Asymmetric Allylboration of Aldehydes and Ketones using 3,3'-Disubstitutedbinaphthol-modified Boronates

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Supporting Information

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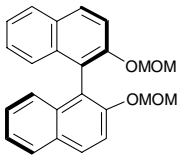
General Experimental

IR spectra were recorded on a Bomem MB-100 infrared spectrophotometer. ^{1}H (250 and 300 MHz), ^{13}C (63 and 75 MHz), and ^{19}F (188 and 182 MHz) NMR spectra were recorded in $CDCl_3$ on Bruker AM250 or AVANCE 300 spectrometers unless otherwise noted. Chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane (TMS). The ^{1}H NMR samples were run in deuteriochloroform containing ca. 0.01% TMS as an internal standard ($\delta = 0.0$). Spectra are tabulated in the order: chemical shift, assignment, numbers of protons, multiplicity, coupling constant. The spectral reference for ^{13}C NMR spectra was $CDCl_3$ ($\delta = 77.0$). The spectral reference for ^{19}F NMR spectra was CF_3COOH ($\delta = 76.53$ upfield of $CFCl_3$). Elemental analyses were conducted by M-H-W Laboratories, Phoenix, Arizona. Mass spectra were recorded on a GC-MS (Hewlett Parkard G 1800A GCD System) or a Kratos MA890 mass spectrometer using electron impact (EI, 70 ev) ionization if the mass was over 430. Optical rotations were recorded in cells with 10 cm path length on a Perkin-Elmer 241 digital polarimeter.

All reactions involving air or moisture sensitive reagents were performed under an argon or nitrogen atmosphere on the bench using standard Schlenk techniques. Solvents were dried prior to use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried by distillation from sodium wire. Dichloromethane (CH_2Cl_2), DMF, HMPA and *n*-pentane were dried by distillation from calcium hydride. Chloromethyl methyl ether was prepared according to the literature.[1] $BrCl_2CCCl_2Br$ was prepared in 85% yield from the reaction of dichloroethene and bromine in dichloromethane under reflux condition for 3 days, followed by the removal of organic solvent. Triallylborane was prepared as reported by Brown.[2] The triallylborane thus prepared was distilled prior to use so was metal-free. BINOL (**1**) was prepared following a literature procedure[3] and was resolved using the Merck method.[4] Methyl fluorosulfonyldifluoroacetate was purchased from SynQuest Laboratories,

Alachua, FL and used without further purification. Unless otherwise noted, other chemicals were purchased from Aldrich Chemical Company.

(±)- and (*R*)-2,2'-Bis(methoxymethoxy)-1,1'-Binaphthyl (2).



The preparation followed literature procedures[5] with some modifications.

NaH (2.92 g, 60% in oil, 73.0 mmol) was mixed in dry THF (150 mL) in a 500 mL round bottom flask at 0 ^{o}C under an argon atmosphere. To the mixture with stirring, was added a solution of (±)-2,2'-dihydroxy- 1,1'-binaphthyl (**1**) (9.50 g, 33.2 mmol) in THF (50 mL) in a dropping funnel. After the addition, the mixture was stirred at 0 ^{o}C for 1 h, then allowed to warm up to room temperature for 15 min. After the mixture was re-cooled to 0 ^{o}C, chloromethyl methyl ether (5.54 mL, 73.0 mmol) was slowly added from the dropping funnel. After the addition, the reaction mixture was warmed to room temperature and stirred for 4.5 h. Saturated aqueous NH_4Cl (50 mL) was added to the flask, then the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (50 mL x 3). The organic layers were combined, washed with brine (50 mL), dried over Na_2SO_4, and concentrated. Crude product was purified by column chromatography (EtOAc/hexane: 1/10) and crystallized from CH_2Cl_2/hexane to give a white crystalline product (±)-**2** in quantitative yield. mp 89-92 ^{o}C (lit[5] mp 88-91 ^{o}C); IR (KBr): υ (max) 1236, 1144, 1028 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.88-8.14 (ArH, 2 H, m), 7.76-7.84 (ArH, 2 H, m), 7.10-7.62 (ArH, 8 H, m), 4.97, 5.08 (OCH_2O, 4 H, d, AB, J_{AB} = 8.5 Hz), 3.10 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 152.6, 130.0, 129.9, 129.3, 127.8, 126.3, 125.5, 124.0, 121.3, 117.3, 95.2, 55.7; MS *m/e* (relative intensity):

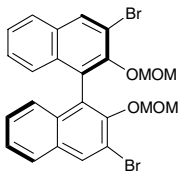
374 (M^+, 100), 298 (90), 270 (71), 239 (23); Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 77.02; H, 5.94. (*R*)-2,2'-Dihydroxy-1,1'-binaphthyl was used to afford (R)-**2** in quantitative yield. mp 98-100 ^oC. The sample showed $[\alpha]^{25}_{589}$ +95.0^o (c = 1.0, THF).

General Procedure A: Preparation of 3,3'-Disubsituted-2,2'-*Bis*(methoxymethoxy) -1,1'-Binaphthyls 3a-3c.

The preparation of 3,3'-disubstituted binaphthyl compounds followed literature procedures[5] with some modifications.

(±)- or (*R*)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (**2**) (1 equiv) was dissolved in dry Et_2O (17 mL/1 mmol of **2**) in a round bottom flask under an argon atmosphere. To the mixture with stirring, was added *n*BuLi (3 equiv) at room temperature by syringe injection. After the reaction mixture was stirred for 3 h, THF (11 mL/1 mmol of **2**) was injected to the flask and then the mixture was stirred for 1 h. After the flask was cooled in an ice water bath for 5 min, the appropriate electrophile (3 equiv) was quickly added in one portion. The reaction mixture was stirred for 15 min, quenched with saturated aqueous NH_4Cl and water. The two phases were separated. The aqueous layer was extracted with Et_2O twice. All organic solutions were combined, washed with brine, dried over Na_2SO_4 and concentrated. Subsequent work-up gave the product.

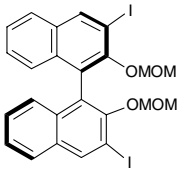
(±)- and (R)-3,3'-Dibromo-2,2'-Bis(methoxymethoxy-1,1'-binaphthyl (3a).



(±)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (**2**) (8.80 g, 23.5 mmol) was treated with

*n*BuLi (44.10 mL of a 1.6 M solution in hexane, 70.5 mmol) at room temperature and resulting mixture was quenched with dibromotetrachloroethane (23.0 g, 70.5 mmol). Crude product was purified by column chromatography (EtOAc/hexane: 1/10) and crystallized from Et_2O/hexane to give a white crystalline product (±)-**3a** (10.60 g) in 85% yield. mp 125-126 ^oC (lit[5] mp 124-126 ^oC); IR (KBr): υ (max) 1235, 1157, 1026 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.25-8.30 (ArH, 2 H, m), 7.78-7.82 (ArH, 2 H, m), 7.18-7.48 (ArH, 6 H, m), 4.81, 4.82 (OCH_2O, 4 H, d, AB, J_{AB} = 6.0 Hz), 2.56 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 153.2, 141.0, 133.6, 131.8, 131.6, 127.2, 126.7, 126.6, 126.2, 125.6, 99.8, 92.8, 56.6; MS *m/e* (relative intensity): 535 (M^++3, 20), 534 (M^++2, 18), 533 (M^++1, 4), 532 (M^+, 9), 457 (24), 455 (47), 453 (28), 376 (20), 268 (23), 45 (100); Anal. Calcd for $C_{24}H_{20}Br_2O_4$: C, 54.16; H, 3.79. Found: C, 54.10; H, 3.87. (R)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**3a** in 84% yield. mp 123-124 ^oC. The sample showed $[\alpha]^{25}_{589}$ +28.3 (c = 1.0, THF).

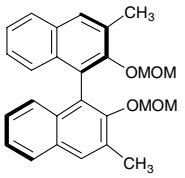
(±)- and (*R*)-3,3'-Diiodo-2,2'-Bis(methoxymethoxy-1,1'-binaphthyl (3b).



(±)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (**2**) (6.50 g, 17.36 mmol) was treated with *n*BuLi (33.0 mL of a 1.6 M solution in hexane, 52.80 mmol) at room temperature and resulting mixture was quenched with iodine (13.20 g, 52.0 mmol). Crude product was purified by column chromatography (EtOAc/hexane: 1/10) and crystallized from CH_2Cl_2/hexane to give a white crystalline product (**3b**) (9.60 g) in 88% yield. mp 129-131 ^oC (lit[5] mp 127-128 ^oC); IR (KBr): υ (max) 1232, 1156, 1026 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.50-8.62 (ArH, 2 H, m), 7.70-7.85 (ArH, 2 H, m), 7.10-7.54 (ArH, 6 H, m), 4.81, 4.69 (OCH_2O, 4 H, d, AB, J_{AB} = 5.7 Hz), 2.59 (OCH_3, 6 H, s);

^{13}C NMR ($CDCl_3$): δ 152.2, 140.0, 133.8, 132.8, 132.2, 127.1, 126.7, 126.5, 126.2, 125.8, 99.4, 92.5, 56.5; MS *m/e* (relative intensity): 626 (M^+, 35), 550 (20), 549 (100), 422 (60), 268 (45), 239 (46), 237 (28), 226 (37), 224 (45); Anal. Calcd for $C_{24}H_{20}I_2O_4$: C, 46.03; H, 3.22. Found: C, 46.05; H, 3.20. (*R*)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**3b**. mp 45-47 ^oC. The sample showed $[\alpha]^{25}_{589}$ -5.3 (c = 1.0, THF).

(*R*)-3,3'-Dimethyl-2,2'-*Bis*(methoxymethoxy)-1,1'-Binaphthyl (3c).



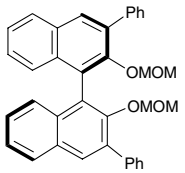
(*R*)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl [(*R*)-**2**] (2.0 g, 5.34 mmol) was treated with *n*-BuLi (10.0 mL of a 1.6 M solution in hexane, 16.0 mmol) at room temperature and resulting mixture was quenched with iodomethane (1.0 mL, 16.0 mmol). Crude product was purified by column chromatography (EtOAc/hexane: 1/10) and crystallized from CH_2Cl_2/hexane to give a white crystalline product (*R*)-**3c** (2.1 g) in 96% yield. mp 91-92 ^oC (lit[5] (S)-**3c** mp 90.5-91.5 ^oC); IR (KBr): υ (max) 1238, 1155, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.72-7.80 (ArH, 4 H, m), 7.26-7.38 (ArH, 2 H, m), 7.14-7.20 (ArH, 4 H, m), 4.46, 4.58 (OCH_2O, 4 H, d, AB, J_{AB} = 5.8 Hz), 2.83 (OCH_3, 6 H, s), 2.57 ($ArCH_3$, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 153.1, 133.0, 131.6, 131.0, 129.6, 127.1, 126.1, 125.5, 125.4, 124.7, 98.5, 56.4, 17.8; MS *m/e* (relative intensity): 402 (M^+, 30), 327 (29), 326 (100), 309 (26), 298 (36), 297 (50), 296 (45), 283 (29), 252 (20), 239 (30), 119 (27), 111 (25); Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.55; H, 6.47. The sample showed $[\alpha]^{25}_{589}$ -86.6 (c = 1.0, THF).

General Procedure B: Preparation of 3,3'-Diaryl-2,2'-*Bis*(methoxymethoxy)-1,1'-Binaphthyls 3d-3i.

The preparation of 3,3'-disubstituted binaphthyl compounds followed literature procedures[5] with some modifications.

(*R*)-3,3'-Dibromo-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (**3a**) (1 equiv) and $Pd(PPh_3)_4$ (10 mol%) were mixed in DME (6.7 mL/1 mmol of **3a**) in a round bottom flask at room temperature under an argon atmosphere. To the mixture, with stirring, were added arylboronic acid (3.5 equiv) and 2 M aqueous Na_2CO_3 solution (5.2 equiv). The resulting mixture was stirred and heated to reflux for 10 h, cooled to room temperature, and passed through a pad of Celite. The organic solution was evaporated to give a residue. The residue was dissolved in CH_2Cl_2, washed with saturated aqueous NH_4Cl, water, brine, dried over Na_2SO_4, and concentrated to give a crude product. Subsequent purification gave the product.

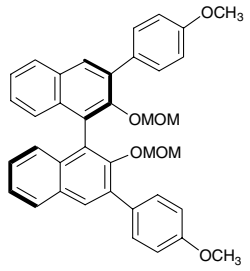
(±)- and (*R*)-3,3'-Diphenyl-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (3d).



Following General Procedure B, (±)-3,3'-Dibromo-2,2'-*Bis*(methoxymethoxy-1,1'-binaphthyl (**3a**) (8.0 g, 15.0 mmol) was treated with $Pd(PPh_3)_4$ (1.73 g, 1.5 mmol), phenylboronic acid (6.40 g, 52.6 mmol) and 2 M aqueous Na_2CO_3 solution (39 mL) in DME (100 mL) in a 500 mL round bottom flask. Purification was carried by column chromatography (EtOAc/hexane: 1/10) to give a foamy product (±)-**3d** (6.7 g) in 85% yield. The product was directly used for deprotection of MOM group with only ^1H NMR and ^{13}C NMR being examined. ^1H NMR ($CDCl_3$): δ 7.65-8.05

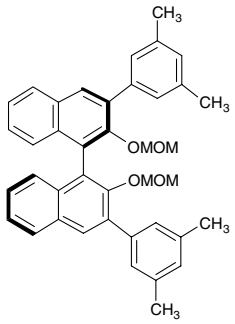
(ArH, 8 H, m), 7.22-7.55 (ArH, 12 H, m), 4.40, 4.37 (OCH_2O, 4 H, d, AB, J_{AB} = 5.8 Hz), 2.34 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 139.0, 135.5, 133.6, 130.9, 130.6, 129.6, 128.3, 127.9, 127.3, 126.5, 126.4, 126.3, 125.2, 98.5, 55.8. (*R*)-3,3'-Dibromo-2,2'-Bis(methoxymethoxy)-1,1'-binaphthyl (**3a**) was used to afford (*R*)-**3d.**

(±)- and (*R*)-3,3'-*Bis*(4-methoxyphenyl)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (3e).



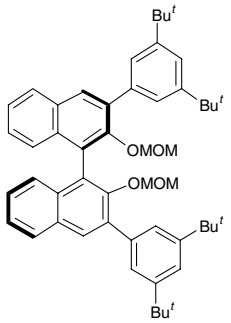
Following General Procedure B, (±)-3,3'-Dibromo-2,2'-*Bis*(methoxymethoxy-1,1'-binaphthyl (**3a**) (1.0 g, 1.88 mmol) was treated with $Pd(PPh_3)_4$ (0.22 g, 0.188 mmol), 4-methoxyphenylboronic acid (1.0 g, 6.58 mmol) and 2 M aqueous Na_2CO_3 solution (4.9 mL) in DME (20 mL) in a 50 mL round bottom flask. Purification was carried by column chromatography (EtOAc/hexane: 1/10) and crystallization from CH_2Cl_2/hexane to give colorless crystals (**3e**) (1.53 g) in 92% yield. mp 75-76 ^oC; IR (KBr): υ (max) 1608, 1513, 1247 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.82-7.96 (ArH, 4 H, m), 7.63-7.78 (ArH, 4 H, m), 7.18-7.47 (ArH, 6 H, m), 6.90-7.08 (ArH, 4 H, m), 4.42, 4.37 (OCH_2O, 4 H, d, AB, J_{AB} = 5.7 Hz), 3.87 (OCH_3, 6 H, s), 2.35 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 159.0, 151.3, 135.0, 133.4, 131.4, 130.9, 130.7, 130.2, 127.7, 126.6, 126.4, 126.1, 125.1, 113.8, 98.3, 55.9, 55.3; Anal. Calcd for $C_{38}H_{34}O_6$: C, 77.80; H, 5.84. Found: C, 77.68; H, 5.78. (*R*)-3,3'-Dibromo-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**yy8**. mp 68-70 ^oC. The sample showed $[\alpha]^{25}_{578}$ -109.6 (c = 1.0, THF).

(±)- and (*R*)-3,3'-Bis(3,5-dimethylphenyl)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (3f).



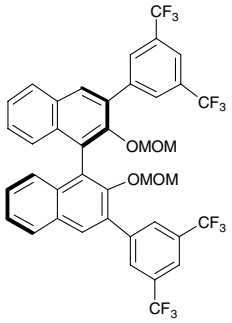
Following General Procedure B, (±)-3,3'-Dibromo-2,2'-*Bis*(methoxymethoxy-1,1'-binaphthyl (**3a**) (2.0 g, 3.76 mmol) was treated with $Pd(PPh_3)_4$ (0.43 g, 0.372 mmol), 3,5-dimethylphenylboronic acid (2.0 g, 13.34 mmol) and 2 M aqueous Na_2CO_3 solution (10 mL) in DME (40 mL) in a 100 mL round bottom flask. Purification was carried by column chromatography (CH_2Cl_2/hexane: 1/1)) and crystallization from CH_2Cl_2/hexane to give colorless crystals (**3f**) (2.25 g) in 93% yield. mp 84-85 ^oC; IR (KBr): υ (max) 1600, 1389, 1233, 1157 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.80-7.97 (ArH, 4 H, m), 7.18-7.48 (ArH, 10 H, m), 7.02-7.08 (ArH, 2 H, m), 4.69, 4.44 (OCH_2O, 4 H, d, AB, J_{AB} = 5.8 Hz), 2.40 ($ArCH_3$, 12 H, s), 2.36 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 151.4, 139.0, 137.7, 135.7, 133.6, 130.8, 130.5, 128.9, 127.7, 127.4, 126.4, 126.1, 125.0, 98.5, 55.8, 21.4; MS *m/e* (relative intensity): 585 (M^++3, 1), 584 (M^++2, 4), 583 (M^++1, 15), 582 (M^+, 35), 518 (12), 507 (41), 506 (100), 478 (28); Anal. Calcd for $C_{40}H_{38}O_4$: C, 82.44; H, 6.57. Found: C, 82.55; H, 6.50. (*R*)-3,3'-Dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**3f**. mp 81-83 ^oC. The sample showed $[\alpha]^{25}_{578}$ -36.8 (c = 1.1, THF).

(*R*)-3,3'-*Bis*[3,5-di(*tert*-butyl)phenyl]-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (3g).



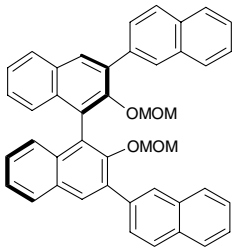
Following General Procedure B, (*R*)-3,3'-Dibromo-2,2'-*Bis*(methoxymethoxy-1,1'-binaphthyl (**3a**) (2.50 g, 4.70 mmol) was treated with $Pd(PPh_3)_4$ (0.54 g, 0.470 mmol), 3,5-di(*tert*-butyl)phenylboronic acid (3.85 g, 16.40 mmol) and 2 M aqueous Na_2CO_3 solution (12.5 mL) in DME (50 mL) in a 100 mL round bottom flask. Purification was carried by column chromatography (CH_2Cl_2/hexane: 1/1) and crystallization from CH_2Cl_2/hexane to give colorless crystals (**3g**) (3.5 g) in 99% yield. mp 97-99 ^oC; IR (KBr): υ (max) 1595, 1390, 1244, 1157 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.84-8.02 (ArH, 4 H, m), 7.54-7.64 (ArH, 4 H, m), 7.20-7.50 (ArH, 8 H, m), 4.42, 4.40 (OCH_2O, 4 H, d, AB, J_{AB} = 5.7 Hz), 2.37 (OCH_3, 6 H, s), 1.39 (($CH_3)_3$, 18 H, s); ^{13}C NMR ($CDCl_3$): δ 151.6, 150.6, 138.2, 136.4, 133.5, 130.8, 130.2, 127.8, 126.5, 126.4, 126.0, 124.9, 123.9, 121.0, 98.3, 55.7, 34.9, 31.5; Anal. Calcd for $C_{52}H_{62}O_4$: C, 83.16; H, 8.32. Found: C, 82.96; H, 8.19. The sample showed $[\alpha]^{25}_{578}$ -73.8 (c = 1.1, THF).

(*R*)-3,3'-*Bis*[3,5-bis(trifluoromethyl)phenyl]-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (3h).



Following General Procedure B, (*R*)-3,3'-Dibromo-2,2'-*Bis*(methoxymethoxy-1,1'-binaphthyl (**3a**) (2.36 g, 4.43 mmol) was treated with $Pd(PPh_3)_4$ (0.512 g, 0.443 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (4.0 g, 15.50 mmol) and 2 M aqueous Na_2CO_3 solution (11.7 mL) in DME (50 mL) in a 100 mL round bottom flask. Purification was carried by column chromatography (CH_2Cl_2/hexane: 2/3) and crystallization from CH_2Cl_2/hexane to give slightly yellow crystals (*R*)-**3h** (3.0 g) in 85% yield. mp 69-71 ^oC; IR (KBr): υ (max) 1621, 1377, 1281, 1153 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.20-8.32 (ArH, 4 H, m), 7.86-8.08 (ArH, 6 H, m), 7.20-7.56 (ArH, 6 H, m), 4.43, 4.37 (OCH_2O, 4 H, d, AB, J_{AB} = 6.0 Hz), 2.50 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 151.3, 141.2, 134.2, 132.8, 132.0, 131.5, 131.1, 130.7, 130.0, 128.3, 127.5, 126.4, 126.3, 125.9, 125.6, 121.1, 99.2, 56.2; ^{19}F NMR ($CDCl_3$): δ -63.43; Anal. Calcd for $C_{40}H_{26}F_{12}O_4$: C, 60.16; H, 3.28. Found: C, 60.35; H, 3.17. The sample showed $[\alpha]^{25}_{578}$ -83.6 (c = 1.1, THF).

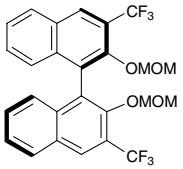
(±)- and (*R*)-3,3'-Bis(2-naphthyl)-2,2'-*Bis*(methoxymethoxy)-1,1'-binaphthyl (3i).



Following General Procedure B, (±)-3,3'-Dibromo-2,2'-*Bis*(methoxymethoxy-1,1'-

binaphthyl (**3a**) (1.2 g, 2.25 mmol) was treated with $Pd(PPh_3)_4$ (0.26 g, 0.225 mmol), 2-naphthylboronic acid (2.02 g, 11.76 mmol) and 2 M aqueous Na_2CO_3 solution (5.9 mL) in DME (25 mL) in a 100 mL round bottom flask. Purification was carried by column chromatography (CH_2Cl_2/hexane: 1/1) and crystallization from CH_2Cl_2/hexane to give colorless crystals (**3i**) (1.4 g) in 85% yield. mp 103-104 ^oC; IR (KBr): υ (max) 1597, 1154 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.14-8.28 (ArH, 2 H, m), 8.01-8.10 (ArH, 2 H, m), 7.70-8.01 (ArH, 10 H, m), 7.22-7.66 (ArH, 10 H, m), 4.45, 4.44 (OCH_2O, 4 H, d, AB, J_{AB} = 5.9 Hz), 2.32 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 151.5, 136.7, 135.3, 133.7, 133.5, 132.5, 130.9, 128.1, 128.0, 127.9, 127.7, 127.6, 126.6, 126.5, 126.4, 126.1, 126.0, 125.2, 98.6, 55.9; MS *m/e* (relative intensity): 627 (M^+, 1), 271 (22), 270 (100), 269 (30), 268 (15), 239 (22); Anal. Calcd for $C_{44}H_{34}O_4$: C, 84.32; H, 5.47. Found: C, 84.23; H, 5.38. (*R*)-3,3'-Dibromo-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**3i** as a yellowish syrup. The sample showed $[\alpha]^{25}_{578}$ -110 (c = 1.1, THF).

Preparation of (*R*)-3,3'-*Bis*(trifluoromethyl)-2,2'-*Bis*(methoxymethoxy)-1,1'-Binaphthyls (3j).



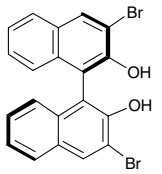
A mixture of $FSO_2CF_2CO_2Me$ (1.63 mL, 12.78 mmol), CuI (1.46 g, 7.67 mmol), HMPA (2.22 mL, 12.78 mmol) and (*R*)-3,3'-diiodo-2,2'-*dis*(methoxymethoxy-1,1'-binaphthyl (**yy3**) (2.0 g, 3.19 mmol) in DMF (40 mL) was stirred under argon atmosphere for 6 h at 70 ^oC. The reaction mixture was then cooled to room temperature. It was diluted with CH_2Cl_2 (400 mL), the solution washed with water (3 x 200 mL), dried over Na_2SO_4, and concentrated to afford a syrup. The purification was done by column chromatography (EtOAc/hexane: 1/20) to give 1.51 g of pure

product **3j** (93%). mp 43-45 ^{o}C; IR (KBr): υ (max) 1230, 1165, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.22-8.32 (ArH, 2 H, m), 7.85-7.98 (ArH, 2 H, m), 7.25-7.55 (ArH, 4 H, m), 7.08-7.25 (ArH, 2 H, m), 4.68, 4.44 (OCH_2O, 4 H, d, AB, J_{AB} = 5.5 Hz), 2.63 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 150.8, 140.3, 135.6, 129.2, 129.1, 129.0, 128.9, 126.9, 126.2, 126.0, 123.9 (q, J = 30.4 Hz), 123.6 (q, 272.7 Hz), 99.7, 56.2; ^{19}F NMR ($CDCl_3$): δ -61.7; Anal. Calcd for $C_{26}H_{20}F_6O_4$: C, 61.18; H, 3.95, F, 22.33. Found: C, 61.10; H, 3.76; F, 22.43. The sample showed $[\alpha]^{25}_{589}$ –57.0 (c = 1.0, THF).

General Procedure C: Preparation of 3,3'-Disubstituted-2,2'-Dihydroxy-1,1'-Binaphthyls 4a-4j.

A mixture of 3,3'-disubstituted-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3**, 2.0 mmol) and Amberlyst 15 resin (1.0 g) in THF/MeOH (1:1) was stirred and heated to reflux under argon atomosphere for 15 h, then cooled to room temperature. The resin was removed by filtration and the filtrate was concentrated by rotary evaporation. Subsequent purification gave the product.

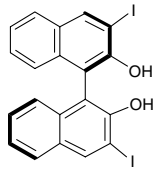
(*R*)-3,3'-Dibromo-2,2'-Dihydroxy-1,1'-Binaphthyl (4a).



(*R*)-3,3'-Dibromo-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3a**) (2.0 g, 3.76 mmol) was treated with Amberlyst 15 (2.0 g) in THF/MeOH (100 mL, 1:1) as described in General Procedure C. Purification was carried out by crystallization (CH_2Cl_2/hexane) to afford 1.6 g of a white crystalline product (*R*)-**4a** (96%). mp 256-257 ^{o}C (lit.[6] mp 243-244 ^{o}C); IR (KBr): υ (max) 3479, 1616, 1577, 1499, 1448, 1421, 1382, 1359, 1255, 1195, 1138 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.20-8.35

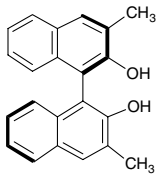
(ArH, 2 H, m), 7.74-7.88 (ArH, 2 H, m), 7.05-7.50 (ArH, 6 H, m), 5.53 (OH, 2 H, s); ^{13}C NMR ($CDCl_3$): δ 148.1, 132.8, 129.8, 127.6, 127.4, 124.9, 124.6, 114.7, 112.3; Anal. Calcd for $C_{20}H_{12}Br_2O_2$: C, 54.09; H, 2.72. Found: C, 54.05; H, 2.68. The sample showed $[\alpha]^{25}_{589}$ +104.7 (c = 1.0, THF); lit[6] $[\alpha]^{25}_{D}$ +43 (c = 0.22, $CHCl_3$)

(*R*)-3,3'-Diiodo-2,2'-Dihydroxy-1,1'-Binaphthyl (4b).



(*R*)-3,3'-Diiodo-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3b**) (3.7 g, 5.91 mmol) was treated with Amberlyst 15 (3.0 g) in THF/MeOH (160 mL, 1:1) as described in General Procedure C. Purification was carried out by column chromatography (EtOAc/hexane: 1:10), and by crystallization (EtOAc/hexane) to afford 3.0 g of a light yellow crystalline product (*R*)-**4b** (94%). mp 312-314 ^{o}C; IR (KBr): υ (max) 3483, 1565, 1355, 1177, 1141 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.40-8.60 (ArH, 2 H, m), 7.70-7.90 (ArH, 2 H, m), 7.02-7.50 (ArH, 6 H, m), 5.41 (OH, 2 H, s); ^{13}C NMR ($CDCl_3$): δ 152.0, 140.4, 133.4, 130.7, 128.0, 127.3, 126.8, 125.2, 124.8, 124.4; Anal. Calcd for $C_{20}H_{12}I_2O_2$: C, 44.64; H, 2.25. Found: C, 44.58; H, 2.27. The sample showed $[\alpha]^{25}_{589}$ +102.7 (c = 1.0, THF).

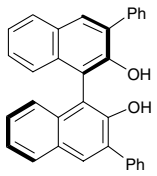
(*R*)-3,3'-Dimethyl-2,2'-Dihydroxy-1,1'-Binaphthyls (4c).



(*R*)-3,3'-Dimethyl-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3c**) (1.80 g, 4.47 mmol) was

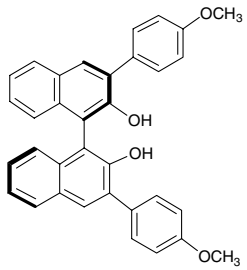
treated with Amberlyst 15 (2.5 g) in THF/MeOH (80 mL, 1:1) as described in General Procedure C. Purification was carried out by column chromatography (EtOAc/hexane: 1:10), and by crystallization (CH_2Cl_2/hexane) to afford 1.40 g of a slightly yellow crystalline product (*R*)-**4c** (100%). mp 201-202 ^oC [lit[7] for (*S*)-**4c**, mp 200-202]; IR, ^1H NMR, and ^{13}C NMR were identical with that of (±)-**4c**.[7] Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.01; H, 5.78. The sample showed $[\alpha]^{25}_{589}$ +43.4 (c = 1.0, THF).

(±)- and (*R*)-3,3'-Diphenyl-2,2'-Dihydroxy-1,1'-Binaphthyl (4d).



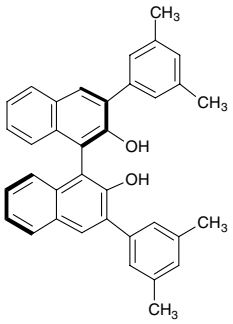
(±)-3,3'-Diphenyl-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3d**) (6.4 g, 12.15 mmol) was treated with Amberlyst 15 (6.0 g) in THF/MeOH (200 mL, 1:1)) as described in General Procedure C. Purification was carried out by column chromatography (EtOAc/hexane: 1:10), followed by crystallization (CH_2Cl_2/hexane) to afford 4.70 g of a white crystalline product (±)-**4d** (89%). mp 209-210 ^oC [lit[7] mp 210-211 ^oC]; IR, ^1H NMR, ^{13}C NMR were identical to that of (±)-(**4d**) in the literature[8]; Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06. Found C, 87.55; H, 4.99. (*R*)-3,3'-Diphenyl-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3d**) was used to afford (*R*)-**4d**. mp 200-202 ^oC [lit[8] mp 197-198 ^oC]; The sample showed $[\alpha]^{25}_{589}$ +135.0 (c = 1.0, THF) [lit[8] $[\alpha]^{25}_{546}$ +132.4^o (c = 1.0, THF)].

(±)- and (*R*)-3,3'-*Bis*(4-methoxyphenyl)-2,2'-Dihydroxy-1,1'-Binaphthyl (4e).



(±)-3,3'-*Bis*(4-methoxyphenyl)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3e**) (1.50 g, 2.56 mmol) was treated with Amberlyst 15 (1.3 g) in THF/MeOH (80 mL, 1:1) as described in General Procedure C. Purification was carried out by crystallization (EtOAc/hexane) to afford 1.15 g of a light yellow crystalline product (±)-**4e** (90%). mp 224-225 ^{o}C; IR (KBr): υ (max) 3480, 1606, 1512, 1244, 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.80-8.10 (ArH, 4 H, m), 7.56-7.75 (ArH, 4 H, m), 7.12-7.45 (ArH, 6 H, m), 6.90-7.06 (ArH, 4 H, m), 5.36 (OH, 2 H, s), 3.83 (OCH_3, 6 H, s); ^{13}C NMR ($CDCl_3$): δ 159.3, 150.2, 132.7, 130.9, 130.7, 130.3, 129.8, 129.5, 128.3, 127.1, 124.2, 113.9, 112.4, 55.3; Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26. Found: C, 82.02; H, 5.16. (*R*)-3,3'-*Bis*(4-methoxyphenyl)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**4e**. mp 109-111 ^{o}C. The sample showed $[\alpha]^{25}_{578}$ +50.1 (c = 1.0, THF).

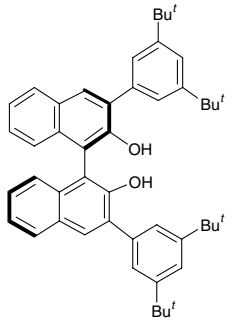
(±)- and (*R*)-3,3'-*Bis*(3,5-dimethylphenyl)-2,2'-Dihydroxy-1,1'-Binaphthyl (4f).



(±)-3,3'-*Bis*(3,5-dimethylphenyl)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3f**) (2.20 g, 3.78 mmol) was treated with Amberlyst 15 (2.0 g) in THF/MeOH (100 mL, 1:1) as described in

General Procedure C. Purification was carried out by crystallization (THF/hexane) to afford 1.74 g of a light yellow crystalline product (±)-**4f** (93%). mp 299-301 ^{o}C; IR (KBr): υ (max) 3476, 1600, 1497, 1411, 1252, 1211 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.82-8.08 (ArH, 4 H, m), 7.18-7.48 (ArH, 10 H, m), 6.98-7.15 (ArH, 2 H, m), 5.39 (OH, 2 H, s), 2.40 ($ArCH_3$, 12 H, s); ^{13}C NMR ($CDCl_3$): δ 150.0, 138.1, 137.3, 133.0, 130.9, 129.5, 129.4, 128.3, 127.3, 127.1, 124.4, 124.1, 112.8, 21.4; Anal. Calcd for $C_{36}H_{30}O_2$: C, 87.42; H, 6.11. Found: C, 87.35; H, 5.98. (*R*)-3,3'-*Bis*(3,5-dimethylphenyl)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**4f**. mp 124-125 ^{o}C. The sample showed $[\alpha]^{25}_{578}$ +53.2 (c = 1.1, THF).

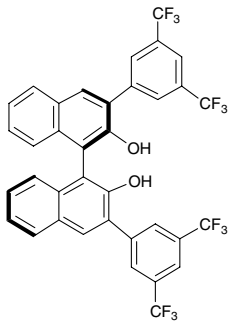
(*R*)-3,3'-*Bis*[3,5-di(*tert*-butyl)phenyl]-2,2'-Dihydroxy-1,1'-Binaphthyl (4g).



(*R*)-3,3'-*Bis*[3,5-di(*tert*-butyl)phenyl]-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3g**) (3.0 g, 3.76 mmol) was treated with Amberlyst 15 (2.0 g) in THF/MeOH (100 mL, 1:1) as described in General Procedure C. Purification was carried out by column chromatography (EtOAc/hexane: 1:10), and by crystallization (EtOAc/hexane) to afford 2.60 g of a white crystalline product (*R*)-**4g** (98%). mp 142-144 ^{o}C; IR (KBr): υ (max) 3490, 1601, 1360, 1209 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.85-8.05 (ArH, 4 H, m), 7.15-7.62 (ArH, 12 H, m), 5.47 (OH, 2 H, s), 1.38 ($C(CH_3)_3$, 18 H, s); ^{13}C NMR ($CDCl_3$): δ 151.0, 150.1, 136.5, 133.0, 131.6, 130.9, 129.4, 128.3, 127.0, 124.5, 124.1, 123.9, 121.9, 113.0, 35.0, 31.5; Anal. Calcd for $C_{48}H_{54}O_2$: C, 86.96; H, 8.21. Found: C, 86.86; H, 8.17.

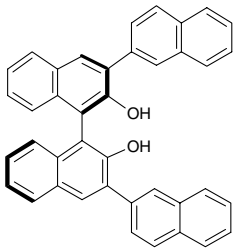
The sample showed $[\alpha]^{25}_{589}$ +27.5 (c = 1.0, THF).

(*R*)-3,3'-*Bis*[3,5-bis(trifluoromethyl)phenyl]-2,2'-Dihydroxy-1,1'-Binaphthyl (4h).



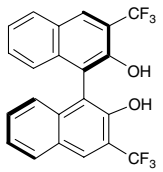
(*R*)-3,3'-*Bis*[3,5-bis(trifluoromethyl)phenyl]-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3h**) (3.0 g, 3.76 mmol) was treated with Amberlyst 15 (2.0 g) in THF/MeOH (100 mL, 1:1) as described in General Procedure C. Purification was carried out by column chromatography (EtOAc/hexane: 1:10), and by crystallization (EtOAc/hexane) to afford 2.60 g of a light yellow crystalline product (*R*)-**4h** (97%). mp 97-99 ^{o}C; IR (KBr): υ (max) 3477, 1603, 1385, 1203, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.80-8.35 (ArH, 10 H, m), 7.10-7.60 (ArH, 6 H, m), 5.37 (OH, 2 H, s); ^{13}C NMR ($CDCl_3$): δ 150.0, 139.7, 133.4, 132.4, 131.7 (q, J = 33.9 Hz), 129.9, 129.6, 128.9, 128.6, 127.9 (q, J = 275.5 Hz), 125.2, 124.1, 121.3, 112.0; ^{19}F NMR (CDCl3): δ -63.49; Anal. Calcd for $C_{36}H_{18}O_2F_{12}$: C, 60.86; H, 2.55; F, 32.09. Found: C, 60.80; H, 2.48; F, 31.99. The sample showed $[\alpha]^{25}_{589}$ -11.9 (c = 1.1, THF).

(±)- and (*R*)-3,3'-*Bis*(2-naphthyl)-2,2'-Dihydroxy-1,1'-Binaphthyl (4i).



(±)-3,3'-*Bis*(2-naphthyl)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3i**) (1.35 g, 2.15 mmol) was treated with Amberlyst 15 (1.1 g) in THF/MeOH (80 mL, 1:1) as described in General Procedure C. Purification was carried out by column chromatography (CH_2Cl_2/hexane: 1:1), then by crystallization (CH_2Cl_2/hexane) to afford 1.05 g of a light yellow crystalline product (±)-**4i** (91%). mp 184-185 ^oC; IR (KBr): υ (max) 3478, 1615, 1501, 1384, 1226, 1169, 1118 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.70-8.40 (ArH, 14 H, m), 7.15-7.60 (ArH, 10 H, m), 5.46 (OH, 2 H, s); ^{13}C NMR ($CDCl_3$): δ 150.3, 135.0, 133.5, 133.0, 132.8, 131.7, 130.6, 129.6, 128.5, 128.2, 127.9, 127.7, 127.4, 126.3, 124.4, 124.3, 112.5; Anal. Calcd for $C_{40}H_{26}O_2$: C, 89.19; H, 4.86. Found: C, 88.98; H, 5.05. (*R*)-3,3'-*Bis*(2-naphthyl)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl was used to afford (*R*)-**4i**: mp 217-218 ^oC (dec.). The sample showed $[\alpha]^{25}_{578}$ -32.9 (c = 1.0, THF).

(*R*)-3,3'-*Bis*(trifluoromethyl)-2,2'-Dihydroxy-1,1'-Binaphthyl (4j).



(*R*)-3,3'-Bis(trifluoromethyl)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**3j**) (1.60 g, 3.13 mmol) was treated with Amberlyst 15 (1.6 g) in THF/MeOH (80 mL, 1:1) as described in General Procedure C. Purification was carried out by column chromatography (EtOAc/hexane: 1:10), and

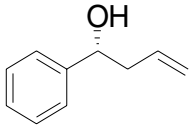
by crystallization (CH_2Cl_2/hexane) to afford 1.30 g of a white crystalline product (*R*)-**4j** (98%). mp 240-242 ^oC; IR (KBr): υ (max) 3490, 1545, 1365, 1179 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.30-8.48 (ArH, 2 H, m), 7.90-8.10 (ArH, 2 H, m), 7.00-7.62(ArH, 6 H, m), 5.30 (OH, 2 H, s); ^{13}C NMR ($CDCl_3$): δ 149.4, 134.6, 130.4 (q, J = 5.5 Hz), 130.0, 129.7, 127.9, 125.5, 123.9, 123.3 (q, J = 272.2 Hz), 118.9 (q, J = 30.9 Hz), 112.2; ^{19}F NMR ($CDCl_3$): δ -63.38; Anal. Calcd for $C_{22}H_{12}F_6O_2$: C, 62.57; H, 2.86; F, 26.99. Found: C, 62.50; H, 2.82; F, 26.88. MS *m/e* (relative intensity): 423 (M^++1, 16), 422 (M^+, 78), 403 (13), 385 (17), 353 (17), 335 (14), 307 (14), 305 (18), 257 (17), 253 (13), 208 (23), 207 (100), 202 (15), 192 (18), 191 (29), 183 (17), 177 (20), 176 (14), 168 (42), 167 (35), 166 (22), 164 (13), 162 (20), 153 (46), 152 (35), 144 (25), 142 (18), 140 (14), 139 (14), 138 (37), 133 (19), 128 (18), 127 (23), 125 (13), 122 (13), 119 (21), 118 (15), 113 (22), 112 (13), 96 (27), 77 (14), 75 (19), 73 (23), 69 (20). The sample showed $[\alpha]^{25}_{589}$ +72.8 (c = 1.0, THF).

General Procedure D: Allylboration of Aldehydes and Ketones using Binaphthol-modified Allylboronates. To a solution of triallylborane (0.75 mmol, 1.5 eq) in dry THF (4 mL) under argon was added the 3,3′-disubstituted BINOL **4** (0.9 mmol, 1.8 eq). This mixture was stirred at room temperature for 2 h and then was heated at reflux for 1 h. The solution was cooled to -78 ^oC (in ketone cases, THF was evaporated, 5 mL toluene was added). The aldehyde (or ketone) (0.5 mmol) was dissolved in 1 mL of dry THF (toluene for ketones) and added dropwise to the solution. Upon completion of the addition, the solution was stirred at –78 ^oC for 1 h (-78^oC ~ -40 ^oC for 48 h for ketones). The reaction was quenched cold with 1 M NaOH and allowed to warm to room temperature. The mixture was diluted with CH_2Cl_2 (20 mL) and the organic layer washed with 0.1 M NaOH then brine, dried with sodium sulfate. The ligand was recovered by neutralizing the aqueous layer with 1 M HCl and extracting with Et_2O. The organic layer was evaporated under

reduced pressure to afford a clear colorless oil, which was purified via flash column chromatography (10:1 hexane:ethyl acetate) to provide the expected homoallylic alcohol in the yields reported in Tables 1, 2, and 3 of the paper**.** The enantiomeric excesses of most alcohols were determined by HPLC (4.6 x 250 mm ChiralCel OD) using racemic mixtures prepared with triallylborane as standards.

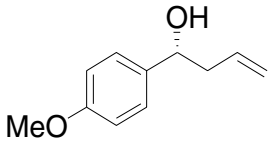
While excess binaphthol was typically used to ensure that no free triallylborane remained, control experiments using 1.0:1.0 binaphthol:triallylborane gave essentially identical enantioselectivities.

(*R*)-1-Phenyl-3-buten-1-ol (6a).



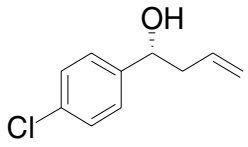
$[\alpha]_D$ = +43.6 (c 1.24, benzene, 86 %ee), lit.[9]for *S* enantiomer: $[\alpha]_D$ = -44.92 (c 7.38, benzene, 96 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ2.06 (1H, br), 2.34-2.57 (2H, m), 4.70 (1H, dd, J = 11.6, 7.0Hz), 5.11-5.17 (2H, m), 5.72-5.86 (1H, m), 7.26-7.60 (5H, m); %ee was determined by HPLC (hexane/iPrOH = 98/2, flow rate = 1 mL/min), t_R = 15.87 min (*R*), t_R = 18.90 min (*S*).

(*R*)-l-(4-Methoxyphenyl)-3-buten-l-o1 (6b).



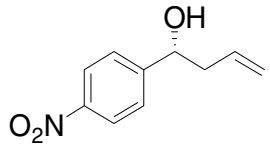
$[\alpha]_D$ = +62.4 (c 0.75, $CHCl_3$, 93 %ee), lit.[10]: $[\alpha]_D$ = +30.5 (c 1.0, benzene, 95 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ2.06 (1H, br s), 2.44 (2H, t, J = 6.6 Hz), 3.74 (3H, s), 4.59 (1 H, dd, J = 6.3, 6.6 Hz), 5.08-5.13 (2 H , m), 5.53-5.93 (1 H, m), 6.82 (2 H, d, J = 8.7 Hz), 2.66-2.62 (1 H, br s); 7.20 (2 H, d, J = 8.7 Hz). %ee was determined by HPLC (hexane/iPrOH = 98/2, flow rate = 1 mL/min), t_R = 21.09 min (*R*), t_R = 26.12 min (*S*).

(*R*)-1-(4-Chlorophenyl)-3-buten-1-ol (6c).



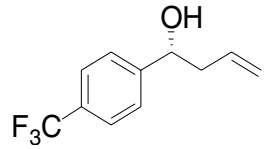
$[\alpha]_D$ = +61.4 (c 1.17, $CHCl_3$, 94 %ee), lit[11]: $[\alpha]_D$ = +26.4 (c 0.38, C_6H_6, 98 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ2.02 (1H, br s), 2.37-2.53 (2H, m), 4.68 (1H, dd, J = 7.5, 5.2 Hz), 5.12-5.17 (2 H, m), 5.68-5.83 (1 H, m), 7.19-7.31 (4H, m); %ee was determined by HPLC (hexane/iPrOH = 98/2, flow rate = 0.6 mL/min), t_R = 23.19 min (*S*), t_R = 25.29 min (*R*).

(*R*)-1-(4-Nitrophenyl)-3-buten-1-ol (6d).



$[\alpha]_D$ = +58.6 (c 0.5, $CHCl_3$, 91 %ee), lit[12]: $[\alpha]_D$ = +40.1 (c 1.4, $CHCl_3$, 89 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ2.22 (1H, br s), 2.38-2.60 (2H, m), 4.85 (1H, dd, J = 4.8, 7.6Hz), 5.14-5.20 (2H, m), 5.70-5.84 (1H, m), 7.52 (2H, d, 8.4Hz), 8.05(2H, d, 8.4Hz); %ee was determined by ^{19}F NMR of its corresponding *R*-Mosher esters (282 MHz, $CDCl_3$), δ-70.83 (for *RR* diastereomer), -70.96 (for *SR* diastereomer).

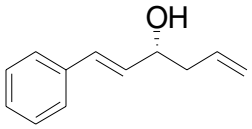
(*R*)-1-(4-Trifluoromethylphenyl)-3-buten-1-ol (6e).



$[\alpha]_D$ = +53.2 (c 0.82, $CHCl_3$, 93 %ee), lit[12]: $[\alpha]_D$ = +43.1 (c 1.24, $CHCl_3$, 96 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ2.37 (1H, br s), 2.40-2.53 (2H, m), 4.74-4.76(1H, m), 5.13-5.17(2H, m), 5.70-5.83(1H, m), 7.44 (2H, d, 8.1Hz), 7.58 (2H, d, 8.1Hz); %ee was determined by ^{19}F NMR of its

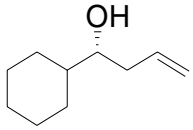
corresponding *R*-Mosher esters (282 MHz, $CDCl_3$), δ-70.89 (for *RR* diastereomer), -71.06 (for *SR* diastereomer).

(*R*)-1-Phenyl-1,5-hexadien-3-ol (6f).



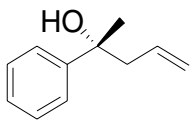
$[\alpha]_D$ = -6.3 (c 0.8, Et_2O, 75%ee), lit[10]: $[\alpha]_D$ = -12.3 (c 1.0, Et_2O, 87 %ee); ^1H NMR (300 MHz, $CDCl_3$) δ1.90 (1H, br s), 2.32-2.49 (2H, m), 4.34-4.38 (1H, m), 5.15-5.21 (2H, m), 5.81-5.87 (1H, m), 6.25 (1H, dd, J = 6.0, 16.0Hz), 6.60 (1H, 16.0Hz), 7.21-7.40 (5H, m); %ee was determined by ^{19}F NMR of its corresponding *R*-Mosher ester [(S)-MTPA-Cl, Et_3N, cat. DMAP, 282 MHz, $CDCl_3$], δ-71.04 (for *RR* diastereomer), -71.15 (for *SR* diastereomer).

(*R*)-1-Cyclohexyl-3-buten-1-ol (6g).



$[\alpha]_D$ = +1.1 (c 0.53, $CHCl_3$, 75 %ee), lit[10]: $[\alpha]_D$ = +13.7 (c 1.0, Ethanol, 93 %ee); ^1H NMR (300 MHz, $CDCl_3$) δ0.95-1.85 (11H, m), 2.06-2.27(3H, m), 3.33-3.39(1H, m), 5.08-5.13 (2H, m), 5.74-5.88 (1H, m); %ee was determined by HPLC analysis (hexane/iPrOH = 99.9/0.1, flow rate = 1 mL/min) of its corresponding benzoate ester, t_R = 7.62 min (*R*), t_R = 8.65 min (*S*).

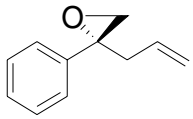
(*R*)-2-Phenyl-4-penten-2-ol (7a).



$[\alpha]_D$ = +61.7 (c 0.36, $CHCl_3$, 91 %ee), lit[13]: $[\alpha]_D$ = +36.3 (c 0.843, $CHCl_3$, 61 %ee); ^1H NMR (300

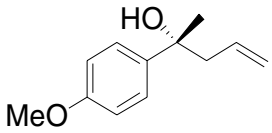
MHz, $CDCl_3$) δ1.54 (3H, s), 1.99 (1H, br s), 2.49 (1H, dd, J = 8.4, 13.7Hz), 2.68 (1H, dd, J = 13.7, 6.9 Hz), 5.10-5.15 (2H, m), 5.54-5.68 (1H, m), 7.20-2.44 (5H, m); %ee was determined by HPLC (hexane/iPrOH = 99/1, flow rate = 1 mL/min) , t_R = 12.58 min (*R*), t_R = 13.98 min (*S*).

(*R*)-1-Phenyl-1-(2-propenyl)-oxirane[14]



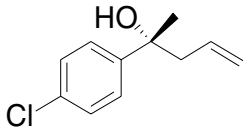
(*R*)-1-Phenyl-1-(2-propenyl)-oxirane was obtained from the allyboration of α-bromoacetophenone after workup with 1 M NaOH. $[\alpha]_D$ = -29.8 (c 0.84 , $CHCl_3$, 93 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ2.64 (1H, dd, J = 7.8, 15.0Hz), 2.75 (1H, d, J = 5.2 Hz), 2.88 (1H, dd, J = 6.3, 15.0Hz), 2.99 (1H, d, J = 5.2 Hz), 5.06-5.14 (2H, m), 5.70-5.84 (1H, m), 7.25-7.38 (5H, m); %ee was determined by HPLC (hexane/iPrOH = 99.5/0.5, flow rate = 1 mL/min) , t_R = 6.54 min (*R*), t_R = 7.93 min (*S*). This compound has not been previously reported in enantiomerically enriched form; the absolute configuration has been assigned based on correlation with results for acetophenone and the assumption that $–CH_2Br$ (A value = 1.79 kcal mol^{-1})[15] and $–CH_3$ (A value = 1.74) behave similarly in the allylation.

(*R*)-2-(4′-Methoxyphenyl)-4-penten-2-ol (7c).[16]



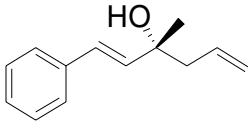
$[\alpha]_D$ = +65.2 (c 0.71 , $CHCl_3$, 98 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ1.51 (3H, s), 2.02 (1H, br, s), 2.46 (1H, dd, J = 8.1, 13.1Hz), 2.64 (1H, dd, J = 6.0, 13.1 Hz), 3,78 (3H, s), 5.07-5.13 (2H, m), 5.54-5.68 (1H, m), 6.85 (2H, d, 8.4Hz), 7.40 (2H, d, 8.4Hz); %ee was determined by HPLC (hexane/iPrOH = 99.5/0.5, flow rate = 0.6 mL/min) , t_R = 34.01 min (*R*), t_R = 37.98 min (*S*).

(*R*)-2-(4′-Chlorophenyl)-4-penten-2-ol (7d).[16]



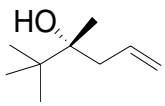
$[\alpha]_D$ = +63.1 (c 0.58, $CHCl_3$, > 98 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ1.50 (3H, s), 2.08 (1H, br, s), 2.46 (1H, dd, J = 6.0, 13.2Hz), 2.63 (1H, dd, J = 7.8, 13.2 Hz), 5.09-5.13 (2H, m), 5.49-5.65 (1H, m), 7.27-7.36 (4H, m); %ee was determined by HPLC (hexane/iPrOH = 99.5/0.5, flow rate = 0.6 mL/min) , t_R = 33.49 min (*S*), t_R = 35.03 min (*R*). The minor (*S*) isomer was not detected but its retention time was determined using authentic racemate.

(*R*)-1-phenyl-3-hydroxy-3-methyl-1,5-hexandiene (7e).[16]



$[\alpha]_D$ = +65.8 (c 1.1, $CHCl_3$, 75 %ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ1.38 (3H, s), 1.78 (1H, br, s), 2.31-2.47 (2H, m), 5.12-5.18 (2H, m), 5.69-5.90 (1H, m), 6.29 (1H, d, J = 15.9), 6.59 (1H, d, J = 15.9),7.21-7.38 (5H, m); %ee was determined by HPLC (hexane/iPrOH = 95/5, flow rate = 1.0 mL/min) , t_R = 11.58 min (*R*), t_R = 13.78 min (*S*).

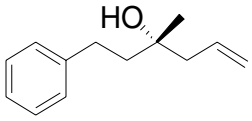
(*R*)-2,2,3-Trimethyl- 5-hexen-3-ol (7f).[17]



^{1}H NMR (300 MHz, C_6D_6) δ0.97 (9H, s), 1.03 (3H, s), 1.19 (1H, br, s), 2.06 (1H, dd, J = 7.8, 13.5 Hz), 2.32 (1H, dd, J = 6.9, 13.5Hz), 5.02-5.13 (2H, m), 5.87-6.00 (1H, m); %ee was determined by

^{1}H NMR (300 MHz, $CDCl_3$) in the presence of chiral shift reagent, $Eu(hfc)_3$.

(*R*)-3-Methyl-1-phenyl-5-hexen-3-ol (7g).



$[\alpha]_D$ = +6.0 (c 1.1, $CHCl_3$, 51 %ee), literature value for *S* enantiomer[18]: $[\alpha]_D$ = -58.0 (c 1.0, $CHCl_3$, 92 %ee);^{1}H NMR (300 MHz, C_6D_6) δ 0.97 (1H, s), 1.07 (3H, s), 1.64-1.70 (2H, m), 2.12-2.14 (2H, m), 2.66-2.70 (2H, m), 5.02-5.10 (2H, m), 5.75-5.90 (1H, m), 7.16-7.23 (5H, m); %ee was determined by HPLC (hexane/iPrOH = 95/5, flow rate = 0.6 mL/min) , t_R = 16.18 min (*S*), t_R = 17.35 min (*R*).

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