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Palladium-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols Bearing a Trisubstituted Double Bond: Application to Chirality Transfer from Hydroxylated Carbon to Benzylic One

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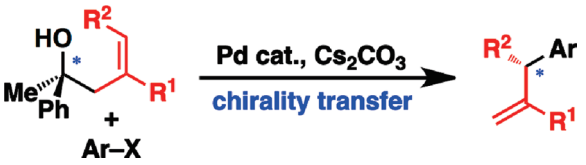

A facile route to homoallyl alcohols bearing a trisubstituted double bond has been devised. The palladium-catalyzed reactions of aryl halides with the alcohols thus synthesized result in regiospecific allyl transfer from the alcohols to aryl halides via retro-allylation, providing allylarenes having two substituents at the 1 and 2 positions of the allyl moiety. Optically active homoallyl alcohols transfer their chirality at the hydroxylated carbon to the benzylic carbon of the product.

Introduction

Allylarenes are a useful class of compounds in organic chemistry, being converted to a wide variety of functionalized alkylarenes.[1] Palladium-catalyzed reaction of aryl halides with allylmetals is likely to be an efficient method for the synthesis of allylarenes of interest. However, highly regio- and stereocontrolled allylation is difficult to achieve when substituted allylmetals such as crotylmetal are used.[2,3] We have been developing the use of homoallyl alcohols as allylmetal equivalents in the palladium-catalyzed allylation of aryl halides (Scheme 1):[4−6] after oxidative addition and halide−alkoxide exchange, retro-allylation provides σ-allyl(aryl)palladium, which undergoes rapid reductive elimination to yield the corresponding allylarene. The allyl transfer is proposed to occur via palladium-mediated retro-allylation that proceeds through a six-membered chairlike transition state. Therefore, design and synthesis of

(1) For recent examples, see: (a) Ohmiya, H.; Makida, Y.; Li, D.; Tanabe, M.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 879–889. (b) Ohta, T.; Kataoka, Y.; Miyoshi, A.; Oe, Y.; Furukawa, I.; Ito, Y. *J. Organomet. Chem.* **2007**, *692*, 671–677. (c) Axet, M. R.; Castillon, S.; Claver, C. *Inorg. Chim. Acta* **2006**, *359*, 2973–2979.

(2) (a) Godschalx, J.; Stille, J. K. *Tetrahedron Lett.* **1980**, *21*, 2599–2602. (b) Takemura, S.; Hirayama, A.; Tokunaga, J.; Kawamura, F.; Inagaki, K.; Hashimoto, K.; Nakata, M. *Tetrahedron Lett.* **1999**, *40*, 7501–7505. (c) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595–2598. (d) Méndez, M.; Echavarren, A. M. *Eur. J. Org. Chem.* **2002**, 15–28. (e) Goliaszewski, A.; Schwartz, J. *Tetrahedron* **1985**, *41*, 5779–5789. (f) Lee, P. H.; Sung, S.-Y.; Lee, K. *Org. Lett.* **2001**, *3*, 3201–3204. (g) Lee, K.; Lee, J.; Lee, P. H. *J. Org. Chem.* **2002**, *67*, 8265–8268.

(3) Examples of selective allylation: (a) Obora, Y.; Tsuji, Y.; Kobayashi, M.; Kawamura, T. *J. Org. Chem.* **1995**, *60*, 4647–4649. (b) Hatanaka, Y.; Ebina, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 7075–7076. (c) Hatanaka, Y.; Goda, K.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 1279–1282. (d) Hatanaka, Y.; Goda, K.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 6511–6514. (e) Hiyama, T.; Matsuhashi, H.; Fujita, A.; Tanaka, M.; Hirabayashi, K.; Shimizu, M.; Mori, A. *Organometallics* **1996**, *15*, 5762–5765. (f) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471–1478. (g) Yamamoto, Y.; Takada, S.; Miyaura, N. *Chem. Lett.* **2006**, *35*, 704–705. (h) Yamamoto, Y.; Takada, S.; Miyaura, N. *Chem. Lett.* **2006**, *35*, 1368–1369. (i) Yamamoto, Y.; Takada, S.; Miyaura, N.; Iyama, T.; Tachikawa, H. *Organometallics* **2009**, *28*, 152–160.

(4) (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. (d) Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 12650–12651. (e) Yorimitsu, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 778–792.

(5) Reviews for palladium-catalyzed C−C bond cleavage of tertiary alcohols: (a) Muzart, J. *Tetrahedron* **2005**, *61*, 9423–9463. (b) Nishimura, T.; Uemura, S. *Synlett* **2004**, 201–216. (c) Satoh, T.; Miura, M. *Top. Organomet. Chem.* **2005**, *14*, 1–20.

(6) Cross-coupling reactions of organic halides with tertiary alcohols via β-carbon elimination: (a) Nakano, M; Satoh, T.; Miura, M. *J. Org. Chem.* **2006**, *71*, 8309–8311. (b) Terao, Y.; Wakui, H.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2001**, *123*, 10407–10408. (c) Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 11010–11011. (d) Larock, R. C.; Reddy, C. K. *Org. Lett.* **2000**, *2*, 3325–3327. (e) Chow, H.-F.; Wan, C.-W.; Low, K.-H.; Yeung, Y.-Y. *J. Org. Chem.* **2001**, *66*, 1910–1913.

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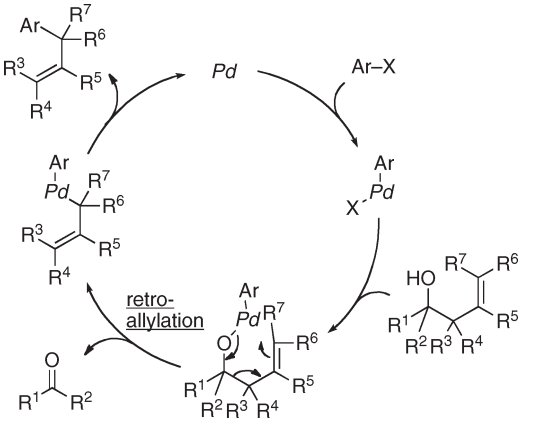
SCHEME 1. Reaction Mechanism of Palladium-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols



proper homoallyl alcohols are quite important to introduce the needed allylic moieties.

Although we have prepared several homoallyl alcohols for the palladium-catalyzed allylation, homoallyl alcohols **1** are the only alcohols that bear a trisubstituted double bond (Figure 1).[7]

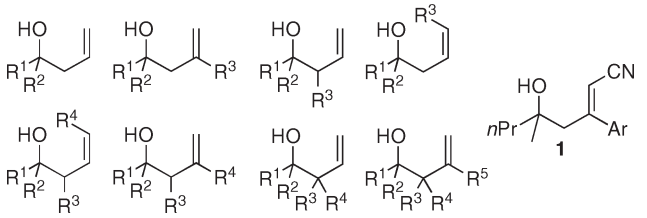
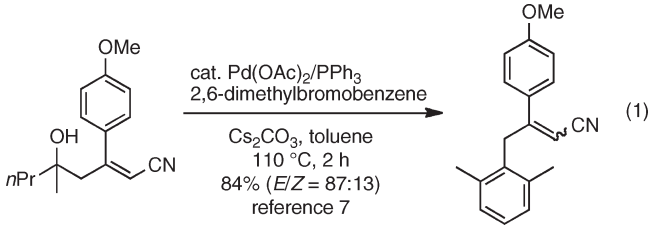


FIGURE 1. Hitherto known substitution patterns.

Unfortunately, the palladium-catalyzed allylation with **1** proceeded without regio- and stereospecificity because the electron-withdrawing nature of the cyano group retarded reductive elimination that is responsible for regio- and stereospecific allylation (eq 1). Hence, there are no examples of regio- and stereospecific allylation with homoallyl alcohols bearing a trisubstituted double bond. In addition, such highly substituted homoallyl alcohols are difficult to synthesize in a stereoselective manner. To expand the scope of homoallyl alcohols, we designed and prepared homoallyl alcohols **2** (Scheme 2) and employed **2** in palladium-catalyzed allylation of aryl halides, which we report herein.



(1)

Results and Discussion

Synthesis of Homoallyl Alcohols. Homoallyl alcohols **2** were readily prepared as demonstrated in Scheme 2. Nucleophilic ring-opening reaction of α-methylstyrene oxide with lithium acetylide afforded tertiary homopropargyl alcohol **3**.

(7) Ohmura, T.; Awano, T.; Suginome, M.; Yorimitsu, H.; Oshima, K. *Synlett* **2008**, 423–427.

SCHEME 2. Representative Scheme for Synthesis of Homoallyl Alcohols Bearing a Trisubstituted Double Bond

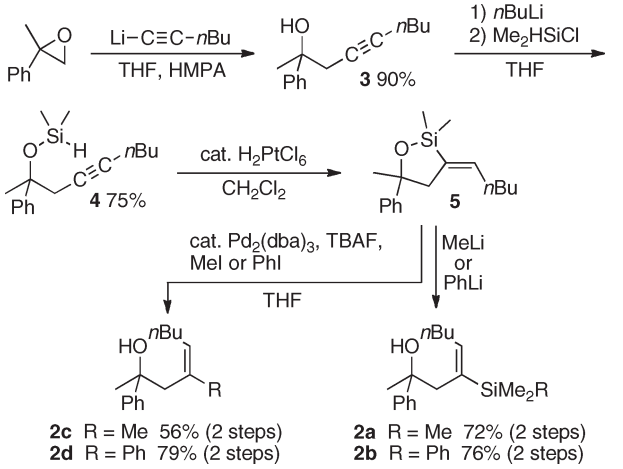
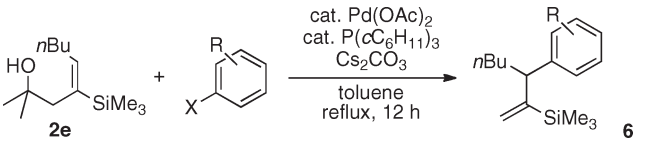


TABLE 1. Scope of Aryl Halides[a]



entry	X	R	6	yield/%
1	Br	H	**6a**	80
2	Cl	H	**6a**	74
3	Br	4-Me	**6b**	68
4	Br	4-OMe	**6c**	67
5	Br	4-CF_3	**6d**	76
6	Cl	4-CO_2Et	**6e**	89
7[b]	Br	4-CHO	**6f**	74
8[b]	Br	4-COPh	**6g**	81
9[b]	Br	4-CN	**6h**	76
10	Br	(1-naphthyl)[c]	**6i**	77
11	I	(3-pyridyl)[d]	**6j**	86

[a]Conditions: **2e** (0.40 mmol), aryl halide (1.5 equiv), $Pd(OAc)_2$ (5 mol %), $P(cC_6H_{11})_3$ (20 mol %), Cs_2CO_3 (1.5 equiv). [b]PPh_3 was used instead of $P(cC_6H_{11})_3$. [c]1-Bromonaphthalene was used as substrate. [d]3-Iodopyridine was used as substrate.

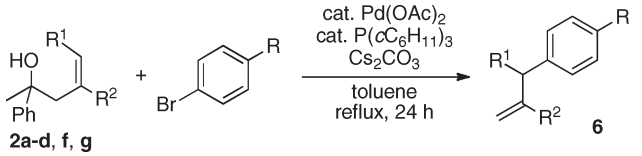
After dimethylsilylation of **3**, platinum-catalyzed intramolecular hydrosilylation of **4**[8] yielded oxasilacyclopentane **5**. Since **5** partially decomposed during silica gel column purification, the crude oil containing **5** was directly treated with organolithium to furnish silyl-substituted homoallyl alcohol **2a** and **2b**. Cross-coupling methylation and phenylation of **5**[9] provided another type of homoallyl alcohols **2c** and **2d**, respectively. Each step was easy to perform and high-yielding. We prepared several additional homoallyl alcohols **2e**–**g** (Tables 1 and 2) according to this procedure.

Allylation Reaction. Treatment of bromobenzene with **2e** in the presence of cesium carbonate under $Pd(OAc)_2/P(cC_6H_{11})_3$ catalysis in refluxing toluene provided the corresponding allylbenzene in 80% yield (Table 1, entry 1). The reaction proceeded

(8) Tamao, K.; Maeda, K.; Tanaka, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 6955–6956.

(9) (a) Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565–568. (b) Denmark, S. E.; Weitao, P. *Org. Lett.* **2001**, *3*, 61–64. (c) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845–853. (d) Takahashi, K.; Minami, T.; Ohara, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2649–2656.

TABLE 2. Scope of Homoallyl Alcohols[a]



entry	R^1	R^2	2	R	6	yield/%
1	*n*Bu	$SiMe_3$	**2a**	H	**6a**	75
2	*n*Bu	$SiMe_3$	**2a**	MeO	**6c**	74
3	*n*Bu	$SiMe_3$	**2a**	CO_2Et	**6e**	87
4[b]	*n*Bu	$SiMe_2Ph$	**2b**	H	**6k**	77
5	*n*Bu	Me	**2c**	H	**6l**	83
6	*n*Bu	Ph	**2d**	H	**6m**	73
7	$TIPSOCH_2$	$SiMe_3$	**2f**	H	**6n**	71
8	*t*Bu	$SiMe_3$	**2g**	H	**6o**	35[c]

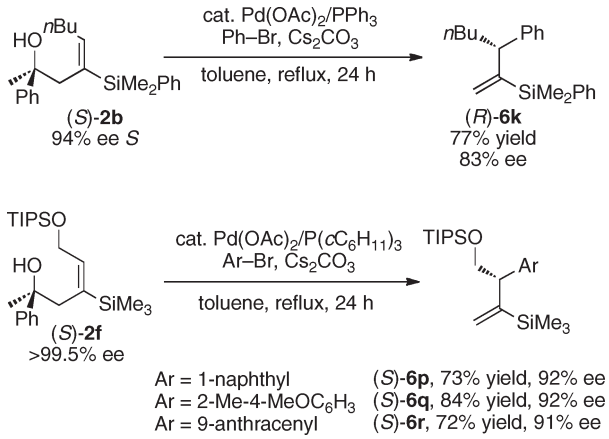
[a]Conditions: **2** (0.40 mmol), 4-RC_6H_4Br (1.5 equiv), $Pd(OAc)_2$ (5 mol %), $P(cC_6H_{11})_3$ (20 mol %), Cs_2CO_3 (1.5 equiv). [b]PPh_3 was used instead of $P(cC_6H_{11})_3$. [c]The phenyl ether of **2g** was obtained as a byproduct in 22% yield.

with perfect regioselectivity, and no 2-trimethylsilyl-2-heptenylbenzene was detected. Chlorobenzene as well as electron-rich 4-bromoanisole reacted smoothly without suffering from slow oxidative addition (entries 2 and 4). Trifluoromethyl and ethoxycarbonyl groups had little effect on the reaction (entries 5 and 6). Aryl bromides bearing the more electron-withdrawing formyl, benzoyl, or cyano group were allylated by using PPh_3 as the ligand (entries 7−9).[10] Sterically demanding 1-bromonaphthalene participated in the reaction (entry 10). A nitrogen-containing heterocycle could be allylated (entry 11).

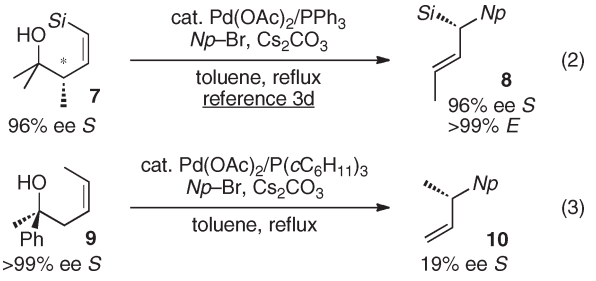
The scope of homoallyl alcohols was examined (Table 2). Compared to **2e**, the increased steric hindrance around the hydroxylated carbons of **2a**−**d** and **2f** led to a prolonged reaction time, although the yields of the products were satisfactory (entries 1−7). Instead of the trimethylsilyl group of **2a**, dimethylphenylsilyl, methyl, and phenyl groups on the internal olefinic carbons were also compatible (entries 4−6). Under the reaction conditions, the triisopropylsilyl ether of **2f** survived (entry 7). Unfortunately, the *tert*-butyl group of **2g** retarded the retro-allylation process (entry 8). Palladium-catalyzed phenylation of the hydroxy group[11] competed to yield the phenyl ether of **2g** as a byproduct.

Previously, we reported successful chirality transfer from an optically active homoallyl alcohol to allylarenes, in which the alcohol having chirality at the allylic position was used (eq 2, Np = 1-naphthyl).[4d] However, a number of attempts to transfer chirality from hydroxylated carbons failed, and we observed only 19% ee at a maximum (eq 3). We were pleased to find that optically enriched alcohol (*S*)-**2b** with a trisubstituted double bond realized satisfactory chirality transfer from the hydroxylated carbon (Scheme 3).[12] In the reaction

SCHEME 3. Chirality Transfer from (*S*)-2b and (*S*)-2f

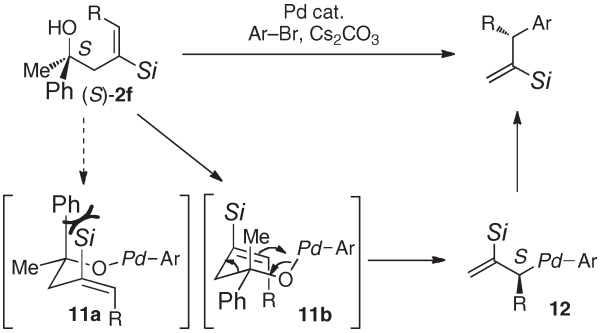


with optically pure (*S*)-**2f**, higher levels of chirality transfer were observed.[13,14]



The high levels of chirality transfer from (*S*)-**2f** are rationalized as follows (Scheme 4). Between two possible chairlike transition states, **11a** and **11b**, of the retro-allylation, **11b** would be more favorable because **11a** would suffer from the stronger 1,3-diaxial repulsion between the phenyl and silyl groups. The palladium center would approach the *Si*(sinister)-face of the alkene moiety, which results in the formation of **12** with *S* configuration. Rapid reductive elimination from **12** without loss of the chirality provides (*R*)-**6k** and (*S*)-**6p**−**r**.

SCHEME 4. Mechanism of Chirality Transfer



Conclusion

We have developed an easy route to homoallyl alcohols bearing a trisubstituted double bond, taking advantage of

(10) The use of $P(c\text{-}C_6H_{11})_3$ resulted in conversion as low as 10%, probably because of deactivation of the palladium catalyst.

(11) Buchwald, A. V.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 8146–8149 and references cited therein.

(12) Because direct determination of the enantiomeric excess of **6k** by chiral HPLC was difficult, **6k** was converted to **6m** according to the literature: Anderson, J. C.; Munday, R. H. *J. Org. Chem.* **2004**, *69*, 8971–8974. The enantiomeric excess of **6m** thus obtained was determined by chiral HPLC. See the Supporting Information.

(13) Because determination of the enantiomeric excess of **6p**−**r** was difficult, the TIPS group was removed by tetrabutylammonium fluoride to yield the corresponding chiral alcohols that were suitable for determination of enantiomeric excess. See the Supporting Information.

(14) The absolute stereochemistry of (*S*)-**6r** was determined by X-ray crystallographic analysis of the corresponding alcohol after desilylation. The absolute stereochemistry of the other products was tentatively assigned. See the Supporting Information.

intramolecular hydrosilylation. The homoallyl alcohols thus synthesized undergo palladium-catalyzed regioselective allyl transfer to aryl halides via retro-allylation. The silyl substituents at the more substituted olefinic carbon realize high levels of chirality transfer from the hydroxylated carbon to the benzylic carbon of the product.

Experimental Section

Preparation of Homoallyl Alcohols 2 (Scheme 2). A 100-mL reaction flask was filled with argon. THF (7.4 mL), 1-hexyne (1.70 mL, 14.8 mmol), and *n*-butyllithium (1.62 M hexane solution, 9.14 mL, 14.8 mmol) were added at 0 °C. The resulting mixture was stirred for 30 min. Hexamethylphosphoramide (1.29 mL, 7.4 mmol) and α-methylstyrene oxide (0.99 g, 7.4 mmol) were added at 0 °C. The mixture was allowed to warm to 40 °C and stirred for 22 h at ambient temperature. After an addition of a saturated ammonium chloride solution (20 mL), extraction, evaporation, and purification on silica gel furnished propargyl alcohol **3** (1.44 g, 6.67 mmol, 90%).

Alcohol **3** (1.44 g, 6.67 mmol) in THF (13 mL) was placed in a 50-mL reaction flask under argon. *n*-Butyllithium (1.62 M hexane solution, 4.8 mL, 7.7 mmol) was added at 0 °C. After the mixture was stirred for 30 min, chlorodimethylsilane (0.97 mL, 8.7 mmol) was added. The resulting mixture was allowed to warm to room temperature and was stirred for 8 h. Hexane (20 mL) was added, and the resulting suspension was filtered through a pad of Celite. The filtrate was concentrated in vacuo. Purification on silica gel (Kanto Chemical, neutral) by using hexane/ethyl acetate = 20:1 as an eluent provided silyl ether **4** (1.38 g, 5.03 mmol, 75%), along with **3** recovered (0.31 g, 1.4 mmol).

$H_2PtCl_6 \cdot 6H_2O$ (13 mg, 0.025 mmol) was placed in a 50-mL reaction flask under argon. Silyl ether **4** (1.38 g, 5.03 mmol) was diluted in dichloromethane (10 mL), and the solution was added to the platinum catalyst. After the mixture was stirred for 1 h, the solvent was removed in vacuo. The crude oxasilacyclopentane **5** was diluted in ether (10 mL) in a 50-mL reaction flask under argon. Phenyllithium (1.15 M in hexane/ether, 6.6 mL, 7.5 mmol) was added at −78 °C. After the mixture was stirred for 1 h, saturated ammonium chloride solution (20 mL) was added at room temperature. Extraction, evaporation, and purification on silica gel (hexane/ethyl acetate =40:1) furnished **2b** (1.34 g, 3.81 mmol, 76%).

In a similar fashion, addition of methyllithium (1.09 M in ether, 6.75 mL, 7.35 mmol) to crude **5** (from 4.9 mmol of **4**) afforded **2a** (1.03 g, 3.54 mmol, 72%).

The procedure for the synthesis of **2d** is as follows. Crude **5** (from 7.03 mmol of **4**) was placed in a 50-mL reaction flask. Tetrabutylammonium fluoride in THF (1.0 M, 14.1 mL, 14.1 mmol), iodobenzene (0.87 mL, 7.7 mmol), and $Pd_2(dba)_3$ (0.160 g, 0.175 mmol) were sequentially added. The mixture was stirred at room temperature for 30 min. Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 10:1) afforded **2d** (1.64 g, 5.58 mmol, 79%).

Alcohol **2c** was prepared in a similar fashion by using iodomethane. It is worth noting that the order of charging iodomethane and $Pd_2(dba)_3$ is important: after an addition of tetrabutylammonium fluoride, $Pd_2(dba)_3$ was added first. Iodomethane was then added. Otherwise, the reaction gave significant amounts of byproducts.

Reaction of Aryl Halides with Homoallyl Alcohols. Synthesis of **6a** (Table 1, entry 1) is representative. Cesium carbonate (0.20 g, 0.60 mmol) was placed in a 20-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 (4.5 mg, 0.020 mmol) was added. The flask was then filled with argon by using the standard Schlenk technique. Tricyclohexylphosphine (0.16 mL, 0.080 mmol, 0.50 M toluene solution) was charged in the reaction flask. Toluene (0.40 mL), homoallyl alcohol **2e** (91 mg, 0.40 mmol), and bromobenzene (94 mg, 0.60 mmol) were sequentially added at ambient temperature. The resulting mixture was heated at reflux for 12 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 **6a** (79 mg, 0.32 mmol) in 80% yield.

Characterization Data. (*E*)-2-Phenyl-4-trimethylsilyl-4-nonen-2-ol (2a): IR (neat) 3472, 2955, 2862, 1605, 1450, 1250, 1065, 841, 756, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H), 0.86−0.90 (m, 3H), 1.21−1.34 (m, 4H), 1.55 (s, 3H), 1.88 (s, 1H), 1.96−2.07 (m, 2H), 2.65 (d, J = 13.5 Hz, 1H), 2.72 (d, J = 13.5 Hz, 1H), 6.02 (t, J = 7.0 Hz, 1H), 7.24 (tt, J = 7.0, 2.0 Hz, 1H), 7.32−7.36 (m, 2H), 7.46−7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.0, 14.2, 22.7, 29.5, 30.4, 31.8, 44.1, 74.9, 125.1, 126.7, 128.2, 136.7, 147.3, 149.3; HRMS (FAB) found 289.1983 (M−H), calcd for $C_{18}H_{29}OSi$ 289.1988.

(*E*)-4-Dimethylphenylsilyl-2-phenyl-4-nonen-2-ol (2b): IR (neat) 3564, 3464, 2955, 2862, 1605, 1450, 1373, 1250, 1111, 1057, 818, 772, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (s, 3H), 0.34 (s, 3H), 0.88 (t, J = 7.0 Hz, 3H), 1.22−1.34 (m, 4H), 1.41 (s, 3H), 1.59 (s, 1H), 1.99−2.08 (m, 2H), 2.61 (d, J = 14.0 Hz, 1H), 2.73 (d, J = 14.0 Hz, 1H), 6.12 (t, J = 7.0 Hz, 1H), 7.20 (tt, J = 7.5, 2.0 Hz, 1H), 7.26−7.30 (m, 2H), 7.32−7.37 (m, 5H), 7.49−7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −1.6, −1.4, 14.2, 22.7, 29.6, 30.0, 31.7, 44.3, 75.1, 125.0, 126.6, 128.0, 128.2, 129.0, 134.4, 134.7, 139.9, 149.07, 149.10. Anal. Calcd for $C_{23}H_{32}OSi$: C, 78.35; H, 9.15. Found: C, 78.54; H, 9.05.

(*Z*)-4-Methyl-2-phenyl-4-nonen-2-ol (2c): IR (neat) 3464, 2924, 2862, 1450, 1373, 1095, 1034, 941, 872, 764, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.22−1.34 (m, 4H), 1.40 (q, J = 1.5 Hz, 3H), 1.58 (s, 3H), 1.97−2.01 (m, 2H), 2.09 (s, 1H), 2.52 (d, J = 13.5 Hz, 1H), 2.68 (d, J = 13.5 Hz, 1H), 5.33−5.36 (m, 1H), 7.22 (tt, J = 7.5, 2.0 Hz, 1H), 7.31−7.34 (m, 2H), 7.45−7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.6, 25.8, 28.5, 30.9, 32.3, 46.6, 74.6, 125.0, 126.7, 128.3, 131.3, 131.4, 148.9. HRMS (DART) found 231.1745(M − H), calcd for $C_{16}H_{23}O$ 231.1749.

(*E*)-2,4-Diphenyl-4-nonen-2-ol (2d): IR (neat) 3456, 3024, 2963, 2924, 2862, 2739, 1597, 1497, 1450, 1373, 1103, 1065, 910, 864, 756, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87−0.90 (t, J = 7.0 Hz, 3H), 1.26−1.33 (m, 4H), 1.42 (s, 3H), 1.83 (s, 1H), 2.02−2.06 (m, 2H), 3.05 (s, 2H), 5.68 (t, J = 7.0 Hz, 1H), 7.16−7.28 (m, 2H), 7.25−7.28 (m, 6H), 7.37−7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22. 7, 29.1, 30.0, 32.0, 44.2, 75.6, 125.0, 126.6, 126.9, 127.0, 128.1, 128.6, 135.1, 136.2, 144.9, 148.3. HRMS (FAB) found 293.1908 (M − H), calcd for $C_{21}H_{25}O$ 293.1905.

(*E*)-2-Methyl-4-trimethylsilyl-4-nonen-2-ol (2e): IR (neat) 3472, 2963, 1605, 1466, 1373, 1250, 1126, 1057, 903, 841, 756, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H), 0.89 (t, J = 7.5 Hz, 3H), 1.20 (s, 6H), 1.23−1.37 (m, 5H), 2.13 (dt, J = 7.5 Hz, 2H), 2.37 (s, 2H), 5.99 (t, J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.2, 14.3, 22.7, 29.6, 30.3, 31.9, 42.8, 71.9, 137.4, 146.1. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.24; H, 12.09.

(*E*)-2-Phenyl-6-triisopropylsiloxy-4-trimethylsilyl-4-hexen-2-ol (2f): IR (neat) 3456, 2947, 2870, 1605, 1466, 1373, 1250, 1065, 1011, 841, 764, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 9H), 1.03−1.05 (m, 21H), 1.55 (s, 3H), 2.30 (s, 1H), 2.64 (d, J = 4.0 Hz, 2H), 3.87 (dd, J = 14.0, 6.0 Hz, 1H), 4.07 (dd, J = 14.0, 6.0 Hz, 1H), 6.11 (t, J = 6.0 Hz, 1H), 7.22 (tt, J = 7.5, 1.0 Hz, 1H), 7.32 (tt, J = 7.5, 1.0 Hz, 2H), 7.41−7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.3, 12.2, 18.2, 30.6, 44.8, 60.9, 74.8, 125.2, 126.8, 128.3, 138.2, 145.7, 148.9. Anal. Calcd for $C_{24}H_{44}O_2Si_2$: C, 68.51; H, 10.54. Found: C, 68.24; H, 10.53.

(*E*)-6,6-Dimethyl-2-phenyl-4-trimethylsilyl-4-hepten-2-ol (2g): IR (neat) 3472, 2955, 1597, 1450, 1366, 1250, 1049, 841, 756, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.13 (s, 9H), 1.54 (s, 3H), 1.86 (s, 1H), 2.69 (d, J = 13.5 Hz, 1H), 3.05 (d, J = 13.5 Hz, 1H), 5.93 (t, J = 7.0 Hz, 1H), 7.21−7.25 (m, 1H), 7.32−7.36 (m, 2H), 7.47−7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.6, 30.4, 31.6, 36.3, 43.0, 73.8, 125.0, 126.7, 128.3, 134.4, 150.0, 155.6; HRMS (FAB) found 289.1975 (M − H), calcd for $C_{18}H_{29}OSi$ 289.1988.

2-Phenyl-4-nonyn-2-ol (3): ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.5 Hz, 3H), 1.28−1.36 (m, 2H), 1.39−1.45 (m, 2H), 1.61 (s, 3H), 2.14 (tt, J = 7.0, 2.5 Hz, 2H), 2.49 (s, 1H), 2.65 (dt, J = 17.0, 2.5 Hz, 1H), 2.72 (dt, J = 17.0, 2.5 Hz, 1H), 7.25 (tt, J = 7.0, 2.0 Hz, 1H), 7.32−7.36 (m, 2H), 7.46−7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 18.6, 22.1, 29.4, 31.2, 35.3, 73.5, 75.9, 84.5, 125.0, 127.1, 128.3, 147.0; HRMS (FAB) found 215.1433 (M − H), calcd for $C_{15}H_{19}O$ 215.1436.

Dimethylsilyl 1-methyl-1-phenyl-3-octynyl ether (4): ^1H NMR ($CDCl_3$) δ 0.16 (d, J = 3.0 Hz, 3H), 0.21 (d, J = 3.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H), 1.31−1.45 (m, 4H), 1.75 (s, 3H), 2.12 (tt, J = 7.0, 2.5 Hz, 2H), 2.62−2.64 (m, 2H), 4.74 (septet, J = 3.0 Hz, 1H), 7.24 (tt, J = 7.5, 1,5 Hz, 1H), 7.30−7.34 (m, 2H), 7.44−7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.7, 13.8, 18.7, 22.1, 27.8, 31.2, 36.3, 77.0, 77.2, 83.1, 125.6, 127.0, 128.0, 147.4; HRMS (EI) found 274.1755, calcd for $C_{17}H_{26}OSi$ 274.1753.

3-Phenyl-2-trimethylsilyl-1-heptene (6a): IR (neat) 3061, 3026, 2957, 2931, 2898, 2859, 1492, 1452, 1248, 926, 837, 760, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.09 (s, 9H), 0.86 (t, J = 7.5 Hz, 3H), 1.10−1.19 (m, 1H), 1.20−1.35 (m, 3H), 1.65−1.74 (m, 1H), 1.78−1.86 (m, 1H), 3.41 (t, J = 7.5 Hz, 1H), 5.51 (dd, J = 2.5, 1.0 Hz, 1H), 5.74 (dd, J = 2.5, 1.5 Hz, 1H), 7.14−7.19 (m, 3H), 7.24−7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.3, 23.0, 30.4, 34.9, 50.5, 123.5, 126.1, 128.3, 128.7, 144.6, 155.2. Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 78.02; H, 10.85.

3-(4-Methylphenyl)-2-trimethylsilyl-1-heptene (6b): IR (neat) 2955, 2862, 1512, 1458, 1412, 1250, 926, 841, 756, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.07 (s, 9H), 0.87 (t, J = 7.5 Hz, 3H), 1.11−1.38 (m, 4H), 1.64−1.72 (m, 1H), 1.77−1.84 (m, 1H), 2.32 (s, 3H), 3.39 (t, J = 7.5 Hz, 1H), 5.50 (dd, J = 2.5, 1.0 Hz, 1H), 5.73 (dd, J = 2.5, 1.5 Hz, 1H), 7.05−7.09 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.3, 21.2, 23.0, 30.5, 35.1, 50.0, 123.4, 128.5, 129.0, 135.5, 141.5, 155.5. Anal. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83. Found: C, 78.63; H, 10.68.

3-(4-Methoxyphenyl)-2-trimethylsilyl-1-heptene (6c): IR (neat) 3676, 2956, 2858, 1610, 1510, 1302, 1248, 1179, 1041, 925, 836, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.09 (s, 9H), 0.86 (t, J = 7.5 Hz, 3H), 1.10−1.35 (m, 4H), 1.61−1.68 (m, 1H), 1.75−1.82 (m, 1H), 3.36 (t, J = 7.5 Hz, 1H), 3.79 (s, 3H), 5.48 (d, J = 2.0 Hz, 1H), 5.72 (s, 1H), 6.81 (d, J = 9.0 Hz, 2H), 7.07 (d, 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.3, 23.0, 30.4, 35.1, 49.6, 55.4, 113.6, 123.2, 129.5, 136.6, 155.6, 158.1. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C,74.01; H, 10.33.

3-(4-Trifluoromethylphenyl)-2-trimethylsilyl-1-heptene (6d): IR (neat) 2955, 2862, 1620, 1327, 1250, 1165, 1026, 1032, 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.08 (s, 9H), 0.86 (t, J = 7.5 Hz, 3H), 1.08−1.16 (m, 1H), 1.18−1.35 (m, 3H), 1.65−1.72 (m, 1H), 1.80−1.87 (m, 1H), 3.48 (t, J = 7.5 Hz, 1H), 5.56 (dd, J = 2.0, 1.0 Hz, 1H), 5.75 (dd, J = 2.0, 1.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.2, 22.9, 30.3, 34.9, 50.3, 124.5, 124.6 (q, J = 270.1 Hz), 125.2 (q, J = 3.75 Hz), 128.6 (q, J = 32.18 Hz), 128.9, 148.9, 154.5. Anal. Calcd for $C_{17}H_{25}F_3Si$: C, 64.93; H, 8.01. Found: C, 64.67; H, 8.06.

Ethyl 4-(2-trimethylsilyl-1-hepten-3-yl)benzoate (6e): IR (neat) 2955, 2870, 1720, 1612, 1273, 1180, 1111, 1026, 926, 841, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.10 (s, 9H), 0.84 (t, J = 7.5 Hz, 3H), 1.06−1.18 (m, 1H), 1.20−1.33 (m, 3H), 1.38 (t, J = 7.0 Hz, 3H), 1.65−1.72 (m, 1H), 1.79−1.86 (m, 1H), 3.47 (t, J = 7.5 Hz, 1H), 4.36 (q, J = 7.0 Hz, 2H), 5.54 (dd, J = 2.0, 1.0 Hz, 1H), 5.76 (dd, J = 2.0, 1.5 Hz, 1H), 7.22−7.24 (m, 2H), 7.93−7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.2, 14.6, 22.9, 30.3, 34.8, 50.4, 61.0, 124.3, 128.5, 128.6, 129.6, 150.1, 154.5, 166.9. Anal. Calcd for $C_{19}H_{30}O_2Si$: C, 71.64; H, 9.49. Found: C, 71.91; H, 9.30.

4-(2-Trimethylsilyl-1-hepten-3-yl)benzaldehyde (6f): IR (neat) 2955, 2862, 2731, 1705, 1604, 1420, 1250, 1211, 1165, 934, 841, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.09 (s, 9H), 0.85 (t, J = 7.5 Hz, 3H), 1.08−1.16 (m, 1H), 1.19−1.34 (m, 3H), 1.67−1.74 (m, 1H), 1.81−1.88 (m, 1H), 3.50 (t, J = 7.5 Hz, 1H), 5.57 (dd, J = 2.0, 0.5 Hz, 1H), 5.77 (dd, J = 2.0, 1.5 Hz, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 9.97 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.2, 22.9, 30.3, 34.8, 50.6, 124.6, 129.3, 129.9, 134.9, 152.3, 154.2, 192.3. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.60; H, 9.42.

Phenyl 4-(trimethylsilyl-1-hepten-3-yl)phenyl ketone (6g): IR (neat) 2955, 2862, 1659, 1605, 1412, 1281, 1180, 1026, 926, 841, 756, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06 (s, 9H), 0.87 (t, J = 7.5 Hz, 3H), 1.12−1.37 (m, 4H), 1.69−1.76 (m, 1H), 1.82−1.89 (m, 1H), 3.51 (t, J = 7.5 Hz, 1H), 5.56 (dd, J = 2.0, 1.0 Hz, 1H), 5.78 (dd, J = 2.0, 1.5 Hz, 1H), 7.27−7.29 (m, 2H), 7.46−7.50 (m, 2H), 7.56−7.59 (m, 1H), 7.72−7.75 (m, 2H), 7.78−7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.2, 23.0, 30.4, 34.9, 50.5, 124.4, 128.4, 128.6, 130.2, 130.4, 132.4, 135.6, 138.2, 150.0, 154.5, 196.8. Anal. Calcd for $C_{23}H_{30}OSi$: C, 78.80; H, 8.63. Found: C, 78.72; H, 8.80.

4-(2-Trimethylsilyl-1-hepten-3-yl)benzonitrile (6h): IR (neat) 2955, 2862, 2230, 1605, 1504, 1412, 1250, 1026, 934, 841, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.09 (s, 9H), 0.85 (t, J = 7.5 Hz, 3H), 1.05−1.14 (m, 1H), 1.18−1.35 (m, 3H), 1.63−1.70 (m, 1H), 1.79−1.86 (m, 1H), 3.47 (t, J = 7.5 Hz, 1H), 5.57 (dd, J = 2.0, 1.0 Hz, 1H), 5.75 (dd, J = 2.0, 1.5 Hz, 1H), 7.26−7.29 (m, 2H), 7.55 (dt, J = 8.5, 2.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.2, 22.9, 30.3, 34.8, 50.5, 110.1, 119.3, 124.9, 129.4, 132.2, 150.5, 154.0. Anal. Calcd for $C_{17}H_{25}NSi$: C, 75.21; H, 9.28. Found: C, 75.26; H, 9.31.

3-(1-Naphthyl)-2-trimethylsilyl-1-heptene (6i): IR (neat) 3055, 2955, 2862, 1597, 1396, 1250, 926, 841, 779 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.15 (s, 9H), 0.85 (t, J = 7.5 Hz, 3H), 1.20−1.40 (m, 4H), 1.80−1.87 (m, 1H), 1.93−1.99 (m, 1H), 4.30 (t, J = 7.0 Hz, 1H), 5.62 (dd, J = 2.5, 1.0 Hz, 1H), 5.78 (dd, J = 2.5, 1.5 Hz, 1H), 7.35 (dd, J = 7.5, 1.5 Hz, 1H), 7.40−7.51 (m, 3H), 7.70 (d, J = 8.0 Hz, 1H), 7.84−7.86 (m, 1H), 8.12 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.7, 14.3, 23.2, 30.7, 34.9, 45.2, 123.8, 124.7, 125.4, 125.5 (overlapped, 2C), 125.8, 126.9, 129.1, 132.5, 134.3, 140.4, 154.6. Anal. Calcd for $C_{20}H_{28}Si$: C, 81.01; H, 9.52. Found: C, 80.95; H, 9.46.

3-(3-Pyridyl)-2-trimethylsilyl-1-heptene (6j): IR (neat) 2955, 2862, 2368, 1574, 1466, 1420, 1250, 1111, 1026, 926, 841, 756, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.08 (s, 9H), 0.85 (t, J = 7.5 Hz, 3H), 1.09−1.18 (m, 1H), 1.19−1.37 (m, 3H), 1.64−1.72 (m, 1H), 1.82−1.88 (m, 1H), 3.43 (t, J = 7.5 Hz, 1H), 5.56 (dd, J = 2.5, 1.0 Hz, 1H), 5.75 (dd, J = 2.5, 1.0 Hz, 1H), 7.18−7.21 (m, 1H), 7.45−7.47 (m, 1H), 8.42−8.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.2, 22.9, 30.3, 34.8, 47.8, 123.4, 124.6, 135.7, 139.9, 147.8, 150.5, 154.3. Anal. Calcd for $C_{15}H_{25}NSi$: C, 72.81; H, 10.18. Found: C, 72.70; H, 10.43.

2-Dimethylphenylsilyl-3-phenyl-1-heptene (6k): IR (neat) 3055, 2955, 2862, 1597, 1458, 1427, 1250, 1111, 1034, 934, 826, 772, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 3H), 0.19 (s, 3H), 0.79 (t, J = 7.5 Hz, 3H), 1.02−1.25 (m, 4H), 1.60−1.67 (m, 1H), 1.72−1.79 (m, 1H), 3.35 (t, J = 7.5 Hz, 1H), 5.55 (d, J = 2.5 Hz, 1H), 5.83 (dd, J = 1.5 Hz, 1H), 7.03−7.06 (m, 2H), 7.12−7.15 (m, 1H), 7.19−7.22 (m, 2H), 7.29−7.36 (m, 3H), 7.39−7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −2.5, −2.2, 14.2, 22.9, 30.3, 35.0, 50.3, 125.6, 126.1, 127.8, 128.2, 128.7, 129.0, 134.3, 138.6, 144.3, 153.5. Anal. Calcd for $C_{21}H_{28}Si$: C, 81.75; H, 9.15. Found: C, 81.56; H, 9.08.

The enantiomeric excess of **6k** was determined after replacement of the silyl group with a phenyl group to give **6m** by the palladium-catalyzed cross-coupling reaction of **6k** with iodobenzene in the presence of potassium trimethylsiloxide and 18-crown-6.[15]

2-Methyl-3-phenyl-1-heptene (6l): IR (neat) 3078, 3024, 2932, 2862, 1643, 1597, 1450, 1373, 1034, 887, 748, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.5 Hz, 3H), 1.12−1.36 (m, 4H), 1.57 (m, 3H), 1.68−1.75 (m, 1H), 1.79−1.86 (m, 1H), 3.19 (t, J = 7.5 Hz, 1H), 4.81−4.82 (m, 1H), 4.90−4.91 (m, 1H), 7.17−7.22 (m, 3H), 7.26−7.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.1, 23.0, 30.3, 32.9, 53.1, 110.4, 126.3, 128.1, 128.4, 144.2, 148.5; HRMS (EI) found 188.1568, calcd for $C_{14}H_{20}$ 188.1565.

2,3-Diphenyl-1-heptene (6m): IR (neat) 3024, 2932, 2862, 1628, 1497, 1450, 1026, 903, 779, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.5 Hz, 3H), 1.19−1.36 (m, 4H), 1.74−1.81 (m, 1H), 1.87−1.93 (m, 1H), 3.75 (t, J = 7.5 Hz, 1H), 5.18 (dd, J = 1.0 Hz, 1H), 5.36 (d, J = 1.0 Hz, 1H), 7.14−7.27 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.2, 23.0, 30.4, 35.1, 50.7, 113.2, 126.3, 127.0, 127.3, 128.2, 128.4, 128.5, 143.0, 143.9, 152.2. Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.13; H, 9.03. HPLC conditions: Daicel CHIRALPAK OJ-H, hexane/2-propnol =98.0/2.0, 0.2 mL/min, retention time: 20.06 min (*R*, major); 21.21 min (*S*, minor).

2-Phenyl-3-trimethylsilyl-3-butenyl triisopropylsilyl ether (6n): IR (neat) 2947, 2869, 1466, 1381, 1250, 1111, 995, 926, 880, 841, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.05 (s, 9H), 0.97−1.03 (m, 21H), 3.67 (t, J = 7.0 Hz, 1H), 3.93 (dd, J = 10.0, 7.0 Hz, 1H), 4.07 (dd, J = 10.0, 7.0 Hz, 1H), 5.59 (dd, J = 2.5, 1.0 Hz, 1H), 5.77 (dd, J = 2.5, 1.0 Hz, 1H), 7.17−7.20 (m, 1H), 7.22−7.28 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −1.1, 12.2, 18.15, 18.19, 52.7, 67.0, 124.7, 126.4, 128.1, 129.2, 142.1, 152.2. Anal. Calcd for $C_{22}H_{40}OSi_2$: C, 70.14; H, 10.70. Found: C, 70.08; H, 10.77.

4,4-Dimethyl-3-phenyl-2-trimethylsilyl-1-pentene (6o): IR (neat) 2955, 1597, 1450, 1366, 1250, 1157, 1119, 1072, 1011, 841, 748, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H), 1.00 (s, 9H), 3.49 (d, J = 1.0 Hz, 1H), 5.63 (d, J = 4.0 Hz, 1H), 6.19 (dd, J = 4.0, 1.0 Hz, 1H), 7.15−7.19 (m, 1H), 7.21−7.28 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −1.2, 29.7, 35.6, 59.1, 124.9, 126.1, 127.4, 131.0, 141.9, 154.2. Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.77; H, 10.60.

2-(1-Naphthyl)-3-trimethylsilyl-3-butenyl triisopropylsilyl ether (6p): IR (neat) 3055, 2947, 2862, 1466, 1389, 1250, 1111, 1010, 926, 841, 764, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 9H), 0.93−1.00 (m, 21H), 4.05 (dd, J = 10.0, 6.5 Hz, 1H), 4.18 (dd, J = 10.0, 6.5 Hz, 1H), 4.55 (t, J = 6.5 Hz, 1H), 5.68 (dd, J = 2.5, 1.0 Hz, 1H), 5.88 (J = 2.5, 1.0 Hz, 1H), 7.38−7.51 (m, 4H), 7.70 (dd, J = 6.5, 3.0 Hz, 1H), 7.82−7.84 (m, 1H), 8.17−8.19 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −0.1, 12.2, 18.2, 47.7, 66.4, 124.0, 125.3, 125.3, 125.76, 125.79, 126.4, 127.1, 129.0, 132.7, 134.2, 137.6, 152.0. Anal. Calcd for $C_{26}H_{42}OSi_2$: C, 73.17; H, 9.92. Found: C, 73.03; H, 10.05.

Direct determination of the enantiomeric excess of **6p** was difficult. For the determination, we deprotected the silyl ether to yield the corresponding alcohol **6p-Si** (vide infra). Desilylation was performed by treatment of **6p** with tetrabutylammonium fluoride in THF at room temperature (84% yield).

2-(1-Naphthyl)-3-trimethylsilyl-3-buten-1-ol (6p-Si): IR (neat) 3387, 3055, 2955, 2893, 1597, 1512, 1396, 1250, 1165, 1049, 934, 841, 779, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 9H), 1.60 (t, J = 6.5 Hz, 1H), 4.01 (m, 1H), 4.11 (m, 1H), 4.63 (t, J = 7.0 Hz, 1H), 5.77 (dd, J = 2.5, 1.5 Hz, 1H), 5.87 (dd, J = 2.5, 1.5 Hz, 1H), 7.40−7.55 (m, 4H), 7.75−7.77 (m, 1H), 7.86−7.88 (m, 1H), 8.15 (dd, J = 8.0, 0.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.9, 47.8, 64.9, 123.6, 125.4, 125.7, 125.9, 126.33, 126.34, 127.8, 129.2, 132.4, 134.4, 136.2, 152.0; HRMS (EI) found 270.1438, calcd for $C_{17}H_{22}OSi$ 270.1440; 92% ee *R*; $[\alpha]^{32}_D$ −65.0 (*c* 1.00, $CHCl_3$). HPLC conditions: Daicel CHIRALPAK AD-H, hexane/2-propanol = 98.0/2.0, 0.4 mL/min, retention time: 28.01 min (*S*, major); 30.30 min (*R*, minor).

2-(4-Methoxy-2-methylphenyl)-3-trimethylsilyl-3-butenyl triisopropylsilyl ether (6q): IR (neat) 2947, 2862, 2361, 1612, 1504, 1466, 1381, 1250, 1111, 1057, 995, 926, 841, 756, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H), 0.97−0.99 (m, 21H), 2.34 (s, 3H), 3.77 (s, 3H), 3.81−3.87 (m, 2H), 4.02 (dd, J = 5.0 Hz, 1H), 5.58 (dd, J = 2.5, 1.0 Hz, 1H), 5.74 (dd, J = 2.5, 1.0 Hz, 1H), 6.63−6.69 (m, 2H), 7.04 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.9, 12.2, 18.18, 18.19, 20.4, 47.5, 55.3, 66.5, 110.8, 115.9, 124.9, 129.5, 132.0, 138.0, 152.0, 158.0. Anal. Calcd for $C_{24}H_{44}O_2Si_2$: C, 68.51; H, 10.54. Found: C, 68.71; H, 10.65.

Direct determination of the enantiomeric excess of **6q** was difficult. For the determination, we deprotected the silyl ether to yield the corresponding alcohol **6q-Si** (vide infra). Desilylation was performed by treatment of **6q** with tetrabutylammonium fluoride in THF at room temperature (80% yield).

2-(4-Methoxy-2-methylphenyl)-3-trimethylsilyl-3-buten-1-ol (6q-Si): IR (neat) 3410, 2955, 1612, 1497, 1466, 1412, 1250, 1196, 1057, 934, 841, 756, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H), 1.50 (t, J = 5.5 Hz, 1H), 2.33 (s, 3H), 3.74−3.81 (m, 4H), 3.91−3.96 (m, 2H), 5.66 (dd, J = 2.0, 1.0 Hz, 1H), 5.71 (dd, J = 2.0, 1.0 Hz, 1H), 6.71 (dt, J = 9.0, 3.0 Hz, 2H), 7.07 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.9, 20.2, 47.8, 55.3, 64.8, 111.2, 116.5, 125.6, 128.9, 130.5, 138.3, 152.0, 158.4; 92% ee *R*, $[\alpha]^{32}_D$ −47.8 (*c* 0.75, $CHCl_3$). Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15. Found: C, 68.40; H, 9.20. HPLC conditions: Daicel CHIRALPAK OD-H, hexane/2-propanol = 99.4/0.6, 0.4 mL/min, retention time: 44.53 min (*S*, major); 51.98 min (*R*, minor).

2-(9-Anthryl)-3-trimethylsilyl-3-butenyl triisopropylsilyl ether (6r): IR (neat) 3055, 2947, 2862, 1466, 1389, 1250, 1103, 1011, 926, 880, 841, 733, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.43 (s, 9H), 0.74−0.89 (m, 21H), 4.43 (dd, J = 9.0, 6.5 Hz, 1H), 4.82 (dd, J = 9.0, 6.5 Hz, 1H), 5.18−5.21 (m, 1H), 5.73 (dd, J = 2.5 Hz, 1H), 6.04 (dd, J = 2.5 Hz, 1H), 7.40 (s, 4H), 7.95−7.97 (m, 2H), 8.35 (s, 1H), 8.47−8.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.8, 12.0, 17.9, 18.0, 48.1, 66.6, 124.4, 124.7 (overlapped, 2C), 125.4, 127.3, 129.3, 131.6, 132.0, 134.2, 154.2. Anal. Calcd for $C_{30}H_{44}OSi_2$: C, 75.56; H, 9.30. Found: C, 75.29; H, 9.17.

Direct determination of the enantiomeric excess of **6r** was difficult. For the determination, we deprotected the silyl ether to yield the corresponding alcohol **6r-Si** (vide infra). Desilylation was performed by treatment of **6r** with tetrabutylammonium fluoride in THF at room temperature (84% yield).

2-(9-Anthryl)-3-trimethylsilyl-3-buten-1-ol (6r-Si): mp = 70−71 °C; IR (Nujol) 3256, 2924, 2854, 2723, 1589, 1458, 1373, 1250, 1180, 1049, 972, 918, 841, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.41 (s, 9H), 1.25 (dd, J = 8.0, 5.0 Hz, 1H), 4.45−4.50 (m, 1H), 4.72−4.77 (m, 1H), 5.25−5.28 (m, 1H), 5.78 (dd, J = 2.5, 2.0 Hz, 1H), 6.02 (dd, J = 2.5, 2.0 Hz, 1H), 7.45−7.48 (m, 4H), 8.01−8.03 (m, 2H), 8.44 (s, 1H), 8.50−8.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −1.0, 47.6, 65.6, 124.1, 125.0 (overlapped, 2C), 125.6, 128.1, 129.5, 131.6, 132.0, 132.1, 154.0; HRMS (EI) found 320.1594, calcd for $C_{21}H_{24}OSi$ 320.1596; 91% ee *R*, $[\alpha]^{32}_D$ −124.3 (*c* 1.01, $CHCl_3$). HPLC conditions: Daicel CHIRALPAK OD-H, hexane/2-propanol =80/20, 1.0 mL/min, retention time: 5.92 min (*S*, major); 7.45 min (*R*, minor).

The absolute stereochemistry of the major isomer of **6r-Si** was determined by using X-ray crystallographic analysis. Crystals of the major isomer of **6r-Si** suitable for X-ray crystallographic analysis were grown from heptane/dichloromethane. The ORTEP drawing of the major isomer of **6r-Si** is shown in the Supporting Information (CCDC No. 772243). The flack parameter was −0.20, which indicates that the structure shown

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below represents the exact absolute stereochemistry, which is *S*. The absolute stereochemistry of **6k-Si**, **6p-Si**, and **6q-Si** was tentatively asigned by taking the reaction mechanism into consideration.

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Supporting Information Available: Copies of NMR spectra and HPLC chromatograms and CIF and ORTEP drawing for **6r-Si**. This material is available free of charge via the Internet at http://pubs.acs.org.