Supporting information for:

Synthesis of Spiro Diphosphine Ligands and Their Application in Asymmetric Hydrogenation of Ketones

Jian-Hua Xie, Li-Xin Wang, Yu Fu, Shuo-Fei Zhu, Bao-Min Fang, Hai-Feng Duan and Qi-Lin Zhou*

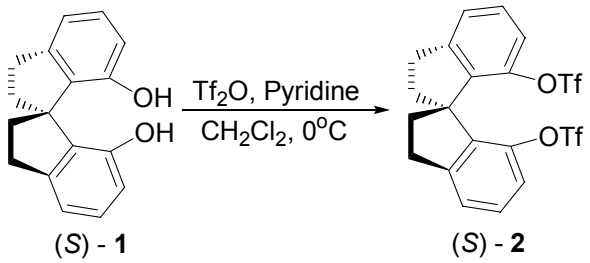
State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China

CONTENTS

General: All reactions and manipulations were performed in an argon-filled glovebox (VAC DRI-LAB HE 493) or using standard Schlenk techniques. Hydrogen gas (99.999%) was purchased from Boc Gas Inc., Tianjin. $[Ru(C_6H_6)Cl_2]_2$, aromatic ketones, hetero-aromatic ketones et al were purchased from Aldrich or Acros chemical company. Anhydrous n-hexane and toluene was distilled from sodium benzophenone ketyl. Anhydrous CH_2Cl_2, DMSO, DMF and *i*-PrOH were freshly distilled from calcium hydride. Melting points were measured on a RY-I apparatus and uncorrected. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Varian MerCury Vx-300 spectrometers. Chemical shifts were reported in ppm down field from internal Me_4Si and external 85% H_3PO_4, respectively. Optical rotations were determined using a Perkin Elmer 241 MC polarimeter. Elemental analyses were performed on Yanaca CDRDER MT-3 instrument. IR spectra were recorded on Bio-Rad FTS 135 spectrometer. Mass spectra were recorded on a VG-7070E spectrometer. GC analyses were performed using a Hewlett Packard Model HP 6890 Series. HPLC analyses were performed using a Hewlett Packard Model HP 1100 Series.

(A) Preparation and Physical Data of Ligands (SDP) [1]

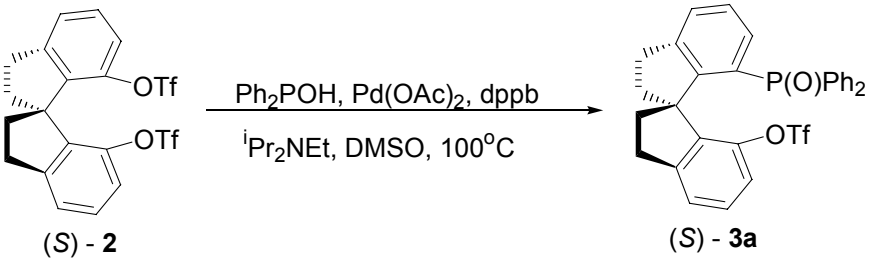
1. Synthesis of (*S*)-7,7'-bis(trifluoromethanesulfonyloxy)-1,1'-spirobiindane ((*S*)-2)



To a solution of (*S*)-1,1'-spirobiindane-7,7'-diol ((*S*)-**1**) (5.0 g, 19.8 mmol) in 100 mL of CH_2Cl_2 was added pyridine (7.0 mL, 86.7 mmol), and followed by dropwise addition of triflic anhydride (8.2 mL, 43.7 mmol) at 0°C. The mixture was stirred at room temperature over night. After removal of the solvent, the residue was diluted with EtOAc (80 mL) and then washed with 5 % aqueous HCl, saturated $NaHCO_3$, and brine (once for each). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure, and passed through a silica gel plug (eluted with CH_2Cl_2) to give (*S*)-7,7'-bis(trifluomethanesulfonyloxy)-1,1'-spirobiindane ((*S*)-**2**) (9.9 g, 97%) as a white solid, m.p. 62-64 °C. $[\alpha]_D$ -64 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (m, 4H, CH_2), 3.10 (m, 4H, CH_2), 7.15 (dd, 2H, *J* = 1.8 and 6.6 Hz, Ar-H), 7.26-7.30 (m, 4H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.1, 38.6, 59.4, 115.9, 118.5, 120.1, 124.4, 129.4, 138.2, 145.8, 147.7. IR (KBr) 2958, 1622, 1579, 1466, 1405, 1214, 1144, 994, 934, 860, 830 cm^{-1}. MS (EI) m/z 516 (M^+). Anal. calcd for $C_{19}H_{14}F_6O_6S_2$: C, 44.19; H, 2.73. Found: C, 43.97; H, 2.83.

2. Synthesis of compounds 3

Synthesis of (*S*)-7-diphenylphosphinyl-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*S*)-3a)



Typical procedure: To a mixture of (*S*)-7,7'-bis(trifluoromethanesulfonyloxy)-1,1'-spirobiindane ((*S*)-**2**) (4.0 g, 7.75 mmol), diphenylphosphine oxide (3.13 g, 15.5 mmol), palladium acetate (87 mg, 0.39 mmol) and 1,4-bis(diphenylphospino)butane (dppb, 166 mg, 0.39 mmol) was added 25 mL of degassed DMSO and diisopropylethylamine (4.1 g, 32 mmol), and the mixture was heated with stirring at 100 °C for 6 hours. After cooling to room temperature, the reaction mixture

was diluted with EtOAc, washed with 5 % aqueous HCl and saturated $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on a silica gel column eluted with petroleum ether/EtOAc (3:1 in volume) to give (*S*)-7-diphenylphosphinyl-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*S*)-**3a**) (4.0 g, 90%) as a white solid, m.p. 173-175 ^oC. $[\alpha]_D$ -74 (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 2.20-2.39 (m, 4H, CH_2), 3.08 (m, 2H, CH_2), 3.23-3.41 (m, 2H, CH_2), 6.21 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.14-7.20 (m, 11H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.79 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 30.8, 31.8, 39.8, 40.1, 61.8, 117.5, 123.9, 126.1, 128.0, 128.2, 131.3, 131.4, 131.7, 131.8, 133.6, 140.7, 144.8, 146.1, 149.8. IR (KBr) 3061, 2943, 1462, 1439, 1415, 1398, 1209, 1142, 853 cm^{-1}. MS (EI) m/z 569 (M^+ + 1). Anal. calcd for $C_{30}H_{24}F_3O_4PS$: C, 63.38; H, 4.25; S, 5.64. Found: C, 63.47; H, 4.15; S, 5.45.

(*R*)-7-Di(*p*-methylphenyl)phosphinyl-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*R*)-3b)

(*R*)-**3b** was synthesized using di(*p*-methylphenyl)phosphine oxide by the same procedure as that for (*S*)-**3a** (81%) as a white solide, m.p. 222-224 ^oC. $[\alpha]_D$ +116 (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 2.18-2.42 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.05 (m, 3H, CH_2), 3.21-3.19 (m, 2H, CH_2), 6.24 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.00-7.10 (m, 2H, Ar-H), 7.10-7.23 (m, 10H, Ar-H), 7.20-7.23 (m, 2H, Ar-H), 7.29(d, 2H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.73(s). ^{13}C NMR (121 MHz, $CDCl_3$) δ 21.5, 30.7, 31.8, 39.8, 40.0, 61.9, 115.6, 117.5, 123.7, 125.9, 126.2, 127.5, 127.6, 127.9, 128.2, 128.6, 128.8, 128.9, 131.3, 131.5, 131.7, 131.8, 132.2, 133.2, 133.4, 133.6, 140.9, 141.3, 144.9, 145.9, 146.1, 149.7, 152.9, 152.9. IR (KBr) 3061, 2943, 1462, 1439, 1415, 1398, 1209, 1142, 853 cm^{-1}. MS (EI) m/z 596 (M^+). Anal. calcd for $C_{32}H_{28}F_3O_4PS$: C, 64.42; H, 4.73. Found: C, 64.16; H, 4.92.

(*R*)-7-Di(*p*-methoxyphenyl)phosphinyl-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*R*)-3c)

(*R*)-**3c** was synthesized using di(*p*-methoxyphenyl)phosphine oxide by the same procedure as that for (*S*)-**3a** (90%) as a white solid, m.p.150-152 ^oC. $[\alpha]_D$ +108 (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 2.20-2.32 (m, 3H, CH_2), 3.04-3.18 (m, 3H, CH_2), 3.20-3.40 (m, 2H, CH_2), 3.78 (s, 3H, OCH_3), 3.85(s, 3H, OCH_3), 6.24 (d, 2H, *J* = 8.1 Hz, Ar-H), 6.80-6.85 (m, 4H, Ar-H), 6.86-7.00 (m, 2H, Ar-H), 7.16-7.21 (m, 4H, Ar-H), 7.21-7.30 (m, 2H, Ar-H), 7.32 (d, 1H, *J* = 7.2 Hz, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.45(s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.7, 30.1, 30.8, 38.7, 38.9, 54.2, 60.8, 112.4, 112.6, 116.3, 118.8, 121.1, 122.6, 124.9, 125.1, 125.9, 126.4, 126.9, 127.2, 127.4, 127.8, 131.9, 132.1, 132.4, 132.5, 139.7, 143.8, 144.8, 145.0, 148.6, 151.7, 160.7, 160.9. IR (CH_2Cl_2) 3048, 2948, 1598, 1570, 1500, 1460, 1412, 1292, 1257, 1214, 1178, 1142, 1029, 931. MS (EI) m/z 628 (M^+). HRMS (FAB) calcd for $C_{32}H_{28}F_3O_6PS + H^+$: 629.1369. Found 629.1362.

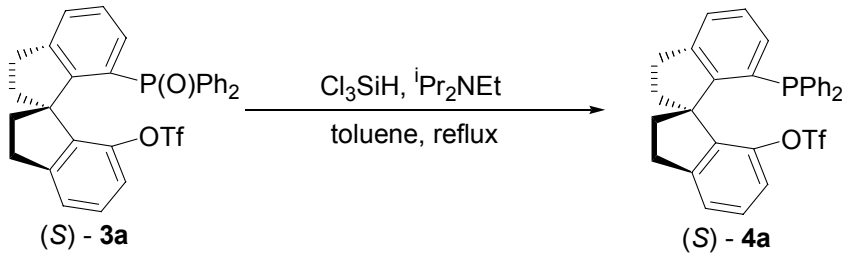
(*S*)-7-Di(3,5-dimethylphenyl)phosphinyl-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*S*)-3d)

(*S*)-**3d** was synthesized using di(3,5-dimethylphenyl)phosphine oxide by the same procedure as that for (*S*)-**3a** (92%) as a white solid, m.p. 183-185 ^oC. $[\alpha]_D$ -128 (*c* 0.5, CH_2Cl_2). ^1H NMR(300 MHz, $CDCl_3$) δ 2.18-2.37 (m, 3H, CH_2), 2.23 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.90-3.18 (m, 3H, CH_2), 3.21-3.42 (m, 2H, CH_2), 6.26 (d, 1H, *J* = 8.1 Hz, Ar-H), 6.85 (d, 2H, *J* = 12 Hz, Ar-H),

6.90-7.10 (m, 6H, Ar-H), 7.10-7.20 (m, 2H, Ar-H), 7.39 (d, 1H, J = 7.8 Hz, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.16(s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 21.5, 21.7, 30.9, 32.1, 39.8, 40.5, 62.1, 115.8, 117.4, 120.0, 123.8, 126.2, 126.5, 127.7, 127.9, 129.1, 129.2, 129.5, 129.6, 130.3, 131.6, 133.1, 133.30, 133.4, 133.6, 135.3, 136.7, 137.5, 137.7, 137.8, 137.9, 140.7, 145.1, 145.9, 146.1, 150.3, 153.1. IR (CH_2Cl_2) 3053, 2943, 1605, 1577, 1460, 1397, 1267, 1219, 1188, 1138, 983, 932, 854. HRMS (FAB) calcd for $C_{34}H_{32}F_3O_4PS + H^+$: 625.1784. Found 625.1782.

3. Synthesis of compounds 4

Synthesis of (*S*)-7-diphenylphosphino-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*S*)-4a)



Typical procedure: To a mixture of (*S*)-7-diphenylphosphinyl-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*S*)-**3a**) (1.4 g, 2.5 mmol) and diisopropylethylamine (13.2 g, 102 mmol) in toluene (25 mL) was added Cl_3SiH (4.0 mL, 39 mmol) at 0 °C. The reaction mixture was stirred at 110 °C for 5 days. After cooling to room temperature, the mixture was diluted with Et_2O and quenched with small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silical gel column chromatography with pretrolum ether/EtOAc (30:1 in volume) as eluent to give (*S*) -7-diphenylphosphino-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((***S***)-**4a**) (1.26 g, 91%) as a white solid, m.p. 72-74 °C. $[\alpha]_D$ -73 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.26-2.33 (m, 3H, CH_2), 2.54 (m, 1H, CH_2), 3.09 (m, 4H, CH_2), 6.65 (d, 1H, J = 8.1 Hz, Ar-H), 6.90-7.04 (m, 5H, Ar-H), 7.04-7.28 (m, 10H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –20.54 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.7, 30.3, 37.9, 39.0, 39.1, 60.6, 114.7, 117.3, 118.9, 123.0, 124.5, 126.4, 126.9, 127.1, 127.2, 127.3, 127.7, 131.1, 131.3, 132.1, 132.3, 132.4, 132.7, 133.4, 134.9, 135.1, 137.5, 137.7, 140.9, 142.7, 142.8, 144.5, 146.9, 151.8. IR (KBr) 3072, 3057, 2948, 2848, 1614, 1578, 1462, 1435, 1415, 1398, 1214, 1141, 995, 978, 929, 852, 829 cm^{-1}. MS (EI) m/z 552 (M^+). Anal. calcd for $C_{30}H_{24}F_3O_3PS$: C, 65.22; H, 4.38. Found: C, 65.20; H, 4.25.

(*R*)-7-Di(*p*-methylphenyl)phosphino-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*R*)-4b)

(*R*)-**4b** was synthesized from (*R*)-**3b** by the same procedure as that for (*S*)-**4a** (81%) as a white solid, m.p 112-114 °C. $[\alpha]_D$ +66 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.25-2.34 (m, 3H, CH_2), 2.42 (m, 1H, CH_2), 3.05 (m, 4H, CH_2), 6.70 (d, 1H, J = 7.8 Hz, Ar-H), 6.88-7.00 (m, 9H, Ar-H), 7.19-7.25 (m, 4H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ

–22.26 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 30.9, 31.6, 39.2, 40.0, 61.8, 116.0, 118.6, 120.2, 124.3, 125.6, 126.5, 127.6, 128.6, 128.9, 129.2, 133.2, 133.4, 133.7, 133.9, 134.7, 135.1, 135.3, 135.4, 138.3, 138.4, 142.3, 144.0, 145.8, 148.1, 152.4, 152.7. IR (CH_2Cl_2) 2947, 2848, 1603, 1577, 1464, 1415, 1398, 1273, 1219, 1141, 932 cm^{-1}. HRMS (FAB) calcd for $C_{32}H_{28}F_3O_3PS$ + H^+: 581.1521. Found: 581.1530.

(*R*)-7-Di(*p*-methoxylphenyl)phosphino-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*R*)-4c)

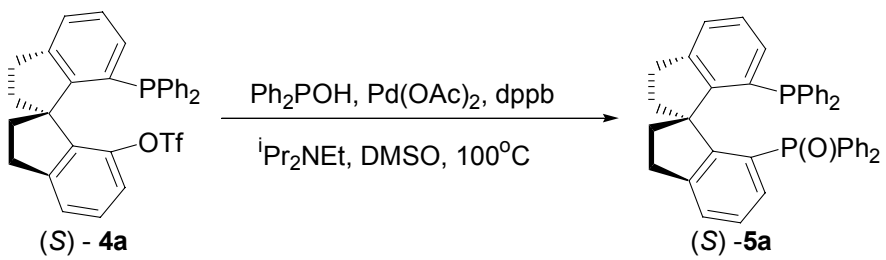
(*R*)-**4c** was synthesized from (*R*)-**3c** by the same procedure as that for (*S*)-**4a** (75 %). (*S*)-**4c** was a colorless oil and solidified slowly by standing. $[\alpha]_D$ +72 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2. 24-2.33 (m, 3H, CH_2), 2.50 (m, 1H, CH_2), 3.04 (m, 4H, CH_2), 3.75 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.70-6.78 (m, 5H, Ar-H), 6.89-7.00 (m, 5H, Ar-H), 7.17-7.25 (m, 4H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –23.65 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.6, 30.1, 30.3, 38.0, 38.6, 54.1, 60.5, 112.3, 112.6, 112.8, 112.9, 114.7, 118.9, 122.9, 124.2, 126.1, 126.3, 127.7, 128.4, 128.5, 132.3, 132.6, 132.7, 133.6, 133.9, 134.1, 140.8, 142.6, 142.7, 144.6, 146.8, 150.8, 151.2, 158.6, 158.9. IR (CH_2Cl_2) 3053, 2968, 2935, 2846, 1595, 1569, 1496, 1462, 1413, 1283, 1243, 1219, 1178, 1140, 1030, 930, 831 cm^{-1}. HRMS (FAB) calcd for $C_{32}H_{28}F_3O_6PS$ + H^+: 613.1420. Found 613.1424.

(*S*)-7-Di(3,5-dimethylphenyl)phosphino-7'-trifluoromethanesulfonyloxy-1,1'-spirobiindane ((*S*)-4d)

(*S*)-**4d** was synthesized from (*S*)-**3d** by the same procedure as that for (*S*)-**4a** (78 %) as a white solid, m.p. 94-96 ^{o}C. $[\alpha]_D$ -78 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.08-2.18 (m, 3H, CH_2), 2.56 (m, 1H, CH_2), 3.08 (m, 4H, CH_2), 6.61-6.70 (m, 5H, Ar-H), 6.84 (s, 1H, Ar-H), 6.98 (s, 1H, Ar-H), 7.00 (m, 1H, Ar-H), 7.11-7.26 (m, 4H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –20.66 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 20.2, 29.6, 30.4, 37.9, 38.9, 60.4, 114.6, 117.1, 118.9, 122.9, 124.1, 126.2, 127.3, 128.7, 129.2, 129.8, 130.0, 130.3, 130.7, 131.8, 132.1, 133.3, 134.4, 134.5, 136.1, 136.2, 136.3, 137.2, 137.3, 140.9, 142.7, 142.4, 144.4, 146.9, 151.2, 151.5. IR (CH_2Cl_2) 3053, 2951, 2854, 1601, 1579, 1462, 1415, 1398, 1267, 1215, 1142, 988, 930, 853 cm^{-1}. MS (EI) m/z 609 (M^+ + 1). Anal. calcd for $C_{34}H_{32}F_3O_3PS$: C, 67.09; H, 5.30. Found: C, 66.87; H, 5.46.

4. Synthesis of compounds 5

Synthesis of (*S*)-7-diphenylphosphino-7'-diphenylphospinyl-1,1'-spirobiindane ((*S*)-5a)



(*S*) - **4a** (*S*) -**5a**

Typic procedure：To a mixture of (*S*)-7-diphenylphosphino-7'-trifluoromethanesulfonyloxy -1,1'-spirobiindane ((*S*)-**4a**) (1.2 g, 2.17 mmol), diphenylphosphine oxide (0.87 g, 4.3 mmol), palladium acetate (22.4 mg, 0.1 mmol) and 1,4-bis(diphenylphospino)butane (dppb, 42.6 mg, 0.1 mmol) was added 15 mL of degassed DMSO and diisopropylethylamine (1.0 g, 8.7 mmol), and the mixture was heated with stirring at 100 °C for 10 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc, washed with 5 % aqueous HCl and saturated $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on a silica gel column eluted with petroleum ether/EtOAc (3:1 in volume) to give (*S*)-7-diphenylphosphino-7'-diphenylphospinyl-1,1'-spirobiindane ((*S*)-**5a**) (1.2 g, 92%) as a white solid, m.p. 80-83 °C. $[\alpha]_D$ –74 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80-2.15 (m, 3H, CH_2), 2.59-3.04 (m, 5H, CH_2), 6.84 (m, 2H, Ar-H), 6.92 (m, 1H, Ar-H), 7.10-7.23 (m, 14H, Ar-H), 7.23-7.42 (m, 9H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –17.29 (s), 30.99 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.9, 31.0, 40.5, 64.3, 125.1, 125.6, 125.8, 126.3, 127.2, 127.7, 127.8, 127.9, 128.2, 128.3, 131.0, 131.6, 131.7, 132.3, 132.5, 132.9, 133.0, 133.1, 133.2, 133.4, 134.1, 134.4, 138.7, 143.3, 143.4, 155.1, 157.7, 158.1. IR (KBr) 3142, 3053, 2935, 1631, 1586, 1435, 1412, 1209, 1114, 744, 696 cm^{-1}. MS (EI) m/z 604 (M^+). HRMS (FAB) calcd for $C_{41}H_{34}OP_2 + H^+$: 605.2157. Found 605.2154.

(*R*)-7-Di(*p*-methylphenyl)phosphino-7'-di(*p*-methylphenyl)phospinyl–1,1'-spirobiindane ((*R*)-5b)

(*R*)-**5b** was synthesized using di(*p*-methylphenyl)phosphine oxide by the same procedure as that for (*S*)-**5a** (90%) as a white solid, m.p. 203-205 °C. $[\alpha]_D$ +90 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80-2.10 (m, 3H, CH_2), 2.27 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.32 (s. 3H, CH_3), 2.35 (s, 3H, CH_3), 2.62-2.80 (m, 2H, CH_2), 2.80-3.05 (m, 3H, CH_2), 6.69 (t, 2H, *J* = 6.9 Hz, Ar-H), 6.88 (d, 2H, *J* = 6.3 Hz, Ar-H), 6.90-7.40 (m, 18H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –19.35 (s), 30.35 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3, 20.5, 30.0, 39.5, 39.7, 63.3, 123.9, 124.5, 124.6, 125.1, 126.7, 127.5, 127.7, 127.8, 129.4, 130.6, 130.7, 131.3, 131.5, 131.7, 131.9, 132.2, 132.5, 133.0, 133.3, 134.1, 134.3, 134.5, 134.6, 135.7, 137.0, 140.0, 142.4, 146.3, 154.1, 156.6, 156.9. IR (CH_2Cl_2) 3053, 2935, 2874, 1604, 1498, 1413, 1269, 1196, 1190, 1018, 811 cm^{-1}. MS (EI) m/z 660 (M^+). Anal. calcd for $C_{45}H_{42}OP_2$: C, 81.80; H, 6.41. Found: C, 81.86; H, 6.50.

(*R*)-7-Di(*p*-methoxylphenyl)phosphino-7'-di(*p*-methoxylphenyl)phospinyl-1,1'-spirobiindan e ((*R*)-5c)

(*R*)-**5c** was synthesized using di(*p*-methoxyphenyl)phosphine oxide by the same procedure as that for (*S*)-**5a** (88%) as a white solid, m.p. 205-207 °C. $[\alpha]_D$ +94 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80-1.98 (m, 1H, CH_2), 2.00-2.10 (m, 2H, CH_2), 2.65-2.80 (m, 2H, CH_2), 3.73 (s. 3H, CH_3), 3.75 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 6.60-6.66 (m, 5H, Ar-H), 6.77 (d, 2H, *J* = 8.4 Hz, Ar-H), 6.86 (dd, 2H, *J* = 1.8 and 8.7 Hz, Ar-H), 6.90 (t, 1H, *J* = 5.1 Hz, Ar-H), 7.00-7.38 (m, 12H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –21.01 (s), 29.80 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.0, 39.3, 39.7, 54.0, 54.1, 63.3, 108.7, 112.3, 112.4, 112.6, 123.8, 124.4, 124.6, 125.1, 125.4, 126.2, 126.6, 127.0, 127.6, 128.4, 128.6, 129.0, 129.2, 130.8, 131.0, 131.3, 131.9, 132.2, 132.3, 132.5, 133.1, 133.2, 133.6, 133.9, 134.4, 134.6, 142.6, 146.0, 154.1, 156.3, 156.7, 158.0, 158.7, 160.6. IR (CH_2Cl_2) 3049, 2939, 2838, 1595, 1567, 1500, 1460, 1283, 1245, 1196, 1182, 1111, 1028,

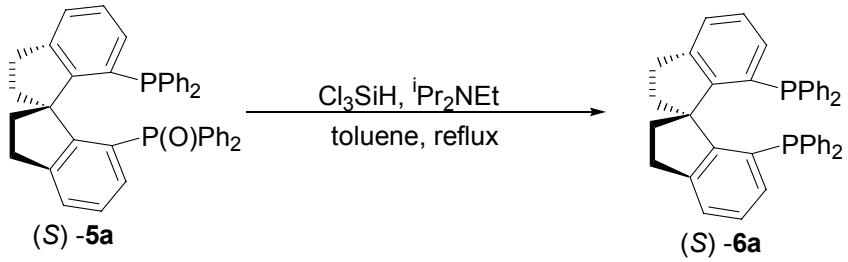
831 cm^{-1}. MS (EI) m/z 725 (M^+ + 1). Anal. calcd for $C_{45}H_{42}O_5P_2$: C, 74.58; H, 5.84. Found: C, 74.52; H, 5.93.

(*S*)-7-Di(3,5-dimethylphenyl)phosphino-7'-di(3,5-dimethylphenyl)phospinyl-1,1'-Spirobiindane ((*S*)-5d)

(*S*)-**5d** was synthesized using di(3,5-dimethylphenyl)phosphine oxide by the same procedure as that for (*S*)-**5a** (91%) as a white solid, m.p. 116-118 °C. $[\alpha]_D$ -42 (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.70 (m, 2H, CH_2), 1.94 (m, 1H, CH_2), 2.20 (s, 12H, CH_3), 2.23 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 2.49 (m, 2H, CH_2), 2.80 (m, 1H, CH_2), 2.92 (m, 2H, CH_2), 6.56 (d, 2H, *J* = 6.6 Hz, Ar-H), 6.73 (s, 1H, Ar-H), 6.85 (d, 2H, *J* = 8.1 Hz, Ar-H), 6.91 (s, 1H, Ar-H), 6.95 (s, 1H, Ar-H), 7.10-7.25 (m, 10H, Ar-H), 7.38 (d, 1H, *J* = 6.6 Hz, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –16.24 (s), 31.05 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.01, 21.3, 30.7, 30.9, 39.8, 40.1, 64.4, 132.6, 124.9, 125.4, 125.6, 126.1, 127.7, 128.7, 129.4, 129.5, 130.2, 130.4, 130.5, 130.7, 132.1, 132.5, 132.7, 133.0, 134.0, 135.4, 136.2, 136.6, 137.1, 137.6, 137.8, 138.0, 139.1, 139.3, 142.2, 142.3, 147.0, 154.4, 158.0. IR (CH_2Cl_2) 3065, 3028, 2980, 2923, 1597, 1413, 1275, 1255, 1196, 1130, 896, 851 cm^{-1}. HRMS (FAB) calcd for $C_{49}H_{50}OP_2 + H^+$: 717.3409. Found 717.3414.

5. Synthesis of ligands 6

Synthesis of (*S*)–7,7'-bis(diphenylphosphino)-1,1'-spirobiindane ((*S*)-6a)



(*S*) -**5a** (*S*) -**6a**

Typic procedure: A mixture of ((*S*)-**5a**) (0.36 g, 0.6 mmol), diisopropylethylamine (3.1 g, 24 mmol) in toluene (10 mL) was added Cl_3SiH (0.9 mL, 9 mmol) at 0 °C. The reaction mixture was stirred at 110 °C for 3 days. After cooling to room temperature, the mixture was diluted with Et_2O and quenched with small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silical gel column chromatography eluted with pretrolum ether/EtOAc (30:1 in volume) to give (*S*) –7,7'-bis(diphenylphosphino)-1,1'-spirobiindane ((*S*)-**6a**) (0.3 g, 86%) as a white solid, m.p. 206-208 °C. $[\alpha]_D$ –81 (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.80-2.00 (m, 4H, CH_2), 2.62-2.80 (m, 2H, CH_2), 2.80-2.96 (m, 2H, CH_2), 6.96 (m, 2H, Ar-H), 7.08-7.30 (m, 14H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –17.26 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.7, 40.1, 64.1, 125.3, 126.9, 127.5, 127.9, 128.2, 128.5, 133.3, 133.4, 133.5, 134.4, 134.5, 134.6, 138.4, 144.5, 144.6, 154.5, 154.7, 154.8. IR (KBr) 3138, 3052, 2999, 2938, 1636, 1586, 1567, 1479, 1434, 1412, 1262, 1091, 1027 cm^{-1}. MS (EI) m/z 588 (M^+). Anal. calcd for $C_{41}H_{34}P_2$: C, 83.65; H, 5.83. Found: C, 83.50; H,

6.05.

(*R*)–7,7'-Bis[di(*p*-methylphenyl)phosphino]-1,1'-spirobiindane ((*R*)-6b)

(*R*)-**6b** was synthesized from (*R*)-**5b** by the same procedure as that for (*S*)-**6a** (85%) as a white solid, m.p 142-144 °C. $[\alpha]_D$ +88 (*c* 0.48, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.94 (m, 4H, CH_2), 2.72 (m, 2H, CH_2), 2.79 (s, 6H, CH_3), 2.73 (s, 6H, CH_3), 2.87 (m, 2H, CH_2), 6.80-6.90 (m, 8H, Ar-H), 6.90-7.10 (m, 10H, Ar-H), 7.21-7.24 (m, 4H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –19.75 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.6, 31.0, 40.4, 64.3, 125.3, 127.0, 128.9, 129.2, 133.4, 133.6, 133.8, 133.9, 134.5, 134.6, 134.8, 135.3, 137.4, 138.4, 144.7, 154.7, 154.9, 155.1. IR (CH_2Cl_2) 2952, 2928, 2861, 1598, 1495, 1452, 1308, 1377, 1270, 1255, 1188, 1088, 1018, 809, 767 cm^{-1}. HRMS (FAB) calcd for $C_{45}H_{42}P_2 + H^+$: 645.2834. Found 645.2839.

(*R*)–7,7'-Bis[di(*p*-methoxylphenyl)phosphino]-1,1'-spirobiindane ((*R*)-6c)

(*R*)-**6c** was synthesized (*R*)-**5c** by the same procedure as that for (*S*)-**6a** (80%) as a white solid, m.p 183-185 °C. $[\alpha]_D$ –106 (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.93 (m, 4H, CH_2), 2.72 (m, 2H, CH_2), 2.85 (m, 2H, CH_2), 3.74 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 6.68 (d, 4H, *J* = 8.1 Hz, Ar-H), 6.79 (d, 4H, *J* = 9.0 Hz, Ar-H), 6.85-6.90 (m, 4H, Ar-H), 7.01-7.09 (m, 6H, Ar-H), 7.15-7.25 (m, 4H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –20.61(s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.0, 40.1, 55.3, 64.2, 113.8, 114.0, 125.2, 127.0, 129.8, 133.0, 134.9, 135.1, 135.1, 135.2, 135.9, 136.0, 136.2, 144.6, 154.4, 154.6, 154.7, 159.5, 160.1. IR (CH_2Cl_2) 2946, 2831, 1598, 1561, 1489, 1452, 1285, 1235, 1177, 1097, 1024, 821 cm^{-1}. MS (EI) m/z 708 (M^+). Anal. calcd for $C_{45}H_{42}O_4P_2$: C, 76.26; H, 5.97. Found: C, 76.07; H, 5.95.

(*S*)–7,7'-Bis[di(3,5-dimethylphenyl)phosphino]-1,1'-spirobiindane ((*S*)-6d)

(*S*)-**6d** was synthesized from (*S*)-**5d** by the same procedure as that for (*S*)-**6a** (83%). (*S*)-**6d** was a colorless oil and solidified slowly by standing. $[\alpha]_D$ –36 (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.71 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 2.05 (s, 6H, CH_3), 2.17 (s, 3H, CH_3), 2.25 (s, 6H, CH_3), 2.28 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.65 (m, 2H, CH_2), 2.87 (m, 2H, CH_2), 6.68 (m, 3H, Ar-H), 6.85 (m, 5H, Ar-H), 6.98-7.50 (m, 10H, Ar-H). ^{31}P NMR (121 MHz, $CDCl_3$) δ –14.80 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 20.3, 28.6, 29.6, 38.4, 63.1, 124.0, 125.7, 126.6, 127.9, 128.5, 129.4, 129.6, 129.7, 129.8, 131.8, 132.1, 133.7, 135.9, 136.2, 137.6, 143.1, 152.7, 152.9, 153.1. IR (CH_2Cl_2) 3054, 2963, 2851, 1591, 1571, 1458, 1415, 1273, 1182, 852 cm^{-1}. HRMS (FAB) calcd for $C_{49}H_{50}P_2 + H^+$: 701.3460. Found 701.3466.

(B) General Procedure for Preparation of SDP-Ru-Diamine Precatalysts [2]

SDP **6a-d** (0.165 mmol) and $[(C_6H_6)RuCl_2]_2$ (0.08 mmol) were dissolved in anhydrous and degassed DMF (3 mL) under nitrogen. The reaction was heated to 100 °C for 1.5-2.0 hours, then the 1,2-diphenylethylenediamine (DPEN) (0.165 mmol) was added and the reaction was allowed to reach room temperature while stirring 18-20 hours. The solvent was removed under high vacuum at room temperature and the residue was used for hydrogenations without further purification. ^{31}P NMR (121 MHz, $CDCl_3$) of precatalysts:

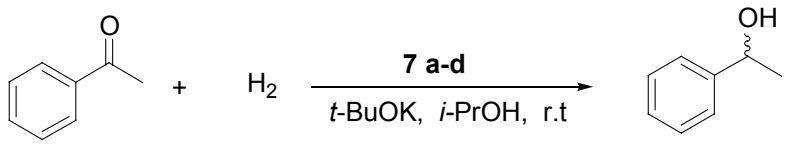
[((*S*)-SDP)Ru((*R*,*R*)-DPEN)Cl_2] (*S*,*RR*-**7a**): δ = 49.94(s)

[((*R*)-Tol-SDP)Ru((*S*,*S*)-DPEN)Cl_2] (*R*,*SS*-**7b**): δ = 47.95(s)

[((*R*)-An-SDP)Ru((*S*,*S*)-DPEN)Cl_2] (*R*,*SS*-**7c**): δ = 46.04 (s)

[((*S*)-Xyl-SDP)Ru((*R*,*R*)-DPEN)Cl_2] (*S*,*RR*-**7d**): δ = 48.3 (s)

(C) General Procedure for Asymmetric Hydrogenation



Standard procedure at S/C = 5000: The catalyst (0.002 mmol) was placed in a 20 mL hydrogenation vessel. The vessel was purged with hydrogen by pressurizing to 10 atm and releasing the pressure. The procedure was repeated three times. Anhydrous *i*-PrOH (3.0 mL) was introduced with syringe via the vessel injection port and the vessel was purged with hydrogen and pressurized to 20 atm for 5 minutes. After releasing the pressure, acetophenone (1.2 g, 10 mmol) and a solution of *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol) were added through the injection port. The vessel was purged with hydrogen and pressurized to 50 atm. After stirring at room temperature for certain hours, the reaction was stopped. The reaction mixture was filtered through a short silica gel column, the filtrate was diluted with acetone and analysed by chiral GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200^{o}C; initial column temperature, 100°C; progress rate, 1 $^{\circ}$C/min; final column temperature, 160 $^{\circ}$C); t_R of (*R*)-1-phenyethanol, 15.51 min; t_R of (*S*)-1-phenylethanol, 16.01 min.[3]

Reaction with (*S*,*RR*-7a) at S/C = 5000: (*S*,*RR*-**7a**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 1.5 h. (*S*)-1-Phenylethanol, 100% conversion, 90% ee.

Reaction with (*R*,*SS*-7b) at S/C = 5000: (*R*,*SS*-**7b**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 mL), *t*-BuONa in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 2.0 h. (*R*)-1-Phenylethanol, 99% conversion, 89% ee.

Reaction with (*R*,*SS*-7c) at S/C = 5000: (*R*,*SS*-**7c**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 2.5 h. (*R*)-1-Phenylethanol, 100% conversion, 92% ee.

Reaction with (*S*,*RR*-7d) at S/C = 5000: (*S*,*RR*-**7d**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 1.5 h. (*S*)-1-Phenylethanol, 100% conversion, 99% ee.

Reaction with (*S*,*SS*-7d) at S/C = 5000: (*S*,*SS*-**7d**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 ml), *t*-BuOK in *i*-PrOH (0.2 mmol/ml, 0.7 ml, 0.14 mmol), 50 atm, r.t., 48 h. (*S*)-1-Phenylethanol, 64% conversion, 28% ee.

Reaction with (*S*,*RR*-7d) at S/C = 5000: (*S*,*RR*-**7d**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 ml), *t*-BuOK in *i*-PrOH (0.2 mmol/ml, 0.7 ml, 0.14 mmol), 50 atm, 40°C, 1.0 h. (*S*)-1-Phenylethanol, 98% conversion, 99% ee.

Reaction with (*S*,*RR*-7d) at S/C = 5000: (*S*,*RR*-**7d**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 ml), *t*-BuOK in *i*-PrOH (0.2 mmol/ml, 0.7 ml, 0.14 mmol), 50 atm, 0°C, 24h. (*S*)-1-Phenylethanol, 69% conversion, 98% ee.

Reaction with (*S*,*RR*-7d) at S/C = 5000: (*S*,*RR*-**7d**) (2.0 mg, 0.002 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (3.0 ml), *t*-BuOK in *i*-PrOH (0.2 mmol/ml, 0.7 ml, 0.14 mmol), 20 atm, r.t., 12 h. (*S*)-1-Phenylethanol, 80% conversion, 99% ee.

Reaction with (*S*,*RR*-7d) at S/C = 10,000: (*S*,*RR*-**7d**) (0.001 mmol/mL, 1.0 mL, 0.001 mmol), acetophenone (1.2 g, 10 mmol), *i*-PrOH (2.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 60 atm, r.t., 22 h. (*S*)-1-Phenylethanol, 100% conversion, 98% ee.

Reaction with (*S*,*RR*-7d) at S/C = 100,000: (*S*,*RR*-**7d**) (8.7 mg, 0.008 mmol) was placed in a 600 mL stainless steel hydrogenation vessel. The vessel was purged with hydrogen by pressurizing to 10 atm and releasing the pressure. The procedure was repeated three times. Anhydrous *i*-PrOH (54 mL) was introduced into the vessel and the vessel was purged with hydrogen and pressurized to 20 atm for 5 minutes. After releasing the pressure, acetophenone (96 g, 0.8 mol) and a solution of *t*-BuOK(896 mg, 0.8 mmol) in *i*-PrOH (50 mL) were added. The vessel was purged with hydrogen and pressurized to 100 atm. The mixture was vigorously stirred at 40°C for 72 hours. The conversion of substrate was determined by GC to be 98 %. After the solvent was removed under reduced pressure, the residue was passed through a short silica gel column and then distilled (54-56°C, 3 mmHg) to give (*S*)-1-phenylethanol (94 g, 96% yield) with 98% ee.

Table 1. Asymmetric hydrogenation of acetophenone catalyzed by **7** [a]

entry	catalyst	S/C M/M	H_2 [b] (atm)	temp. (°C)	time (h)	conv (%)	ee [c] (%)
1	(*S,RR*)-**7a**	5000	50	r.t.	1.5	100	90(*S*)
2	(*R,SS*)-**7b**	5000	50	r.t.	2.0	99	89(*R*)
3	(*R,SS*)-**7c**	5000	50	r.t.	2.5	100	92(*R*)
4	(*S,RR*)-**7d**	5000	50	r.t.	1.5	100	99(*S*)
5	(*S,RR*)-**7d**	10,000	60	r.t.	22	100	98(*S*)
6	(*S,RR*)-**7d**	100,000	100	40	72	98	98(*S*)
7	(*S,SS*)-**7d**	5000	50	r.t.	48	64	28(S)
8	(*S,RR*)-**7d**	5000	50	40	1.0	98	99(*S*)

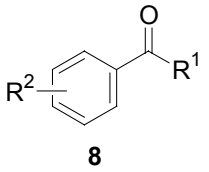
9	(*S,RR*)-**7d**	5000	50	0	24	69	98(*S*)
10	(*S,RR*)-**7d**	5000	20	r.t.	12	80	99(*S*)

[a] S/C = 70, r.t. = 20-25 °C. [b] Initial H_2 pressure. [c] Determined by chiral GC using a Suplco β-DEX 120 column.

(D) Representative Examples, Reaction Conditions and Analytical Data of Products.

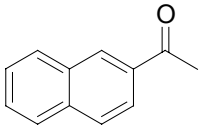
Hydrogenations of other ketones with (*S,RR*-**7d**) were carried out using the standard procedure as that for the hydrogenation of acetophenone. When the reactions were complete, the reaction mixtures were filtered through a short silica gel column, the filtrate was concentrated and the residue was analysed by NMR and chiral GC or HPLC. The stereochemistry of products was assigned by comparing the optical rotation with literature data.

Ketones:



8

	R^1	R^2		R^1	R^2
8a	CH_3	*o*-Cl	**8f**	CH_3	*p*-MeO
8b	CH_3	*o*-Br	**8g**	CH_3	*p*-Cl
8c	CH_3	*m*-Br	**8h**	CH_3	*p*-Br
8d	CH_3	*m*-CF_3	**8i**	Et	H
8e	CH_3	*p*-Me	**8j**	$PhCH_2$	H



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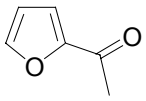

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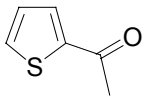

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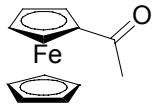

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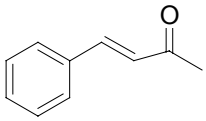

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(*S*)-1-(2'-Chlorophenyl)ethanol:[3] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), 2'-chloroacetophenone (**8a**) (1.55 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 3.5 h. (*S*)-1-(2'-Chlorophenyl)ethanol, 99% conversion, 98% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200°C; column temp: initial temperature, 100°C; rate, 1 °C/min; final temperature, 160 °C; t_R of (*R*) isomer, 21.43 min; t_R of (*S*) isomer, 23.36 min.

(*S*)-1-(2'-Bromophenyl)ethanol:[2] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), 2'-bromoacetophenone (**8b**) (1.99 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 6.5 h. 100% conversion, 99.2% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200°C; column temp: initial temperature, 100°C; rate, 2 °C/min; final temperature, 160 °C; t_R of (*R*) isomer, 26.39 min; t_R of (*S*) isomer, 28.62 min.

(*S*)-1-(3'-Bromophenyl)ethanol:[4] (*S,RR*-7d) (2.2 mg, 0.002 mmol), 3'-bromoacetophenone (**8c**)

(1.99 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 3 h. 99% conversion, 99.2% ee. GC (Suplco β- DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200^{o}C; column temp: initial temperature, 100^{o}C; rate, 1 ^{o}C/min; final temperature, 160 ^{o}C; t_R of (*R*) isomer, 41.95 min; t_R of (*S*) isomer, 43.03 min.

(*S*)-1-(3'-Trifluoromethylphenyl)ethanol:[5] (*S*,*RR*-7d) (2.2 mg, 0.002 mmol), 3'-trifluoromethylacetophenone (**8d**) (1.88 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t, 2 h. 99% conversion, 99% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200^{o}C; column temp: initial temperature, 100^{o}C; rate, 1 ^{o}C/min; final temperature, 160 ^{o}C); t_R of (*R*) isomer, 15.78 min; t_R of (*S*) isomer, 16.70 min.

(*S*)-1-(4'-Methylphenyl)ethanol:[4] (*S*,*RR*-**7d**) (2.2 mg, 0.002 mmol), 4'-methylacetophenone (**8e**) (1.34 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 1.5 h. 100% conversion, 99.2% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200^{o}C; column temp: initial temperature, 100^{o}C; rate, 2 ^{o}C/min; final temperature, 160 ^{o}C; t_R of (*R*) isomer, 15.34 min; t_R of (*S*) isomer, 15.92 min.

(*S*)-1-(4'-Methoxyphenyl)ethanol:[4] (*S*,*RR*-**7d**) (2.2 mg, 0.002 mmol), 4'-methoxylacetophenone (**8f**) (1.50 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 4.5 h. 100% conversion, 98% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200^{o}C; column temp: initial temperature, 100^{o}C; rate, 1 ^{o}C/min; final temperature, 160 ^{o}C; t_R of (*R*) isomer, 36.04 min; t_R of (*S*) isomer, 36.65 min.

(*S*)-1-(4'-Chlorophenyl)ethanol:[3] (*S*,*RR*-**7d**) (2.2 mg, 0.002 mmol), 4'-chloroacetophenone (**8g**) (1.55 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 1.5 h. 100% conversion, 99% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200^{o}C; column temp: initial temperature, 100^{o}C; rate, 2 ^{o}C/min; final temperature, 160 ^{o}C; t_R of (*R*) isomer, 22.85 min; t_R of (*S*) isomer, 23.65 min.

(*S*)-1-(4'-Bromophenyl)ethanol:[4] (*S*,*RR*-**7d**) (2.2 mg, 0.002 mmol), 4'-bromoacetophenone (**8h**) (1.99 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 3 h. 100% conversion, 99% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200^{o}C; column temp: initial temperature, 100^{o}C; rate, 2 ^{o}C/min; final temperature, 160 ^{o}C; t_R of (*R*) isomer, 29.23 min; t_R of (*S*) isomer, 29.99 min.

(*S*)-Phenylpropanol:[3] (*S*,*RR*-**7d**) (2.2 mg, 0.002 mmol), phenylpropanone (**8i**) (1.34 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t.,

3.5 h. 99% conversion, 99.5% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 1 mL/min); injection temp, 200°C; column temp: initial temperature, 90°C; rate, 1 °C/min; final temperature, 160 °C; t_R of (*R*) isomer, 36.69 min; t_R of (*S*) isomer, 37.13 min.

(*S*)-1,2-Diphenylethanol:[6] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), deoxybenzoin (**8j**) (1.96 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 46 h. 100% conversion, 98% ee. HPLC (column, Chiralcel OD; eluent, 2-propanol/hexane 4:96; temp, r.t.; flow rate, 1.0 mL/min; detection, 254 nm light); t_R of (*R*) isomer, 12.85 min; t_R of (*S*) isomer, 16.52 min.

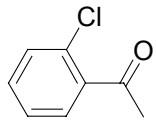
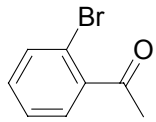
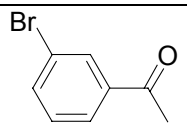
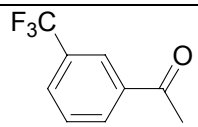
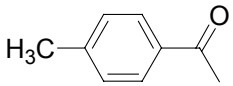
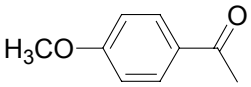
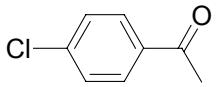
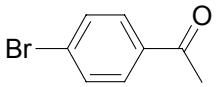
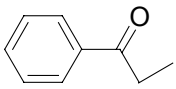
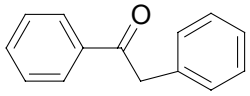
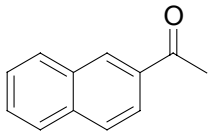
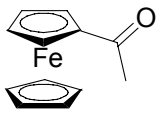
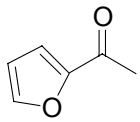
(*S*)-1-(2'-Naphtyl)ethanol:[3] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), 2'-acetonaphthone (**9**) (1.70 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 4 h. 98% conversion, 99.2 % ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200°C; column temp: initial temperature, 140°C; rate, 0.5 °C/min; final temperature, 200 °C; t_R of (*R*) isomer, 40.97 min; t_R of (*S*) isomer, 41.89 min.

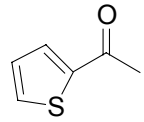
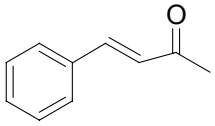
(S)-1-Ferrocenylethanol:[7] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), acetylferrocene (**10**) (2.28 g, 10 mmol, S/C 5000), *i*-PrOH (9.3 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm,r.t., 5 h. 100% conversion, 98% ee. HPLC (column, Chirapack AD-H; eluent, 2-propanol/hexane 5:95; temp, r.t.; flow rate, 0.6 mL/min; detection, 254 nm light); t_R of (*R*) isomer, 28.95 min; t_R of (*S*) isomer, 30.74 min.

(*S*)-1-(2-Furyl)ethanol:[8] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), acetylfuran (**11**) (1.10 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 5 h. 99% conversion, 98% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200°C; column temp: initial temperature, 100°C; rate, 1 °C/min; final temperature, 160 °C; t_R of (*R*) isomer, 33.22 min; t_R of (*S*) isomer, 33.85 min.

(*S*)-1-(2-Thienyl)ethanol:[3] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), 2-acetylthiophene (**12**) (1.26 g, 10 mmol, S/C = 5000), *i*-PrOH (3.0 mL), *t*-BuOK in *i*-PrOH (0.2 mmol/mL, 0.7 mL, 0.14 mmol), 50 atm, r.t., 5 h. 98% conversion, 98% ee. GC (Suplco β-DEX^{TM} 120, df = 0.25 μm, 0.25 mm i.d. x 25 m, fused silica capillary column); carrier gas, N_2 (flow 2 mL/min); injection temp, 200°C; column temp: initial temperature, 100°C; rate, 1 °C/min; final temperature, 160 °C; t_R of (*R*) isomer, 16.38 min; t_R of (*S*) isomer, 17.21 min.

(*S*)-(*E*)-4-Phenyl-3-buten-2-ol:[9] (*S,RR*-**7d**) (2.2 mg, 0.002 mmol), (E)-4-phenyl-3-butenone (**13**) (1.45 g, 4 mmol, S/C = 5000), *i*-PrOH (3.0 ml), *t*-BuOK in *i*-PrOH (0.2 mmol/ml, 0.7 ml, 0.14 mmol), 50 atm, r.t., 3 h. 100% conversion, 96% ee. HPLC (column, Chiralcel OD; eluent, 2-propanol/hexane 4:96; temp, r.t.; flow rate, 1.0 mL/min; detection, 254 nm light); t_R of (*R*) isomer, 13.14 min; t_R of (*S*) isomer, 17.60 min.

Ketones	S/C	B/C	H_2(atm)	Time(h)	Conv.(%)	e.e.(%)	config
	5000	70	50	3.5	99	98	*S*
	5000	70	50	6.5	100	99.2	*S*
	5000	70	50	3	99	99.2	*S*
	5000	70	50	2	99	99	*S*
	5000	70	50	1.5	100	99.2	*S*
	5000	70	50	4.5	100	98	*S*
	5000	70	50	1.5	100	99	*S*
	5000	70	50	3	100	99	*S*
	5000	70	50	3.5	99	99.5	*S*
	5000	70	50	46	100	98	*S*
	5000	70	50	4	98	99.2	*S*
	5000	50	50	5	100	98	*S*
	5000	70	50	5	99	98	*S*

	5000	70	50	5	98	98	*S*
	5000	50	50	3	100	96	*S*

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