Supplementary: Chiral Imidazolylidine Ligands for Asymmetric Hydrogenation of Aryl Alkenes

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General Procedures. High field NMR spectra were recorded on Varian Unity Plus 300 spectrometer (^{1}H at 300 MHz, ^{2}H at 46 MHz, and ^{13}C at (75 MHz). Chemical shifts of ^{1}H and ^{13}C spectra were referenced to the NMR solvents;. IR spectra were recorded on a FTIR instrument. Melting points were uncorrected. Optical rotations were measured on Jasco DIP-360 digital polarimeter. Flash chromatography was performed using silica gel (230–600 mesh). Thin layer chromatography was performed on glass plates coated with silica gel 60 F254 (E. Merck, Darmstadt, Germany). Micro analyses were performed by Atlantic Microlab, Norcross, GA. CH_2Cl_2 was distilled over CaH_2, Et_20 and THF over Na/benzophenone , and acetone over $CaSO_4$. Other solvents and reagents were used as received. Chloro-1,5-cyclooctadiene iridium (I) dimer was provided by Johnson Matthey. Deuterium Gas under high pressure was purchased from Praxair Inc. Danbury, CT. Intermediates used in the syntheses of compounds **1a** - **d** were prepared via known procedures.

(*S*)-2-Phenyl-4-(2-iodoethyl)oxazoline 1a. NaI (5.7 g, 38 mmol) was added in one portion to a solution of the corresponding tosylate (1.32 g, 3.8

mmol) in acetone (25 mL) at 25 ˚C. The reaction was heated to 50 ˚C for 12 h. Upon completion the reaction was diluted with H_2O (25 mL) and extracted with Et_2O (3 x 20 mL). The organics were combined and washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude oil was purified via filtration through a silica plug using 10 % EtOAc/hexanes as the eluent to yield the title compound (1.15 g, 99 %). R_f 0.23 (15 % EtOAc/hexanes); ^{1}H NMR ($CDCl_3$): δ 8.00 – 7.90 (m, 2H), 7.55 – 7.38 (m, 3H), 4.40 – 4.60 (m, 2H), 4.15 – 4.30 (m, 1H), 3.45 (dd, *J* = 9 Hz, *J* = 4 Hz, 1H), 3.25 – 3.17 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 168.1, 131.8, 130.4, 128.4, 73.2, 67.2, 38.4 10.5; IR (film): υ (cm^{-1}) 3109, 3018, 2965, 1648, 1450; HRMS (FAB):calcd for [$C_{11}H_{12}INO$ + H] 302.0042, found 302.0042.

(*S*)-2-Diphenylmethyl-4-(2-iodoethyl)oxazoline 1b. This compound was prepared via the same procedure described for **1a** using NaI (1.1 g, 7.4 mmol), **5d** (0.5 g, 1.2 mmol), and acetone (10 mL). Upon completion the reaction was diluted with H_2O (5 mL) and extracted with Et_2O (3 x 10 mL). The organics were combined and washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude oil was purified via filtration through a silica plug using 10 % EtOAc/hexanes as the eluent to yield the title compound (0.37 g, 82 %). R_f 0.69 (50 % EtOAc/hexanes)**;** ^{1}H NMR ($CDCl_3$) δ 7.39 – 7.26 (m, 10H), 5.16 (s, 1H), 4.43 (t, *J* = 8.3 Hz), 4.39 – 4.23 (m, 1H) 3.95 (t, *J* = 8.1 Hz, 1H), 3.30 (t, *J* = 7.4 Hz, 2H) 2.21 – 2.05 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 167.9, 139.1, 128.6, 128.5, 127.1, 72.1, 66.5, 50.9, 39.9, 1.6; IR (film):υ (cm^{-1}) 3026, 2918, 1654, 1494, 1450; HRMS (ESI):calcd for [$C_{18}H_{18}INO$ + H] 392.0511, found 392.0553

(*S*)-2-*tert*-Butyl-4-(2-iodoethyl)oxazoline 1c. This compound was prepared via the same procedure described for **1a** using NaI (2.8 g, 18.8 mmol), Ots (1.3 g, 3.7 mmol), and acetone (20 mL). Upon completion, the reaction was diluted with H_2O (10 mL) and extracted with Et_2O (4 x 10 mL). The organics were combined and washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude oil was purified via filtration through a silica plug using 10 % EtOAc/hexanes as the eluent to yield the title compound (1.0 g, 95 %). R_f 0.84 (30 % EtOAc/hexanes); ^{1}H NMR ($CDCl_3$): δ 4.29 (t, *J* = 8.2 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.85 (t, *J* = 7.1 Hz, 1H), 3.25 (t, *J* = 7.3 Hz), 2.17 – 1.96 (m, 2H), 1.20 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 174.7, 71.9, 66.7, 40.3, 28.0, 1.6; IR (film):υ (cm^{-1}) 2925, 1741, 1598, 1366; HRMS (ESI):calcd for [$C_9H_{16}INO$ + H] 282.0355, found 282.0355

(*S*)-2-Adamantyl-4-(2-iodoethyl)oxazoline 1d. This compound was prepared via the same procedure described for **1a** using NaI (1.3 g, 8.4 mmol), (*S)*-2-(1-Adamantyl)-4-[2-(p-toluenesulfonyl)ethyl]oxazoline (0.34 g, 0.84 mmol), and acetone (5 mL). Upon completion the reaction was diluted with H_2O (5 mL) and extracted with Et_2O (3 x 10 mL). The organics were combined and washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude oil was purified via filtration through a silica plug using 10 % EtOAc/hexanes as the eluent to yield the title compound (0.32 g, 95 %).R_f 0.90 (50 % EtOAc/hexanes)**;** ^{1}H NMR ($CDCl_3$) δ 4.28 – 4.08 (m, 2H), 3.81 (t, *J* = 6.8 Hz, 1H), 3.23 (t, *J* = 7.3 Hz, 1H), 2.20 – 1.95 (m, 6H), 1.90 (s, 6H). 1.70 (s, 5H); ^{13}C NMR ($CDCl_3$) δ 174.0, 71.9,

63.3, 48.2, 39.6, 36.5, 28.0; IR (film): υ (cm^{-1}) 3055, 2925, 1741, 1598, 1365, 1265. MS (FAB) 360 (M + H).

1-(((*S*)-4',5'-Dihydro-2'-phenyl-4'-oxazolyl) ethyl)-3-(2,6)-diisopropylphenyl)imidazolium iodide 2a. A solution of iodide **1a** (2.5 g, 8.3 mmol) in DMF (5 mL) was added in one portion to 2,6-diisopropylphenyl imidazole (2.7 g, 12.0 mmol) in DMF (5 mL) under N_2 atmosphere at 25 ˚C. The reaction was stirred and warmed to 80 ˚C for 8 h. Upon completion the reaction was cooled to 25 ˚C and Et_2O (5 mL) was added. The white precipitate was filtered and dried *in vacuo* to yield the title compound (3.25 g, 74 %). m.p. 207 – 209 ˚C; R_f 0.25 (1 % MeOH/CH_2Cl_2); ^{1}H NMR (DMSO) δ 9.62 (s, 1H), 8.21 (s, 1H), 8.12 (s, 1H), 7.88 – 7.42 (m, 8H), 4.58 – 4.47 (m, 3H), 4.18 – 4.15 (m, 2H), 2.4 – 2.05 (m, 4H), 1.10 (t, *J* = 6.6 Hz, 12H); ^{13}C NMR (DMSO) δ 162.7, 145.2, 137.6, 131.6, 131.4, 130.5, 128.5, 127.8, 127.1, 125.0, 124.3, 123.5, 72.0, 61.9, 47.1, 34.9, 28.0, 22.1; IR (film) υ (cm^{-1}) 3444, 3056, 2966, 2870, 1649, 1450; MS (MALDI): 403 (M + H); Combustion Analysis calcd for $C_{26}H_{32}IN_3O$ C, 58.98; H, 6.09; found C, 58.87; H, 6.13.

1-(((*S*)-4',5'-Dihydro-2'-(diphenylmethyl)-4'-oxazolyl) ethyl)-3-(2,6)-diisopropylphenyl)imidazolium iodide 2b. This compound was prepared via the same procedure described for **2a** using iodide **1b** (0.30 g, 0.77 mmol), 2,6-diisopropylphenyl imidazole (0.26 g, 1.2 mmol), DMF (1 mL). Upon completion, the reaction was concentrated *in vacuo* and the residue was purified via flash chromatography using 5 % EtOH/EtOAc as the eluent to yield the title compound (0.30 g, 63 %). R_f 0.20 (5 % EtOH/EtOAc)**;** ^{1}H

NMR (DMSO) δ 9.60 (s, 1H), 8.20 (s, 1H), 8.19 (s, 1H), 7.70 – 7.50 (m, 3H), 7.45 – 7.20 (m, 10 H), 5.17 (s, 1H), 4.55 – 4.35 (m, 3H) 4.20 – 3.99 (m, 2H), 2.40 – 2.05 (m, 4H), 1.25 – 1.05 (m, 12H); IR (film):υ (cm^{-1}) 3300, 3070, 2966, 1697, 1654; $[\alpha]_D$ –16.2° (c 0.9, CH_3OH, 25 ˚C); HRMS (FAB):calcd for [$C_{31}H_{39}N_4O_2$ + H] 492.3015 found 492.3024.

1-(((*S*)-4',5'-Dihydro-2'-(*tert*-Butyl)-4'-oxazolyl) ethyl)-3-(2,6)-diisopropylphenyl)imidazolium iodide 2c. This compound was prepared via the same procedure described for **2a** using iodide **1c** (0.57 g, 2.0 mmol), 2,6-diisopropylphenyl imidazole (0.58 g, 2.5 mmol), DMF (1.5 mL). Upon completion, the reaction was cooled to 25 ˚C and concentrated *in vacuo*. The crude residue was purified by flash chromatography using 1 % MeOH/CH_2Cl_2 as the eluent to yield the title compound (0.40 g, 39 %).R_f 0.15 (1 % MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.75 (s, 1H), 7.47 - 7.30 (m, 4H), 7.20 (s, 1H), 4.66 – 4.45 (m, 1H), 4.38 – 4.20 (m, 2H), 3.86 – 3.60 (m, 2H), 2.20 – 2.00 (m, 3H), 1.82 – 1.65 (m, 1H), 1.10 (m, 21H). ^{13}C NMR ($CDCl_3$) δ 176.7, 162.8, 162.2, 161.6, 160.9, 145.4, 137.1, 135.0, 132.9, 126.6, 125.5, 125.3, 125.2, 122.9, 117.7, 72.3, 62.0, 48.3, 35.2, 29.1, 29.0, 27.7, 24.3, 24.1, 23.7. IR (film):υ (cm^{-1})2987, 1634, 1446; HRMS (FAB):calcd for [$C_{24}H_{35}N_3O$ + H] 382.2858, found 382.2858

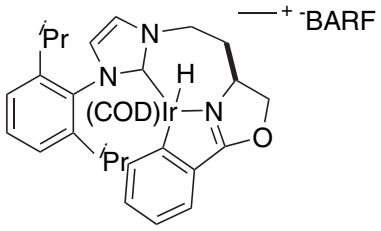
1-(((*S*)-4',5'-Dihydro-2'-(1-adamantyl)-4'-oxazolyl) ethyl)-3-(2,6)-diisopropylphenyl)imidazolium iodide 2d. This compound was prepared via the same procedure described for **2a** using iodide **1d** (0.20 g, 0.56 mmol), 2,6-diisopropylphenyl imidazole (0.16 g, 0.7 mmol), DMF (1 mL). Upon completion, the reaction was triturated with Et_2O and concentrated *in*

vacuo to yield the title compound (0.13 g, 50 %). R_f 0.20 (5 % EtOH/EtOAc)**;** ^{1}H NMR (DMSO) δ 9.60 (s, 1H), 8.20 (s, 1H), 8.15 (s, 1H), 7.70 – 7.50 (m, 3H), 4.45 – 4.30 (m, 3H) 4.10 – 3.85 (m, 2H), 2.37 – 2.10 (m, 4H),2.05 – 1.95 (m, 6H), 1.8 (s, 6H). 1.65 (s, 5H) 1.20 – 1.05 (m, 12H);^{13}C NMR (DMSO) δ 162.9, 146.5, 145.8, 138.4, 132.1, 130.3, 129.3, 125.1, 124.3, 124.2, 71.7, 63.4, 47.7, 36.7, 35.8, 35.3, 31.5, 28.7, 28.0, 24.7, 24.5; HRMS (FAB):calcd for [$C_{30}H_{42}N_3O$ + H] 461.3406 found 461.3406.

General Procedure for Synthesis of 3. Imidazolium salt **2** was added to a Schlenk tube along with 1.5 equivalents lithium *tert*-butoxide and 0.5 equivalents of $[Ir(COD)Cl]_2$. Enough THF was syringed in to make the solution 0.03 M in imidazolium salt. The mixture was heated to 70 ˚C in an oil bath and stirred for 16 h. Upon cooling the volatiles were removed *in vacuo* and 1.5 equivlents of NaBARF dissolved in 5 mL CH_2Cl_2 was added. Water (5 mL) was added and the mixture was stirred vigorously for 15 min. The organic layer was removed and the aqueous layer was washed with an additional 5 mL CH_2Cl_2. The organic layers were combined, dried (Na_2SO_4) and the volatiles were removed *in vacuo*. The residue was chromatographed using a short silica column and 10 % hexanes/CH_2Cl_2 as the eluent.

(η^4-1,5-Cyclooctadiene)(1-[(4S)-(2-phenyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (3a). The above procedure was followed using **2a** (53 mg, 0.1 mmol), LiO^tBu (12 mg, 0.15 mmol), $[Ir(COD)Cl]_2$ (34 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as a yellow-orange solid (149 mg, 95%); Mp 183-186

(dec.). This solid was composed of **3a** (81%) and **7**(19%). **3a**; ^{1}H NMR ($CDCl_3$) 300 MHz δ 8.65 (dd, J = 8.4, 0.9 Hz, 2H), 7.73 (bs, 8H), 7.65 (m, 1H), 7.55 (bs, 4H), 7.37 (m, 3H), 7.11 (dd, J = 7.5, 1.5 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 6.87 (d, J = 2.1 Hz, 1H), 5.41 (dd, J = 14.7, 8.7 Hz, 1H)' 4.70 (m, 2H), 4.34 (dd, J = 14.4, 7.8 Hz, 1H), 4.07(m, 1H), 3.93 (m, 2H), 3.55 (m, 1H), 1.61-2.14 (m, 11H), 1.57 (s, 3H), 1.28 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.6 Hz, 3H), 0.70 (d, J = 6.6 Hz, 3H), 0.36 (d, J = 6.6 Hz, 3H); MS (+FAB) 702 $[C_{34}H_{43}IrN_3O]^+$. ^{13}C-NMR was not run on **3a**, because it is converted to **7** when sitting in solution. A crystal structure determination has been performed on **7** and will be reported in a future publication.



7

(η^4-1,5-Cyclooctadiene)(1-[(4S)-(2-diphenylmethyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (3b). The above procedure was followed using **2b** (40 mg, 0.065 mmol), LiO^{t}Bu (8 mg, 0.098 mmol), $[Ir(COD)Cl]_2$ (22 mg, 0.033 mmol) and NaBARF (82 mg, 0.098 mmol). The complex was isolated as an orange solid (49 mg, 46%)**;** Mp 68-70 ˚C (dec.); ^{1}H NMR ($CDCl_3$) 300 MHz δ 7.73 (bs, 8H), 7.55 (bs, 4H), 7.48 (t, J = 7.5 Hz, 1H), 7.45 (s, 5H), 7.24 (m, 5H), 7.08 (d, J = 1.8 Hz, 1H), 6.86 (d, J= 1.8 Hz, 1H), 6.49 (dd, J = 7.2, 0.9 Hz, 2H), 5.41 (s, 1H), 5.03 (m, 1H), 4.56 (m, 1H), 4.46 (t, J = 9.0 Hz, 1H), 4.20 (m, 2H),

3.99 (m,1H), 3.71 (m, 2H), 2.88 (m, 1H), 2.81 (h, J=7.2 Hz, 1H), 1.76-2.24 (m, 7H), 1.62 (m, 2H),1.24-1.32 (m, 1H), 1.21 (d, J = 6.9 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H), 1.05 (d, J = 6.6 Hz, 3H), 0.83-0.99 (m, 1H), 0.35 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 175.6, 173.3, 162.0 (q, J = 49.8 Hz), 147.4, 145.1, 137.1, 135.1, 134.5, 131.2, 130.2, 129.8, 129.7, 129.5 (qq, J = 31.4, 2.7 Hz), 129.3, 129.2, 128.8, 128.4, 127.2, 126.9, 126.7, 126.6, 124.5, 124.2, 123.0, 121.9, 119.4, 117.8 (h, J = 3.5 Hz), 84.4, 82.5, 77.3, 74.7, 69.3, 65.9, 63.6, 52.0, 50.2, 36.8, 34.3, 31.7, 30.6, 28.9, 28.4, 26.8, 25.2, 22.9, 22.4, 14.3; MS (+FAB) 793 $[C_{41}H_{49}IrN_3O]^+$.

(η^4-1,5-Cyclooctadiene)(1-[(4S)-(2-*tert*-butyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (3c). The above procedure was followed using **2c** (153 mg, 0.3 mmol), LiO^{t}Bu (36 mg, 0.45 mmol), $[Ir(COD)Cl]_2$ (101 mg, 0.15 mmol) and NaBARF (399 mg, 0.45 mmol). The complex was isolated as an orange solid (403 mg, 87%)**;** Mp 157-159 ˚C (dec.); ^{1}H NMR ($CDCl_3$) 300 MHz δ 7.73 (bs, 8H), 7.55 (bs, 4H), 7.49 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 7.8, 1.2 Hz, 1H), 7.21 (dd, J = 7.8, 1.5 Hz, 1H), 6.93 (d, J = 1.8 Hz, 1H), 6.80 (d, J = 1.8 Hz, 1H), 4.96 (m, 1H), 4.70 (m, 1H), 4.36 (t, J = 9.6 Hz, 1H), 4.16 (m, 1H), 3.98 (dd, J = 9.6, 4.9 Hz, 1H), 3.61-3.83 (m, 3H), 3.15 (m, 1H), 2.94 (m,1H), 1.94-2.21 (m, 3H), 1.79 (m, 3H), 1.76 (h, J = 6.9 Hz, 1H), 1.43-1.69 (m, 2H), 1.38 (d, J = 6.9 Hz, 3H), 1.34 (s, 9H), 1.28 (m, 2H) 1.18 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H) ; ^{13}C NMR ($CDCl_3$) δ 180.1, 162.3 (q, J = 49.8 Hz), 147.5, 144.8, 135.0, 131.3, 130.2, 129.2 (qq, J = 31.4, 2.7 Hz), 127.2, 126.6, 124.5, 124.2, 123.0, 122.1, 119.4, 117.7 (h, J = 4.0 Hz), 84.9,

81.3, 77.4, 72.5, 70.1, 62.6, 60.2, 49.9, 36.5, 34.0, 33.8, 31.7, 29.5, 29.0, 28.7, 28.6, 28.5, 27.2, 26.0, 23.0, 22.8, 22.3, 14.3; MS (+FAB) 683 $[C_{32}H_{47}IrN_3O]^+$; Anal. Calcd for ($C_{64}H_{59}BF_{24}IrN_3O$): C, 49.95; H, 3.85; N, 2.72. Found: C, 49.89; H, 3.85; N, 2.72.

(η^4-1,5-Cyclooctadiene)(1-[(4S)-(2-(1-adamantyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (3d). The above procedure was followed using **2d** (135 mg, 0.23 mmol), LiO^{t}Bu (28 mg, 0.34 mmol), $[Ir(COD)Cl]_2$ (77 mg, 0.12 mmol) and NaBARF (301 mg, 0.34 mmol). The complex was isolated as an orange solid (240 mg, 64%); Mp 60-62 ˚C (dec.); ^{1}H NMR ($CDCl_3$) 300 MHz δ 7.72 (bs, 8H), 7.55 (bs, 4H), 7.49 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 7.8, 1.2 Hz, 1H), 7.22 (dd, J = 7.8, 1.5 Hz, 1H), 6.90 (d, J = 1.8 Hz, 1H), 6.78 (d, J = 1.8 Hz, 1H), 4.78 (m, 1H), 4.41 (t, J = 10.2 Hz, 1H), 4.01 (m, 3H), 3.89 (dd, J = 9.0, 7.1 Hz, 1H), 3.60 (m, 1H), 3.00 (m, 1H),1.61-2.19 (m, 21H), 1.56 (s, 3H), 1.43 (d, J = 6.9 Hz, 3H), 1.27 (m, 2H), 1.22 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 179.5, 161.9 (q, J = 49.8 Hz), 146.8, 144.9, 135.0, 131.2, 129.1 (qq, J = 31.4, 2.7 Hz), 127.1, 126.5, 1222.9, 119.3,117.7 (h, J = 4.0 Hz), 84.0, 77.4, 71.3, 62.7, 39.5, 36.5, 36.0, 34.9, 31.8, 30.5, 29.4, 28.6, 27.7, 27.1, 25.5, 25.2, 23.1, 22.9, 22.5, 14.3; MS (+FAB) 761 $[C_{38}H_{53}IrN_3O]^+$; Anal. Calcd for ($C_{70}H_{65}BF_{24}IrN_3O$): C, 51.79; H, 4.03; N, 2.59. Found: C, 51.88; H, 4.25; N, 2.59.

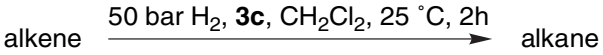
General Hydrogenation Procedure. Alkene substrate (0.2 mmol), iridium complex **3** (0.0012 mmol, 0.6 mol%), and CH_2Cl_2 (100 μL) were added to a test tube containing a small stir bar. The tube was placed in a bomb which was pressurized to 50 bar with hydrogen(deuterium). The mixture was stirred at 300 rpm's for two hours. Upon completion, the bomb was vented, and the reaction mixture was passed through a short silica plug using 50% EtOAc/Hexanes as the eluent. The solution was collected in a vial containing a known amount of dodecane. The yield and ee of the reaction were then determined by GC analysis using a chiral column prepared by Vigh *et al.*;[1] (30.7 m x 0.25 mm, 30% β-*tert*-butyldimethylsilyl cyclodextrin derivative in OV-1701-vi of 0.25 μm film thickness).

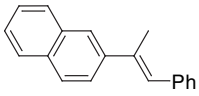
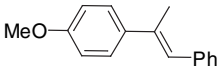
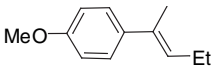
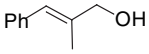
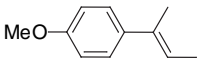
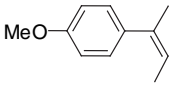
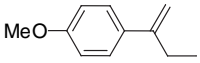
Assignments of Absolute Configurations. The absolute configuration of 2-(2'-naphthyl)-1-phenylpropane was determined by comparison of the optical rotation with those reported by Givens.[2] The absolute configuration of both 1,2-diphenylpropane and 2-(4'-methoxyphenyl)butane were determined by comparison of their optical rotations with those reported by Buchwald.[3] We were unable to find a literature optical rotation (or similar data) for 2-(4'-methoxyphenyl)-1-phenylpropane; the configuration shown in Table 1 of the text was assigned on the basis of the assumption that this material probably has the same sign of rotation as 1,2-diphenylpropane (*vide supra*). This assumption is probably, though not certainly, correct, so the assignment given is tentative.

Solvent Effects in the Hydrogenation Studies. The narrow solvent tolerance of these types of reactions has been known since Crabtree's original studies.[4] In these initial studies, only the solvents that were shown

by Pfaltz[5] to work well in an analogous phosphine-oxazoline system were investigated (*ie* CH_2Cl_2 and $CHCl_3$). These solvent tend to give very similar results. For example, hydrogenation of 2-(2-naphthyl)-1-phenylpropene using 0.6 mol% **3d** under the standard reaction conditions gave 60% yield and 93% ee in both $CHCl_3$ and CH_2Cl_2.

Hydrogenation Data Using Complex 3c.



Entry	Alkene	**3c** (mol %)	Yield[a] (%)	E.e.[a] (%)
1		0.6	34	55
2		0.6	45	45
3		0.6	35	44
4		0.6	25	59
5		0.6	99	59
6[b]		0.6	28	21
7		0.3	95	19

[a] Determined via GC on a chiral column versus an internal standard.

(1) Shitangkoon, A.; Vigh, G. *J. Chromatography A* **1996**, *738*, 31.

(2) Givens, R. S.; Hrinczenko, B. *J. Am. Chem. Soc.* **1984**, *106*, 1779.

(3) Broene, R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 12569.

(4) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331; Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994.

(5) Blackmond, D. G.; Lightfoot, A.; Pfaltz, A.; Rosner, T.; Schnider, P.; Zimmermann, N. *Chirality* **2000**, *12*, 442.