Studies on New Synthetic Reactions of Unsaturated Alcohols and Amines with Aryl Halides under Palladium Catalysis

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Abbreviations

Ac	acetyl
acac	acetylacetonate
aq.	aqueous
Ar	aryl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
brs	broad singlet (spectral)
Bu	butyl
c	cyclo
°C	degrees Celsius
ca.	circa
calcd	calculated
cat.	catalytic
cm	centimeter(s)
Co.	company
COD (cod)	1,5-cyclooctadiene
conc.	concentrated
δ	chemical shift in parts per million downfield from tetramethylsilane
d	doublet (spectral)
dba	dibenzylideneacetone
DIBAL-H	diisobutylaluminum hydride
DMA	*N,N*-dimethylacetamide
DME	dimethoxyethane
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulfoxide
DPPE (dppe)	1,2-bis(diphenylphosphino)ethane
DPPP (dppp)	1,3-bis(diphenylphosphino)propane
DPPB (dppb)	1,4-bis(diphenylphosphino)butane
DPPF	1,1'-bis(diphenylphosphino)ferrocene
de	diastereomeric excess
Ed(s).	editor(s)
ee	enantiomeric excess
eq	equation
equiv	equivalent(s)
Et	ethyl
g	gram(s)
h	hour(s)
Hex	hexyl
HMPA	hexamethylphosphoramide
Hz	hertz (s^{-1})
i	iso
i.e.	that is
IR	infrared (spectrum)
J	coupling constant (in NMR)
m	multiplet (spectral), meter(s), milli
M	molar (1 M = 1 mol dm^{-3})
Me	methyl
Mes	mesityl
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mmol	millimole
n	normal
nd	not determined
NMR	nuclear magnetic resonance
Np	naphthyl
Oct	octyl
p.	page(s)
Ph	phenyl
PMB	*p*-methoxybenzyl
ppm	parts per million (in NMR)
Pr	propyl
q	quartet (spectral)
quant.	quantitative
quint	quintet (spectral)
ref(s)	reference(s)
R_f	retention factor (in TLC)
RI	index of refraction
R^L	larger group
R^S	smaller group
r.t.	room temperature (25 ± 3 °C)
s (*sec*)	secondary
s	singlet (spectral)
sept	septet (spectral)
t	triplet (spectral)
t (*tert*)	tertiary
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	trimethylsilyl
Tol	tolyl
Torr	1 mmHg, 1/760 atm, 133.322 Pa
Ts	*p*-toluenesulfonyl
UV	ultraviolet
vide infra	see below

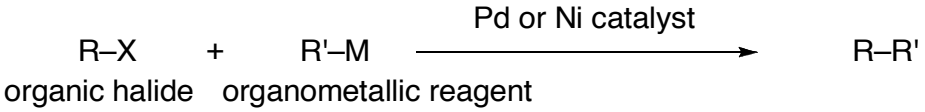
General Introduction

1. Palladium-Catalyzed Cross-Coupling Reaction

1.1 Carbon-Carbon Bond Forming Cross-Coupling Reaction of Organic Halides or Pseudohalides with Organometallic Reagents

Cross-coupling reaction of organic halides with organometallic reagents is one of the most straightforward and reliable synthetic strategies for carbon-carbon bond formation (Scheme 1). In 1972, Kumada and Tamao[1] and Corriu[2] independently reported the first discovery of the cross-coupling reaction of aryl or alkenyl halides with Grignard reagents in the presence of a catalytic amount of a nickel-phosphine complex. Since the palladium-catalyzed cross-coupling reaction of alkenyl halides with Grignard reagents was presented by Murahashi,[3] a variety of organometallic reagents such as organolithium,[4] -aluminum,[5] -zinc,[6] -zirconium,[7] -tin,[8] -copper,[9] -boron,[10] and -silicon[11] proved to participate in the cross-coupling reaction.

Scheme 1.



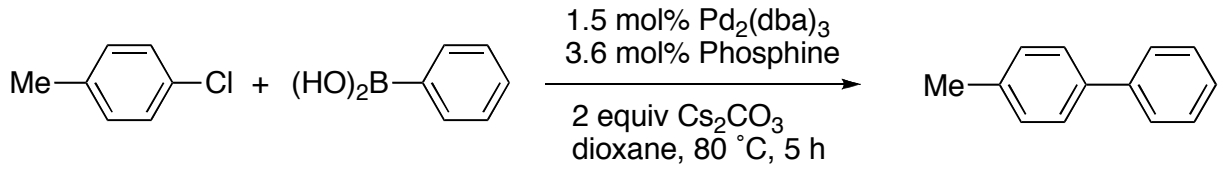
Unlike magnesium and zinc reagents which undergo transmetalation without any difficulty, organoborons and organosilicons lack enough nucleophilicity for transfer of organic groups from boron and silicon to palladium center. In 1979, Suzuki and Miyaura revealed the fact that an additional base coordinates to boron to activate the organoboron reagent and allows efficient transmetalation between organoboron and palladium.[10] Subsequently, the method for the utilization of organosilicons in the cross-coupling methodology was developed by Hiyama and Hatanaka.[11] Thus, the cross-coupling reaction made progress at an accelerated rate during the three decades since 1972 and brought significant innovation in the field of carbon-carbon bond formation. Among them, the cross-coupling reaction using organoborons, so called Suzuki-Miyaura cross-coupling reaction, has emerged as the most practical synthetic method,[12]

particularly for the preparation of biaryls found not only in natural or biologically active compounds but also in industrial materials. The advantages of the use of organoborons in the cross-coupling reaction are their inertness toward water and oxygen, thermal stability, and functional group compatibility. It is also noteworthy that the organoborons and their byproducts generated after the reaction have low toxicity. The recent progress of the cross-coupling reactions is described below mainly with a focus on Suzuki-Miyaura cross-coupling reaction.

Recognizing the limitation of substrates for the conventional cross-coupling reaction, many researchers began to turn their attention to the development of a new ligand, which coordinates to palladium center and enhances catalytic activity toward generally unreactive substrates.

The first example of palladium-catalyzed Suzuki-Miyaura reaction of aryl chlorides was reported by Fu in 1998 (Scheme 2).[13] The sterically demanding and strongly σ-donating nature of the ligand was found to be effective for the reaction of unreactive aryl chlorides under mild conditions. Subsequently, several groups developed a series of ligands bearing similar characteristics[14] and enabled the use of aryl tosylate[15] and heteroaryl halides. The latest studies demonstrated by Hartwig provided satisfactory explanation for the efficiency of bulky and strongly σ-donating ligands in oxidative addition step of aryl halides to zelovalent palladium.[16]

Scheme 2.

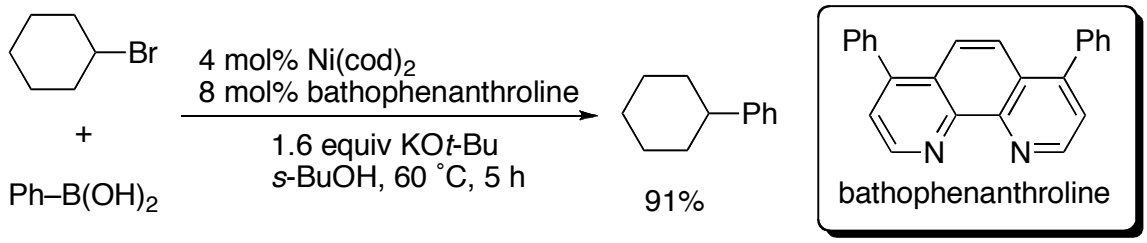


Phosphine	
PPh_3	0%
P(*o*-tol)$_3$	10%
binap	0%
dppf	0%
P(*c*-Hex)$_3$	**75%**
P(*t*-Bu)$_3$	**86%**

As mentioned above, the successful results were obtained in palladium-catalyzed sp^2C–sp^2C cross-coupling reactions as represented by the synthesis of biaryls. On the other hand,

cross-coupling of unactivated alkyl halides/sulfonates containing β-hydrogens were presented by the pioneering work of Suzuki in 1992 and Knochel in 1995, which focused on the reaction with organoboron reagents under palladium catalysis[17,18] and organozincs under nickel catalysis,[19] respectively. There was a significant progress for the cross-coupling reaction of primary alkyl halides with various organometallic reagents,[20] while the reaction of secondary alkyl halides often resulted in failure because of the faster β-hydride elimination of the corresponding alkylpalladium intermediate prior to transmetalation with organometallic reagents. In 2003, Fu discovered the breakthrough for such problematic cross-coupling reaction of secondary alkyl halides with alkylzinc reagents,[21] and then he succeeded in the reaction with arylboronic acid by using a $Ni(cod)_2$/bathophenanthroline catalyst (Scheme 3).[22] Unfortunately, the use of palladium precursors such as $Pd_2(dba)_3$ and $Pd(OAc)_2$ instead of $Ni(cod)_2$ was entirely ineffective for the formation of the desired coupling product. It is apparent that nickel catalysis is much superior to palladium one in the cross-coupling reaction of alkyl electrophiles with organometallic reagents, especially in the reaction of secondary alkyl halides. Different from palladium catalysis, the reaction catalyzed by a nickel complex would proceed through a radical pathway, which begins with a single electron transfer from electron-rich metal complex to alkyl halides.[23]

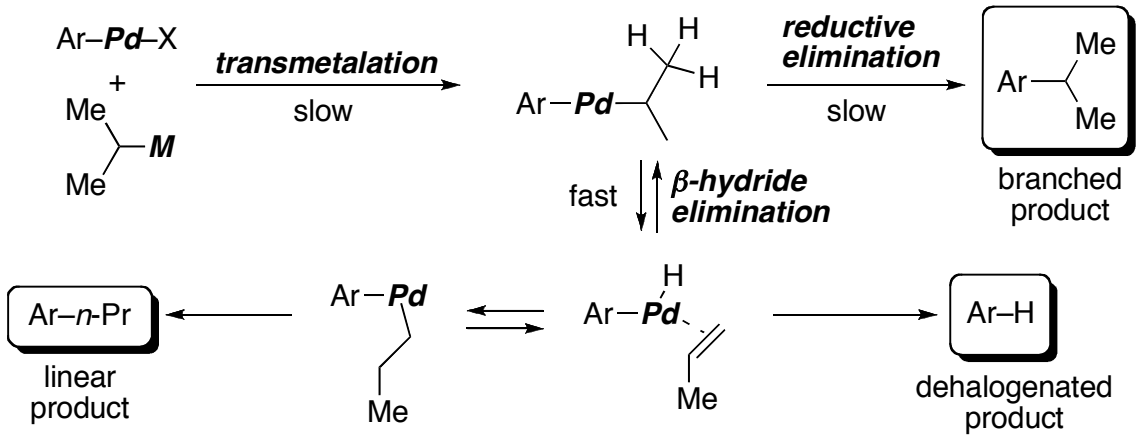
Scheme 3.



Meanwhile, its complementary process, that is, the cross-coupling reaction of aryl halides with secondary alkylmetals was accomplished with the aid of well-defined palladium catalysts. There are two problems to solve for the success of this type of transformation (Scheme 4). The first problematic step is the slow transmetalation due to their bulkiness of secondary alkyl groups.

The second one is the reductive elimination which inevitably competes β-hydride elimination to yield dehalogenated arenes. Another possibility is the initial β-hydride elimination followed by re-insertion of palladium hydride intermediate to alkenes in anti-Markovnikov fashion, finally affording undesirable primary linear product.

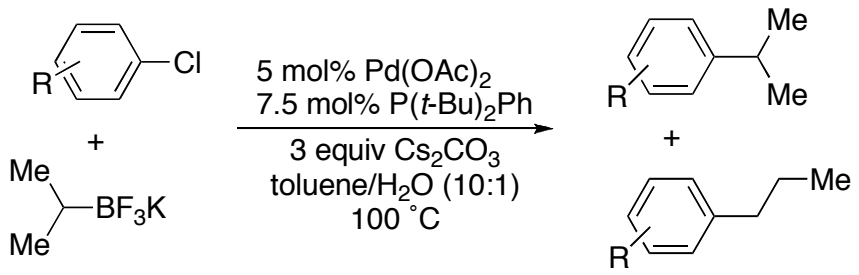
Scheme 4.



Some special substrates were known to readily couple with secondary Grignard reagents in the presence of $NiCl_2$(dppp)[24a] or $PdCl_2$(dppf).[24b] Although there were some reports for the reactions using secondary alkyl-substituted organometallic reagents, most of them suffered from low yield, undesirable β-hydride elimination, and production of the regioisomer.[25] Recent progress was made by Molander in the field of Suzuki-Miyaura coupling reaction of secondary organoboron reagents.[26] Although the coupling with secondary alkylborons was strongly desired because of their broad range of functional group compatibility, it was regarded as one of the most challenging coupling patterns due to its lower reactivity for transmetalation. Molander conducted the reaction of aryl chlorides with secondary alkyltrifluoroborates under various conditions and clearly demonstrated the efficiency of the sterically demanding phosphine ligand having at least two *t*-butyl groups on phosphorus, albeit in moderate isomeric purity in some cases (Scheme 5). In the Negishi cross-coupling reaction, Buchwald developed the most practical ligand, CPhos, and succeeded in cross-coupling of a wide range of aryl halides and secondary alkylzinc reagents without erosion of regiochemical information of the starting

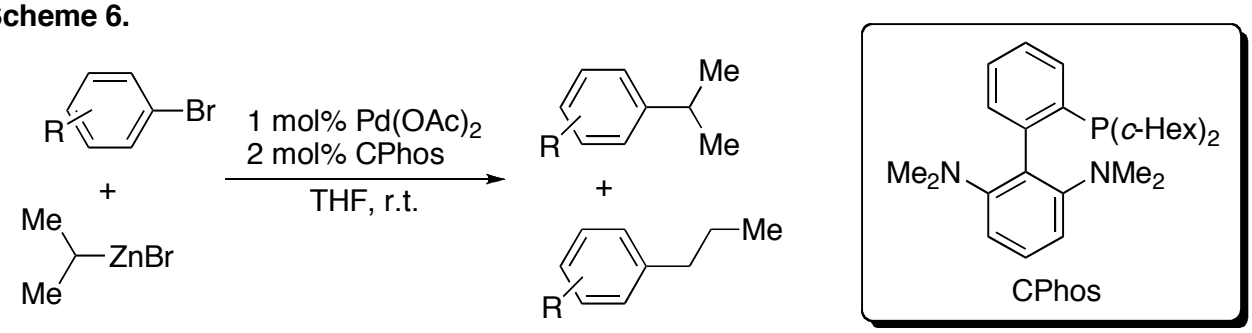
materials (Scheme 6).[27]

Scheme 5.



R = 4-MeO 79% branched/linear = 8.2:1
2-MeO 57% branched/linear = 1.4:1

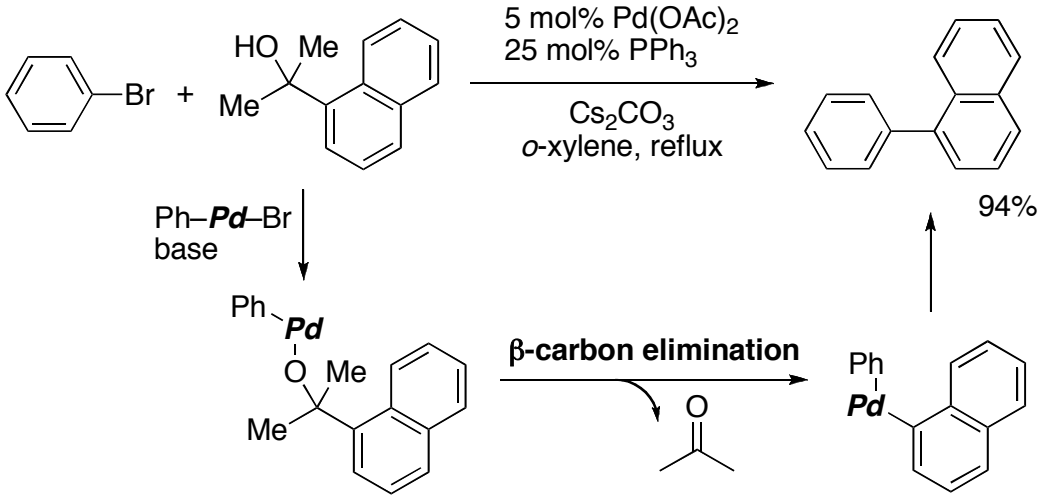
Scheme 6.



R = 4-MeO 92% branched/linear = 37:1
2-MeO 97% branched/linear = 27:1

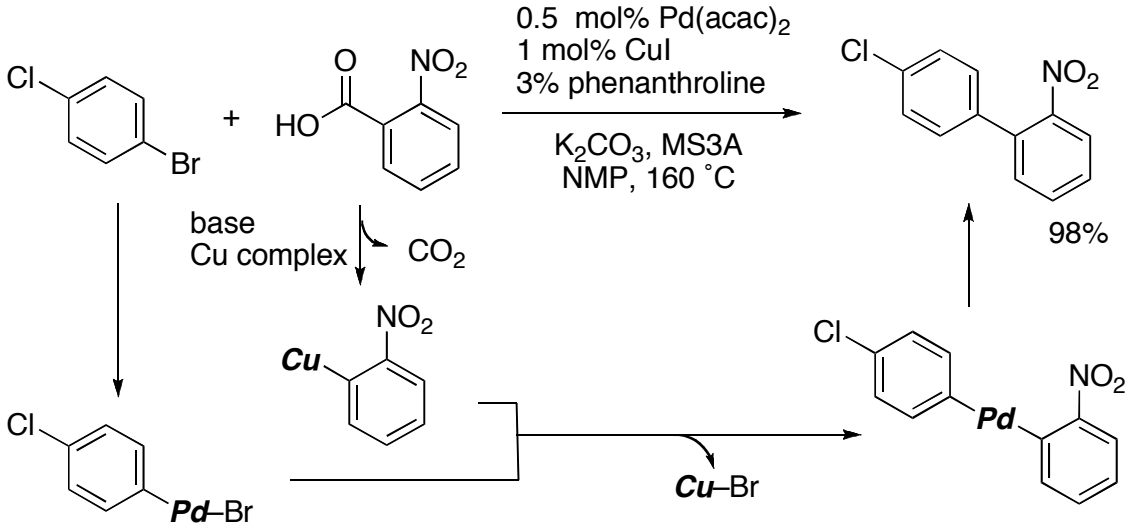
Needless to say, the traditional cross-coupling reaction requires organometallic reagents as coupling partners, some of which are so reactive that they should be handled carefully, and sometimes need tedious steps for preparation. Recently, stable and easy-to-handle tertiary alcohols and carboxylic acids were found to participate as alternatives to organometallic reagents in the cross-coupling reaction. For instance, synthesis of biaryls via palladium-catalyzed reaction of tertiary benzyl alcohols with aryl halides was reported by Miura in 2001 (Scheme 7).[28] The key step of the reaction is β-carbon elimination from palladium alkoxide generated from ligand exchange between the arylpalladium halide intermediate and the tertiary alcohol in the presence of cesium carbonate, producing diarylpalladium intermediate in situ. The reaction indicated that aryl-substituted tertiary alcohol served as arylmetal equivalent. Uemura[29] and Chow[30] reported similar transformations, using other tertiary alcohols such as cyclobutanols and propargyl alcohols, respectively.

Scheme 7.



Goossen disclosed a new synthetic strategy for the construction of biaryls by palladium/copper-co-catalyzed decarboxylative coupling of aromatic carboxylic acids with aryl halides and triflates (Scheme 8).[31] The copper phenanthroline complex facilitated extrusion of carbon dioxide from copper carboxylate to provide arylcopper intermediate. The resulting arylcopper underwent transmetalation with arylpalladium halide to furnish biarylpalladium, en route to unsymmetrical biaryl.

Scheme 8.

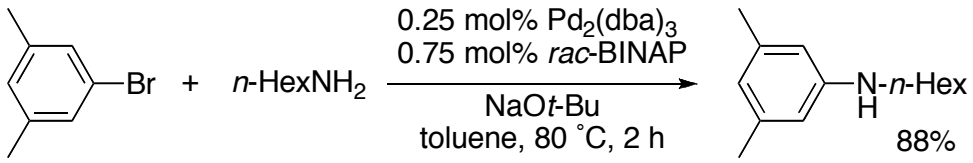


1.2 Palladium-Catalyzed Cross-Coupling Reaction Forming Carbon-Nitrogen and Carbon-Oxygen Bond

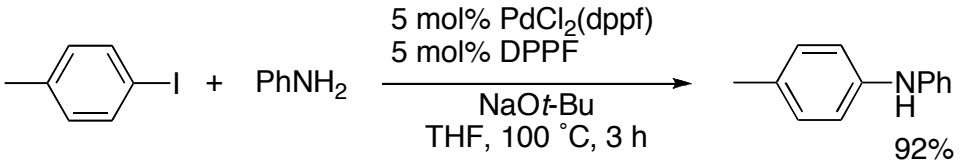
Palladium-catalyzed cross-coupling amination which provides a rapid access to substituted amines has been developed in the past twenty years. The first amination reaction of aryl bromides was stimulated by Kosugi and Migita using tin amides in the presence of a catalytic amount of $[P(o\text{-tol})_3]_2PdCl_2$.[32] In 1995, practical methods for the amination reaction using amines as coupling partners were independently reported by Buchwald[33a] and Hartwig.[33b] They indicated that aromatic bisphosphines such as BINAP[34] and DPPF[35] served as suitable ligands for the amination reaction of aryl halides (Scheme 9).

Scheme 9.

Buchwald



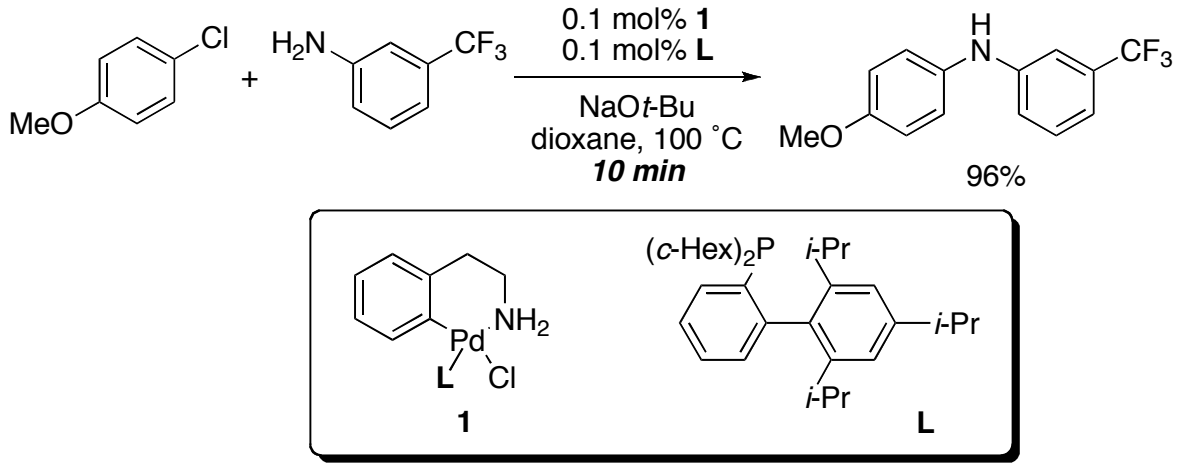
Hartwig



Nowadays, it is known that a wide range of nitrogen nucleophiles such as primary amines, secondary amines, imines, hydrazones, amides, and sulfonamides coupled with aryl halides efficiently.[36] The use of bulky and electron-rich phosphine ligands allowed unreactive aryl chlorides to participate in the cross-coupling amination reaction.[37,38] In addition, preparation of palladium(0) precatalyst ligated by only one phosphine ligand which is believed to be active species has been studied during recent years. Buchwald demonstrated that a new class of easily activated and air-stable palladium precatalysts bearing one biarylphosphine ligand catalyzed the amination reaction of aryl chloride with low catalyst loading in very short reaction times (Scheme 10).[39a] He also described a simple and practical method for the preparation of remarkably active

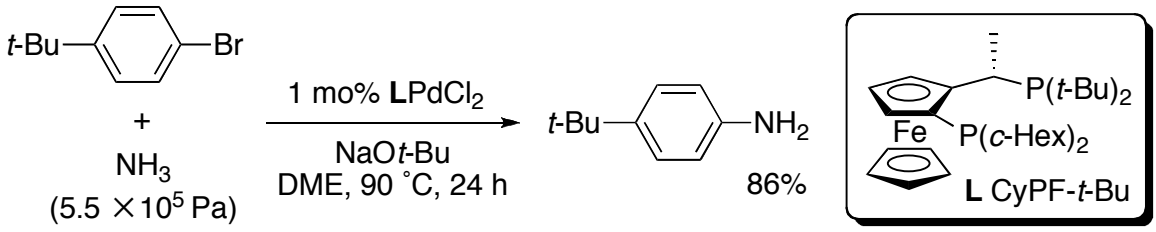
palladium(0) complex by mixing $Pd(OAc)_2$, phosphine ligand, and water.[39b]

Scheme 10.



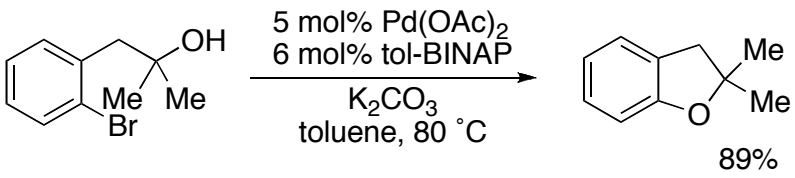
It is no wonder that ammonia is the most simple and abundant nitrogen source and the least expensive bulk chemical. However, successful examples of its use in the transition-metal-catalyzed reactions are rare due to its high coordination ability to metal center derived from the strong basicity and small size to cause deactivation of the catalyst. During the course of the development of reliable and robust catalysts for palladium-catalyzed amination reaction described above, Hartwig disclosed that ammonia underwent coupling smoothly with aryl halides to afford the corresponding anilines by the use of $PdCl_2$/CyPF-*t*-Bu catalytic system (Scheme 11).[40a] Tight coordination ability of the ligand would contribute to stabilization of the catalyst, suppressing the undesirable deactivation pathway even under high pressure of ammonia. Moreover, he devised a palladium precursor to generate highly active catalyst more easily and broadened the scope of aryl halides.[40b] Later, Buchwald[41] and Beller[42] independently reported the same reaction by the use of bulky monophosphine ligand.

Scheme 11.



Together with the studies on the carbon-nitrogen bond forming cross-coupling reaction of aryl halides, researches for carbon-oxygen bond formation to synthesize aryl ethers have been subsequently carried out. Unfortunately, etherification reaction is inferior to amination in scope and generality. The initial report for the etherification reaction was an intramolecular version to form oxygen heterocycles (Scheme 12).[43] Subsequently, the intermolecular etherification reaction using tertiary alcohols and phenols was accomplished.[44] However, the reaction of primary or secondary alcohols with unactivated aryl halides was troublesome due to the competitive β-hydride elimination from the palladium alkoxide intermediate. It is essential to use the tunable ligand for each substrate in the present catalytic system.[45] The cross-coupling etherification reaction was also applied to the reaction with hydroxide base, which provided a new method for the synthesis of phenols.[46]

Scheme 12.

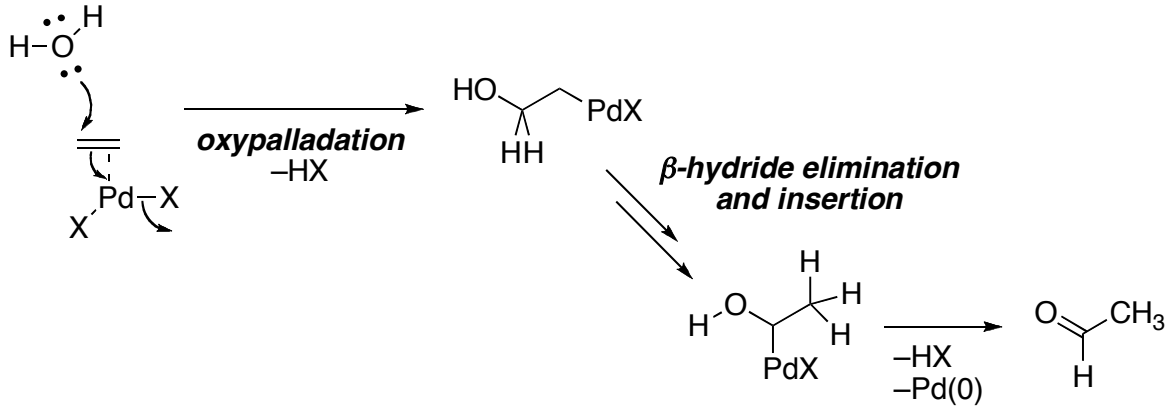


2. Palladium-Catalyzed Reactions Involving Oxy- or Aminopalladation

Among various modes of the reaction catalyzed by palladium complexes, oxypalladation of carbon-carbon unsaturated bond is one of the most useful and powerful methods for formation of carbon-oxygen bond. In particular, Wacker oxidation is a fundamental and important transformation involving the oxypalladation process, where terminal alkene is converted into

methyl ketones by addition of water (Scheme 13).

Scheme 13.



The initial stoichiometric reaction using palladium(II) salt was first reported by Phillips in 1894,[47] and Smidt then rendered the process catalytic in palladium by using copper(II) chloride under oxygen atmosphere.[48] It is noteworthy that a catalytic amount of copper is sufficient to operate the palladium-catalyzed process, since the resulting copper(I) chloride is oxidized by oxygen under air. The whole catalytic cycle is described in Scheme 14. Nowadays, the Wacker oxidation has been used extensively in not only laboratory but also industrial scale synthesis.

Scheme 14.

$[PdCl_4]^{2-} + C_2H_4 + H_2O \longrightarrow CH_3CHO + Pd(0) + 2HCl + 2Cl^-$

$Pd(0) + 2CuCl_2 + 2Cl^- \longrightarrow [PdCl_4]^{2-} + 2CuCl$

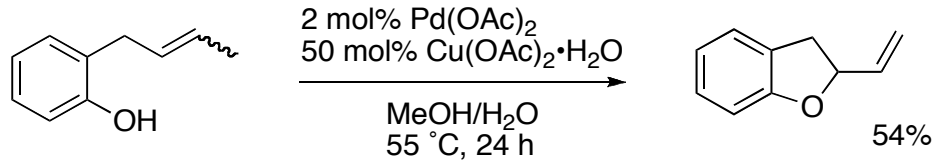
$2CuCl + 1/2O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$

Very recently, Sigman demonstrated that a novel carbene-ligated palladium complex catalyzed facile oxypalladation to afford a variety of methyl ketones under copper-free conditions using oxygen as the sole oxidant.[49] Moreover, he devised reaction conditions where hydrogen peroxide served as an oxidant with cationic palladium/quinox complex and succeeded in the synthesis of methyl ketones from conventionally challenging substrates.[50]

It is well known that oxypalladation also occurs by using other oxygen nucleophiles such as

alcohols and carboxylic acids to yield ethers and esters, respectively.[51] Especially, reactions promoted by intramolecular oxypalladation provide convenient ways to construct oxygen-containing heterocycles. In 1973, Hosokawa reported stoichiometric intramolecular oxypalladation reaction, in which sodium 2-allylphenoxide was transformed to 2-methylbenzofuran, and subsequently disclosed its catalytic version (Scheme 15).[52] Thus, the reaction including intramolecular oxypalladation and subsequent β-hydride elimination is widely applicable to substrates bearing hydroxy, carboxy, and aminohydroxy groups.[53] The use of asymmetric ligand such as bisoxazoline ligand, boxax (also see Scheme 18), made the reaction asymmetric.[54]

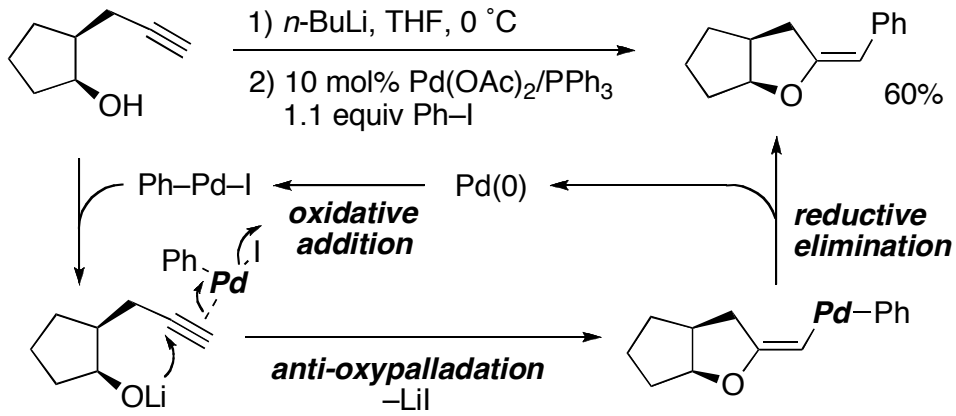
Scheme 15.



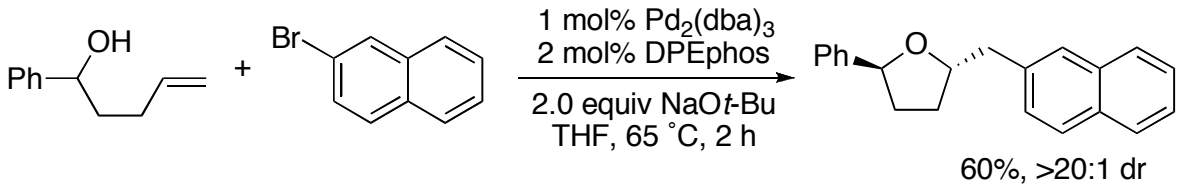
As one can easily expect, further functionalization of alkenes is also possible by trapping alkylpalladium intermediate generated from oxypalladation of alkene, leading to prepare complex heterocycles from relatively simple starting materials. In 1992, Luo developed a novel reaction of *cis*-2-propargylcyclopentanol with aryl iodides, where both C–O and C–C bond were formed in a single operation (Scheme 16).[55] Unlike the reactions conducted under oxidative conditions as shown in Scheme 14 and 15, the present transformation was accomplished under basic conditions in the absence of an oxidant. Based on the stereochemistry of the product, Luo assumed the reaction mechamism as follows: i) the oxidative addition of aryl iodide to zerovalent palladium to generate arylpalladium iodide, ii) coordination of the alkyne moiety of alkoxide to arylpalladium intermediate, iii) the intramolecular attack of alkoxide to alkyne activated by palladium(II), that is, *anti*-oxypalladation to give β-alkoxyalkyl(aryl)palladium, iv) reductive elimination from the palladium intermediate. Since then, there have been many reports for arylative cyclization reaction of alkynes having various pendant oxygen nucleophiles.[56] On the

other hand, the arylative cyclization reaction of alkenol was regarded to be difficult because it would suffer from a competitive Mizoroki-Heck reaction.[57] However, Wolfe overcame such a problem and succeeded in the arylative cyclization reaction of bishomoallyl alcohols with aryl halides to form multisubstituted tetrahydrofurans (Scheme 17).[58]

Scheme 16.



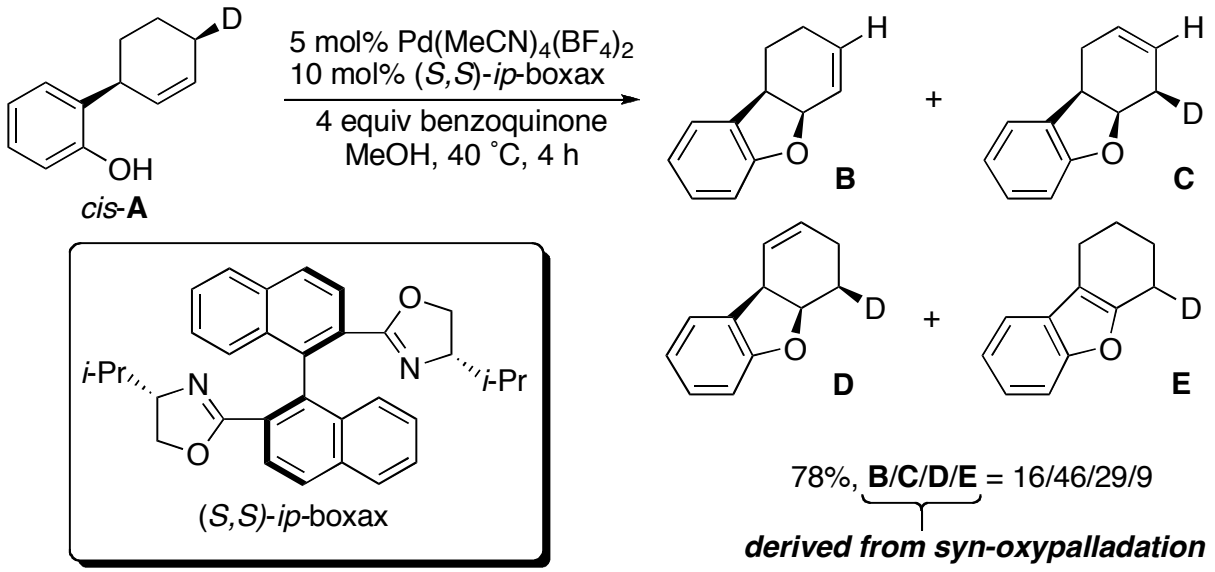
Scheme 17.



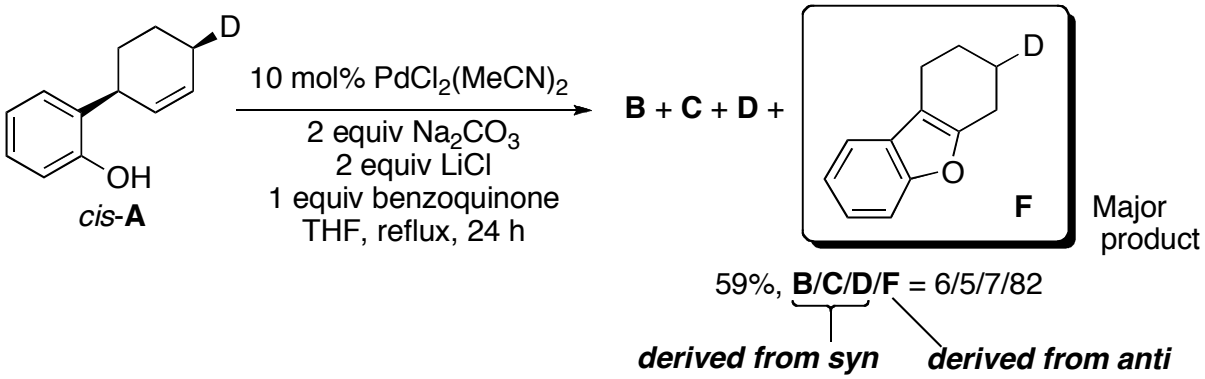
Along with the development of many transformations using oxypalladation, the stereochemistry of oxypalladation has been well investigated for a long time. In early studies by Bäckvall, Stille, and Kurosawa, the oxypalladation step was considered to proceed via an *anti* fashion, that is, alkene would coordinate to electrophilic palladium followed by the attack of oxygen atom to alkene from the backside of the alkene.[59] Thus, the stereochemistry of oxypalladation was generally believed to be *anti*. On the other hand, in 1990s, Henry and others reported that the stereochemistry of oxypalladation would be affected by the concentration of the chloride ion.[60] Although Henry et al. devised several reaction systems including oxypalladation reaction, the stereochemistry of these reactions was still ambiguous.

In 2004, Hayashi eventually confirmed the stereochemistry in the Wacker-type cyclization by conducting experiments with deuterium-labeled allylphenols.[61] The complete consumption of starting material was observed in the reaction, and all of the products were likely produced through oxypalladation/β-hydride elimination, or further reinsertion-elimination sequence of palladium hydride species, which gave olefin isomerization products. Hayashi elucidated that the oxypalladation proceeded through a *syn* fashion in the absence of chloride ion, while the stereochemistry became mainly *anti* in the presence of chloride ion (Scheme 18 and 19).

Scheme 18.

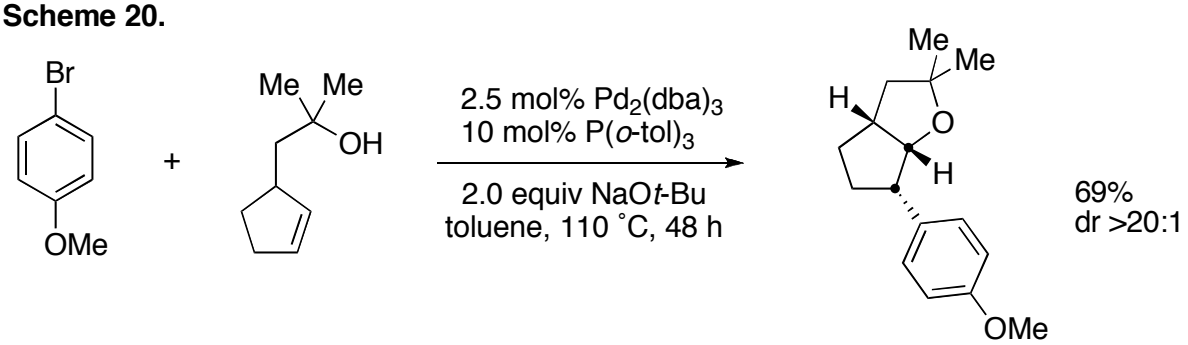


Scheme 19.



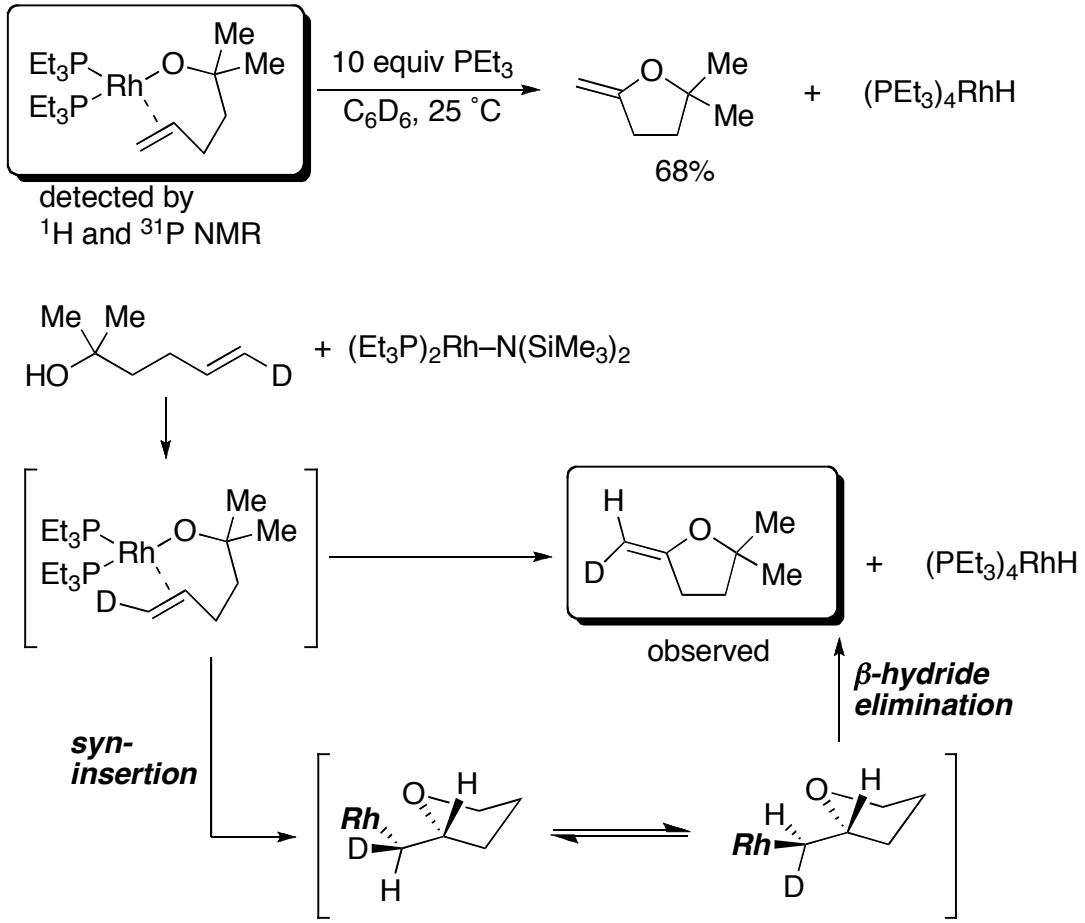
Around the same time, Stoltz reported that the cyclization reaction of primary alkenol under oxidative conditions proceeded via a *syn* fashion, except for the substrate bearing a carboxy group, which would undergo oxypalladation via an *anti* fashion albeit in low yield.[62] In the case of the arylative cyclization reaction of δ-alkenol reported by Wolfe, a *syn*-oxypalladation pathway was strongly supported by the stereochemical analysis of the product prepared from the reaction with an internal cyclic alkenol (Scheme 20).[63]

Scheme 20.



Most recently, Hartwig gave deep mechanistic insights of the insertion step by using a rhodium alkoxide complex bearing a tethered olefin moiety. He observed that the prepared rhodium alkoxide complex was converted to a tetrahydrofuran derivative and a rhodium hydride complex by addition of excess of ligands (Scheme 21).[64] This is the first observation of olefin-ligated late transition metal alkoxo complex and the olefin insertion into metal-alkoxide bond. The result of the deuterium-labeling experiment is strongly suggestive of *syn*-insertion pathway, which is similar to that of Wolfe's palladium-catalyzed cyclization reaction of δ-alkenol.[58,63]

Scheme 21.

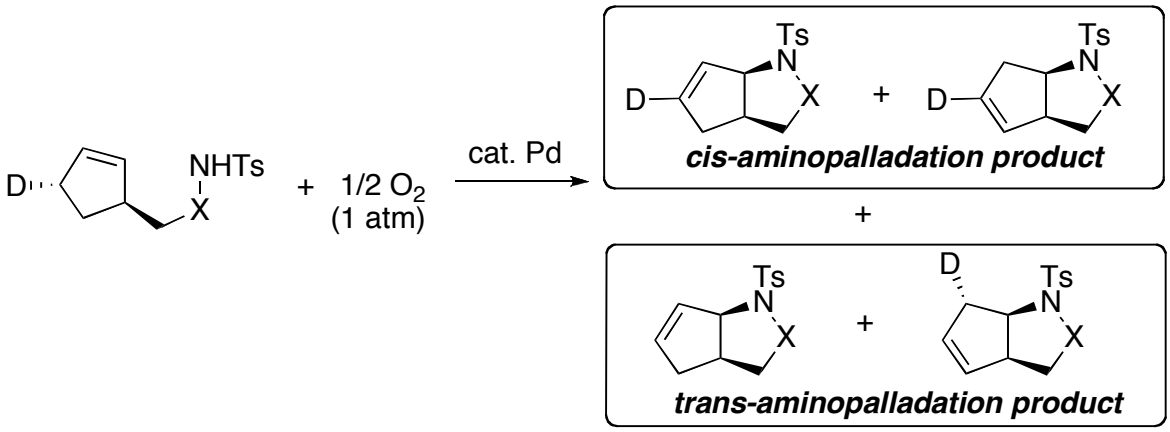


Similar development has been made in aminopalladation chemistry, especially for intramolecular versions. In the reaction involving aminopalladation and dehydropalladation steps, nitrogen nucleophiles such as anilines,[65] amides,[66] sulfonamides,[67] and carbamates[68] are mainly used. However, aliphatic amines are not suitable substrates for the aminopalladation reaction, since their high coordination ability to palladium center is prone to deactivate the palladium catalyst. On the other hand, aminopalladation/cross-coupling reaction of aryl halides with alkynylamines[69] or alkenylamines[70] was well investigated mainly by Cacchi or Wolfe, respectively.

The stereochemistry of aminopalladation was also probed. Stahl found that alkenes bearing a sulfonamide moiety readily cyclized through a *syn* fashion in the presence of various palladium catalysts under oxygen atmosphere (Scheme 22).[71] Although an *anti* adduct was observed

simultaneously when $Pd(IMes)(O_2CCF_3)_2$ was used as a catalyst, the addition of a base such as Na_2CO_3 completely suppressed the formation of the *anti* adduct. He also noted that *anti*-aminopalladation was favorable when the substrate has an acidic proton on nitrogen. Thus, the stereochemistry of aminopalladation reaction would be strongly affected by starting materials and reaction conditions.

Scheme 22.



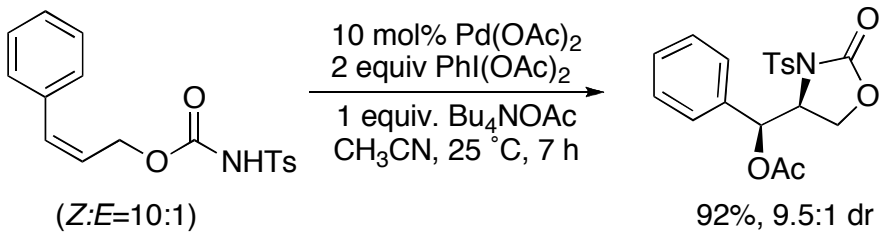
X	Pd catalysts	product ratio cis : trans
CH_2	$Pd(OAc)_2$/DMSO (**cat. A**)	100 : 0
CH_2	$Pd(IMes)(O_2CCF_3)_2$/PhCOOH (**cat. B**)	51 : 49
CH_2	$Pd(IMes)(O_2CCF_3)_2/Na_2CO_3$ (**cat. C**)	100 : 0
C=O	**cat. A**	0 : 100
C=O	**cat. B**	54 : 46
C=O	**cat. C**	67 : 33

In the case of intramolecular aminopalladation/arylation reaction of alkynes and alkenes described above, the stereochemistry of aminopalladation of alkynes was exclusively *anti*,[69] whereas that of alkenes was found to be *syn*.[70,72]

As mentioned above, the alkylpalladium(II) intermediate generated from oxypalladation or aminopalladation is prone to undergo β-hydride elimination under oxidative conditions. Recently, further transformations of the alkylpalldaium(II) intermediate were accomplished by oxidizing a palladium(II) intermediate to palladium(IV) species, from which reductive elimination or substitution reaction took place much faster than β-hydride elimination to yield

alkene difunctionalization product.[73] Sorensen reported palladium-catalyzed ring forming aminoacetoxylation reaction of alkenes in the presence of $PhI(OAc)_2$ as a oxidant (Scheme 23).[74] He mentioned that the use of $Cu(OAc)_2$, a standard oxidant for Pd(0)/Pd(II) redox cycle, instead of $PhI(OAc)_2$ was ineffective for the transformation.

Scheme 23.



3. Overview of This Thesis

The author focused on the potential ability of palladium complexes in organic synthesis. She found some new reactions of sterically demanding unsaturated alcohols with aryl and alkenyl halides under palladium catalysis. In Chapters 1 and 2, palladium-catalyzed regio- and stereospecific allylation of aryl halides with bulky homoallyl alcohols via retro-allylation is described. In Chapter 3, synthesis of arylallenes by palladium-catalyzed reactions of aryl halides with tertiary homopropargyl alcohols via retro-propargylation which is analogous to retro-allylation is presented. In Chapters 4 and 5, unexpected cyclization reaction to form three-membered heterocycles by palladium-catalyzed reactions of tertiary allyl alcohols or amines with aryl or alkenyl halides is disclosed. The overview of this thesis is described below.

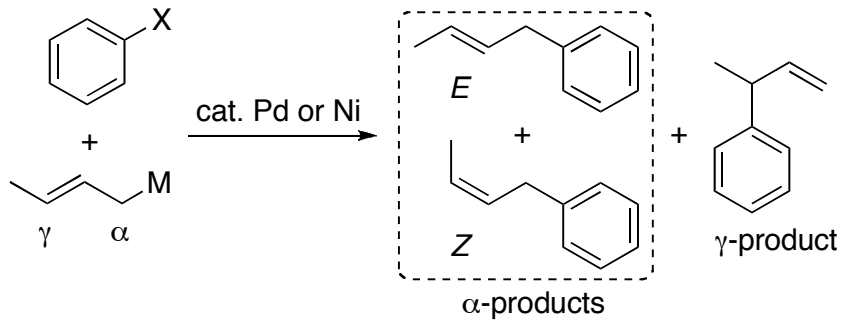
3.1. Palladium-Catalyzed Regio- and Stereospecific Allylation Reactions via Retro-Allylation (Chapters 1, 2, and 3)

Palladium- or nickel-catalyzed cross-coupling reactions of organic halides with organometallic reagents are among the most important discoveries in the late twentieth century and have been significantly advancing the strength and sophistication of organic synthesis as described in Section 1.1. Nowadays, the cross-coupling strategy seems to be able to construct any

carbon-carbon bonds as one likes. However, despite their seeming simplicity and apparent usefulness, the cross-coupling reactions of aryl halides with allylmetals are rarely reported and difficult to achieve.[75–79] The combination often suffers from low reaction efficiency and unsatisfactory chemo-, regio-, and stereoselectivities. The importance of allylation reaction in organic synthesis clearly demands further studies on rare cross-coupling reactions to establish the universality of cross-coupling reactions.

To this end, the most important issue is the regio- and stereochemical control of the allylation when substituted allylmetals such as crotylmetals are employed.[76b,76e–i,77,78e–g,79] As exemplified in Scheme 24, a bond-forming event in the cross-coupling reaction with a crotylmetal reagent can take place competitively at the α- and γ-positions of the crotyl group. Furthermore, the α-product is usually comprised of *E* and *Z* isomers. Hence, high degrees of regio- and stereochemical control must be established to utilize such reactions in modern organic synthesis.

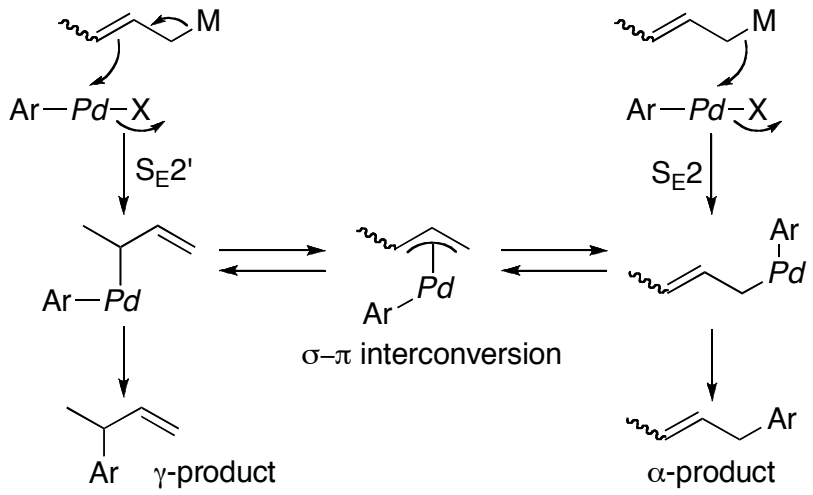
Scheme 24.



Hatanaka and Hiyama developed regioselective cross-coupling reactions of aryl halides with substituted allylfluorosilanes.[77] They used monodentate triphenylphosphine and bidentate 1,3-bis(diphenylphosphino)propane for the synthesis of γ-[77a] and α-products,[77c] respectively. However, the reactions required heating in sealed tubes and the use of difficult-to-handle allylfluorosilanes and failed to universally control the stereoselectivity of the α-products. Tributylcrotylstannane reacted with 1-iodonaphthalene regioselectively to yield the corresponding (*E*)-α- and γ-products by using triphenylarsine and triphenylphosphine,

respectively.[76e] Unfortunately, the generality and efficiency of the tin-based reaction are unsatisfactory, and one cannot obtain (*Z*)-α-product. Very recently, perfectly γ-selective cross-coupling reactions with potassium (*E*)-crotyltrifluoroborate, including enantioselective ones, were reported, wherein no α-selectivity was attained.[78e–g]

Scheme 25.

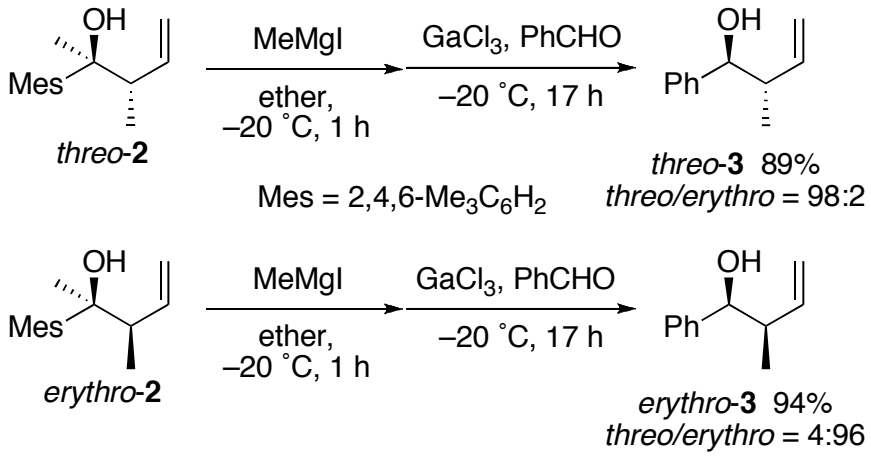


The exclusive γ-selectivity observed in the reactions of crotyltrifluoroborate was explained as follows (Scheme 25).[78g] The transmetalation between the crotylboron and arylpalladium halide proceeds in an S_E2' mode. Aryl(1-methyl-2-propenyl)palladium, a σ-allylpalladium formed by the transmetalation, then undergoes rapid reductive elimination of 1-methyl-2-propenylarene prior to σ-π interconversion. However, the ideal path is not general. Preparation of allylmetals having an arbitrary substitution pattern is usually difficult. Moreover, there remains a moderate possibility that an S_E2 transmetalation may operate. Slow reductive elimination from σ-allyl(aryl)palladium intermediates gives rise to σ-π interconversion with the loss of the initial regio- and stereochemical information of σ-allylmetals. Thus, the innovative and reliable method for the cross-coupling reactions of aryl halides with allylmetals is strongly desired.

In 2005, the author found gallium-mediated stereospecific allyl transfer from bulky homoallyl alcohols to aldehydes.[80] By the action of gallium trichloride, homoallyl alcohols *threo*- and

erythro-**2**, bearing bulky mesityl and small methyl groups at the oxygenated carbon, transferred the allyl moiety stereospecifically to benzaldehyde to afford *threo*- and *erythro*-**3**, respectively (Scheme 26). The stereospecifity of the reaction would be explained as follows: First, retro-allylation[81–84] would proceed via configurationally regulated six-membered cyclic transition state, which is the exactly reverse reaction of the allylation reaction of ketones with crotylmetals such as crotylboron and crotyltitanium. The resulting crotylgallium reagents should immediately react with benzaldehyde to furnish the corresponding secondary alcohols with perfect diastereoselectivity. These results clearly suggest that the stereoselective generation of crotylgallium reagents, which is very difficult via the conventional routes such as transmetalation and Barvier/Grignard methods, would be possible by taking advantage of the retro-allylation strategy.

Scheme 26.

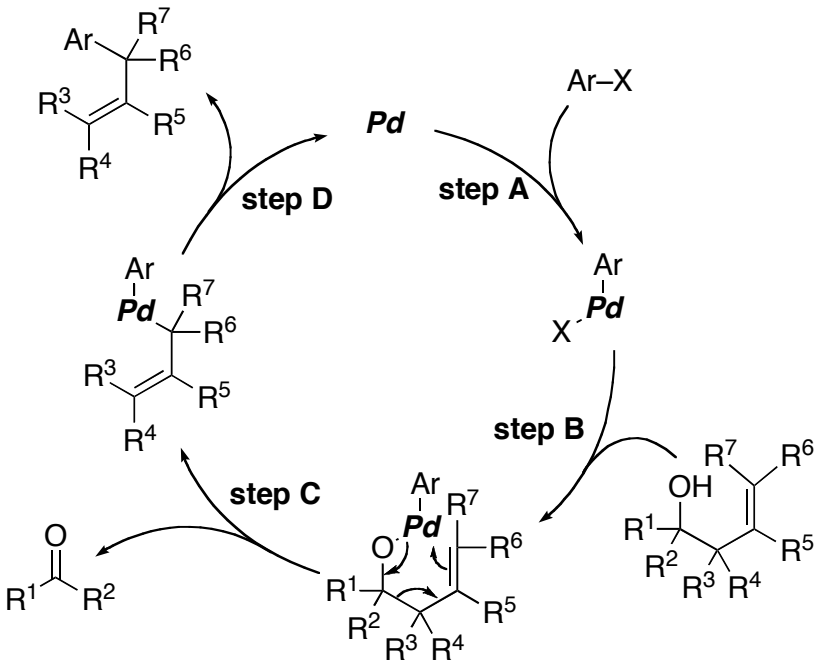


On the other hand, several precedent reports for palladium-catalyzed cross-coupling reaction where tertiary alcohols served as organometallic reagents encouraged the author to develop a new method for palldium-catalyzed allylation of aryl halides by using homoallyl alcohols as allylmetal equivalents.[28–30]

3.1.1. Palladium-Catalyzed Regio- and Stereospecific Allylation Reaction of Aryl Halides with Homoallyl Alcohols via Retro-Allylation (Chapter 1)

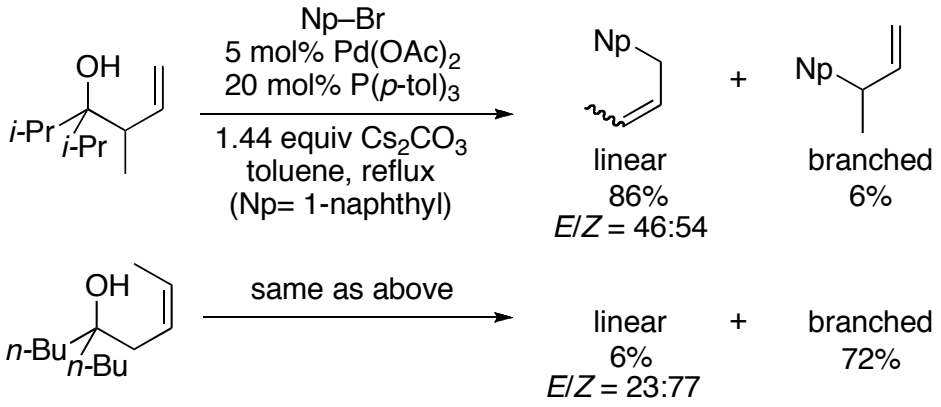
In Chapter 1, the author describes the palladium-catalyzed cross-coupling allylation reactions of aryl halides with tertiary homoallyl alcohols based on the concept of 'selective preparation of σ-allylmetals via retro-allylation'. The working hypothesis is depicted in Scheme 27: After oxidative addition of aryl halide to zelovalent palladium (**step A**), ligand exchange between arylpalladium halide and homoallyl alcohol in the presence of a base would occur to generate arylpalladium alkoxide (**step B**). A retro-allylation then takes place via a six-membered cyclic transition state to afford σ-allylpalladium intermediate along with extrusion of a ketone (**step C**). Given that subsequent reductive elimination (**step D**) is much faster than isomerization to π-allylpalladium, the regio- and stereochemical information of the starting homoallyl alcohol would be completely transferred to the allylated product.

Scheme 27.



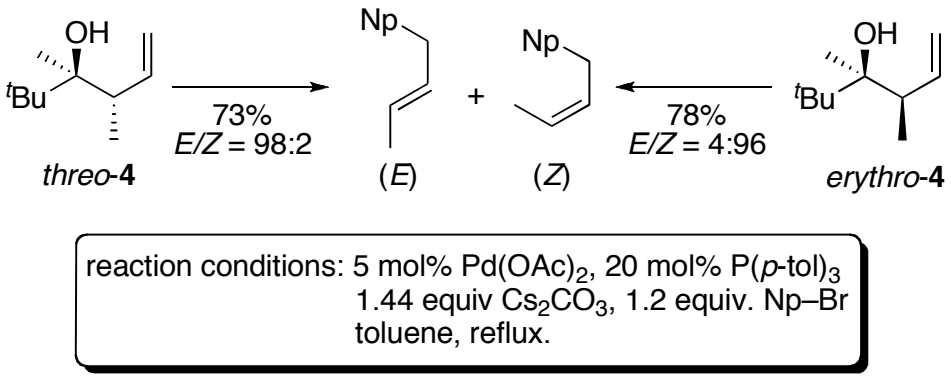
Treatment of homoallyl alcohol bearing a methyl group at the allylic position with 1-bromonaphthalene in the presence of cesium carbonate under palladium catalysis in boiled toluene provided the linear product regioselectively. On the other hand, the reaction of homoallyl alcohol having a methyl group at the olefin terminus gave the branched product exclusively (Scheme 28).

Scheme 28.



The stereospecific allylation reaction was then conducted. Starting from *threo*- or *erythro*-**4**, 1-crotylnaphthalene was obtained, the stereochemistry of which was *E* and *Z*, respectively (Scheme 29). The experimental results were consistent with her hypothesis.

Scheme 29.

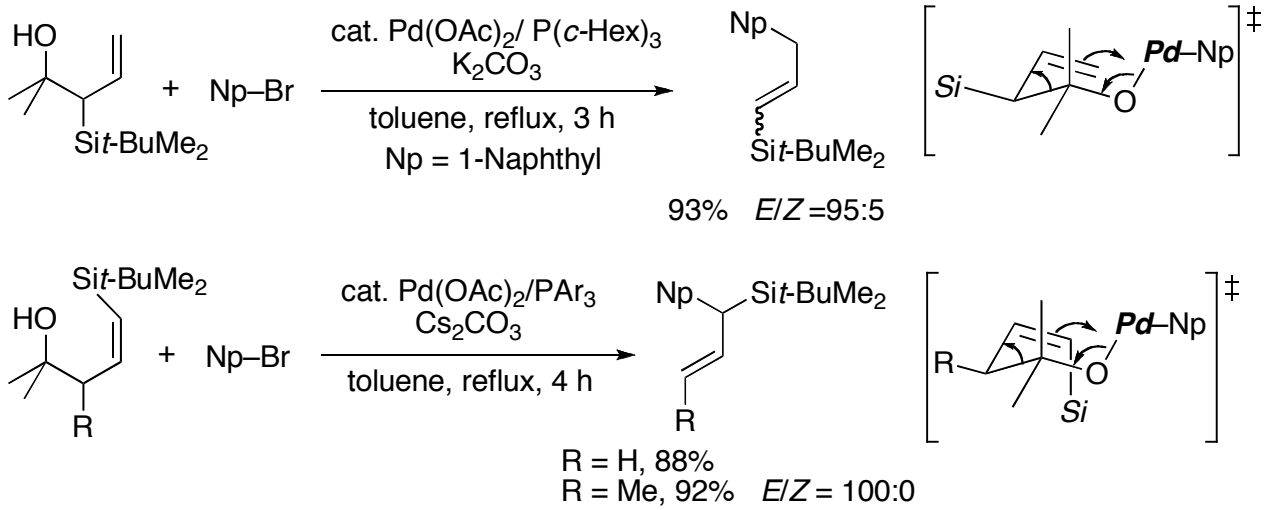


3.1.2. Synthesis of (Arylalkenyl)silanes by Palladium-Catalyzed Regiospecific and Stereoselective Allyl Transfer from Silyl-Substituted Homoallyl Alcohols to Aryl Halides (Chapter 2)

The studies for palladium-catalyzed allylation reaction via retro-allylation in Chapter 1 shed light on the usefulness of homoallyl alcohols as allylmetal equivalents. It is noteworthy that the homoallyl alcohols are stable to air and moisture, and able to be handled without special care. Therefore, the synthesis of more complex homoallyl alcohols seems to be relatively easy, leading to prepare highly functionalized allylmetal equivalents which is difficult to achieve by other methods.

In Chapter 2, the author presents synthesis of aryl(alkenyl)silanes by palladium-catalyzed retro-allylation reactions of silyl-substituted homoallyl alcohols with aryl halides. The reaction proceeded in regio- and stereospecific manner as expected, and various aryl halides enabled to take part in the allylation reaction (Scheme 30).

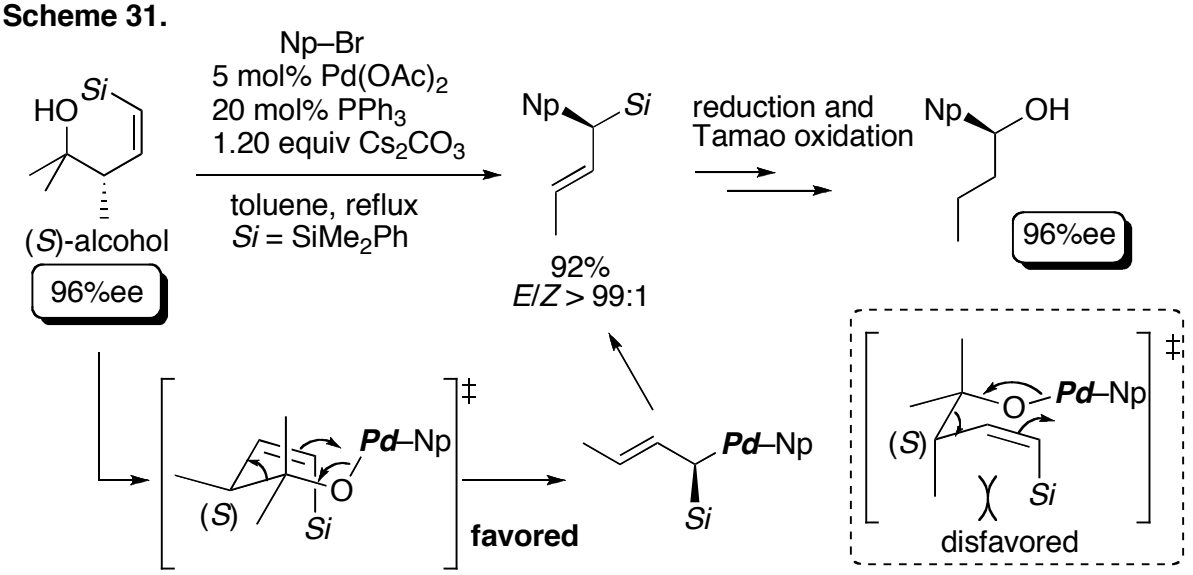
Scheme 30.



The stereochemistry of the product indicated that the reaction would proceed via the most stable six-membered cyclic chair-like transition state in which the allylic substituent of the palladium alkoxide is located at the equatorial position. Encouraged by the result, the author performed asymmetric transfer reaction by using an enantiomerically-pure homoallyl alcohol

bearing a stereogenic center at the allylic position, and succeeded in transfer of the chirality to the product, α-arylcrotylsilane, without loss of enantiomeric excess (Scheme 31).

Scheme 31.

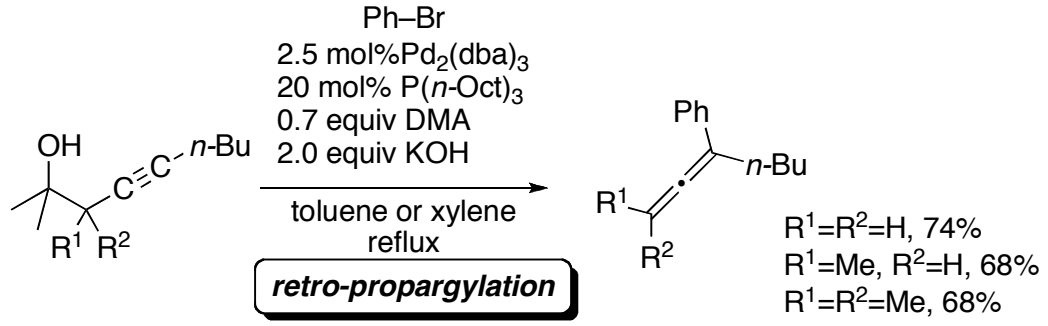


3.1.3. Synthesis of Arylallenes by Palladium-Catalyzed Retro-Propargylation of Homopropargyl Alcohols (Chapter 3)

As a wide range of homoallyl alcohols bearing substituents at the allyl moiety became applicable to the regio- and stereoselective allylation reaction with aryl halides, the author expected the retro-allylation chemistry would be extended to retro-propargylation. Homopropargyl alcohols instead of homoallyl alcohols should be subjected to palladium-catalyzed cross-coupling reaction as allenylmetal equivalents via retro-propargylation.

In Chapter 3, the author reports synthesis of arylallenes by palladium-catalyzed reaction of homopropargyl alcohols with aryl halides. After a series of reaction optimization, *gem*-di-, tri- and tetrasubstituted arylallenes were successfully obtained regioselectively in moderate to good yield from relatively simple homopropargyl alcohols (Scheme 32).

Scheme 32.



3.2. Synthesis of Three-Membered Rings by Palladium-Catalyzed Reactions of Aryl or Alkenyl Halides with Allylic Alcohols or Amines (Chapters 4 and 5)

Palladium-catalyzed intramolecular carboetherification or carboamination reaction of alkenes with organic halides emerged as an attractive method to construct heterocycles, forming both carbon-heteroatom and carbon-carbon bonds in a single operation as described in Section 2. A number of five-membered heterocycles have been synthesized by the methodology. Meanwhile, the preparation of strained three-membered heterocycles has remained a challenge. The author overcame such limitation and opened the door to construct three-membered heterocycles such as epoxides and aziridines.

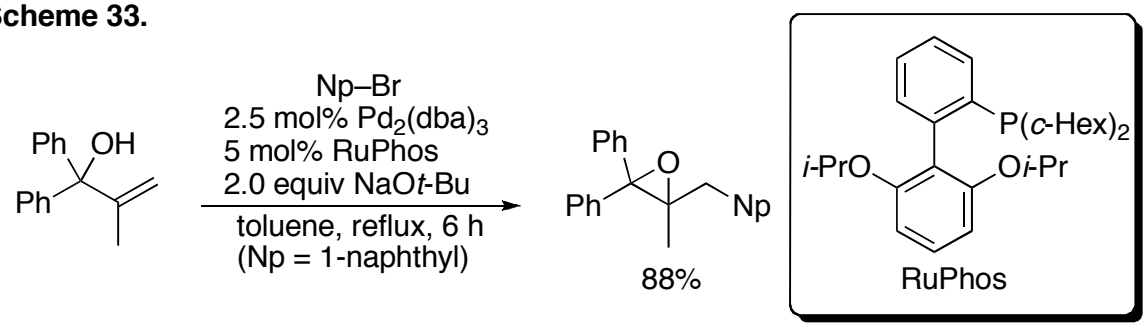
3.2.1. Synthesis of Epoxides by Palladium-Catalyzed Reaction of Tertiary Allyl Alcohols with Aryl and Alkenyl Halides (Chapter 4)

Epoxides are among the most synthetically useful intermediates and are found in many natural products and biologically active compounds. Numerous methods for the preparation of epoxides have been reported so far. However, novel synthetic methods for the construction of epoxides have been still required because of their synthetic importance in organic chemistry.

During the course of her investigation on palladium-catalyzed reactions of unsaturated alcohols with aryl halides, the author serendipitously found that carboetherification/arylation reaction is applicable for the reaction of tertiary allyl alcohols with aryl halides, which provides a new

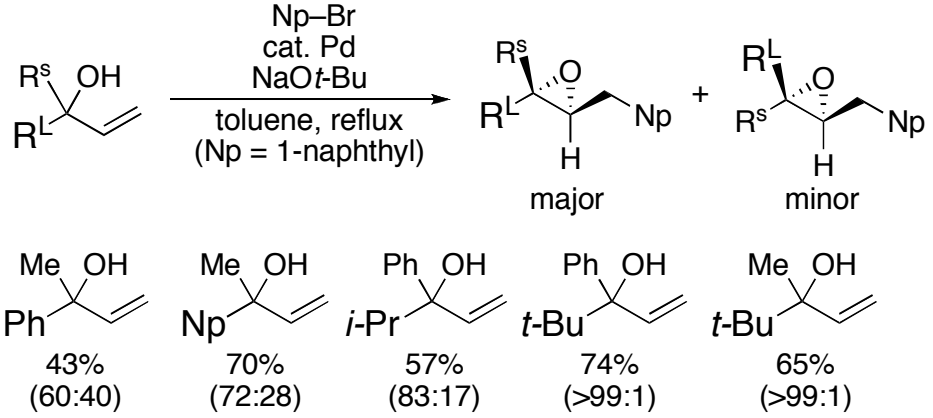
synthetic strategy for preparation of epoxides (Scheme 33). In the epoxidation reaction, the choice of ligand is quite important. Only the use of biarylphosphine ligands such as RuPhos or Xantphos was effective for the epoxidation reaction. Otherwise, a competitive Mizoroki-Heck reaction predominated or exclusively proceeded under the reaction conditions.

Scheme 33.



The reaction of tertiary allyl alcohols having a stereogenic center at the oxygenated carbon was also examined. Interestingly, both yield and diastereoselectivity became better as substituents at the stereogenic carbon became larger (Scheme 34).

Scheme 34.

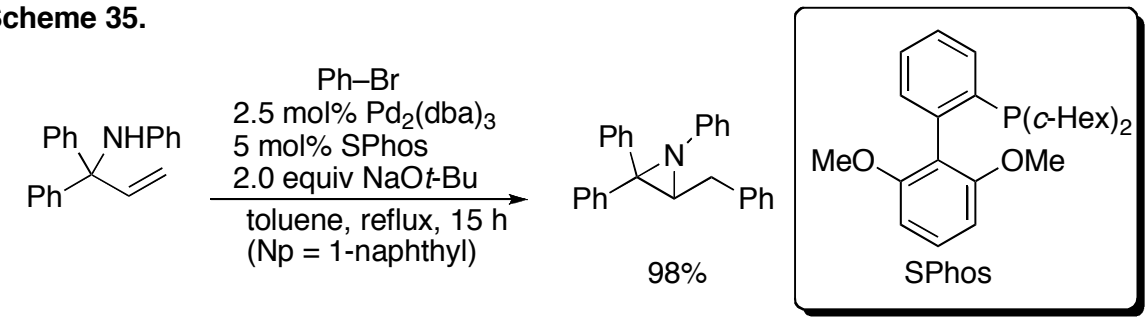


3.2.2. Synthesis of Aziridines by Palladium-Catalyzed Reaction of Allylamines with Aryl and Alkenyl Halides : Evidence of a *syn*-Carboamination Pathway (Chapter 5)

Taking into consideration the fact that allyl alcohols undergo carboetherification reaction, the author expected that allylamines would also be able to undergo arylative cyclization reaction to

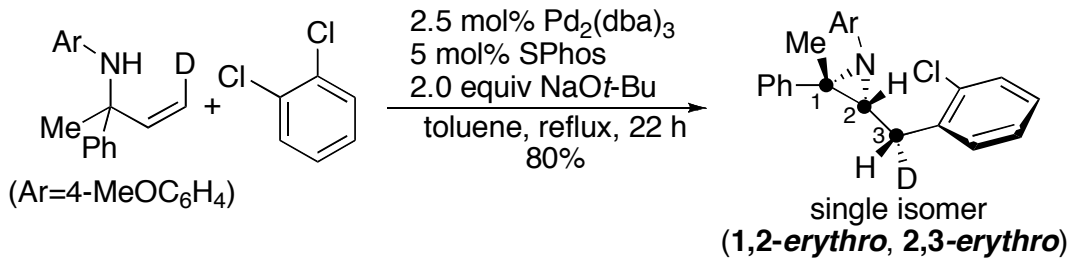
afford the corresponding aziridine. In Chapter 5, the author describes the synthesis of aziridines by palladium-catalyzed reaction of *N*-arylallylamines with aryl and alkenyl halides (Scheme 35). It should be noted that the yields of the aziridination reaction were superior to those of epoxidation reaction due to the absence of a competitive Mizoroki-Heck reaction.

Scheme 35.



Moreover, the author disclosed the evidence that the reaction would proceed through a *syn*-aminopalladation pathway by a deuterium-labeling experiment (Scheme 36).

Scheme 36.



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Chapter 1

Palladium-Catalyzed Regio- and Stereospecific Allylation Reaction of Aryl Halides with Homoallyl Alcohols via Retro-Allylation

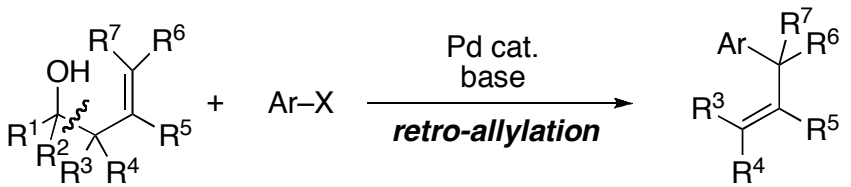
Treatment of tertiary homoallyl alcohol with aryl halide under palladium catalysis resulted in the transfer of the allyl moiety of the homoallyl alcohol to aryl halide and yielded the corresponding allylarene regio- and stereospecifically. The transfer process includes retro-allylation, which proceeds via a conformationally regulated six-membered transition state. The retro-allylation can be regarded as a method for the regio- and stereospecific preparation of σ-allylpalladium.

Introduction

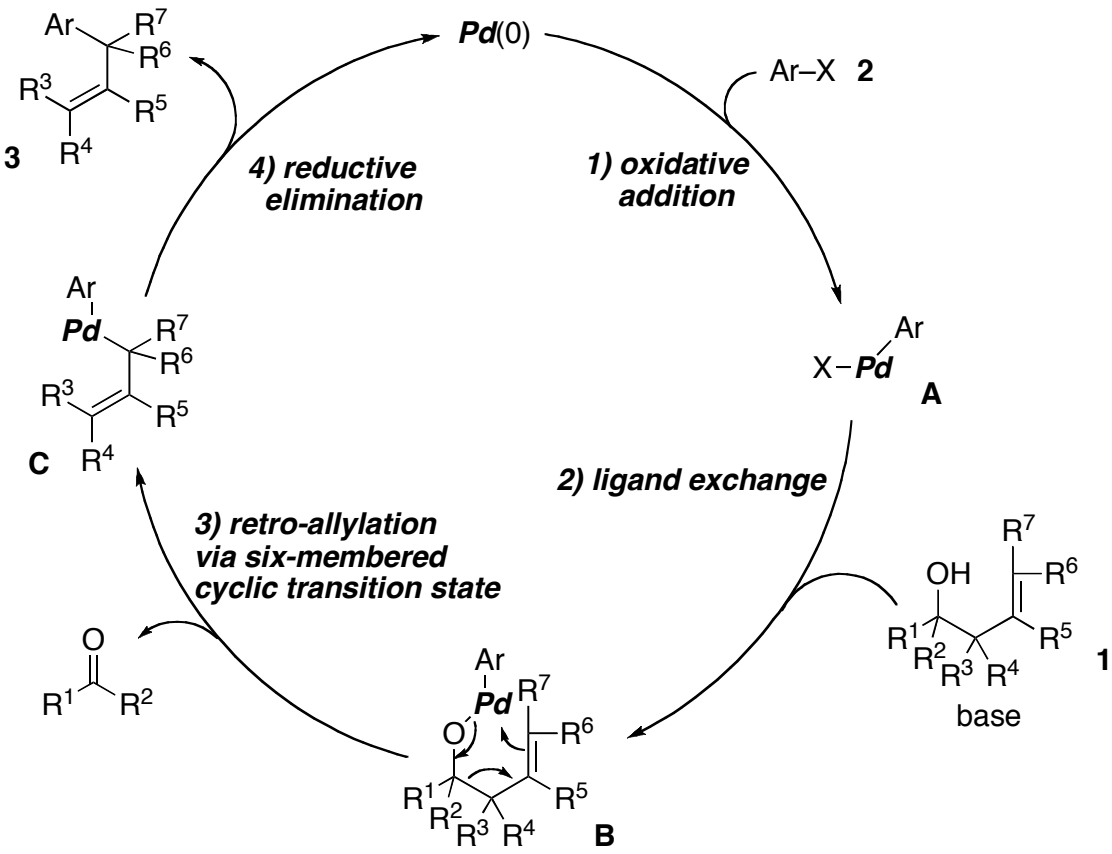
Allylation reactions are not only fundamental but also useful transformations in organic synthesis. Among them, transition metal-catalyzed cross-coupling allylation of aryl halides with allylmetal reagents ranks as one of the most attractive allylation reactions.[1] In the case of palladium catalysis, allylmetal reagents such as allylstannane and allylboron reagents serve as the allyl sources and effect transmetalation to yield allyl(aryl)palladium intermediates. The intermediate occupies the last place in the catalytic cycle of the cross-coupling allylation reaction, thereby being most responsible for the control of the regio- and stereoselectivity of the allylation reaction when a substituted allyl group is to be introduced. However, such regio- and stereoselective allylations are very difficult processes.[2,3]

In Chapter 1, the author reports a new protocol for allylation reaction of aryl halides with homoallyl alcohols as the allyl sources (Scheme 1). The working hypothesis is depicted in Scheme 2. After oxidative addition of aryl halide **2** to zerovalent palladium to generate arylpalladium halide **A**, ligand exchange between **A** and homoallyl alcohol **1** in the presence of a base occurs to afford alkoxy(aryl)palladium **B**. Then, retro-allylation[4–8] of intermediate **B**, the key step of her strategy, takes place to provide σ-allyl(aryl)palladium **C**. Finally, reductive elimination from **C** gives the allylated product **3**. Given that the retro-allylation would proceed in a concerted fashion via a conformationally regulated six-membered cyclic transition state and that the reductive elimination from **C** is faster than isomerization of **C** to π-allyl(aryl)palladium, the stereo- and regiochemical information of homoallyl alcohol **1** can be transferred to the allylated product **3**.[9]

Scheme 1.



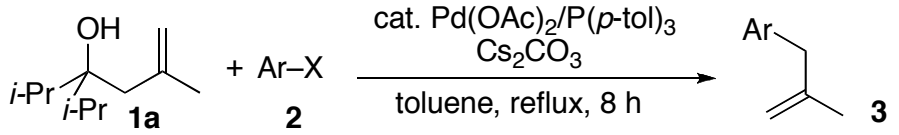
Scheme 2.

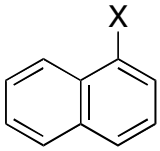
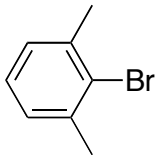
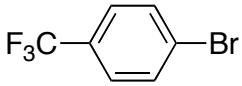
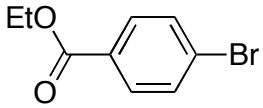
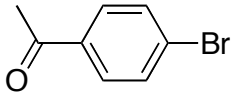
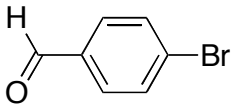
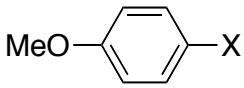


Results and Discussion

Treatment of 1-bromonaphthalene (**2a**) with homoallyl alcohol **1a** in the presence of cesium carbonate under palladium catalysis in refluxing toluene provided 1-methallylnaphthalene (**3a**) in good yield (Table 1, entry 1). Sterically demanding **2d** as well as electron deficient **2e**–**2h** underwent the methallylation reaction. The reaction of electron-rich *p*-bromoanisole (**2i**) resulted in a lower yield of coupling product **3g**. However, the use of *p*-iodoanisole (**2j**) provided a better yield of 59%. 1-Chloronaphthalene (**2b**) remained untouched under the reaction conditions (entry 2). In the reactions of aryl triflates, no significant differences in rate and yield were observed (entries 1 and 3). Although the present catalytic system provides a new access for the methallylarenes, the scope of the reaction was somewhat limited.

Table 1. $Pd(OAc)_2/P(p\text{-tol})_3$-Catalyzed Methallylation of Aryl Halides **2** with Homoallyl Alclhol **1a** via Retro-Allylation[a]

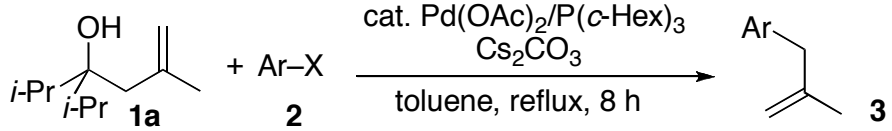


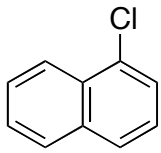
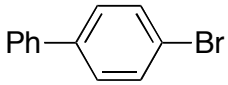
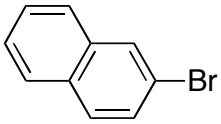
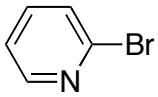
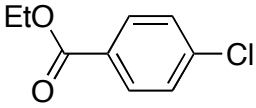
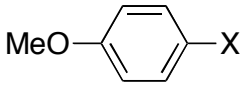
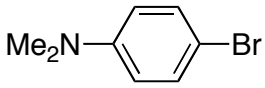
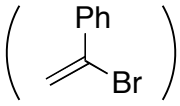
entry	Ar–X	2	3, yield (%)
1		**2a** : X=Br	**3a**, 86
2		**2b** : X=Cl	**3a**, 6
3		**2c** : X=OTf	**3a**, 87
4		**2d**	**3b**, 90
5		**2e**	**3c**, 64
6		**2f**	**3d**, 83[b]
7		**2g**	**3e**, 71[c]
8		**2h**	**3f**, 57
9		**2i** : X=Br	**3g**, 29
10		**2j** : X=I	**3g**, 59
11		**2k** : X=OTf	**3g**, 61

[a] A mixture of $Pd(OAc)_2$ (0.025 mmol), $P(p\text{-tol})_3$ (0.10 mmol), Cs_2CO_3 (0.72 mmol), **1** (0.60 mmol), and **2** (0.50 mmol) was boiled in toluene (3.0 mL) for 8 h. [b] A catalyst prepared from $Pd(OAc)_2$ (0.013 mmol) and $P(p\text{-tol})_3$ (0.050 mmol) was used. [c] A catalyst prepared from $Pd(OAc)_2$ (0.013 mmol) and PPh_3 (0.050 mmol) was used.

After additional screening of ligands, the author found that the combination of $Pd(OAc)_2$ and $P(c\text{-Hex})_3$ was the best catalyst. The reaction of **1a** with 1-chloronaphthalene (**2b**) was dramatically accelerated by using 5 mol% $Pd(OAc)_2$ and 10 mol% $P(c\text{-Hex})_3$ (Table 2, entry 1). The use of $P(c\text{-Hex})_3$ also promoted the methallylation of 4-bromobiphenyl and 2-bromonaphthalene, wherein the use of $P(p\text{-tol})_3$ failed to attain satisfactory yields (entries 2 and 3). The bulkier $P(c\text{-Hex})_3$ would increase steric hindrance around the palladium center of the alkoxy(aryl)palladium **B**, preventing the vacant coordination site that is responsible for the indispensable interaction with the double bond of **1a** from being occupied through the coordination of an additional $P(c\text{-Hex})_3$ and/or the dimerization of the palladium complex.[10] 2-Bromopyridine (**2n**) was converted to 2-methallylpyridine (**3j**) in moderate yield, the remainder being **2n** untouched (entry 4). Electron-deficient aryl chloride **2o** smoothly underwent the methallylation reaction (entry 5). Although the reaction of electron-rich *p*-bromoanisole (**2i**) with $P(p\text{-tol})_3$ resulted in a lower yield of coupling product **3g**, $P(c\text{-Hex})_3$ was the better ligand (entry 6). The reactions of electron-rich, much less reactive *p*-chloroanisole (**2p**) and *p*-bromo-*N*,*N*-dimethylaniline (**2q**) proceeded smoothly with the aid of $P(c\text{-Hex})_3$ (entries 7 and 8). Tri(*tert*-butyl)phosphine was also a highly effective ligand (entry 9). In this case, a catalyst prepared from equimolar amounts of $Pd(OAc)_2$ and $P(t\text{-Bu})_3$ was essential to attain high catalytic activity; otherwise the yields were poor (entry 10). Thus electron-rich trialkylphosphines have significantly expanded the scope of organic halides. Attempted methallylations of alkenyl halides resulted in poor to fair yields. The highest yield was observed when α-bromostyrene (**2r**) reacted with the aid of (*R*)-MONOPHOS ligand (entry 11). Tricyclohexylphosphine did not work well in the reaction of **2r** (entry 12).

Table 2. $Pd(OAc)_2/P(c\text{-Hex})_3$-Catalyzed Methallylation of Aryl Halides **2** with Homoallyl Alcohol **1a** via Retro-Allylation[a]

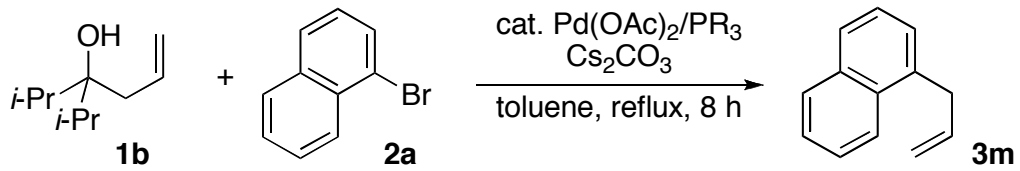


entry	Ar–X	2	3, yield[b] (%)
1		**2b**	**3a**, 79[c](6)
2		**2l**	**3h**, 83 (34)
3		**2m**	**3i**, 86 (<30)
4		**2n**	**3j**, 56
5		**2o**	**3d**, 79
6		**2i** : X=Br	**3g**, 67 (29)
7		**2p** : X=Cl	**3g**, 70
8		**2q**	**3k**, 80
9		**2q**	**3k**, 57[d]
10		**2q**	**3k**, 12[e]
11		**2r**	**3l**, 45[f,g]
12		**2r**	**3l**, 5

[a] A mixture of $Pd(OAc)_2$ (0.025 mmol), $P(c\text{-Hex})_3$ (0.050 mmol), Cs_2CO_3 (0.72 mmol), **1a** (0.60 mmol), and **2** (0.50 mmol) was boiled in toluene (3.0 mL). [b] Isolated yields. Yields in the reaction under $Pd(OAc)_2/P(p\text{-tol})_3$ catalysis are in parentheses. [c] As a byproduct, 2-methallylnaphthalene was obtained in 8% yield. [d] $P(t\text{-Bu})_3$ (0.025 mmol) was used. [e] $P(t\text{-Bu})_3$ (0.050 mmol) was used.74% of **2q** was recovered. [f] (*R*)-MONOPHOS, a monodentate phosphoramidite ligand, [(*R*)-(binaphthoxy)]$PNMe_2$ (0.050 mmol) was used. [g] Alcohol **1a** (1.0 mmol) and Cs_2CO_3 (1.2 mmol) were used.

Homoallyl alcohol **1b** effected allylation of **2a** to yield 1-allylnaphthalene (**3m**) in excellent yield (Scheme 3). The reaction of **1b** implies the generality of the allyl transfer reaction in $Pd(OAc)_2/PR_3$ system. Both P(*p*-tol)$_3$ and P(*c*-Hex)$_3$ served as suitable ligands for the allylation reaction, so all of the allyl transfer reactions described below were conducted with comparing the efficiency of these two ligands.

Scheme 3.



5 mol% $Pd(OAc)_2$/ 20 mol% P(*p*-tol)$_3$ (conditions A) 89%
5 mol% $Pd(OAc)_2$/ 10 mol% P(*c*-Hex)$_3$ (conditions B) 83%

To justify her idea depicted in Scheme 2, she subsequently prepared a variety of homoallyl alcohols having unsymmetrically substituted allyl moieties that are to be transferred. As Table 3 clearly shows, the reactions with the homoallyl alcohols indeed proceeded with high regiospecificity. In the reaction of **1c** (entries 1 and 2), the carbon-carbon bond formation took place at the terminal olefinic carbon of **1c** to provide trisubstituted alkene **3n** exclusively. The corresponding regioisomer **3o** was hardly detected. Notably the **3n**/**3o** selectivity obtained by using P(*c*-Hex)$_3$ was much better than that obtained by using P(*p*-tol)$_3$. By changing P(*p*-tol)$_3$ to P(*c*-Hex)$_3$, increasing the steric bulk around the palladium would accelerate the rate of the reductive elimination,[10] thereby avoiding undesirable isomerization of the initially formed σ-allylpalladium. The formation of linear coupling product **3p** predominated over that of branched **3q** in the reaction of **1d** (entries 3 and 4). In contrast, the use of **1e** led to the opposite regioselectivity (entries 5 and 6). The regiospecificity is highly suggestive of the retro-allylation of **B** followed by rapid reductive elimination (Scheme 2). In addition, the yield of **3q** diminished when P(*c*-Hex)$_3$ was used as a ligand. In contrast to the reaction with homoallyl alcohols bearing no substituents at olefin terminus, the reaction with **1e** having a methyl group at

the *cis* position was significantly affected by the steric hindrance at palladium complexes. The bulkier palladium complex ligated by P(*c*-Hex)$_3$ would have difficulty in approaching an internal alkene to undergo retro-allylation.

It is worth noting that alcohol **1f**, the stereoisomer of **1e**, resisted the transformation under either palladium catalysis (entries 7 and 8). The methyl substituent located at the *trans* position to the hydroxylated moiety would retard the reaction. The author is tempted to assume that, on the transition state of the retro-allylation reaction, the methyl group and one of the ligands on the palladium of square planar geometry would create so strong repulsion that the palladium could not approach the carbon–carbon double bond (Scheme 4).

Thus, the substituents on the carbon-carbon double bonds proved to influence the efficiency of the allyl transfer reaction. In contrast, the substituents at the allylic positions had little effect on the efficiency. These facts strongly suggest that the reactions proceed via a retro-allylation process. From a mechanistic point of view, her carbon-carbon bond cleavage is completely different from the palladium-catalyzed β-carbon elimination.[9]

Scheme 4.

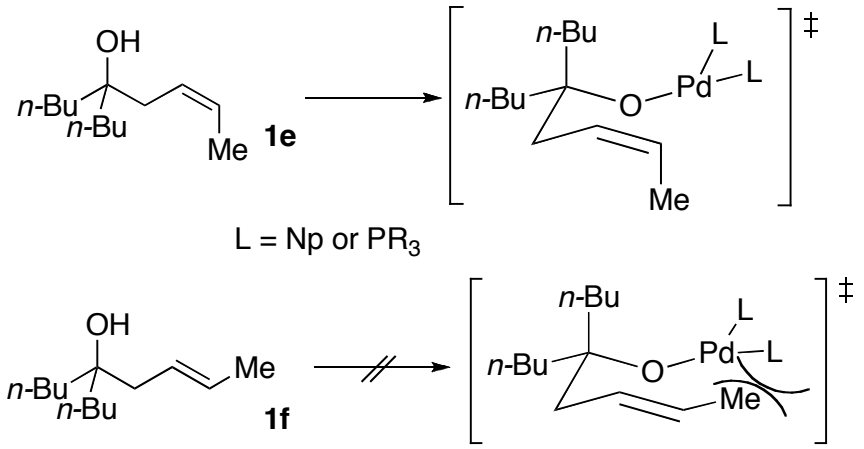
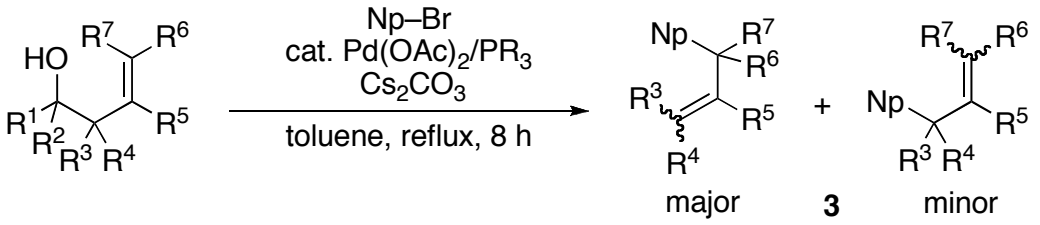
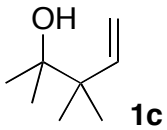
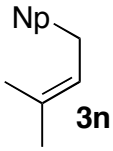
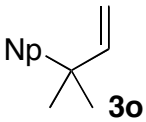
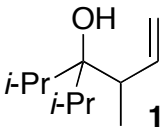
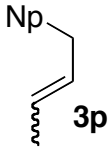
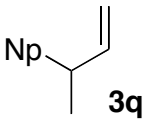
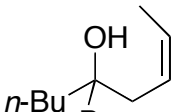
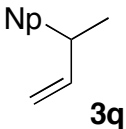
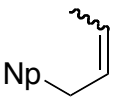
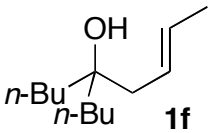
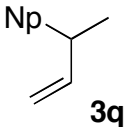
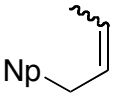


Table 3. Regiospecific Allylation of 1-Bromonaphthalene **2a** with Homoallyl Alcohols[a]



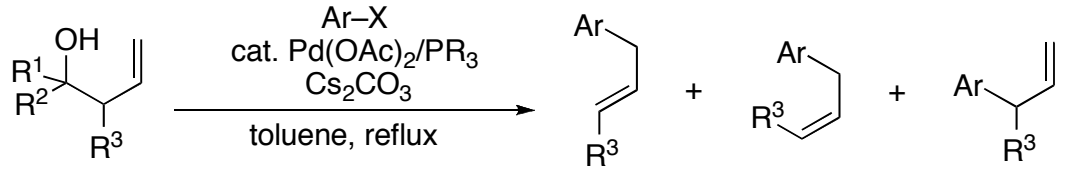
entry	1	PR_3	major 3		minor 3	
1	 **1c**	P(*p*-tol)$_3$	 **3n**	96%	 **3o**	3%
2		P(*c*-Hex)$_3$		92%		0%
3	 **1d**	P(*p*-tol)$_3$	 **3p**	86% (*E*/*Z* = 46:54)	 **3q**	6%
4		P(*c*-Hex)$_3$		80% (*E*/*Z* = 63:37)		5%
5	 **1e**	P(*p*-tol)$_3$	 **3q**	72%	 **3p**	6% (*E*/*Z* = 23:77)
6[b]		P(*c*-Hex)$_3$		48%		0%
7	 **1f**	P(*p*-tol)$_3$	 **3q**	5%	 **3p**	<1%
8		P(*c*-Hex)$_3$		11%		0%

[a] The reactions were performed under the same conditions as Table 1, entry 1 or Table 2, entry 1. [b] Substrate **1e** (1.0 mmol) and Cs_2CO_3 (1.2 mmol) were used. More than 30% of naphthalene was obtained.

Although the reactions of **1d** selectively yielded the linear coupling product **3p**, **3p** comprised a mixture of (*E*) and (*Z*) isomers (Table 3, entries 3 and 4). The author thus designed diastereomerically pure **1g**, having *tert*-butyl and methyl groups at the oxygenated carbon (Table 4). To her delight, **1g** realized stereospecific synthesis of (*E*)- and (*Z*)-**3p**. Treatment of **2a** with *threo*-**1g**[11] under the palladium catalysis afforded (*E*)-**3p** stereoselectively (entries 1 and 2).

On the other hand, formation of (*Z*)-**3p** predominated over that of (*E*)-**3p** in the reaction of *erythro*-**1g** (entries 3 and 4). Electron-deficient aryl halides **2f** and **2o** as well as electron-rich aryl halide **2p** also participated in stereospecific allylations (entries 5–10). The formations of (*Z*)-**3** from *erythro*-**1g** were always exclusive when P(*c*-Hex)$_3$ was used. The allyl transfer reaction was applied to stereospecific synthesis of vinyl ether **3v** starting from diastereomerically pure **1h** (Table 4, entries 11–14). Highly stereoselective synthesis of silyl enolate (*E*)-**3x** also highlights the utility of the retro-allylation strategy (entries 15 and 16).

Table 4. Stereospecific Allylation of **2** with Diastereomerically Pure Homoallyl Alcohols **1g–1i**[a]



(*E*)-**3** (*Z*)-**3** branched **3**

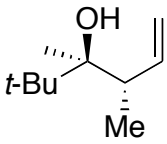
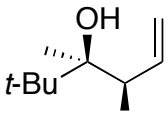
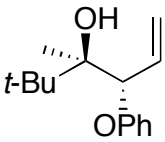
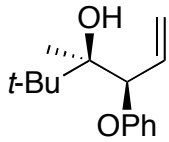
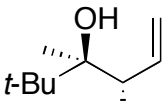
entry	**1**	**2**	PR_3	(*E*)- and (*Z*)- **3**	branched **3**
1	 *threo*-**1g**	**2a**	P(*p*-tol)$_3$	**3p**, 73%, *E/Z* = 98:2	**3q**, 4%
2		**2a**	P(*c*-Hex)$_3$	**3p**, 95%, *E/Z* = 97:3	**3q**, 2%
3	 *erythro*-**1g**	**2a**	P(*p*-tol)$_3$	**3p**, 78%, *E/Z* = 4:96	**3q**, 3%
4		**2a**	P(*c*-Hex)$_3$	**3p**, 70%, *E/Z* = 0:100	**3q**, 2%
5	*threo*-**1g**	**2f**	P(*p*-tol)$_3$	**3r**, 84%, *E/Z* = 97:3	**3s,** 2%
6	*erythro*-**1g**	**2f**	P(*p*-tol)$_3$	**3r**, 74%, *E/Z* = 8:92	**3s,** 2%
7	*threo*-**1g**	**2o**	P(*c*-Hex)$_3$	**3r**, 78%, *E/Z* = 95:5	**3s,** 4%
8	*erythro*-**1g**	**2o**	P(*c*-Hex)$_3$	**3r**, 73%, *E/Z* = 0:100	**3s,** 6%[b]

Table 4. (Continued)

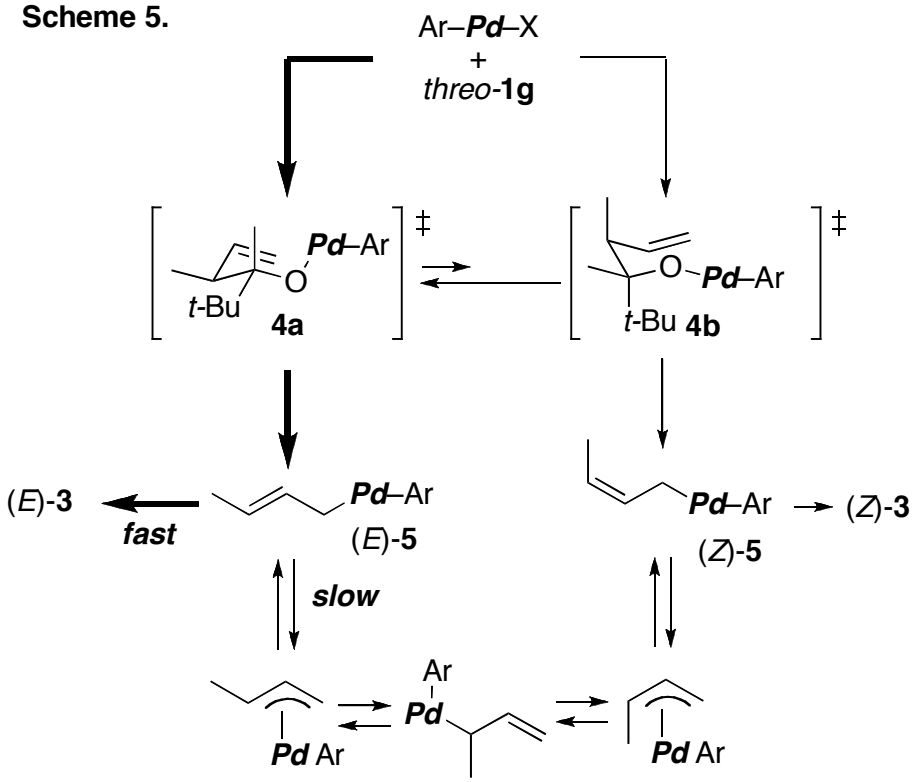
entry	**1**	**2**	PR_3	(*E*)- and (*Z*)- **3**	branched **3**
9	*threo*-**1g**	**2p**	P(*c*-Hex)$_3$	**3t**, 67%, *E/Z* = 96:4	**3u**, 4%
10	*erythro*-**1g**	**2p**	P(*c*-Hex)$_3$	**3t**, 77%, *E/Z* = 0:100	**3u**, 3%
11	 *erythro*-**1h**	**2a**	P(*p*-tol)$_3$	**3v**, 89%, *E/Z* = 94:6	**3w**, 0%
12		**2a**	P(*c*-Hex)$_3$	**3v**, 88%, *E/Z* = 99:1	**3w**, 0%
13	 *threo*-**1h**	**2a**	P(*p*-tol)$_3$	**3v**, 75%, *E/Z* = 4:96	**3w**, 0%
14		**2a**	P(*c*-Hex)$_3$	**3v**, 67%, *E/Z* = 0:100	**3w**, 0%
15[c]	 *erythro*-**1i**	**2a**	P(*p*-tol)$_3$	**3x**, 84%, *E/Z* = 99:1	**3y**, 0%
16[c]		**2a**	P(*c*-Hex)$_3$	**3x**, 87%, *E/Z* = 97:3	**3y**, 0%

[a] The reactions were performed under the conditions in Table 1, entry 1 or Table 2, entry 1.
[b] The branched product was contaminated with ethyl *p*-[(*E*)-1-methyl-1-propenyl]benzoate.
[c] The alcohol **1i** used was a 9:1 mixture of *erythro*-**1i** and *threo*-**1i**.

The author rationalizes the mechanism of the stereospecific allyl transfer reaction as follows (Scheme 5). Upon the retro-allylation reaction of *threo*-**1g**, a chairlike transition state **4a** that locates the *tert*-butyl group at the equatorial position would be most stable among possible transition states including another chairlike transition state **4b** and twist-boatlike transition states, on the basis of the conventional conformational analysis. Formation of aryl[(*E*)-crotyl]palladium (*E*)-**5** is thus favored. The intermediate probably undergoes reductive elimination so rapidly that its isomerization into π-allylpalladium and any other isomers is negligible. A similar explanation is applicable to the reaction of *erythro*-**1g**, where a chairlike transition state having the *tert*-butyl group at the equatorial position and the two methyl groups at

the axial positions would be preferred.

Scheme 5.



Conclusion

The author has devised a new method for the preparation of σ-allylpalladium, which is difficult to generate in a stereo- and regioselective manner, by taking advantage of retro-allylation as a bond-cleavage strategy. Coupled with immediate use of the σ-allylpalladium, the retro-allylation realizes stereo- and regiospecific allylations of aryl halides.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on Varian Mercury 300 spectrometers and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to residual $CHCl_3$ at 77.23 ppm for ^{13}C unless otherwise noted. ^{19}F NMR spectra were obtained in $CDCl_3$ with fluorotrichloromethane as an external standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra (EI unless otherwise noted) were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) and silica gel 60N (KANTO Co. Ltd. 40–100 mesh) were used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 3.80 mL/min, RI detector). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Tri(*p*-tolyl)phosphine, triphenylphosphine, tri(*tert*-butyl)phosphine, and cesium carbonate were purchased from Wako Pure Chemical Co. Tricyclohexylphosphine was purchased from Strem. Tricyclohexyphosphine and tri(*tert*-butyl)phosphine were dissolved in degassed toluene and hexane, respectively and stored strictly under argon. Palladium acetate was obtained from TCI. All reactions were carried out under argon atmosphere. The preparation of homoallyl alcohols **1a–1i** were descrived below.

Preparation of 1a–1d

Preparation of **1a** is representative. Under argon atmosphere, a solution of methallylmagnesium chloride (1.00 M THF solution, 28.0 mL, 28.0 mmol) and THF (20 mL) were placed in a 100-mL reaction flask. At 0 °C, 2,4-dimethyl-3-pentanone (3.28 mL, 23.0 mmol) was added dropwise via a syringe to the solution. The mixture was stirred for 1.5 h at room temperature. The mixture was poured into 1 M hydrochloric acid (30 mL). Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 10:1) provided **1a** (3.66 g, 21.5 mmol, 93%).

Preparation of 1e and 1f

Sodium hydride (60% suspension in oil, 1.20 g, 30 mmol) was placed in a 100-mL reaction flask equipped with a Dimroth condenser under argon. The hydride was washed with hexane (10 mL × 3) and THF (10 mL × 1). THF (50 mL) and methyltriphenylphosphonium iodide (11

g, 27 mmol) were added at 0 ˚C. After the resulting mixture was stirred for 1 h at ambient temperature, 5-nonanone (4.34 mL, 25.0 mmol) was added. The whole mixture was heated at 50 ˚C for 2 h. Triphenylphosphine oxide was removed to yield 2-butyl-1-hexene. The crude oil was dissolved in 30 mL of dichloromethane in a 100-mL round-bottomed flask. *m*-Chloroperbenzoic acid (77% purity, 5.6 g, 25 mmol) was added portionwise at 0 ˚C. After being stirred for 1 h at room temperature, the mixture was quenched with saturated sodium thiosulfate (5 mL). Sodium hydroxide solution (1 M, 30 mL) was then added. Organic components were extracted with hexane/ethyl acetate = 10:1 three times. The organic layer was washed with sodium hydroxide solution (1 M, 30 mL). Concentration followed by purification on silica gel (hexane/ethyl acetate = 10:1) yielded 1,2-epoxy-2-butylhexane (2.70 g, 17.3 mmol, 69%) as a colorless oil.

A 200-mL three-necked reaction flask equipped with a dropping funnel and a Dimroth condenser was allowed to cool to –78 ˚C under argon. Gaseous propyne was charged into the reaction flask to obtain ca. 2 mL (40 mmol) of liquid propyne. THF (50 mL) and then butyllithium (1.62 M hexane solution, 21.4 mL, 34.6 mmol) were added dropwise through the dropping funnel at –78 ˚C. After completion of the addition, hexamethylphosphoramide (15 mL) and 1,2-epoxy-2-butylhexane (2.70 g, 17.3 mmol in 10 mL of THF) were added via syringes. The resulting solution was stirred at –78 ˚C for 15 min and was allowed to warm gradually to room temperature by removing the bath. The mixture was heated at 50 ˚C for 60 h. The reaction was quenched with saturated ammonium chloride solution (40 mL). Extraction, concentration, and purification furnished 5-butyl-2-nonyn-5-ol (2.86 g, 14.6 mmol, 84%).

The reduction of the alkynol to yield **1e** was performed according to the literature.[12] Under an atmosphere of argon, diethyl ether (8 mL), 5-butyl-2-nonyn-5-ol (1.62 g, 8.26 mmol), and isopropylmagnesium bromide (0.98 M ethereal solution, 8.5 mL, 8.3 mmol) were sequentially added at 0 ˚C. After being stirred for 10 min at 0 ˚C, the mixture was cooled to –78 ˚C. Titanium tetraisopropoxide (3.05 mL, 10.3 mmol) and isopropylmagnesium bromide (21.1 mL, 20.7 mmol) were added to obtain a black solution. The mixture was allowed to warm to –50 ˚C and stirred for 3 h at the same temperature. The mixture was carefully poured into ice-cold 1 M hydrochloric acid (40 mL). The resulting mixture was stirred for 30 min at ambient temperature. Extractive workup and silica gel column purification afforded 1.36 g of **1e** (6.85 mmol, 83%) as a colorless oil.

Preparation of **1f** also started from 5-butyl-2-nonyn-5-ol. Lithium aluminum hydride (0.911 g, 24 mmol) was placed in a 100-mL reaction flask. THF (32 mL) and the alcohol (1.18 g, 6.0 mmol, dissolved in 13 mL of THF) were added through a dropping funnel. After completion of the addition, the whole mixture was stirred for 24 h at reflux. After being cooled to room temperature, the mixture was poured into ice-cold hydrochloric acid (1 M). The products were

extracted with hexane/ethyl acetate = 10:1. The organic layer was dried over magnesium sulfate and concentrated in vacuo. Purification of the crude product was performed on silica gel neutral (Kanto Chemical, spherical, neutral, 60N) with hexane/ethyl acetate = 10:1 as an eluent. (*E*)-5-Butyl-2-nonen-5-ol (**1f**) was obtained in 89% yield (1.05 g, 5.32 mmol, a colorless oil).

Preparation of *threo*- and *erythro*-1g

Crotylmagnesium chloride (0.95 M THF solution, 25.3 mL, 24 mmol) was added to a solution of pinacolone (2.47 mL, 20.0 mmol) in ether (30 mL) at 0 ˚C under an atmosphere of argon. The mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into 1 M hydrochloric acid (30 mL), and products were extracted with ether. Silica gel column purification (hexane/ethyl acetate = 20:1) provided *threo*-**1g** (R_f = 0.45, 1.89 g, 12.1 mmol, 60%) and *erythro*-**1g** (R_f = 0.36, 0.24 g, 1.5 mmol, 8%). The relative stereochemistry was determined according to the literature.[13]

Preparation of *threo*- and *erythro*-1h

Ether (60 mL) and allyl phenyl ether (1.37 mL, 10.0 mmol) were placed in a 100-mL reaction flask under argon. At –78 ˚C, *sec*-butyllithium (1.01 M cyclohexane solution, 9.90 mL, 10.0 mmol) was added dropwise via a syringe. After the mixture was stirred for 30 min at –78 ˚C, triethylaluminum (0.92 M hexane solution, 10.9 mL, 10.0 mmol) and pinacolone (1.24 mL, 10.0 mmol) were added.[14] The resulting mixture was allowed to warm to room temperature and stirred for 8 h. The reaction was quenched with 1 M hydrochloric acid (30 mL). Extraction with hexane/ethyl acetate = 5:1 and concentration in vacuo provided a crude oil that mainly consisted of *threo*-**1h** and *erythro*-**1h**. Purification on silica gel (gradient starting from hexane/ethyl acetate = 40:1) afforded *threo*-**1h** (R_f = 0.38 (hexane/ethyl acetate = 10:1), 0.542 g, 2.31 mmol, 23%) and *erythro*-**1h** (R_f = 0.25 (hexane/ethyl acetate = 10:1), 0.689 g, 2.94 mmol, 29%). The relative stereochemistry was determined by further derivatization shown below.

Preparation of 1i

A 100-mL reaction flask was filled with argon, and THF (15 mL), allyl alcohol (1.22 mL, 18.0 mmol), and butyllithium (1.60 M hexane solution, 10.3 mL, 16.5 mmol) were added at –78 ˚C. The resulting mixture was stirred for 30 min. Chlorotriisopropylsilane (3.21 mL, 15.0 mmol) was added at –78 ˚C. The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated ammonium chloride. Extraction and silica gel column purification (hexane/ethyl acetate = 10:1) provided allyl triisopropylsilyl ether (2.84 g, 13.3 mmol, 88%).

Ether (39 mL) and allyl triisopropylsilyl ether (2.84 g, 13.3 mmol) were placed in a 100-mL reaction flask under argon. At –78 ˚C, *sec*-butyllithium (1.00 M cyclohexane solution, 13.3 mL,

13.3 mmol) was added dropwise via a syringe. The mixture was stirred for 30 min at –40 °C. After the mixture was cooled to –78 °C, triethylaluminum (0.92 M hexane solution, 14.4 mL, 13.3 mmol) and pinacolone (1.64 mL, 13.3 mmol) were added.[14] The resulting mixture was stirred for 5 min at the same temperature, then allowed to warm to room temperature, and stirred for 5 h. The reaction was quenched with saturated ammonium chloride solution. A crude oil was purified on silica gel (hexane/ethyl acetate = 40:1) provided **1i** as a mixture of *erythro* and *threo* isomers in a ratio of 9:1 (2.09 g, 6.65 mmol, 50%, not optimized). Homoallyl alcohol **1i** was used as the mixture. The relative stereochemistry was inversely deduced from the product **3x**.

Typical Procedure for $Pd(OAc)_2$/P(*p*-tol)$_3$-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohol

Cesium carbonate (0.23 g, 0.72 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. The cesium carbonate was dried in vacuo with heating with a hair dryer for 2 min. Palladium acetate (5.6 mg, 0.025 mmol) and tri(*p*-tolyl)phosphine (30 mg, 0.10 mmol) were added in the reaction flask. The flask was then filled with argon by using the standard Schlenk technique. Toluene (3.0 mL), homoallyl alcohol **1a** (0.10 g, 0.60 mmol), and 1-bromonaphthalene (**2a**, 0.10 g, 0.50 mmol) were sequentially added at ambient temperature. The resulting mixture was heated at reflux for 8 h. After the mixture was cooled to room temperature, water (20 mL) was added. The product was extracted with hexane (20 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification with hexane as an eluent gave 1-methallylnaphthalene (**3a**, 0.078 g, 0.43 mmol) in 86% yield.

Typical Procedure for $Pd(OAc)_2$/P(*c*-Hex)$_3$-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohol

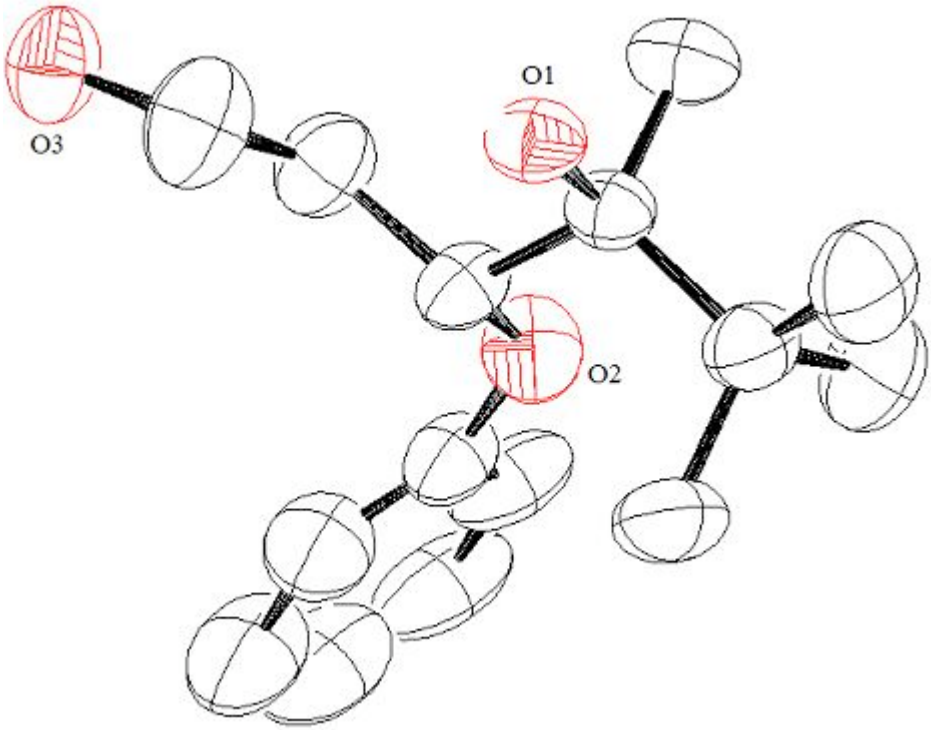
The procedure was similar to that described above except for the order of the addition of reagents. After dried cesium carbonate (0.23 g, 0.72 mmol) and palladium acetate (5.6 mg, 0.025 mmol) were placed in a reaction flask, the flask was filled with argon by using the standard Schlenk technique. Tricyclohexylphosphine (0.50 M in toluene, 0.10 mL, 0.050 mmol) and toluene (1.0 mL) were added, and the resulting mixture was stirred for 10 min at room temperature. The rest of the procedure was similar to those described above. .

Stereochemical Assignment of *erythro*-1h

One of the two isomers of **1h** (0.117 g, 0.50 mmol), which was the slower moving band of R_f = 0.29 (hexane/ethyl acetate = 10:1, the other isomer showed R_f = 0.42), was dissolved in THF (1.0

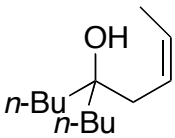
mL), and the solution was placed in a 30-mL reaction flask under argon. Borane dimethyl sulfide complex (0.095 mL, 1.0 mmol) was added at 0 ˚C. After the mixture was stirred at ambient temperature for 15 h, water (0.30 mL), 6 M NaOH (0.30 mL, 1.8 mmol), and 30% hydrogen peroxide (0.60 mL, 5.4 mmol) were sequentially added. A slightly exothermic reaction took place. The whole mixture was heated at reflux for 1 h. The reaction was quenched with aqueous sodium thiosulfate, and the products were extracted with ethyl acetate. After removal of solvent, silica gel column purification yielded 0.044 g of *erythro*-4,5,5-trimethyl-3-phenoxyhexane-1,4-diol (0.174 mmol, 35% yield, unoptimized). X-ray quality crystals were grown from heptane (Figure 1). The stereochemistry of *erythro*-**1i** was tentatively assigned according to the stereochemisty of the allyl transfer.

Figure 1. ORTEP Diagram of *erythro*-4,5,5-trimethyl-3-phenoxyhexane-1,4-diol. Hydrogen atoms are omitted for clarity.

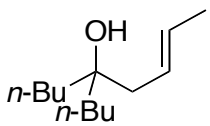


Characterization Data for New Compounds

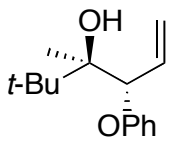
(*Z*)-5-Butyl-2-nonen-5-ol (1e): IR (neat) 3387, 3020, 2934, 2862, 1456, 1379, 1259, 1217, 1142, 1015, 907, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.0 Hz, 6H), 1.26–1.33 (m, 8H), 1.42–1.45 (m, 5H), 1.64 (ddt, *J* = 7.0, 1.5, 1.0 Hz, 3H), 2.21 (dm, *J* = 7.5 Hz, 2H), 5.46 (dtq, *J* = 11.0, 7.5, 1.5 Hz, 1H), 5.65 (dqt, *J* = 11.0, 7.0 ,1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.33, 14.35, 23.54, 26.01, 36.80, 39.08, 74.87, 125.47, 127.46. Found: C, 78.58; H, 12.93%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.



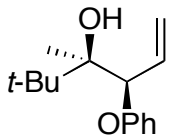
(*E*)-5-Butyl-2-nonen-5-ol (1f): IR (neat) 3402, 3025, 2934, 2861, 1458, 1379, 1341, 1259, 1217, 1142, 1001, 971, 906, 403 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.0 Hz, 6H), 1.24–1.33 (m, 8H), 1.39–1.43 (m, 5H), 1.69 (dm, *J* = 6.0 Hz, 3H), 2.12 (dm, *J* = 7.0 Hz, 2H), 5.44 (dtq, *J* = 15.0, 7.0, 1.0 Hz, 1H), 5.53 (dqt, *J* = 15.0, 6.0 ,1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.36, 18.42, 23.53, 25.94, 38.98, 42.80, 74.14, 126.34, 129.56. Found: C, 78.42; H, 12.99%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.



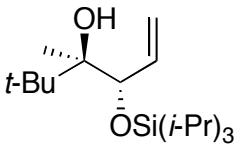
***erythro*-4-Phenoxy-2,2,3-trimethyl-5-hexen-3-ol (*erythro*-1h):** IR (neat) 3493, 2959, 2877, 1587, 1495, 1456, 1366, 1335, 1287, 1240, 1078, 1045, 993, 925, 751, 691, 402 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.09 (s, 1H), 1.30 (s, 3H), 4.78 (dt, *J* = 6.0, 1.0 Hz, 1H), 5.33 (dt, *J* = 17.5, 1.5 Hz, 1H), 5.38 (dt, *J* = 10.5, 1.5 Hz, 1H), 6.00 (ddd, *J* = 17.5, 10.5, 6.0 Hz, 1H), 6.88 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.92 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.25 (dd, *J* = 8.5, 7.5 Hz, 2H); ^{13}C NMR (C_6D_6) δ 19.09, 26.80, 38.60, 76.98, 81.54, 116.07, 119.09, 121.04, 130.12, 136.06, 158.28. Found: C, 76.71; H, 9.64%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.



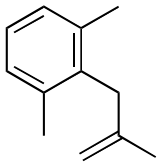
***threo*-4-Phenoxy-2,2,3-trimethyl-5-hexen-3-ol (*threo*-1h):** IR (neat) 3583, 2959, 2876, 1588, 1495, 1396, 1373, 1223, 1101, 1073, 992, 958, 930, 752, 691, 408 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.22 (s, 3H), 2.74 (s, 1H), 4.72 (d, *J* = 7.5 Hz, 1H), 5.27 (dm, *J* = 17.5 Hz, 1H), 5.29 (dm, *J* = 10.5 Hz, 1H), 5.89 (ddd, *J* = 17.5, 10.5, 7.5 Hz, 1H), 6.92 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.96 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.27 (dd, *J* = 8.5, 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.45, 26.75, 37.85, 77.73, 82.88, 116.91, 119.70, 121.60, 129.59, 134.90, 157.30. Found: C, 76.85; H, 9.59%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.



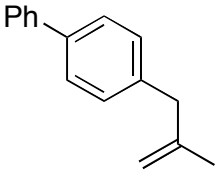
***erythro*-4-Triisopropylsiloxy-2,2,3-trimethyl-5-hexen-3-ol (*erythro*-1i):** IR (neat) 2946, 2868, 1464, 1421, 1384, 1370, 1094, 1065, 1007, 922, 883, 812, 684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 9H), 1.05–1.13 (m, 22H), 1.18 (s, 3H), 4.26 (d, J = 9.0 Hz, 1H), 5.20 (dm, J = 17.0 Hz, 1H), 5.21 (dm, J = 10.5 Hz, 1H), 6.00 (ddd, J = 17.0, 10.5, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.09, 18.44, 18.49, 20.34, 26.98, 37.85, 81.87, 118.04, 139.48. Found: C, 68.78; H, 12.40%. Calcd for $C_{18}H_{38}O_2Si$: C, 68.72; H, 12.18%.



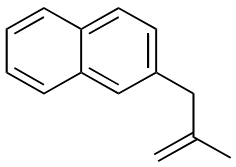
3-(2,6-Dimethylphenyl)-2-methyl-1-propene (3b): IR (neat) 3076, 3020, 2958, 2918, 2856, 1651, 1470, 1447, 1375, 1096, 893, 768 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83–1.84 (m, 3H), 2.25 (s, 6H), 3.28 (bs, 2H), 4.20–4.22 (m, 1H), 4.69–4.71 (m, 1H), 7.00–7.06 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 20.04, 23.71, 37.53, 109.97, 126.13, 128.00, 136.81, 137.24, 143.11; Found: C, 89.70; H, 9.99%. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06%.



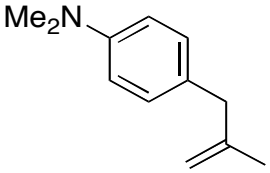
4-(2-Methyl-2-propenyl)biphenyl (3h): IR (neat) 3029, 2913, 2852, 1647, 1517, 1486, 1436, 1409, 1374, 1009, 892, 804, 760, 743, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (s, 3H), 3.37 (s, 2H), 4.78 (m, 1H), 4.84 (m, 1H), 7.26–7.28 (m, 2H), 7.32–7.35 (m, 1H), 7.42–7.45 (m, 2H), 7.52–7.54 (m, 2H), 7.58–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.34, 44.49, 112.26, 127.22, 127.24 (overlapped), 128.93, 129.52, 139.10, 139.22, 141.27, 145.27. Found: C, 92.31; H, 7.77%. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74%.



2-(2-Methyl-2-propenyl)naphthalene (3i): IR (neat) 3053, 3021, 2969, 2909, 2854, 1652, 1635, 1600, 1508, 1436, 1374, 892, 857, 807, 758, 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (s, 3H), 3.50 (s, 2H), 4.79–4.81 (m, 1H), 4.86–4.88 (m, 1H), 7.35 (dd, J = 8.0, 1.5 Hz, 1H), 7.45 (quintet of doublet, J = 7.0, 1.5 Hz, 2H), 7.64 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.79–7.83 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.36, 45.02, 112.39, 125.45, 126.08, 127.36, 127.70, 127.76, 127.82, 128.02, 132.35, 133.76, 137.50, 145.25. Found: C, 92.39; H, 7.88%. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74%.



4-(2-Methyl-2-propenyl)-*N*,*N*-dimethylaniline (3k): IR (neat) 3072, 2852, 2800, 1649, 1615, 1520 ,1444, 1346, 1227, 1163, 948, 888, 797, 567 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (s, 3H), 2.92 (s, 6H), 3.23 (s, 2H), 4.71–4.73 (m, 1H), 4.76–4.78 (m, 1H), 6.70 (d, J = 9.0 Hz, 2H), 7.06 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.23, 31.13, 41.08, 43.87, 111.34, 113.06, 128.11,



129.68, 146.20, 149.41. Found: C, 82.11; H, 9.84%. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78%.

(*E*)-3-Naphthyl-1-phenoxypropene ((*E*)-3v): IR (neat) 3042, 2924, 1672 1593, 1510, 1491, 1396, 1306, 1167, 1109, 935, 793, 777, 754, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.85 (dd, *J* = 7.0, 1.5 Hz, 2H), 5.72 (dt, *J* = 12.0, 7.0 Hz, 1H), 6.49 (dt, *J* = 12.0, 1.5 Hz, 1H), 6.95 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.03 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.29 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.41–7.46 (m, 2H), 7.49–7.52 (m, 1H), 7.54–7.57 (m, 1H), 7.75–7.77 (m, 1H), 7.87–7.89 (m, 1H), 8.09–8.10 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 30.92, 111.92, 116.62, 122.81, 123.94, 125.82, 125.85, 126.11, 126.16, 127.28, 128.98, 129.78, 132.00, 134.01, 136.54, 143.44, 157.44; Found: C, 87.38; H, 6.16%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

(*Z*)-3-Naphthyl-1-phenoxypropene ((*Z*)-3v): IR (neat) 3042, 2957, 2924, 1666, 1595, 1510, 1491, 1383, 1227, 1167, 1090, 1074, 791, 779, 754, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.03 (dd, *J* = 7.0, 1.5 Hz, 2H), 5.08 (dt, *J* = 7.0, 6.0 Hz, 1H), 6.51 (dt, *J* = 6.0, 1.5 Hz, 1H), 7.08–7.11 (m, 3H), 7.34–7.39 (m, 2H), 7.41–7.44 (m, 2H), 7.47–7.50 (m, 2H), 7.73–7.75 (m, 1H), 7.85–7.88 (m, 1H), 8.12–8.15 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 28.28, 114.47, 116.65, 122.95, 124.30, 125.77, 125.86, 126.05, 126.08, 127.08, 128.86, 129.88, 132.17, 134.05, 137.17, 140.75, 157.65; Found: C, 87.66; H, 6.25%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

(*E*)-3-(1-Naphthyl)-1-triisopropylsiloxy-1-propene ((*E*)-3x): IR (neat) 3042, 2944, 2892, 2866, 1664, 1463, 1253, 1169, 924, 883, 790, 776, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04–1.17 (m, 21H), 3.70 (d, *J* = 7.5 Hz, 2H), 5.32 (dt, *J* = 12.0, 7.5 Hz, 1H), 6.44 (dt, *J* = 12.0, 1.5 Hz, 1H), 7.35–7.36 (m, 1H), 7.39–7.42 (m, 1H), 7.45–7.51 (m, 2H), 7.71–7.72 (m, 1H), 7.84–7.86 (m, 1H), 8.06–8.07 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 12.16, 17.94, 30.94, 109.30, 124.09, 125.64, 125.79, 125.81, 125.89, 126.86, 128.82, 132.10 ,133.94, 137.72, 142.44. Found: C, 77.52; H, 9.48%. Calcd for $C_{22}H_{32}OSi$: C, 77.59; H, 9.47%.

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Chapter 2

Synthesis of (Arylalkenyl)silanes by Palladium-Catalyzed Regiospecific and Stereoselective Allyl Transfer from Silyl-Substituted Homoallyl Alcohols to Aryl Halides

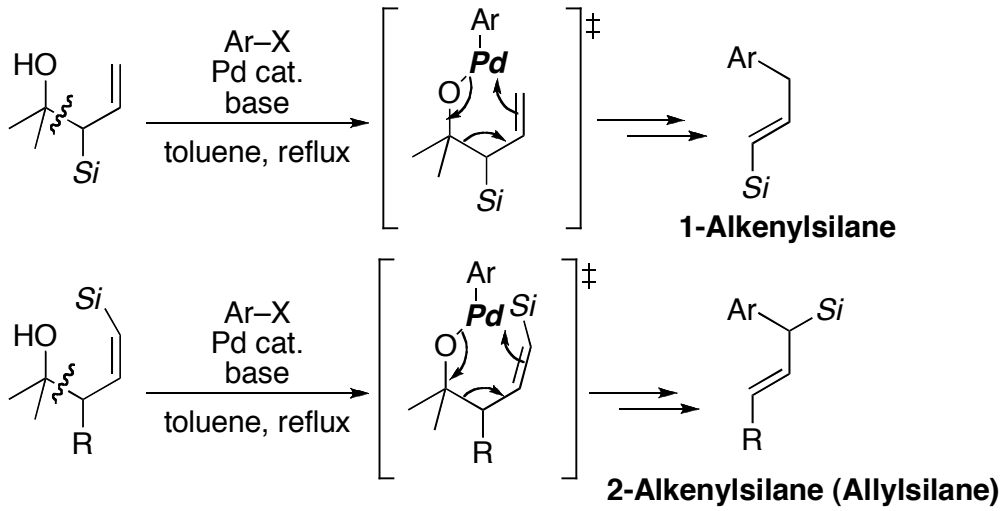
The reactions of silyl-substituted homoallyl alcohols with aryl halides under palladium catalysis result in regiospecific and stereoselective allyl transfer from the alcohols to aryl halides, offering modular synthesis of (*E*)-3-aryl-1-alkenyl-, (*E*)-1-aryl-2-alkenyl-, and optically active (*E*)-1-aryl-2-butenylsilanes.

Introduction

Alkenylsilanes are indispensable reagents in modern organic synthesis.[1] For instance, alkenylsilanes serves as coupling partners of organic halides in Hiyama cross-coupling reaction, forming a new carbon-carbon bond. Allylsilanes are representative reagents for the allylation of carbonyl compounds. The transformation of a carbon-silicon bond to a carbon-oxygen bond is also possible by using Tamao-Fleming oxidation. Developing new methods for highly selective synthesis of vinyl- and allylsilanes, including optically active ones, is thus still quite important.[2]

In Chapter 1, the author reported palladium-catalyzed allyl transfer from homoallyl alcohols to aryl halides through carbon-carbon bond cleavage.[3,4] The allyl transfer proceeds in a regio- and stereospecific manner, reflecting the structure of homoallyl alcohols used. In Chapter 2, she presents regiospecific and stereoselective allyl transfer reaction for the synthesis of aryl-substituted (*E*)-1- or 2-alkenylsilanes from silyl-substituted homoallyl alcohols (Scheme 1).

Scheme 1.

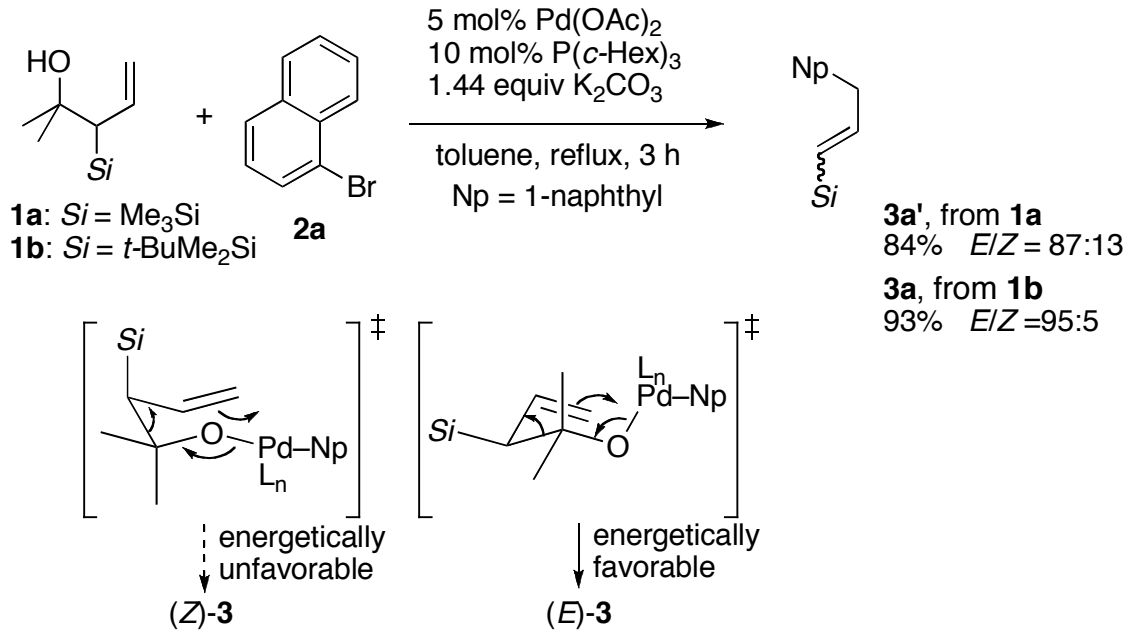


Results and Discussion

Treatment of 1-bromonaphthalene (**2a**) with **1a**, containing an allylic silane moiety, in the presence of K_2CO_3 under $Pd(OAc)_2/P(c\text{-Hex})_3$ catalysis provided vinylsilane **3a'** in good yield with moderate *E* selectivity (Scheme 2). The reaction with **1b** having a bulkier *t*-$BuMe_2Si$

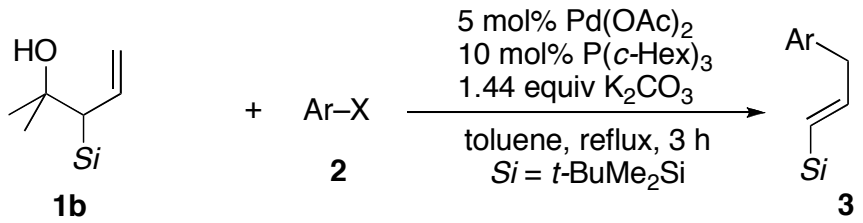
group proceeded to yield **3a** with excellent selectivity of *E*/*Z* = 95:5. The improvement of the stereoselectivity would originate from the stronger preference of the *t*-$BuMe_2Si$ group being at the pseudoequatorial position in the transition state of the retro-allylation. It is worth noting that only one silyl group at the allylic position can be a decisive factor in determining the stereoselectivity, whereas tedious preparation of diastereomerically pure and differently 1,1,2-trisubstituted homoallyl alcohols was essential to attain high *E* selectivity in the previous report.[3]

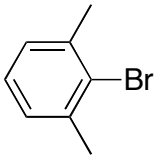
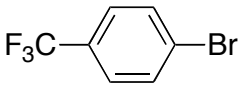
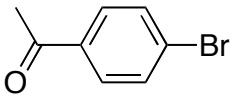
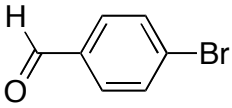
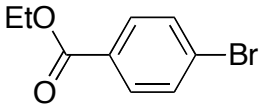
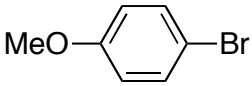
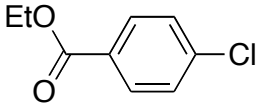
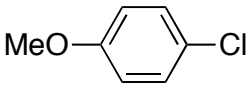
Scheme 2.



The scope of aryl halides is wide enough to afford a variety of (*E*)-3-aryl-1-propenylsilanes in excellent yields (Table 1[5,6]). Sterically demanding (entry 1), electron-deficient (entries 2–5), and electron-rich (entry 6) aryl bromides participated in the reaction. The use of P(*c*-Hex)$_3$ as a ligand allowed her to use aryl chlorides as substrates (entries 7 and 8).

Table 1. Synthesis of (*E*)-3-aryl-1-propenylsilanes **3**



entry	Ar–X **2**		**3**, yield(%)	*E*/*Z*
1		**2b**	**3b**, 92	93:7
2		**2c**	**3c**, 75	96:4
3		**2d**	**3d**, 89	95:5
4		**2e**	**3e**, 87	96:4
5		**2f**	**3f**, 97	95:5
6		**2g**	**3g**, 92	94:6
7		**2f-Cl**	**3f**, 89	97:3
8		**2g-Cl**	**3g**, 92	95:5

The author then focused on homoallyl alcohol **4a**, containing a (*Z*)-1-alkenylsilane moiety. The reactions of **4a** with aryl bromides in the presence of Cs_2CO_3 under $Pd(OAc)_2/PAr_3$ catalysis provided 1-aryl-2-propenylsilanes in high yields (Table 2,[5] entries 1–6). P(*c*-Hex)Ph_2 was exceptionally essential to attain high yield when electron-rich aryl bromide **2g** was used (entry 7).

Interestingly, silylated homoallyl alcohols **4b–d** having one methyl group at the allylic position were converted to (*E*)-1-aryl-2-butenylsilanes stereoselectively (entries 8–16). Fortunately, the allyl transfer reaction to 1-bromonaphthalene (**2a**) always provided the *E* isomers exclusively (entries 8, 10, and 15). The exclusive formation of the *E* isomers would result from the steric factor of the 1-naphthyl group on palladium in the transition state of the retro-allylation. The Me_3Si, *t*-$BuMe_2Si$, and Me_2PhSi groups were compatible under the reaction conditions. The bulkiness of the silyl groups had little influence on stereoselectivity (entries 9 vs 11 and 13 vs 16). On the other hand, when the larger substituent, *n*-Bu, was introduced at the allylic position, the *E* selectivity of the reaction was excellent (entries 13 vs 17). The *E* selective formation of **5** was explained in a fashion similar to that in Scheme 2. In addition, the steric repulsion between the substituent at the allylic position and the silyl substituent at the olefin terminus also contributed to preferable *E* selectivity (Scheme 3).

Scheme 3.

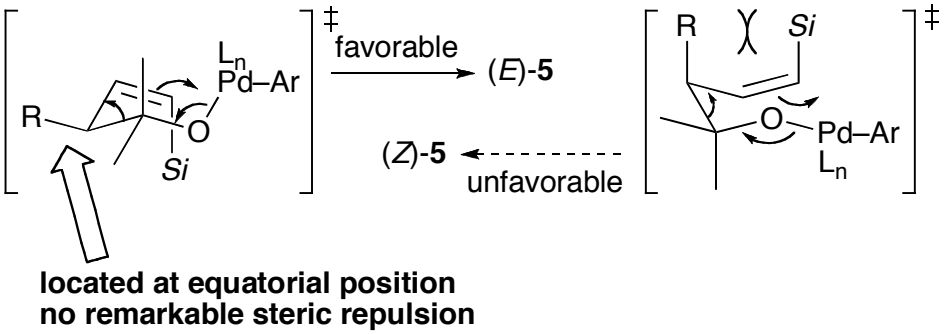
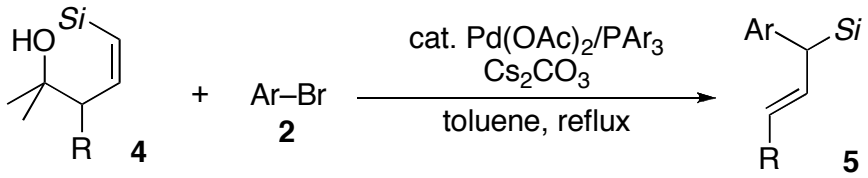


Table 2. Synthesis of 1-aryl-2-alkenylsilanes



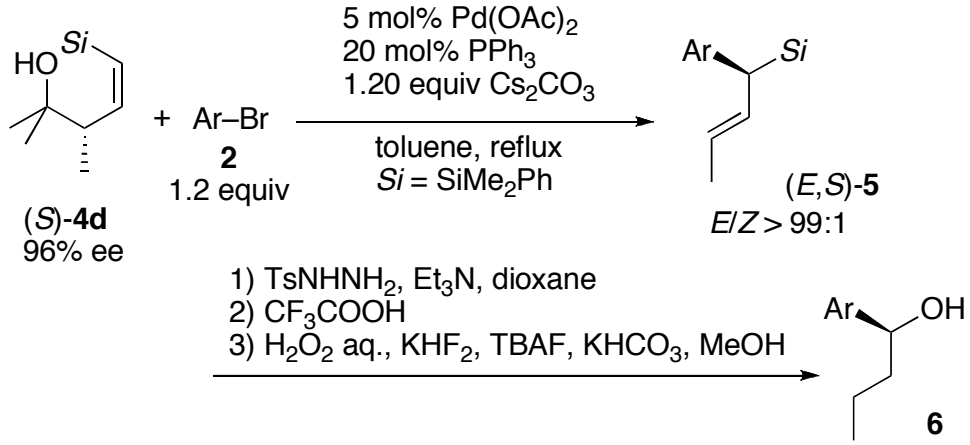
entry	**2**	*Si*	R	**4**	conditions[a]	**5**, yield (%)[b]
1	**2a**	*t*-BuMe$_2$Si	H	**4a**	A[c]	**5aa**, 88
2	**2b**			**4a**	A	**5ba**, 66
3	**2c**			**4a**	A	**5ca**, 81
4	**2d**			**4a**	A[c,d]	**5da**, 61
5	**2e**			**4a**	A	**5ea**, 68
6	**2f**			**4a**	A[d]	**5fa**, 88
7	**2g**			**4a**	A[e]	**5ga**, 74
8	**2a**	*t*-BuMe$_2$Si	Me	**4b**	B	**5ab**, 92 (100:0)
9	**2d**			**4b**	B	**5db**, 83 (89:11)
10	**2a**	Me$_3$Si	Me	**4c**	B	**5ac**, 92 (100:0)
11	**2d**			**4c**	B	**5dc**, 68 (95:5)
12	**2e**			**4c**	B	**5ec**, 46 (96:4)
13	**2f**			**4c**	B	**5fc**, 91 (96:4)
14	**2g**			**4c**	B[f]	**5gc**, 46 (100:0)
15	**2a**	Me$_2$PhSi	Me	**4d**	B	**5ad**, 93 (100:0)
16	**2f**			**4d**	C	**5fd**, 84 (94:6)
17	**2f**	Me$_3$Si	*n*-Bu	**4e**	C[g]	**5fe**, 92 (100:0)

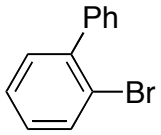
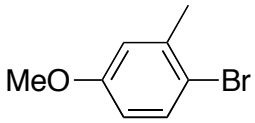
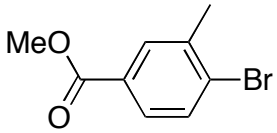
[a] Conditions A: 5 mol% Pd(OAc)$_2$, 20 mol% P(*p*-tol)$_3$, 1.44 equiv Cs$_2$CO$_3$, reflux, 4–15 h. Conditions B: 5 mol% Pd(OAc)$_2$, 20 mol% PPh$_3$, 1.20 equiv Cs$_2$CO$_3$, reflux, 4–7 h. Conditions C: 2.5 mol% Pd(OAc)$_2$, 10 mol% PPh$_3$, 1.20 equiv Cs$_2$CO$_3$, reflux, 45 min. [b] *E*/*Z* Ratios of **5** are in parentheses. [c] PPh$_3$ was used instead of P(*p*-tol)$_3$. [d] Reaction run using 2.5 mol% of Pd(OAc)$_2$ and 10 mol% of the ligand. [e] P(*c*-Hex)Ph$_2$ (10 mol%) was used. [f] P(*t*-Bu)$_3$ (5 mol%) was used instead. [g] The reaction time was 5 h.

The reactions of optically active (*S*)-**4d** (96% ee) with 2-substituted aryl bromides resulted in excellent chirality transfer to (*E*)-1-aryl-2-butenylsilanes **5** (Table 3[5]). The enantiomeric excesses of the products were indirectly determined after converting allylsilanes **5** to the corresponding 1-aryl-1-butanols **6**. The conversion consisted of hydrogenation with hydrazine,

acid-mediated conversion of the phenyl group on silicon to a trifluoroacetoxy group, and Tamao-Fleming oxidation with retention of configuration of the chiral carbon.[7]

Table 3.

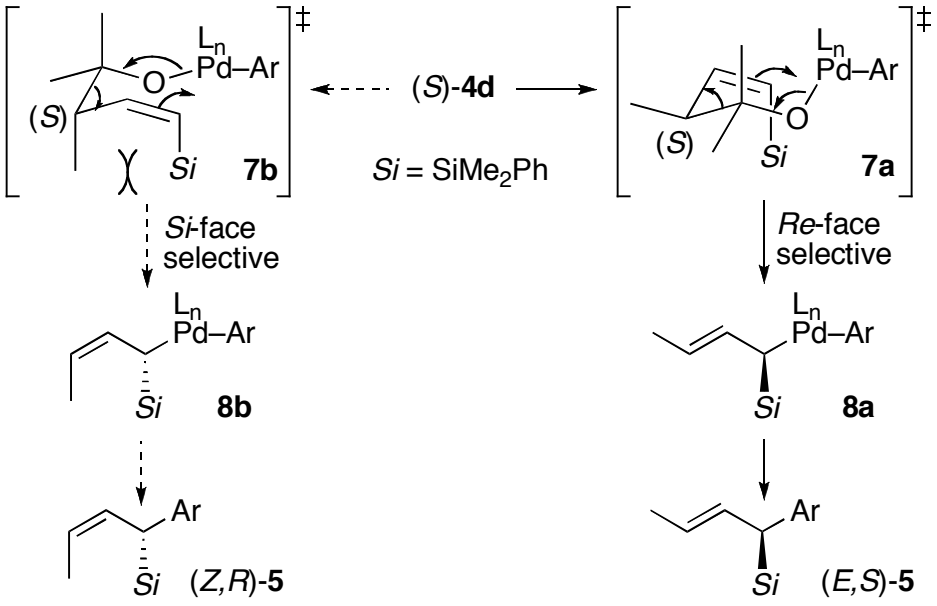


entry	2		5, yield (%)	ee of 6 (%)
1	**2a**		**5ad**, 92	**6ad**, 96
2	**2b**		**5bd**, 97	**6bd**, 96
3		**2h**	**5hd**, 94	**6hd**, 94
4		**2i**	**5id**, 90	**6id**, 96
5		**2j**	**5jd**, 87	**6jd**, 95

The excellent chirality transfer is rationalized as follows (Scheme 4). Comparing **7a** and **7b**, two possible chairlike transition states of the retro-allylation step, **7a** would be the more preferable because the methyl group at the allylic position occupies the pseudoequatorial position. The palladium center would approach the *Re* face of the alkene moiety, which leads to the

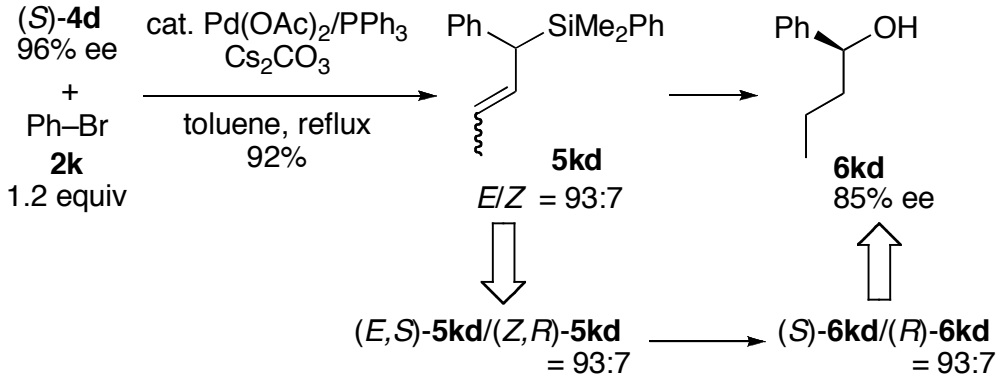
formation of **8a** having *E,R* configuration. Immediate reductive elimination from **8a** without loss of the chirality provides (*E,S*)-**5**.

Scheme 4.



The reaction of optically active (*S*)-**4d** (96% ee) with bromobenzene provided a mixture of (*E*)- and (*Z*)-**5kd** in a ratio of 93:7 (Scheme 5). Since the author could not determine the enantiomeric excess of each isomer, the mixture was converted to 1-phenylbutanol according to the procedure described in Table 3. The enantiomeric excess of **6kd** was 85% ee. The ee value of **6kd** strongly supports that complete chirality transfer to both (*E*)- and (*Z*)-**5kd** took place according to the mechanism shown in Scheme 4.

Scheme 5.



Conclusion

The author applied the allyl transfer reaction to silyl-substituted homoallyl alcohols and developed a new method for the preparation of (arylalkenyl)silanes. Starting from optically active homoallyl alcohol bearing a stereogenic center at the allylic position, the corresponding allylic silanes were obtained in excellent yields with perfect chirality transfer.

Experimental Procedure

Instrumentation and Chemicals

All experiments were conducted using the same instruments described in Chapter 1. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Tri(*p*-tolyl)phosphine, triphenylphosphine, cesium carbonate, and potassium carbonate were purchased from Wako Pure Chemical Co. Palladium acetate was obtained from TCI. Tricyclohexylphosphine was obtained from Strem. Tricyclohexylphosphine was dissolved in degassed toluene to prepare 0.5 M solution and stored strictly under argon. The preparations of the homoallyl alcohols are described in the following section. All reactions were carried out under argon atmosphere.

Preparation of 1a and 1b

Under argon atmosphere, allyl(*tert*-butyl)dimethylsilane (1.80 g, 11.5 mmol), *N,N,N', N'*-tetramethylethylenediamine (1.58 mL, 10.5 mmol), and THF (30 mL) were placed in a 100-mL reaction flask. At –78 ˚C, *tert*-butyllithium (1.59 M pentane solution, 6.60 mL, 10.5 mmol) was added dropwise via a syringe to the solution. The mixture was stirred for 2 h at –30 ˚C. The reaction mixture was again cooled to –78 ˚C before titanium tetraisopropoxide (3.39 mL, 11.5 mmol) was added. After stirring for 1 h at the same temperature, acetone (0.71 mL, 9.6 mmol) was added. The resulting mixture was stirred for 3 h. The mixture was poured into 1 M hydrochloric acid (40 mL) at 0 ˚C and stirred for 10 min. Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 20:1) provided **1b** (1.14 g, 5.34 mmol, 56%). A similar procedure gave **1a**, starting from allyltrimethylsilane (45%).

Preparation of 4a

A 100-mL reaction flask was filled with argon. THF (10 mL), *tert*-butyldimethylsilylacetylene (2.65 mL, 14.2 mmol), and butyllithium (1.60 M hexane solution, 9.37 mL, 14.9 mmol) were added at 0 ˚C. The resulting mixture was stirred for 30 min. Hexamethylphosphoramide (2.49 mL, 14.9 mmol) and isobutylene oxide (1.38 mL, 15.6 mmol) were added at 0 ˚C. The mixture was allowed to warm to room temperature and stirred for 20 h at ambient temperature. The reaction was quenched with saturated ammonium chloride solution (20 mL). Extraction, evaporation, and purification furnished 5-(*tert*-butyldimethylsilyl)-2-methyl-4-pentyn-2-ol (2.77 g, 13.0 mmol, 92%) as a white solid.

The reduction of the alkynol to yield **4a** was performed according to the literature.[8] Under an atmosphere of argon, diethyl ether (13 mL), 5-(*tert*-butyldimethylsilyl)-2-methyl-4-pentyn-2-ol (2.77 g, 13.0 mmol), and isopropylmagnesium bromide (1.00 M ethereal solution, 13.5 mL, 13.5

mmol) were sequentially added at 0 ˚C. After being stirred for 10 min at 0 ˚C, the mixture was cooled to –78 ˚C. Titanium tetraisopropoxide (7.69 mL, 26.0 mmol) and isopropylmagnesium bromide (52.0 mL, 52.0 mmol) were added. The resulting black solution was allowed to warm to –50 ˚C and stirred for 3 h at the same temperature. The mixture was carefully poured into ice-cold 1 M hydrochloric acid (100 mL). The resulting mixture was stirred for 30 min at ambient temperature. Extractive workup and silica gel column purification afforded 2.47 g of **4a** (11.5 mmol, 88%) as a colorless oil.

Preparation of 4b–4e

Preparation of **4c** is representative. Under argon atmosphere, *n*-butyllithium (1.60 M hexane solution, 22.0 mL, 36.0 mmol) was added dropwise to a solution of trimethylsilylacetylene (4.24 mL, 30.0 mmol) in THF (30 mL) at –78 ˚C. After stirring for 15 min at this temperature, acetaldehyde (3.35 mL, 60.0 mmol) was added. The reaction mixture was stirred at the same temperature for 2 h before quenching with saturated ammonium chloride solution (40 mL). Extraction and silica gel column purification provided 4-trimethylsilyl-3-butyn-2-ol (4.11 g, 28.9 mmol).

4-Dimethylaminopyridine (ca. 0.1 g) was placed in a 100-mL reaction flask under argon. A solution of 4-trimethylsilyl-3-butyn-2-ol (4.11 g, 28.9 mmol) in dichloromethane (30 mL), pyridine (3.51 mL, 43.4 mmol), and ethyl chloroformate (3.32 mL, 34.7 mmol) were sequentially added at 0 ˚C. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The mixture was poured into saturated sodium hydrogencarbonate solution, and the product was extracted with ethyl acetate three times. The combined organic layer was dried and concentrated in vacuo. Silica gel column purification provided the carbonate (5.53 g, 25.8 mmol, 89% in 2 steps) as a colorless oil.

Diethyl ether (50 mL) and the carbonate (4.5 g, 21 mmol) were placed in a 100-mL reaction flask under argon. The flask was cooled to –50 ˚C, and then titanium tetraisopropoxide (6.20 mL, 21.0 mmol) and isopropylmagnesium bromide (1.00 M ether solution, 40.0 mL, 40.0 mmol) were added and the whole mixture was stirred for 1 h at this temperature. After the obtained black solution was cooled to –78 ˚C, acetone (1.10 mL, 15.0 mmol) was added. The reaction mixture was warmed to –20 ˚C and stirring for 3 h at this temperature.[9] The mixture was carefully poured into ice-cold 1 M hydrochloric acid (100 mL). Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 10:1) afforded 2,3-dimethyl-5-trimethylsilyl-4-pentyn-2-ol (1.38 g, 7.49 mmol, 50%) and the starting carbonate (5.54 mmol).

The reduction of 2,3-dimethyl-5-trimethylsilyl-4-pentyn-2-ol to yield **4c** was accomplished by a similar procedure for the preparaton of **4a**. Note that 1.5 equivalent of titanium

tetraisopropoxide and 3.0 equivalent of isopropylmagnesium bromide were used for the reduction of 2,3-dimethyl-5-trimethylsilyl-4-pentyn-2-ol. Alcohol **4c** was obtained in 82% yield as colorless oil.

Preparation of **4d** is different from that of **4c** in the first step. A 300-mL three-necked reaction flask equipped with a Dimroth condenser was cooled to 0 ˚C under argon atmosphere. Butyllithium (1.60 M hexane solution, 46.9 mL, 75.0 mmol) was added dropwise to the solution of 3-butyn-2-ol (2.35 mL, 30.0 mmol) in THF (60 mL) via a syringe at 0 ˚C. After stirring for 30 min at this temperature, chlorodimethylphenylsilane (12.5 mL, 75.0 mmol) was added at 0 ˚C. The reaction mixture was refluxed for 2 h. After cooling to 0 ˚C, 1.4 M sulfuric acid (33 mL, 150 mmol) was added dropwise below 45 ˚C and stirred for another 5 min. Extraction, evaporation, purification by silica gel column provided a mixture of 4-dimethylphenylsilyl-3-butyn-2-ol (21.7 mmol, 72%) and tetramethyldiphenyldisiloxane. The disiloxane was separated in the next step by silica gel column purification.

Preparation of (*S*)-4d

Preparations of 4-methoxybenzyl trichloroacetimidate and methyl (*S*)-3-[(4-methoxybenzyl)oxy]-2-methylpropanoate were performed according to the literature.[10] Sodium hydride (60% suspension in oil, 0.56 g, 14 mmol) was placed in a 100-mL reaction flask under argon. The hydride was washed with hexane (9 mL × 3). Diethyl ether (25 mL) and 4-methoxybenzyl alcohol were slowly added at 0 ˚C. The reaction mixture was allowed to warm to room temperature, stirred for 30 min, and then cooled to 0 ˚C. Trichloroacetonitrile (5.61 mL, 56.0 mmol) was added dropwise via a syringe and the resulting mixture was allowed to warm gradually to room temperature by removing the ice bath. After stirring for 2 h, the reaction was quenched with saturated sodium hydrogencarbonate solution. The mixture was extracted with ether three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo to afford crude 4-methoxybenzyl trichloroacetimidate.

Under argon atmosphere, pyridinium *p*-toluenesulfonate (1.01 g, 4.0 mmol) was added to a solution of methyl (*S*)-3-hydroxy-2-methylpropionate (4.73 mL, 40.0 mmol) and 4-methoxybenzyltrichloroacetimidate (ca. 56 mmol) in dichloromethane (80 mL) at room temperature. After stirring for 17 h, saturated sodium hydrogencarbonate solution (50 mL) was added. The product was extracted with hexane/ethyl acetate = 10:1 three times, and the organic layer was washed with water and brine. Evaporation followed by silica gel column purification (hexane/ethyl acetate = 10:1) provided methyl (*S*)-3-[(4-methoxybenzyl)oxy]-2-methylpropanoate (8.80 g, 36.9 mmol, 92%).

A 300-mL reaction flask was filled with argon. Methylmagnesium iodide (1.00 M ether solution, 88.6 mL, 88.6 mmol) was placed in the flask at 0 ˚C and a solution of methyl

(*S*)-3-[(4-methoxybenzyl)oxy]-2-methylpropanoate (8.80 g, 36.9 mmol) in diethyl ether (30 mL) was added dropwise through a syringe. The resulting mixture was stirred for 2 h at room temperature, before quenching with saturated ammonium chloride solution (100 mL). Extractive workup followed by silica gel column purification furnished (*S*)-4-[(4-methoxybenzyl)oxy]-2,3-dimethyl-2-butanol (6.35 g, 26.6 mmol, 72%) as a colorless oil.

A solution of (*S*)-4-[(4-methoxybenzyl)oxy]-2,3-dimethyl-2-butanol (6.35 g, 26.6 mmol) in THF (27 mL) was placed in a 100-mL flask under argon. The flask was cooled to 0 ˚C, and then butyllithium (1.60 M hexane solution, 16.9 mL, 27.0 mmol) was added dropwise via a syringe. After stirring for 15 min at 0 ˚C, chlorotriethylsilane (5.36 mL, 31.9 mmol) was added at ambient temperature. The reaction mixture was heated at 50 ˚C for 12 h. After the reaction mixture was cooled to room temperature, water was added. Extraction, evaporation and silica gel column purification provided silyl-protected alcohol (8.13 g, 23.1 mmol, 87%) as a colorless oil.

Pd/C (10% Pd, 1.05 g) was placed in a 100-mL reaction flask. A solution of silyl-protected alcohol (8.13 g, 23.1 mmol) in ethanol (92 mL) was added under argon atmosphere. The flask was then flushed with hydrogen. After stirring for 12 h at atmospheric pressure of H_2, starting material was detected by TLC. The hydrogen balloon was then replaced by a new one and the reaction mixture was heated at 40 ˚C for 2 h. The reaction mixture was filtrated and the filtrate was concentrated. Silica gel column purification afforded (*S*)-3-triethylsiloxy-2,3-dimethyl-1-butanol (3.67 g, 15.8 mmol, 68%) as a colorless oil.

Molecular sieves 4A (powdered, 15.8 g) was placed in a reaction flask. Under argon atmosphere, a solution of (*S*)-3-triethylsiloxy-2,3-dimethyl-1-butanol (3.67 g, 15.8 mmol) in dichloromethane (100 mL), *N*-methylmorpholine *N*-oxide (5.55 g, 47.3 mmol), and tetra-propylammonium perruthenate (0.39 g, 1.1 mmol) were sequentially added. After stirring for 1 h, the mixture was concentrated in vacuo, which was followed by filtration through a pad of neutral silica gel with the aid of hexane/ethyl acetate = 5:1. (*S*)-3-Triethylsiloxy-2,3-dimethylbutanal was obtained as an oil.

Tetrabromomethane (7.46 mmol, 22.5 mmol) was placed in a 300-mL flask under argon. Dichloromethane (80 mL) and triphenylphosphine (11.8 g, 45.0 mmol) were added at 0 ˚C. The reaction mixture was turned to red brown solution. After stirring for 1 h, the mixture was cooled to –78 ˚C, a solution of crude (*S*)-3-triethylsiloxy-2,3-dimethylbutanal in dichloromethane (20 mL) was added and the resulting mixture was stirred for 1 h at ambient temperature. The mixture was concentrated in vacuo. Hexane (100 mL) was added to precipitate phosphine oxide. Filtration, evaporation, purification by neutral silica gel column (hexane) provided (*S*)-(4,4-dibromo-1,1,2-trimethyl-3-butenyloxy)triethylsilane (3.00 g, 7.8 mmol, 49% in two steps) as a colorless oil.

THF (25 mL) and (*S*)-(4,4-dibromo-1,1,2-trimethyl-3-butenyloxy)triethylsilane (3.00 g, 7.8 mmol) were placed in a 100-mL flask under argon. The solution was cooled to –78 ˚C, then butyllithium (1.60 M hexane solution, 12.1 mL, 19.4 mmol) was added dropwise via a syringe. The mixture was allowed to warm to –20 ˚C and stirred at ambient temperature. After 1 h, the mixture was recooled to –78 ˚C, chlorodimethylphenylsilane (3.9 mL, 23.3 mmol) was added to the mixture and the resulting mixture was stirred for 2.5 h at –20 ˚C. The reaction was quenched with saturated ammonium chloride solution. Extractive workup followed by column purification on neutral silica gel afforded (*S*)-(4-dimethylphenylsilyl-1,2,2-trimethyl-3-butynyloxy)triethylsilane (3.72 g, 7.4 mmol, 94%) as a colorless oil.

Under argon atmosphere, diethyl ether (10 mL), (*S*)-(4-dimethylphenylsilyl-1,2,2-trimethyl-3-butynyloxy)triethylsilane (3.72 g, 7.4 mmol,), titanium tetraisopropoxide (3.29 mL, 11.1 mmol), and isopropylmagnesium bromide (1.0 M ether solution, 22.3 mL, 22.3 mmol) were added to a 100-mL flask at –78 ˚C. The resulting black solution was stirred for 2 h at –50 ˚C, then warmed to –40 ˚C, and stirred for another 1 h. The reaction was quenched with ice-cold 1 M hydrochloric acid (40 mL). Extraction, evaporation, and purification by neutral silica gel column (hexane) provided (*Z*)-(*S*)-(4-dimethylphenylsilyl-1,2,2-trimethyl-3-butenyloxy)triethylsilane (2.26 g, 5.8 mmol, 78%) as a colorless oil.

(*Z*)-(*S*)-(4-Dimethylphenylsilyl-1,2,2-trimethyl-3-butenyloxy)triethylsilane (2.26 g, 5.8 mmol) was placed in a 100-mL flask. Methanol (60 mL), THF (12 mL), and *p*-toluenesulfonic acid monohydrate (0.06 g, 0.3 mmol) were added and the resulting mixture was stirred for 2 h at room temperature. The mixture was then concentrated in vacuo and purified on neutral silica gel column. **(*S*)-4d** was obtained (1.35 g, 5.5 mmol, 95%) as a colorless oil. Total yield was 14 % starting from methyl (*S*)-3-hydroxy-2-methylpropanoate.

Preparation of carbamate for determination of enantiomeric excess of (*S*)-4d

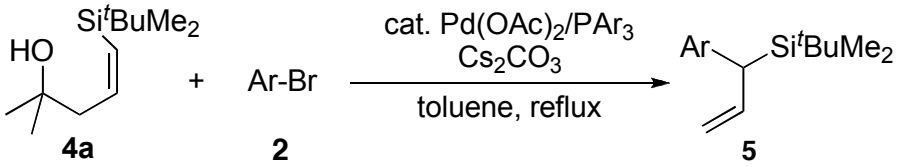
(*S*)-4d (0.075 g, 0.30 mmol) was placed in a 20-mL reaction flask under argon. Pyridine (0.30 mL) and phenylisocyanate (0.049 mL, 0.45 mmol) were added at room temperature. After the mixture was stirred for 24 h at ambient temperature, brine (15 mL) was added. Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 30:1 then 10:1) afforded the carbamate (0.067 g, 0.18 mmol, 60%). The enantiomeric excess was determined to be 96% ee according to HPLC analysis. HPLC conditions : Daicel CHIRALPAK AD-H, hexane/2-propanol = 98/2, 1.0 mL/min, retention time : 6.19 min (*R*, minor); 6.98 min (*S*, major).

Typical procedure for the synthesis of (*E*)-3-aryl-1-propenylsilanes

Potassium carbonate (0.083 g, 0.58 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. The potassium carbonate was dried in vacuo with heating with a hair dryer for 2 min. Palladium acetate (4.5 mg, 0.020 mmol) was added in the reaction flask. The flask was filled with argon by using the standard Schlenk technique. Tricyclohexylphosphine (0.5 M toluene solution, 0.080 mL, 0.04 mmol) and toluene (0.4 mL) were then added at room temperature. After the mixture was stirred for 10 min, a solution of homoallyl alcohol **1b** (0.10 g, 0.48 mmol) and 1-bromonaphthalene (0.083 g, 0.40 mmol) in toluene (2.0 mL) was added at ambient temperature. The resulting mixture was heated at reflux for 3 h. After the resulting mixture was cooled to room temperature, water (20 mL) was added. The product was extracted with hexane/ethyl acetate = 5:1 three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Silica gel column purification provided *tert*-butyldimethyl[3-(1-naphthyl)-1-propenyl]silane (**3a**, 0.11 g, 0.37 mmol, *E*/*Z* = 95:5, 93%) as a colorless oil.

Typical procedure for the synthesis of (*E*)-1-aryl-2-alkenylsilanes

The volume of the solvent is very important in the reactions with **4a**. Reaction conditions of each aryl bromide are showed in the next page. The reactions of **4b**-**4e** were performed with 0.17 M.



entry	2	Pd (mol%) / Ligand (mol%)	Ligand	conc. of **2** (mmol/mL)	time (h)
1	**2a**	5/20	PPh_3	0.50	4
2	**2b**	2.5/10	P(*p*-tol)$_3$	0.50	4
3	**2c**	5/20	P(*p*-tol)$_3$	0.50	4
4	**2d**	5/20	P(*p*-tol)$_3$	0.17	15
5	**2e**	2.5/10	PPh_3	0.17	12
6	**2f**	5/10	P(*p*-tol)$_3$	0.067	12
7	**2g**	5/10	P(*c*-Hex)Ph_2	0.50	4

Cesium carbonate (0.19 g, 0.58 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. The cesium carbonate was dried by the same procedure mentioned above. Palladium acetate (4.5 mg, 0.020 mmol) and triphenylphosphine (0.021 g, 0.080 mmol) were added in the reaction flask. The flask was filled with argon by using the

standard Schlenk technique. Toluene (0.2 mL) was added at room temperature and the mixture was stirred for 10 min. Toluene (0.6 mL), homoallyl alcohol **4a** (0.10 g, 0.48 mmol), and 1-bromonaphthalene (0.083 g, 0.40 mmol) were added to the yellow solution obtained at ambient temperature. The resulting mixture was then heated at reflux for 4 h. After the resulting mixture was cooled to room temperature, water (20 mL) was added. Extractive workup followed by silica gel column purification afforded *tert*-butyldimethyl[1-(1-naphthyl)allyl]silane (**5aa**, 0.099 g, 0.35 mmol, 88%) as a colorless oil. The product was contaminated with 2% of **3a**.

Typical procedure for chirality transfer from optically active (*S*)-4d to (*E*)-1-aryl-2-butenylsilanes

Dried cesium carbonate (0.20 g, 0.60 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. Palladium acetate (5.6 mg, 0.025 mmol) and triphenylphosphine (0.026 g, 0.10 mmol) were added in the reaction flask. The flask was filled with argon by using the standard Schlenk technique. Toluene (1.0 mL) was added at room temperature and the mixture was stirred for 10 min to obtain a yellow solution. A solution of **(*S*)-4d** (0.12 g, 0.50 mmol) and 1-bromonaphthalene (0.10 g, 0.60 mmol) in toluene (2.0 mL) was added at ambient temperature. The resulting mixture was then heated at reflux for 8 h. After the resulting mixture was cooled to room temperature, water (20 mL) was added. Extraction, evaporation, column purification on neutral silica gel gave (*E*)-dimethyl[1-(1-naphthyl)-2-butenyl]phenylsilane (**5ad**, 0.15 g, 0.46 mmol, 92%) as a colorless oil.

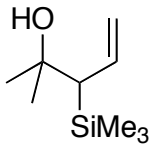
p-Toluenesulfonyl hydrazide (0.931 g, 5.00 mmol) was added to a 30-mL two-necked reaction flask equipped with a Dimroth condenser. Under argon atmosphere, (*E*)-dimethyl[1-(1-naphthyl)-2-butenyl]phenylsilane (**5ad**, 0.46 mmol), dioxane (5.55 mL), and triethylamine (0.697 mL, 5.00 mmol) were sequentially added to the reaction flask at room temperature. The resulting mixture was then refluxed for 10 h. After the mixture was cooled to room tempeature, water was added. The mixture was extracted (hexane/ethyl acetate = 30:1) three times and dried over sodium sulfate. The combined organic layer was then concentrated in vacuo. The residue was purified by gel permeation chromatography. The hydrogenated product was obtained as a colorless oil (0.13 g, 0.39 mmol, 85%).

A 20-mL two-necked reaction flask containing the reduced product (0.13 g, 0.39 mmol) was filled with argon. Trifluoroacetic acid (1.95 mL) was added at ambient temperature. After stirring for 1 h, the solvent was removed in vacuo. Methanol (0.78 mL), potassium hydrogenfluoride (0.122 g, 1.56 mmol), tetrabutylammonium fluoride (1.0 M THF solution, 0.78 mL, 0.8 mmol), aqueous 30% hydrogen peroxide (ca. 0.47 mL, 5.8 mmol), and potassium hydrogencarbonate

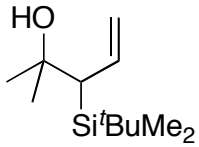
(0.331 g, 3.31 mmol) were sequentially added at room temperature. The resulting mixture was then heated at 50 °C for 30 min. The reaction was quenched with saturated sodium thiosulfate solution (15 mL). Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 5:1) provided 1-(1-naphthyl)-1-butanol (**6ad**, 0.14 mmol, 36%) as a colorless oil. The reaction conditions were not optimized.

Characterization Data for New Compounds

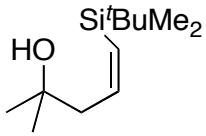
2-Methyl-3-trimethylsilyl-4-penten-2-ol (1a): IR (neat) 3444, 2970, 1625, 1370, 1249, 1156, 901, 857, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 1.25 (s, 3H), 1.28 (s, 3H), 1.64 (s, 1H), 1.83 (d, *J* = 11.5 Hz, 1H), 4.96 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.06 (dd, *J* = 10.0 2.0 Hz, 1H), 5.76 (ddd, *J* = 17.0, 11.5, 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –0.34, 30.08, 30.24, 50.54, 72.88, 116.59, 136.96. Found: C, 62.43; H, 11.88%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.



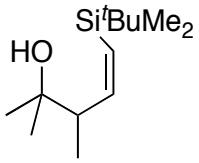
3-(*tert*-Butyldimethylsilyl)-2-methyl-4-penten-2-ol (1b): IR (neat) 3463, 3074, 2930, 2857, 1626, 1465, 1364, 1334, 1250, 1155, 1117, 1008, 904, 826, 801, 766, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 1.24 (s, 3H), 1.28 (s, 3H), 1.84 (s, 1H), 2.01 (d, *J* = 11.5 Hz, 1H), 5.03 (dd, *J* = 17.0, 2.5 Hz, 1H), 5.12 (dd, *J* = 10.0, 2.5 Hz, 1H), 5.81 (ddd, *J* = 17.0, 11.5, 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.88, –2.79, 18.27, 27.39, 29.85, 30.01, 46.45, 72.49, 117.89, 138.64. Found: C, 67.28; H, 12.12%. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22%.



(*Z*)-5-(*tert*-Butyldimethylsilyl)-2-methyl-4-penten-2-ol (4a): IR (neat) 3351, 2955, 2928, 2884, 2857, 1607, 1472, 1463, 1249, 826, 812, 772 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6H), 0.89 (s, 9H), 1.24 (s, 6H), 1.44 (bs, 1H), 2.33 (dd, *J* = 7.5, 1.5 Hz, 2H), 5.70 (dt, *J* = 14.5, 1.5 Hz, 1H), 6.39 (dt, *J* = 14.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.70, 17.07, 26.62, 29.54, 47.23, 70.82, 130.17, 144.76. Found: C, 67.02; H, 12.49%. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22%.



(*Z*)-5-(*tert*-Butyldimethylsilyl)-2,3-dimethyl-4-penten-2-ol (4b): IR (neat) 3389, 2955, 2929, 2857, 1608, 1463, 1363, 1251, 1140, 826, 811, 779 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.89 (s, 9H), 1.00 (d, *J* = 6.5 Hz, 3H), 1.17 (s, 3H), 1.19 (s, 3H), 1.45 (s, 1H), 2.39 (dq, *J* = 10.5, 6.5 Hz, 1H), 5.62 (d, *J* = 14.0 Hz, 1H), 6.30 (dd, *J* = 14.0, 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.60, –3.53, 16.42, 16.79, 26.62, 26.93, 27.37, 48.41, 72.44, 128.13, 151.13. Found: C, 68.08; H, 12.43%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.



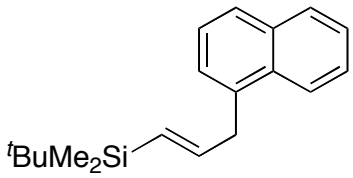
(*Z*)-2,3-Dimethyl-5-trimethylsilyl-4-penten-2-ol (4c): IR (neat) 3394, 2968, 2900, 1601, 1374, 1248, 837, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9H), 1.00 (d, *J* = 7.0 Hz, 3H), 1.17, (s, 3H), 1.19 (s, 3H), 1.45 (bs, 1H), 2.39, (dq, *J* = 11.0, 7.0 Hz, 1H), 5.59 (d, *J* = 14.0 Hz, 1H), 6.22 (dd, *J* = 14.0, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.68, 16.27, 27.03, 27.27, 48.68, 72.43, 131.13, 150.30. Found: C, 64.27; H, 11.68%. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90%.

(*Z*)-5-(Dimethylphenylsilyl)-2,3-dimethyl-4-penten-2-ol (4d): IR (neat) 3402, 2970, 2936, 1605, 1373, 1248, 1112, 835, 821, 784, 731, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 0.89 (d, *J* = 6.5 Hz, 3H, 1.06 (s, 6H), 1.20 (s, 1H), 2.29 (dq, *J* = 10.5, 6.5 Hz, 1H), 5.74 (d, *J* = 14.5 Hz, 1H), 6.33 (dd, *J* = 14.5, 10.5 Hz, 1H), 7.34–7.37 (m, 3H), 7.54–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.66, –0.52, 16.02, 26.62, 27.41, 48.48, 72.43, 128.06, 128.86, 129.20, 133.96, 139.86, 151.98. Found: C, 72.71; H, 10.00%. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74%.

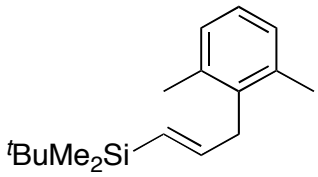
(*Z*)-2-Methyl-3-[2-(trimethylsilyl)ethenyl]-2-heptanol (4e): IR (neat) 3404, 2957, 2933, 2900, 2861, 1610, 1462, 1378, 1247, 1135, 838, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 0.89 (t, *J* = 7.0 Hz, 3H), 1.13 (s, 3H), 1.10–1.17 (m, 2H), 1.20 (s, 3H), 1.24–1.38 (m, 3H), 1.51–1.57 (m, 1H), 1.61 (bs, 1H), 2.18 (td, *J* = 10.5, 2.0 Hz, 1H), 5,72 (d, *J* = 14.5 Hz, 1H), 6.06 (dd, *J* = 14.5, 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.86, 14.23, 23.23, 26.75, 27.57, 30.03, 30.84, 54.50, 72.26, 133.89, 148.96. Found: C, 68.07; H, 12.49%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

(*E*)-Trimethyl[3-(1-naphthyl)-1-propenyl]silane (3a'): IR (neat) 3045, 2955, 2897, 1612, 1597, 1396, 1248, 991, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 3.91 (dd, *J* = 6.0, 1.5 Hz, 2H), 5.76 (dt, *J* = 18.0, 1.5 Hz, 1H), 6.28 (dt, *J* = 18.0, 6.0 Hz, 1H), 7.34–7.36 (m, 1H), 7.41–7.45 (m, 1H), 7.47–7.55 (m, 2H), 7.74–7.76 (m, 1H), 7.85–7.88 (m, 1H), 8.01–8.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –1.01, 40.56, 124.46, 125.71, 125.83, 125.93, 126.64, 127.11, 128.83, 132.06, 132.33, 134.03, 136.42, 144.79. Found: C, 79.67; H, 8.65%. Calcd for $C_{16}H_{20}Si$: C, 79.93; H, 8.38%.

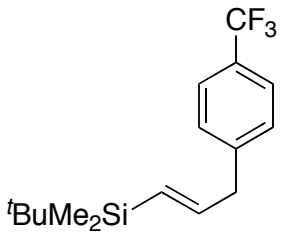
(*E*)-*tert*-Butyldimethyl[3-(1-naphthyl)-1-propenyl]silane (3a): IR (neat) 3045, 2926, 2855, 1611, 1597, 1581, 1511, 1463, 1397, 1361, 1247, 1008, 991, 828, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 6H), 0.85 (s, 9H), 3.93 (dd, *J* = 6.0, 1.5 Hz, 2H), 5.76 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.29 (dt, *J* = 18.5, 6.0 Hz, 1H), 7.33–7.35 (m, 1H), 7.42–7.45 (m, 1H), 7.47–7.52 (m, 2H), 7.75–7.76 (m, 1H), 7.86–7.88 (m, 1H), 8.03–8.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –5.93, 16.77, 26.64, 40.87, 124.55, 125.71, 125.81, 125.89, 126.59, 127.12, 128.79, 129.23, 132.32, 134.01, 136.42, 146.23. Found: C, 81.07; H, 9.43%. Calcd for $C_{19}H_{26}Si$: C, 80.78; H, 9.28%.



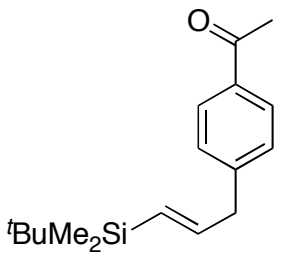
(*E*)-*tert*-Butyl[3-(2,6-dimethylphenyl)-1-propenyl]dimethylsilane (3b): IR (neat) 2927, 2856, 1615, 1464, 1248, 989, 826, 810, 766 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.02 (s, 6H), 0.83 (s, 9H), 2.29 (s, 6H), 3.49 (dd, *J* = 5.5, 2.0 Hz, 2H), 5.50 (dt, *J* = 18.5, 2.0 Hz, 1H), 6.08 (dt, *J* = 18.5, 5.5 Hz, 1H), 7.02–7.07 (m, 3H); ^{13}C NMR ($CDCl_3$) δ –5.93, 16.75, 20.14, 26.66, 37.02, 126.15, 127.42, 128.13, 136.42, 137.03, 144.34. Found: C, 78.14; H, 11.07%. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83%.



(*E*)-*tert*-Butyl[3-(4-trifluoromethylphenyl)-1-propenyl]dimethylsilane (3c): IR (neat) 2954, 2929, 2856, 1326, 1165, 1127, 1106, 1069, 858, 826, 811, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.87 (s, 9H), 3.51 (d, *J* = 6.0 Hz, 2H), 5.73 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.12 (dt, *J* = 18.5, 6.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.90, 16.73, 26.65, 43,35, 124.58 (q, *J* = 272.2 Hz), 125.55 (q, *J* = 3.8 Hz), 128.65 (q, *J* = 32.2 Hz), 129.18, 130.18, 144.44 (q, *J* = 1.0 Hz), 145.32. Found: C, 63.82; H, 7.94%. Calcd for $C_{16}H_{23}F_3Si$: C, 63.97; H, 7.72%.



(*E*)-1-{4-[3-(*tert*-Butyldimethylsilyl)-2-propenyl]phenyl}ethanone (3d): IR (neat) 2953, 2927, 2855, 1687, 1606, 1360, 1267, 1248, 826, 812, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.86 (s, 9H), 2.59 (s, 3H), 3.52 (dd, *J* = 6.5, 1.5 Hz, 2H), 5.72 (dt, *J* = 18.0, 1.5 Hz, 1H), 6.13 (dt, *J* = 18.0, 6.5 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.92, 16.74, 26.64, 26.80, 43.53, 128.81, 129.11, 130.04, 135.44, 145.33, 146.10, 198.11. Found: C, 74.58; H, 9.78%. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55%.



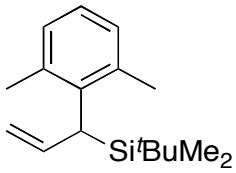
(*E*)-4-[3-(*tert*-Butyldimethylsilyl)-2-propenyl]benzaldehyde (3e): IR (neat) 2953, 2927, 2883, 2855, 1704, 1699, 1605, 1471, 1248, 1211, 1168, 827, 811, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.86 (s, 9H), 3.54 (dd, *J* = 6.0, 1.0 Hz, 2H), 5.73 (dt, *J* = 18.5, 1.0 Hz, 1H), 6.13 (dt, *J* = 18.5, 6.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 9.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –5.93, 16.73, 26.62, 43.71, 129.57, 130.23, 130.38, 134.86, 145.01, 147.74, 192.27. Found: C, 73.60; H, 9.33%. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.29%.

Ethyl (*E*)-4-[3-(*tert*-butyldimethylsilyl)-2-propenyl]benzoate (3f): IR (neat) 2928, 2855, 1721, 1609, 1275, 1100, 828, 808, 779, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 6H), 0.86 (s, 9H), 1.39 (t, *J* = 7.0 Hz, 3H), 3.51 (dd, *J* = 6.0, 1.5 Hz, 2H), 4.36 (q, *J* = 7.0 Hz, 2H), 5.71 (dt, *J* = 18.0, 1.5 Hz, 1H), 6.13 (dt, *J* = 18.0, 6.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.92, 14.57, 16.74, 26.64, 43.54, 61.03, 128.57, 128.89, 129.86, 129.94, 145.52, 145.67, 166.89. Found: C, 70.71; H, 9.22%. Calcd for $C_{18}H_{28}OSi$: C, 71.00; H, 9.27%.

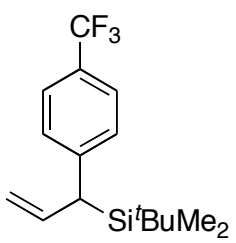
(*E*)-*tert*-Butyl[3-(4-methoxyphenyl)-1-propenyl]dimethylsilane (3g): IR (neat) 2953, 2927, 2885, 2854, 1615, 1511, 1464, 1248, 1176, 1040, 857, 827, 811, 777 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 6H), 0.86 (s, 9H), 3.40 (dd, *J* = 6.5, 1.5 Hz, 2H), 3.79 (s, 3H), 5.68 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.13 (dt, *J* = 18.5, 6.5 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.87, 16.75, 26.67, 42.77, 55.47, 114.00, 128.45, 129.81, 132.36, 147.10, 158.10. Found: C, 73.28; H, 10.08%. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98%.

***tert*-Butyldimethyl[1-(1-naphthyl)-2-propenyl]silane (5aa):** IR (neat) 3048, 2929, 2856, 1626, 1471, 1464, 1392, 1363, 1250, 1080, 901, 824, 782, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 3H), 0.15 (s, 3H), 0.88 (s, 9H), 4.06 (d, *J* = 10.0 Hz, 1H), 5.01 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.05 (dd, *J* = 16.5, 1.5 Hz, 1H), 6.34 (dt, *J* = 16.5, 10.0 Hz, 1H), 7.35–7.36 (m, 1H), 7.40–7.51 (m, 3H), 7.63–7.65 (m, 1H), 7.83–7.84 (m, 1H), 8.09–8.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –6.76, –6.00, 18.41, 27.44, 35.11, 113.71, 123.80, 125.08, 125.49 (overrapped 2C), 125.53, 125.64, 129.20, 131.46, 134.43, 139.76, 140.00. Found: C, 80.86; H, 9.30%. Calcd for $C_{19}H_{26}Si$: C, 80.78; H, 9.28%.

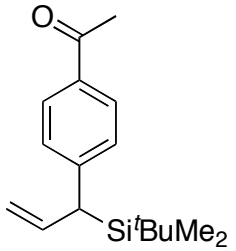
***tert*-Butyl[1-(2,6-dimethylphenyl)-2-propenyl]dimethylsilane (5ba):** IR (neat) 3071, 2956, 2929, 2857, 1622, 1464, 1252, 902, 856, 832, 822, 807, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.25 (s, 3H), 0.23 (s, 3H), 0.94 (s, 9H), 2.28 (s, 3H), 2.34 (s, 3H), 3.68 (dt, *J* = 6.5, 2.0 Hz, 1H), 4.74 (dt, *J* = 16.5, 2.0 Hz, 1H), 4.92 (dt, *J* = 10.0, 2.0 Hz, 1H), 6.17 (ddd, *J* = 16.5, 10.0, 6.5 Hz, 1H), 6.94–7.03 (m, 3H); ^{13}C NMR ($CDCl_3$) δ –5.69, –4.39 18.48, 22.21, 22.60, 27.19, 34.16, 113.35, 125.05, 128.53, 129.38, 136.16, 136.73, 137.93, 139.69. Found: C, 78.35; H, 11.07%. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83%.



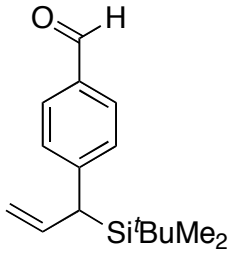
***tert*-Butyl[1-(4-trifluoromethylphenyl)-2-propenyl]dimethylsilane (5ca):** IR (neat) 2931, 2859, 1615, 1326, 1253, 1164, 1125, 1106, 1070, 1017, 905, 858, 837, 822, 803, 782 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.13 (s, 3H), 0.06 (s, 3H), 0.83 (s, 9H), 3.21 (d, *J* = 10.0 Hz, 1H), 5.00 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.00 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.17 (dt, *J* = 17.0, 10.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.96, –6.50, 18.21, 27.21, 42.50, 113.97, 124.66 (q, *J* = 271.7 Hz), 125.48 (q, *J* = 3.9 Hz), 127.28 (q, *J* = 32.1 Hz), 128.08, 138.49, 147.81 (q, *J* = 1.5 Hz); ^{19}F NMR ($CDCl_3$) δ –62.72. Found: C, 64.21; H, 7.85%. Calcd for $C_{16}H_{23}F_3Si$: C, 63.97; H, 7.72%.



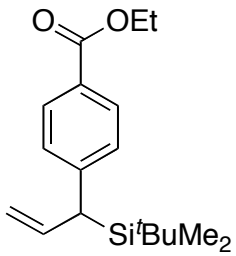
1-{4-[1-(*tert*-Butyldimethylsilyl)-2-propenyl]phenyl}ethanone (5da): IR (neat) 2957, 2929, 2883, 2857, 1684, 1602, 1406, 1359, 1271, 1252, 1181, 858, 836, 823, 803, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.13 (s, 3H), 0.06 (s, 3H), 0.83 (s, 9H), 2.57 (s, 3H), 3.22 (d, *J* = 10.0 Hz, 1H), 4.90 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.91 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.19 (dt, *J* = 17.0, 10.0 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.90, –6.49, 18.28, 26.65, 27.21, 42.96, 113.92, 127.97, 128.83, 134.25, 138.39, 149.70, 197.89. Found: C, 74.15; H, 9.66%. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55%.



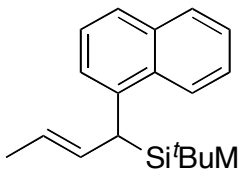
4-[1-(*tert*-Butyldimethylsilyl)-2-propenyl]benzaldehyde (5ea): IR (neat) 2929, 2857, 1699, 1602, 1250, 1215, 1168, 834, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.12 (s, 3H), 0.07 (s, 3H), 0.83 (s, 9H), 3.26 (d, *J* = 10.0 Hz, 1H), 5.01 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.01 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.19 (dt, *J* = 17.0, 10.0 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 9.94 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –6.91, –6.49, 18.31, 27.19, 43.31, 114.19, 128.40, 130.21, 133.77, 138.11, 151.46, 192.01. Found: C, 73.60; H, 9.48%. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.29%.



Ethyl 4-[1-(*tert*-butyldimethylsilyl)-2-propenyl]benzoate (5fa): IR (neat) 3077, 2930, 2857, 1717, 1607, 1464, 1408, 1367, 1277, 1252, 1178, 1101, 1021, 822, 803, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.13 (s, 3H), 0.05 (s, 3H), 0.82 (s, 9H), 1.38 (t, *J* = 7.5 Hz, 3H), 3.21 (d, *J* = 9.5 Hz, 1H), 4.35 (q, *J* = 7.5 Hz, 2H), 4.98–5.01 (m, 2H), 6.15–6.22 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.91, –6.55, 14.58, 18.26, 27.20, 42.88, 60.92, 113.78, 127.21, 127.78, 129.92, 138.53, 149.14, 166.93. Found: C, 70.79; H, 9.39%. Calcd for $C_{18}H_{28}O_2Si$: C, 71.00; H, 9.27%.

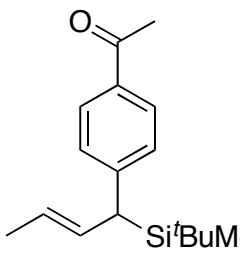


***tert*-Butyl[1-(4-methoxyphenyl)-2-propenyl]dimethylsilane (5ga):** IR (neat) 2955, 2929, 2883, 2856, 2835, 1626, 1511, 1464, 1298, 1248, 1178, 1040, 899, 823, 806, 785, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.11 (s, 3H), 0.04 (s, 3H), 0.81 (s, 9H), 3.06 (d, *J* = 10.0 Hz, 1H), 3.78 (s, 3H), 4.93 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.94 (dd, *J* = 17.0, 2.0 Hz, 1H), 6.14 (dt, *J* = 17.0, 10.0 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.74, –6.57, 18.10, 27.25, 41.08, 55.45, 112.73, 114.05, 128.88, 135.20, 139.95, 157.25. Found: C, 73.39; H, 10.10%. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98%.

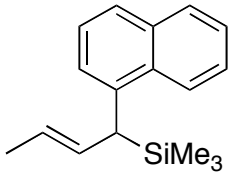


(*E*)-*tert*-Butyldimethyl[1-(1-naphthyl)-2-butenyl]silane (5ab): IR (neat) 3046, 2956, 2928, 2882, 2855, 1471, 1463, 1392, 1256, 1248, 1082, 966, 835, 826, 806, 791, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.35 (s, 3H), 0.11 (s, 3H), 0.88 (s, 9H), 1.68 (dd, *J* = 6.5, 1.5 Hz, 3H), 4.00 (d, *J* = 10.0 Hz, 1H), 5.49 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.95 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.32–7.34 (m, 1H), 7.40–7.50 (m, 3H), 7.61–7.62 (m, 1H), 7.81–7.83 (m, 1H), 8.08–8.10 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –6.98, –5.90, 18.26, 18.29, 27.44, 33.42, 123.89, 124.53, 124.78, 125.23, 125.42, 125.52, 125.58, 129.16, 131.39, 132.19, 134.38, 140.78. Found: C, 81.17; H, 9.69%. Calcd for $C_{20}H_{28}Si$: C, 81.01; H, 9.52%.

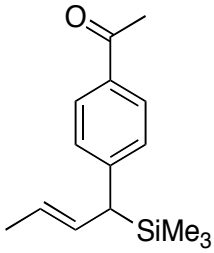
(*E*)-1-{4-[1-(*tert*-Butyldimethylsilyl)-2-butenyl]phenyl}ethanone (5db): IR (neat) 2958, 2929, 2882, 2856, 1682, 1602, 1359, 1270, 1249, 1179, 834, 823, 803 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.16 (s, 3H), 0.02 (s, 3H), 0.83 (s, 9H), 1.68 (dd, *J* = 7.0, 1.5 Hz, 3H), 2.56 (s, 3H), 3.16 (d, *J* = 10.0 Hz, 1H), 5.43 (dq, *J* = 15.0, 7.0 Hz, 1H), 5.80 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –7.12, –6.42, 18.17, 18.25, 26.67, 27.21, 41.27, 124.91, 127.80, 128.77, 130.51, 134.02, 150.63, 197.96. Found: C, 74.70; H, 9.52%. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78%.



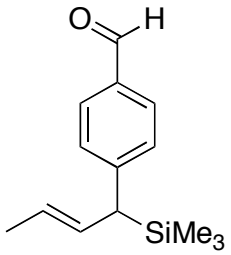
(*E*)-Trimethyl[1-(1-naphthyl)-2-butenyl]silane (5ac): IR (neat) 3046, 2959, 2898, 1511, 1393, 1249, 1086, 964, 838, 794, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.03 (s, 9H), 1.72 (dd, *J* = 6.5, 1.5 Hz, 3H), 3.80 (d, *J* = 9.5 Hz, 1H), 5.49 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.94 (ddq, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.32–7.34 (m, 1H), 7.41–7.49 (m, 3H), 7.62–7.63 (m, 1H), 7.82–7.84 (m, 1H), 8.05–8.07 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –2.28, 18.34, 36.55, 123.96, 124.01, 124.13, 125.15, 125.40, 125.42, 125.60, 129.06, 130.07, 131.61, 134.32, 139.99. Found: C, 80.20; H, 8.66%. Calcd for $C_{17}H_{22}Si$: C, 80.25; H, 8.72%.



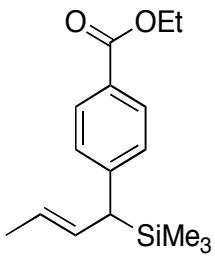
(*E*)-1-[4-(1-Trimethylsilyl-2-butenyl)phenyl]ethanone (5dc): IR (neat) 2959, 1683, 1603, 1414, 1358, 1271, 1249, 1179, 962, 866, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.05 (s, 9H), 1.72 (dd, *J* = 6.5, 1.5 Hz, 3H), 2.57 (s, 3H), 2.99 (d, *J* = 10.0 Hz, 1H), 5.43 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.80 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.84, 18.34, 26.67, 43.82, 124.71, 127.24, 128.73, 129.12, 133.95, 149.84, 198.00. Found: C, 73.27; H, 9.19%. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00%.



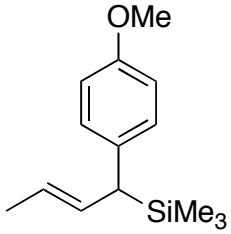
(*E*)-4-(1-Trimethylsilyl-2-butenyl)benzaldehyde (5ec): IR (neat) 2959, 1700, 1602, 1570, 1249, 1213, 1168, 843, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.04 (s, 9H), 1.72 (dd, *J* = 6.5, 1.5 Hz, 3H), 3.02 (d, *J* = 10.0 Hz, 1H), 5.45 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.81 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 9.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –2.85, 18.34, 44.20, 124.98, 127.67, 128.84, 130.13, 133.49, 151.63, 192.12. Found: C, 72.07; H, 8.77%. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67%.



Ethyl (*E*)-4-(1-trimethylsilyl-2-butenyl)benzoate (5fc): IR (neat) 2960, 1718, 1607, 1367, 1276, 1249, 1178, 1101, 869, 839, 708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.06 (s, 9H), 1.38 (t, *J* = 7.5 Hz, 3H), 1.71 (dd, *J* = 6.0, 1.5 Hz, 3H), 2.98 (d, *J* = 10.0 Hz, 1H), 4.35 (q, *J* = 7.5 Hz, 2H), 5.43 (dq, *J* = 15.0, 6.0 Hz, 1H), 5.80 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.86, 14.59, 18.34, 43.72, 60.87, 124.55, 126.88, 127.07, 129.29, 129.80, 149.28, 167.03. Found: C, 69.27; H, 8.73%. Calcd for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75%.

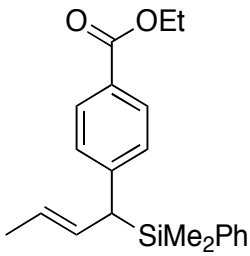


(*E*)-[1-(4-Methoxyphenyl)-2-butenyl]trimethylsilane (5gc): IR (neat) 2956, 2834, 1611, 1509, 1247, 1178, 1039, 868, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.06 (s, 9H), 1.69 (dd, *J* = 6.0, 1.5 Hz, 3H), 2.80 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 5.38 (dq, *J* = 15.0, 6.0 Hz, 1H), 5.74 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.74, 18.34, 41.80, 55.46, 113.94, 123.49, 128.18, 130.81, 135.41, 156.99. Found: C, 71.60; H, 9.46%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

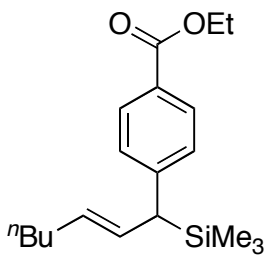


(*E*)-Dimethyl[1-(1-naphthyl)-2-butenyl]phenylsilane (5ad): IR (neat) 3047, 3013, 2959, 2915, 2853, 1427, 1393, 1248, 1114, 833, 809, 794, 777, 732, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 3H), 0.23 (s, 3H), 1.68 (ddd, *J* = 6.5, 1.5, 1.0 Hz, 3H), 3.98 (d, *J* = 9.5 Hz, 1H), 5.39 (dqd, *J* = 15.0, 6.5, 1.0 Hz, 1H), 5.86 (ddq, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.14–7.15 (m, 1H), 7.27–7.33 (m, 2H), 7.33–7.43 (m, 6H), 7.61–7.62 (m, 1H), 7.80–7.81 (m, 1H), 7.97–7.99 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –4.35, –3.38, 18.28, 36.27, 123.88, 124.44, 124.57, 125.34, 125.35, 125.38, 125.48, 127.64, 128.98, 129.23, 130.74, 131.62, 134.24, 134.55, 137.55, 139.27. Found: C, 83.21; H, 7.57%. Calcd for $C_{22}H_{24}Si$: C, 83.48; H, 7.64%.

Ethyl (*E*)-4-[1-(dimethylphenylsilyl)-2-butenyl]benzoate (5fd): IR (neat) 2960, 1715, 1607, 1276, 1249, 1178, 1101, 831, 809, 736, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.24 (s, 3H), 1.38 (t, *J* = 7.0 Hz 3H), 1.68 (dd, *J* = 6.5, 1.5 Hz, 3H), 3.15 (d, *J* = 10.0 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 5.37 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.73 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.30–7.31 (m, 4H), 7.34–7.38 (m, 1H), 7.85 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –4.52, –4.29, 14.58, 18.29, 43.43, 60.88, 125.02, 126.96, 127.36, 127.73, 129.04, 129.45, 129.63, 134.50, 136.59, 148.53, 167.04. Found: C, 74.25; H, 7.73%. Calcd for $C_{21}H_{26}O_2Si$: C, 74.51; H, 7.74%.

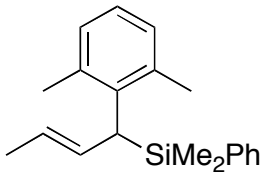


Ethyl (*E*)-4-[1-(trimethylsilyl)-2-heptenyl]benzoate (5fe): IR (neat) 2958, 2929, 2859, 1718, 1608, 1276, 1249, 1177, 1104, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.05 (s, 9H), 0.89 (t, *J* = 7.5 Hz, 3H), 1.28–1.37 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 3H), 2.05 (td, *J* = 7.0, 6.5 Hz, 2H), 2.89 (d, *J* = 9.5 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 5.41 (dt, *J* = 15.0, 6.5 Hz, 1H), 5.77 (ddt, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.86, 14.15, 14.59, 22.41, 32.21, 32.71, 43.68, 60.86, 126.86, 127.06, 128.10, 129.79, 130.25, 149.34, 167.03. Found: C, 71.59; H, 9.34%.

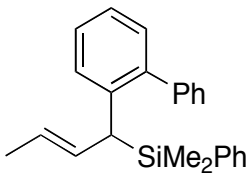


Calcd for $C_{19}H_{30}O_2Si$: C, 71.64; H, 9.49%.

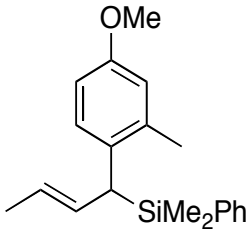
(*E*)-[1-(2,6-Dimethylphenyl)-2-butenyl]dimethylphenylsilane (5bd): IR (neat) 3069, 3017, 2957, 2915, 1427, 1249, 1112, 830, 813, 767, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 3H), 0.35 (s, 3H), 1.65 (dt, *J* = 6.5, 1.5 Hz, 3H), 2.15 (s, 3H), 2.22 (s, 3H), 3.72 (d, *J* = 8.0 Hz, 1H), 5.27 (dqd, *J* = 15.0, 6.5, 1.5 Hz, 1H), 5.83 (ddq, *J* = 15.0, 8.0, 1.5 Hz, 1H), 6.90–6.94 (m, 3H), 7.30–7.37 (m, 3H), 7.43–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –2.33, –2.00, 18.20, 22.29, 22.64, 36.88, 124.76, 124.83, 127.84, 128.33, 129.11, 129.46, 129.54, 134.06, 135.88, 136.13, 139.61, 140.02. Found: C, 81.53; H, 9.00%. Calcd for $C_{20}H_{26}Si$: C, 81.56; H, 8.90%.



(*E*)-[1-(2-Phenylphenyl)-2-butenyl]dimethylphenylsilane (5hd): IR (neat) 3056, 3020, 2958, 2915, 1476, 1427, 1245, 831, 748, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.15 (s, 3H), 1.67 (dd, *J* = 6.0, 1.5 Hz, 3H), 3.33 (d, *J* = 9.5 Hz, 1H), 5.22 (dq, *J* = 15.0, 6.0 Hz, 1H), 5.71 (ddq, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.04–7.09 (m, 2H), 7.10–7.13 (m, 3H), 7.17–7.18 (m, 2H), 7.20–7.26 (m, 3H), 7.29–7.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –4.42, –3.50, 18.27, 37.88, 123.56, 124.60, 126.73, 127.23, 127.60, 128.13 (overrapped, 2C), 129.09, 129.70, 130.47, 131.59, 134.44, 137.71, 140.20, 141.53, 142.25. Found: C, 84.35; H, 7.89%. Calcd for $C_{24}H_{26}Si$: C, 84.15; H, 7.65%.



(*E*)-[1-(4-Methoxy-2-methylphenyl)-2-butenyl]dimethylphenylsilane (5id): IR (neat) 2956, 2914, 1608, 1500, 1427, 1253, 1196, 1113, 1049, 849, 830, 818, 737, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.28 (s, 3H), 1.65 (ddd, *J* = 6.5, 1.5, 1.0 Hz, 3H), 2.05 (s, 3H), 3.22 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 5.28 (dqd, *J* = 15.0, 6.5, 1.0 Hz, 1H), 5.66 (ddq, *J* = 15.0, 9.0, 1.5 Hz, 1H), 6.63–6.66 (m, 2H), 6.87–6.89 (m, 1H), 7.28–7.31 (m, 2H), 7.34–7.37 (m, 3H); ^{13}C NMR ($CDCl_3$) δ –4.50, –3.74, 18.26, 20.62, 26.35, 55.36, 111.24, 116.08, 123.85, 127.63, 128.19, 129.17, 131.17, 133.15, 134.47, 136.34, 137.92, 156.65. Found: C, 77.42; H, 8.68%. Calcd for $C_{20}H_{26}OSi$: C, 77.36; H, 8.44%.



Methyl (*E*)-4-(1-dimethylphenysilyl-2-butenyl)-3-methylbenzoate (5jd): IR (neat) 2953, 2916, 1720, 1608, 1436, 1428, 1292, 1270, 1249, 1211, 1143, 1113, 831, 812, 768, 737, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 3H), 0.29 (s, 3H), 1.68 (dd, J = 6.0, 1.5 Hz, 3H), 2.08 (s, 3H), 3.37 (d, J = 9.0 Hz, 1H), 3.89 (s, 3H), 5.35 (dq, J = 6.0, 1.5 Hz, 1H), 5.72 (ddq, J = 15.0, 9.0, 1.5 Hz, 1H), 7.01–7.03 (m, 1H), 7.28–7.31 (m, 4H), 7.33–7.37 (m, 1H), 7.74–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.66, –4.08, 18.26, 20.34, 38.33, 52.05, 124.88, 126.20, 126.99, 127.18, 127.74, 129.46, 129.86, 131.63, 134.39, 135.02, 136.90, 147.16, 167.65. Found: C, 74.58; H, 7.60%. Calcd for $C_{21}H_{26}O_2Si$: C, 74.51; H, 7.74%.

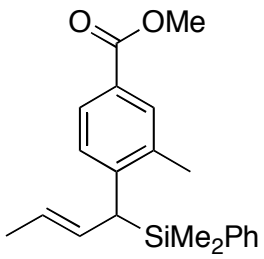


Table S1. Conditions for determining the enantiomeric excesses of **6**

6	column	eluent hexane/*i*-PrOH	Flow /mL•min^{-1}	Retention time /min *S*, major	*R*, minor
6ad	AD-H	95/5	1.5	6.62	7.62
6bd	OD-H	95/5	1.0	5.14	6.00
6hd	OD-H	95/5	1.0	5.19	5.83
6id	OD-H	95/5	1.0	7.61	8.79
6jd	AD-H	95/5	1.5	9.58	8.78
6kd	OD-H	98/2	1.2	9.74	8.72

References and Notes

(1) (a) Miura, K., Hosomi, A., In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004, Vol. 2, Chapter 10. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-VCH: New York, 2000. (c) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063–2192. (d) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375–1408. (e) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, 3173–3199.

(2) Very recent selected examples: (a) Terao, J.; Kambe, N. *Chem. Rec.* **2007**, *7*, 57–67. (b) Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 6094–6095. (c) Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 3070–3071. (d) Perrone, S.; Knochel, P. *Org. Lett.* **2007**, *9*, 1041–1044. (e) Kacprzynski, M. A.; May, T. L.; Kazane, S. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4554–4558. (f) Ohmura, T.; Taniguchi, H.; Suginome, M. *J. Am. Chem. Soc.* **2006**, *128*, 13682–13683. (g) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17644–17655. (h) Schmidtmann, E. S.; Oestrich, M. *Chem. Commun.* **2006**, 3643–3645.

(3) (a) Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2006**, *128*, 2210–2211. (b) Iwasaki, M.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4463–4469. (c) Iwasaki, M.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Tetrahedron* **2007**, *63*, 5200–5203.

(4) Examples of palladium-catalyzed carbon-carbon bond cleavage of tertiary alcohols are summarized: Muzart, J. *Tetrahedron* **2005**, *61*, 9423–9463.

(5) The regioselectivity of each reaction was greater than 99:1. One exception is the reaction in entry 6, Table 1, wherein the regioselectivity was 98:2. We assume that the bulky silyl groups would accelerate the reductive elimination steps and that the conceivable isomerization of the σ-allyl(aryl)palladium intermediates scarcely took place.

(6) When allylsilane having an aryl or an isopropoxy group on the silicon was employed, decomposition of the allylsilane was observed and no coupling products were obtained.

(7) Suginome, M.; Iwanami, T.; Ohmori, Y.; Matsumoto, A.; Ito, Y. *Chem. Eur. J.* **2005**, *11*, 2954–2965.

(8) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2789–2834.

(9) Nakagawa, T.; Kasatkin, A.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3207–3210.

(10) Fürstner, A.; Kattnig, E.; Lepage, O. *J. Am. Chem. Soc.* **2006**, *128*, 9194–9204.

Chapter 3

Synthesis of Arylallenes by Palladium-Catalyzed Retro-Propargylation of Homopropargyl Alcohols

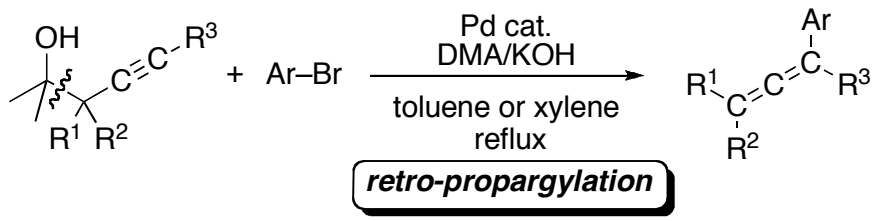
Treatment of tertiary homopropargyl alcohols with aryl halides under palladium catalysis provided arylallenes regioselectively. The reaction includes retro-propargylation, which proceeds in a concerted fashion via a cyclic transition state and transfers the stereochemistry of homopropargyl alcohols through C–C bond cleavage. The present method enables to use homopropargyl alcohols as allenylmetal equivalents.

Introduction

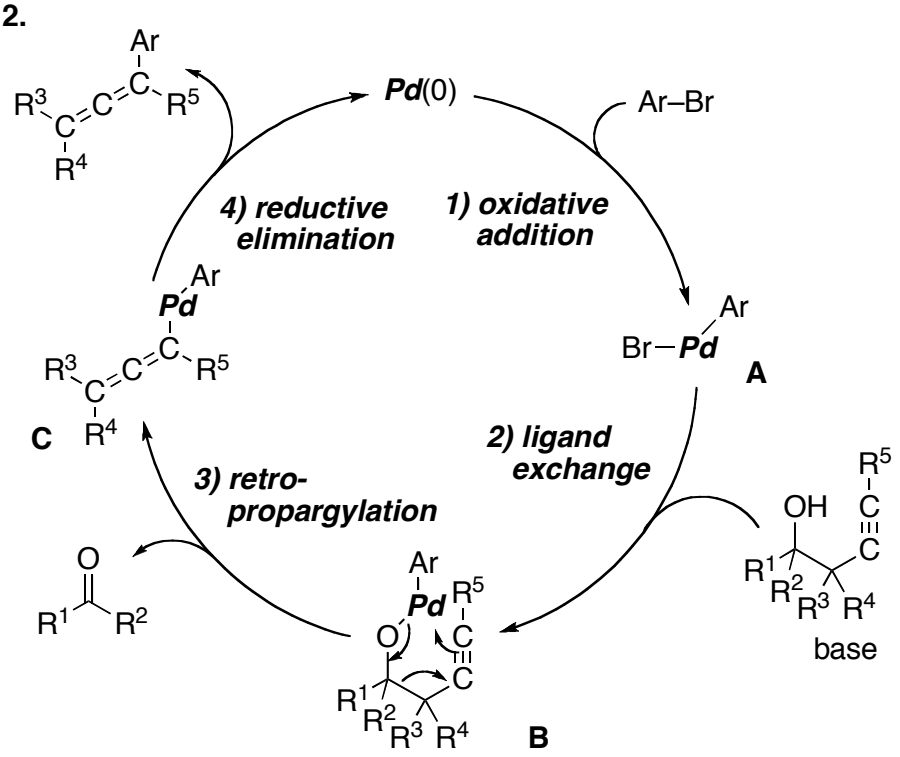
Allenes are a class of compounds that have interesting reactivity due to the two orthogonal π-bonds[1] and have been found in many natural products.[2] Transition-metal-catalyzed cross-coupling reaction of aryl halides with allenylmetals is one of the most convenient ways to prepare arylallenes.[3] In the case of palladium catalysis, allenylzinc and allenylcopper reagents have been mainly used. These reagents can easily undergo transmetalation with the arylpalladium halide intermediates formed in situ through oxidative addition of aryl halides to palladium. However, the preparation of these allenylmetals requires multiple steps, and they should be handled carefully because of their high reactivity. Moreover, they are in equilibrium with the corresponding propargylmetals[4] so that the control of regioselectivity in the coupling reaction can be difficult.

In Chapter 3, the author reports a new allenylation reaction of aryl halides with homopropargyl alcohols as allenylmetal equivalents (Scheme 1). During the studies on palladium-catalyzed regio- and stereospecific allyl transfer from homoallyl alcohols to aryl halides via retro-allylation described in Chapters 1 and 2,[5] the author expected the retro-allylation would be extended to retro-propargylation (Scheme 2). If retro-propargylation from intermediate **B** occurs via a cyclic transition state to provide σ-allenyl(aryl)palladium **C** and subsequent reductive elimination proceeds faster than isomerization of **C** to π-allenyl- or propargylpalladium, regioselective allenylated product can be obtained. It is noteworthy that tertiary homopropargyl alcohols are stable to air and moisture. In addition, they are readily accessible in short steps.

Scheme 1.



Scheme 2.

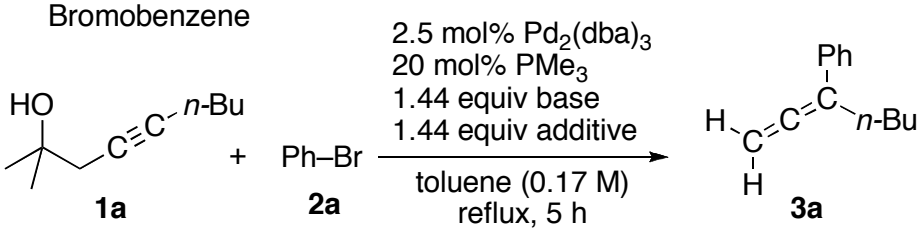


Results and Discussion

Homopropargyl alcohol **1a** and bromobenzene **2a** was chosen as model substrates, and the effect of a base and an additive in the allenylation was investigated under $Pd_2(dba)_3/PMe_3$ catalysis. The use of bases such as potassium phosphate and cesium carbonate which prompted the allyl transfer reaction described in Chapters 1 and 2 gave disappointing results, and most of the starting material was recovered intact (entries 1 and 2). The catalytic cycle worked better in the presence of cesium hydroxide monohydrate (entry 4). The addition of dehydrating reagents suppressed the reaction (entries 5 and 6). A positive effect of the addition of water was observed in the case of potassium hydroxide and cesium carbonate, while the effect on the latter was trivial (compare entries 2 with 3 and 7 with 8, respectively). Although the exact role of water was not clear at this stage, the oxygen atom on water might coordinate to palladium as a Lewis base to protect palladium from undesirable deactivation. Encouraged by the results, the

author evaluated various Lewis bases in the presence of potassium hydroxide. Indeed, some Lewis bases dramatically promoted the allenylation reaction (entries 9, 12, 13 and 15). In contrast, Lewis bases bearing a bulky substituent near the coordinating site diminished the yields (entries 10 and 11). The use of a much stronger base, DMSO, and bidentate coordinating molecules such as DME and 1,10-phenanthroline resulted in no formation of the allenylation product (entries 16–18). Finally, the combination of KOH and DMA was found to be optimal from the viewpoint of reproducibility and the yield (entry 13).

Table 1. Screening of Base and Additive for Palladium-Catalyzed Allenylation of Bromobenzene

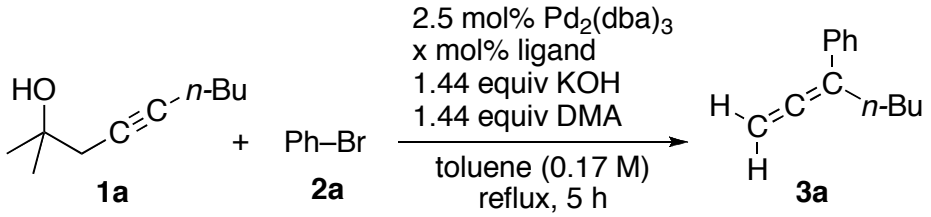


entry	base	additive	**3a**, yield[a](%)
1	K_3PO_4	–	7
2	Cs_2CO_3	–	8
3	Cs_2CO_3	H_2O	18
4	$CsOH{\bullet}H_2O$	–	47
5	$CsOH{\bullet}H_2O$	MS4A	22
6	$CsOH{\bullet}H_2O$	Na_2SO_4	29
7	KOH	–	8
8	KOH	H_2O	35–61
9	KOH	MeOH	47–61
10	KOH	*i*-PrOH	19
11	KOH	*t*-BuOH	18
12	KOH	pyridine	45
13	KOH	DMA	56
14	KOH	DMF	20
15	KOH	Et_2O	44
16	KOH	DMSO	0[b]
17	KOH	DME	0
18	KOH	1,10-phenanthroline	0[b]

[a] ^{1}H NMR yields. [b] Complex mixture.

Subsequently, various phosphorus ligands were assessed under the conditions shown in Table 1, entry 13 (Table 2). Arylallene **3a** was obtained exclusively only when primary alkyl-substituted trialkylphosphines were used (entries 1, 4, 5, and 7). The best ratio of palladium to ligand was 1 to 4, less of which was prone to cause precipitation of palladium black (entry 4–6). Among a series of trialkylphosphines, trioctylphosphine bearing longer alkyl chains showed the highest catalytic activity (entry 7). Other phosphine ligands and phosphite ligands were not effective for the formation of **3a** (entries 8–13). It should be noted that the reaction scarcely proceeded and most of the starting materials were recovered when divalent palladium complex such as $Pd(OAc)_2$ and $[(allyl)PdCl]_2$ were used (entries 2 and 3). This was probably because homopropargyl alcohol **1a** might coordinate tightly to palladium(II) to suppress the generation of active palladium(0) catalyst prior to the initial oxidative addition step as outlined in Scheme 2. The additional fine-tuning of the amounts of KOH and DMA under $Pd_2(dba)_3/P(n\text{-Oct})_3$ catalysis gave her the best result (entry 14).

Table 2. The Effect of Ligand in Palladium-Catalyzed Allenylation of Bromobenzene



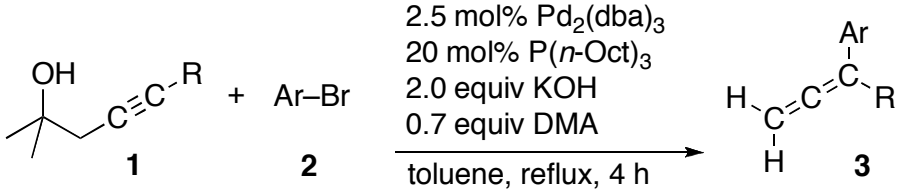
entry	ligand (mol%)	**3a**, yield[a](%)
1	PMe_3 (20)	56
2	PMe_3 (20)	4[b]
3	PMe_3 (20)	8[c]
4	P(*n*-Bu)$_3$ (20)	44–63
5	P(*n*-Bu)$_3$ (10)	58
6	P(*n*-Bu)$_3$ (5)	16[d]
7	P(*n*-Oct)$_3$ (20)	65
8	P(*c*-Hex)$_3$ (20)	14[e]
9	P(*c*-Hex)$_3$ (10)	11[e]
10	P(*t*-Bu)$_3$ (5)	0[e]
11	PPh_3 (20)	0[e]
12	P(OMe)$_3$ (20)	0[e]
13	P(OPh)$_3$ (20)	0[e]
14	P(*n*-Oct)$_3$ (20)	74[f]

[a] ^{1}H NMR yields. [b] $Pd(OAc)_2$ (5 mol%) was used. [c] $[(allyl)PdCl]_2$ was used. [d] Pd black was detected. [e] Complex mixture. [f] KOH (2.0 equiv) and DMA (0.7 equiv) were used.

With optimized conditions in hand, the author performed the allenylation reaction of various aryl halides with homopropargyl alcohol **1a** (Table 3). The reaction of bromobenzene (**2a**) with **1a** provided arylallene **3a** in 74% yield. In the reaction, no propargylated product was detected. This result is strongly suggestive of her hypothesis. A wide range of *p*-substituted aryl bromides including electron-deficient as well as electron-rich ones could be employed (entries 2–7). Sterically demanding **2h** and **2i** also participated in the allenylation reaction. Aryl bromides that possess carbonyl groups except for **2f** decomposed under the strongly basic conditions. Instead, acetal-protected substrates such as **2j** and **2k** gave good results (entries 10 and 11). Scope of the substituents at the alkyne terminus was then examined. Not only

primary but also secondary alkyl groups did not interfere with the reaction (entries 12–14). Notably, allenylation of **2a** with **1c** proceeded to furnish **3m**, leaving the benzyl ether moiety untouched. Unfortunately, the bulky *tert*-butyl group of **1e** suppressed the reaction (entry 15).[6]

Table 3. Palladium-Catalyzed Allenylation of Aryl Bromides **2** with Homopropargyl Alcohols **1** via Retro-Propargylation[a]



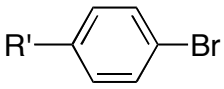
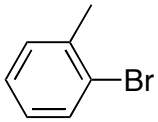
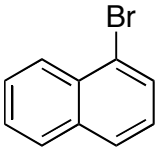
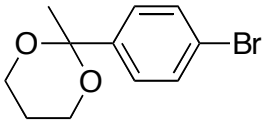
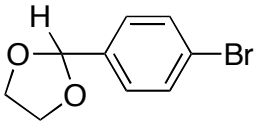
entry	R **1**	Ar–Br **2**		**3**, yield[b](%)
1	*n*-Bu **1a**		**2a:** R' = H	**3a**, 74
2			**2b:** Me	**3b**, 67
3			**2c:** Ph	**3c**, 68
4			**2d:** F	**3d**, 62
5			**2e:** CF_3	**3e**, 63
6			**2f :** *t*-BuCO	**3f**, 85
7			**2g:** OMe	**3g**, 63[c]
8			**2h**	**3h**, 65
9			**2i**	**3i**, 64

Table 3. (Continued)

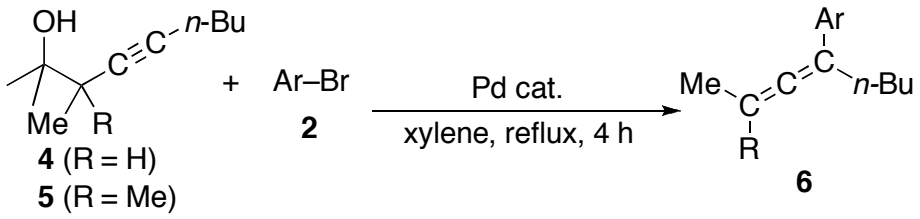
entry	R **1**	Ar–Br **2**		**3**, yield[b](%)
10			**2j**	**3j**, 82
11			**2k**	**3k**, 69
12	-$(CH_2)_3$Ph **1c**		**2a**	**3l**, 81
13	-$(CH_2)_3OCH_2$Ph **1d**		**2a**	**3m**, 56[d]
14	*i*-Pr **1d**		**2j**	**3n**, 62
15	*t*-Bu **1e**		**2a**	**3o**, 0

[a] A mixture of $Pd_2(dba)_3$ (0.010 mmol), P(*n*-Oct)$_3$ (0.080 mmol), DMA (0.28 mmol), KOH (0.80 mmol), **1** (0.48 mmol), and **2** (0.40 mmol) was boiled in toluene (6.0 mL) for 4 h. [b] Isolated yields. [c] With 2.0 equiv of **1a**. [d] Xylene was used instead of toluene.

Homopropargyl alcohols having one or two methyl groups at the propargylic position were converted to tri- or tetrasubstituted arylallenes, respectively (Table 4). Although higher temperature was required, a variety of aryl bromides reacted with **4** and **5** to produce the corresponding allenes **6** in moderate to good yields.

Finally, the author attempted diastereoselective synthesis of tetrasubstituted arylallenes as depicted in Scheme 3. Taking advantage of the retro-propargylation that would proceed in a concerted fashion via a cyclic transition state, the stereochemical information of homopropargyl alcohols would be transferred to the corresponding allenes through C–C bond cleavage.[7] The reaction of diastereomerically pure homopropargyl alcohol *anti*-**7** with bromobenzene (**2a**) provided tetrasubstituted allene **8a** in good yield with perfect *anti* selectivity (Table 5, entry 1). On the other hand, *syn*-**8a** was obtained as the sole product in the reaction of *syn*-**7** (entry 2). Other aryl bromides also underwent the stereospecific allenylation reaction with both diastereomers (entries 3–8).

Table 4. Synthesis of Tri- and Tetrasubstituted Arylallenes[a]



entry	alcohol	Ar–Br **2**	**6**, yield[b](%)
1	**4**	**2a**	**6a**, 68
2		**2b**	**6b**, 64
3		**2d**	**6c**, 60
4		**2f**	**6d**, 62
5		**2j**	**6e**, 71
6		**2k**	**6f**, 63
7	**5**	**2a**	**6g**, 68
8		**2f**	**6h**, 80
9		**2j**	**6i**, 79

[a] The reaction conditions are the same as those in Table 3 except for the use of xylene instead of toluene. [b] Isolated yields.

Scheme 3.

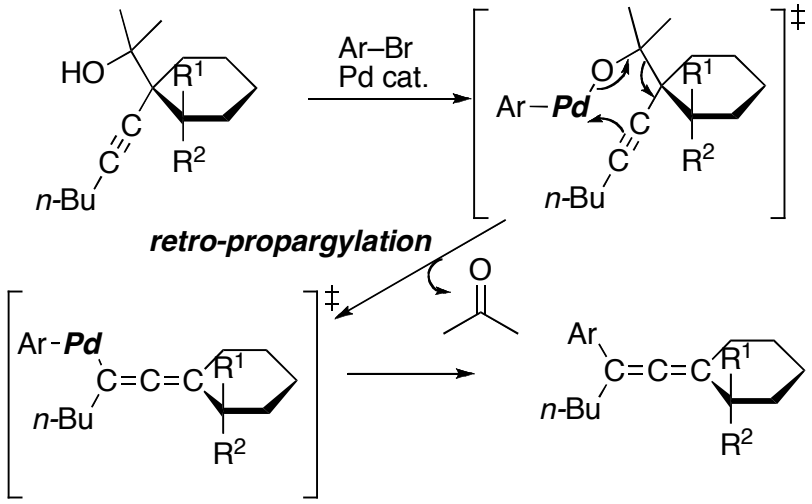
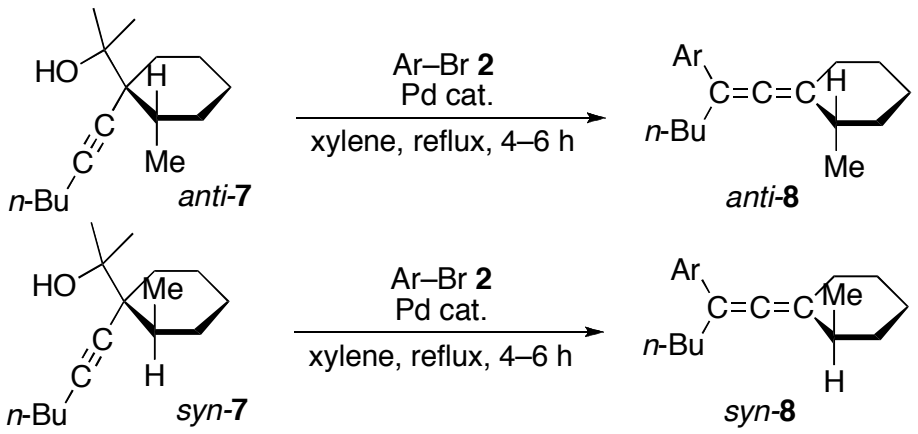


Table 5. Stereospecific Synthesis of Tetrasubstituted Arylallenes[a,b]



entry	**7**	Ar–Br **2**	**8**, yield[c](%)
1	*anti*	**2a**	*anti*-**8a**, 77
2	*syn*	**2a**	*syn*-**8a**, 77
3	*anti*	**2c**	*anti*-**8b**, 82
4	*syn*	**2c**	*syn*-**8b**, 62
5	*anti*	**2d**	*anti*-**8c**, 72
6	*syn*	**2d**	*syn*-**8c**, 50
7	*anti*	**2j**	*anti*-**8d**, 72
8	*syn*	**2j**	*syn*-**8d**, 77

[a] The reaction conditions were the same as those in Table 4. Both diastereomers were racemic. [b] Relative configurations of alcohol **7** and allene **8** were assigned by X-ray crystallographic analysis. [c] Isolated yields. Isomeric purity >99:1.

Conclusion

The author has developed a new method for the generation of σ–allenylpalladium from homopropargyl alcohols via retro-propargylation and applied it to the highly regioselective synthesis of *gem*-di-, tri- and tetrasubstituted arylallenes.

Experimental Section

Instrumentation and Chemicals

All experiments were conducted using the same instruments described in Chapter 1. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Xylene was purchased from Nacalai Tesque Co. and stored as the same above. *N,N*-Dimethylacetamide (DMA) was purchased from Aldrich and dried over molecular sieves 4A. Potassium hydroxide (pellet) was purchased from Wako Pure Chemical Co. and powdered under argon atmosphere prior to use. Trioctylphosphine was purchased from Strem and diluted to prepare a 1.0 M degassed hexane solution and stored strictly under argon. Tris(dibenzylideneacetone)dipalladium was from Aldrich. All reactions were carried out under argon atmosphere. Homopropargyl alcohols **1a**–**1e** were prepared by the ring-opening reaction of 2,2-dimethyloxirane with alkynyllithium. Alcohols **4** and **5** were prepared by the procedure of Sato.[8]

Preparation of 7

A 300–mL reaction flask was filled with argon. THF (60 mL) and 1-hexyne (8.28 mL, 72.0 mmol) were placed in the flask. At –78 ºC, butyllithium (1.60 M hexane solution, 41.2 mL, 66.0 mmol) was added dropwise to the solution via a syringe. After 15 min, hexamethylphosphoramide (HMPA, 6.00 mL) and 2-methylcyclohexanone (7.28 mL, 60.0 mmol) were sequentially added, and the resulting mixture was stirred for 2 h at –78 ºC. The reaction was quenched with saturated ammonium chloride solution (60 mL). Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 10:1) provided 1-(1-hexynyl)-2-methylcyclohexanol (7.09 g, 36.5 mmol, 61%) as a colorless liquid.

Under argon atmosphere, THF (35 mL), 1-(1-hexynyl)-2-methylcyclohexanol (7.09 g, 36.5 mmol), and butyllithium (1.60 M hexane solution, 22.8 mL, 36.5 mmol) were added at –78 ºC, and the resulting mixture was stirred for 1 h at this temperature. Ethyl chloroformate (4.36 mL, 45.6 mmol) was added at –78 ºC. The resulting mixture was then warmed to 60 ºC. After being stirred for 12 h, the mixture was poured into saturated ammonium chloride solution (40 mL). Extraction, evaporation, and purification on silica gel afforded ethyl 1-(1-hexynyl)-2-methylcyclohexyl carbonate (9.36 g, 35.1 mmol, 96%) as a colorless liquid.

A solution of the carbonate (10.5 g, 39.4 mmol) in diethyl ether (80 mL) was placed in the 300–mL reaction flask under argon atmosphere. The flask was cooled to –50 ºC. Titanium tetraisopropoxide (11.6 mL, 39.4 mmol) and isopropylmagnesium bromide (1.00 M ether solution, 74.9 mL, 74.9 mmol) were added. The resulting black solution was stirred for 1 h at this temperature and then cooled to –78 ºC. Acetaldehyde (2.21 mL, 39.4 mmol) was added,

and the mixture was allowed to warm up to –20 ºC. After being stirred for 3 h, the reaction was quenched with ice-cold 1 M hydrochloric acid (150 mL). Extraction followed by silica gel column purification furnished 1-[1-(1-hexynyl)-2-methylcyclohexyl]ethanol (2.93 g, 13.2 mmol, 33%) as a colorless liquid.

In a 100–mL reaction flask, pyridinium chlorochromate (4.27 g, 19.8 mmol) and neutral silica gel (4.27 g) were added and the flask was flushed with argon. Dichloromethane (30 mL) and 1-[1-(1-hexynyl)-2-methylcyclohexyl]ethanol (2.93 g, 13.2 mmol) were added at 0 ºC. The resulting mixture was stirred at ambient temperature. After 10 h, the mixture was passed through a pad of celite, dried over sodium sulfate, and evaporated. 1-[1-(1-Hexynyl)-2-methylcyclohexyl]ethanone (2.50 g, 11.3 mmol, 86%) was obtained after silica gel column purification as a colorless liquid.

Under an atmosphere of argon, methyllithium (1.09 M ether solution, 15.6 mL, 17.0 mmol) was placed in the reaction flask at –78 ºC. 1-[1-(1-Hexynyl)-2-methylcyclohexyl]ethanone (2.50 g, 11.3 mmol) in ether solution (15 mL) was added dropwise through a syringe at this temperature, and the mixture was stirred for 4 h at the same temperature. The reaction was quenched with 1 M hydrochloric acid (20 mL). After extractive workup, the starting material, along with the desired product, was detected in the crude mixture by NMR. The residue was treated with the same reaction conditions for additional two times. Purification on silica gel (hexane/ethyl acetate = 20:1) afforded *anti*-**7** (R_f = 0.31, 1.81 g, 7.67 mmol, 68%) and *syn*-**7** (R_f= 0.24, 0.58 g, 2.46 mmol, 22%). Both of the diastereomers were obtained as colorless liquids.

Typical Procedure for Palladium-catalyzed Cross-coupling Allenylation of Aryl Halides with Homopropargyl Alcohol

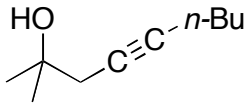
Tris(dibenzylideneacetone)dipalladium (9.1 mg, 0.010 mmol) was placed in a 30–mL two-necked reaction flask equipped with a Dimroth condenser. With a glovebox filled with argon, powdered potassium hydroxide (0.045 g, 0.80 mmol) was added. *N*, *N*-Dimethylacetamide (DMA, 26 μL, 0.28 mmol) was added to the reaction flask via a microsyringe at room temperature. Trioctylphoshine (1.0 M hexane solution, 0.080 mL, 0.080 mmol) and toluene (2.0 mL) were sequentially added, and the mixture was stirred for 10 min at ambient temperature. A solution of homopropargyl alcohol **1a** (0.074 g, 0.48 mmol) and bromobenzene (0.063 g, 0.40 mmol) in toluene (4.0 mL) was added to the resulting brown solution. The reaction mixture was heated at reflux for 4 h. After the mixture was cooled to room temperature, the reaction was quenched with water (20 mL). The product was extracted with hexane/ethyl acetate = 5:1 three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Purification on silica gel with hexane as an eluent provided

3-phenyl-1,2-heptadiene (0.051 g, 0.30 mmol, 74%) as a colorless liquid.

Characterization Data for Compounds

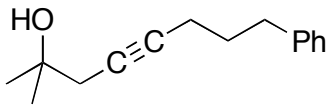
Spectral data for some compounds (**3a**[9] and **4**[10]) are found in the literature.

2-Methyl-4-nonyn-2-ol (1a): IR (neat) 3374, 2963, 2933, 2863, 1467, 1378, 1146, 907 cm^{-1};



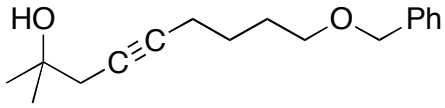
^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.0 Hz, 3H), 1.28 (s, 6H), 1.41 (tq, J = 7.0, 7.0 Hz, 2H), 1.49 (tt, J = 7.0, 7.0 Hz, 2H), 1.94 (s, 1H), 2.19 (tt, J = 7.0, 2.5 Hz, 2H), 2.33 (t, J = 2.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.82, 18.62, 22.18, 28.74, 31.31, 34.72, 70.08, 76.42, 83.90.

2-Methyl-8-phenyl-4-octyn-2-ol (1b): IR (neat) 3384, 2973, 2933, 1497, 1454, 1376, 1145, 907, 746 cm^{-1};



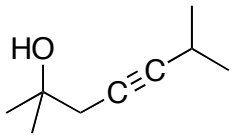
^{1}H NMR ($CDCl_3$) δ 1.31 (s, 6H), 1.83 (tt, J = 7.5, 7.0 Hz, 2H), 1.91 (s, 1H), 2.22 (tt, J = 7.0, 2.5 Hz, 2H), 2.36 (t, J = 2.5 Hz, 2H), 2.72 (t, J = 7.5 Hz, 2H), 7.18–7.21 (m, 3H), 7.27–7.31 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.44, 28.79, 30.86, 34.74, 35.10, 70.12, 76.97, 83.35, 126.10, 128.57, 128.71, 141.85.

9-Benzyloxy-2-methyl-4-nonyn-2-ol (1c): IR (neat) 3415, 2934, 2862, 1454, 1363, 1113, 907, 737 cm^{-1};



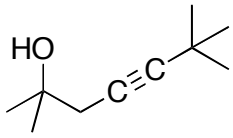
^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6H), 1.58–1.64 (m, 2H), 1.70–1.75 (m, 2H), 1.93 (s, 1H), 2.22 (tt, J = 7.5, 2.5 Hz, 2H), 2.33 (t, J = 2.5 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 4.50 (s, 2H), 7.27 –7.31 (m, 1H), 7.33–7.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ; 18.79, 25.97, 28.77, 29.13, 34.71, 70.00, 70.08, 73.09, 76.81, 83.51, 127.74, 127.84, 128.58, 138.75.

2,6-Dimethyl-4-heptyn-2-ol (1d): IR (neat) 3373, 2971, 2933, 1466, 1378, 1364, 1321, 1146, 907 cm^{-1};



^{1}H NMR ($CDCl_3$) δ 1.16 (d, J = 7.0 Hz, 6H), 1.28 (s, 6H), 1.94 (s, 1H), 2.33 (d, J = 2.5 Hz, 2H), 2.56 (sept of t, J = 7.0, 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.75, 23.56, 28.69, 34.64, 70.00, 75.62, 89.74.

2,6,6-Trimethyl-4-heptyn-2-ol (1e): IR (nujol) 3230, 2866, 2360, 1456, 1363, 1266, 1158, 984, 907 cm^{-1};



^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H), 1.28 (s, 6H), 1.93 (s, 1H), 2.32 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 27.66, 28.65, 31.50, 34.62, 69.98, 74.87, 92.75.

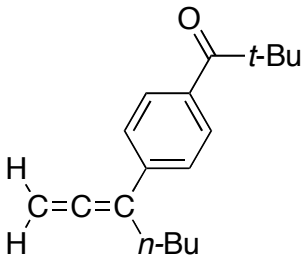
1-(1-Butyl-1,2-propadienyl)-4-methylbenzene (3b): IR (neat) 3024, 2958, 2928, 2860, 1939, 1511, 848, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.41 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.53 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.33 (s, 3H), 2.40 (tt, *J* = 7.5, 3.5 Hz, 2H), 5.04 (t, *J* = 3.5 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.19, 21.27, 22.73, 29.50, 30.27, 78.06, 105.02, 126.09, 129.28, 133.74, 136.42, 208.66; Found: C, 89.96; H, 9.72%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%.

4-(1-Butyl-1,2-propadienyl)biphenyl (3c): IR (neat) 3030, 2956, 2929, 2859, 1938, 1486, 841, 765, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.5 Hz, 3H), 1.44 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.57 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.46 (tt, *J* = 7.5, 3.5 Hz, 2H), 5.10 (t, *J* = 3.5 Hz, 2H), 7.34 (tt, *J* =7.5, 1.5 Hz, 1H), 7.44 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.60 (dd, *J* = 7.5, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.21, 22.75, 29.42, 30.29, 78.36, 104.95, 126.58, 127.15, 127.26, 127.38, 128.97, 135.79, 139.52, 141.05, 209.02; Found: C, 91.82; H, 8.12%. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12%.

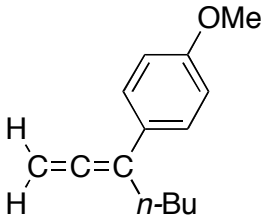
4-(1-Butyl-1,2-propadienyl)-1-fluorobenzene (3d): IR (neat) 2959, 2931, 2861, 1941, 1602, 1508, 1232, 1159, 852, 836, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.0 Hz, 3H), 1.42 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.50–1.56 (m, 2H), 2.39 (tt, *J* = 7.0, 3.0 Hz, 2H), 5.06 (t, *J* = 3.0 Hz, 2H), 7.00 (t, *J* = 9.0 Hz, 2H), 7.36 (dd, *J* = 9.0, 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.16, 22.70, 29.63, 30.19, 78.40, 104.45, 115.39 (d, *J* = 21.6 Hz), 127.69 (d, *J* = 8.2 Hz), 132.71 (d, *J* = 3.4 Hz), 161.92 (d, *J* = 245.7 Hz), 208.68 (d, *J* = 1.4 Hz); ^{19}F NMR ($CDCl_3$) δ –116.71; Found: C, 82.00; H, 7.98%. Calcd for $C_{13}H_{15}F$: C, 82.07; H, 7.98%.

4-(1-Butyl-1,2-propadienyl)-1-trifluoromethylbenzene (3e): IR (neat) 2960, 2933, 2863, 1940, 1617, 1328, 1167, 1125, 1070, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.42 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.54 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.42 (tt, *J* = 7.5, 3.0 Hz, 2H), 5.13 (t, *J* = 3.0 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.16, 22.67, 29.25, 30.13, 78.88, 104.60, 124.52 (q, *J* = 272.2 Hz), 125.43 (q, *J* = 3.9 Hz), 126.34, 128.63 (q, *J* = 32.7 Hz), 140.73, 209.36; ^{19}F NMR ($CDCl_3$) δ –62.94; Found: C, 69.95; H, 6.41%. Calcd for $C_{14}H_{15}F_3$: C, 69.99; H, 6.29%.

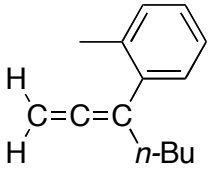
***tert*-Butyl 4-(1-butyl-1,2-propadienyl)phenyl ketone (3f):** IR (neat) 2958, 2931, 2872, 1938, 1671, 1602, 1174, 961, 849 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.36 (s, 9H), 1.42 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.55 (tt, *J* = 7.5, 3.5 Hz, 2H), 2.42 (tt, *J* = 7.5, 3.5 Hz, 2H), 5.11 (t, *J* = 3.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.15, 22.68, 28.37, 29.22, 30.21, 44.31, 78.65, 104.89, 125.71, 128.68, 136.25, 139.87, 208.26, 209.48; Found: C, 84.06; H, 9.40%. Calcd for $C_{18}H_{24}O$: C, 84.33; H, 9.44%.



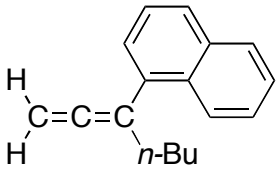
4-(1-Butyl-1,2-propadienyl)-1-methoxybenzene (3g): IR (neat) 2957, 2931, 2859, 2835, 1939, 1608, 1510, 1250, 1178, 1039, 832 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.41 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.53 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.39 (tt, *J* = 7.5, 3.5 Hz, 2H), 3.81 (s, 3H), 5.04 (t, *J* = 3.5 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 9.0, 2H); ^{13}C NMR ($CDCl_3$) δ 14.18, 22.73, 29.63, 30.27, 55.51, 78.09, 104.71, 114.05, 127.28, 129.00, 158.63, 208.51; Found: C, 82.83; H, 9.09%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.



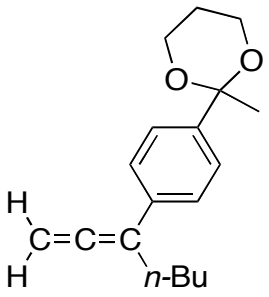
1-(1-Butyl-1,2-propadienyl)-2-methylbenzene (3h): IR (neat) 3017, 2957, 2929, 2859, 1952, 1458, 843, 762, 726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.5 Hz, 3H), 1.37 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.44 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.31 (tt, *J* = 7.5, 3.5 Hz, 2H), 2.34 (s, 3H), 4.78 (t, *J* = 3.5 Hz, 2H), 7.13–7.20 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.16, 20.42, 22.63, 30.08, 33.48, 75.36, 104.05, 125.97, 127.03, 128.12, 130.63, 136.23, 137.75, 206.89; Found: C, 90.04; H, 9.94%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%.



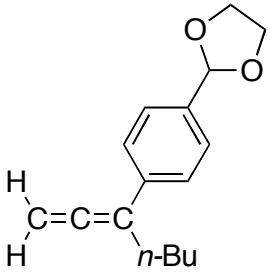
1-(1-Butyl-1,2-propadienyl)naphthalene (3i): IR (neat) 3045, 2957, 2930, 2871, 2858, 1952, 1466, 1394, 845, 799, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.5 Hz, 3H), 1.41 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.51 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.47 (tt, *J* = 7.5, 3.5 Hz, 2H), 4.86 (t, *J* = 3.5 Hz, 2H), 7.39–7.41 (m, 1H), 7.44–7.52 (m, 3H), 7.76–7.77 (m, 1H), 7.84–7.86 (m, 1H), 8.13–8.15 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.17, 22.63, 30.29, 34.26, 75.38, 103.28, 125.55, 125.62, 125.76, 125.90, 126.01, 127.57, 128.60, 131.52, 134.18, 136.41, 207.57; Found: C, 92.09; H, 8.29%. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16%.



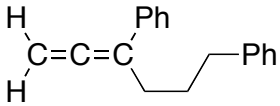
2-[4-(1-Butyl-1,2-propadienyl)phenyl]-2-methyl-1,3-dioxane (3j): IR (neat) 2959, 2932, 2870, 1939, 1369, 1250, 1192, 1147, 1084, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.24 (dm, *J* = 13.5 Hz, 1H), 1.41 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.50 (s, 3H), 1.56 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.12 (dtt, *J* = 13.5, 12.0, 5.5 Hz, 1H), 2.43 (tt, *J* = 7.5, 3.5 Hz, 2H), 3.79–3.88 (m, 4H), 5.08 (t, *J* = 3.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.19, 22.75, 25.70, 29.40, 30.29, 32.59, 61.47, 78.36, 100.74, 104.96, 126.50, 127.16, 136.19, 139.67, 208.99; Found: C, 79.18; H, 8.96%. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88%.



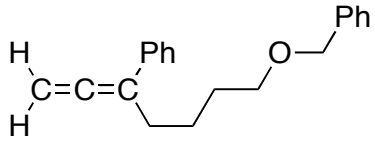
2-[4-(1-Butyl-1,2-propadienyl)phenyl]-1,3-dioxolane (3k): IR (neat) 2957, 2930, 2873, 2862, 1939, 1083, 943, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.40 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.52 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.41 (tt, *J* = 7.5, 3.0 Hz, 2H), 4.00–4.07 (m, 2H), 4.09–4.16 (m, 2H), 5.06 (t, *J* = 3.0 Hz, 2H), 5.81 (s, 1H), 7.42 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.18, 22.68, 29.45, 30.19, 65.49, 78.27, 103.84, 104.96, 126.21, 126.65, 136.25, 137.80, 209.02; Found: C, 78.38; H, 8.40%. Calcd for $C_{16}H_{20}O$: C, 78.65; H, 8.25%.



3,6-Diphenyl-1,2-hexadiene (3l): IR (neat) 3084, 3061, 3026, 2936, 2859, 1940, 1597, 1495, 1452, 852, 764, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91 (quint, *J* = 7.5 Hz, 2H), 2.47 (tt, *J* = 7.5, 3.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 5.10 (t, *J* = 3.5 Hz, 2H), 7.17–7.22 (m, 4H), 7.27–7.33 (m, 4H), 7.38–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 29.10, 29.73, 35.76, 78.61, 104.96, 125.96, 126.19, 126.82, 128.52, 128.58, 128.72, 136.62, 142.56, 208.81; Found: C, 92.51; H, 7.78%. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74%.



7-Benzyloxy-3-phenyl-1,2-heptadiene (3m): IR (neat) 3031, 2938, 2859, 1940, 1494, 1452, 1106, 1076, 852, 765, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (tt, *J* = 8.0, 7.5 Hz, 2H), 1.74 (tt, *J* = 8.0, 6.5 Hz, 2H), 2.45 (tt, *J* = 7.5, 3.5 Hz, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 4.51 (s, 2H), 5.07 (t, *J* = 3.5 Hz, 2H), 7.19–7.22 (m, 1H), 7.26–7.35(m, 7H), 7.40–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.69, 29.47, 29.64, 70.43, 73.09, 78.42, 104.99, 126.19, 126.78, 127.70, 127.85, 128.57 (overlapped), 136.58, 138.85, 208.82; Found: C, 86.42; H, 8.19%. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97%.



2-Methyl-2-[4-{1-(1-methylethyl)-1,2-propadienyl}phenyl]-1,3-dioxane (3n): IR (neat) 2963, 2932, 2869, 1940, 1243, 1192, 1147, 1085, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (d, J = 7.0 Hz, 6H), 1.22–1.27 (dm, J = 13.0 Hz, 1H), 1.51 (s, 3H), 2.12 (dtt, J = 13.0, 6.5, 5.5 Hz, 1H), 2.82 (sept.t, J = 7.0, 2.5 Hz, 1H), 3.79–3.88 (m, 4H), 5.11 (d, J = 2.5 Hz, 2H), 7.38 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.43, 25.69, 27.53, 32.58, 61.47, 79.47, 100.73, 112.11, 126.95, 127.18, 136.00, 139.61, 207.97; Found: C, 79.29; H, 8.84%. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%.

2,3,3-Trimethyl-4-nonyn-2-ol (5): IR (neat) 3448, 2961, 2934, 2874, 1458, 1375, 1143 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.5 Hz, 3H), 1.20 (s, 6H), 1.25 (s, 6H), 1.40 (tt, J = 7.5, 7.0 Hz, 2H), 1.47 (tt, J = 7.0 ,7.0 Hz, 2H), 1.95 (s, 1H), 2.17 (t, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.83, 18.56, 22.17, 24.88, 25.12, 31.40, 41.06, 74.14, 82.65, 85.77.

4-Phenyl-2,3-octadiene (6a): IR (neat) 3025, 2957, 2927, 2860, 1947, 1597, 1494, 1458, 782, 747 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 3H), 1.38–1.45 (m, 2H), 1.49–1.55 (m, 2H), 1.77 (d, J = 7.0 Hz, 3H), 2.40 (dtd, J = 10.0, 4.5, 3.0 Hz, 2H), 5.46 (qt, J = 7.0, 3.0 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.40 (dd, J = 8.0, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.25, 14.61, 22.68, 29.82, 30.31, 88.95, 105.19, 126.18, 126.50, 128.46, 137.83, 204.89.

1-(1-Butyl-3-methyl-1,2-butadienyl)-4-methylbenzene (6b): IR (neat) 3023, 2957, 2926, 2860, 1947, 1511, 821 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 3H), 1.40 (tq, J = 7.5, 7.5 Hz, 2H), 1.51 (tt, J = 7.5, 5.0 Hz, 2H), 1.75 (d, J = 7.0 Hz, 3H), 2.33 (s, 3H), 2.39 (dtd, J = 10.0, 5.0, 3.0 Hz, 2H), 5.43 (qt, J = 7.0, 3.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.24, 14.67, 21.26, 22.68, 29.93, 30.34, 88.74, 105.53, 126.10, 129.19, 134.87, 136.17, 204.64; Found: C, 89.97; H, 10.19%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

4-(1-Butyl-3-methyl-1,2-butadienyl)-1-fluorobenzene (6c): IR (neat) 2958, 2928, 2861, 1950, 1507, 1232, 1159, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.40 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.50 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.76 (d, *J* = 7.0 Hz, 3H), 2.37 (dtd, *J* = 8.5, 7.5, 3.0 Hz, 2H), 5.46 (qt, *J* = 7.0, 3.0 Hz, 1H), 6.99 (dd, *J* = 9.0, 9.0 Hz, 2H), 7.34 (d, *J* = 9.0, 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.22, 14.60, 22.65, 30.03, 30.24, 89.17, 104.41, 115.26 (d, *J* = 21.6 Hz), 127.63 (d, *J* = 7.7 Hz), 133.77 (d, *J* = 2.9 Hz), 161.79 (d, *J* = 245.2 Hz), 204.66; ^{19}F NMR ($CDCl_3$) δ –117.08; Found: C, 82.33; H, 8.51%. Calcd for $C_{14}H_{17}F$: C, 82.31; H, 8.39%.

***tert*-Butyl 4-(1-Butyl-3-methyl-1,2-butadienyl)phenyl ketone (6d):** IR (neat) 2958, 2930, 2861, 1943, 1670, 1602, 1174, 961, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.36 (s, 9H), 1.41 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.52 (tt, *J* = 7.5, 5.0 Hz, 2H), 1.78 (d, *J* = 7.0 Hz, 3H), 2.41 (dtd, *J* = 10.0, 5.0, 3.0 Hz, 2H), 5.51 (qt, *J* = 7.0, 3.0 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.21, 14.39, 22.64, 28.40, 29.63, 30.27, 44.29, 89.44, 104.89, 125.68, 128.69, 135.94, 140.99, 205.74, 208.20; Found: C, 84.65; H, 9.98%. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69%.

2-[4-(1-Butyl-3-methyl-1,2-butadienyl)phenyl]-2-methyl-1,3-dioxane (6e): IR (neat) 2958, 2927, 2870, 1192, 1147, 1085, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.23 (dm, *J* = 13.0 Hz, 1H), 1.42 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.50 (s, 3H), 1.51–1.57 (m, 2H), 1.77 (d, *J* = 7.0 Hz, 3H), 2.12 (dm, *J* = 13.0 Hz, 1H), 2.41 (dtd, *J* = 10.5, 4.5, 3.0 Hz, 2H), 3.79–3.89 (m, 4H), 5.48 (qt, *J* = 7.0, 3.0 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.24, 14.59, 22.70, 25.70, 29.80, 30.35, 32.63, 61.46, 89.14, 100.77, 104.93, 126.47, 127.08, 137.25, 139.34, 205.03; Found: C, 79.72; H, 9.31%. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15%.

2-[4-(1-Butyl-3-methyl-1,2-butadienyl)phenyl]-1,3-dioxolane (6f): IR (neat) 2956, 2928, 2860, 1947, 1083, 943, 832 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 3H), 1.40 (tq, J = 7.5, 7.5 Hz, 2H), 1.51 (tt, J = 7.5, 5.0 Hz, 2H), 1.76 (d, J = 7.0 Hz, 3H), 2.40 (dtd, J = 10.0, 5.0, 3.0 Hz, 2H), 4.00–4.06 (m, 2H), 4.09–4.15 (m, 2H), 5.46 (qt, J = 7.0, 3.0 Hz, 1H), 5.81 (s, 1H), 7.38–7.42 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.22, 14.53, 22.63, 29.87, 30.27, 65.47, 88.96, 103.89, 104.98, 126.19, 126.55, 136.03, 138.90, 205.14; Found: C, 78.75; H, 8.52%. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%.

2-Methyl-4-phenyl-2,3-octadiene (6g): IR (neat) 3025, 2957, 2930, 2859, 1953, 1598, 1493, 1466, 1447, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.0 Hz, 3H), 1.41 (tq, J = 7.0, 7.0 Hz, 2H), 1.50 (tt, J = 7.5, 7.0 Hz, 2H), 1.80 (s, 6H), 2.39 (t, J = 7.5 Hz, 2H), 7.16 (tt, J = 7.0, 1.0 Hz, 1H), 7.30 (dd, J = 8.5, 7.0 Hz, 2H), 7.37 (dd, J = 8.5, 1.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.29, 20.64, 22.67, 30.09, 30.35, 98.27, 103.53, 126.22 (overlapped), 128.39, 138.77, 202.01; Found: C, 89.96; H, 9.99%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

***tert*-Butyl 4-(1-butyl-3-methyl-1,2-butadienyl)phenyl ketone (6h):** IR (neat) 2958, 2931, 2861, 1951, 1672, 1602, 1173, 961, 849 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.0 Hz, 3H), 1.36 (s, 9H), 1.40 (tq, J = 7.5, 7.5 Hz, 2H), 1.49 (tt, J = 7.5, 7.0 Hz, 2H), 1.81 (s, 6H), 2.38 (t, J = 7.0 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.25, 20.47, 22.62, 28.42, 29.88, 30.30, 44.27, 98.87, 103.24, 125.68, 128.71, 135.58, 141.95, 202.98, 208.10; Found: C, 84.72; H, 10.21%. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92%.

2-[4-(1-Butyl-3-methyl-1,2-butadienyl)phenyl]-2-methyl-1,3-dioxane (6i): IR (neat) 2958, 2932, 2870, 1369, 1250, 1192, 1147, 1085, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.0 Hz, 3H), 1.23 (dm, J = 13.5 Hz, 1H), 1.41 (tq, J = 8.0, 7.5 Hz, 2H), 1.48–1.53 (m, 2H), 1.50 (s, 3H), 1.81 (s, 6H), 2.12 (dtt, J = 13.5, 9.5, 6.0 Hz, 1H), 2.39 (t, J = 7.5 Hz, 2H), 3.80–3.87 (m, 4H), 7.35 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.29, 20.63, 22.69, 25.70, 30.04, 30.37, 32.68, 61.45, 98.54, 100.80, 103.21, 126.47, 127.02, 138.11, 138.98, 202.10; Found: C, 79.93; H, 9.50%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%.

***anti*-2-[1-(1-Hexynyl)-2-methylcyclohexyl]-2-propanol (*anti*-7):** IR (neat) 3560, 2958, 2930, 2857, 2360, 2341, 1448, 1338, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.06 (d, *J* = 6.5 Hz, 3H), 1.10–1.18 (m, 2H), 1.20 (s, 3H), 1.24 (s, 3H), 1.36–1.66 (m, 10H), 1.70–1.74 (m, 1H), 2.27 (t, *J* = 6.5 Hz, 2H), 2.36 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.81, 18.63, 20.27, 22.22, 22.47, 24.12, 26.60, 28.96, 31.63, 34.01, 34.54, 37.41, 51.42, 75.04, 80.01, 87.61; Found: C, 81.20; H, 12.08%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

***syn*-2-[1-(1-Hexynyl)-2-methylcyclohexyl]-2-propanol (*syn*-7):** IR (neat) 3504, 2934, 2861, 2360, 2331, 1466, 1459, 1376, 1368, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.26 (s, 3H), 1.33 (s, 3H), 1.31–1.54 (m, 7H), 1.57–1.64 (m, 4H), 1.67–1.74 (m, 1H), 2.01–2.03 (m, 1H), 2.14–2.29 (m, 1H), 2.23 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.82, 16.38, 18.66, 20.23, 22.25, 23.81, 24.78, 25.19, 27.21, 31.46, 33.06, 35.09, 49.28, 74.47, 85.39, 85.85; Found: C, 81.05; H, 12.17%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

***anti*-1-Butyl-2-(2-methylcyclohexylidene)ethenylbenzene (*anti*-8a):** IR (neat) 3029, 2956, 2925, 2853, 1949, 1494, 1449, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.5 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H), 1.13–1.21 (m, 1H), 1.37–1.49 (m, 4H), 1.51 (quint, *J* = 7.5 Hz, 2H), 1.80–1.90 (m, 3H), 2.07–2.13 (m, 1H), 2.14–2.20 (m, 1H), 2.37–2.39 (m, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 7.16, (t, *J* = 8.5 Hz, 1H), 7.30 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.40 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.34, 19.87, 22.80, 26.47, 27.97, 30.01, 30.56, 32.21, 35.56, 36.80, 105.75, 111.87, 125.89, 126.10, 128.35, 139.11, 197.96; Found: C, 89.56; H, 10.42%. Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30%.

***syn*-1-Butyl-2-(2-methylcyclohexylidene)ethenylbenzene (*syn*-8a):** IR (neat) 2956, 2925, 2853, 1949, 1494, 1448, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H), 1.20–1.28 (m, 1H), 1.37–1.55 (m, 6H), 1.82–1.93 (m, 3H), 2.04–2.16 (m, 2H), 2.38–2.41 (m, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 7.17, (td, *J* = 7.5, 1.0 Hz, 1H), 7.31 (dd, *J* = 8.0, 7.5 Hz, 2H), 7.45 (dd, *J* = 8.0, 1.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.32, 19.86, 22.86, 26.46, 28.25, 30.19, 30.62, 32.19, 35.70, 36.98, 105.62, 111.75, 125.77, 126.08, 128.41, 138.87, 197.99; Found: C, 89.67; H, 10.50%. Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30%.

***anti*-4-[1-Butyl-2-(2-methylcyclohexylidene)ethenyl]biphenyl (*anti*-8b):** IR (neat) 2924, 2846, 1952, 1598, 1487, 1433, 837, 762, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 1.15–1.22 (m, 1H), 1.42–1.51 (m, 4H), 1.57 (quint, *J* = 7.5 Hz, 2H), 1.82–1.91 (m, 3H), 2.10–2.23 (m, 2H), 2.37–2.42 (m, 1H), 2.45 (t, *J* = 7.5 Hz, 2H), 7.32–7.35 (m, 1H), 7.42–7.49 (m, 4H), 7.53–7.56 (m, 2H), 7.59–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.36, 19.91, 22.82, 26.48, 27.98, 30.05, 30.60, 32.24, 35.61, 36.82, 105.50, 112.03, 126.27, 127.11, 127.13, 127.21, 128.93, 138.18, 138.92, 141.29, 198.18; Found: C, 91.14; H, 8.99%. Calcd for $C_{25}H_{30}$: C, 90.85; H, 9.15%. m.p. 88.7–89.3 ºC.

***syn*-4-[1-Butyl-2-(2-methylcyclohexylidene)ethenyl]biphenyl (*syn*-8b):** IR (neat) 3029, 2955, 2925, 2853, 1947, 1486, 1448, 840, 764, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.5 Hz, 3H), 1.03 (d, *J* = 6.5 Hz, 3H), 1.22–1.30 (m, 1H), 1.40–1.57 (m, 6H), 1.84–1.94 (m, 3H), 2.06–2.17 (m, 2H), 2.40–2.43 (m, 1H), 2.45 (t, *J* = 7.5 Hz, 2H), 7.34 (tt, *J* = 8.0, 1.5 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.61 (dd, *J* = 8.0, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.33, 19.89, 22.87, 26.46, 28.29, 30.22, 30.65, 32.21, 35.75, 37.02, 105.38, 111.90, 126.15, 127.12, 127.16, 127.21, 128.93, 137.95, 138.89, 141.26, 198.20; Found: C, 91.00; H, 9.29%. Calcd for $C_{25}H_{30}$: C, 90.85; H, 9.15%.

***anti*-4-[1-Butyl-2-(2-methylcyclohexylidene)ethenyl]-1-fluorobenzene (*anti*-8c):** IR (neat) 2957, 2926, 2854, 1950, 1507, 1231, 1158, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 1.12–1.20 (m, 1H), 1.37–1.47 (m, 4H), 1.52 (quint, *J* = 7.5 Hz, 2H), 1.80–1.90 (m, 3H), 2.06–2.19 (m, 2H), 2.34–2.39 (m, 1H), 2.37 (t, *J* = 7.5 Hz, 2H), 6.98 (t, *J* = 9.0 Hz, 2H), 7.33 (dd, *J* = 9.0, 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.32, 19.86, 22.77, 26.45, 27.97, 30.22, 30.50, 32.24, 35.57, 36.79, 104.96, 112.12, 115.11 (d, *J* = 21.1 Hz), 127.25 (d, *J* = 7.7 Hz), 135.03 (d, *J* = 3.4 Hz), 161.61 (d, *J* = 244.9 Hz), 197.68; ^{19}F NMR ($CDCl_3$) δ –117.75; Found: C, 83.63; H, 9.47%. Calcd for $C_{19}H_{25}F$: C, 83.78; H, 9.25%.

***syn*-4-[1-Butyl-2-(2-methylcyclohexylidene)ethenyl]-1-fluorobenzene (*syn*-8c):** IR (neat) 2956, 2926, 2854, 1949, 1507, 1231, 1158, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.5 Hz, 3H), 0.99 (d, J = 6.5 Hz, 3H), 1.17–1.25 (m, 1H), 1.37–1.52 (m, 6H), 1.82–1.93 (m, 3H), 2.03–2.16 (m, 2H), 2.36–2.40 (m, 1H), 2.37 (t, J = 7.5 Hz, 2H), 6.99 (t, J = 9.0 Hz, 2H), 7.38 (dd, J = 9.0, 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.30, 19.86, 22.82, 26.41, 28.25, 30.40, 30.53, 32.18, 35.68, 36.98, 104.83, 112.01, 115.17 (d, J = 21.6 Hz), 127.12 (d, J = 7.8 Hz), 134.80, 161.58 (d, J = 244.8 Hz), 197.72; ^{19}F NMR ($CDCl_3$) δ –117.75; Found: C, 83.80; H, 9.29%. Calcd for $C_{19}H_{25}F$: C, 83.78; H, 9.25%.

***anti*-2-[{1-Butyl-2-(2-methylcyclohexylidene)ethenyl}phenyl]-2-methyl-1,3-dioxane (*anti*-8d):** IR (neat) 2957, 2926, 2855, 1947,1369, 1250, 1192, 1147, 1085, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, J = 7.5 Hz, 3H), 1.01 (d, J = 6.5 Hz, 3H), 1.13–1.27 (m, 2H), 1.37–1.49 (m, 4H), 1.51 (s, 3H), 1.52–1.64 (m, 2H), 1.78–1.90 (m, 3H), 2.08–2.22 (m, 3H), 2.36–2.39 (m, 1H), 2.42 (td, J = 7.5, 2.5 Hz, 2H), 3.82–3.87 (m, 4H), 7.36 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.37, 19.91, 22.82, 25.70, 26.45, 27.97, 29.98, 30.58, 32.22, 32.67, 35.59, 36.80, 61.44, 100.81, 105.44, 112.11, 126.13, 126.97, 138.46, 138.84, 198.05; Found: C, 81.03; H, 9.57%. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67%.

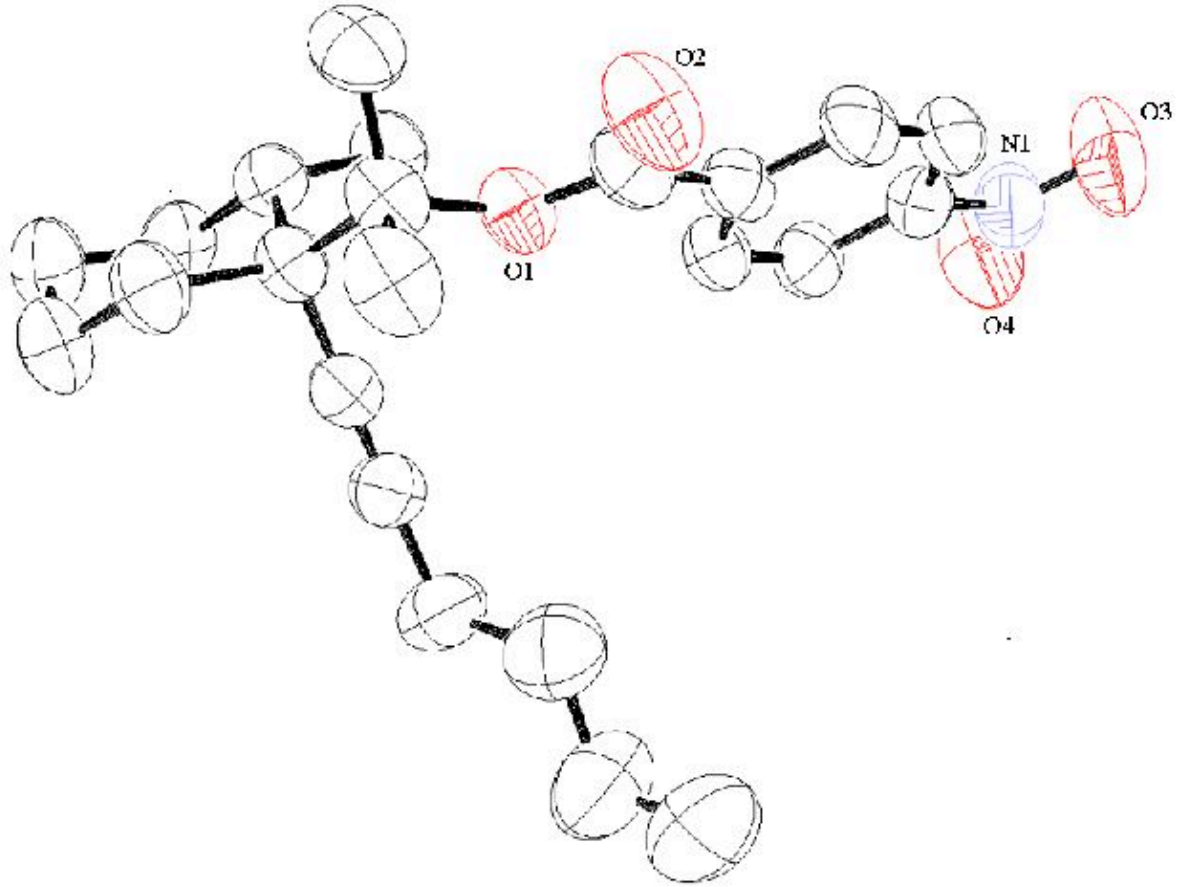
***syn*-2-[{1-Butyl-2-(2-methylcyclohexylidene)ethenyl}phenyl]-2-methyl-1,3-dioxane (*syn*-8d):** IR (neat) 2957, 2926, 2855, 1947,1369, 1243, 1192, 1147, 1086, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.5 Hz, 3H), 1.02 (d, J = 7.0 Hz, 3H), 1.23–1.30 (m, 2H), 1.39–1.56 (m, 6H), 1.52 (s, 3H), 1.83–1.94 (m, 3H), 2.04–2.18 (m, 3H), 2.37–2.42 (m, 1H), 2.42 (td, J = 7.0, 2.0 Hz, 2H), 3.85–3.88 (m, 4H), 7.37 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.33, 19.90, 22.89, 25.72, 26.43, 28.27, 30.17, 30.64, 32.19, 32.66, 35.73, 37.00, 61.46, 100.81, 105.31, 112.02, 125.99, 127.03, 138.20, 138.85, 198.07; HRMS Found: m/z 354.2554. Calcd for $C_{24}H_{34}O_2$: 354.2559.

Stereochemical Assignment of *anti*-7

One of the two isomers of **7** (0.085 g, 0.30 mmol), which was the faster moving band of R_f = 0.31 (hexane/ethyl acetate = 20:1, the other isomer showed R_f = 0.24), was dissolved in THF (1.0

mL), and the solution was placed in a 30-mL reaction flask under argon. Butyllithium (1.6 M hexane solution, 0.23 mL, 0.36 mmol) was added dropwise via a syringe at –78 ºC. After the mixture was stirred for 1 h at the same temperature, *p*-nitrobenzoyl chloride (0.069 g, 0.36 mmol) was added at once to the mixture at –78 ºC. The resulting mixture was allowed to warm gradually up to room temperature and heated at 60 ºC by using an oil bath for 2 h. The reaction was quenched with saturated ammonium chloride solution. Extractive workup followed by silica gel column purification yielded a mixture of *anti*-1-(1-hexynyl-2-methylcyclohexyl)-1-methylethyl 4-nitrobenzoate and starting material. The residue was purified by gel permeation chromatography. The pure ester was obtained as a white solid (0.066 g, 0.18 mmol, 60 % yield, unoptimized). X-ray quality crystals were grown from acetonitrile (Figure 1).

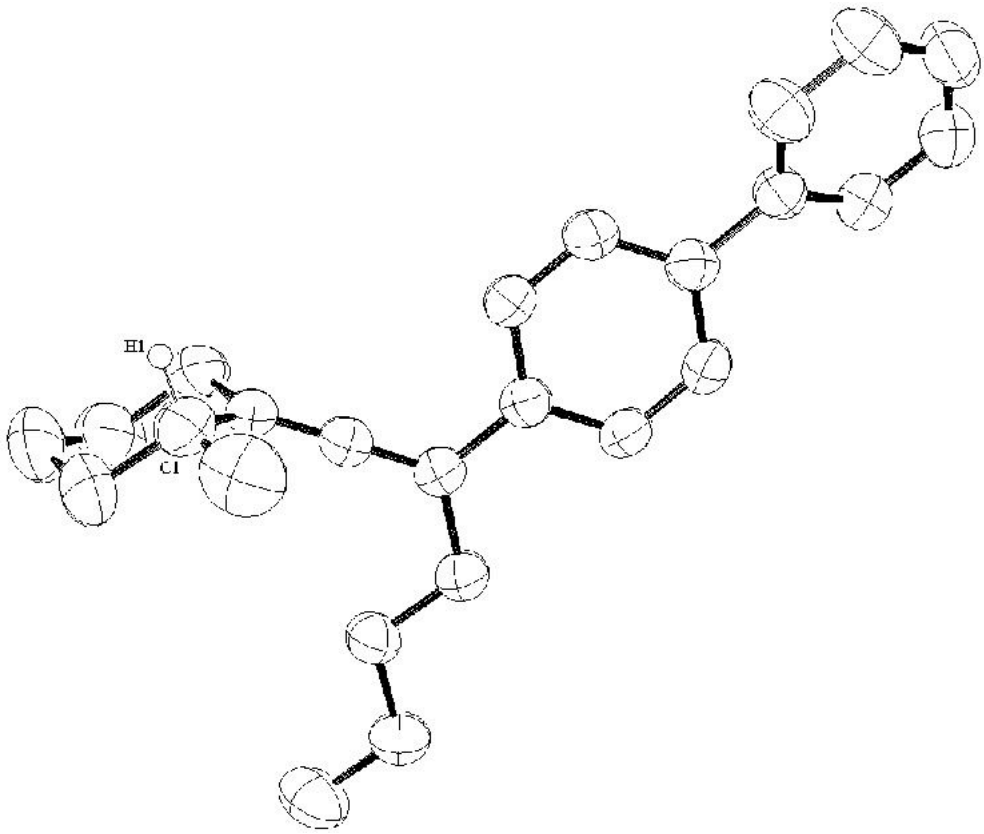
Fugure 1. Ortep diagram of *anti*-1-(1-hexynyl-2-methylcyclohexyl)-1-methylethyl 4-nitrobenzoate. Hydrogen atoms are omitted for clarity.



Stereochemical Assignment of *anti*-8b

X-ray quality crystals were grown from 2-propanol (Figure 2).

Figure 2. Ortep diagram of *anti*-**8b**. Hydrogen atoms are omitted for clarity except for that at the C1.



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Chapter 4

Synthesis of Epoxides by Palladium-Catayzed Reaction of Tertiary Allyl Alcohols with Aryl and Alkenyl Halides

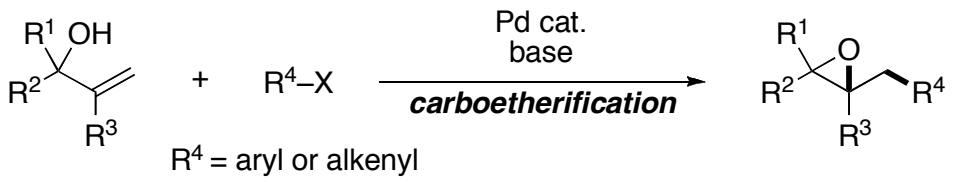
A novel synthetic method for the preparation of tri- or tetrasubstituted epoxides is developed. Treatment of readily available tertiary allyl alcohol with aryl or alkenyl halide under palladium catalysis resulted in arylative cyclization to form the epoxide. The reaction includes intramolecular C–O bond and intermolecular C–C bond construction.

Introduction

Epoxides are among the most synthetically useful intermediates and are found in many natural products and biologically active compounds.[1] Numerous methods for the preparation of epoxides have been reported so far, such as epoxidation of olefins, reaction of carbonyl compounds with sulfur ylides, and ring closure of *vic*-halohydrins.[2] However, novel synthetic methods for the construction of epoxides have been still required because of their synthetic importance in organic chemistry.

Recently, palladium-catalyzed carboetherification/arylation reactions of alkenes with aryl bromides have provided a very efficient way to construct multisubstituted five-membered heterocycles.[3,4] During the course of the studies for palladium-catalyzed reactions of unsaturated alcohols with aryl halides (Chapters 1–3), the author serendipitously found that Wolfe's carboetherification is applicable to more rigid three-membered ring construction, which is a new synthetic strategy for the preparation of epoxides (Scheme 1). In Chapter 4, she reports palladium-catalyzed reactions of readily accessible tertiary allyl alcohols with aryl and alkenyl halides.

Scheme 1.

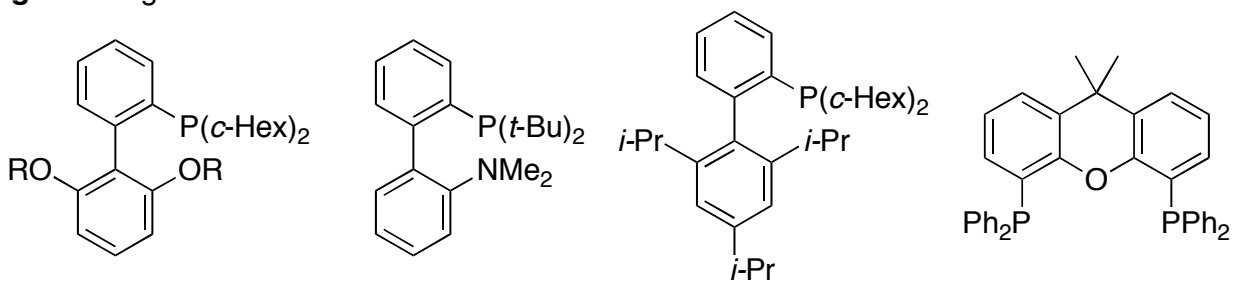


Results and Discussion

Treatment of tertiary allyl alcohol **1a** with 1-bromonaphthalene in the presence of sodium *tert*-butoxide under palladium catalysis provided epoxide **2a** in 88% yield (Table 1, entry 1). It is noteworthy that the reaction constructs both C–C and C–O bonds in a single operation. In the reaction, the choice of ligand is quite important: Only Buchwald's biaryl phosphines **P1–P4** and Xantphos **P5** (Figure 1) served as suitable ligands for the epoxidation reaction. The

Mizoroki–Heck reaction of tertiary allyl alcohols with 1-bromonaphthalene predominated or exclusively proceeded when other phosphine ligands were used. The reaction with not only aryl bromide but also aryl chloride gave the corresponding epoxide **2a** in good yield (entry 2). However, the use of naphthyl triflate as a starting material failed to afford the product (entry 3). Sterically demanding aryl bromides also participated in the epoxidation reaction (entries 4–7 and 9) except for bulkier 2-bromobiphenyl (entry 8). Aryl bromides bearing electron-donating groups as well as electron-deficient ones were converted to the corresponding epoxides in moderate yields (entries 10–12). Notably, alkenyl halides were also applicable to the epoxidation reaction (entries 13–15). Products **2k–2m** would be difficult to synthesize in one step from simple starting materials using traditional methods. In the reactions with alkenyl halides, the combination of $Pd_2(dba)_3$ and **P3** showed the highest catalytic activity.

Figure 1. Ligands used in the reactions



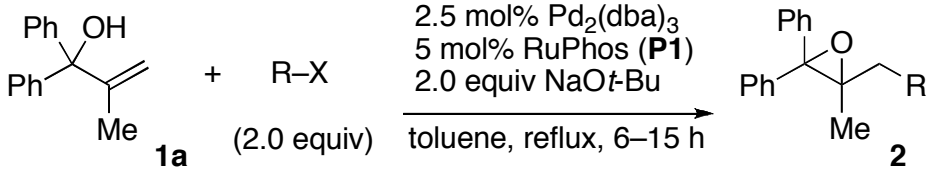
R=*i*-Pr RuPhos (**P1**)
Me SPhos (**P2**)

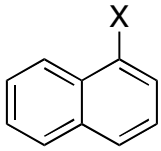
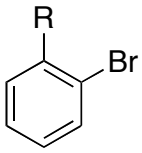
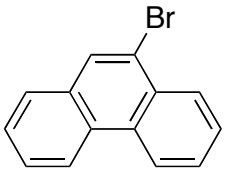
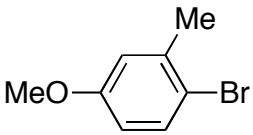
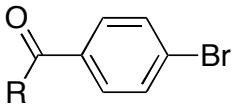
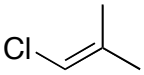
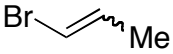
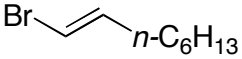
P3

XPhos (**P4**)

Xantphos (**P5**)

Table 1. Scope of Aryl and Alkenyl Halides in Palladium-Catalyzed Epoxidation/Arylation or /Alkenylation[a]

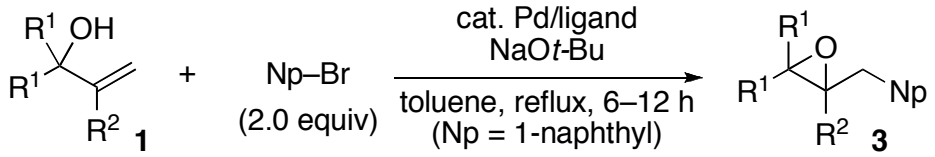


entry	R–X		**2**, yield[b](%)
1		X = Br	**2a**, 88
2		Cl	72
3		OTf	0
4		R = Me	**2b**, 82
5		Et	**2c**, 90
6		*i*-Pr	**2d**, 56
7		$CH{=}CH_2$	**2e**, 49
8		Ph	**2f**, 0[c]
9			**2g**, 91
10			**2h**, 67
11		R = Ph	**2i**, 47
12		*t*-Bu	**2j**, 50
13[d]			**2k**, 77
14[d,e]			**2l**, 74
15[d]			**2m**, 62

[a] A mixture of $Pd_2(dba)_3$ (0.0075 mmol), **P1** (0.015 mmol), NaO*t*-Bu (0.60 mmol), **1a** (0.30 mmol), and R–X (0.60 mmol) was boiled in toluene (3.0 mL) for 6–15 h. [b] Isolated yields. [c] No reaction. [d] **P3** as a ligand. [e] The *E/Z* ratio of both 1-bromopropene and the product was 76:24.

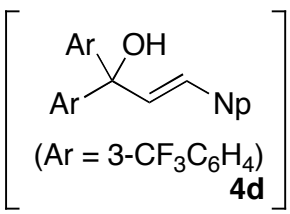
Reactions of a variety of tertiary allyl alcohols with 1-bromonaphthalene were then examined (Table 2). The methyl group of **1a** is not essential, and alcohol **1b** having hydrogen at the internal vinylic carbon underwent the epoxidation smoothly to yield trisubstituted epoxide **3b** (entry 1). With **1b**, the use of Xantphos improved the yield slightly (entry 2). The reaction of alcohol having an electron-rich aryl group at the tertiary carbon center furnished the corresponding product in 75% yield (entry 3). On the other hand, an electron-withdrawing group on the benzene rings interfered with the formation of the epoxide due to the predominance of a competitive Heck reaction (entry 4). Alcohols with small alkyl substituents such as a butyl group showed lower reactivity than those with aryl substituents (entry 5). The reactions of allyl alcohols bearing ethyl and phenyl substituents at the internal olefin moiety also proceeded to give the corresponding tetrasubstituted epoxides in moderate yields (entries 6 and 7).

Table 2. Reactions with Tertiary Allyl Alcohols with 1-Bromonaphthalene[a]

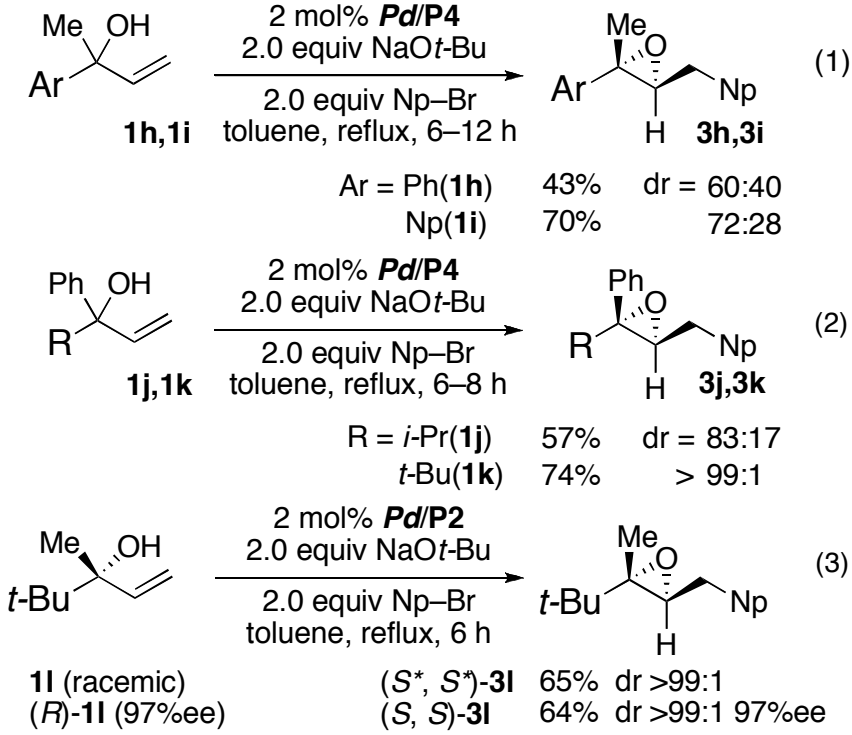


entry	R^1	R^2		ligand	**3**, yield[b] (%)
1	Ph	H	(**1b**)	**P1**	**3b**, 69
2[c]	Ph	H	(**1b**)	**P5**	**3b**, 75
3	4-$MeOC_6H_4$	H	(**1c**)	**P1**	**3c**, 60 (75[d])
4[e]	3-$CF_3C_6H_4$	H	(**1d**)	**P1**	**3d**, 23
5[f]	*n*-Bu	H	(**1e**)	**P4**	**3e**, 35
6	Ph	Et	(**1f**)	**P1**	**3f**, 62
7	Ph	Ph	(**1g**)	**P1**	**3g**, 44

[a] Conditions: $Pd_2(dba)_3$ (2.5 mol%), ligand (5 mol% with **P1**, **P4** or 10 mol% with **P5**), NaO*t*-Bu (2.0 equiv), toluene (0.1 M). [b] Isolated yields. [c] Cs_2CO_3 as a base. [d] ^{1}H NMR yield. [e] Product **4d** was obtained in 24% yield. [f] 2 mol% of [Pd] and **P4** were used.



Scheme 2.

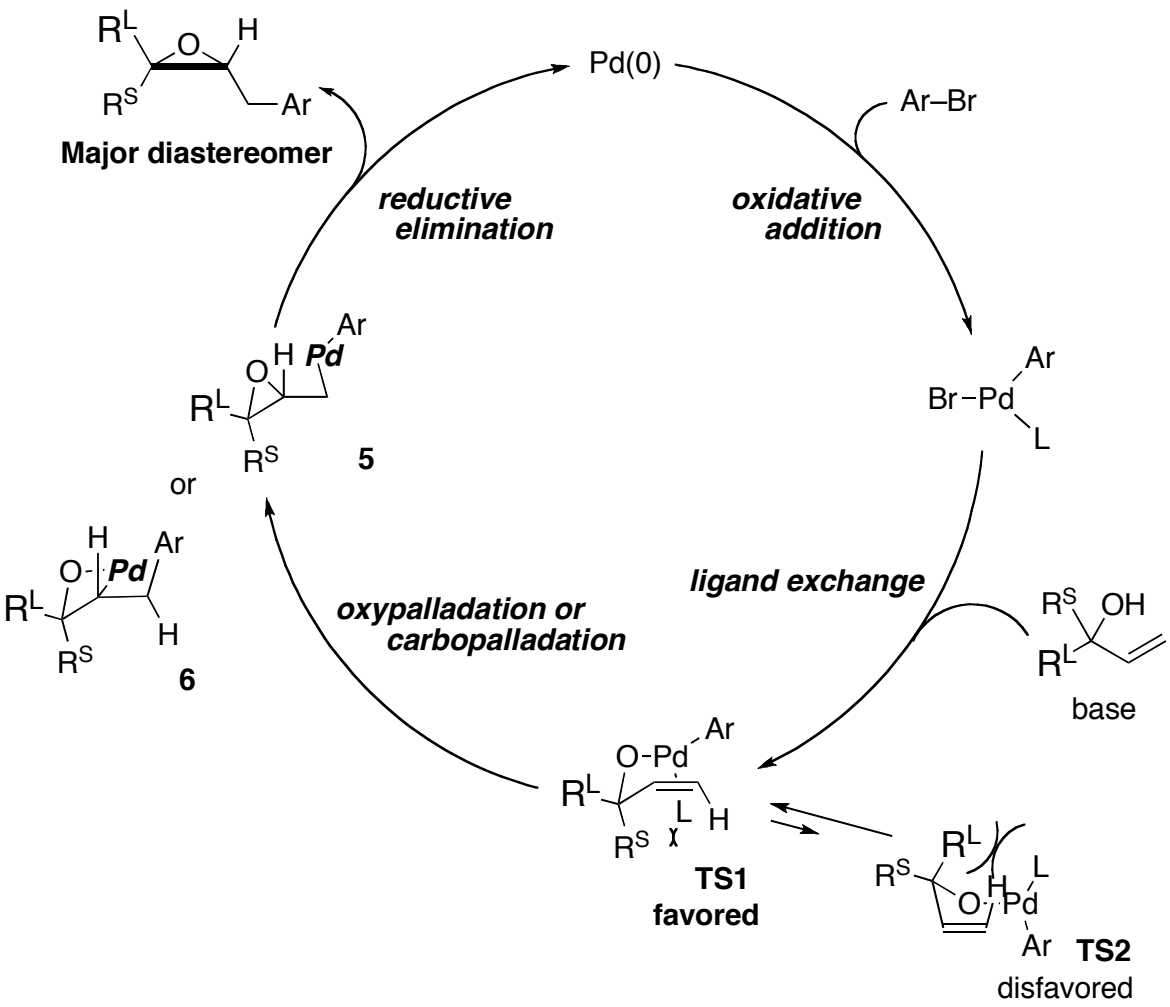


Subsequently, the reactions of tertiary alcohols that possess a stereogenic center at the oxygenated carbon were conducted (Scheme 2). Both yield and diastereoselectivity became better as the substituents at the oxygenated carbon of alcohols **1h**–**1k** became larger. As depicted in eq 1, 2-naphthyl-3-buten-2-ol (**1i**) gave a better result than 2-phenyl-3-buten-2-ol (**1h**). The reactions with alcohols **1j** and **1k** afforded the corresponding epoxides **3j** and **3k**, respectively, with good diastereoselectivity, bearing phenyl and naphthylmethyl substituents in a *cis* configuration (eq 2). As expected, bulkier *tert*-butyl-substituted alcohol **1l** underwent a smooth reaction to afford the corresponding epoxide **3l** in good yield as a single diastereomer (eq 3). Finally, the reaction was applied to the synthesis of an optically active epoxide. Starting from enantiomerically enriched tertiary alcohol **1l**, which was prepared in three steps from

2,3,3-trimethyl-1-butene, we obtained (*S*, *S*)-**3l** as a sole product without a loss of enantiomeric excess (eq 3).

Based on the results and Wolfe's report,[3,4] the author is tempted to assume the reaction mechanism as follows (Scheme 3). Initial oxidative addition of aryl halide to zerovalent palladium occurs to afford arylpalladium halide. Subsequent ligand exchange between the palladium intermediate and allyl alcohol in the presence of the base provides palladium alkoxide. Intramolecular oxypalladation then takes place to generate alkylpalladium intermediate **5**. Another possibility is a carbopalladation pathway, en route to oxapalladacyclobutane **6**. Finally, reductive elimination from these intermediates gives the desired product and regenerates Pd(0). The diastereoselectivity would be determined in the oxypalladation or carbopalladation step. **TS1** is the more favorable transition state than **TS2** because the larger substituent R^L is located at the pseudoequatorial position, thus minimizing the steric repulsion from the vinylic proton or the ligand L which coordinates to the palladium center. [6,7]

Scheme 3. Reaction Mechanism



Conclusion

The author has reported a new method for the synthesis of epoxides by palladium-catalyzed reactions of tertiary allyl alcohols with aryl halides. Moreover, the diastereoselective synthesis of trisubstituted epoxides was accomplished by the use of tertiary alcohols bearing stereogenic center at the allylic position.

Experimental Section

Instrumentation and Chemicals

All experiments were conducted using the same instruments described in Chapter 1. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Sodium *tert*-butoxide and cesium carbonate were purchased from Wako Pure Chemical Co. Buchwald's biarylphosphines (RuPhos (**P1**), SPhos (**P2**), **P3** and XPhos (**P4**)), xantphos (**P5**), and tris(dibenzylideneacetone)dipalladium were purchased from Aldrich. All reactions were carried out under argon atmosphere. Tertiary allyl alcohols **1a**–**1e** and **1h**–**1l** were prepared by the addition reaction of vinylmagnesium bromide with ketones. Alcohols **1f** and **1g** were synthesized by the reaction of ketones with alkenyllithium reagents generated by the Shapiro reaction. Preparation of (*R*)-**1l** was shown below.

Preparation of 1f and 1g

Preparation of **1f** is representative. *p*-Toluenesulfonyl hydrazide (2.79 g, 15.0 mmol) was placed in a 100–mL reaction flask and the flask was filled with argon. Hexane (75.0 mL) and 2-butanone (2.01 mL, 22.5 mmol) were added at room temperature. The mixture was then warmed to 50 °C and stirred for 7 h. A white precipitate was observed during the reaction. After the mixture was cooled to room temperature, the resulting white solid was collected through a Hirsch funnel. The solid was washed with hexane three times to yield *N'*-2-butanylidene-4-methylbenzenesulfonyl hydrazide (3.47 g, 14.4 mmol) in 96 % yield.[7]

N'-Butan-2-ylidene-4-methylbenzenesulfonyl hydrazide (3.47 g, 14.4 mmol) was placed in a 200–mL reaction flask. Under argon atmosphere, *N,N,N',N'*-tetramethylethylenediamine (28 mL) was added, and the solution was cooled to –78 °C. Butyllithium (1.60 M hexane solution, 31.5 mL, 50.4 mmol) was added dropwise via a syringe at –78 °C. The mixture was then allowed to warm to room temperature and stirred for 5 h. Benzophenone (2.10 g, 11.5 mmol) was added to the resulting mixture at ambient temperature and the mixture was stirred overnight. The mixture was poured into saturated ammonium chloride solution (100 mL) and stirred for 10 min. After extractive workup, a small amount of starting benzophenone was detected along with the desired product in the crude mixture. The residue was treated with LAH to convert remaining benzophenone to diphenylmethanol. Finally, **1f** (1.41 g, 5.90 mmol, 51% yield) was obtained as a white solid after purification on silica gel (hexane/AcOEt = 10 : 1).

Preparation of (*R*)-1l

Osmium-catalyzed dihydroxylation of olefins[8] and kinetic resolution of 1,2-diols[9] were performed according to the literature procedure. Microencapsulated osmium tetraoxide (10 wt%

MC OsO_4, purchased from Wako Pure Chemical Co., 1.00 g, 0.39 mmol) and *N*-methylmorpholine oxide (1.20 g, 10.2 mmol) were placed in a 50–mL reaction flask. Under argon atmosphere, water (2.4 mL), acetone (2.4 mL), acetonitrile (2.4 mL) and 2,3,3-trimethyl-1-butene were sequentially added at room temperature. The mixture was stirred for two days. Methanol was added to the resulting brown solution and the mixture was filtered through a Hirsch funnel. The filtrate was concentrated under a reduced pressure. Purification on silica gel (hexane/AcOEt = 1 : 1) provided 2,3,3-trimethylbutane-1,2-diol (0.96 g, 7.2 mmol, 91%) as a white solid. Although the resulting catalyst could be used three times, the catalytic activity was gradually decreased in our hands (74% yield in the second use and 20% yield in the third one).

A catalyst for the asymmetric silylation of 2,3,3-trimethylbutane-1,2-diol was prepared according to the literature procedure.[10] The catalyst (0.62 g, 2.0 mmol) and 2,3,3-trimethylbutane-1,2-diol (1.33 g, 10.0 mmol) were placed in a 50–mL reaction flask. The mixture was dissolved in diisopropylethylamine (2.18 mL, 12.5 mmol) and THF (2.0 mL) at room temperature under argon. At –78 ºC, a solution of *tert*-butyldimethylsilyl chloride in THF (6.0 mL) was added and the resulting mixture was stirred for 24 h at the same temperature. Methanol (0.5 mL) was added before the mixture was allowed to warm to room temperature. The mixture was poured into 10 wt% citric acid solution (30 mL) and extracted with AcOEt three times. Evaporation and purification on neutral silica gel afforded the starting alcohol (0.82 g, 6.2 mmol, 62%) and silyl-protected alcohol (0.93 g, 3.8 mmol, 38%). The silylated alcohol should have (*S*) configuration according to the literature.[10] The same reaction was repeated three times to obtain a sufficient amount of the (*S*)-enriched silyl-protected alcohol.

Under argon atmosphere, the (*S*)-enriched silyl-protected alcohol was treated with tetrabutylammonium fluoride (1.0 M THF solution, 12.0 mL, 12 mmol) in THF (10 mL) at 0 ºC. After 3 h, extractive workup followed by silica gel column purification furnished optically active 2,3,3-trimethylbutane-1,2-diol (1.10 g, 8.34 mmol, 72%).

Dimethyl sulfoxide (6.22 mL, 87.6 mmol), CH_2Cl_2 (25 mL), and diisopropylethylamine (7.56 mL, 43.3 mmol) were added to a flask containing 2,3,3-trimethylbutane-1,2-diol (1.10 g, 8.34 mmol) under argon. The flask was then cooled to 0 ºC, and pyridine sulfur trioxide complex (4.11g, 25.9 mmol) was added. After being stirred for 2 h, the mixture was poured into 1 M hydrochloric acid solution (30 mL). The mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with saturated sodium hydrogencarbonate solution (30 mL). Evaporation followed by silica gel column purification (hexane/AcOEt = 10 : 1) gave 2-hydroxy-2,3,3-trimethylbutanal (0.725 g, 5. 57 mmol, 67%).

A suspension of methyltriphenylphosphonium bromide (5.78 g, 16.2 mmol) in THF (10 mL) was placed in a 100–mL flask. Under argon atmosphere, potassium *tert*-butoxide (1.75 g, 15.6

mmol) was added at once, and the mixture was stirred for 30 min at ambient temperature. 2-Hydroxy-2,3,3-trimethylbutanal (0.725 g, 5. 57 mmol) dissolved in THF (8 mL) was added, and the resulting mixture was warmed to 50 ºC for 2 h. The reaction was quenched with saturated sodium hydrogencarbonate solution (30 mL). Extraction, evaporation, and purification by a silica gel column provided 2,2,3-trimethyl-4-penten-3-ol ((*R*)-**1l**, 0.308 g, 2.40 mmol, 43%) as a colorless oil. (Caution : careful concentration under a reduced pressure was required, since the product was volatile.)

Preparation of the carbamate for the determination of enantiomeric excess of (*R*)-1l

A solution of (*R*)-**1l** (0.0513 g, 0.40 mmol) in THF (0.80 mL) was placed in a 30–mL reaction flask under argon. The flask was then cooled to 0 ºC with an ice bath. Butyllithium (1.60 M hexane solution, 0.25 mL, 0.40 mmol) was added via a syringe at 0 ºC, and the mixture was stirred for 30 min. Phenyl isocyanate (0.0652 mL, 0.60 mmol) was added at 0 ºC, and the mixture was allowed to warm to room temperature. After the mixture was stirred for 12 h, water (20 mL) was added. Extractive workup followed by silica gel column purification provided the carbamate (0.0620 g, 0.251 mmol, 63%) as a white solid. HPLC conditions: Daicel CHRALCEL OD-H, hexane/2-propanol = 95/5, 1.0 mL/min, retention time: 6.17 min (*R*, major); 7.31 min (*S*, minor).

Typical Procedure for Palladium-catalyzed Reactions of Tertiary Allyl Alcohols with Aryl or Alkenyl Halides

The synthesis of **2a** (Table 1, entry 1) is representative. Sodium *tert*-butoxide (0.058 g, 0.60 mmol) was placed in a 30–mL two-necked reaction flask equipped with a Dimroth condenser, and dried in vacuo with heating with a hair dryer for 1 min. Tris(dibenzylideneacetone)dipalladium (0.0069 g, 0.0075 mmol) and 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (Ruphos, 0.0070 g, 0.015 mmol) were added, and the flask was filled with argon by using the standard Schlenck technique. Toluene (1.0 mL) was added to the flask, and the mixture was stirred at room temperature. After 10 min, a solution of alcohol **1a** (0.067 g, 0.30 mmol) and 1-bromonaphthalene (0.12 g, 0.60 mmol) in toluene (2.0 mL) was added. The resulting brown mixture was then heated at reflux for 6 h. After the mixture was cooled to room temperature, water (20 mL) was added. The mixture was extracted with hexane/AcOEt = 5 : 1 three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on neutral silica gel with hexane/AcOEt/triethylamine = 20 : 1 : 0.1 as an eluent. 2-Methyl-2-(1-naphthalenylmethyl)-3,3-diphenyloxirane (**2a**) was obtained as a white solid

(0.092 g, 0.26 mmol, 88%).

Characterization Data

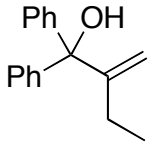
2-Methyl-1,1-diphenyl-2-propen-1-ol (1a): IR (neat) 3475, 3059, 1642, 1599, 1492, 1448, 1025, 907, 759, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.81 (dd, J = 1.5, 0.5 Hz, 3H), 2.46 (s, 1H), 4.73–4.74 (m, 1H), 5.15 (dq, J = 1.5, 1.5 Hz, 1H), 7.26–7.30 (m, 2H), 7.31–7.38 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 20.27, 83.20, 115.74, 127.47, 127.84, 128.12, 145.09, 149.30; HRMS Found: m/z 224.1205. Calcd for $C_{16}H_{16}O$: 224.1201.

1,1-Di(4-methoxyphenyl)-2-propen-1-ol (1c): IR (neat) 3478, 1609, 1511, 1250, 1176, 1035, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 1H), 3.78 (s, 6H), 5.27 (dd, J = 10.5, 1.5 Hz, 1H), 5.29 (dd, J = 17.0, 1.5 Hz, 1H), 6.46 (dd, J = 17.0, 10.5 Hz, 1H), 6.85 (d, J = 9.0 Hz, 4H), 7.29 (d, J = 9.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.47, 79.05, 113.61 (two peaks merge), 128.34, 138.39, 144.12, 158.89; HRMS Found: m/z 270.1255. Calcd for $C_{17}H_{18}O_3$: 270.1256.

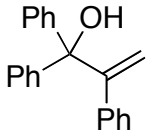
1,1-Di(3-trifluoromethylphenyl)-2-propen-1-ol (1d): IR (neat) 3443, 1680, 1440, 1330, 1124, 1075, 804, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 1H), 5.34 (dd, J = 17.0, 0.5 Hz, 1H), 5.43 (dd, J = 10.5, 0.5 Hz, 1H), 6.49 (dd, J = 17.0, 10.5 Hz, 1H), 7.40–7.48 (m, 2H), 7.49–7.52 (m, 2H), 7.55–7.58 (m, 2H), 7.71–7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 79.08, 116.17, 123.64 (q, J = 3.8 Hz), 124.24 (q, J = 272.7 Hz), 124.79 (q, J = 3.9 Hz), 129.09, 130.62, 131.00 (q, J = 32.2 Hz), 142.33, 146.19; ^{19}F NMR ($CDCl_3$) δ –63.12; HRMS Found: m/z 346.0788. Calcd for $C_{17}H_{12}OF_6$: 346.0792.

3-Butyl-1-hepten-3-ol (1e): IR (neat) 3426, 2935, 2862, 1458, 997, 919 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 6H), 1.23–1.34 (m, 8H), 1.38 (s, 1H), 1.44–1.56 (m, 4H), 5.09 (dd, J = 11.0, 1.5 Hz, 1H), 5.19 (dd, J = 17.5, 1.5 Hz, 1H), 5.82 (dd, J = 17.5, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.30, 23.39, 25.86, 40.75, 75.68, 112.27, 114.49; HRMS Found: m/z 170.1669. Calcd for $C_{11}H_{22}O$: 170.1671.

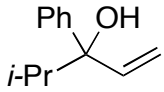
2-Methylene-1,1-diphenylbutan-1-ol (1f): IR (nujol) 3420, 1639, 1598, 1447, 1162, 1002, 907, 756, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.0 Hz, 3H), 2.09 (q, J = 7.0 Hz, 2H), 2.46–2.48 (m, 1H), 4.83–4.84 (m, 1H) 5.17–5.19 (m, 1H), 7.26–7.29 (m, 2H), 7.30–7.36 (m, 8H); ^{13}CNMR($CDCl_3$) δ 12.87, 25.04, 83.76, 113.06, 127.43, 127.92, 128.08, 145.49, 155.21; HRMS Found: m/z 238.1361. Calcd for $C_{17}H_{18}O$: 238.1358. m.p. 61.5–62.0 °C.



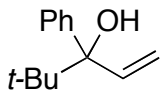
1,1,2-Triphenyl-2-propen-1-ol (1g): IR (neat) 3565, 3474, 1598, 1493, 1447, 1336, 1162, 1031, 968, 918, 779, 751, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 1H), 4.82 (d, J = 1.0 Hz, 1H), 5.52 (d, J = 1.0 Hz, 1H), 7.17–7.20 (m, 2H), 7.21–7.26 (m, 3H), 7.29–7.33 (m, 2H), 7.34–7.38 (m, 4H), 7.45–7.49 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 83.19, 119.83, 127.61, 127.95, 128.16 (two peaks merge), 128.52, 128.70, 139.92, 145.55, 154.47; HRMS Found: m/z 286.1359. Calcd for $C_{21}H_{18}O$: 286.1358.



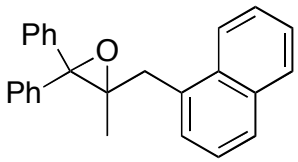
4-Methyl-3-phenyl-1-penten-3-ol (1j): IR (neat) 3479, 2965, 1447, 990, 920, 760, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H), 1.77 (s, 1H), 2.19 (qq, J = 7.0, 7.0 Hz, 1H), 5.19 (dd, J = 11.0, 1.5 Hz, 1H), 5.33 (dd, J = 17.5, 1.5 Hz, 1H), 6.30 (dd, J = 17.5, 11.0 Hz, 1H), 7.21–7.25 (m, 1H), 7.31–7.36 (m, 2H), 7.42–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 16.92, 17.29, 37.47, 79.51, 112.88, 125.66, 126.80, 128.29, 143.42, 145.91; HRMS Found: m/z 176.1203. Calcd for $C_{12}H_{16}O$: 176.1201.



4,4-Dimethyl-3-phenyl-1-penten-3-ol (1k): IR (neat) 3478, 2957, 1481, 1447, 1394, 1365, 1145, 968, 922, 756, 708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9H), 1.78 (s, 1H), 5.26 (dd, J = 17.0, 1.5 Hz, 1H), 5.36 (dd, J = 17.0, 1.5 Hz, 1H), 6.80 (dd, J = 17.0, 11.0 Hz, 1H), 7.21–7.25 (m, 1H), 7.29–7.33 (m, 2H), 7.48–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.74, 38.41, 80.74, 113.68, 126.77, 127.41, 127.53, 142.12, 144.44; HRMS Found: m/z 190.1355. Calcd for $C_{13}H_{18}O$: 190.1358.



2-Methyl-2-(1-naphthylmethyl)-3,3-diphenyloxirane (2a): IR (nujol) 3028, 2924, 2853, 1597, 1495, 1447, 1171, 938, 782, 749, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 3H), 3.06 (d, J = 15.0 Hz, 1H), 3.28 (d, J = 15.0 Hz, 1H), 7.22–7.30 (m, 2H), 7.31–7.35 (m, 2H), 7.38–7.44 (m, 4H), 7.46–7.50 (m, 1H), 7.51–7.55 (m, 3H), 7.68–7.72 (m, 2H), 7.73–7.76 (m, 1H), 7.82–7.84 (m, 1H), 8.08–8.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.46, 38.30, 68.26, 71.65, 125.05, 125.55, 125.75, 126.11, 127.34, 127.39, 127.43, 127.45, 127.61,



128.08, 128.45, 128.57, 128.75, 132.87, 134.08, 134.80, 140.31, 140.53; Found: C, 88.86; H, 6.33%. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.41%. m.p. 84.0–84.4 ºC.

2-Methyl-2-(2-methylphenyl)methyl-3,3-diphenyloxirane (2b): IR (nujol) 3060, 2927, 1603, 1494, 1448, 1380, 1063, 1016, 746, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 3H), 2.27 (s, 3H), 2.60 (d, *J* = 15.0 Hz, 1H), 2.84 (d, *J* = 15.0 Hz, 1H), 7.09–7.17 (m, 3H), 7.22–7.26 (m, 2H), 7.26–7.29 (m, 1H), 7.31–7.36 (m, 4H), 7.49–7.52 (m, 2H), 7.57–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.43, 20.37, 37.68, 68.37, 71.27, 126.02, 126.60, 127.31, 127.35, 127.42, 127.48, 128.44, 128.45, 130.23, 130.48, 136.67, 136.99, 140.26, 140.60; Found: C, 87.88; H, 7.08%. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05%. m.p. 67.9–68.2 ºC.

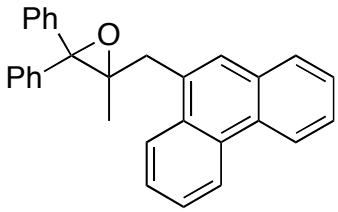
2-(2-Ethylphenyl)methyl-2-methyl-3,3-diphenyloxirane (2c): IR (nujol) 2854, 1601, 1495, 1058, 1015, 761, 749, 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 3H), 1.10 (t, *J* = 7.5 Hz, 3H), 2.56–2.69 (m, 3H), 2.85 (d, *J* = 10.5 Hz, 1H), 7.14–7.17 (m, 3H), 7.22–7.26 (m, 2H), 7.30–7.35 (m, 5H), 7.49–7.52 (m, 2H), 7.57–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.34, 19.56, 26.28, 36.90, 68.38, 71.32, 125.95, 126.81, 127.32, 127.40, 127.44, 127.48, 128.43, 128.45, 128.77, 130.36, 135.93, 140.27, 140.63, 142.98; Found: C, 87.62; H, 7.50%. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37%. m.p. 70.9– 71.5 ºC.

2-(2-Isopropylphenylmethyl)-2-methyl-3,3-diphenyloxirane (2d): IR (neat) 3060, 2963, 1602, 1493, 1448, 1383, 1034, 1016, 761, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 2.66 (d, *J* = 14.5 Hz, 1H), 2.89 (d, *J* = 14.5 Hz, 1H), 3.15 (qq, *J* = 7.0, 7.0 Hz, 1H), 7.12–7.16 (m, 1H), 7.18–7.36 (m, 9H), 7.49–7.52 (m, 2H), 7.57–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.64, 23.80, 24.07, 29.08, 36.76, 68.35, 71.45, 125.46, 125.69, 126.99, 127.33, 127.42, 127.48, 128.36, 128.42, 128.45, 130.55, 135.15, 140.26, 140.64, 147.54; HRMS Found: m/z 342.1979. Calcd for $C_{25}H_{26}O$: 342.1984.

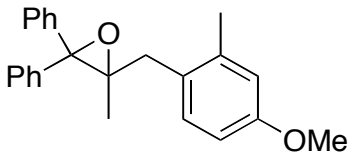
2-Methyl-3,3-diphenyl-2-(2-vinylphenyl)methyloxirane (2e): IR (nujol) 3059, 1601, 1495, 1057, 911, 761, 749, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (s, 3H), 2.65 (d, *J* = 15.0 Hz, 1H), 2.95 (d, *J* = 15.0 Hz, 1H), 5.29 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.62 (dd, *J* = 17.5, 1.5 Hz, 1H), 6.98 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.20–7.28 (m, 5H), 7.30–7.38 (m, 4H), 7.47–7.51 (m, 3H), 7.59–7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.47, 37.52, 68.41, 71.54, 115.81, 126.06, 126.98, 127.35 (two

peaks merge), 127.43, 127.55, 127.88, 128.42, 128.48, 130.87, 135.48, 135.78, 137.65, 140.18, 140.52; Found: C, 88.32; H, 6.84%. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79%. m.p. 71.0–71.2 ºC.

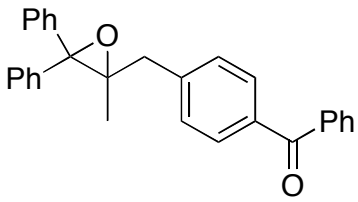
2-Methyl-2-(9-phenanthrenylmethyl)-3,3-diphenyloxirane (2g): IR (nujol) 1496, 1055, 1019, 925, 765, 753, 730, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 3H), 3.12 (d, J = 15.5 Hz, 1H), 3.32 (d, J = 15.5 Hz, 1H), 7.22–7.26 (m, 1H), 7.27–7.30 (m, 1H), 7.31–7.35 (m, 2H), 7.38–7.42 (m, 2H), 7.52–7.55 (m, 2H), 7.57–7.64 (m, 2H), 7.65–7.68 (m, 2H), 7.71–7.74 (m, 2H), 7.84–7.87 (m, 2H), 8.17–8.21 (m, 1H), 8.65–8.68 (m, 1H), 8.71–8.74(m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.60, 39.17, 68.06, 71.53, 122.68, 123.19, 125.85, 126.49, 126.55, 126.82, 126.85, 127.37, 127.42, 127.49, 127.66, 128.41, 128.49, 128.59, 128.66, 130.11, 130.84, 131.85, 131.95, 133.30, 140.28, 140.51; Found: C, 89.76; H, 5.96%. Calcd for $C_{30}H_{24}O$: C, 89.97; H, 6.04%. m.p. 135.0–135.6 ºC.



2-(4-Methoxy-2-methylphenyl)methyl-2-methyl-3,3-diphenyloxirane (2h): IR (neat) 2926, 1613, 1498, 1448, 1256, 1153, 1112, 1054, 768, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 3H), 2.24 (s, 3H), 2.52 (d, J = 15.0 Hz, 1H), 2.77 (d, J = 15.0 Hz, 1H), 3.77 (s, 3H), 6.69–6.71 (m, 2H), 7.14–7.17 (m, 1H), 7.22–7.26 (m, 2H), 7.30–7.35 (m, 4H), 7.48–7.50 (m, 2H), 7.56–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.35, 20.65, 36.96, 55.34, 68.52, 71.32, 111.25, 115.93, 127.31, 127.32, 127.39, 127.44, 128.43 (two peaks merge), 128.78, 131.20, 138.30, 140.31, 140.67, 158.18; Found: C, 83.88; H, 7.08%. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02%. m.p. 83.9–84.2 ºC.



4-(2,3-Epoxy-2-methyl-3,3-diphenylpropyl)phenyl phenyl ketone (2i): IR (nujol) 3027, 1653, 1607, 1495, 1448, 1277, 1178, 1019, 938, 924, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3H), 2.71 (d, J = 14.0 Hz, 1H), 2.87 (d, J = 14.0 Hz, 1H), 7.23–7.29 (m, 2H), 7.30–7.39 (m, 6H), 7.46–7.50 (m, 4H), 7.56–7.61 (m, 3H), 7.73–7.76 (m, 2H), 7.78-–7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.63, 40.94, 68.06, 71.60, 127.34 (two peaks merge), 127.57, 127.66, 128.45, 128.50, 128.57, 129.69, 130.21, 130.47, 132.51, 136.02, 137.95, 139.98, 140.21, 143.33. 196.70; HRMS Found: m/z 404.1779. Calcd for $C_{29}H_{24}O_2$: 404.1779.



***tert*-Butyl 4-(2,3-epoxy-2-methyl-3,3-diphenylpropyl)phenyl ketone (2j):** IR (nujol) 2854, 1673, 1608, 1457, 1178, 1019, 962, 951, 763, 726, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, 3H), 1.35 (s, 9H), 2.66 (d, J = 14.0 Hz, 1H), 2.80 (d, J = 14.0 Hz, 1H), 7.22–7.28 (m, 4H), 7.30–7.37 (m, 4H), 7.45–7.48 (m, 2H), 7.56–7.59(m, 2H), 7.64–7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.62, 28.33, 40.75, 44.34, 68.10, 71.57, 127.37, 127.38, 127.55, 12.63, 128.45, 128.49, 128.55, 129.42, 136.71, 140.06, 140.31, 141.56, 208.73; Found: C, 84.08; H, 7.39%. Calcd for $C_{27}H_{28}O_2$: C, 84.34; H, 7.34%. m.p. 102.1–102.8 °C.

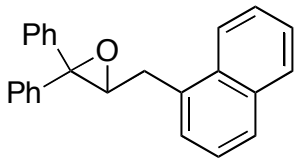
2-Methyl-2-(3-methyl-2-butenyl)-3,3-diphenyloxirane (2k): IR (neat) 2928, 1603, 1495, 1448, 1377, 1067, 1024, 766, 753, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (s, 3H), 1.43 (d, J = 1.0 Hz, 3H), 1.71 (d, J = 1.0 Hz, 3H), 2.05 (dd, J = 14.5, 7.5 Hz, 1H), 2.12 (dd, J = 14.5, 7.5 Hz, 1H), 5.19 (t of sept., J = 7.5, 1.0 Hz, 1H), 7.19–7.24 (m, 2H), 7.27–7.33 (m, 4H), 7.44–7.50 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.04, 19.62, 26.11, 33.99, 68.34, 71.79, 119.19, 127.27 (two peaks merge), 127.31, 127.34, 128.29, 128.37, 134.54, 140.42, 140.79; Found: C, 86.30; H, 8.11%. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97%.

2-(2-Butenyl)-2-methyl-3,3-diphenyloxirane (2l, *E*/*Z* = 76:24): IR (neat) 3026, 2927, 1602, 1495, 1448, 1018, 968, 926, 750, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 0.24 x 3H), 1.18 (s, 0.76 x 3H), 1.42–1.45 (m, 0.76 x 3H), 1.65–1.68 (m, 0.24 x 3H), 2.03–2.15 (m, 0.76 x 1H, 0.24 x 2H), 2.19 (dd, J = 14.5, 7.5 Hz, 0.76 x 1H), 5.35–5.49 (m, 0.76 x 1H, 0.24 x 2H), 5.54–5.61 (m, 0.76 x 1H), 7.20–7.25 (m, 2H), 7.28–7.34 (m, 4H), 7.45–7.51 (m, 4H); ^{13}C NMR ($CDCl_3$, unable to assign all peaks completely) δ 13.07 (0.76 x 1C), 18.29 (0.24 x 1C), 19.55 (0.24 x 1C), 19.61 (0.76 x 1C), 32.80 (0.76 x 1C), 38.51 (0.24 x 1C), 67.75 (0.24 x 1C), 68.05 (0.76 x 1C), 71.73 (0.76 x 1C, 0.24 x 1C), 125.11 (0.76 x 1C), 125.92 (0.24 x 1C), 126.95, 127.25, 127.30, 127.32, 127.33, 127.36, 128.27, 128.34, 128.40, 128.84 (0.76 x 7C, 0.24 x 7C), 140.29 (0.76 x 1C, 0.24 x 1C), 140.65 (0.76 x 1C), 140.71 (0.24 x 1C); Found: C, 86.44; H, 7.72%. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%.

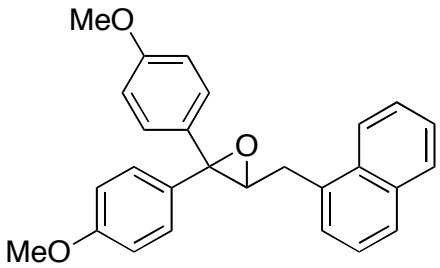
2-Methyl-2-(2-nonenyl)-3,3-diphenyloxirane (2m): IR (neat) 2926, 1602, 1495, 1448, 1377, 1017, 969, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.17 (s, 3H), 1.24–1.36 (m, 8H), 1.99 (td, J = 6.5, 6.0 Hz, 2H), 2.05 (dd, J = 14.0, 6.0 Hz, 1H), 2.11 (dd, J =

14.0, 6.0 Hz, 1H), 5.32–5.43 (m, 2H), 7.19–7.24 (m, 2H), 7.27–7.33 (m, 4H), 7.43–7.49 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.33, 19.57, 22.88, 29.05, 29.59, 31.95, 32.89, 38.58, 67.80, 71.69, 124.65, 127.13, 127.33 (two peaks merge), 127.92, 128.26, 128.39, 134.60, 140.30, 140.73; Found: C, 85.92; H, 8.91%. Calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04%.

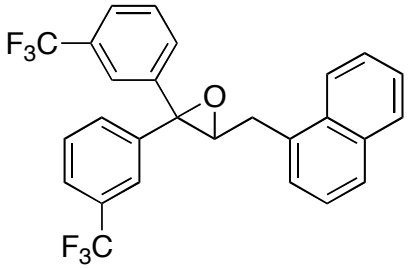
3-(1-Naphthylmethyl)-2,2-diphenyloxirane (3b): IR (nujol) 2922, 2853, 1596, 1448, 1260, 1014, 887, 796, 777, 757, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.11 (dd, *J* = 15.5, 6.0 Hz, 1H), 3.19 (dd, *J* = 15.5, 6.0 Hz, 1H), 3.79 (t, *J* = 6.0 Hz, 1H), 7.24–7.33 (m, 6H), 7.36–7.46 (m, 4H), 7.47–7.52 (m, 2H), 7.54–7.57 (m, 2H), 7.75–7.78 (m, 1H), 7.84–7.88 (m, 1H), 7.94–7.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 33.34, 66.49, 66.90, 124.05, 125.78, 125.89, 126.28, 126.81, 127.26, 127.58, 128.04, 128.08, 128.42, 128.50 (two peaks merge), 128.93, 132.28, 134.04, 134.19, 137.52, 140.88; HRMS Found: m/z 336.1506. Calcd for $C_{25}H_{20}O$: 336.1514. m.p. 84.5–85.0 ºC.



2,2-Di(4-methoxyphenyl)-3-(1-naphthylmethyl)oxirane (3c): IR (neat) 2930, 2837, 1520, 1505, 1252, 1174, 1031, 895, 778, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.12 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.17 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.76 (s, 3H), 3.77 (t, *J* = 6.0 Hz, 1H), 3.85 (s, 3H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 2H), 7.28–7.32 (m, 1H), 7.39–7.43 (m, 1H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.46–7.52 (m, 2H), 7.74–7.78 (m, 1H), 7.84-–7.88 (m, 1H), 7.94–7.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 33.24, 55.48, 55.50, 66.41 (two peaks merge), 113.83 (two peaks merge), 124.11, 125.78, 125.87, 126.24, 126.76, 127.51, 128.61, 128.91, 129.57, 129.98, 132.31, 133.44, 134.04, 134.37, 159.33, 159.40; HRMS Found: m/z 396.1725. Calcd for $C_{27}H_{24}O_3$: 396.1723.

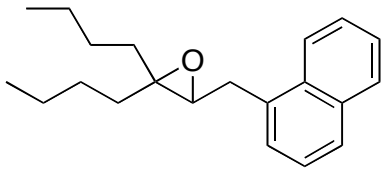


2,2-Di(3-trifluoromethylphenyl)-3-(1-naphthylmethyl)oxirane (3d): IR (neat) 3048, 2925, 2855, 1598, 1441, 1259, 1072, 892, 775, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.09 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.17 (dd, *J* = 15.0, 5.0 Hz, 1H), 3.79 (dd, *J* = 6.0, 5.0 Hz, 1H), 7.24–7.28 (m, 1H), 7.40–7.44 (m, 2H), 7.45–7.48 (m, 1H), 7.49–7.53 (m, 2H), 7.54–7.60 (m, 2H), 7.60–7.63 (m, 1H), 7.68–7.72 (m, 1H), 7.72–7.76 (m, 1H), 7.77–7.80 (m, 1H), 7.84 (s, 1H), 7.88–7.90 (m, 1H), 7.90–7.93(m, 1H); ^{13}C NMR ($CDCl_3$) δ 33.33, 65.99, 66.84, 123.71 (q, *J* = 3.8 Hz), 123.74, 124.03 (q, *J* = 272.6 Hz), 124.12 (q, *J* = 272.6 Hz), 125.22 (q, *J* = 3.8 Hz), 125.28 (q, *J* =

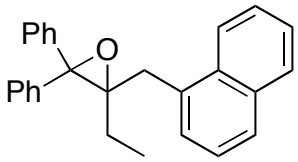


3.8 Hz), 125.47 (q, J = 3.8 Hz), 125.76, 126.06, 126.50, 126.90, 127.98, 129.08, 129.24, 129.35, 130.62, 131.30 (q, J = 32.7 Hz), 131.34 (q, J = 32.6 Hz), 131.72, 132.14, 133.27, 134.13, 137.82, 141.02; HRMS Found: m/z 472.1262. Calcd for $C_{27}H_{18}OF_6$: 472.1262.

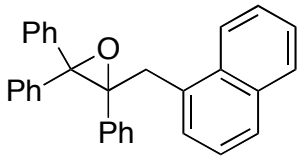
2,2-Dibutyl-3-(1-naphthylmethyl)oxirane (3e): IR (neat) 3046, 2932, 2861, 1598, 1511, 1460, 1397, 961, 791, 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.0 Hz, 3H), 1.22–1.54 (m, 9H), 1.61–1.79 (m, 3H), 3.08 (t, J = 5.5 Hz, 1H), 3.33 (d, J = 5.5 Hz, 2H), 7.39–7.45 (m, 2H), 7.48–7.52 (m, 1H), 7.53–7.57 (m, 1H), 7.75–7.78 (m, 1H), 7.85–7.89 (m, 1H), 8.08–8.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.21, 14.31, 23.05, 23.39, 27.13, 27.69, 30.33, 32.33, 35.18, 63.63, 64.32, 124.14, 125.78, 125.89, 126.29, 126.56, 127.46, 128.94, 132.35, 134.08, 135.09; Found: C, 84.85; H, 9.28%. Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52%.



2-Ethyl-2-(1-naphthylmethyl)-3,3-diphenyloxirane (3f): IR (nujol) 2854, 1601, 1448, 1375, 1077, 929, 848, 789, 778, 763, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.0 Hz, 3H), 1.20 (dq, J = 14.0, 7.0 Hz, 1H), 1.49 (dq, J = 14.0, 7.0 Hz, 1H), 3.02 (d, J = 15.5 Hz, 1H), 3.39 (d, J = 15.5 Hz, 1H), 7.23–7.30 (m, 2H), 7.31–7.36 (m, 2H), 7.37–7.56 (m, 6H), 7.58–7.63 (m, 2H), 7.68–7.72 (m, 2H), 7.73–7.77 (m, 1H), 7.82–7.86 (m, 1H), 8.12–8.16 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 9.71, 24.07, 35.37, 71.77, 71.87, 125.08, 125.45, 125.74, 126.07, 127.30, 127.37, 127.39, 127.50, 127.61, 127.82, 128.30, 128.60, 128.73, 132.98, 134.10, 134.58, 140.24, 140.56; Found: C, 88.85; H, 6.77%. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64%. m.p. 123.5–123.9 °C.



2-(1-Naphthylmethyl)-2,3,3-triphenyloxirane (3g): IR (nujol) 2923, 2854, 1654, 1559, 1507, 1457, 1448, 1374, 1023, 933, 790, 774, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (d, J = 15.0 Hz, 1H), 3.86 (d, J = 15.0 Hz, 1H), 6.90–7.01 (m, 4H), 7.02–7.09 (m, 5H), 7.17–7.21 (m, 1H), 7.24–7.28 (m, 2H), 7.34–7.43 (m, 3H), 7.46–7.50 (m, 2H), 7.58–7.62 (m, 1H), 7.73–7.76 (m, 1H), 7.77–7.81 (m, 2H), 7.88–7.92 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 38.09, 72.85 (two peaks merge), 124.91, 125.23, 125.42, 125.69, 126.86, 126.94, 127.10, 127.47, 127.58, 127.60, 127.70 (two peaks merge), 127.91, 128.38, 128.54, 128.80, 132.90, 133.66, 133.82, 137.87, 139.24, 139.95; HRMS Found: m/z 412.1829. Calcd for $C_{31}H_{24}O$: 412.1827. m.p. 151.0–152.0 °C.



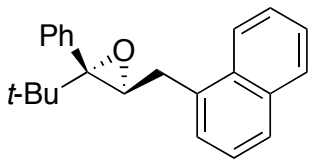
2-Methyl-3-(1-naphthylmethyl)-2-phenyloxirane (3h, diastereomer ratio = 60:40): IR (neat) 3048, 2967, 1598, 1496, 1446, 1396, 1380, 1067, 1027, 788, 775, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69 (s, 0.40 × 3H), 1.88 (s, 0.60 × 3H), 2.87 (dd, J = 15.0, 6.0 Hz, 0.40 × 1H), 3.09 (dd, J = 15.0, 6.0 Hz, 0.40 × 1H), 3.21 (t, J = 6.0 Hz, 0.60 × 1H), 3.44 (t, J = 6.0 Hz, 0.40 × 1H), 3.46 (dd, J = 15.0, 6.0 Hz, 0.60 × 1H), 3.54 (dd, J = 15.0, 6.0 Hz, 0.60 × 1H), 7.14–7.17 (m, 0.40 × 1H), 7.24–7.28 (m, 1H), 7.30–7.51 (m, 0.60 × 6H, 0.40 × 7H), 7.51–7.54 (m, 0.60 × 1H), 7.54–7.59 (m, 0.60 × 1H), 7.73–7.76 (m, 0.40 × 1H), 7.76–7.81 (m, 0.60 × 1H), 7.83–7.87 (m, 0.40 × 1H), 7.87–7.92 (m, 1H), 8.10–8.14 (m, 0.60 × 1H); ^{13}C NMR ($CDCl_3$, The peaks of the major diastereomer were underlined.) δ 18.11, 24.61, 32.46, 32.97, 61.25, 63.38, 65.54, 66.72, 123.98, 124.04, 125.24, 125.73, 125.82, 125.84, 125.97, 126.19, 126.42, 126.51, 126.79, 126.91, 127.43, 127.55, 127.64, 127.68, 128.44, 128.57, 128.88, 129.00, 132.29 (two peaks merge), 133.99, 134.08, 134.31, 134.34, 139.61, 142.82; Found: C, 87.76; H, 6.72%. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.61%.

2-Methyl-2-(1-naphthyl)-3-(1-naphthylmethyl)oxirane (3i, diastereomer ratio = 72:28): IR (neat) 3047, 2962, 2926, 1597, 1511, 1444, 1396, 1377, 1249, 109, 862, 777 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.79 (s, 0.28 × 3H), 1.94 (s, 0.72 × 3H), 2.71 (dd, J = 15.0, 7.5 Hz, 0.28 × 1H), 3.04 (dd, J = 15.0, 4.5 Hz, 0.28 × 1H), 3.44 (t, J = 6.0 Hz, 0.72 × 1H), 3.63 (dd, J = 15.0, 6.5 Hz, 0.72 × 1H), 3.66–3.72 (m, 0.72 × 1H, 0.28 × 1H), 7.06–7.09 (m, 0.28 × 1H), 7.27–7.33 (m, 0.72 × 1H, 0.28 × 1H), 7.38–7.58 (m, 0.72 × 5H, 0.28 × 8H), 7.58–7.61 (m, 0.72 × 1H), 7.69–7.79 (m, 0.72 × 2H, 0.28 × 1H), 7.79–8.00 (m, 0.72 × 4H, 0.28 × 3H), 8.16–8.20 (m, 0.72 × 1H); ^{13}C NMR ($CDCl_3$, unable to assign all peaks completely) δ 20.47, 25.34, 32.84, 33.40, 62.55, 63.16, 64.05, 65.80, 123.89, 124.01, 124.15, 124.25, 124.58, 125.43, 125.60, 125.67, 125.74, 125.78, 125.84, 125.96, 126.00 (two peaks merge), 126.10, 126.22, 126.31, 126.48, 127.11, 127.25, 127.43, 127.83, 128.10, 128.21, 128.83 (two peaks merge), 129.04, 129.05, 130.30, 130.40, 132.31, 132.35, 133.61, 133.77, 133.99, 134.17, 134.22, 134.42, 136.78, 139.56; HRMS Found: m/z 324.1512. Calcd for $C_{24}H_{20}O$: 324.1514.

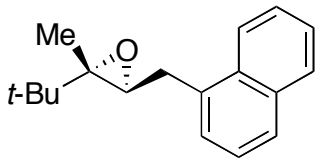
2-Isopropyl-3-(1-naphthylmethyl)-2-phenyloxirane (3j, diastereomer ratio = 88:12): IR (neat) 3047, 1598, 1511, 1446, 1397, 941, 788, 775, 761 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (d, J = 7.0 Hz, 0.88 × 3H), 0.98 (d, J = 7.0 Hz, 0.88 × 3H), 1.04 (d, J = 7.0 Hz, 0.12 × 3H), 1.09 (d, J = 7.0 Hz, 0.12 × 3H), 1.99 (sept, J = 7.0 Hz, 0.88 × 1H), 2.15 (sept, J = 7.0 Hz, 0.12 ×

1H), 2.82 (dd, J = 15.0, 6.5 Hz, 0.88 × 1H), 2.97 (dd, J = 15.0, 5.0 Hz, 0.88 × 1H), 3.36 (dd, J = 6.5, 5.0 Hz, 0.12 × 1H), 3.48 (dd, J = 6.5, 5.0 Hz, 0.88 × 1H), 3.51 (dd, J = 15.0, 6.5 Hz, 0.12 × 1H), 3.59 (dd, J = 15.0, 5.0 Hz, 0.12 × 1H), 7.26–7.36 (m, 2H), 7.37–7.53 (m, 0.88 × 7H, 0.12 × 6H), 7.53–7.57 (m, 0.12 × 1H), 7.71–7.76 (m, 0.88 × 1H), 7.76–7.80 (m, 0.12 × 1H), 7.82–7.89 (m, 1H), 7.91–7.95 (m, 0.88 × 1H), 8.11–8.14 (m, 0.12 × 1H); ^{13}C NMR ($CDCl_3$ for the major isomer) δ 17.69, 19.12, 33.30, 35.04, 63.18, 69.94, 124.12, 125.73, 125.81, 126.17, 126.55, 127.37, 127.60, 128.10, 128.19, 128.86, 132.32, 134.00, 134.80, 137.50; Found: C, 87.60; H, 7.49%. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33%.

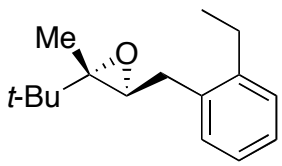
2-*tert*-butyl-3-(1-naphthylmethyl)-2-phenyloxirane (3k): IR (nujol) 2924, 2854, 1596, 1558, 1456, 1364, 1317, 908, 806, 788, 775, 756, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9H), 2.62 (dd, J = 15.5, 7.5 Hz, 1H), 3.03 (dd, J = 15.5, 4.0 Hz, 1H), 3.59 (dd, J = 7.5, 4.0 Hz, 1H), 7.28–7.34 (m, 3H), 7.34–7.37 (m, 1H), 7.40–7.45 (m, 2H), 7.45–7.52 (m, 2H), 7.54–7.58 (m, 1H), 7.72–7.76 (m, 1H), 7.82–7.86 (m, 1H), 7.89–7.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 26.74, 34.10, 34.77, 60.33, 71.39, 124.20, 125.73, 125.80, 126.15, 126.42, 126.98, 127.35, 127.47, 128.36, 128.56, 128.84, 130.04, 132.38, 134.03, 135.19, 137.60; HRMS Found: m/z 316.1815. Calcd for $C_{23}H_{24}O$: 316.1827. m.p. 64.5–64.9 ºC.



2-(1,1-Dimethylethyl)-2-methyl-3-(1-naphthylmethyl)oxirane (3l): IR (neat) 3046, 2966, 1598, 1511, 1466, 1379, 1166, 1078, 792, 781 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9H), 1.46 (s, 3H), 3.26–3.58 (m, 3H), 7.38–7.46 (m, 2H), 7.48–7.53 (m, 1H), 7.53–7.58 (m, 1H), 7.75–7.79 (m, 1H), 7.86–7.90 (m, 1H), 8.06–8.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.48, 26.12, 32.78, 34.60, 60.13, 66.14, 124.15, 125.79, 125.91, 126.33, 126.43, 127.45, 128.95, 132.37, 134.07, 135.29; Found: C, 84.93; H, 8.71%. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72%. HPLC conditions: Daicel CHRALCEL OD-H, hexane/2-propanol = 99/1, 0.7 mL/min, retention time: 11.53 min ((*S*,*S*), major); 13.80 min ((*R*,*R*), minor).

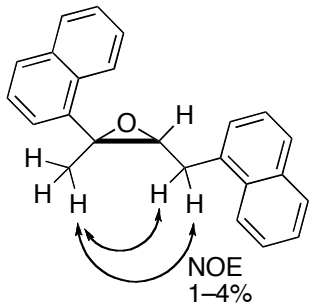


3-(2-Ethylphenyl)methyl-2-(1,1-dimethylethyl)-2-methyloxirane (3m): IR (neat) 2966, 2934, 1605, 1454,1379, 1364, 1165, 1076, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9H), 1.23 (t, J = 7.5 Hz, 3H), 1.37 (s, 3H), 2.70 (qd, J = 7.5, 4.5 Hz, 2H), 2.85 (dd, J = 15.0, 6.0 Hz, 1H), 2.93 (dd, J = 15.0, 6.0 Hz, 1H), 3.15 (t, J = 6.0 Hz, 1H), 7.14–7.24 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.40, 15.37, 26.12 (two peaks merge), 31.97, 34.55, 60.29, 65.92, 126.27, 126.93, 128.75, 129.34, 136.53, 142.48; Found: C, 82.69; H, 10.50%. Calcd for

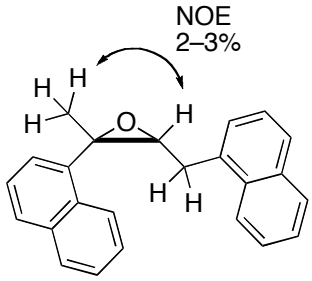


$C_{16}H_{24}O$: C, 82.70; H, 10.41%.

Stereochemical Assignment of 3h and 3i



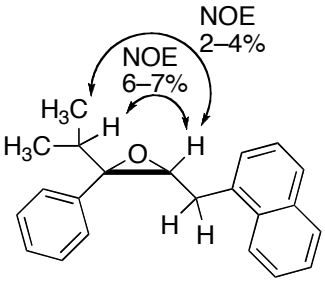
major diastereomer of **3i**



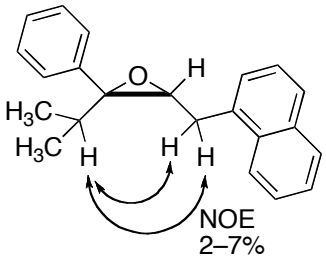
minor diastereomer of **3i**

The relative stereochemistry of diastereomers of **3i** was assigned based on NOE experiments. The major diastereomer showed a correlation between the benzylic protons and the protons of the methyl group. In contrast, a correlation was observed between the proton attached to the oxygenated carbon and the protons of the methyl group in the minor diastereomer. The NOE experiments of the diastereomeric mixture of **3h** failed because all the expected correlations were too weak. The relative stereochemistry of diastereomers **3h** was assigned based on the structural analogy of **3i**. Both diastereomers showed similar ^{1}H NMR spectrum.

Stereochemical Assignment of 3j



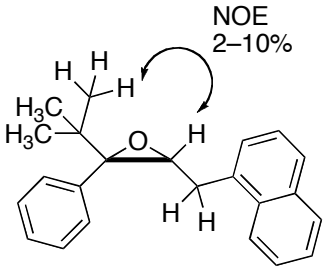
major diastereomer of **3i**



minor diastereomer of **3j**

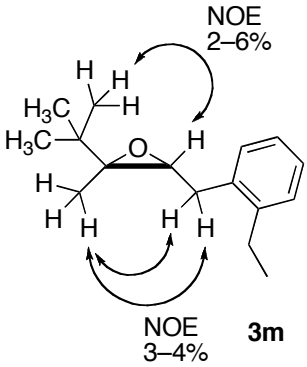
The relative stereochemistry of diastereomers **3j** was also assigned based on NOE experiments. In the case of the major diastereomer, a correlation between the proton attached to the oxygenated carbon and the protons of the isopropyl group (both C–<u>H</u> and $CH(C\underline{H}_3)_2$ was observed. On the other hand, the minor diastereomer showed a correlation between the benzylic protons and the methyne proton of the isopropyl group.

Stereochemical Assignment of (*R,*S**)-3k**



The stereochemistry of **3k** was assigned based on a correlation between the proton at the oxygenated carbon and the protons of the *tert*-butyl group. The similarity of the ^{1}H NMR spectrum of **3k** to that of the major diastereomer of **3j** also supports the stereochemistry of **3k**.

Stereochemical Assignment of (*S,*S**)-3l**



The relative stereochemistry of **3l** was determined based on the structural analogy of **3m**. Oxirane **3m** was prepared by the reaction of **1l** with 1-bromo-2-ethylbenzene (59% yield). The trans stereochemistry was assigned based on a correlation between the benzylic protons and the protons of the methyl group. A NOE correlation was also observed between the proton attached to the oxygenated carbon and the protons of the *tert*-butyl group.

References and Notes

(1) (a) Aggarwal, V. K.; Badine, D. M.; Moorthie, V. A. In *Aziridines and Epoxides in Organic Synthesis*; Yudin, A. K., Ed.; Wiley-VCH Verlag: Weinheim, 2006; pp1–22. (b) Erden, I. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriren, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 1A, pp97–171.

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(3) (a) Nakhla, J. S.; Kampf, J. W.; Wolfe, J. P. *J. Am. Chem. Soc.* **2006**, *128*, 2893–2901. (b) Hay, M. B.; Wolfe, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 16468–16476. (c) Hay, M. B.; Hardin, A. R.; Wolfe, J. P. *J. Org. Chem.* **2005**, *70*, 3099–3107. (d) Wolfe, J. P.; Rossi, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 1620–1621. (e) Wolfe, J. P. *Synlett* **2008**, 2913–2937.

(4) Palladium-catalyzed carboetherification reactions affording isoxazolines and isoxazolidines were reported. (a) Jiang, D.; Peng, J.; Chen, Y. *Org. Lett.* **2008**, *10*, 1695–1698. (b) Dongol, K. G.; Tay, B. Y. *Tetrahedron Lett.* **2006**, *47*, 927–930. (c) Hay, M. B.; Wolfe, J. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6492–6494. (d) Jiang, D.; Peng, J.; Chen, Y. *Tetrahedron* **2008**, *64*, 1641–1647.

(5) It is possible that other undesired reactions might proceed under the reaction conditions such as β-vinyl elimination from palladium alkoxide. These reactions would be suppressed by the proper choice of the ligand. Reviews for palladium-catalyzed reactions with tertiary alcohols: (a) Muzart, J. *Tetrahedron* **2005**, *61*, 9423–9463. (b) Satoh, T.; Miura, M. *J. Synth. Org. Chem. Jpn.* **2006**, *64*, 1199–1207.

(6) The possibility that the insertion reaction proceeds through an *anti*-oxypalladation pathway cannot be excluded at this stage. See Chapter 5.

(7) Wu, P.-L.; Peng, S.-Y.; Magrath, J. *Synthesis* **1996**, 249–252.

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(10) Zhao, Y.; Mitra, A. W.; Hoveyda, A. H.; Snapper, M. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8471–8474.

Chapter 5

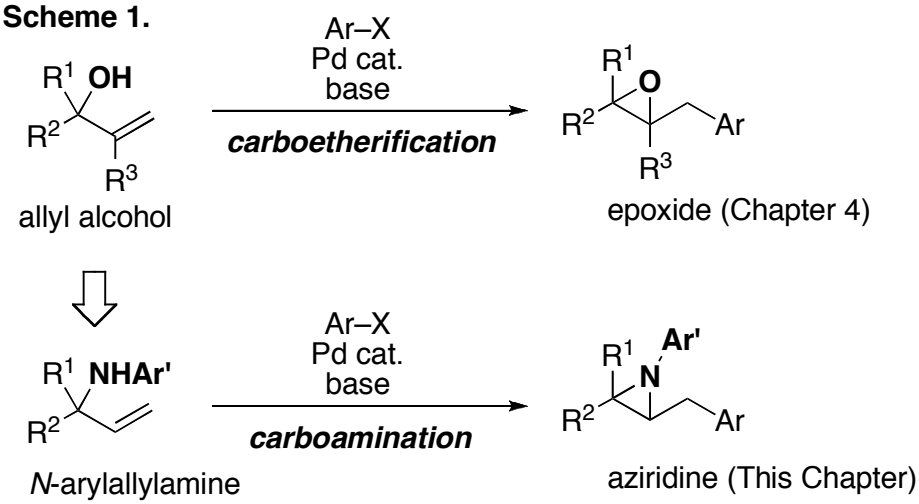
Synthesis of Aziridines by Palladium-Catalyzed Reaction of Allylamines with Aryl and Alkenyl Halides : Evidence of a *syn*-Carboamination Pathway

Treatment of *N*-arylallylamine with aryl or alkenyl halide under palladium catalysis resulted in intramolecular cyclization to form the arylmethyl-substituted aziridine with concomitant C–C bond formation. The deuterium-labeling experiments for the elucidation of the reaction mechanism revealed that the reaction proceeded through *syn*-carboamination.

Introduction

Palladium-catalyzed intramolecular carboetherification or carboamination reaction of alkenes with organic halides emerged as an attractive method to construct heterocycles, forming both carbon-heteroatom and carbon-carbon bonds in a single operation.[1] A number of five-membered heterocycles have been synthesized by the methodology.[2,3] Meanwhile, the preparation of strained three-membered heterocycles has remained a challenge. In Chapter 4, the author has reported palladium-catalyzed carboetherification reactions of tertiary allyl alcohols with aryl or alkenyl halides, which provide multisubstituted epoxides.[4] She then expected that the reaction would be extended to carboamination for the synthesis of aziridines starting from allylamines (Scheme 1). In Chapter 5, she presents the results of the carboamination along with evidence for a plausible reaction mechanism.

Scheme 1.

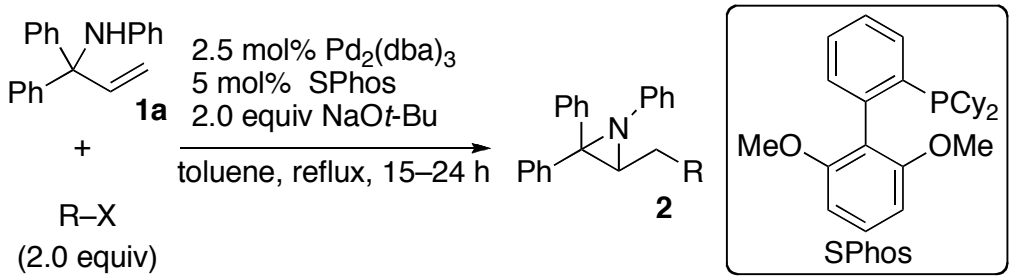


Results and Discussion

Her investigation began with a reaction of *N*-phenylallylamine **1a** bearing two phenyl groups at the allylic position. Treatment of **1a** with bromobenzene in the presence of sodium *tert*-butoxide under palladium catalysis led to aziridination and C–C bond formation, providing the corresponding arylated aziridine **2a** in 98% yield (Table 1, entry 1). In contrast to her

previous epoxidation reactions, the aziridination reaction did not suffer from a competitive Mizoroki-Heck reaction.[4] A wide range of aryl bromides and chlorides were incorporated to the corresponding aziridines **2a**–**2h** in excellent yields (entries 2–9). Alkenyl chlorides also proved to be suitable substrates for the aziridination reactions (entries 10 and 11).

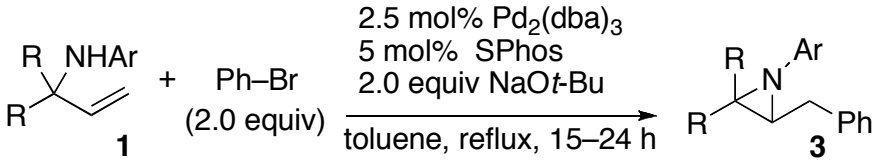
Table 1. Scope of Aryl and Alkenyl Halides in Palladium-Catalyzed Aziridination/Arylation or /Alkenylation with **1a**



entry	R–X	**2**, yield (%)
1	C_6H_5Br	**2a,** 98
2	C_6H_5Cl	**2a**, 98
3	1-$C_{10}H_7Br$	**2b**, 90
4	2-$MeOC_6H_4Br$	**2c**, 83
5	4-$MeOC_6H_4Br$	**2d**, 97
6	4-$Me_2NC_6H_4Br$	**2e**, 88
7	4-$F_3CC_6H_4Cl$	**2f**, 99
8	4-(*t*-BuO_2C)C_6H_4Cl	**2g**, 81
9	4-(Et_2NOC)C_6H_4Cl	**2h**, 81
10	$(CH_3)_2C{=}CHCl$	**2i**, 94
11	(*E*)-*n*-$C_5H_{11}CH{=}CHCl$	**2j**, 90

The reactions of several *N*-arylallylamines with bromobenzene were then examined (Table 2). The electronic nature of aryl substituents on the nitrogen atom as well as at the allylic position did not affect the reaction efficiency (entries 1–4). Gratifyingly, alkyl-substituted allylamines **1f** and **1g** also underwent the reaction in satisfactory yields (entries 5 and 6).

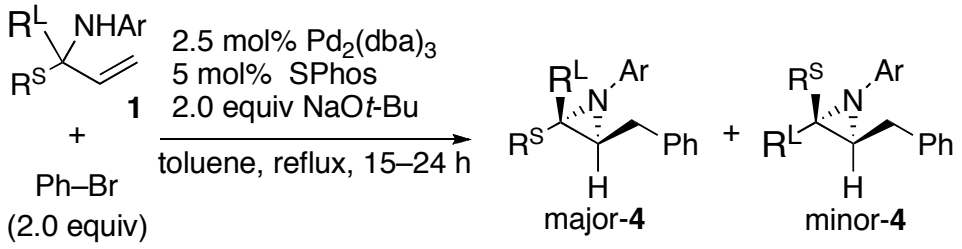
Table 2. Reactions with Various *N*-Arylallylamines with Bromobenzene



entry	R	Ar		**3**, yield (%)
1	Ph	4-$MeOC_6H_4$	(**1b**)	**3a**, 92
2	Ph	4-FC_6H_4	(**1c**)	**3b**, 96
3	4-$MeOC_6H_4$	Ph	(**1d**)	**3c**, 98
4	4-FC_6H_4	Ph	(**1e**)	**3d**, 98
5	*n*-C_3H_7	Ph	(**1f**)	**3e**, 92
6	-$(CH_2)_5$-	Ph	(**1g**)	**3f**, 76

Next, the author turned her attention to reactions of allylamines bearing a stereogenic center at the aminated carbon, in which two diastereomers could be obtained (Table 3). It was found that the larger substituent R^L and the benzyl moiety were oriented in a *cis* configuration in the major diastereomer. Interestingly, the major diastereomer obtained in the aziridination reaction possessed configuration opposite of the epoxides.[4] For instance, the reaction with *N*-aryl-2-phenylbutenamines **1h** and **1i** afforded **4a** and **4b** as a single diastereomer in 90% and 73% yields, respectively (entries 1 and 2). Moreover, allylamine **1j** bearing a trifluoromethyl group also took part in the reaction with high diastereoselectivity (entry 3). Dialkyl-substituted allylamines were then subjected to the aziridination reaction. Allylamine **1k** having an isopropyl group at the allylic position was converted to **4d** with slightly lower diastereoselectivity (entry 4). Surprisingly, both yield and diastereoselectivity diminished when the more bulky *tert*-butyl-substituted allylamine **1m** was used as a substrate (entry 5).

Table 3. Diastereoselective Synthesis of Aziridines

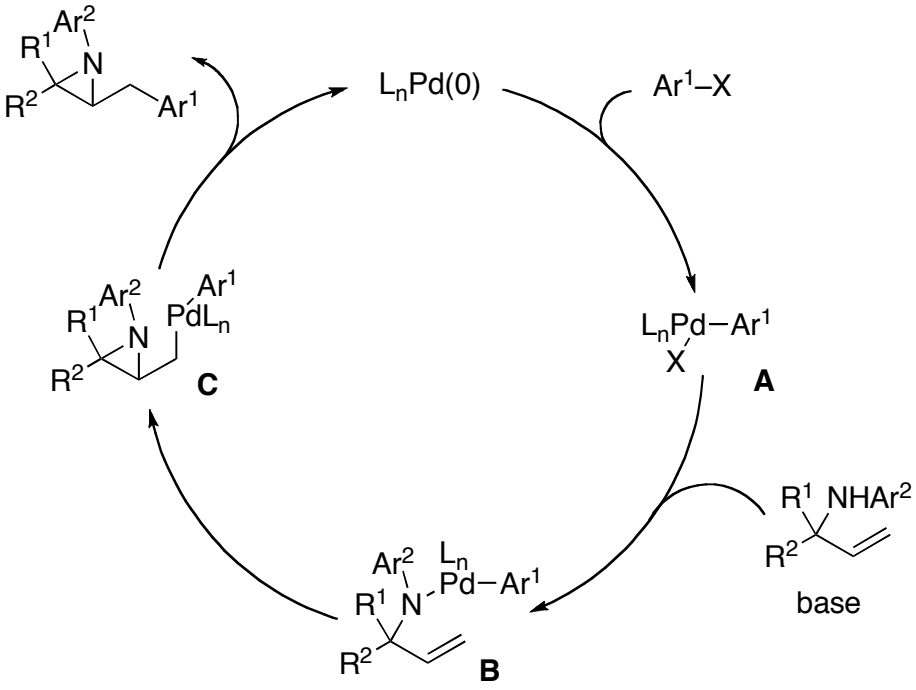


entry	R^L	R^S	Ar		**4**, yield (%)	dr
1	Ph	Me	Ph	(**1h**)	**4a**, 90	>99:1
2	Ph	Me	4-$MeOC_6H_4$	(**1i**)	**4b**, 73	>99:1
3	Ph	CF_3	Ph	(**1j**)	**4c**, 90	93:7
4	*i*-Pr	Me	Ph	(**1k**)	**4d**, 83	79:21
5[a]	*t*-Bu	Me	Ph	(**1l**)	**4e**, 42	59:41

[a] Xylene was used instead of toluene. An amount of 47% of **1l** was recovered.

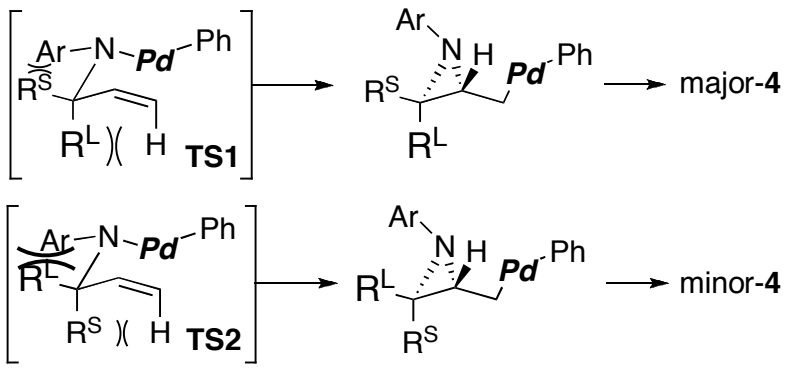
A mechanism of the reaction based on related precedent[1,2,4] is proposed as shown in Scheme 2. Initial oxidative addition of aryl halide to zerovalent palladium occurs to provide arylpalladium halide **A**. Subsequent ligand exchange between **A** and allylamine in the presence of sodium *tert*-butoxide affords palladium amide **B**. It seems likely that **B** would undergo reductive elimination to give N-arylated product under the reaction conditions.[5] However, intramolecular coordination of the alkene moiety of **B** to the palladium center would prevent such reductive elimination. The coordination followed by *syn*-aminopalladation then furnishes alkylpalladium intermediate **C**.[6] Finally, reductive elimination from **C** takes place to give the corresponding aziridine and to regenerate Pd(0).

Scheme 2. Plausible Reaction Mechanism



The observed diastereoselectivity in Table 3 would be explained as follows (Scheme 3). There are two presumable chair-like transition states **TS1** and **TS2** in the aminopalladation step, in which diastereoselectivity would be determined. Two sets of steric interactions should be considered in both transition states: one is 1,3-allylic interaction between the pseudoaxial substituent, R^L or R^S, and the hydrogen at the alkene terminus, and the other is 1,2-pseudoequatorial repulsion between the aryl group attached to nitrogen and R^L or R^S. Generally, **TS1** would be more favorable due to its smaller repulsion energy than that of **TS2**, which involves a larger repulsive interaction between R^L and the aryl group (Table 3, entries 1–3). However, as R^L becomes much bulkier (entries 4 and 5), 1,3-allylic interaction could not be negligible in **TS1**. As a result, the difference of the energy between the two transition states would be smaller, leading to the lower diastereoselectivity in the case of the reaction with **1k** and **1l**.

Scheme 3.



As described above, the author hypothesizes that the reaction proceeds through *syn*-aminopalladation of palladium amide intermediate **B**. However, an intermolecular *anti*-aminopalladation pathway[7] is also conceivable. To confirm *syn*-aminopalladation, she performed the reaction of (*Z*)-deuterio-**1i** with 1,2-dichlorobenzene (Scheme 4). As a consequence, aziridine deuterio-**5** bearing three stereogenic centers was obtained as a single diastereomer. The relative configuration of **5** on the aziridine ring would be *erythro*, the same as **4b**.[8] The other relative configuration between the secondary aminated carbon and the deuterium-substituted one (2,3-position) was not known at this stage and should be determined after further derivatization. Oxidative removal of the 4-methoxyphenyl group followed by intramolecular amination of the aryl chloride gave an azabicyclo[3.1.0]hexane derivative deuterio-**6**. The corresponding nondeuterated analog **6** was prepared in the same manner. The rigid conformation of **6** gave the characteristic coupling constants in the ^{1}H NMR spectrum, allowing the assignment of the signals corresponding to H_A, H_B, and H_C (Figure 1, left). On the other hand, the H_B signal was not observed in the ^{1}H NMR spectrum of deuterio-**6** (Figure 1, right). Thus, the relative stereochemistry of the newly created stereogenic centers of deuterio-**6** was assigned to *erythro*. Thereby, deuterio-**5** should have 1,2-*erythro,* 2,3-*erythro* configuration.

Scheme 4. Validation of the Reaction Mechanism

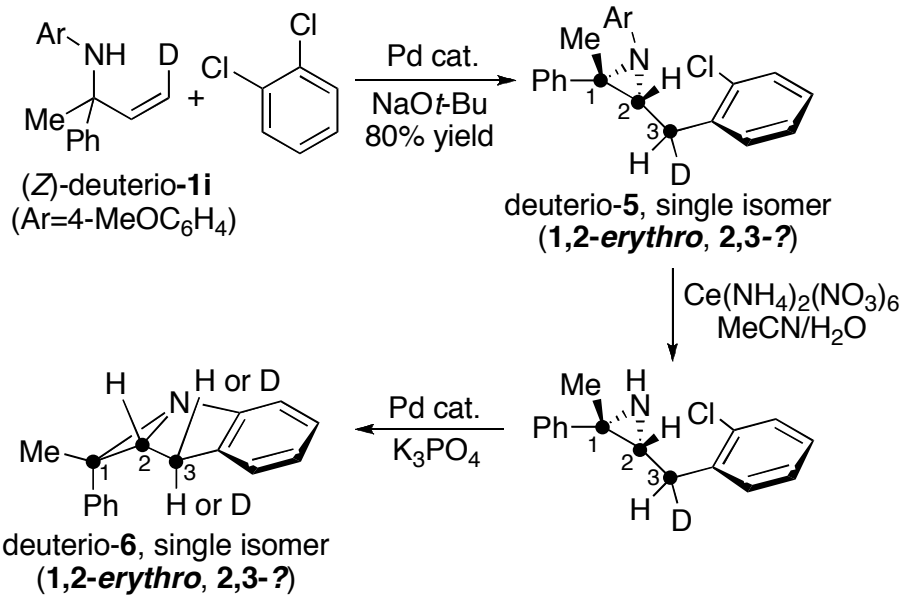
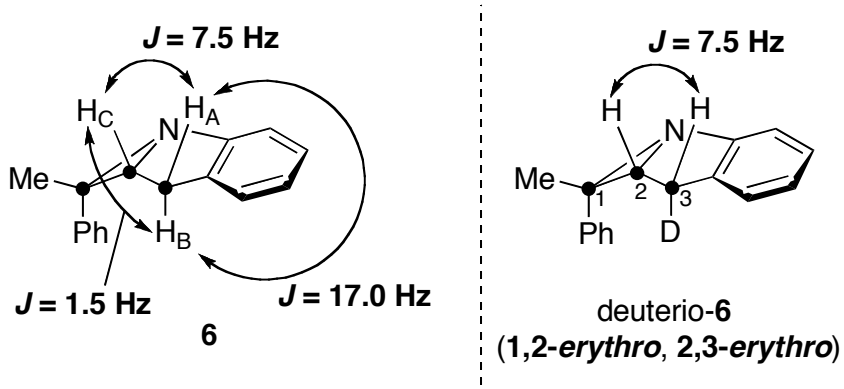
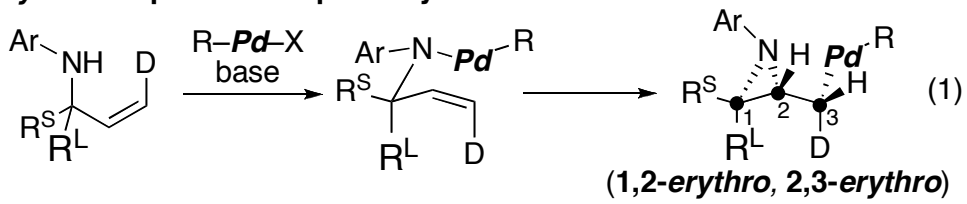


Figure 1. ^{1}H NMR coupling constant analysis of **6** and deuterio-**6**

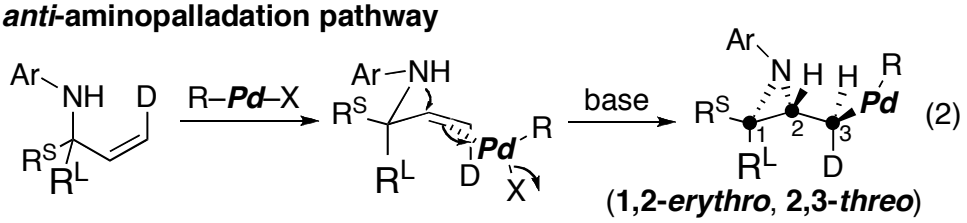


Suppose that the aminopalladation reaction proceeds in a *syn* fashion, (1,2-*erythro*, 2,3-*erythro*)-deuterio-**5** would be produced (eq 1). In contrast, *anti*-aminopalladation pathway would result in the formation of (1,2-*erythro,* 2,3-*threo*)-deuterio-**5** (eq 2). Therefore, the experimental result is consistent with her hypothesis.

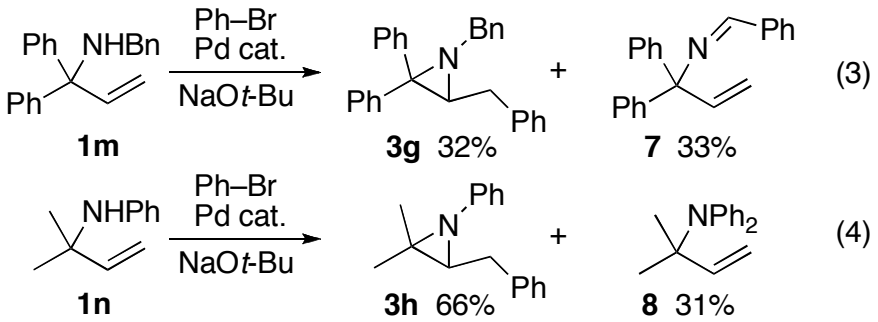
***syn*-aminopalladation pathway**



***anti*-aminopalladation pathway**



In addition, the reaction of **1m** bearing a benzyl moiety on nitrogen provided a mixture of the aziridinated product **3g** and imine **7**, which would be generated from β-hydride elimination from the palladium amide intermediate corresponding to **B** in Scheme 2 (eq 3). Moreover, the reaction of **1n** gave aziridine **3h** along with N-arylated allylamine **8** (eq 4). The results are also suggestive of the existence of the palladium amide intermediate.



Conclusion

The author has found a new synthetic method for the preparation of aziridines by palladium-catalyzed reactions of allylamines with aryl or alkenyl halides. The reaction proceeds through *syn*-aminopalladation, producing carbon-nitrogen bond with concomitant carbon-carbon bond formation.

Experimental Section

Instrumentation and Chemicals

All experiments were conducted using the same instruments described in Chapter 1. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Sodium *tert*-butoxide was purchased from Wako Pure Chemical Co. 2-Dicyclohexyphosphino-2',6'-dimethoxybiphenyl (SPhos) and tris(dibenzylideneacetone)dipalladium were purchased from Aldrich. All reactions were carried out under argon atmosphere. Preparation of allylamines **1a–1n** was shown below.

Experimental Procedure for the Synthesis of Starting Materials

The reaction conditions for the preparation of allylamines were not optimized completely.

Preparation of allylamines (Method 1)

Allylamines **1a–1e** and **1h–1j** were synthesized as described in method 1. Preparation of **1a** is representative. Benzophenone (9.11 g, 50.0 mmol) and activated molecular sieves 5A (20.0 g) were placed in a 100–mL reaction flask equipped with a Dimroth condenser. Under argon atmosphere, benzene (20.0 mL) and aniline (5.47 mL, 60 mmol) were added, and the mixture was heated under reflux overnight. After being cooled, the resulting mixture was filtered through a filter paper to remove the molecular sieves. The filtrate was evaporated, and the resulting pale yellow solid was recrystallized from ethanol. *N*-(Diphenylmethylene)aniline[9] was obtained as a yellow plate (9.35 g, 36.3 mmol, 73%).

Trimethylsilylacetylene (3.53 mL, 25.0 mmol) and THF (15 mL) were added to a 100–mL reaction flask filled with argon. At 0 ºC, butyllithium (1.60 M in hexane solution, 15.0 mL, 24.0 mmol) was added dropwise via a syringe, and the mixture was stirred for 30 min at the same temperature. Hexamethylphosphoramide (20.0 mL) and *N*-(diphenylmethylene)aniline (5.15 g, 20.0 mmol) were sequentially added, and the resulting brown mixture was allowed to warm to room temperature. After being stirred for 2 h, the mixture was poured into saturated ammonium chloride solution (40 mL). The mixture was extracted three times (hexane/EtOAc = 5/1), and the combined organic layer was dried over sodium sulfate and concentrated in vacuo. A residue, which contained *N*-(1,1-diphenyl-3-trimethylsilyl-2-propynyl)aniline and *N*-(1,1-diphenyl -2-propynyl)aniline, was used in the following reaction without further purification.

The residue was dissolved in methanol (50.0 mL) under air. Four teaspoons of potassium carbonate (6.6 g, 48 mmol) was added to the solution at room temperature. The suspension was stirred until consumption of *N*-(1,1-diphenyl-3-trimethylsilyl-2-propynyl)aniline was observed by thin layer chromatography. After the reaction was completed, brine (50 mL) was added. Extraction, evaporation, and purification on silica gel afforded

N-(1,1-diphenyl-2-propynyl)aniline as a white solid (5.66 g, 20.0 mmol, quantative yield in two steps).

Lithium aluminum hydride (2.28 g, 60 mmol) was placed in a reaction flask equipped with a Dimroth condenser under argon, and THF (40.0 mL) was added to the flask. A solution of *N*-(1,1-diphenyl-2-propynyl)aniline (5.66 g, 20.0 mmol) dissolved in THF (40.0 mL) was added to the slurry at room temperature. The mixture was heated at reflux overnight. After the mixture was cooled to room temperature, methanol (42.0 mL) was carefully added dropwise at 0 ºC. The mixture was stirred vigorously until the generation of hydrogen gas ceased. A 30 wt% Rochelle salt solution (72.0 mL) was added, and the mixture was stirred for another 30 min at room temperature. The resulting colloidal mixture was filtered through a Buchner funnel. The filtrate was washed with brine and extracted three times (hexane:AcOEt = 5/1), and the combined organic layer was dried over sodium sulfate. Evaporation under reduced pressure generated a pale-yellow solid. The solid was washed with cold hexane three times. *N*-(1,1-Diphenyl -2-propenyl)aniline **1a** was obtained as a white solid (4.46 g, 15.6 mmol, 78%). In the case that an oily residue was obtained, it was purified by silica gel column chromatography.

Preparation of allylamines (Method 2)

Allylamines **1f**, **1g**, **1k**, **1l**, and **1n** were synthesized as outlined in method 2. Preparation of **1g** is representative. Sodium hydride (60 wt% in oil, 3.28 g, 82.0 mmol) was placed in a flask. Under argon atmosphere, sodium hydride was washed with hexane (15 mL) three times. THF (60.0 mL) and ethyl (diethoxyphosphoryl)acetate (18.2 mL, 81.0 mmol) were added to the flask at room temperature. After 30 min, cyclohexanone (8.29 mL, 80.0 mmol) was added, and the resulting mixture was stirred at ambient temperature for 8 h. Water (200 mL) was then added to the flask to quench the reaction. Extraction and evaporation followed by distillation under reduced pressure (84 ºC/4–5 Torr) provided ethyl 2-cyclohexylideneacetate as a colorless liquid (11.7 g, 69.4 mmol, 87%).

A suspension of lithium aluminum hydride (5.27 g, 139 mmol) in Et_2O (220 mL) was placed in a reaction flask. After the flask was cooled to –78 ºC, a solution of ethyl 2-cyclohexylideneacetate (11.7 g, 69.4 mmol) in Et_2O (50 mL) was added through a dropping funnel. The bath temperature was kept at –78 ºC during the addition of the ester. The flask was then allowed to warm to room temperature. After 10 min, the flask was cooled to –78 ºC, and ethyl acetate (153 mL) and water (153 mL) was subsequently added to the mixture. The resulting colloidal mixture was filtered through a Buchner funnel. The solid on the funnel was washed three times with ethyl acetate, and the bilayer filtrate was extracted three times with ethyl acetate. Evaporation followed by purification on silica gel gave 2-cyclohexylideneethanol (4.36

g, 25.9 mmol, 37%) with the recovery of the starting material (4.56 g, 36.1 mmol, 52%).

A solution of 2-cyclohexylideneethanol (1.01 g, 8.0 mmol) in THF (11.0 mL) was placed in a flask. Under argon atmosphere, butyllithium (1.60 M in hexane solution, 5.50 mL, 8.8 mmol) was added at –78 ºC, and the resulting reddish brown mixture was stirred for 30 min at the same temperature. 2,2,2-Trifluoromethyl-*N*-phenylacetoimidoyl chloride[10] (2.28 g, 9.6 mmol) dissolved in THF (5.0 mL) was added at –78 ºC, and the mixture was warmed to 0 ºC. After being stirred for 3 h, the mixture was poured into saturated ammonium chloride solution (20 mL). Extraction, evaporation, and purification afforded 2-cyclohexylideneethyl 2,2,2-trifluoro-*N*-phenylacetimidate along with unidentified byproduct (yield could not be calculated at the current step).

Palladium-mediated rearrangement of allylic trifluoroacetimidates was performed according to the literature procedure.[11] Bis(benzonitrile)dichloropalladium (0.15 g, 0.40 mmol) was placed in a 50 mL reaction flask. A solution of 2-cyclohexylideneethyl 2,2,2-trifluoro-*N*-phenylacetimidate (ca. 8 mmol) in benzene (24 mL) was added under argon at room temperature. After the mixture was stirred for 10 h, water (20 mL) was added to the flask. Extractive workup followed by purification on silica gel provided 2,2,2-trifluoro-*N*-phenyl-*N*-(1-vinylcyclohexyl)acetamide (1.84 g, 6.2 mmol, 77% in 2 steps) as a colorless liquid.

A reaction flask containing a solution of 2,2,2-trifluoro-*N*-phenyl-*N*-(1-vinylcyclohexyl)acetamide (1.84 g, 6.2 mmol) in ethanol (13.0 mL) was cooled to 0 ºC. With vigorous stirring, sodium tetrahydroborate (1.18 g, 31.0 mmol) was added to the flask in five parts every 10 minutes. After the addition of sodium tetrahydroborate was finished, the mixture was gradually warmed to room temperature over 2 h and stirred at ambient temperature for 12 h. The mixture was then concentrated to remove ethanol, and water was added to the residue. Extraction, evaporation and purification on silica gel furnished *N*-(1-vinylcyclohexyl)aniline **1g** as a colorless oil (1.09 g, 5.4 mmol, 87%).

Preparation of 1m

A solution of benzophenone imine (3.62 g, 20.0 mmol) in toluene (10 mL) was placed in a flask under argon. Triethylamine (5.58 mL, 40.0 mmol) and benzoyl chloride (2.38 mL, 21.0 mmol) were sequentially added to the flask at room temperature. The ammonium salt was precipitated immediately. The resulting mixture was stirred for 2 h at 90 ºC. After the flask was cooled to room temperature, saturated ammonium chloride solution was added to the flask. The mixture was extracted with dichloromethane three times, and combined organic layer was evaporated in vacuo. The resulting white solid was washed with cold hexane to afford

N-(diphenylmethylene)benzamide as a white solid (5.13 g, 18.0 mmol, 90%).

Under argon atmosphere, vinylmagnesium bromide (1.00 M in THF solution, 15.0 mL, 15.0 mmol), prepared from Mg and vinyl bromide in THF, was placed in a flask. A solution of *N*-(diphenylmethylene)benzamide (2.85 g, 10.0 mmol) in THF (10 mL) was added to the flask at 0 ºC. The mixture was allowed to warm up to room temperature and stirred for 3 h. The reaction was quenched with saturated ammonium chloride solution (30 mL). Extractive workup followed by silica gel column purification provided *N*-(1,1-dipheny-2-propenyl)benzamide (3.04 g, 9.70 mmol, 97%) as a white solid.

Diisobutylaluminum hydride (1.0 M in hexane solution, 4.0 mL, 4.0 mmol) was placed in a flask under argon. Toluene (4.0 mL) and *N*-(1,1-diphenyl-2-propenyl)benzamide (0.63 g, 2.0 mmol) were added to the flask at room temperature. The mixture was refluxed for 1 h. After the flask was cooled to room temperature, methanol (2.8 mL) and 30 wt% Rochell salt solution (5.0 mL) were sequentially added to the mixture to quench the reaction. Extraction, evaporation, and purification by silica gel column gave the mixture of *N*-benzyl-1,1-diphenyl-2-propenamine (**1m**) (0.58 mmol, 29%) and *N*-benzylidene-1,1-diphenyl-2-propenamine (0.87 mmol, 44%). The mixture dissolved in toluene (3.0 mL) was treated again with diisobutylaluminum hydride (2.32 mL, 2.32 mmol) at 0 ºC for 1 h. Extractive workup followed by silica gel column purification provided pure **1m** (0.390 g, 1.30 mmol, 65% in 2 steps) as a colorless liquid.

Preparation of (*Z*)-deuterio-1i

A 100–mL reaction flask was filled with argon. A solution of 4-methoxy-*N*-(2-phenyl-3-butyn-2-yl)aniline (1.31 g, 5.21 mmol), prepared by the method described in method 1, in THF (20.0 mL) and diisobutylaluminum hydride (1.0 M in hexane solution, 31.2 mL, 31.2 mmol) were added to the flask at room temperature. The mixture was heated at reflux overnight. After the flask was cooled to 0 ºC with an ice bath, methanol-*d* (21.8 mL) was carefully added, and the mixture was stirred at room temperature for 30 min. At ambient temperature, 30 wt% Rochell salt solution (37.4 mL) was added to the resulting colloidal mixture, and the mixture was extracted with diethyl ether three times. Evaporation and purification through a silica gel column provided (*Z*)-deuterio-4-methoxy-*N*-(2-phenyl-3-buten-2-yl)aniline [(*Z*)-deuterio-**1i**] (1.24 g, 4.88 mmol, 94%) as a pale yellow liquid. The deuteration degree was 91% estimated from ^{2}H NMR spectra.

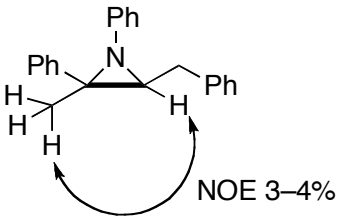
Typical procedure for palladium-catalyzed reactions of allylamines with aryl or alkenyl halides

The reaction of *N*-(1,1-diphenyl-2-propenyl)aniline (**1a**) with bromobenzene (Table 1, entry 1) is representative. Sodium *tert*-butoxide (0.058 g, 0.60 mmol) was added to a 30–mL

two-necked reaction flask equipped with a Dimroth condenser and was dried in vacuo with heating by a hair dryer for 1 min. (Trisdibenzylideneacetone)dipalladium (6.9 mg, 0.0075 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 6.2 mg, 0.015 mmol) were added to the flask, and the flask was filled with argon by using the standard Schlenck technique. Toluene (1.0 mL) was then added at room temperature. After the suspension was stirred for 10 min, **1a** (0.0856 g 0.30 mmol) and bromobenzene (0.0942 g, 0.60 mmol) dissolved in toluene (2.0 mL) were added to the flask at ambient temperature. The mixture was heated at reflux for 15 h with an oil bath. After the flask was cooled to room temperature, water (20 mL) was added to quench the reaction. The mixture was extracted with hexane:AcOEt = 5/1 three times. The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. The resulting brown residue was purified by silica gel column chromatography under basic conditions (silica gel 60N was used with an eluent (hexane:AcOEt:triethylamine = 30/1/0.1)) to provide 3-benzyl-1,2,2-triphenylaziridine **2a** (0.106 g, 0.294 mmol, 98%).

Stereochemical Assignment of 4a

The relative stereochemistry of **4a** was assigned based on NOE experiments. A correlation between the protons of the methyl group and the proton attached to the aminated carbon was observed.



The author performed the reaction of **1i** with *tert*-butyl 2-chlorobenzoate to afford the corresponding aziridine **10**, which would possess a similar structure of **4a**, as a single diastereomer. The X-ray crystallographic structure of **10** also supports the relative stereochemistry of **4a** (Figure 2).

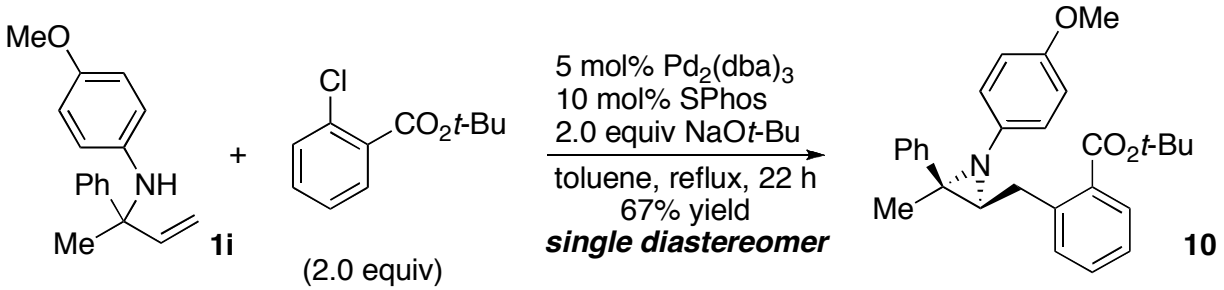
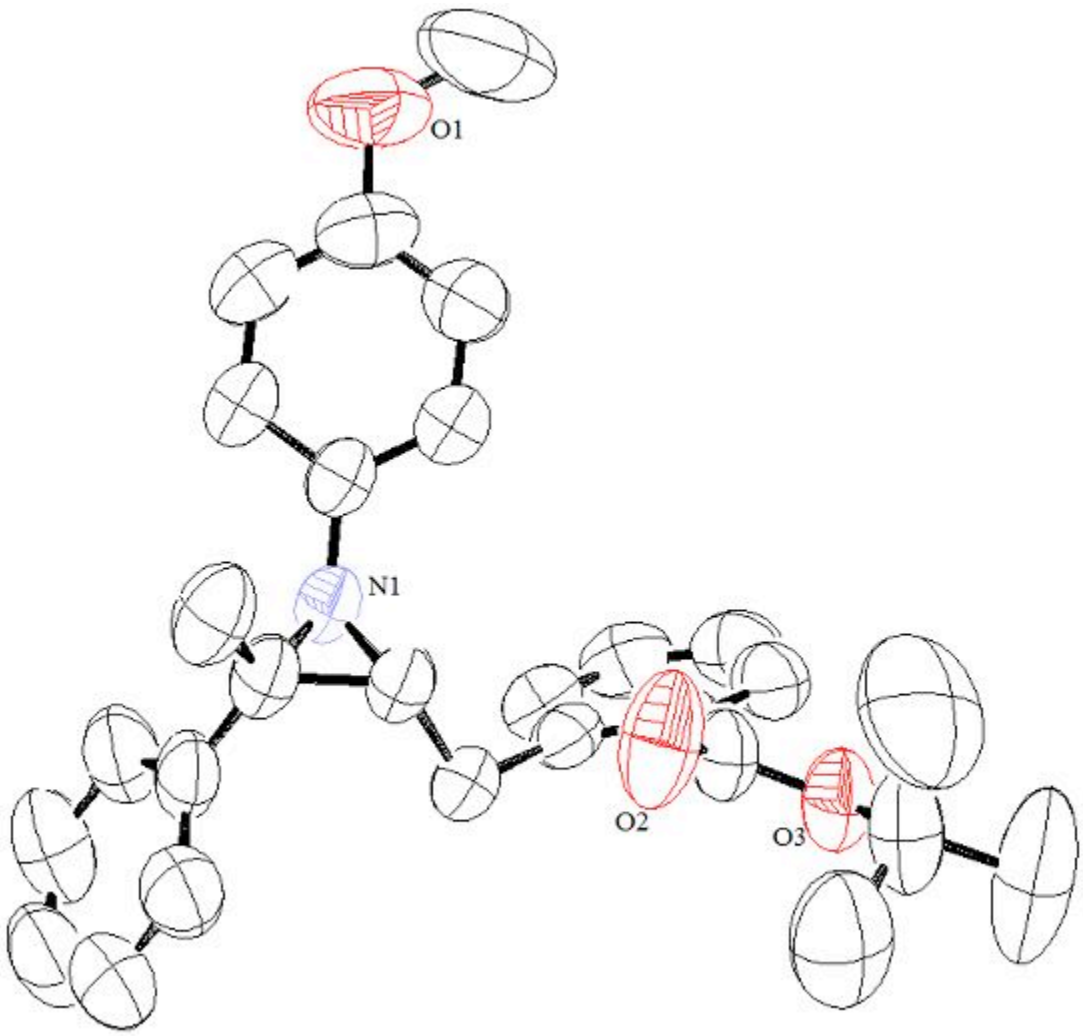


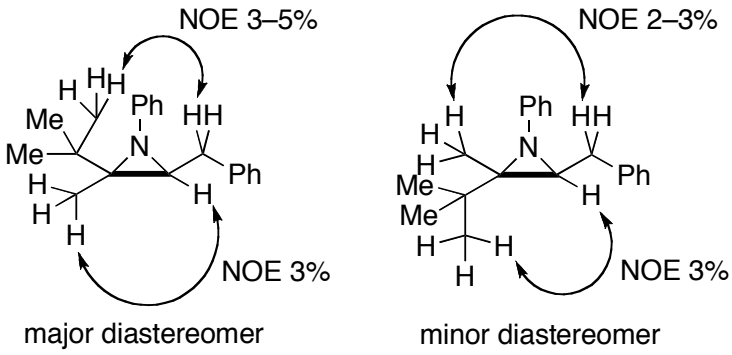
Figure 2. ORTEP Diagram of **10**. Hydrogen atoms are omitted for clarity.



Stereochemical Assignment of 4c

The NOE experiments of **4c** did not show any characteristic correlations between the protons of the substituents at the aminated carbon. The author assumed the relative stereochemistry of the major diastereomer of **4c** on the basis of A value, which indicates that the phenyl group would be larger than the trifluoromethyl group.

Stereochemical Assignment of 4e



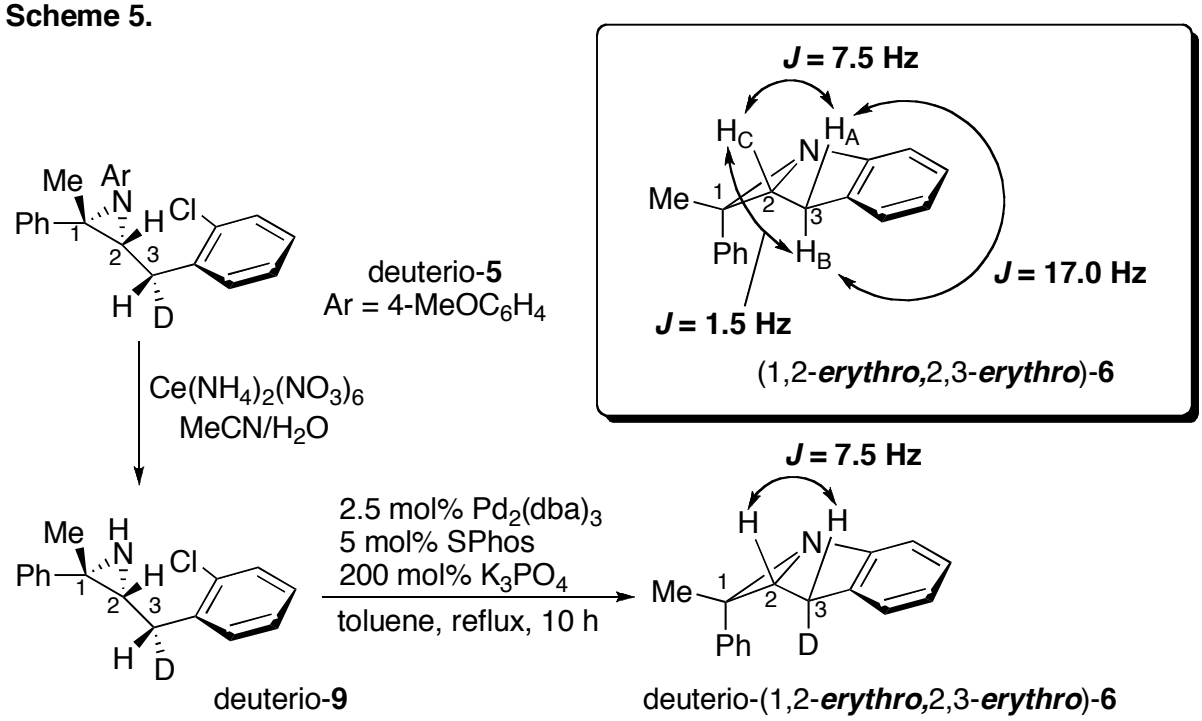
The relative stereochemistry of the both diastereomers of **4e** was also determined based on NOE experiments. In the case of the major diastereomer, the correlation between the protons of the methyl group and the protons at the aminated carbon was observed. Moreover, the protons of the *tert*-butyl group and the benzylic protons showed the correlation. On the other hand, the minor diastereomer showed the correlation between the protons of the methyl group and the benzylic protons along with that between the methyl protons of the *tert*-butyl group and the proton at the aminated carbon.

Stereochemical Assignment of (*erythro*, *erythro*)-deuterio-5

The relative stereochemistry of deuterio-**5** was assigned by further transformation (Scheme 5). The experimental procedure is as follows. Acetonitrile (2.8 mL) and water (2.0 mL) were added to a 50–mL flask containing deuterio-**5** (0.0875 g, 0.240 mmol). After the flask was cooled to 0 ºC, diammonium cerium(IV) nitrate (0.329 g, 0.60 mmol) was added in one portion. The mixture immediately turned brown. The mixture was stirred at 0 ºC for 3 h, and then saturated sodium hydrogencarbonate solution and saturated sodium thiosulfate solution were added to quench the reaction. Extractive workup followed by silica gel column purification yielded secondary amine deuterio-**9** (0.0412 g, 0.155 mmol, 65%).

The procedure of palladium-catalyzed intramolecular amination reaction was similar to that of carboamination reaction described in main text, in which sodium *tert*-butoxide was used instead of potassium phosphate. The resulting crude mixture involved deuterio-**6** along with deuterio-**9** and some unidentified products. After purification on neutral silica gel 60N using hexane:AcOEt = 3:1 as an eluent, deuterio-**6** was obtained in 28 % yield.

Scheme 5.



In the ^{1}H NMR spectrum of nondeuterated **6**, the two benzylic protons showed characteristic signals. One signal appeared at 3.27 ppm with coupling constants of 7.5 Hz and 17.0 Hz, while the other appeared at 3.13 ppm with coupling constants of 1.5 Hz and 17.0 Hz. On the basis of the conventional coupling constant analysis proposed by Karplus,[12,13] we were able to assign each signal to each benzylic proton since **6** is conformationally restricted. The proton H_A on the convex face should correspond to the signal with the larger coupling constant of 7.5 Hz since H_A and H_C are nearly eclipsed. Meanwhile, the signal with the smaller coupling constant of 1.5 Hz should be assigned to H_B on the concave face because the relevant dihedral angle of H_C-C-C and H_B-C-C is almost orthogonal.

In the ^{1}H NMR spectrum of deuterated **6**, the signal corresponding to H_A remained at the same position while the signal corresponding to H_B disappeared almost completely. Thus deuterium must be on the concave face, and the relative stereochemistry at 2,3-position was assigned to be *erythro*. Thereby, deuterio-**5** should have *erythro, erythro* configuration.

Characterization Data

***N*-(1,1-Diphenyl-2-propenyl)aniline (1a):** IR (nujol) 3418, 2923, 2853, 1599, 1490, 1445, 1320, 931, 763, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.59 (s, 1H), 5.28 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.43 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.43 (dd, *J* = 8.5, 1.5 Hz, 2H), 6.57 (dd, *J* = 17.0, 10.5 Hz, 1H), 6.62 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.01 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.24 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.39 (dd, *J* = 7.5, 1.5 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 68.19, 116.35, 117.21, 117.39, 127.28, 128.23, 128.51, 128.54, 139.52, 114.94, 145.79; Found: C, 88.15; H, 6.90%. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71%. m.p. 126.0–127.1 ºC.

4-Methoxy-*N*-(1,1-diphenyl-2-propenyl)aniline (1b): IR (nujol) 3419, 2924, 2853, 2826, 1507, 1447, 1436, 1237, 1180, 1041, 1007, 928, 820, 805, 778, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 3H), 4.35 (s, 1H), 5.27 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.42 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.39 (d, *J* = 9.0 Hz, 2H), 6.54 (dd, *J* = 17.0, 10.5 Hz, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 7.24 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.43 (dd, *J* = 7.5, 1.5 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.76, 68.36, 114.13, 117.07, 117.60, 127.18, 128.26, 128.46, 139.81, 140.12, 145.19, 152.00; Found: C, 83.93; H, 6.87%. Calcd for $C_{22}H_{21}NO$: C, 83.78; H, 6.71%. m.p. 84.2–85.5 ºC.

***N*-(1,1-Diphenyl-2-propenyl)-4-fluoroaniline (1c):** IR (nujol) 3425, 2923, 2854, 1490, 1447, 1225, 1101, 1009, 932, 818, 791, 759, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.49 (s, 1H), 5.28 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.43 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.34–6.38 (m, 2H), 6.53 (dd, *J* = 17.0, 10.5 Hz, 1H), 6.69–6.74 (m, 2H), 7.25 (tt, *J* = 7.0, 1.5 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 4H), 7.38 (dd, *J* = 7.0, 1.5 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 68.37, 114.98 (d, *J* = 22.5 Hz), 117.13 (d, *J* = 7.2 Hz), 127.34, 128.21, 128.56, 139.61, 142.04, 142.05, 144.81, 155.82 (d, *J* = 235.1 Hz); ^{19}F NMR ($CDCl_3$) δ –128.38—128.29 (m); Found: C, 83.32; H, 6.18%. Calcd for $C_{21}H_{18}FN$: C, 83.14; H, 5.98%. m.p. 124.2–125.5 ºC.

***N*-[1,1-Di(4-methoxyphenyl)-2-propenyl]aniline (1d):** IR (nujol) 3406, 2926, 2854, 1602, 1578, 1505, 1452, 1444, 1306, 1247, 1184, 1166, 1033, 1017, 998, 919, 819, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 6H), 4.51 (s, 1H), 5.24 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.38 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.43 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.53 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.61 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 4H), 7.01 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.45, 67.30, 113.77, 116.29, 116.49, 117.22, 128.51, 129.40, 137.23, 139.89, 145.94, 158.68; Found: C, 80.09; H, 6.84%. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71%. m.p. 121.0–122.5 ºC.

***N*-[1,1-Di(4-fluorophenyl)-2-propenyl]aniline (1e):** IR (nujol) 3419, 2924, 2854, 1599, 1505, 1430, 1320, 1230, 1160, 1013, 995, 925, 853, 833, 817, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.48 (s, 1H), 5.24 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.44 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.39–6.47 (m, 2H), 6.50 (dd, *J* = 17.0, 10.5 Hz, 1H), 6.65 (tt, *J* = 7.0, 1.0 Hz, 1H), 6.97–7.04 (m, 6H), 7.31–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 67.41, 115.40 (d, *J* = 21.1 Hz), 116.39, 117.50, 117.79, 128.63, 129.94 (d, *J* = 7.7 Hz), 139.43, 140.39 (d, *J* = 3.3 Hz), 145.39, 162.00 (d, *J* = 246.7 Hz); ^{19}F NMR ($CDCl_3$) δ 46.05; Found: C, 78.74; H, 5.43%. Calcd for $C_{21}H_{17}F_2N$: C, 78.49; H, 5.33%. m.p. 65.9–66.5 ºC.

***N*-(4-Vinyl-4-heptanyl)aniline (1f):** IR (neat) 3412, 2934, 2872, 1602, 1497, 1458, 1320, 1258, 1153, 1002, 917, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.5 Hz, 6H), 1.21–1.34 (m, 4H), 1.51–1.60 (m, 2H), 1.69–1.76 (m, 2H), 3.63 (s, 1H), 5.15 (dd, *J* = 18.0, 1.0 Hz, 1H), 5.19 (dd, *J* = 11.0, 1.0 Hz, 1H), 5.89 (dd, *J* = 18.0, 11.0 Hz, 1H), 6.65 (t, *J* = 7.0 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 2H), 7.09 (dd, *J* = 8.5, 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.70, 16.55, 39.15, 59.85, 113.99, 115.41, 117.13, 128.92, 145.12, 146.88; HRMS Found: m/z 217.1830. Calcd for $C_{15}H_{23}N$: 217.1830.

***N*-(1-Vinylcyclohexyl)aniline (1g):** IR (neat) 3421, 2932, 2855, 1601, 1497, 1449, 1426, 1317, 1277, 1255, 1180, 1164, 998, 906, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26–1.34 (m, 1H), 1.45–1.63 (m, 7H), 1.89–1.96 (m, 2H), 3.77 (s, 1H), 5.14 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.22 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.95 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.67 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.70 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.11 (dd, *J* = 8.5, 7.5 Hz, 2H); ^{13}C NMR($CDCl_3$) δ 21.79, 25.80, 35.52, 56.46, 113.50, 115.95, 117.30, 128.84, 145.96, 146.33; Found: C, 83.74; H, 9.69%. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51%.

***N*-(2-Phenyl-3-buten-2-yl)aniline (1h):** IR (neat) 3414, 3054, 2982, 1601, 1498, 1446, 1411, 1317, 1258, 1216, 1181, 1028, 995, 923, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (s, 3H), 4.15 (s, 1H), 5.22 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.26 (dd, *J* = 17.5, 1.0 Hz, 1H), 6.38 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.41 (dd, *J* = 7.5, 1.0 Hz, 2H), 6.63 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.02 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.25 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.52 (dd, *J* = 7.5, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 29.47, 60.46, 114.05, 115.96, 117.55, 126.47, 126.89, 128.73, 128.81, 143.09, 145.49, 145.91; Found: C, 86.14; H, 7.79%. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67%.

4-Methoxy-*N*-(2-phenyl-3-buten-2-yl)aniline (1i): IR (neat) 3402, 2831, 1510, 1492, 1446, 1408, 1366, 1296, 1227, 1179, 1039, 922, 822, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (s, 3H), 3.69 (s, 3H), 3.84 (s, 1H), 5.20 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.24 (dd, *J* = 17.5, 1.0 Hz, 1H), 6.32 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.39 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 7.25 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.53 (dd, *J* = 7.5, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.99, 55.79, 60.74, 113.80, 114.42, 117.85, 126.61, 126.86, 128.66, 139.86, 143.69, 145.87, 152.45; Found: C, 80.47; H, 7.54%. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56%.

(*Z*)-4-Methoxy-*N*-(4-deuterio-2-phenyl-3-buten-2-yl)aniline ((*Z*)-deuterio-1i): IR (neat) 3403, 2932, 2831, 1511, 1492, 1445, 1372, 1295, 1236, 1179, 1039, 820, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (s, 3H), 3.69 (s, 3H), 3.83 (s, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 6.32 (dt, *J* = 10.5, 2.5 Hz, 1H), 6.39 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 7.25 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.34 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.53 (dd, *J* = 8.5, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.99, 55.79, 60.73, 113.54 (t, *J* = 23.5 Hz), 114.41, 117.85, 126.60, 126.86, 128.65, 139.86, 143.60, 145.87, 152.45; HRMS Found: m/z 254.1528. Calcd for $C_{17}H_{18}DNO$: 254.1529.

***N*-(1,1,1-Trifluoro-2-phenyl-3-buten-2-yl)aniline (1j):** IR (nujol) 3410, 3064, 3031, 1600, 1496, 1455, 1318, 1242, 1172, 1142, 962, 939, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.55 (s, 1H), 5.56 (d, *J* = 17.0 Hz, 1H), 5.57 (d, *J* = 10.5 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 2H), 6.47 (dd, *J* = 17.0, 10.5 Hz, 1H), 6.69 (t, 7.5 Hz, 1H), 7.01 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.36–7.41 (m, 3H), 7.61–7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 67.26 (q, *J* = 26.4 Hz), 116.83, 118.83, 121.47, 125.48 (q, *J* = 286.5 Hz), 128.71, 128.76, 128.86 (two peaks merge), 131.81, 134.90, 143.68; ^{19}F NMR ($CDCl_3$) δ –76.44; HRMS Found: m/z 277.1082. Calcd for $C_{16}H_{14}F_3N$: 277.1078. m.p. 76.7–77.0 °C.

***N*-(3,4-Dimethyl-1-penten-3-yl)aniline (1k):** IR (neat) 3424, 2965, 2937, 2877, 1602, 1500, 1459, 1388, 1372, 1312, 1257, 1173, 917, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (d, *J* = 6.5 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 1.33 (s, 3H), 1.83 (sept, *J* = 6.5 Hz, 1H), 3.67 (s, 1H), 5.16 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.24 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.94 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.67 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.71 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.10 (dd, *J* = 8.5, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 17.30, 17.60, 20.24, 38.30, 60.19, 115.04, 116.00, 117.39, 128.91, 143.32, 147.05; Found: C, 82.48; H, 10.38%. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12%.

***N*-(3,4,4-Trimethyl-1-penten-3-yl)aniline (1l):** IR (neat) 3441, 2971, 2875, 1602, 1500, 1397, 1374, 1316, 1255, 1107, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.36 (s, 3H), 3.86 (s, 1H), 5.14 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.28 (dd, *J* = 11.0, 1.5 Hz, 1H), 6.00 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.66 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.73 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.09 (dd, *J* = 8.5, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 17.24, 25.48, 38.05, 62.18, 115.92, 116.16, 117.34, 128.86, 143.13, 147.27; HRMS Found: m/z 203.1674. Calcd for $C_{14}H_{21}N$: 203.1674.

***N*-Benzyl-1,1-diphenylallylamine (1m):** IR (neat) 3321, 3060, 3028, 2850, 1599, 1492, 1452, 1029, 924, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 1H), 3.51 (s, 2H), 5.27 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.33 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.47 (dd, *J* = 17.5, 10.5 Hz, 1H), 7.22–7.25 (m, 3H), 7.30–7.35 (m, 6H), 7.39–7.42 (m, 2H), 7.43–7.47 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 47.85, 68.26, 114.62, 126.81, 127.01, 128.20, 128.23, 128.27, 128.54, 141.38, 142.89, 145.69; HRMS Found: m/z 299.1673. Calcd for $C_{22}H_{21}N$: 299.1674.

***N*-(2-Methyl-3-buten-2-yl)aniline (1n):** IR (neat) 3407, 3052, 2981, 2930, 1603, 1498, 1411, 1317, 1261, 1180, 996, 917, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 6H), 3.70 (s, 1H), 5.11 (dd, *J* = 11.0, 1.0 Hz, 1H), 5.19 (dd, *J* = 17.5, 1.0 Hz, 1H), 6.02 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.67–6.72 (m, 3H), 7.09–7.14 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 28.53, 54.82, 112.90, 115.94, 117.65, 128.94, 146.63, 146.86; HRMS Found: m/z 161.1207. Calcd for $C_{11}H_{15}N$: 161.1204.

3-Benzyl-1,2,2-triphenylaziridine (2a): IR (nujol) 3060, 3026, 2917, 1596, 1494, 1446, 1405, 1309, 1266, 1233, 1077, 1029, 770, 753, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.53 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.74 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.54 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.57 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.75 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.94–6.98 (m, 4H), 7.06–7.09 (m, 3H), 7.22–7.28 (m, 3H), 7.30–7.36 (m, 3H), 7.39–7.42 (m, 2H), 7.56–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 36.46, 49.94, 57.05, 121.00, 121.87, 126.55, 127.37, 127.51, 127.89, 128.24, 128.44, 128.77, 129.17, 129.72, 130.18, 137.56, 139.79, 140.81, 149.46; HRMS Found: m/z 360.1741. Calcd for $[C_{27}H_{23}N - H]^+$: 360.1747.

3-(1-Naphthalenyl)methyl-1,2,2-triphenylaziridine (2b): IR (nujol) 2965, 2870, 1597, 1507, 1490, 1457, 1379, 1364, 1339, 1249, 1076, 760, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.96 (dd, *J* = 15.0, 7.5 Hz, 1H), 3.21 (dd, *J* = 15.0, 5.0 Hz, 1H), 3.63 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.42 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.69 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.87 (dd, *J* = 8.5, 7.5 Hz, 2H), 6.92–6.94 (m, 2H), 7.05–7.08 (m, 3H), 7.34–7.46 (m, 5H), 7.49–7.55 (m, 2H), 7.65–7.67 (m, 2H), 7.77–7.79 (m, 1H), 7.89–7.91 (m, 1H), 8.17–8.18 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 33.73, 49.42, 57.21, 120.90, 121.80, 124.32, 125.82, 125.93, 126.31, 127.13, 127.36, 127.47, 127.52, 127.89, 128.35, 128.37, 128.96, 129.77, 130.13, 132.29, 134.16, 136.07, 137.52, 140.80, 149.27; Found: C, 90.67; H, 6.24%. Calcd for $C_{31}H_{25}N$: C, 90.47; H, 6.12%. m.p. 51.5–52.2 ºC.

3-(2-Methoxyphenyl)methyl-1,2,2-triphenylaziridine (2c): IR (neat) 3025, 3002, 2935, 2834, 1594, 1489, 1447, 1404, 1241, 1173, 1119, 1077, 1029, 753, 728 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.81 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.67 (dd, *J* = 7.0, 5.0 Hz, 1H), 3.92 (s, 3H), 6.58 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.74 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.83–6.86 (m, 1H), 6.92–6.98 (m, 5H), 7.00–7.01 (m, 1H), 7.06–7.10 (m, 3H), 7.21–7.25 (m, 1H), 7.32–7.35 (m, 1H), 7.38–7.41 (m, 2H), 7.54–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 31.08, 48.59, 55.64, 57.17, 110.46, 120.85, 120.99, 121.67, 127.24, 127.38, 127.82 (two peaks merge), 128.03, 128.15, 128.39, 129.87, 130.25, 131.09, 137.90, 140.97, 149.84, 157.74; Found: C, 85.74; H, 6.67%. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44%.

3-(4-Methoxyphenyl)methyl-1,2,2-triphenylaziridine (2d): IR (nujol) 2924, 2854, 1652, 1595, 1558, 1507, 1490, 1447, 1247, 1177, 1036, 768, 708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.47 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.69 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.51 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.81 (s, 3H), 6.59 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.76 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.94–6.99 (m, 4H), 7.07–7.10 (m, 3H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.32–7.36 (m, 1H), 7.38–7.42 (m, 2H), 7.55–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 35.55, 50.12, 55.46, 57.04, 114.17, 121.02, 121.84, 127.32, 127.48, 127.88, 128.22, 128.45, 129.71, 130.15, 130.18, 131.81, 137.61, 140.86, 149.53, 158.37; Found: C, 85.90; H, 6.49%. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44%. m.p. 77.5–79.0 ºC.

3-(4-Dimethylaminophenyl)methyl-1,2,2-triphenylaziridine (2e): IR (nujol) 2925, 1613, 1596, 1521, 1490, 1410, 1227, 763, 708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.47 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.63 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.93 (s, 6H), 3.51 (dd, *J* = 7.5, 5.5 Hz, 1H), 6.62 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.75 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.94–6.99 (m, 4H), 7.05–7.08 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.31–7.34 (m, 1H), 7.37–7.41 (m, 2H), 7.54–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 35.37, 41.08, 50.25, 57.03, 113.32, 121.12, 121.75, 127.25, 127.41, 127.78, 127.85, 128.18, 128.43, 129.77, 129.80, 130.23, 137.79, 140.98, 149.57, 149.67; Found: C, 86.00; H, 6.94%. Calcd for $C_{29}H_{28}N_2$: C, 86.10; H, 6.98%. m.p. 114.0–114.3 ºC.

3-(4-Trifluoromethylphenyl)methyl-1,2,2-triphenylaziridine (2f): IR (neat) 3027, 2923, 1618, 1596, 1489, 1447, 1405, 1323, 1233, 1111, 1067, 1019, 853, 820, 770, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.58 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.81 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.55 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.57 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.78 (td, *J* = 7.5, 1.0 Hz, 1H), 6.95–7.00 (m, 4H), 7.08–7.11 (m, 3H), 7.34–7.44 (m, 5H), 7.55–7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 36.34, 49.23, 57.15, 120.92, 122.11, 124.55 (q, *J* = 271.7 Hz), 125.67 (q, *J* = 3.8 Hz), 127.54, 127.66, 127.98, 128.34, 128.55, 128.97 (q, *J* = 32.2 Hz), 129.55, 129.65, 130.15, 137.25, 140.59, 143.96, 149.13; ^{19}F NMR ($CDCl_3$) δ –62.84 ; HRMS Found: m/z 428.1630. Calcd for $[C_{28}H_{22}F_3N - H]^+$: 428.1621.

***tert*-Butyl 4-[(1,3,3-triphenyl-2-aziridinyl)methyl]benzoate (2g):** IR (nujol) 2853, 1717, 1596, 1447, 1367, 1258, 1162, 1113, 1077, 1020, 850, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 9H), 2.56 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.77 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.54 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.57 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.76 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.93–6.99 (m, 4H), 7.06–7.10 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.32–7.36 (m, 1H), 7.38–7.42 (m, 2H), 7.54–7.58 (m, 2H), 7.93 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.45, 36.52, 49.39, 57.09, 81.09, 120.98, 122.02, 127.48, 127.60, 127.95, 128.31, 128.53, 129.09, 129.69, 129.95, 130.18, 130.44, 137.36, 140.68, 144.71, 149.24, 166.08; HRMS Found: m/z 461.2352. Calcd for $C_{32}H_{31}NO_2$: 461.2355. m.p. 56.9–58.0 ºC.

***N,N*-Diethyl-4-[(1,3,3-triphenyl-2-aziridinyl)methyl]benzamide (2h):** IR (nujol) 2923, 2853, 1717, 1684, 1595, 1558, 1507, 1490, 1420, 1363, 1287, 1077, 1022, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–1.17 (bs, 3H), 1.18–1.30 (bs, 3H), 2.53 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.77 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.20–3.34 (bs, 2H), 3.48–3.62 (bs, 2H), 3.54 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.56 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.75 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.93–6.98 (m, 4H), 7.07–7.10 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.32–7.37 (m, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.38–7.43 (m, 2H), 7.54–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.14, 14.43, 36.31, 39.46, 43.50, 49.68, 57.06, 120.92, 121.94, 126.84, 127.41, 127.56, 127.91, 128.26, 128.44, 129.20, 129.65, 130.12, 135.51, 137.33, 140.67, 140.97, 149.28, 171.55; HRMS Found: m/z 459.2440. Calcd for $[C_{32}H_{32}N_2O - H]^+$: 459.2431. m.p. 52.0–53.1 ºC.

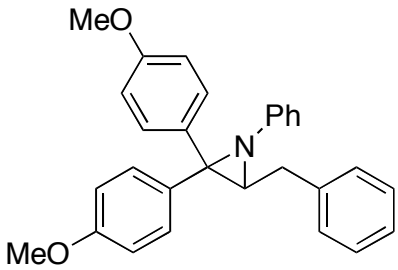
3-(3-Methyl-2-butenyl)-1,2,2-triphenylaziridine (2i): IR (neat) 3060, 3025, 2978, 2913, 2855, 1597, 1492, 1446, 1310, 1234, 769 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 3H), 1.74 (s, 3H), 1.96–2.04 (m, 1H), 2.05–2.13 (m, 1H), 3.30 (dd, *J* = 7.0, 6.0 Hz, 1H), 5.33 (t, *J* = 7.0 Hz, 1H), 6.76–6.81 (m, 3H), 6.94–6.99 (m, 2H), 7.01–7.07 (m, 2H), 7.07–7.12 (m, 3H), 7.28–7.33 (m, 1H), 7.34–7.39 (m, 2H), 7.49–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.17, 26.08, 28.95, 48.63, 56.95, 120.82, 121.06, 121.82, 127.16, 127.41, 127.85, 128.16, 128.50, 129.63, 130.16, 134.04, 137.81, 140.92, 149.77; HRMS Found: m/z 339.1982. Calcd for $C_{25}H_{25}N$: 339.1987.

3-(*E*)-(2-Octenyl)-1,2,2-triphenylaziridine (2j): IR (neat) 3026, 2957, 2926, 2855, 1597, 1493, 1446, 1409, 1311, 1232, 971, 769, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 3H), 1.25–1.41 (m, 6H), 1.98–2.12 (m, 4H), 3.33 (dd, *J* = 7.0, 6.0 Hz, 1H), 5.51 (dt, *J* = 15.5, 6.0 Hz, 1H), 5.56 (dt, *J* = 15.5, 6.0 Hz, 1H), 6.78–6.81 (m, 3H), 6.96–6.99 (m, 2H), 7.02–7.06 (m, 2H), 7.07–7.12 (m, 3H), 7.29–7.33 (m, 1H), 7.34–7.38 (m, 2H), 7.49–7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.30, 22.77, 29.35, 31.60, 32.89, 33.43, 48.49, 57.01, 121.12, 121.88, 126.54, 127.21, 127.44, 127.87, 128.12, 128.49, 129.67, 130.15, 133.41, 137.74, 140.82, 149.69; Found: C, 88.13; H, 8.08%. Calcd for $C_{28}H_{31}N$: C, 88.14; H, 8.19%.

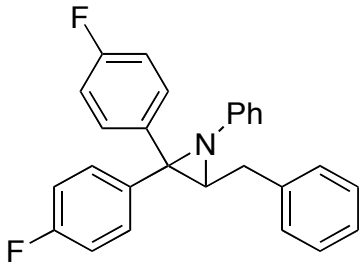
3-Benzyl-1-(4-methoxyphenyl)-2,2-diphenylaziridine (3a): IR (nujol) 2924, 2852, 1602, 1506, 1496, 1447, 1239, 1180, 1036, 826, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.53 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.72 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.49 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.64 (s, 3H), 6.51–6.53 (m, 4H), 6.95–6.98 (m, 2H), 7.07–7.11 (m, 3H), 7.22–7.26 (m, 1H), 7.26–7.35 (m, 5H), 7.37–7.41 (m, 2H), 7.54–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 36.40, 49.90, 55.52, 57.17, 113.84, 121.85, 126.52, 127.27, 127.45, 127.91, 128.20, 128.75, 129.20, 129.69, 130.34, 137.73, 139.88, 141.02, 142.68, 154.81; Found: C, 85.61; H, 6.48%. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44%.

3-Benzyl-1-(4-fluorophenyl)-2,2-diphenylaziridine (3b): IR (neat) 3028, 1602, 1505, 1446, 1312, 1212, 1153, 1094, 1030, 831, 818, 763, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.51 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.74 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.51 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.49 (dd, *J* = 9.0, 5.0 Hz, 2H), 6.65 (t, *J* = 9.0 Hz, 2H), 6.93–6.98 (m, 2H), 7.08–7.12 (m, 3H), 7.21–7.28 (m, 3H), 7.29–7.36 (m, 3H), 7.38–7.42 (m, 2H), 7.54–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 36.32, 50.18, 57.29, 115.06 (d, *J* = 22.5 Hz), 121.98 (d, *J* = 8.2 Hz), 126.62, 127.44, 127.66, 128.01, 128.28, 128.81, 129.17, 129.62, 130.20, 137.35, 139.69, 140.63, 145.50, 158.35 (d, *J* = 239.5 Hz); Found: C, 85.19; H, 5.75%. Calcd for $C_{27}H_{22}FN$: C, 85.46; H, 5.84%.

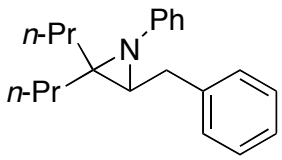
3-Benzyl-2,2-di(4-methoxyphenyl)-1-phenylaziridine (3c): IR (nujol) 2839, 1583, 1507, 1490, 1443, 1246, 1171, 1107, 1033, 833, 752, 734, 717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.56 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.71 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.44 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.68 (s, 3H), 3.85 (s, 3H), 6.56 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 6.75 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.97 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.21–7.29 (m, 3H), 7.29–7.33 (m, 2H), 7.43–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 36.36, 50.14, 55.26, 55.50, 56.26, 113.23, 113.56, 121.03, 121.72, 126.49, 128.47, 128.75, 129.21, 130.01, 130.67, 131.28, 133.28, 139.93, 149.74, 158.77, 158.86; Found: C, 82.51; H, 6.58%. Calcd for $C_{29}H_{27}NO_2$: C, 82.63; H, 6.46%. m.p. 43.0–44.2 °C.



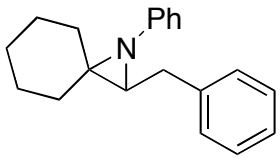
3-Benzyl-2,2-di(4-fluorophenyl)-1-phenylaziridine (3d): IR (nujol) 2360, 2333, 1597, 1512, 1222, 1153, 1094, 1075, 1014, 893, 795, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.70 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.49 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.53–6.59 (m, 2H), 6.75–6.82 (m, 3H), 6.90–6.95 (m, 2H), 6.96–7.02 (m, 2H), 7.07–7.13 (m, 2H), 7.23–7.29 (m, 3H), 7.29–7.35 (m, 2H), 7.48–7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 36.24, 49.94, 55.92, 114.97 (d, *J* = 21.1 Hz), 115.24 (d, *J* = 21.6 Hz), 120.97, 122.22, 126.69, 128.62, 128.85, 129.13, 131.14 (d, *J* = 8.2 Hz), 131.75 (d, *J* = 8.2 Hz), 133.30, 136.44, 139.39, 149.04, 162.13 (d, *J* = 247.7 Hz), 162.30 (d, *J* = 245.7 Hz); ^{19}F NMR ($CDCl_3$) δ –115.41—115.31 (m), –114.69-—114.60 (m); Found: C, 81.55; H, 5.50%. Calcd for $C_{27}H_{21}F_2N$: C, 81.59; H, 5.33%. m.p. 111.4–112.0 °C.



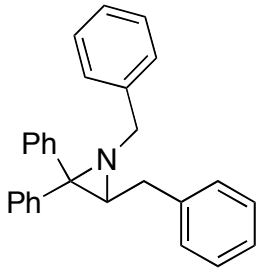
3-Benzyl-1-phenyl-2,2-dipropylaziridine (3e): IR (neat) 3062, 3029, 2959, 2932, 2872, 1598, 1492, 1453, 1424, 1277, 1258, 766, 749, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.28 (ddd, *J* = 13.5, 11.0, 6.0 Hz, 1H), 0.76 (t, *J* = 7.5 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H), 1.16–1.27 (m, 1H), 1.37–1.51 (m, 2H), 1.65–1.85 (m, 4H), 2.19 (t, *J* = 7.0 Hz, 1H), 2.94 (d, *J* = 7.0 Hz, 2H), 6.65 (d, *J* = 7.5 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.24–7.28 (m, 1H), 7.33–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.33, 14.92, 19.59, 20.05, 33.48, 34.97, 35.77, 49.59, 52.28, 120.60, 121.65, 126.51, 128.79, 128.81, 129.17, 140.24, 150.66; Found: C, 85.70; H, 9.39%. Calcd for $C_{21}H_{27}N$: C, 85.95; H, 9.27%.



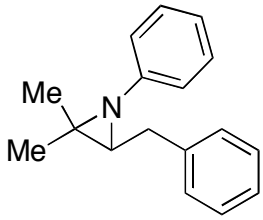
2-Benzyl-1-phenyl-1-azaspiro[2.5]octane (3f): IR (neat) 3062, 3028, 2929, 2853, 1597, 1491, 1451, 1428, 1274, 766 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.74–0.81 (m, 1H), 1.30–1.49 (m, 3H), 1.49–1.56 (m, 1H), 1.64–1.72 (m, 1H), 1.72–1.90 (m, 4H), 2.23 (dd, *J* = 8.0, 4.5 Hz, 1H), 2.87 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.02 (dd, *J* = 14.5, 4.5 Hz, 1H), 6.65 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.88 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.11 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.24–7.28 (m, 1H), 7.32–7.39 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.75, 25.85, 26.12, 32.65, 33.46, 35.80, 48.81, 51.48, 120.80, 121.79, 126.50, 128.68, 128.82, 129.15, 140.43, 150.67; Found: C, 86.29; H, 8.36%. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36%.



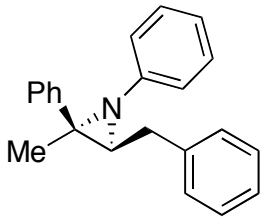
1,3-Dibenzyl-2,2-diphenylaziridine (3g): IR (nujol) 3025, 2922, 2853, 1644, 1602, 1495, 1446, 1357, 1118, 1027, 753, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.46 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.60 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.72 (t, *J* = 6.5 Hz, 1H), 3.22 (d, *J* = 14.5 Hz, 1H), 3.44 (d, *J* = 14.5 Hz, 1H), 7.02–7.05 (m, 2H), 7.14–7.36 (m, 15H), 7.42–7.46 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 35.44, 50.99, 55.83, 58.40, 126.15, 126.75, 126.80, 127.74, 127.89, 128.17, 128.27, 128.37, 128.46, 128.97, 129.33, 131.57, 139.11, 140.02, 140.33, 142.12; HRMS Found: m/z 375.1987. Calcd for $C_{28}H_{25}N$: 375.1987. m.p. 90.9–91.8 ºC.



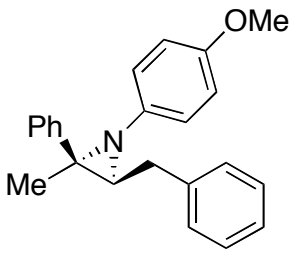
3-Benzyl-2,2-dimethyl-1-phenylaziridine (3h): IR (neat) 3061, 3029, 2955, 2921, 1597, 1493, 1453, 1412, 1376, 1319, 1259, 1113, 768, 750, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 3H), 1.46 (s, 3H), 2.20 (dd, *J* = 7.0, 6.0 Hz, 1H), 2.93 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.96 (dd, *J* = 16.5, 6.0 Hz, 1H), 6.66 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.90 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.14 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.24–7.29 (m, 1H), 7.32–7.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.81, 21.84, 36.18, 42.90, 51.63, 120.64, 121.84, 126.52, 128.81, 128.85, 129.03, 140.17, 150.97; Found: C, 85.88; H, 8.08%. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07%.



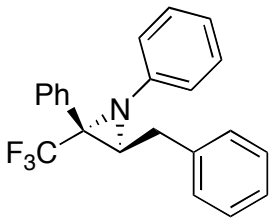
3-Benzyl-2-methyl-1,2-diphenylaziridine (4a, *erythro/threo* >99:1): IR (neat) 3027, 3061, 2963, 2923, 1599, 1495, 1454, 1411, 1330, 1268, 1226, 767, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (s, 3H), 2.41 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.52 (dd, *J* = 7.5, 5.0 Hz, 1H), 2.62 (dd, *J* = 14.0, 5.0 Hz, 1H), 6.75 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.95 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.19 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.21–7.25 (m, 3H), 7.27–7.33 (m, 3H), 7.38–7.43 (m, 2H), 7.57–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.50, 36.45, 49.16, 53.12, 120.43, 121.96, 126.43, 127.16, 128.04, 128.41, 128.69, 128.96, 129.15, 140.00, 141.83, 150.56; HRMS Found: m/z 298.1590. Calcd for $[C_{22}H_{21}N - H]^+$: 298.1590.



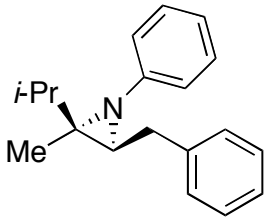
3-Benzyl-1-methoxyphenyl-2-methyl-2-phenylaziridine (4b, *erythro/threo* >99:1): IR (neat) 3059, 3027, 2960, 2925, 2832, 1603, 1505, 1496, 1454, 1443, 1241, 1224, 1040, 832, 767, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 3H), 2.39 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.47 (dd, *J* = 7.5, 4.5 Hz, 1H), 2.61 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.75 (s, 3H), 6.68 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 7.20–7.25 (m, 3H), 7.27–7.32 (m, 3H), 7.38–7.42 (m, 2H), 7.56–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.31, 36.47, 49.11, 53.17, 55.72, 114.37, 121.20, 126.39, 127.09, 128.07, 128.38, 128.66, 129.13, 140.10, 141.99, 143.81, 155.06.



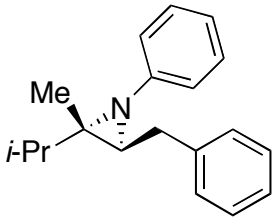
3-Benzyl-2-trifluoromethyl-1,2-diphenylaziridine (4c, *erythro/threo* = 7:93): IR (neat) 3064, 3030, 1600, 1495, 1455, 1318, 1240, 1174, 1141, 765, 755 cm^{-1}; ^1H NMR ($CDCl_3$) major diastereomer δ 2.27 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.81 (dd, *J* = 14.5, 4.0 Hz, 1H), 3.17 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.80 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.98 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.19 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.22–7.29 (m, 3H), 7.30–7.34 (m, 2H), 7.44–7.49 (m, 3H), 7.67–7.72 (m, 2H); Signals corresponding to the minor diastereomer were so weak that only the protons located at aminated and benzylic carbon were detected clearly. δ 3.22–3.26 (m, 1H), 3.29–3.33 (m, 2H); ^{13}C NMR ($CDCl_3$) major diastereomer δ 36.27, 46.14, 52.04 (q, *J* = 31.3 Hz), 119.02, 122.84, 124.72 (q, *J* = 282.2 Hz), 126.99, 128.67, 128.97, 129.15 (two peaks merge), 129.17, 130.25, 132.20, 138.40, 148.14; ^{19}F NMR ($CDCl_3$) δ –64.79 (major), –66.57 (minor); Found: C, 74.86; H, 5.15%. Calcd for $C_{22}H_{18}F_3N$: C, 74.77; H, 5.15%.



3-Benzyl-2-isopropyl-2-methyl-1-phenylaziridine (4d, *erythro*/*threo* = 79:21): major diastereomer: IR (neat) 3029, 2963, 2932, 2871, 1599, 1492, 1454, 1420, 1296, 1234, 1066, 768, 754, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (s, 3H), 1.03 (d, J = 7.0 Hz, 3H), 1.25 (d, J = 7.0 Hz, 3H), 1.83 (sept, J = 7.0 Hz, 1H), 2.20 (dd, J = 8.5, 4.5 Hz, 1H), 2.87 (dd, J = 14.0, 8.5 Hz, 1H), 3.05 (dd, J = 14.0, 4.5 Hz, 1H), 6.57 (dd, J = 8.5, 1.5 Hz, 2H), 6.88 (tt, J = 7.5, 1.5 Hz, 1H), 7.10 (dd, J = 8.5, 7.5 Hz, 2H), 7.24–7.28 (m, 1H), 7.32–7.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.70, 19.09, 19.14, 32.30, 35.30, 50.31, 53.58, 120.56, 121.72, 126.50, 128.75, 128.83, 129.23, 140.50, 150.76; HRMS Found: m/z 265.1832. Calcd for $C_{19}H_{23}N$: 265.1830. m.p. 37.8–39.9 °C.



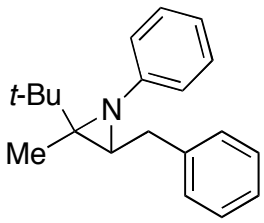
major



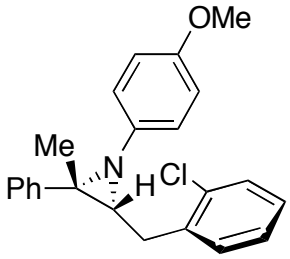
minor

minor diastereomer: IR (neat) 3026, 2962, 2931, 2875, 1601, 1494, 1453, 1319, 1254, 1089, 747 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (d, J = 6.5 Hz, 3H), 0.98 (d, J = 5.0 Hz, 3H), 0.96–1.05 (m, 1H), 1.33 (s, 3H), 2.26 (t, J = 6.5 Hz, 1H), 2.82 (dd, J = 14.0, 6.5 Hz, 1H), 2.97 (dd, J = 14.0, 6.5 Hz, 1H), 6.80 (dd, J = 8.5, 1.5 Hz, 2H), 6.91 (tt, J = 7.5, 1.5 Hz, 1H), 7.16 (dd, J = 8.5, 7.5 Hz, 2H), 7.22–7.26 (m, 1H), 7.29–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.18, 17.86, 21.18, 33.08, 35.35, 49.50, 51.08, 121.53, 121.86, 126.49, 128.78 (two peaks merge), 129.05, 140.10, 149.75; HRMS Found: m/z 265.1835. Calcd for $C_{19}H_{23}N$: 265.1830.

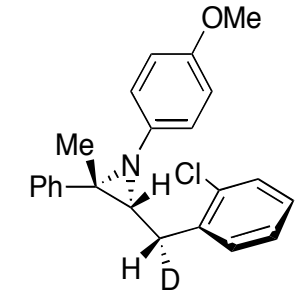
3-Benzyl-2-*tert*-butyl-2-methyl-1-phenylaziridine (4e, *erythro*/*threo* = 59:41): IR (neat) 2965, 2870, 1654, 1597, 1559, 1507, 1490, 1457, 1379, 1362, 1339, 1249, 1076, 760, 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (s, 0.59 × 3H), 0.96 (s, 0.41 × 9H), 1.14 (s, 0.41 ×3H), 1.17 (s, 0.59 × 9H), 2.10 (dd, J = 7.5, 5.5 Hz, 0.59 × 1H), 2.40 (dd, J = 15.0, 9.0 Hz, 0.41 × 1H), 2.93 (dd, J = 9.0, 5.0 Hz, 0.41 × 1H), 3.13–3.18 (m, 0.59 × 2H), 3.18 (dd, J = 15.0, 5.0 Hz, 0.41 × 1H), 6.50 (dd, J = 8.5, 1.0 Hz, 0.59 × 2H), 6.79 (dd, J = 8.5, 1.0 Hz, 0.41 × 2H), 6.86 (tt, J = 7.5, 1.0 Hz, 0.59 × 1H), 6.90 (tt, J = 7.5, 1.0 Hz, 0.41 × 1H), 7.09 (dd, J = 8.5, 7.5 Hz, 0.59 × 2H), 7.21–7.38 (m, 0.59 × 5H, 0.41 × 7H); ^{13}C NMR ($CDCl_3$) δ 11.63, 18.70, 26.61, 28.72, 31.47, 34.78, 36.81, 43.56, 49.63, 51.85, 54.59 (two peaks merge), 120.37, 120.40, 120.57, 121.46, 126.39, 126.50, 128.68, 128.71 (two peaks merge), 128.88, 128.98, 129.21, 139.77, 141.34, 147.99, 151.34; HRMS Found: m/z 279.1997. Calcd for $C_{20}H_{25}N$: 279.1987.



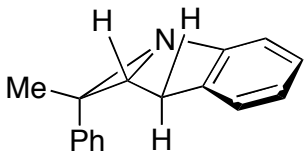
***erythro*-3-(2-Chlorophenyl)methyl-1-(4-methoxyphenyl)-2-methyl-2-phenylaziridine (erythro-5):** IR (neat) 2928, 2832, 1505, 1444, 1330, 1289, 1241, 1223, 1039, 832, 767, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3H), 2.45 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.60 (dd, *J* = 7.5, 5.0 Hz, 1H), 2.82 (dd, *J* = 14.0, 5.0 Hz, 1H), 3.75 (s, 3H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 7.06 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.5 Hz, 1H), 7.17 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.38–7.43 (m, 3H), 7.57–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.23, 34.03, 49.44, 51.20, 55.72, 114.40, 121.11, 127.13, 127.18, 127.97, 128.12, 128.42, 129.54, 131.61, 134.05, 137.70, 141.85, 143.71, 155.08; HRMS Found: m/z 363.1396. Calcd for $C_{23}H_{22}ClNO$: 363.1390.



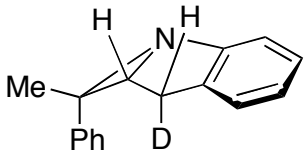
(*erythro,erythro*)-3-(2-Chlorophenyl)deuteriomethyl-1-(4-methoxyphenyl)-2-methyl-2-phenylaziridine ((*erythro,erythro*)-deuterio-5): IR (neat) 2959, 2928, 1505, 1472, 1442, 1327, 1289, 1240, 1221, 1180, 1110, 1039, 832, 766, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3H), 2.60 (d, *J* = 5.5 Hz, 1H), 2.80 (d, *J* = 5.5 Hz, 1H), 3.74 (s, 3H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 7.06 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.5 Hz, 1H), 7.17 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.37–7.43 (m, 3H), 7.57–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.23, 33.71 (t, *J* = 19.2 Hz), 49.42, 51.15, 55.73, 114.40, 121.10, 127.13, 127.18, 127.97, 128.12, 128.42, 129.53, 131.60, 134.04, 137.67, 141.86, 143.72, 155.08; HRMS Found: m/z 364.1449. Calcd for $C_{23}H_{21}ClDNO$: 364.1453.



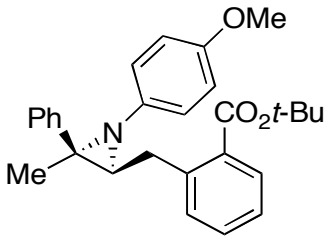
***erythro*-1,2-[(1-Methyl-1-phenyl)methylene]indoline (*erythro*-6):** IR (nujol) 1602, 1579, 1498, 1320, 1243, 1159, 1108, 1083, 1062, 1039, 1016, 943, 926, 862, 790, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 3H), 3.13 (dd, *J* = 17.0, 1.5 Hz, 1H), 3.18 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.27 (dd, *J* = 17.0, 7.5 Hz, 1H), 6.73–6.78 (m, 2H), 7.00–7.12 (m, 6H), 7.29–7.32 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 29.74, 31.76, 52.04, 52.09, 121.66, 124.32, 124.67, 126.73, 126.91, 128.03, 129.71, 137.43, 137.69, 153.55; HRMS Found: m/z 221.1203. Calcd for $C_{16}H_{15}N$: 221.1204. m.p. 101.5–102.0 ºC.



(*erythro,erythro*)-3-deuterio-1,2-[(1-Methyl-1-phenyl)methylene]indoline ((*erythro,erythro*)-deuterio-6): IR (nujol) 1602, 1498, 1457, 1442, 1373, 1287, 1242, 1054, 906, 790, 761, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 3H), 3.18 (d, *J* = 7.5 Hz, 1H), 3.25 (d, *J* = 7.5 Hz, 1H), 6.73–6.78 (m, 2H), 7.00–7.11 (m, 6H), 7.29–7.32 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 29.73, 31.46 (t, *J* = 19.6 Hz), 52.02, 52.08, 121.65, 124.33, 124.69, 126.74, 126.92, 128.03, 129.71, 137.43, 137.65, 153.56; HRMS Found: m/z 222.1262. Calcd for $C_{16}H_{14}DN$: 222.1267. m.p. 102.5–103.0 ºC.



***tert*-Butyl 2-[1-(4-methoxyphenyl)-3-methyl-3-phenyl-2-aziridinylmethyl]benzoate (10, *erythro*/*thoreo* >99:1):** IR (nujol) 2924, 2854, 1712, 1506, 1442, 1369, 1296, 1238, 1224, 1177, 1139, 1079, 1038, 837, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.62 (s, 9H), 2.39 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.63 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.17 (dd, *J* = 13.5, 4.0 Hz, 1H), 3.73 (s, 3H), 6.60 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 7.10 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.25 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38–7.42 (m, 2H), 7.57–7.61 (m, 2H), 7.83 (dd, *J* = 7.5, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.40, 28.51, 34.89, 49.36, 53.14, 55.72, 81.48, 114.31, 121.15, 126.36, 127.04, 128.13, 128.38, 130.46, 131.68, 131.93, 131.99, 141.00, 142.25, 144.11, 154.95, 167.52; HRMS Found: m/z 429.2292. Calcd for $C_{28}H_{31}NO_3$: 429.2304. m.p. 104.6–106.0 ºC.



References and Notes

(1) For reviews, see: (a) Wolfe, J. P. *Eur. J. Org. Chem.* **2007**, 571–582. (b) Wolfe, J. P. *Synlett* **2008**, 2913–2937.

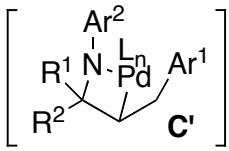
(2) Recent work reported by Wolfe: (a) Ward, R. F.; Wolfe, J. P. *Org. Lett.* **2009**, *11*, 2209–2212. (b) Lemen, G. S.; Giampietro, N. C.; Hay, M. B.; Wolfe, J. P. *J. Org. Chem.* **2009**, *74*, 2533–2540. (c) Bertrand, M. B.; Neukom, J. D.; Wolfe, J. P. *J. Org. Chem.* **2008**, *73*, 8851–8860.

(3) Representative examples reported by other groups: (a) Jiang, D.; Peng, J.; Chen, Y. *Org. Lett.* **2008**, *10*, 1695–1698. (b) Dongol, K. G.; Tay, B. Y. *Tetrahedron Lett.* **2006**, *47*, 927–930.

(4) Hayashi, S.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2009**, *131*, 2052–2053.

(5) The palladium amide intermediate bearing a bulky monophosphine ligand is known to undergo rapid reductive elimination to produce *N*-arylated product. (a) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338–6361. (b) Yamashita, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5344–5345.

(6) We cannot exclude another possibility that the reaction proceeds through *syn*-carbopalladation, yielding azapalladacyclobutane **C'**. However, examples of reductive elimination to form sp^3-C–N bond are rare. On the other hand, *syn*-aminopalladation and subsequent reductive elimination from **C** is a prevailing pathway as shown in ref. 1.



(7) Although *anti*-aminopalladation of olefin has been well studied, the reactions of amines tend to suffer from catalyst deactivation by the strong coordination of amine to the palladium center except for the reaction of substrate bearing a electron-withdrawing group on nitrogen. For leading reviews: (a) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415–2434. (b) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675–704.

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Publication List

I. Parts of the present thesis have been published in the following journals.

Chapter 1 Palladium-Catalyzed Stereo- and Regioselective Allylation of Aryl Halides with Homoallyl Alcohols via Retro-Allylation: Selective Generation and Use of σ-Allylpalladium.

Sayuri Hayashi, Koji Hirano, Hideki Yorimitsu, and Koichiro Oshima

J. Am. Chem. Soc. **2006**, *128*, 2210–2211.

$Pd(OAc)_2/P(^cC_6H_{11})_3$-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols via Retro-Allylation.

Masayuki Iwasaki, Sayuri Hayashi, Koji Hirano, Hideki Yorimitsu, and Koichiro Oshima

J. Am. Chem. Soc. **2007**, *129*, 4463–4469.

Chapter 2 Synthesis of (Arylalkenyl)silanes by Palladium-Catalyzed Regiospecific and Stereoselective Allyl Transfer from Silyl-Substituted Homoallyl Alcohols to Aryl Halides.

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Chapter 3 Synthesis of Arylallenes by Palladium-Catalyzed Retro-Propargylation of Homopropargyl Alcohols.

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Chapter 4 Synthesis of Epoxides by Palladium-Catalyzed Reactions of Tertiary Allyl Alcohols with Aryl or Alkenyl Halides.

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Chapter 5 Synthesis of Aziridines by Palladium-Catalyzed Reactions of Allylamines with Aryl or Alkenyl Halides: Evidence of Intramolecular *syn*-Carboamination Pathway.

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II. Other Publications not included in this thesis.

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