

# **Studies on Design of 3d Transition Metal Lewis Acid Catalysts for Efficient Activation of Aldehydes and Imines**

**Rei Tomifuji**

**2020**



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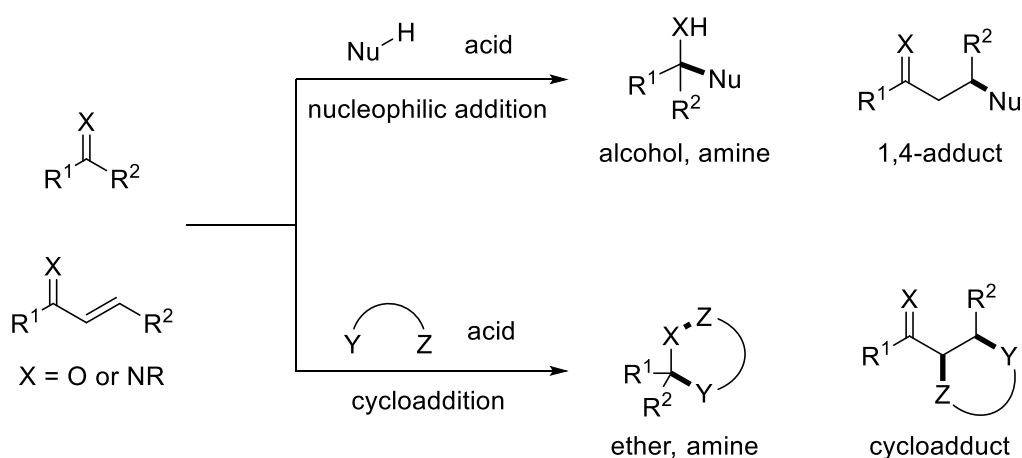
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## Abbreviations

|            |                                          |                 |                                       |
|------------|------------------------------------------|-----------------|---------------------------------------|
| $\alpha$   | observed optical rotation                | m               | multiplet (spectral)                  |
| Å          | ångström                                 | M               | molar (1 M = 1 mol dm <sup>-3</sup> ) |
| Ac         | acetyl                                   | Me              | methyl                                |
| aq         | Aqueous                                  | mg              | milligram(s)                          |
| BINOL      | 1,1'-Bi-2-naphthol                       | MHz             | megahertz                             |
| br         | broad (spectral)                         | min             | minute(s)                             |
| Bn         | benzyl                                   | mL              | milliliter(s)                         |
| Bu         | butyl                                    | mm              | millimeter(s)                         |
| <i>c</i>   | concentration                            | mmol            | millimole(s)                          |
| °C         | degrees Celsius                          | mol             | mole(s)                               |
| calcd      | calculated                               | mp.             | melting point                         |
| $\delta$   | chemical shift in perts per million      | Naph            | naphthyl                              |
| d          | doublet (spectral)                       | nm              | nanometer(s)                          |
| d          | day(s)                                   | Nu              | nucleophile                           |
| $\Delta$   | delta                                    | Ns              | nitrobenzenesulfonyl                  |
| DFT        | density functional theory                | <i>o</i>        | ortho                                 |
| d.r.       | diastereomer ratio                       | <i>p</i>        | para                                  |
| Ed(s)      | editor(s)                                | Ph              | phenyl                                |
| <i>ee</i>  | enantiomeric excess                      | pp.             | page(s)                               |
| <i>ent</i> | enantiomer                               | ppm             | parts per million (spectral)          |
| equiv      | equivalent(s)                            | Pr              | propyl                                |
| e.r.       | enantiomer ratio                         | q               | quartet (spectral)                    |
| ESI        | electrospray ionization                  | <i>R</i>        | rectus                                |
| Et         | ethyl                                    | R               | gas constant                          |
| EXAFS      | extended X-ray absorption fine structure | rt              | room temperature ( <i>ca.</i> 25 °C)  |
| <i>G</i>   | Gibbs free energy                        | s               | singlet                               |
| h          | hour(s)                                  | <i>S</i>        | sinister                              |
| HPLC       | high performance liquid chromatography   | <i>S</i>        | entropy                               |
| HRMS       | high-resolution mass spectrum            | sept            | septet                                |
| Hz         | hertz (s <sup>-1</sup> )                 | t               | triplet                               |
| <i>i</i>   | iso                                      | <i>t (tert)</i> | tertiary                              |
| IR         | infrared (spectral)                      | TBS             | tert-butyldimethylsilyl               |
| <i>J</i>   | coupling constant (spectral)             | TMS             | trimethyl silyl                       |
| J          | Joule                                    | TLC             | thin-layer chromatography             |
| k          | kilo                                     | Ts              | 4-methylbenzenesulfonyl               |
| K          | kelvin                                   | XANES           | X-ray Absorption Near Edge Structure  |
|            |                                          | XAS             | X-ray absorption spectroscopy         |

## General Introduction

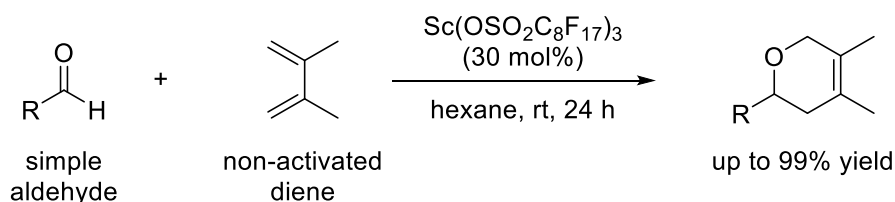
The coordination of an acid to carbonyl groups and their derivatives such as imines efficiently lowers the LUMO energy level of the electrophiles, and facilitates the addition of a nucleophile. This is a fundamental and important reactions in synthetic chemistry to prepare various organic compounds such as alcohols, ethers, amines, and functionalized ketones or imines in a stereo- and chemoselective manner (Scheme 1). Ever since Charles Friedel and James Crafts reported the alkylation reaction of aromatic compounds in the presence of aluminum chloride, a.k.a. Friedel–Crafts alkylation, metal-based Lewis acids have emerged as a useful class of catalysts. Indeed, the Diels–Alder reaction, Mukaiyama aldol reaction, ene reaction, and many other Lewis acid-catalyzed reactions play pivotal roles in the formation and cleavage of chemical bonds, and are widely used in the synthesis of natural products, pharmaceuticals, and agrochemicals.<sup>1</sup> Although many Lewis acid-catalyzed reactions have been reported to date, the discovery of novel acid catalysts which can offer the new transformations with high reactivity and improved/different selectivity are of great research interest. Over the last few decades, the growing importance of synthesizing asymmetric compounds has led to the design of novel chiral Lewis acid catalysts becoming one of the main goals in this research area.<sup>2</sup>



**Scheme 1.** Acid-catalyzed nucleophilic addition and cycloaddition reactions.

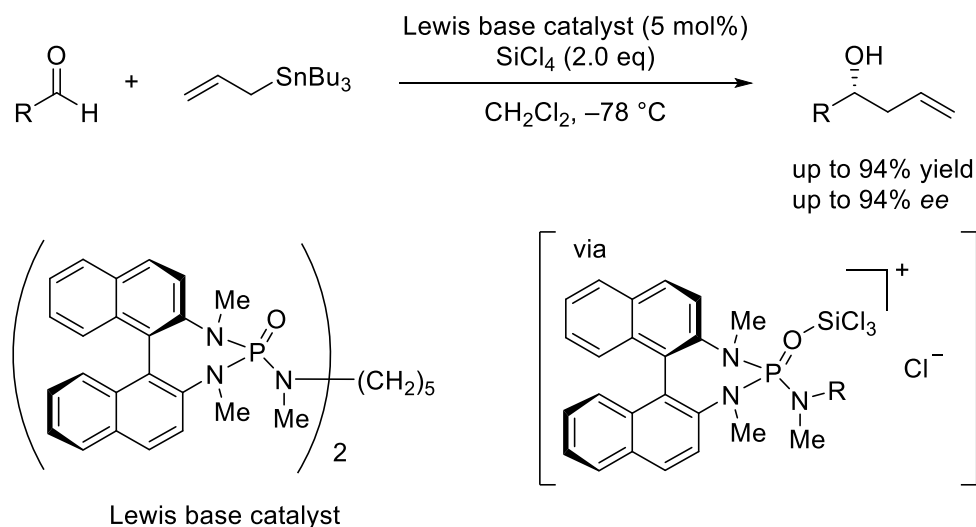


activated substrates in the presence of  $\text{Sc(OPf)}_3$  ( $\text{OPf} = \text{OSO}_2\text{C}_8\text{F}_{17}$ ), although 30 mol% of the scandium catalyst was required for substantial conversion due to its low catalytic turn-over (Scheme 3).<sup>4</sup>



**Scheme 3.** Oxa-Diels–Alder reaction of non-activated substrates using scandium Lewis acid catalyst.

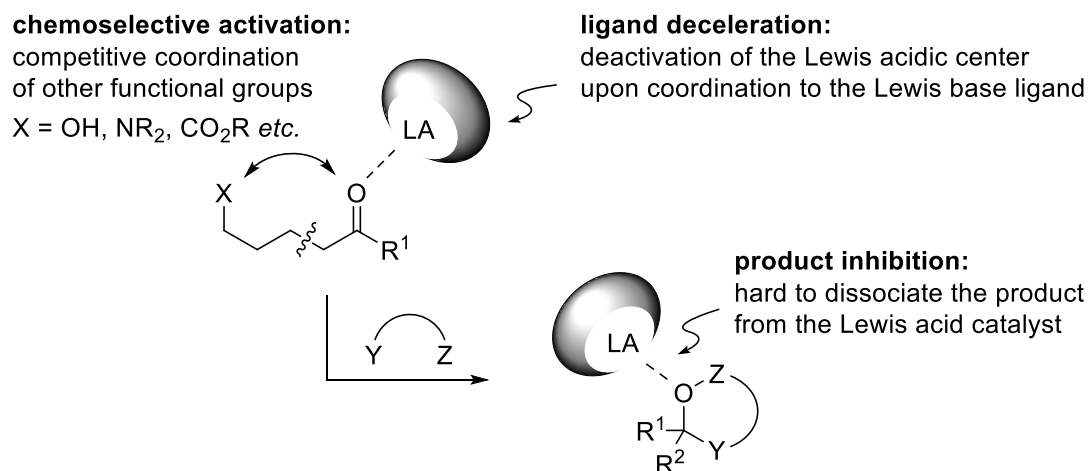
For enantioselective reactions, it is more challenging to design a highly active chiral Lewis acid because chiral ligands are, in general, Lewis bases. Lewis basic ligand coordination results in the deactivation of the Lewis acidity and activation of the substrates becomes more difficult. Several attempts to realize highly active Lewis acid have been carried out, and Denmark and co-workers successfully developed a method based on the concept of Gutmann's rule, which described that the coordination of a chiral Lewis base causes an electronic charge redistribution and cationic Lewis acid was formed in situ.<sup>5,6</sup> The Denmark group reported a series of works related to Lewis base activation of Lewis acid methodology. For example, the asymmetric allylation reaction of aldehydes catalyzed using a combination of a chiral Lewis base catalyst and tetrachloro silane (Scheme 4).<sup>6a</sup> The reaction did not proceed without the chiral Lewis base because the active chiral cationic acid species was not formed in the absence of the catalyst. The reaction mechanism was investigated in detail and a wide range of reactions were achieved using this strategy. However, a stoichiometric amount of the Lewis acid was required in the reaction because the activated Lewis acid strongly coordinates with the product, which prevents the regeneration of the active Lewis acid as the catalyst.



**Scheme 4.** Allylation of aldehydes using chiral Lewis base activation of Lewis acid.

In brief, although the chemistry of Lewis acids has been developed over the century, the contradiction between acid activity and catalytic turn-over has limited the potential of Lewis acids especially when used as a catalyst. The key requirement for novel acid catalysts is to overcome the following major drawbacks: (i) Chemoselectivity, which implies the selective activation of the desired functional group is difficult in the presence of other coordinative functional groups possessing a basic moiety. (ii) Product inhibition, which is caused by strong coordination to the product, preventing the catalyst from being regenerated due to the higher basicity of the product when compared to the starting material (i.e.  $sp^2$  ketone  $\rightarrow$   $sp^3$  alcohol or ether, the lower the  $s$ -character in the hybrid orbital represents the stronger Lewis basicity of the lone pair electrons on the heteroatom). (iii) Ligand deceleration, the effect of the ligand in decreasing the Lewis acidity upon its coordination. This problem is crucial since the coordination of the ligand to Lewis acid controls the reactivity and selectivity. However, this coordination causes difficulties in the electrophilic activation (Scheme 5).

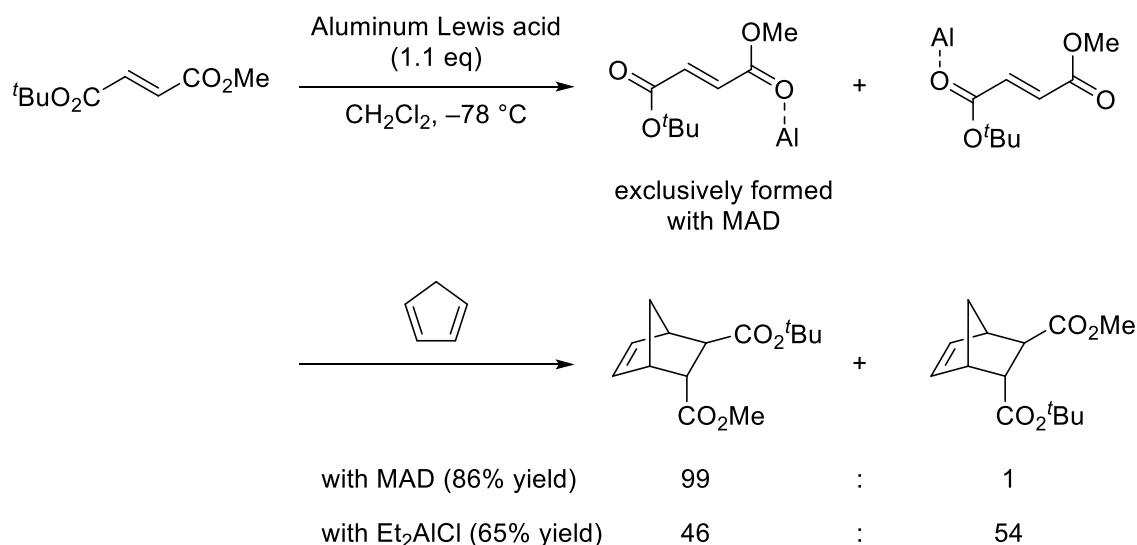
To overcome the problems in conventional Lewis acid, several elaborate designs have been reported over the past few decades. These seminal works are summarized in following section.



**Scheme 5.** Common problems in Lewis acid catalysis.

## 2. Designs for chemoselective activation

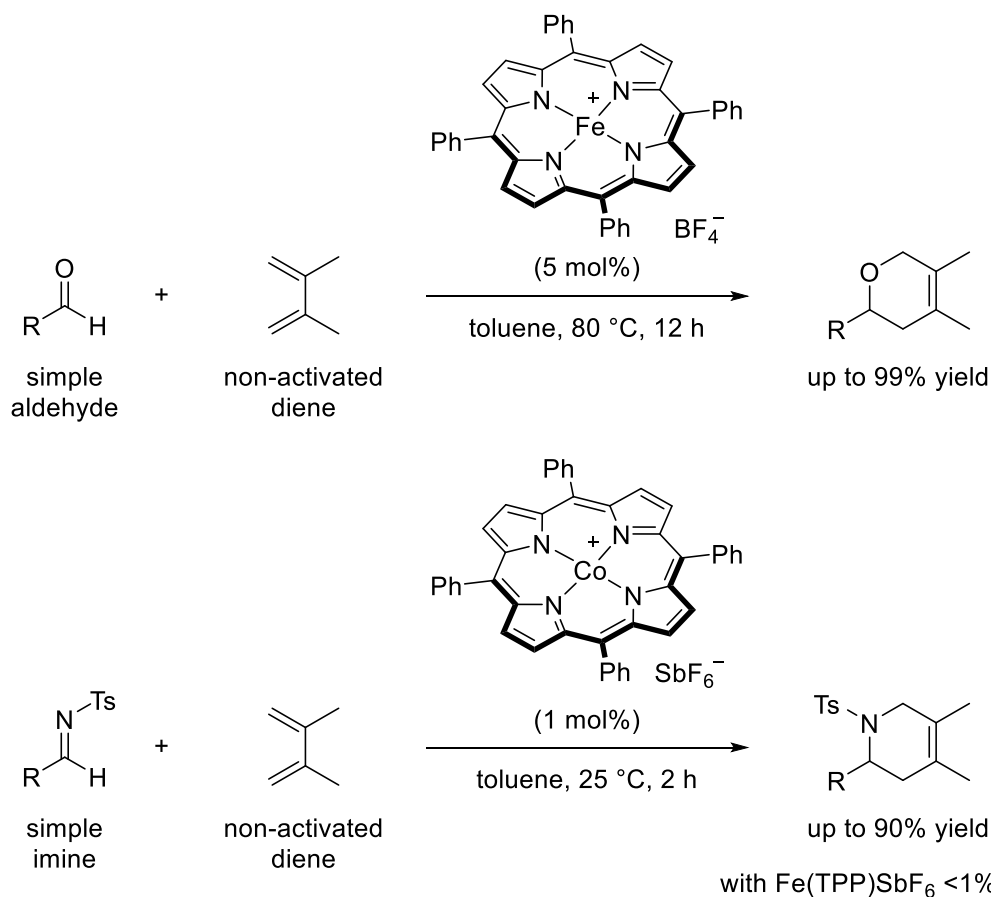
Yamamoto and co-workers have demonstrated excellent chemoselective coordination of a Lewis acid to an ester carbonyl group utilizing a bulky aluminum Lewis acid. For example, a mixture of *tert*-butyl methyl fumarate and bulky aluminum Lewis acid methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) exclusively forms a methyl ester coordinated organoaluminum complex (Scheme 6),<sup>7</sup> which reacts with cyclopentadiene to give the corresponding Diels–Alder cycloadduct, while sterically less hindered diethylaluminum chloride gave the product as a mixture of regioisomers. Both the kinetic and thermodynamic effects of the bulky Lewis acidic center can realize selective activation even though a stoichiometric amount of Lewis acid is required.



**Scheme 6.** Regioselective Diels–Alder reaction and steric effects of the Lewis acid.

### 3. Designs to reduce product inhibition and promote chemoselective activation

Kurahashi and Matsubara have developed a series of cationic metalloporphyrin Lewis acid catalysts, and demonstrated their use in the catalytic hetero-Diels–Alder reactions with non-activated substrates.<sup>8</sup> The high Lewis acidity of the cationic metalloporphyrin complex facilitates the reaction of electronically unbiased substrates and the repulsive interactions between the product and bulky metalloporphyrin complex allows facile dissociation of the acid catalyst from the product. Moreover, chemoselective activation was achieved by choosing an appropriate metal center. The cationic iron(III) porphyrin catalyst can catalyze the oxa-Diels–Alder reaction,<sup>8a</sup> while a cationic cobalt(III) porphyrin catalyst was suitable for the aza-Diels–Alder reaction (Scheme 7).<sup>8b</sup> As seen in this series of cationic metalloporphyrin catalyzed reactions, suitable choice of the transition metal (Fe, Co, Ru, Mn etc.) is crucial toward promoting each reaction.



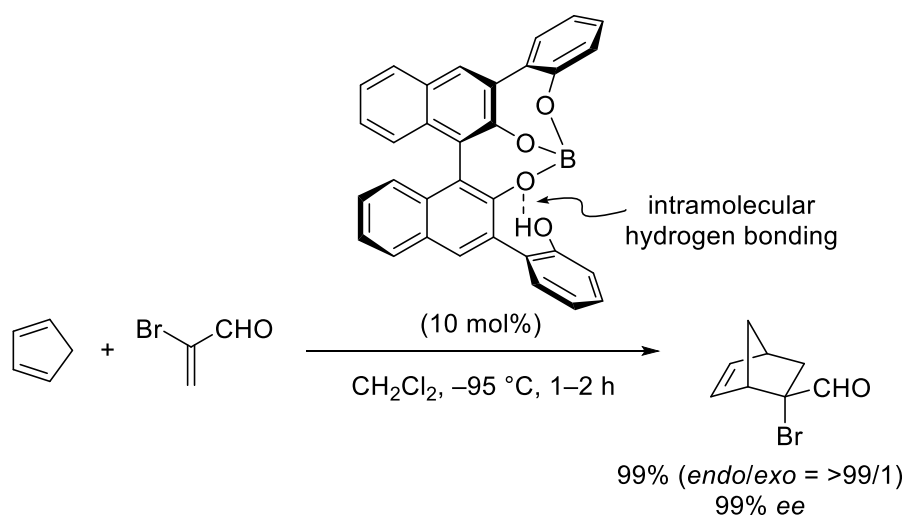
**Scheme 7.** Oxa- and aza-Diels–Alder reaction of non-activated substrates using cationic metalloporphyrin complex.

#### 4. Designs to overcome ligand deceleration

As mentioned beforehand, substrate activation in enantioselective reactions is challenging because conventional chiral ligands are Lewis basic. To avoid any undesired background reactions, strongly coordinative ligands such as salens, bisphosphines and bisalkoxides bearing a binaphthyl backbone are favorable toward the construction of a rigid asymmetric environment, however, the use of these ligands can cause a serious ligand deceleration.<sup>2</sup> In this section, some of the innovative strategies used for highly active chiral acid catalysts reported over the last several decades were presented.

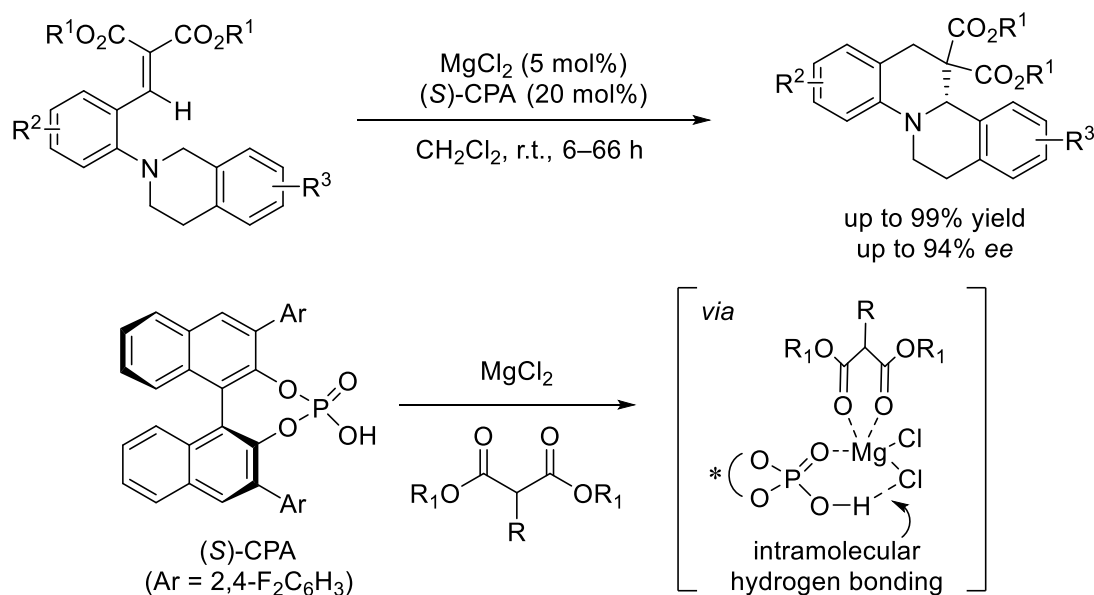
#### 4.1. Brønsted acid-assisted Lewis acid (BLA)

A pioneering Lewis acid activation strategy has been reported by Yamamoto and Ishihara, which is known as a Brønsted acid-assisted Lewis acid (BLA).<sup>9</sup> They demonstrated the enantioselective Diels–Alder reaction of acrolein and dienes using a catalyst, obtained upon mixing (R)-3,3'-di(2-hydroxyphenyl)-2,2'-dihydroxy-1,1'-binaphthyl and B(OMe)<sub>3</sub> (Scheme 8). In this reaction, intramolecular hydrogen bonding between the phenol acidic proton and oxygen atom attached to the Lewis acidic boron was essential to enhance the Lewis acidity and achieving high reactivity and enantioselectivity.



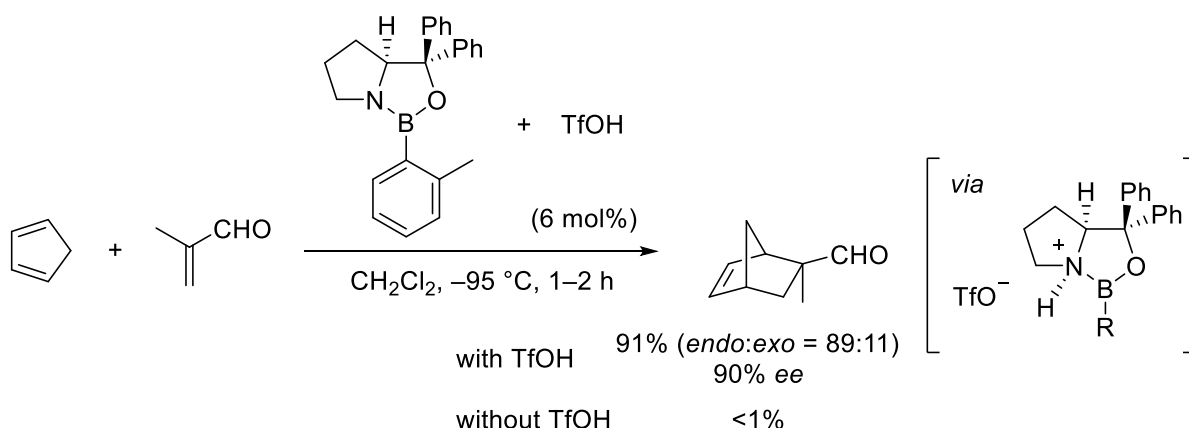
**Scheme 8.** Brønsted acid-assisted Lewis acid catalyst via intramolecular hydrogen bonding for the enantioselective Diels–Alder reaction.

Lately, a binary acid catalyst combining the use of a main group metal Lewis acid and chiral phosphoric acid, has been demonstrated using a similar concept by the Luo group.<sup>10</sup> MgCl<sub>2</sub> and a chiral phosphoric acid can catalyze an enantioselective 1,5-hydride transfer and subsequent *tert*-aminocyclization reaction (Scheme 9). The chiral phosphoric acid not only acts as a ligand, but also as a hydrogen bonding donor during the intramolecular activation of the Lewis acid catalyst.



**Scheme 9.** Binary acid catalyst for enantioselective 1,5-hydride transfer and subsequent *tert*-aminocyclization reaction.

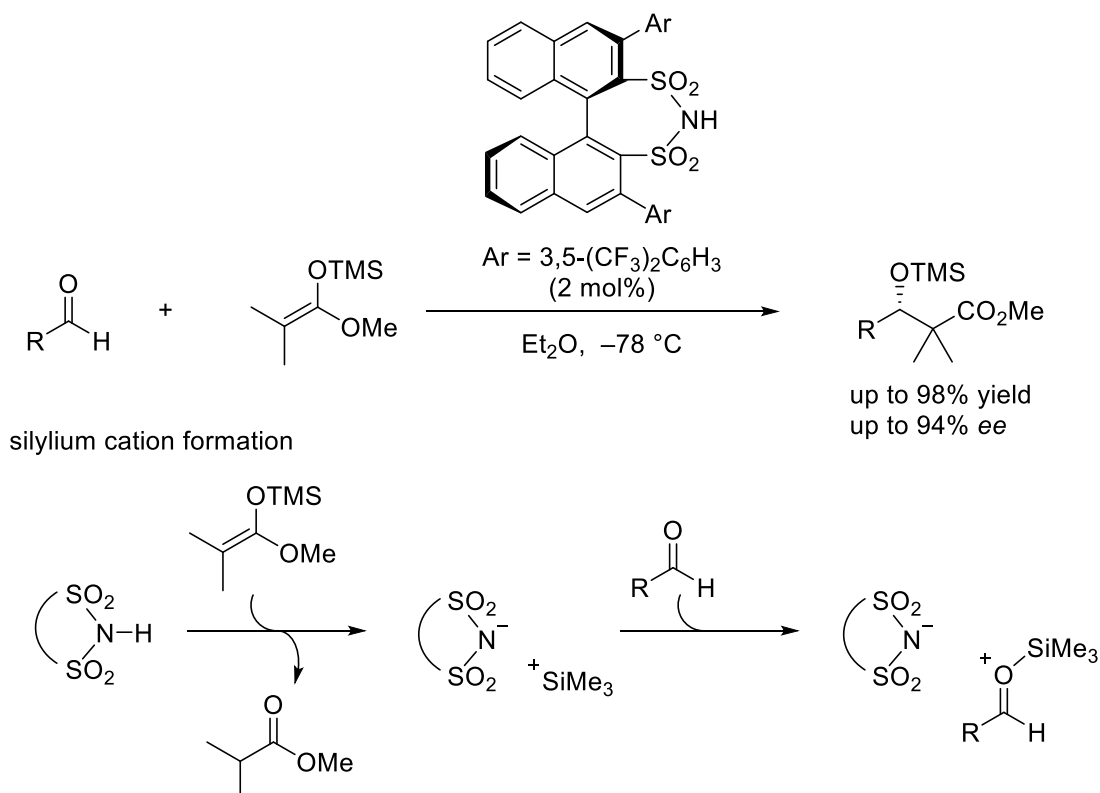
In 2002, Corey and co-workers exploited another method for Lewis acid activation by using external proton addition.<sup>11</sup> An enantioselective Diels–Alder reaction was performed in the presence of a chiral oxazaborolidine and triflic acid, which gave the desired product in high yield and selectivity. The chiral oxazaborolidine alone could not catalyze the reaction (Scheme 10). This result indicates that a highly active cationic chiral acid catalyst was generated via protonation of the chiral oxazaborolidine catalyst by using triflic acid.



**Scheme 10.** Triflic acid activated oxazaborolidine-catalyzed enantioselective Diels–Alder reaction.

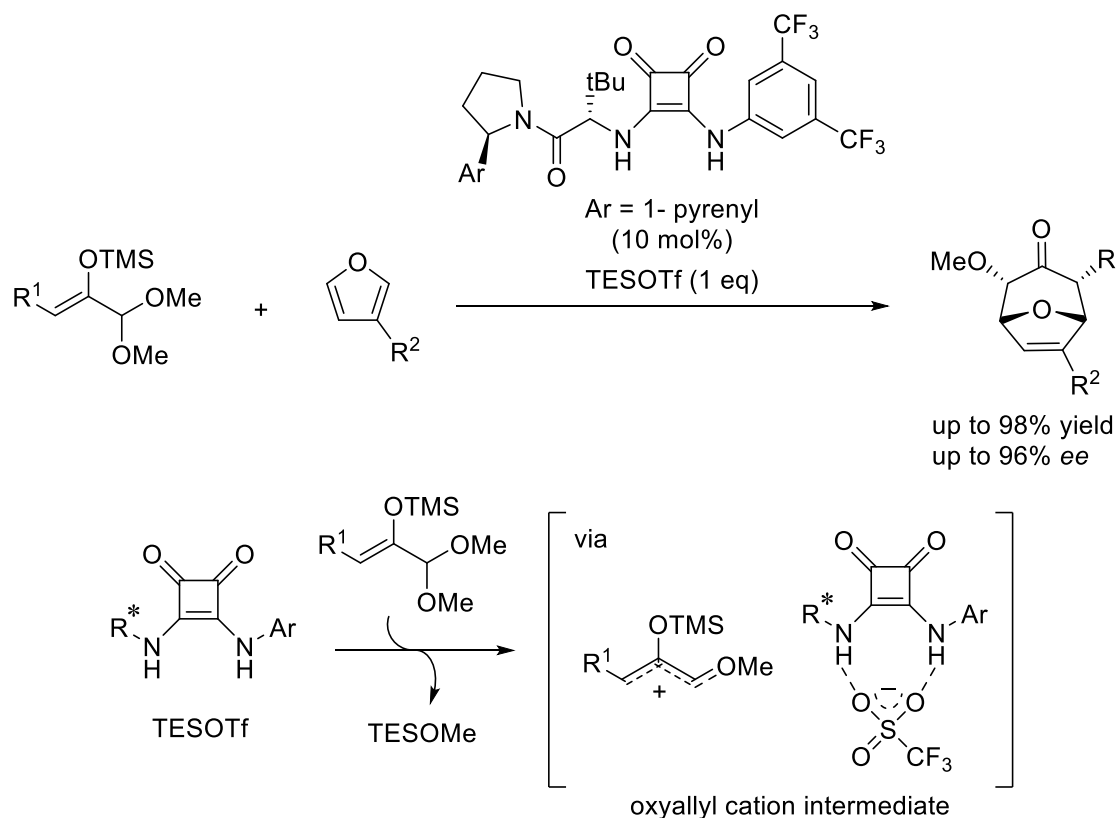
#### 4.2. Silylium cation-based asymmetric catalysis

Silylium cation formation using a combination of a chiral catalyst and silylating reagent has been reported by several research groups. The List group has developed and expanded the concept of asymmetric counteranion directed catalysis in highly active silylium cation Lewis acid chemistry.<sup>12</sup> The Mukaiyama aldol reaction proceeded in high yield and enantioselectivity in the presence of a binaphthyl-derived chiral disulfonimide catalyst. List and co-workers confirmed that the catalyst was first silylated and the silylium cation was formed in situ (Scheme 11). The general disadvantage of using silylium cations as a Lewis acid catalyst is their instability for water. However, in this reaction, the silylium cation was regenerated by the existing silylating reagent if the silylium cation was deactivated, and thus, the reaction proceeds in the presence of a small amount of water.<sup>12c</sup>



**Scheme 11.** Catalytic enantioselective Mukaiyama aldol reaction and mechanism for the formation of the silylium cation.

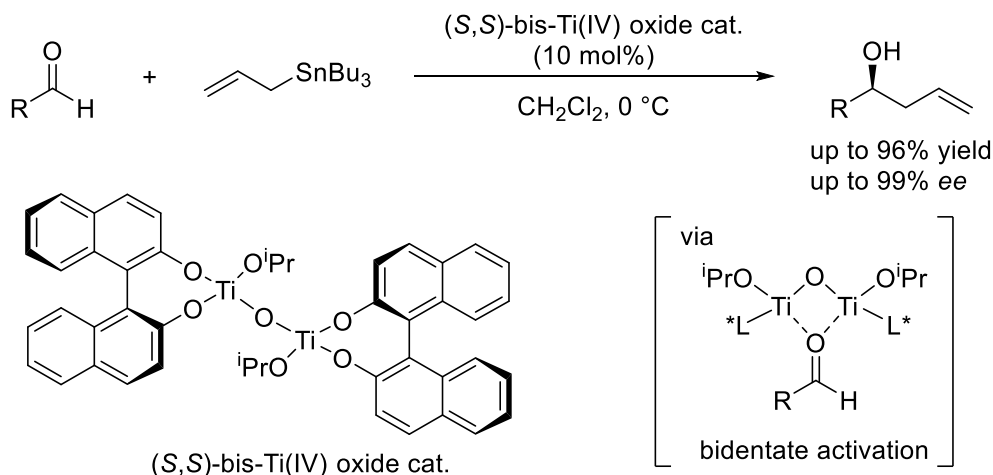
More recently, the Jacobsen group have provided a new strategy for generating a silylium cation bearing a chiral moiety. Dual hydrogen bond donors such as urea and thiourea are well-known scaffolds in organocatalysis, which are used to abstract and bind anions. Jacobsen and co-workers used this character to activate a Lewis acid catalyst by abstracting a triflate anion from silyl triflate using a chiral squaramide to form the requisite silylium cation. They demonstrated a [4+3] cycloaddition reaction utilizing this Lewis acid enhancement methodology (Scheme 12).<sup>13</sup> The seven-membered cycloadduct was obtained using this catalyst system, while TESOTf alone did not catalyze the reaction.



**Scheme 12.** [4+3] cycloaddition reaction by Lewis acid enhancement via anion binding strategy

#### 4.3. Bidentate activation of carbonyl compounds

Bidentate activation is another beneficial strategy used toward the efficient activation of carbonyl compounds. Maruoka and co-workers demonstrated the enantioselective allylation reaction of aldehydes utilizing a chiral bis-Ti(IV) oxide complex as the catalyst (Scheme 13).<sup>14</sup> This bis-Ti(IV) complex coordinates to both lone pairs on carbonyl oxygen atom and strongly activate the aldehyde. On the other hand, the mono-Ti(IV) catalyst gave the product in low yield and selectivity. Hence this bidentate activation strategy provides a beneficial way of realizing high activity.



**Scheme 13.** Allylation of aldehydes via bidentate activation

As reviewed above, designing the steric effects around the Lewis acidic center is crucial to enhancing the chemoselectivity and reducing the product inhibition. Hence, a suitable choice of Lewis acidic center and ligand design is essential toward regulating the character of the Lewis acid catalyst. Moreover, even in the predominant pioneering works used to overcome ligand deceleration, a pre-activated substrate and/or relatively high acid loading are still needed. Thus, the exploitation of highly active acid catalysts is still an underdeveloped research area.

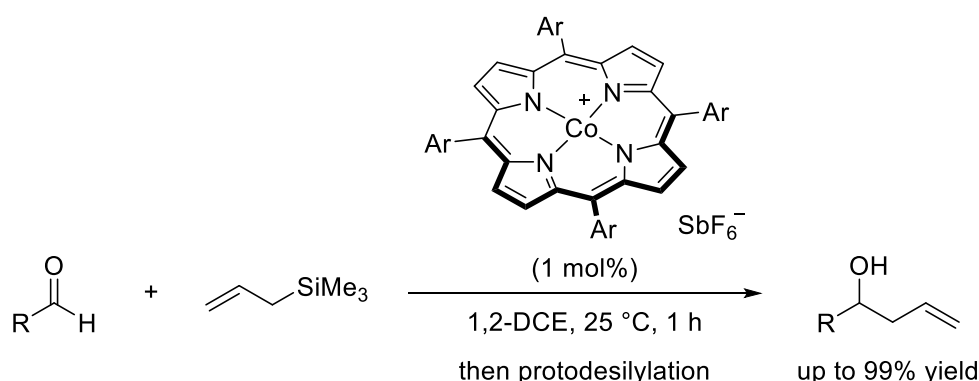
## 5. Overview of this thesis

The author has coped with establishing the novel strategy for the preparation of highly active acid catalysts, which offers solutions to the major limitations of Lewis acid chemistry, i.e. chemoselectivity, product inhibition, and ligand deceleration. His research has focused on exploring the formation and employment of the cationic species, especially 3d transition metal Lewis acids. The metal Lewis acids should be more accessible for flexible design, since transition metals allow the formation of several coordinated species and geometrical changes to occur (tetrahedral, square planar, octahedral etc.), while aluminum or boron Lewis acid can only form tetrahedral structural arrays. By disclosing the character of the 3d transition metal Lewis acid, he

have demonstrated various catalytic reactions utilizing an isolable cationic Lewis acid (Chapter 1) and highly active cationic species generated in situ (Chapter 2 and 3). Furthermore, the concept of in situ formed cationic Lewis acids was developed for use in asymmetric synthesis (Chapter 4 and 5). In each reaction, higher catalytic activities were achieved compared to previously reported works decreased catalyst loading and a broad functional group tolerance was exhibited.

### 5.1. Cationic Co porphyrin-catalyzed allylation of aldehydes (Chapter 1)

Taking note of the high Lewis acidity of cationic metalloporphyrin complexes, the author has investigated the Hosomi–Sakurai allylation reaction of aldehydes with a readily available allyltrimethylsilane. The reaction was efficiently catalyzed in the presence of 1 mol% of cationic Co(III) porphyrin complex within a short reaction time under mild conditions (Scheme 14).<sup>15</sup> Density functional theory (DFT) calculations revealed the strong interaction formed between the cationic Co porphyrin complex and aldehyde. Moreover, DFT studies also implied that the dissociation of the product was accelerated due to the bulkiness of the porphyrin ligand, which led to a high catalytic turn-over.



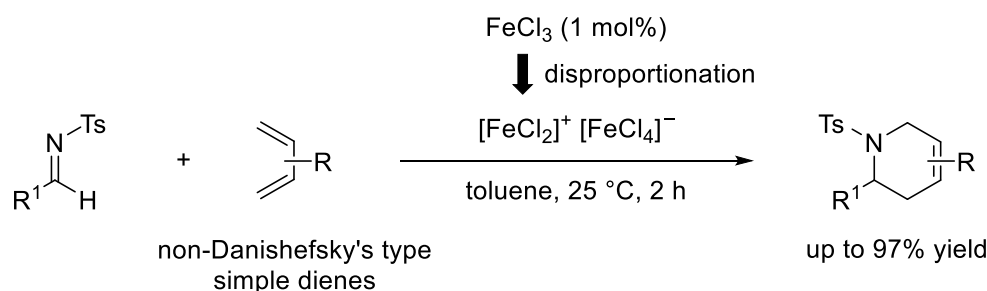
**Scheme 14.** Cationic cobalt porphyrin-catalyzed Hosomi–Sakurai allylation reaction of aldehydes

## 5.2. Fe(III)-catalyzed cycloaddition reaction

In modern synthetic chemistry, iron is regarded as an attractive catalyst due to its high availability, low toxicity, and environmentally benign character. Thus, the development of iron-catalyzed reactions is one of the current hot topics in scientific research.<sup>16,17</sup> Obviously, iron(III) halides (i.e. FeCl<sub>3</sub>, FeBr<sub>3</sub>) are one of the most conventional metal Lewis acid catalysts used to date. Despite their wide range of applications, the activation mechanism has been slightly neglected. The author has engaged in developing iron Lewis acid catalyst chemistry from a mechanistic viewpoint.

### 5.2.1. FeCl<sub>3</sub>-catalyzed aza-Diels–Alder reaction of aldimines and non-activated dienes, and the investigation of its mechanistic insight (Chapter 2)

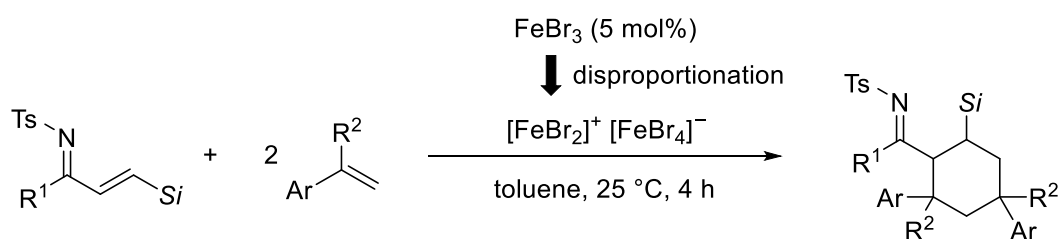
The author has found that the aza-Diels–Alder reaction of *N*-tosylated aldimines and non-activated dienes can be successfully catalyzed using 1 mol% FeCl<sub>3</sub> (Scheme 15).<sup>18</sup> A precise mechanistic investigation revealed that the key step in the reaction was the formation of an ion-paired species, i.e. [FeCl<sub>2</sub>]<sup>+</sup>[FeCl<sub>4</sub>]<sup>−</sup>, via the in situ disproportionation of FeCl<sub>3</sub>.<sup>19</sup> This type of disproportionation is known to occur in coordinative solvents, however it is difficult to utilize as a Lewis acid catalyst because of its deactivation by solvent. In the present case, coordination of the tosyl group induces the disproportionation reaction even in a non-coordinative solvent. Thus, the resulting cationic species acts as a Lewis acid catalyst. The as-formed cationic Lewis acid, [FeCl<sub>2</sub>]<sup>+</sup>, is a strong Lewis acid, which can efficiently lower the activation energy of the diene addition reaction, and provide various *N*-contained six-membered heterocycles.



**Scheme 15.** Aza-Diels–Alder reaction of aldimines and non-activated dienes promoted by the in situ generated ion-paired Lewis acid catalyst.

### 5.2.2. $FeBr_3$ -catalyzed [2+2+2] cycloaddition reaction (Chapter 3)

Encouraged by the results described in Chapter 2, the author envisaged that  $\alpha,\beta$ -unsaturated  $N$ -tosylated imines can be also strongly activated by iron(III) halides and react with a range of nucleophiles. In fact, the [2+2+2] reaction proceeded by employing styrene derivatives as substrate, and corresponding multi-substituted cyclohexane products were obtained in a diastereoselective manner (Scheme 16).<sup>20</sup> While the construction of six-membered carbon rings is one of the most important reactions in organic chemistry represented by the Diels–Alder reaction, the Lewis acid-catalyzed [2+2+2] cycloaddition reaction between three alkenes has not been reported to date. Hence, this synthetic approach is expected to be a new route to construct the cyclohexane scaffold.



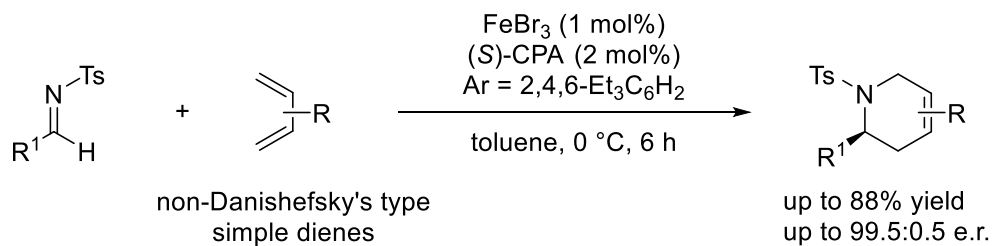
**Scheme 16.**  $FeBr_3$ -catalyzed [2+2+2] cycloaddition reaction of  $\alpha,\beta$ -unsaturated  $N$ -tosylated imines and styrene derivatives

### 5.3. Bidentate activation chiral catalyst for asymmetric hetero-Diels–Alder reaction using non-activated substrates (Chapter 4 and 5)

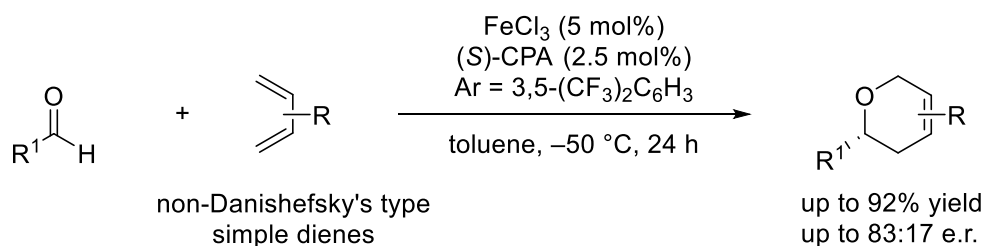
The author has further developed this protocol using the in situ generation of a highly active cationic Lewis acid via  $\text{FeX}_3$  disproportionation in asymmetric synthesis. Since the coordination of the Lewis basic moiety induces the disproportionation of  $\text{FeX}_3$ , he envisioned that cationic  $[\text{FeX}_2]^+$  can also be formed via the coordination of a chiral Lewis base. Furthermore, bidentate activation is an attractive strategy used to compensate for the reduced acidity upon the coordination of the Lewis basic ligand (Scheme 13). To achieve bidentate activation, two acidic moieties need to be located in appropriate positions. Based on these facts, the author envisaged that the combination of  $\text{FeX}_3$  and a chiral phosphoric acid should satisfy the conditions required for chiral bidentate activation. BINOL-derived chiral phosphoric acid is one of the most established chiral organocatalysts and it is known that the Brønsted acidic proton (O-H) and Lewis basic phosphoryl oxygen ( $\text{P}=\text{O}$ ) works synergistically as an acid–base catalyst.<sup>21</sup> Hence, the  $[\text{FeX}_2]^+[\text{FeX}_4]^-$  species should be formed via the coordination of the phosphoryl oxygen to both the cationic Lewis acid and neighboring Brønsted acidic proton, which activates the substrates.

To prove this hypothesis, a hetero-Diels–Alder reaction of non-activated substrates was conducted in the presence of both  $\text{FeX}_3$  and the chiral phosphoric acid. The reactions proceed for both imine and aldehyde substrate and corresponding cycloadducts were obtained in high yield and enantioselectivity (Scheme 17).<sup>22,23</sup> Although a limited number of catalytic hetero-Diels–Alder reactions of non-activated substrates has been reported to date, a notably low catalyst loading and mild reaction conditions were achieved compared to those previously reported examples. Furthermore, DFT calculations and spectroscopic analysis revealed the importance of the multiple activation system.

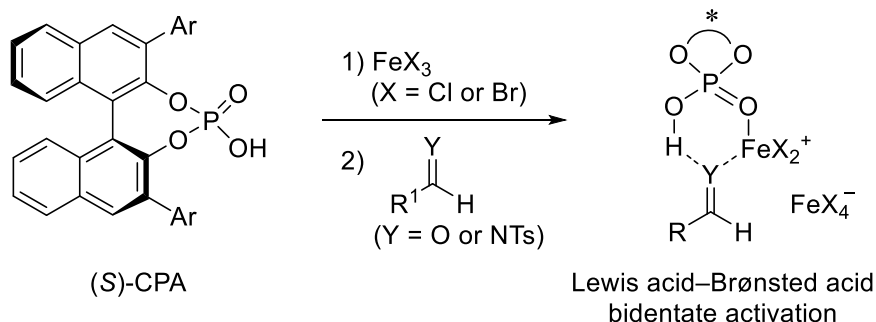
**Asymmetric aza-Diels–Alder reaction of non-activated substrates (Chapter 4)**



**Asymmetric oxa-Diels–Alder reaction of non-activated substrates (Chapter 5)**



Formation of active catalyst species



**Scheme 17.** Asymmetric hetero-Diels–Alder reaction of non-activated substrates via bidentate activation

## References and Notes

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## Instrumental and Materials

All manipulations of oxygen- and moisture-sensitive materials were conducted in a dry box. Nuclear magnetic resonance (NMR) spectra were acquired on Varian UNITY INOVA 500 ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}$ , 125.7 MHz) spectrometer using  $\text{CHCl}_3$  as an internal standard for  $^1\text{H}$  NMR ( $\delta = 7.26$  ppm) and  $\text{CDCl}_3$  as an internal standard for  $^{13}\text{C}$  NMR ( $\delta = 77.0$  ppm).  $^1\text{H}$  NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher SCIENTIFIC EXACTIVE spectrometer. X-Ray data were recorded on a Rigaku XtaLAB mini diffractometer equipped with a CCD detector. Infrared (IR) spectra were acquired on a SHIMADZU IR Affinity-1 spectrometer. High-performance liquid chromatography (HPLC) was performed with a SHIMADZU Prominence. Optical rotations were measured on a HORIBA SEPA-200. Melting points were determined using a YANAKO MP-500D. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F<sub>254</sub> (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or such as an aqueous alkaline  $\text{KMnO}_4$  solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50  $\mu\text{m}$ ). Unless otherwise noted, commercially available reagents were used without purification. Extended X-ray absorption fine structure (EXAFS) analysis was conducted at the SPring-8 beamline BL14B2 using Si(111) (for Co and Fe *K*-edge) double-crystal monochromated synchrotron radiation.

# Chapter 1

## **Cationic Cobalt Porphyrin-Catalyzed Allylation of Aldehydes with Allyltrimethylsilanes**

Cationic cobalt porphyrin-catalyzed allylation of aldehydes with allyltrimethylsilanes has been developed. The formation of the aldehyde–cobalt porphyrin complex, the key intermediate for the addition of allylsilanes, is confirmed by theoretical studies and synchrotron-based X-ray absorption fine-structure measurements. Facile dissociation of the produced homoallylic alcohol from the cobalt complex regenerates the active complex with the aldehyde. The readily obtainable [Co(TPP)]SbF<sub>6</sub> complex serves as an efficient catalyst for this allylation.

## Introduction

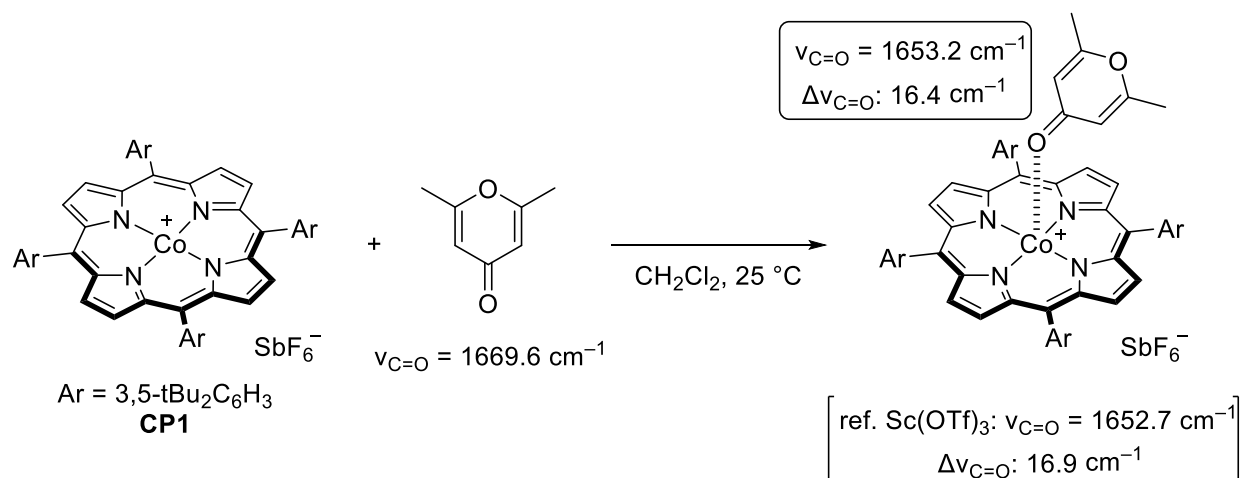
Metalloporphyrins are well-known to have important biochemical functions in nature. Therefore, there has been much interest in exploiting the unique character of metalloporphyrins in organic synthesis.<sup>1,2</sup> Recently, it has been demonstrated that metalloporphyrins could serve as a Lewis acid to catalyze various reactions such as the hetero-Diels–Alder reaction, cycloisomerization, and cycloaddition.<sup>3</sup> Herein, the author developed the allylation reaction of aldehydes via the addition of allyltrimethylsilanes to give homoallylic alcohols by employing cationic cobalt porphyrin catalyst.

Allylation of aldehydes in the presence of a Lewis acid catalyst is a fundamental transformation involving C–C bond formation to afford homoallylic alcohols.<sup>4</sup> The reaction mechanism involves coordination and activation of the aldehyde with a strong Lewis acid as the key step. Consequently, there is often a trade-off between the activation of the aldehyde for coordination with the Lewis acid and product dissociation from the Lewis acid, thereby necessitating the use of a stoichiometric or substoichiometric amount of the Lewis acid catalyst. Therefore, the development of an efficient, easy-to-prepare catalyst for the allylation, especially for reactions with less reactive and thermodynamically stable allylsilanes (e.g., allyltrimethylsilanes), remains a topic of interest. The author hypothesized that the cationic cobalt porphyrin complex, by virtue of its high Lewis acidity, would catalytically facilitate the activation of the aldehyde and promote the addition of allyltrimethylsilane to afford the corresponding homoallylic alcohol. Moreover, the steric hindrance of the porphyrin ligand would promote the dissociation of the alcohol so that a high turnover frequency and high turnover number can be achieved.

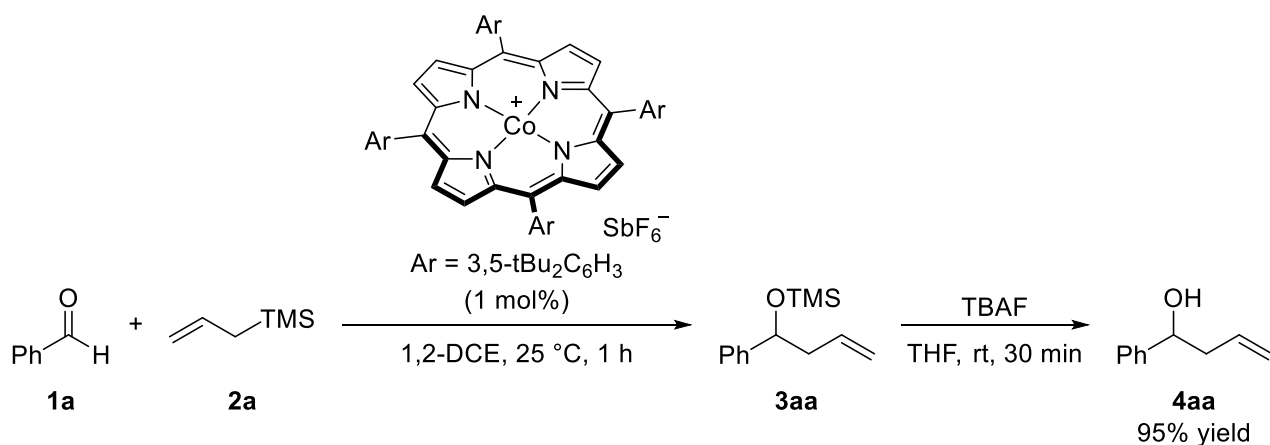
## Results and Discussion

The author initially examined the Lewis acidity of cationic cobalt porphyrin **CP1** by IR spectroscopy by means of measuring the carbonyl stretching vibration of the 2,6-dimethyl- $\gamma$ -pyrone

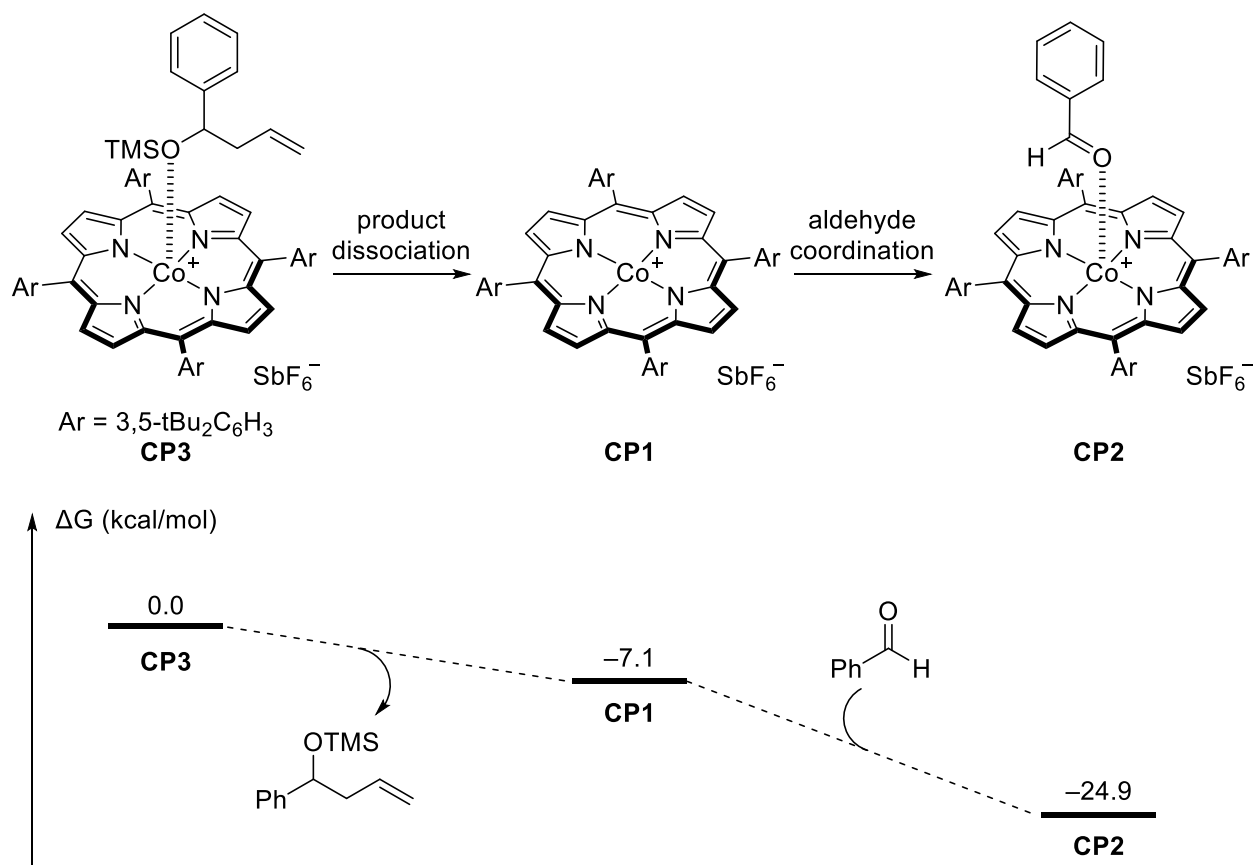
complexes of Lewis acid in 30 mM CH<sub>2</sub>Cl<sub>2</sub> solution in a sealed liquid cell at 25 °C (Scheme 1); a larger shift ( $\Delta\nu_{\text{C=O}}$ ) of the carbonyl absorption peak indicated higher Lewis acidity.<sup>5</sup> The Lewis acidity of **CP1** was comparable to that of the rare-earth Lewis acid Sc(OTf)<sub>3</sub>.<sup>4a</sup> Encouraged by these results, the author next investigated the reaction of aldehyde **1a** and allylsilane **2a** in the presence of a catalytic amount of **CP1** (1 mol%). As shown in Scheme 2, the reaction proceeded at 25 °C and was completed in 1 h to afford homoallylic alcohol **4aa** in 95% yield after protodesilylation of **3aa**. To understand the efficiency of the cobalt porphyrin catalyst, density functional theory (DFT) calculations were conducted to determine the Gibbs free energy change for the dissociation of **3aa** in cobalt porphyrin **CP3** to regenerate active catalyst **CP1** for the next catalytic cycle and the coordination of **1a** to **CP1** to generate active species **CP2** for the addition of **2a** (Scheme 3). The Gibbs free energy change for the dissociation of **3aa** in **CP3** was calculated to be −7.1 kcal/mol; that is, the reaction is exergonic, has a favorable equilibrium constant, and can occur spontaneously. Meanwhile, the Gibbs free energy change for the coordination of **1a** to **CP1** was calculated to be −24.9 kcal/mol relative to the Gibbs energy of **CP3**; this reaction also has a favorable equilibrium constant and would be spontaneous. Thus, the dissociation of **3aa** in **CP3** to afford **CP1** and the subsequent coordination of **1a** to **CP1** are exergonic, consistent with the short reaction time under mild conditions.



**Scheme 1.** Lewis acidity of **CP1**.

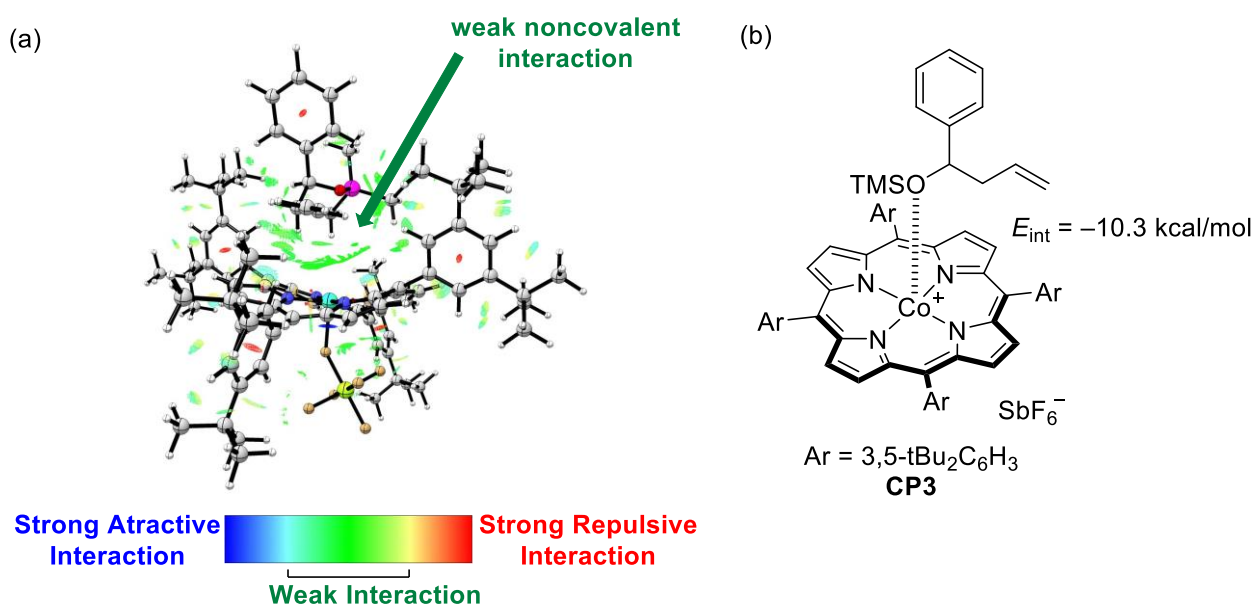


**Scheme 2.** [Co(TArP)]SbF<sub>6</sub>-catalyzed allylation reaction of aldehyde **1a**.

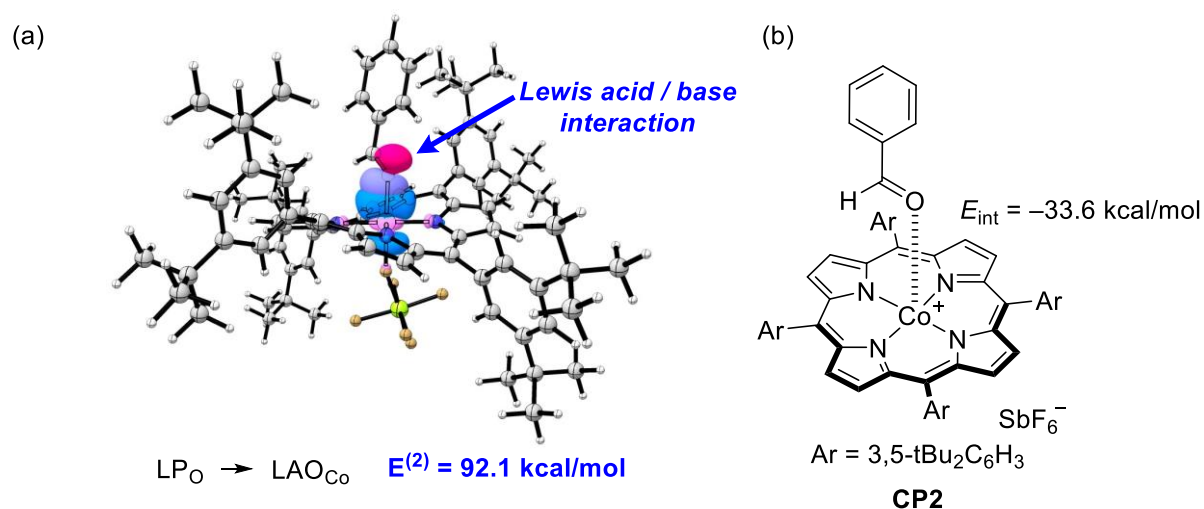


**Scheme 3.** Gibbs free energy change for dissociation of product **3aa** from **CP1** and coordination of aldehyde **1a** to **CP1**.

To understand why the dissociation of product **3aa** and the coordination of aldehyde **1a** are facilitated, the interaction energy of **3aa** and the cobalt porphyrin in **CP3**, as well as that of **1a** and the cobalt porphyrin in **CP2**, were investigated. The weak interactions in **CP3** could be confirmed by the analysis of noncovalent interactions. As shown in Figure 1a, only weak interactions were observed between **3aa** and the cobalt porphyrin. The counterpoise-corrected interaction energy ( $E_{\text{int}}$ ) analysis based on the fragment molecular orbital scheme involved in the complex formation also suggested weak interactions (Figure 1b,  $-10.3$  kcal/mol). On the other hand, the interaction between **1a** and the cobalt porphyrin in **CP2** was found to be strong. The Lewis acid–Lewis base interaction was calculated to be  $92.1$  kcal/mol by NBO analysis (Figure 2a). Furthermore,  $E_{\text{int}}$  analysis suggested strong interaction between **1a** and cobalt porphyrin (Figure 2b,  $-33.6$  kcal/mol).



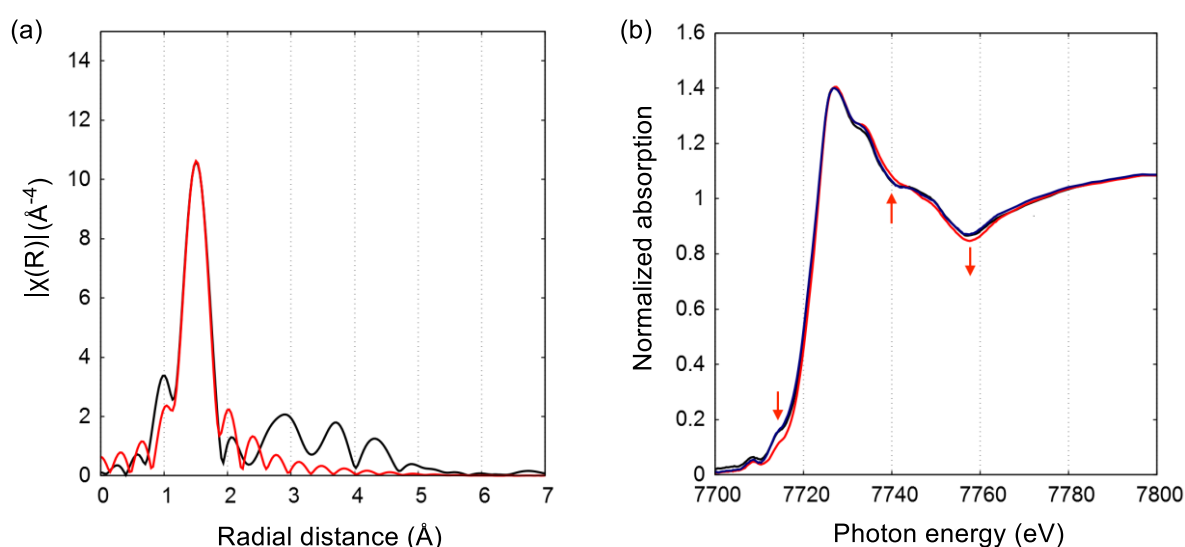
**Figure 1.** (a) NCI (noncovalent interactions) plot of **CP3**. The gradient isosurfaces ( $s = 0.5$  au) are colored over the range  $-0.02$  to  $+0.02$  au in terms of  $\text{sign}(\lambda^2)\rho$ . (b) Counterpoise-corrected interaction energy ( $E_{\text{int}}$ ) analysis based on the fragment molecular orbital scheme.



**Figure 2.** (a) Major contributor to the aldehyde–cobalt porphyrin interactions in second-order perturbation theory analysis of the Fock matrix in NBO basis of **CP2**. LP and LAO denote lone pair and Lewis acceptor orbital, respectively. (b) Counterpoise-corrected interaction energy ( $E_\text{int}$ ) analysis based on the fragment molecular orbital scheme.

To gain further insight of the reaction solution, the author performed solution-phase in situ Co *K*-edge X-ray absorption spectroscopy (XAS) at a synchrotron radiation facility. XAS measurements were carried out using a toluene solution of **CP1** and **1a** at 25 °C. The results of extended X-ray absorption fine structure (EXAFS) analysis are shown in Figure 3a. The spectral features arising from the coordination sphere of the cobalt atoms, i.e., the radial distance of 1.1–2.2 Å, matched well with the spectra simulated using the DFT-calculated structure of complex **CP2** ( $R_\text{f} = 1.7\%$ ), in which **1a** and counteranion  $\text{SbF}_6^-$  were coordinated to the cationic cobalt porphyrin. EXAFS analysis of the coordination sphere of cobalt indicated that the cobalt atoms had octahedral coordination geometry, with the oxygen atom of **1a** and the nearest fluoride atom of  $\text{SbF}_6^-$  located at a distance of 1.89 and 2.01 Å from cobalt, respectively. The structure of complex **CP2** calculated by DFT was consistent with the observed coordination geometry of the cobalt atoms and bond lengths in the coordination sphere (Co–O: 1.91 Å, and Co–F: 2.02 Å). The Co *K*-edge XANES spectra of three different solutions are shown in Figure 4 for the following cases: (1) solution of **CP1** without the addition of **1a** or **3aa**; (2) mixture of **CP1** with **1a** as a representative solution of

**CP2**; and (3) mixture of **CP1** with **3aa** as a representative solution of **CP3**. Clearly, the unique spectral feature was observed only for the mixture of **CP1** with **1a**, suggesting the formation of **CP2**. Meanwhile the addition of **3aa** to **CP1** did not lead to any change in the spectra as compared with that of **CP1**. Thus, the Gibbs energy changes calculated by DFT for the dissociation of **3aa** and coordination of **1a** were also consistent with the observed changes in these three XANES spectra (Figure 3b).



**Figure 3.** (a) Solution-phase Co *K*-edge EXAFS analysis (Fourier transform of  $k^3$ -weighted spectrum,  $\Delta k = 3.0\text{--}11.8 \text{ \AA}^{-1}$ ,  $\Delta R = 1.1\text{--}2.2 \text{ \AA}$ , spatial resolution  $\delta R = 0.133 \text{ \AA}$ ,  $R_f = 1.7\%$ ): simulated spectrum based on DFT structure of **CP2** (red line) and experimental spectrum (black line; mixture of **CP1** and **1a**). (b) Solution-phase Co *K*-edge XANES spectra: **CP1** (black line), **CP2** (red line; mixture of **CP1** and **1a**), and **CP3** (blue line; mixture of **CP1** and **3aa**).

Based on the theoretical study and X-ray spectroscopic analysis, the cobalt porphyrin complex  $[\text{Co}(\text{TPP})]\text{SbF}_6$ , which can be readily prepared using the commercially available  $[\text{Co}(\text{TPP})]\text{Cl}$  and  $\text{AgSbF}_6$ , would be expected to promote the allylation as well. When using  $[\text{Co}(\text{TPP})]\text{SbF}_6$  in place of **CPI**, the reaction temperature had to be elevated to address the insolubility of the complex in organic solvents attributed to the strong  $\pi$ - $\pi$  stacking intermolecular interactions. Nonetheless, the reaction of aldehyde **1a** with allylsilane **2a** in the presence of cationic cobalt porphyrin catalyst  $[\text{Co}(\text{TPP})]\text{SbF}_6$  (1 mol%) afforded homoallylic alcohol **4aa** in 97% yield at 100 °C. Thus, the cationic cobalt porphyrin  $[\text{Co}(\text{TPP})]\text{SbF}_6$ -catalyzed allylation of aldehydes was briefly examined; the results are summarized in Table 1. Under the optimized conditions, aromatic aldehydes possessing variety of functional groups on the phenyl moiety reacted with allylsilane **2a** to afford the corresponding substituted product in good to moderate yields. Aliphatic aldehydes could also participate in the reaction to afford homoallylic alcohols. Of note, the reaction of dicarbonyl compounds such as **1m** and **1s** afforded **4ma** and **4sa** in 99% and 57% yields, respectively, while the use of  $\text{Sc}(\text{OTf})_3$  as the catalyst resulted in lower yields (52% and 14%, respectively). These results highlight the unique reactivity of the  $[\text{Co}(\text{TPP})]\text{SbF}_6$  catalyst. For example, in case of the reaction using **1s**, which has two carbonyl moieties, **1s** acts as a bidentate chelating ligand toward  $\text{Sc}(\text{OTf})_3$ ; thus, dissociation of the product is prevented. Meanwhile, the Co porphyrin has only one d-orbital for available coordination sites, so **1s** behaves as a monodentate ligand; consequently, a higher yield of the product is obtained as compared with that in the case of the  $\text{Sc}(\text{OTf})_3$  catalyst. The use of methylallyltrimethylsilane **2b** instead of **2a** also provided the corresponding product **4pb**. However, the reaction with crotyltrimethylsilane did not afford the desired product. Note that the drawback of the  $[\text{Co}(\text{TPP})]\text{SbF}_6$ -catalyzed reaction is the formation of a side product when employing an aromatic aldehyde with an electron-donating substituent, as is commonly observed with other Lewis acid and Brønsted acid systems.<sup>6</sup> For example, the reaction of anisaldehyde with **2a** afforded a diallylated product **5ua** in 32% yield as the major product, while the desired homoallylic alcohol was not formed (see Experimental section).

To investigate the diastereoselectivity of the cobalt porphyrin-catalyzed allylation, the reaction

of **2a** with 2-phenylpropionaldehyde **1t** was examined, and homoallylic alcohol **4ta** was obtained in 92% yield as a 1:1 diastereomeric mixture. This result indicated that the allylation proceeded via an acyclic transition state for the addition of the allylsilane to the carbonyl carbon of the aldehyde and not via a chairlike sixmembered transition state (the Zimmerman–Traxler model). In order to elucidate the reaction mechanism, the author examined the allylation with allylsilane **2d** possessing a sterically hindered TBDMS group. The reaction did not afford the allylation product **4aa**. This result, along with the reaction scope provided in Table 1, clearly suggested that the plausible ratedetermining step in the catalytic cycle is silyl group migration and not addition of the allylsilane to the aldehyde carbonyl carbon or dissociation to regenerate the initial active Lewis acid cobalt porphyrin complex.

**Table 1.** Allylation reaction of aldehydes **1** with allylsilane **2**<sup>a</sup>

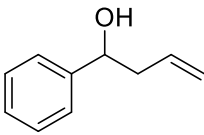
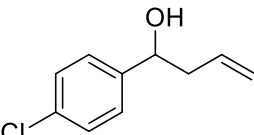
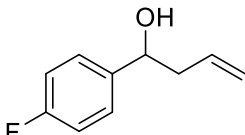
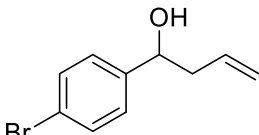
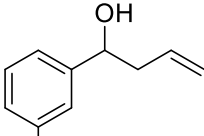
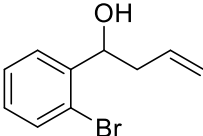
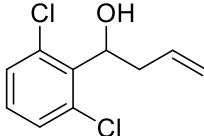
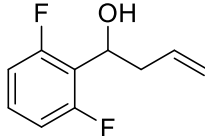
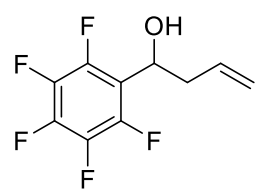
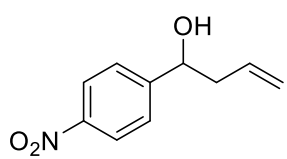
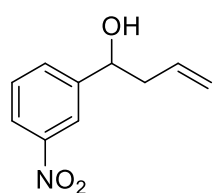
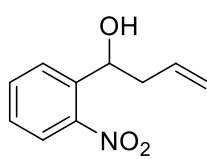
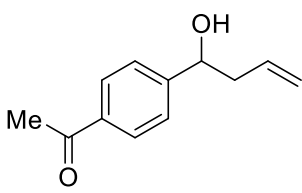
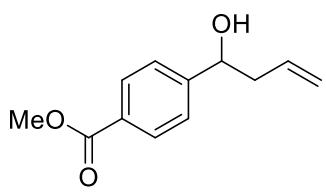
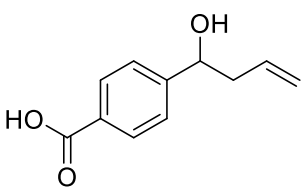
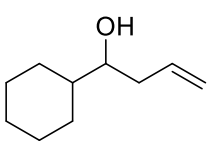
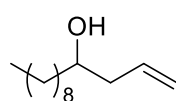
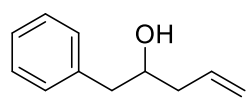
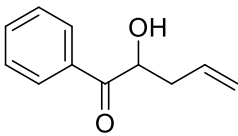
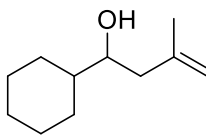
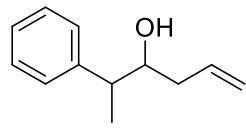
| $  \begin{array}{c} \text{R}^1 \\   \\ \text{O} \\    \\ \text{R}^1-\text{C}-\text{H} \\ \mathbf{1} \end{array}  +   \begin{array}{c} \text{R}^4 \\   \\ \text{R}^2-\text{C}=\text{C}-\text{CH}_2-\text{TMS} \\   \\ \text{R}^3 \\ \mathbf{2} \end{array}  \xrightarrow[2) \text{ TBAF, THF, 25 }^\circ\text{C, 30 min}]{1) [\text{Co}(\text{TPP})]\text{SbF}_6 \text{ (1 mol\%)} \\ 1,2\text{-DCE, 100 }^\circ\text{C, 4 h}}  \begin{array}{c} \text{OH} \quad \text{R}^4 \\   \quad   \\ \text{R}^1-\text{C}-\text{C}-\text{CH}=\text{CH}_2 \\   \quad   \\ \text{R}^2 \quad \text{R}^3 \\ \mathbf{4} \end{array}  $ |  | products <sup>b</sup>                                                                                 |                                                                                                       |                                                                                                        |                                                                                                         |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|-------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | <br><b>4aa</b> 99% | <br><b>4ba</b> 82% | <br><b>4ca</b> 98% | <br><b>4da</b> 95% |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | <br><b>4ea</b> 83% | <br><b>4fa</b> 99% | <br><b>4ga</b> 99% | <br><b>4ha</b> 77% |

Table 1. (continued)

|                                                                                     |                                                                                     |                                                                                       |                                                                                     |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|    |    |     |  |
| <b>4ia</b> 74%                                                                      | <b>4ja</b> 93%                                                                      | <b>4ka</b> 99%                                                                        | <b>4la</b> 12%                                                                      |
|    |    |    |                                                                                     |
| <b>4ma</b> 99% (52%) <sup>c</sup>                                                   | <b>4na</b> 99%                                                                      | <b>4oa</b> 76%                                                                        |                                                                                     |
|   |    |    |                                                                                     |
| <b>4pa</b> 77%                                                                      | <b>4qa</b> 53%                                                                      | <b>4ra</b> 55%                                                                        |                                                                                     |
|  |  |  |                                                                                     |
| <b>4sa</b> 57% (14%) <sup>c</sup>                                                   | <b>4pb</b> 64%                                                                      | <b>4ta</b> 92% ( <i>syn/anti</i> = 1/1) <sup>d</sup>                                  |                                                                                     |

<sup>a</sup>Reaction conditions were carried out using [Co(TPP)]SbF<sub>6</sub> (1 mol %), aldehyde **1** (0.2 mmol), and allylsilane **2** (0.5 mmol) in 1 mL of 1,2-DCE for 4 h. <sup>b</sup>Isolated yields. <sup>c</sup>Reaction with Sc(OTf)<sub>3</sub> catalyst instead of cobalt porphyrin catalyst [Co(TPP)]SbF<sub>6</sub>. <sup>d</sup>Ratio of isomers was determined by <sup>1</sup>H NMR analysis of the crude mixture.

## Conclusion

The author have demonstrated that a cobalt porphyrin Lewis acid can catalyze the allylation of aldehydes with allyltrimethylsilanes for the first time. The use of a cationic cobalt porphyrin complex as the Lewis acid catalyst facilitates activation of the aldehyde via coordination and dissociation of the product, so that the reaction can proceed to completion within a short time under mild conditions. The allylation proceeds with 1 mol% of the cobalt porphyrin catalyst **CP1** at 25 °C within 1 h. The coordination of the aldehyde to the cobalt porphyrin catalyst is demonstrated by Co *K*-edge XAS analysis and DFT calculations. Moreover, allylation with a diverse range of aldehydes can be promoted by the readily available [Co(TPP)]SbF<sub>6</sub>.

## Experimental Section

### Materials.

Unless otherwise noted, commercially available reagents were used without purification.

### Experimental procedure and characterization data for products

#### Preparation of [Co(TArP)]SbF<sub>6</sub> (**CP1**)<sup>7,8</sup>

[Co(TArP)]Cl (0.5 mmol, 531 mg) and AgSbF<sub>6</sub> (0.5 mmol, 171 mg) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (8 mL) and stirred for 12 h in dry box. The reaction mixture was filtered and concentrated to dryness. The complex was used without further purification.

#### *General procedure.*

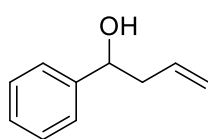
To a screw cap vial was added [Co(TPP)]SbF<sub>6</sub> (0.002 mmol, 1.8 mg), followed by the aldehyde (0.2 mmol), the allylsilane (0.5 mmol) and dry dichloroethane (1.0 mL) in a dry box. The vial was sealed and stirred under the indicated condition. The reaction mixture was diluted with

hexane, passed through a short silica gel pad and washed with diethylether, concentrated in vacuo. The solution was dissolved in THF 2 mL and was added TBAF (in THF 1M 0.4 mL). The solution was stirred for 30 min, and added water (20 mL). The mixture was extracted with diethylether. The organic layer was washed with brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated under reduced pressure. The residue was purified by column chromatography (20 x 300, SiO<sub>2</sub>, hexane/ethylacetate = 5/1 or hexane/ diethylether = 5/1).

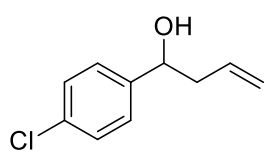
### Representative examples at 1mmol scale reaction

To a screw cap vial was added **CP1** (0.01 mmol), followed by aldehyde **1a** (1.0 mmol), allylsilane **2a** (2.5 mmol) and dry dichloroethane (5.0 mL) in a dry box. The vial was stirred under the indicated condition. The reaction mixture was diluted with hexane, passed through a short silica gel pad and washed with diethylether, concentrated in vacuo. The solution was dissolved in THF 2 mL and was added TBAF (in THF 1M 1.0 mL). The solution was stirred for 30 min, and added water (20 mL). The mixture was extracted with diethylether. The organic layer was washed with brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated under reduced pressure. The residue was purified by column chromatography (20 x 300, SiO<sub>2</sub>, hexane/ethylacetate = 5/1 or hexane/ diethylether = 5/1). The product **4aa** were obtained in 98% yield (145 mg).

#### 1-Phenylbut-3-en-1-ol (**4aa**).



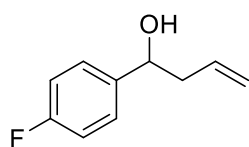
Yield: 99%, colorless oil. TLC: R<sub>f</sub> = 0.17 (hexane/ diethyl ether = 5/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.38–7.34 (m, 4H), 7.31–7.28 (m, 1H), 5.86–5.78 (m, 1H), 5.20–5.14 (m, 2H), 4.76–4.73 (m, 1H), 2.57–2.46 (m, 2H), 2.05 (d, *J* = 3.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.8, 134.4, 128.4, 127.5, 125.8, 118.5, 73.2, 43.9. IR (neat): 3375, 3076, 2907, 2360, 1641, 1494, 1454, 1048, 916, 758, 700 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 171.0778, calcd for [M+Na]<sup>+</sup> 171.0780.

1-(4-Chlorophenyl)but-3-en-1-ol (**4ba**).

Yield: 82%, brown oil. TLC:  $R_f$  = 0.27 (hexane/ethyl acetate = 5/1).  $^1\text{H}$

NMR ( $\text{CDCl}_3$ )  $\delta$  7.33–7.28 (m, 5H), 5.83–5.74 (m, 1H), 5.19–5.15 (m, 1H),  
5.15 (t,  $J$  = 1.0 Hz, 1H), 4.73, (dd,  $J$  = 8.0, 5.0 Hz, 1H), 2.54–2.42 (m, 2H),

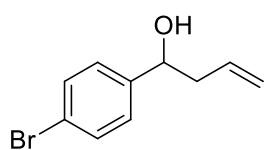
2.00 (br s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  142.3, 134.0, 133.2, 128.5, 127.2, 118.9, 72.5, 43.9. IR (neat):  
3362, 3079, 2933, 2377, 1641, 1297, 1493, 1411, 1092, 919, 830  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found  
205.0380, calcd for  $[\text{M}+\text{Na}]^+$  205.0391.

1-(4-Fluorophenyl)but-3-en-1-ol (**4ca**).

Yield: 98%, colorless oil. TLC:  $R_f$  = 0.31 (hexane/ethyl acetate = 5/1).  $^1\text{H}$

NMR ( $\text{CDCl}_3$ )  $\delta$  7.35–7.31 (m, 2H), 7.06–7.01 (m, 2H), 5.83–5.74 (m, 1H),  
5.19–5.16 (m, 1H), 5.16–5.14 (m, 1H), 4.75–4.70 (m, 1H), 2.54–2.42 (m, 2H),

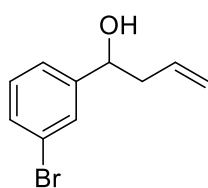
2.08 (d,  $J$  = 2.0 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  162.1 (d,  $J$  = 244 Hz), 139.5 (d,  $J$  = 3.4 Hz), 134.1,  
127.4 (d,  $J$  = 8.1 Hz), 118.8, 115.2 (d,  $J$  = 14.8), 72.5, 44.0. IR (neat): 3384, 3078, 2932, 2362,  
1605, 1510, 1224, 1157, 1051, 920, 836  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 189.0685, calcd for  $[\text{M}+\text{Na}]^+$   
189.0686.

1-(4-Bromophenyl)but-3-en-1-ol (**4da**).

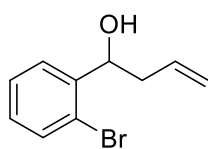
Yield: 95%, red brown oil. TLC:  $R_f$  = 0.60 (hexane/ethyl acetate = 2/1).  $^1\text{H}$

NMR ( $\text{CDCl}_3$ )  $\delta$  7.50 (dd,  $J$  = 3.0, 1.5 Hz, 1H), 7.48 (dd,  $J$  = 2.5, 2.0 Hz,  
1H), 7.26–7.25 (m, 1H), 7.25–7.23 (m, 1H), 5.83–5.75 (m, 1H), 5.20–5.18

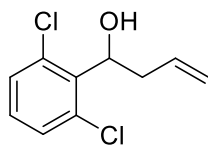
(m, 1H), 5.17–5.15 (m, 1H), 4.72 (t,  $J$  = 4.0 Hz, 1H), 2.54–2.42 (m, 2H), 2.11 (s, 1H).  $^{13}\text{C}$  NMR  
( $\text{CDCl}_3$ )  $\delta$  142.7, 133.9, 131.4, 127.5, 121.2, 119.0, 72.5, 43.9. IR (neat): 3363, 3077, 2932, 2362,  
1902, 1641, 1489, 1404, 1071, 919, 826  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 248.9879, calcd for  $[\text{M}+\text{Na}]^+$   
248.9885.

1-(3-Bromophenyl)but-3-en-1-ol (**4ea**).

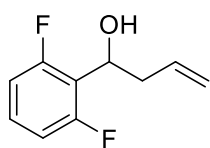
Yield: 83%, yellow oil. TLC:  $R_f$  = 0.34 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.53 (t,  $J$  = 2.0 Hz, 1H), 7.42–7.39 (m, 1H), 7.29–7.27 (m, 1H), 7.22 (t,  $J$  = 8.0 Hz, 1H), 5.83–5.75 (m, 1H), 5.20–5.18 (m, 1H), 5.17 (t,  $J$  = 1.0 Hz, 1H), 4.73–4.69 (m, 1H), 2.55–2.49 (m, 1H), 2.48–2.42 (m, 1H), 2.10 (d,  $J$  = 3.5 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.1, 133.8, 130.5, 130.0, 128.9, 124.4, 122.5, 119.1, 72.4, 43.9. IR (neat): 3363, 3076, 2931, 2362, 1641, 1570, 1430, 1296, 1193, 1071, 919, 784, 679  $\text{cm}^{-1}$ ; HRMS ( $\text{ESI}^+$ ) found 248.9879, calcd for  $[\text{M}+\text{Na}]^+$  248.9855.

1-(2-bromophenyl)but-3-en-1-ol (**4fa**).

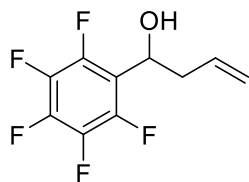
Yield: 99%, yellow solid. Mp. 32 °C. TLC:  $R_f$  = 0.36 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.56 (dd,  $J$  = 8.0, 2.0 Hz, 1H), 7.52 (dd,  $J$  = 8.0, 2.0 Hz, 1H), 7.36–7.33 (m, 1H), 7.15–7.12 (m, 1H), 5.93–5.84 (m, 1H), 5.23–5.18 (m, 2H), 5.12–5.09 (m, 1H), 2.68–2.62 (m, 1H), 2.38–2.32 (m, 1H), 2.19 (d,  $J$  = 3.5 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  142.6, 134.2, 132.6, 128.8, 127.6, 127.3, 121.7, 118.8, 71.7, 42.1. IR (KBr): 3302, 3072, 2940, 1925, 1833, 1641, 1430, 1350, 1220, 1126, 1065, 917, 871, 752  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 248.9881, calcd for  $[\text{M}+\text{Na}]^+$  248.9886.

1-(2,6-Dichlorophenyl)but-3-en-1-ol (**4ga**).

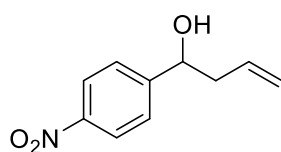
Yield: 99%, red oil. TLC:  $R_f$  = 0.58 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J$  = 8.0 Hz, 2H), 7.14 (dd,  $J$  = 8.5, 7.5 Hz, 1H), 5.88–5.80 (m, 1H), 5.52–5.47 (m, 1H), 5.16–5.08 (m, 2H), 2.91 (d,  $J$  = 10.0 Hz, 1H), 2.88–2.82 (m, 1H), 2.71–2.65 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  137.1, 134.2, 133.8, 129.3, 128.9, 118.2, 71.4, 39.9. IR (neat): 3441, 3079, 2980, 1933, 1859, 1642, 1562, 1438, 1182, 1086, 919, 777  $\text{cm}^{-1}$ ; HRMS ( $\text{ESI}^+$ ) found 238.9996, calcd for  $[\text{M}+\text{Na}]^+$  239.0001.

1-(2,6-Difluorophenyl)but-3-en-1-ol (**4ha**).

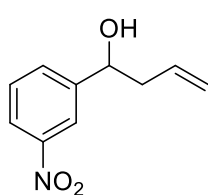
Yield: 77%, colorless oil. TLC:  $R_f$  = 0.36 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.25–7.19 (m, 1H), 6.90–6.84 (m, 2H), 5.83–5.74 (m, 1H), 5.17–5.12 (m, 2H), 5.12–5.08 (m, 1H), 2.78–2.73 (m, 1H), 2.63–2.57 (m, 1H), 2.35 (d,  $J$  = 8.5 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  160.9 (dd,  $J$  = 246.3, 8.6 Hz), 133.5, 129.2 (t,  $J$  = 10.5 Hz), 118.8 (t,  $J$  = 16.5 Hz), 111.5, 111.7 (dd,  $J$  = 20.5, 5.8 Hz), 65.8, 41.7. IR (neat): 2929, 1595, 1460  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 207.0589, calcd for  $[\text{M}+\text{Na}]^+$  207.0592.

1-(Perfluorophenyl)but-3-en-1-ol (**4ia**).

Yield: 74%, brown oil. TLC:  $R_f$  = 0.36 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.79–5.70 (m, 1H), 5.19–5.09 (m, 3H), 2.80–2.74 (m, 1H), 2.63–2.57 (m, 1H), 2.34 (d,  $J$  = 7.0 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.7, 145.6, 145.5, 143.8, 143.7, 141.6, 141.5, 139.6, 139.5, 138.6, 138.5, 136.6, 136.5, 132.4, 119.7, 116.4, 116.2, 65.6, 41.3. IR (neat): 3356, 3085, 2925, 2370, 1653, 1505, 1306, 1127, 992, 928, 874, 780  $\text{cm}^{-1}$ ; HRMS ( $\text{ESI}^+$ ) found 273.0115, calcd for  $[\text{M}+\text{Cl}]^+$  273.0100.

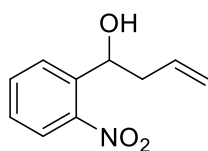
1-(4-Nitrophenyl)but-3-en-1-ol (**4ja**).

Yield: 93%, brown oil. TLC:  $R_f$  = 0.43 (hexane/ethyl acetate = 2/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.23–8.20 (m, 2H), 7.55–7.52 (m, 2H), 5.83–5.75 (m, 1H), 5.22–5.17 (m, 2H), 4.87 (dd,  $J$  = 8.0, 2.5 Hz, 1H), 2.60–2.54 (m, 1H), 2.49–2.43 (m, 1H), 2.19 (br s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  151.0, 147.3, 133.2, 126.6, 123.6, 119.7, 72.2, 43.9. IR (neat): 3405, 3078, 2933, 2360, 1606, 1518, 1347, 1056, 921, 855, 700  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 216.0631, calcd for  $[\text{M}+\text{Na}]^+$  216.0631.

1-(3-Nitrophenyl)but-3-en-1-ol (**4ka**).

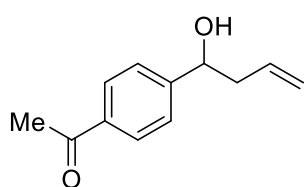
Yield: 99%, colorless oil. TLC:  $R_f$  = 0.49 (hexane/ethyl acetate = 2/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.25–8.24 (m, 1H), 8.15–8.13 (m, 1H), 7.72–7.69 (m, 1H), 7.53 (t,  $J$  = 8.0 Hz, 1H), 5.84–5.76 (m, 1H), 5.23–5.21 (m, 1H), 5.21–5.18 (m, 1H), 4.88–4.85 (m, 1H), 2.61–2.56 (m, 1H), 2.50–2.44 (m, 1H), 2.27 (d,  $J$  = 3.0 Hz, 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  148.2, 145.8, 133.2, 131.9, 129.3, 122.5, 120.8, 119.8, 71.9, 44.0. IR (neat): 3405, 3079, 2916, 2360, 1641, 1529, 1350, 1056, 923, 809, 739, 691  $\text{cm}^{-1}$ ; HRMS ( $\text{ESI}^+$ ) found 216.0629, calcd for  $[\text{M}+\text{Na}]^+$  216.0631.

1-(2-Nitrophenyl)but-3-en-1-ol (**4la**).

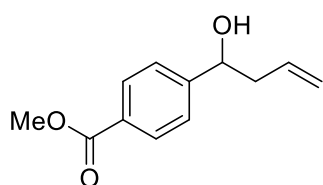
Yield: 12%, brown solid. Mp. 54–55 °C. TLC:  $R_f$  = 0.34 ( $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J$  = 8.5, 1.5 Hz, 1H), 7.84 (dd,  $J$  = 8.5, 1.5 Hz, 1H), 7.68–7.64 (m, 1H), 7.45–7.42 (m, 1H), 5.95–5.86 (m, 1H), 5.32 (dd,  $J$  = 8.5, 4.0 Hz, 1H), 5.24–5.22 (m, 1H), 5.20 (t,  $J$  = 1.5 Hz, 1H), 2.76 (m, 1H), 2.45–2.38 (m, 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  147.7, 139.2, 134.0, 133.5, 128.2, 128.1, 124.5, 119.3, 68.3, 42.9. IR (KBr): 3302, 2917, 1641, 1523, 1338, 1059, 990, 935, 859, 792, 702  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 216.0629, calcd for  $[\text{M}+\text{Na}]^+$  216.0631.

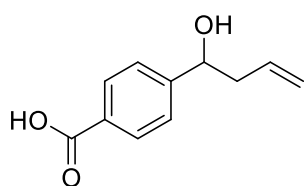
1-(4-(1-Hydroxybut-3-en-1-yl)phenyl)ethanone (**4ma**).

Yield: 99%, yellow oil. TLC:  $R_f$  = 0.33 (hexane/ethyl acetate = 2/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.96–7.93 (m, 2H), 7.47–7.44 (m, 2H), 5.83–5.75 (m, 1H), 5.20–5.18 (m, 1H), 5.17–5.16 (m, 1H), 4.82 (dd, 1H), 2.61 (s, 3H), 2.60–2.52 (m, 1H), 2.50–2.43 (m, 1H), 2.12 (br s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

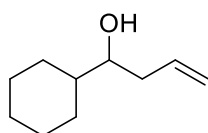
$\delta$  197.9, 149.1, 136.2, 133.7, 128.5, 125.9, 119.2, 72.6, 43.9, 26.7. IR (neat): 3410, 3077, 2927, 2358, 1678, 1668, 1609, 1413, 1360, 1270, 1057, 918, 835  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 191.1064, calcd for  $[\text{M}+\text{H}]^+$  191.1067.

Methyl 4-(1-hydroxybut-3-en-1-yl)benzoate (**4na**).

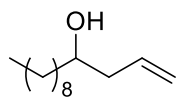
Yield: 99%, yellow oil. TLC:  $R_f$  = 0.47 (hexane/ethyl acetate = 2/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.03–8.01 (m, 2H), 7.44–7.42 (m, 2H), 5.83–5.75 (m, 1H), 5.20–5.18 (m, 1H), 5.17–5.15 (m, 1H), 3.91 (s, 3H), 2.57–2.52 (m, 1H), 2.50–2.43 (m, 1H), 2.19 (d,  $J$  = 3.0 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  166.9, 148.9, 133.8, 129.7, 129.2, 125.7, 119.2, 72.6, 52.1, 43.9. IR (neat): 3461, 3077, 2952, 2362, 1942, 1723, 1699, 1641, 1612, 1436, 1282, 1193, 1114, 1019, 918, 771  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 207.1013, calcd for  $[\text{M}+\text{H}]^+$  207.1016.

4-(1-Hydroxybut-3-en-1-yl)benzoic acid (**4oa**).

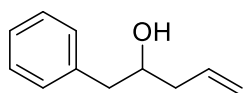
Yield: 76%, brown solid. Mp. 105–107 °C (hexane/ethyl acetate). TLC:  $R_f$  = 0.28 (hexane/ethyl acetate = 1/3).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J$  = 8.0 Hz, 2H), 7.47 (d,  $J$  = 8.0 Hz, 2H), 5.85–5.75 (m, 1H), 5.22–5.19 (m, 1H), 5.18–5.16 (m, 1H), 4.84 (dd,  $J$  = 8.0, 4.5 Hz, 1H), 2.60–2.54 (m, 1H), 2.51–2.44 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  171.7, 149.8, 133.7, 130.4, 128.3, 125.8, 119.3, 72.6, 43.9. IR (KBr): 3362, 2888, 2671, 2547, 2696, 1680, 1612, 1425, 1290, 1181, 1054, 990, 918  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 215.0675, calcd for  $[\text{M}+\text{Na}]^+$  215.0679.

1-Cyclohexylbut-3-en-1-ol (**4pa**).

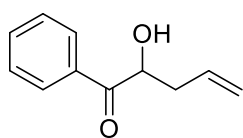
Yield: 77%, colorless oil. TLC:  $R_f$  = 0.29 (hexane/diethyl ether = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.87–5.79 (m, 1H), 5.16–5.13 (m, 1H), 5.13–5.12 (m, 1H), 3.40–3.36 (m, 1H), 2.35–2.30 (m, 1H), 2.15–2.09 (m, 1H), 1.87–0.98 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  135.4, 118.1, 74.6, 43.0, 38.8, 29.0, 28.1, 26.5, 26.2, 26.1. IR (neat): 3392, 2852, 1640, 1451, 986, 910  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 177.1246, calcd for  $[\text{M}+\text{Na}]^+$  177.1250.

Tridec-1-en-4-ol (**4qa**).

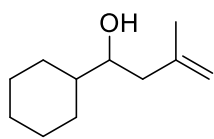
Yield: 53%, yellow oil. TLC:  $R_f$  = 0.20 (hexane/ diethyl ether = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.87–5.79 (m, 1H), 5.16–5.14 (m, 1H), 5.13–5.11 (m, 1H), 3.67–3.61 (m, 1H), 2.33–2.28 (m, 1H), 2.17–2.10 (m, 1H), 1.57 (d,  $J$  = 4.0 Hz, 1H), 1.49–1.40 (m, 3H), 1.34–1.21 (m, 13H), 0.88 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  134.9, 118.1, 70.6, 41.9, 36.8, 31.9, 29.63, 29.60, 29.56, 29.3, 25.7, 22.7, 14.1. IR (neat): 3346, 3078, 2925, 1641, 1466, 994, 912  $\text{cm}^{-1}$ .  $^1$ . HRMS ( $\text{ESI}^+$ ) found 221.1873, calcd for  $[\text{M}+\text{Na}]^+$  221.1876.

1-Phenylpent-4-en-2-ol (**4ra**).

Yield: 55%, colorless oil. TLC:  $R_f$  = 0.33 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.34–7.29 (m, 2H), 7.26–7.22 (m, 3H), 5.91–5.83 (m, 1H), 5.19–5.16 (m, 1H), 5.15 (t,  $J$  = 1.5 Hz, 1H), 3.92–3.86 (m, 1H), 2.84–2.81 (m, 1H), 2.75–2.71 (m, 1H), 2.38–2.32 (m, 1H), 2.38–2.32 (m, 1H), 2.26–2.20 (m, 1H), 1.71 (d,  $J$  = 3.0 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  142.0, 134.6, 128.42, 128.38, 125.8, 118.5, 69.8, 42.1, 38.4, 32.0. IR (neat): 3393, 3064, 2925, 2362, 1641, 1604, 1496, 1454, 1079, 915, 745, 700  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 185.0936, calcd for  $[\text{M}+\text{Na}]^+$  185.0937.

2-Hydroxy-1-phenylpent-4-en-1-one (**4sa**).

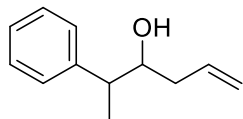
Yield: 57%, brown oil. TLC:  $R_f$  = 0.29 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.93–7.90 (m, 2H), 7.66–7.62 (m, 1H), 7.54–7.50 (m, 2H), 5.84–5.75 (m, 1H), 5.20–5.16 (m, 1H), 5.10–5.07 (m, 1H), 5.04–4.99 (m, 1H), 3.76 (d,  $J$  = 6.5 Hz, 1H), 2.71–2.65 (m, 1H), 2.39–2.32 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  201.2, 134.1, 133.5, 132.3, 128.9, 128.5, 118.5, 72.6, 40.4. IR (neat): 3454, 3078, 2948, 2356, 1684, 1262, 1074, 963, 922, 698  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 215.0675, calcd for  $[\text{M}+\text{H}]^+$  215.0679.

1-Cyclohexyl-3-methylbut-3-en-1-ol (**4pb**).

Yield: 64%, colorless oil. TLC:  $R_f$  = 0.35 (hexane/ diethyl ether = 5/1).  $^1\text{H}$  NMR

( $\text{CDCl}_3$ )  $\delta$  4.90–4.88 (m, 1H), 4.81–4.79 (m, 1H), 3.49–3.45 (m, 1H), 2.26–2.22 (m, 1H), 2.09–2.03 (m, 1H), 1.89–1.83 (m, 1H), 1.79–1.74 (m, 5H), 1.72–1.64

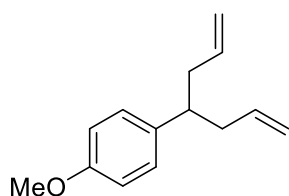
(m, 3H), 1.40–1.32 (m, 1H), 1.30–1.00 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  143.3, 113.5, 72.4, 43.4, 43.0, 29.0, 28.2, 26.6, 26.3, 26.2, 22.2. IR (neat): 3436, 3074, 2926, 1654, 1451, 1102, 1045, 891  $\text{cm}^{-1}$ ; HRMS ( $\text{ESI}^+$ ) found 191.1404, calcd for  $[\text{M}+\text{Na}]^+$  191.1406.

2-Phenylhex-5-en-3-ol (**4ta**).

Yield: 92%, colorless oil. TLC:  $R_f$  = 0.47 (hexane/ethyl acetate = 5/1).  $^1\text{H}$  NMR

( $\text{CDCl}_3$ )  $\delta$  7.35–7.31 (m, 2H), 7.27–7.23 (m, 3H), 5.93–5.85 (m, 1H), 5.16–5.14 (m, 1H), 5.12 (t,  $J$  = 1.5 Hz, 1H), 3.77–3.72 (m, 1H), 2.84–2.78 (m,

1H), 2.43–2.37 (m, 1H), 2.15–2.08 (m, 1H), 1.51 (d,  $J$  = 3.5 Hz, 1H), 1.30 (d,  $J$  = 8.0 Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  143.2, 135.0, 128.5, 128.1, 126.7, 117.8, 73.9, 45.3, 38.9, 17.7 (for anti);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.34–7.30 (m, 2H), 7.24–7.20 (m, 3H), 5.84–5.75 (m, 1H), 5.14–5.08 (m, 2H), 3.75–3.69 (m, 1H), 2.81–2.75 (m, 1H), 2.22–2.16 (m, 1H), 2.06–1.99 (m, 1H), 1.66 (d,  $J$  = 4.0 Hz, 1H), 1.35 (d,  $J$  = 7.5 Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  144.3, 135.0, 128.5, 127.8, 126.5, 118.3, 74.9, 45.3, 39.5, 16.4 (for syn); IR (neat): 3394, 3080, 2964, 2364, 1654, 1602, 1452, 1262, 1081, 1011, 912, 798, 701  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 199.1090, calcd for  $[\text{M}+\text{Na}]^+$  199.1093.

1-(Hepta-1,6-dien-4-yl)-4-methoxybenzene (**5ua**).

Yield: 32%, colorless oil. TLC:  $R_f$  = 0.36 (hexane/ethyl acetate = 20/1).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.09–7.05 (m, 2H), 6.87–6.82 (m, 2H), 5.71–5.62 (m, 2H), 5.00–4.91 (m, 4H), 3.79 (s, 3H), 2.70–2.64 (m, 1H), 2.50–2.28 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  157.8, 136.9, 136.7, 128.5, 116.0, 113.6, 55.2,

44.7, 40.5. IR (neat): 2921, 2362, 1641, 1612, 1513, 1442, 1248, 1178, 1039, 911, 828  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 201.1274, calcd for  $[\text{M}+\text{H}]^+$  201.1285.

## Supplemental Data

### Computational Details

General Methods. Calculations were performed on Gaussian 09 E.01.<sup>3</sup> For geometry optimization and frequency calculations ONIOM (B3LYP: UFF) was used and M06 was used for single-point energy calculations. Geometry optimization and frequency calculations were carried out using 6-31+G(d) (H, C, N, F) and f polarization function added Lanl2dz(f) (Co, Sb) basis sets. Solvation effects of toluene were added all calculations using ONIOM-PCM-X (toluene). Single-point calculations were performed with M06 functional and CPCM (toluene). Def2-TZVP basis sets were used for all atoms. Second order perturbation theory analysis of Fock matrix in NBO basis was calculated with the NBO 6.0 program. The weak interactions are further confirmed by analysis of non-covalent interactions with NCIPLOT.

Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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#### Cartesian Coordinates for **CP1**

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## Chapter 1

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C -3.22598500000 -8.16072400000 5.45840400000  
H -2.44901700000 -8.83632500000 5.87281100000  
H -4.19044500000 -8.43003200000 5.94127100000  
H -3.31408800000 -8.35794500000 4.36802600000  
C 1.60643600000 5.08928200000 3.88473500000  
C 0.96535500000 6.48201500000 3.69921200000  
H 0.38875800000 6.79084500000 4.59591000000  
H 1.74497100000 7.25498100000 3.52435500000  
H 0.27675300000 6.47655600000 2.82658700000  
C 2.51247300000 4.82389700000 2.65718700000  
H 3.03187600000 3.84573100000 2.75164500000  
H 1.92035800000 4.83711800000 1.71642400000  
H 3.29540900000 5.60820400000 2.56786600000  
C 2.50938500000 5.10165600000 5.13756500000  
H 3.34512400000 5.82428000000 5.01422000000  
H 1.94612600000 5.39966700000 6.04629600000

H 7.043389000000 -4.938944000000 -5.059441000000  
 H 5.665221000000 -5.420177000000 -6.093896000000  
 H 5.686007000000 -3.786433000000 -5.337510000000  
 C 5.787958000000 -4.665294000000 -2.695301000000  
 H 5.621980000000 -3.568967000000 -2.774170000000  
 H 5.324536000000 -5.041979000000 -1.757725000000  
 H 6.884472000000 -4.829854000000 -2.613027000000  
 C 2.110503000000 -7.506457000000 5.064990000000  
 C 2.397104000000 -7.292201000000 6.567353000000  
 H 1.576928000000 -7.687861000000 7.201903000000  
 H 3.330824000000 -7.814665000000 6.869122000000  
 H 2.516226000000 -6.209025000000 6.786765000000  
 C 1.885565000000 -9.010285000000 4.793875000000  
 H 1.632393000000 -9.175782000000 3.724209000000  
 H 2.800811000000 -9.595109000000 5.030880000000  
 H 1.061739000000 -9.420486000000 5.414260000000

#### Cartesian Coordinates for **CP2**

N -0.207433000000 -3.531587000000 -0.179242000000  
 N -0.359413000000 -1.626117000000 1.827223000000  
 C -0.517646000000 -4.053362000000 2.206958000000  
 C -0.282492000000 -4.407180000000 0.872046000000  
 C 0.526058000000 -5.596209000000 -0.873736000000  
 H 0.908517000000 -6.377254000000 -1.518668000000  
 C 0.331088000000 -3.717852000000 -2.568168000000  
 C -0.452658000000 -2.725825000000 2.648441000000  
 C 0.270326000000 -4.225782000000 -1.265274000000  
 C 0.123076000000 -5.722553000000 0.419462000000  
 H 0.138981000000 -6.618442000000 1.027755000000  
 C -0.121163000000 -0.532611000000 2.622123000000  
 C -0.304955000000 -2.296037000000 4.024187000000  
 H -0.366133000000 -2.934243000000 4.896540000000  
 C -0.039495000000 -0.962593000000 4.003348000000  
 H 0.137031000000 -0.316183000000 4.854258000000  
 N -0.977796000000 0.304672000000 -0.066150000000  
 N -0.830042000000 -1.606560000000 -2.059057000000  
 C -2.017925000000 0.531640000000 -2.292980000000  
 C -1.654522000000 1.016656000000 -1.029778000000  
 C -1.103429000000 2.506743000000 0.580111000000  
 H -0.974048000000 3.404264000000 1.171868000000  
 C -0.145364000000 0.802539000000 2.196101000000  
 C -1.532107000000 -0.680946000000 -2.796383000000  
 C -0.656237000000 1.179786000000 0.946758000000  
 C -1.768305000000 2.394122000000 -0.602136000000  
 H -2.259932000000 3.184474000000 -1.155959000000  
 C -0.316452000000 -2.530960000000 -2.936329000000

H 2.942565000000 4.092733000000 5.310867000000  
 C -2.406766000000 3.392758000000 6.545654000000  
 C -3.133595000000 4.750019000000 6.424396000000  
 H -3.862449000000 4.882481000000 7.253305000000  
 H -2.422940000000 5.601372000000 6.469747000000  
 H -3.685532000000 4.807429000000 5.461237000000  
 C -1.595846000000 3.359434000000 7.859757000000  
 H -0.873031000000 4.199700000000 7.917438000000  
 H -2.268863000000 3.441001000000 8.740813000000  
 H -1.029653000000 2.406168000000 7.939614000000  
 C -3.488121000000 2.288512000000 6.635704000000  
 H -4.132023000000 2.289232000000 5.729646000000  
 H -3.022159000000 1.286439000000 6.756109000000  
 H -4.150022000000 2.455202000000 7.513365000000  
 Co -0.506470000000 -1.456848000000 -0.011386000000

H -8.507561000000 3.081680000000 -4.151156000000  
 H -7.093728000000 4.172955000000 -4.291750000000  
 H -7.305617000000 2.790287000000 -5.447451000000  
 C -6.874791000000 2.683640000000 -1.994739000000  
 H -7.964644000000 2.733154000000 -1.781159000000  
 H -6.421723000000 2.000852000000 -1.245921000000  
 H -6.443387000000 3.697536000000 -1.848087000000  
 C -7.171264000000 0.762129000000 -3.599484000000  
 H -6.954878000000 0.378167000000 -4.619932000000  
 H -6.721402000000 0.064616000000 -2.862312000000  
 H -8.271945000000 0.742381000000 -3.444718000000  
 C 0.596087000000 -7.537436000000 -5.850250000000  
 C 1.494571000000 -8.208431000000 -6.917323000000  
 H 0.991902000000 -9.099861000000 -7.351919000000  
 H 1.708334000000 -7.507684000000 -7.753312000000  
 H 2.452139000000 -8.552609000000 -6.469848000000  
 C 0.305420000000 -8.588716000000 -4.756515000000  
 H 1.241433000000 -8.856219000000 -4.219911000000  
 H -0.427343000000 -8.213702000000 -4.011853000000  
 H -0.119113000000 -9.514592000000 -5.201906000000  
 C -0.726189000000 -7.134649000000 -6.539299000000  
 H -1.467704000000 -6.748585000000 -5.809166000000  
 H -0.540486000000 -6.344366000000 -7.298629000000  
 H -1.187352000000 -8.008147000000 -7.049392000000  
 C 4.506329000000 -4.205307000000 -5.396375000000  
 C 5.530790000000 -5.330300000000 -5.131795000000  
 H 5.314510000000 -6.233916000000 -5.738754000000  
 H 6.558982000000 -4.996297000000 -5.390911000000  
 H 5.517598000000 -5.619301000000 -4.058512000000

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C -1.502201000000 -1.072021000000 -4.188909000000  
H -2.001836000000 -0.556848000000 -4.999666000000  
C -0.701685000000 -2.169880000000 -4.282401000000  
H -0.448012000000 -2.725175000000 -5.177001000000  
Sb -4.279135000000 -2.844577000000 -0.133360000000  
F -4.070591000000 -2.517388000000 -1.980385000000  
F -5.955261000000 -3.664354000000 -0.393708000000  
F -5.062882000000 -1.139585000000 0.073265000000  
F -4.357278000000 -3.110488000000 1.733539000000  
F -2.546611000000 -1.958109000000 0.173139000000  
F -3.365581000000 -4.483574000000 -0.328776000000  
C 0.264624000000 1.854690000000 3.153794000000  
C -0.700428000000 2.570930000000 3.867796000000  
C 1.623015000000 2.106611000000 3.360085000000  
C -0.325578000000 3.567773000000 4.792258000000  
H -1.737055000000 2.330520000000 3.682572000000  
C 2.469990000000 -6.250315000000 5.836315000000  
H 2.902793000000 -6.375302000000 4.820128000000  
H 2.307367000000 -5.169165000000 6.037368000000  
H 3.225723000000 -6.614333000000 6.566069000000  
C -3.604210000000 -7.565228000000 4.180886000000  
C -4.218472000000 -7.399688000000 5.588175000000  
H -5.218386000000 -7.882602000000 5.641345000000  
H -3.584075000000 -7.866356000000 6.370238000000  
H -4.337526000000 -6.321925000000 5.832826000000  
C -4.633722000000 -7.030893000000 3.154953000000  
H -4.856872000000 -5.957622000000 3.339178000000  
H -4.259955000000 -7.156189000000 2.115549000000  
H -5.593014000000 -7.587570000000 3.232274000000  
C -3.388474000000 -9.066047000000 3.887445000000  
H -2.746595000000 -9.545952000000 4.655294000000  
H -4.358110000000 -9.609736000000 3.879455000000  
H -2.904791000000 -9.199552000000 2.895541000000  
C 3.536867000000 3.402544000000 4.533016000000  
C 3.821381000000 4.880443000000 4.186307000000  
H 3.249559000000 5.572457000000 4.838988000000  
H 4.899756000000 5.116028000000 4.318502000000  
H 3.545121000000 5.089029000000 3.130005000000  
C 4.495961000000 2.530275000000 3.686504000000  
H 4.361514000000 1.451848000000 3.920109000000  
H 4.327995000000 2.695779000000 2.600192000000  
H 5.556142000000 2.787034000000 3.901603000000  
C 3.867206000000 3.150799000000 6.020565000000  
H 4.947199000000 3.323717000000 6.219511000000  
H 0.585308000000 -9.179152000000 5.919110000000  
C 3.246409000000 -0.595226000000 -1.435208000000

C 4.493995000000 -3.864296000000 -6.902369000000  
H 5.484640000000 -3.478499000000 -7.227410000000  
H 4.266370000000 -4.755817000000 -7.523014000000  
H 3.729110000000 -3.086333000000 -7.115349000000  
C 4.989525000000 -2.945746000000 -4.635330000000  
H 4.308881000000 -2.085914000000 -4.817242000000  
H 5.050529000000 -3.142214000000 -3.543024000000  
H 6.003909000000 -2.642830000000 -4.974807000000  
C 1.147018000000 -7.042457000000 5.974363000000  
C 0.643308000000 -6.860219000000 7.423008000000  
H -0.244119000000 -7.493294000000 7.631649000000  
H 1.431623000000 -7.144548000000 8.153474000000  
H 0.365301000000 -5.799299000000 7.604187000000  
C 1.466354000000 -8.532718000000 5.724759000000  
H 1.786928000000 -8.687489000000 4.671719000000  
H 2.284492000000 -8.878099000000 6.393508000000  
C 3.730084000000 0.219746000000 -2.477924000000  
C 5.092633000000 0.239302000000 -2.768360000000  
C 5.971054000000 -0.551593000000 -2.019193000000  
H 6.186739000000 -1.975291000000 -0.406995000000  
H 3.749283000000 -2.018579000000 0.112861000000  
H 3.035976000000 0.824160000000 -3.056261000000  
H 5.469081000000 0.861382000000 -3.574594000000  
H 7.033158000000 -0.540478000000 -2.248041000000  
C 1.818101000000 -0.620811000000 -1.194260000000  
O 1.304888000000 -1.335199000000 -0.309770000000  
H 1.178272000000 -0.000199000000 -1.829144000000  
H 3.295479000000 3.828536000000 6.688162000000  
H 3.624411000000 2.102010000000 6.297559000000  
C -1.357914000000 4.389566000000 5.593632000000  
C -1.186327000000 5.889674000000 5.268503000000  
H -1.951041000000 6.498148000000 5.798441000000  
H -0.190079000000 6.266007000000 5.581088000000  
H -1.297566000000 6.062833000000 4.176117000000  
C -1.136026000000 4.162441000000 7.105047000000  
H -0.139106000000 4.524346000000 7.432245000000  
H -1.898723000000 4.708149000000 7.702006000000  
H -1.211055000000 3.080258000000 7.347679000000  
C -2.823050000000 4.006136000000 5.272465000000  
H -3.052087000000 4.180479000000 4.198741000000  
H -3.018062000000 2.940816000000 5.522768000000  
H -3.531634000000 4.622205000000 5.867906000000  
Co -0.571637000000 -1.610040000000 -0.119991000000  
C 5.494320000000 -1.364182000000 -0.978151000000  
C 4.136704000000 -1.390991000000 -0.683275000000

Cartesian Coordinates for **CP3**

N -0.083026000000 -3.275207000000 -0.078249000000  
 N -0.303056000000 -1.318119000000 1.855882000000  
 C -0.281867000000 -3.736763000000 2.319316000000  
 C -0.149634000000 -4.144884000000 1.005949000000  
 C 0.458880000000 -5.409097000000 -0.764170000000  
 H 0.746921000000 -6.211777000000 -1.431048000000  
 C 0.405723000000 -3.521218000000 -2.480208000000  
 C -0.212063000000 -2.364903000000 2.706757000000  
 C 0.289741000000 -4.012342000000 -1.142930000000  
 C 0.132400000000 -5.499555000000 0.547199000000  
 H 0.118483000000 -6.390795000000 1.161429000000  
 C -0.025437000000 -0.175632000000 2.593192000000  
 C 0.115454000000 -1.899263000000 4.047466000000  
 H -0.076468000000 -2.422483000000 -5.160098000000  
 Sb -4.370311000000 -2.955936000000 -0.314493000000  
 F -3.855619000000 -2.644713000000 -2.112705000000  
 F -5.846884000000 -3.989136000000 -0.883095000000  
 F -5.412010000000 -1.374355000000 -0.342696000000  
 F -4.821983000000 -3.237861000000 1.503136000000  
 F -2.869560000000 -1.901019000000 0.272753000000  
 F -3.260544000000 -4.492970000000 -0.274978000000  
 C 0.357722000000 2.229166000000 2.947377000000  
 C -0.490029000000 3.032601000000 3.714231000000  
 C 1.738269000000 2.443152000000 2.967769000000  
 C 0.025919000000 4.086274000000 4.497938000000  
 H -1.547432000000 2.815035000000 3.681211000000  
 C 2.301812000000 3.475586000000 3.743402000000  
 H 2.352163000000 1.786507000000 2.368503000000  
 C 1.424510000000 4.288323000000 4.494677000000  
 H 1.837376000000 5.088752000000 5.089446000000  
 C -0.370640000000 -4.758705000000 3.385253000000  
 C -1.606915000000 -5.040988000000 3.970014000000  
 C 0.780562000000 -5.425407000000 3.813664000000  
 C -1.721347000000 -6.007872000000 4.990180000000  
 H -2.465526000000 -4.494517000000 3.607784000000  
 C 0.716288000000 -6.400304000000 4.830265000000  
 H 1.713587000000 -5.164483000000 3.336342000000  
 C -0.545964000000 -6.674527000000 5.401917000000  
 H -0.614632000000 -7.418679000000 6.180606000000  
 C -2.959935000000 1.388635000000 -3.246851000000  
 C -2.526861000000 2.572287000000 -3.850828000000  
 C -4.217970000000 0.867490000000 -3.552593000000  
 C -3.355015000000 3.269834000000 -4.755271000000  
 H -1.537866000000 2.926061000000 -3.599305000000  
 C -5.079038000000 1.520631000000 -4.454031000000

H 0.226990000000 -2.525211000000 4.923869000000  
 C 0.287886000000 -0.556778000000 3.965108000000  
 H 0.543579000000 0.125833000000 4.765946000000  
 N -1.068889000000 0.523610000000 -0.083442000000  
 N -0.801382000000 -1.437732000000 -2.029405000000  
 C -2.073542000000 0.652486000000 -2.316603000000  
 C -1.818282000000 1.172999000000 -1.059785000000  
 C -1.458058000000 2.700047000000 0.567603000000  
 H -1.425792000000 3.600491000000 1.166746000000  
 C -0.185345000000 1.119794000000 2.132000000000  
 C -1.439833000000 -0.533946000000 -2.798768000000  
 C -0.843919000000 1.422700000000 0.901066000000  
 C -2.112419000000 2.526081000000 -0.607235000000  
 H -2.705085000000 3.259823000000 -1.138209000000  
 C -0.196152000000 -2.346905000000 -2.893347000000  
 C -1.258499000000 -0.850361000000 -4.210223000000  
 H -1.677390000000 -0.296817000000 -5.041004000000  
 C -0.439115000000 -1.927423000000 -4.268744000000  
 H -3.585125000000 6.683584000000 -5.490945000000  
 H -4.929908000000 5.505179000000 -5.431671000000  
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 C -1.502349000000 5.049690000000 -5.010012000000  
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 H -0.737836000000 4.294066000000 -5.293129000000  
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 C -6.459657000000 0.901618000000 -4.761785000000  
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 H -8.273565000000 1.249258000000 -5.962458000000  
 H -7.491794000000 2.750356000000 -5.374884000000  
 H -6.763882000000 1.811485000000 -6.746385000000  
 C -7.279103000000 0.796051000000 -3.456720000000  
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 H -6.796812000000 0.116296000000 -2.723672000000  
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 H -5.778589000000 -1.197815000000 -4.642744000000  
 H -7.248075000000 -0.957442000000 -5.635560000000  
 C 0.620316000000 -6.517301000000 -6.535976000000  
 C 1.582713000000 -7.295651000000 -7.465569000000  
 H 1.019239000000 -7.812062000000 -8.273041000000  
 H 2.305947000000 -6.606958000000 -7.953695000000

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H -4.519611000000 -0.057076000000 -3.078654000000  
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C 0.589011000000 -5.019499000000 -4.474578000000  
C 2.593177000000 -4.376822000000 -3.280735000000  
C 1.344485000000 -5.774422000000 -5.392622000000  
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C 3.393396000000 -5.128763000000 -4.164017000000  
H 3.024637000000 -3.822070000000 -2.460521000000  
C 2.748827000000 -5.813487000000 -5.219585000000  
H 3.360223000000 -6.378745000000 -5.902161000000  
C -2.918620000000 4.587732000000 -5.432102000000  
C -3.907009000000 5.713063000000 -5.054649000000  
H 6.707130000000 -4.653592000000 -5.179410000000  
H 5.340430000000 -5.222656000000 -6.186589000000  
H 5.278091000000 -3.586118000000 -5.437943000000  
C 5.471292000000 -4.436860000000 -2.795000000000  
H 5.241283000000 -3.354025000000 -2.884001000000  
H 5.039519000000 -4.828411000000 -1.848475000000  
H 6.576407000000 -4.534286000000 -2.721959000000  
C 1.961119000000 -7.165681000000 5.327929000000  
C 2.159481000000 -6.902044000000 6.836739000000  
H 1.308235000000 -7.286807000000 7.436030000000  
H 3.079057000000 -7.404878000000 7.207413000000  
H 2.256239000000 -5.811369000000 7.028336000000  
C 1.763099000000 -8.678918000000 5.091878000000  
H 1.575045000000 -8.879938000000 4.014890000000  
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H 3.193499000000 -6.944372000000 3.513223000000  
H 3.477455000000 -5.667486000000 4.770608000000  
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C -2.981454000000 -6.066832000000 7.173571000000  
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H -1.170934000000 -7.031608000000 -5.348517000000  
H -0.878580000000 -8.114241000000 -6.743344000000  
C -0.146703000000 -5.497476000000 -7.406471000000  
H -0.939139000000 -4.978513000000 -6.827812000000  
H 0.550866000000 -4.730373000000 -7.807191000000  
H -0.640501000000 -6.003358000000 -8.264424000000  
C 4.928290000000 -5.218969000000 -4.016389000000  
C 5.345547000000 -6.696100000000 -3.843242000000  
H 5.098124000000 -7.301556000000 -4.739717000000  
H 6.442256000000 -6.779933000000 -3.681719000000  
H 4.828360000000 -7.142547000000 -2.966387000000  
C 5.600051000000 -4.638310000000 -5.279336000000  
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C -0.701552000000 6.470867000000 4.876094000000  
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H -0.942526000000 6.559411000000 3.794539000000  
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H 0.566528000000 5.244733000000 7.004765000000  
H -1.139911000000 5.518696000000 7.469565000000  
H -0.549085000000 3.841765000000 7.174130000000  
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H -2.733787000000 4.753982000000 4.189371000000  
H -2.572206000000 3.626633000000 5.601432000000  
H -2.990008000000 5.349485000000 5.860085000000  
C 4.680818000000 -0.897807000000 0.701395000000  
H 4.445890000000 0.105552000000 1.088161000000  
C 6.176529000000 -1.126743000000 0.881174000000  
C 6.837935000000 -0.563546000000 1.982275000000  
C 6.910098000000 -1.922688000000 -0.007821000000  
C 8.201247000000 -0.790247000000 2.193614000000  
H 6.286381000000 0.062275000000 2.681282000000  
C 8.274415000000 -2.150060000000 0.197647000000  
H 6.409195000000 -2.355146000000 -0.866987000000  
C 8.925449000000 -1.586001000000 1.299568000000  
H 8.697289000000 -0.340153000000 3.050052000000  
H 8.828312000000 -2.768764000000 -0.504362000000  
H 9.986590000000 -1.760576000000 1.457969000000  
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H 4.356364000000 -5.364349000000 1.512212000000  
Co -0.622212000000 -1.392512000000 -0.076194000000

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## Chapter 2

### **FeCl<sub>3</sub>-Catalyzed Aza-Diels–Alder Reaction of Non-Activated Substrates: New Insight on FeCl<sub>3</sub> as Lewis Acid Catalyst**

The new aspect on FeCl<sub>3</sub> as a Lewis acid catalyst have been disclosed. The ion-paired species, [FeCl<sub>2</sub>]<sup>+</sup>[FeCl<sub>4</sub>]<sup>−</sup>, was generated by the in situ disproportionation of FeCl<sub>3</sub>, and this ionic species acting as an ion-paired catalyst attributed to both the highly Lewis acidic [FeCl<sub>2</sub>]<sup>+</sup> and thermodynamically stable [FeCl<sub>4</sub>]<sup>−</sup>. Synchrotron-based X-ray absorption fine structure measurements provided insight into the disproportionation and structure of the resulting ion-paired iron complex. A theoretical study was performed to analyze the catalytic reaction and better understand the “ion-pairing effect” which transforms simple FeCl<sub>3</sub> into a high turnover frequency Lewis acid catalyst in the aza-Diels–Alder reaction of non-activated dienes and imines.

## Introduction

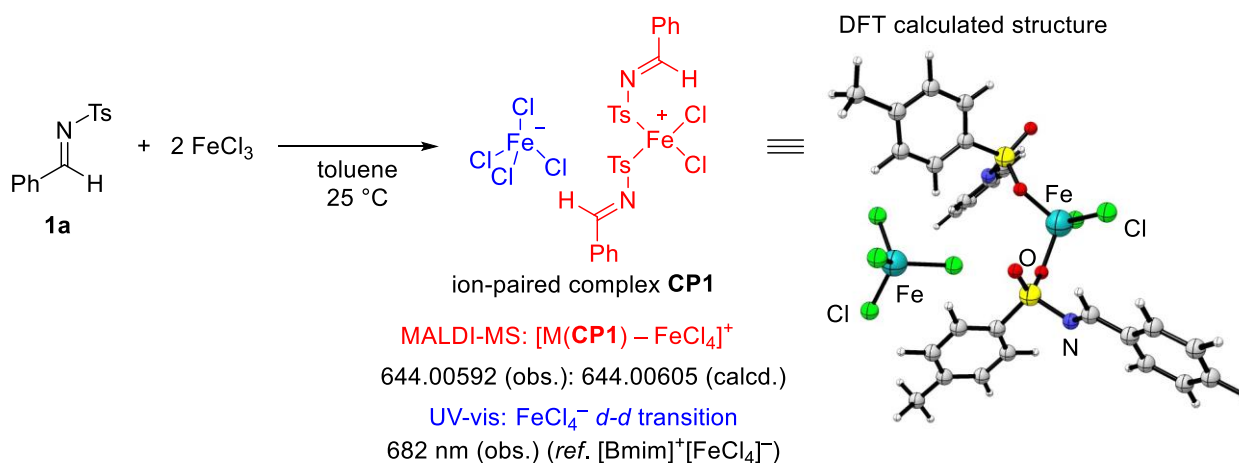
Understanding the unique character of first-row transition metals as abundant, nontoxic metal catalysts has become an important topic of research since such fundamental findings can help develop new transformations that can realize the practical chemical production of valuable organic materials.<sup>1</sup> Herein, the author described that  $\text{FeCl}_3$  could successfully catalyze aza-Diels–Alder reactions of simple imines and non-activated dienes, and precise mechanistic investigation provided the new insight on  $\text{FeCl}_3$  as a Lewis acid catalyst. Although  $\text{FeCl}_3$  is one of the most conventional metal Lewis acid catalysts, the origin of its high activity has not been studied in detail.

Swanson and Laurie originally reported that the disproportionation of  $\text{FeCl}_3$  was confirmed in coordinative solvents such as DMF and pyridine.<sup>2</sup> On the basis of their findings,  $\text{FeCl}_3$  disproportionation has been applied to generate reactive oxidation catalysts in organic synthesis, as exemplified by the independent seminal works of Tobinaga, Frazier, Jr., Overmann, and MacMillan.<sup>3</sup> The author envisioned that the disproportionation of  $\text{FeCl}_3$  would also be triggered in non-coordinative solvents upon coordination with a Lewis basic molecules such as imine, instead of a coordinative solvent molecule, and forming the highly Lewis acidic  $[\text{FeCl}_2]^+$  species along with the thermodynamically stable  $[\text{FeCl}_4]^-$ . Consequently, the LUMO of the imine would be sufficiently lowered and the reactivity toward nucleophile, e.g. dienes, should be enhanced.

The aza-Diels–Alder reaction of non-activated substrates is recognized as a simple reaction, it is, in fact, difficult to accomplish due to the low energy level of the HOMO of the diene (compared to those of activated dienes such as the Danishefsky's and Rawal's dienes) as well as the high energy level of the LUMO of imine (compared to those of activated substrates such as glyoxal type 1,2-dicarbonyl derived imines).<sup>4,5</sup> Considering that a late-stage aza-Diels–Alder reaction with a non-activated diene and imine could be a powerful tool that would offer an alternative strategy for the total synthesis of natural compounds and manufacture of medicinal drugs, the development of a practical Lewis catalyst that promotes the reaction in high chemoselectivity reaction based on an abundant, nontoxic metal would be quite desirable.

## Results and Discussion

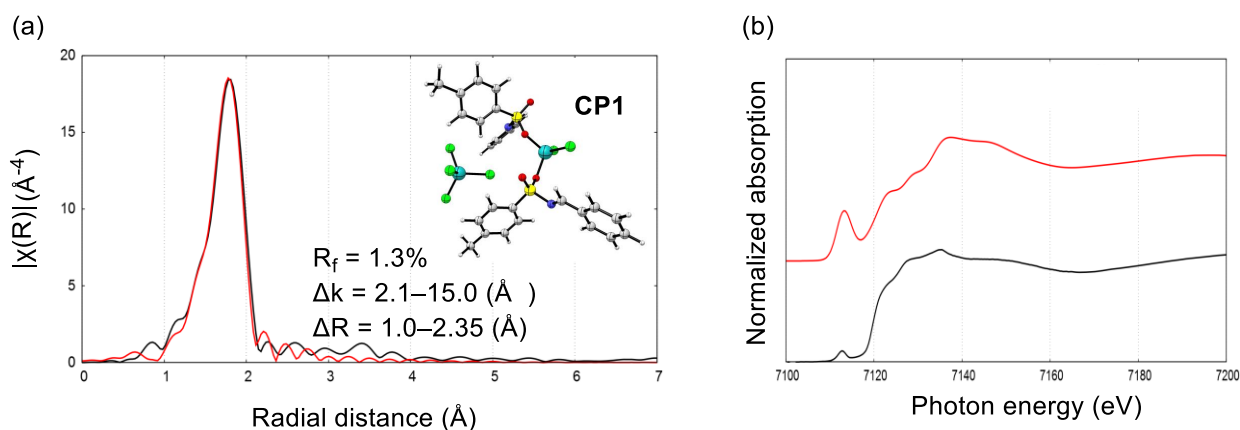
The author initially investigated the disproportionation of  $\text{FeCl}_3$  upon coordination with *N*-sulfonylated imine **1a**, which contains a Lewis basic oxygen atom to coordinate with the Lewis acid (Figure 1). The disproportionation and formation of ion-paired complex  $[\text{FeCl}_2(\mathbf{1a})_2]^+[\text{FeCl}_4]^-$  (**CP1**) was confirmed spectroscopically (Figure 1). Formula determination by MALDI-MS was consistent with that theoretically calculated for a cationic iron complex with two imine and two chloride ligands, which is identical to that of  $[\text{M}(\mathbf{CP1})-\text{FeCl}_4]^-$ , i.e.,  $[\text{FeCl}_2(\mathbf{1a})_2]^+$ . Furthermore, the UV-vis spectrum revealed the formation of  $[\text{FeCl}_4]^-$  by comparison with the spectrum for  $[\text{Bmim}][\text{FeCl}_4]$  as a reference compound.



**Figure 1.** Disproportionation of  $\text{FeCl}_3$  upon coordination with imine **1a** to form ion-paired complex  $[\text{FeCl}_2(\mathbf{1a})_2]^+[\text{FeCl}_4]^-$  (**CP1**).

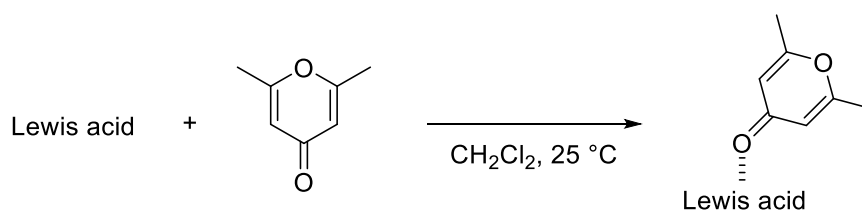
To gain further insight into **CP1**, Fe *K*-edge X-ray absorption spectroscopy (XAS) was performed using a synchrotron radiation beamline, where the ultrahigh brightness made solution-phase XAS accessible for in situ structural investigation. Analysis of the extended X-ray absorption fine structure (EXAFS) spectrum of the solution of  $\text{FeCl}_3$  with imine **1a** in toluene clearly indicated good agreement with the theoretically calculated **CP1** model (Figure 2a). A significant pre-edge

peak in the X-ray absorption near edge structure (XANES) also indicated the formation of an iron species with tetrahedral geometry (Figure 2b).<sup>7</sup> Furthermore, a calculated absorption spectrum using the finite difference method for postulated complex **CP1** resulted in good agreement with the experimentally obtained XANES spectrum. Based on these results, it was confirmed that the disproportionation of  $\text{FeCl}_3$  generates the highly Lewis acidic  $[\text{FeCl}_2]^+$  via the coordination of two imine molecules along with the formation of the thermodynamically stable  $[\text{FeCl}_4]^-$ , which leads to the in situ generation of ion-paired iron complex **CP1**.



**Figure 2.** (a) Solution-phase Fe *K*-edge EXAFS analysis (Fourier transform of  $k^3$ -weighted spectrum: experimental spectrum (black line) and FEFF-calculated fitting of DFT model **CP1** (red line). (b) Solution-phase Fe *K*-edge XANES spectra: experimental spectrum (black line) and calculated spectrum of **CP1** (red line).

Next, the Lewis acidity of  $\text{FeCl}_3$  was examined by IR spectroscopy, measuring the carbonyl stretching vibration of its 2,6-dimethyl- $\gamma$ -pyrone complex in non-coordinative solvent  $\text{CH}_2\text{Cl}_2$  (Table 1), where a larger shift ( $\Delta\nu_{\text{C=O}}$ ) in the carbonyl absorption peak indicates higher Lewis acidity.<sup>6</sup> In the event,  $\text{FeCl}_3$ , which disproportionates to  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$ , shows high Lewis acidity relative to various common Lewis acids.

**Table 1.** Investigation of Lewis acidity via IR measurement<sup>a</sup>

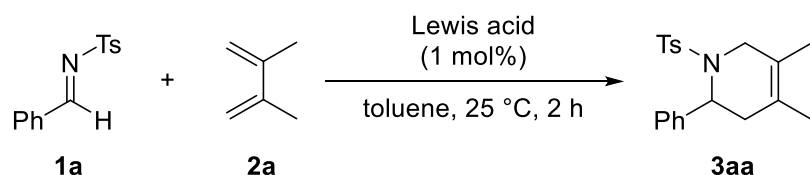
| Lewis acid                                                     | $\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ ) | $\Delta\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ ) |
|----------------------------------------------------------------|-----------------------------------------|-----------------------------------------------|
| None                                                           | 1669.6                                  | —                                             |
| $\text{FeCl}_3 = [\text{FeCl}_2]^+[\text{FeCl}_4]^-$ (in situ) | 1646.4                                  | 23.2                                          |
| $\text{FeCl}_2$                                                | 1668.6                                  | 1.0                                           |
| $\text{AlCl}_3$                                                | 1649.8                                  | 19.8                                          |
| MAD <sup>b</sup>                                               | 1653.7                                  | 15.9                                          |
| $\text{B}(\text{C}_6\text{F}_5)_3$                             | 1650.3                                  | 19.3                                          |
| $\text{RuCl}_3$                                                | 1669.6                                  | <0.1                                          |
| $\text{FeCl}_3 + \text{Cl}^-$ <sup>c</sup>                     | 1669.6                                  | <0.1                                          |
| $\text{FeCl}_3 + \text{SbF}_6^-$ <sup>c</sup>                  | 1646.4                                  | 23.2                                          |
| $\text{FeCl}_3 + \text{FeCl}_4^-$ <sup>c</sup>                 | 1647.2                                  | 22.4                                          |

<sup>a</sup>IR measurement was carried out for  $\text{CH}_2\text{Cl}_2$  solution of 2,6-dimethyl- $\gamma$ -pyrone and 1 equiv of Lewis acid. <sup>b</sup>MAD: methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide). <sup>c</sup>With addition of an equivalent amount of the 1-butyl-3-methylimidazolium salt  $[\text{Bmim}]^+[\text{X}]^-$ .

To assess the catalytic reactivity of in situ generated **CP1**, the author next examined the aza-Diels–Alder reaction of imine **1a** and diene **2a** in the presence of  $\text{FeCl}_3$  in toluene at 25 °C for 2 h (Table 2). The reaction afforded cycloadduct **3aa** in almost quantitative yield, even with 1 mol % catalytic loading. The reaction with other Lewis acids such as  $\text{AlCl}_3$ , MAD,  $\text{B}(\text{C}_6\text{F}_5)_3$ , and  $\text{RuCl}_3$  resulted in lower yields (for further investigation of the effect of Lewis acid see Supplemental Data). To gain insight into the disproportionation of  $\text{FeCl}_3$  to form cationic  $[\text{FeCl}_2]^+$  and anionic  $[\text{FeCl}_4]^-$  in terms of catalytic reactivity, the reaction was examined with  $\text{FeCl}_3$  in the presence of

imidazolium salts which possessed the counteranions  $\text{Cl}^-$ ,  $\text{SbF}_6^-$ , and  $\text{FeCl}_4^-$ . The addition of  $\text{Cl}^-$  dramatically retarded the reaction because the excess  $\text{Cl}^-$  coordinated with  $\text{FeCl}_3$  to form the stable but inactive anion  $[\text{FeCl}_4]^-$ . In contrast, in the presence of  $\text{SbF}_6^-$ , the reaction proceeded without any inhibition of reactivity. Notably, with the addition of  $[\text{FeCl}_4]^-$ , the reaction was not impeded, since  $[\text{FeCl}_4]^-$  behaves as a noncoordinating anion. These results are consistent with the aforementioned IR-based Lewis acidity estimates for the 2,6-dimethyl- $\gamma$ -pyrone-coordinated iron complexes with or without imidazolium salts. Therefore, the disproportionation of  $\text{FeCl}_3$  concomitantly generates the strongly Lewis acidic  $[\text{FeCl}_2]^+$  with coordination of imine **1a**, which indeed facilitates the aza-Diels–Alder reaction with nonactivated diene **2a**.

**Table 2.** Effect of Lewis acid catalysts on the reaction of imine **1a** with diene **2a**<sup>a</sup>



| entry | Lewis acid      | yield (%) <sup>b</sup> | entry | Lewis acid                                       | yield (%) <sup>b</sup> |
|-------|-----------------|------------------------|-------|--------------------------------------------------|------------------------|
| 1     | none            | <1                     | 6     | $\text{B}(\text{C}_6\text{F}_5)_3$               | <1                     |
| 2     | $\text{FeCl}_3$ | >99 (92) <sup>c</sup>  | 7     | $\text{RuCl}_3$                                  | <1                     |
| 3     | $\text{FeCl}_2$ | <1                     | 8     | $\text{FeCl}_3 + \text{Cl}^-$ <sup>d</sup>       | <1                     |
| 4     | $\text{AlCl}_3$ | 22                     | 9     | $\text{FeCl}_3 + \text{SbF}_6^-$ <sup>d</sup>    | >99                    |
| 5     | MAD             | <1                     | 10    | $\text{FeCl}_3 + [\text{FeCl}_4]^-$ <sup>d</sup> | >99                    |

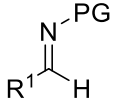
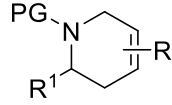
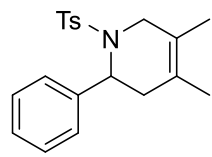
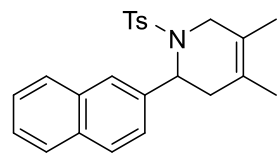
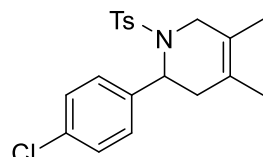
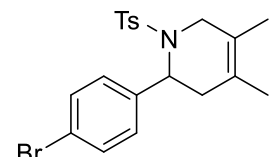
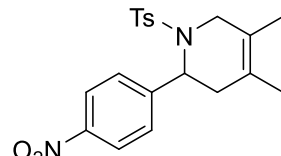
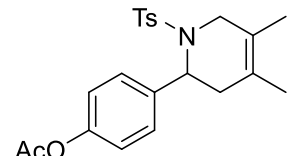
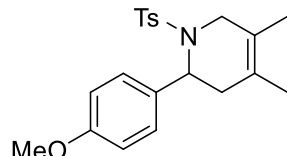
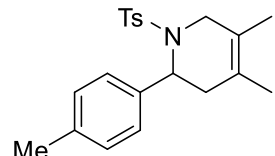
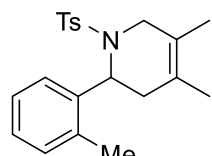
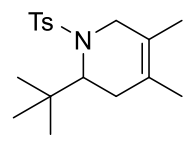
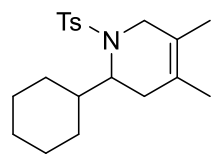
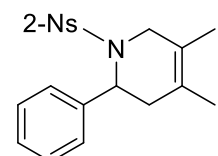
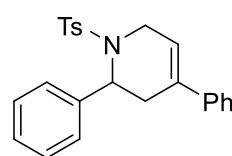
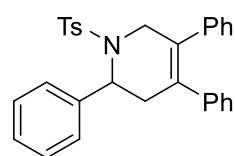
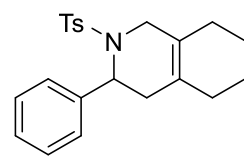
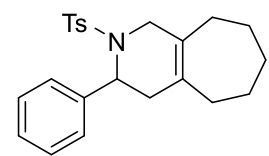
<sup>a</sup>Reactions were carried out using Lewis acid (1 mol%), imine **1a** (0.2 mmol), diene **2a** (0.4 mmol), toluene (2 mL), 25 °C, 2 h. <sup>b</sup>NMR yields. <sup>c</sup>Isolated yields. <sup>d</sup>Reactions were carried out with the addition of imidazolium salt  $[\text{Bmim}]^+[\text{X}]^-$  (1 mol%) in dichloromethane.

To demonstrate the scope of the in situ generated **CP1**-catalyzed aza-Diels–Alder reaction, the author examined the reactions of various imines **1** with conjugated dienes **2** (Table 3). Under the optimized reaction conditions, functional groups such as nitro, ester, ether, and halogen groups

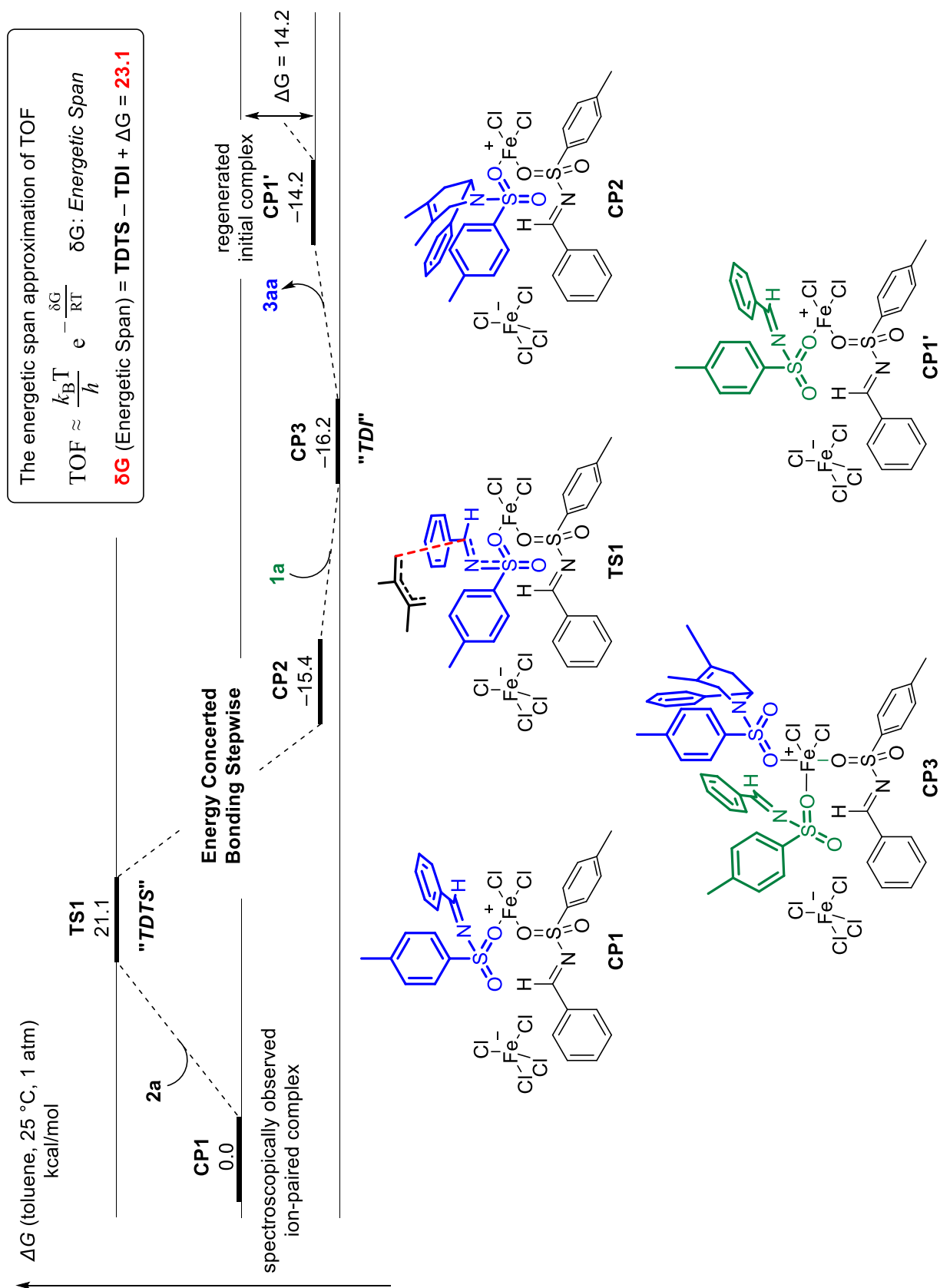
were tolerated, giving the corresponding substituted cycloadducts in high yields (**3ba–3ia**). These results highlight the excellent functional group compatibility of the **CP1**-catalyzed reaction, which is ascribed to the selective and substantial Lewis acid/base affinity of **CP1** toward the oxygen atom on the *N*-sulfonylated imine. The reaction using *N*-substituted imines with simple alkyl or aryl substitutes resulted in low yields.

To understand the electronic character of the ion-paired Lewis acid catalyst **CP1** in the aza-Diels–Alder reaction, the author performed a series of DFT calculations. Based on spectroscopic observations, the  $[\text{FeCl}_2(\mathbf{1a})_2]^+[\text{FeCl}_4]^-$  (**CP1**) species formed via the coordination of two molecules of imine **1a** to  $\text{FeCl}_3$  was reasonably employed as the active species of this catalytic reaction. The DFT calculations supported the catalytic cycle involving the  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$  complex, as shown in Figure 3. First, the coordination of imine **1a** to  $\text{FeCl}_3$  forms **CP1**; then C–C bond formation with the addition of diene **2a** occurs with a Gibbs activation energy of 21.1 kcal/mol via **TS1**, which is the TOF-determining transition state (TDTS, vide infra). This is followed by cyclization to form the C–N bond in an “energy-concerted bonding stepwise manner” to afford **CP2**.<sup>8</sup> The dissociation of **3aa** from an iron atom proceeds via coordination of another imine **1aa** to form thermodynamically stable five-coordination trigonal bipyramidal complex **CP3**, which is the TOF-determining intermediate (TDI). Finally, cycloadduct **3aa** is dissociated from iron with small endergonic energy (2.0 kcal/mol) to regenerate initial active species **CP1'**.

**Table 3.** Substrate scope<sup>a</sup>

|                                                                                                                   |                                                                                                                    |                                                                                                                     |                                                                                                                      |                                                                                                 |
|-------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| <br><b>1a-1l</b>                 | +                                                                                                                  | <br><b>2a-2e</b>                   | $\xrightarrow[\text{toluene, 25 } ^\circ\text{C, 2 h}]{\text{FeCl}_3 \text{ (1 mol\%)}}$                             | <br><b>3</b> |
| Products <sup>b</sup>                                                                                             |                                                                                                                    |                                                                                                                     |                                                                                                                      |                                                                                                 |
| <br><b>3aa</b> 92%               | <br><b>3ba</b> 90% <sup>c</sup>   | <br><b>3ca</b> 92%                | <br><b>3da</b> 74%                |                                                                                                 |
| <br><b>3ea</b> 88% <sup>c</sup> | <br><b>3fa</b> 95%               | <br><b>3ga</b> 78% <sup>c</sup>  | <br><b>3ha</b> 87%               |                                                                                                 |
| <br><b>3ia</b> 87%             | <br><b>3ja</b> 71%              | <br><b>3ka</b> 97% <sup>c</sup> | <br><b>3la</b> 90% <sup>d</sup> |                                                                                                 |
| <br><b>3ab</b> 92%             | <br><b>3ac</b> 88% <sup>d</sup> | <br><b>3ad</b> 72% <sup>e</sup> | <br><b>3ae</b> 90% <sup>e</sup> |                                                                                                 |

<sup>a</sup>Reactions were carried out using **1** (0.2 mmol), **2** (0.4 mmol), FeCl<sub>3</sub> (0.002 mmol) in 2 mL of toluene for 2 h under 25 °C unless otherwise noted. <sup>b</sup>Isolated yield. <sup>c</sup>Reaction time 6 h. <sup>d</sup>FeCl<sub>3</sub> (3 mol %), reaction time 6 h. <sup>e</sup>FeCl<sub>3</sub> (5 mol %), reaction temperature 50 °C, reaction time 6 h.

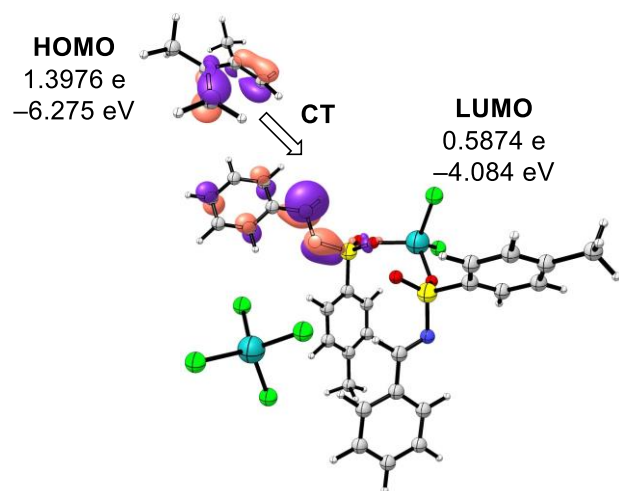


**Figure 3.** Calculated free energy profile for the transformation.

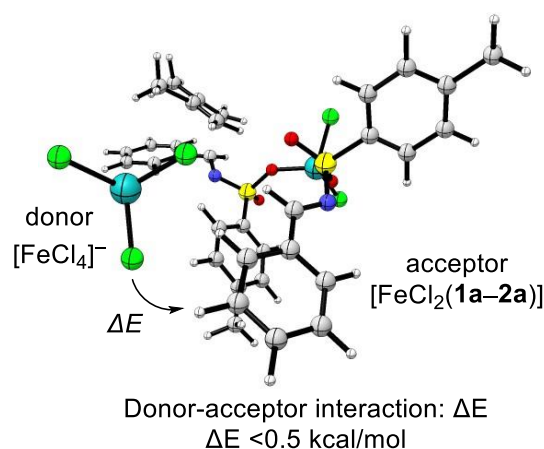
To better understand how the  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$  catalyst accelerates the addition of diene to imine with **TS1**, the step electronically through fragment molecular orbital (FMO) analysis was investigated (Figure 4a).<sup>9</sup> During formation of the C–C bond at **TS1**, the dienyl HOMO overlaps well with the imino LUMO ( $\pi^*\text{C}=\text{N}$  antibonding orbital). The population of the imino LUMO considerably increases to 0.587 e in **TS1**, while the population of the dienyl HOMO considerably decreases to 1.398 e. These results clearly indicate that charge transfer (CT) substantially occurs from the diene  $\pi$  orbital to the antibonding LUMO of the imine. That is, this CT stabilizes the **TS1** and increases the electron population of the imine moiety, which contributes to C–C bond formation. Next, the proposed catalytic cycle for the aza-Diels–Alder reaction was analyzed by the energetic span model.<sup>10</sup> In this model, the TOF of the catalytic cycle can be measured with the energetic span  $\delta G$ , which is the difference in the Gibbs energy between the TOF-determining transition state (TDTS) and the TOF-determining intermediate (TDI), with the addition of the global Gibbs energy of the reaction when the TDTS appears before the TDI. TDTS and TDI are the most unstable and most stable species in the catalytic cycle, respectively. Therefore,  $\delta G$  is a genuinely effective barrier of the global reaction in the catalytic cycle, which can be subsequently used to estimate the TOF. Calculated  $\delta G$  values for this reaction and other catalytic systems are summarized in Figure 5, to compare the unique catalytic reactivity of  $\text{FeCl}_3$  with analogous ion-paired catalysts  $[\text{AlCl}_2]^+[\text{AlCl}_4]^-$  (via disproportionation of  $\text{AlCl}_3$ ),<sup>11</sup> and non-ion-paired cationic iron catalyst  $[\text{FeCl}_2]^+$  without  $[\text{FeCl}_4]^-$ . The reaction with  $[\text{AlCl}_2]^+[\text{AlCl}_4]^-$  has slightly larger  $\delta G$  (27.5 kcal/mol) and slightly lower relative TOF (*rel*/TOF) values compared to  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$ . Furthermore, the reaction of the  $[\text{FeCl}_2]^+$  catalyst without a counteranion has an energetically high-lying TDTS leading to a high  $\delta G$  (40.6 kcal/mol). Therefore, in the ion-paired complex  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$ , both  $[\text{FeCl}_2]^+$  and  $[\text{FeCl}_4]^-$  promote the reaction efficiently by lowering the TDTS and also raising the TDI, respectively, narrowing the  $\delta G$  in the catalytic cycle. Of note, second-order perturbation theory analysis in NBO basis for donor–acceptor orbital interactions corresponding to the **TS1** of  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$  catalysis shows only faint orbital interactions between  $[\text{FeCl}_4]^-$  and the remainder of the reacting fragment (Figure 4b), suggesting that a long-

range electrostatic interaction dominates over the short-range orbital interaction for thermodynamic stabilization to realize the low-lying activation energy of **TS1** as TDTS. Indeed, some attractive or weak interactions between  $[\text{FeCl}_4]^-$  and  $[\text{FeCl}_2(\mathbf{1a})_2]^+$  complex were confirmed (Figure 4c).

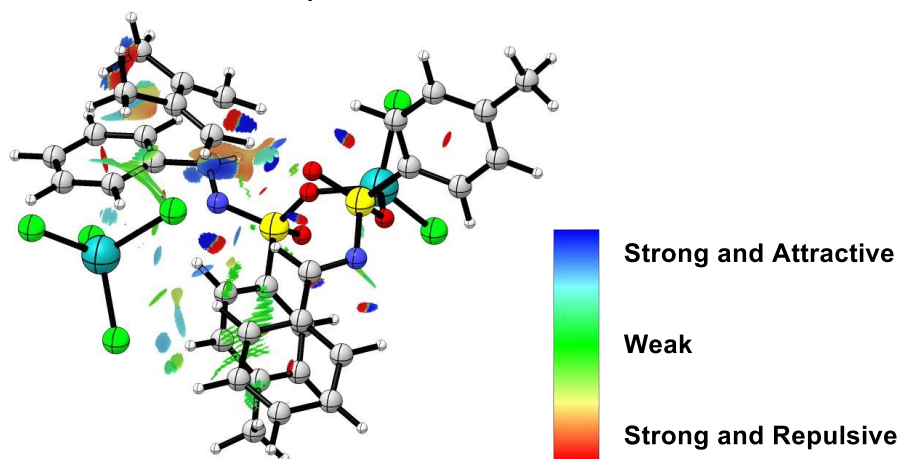
(a) electron population and energy



(b) natural bond orbital analysis



(c) noncovalent interaction analysis



**Figure 4.** (a) Important Kohn–Sham MOs (electron population and orbital energy) of imine and diene moieties of **TS1**. (b) Natural bond orbital analysis of **TS1**. (c) Noncovalent interaction analysis of **TS1**.

| Lewis acid                           | TDTS <sup>a</sup>   | TDI <sup>a</sup>      | $\delta G^b$ | <i>rel</i> TOF <sup>c</sup> |
|--------------------------------------|---------------------|-----------------------|--------------|-----------------------------|
| $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$ | 21.1 ( <b>TS1</b> ) | -16.2 ( <b>CP3</b> )  | 23.1         | 1                           |
| $[\text{AlCl}_2]^+[\text{AlCl}_4]^-$ | 24.5 ( <b>TS1</b> ) | -17.2 ( <b>CP3</b> )  | 27.5         | $1.2 \times 10^{-2}$        |
| $[\text{FeCl}_2]^+$                  | 40.6 ( <b>TS1</b> ) | -14.2 ( <b>CP1'</b> ) | 40.6         | $2.6 \times 10^{-8}$        |

**Figure 5.** Energetic spans in several catalytic systems. (a) Gibbs free energy (kcal/mol). (b) Energetic span (kcal/mol). (c) Relative turnover frequency normalized to the value for  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$ .

## Conclusion

The author succeeded in developing a practical catalyst for the aza-Diels–Alder reactions of non-activated dienes and imines using  $\text{FeCl}_3$ , which forms the highly Lewis acidic  $\text{FeCl}_2^+$  and thermodynamically stable  $[\text{FeCl}_4]^-$  that act as the ion-paired catalyst  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$  after in situ disproportionation upon imine coordination. The disproportionation was confirmed spectroscopically, and the catalytic cycle was analyzed theoretically. The high TOF reactivity of the catalyst was rationalized with the energetic span model;  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$  realizes both a low-energy TOF-determining transition state (TDTS) and a high-energy TOF-determining intermediate (TDI). The obtained fundamental understanding of this first-row transition metal Lewis acid catalyst will provide new ideas for promoting catalytic reactions with high TOFs in other reactions.

## Experimental Section

### Materials.

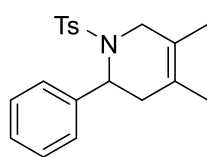
Toluene was purchased from Wako Pure Chemical Co. Iron(III) chloride was purchased from Sigma-Aldrich Co.. 2,3-Dimethyl-1,3-butadiene was purchased from TCI. Aldimines and dienes were prepared according to the reported procedure. Unless otherwise noted, commercially available reagents were used without purification

## Experimental Procedure and Characterization Data for Products.

### General procedure.

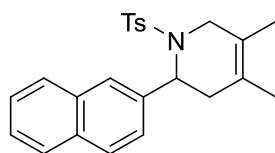
The reaction was performed in a 15 mL sealed tube equipped with a Teflon-coated magnetic stirrer bar. A diene (0.4 mmol) were added to a solution of imine (0.2 mmol) and FeCl<sub>3</sub> (0.3 mg, 2.0 μmol) in toluene (2 mL) in a dry box. The vial was taken outside the dry box and stirred at 25 °C for the indicated time. The reaction mixture was passed through a short silica gel pad, washed with ethylacetate, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with given eluent.

#### 4,5-Dimethyl-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3aa**).



Yield: 92%. Mp. 87–89 °C (ethyl acetate). TLC: R<sub>f</sub> = 0.37 (hexane/ethyl acetate = 7:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.65 (dt, *J* = 7.0, 2.0 Hz, 2H), 7.20–7.28 (m, 7H), 5.23 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.21–3.25 (m, 1H), 2.40 (s, 3H), 2.31–2.37 (m, 1H), 2.19 (d, *J* = 17.5 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.1, 140.0, 138.0, 129.6, 128.6, 127.6, 127.5, 127.3, 123.4, 122.5, 53.8, 45.2, 32.8, 21.7, 18.8, 16.2. IR (KBr): 2919, 1927, 1596, 1522, 1517, 1352, 1330, 1279, 1162, 1090, 1009, 856, 814 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 342.1512, calcd for [M+H]<sup>+</sup> 342.1522.

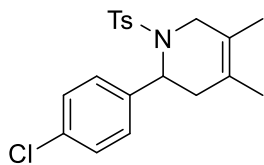
#### 4,5-Dimethyl-2-(naphthalen-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ba**).



Yield: 90%. Mp. 100–102 °C (ethyl acetate). TLC: R<sub>f</sub> = 0.41 (hexane/ethyl acetate = 5:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.71–7.81 (m, 3H), 7.68–7.70 (m, 2H), 7.56 (s, 1H), 7.44–7.47 (m, 3H), 7.20–7.22 (m, 2H), 5.39 (d, *J* = 6.5 Hz, 1H), 3.93 (d *J* = 18.5 Hz, 1H), 3.27 (d, *J* = 18.5 Hz, 1H), 2.32–2.43 (m, 2H), 2.39 (s, 3H), 1.62 (s, 3H), 1.52 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.2, 138.0, 137.2, 133.3, 132.9, 129.6, 128.3, 128.3, 127.7, 127.2, 126.2, 126.1, 126.0, 126.0, 123.3, 122.6, 53.9, 45.3, 32.6, 21.6, 18.8, 16.2. IR (KBr): 2978, 2880, 1596, 1507, 1493, 1457, 1437, 1386, 1378, 1339, 1320, 1292, 1107, 949, 841 cm<sup>-1</sup>. HRMS

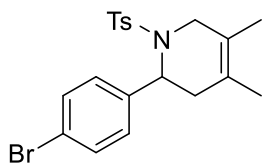
(ESI<sup>+</sup>) found 392.1666, calcd for [M+H]<sup>+</sup> 392.1679.

2-(4-Chlorophenyl)-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ca**).



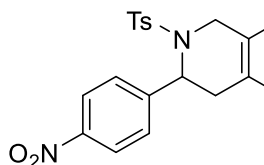
Yield: 92%. Mp. 110–112 °C (ethyl acetate). TLC: R<sub>f</sub> = 0.41 (hexane/ethyl acetate = 7:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.64 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.20–7.24 (m, 4H), 7.15–7.18 (m, 2H), 5.18 (d, *J* = 6.5 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.19–3.23 (m, 1H), 2.40 (s, 3H), 2.30–2.36 (m, 1H), 2.14 (d, *J* = 17.5 Hz, 1H), 1.56 (s, 3H), 1.52 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.4, 138.4, 137.7, 133.4, 129.7, 128.9, 128.7, 127.2, 123.2, 122.6, 53.1, 45.1, 32.7, 21.7, 18.8, 16.2. IR (KBr): 2922, 2856, 1595, 1492, 1447, 1325, 1292, 1159, 1089, 1011, 922, 816, 715 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 376.1121, calcd for [M+H]<sup>+</sup> 376.1123.

2-(4-bromophenyl)-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3da**).



Yield: 74%. Mp. 102–104 °C (hexane). TLC: R<sub>f</sub> = 0.45 (hexane/ethyl acetate = 5:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.63 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.37 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.11 (dt, *J* = 8.5, 1.5 Hz, 2H), 5.16 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.20 (dt, *J* = 17.5, 1.0 Hz, 1H), 2.40 (s, 3H), 2.28–2.36 (m, 1H), 2.13 (d, *J* = 17.5 Hz, 1H), 1.56 (s, 3H), 1.51 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.1, 138.6, 137.3, 131.4, 129.4, 129.1, 126.9, 122.9, 122.3, 121.3, 52.9, 44.8, 32.2, 21.5, 18.6, 16.0. IR (KBr): 2920, 2858, 1596, 1485, 1443, 1352, 1162, 1130, 1006, 908 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 420.0628, calcd for [M+H]<sup>+</sup> 420.0627.

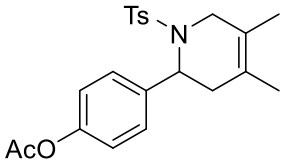
4,5-Dimethyl-2-(4-nitrophenyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ea**).



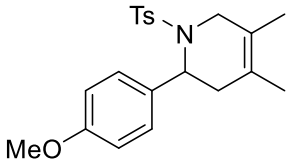
Yield: 88%. Mp. 141–143 °C (ethyl acetate). TLC: R<sub>f</sub> = 0.35 (hexane/ethyl acetate = 3:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.12 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.66 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.40–7.43 (m, 2H), 7.25–7.26 (m, 2H), 5.29 (d, *J* = 6.5 Hz, 1H), 3.89 (d, *J* = 17.5 Hz, 1H), 3.21–3.26 (m, 1H), 2.42 (s, 3H), 2.38–2.40 (m, 1H), 2.20 (d, *J* = 17.5 Hz, 1H), 1.59 (s, 3H), 1.53 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 147.5, 147.4, 143.7, 137.4, 129.8,

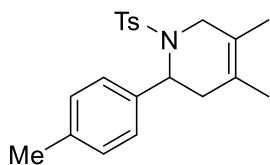
128.4, 127.2, 123.8, 123.0, 122.9, 53.3, 45.3, 32.7, 21.7, 18.9, 16.2. IR (KBr): 2919, 1927, 1596, 1522, 1517, 1352, 1330, 1279, 1162, 1090, 1009, 856, 814  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 387.1361, calcd for [M+H]<sup>+</sup> 387.1373.

4-(4,5-Dimethyl-1-tosyl-1,2,3,6-tetrahydropyridin-2-yl)phenyl acetate (**3fa**).

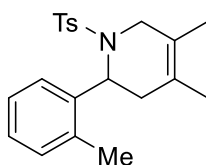
 Yield: 95%. Mp. 125–127 °C (ethyl acetate). TLC: R<sub>f</sub> = 0.30 (hexane/ethyl acetate = 3:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.64 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.21–7.25 (m, 4H), 6.97 (dt, *J* = 8.5, 2.0 Hz, 2H), 5.20 (d, *J* = 6.5 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.23 (d, *J* = 17.5 Hz, 1H), 2.30–2.36 (m, 1H), 2.28 (s, 3H), 2.15 (d, *J* = 17.5 Hz, 1H), 1.56 (s, 3H), 1.52 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 169.5, 150.0, 143.2, 137.8, 137.4, 129.6, 128.6, 127.2, 123.2, 122.5, 121.5, 53.2, 45.0, 32.8, 21.6, 21.3, 18.8, 16.2. IR (KBr): 2923, 2860, 1754, 1597, 1508, 1447, 1322, 1220, 1209, 1156, 1066, 1012, 912, 805  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 400.1563, calcd for [M+H]<sup>+</sup> 400.1577.

2-(4-Methoxyphenyl)-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ga**).

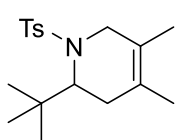
 Yield: 78%. Mp. 120–122 °C (ethyl acetate). TLC: R<sub>f</sub> = 0.37 (hexane/ethyl acetate = 5:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.63–7.65 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 (dt, *J* = 8.5, 2.0 Hz, 2H), 6.78 (dt, *J* = 8.5, 2.0 Hz, 2H), 5.18 (d, *J* = 7.0 Hz, 1H), 3.84 (d, *J* = 17.5 Hz, 1H), 3.77 (s, 3H), 3.18–3.22 (m, 1H), 2.40 (s, 3H), 2.30–2.36 (m, 1H), 2.14 (d, *J* = 17.5 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 159.0, 143.1, 138.0, 131.9, 129.6, 128.8, 127.2, 123.4, 122.5, 113.8, 55.4, 53.2, 45.0, 32.9, 21.7, 18.8, 16.2. IR (KBr): 2906, 2842, 1609, 1513, 1442, 1379, 1333, 1302, 1254, 1167, 1138, 1088, 1031, 916, 816  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 372.1616, calcd for [M+H]<sup>+</sup> 372.1628.

4,5-dimethyl-2-(p-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ha**).

Yield: 87%. Mp. 125–127 °C (hexane). TLC:  $R_f$  = 0.45 (hexane/ethyl acetate = 5:1)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.65 (dt,  $J$  = 8.0, 1.5 Hz, 2H), 7.22 (d,  $J$  = 8.0 Hz, 2H), 7.13 (d,  $J$  = 8.0 Hz, 2H), 7.06 (d,  $J$  = 8.0 Hz, 2H), 5.19 (d,  $J$  = 6.5 Hz, 1H), 3.85 (d,  $J$  = 17.5 Hz, 1H), 3.23 (dt,  $J$  = 17.5, 1.0 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.28–2.35 (m, 1H), 2.16 (d,  $J$  = 17.5 Hz, 1H), 1.56 (s, 3H), 1.51 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  142.9, 137.6, 136.9, 136.5, 129.3, 128.9, 127.2, 126.9, 123.2, 122.1, 53.2, 44.8, 32.3, 21.5, 21.0, 18.6, 16.0. IR (KBr): 2912, 2880, 1590, 1439, 1375, 1319, 1282, 1184, 1155, 1039, 814  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 356.1682, calcd for  $[\text{M}+\text{H}]^+$  356.1679.

4,5-dimethyl-2-(o-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ia**).

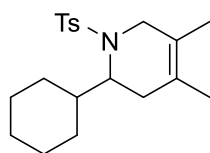
Yield: 87%. Mp. 123–124 °C (hexane). TLC:  $R_f$  = 0.50 (hexane/ethyl acetate = 5:1)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.65 (dt,  $J$  = 8.0, 2.0 Hz, 2H), 7.20 (d,  $J$  = 8.0 Hz, 2H), 7.14–7.20 (m, 2H), 7.03 (dd,  $J$  = 6.5, 2.0 Hz, 1H), 6.98 (d, 8.0 Hz, 1H), 5.40 (d,  $J$  = 7.5 Hz, 1H), 3.80 (d,  $J$  = 18.0 Hz, 1H), 3.22 (dt,  $J$  = 18.0, 1.0 Hz, 1H), 2.53 (s, 3H), 2.40 (s, 3H), 2.28–2.38 (m, 1H), 2.00 (d,  $J$  = 18.0 Hz, 1H), 1.51 (s, 3H), 1.40 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  143.0, 137.8, 137.6, 137.1, 130.9, 129.0, 127.7, 127.2, 126.2, 125.5, 123.9, 122.5, 51.2, 45.1, 32.3, 21.4, 19.8, 18.1, 16.2. IR (KBr): 2907, 2856, 1592, 1435, 1343, 1333, 1167, 1087, 999, 905, 820  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 356.1680, calcd for  $[\text{M}+\text{H}]^+$  356.1679.

2-*tert*-Butyl-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ja**).

Yield: 71%. Mp. 104–106 °C (ethyl acetate). TLC:  $R_f$  = 0.33 (hexane/ethyl acetate = 10:1)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.61–7.64 (m, 2H), 7.21–7.23 (m, 2H), 3.95 (d,  $J$  = 18.5 Hz, 1H), 3.74 (d,  $J$  = 8.0 Hz, 1H), 3.59 (d,  $J$  = 18.5, 1H), 2.39 (s, 3H), 1.72–1.84 (m, 2H), 1.48 (s, 3H), 1.44 (s, 3H), 0.93 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  142.9, 138.3, 129.6, 127.0, 124.1, 120.8, 58.4, 46.8, 36.3, 29.1, 28.2, 21.7, 18.7, 16.0. IR (KBr): 2972, 2935, 2865, 1595, 1476, 1400, 1328, 1182, 1160, 1142, 1089, 1011, 920, 817, 732  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found

322.1824, calcd for  $[M+H]^+$  322.1835.

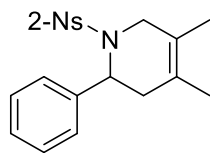
2-Cyclohexyl-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ka**).



Yield: 97%. Mp. 133–135 °C (ethyl acetate). TLC:  $R_f$  = 0.42 (hexane/ethyl acetate = 7:1)  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.62–7.64 (m, 2H), 7.21–7.23 (m, 2H), 3.86 (d,  $J$  = 18.0 Hz, 1H), 3.63 (td,  $J$  = 4.5, 2.5 Hz, 1H), 3.43 (d,  $J$  = 18.0, 1H), 2.39

(s, 3H), 1.70–1.86 (m, 5H), 1.59–1.64 (m, 2H), 1.53 (s, 3H), 1.44 (s, 3H), 1.31–1.39 (m, 1H), 1.12–1.25 (m, 3H), 0.96–1.04 (m, 1H), 0.86–0.92 (m, 1H).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  142.8, 138.7, 129.5, 127.0, 123.2, 121.2, 56.6, 45.6, 37.6, 31.1, 30.5, 30.4, 26.5, 26.4, 26.3, 21.7, 19.1, 16.0. IR (KBr): 2926, 2856, 2848, 1595, 1452, 1437, 1327, 1266, 1163, 1080, 1005, 925, 816  $cm^{-1}$ . HRMS (ESI $^+$ ) found 348.1980, calcd for  $[M+H]^+$  348.1992.

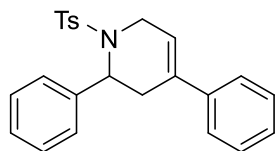
4,5-Dimethyl-1-(2-nitrophenylsulfonyl)-2-phenyl-1,2,3,6-tetrahydropyridine (**3la**).



Yield: 74%. TLC:  $R_f$  = 0.41 (hexane/ethyl acetate = 2:1)  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.98 (dd,  $J$  = 7.5, 1.0 Hz, 1H), 7.60–7.69 (m, 3H), 7.21–7.28 (m, 5H), 5.26 (d,  $J$  = 6.5 Hz, 1H), 3.83 (d,  $J$  = 18.0 Hz, 1H), 3.36 (d,  $J$  = 18.0 Hz, 1H), 2.62–2.68

(m, 1H), 2.34 (d,  $J$  = 17.5 Hz, 1H), 1.68 (s, 3H), 1.57 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  139.3, 133.5, 131.8, 130.8, 128.7, 127.8, 127.5, 124.5, 123.6, 122.6, 110.0, 54.3, 45.4, 33.3, 18.9, 16.2. (One signal emerged.) IR (neat): 2916, 2856, 1547, 1538, 1451, 1372, 1346, 1173, 1068, 1012, 777  $cm^{-1}$ . HRMS (ESI $^+$ ) found 373.1205, calcd for  $[M+H]^+$  373.1217.

2,4-Diphenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ab**).

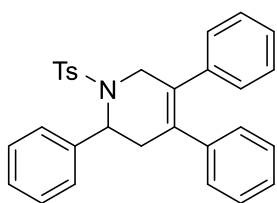


Yield: 92%. Mp. 33–35 °C (ethyl acetate). TLC:  $R_f$  = 0.26 (hexane/ethyl acetate = 7:1)  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.73 (dd,  $J$  = 8.0, 1.0 Hz, 2H), 7.30–7.35 (m, 4H), 7.21–7.27 (m, 8H), 5.90 (t,  $J$  = 2.0 Hz, 1H), 5.47 (d,  $J$  = 6.0 Hz, 1H), 4.33 (d,  $J$  = 19.0 Hz, 1H), 3.55 (dd,  $J$  = 19.0, 2.0 Hz, 1H), 2.81 (d,  $J$  = 17.5 Hz, 1H), 2.67–2.72

(m, 1H), 2.37 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  143.4, 140.4, 139.2, 137.8, 134.4, 129.7, 128.6, 128.6,

127.7, 127.7, 127.4, 127.2, 125.2, 120.2, 53.4, 41.5, 28.7, 21.6. IR (KBr): 3060, 3030, 2923, 1598, 1494, 1446, 1372, 1345, 1324, 1304, 1289, 1155, 1090, 927, 820  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 390.1507, calcd for  $[\text{M}+\text{H}]^+$  390.1522.

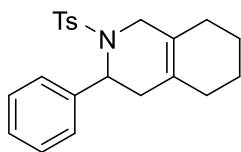
2,4,5-Triphenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ac**).



Yield: 88%. Mp. 134–136 °C (ethyl acetate). TLC:  $R_f$  = 0.39 (hexane/ethyl acetate = 5:1) <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J$  = 8.0 Hz, 2H), 7.47 (d,  $J$  = 8.0 Hz, 2H), 7.35 (t,  $J$  = 7.0 Hz, 2H), 7.28–7.31 (m, 3H), 7.08–7.12 (m, 6H), 6.84–6.86 (m, 2H), 6.75–6.77 (m, 2H) 5.46 (t,  $J$  = 4.0 Hz, 1H), 4.48 (d,  $J$

= 18.5 Hz, 1H), 3.68 (dt,  $J$  = 18.5, 3.0 Hz, 1H), 2.74–2.76 (m, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  143.6, 141.4, 139.5, 139.3, 137.8, 132.3, 131.8, 129.8, 128.9, 128.8, 128.7, 128.3, 128.2, 127.9, 127.6, 127.5, 127.1, 126.9, 53.8, 45.2, 32.4, 21.7. IR (KBr): 3049, 2922, 1598, 1493, 1344, 1165, 1094, 1070, 981, 912, 812  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 466.1820, calcd for  $[\text{M}+\text{H}]^+$  466.1835.

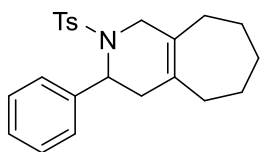
3-Phenyl-2-tosyl-1,2,3,4,5,6,7,8-octahydroisoquinoline (**3ad**).



Yield: 72%. Mp. 88–90 °C (hexane). TLC:  $R_f$  = 0.52 (hexane/ethyl acetate = 5:1) <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.66 (dt,  $J$  = 8.5, 2.0 Hz, 2H), 7.20–7.29 (m, 7H), 5.25 (d,  $J$  = 7.0 Hz, 1 H), 3.84 (d,  $J$  = 17.5 Hz, 1H), 3.17 (d,  $J$  = 17.5 Hz, 1H),

2.40 (s, 3H), 2.23–2.32 (m, 1H), 2.12 (d,  $J$  = 17.5 Hz, 1H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  142.9, 139.6, 137.5, 129.3, 128.3, 127.4, 127.3, 127.0, 125.5, 124.8, 53.5, 44.0, 31.0, 29.5, 27.0, 22.6, 22.4, 21.5. IR (KBr): 2924, 1596, 1436, 1340, 1162, 1138, 1089, 1032, 817  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 368.1682, calcd for  $[\text{M}+\text{H}]^+$  368.1679.

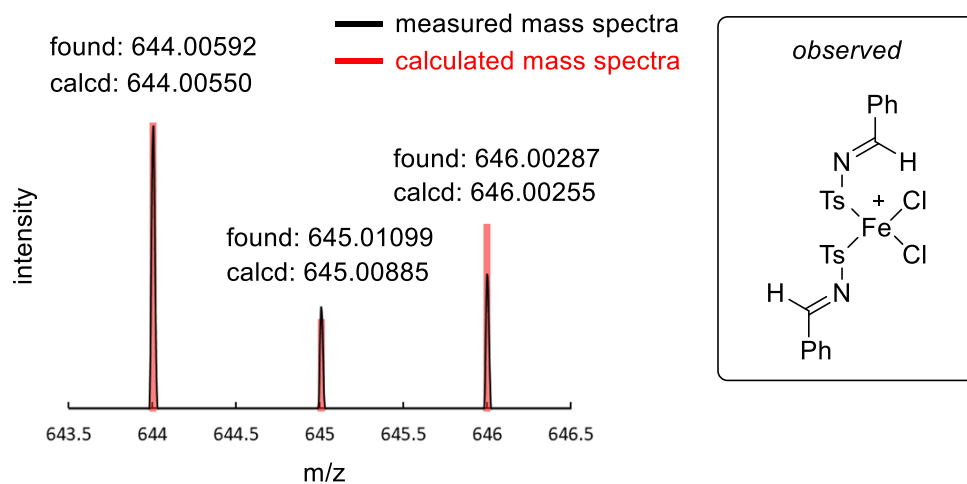
3-Phenyl-2-tosyl-2,3,4,5,6,7,8,9-octahydro-1H-cyclohepta[c]pyridine (**3ae**).



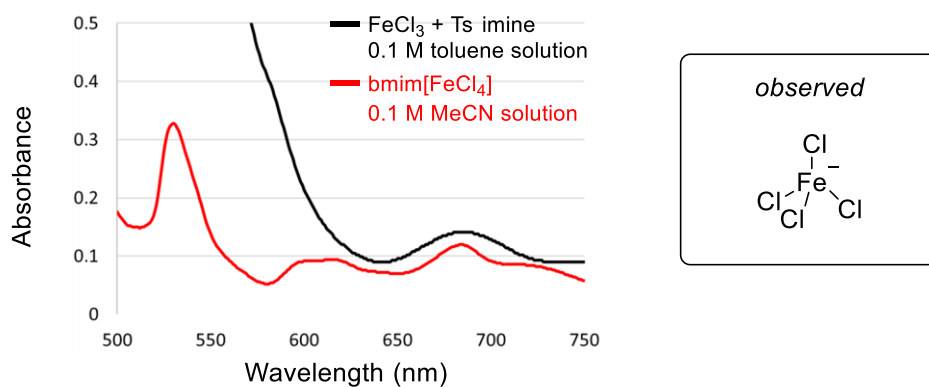
Yield: 90%. Mp. 88–89 °C (ethyl acetate). TLC:  $R_f$  = 0.53 (hexane/ethyl acetate = 5:1) <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J$  = 8.5 Hz, 2H), 7.23–7.33 (m, 7H), 5.22 (d,  $J$  = 6.5 Hz, 1H), 3.92 (d,  $J$  = 18.5 Hz, 1H), 3.27 (d,  $J$  = 18.5

Hz, 1H), 2.42 (s, 3H), 2.37–2.39 (m, 1H), 2.21 (d,  $J = 18.0$  Hz, 1H), 2.09–2.15 (m, 1H), 1.88–1.93 (m, 3H), 1.61–1.75 (m, 2H), 1.27–1.45 (m, 3H), 1.15–1.22 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  143.2, 139.9, 137.9, 131.1, 130.2, 129.6, 128.5, 127.6, 127.5, 127.3, 53.3, 45.0, 34.8, 32.6, 32.3, 31.9, 26.1, 26.1, 21.7. IR (neat): 2915, 2845, 1597, 1451, 1343, 1329, 1165, 1156, 1101, 1087, 816  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 382.1822, calcd for  $[\text{M}+\text{H}]^+$  382.1835.

## Supplemental Data

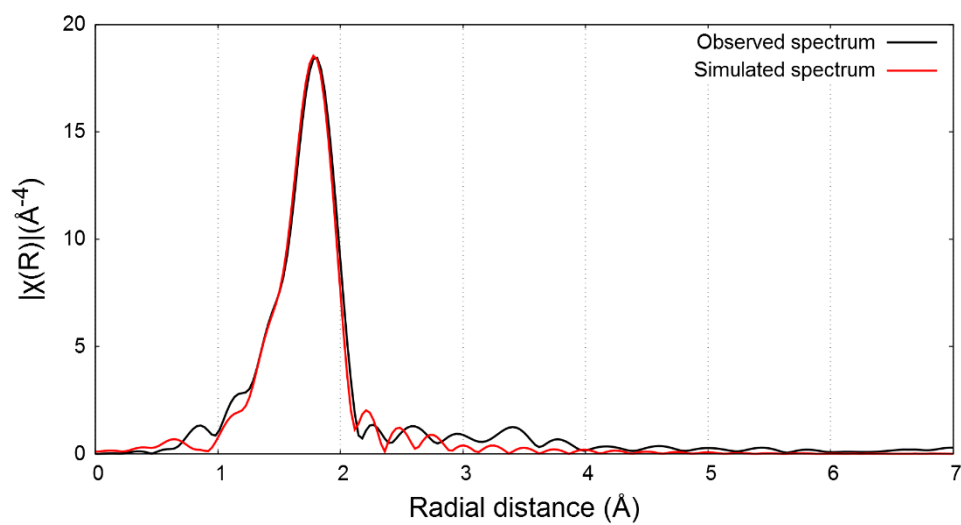


**Figure S1.** MALDI-MS measurement to detect  $[\text{FeCl}_2(\mathbf{1a})_2]^+$ .

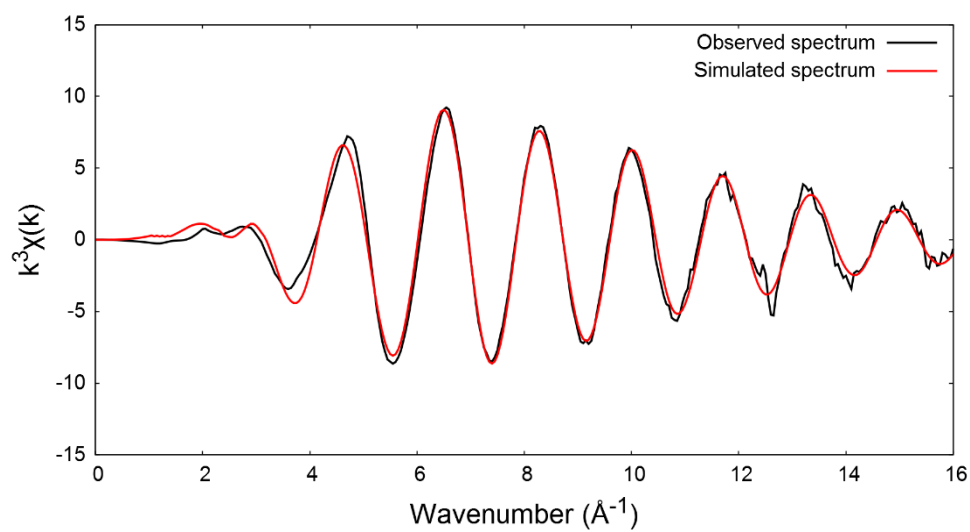


**Figure S2.** UV-vis measurement to detect  $[\text{FeCl}_4]^-$ .

## S3. XAS measurement



**Figure S3-1.** Fourier-transformed Fe *K*-edge extended X-ray absorption fine Structure in R-space.



**Figure S3-2.** Fourier-transformed Fe *K*-edge extended X-ray absorption fine Structure in K-space.

## Structural parameters obtained from EXAFS analysis

| Ab–Sc | R (Å)   | N | S <sub>0</sub> <sup>2</sup> | ΔR (Å)   | ΔE <sub>0</sub> (eV) | Δσ <sup>2</sup> (Å <sup>2</sup> ) |
|-------|---------|---|-----------------------------|----------|----------------------|-----------------------------------|
| Fe–O  | 1.92770 | 2 | 1                           | 0.09642  | –1.674               | 0.01025                           |
| Fe–Cl | 2.19830 | 2 | 1                           | 0.09642  | –1.674               | 0.01025                           |
| Fe–Cl | 2.22400 | 1 | 1                           | –0.07882 | 6.548                | 0.00410                           |
| Fe–Cl | 2.25990 | 3 | 1                           | –0.07882 | 6.548                | 0.00410                           |

$R_{\text{factor}} = 1.25\%$ ,  $\Delta k = 2.1 - 15.0$ ,  $\Delta R = 1.0 - 2.35$  (*spatial resolution*  $\delta R \geq \pi/2k_{\text{max}} = 0.105 \text{ Å}$ )

Ab–Sc: X-ray absorbing atom and scattering atom

R (Å): atomic distance (DFT model of **CP1**)

N: coordination number

S<sub>0</sub><sup>2</sup>: passive electron reduction factor

*parameter* ΔR(Å): change in half-path length

*parameter* ΔE<sub>0</sub> (eV): edge shift

*parameter* Δσ<sup>2</sup> (Å<sup>2</sup>): mean squared displacement (Debye–Waller factor)

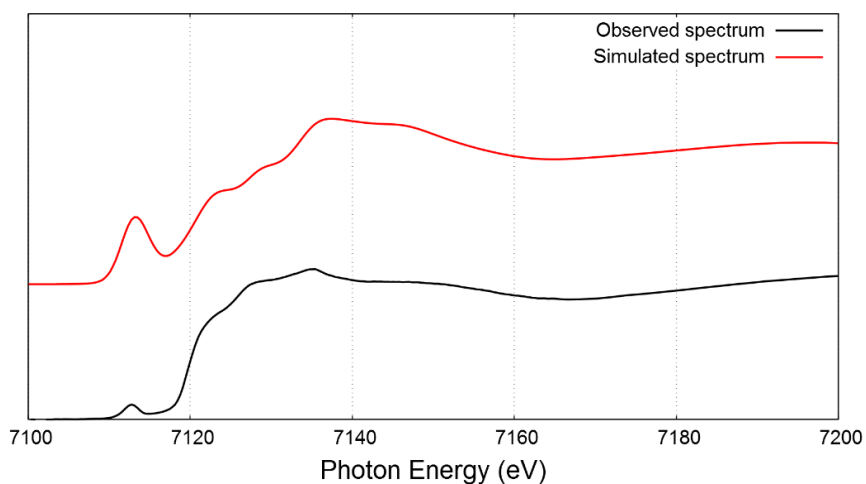
*The total number of parameters used in the model is less than that given by the Nyquist theorem.*

$N_{\text{idp}} \approx 2\Delta k\Delta R/\pi = 11.1 > N_{\text{used}} = 6$  (ΔR, ΔE<sub>0</sub> and Δσ<sup>2</sup>)

J. J. Rehr, J. J. Kas, M. P. Prange, A. P. Sorini, Y. Takimoto, and F. Vila, Ab initio theory and calculations of X-ray spectra *C. R. Phys.* **2009**, *10*, 548.

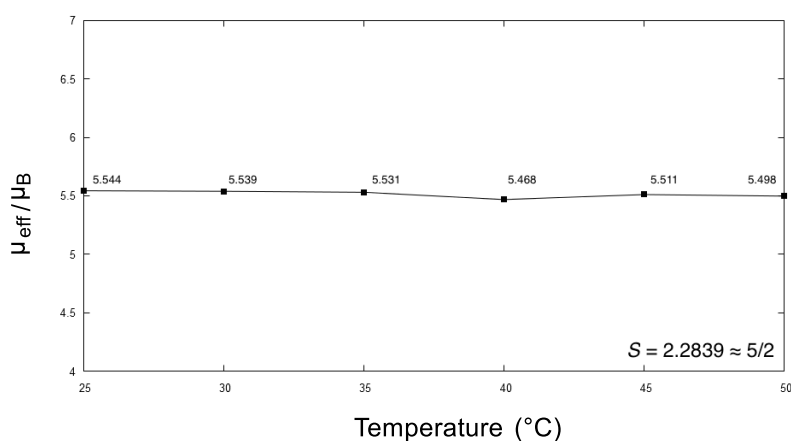
B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchrotron Rad.* **2005**, *12*, 537.

M. Newville, IFEFFIT: interactive EXAFS analysis and FEFF fitting *J. Synchrotron Rad.* **2001**, *8*, 322.



**Figure S3-3.** Fe *K*-edge X-ray absorption near edge structure (XANES)

**S4.** Paramagnetic susceptibility measurement (Evans method).



**Figure S4.** Paramagnetic susceptibility measurement.

A solution-state magnetic moment of  $5.515 \mu_B$  was measured by the Evans method (25 – 50 °C), consist with an  $S = 5/2$  ground state for the iron complex **CP1** with negligible magnetic coupling between two iron atoms. This result indicates that the two iron atoms have a spin state of  $S = 5/2$  with tetrahedral geometry, and are not connected to each other to form halide bridge dimer species. In situ-generated iron complex is  $[\text{FeCl}_2(\mathbf{1a})_2]^+$  with  $[\text{FeCl}_4]^-$ , but not dimeric species  $(\text{FeCl}_3)_2$  as proposed in different reaction systems.

## Computational Details

General Methods. Calculations were performed on Gaussian 09 E.01. For geometry optimization and frequency calculations B3LYP was used and M06 was used for single-point energy calculations. Geometry optimization and frequency calculations were carried out using 6-31G(d) (H, C, N, O, Al), 6-31+G(d) (Cl, S) and f polarization function added Lanl2dz(f) (Fe) basis sets. Single-point calculations were performed with def2-TZVP basis sets. Solvation effects of toluene were added all calculations using CPCM. Second order perturbation theory analysis of Fock matrix in NBO basis was calculated with the NBO6.0 program. Monte-Carlo simulated annealing method was initially employed to generate conformers, and followed by geometry optimization and thermodynamic calculation to obtain Boltzmann distribution of these conformers. Among conformers examined, the most stable conformer was found to be ion-pair complex **CP1**.

Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Ehlers, A. W., Böhme, M., Dapprich, S., Gobbi, A., Höllwarth, A., Jonas, V., Köhler, K. F., Stegmann, R., Veldkamp, A. & Frenking, G. A set of f-polarization functions for pseudo-potential

basis sets of the transition metals Sc-Cu, Y-Ag and La-Au. *Chem. Phys. Lett.* **1993**, *208*, 111.

Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural Population Analysis. *J. Chem. Phys.* 1985, *83*, 735–746. Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 6.0: Natural Bond Orbital Analysis Program. *J. Comput. Chem.* **2013**, *34*, 1429.

#### Cartesian Coordinates for **CP1**

Fe 1.399199000000 1.361187000000 0.835267000000  
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 Cl -1.292986000000 -2.246761000000 0.137855000000  
 Cl -0.487158000000 -5.151587000000 -1.857630000000  
 Cl -2.163774000000 -2.282774000000 -3.424206000000  
 Cl -4.032941000000 -4.405791000000 -1.049827000000

## Chapter 2

### Cartesian Coordinates for **TS1**

Fe 1.484496000000 -0.431260000000 3.897542000000  
N -0.143369000000 -3.943844000000 1.830683000000  
C -0.720971000000 -3.815937000000 0.671280000000  
S -0.476398000000 -2.757977000000 2.956898000000  
H -1.395234000000 -2.978941000000 0.459116000000  
O 0.916405000000 -2.214242000000 3.278526000000  
O -1.480299000000 -1.764009000000 2.572601000000  
N 0.759032000000 2.570034000000 0.701445000000  
H -1.050810000000 5.496950000000 -2.749187000000  
H 0.424104000000 8.312565000000 0.155997000000  
H -0.590671000000 7.847863000000 -2.067411000000  
C -0.504249000000 -4.770013000000 -0.397429000000  
C -1.153686000000 -4.545203000000 -1.626604000000  
C 0.336033000000 -5.892690000000 -0.239975000000  
C -0.963128000000 -5.430098000000 -2.685999000000  
H -1.794621000000 -3.677628000000 -1.750066000000  
C 0.515317000000 -6.771347000000 -1.298237000000  
H 0.834936000000 -6.054018000000 0.710092000000  
C -0.133162000000 -6.540334000000 -2.520991000000  
H -1.458258000000 -5.243171000000 -3.633548000000  
H 1.159888000000 -7.637691000000 -1.181248000000  
H 0.014820000000 -7.231280000000 -3.346610000000  
C -1.000122000000 -3.663964000000 4.389248000000  
C -0.114204000000 -4.546201000000 5.017676000000  
C -2.299981000000 -3.466659000000 4.856074000000  
C -0.555695000000 -5.240992000000 6.137305000000  
H 0.894345000000 -4.680090000000 4.641443000000  
C -2.716037000000 -4.175397000000 5.981803000000  
H -2.962976000000 -2.771087000000 4.353215000000  
C -1.857255000000 -5.066565000000 6.638575000000  
H 0.121906000000 -5.929663000000 6.634908000000  
H -3.725576000000 -4.029072000000 6.355546000000  
C 2.108746000000 0.359639000000 0.109426000000  
C 1.152276000000 0.087665000000 -0.874927000000  
C 3.319893000000 -0.333453000000 0.171685000000  
C 1.427784000000 -0.903225000000 -1.812423000000  
H 0.226924000000 0.649575000000 -0.926257000000  
C 3.568869000000 -1.323032000000 -0.778293000000  
H 4.054974000000 -0.094966000000 0.933446000000  
C 2.633190000000 -1.625100000000 -1.777249000000  
H 0.692952000000 -1.109528000000 -2.586703000000  
H 4.511559000000 -1.862635000000 -0.744218000000  
C -2.306011000000 -5.807962000000 7.873423000000

C 0.596058000000 3.805785000000 1.280666000000  
S 1.807160000000 1.573630000000 1.367396000000  
O 3.062403000000 2.130023000000 1.887283000000  
O 1.057306000000 0.779302000000 2.525587000000  
Cl 0.262909000000 0.113084000000 5.660259000000  
Cl 3.624033000000 -0.643249000000 4.332008000000  
C 0.243915000000 4.912611000000 0.343950000000  
C -0.319958000000 4.653896000000 -0.914455000000  
C 0.506402000000 6.237735000000 0.721006000000  
C -0.620532000000 5.709899000000 -1.774653000000  
H -0.506583000000 3.629782000000 -1.220859000000  
C 0.206892000000 7.290754000000 -0.142663000000  
H 0.959337000000 6.444173000000 1.688807000000  
C -0.360218000000 7.028693000000 -1.391849000000  
Cl -1.679331000000 -1.830445000000 -4.140712000000  
C -2.640494000000 2.552408000000 1.343592000000  
C -2.047737000000 3.712939000000 1.974980000000  
C -2.723197000000 5.037850000000 1.784565000000  
H -2.219141000000 5.839784000000 2.325739000000  
H -2.749529000000 5.301865000000 0.718712000000  
H -3.767597000000 4.986776000000 2.116964000000  
C -3.896267000000 2.713213000000 0.512005000000  
H -3.746593000000 3.409212000000 -0.320521000000  
H -4.195878000000 1.754322000000 0.084940000000  
H -4.730914000000 3.092961000000 1.114609000000  
C -0.803219000000 3.688985000000 2.636958000000  
H -0.576687000000 4.567280000000 3.237295000000  
H -0.459673000000 2.761884000000 3.083337000000  
C -2.057219000000 1.328518000000 1.459085000000  
H -1.200023000000 1.134353000000 2.089026000000  
H -2.457542000000 0.474156000000 0.920595000000  
H 1.339409000000 4.105769000000 2.025160000000  
H -3.396578000000 -5.828317000000 7.955794000000  
H -1.942223000000 -6.840922000000 7.873337000000  
H -1.914407000000 -5.325997000000 8.778522000000  
C 2.904803000000 -2.697605000000 -2.803332000000  
H 2.834485000000 -2.294505000000 -3.820321000000  
H 3.900355000000 -3.133543000000 -2.676978000000  
H 2.166842000000 -3.505560000000 -2.729891000000  
Fe -3.021557000000 -0.475158000000 -2.944680000000  
Cl -2.000570000000 1.505641000000 -2.621281000000  
Cl -4.988733000000 -0.202918000000 -3.928216000000  
Cl -3.302242000000 -1.439780000000 -0.895546000000

Cartesian Coordinates for **CP2**

Fe 2.067833000000 -0.719526000000 2.480076000000  
 N -0.360679000000 -4.055171000000 0.955614000000  
 C -0.982798000000 -4.061637000000 -0.190730000000  
 S -0.365699000000 -2.625869000000 1.797865000000  
 H -1.475014000000 -3.164415000000 -0.577090000000  
 O 1.136285000000 -2.352669000000 1.994448000000  
 O -1.130116000000 -1.513435000000 1.231637000000  
 N 0.900979000000 2.510974000000 0.798561000000  
 C 0.866400000000 3.958676000000 1.175302000000  
 S 2.371518000000 1.806241000000 0.549909000000  
 Cl 0.925511000000 0.337933000000 4.033238000000  
 Cl 4.075403000000 -1.281680000000 3.144925000000  
 C 1.002542000000 4.926618000000 0.004711000000  
 C 0.005235000000 5.106652000000 -0.967248000000  
 C 2.174084000000 5.692237000000 -0.091464000000  
 C 0.188566000000 6.012733000000 -2.012466000000  
 H -0.924560000000 4.552013000000 -0.901923000000  
 C 2.354966000000 6.604320000000 -1.132654000000  
 H 2.949873000000 5.577455000000 0.662648000000  
 C 1.362991000000 6.762722000000 -2.100399000000  
 H -0.593103000000 6.133887000000 -2.757318000000  
 H 3.268236000000 7.191361000000 -1.183318000000  
 H 1.500116000000 7.469203000000 -2.914500000000  
 C -1.064512000000 -5.260939000000 -0.998242000000  
 C -1.766353000000 -5.194712000000 -2.217958000000  
 C -0.465951000000 -6.473413000000 -0.597114000000  
 C -1.869544000000 -6.326437000000 -3.022374000000  
 H -2.214358000000 -4.256622000000 -2.529455000000  
 C -0.574167000000 -7.596046000000 -1.404793000000  
 H 0.078287000000 -6.512245000000 0.340791000000  
 C -1.275508000000 -7.523014000000 -2.616823000000  
 H -2.405372000000 -6.269935000000 -3.964736000000  
 H -0.112448000000 -8.530737000000 -1.100295000000  
 H -1.353546000000 -8.405051000000 -3.246773000000  
 C -0.998166000000 -3.080184000000 3.393182000000  
 C -0.386461000000 -4.108175000000 4.120190000000  
 C -2.096302000000 -2.378187000000 3.889822000000  
 C -0.900999000000 -4.429862000000 5.370558000000  
 H 0.467181000000 -4.641130000000 3.715415000000  
 C -2.590701000000 -2.721590000000 5.147404000000  
 H -2.546544000000 -1.582554000000 3.306552000000  
 H 4.421064000000 0.911263000000 -5.615952000000  
 Fe -1.632546000000 -1.118828000000 -3.600500000000

H 4.906646000000 3.470299000000 -3.258863000000  
 C -2.529009000000 -4.092612000000 7.275942000000  
 H -3.526696000000 -3.676487000000 7.442475000000  
 H -2.581819000000 -5.177453000000 7.418114000000  
 H -1.868437000000 -3.695232000000 8.057160000000  
 C 4.006777000000 1.875416000000 -5.298147000000  
 H 3.132958000000 2.072954000000 -5.930436000000  
 H 4.753681000000 2.648946000000 -5.499204000000  
 O 3.369065000000 2.487684000000 1.367709000000  
 O 2.118318000000 0.320404000000 0.854073000000  
 Cl -1.323636000000 1.101790000000 -3.710298000000  
 Cl -2.117582000000 -2.004986000000 -5.579273000000  
 Cl -3.259360000000 -1.624330000000 -2.114853000000  
 Cl 0.279351000000 -2.056046000000 -2.804787000000  
 C -1.582231000000 2.450020000000 0.636537000000  
 C -1.644171000000 3.451453000000 1.530538000000  
 C -2.911522000000 3.976276000000 2.158783000000  
 H -2.823014000000 3.970964000000 3.254162000000  
 H -3.088037000000 5.020889000000 1.866526000000  
 H -3.799275000000 3.399056000000 1.896040000000  
 C -2.752416000000 1.697684000000 0.052303000000  
 H -2.703280000000 1.692858000000 -1.043794000000  
 H -2.733399000000 0.644711000000 0.360767000000  
 H -3.716220000000 2.120994000000 0.340034000000  
 C -0.394217000000 4.140890000000 2.038849000000  
 H -0.579168000000 5.218878000000 2.134521000000  
 H -0.174610000000 3.776499000000 3.052803000000  
 C -0.264510000000 1.955737000000 0.075470000000  
 H -0.231384000000 0.866806000000 0.174478000000  
 H -0.206534000000 2.186332000000 -0.999102000000  
 H 1.730239000000 4.107313000000 1.823655000000  
 C -2.004491000000 -3.743403000000 5.905227000000  
 H -0.436786000000 -5.228143000000 5.944309000000  
 H -3.446032000000 -2.182159000000 5.544384000000  
 C 2.872725000000 1.774777000000 -1.155636000000  
 C 2.300768000000 0.857850000000 -2.044427000000  
 C 3.807950000000 2.724136000000 -1.577757000000  
 C 2.681368000000 0.903106000000 -3.380952000000  
 H 1.587797000000 0.110168000000 -1.717578000000  
 C 4.173968000000 2.742419000000 -2.921210000000  
 H 4.245960000000 3.419331000000 -0.871375000000  
 C 3.616852000000 1.842968000000 -3.841386000000  
 H 2.233392000000 0.192193000000 -4.069065000000

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### Cartesian Coordinates for **CP3**

Fe -0.659731000000 -0.726273000000 3.798085000000  
N -1.222215000000 -5.278014000000 4.562899000000  
C -1.517537000000 -4.951601000000 5.783293000000  
S -0.971010000000 -4.042472000000 3.454890000000  
H -1.627837000000 -3.904212000000 6.079620000000  
O -1.200257000000 -2.710728000000 4.129407000000  
O 0.331143000000 -4.263278000000 2.821584000000  
N 0.255543000000 3.182961000000 5.629695000000  
C 0.929793000000 4.413234000000 5.134070000000  
S -0.820810000000 2.402910000000 4.647300000000  
H -0.230539000000 5.884844000000 3.204498000000  
C -1.353479000000 8.085667000000 5.540672000000  
H -0.991212000000 7.917059000000 7.659718000000  
H -1.526476000000 7.982925000000 3.392555000000  
H -1.924671000000 9.006052000000 5.627848000000  
C -1.729020000000 -5.948775000000 6.817568000000  
C -2.076410000000 -5.501065000000 8.105909000000  
C -1.598392000000 -7.329545000000 6.565442000000  
C -2.294248000000 -6.421397000000 9.128887000000  
H -2.179514000000 -4.438121000000 8.302914000000  
C -1.816075000000 -8.239922000000 7.590065000000  
H -1.327570000000 -7.663215000000 5.568885000000  
C -2.164479000000 -7.787069000000 8.870818000000  
H -2.564240000000 -6.065672000000 10.118383000000  
H -1.716464000000 -9.304736000000 7.399713000000  
H -2.334156000000 -8.506196000000 9.667795000000  
C -2.272630000000 -4.269575000000 2.266736000000  
C -3.543130000000 -3.745575000000 2.524503000000  
C -1.998720000000 -4.996087000000 1.107119000000  
C -4.551401000000 -3.961080000000 1.590802000000  
H -3.733816000000 -3.164042000000 3.419850000000  
C -3.025442000000 -5.194400000000 0.186408000000  
H -1.002411000000 -5.385392000000 0.928580000000  
C -4.311109000000 -4.682549000000 0.410551000000  
H -5.540194000000 -3.551234000000 1.778268000000  
H -2.822415000000 -5.755215000000 -0.721971000000  
C -2.492238000000 2.703466000000 5.191789000000  
C -3.070587000000 1.893918000000 6.173456000000  
C -3.176252000000 3.793590000000 4.646650000000  
C -4.358617000000 2.188577000000 6.612016000000  
H -2.544068000000 1.038017000000 6.577633000000  
C -4.465292000000 4.064418000000 5.098445000000  
H -2.714915000000 4.408941000000 3.882750000000  
C -5.075028000000 3.272487000000 6.082932000000  
H -4.807202000000 1.558467000000 7.375747000000

H 1.053265000000 4.263891000000 4.061607000000  
O -0.629715000000 2.874224000000 3.279642000000  
O -0.568599000000 0.931412000000 4.941998000000  
Cl -2.724535000000 -0.280379000000 3.016986000000  
Cl 0.603450000000 -0.610643000000 1.978027000000  
C 0.128230000000 5.698887000000 5.321293000000  
C -0.092590000000 6.293240000000 6.573727000000  
C -0.398979000000 6.327783000000 4.183354000000  
C -0.829999000000 7.473168000000 6.680828000000  
H 0.326571000000 5.842514000000 7.467287000000  
C -1.132463000000 7.510892000000 4.288837000000  
Cl -2.381202000000 -2.742828000000 10.755366000000  
Cl -1.915463000000 0.797840000000 9.845661000000  
Cl -2.588187000000 -1.682799000000 7.270355000000  
C 1.395707000000 3.387184000000 7.832156000000  
C 2.393465000000 4.059170000000 7.233850000000  
C 3.677990000000 4.480806000000 7.903241000000  
H 4.540418000000 4.098161000000 7.339975000000  
H 3.773327000000 5.575640000000 7.910575000000  
H 3.772446000000 4.126432000000 8.931168000000  
C 1.347538000000 2.971054000000 9.282761000000  
H 0.370986000000 3.209008000000 9.723555000000  
H 1.471044000000 1.884823000000 9.383675000000  
H 2.113401000000 3.457286000000 9.889936000000  
C 2.334760000000 4.416768000000 5.762451000000  
H 2.773732000000 5.410809000000 5.605246000000  
H 2.962042000000 3.707249000000 5.204853000000  
C 0.152536000000 2.961380000000 7.079642000000  
H -0.011772000000 1.891948000000 7.247817000000  
H -0.724950000000 3.484504000000 7.493663000000  
N 3.481964000000 -1.861197000000 5.017155000000  
C 3.176386000000 -2.758047000000 4.138486000000  
S 2.244768000000 -0.835582000000 5.542717000000  
H 2.149704000000 -2.888099000000 3.786378000000  
O 2.607555000000 0.523922000000 5.146098000000  
O 0.899600000000 -1.373471000000 5.116077000000  
C 4.178273000000 -3.653068000000 3.572068000000  
C 5.539770000000 -3.561708000000 3.917701000000  
C 3.755063000000 -4.629398000000 2.652801000000  
C 6.457918000000 -4.436963000000 3.352196000000  
H 5.855544000000 -2.800255000000 4.623342000000  
C 4.682165000000 -5.504138000000 2.089533000000  
H 2.702682000000 -4.694512000000 2.392774000000  
C 6.030473000000 -5.408721000000 2.438181000000  
H 7.508965000000 -4.366028000000 3.617148000000  
H 4.353676000000 -6.257997000000 1.380071000000

H -5.007206000000 4.906569000000 4.676096000000  
 C -5.410668000000 -4.876072000000 -0.604578000000  
 H -5.181289000000 -5.692956000000 -1.295356000000  
 H -6.367720000000 -5.095415000000 -0.119319000000  
 H -5.551450000000 -3.966247000000 -1.202237000000  
 C -6.480390000000 3.559949000000 6.551242000000  
 H -6.565437000000 3.454765000000 7.638031000000  
 H -6.798022000000 4.570510000000 6.276292000000  
 H -7.191366000000 2.853852000000 6.103185000000  
 Fe -3.070621000000 -1.074552000000 9.412263000000  
 Cl -5.258251000000 -0.700762000000 9.584860000000  
 C 2.495899000000 -1.372755000000 11.592397000000  
 H 1.557847000000 -1.053778000000 12.057660000000

Cartesian Coordinates for **TS1** (antiferromagnetic singlet state)

Fe 3.949290000000 0.213097000000 -0.979740000000  
 N 4.191836000000 -3.215914000000 -3.761342000000  
 C 4.131966000000 -2.244782000000 -4.629526000000  
 S 4.230781000000 -2.823072000000 -2.145653000000  
 H 4.182609000000 -1.200818000000 -4.310236000000  
 O 4.588827000000 -1.336483000000 -1.988015000000  
 O 2.994704000000 -3.256418000000 -1.500950000000  
 N 2.112397000000 2.860721000000 -3.715356000000  
 C 2.928658000000 3.863296000000 -3.227315000000  
 S 2.462639000000 1.361016000000 -3.385702000000  
 H 3.750943000000 3.562776000000 -2.570209000000  
 O 3.755973000000 0.870521000000 -3.917008000000  
 O 2.455819000000 1.068789000000 -1.827666000000  
 Cl 3.204174000000 -0.447709000000 0.981748000000  
 Cl 5.631960000000 1.631944000000 -0.757018000000  
 C 3.332006000000 4.936072000000 -4.180929000000  
 C 2.715125000000 5.074729000000 -5.432775000000  
 C 4.381850000000 5.800576000000 -3.829435000000  
 C 3.144002000000 6.066080000000 -6.316589000000  
 H 1.925484000000 4.392634000000 -5.728322000000  
 C 4.805234000000 6.790184000000 -4.713281000000  
 H 4.879880000000 5.685608000000 -2.868337000000  
 C 4.184456000000 6.926190000000 -5.958631000000  
 H 2.670601000000 6.148283000000 -7.290456000000  
 H 5.626050000000 7.446123000000 -4.436737000000  
 H 4.519948000000 7.692269000000 -6.652179000000  
 C 3.971826000000 -2.475161000000 -6.047124000000  
 C 3.816158000000 -1.345916000000 -6.877908000000  
 C 3.922891000000 -3.770764000000 -6.604427000000  
 C 3.601564000000 -1.507592000000 -8.244308000000  
 H 3.846228000000 -0.347992000000 -6.449316000000

H 6.753283000000 -6.090251000000 1.997650000000  
 C 2.318302000000 -1.032777000000 7.309256000000  
 C 3.516545000000 -0.732823000000 7.966630000000  
 C 1.176327000000 -1.420690000000 8.012563000000  
 C 3.561850000000 -0.843173000000 9.353126000000  
 H 4.390542000000 -0.418077000000 7.406215000000  
 C 1.244456000000 -1.516013000000 9.401643000000  
 H 0.247030000000 -1.627878000000 7.494186000000  
 C 2.433494000000 -1.237004000000 10.090831000000  
 H 4.488463000000 -0.614256000000 9.873318000000  
 H 0.351136000000 -1.797262000000 9.952433000000  
 H 2.661222000000 -2.418982000000 11.881311000000  
 H 3.312865000000 -0.780741000000 12.016903000000

C 6.490684000000 -5.658598000000 -0.406712000000  
 H 4.391324000000 -5.341359000000 -0.819075000000  
 C 7.793051000000 -5.147473000000 -0.497596000000  
 H 8.985609000000 -3.483325000000 -1.181405000000  
 H 6.325514000000 -6.625051000000 0.061525000000  
 C 1.084739000000 0.428463000000 -4.008073000000  
 C 0.584619000000 0.734464000000 -5.278562000000  
 C 0.601903000000 -0.657028000000 -3.271402000000  
 C -0.430879000000 -0.058693000000 -5.803833000000  
 H 0.967975000000 1.574240000000 -5.845974000000  
 C -0.414934000000 -1.436112000000 -3.822900000000  
 H 0.993714000000 -0.885504000000 -2.286711000000  
 C -0.944914000000 -1.152840000000 -5.089120000000  
 H -0.814922000000 0.179259000000 -6.792119000000  
 H -0.798846000000 -2.278425000000 -3.253595000000  
 C 8.965015000000 -5.909689000000 0.069548000000  
 H 8.746613000000 -6.978462000000 0.152877000000  
 H 9.858677000000 -5.788831000000 -0.551286000000  
 H 9.215200000000 -5.544837000000 1.074227000000  
 C -2.050713000000 -1.993112000000 -5.678604000000  
 H -1.801315000000 -2.311699000000 -6.696831000000  
 H -2.244688000000 -2.885647000000 -5.076188000000  
 H -2.984263000000 -1.420480000000 -5.744042000000  
 Fe 0.733154000000 2.783817000000 -8.975911000000  
 Cl 2.770756000000 2.225214000000 -8.162978000000  
 Cl 0.938028000000 4.157078000000 -10.711480000000  
 Cl -0.401612000000 3.804968000000 -7.294074000000  
 Cl -0.334867000000 0.885724000000 -9.533988000000  
 C -0.332838000000 4.516825000000 -2.690210000000  
 C 0.834349000000 5.288255000000 -2.330333000000  
 C 0.908809000000 6.719544000000 -2.763845000000  
 H 1.789557000000 7.224842000000 -2.365054000000

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C 3.723519000000 -3.922863000000 -7.968374000000  
H 4.038443000000 -4.633532000000 -5.956112000000  
C 3.558553000000 -2.794047000000 -8.786056000000  
H 3.455166000000 -0.632708000000 -8.869651000000  
H 3.686674000000 -4.917202000000 -8.403850000000  
H 3.389594000000 -2.922459000000 -9.851669000000  
C 5.626260000000 -3.707324000000 -1.497949000000  
C 6.910757000000 -3.165793000000 -1.607099000000  
C 5.399140000000 -4.949115000000 -0.902200000000  
C 7.983072000000 -3.895536000000 -1.104881000000  
H 7.067013000000 -2.193804000000 -2.062873000000  
H -1.238838000000 2.591271000000 -2.705864000000

Cartesian Coordinates for **CPI** ( $[\text{AlCl}_2]^+[\text{AlCl}_4]^-$ )

N -1.341728000000 -0.089939000000 -3.069889000000  
C -0.531946000000 0.913286000000 -2.926854000000  
S -1.692165000000 -1.011169000000 -1.710705000000  
H -0.066349000000 1.140809000000 -1.967297000000  
O -1.840433000000 -2.401558000000 -2.150376000000  
O -0.690589000000 -0.749363000000 -0.605074000000  
Cl -0.237273000000 -2.477367000000 1.829027000000  
Cl 2.249164000000 -0.391457000000 -1.335678000000  
C -0.214059000000 1.804593000000 -4.030936000000  
C -0.724673000000 1.608972000000 -5.328272000000  
C 0.616445000000 2.908200000000 -3.764116000000  
C -0.403641000000 2.505761000000 -6.338586000000  
H -1.371091000000 0.758400000000 -5.519168000000  
C 0.930553000000 3.806303000000 -4.781535000000  
H 0.995515000000 3.057150000000 -2.756948000000  
C 0.422433000000 3.604312000000 -6.066075000000  
H -0.798911000000 2.359787000000 -7.339799000000  
H 1.562685000000 4.663738000000 -4.571664000000  
H 0.664128000000 4.306680000000 -6.859309000000  
C -3.246934000000 -0.375128000000 -1.130726000000  
C -4.382624000000 -1.173899000000 -1.281660000000  
C -3.315087000000 0.908610000000 -0.576700000000  
C -5.609023000000 -0.672164000000 -0.849792000000  
H -4.301996000000 -2.161101000000 -1.723579000000  
C -4.553055000000 1.388307000000 -0.161210000000  
H -2.432432000000 1.530314000000 -0.462725000000  
C -5.715676000000 0.610068000000 -0.291726000000  
H -6.499513000000 -1.286880000000 -0.955528000000  
H -4.612356000000 2.383305000000 0.269969000000  
C -7.051816000000 1.164795000000 0.134800000000  
H -6.945777000000 1.842505000000 0.987033000000  
H -7.503623000000 1.745194000000 -0.680425000000

H 0.955948000000 6.771375000000 -3.862041000000  
H 0.011233000000 7.272032000000 -2.462679000000  
C -1.415856000000 5.146661000000 -3.539892000000  
H -1.030818000000 5.450151000000 -4.520108000000  
H -2.228685000000 4.438288000000 -3.714862000000  
H -1.842395000000 6.034949000000 -3.059141000000  
C 1.986100000000 4.692487000000 -1.774857000000  
H 2.738475000000 5.376063000000 -1.389384000000  
H 1.879460000000 3.793163000000 -1.176293000000  
C -0.417038000000 3.202647000000 -2.345431000000  
H 0.275199000000 2.713935000000 -1.672213000000

C 6.041119000000 -1.852168000000 -1.960092000000  
C 6.608907000000 -0.819932000000 -2.726066000000  
C 6.154424000000 -3.186409000000 -2.393814000000  
C 7.283615000000 -1.114122000000 -3.908537000000  
H 6.513835000000 0.209696000000 -2.390925000000  
C 6.830917000000 -3.474246000000 -3.572553000000  
H 5.706997000000 -3.973620000000 -1.795849000000  
C 7.396189000000 -2.440500000000 -4.329874000000  
H 7.719728000000 -0.313698000000 -4.498651000000  
H 6.921192000000 -4.503532000000 -3.907553000000  
H 7.924307000000 -2.671908000000 -5.250938000000  
C 4.511025000000 -2.997499000000 2.652840000000  
C 5.347538000000 -2.576728000000 3.686501000000  
C 4.034407000000 -4.310050000000 2.572496000000  
C 5.714605000000 -3.500352000000 4.664051000000  
H 5.694007000000 -1.549785000000 3.726624000000  
C 4.419058000000 -5.210379000000 3.559913000000  
H 3.381851000000 -4.612979000000 1.760404000000  
C 5.257859000000 -4.823937000000 4.618457000000  
H 6.363282000000 -3.183988000000 5.476484000000  
H 4.055743000000 -6.233658000000 3.510995000000  
C 5.635551000000 -5.812415000000 5.694582000000  
H 5.883373000000 -6.790728000000 5.268576000000  
H 6.494489000000 -5.465325000000 6.276602000000  
H 4.802444000000 -5.965618000000 6.392687000000  
N 0.057488000000 -5.507295000000 -0.949625000000  
C -1.041266000000 -5.040981000000 -0.451784000000  
S 1.342534000000 -4.433538000000 -1.141055000000  
H -1.141910000000 -3.988634000000 -0.186351000000  
O 0.907137000000 -3.017456000000 -0.891795000000  
O 2.476518000000 -4.959955000000 -0.380019000000  
C -2.198882000000 -5.891185000000 -0.208850000000  
C -3.343388000000 -5.302398000000 0.357138000000

H -7.753404000000 0.366874000000 0.399658000000  
 Cl -2.840579000000 4.878765000000 -0.236323000000  
 Cl -2.230439000000 5.766502000000 3.131526000000  
 Cl -5.358593000000 4.423168000000 2.197898000000  
 Cl -4.475451000000 7.722981000000 1.168841000000  
 N 4.817173000000 -2.399515000000 0.035416000000  
 C 5.352975000000 -1.502690000000 -0.724823000000  
 S 4.039756000000 -1.815187000000 1.415919000000  
 H 5.320380000000 -0.441775000000 -0.461595000000  
 O 4.478839000000 -0.470003000000 1.807950000000  
 O 2.569325000000 -2.044008000000 1.206694000000  
 H 0.219972000000 -3.046276000000 -3.435283000000  
 C 2.903503000000 -5.562740000000 -4.679852000000  
 H 3.182030000000 -6.061659000000 -2.592853000000  
 C 2.215053000000 -4.774997000000 -5.612598000000  
 H 0.703031000000 -3.254020000000 -5.853337000000  
 H 3.650527000000 -6.272637000000 -5.025567000000  
 C 2.516055000000 -4.877764000000 -7.088076000000  
 H 3.049973000000 -5.802673000000 -7.326489000000  
 H 1.598298000000 -4.849551000000 -7.685276000000  
 H 3.142113000000 -4.038664000000 -7.418327000000  
 N -0.940319000000 1.762159000000 2.365048000000  
 C -1.300759000000 0.720467000000 3.044528000000  
 S 0.348524000000 1.637517000000 1.313299000000  
 H -0.783415000000 -0.237155000000 2.935622000000  
 O 0.983973000000 0.253725000000 1.364174000000  
 O -0.093408000000 2.110623000000 -0.000337000000  
 C -2.413467000000 0.766386000000 3.976574000000  
 C -2.734630000000 -0.408353000000 4.683325000000  
 C -3.165717000000 1.939730000000 4.182305000000  
 C -3.792259000000 -0.408968000000 5.587691000000  
 H -2.151216000000 -1.310081000000 4.513767000000  
 C -4.223807000000 1.929031000000 5.083615000000  
 Al 0.970680000000 -1.374849000000 0.251502000000

Cartesian Coordinates for **TS1** ( $[\text{AlCl}_2]^+[\text{AlCl}_4]^-$ )

N 2.590801000000 1.701378000000 -3.692835000000  
 C 3.843182000000 2.068623000000 -4.113872000000  
 S 2.500588000000 0.520482000000 -2.604123000000  
 H 4.702254000000 1.589608000000 -3.634901000000  
 O 2.546692000000 -0.821178000000 -3.227025000000  
 O 3.548861000000 0.707828000000 -1.499021000000  
 Cl 3.488108000000 -1.231185000000 0.827523000000  
 Cl 6.534742000000 0.897335000000 -1.806044000000  
 C 4.026148000000 2.246738000000 -5.588821000000  
 C 2.930007000000 2.371282000000 -6.454251000000

C -2.200194000000 -7.264098000000 -0.517728000000  
 C -4.475014000000 -6.074675000000 0.609691000000  
 H -3.333216000000 -4.242996000000 0.599186000000  
 C -3.332396000000 -8.028584000000 -0.265804000000  
 H -1.310288000000 -7.708717000000 -0.951344000000  
 C -4.469587000000 -7.435581000000 0.297533000000  
 H -5.356721000000 -5.618014000000 1.049369000000  
 H -3.335415000000 -9.088140000000 -0.504986000000  
 H -5.351825000000 -8.038943000000 0.493631000000  
 C 1.684394000000 -4.539413000000 -2.885125000000  
 C 0.973179000000 -3.742744000000 -3.786446000000  
 C 2.646220000000 -5.454639000000 -3.314647000000  
 C 1.248930000000 -3.870954000000 -5.144378000000  
 H -2.919641000000 2.844176000000 3.636012000000  
 C -4.535522000000 0.758596000000 5.785994000000  
 H -4.039845000000 -1.314410000000 6.134410000000  
 H -4.807249000000 2.832594000000 5.229535000000  
 H -5.364046000000 0.757121000000 6.489560000000  
 C 1.517278000000 2.770298000000 2.022436000000  
 C 2.826927000000 2.370646000000 2.280988000000  
 C 1.074351000000 4.078668000000 2.260639000000  
 C 3.713294000000 3.316025000000 2.798591000000  
 H 3.151098000000 1.355776000000 2.083797000000  
 C 1.980762000000 4.995285000000 2.780084000000  
 H 0.049009000000 4.375119000000 2.062433000000  
 C 3.309434000000 4.631740000000 3.057277000000  
 H 4.738365000000 3.018301000000 3.003899000000  
 H 1.643139000000 6.009812000000 2.974697000000  
 C 4.270914000000 5.644249000000 3.630787000000  
 H 3.955318000000 5.962191000000 4.632206000000  
 H 5.283552000000 5.237577000000 3.711087000000  
 H 4.314526000000 6.545668000000 3.008304000000  
 Al -3.735444000000 5.737726000000 1.550807000000

C 0.739181000000 1.462031000000 -0.678380000000  
 C -1.474073000000 0.358450000000 -1.977362000000  
 H -0.058418000000 -0.423428000000 -3.412518000000  
 C -0.542075000000 1.649491000000 -0.167059000000  
 H 1.594643000000 1.899848000000 -0.180149000000  
 C -1.667282000000 1.111872000000 -0.811179000000  
 H -2.333758000000 -0.069453000000 -2.487309000000  
 H -0.665829000000 2.247098000000 0.732222000000  
 C -3.048011000000 1.364528000000 -0.258106000000  
 H -3.133602000000 1.003258000000 0.773720000000  
 H -3.261781000000 2.439750000000 -0.238627000000

## Chapter 2

C 5.322121000000 2.249529000000 -6.126989000000  
C 3.129482000000 2.510959000000 -7.828084000000  
H 1.928231000000 2.337183000000 -6.038504000000  
C 5.519281000000 2.384922000000 -7.501237000000  
H 6.177318000000 2.136856000000 -5.463859000000  
C 4.422948000000 2.520469000000 -8.356267000000  
H 2.271644000000 2.603612000000 -8.489078000000  
H 6.528712000000 2.380879000000 -7.904381000000  
H 4.575171000000 2.625874000000 -9.427141000000  
C 0.897020000000 0.722455000000 -1.852433000000  
C -0.199829000000 0.157266000000 -2.507155000000  
H 0.251682000000 5.900637000000 -3.937536000000  
H 1.645041000000 6.903734000000 -4.341566000000  
C 4.327669000000 3.764519000000 -3.290368000000  
H 5.389547000000 3.810627000000 -3.520916000000  
H 4.125522000000 3.442269000000 -2.275003000000  
C 1.621691000000 4.330611000000 -2.419837000000  
H 2.227469000000 3.772037000000 -1.722143000000  
H 0.573195000000 4.441571000000 -2.159635000000  
N 8.781416000000 -1.379480000000 -0.271471000000  
C 9.455829000000 -0.446165000000 -0.855406000000  
S 7.817607000000 -0.885204000000 1.025955000000  
H 9.421535000000 0.587643000000 -0.500535000000  
O 8.244115000000 0.391760000000 1.614853000000  
O 6.393936000000 -1.018771000000 0.575347000000  
C 10.310184000000 -0.719137000000 -2.004216000000  
C 11.036180000000 0.343095000000 -2.568668000000  
C 10.427696000000 -2.011415000000 -2.549036000000  
C 11.871815000000 0.119605000000 -3.660483000000  
H 10.938298000000 1.340903000000 -2.148595000000  
C 11.264192000000 -2.229135000000 -3.636792000000  
H 9.856581000000 -2.821743000000 -2.107841000000  
C 11.987004000000 -1.166137000000 -4.192607000000  
H 12.431018000000 0.943254000000 -4.094295000000  
H 11.356961000000 -3.226329000000 -4.057291000000  
H 12.639828000000 -1.342670000000 -5.043194000000  
C 8.055528000000 -2.201250000000 2.194351000000  
C 8.734851000000 -1.922370000000 3.379855000000  
C 7.555717000000 -3.476277000000 1.909113000000  
C 8.916995000000 -2.952399000000 4.301939000000  
H 9.104054000000 -0.921589000000 3.576168000000  
C 7.754501000000 -4.484916000000 2.845467000000  
H 7.028238000000 -3.668389000000 0.980451000000  
C 8.431917000000 -4.242512000000 4.052218000000  
H 9.442401000000 -2.746913000000 5.230770000000  
H 7.371324000000 -5.480640000000 2.637291000000

H -3.819930000000 0.871512000000 -0.857398000000  
Cl -1.510906000000 5.547421000000 -0.547208000000  
Cl 1.698241000000 6.635082000000 0.470239000000  
Cl -0.214309000000 4.491240000000 2.564036000000  
Cl -1.189076000000 7.887606000000 2.128902000000  
C 2.143310000000 4.963637000000 -3.506864000000  
C 3.521393000000 4.756607000000 -3.879368000000  
C 4.064497000000 5.524120000000 -5.050784000000  
H 5.120933000000 5.312031000000 -5.223879000000  
H 3.510818000000 5.279426000000 -5.967261000000  
H 3.943041000000 6.602844000000 -4.890373000000  
C 1.266296000000 5.874386000000 -4.341492000000  
H 1.211546000000 5.548251000000 -5.387411000000  
C 0.510877000000 -3.789476000000 -1.229179000000  
C 1.677954000000 -5.779120000000 -2.005929000000  
C -0.675775000000 -4.515956000000 -1.155072000000  
H 0.530579000000 -2.737293000000 -0.958879000000  
C 0.491357000000 -6.497335000000 -1.931096000000  
H 2.598788000000 -6.252473000000 -2.331121000000  
C -0.685429000000 -5.867224000000 -1.505778000000  
H -1.588532000000 -4.029443000000 -0.824434000000  
H 0.476088000000 -7.549331000000 -2.201546000000  
H -1.610580000000 -6.434500000000 -1.448050000000  
C 5.882616000000 -3.069497000000 -3.792623000000  
C 5.263541000000 -2.184300000000 -4.679657000000  
C 6.871763000000 -3.959427000000 -4.211677000000  
C 5.665188000000 -2.193723000000 -6.012181000000  
H 4.482132000000 -1.514359000000 -4.335327000000  
C 7.254001000000 -3.949603000000 -5.551970000000  
H 7.332426000000 -4.636964000000 -3.500850000000  
C 6.663372000000 -3.068978000000 -6.468436000000  
H 5.195998000000 -1.503064000000 -6.708140000000  
H 8.023524000000 -4.638706000000 -5.890569000000  
C 7.100295000000 -3.044765000000 -7.913222000000  
H 7.655816000000 -3.948754000000 -8.181032000000  
H 6.241602000000 -2.959045000000 -8.587843000000  
H 7.752456000000 -2.183974000000 -8.110500000000  
N 3.570793000000 2.600717000000 2.560962000000  
C 3.461944000000 1.453726000000 3.148541000000  
S 4.386411000000 2.677553000000 1.100010000000  
H 3.926255000000 0.554882000000 2.733139000000  
O 5.075473000000 1.364119000000 0.792975000000  
O 3.456066000000 3.200366000000 0.101485000000  
C 2.701979000000 1.299645000000 4.379228000000  
C 2.726312000000 0.050821000000 5.026168000000  
C 1.941715000000 2.355995000000 4.917943000000

C 8.611389000000 -5.349094000000 5.062905000000  
 H 8.945334000000 -6.276022000000 4.583546000000  
 H 9.343143000000 -5.078973000000 5.830010000000  
 H 7.664278000000 -5.572043000000 5.570770000000  
 N 4.040985000000 -4.114203000000 -2.094720000000  
 C 2.909535000000 -3.613994000000 -1.714914000000  
 S 5.384317000000 -3.099003000000 -2.082884000000  
 H 2.821150000000 -2.568749000000 -1.421204000000  
 O 4.997993000000 -1.688121000000 -1.748724000000  
 O 6.419366000000 -3.748937000000 -1.276324000000  
 C 1.695190000000 -4.416087000000 -1.655822000000  
 H 7.272146000000 2.457652000000 1.516098000000  
 C 6.204856000000 6.187268000000 1.762755000000  
 H 4.201878000000 5.497643000000 1.347695000000  
 C 7.554509000000 5.842099000000 1.946090000000  
 H 8.962890000000 4.211248000000 1.986462000000  
 H 5.900265000000 7.228718000000 1.826960000000  
 C 8.579837000000 6.911083000000 2.237566000000

Cartesian Coordinates for **CP2** ([AlCl<sub>2</sub>]<sup>+</sup>[AlCl<sub>4</sub>]<sup>-</sup>)

N -1.040749000000 1.497154000000 -2.672431000000  
 C 0.103202000000 1.426301000000 -3.633023000000  
 S -1.424994000000 0.089353000000 -1.889358000000  
 H 0.784412000000 0.631235000000 -3.317449000000  
 O -1.216223000000 -1.017784000000 -2.830185000000  
 O -0.720567000000 -0.040585000000 -0.554874000000  
 Cl -0.635348000000 -2.035986000000 1.677193000000  
 Cl 2.263801000000 0.350190000000 -0.868898000000  
 C -0.356707000000 1.135474000000 -5.055965000000  
 C -1.611908000000 1.517165000000 -5.540809000000  
 C 0.542790000000 0.516665000000 -5.935289000000  
 C -1.960255000000 1.282395000000 -6.873107000000  
 H -2.317567000000 1.996552000000 -4.870543000000  
 C 0.198902000000 0.284795000000 -7.267438000000  
 H 1.524243000000 0.217201000000 -5.571266000000  
 C -1.058142000000 0.666501000000 -7.741307000000  
 H -2.940417000000 1.585264000000 -7.232416000000  
 H 0.911866000000 -0.192697000000 -7.935410000000  
 H -1.331478000000 0.484672000000 -8.777243000000  
 C -3.145774000000 0.239853000000 -1.468261000000  
 C -4.076399000000 -0.091291000000 -2.459284000000  
 C -3.543366000000 0.686528000000 -0.204485000000  
 C -5.431721000000 0.033732000000 -2.165711000000  
 H -3.745339000000 -0.445588000000 -3.430038000000  
 C -4.905397000000 0.808557000000 0.060290000000  
 H -2.812930000000 0.959127000000 0.547913000000

C 2.013825000000 -0.136634000000 6.207381000000  
 H 3.302391000000 -0.763647000000 4.594089000000  
 C 1.227799000000 2.158520000000 6.094037000000  
 H 1.899331000000 3.305104000000 4.393591000000  
 C 1.266517000000 0.916955000000 6.740357000000  
 H 2.033797000000 -1.100661000000 6.707401000000  
 H 0.632668000000 2.969095000000 6.503720000000  
 H 0.703741000000 0.769107000000 7.658322000000  
 C 5.650291000000 3.882476000000 1.418718000000  
 C 6.978857000000 3.498716000000 1.592104000000  
 C 5.241737000000 5.220228000000 1.497860000000  
 C 7.921668000000 4.493647000000 1.853532000000  
 H 8.354620000000 7.426273000000 3.179378000000  
 H 9.587313000000 6.491738000000 2.316424000000  
 H 8.590940000000 7.674313000000 1.450236000000  
 Al -0.315744000000 6.166168000000 1.171333000000  
 Al 4.955955000000 -0.134132000000 -0.514504000000

H 4.006614000000 -6.027306000000 6.478390000000  
 N -0.342875000000 -4.624538000000 -1.268382000000  
 C -1.440156000000 -3.996487000000 -0.996552000000  
 S 1.102728000000 -3.766641000000 -1.165410000000  
 H -1.436361000000 -2.941526000000 -0.724956000000  
 O 0.867173000000 -2.297737000000 -0.937427000000  
 O 1.982151000000 -4.484143000000 -0.241841000000  
 C -2.736640000000 -4.658309000000 -1.022471000000  
 C -3.871652000000 -3.905002000000 -0.672957000000  
 C -2.878844000000 -6.012835000000 -1.377887000000  
 C -5.132615000000 -4.497358000000 -0.680766000000  
 H -3.756638000000 -2.862744000000 -0.387988000000  
 C -4.139105000000 -6.596421000000 -1.386538000000  
 H -1.995471000000 -6.585317000000 -1.641588000000  
 C -5.265976000000 -5.840234000000 -1.038269000000  
 H -6.006175000000 -3.913581000000 -0.407095000000  
 H -4.250907000000 -7.641283000000 -1.661627000000  
 H -6.249175000000 -6.303013000000 -1.044615000000  
 C 1.739197000000 -3.895317000000 -2.824605000000  
 C 1.288506000000 -3.017669000000 -3.814630000000  
 C 2.646425000000 -4.917121000000 -3.105555000000  
 C 1.768417000000 -3.179450000000 -5.110889000000  
 H 0.577125000000 -2.233078000000 -3.578149000000  
 C 3.116320000000 -5.053156000000 -4.411073000000  
 H 2.975505000000 -5.585913000000 -2.317456000000  
 C 2.686902000000 -4.192222000000 -5.430017000000  
 H 1.416296000000 -2.504677000000 -5.886945000000

## Chapter 2

C -5.866051000000 0.491588000000 -0.911629000000  
H -6.164653000000 -0.223172000000 -2.926249000000  
H -5.211854000000 1.183126000000 1.032953000000  
C -7.333747000000 0.668500000000 -0.611165000000  
H -7.607358000000 0.181164000000 0.331365000000  
H -7.575999000000 1.732356000000 -0.499606000000  
H -7.963012000000 0.259004000000 -1.407496000000  
Cl -4.317386000000 4.593526000000 0.599205000000  
Cl -2.784440000000 5.466175000000 3.693014000000  
Cl -4.808933000000 2.561580000000 3.459182000000  
Cl -6.305876000000 5.777412000000 3.295401000000  
C -1.090485000000 3.971205000000 -2.842045000000  
C -0.008203000000 3.968770000000 -3.637763000000  
C 0.393300000000 5.045625000000 -4.608279000000  
H 1.406834000000 5.409018000000 -4.387689000000  
H 0.418231000000 4.650636000000 -5.633449000000  
H -0.279159000000 5.906149000000 -4.596497000000  
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Cartesian Coordinates for **CP3** ([AlCl<sub>2</sub>]<sup>+</sup>[AlCl<sub>4</sub>]<sup>-</sup>)

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## Chapter 2

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## Chapter 3

### **Iron(III)-Catalyzed Intermolecular [2+2+2] Cycloaddition Reaction of Alkenes**

A novel methodology for the synthesis of cyclohexane scaffolds has been developed. The unprecedented intermolecular [2+2+2] cycloaddition reaction of three alkenes was catalyzed by an iron(III)-based Lewis acid catalyst to give multi-substituted cyclohexane products in a diastereoselective manner. The ionic species  $[\text{FeBr}_2]^+[\text{FeBr}_4]^-$  generated via disproportionation of  $\text{FeBr}_3$  is crucial for this catalysis: the strong Lewis acidity of  $[\text{FeBr}_2]^+$  facilitates the addition reaction of a nucleophile, and  $[\text{FeBr}_4]^-$  prevents the fast polymerization reaction by forming a dormant-like species. This protocol offers a new synthetic way to obtain multi-substituted cyclohexane cycloadduct which is a core structure for many natural products and pharmaceuticals.

## Introduction

The cyclohexane scaffold is the core structure of many natural products, such as steroidal compounds. Therefore, the development of a method for six-membered carbocycle construction has remained arguably important, and many approaches to control the regio- and stereochemistry have been examined by several researchers to date, including the Diels–Alder reaction followed by reduction,<sup>1</sup> hydrogenation of the benzene ring,<sup>2</sup> dimerization of donor–acceptor cyclopropane compounds,<sup>3</sup> and double alkylation of the carbonyl  $\alpha$ -position.<sup>4</sup>

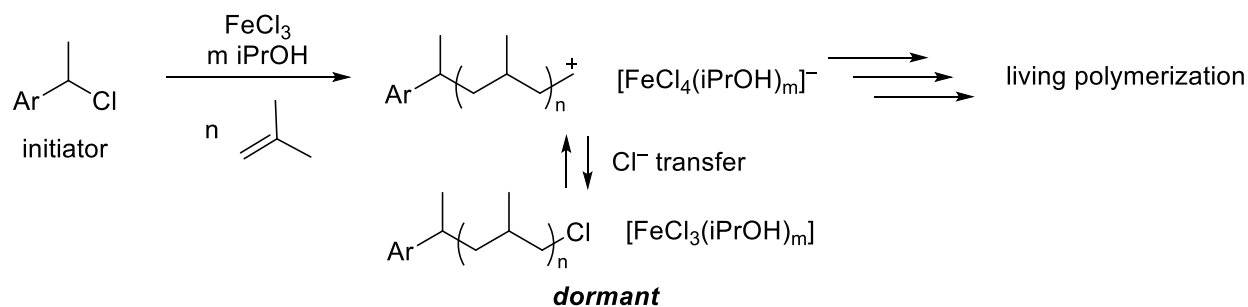
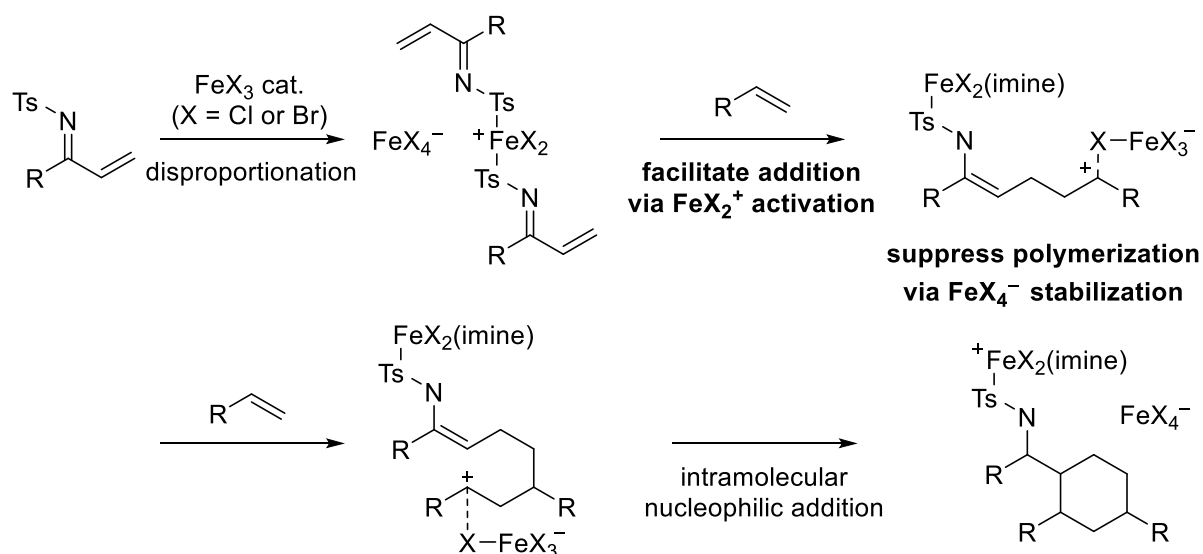
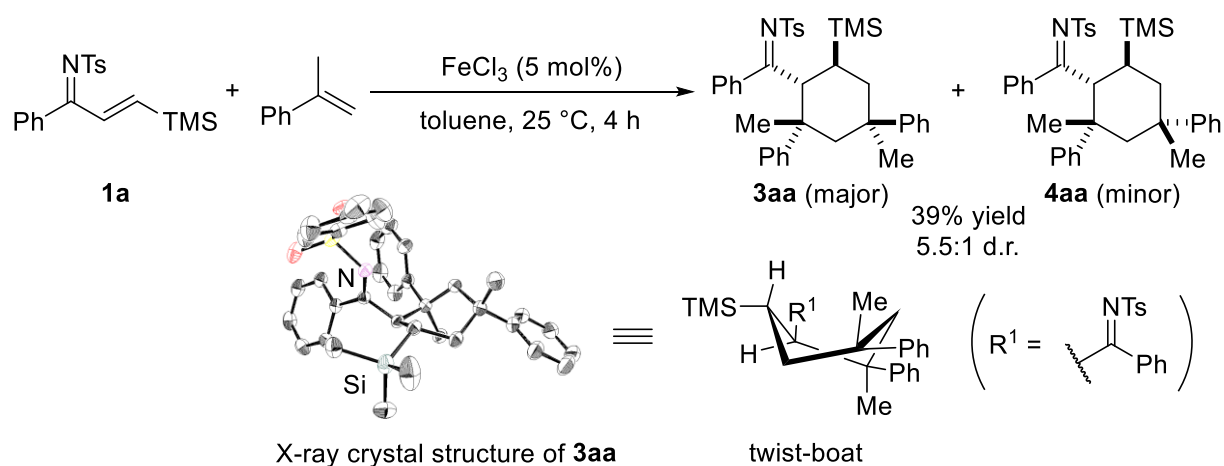
The catalytic [2+2+2] cycloaddition reaction is an established synthetic method for one-step construction of a six-membered ring. In particular, the intermolecular [2+2+2] reaction provides a powerful approach for diverse synthesis. Although many low-valent transition metals, i.e. Ni(0), Co(I), and Rh(I), can promote the [2+2+2] reaction, transition metal-catalyzed [2+2+2] reactions generally required at least one triple bond, such as C $\equiv$ C or C $\equiv$ N, to produce an aromatic ring or partially unsaturated six-membered product.<sup>5</sup> The only example of a transition metal-catalyzed alkene trimerization reaction were reported by McMeeking in 1974 utilizing highly strained 3,3-dimethylcyclopropene as the alkene.<sup>6</sup> Although some protocols utilizing nucleophilic organocatalysts have been reported to date,<sup>7</sup> the intermolecular [2+2+2] cyclization reaction between three molecules of alkenes is still an underdeveloped research topic. In this chapter, the author described the first Lewis acid-catalyzed [2+2+2] cycloaddition reaction of three alkenes. This protocol can provide an alternative strategy for the preparation of cyclohexane rings.

## Results and Discussion

Because various alkenes, such as styrene, often undergo fast non-living polymerization under acidic conditions, the challenge in achieving a Lewis acid-catalyzed [2+2+2] cycloaddition is suppression of cationic polymerization. However, the use of an appropriate Lewis acid is effective for living polymerization by forming a dormant species, and FeCl<sub>3</sub> is a candidate for such living

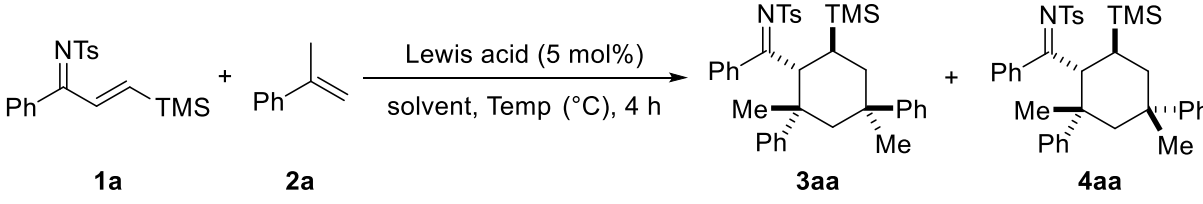
polymerization. Indeed, the complex of  $\text{FeCl}_3$ /isopropanol is crucial for the living polymerization of isobutylene, because the  $[\text{FeCl}_4(\text{iPrOH})_m]^-$  species transfers chloride atom to a cationic intermediate to form the corresponding dormant species (Scheme 1a).<sup>8a</sup> Encouraged by this fact, the author envisioned that  $\text{FeX}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) would catalyze the  $[2+2+2]$  reaction of alkenes by employing the  $\alpha,\beta$ -unsaturated *N*-tosylated imine as the substrate (Scheme 1b). As described in Chapter 2, *N*-tosylated imine is strongly activated by  $\text{FeX}_3$  via generating  $[\text{FeX}_2]^+[\text{FeX}_4]^-$  upon substrate coordination.<sup>9</sup> Therefore, the coordination of  $\alpha,\beta$ -unsaturated-*N*-tosylated imine to  $\text{FeX}_3$  would induce the disproportionation as well and facilitate the 1,4-addition reaction of the alkene. Moreover, the simultaneously generated  $[\text{FeX}_4]^-$  acts as a stabilizer of the generated carbocation to form a dormant-like species. After the second addition reaction of alkene occurs, the nucleophilic enamine moiety attacks to the carbocation and afford the six-membered product. Because this cyclization step is an intermolecular reaction, it should be faster than the intramolecular further alkene addition and suppress the cationic polymerization process.

To prove this hypothesis, the author initially examined the reaction of a chalcone-derived *N*-tosylated imine and  $\alpha$ -methylstyrene in the presence of  $\text{FeCl}_3$ . However, the desired cycloadduct was not obtained, and the starting material was recovered quantitatively. On the other hand, the use of  $\beta$ -silyl- $\alpha,\beta$ -unsaturated *N*-tosylated imine **1a** as the substrate gave the desired  $[2+2+2]$  products, **3aa** and **4aa**, in a 39% yield and in a ratio of 5.5:1 diastereoselectivity, and other diastereomers were not observed (Scheme 2).<sup>10</sup> The reactivity of  $\beta$ -silyl- $\alpha,\beta$ -unsaturated *N*-tosylated imine was expounded by following two major reasons: (i) lowering the energy of the transition state by stabilizing the cationic character of the Si–C carbon atom due to the small electronegativity of the silicon atom and (ii) stabilizing the intermediate after the first styrene addition owing to the  $\gamma$ -silicon effect.<sup>11</sup> The stereochemistry was determined by single crystal X-ray diffraction analysis. Interestingly, the conformation of the major isomer **3aa** was a twist-boat form in the crystalline state, while the minor isomer **4aa** existed as a chair conformation.

(a) living cationic polymerization using  $\text{FeCl}_3$ (b) working hypothesis for the  $\text{FeX}_3$ -catalyzed [2+2+2] reaction**Scheme 1.** Outline of the  $\text{FeX}_3$ -catalyzed [2+2+2] reaction of alkenes.**Scheme 2.**  $\text{FeCl}_3$ -catalyzed [2+2+2] cycloaddition reaction of three alkenes.

The author further examined the reaction to investigate the effect of the Lewis acid catalyst (Table 1), and studies on the acidity of each Lewis acid are summarized in Table 2. The use of FeBr<sub>3</sub> instead of FeCl<sub>3</sub> could catalyze the reaction in a higher yield and diastereoselectivity (83%, 5.6:1 d.r.), even though there was the negligible difference in the Lewis acidity. This implied that the counteranion ([FeX<sub>4</sub>]<sup>−</sup>) played a crucial role in the catalysis to stabilize the cationic intermediate. The use of AlCl<sub>3</sub> and GaCl<sub>3</sub>, which are also known to form [AlCl<sub>4</sub>]<sup>−</sup> or [GaCl<sub>4</sub>]<sup>−</sup> and promote the living polymerization reaction,<sup>12</sup> could catalyze the reaction, however yield was inferior to the case of FeBr<sub>3</sub> owing its lower Lewis acidity. A similar result was observed when using the cationic metalloporphyrin complex as a catalyst, and the highly Lewis acidic Fe-porphyrin gave the product only in a 13%, whereas, Co-porphyrin promoted the reaction the same as AlCl<sub>3</sub> or GaCl<sub>3</sub>. These results suggest that both a strong Lewis acidity and counterion stabilization are crucial to catalyze the reaction sufficiently. After several solvents were investigated, the use of toluene gave the best result. Solvents, such as THF or MeCN, may not be suitable for the reaction because of the deactivation of the Lewis acid catalyst upon solvent coordination.

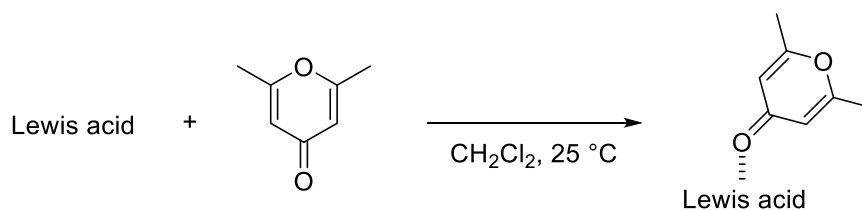
**Table 1.** Optimization of conditions<sup>a</sup>

|  |                                       |         |                  |                        |                             |
|--------------------------------------------------------------------------------------|---------------------------------------|---------|------------------|------------------------|-----------------------------|
| entry                                                                                | Lewis acid                            | solvent | Temperature (°C) | yield (%) <sup>b</sup> | <b>3aa:4aa</b> <sup>c</sup> |
| 1                                                                                    | FeCl <sub>3</sub>                     | toluene | 25               | 39                     | 5.5:1                       |
| 2                                                                                    | FeBr <sub>3</sub>                     | toluene | 25               | 83                     | 5.6:1                       |
| 3                                                                                    | AlCl <sub>3</sub>                     | toluene | 25               | 45                     | 5.0:1                       |
| 4                                                                                    | GaCl <sub>3</sub>                     | toluene | 25               | 61                     | 5.1:1                       |
| 5                                                                                    | Fe(TArP)SbF <sub>6</sub> <sup>d</sup> | toluene | 25               | 13                     | 6.1:1                       |
| 6                                                                                    | Co(TArP)SbF <sub>6</sub> <sup>d</sup> | toluene | 25               | 53                     | 6.2:1                       |

**Table 1.** (Continued)

|    |                                |             |    |    |       |
|----|--------------------------------|-------------|----|----|-------|
| 7  | FeBr <sub>3</sub> <sup>e</sup> | toluene     | 25 | 36 | 5.6:1 |
| 8  | FeBr <sub>3</sub>              | toluene     | 0  | 74 | 5.6:1 |
| 9  | FeBr <sub>3</sub>              | toluene     | 80 | 78 | 5.6:1 |
| 10 | FeBr <sub>3</sub>              | 1,2-DCE     | 25 | 84 | 3.9:1 |
| 11 | FeBr <sub>3</sub>              | cyclohexane | 25 | 14 | 3.7:1 |
| 12 | FeBr <sub>3</sub>              | THF         | 25 | <1 | —     |

<sup>a</sup>Reactions were carried out using **1a** (0.1 mmol), **2a** (0.4 mmol), and Lewis acid (0.005 mmol) in 1 mL of solvent for 4 h. <sup>b</sup>NMR yields. <sup>c</sup>Diastereomer ratio was determined by <sup>1</sup>H NMR. <sup>d</sup>TArP: 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-21*H*,23*H*-porphyrinoate. <sup>e</sup>Reaction was carried out using 2 mol% of FeBr<sub>3</sub>.

**Table 2.** Investigation of Lewis acidity via IR measurements<sup>a</sup>

| entry | Lewis acid                           | $\nu_{\text{C=O}}$ (cm <sup>-1</sup> ) | $\Delta\nu_{\text{C=O}}$ (cm <sup>-1</sup> ) |
|-------|--------------------------------------|----------------------------------------|----------------------------------------------|
| 1     | none                                 | 1669.6                                 | —                                            |
| 2     | FeCl <sub>3</sub>                    | 1646.4                                 | 23.2                                         |
| 3     | FeBr <sub>3</sub>                    | 1647.0                                 | 22.6                                         |
| 4     | AlCl <sub>3</sub>                    | 1649.8                                 | 19.8                                         |
| 5     | GaCl <sub>3</sub>                    | 1652.2                                 | 17.4                                         |
| 6     | Fe(TPP)SbF <sub>6</sub> <sup>b</sup> | 1647.3                                 | 22.3                                         |
| 7     | Co(TPP)SbF <sub>6</sub> <sup>b</sup> | 1653.2                                 | 16.4                                         |

<sup>a</sup>IR measurements were carried out for a CH<sub>2</sub>Cl<sub>2</sub> solution of 2,6-dimethyl- $\gamma$ -pyrone and 1 equiv of Lewis acid. <sup>b</sup>TPP: 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrinoate.

After optimizing the reaction conditions, various substrates were examined for the FeBr<sub>3</sub>-catalyzed [2+2+2] reaction (Table 3). Alkenes **2a** and **2b**,  $\alpha$ -methylstyrene and its derivative, respectively, reacted with **1a**, and corresponding cycloadducts were obtained in high yield and moderate diastereoselectivity. Of note, although the yield was decreased, styrene derivatives afforded the product as a single diastereomer (**3ac**, **3ad**). CF<sub>3</sub>-substituted imine **1b** also afforded the desired product, however, the polymerization of **2a** was a considerable side reaction probably due to the low reaction rate of the last cyclization process. Furthermore, the effect of the substituent on the silane was investigated. The substrate with a sterically bulkier substituent, such as SiMe<sub>2</sub>Ph, TBS, and SiPh<sub>3</sub>, was also converted to the corresponding products, and gave the product in a higher diastereoselectivity (7.3:1, >10:1, and 6.1:1, respectively).

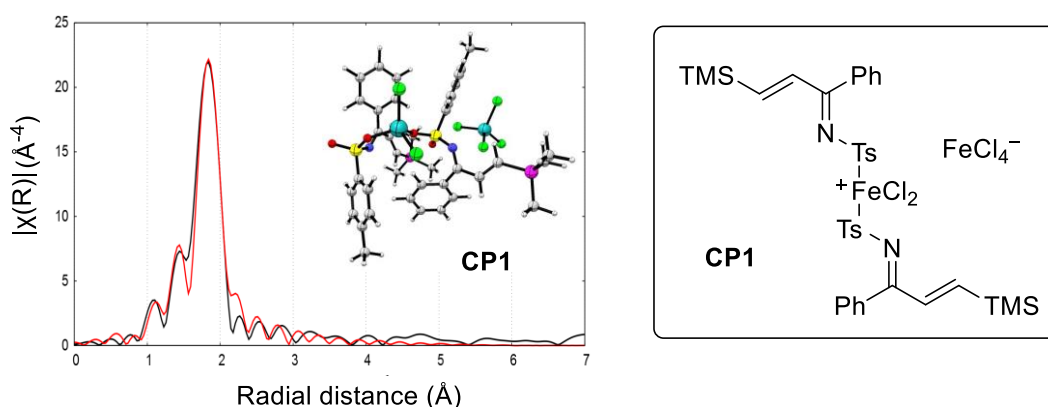
**Table 3.** Substrate scope<sup>a</sup>

|                                                                                                                         |
|-------------------------------------------------------------------------------------------------------------------------|
|                                                                                                                         |
| <b>1</b> + <b>2</b> $\xrightarrow[\text{toluene, 25 } ^\circ\text{C, 4 h}]{\text{FeBr}_3 \text{ (5 mol\%)}}$ <b>3/4</b> |
| <b>Products<sup>b,c</sup></b>                                                                                           |
|                                                                                                                         |
| <b>3aa/4aa</b><br>83%, 5.6:1 d.r.                                                                                       |
|                                                                                                                         |
| <b>3ab/4ab</b><br>94%, 6.0:1 d.r.                                                                                       |
|                                                                                                                         |
| <b>3ac</b><br>35%, >20:1 d.r.                                                                                           |
|                                                                                                                         |
| <b>3ad</b><br>22% >20:1 d.r.                                                                                            |
|                                                                                                                         |
| <b>3ba/4ba</b><br>30%, 6.0:1 d.r.                                                                                       |
|                                                                                                                         |
| <b>3ca/4ca</b><br>83%, 7.3:1 d.r.                                                                                       |
|                                                                                                                         |
| <b>3da/4da</b><br>40%, 6.8:1 d.r.                                                                                       |
|                                                                                                                         |
| <b>3ea/4ea</b><br>48%, 6.1:1 d.r.                                                                                       |

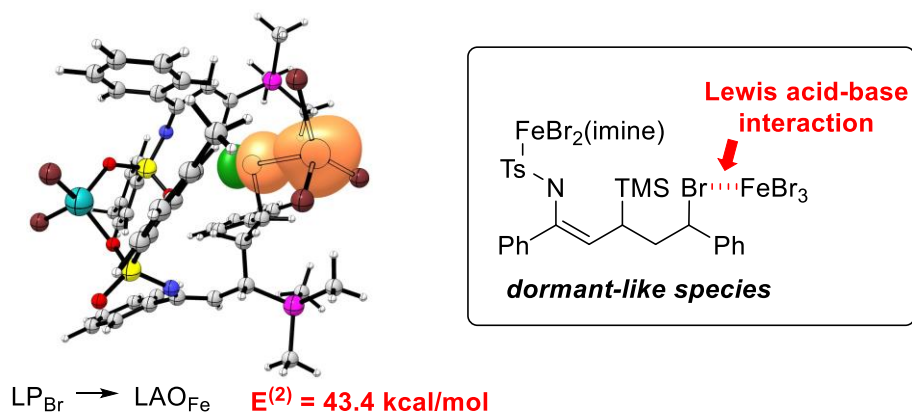
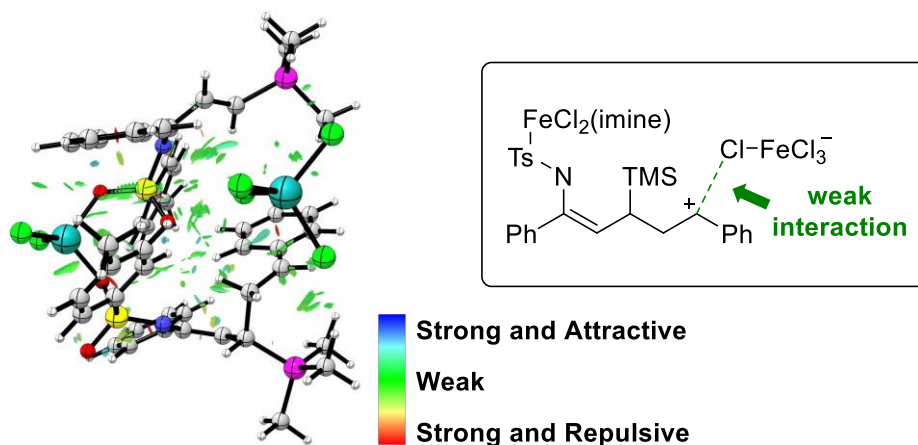
<sup>a</sup>Reactions were carried out using **1** (0.1 mmol), **2** (0.4 mmol), and FeBr<sub>3</sub> (0.005 mmol) in 1 mL of toluene for 4 h. <sup>b</sup>Yields were isolated yield. <sup>c</sup>Diastereomer ratio was determined by <sup>1</sup>H NMR.

To obtain insight regarding the solution-phase structure of **CP1**, which is the initial complex formed by mixing  $\text{FeCl}_3$  and imine **1a**, in situ Fe *K*-edge X-ray absorption spectroscopy (XAS) was conducted at a synchrotron radiation facility. The XAS measurement was performed using toluene solution of  $\text{FeCl}_3$  and imine **1a**, and the result of the extended X-ray absorption fine structure (EXAFS) analysis is shown in Figure 1. The spectral features arising from the coordination sphere of the iron atoms agreed well with the spectra simulated using the DFT-calculated structure of the complex ( $R_f = 2.0\%$ ). Two imines were coordinated to  $[\text{FeCl}_2]^+$  along with the formation of  $[\text{FeCl}_4]^-$ .

To elucidate the reason of the difference between  $\text{FeCl}_3$  and  $\text{FeBr}_3$  (Table 1, entries 1 and 2), DFT calculations were performed. In **Int<sup>Br</sup>** (which is the intermediate formed after the addition of a styrene using  $\text{FeBr}_3$ ), the formation of a dormant-like species was proposed to be plausible. Natural bond orbital analysis of **Int<sup>Br</sup>** confirmed the Lewis acid-base interaction between Br atom and the  $\text{FeBr}_3$  (Figure 2a). Whereas, in the case of calculation using  $\text{FeCl}_3$ , only weak interaction between  $[\text{FeCl}_4]^-$  and cationic moiety was confirmed by noncovalent analysis of **Int<sup>Cl</sup>** (Figure 2b). Thus, both the high Lewis acidity of  $[\text{FeBr}_2]^+$  and cation stabilization effect of  $[\text{FeBr}_4]^-$  were crucial to catalyze the [2+2+2] cycloaddition reaction of three alkenes.



**Figure 1.** Solution-phase Fe *K*-edge EXAFS analysis (Fourier transform of  $k^3$ -weighted spectrum: experimental spectrum (black line) and FEFF-calculated fitting of DFT model **CP1** (red line).

(a) NBO analysis of **Int<sup>Br</sup>**(b) NCI analysis of **Int<sup>Cl</sup>**

**Figure 2.** (a) Natural bond orbital analysis of **Int<sup>Br</sup>**. LP and LAO denote the lone pair and Lewis acceptor orbital, respectively. (b) Noncovalent interaction analysis in **Int<sup>Cl</sup>**.

## Conclusion

The author has presented a novel method for the construction of fully saturated cyclohexane scaffolds by the Lewis acid-catalyzed [2+2+2] cycloaddition reaction of alkenes.  $[\text{FeBr}_2]^+[\text{FeBr}_4]^-$  generated via disproportionation of  $\text{FeBr}_3$  successfully catalyzed the reaction, and following two factors were crucial for efficient conversion: (i) the highly Lewis acidic  $[\text{FeBr}_2]^+$  facilitated the addition reaction of the alkene to activate the substrate, (ii) the electronic interaction between

$[\text{FeBr}_4]^-$  and the carbocation intermediate suppressed the undesired polymerization reaction. Furthermore, the conformation of the obtained multi-substituted cyclohexane product was uncommon twist-boat structure.

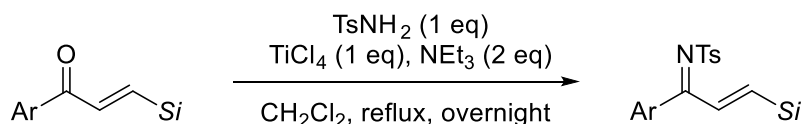
## Experimental Section

### Materials.

Iron(III) bromide was purchased from Strem Chemicals, Inc., iron(III) chloride was purchased from Sigma-Aldrich Co.. Styrene and  $\alpha$ -methylstyrene were purchased from TCI. Unless otherwise noted, commercially available reagents were used without purification

### Experimental Procedure and Characterization Data for Products.

#### Preparation of $\beta$ -silyl- $\alpha,\beta$ -unsaturated *N*-tosylated imine



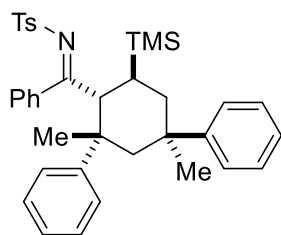
$\beta$ -Silylenones were prepared according to the literature procedures.<sup>13</sup> To a solution of  $\beta$ -silylenone and  $\text{TsNH}_2$  (1 eq) in  $\text{CH}_2\text{Cl}_2$  was added  $\text{NEt}_3$  (2 eq) and  $\text{TiCl}_4$  (1 eq) subsequently at ambient temperature. The reaction mixture was stirred at 60 °C for 12 h. after completion of the reaction, the reaction was quenched with water, and extracted with  $\text{CH}_2\text{Cl}_2$  and washed with brine, the combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated *in vacuo*. The crude product was purified by silica gel column chromatography, then the obtained solid was recrystallized with hexane/EtOAc.

**General procedure.**

The reaction was performed in a 15 mL sealed tube equipped with a Teflon-coated magnetic stirrer bar. A styrene derivatives (0.4 mmol) were added to a solution of imine (0.1 mmol) and FeBr<sub>3</sub> (0.005 mmol) in toluene (1 mL) in a dry box. The vial was taken outside the dry box and stirred at 25 °C for the 4 hours. The reaction mixture was passed through a short silica gel pad, washed with ethylacetate, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with given eluent.

*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*S*<sup>\*</sup>,6*S*<sup>\*</sup>)-2,4-dimethyl-2,4-diphenyl-6-

(trimethylsilyl)cyclohexyl)(phenyl)methylene)-4-methylbenzenesulfonamide (**3aa**).



Yield: 70%, white solid. Mp. 69–71 °C (hexane). TLC: *R*<sub>f</sub> = 0.24

(hexane/ethyl acetate = 10:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.5 Hz, 2H),

7.43 (d, *J* = 7.5 Hz, 2H), 7.29–7.35 (m, 5H), 7.07–7.20 (m, 8H), 6.97 (d, *J* = 8.5 Hz, 2H), 3.36 (d, *J* = 10.5 Hz, 1H), 2.72 (d, *J* = 14.5 Hz, 1H), 2.47

(s, 3H), 2.39 (d, *J* = 14.0 Hz, 1H), 2.28 (t, *J* = 14.5 Hz, 1H), 1.88–1.94 (m, 2H), 1.34 (s, 3H), 1.17

(s, 3H), –0.08 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 186.9, 152.3, 147.1, 143.0, 139.0, 138.1, 131.0, 129.1,

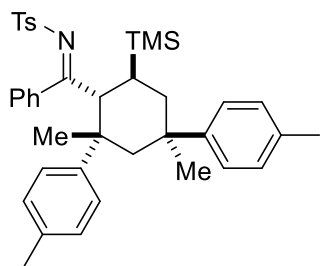
128.6, 128.2, 128.0, 127.7, 127.4, 127.2, 127.1, 125.6, 125.3, 125.2, 57.9, 42.6, 42.0, 37.1, 35.1,

33.9, 30.7, 22.8, 21.5, –2.4. IR (KBr): 1608, 1588, 1496, 1320, 1252, 1154, 1089, 852 cm<sup>–1</sup>. HRMS

(ESI<sup>+</sup>) found 616.2668, calcd for [M+Na]<sup>+</sup> 616.2676.

*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*S*<sup>\*</sup>,6*S*<sup>\*</sup>)-2,4-dimethyl-2,4-di-*p*-tolyl-6-

(trimethylsilyl)cyclohexyl)(phenyl)methylene)-4-methylbenzenesulfonamide (**3ab**).



Yield: 78%, white solid. Mp. 67–68 °C (hexane). TLC: *R*<sub>f</sub> = 0.30

(hexane/ethyl acetate = 10:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.5 Hz,

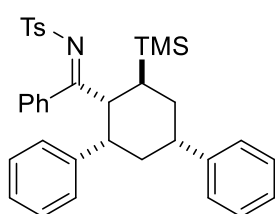
2H), 7.35 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.96–7.20 (m,

9H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.36 (d, *J* = 10.5 Hz, 1H), 2.69 (d, *J* =

14.5 Hz, 1H), 2.48 (s, 3H), 2.45 (d, *J* = 12.5 Hz, 1H), 2.35 (s, 3H), 2.32

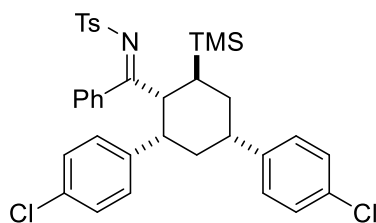
(s, 3H), 2.30–2.34 (m, 1H), 1.88–1.94 (m, 2H), 1.34 (s, 3H), 1.19 (s, 3H), –0.08 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  187.0, 149.4, 144.2, 142.9, 139.0, 138.2, 135.0, 134.6, 130.9, 129.1, 128.8, 128.6, 128.3, 127.2, 127.2, 127.0, 125.1, 58.0, 42.2, 41.8, 36.7, 35.2, 34.0, 30.7, 22.7, 21.5, 20.8, 20.7, –2.4. IR (KBr): 1602 1444, 1322, 1093, 849  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 644.2983, calcd for  $[\text{M}+\text{Na}]^+$  644.2989.

*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*R*<sup>\*</sup>,6*S*<sup>\*</sup>)-2,4-diphenyl-6-(trimethylsilyl)cyclohexyl)(phenyl)methylene)-4-methylbenzenesulfonamide (**3ac**).



Yield: 35%, white solid. Mp. 142–143 °C (hexane). TLC:  $R_f$  = 0.25 (hexane/ethyl acetate = 10:1)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J$  = 8.0 Hz, 2H), 7.16–7.34 (m, 13H), 7.04–7.07 (m, 2H), 6.95 (d,  $J$  = 7.0 Hz, 2H), 3.39 (d,  $J$  = 5.0 Hz, 1H), 3.17 (dt,  $J$  = 13.0, 4.0 Hz, 1H), 2.84 (q,  $J$  = 12.5 Hz, 1H), 2.66–2.72 (m, 1H), 2.47 (s, 3H), 2.36 (ddd,  $J$  = 14.0, 6.5 Hz, 1H), 1.85 (dt,  $J$  = 14.0, 2.0 Hz, 1H), 1.77 (dt,  $J$  = 12.5, 3.0 Hz, 1H), 1.41 (d,  $J$  = 5.0 Hz, 1H), –0.08 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  187.4, 147.2, 143.5, 143.3, 139.0, 138.7, 129.9, 129.3, 128.4, 128.2, 127.8, 127.8, 127.4, 126.9, 126.3, 126.2, 126.1, 51.1, 43.7, 42.5, 32.3, 28.3, 27.8, 21.6, –0.8. IR (KBr): 1613, 1324, 1257, 1157, 1090, 1027, 861, 700  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 588.2360, calcd for  $[\text{M}+\text{Na}]^+$  588.2363.

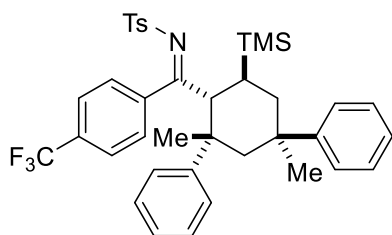
*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*R*<sup>\*</sup>,6*S*<sup>\*</sup>)-2,4-bis(4-chlorophenyl)-6-(trimethylsilyl)cyclohexyl)(phenyl)methylene)-4-methylbenzenesulfonamide (**3ad**).



Yield: 22%, white solid. Mp. 173–175 °C (hexane). TLC:  $R_f$  = 0.28 (hexane/ethyl acetate = 10:1)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J$  = 8.0 Hz, 2H), 7.34–7.38 (m, 1H), 7.26–7.32 (m, 6H), 7.08–7.13 (m, 4H), 7.00 (d,  $J$  = 7.0 Hz, 2H), 6.96 (d,  $J$  = 7.0 Hz, 2H), 3.35 (d,  $J$  = 5.0 Hz, 1H), 3.12 (dt,  $J$  = 13.0, 4.0 Hz, 1H), 2.74 (q,  $J$  = 12.5 Hz, 1H), 2.60–2.69 (m, 1H), 2.48 (s, 3H), 2.26 (ddd,  $J$  = 13.5, 6.0 Hz, 1H), 1.81 (dt,  $J$  = 13.5, 1.5 Hz, 1H), 1.72 (dt,  $J$  = 12.0, 3.0 Hz, 1H), 1.38 (d,  $J$  = 5.0 Hz, 1H), –0.06 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  186.7, 145.3, 143.6,

141.8, 138.5, 138.4, 132.0, 131.8, 130.1, 129.4, 129.0, 128.5, 128.3, 128.2, 127.9, 127.3, 126.2, 50.8, 42.9, 41.8, 32.4, 28.3, 27.6, 21.6, -0.8. IR (KBr): 2958, 1616, 1490, 1325, 1251, 1160, 1090, 1013, 861, 711  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 656.1579, calcd for  $[\text{M}+\text{Na}]^+$  656.1584.

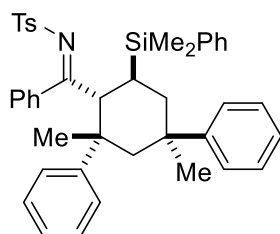
*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*S*<sup>\*</sup>,6*S*<sup>\*</sup>)-2,4-dimethyl-2,4-diphenyl-6-(trimethylsilyl)cyclohexyl)(4-(trifluoromethyl)phenyl)methylene)-4-methylbenzenesulfonamide (**3ba**).



Yield: 25%, white solid. Mp. 73–75 °C (hexane). TLC:  $R_f$  = 0.10 (hexane/ethyl acetate = 30:1) <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J$  = 8.5 Hz, 2H), 7.33–7.41 (m, 6H), 7.29 (t,  $J$  = 8.5 Hz, 2H), 7.07–7.18 (m, 6H), 6.98 (d,  $J$  = 8.5 Hz, 2H), 3.28 (d,  $J$  = 10.5 Hz, 1H), 2.65

(d,  $J$  = 15.0 Hz, 1H), 2.47 (s, 3H), 2.36 (d,  $J$  = 14.0 Hz, 1H), 2.26 (t,  $J$  = 15.0 Hz, 1H), 1.88–1.94 (m, 2H), 1.31 (s, 3H), 1.14 (s, 3H), -0.09 (s, 9H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  185.3, 152.1, 147.1, 143.5, 141.4, 138.4, 129.3, 128.6, 128.3, 128.0, 127.8 (q,  $J$  = 59.5 Hz), 127.5, 127.3, 126.0, 125.4, 125.2, 124.2 (q,  $J$  = 3.9 Hz), 123.5 (q,  $J$  = 272.4 Hz), 58.6, 42.7, 42.0, 37.1, 35.2, 33.9, 30.6, 22.8, 21.6, -2.3. IR (KBr): 1608, 1331, 1251, 1166, 1131, 843, 768  $\text{cm}^{-1}$ . HRMS (ESI<sup>+</sup>) found 684.2546, calcd for  $[\text{M}+\text{Na}]^+$  684.2550.

*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*S*<sup>\*</sup>,6*S*<sup>\*</sup>)-6-(dimethyl(phenyl)silyl)-2,4-dimethyl-2,4-diphenylcyclohexyl)(phenyl)methylene)-4-methylbenzenesulfonamide (**3ca**).

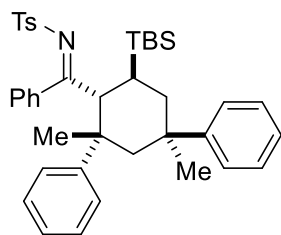


Yield: 73%, white solid. Mp. 65–66 °C (hexane). TLC:  $R_f$  = 0.25 (hexane/ethyl acetate = 10:1) <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J$  = 8.5 Hz, 2H), 7.40 (d,  $J$  = 8.0 Hz, 2H), 7.06–7.36 (m, 18H), 6.88 (d,  $J$  = 7.5 Hz, 2H), 3.41 (d,  $J$  = 10.0 Hz, 1H), 2.74 (d,  $J$  = 14.5 Hz, 1H), 2.54 (s, 3H), 2.39 (d,

$J$  = 14.0 Hz, 1H), 2.16–2.32 (m, 2H), 1.73–1.80 (m, 1H), 1.21 (s, 3H), 1.15 (s, 3H), 0.33 (s, 3H), 0.05 (s, 3H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  186.9, 152.3, 147.1, 143.2, 139.3, 138.2, 137.8, 133.7, 131.1, 129.4, 129.1, 128.7, 128.2, 127.8, 127.6, 127.5, 127.3, 125.8, 125.3, 57.6, 42.8, 41.5, 37.2, 35.1, 33.8, 30.5, 22.5, 21.7, -2.0, -5.4. IR (KBr): 1605, 1573, 1443, 1319, 1155, 1092, 1031, 875, 842

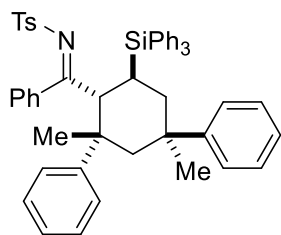
$\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 678.2830, calcd for  $[\text{M}+\text{Na}]^+$  678.2832.

*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*S*<sup>\*</sup>,6*S*<sup>\*</sup>)-6-(*tert*-butyldimethylsilyl)-2,4-dimethyl-2,4-diphenylcyclohexyl)(phenyl)methylene)-4-methylbenzenesulfonamide (**3da**).

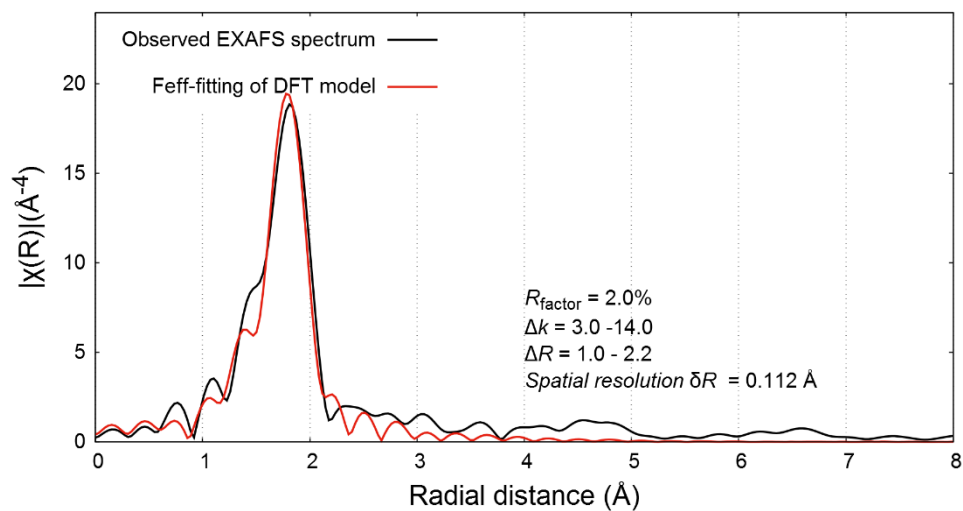
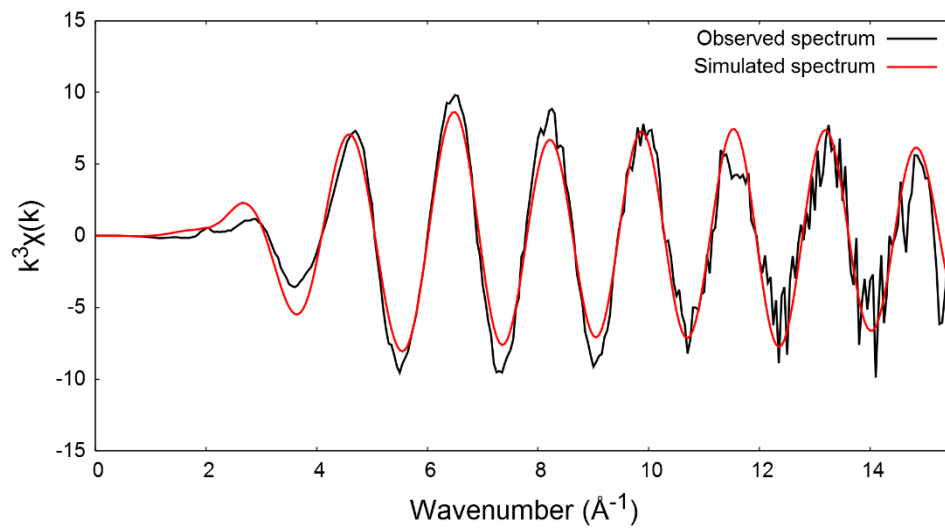


Yield: 36%, white solid. Mp. 68–69 °C (hexane). TLC:  $R_f$  = 0.30 (hexane/ethyl acetate = 10:1)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J$  = 8.5 Hz, 2H), 7.37 (d,  $J$  = 7.5 Hz, 2H), 7.27–7.32 (m, 4H), 6.98–7.16 (m, 11H), 3.44 (d,  $J$  = 10.5 Hz, 1H), 2.68 (d,  $J$  = 14.5 Hz, 1H), 2.43 (s, 3H), 2.28–2.37 (m, 3H), 2.02–2.30 (m, 1H), 1.33 (s, 3H), 1.16 (s, 3H), 0.76 (s, 9H), –0.01 (s, 3H), –0.34 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  186.6, 152.4, 147.2, 143.1, 139.1, 138.0, 131.1, 129.2, 129.1, 128.2, 127.7, 127.4, 127.4, 127.2, 125.7, 125.3, 125.3, 57.7, 42.9, 41.3, 37.3, 35.1, 34.7, 30.5, 27.6, 21.5, 21.3, 17.6, –4.6, –7.3. IR (KBr): 1597, 1444, 1322, 1154, 1093, 876, 827, 764  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 658.3140, calcd for  $[\text{M}+\text{Na}]^+$  658.3145.

*N*-((*Z*)-((1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,4*S*<sup>\*</sup>,6*S*<sup>\*</sup>)-2,4-dimethyl-2,4-diphenyl-6-(triphenylsilyl)cyclohexyl)(phenyl)methylene)-4-methylbenzenesulfonamide (**3ea**).



Yield: 48%, white solid. Mp. 104–105 °C (hexane). TLC:  $R_f$  = 0.25 (hexane/ethyl acetate = 10:1)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J$  = 8.0 Hz, 2H), 7.55 (dd,  $J$  = 7.5, 1.5 Hz, 6H), 7.31–7.40 (m, 14H), 7.06–7.22 (m, 8H), 6.77 (t,  $J$  = 8.0 Hz, 2H), 6.19 (d,  $J$  = 7.5 Hz, 2H), 3.72 (d,  $J$  = 9.0 Hz, 1H), 3.08–3.14 (m, 1H), 2.97 (d,  $J$  = 14.5 Hz, 1H), 2.53 (s, 3H), 2.46 (s, 1H), 2.26 (t,  $J$  = 14.5 Hz, 1H), 1.99 (dd,  $J$  = 14.5, 3.5 Hz, 1H), 1.46 (s, 3H), 1.34 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  187.8, 152.5, 147.2, 143.1, 139.3, 138.2, 135.9, 135.8, 133.4, 130.0, 129.6, 129.4, 128.1, 128.1, 128.0, 127.6, 127.2, 127.0, 126.4, 125.7, 125.1, 56.5, 42.8, 39.7, 37.2, 35.0, 34.8, 29.6, 21.6, 20.3. IR (KBr): 1599, 1565, 1428, 1321, 1156, 1108, 1089, 911, 871  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 802.3143, calcd for  $[\text{M}+\text{Na}]^+$  802.3145.

**Supplemental Data****S1. XAS measurement of CP1****Figure S1-1.** Fourier-transformed Fe *K*-edge EXAFS spectra in R-space.**Figure S1-2.** Fourier-transformed Fe *K*-edge EXAFS spectra in k-space.

## Structural Parameters Obtained from EXAFS Analysis

| Ab–Sc  | R (Å)   | N | S <sub>0</sub> <sup>2</sup> | ΔR (Å)   | ΔE <sub>0</sub> (eV) | Δσ <sup>2</sup> (Å <sup>2</sup> ) |
|--------|---------|---|-----------------------------|----------|----------------------|-----------------------------------|
| Fe– O  | 1.83281 | 1 | 0.484                       | –0.05449 | 0.838                | 0.00114                           |
| Fe– O  | 1.86681 | 1 | 0.484                       | –0.05449 | 0.838                | 0.00114                           |
| Fe–Cl  | 2.15381 | 2 | 0.484                       | –0.05449 | 0.838                | 0.00114                           |
| Fe– Cl | 2.19501 | 4 | 0.484                       | –0.05449 | 0.838                | 0.00114                           |

$R_{\text{factor}} = 3.6\%$ ,  $\Delta k = 3.5\text{--}14.8$ ,  $\Delta R = 1.2\text{--}2.4$  (*spatial resolution*  $\delta R \geq \pi/2k_{\text{max}} = 0.1061\text{ Å}$ )

Ab–Sc: X-ray absorbing atom and scattering atom

R (Å): atomic distance

N: coordination number

S<sub>0</sub><sup>2</sup>: passive electron reduction factor

*parameter* ΔR(Å): change in half-path length

*parameter* ΔE<sub>0</sub> (eV): edge shift

*parameter* Δσ<sup>2</sup> (Å<sup>2</sup>): mean squared displacement (Debye–Waller factor)

*The total number of parameters used in the model is less than that given by the Nyquist theorem.*

$N_{\text{idp}} \approx 2\Delta k\Delta R/\pi = 8.64 > N_{\text{used}} = 4$  (S<sub>0</sub><sup>2</sup>, ΔR, ΔE<sub>0</sub> and Δσ<sup>2</sup>)

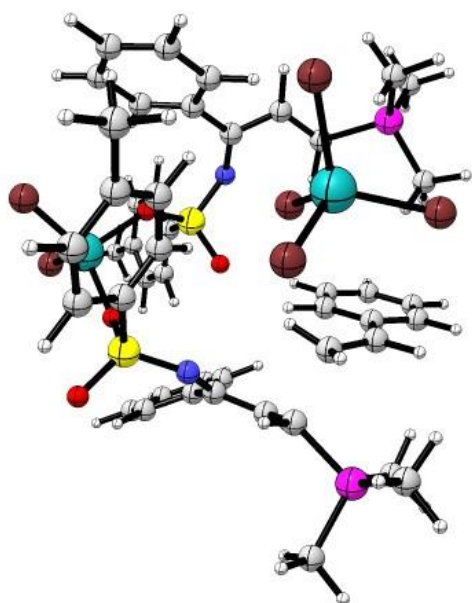
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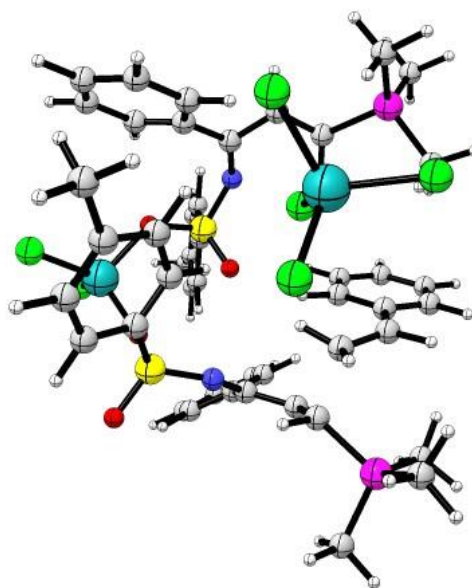
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## S2. DFT-calculated structure of TS1<sup>Br</sup> and TS1<sup>Cl</sup>



(a) Structure of TS1<sup>Br</sup>



(b) Structure of TS1<sup>Cl</sup>

## S3. Computational details for DFT calculation

General Methods. Calculations were performed on Gaussian 09 E.01. For geometry optimization and frequency calculations B3LYP augmented with an empirical dispersion (GD3) was used and M06 was used for single-point energy calculations. Geometry optimization and frequency calculations were carried out using 6-31G(d) (C, H, O, N), 6-31+G(d) (S, Cl, Si), and f polarization function added Lanl2dz(f) (Fe) basis sets. Single-point calculations were performed with def2-TZVP basis sets. The solvation effects of toluene were incorporated in all calculations using PCM (toluene). The Monte-Carlo simulated annealing method was initially employed to generate conformers, followed by geometry optimization and thermodynamic calculation to obtain the Boltzmann distribution of these conformers to determine the energetically global minimum conformer.

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#### Cartesian Coordinates for **CPI**

|    |                |                 |                 |    |                 |                 |                 |
|----|----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| S  | 5.065537000000 | -1.384271000000 | 22.609897000000 | H  | 10.340808000000 | 0.948892000000  | 17.239739000000 |
| Si | 7.880115000000 | 1.042548000000  | 17.648698000000 | H  | 4.329979000000  | 4.289933000000  | 24.982773000000 |
| O  | 5.645404000000 | -0.851903000000 | 23.836861000000 | S  | 0.358263000000  | -0.842058000000 | 24.428053000000 |
| O  | 3.532451000000 | -1.615008000000 | 22.767878000000 | Si | 5.864140000000  | 0.066431000000  | 27.283229000000 |
| N  | 5.259286000000 | -0.570513000000 | 21.207710000000 | O  | 0.567977000000  | -1.469564000000 | 23.032528000000 |
| C  | 5.745323000000 | -2.967468000000 | 22.229508000000 | O  | -0.867956000000 | -1.322514000000 | 25.071033000000 |
| C  | 5.162286000000 | 1.695477000000  | 22.216930000000 | N  | 1.668669000000  | -0.925723000000 | 25.388147000000 |
| C  | 6.854552000000 | 0.445744000000  | 19.121317000000 | C  | 0.282198000000  | 0.910865000000  | 24.139459000000 |
| C  | 5.482270000000 | 0.724113000000  | 21.151850000000 | C  | 2.344044000000  | -3.321448000000 | 25.105590000000 |
| C  | 7.204820000000 | -4.757964000000 | 22.848276000000 | C  | 4.243680000000  | -0.379522000000 | 26.403375000000 |
| C  | 6.690405000000 | -3.492459000000 | 23.110965000000 | C  | 2.490841000000  | -1.935861000000 | 25.590464000000 |
|    |                |                 |                 | C  | 0.178658000000  | 2.785035000000  | 22.648711000000 |

## Chapter 3

|                                                   |                |                 |                 |    |                 |                 |                 |
|---------------------------------------------------|----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C                                                 | 5.307134000000 | -3.664166000000 | 21.101229000000 | C  | 0.260993000000  | 1.406142000000  | 22.836392000000 |
| C                                                 | 7.614067000000 | 2.897276000000  | 17.425075000000 | C  | 0.188531000000  | 1.757773000000  | 25.249985000000 |
| C                                                 | 6.100308000000 | 1.227415000000  | 19.925067000000 | C  | 5.385175000000  | 1.237243000000  | 28.694079000000 |
| C                                                 | 6.791485000000 | -5.491565000000 | 21.726040000000 | C  | 3.693153000000  | -1.612221000000 | 26.365343000000 |
| C                                                 | 3.939491000000 | 1.626328000000  | 22.907021000000 | C  | 0.102689000000  | 3.665041000000  | 23.736045000000 |
| C                                                 | 5.836454000000 | -4.928249000000 | 20.863135000000 | C  | 1.093338000000  | -3.955731000000 | 24.986673000000 |
| C                                                 | 6.075763000000 | 2.719163000000  | 22.522710000000 | C  | 0.096355000000  | 3.128732000000  | 25.035220000000 |
| C                                                 | 7.313528000000 | 0.085361000000  | 16.121799000000 | C  | 3.507543000000  | -4.027672000000 | 24.738182000000 |
| C                                                 | 3.640346000000 | 2.562820000000  | 23.891963000000 | C  | 6.994249000000  | 0.953654000000  | 26.068939000000 |
| C                                                 | 7.402234000000 | -6.838442000000 | 21.435292000000 | C  | 1.014905000000  | -5.256033000000 | 24.494416000000 |
| C                                                 | 5.780946000000 | 3.638986000000  | 23.525955000000 | C  | 0.073784000000  | 5.156699000000  | 23.520031000000 |
| C                                                 | 9.677664000000 | 0.646039000000  | 18.059759000000 | C  | 3.420324000000  | -5.312467000000 | 24.216936000000 |
| C                                                 | 4.562182000000 | 3.565008000000  | 24.207513000000 | C  | 6.632776000000  | -1.515865000000 | 27.957897000000 |
| H                                                 | 6.939176000000 | -0.602854000000 | 19.412434000000 | C  | 2.172028000000  | -5.930546000000 | 24.096551000000 |
| H                                                 | 7.964754000000 | -5.162514000000 | 23.509222000000 | H  | 3.732793000000  | 0.399324000000  | 25.834668000000 |
| H                                                 | 7.037832000000 | -2.917368000000 | 23.960846000000 | H  | 0.178945000000  | 3.178666000000  | 21.636303000000 |
| H                                                 | 4.573456000000 | -3.234265000000 | 20.429165000000 | H  | 0.320791000000  | 0.739340000000  | 21.985687000000 |
| H                                                 | 7.926167000000 | 3.454021000000  | 18.317135000000 | H  | 0.204939000000  | 1.354809000000  | 26.256980000000 |
| H                                                 | 6.561126000000 | 3.132132000000  | 17.226975000000 | H  | 4.711780000000  | 0.750571000000  | 29.409805000000 |
| H                                                 | 8.204231000000 | 3.269309000000  | 16.578766000000 | H  | 4.884106000000  | 2.134772000000  | 28.310247000000 |
| H                                                 | 6.001576000000 | 2.295590000000  | 19.748261000000 | H  | 6.281869000000  | 1.561068000000  | 29.237617000000 |
| H                                                 | 3.215988000000 | 0.859460000000  | 22.655656000000 | H  | 4.180635000000  | -2.454096000000 | 26.849845000000 |
| H                                                 | 5.505830000000 | -5.484123000000 | 19.990434000000 | H  | 0.189261000000  | -3.450733000000 | 25.306119000000 |
| H                                                 | 7.029193000000 | 2.760606000000  | 22.005718000000 | H  | 0.028422000000  | 3.795377000000  | 25.890376000000 |
| H                                                 | 7.421158000000 | -0.995437000000 | 16.273282000000 | H  | 4.476557000000  | -3.549792000000 | 24.817763000000 |
| H                                                 | 7.919062000000 | 0.364486000000  | 15.250318000000 | H  | 7.342422000000  | 0.279962000000  | 25.281907000000 |
| H                                                 | 6.263036000000 | 0.292897000000  | 15.886255000000 | H  | 7.873940000000  | 1.344677000000  | 26.595543000000 |
| H                                                 | 2.688428000000 | 2.512152000000  | 24.407754000000 | H  | 6.476358000000  | 1.792858000000  | 25.591813000000 |
| H                                                 | 8.413911000000 | -6.712283000000 | 21.029211000000 | H  | 0.046680000000  | -5.740590000000 | 24.416094000000 |
| H                                                 | 6.814135000000 | -7.402175000000 | 20.705071000000 | H  | -0.406906000000 | 5.415809000000  | 22.571848000000 |
| H                                                 | 7.493985000000 | -7.438695000000 | 22.346782000000 | H  | 1.096634000000  | 5.554577000000  | 23.488823000000 |
| H                                                 | 6.502493000000 | 4.409868000000  | 23.778193000000 | H  | -0.454465000000 | 5.670494000000  | 24.328990000000 |
| H                                                 | 9.812418000000 | -0.428864000000 | 18.228148000000 | H  | 4.323889000000  | -5.821306000000 | 23.895302000000 |
| H                                                 | 9.999011000000 | 1.163947000000  | 18.970645000000 | H  | 6.866735000000  | -2.212898000000 | 27.145569000000 |
| H                                                 | 5.970130000000 | -2.017634000000 | 28.674012000000 | Fe | 10.027998000000 | -1.643119000000 | 23.235299000000 |
| H                                                 | 7.575913000000 | -1.291778000000 | 28.470139000000 | Cl | 9.179022000000  | -2.059219000000 | 25.287286000000 |
| H                                                 | 2.100889000000 | -6.936506000000 | 23.693566000000 | Cl | 11.939354000000 | -0.492963000000 | 23.455035000000 |
| Fe                                                | 1.954186000000 | -1.887859000000 | 21.769612000000 | Cl | 8.592116000000  | -0.421174000000 | 22.010519000000 |
| Cl                                                | 1.761395000000 | -3.966534000000 | 21.077573000000 | Cl | 10.414613000000 | -3.594160000000 | 22.186533000000 |
| Cl                                                | 1.944011000000 | -0.433920000000 | 20.095694000000 |    |                 |                 |                 |
| Cartesian Coordinates for <b>TS1<sup>Br</sup></b> |                |                 |                 | O  | 1.400181000000  | -2.193997000000 | 22.942694000000 |
| S                                                 | 5.033654000000 | -1.613707000000 | 22.303943000000 | O  | -0.832519000000 | -2.134542000000 | 24.067498000000 |
| Si                                                | 8.946631000000 | 1.894962000000  | 25.215618000000 | N  | 1.298327000000  | -1.788173000000 | 25.506700000000 |
| O                                                 | 4.774522000000 | -2.042742000000 | 23.681346000000 | C  | 0.559637000000  | 0.136034000000  | 23.862956000000 |
| O                                                 | 3.810269000000 | -0.931016000000 | 21.673393000000 | C  | 6.522850000000  | -2.393086000000 | 26.272809000000 |

|    |                |                |                |   |                |                |                |
|----|----------------|----------------|----------------|---|----------------|----------------|----------------|
| N  | 6.36655000000  | -0.68946500000 | 22.23103300000 | C | 2.28700600000  | -4.09874400000 | 25.25369500000 |
| C  | 5.43588700000  | -3.02513500000 | 21.31135800000 | C | 1.98615100000  | -1.69630800000 | 28.21209900000 |
| C  | 5.51508500000  | 1.49121900000  | 21.34346800000 | C | 1.96682500000  | -2.85547900000 | 26.01063900000 |
| C  | 8.02920500000  | 0.83019600000  | 23.93763300000 | C | 5.45334100000  | -1.07157400000 | 28.01555300000 |
| C  | 6.45538800000  | 0.61651500000  | 22.07129000000 | C | 1.84142000000  | 2.11544600000  | 23.45190100000 |
| C  | 5.17794800000  | -5.37787000000 | 20.94692500000 | C | 4.35190200000  | -0.32727200000 | 28.53722700000 |
| C  | 4.95980100000  | -4.26070800000 | 21.74767600000 | C | 5.42256400000  | -1.67706900000 | 26.73571200000 |
| C  | 6.11007200000  | -2.87954500000 | 20.09741100000 | C | 1.80029800000  | 0.75869200000  | 23.73107000000 |
| C  | 8.13869400000  | 3.59662300000  | 25.16515700000 | C | -0.63682000000 | 0.83170100000  | 23.71590700000 |
| C  | 7.57955100000  | 1.27476100000  | 22.74283500000 | C | 0.31440500000  | -3.05958100000 | 30.34775600000 |
| C  | 5.84648600000  | -5.27178700000 | 19.71964100000 | C | 3.10616600000  | -0.14293200000 | 27.93359500000 |
| C  | 4.89941600000  | 1.08604700000  | 20.14626600000 | C | 2.37508500000  | -2.76482500000 | 27.34922200000 |
| C  | 6.31231100000  | -4.01035400000 | 19.31249300000 | C | 0.65970200000  | 2.85740000000  | 23.30929900000 |
| C  | 5.23431700000  | 2.76891500000  | 21.86628300000 | C | 1.31972200000  | -4.75783200000 | 24.47640800000 |
| C  | 10.78314100000 | 1.99206000000  | 24.77583600000 | C | -0.57114900000 | 2.19977400000  | 23.44138700000 |
| C  | 4.00288900000  | 1.92950300000  | 19.49957800000 | C | 3.57031100000  | -4.66341100000 | 25.35831400000 |
| C  | 6.03094500000  | -6.48042000000 | 18.83648500000 | C | 1.68737400000  | -0.36609900000 | 30.98710500000 |
| C  | 4.31719000000  | 3.59898100000  | 21.22736900000 | C | 1.63238900000  | -5.94376600000 | 23.81390800000 |
| C  | 8.67029600000  | 1.05019400000  | 26.87416300000 | C | 0.74151100000  | 4.34235000000  | 23.06770400000 |
| C  | 3.70032400000  | 3.18122500000  | 20.04571100000 | C | 7.68997900000  | -1.97852400000 | 28.36293300000 |
| H  | 7.64112700000  | -0.13419400000 | 24.27051100000 | C | 3.87869100000  | -5.85192100000 | 24.69796100000 |
| H  | 4.80972700000  | -6.34392000000 | 21.28108500000 | C | 3.39227500000  | -2.96296000000 | 30.66423700000 |
| H  | 4.41874600000  | -4.34491000000 | 22.68224900000 | C | 2.91157600000  | -6.49531700000 | 23.92085400000 |
| H  | 6.48686900000  | -1.91226100000 | 19.78111100000 | C | 7.64977200000  | -2.55247000000 | 27.08372000000 |
| H  | 7.07835900000  | 3.52068500000  | 25.42338500000 | C | 6.60997800000  | -1.23973500000 | 28.81940800000 |
| H  | 8.20899800000  | 4.05150600000  | 24.16939600000 | H | 6.49112400000  | -2.82005200000 | 25.27626700000 |
| H  | 8.60755600000  | 4.27921800000  | 25.88415400000 | H | 1.12677300000  | -1.14931200000 | 27.81534400000 |
| H  | 7.85576700000  | 2.25441100000  | 22.36170600000 | H | 2.80157000000  | 2.61415100000  | 23.38465400000 |
| H  | 5.12046200000  | 0.11221900000  | 19.72502000000 | H | 4.48259500000  | 0.06666500000  | 29.54270600000 |
| H  | 6.84277400000  | -3.91415800000 | 18.36929600000 | H | 4.56377900000  | -1.55612500000 | 26.09185700000 |
| H  | 5.69059600000  | 3.09178900000  | 22.79547700000 | H | 2.71533900000  | 0.19533300000  | 23.85526100000 |
| H  | 11.24290800000 | 0.99649400000  | 24.76070800000 | H | -1.58747300000 | 0.31842300000  | 23.81016400000 |
| H  | 11.31976900000 | 2.60192500000  | 25.51387100000 | H | 0.38439700000  | -4.00942800000 | 29.80460300000 |
| H  | 10.93069200000 | 2.44952600000  | 23.78996600000 | H | -0.58038600000 | -2.53429600000 | 29.99210700000 |
| H  | 3.52559100000  | 1.60400300000  | 18.58093500000 | H | 0.17282200000  | -3.28486500000 | 31.41238300000 |
| H  | 6.11318900000  | -7.39897700000 | 19.42597900000 | H | 3.03418900000  | -0.16382700000 | 26.85031600000 |
| H  | 6.92381700000  | -6.38956400000 | 18.21007600000 | H | 2.47783300000  | 0.61363200000  | 28.39032500000 |
| H  | 5.16921000000  | -6.59644900000 | 18.16649200000 | H | 2.98121500000  | -3.57691600000 | 27.73706700000 |
| H  | 4.08066000000  | 4.56402700000  | 21.66510000000 | H | 0.31468900000  | -4.35738500000 | 24.40134700000 |
| H  | 9.23595900000  | 0.11414700000  | 26.94409500000 | H | -1.49410100000 | 2.76270900000  | 23.33198600000 |
| H  | 7.60986000000  | 0.80963900000  | 27.00748300000 | H | 4.33545100000  | -4.15370000000 | 25.93311500000 |
| H  | 8.97151400000  | 1.69709200000  | 27.70658300000 | H | 8.50451200000  | -3.11492300000 | 26.71776200000 |
| H  | 2.98265000000  | 3.82768400000  | 19.54851400000 | H | 6.64251600000  | -0.77316200000 | 29.80058400000 |
| Fe | 2.00895600000  | -1.55640000000 | 21.27617400000 | H | 4.32033400000  | -2.42465200000 | 30.44370400000 |
| Fe | 4.15369600000  | 2.97601600000  | 26.24747300000 | H | 3.45364600000  | -3.94490600000 | 30.17939700000 |
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## Chapter 3

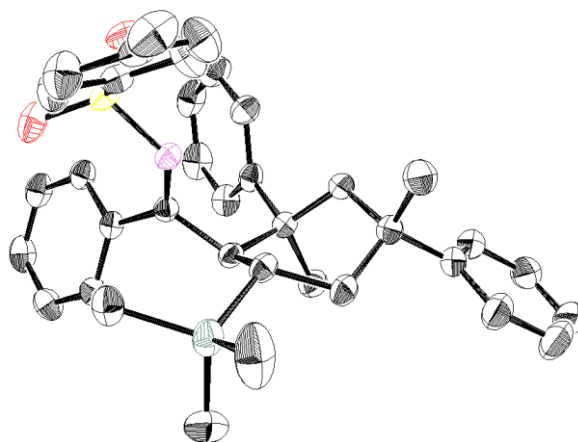
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| H  | 2.598303000000  | 0.241489000000  | 30.944785000000 | H  | 4.879751000000 | -6.266555000000 | 24.779786000000 |
| H  | 1.451159000000  | -0.536227000000 | 32.044759000000 | Br | 5.454930000000 | 2.990973000000  | 28.241967000000 |
| H  | 0.871508000000  | 0.227083000000  | 30.555684000000 | Br | 4.476106000000 | 4.903939000000  | 24.878703000000 |
| H  | 0.870214000000  | -6.441459000000 | 23.221451000000 | Br | 1.839998000000 | 2.868531000000  | 26.760177000000 |
| H  | 1.145044000000  | 4.844280000000  | 23.956373000000 | Br | 4.949188000000 | 1.113656000000  | 25.036235000000 |
| H  | -0.237834000000 | 4.774933000000  | 22.842151000000 | Br | 0.937098000000 | 0.257652000000  | 20.296350000000 |
| H  | 1.420762000000  | 4.566623000000  | 22.237352000000 | Br | 2.191451000000 | -3.391867000000 | 19.832296000000 |
| H  | 8.569631000000  | -2.099614000000 | 28.987774000000 |    |                |                 |                 |

Cartesian Coordinates for **TS1<sup>Cl</sup>**

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| S  | 4.770295000000  | -1.440416000000 | 22.194292000000 | H  | 10.868658000000 | 2.061064000000  | 23.828581000000 |
| Si | 8.782446000000  | 1.954973000000  | 25.216616000000 | H  | 3.482278000000  | 1.896421000000  | 18.436053000000 |
| O  | 4.284384000000  | -1.670580000000 | 23.559719000000 | H  | 6.224555000000  | -7.538008000000 | 20.312401000000 |
| O  | 3.647335000000  | -0.941671000000 | 21.263726000000 | H  | 7.473176000000  | -6.711124000000 | 19.357869000000 |
| N  | 6.084898000000  | -0.495640000000 | 22.195422000000 | H  | 5.820345000000  | -6.831361000000 | 18.744676000000 |
| C  | 5.352026000000  | -2.960256000000 | 21.495609000000 | H  | 3.651288000000  | 4.697429000000  | 21.710100000000 |
| C  | 5.210705000000  | 1.690912000000  | 21.363889000000 | H  | 8.541427000000  | 0.202251000000  | 26.980195000000 |
| C  | 7.753785000000  | 0.964719000000  | 23.964165000000 | H  | 7.291900000000  | 1.450916000000  | 27.139468000000 |
| C  | 6.140156000000  | 0.820986000000  | 22.106635000000 | H  | 8.941804000000  | 1.778788000000  | 27.696974000000 |
| C  | 5.042948000000  | -5.324423000000 | 21.279365000000 | H  | 2.775407000000  | 4.045262000000  | 19.464573000000 |
| C  | 4.673703000000  | -4.120538000000 | 21.872569000000 | Fe | 1.838792000000  | -1.637327000000 | 21.053632000000 |
| C  | 6.368613000000  | -2.974376000000 | 20.538119000000 | Cl | 2.004201000000  | -3.402204000000 | 19.706450000000 |
| C  | 8.294137000000  | 3.768116000000  | 25.051901000000 | Cl | 0.642944000000  | -0.001883000000 | 20.175389000000 |
| C  | 7.227878000000  | 1.479025000000  | 22.830020000000 | Fe | 4.167652000000  | 3.414650000000  | 26.318307000000 |
| C  | 6.059245000000  | -5.380324000000 | 20.315953000000 | Cl | 2.067374000000  | 3.122992000000  | 27.058059000000 |
| C  | 4.720798000000  | 1.330235000000  | 20.095639000000 | Cl | 5.550096000000  | 3.792391000000  | 28.047073000000 |
| C  | 6.717038000000  | -4.191555000000 | 19.960232000000 | Cl | 4.220676000000  | 5.084818000000  | 24.805217000000 |
| C  | 4.840713000000  | 2.928912000000  | 21.923076000000 | Cl | 4.879367000000  | 1.553146000000  | 25.298104000000 |
| C  | 10.616909000000 | 1.693796000000  | 24.830738000000 | S  | 0.596602000000  | -1.667818000000 | 24.006880000000 |
| C  | 3.856130000000  | 2.180494000000  | 19.414877000000 | Si | 1.913557000000  | -2.045850000000 | 29.921628000000 |
| C  | 6.419377000000  | -6.686494000000 | 19.652887000000 | O  | 1.384213000000  | -2.250761000000 | 22.765631000000 |
| C  | 3.956811000000  | 3.764544000000  | 21.246752000000 | O  | -0.778853000000 | -2.192935000000 | 23.993575000000 |
| C  | 8.350699000000  | 1.279598000000  | 26.919362000000 | N  | 1.407758000000  | -1.840474000000 | 25.344063000000 |
| C  | 3.463247000000  | 3.392067000000  | 19.993929000000 | C  | 0.595254000000  | 0.090998000000  | 23.777437000000 |
| H  | 7.420911000000  | -0.037214000000 | 24.241694000000 | C  | 6.396936000000  | -2.401713000000 | 25.867379000000 |
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| H  | 6.885008000000  | -2.060252000000 | 20.264615000000 | C  | 2.077848000000  | -2.893911000000 | 25.870508000000 |
| H  | 7.227694000000  | 3.896519000000  | 25.268990000000 | C  | 5.470354000000  | -1.176016000000 | 27.757733000000 |
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| H  | 7.514079000000  | -4.219701000000 | 19.222377000000 | C  | -0.609547000000 | 0.733861000000  | 23.502895000000 |
| H  | 5.193587000000  | 3.210364000000  | 22.908691000000 | C  | 0.334209000000  | -3.059379000000 | 30.131585000000 |
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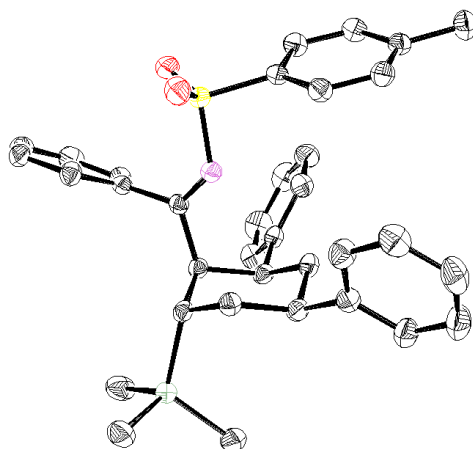
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| H | 4.409700000000  | -4.261199000000 | 25.889141000000 | H | 0.946702000000  | -6.520856000000 | 23.153682000000 |
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| H | 1.513439000000  | -0.614787000000 | 31.916940000000 |   |                 |                 |                 |

ORTEP Drawing of **3aa** ( $C_{37}H_{43}NO_2SSi$ ,  $M = 593.90$ ,  $T = 293(0)$  K)



|                                       |                                                                                      |
|---------------------------------------|--------------------------------------------------------------------------------------|
| Wavelength                            | MoK $\alpha$ ( $\lambda = 0.71075$ Å)                                                |
| Crystal System                        | monoclinic                                                                           |
| Space Group                           | P-1 (#2)                                                                             |
| Crystal Dimensions                    | $0.700 \times 0.650 \times 0.300$ mm                                                 |
| Lattice Parameters                    | $a = 9.046(2)$ Å<br>$b = 11.482(3)$ Å $\beta = 81.706(6)^\circ$<br>$c = 16.404(4)$ Å |
| Volume                                | $V = 1681.0(7)$ Å <sup>3</sup>                                                       |
| Z value                               | 2                                                                                    |
| $D_{\text{calc}}$                     | $1.173$ g/cm <sup>3</sup>                                                            |
| $2\theta_{\text{max}}$                | $55.0^\circ$                                                                         |
| Reflections collected                 | 14522                                                                                |
| Independent reflections               | 7446 ( $R_{\text{int}} = 0.0317$ )                                                   |
| No. Variables                         | 379                                                                                  |
| Goodness of Fit Indicator             | 1.047                                                                                |
| Residuals: $R_1$ ( $I > 2\sigma(I)$ ) | $R_1 = 0.0573$                                                                       |
| Residuals: $R$ (All reflections)      | $R_1 = 0.0679$ , $wR_2 = 0.1591$                                                     |

ORTEP Drawing of **3ac** ( $\text{C}_{35}\text{H}_{39}\text{NO}_2\text{SSi}$ ,  $M = 565.84$ ,  $T = 293(0)$  K)



|                                       |                                                                               |
|---------------------------------------|-------------------------------------------------------------------------------|
| Wavelength                            | MoK $\alpha$ ( $\lambda = 0.71075$ Å)                                         |
| Crystal System                        | orthorhombic                                                                  |
| Space Group                           | Pbcn (#60)                                                                    |
| Crystal Dimensions                    | $0.480 \times 0.260 \times 0.200$ mm                                          |
| Lattice Parameters                    | $a = 13.941(9)$ Å<br>$b = 12.992(9)$ Å $\beta = 90^\circ$<br>$c = 33.61(2)$ Å |
| Volume                                | $V = 6087(7)$ Å <sup>3</sup>                                                  |
| Z value                               | 8                                                                             |
| $D_{\text{calc}}$                     | $1.235$ g/cm <sup>3</sup>                                                     |
| $2\theta_{\text{max}}$                | $55.0^\circ$                                                                  |
| Reflections collected                 | 60621                                                                         |
| Independent reflections               | 6955 ( $R_{\text{int}} = 0.0716$ )                                            |
| No. Variables                         | 361                                                                           |
| Goodness of Fit Indicator             | 1.086                                                                         |
| Residuals: $R_1$ ( $I > 2\sigma(I)$ ) | $R_1 = 0.0542$                                                                |
| Residuals: $R$ (All reflections)      | $R_1 = 0.0711$ , $wR_2 = 0.1270$                                              |

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## Chapter 4

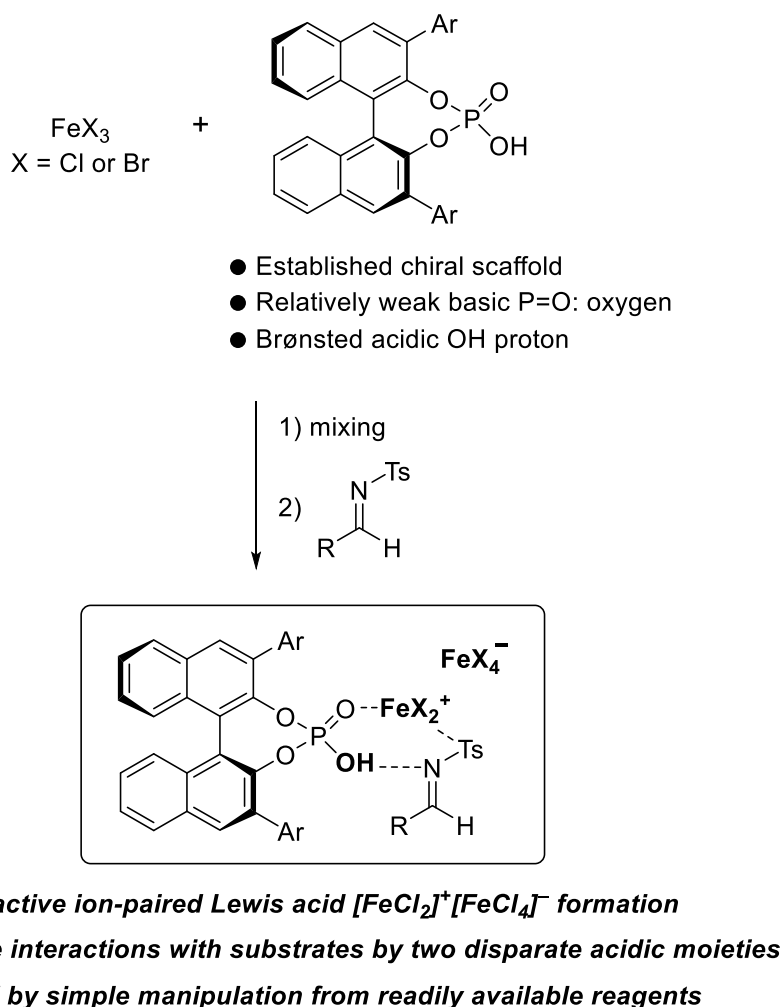
### **Multiple Activation Catalyst for Asymmetric Aza-Diels–Alder Reaction of Non-Activated Substrates**

A novel acid catalyst that has two acidic sites in single catalyst has been developed. The active catalyst species was generated in situ by a simple manipulation involving the mixing of  $\text{FeX}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and BINOL-derived chiral phosphoric acid. This catalyst system efficiently activates imines and catalyzes the asymmetric intermolecular aza-Diels–Alder reaction with non-activated dienes. Furthermore, insight on this novel catalyst system was revealed via mechanistic investigations.

## Introduction

As mentioned in the general introduction, ligand deceleration (in which the coordination of the Lewis basic ligand reduce its acidity) is a considerable problem, especially in enantioselective reactions.<sup>1</sup> As described in Chapter 2 and 3, the coordination of a Lewis basic moiety to  $\text{FeX}_3$  induced the formation of  $[\text{FeX}_2]^+[\text{FeX}_4]^-$  and produced highly active species for the Lewis acid catalyst. Stimulated by this result, the author exploited the novel chiral acid catalyst by employing the combination of  $\text{FeX}_3$  and chiral phosphoric acid. BINOL-derived chiral phosphoric acid is one of the most established chiral organocatalysts, and several highly enantioselective reactions have been accomplished by the acid–base interaction by utilizing a Brønsted acidic proton (O–H) and Lewis basic phosphoryl oxygen (P=O).<sup>2</sup> Hence, the combined use of  $\text{FeX}_3$  and chiral phosphoric acid would similarly cause the formation of  $[\text{FeX}_2]^+[\text{FeX}_4]^-$  upon coordination of the Lewis basic phosphoryl oxygen to  $\text{FeX}_3$ . Two unrelated acidic sites, a Lewis acidic Fe(III) cationic moiety and a Brønsted acidic proton moiety, are expected to activate the substrate as a dual acid catalyst (Figure 1).<sup>3,4</sup> Moreover,  $[\text{FeX}_4]^-$  could stabilize the cationic intermediate, as described in Chapter 3, and these multiple interactions should work synergistically. This catalyst system can be promising for solving the problem of ligand deceleration, because the advantage of multiple acid activation have been demonstrated recently for several types of reactions.

Herein, the author demonstrated the aza-Diels–Alder reaction of non-activated substrates by employing this Lewis acid and Brønsted acid multiple activation catalyst system. The intermolecular aza-Diels–Alder reaction is one of the most efficient tools for rapid and atom-economical construction of heterocycles; therefore, the aza-Diels–Alder reaction has played a significant role in the synthesis of natural products.<sup>5</sup> Because of its importance, several racemic and asymmetric aza-Diels–Alder reactions have been developed in recent decades, although most required pre-activated substrates (i.e. Danishefsky's and Rawal's dienes, which possess high HOMO energy levels).<sup>6,7</sup> The asymmetric aza-Diels–Alder reaction of non-activated substrates remains challenging, and an efficient catalyst system is in high demand.



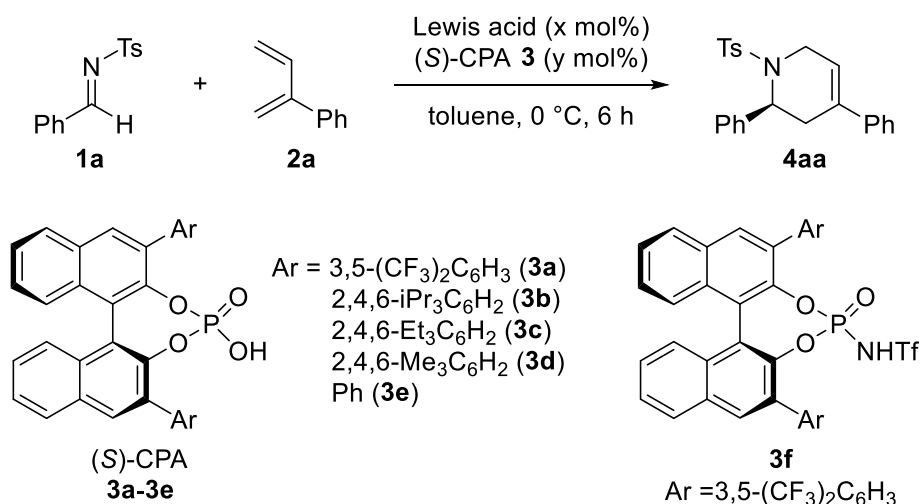
**Figure 1.** Designs of multiple activation catalyst.

## Results and Discussion

The author initially conducted the reaction of *N*-tosylated aldimine (**1a**) and 2-phenyl-1,3-butadiene (**2a**) in the presence of  $\text{FeCl}_3$  and chiral phosphoric acid **3a** ( $\text{Ar} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ). The reaction was proceeded enantioselective manner within 6 hours (Table 1, entry 1), while  $\text{FeCl}_3$  alone could catalyze the reaction but gave racemic product (entry 2). Considering that sole use of chiral phosphoric acid could not promote the reaction (entry 3), both of  $\text{FeCl}_3$  and chiral phosphoric acid are necessary for achieving enantioselective reaction. After various substituents on chiral phosphoric acid were investigated, objective cycloadduct was obtained in good yield and excellent

enantioselectivity by using  $\text{FeCl}_3$  and chiral phosphoric acid **3c** ( $\text{Ar} = 2,4,6\text{-Et}_3\text{C}_6\text{H}_2$ ) (entry 5). In addition, a chiral phosphoramidate, which possesses stronger Brønsted acidic proton, could not catalyze the reaction (entry 8), indicating this catalyst system is not likely proceeded via Lewis acid assisted Brønsted acid (LBA) catalyst.<sup>8,9</sup> Next, the effect of Lewis acid was examined. Using  $\text{FeBr}_3$  instead of  $\text{FeCl}_3$  slightly raised enantioselectivity (entry 9). Although  $\text{AlCl}_3$  and  $\text{Sc}(\text{OTf})_3$  could catalyze the reaction, results were inferior to the case of  $\text{FeBr}_3$ . Other metal halide even  $\text{FeCl}_2$  did not give the product at all (entry 11-13, see Supplemental Data for detail), and these facts implied that the nature of in situ disproportionation of  $\text{FeX}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) is crucial for the catalysis.

**Table 1.** Optimization for asymmetric aza-Diels–Alder reaction of **1a** and **2a**<sup>a</sup>



| entry | Lewis acid<br>(x mol%) | (S)-CPA<br>(y mol%) | Yield of <b>4aa</b><br>(%) <sup>b</sup> | e.r. of <b>4aa</b> <sup>c</sup> |
|-------|------------------------|---------------------|-----------------------------------------|---------------------------------|
| 1     | $\text{FeCl}_3$ (1)    | <b>3a</b> (5)       | 85                                      | 60:40                           |
| 2     | $\text{FeCl}_3$ (1)    | none                | 92                                      | racemic                         |
| 3     | none                   | <b>3a</b> (5)       | <1                                      | —                               |
| 4     | $\text{FeCl}_3$ (1)    | <b>3b</b> (5)       | 85                                      | 79:21                           |
| 5     | $\text{FeCl}_3$ (1)    | <b>3c</b> (5)       | 90                                      | 96:4                            |
| 6     | $\text{FeCl}_3$ (1)    | <b>3d</b> (5)       | 39                                      | 96:4                            |
| 7     | $\text{FeCl}_3$ (1)    | <b>3e</b> (5)       | <5                                      | —                               |

**Table 1.** (Continued)

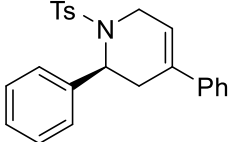
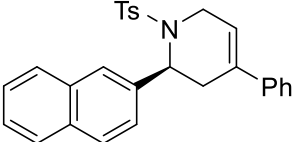
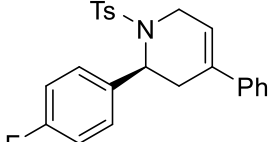
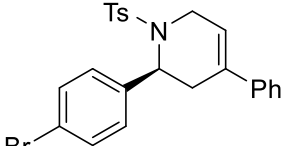
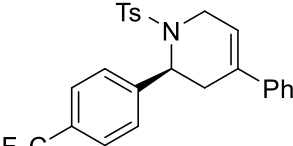
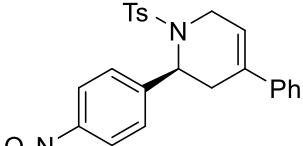
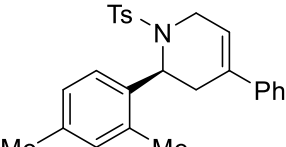
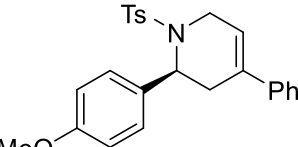
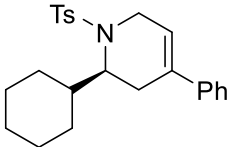
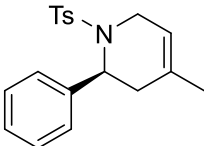
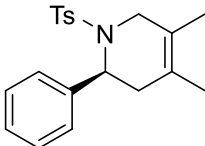
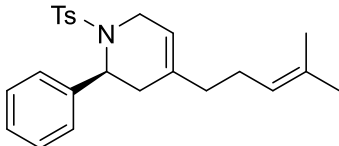
|    |                       |               |    |       |
|----|-----------------------|---------------|----|-------|
| 8  | FeCl <sub>3</sub> (1) | <b>3f</b> (5) | <1 | —     |
| 9  | FeBr <sub>3</sub> (1) | <b>3c</b> (5) | 88 | 98:2  |
| 10 | FeBr <sub>3</sub> (1) | <b>3c</b> (2) | 88 | 98:2  |
| 11 | FeCl <sub>2</sub>     | <b>3c</b> (5) | <1 | —     |
| 12 | AlCl <sub>3</sub>     | <b>3c</b> (5) | 21 | 97:3  |
| 13 | Sc(OTf) <sub>3</sub>  | <b>3c</b> (5) | 37 | 58:42 |

<sup>a</sup>Reactions were carried out using Lewis acid and chiral phosphoric acid as indicated loading, **1a** (0.2 mmol), and **2a** (0.4 mmol) in 1.5 mL of toluene for 6 h under 0 °C. <sup>b</sup>Isolated yield.

<sup>c</sup>Determined by chiral HPLC analysis.

Under the optimized reaction conditions, various imines and dienes were transformed to the corresponding cycloadducts using the multiple activation catalyst system (Table 2). Imines with electron-withdrawing groups, such as F, Br, and CF<sub>3</sub>, were successfully converted to the corresponding desired products in excellent yield and enantioselectivity, and the absolute configuration of the products was determined to be (*S*) by single crystal X-ray diffraction analysis of **4da**. NO<sub>2</sub> substituent on the imine also gave the desired product in high selectivity. Although electron-donating substituents lowered the reactivity, enantioselectivity was not affected. Aliphatic imines were also applicable as substrates, but the corresponding products were obtained in slightly low yields and enantioselectivities. Notably, simple dienes like isoprene, 2,3-dimethyl-1,3-butadiene, and myrcene afforded the corresponding products in good enantioselectivities.

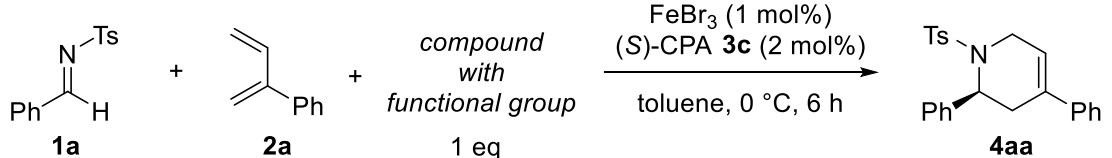
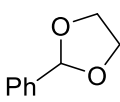
**Table 2.** Substrate scope<sup>a</sup>

| $  \begin{array}{c}  \text{Ts} \\    \\  \text{R}^1\text{C}=\text{N} \\    \\  \text{H} \\  \mathbf{1}  \end{array}  +  \begin{array}{c}  \text{R} \\    \\  \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \\  \mathbf{2}  \end{array}  \xrightarrow[\text{toluene, 0 } ^\circ\text{C, 6 h}]{\text{FeBr}_3 \text{ (1 mol\%)} \\ \text{(S)-CPA } \mathbf{3c} \text{ (2 mol\%)}}  \begin{array}{c}  \text{Ts} \\    \\  \text{R}^1\text{C}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{N} \\  \mathbf{4}  \end{array}  $ |                                                                                                                                                                              |                                                                                                                                            |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| products <sup>b</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                              |                                                                                                                                            |
|  <p><b>4aa</b><br/>88%, 98:2 e.r.</p>                                                                                                                                                                                                                                                                                                                                                                                                     |  <p><b>4ba</b><br/>75%, 98:2 e.r.</p>                                                       |  <p><b>4ca</b><br/>87%, 98:2 e.r.</p>                   |
|  <p><b>4da</b><br/>88%, 99:1 e.r.</p>                                                                                                                                                                                                                                                                                                                                                                                                    |  <p><b>4ea</b><br/>86%, 99:1 e.r.</p>                                                      |  <p><b>4fa</b><br/>55%, 99.5:0.5 e.r.<br/>(18 h)</p>   |
|  <p><b>4ga</b><br/>78%, 97.5:2.5 e.r.</p>                                                                                                                                                                                                                                                                                                                                                                                               |  <p><b>4ha</b><br/>49%, 96.5:3.5 e.r.</p>                                                 |  <p><b>4ia</b><br/>56%, 87.5:12.5 e.r.<br/>(18 h)</p> |
|  <p><b>4ab</b><br/>87%, 98:2 e.r. (48 h)<br/>87%, 93:7 (25 °C, 18 h)</p>                                                                                                                                                                                                                                                                                                                                                                |  <p><b>4ac</b><br/>56%, 96.5:3.5 e.r. (10 °C, 18 h)<br/>88%, 82:18 e.r. (25 °C, 18 h)</p> |  <p><b>4ad</b><br/>15%, 99.5:0.5 e.r. (18 h)</p>      |

<sup>a</sup>Reactions were carried out using FeBr<sub>3</sub> (1 mol%), chiral phosphoric acid **3c** (2 mol%), **1** (0.2 mmol), and **2** (0.4 mmol) in 1.5 mL of toluene for 6 h under 0 °C unless otherwise noted. <sup>b</sup>Yields were isolated yield, and enantioselectivity was determined by chiral HPLC analysis.

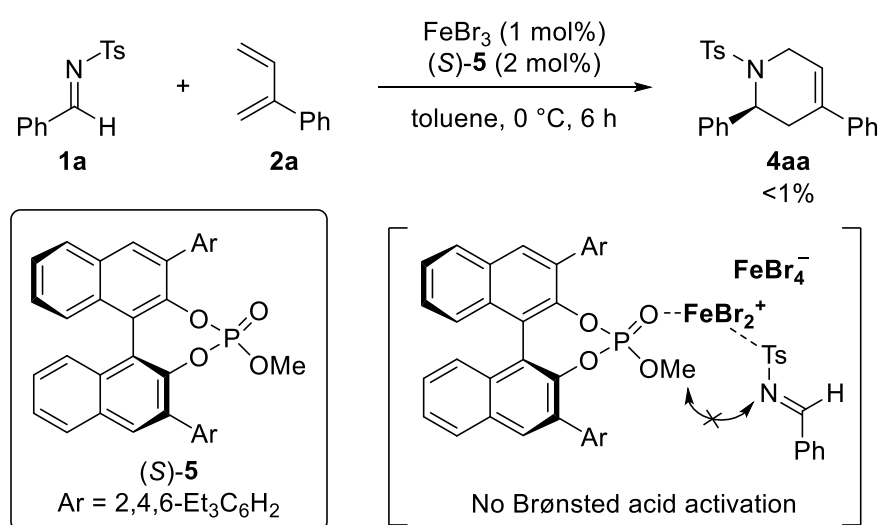
Furthermore, functional-group tolerance studies were conducted to show the high chemoselectivity of this catalyst system.<sup>10</sup> Reactions were conducted in the presence of one equivalent of the tested compounds (Table 3). Aldehyde did not react and cycloadduct from imine was selectively obtained. Presence of ketones, esters, and even phenols had little influence on the results. Notably, acetals that can decompose under Brønsted acidic conditions were also tolerated but the desired products were obtained in low yields. All the tested compounds were recovered quantitatively after the reaction, indicating that a highly imine selective activation was achieved by the multiple-activation catalyst system used herein.

**Table 3.** Examination of the functional group tolerance<sup>a</sup>

|  |                                                                                     |                                             |                                         |                                 |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------|-----------------------------------------|---------------------------------|
| entry                                                                               | compound                                                                            | Conversion of <b>1a</b><br>(%) <sup>a</sup> | Yield of <b>4aa</b><br>(%) <sup>b</sup> | e.r. of <b>4aa</b> <sup>d</sup> |
| 1                                                                                   | PhCHO                                                                               | 78                                          | 68                                      | 98.5:1.5                        |
| 2                                                                                   | PhC(O)Me                                                                            | 68                                          | 61                                      | 99:1                            |
| 3                                                                                   | PhCO <sub>2</sub> Me                                                                | >99                                         | 90                                      | 97.5:2.5                        |
| 4                                                                                   | PhOH                                                                                | >99                                         | 92                                      | 95:5                            |
| 5                                                                                   |  | 26                                          | 22                                      | 96:4                            |
| 6                                                                                   | PhCO <sub>2</sub> H                                                                 | 30                                          | 22                                      | 89.5:10.5                       |

<sup>a</sup>Reactions were carried out using FeBr<sub>3</sub> (1 mol%), chiral phosphoric acid **3c** (2 mol%), **1a** (0.2 mmol), **2a** (0.4 mmol), and corresponding compound (0.2 mmol) in 1.5 mL of toluene for 6 h at 0 °C. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR spectroscopic analysis using CHBr<sub>3</sub> as an internal standard. <sup>c</sup>Isolated yield. <sup>d</sup>Determined by chiral HPLC spectroscopic analysis.

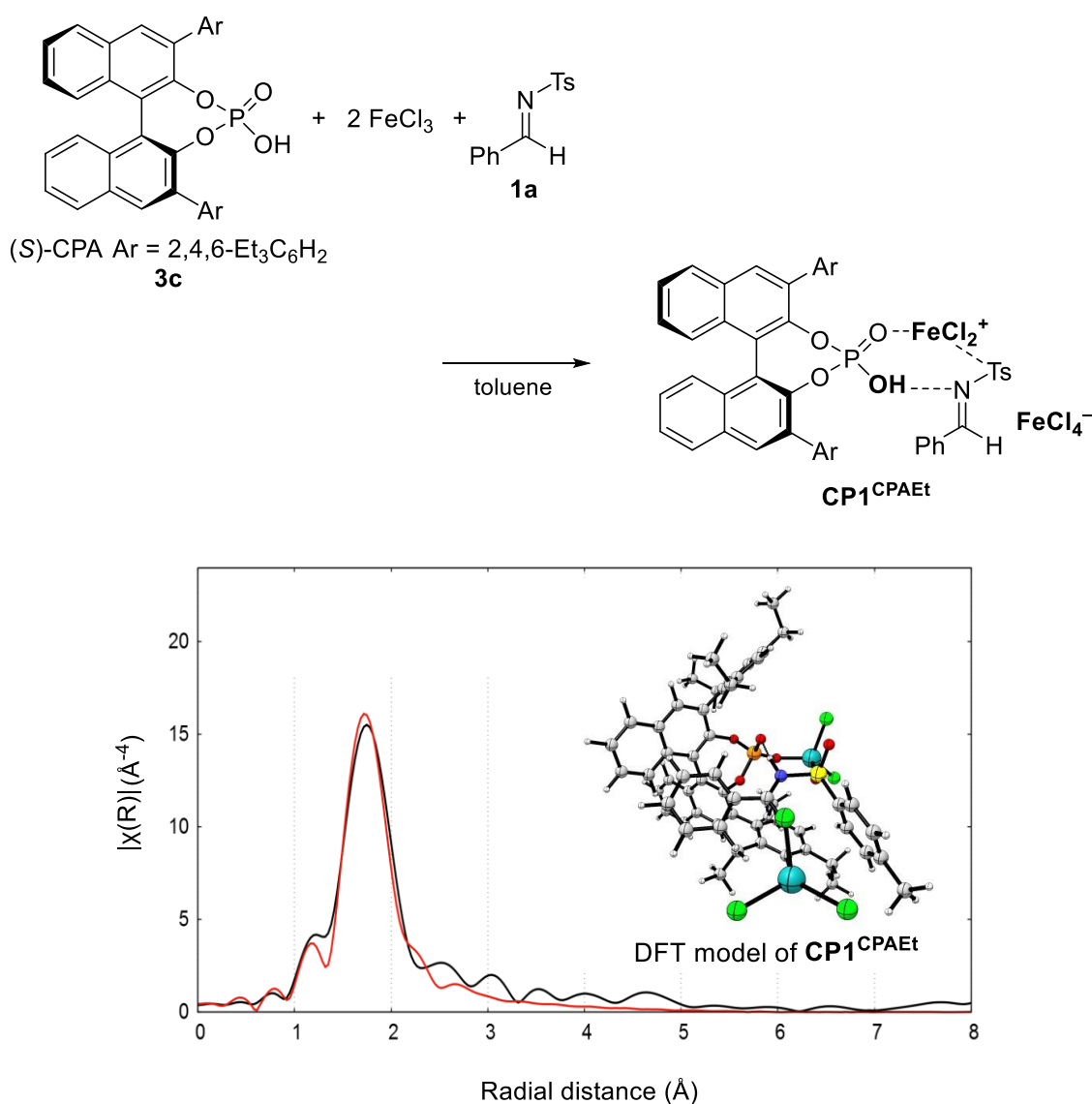
To obtain mechanistic information,  $\text{FeBr}_3$  and chiral methyl phosphate (*S*)-**5** (without Brønsted acidic proton) were used under the optimized reaction conditions for elucidating the effect of Brønsted acid in the catalyst system (Figure 2). The combined use of  $\text{FeBr}_3$  and chiral phosphate (*S*)-**5** did not give any products (<1% yield), underlining the importance of the Brønsted acidic proton in promoting the reaction; therefore, the multiple-activation catalyst system is efficient for the non-pre-activated imine as a dienophile.



**Figure 2.** Reaction using chiral phosphate.

To gain further detailed insight regarding the in situ formation of ion-paired Lewis acid by the coordination of the imine and the chiral phosphoric acid, the author performed solution-phase in situ Fe *K*-edge X-ray absorption spectroscopy (XAS) at a synchrotron radiation facility. The XAS measurement was carried out using a toluene solution of chiral phosphoric acid **3c**, imine **1a**, and  $\text{FeCl}_3$  at 0 °C, and the result of extended X-ray absorption fine structure (EXAFS) analysis is shown in Figure 3. The spectral features arising from the coordination sphere of the iron atoms, i.e. the radial distance of 1.0–2.2 Å, matched well with the spectra simulated using the DFT-calculated structure of complex **CP1**<sup>CPA<sup>Et</sup></sup> ( $R_f = 2.0\%$ ), in which one imine and one chiral phosphoric acid were coordinated to  $[\text{FeCl}_2]^+$  ion-paired with  $[\text{FeCl}_4]^-$ . The XAS analysis of the coordination sphere

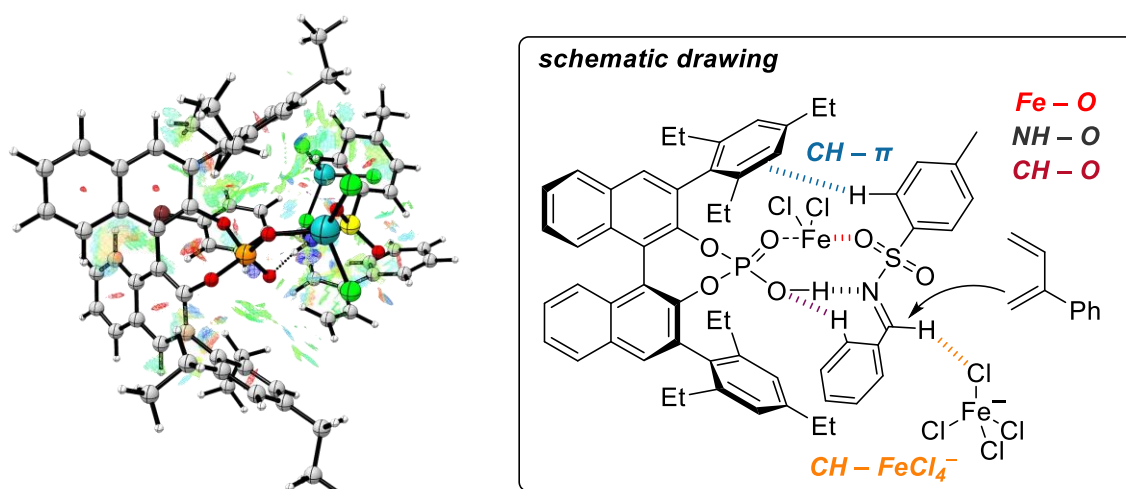
of iron indicated that the two iron atoms had tetrahedral coordination geometry and showed that the six chloride atoms were located at distances of 2.13–2.18 Å from iron, and the two oxygen atoms were at distances 1.81–1.95 Å. The DFT calculated structure of complex **CP1**<sup>CPA<sup>Et</sup></sup> was consistent with the observed coordination geometry of the iron atoms and bond lengths in the coordination sphere, which was found to be the most thermodynamically stable iron species and the TOF-determining intermediate by DFT calculations in the catalytic cycle.



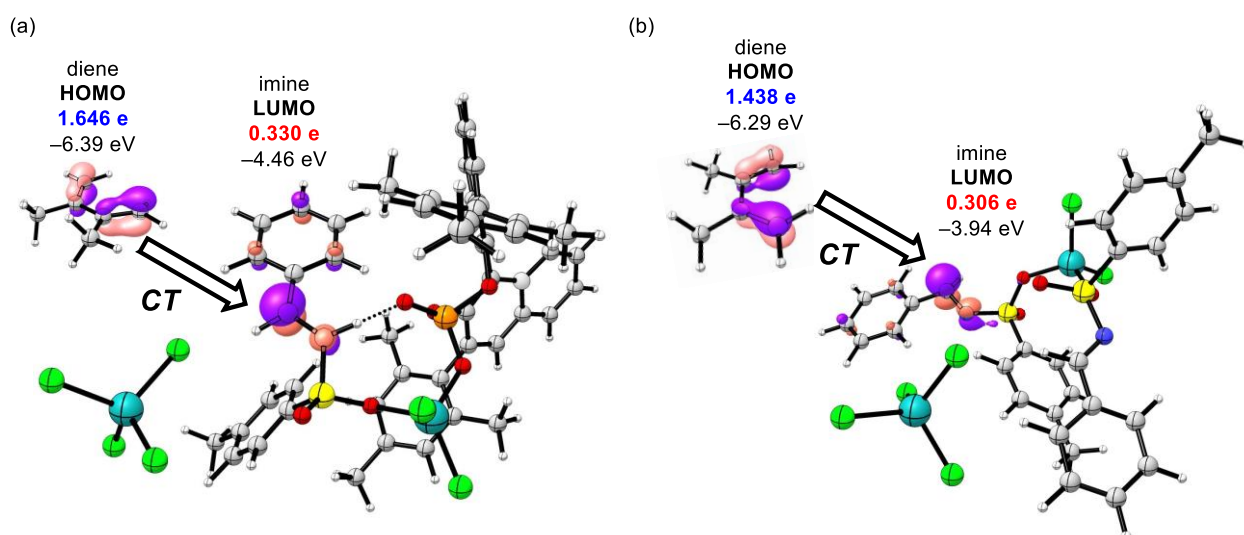
**Figure 3.** Solution-phase in situ Fe *K*-edge EXAFS analysis.

To elucidate the multiple activation of the ion-paired Lewis acid and the chiral Brønsted acid in the transition state, and to clarify the origin of the enantioselective reaction prior to racemic reaction, DFT calculations for the catalytic cycle were performed based on the observed spectroscopic results obtained for imine **1a**, diene **2c**, chiral phosphoric acid **3d**, and FeCl<sub>3</sub> as the model case (computational details are provided in the Supplemental Data). The author investigated the catalytic reaction pathway of FeCl<sub>3</sub> upon coordination of imine and chiral phosphoric acid to form the transition state (**TS1**<sup>CPAMe</sup>), which was controlled by multiple coordination by the ion-paired Lewis acid and the chiral Brønsted acid. The *exo*-addition of diene to imine on the iron complex takes place from the *Si*-face with an activation energy of 14.5 kcal/mol. This was the TOF-determining transition state in the asymmetric catalytic cycle, and the activation energy was estimated by an energetic span model.<sup>11</sup> On the other hand, the formation of the TOF-determining transition state in the racemic reaction takes place with [FeCl<sub>2</sub>]<sup>+</sup>[FeCl<sub>4</sub>]<sup>−</sup> catalyst via disproportionation of FeCl<sub>3</sub>, with an activation energy of 25.9 kcal/mol. Thus, the energy difference is large enough for the reaction to proceed by the asymmetric reaction path (see Supplemental Data for detail).

The weak interactions in the transition state (**TS1**<sup>CPAEt</sup>), giving rise to the asymmetric product, are confirmed by analysis of noncovalent interactions (Figure 4).<sup>12</sup> Several interactive noncovalent interactions are confirmed: 1) interaction between C–H hydrogen of phenyl group on the imine and oxygen atom of the chiral phosphoric acid, 2) interaction between the C–H hydrogen of imine and chloride atom of neighboring [FeCl<sub>4</sub>]<sup>−</sup>, and 3) interaction between the C–H hydrogen of tosyl group and aromatic substituent on 3,3'-position of chiral phosphoric acid. Furthermore, the transition-state **TS1**<sup>CPAEt</sup> was investigated through fragment Kohn–Sham molecular orbital analysis. During the C–C bond formation in the transition state, the electronic transition in the transition-state **TS1**<sup>CPAMe</sup> is facilitated because the LUMO of the imine is lowered by the multiple activation (−4.46 eV), compared to that of the possible background racemic pathway catalyzed by [FeCl<sub>2</sub>]<sup>+</sup> iron complex without multiple activation (−3.94 eV) (Figure 5).



**Figure 4.** Noncovalent interaction analysis in  $\text{TS1}^{\text{CPA}^{\text{Et}}}$ .



**Figure 5.** Charge decomposition analysis using fragment Kohn–Sham molecular orbitals.

## Conclusion

The author has developed a multiple-activation catalyst system with ion-paired Lewis acid and chiral Brønsted acid and applied the catalyst for the asymmetric aza-Diels–Alder reaction of nonactivated substrates. The catalyst was spontaneously generated in situ by mixing  $\text{FeBr}_3$  and chiral phosphoric acid, in which the formation of ion-paired Lewis acid with weakly coordinating

phosphoryl oxygen (P=O:) realized efficient activation. The multiple coordination at the Lewis and Brønsted acid sites was crucial for substrate-selective activation. Importance of both in situ formation of ion-paired Lewis acid ( $[\text{FeBr}_2]^+[\text{FeBr}_4]^-$ ) and the Brønsted acidic proton were experimentally and theoretically confirmed. This multiple-activation catalyst system would potentially solve the problem of conventional chiral Lewis acids and/or Brønsted acid catalysts, because the catalyst system may overcome the tradeoff between selectivity and reactivity of the reaction using nonactivated substrates that could not be employed due to their low electrophilicities.

## Experimental Section

### Materials.

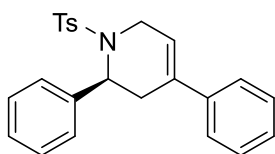
Iron(III) chloride was purchased from Sigma-Aldrich Co., Iron(III) bromide was purchased from Strem Chemicals, Inc., 2,3-Dimethyl-1,3-butadiene was purchased from TCI. Aldimines,<sup>13</sup> dienes,<sup>14</sup> and chiral phosphoric acid<sup>15</sup> were prepared according to the reported procedure. Unless otherwise noted, commercially available reagents were used without purification.

### Experimental Procedure and Characterization Data for Products.

#### *General procedure.*

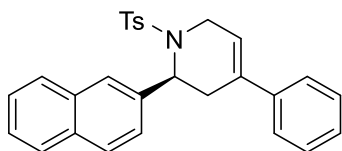
The reaction was performed in a 15 mL sealed tube equipped with a Teflon-coated magnetic stirrer bar. In a glove box,  $\text{FeBr}_3$  (0.002 mmol, 1 mol%) and chiral phosphoric acid (0.004 mmol, 2 mol%) were stirred in toluene (1 mL) at 0 °C. After  $\text{FeBr}_3$  was dissolved completely, imines (0.2 mmol) in toluene (0.5 mL) were added and stirred for a while, then dienes (0.4 mmol) were added to a solution. After the reaction mixture was stirred at 0 °C for the indicated time, the solution was passed through a short silica gel pad, washed with ethyl acetate, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with given eluent.

(*R*)-2-(naphthalen-2-yl)-4-phenyl-3,6-dihydro-2*H*-pyran (**4aa**).

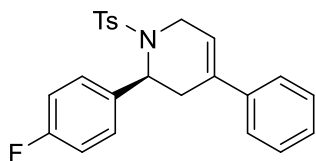


Yield: 88%, 96% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +43.5$  (*c* 1.29, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 33–35 °C (Hexane). TLC:  $R_f = 0.30$  (hexane/ethyl acetate = 8:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.73 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.22–7.36 (m, 12H), 5.91 (dd, *J* = 4.5, 2.5 Hz, 1H), 5.47 (d, *J* = 6.0 Hz, 1H), 4.33 (ddd, *J* = 19.0, 4.5, 2.5 Hz, 1H), 3.51–3.59 (m, 1H), 2.82 (d, *J* = 17.5 Hz, 1H), 2.66–2.84 (m, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  143.2, 140.3, 138.9, 137.5, 134.2, 129.6, 128.5, 128.4, 127.6, 127.5, 127.3, 127.0, 125.0, 120.1, 53.1, 41.3, 28.4, 21.5. IR (KBr): 3060, 3030, 2923, 1598, 1494, 1446, 1372, 1345, 1324, 1304, 1289, 1155, 1090, 927, 820 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 390.1507, calcd for [M+H]<sup>+</sup> 390.1522. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90/10, flow rate = 2.5 ml/min,  $\lambda$  = 254 nm, 40 °C):  $t_{\text{major}} = 9.3$  min,  $t_{\text{minor}} = 11.3$  min.

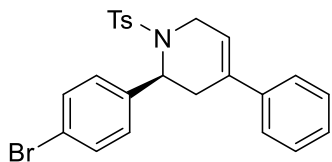
(*S*)-2-(naphthalen-2-yl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**4ba**).



Yield: 75%, 96% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +79.9$  (*c* 0.67, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 51–53 °C (Hexane). TLC:  $R_f = 0.23$  (hexane/ethyl acetate = 8/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.76–7.82 (m, 4H), 7.69 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.64 (s, 1H), 7.56 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.42–7.48 (m, 2H), 7.27–7.38 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.91–5.93 (m, 1H), 5.62 (d, *J* = 6.5 Hz, 1H), 4.38 (ddd, *J* = 7.0, 4.0, 2.5 Hz, 1H), 3.57 (ddt, *J* = 19.0, 4.0, 1.5 Hz, 1H), 2.94 (d, *J* = 17.0 Hz, 1H), 2.73–2.80 (m, 1H), 2.38 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  143.3, 140.4, 137.6, 136.2, 134.2, 132.9, 132.6, 129.6, 128.5, 128.3, 127.6, 127.5, 127.0, 126.1, 126.0, 125.8, 125.8, 125.0, 120.2, 53.3, 41.4, 28.3, 21.5. IR (KBr): 3059, 2933, 2845, 1599, 1448, 1343, 1328, 1160, 1095, 931, 859, 812, 750, 733, 682, 573, 548 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 462.1493, calcd for [M+Na]<sup>+</sup> 462.1498. HPLC (Daicel Chiralpak IF, hexane/*i*-PrOH = 80/20, flow rate = 2.0 ml/min,  $\lambda$  = 254 nm, 40 °C):  $t_{\text{major}} = 8.4$  min,  $t_{\text{minor}} = 9.9$  min.

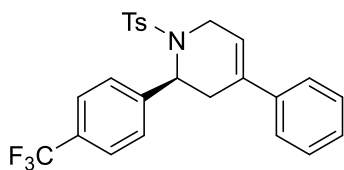
**(S)-2-(4-fluorophenyl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (4ca).**

Yield: 87%, 96% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +46.8$  (*c* 0.80, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 33–34 °C (Hexane). TLC: *R<sub>f</sub>* = 0.25 (hexane/ethyl acetate = 8:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.73 (d, *J* = 8.5 Hz, 2H), 7.24–7.35 (m, 9H), 6.95 (t, *J* = 8.5 Hz, 2H), 5.93 (s, 1H), 5.44 (d, *J* = 8.5 Hz, 1H), 4.33 (d, *J* = 19.0 Hz, 1H), 3.54 (d, *J* = 18.5 Hz), 2.78 (d, *J* = 19 Hz, 1H), 2.67–2.74 (m, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  162.0 (d, *J* = 246.4 Hz), 143.3, 140.0, 137.3, 134.7 (d, *J* = 2.9 Hz), 133.9, 129.6, 129.0 (d, *J* = 8.5 Hz), 128.5, 127.7, 126.9, 124.9, 120.0, 115.2 (d, *J* = 22.1 Hz), 52.5, 41.2, 28.5, 21.5. IR (KBr): 3066, 2940, 2852, 1604, 1507, 1446, 1330, 1231, 1165, 1099, 1076, 916, 834, 740, 731, 683, 678, 579 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 430.1228, calcd for [M+Na]<sup>+</sup> 430.1247. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90/10, flow rate = 2.5 ml/min,  $\lambda$  = 254 nm, 40 °C): *t*<sub>major</sub> = 7.9 min, *t*<sub>minor</sub> = 10.9 min.

**(S)-2-(4-bromophenyl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (4da).**

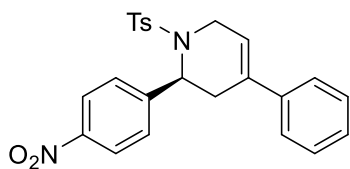
Yield: 88%, 98% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +50.9$  (*c* 0.49, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 41–43 °C (Hexane). TLC: *R<sub>f</sub>* = 0.18 (hexane/ethyl acetate = 10:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.71 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.38 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.18–7.35 (m, 9H), 5.91 (dd, *J* = 6.5, 2.5 Hz, 1H), 5.40 (d, *J* = 6.0 Hz, 1H), 4.32 (ddd, *J* = 19.0, 4.0, 2.5 Hz, 1H), 3.50–3.57 (m, 1H), 2.76 (d, *J* = 17.5 Hz, 1H), 2.65–2.72 (m, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  143.4, 140.0, 138.0, 137.3, 133.9, 131.5, 129.7, 129.1, 128.5, 127.7, 127.0, 124.9, 121.5, 120.0, 52.7, 41.3, 28.4, 21.5. IR (KBr): 3065, 2925, 2852, 1597, 1487, 1444, 1344, 1327, 1158, 1094, 1070, 923, 814, 749, 710, 682, 668, 647, 568, 552 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 492.0419, calcd for [M+Na]<sup>+</sup> 492.0426. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90/10, flow rate = 2.5 ml/min,  $\lambda$  = 254 nm, 40 °C): *t*<sub>major</sub> = 8.4 min, *t*<sub>minor</sub> = 10.8 min.

(*S*)-4-phenyl-1-tosyl-2-(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyridine (**4ea**).



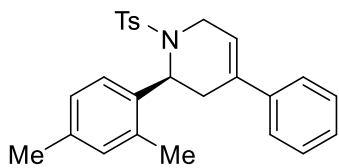
Yield: 86%, 98% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +44.3$  (*c* 1.57, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 36–38 °C (Hexane). TLC: *R*<sub>f</sub> = 0.27 (hexane/ethyl acetate = 10:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.73 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.24–7.36 (m, 7H), 5.94 (dd, *J* = 4.5, 2.0 Hz, 1H), 5.50 (d, *J* = 6.0 Hz, 1H), 4.36 (dt, *J* = 19.0, 3.0 Hz, 1H), 3.54–3.60 (m, 1H), 2.83 (d, *J* = 17.5 Hz, 1H), 2.72–2.79 (m, 1H), 2.40 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.5, 143.1, 139.9, 137.1, 133.8, 129.7 (q, *J* = 32.6 Hz), 129.7, 128.5, 127.8, 127.7, 126.9, 125.4 (q, *J* = 3.8 Hz), 124.9, 123.9 (q, *J* = 271.4 Hz), 119.9, 52.9, 41.5, 28.5, 21.4. IR (KBr): 3050, 2867, 1619, 1601, 1446, 1326, 1162, 1114, 1098, 1069, 1017, 923, 842, 816, 759, 741, 684, 568, 550 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 480.1204, calcd for [M+Na]<sup>+</sup> 480.1216. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90/10, flow rate = 2.5 ml/min, λ = 254 nm, 40 °C): *t*<sub>major</sub> = 5.7 min, *t*<sub>minor</sub> = 7.2 min.

(*S*)-2-(4-nitrophenyl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**4fa**).



Yield: 55%, 99% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +49.2$  (*c* 0.95, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 47–49 °C (Hexane). TLC: *R*<sub>f</sub> = 0.20 (hexane/ethyl acetate = 5:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.12 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.74 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.22–7.36 (m, 7H), 5.94 (dd, *J* = 4.0, 2.5, 1H), 5.53 (d, *J* = 5.5 Hz, 1H), 4.36 (dt, *J* = 18.0, 3.5 Hz, 1H), 3.54–3.61 (m, 1H), 2.84 (d, *J* = 17.5 Hz, 1H), 2.72–2.78 (m, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 147.2, 146.5, 143.7, 139.6, 136.9, 133.6, 129.8, 128.6, 128.2, 127.9, 126.9, 124.8, 123.6, 119.9, 52.8, 41.5, 28.5, 21.5. IR (KBr): 2852, 1598, 1515, 1445, 1343, 1160, 1096, 926, 857, 684, 572 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 457.1191, calcd for [M+Na]<sup>+</sup> 457.1192. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 85/15, flow rate = 2.5 ml/min, λ = 254 nm, 40 °C): *t*<sub>major</sub> = 15.3 min, *t*<sub>minor</sub> = 25.6 min.

(*S*)-2-(2,4-dimethylphenyl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**4ga**).



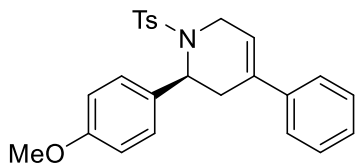
Yield: 78%, 95% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +41.9$  (*c* 1.40, CH<sub>2</sub>Cl<sub>2</sub>). Mp.

36–38 °C (Hexane). TLC: *R*<sub>f</sub> = 0.27 (hexane/ethyl acetate = 10:1). <sup>1</sup>H

NMR (CDCl<sub>3</sub>) δ 7.75 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.23–7.32 (m, 3H),

7.19 (d, *J* = 8.0 Hz, 2H), 7.09–7.12 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.84 (dd, *J* = 9.5, 1.5 Hz, 1H), 5.86–5.88 (m, 1H), 5.60 (d, *J* = 7.0 Hz, 1H), 4.27 (dd, *J* = 19.0, 5.0 Hz, 1H), 3.52 (ddd, *J* = 19.0, 5.0, 2.5 Hz, 1H), 2.71–2.79 (m, 1H), 2.60 (dd, *J* = 18.0, 2.0 Hz, 1H), 2.57 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.2, 140.4, 137.6, 137.5, 137.0, 135.4, 134.2, 131.8, 129.3, 128.3, 127.5, 127.4, 126.2, 126.1, 125.1, 120.6, 50.9, 41.3, 28.7, 21.3, 20.9, 19.8. IR (KBr): 3029, 2925, 1597, 1502, 1444, 1345, 1332, 1156, 1092, 1059, 921, 812, 763, 739, 678, 581, 561 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 440.1651, calcd for [M+Na]<sup>+</sup> 440.1655. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90/10, flow rate = 2.5 ml/min, λ = 254 nm, 40 °C): *t*<sub>minor</sub> = 6.6 min, *t*<sub>major</sub> = 8.0 min.

(*S*)-2-(4-methoxyphenyl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**4ha**).



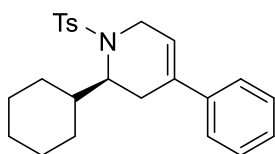
Yield: 49%, 93% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +53.1$  (*c* 1.07, CH<sub>2</sub>Cl<sub>2</sub>). Mp.

36–37 °C (Hexane). TLC: *R*<sub>f</sub> = 0.20 (hexane/ethyl acetate = 8:1). <sup>1</sup>H

NMR (CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.23–7.36 (m, 9H), 6.80

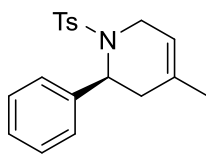
(dt, *J* = 9.0, 2.5 Hz, 2H), 5.92 (ddd, *J* = 4.5, 2.5, 2.0 Hz, 1H), 5.42 (d, *J* = 6.0 Hz, 1H), 4.32 (ddd, *J* = 19.0, 4.5, 2.0 Hz, 1H), 3.78 (s, 3H), 3.51–3.57 (m, 1H), 2.78 (d, *J* = 17.5 Hz, 1H), 2.60–2.72 (m, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.8, 143.2, 140.3, 137.6, 134.2, 130.9, 129.5, 128.5, 128.5, 127.6, 127.0, 125.0, 120.1, 113.6, 55.2, 52.6, 41.1, 28.5, 21.5. IR (KBr): 3059, 2933, 2853, 1609, 1512, 1496, 1444, 1333, 1305, 1252, 1159, 1097, 1031, 919, 830, 756, 732, 649, 576 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 442.1440, calcd for [M+Na]<sup>+</sup> 442.1447. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90/10, flow rate = 2.5 ml/min, λ = 254 nm, 40 °C): *t*<sub>major</sub> = 14.7 min, *t*<sub>minor</sub> = 22.8 min.

(*S*)-2-cyclohexyl-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**4ia**).

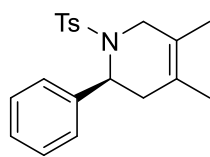


Yield: 56%, 75% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} -1.35$  (*c* 1.18, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 33–34 °C (Hexane). TLC: *R<sub>f</sub>* = 0.32 (hexane/ethyl acetate = 10/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.70 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.27–7.32 (m, 2H), 7.18–7.26 (m, 5H), 5.90 (ddd, 4.5, 2.5, 2.0 Hz, 1H), 4.34 (dt, *J* = 19.5, 3.5 Hz, 1H), 3.87 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.77–3.83 (m, 1H), 2.44 (d, *J* = 17.0 Hz, 1H), 2.37 (s, 3H), 2.16–2.25 (m, 1H), 1.94 (d, *J* = 13.0 Hz, 1H), 1.60–1.84 (m, 4H), 1.45–1.54 (m, 1H), 1.04–1.22 (m, 4H), 0.93–1.02 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  142.9, 140.7, 138.2, 133.8, 129.5, 128.3, 127.3, 126.7, 124.9, 119.2, 56.1, 41.4, 37.1, 30.7, 30.3, 26.5, 26.2, 26.1, 26.0, 21.4. IR (KBr): 3059, 2915, 2851, 1598, 1448, 1335, 1267, 1159, 1100, 928, 815, 749, 734, 683, 649, 575, 558 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 418.1802, calcd for [M+Na]<sup>+</sup> 418.1811. HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90/10, flow rate = 1.5 ml/min,  $\lambda$  = 254 nm, 40 °C): *t<sub>major</sub>* = 10.0 min, *t<sub>minor</sub>* = 11.7 min.

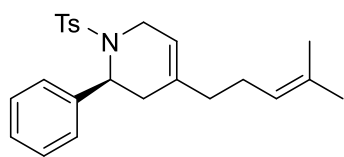
(*S*)-4-methyl-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**4ab**).



Yield: 87%, 96% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} -11.8$  (*c* 0.49, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 101–103 °C (Hexane). TLC: *R<sub>f</sub>* = 0.28 (hexane/ethyl acetate = 10/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.67 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.21–7.30 (m, 7H), 5.29 (d, *J* = 6.0 Hz, 2H), 4.07 (dt, *J* = 18.0, 2.0 Hz, 1H), 3.33 (ddd, *J* = 18.0, 3.5, 1.5 Hz, 1H), 2.40 (s, 3H), 2.28–2.36 (m, 1H), 2.23 (d, *J* = 18.0 Hz, 1H), 1.65 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  143.0, 139.3, 137.6, 131.4, 129.4, 128.3, 127.4, 127.2, 127.0, 117.4, 53.1, 40.8, 31.1, 23.2, 21.5. IR (KBr): 3027, 2851, 1595, 1493, 1451, 1368, 1324, 1258, 1147, 1093, 1030, 923, 815 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 350.1175, calcd for [M+Na]<sup>+</sup> 350.1185. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 97/3, flow rate = 1.0 ml/min,  $\lambda$  = 254 nm, 40 °C): *t<sub>major</sub>* = 10.4 min, *t<sub>minor</sub>* = 12.7 min.

**(S)-4,5-dimethyl-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (4ac).**

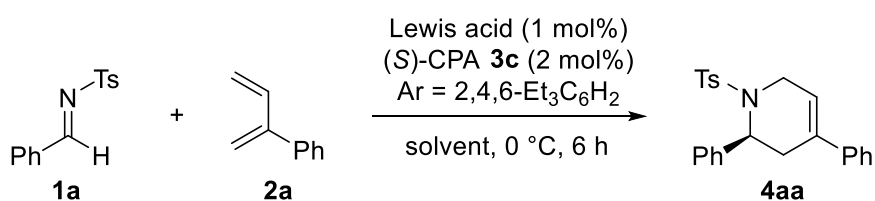
Yield: 56%, 93% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +26.8$  (*c* 1.32, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 87–89 °C (Hexane). TLC: *R*<sub>f</sub> = 0.30 (hexane/ethyl acetate = 8/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.65 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.20–7.28 (m, 7H), 5.23 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.20–3.25 (m, 1H), 2.40 (s, 3H), 2.31–2.37 (m, 1H), 2.18 (d, *J* = 17.5 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 142.9, 139.6, 137.5, 129.3, 128.3, 127.3, 127.3, 127.0, 123.1, 122.2, 53.4, 44.9, 32.3, 21.5, 18.6, 16.0. IR (KBr): 2919, 1927, 1596, 1522, 1517, 1352, 1330, 1279, 1162, 1090, 1009, 856, 814 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 364.1335, calcd for [M+Na]<sup>+</sup> 364.1342. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 97/3, flow rate = 1.0 ml/min, λ = 254 nm, 40 °C): *t*<sub>major</sub> = 8.4 min, *t*<sub>minor</sub> = 10.2 min.

**(S)-4-(4-methylpent-3-en-1-yl)-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (4ad).**

Yield: 15%, 99% *ee*, colorless oil.  $[\alpha]_{\text{D}}^{23} +27.9$  (*c* 0.14, CH<sub>2</sub>Cl<sub>2</sub>). TLC: *R*<sub>f</sub> = 0.30 (hexane/ethyl acetate = 10/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.67 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.21–7.30 (m, 7H), 5.30 (d, *J* = 5.5 Hz, 2H), 4.94–4.99 (m, 1H), 4.10 (d, *J* = 17.0 Hz, 1H), 3.36 (dt, *J* = 18.0, 2.0 Hz, 1H), 2.40 (s, 3H), 2.28–2.36 (m, 1H), 2.24 (d, *J* = 18.0 Hz, 1H), 1.87–2.05 (m, 1H), 1.66 (s, 3H), 1.56 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.0, 139.4, 137.6, 135.0, 131.9, 129.4, 128.3, 127.4, 127.3, 127.1, 123.5, 117.2, 53.2, 40.8, 37.3, 29.5, 25.7, 25.7, 21.5, 17.7. IR (neat): 2957, 2923, 2868, 1598, 1495, 1447, 1376, 1337, 1163, 1094, 1069, 931, 813, 688, 543 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 418.1806, calcd for [M+H]<sup>+</sup> 418.1811. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 97/3, flow rate = 1.0 ml/min, λ = 254 nm, 40 °C): *t*<sub>major</sub> = 9.2 min, *t*<sub>minor</sub> = 10.7 min.

## Supplemental Data

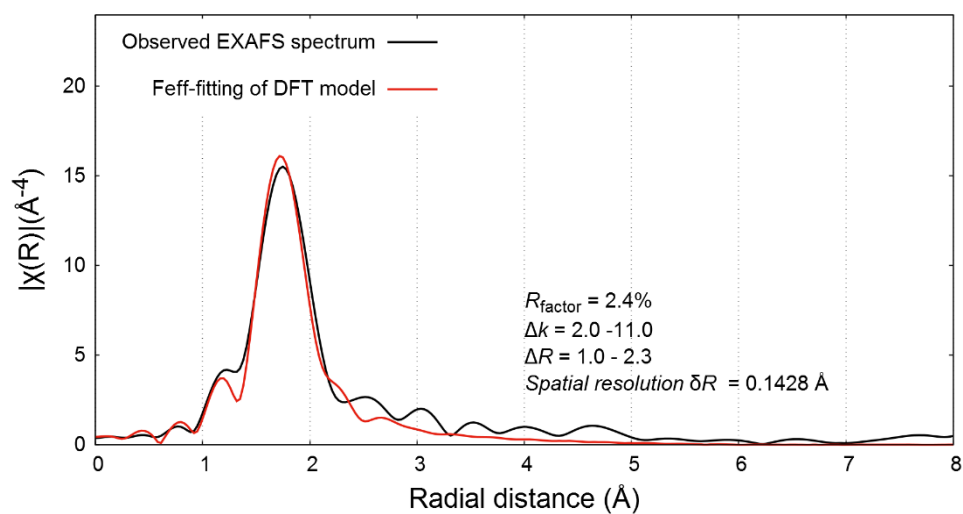
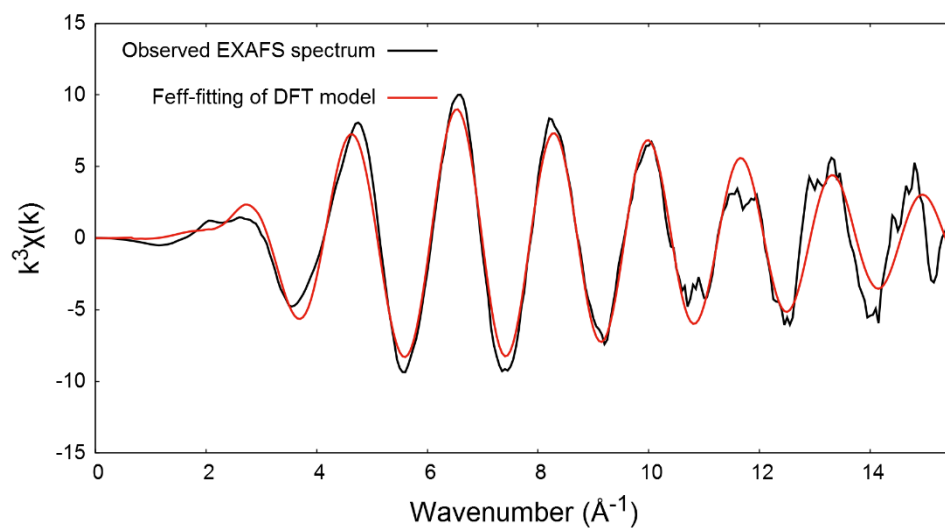
## S1. Investigation of Lewis acid and solvent

Table S1. Effect of Lewis acid and solvent<sup>a</sup>

| entry           | Lewis acid           | solvent | Yield of <b>4aa</b> (%) <sup>b</sup> | e.r. of <b>4aa</b> <sup>c</sup> |
|-----------------|----------------------|---------|--------------------------------------|---------------------------------|
| 1               | FeBr <sub>3</sub>    | toluene | 88                                   | 98:2                            |
| 2               | FeCl <sub>2</sub>    | toluene | <1                                   | —                               |
| 3               | AlCl <sub>3</sub>    | toluene | 21                                   | 97:3                            |
| 4               | Sc(OTf) <sub>3</sub> | toluene | 37                                   | 58:42                           |
| 5               | RuCl <sub>3</sub>    | toluene | <1                                   | —                               |
| 6               | CoCl <sub>2</sub>    | toluene | 21                                   | —                               |
| 7               | NiCl <sub>2</sub>    | toluene | <5                                   | —                               |
| 8               | CuCl <sub>2</sub>    | toluene | <1                                   | —                               |
| 9               | FeBr <sub>3</sub>    | EtOAc   | <1                                   | —                               |
| 10              | FeBr <sub>3</sub>    | acetone | <1                                   | —                               |
| 11 <sup>c</sup> | FeBr <sub>3</sub>    | THF     | <1                                   | —                               |

<sup>a</sup>Reactions were carried out using Lewis acid (1 mol%) and chiral phosphoric acid **3c** (2 mol%), **1a** (0.2 mmol), and **2a** (0.4 mmol) in 1.5 mL of solvent for 6 h under 0 °C. <sup>b</sup>Isolated yield.

<sup>c</sup>Determined by chiral HPLC analysis.

S2. XAS measurement of **CP1**<sup>CPAEt</sup>**Figure S2-1.** Fourier-transformed Fe K-edge EXAFS spectra in R-space.**Figure S2-2.** Fourier-transformed Fe K-edge EXAFS spectra in k-space.

## Structural Parameters Obtained from EXAFS Analysis

| Ab–Sc | R (Å)   | N | $S_0^2$ | $\Delta R$ (Å) | $\Delta E_0$ (eV) | $\Delta\sigma^2$ (Å <sup>2</sup> ) |
|-------|---------|---|---------|----------------|-------------------|------------------------------------|
| Fe–O  | 1.81971 | 2 | 0.541   | –0.06689       | 1.857             | 0.00241                            |
| Fe–O  | 1.96231 | 2 | 0.541   | –0.06689       | 1.857             | 0.00241                            |
| Fe–Cl | 2.13791 | 2 | 0.541   | –0.06689       | 1.857             | 0.00241                            |
| Fe–Cl | 2.18401 | 4 | 0.541   | –0.06689       | 1.857             | 0.00241                            |

$R_{\text{factor}} = 2.0\%$ ,  $\Delta k = 3.0\text{--}14.0$ ,  $\Delta R = 1.0\text{--}2.2$  (*spatial resolution*  $\delta R \geq \pi/2k_{\text{max}} = 0.1122$  Å)

Ab–Sc: X-ray absorbing atom and scattering atom

R (Å): atomic distance

N: coordination number

$S_0^2$ : passive electron reduction factor

*parameter*  $\Delta R$ (Å): change in half-path length

*parameter*  $\Delta E_0$  (eV): edge shift

*parameter*  $\Delta\sigma^2$  (Å<sup>2</sup>): mean squared displacement (Debye–Waller factor)

*The total number of parameters used in the model is less than that given by the Nyquist theorem.*

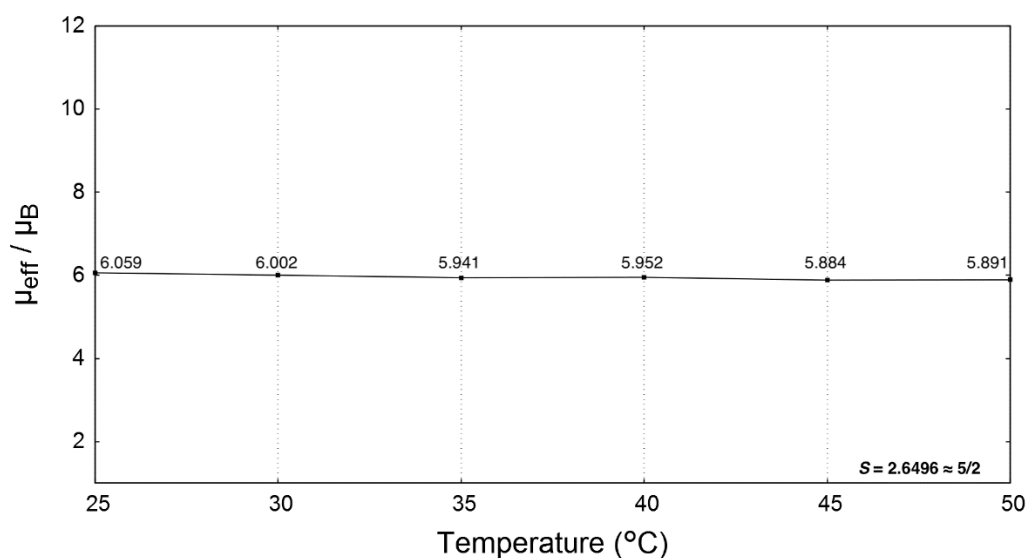
$N_{\text{idp}} \approx 2\Delta k\Delta R/\pi = 8.40 > N_{\text{used}} = 4$  ( $S_0^2$ ,  $\Delta R$ ,  $\Delta E_0$  and  $\Delta\sigma^2$ )

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Rehr, J. J.; Kas, J. J.; Prange, M. P.; Sorini, A. P.; Takimoto, Y.; Vila, F. C. *R. Phys.* **2009**, *10*, 548.

Ravel, B.; Newville, M. *J. Synchrotron Rad.* **2005**, *12*, 537.

Newville, M. *J. Synchrotron Rad.* **2001**, *8*, 322.

**S3.** Measurement of magnetic susceptibility (Evans method)**Figure S3.** Paramagnetic susceptibility measurement.

A solution-state magnetic moment of 5.955  $\mu_{\text{B}}$  was measured by the Evans method (25 – 50 °C), consist with an  $S = 5/2$  ground state for the iron complex **CP1**<sup>CPA</sup>Et with negligible magnetic coupling between two iron atoms. This result indicates that the two iron atoms have a spin state of  $S = 5/2$  with tetrahedral geometry, and are not connected to each other to form halide bridge dimer species. In situ-generated iron complex is  $[\text{FeCl}_2\text{L}_2]^+$  with  $[\text{FeCl}_4]^-$ , but not dimeric species  $(\text{FeCl}_3)_2$  as proposed in different reaction systems.

## references

Evans, D. F. *J. Chem. Phys.* **1959**, 2003.

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#### S4. Computational details for DFT calculation

General Methods. Calculations were performed on Gaussian 09 E.01. For geometry optimization and frequency calculations B3LYP augmented with an empirical dispersion (GD3) was used and M06 was used for single-point energy calculations. Geometry optimization and frequency calculations were carried out using 6-31G(d) (H, C, N, O), 6-31+G(d) (Cl, S, P), 6-31++G(d,p) (acidic proton on chiral phosphoric acid), and f polarization function added Lanl2dz(f) (Fe) basis sets. Single-point calculations were performed with def2-TZVP basis sets. The solvation effects of toluene were incorporated in all calculations using CPCM (toluene). The Monte-Carlo simulated annealing method was initially employed to generate conformers, followed by geometry optimization and thermodynamic calculation to obtain the Boltzmann distribution of these conformers to determine the energetically global minimum conformer.

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#### **S4-1. Reaction energy diagram for enantioselective path and racemic background path.**

The proposed catalytic cycle for the aza-Diels–Alder reaction was analyzed by the energetic span model. In this model, the TOF of the catalytic cycle can be measured with the energetic span  $\delta G$ , which is the difference in the Gibbs energy between the **TDTS** and **TDI**, with the addition of the global Gibbs energy of the reaction when the **TDTS** appears before the **TDI**. **TDTS** and **TDI** are the most unstable and most stable species in the catalytic cycle, respectively. Therefore,  $\delta G$  is the genuine effective barrier of the global reaction in the catalytic cycle, which can be subsequently used to estimate the TOF. The calculated  $\delta G$  values for the enantioselective reaction are summarized in the table below. The enantioselectivity of the present asymmetric reaction can be rationalized with the difference in the TOFs.

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(a) Gibbs energy profile for the cycloaddition of imine **1a** and diene **2c** catalyzed by FeCl<sub>3</sub> ion-pairing complex with chiral phosphoric acid **3d**

Plausible reaction path to yield (*S*)-**4ac** with FeCl<sub>3</sub> and chiral phosphoric acid **3d**

(*exo*-addition of the diene to *si*-face of the imine on CP1<sup>CPAMe</sup>)

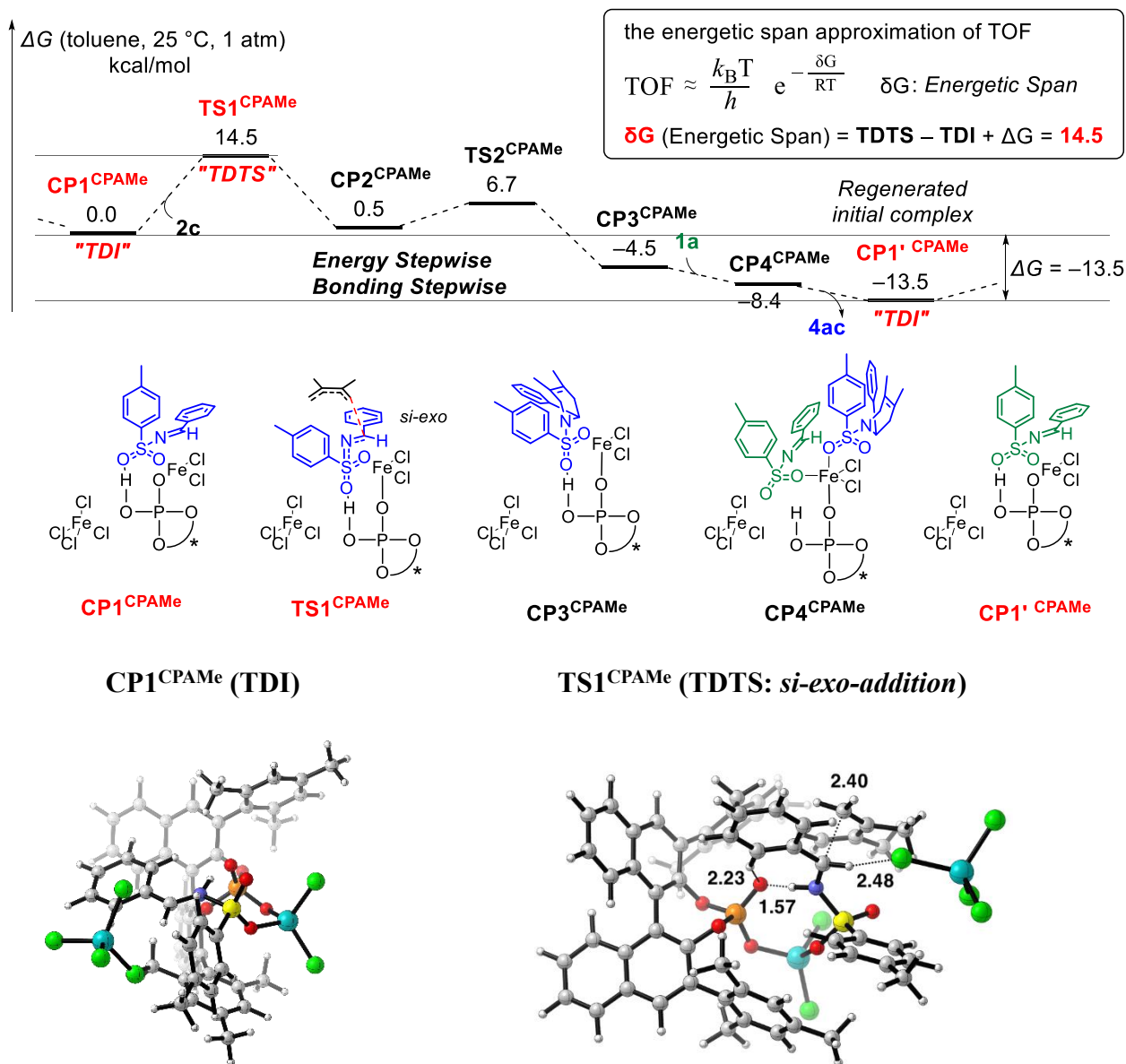
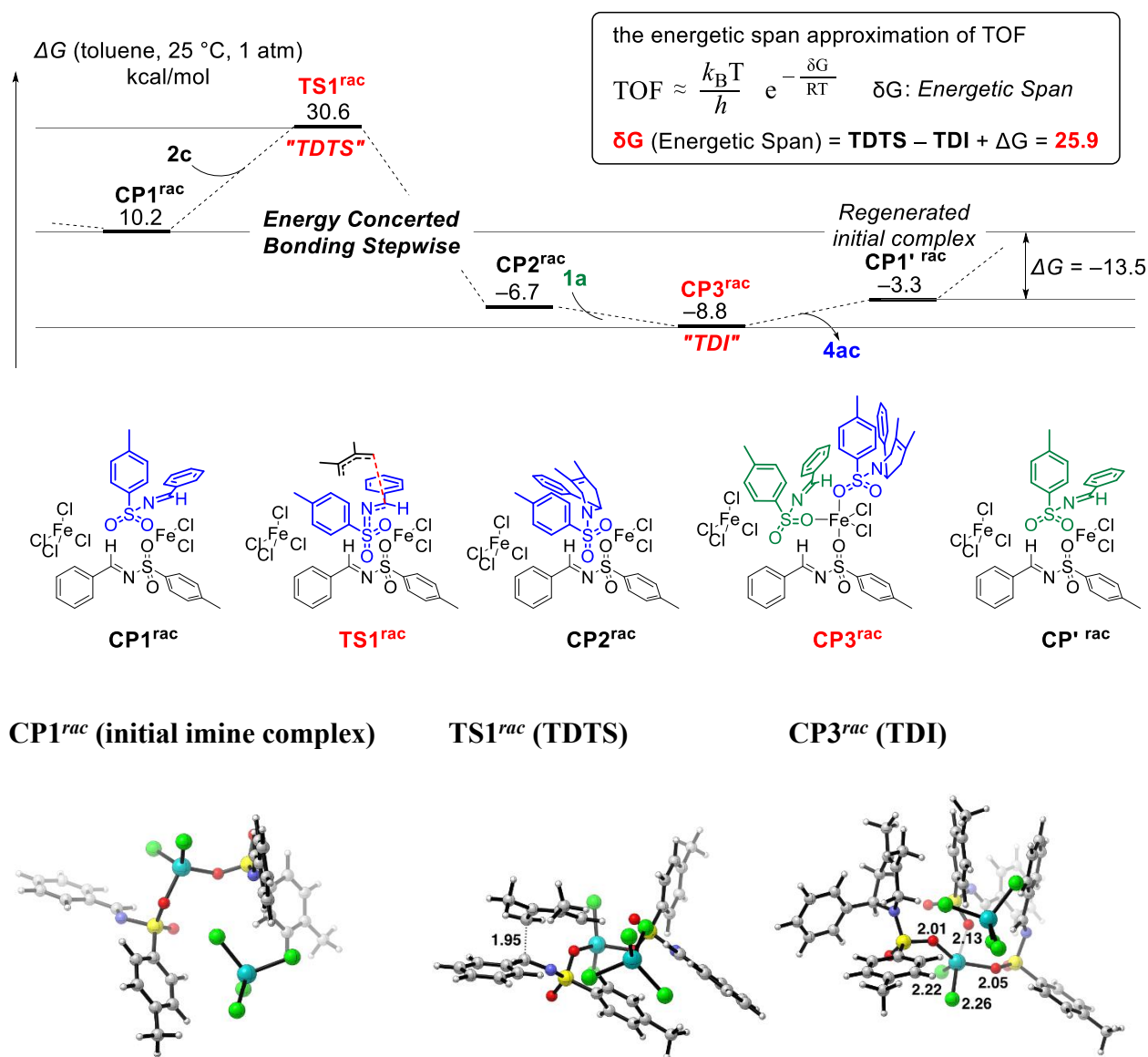


Figure S4-1a. DFT model of CP1<sup>CPAMe</sup> and TS1<sup>CPAMe</sup>.

(b) Gibbs energy profile for the cycloaddition of imine **1a** and diene **2c** catalyzed by FeCl<sub>3</sub> ion-pairing complex

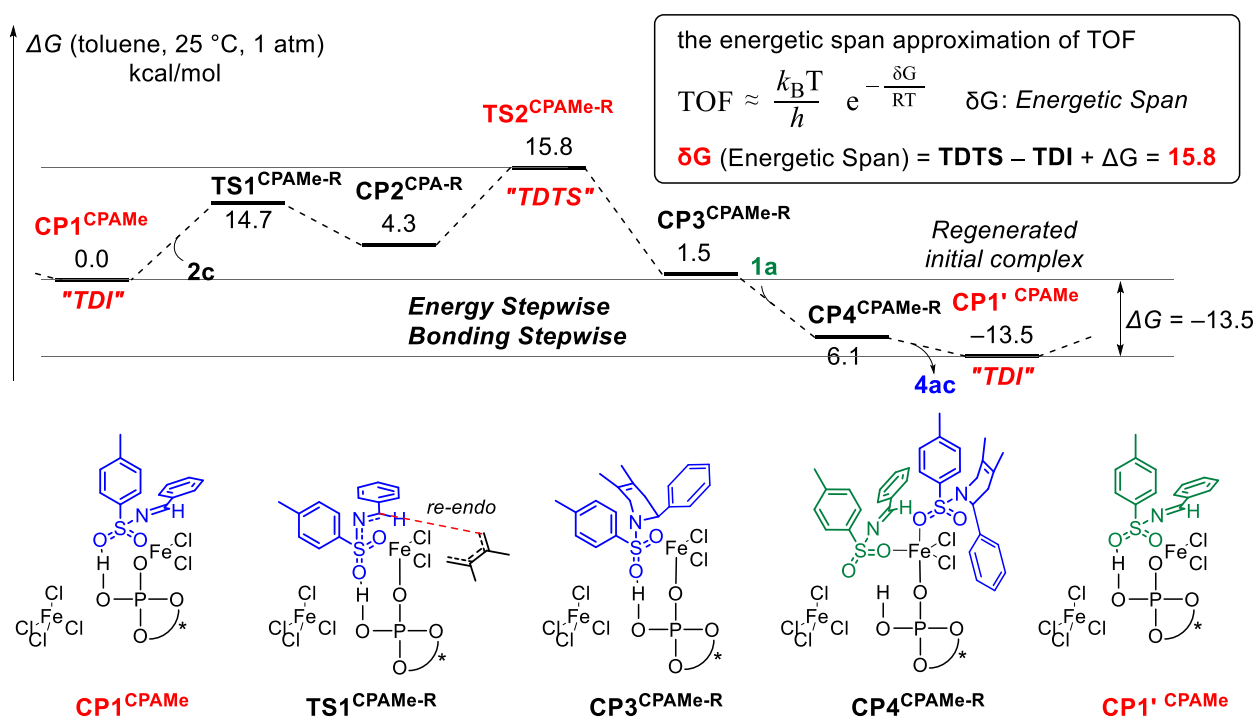
**Plausible competing background reaction path to yield *racemic*-4ac**



**Figure S4-1b.** DFT model of **CP1<sup>rac</sup>**, **TS1<sup>rac</sup>**, and **CP3<sup>rac</sup>**.

(c) Gibbs energy profile for the cycloaddition of imine **1a** and diene **2c** catalyzed by FeCl<sub>3</sub> ion-pairing complex with chiral phosphoric acid **3d**

**Plausible competing reaction path to yield (*R*)-4ac with FeCl<sub>3</sub> and chiral phosphoric acid **3d** (*endo*-addition of the diene to *re*-face of the imine on CP1<sup>CPAMe</sup>)**



TS1<sup>CPAMe-R</sup> (*re-endo*-addition)

TS2<sup>CPAMe-R</sup> (TDTS)

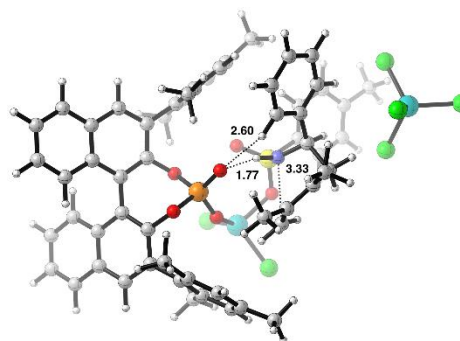
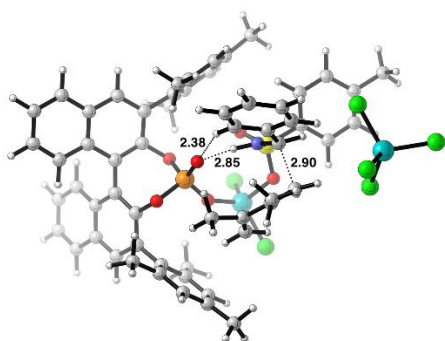


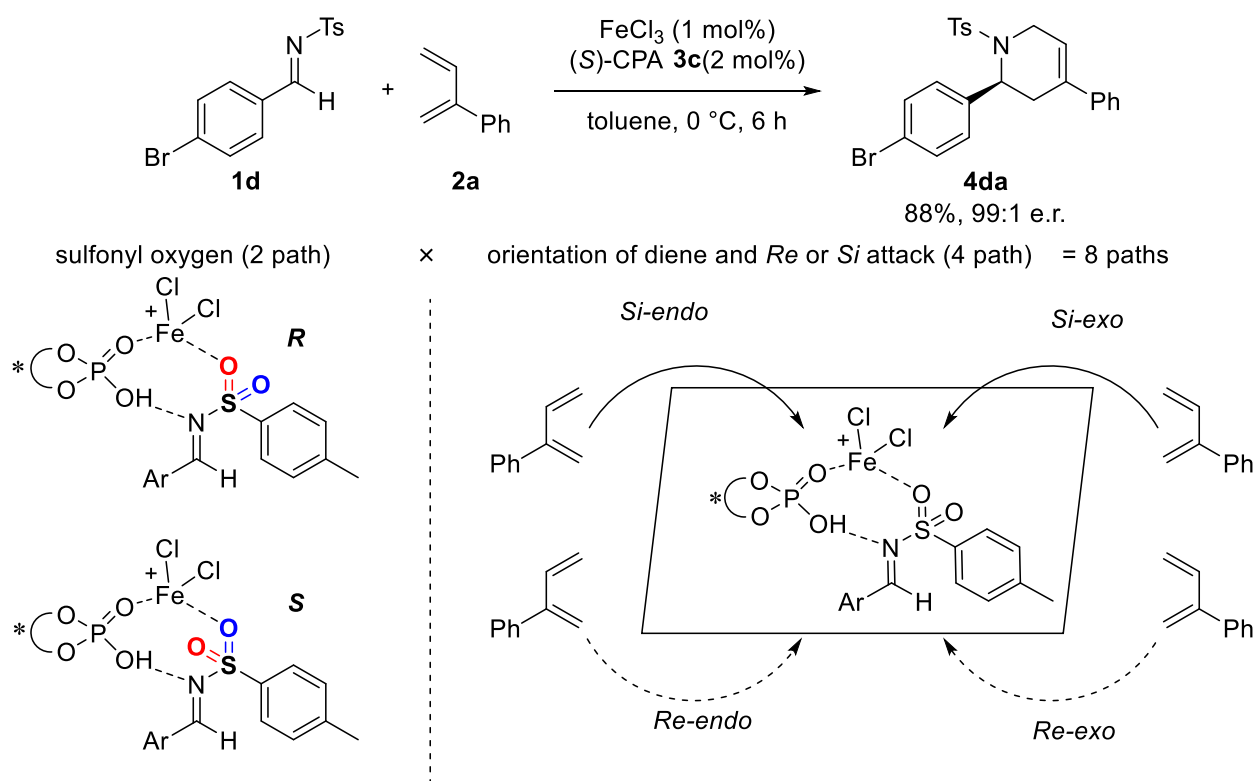
Figure S4-1c. DFT model of TS1<sup>CPAMe-R</sup> and TS2<sup>CPAMe-R</sup>.

## references

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**S4-2.** Calculations to account for enantioselectivity of reaction **1d** and **2a**



**Figure S4-2a.** Considerable eight paths for addition reaction.

| Reaction path     | $\Delta G$ (TS1) <sup>a</sup> | $\Delta G$ (TS2) <sup>a</sup> | $\delta G$ <sup>b</sup> | <i>rel</i> -TOF <sup>c</sup> | Path selectivity | Calculated e.r.   |
|-------------------|-------------------------------|-------------------------------|-------------------------|------------------------------|------------------|-------------------|
| R-Si- <i>exo</i>  | 22.5                          | 16.8                          | 22.5                    | 1.0                          | 62               | 69<br>(S)-product |
| R-Si- <i>endo</i> | 21.9                          | 23.8                          | 23.8                    | $1.1 \times 10^{-1}$         | 7                |                   |
| S-Si- <i>exo</i>  | 35.6                          | 27.0                          | 35.6                    | $2.5 \times 10^{-10}$        | <1               |                   |
| S-Si- <i>endo</i> | 32.2                          | 32.5                          | 32.5                    | $4.7 \times 10^{-8}$         | <1               |                   |
| R-Re- <i>exo</i>  | 24.7                          | 16.8                          | 24.7                    | $2.4 \times 10^{-2}$         | 2                | 31<br>(R)-product |
| R-Re- <i>endo</i> | 19.7                          | 23.0                          | 23.0                    | $4.0 \times 10^{-1}$         | 27               |                   |
| S-Re- <i>exo</i>  | 24.8                          | 22.6                          | 24.8                    | $2.1 \times 10^{-2}$         | <1               |                   |
| S-Re- <i>endo</i> | 24.7                          | 24.2                          | 24.7                    | $2.4 \times 10^{-2}$         | 2                |                   |

**Figure S4-2b.** Energetic spans in several paths. (a) Gibbs free energy (kcal/mol). (b) Energetic span (kcal/mol). (c) Relative turnover frequency normalized to the value for R-Si-*exo*.

Energetic spans were estimated for considerable eight paths of the reaction of **1d** and **2a** as shown in Figure S4-2a, and the results were summarized in S4-2b. Calculated selectivity was 69:31 e.r. as (*S*)-product was major isomer. This result was consistent with the fact that the obtained isomer was (*S*)-product, although the calculated enantioselectivity was not good enough compared to experimentally observed.

## Chapter 4

Cartesian Coordinates for **CPI<sup>CPAME</sup>**

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 6.246350000000  | 1.352339000000  | 3.939250000000  | C  | -2.303506000000 | 3.891375000000  | -2.181917000000 |
| C | 6.389109000000  | 0.491665000000  | 2.874265000000  | C  | -2.666517000000 | 3.432816000000  | 0.148820000000  |
| C | 5.695029000000  | 0.717965000000  | 1.653977000000  | C  | -3.187718000000 | 3.596160000000  | -1.138455000000 |
| C | 4.861079000000  | 1.877669000000  | 1.528953000000  | Fe | -0.455299000000 | 0.421803000000  | -3.549661000000 |
| C | 4.731032000000  | 2.742195000000  | 2.650361000000  | Cl | -1.663800000000 | 1.680376000000  | -4.893232000000 |
| C | 5.402281000000  | 2.483266000000  | 3.825286000000  | Cl | -0.025408000000 | -1.544366000000 | -4.441587000000 |
| H | 6.431712000000  | -1.071535000000 | 0.685820000000  | N  | -0.625877000000 | -0.700047000000 | 0.328702000000  |
| H | 6.772413000000  | 1.161962000000  | 4.870171000000  | C  | -0.910112000000 | -0.266259000000 | 1.531936000000  |
| H | 7.022829000000  | -0.387667000000 | 2.955514000000  | S  | -1.761145000000 | -1.096552000000 | -0.931815000000 |
| C | 5.778763000000  | -0.209435000000 | 0.582936000000  | H  | -1.961933000000 | -0.139334000000 | 1.781453000000  |
| C | 4.130452000000  | 2.074971000000  | 0.308720000000  | O  | -1.568169000000 | 0.045117000000  | -1.897049000000 |
| H | 4.076596000000  | 3.603161000000  | 2.582166000000  | O  | -1.402787000000 | -2.440668000000 | -1.348145000000 |
| H | 5.278162000000  | 3.149917000000  | 4.673828000000  | C  | 0.069649000000  | 0.060029000000  | 2.522389000000  |
| C | 4.195133000000  | 1.077871000000  | -0.647346000000 | C  | -0.408522000000 | 0.562966000000  | 3.755221000000  |
| C | 5.022395000000  | -0.072194000000 | -0.561932000000 | C  | 1.463699000000  | -0.092758000000 | 2.320222000000  |
| C | 3.266793000000  | 3.268096000000  | 0.082574000000  | C  | 0.485341000000  | 0.922554000000  | 4.754592000000  |
| C | 3.791885000000  | 4.604362000000  | 0.115124000000  | H  | -1.473651000000 | 0.665357000000  | 3.920477000000  |
| C | 1.921985000000  | 3.106160000000  | -0.205086000000 | C  | 2.345583000000  | 0.259788000000  | 3.328672000000  |
| C | 5.177928000000  | 4.884943000000  | 0.268300000000  | H  | 1.850303000000  | -0.475566000000 | 1.384103000000  |
| C | 2.888601000000  | 5.706736000000  | -0.042343000000 | C  | 1.859011000000  | 0.773974000000  | 4.540175000000  |
| C | 1.009868000000  | 4.176546000000  | -0.374109000000 | H  | 0.110388000000  | 1.308759000000  | 5.696598000000  |
| C | 5.637813000000  | 6.182929000000  | 0.299596000000  | H  | 3.412631000000  | 0.142124000000  | 3.179682000000  |
| H | 5.879480000000  | 4.063154000000  | 0.354167000000  | H  | 2.562260000000  | 1.055719000000  | 5.318267000000  |
| C | 3.395224000000  | 7.033848000000  | 0.007469000000  | C  | -3.384157000000 | -0.973641000000 | -0.295600000000 |
| C | 1.510584000000  | 5.456750000000  | -0.265832000000 | C  | -4.181723000000 | 0.117112000000  | -0.664126000000 |
| C | 4.739602000000  | 7.270588000000  | 0.179640000000  | C  | -3.865395000000 | -2.031149000000 | 0.490705000000  |
| H | 6.701205000000  | 6.373754000000  | 0.412420000000  | C  | -5.500480000000 | 0.130807000000  | -0.231164000000 |
| H | 2.697806000000  | 7.860133000000  | -0.103971000000 | H  | -3.774521000000 | 0.919657000000  | -1.265194000000 |
| H | 0.833617000000  | 6.299648000000  | -0.376944000000 | C  | -5.181171000000 | -1.970521000000 | 0.927763000000  |
| H | 5.116461000000  | 8.288723000000  | 0.211876000000  | H  | -3.231756000000 | -2.868233000000 | 0.760449000000  |
| P | 1.824621000000  | 0.814946000000  | -1.494907000000 | C  | -6.015854000000 | -0.895670000000 | 0.576046000000  |
| O | 1.394703000000  | 1.808423000000  | -0.286489000000 | H  | -6.139151000000 | 0.961489000000  | -0.512598000000 |
| O | 3.363353000000  | 1.190691000000  | -1.784005000000 | H  | -5.563480000000 | -2.760964000000 | 1.564797000000  |
| O | 1.594207000000  | -0.585987000000 | -0.996017000000 | C  | -7.422723000000 | -0.821913000000 | 1.100547000000  |
| H | 0.365351000000  | -0.742744000000 | -0.090176000000 | H  | -8.056559000000 | -0.190808000000 | 0.471020000000  |
| O | 1.073426000000  | 1.221144000000  | -2.790666000000 | H  | -7.874725000000 | -1.815234000000 | 1.178887000000  |
| C | 5.032469000000  | -1.079857000000 | -1.662386000000 | H  | -7.408194000000 | -0.394519000000 | 2.111107000000  |
| C | 5.564529000000  | -0.734034000000 | -2.922025000000 | Fe | -4.051318000000 | -0.671449000000 | 4.290259000000  |
| C | 4.488175000000  | -2.363852000000 | -1.449389000000 | Cl | -4.014592000000 | 1.024075000000  | 2.792968000000  |
| C | 5.529789000000  | -1.675969000000 | -3.954111000000 | Cl | -2.536148000000 | -2.233480000000 | 3.672585000000  |
| C | 4.466594000000  | -3.271283000000 | -2.513356000000 | Cl | -6.080272000000 | -1.605018000000 | 4.420095000000  |
| C | 4.972987000000  | -2.945786000000 | -3.775100000000 | Cl | -3.349744000000 | 0.211191000000  | 6.229377000000  |
| C | -0.436356000000 | 3.925269000000  | -0.649328000000 | H  | 4.037249000000  | -4.258067000000 | -2.352847000000 |
| C | -0.933483000000 | 4.062938000000  | -1.961202000000 | H  | 5.947170000000  | -1.410046000000 | -4.923237000000 |
| C | -1.301168000000 | 3.598564000000  | 0.412220000000  | H  | -3.336149000000 | 3.193010000000  | 0.971470000000  |
|   |                 |                 |                 | H  | -2.690210000000 | 4.002108000000  | -3.191910000000 |

|   |                 |                |                 |   |                |                 |                 |
|---|-----------------|----------------|-----------------|---|----------------|-----------------|-----------------|
| C | -4.673738000000 | 3.502853000000 | -1.399316000000 | H | 5.391741000000 | 1.399026000000  | -3.245668000000 |
| H | -4.898355000000 | 2.832570000000 | -2.238484000000 | C | 4.897045000000 | -3.930055000000 | -4.918488000000 |
| H | -5.212876000000 | 3.145613000000 | -0.516636000000 | H | 5.697336000000 | -3.761973000000 | -5.646988000000 |
| H | -5.085702000000 | 4.485211000000 | -1.661550000000 | H | 4.967991000000 | -4.963886000000 | -4.563734000000 |
| C | -0.779773000000 | 3.486351000000 | 1.826379000000  | H | 3.942836000000 | -3.834648000000 | -5.453370000000 |
| H | 0.073083000000  | 2.803621000000 | 1.892635000000  | C | 3.919767000000 | -2.774164000000 | -0.109069000000 |
| H | -0.433208000000 | 4.459971000000 | 2.195060000000  | H | 3.377782000000 | -3.721061000000 | -0.192024000000 |
| H | -1.557071000000 | 3.123958000000 | 2.505428000000  | H | 4.704830000000 | -2.905534000000 | 0.645011000000  |
| C | -0.013092000000 | 4.407857000000 | -3.110053000000 | H | 3.225416000000 | -2.019500000000 | 0.269580000000  |
| H | -0.559966000000 | 4.424519000000 | -4.056338000000 | H | 6.840778000000 | 0.928176000000  | -2.356953000000 |
| H | 0.456639000000  | 5.387674000000 | -2.966282000000 | H | 6.739615000000 | 0.641068000000  | -4.103597000000 |
| H | 0.794200000000  | 3.673403000000 | -3.202091000000 | C | 6.169391000000 | 0.629536000000  | -3.169915000000 |

Cartesian Coordinates for **TS1**<sup>CPAME</sup>

|   |                 |                 |                 |    |                  |                 |                 |
|---|-----------------|-----------------|-----------------|----|------------------|-----------------|-----------------|
| C | -2.639125000000 | 0.566861000000  | 1.650469000000  | O  | -5.796321000000  | -0.756076000000 | -3.784423000000 |
| C | -2.535443000000 | -0.485851000000 | 0.770669000000  | O  | -7.583944000000  | -2.432116000000 | -2.870494000000 |
| C | -3.332980000000 | -0.535587000000 | -0.405368000000 | H  | -8.979777000000  | -2.885151000000 | -2.308756000000 |
| C | -4.229474000000 | 0.546302000000  | -0.691073000000 | O  | -8.081926000000  | -0.765551000000 | -4.801140000000 |
| C | -4.329582000000 | 1.606142000000  | 0.252613000000  | C  | -4.152037000000  | -2.999420000000 | -3.211280000000 |
| C | -3.556126000000 | 1.614315000000  | 1.392515000000  | C  | -3.707310000000  | -2.974168000000 | -4.547832000000 |
| H | -2.603581000000 | -2.468514000000 | -1.043174000000 | C  | -4.663872000000  | -4.193270000000 | -2.656405000000 |
| H | -2.029523000000 | 0.591354000000  | 2.549109000000  | C  | -3.800381000000  | -4.140504000000 | -5.316251000000 |
| H | -1.850556000000 | -1.306538000000 | 0.968284000000  | C  | -4.731348000000  | -5.335196000000 | -3.457889000000 |
| C | -3.285045000000 | -1.654516000000 | -1.274699000000 | C  | -4.315184000000  | -5.329113000000 | -4.793508000000 |
| C | -5.016087000000 | 0.494122000000  | -1.891843000000 | C  | -9.664268000000  | 1.948857000000  | -3.022466000000 |
| H | -5.029908000000 | 2.413055000000  | 0.071016000000  | C  | -10.198251000000 | 1.890473000000  | -4.325256000000 |
| H | -3.652839000000 | 2.431369000000  | 2.101800000000  | C  | -10.469171000000 | 1.642133000000  | -1.908216000000 |
| C | -4.957820000000 | -0.660005000000 | -2.654721000000 | C  | -11.528641000000 | 1.485826000000  | -4.491036000000 |
| C | -4.109224000000 | -1.763328000000 | -2.375989000000 | C  | -11.804118000000 | 1.286003000000  | -2.117419000000 |
| C | -5.928657000000 | 1.602572000000  | -2.291413000000 | C  | -12.346013000000 | 1.172475000000  | -3.401402000000 |
| C | -5.462740000000 | 2.943425000000  | -2.511527000000 | Fe | -9.555931000000  | -1.686851000000 | -5.540404000000 |
| C | -7.272470000000 | 1.343554000000  | -2.499530000000 | Cl | -10.634390000000 | -0.680059000000 | -7.181992000000 |
| C | -4.086213000000 | 3.298724000000  | -2.468294000000 | Cl | -8.920639000000  | -3.688173000000 | -6.227795000000 |
| C | -6.419110000000 | 3.966222000000  | -2.822162000000 | N  | -9.903018000000  | -3.279676000000 | -1.962978000000 |
| C | -8.235922000000 | 2.330850000000  | -2.823192000000 | C  | -10.073430000000 | -3.817109000000 | -0.736775000000 |
| C | -3.683307000000 | 4.598320000000  | -2.683118000000 | S  | -11.158473000000 | -3.150888000000 | -3.098750000000 |
| H | -3.346716000000 | 2.531316000000  | -2.270543000000 | H  | -11.056042000000 | -4.227349000000 | -0.526563000000 |
| C | -5.970235000000 | 5.299789000000  | -3.023718000000 | O  | -10.668792000000 | -1.957377000000 | -3.898907000000 |
| C | -7.791097000000 | 3.629437000000  | -2.950704000000 | O  | -11.424093000000 | -4.375667000000 | -3.836361000000 |
| C | -4.632551000000 | 5.613601000000  | -2.951859000000 | C  | -9.287803000000  | -3.358025000000 | 0.403456000000  |
| H | -2.626043000000 | 4.845571000000  | -2.651084000000 | C  | -8.213351000000  | -2.452790000000 | 0.277898000000  |
| H | -6.707054000000 | 6.066524000000  | -3.249186000000 | C  | -9.678233000000  | -3.796490000000 | 1.686815000000  |
| H | -8.505980000000 | 4.414169000000  | -3.183353000000 | C  | -7.540895000000  | -2.010991000000 | 1.412362000000  |
| H | -4.300465000000 | 6.635018000000  | -3.113579000000 | H  | -7.908743000000  | -2.083220000000 | -0.691711000000 |
| P | -7.345748000000 | -1.079193000000 | -3.470006000000 | C  | -9.001772000000  | -3.345719000000 | 2.814312000000  |
| O | -7.740216000000 | 0.027790000000  | -2.351219000000 | H  | -10.514941000000 | -4.481256000000 | 1.789850000000  |
|   |                 |                 |                 | C  | -7.928442000000  | -2.457844000000 | 2.680014000000  |

## Chapter 4

|                                                |                  |                 |                 |   |                  |                 |                 |
|------------------------------------------------|------------------|-----------------|-----------------|---|------------------|-----------------|-----------------|
| C                                              | -16.005330000000 | -1.639697000000 | 0.177234000000  | H | -6.715671000000  | -1.312887000000 | 1.304268000000  |
| H                                              | -15.860893000000 | -0.719461000000 | 0.750538000000  | H | -9.311982000000  | -3.683622000000 | 3.798129000000  |
| H                                              | -16.900219000000 | -1.531907000000 | -0.444054000000 | H | -7.400545000000  | -2.109006000000 | 3.562703000000  |
| H                                              | -16.200957000000 | -2.458793000000 | 0.880116000000  | C | -12.556435000000 | -2.669254000000 | -2.143645000000 |
| Fe                                             | -14.791297000000 | -6.347707000000 | -0.203180000000 | C | -12.417927000000 | -1.734972000000 | -1.111342000000 |
| Cl                                             | -13.016624000000 | -5.206485000000 | 0.649888000000  | C | -13.786219000000 | -3.253054000000 | -2.462632000000 |
| Cl                                             | -14.636917000000 | -6.564625000000 | -2.444466000000 | C | -13.547567000000 | -1.400435000000 | -0.375654000000 |
| Cl                                             | -16.685667000000 | -5.273450000000 | 0.364165000000  | H | -11.459144000000 | -1.282106000000 | -0.887472000000 |
| Cl                                             | -14.812981000000 | -8.420856000000 | 0.658317000000  | C | -14.899988000000 | -2.892410000000 | -1.713458000000 |
| H                                              | -5.139425000000  | -6.251092000000 | -3.035126000000 | H | -13.863136000000 | -3.992198000000 | -3.249742000000 |
| H                                              | -3.459838000000  | -4.117292000000 | -6.349350000000 | C | -14.799346000000 | -1.971629000000 | -0.658647000000 |
| H                                              | -12.435985000000 | 1.083418000000  | -1.256950000000 | H | -13.455656000000 | -0.684274000000 | 0.435560000000  |
| H                                              | -11.932708000000 | 1.413283000000  | -5.497204000000 | H | -15.854102000000 | -3.361561000000 | -1.929309000000 |
| C                                              | -13.760523000000 | 0.683059000000  | -3.600990000000 | C | -9.238752000000  | -6.002551000000 | -0.719087000000 |
| H                                              | -14.417017000000 | 1.002876000000  | -2.784802000000 | H | -8.212513000000  | -5.663924000000 | -0.640474000000 |
| H                                              | -14.183299000000 | 1.042630000000  | -4.544722000000 | H | -9.730763000000  | -6.248067000000 | 0.215582000000  |
| H                                              | -13.789029000000 | -0.414532000000 | -3.624711000000 | C | -9.634453000000  | -6.996606000000 | -4.405188000000 |
| C                                              | -9.905409000000  | 1.677249000000  | -0.505984000000 | H | -9.628105000000  | -8.083749000000 | -4.261649000000 |
| H                                              | -9.211659000000  | 0.842127000000  | -0.343415000000 | H | -9.037828000000  | -6.763680000000 | -5.290597000000 |
| H                                              | -9.345159000000  | 2.599301000000  | -0.315064000000 | H | -10.667393000000 | -6.697615000000 | -4.608322000000 |
| H                                              | -10.701434000000 | 1.600319000000  | 0.241341000000  | H | -5.639631000000  | -5.221461000000 | -1.028289000000 |
| C                                              | -9.356037000000  | 2.245740000000  | -5.530002000000 | H | -4.380168000000  | -4.105109000000 | -0.497278000000 |
| H                                              | -9.915996000000  | 2.092923000000  | -6.455565000000 | H | -5.924477000000  | -3.471041000000 | -1.056878000000 |
| H                                              | -9.028023000000  | 3.290677000000  | -5.496545000000 | C | -8.035802000000  | -5.439549000000 | -3.316381000000 |
| H                                              | -8.454326000000  | 1.625372000000  | -5.575441000000 | H | -7.564302000000  | -5.265933000000 | -4.275953000000 |
| C                                              | -3.137504000000  | -1.715470000000 | -5.161370000000 | H | -7.609537000000  | -4.884462000000 | -2.492977000000 |
| H                                              | -2.441224000000  | -1.214808000000 | -4.479406000000 | C | -9.088839000000  | -6.278024000000 | -3.192861000000 |
| H                                              | -2.603626000000  | -1.938725000000 | -6.089915000000 | C | -9.762088000000  | -6.470275000000 | -1.901253000000 |
| H                                              | -3.931856000000  | -0.997401000000 | -5.396238000000 | C | -11.102679000000 | -7.145600000000 | -1.896236000000 |
| C                                              | -4.407269000000  | -6.583022000000 | -5.630735000000 | H | -11.811508000000 | -6.614174000000 | -2.540355000000 |
| H                                              | -3.621605000000  | -7.299958000000 | -5.358639000000 | H | -11.532802000000 | -7.202388000000 | -0.894999000000 |
| H                                              | -5.368845000000  | -7.088190000000 | -5.482502000000 | H | -11.021442000000 | -8.162570000000 | -2.300033000000 |
| H                                              | -4.299769000000  | -6.363001000000 | -6.697518000000 | C | -5.177270000000  | -4.250585000000 | -1.234316000000 |
| Cartesian Coordinates for CP2 <sup>CPAMe</sup> |                  |                 |                 | O | -1.767930000000  | 0.321702000000  | -1.647683000000 |
| C                                              | 7.537773000000   | 2.833707000000  | 3.281756000000  | O | -2.064130000000  | -2.181961000000 | -1.502747000000 |
| C                                              | 7.423634000000   | 1.730533000000  | 2.468197000000  | C | -0.495366000000  | -0.964973000000 | 2.784630000000  |
| C                                              | 6.414751000000   | 1.662465000000  | 1.468631000000  | C | 0.602583000000   | -0.095419000000 | 2.857895000000  |
| C                                              | 5.531106000000   | 2.776319000000  | 1.282076000000  | C | -1.316697000000  | -1.132774000000 | 3.904766000000  |
| C                                              | 5.656187000000   | 3.885296000000  | 2.164700000000  | C | 0.869928000000   | 0.596786000000  | 4.038617000000  |
| C                                              | 6.632622000000   | 3.912357000000  | 3.135791000000  | H | 1.237672000000   | 0.060169000000  | 1.992271000000  |
| H                                              | 6.889342000000   | -0.360668000000 | 0.872145000000  | C | -1.045558000000  | -0.437391000000 | 5.086230000000  |
| H                                              | 8.308292000000   | 2.873639000000  | 4.046211000000  | H | -2.172240000000  | -1.799996000000 | 3.852706000000  |
| H                                              | 8.094426000000   | 0.883397000000  | 2.586884000000  | C | 0.046782000000   | 0.428457000000  | 5.155851000000  |
| C                                              | 6.234635000000   | 0.488594000000  | 0.695680000000  | H | 1.719834000000   | 1.272442000000  | 4.082069000000  |
| C                                              | 4.538492000000   | 2.709295000000  | 0.244010000000  | H | -1.693259000000  | -0.572002000000 | 5.947938000000  |

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H  | 4.968512000000  | 4.717284000000  | 2.072873000000  | H  | 0.255432000000  | 0.971336000000  | 6.073461000000  |
| H  | 6.705730000000  | 4.769144000000  | 3.799514000000  | C  | -3.576807000000 | -0.669585000000 | 0.058758000000  |
| C  | 4.410700000000  | 1.516834000000  | -0.452497000000 | C  | -3.630785000000 | 0.099609000000  | 1.224298000000  |
| C  | 5.219357000000  | 0.371862000000  | -0.231060000000 | C  | -4.709793000000 | -1.290670000000 | -0.476933000000 |
| C  | 3.604774000000  | 3.839973000000  | -0.032210000000 | C  | -4.853720000000 | 0.220917000000  | 1.876135000000  |
| C  | 4.058453000000  | 5.163466000000  | -0.358638000000 | H  | -2.738859000000 | 0.571709000000  | 1.618320000000  |
| C  | 2.237529000000  | 3.619044000000  | -0.004634000000 | C  | -5.919454000000 | -1.141635000000 | 0.187902000000  |
| C  | 5.428091000000  | 5.479572000000  | -0.574754000000 | H  | -4.635659000000 | -1.906792000000 | -1.364511000000 |
| C  | 3.088034000000  | 6.209549000000  | -0.506802000000 | C  | -6.008143000000 | -0.401605000000 | 1.378666000000  |
| C  | 1.253526000000  | 4.620444000000  | -0.205964000000 | H  | -4.907059000000 | 0.796923000000  | 2.795497000000  |
| C  | 5.819604000000  | 6.765333000000  | -0.876407000000 | H  | -6.800659000000 | -1.643074000000 | -0.197727000000 |
| H  | 6.170246000000  | 4.692457000000  | -0.506186000000 | C  | -7.315720000000 | -0.330944000000 | 2.121342000000  |
| C  | 3.528603000000  | 7.528947000000  | -0.800687000000 | H  | -7.280761000000 | 0.392327000000  | 2.940991000000  |
| C  | 1.705331000000  | 5.907437000000  | -0.408958000000 | H  | -8.137992000000 | -0.059320000000 | 1.450166000000  |
| C  | 4.864772000000  | 7.805557000000  | -0.977299000000 | H  | -7.554367000000 | -1.317353000000 | 2.538355000000  |
| H  | 6.870853000000  | 6.982072000000  | -1.043481000000 | Fe | -5.303062000000 | -4.749064000000 | 1.232817000000  |
| H  | 2.783681000000  | 8.314383000000  | -0.899822000000 | Cl | -4.020551000000 | -3.389163000000 | 2.521883000000  |
| H  | 0.983207000000  | 6.707526000000  | -0.546907000000 | Cl | -4.584399000000 | -4.735295000000 | -0.910752000000 |
| H  | 5.188635000000  | 8.816079000000  | -1.209041000000 | Cl | -7.448340000000 | -4.100464000000 | 1.348079000000  |
| P  | 1.900699000000  | 1.214572000000  | -0.918023000000 | Cl | -5.091261000000 | -6.847309000000 | 2.000803000000  |
| O  | 1.770698000000  | 2.321428000000  | 0.252683000000  | H  | 3.853952000000  | -4.074454000000 | -0.183464000000 |
| O  | 3.416672000000  | 1.417037000000  | -1.443893000000 | H  | 5.174148000000  | -2.476237000000 | -3.937419000000 |
| O  | 1.629564000000  | -0.127663000000 | -0.310376000000 | H  | -2.770429000000 | 3.072659000000  | 1.594365000000  |
| H  | -0.011600000000 | -0.390185000000 | 0.044908000000  | H  | -2.646304000000 | 3.876441000000  | -2.612888000000 |
| O  | 1.020717000000  | 1.631465000000  | -2.125473000000 | C  | -4.294959000000 | 2.921737000000  | -0.681677000000 |
| C  | 4.945639000000  | -0.932025000000 | -0.909520000000 | H  | -4.794457000000 | 2.811489000000  | 0.285121000000  |
| C  | 5.205706000000  | -1.102382000000 | -2.287216000000 | H  | -4.885670000000 | 3.607637000000  | -1.299549000000 |
| C  | 4.439481000000  | -2.004201000000 | -0.148931000000 | H  | -4.314917000000 | 1.941033000000  | -1.173654000000 |
| C  | 4.968076000000  | -2.348701000000 | -2.876933000000 | C  | -0.231554000000 | 3.755381000000  | 2.209070000000  |
| C  | 4.220858000000  | -3.240171000000 | -0.777398000000 | H  | 0.431481000000  | 2.886846000000  | 2.289748000000  |
| C  | 4.489791000000  | -3.435495000000 | -2.139303000000 | H  | 0.376138000000  | 4.647708000000  | 2.395522000000  |
| C  | -0.189737000000 | 4.244614000000  | -0.287421000000 | H  | -0.976309000000 | 3.674701000000  | 3.006938000000  |
| C  | -0.831096000000 | 4.285764000000  | -1.546110000000 | C  | -0.100785000000 | 4.743389000000  | -2.789387000000 |
| C  | -0.892041000000 | 3.804567000000  | 0.850663000000  | H  | -0.725351000000 | 4.609877000000  | -3.675553000000 |
| C  | -2.159986000000 | 3.863832000000  | -1.640681000000 | H  | 1.688514000000  | -2.085982000000 | -0.953415000000 |
| C  | -2.225761000000 | 3.398251000000  | 0.710608000000  | C  | 0.509627000000  | -3.916694000000 | -1.090413000000 |
| C  | -2.873899000000 | 3.407496000000  | -0.526711000000 | C  | -0.100277000000 | -3.798247000000 | 0.181931000000  |
| Fe | -0.424664000000 | 0.785283000000  | -2.983348000000 | C  | -1.205773000000 | -4.715415000000 | 0.543976000000  |
| Cl | -1.408888000000 | 1.931571000000  | -4.601587000000 | H  | -2.064050000000 | -4.526836000000 | -0.121203000000 |
| Cl | 0.403298000000  | -1.098012000000 | -3.862265000000 | H  | -1.545095000000 | -4.600765000000 | 1.573373000000  |
| N  | -0.915207000000 | -0.761707000000 | 0.391854000000  | H  | -0.925402000000 | -5.760801000000 | 0.361819000000  |
| C  | -0.809226000000 | -1.723158000000 | 1.503938000000  | C  | 0.297138000000  | -2.796988000000 | 1.213817000000  |
| S  | -2.043788000000 | -0.911356000000 | -0.773514000000 | H  | 1.229651000000  | -2.281410000000 | 0.991043000000  |
| H  | -1.775875000000 | -2.218169000000 | 1.619666000000  | H  | 0.438502000000  | -3.349559000000 | 2.151272000000  |
| H  | 0.184947000000  | 5.799144000000  | -2.730961000000 | C  | 0.084568000000  | -5.024713000000 | -2.028356000000 |
| H  | 0.819526000000  | 4.167170000000  | -2.936254000000 | H  | 0.242719000000  | -6.015285000000 | -1.587827000000 |

## Chapter 4

|                                    |                 |                 |                 |    |                 |                 |                 |
|------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C                                  | 5.740273000000  | 0.037410000000  | -3.120622000000 | H  | 0.644984000000  | -4.975409000000 | -2.964543000000 |
| H                                  | 6.583188000000  | 0.531986000000  | -2.625020000000 | H  | -0.981150000000 | -4.934084000000 | -2.266575000000 |
| H                                  | 6.075167000000  | -0.312702000000 | -4.101165000000 | H  | 3.626499000000  | -5.422645000000 | -2.189321000000 |
| H                                  | 4.968012000000  | 0.799051000000  | -3.278016000000 | H  | 3.840672000000  | -4.681146000000 | -3.787642000000 |
| C                                  | 4.281451000000  | -4.782621000000 | -2.789488000000 | C  | 4.096185000000  | -1.843800000000 | 1.315230000000  |
| H                                  | 5.235951000000  | -5.310362000000 | -2.911336000000 | H  | 3.586231000000  | -2.734356000000 | 1.695714000000  |
| H                                  | 3.440047000000  | -0.980660000000 | 1.467856000000  | H  | 4.986897000000  | -1.684051000000 | 1.932032000000  |
| C                                  | 1.419456000000  | -2.972283000000 | -1.511468000000 | H  | 1.849955000000  | -3.043177000000 | -2.501469000000 |
| Cartesian Coordinates for CP2CPAMe |                 |                 |                 | O  | 1.020717000000  | 1.631465000000  | -2.125473000000 |
| C                                  | 7.537773000000  | 2.833707000000  | 3.281756000000  | C  | 4.945639000000  | -0.932025000000 | -0.909520000000 |
| C                                  | 7.423634000000  | 1.730533000000  | 2.468197000000  | C  | 5.205706000000  | -1.102382000000 | -2.287216000000 |
| C                                  | 6.414751000000  | 1.662465000000  | 1.468631000000  | C  | 4.439481000000  | -2.004201000000 | -0.148931000000 |
| C                                  | 5.531106000000  | 2.776319000000  | 1.282076000000  | C  | 4.968076000000  | -2.348701000000 | -2.876933000000 |
| C                                  | 5.656187000000  | 3.885296000000  | 2.164700000000  | C  | 4.220858000000  | -3.240171000000 | -0.777398000000 |
| C                                  | 6.632622000000  | 3.912357000000  | 3.135791000000  | C  | 4.489791000000  | -3.435495000000 | -2.139303000000 |
| H                                  | 6.889342000000  | -0.360668000000 | 0.872145000000  | C  | -0.189737000000 | 4.244614000000  | -0.287421000000 |
| H                                  | 8.308292000000  | 2.873639000000  | 4.046211000000  | C  | -0.831096000000 | 4.285764000000  | -1.546110000000 |
| H                                  | 8.094426000000  | 0.883397000000  | 2.586884000000  | C  | -0.892041000000 | 3.804567000000  | 0.850663000000  |
| C                                  | 6.234635000000  | 0.488594000000  | 0.695680000000  | C  | -2.159986000000 | 3.863832000000  | -1.640681000000 |
| C                                  | 4.538492000000  | 2.709295000000  | 0.244010000000  | C  | -2.225761000000 | 3.398251000000  | 0.710680000000  |
| H                                  | 4.968512000000  | 4.717284000000  | 2.072873000000  | C  | -2.873899000000 | 3.407496000000  | -0.526711000000 |
| H                                  | 6.705730000000  | 4.769144000000  | 3.799514000000  | Fe | -0.424664000000 | 0.785283000000  | -2.983348000000 |
| C                                  | 4.410700000000  | 1.516834000000  | -0.452497000000 | Cl | -1.408888000000 | 1.931571000000  | -4.601587000000 |
| C                                  | 5.219357000000  | 0.371862000000  | -0.231060000000 | Cl | 0.403298000000  | -1.098012000000 | -3.862265000000 |
| C                                  | 3.604774000000  | 3.839973000000  | -0.032210000000 | N  | -0.915207000000 | -0.761707000000 | 0.391854000000  |
| C                                  | 4.058453000000  | 5.163466000000  | -0.358638000000 | C  | -0.809226000000 | -1.723158000000 | 1.503938000000  |
| C                                  | 2.237529000000  | 3.619044000000  | -0.004634000000 | S  | -2.043788000000 | -0.911356000000 | -0.773514000000 |
| C                                  | 5.428091000000  | 5.479572000000  | -0.574754000000 | H  | -1.775875000000 | -2.218169000000 | 1.619666000000  |
| C                                  | 3.088034000000  | 6.209549000000  | -0.506802000000 | O  | -1.767930000000 | 0.321702000000  | -1.647683000000 |
| C                                  | 1.253526000000  | 4.620444000000  | -0.205964000000 | O  | -2.064130000000 | -2.181961000000 | -1.502747000000 |
| C                                  | 5.819604000000  | 6.765333000000  | -0.876407000000 | C  | -0.495366000000 | -0.964973000000 | 2.784630000000  |
| H                                  | 6.170246000000  | 4.692457000000  | -0.506186000000 | C  | 0.602583000000  | -0.095419000000 | 2.857895000000  |
| C                                  | 3.528603000000  | 7.528947000000  | -0.800687000000 | C  | -1.316697000000 | -1.132774000000 | 3.904766000000  |
| C                                  | 1.705331000000  | 5.907437000000  | -0.408958000000 | C  | 0.869928000000  | 0.596786000000  | 4.038617000000  |
| C                                  | 4.864772000000  | 7.805557000000  | -0.977299000000 | H  | 1.237672000000  | 0.060169000000  | 1.992271000000  |
| H                                  | 6.870853000000  | 6.982072000000  | -1.043481000000 | C  | -1.045558000000 | -0.437391000000 | 5.086230000000  |
| H                                  | 2.783681000000  | 8.314383000000  | -0.899822000000 | H  | -2.172240000000 | -1.799996000000 | 3.852706000000  |
| H                                  | 0.983207000000  | 6.707526000000  | -0.546907000000 | C  | 0.046782000000  | 0.428457000000  | 5.155851000000  |
| H                                  | 5.188635000000  | 8.816079000000  | -1.209041000000 | H  | 1.719834000000  | 1.272442000000  | 4.082069000000  |
| P                                  | 1.900699000000  | 1.214572000000  | -0.918023000000 | H  | -1.693259000000 | -0.572002000000 | 5.947938000000  |
| O                                  | 1.770698000000  | 2.321428000000  | 0.252683000000  | H  | 0.255432000000  | 0.971336000000  | 6.073461000000  |
| O                                  | 3.416672000000  | 1.417037000000  | -1.443893000000 | C  | -3.576807000000 | -0.669585000000 | 0.058758000000  |
| O                                  | 1.629564000000  | -0.127663000000 | -0.310376000000 | C  | -3.630785000000 | 0.099609000000  | 1.224298000000  |
| H                                  | -0.011600000000 | -0.390185000000 | 0.044908000000  | C  | -4.709793000000 | -1.290670000000 | -0.476933000000 |
| H                                  | -7.554367000000 | -1.317353000000 | 2.538355000000  | C  | -4.853720000000 | 0.220917000000  | 1.876135000000  |

|                                                      |                 |                 |                 |   |                 |                 |                 |
|------------------------------------------------------|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| Fe                                                   | -5.303062000000 | -4.749064000000 | 1.232817000000  | H | -2.738859000000 | 0.571709000000  | 1.618320000000  |
| Cl                                                   | -4.020551000000 | -3.389163000000 | 2.521883000000  | C | -5.919454000000 | -1.141635000000 | 0.187902000000  |
| Cl                                                   | -4.584399000000 | -4.735295000000 | -0.910752000000 | H | -4.635659000000 | -1.906792000000 | -1.364511000000 |
| Cl                                                   | -7.448340000000 | -4.100464000000 | 1.348079000000  | C | -6.008143000000 | -0.401605000000 | 1.378666000000  |
| Cl                                                   | -5.091261000000 | -6.847309000000 | 2.008030000000  | H | -4.907059000000 | 0.796923000000  | 2.795497000000  |
| H                                                    | 3.853952000000  | -4.074454000000 | -0.183464000000 | H | -6.800659000000 | -1.643074000000 | -0.197727000000 |
| H                                                    | 5.174148000000  | -2.476237000000 | -3.937419000000 | C | -7.315720000000 | -0.330944000000 | 2.121342000000  |
| H                                                    | -2.770429000000 | 3.072659000000  | 1.594365000000  | H | -7.280761000000 | 0.392327000000  | 2.940991000000  |
| H                                                    | -2.646304000000 | 3.876441000000  | -2.612888000000 | H | -8.137992000000 | -0.059320000000 | 1.450166000000  |
| C                                                    | -4.294959000000 | 2.921737000000  | -0.681677000000 | C | 0.084568000000  | -5.024713000000 | -2.028356000000 |
| H                                                    | -4.794457000000 | 2.811489000000  | 0.285121000000  | H | 0.242719000000  | -6.015285000000 | -1.587827000000 |
| H                                                    | -4.885670000000 | 3.607637000000  | -1.299549000000 | H | 0.644984000000  | -4.975409000000 | -2.964543000000 |
| H                                                    | -4.314917000000 | 1.941033000000  | -1.173654000000 | H | -0.981150000000 | -4.934084000000 | -2.266575000000 |
| C                                                    | -0.231554000000 | 3.755381000000  | 2.209070000000  | H | 3.440047000000  | -0.980660000000 | 1.467856000000  |
| H                                                    | 0.431481000000  | 2.886846000000  | 2.289748000000  | C | 1.419456000000  | -2.972283000000 | -1.511468000000 |
| H                                                    | 0.376138000000  | 4.647708000000  | 2.395522000000  | H | 1.849955000000  | -3.043177000000 | -2.501469000000 |
| H                                                    | -0.976309000000 | 3.674701000000  | 3.006938000000  | H | 1.688514000000  | -2.085982000000 | -0.953415000000 |
| C                                                    | -0.100785000000 | 4.743389000000  | -2.789387000000 | C | 0.509627000000  | -3.916694000000 | -1.090413000000 |
| H                                                    | -0.725351000000 | 4.609877000000  | -3.675553000000 | C | -0.100277000000 | -3.798247000000 | 0.181931000000  |
| H                                                    | 0.184947000000  | 5.799144000000  | -2.730961000000 | C | -1.205773000000 | -4.715415000000 | 0.543976000000  |
| H                                                    | 0.819526000000  | 4.167170000000  | -2.936254000000 | H | -2.064050000000 | -4.526836000000 | -0.121203000000 |
| C                                                    | 5.740273000000  | 0.037410000000  | -3.120622000000 | H | -1.545095000000 | -4.600765000000 | 1.573373000000  |
| H                                                    | 6.583188000000  | 0.531986000000  | -2.625020000000 | H | -0.925402000000 | -5.760801000000 | 0.361819000000  |
| H                                                    | 6.075167000000  | -0.312702000000 | -4.101165000000 | C | 0.297138000000  | -2.796988000000 | 1.213817000000  |
| H                                                    | 4.968012000000  | 0.799051000000  | -3.278016000000 | H | 1.229651000000  | -2.281410000000 | 0.991043000000  |
| C                                                    | 4.281451000000  | -4.782621000000 | -2.789488000000 | H | 0.438502000000  | -3.349559000000 | 2.151272000000  |
| H                                                    | 5.235951000000  | -5.310362000000 | -2.911336000000 | C | 4.096185000000  | -1.843800000000 | 1.315230000000  |
| H                                                    | 3.626499000000  | -5.422645000000 | -2.189321000000 | H | 3.586231000000  | -2.734356000000 | 1.695714000000  |
| H                                                    | 3.840672000000  | -4.681146000000 | -3.787642000000 | H | 4.986897000000  | -1.684051000000 | 1.932032000000  |
| Cartesian Coordinates for <b>TS2<sup>CPAME</sup></b> |                 |                 |                 | C | -0.138235000000 | 0.739461000000  | 3.694362000000  |
| C                                                    | 7.570404000000  | 2.492953000000  | 3.337248000000  | H | 0.927151000000  | -0.329847000000 | 2.171992000000  |
| C                                                    | 7.393590000000  | 1.445711000000  | 2.462633000000  | C | -2.425752000000 | 0.066813000000  | 4.072875000000  |
| C                                                    | 6.360614000000  | 1.475947000000  | 1.486227000000  | H | -3.146835000000 | -1.549197000000 | 2.848869000000  |
| C                                                    | 5.517664000000  | 2.632870000000  | 1.392486000000  | C | -1.346905000000 | 0.897095000000  | 4.378174000000  |
| C                                                    | 5.710507000000  | 3.683961000000  | 2.331001000000  | H | 0.708750000000  | 1.378778000000  | 3.925772000000  |
| C                                                    | 6.709111000000  | 3.614826000000  | 3.277241000000  | H | -3.371372000000 | 0.180286000000  | 4.595301000000  |
| H                                                    | 6.769760000000  | -0.508025000000 | 0.727093000000  | H | -1.444262000000 | 1.662104000000  | 5.143370000000  |
| H                                                    | 8.359039000000  | 2.456121000000  | 4.083189000000  | C | -3.440511000000 | -0.797922000000 | -0.125869000000 |
| H                                                    | 8.033609000000  | 0.568515000000  | 2.513760000000  | C | -3.531960000000 | 0.506214000000  | 0.372376000000  |
| C                                                    | 6.127927000000  | 0.364141000000  | 0.636516000000  | C | -4.369859000000 | -1.792821000000 | 0.195986000000  |
| C                                                    | 4.496050000000  | 2.667205000000  | 0.382463000000  | C | -4.602155000000 | 0.813175000000  | 1.203490000000  |
| H                                                    | 5.056220000000  | 4.547446000000  | 2.300156000000  | H | -2.788467000000 | 1.257239000000  | 0.127144000000  |
| H                                                    | 6.834476000000  | 4.427716000000  | 3.986795000000  | C | -5.426736000000 | -1.453712000000 | 1.035787000000  |
| C                                                    | 4.298381000000  | 1.519485000000  | -0.368769000000 | H | -4.265862000000 | -2.803343000000 | -0.185013000000 |
| C                                                    | 5.084273000000  | 0.342069000000  | -0.264788000000 | C | -5.558610000000 | -0.154529000000 | 1.550216000000  |

## Chapter 4

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C  | 3.633377000000  | 3.862443000000  | 0.147184000000  | H  | -4.686410000000 | 1.819122000000  | 1.602286000000  |
| C  | 4.179771000000  | 5.155681000000  | -0.164176000000 | H  | -6.144335000000 | -2.221860000000 | 1.304685000000  |
| C  | 2.253547000000  | 3.732461000000  | 0.150173000000  | C  | -6.715386000000 | 0.195642000000  | 2.449951000000  |
| C  | 5.571448000000  | 5.385293000000  | -0.349483000000 | H  | -6.462927000000 | 1.018736000000  | 3.125558000000  |
| C  | 3.283620000000  | 6.263017000000  | -0.334624000000 | H  | -7.580921000000 | 0.511341000000  | 1.853243000000  |
| C  | 1.344991000000  | 4.793592000000  | -0.093133000000 | H  | -7.027665000000 | -0.665753000000 | 3.048265000000  |
| C  | 6.051500000000  | 6.644722000000  | -0.633943000000 | Fe | -4.470565000000 | -5.602839000000 | 1.504726000000  |
| H  | 6.261544000000  | 4.553596000000  | -0.272014000000 | Cl | -3.253796000000 | -4.336402000000 | 2.941988000000  |
| C  | 3.814007000000  | 7.552899000000  | -0.610442000000 | Cl | -3.613491000000 | -5.410723000000 | -0.575408000000 |
| C  | 1.882643000000  | 6.048157000000  | -0.286799000000 | Cl | -6.609506000000 | -4.906103000000 | 1.539637000000  |
| C  | 5.168922000000  | 7.745079000000  | -0.750935000000 | Cl | -4.301350000000 | -7.733376000000 | 2.164784000000  |
| H  | 7.118196000000  | 6.793332000000  | -0.775620000000 | H  | 3.495388000000  | -4.014165000000 | -0.681230000000 |
| H  | 3.122617000000  | 8.383860000000  | -0.725217000000 | H  | 4.624505000000  | -1.987768000000 | -4.283186000000 |
| H  | 1.216434000000  | 6.889066000000  | -0.460016000000 | H  | -2.907100000000 | 3.764211000000  | 1.550055000000  |
| H  | 5.562508000000  | 8.733814000000  | -0.968252000000 | H  | -2.477747000000 | 4.315661000000  | -2.681830000000 |
| P  | 1.764016000000  | 1.327295000000  | -0.712773000000 | C  | -4.341542000000 | 3.746804000000  | -0.793147000000 |
| O  | 1.690827000000  | 2.475912000000  | 0.420687000000  | H  | -4.903972000000 | 3.851988000000  | 0.140289000000  |
| O  | 3.255888000000  | 1.503168000000  | -1.310630000000 | H  | -4.769127000000 | 4.439960000000  | -1.525837000000 |
| O  | 1.484298000000  | 0.006130000000  | -0.074026000000 | H  | -4.516287000000 | 2.731091000000  | -1.170102000000 |
| H  | -0.079929000000 | -0.701852000000 | -0.004604000000 | C  | -0.327510000000 | 4.177175000000  | 2.263917000000  |
| O  | 0.855867000000  | 1.737150000000  | -1.907092000000 | H  | 0.365587000000  | 3.335089000000  | 2.364781000000  |
| C  | 4.742472000000  | -0.870714000000 | -1.068283000000 | H  | 0.236192000000  | 5.090280000000  | 2.487940000000  |
| C  | 4.896359000000  | -0.868317000000 | -2.472389000000 | H  | -1.106213000000 | 4.058631000000  | 3.023239000000  |
| C  | 4.230061000000  | -2.010767000000 | -0.418433000000 | C  | 0.162202000000  | 4.856187000000  | -2.755114000000 |
| C  | 4.512954000000  | -1.997606000000 | -3.200943000000 | H  | -0.417076000000 | 4.711494000000  | -3.670310000000 |
| C  | 3.875534000000  | -3.129051000000 | -1.186449000000 | H  | 0.538654000000  | 5.885177000000  | -2.748070000000 |
| C  | 3.990617000000  | -3.136604000000 | -2.579709000000 | H  | 1.032999000000  | 4.193522000000  | -2.799977000000 |
| C  | -0.117448000000 | 4.524746000000  | -0.241181000000 | C  | 5.455183000000  | 0.334643000000  | -3.195814000000 |
| C  | -0.681216000000 | 4.558462000000  | -1.535569000000 | H  | 6.312754000000  | 0.762002000000  | -2.665051000000 |
| C  | -0.919589000000 | 4.221958000000  | 0.874869000000  | H  | 5.775092000000  | 0.070454000000  | -4.208091000000 |
| C  | -2.045397000000 | 4.296285000000  | -1.684367000000 | H  | -1.370453000000 | -5.784392000000 | 1.006902000000  |
| C  | -2.284774000000 | 3.973415000000  | 0.681749000000  | H  | -0.215608000000 | -5.729081000000 | 2.339159000000  |
| C  | -2.867807000000 | 4.010602000000  | -0.589218000000 | H  | 0.227092000000  | -6.480045000000 | 0.774287000000  |
| Fe | -0.256604000000 | 0.764628000000  | -3.039386000000 | C  | 0.161661000000  | -3.157686000000 | 1.659570000000  |
| Cl | -1.360115000000 | 2.010566000000  | -4.492949000000 | H  | 1.115073000000  | -2.618638000000 | 1.636577000000  |
| Cl | 0.946548000000  | -0.812969000000 | -4.032345000000 | H  | -0.017361000000 | -3.466589000000 | 2.690528000000  |
| N  | -0.728582000000 | -1.515352000000 | -0.021827000000 | C  | 0.084392000000  | -5.201245000000 | -1.643448000000 |
| C  | -0.980890000000 | -2.127980000000 | 1.303534000000  | H  | 0.801080000000  | -6.028863000000 | -1.576698000000 |
| S  | -2.026172000000 | -1.250822000000 | -1.074733000000 | H  | 0.145234000000  | -4.790165000000 | -2.654053000000 |
| H  | -1.911619000000 | -2.694027000000 | 1.245762000000  | H  | -0.919225000000 | -5.611287000000 | -1.497114000000 |
| O  | -1.609351000000 | 0.011242000000  | -1.806836000000 | H  | 4.934098000000  | -1.938676000000 | 1.643887000000  |
| O  | -2.263159000000 | -2.455761000000 | -1.853740000000 | H  | 3.355029000000  | -1.204212000000 | 1.380397000000  |
| C  | -1.095983000000 | -1.069418000000 | 2.393568000000  | C  | 0.833922000000  | -2.872315000000 | -1.017198000000 |
| C  | -0.010839000000 | -0.238826000000 | 2.708543000000  | H  | 0.799009000000  | -2.583447000000 | -2.062675000000 |
| C  | -2.301299000000 | -0.913648000000 | 3.085931000000  | H  | 1.437000000000  | -2.226883000000 | -0.398459000000 |
| H  | 4.698996000000  | 1.124005000000  | -3.278237000000 | C  | 0.400738000000  | -4.139630000000 | -0.613226000000 |

|                                                |                 |                 |                 |    |                 |                 |                 |
|------------------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C                                              | 3.552710000000  | -4.328160000000 | -3.397747000000 | C  | 0.160844000000  | -4.334548000000 | 0.741766000000  |
| H                                              | 4.346388000000  | -4.660048000000 | -4.077134000000 | C  | -0.307249000000 | -5.653693000000 | 1.254130000000  |
| H                                              | 3.275432000000  | -5.174452000000 | -2.761050000000 | C  | 4.002428000000  | -2.035197000000 | 1.077207000000  |
| H                                              | 2.683359000000  | -4.077346000000 | -4.019044000000 | H  | 3.529320000000  | -2.974114000000 | 1.382966000000  |
| Cartesian Coordinates for CP3 <sup>CPAmc</sup> |                 |                 |                 | C  | 4.448141000000  | -1.823335000000 | -3.143393000000 |
| C                                              | 7.160900000000  | 2.571093000000  | 3.630323000000  | C  | 3.670559000000  | -2.960814000000 | -1.181694000000 |
| C                                              | 7.040188000000  | 1.533347000000  | 2.734962000000  | C  | 3.847206000000  | -2.947215000000 | -2.568037000000 |
| C                                              | 6.074825000000  | 1.576522000000  | 1.692229000000  | C  | -0.303434000000 | 4.626720000000  | -0.297064000000 |
| C                                              | 5.241960000000  | 2.736717000000  | 1.555666000000  | C  | -0.861881000000 | 4.638336000000  | -1.593175000000 |
| C                                              | 5.374845000000  | 3.777955000000  | 2.515165000000  | C  | -1.108189000000 | 4.337430000000  | 0.821083000000  |
| C                                              | 6.308531000000  | 3.696316000000  | 3.524736000000  | C  | -2.221750000000 | 4.351741000000  | -1.744625000000 |
| H                                              | 6.528844000000  | -0.401701000000 | 0.943682000000  | C  | -2.469893000000 | 4.075931000000  | 0.626211000000  |
| H                                              | 7.898040000000  | 2.524053000000  | 4.426643000000  | C  | -3.045452000000 | 4.073127000000  | -0.648753000000 |
| H                                              | 7.673341000000  | 0.653766000000  | 2.819334000000  | Fe | -0.383254000000 | 0.916680000000  | -3.090327000000 |
| C                                              | 5.897341000000  | 0.473466000000  | 0.817612000000  | Cl | -1.652875000000 | 1.988128000000  | -4.531314000000 |
| C                                              | 4.287782000000  | 2.782238000000  | 0.482194000000  | Cl | 0.662730000000  | -0.818216000000 | -3.987709000000 |
| H                                              | 4.726307000000  | 4.643905000000  | 2.449668000000  | N  | -0.635015000000 | -1.610817000000 | -0.000091000000 |
| H                                              | 6.388888000000  | 4.501800000000  | 4.249109000000  | C  | -0.999810000000 | -2.083481000000 | 1.420729000000  |
| C                                              | 4.141725000000  | 1.644005000000  | -0.293324000000 | S  | -2.088041000000 | -1.042604000000 | -1.026138000000 |
| C                                              | 4.917130000000  | 0.463181000000  | -0.152215000000 | H  | -2.005249000000 | -2.499585000000 | 1.356628000000  |
| C                                              | 3.433592000000  | 3.975500000000  | 0.209158000000  | O  | -1.549454000000 | 0.255176000000  | -1.563397000000 |
| C                                              | 3.987942000000  | 5.275168000000  | -0.057289000000 | O  | -2.391384000000 | -2.133673000000 | -1.932864000000 |
| C                                              | 2.056660000000  | 3.838944000000  | 0.134816000000  | C  | -0.969802000000 | -0.930317000000 | 2.400392000000  |
| C                                              | 5.386796000000  | 5.513474000000  | -0.157574000000 | C  | 0.205185000000  | -0.199325000000 | 2.630941000000  |
| C                                              | 3.096416000000  | 6.378781000000  | -0.271901000000 | C  | -2.119226000000 | -0.623959000000 | 3.138610000000  |
| C                                              | 1.155665000000  | 4.900681000000  | -0.131630000000 | C  | 0.217262000000  | 0.840302000000  | 3.559977000000  |
| C                                              | 5.875339000000  | 6.777394000000  | -0.405133000000 | H  | 1.109655000000  | -0.422617000000 | 2.077906000000  |
| H                                              | 6.075641000000  | 4.684866000000  | -0.043853000000 | C  | -2.103376000000 | 0.411344000000  | 4.074582000000  |
| C                                              | 3.634697000000  | 7.672973000000  | -0.508849000000 | H  | -3.028569000000 | -1.192740000000 | 2.977374000000  |
| C                                              | 1.695237000000  | 6.158428000000  | -0.294032000000 | C  | -0.937883000000 | 1.150392000000  | 4.282652000000  |
| C                                              | 4.994513000000  | 7.873265000000  | -0.568066000000 | H  | 1.131586000000  | 1.404810000000  | 3.718870000000  |
| H                                              | 6.947649000000  | 6.933163000000  | -0.481431000000 | H  | -3.006013000000 | 0.641094000000  | 4.633320000000  |
| H                                              | 2.946712000000  | 8.501332000000  | -0.657661000000 | H  | -0.926688000000 | 1.961844000000  | 5.004719000000  |
| H                                              | 1.033753000000  | 6.999106000000  | -0.485404000000 | C  | -3.414313000000 | -0.629164000000 | 0.034128000000  |
| H                                              | 5.394418000000  | 8.865580000000  | -0.755363000000 | C  | -3.493024000000 | 0.669442000000  | 0.552575000000  |
| P                                              | 1.635899000000  | 1.458714000000  | -0.814546000000 | C  | -4.348723000000 | -1.629726000000 | 0.339025000000  |
| O                                              | 1.484863000000  | 2.573210000000  | 0.344197000000  | C  | -4.559646000000 | 0.963440000000  | 1.391672000000  |
| O                                              | 3.162562000000  | 1.642692000000  | -1.302629000000 | H  | -2.751384000000 | 1.422565000000  | 0.311536000000  |
| O                                              | 1.310627000000  | 0.119502000000  | -0.239709000000 | C  | -5.392542000000 | -1.302634000000 | 1.193579000000  |
| H                                              | -0.014239000000 | -0.750010000000 | 0.033529000000  | H  | -4.256845000000 | -2.629742000000 | -0.070244000000 |
| O                                              | 0.818572000000  | 1.901143000000  | -2.065845000000 | C  | -5.514743000000 | -0.008894000000 | 1.730406000000  |
| C                                              | 4.609753000000  | -0.737129000000 | -0.986360000000 | H  | -4.642357000000 | 1.964291000000  | 1.802473000000  |
| C                                              | 4.833482000000  | -0.718144000000 | -2.378751000000 | H  | -6.111129000000 | -2.073254000000 | 1.453426000000  |
| C                                              | 4.035993000000  | -1.873693000000 | -0.379118000000 | C  | -6.662023000000 | 0.318158000000  | 2.648150000000  |
| Cl                                             | -6.695216000000 | -4.771545000000 | 1.326010000000  | H  | -6.503599000000 | 1.263194000000  | 3.174919000000  |

## Chapter 4

|                                                |                 |                 |                 |    |                 |                 |                 |
|------------------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| Cl                                             | -4.320253000000 | -7.466780000000 | 2.338260000000  | H  | -7.594480000000 | 0.401688000000  | 2.075802000000  |
| H                                              | 3.221912000000  | -3.834770000000 | -0.712383000000 | H  | -6.808412000000 | -0.476525000000 | 3.387359000000  |
| H                                              | 4.617114000000  | -1.803760000000 | -4.218187000000 | Fe | -4.536274000000 | -5.359008000000 | 1.604584000000  |
| H                                              | -3.094960000000 | 3.882710000000  | 1.496209000000  | Cl | -3.547600000000 | -3.960941000000 | 3.092010000000  |
| H                                              | -2.649112000000 | 4.347666000000  | -2.744403000000 | Cl | -3.478142000000 | -5.131488000000 | -0.370685000000 |
| C                                              | -4.509551000000 | 3.761089000000  | -0.852107000000 | H  | 3.229441000000  | -5.007180000000 | -2.839251000000 |
| H                                              | -5.084761000000 | 3.902525000000  | 0.068801000000  | H  | 2.417024000000  | -3.851841000000 | -3.905654000000 |
| H                                              | -4.947730000000 | 4.397826000000  | -1.628175000000 | C  | 3.776255000000  | -1.929056000000 | 1.109695000000  |
| H                                              | -4.651468000000 | 2.719960000000  | -1.170166000000 | H  | 3.205392000000  | -2.825703000000 | 1.370508000000  |
| C                                              | -0.520647000000 | 4.309194000000  | 2.212333000000  | H  | 4.704566000000  | -1.952619000000 | 1.690865000000  |
| H                                              | 0.148592000000  | 3.450251000000  | 2.334133000000  | H  | 3.214122000000  | -1.050520000000 | 1.443066000000  |
| H                                              | 0.066384000000  | 5.211301000000  | 2.418854000000  | C  | 0.207378000000  | -2.611583000000 | -0.804510000000 |
| H                                              | -1.304152000000 | 4.226938000000  | 2.971590000000  | H  | 0.081954000000  | -2.374312000000 | -1.859774000000 |
| C                                              | -0.019747000000 | 4.946547000000  | -2.810844000000 | H  | 1.229979000000  | -2.324508000000 | -0.544325000000 |
| H                                              | -0.581510000000 | 4.753219000000  | -3.728761000000 | C  | -0.091825000000 | -4.050336000000 | -0.493173000000 |
| H                                              | 0.301847000000  | 5.994428000000  | -2.822745000000 | C  | -0.175466000000 | -4.384023000000 | 0.805547000000  |
| H                                              | 0.884607000000  | 4.330510000000  | -2.831800000000 | C  | -0.431724000000 | -5.751259000000 | 1.367925000000  |
| C                                              | 5.470520000000  | 0.474872000000  | -3.053707000000 | H  | -1.389180000000 | -5.765062000000 | 1.901275000000  |
| H                                              | 6.312504000000  | 0.865682000000  | -2.472106000000 | H  | 0.346039000000  | -6.013080000000 | 2.097882000000  |
| H                                              | 5.836401000000  | 0.212087000000  | -4.050806000000 | H  | -0.464235000000 | -6.529604000000 | 0.604058000000  |
| H                                              | 4.748341000000  | 1.291935000000  | -3.166905000000 | C  | -0.069090000000 | -3.249338000000 | 1.802505000000  |
| C                                              | 3.375483000000  | -4.095480000000 | -3.427720000000 | H  | 0.961045000000  | -2.881900000000 | 1.900135000000  |
| H                                              | 4.087609000000  | -4.316842000000 | -4.230378000000 | H  | -0.387974000000 | -3.570248000000 | 2.798269000000  |
| H                                              | 0.658123000000  | -4.887737000000 | -2.331360000000 | C  | -0.230132000000 | -4.949828000000 | -1.688853000000 |
| H                                              | -1.091687000000 | -4.636124000000 | -2.291424000000 | H  | -0.378627000000 | -5.994241000000 | -1.411521000000 |
| Cartesian Coordinates for CP4 <sup>CPAMe</sup> |                 |                 |                 | C  | 5.498213000000  | 5.226881000000  | 0.289695000000  |
| C                                              | 6.884674000000  | 1.876733000000  | 3.825695000000  | C  | 3.278395000000  | 6.189661000000  | -0.088787000000 |
| C                                              | 6.795726000000  | 0.938705000000  | 2.822883000000  | C  | 1.268560000000  | 4.806087000000  | -0.203306000000 |
| C                                              | 5.899461000000  | 1.116304000000  | 1.733691000000  | C  | 6.061944000000  | 6.478914000000  | 0.168428000000  |
| C                                              | 5.110102000000  | 2.311467000000  | 1.663724000000  | H  | 6.137714000000  | 4.369628000000  | 0.460124000000  |
| C                                              | 5.205178000000  | 3.245192000000  | 2.732463000000  | C  | 3.892438000000  | 7.466370000000  | -0.206727000000 |
| C                                              | 6.068270000000  | 3.032582000000  | 3.784855000000  | C  | 1.880718000000  | 6.037199000000  | -0.281183000000 |
| H                                              | 6.336817000000  | -0.795472000000 | 0.822397000000  | C  | 5.253820000000  | 7.614387000000  | -0.074997000000 |
| H                                              | 7.567042000000  | 1.726026000000  | 4.657179000000  | H  | 7.139104000000  | 6.592187000000  | 0.253017000000  |
| H                                              | 7.398413000000  | 0.034623000000  | 2.856700000000  | H  | 3.260867000000  | 8.327009000000  | -0.411750000000 |
| C                                              | 5.740267000000  | 0.109535000000  | 0.746913000000  | H  | 1.284792000000  | 6.912334000000  | -0.526033000000 |
| C                                              | 4.228584000000  | 2.496497000000  | 0.544956000000  | H  | 5.710693000000  | 8.595319000000  | -0.167394000000 |
| H                                              | 4.582388000000  | 4.132540000000  | 2.715507000000  | P  | 1.585713000000  | 1.340771000000  | -0.910490000000 |
| H                                              | 6.119622000000  | 3.756382000000  | 4.593226000000  | O  | 1.439160000000  | 2.457766000000  | 0.261552000000  |
| C                                              | 4.078329000000  | 1.437512000000  | -0.339431000000 | O  | 3.135129000000  | 1.555492000000  | -1.373193000000 |
| C                                              | 4.809481000000  | 0.220238000000  | -0.264636000000 | O  | 1.329233000000  | -0.002682000000 | -0.313453000000 |
| C                                              | 3.455697000000  | 3.753819000000  | 0.316880000000  | H  | -0.004279000000 | -0.834906000000 | 0.125826000000  |
| C                                              | 4.090867000000  | 5.039171000000  | 0.187239000000  | O  | 0.782323000000  | 1.789695000000  | -2.146188000000 |
| C                                              | 2.084305000000  | 3.689470000000  | 0.121653000000  | C  | 4.502442000000  | -0.900155000000 | -1.204751000000 |
| C                                              | -0.863224000000 | 1.350328000000  | 4.273630000000  | C  | 4.791023000000  | -0.782653000000 | -2.579972000000 |

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H  | 1.168366000000  | 1.598221000000  | 3.581280000000  | C  | 3.869215000000  | -2.062697000000 | -0.716513000000 |
| H  | -2.905647000000 | 0.844327000000  | 4.755191000000  | C  | 4.390597000000  | -1.800928000000 | -3.449746000000 |
| H  | -0.822250000000 | 2.195041000000  | 4.955532000000  | C  | 3.485436000000  | -3.057530000000 | -1.623236000000 |
| C  | -3.405168000000 | -0.537494000000 | 0.181592000000  | C  | 3.707765000000  | -2.933911000000 | -2.996949000000 |
| C  | -3.466288000000 | 0.776946000000  | 0.653459000000  | C  | -0.172932000000 | 4.591216000000  | -0.527640000000 |
| C  | -4.350240000000 | -1.511545000000 | 0.529733000000  | C  | -0.583938000000 | 4.583681000000  | -1.876721000000 |
| C  | -4.519620000000 | 1.117183000000  | 1.493575000000  | C  | -1.099080000000 | 4.326472000000  | 0.497849000000  |
| H  | -2.715912000000 | 1.506082000000  | 0.371969000000  | C  | -1.909635000000 | 4.257957000000  | -2.178791000000 |
| C  | -5.379551000000 | -1.143493000000 | 1.386333000000  | C  | -2.425088000000 | 4.042340000000  | 0.154463000000  |
| H  | -4.277471000000 | -2.525126000000 | 0.151868000000  | C  | -2.844578000000 | 3.971353000000  | -1.177837000000 |
| C  | -5.480601000000 | 0.169410000000  | 1.878988000000  | Fe | -0.467850000000 | 0.980175000000  | -3.344686000000 |
| H  | -4.586319000000 | 2.132990000000  | 1.871142000000  | Cl | -2.553595000000 | 1.192148000000  | -4.157127000000 |
| H  | -6.104612000000 | -1.895635000000 | 1.681326000000  | Cl | 0.347471000000  | -1.042445000000 | -3.797788000000 |
| C  | -6.612130000000 | 0.540742000000  | 2.801036000000  | N  | -0.669242000000 | -1.655332000000 | 0.150241000000  |
| H  | -6.450427000000 | 1.515622000000  | 3.269567000000  | C  | -1.037238000000 | -2.027823000000 | 1.586110000000  |
| H  | -7.558332000000 | 0.583797000000  | 2.247308000000  | S  | -2.094151000000 | -0.981007000000 | -0.897881000000 |
| H  | -6.734810000000 | -0.210235000000 | 3.589008000000  | H  | -2.051145000000 | -2.426744000000 | 1.553230000000  |
| Fe | -4.588966000000 | -5.214198000000 | 1.906657000000  | O  | -1.467423000000 | 0.261436000000  | -1.403154000000 |
| Cl | -3.591713000000 | -3.811959000000 | 3.381038000000  | O  | -2.467888000000 | -2.069518000000 | -1.785730000000 |
| Cl | -3.548970000000 | -5.031716000000 | -0.079664000000 | C  | -0.974275000000 | -0.818509000000 | 2.495874000000  |
| Cl | -6.748743000000 | -4.622075000000 | 1.635811000000  | C  | 0.201800000000  | -0.064808000000 | 2.624818000000  |
| Cl | -4.379828000000 | -7.322073000000 | 2.651122000000  | C  | -2.086301000000 | -0.485168000000 | 3.278019000000  |
| H  | 2.985041000000  | -3.947364000000 | -1.245841000000 | C  | 0.253555000000  | 1.017534000000  | 3.502625000000  |
| H  | 4.617128000000  | -1.703217000000 | -4.509260000000 | H  | 1.076626000000  | -0.302070000000 | 2.030313000000  |
| H  | -3.145484000000 | 3.864873000000  | 0.950533000000  | C  | -2.030874000000 | 0.593523000000  | 4.162077000000  |
| H  | -2.217505000000 | 4.209694000000  | -3.220762000000 | H  | -2.999165000000 | -1.064162000000 | 3.186745000000  |
| C  | -4.249874000000 | 3.554835000000  | -1.537650000000 | H  | 2.229234000000  | -3.650158000000 | -4.387659000000 |
| H  | -4.919775000000 | 3.597043000000  | -0.672935000000 | C  | 3.563838000000  | -2.243958000000 | 0.753891000000  |
| H  | -4.667304000000 | 4.188555000000  | -2.327973000000 | H  | 2.966021000000  | -3.146499000000 | 0.917105000000  |
| H  | -4.254829000000 | 2.524587000000  | -1.917011000000 | H  | 4.473855000000  | -2.342127000000 | 1.355371000000  |
| C  | -0.670155000000 | 4.326790000000  | 1.945659000000  | H  | 3.010013000000  | -1.384192000000 | 1.143955000000  |
| H  | -0.010004000000 | 3.477373000000  | 2.153234000000  | C  | 0.088002000000  | -2.729487000000 | -0.629302000000 |
| H  | -0.119600000000 | 5.238818000000  | 2.203388000000  | H  | -0.135328000000 | -2.586762000000 | -1.684889000000 |
| H  | -1.531960000000 | 4.243553000000  | 2.614718000000  | H  | 1.131765000000  | -2.438905000000 | -0.495698000000 |
| C  | 0.376234000000  | 4.908905000000  | -2.997477000000 | C  | -0.180597000000 | -4.139983000000 | -0.185017000000 |
| H  | 0.014062000000  | 4.510127000000  | -3.948334000000 | C  | -0.245112000000 | -4.378680000000 | 1.134674000000  |
| H  | 0.504748000000  | 5.993213000000  | -3.108140000000 | C  | -0.494006000000 | -5.703267000000 | 1.796028000000  |
| H  | 1.367428000000  | 4.489836000000  | -2.809102000000 | H  | -1.445079000000 | -5.676367000000 | 2.341931000000  |
| C  | 5.518622000000  | 0.424663000000  | -3.121073000000 | H  | 0.291611000000  | -5.916195000000 | 2.533566000000  |
| H  | 6.405598000000  | 0.663812000000  | -2.523513000000 | H  | -0.538141000000 | -6.534363000000 | 1.090188000000  |
| H  | 5.837737000000  | 0.264809000000  | -4.155854000000 | C  | -0.126800000000 | -3.178967000000 | 2.050217000000  |
| H  | 4.876629000000  | 1.309490000000  | -3.104477000000 | H  | 0.908791000000  | -2.820358000000 | 2.123506000000  |
| C  | 3.190441000000  | -3.971255000000 | -3.964217000000 | H  | -0.449772000000 | -3.427845000000 | 3.065169000000  |
| H  | 3.879919000000  | -4.125855000000 | -4.801824000000 | C  | -0.304524000000 | -5.132203000000 | -1.307812000000 |
| H  | 3.029172000000  | -4.936611000000 | -3.473218000000 | H  | -0.422153000000 | -6.157118000000 | -0.953166000000 |
| H  | -1.176282000000 | -4.887385000000 | -1.927402000000 | H  | 0.578897000000  | -5.095020000000 | -1.960813000000 |

## Chapter 4

|   |                |                 |                 |   |                 |                 |                 |
|---|----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| N | 2.550000000000 | 2.652719000000  | -6.084870000000 | H | 7.136489000000  | 4.439999000000  | -6.322942000000 |
| C | 2.965099000000 | 2.987674000000  | -4.901848000000 | H | 7.742203000000  | 5.168465000000  | -4.026180000000 |
| S | 0.990703000000 | 2.048739000000  | -6.200844000000 | C | 1.208159000000  | 0.362269000000  | -6.701492000000 |
| H | 2.338799000000 | 2.830834000000  | -4.018334000000 | C | 2.375754000000  | -0.337986000000 | -6.392685000000 |
| O | 0.362904000000 | 2.081001000000  | -4.820438000000 | C | 0.119645000000  | -0.254077000000 | -7.324346000000 |
| O | 0.248905000000 | 2.799285000000  | -7.211564000000 | C | 2.446504000000  | -1.685990000000 | -6.729611000000 |
| C | 4.271577000000 | 3.579504000000  | -4.692601000000 | H | 3.207305000000  | 0.148779000000  | -5.896656000000 |
| C | 4.620630000000 | 3.990274000000  | -3.391988000000 | C | 0.210466000000  | -1.607527000000 | -7.633856000000 |
| C | 5.184819000000 | 3.748306000000  | -5.752849000000 | H | -0.775310000000 | 0.310356000000  | -7.555892000000 |
| C | 5.866683000000 | 4.565515000000  | -3.157759000000 | C | 1.367014000000  | -2.344397000000 | -7.335876000000 |
| H | 3.921196000000 | 3.848150000000  | -2.572908000000 | H | 3.351779000000  | -2.240839000000 | -6.504587000000 |
| C | 6.429122000000 | 4.313373000000  | -5.509022000000 | H | -0.631390000000 | -2.099079000000 | -8.113024000000 |
| H | 4.903417000000 | 3.429937000000  | -6.751171000000 | C | 1.437354000000  | -3.822455000000 | -7.625437000000 |
| C | 6.768878000000 | 4.723226000000  | -4.212540000000 | H | 1.101215000000  | -4.394932000000 | -6.751058000000 |
| H | 6.129695000000 | 4.890721000000  | -2.158230000000 | H | 0.794604000000  | -4.099763000000 | -8.466333000000 |
| H | 2.460668000000 | -4.139494000000 | -7.849629000000 |   |                 |                 |                 |

### Cartesian Coordinates for **CP1<sup>rac</sup>**

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| Fe | 2.963890000000  | -0.753951000000 | 1.963401000000  | H  | -1.708961000000 | 4.696026000000  | 2.863267000000  |
| N  | 0.256889000000  | -3.795017000000 | 0.569113000000  | H  | -1.353740000000 | 5.032804000000  | 4.555609000000  |
| C  | 0.335205000000  | -4.330432000000 | -0.615374000000 | C  | -1.985381000000 | 2.365899000000  | 4.851514000000  |
| S  | 0.537322000000  | -2.157768000000 | 0.614187000000  | H  | -2.778622000000 | 2.942320000000  | 4.358082000000  |
| H  | 0.600850000000  | -3.730336000000 | -1.489208000000 | H  | -2.380069000000 | 1.369002000000  | 5.069146000000  |
| O  | 1.514167000000  | -2.032918000000 | 1.804330000000  | H  | -1.778451000000 | 2.867835000000  | 5.805482000000  |
| O  | 1.007629000000  | -1.540478000000 | -0.627337000000 | C  | 1.284536000000  | 3.610201000000  | 3.470156000000  |
| N  | 0.914918000000  | 2.417335000000  | -0.243014000000 | H  | 1.782120000000  | 4.543208000000  | 3.217505000000  |
| C  | 0.542103000000  | 3.612098000000  | 0.098737000000  | H  | 1.920917000000  | 2.736758000000  | 3.575383000000  |
| S  | 2.439875000000  | 1.946304000000  | 0.225450000000  | C  | -0.315701000000 | 1.098734000000  | 3.519055000000  |
| O  | 3.294811000000  | 2.969688000000  | 0.831055000000  | H  | 0.535908000000  | 1.022831000000  | 2.855733000000  |
| O  | 2.102937000000  | 0.779695000000  | 1.170947000000  | H  | -0.821319000000 | 0.171558000000  | 3.770488000000  |
| Cl | 3.343551000000  | -0.323806000000 | 4.093430000000  | H  | 1.208213000000  | 4.275008000000  | 0.657032000000  |
| Cl | 4.746305000000  | -1.371316000000 | 0.817857000000  | C  | 2.968965000000  | 0.073296000000  | -3.298591000000 |
| C  | -0.772474000000 | 4.116433000000  | -0.242602000000 | H  | 1.286568000000  | 0.514305000000  | -2.036706000000 |
| C  | -1.689376000000 | 3.340700000000  | -0.981391000000 | C  | 5.123914000000  | 0.868195000000  | -2.542070000000 |
| C  | -1.130504000000 | 5.410684000000  | 0.177193000000  | H  | 5.132055000000  | 1.954066000000  | -0.673309000000 |
| C  | -2.945550000000 | 3.851958000000  | -1.278917000000 | C  | 4.355385000000  | 0.183310000000  | -3.496137000000 |
| H  | -1.403202000000 | 2.352741000000  | -1.322908000000 | H  | 2.357917000000  | -0.462259000000 | -4.018488000000 |
| C  | -2.392692000000 | 5.917063000000  | -0.122432000000 | H  | 6.197244000000  | 0.959888000000  | -2.680628000000 |
| H  | -0.420756000000 | 6.008671000000  | 0.741367000000  | C  | -4.589668000000 | 0.469512000000  | 2.463203000000  |
| C  | -3.299396000000 | 5.137914000000  | -0.846536000000 | H  | -5.046219000000 | 1.074415000000  | 1.673895000000  |
| H  | -3.648405000000 | 3.253926000000  | -1.850986000000 | H  | -5.331509000000 | -0.249987000000 | 2.823317000000  |
| H  | -2.668985000000 | 6.914150000000  | 0.205847000000  | H  | -4.349706000000 | 1.141518000000  | 3.297402000000  |
| H  | -4.283535000000 | 5.533459000000  | -1.080813000000 | C  | 4.992592000000  | -0.410367000000 | -4.726442000000 |
| C  | 0.073400000000  | -5.734048000000 | -0.846442000000 | H  | 4.816639000000  | 0.233631000000  | -5.597615000000 |
| C  | 0.107460000000  | -6.195922000000 | -2.176709000000 | H  | 6.074087000000  | -0.523636000000 | -4.607481000000 |
| C  | -0.226910000000 | -6.626045000000 | 0.202601000000  | H  | 4.562448000000  | -1.390638000000 | -4.957356000000 |
|    |                 |                 |                 | Fe | -1.419343000000 | -1.907577000000 | -3.557028000000 |

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | -0.158416000000 | -7.534205000000 | -2.453506000000 | Cl | -1.274956000000 | 0.294600000000  | -3.066232000000 |
| H | 0.327421000000  | -5.497019000000 | -2.979350000000 | Cl | -2.696716000000 | -2.184235000000 | -5.373899000000 |
| C | -0.486250000000 | -7.959916000000 | -0.081740000000 | Cl | -2.325412000000 | -3.012559000000 | -1.814720000000 |
| H | -0.250201000000 | -6.259118000000 | 1.223585000000  | Cl | 0.649225000000  | -2.733701000000 | -3.970615000000 |
| C | -0.453231000000 | -8.413599000000 | -1.408128000000 | C  | -0.745680000000 | 2.279979000000  | 3.987700000000  |
| H | -0.137173000000 | -7.890680000000 | -3.478605000000 | C  | -0.044933000000 | 3.555636000000  | 3.661970000000  |
| H | -0.716255000000 | -8.651629000000 | 0.722914000000  | C  | -0.891582000000 | 4.807252000000  | 3.586597000000  |
| H | -0.659565000000 | -9.458088000000 | -1.624139000000 | H  | -0.291903000000 | 5.674323000000  | 3.293962000000  |
| C | -0.985703000000 | -1.436848000000 | 1.145342000000  | C  | -3.339835000000 | -0.218846000000 | 1.977281000000  |
| C | -1.734520000000 | -2.041757000000 | 2.159871000000  | H  | -3.513037000000 | -1.882110000000 | 3.343279000000  |
| C | -1.379464000000 | -0.246012000000 | 0.534610000000  | H  | -2.877297000000 | 1.282442000000  | 0.500189000000  |
| C | -2.914088000000 | -1.423908000000 | 2.561445000000  | C  | 3.153576000000  | 1.295558000000  | -1.250395000000 |
| H | -1.409165000000 | -2.971589000000 | 2.612841000000  | C  | 2.353575000000  | 0.619802000000  | -2.179176000000 |
| C | -2.560698000000 | 0.352266000000  | 0.961893000000  | C  | 4.536248000000  | 1.429262000000  | -1.411802000000 |
| H | -0.784122000000 | 0.192923000000  | -0.255810000000 |    |                 |                 |                 |

Cartesian Coordinates for **TS1<sup>rac</sup>**

|    |                 |                 |                 |   |                 |                 |                 |
|----|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| Fe | 1.540262000000  | -0.418124000000 | 4.028329000000  | C | -0.990256000000 | -5.232235000000 | -2.911582000000 |
| N  | 0.042906000000  | -3.778978000000 | 1.573259000000  | H | -1.792074000000 | -3.505484000000 | -1.908872000000 |
| C  | -0.593906000000 | -3.658357000000 | 0.444706000000  | C | 0.569844000000  | -6.577321000000 | -1.619198000000 |
| S  | -0.282686000000 | -2.600030000000 | 2.708573000000  | H | 0.977839000000  | -5.889067000000 | 0.383317000000  |
| H  | -1.285196000000 | -2.828733000000 | 0.271602000000  | C | -0.137267000000 | -6.333448000000 | -2.806423000000 |
| O  | 1.114227000000  | -2.048239000000 | 3.010806000000  | H | -1.529648000000 | -5.035526000000 | -3.832494000000 |
| O  | -1.292800000000 | -1.610522000000 | 2.323509000000  | H | 1.230575000000  | -7.435956000000 | -1.548060000000 |
| N  | 0.750984000000  | 2.552646000000  | 0.854277000000  | H | -0.017262000000 | -7.006009000000 | -3.650998000000 |
| C  | 0.576833000000  | 3.799349000000  | 1.403704000000  | C | -0.780619000000 | -3.478881000000 | 4.159503000000  |
| S  | 1.772132000000  | 1.560813000000  | 1.551212000000  | C | 0.178797000000  | -4.162102000000 | 4.913121000000  |
| O  | 3.122921000000  | 2.055885000000  | 1.853496000000  | C | -2.128925000000 | -3.450847000000 | 4.519580000000  |
| O  | 1.109683000000  | 1.019880000000  | 2.894161000000  | C | -0.238049000000 | -4.831971000000 | 6.057630000000  |
| Cl | 0.162966000000  | -0.355306000000 | 5.769817000000  | H | 1.222834000000  | -4.153804000000 | 4.619367000000  |
| Cl | 3.696080000000  | -0.589750000000 | 4.493183000000  | C | -2.518562000000 | -4.130067000000 | 5.671170000000  |
| C  | 0.210713000000  | 4.872454000000  | 0.440713000000  | H | -2.847752000000 | -2.901171000000 | 3.921630000000  |
| C  | -0.305395000000 | 4.557419000000  | -0.824602000000 | C | -1.585840000000 | -4.824461000000 | 6.455827000000  |
| C  | 0.354650000000  | 6.215809000000  | 0.813413000000  | H | 0.494668000000  | -5.364842000000 | 6.656994000000  |
| C  | -0.675581000000 | 5.576165000000  | -1.701873000000 | H | -3.563542000000 | -4.114707000000 | 5.966923000000  |
| H  | -0.413501000000 | 3.518603000000  | -1.114042000000 | C | 1.842764000000  | 0.171992000000  | 0.448704000000  |
| C  | -0.012923000000 | 7.232752000000  | -0.067603000000 | C | 0.807002000000  | -0.093207000000 | -0.448199000000 |
| H  | 0.753978000000  | 6.464771000000  | 1.794039000000  | C | 2.980697000000  | -0.639411000000 | 0.521162000000  |
| C  | -0.531499000000 | 6.915270000000  | -1.326056000000 | C | 0.935442000000  | -1.180603000000 | -1.310973000000 |
| H  | -1.073563000000 | 5.320612000000  | -2.679878000000 | H | -0.061416000000 | 0.549115000000  | -0.501247000000 |
| H  | 0.107151000000  | 8.271287000000  | 0.227236000000  | C | 3.078855000000  | -1.725454000000 | -0.342178000000 |
| H  | -0.818476000000 | 7.707562000000  | -2.011585000000 | H | 3.773586000000  | -0.417591000000 | 1.228203000000  |
| C  | -0.428590000000 | -4.604096000000 | -0.637517000000 | C | 2.072067000000  | -2.002610000000 | -1.281908000000 |
| C  | -1.141046000000 | -4.369513000000 | -1.829060000000 | H | 0.147632000000  | -1.371888000000 | -2.033087000000 |
| C  | 0.430099000000  | -5.718557000000 | -0.537831000000 | H | 3.962196000000  | -2.356853000000 | -0.301087000000 |
| H  | -3.837452000000 | 4.812949000000  | 1.815898000000  | C | -2.011717000000 | -5.523839000000 | 7.721912000000  |
|    |                 |                 |                 | H | -3.070701000000 | -5.797107000000 | 7.693543000000  |

## Chapter 4

|   |                 |                |                 |    |                 |                 |                 |
|---|-----------------|----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | -3.528379000000 | 2.565261000000 | 0.169404000000  | H  | -1.422995000000 | -6.430323000000 | 7.894674000000  |
| H | -3.243792000000 | 3.286882000000 | -0.603555000000 | H  | -1.862672000000 | -4.867013000000 | 8.588571000000  |
| H | -3.681839000000 | 1.602186000000 | -0.321330000000 | C  | 2.237828000000  | -3.139099000000 | -2.258309000000 |
| H | -4.486547000000 | 2.892427000000 | 0.590929000000  | H  | 3.043245000000  | -2.915656000000 | -2.968805000000 |
| C | -0.877223000000 | 3.688939000000 | 2.732909000000  | H  | 2.505198000000  | -4.067581000000 | -1.742974000000 |
| H | -0.717861000000 | 4.592529000000 | 3.316080000000  | H  | 1.323495000000  | -3.317805000000 | -2.828776000000 |
| H | -0.507929000000 | 2.786930000000 | 3.208702000000  | Fe | -2.755140000000 | -0.306149000000 | -2.924231000000 |
| C | -1.871880000000 | 1.260903000000 | 1.497460000000  | Cl | -1.475491000000 | 1.524083000000  | -2.648920000000 |
| H | -1.163091000000 | 1.102472000000 | 2.297985000000  | Cl | -4.715081000000 | 0.304716000000  | -3.817954000000 |
| H | -2.133771000000 | 0.380152000000 | 0.922685000000  | Cl | -3.138701000000 | -1.277295000000 | -0.909848000000 |
| H | 1.285299000000  | 4.123884000000 | 2.170723000000  | Cl | -1.681445000000 | -1.794751000000 | -4.238562000000 |
| C | -2.758479000000 | 4.931944000000 | 1.661065000000  | C  | -2.463497000000 | 2.457142000000  | 1.240516000000  |
| H | -2.396290000000 | 5.753037000000 | 2.280948000000  | C  | -2.041882000000 | 3.648320000000  | 1.946327000000  |
| H | -2.621821000000 | 5.209501000000 | 0.606919000000  |    |                 |                 |                 |

### Cartesian Coordinates for CP2<sup>rac</sup>

|    |                 |                 |                 |   |                 |                 |                 |
|----|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| Fe | 1.959746000000  | -0.696600000000 | 2.625237000000  | H | -2.221953000000 | -4.018454000000 | -2.658225000000 |
| N  | -0.397658000000 | -3.972425000000 | 0.836559000000  | C | -0.647786000000 | -7.432016000000 | -1.668677000000 |
| C  | -1.054172000000 | -3.958285000000 | -0.289445000000 | H | -0.044326000000 | -6.453711000000 | 0.155795000000  |
| S  | -0.388908000000 | -2.535088000000 | 1.672826000000  | C | -1.307618000000 | -7.284971000000 | -2.897203000000 |
| H  | -1.571970000000 | -3.058183000000 | -0.628652000000 | H | -2.383557000000 | -5.948798000000 | -4.209927000000 |
| O  | 1.118557000000  | -2.274804000000 | 1.844861000000  | H | -0.204670000000 | -8.386491000000 | -1.401299000000 |
| O  | -1.150583000000 | -1.433525000000 | 1.079058000000  | H | -1.371076000000 | -8.129450000000 | -3.577662000000 |
| N  | 1.023189000000  | 2.372099000000  | 1.051422000000  | C | -0.997054000000 | -2.923824000000 | 3.286834000000  |
| C  | 0.905999000000  | 3.839941000000  | 1.320856000000  | C | -0.260481000000 | -3.780272000000 | 4.112299000000  |
| S  | 2.539505000000  | 1.801496000000  | 0.716833000000  | C | -2.189768000000 | -2.331127000000 | 3.702306000000  |
| O  | 3.522490000000  | 2.586457000000  | 1.456728000000  | C | -0.747591000000 | -4.043920000000 | 5.386822000000  |
| O  | 2.443835000000  | 0.306255000000  | 1.050788000000  | H | 0.671136000000  | -4.217456000000 | 3.769170000000  |
| Cl | 0.493749000000  | 0.317972000000  | 3.923947000000  | C | -2.653959000000 | -2.612567000000 | 4.985441000000  |
| Cl | 3.733929000000  | -1.387573000000 | 3.743062000000  | H | -2.727853000000 | -1.658309000000 | 3.043724000000  |
| C  | 1.066529000000  | 4.705121000000  | 0.078470000000  | C | -1.944832000000 | -3.464978000000 | 5.843714000000  |
| C  | 0.165820000000  | 4.679332000000  | -0.998358000000 | H | -0.189322000000 | -4.707070000000 | 6.041617000000  |
| C  | 2.186957000000  | 5.543639000000  | -0.005327000000 | H | -3.579329000000 | -2.156630000000 | 5.325054000000  |
| C  | 0.404345000000  | 5.446448000000  | -2.139480000000 | C | 2.892212000000  | 1.783057000000  | -1.018310000000 |
| H  | -0.729513000000 | 4.071217000000  | -0.946741000000 | C | 2.389315000000  | 0.745718000000  | -1.809916000000 |
| C  | 2.420444000000  | 6.320690000000  | -1.141649000000 | C | 3.570602000000  | 2.873273000000  | -1.569894000000 |
| H  | 2.891813000000  | 5.576733000000  | 0.822181000000  | C | 2.577827000000  | 0.809552000000  | -3.184464000000 |
| C  | 1.534188000000  | 6.264622000000  | -2.218310000000 | H | 1.860554000000  | -0.090917000000 | -1.371657000000 |
| H  | -0.298758000000 | 5.404422000000  | -2.966742000000 | C | 3.741059000000  | 2.913403000000  | -2.950835000000 |
| H  | 3.296664000000  | 6.961748000000  | -1.186044000000 | H | 3.946305000000  | 3.670009000000  | -0.940676000000 |
| H  | 1.717081000000  | 6.858637000000  | -3.109385000000 | C | 3.245491000000  | 1.892915000000  | -3.776532000000 |
| C  | -1.135300000000 | -5.119902000000 | -1.147706000000 | H | 2.174220000000  | 0.012499000000  | -3.801145000000 |
| C  | -1.798268000000 | -4.979149000000 | -2.383337000000 | H | 4.262236000000  | 3.757617000000  | -3.392725000000 |
| C  | -0.556765000000 | -6.356172000000 | -0.795775000000 | C | -2.435817000000 | -3.738700000000 | 7.242838000000  |
| C  | -1.880344000000 | -6.061186000000 | -3.254711000000 | H | -3.498108000000 | -3.501485000000 | 7.350612000000  |
| Cl | -1.637586000000 | -1.780601000000 | -5.413372000000 | H | -2.284450000000 | -4.787450000000 | 7.518908000000  |
|    |                 |                 |                 | H | -1.882791000000 | -3.128336000000 | 7.968139000000  |

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| Cl | -3.117520000000 | -1.383549000000 | -2.085069000000 | C  | 3.410738000000  | 1.947155000000  | -5.273937000000 |
| Cl | 0.476046000000  | -2.120304000000 | -2.464224000000 | H  | 2.435765000000  | 1.879670000000  | -5.770923000000 |
| C  | -1.447888000000 | 2.222413000000  | 0.743457000000  | H  | 3.897326000000  | 2.872278000000  | -5.595663000000 |
| C  | -1.596042000000 | 3.277994000000  | 1.560154000000  | H  | 4.012897000000  | 1.102641000000  | -5.630237000000 |
| C  | -2.914609000000 | 3.823664000000  | 2.046333000000  | Fe | -1.285219000000 | -0.997636000000 | -3.341498000000 |
| H  | -2.899408000000 | 3.926028000000  | 3.140043000000  | Cl | -0.858158000000 | 1.207149000000  | -3.397263000000 |
| H  | -3.087227000000 | 4.830336000000  | 1.641029000000  | H  | -0.616878000000 | 5.101554000000  | 2.135636000000  |
| H  | -3.770768000000 | 3.200645000000  | 1.782806000000  | H  | -0.227801000000 | 3.716771000000  | 3.146305000000  |
| C  | -2.559575000000 | 1.430317000000  | 0.103347000000  | C  | -0.086593000000 | 1.722149000000  | 0.314079000000  |
| H  | -2.413050000000 | 1.375117000000  | -0.981778000000 | H  | -0.031534000000 | 0.646759000000  | 0.501632000000  |
| H  | -2.561852000000 | 0.395802000000  | 0.461467000000  | H  | 0.029046000000  | 1.865277000000  | -0.770145000000 |
| H  | -3.545759000000 | 1.861127000000  | 0.284150000000  | H  | 1.726919000000  | 4.077135000000  | 1.997966000000  |
| C  | -0.399987000000 | 4.026236000000  | 2.105853000000  |    |                 |                 |                 |

Cartesian Coordinates for **CP3<sup>rac</sup>**

|    |                 |                 |                |   |                 |                 |                |
|----|-----------------|-----------------|----------------|---|-----------------|-----------------|----------------|
| Fe | -1.225124000000 | -0.266221000000 | 3.220330000000 | H | -1.462603000000 | -3.473821000000 | 7.462136000000 |
| N  | -0.278236000000 | -4.214523000000 | 3.777889000000 | C | 1.896618000000  | -5.416619000000 | 7.260376000000 |
| C  | -0.640787000000 | -3.853237000000 | 4.970087000000 | H | 1.693510000000  | -5.254938000000 | 5.119844000000 |
| S  | -1.050858000000 | -3.473986000000 | 2.480208000000 | C | 1.324210000000  | -5.112048000000 | 8.504781000000 |
| H  | -1.458428000000 | -3.147314000000 | 5.130446000000 | H | -0.332132000000 | -4.181232000000 | 9.539701000000 |
| O  | -1.772861000000 | -2.217114000000 | 2.927299000000 | H | 2.844152000000  | -5.944814000000 | 7.212011000000 |
| O  | -0.041942000000 | -3.343481000000 | 1.427067000000 | H | 1.832798000000  | -5.409894000000 | 9.417485000000 |
| N  | 0.129061000000  | 2.799288000000  | 6.049766000000 | C | -2.350436000000 | -4.573292000000 | 1.988672000000 |
| C  | 1.318709000000  | 3.663891000000  | 5.819526000000 | C | -3.632212000000 | -4.406384000000 | 2.523211000000 |
| S  | -0.921936000000 | 2.519496000000  | 4.813576000000 | C | -2.041409000000 | -5.615090000000 | 1.111199000000 |
| H  | 1.625775000000  | 3.489175000000  | 4.788663000000 | C | -4.622460000000 | -5.311312000000 | 2.154361000000 |
| O  | -0.429817000000 | 3.159133000000  | 3.594913000000 | H | -3.848618000000 | -3.583815000000 | 3.196625000000 |
| O  | -1.080395000000 | 1.007065000000  | 4.769474000000 | C | -3.052059000000 | -6.506018000000 | 0.759741000000 |
| Cl | -3.273165000000 | 0.444385000000  | 2.591727000000 | H | -1.039505000000 | -5.717459000000 | 0.707886000000 |
| Cl | 0.095586000000  | 0.247224000000  | 1.511928000000 | C | -4.351348000000 | -6.369342000000 | 1.271617000000 |
| C  | 0.975862000000  | 5.140352000000  | 5.972914000000 | H | -5.624359000000 | -5.191574000000 | 2.556935000000 |
| C  | 0.836025000000  | 5.760395000000  | 7.223461000000 | H | -2.828211000000 | -7.318742000000 | 0.074553000000 |
| C  | 0.725411000000  | 5.896087000000  | 4.817419000000 | C | -2.519492000000 | 3.121041000000  | 5.298729000000 |
| C  | 0.437261000000  | 7.095359000000  | 7.314355000000 | C | -3.524485000000 | 2.220625000000  | 5.654577000000 |
| H  | 1.039596000000  | 5.199484000000  | 8.129377000000 | C | -2.704234000000 | 4.506840000000  | 5.368017000000 |
| C  | 0.327380000000  | 7.231397000000  | 4.907405000000 | C | -4.748453000000 | 2.728334000000  | 6.082919000000 |
| H  | 0.827091000000  | 5.427889000000  | 3.843007000000 | H | -3.354595000000 | 1.152806000000  | 5.607106000000 |
| C  | 0.175898000000  | 7.833930000000  | 6.158321000000 | C | -3.937253000000 | 4.986377000000  | 5.797047000000 |
| H  | 0.330312000000  | 7.557582000000  | 8.292084000000 | H | -1.904773000000 | 5.191200000000  | 5.100226000000 |
| H  | 0.137132000000  | 7.798776000000  | 4.000411000000 | C | -4.974769000000 | 4.109437000000  | 6.159499000000 |
| H  | -0.137487000000 | 8.871756000000  | 6.231536000000 | H | -5.529080000000 | 2.032907000000  | 6.378521000000 |
| C  | 0.035647000000  | -4.333433000000 | 6.157726000000 | H | -4.096157000000 | 6.059433000000  | 5.858411000000 |
| C  | -0.530038000000 | -4.026629000000 | 7.408809000000 | C | -5.447000000000 | -7.319950000000 | 0.858973000000 |
| C  | 1.256369000000  | -5.036538000000 | 6.088662000000 | H | -5.042678000000 | -8.284119000000 | 0.536237000000 |
| C  | 0.110826000000  | -4.424345000000 | 8.578946000000 | H | -6.151988000000 | -7.495512000000 | 1.677751000000 |
| C  | 0.142900000000  | 2.363593000000  | 9.838425000000 | H | -6.018780000000 | -6.903427000000 | 0.019623000000 |
|    |                 |                 |                | C | -6.313077000000 | 4.643363000000  | 6.604982000000 |

## Chapter 4

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H | -0.406064000000 | 3.257077000000  | 10.169076000000 | H  | -6.791393000000 | 3.969131000000  | 7.322368000000  |
| H | -0.573627000000 | 1.536140000000  | 9.851069000000  | H  | -6.217978000000 | 5.631302000000  | 7.066383000000  |
| H | 0.915205000000  | 2.156963000000  | 10.580929000000 | H  | -6.990575000000 | 4.744011000000  | 5.747121000000  |
| C | 2.425607000000  | 3.112095000000  | 6.730821000000  | Fe | -4.010989000000 | -1.119496000000 | 8.218384000000  |
| H | 3.226815000000  | 3.861188000000  | 6.781433000000  | Cl | -6.247880000000 | -1.084845000000 | 8.230297000000  |
| H | 2.854457000000  | 2.226268000000  | 6.245823000000  | Cl | -3.183439000000 | -2.691637000000 | 9.607019000000  |
| C | -0.395266000000 | 2.701898000000  | 7.419305000000  | Cl | -3.214378000000 | 0.886892000000  | 8.841959000000  |
| H | -1.032995000000 | 1.815467000000  | 7.477996000000  | Cl | -3.302939000000 | -1.582318000000 | 6.113870000000  |
| H | -1.034977000000 | 3.569324000000  | 7.649719000000  | C  | 0.698534000000  | 2.584079000000  | 8.453924000000  |
| N | 2.798737000000  | -1.921110000000 | 4.654092000000  | C  | 1.992882000000  | 2.748286000000  | 8.136282000000  |
| C | 2.599084000000  | -2.686502000000 | 3.628629000000  | C  | 3.146622000000  | 2.599478000000  | 9.094496000000  |
| S | 1.628360000000  | -0.737807000000 | 4.927292000000  | H  | 3.910199000000  | 1.943042000000  | 8.656277000000  |
| H | 1.725148000000  | -2.565503000000 | 2.986242000000  | H  | 3.630665000000  | 3.569131000000  | 9.275714000000  |
| O | 2.139641000000  | 0.563693000000  | 4.484576000000  | H  | 2.861761000000  | 2.175797000000  | 10.059236000000 |
| O | 0.320320000000  | -1.214080000000 | 4.338423000000  | C  | 2.574250000000  | -0.858820000000 | 7.501003000000  |
| C | 3.498718000000  | -3.772195000000 | 3.280450000000  | C  | 0.149384000000  | -0.807236000000 | 7.221484000000  |
| C | 4.652925000000  | -4.061485000000 | 4.034050000000  | C  | 2.399840000000  | -0.917106000000 | 8.879747000000  |
| C | 3.166758000000  | -4.569350000000 | 2.168780000000  | H  | 3.567765000000  | -0.859735000000 | 7.066582000000  |
| C | 5.461383000000  | -5.131933000000 | 3.673768000000  | C  | 0.003441000000  | -0.870647000000 | 8.603173000000  |
| H | 4.896467000000  | -3.442707000000 | 4.891608000000  | H  | -0.719739000000 | -0.763291000000 | 6.577829000000  |
| C | 3.983524000000  | -5.640593000000 | 1.813465000000  | C  | 1.117233000000  | -0.935009000000 | 9.449382000000  |
| H | 2.268130000000  | -4.344230000000 | 1.601216000000  | H  | 3.273977000000  | -0.953679000000 | 9.523920000000  |
| C | 5.127996000000  | -5.921106000000 | 2.564058000000  | H  | -0.995581000000 | -0.882148000000 | 9.023551000000  |
| H | 6.352599000000  | -5.357274000000 | 4.251799000000  | C  | 0.936488000000  | -1.055977000000 | 10.940646000000 |
| H | 3.728435000000  | -6.255472000000 | 0.955789000000  | H  | -0.010087000000 | -0.613785000000 | 11.264980000000 |
| H | 5.764108000000  | -6.757179000000 | 2.287283000000  | H  | 0.923466000000  | -2.112885000000 | 11.237940000000 |
| C | 1.437509000000  | -0.817718000000 | 6.687129000000  | H  | 1.753056000000  | -0.571368000000 | 11.485735000000 |

### Cartesian Coordinates for TS1<sup>CPAME-R</sup>

|   |                |                 |                 |   |                 |                 |                 |
|---|----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| C | 7.430413000000 | -1.973649000000 | 1.191636000000  | C | -1.310053000000 | -3.531454000000 | 3.446972000000  |
| C | 6.422506000000 | -2.580458000000 | 0.478458000000  | H | -0.707348000000 | -2.113733000000 | 1.961618000000  |
| C | 5.308337000000 | -1.832371000000 | 0.009055000000  | C | -2.368805000000 | -4.242026000000 | 4.021662000000  |
| C | 5.254736000000 | -0.421975000000 | 0.258659000000  | H | -4.495417000000 | -4.618393000000 | 3.976396000000  |
| C | 6.302114000000 | 0.168510000000  | 1.018934000000  | H | -0.298763000000 | -3.657570000000 | 3.821814000000  |
| C | 7.359806000000 | -0.587794000000 | 1.473266000000  | H | -2.181417000000 | -4.922175000000 | 4.847375000000  |
| H | 4.307123000000 | -3.526396000000 | -0.887543000000 | C | -3.579297000000 | -1.511349000000 | -2.361813000000 |
| H | 8.274610000000 | -2.555652000000 | 1.550049000000  | C | -3.387237000000 | -2.873133000000 | -2.630797000000 |
| H | 6.455886000000 | -3.647067000000 | 0.271143000000  | C | -4.752686000000 | -0.834113000000 | -2.705423000000 |
| C | 4.244412000000 | -2.460455000000 | -0.685469000000 | C | -4.413484000000 | -3.565400000000 | -3.256983000000 |
| C | 4.132560000000 | 0.325159000000  | -0.235444000000 | H | -2.458806000000 | -3.363777000000 | -2.360848000000 |
| H | 6.259303000000 | 1.227267000000  | 1.247030000000  | C | -5.764228000000 | -1.558610000000 | -3.325735000000 |
| H | 8.145879000000 | -0.116966000000 | 2.056761000000  | H | -4.876232000000 | 0.217091000000  | -2.477889000000 |
| C | 3.094989000000 | -0.375291000000 | -0.829705000000 | C | -5.617886000000 | -2.925802000000 | -3.599932000000 |
| C | 3.121090000000 | -1.768526000000 | -1.091578000000 | H | -4.286503000000 | -4.622372000000 | -3.470966000000 |
| C | 4.044042000000 | 1.807040000000  | -0.101851000000 | H | -6.693552000000 | -1.055228000000 | -3.573179000000 |
| C | 5.042866000000 | 2.680358000000  | -0.653856000000 | C | -6.759889000000 | -3.709249000000 | -4.188310000000 |
|   |                |                 |                 | H | -6.409748000000 | -4.590747000000 | -4.733637000000 |

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C  | 2.947992000000  | 2.383753000000  | 0.517281000000  | H  | -7.414562000000 | -4.055446000000 | -3.377539000000 |
| C  | 6.131849000000  | 2.211553000000  | -1.440058000000 | H  | -7.365782000000 | -3.095283000000 | -4.861593000000 |
| C  | 4.924567000000  | 4.092206000000  | -0.434219000000 | Fe | -7.574090000000 | -1.695512000000 | 0.530764000000  |
| C  | 2.784968000000  | 3.779856000000  | 0.709284000000  | Cl | -6.257585000000 | -3.342456000000 | -0.274897000000 |
| C  | 7.071452000000  | 3.085083000000  | -1.941422000000 | Cl | -7.014390000000 | 0.286469000000  | -0.390057000000 |
| H  | 6.215846000000  | 1.152214000000  | -1.652117000000 | Cl | -7.232484000000 | -1.547084000000 | 2.769709000000  |
| C  | 5.920797000000  | 4.964396000000  | -0.951778000000 | Cl | -9.701141000000 | -2.174417000000 | 0.054600000000  |
| C  | 3.797862000000  | 4.600706000000  | 0.259300000000  | H  | 0.738447000000  | -2.895687000000 | -4.927797000000 |
| C  | 6.976228000000  | 4.474203000000  | -1.685482000000 | H  | -0.336850000000 | -4.881810000000 | -1.283375000000 |
| H  | 7.891139000000  | 2.704383000000  | -2.544067000000 | H  | -1.249756000000 | 6.082468000000  | 0.498365000000  |
| H  | 5.822763000000  | 6.031231000000  | -0.767431000000 | H  | -0.050782000000 | 4.570030000000  | 4.326364000000  |
| H  | 3.714419000000  | 5.673762000000  | 0.409006000000  | C  | -2.092812000000 | 5.885828000000  | 3.086429000000  |
| H  | 7.728541000000  | 5.149970000000  | -2.081881000000 | H  | -1.963770000000 | 6.173849000000  | 4.135266000000  |
| P  | 0.960243000000  | 0.777320000000  | -0.007918000000 | H  | -2.487440000000 | 6.747968000000  | 2.538974000000  |
| O  | 1.939807000000  | 1.547996000000  | 1.023424000000  | H  | -2.860287000000 | 5.100369000000  | 3.055954000000  |
| O  | 1.944182000000  | 0.335685000000  | -1.215868000000 | C  | 0.865515000000  | 5.245606000000  | -0.951159000000 |
| O  | 0.304754000000  | -0.346839000000 | 0.729181000000  | H  | 1.708062000000  | 5.921966000000  | -1.135015000000 |
| H  | -1.157672000000 | -0.968844000000 | 0.319288000000  | H  | 1.106403000000  | 4.301580000000  | -1.453472000000 |
| O  | 0.026258000000  | 1.840414000000  | -0.653094000000 | H  | -0.019423000000 | 5.668200000000  | -1.432776000000 |
| C  | 2.012417000000  | -2.475739000000 | -1.801501000000 | C  | 2.292090000000  | 3.433566000000  | 3.588606000000  |
| C  | 1.216561000000  | -3.406542000000 | -1.107392000000 | H  | 2.036411000000  | 3.544110000000  | 4.646635000000  |
| C  | 1.819230000000  | -2.268665000000 | -3.184228000000 | H  | 2.306939000000  | 2.362303000000  | 3.355448000000  |
| C  | 0.267466000000  | -4.152029000000 | -1.819648000000 | H  | 3.312161000000  | 3.806438000000  | 3.442199000000  |
| C  | 0.872111000000  | -3.041849000000 | -3.857653000000 | C  | 1.372936000000  | -3.616915000000 | 0.382695000000  |
| C  | 0.098141000000  | -4.002411000000 | -3.198172000000 | H  | 2.283976000000  | -4.179024000000 | 0.621331000000  |
| C  | 1.547314000000  | 4.335012000000  | 1.331702000000  | H  | 1.436936000000  | -2.659264000000 | 0.908686000000  |
| C  | 1.305526000000  | 4.168673000000  | 2.710513000000  | H  | 0.522752000000  | -4.173983000000 | 0.788597000000  |
| C  | 0.626859000000  | 5.040603000000  | 0.528725000000  | C  | -0.874429000000 | -4.862084000000 | -3.973422000000 |
| C  | 0.135451000000  | 4.700105000000  | 3.262155000000  | H  | -1.479261000000 | -5.488873000000 | -3.309022000000 |
| C  | -0.532031000000 | 5.554948000000  | 1.121895000000  | H  | -1.555658000000 | -4.252147000000 | -4.578595000000 |
| C  | -0.801019000000 | 5.388110000000  | 2.483579000000  | H  | -0.344112000000 | -5.530208000000 | -4.663507000000 |
| Fe | -1.250722000000 | 2.237571000000  | -1.940604000000 | C  | 2.615587000000  | -1.228379000000 | -3.936649000000 |
| Cl | -2.466048000000 | 4.059461000000  | -1.636818000000 | H  | 2.493287000000  | -1.343829000000 | -5.017730000000 |
| Cl | -0.489640000000 | 2.010398000000  | -3.993416000000 | H  | 2.280244000000  | -0.219441000000 | -3.667253000000 |
| N  | -2.113013000000 | -1.205964000000 | -0.051022000000 | H  | 3.685057000000  | -1.287010000000 | -3.704709000000 |
| C  | -3.153261000000 | -1.597957000000 | 0.756551000000  | C  | -4.092504000000 | 0.117814000000  | 1.491812000000  |
| S  | -2.241068000000 | -0.651338000000 | -1.627912000000 | H  | -5.061805000000 | -0.319880000000 | 1.702750000000  |
| H  | -4.072634000000 | -1.826978000000 | 0.220182000000  | H  | -4.020358000000 | 0.661952000000  | 0.555527000000  |
| O  | -2.637695000000 | 0.821689000000  | -1.583237000000 | C  | -3.279484000000 | 0.459168000000  | 2.568561000000  |
| O  | -0.943986000000 | -0.915562000000 | -2.235194000000 | C  | -2.101391000000 | 1.311577000000  | 2.423947000000  |
| C  | -2.847014000000 | -2.494153000000 | 1.885681000000  | C  | -0.954681000000 | 1.140149000000  | 3.395223000000  |
| C  | -3.908876000000 | -3.203723000000 | 2.473246000000  | H  | -0.589481000000 | 0.108322000000  | 3.392702000000  |
| C  | -1.542663000000 | -2.656430000000 | 2.388420000000  | H  | -0.126039000000 | 1.794610000000  | 3.121866000000  |
| C  | -3.667079000000 | -4.073681000000 | 3.533911000000  | H  | -1.258439000000 | 1.384691000000  | 4.419927000000  |
| H  | -4.918635000000 | -3.068689000000 | 2.103883000000  | C  | -2.076210000000 | 2.278535000000  | 1.480294000000  |
| H  | -3.519507000000 | 0.604587000000  | 4.690528000000  | H  | -2.907224000000 | 2.463772000000  | 0.808745000000  |

## Chapter 4

|                                      |                 |                 |                 |    |                 |                 |                 |
|--------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H                                    | -4.509797000000 | -0.671806000000 | 3.930578000000  | H  | -1.227287000000 | 2.943764000000  | 1.381789000000  |
| H                                    | -2.756952000000 | -0.883840000000 | 4.144028000000  | C  | -3.547545000000 | -0.158812000000 | 3.903920000000  |
| Cartesian Coordinates for CP2CPAMe-R |                 |                 |                 | C  | 1.600808000000  | -3.489165000000 | -3.044403000000 |
| C                                    | 8.481913000000  | -1.661067000000 | 1.274471000000  | C  | 0.947926000000  | -4.407714000000 | -2.218169000000 |
| C                                    | 7.452886000000  | -2.357045000000 | 0.683818000000  | C  | 2.428653000000  | 4.407239000000  | 1.613522000000  |
| C                                    | 6.269280000000  | -1.690667000000 | 0.263342000000  | C  | 2.330796000000  | 4.304041000000  | 3.015504000000  |
| C                                    | 6.164287000000  | -0.271871000000 | 0.429030000000  | C  | 1.439669000000  | 5.093309000000  | 0.879311000000  |
| C                                    | 7.236536000000  | 0.412476000000  | 1.066752000000  | C  | 1.226986000000  | 4.872491000000  | 3.660918000000  |
| C                                    | 8.362969000000  | -0.264773000000 | 1.478278000000  | C  | 0.349070000000  | 5.643987000000  | 1.563195000000  |
| H                                    | 5.277137000000  | -3.482677000000 | -0.423956000000 | C  | 0.221001000000  | 5.540685000000  | 2.952213000000  |
| H                                    | 9.380054000000  | -2.179804000000 | 1.597128000000  | Fe | -0.466560000000 | 2.223929000000  | -1.553865000000 |
| H                                    | 7.522394000000  | -3.432256000000 | 0.539456000000  | Cl | -1.747695000000 | 3.929086000000  | -0.924464000000 |
| C                                    | 5.182427000000  | -2.407950000000 | -0.293098000000 | Cl | 0.401731000000  | 2.410073000000  | -3.579125000000 |
| C                                    | 4.972434000000  | 0.388525000000  | -0.024096000000 | N  | -1.206342000000 | -1.259931000000 | 0.087419000000  |
| H                                    | 7.159631000000  | 1.480241000000  | 1.235151000000  | C  | -2.398009000000 | -1.424266000000 | 0.916446000000  |
| H                                    | 9.167097000000  | 0.277474000000  | 1.967611000000  | S  | -1.247380000000 | -0.730365000000 | -1.452012000000 |
| C                                    | 3.924480000000  | -0.389343000000 | -0.490078000000 | H  | -3.273121000000 | -1.391603000000 | 0.259375000000  |
| C                                    | 3.994104000000  | -1.797884000000 | -0.644751000000 | O  | -1.733834000000 | 0.727755000000  | -1.524247000000 |
| C                                    | 4.829312000000  | 1.868961000000  | 0.035521000000  | O  | 0.093871000000  | -0.902958000000 | -2.005676000000 |
| C                                    | 5.755496000000  | 2.743190000000  | -0.629555000000 | C  | -2.387408000000 | -2.770976000000 | 1.618108000000  |
| C                                    | 3.766962000000  | 2.437878000000  | 0.718615000000  | C  | -3.562188000000 | -3.220831000000 | 2.238077000000  |
| C                                    | 6.781458000000  | 2.268800000000  | -1.493463000000 | C  | -1.239228000000 | -3.569011000000 | 1.666364000000  |
| C                                    | 5.626821000000  | 4.157950000000  | -0.444389000000 | C  | -3.578775000000 | -4.442605000000 | 2.908892000000  |
| C                                    | 3.603792000000  | 3.836719000000  | 0.893224000000  | H  | -4.465516000000 | -2.621671000000 | 2.188679000000  |
| C                                    | 7.651272000000  | 3.143405000000  | -2.106261000000 | C  | -1.258789000000 | -4.793839000000 | 2.339581000000  |
| H                                    | 6.870251000000  | 1.204493000000  | -1.677218000000 | H  | -0.335608000000 | -3.250640000000 | 1.160443000000  |
| C                                    | 6.551795000000  | 5.032550000000  | -1.077278000000 | C  | -2.424966000000 | -5.231827000000 | 2.966643000000  |
| C                                    | 4.558812000000  | 4.662517000000  | 0.337335000000  | H  | -4.497180000000 | -4.780971000000 | 3.379915000000  |
| C                                    | 7.547146000000  | 4.538554000000  | -1.888204000000 | H  | -0.359605000000 | -5.403433000000 | 2.368328000000  |
| H                                    | 8.421825000000  | 2.759003000000  | -2.768404000000 | H  | -2.440775000000 | -6.183752000000 | 3.489635000000  |
| H                                    | 6.446269000000  | 6.102792000000  | -0.918739000000 | C  | -2.516097000000 | -1.671854000000 | -2.226940000000 |
| H                                    | 4.468595000000  | 5.737154000000  | 0.470759000000  | C  | -2.450931000000 | -3.064393000000 | -2.101004000000 |
| H                                    | 8.244498000000  | 5.215160000000  | -2.373643000000 | C  | -3.491739000000 | -1.036198000000 | -2.999172000000 |
| P                                    | 1.793804000000  | 0.751255000000  | 0.375540000000  | C  | -3.400321000000 | -3.829568000000 | -2.765691000000 |
| O                                    | 2.813278000000  | 1.596891000000  | 1.316844000000  | H  | -1.682344000000 | -3.529648000000 | -1.493990000000 |
| O                                    | 2.728846000000  | 0.259438000000  | -0.852137000000 | C  | -4.428242000000 | -1.829693000000 | -3.653530000000 |
| O                                    | 1.185313000000  | -0.348064000000 | 1.186845000000  | H  | -3.529680000000 | 0.044442000000  | -3.059255000000 |
| H                                    | -0.294984000000 | -1.027551000000 | 0.527873000000  | C  | -4.404355000000 | -3.227552000000 | -3.541473000000 |
| O                                    | 0.798169000000  | 1.773006000000  | -0.250453000000 | H  | -3.370173000000 | -4.910972000000 | -2.670570000000 |
| C                                    | 2.870668000000  | -2.629353000000 | -1.174620000000 | H  | -5.206093000000 | -1.351870000000 | -4.241758000000 |
| C                                    | 2.201397000000  | -3.523028000000 | -0.313694000000 | C  | -5.474152000000 | -4.065142000000 | -4.190794000000 |
| C                                    | 2.550446000000  | -2.593450000000 | -2.546376000000 | H  | -5.112490000000 | -5.070773000000 | -4.426554000000 |
| C                                    | 1.247277000000  | -4.394484000000 | -0.852507000000 | H  | -6.325297000000 | -4.170205000000 | -3.505301000000 |
| Cl                                   | -8.425674000000 | 0.034891000000  | -0.363939000000 | H  | -5.846777000000 | -3.601811000000 | -5.109489000000 |
| H                                    | 1.363495000000  | -3.466851000000 | -4.106148000000 | Fe | -6.370259000000 | -0.493215000000 | 0.351467000000  |

|                                                        |                 |                 |                 |    |                 |                 |                 |
|--------------------------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H                                                      | 0.735917000000  | -5.091065000000 | -0.191055000000 | Cl | -5.795434000000 | -2.526616000000 | -0.422721000000 |
| H                                                      | -0.421363000000 | 6.158161000000  | 0.993697000000  | Cl | -4.888686000000 | 1.014746000000  | -0.432713000000 |
| H                                                      | 1.153007000000  | 4.795801000000  | 4.743845000000  | Cl | -6.257154000000 | -0.517048000000 | 2.619096000000  |
| C                                                      | -0.989323000000 | 6.099893000000  | 3.662430000000  | H  | -0.671980000000 | -5.836066000000 | -2.019855000000 |
| H                                                      | -0.755842000000 | 6.379646000000  | 4.695086000000  | H  | -0.663983000000 | -4.956070000000 | -3.559483000000 |
| H                                                      | -1.383334000000 | 6.982515000000  | 3.148140000000  | H  | 0.507394000000  | -6.244906000000 | -3.269794000000 |
| H                                                      | -1.799371000000 | 5.358969000000  | 3.700162000000  | C  | 3.201596000000  | -1.591995000000 | -3.469498000000 |
| C                                                      | 1.552114000000  | 5.257618000000  | -0.619308000000 | H  | 2.993833000000  | -1.825913000000 | -4.517907000000 |
| H                                                      | 2.315254000000  | 6.000020000000  | -0.881768000000 | H  | 2.816332000000  | -0.585521000000 | -3.266169000000 |
| H                                                      | 1.847522000000  | 4.321654000000  | -1.105143000000 | H  | 4.288640000000  | -1.558174000000 | -3.334362000000 |
| H                                                      | 0.602570000000  | 5.582495000000  | -1.050251000000 | C  | -2.633244000000 | -0.171067000000 | 1.863908000000  |
| C                                                      | 3.410668000000  | 3.611207000000  | 3.815011000000  | H  | -3.596874000000 | -0.356693000000 | 2.355907000000  |
| H                                                      | 3.226507000000  | 3.701965000000  | 4.889646000000  | H  | -2.759361000000 | 0.676613000000  | 1.195755000000  |
| H                                                      | 3.466786000000  | 2.544316000000  | 3.569500000000  | C  | -1.609551000000 | 0.051984000000  | 2.906307000000  |
| H                                                      | 4.396771000000  | 4.038904000000  | 3.599934000000  | C  | -0.724156000000 | 1.173909000000  | 2.921702000000  |
| C                                                      | 2.484562000000  | -3.541584000000 | 1.173026000000  | C  | 0.448786000000  | 1.193708000000  | 3.875817000000  |
| H                                                      | 3.517656000000  | -3.831898000000 | 1.392347000000  | H  | 1.031970000000  | 0.273632000000  | 3.790597000000  |
| H                                                      | 2.327781000000  | -2.547510000000 | 1.606634000000  | H  | 1.102791000000  | 2.032372000000  | 3.640818000000  |
| H                                                      | 1.827307000000  | -4.249517000000 | 1.688075000000  | H  | 0.117528000000  | 1.303913000000  | 4.914951000000  |
| C                                                      | -0.024886000000 | -5.410469000000 | -2.794811000000 | C  | -0.961866000000 | 2.247947000000  | 2.108736000000  |
| H                                                      | -1.142717000000 | -0.552997000000 | 4.916527000000  | H  | -1.811369000000 | 2.321864000000  | 1.441721000000  |
| H                                                      | -2.362869000000 | -1.580104000000 | 4.088472000000  | H  | -0.307651000000 | 3.112888000000  | 2.129548000000  |
| H                                                      | -0.661792000000 | -1.663800000000 | 3.637494000000  | C  | -1.464805000000 | -0.976891000000 | 3.962232000000  |
| Cartesian Coordinates for <b>TS2<sup>CPA</sup>Me-R</b> |                 |                 |                 | H  | -2.652393000000 | -5.822032000000 | 1.425341000000  |
| C                                                      | 8.626397000000  | -1.953979000000 | 0.986288000000  | H  | 0.203099000000  | -3.602628000000 | 3.764864000000  |
| C                                                      | 7.544046000000  | -2.602677000000 | 0.439251000000  | H  | -0.867836000000 | -5.767749000000 | 3.169564000000  |
| C                                                      | 6.364198000000  | -1.888436000000 | 0.093483000000  | C  | -2.540352000000 | -1.144542000000 | -2.301637000000 |
| C                                                      | 6.316937000000  | -0.469455000000 | 0.283509000000  | C  | -2.499040000000 | -2.545058000000 | -2.331433000000 |
| C                                                      | 7.443209000000  | 0.163479000000  | 0.880750000000  | C  | -3.594170000000 | -0.411329000000 | -2.853887000000 |
| C                                                      | 8.564764000000  | -0.559297000000 | 1.222266000000  | C  | -3.565567000000 | -3.219323000000 | -2.907751000000 |
| H                                                      | 5.258328000000  | -3.641768000000 | -0.519433000000 | H  | -1.659176000000 | -3.079888000000 | -1.904480000000 |
| H                                                      | 9.521263000000  | -2.508991000000 | 1.252788000000  | C  | -4.638167000000 | -1.117284000000 | -3.443364000000 |
| H                                                      | 7.566325000000  | -3.677129000000 | 0.275630000000  | H  | -3.596491000000 | 0.671914000000  | -2.816776000000 |
| C                                                      | 5.218726000000  | -2.562855000000 | -0.394231000000 | C  | -4.655405000000 | -2.519986000000 | -3.456258000000 |
| C                                                      | 5.129067000000  | 0.242887000000  | -0.103748000000 | H  | -3.565680000000 | -4.304386000000 | -2.916240000000 |
| H                                                      | 7.412960000000  | 1.228529000000  | 1.076901000000  | H  | -5.470749000000 | -0.567866000000 | -3.871570000000 |
| H                                                      | 9.409202000000  | -0.054027000000 | 1.682402000000  | C  | -5.843036000000 | -3.273571000000 | -3.988450000000 |
| C                                                      | 4.027752000000  | -0.495979000000 | -0.511649000000 | H  | -5.535916000000 | -4.164465000000 | -4.545839000000 |
| C                                                      | 4.034422000000  | -1.906034000000 | -0.661227000000 | H  | -6.457793000000 | -3.614083000000 | -3.145220000000 |
| C                                                      | 5.056870000000  | 1.728043000000  | -0.016586000000 | H  | -6.465549000000 | -2.648865000000 | -4.635061000000 |
| C                                                      | 6.008921000000  | 2.579786000000  | -0.676393000000 | Fe | -6.517978000000 | -3.274278000000 | 0.642694000000  |
| C                                                      | 4.046625000000  | 2.332904000000  | 0.710864000000  | Cl | -5.625833000000 | -4.970308000000 | -0.559516000000 |
| C                                                      | 6.980058000000  | 2.088185000000  | -1.591729000000 | Cl | -5.972724000000 | -1.312298000000 | -0.337948000000 |
| C                                                      | 5.964693000000  | 3.990617000000  | -0.427299000000 | Cl | -5.709219000000 | -3.238651000000 | 2.754887000000  |
| C                                                      | 3.952741000000  | 3.731292000000  | 0.937937000000  | Cl | -8.741034000000 | -3.516102000000 | 0.683613000000  |

## Chapter 4

|                                                  |                 |                 |                 |   |                 |                 |                 |
|--------------------------------------------------|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| C                                                | 7.881639000000  | 2.938822000000  | -2.192555000000 | H | 1.069418000000  | -3.720008000000 | -3.770905000000 |
| H                                                | 7.001604000000  | 1.029646000000  | -1.823228000000 | H | 0.535796000000  | -4.792615000000 | 0.346752000000  |
| C                                                | 6.922633000000  | 4.838096000000  | -1.047996000000 | H | -0.046512000000 | 6.090062000000  | 1.050042000000  |
| C                                                | 4.943578000000  | 4.524335000000  | 0.398797000000  | H | 1.299310000000  | 4.344214000000  | 4.727367000000  |
| C                                                | 7.865464000000  | 4.325744000000  | -1.909085000000 | C | -0.807873000000 | 5.691002000000  | 3.645091000000  |
| H                                                | 8.609335000000  | 2.541860000000  | -2.894550000000 | H | -0.633353000000 | 5.953248000000  | 4.694295000000  |
| H                                                | 6.884074000000  | 5.904415000000  | -0.840138000000 | H | -1.255557000000 | 6.556142000000  | 3.145282000000  |
| H                                                | 4.918171000000  | 5.596324000000  | 0.573213000000  | H | -1.554629000000 | 4.884891000000  | 3.633052000000  |
| H                                                | 8.587959000000  | 4.983143000000  | -2.384047000000 | C | 2.049786000000  | 5.423344000000  | -0.505838000000 |
| P                                                | 1.955107000000  | 0.834307000000  | 0.342348000000  | H | 2.834556000000  | 6.179935000000  | -0.623238000000 |
| O                                                | 3.057782000000  | 1.526610000000  | 1.299059000000  | H | 2.365991000000  | 4.554673000000  | -1.094303000000 |
| O                                                | 2.841014000000  | 0.181454000000  | -0.844229000000 | H | 1.133860000000  | 5.820304000000  | -0.947498000000 |
| O                                                | 1.120914000000  | -0.100272000000 | 1.155690000000  | C | 3.602208000000  | 3.254172000000  | 3.837558000000  |
| H                                                | -0.512386000000 | -0.491770000000 | 0.604931000000  | H | 3.458273000000  | 3.404296000000  | 4.911927000000  |
| O                                                | 1.157726000000  | 1.977394000000  | -0.373530000000 | H | 3.509399000000  | 2.181294000000  | 3.632196000000  |
| C                                                | 2.824731000000  | -2.696236000000 | -1.045554000000 | H | 4.628817000000  | 3.542086000000  | 3.586419000000  |
| C                                                | 2.138558000000  | -3.419040000000 | -0.048234000000 | C | 2.525463000000  | -3.299416000000 | 1.408503000000  |
| C                                                | 2.422067000000  | -2.783024000000 | -2.390365000000 | H | 3.588063000000  | -3.508192000000 | 1.569098000000  |
| C                                                | 1.072771000000  | -4.243309000000 | -0.422822000000 | H | 2.332577000000  | -2.283028000000 | 1.772484000000  |
| C                                                | 1.368903000000  | -3.639807000000 | -2.727659000000 | H | 1.945245000000  | -3.992442000000 | 2.021399000000  |
| C                                                | 0.691641000000  | -4.388657000000 | -1.760995000000 | C | -0.397149000000 | -5.366431000000 | -2.144783000000 |
| C                                                | 2.781368000000  | 4.299920000000  | 1.665489000000  | H | -1.178029000000 | -5.418954000000 | -1.376869000000 |
| C                                                | 2.591779000000  | 4.045462000000  | 3.039304000000  | H | -0.866111000000 | -5.098696000000 | -3.098032000000 |
| C                                                | 1.839388000000  | 5.068804000000  | 0.949521000000  | H | 0.008647000000  | -6.380287000000 | -2.257546000000 |
| C                                                | 1.442588000000  | 4.536861000000  | 3.665723000000  | C | 3.100791000000  | -1.948536000000 | -3.450178000000 |
| C                                                | 0.690258000000  | 5.518435000000  | 1.610028000000  | H | 2.760266000000  | -2.224146000000 | -4.452876000000 |
| C                                                | 0.466216000000  | 5.251342000000  | 2.963526000000  | H | 2.877008000000  | -0.884993000000 | -3.298388000000 |
| Fe                                               | 0.171380000000  | 2.467510000000  | -1.869040000000 | H | 4.191162000000  | -2.056442000000 | -3.416572000000 |
| Cl                                               | -1.154101000000 | 4.227138000000  | -1.532606000000 | C | -3.444597000000 | -0.373884000000 | 1.766976000000  |
| Cl                                               | 1.249200000000  | 2.447724000000  | -3.794973000000 | H | -4.197046000000 | -1.065618000000 | 2.147986000000  |
| N                                                | -1.464409000000 | -0.379576000000 | 0.192876000000  | H | -3.961301000000 | 0.361215000000  | 1.141877000000  |
| C                                                | -2.527675000000 | -1.218485000000 | 0.776588000000  | C | -2.676475000000 | 0.265072000000  | 2.860656000000  |
| S                                                | -1.206237000000 | -0.333090000000 | -1.501643000000 | C | -1.716649000000 | 1.229626000000  | 2.542507000000  |
| H                                                | -3.225082000000 | -1.489570000000 | -0.015131000000 | C | -0.639375000000 | 1.654722000000  | 3.518935000000  |
| O                                                | -1.335193000000 | 1.140433000000  | -1.854365000000 | H | -0.097803000000 | 0.792114000000  | 3.919769000000  |
| O                                                | 0.087196000000  | -0.945751000000 | -1.776939000000 | H | 0.084994000000  | 2.315955000000  | 3.041172000000  |
| C                                                | -1.993102000000 | -2.482875000000 | 1.419214000000  | H | -1.076238000000 | 2.202180000000  | 4.361624000000  |
| C                                                | -2.581201000000 | -3.703843000000 | 1.074818000000  | C | -1.679999000000 | 1.691163000000  | 1.226260000000  |
| C                                                | -0.974664000000 | -2.456832000000 | 2.380277000000  | H | -2.556265000000 | 1.740860000000  | 0.594757000000  |
| C                                                | -2.175179000000 | -4.885159000000 | 1.697509000000  | H | -0.820954000000 | 2.250930000000  | 0.873109000000  |
| H                                                | -3.374735000000 | -3.736125000000 | 0.336723000000  | C | -2.851705000000 | -0.291219000000 | 4.230320000000  |
| C                                                | -0.578713000000 | -3.635754000000 | 3.012212000000  | H | -2.203133000000 | 0.160783000000  | 4.980588000000  |
| H                                                | -0.477982000000 | -1.524577000000 | 2.635883000000  | H | -3.900477000000 | -0.150771000000 | 4.528470000000  |
| C                                                | -1.179067000000 | -4.852166000000 | 2.674941000000  | H | -2.693458000000 | -1.377210000000 | 4.213235000000  |
| Cartesian Coordinates for CP3 <sup>CPAMe-R</sup> |                 |                 |                 | C | 1.762524000000  | 5.287032000000  | 1.179898000000  |

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 8.516401000000  | -1.799661000000 | 1.098956000000  | C  | 1.478623000000  | 4.763060000000  | 3.911601000000  |
| C | 7.447149000000  | -2.460520000000 | 0.540496000000  | C  | 0.704124000000  | 5.836461000000  | 1.912797000000  |
| C | 6.257446000000  | -1.762071000000 | 0.196828000000  | C  | 0.542302000000  | 5.585867000000  | 3.277741000000  |
| C | 6.185804000000  | -0.346847000000 | 0.405686000000  | Fe | 0.362167000000  | 2.482244000000  | -1.951450000000 |
| C | 7.300589000000  | 0.299806000000  | 1.008956000000  | Cl | -0.953510000000 | 4.266037000000  | -1.909043000000 |
| C | 8.432655000000  | -0.408180000000 | 1.346793000000  | Cl | 1.686241000000  | 2.175448000000  | -3.674417000000 |
| H | 5.195886000000  | -3.518959000000 | -0.482423000000 | N  | -1.676538000000 | 0.003849000000  | 0.411572000000  |
| H | 9.418959000000  | -2.342854000000 | 1.363734000000  | C  | -2.710780000000 | -0.997769000000 | 0.958906000000  |
| H | 7.488576000000  | -3.532431000000 | 0.364638000000  | S  | -1.271199000000 | -0.267939000000 | -1.430327000000 |
| C | 5.131042000000  | -2.446035000000 | -0.321845000000 | H  | -3.379197000000 | -1.232809000000 | 0.130867000000  |
| C | 4.986829000000  | 0.350215000000  | 0.026336000000  | O  | -1.209957000000 | 1.136763000000  | -1.959218000000 |
| H | 7.252213000000  | 1.362894000000  | 1.213059000000  | O  | -0.070215000000 | -1.079594000000 | -1.393593000000 |
| H | 9.268288000000  | 0.106116000000  | 1.812885000000  | C  | -2.048111000000 | -2.261294000000 | 1.454189000000  |
| C | 3.899221000000  | -0.401776000000 | -0.389839000000 | C  | -2.525804000000 | -3.490555000000 | 0.989142000000  |
| C | 3.938237000000  | -1.804753000000 | -0.588512000000 | C  | -1.084214000000 | -2.236725000000 | 2.472633000000  |
| C | 4.901508000000  | 1.834740000000  | 0.104637000000  | C  | -2.057131000000 | -4.685605000000 | 1.536074000000  |
| C | 5.838024000000  | 2.681108000000  | -0.583309000000 | H  | -3.299019000000 | -3.522134000000 | 0.230153000000  |
| C | 3.898012000000  | 2.442859000000  | 0.838193000000  | C  | -0.619511000000 | -3.431239000000 | 3.020225000000  |
| C | 6.796132000000  | 2.181611000000  | -1.508254000000 | H  | -0.701970000000 | -1.291480000000 | 2.844991000000  |
| C | 5.787354000000  | 4.094807000000  | -0.355813000000 | C  | -1.105693000000 | -4.657808000000 | 2.556435000000  |
| C | 3.805474000000  | 3.842091000000  | 1.058789000000  | H  | -2.456205000000 | -5.629086000000 | 1.175478000000  |
| C | 7.677500000000  | 3.029991000000  | -2.141403000000 | H  | 0.123212000000  | -3.403399000000 | 3.811821000000  |
| H | 6.822999000000  | 1.119712000000  | -1.722777000000 | H  | -0.744360000000 | -5.585146000000 | 2.991837000000  |
| C | 6.725229000000  | 4.940289000000  | -1.009266000000 | C  | -2.620028000000 | -1.056045000000 | -2.199625000000 |
| C | 4.783071000000  | 4.631165000000  | 0.487699000000  | C  | -2.586168000000 | -2.457144000000 | -2.253467000000 |
| C | 7.654357000000  | 4.421484000000  | -1.881241000000 | C  | -3.687812000000 | -0.301410000000 | -2.706348000000 |
| H | 8.394738000000  | 2.627521000000  | -2.850956000000 | C  | -3.669256000000 | -3.111222000000 | -2.820532000000 |
| H | 6.682242000000  | 6.009380000000  | -0.817344000000 | H  | -1.736886000000 | -3.002158000000 | -1.860703000000 |
| H | 4.760589000000  | 5.703929000000  | 0.656774000000  | C  | -4.752813000000 | -0.990074000000 | -3.269144000000 |
| H | 8.361185000000  | 5.076772000000  | -2.381951000000 | H  | -3.680378000000 | 0.781646000000  | -2.657688000000 |
| P | 1.818537000000  | 0.940132000000  | 0.474709000000  | C  | -4.776742000000 | -2.395436000000 | -3.307778000000 |
| O | 2.911608000000  | 1.633871000000  | 1.434092000000  | H  | -3.672594000000 | -4.194888000000 | -2.857841000000 |
| O | 2.695492000000  | 0.254899000000  | -0.698250000000 | H  | -5.597165000000 | -0.430095000000 | -3.658261000000 |
| O | 0.936760000000  | 0.040272000000  | 1.278673000000  | C  | -5.993438000000 | -3.128696000000 | -3.794740000000 |
| H | -0.716400000000 | -0.177812000000 | 0.815228000000  | H  | -5.726388000000 | -4.054414000000 | -4.313447000000 |
| O | 1.039859000000  | 2.073833000000  | -0.281278000000 | H  | -6.603707000000 | -3.407798000000 | -2.925567000000 |
| C | 2.758583000000  | -2.594763000000 | -1.054380000000 | H  | -6.605829000000 | -2.510262000000 | -4.456775000000 |
| C | 2.064557000000  | -3.399342000000 | -0.129480000000 | Fe | -6.443276000000 | -3.475723000000 | 0.703180000000  |
| C | 2.390635000000  | -2.592501000000 | -2.413006000000 | Cl | -5.455993000000 | -5.046445000000 | -0.590618000000 |
| C | 1.027744000000  | -4.217513000000 | -0.589025000000 | Cl | -6.074479000000 | -1.424977000000 | -0.188197000000 |
| C | 1.359913000000  | -3.438740000000 | -2.835600000000 | Cl | -5.573576000000 | -3.511542000000 | 2.780579000000  |
| C | 0.676210000000  | -4.268657000000 | -1.941430000000 | Cl | -8.658556000000 | -3.800800000000 | 0.763762000000  |
| C | 2.679899000000  | 4.437791000000  | 1.835730000000  | H  | 1.086534000000  | -3.450052000000 | -3.889132000000 |
| C | 2.541625000000  | 4.179442000000  | 3.216661000000  | H  | 0.484834000000  | -4.829811000000 | 0.126202000000  |
| H | 1.380639000000  | 4.571931000000  | 4.978471000000  | H  | -0.006437000000 | 6.483949000000  | 1.402817000000  |
| C | -0.625401000000 | 6.160712000000  | 4.043742000000  | H  | 1.802032000000  | -4.083269000000 | 1.899439000000  |

## Chapter 4

|   |                 |                 |                 |   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| H | -0.346828000000 | 6.406482000000  | 5.074256000000  | C | -0.390680000000 | -5.227323000000 | -2.422074000000 |
| H | -1.012059000000 | 7.067830000000  | 3.567922000000  | H | -1.155012000000 | -5.395217000000 | -1.654174000000 |
| H | -1.452089000000 | 5.439553000000  | 4.095132000000  | H | -0.885876000000 | -4.862125000000 | -3.328714000000 |
| C | 1.906320000000  | 5.644078000000  | -0.283425000000 | H | 0.041383000000  | -6.207438000000 | -2.662816000000 |
| H | 2.664480000000  | 6.423354000000  | -0.430692000000 | C | 3.084232000000  | -1.680673000000 | -3.397627000000 |
| H | 2.219368000000  | 4.787855000000  | -0.888914000000 | H | 2.780484000000  | -1.901326000000 | -4.425543000000 |
| H | 0.963165000000  | 6.019648000000  | -0.686725000000 | H | 2.837141000000  | -0.631256000000 | -3.192396000000 |
| C | 3.527603000000  | 3.305897000000  | 3.958445000000  | H | 4.174886000000  | -1.771813000000 | -3.336162000000 |
| H | 3.459673000000  | 3.469336000000  | 5.038210000000  | C | -3.568108000000 | -0.298927000000 | 2.045231000000  |
| H | 3.335465000000  | 2.244043000000  | 3.766591000000  | H | -4.056245000000 | -1.094303000000 | 2.613038000000  |
| H | 4.558442000000  | 3.507438000000  | 3.647168000000  | H | -4.375415000000 | 0.252870000000  | 1.546450000000  |
| C | 2.410915000000  | -3.368648000000 | 1.341961000000  | C | -2.767337000000 | 0.632659000000  | 2.926742000000  |
| H | 3.465466000000  | -3.603384000000 | 1.520112000000  | C | -1.986049000000 | 1.523395000000  | 2.289122000000  |
| H | 2.224162000000  | -2.371938000000 | 1.760489000000  | C | -1.061805000000 | 2.547207000000  | 2.883834000000  |
| H | -1.228701000000 | 2.075191000000  | 0.344864000000  | H | -0.013864000000 | 2.276744000000  | 2.706017000000  |
| C | -2.914919000000 | 0.468412000000  | 4.410592000000  | H | -1.210191000000 | 3.529609000000  | 2.421218000000  |
| H | -2.349781000000 | 1.205913000000  | 4.984214000000  | H | -1.198704000000 | 2.659483000000  | 3.961215000000  |
| H | -3.971683000000 | 0.541545000000  | 4.698395000000  | C | -1.997146000000 | 1.443530000000  | 0.778406000000  |
| H | -2.578314000000 | -0.533324000000 | 4.708872000000  | H | -2.962023000000 | 1.688992000000  | 0.325433000000  |

### Cartesian Coordinates for CP4<sup>CPAMe-R</sup>

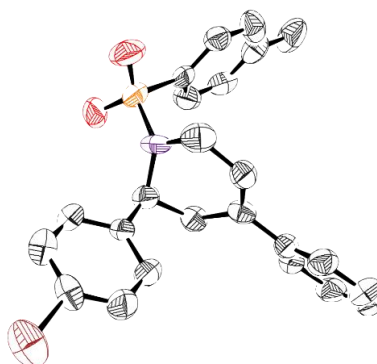
|   |                |                 |                 |    |                 |                 |                 |
|---|----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 8.326056000000 | -2.019842000000 | -0.411212000000 | C  | -3.448086000000 | -2.439969000000 | -1.914957000000 |
| C | 7.182229000000 | -2.683073000000 | -0.790226000000 | C  | -4.488350000000 | -0.242642000000 | -2.277549000000 |
| C | 5.951810000000 | -1.987738000000 | -0.945719000000 | C  | -4.653029000000 | -3.047623000000 | -2.236191000000 |
| C | 5.913097000000 | -0.568164000000 | -0.749582000000 | H  | -2.573083000000 | -3.023026000000 | -1.653818000000 |
| C | 7.106244000000 | 0.076655000000  | -0.318119000000 | C  | -5.678283000000 | -0.883412000000 | -2.598952000000 |
| C | 8.277750000000 | -0.628935000000 | -0.154023000000 | H  | -4.407431000000 | 0.838648000000  | -2.292838000000 |
| H | 4.787675000000 | -3.770607000000 | -1.331484000000 | C  | -5.788910000000 | -2.283289000000 | -2.553655000000 |
| H | 9.259130000000 | -2.561842000000 | -0.287188000000 | H  | -4.725718000000 | -4.129276000000 | -2.208343000000 |
| H | 7.194428000000 | -3.757090000000 | -0.957575000000 | H  | -6.547200000000 | -0.286985000000 | -2.859001000000 |
| C | 4.752207000000 | -2.689364000000 | -1.227037000000 | C  | -7.115658000000 | -2.956920000000 | -2.764778000000 |
| C | 4.672214000000 | 0.132569000000  | -0.963412000000 | H  | -7.003738000000 | -3.920039000000 | -3.272182000000 |
| H | 7.089011000000 | 1.138477000000  | -0.104962000000 | H  | -7.805858000000 | -2.329823000000 | -3.336315000000 |
| H | 9.171912000000 | -0.112605000000 | 0.183565000000  | Fe | -6.819891000000 | -3.227727000000 | 1.647062000000  |
| C | 3.533411000000 | -0.636231000000 | -1.172992000000 | Cl | -6.059741000000 | -4.906313000000 | 0.334936000000  |
| C | 3.531328000000 | -2.051356000000 | -1.291549000000 | Cl | -6.497747000000 | -1.217740000000 | 0.666026000000  |
| C | 4.605683000000 | 1.624634000000  | -0.899541000000 | Cl | -5.658178000000 | -3.227986000000 | 3.574071000000  |
| C | 5.486973000000 | 2.474688000000  | -1.661298000000 | Cl | -9.005644000000 | -3.501401000000 | 2.057958000000  |
| C | 3.692550000000 | 2.246023000000  | -0.061831000000 | H  | 0.029421000000  | -4.127784000000 | -3.599286000000 |
| C | 6.372229000000 | 1.981294000000  | -2.658549000000 | H  | 0.154693000000  | -4.564226000000 | 0.661255000000  |
| C | 5.467413000000 | 3.889188000000  | -1.424841000000 | H  | -0.035305000000 | 6.085182000000  | 1.695862000000  |
| C | 3.661097000000 | 3.640473000000  | 0.201386000000  | H  | 2.590104000000  | 4.429100000000  | 4.650300000000  |
| C | 7.193808000000 | 2.827753000000  | -3.368643000000 | C  | 0.308808000000  | 5.906548000000  | 4.394888000000  |
| H | 6.387368000000 | 0.922273000000  | -2.873477000000 | H  | 0.887373000000  | 6.129767000000  | 5.297504000000  |
| C | 6.359195000000 | 4.731411000000  | -2.143751000000 | H  | -0.192799000000 | 6.825272000000  | 4.072784000000  |
| C | 4.562616000000 | 4.432279000000  | -0.475844000000 | H  | -0.474395000000 | 5.190392000000  | 4.677727000000  |

|    |                 |                 |                 |   |                 |                 |                 |
|----|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| C  | 7.200815000000  | 4.217250000000  | -3.102143000000 | C | 1.157495000000  | 5.138149000000  | -0.498708000000 |
| H  | 7.841547000000  | 2.421373000000  | -4.139881000000 | H | 1.442864000000  | 6.126881000000  | -0.881888000000 |
| H  | 6.347783000000  | 5.796916000000  | -1.934922000000 | H | 1.566377000000  | 4.378701000000  | -1.165837000000 |
| H  | 4.587807000000  | 5.500177000000  | -0.276908000000 | H | 0.067865000000  | 5.077761000000  | -0.570888000000 |
| H  | 7.863260000000  | 4.874934000000  | -3.657366000000 | C | 4.326515000000  | 3.191649000000  | 2.990800000000  |
| P  | 1.542225000000  | 0.800719000000  | -0.180626000000 | H | 4.518727000000  | 3.248078000000  | 4.066227000000  |
| O  | 2.767061000000  | 1.469095000000  | 0.643049000000  | H | 4.188157000000  | 2.135404000000  | 2.729729000000  |
| O  | 2.303065000000  | -0.004004000000 | -1.368893000000 | H | 5.223988000000  | 3.536624000000  | 2.464426000000  |
| O  | 0.739370000000  | -0.009486000000 | 0.781899000000  | C | 2.351895000000  | -3.072800000000 | 1.153637000000  |
| H  | -0.955306000000 | -0.245090000000 | 0.658426000000  | H | 3.417646000000  | -3.325989000000 | 1.169713000000  |
| O  | 0.770599000000  | 1.899235000000  | -0.969642000000 | H | 2.263408000000  | -2.006495000000 | 1.393129000000  |
| C  | 2.262512000000  | -2.843647000000 | -1.379807000000 | H | 1.853720000000  | -3.632346000000 | 1.948928000000  |
| C  | 1.721429000000  | -3.370548000000 | -0.188103000000 | C | -1.243447000000 | -5.381859000000 | -1.525679000000 |
| C  | 1.641468000000  | -3.108774000000 | -2.613421000000 | H | -1.919608000000 | -5.199430000000 | -0.683162000000 |
| C  | 0.575299000000  | -4.167374000000 | -0.257951000000 | H | -1.807682000000 | -5.260045000000 | -2.456880000000 |
| C  | 0.502281000000  | -3.920172000000 | -2.641388000000 | H | -0.937915000000 | -6.434816000000 | -1.466641000000 |
| C  | -0.042166000000 | -4.464924000000 | -1.476676000000 | C | 2.181342000000  | -2.527935000000 | -3.896572000000 |
| C  | 2.761345000000  | 4.201827000000  | 1.256486000000  | H | 1.625112000000  | -2.896505000000 | -4.763754000000 |
| C  | 3.111038000000  | 4.006829000000  | 2.612291000000  | H | 2.099375000000  | -1.435837000000 | -3.897195000000 |
| C  | 1.613230000000  | 4.943772000000  | 0.927339000000  | H | 3.237715000000  | -2.781411000000 | -4.041948000000 |
| C  | 2.316257000000  | 4.578039000000  | 3.607768000000  | C | -3.630134000000 | -0.089137000000 | 2.299698000000  |
| C  | 0.851587000000  | 5.510296000000  | 1.957344000000  | H | -4.124541000000 | -0.809884000000 | 2.955680000000  |
| C  | 1.181550000000  | 5.338301000000  | 3.301481000000  | H | -4.433109000000 | 0.505136000000  | 1.844611000000  |
| Fe | 0.180907000000  | 2.168296000000  | -2.755827000000 | C | -2.667441000000 | 0.807636000000  | 3.043312000000  |
| Cl | -1.146928000000 | 3.944470000000  | -2.978834000000 | C | -1.890811000000 | 1.597222000000  | 2.279997000000  |
| Cl | 0.053592000000  | 0.743231000000  | -4.478659000000 | C | -0.831539000000 | 2.563262000000  | 2.724564000000  |
| N  | -1.953842000000 | -0.004235000000 | 0.430181000000  | H | 0.156740000000  | 2.249377000000  | 2.366056000000  |
| C  | -2.934884000000 | -0.907754000000 | 1.183456000000  | H | -1.008612000000 | 3.561076000000  | 2.307605000000  |
| S  | -1.880430000000 | -0.290493000000 | -1.462309000000 | H | -0.779802000000 | 2.660546000000  | 3.810973000000  |
| H  | -3.709243000000 | -1.196071000000 | 0.473255000000  | C | -2.082290000000 | 1.466156000000  | 0.784264000000  |
| O  | -1.824349000000 | 1.090733000000  | -1.987018000000 | H | -3.066773000000 | 1.796619000000  | 0.438694000000  |
| O  | -0.755288000000 | -1.200519000000 | -1.604316000000 | H | -1.316493000000 | 1.997960000000  | 0.223413000000  |
| C  | -2.255290000000 | -2.147814000000 | 1.719427000000  | C | -2.658059000000 | 0.710369000000  | 4.540766000000  |
| C  | -2.862378000000 | -3.386224000000 | 1.488418000000  | H | -1.970472000000 | 1.413735000000  | 5.015406000000  |
| C  | -1.138360000000 | -2.076902000000 | 2.564829000000  | H | -3.664610000000 | 0.889036000000  | 4.940834000000  |
| C  | -2.379210000000 | -4.539806000000 | 2.107491000000  | H | -2.376513000000 | -0.306648000000 | 4.844758000000  |
| H  | -3.744951000000 | -3.448568000000 | 0.861348000000  | N | 3.509338000000  | 4.724005000000  | -4.593874000000 |
| C  | -0.656369000000 | -3.230402000000 | 3.182808000000  | C | 3.353050000000  | 5.527070000000  | -3.593146000000 |
| H  | -0.651234000000 | -1.125313000000 | 2.751794000000  | S | 2.525873000000  | 3.370346000000  | -4.683491000000 |
| C  | -1.278491000000 | -4.463217000000 | 2.962272000000  | H | 2.643118000000  | 5.305750000000  | -2.794422000000 |
| H  | -2.879657000000 | -5.487629000000 | 1.932456000000  | O | 1.947463000000  | 3.062524000000  | -3.306441000000 |
| H  | 0.203077000000  | -3.163490000000 | 3.843422000000  | O | 1.573609000000  | 3.568886000000  | -5.775045000000 |
| H  | -0.904770000000 | -5.357206000000 | 3.453482000000  | C | 4.132441000000  | 6.746733000000  | -3.466034000000 |
| C  | -3.389751000000 | -1.039625000000 | -1.932661000000 | C | 3.925838000000  | 7.562630000000  | -2.339752000000 |
| H  | 3.166523000000  | 7.293978000000  | -1.611788000000 | C | 5.118036000000  | 7.095666000000  | -4.409290000000 |
| C  | 5.886201000000  | 8.236642000000  | -4.217537000000 | C | 4.699447000000  | 8.705392000000  | -2.150987000000 |

## Chapter 4

|   |                |                 |                 |   |                |                 |                 |
|---|----------------|-----------------|-----------------|---|----------------|-----------------|-----------------|
| H | 5.275855000000 | 6.456780000000  | -5.271521000000 | C | 5.522892000000 | 0.067886000000  | -5.618624000000 |
| C | 5.680998000000 | 9.040125000000  | -3.087436000000 | H | 4.612327000000 | -0.979583000000 | -3.969985000000 |
| H | 4.539575000000 | 9.330701000000  | -1.278174000000 | H | 6.205845000000 | 1.378816000000  | -7.191733000000 |
| H | 6.649524000000 | 8.503846000000  | -4.941964000000 | C | 6.548718000000 | -1.004820000000 | -5.884053000000 |
| H | 6.287865000000 | 9.928819000000  | -2.939794000000 | H | 6.146022000000 | -2.001101000000 | -5.675701000000 |
| C | 3.697984000000 | 2.088555000000  | -5.035919000000 | H | 6.899792000000 | -0.981137000000 | -6.920108000000 |
| C | 3.682266000000 | 0.922004000000  | -4.274075000000 | H | 7.423276000000 | -0.864825000000 | -5.234902000000 |
| C | 4.592516000000 | 2.266809000000  | -6.096539000000 | C | 5.500140000000 | 1.250151000000  | -6.375884000000 |
| C | 4.599399000000 | -0.080254000000 | -4.576017000000 | H | 4.587096000000 | 3.180711000000  | -6.680248000000 |
| H | 2.985964000000 | 0.809463000000  | -3.455263000000 |   |                |                 |                 |

ORTEP Drawing of **4da** ( $\text{C}_{24}\text{H}_{22}\text{BrNO}_2\text{S}$ ,  $M = 468.41$ ,  $T = 293(0)$  K)



|                                       |                                                                                     |
|---------------------------------------|-------------------------------------------------------------------------------------|
| Wavelength                            | MoK $\alpha$ ( $\lambda = 0.71075$ Å)                                               |
| Crystal System                        | monoclinic                                                                          |
| Space Group                           | C2 (#5)                                                                             |
| Crystal Dimensions                    | $0.200 \times 0.100 \times 0.100$ mm                                                |
| Lattice Parameters                    | $a = 18.031(2)$ Å<br>$b = 8.3779(9)$ Å $\beta = 106.372^\circ$<br>$c = 29.676(3)$ Å |
| Volume                                | $V = 4301.2(8)$ Å <sup>3</sup>                                                      |
| Z value                               | 8                                                                                   |
| $D_{\text{calc}}$                     | $1.447$ g/cm <sup>3</sup>                                                           |
| $2\theta_{\text{max}}$                | $55.0^\circ$                                                                        |
| Reflections collected                 | 20778                                                                               |
| Independent reflections               | 9715 ( $R_{\text{int}} = 0.0944$ )                                                  |
| No. Variables                         | 527                                                                                 |
| Goodness of Fit Indicator             | 0.983                                                                               |
| Residuals: $R_1$ ( $I > 2\sigma(I)$ ) | $R_1 = 0.0651$                                                                      |
| Residuals: $R$ (All reflections)      | $R_1 = 0.1721$ , $wR_2 = 0.1099$                                                    |
| Flack Parameter                       | $0.003(10)$                                                                         |

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## Chapter 5

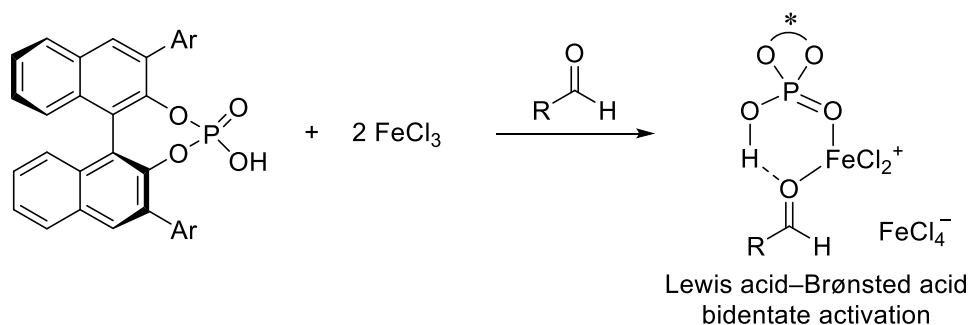
### **Multiple Activation Catalyst for Asymmetric Oxa-Diels–Alder Reaction of Non-Activated Substrates**

The enantioselective oxa-Diels–Alder reaction of non-activated substrates by utilizing  $\text{FeCl}_3$  and a BINOL-derived chiral phosphoric acid as a multiple activation catalyst is reported. Various oxygen containing six-membered hetero cycles were obtained in high yields and in an enantioselective manner. Density functional theory (DFT) calculations elucidate that two acidic moieties in the catalyst system are crucial for efficient activation and enantioselective addition reaction of dienes.

## Introduction

The oxa-Diels–Alder reaction is one of the most attractive methods to afford an oxygen containing six-membered heterocycle which is an important structure especially for marine natural products and pharmaceuticals.<sup>1</sup> Although many studies on catalytic enantioselective oxa-Diels–Alder reactions have been investigated, most required electronically-biased substrates to obtain satisfying yields and enantioselectivity. Recently, the List group reported the well-designed Brønsted acid catalyst to apply non-activated substrates; however, the development of a practical catalyst system is still in demand.<sup>2,3</sup>

In Chapter 4, the combination of  $\text{FeCl}_3$  and a chiral phosphoric acid was demonstrated to be beneficial for efficient activation of imines. This catalyst system has two disparate acidic sites, the Lewis acidic  $[\text{FeCl}_2]^+$  via disproportionation of  $\text{FeCl}_3$  and a Brønsted acidic proton, and these acidic sites synergistically activate the substrate;  $[\text{FeCl}_2]^+$  coordinates to the oxygen atom of sulfonyl groups, and the Brønsted acidic proton coordinates to the nitrogen atom of imine.<sup>4,5</sup> Hence, the author envisioned that this multiple activation system may be also employed for the efficient activation of aldehydes. Bidentate activation of carbonyl groups, where two acidic sites coordinate to each lone pair of a carbonyl oxygen atom, widely occurs in enzymatic reactions, and some organocatalysts, such as thiourea, which mimics these enzymes, have accomplished many sufficient reactions, according to studies in recent decades.<sup>6</sup> Furthermore, Maruoka and co-workers reported seminal works on the bidentate Lewis acid catalyst.<sup>7</sup> However, a catalyst which coordinates to carbonyls via the Lewis acid and Brønsted acid bidentate activation of the catalyst has not been reported to date. The Lewis acid and Brønsted acid bidentate activation would provide the advantage of fixing the orientation of the aldehyde by selectively coordinating the specific lone pair among two lone pairs in the carbonyl group.



**Scheme 1.** Lewis acid and Brønsted acid bidentate activation catalyst for aldehydes.

## Results and Discussion

At the outset, the reaction of 2-naphthaldehyde **1a** and diene **2a** was conducted in the presence of  $\text{FeCl}_3$  and chiral phosphoric acid **3a**, and the desired cycloadduct **4aa** was obtained in high yield and with moderate enantioselectivity (Table 1, entry 1). The use of  $\text{FeCl}_3$  or chiral phosphoric acid alone did not catalyze the reaction (entry 2 and 3), and employing  $\text{FeCl}_2$  or other metal halide Lewis acids ( $\text{AlCl}_3$ ,  $\text{RuCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{ScCl}_3$ ,  $\text{Sc}(\text{OTf})_3$ , etc.) did not give any products. This indicated that the formation of  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$  upon coordination of the chiral phosphoric acid to  $\text{FeCl}_3$  is the key for promoting the reaction. Then, the investigation on the effect of 3,3'-position substituents of chiral phosphoric acid catalyst was conducted, and the catalyst **3a** was determined as a suitable catalyst in terms of product yields and enantioselectivity (for further optimization of the reaction conditions, see the Supplemental Data). Performing the reaction at lower temperature ( $-50\text{ }^\circ\text{C}$ ) improved the enantioselectivity and gave the cycloadduct in an 83:17 enantiomeric ratio (entry 8). When benzaldehyde **1b** was used as the substrate, almost the same enantioselectivity was observed, and the product yield increased.

Notably, the disproportionation of  $\text{FeCl}_3$  was strongly indicated by the effect of catalyst loading. Regarding the use of 5 mol%  $\text{FeCl}_3$  and 2.5 mol% chiral phosphoric acid, both yield and enantioselectivity were not significantly affected (80% yields, 83:17 e.r.) (entry 10). In contrast, in the case of 2.5 mol%  $\text{FeCl}_3$  and 5 mol% chiral phosphoric acid, the desired product was obtained

in only 26% yield, although enantioselectivity was maintained (entry 11). Namely, only half the amount of chiral phosphoric acid compared to  $\text{FeCl}_3$  was sufficient to promote the reaction, which supported the fact that  $\text{FeCl}_3$  was disproportionated to generate the  $[\text{FeCl}_2]^+[\text{FeCl}_4]^-$  complex. Furthermore, the stronger Brønsted acidic chiral phosphoramidate **3f** or methyl ester **5** did not catalyze the reaction; thus, bidentate activation was strongly suggested (entry 12 and 13).

**Table 1.** Optimization for asymmetric oxa-Diels–Alder reaction of **1** and **2a**<sup>a</sup>

$\text{Ar}-\text{CHO} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{Ph} \xrightarrow[\text{toluene, } T\text{ }^\circ\text{C, 24 h}]{\text{FeCl}_3\text{ (x mol\%)} \text{ (S)-CPA } \mathbf{3}\text{ (y mol\%)}}$

**1a** (Ar = 2-Naphthyl)      **2a**      **4aa or 4ba**

**(S)-CPA 3a-3f**

**3a:**  $\text{R}_1 = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$ ,  $\text{R}_2 = \text{OH}$   
**3b:**  $\text{R}_1 = 2,4,6\text{-iPr}_3\text{C}_6\text{H}_2$ ,  $\text{R}_2 = \text{OH}$   
**3c:**  $\text{R}_1 = 2,4,6\text{-Et}_3\text{C}_6\text{H}_2$ ,  $\text{R}_2 = \text{OH}$   
**3d:**  $\text{R}_1 = 9\text{-anthracenyl}$ ,  $\text{R}_2 = \text{OH}$   
**3e:**  $\text{R}_1 = \text{SiPh}_3$ ,  $\text{R}_2 = \text{OH}$   
**3f:**  $\text{R}_1 = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$ ,  $\text{R}_2 = \text{NHTf}$

**(S)-5**  
Ar = 2,4,6-Et<sub>3</sub>C<sub>6</sub>H<sub>2</sub>

| entry | <b>1</b>  | $\text{FeCl}_3$<br>(x mol%) | (S)-CPA<br>(y mol%) | Temperature<br>(°C) | yield of <b>4</b><br>(%) <sup>b</sup> | e.r. of <b>4</b> <sup>c</sup> |
|-------|-----------|-----------------------------|---------------------|---------------------|---------------------------------------|-------------------------------|
| 1     | <b>1a</b> | 5                           | <b>3a</b> (5)       | 0                   | 90                                    | 74:26                         |
| 2     | <b>1a</b> | 5                           | none                | 0                   | <1                                    | —                             |
| 3     | <b>1a</b> | none                        | <b>3a</b> (5)       | 0                   | <1                                    | —                             |
| 4     | <b>1a</b> | 5                           | <b>3b</b> (5)       | 0                   | 39                                    | 77.5:22.5                     |
| 5     | <b>1a</b> | 5                           | <b>3c</b> (5)       | 0                   | 62                                    | 75.5:24:5                     |
| 6     | <b>1a</b> | 5                           | <b>3d</b> (5)       | 0                   | 11                                    | 79:21                         |
| 7     | <b>1a</b> | 5                           | <b>3e</b> (5)       | 0                   | 50                                    | 24:76                         |
| 8     | <b>1a</b> | 5                           | <b>3a</b> (5)       | −50                 | 53                                    | 83:17                         |

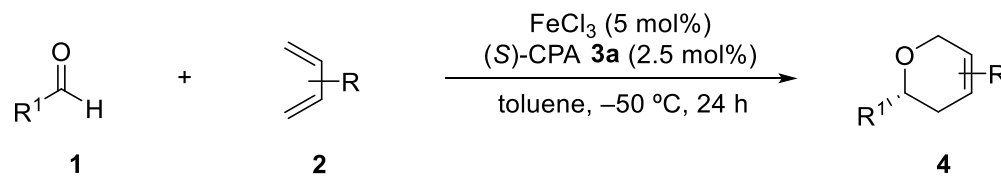
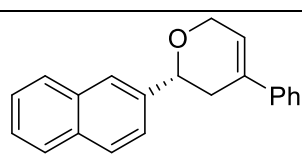
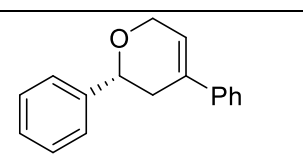
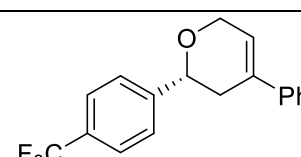
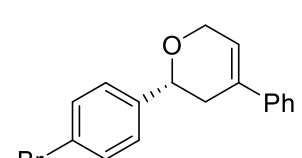
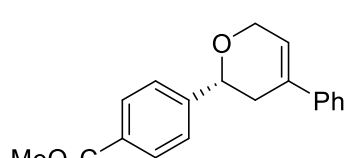
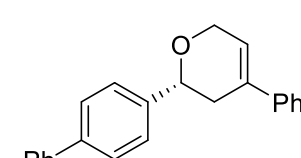
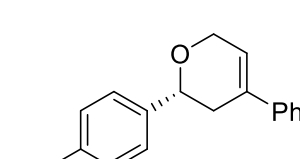
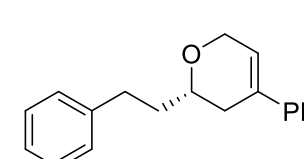
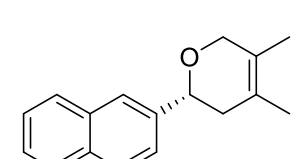
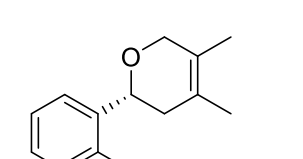
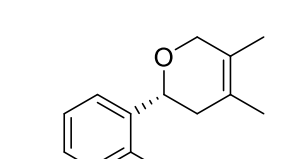
**Table 1.** (Continued)

|                 |           |     |                 |     |    |       |
|-----------------|-----------|-----|-----------------|-----|----|-------|
| 9               | <b>1b</b> | 5   | <b>3a</b> (5)   | −50 | 88 | 84:16 |
| 10              | <b>1b</b> | 5   | <b>3a</b> (2.5) | −50 | 80 | 83:17 |
| 11              | <b>1b</b> | 2.5 | <b>3a</b> (5)   | −50 | 26 | 84:16 |
| 12 <sup>c</sup> | <b>1a</b> | 5   | <b>3f</b> (5)   | 0   | <1 | —     |
| 13              | <b>1a</b> | 5   | <b>5</b> (5)    | 0   | <1 | —     |

<sup>a</sup>Reactions were carried out using **1** (0.15 mmol), **2a** (0.3 mmol), FeCl<sub>3</sub>, and chiral phosphoric acid with the indicated loading, in 1 mL of toluene for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by chiral HPLC analysis. <sup>c</sup>2,3-dimethyl-1,3-butadiene was used instead of **2a**.

Under the optimized reaction conditions, various aldehydes and dienes were examined for the asymmetric oxa-Diels–Alder reaction (Table 2). Aldehydes possessing electron-withdrawing groups, such as CF<sub>3</sub>, Br, and CO<sub>2</sub>Me, were successfully converted to the corresponding cycloadduct (**4ca–4ea**). The absolute configuration of the product was determined to be (*R*) by single crystal X-ray diffraction analysis of product **4da**. Of note, the less reactive 2,3-dimethyl-1,3-butadiene also reacted with various aldehydes, and even with *o*-anisaldehyde, which has an electron-donating substituent. The aliphatic aldehyde afforded the product in high yield, but the enantioselectivity significantly decreased.

**Table 2.** Substrate scope<sup>a</sup>

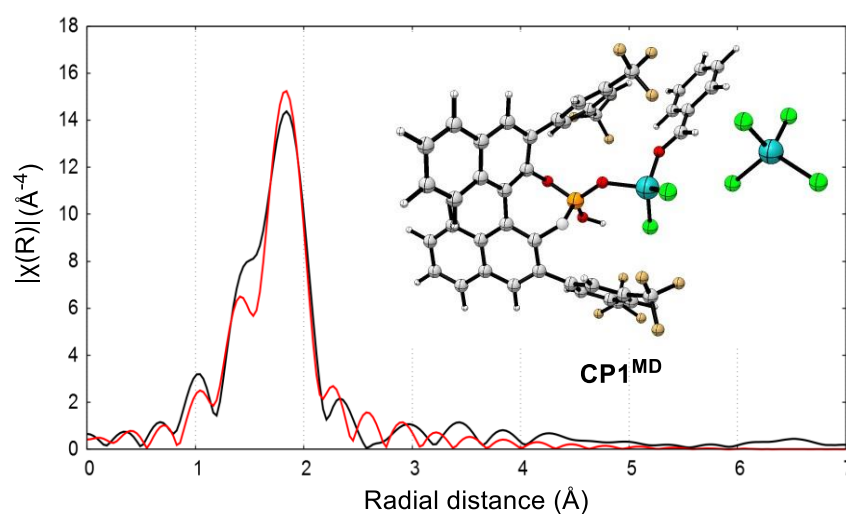
|                                                                                                                                      |                                                                                                                                       |                                                                                                                                        |
|--------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
|                                                    |                                                                                                                                       |                                                                                                                                        |
| <b>1</b> <b>2</b> <b>4</b>                                                                                                           |                                                                                                                                       |                                                                                                                                        |
| products <sup>b</sup>                                                                                                                |                                                                                                                                       |                                                                                                                                        |
| <br><b>4aa</b><br>53%, 83:17 e.r.                   | <br><b>4ba</b><br>80%, 83:17 e.r.                    | <br><b>4ca</b><br>92%, 77.5:22.5 e.r.               |
| <br><b>4da</b><br>90%, 81:19 e.r.                   | <br><b>4ea</b><br>83%, 81:19 e.r.                    | <br><b>4fa</b><br>48%, 80:20 e.r.                   |
| <br><b>4ga<sup>c</sup></b><br>78%, 64.5:35.5 e.r. | <br><b>4ha<sup>c</sup></b><br>49%, 57.5:42.5 e.r. |                                                                                                                                        |
| <br><b>4ab<sup>c</sup></b><br>92%, 73:27 e.r.     | <br><b>4ib<sup>c</sup></b><br>80%, 71.5:28.5 e.r.  | <br><b>4jb<sup>c</sup></b><br>56%, 53.5:46.5 e.r. |

<sup>a</sup>Reactions were carried out using FeCl<sub>3</sub> (5 mol%), chiral phosphoric acid **3a** (2.5 mol%), **1** (0.15 mmol), and **2** (0.3 mmol) in 1 mL of toluene for 24 h under –50 °C unless otherwise noted.

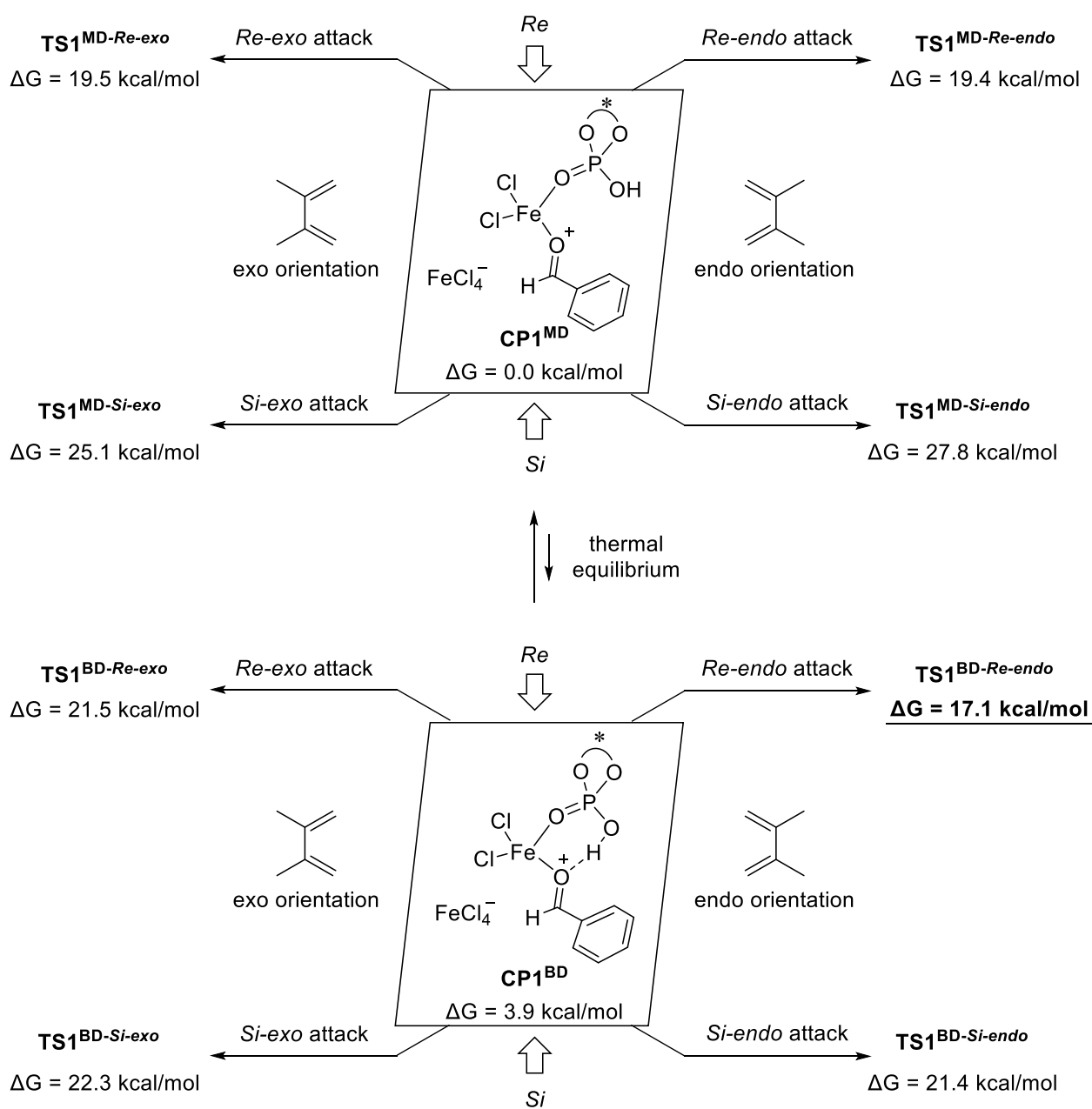
<sup>b</sup>Yields were isolated yield, and enantioselectivity was determined by chiral HPLC analysis.

<sup>c</sup>Reaction was conducted at 0 °C.

To obtain mechanistic insight, DFT calculations were conducted (the computational details are provided in the Supplemental Data). First, a mixture of  $\text{FeCl}_3$ , the chiral phosphoric acid **3a**, and aldehyde **1b** resulted in the formation of thermodynamically stable **CP1<sup>MD</sup>**, which is the monodentate complex in which aldehyde **1b** coordinated only to  $\text{FeCl}_2^+$  and not to the Brønsted acidic proton (Scheme 2); subsequently bidentate complex **CP1<sup>BD</sup>** was formed via thermal equilibrium ( $\Delta G = 3.9$  kcal/mol). The thermodynamically more stable complex **CP1<sup>MD</sup>** was spectroscopically confirmed by using in situ Fe *K*-edge X-ray absorption spectroscopy (XAS) at a synchrotron radiation facility. The XAS measurements were carried out using a toluene solution of chiral phosphoric acid **3a**, aldehyde **1b**, and  $\text{FeCl}_3$  at 0 °C, and the result of the extended X-ray absorption fine structure (EXAFS) analysis is shown in Figure 1. The spectral features arising from the coordination sphere of the iron atoms matched the spectra simulated using the DFT-calculated structure of complex **CP1<sup>MD</sup>** ( $R_f = 2.5$  %).



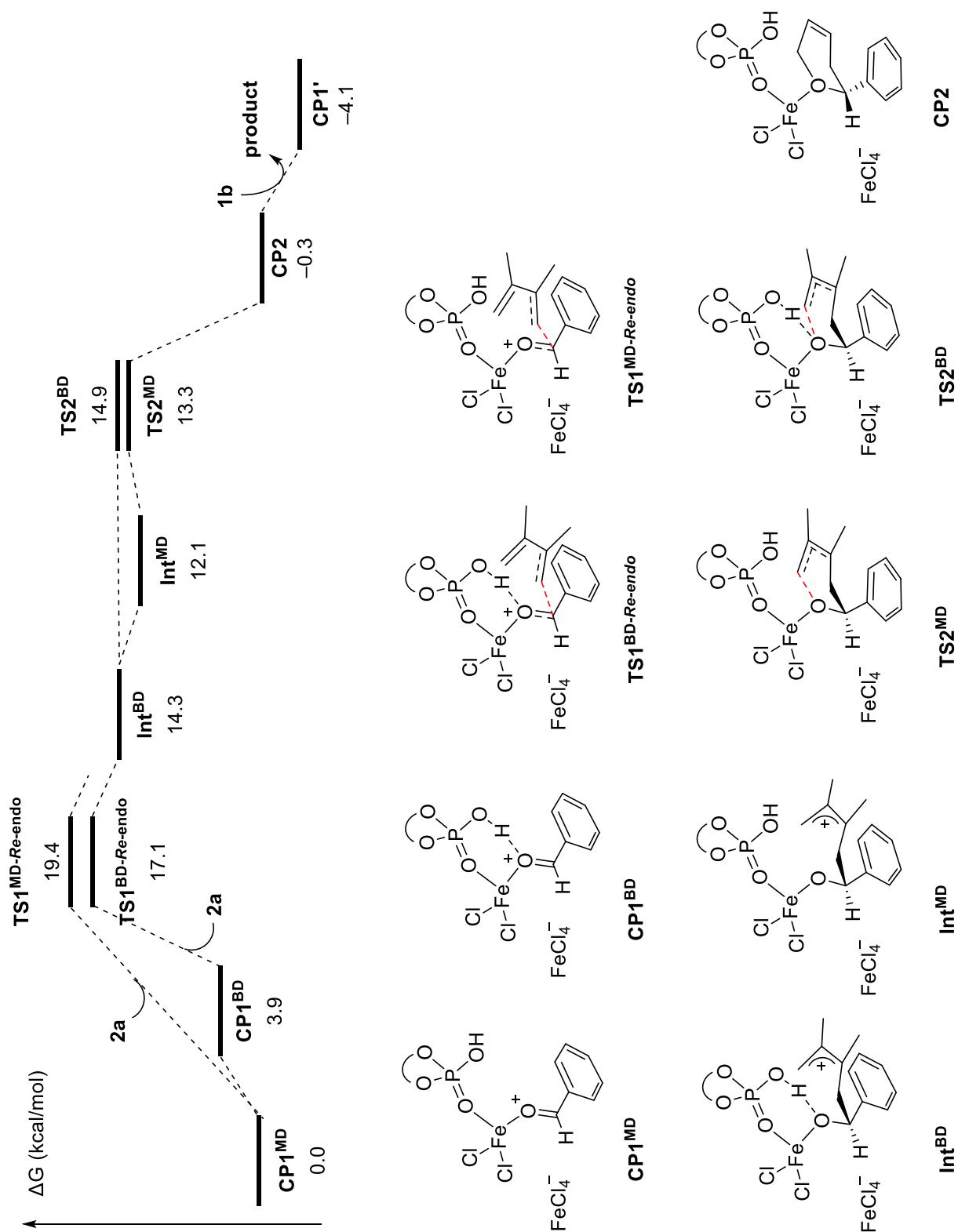
**Figure 1.** Solution-phase Fe *K*-edge EXAFS analysis (Fourier transform of  $k^3$ -weighted spectrum: experimental spectrum (black line) and FEFF-calculated fitting of DFT model **CP1** (red line).



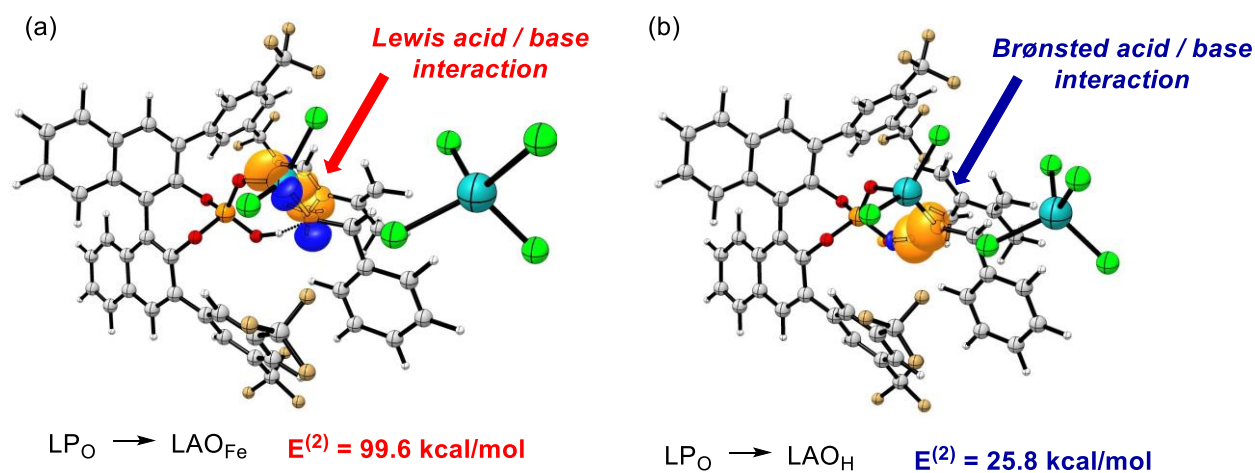
**Scheme 2.** Gibbs free activation energies of diene addition from **CP1<sup>MD</sup>** and **CP1<sup>BD</sup>**.

Then, the Gibbs activation energies of the addition reaction of diene **2b** were estimated for eight considered paths (*Re*, *Si* addition and endo, exo orientation of the diene for each **CP1<sup>MD</sup>** and **CP1<sup>BD</sup>**). As a result, the *Re*-endo attack to **CP1<sup>BD</sup>** path was found to have the lowest Gibbs activation energy of 13.2 kcal/mol (**TS1<sup>BD-Re-endo</sup>**:  $\Delta G = 17.1$  kcal/mol from **CP1<sup>MD</sup>**) (Scheme 2). For this path (*Re*-endo attack to **CP1<sup>BD</sup>**), the Gibbs free energies of the catalytic cycle were calculated (Figure 2). After the addition reaction, bidentate intermediate **Int<sup>BD</sup>** was formed ( $\Delta G = 14.3$  kcal/mol), and subsequently, monodentate intermediate **Int<sup>MD</sup>** was formed in an exothermal process ( $\Delta G = 12.1$  kcal/mol) by dissociation of the Brønsted acidic proton. The subsequent C–O bond formation via **TS2<sup>MD</sup>**, with an activation energy of 1.2 kcal/mol to afford **CP2**, followed by product dissociation gave the desired (*R*)-product. Since the enantio-determining step is suggested to involve addition of a diene, the dominant catalytic process is thought to involve *Re*-endo attack to **CP1<sup>BD</sup>**. In the catalytic cycle, the labile character of a proton is crucial: lowering the activation energy of the addition step by forming bidentate complex **TS1<sup>BD-Re-endo</sup>** and providing the thermodynamically stable intermediate **Int<sup>MD</sup>** via dissociation to form monodentate intermediate.

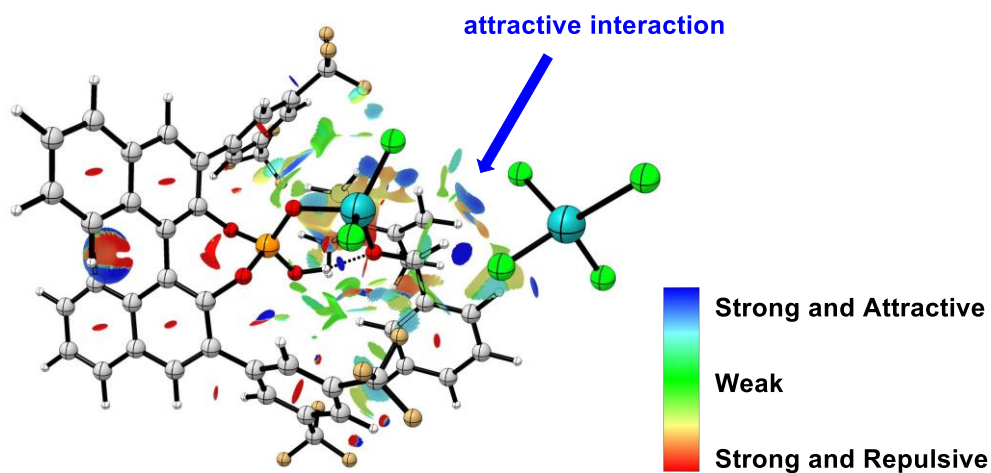
Additionally, the interaction between the catalyst and aldehyde was calculated via natural bond orbital (NBO) analysis (Figure 3). The Lewis basic aldehyde–Lewis acidic  $[\text{FeCl}_2]^+$  interaction was calculated to be 99.6 kcal/mol (Figure 3a), and the Lewis basic aldehyde–Brønsted acidic OH proton interaction was calculated to be 25.8 kcal/mol (Figure 3b). These interactions implied the importance of two acidic moieties in **TS1<sup>BD-Re-endo</sup>**. Furthermore, the noncovalent interaction (NCI) analysis in **TS1<sup>BD-Re-endo</sup>** was conducted, and several attractive interactions were confirmed, such as the interaction between the C–H hydrogen of aldehyde and the chloride atom of the neighboring  $[\text{FeCl}_4]^-$  (Figure 4).<sup>8</sup> This result indicated that  $[\text{FeCl}_4]^-$  acted as a thermodynamically stable counteranion and molded the conformation of **TS1<sup>BD-Re-endo</sup>**. Thus, DFT calculations and spectroscopic analysis revealed that the multiple activation catalyst system proposed herein is an efficient tool for sufficient activation of carbonyls.



**Figure 2.** Energy diagram of the *Re-endo* path.



**Figure 3.** NBO analysis in  $\text{TS1}^{\text{BD-Re-endo}}$ : (a) aldehyde–Lewis acidic Fe interaction, and (b) aldehyde–Brønsted acidic proton (OH) interaction. LP and LAO denote the lone pair and Lewis acceptor orbital, respectively.



**Figure 4.** Noncovalent interaction analysis in  $\text{TS1}^{\text{BD-Re-endo}}$ .

## Conclusion

The author demonstrated the asymmetric oxa-Diels–Alder reaction of non-activated substrates by utilizing  $\text{FeCl}_3$  and a chiral phosphoric acid as a multiple activation catalyst. Various dihydropyran products were prepared using this method, which can offer new synthetic routes for natural product synthesis. The synergistically activations of the carbonyl groups by Lewis acidic  $[\text{FeCl}_2]^+$  and the Brønsted acidic proton play a crucial role in this catalyst system. DFT calculations and spectroscopic analysis provided mechanistic insights into this multiple activation catalysis; labile proton coordination and dissociation to carbonyl groups successfully stabilized the rate-determining transition state and reaction intermediates.

## Experimental Section

### Materials.

Iron(III) chloride was purchased from Sigma-Aldrich Co., Iron(III) bromide was purchased from Strem Chemicals, Inc., aldehydes and 2,3-dimethyl-1,3-butadiene was purchased from TCI. Dienes and chiral phosphoric acid were prepared according to the reported procedure.<sup>9,10</sup> Unless otherwise noted, commercially available reagents were used without purification.

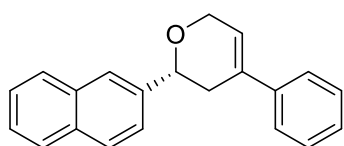
### Experimental Procedure and Characterization Data for Products.

#### *General procedure.*

The reaction was performed in a 15 mL sealed tube equipped with a Teflon-coated magnetic stirrer bar. In a glove box,  $\text{FeCl}_3$  (0.0075 mmol, 5 mol%) and chiral phosphoric acid (0.00375 mmol, 2.5 mol%) were stirred in toluene (1 mL) at  $-50\text{ }^\circ\text{C}$ . After  $\text{FeCl}_3$  was dissolved completely, aldehydes (0.15 mmol) were added and stirred for a while, then dienes (0.3 mmol) were added to a solution. After the reaction mixture was stirred at  $-50\text{ }^\circ\text{C}$  for the indicated time, the solution

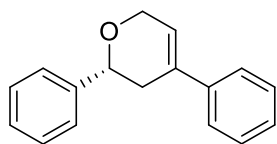
was passed through a short silica gel pad, washed with ethyl acetate, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with given eluent.

(*R*)-2-(naphthalen-2-yl)-4-phenyl-3,6-dihydro-2*H*-pyran (**4aa**).



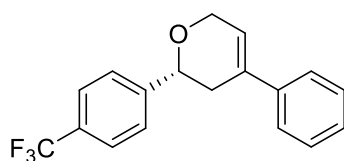
Yield: 53%, 66% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +25.8$  (*c* 0.83, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 83–84 °C (Hexane). TLC: *R*<sub>f</sub> = 0.25 (hexane/ethyl acetate = 30/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.84–7.92 (m, 4H), 7.57 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.47–7.50 (m, 2H), 7.42–7.55 (m, 2 H), 7.33–7.39 (m, 2H), 7.28 (dt, *J* = 7.0, 1.5 Hz, 1H), 6.24–6.28 (m, 1H), 4.85 (dd, *J* = 9.5, 4.5 Hz, 1H), 4.55–4.67 (m, 2H), 2.73–2.85 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 140.0, 139.7, 134.4, 133.3, 132.9, 128.5, 128.2, 128.0, 127.7, 127.4, 126.1, 125.8, 124.8, 124.5, 124.1, 122.2, 76.0, 66.9, 35.9. IR (KBr): 2824, 1600, 1446, 1372, 1119, 826, 752, 693 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 285.1278, calcd for [M+H]<sup>+</sup> 285.1285. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 98.5/1.5, flow rate = 1.0 ml/min, λ = 254 nm, 40 °C): *t*<sub>minor</sub> = 13.1 min, *t*<sub>major</sub> = 16.0 min.

(*R*)-2,4-diphenyl-3,6-dihydro-2*H*-pyran (**4ba**).



Yield: 80%, 66% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +77.2$  (*c* 0.84, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 62 °C (Hexane). TLC: *R*<sub>f</sub> = 0.30 (hexane/ethyl acetate = 30/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.27–7.48 (m, 10H), 6.22–6.24 (m, 1H), 4.68 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.50–4.62 (m, 2H), 2.64–2.78 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 142.3, 140.0, 134.3, 128.5, 128.4, 127.6, 127.4, 125.9, 124.7, 122.2, 76.0, 66.8, 34.9. IR (KBr): 2920, 2360, 1124, 745 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 235.1120, calcd for [M+H]<sup>+</sup> 235.1128. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 98.5/1.5, flow rate = 1.0 ml/min, λ = 254 nm, 40 °C): *t*<sub>major</sub> = 6.6 min, *t*<sub>minor</sub> = 14.8 min.

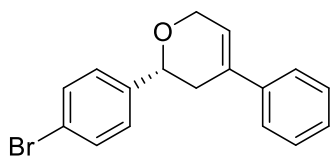
(*R*)-4-phenyl-2-(4-(trifluoromethyl)phenyl)-3,6-dihydro-2*H*-pyran (**4ca**).



Yield: 92%, 55% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +67.0$  (*c* 1.26, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 67–68 °C (Hexane). TLC: *R*<sub>f</sub> = 0.33 (hexane/ethyl acetate = 30/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H),

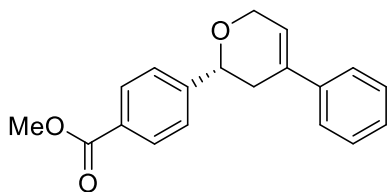
7.40–7.44 (m, 2H), 7.34–7.38 (m, 2H), 7.29 (dd,  $J = 7.0, 2.0, 1.0$  Hz, 1H), 6.22–6.26 (m, 1H), 4.75 (dd,  $J = 9.5, 4.0$  Hz, 1H), 4.51–4.64 (m, 2H), 2.62–2.74 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.4, 139.8, 134.0, 129.7 (q,  $J = 32.7$  Hz), 128.5, 127.5, 126.1, 125.4 (q,  $J = 3.9$  Hz), 124.7, 124.2 (q,  $J = 272.4$  Hz), 122.2, 75.2, 66.7, 34.9. IR (KBr): 2928, 2849, 1620, 1420, 1321, 1150, 1023, 835, 606  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 304.1025, calcd for  $[\text{M}+\text{H}]^+$  304.1036. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 98.5/1.5, flow rate = 1.0 ml/min,  $\lambda = 254$  nm, 40  $^\circ\text{C}$ ):  $t_{\text{minor}} = 6.1$  min,  $t_{\text{major}} = 7.3$  min.

(*R*)-2-(4-bromophenyl)-4-phenyl-3,6-dihydro-2*H*-pyran (**4da**).



Yield: 90%, 62% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +62.6$  ( $c$  1.71,  $\text{CH}_2\text{Cl}_2$ ). Mp. 90–92  $^\circ\text{C}$  (Hexane). TLC:  $R_f = 0.30$  (hexane/ethyl acetate = 30/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.51 (dt,  $J = 8.5, 2.0$  Hz, 2H), 7.41 (dt,  $J = 7.0, 1.5$  Hz, 2H), 7.31–7.38 (m, 4H), 7.28 (dt,  $J = 7.0, 1.5$  Hz, 1H), 6.19–6.24 (m, 1H), 4.64 (t,  $J = 7.0$  Hz, 1H), 4.39–4.60 (m, 2H), 2.62–2.67 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  141.4, 139.8, 134.1, 131.5, 128.5, 127.6, 127.5, 124.7, 122.2, 121.4, 75.2, 66.8, 34.8. IR (KBr): 2919, 148, 1443, 1367, 1119, 1007, 818, 748  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 313.0228, calcd for  $[\text{M}+\text{H}]^+$  313.0234. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99/1, flow rate = 1.5 ml/min,  $\lambda = 254$  nm, 40  $^\circ\text{C}$ ):  $t_{\text{minor}} = 7.0$  min,  $t_{\text{major}} = 7.8$  min.

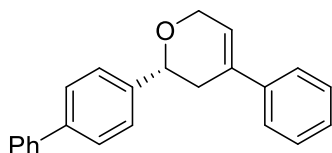
Methyl (*R*)-4-(4-phenyl-3,6-dihydro-2*H*-pyran-2-yl)benzoate (**4ea**).



Yield: 83%, 62% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +74.8$  ( $c$  1.00,  $\text{CH}_2\text{Cl}_2$ ). Mp. 52  $^\circ\text{C}$  (Hexane). TLC:  $R_f = 0.40$  (hexane/ethyl acetate = 10/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.0$  Hz, 2H), 7.52 (d,  $J = 8.5$  Hz, 2H), 7.41 (d,  $J = 7.5$  Hz, 2H), 7.35 (t,  $J = 8.0$  Hz, 2H), 7.28 (t,  $J = 7.5$  Hz, 1H), 6.22 (d,  $J = 2.0$  Hz, 1H), 4.74 (dd,  $J = 9.5, 4.5$  Hz, 1H), 4.51–4.64 (m, 2H), 3.93 (s, 3H), 2.62–2.74 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  166.9, 147.5, 139.8, 134.1, 129.8, 129.3, 128.5, 127.4, 125.7, 124.7, 122.1, 75.4, 66.7, 52.1, 34.8. IR (KBr): 2816, 1711, 1612, 1432, 1372, 1270, 1116, 859, 745, 696  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 293.1166, calcd for  $[\text{M}+\text{H}]^+$  293.1183. HPLC (Daicel

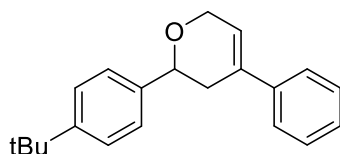
Chiralpak IB, hexane/*i*-PrOH = 90/10, flow rate = 2.0 ml/min,  $\lambda$  = 254 nm, 40 °C):  $t_{\text{major}}$  = 8.8 min,  $t_{\text{minor}}$  = 10.8 min.

(*R*)-2-([1,1'-biphenyl]-4-yl)-4-phenyl-3,6-dihydro-2*H*-pyran (**4fa**).

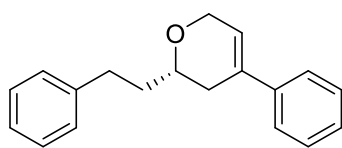


Yield: 48%, 60% *ee*, white solid.  $[\alpha]_{\text{D}}^{23}$  +49.0 (*c* 0.66, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 91–92 °C (Hexane). TLC:  $R_{\text{f}}$  = 0.20 (hexane/ethyl acetate = 30/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.60–7.64 (m, 4H), 7.53 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.42–7.47 (m, 4H), 7.33–7.38 (m, 3H), 7.29 (dt, *J* = 7.0, 1.5, 1H), 6.22–6.26 (m, 1H), 4.73 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.52–4.62 (m, 2H), 2.68–2.82 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  141.4, 140.9, 140.6, 140.0, 134.3, 128.7, 128.5, 127.4, 127.3, 127.1, 126.4, 124.8, 122.2, 75.7, 66.8, 34.8. IR (KBr): 2823, 1487, 1446, 1367, 1119, 1008, 834, 767 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 311.1435, calcd for [M+H]<sup>+</sup> 311.1441. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90/10, flow rate = 2.0 ml/min,  $\lambda$  = 254 nm, 40 °C):  $t_{\text{major}}$  = 5.2 min,  $t_{\text{minor}}$  = 13.0 min.

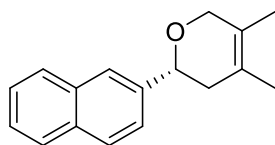
(*R*)-2-(4-(*tert*-butyl)phenyl)-4-phenyl-3,6-dihydro-2*H*-pyran (**4ga**).



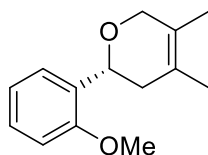
Yield: 78%, 29% *ee*, white solid.  $[\alpha]_{\text{D}}^{23}$  +24.7 (*c* 0.59, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 64 °C (Hexane). TLC:  $R_{\text{f}}$  = 0.33 (hexane/ethyl acetate = 30:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.30–7.45 (m, 8H), 7.28 (dt, *J* = 7.0, 1.5 Hz, 1H), 6.21–6.24 (m, 1H), 4.66 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.50–4.61 (m, 2H), 2.73–2.81 (m, 1H), 2.67 (dt, *J* = 16.5, 3.0 Hz, 1H), 1.35 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  150.6, 140.1, 139.2, 134.4, 128.4, 127.3, 125.8, 125.4, 124.7, 122.2, 75.8, 66.8, 34.6, 34.5, 31.3. IR (KBr): 2964, 1597, 1446, 1371, 1118, 829, 740, 689, 580 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 291.1748, calcd for [M+H]<sup>+</sup> 291.1754. HPLC (Daicel Chiralpak IA, hexane/*i*-PrOH = 99/1, flow rate = 1.5 ml/min,  $\lambda$  = 254 nm, 40 °C):  $t_{\text{minor}}$  = 6.2 min,  $t_{\text{major}}$  = 7.4 min.

**(S)-2-phenethyl-4-phenyl-3,6-dihydro-2H-pyran (4ha).**

Yield: 49%, 15% *ee*, colorless oil.  $[\alpha]_{\text{D}}^{23} +10.4$  (*c* 0.48, CH<sub>2</sub>Cl<sub>2</sub>). TLC: *R<sub>f</sub>* = 0.25 (hexane/ethyl acetate = 30/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.18–7.40 (m, 10H), 6.11–6.14 (m, 1H), 4.40–4.47 (m, 1H) 4.54 (ddd, *J* = 17.5, 5.5, 3.5 Hz, 1H), 3.59 (sept, *J* = 4.5 Hz, 1H), 2.84–2.92 (m, 1H), 2.72–2.81 (m, 1H), 2.35–2.45 (m, 2H), 1.96–2.02 (m, 1H), 1.85–1.93 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  142.1, 140.3, 134.1, 128.5, 128.4, 128.4, 127.2, 125.8, 124.8, 122.3, 72.9, 66.3, 37.6, 32.9, 31.7. IR (neat) 2924, 1495, 1446, 1129, 748, 696 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 263.1435, calcd for [M+H]<sup>+</sup> 263.1441. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99/1, flow rate = 1.5 ml/min,  $\lambda$  = 254 nm, 40 °C): *t*<sub>major</sub> = 7.1 min, *t*<sub>minor</sub> = 18.9 min.

**(R)-4,5-dimethyl-2-(naphthalen-2-yl)-3,6-dihydro-2H-pyran (4ab).**

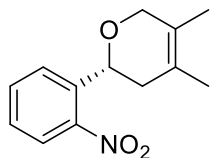
Yield: 92%, 46% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +81.5$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>). Mp. 28–29 °C (Hexane). TLC: *R<sub>f</sub>* = 0.32 (hexane/ethyl acetate = 30/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.83–7.85 (m, 4H), 7.43–7.83 (m, 3H), 4.70–4.74 (m, 1H), 4.28 (d, *J* = 15.5 Hz, 1H), 4.17 (d, *J* = 15.5 Hz, 1H), 2.36–2.42 (m, 1H), 2.19 (d, *J* = 13.5 Hz, 1H), 1.72 (s, 3H), 1.63 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  140.1, 133.4, 132.8, 128.1, 128.0, 127.6, 126.0, 125.6, 124.5, 124.3, 124.1, 123.9, 76.3, 70.3, 38.6, 18.3, 13.9. IR (KBr): 2908, 1100 cm<sup>-1</sup>. HRMS (ESI<sup>+</sup>) found 237.1279, calcd for [M+H]<sup>+</sup> 237.1280. HPLC (Daicel Chiralpak IE, hexane/*i*-PrOH = 99/1, flow rate = 1.5 ml/min,  $\lambda$  = 254 nm, 40 °C): *t*<sub>major</sub> = 6.2 min, *t*<sub>minor</sub> = 6.9 min.

**(R)-2-(2-methoxyphenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran (4ib).**

Yield: 80%, 43% *ee*, colorless oil.  $[\alpha]_{\text{D}}^{23} +63.0$  (*c* 1.12, CH<sub>2</sub>Cl<sub>2</sub>). TLC: *R<sub>f</sub>* = 0.33 (hexane/ethyl acetate = 30/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.47 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.22–7.26 (m, 1H), 6.99 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.90 (dd, *J* = 9.5, 5.0 Hz, 1H), 4.18–4.26 (m, 1H), 4.12 (d, *J* = 15.0 Hz, 1H), 3.82 (s, 3H), 2.10–2.21 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  155.7, 131.2, 128.0, 126.0, 124.3,

124.2, 120.8, 110.1, 70.7, 70.4, 55.3, 37.3, 18.3, 13.9. IR (neat): 2917, 1494, 1244, 1099, 754  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 241.1194, calcd for  $[\text{M}+\text{H}]^+$  241.1199. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99/1, flow rate = 1.5 ml/min,  $\lambda$  = 254 nm, 40  $^{\circ}\text{C}$ ):  $t_{\text{major}}$  = 4.9 min,  $t_{\text{minor}}$  = 6.9 min.

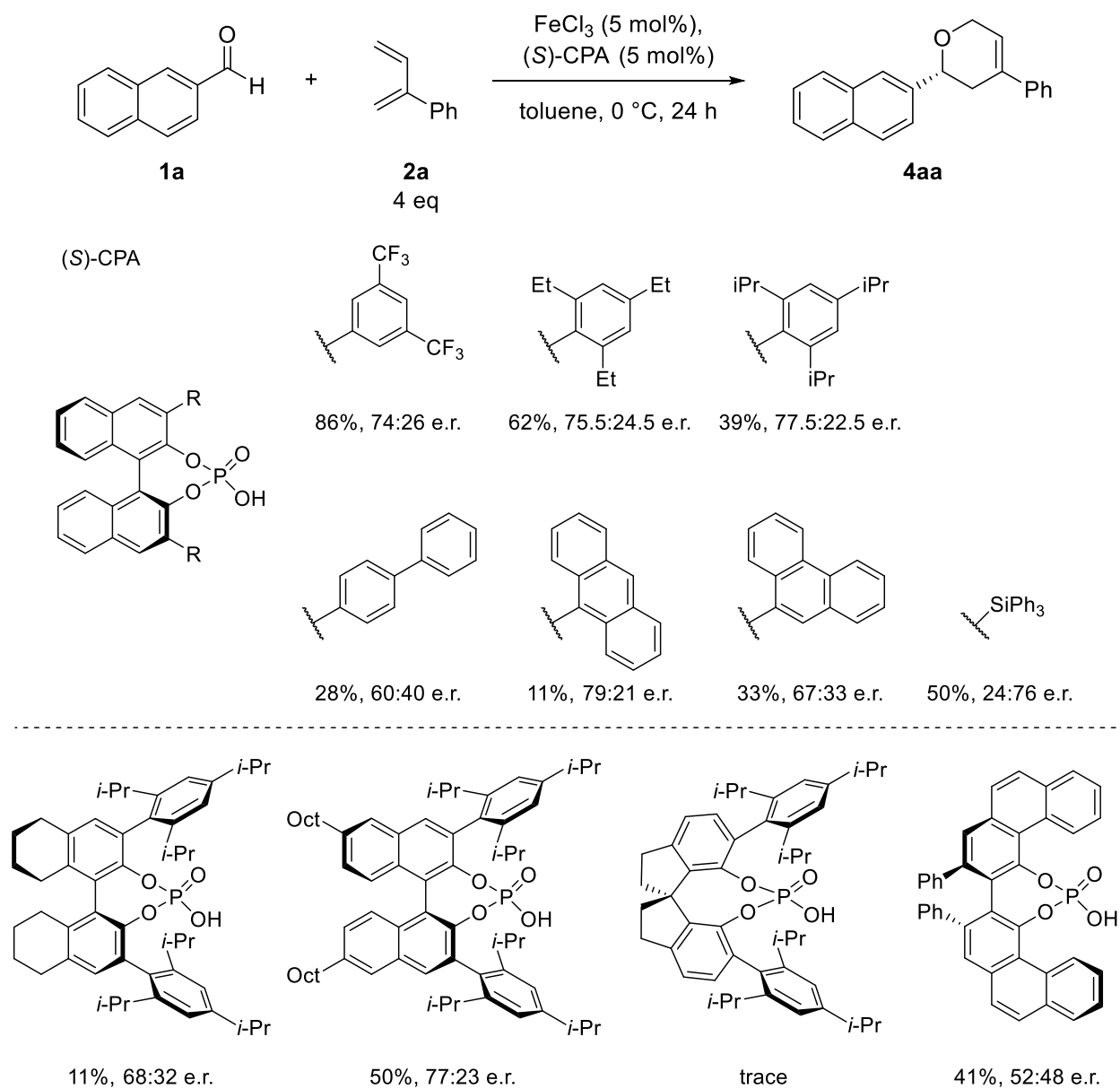
(*R*)-4,5-dimethyl-2-(2-nitrophenyl)-3,6-dihydro-2*H*-pyran (**4jc**).



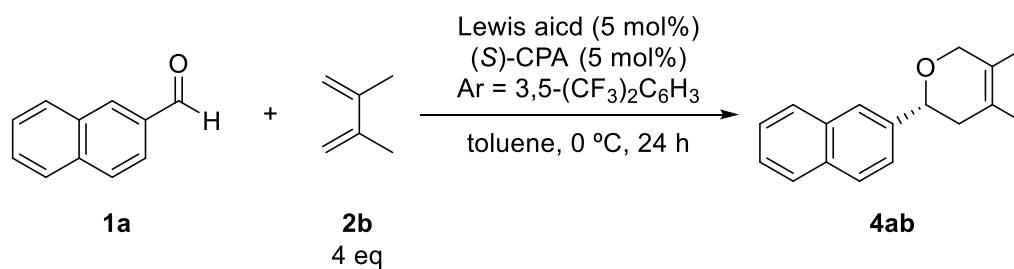
Yield: 56%, 7% *ee*, white solid.  $[\alpha]_{\text{D}}^{23} +1.67$  (*c* 0.54,  $\text{CH}_2\text{Cl}_2$ ). Mp. 67–68  $^{\circ}\text{C}$  (Hexane). TLC:  $R_{\text{f}}$  = 0.30 (hexane/ethyl acetate = 8/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.89 (dd,  $J$  = 8.0, 1.0 Hz, 1H), 7.81 (dd,  $J$  = 8.0, 0.5 Hz, 1H), 7.64 (dt,  $J$  = 8.0, 1.0 Hz, 1H), 7.41 (dt,  $J$  = 8.5, 1.5 Hz, 1H), 5.08 (dd,  $J$  = 10.5, 3.0 Hz, 1H), 4.18 (d,  $J$  = 15.5 Hz, 1H), 4.10 (d,  $J$  = 15.5 Hz, 1H), 2.34 (d,  $J$  = 16.5 Hz, 1H), 2.14–2.24 (m, 1H), 1.69 (s, 3H), 1.60 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  147.7, 138.1, 133.5, 127.9, 124.2, 124.0, 123.7, 110.0, 72.0, 70.3, 37.7, 18.3, 13.8. IR (KBr): 2832, 1609, 1519, 1346, 1095, 885, 791, 746, 715  $\text{cm}^{-1}$ . HRMS ( $\text{ESI}^+$ ) found 256.0945, calcd for  $[\text{M}+\text{Na}]^+$  256.0944. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99/1, flow rate = 1.5 ml/min,  $\lambda$  = 254 nm, 40  $^{\circ}\text{C}$ ):  $t_{\text{major}}$  = 5.0 min,  $t_{\text{minor}}$  = 6.0 min.

## Supplemental Data

### S1. Investigation of chiral phosphoric acid.

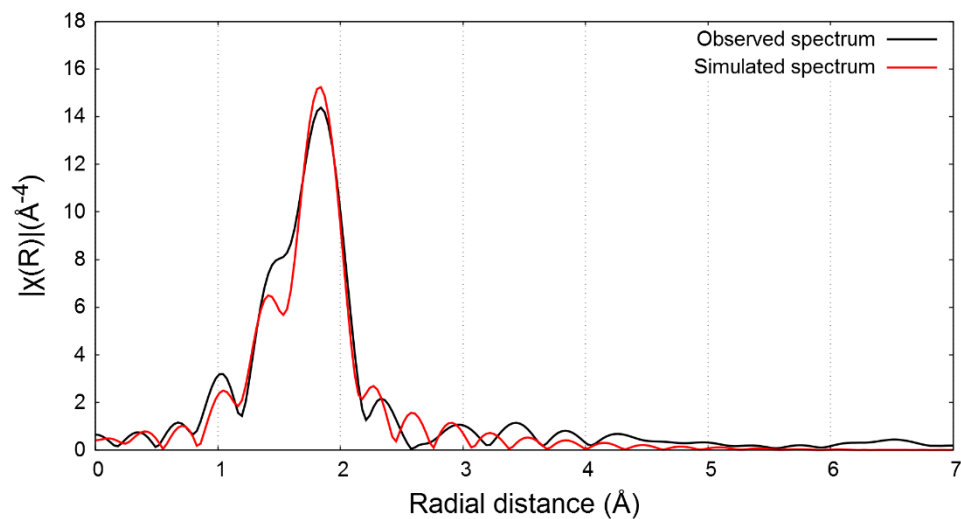
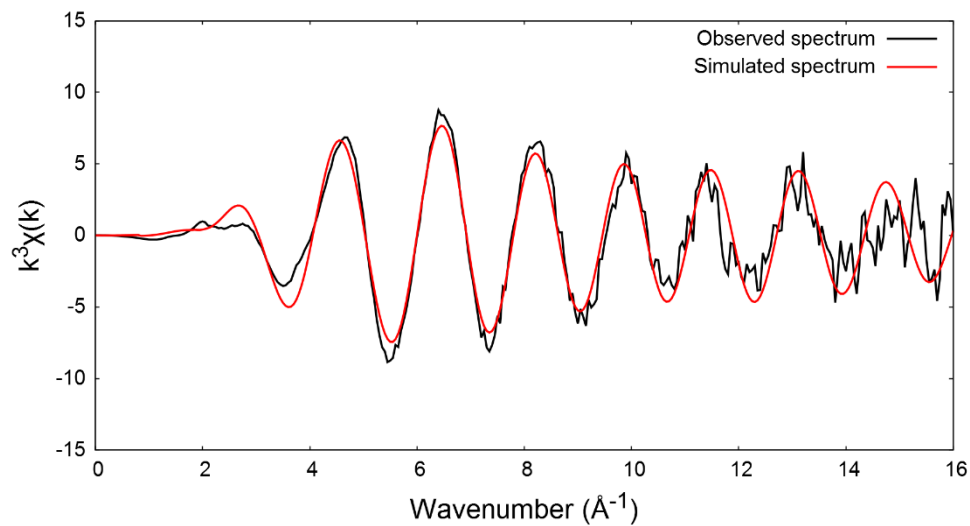


## S2. Investigation of Lewis acid.



| Lewis acid           | Yield (%) | e.r.  | Lewis acid        | Yield (%) | e.r. |
|----------------------|-----------|-------|-------------------|-----------|------|
| FeCl <sub>3</sub>    | 92        | 73:27 | CoCl <sub>2</sub> | <1        | —    |
| FeCl <sub>2</sub>    | <1        | —     | NiCl <sub>2</sub> | <1        | —    |
| AlCl <sub>3</sub>    | <1        | —     | MnCl <sub>2</sub> | <1        | —    |
| Sc(OTf) <sub>3</sub> | <1        | —     | CuCl              | <1        | —    |
| ZnCl <sub>2</sub>    | <1        | —     | RuCl <sub>3</sub> | <1        | —    |

Reactions were carried out using FeCl<sub>3</sub> (5 mol%), chiral phosphoric acid **3a** (5 mol%), **1** (0.15 mmol), and **2** (0.3 mmol) in 1 mL of toluene for 24 h under 0 °C unless otherwise noted. Yields were isolated yield, and enantioselectivity was determined by chiral HPLC analysis.

**S3. XAS measurement of CP1<sup>MD</sup>.****Figure S3-1.** Fourier-transformed Fe K-edge EXAFS spectra in R-space.**Figure S3-2.** Fourier-transformed Fe K-edge EXAFS spectra in k-space.

## Structural Parameters Obtained from EXAFS Analysis

| Ab–Sc  | R (Å)   | N | $S_0^2$ | $\Delta R$ (Å) | $\Delta E_0$ (eV) | $\Delta\sigma^2$ (Å <sup>2</sup> ) |
|--------|---------|---|---------|----------------|-------------------|------------------------------------|
| Fe– O  | 1.9124  | 1 | 0.453   | –0.05164       | 2.573             | 0.00163                            |
| Fe– O  | 1.9453  | 1 | 0.453   | –0.05164       | 2.573             | 0.00163                            |
| Fe–Cl  | 2.11446 | 1 | 0.453   | –0.05164       | 2.573             | 0.00163                            |
| Fe– Cl | 2.19446 | 1 | 0.453   | –0.05164       | 2.573             | 0.00163                            |
| Fe– Cl | 2.18316 | 2 | 0.453   | –0.05164       | 2.573             | 0.00163                            |
| Fe– Cl | 2.21476 | 2 | 0.453   | –0.05164       | 2.573             | 0.00163                            |

$R_{\text{factor}} = 2.5\%$ ,  $\Delta k = 3.5\text{--}13.6$ ,  $\Delta R = 1.2\text{--}2.2$  (spatial resolution  $\delta R \geq \pi/2k_{\text{max}} = 0.1154$  Å)

Ab–Sc: X-ray absorbing atom and scattering atom

R (Å): atomic distance

N: coordination number

$S_0^2$ : passive electron reduction factor

parameter  $\Delta R$ (Å): change in half-path length

parameter  $\Delta E_0$  (eV): edge shift

parameter  $\Delta\sigma^2$  (Å<sup>2</sup>): mean squared displacement (Debye–Waller factor)

*The total number of parameters used in the model is less than that given by the Nyquist theorem.*

$N_{\text{idp}} \approx 2\Delta k\Delta R/\pi = 6.43 > N_{\text{used}} = 4$  ( $S_0^2$ ,  $\Delta R$ ,  $\Delta E_0$  and  $\Delta\sigma^2$ )

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Newville, M. *J. Synchrotron Rad.* **2001**, *8*, 322.

#### S4. Computational details for DFT calculation

General Methods. Calculations were performed on Gaussian 09 E.01. For geometry optimization and frequency calculations B3LYP augmented with an empirical dispersion (GD3) was used and M06 was used for single-point energy calculations. Geometry optimization and frequency calculations were carried out using 6-31++G(d,p) (for Bronsted acidic proton on chiral phosphoric acid), 6-31G(d) (C, other H, O, F), 6-31+G(d) (Cl, P), and f polarization function added Lanl2dz(f) (Fe) basis sets. Single-point calculations were performed with def2-TZVP basis sets. The solvation effects of toluene were incorporated in all calculations using PCM (toluene). The Monte-Carlo simulated annealing method was initially employed to generate conformers, followed by geometry optimization and thermodynamic calculation to obtain the Boltzmann distribution of these conformers to determine the energetically global minimum conformer.

Gaussian 09, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. W.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. F.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

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Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. A Set of f-Polarization Functions for Pseudo-Potential Basis Sets of the Transition Metals Sc–Cu, Y–Ag and La–Au. *Chem. Phys. Lett.* **1993**, 208, 111.

| Cartesian Coordinates for CP1 <sup>MD</sup> |                |                 |                 | O  | 0.962213000000  | 0.913114000000  | -1.434653000000 |
|---------------------------------------------|----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C                                           | 7.879720000000 | 3.292609000000  | 3.011713000000  | C  | 5.297697000000  | -0.611242000000 | -1.089817000000 |
| C                                           | 7.811689000000 | 2.198390000000  | 2.180591000000  | C  | 4.972106000000  | -0.599588000000 | -2.455119000000 |
| C                                           | 6.714429000000 | 2.023086000000  | 1.294297000000  | C  | 5.276855000000  | -1.827343000000 | -0.400721000000 |
| C                                           | 5.684445000000 | 3.022812000000  | 1.250121000000  | C  | 4.609376000000  | -1.776448000000 | -3.102869000000 |
| C                                           | 5.773168000000 | 4.125939000000  | 2.141543000000  | C  | 4.911074000000  | -3.003493000000 | -1.060182000000 |
| C                                           | 6.843366000000 | 4.256340000000  | 2.998759000000  | C  | 4.572528000000  | -2.988159000000 | -2.410047000000 |
| H                                           | 7.389142000000 | 0.104824000000  | 0.547801000000  | C  | -0.325805000000 | 3.611585000000  | -0.001097000000 |
| H                                           | 8.720662000000 | 3.413528000000  | 3.687972000000  | C  | -1.079050000000 | 3.784221000000  | -1.169709000000 |
| H                                           | 8.592207000000 | 1.442522000000  | 2.197303000000  | C  | -0.830430000000 | 2.781825000000  | 1.009815000000  |
| C                                           | 6.610077000000 | 0.859937000000  | 0.488113000000  | C  | -2.306515000000 | 3.139686000000  | -1.322233000000 |
| C                                           | 4.586706000000 | 2.847228000000  | 0.341531000000  | C  | -2.054005000000 | 2.136197000000  | 0.842470000000  |
| H                                           | 4.984491000000 | 4.869496000000  | 2.145558000000  | C  | -2.806368000000 | 2.316165000000  | -0.317558000000 |
| H                                           | 6.890316000000 | 5.105500000000  | 3.674151000000  | Fe | 0.190967000000  | -0.455547000000 | -2.581566000000 |
| C                                           | 4.548432000000 | 1.674930000000  | -0.390113000000 | Cl | 0.523621000000  | 0.168125000000  | -4.629120000000 |
| C                                           | 5.530480000000 | 0.653220000000  | -0.344933000000 | Cl | 1.213389000000  | -2.309786000000 | -1.832032000000 |
| C                                           | 3.476784000000 | 3.834647000000  | 0.186254000000  | C  | -2.679833000000 | -0.371691000000 | -2.783888000000 |
| C                                           | 3.700608000000 | 5.188791000000  | -0.241726000000 | H  | -2.557820000000 | -0.181836000000 | -3.851341000000 |
| C                                           | 2.166511000000 | 3.418625000000  | 0.334190000000  | C  | -3.996947000000 | -0.506770000000 | -2.250660000000 |
| C                                           | 4.992313000000 | 5.702171000000  | -0.538675000000 | C  | -5.088842000000 | -0.336580000000 | -3.129378000000 |
| C                                           | 2.568602000000 | 6.052164000000  | -0.426039000000 | C  | -4.208718000000 | -0.777026000000 | -0.878064000000 |
| C                                           | 1.026842000000 | 4.221632000000  | 0.070268000000  | C  | -6.383775000000 | -0.428070000000 | -2.632610000000 |
| C                                           | 5.158122000000 | 7.009144000000  | -0.941121000000 | H  | -4.907837000000 | -0.143561000000 | -4.181466000000 |
| H                                           | 5.856366000000 | 5.054780000000  | -0.452337000000 | C  | -5.503239000000 | -0.857288000000 | -0.394788000000 |
| C                                           | 2.777512000000 | 7.399891000000  | -0.826486000000 | H  | -3.355103000000 | -0.900596000000 | -0.221461000000 |
| C                                           | 1.256875000000 | 5.537713000000  | -0.275910000000 | C  | -6.587355000000 | -0.685081000000 | -1.273115000000 |
| C                                           | 4.045119000000 | 7.873020000000  | -1.072911000000 | H  | -7.229949000000 | -0.306983000000 | -3.300489000000 |
| H                                           | 6.154364000000 | 7.378692000000  | -1.165430000000 | H  | -5.679125000000 | -1.049450000000 | 0.658542000000  |
| H                                           | 1.912156000000 | 8.045168000000  | -0.951179000000 | H  | -7.600759000000 | -0.754927000000 | -0.888119000000 |
| H                                           | 0.410919000000 | 6.189801000000  | -0.475396000000 | Fe | -3.158239000000 | -2.191333000000 | -6.170029000000 |
| H                                           | 4.193792000000 | 8.902297000000  | -1.385207000000 | Cl | -2.948779000000 | 0.061122000000  | -6.307875000000 |
| P                                           | 2.096004000000 | 0.978071000000  | -0.431248000000 | Cl | -2.538212000000 | -3.152866000000 | -8.079711000000 |
| O                                           | 1.921500000000 | 2.069567000000  | 0.711468000000  | Cl | -5.299912000000 | -2.663561000000 | -5.696974000000 |
| O                                           | 3.416895000000 | 1.422727000000  | -1.209617000000 | Cl | -1.895602000000 | -2.928077000000 | -4.438243000000 |
| O                                           | 2.311183000000 | -0.339061000000 | 0.400503000000  | O  | -1.646632000000 | -0.427390000000 | -2.052711000000 |
| H                                           | 2.067693000000 | -1.151021000000 | -0.104438000000 | H  | 4.254223000000  | -3.897090000000 | -2.906882000000 |
| F                                           | 3.169634000000 | -2.550390000000 | -4.807358000000 | H  | 5.498161000000  | -1.850334000000 | 0.661244000000  |

## Chapter 5

|   |                 |                 |                 |   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| F | 5.246846000000  | -2.196209000000 | -5.343009000000 | H | 4.969009000000  | 0.335785000000  | -3.001281000000 |
| F | 4.815107000000  | -5.371645000000 | -1.013592000000 | H | -0.686229000000 | 4.390527000000  | -1.979186000000 |
| F | 5.649088000000  | -4.362184000000 | 0.731900000000  | H | -0.262166000000 | 2.625097000000  | 1.918950000000  |
| F | 3.510962000000  | -4.276196000000 | 0.343086000000  | H | -3.756002000000 | 1.812312000000  | -0.441216000000 |
| F | -2.129487000000 | 1.471643000000  | 3.117158000000  | C | -3.018881000000 | 3.234568000000  | -2.644637000000 |
| F | -1.940868000000 | -0.087565000000 | 1.611262000000  | C | -2.499321000000 | 1.130397000000  | 1.868118000000  |
| F | -3.837837000000 | 0.948696000000  | 1.863018000000  | C | 4.234403000000  | -1.755241000000 | -4.563347000000 |
| F | -4.313700000000 | 2.867663000000  | -2.557070000000 | C | 4.732341000000  | -4.261917000000 | -0.255621000000 |
| F | -2.435442000000 | 2.403641000000  | -3.555868000000 | F | 3.918178000000  | -0.508971000000 | -4.981816000000 |
| F | -2.966587000000 | 4.475808000000  | -3.162349000000 |   |                 |                 |                 |

### Cartesian Coordinates for **CP1<sup>BD</sup>**

|   |                |                 |                 |    |                 |                 |                 |
|---|----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 6.962947000000 | 3.179799000000  | 3.471637000000  | O  | 1.260282000000  | 0.332973000000  | -0.137103000000 |
| C | 6.794212000000 | 1.989985000000  | 2.802256000000  | H  | 0.508014000000  | -0.185252000000 | -0.518773000000 |
| C | 5.897544000000 | 1.892078000000  | 1.704030000000  | O  | 0.776257000000  | 1.716094000000  | -2.275434000000 |
| C | 5.186443000000 | 3.062316000000  | 1.271449000000  | C  | 4.385577000000  | -0.778336000000 | -0.578712000000 |
| C | 5.362933000000 | 4.266886000000  | 2.005498000000  | C  | 4.605845000000  | -1.041541000000 | -1.934681000000 |
| C | 6.228694000000 | 4.322738000000  | 3.075349000000  | C  | 3.680437000000  | -1.710648000000 | 0.190859000000  |
| H | 6.192585000000 | -0.236007000000 | 1.421233000000  | C  | 4.122487000000  | -2.216402000000 | -2.510586000000 |
| H | 7.647379000000 | 3.241955000000  | 4.312416000000  | C  | 3.177908000000  | -2.870227000000 | -0.399548000000 |
| H | 7.336042000000 | 1.100123000000  | 3.111380000000  | C  | 3.398437000000  | -3.134226000000 | -1.751785000000 |
| C | 5.667037000000 | 0.645930000000  | 1.065462000000  | C  | -0.184526000000 | 4.697744000000  | -1.194730000000 |
| C | 4.291602000000 | 2.959806000000  | 0.151302000000  | C  | -0.767631000000 | 4.949084000000  | -2.444856000000 |
| H | 4.803844000000 | 5.149981000000  | 1.719815000000  | C  | -0.959988000000 | 4.072697000000  | -0.209379000000 |
| H | 6.345458000000 | 5.253170000000  | 3.623194000000  | C  | -2.081870000000 | 4.561070000000  | -2.705985000000 |
| C | 4.111879000000 | 1.705483000000  | -0.403473000000 | C  | -2.260380000000 | 3.657793000000  | -0.491922000000 |
| C | 4.768997000000 | 0.526299000000  | 0.027590000000  | C  | -2.835848000000 | 3.897037000000  | -1.739347000000 |
| C | 3.499421000000 | 4.115721000000  | -0.367214000000 | Fe | -0.315553000000 | 0.416504000000  | -3.270548000000 |
| C | 4.101718000000 | 5.317719000000  | -0.872494000000 | Cl | -1.532637000000 | 1.547501000000  | -4.654063000000 |
| C | 2.123685000000 | 4.008667000000  | -0.446448000000 | Cl | 1.133746000000  | -1.025851000000 | -4.067753000000 |
| C | 5.508463000000 | 5.501812000000  | -0.951880000000 | C  | -2.026881000000 | -0.719491000000 | -1.099541000000 |
| C | 3.248043000000 | 6.365002000000  | -1.358194000000 | H  | -2.883406000000 | -0.209384000000 | -1.540496000000 |
| C | 1.255415000000 | 4.996455000000  | -0.982474000000 | C  | -2.240054000000 | -1.625924000000 | -0.018873000000 |
| C | 6.040532000000 | 6.675876000000  | -1.437757000000 | C  | -3.545886000000 | -1.723218000000 | 0.510968000000  |
| H | 6.168203000000 | 4.704998000000  | -0.629333000000 | C  | -1.191442000000 | -2.417271000000 | 0.501671000000  |
| C | 3.831395000000 | 7.569172000000  | -1.838169000000 | C  | -3.788506000000 | -2.589914000000 | 1.569338000000  |
| C | 1.843914000000 | 6.172677000000  | -1.402655000000 | H  | -4.342952000000 | -1.120005000000 | 0.085065000000  |
| C | 5.197512000000 | 7.726198000000  | -1.872402000000 | C  | -1.445507000000 | -3.281527000000 | 1.553150000000  |
| H | 7.118676000000 | 6.794567000000  | -1.492225000000 | H  | -0.206377000000 | -2.374890000000 | 0.053022000000  |
| H | 3.175105000000 | 8.359505000000  | -2.192485000000 | C  | -2.741584000000 | -3.361949000000 | 2.087337000000  |
| H | 1.219492000000 | 6.965895000000  | -1.804469000000 | H  | -4.786032000000 | -2.672142000000 | 1.988004000000  |
| H | 5.632515000000 | 8.648147000000  | -2.246438000000 | H  | -0.644804000000 | -3.895718000000 | 1.949875000000  |
| P | 1.627441000000 | 1.574930000000  | -1.029531000000 | H  | -2.937277000000 | -4.043290000000 | 2.910379000000  |
| O | 1.526557000000 | 2.796888000000  | -0.012117000000 | Fe | -4.812267000000 | -0.496039000000 | -4.076640000000 |
| O | 3.165741000000 | 1.541634000000  | -1.448597000000 | Cl | -4.830072000000 | 0.956566000000  | -2.331740000000 |
| C | 2.375288000000 | -3.846488000000 | 0.417061000000  | Cl | -4.799245000000 | 0.588703000000  | -6.009957000000 |
|   |                |                 |                 | Cl | -6.605489000000 | -1.817729000000 | -3.898882000000 |

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| F | 4.454151000000  | -1.365833000000 | -4.693299000000 | Cl | -2.971250000000 | -1.821849000000 | -3.828654000000 |
| F | 3.479285000000  | -3.310587000000 | -4.510397000000 | O  | -0.870320000000 | -0.456296000000 | -1.557594000000 |
| F | 5.608450000000  | -3.113678000000 | -4.113226000000 | H  | 2.987207000000  | -4.023497000000 | -2.215146000000 |
| F | 1.347504000000  | -4.361584000000 | -0.300010000000 | H  | 3.474160000000  | -1.499006000000 | 1.233769000000  |
| F | 3.114583000000  | -4.885353000000 | 0.854457000000  | H  | 5.125973000000  | -0.315483000000 | -2.549725000000 |
| F | 1.828146000000  | -3.256514000000 | 1.512714000000  | H  | -0.177668000000 | 5.403679000000  | -3.233282000000 |
| F | -4.314861000000 | 2.809394000000  | 0.348299000000  | H  | -0.544018000000 | 3.884807000000  | 0.772873000000  |
| F | -2.762460000000 | 3.303827000000  | 1.795321000000  | H  | -3.837132000000 | 3.551216000000  | -1.962757000000 |
| F | -2.544893000000 | 1.548692000000  | 0.533160000000  | C  | -2.698303000000 | 4.886203000000  | -4.043229000000 |
| F | -3.219835000000 | 6.136915000000  | -4.045861000000 | C  | -2.986849000000 | 2.847969000000  | 0.545156000000  |
| F | -3.694555000000 | 4.037626000000  | -4.362561000000 | C  | 4.410377000000  | -2.501328000000 | -3.962263000000 |
| F | -1.780937000000 | 4.843881000000  | -5.037211000000 |    |                 |                 |                 |

Cartesian Coordinates for TS1<sup>MD-Re-exo</sup>

|   |                 |                |                 |    |                 |                 |                 |
|---|-----------------|----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 7.210076000000  | 4.906815000000 | 2.808736000000  | P  | 1.890812000000  | 0.979671000000  | 0.080193000000  |
| C | 7.276385000000  | 3.571188000000 | 2.486592000000  | O  | 1.619390000000  | 2.356267000000  | 0.831395000000  |
| C | 6.284920000000  | 2.970955000000 | 1.664217000000  | O  | 3.300122000000  | 1.165466000000  | -0.663024000000 |
| C | 5.220335000000  | 3.779490000000 | 1.142820000000  | O  | 2.069637000000  | -0.016616000000 | 1.301422000000  |
| C | 5.168350000000  | 5.149823000000 | 1.518226000000  | H  | 2.300736000000  | -0.911585000000 | 0.984033000000  |
| C | 6.138539000000  | 5.696943000000 | 2.328268000000  | O  | 0.836280000000  | 0.586118000000  | -0.924853000000 |
| H | 7.116061000000  | 0.976098000000 | 1.801162000000  | C  | 5.310409000000  | -0.496888000000 | 0.400609000000  |
| H | 7.970282000000  | 5.355191000000 | 3.441389000000  | C  | 5.564227000000  | -1.044674000000 | -0.861097000000 |
| H | 8.083517000000  | 2.950001000000 | 2.865739000000  | C  | 4.975544000000  | -1.349864000000 | 1.460124000000  |
| C | 6.314949000000  | 1.580772000000 | 1.385107000000  | C  | 5.500979000000  | -2.424308000000 | -1.053218000000 |
| C | 4.229785000000  | 3.166156000000 | 0.303390000000  | C  | 4.893096000000  | -2.727972000000 | 1.250435000000  |
| H | 4.351794000000  | 5.767568000000 | 1.163796000000  | C  | 5.170378000000  | -3.275105000000 | -0.000786000000 |
| H | 6.078100000000  | 6.745435000000 | 2.604768000000  | C  | -0.734502000000 | 3.617426000000  | -0.139091000000 |
| C | 4.317399000000  | 1.802769000000 | 0.092081000000  | C  | -1.680074000000 | 3.421977000000  | -1.152686000000 |
| C | 5.340442000000  | 0.976589000000 | 0.620100000000  | C  | -1.087525000000 | 3.308624000000  | 1.181151000000  |
| C | 3.077931000000  | 3.923365000000 | -0.267187000000 | C  | -2.949006000000 | 2.927010000000  | -0.848228000000 |
| C | 3.245907000000  | 5.026265000000 | -1.170211000000 | C  | -2.353839000000 | 2.808810000000  | 1.472564000000  |
| C | 1.788788000000  | 3.516345000000 | 0.022234000000  | C  | -3.297360000000 | 2.614216000000  | 0.463254000000  |
| C | 4.519466000000  | 5.459234000000 | -1.629169000000 | Fe | 0.186554000000  | -1.238822000000 | -1.420945000000 |
| C | 2.077565000000  | 5.693983000000 | -1.666913000000 | Cl | -0.273115000000 | -1.120288000000 | -3.580812000000 |
| C | 0.613785000000  | 4.141748000000 | -0.467122000000 | Cl | 2.248427000000  | -2.239886000000 | -1.239362000000 |
| C | 4.631554000000  | 6.520330000000 | -2.500145000000 | C  | -0.047189000000 | -2.679651000000 | 1.138557000000  |
| H | 5.410344000000  | 4.941865000000 | -1.292604000000 | H  | 1.027427000000  | -2.880341000000 | 1.142303000000  |
| C | 2.230946000000  | 6.794976000000 | -2.552886000000 | C  | -0.667590000000 | -2.494498000000 | 2.470179000000  |
| C | 0.790334000000  | 5.235358000000 | -1.292110000000 | C  | 0.027216000000  | -2.915200000000 | 3.616509000000  |
| C | 3.479982000000  | 7.203921000000 | -2.958672000000 | C  | -1.938348000000 | -1.914994000000 | 2.587007000000  |
| H | 5.613783000000  | 6.832797000000 | -2.842487000000 | C  | -0.550858000000 | -2.748908000000 | 4.872414000000  |
| H | 1.338931000000  | 7.300072000000 | -2.913550000000 | H  | 1.012165000000  | -3.364689000000 | 3.518992000000  |
| H | -0.083610000000 | 5.754673000000 | -1.675332000000 | C  | -2.514280000000 | -1.760453000000 | 3.844516000000  |
| H | 3.585832000000  | 8.042385000000 | -3.640594000000 | H  | -2.465819000000 | -1.591130000000 | 1.698616000000  |
| C | -3.947901000000 | 2.776486000000 | -1.965834000000 | C  | -1.823574000000 | -2.177801000000 | 4.986205000000  |
|   |                 |                |                 | H  | -0.012577000000 | -3.064854000000 | 5.761366000000  |

## Chapter 5

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | -2.662912000000 | 2.411214000000  | 2.890327000000  | H  | -3.498846000000 | -1.311580000000 | 3.921781000000  |
| C | 5.765089000000  | -3.003390000000 | -2.418615000000 | H  | -2.275323000000 | -2.055820000000 | 5.966633000000  |
| C | 4.363001000000  | -3.623331000000 | 2.334114000000  | Fe | -4.781010000000 | -1.450110000000 | -0.148013000000 |
| F | 5.434620000000  | -2.137171000000 | -3.398715000000 | Cl | -3.010081000000 | -0.605530000000 | -1.250433000000 |
| F | 5.054646000000  | -4.138743000000 | -2.618612000000 | Cl | -4.331587000000 | -3.589970000000 | 0.445420000000  |
| F | 7.069181000000  | -3.319811000000 | -2.585798000000 | Cl | -6.571554000000 | -1.418201000000 | -1.480923000000 |
| F | 3.009437000000  | -3.812661000000 | 2.175654000000  | Cl | -5.142361000000 | -0.257759000000 | 1.707384000000  |
| F | 4.917451000000  | -4.848581000000 | 2.308125000000  | O  | -0.482391000000 | -1.909172000000 | 0.167200000000  |
| F | 4.530865000000  | -3.107575000000 | 3.564699000000  | H  | 5.087914000000  | -4.343348000000 | -0.163676000000 |
| F | -3.981675000000 | 2.456980000000  | 3.162916000000  | H  | 4.755707000000  | -0.933391000000 | 2.437423000000  |
| F | -2.034871000000 | 3.214712000000  | 3.783056000000  | H  | 5.785674000000  | -0.392123000000 | -1.698233000000 |
| F | -2.239181000000 | 1.148173000000  | 3.144403000000  | H  | -1.416064000000 | 3.628008000000  | -2.184949000000 |
| F | -5.024528000000 | 2.050996000000  | -1.604168000000 | H  | -0.376857000000 | 3.463778000000  | 1.984238000000  |
| F | -3.394436000000 | 2.191690000000  | -3.051909000000 | H  | -4.271729000000 | 2.202938000000  | 0.693675000000  |
| F | -4.402688000000 | 3.989960000000  | -2.372417000000 | H  | 1.262136000000  | -6.575616000000 | -0.660416000000 |
| C | -1.549555000000 | -3.704768000000 | -1.907656000000 | H  | 2.143713000000  | -5.080425000000 | -0.969418000000 |
| H | -1.886468000000 | -3.388687000000 | -2.888461000000 | H  | 1.740446000000  | -5.540447000000 | 0.700270000000  |
| H | -2.184551000000 | -3.417814000000 | -1.081676000000 | C  | 0.399921000000  | -4.826893000000 | -2.987743000000 |
| C | -0.407242000000 | -4.438214000000 | -1.770269000000 | H  | 1.374863000000  | -4.327733000000 | -2.989117000000 |
| C | 0.062535000000  | -4.828476000000 | -0.451260000000 | H  | 0.578502000000  | -5.907699000000 | -3.017180000000 |
| C | -0.634815000000 | -4.509889000000 | 0.724067000000  | H  | -0.122639000000 | -4.539953000000 | -3.902603000000 |
| H | -0.308605000000 | -5.008600000000 | 1.632228000000  | C  | 1.380605000000  | -5.533242000000 | -0.330802000000 |
| H | -1.698326000000 | -4.297478000000 | 0.688490000000  |    |                 |                 |                 |

### Cartesian Coordinates for **TS1<sup>MD-Re-endo</sup>**

|    |                 |                 |                 |   |                 |                 |                 |
|----|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| C  | 7.375750000000  | 5.396534000000  | 2.360367000000  | C | 0.510208000000  | 3.874516000000  | -0.197202000000 |
| C  | 7.508681000000  | 4.040960000000  | 2.166178000000  | C | 4.350033000000  | 6.097380000000  | -2.673690000000 |
| C  | 6.452503000000  | 3.280556000000  | 1.596020000000  | H | 5.236262000000  | 4.751509000000  | -1.280320000000 |
| C  | 5.246952000000  | 3.946160000000  | 1.194014000000  | C | 1.941695000000  | 6.264577000000  | -2.681770000000 |
| C  | 5.135923000000  | 5.343507000000  | 1.427614000000  | C | 0.607165000000  | 4.838347000000  | -1.176591000000 |
| C  | 6.172893000000  | 6.048156000000  | 1.997851000000  | C | 3.157955000000  | 6.660340000000  | -3.187105000000 |
| H  | 7.487212000000  | 1.380541000000  | 1.738234000000  | H | 5.307317000000  | 6.389558000000  | -3.095316000000 |
| H  | 8.186679000000  | 5.967320000000  | 2.802778000000  | H | 1.016743000000  | 6.669162000000  | -3.083917000000 |
| H  | 8.420657000000  | 3.527267000000  | 2.458393000000  | H | -0.299989000000 | 5.231539000000  | -1.626536000000 |
| C  | 6.566096000000  | 1.874080000000  | 1.441256000000  | H | 3.206085000000  | 7.390409000000  | -3.989473000000 |
| C  | 4.189777000000  | 3.178311000000  | 0.594528000000  | P | 1.887583000000  | 0.903119000000  | 0.809148000000  |
| H  | 4.218666000000  | 5.854597000000  | 1.158255000000  | O | 1.595736000000  | 2.370029000000  | 1.345538000000  |
| H  | 6.064437000000  | 7.114039000000  | 2.175269000000  | O | 3.293778000000  | 0.996852000000  | 0.056402000000  |
| C  | 4.335874000000  | 1.803556000000  | 0.574670000000  | O | 1.978275000000  | 0.098988000000  | 2.161853000000  |
| C  | 5.515842000000  | 1.120719000000  | 0.967662000000  | H | 1.862436000000  | -0.868360000000 | 2.084749000000  |
| C  | 2.981803000000  | 3.806781000000  | -0.012291000000 | O | 0.866988000000  | 0.350383000000  | -0.160970000000 |
| C  | 3.074389000000  | 4.768848000000  | -1.079794000000 | C | 5.547258000000  | -0.361971000000 | 0.835895000000  |
| C  | 1.718190000000  | 3.393814000000  | 0.362749000000  | C | 6.175151000000  | -0.984341000000 | -0.248217000000 |
| C  | 4.311516000000  | 5.176732000000  | -1.649777000000 | C | 4.808173000000  | -1.138261000000 | 1.728721000000  |
| C  | 1.864732000000  | 5.304363000000  | -1.636931000000 | C | 6.033837000000  | -2.358632000000 | -0.444602000000 |
| Cl | -4.502002000000 | -3.680029000000 | 4.256978000000  | C | 4.633092000000  | -2.501699000000 | 1.495922000000  |
|    |                 |                 |                 | C | 5.245766000000  | -3.125675000000 | 0.413522000000  |

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| Cl | -7.486064000000 | -1.560705000000 | 4.608286000000  | C  | -0.787190000000 | 3.270709000000  | 0.205933000000  |
| Cl | -4.197183000000 | -0.272293000000 | 5.588850000000  | C  | -1.485829000000 | 2.479206000000  | -0.711574000000 |
| O  | -0.418684000000 | -2.247418000000 | -0.737773000000 | C  | -1.289041000000 | 3.420584000000  | 1.502479000000  |
| H  | 5.084223000000  | -4.178788000000 | 0.218678000000  | C  | -2.667516000000 | 1.845397000000  | -0.328198000000 |
| H  | 4.326294000000  | -0.665371000000 | 2.576915000000  | C  | -2.480696000000 | 2.794879000000  | 1.868737000000  |
| H  | 6.731360000000  | -0.389689000000 | -0.964420000000 | C  | -3.178991000000 | 2.001314000000  | 0.959757000000  |
| H  | -1.086823000000 | 2.327079000000  | -1.709109000000 | Fe | 0.707241000000  | -1.028712000000 | -1.537813000000 |
| H  | -0.751782000000 | 4.025323000000  | 2.225606000000  | Cl | -0.005336000000 | -0.140977000000 | -3.425604000000 |
| H  | -4.090115000000 | 1.498110000000  | 1.257290000000  | Cl | 2.691309000000  | -2.029470000000 | -1.605762000000 |
| C  | -3.313468000000 | 0.881581000000  | -1.283386000000 | C  | -0.284355000000 | -3.081303000000 | 0.249416000000  |
| C  | -2.958529000000 | 2.919399000000  | 3.292273000000  | H  | 0.519787000000  | -3.815308000000 | 0.161439000000  |
| C  | 6.707218000000  | -3.022069000000 | -1.617606000000 | C  | -0.708511000000 | -2.697946000000 | 1.587729000000  |
| C  | 3.618110000000  | -3.218146000000 | 2.330913000000  | C  | -0.387204000000 | -3.526962000000 | 2.680407000000  |
| F  | 6.881381000000  | -2.163031000000 | -2.644250000000 | C  | -1.384546000000 | -1.481166000000 | 1.801591000000  |
| F  | 5.982679000000  | -4.067515000000 | -2.076450000000 | C  | -0.728683000000 | -3.136871000000 | 3.968644000000  |
| F  | 7.927964000000  | -3.501271000000 | -1.285899000000 | H  | 0.134503000000  | -4.465219000000 | 2.510868000000  |
| F  | 2.346750000000  | -2.753609000000 | 1.998135000000  | C  | -1.712131000000 | -1.093218000000 | 3.096796000000  |
| F  | 3.588490000000  | -4.541780000000 | 2.133636000000  | H  | -1.648480000000 | -0.861365000000 | 0.952558000000  |
| F  | 3.752467000000  | -2.978534000000 | 3.645422000000  | C  | -1.389526000000 | -1.919537000000 | 4.177512000000  |
| F  | -4.260162000000 | 2.608917000000  | 3.425830000000  | H  | -0.492374000000 | -3.778703000000 | 4.811540000000  |
| F  | -2.775963000000 | 4.170983000000  | 3.769883000000  | H  | -2.233883000000 | -0.161127000000 | 3.272096000000  |
| F  | -2.253921000000 | 2.087853000000  | 4.104360000000  | H  | -1.681203000000 | -1.622445000000 | 5.178917000000  |
| F  | -2.704552000000 | -0.338121000000 | -1.201896000000 | Fe | -5.296342000000 | -1.578569000000 | 4.132301000000  |
| F  | -3.199533000000 | 1.280591000000  | -2.568831000000 | Cl | -5.025833000000 | -0.850299000000 | 2.008910000000  |
| F  | -4.619244000000 | 0.683246000000  | -1.026489000000 | C  | -3.568018000000 | -4.169877000000 | 0.904823000000  |
| C  | -2.497781000000 | -3.075380000000 | -2.558662000000 | H  | -3.616889000000 | -3.161681000000 | 1.338442000000  |
| H  | -2.845993000000 | -2.410044000000 | -3.342246000000 | H  | -4.608133000000 | -4.465849000000 | 0.728134000000  |
| H  | -1.503056000000 | -3.481425000000 | -2.694046000000 | H  | -3.137787000000 | -4.835355000000 | 1.653761000000  |
| C  | -3.271323000000 | -3.336384000000 | -1.480579000000 | C  | -4.651305000000 | -2.729718000000 | -1.367389000000 |
| C  | -2.776900000000 | -4.153169000000 | -0.365520000000 | H  | -5.420357000000 | -3.509072000000 | -1.301952000000 |
| C  | -1.561091000000 | -4.805144000000 | -0.394114000000 | H  | -4.748294000000 | -2.106514000000 | -0.473761000000 |
| H  | -1.297639000000 | -5.470040000000 | 0.422248000000  | H  | -4.873041000000 | -2.106579000000 | -2.236818000000 |
| H  | -1.008500000000 | -4.949092000000 | -1.316124000000 |    |                 |                 |                 |

Cartesian Coordinates for **TS1<sup>MD-Si-exo</sup>**

|   |                |                |                |    |                 |                 |                 |
|---|----------------|----------------|----------------|----|-----------------|-----------------|-----------------|
| C | 7.667670000000 | 4.588021000000 | 2.139292000000 | C  | 1.591764000000  | -6.501438000000 | 0.133164000000  |
| C | 7.555820000000 | 3.217004000000 | 2.168993000000 | H  | 0.945119000000  | -4.891187000000 | 1.395001000000  |
| C | 6.425318000000 | 2.565757000000 | 1.606561000000 | C  | 1.408746000000  | -6.122916000000 | -2.252478000000 |
| C | 5.404112000000 | 3.353250000000 | 0.974835000000 | H  | 0.627420000000  | -4.200904000000 | -2.841748000000 |
| C | 5.542115000000 | 4.767443000000 | 0.981833000000 | C  | 1.755467000000  | -6.949624000000 | -1.181621000000 |
| C | 6.643829000000 | 5.367355000000 | 1.550796000000 | H  | 1.829570000000  | -7.154799000000 | 0.966588000000  |
| H | 7.069451000000 | 0.569119000000 | 2.160877000000 | H  | 1.522410000000  | -6.476504000000 | -3.272347000000 |
| H | 8.533629000000 | 5.075469000000 | 2.576857000000 | H  | 2.133685000000  | -7.949345000000 | -1.368231000000 |
| H | 8.326967000000 | 2.609460000000 | 2.635075000000 | Fe | -2.507896000000 | -7.425632000000 | -0.555783000000 |
| C | 6.286673000000 | 1.153863000000 | 1.686469000000 | Cl | -1.941934000000 | -6.601437000000 | 1.471449000000  |
| C | 4.271242000000 | 2.689550000000 | 0.385595000000 | Cl | -2.525790000000 | -5.751758000000 | -2.082513000000 |
|   |                |                |                | Cl | -4.569374000000 | -8.294047000000 | -0.433090000000 |

## Chapter 5

|                                                            |                 |                 |                 |    |                 |                 |                 |
|------------------------------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H                                                          | 4.764581000000  | 5.378359000000  | 0.538110000000  | Cl | -1.051143000000 | -9.012641000000 | -1.170005000000 |
| H                                                          | 6.725356000000  | 6.450276000000  | 1.550801000000  | O  | 0.048202000000  | -2.253970000000 | -1.498602000000 |
| C                                                          | 4.171089000000  | 1.328334000000  | 0.586991000000  | H  | 3.422023000000  | -4.546316000000 | 1.313540000000  |
| C                                                          | 5.160304000000  | 0.526662000000  | 1.209034000000  | H  | 3.795369000000  | -0.678532000000 | 3.167007000000  |
| C                                                          | 3.245367000000  | 3.406880000000  | -0.426589000000 | H  | 5.775261000000  | -1.480473000000 | -0.556197000000 |
| C                                                          | 3.614842000000  | 4.169044000000  | -1.589478000000 | H  | -1.165494000000 | 3.720758000000  | -2.602891000000 |
| C                                                          | 1.898144000000  | 3.296429000000  | -0.130314000000 | H  | -0.383507000000 | 3.713503000000  | 1.629633000000  |
| C                                                          | 4.942200000000  | 4.220577000000  | -2.094838000000 | H  | -4.396910000000 | 3.276995000000  | 0.182529000000  |
| C                                                          | 2.591925000000  | 4.878878000000  | -2.299043000000 | C  | -3.838722000000 | 3.401137000000  | -2.466720000000 |
| C                                                          | 0.855021000000  | 3.952716000000  | -0.838409000000 | C  | -2.869441000000 | 3.169665000000  | 2.439703000000  |
| C                                                          | 5.244131000000  | 4.970857000000  | -3.210005000000 | C  | 4.916851000000  | -4.027462000000 | -0.879221000000 |
| H                                                          | 5.723658000000  | 3.652747000000  | -1.605407000000 | C  | 2.444075000000  | -2.977158000000 | 3.340962000000  |
| C                                                          | 2.941406000000  | 5.662800000000  | -3.432437000000 | F  | 6.134248000000  | -3.823008000000 | -1.424517000000 |
| C                                                          | 1.242881000000  | 4.762779000000  | -1.890257000000 | F  | 4.000431000000  | -3.797958000000 | -1.848856000000 |
| C                                                          | 4.241205000000  | 5.712984000000  | -3.878034000000 | F  | 4.823486000000  | -5.329179000000 | -0.540806000000 |
| H                                                          | 6.263513000000  | 4.987857000000  | -3.583966000000 | F  | 1.256476000000  | -2.359791000000 | 2.905571000000  |
| H                                                          | 2.156272000000  | 6.206484000000  | -3.950791000000 | F  | 2.158926000000  | -4.278863000000 | 3.438968000000  |
| H                                                          | 0.488858000000  | 5.319630000000  | -2.438353000000 | F  | 2.669087000000  | -2.484239000000 | 4.564756000000  |
| H                                                          | 4.498312000000  | 6.305961000000  | -4.750509000000 | F  | -4.182215000000 | 3.406648000000  | 2.623391000000  |
| P                                                          | 1.607428000000  | 0.896798000000  | 0.749998000000  | F  | -2.182884000000 | 3.892356000000  | 3.349224000000  |
| O                                                          | 1.515222000000  | 2.468918000000  | 0.961544000000  | F  | -2.655983000000 | 1.857305000000  | 2.745831000000  |
| O                                                          | 3.038711000000  | 0.632312000000  | 0.108700000000  | F  | -5.022507000000 | 3.985226000000  | -2.183276000000 |
| O                                                          | 1.509227000000  | 0.416407000000  | 2.250612000000  | F  | -4.104544000000 | 2.097587000000  | -2.744583000000 |
| H                                                          | 1.331086000000  | -0.535308000000 | 2.383177000000  | F  | -3.363367000000 | 3.953995000000  | -3.601118000000 |
| O                                                          | 0.570296000000  | 0.247003000000  | -0.137750000000 | C  | -2.850022000000 | -1.848784000000 | -1.621086000000 |
| C                                                          | 4.862630000000  | -0.929610000000 | 1.318124000000  | H  | -3.270628000000 | -1.256026000000 | -2.427094000000 |
| C                                                          | 5.176570000000  | -1.817490000000 | 0.283314000000  | H  | -2.629861000000 | -2.884223000000 | -1.852265000000 |
| C                                                          | 4.056646000000  | -1.367542000000 | 2.370809000000  | C  | -2.634965000000 | -1.289662000000 | -0.400903000000 |
| C                                                          | 4.677272000000  | -3.120901000000 | 0.302695000000  | C  | -1.985960000000 | -2.042845000000 | 0.658063000000  |
| C                                                          | 3.524657000000  | -2.657256000000 | 2.356040000000  | C  | -1.499369000000 | -3.337152000000 | 0.470550000000  |
| C                                                          | 3.840727000000  | -3.548930000000 | 1.332423000000  | H  | -1.162214000000 | -3.880736000000 | 1.345849000000  |
| C                                                          | -0.583130000000 | 3.758482000000  | -0.522924000000 | H  | -1.893966000000 | -3.972549000000 | -0.313342000000 |
| C                                                          | -1.509468000000 | 3.685010000000  | -1.576747000000 | C  | -1.722993000000 | -1.350336000000 | 1.963381000000  |
| C                                                          | -1.062762000000 | 3.647831000000  | 0.789675000000  | H  | -1.213901000000 | -0.392325000000 | 1.810772000000  |
| C                                                          | -2.869171000000 | 3.533093000000  | -1.321482000000 | H  | -2.672912000000 | -1.108083000000 | 2.457438000000  |
| C                                                          | -2.423072000000 | 3.455144000000  | 1.032489000000  | H  | -1.137147000000 | -1.973091000000 | 2.641494000000  |
| C                                                          | -3.340263000000 | 3.415164000000  | -0.014175000000 | C  | -2.976679000000 | 0.160791000000  | -0.157433000000 |
| Fe                                                         | 0.475348000000  | -0.531649000000 | -1.976682000000 | H  | -3.572453000000 | 0.297156000000  | 0.750679000000  |
| Cl                                                         | -0.944652000000 | 0.706396000000  | -3.143742000000 | H  | -2.064058000000 | 0.754359000000  | -0.035057000000 |
| Cl                                                         | 2.519607000000  | -0.513024000000 | -2.841911000000 | H  | -3.526556000000 | 0.578877000000  | -1.000000000000 |
| C                                                          | 0.293487000000  | -3.007349000000 | -0.449119000000 | C  | 1.090945000000  | -5.227673000000 | 0.374074000000  |
| H                                                          | 0.741119000000  | -2.497627000000 | 0.408128000000  | C  | 0.899770000000  | -4.849176000000 | -2.016988000000 |
| C                                                          | 0.755600000000  | -4.386196000000 | -0.699758000000 |    |                 |                 |                 |
| Cartesian Coordinates for <b>TS1</b> <sup>BD-Si-endo</sup> |                 |                 |                 | C  | -2.037697000000 | 4.346297000000  | -1.446512000000 |
| C                                                          | 6.308349000000  | 4.052606000000  | 4.111545000000  | C  | -2.386605000000 | 4.576042000000  | -2.780370000000 |

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 6.237417000000  | 2.827987000000  | 3.489491000000  | Fe | 0.179923000000  | 1.072820000000  | -3.623377000000 |
| C | 5.543806000000  | 2.675900000000  | 2.258287000000  | Cl | -1.595557000000 | 1.814486000000  | -4.649657000000 |
| C | 4.943136000000  | 3.824889000000  | 1.642443000000  | Cl | 1.576711000000  | -0.071412000000 | -4.899764000000 |
| C | 5.008944000000  | 5.067511000000  | 2.329572000000  | C  | -1.700981000000 | -0.255258000000 | -1.844179000000 |
| C | 5.674685000000  | 5.176690000000  | 3.530520000000  | H  | -2.441064000000 | 0.354376000000  | -2.363778000000 |
| H | 5.837206000000  | 0.534596000000  | 2.153359000000  | C  | -1.996289000000 | -0.566685000000 | -0.435245000000 |
| H | 6.836049000000  | 4.157358000000  | 5.054765000000  | C  | -3.278477000000 | -0.294949000000 | 0.066136000000  |
| H | 6.699812000000  | 1.952351000000  | 3.937112000000  | C  | -1.021990000000 | -1.138143000000 | 0.402996000000  |
| C | 5.399642000000  | 1.398753000000  | 1.660880000000  | C  | -3.571284000000 | -0.565771000000 | 1.402248000000  |
| C | 4.262048000000  | 3.664747000000  | 0.386635000000  | H  | -4.037581000000 | 0.136477000000  | -0.576007000000 |
| H | 4.523762000000  | 5.937590000000  | 1.903999000000  | C  | -1.323164000000 | -1.411778000000 | 1.734035000000  |
| H | 5.709385000000  | 6.135598000000  | 4.039083000000  | H  | -0.043751000000 | -1.394853000000 | 0.010709000000  |
| C | 4.157577000000  | 2.383936000000  | -0.125173000000 | C  | -2.597531000000 | -1.119798000000 | 2.236629000000  |
| C | 4.694795000000  | 1.223821000000  | 0.487900000000  | H  | -4.561864000000 | -0.335704000000 | 1.782340000000  |
| C | 3.594545000000  | 4.799482000000  | -0.317733000000 | H  | -0.565865000000 | -1.857219000000 | 2.371488000000  |
| C | 4.297379000000  | 5.972918000000  | -0.755446000000 | H  | -2.829362000000 | -1.328945000000 | 3.277014000000  |
| C | 2.251034000000  | 4.704387000000  | -0.627611000000 | Fe | -6.526449000000 | 1.793840000000  | -2.363803000000 |
| C | 5.701615000000  | 6.132035000000  | -0.606906000000 | Cl | -6.018574000000 | 3.863063000000  | -3.069325000000 |
| C | 3.557566000000  | 7.015552000000  | -1.407903000000 | Cl | -8.561679000000 | 1.228069000000  | -3.108535000000 |
| C | 1.503472000000  | 5.687694000000  | -1.328676000000 | Cl | -6.450423000000 | 1.590438000000  | -0.123837000000 |
| C | 6.331313000000  | 7.279323000000  | -1.036715000000 | Cl | -5.030931000000 | 0.333582000000  | -3.247974000000 |
| H | 6.281777000000  | 5.336900000000  | -0.153446000000 | O  | -0.422970000000 | 0.003909000000  | -2.148897000000 |
| C | 4.237032000000  | 8.193218000000  | -1.823086000000 | H  | 3.503496000000  | -3.636962000000 | -1.488613000000 |
| C | 2.176366000000  | 6.842657000000  | -1.675666000000 | H  | 3.590739000000  | -0.854384000000 | 1.784499000000  |
| C | 5.593436000000  | 8.326945000000  | -1.637707000000 | H  | 5.098065000000  | 0.308542000000  | -2.069725000000 |
| H | 7.406110000000  | 7.379043000000  | -0.916958000000 | H  | 0.487575000000  | 6.085610000000  | -3.790886000000 |
| H | 3.664203000000  | 8.981273000000  | -2.304483000000 | H  | -0.575051000000 | 4.586693000000  | 0.096879000000  |
| H | 1.641140000000  | 7.631725000000  | -2.196502000000 | H  | -3.330179000000 | 4.214567000000  | -3.171995000000 |
| H | 6.103437000000  | 9.228224000000  | -1.964433000000 | C  | -1.788817000000 | 5.478415000000  | -5.054807000000 |
| P | 1.825492000000  | 2.247437000000  | -1.192976000000 | C  | -2.974336000000 | 3.543317000000  | -0.583227000000 |
| O | 1.568124000000  | 3.513493000000  | -0.263046000000 | C  | 4.639171000000  | -2.037192000000 | -3.351106000000 |
| O | 3.416154000000  | 2.177518000000  | -1.317406000000 | C  | 2.745672000000  | -3.314186000000 | 1.113284000000  |
| O | 1.270990000000  | 1.038850000000  | -0.363852000000 | F  | 4.768371000000  | -0.939135000000 | -4.121545000000 |
| H | 0.592707000000  | 0.513993000000  | -0.879135000000 | F  | 3.658129000000  | -2.805496000000 | -3.890746000000 |
| O | 1.235815000000  | 2.345924000000  | -2.589196000000 | F  | 5.786139000000  | -2.743391000000 | -3.455965000000 |
| C | 4.409188000000  | -0.123084000000 | -0.068731000000 | F  | 1.434745000000  | -2.952750000000 | 1.233018000000  |
| C | 4.658988000000  | -0.433822000000 | -1.414311000000 | F  | 2.757990000000  | -4.570302000000 | 0.619618000000  |
| C | 3.819685000000  | -1.091169000000 | 0.750639000000  | F  | 3.247993000000  | -3.351958000000 | 2.362185000000  |
| C | 4.330828000000  | -1.689850000000 | -1.917613000000 | F  | -4.080285000000 | 4.223656000000  | -0.233184000000 |
| C | 3.485913000000  | -2.344973000000 | 0.234348000000  | F  | -2.379713000000 | 3.118761000000  | 0.557817000000  |
| C | 3.748681000000  | -2.657572000000 | -1.096030000000 | F  | -3.374584000000 | 2.430982000000  | -1.253094000000 |
| C | 0.118659000000  | 5.401319000000  | -1.780539000000 | F  | -1.854169000000 | 6.801534000000  | -5.333261000000 |
| C | -0.233363000000 | 5.638943000000  | -3.113537000000 | F  | -2.952849000000 | 4.921682000000  | -5.436395000000 |
| C | -0.817025000000 | 4.776059000000  | -0.940244000000 | F  | -0.810642000000 | 4.967239000000  | -5.846335000000 |
| C | -1.480581000000 | 5.239046000000  | -3.600275000000 | H  | -3.240583000000 | -1.587510000000 | -3.233581000000 |
| C | 0.504289000000  | -2.914269000000 | -2.924834000000 | C  | -2.913668000000 | -3.463156000000 | -1.393956000000 |

## Chapter 5

|   |                 |                 |                 |   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| H | 0.349008000000  | -2.183039000000 | -3.706172000000 | H | -2.972984000000 | -4.550113000000 | -1.529320000000 |
| H | 1.524681000000  | -3.261593000000 | -2.815307000000 | H | -2.659699000000 | -3.293091000000 | -0.338793000000 |
| C | -0.489217000000 | -3.396922000000 | -2.142810000000 | H | -3.893148000000 | -3.025429000000 | -1.589724000000 |
| C | -1.851990000000 | -2.885608000000 | -2.274831000000 | C | -0.206960000000 | -4.458579000000 | -1.102672000000 |
| C | -2.187162000000 | -1.791741000000 | -3.074150000000 | H | -0.470752000000 | -4.116113000000 | -0.097268000000 |
| H | -1.540582000000 | -1.474560000000 | -3.884842000000 | H | -0.780644000000 | -5.370968000000 | -1.300886000000 |
| H | 0.851838000000  | -4.723320000000 | -1.091243000000 |   |                 |                 |                 |

### Cartesian Coordinates for TS1<sup>BD-Re-exo</sup>

|   |                |                 |                 |    |                 |                 |                 |
|---|----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 7.252416000000 | 3.199197000000  | 3.150776000000  | C  | 4.206590000000  | -0.940059000000 | -0.312203000000 |
| C | 6.971322000000 | 1.977678000000  | 2.584882000000  | C  | 3.901991000000  | -1.255717000000 | -1.647525000000 |
| C | 5.962643000000 | 1.851971000000  | 1.590665000000  | C  | 4.167729000000  | -1.968855000000 | 0.640190000000  |
| C | 5.258446000000 | 3.020492000000  | 1.153094000000  | C  | 3.582193000000  | -2.566091000000 | -2.004300000000 |
| C | 5.555923000000 | 4.262437000000  | 1.777234000000  | C  | 3.862348000000  | -3.277371000000 | 0.268004000000  |
| C | 6.527089000000 | 4.347223000000  | 2.750213000000  | C  | 3.567022000000  | -3.588289000000 | -1.055520000000 |
| H | 6.177783000000 | -0.282660000000 | 1.393047000000  | C  | -0.124549000000 | 4.999230000000  | -0.988665000000 |
| H | 8.020680000000 | 3.284967000000  | 3.913409000000  | C  | -0.799621000000 | 5.180086000000  | -2.204601000000 |
| H | 7.506938000000 | 1.085565000000  | 2.898504000000  | C  | -0.864524000000 | 4.672939000000  | 0.153065000000  |
| C | 5.624018000000 | 0.587483000000  | 1.053042000000  | C  | -2.183830000000 | 5.038031000000  | -2.271430000000 |
| C | 4.267753000000 | 2.880482000000  | 0.124444000000  | C  | -2.249612000000 | 4.526519000000  | 0.074983000000  |
| H | 5.008372000000 | 5.150537000000  | 1.484051000000  | C  | -2.920852000000 | 4.711230000000  | -1.132310000000 |
| H | 6.736865000000 | 5.305062000000  | 3.217209000000  | Fe | -0.001530000000 | 0.746057000000  | -3.493104000000 |
| C | 3.963431000000 | 1.605303000000  | -0.320976000000 | Cl | -1.518435000000 | 1.796499000000  | -4.690265000000 |
| C | 4.608772000000 | 0.422315000000  | 0.127146000000  | Cl | 1.834231000000  | 0.364177000000  | -4.621429000000 |
| C | 3.536890000000 | 4.054605000000  | -0.434821000000 | C  | -0.781388000000 | -1.869043000000 | -2.349321000000 |
| C | 4.210723000000 | 5.139946000000  | -1.093328000000 | H  | -0.849909000000 | -2.160575000000 | -3.396613000000 |
| C | 2.156458000000 | 4.081606000000  | -0.401426000000 | C  | -0.301443000000 | -2.921978000000 | -1.422926000000 |
| C | 5.616873000000 | 5.164312000000  | -1.297768000000 | C  | -0.081896000000 | -4.206193000000 | -1.943441000000 |
| C | 3.428826000000 | 6.224441000000  | -1.613903000000 | C  | -0.089594000000 | -2.679633000000 | -0.056489000000 |
| C | 1.354067000000 | 5.114219000000  | -0.950783000000 | C  | 0.368866000000  | -5.227585000000 | -1.108847000000 |
| C | 6.218208000000 | 6.224312000000  | -1.939815000000 | H  | -0.235331000000 | -4.397774000000 | -3.000726000000 |
| H | 6.220247000000 | 4.333937000000  | -0.951653000000 | C  | 0.361072000000  | -3.701870000000 | 0.772050000000  |
| C | 4.083550000000 | 7.310559000000  | -2.255497000000 | H  | -0.297399000000 | -1.704003000000 | 0.372229000000  |
| C | 2.015393000000 | 6.180386000000  | -1.525795000000 | C  | 0.590462000000  | -4.978735000000 | 0.247437000000  |
| C | 5.450011000000 | 7.315149000000  | -2.411734000000 | H  | 0.552240000000  | -6.214351000000 | -1.523446000000 |
| H | 7.293568000000 | 6.219367000000  | -2.090966000000 | H  | 0.542768000000  | -3.506081000000 | 1.823036000000  |
| H | 3.479889000000 | 8.130414000000  | -2.635345000000 | H  | 0.954981000000  | -5.769348000000 | 0.894584000000  |
| H | 1.437794000000 | 6.998920000000  | -1.946252000000 | Fe | 0.308913000000  | -3.436015000000 | -6.827514000000 |
| H | 5.940607000000 | 8.145453000000  | -2.910712000000 | Cl | -1.015935000000 | -1.853090000000 | -5.871859000000 |
| P | 1.425676000000 | 1.733216000000  | -0.889758000000 | Cl | 2.334336000000  | -2.596150000000 | -7.217940000000 |
| O | 1.474279000000 | 2.949750000000  | 0.137623000000  | Cl | -0.668327000000 | -4.065829000000 | -8.745794000000 |
| O | 2.947312000000 | 1.459003000000  | -1.292666000000 | Cl | 0.403910000000  | -5.221227000000 | -5.452563000000 |
| O | 0.826952000000 | 0.534116000000  | -0.070865000000 | O  | -0.370747000000 | -0.619292000000 | -2.146119000000 |
| H | 0.359675000000 | -0.077263000000 | -0.719798000000 | H  | 3.322852000000  | -4.601869000000 | -1.344211000000 |
| O | 0.631834000000 | 2.029039000000  | -2.146979000000 | H  | 4.370220000000  | -1.746948000000 | 1.682987000000  |
| F | 3.443279000000 | -4.174412000000 | -3.739314000000 | H  | 3.927675000000  | -0.489695000000 | -2.413015000000 |
|   |                |                 |                 | H  | -0.236615000000 | 5.393890000000  | -3.105972000000 |

|   |                 |                 |                 |   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| F | 3.564318000000  | -5.560760000000 | 0.854564000000  | H | -0.363112000000 | 4.530382000000  | 1.103453000000  |
| F | 5.097913000000  | -4.432732000000 | 1.914194000000  | H | -3.997550000000 | 4.599179000000  | -1.184868000000 |
| F | 3.002595000000  | -4.058137000000 | 2.331430000000  | C | -2.906691000000 | 5.278848000000  | -3.571244000000 |
| F | -4.318441000000 | 4.329185000000  | 1.217928000000  | C | -2.997859000000 | 4.072605000000  | 1.297950000000  |
| F | -2.527762000000 | 4.649450000000  | 2.422172000000  | C | 3.214984000000  | -2.880362000000 | -3.434854000000 |
| F | -2.865335000000 | 2.726070000000  | 1.467040000000  | C | 3.879664000000  | -4.339620000000 | 1.333453000000  |
| F | -3.408592000000 | 6.534242000000  | -3.628252000000 | F | 3.910821000000  | -2.121102000000 | -4.302532000000 |
| F | -3.955058000000 | 4.432915000000  | -3.718003000000 | F | 1.894824000000  | -2.649220000000 | -3.657101000000 |
| F | -2.099529000000 | 5.121708000000  | -4.638839000000 | H | -4.957196000000 | -1.156251000000 | -4.086464000000 |
| C | -2.783981000000 | 0.803422000000  | -1.130102000000 | H | -3.433642000000 | -0.634886000000 | -4.796081000000 |
| H | -2.117040000000 | 0.163823000000  | -0.567707000000 | H | -3.648282000000 | -2.337716000000 | -4.346378000000 |
| H | -2.833001000000 | 1.835612000000  | -0.805290000000 | C | -4.445745000000 | 1.309700000000  | -2.915484000000 |
| C | -3.507544000000 | 0.372688000000  | -2.192652000000 | H | -4.195803000000 | 1.395622000000  | -3.975960000000 |
| C | -3.366174000000 | -0.994648000000 | -2.681330000000 | H | -5.479266000000 | 0.948960000000  | -2.845941000000 |
| C | -2.728788000000 | -1.992910000000 | -1.933381000000 | H | -4.400890000000 | 2.311988000000  | -2.488060000000 |
| H | -2.664238000000 | -1.876036000000 | -0.857283000000 | C | -3.869874000000 | -1.311642000000 | -4.051786000000 |
| H | -2.869859000000 | -3.018323000000 | -2.262292000000 |   |                 |                 |                 |

Cartesian Coordinates for **TS1<sup>BD-Re-endo</sup>**

|   |                |                 |                 |    |                 |                 |                 |
|---|----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 7.369876000000 | 3.866772000000  | 3.074084000000  | H  | 7.039124000000  | 6.572350000000  | -2.402856000000 |
| C | 7.169681000000 | 2.588955000000  | 2.606432000000  | H  | 3.056466000000  | 8.121085000000  | -2.886638000000 |
| C | 6.168333000000 | 2.318615000000  | 1.634128000000  | H  | 1.143402000000  | 6.885048000000  | -2.008243000000 |
| C | 5.384123000000 | 3.400477000000  | 1.113666000000  | H  | 5.494016000000  | 8.326449000000  | -3.267055000000 |
| C | 5.598018000000 | 4.703202000000  | 1.640231000000  | P  | 1.663584000000  | 1.671791000000  | -0.852035000000 |
| C | 6.565805000000 | 4.928306000000  | 2.594270000000  | O  | 1.598032000000  | 2.911247000000  | 0.152791000000  |
| H | 6.496995000000 | 0.185088000000  | 1.631998000000  | O  | 3.208404000000  | 1.504964000000  | -1.213882000000 |
| H | 8.134000000000 | 4.062790000000  | 3.820295000000  | O  | 1.141419000000  | 0.445806000000  | -0.020872000000 |
| H | 7.765934000000 | 1.762073000000  | 2.982838000000  | H  | 0.598824000000  | -0.148756000000 | -0.622246000000 |
| C | 5.905799000000 | 0.993131000000  | 1.210365000000  | O  | 0.884366000000  | 1.886475000000  | -2.135473000000 |
| C | 4.400207000000 | 3.115305000000  | 0.107305000000  | C  | 4.529697000000  | -0.710728000000 | 0.007770000000  |
| H | 4.990146000000 | 5.527513000000  | 1.286558000000  | C  | 4.254642000000  | -1.172060000000 | -1.290062000000 |
| H | 6.711402000000 | 5.931235000000  | 2.984673000000  | C  | 4.411564000000  | -1.609555000000 | 1.076412000000  |
| C | 4.196704000000 | 1.794476000000  | -0.246482000000 | C  | 3.867291000000  | -2.494803000000 | -1.496368000000 |
| C | 4.908019000000 | 0.695267000000  | 0.301229000000  | C  | 4.031843000000  | -2.933411000000 | 0.855275000000  |
| C | 3.550364000000 | 4.181221000000  | -0.498280000000 | C  | 3.753499000000  | -3.387360000000 | -0.430378000000 |
| C | 4.099426000000 | 5.289615000000  | -1.229106000000 | C  | -0.200060000000 | 4.854965000000  | -0.807380000000 |
| C | 2.173534000000 | 4.087901000000  | -0.417185000000 | C  | -1.000821000000 | 4.718791000000  | -1.949639000000 |
| C | 5.490335000000 | 5.422957000000  | -1.489354000000 | C  | -0.799766000000 | 4.807805000000  | 0.456025000000  |
| C | 3.207473000000 | 6.275817000000  | -1.768329000000 | C  | -2.378823000000 | 4.554207000000  | -1.821428000000 |
| C | 1.268597000000 | 5.042861000000  | -0.941603000000 | C  | -2.182245000000 | 4.654079000000  | 0.572617000000  |
| C | 5.973504000000 | 6.493175000000  | -2.209271000000 | C  | -2.980959000000 | 4.532554000000  | -0.562581000000 |
| H | 6.174976000000 | 4.666852000000  | -1.123824000000 | Fe | 0.311443000000  | 0.517696000000  | -3.431068000000 |
| C | 3.741732000000 | 7.375636000000  | -2.492317000000 | Cl | -1.528307000000 | 1.190277000000  | -4.412002000000 |
| C | 1.807355000000 | 6.129180000000  | -1.598019000000 | Cl | 2.099609000000  | 0.206660000000  | -4.653211000000 |
| C | 5.096114000000 | 7.486351000000  | -2.705874000000 | C  | -0.856792000000 | -1.842686000000 | -2.243978000000 |
| H | 4.339906000000 | -0.504740000000 | -2.139245000000 | H  | -1.170021000000 | -1.997511000000 | -3.278542000000 |
|   |                |                 |                 | C  | -0.538648000000 | -3.086152000000 | -1.516993000000 |

## Chapter 5

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H | -0.542651000000 | 4.716234000000  | -2.931873000000 | C  | -1.062183000000 | -4.285219000000 | -2.026317000000 |
| H | -0.190285000000 | 4.901359000000  | 1.348302000000  | C  | 0.258474000000  | -3.111556000000 | -0.362632000000 |
| H | -4.054095000000 | 4.408778000000  | -0.468398000000 | C  | -0.796285000000 | -5.492746000000 | -1.386822000000 |
| C | -3.252610000000 | 4.331761000000  | -3.028963000000 | H  | -1.652893000000 | -4.276442000000 | -2.936331000000 |
| C | -2.799047000000 | 4.508585000000  | 1.937295000000  | C  | 0.514789000000  | -4.321660000000 | 0.280006000000  |
| C | 3.462455000000  | -2.945815000000 | -2.876374000000 | H  | 0.699308000000  | -2.198747000000 | 0.024320000000  |
| C | 3.843765000000  | -3.832452000000 | 2.045733000000  | C  | -0.013142000000 | -5.512126000000 | -0.229288000000 |
| F | 4.156243000000  | -2.309835000000 | -3.841343000000 | H  | -1.192959000000 | -6.414569000000 | -1.800935000000 |
| F | 2.147784000000  | -2.685875000000 | -3.085497000000 | H  | 1.127110000000  | -4.335398000000 | 1.174166000000  |
| F | 3.634599000000  | -4.272336000000 | -3.045518000000 | H  | 0.193599000000  | -6.452911000000 | 0.272702000000  |
| F | 3.714327000000  | -5.128384000000 | 1.698784000000  | Fe | -2.096142000000 | -3.574921000000 | -5.982062000000 |
| F | 4.868349000000  | -3.734467000000 | 2.918781000000  | Cl | -3.461175000000 | -2.053616000000 | -5.015813000000 |
| F | 2.717352000000  | -3.493002000000 | 2.733399000000  | Cl | -2.330438000000 | -3.585186000000 | -8.201031000000 |
| F | -4.082487000000 | 4.918182000000  | 1.960530000000  | Cl | -2.611743000000 | -5.601335000000 | -5.136637000000 |
| F | -2.122402000000 | 5.202777000000  | 2.875216000000  | Cl | 0.007452000000  | -3.036464000000 | -5.398830000000 |
| F | -2.792644000000 | 3.206187000000  | 2.330623000000  | O  | -0.093019000000 | -0.763770000000 | -2.057597000000 |
| F | -4.280195000000 | 5.207622000000  | -3.061597000000 | H  | 3.441820000000  | -4.409642000000 | -0.602243000000 |
| F | -3.800814000000 | 3.090152000000  | -2.994325000000 | H  | 4.594958000000  | -1.269476000000 | 2.090443000000  |
| F | -2.573248000000 | 4.446464000000  | -4.185328000000 | H  | -3.244207000000 | -2.185809000000 | -2.148148000000 |
| C | -1.958599000000 | 1.258361000000  | -0.643110000000 | C  | -2.930869000000 | -2.216305000000 | 0.503698000000  |
| H | -2.251496000000 | 1.311236000000  | -1.683981000000 | H  | -2.007462000000 | -2.527659000000 | 1.013049000000  |
| H | -1.534463000000 | 2.164361000000  | -0.227184000000 | H  | -3.633048000000 | -1.908140000000 | 1.287633000000  |
| C | -2.134296000000 | 0.166022000000  | 0.138387000000  | H  | -3.336693000000 | -3.081579000000 | -0.021533000000 |
| C | -2.641624000000 | -1.081049000000 | -0.424270000000 | C  | -1.776374000000 | 0.217145000000  | 1.607788000000  |
| C | -2.708595000000 | -1.308065000000 | -1.800867000000 | H  | -2.646478000000 | -0.002644000000 | 2.236559000000  |
| H | -2.730627000000 | -0.479176000000 | -2.500751000000 | H  | -1.001376000000 | -0.515623000000 | 1.859261000000  |
| H | -1.412670000000 | 1.208038000000  | 1.882788000000  |    |                 |                 |                 |

### Cartesian Coordinates for TS1<sup>BD-Si-exo</sup>

|   |                 |                 |                 |   |                |                |                 |
|---|-----------------|-----------------|-----------------|---|----------------|----------------|-----------------|
| C | 7.162394000000  | 3.404579000000  | 3.393277000000  | C | 4.101868000000 | 5.269531000000 | -0.935069000000 |
| C | 6.977130000000  | 2.176770000000  | 2.801175000000  | C | 2.154252000000 | 3.979120000000 | -0.361069000000 |
| C | 6.033038000000  | 2.007857000000  | 1.752673000000  | C | 5.502925000000 | 5.452520000000 | -1.085495000000 |
| C | 5.287595000000  | 3.144320000000  | 1.288748000000  | C | 3.222230000000 | 6.282130000000 | -1.449338000000 |
| C | 5.483904000000  | 4.390656000000  | 1.943758000000  | C | 1.257833000000 | 4.943802000000 | -0.890114000000 |
| C | 6.397546000000  | 4.516040000000  | 2.966811000000  | C | 6.007870000000 | 6.593111000000 | -1.670186000000 |
| H | 6.342468000000  | -0.130490000000 | 1.575883000000  | H | 6.179885000000 | 4.679776000000 | -0.740775000000 |
| H | 7.883520000000  | 3.521130000000  | 4.196761000000  | C | 3.778924000000 | 7.452770000000 | -2.032069000000 |
| H | 7.542515000000  | 1.310936000000  | 3.135512000000  | C | 1.816201000000 | 6.091669000000 | -1.410579000000 |
| C | 5.790239000000  | 0.724452000000  | 1.195709000000  | C | 5.141637000000 | 7.610005000000 | -2.136602000000 |
| C | 4.346951000000  | 2.971899000000  | 0.215275000000  | H | 7.082101000000 | 6.710281000000 | -1.778797000000 |
| H | 4.902202000000  | 5.250808000000  | 1.634204000000  | H | 3.103968000000 | 8.217224000000 | -2.407413000000 |
| H | 6.528372000000  | 5.477589000000  | 3.454428000000  | H | 1.168086000000 | 6.860392000000 | -1.822294000000 |
| C | 4.153317000000  | 1.685683000000  | -0.254528000000 | H | 5.555132000000 | 8.506129000000 | -2.589530000000 |
| C | 4.843991000000  | 0.541388000000  | 0.213109000000  | P | 1.648018000000 | 1.571971000000 | -0.930273000000 |
| C | 3.530600000000  | 4.092833000000  | -0.339337000000 | O | 1.570367000000 | 2.769835000000 | 0.111729000000  |
| H | -1.524980000000 | -2.051171000000 | 2.491533000000  | O | 3.201970000000 | 1.450700000000 | -1.273124000000 |
|   |                 |                 |                 | O | 1.129819000000 | 0.331968000000 | -0.113299000000 |

|                                                            |                 |                 |                 |    |                 |                 |                 |
|------------------------------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H                                                          | -3.752336000000 | -1.038375000000 | 2.957651000000  | H  | 0.481524000000  | -0.203304000000 | -0.638725000000 |
| Fe                                                         | -6.625076000000 | 1.254344000000  | -3.126688000000 | O  | 0.889874000000  | 1.775406000000  | -2.230528000000 |
| Cl                                                         | -6.221409000000 | 1.975332000000  | -1.029530000000 | C  | 4.446938000000  | -0.792694000000 | -0.325030000000 |
| Cl                                                         | -6.959354000000 | 2.988293000000  | -4.494792000000 | C  | 4.889619000000  | -1.231265000000 | -1.575785000000 |
| Cl                                                         | -8.418937000000 | -0.095443000000 | -3.105381000000 | C  | 3.509103000000  | -1.558875000000 | 0.376647000000  |
| Cl                                                         | -4.844575000000 | 0.040090000000  | -3.815214000000 | C  | 4.399928000000  | -2.422147000000 | -2.114748000000 |
| O                                                          | -0.448744000000 | -0.723821000000 | -2.129825000000 | C  | 3.007760000000  | -2.735115000000 | -0.179426000000 |
| H                                                          | 3.063294000000  | -4.092093000000 | -1.857106000000 | C  | 3.458639000000  | -3.180983000000 | -1.422305000000 |
| H                                                          | 3.133977000000  | -1.207908000000 | 1.330638000000  | C  | -0.190680000000 | 4.620784000000  | -0.949607000000 |
| H                                                          | 5.587700000000  | -0.627924000000 | -2.145171000000 | C  | -0.869287000000 | 4.629329000000  | -2.175891000000 |
| H                                                          | -0.357210000000 | 4.956670000000  | -3.073594000000 | C  | -0.860610000000 | 4.161516000000  | 0.187794000000  |
| H                                                          | -0.354626000000 | 4.151529000000  | 1.146716000000  | C  | -2.175680000000 | 4.149920000000  | -2.257172000000 |
| H                                                          | -3.832121000000 | 3.239137000000  | -1.204613000000 | C  | -2.160435000000 | 3.666040000000  | 0.093535000000  |
| C                                                          | -2.909142000000 | 4.154792000000  | -3.574823000000 | C  | -2.829315000000 | 3.646150000000  | -1.128188000000 |
| C                                                          | -2.755915000000 | 3.054732000000  | 1.332507000000  | Fe | 0.395927000000  | 0.334337000000  | -3.478323000000 |
| C                                                          | 4.903268000000  | -2.905893000000 | -3.449117000000 | Cl | -1.066531000000 | 0.937993000000  | -4.987930000000 |
| C                                                          | 1.955247000000  | -3.531205000000 | 0.542600000000  | Cl | 2.366589000000  | -0.338642000000 | -4.221782000000 |
| F                                                          | 5.328186000000  | -1.890978000000 | -4.228546000000 | C  | -1.762825000000 | -0.871698000000 | -2.000798000000 |
| F                                                          | 3.936462000000  | -3.570706000000 | -4.133334000000 | H  | -2.380842000000 | -0.352038000000 | -2.732865000000 |
| F                                                          | 5.938002000000  | -3.763744000000 | -3.309187000000 | C  | -2.307547000000 | -0.968472000000 | -0.637385000000 |
| F                                                          | 0.957977000000  | -3.907983000000 | -0.311711000000 | C  | -3.573837000000 | -0.418118000000 | -0.380235000000 |
| F                                                          | 2.442765000000  | -4.663504000000 | 1.082984000000  | C  | -1.574112000000 | -1.566430000000 | 0.402602000000  |
| F                                                          | 1.368023000000  | -2.824361000000 | 1.533860000000  | C  | -4.087012000000 | -0.441177000000 | 0.914738000000  |
| F                                                          | -4.062996000000 | 2.770085000000  | 1.204007000000  | H  | -4.145423000000 | 0.038377000000  | -1.180502000000 |
| F                                                          | -2.611537000000 | 3.866311000000  | 2.405826000000  | C  | -2.094743000000 | -1.588615000000 | 1.691033000000  |
| F                                                          | -2.115171000000 | 1.894496000000  | 1.641255000000  | H  | -0.619176000000 | -2.037458000000 | 0.196653000000  |
| F                                                          | -3.831572000000 | 5.142165000000  | -3.622235000000 | C  | -3.350565000000 | -1.023144000000 | 1.948685000000  |
| F                                                          | -3.560513000000 | 2.990394000000  | -3.775727000000 | H  | -5.054760000000 | 0.010619000000  | 1.105747000000  |
| F                                                          | -2.070133000000 | 4.339092000000  | -4.621196000000 | C  | -2.866343000000 | -2.447807000000 | -5.037262000000 |
| C                                                          | 0.574812000000  | -3.102149000000 | -3.583344000000 | H  | -2.715326000000 | -1.449326000000 | -5.469175000000 |
| H                                                          | 0.416715000000  | -3.265783000000 | -2.525907000000 | H  | -2.796568000000 | -3.160843000000 | -5.867281000000 |
| H                                                          | 1.602921000000  | -3.151610000000 | -3.921684000000 | H  | -3.871065000000 | -2.481032000000 | -4.617817000000 |
| C                                                          | -0.429499000000 | -2.856348000000 | -4.462661000000 | C  | -0.115679000000 | -2.664584000000 | -5.930287000000 |
| C                                                          | -1.815313000000 | -2.737812000000 | -4.012053000000 | H  | -0.576697000000 | -3.448638000000 | -6.542103000000 |
| C                                                          | -2.174454000000 | -2.788465000000 | -2.665249000000 | H  | -0.490806000000 | -1.702402000000 | -6.294492000000 |
| H                                                          | -1.519517000000 | -3.249421000000 | -1.934906000000 | H  | 0.963149000000  | -2.689199000000 | -6.098902000000 |
| H                                                          | -3.231582000000 | -2.825920000000 | -2.422716000000 |    |                 |                 |                 |
| Cartesian Coordinates for <b>TS1</b> <sup>BD-Si-endo</sup> |                 |                 |                 | H  | -2.441064000000 | 0.354376000000  | -2.363778000000 |
| C                                                          | 6.308349000000  | 4.052606000000  | 4.111545000000  | C  | -1.996289000000 | -0.566685000000 | -0.435245000000 |
| C                                                          | 6.237417000000  | 2.827987000000  | 3.489491000000  | C  | -3.278477000000 | -0.294949000000 | 0.066136000000  |
| C                                                          | 5.543806000000  | 2.675900000000  | 2.258287000000  | C  | -1.021990000000 | -1.138143000000 | 0.402996000000  |
| C                                                          | 4.943136000000  | 3.824889000000  | 1.642443000000  | C  | -3.571284000000 | -0.565771000000 | 1.402248000000  |
| C                                                          | 5.008944000000  | 5.067511000000  | 2.329572000000  | H  | -4.037581000000 | 0.136477000000  | -0.576007000000 |
| C                                                          | 5.674685000000  | 5.176690000000  | 3.530520000000  | C  | -1.323164000000 | -1.411778000000 | 1.734035000000  |
| H                                                          | 5.837206000000  | 0.534596000000  | 2.153359000000  | H  | -0.043751000000 | -1.394853000000 | 0.010709000000  |

## Chapter 5

|    |                 |                 |                 |    |                 |                 |                 |
|----|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| H  | 6.836049000000  | 4.157358000000  | 5.054765000000  | C  | -2.597531000000 | -1.119798000000 | 2.236629000000  |
| H  | 6.699812000000  | 1.952351000000  | 3.937112000000  | H  | -4.561864000000 | -0.335704000000 | 1.782340000000  |
| C  | 5.399642000000  | 1.398753000000  | 1.660880000000  | H  | -0.565865000000 | -1.857219000000 | 2.371488000000  |
| C  | 4.262048000000  | 3.664747000000  | 0.386635000000  | H  | -2.829362000000 | -1.328945000000 | 3.277014000000  |
| H  | 4.523762000000  | 5.937590000000  | 1.903999000000  | Fe | -6.526449000000 | 1.793840000000  | -2.363803000000 |
| H  | 5.709385000000  | 6.135598000000  | 4.039083000000  | Cl | -6.018574000000 | 3.863063000000  | -3.069325000000 |
| C  | 4.157577000000  | 2.383936000000  | -0.125173000000 | Cl | -8.561679000000 | 1.228069000000  | -3.108535000000 |
| C  | 4.694795000000  | 1.223821000000  | 0.487900000000  | Cl | -6.450423000000 | 1.590438000000  | -0.123837000000 |
| C  | 3.594545000000  | 4.799482000000  | -0.317733000000 | Cl | -5.030931000000 | 0.333582000000  | -3.247974000000 |
| C  | 4.297379000000  | 5.972918000000  | -0.755446000000 | O  | -0.422970000000 | 0.003909000000  | -2.148897000000 |
| C  | 2.251034000000  | 4.704387000000  | -0.627611000000 | H  | 3.503496000000  | -3.636962000000 | -1.488613000000 |
| C  | 5.701615000000  | 6.132035000000  | -0.606906000000 | H  | 3.590739000000  | -0.854384000000 | 1.784499000000  |
| C  | 3.557566000000  | 7.015552000000  | -1.407903000000 | H  | 5.098065000000  | 0.308542000000  | -2.069725000000 |
| C  | 1.503472000000  | 5.687694000000  | -1.328676000000 | H  | 0.487575000000  | 6.085610000000  | -3.790886000000 |
| C  | 6.331313000000  | 7.279323000000  | -1.036715000000 | H  | -0.575051000000 | 4.586693000000  | 0.096879000000  |
| H  | 6.281777000000  | 5.336900000000  | -0.153446000000 | H  | -3.330179000000 | 4.214567000000  | -3.171995000000 |
| C  | 4.237032000000  | 8.193218000000  | -1.823086000000 | C  | -1.788817000000 | 5.478415000000  | -5.054807000000 |
| C  | 2.176366000000  | 6.842657000000  | -1.675666000000 | C  | -2.974336000000 | 3.543317000000  | -0.583227000000 |
| C  | 5.593436000000  | 8.326945000000  | -1.637707000000 | C  | 4.639171000000  | -2.037192000000 | -3.351106000000 |
| H  | 7.406110000000  | 7.379043000000  | -0.916958000000 | C  | 2.745672000000  | -3.314186000000 | 1.113284000000  |
| H  | 3.664203000000  | 8.981273000000  | -2.304483000000 | F  | 4.768371000000  | -0.939135000000 | -4.121545000000 |
| H  | 1.641140000000  | 7.631725000000  | -2.196502000000 | F  | 3.658129000000  | -2.805496000000 | -3.890746000000 |
| H  | 6.103437000000  | 9.228224000000  | -1.964433000000 | F  | 5.786139000000  | -2.743391000000 | -3.455965000000 |
| P  | 1.825492000000  | 2.247437000000  | -1.192976000000 | F  | 1.434745000000  | -2.952750000000 | 1.233018000000  |
| O  | 1.568124000000  | 3.513493000000  | -0.263046000000 | F  | 2.757990000000  | -4.570302000000 | 0.619618000000  |
| O  | 3.416154000000  | 2.177518000000  | -1.317406000000 | F  | 3.247993000000  | -3.351958000000 | 2.362185000000  |
| O  | 1.270990000000  | 1.038850000000  | -0.363852000000 | F  | -4.080285000000 | 4.223656000000  | -0.233184000000 |
| H  | 0.592707000000  | 0.513993000000  | -0.879135000000 | F  | -2.379713000000 | 3.118761000000  | 0.557817000000  |
| O  | 1.235815000000  | 2.345924000000  | -2.589196000000 | F  | -3.374584000000 | 2.430982000000  | -1.253094000000 |
| C  | 4.409188000000  | -0.123084000000 | -0.068731000000 | F  | -1.854169000000 | 6.801534000000  | -5.333261000000 |
| C  | 4.658988000000  | -0.433822000000 | -1.414311000000 | F  | -2.952849000000 | 4.921682000000  | -5.436395000000 |
| C  | 3.819685000000  | -1.091169000000 | 0.750639000000  | F  | -0.810642000000 | 4.967239000000  | -5.846335000000 |
| C  | 4.330828000000  | -1.689850000000 | -1.917613000000 | C  | 0.504289000000  | -2.914269000000 | -2.924834000000 |
| C  | 3.485913000000  | -2.344973000000 | 0.234348000000  | H  | 0.349008000000  | -2.183039000000 | -3.706172000000 |
| C  | 3.748681000000  | -2.657572000000 | -1.096030000000 | H  | 1.524681000000  | -3.261593000000 | -2.815307000000 |
| C  | 0.118659000000  | 5.401319000000  | -1.780539000000 | C  | -0.489217000000 | -3.396922000000 | -2.142810000000 |
| C  | -0.233363000000 | 5.638943000000  | -3.113537000000 | C  | -1.851990000000 | -2.885608000000 | -2.274831000000 |
| C  | -0.817025000000 | 4.776059000000  | -0.940244000000 | C  | -2.187162000000 | -1.791741000000 | -3.074150000000 |
| C  | -1.480581000000 | 5.239046000000  | -3.600275000000 | H  | -1.540582000000 | -1.474560000000 | -3.884842000000 |
| C  | -2.037697000000 | 4.346297000000  | -1.446512000000 | H  | -3.240583000000 | -1.587510000000 | -3.233581000000 |
| C  | -2.386605000000 | 4.576042000000  | -2.780370000000 | C  | -2.913668000000 | -3.463156000000 | -1.393956000000 |
| Fe | 0.179923000000  | 1.072820000000  | -3.623377000000 | H  | -2.972984000000 | -4.550113000000 | -1.529320000000 |
| Cl | -1.595557000000 | 1.814486000000  | -4.649657000000 | H  | -2.659699000000 | -3.293091000000 | -0.338793000000 |
| Cl | 1.576711000000  | -0.071412000000 | -4.899764000000 | H  | -3.893148000000 | -3.025429000000 | -1.589724000000 |
| C  | -1.700981000000 | -0.255258000000 | -1.844179000000 | C  | -0.206960000000 | -4.458579000000 | -1.102672000000 |
| H  | -0.780644000000 | -5.370968000000 | -1.300886000000 | H  | -0.470752000000 | -4.116113000000 | -0.097268000000 |

H 0.851838000000 -4.723320000000 -1.091243000000

# Cartesian Coordinates for Int<sup>BP</sup>

C 6.726839000000 3.193265000000 4.631245000000  
 C 6.456640000000 1.948121000000 4.113620000000  
 C 5.416354000000 1.766053000000 3.161569000000  
 C 4.668387000000 2.903201000000 2.712211000000  
 C 4.955134000000 4.170327000000 3.289059000000  
 C 5.957629000000 4.309541000000 4.223339000000  
 H 5.661320000000 -0.372404000000 3.045068000000  
 H 7.519500000000 3.321667000000 5.362288000000  
 H 7.025469000000 1.079759000000 4.435187000000  
 C 5.084079000000 0.474828000000 2.686175000000  
 C 3.647295000000 2.707309000000 1.722429000000  
 H 4.374483000000 5.035108000000 2.990177000000  
 H 6.158171000000 5.286241000000 4.653921000000  
 C 3.362642000000 1.410674000000 1.328168000000  
 C 4.040670000000 0.257195000000 1.804154000000  
 C 2.855949000000 3.842098000000 1.161599000000  
 C 3.462158000000 4.941064000000 0.460783000000  
 C 1.477000000000 3.819498000000 1.242762000000  
 C 4.858308000000 5.015445000000 0.205765000000  
 C 2.620984000000 5.986198000000 -0.049529000000  
 C 0.617339000000 4.813159000000 0.708131000000  
 C 5.396241000000 6.086704000000 -0.472819000000  
 H 5.504493000000 4.214286000000 0.543679000000  
 C 3.211549000000 7.085177000000 -0.730227000000  
 C 1.213147000000 5.891928000000 0.089229000000  
 C 4.570795000000 7.139622000000 -0.933726000000  
 H 6.465272000000 6.120257000000 -0.661033000000  
 H 2.564457000000 7.875676000000 -1.100820000000  
 H 0.589263000000 6.678756000000 -0.325802000000  
 H 5.011465000000 7.980252000000 -1.461210000000  
 P 0.808504000000 1.431462000000 0.828951000000  
 O 0.851769000000 2.678745000000 1.822899000000  
 O 2.330435000000 1.206784000000 0.388927000000  
 O 0.268695000000 0.244186000000 1.692260000000  
 H -0.212286000000 -0.404902000000 1.056369000000  
 O -0.014106000000 1.666458000000 -0.424862000000  
 C 3.619358000000 -1.125869000000 1.455477000000  
 C 3.254314000000 -1.516611000000 0.155407000000  
 C 3.602792000000 -2.094144000000 2.469811000000  
 C 2.888790000000 -2.838084000000 -0.103936000000  
 C 3.251252000000 -3.414929000000 2.194415000000  
 C 2.886906000000 -3.798401000000 0.908041000000  
 F -2.955589000000 2.543459000000 3.722383000000

C -0.854644000000 4.622521000000 0.736543000000  
 C -1.583806000000 4.658021000000 -0.460994000000  
 C -1.525256000000 4.327568000000 1.926875000000  
 C -2.950033000000 4.386318000000 -0.462882000000  
 C -2.894199000000 4.054022000000 1.914718000000  
 C -3.617005000000 4.077088000000 0.724371000000  
 Fe -0.624757000000 0.246111000000 -1.657407000000  
 Cl -2.538418000000 0.945472000000 -2.502931000000  
 Cl 1.121301000000 -0.015588000000 -2.965028000000  
 C -1.469545000000 -2.247245000000 -0.385224000000  
 H -1.301501000000 -2.587672000000 -1.410784000000  
 C -0.934194000000 -3.272160000000 0.586541000000  
 C -0.760509000000 -4.587834000000 0.141342000000  
 C -0.660827000000 -2.961459000000 1.924940000000  
 C -0.328446000000 -5.579072000000 1.024729000000  
 H -0.972285000000 -4.836565000000 -0.894143000000  
 C -0.220188000000 -3.950385000000 2.805064000000  
 H -0.797144000000 -1.951248000000 2.297373000000  
 C -0.056272000000 -5.263456000000 2.357352000000  
 H -0.199809000000 -6.596119000000 0.665880000000  
 H 0.011502000000 -3.692856000000 3.832949000000  
 H 0.299660000000 -6.028490000000 3.039446000000  
 Fe -3.631001000000 -3.510170000000 -3.838714000000  
 Cl -5.152822000000 -2.020627000000 -3.104450000000  
 Cl -4.214925000000 -4.339378000000 -5.826460000000  
 Cl -3.491133000000 -5.195621000000 -2.321767000000  
 Cl -1.621116000000 -2.498493000000 -3.933419000000  
 O -0.902744000000 -0.975532000000 -0.225202000000  
 H 2.599038000000 -4.819779000000 0.697303000000  
 H 3.854363000000 -1.813397000000 3.487387000000  
 H 3.265616000000 -0.800725000000 -0.657574000000  
 H -1.070722000000 4.848596000000 -1.396761000000  
 H -0.977473000000 4.290238000000 2.862222000000  
 H -4.675214000000 3.844675000000 0.716217000000  
 C -3.734750000000 4.446602000000 -1.748777000000  
 C -3.545521000000 3.670575000000 3.213842000000  
 C 2.463816000000 -3.235908000000 -1.495461000000  
 C 3.297328000000 -4.409148000000 3.322826000000  
 F 3.148618000000 -2.560587000000 -2.439753000000  
 F 1.144977000000 -2.983922000000 -1.701599000000  
 F 2.644483000000 -4.554820000000 -1.717335000000  
 F 2.937050000000 -5.650397000000 2.938181000000  
 F 4.541404000000 -4.492550000000 3.849456000000  
 F 2.477059000000 -4.044930000000 4.341312000000

## Chapter 5

|   |                 |                 |                 |   |                 |                 |                |
|---|-----------------|-----------------|-----------------|---|-----------------|-----------------|----------------|
| F | -4.367137000000 | 5.636685000000  | -1.879298000000 | F | -4.857025000000 | 3.400443000000  | 3.081993000000 |
| F | -4.688244000000 | 3.488959000000  | -1.788173000000 | F | -3.406242000000 | 4.624195000000  | 4.154619000000 |
| F | -2.945642000000 | 4.292967000000  | -2.830952000000 | C | -4.082124000000 | -3.211774000000 | 1.687632000000 |
| C | -3.068247000000 | 0.367968000000  | 1.120300000000  | H | -3.270187000000 | -3.595020000000 | 2.328976000000 |
| H | -3.005513000000 | 0.454388000000  | 0.044658000000  | H | -4.924344000000 | -2.995209000000 | 2.352922000000 |
| H | -2.871855000000 | 1.270815000000  | 1.687576000000  | H | -4.346479000000 | -3.997672000000 | 0.979407000000 |
| C | -3.438329000000 | -0.778724000000 | 1.762174000000  | C | -3.658926000000 | -0.788819000000 | 3.259459000000 |
| C | -3.582207000000 | -1.990628000000 | 1.008856000000  | H | -4.699001000000 | -1.033920000000 | 3.502136000000 |
| C | -3.085199000000 | -2.127094000000 | -0.355903000000 | H | -3.024569000000 | -1.535995000000 | 3.749033000000 |
| H | -3.303945000000 | -1.277750000000 | -1.006458000000 | H | -3.438948000000 | 0.189678000000  | 3.688552000000 |
| H | -3.467076000000 | -3.032067000000 | -0.823851000000 |   |                 |                 |                |

### Cartesian Coordinates for **Int<sup>MD</sup>**

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 7.135185000000  | 2.192959000000  | 3.791823000000  | O  | 2.253119000000  | 1.214346000000  | -0.265236000000 |
| C | 6.877307000000  | 1.179959000000  | 2.897878000000  | O  | 0.912399000000  | -0.529308000000 | 1.081323000000  |
| C | 5.714700000000  | 1.206831000000  | 2.080382000000  | H  | 0.110569000000  | -1.082507000000 | 0.926630000000  |
| C | 4.819829000000  | 2.326230000000  | 2.168282000000  | O  | -0.291301000000 | 1.249586000000  | -0.385724000000 |
| C | 5.101560000000  | 3.338645000000  | 3.125569000000  | C  | 3.814107000000  | -1.101144000000 | -0.293050000000 |
| C | 6.229234000000  | 3.273208000000  | 3.913927000000  | C  | 3.403901000000  | -1.038120000000 | -1.633815000000 |
| H | 6.077349000000  | -0.735644000000 | 1.197251000000  | C  | 3.697714000000  | -2.315311000000 | 0.391854000000  |
| H | 8.023911000000  | 2.159592000000  | 4.414986000000  | C  | 2.886839000000  | -2.170392000000 | -2.260458000000 |
| H | 7.552817000000  | 0.332989000000  | 2.811845000000  | C  | 3.161005000000  | -3.437595000000 | -0.241878000000 |
| C | 5.407057000000  | 0.119157000000  | 1.224066000000  | C  | 2.753900000000  | -3.377409000000 | -1.570979000000 |
| C | 3.658409000000  | 2.353847000000  | 1.321899000000  | C  | -1.150240000000 | 3.749623000000  | 1.615543000000  |
| H | 4.415837000000  | 4.169993000000  | 3.237813000000  | C  | -2.066241000000 | 4.398757000000  | 0.772336000000  |
| H | 6.422543000000  | 4.057317000000  | 4.640175000000  | C  | -1.613476000000 | 2.677365000000  | 2.396152000000  |
| C | 3.429937000000  | 1.250633000000  | 0.519017000000  | C  | -3.393797000000 | 3.979240000000  | 0.702867000000  |
| C | 4.261398000000  | 0.103245000000  | 0.455815000000  | C  | -2.925930000000 | 2.228664000000  | 2.272957000000  |
| C | 2.665109000000  | 3.471535000000  | 1.342581000000  | C  | -3.831674000000 | 2.880059000000  | 1.436725000000  |
| C | 3.020603000000  | 4.832130000000  | 1.053806000000  | Fe | -0.745325000000 | 1.555036000000  | -2.286925000000 |
| C | 1.330987000000  | 3.190835000000  | 1.581820000000  | Cl | -1.900072000000 | 3.460027000000  | -2.535775000000 |
| C | 4.329739000000  | 5.222934000000  | 0.663482000000  | Cl | 1.162198000000  | 1.528004000000  | -3.414462000000 |
| C | 2.001725000000  | 5.839460000000  | 1.127526000000  | C  | -1.955352000000 | -1.169819000000 | -2.677070000000 |
| C | 0.281407000000  | 4.152166000000  | 1.574293000000  | H  | -1.301645000000 | -1.529140000000 | -3.477374000000 |
| C | 4.625224000000  | 6.544231000000  | 0.410035000000  | C  | -1.596839000000 | -1.849854000000 | -1.369697000000 |
| H | 5.100628000000  | 4.468773000000  | 0.558838000000  | C  | -0.835311000000 | -3.021218000000 | -1.396980000000 |
| C | 2.346179000000  | 7.196404000000  | 0.878478000000  | C  | -2.035281000000 | -1.342341000000 | -0.139704000000 |
| C | 0.659795000000  | 5.469329000000  | 1.388476000000  | C  | -0.514234000000 | -3.689531000000 | -0.214916000000 |
| C | 3.630952000000  | 7.544298000000  | 0.532281000000  | H  | -0.492274000000 | -3.415169000000 | -2.345663000000 |
| H | 5.630979000000  | 6.820697000000  | 0.107697000000  | C  | -1.721187000000 | -2.011930000000 | 1.049581000000  |
| H | 1.568553000000  | 7.952344000000  | 0.948731000000  | H  | -2.602311000000 | -0.417772000000 | -0.103025000000 |
| H | -0.095688000000 | 6.249457000000  | 1.409918000000  | C  | -0.955423000000 | -3.188108000000 | 1.011262000000  |
| H | 3.882159000000  | 8.582256000000  | 0.335660000000  | H  | 0.074220000000  | -4.598738000000 | -0.261200000000 |
| P | 0.885827000000  | 0.925041000000  | 0.497689000000  | H  | -2.079299000000 | -1.620550000000 | 1.996456000000  |
| O | 0.975984000000  | 1.839820000000  | 1.807584000000  | H  | -0.702464000000 | -3.703326000000 | 1.932699000000  |
| C | 2.366172000000  | -2.074447000000 | -3.671223000000 | Fe | -1.442147000000 | -5.642037000000 | -4.072634000000 |
|   |                 |                 |                 | Cl | -3.167491000000 | -5.386590000000 | -2.632141000000 |

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 2.951213000000  | -4.683121000000 | 0.575238000000  | Cl | -1.847435000000 | -7.306322000000 | -5.501764000000 |
| F | 3.012396000000  | -1.134430000000 | -4.389557000000 | Cl | 0.426450000000  | -6.028123000000 | -2.883298000000 |
| F | 1.045504000000  | -1.739071000000 | -3.672943000000 | Cl | -1.254720000000 | -3.692233000000 | -5.188050000000 |
| F | 2.469466000000  | -3.245034000000 | -4.331239000000 | O  | -1.896753000000 | 0.210182000000  | -2.597977000000 |
| F | 2.482102000000  | -5.711616000000 | -0.158324000000 | H  | 2.322336000000  | -4.243452000000 | -2.058134000000 |
| F | 4.091638000000  | -5.086819000000 | 1.176980000000  | H  | 3.979720000000  | -2.370714000000 | 1.438575000000  |
| F | 2.049174000000  | -4.460520000000 | 1.570136000000  | H  | 3.465918000000  | -0.104250000000 | -2.180246000000 |
| F | -4.350013000000 | 1.258710000000  | 3.906136000000  | H  | -1.734567000000 | 5.200232000000  | 0.124364000000  |
| F | -2.380589000000 | 0.362743000000  | 3.640016000000  | H  | -0.944580000000 | 2.169270000000  | 3.075790000000  |
| F | -3.919034000000 | 0.094667000000  | 2.121915000000  | H  | -4.854611000000 | 2.529552000000  | 1.350154000000  |
| F | -5.347589000000 | 5.293053000000  | 0.561943000000  | C  | -4.388422000000 | 4.689959000000  | -0.175502000000 |
| F | -5.039306000000 | 3.813825000000  | -0.994849000000 | C  | -3.387551000000 | 0.997948000000  | 3.001732000000  |
| F | -3.824825000000 | 5.627549000000  | -0.955962000000 | H  | -4.306777000000 | -3.209548000000 | -1.362982000000 |
| C | -4.404295000000 | 1.090986000000  | -2.837869000000 | H  | -5.087646000000 | -1.994242000000 | -0.298292000000 |
| H | -3.854665000000 | 0.898772000000  | -3.747868000000 | H  | -5.936953000000 | -2.618454000000 | -1.708107000000 |
| H | -4.597949000000 | 2.134559000000  | -2.613407000000 | C  | -5.766342000000 | 0.451663000000  | -0.840401000000 |
| C | -4.870588000000 | 0.101713000000  | -2.010851000000 | H  | -6.706523000000 | -0.108538000000 | -0.882363000000 |
| C | -4.442358000000 | -1.243011000000 | -2.218474000000 | H  | -5.285533000000 | 0.218361000000  | 0.115627000000  |
| C | -3.417699000000 | -1.597035000000 | -3.209847000000 | H  | -6.004197000000 | 1.517007000000  | -0.845640000000 |
| H | -3.526713000000 | -1.076242000000 | -4.162859000000 | C  | -4.942026000000 | -2.323640000000 | -1.330475000000 |
| H | -3.378375000000 | -2.673129000000 | -3.387804000000 |    |                 |                 |                 |

Cartesian Coordinates for **TS2<sup>BD</sup>**

|    |                 |                 |                 |   |                 |                 |                 |
|----|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|
| C  | 5.905400000000  | 3.521104000000  | 5.129364000000  | H | 5.384453000000  | 4.191698000000  | 0.793936000000  |
| C  | 5.864262000000  | 2.233974000000  | 4.646365000000  | C | 3.106992000000  | 6.800463000000  | -0.977092000000 |
| C  | 5.047732000000  | 1.901165000000  | 3.531177000000  | C | 1.102609000000  | 5.478699000000  | -0.404979000000 |
| C  | 4.287541000000  | 2.931266000000  | 2.885301000000  | C | 4.472443000000  | 6.965669000000  | -0.963696000000 |
| C  | 4.333327000000  | 4.244566000000  | 3.426457000000  | H | 6.372528000000  | 6.130286000000  | -0.335651000000 |
| C  | 5.121399000000  | 4.529692000000  | 4.519706000000  | H | 2.467375000000  | 7.518235000000  | -1.483548000000 |
| H  | 5.539962000000  | -0.199296000000 | 3.575606000000  | H | 0.488577000000  | 6.215227000000  | -0.915764000000 |
| H  | 6.528094000000  | 3.764563000000  | 5.985001000000  | H | 4.924469000000  | 7.821694000000  | -1.455594000000 |
| H  | 6.446793000000  | 1.446927000000  | 5.117767000000  | P | 1.017662000000  | 0.959147000000  | 0.447251000000  |
| C  | 4.952707000000  | 0.564320000000  | 3.073617000000  | O | 0.736843000000  | 2.265479000000  | 1.330510000000  |
| C  | 3.493096000000  | 2.585466000000  | 1.739714000000  | O | 2.600276000000  | 0.897640000000  | 0.286067000000  |
| H  | 3.737521000000  | 5.028283000000  | 2.973691000000  | O | 0.483460000000  | -0.224026000000 | 1.319899000000  |
| H  | 5.139313000000  | 5.539199000000  | 4.919689000000  | H | -0.217434000000 | -0.753064000000 | 0.809407000000  |
| C  | 3.425883000000  | 1.253149000000  | 1.378054000000  | O | 0.404523000000  | 1.019542000000  | -0.940182000000 |
| C  | 4.129560000000  | 0.202104000000  | 2.023574000000  | C | 3.949871000000  | -1.221258000000 | 1.640037000000  |
| C  | 2.708840000000  | 3.604228000000  | 0.981341000000  | C | 3.886002000000  | -1.634356000000 | 0.297276000000  |
| C  | 3.331665000000  | 4.729393000000  | 0.340481000000  | C | 3.830625000000  | -2.191525000000 | 2.641892000000  |
| C  | 1.343031000000  | 3.451357000000  | 0.829114000000  | C | 3.689945000000  | -2.974434000000 | -0.018269000000 |
| C  | 4.740079000000  | 4.918861000000  | 0.314296000000  | C | 3.661410000000  | -3.538454000000 | 2.313243000000  |
| C  | 2.503952000000  | 5.679311000000  | -0.345103000000 | C | 3.584776000000  | -3.940634000000 | 0.985027000000  |
| C  | 0.498562000000  | 4.370509000000  | 0.154918000000  | C | -0.964439000000 | 4.146033000000  | 0.034114000000  |
| C  | 5.293514000000  | 6.007978000000  | -0.322073000000 | C | -1.586704000000 | 4.239282000000  | -1.216813000000 |
| Cl | -4.691571000000 | -2.052345000000 | -2.878293000000 | C | -1.750851000000 | 3.867605000000  | 1.161570000000  |
|    |                 |                 |                 | C | -2.964037000000 | 4.050106000000  | -1.338995000000 |

## Chapter 5

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| O | -1.406710000000 | -1.058548000000 | -0.242673000000 | C  | -3.126172000000 | 3.682288000000  | 1.029538000000  |
| H | 3.425641000000  | -4.981217000000 | 0.731510000000  | C  | -3.744479000000 | 3.767241000000  | -0.220406000000 |
| H | 3.842516000000  | -1.895654000000 | 3.685977000000  | Fe | -0.793892000000 | -0.226502000000 | -1.867362000000 |
| H | 3.985336000000  | -0.911272000000 | -0.501005000000 | Cl | -2.394183000000 | 0.900900000000  | -2.816589000000 |
| H | -0.990491000000 | 4.430667000000  | -2.101801000000 | Cl | 0.322076000000  | -1.753625000000 | -2.983623000000 |
| H | -1.290390000000 | 3.801594000000  | 2.140121000000  | C  | -2.051833000000 | -2.345932000000 | -0.295060000000 |
| H | -4.810518000000 | 3.596204000000  | -0.321958000000 | H  | -2.270097000000 | -2.572133000000 | -1.343730000000 |
| C | -3.632765000000 | 4.211447000000  | -2.682253000000 | C  | -1.138781000000 | -3.408164000000 | 0.273241000000  |
| C | -3.973468000000 | 3.353526000000  | 2.230532000000  | C  | -0.784429000000 | -4.499262000000 | -0.527113000000 |
| C | 3.591381000000  | -3.424526000000 | -1.453307000000 | C  | -0.643781000000 | -3.331974000000 | 1.583099000000  |
| C | 3.566905000000  | -4.537108000000 | 3.434463000000  | C  | 0.032146000000  | -5.511965000000 | -0.019560000000 |
| F | 3.613470000000  | -2.389338000000 | -2.318591000000 | H  | -1.144804000000 | -4.553763000000 | -1.550702000000 |
| F | 2.447525000000  | -4.115086000000 | -1.667355000000 | C  | 0.173985000000  | -4.340394000000 | 2.089635000000  |
| F | 4.611595000000  | -4.251071000000 | -1.780655000000 | H  | -0.895931000000 | -2.485349000000 | 2.216013000000  |
| F | 3.223927000000  | -5.770201000000 | 3.003258000000  | C  | 0.507490000000  | -5.437188000000 | 1.289479000000  |
| F | 4.739164000000  | -4.651951000000 | 4.096321000000  | H  | 0.300945000000  | -6.352513000000 | -0.652360000000 |
| F | 2.641314000000  | -4.159447000000 | 4.354104000000  | H  | 0.560990000000  | -4.265849000000 | 3.100284000000  |
| F | -4.505117000000 | 2.105017000000  | 2.125289000000  | H  | 1.148323000000  | -6.217780000000 | 1.686119000000  |
| F | -5.007250000000 | 4.204273000000  | 2.365294000000  | Fe | -6.420282000000 | -1.166863000000 | -1.729596000000 |
| F | -3.263430000000 | 3.375348000000  | 3.381463000000  | Cl | -5.744826000000 | 0.758053000000  | -0.761422000000 |
| F | -4.173588000000 | 5.447765000000  | -2.802740000000 | Cl | -8.177353000000 | -0.834213000000 | -3.052240000000 |
| F | -4.630570000000 | 3.323724000000  | -2.856838000000 | Cl | -6.915115000000 | -2.586312000000 | -0.041928000000 |
| F | -2.758649000000 | 4.061508000000  | -3.702073000000 | H  | -3.253799000000 | -3.621194000000 | 2.819173000000  |
| C | -2.684615000000 | 0.280538000000  | 0.852363000000  | H  | -3.746398000000 | -2.263356000000 | 3.874284000000  |
| H | -3.302881000000 | 0.226770000000  | -0.032861000000 | H  | -4.884593000000 | -2.978689000000 | 2.704975000000  |
| H | -2.065304000000 | 1.169336000000  | 0.914375000000  | C  | -2.540495000000 | 0.035214000000  | 3.361250000000  |
| C | -2.929764000000 | -0.490171000000 | 1.995128000000  | H  | -3.432062000000 | 0.331649000000  | 3.923617000000  |
| C | -3.439138000000 | -1.766373000000 | 1.781017000000  | H  | -1.996195000000 | -0.710058000000 | 3.949266000000  |
| C | -3.466311000000 | -2.283478000000 | 0.390705000000  | H  | -1.908158000000 | 0.921857000000  | 3.269057000000  |
| H | -4.073604000000 | -1.628745000000 | -0.240056000000 | C  | -3.836476000000 | -2.692979000000 | 2.876015000000  |
| H | -3.912724000000 | -3.277179000000 | 0.330050000000  |    |                 |                 |                 |

### Cartesian Coordinates for TS2<sup>MD</sup>

|   |                 |                 |                 |   |                |                 |                |
|---|-----------------|-----------------|-----------------|---|----------------|-----------------|----------------|
| C | 7.017100000000  | 2.089443000000  | 4.193562000000  | H | 4.421918000000 | 4.150060000000  | 3.399108000000 |
| C | 6.766254000000  | 1.048843000000  | 3.329908000000  | H | 6.340439000000 | 4.018180000000  | 4.918810000000 |
| C | 5.652714000000  | 1.086531000000  | 2.446912000000  | C | 3.457523000000 | 1.149333000000  | 0.761418000000 |
| C | 4.803681000000  | 2.243654000000  | 2.436393000000  | C | 4.246614000000 | -0.029314000000 | 0.785482000000 |
| C | 5.075777000000  | 3.286836000000  | 3.362831000000  | C | 2.763008000000 | 3.445846000000  | 1.432536000000 |
| C | 6.153730000000  | 3.210616000000  | 4.216958000000  | C | 3.211685000000 | 4.767413000000  | 1.095894000000 |
| H | 5.994295000000  | -0.894896000000 | 1.651746000000  | C | 1.404769000000 | 3.252261000000  | 1.613218000000 |
| H | 7.867210000000  | 2.047832000000  | 4.867980000000  | C | 4.559295000000 | 5.063549000000  | 0.756363000000 |
| H | 7.408686000000  | 0.172385000000  | 3.318465000000  | C | 2.251263000000 | 5.832548000000  | 1.067092000000 |
| C | 5.350335000000  | -0.020540000000 | 1.615100000000  | C | 0.415457000000 | 4.269976000000  | 1.509210000000 |
| C | 3.693662000000  | 2.279141000000  | 1.524506000000  | C | 4.943383000000 | 6.351030000000  | 0.452740000000 |
| H | -0.283359000000 | -3.148922000000 | -1.996656000000 | H | 5.289356000000 | 4.263377000000  | 0.730558000000 |
|   |                 |                 |                 | C | 2.686027000000 | 7.153123000000  | 0.768762000000 |

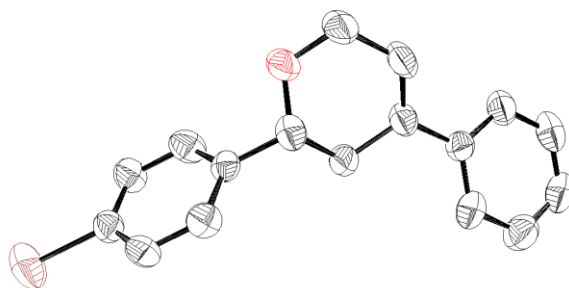
|                                      |                 |                 |                 |    |                 |                 |                 |
|--------------------------------------|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C                                    | -2.008010000000 | -1.670280000000 | 1.143349000000  | C  | 0.879330000000  | 5.552452000000  | 1.278893000000  |
| H                                    | -2.810639000000 | -0.180616000000 | -0.186158000000 | C  | 4.004253000000  | 7.410002000000  | 0.472516000000  |
| C                                    | -1.186868000000 | -2.802672000000 | 1.260291000000  | H  | 5.977310000000  | 6.554623000000  | 0.190192000000  |
| H                                    | 0.080259000000  | -4.197726000000 | 0.204373000000  | H  | 1.951193000000  | 7.953723000000  | 0.761451000000  |
| H                                    | -2.486236000000 | -1.249277000000 | 2.020418000000  | H  | 0.171185000000  | 6.374403000000  | 1.225149000000  |
| H                                    | -1.034207000000 | -3.264265000000 | 2.231656000000  | H  | 4.325058000000  | 8.420440000000  | 0.237499000000  |
| Fe                                   | -1.373769000000 | -5.686754000000 | -3.427198000000 | P  | 0.904769000000  | 0.943204000000  | 0.634681000000  |
| Cl                                   | -3.187405000000 | -5.211331000000 | -2.161513000000 | O  | 0.962104000000  | 1.936696000000  | 1.886594000000  |
| Cl                                   | -1.752905000000 | -7.517839000000 | -4.647682000000 | O  | 2.317515000000  | 1.127069000000  | -0.076756000000 |
| Cl                                   | 0.395015000000  | -6.006793000000 | -2.074456000000 | O  | 0.846626000000  | -0.466642000000 | 1.312494000000  |
| Cl                                   | -1.028237000000 | -3.921789000000 | -4.787856000000 | H  | 0.041061000000  | -1.016220000000 | 1.169254000000  |
| O                                    | -1.834947000000 | 0.370012000000  | -2.611685000000 | O  | -0.205746000000 | 1.254676000000  | -0.336853000000 |
| H                                    | 2.638817000000  | -4.474121000000 | -1.799272000000 | C  | 3.834136000000  | -1.245106000000 | 0.035903000000  |
| H                                    | 4.042081000000  | -2.521747000000 | 1.761440000000  | C  | 3.459340000000  | -1.200230000000 | -1.315329000000 |
| H                                    | 3.487725000000  | -0.264170000000 | -1.860616000000 | C  | 3.776440000000  | -2.472186000000 | 0.710834000000  |
| H                                    | -1.456302000000 | 5.360098000000  | -0.085486000000 | C  | 3.038971000000  | -2.361189000000 | -1.964750000000 |
| H                                    | -1.003585000000 | 2.442325000000  | 3.044124000000  | C  | 3.350115000000  | -3.624720000000 | 0.051370000000  |
| H                                    | -4.787170000000 | 2.928876000000  | 1.083215000000  | C  | 2.979566000000  | -3.580636000000 | -1.291177000000 |
| C                                    | -4.102008000000 | 4.946701000000  | -0.551005000000 | C  | -1.037970000000 | 3.953202000000  | 1.498641000000  |
| C                                    | -3.517639000000 | 1.438320000000  | 2.924400000000  | C  | -1.868805000000 | 4.610583000000  | 0.577302000000  |
| C                                    | 2.577043000000  | -2.285717000000 | -3.397366000000 | C  | -1.604665000000 | 2.952419000000  | 2.304838000000  |
| C                                    | 3.207785000000  | -4.909179000000 | 0.823845000000  | C  | -3.210912000000 | 4.259104000000  | 0.448151000000  |
| F                                    | 3.272537000000  | -1.371099000000 | -4.105078000000 | C  | -2.935306000000 | 2.576665000000  | 2.133941000000  |
| F                                    | 1.266196000000  | -1.922410000000 | -3.464096000000 | C  | -3.752519000000 | 3.228119000000  | 1.211520000000  |
| F                                    | 2.685627000000  | -3.469834000000 | -4.030413000000 | Fe | -0.533930000000 | 1.592291000000  | -2.249237000000 |
| F                                    | 3.324451000000  | -5.993707000000 | 0.034359000000  | Cl | -1.370480000000 | 3.634488000000  | -2.565568000000 |
| F                                    | 4.131300000000  | -5.009395000000 | 1.806136000000  | Cl | 1.356155000000  | 1.314143000000  | -3.351845000000 |
| F                                    | 1.991018000000  | -4.986174000000 | 1.428155000000  | C  | -1.845974000000 | -1.031610000000 | -2.627400000000 |
| F                                    | -4.411899000000 | 1.848677000000  | 3.844284000000  | H  | -1.082731000000 | -1.389140000000 | -3.325287000000 |
| F                                    | -2.569880000000 | 0.719447000000  | 3.567606000000  | C  | -1.598881000000 | -1.618482000000 | -1.248894000000 |
| F                                    | -4.176559000000 | 0.571558000000  | 2.101344000000  | C  | -0.769553000000 | -2.737090000000 | -1.120828000000 |
| F                                    | -5.162403000000 | 5.526240000000  | 0.053271000000  | C  | -2.204975000000 | -1.076971000000 | -0.107393000000 |
| F                                    | -4.621063000000 | 4.053989000000  | -1.445290000000 | C  | -0.563435000000 | -3.330471000000 | 0.125317000000  |
| F                                    | -3.463788000000 | 5.894426000000  | -1.258743000000 | H  | -5.417788000000 | -2.976003000000 | -2.360683000000 |
| C                                    | -3.970605000000 | 1.137707000000  | -3.057079000000 | C  | -5.581865000000 | 0.722621000000  | -1.173379000000 |
| H                                    | -3.551234000000 | 0.886652000000  | -4.020533000000 | H  | -6.613614000000 | 0.398728000000  | -1.348012000000 |
| H                                    | -3.957527000000 | 2.193113000000  | -2.801866000000 | H  | -5.276599000000 | 0.346417000000  | -0.191555000000 |
| C                                    | -4.666890000000 | 0.228296000000  | -2.278011000000 | H  | -5.578184000000 | 1.813749000000  | -1.136275000000 |
| C                                    | -4.378383000000 | -1.138888000000 | -2.448398000000 | H  | -3.140366000000 | -2.639031000000 | -3.342179000000 |
| C                                    | -3.213704000000 | -1.553727000000 | -3.263348000000 | C  | -5.066876000000 | -2.198611000000 | -1.668642000000 |
| H                                    | -3.237974000000 | -1.135207000000 | -4.274851000000 | H  | -4.335924000000 | -2.712161000000 | -1.028792000000 |
| H                                    | -5.898867000000 | -1.841254000000 | -1.062786000000 |    |                 |                 |                 |
| Cartesian Coordinates for <b>CP2</b> |                 |                 |                 | C  | -3.825424000000 | 3.106713000000  | 1.274444000000  |
| C                                    | 7.053209000000  | 2.218624000000  | 4.115680000000  | Fe | -0.493470000000 | 1.500024000000  | -2.070412000000 |
| C                                    | 6.821987000000  | 1.147764000000  | 3.284183000000  | Cl | -0.733388000000 | 3.669537000000  | -2.333239000000 |

## Chapter 5

|   |                 |                 |                 |    |                 |                 |                 |
|---|-----------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|
| C | 5.695451000000  | 1.128625000000  | 2.417440000000  | Cl | 1.147716000000  | 0.696166000000  | -3.270201000000 |
| C | 4.810835000000  | 2.258387000000  | 2.389843000000  | C  | -2.061522000000 | -0.969998000000 | -2.561005000000 |
| C | 5.064170000000  | 3.334308000000  | 3.283677000000  | H  | -1.244410000000 | -1.147925000000 | -3.261752000000 |
| C | 6.156468000000  | 3.313560000000  | 4.122449000000  | C  | -1.718898000000 | -1.557837000000 | -1.211117000000 |
| H | 6.090367000000  | -0.858159000000 | 1.658036000000  | C  | -0.627693000000 | -2.425508000000 | -1.118506000000 |
| H | 7.914030000000  | 2.221275000000  | 4.777573000000  | C  | -2.475243000000 | -1.279447000000 | -0.060056000000 |
| H | 7.491052000000  | 0.291467000000  | 3.285650000000  | C  | -0.321614000000 | -3.050894000000 | 0.097125000000  |
| C | 5.418434000000  | -0.005561000000 | 1.613885000000  | H  | -0.026585000000 | -2.641601000000 | -1.994999000000 |
| C | 3.686084000000  | 2.235143000000  | 1.495855000000  | C  | -2.179234000000 | -1.903182000000 | 1.148497000000  |
| H | 4.385014000000  | 4.178137000000  | 3.307681000000  | H  | -3.289757000000 | -0.567623000000 | -0.103239000000 |
| H | 6.328925000000  | 4.145164000000  | 4.799336000000  | C  | -1.107760000000 | -2.803570000000 | 1.228583000000  |
| C | 3.475308000000  | 1.081140000000  | 0.762984000000  | H  | 0.501803000000  | -3.752238000000 | 0.147871000000  |
| C | 4.306595000000  | -0.065746000000 | 0.797994000000  | H  | -2.772337000000 | -1.677233000000 | 2.027373000000  |
| C | 2.721429000000  | 3.370747000000  | 1.389015000000  | H  | -0.881855000000 | -3.303927000000 | 2.166154000000  |
| C | 3.132352000000  | 4.692309000000  | 1.009471000000  | Fe | -1.400856000000 | -5.445295000000 | -3.155466000000 |
| C | 1.372511000000  | 3.147358000000  | 1.602305000000  | Cl | -3.113995000000 | -4.957839000000 | -1.768422000000 |
| C | 4.463593000000  | 5.010042000000  | 0.627649000000  | Cl | -1.856485000000 | -7.312389000000 | -4.301221000000 |
| C | 2.148297000000  | 5.734600000000  | 0.986425000000  | Cl | 0.479351000000  | -5.750521000000 | -1.956022000000 |
| C | 0.356078000000  | 4.138127000000  | 1.497519000000  | Cl | -1.145676000000 | -3.730410000000 | -4.596334000000 |
| C | 4.809411000000  | 6.298896000000  | 0.286146000000  | O  | -2.130511000000 | 0.522039000000  | -2.428369000000 |
| H | 5.211166000000  | 4.226220000000  | 0.599998000000  | H  | 2.979706000000  | -4.590580000000 | -1.799852000000 |
| C | 2.544114000000  | 7.058368000000  | 0.649739000000  | H  | 4.056375000000  | -2.537714000000 | 1.819173000000  |
| C | 0.790415000000  | 5.427098000000  | 1.239917000000  | H  | 3.711361000000  | -0.357722000000 | -1.873292000000 |
| C | 3.847286000000  | 7.337254000000  | 0.310396000000  | H  | -1.555997000000 | 5.276022000000  | -0.003100000000 |
| H | 5.830740000000  | 6.519911000000  | -0.009368000000 | H  | -1.030465000000 | 2.229858000000  | 2.991763000000  |
| H | 1.791451000000  | 7.842182000000  | 0.646858000000  | H  | -4.868487000000 | 2.831793000000  | 1.175983000000  |
| H | 0.066480000000  | 6.235249000000  | 1.194707000000  | C  | -4.163053000000 | 4.872959000000  | -0.470870000000 |
| H | 4.138624000000  | 8.349119000000  | 0.045285000000  | C  | -3.550918000000 | 1.248072000000  | 2.908255000000  |
| P | 0.937701000000  | 0.777077000000  | 0.733107000000  | C  | 3.009196000000  | -2.464931000000 | -3.449089000000 |
| O | 0.972444000000  | 1.827598000000  | 1.929967000000  | C  | 3.321128000000  | -4.953970000000 | 0.878994000000  |
| O | 2.312379000000  | 0.995790000000  | -0.047063000000 | F  | 3.525017000000  | -1.385915000000 | -4.078680000000 |
| O | 0.910107000000  | -0.579634000000 | 1.503888000000  | F  | 1.668270000000  | -2.445294000000 | -3.657455000000 |
| H | 0.414666000000  | -1.334001000000 | 1.091913000000  | F  | 3.482365000000  | -3.566366000000 | -4.065311000000 |
| O | -0.209197000000 | 0.988885000000  | -0.235871000000 | F  | 3.445493000000  | -6.057982000000 | 0.121006000000  |
| C | 3.943485000000  | -1.301776000000 | 0.057134000000  | F  | 4.207751000000  | -5.043707000000 | 1.895444000000  |
| C | 3.663480000000  | -1.286908000000 | -1.318164000000 | F  | 2.082066000000  | -4.990930000000 | 1.442162000000  |
| C | 3.862052000000  | -2.514238000000 | 0.751976000000  | F  | -4.381526000000 | 1.639814000000  | 3.894836000000  |
| C | 3.332145000000  | -2.469845000000 | -1.976465000000 | F  | -2.587885000000 | 0.481268000000  | 3.465157000000  |
| C | 3.508672000000  | -3.688619000000 | 0.085164000000  | F  | -4.277172000000 | 0.440865000000  | 2.085024000000  |
| C | 3.252305000000  | -3.678998000000 | -1.283132000000 | F  | -5.469255000000 | 4.821353000000  | -0.139755000000 |
| C | -1.094017000000 | 3.804411000000  | 1.508539000000  | F  | -4.056768000000 | 4.307663000000  | -1.709037000000 |
| C | -1.949038000000 | 4.495784000000  | 0.636059000000  | F  | -3.814808000000 | 6.166639000000  | -0.609882000000 |
| C | -1.645082000000 | 2.771233000000  | 2.287125000000  | H  | -3.352309000000 | -2.554872000000 | -3.156936000000 |
| C | -3.298008000000 | 4.158970000000  | 0.532716000000  | C  | -5.581431000000 | -1.909843000000 | -1.930165000000 |
| C | -2.982454000000 | 2.411114000000  | 2.141125000000  | H  | -5.094534000000 | -2.611520000000 | -1.240048000000 |
| C | -3.428136000000 | 1.189706000000  | -2.750925000000 | H  | -6.428149000000 | -1.447653000000 | -1.417802000000 |

|   |                |                |                |   |                |                |                |
|---|----------------|----------------|----------------|---|----------------|----------------|----------------|
| H | -3.43917000000 | 1.28015100000  | -3.84268700000 | H | -5.96329300000 | -2.51653100000 | -2.76123000000 |
| H | -3.33920900000 | 2.18196500000  | -2.31247600000 | C | -5.61959900000 | 1.16538500000  | -1.39892000000 |
| C | -4.59100300000 | 0.41158900000  | -2.20744800000 | H | -6.62302800000 | 0.75213800000  | -1.53057300000 |
| C | -4.57614000000 | -0.91613900000 | -2.43079400000 | H | -5.38372900000 | 1.11457000000  | -0.32680200000 |
| C | -3.37901200000 | -1.46366200000 | -3.17293600000 | H | -5.65416600000 | 2.22359300000  | -1.67602200000 |
| H | -3.39929400000 | -1.16344300000 | -4.22965700000 |   |                |                |                |

ORTEP Drawing of **4da** ( $C_{17}H_{15}BrO$ ,  $M = 315.21$ ,  $T = 293(0)$  K)



|                                       |                                                                                     |
|---------------------------------------|-------------------------------------------------------------------------------------|
| Wavelength                            | MoK $\alpha$ ( $\lambda = 0.71075$ Å)                                               |
| Crystal System                        | orthorhombic                                                                        |
| Space Group                           | C2 (#5)                                                                             |
| Crystal Dimensions                    | $0.300 \times 0.160 \times 0.140$ mm                                                |
| Lattice Parameters                    | $a = 5.6483(8)$ Å<br>$b = 13.801(2)$ Å $\beta = 106.372^\circ$<br>$c = 18.475(3)$ Å |
| Volume                                | $V = 1440.1(4)$ Å <sup>3</sup>                                                      |
| Z value                               | 4                                                                                   |
| $D_{\text{calc}}$                     | $1.454$ g/cm <sup>3</sup>                                                           |
| $2\theta_{\text{max}}$                | $55.0^\circ$                                                                        |
| Reflections collected                 | 15254                                                                               |
| Independent reflections               | 3312 ( $R_{\text{int}} = 0.1247$ )                                                  |
| No. Variables                         | 172                                                                                 |
| Goodness of Fit Indicator             | 1.020                                                                               |
| Residuals: $R_1$ ( $I > 2\sigma(I)$ ) | $R_1 = 0.0642$                                                                      |
| Residuals: $R$ (All reflections)      | $R_1 = 0.1089$ , $wR_2 = 0.1510$                                                    |
| Flack Parameter                       | $0.019(19)$                                                                         |

## References and Notes

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## Publication List

1. Parts of present Thesis have been or are to be published in the following journals.

**Chapter 1** Cationic Cobalt Porphyrin-Catalyzed Allylation of Aldehydes with Allyltrimethylsilanes

Rei Tomifuji, Shota Masuda, Takuya Kurahashi and Seijiro Matsubara

(Chapter 1 is the edited version of the accepted publication in *Org. Lett.* **2019**, *21*, 3834-3837 (Copyright 2019 American Chemical Society). To access the final edited and published work, see the following website: <https://pubs.acs.org/doi/10.1021/acs.orglett.9b01303>)

**Chapter 2** FeCl<sub>3</sub> as an Ion-Pairing Lewis Acid Catalyst. Formation of Highly Lewis Acidic FeCl<sub>2</sub><sup>+</sup> and Thermodynamically Stable FeCl<sub>4</sub><sup>-</sup> To Catalyze the Aza-Diels–Alder Reaction with High Turnover Frequency

Rei Tomifuji, Kazuki Maeda, Toshifumi Takahashi, Takuya Kurahashi and Seijiro Matsubara

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**Chapter 3** Iron(III)-Catalyzed Intermolecular [2+2+2] Cycloaddition Reaction of Alkenes

Rei Tomifuji, Takuya Kurahashi and Seijiro Matsubara

*To be submitted.*

**Chapter 4** Asymmetric Aza-Diels–Alder Reaction with Ion-Paired–Iron Lewis Acid–Brønsted Acid Catalyst

Rei Tomifuji, Takuya Kurahashi and Seijiro Matsubara

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**Chapter 5** Multiple Activation Catalyst for Asymmetric Oxa-Diels–Alder Reaction of Non-Activated Substrates

Rei Tomifuji, Satoru Teranishi, Daiki Kuroda, Takuya Kurahashi and Seijiro Matsubara

*To be submitted.*

2. Following publication is not included in this Thesis.

Ligand-controlled Behavior of Ag(I)– $\pi$  Complex as  $\sigma$ -Lewis Acid

Kazuki Maeda, Toshifumi Takahashi, Rei Tomifuji, Naoya Hirao, Takuya Kurahashi and Seijiro Matsubara

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Rei Tomifuji  
Department of Material Chemistry  
Graduate School of Engineering  
Kyoto University