2,6-Bis(2-alkylphenyl)-3,5-dimethylphenol as a New Chiral Phenol with C_2-Symmetry. Application to the Asymmetric Alkylation of Aldehydes

Susumu Saito, Taichi Kano, Keiko Hatanaka, and Hisashi Yamamoto*

Graduate School of Engineering, Nagoya University, CREST, Japan Science and Technology Corporation (JST), Furo-cho, Chikusa, Nagoya 464-01, Japan

Received April 28, 1997[⊗]

The desire to control the selectivity of carbon−carbon bond-forming reactions in organic synthesis has led to the design of various Lewis acid catalysts, which are required to attach the proper ligands to an acidic metal center. Various Lewis acid catalysts have been used for this purpose in our laboratory,[1] and each reagent has characteristic features due to its unique steric factors. In particular, aluminum tris(2,6-diphenylphenoxide) (ATPH)[2] has been used as a typical designer Lewis acid catalyst for regio-, chemo-, and stereoselective organic reactions, and the structure of ATPH has been successfully extended to the chiral analogue aluminum tris((*R*)-1-α-naphthyl-2-naphthoxide) ((*R*)-ATBN) for asymmetric Claisen rearrangement.[2c] This result encouraged us to explore the possibility of a new chiral phenol with C_2-symmetry. We report here the synthesis and optical resolution of racemic 3,5-dimethyl-2,6-bis(2-methylphenyl)phenol (*dl*-**1**) and analogous 2,6-bis(2-isopropylphenyl)-3,5-dimethylphenol (*dl*-**2**) for chiral aluminum reagents, which were found to be effective for the enantioselective alkylation of aldehydes (Figure 1).

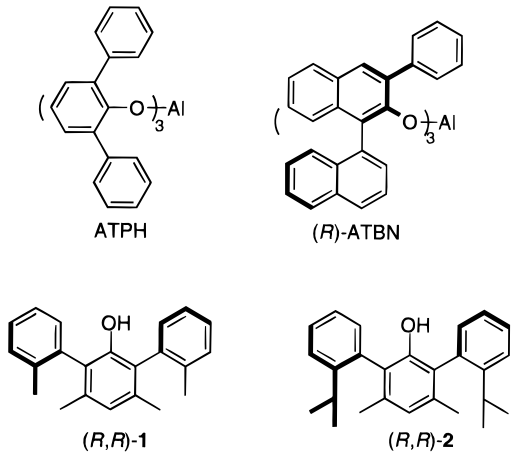


Figure 1.

Optically active **1** and **2** were synthesized as follows. Regioselective dibromination of commercially available 3,5-dimethylphenol (**3**) with Br_2 in the presence of 4 equiv of *t*-$BuNH_2$ followed by methylation of **4** with MeI and K_2CO_3 in MeOH gave methyl ether **5** (68% yield from **3**). Subsequent Suzuki coupling[3] of **5** with (2-methylphenyl)-boronic acid [$Pd(OAc)_2$, (*o*-tolyl)$_3$P, $Ba(OH)_2$, DME−H_2O (5:1); reflux for 4 h] gave racemic *dl*-**6** and *meso*-**6** in a ratio of 1:1, which was then recrystallized from methanol to give *meso*-**6** in a yield of 45% as a colorless crystal. The filtrate, which contained a 10:1 mixture of *dl*- and *meso*-**6**, was purified by column chromatography on silica gel to give *dl*-**6** in a yield of 38%, which was demethylated (BBr_3, CH_2Cl_2), and the resulting *dl*-**1** was converted into camphorsulfonyl esters (*R*,*R*,*S*)-**7** and (*S*,*S*,*S*)-**7** (94%) by sequential treatment with NaH and (+)-(*S*)-camphorsulfonyl chloride. The mixture of diastereomers (*R*,*R*,*S*)-**7** and (*S*,*S*,*S*)-**7** was separated by fractional recrystallization from ether to give enantiomerically pure (*S*,*S*,*S*)-**7** (17%), which was subjected to desulfonylation (Na, naphthalene, THF; −78 °C for 30 min) to furnish (*S*,*S*)-**1** (>99% ee)[4] in 68% yield (Scheme 1). (*R*,*R*)-**1** can be obtained readily by using (−)-camphorsulfonyl chloride. The synthesis of (*R*,*R*)-**2** and (*S*,*S*)-**2** was initiated with the introduction of sterically hindered 2-isopropylphenyl groups to **5** by Suzuki coupling, which was carried out using a sealed tube to give *dl*-**8** in 46% yield.[5] It should be noted that no *meso*-**8** could be detected. Sulfonylation of *dl*-**2** with *n*-BuLi and (+)-camphorsulfonyl chloride after treatment of *dl*-**8** with BBr_3 gave a diastereomixture of (*R*,*R*,*S*)-**9** and (*S*,*S*,*S*)-**9**, which were separated by silica gel column chromatography to furnish (*R*,*R*,*S*)-**9** in 46% yield together with a slightly impure (*S*,*S*,*S*)-**9**, which was recrystallized from EtOAc to give enantiomerically pure (*S*,*S*,*S*)-**9** in 38% yield. Subsequent reduction of (*R*,*R*,*S*)-**9** or (*S*,*S*,*S*)-**9** with $LiAlH_4$ in THF at reflux gave rise to (*R*,*R*)-**2** or (*S*,*S*)-**2** in 82% yield. The absolute configuration of (*S*,*S*)-**2** was rigorously established by X-ray crystal analysis of (*S*,*S*,*S*)-**9**,[6] and those of (*R*,*R*)-**2**, (*R*,*R*)-**1**, and (*S*,*S*)-**1** could be assigned by correlating among the CD spectra of these phenols.[6]

Scheme 2 shows an alternative approach to this type of phenol. Tribromination of aniline **10** followed by diazotization and iodination[7] of **11** with KI gave tribromoiodobenzene **12** in an overall yield of 88%. The successive generation of two different benzynes from **12** was promoted by treatment with 2 equiv of the Grignard reagent,[8] and transmetalation of the resulting (2,6-diarylphenyl)magnesium species to BH_3 was followed by hydrolysis with H_2O_2−aqueous NaOH[9] to give bromophenol **13** in 42% yield in a *dl*:*meso* ratio of ca. 2:1. Subsequent reduction with Bu_3SnH proceeded smoothly to give *dl*-**2** and *meso*-**2** (66:34) in 70% yield (overall yield of *dl*-**2** from **10** = 17%).

Neither the reaction of (*R*,*R*)-**1** with Me_3Al in CH_2Cl_2 or toluene upon reflux gave aluminum trisphenoxide **14**, but resulted in the formation of aluminum bisphenoxide methylaluminum bis((*R*,*R*)-3,5-dimethyl-2,6-bis(2-meth-

(1) Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD): (a) Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588. (b) Maruoka, K.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1992**, *114*, 1089. Methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR): (c) Maruoka, K.; Ooi, T; Yamamoto, H. *ibid.* **1989**, *111*, 6431. (d) Maruoka, K.; Ooi, T.; Yamamoto, H. *ibid.* **1990**, *112*, 9011. (e) Maruoka, K.; Sato, J.; Yamamoto, H.; *ibid.* **1993**, *113*, 5449 (f) Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *ibid.* **1988**, *110*, 7922.

(2) (a) Maruoka, K.; Imoto, H.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 4131. (b) Maruoka, K.; Imoto, H.; Yamamoto, H. *ibid.* **1994**, *116*, 12115. ATPH for Claisen rearrangement: (c) Maruoka, K.; Saito, S.; Yamamoto, H. *ibid.* **1995**, *117*, 1165. (d) Maruoka, K.; Ito, M.; Yamamoto, H. *ibid.* **1995**, *117*, 9091. (e) Saito, S.; Ito, M.; Yamamoto, H. *ibid.* **1997**, *119*, 611.

(3) (a) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314. (b) Oh-e, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, *58*, 2201.

(4) The optical purity was determined by chiral HPLC using a Daicel column OD-H.

(5) Otherwise, the yield of *dl*-**9** decreased significantly.

(6) See the Supporting Information.

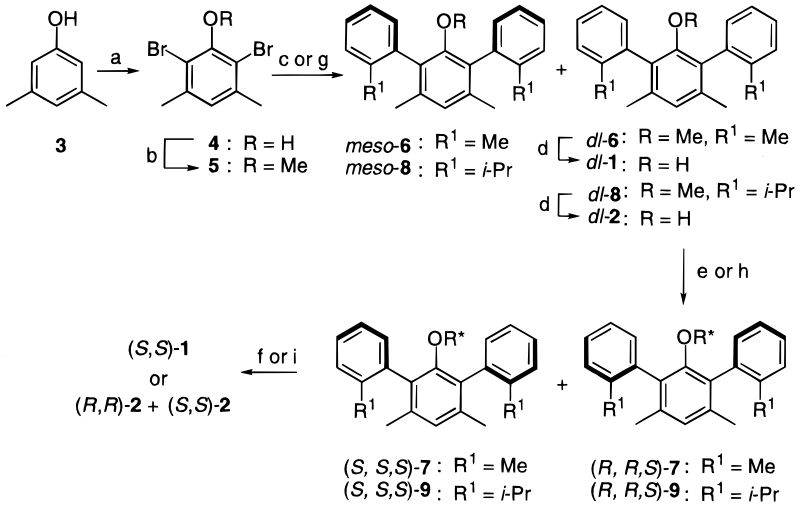
(7) Hodgson, H. H.; Mahadevan, A. P. *J. Chem. Soc.* **1947**, 173.

(8) Du, C.-J. F.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162.

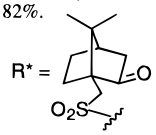
(9) (a) Breuer, S. W.; Broster, F. A. *J. Organomet. Chem.* **1972**, *35*, C5. (b) Brown, H. C.; Zweifel, G. *Org. React.* **1963**, *13*, 1.

S0022-3263(97)00747-0 CCC: $14.00

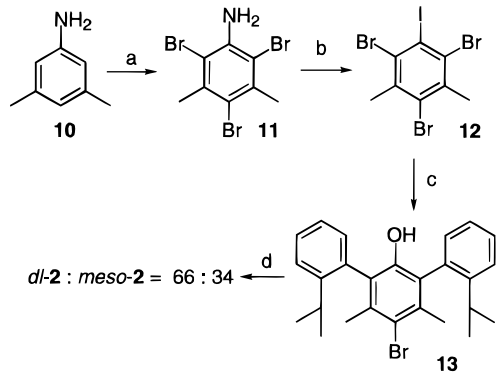
Scheme 1



For (*S*,*S*)-**1**: (a) Br_2, *t*-$BuNH_2$, toluene, 0 °C, 70% (b) MeI, K_2CO_3, MeOH, reflux, 97% (c) (2-methyl)phenyl boronic acid, $Pd(OAc)_2$, (*o*-tolyl)$_3$P, $Ba(OH)_2$, DME-H_2O (5: 1), reflux, 97% (*dl*-**6** = 38%) (d) BBr_3, CH_2Cl_2, 0 °C, 99% (e) NaH, (+)-camphorsulfonyl chloride, THF, rt, 75% ((*S*,*S*)-**8** = 17%) (f) Na, naphthalene, THF, -78 °C, 68%. For (*R*,*R*)- and (*S*,*S*,)-**2**: (g) (2-isopropyl)phenyl boronic acid, $Pd(OAc)_2$, (*o*-tolyl)$_3$P, $Ba(OH)_2$, DME-H_2O (10 : 1) in a sealed tube, reflux, 46% (h) *n*-BuLi, (+)-camphorsulfonyl chloride, THF, rt, 88% ((*S*,*S*)-**10** = 38%, (*R*,*R*)-**10** = 46%) (i) $LiAlH_4$, THF, 50 °C, 82%.

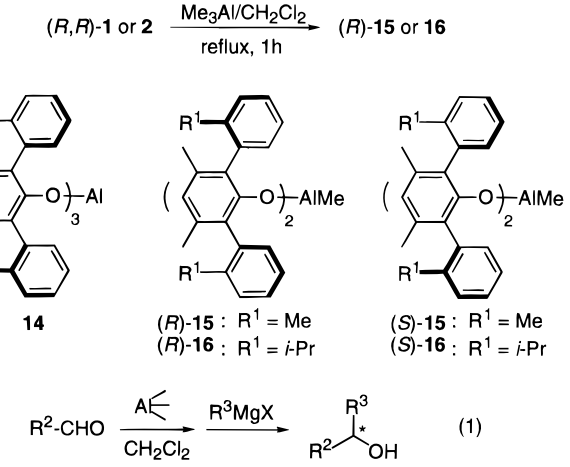


Scheme 2



(a) Br_2, CCl_4, CH_2Cl_2, 0 °C, 90% (b) (i) $NaNO_2$, H_2SO_4-AcOH, 0 °C (ii) KI, 80 °C, 98% (c) (i) (2-isopropylphenyl)-magnesium iodide, THF, rt (ii) BH_3, rt (iii) H_2O_2, NaOH, rt, 42% (d) Bu_3SnH, 140 °C, 70%

Scheme 3. Preparation of Optically Active Aluminum Bisphenoxides

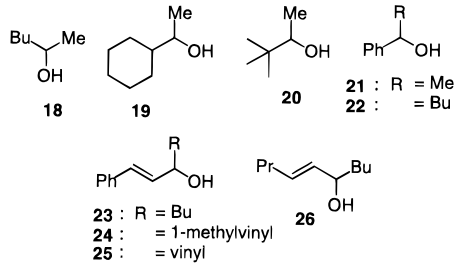


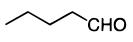
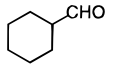
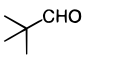
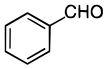
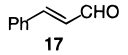
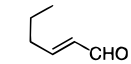
ylphenyl)phenoxide) [(*R*)-**15**], which was rigorously confirmed by ^{1}H NMR measurement.[10] A similar trend was also observed with sterically more-hindered (*R*,*R*)-**2** upon reaction with Me_3Al to produce methylaluminum bis((*R*,*R*)-2,6-bis(2-isopropylphenyl)-3,5-dimethylphenoxide) [(*R*)-**16**] as a sole product (Scheme 3).[10] To determine the potential of chiral phenols **1** and **2**, asymmetric alkylation of aldehydes[11] was demonstrated by the combined use of Grignard reagents and the optically active aluminum reagents **15** and **16** (eq 1), and the results are summarized in Table 1. This reaction had several characteristic features: (1) Asymmetric induction of aliphatic aldehydes was most highly promoted by using 3 equiv of **15**, i.e., the % ee decreased with less **15** (<3 equiv) or with 3 equiv of **16**. In contrast, reagent **16** was more efficient for conjugated aldehydes such as benzaldehyde or cinnamaldehyde (**17**). Vinylation of **17** gave allylic alcohols **24** and **25** with low to moderate selectivities. (2) The choice of the solvent for Grignard reagents is crucial for obtaining higher % ee. For instance,

(10) The ^{1}H NMR (300 MHz, toluene-d_8) data of (*R*)-**15**: δ 7.20−5.60 (m, 16H), 6.66 (s, 2H), 1.92 (s, 12H), 1.89 (s, 12H), −2.13 (s, 3H, $AlCH_3$). (*R*)-**16**: δ 7.60−6.70 (m, 16H), 6.57 (s, 2H), 2.95−2.41 (b, 4H), 2.05−1.62 (b, 12H), 1.14 (bd, 12H, J = 6.1 Hz), 0.90−0.445 (b, 12H), −2.54 (s, 3H, $AlCH_3$).

(11) (a) Weber, B.; Seebach, D. *Tetrahedron*, **1994**, *50*, 7473. (b) Weber, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 84. (c) Greeves, N.; Pease, J. E. *Tetrahedron Lett.* **1996**, *37*, 5821. (d) Chibale, K.; Greeves, N.; Lyford, L.; Pease, J. E. *Tetrahedron: Asymmetry* **1993**, *4*, 2407. (e) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49. Dialkylzincs as alkylating agents: (f) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1321. (g) Nowotny, S.; Vettel, S.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 4539. (h) Rozema, M. J.; Sidduri, A.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956. (i) Chaloner, P. A.; Langadianou, E. *Tetrahedron Lett.* **1990**, *31*, 5185. (j) Soai, K.; Niwa, S.; Hatanaka, T. *J. Chem. Soc., Chem. Commun.* **1990**, 709. (k) Zhang, H.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Org. Chem.* **1996**, *61*, 8002.

Table 1. Asymmetric Alkylation of Aldehydes with Grignard Reagents in the Presence of Optically Active 15 or 16[a]



entry	aldehyde	aluminum reagent (equiv)	Grignard reagent (equiv, solvent)	alcohol	yield[b] %	ee[c] %	absolute config[d] (rotation)
1		(*S*)-**15** (3.0)	MeMgI (3.0, ether)	**18**	99	52[f]	*S* (+)
2		(*S*)-**15** (3.0)	MeMgI (3.0, ether)	**19**	99	84[f]	*S* (+)
3		(*S*)-**15** (3.0)	MeMgI (3.0, ether)	**20**	90[e]	86[f]	*S* (+)
4		(*S*)-**15** (1.2)	MeMgBr (2.0, ether)	**21**	83	42	*R* (+)
5		(*R*)-**16** (1.2)	MeMgBr (2.0, ether)	**21**	61	65	*S* (-)
6		(*R*)-**16** (1.2)	BuMgCl (2.0, ether)	**22**	99	73	*S* (-)
7		(*R*)-**16** (1.2)	BuMgCl (2.0,THF)	**22**	90	75	*S* (-)
8	 **17**	(*R*)-**16** (2.0)	BuMgCl (2.0, ether)	**23**	86	83	*S*(+)
9		(*R*)-**16** (1.2)	 (2.0, THF)	**24**	95	80[g]	(-)[h]
10		(*R*)-**16** (1.2)	 (2.0, THF)	**25**	82	42[g]	*S* (+)
11		(*S*)-**16** (1.2)	BuMgBr (2.0, ether)	**26**	99	82[f]	*S* (+)

[a] Unless otherwise specified, the reactions were carried out using **15** or **16**, an aldehyde, and a Grignard reagent in CH_2Cl_2 at −78 °C for 30 min-2 h under the conditions as indicated in Table 1. [b] Isolated yields. [c] Determined by chiral HPLC (column, OB-H) analysis. [d] Determined by comparison of reported optical rotation. [e] GC yield. [f] Determined by HPLC using OD-H after converting the products into phenyl carbamate (pyridine, phenyl isocyanate, room temperature). [g] Determined by chiral HPLC (column, OD-H). [h] Absolute configuration was not determined.

alkylation of **17** complexed with (*R*)-**16** with a THF solution of vinylmagnesium bromide gave alcohol **25** with 42% ee, whereas replacing THF with diglyme gave **25** with 6% ee. (3) The alkylation of aliphatic aldehydes and (*E*)-2-hexenal with (*S*)-**15** or (*S*)-**16** proceeded favorably from the *si* face of the carbonyl plane, while the *re* face was preferred with benzaldehyde and **17**. The origin of this face reversibility is now under investigation in our laboratory.[12]

The present result is one of the successful applications of a Lewis acid−base complexation system to Grignard reagents that is generally useful for asymmetric alkylation of aldehydes.

Experimental Section

General Methods. All experiments were carried out under an atmosphere of dry argon. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (E. Merck no. 9385). Optical rotations were measured using a 3.5 mm × 0.5 dm Pyrex cell. Microanalyses were performed at the Faculty of Agriculture, Nagoya University. Phenol **3**, aniline **10**, and cinnamaldehyde (**17**) were obtained commercially. Aniline derivative **11**[14] and chiral secondary alcohols **18**,[15] **19**,[16] **20**,[15] **21**,[15] **22**,[17] **23**,[18] **25**,[19] and **26**[17] are all known compounds, and the spectral data, optical data, and analytical data of these compounds which we obtained agreed with those in the literature.

2,6-Dibromo-3,5-dimethylphenol (4). To a solution of *t*-$BuNH_2$ (84.0 mL, 800 mmol) in dry toluene (800 mL) was added Br_2 (20.6 mL, 400 mmol) at −20 °C from a dripping funnel over a period of 10 min. After the reaction mixture was cooled to −78 °C, 3,5-dimethylphenol (24.4 g, 200 mmol) in CH_2Cl_2 (80 mL) was added over 5 min. The mixture was allowed to warm to rt and then stirred for 20 h. The reaction was quenched with 1 M HCl, and the resulting mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated. The residue was recrystallized from Et_2O−hexane at rt to yield the product (33.9 g, yield 61%). **4**: IR (KBr) 3457, 1294, 1239, 1194, 1058 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.75 (s, 1H), 5.96 (s, 1H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.0, 137.4, 123.9, 109.3, 22.8. Anal. Calcd for $C_8H_8OBr_2$: C, 34.32; H, 2.88. Found: C, 34.21; H, 2.88.

2,6-Dibromo-3,5-dimethylanisole (5). A 200-mL, round-bottomed flask was charged with **4** (3.23 g, 11.5 mmol), MeOH (50 mL), and K_2CO_3 (4.77 g, 34.5 mmol). To this suspension was added MeI (2.15 mL, 34.5 mmol), and the reaction mixture was heated at reflux for 2 h, followed by the addition of MeI (2.15 mL, 34.5 mmol). After stirring during reflux for 10 h, the reaction mixture was cooled to rt, poured into aqueous NH_4Cl, and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated at reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel (Et_2O/hexane = 1/50 as the eluent) to give a colorless solid (3.28 g, yield 97%). **5**: IR (KBr) 1456, 1437, 1312, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.93 (s, 1H), 3.86 (s, 3H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.9, 138.0, 127.8, 117.5, 60.1, 22.9. Anal. Calcd for $C_9H_{10}OBr_2$: C, 36.77; H, 3.43. Found: C, 36.77; H, 3.43.

***meso*- and *dl*-3,5-Dimethyl-2,6-bis(2-methylphenyl)anisole (*meso*- and *dl*-6).** A 300-mL, three-necked flask, equipped with a magnetic stirring bar, reflux condenser, and a rubber septum, was charged with tri-*o*-tolylphosphine (1.83 g, 6.0 mmol), $Pd(OAc)_2$ (673 mg, 3.0 mmol), *o*-tolylboronic acid (12.2 g, 90.0 mmol), $Ba(OH)_2 \cdot 8H_2O$ (28.4 g, 90.0 mmol), methyl ether **5** (8.70 g, 29.6 mmol), DME (120 mL), and H_2O (24.0 mL). The mixture was degassed at reduced pressure *in vacuo* at −20 °C for ca. 20 min and then heated at reflux for 3 h. After being cooled to rt, the mixture was poured into aqueous NH_4Cl and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (Et_2O/hexane = 1/200 to 1/10 as the eluent) to give a mixture of the diastereomers (8.80 g, yield 94%) as colorless solids. Recrystallization of the isomeric phenols from MeOH gave *meso*-**6** (4.2 g, yield 45%) as a colorless crystal after filtration and rinsing the cake with MeOH. The filtrate which included a 1:10 (*meso*/*dl*) mixture of **6** was concentrated, and the residue was purified by column chromatography on silica gel (benzene/hexane = 1/25 as the eluent) to give *dl*-**6** (3.60 g,

(12) Optically active **15** and **16** were demonstrated to be more effective than methylaluminum (*R*)-3,3′-bis(tris(4-methylphenyl)silyl)-1,1′-bi-2-naphthoxide [(*R*)-**27**]:[13] treatment of **17** with (*R*)-**27** (1.2 equiv) at −78 °C in toluene followed by the addition of an ether solution of BuMgCl (2.0 equiv) gave, after 30 min, **23** in a yield of 89% with 5% ee.

(13) (a) Maruoka, K.; Itoh, T.; Araki, Y.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975. (b) Maruoka, K.; Concepcion, A. B.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3501.

(14) (a) Kajigaeshi, S.; Kakinami, T.; Inoue, K.; Kondo, M.; Nakamura, H.; Fujikawa, M.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 597. (b) Jaeger, F.; Blanksma, J. *Recl. Trav. Chim. Pays-Bas* **1906**, *25*, 253.

(15) Sada, K.; Kondo, T.; Miyata, M. *Tetrahedron: Asymmetry* **1995**, *6*, 2655.

(16) Terashima, S.; Tanno, N.; Koga, K. *Chem Lett.* **1980**, 981.

(17) Weber, B.; Seebach, D. *Tetrahedron* **1994**, *50*, 7473.

(18) Rozema, M. J.; Rajagopal, D.; Tucker, C. E.; Knochel, P. *J. Organomet. Chem.* **1992**, *438*, 11.

(19) Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 6129.

yield 38%) as a colorless solid. ***meso*-6**: IR (KBr) 1454, 1393, 1308, 1287, 1271, 1073 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.29−7.18 (m, 8H), 7.01 (s, 1H), 3.01 (s, 3H), 2.08 (s, 6H), 2.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.0, 137.6, 136.8, 136.4, 132.6, 129.8, 129.7, 127.0 (two overlapped signals), 125.3, 60.4, 20.0, 19.8. Anal. Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.64. Found: C, 87.29; H, 7.75. ***dl*-6**: IR (KBr) 1453, 1393, 1285, 1269, 1111, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.28−7.13 (m, 8H), 6.98 (s, 1H), 2.96 (s, 3H), 2.14 (s, 6H), 2.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.8, 137.6, 136.4, 136.3, 132.5, 130.0, 129.7, 127.0, 126.7, 125.4, 59.7, 19.9, 19.7. Anal. Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.64. Found: C, 87.32; H, 7.71.

***dl*-3,5-Dimethyl-2,6-bis(2-methylphenyl)phenol (*dl*-1).** To a solution of *dl*-**6** (1.00 g, 3.16 mmol) in CH_2Cl_2 (13.0 mL) was added an excess of BBr_3 dropwise at 0 °C under argon, and the reaction mixture was stirred at 0 °C for 30 min. H_2O was added slowly and cautiously at the same temperature, followed by dropwise addition of aqueous $NaHCO_3$ over a few minutes, during which time gas evolved vigorously. After the evolution of gas was complete, the mixture was extracted with CH_2Cl_2. The organic layer was dried and concentrated. The residue was purified by column chromatography on silica gel (Et_2O/hexane = 1/9 as the eluent) to give a colorless solid (944 mg, yield 99%). ^1H NMR, ^{13}C NMR, and elemental analysis data of *dl*-**1** were consistent with those of (+)-(*S,S*)-**1**. Chiral HPLC analytical data (column, OD-H) of *dl*-**1**: retention times t_R = 10.8 min for (*S,S*)-**1** and t_R = 13.8 min for (*R,R*)-**1** using *i*-PrOH/hexane (1/100) as the eluent at a flow rate of 0.5 mL/min.

(*S,S*)-3,5-Dimethyl-2,6-bis(2-methylphenyl)phenyl (+)-(*S*)-Camphor-10-sulfonate [(*S,S,S*)-7]. To a suspension of NaH (60% in oil; 322 mg, 13.4 mmol) in THF (100 mL) was added *dl*-**1** (4.06 g, 13.4 mmol) portionwise at 0 °C, and the reaction mixture was stirred at rt under argon for 30 min. To the resulting solution was added (+)-camphor-10-sulfonyl chloride (3.36 g, 13.4 mmol) in one portion, and the mixture was stirred for 2 h at rt. After the mixture was cooled to 0 °C, H_2O was added, and the resulting mixture was poured into aqueous NH_4Cl, extracted with Et_2O, dried, and concentrated. The residue was purified by column chromatography on silica gel (Et_2O/hexane = 1/4) to give (*S,S,S*)-**7** and (*R,R,S*)-**7** as colorless solids (5.17 g, yield 75%). Recrystallization of the diastereomixture **7** from Et_2O at rt with slow evaporation of the solvent gave one diastereomer, (*S,S,S*)-**7** (1.17 g, yield 17%, based on *dl*-**1**). HPLC analytical data (column, Finepak SIL) of (*R,R,S*)-**7** and (*S,S,S*)-**7**: t_R = 19.8 min for (*R,R,S*)-**7** and t_R = 20.7 min for (*S,S,S*)-**7** using EtOAc/hexane (1/10) as the eluent at a flow rate of 1.0 mL/min. **(*S,S,S*)-7**: IR (KBr) 1750, 1456, 1395, 1368, 1250, 1173, 1024 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.27−7.19 (m, 8H), 7.16 (s, 1H), 2.60 (d, 1H, J = 14.9 Hz), 2.27−1.71 (m, 5H), 2.16 (s, 6H), 2.05 (s, 6H), 1.67 (d, 1H, J = 14.9 Hz), 1.42−1.19 (m, 2H), 0.86 (s, 3H), 0.58 (s. 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 213.3, 145.8, 137.0, 136.9, 136.2, 133.2, 130.8, 130.0 (two overlapped signals), 127.9, 125.7, 57.6, 48.4, 47.6, 42.8, 42.3, 26.6, 25.0, 19.9, 19.7, 19.5 (two overlapped signals). Anal. Calcd for $C_{32}H_{36}O_4S$: C, 74.39; H, 7.02. Found: C, 74.40; H,7.20; $[\alpha]^{25}_D$ = +19.6° (*c* 1.00, $CHCl_3$).

(+)-(*S,S*)-3,5-Dimethyl-2,6-bis(2-methylphenyl)phenol [(+)-(*S,S*)-1]. An oven-dried, 25-mL, Schlenk tube was charged with naphthalene (497 mg, 3.88 mmol) and THF (5 mL). To this mixture was added small pieces of sodium (89 mg, 3.88 mmol) portionwise at rt under a gentle stream of argon, and the resulting dark purple suspension was stirred at rt for 2 h. After the mixture was cooled to −78 °C, optically active (*S,S,S*)-**7** (100 mg, 0.19 mmol) in THF (1 mL) was added, and the mixture was maintained at −78 °C with stirring for an additional 20 min. The reaction was quenched by dropwise addition of MeOH at −78 °C until the dark color disappeared. The mixture was poured into 1 M HCl, extracted with Et_2O, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 1/2 as the eluent) to give colorless solids (40 mg, yield 68%). **(+)-(*S,S*)-1**: IR (KBr) 3497, 1449, 1402, 1291, 1233, 1152, 1049 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30−7.16 (m, 8H), 6.82 (s, 1H), 4.42 (s, 1H), 2.12 (s, 6H), 2.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.4, 137.4, 135.8, 130.4, 130.3, 127.9, 126.2, 125.0, 123.1, 19.8, 19.6. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.39; H, 7.61; $[\alpha]^{25}_D$ = +15.0° (*c* 1.00, $CHCl_3$).

2-Isopropyliodobenzene. The reaction was carried out as described in the literature.[20] A 2-L, round-bottomed flask, equipped with a magnetic stirring bar, was charged with 2-isopropylaniline (84.9 mL, 600 mmol), H_2O (250 mL), and 12 M HCl (250 mL, 3.0 mol). To the vigorously stirred mixture were added ice (500 g) and $NaNO_2$ (43.5 g, 630 mmol) in one portion. After 10 min, to the resulting brown mixture was added a H_2O (250 mL) solution of KI (100.3 g, 604 mmol), and the mixture was stirred at rt for 5 h, poured into H_2O (250 mL), and extracted with CH_2Cl_2. The organic layer was dried and concentrated, and the residue was filtered through a short-path column of silica gel (EtOAc/hexane = 1/100 as the eluent). Fractions were collected and concentrated, and the residual crude mixture was distilled through a 40-cm Vigreux column to give 1-iodocumene (70.9 g, yield 47%) as a wine-red liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, 1H, J = 7.9 Hz), 7.38−7.18 (m, 2H), 6.87 (t, 1H, J = 7.6 Hz), 3.19 (heptet, 1H, J = 6.8 Hz), 1.23 (d, 6H, J = 6.8 Hz).

(2-Isopropylphenyl)boronic Acid. A 50-mL three-necked flask, equipped with a magnetic stirring bar, a reflux condenser, and a rubber septum, was charged with magnesium (729 mg, 30.0 mmol), which was activated as usual with heat under reduced pressure, and furnished with an atmosphere of dry argon. THF (25 mL) and 1,2-dibromoethane (100 μL) were added to the flask, and to the resulting suspension was added 1-iodocumene (6.15 g, 25.0 mmol) dropwise with gentle heating. When the reaction started, heating was discontinued, and the reaction mixture was stirred as the remainder of the iodide was added dropwise at a rate such that gentle reflux was maintained. After the addition was complete, the mixture was stirred for an additional 30−60 min and transferred *via* a steel cannula to a THF (25 mL) solution of trimethylborate (5.88 mL, 50.0 mmol) which was precooled to −78 °C under an argon atmosphere. The entire mixture was then allowed to warm to rt and, after being stirred for 1 h, was poured into 1 M HCl, extracted with Et_2O, dried, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1/3 as the eluent) to give (2-isopropylphenyl)boronic acid (2.68 g, yield 65%) as a colorless solid.

***dl*-2,6-Bis(2-isopropylphenyl)-3,5-dimethylanisole (*dl*-8).** A 100-mL sealed tube equipped with a magnetic stirring bar was charged with tri-*o*-tolylphosphine (365 mg, 1.20 mmol), $Pd(OAc)_2$ (135 mg, 0.60 mmol), (2-isopropylphenyl)boronic acid (5.90 g, 36.0 mmol), K_3PO_4 (9.55 g, 45.0 mmol), **5** (4.4 g, 15.0 mmol), DME (60.0 mL), and H_2O (12.0 mL). The mixture was degassed at reduced pressure *in vacuo* at −20 °C for ca. 20 min and heated at reflux for 5 h. After being cooled to rt, the mixture was poured into aqueous NH_4Cl and was extracted with Et_2O. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1/300 to 1/50 as the eluent) to give a colorless solid (yield 46%). ***dl*-8**: IR (KBr) 1605, 1306, 1283, 1084, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.39−7.10 (m, 8H), 6.96 (s, 1H), 3.00 (s, 3H), 2.79 (m, 2H), 2.02 (s, 6H), 1.17 (d, 6H, J = 6.8 Hz), 1.15 (d, 6H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.6, 147.1, 136.6, 136.4, 131.9, 130.5, 127.5, 126.3, 125.3, 125.2, 60.3, 30.0, 24.3, 23.9, 20.3. Anal. Calcd for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 87.04; H, 8.91. The procedure for demethylation of *dl*-**6** was followed except that *dl*-**8** (4.30 g, 11.6 mmol) was used to give *dl*-2,6-bis(2-isopropylphenyl)-3,5-dimethylphenol (*dl*-**2**) (3.80 g, yield 91%) as a colorless solid. IR, ^1H NMR, ^{13}C NMR, and elemental analysis data of *dl*-**2** were consistent with those of (−)-(*R,R*)-**2**.

(*R,R*)- and (*S,S*)-2,6-Bis(2-isopropylphenyl)-3,5-dimethylphenyl (+)-(*S*)-Camphor-10-sulfonate [(*R,R,S*)- and (*S,S,S*)-9]. To a solution of *dl*-phenol **2** (2.76 g, 7.70 mmol) in THF (50 mL) was added a 1.58 M hexane solution of *n*-BuLi (6.30 mL, 10.0 mmol) dropwise at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 30 min, followed by the addition of (+)-(*S*)-camphor-10-sulfonyl chloride (3.86 g, 15.0 mmol) in

(20) Bolton, R.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1977**, 278.

one portion, and the resulting mixture was stirred at rt for 3 h. The reaction mixture was poured into aqueous NH_4Cl and extracted with Et_2O. The organic layer was dried and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1/50 as the eluent) to give pure (*R,R,S*)-**9** (1.85 g, yield 42%) and a ca. 1:20 diastereomixture of (*R,R,S*)-**9** and (*S,S,S*)-**9** (yield 46%), which was recrystallized from EtOAc at rt to give pure (*S,S,S*)-**9** (1.68 g, yield 38%). **(*R,R,S*)-9**: IR (KBr) 1748, 1474, 1397, 1368, 1250, 1177, 1026 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44−7.15 (m, 9H), 2.80−2.70 (m, 3H), 2.26−1.69 (m, 5H), 2.07 (s, 6H), 1.43 (d, 1H, J = 14.9 Hz), 1.37−1.12 (m, 2H), 1.26 (d, 6H, J = 6.8 Hz), 1.16 (d, 6H, J = 6.8 Hz), 0.88 (s, 3H), 0.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 213.4, 147.7, 146.1, 137.3, 134.7, 133.2, 130.8, 129.8, 128.3, 125.8, 125.4, 57.8, 48.6, 47.4, 42.9, 42.2, 30.2, 26.6, 25.0, 24.5, 23.8, 20.4, 19.6, 19.5. Anal. Calcd for $C_{36}H_{44}O_4S$: C, 75.49; H, 7.74. Found: C, 75.50; H, 8.07. $[\alpha]^{25}_D$ = −13.0° (*c* 1.00, $CHCl_3$). **(*S,S,S*)-9**: IR (KBr) 1748, 1474, 1395, 1372, 1250, 1173, 1026 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42−7.15 (m, 9H), 2.74 (m, 2H), 2.24 (d, 1H, J = 14.8 Hz), 2.16−1.13 (m, 7H), 2.08 (s, 6H), 1.88 (d, 1H, J = 14.8 Hz), 1.25 (d, 6H, J = 6.8 Hz), 1.18 (d, 6H, J = 6.8 Hz), 0.80 (s, 3H), 0.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 213.0, 147.6, 146.5, 137.3, 134.7, 133.1, 131.1, 130.0, 128.3, 125.8, 125.5, 57.6, 48.9, 47.7, 42.9, 42.3, 30.1, 26.7, 25.2, 24.4, 24.1, 20.4, 19.6, 19.5. Anal. Calcd for $C_{36}H_{44}O_4S$: C, 75.49; H, 7.74. Found: C, 75.48; H, 8.01. $[\alpha]^{25}_D$ = +51.2° (*c* 1.00, $CHCl_3$).

(−)-(*R,R*)-2,6-Bis(2-isopropylphenyl)-3,5-dimethylphenol [(−)-(*R,R*)-2]. To a suspension of $LiAlH_4$ (53 mg, 1.40 mmol) in THF (17.5 mL) was added (*R,R,S*)-**9** (100 mg, 0.18 mmol) portionwise at rt. The mixture was immersed in an oil bath at 50 °C and maintained at this temperature for 9 h. After the reaction mixture was cooled to 0 °C, H_2O was added dropwise until no gas evolution was observed. The mixture was poured into 1 M HCl, extracted with Et_2O, dried over Na_2SO_4, and concentrated. The residual crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1/60 as the eluent) to give a colorless solid (52 mg, yield 82%). **(−)-(*R,R*)-2**: IR (KBr) 3530, 1445, 1306, 1242, 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.10 (m, 8H), 6.81 (s, 1H), 4.38 (s, 1H), 2.76 (m, 2H, J = 6.9 Hz), 2.01 (s, 6H), 1.16 (d, 6H, J = 6.9 Hz), 1.11 (d, 6H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.2, 148.2, 136.1, 134.5, 130.4, 128.4, 126.2, 125.8, 124.9, 122.9, 30.2, 24.2, 23.7, 20.1. Anal. Calcd for $C_{26}H_{30}O$: C, 87.10; H, 8.43. Found: C, 87.10; H, 8.78. $[\alpha]^{25}_D$ = −58.1° (*c* 1.00, $CHCl_3$).

2,4,6-Tribromoiodobenzene (12). **12** was prepared as described in the literature.[7] **12**: IR (KBr) 1375, 1337, 963 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.79 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.5, 130.4, 127.9, 110.8, 29.1. Anal. Calcd for $C_8H_6Br_3I$: C, 20.50; H, 1.29. Found: C, 20.60; H, 1.28.

***dl*- and *meso*-4-Bromo-2,6-bis(2-isopropylphenyl)-3,5-dimethylphenol (*dl*- and *meso*-13).**[8,9] To a THF solution of (2-isopropylphenyl)magnesium iodide (3.5 mL, 1.5 mmol) was added **12** (236 mg, 0.5 mmol) in THF (7.0 mL) dropwise over 1h at rt under argon, and the mixture was stirred at rt for 3.5 h. The mixture was cooled to −78 °C, a 1.0 M THF solution of BH_3 (2.5 mL, 2.5 mmol) was added, and the resulting mixture was stirred at rt for 3 h. To this mixture were added sequentially a 3.0 M aqueous solution of NaOH (2.2 mL, 6.6 mmol) and 30 wt % aqueous H_2O_2 (2.2 mL, 20 mmol) at the same temperature. After 4 days of stirring, 4 g of K_2CO_3 was added. The entire mixture was then extracted twice with THF. The organic layer was dried, concentrated, and purified by column chromatography on silica gel (hexane only to EtOAc/hexane = 1/20 as the eluent) to give a mixture of *dl*- and *meso*-**13** (yield 28% and 14%, respectively). ***dl*-13:** IR (KBr) 3530, 1441, 1235, 1084 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.07 (m, 8H), 4.38 (s, 1H), 2.73 (m, 2H), 2.15 (s, 6H), 1.15 (d, 6H, J = 6.9 Hz), 1.10 (d, 6H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.3, 148.0, 136.2, 134.5, 130.2, 128.7, 126.3, 126.0 (two overlapped signals), 119.4, 30.3, 24.1, 23.6, 21.9. Anal. Calcd for $C_{26}H_{29}OBr$: C, 71.39; H, 6.68. Found: C, 71.34; H, 6.59. ***meso*-13:** IR (KBr) 3528, 1445, 1283, 1232, 1157, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.10 (m, 8H), 4.40 (s, 1H), 2.70 (m, 2H), 2.16 (s, 6H), 1.15 (d, 6H, J = 6.9 Hz), 1.08 (d, 6H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.3, 148.0, 136.2, 134.3, 130.2, 128.7, 126.3, 126.0, 125.5, 119.5, 30.2, 24.1, 23.7, 21.9. Anal. Calcd for $C_{26}H_{29}OBr$: C, 71.39; H, 6.68. Found: C, 71.33; H, 6.64.

Reduction of *dl*-13 and *meso*-13 with Bu_3SnH. A 2:1 mixture of *dl*-**13** and *meso*-**13** (39.5 mg, 0.09 mmol) in Bu_3SnH (500 μL) was heated at 140 °C for 3 h and purified by column chromatography on silica gel (hexane only to EtOAc/hexane = 1/30 as the eluent) to give *dl*-**2** and *meso*-**2** (22.6 mg, 0.063 mmol) in 70% yield in a ratio of 2:1. ***meso*-2:** IR (KBr) 3584, 1443, 1291, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.15 (m, 8H), 6.83 (s, 1H), 4.41 (s, 1H), 2.75 (m, 2H), 2.02 (s, 6H), 1.16 (d, 6H, J = 6.9 Hz), 1.10 (d, 6H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.1, 148.1, 136.1, 134.2, 130.3, 128.4, 126.2, 125.8, 124.8, 123.0, 30.1, 24.2, 23.8, 20.1. Anal. Calcd for $C_{26}H_{30}O$: C, 87.10; H, 8.43. Found: C, 87.02; H, 8.59.

Preparation of (*R*)-15. To a toluene (4.0 mL) solution of phenol (*R,R*)-**1** (258 mg, 0.72 mmol; 2 equiv) was added a 1.0 M hexane solution of Me_3Al (0.36 mL, 0.36 mmol; 1 equiv) dropwise at 50 °C under argon with rigorous exclusion of air and moisture, and the mixture was stirred for 1 h. When CH_2Cl_2 was used as a solvent, the preparation was conducted at reflux for 1 h. (*R*)-**16** could be prepared similarly. Both the solutions of the reagents were used for the following alkylation experiments without further purification.

General Procedure for Enantioselective Alkylation of Aldehydes. To a CH_2Cl_2 (4.0 mL) solution of (*R*)-**16** (1.2 equiv) was added cinnamaldehyde (**17**) (38 μL, 0.3 mmol) at −78 °C under argon, and the mixture was stirred for ca. 10 min. To this solution was added a 1.86 M Et_2O solution of BuMgCl (0.32 mL, 0.6 mmol) dropwise at −78 °C, and the mixture was stirred for 0.5−1 h, quenched with 1 M HCl, and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1/20 to Et_2O/hexane = 1/3 as the eluent) to give 1-phenyl-1-hepten-3-ol (**23**) (49 mg, yield 86%) as a colorless liquid.

Chiral HPLC analysis of 21−25. **21** (column, OB-H): retention times t_R = 13.0 min for (*R*)-**21** and t_R = 17.4 min for (*S*)-**21** using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 0.5 mL/min. **22** (column: OB-H): retention times t_R = 14.9 min for (*S*)-**22** and t_R = 18.0 min for (*R*)-**22** using *i*-PrOH/hexane (1/20) as the eluent at a flow rate of 0.5 mL/min. **23** (column, OB-H): retention times t_R = 15.1 min for (*R*)-**23** and t_R = 18.2 min for (*S*)-**23** using *i*-PrOH/hexane (1/9) as eluent at a flow rate of 0.5 mL/min. **24** (column, OD-H); retention times t_R = 8.95 min and t_R = 12.61 min (the later peak for the major enantiomer when (*R*)-**16** was used) using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 1.0 mL/min. **25** (column, OD-H); retention times t_R = 10.6 min for (*R*)-**25** and t_R = 15.4 min for (*S*)-**25** using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 1.0 mL/min.

4-Methyl-1-phenyl-1,4-penten-3-ol (24): IR (neat) 3083, 3029, 1449, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.21 (m, 5H), 6.63 (d, 1H, J = 15.9 Hz), 6.20 (dd, 1H, J = 15.9, 6.6 Hz), 5.10 (s, 1H), 4.91 (s, 1H), 4.71 (d, 1H, J = 6.6 Hz), 1.90 (bs, 1H), 1.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.2, 136.5, 131.1, 130.2, 128.5, 127.8, 126.4, 111.2, 76.3, 18.3. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.40; H, 8.49. $[\alpha]^{25}_D$ = −11.0° (*c* 0.94, $CHCl_3$) for an 80% ee of **24**.

Preparation of Phenyl Carbamates from Alcohols for HPLC Analysis. To a pyridine solution of an alcohol was added phenyl isocyanate at rt, and the mixture was stirred for 0.5 h. Pyridine was removed under reduced pressure (1−3 mmHg). The residue was purified by column chromatography on silica gel.

HPLC Analytical Data of Some Carbamates Using the Column OD-H. Phenyl carbamate from 18: retention times t_R = 16.5 min for (*S*)-**18** and t_R = 39.8 min for (*R*)-**18** using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 0.5 mL/min. **Phenyl carbamate from 19:** retention times t_R = 6.87 min for (*S*)-**19** and t_R = 14.3 min for (*E*)-**19** using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 1.0 mL/min. **Phenyl carbamate from 20:** retention times t_R = 13.7 min for (*S*)-**20** and t_R = 21.7 min for (*R*)-**20** using *i*-PrOH/hexane (1/20) as the eluent at a flow rate of 1.0 mL/min. **Phenyl carbamate from 26:** retention times t_R = 5.97 min for (*R*)-**26** and t_R = 7.65 min for (*S*)-**26** using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 0.5 mL/min.

Acknowledgment. We gratefully acknowledge financial support from the Ministry of Education, Science, and Culture of Japan. We also appreciate the assistance

of A. Nakao (MAC Science Co., Ltd.) for the X-ray crystal analysis of sulfonate (*S*,*S*,*S*)-**9** and A. Takakuwa (JASCO., Ltd.) for the CD spectral analysis of (*R*,*R*)- and (*S*,*S*)-**1** and **2**.

Supporting Information Available: CD spectra of (*S*,*S*)- and (*R*,*R*)-**1** and **2** (black and white version is available on microfiche and in microfilm version; color spectra are available electronically) and the X-ray crystal data of (*S*,*S*,*S*)-**9** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information and instructions on accessing the color image.

JO970747G

Additions and Corrections

Vol. 61, 1996

Naoki Asao, Tomoko Sudo, and Yoshinori Yamamoto*. Lewis Acid-Catalyzed *trans*-Hydrosilylation of Alkynes.

Page 7654, Table 1. The structures of **1d** and **2d** should read as follows: $R^1 = H$, $R^2 = Me_3Si$.

JO974013F

S0022-3263(97)04013-9

Vol. 62, 1997

Paul S. Engel,* Shu-Lin He, J. T. Banks, K. U. Ingold, and J. Lusztyk. Clocking Tertiary Cyclopropylcarbinyl Radical Rearrangements.

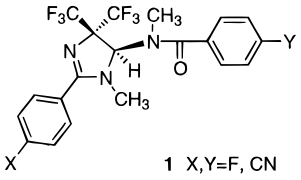
Page 1210. The units given for k_1 in the abstract should be s^{-1}, not $M^{-1}\ s^{-1}$. The authors at Rice University gratefully acknowledge the National Science Foundation and the Robert A. Welch Foundation for support of this research.

JO974012N

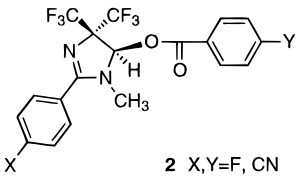
S0022-3263(97)04012-7

Hui-Yin Li,* Indawati DeLucca, Spencer Drummond, and George A. Broswell. An Unusual Trifluoromethyl Elimination Reaction From the 4,4-Bis(trifluoromethyl)-5-hydroxyimidazoline Ring System.

Page 2250, column 2. The following structures should be inserted before the Results and Discussions section.



1 X,Y=F, CN



2 X,Y=F, CN

Page 2554. The preparation of **22** and **23** should read as follows: The residue was purified by flash column chromatography to give compound **22** (96 mg, 12% from **9**) and **23** (248 mg, 30% from **9**).

JO974011V

S0022-3263(97)04011-5

John D. Tovar, Norbert Jux, Thibaut Jarrosson, Saeed I. Khan, and Yves Rubin*. Synthesis and X-ray Characterization of an Octaalkynyldibenzooctadehydro[12]-annulene.

Page 3432, column 2. During the production of the journal, text was deleted from the paragraph beginning at the bottom of the page (the electronic file is correct). The entire paragraph is given below:

Interestingly, bis(trimethyl)silyl)hexatriyne (**5f**)[10] did not add to dienones **1a,b** across its central, least sterically hindered C≡C bond[11] to give the desired C_{2v}-symmetric HEBs, but rather at one of the two peripheral triple bonds to give **6f** and **6j**. This can be understood as a result of the large steric repulsion created between the TMS and *t*-Bu/TIPS groups at the transition state (T.S., Figure 2);[12] an unsymmetrical approach is more favorable. Since the more extended diynyl system of the green cyclopentadienone **1c** should not display this steric bias, its reaction with hexatriyne **5f** was attempted. Unfortunately, the expected symmetrical adduct **6k** was not observed among a complex mixture of highly colored compounds.

JO9740148

S0022-3263(97)04014-0