

Inverse Kinetic Isotope Effect in Singlet-to-Triplet Intersystem Crossing Contributes to Greater Robustness of Deuterated Organocatalyst

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Abstract

Precisely defined deuterium labeling of simplified Maruoka Catalyst[®] markedly increases its robustness under basic conditions, but the reason for this has remained unclear. Based on MC_DFT calculations, we find that an inverse kinetic isotope effect in singlet-to-triplet intersystem crossing contributes to the greater robustness of the deuterated catalyst.

Keywords: Deuterated Organocatalyst, Phase-Transfer Catalyst, Kinetic Isotope Effect

1. Introduction

Discovery of design principles for sustainable molecular catalysts is an important issue in modern catalysis science. In this context, catalyst deuteration is an emerging concept: precisely controlled deuteration of molecular catalysts can result in higher robustness in oxidative reaction media and can also extend the catalyst lifetime.¹⁻⁵ The higher stability of these deuterated catalysts originates from a primary kinetic isotope effect (KIE) based on the fact that carbon–deuterium (C–D) bonds are stronger than the corresponding C–H bonds.⁶⁻¹⁰ This phenomenon has also contributed to the recent development of deuterated drugs.¹¹⁻¹⁶

Quaternary ammonium salts are widely used as phase-transfer catalysts in asymmetric syntheses.¹⁷⁻²³ A binaphthyl-based chiral azepinium salt **1**, known as simplified Maruoka Catalyst[®], is a privileged phase-transfer catalyst for the asymmetric synthesis of non-standard amino acids (Figure 1A).²⁴⁻²⁶ Catalyst **1** is more active than its prototype Maruoka Catalyst[®] (**2**)²⁷ or traditional cinchona-alkaloid-based catalysts.²⁴ However, while the yield and enantioselectivity in the asymmetric alkylation of amino acid derivatives are excellent at a catalyst loading of 0.1 mol % (*S*)-**1** (95% yield, 99% ee), the performance at lower catalyst loading (0.005 mol%) is not satisfactory (70% yield, 64% ee, Figure 1B).²⁸ To address this limitation, Liu, Maruoka, and we have recently designed site-specifically deuterated chiral organocatalysts [ax-D₂]**1** and [D₄]**1** (Figure 1A).²⁹ Axial hydrogens in the azepinium ring are labeled with deuterium in [ax-D₂]**1**, and both axial and equatorial hydrogens are deuterated in [D₄]**1** (See Figure 1B for detailed geometries). While the performance of di-deuterated catalyst [ax-D₂]**1** is similar to that of the non-deuterated analog **1**, the tetra-deuterated catalyst [D₄]**1** performs better than **1** in the asymmetric alkylation of amino acid derivatives at 0.005 mol% catalyst loading (72% yield, 90% ee, Figure 1C).²⁸

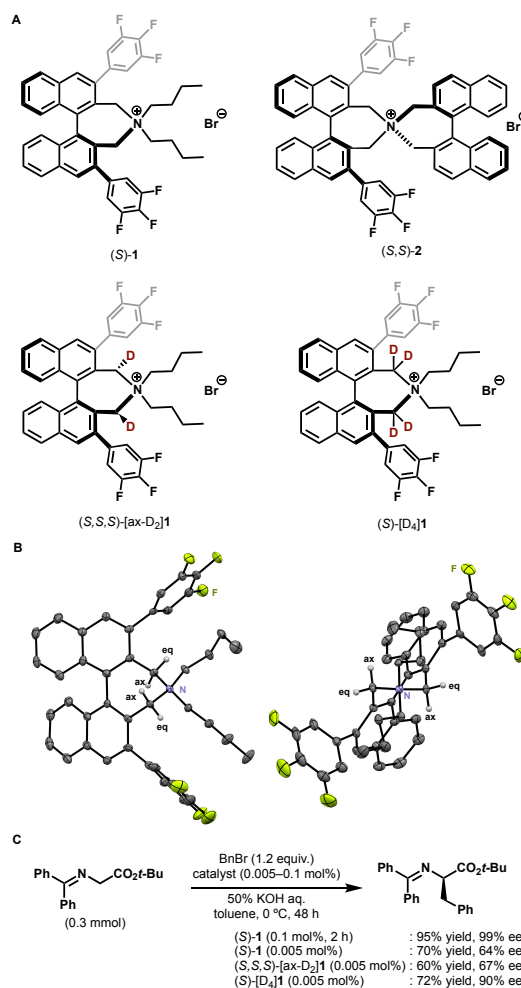


Figure 1. A) Deuterated and non-deuterated chiral phase-transfer catalysts. B) Top(left) and side(right) view for the X-ray crystal structure of (*S*)-**1** reported in ref²⁶ with thermal ellipsoids drawn at the 50% probability level. Axial and equatorial hydrogens are labeled as ax and eq, respectively. Other hydrogen, bromide, and solvent atoms are omitted for clarity. C) Asymmetric benzoylation with deuterated catalysts.²⁸

What is the origin of the better catalytic performance of [D₄]**1** compared to [ax-D₂]**1** and **1**? Because the catalytic activity and selectivity of these deuterated catalysts are very similar to those of the non-deuterated analogs at higher catalyst loadings, we proposed that the higher performance of [D₄]**1** arises from its greater stability.²⁸ Under basic conditions, **1** decomposes into amine **3** via Stevens rearrangement, involving deprotonation at the α-positions, C–N bond cleavage, and C–C bond formation (Figure 2A).²⁹⁻³³ Similarly, [ax-D₂]**1** and [D₄]**1** decompose into [D₁]**3** and [D₃]**3**, respectively. Consistent with the trends of catalytic activity, no significant KIE was observed in the decomposition of catalyst [ax-D₂]**1** vs **1** (*k_H*/*k_D* = 0.9 in KOH/H₂O/toluene), and a large KIE was observed for the decomposition of catalyst [D₄]**1** vs [ax-D₂]**1** (*k_H*/*k_D* = 3.1 in KOH/H₂O/toluene).²⁸

The lack of positive KIE for [ax-D₂]**1** vs **1** is due to rapid and reversible hydrogen–deuterium (H/D) exchange at the α-protons of **1** prior to the Stevens rearrangement.²⁸ Rearrangement of [ax-D₂]**1** gives [D₁]**3** with only 6% deuterium incorporation, suggesting that 94% of deuterium atoms in [ax-D₂]**1** were replaced with hydrogens (¹H) by base-mediated H/D exchange with H₂O (Figure 2B, left). Similar rapid H/D exchange occurs with [D₄]**1**, as suggested by only 8% deuterium incorporation in [D₃]**3** at the hydrogen *trans* position to the

amino group, while the other two deuterium atoms are completely retained (> 98% D, Figure 2B, right). Therefore, the overall KIE of 3.1 for [D₄]**1** is considered to arise *not* from primary KIE due to the C–H cleavage of the axial hydrogens, but from secondary KIE derived from the deuterium at equatorial positions. In fact, the treatment of [ax-D₂]**1** or [D₄]**1** in KOD/D₂O/toluene gives [D₁]**3** or [D₃]**3**, respectively, where no axial H/D exchange occurs, with k_H/k_D as large as 3.8.²⁸ As typical secondary KIEs for α -hydrogens range from 0.8 to 1.2 based on conventional vibrational mechanisms, the reason for the secondary KIEs of 3.1–3.8 is unclear.

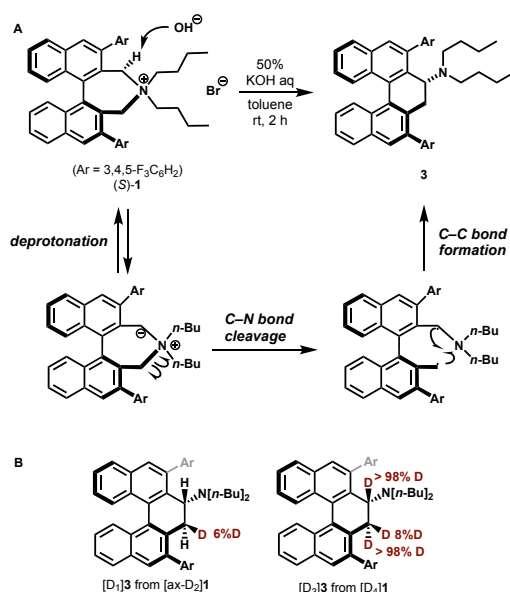


Figure 2. A) Postulated mechanism of the decomposition of **1** to **3** via Stevens rearrangement. The deprotonation of **1** is reversible. B) Products of Stevens rearrangement of [ax-D₂]**1** and [D₄]**1** in KOH aq/toluene. Degrees of deuteration in [D₁]**3** and [D₃]**3** are indicated.^{28, 29}

As we were interested in the origin of this large secondary KIE, in the present work we conducted a computational study on the mechanism of Stevens rearrangement of **1**. The results of multicomponent DFT (MC_DFT) calculations^{34–42} indicated that an inverse deuterium KIE in singlet-to-triplet intersystem crossing contributes substantially to the greater robustness of the chiral deuterated phase transfer catalyst.

2. Computational Methods

All calculations were carried out with a Gaussian 16 (G16) program package⁴³ using unrestricted Truhlar's M06 functionals⁴⁴ in combination with the 6-31G** basis set for the [(CH₂)₂N(CH₃)₂] core of **SM1** (see below) and 3-21G for the other atoms. Geometry optimization and vibrational analysis were performed at the same level. All stationary points were characterized by normal coordinate analysis at the same level of theory (the number of imaginary frequencies, NIMAG, 0 for minima, and 1 for transition states (TSs)). Intrinsic reaction coordinate (IRC) analysis was carried out throughout the reaction pathways to confirm that all stationary points are smoothly connected to each other. The solvent effect was implemented by the energy correction using the results of single-point calculation using the SCRF calculation (SMD, solvent = toluene). Energies of calculated structures in the gas phase and toluene are summarized in Table S1 in the Supporting Information. The natural population analysis (NPA) and MC_DFT calculations^{34–42} were carried out using the G16

program. In the MC_DFT calculations, the equatorial protons and deuterons of the α -carbons were treated as quantum waves along with the electrons in the fields of C, N, and other H nuclear point charges. Gibbs free energy changes at 0 °C (273.15 K) from **IM1** to **TS1** (see below) were used as the energy barrier ($\Delta G^\ddagger$) for calculating the ratio of rate constants k_H and k_D .

3. Results and Discussion

Initial Hypothesis. We first explored the reaction pathway of the Stevens rearrangement using a model compound **SM1** in which the six fluorine atoms and the two alkyl groups of **1** were replaced with hydrogens and methyl groups, respectively (Figure 3). The calculations were conducted at the M06 level of theory. We initially postulated a pathway that starts from the deprotonation of **SM1** to give an intermediate **IM1**, followed by C–N bond cleavage leading to a biradical intermediate **IM2** via a transition state **TS1**. Intramolecular biradical recombination of **IM2** gives the product amine **PD** via **TS2** (Figure 3).

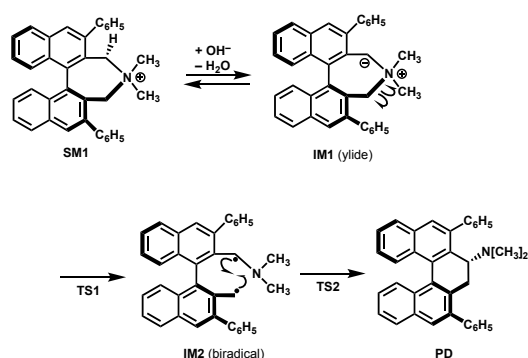


Figure 3. Initial hypothesis for the Stevens rearrangement of a model substrate **SM1** to give a product **PD**. The [(CH₂)₂N(CH₃)₂] core of **SM1** and the other atoms were treated using 6-31G** and 3-21G basis sets, respectively. Energies were corrected with the results of single-point calculation using the SCRF calculation (SMD, solvent = toluene).

Reaction Coordinates. The DFT calculations indicated a barrierless conversion of **SM1** and OH[−] to **IM1** and H₂O. **IM1** was lower than **SM1** in Gibbs free energy (ΔG) by −72.8 kcal mol^{−1} (Figure 4A). A transition state for the C–N bond cleavage of **IM1** (**TS1**) was identified. Its Gibbs free energy ($\Delta G^\ddagger$) was higher than that of **IM1** by +10.9 kcal mol^{−1}. Whereas the transition state search was conducted with unrestricted DFT, the spin state of **TS1** was found to be a closed shell. The IRC analysis of this **TS1** with unrestricted DFT followed by geometrical optimization gave **IM1** and the final product amine **PD** ($\Delta G = -46.4$ kcal mol^{−1} with respect to **IM1**) as stationary points. Unexpectedly, the putative intermediary biradical **IM2** was not identified during this process.

Structural analysis of **IM1**, **TS1**, and **PD** indicated that **TS1** is a transition state for C–N bond cleavage, with the carbon–nitrogen distance ($d(\text{C}\cdots\text{N})$) being elongated to 2.17 Å in **TS1** from 1.55 Å in **IM1**, and the carbon–carbon distance of α -carbons ($d(\text{C}\cdots\text{C})$) also being increased to 2.84 Å in **TS1** from 2.50 Å in **IM1** (Figure 4B). The binaphthyl C–C–C–C dihedral angle (φ) was also expanded from 54.8° to 57.0°. While this tendency continued during the IRC analysis, the optimization of the final IRC product gave a contracted **PD** containing the C–C bond ($d(\text{C}\cdots\text{C}) = 1.54$ Å).

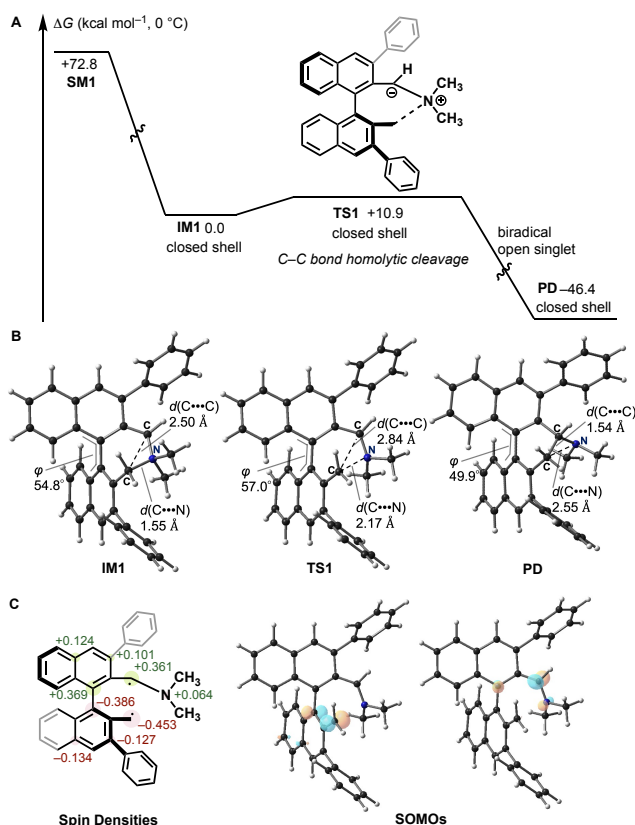


Figure 4. A) Calculated Gibbs free energies (kcal mol⁻¹) and reaction coordinates of the Stevens rearrangement at the uM06 level of theory at 0 °C. The [(CH₂)N(CH₃)₂] core of **SM1** and the other atoms were treated using 6-31G** and 3-21G basis sets, respectively. Energies were corrected with the results of single-point calculation using the SCRf calculation (SMD, solvent = toluene). B) Structures of **IM1**, **TS1**, and **PD** at the uM06 level of theory. Key bond distances (Å) and angles (°) for these structures are shown. C) Spin densities (with hydrogens summed into heavy atoms) and two SOMOs of a biradical form of the last structure in IRC analysis from **TS1** to **PD**.

The biradical nature of the IRC structures between **TS1** and **PD** was confirmed by analyzing the spin densities and frontier orbitals. Spin densities and singly occupied molecular orbitals (SOMOs) of an IRC structure (the last structure in the IRC analysis from **TS1** to **PD**) indicate biradical generation at each α -carbon (Figure 4C). Both of the electrons are delocalized with each adjacent naphthyl ring through π -conjugation.

Based on closed-shell calculations, an alternative pathway from **IM1** to **PD** with heterolytic cleavage was also identified (Figure 5A). While the TS for the C–N bond from **IM1** was identical to **TS1**, the closed-shell IRC search gave a metastable zwitterionic intermediate **IM2zi** ($\Delta G = +7.7$ kcal mol⁻¹ with respect to **IM1**). The C $\cdots$ N and C $\cdots$ C distances are 3.01 Å and 3.04 Å, respectively, in **IM2zi** (Figure 5B, left). The NPA charges of **IM2zi** indicate that the positive charge is located mainly at the CHN[CH₃]₂ moiety (+0.606) while the negative charge is delocalized to the naphthyl rings (upper ring -0.126; lower ring -0.401) from the methylene edge (CH₂, -0.065). The C–C bond formation from **IM2zi** gave **PD** via a transition state **TS2** ($\Delta G^\ddagger = +1.7$ kcal mol⁻¹ vs **IM2zi**; +9.4 kcal mol⁻¹ vs **IM1**, Figure 5A). **TS2** is a transition state for the C–C bond-forming reaction, though the C–C bond distance (3.28 Å) is longer than that in the reactant (3.04 Å, Figure 5B). As this process requires a barrier of $\Delta G^\ddagger = +1.7$ kcal mol⁻¹, the ionic pathway is

energetically less likely than the biradical pathway shown above, in which **PD** is formed directly from **TS1** in a barrierless manner.

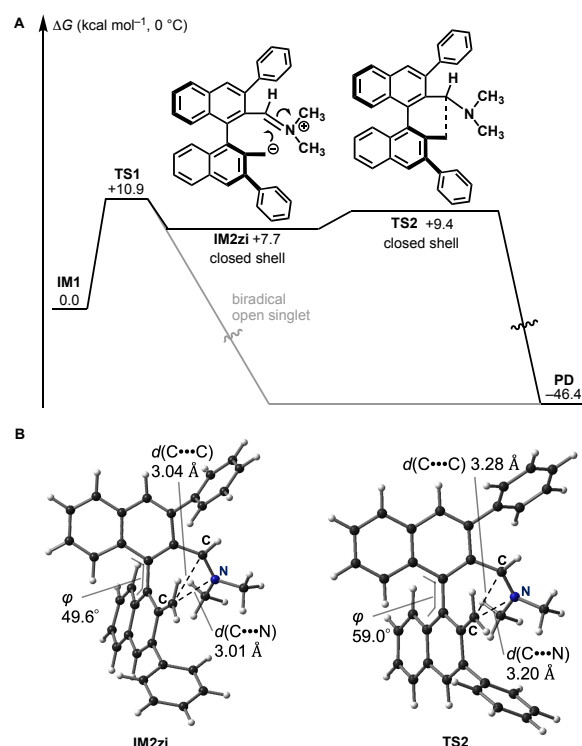
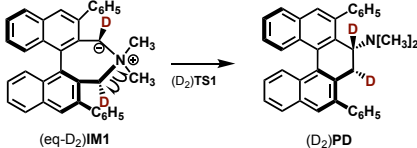


Figure 5. A) Calculated Gibbs free energies (kcal mol⁻¹) and reaction coordinates at the closed-shell M06 level of theory at 0 °C in toluene. B) Molecular structures of **IM2zi** and **TS2** at the closed-shell M06 level of theory. Relevant bond distances (Å) and angles (°) for these structures are shown.

Consideration of Secondary KIE in TS1. Because the above results suggested that the rate-limiting step is the C–N bond cleavage step (**TS1**), we next investigated the secondary kinetic isotope effect for this step. In KOH aq/toluene mixture, axial deuterons of the deuterated catalysts [ax-D₂]**1** and [D₄]**1** are rapidly exchanged to protons to give a non-deuterated catalyst **1** and a catalyst di-deuterated only at equatorial positions (eq-D₂]**1**, respectively, as major products. Therefore, the k_H/k_D of the di-deuterated (eq-D₂]**IM1** vs non-deuterated **IM1** was computationally predicted for the process from **IM1** to **PD** through **TS1** at 0 °C by calculating the harmonic vibrational frequency of **IM1** and **TS1** with or without treating the quantum effects of the nuclei using the MC_DFT method (Table 1). The KIEs were calculated using the following equation: $k_H/k_D = \exp[-(\Delta G_D^\ddagger - \Delta G_H^\ddagger)/RT]$, where R and T are the gas constant and temperature (273.15 K), respectively. As a result, the predicted KIE was found to be 1.27 when the zero-point vibrational energy was considered. When the quantum effects of hydrogen and deuterium nuclei were additionally considered with the MC_DFT method, the predicted KIE was slightly smaller ($k_H/k_D = 1.18$). These values of 1.18–1.27 are broadly consistent with that expected according to the classical theory for secondary KIE in the conformational change from sp³ carbon centers to sp² carbon centers (e.g., 1.22 for S_N1 reaction of α -deuterated isopropyl tosylate with trifluoroacetic acid at 25 °C, where the sp³ carbon is converted to the sp² carbon in the carbocation intermediate).⁴⁵ However, these predicted values are still markedly smaller than the experimental value of 3.1 for [D₄]**1** and [ax-D₂]**1**. Thus, the secondary isotope effect in this C–N bond scission process alone does not account for the large

experimental isotope effect.

Table 1. Predicted secondary KIEs of (eq-D₂)**1** vs **1** based on the energy difference between **IM1** and **TS1** and experimental KIE observed for [D₄]**1** and [ax-D₂]**1** at 0 °C in toluene (SMD).



(eq-D₂)IM1 $\xrightarrow{(D_2)TS1}$ (D₂)PD

	Predicted	Predicted with MC_DFT	Experimental ([D ₄] 1 vs [ax-D ₂] 1) ²⁸
k_H/k_D	1.27	1.18	3.1

Consideration of the Effect of Intersystem Crossing. As has been discussed in the previous section, potential energy surface search on the open-shell singlet and prediction of KIE does not account for the large experimental KIE. Because the presence of an open-shell biradical species was indicated in the IRC analysis from **TS1** to **PD**, we next considered the effect of intersystem crossing from singlet to triplet on the overall reaction rate. We could locate a triplet reaction pathway from the triplet analog of **IM1** (**IM1t**, $\Delta G = +33.3$ with respect to **IM1**) to give a biradical intermediate **IM2t** via a transition state **TS1t** ($\Delta G^\ddagger = +33.5$ with respect to **IM1**, Figure S1 and Table S1). While this triplet pathway is much higher in energy than the singlet pathway and is thus considered unrealistic, we could optimize **IM2t** in the triplet state as a stationary point (Figure 6A). **IM2t** is less stable than **IM1** by 1.1 kcal mol⁻¹. The overall geometry of **IM2t** resembled that of **TS1**, but its C–N bond distance was longer than that of **TS1** by 1.26 Å (3.43 Å vs. 2.17 Å), and the dihedral angle of the binaphthyl ring (76.7°) was larger than that of **TS1** (57.0°, Figure 6A). This geometrical difference indicates further cleavage of the C–N bond and biradical generation in **IM2t**.

To qualitatively estimate the likelihood of intersystem crossing, we conducted a single point and frequency calculation with the molecular structure of **IM2t** at the open-singlet state without geometrical optimization. The result indicated that the total electronic energy (ΔE) and Gibbs free energy (ΔG) at the open-singlet state are slightly lower than that of the triplet state by 0.63 and 1.0 kcal mol⁻¹, respectively. While we could not directly locate the S–T seam of crossing, the small S–T gap around **IM2t** and the decrease in energy for both singlet and triplet pathways from **TS1(t)** to **IM2t** implies that C–N bond cleavage leads to an intersystem crossing of the potential energy curves of singlet and triplet states. These results suggest the presence of a pathway in which a singlet–triplet intersystem crossing occurs during the C–C bond formation to give a triplet biradical intermediate (Figure 6B).

Likewise, triplet intermediate **IM2t** would be reverted to **IM1** via the same triplet to singlet seam of crossing and **TS1**. Selective conversion of **IM2t** to **IM1** over to **PD** is supported based on this reverse trajectory from **IM2t** to **IM1** and the unlikelihood of the spin-forbidden direct conversion of **IM2t** to **PD**.

Inverse KIE in the Intersystem Crossing. Inverse kinetic isotope effects in intersystem crossing from singlet to triplet have been reported. For example, inverse deuterium KIE is considered the reason for the different product distributions in photochemical reactions of (γ -di-deuterated)-ketones.⁴⁶ Another example of an inverse kinetic isotope effect has been observed in the singlet-to-triplet term crossing of diphenyl carbene-*h*₁₀ and

-*d*₁₀ (KIE 0.84–0.92).⁴⁷ Also, the longer fluorescence lifetime of anthracene as compared with that of perdeuterated anthracene^{48, 49} was explained by suggesting that the rate of the intersystem crossing of the perdeuterated anthracene was faster than that of non-deuterated anthracene.^{50–52} Similarly, deuterium atoms at the benzyl positions in **IM1** promote the pathway leading to the non-productive triplet intermediate **IM2t**, thereby inhibiting the formation of the desired 6-membered ring product **PD**. In fact, the triplet free energy (ΔG) of the structure of **IM2t** is lower than the open-singlet free energy of **IM2t** when the hydrogens are replaced with deuterium at the α -positions by 3.1 kcal mol⁻¹ (by 0.99 kcal mol⁻¹ with MC_DFT), implying higher efficiency of intersystem crossing in the deuterated systems.

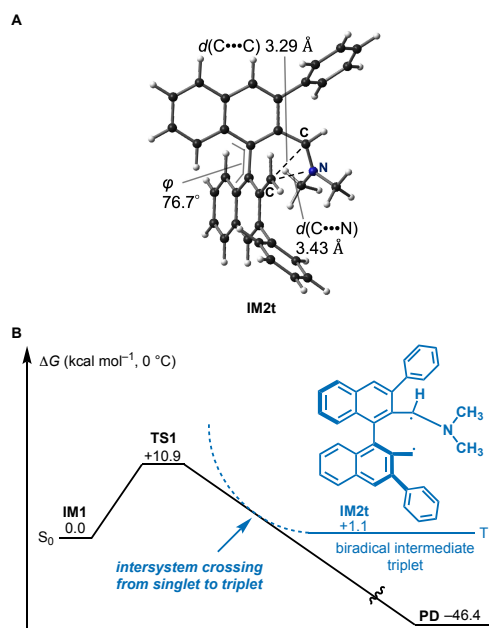


Figure 6. A) Optimized biradical structure of **IM2t** (triplet) at the uM06 level of theory at 0 °C in toluene. The [(CH)(CH₂)N(CH₃)₂] core and the other atoms were treated using 6-31G** and 3-21G basis sets, respectively. Relevant bond distances (Å) and angles (°) for these structures are shown. B) Schematic representation of calculated Gibbs free energy diagram of open-singlet and triplet states.

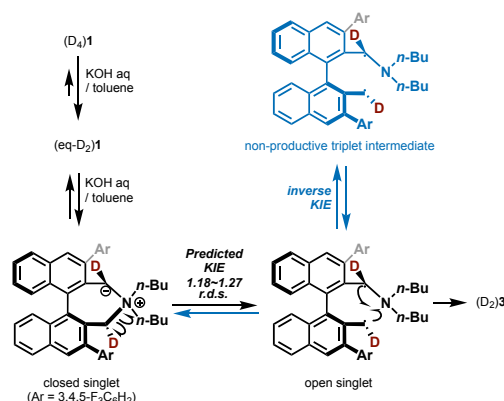


Figure 7. Interpretation of the secondary KIE: a major pathway from (D₄)**1** to (D₂)**3** is presented.

Proposed Mechanism. Based on the above computational analyses, the origin of the large second-order KIE is proposed to be as follows (Figure 7): 1) C–N bond cleavage of the ylide intermediate is the rate-limiting step in the rearrangement of **1** to amine **3**; 2) KIE for the deuteration of the equatorial position in

the reaction pathway from the ylide to the amine product is predicted to be 1.18–1.27, which is less than the large secondary KIE of 3.1; 3) deuterium labeling of the equatorial benzyl positions facilitates intersystem crossing from singlet to triplet, leading to a non-productive triplet biradical intermediate. Since this triplet biradical does not give the amine **3** but instead reverts to the ammonium cation **1**, the formation of **3** is slower from deuterated catalyst [D₄]**1** than from **1** or [ax-D₂]**1**. This difference results in the large difference of secondary KIE between [D₄]**1** and [D₂]**1**.

4. Conclusion

We have shown that the large secondary kinetic isotope effect observed for deuterium-labeled organocatalyst [D₄]**1** vs [D₂]**1** cannot be explained only in terms of a conventional secondary kinetic isotope effect. Instead, deuterium-labeling-enhanced singlet-to-triplet intersystem crossing contributes substantially to the outcome. This result opens up a new direction for molecular design utilizing deuterium labeling to construct functional molecules via radical intermediates.

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Supporting Information

Cartesian coordinates for structures discussed in this article and Figure S1. This material is available on <https://XXXXXXXXX>.

References

- 1 Z. Codolà, I. Gamba, F. Acuña-Parés, C. Casadevall, M. Clémancey, J.-M. Latour, J. M. Luis, J. Lloret-Fillol, M. Costas, *Journal of the American Chemical Society* **2019**, *141*, 323–333 10.1021/jacs.8b10211.
- 2 J. Chen, R. J. M. Klein Gebbink, *ACS Catalysis* **2019**, *9*, 3564–3575 10.1021/acscatal.8b04463.
- 3 F. Li, I. Meijer, B. Kniestedt, M. Lutz, D. L. J. Broere, R. J. M. Klein Gebbink, *ChemCatChem* **2023**, 10.1002/cctc.202301128.
- 4 M. Taki, S. Itoh, S. Fukuzumi, *Journal of the American Chemical Society* **2001**, *123*, 6203–6204 10.1021/ja015721s.
- 5 H. Naka, Y. Kondo, S. Usui, Y. Hashimoto, M. Uchiyama, *Advanced Synthesis & Catalysis* **2007**, *349*, 595–600 10.1002/adsc.200600557.
- 6 S. Kopf, F. Bourriquen, W. Li, H. Neumann, K. Junge, M. Beller, *Chemical Reviews* **2022**, *122*, 6634–6718 10.1021/acs.chemrev.1c00795.
- 7 J. Atzrodt, V. Derdau, W. J. Kerr, M. Reid, *Angew Chem Int Ed Engl* **2018**, *57*, 1758–1784 10.1002/anie.201704146.
- 8 J. Atzrodt, V. Derdau, W. J. Kerr, M. Reid, *Angewandte Chemie International Edition* **2018**, *57*, 3022–3047 10.1002/anie.201708903.
- 9 M. Gómez-Gallego, M. A. Sierra, *Chemical Reviews* **2011**, *111*, 4857–4963 10.1021/cr100436k.
- 10 J. P. Klinman, A. R. Offenbacher, *Accounts of Chemical Research* **2018**, *51*, 1966–1974 10.1021/acs.accounts.8b00226.
- 11 S. H. Dewitt, B. E. Maryanoff, *Biochemistry* **2018**, *57*, 472–473 10.1021/acs.biochem.7b00765.
- 12 R. D. Jansen-Van Vuuren, L. Jedlovčnik, J. Košmrlj, T. E. Massey, V. Derdau, *ACS Omega* **2022**, *7*, 41840–41858 10.1021/acsomega.2c04160.
- 13 F. Liu, B. Wang, Y. Liu, W. Shi, X. Tang, X. Wang, Z. Hu, Y. Zhang, Y. Guo, X. Chang, X. He, H. Xu, Y. He, *ACS Medicinal Chemistry Letters* **2022**, *13*, 1730–1738 10.1021/acsmchemlett.2c00334.
- 14 L.-M. Wang, K. Jenkinson, A. E. H. Wheatley, K. Kuwata, S. Saito, H. Naka, *Acs Sustainable Chemistry & Engineering* **2018**, *6*, 15419–15424 10.1021/acssuschemeng.8b03855.
- 15 L.-M. Wang, Y. Morioka, K. Jenkinson, A. E. H. Wheatley, S. Saito, H. Naka, *Scientific Reports* **2018**, *8*, 10.1038/s41598-018-27270-y.
- 16 M. Itoga, M. Yamanishi, T. Udagawa, A. Kobayashi, K. Maekawa, Y. Takemoto, H. Naka, *Chemical Science* **2022**, *13*, 8744–8751 10.1039/d2sc01805e.
- 17 T. Hashimoto, K. Maruoka, *Chemical Reviews* **2007**, *107*, 5656–5682 10.1021/cr068368n.
- 18 M. Ikunaka, *Organic Process Research & Development* **2008**, *12*, 698–709 10.1021/op700262h.
- 19 J. Tan, N. Yasuda, *Organic Process Research & Development* **2015**, *19*, 1731–1746 10.1021/acs.oprd.5b00304.
- 20 D. C. M. Albanese, F. Foschi, M. Penso, *Organic Process Research & Development* **2016**, *20*, 129–139 10.1021/acs.oprd.5b00385.
- 21 S. Kaneko, Y. Kumatabara, S. Shirakawa, *Organic & Biomolecular Chemistry* **2016**, *14*, 5367–5376 10.1039/c5ob02446c.
- 22 L. Zong, C.-H. Tan, *Accounts of Chemical Research* **2017**, *50*, 842–856 10.1021/acs.accounts.6b00604.
- 23 N. Patel, R. Sood, P. V. Bharatam, *Chemical Reviews* **2018**, *118*, 8770–8785 10.1021/acs.chemrev.8b00169.
- 24 K. Maruoka, *The Chemical Record* **2010**, *10*, 254–259 10.1002/tcr.201000019.
- 25 K. Maruoka, *Proceedings of the Japan Academy, Series B* **2019**, *95*, 1–16 10.2183/pjab.95.001.
- 26 M. Kitamura, S. Shirakawa, Y. Arimura, X. Wang, K. Maruoka, *Chemistry - An Asian Journal* **2008**, *3*, 1702–1714 10.1002/asia.200800107.
- 27 T. Ooi, M. Kameda, K. Maruoka, *Journal of the American Chemical Society* **2003**, *125*, 5139–5151 10.1021/ja021244h.
- 28 S. Murayama, Z. Li, H. Liang, Y. Liu, H. Naka, K. Maruoka, *Chemistry – A European Journal* **2023**, 10.1002/chem.202301866.
- 29 H. T. Liang, Z. R. Li, Y. Liu, S. Murayama, H. Naka, K. Maruoka, *Tetrahedron Letters* **2022**, *96*, 153753 ARTN 153753 10.1016/j.tetlet.2022.153753.
- 30 I. G. Stara, I. Stary, M. Tichy, J. Zavada, V. Hanus, *Journal of the American Chemical Society* **1994**, *116*, 5084–5088 10.1021/ja00091a009.
- 31 M.-H. Gonçalves-Farbos, L. Vial, J. Lacour, *Chem. Commun.* **2008**, 829–831 10.1039/b716488b.
- 32 M. Waser, K. Gratzner, *Synthesis* **2012**, *44*, 3661–3670 10.1055/s-0032-1316804.
- 33 Z. Schwartz, C. Valiton, M. Lovasz, A. G. Roberts, *Synthesis* **2023**, 10.1055/s-0042-1751446.
- 34 T. Ishimoto, M. Tachikawa, U. Nagashima, *International Journal of Quantum Chemistry* **2009**, *109*, 2677–2694 10.1002/qua.22069.
- 35 M. Tachikawa, *Molecular Physics* **2002**, *100*, 881–901 10.1080/00268970110099602.
- 36 T. Udagawa, M. Tachikawa, *Journal of Chemical Physics* **2006**, *125*, 9 10.1063/1.2403857.
- 37 Y. Kita, T. Udagawa, M. Tachikawa, *Chemistry Letters* **2009**, 38, 1156–1157 10.1246/cl.2009.1156.
- 38 Y. Kanematsu, M. Tachikawa, *Journal of Chemical Physics* **2014**, *140*, 10.1063/1.4872006.
- 39 T. Udagawa, T. Tsuneda, M. Tachikawa, *Physical Review A* **2014**, *89*, 10.1103/PhysRevA.89.052519.
- 40 Y. Kimura, Y. Kanematsu, H. Sakagami, D. S. R. Rocabado, T.

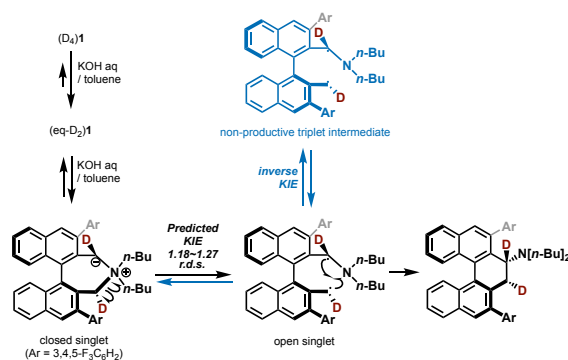
- Shimazaki, M. Tachikawa, T. Ishimoto, *Journal of Physical Chemistry A* **2022**, *126*, 155-163 10.1021/acs.jpca.1c08514.
- 41 K. Nasu, H. Sakagami, Y. Kanematsu, D. S. Rivera Rocabado, T. Shimazaki, M. Tachikawa, T. Ishimoto, *AIP Advances* **2023**, *13*, 10.1063/5.0151660.
- 42 T. Udagawa, R. B. Murphy, T. A. Darwish, M. Tachikawa, S. Mori, *Bulletin of the Chemical Society of Japan* **2021**, *94*, 1954-1962 10.1246/bcsj.20210083.
- 43 Gaussian 16, Revision C.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. V. 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. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. 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.
- 44 Y. Zhao, D. G. Truhlar, *Theoretical Chemistry Accounts* **2008**, *120*, 215-241 10.1007/s00214-007-0310-x.
- 45 F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*. Editor, Springer New York, NY, **2007**.
- 46 D. R. Coulson, N. C. Yang, *Journal of the American Chemical Society* **1966**, *88*, 4511-4513 10.1021/ja00971a041.
- 47 J. G. Langan, E. V. Sitzmann, K. B. Eisenthal, *Chemical Physics Letters* **1986**, *124*, 59-62 10.1016/0009-2614(86)85013-8.
- 48 A. Beckett, *Nature* **1966**, *211*, 410-411 10.1038/211410b0.
- 49 A. Amirav, M. Sonnenschein, J. Jortner, *Chemical Physics Letters* **1983**, *100*, 488-493 10.1016/0009-2614(83)87414-4.
- 50 C. N. Filer, *Journal of Labelled Compounds and Radiopharmaceuticals* **2023**, *66*, 372-383 10.1002/jlcr.4056.
- 51 E. C. Lim, Bhattach.Hr, *Chemical Physics Letters* **1971**, *9*, 249- & 10.1016/0009-2614(71)85042-x.
- 52 S. Okajima, B. E. Forch, E. C. Lim, *Journal of Physical Chemistry* **1983**, *87*, 4571-4573 10.1021/j100246a008.

Graphical Abstract

Inverse Kinetic Isotope Effect in Singlet-to-Triplet Intersystem Crossing Contributes to Greater Robustness of Chiral Deuterated Phase-Transfer Catalyst

Sei Murayama, Takayoshi Ishimoto, and Hiroshi Naka*

The precisely located deuterium labeling of simplified Maruoka Catalyst[®] significantly increases its robustness under basic conditions, but the reason for this has remained unclear. Based on MC_DFT calculations, we find that an inverse kinetic isotope effect in singlet-to-triplet intersystem crossing contributes dramatically to the higher robustness of the deuterated catalyst.



Supporting Information for
**Inverse Kinetic Isotope Effect in Singlet-to-Triplet Intersystem Crossing
 Contributes to Greater Robustness of Deuterated Organocatalyst**

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Table S1. Energies of calculated structures in gas phase and toluene.

	ΔE (kcal mol ⁻¹)		ΔG (kcal mol ⁻¹)	
	gas phase	toluene (SMD)	gas phase	toluene (SMD)
SM1	130.42	70.19	133.02	72.79
IM1	0.00	0.00	0.00	0.00
TS1	9.91	12.86	7.97	10.92
PD	-51.20	-47.06	-50.51	-46.37
IM2zi	7.97	11.04	4.64	7.72
TS2zi	10.73	12.86	7.28	9.41
IM1t (triplet)	37.40	36.58	34.07	33.26
TS1t (triplet)	37.53	37.15	33.82	33.45
IM2t (triplet)	3.20	7.72	-3.39	1.13
IM2ts (frequency calculation of IM2t with open singlet)	2.57	7.09	-4.39	0.13
IRC path8	8.22	11.67	4.08	7.53

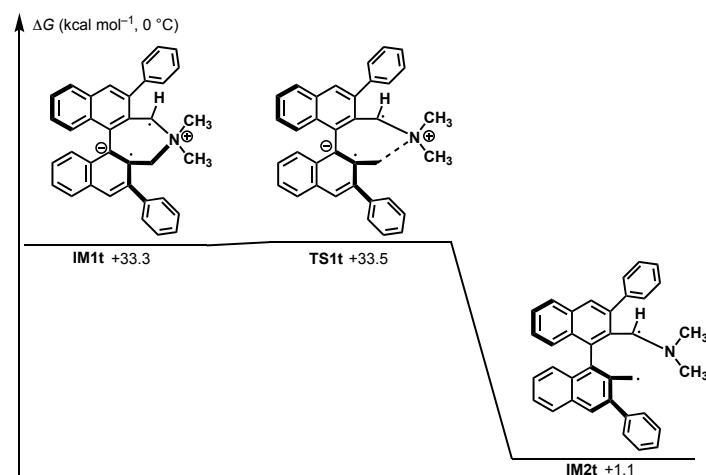


Figure S1. Calculated Gibbs free energies (kcal mol⁻¹) and reaction coordinates at the closed-shell M06 level of theory at 0 °C in the gas phase. The [(CH)(CH₂)N(CH₃)₂] core and the other atoms were treated using 6-31G** and 3-21G basis sets, respectively. Energies were corrected with the results of single-point calculation using the SCRF calculation (SMD, solvent = toluene).

Energies and Geometries

SM1 SMR3912b

SCF Done: E(RM06) = -1436.99580061 A.U.

Sum of electronic and zero-point Energies= -1436.434296

Sum of electronic and thermal Energies= -1436.410424

Sum of electronic and thermal Enthalpies= -1436.409559

Sum of electronic and thermal Free Energies= -1436.486104

SCF Done (single point, scrf=(smd,solvent=toluene)): E(RM06) = -1437.06665808 A.U.

no imaginary frequency

7	-1.338537	10.287899	9.018946
6	-0.466468	9.419811	9.934794
6	-2.206487	11.144695	9.876624
6	-2.209822	9.424009	8.098382
6	-0.471353	11.150113	8.165927
1	0.260138	10.105516	10.379075
1	-1.571892	11.705318	10.568042
1	-2.897425	10.501706	10.426704
1	-2.777529	11.829631	9.243650
1	-2.937233	10.111405	7.658052
1	-1.540410	9.053862	7.316663
1	-1.106475	11.714089	7.477727
1	0.219958	10.510698	7.612161
1	0.099288	11.831934	8.802608
6	-0.622472	7.234750	8.796903
6	0.176602	8.308412	9.179765
6	1.548856	8.375173	8.784636
6	2.063319	7.373899	7.992500
6	1.266511	6.294498	7.544377
6	1.797064	5.290779	6.693859
6	1.002633	4.270761	6.237750
6	-0.361562	4.210818	6.605656
6	-0.904448	5.159220	7.434798
6	-0.105041	6.218323	7.940677
6	2.415187	9.506449	9.208800
6	2.994131	10.341948	8.247301
6	3.784250	11.420881	8.635961
6	4.006693	11.672201	9.987800
6	3.450537	10.832416	10.951291
6	2.662467	9.751872	10.565848
1	3.112028	7.408514	7.703329
1	2.844275	5.350621	6.407149
1	1.414661	3.507015	5.585043
1	-0.982225	3.405968	6.223230
1	-1.952448	5.111137	7.714142
1	2.821474	10.139668	7.191361
1	4.624696	12.512330	10.290542
1	2.257594	9.073054	11.314823
6	-2.051241	7.232669	9.223688
6	-2.851560	8.307675	8.847213
6	-4.223779	8.370678	9.243055
6	-4.737011	7.364195	10.029393
6	-3.938953	6.283037	10.471019
6	-4.468232	5.273806	11.315775
6	-3.672572	4.252063	11.765841
6	-2.308360	4.195798	11.397373
6	-1.766696	5.149623	10.573670
6	-2.567384	6.210730	10.074088
6	-5.091377	9.503729	8.826252
6	-5.670812	10.332416	9.793353
6	-6.685563	11.672708	8.061874

6	-5.339514	9.757576	7.470921
1	-5.785679	7.396022	10.319028
1	-5.515460	5.330791	11.603003
1	-4.083624	3.484092	12.414195
1	-1.686731	3.389436	11.775016
1	-0.718691	5.104380	10.293887
1	-5.497482	10.123534	10.847898
1	-7.304636	12.514066	7.764788
1	-4.934272	9.084003	6.717420
1	4.231706	12.063355	7.882913
1	3.647501	11.009850	12.004763
6	-6.128923	10.839734	7.092769
1	-6.326556	11.023696	6.040539
6	-6.462258	11.412970	9.411976
1	-6.910111	12.050110	10.169307
1	-1.135584	9.044579	10.714338

H₂O SMR40201a

SCF Done: E(RM06) = -76.3842753194 A.U.
Sum of electronic and zero-point Energies= -76.362477
Sum of electronic and thermal Energies= -76.359881
Sum of electronic and thermal Enthalpies= -76.359016
Sum of electronic and thermal Free Energies= -76.378933
SCF Done (single point, scrf=(smd,solvent=toluene)): E(RM06) = -76.3900235310 A.U.
no imaginary frequency

8	-1.659989	0.376260	0.000000
1	-0.701117	0.419051	0.000000
1	-1.939737	1.294424	0.000000

OH⁻ SMR40201b

SCF Done: E(RM06) = -75.6898388894 A.U.
Sum of electronic and zero-point Energies= -75.681420
Sum of electronic and thermal Energies= -75.679257
Sum of electronic and thermal Enthalpies= -75.678392
Sum of electronic and thermal Free Energies= -75.696055
SCF Done (single point, scrf=(smd,solvent=toluene)): E(RM06) = -75.7617616732 A.U.
no imaginary frequency

8	-1.652147	0.394933	0.000000
1	-0.681445	0.394933	0.000000

IM1 SMR3927aro

SCF Done: E(UM06) = -1436.50917663 A.U.
Sum of electronic and zero-point Energies= -1435.963107
Sum of electronic and thermal Energies= -1435.939045
Sum of electronic and thermal Enthalpies= -1435.938180
Sum of electronic and thermal Free Energies= -1436.015239
SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.55028216 A.U.
no imaginary frequency

7	-0.157165	2.172300	0.030276
6	1.186554	1.599923	0.219803
6	-0.890455	2.302353	1.327869
6	-1.000319	1.352441	-0.973365
6	0.002224	3.535213	-0.549011
1	1.931862	2.366749	0.381807
1	-0.311452	2.977810	1.962608
1	-0.945976	1.318191	1.793436
1	-1.899766	2.695486	1.146242
1	-1.765712	2.036861	-1.348347
1	-0.298849	1.083402	-1.769619
1	-0.977355	4.017795	-0.627428

1	0.465273	3.434405	-1.533088
1	0.655557	4.119879	0.103294
6	0.698285	-0.838088	-0.339646
6	1.542527	0.296203	-0.080198
6	2.993153	0.044060	-0.139911
6	3.489415	-1.119923	-0.632145
6	2.647987	-2.162959	-1.122032
6	3.180222	-3.313181	-1.736056
6	2.357059	-4.310045	-2.214848
6	0.962950	-4.161492	-2.092995
6	0.418686	-3.047761	-1.492068
6	1.239892	-2.014373	-0.966319
6	3.943620	1.091844	0.320156
6	4.805801	1.708676	-0.590052
6	5.720056	2.669420	-0.161390
6	5.778264	3.026738	1.182448
6	4.919538	2.417625	2.097841
6	4.008375	1.458254	1.670576
1	4.569618	-1.262240	-0.669386
1	4.262338	-3.395817	-1.829713
1	2.773895	-5.193184	-2.690774
1	0.304485	-4.931102	-2.489145
1	-0.660186	-2.943956	-1.421814
1	4.749348	1.426770	-1.638910
1	6.491516	3.774857	1.518515
1	3.335560	0.978413	2.377538
6	-0.717956	-0.853714	0.064537
6	-1.586903	0.171394	-0.307683
6	-2.963463	0.165932	0.082742
6	-3.450230	-0.864829	0.846825
6	-2.597017	-1.901985	1.301357
6	-3.085546	-2.926128	2.152176
6	-2.242492	-3.887042	2.650150
6	-0.868197	-3.852868	2.329127
6	-0.370573	-2.882763	1.494097
6	-1.219767	-1.897059	0.929931
6	-3.883685	1.256758	-0.334433
6	-4.503755	2.055104	0.633226
6	-5.359975	3.087231	0.256332
6	-5.607726	3.331406	-1.092139
6	-5.004467	2.532966	-2.062565
6	-4.150789	1.499809	-1.687534
1	-4.504567	-0.889837	1.116892
1	-4.143090	-2.925619	2.409215
1	-2.624280	-4.666004	3.304713
1	-0.199192	-4.596767	2.752683
1	0.684897	-2.851957	1.248178
1	-4.305901	1.855437	1.685091
1	-6.274935	4.136611	-1.387009
1	-3.694246	0.859645	-2.440090
1	-5.835563	3.701121	1.016641
1	-5.209865	2.709216	-3.115107
1	6.386885	3.140484	-0.879265
1	4.969084	2.686740	3.150045

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	-0.393628	0.000000
2	C	0.114251	0.000000
3	C	0.279043	0.000000
4	C	0.305935	0.000000

5	C	0.261675	0.000000
15	C	-0.169898	0.000000
16	C	-0.018852	0.000000
17	C	-0.047979	0.000000
18	C	0.010005	0.000000
19	C	-0.015916	0.000000
20	C	-0.019684	0.000000
21	C	-0.037138	0.000000
22	C	-0.008346	0.000000
23	C	-0.013826	0.000000
24	C	-0.007723	0.000000
25	C	-0.080718	0.000000
26	C	0.009264	0.000000
27	C	-0.004786	0.000000
28	C	-0.009760	0.000000
29	C	-0.006401	0.000000
30	C	0.016726	0.000000
39	C	-0.033660	0.000000
40	C	-0.086580	0.000000
41	C	-0.043992	0.000000
42	C	-0.002200	0.000000
43	C	0.003046	0.000000
44	C	-0.009712	0.000000
45	C	0.000780	0.000000
46	C	-0.001020	0.000000
47	C	0.066371	0.000000
48	C	-0.023068	0.000000
49	C	-0.059279	0.000000
50	C	0.004263	0.000000
51	C	0.006552	0.000000
52	C	0.003474	0.000000
53	C	0.010520	0.000000
54	C	0.002264	0.000000

TS1 SMR3927b

SCF Done: E(UM06) = -1436.49336108 A.U.

Sum of electronic and zero-point Energies= -1435.950314

Sum of electronic and thermal Energies= -1435.926133

Sum of electronic and thermal Enthalpies= -1435.925268

Sum of electronic and thermal Free Energies= -1436.002491

SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.52980879 A.U.

ν^i = -196.9444 cm^{-1}

7	0.021105	2.174246	0.437295
6	1.287149	1.661439	0.260593
6	-0.704092	1.726691	1.627017
6	-1.133769	1.308935	-1.187571
6	-0.080486	3.619406	0.257809
1	2.068514	2.405714	0.125435
1	-0.300924	2.248868	2.504198
1	-0.584685	0.650840	1.766204
1	-1.770256	1.951373	1.511758
1	-1.809118	2.104459	-1.491503
1	-0.200978	1.221881	-1.735662
1	-1.135083	3.910795	0.300555
1	0.325116	3.893008	-0.720507
1	0.476042	4.152917	1.042118
6	0.697806	-0.774950	-0.300132
6	1.589284	0.334023	-0.056426
6	3.034493	0.077187	-0.177854
6	3.519279	-1.115732	-0.596694

6	2.653649	-2.175151	-1.005595
6	3.170860	-3.359200	-1.567925
6	2.331026	-4.346295	-2.036045
6	0.940669	-4.149655	-1.976470
6	0.416893	-3.000742	-1.424784
6	1.251888	-1.994261	-0.877492
6	4.010107	1.139373	0.193288
6	4.811899	1.727520	-0.787840
6	5.753129	2.696020	-0.443516
6	5.900310	3.084556	0.884874
6	5.103870	2.500810	1.870196
6	4.162998	1.536286	1.527375
1	4.596149	-1.270589	-0.649256
1	4.251538	-3.471023	-1.636856
1	2.736105	-5.255164	-2.472166
1	0.271494	-4.901463	-2.386687
1	-0.657427	-2.850425	-1.411525
1	4.686952	1.419196	-1.823196
1	6.635089	3.838481	1.154636
1	3.539328	1.074657	2.289217
6	-0.739381	-0.800666	-0.018820
6	-1.630694	0.206934	-0.493511
6	-3.030929	0.175589	-0.098149
6	-3.506531	-0.831660	0.679088
6	-2.647601	-1.854496	1.185949
6	-3.153144	-2.838992	2.063247
6	-2.320196	-3.767589	2.643486
6	-0.939214	-3.715457	2.378923
6	-0.424552	-2.771267	1.520117
6	-1.261753	-1.838240	0.856657
6	-3.945631	1.262211	-0.534693
6	-4.544884	2.093499	0.417039
6	-5.405492	3.116184	0.023246
6	-5.676471	3.318068	-1.327020
6	-5.089006	2.489517	-2.282475
6	-4.229553	1.468579	-1.890706
1	-4.562313	-0.860058	0.945237
1	-4.219690	-2.838090	2.280870
1	-2.717927	-4.519892	3.318892
1	-0.269872	-4.418851	2.867003
1	0.643202	-2.733576	1.336571
1	-4.333595	1.925915	1.471626
1	-6.347304	4.115180	-1.635792
1	-3.776326	0.813339	-2.631002
1	-5.865485	3.755247	0.772468
1	-5.308584	2.636340	-3.336721
1	6.371800	3.147842	-1.214550
1	5.223401	2.795490	2.909614

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	-0.357899	0.000000
2	C	0.257652	0.000001
3	C	0.251189	0.000000
4	C	0.132844	-0.000001
5	C	0.207717	0.000000
15	C	-0.105002	0.000001
16	C	-0.075727	0.000000
17	C	-0.030662	0.000001
18	C	0.010193	0.000000
19	C	-0.002095	0.000000

20	C	-0.013231	0.000000
21	C	-0.013668	0.000000
22	C	-0.002764	0.000000
23	C	0.030670	0.000000
24	C	-0.020300	0.000000
25	C	-0.095546	0.000000
26	C	0.014780	0.000000
27	C	0.001424	0.000000
28	C	-0.003257	0.000000
29	C	-0.000760	0.000000
30	C	0.022122	0.000000
39	C	-0.120208	-0.000001
40	C	-0.017857	0.000000
41	C	-0.050169	0.000000
42	C	0.001843	0.000000
43	C	-0.002422	0.000000
44	C	-0.008718	0.000000
45	C	-0.008818	0.000000
46	C	-0.000546	0.000000
47	C	0.041029	0.000000
48	C	-0.012446	0.000000
49	C	-0.053781	0.000000
50	C	0.003376	0.000000
51	C	0.002682	0.000000
52	C	0.000433	0.000000
53	C	0.007000	0.000000
54	C	0.010921	0.000000

IM2zi SMR3907g

SCF Done: E(RM06) = -1436.49650432 A.U.

Sum of electronic and zero-point Energies= -1435.953779

Sum of electronic and thermal Energies= -1435.928471

Sum of electronic and thermal Enthalpies= -1435.927606

Sum of electronic and thermal Free Energies= -1436.007752

SCF Done (single point, scrf=(smd,solvent=toluene)): E(RM06) = -1436.53266879 A.U.

no imaginary frequency

7	0.275429	1.794041	1.678204
6	1.333408	1.420155	0.947838
6	-0.603791	0.892353	2.393979
6	-0.961183	1.494829	-1.049070
6	0.094986	3.198739	1.996493
1	2.075225	2.213472	0.860442
1	-0.784589	1.325453	3.384941
1	-0.138869	-0.086417	2.520186
1	-1.564377	0.761154	1.880622
1	-1.616174	2.184646	-1.569842
1	0.105236	1.672679	-1.126564
1	-0.925331	3.503441	1.733664
1	0.789431	3.809260	1.414771
1	0.253300	3.389088	3.066935
6	0.714476	-0.854126	-0.004721
6	1.620504	0.249750	0.247959
6	3.037117	0.122697	-0.122581
6	3.552958	-1.082934	-0.452325
6	2.715618	-2.234743	-0.623474
6	3.277009	-3.445811	-1.076901
6	2.477590	-4.506546	-1.443312
6	1.082220	-4.355378	-1.413191
6	0.515582	-3.181129	-0.966215
6	1.305939	-2.108758	-0.488930

6	3.925416	1.315541	-0.129406
6	3.681298	2.365689	-1.024758
6	4.517709	3.475861	-1.050883
6	5.610056	3.550443	-0.186563
6	5.861021	2.508927	0.702126
6	5.021006	1.397620	0.733169
1	4.610577	-1.173220	-0.694995
1	4.360281	-3.516029	-1.155065
1	2.919950	-5.435601	-1.792001
1	0.442311	-5.159906	-1.765015
1	-0.561896	-3.070913	-0.976810
1	2.834639	2.293439	-1.705416
1	6.264066	4.417916	-0.209117
1	5.203504	0.584471	1.431900
6	-0.707183	-0.744241	0.106578
6	-1.475986	0.388078	-0.452686
6	-2.951220	0.255292	-0.430895
6	-3.569463	-0.835634	0.070093
6	-2.846985	-1.883044	0.738972
6	-3.532188	-2.899852	1.425036
6	-2.853478	-3.816039	2.206589
6	-1.463955	-3.694396	2.345919
6	-0.774899	-2.702619	1.675128
6	-1.432078	-1.802899	0.800909
6	-3.791625	1.365045	-0.955040
6	-3.849753	2.592445	-0.284139
6	-4.669959	3.613352	-0.750163
6	-5.443072	3.421640	-1.895259
6	-5.391138	2.204506	-2.567968
6	-4.568967	1.181049	-2.100404
1	-4.657687	-0.890044	0.057754
1	-4.617267	-2.939499	1.344664
1	-3.391743	-4.599017	2.733160
1	-0.923522	-4.375190	2.998632
1	0.300247	-2.614668	1.803198
1	-3.245947	2.732036	0.611262
1	-6.083716	4.220175	-2.259782
1	-4.516219	0.229763	-2.624351
1	-4.713897	4.560178	-0.217985
1	-5.989545	2.051181	-3.462248
1	4.325888	4.281799	-1.754463
1	6.710469	2.563400	1.377920

Mulliken charges with hydrogens summed into heavy atoms:

1	N	-0.298603
2	C	0.436536
3	C	0.280278
4	C	-0.061433
5	C	0.225726
15	C	-0.031302
16	C	-0.140382
17	C	-0.010793
18	C	-0.007120
19	C	0.006764
20	C	-0.010861
21	C	0.004594
22	C	-0.000300
23	C	0.065861
24	C	-0.025607
25	C	-0.092793

26	C	0.020326
27	C	0.009700
28	C	0.003892
29	C	0.005019
30	C	0.005489
39	C	-0.211850
40	C	0.047958
41	C	-0.094016
42	C	0.008752
43	C	-0.024398
44	C	-0.013844
45	C	-0.036464
46	C	-0.003758
47	C	-0.022229
48	C	0.000232
49	C	-0.040976
50	C	-0.008183
51	C	-0.004201
52	C	-0.003733
53	C	0.004428
54	C	0.017294

Summary of Natural Population Analysis:

Atom	No	Natural Charge	Natural Population			Total
			Core	Valence	Rydberg	
N	1	-0.35335	1.99905	5.34281	0.01149	7.35335
C	2	0.17767	1.99911	3.79941	0.02380	5.82233
C	3	-0.49095	1.99922	4.47704	0.01469	6.49095
C	4	-0.50185	1.99906	4.48658	0.01621	6.50185
C	5	-0.48458	1.99925	4.47354	0.01178	6.48458
H	6	0.24380	0.00000	0.75357	0.00263	0.75620
H	7	0.23975	0.00000	0.75860	0.00165	0.76025
H	8	0.26543	0.00000	0.73202	0.00256	0.73457
H	9	0.26332	0.00000	0.73302	0.00367	0.73668
H	10	0.22005	0.00000	0.77788	0.00206	0.77995
H	11	0.21670	0.00000	0.78167	0.00163	0.78330
H	12	0.26126	0.00000	0.73590	0.00283	0.73874
H	13	0.24780	0.00000	0.75085	0.00136	0.75220
H	14	0.23634	0.00000	0.76173	0.00193	0.76366
C	15	0.05017	1.99869	3.93988	0.01126	5.94983
C	16	-0.17833	1.99829	4.16949	0.01055	6.17833
C	17	-0.01772	1.99859	4.00755	0.01159	6.01772
C	18	-0.22349	1.99851	4.21357	0.01141	6.22349
C	19	-0.04314	1.99863	4.03356	0.01096	6.04314
C	20	-0.22842	1.99857	4.21886	0.01098	6.22842
C	21	-0.22895	1.99855	4.21937	0.01104	6.22895
C	22	-0.25122	1.99855	4.24133	0.01134	6.25122
C	23	-0.18915	1.99858	4.17928	0.01129	6.18915
C	24	-0.06159	1.99861	4.05223	0.01075	6.06159
C	25	-0.06846	1.99849	4.05836	0.01161	6.06846
C	26	-0.22386	1.99851	4.21399	0.01136	6.22386
C	27	-0.23909	1.99855	4.22937	0.01117	6.23909
C	28	-0.24346	1.99855	4.23387	0.01103	6.24346
C	29	-0.24311	1.99854	4.23338	0.01118	6.24311
C	30	-0.22925	1.99850	4.21956	0.01118	6.22925
H	31	0.24510	0.00000	0.75389	0.00101	0.75490
H	32	0.24082	0.00000	0.75827	0.00091	0.75918
H	33	0.24551	0.00000	0.75373	0.00076	0.75449
H	34	0.24805	0.00000	0.75118	0.00077	0.75195

H	35	0.26592	0.00000	0.73283	0.00125	0.73408
H	36	0.25449	0.00000	0.74458	0.00093	0.74551
H	37	0.24760	0.00000	0.75165	0.00075	0.75240
H	38	0.25133	0.00000	0.74782	0.00085	0.74867
C	39	-0.16263	1.99861	4.15217	0.01185	6.16263
C	40	-0.06864	1.99830	4.05885	0.01148	6.06864
C	41	-0.05960	1.99850	4.04936	0.01174	6.05960
C	42	-0.19821	1.99847	4.18889	0.01085	6.19821
C	43	-0.10167	1.99858	4.09198	0.01110	6.10167
C	44	-0.20958	1.99858	4.20028	0.01072	6.20958
C	45	-0.28083	1.99854	4.27090	0.01138	6.28083
C	46	-0.23376	1.99856	4.22412	0.01109	6.23376
C	47	-0.25629	1.99859	4.24668	0.01101	6.25629
C	48	-0.03405	1.99859	4.02498	0.01048	6.03405
C	49	-0.04458	1.99852	4.03388	0.01218	6.04458
C	50	-0.24216	1.99850	4.23237	0.01129	6.24216
C	51	-0.24278	1.99854	4.23317	0.01106	6.24278
C	52	-0.24909	1.99855	4.23954	0.01100	6.24909
C	53	-0.23953	1.99855	4.22993	0.01105	6.23953
C	54	-0.22547	1.99848	4.21577	0.01122	6.22547
H	55	0.24133	0.00000	0.75757	0.00110	0.75867
H	56	0.23483	0.00000	0.76420	0.00097	0.76517
H	57	0.23898	0.00000	0.76027	0.00075	0.76102
H	58	0.24012	0.00000	0.75906	0.00081	0.75988
H	59	0.24413	0.00000	0.75441	0.00146	0.75587
H	60	0.23988	0.00000	0.75912	0.00100	0.76012
H	61	0.24433	0.00000	0.75491	0.00076	0.75567
H	62	0.25722	0.00000	0.74189	0.00088	0.74278
H	63	0.24371	0.00000	0.75549	0.00080	0.75629
H	64	0.24627	0.00000	0.75293	0.00079	0.75373
H	65	0.24909	0.00000	0.75013	0.00078	0.75091
H	66	0.24783	0.00000	0.75139	0.00078	0.75217

* Total *	0.00000	73.94888	177.57648	0.47464	252.00000
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TS2 SMR3907h

SCF Done: E(RM06) = -1436.49214776 A.U.

Sum of electronic and zero-point Energies= -1435.950537

Sum of electronic and thermal Energies= -1435.925811

Sum of electronic and thermal Enthalpies= -1435.924946

Sum of electronic and thermal Free Energies= -1436.003557

SCF Done (single point, scrf=(smd,solvent=toluene)): E(RM06) = -1436.52982820 A.U.

$\nu^i = -24.40 \text{ cm}^{-1}$

7	0.197035	1.794335	1.210600
6	1.106826	1.449714	0.342516
6	-0.410231	0.885126	2.169754
6	-1.023406	1.027217	-1.673520
6	-0.398608	3.122871	1.157640
1	1.541008	2.296934	-0.196078
1	-0.441939	1.400664	3.136599
1	0.176610	-0.030505	2.248924
1	-1.426113	0.631276	1.848702
1	-1.654811	1.793979	-2.107487
1	-0.025348	0.911052	-2.087698
1	-1.401122	3.040205	0.716246
1	0.207210	3.779039	0.528476
1	-0.471376	3.537202	2.167993
6	0.729728	-0.944399	-0.270699
6	1.594649	0.157236	-0.012811

6	3.004700	0.089993	-0.308145
6	3.560771	-1.070525	-0.761652
6	2.747461	-2.206794	-1.037391
6	3.310996	-3.388066	-1.571357
6	2.512495	-4.448500	-1.932617
6	1.113584	-4.354147	-1.798625
6	0.542078	-3.219482	-1.271940
6	1.338580	-2.134954	-0.831049
6	3.859089	1.273724	-0.040662
6	4.594565	1.856140	-1.078350
6	5.389404	2.973048	-0.837238
6	5.457505	3.521058	0.441933
6	4.731915	2.944758	1.482669
6	3.937239	1.827383	1.244782
1	4.635565	-1.136115	-0.918749
1	4.389965	-3.435509	-1.703803
1	2.955957	-5.350196	-2.346442
1	0.483561	-5.175270	-2.128208
1	-0.535012	-3.129023	-1.180011
1	4.524117	1.430573	-2.076392
1	6.078138	4.393150	0.628457
1	3.394246	1.354957	2.061121
6	-0.712244	-0.881705	-0.071113
6	-1.495897	0.181602	-0.712840
6	-2.895349	0.300684	-0.252514
6	-3.448169	-0.601490	0.594172
6	-2.710844	-1.695764	1.156212
6	-3.310006	-2.565084	2.082459
6	-2.577669	-3.536165	2.738909
6	-1.197816	-3.616229	2.491796
6	-0.583864	-2.773377	1.588006
6	-1.321243	-1.811155	0.839512
6	-3.708981	1.467184	-0.685838
6	-4.076907	2.437916	0.251989
6	-4.843887	3.538761	-0.125998
6	-5.254920	3.677981	-1.448550
6	-4.903365	2.709028	-2.387762
6	-4.137203	1.610663	-2.010701
1	-4.491144	-0.482848	0.890639
1	-4.374056	-2.446557	2.285208
1	-3.051555	-4.206677	3.449868
1	-0.596549	-4.346567	3.029093
1	0.488337	-2.851277	1.432271
1	-3.766252	2.309535	1.288749
1	-5.853692	4.534435	-1.746985
1	-3.862431	0.849938	-2.737055
1	-5.126660	4.283916	0.613489
1	-5.235149	2.807969	-3.418178
1	5.953079	3.421139	-1.651014
1	4.796457	3.359765	2.484998

PD from TS1 with UM06 SMR3927afo

SCF Done: E(UM06) = -1436.59082103 A.U.

Sum of electronic and zero-point Energies= -1436.043838

Sum of electronic and thermal Energies= -1436.019804

Sum of electronic and thermal Enthalpies= -1436.018939

Sum of electronic and thermal Free Energies= -1436.095673

SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.62525918 A.U.
no imaginary frequency

7	0.463977	1.872617	1.278247
6	0.629786	1.401316	-0.095683

6	-0.209407	1.007024	2.224949
6	-0.655985	1.263612	-0.929670
6	-0.047483	3.222180	1.339572
1	1.250831	2.166400	-0.585678
1	-0.035214	1.393547	3.237826
1	0.198032	-0.007362	2.174803
1	-1.303848	0.942327	2.072161
1	-1.236028	2.192072	-0.911220
1	-0.358189	1.094984	-1.975988
1	-1.116580	3.306239	1.055063
1	0.538429	3.874825	0.678780
1	0.048250	3.604899	2.363683
6	0.659902	-1.081915	-0.311182
6	1.389547	0.101547	-0.206832
6	2.805033	0.096738	-0.387681
6	3.441283	-1.087205	-0.693257
6	2.719395	-2.280113	-0.918312
6	3.372857	-3.464505	-1.350305
6	2.654185	-4.587052	-1.668105
6	1.243025	-4.569123	-1.581351
6	0.584274	-3.449083	-1.141054
6	1.300122	-2.280445	-0.762839
6	3.608533	1.346136	-0.315610
6	4.462611	1.671733	-1.377065
6	5.242390	2.823357	-1.332847
6	5.176687	3.668048	-0.227717
6	4.327562	3.354020	0.831444
6	3.550397	2.200422	0.793045
1	4.524368	-1.101264	-0.803651
1	4.457099	-3.452297	-1.442043
1	3.160979	-5.486582	-2.006510
1	0.677228	-5.449178	-1.874550
1	-0.499380	-3.439531	-1.084399
1	4.495076	1.020596	-2.247755
1	5.782981	4.569330	-0.193134
1	2.873368	1.961369	1.608290
6	-0.795225	-1.018989	-0.008255
6	-1.475591	0.127658	-0.403548
6	-2.862520	0.279505	-0.121817
6	-3.525920	-0.696031	0.585133
6	-2.841073	-1.819239	1.103307
6	-3.503285	-2.756278	1.938886
6	-2.810821	-3.773277	2.542345
6	-1.415723	-3.884660	2.347299
6	-0.752071	-3.013733	1.519732
6	-1.445565	-1.977235	0.836231
6	-3.579734	1.514279	-0.529383
6	-4.131952	2.349284	0.447218
6	-4.798278	3.516395	0.081866
6	-4.918135	3.859732	-1.262222
6	-4.369021	3.032739	-2.240951
6	-3.702413	1.867278	-1.877530
1	-4.589956	-0.586100	0.789198
1	-4.571210	-2.632730	2.107877
1	-3.323140	-4.480289	3.188907
1	-0.862817	-4.663471	2.865419
1	0.320319	-3.103716	1.384712
1	-4.021416	2.079107	1.495688
1	-5.437007	4.770727	-1.547848
1	-3.275959	1.215278	-2.637106

1	-5.220386	4.161313	0.848000
1	-4.464788	3.296232	-3.290920
1	5.896101	3.066178	-2.166507
1	4.275093	4.008496	1.697680

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	-0.385142	0.000000
2	C	0.234722	0.000000
3	C	0.154274	0.000000
4	C	0.113394	0.000000
5	C	0.129108	0.000000
15	C	-0.045488	0.000000
16	C	-0.026722	0.000000
17	C	-0.031418	0.000000
18	C	0.007448	0.000000
19	C	0.002541	0.000000
20	C	0.000252	0.000000
21	C	0.000057	0.000000
22	C	0.003928	0.000000
23	C	0.021206	0.000000
24	C	-0.034978	0.000000
25	C	-0.066203	0.000000
26	C	0.007159	0.000000
27	C	-0.000144	0.000000
28	C	-0.001065	0.000000
29	C	-0.003703	0.000000
30	C	0.041739	0.000000
39	C	-0.059242	0.000000
40	C	-0.015084	0.000000
41	C	-0.050770	0.000000
42	C	0.010351	0.000000
43	C	0.001996	0.000000
44	C	0.000936	0.000000
45	C	-0.001555	0.000000
46	C	0.005384	0.000000
47	C	0.021139	0.000000
48	C	-0.021441	0.000000
49	C	-0.056625	0.000000
50	C	0.016343	0.000000
51	C	0.005718	0.000000
52	C	0.002426	0.000000
53	C	0.007788	0.000000
54	C	0.011674	0.000000

PD from **TS2** with RM06 SMR3907f

SCF Done: E(RM06) = -1436.59083480 A.U.

Sum of electronic and zero-point Energies= -1436.043755

Sum of electronic and thermal Energies= -1436.019751

Sum of electronic and thermal Enthalpies= -1436.018886

Sum of electronic and thermal Free Energies= -1436.095556

SCF Done (single point, scrf=(smd,solvent=toluene)): E(RM06) = -1436.62527281 A.U.

no imaginary frequency

7	0.417382	1.831514	1.332878
6	0.611185	1.378830	-0.043801
6	-0.270101	0.950279	2.254938
6	-0.658287	1.243280	-0.902464
6	-0.103822	3.177159	1.401094
1	1.235357	2.154371	-0.512809
1	-0.117361	1.324083	3.275991
1	0.142554	-0.061690	2.199214

1	-1.361044	0.882923	2.079843
1	-1.244856	2.167564	-0.882339
1	-0.340654	1.090428	-1.945364
1	-1.167503	3.258203	1.096067
1	0.491118	3.841865	0.760685
1	-0.031235	3.547122	2.431761
6	0.662409	-1.101178	-0.288817
6	1.381912	0.085823	-0.157590
6	2.800309	0.092788	-0.314085
6	3.449890	-1.083449	-0.621680
6	2.740394	-2.278471	-0.873042
6	3.409650	-3.453109	-1.307497
6	2.704514	-4.576465	-1.651686
6	1.291934	-4.569005	-1.589872
6	0.617730	-3.458809	-1.148019
6	1.318651	-2.290062	-0.743063
6	3.594125	1.346654	-0.217406
6	4.465479	1.684625	-1.260876
6	5.237452	2.840338	-1.194810
6	5.146521	3.677174	-0.085467
6	4.279860	3.351132	0.955749
6	3.510353	2.193295	0.895577
1	4.534783	-1.088956	-0.713438
1	4.495227	-3.432447	-1.379843
1	3.223471	-5.468357	-1.991878
1	0.737475	-5.449186	-1.903639
1	-0.466818	-3.457405	-1.110442
1	4.517577	1.039802	-2.135268
1	5.746710	4.581710	-0.033684
1	2.819914	1.944708	1.696721
6	-0.798464	-1.051642	-0.012079
6	-1.479464	0.095116	-0.406051
6	-2.872484	0.233821	-0.148646
6	-3.542021	-0.754972	0.533695
6	-2.858977	-1.879720	1.050885
6	-3.530050	-2.831647	1.862221
6	-2.841793	-3.851256	2.466060
6	-1.442471	-3.950353	2.296251
6	-0.769606	-3.064572	1.492269
6	-1.457577	-2.024648	0.808325
6	-3.590830	1.468557	-0.554307
6	-4.167712	2.287060	0.422032
6	-4.835615	3.453911	0.058769
6	-4.932524	3.813451	-1.282929
6	-4.358767	3.002983	-2.261344
6	-3.690523	1.837810	-1.899989
1	-4.610444	-0.654943	0.719077
1	-4.601845	-2.717688	2.012404
1	-3.361072	-4.569786	3.094103
1	-0.893834	-4.731601	2.815240
1	0.305814	-3.145187	1.376811
1	-4.075247	2.004270	1.468922
1	-5.452627	4.724263	-1.566897
1	-3.244928	1.198616	-2.659454
1	-5.276969	4.085965	0.824771
1	-4.436397	3.279232	-3.309528
1	5.904796	3.092612	-2.014745
1	4.207507	3.999518	1.825118

SCF Done: E(UM06) = -1436.49605754 A.U.
 Sum of electronic and zero-point Energies= -1435.954468
 Sum of electronic and thermal Energies= -1435.929189
 Sum of electronic and thermal Enthalpies= -1435.928324
 Sum of electronic and thermal Free Energies= -1436.008679
 SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.53165356 A.U.
 no imaginary frequency

7	-2.771318	-0.503876	0.000000
6	-1.555811	-1.054839	-0.275563
6	-3.549071	-0.989642	1.125437
6	-4.042282	-1.493053	-1.878477
6	-2.912227	0.920214	-0.234809
1	-0.761336	-0.328979	-0.445963
1	-3.225016	-0.481837	2.046406
1	-3.418153	-2.066080	1.250180
1	-4.612981	-0.788938	0.954997
1	-4.709714	-0.697416	-2.192451
1	-3.053442	-1.529496	-2.322234
1	-3.979026	1.172518	-0.245890
1	-2.488227	1.178616	-1.209844
1	-2.413893	1.519216	0.544835
6	-2.148662	-3.494229	-0.835357
6	-1.254569	-2.392705	-0.580757
6	0.186838	-2.641310	-0.713901
6	0.672904	-3.833744	-1.138972
6	-0.194726	-4.888843	-1.546832
6	0.319940	-6.077236	-2.103527
6	-0.522524	-7.062042	-2.570437
6	-1.913847	-6.864552	-2.511108
6	-2.436921	-5.716190	-1.959279
6	-1.598958	-4.705524	-1.420941
6	1.162817	-1.580134	-0.341772
6	1.964525	-0.992360	-1.323274
6	2.903767	-0.022036	-0.978935
6	3.049925	0.367316	0.349323
6	2.253752	-0.216502	1.334860
6	1.313778	-1.181812	0.992241
1	1.749340	-3.988825	-1.193807
1	1.400207	-6.192854	-2.169890
1	-0.119198	-7.973130	-3.003555
1	-2.582936	-7.618245	-2.917544
1	-3.511135	-5.566758	-1.936809
1	1.840085	-1.300979	-2.358587
1	3.783355	1.122560	0.618819
1	0.690803	-1.643972	1.754585
6	-3.594925	-3.514622	-0.550784
6	-4.489832	-2.521318	-1.069204
6	-5.888516	-2.548214	-0.647463
6	-6.353615	-3.542174	0.152108
6	-5.496005	-4.564932	0.660315
6	-6.001487	-5.554147	1.529954
6	-5.168480	-6.486373	2.106785
6	-3.787541	-6.431755	1.842374
6	-3.270821	-5.481212	0.991160
6	-4.107185	-4.539212	0.335056
6	-6.804946	-1.461224	-1.077224
6	-7.395482	-0.626990	-0.122359
6	-8.253825	0.399312	-0.512110
6	-8.528484	0.604068	-1.861070
6	-7.950009	-0.227575	-2.819256

6	-7.097497	-1.254876	-2.431362
1	-7.405868	-3.561481	0.433533
1	-7.068533	-5.555831	1.745412
1	-5.566501	-7.243636	2.776340
1	-3.118750	-7.140862	2.323088
1	-2.202866	-5.446749	0.807516
1	-7.177737	-0.793482	0.931050
1	-9.195305	1.405726	-2.166801
1	-6.653276	-1.913112	-3.174174
1	-8.707470	1.040313	0.239351
1	-8.172737	-0.079001	-3.872613
1	3.521592	0.430770	-1.749993
1	2.372094	0.079397	2.373989

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	-0.348370	0.064226
2	C	0.307202	0.361118
3	C	0.229393	0.008381
4	C	0.083145	-0.452642
5	C	0.189977	0.004160
15	C	-0.085268	0.368694
16	C	-0.093506	-0.165528
17	C	-0.023872	0.101066
18	C	0.008922	-0.089810
19	C	0.003145	0.123769
20	C	-0.011686	-0.077987
21	C	-0.007458	0.105379
22	C	-0.001250	-0.074520
23	C	0.040302	0.104000
24	C	-0.023808	-0.136435
25	C	-0.100015	-0.013348
26	C	0.016171	0.007518
27	C	0.003677	-0.000100
28	C	-0.001352	0.004350
29	C	0.002083	0.001425
30	C	0.020429	0.003577
39	C	-0.128594	-0.385629
40	C	-0.000411	0.202764
41	C	-0.053909	-0.126604
42	C	0.004558	0.108019
43	C	-0.002458	-0.134956
44	C	-0.008961	0.085859
45	C	-0.010928	-0.112492
46	C	-0.000636	0.079776
47	C	0.032533	-0.110280
48	C	-0.010955	0.144248
49	C	-0.047840	0.013669
50	C	0.002817	-0.005188
51	C	0.001699	0.001067
52	C	-0.000527	-0.003367
53	C	0.006245	0.000982
54	C	0.009507	-0.005162

IM1t SMR3927h1r2o

SCF Done: E(UM06) = -1436.44958414 A.U.

Sum of electronic and zero-point Energies= -1435.907443

Sum of electronic and thermal Energies= -1435.882975

Sum of electronic and thermal Enthalpies= -1435.882110

Sum of electronic and thermal Free Energies= -1435.960945

SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.49204937 A.U.

no imaginary frequency

7	-0.192769	2.141110	0.076741
6	1.155254	1.585151	0.188879
6	-0.890519	2.104109	1.403247
6	-1.056338	1.364758	-1.021217
6	-0.074022	3.549797	-0.376734
1	1.882223	2.326941	0.505744
1	-0.291387	2.686409	2.109142
1	-0.967639	1.062481	1.721398
1	-1.891012	2.535059	1.289399
1	-1.814630	2.089316	-1.328295
1	-0.317373	1.212320	-1.818864
1	-1.073955	3.992455	-0.417301
1	0.384459	3.555754	-1.369377
1	0.554854	4.111274	0.320485
6	0.693509	-0.819243	-0.422917
6	1.564903	0.293619	-0.127780
6	3.004518	0.081639	-0.192012
6	3.519118	-1.085735	-0.692942
6	2.677360	-2.119657	-1.179714
6	3.201063	-3.297108	-1.757778
6	2.364566	-4.280308	-2.238803
6	0.965402	-4.119897	-2.167014
6	0.428232	-2.992379	-1.588525
6	1.259378	-1.972747	-1.062977
6	3.937533	1.136364	0.282663
6	4.805939	1.764776	-0.615242
6	5.698395	2.738176	-0.172694
6	5.730805	3.097781	1.172221
6	4.871252	2.473759	2.075952
6	3.982920	1.497912	1.636458
1	4.598264	-1.226174	-0.719426
1	4.281761	-3.410875	-1.818555
1	2.781463	-5.180490	-2.682906
1	0.312404	-4.887566	-2.572028
1	-0.647123	-2.860009	-1.515795
1	4.770243	1.481995	-1.664730
1	6.427496	3.856699	1.517870
1	3.322641	0.993530	2.339183
6	-0.713708	-0.854494	-0.000312
6	-1.624321	0.160542	-0.439416
6	-2.978128	0.138565	-0.012894
6	-3.427043	-0.855830	0.830758
6	-2.541494	-1.863905	1.336432
6	-2.992530	-2.830348	2.250628
6	-2.132544	-3.783829	2.780549
6	-0.788046	-3.776526	2.401925
6	-0.313635	-2.841528	1.494354
6	-1.167383	-1.870616	0.919243
6	-3.914295	1.211786	-0.434419
6	-4.566820	1.990360	0.529600
6	-5.423979	3.020293	0.149693
6	-5.642219	3.285851	-1.200500
6	-5.007178	2.509224	-2.168277
6	-4.153204	1.477128	-1.789739
1	-4.475309	-0.888388	1.121699
1	-4.041462	-2.814039	2.542984
1	-2.501852	-4.524666	3.484598
1	-0.102660	-4.511263	2.817691
1	0.733036	-2.853715	1.207303

1	-4.393395	1.771877	1.582039
1	-6.311332	4.088770	-1.497998
1	-3.671854	0.851805	-2.538905
1	-5.923143	3.617395	0.908661
1	-5.189980	2.700391	-3.222691
1	6.369062	3.218826	-0.880285
1	4.905300	2.739486	3.129462

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	-0.403117	-0.017356
2	C	0.292120	0.598403
3	C	0.302762	0.031024
4	C	0.246560	0.057185
5	C	0.269597	0.012647
15	C	-0.070220	0.450667
16	C	-0.069859	-0.182540
17	C	-0.036263	0.165149
18	C	-0.005797	-0.024367
19	C	0.012988	0.155208
20	C	-0.017340	-0.085098
21	C	0.004975	0.136987
22	C	-0.010412	-0.061183
23	C	0.060953	0.123211
24	C	-0.034587	-0.104720
25	C	-0.086080	-0.020219
26	C	0.014116	0.010847
27	C	0.003155	-0.005973
28	C	-0.002772	0.012582
29	C	0.003156	-0.005999
30	C	0.002439	0.011966
39	C	-0.129843	0.241428
40	C	-0.078682	0.177439
41	C	-0.045555	-0.109698
42	C	-0.041273	0.255343
43	C	-0.001574	-0.010413
44	C	-0.039595	0.045721
45	C	-0.033197	0.078103
46	C	-0.016354	-0.015367
47	C	-0.019503	0.118130
48	C	-0.000515	-0.049889
49	C	-0.058293	0.012071
50	C	-0.002083	-0.008238
51	C	-0.001505	0.008484
52	C	-0.005456	-0.006174
53	C	0.002784	0.005413
54	C	-0.005730	-0.000774

TS1t SMR3927h1

SCF Done: E(UM06) = -1436.44942468 A.U.

Sum of electronic and zero-point Energies= -1435.908216

Sum of electronic and thermal Energies= -1435.884031

Sum of electronic and thermal Enthalpies= -1435.883166

Sum of electronic and thermal Free Energies= -1435.961262

SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.49105267 A.U.

$\nu^i = -261.19 \text{ cm}^{-1}$

7	-0.175916	2.133105	0.121293
6	1.162610	1.569530	0.220246
6	-0.886132	2.061864	1.431262
6	-1.074933	1.331644	-1.044673
6	-0.064393	3.540890	-0.316058

1	1.906095	2.301245	0.526218
1	-0.309946	2.634617	2.164839
1	-0.959759	1.013430	1.727476
1	-1.890083	2.483250	1.310717
1	-1.812229	2.080506	-1.342816
1	-0.297238	1.200590	-1.806863
1	-1.066371	3.979667	-0.354439
1	0.392455	3.562050	-1.309937
1	0.560504	4.105970	0.383972
6	0.691806	-0.824450	-0.422966
6	1.562963	0.278703	-0.109762
6	3.006708	0.065287	-0.193176
6	3.508940	-1.083657	-0.737171
6	2.659359	-2.106804	-1.236987
6	3.176425	-3.268118	-1.850155
6	2.334254	-4.248539	-2.326501
6	0.935915	-4.100880	-2.208080
6	0.405275	-2.989543	-1.596574
6	1.244358	-1.965836	-1.085377
6	3.947372	1.100744	0.307693
6	4.819008	1.746529	-0.574416
6	5.720062	2.699981	-0.106354
6	5.757614	3.021050	1.247945
6	4.893958	2.379605	2.135562
6	3.996310	1.424488	1.670763
1	4.587486	-1.225077	-0.784546
1	4.255905	-3.372876	-1.941038
1	2.744073	-5.137386	-2.798699
1	0.278104	-4.869844	-2.602929
1	-0.668180	-2.867693	-1.487854
1	4.778785	1.494881	-1.631651
1	6.460903	3.764334	1.613466
1	3.331257	0.908222	2.360119
6	-0.721234	-0.859235	0.003757
6	-1.636529	0.143635	-0.464777
6	-2.988388	0.129095	-0.004693
6	-3.416434	-0.835892	0.873271
6	-2.520223	-1.829317	1.397698
6	-2.953220	-2.769529	2.343230
6	-2.082153	-3.708223	2.884925
6	-0.744238	-3.709706	2.480695
6	-0.285531	-2.800182	1.541575
6	-1.151707	-1.840606	0.957925
6	-3.934708	1.182650	-0.451222
6	-4.597888	1.976273	0.492646
6	-5.469991	2.983713	0.086642
6	-5.690649	3.212102	-1.269596
6	-5.041587	2.422298	-2.217513
6	-4.172266	1.413560	-1.812929
1	-4.460196	-0.864477	1.181702
1	-3.997049	-2.747210	2.653362
1	-2.437445	-4.430086	3.615193
1	-0.051630	-4.434180	2.902951
1	0.755817	-2.819287	1.235304
1	-4.421446	1.787922	1.550340
1	-6.371025	3.997582	-1.587573
1	-3.677117	0.779966	-2.545648
1	-5.977978	3.592612	0.830229
1	-5.224640	2.585773	-3.276511
1	6.393050	3.195187	-0.801501

1 4.931128 2.616186 3.195802
 Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	-0.407686	-0.001307
2	C	0.301232	0.609086
3	C	0.294444	0.029410
4	C	0.225476	0.099870
5	C	0.257262	0.012692
15	C	-0.074068	0.454250
16	C	-0.066454	-0.215835
17	C	-0.033355	0.181525
18	C	0.004513	-0.081697
19	C	0.009573	0.180548
20	C	-0.013591	-0.109052
21	C	0.005699	0.157160
22	C	-0.005419	-0.085494
23	C	0.064752	0.138502
24	C	-0.027256	-0.126965
25	C	-0.086667	-0.022325
26	C	0.013734	0.012949
27	C	0.004651	-0.006875
28	C	-0.000944	0.013466
29	C	0.005111	-0.006160
30	C	0.005977	0.012331
39	C	-0.134787	0.294955
40	C	-0.071602	0.160816
41	C	-0.044195	-0.091747
42	C	-0.040999	0.191866
43	C	-0.002357	0.038517
44	C	-0.040111	0.008586
45	C	-0.036390	0.123076
46	C	-0.015509	-0.050914
47	C	-0.025659	0.153698
48	C	0.000682	-0.084521
49	C	-0.054572	0.010474
50	C	-0.003252	-0.007235
51	C	-0.002157	0.008876
52	C	-0.005536	-0.007710
53	C	0.001570	0.007544
54	C	-0.002111	-0.002360

IM2t SMR3927h1fo

SCF Done: E(UM06) = -1436.50414293 A.U.
 Sum of electronic and zero-point Energies= -1435.964141
 Sum of electronic and thermal Energies= -1435.938341
 Sum of electronic and thermal Enthalpies= -1435.937476
 Sum of electronic and thermal Free Energies= -1436.020587
 SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.53804034 A.U.
 no imaginary frequency

IM2ts (a single point and frequency calculation with the molecular structure of IM2t at the open-singlet state without geometrical optimization)

SCF Done: E(UM06) = -1436.50514945 A.U.
 Sum of electronic and zero-point Energies= -1435.965397
 Sum of electronic and thermal Energies= -1435.939483
 Sum of electronic and thermal Enthalpies= -1435.938618
 Sum of electronic and thermal Free Energies= -1436.022231
 SCF Done (single point, scrf=(smd,solvent=toluene)): E(UM06) = -1436.51652685 A.U.
 no imaginary frequency

7	0.192859	1.817673	1.462889
6	1.259958	1.509742	0.669406

6	-0.311150	0.986300	2.528589
6	-1.021722	0.956349	-1.629897
6	-0.452241	3.096789	1.310933
1	1.870539	2.372079	0.395151
1	-0.251914	1.541719	3.478536
1	0.290384	0.079826	2.619605
1	-1.356782	0.692009	2.370629
1	-1.638692	1.688430	-2.141128
1	0.012377	0.837467	-1.937193
1	-1.412927	2.996185	0.776301
1	0.183752	3.771948	0.728461
1	-0.648683	3.553751	2.290901
6	0.742212	-0.805700	-0.197260
6	1.627680	0.269584	0.106112
6	3.007010	0.159369	-0.353559
6	3.428455	-0.928136	-1.060194
6	2.550168	-1.995911	-1.396567
6	2.987850	-3.100012	-2.156129
6	2.115365	-4.104334	-2.514789
6	0.764000	-4.023992	-2.123813
6	0.310292	-2.964053	-1.373586
6	1.189109	-1.921169	-0.968069
6	3.989361	1.229866	-0.039749
6	4.641175	1.904414	-1.076391
6	5.593468	2.882252	-0.796026
6	5.903996	3.196162	0.523608
6	5.259049	2.527386	1.564268
6	4.307423	1.553160	1.286116
1	4.470845	-0.993475	-1.369473
1	4.031657	-3.137204	-2.462951
1	2.460815	-4.949730	-3.103155
1	0.072179	-4.808002	-2.420780
1	-0.733651	-2.909249	-1.080342
1	4.385815	1.660943	-2.105070
1	6.646328	3.958709	0.743439
1	3.807244	1.024229	2.093933
6	-0.709033	-0.729959	0.122879
6	-1.538856	0.178076	-0.604098
6	-2.938984	0.289222	-0.209653
6	-3.439985	-0.486596	0.793570
6	-2.635600	-1.438116	1.488377
6	-3.162445	-2.228821	2.529829
6	-2.361245	-3.109986	3.224335
6	-0.994930	-3.225237	2.896238
6	-0.453294	-2.469654	1.882252
6	-1.254466	-1.557898	1.143177
6	-3.829484	1.267533	-0.885077
6	-4.379845	2.324664	-0.153600
6	-5.232812	3.239192	-0.766562
6	-5.544751	3.105355	-2.116683
6	-5.003965	2.051283	-2.851548
6	-4.152011	1.136920	-2.240995
1	-4.489953	-0.394487	1.068884
1	-4.216871	-2.126003	2.779432
1	-2.777321	-3.713290	4.026309
1	-0.366890	-3.918254	3.449467
1	0.598787	-2.557059	1.624396
1	-4.128838	2.422322	0.900923
1	-6.209199	3.818988	-2.596224
1	-3.735693	0.307024	-2.807389

1	-5.652799	4.058817	-0.189516
1	-5.253261	1.938354	-3.903291
1	6.090261	3.402327	-1.610931
1	5.505411	2.763354	2.596255

Mulliken charges and spin densities with hydrogens summed into heavy atoms (**IM2t**):

		1	2
1	N	-0.350266	0.156727
2	C	0.290174	0.481621
3	C	0.201718	0.009702
4	C	0.094568	0.637322
5	C	0.168477	0.008980
15	C	-0.128623	0.344573
16	C	-0.083077	-0.147966
17	C	-0.025470	0.116523
18	C	0.005310	-0.093738
19	C	-0.001835	0.159960
20	C	-0.011273	-0.100679
21	C	-0.012012	0.146827
22	C	-0.001282	-0.096968
23	C	0.013029	0.137903
24	C	0.011841	-0.137294
25	C	-0.074811	-0.019019
26	C	0.009664	0.014200
27	C	0.002083	-0.001861
28	C	-0.002862	0.008914
29	C	0.000677	0.001615
30	C	0.016089	0.005990
39	C	-0.090185	0.495152
40	C	0.032345	-0.262166
41	C	-0.057611	0.192146
42	C	0.008983	-0.158374
43	C	-0.006035	0.209197
44	C	-0.005833	-0.132871
45	C	-0.000240	0.178021
46	C	0.002657	-0.122989
47	C	0.024835	0.169351
48	C	-0.017121	-0.196967
49	C	-0.050028	-0.019836
50	C	0.009486	0.008020
51	C	0.004222	-0.002580
52	C	0.001875	0.005521
53	C	0.008210	-0.002979
54	C	0.012319	0.008023

Mulliken charges and spin densities with hydrogens summed into heavy atoms (**IM2ts**):

		1	2
1	N	-0.350381	-0.151755
2	C	0.290638	-0.485727
3	C	0.200978	-0.007662
4	C	0.089524	0.632028
5	C	0.169345	-0.005560
15	C	-0.128073	-0.465621
16	C	-0.082076	0.196291
17	C	-0.025751	-0.133323
18	C	0.006243	0.117759
19	C	-0.001752	-0.167865
20	C	-0.010917	0.106346
21	C	-0.011534	-0.150018
22	C	-0.001056	0.101360
23	C	0.014058	-0.145803
24	C	0.012116	0.172917

25	C	-0.074809	0.021596
26	C	0.009803	-0.015480
27	C	0.002287	0.002810
28	C	-0.002779	-0.010030
29	C	0.000880	-0.000664
30	C	0.015895	-0.007229
39	C	-0.091928	0.571038
40	C	0.034161	-0.286338
41	C	-0.058014	0.194431
42	C	0.009102	-0.161876
43	C	-0.006178	0.210707
44	C	-0.005744	-0.133885
45	C	-0.000242	0.177639
46	C	0.002622	-0.123319
47	C	0.024114	0.171178
48	C	-0.016463	-0.218288
49	C	-0.049773	-0.021589
50	C	0.009303	0.008697
51	C	0.004083	-0.003328
52	C	0.001738	0.005752
53	C	0.008032	-0.003622
54	C	0.012548	0.008432