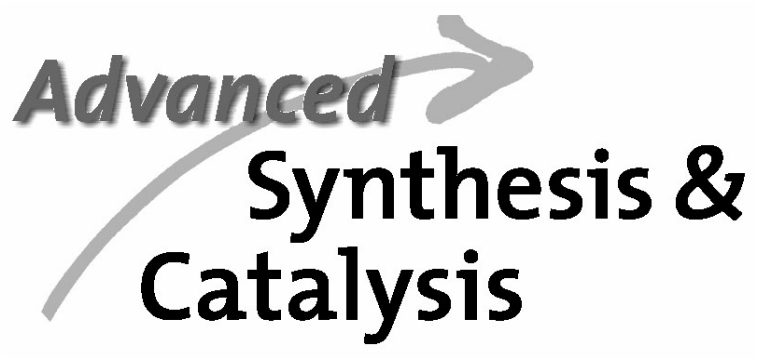

Supporting Information

Iridium catalysts with chiral imidazole-phosphine ligands for asymmetric hydrogenation of vinylfluorides and other olefins

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Supporting Information

Experimental section

THF was freshly distilled under N_2 from a deep-blue solution of sodium-benzophenone ketyl prior to use. CH_2Cl_2 was freshly distilled under N_2 from powdered CaH_2 prior to use. Flash chromatography was performed using silica gel 60 Å (37-70 μm). Analytical TLC was carried out utilizing 0.25 mm plates precoated with silica gel 60 UV_{254} and spots were visualized by the use of UV light or ethanolic phosphomolybdic acid (5%) followed by heating. For NMR spectroscopy, samples were dissolved in $CDCl_3$ and analysed at room temp ^1H (300, 400 or 500 MHz), ^{13}C (75 or 100 MHz) and ^{19}F (282 or 376 MHz) NMR spectra were recorded on a 300, 400 or 500 MHz spectrometer whereas ^{31}P (121 MHz) NMR spectra were recorded on a 300 MHz spectrometer in C_6D_6. The relative shifts for phosphorus are reported relative to external H_3PO_4. Chemical shifts for protons are reported using the residual $CHCl_3$ as internal reference (d 7.26). Carbon signals are referenced to the shift from the ^{13}C signal of $CDCl_3$ (d 77.0). The chemical shifts for fluorine are reported relative to external $CFCl_3$. Mass spectra were measured at 70 eV (EI). IR spectra were measured using a FT-IR apparatus. Optical rotation was measured using a sodium lamp (589 nm). The samples were directly infused into an orthogonal acceleration time-of-flight mass spectrometer Agilent LC/MSD TOF (AgilentTechnologies, Santa Clara, CA, USA). Detection was performed in positive ion mode. The voltage applied at the sampling capillary at the entrance of the mass spectrometer was 4.0 kV. Nitrogen at 300°C and 7 L/min was used as drying gas. Nebulizer gas at 15 L/min was used. Voltage fixed at fragmentor, skimmer and octopole guides were 215 V, 60 V and 250 V, respectively. The ion pulser at the TOF analyzer was set up to a measurement frequency of 0.5 cycles/s. Agilent TOF software and Agilent TM QS software were used to record and analyze mass spectra, respectively. Standard autotune of masses was performed in the TOF-MS instrument before the experimental runs, and typical mass errors of 1-3 ppm were achieved in the calibration. Melting points are reported as their uncorrected values.

Ethyl 2-phenylimidazo[1,1-*a*]pyridine-8-carboxylate (2). R_f (toluene:EtOAc 7:3) = 0.35; IR (neat) υ_{max} 2984, 2250, 1721, 1549, 1498, 1479, 1448, 1364, 1284, 1267, 1216, 1187, 1144, 1040 and 906 cm^{-1}; ^1H NMR δ: 1.51 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 4.54 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 6.84-6.87 (m, 1 H, ArH), 7.32-7.36 (m, 1 H, ArH), 7.42-7.46 (m, 2 H, ArH), 7.94-7.96 (m, 2 H, ArH), 8.03-8.05 (m, 2 H, ArH), 8.29-8.31 (m, 1H, ArH); ^{13}C NMR δ: 14.3, 61.6, 108.5, 111.2, 119.9, 126.3, 128.6, 128.9, 129.2, 133.4, 143.0, 146.9, 164.5; MS (EI) (*m/z*) (rel. intensity) 267.43 (MH^+, 94%), 266.52 (M^+, 58%), 239.33 (10%), 195.79 (32%), 194.46 (100%), 193.43 (50%), 192.25 (10%). HR-MS (ESI): *m/z*= 267.1162 (100%), 268.1163 (22%), calcd for $C_{16}H_{15}N_2O_2^+$ $[M + H]^+$: 267.1134 (100%), 268.1167 (17%).

Ethyl 2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine-8-carboxylate (3). R_f (toluene:EtOAc 3:2)= 0.34; IR (neat) υ_{max} 2958, 1732, 1606, 1476, 1448, 1380, 1215, 1184, 1027 and 950 cm^{-1}; ^1H NMR δ: 1.30 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.96-2.02 (m, 1 H, CH_2), 2.12-2.25 (m, 2 H, CH_2), 2.28-2.34 (m, 1 H, CH_2), 3.92-3.98 (m, 1 H, CH_2) 4.03-4.11 (m, 2 H, CH_2), 4.18-4.28 (m, 2 H, $CO_2CH_2CH_3$), 7.10 (s, 1 H, imidazole-H), 7.19-7.22 (m, 1 H, ArH), 7.32-7.35 (m, 2 H, ArH), 7.73-7.75 (m, 2 H, ArH); ^{13}C NMR δ: 14.1, 20.3, 25.1, 41.3, 44.6, 61.3, 114.3, 124.9, 126.5, 128.3, 134.3, 141.2, 141.6, 171.9; MS (EI) (*m/z*) (rel. intensity) 271.32 (MH^+, 56%), 270.38 (M^+, 74%), 198.43 (22%), 197.38 (100%) and 195.49 (10%). HR-MS (ESI): *m/z*= 271.1447, calcd for $C_{16}H_{19}N_2O_2^+$ $[M + H]^+$: 271.1447.

(*R*)-(2-Phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridin-8-yl)methanol (4). $[\alpha]^{23.2°C}_D$ -53° (t_{R1}, *R*) (*c* 1.2, $CHCl_3$); IR (neat) υ_{max} 2950, 2869, 1606, 1508, 1448, 1434, 1379, 1216, 1193, 1091, 1058, 1021, 958, 844 cm^{-1}; ^1H NMR δ: 1.46-1.54 (m, 1 H, CH_2), 1.97-2.07 (m, 2 H, CH_2), 2.12-2.17 (m, 1 H, CH_2), 3.09-3.15 (m, 1 H, CH), 3.73 (dd, *J* = 10.5 Hz, 9.6 Hz, 1 H, CH_2OH), 3.86 (dd, *J* = 10.5 Hz, 4.8 Hz, 1 H, CH_2OH), 3.88-3.93 (m, 1 H, CH_2), 4.04-4.09 (m, 1 H, CH_2), 7.09 (s, 1 H, imidazole-H), 7.21-7.25 (m, 1 H, ArH), 7.34-7.37 (m, 2 H, ArH), 7.73-7.75 (m, 2 H, ArH); ^{13}C NMR δ: 22.1, 23.4, 37.3, 44.5, 65.8, 113.6, 124.6, 126.6, 128.4, 133.9, 140.3, 147.9; MS (EI) (*m/z*) (rel. intensity) 229.30 (MH^+, 46%), 198.30 (100%), 195.39 (18%) and 83.12 (12%). HR-MS (ESI): *m/z*= 229.1289, calcd for $C_{14}H_{20}N_2O^+$ $[M + H]^+$: 229.1341.

(*R*)-(2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridin-8-yl)methyl 4-methylbenzenesulfonate (5). R_f (EtOAc:toluene 1:4) = 0.18; mp: 103.9-105.0; $[\alpha]^{23.5°C}_D$ -35° (*R*) (*c* 0.7, $CHCl_3$); IR (neat) υ_{max} 3020, 2958, 1599, 1449, 1360, 1216, 1189, 1176, 958, 814, 666 cm^{-1}; ^1H NMR δ: 1.84-1.98 (m, 2 H, CH_2), 2.10-2.16 (m, 1 H, CH_2), 2.18-2.24 (m, 1 H, CH_2), 2.40 (s, 3 H, $ArCH_3$), 3.27-3.32 (m, 1 H, CH), 3.91-4.01 (m, 2 H, CH_2), 4.28 (dd, *J* = 9.5 Hz, 8.4 Hz, 1 H, CH_2OH), 4.59 (dd, *J* = 9.5 Hz, 3.8 Hz, 1 H, CH_2OH), 7.05 (s, 1 H, imidazole-H), 7.19-7.23 (m, 1 H, ArH), 7.27-7.29 (m, 2 H, TsH), 7.31-7.35 (m, 2 H, ArH), 7.61-7.64 (m, 2 H, TsH), 7.74-7.77 (m, 2 H, ArH); ^{13}C NMR δ: 21.2, 21.6, 24.0, 34.9, 44.8, 71.6, 114.4, 124.7, 126.6, 128.0, 128.4, 129.8, 132.58, 134.2, 140.9, 143.2, 144.8; MS (EI) (*m/z*) (rel. intensity) 383.31 (MH^+, 6%), 211.33 (26%), 210.34 (100%), 209.44 (22%), 195.42 (14%) and 83.11 (10%). HR-MS (ESI): *m/z*= 383.1248, calcd for $C_{21}H_{23}N_2O_3S^+$ $[M + H]^+$: 383.1429.

(*R*)-8-((diphenylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine Borane adduct (6). R_f (EtOAc:toluene 1:19)= 0.20; $[\alpha]^{25.3°C}_D$ –1.8° (*R*) (*c* 1.5, $CHCl_3$); IR (neat) υ_{max} 3008, 2958, 2381, 1605, 1503, 1485, 1437, 1380, 1335, 1216, 1108, 1059, 950 and 924 cm^{-1}; ^1H NMR δ: 0.80-1.45 (m, 3 H, BH_3), 1.49-1.56 (m, 1 H, CH_2), 1.84-1.91 (m, 1 H, CH_2), 1.99-2.04 (m, 1 H, CH_2), 2.34-2.45 (m, 2 H, 1×CH_2, 1×CH_2P), 3.26-3.34 (m, 1 H, CH), 3.69-2.75 (m, 1 H, CH_2), 3.88 (ddd, *J* = 5.1 Hz, 11.3 Hz, 16.1 Hz, 1 H, CH_2P), 3.97-4.01 (m, 1 H, CH_2), 7.07 (s, 1 H, imidazole-H), 7.39-7.42 (m, 2 H, ArH), 7.45-7.54 (m, 7 H, ArH), 7.77-7.82 (m, 4 H, ArH), 7.99-8.03 (m, 2 H, ArH); ^{13}C NMR δ: 22.0, 28.5, 29.5 (d, J_{CP}= 36.8 Hz, CP), 32.0 (d, J_{CP}= 3.2 Hz), 44.8, 114.4, 124.7, 126.5, 128.1-129.0 (ArC), 131.1 (d, J_{CP}= 16.5 Hz), 132.0 (d, J_{CP}= 9.4 Hz), 132.5 (d, J_{CP}= 9.1 Hz), 134.5, 140.6, 147.7 (d, J_{CP}= 15.4 Hz); ^{31}P NMR δ: 15.4; MS (EI) (*m/z*) (rel. intensity) 410.35 (M^+, 26 %), 409.42 (38%), 319.36 (100%), 225.30 (34%), 197.34 (58%), 183.31 (38%), 108.18 (20%), 107.18 (36%), 83.13 (28%). HR-MS (ESI): *m/z*= 411.2221 (100%), 412.2167 (40%), 410.2154 (34%), calcd for $C_{26}H_{29}BN_2P^+$ $[M + H]^+$: 411.2161 (100%), 412.2195 (28%), 410.2198 (25%).

(*R*)-(8)-((di*o*-tolylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine Borane adduct (7). Synthesized according to the general procedure except purification of the crude product was performed by using 2% EtOAc in toluene. Clear oil, 80%. R_f (EtOAc:toluene 1:9)= 0.44; $[\alpha]^{22.7°C}_D$ – 8.2° (*R*) (*c* 1.3, $CHCl_3$); IR (neat) υ_{max} 3008, 2960, 2378, 2349, 2333, 1503, 1474, 1449, 1381, 1068, 1068, 950 cm^{-1}; ^1H NMR δ: 0.80-1.47 (m, 3H, BH_3), 1.62-1.71 (m, 1H, CH_2), 1.81-1.90 (m, 1H, CH_2), 2.01-2.08 (m, 1H, CH_2), 2.14 (s, 3H, $ArCH_3$), 2.32 (s, 3H, $ArCH_3$), 2.41-2.50 (m, 2H, CH_2, CH_2P), 3.06-3.14 (m, 1H, CH), 3.89-4.01 (m, 3H, 2×CH_2, CH_2P), 7.07 (s, 1H, imidazole-H), 7.18-7.25 (m, 3H, ArH), 7.32-7.47 (m, 6H, ArH), 7.77-7.79 (m, 2H, ArH), 7.81-7.85 (m, 1H, ArH), 8.26-8.30 (m, 1H, ArH); ^{13}C NMR δ: 21.48 (d, J_{CP}= 4.0 Hz), 21.46 (d, J_{CP}= 4.6 Hz), 22.03, 28.43, 28.75, 31.78 (d, J_{CP}= 3.3 Hz), 44.84, 114.28, 124.64, 126.24-126.65 (ArC), 128.20, 128.45, 129.01, 130.94-132.27 (ArC), 134.50-134.75 (ArC), 140.49, 141.74 (d, J_{CP}= 6.8 Hz), 142.75 (d, J_{CP}= 4.8 Hz), 147.99 (d, J_{CP}= 14.3 Hz); ^{31}P NMR δ: 16.8; MS (EI) (*m/z*) (rel. intensity) 438.08 (M^+, 10%), 437.16 (20%), 424.24 (20%), 334.11 (24%), 333.10 (100%), 225.13 (26%), 211.27 (84%), 197.21 (30%), 78.09 (12%). HR-MS (ESI): *m/z*= 439.2483, calcd for $C_{28}H_{33}BN_2P^+$ $[M + H]^+$: 439.2474 .

(*S*)-8-((bis(3,5-dimethylphenyl)phosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine Borane adduct (8). Synthesized according to the general procedure from the corresponding (*S*)-enantiomer of tosylate **5**. Clear oil, 90%. R_f (EtOAc:toluene 1:9)= 0.35; $[\alpha]^{22.7°C}_D$= -16.9° (*S*) (*c* 1.1, $CHCl_3$); IR (neat) υ_{max} 3007, 2923, 1604, 1503, 1448, 1380, 1219, 1133, 1059, 950, 851 cm^{-1}; ^1H NMR δ: 0.73-1.41 (m, 3 H, BH_3), 1.49-1.57 (m, 1 H, CH_2), 1.82-1.92 (m, 1 H, CH_2), 1.98-2.04 (m, 1 H, CH_2), 2.26-2.41 (m overlapping with 2×s, 2 H, CH_2, CH_2P), 2.32 (s, 6 H, $ArCH_3$), 2.36 (s, 6 H, $ArCH_3$), 3.19-3.27 (m, 1 H, CH), 3.59 -3.66 (m, 1 H, CH_2), 3.88 (ddd, *J* = 14.1 Hz, 4.6 Hz, 2.7 Hz, 1 H, CH_2P), 3.96-4.00 (m, 1 H,

CH_2), 7.05 (s, 1 H, imidazole-H), 7.07 (m, 1 H, ArH), 7.10 (m, 1 H, ArH), 7.20-7.23 (m, 1 H, ArH), 7.31-7.33 (m, 2 H, ArH), 7.34-7.38 (m, 2 H, ArH), 7.57-7.60 (m, 2 H, ArH), 7.77-7-79 (m, 2 H, ArH); ^{13}C NMR δ: 21.3, 22.1, 28.6, 29.1, 29.6, 31.9 (d, J_{CP}= 2.8), 44.9, 114.3, 126.5, 128.2-130.2 (ArC), 132.8 (d, J_{CP}= 2.5 Hz), 133.0 (d, J_{CP}= 2.8 Hz), 138.3 (d, J_{CP}= 10.3 Hz), 138.5 (d, J_{CP}=10.6 Hz), 140.6, 148.1 (d, J_{CP}=14.6 Hz); ^{31}P NMR δ: 14.0; MS (EI) (*m/z*) (rel. intensity) 466.04 (M^+, 48%), 465.2 (78%), 464.2 (20%), 451.9 (15%), 347.1 (100%), 329.1 (22%), 242.0 (42%), 225.1 (68%), 211.2 (55%), 197.1 (52%), 147.1 (40%). HR-MS (ESI): *m/z*= 467.2800 (100%), 468.2817 (37%), 466.2813 (24%), calcd for $C_{30}H_{37}BN_2P^+$ $[M + H]^+$: 467.2787 (100%), 468.2821 (32%), 466.2824 (25%).

(*R*)-(8)-((diphenylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine (9). R_f (3% Et_3N in toluene) = 0.22; $[\alpha]^{25.0°C}_D$ –25.2° (*R*) (*c* 0.5, benzene); IR (neat) υ_{max} 3052, 2944, 2862, 1605, 1503, 1481, 1433, 1380, 1190, 1070, 1027, 949, 740 cm^{-1}; ^{1}H NMR δ: 0.95-1.04 (m, 1 H, CH_2), 1.19-1.33 (m, 2 H, CH_2), 1.97-2.03 (m, 1 H, CH_2), 2.14 (ddd, *J* = 14.3 Hz, 11.3 Hz, 4.8 Hz, 1 H, CH_2P), 2.89-2.97 (m, 1 H, CH), 2.99-3.03 (m, 2 H, CH_2), 3.67 (ddd, *J* = 14.3 Hz, 4.8 Hz, 3.2 Hz, 1 H, CH_2P), 6.56 (s, 1 H, imidazole-H), 7.00-7.15 (m, 7 H, ArH), 7.31-7.35 (m, 2 H, ArH), 7.50-7.53 (m, 2 H, ArH), 7.74-7.78 (m, 2 H, ArH), 8.13-8.15 (m, 2 H, ArH); ^{13}C NMR δ: 21.9, 28.1 (d, J_{CP}= 10.5 Hz), 33.5 (d, J_{CP}= 13.1 Hz), 33.9 (d, J_{CP}= 17.5 Hz), 44.4, 114.0, 125.4, 126.6, 127.7-129.0 (ArC), 133.0 (d, J_{CP}= 18.6 Hz), 133.6 (d, J_{CP}= 19.3 Hz), 135.9, 138.5 (d, J_{CP}= 13.9 Hz), 140.4 (d, J_{CP}= 13.9 Hz), 141.3, 148.5 (d, J_{CP}= 13.1 Hz); ^{31}P NMR δ: -20.0; MS (EI) (*m/z*) (rel. intensity) 397.24 (MH^+, 5%), 396.23 (M^+, 15%), 320.35 (25%), 319.37 (100%), 211.36 (28%), 198.34 (12%). HR-MS (ESI): *m/z*= 397.1866 (100%), 398.1896 (24%), calcd for $C_{26}H_{26}N_2P^+$ $[M + H]^+$: 397.1834 (100%), 398.1867 (28%).

(*R*)-(8)-((di*o*-tolylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine (10). Synthesized according to the general procedure. Clear oil, 50%. R_f (3% Et_3N in toluene) = 0.15; $[\alpha]^{22.8°C}_D$ –40.6° (*R*) (*c* 1.1, benzene); IR (neat) υ_{max} 3055, 3003, 2923, 2856, 1606, 1503, 1470, 1449, 1378, 1260, 1189, 1069, 1015, 796, 747, 695 cm^{-1}; ^{1}H NMR δ: 1.00-1.08 (m, 1 H, CH_2), 1.22-1.34 (m, 2 H, CH_2), 1.96 (ddd, *J* = 14.6 Hz, 11.3 Hz, 5.5 Hz, 1 H, CH_2P), 2.01-2.10 (m, 1 H, CH_2), 2.26-2.32 (m, 1 H, CH_2), 2.44 (s, 3 H, CH_3), 2.54 (s, 3 H, CH_3), 2.90-2.97 (m, 1 H, CH), 3.02-3.05 (m, 2 H, CH_2), 3.58 (ddd, *J* = 14.6 Hz, 4.6 Hz, 3.0 Hz, 1 H, CH_2), 6.58 (s, 1 H, imidazole-H), 6.92-6.96 (m, 1 H, ArH), 7.00-7.06 (m, 3 H, ArH), 7.08-7.20 (m, 3 H, ArH), 7.30-7.34 (m, 3 H, ArH), 7.99-8.04 (m, 1 H, ArH), 8.12-8.14 (m, 2 H, ArH); ^{13}C NMR δ: 11.4, 21.4 (d, J_{CP}= 22.6 Hz), 28.2 (d, J_{CP}= 10.3 Hz), 31.9 (d, J_{CP}= 12.7 Hz), 33.9 (d, J_{CP}= 17.4 Hz), 44.4, 48.6, 113.9, 125.4, 126.6-132.4 (ArC), 136.4 (d, J_{CP}= 14.2 Hz), 138.0 (d, J_{CP}= 11.4 Hz), 141.3, 141.8, 142.0, 142.9, 148.6 (d, J_{CP}= 11.8 Hz); ^{31}P NMR δ: -41.4. MS (EI) (*m/z*) (rel. intensity) 425.10 (MH^+, 10%), 424.05 (M^+, 20%), 334.17 (22%), 333.20 (100%), 212.22 (20%), 211.22 (80%), 197.20 (22%). HR-MS (ESI): *m/z*= 425.2215 (100%), 426.2225 (43%), calcd for $C_{28}H_{30}N_2P^+$ $[M + H]^+$: 425.2147 (100%), 426.2180 (30%).

(*S*)-8-((bis(3,5-dimethylphenyl)phosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine (11). Synthesized according to the general procedure. Clear oil, 77%. R_f (3% Et_3N in toluene) = 0.21; $[\alpha]^{22.7\,^{\circ}C}_{D}$ -0.92° (*S*) (*c*= 1.2 , Benzene); IR (neat) υ_{max} 2923, 2856, 1600, 1504, 1456, 1379, 1189, 1125, 1038, 949, 848, 740 cm^{-1}; ^1H NMR δ: 0.89-1.08 (m, 1 H, CH_2), 1.22-1.45 (m, 2 H, CH_2), 1.92-2.11 (m, 1 H, CH_2), 2.06 (s, 6 H, $ArCH_3$), 2.14 (s, 6 H, $ArCH_3$), 2.25 (ddd, *J* = 14.3 Hz, 11.0 Hz, 5.3 Hz, 1 H, CH_2P), 2.97-3.09 (m, 3 H, CH_2×2, CH), 3.78-3.82 (ddd, *J* = 14.3 Hz, 4.6 Hz, 2.8 Hz, 1 H, CH_2P), 6.56 (s, 1 H, imidazole-H), 6.72-6.74 (m, 1 H, ArH), 6.78-6.80 (m, 1 H, ArH), 7.31-7.35 (m, 2 H, ArH), 7.36-7.39 (m, 2 H, ArH), 7.65-7.68 (m, 2 H, ArH), 8.12-8.15 (m, 2 H, ArH); ^{13}C NMR δ: 21.3 (d, J_{CP}= 5.5 Hz), 21.9, 28.3 (d, J_{CP}= 10.1 Hz), 33.5 (d, J_{CP}= 13.3 Hz), 34.1 (d, J_{CP}= 17.7 Hz), 44.4, 113.9, 125.4, 126.6-131.7 (ArC), 136.0, 138.0 (d, J_{CP}= 7.1 Hz), 138.4 (d, J_{CP}= 7.4 Hz), 138.6, 140.5, 140.6, 141.3, 148.7 (d, J_{CP}= 7.1 Hz); ^{31}P NMR δ: -20.2; MS (EI) (*m/z*) (rel. intensity) 453.01 (MH^+, 10%), 451.92 (32%), 348.15 (25%), 347.17 (100%), 211.29 (32%), 198.27 (16%). HR-MS (ESI): *m/z*= 453.2442, calcd for $C_{30}H_{34}N_2P^+$ $[M + H]^+$: 453.2460.

Complex **(*R*)-12.** $[\alpha]^{22.6^{\circ}C}_{D}$ -8.3° (*R*) (*c* 1.6, $CHCl_3$); IR (neat) υ_{max} 3728, 2965, 2355, 1610, 1485, 1438, 1353, 1274, 1117, 886, 839, 737, 681 cm^{-1}; ^1H NMR δ: 1.22-1.37 (m, 2 H), 1.41-1.48 (m, 1 H), 1.71-1.77 (m, 1 H), 1.84-1.90 (m, 1 H), 1.97-2.02 (m, 2 H), 2.07-2.12 (m, 2 H), 2.22-2.34 (m, 2 H), 2.41-2.49 (m, 3 H), 2.64-2.70 (m, 1 H), 3.62-3.68 (m, 1 H), 3.81-3.84 (m, 1 H, COD), 3.89-3.91 (m, 3 H), 4.62-4.65 (m, 1 H, COD), 6.93 (s, 1 H, imidazole-H), 7.12-7.16 (m, 2 H, ArH), 7.41-7.43 (m, 2 H, ArH), 7.45-7.47 (m, 2 H, ArH), 7.51-7.53 (m, 4 H, BAr_F), 7.54-7.57 (m, 4 H, ArH), 7.58-7.61 (m, 2 H, ArH), 7.70-7.73 (m, 8 H, BAr_F), 7.82-7.86 (m, 2 H, ArH); ^{13}C NMR δ: 20.4, 25.9, 28.2, 33.0, 35.4 (d, J_{CP}= 5.5 Hz), 36.5 (d, J_{CP}= 4.0 Hz), 46.0, 62.0, 64.2, 91.9 (d, J_{CP}= 14.4 Hz), 97.2 (d, J_{CP}= 9.6 Hz), 117.5 (m, BAr_F), 118.1,120.6, 123.3, 126.0, 128.0-132.4 (ArC), 134.8 (m, BAr_F), 142.4, 147.4, 161.8 (q, J_{CB}= 48.6 Hz); ^{31}P NMR δ: 15.2; ^{19}F NMR δ: -62.8. HR-MS (ESI): *m/z*= 697.2317 (100%), 695.2287 (57%), 698.2342 (35%), calcd. for $[C_{34}H_{37}IrN_2P]^+$: 697.2324 (100%), 695.2300 (60%), 698.2357 (37%).

Complex **(*R*)-13.** Synthesized according to the general procedure. Orange solid, 60%. $[\alpha]^{22.4^{\circ}C}_{D}$ +5.7° (*R*) (*c* 1.6, $CHCl_3$); IR (neat) υ_{max} 2965, 2298, 1610, 1485, 1451, 1354, 1275, 1123, 887, 839, 755, 713, 682 cm^{-1}; ^1H NMR δ: 1.21-1.45 (m, 3 H), 1.78-1.85 (m, 2 H), 1.98-2.04 (m, 2 H), 2.10 (s, 6 H), 2.12-2.19 (m, 3 H), 2.37-2.46 (m, 2 H), 2.53-2.61 (m, 1 H), 2.73-2.84 (m, 2 H), 3.56-3.62 (m, 1 H, CH), 3.79-3.83 (m, 1 H, COD), 3.88-4.03 (m, 3 H), 4.71-4.75 (m, 1 H, COD), 6.66-6.82 (m, 1 H), 6.97 (s, 1 H imidazole-H), 7.13-7.19 (m, 1 H), 7.36-7.41 (m, 3 H), 7.51-7.55 (m, 3 H), 7.55-7.59 (m, 4 H, BAr_F), 7.70-7.73 (m, 2 H), 7.74-7.80 (m, 8 H, BAr_F), 8.73-8.80 (m, 1 H); ^{13}C NMR δ: 20.6, 22.4 (d, J_{CP}= 5.9 Hz), 22.7, 25.5, 27.7, 28.2 (d, J_{CP}= 16.1 Hz), 33.6, 34.4 (d, J_{CP}= 5.1 Hz), 36.7 (d, J_{CP}= 5.0 Hz), 46.0, 63.6, 63.8, 89.6 (d, J_{CP}= 14.1 Hz), 95.8 (d, J_{CP}= 9.7 Hz), 117.4-117.5 (m, BAr_F), 118.4, 119.1, 125.8 (d, J_{CP}= 16.0 Hz), 126.3-133.2 (ArC), 134.8 (m, BAr_F), 142.1, 142. 4, 146.9 (d, J_{CP}= 4.3 Hz), 161.7 (q, J_{CB}= 50.6 Hz); ^{31}P NMR δ: 19.6; ^{19}F NMR

δ: -62.8. HR-MS (ESI): *m/z*= 725.2656 (100%), 723.2603 (64%), 726.2654 (47%), calcd. for $[C_{36}H_{41}IrN_2P]^+$: 725.2637 (100%), 723.2613 (60%), 726.2670 (39%).

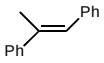
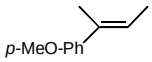
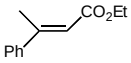
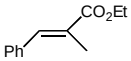
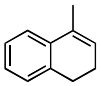
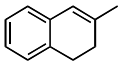
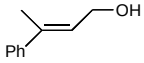
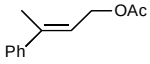
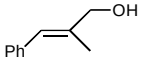
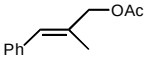
Complex **(*S*)-14.** Synthesized according to the general procedure. Orange solid, 90%. $[\alpha]^{22.4°C}_D$ +19.9° (*S*) (*c* 1.6, $CHCl_3$); IR (neat) υ_{max} 3737, 2926, 2333, 1610, 1485, 1353, 1273, 1117, 887, 839, 744, 713, 682 cm^{-1}; ^1H NMR δ: 1.21-1.36 (m, 2 H), 1.43-1.49 (m, 1 H), 1.72-1.78 (m, 1 H), 1.85-1.92 (m, 1 H), 1.95-2.02 (m, 2 H), 2.06-2.35 (m, 4 H), 2.28 (s, 6 H, $ArCH_3$), 2.38 (s, 6 H, $ArCH_3$), 2.41-2.51 (m, 3 H), 2.62-2.68 (m, 1 H), 3.60-3.66 (m, 1 H, CH), 3.73-3.83 (m, 1 H, COD), 3.88-3.99 (m, 3 H), 4.56-4.60 (m, 1 H, COD), 6.70-6.74 (m, 2 H, ArH), 6.93 (s, 1 H, imidazole-H), 7.05-7.07 (m, 1 H, ArH), 7.19-7.20 (m, 1 H, ArH), 7.46-7.49 (m, 4 H, ArH), 7.52-7.54 (m, 4 H, BAr_F), 7.64-7.66 (m, 2 H, ArH), 7.71-7.75 (m, 8 H, BAr_F); ^{13}C NMR δ: 20.4, 21.2, 21.4, 25.9, 28.1, 28.3, 33.0, 35.4 (d, J_{CP}= 5.8 Hz), 36.6 (d, J_{CP}= 4.7 Hz), 45.9, 61.8, 63.8, 90.9 (d, J_{CP}= 13.9 Hz), 96.3 (d, J_{CP}= 10.0 Hz), 117.4-117.95 (BAr_F, 4C), 119.1, 126.4, 128.0-133.9 (ArC), 134.8 (m, BAr_F), 138.8 (d, J_{CP}= 11.1 Hz), 139.2 (d, J_{CP}= 10.8 Hz), 142.1, 147.3 (d, J_{CP}= 4.4 Hz), 161.7 (q, J_{CB}= 49.8 Hz); ^{31}P NMR δ: 15.1; ^{19}F NMR δ: -62.8. HR-MS (ESI): *m/*z=753.2939 (100%), 751.2913 (51%), 754.2974 (35%), calcd. for $[C_{38}H_{45}IrN_2P]^+$: 753.2950 (100%), 751.2926 (60%), 754.2983 (41%).

General procedure for racemate synthesis

A round-bottomed flask was charged with olefin (100 mg), Pd/C (2 mol %) and EtOH (abs, 2 mL) or EtOAc. The mixture was hydrogenated with H_2 (1 atm) for 12-72 h. The product mixture was filtered through a plug of Celite® and the solvent was removed *in vacuo*.

General procedure for the hydrogenation of olefins (Table 1)

A vial was charged with a substrate (0.25 mmol) and catalyst (0.5 mol%) and 1 mL of anhydrous CH_2Cl_2 was added. The vial was placed in a high-pressure equipment which was purged with three times with H_2 before it was pressurized to 50 bars. The mixture was stirred at rt o.n.. The pressure was released and solvent was removed *in vacuo*. The residue was dissolved in Et_2O:pentane (1:5) and filtered through short plug of silica. The solvent was evaporated and the conversion was determined by ^1H NMR and enantiomer excess by GC/MS (G-TA) or chiral HPLC. Separation details, retention times for enantiomers and starting materials are shown in the table below.

Entry	Substrate		Substrate T_R (min)	T_{R1} (min)	T_{R2} (min)	Separation method
1		**15**	24.5	13.3 (*R*)	21.8 (*S*)	HPLC (chiracel OJ-H column, 254 nm, 20°C, n-hexane: *i*PrOH 99/1
2		**16**	43.1	37.4 (*S*)	37.6 (*R*)	GC (G-TA 60°C, 30 min, 5°C/min, 175°C, 100kPa)
3		**17**	47.93	43.80 (*S*)	43.95 (*R*)	GC (G-TA 60°C, 30 min, 3°C/min, 175°C, 100kPa)
4		**18**	21.1	11.2 (*S*)	13.8 (*R*)	HPLC (chiracel OB-H column, 254 nm, 20°C, n-hexane: *i*PrOH 99.5/0.5
5		**19**	39.5	35.4 (*R*)	37.4 (*S*)	GC (G-TA 60°C, 30 min, 3°C/min, 175°C, 100kPa)
6		**20**	39.0	33.9 (*S*)	34.3 (*R*)	GC (G-TA 60°C, 30 min, 3°C/min, 175°C, 100kPa
7		**21**	29.4	18.1 (*S*)	20.4 (*R*)	HPLC (chiracel AS-H column, 254 nm, 20°C, n-hexane: *i*PrOH 96.5/3.5
8		**22**	as above	as above	as above	Reflux of the acetate in EtOH with K_2CO_3 yields the free alcohol
9		**23**	21.7	14.9 (*S*)	17.5 (*R*)	HPLC (chiracel AS-H column, 254 nm, 20°C, n-hexane: *i*PrOH 96.5/3.5
10		**24**	as above	as above	as above	Reflux of the acetate in EtOH with K_2CO_3 yields the free alcohol

General procedure for hydrogenations of vinyl fluorides

A vial was charged with substrate and catalyst (0.5-1.5 mol %) and CH_2Cl_2 (1-2 mL) was added. For 100 bar hydrogenations: The vial was placed in high-pressure steel equipment, which was purged three times with H_2 before it was pressurized to 100 bars, heated to working temperature and held at this pressure for 63 – 72 hours. One hour before the end of the reaction, the heating was turned off. The pressure was released and the solvent was evaporated off. For hydrogenations at pressures up to 30 bar: The vial was placed in a Endeavor™ Catalyst screening system. Vessels were purged three times with Ar (10 atm), and then flushed and pressurized with H_2 to working pressure and stirred at 700 rpm for 24 hours. In all cases, conversions were measured by ^{1}H NMR after evaporation of solvent. 1.5 mL of Et_2O:pentane (1:1) was added, the solution was filtered through a short plug of silica. The silica plug was rinsed with 3 mL Et_2O:pentane (1:1). The solvent was evaporated and the *ee* was determined by GC-MS (G-TA or B-DM, 90°C 30 min, 1°C/min 130°C, 20°C/min 175°C, 14.5 psi, 1.5 ml/min) or HPLC (*Chiralcel* OB-H, i.d. 4.6 mm × 25 cm 3% *i*-PrOH: 97% *n*-hexane 0.5 mL/min, 220 nm).

Hydrogenation of 1:10 Z:E ethyl 2-fluoro-3-phenylacrylate (25) (Table 3, entry 1):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1 mol % of catalyst, 1 mL CH_2Cl_2; (*R*)-2-fluoro-3-phenylpropanoate. The *ee* was determined on GC-MS (B-DM column): t_R = 48.5 min (major), 52.8 min (minor).

Complex (*R*)-**12***:* Conditions: 100 bar, 40 °C, 63 h, 0.5 mol %, 2 mL CH_2Cl_2; (*S*)-2-fluoro-3-phenylpropanoate. The *ee* was determined on GC-MS (T-GA column): t_R = 34.2 min (minor), 38.5 min (major).

Hydrogenation of (Z)-ethyl 2-fluoro-3-phenylacrylate (26) (Table 3, entry 2):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1 mol % of catalyst, 1 mL CH_2Cl_2; (*S*)-2-fluoro-3-phenylpropanoate. The *ee* was determined on GC-MS (B-DM column): t_R = 48.5 min (minor), 52.8 min (major).

Complex (*R*)-**12***:* Conditions: 100 bar, 40 °C, 72 h, 1 mol %, 2 mL CH_2Cl_2; (*R*)-2-fluoro-3-phenylpropanoate. The *ee* was determined on GC-MS (T-GA column): t_R = 34.2 min (major), 38.5 min (minor).

Hydrogenation of (E)- 2-fluoro-3-phenylbut-2-enyl acetate (27) (Table 3, entry 3):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1 mol %, 1 mL CH_2Cl_2; (*S*)-2-fluoro-3-phenylpropyl acetate. The *ee* was determined by GC-MS (B-DM column), t_R = 53.6 min (major), 54.3 min (minor).

Complex (*R*)-**12***:* Conditions: 100 bar, room temp, 72 h, 1 mol %, 1 mL CH_2Cl_2; (*R*)-2-fluoro-3-phenylpropyl acetate. The *ee* was determined by GC-MS (B-DM), t_R = 53.6 min (minor), 54.3 min (major).

Hydrogenation of (Z)- 2-fluoro-3-phenylbut-2-enyl acetate (28) (Table 3, entry 4):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1 mol %, 1 mL CH_2Cl_2; (*S*)-2-fluoro-3-phenylpropyl acetate. The *ee* was determined by GC-MS (B-DM column), t_R = 53.6 min (major), 54.3 min (minor).

Complex (*R*)-**12***:* Conditions: 30 bar, room temp, 24 h, 1 mol %, 2 mL CH_2Cl_2; (*R*)-2-fluoro-3-phenylpropyl acetate. The *ee* was determined by GC-MS (T-GA), t_R = 39.3 min (major), 40.1 min (minor).

Hydrogenation of (E)-2-fluoro-3-phenylprop-2-en-1-ol (29) (Table 3, entry 5):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1 mol %, 1 mL CH_2Cl_2; (*R*)-2-fluoro-3-phenylpropan-1-ol. The *ee* was determined on chiral HPLC (OB-H, 3% *i*-PrOH: 97% n-hexane), t_R = 36.0 min (major), 39.5 min (minor).

Complex (*R*)-**12***:* Conditions: 100 bar, room temp, 72 h, 1 mol %, 1 mL CH_2Cl_2; (*S*)-2-fluoro-3-phenylpropyl acetate. The *ee* was determined by HPLC (OB-H, 3% *i*-PrOH: 97% n-hexane), t_R = 36.0 min (minor), 39.5 min (major).

Hydrogenation of (Z)-2-fluoro-3-phenylprop-2-en-1-ol (30) (Table 3, entry 6):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1.5 mol %, 1 mL CH_2Cl_2; (*S*)-2-fluoro-3-phenylpropan-1-ol. The *ee* was determined on chiral HPLC (OB-H, 3% *i*-PrOH: 97% n-hexane), t_R = 36.0 min (minor), 39.5 min (major).

Complex (*R*)-**12***:* Conditions: 30 bar, room temp, 24 h, 1 mol %, 2 mL CH_2Cl_2; (*R*)-2-fluoro-3-phenylpropyl acetate. The *ee* was determined by HPLC (OB-H, 3% *i*-PrOH: 97% n-hexane), t_R = 36.0 min (major), 39.5 min (minor).

Hydrogenation of (E)-ethyl 2-fluoro-3-phenylbut-2-enoate (31) (Table 3, entry 7):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1 mol %, 1 mL CH_2Cl_2; (+)-(*2S**,*3S**)-ethyl-2-fluoro-3-phenylbutanoate. The *ee* was determined by GC-MS (B-DM column), t_R = 46.9 min (major), 47.4 min (minor).

Hydrogenation of (Z)-ethyl 2-fluoro-3-phenylbut-2-enoate (32) (Table 3, entry 8):

Complex (*S*)-**14***:* Conditions: 100 bar, room temp, 72 h, 1 mol %, 1 mL CH_2Cl_2; (+)-(*2R**,*3S**)-ethyl-2-fluoro-3-phenylbutanoate. The *ee* was determined by GC-MS (B-DM column), t_R = 48.7 min (minor), 49.3 min (major).