

Iridium-Catalyzed Enantioselective Hydrogenation of Terminal Alkenes

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– Supporting Information –

1. Synthesis and Characterization of Substrates and Hydrogenation Products

General Remarks:

NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. References were for ^1H NMR: TMS \equiv 0 ppm or $\text{CHCl}_3 \equiv$ 7.26 ppm and for ^{13}C NMR: TMS \equiv 0 ppm or $\text{CDCl}_3 \equiv$ 77.0 ppm. IR spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer. Spectra of liquids were measured neat as thin films between two sodium chloride plates, those of solids as KBr disks. EI and FAB mass spectra were measured on mass spectrometers VG70-250 (EI) and Finnigan MAT 312 (FAB). The ions were generated by electron ionization (EI, 70 eV) or bombardment with fast xenon atoms (FAB), using 3-nitrobenzyl alcohol (3-NBA) as matrix and sometimes potassium chloride as additive in the latter case. The data are given in mass units per charge (m/e), and the intensities of the signals are indicated in percent of the basis ion. The elemental analyses were carried out on Leco CHN-900 (C-, H-, N-detection) and Leco RO-478 (O-detection) analyzers. The data are indicated in mass percents. For gas chromatographic analysis, Carlo Erba HRGC Mega2 Series MFC 800 chromatographs were used. Conversions were determined by GC with a Restek Rtx-1701 column, 0.25 μm , 30 m, 60 kPa He using the following temperature program: 100 $^\circ\text{C}$ for 2 min, 7 K/min to 250 $^\circ\text{C}$ for 10 min, separations of the enantiomers were performed on β - or γ -CD modified capillary columns. For HPLC analysis, Shimadzu systems with a SCL-10A System Controller, CTO-10AC column oven, LC10-AD pump system, DGU-14A degasser, and a SPD-M10A Diode Array Detector or a UV-vis detector (220 nm and 254 nm) were used. For separation of the enantiomers by HPLC Chiracel OD-H column from Daicel Chemical Industries Ltd. was used (250 mm x 4.6 mm). Optical rotations were measured in a Perkin Elmer Polarimeter 341, sodium lamp, 1 dm cuvette lengths, c in g/100 ml. Melting points were measured with a Büchi 535 melting point apparatus and are not corrected.

For thin-layer chromatography (TLC), Macherey-Nagel Polygram plates SIL G/UV254, 0.2 mm silica with fluorescence indicator, were used. Column chromatographic separations were

performed on silica 60 (particle size 40-63 μm , 230-400 mesh) purchased at Merck-Schuchardt (now VWR), or Uetikon Chemie, accelerated by pressurized air or nitrogen (flash chromatography). High-pressure hydrogenations (up to 100 bar) were carried out in 60 ml autoclaves of Premex AG, Lengnau, Switzerland. Hydrogen gas used in all experiments was purchased at Carbagas Switzerland at quality 45 (99.995%).

Reactions with air- or moisture-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques, or in a nitrogen atmosphere in a M. Braun glove box ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 2$ ppm). Glassware was oven-dried and then flame-dried under vacuum prior to use.

Solvents were purchased dry from Fluka or Aldrich in septum sealed bottles and kept in an inert atmosphere over molecular sieves. 2-(4-methoxyphenyl)-1-butene (**7a**) was prepared and its hydrogenation products was analyzed following literature procedures.^[1] 2-(4-methylphenyl)-1-butene (**7b**), 2-(4-trifluoromethylphenyl)-1-butene (**7c**), 2-(4-chlorophenyl)-1-butene (**7d**), 2-(4-bromophenyl)-1-butene (**7e**), 2-(3-chlorophenyl)-1-butene (**7f**), and 2-(3-bromophenyl)-1-butene (**7g**) were prepared by standard Wittig olefinations.^[2] 2-(4-Chloro-phenyl)-prop-2-en-1-ol (**9**) was prepared according to literature procedure.^[3] Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr_F) was prepared according to literature procedures.^[4] Chiral ligands and their Iridium complexes were prepared according to literature procedures.^[5]

Experimental Data of Substrates **7a-g** and Hydrogenation Products **8a-g**

2-(4-Methoxyphenyl)-1-butene (**7a**)

To a suspension of methyltriphenylphosphonium bromide (21.8 g, 61.0 mmol, 1.0 equiv.) in THF (400 mL) at 0-5°C under N_2 was added *n*-butyllithium (2.5 M, 26.4 mL., 65.8 mmol, 1.1 equiv.) dropwise over 30 minutes. The resulting orange solution was stirred at 0-5°C for 3 hours. A solution of 4-methoxypropiophenone (9.84 g, 60.0 mmol, 0.98 equiv.) in THF (20 mL) was added and the resulting yellow solution was allowed to warm to ambient temperature for 30 minutes before warming to reflux for 16 hours by which time, TLC indicated complete reaction. The solution was cooled to ambient temperature, water (10 mL) was added and the THF was removed *in vacuo* at 35-40°C. Diethylether (200 ml) was added to the residue and the precipitate was removed by filtration through a pad of silica. The collected solids were washed with further diethylether (3×50 mL) and the filtrate was concentrated *in vacuo*. The crude product was purified on silica eluting with hexane/ethylacetate (99:1) and the product after chromatography was distilled under reduced pressure to furnish the title compound as a colorless liquid (7.18 g, 44.3 mmol, 74%).

¹H-NMR (400.1 MHz, CDCl₃, 300 K): *d* = 1.07 (t, *J* = 7.3 Hz, 3H, CH₂CH₃), 2.45 (q, *J* = 7.3 Hz, 2H, CH₂CH₃), 3.76 (s, 3H, OCH₃), 4.94 (s, 1H, C=CH₂), 5.17 (s, 1H, C=CH₂), 6.82 (d, *J* = 8.9 Hz, Ar-H), 7.33 (d, *J* = 8.9 Hz, Ar-H) ppm.

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 300 K): *d* = 13.0 (CH₃), 28.1 (CH₂), 55.2 (OCH₃), 109.4 (C=CH₂), 113.6 (Ar-CH), 127.0 (Ar-CH), 133.9 (Ar-C), 149.3 (C=CH₂), 160.0 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 3082m, 3040m, 2965s, 2836m, 2053w, 1886w, 1785w, 1609s, 1574m, 1511s, 1461s, 1373w, 1292s, 1245s, 1180s, 1118m, 1035s, 888s, 834s, 803m, 744w cm⁻¹.

MS (EI): *m/z* (%) = 162 (M⁺, 100), 147 (40), 133 (86), 115 (8), 91 (13), 77 (10).

HRMS calculated for C₁₁H₁₄O: *m/z* = 162.1045. Found: 162.1048.

R_f (GC, Restek Rtx-1701, 60 kPa He) = 13.0 min.

2-(4-Methylphenyl)-1-butene (7b)

4-Methylpropiophenone (3.0 g, 20.3 mmol) was treated as above to furnish the title compound as a colorless liquid (1.51g, 10.3 mmol, 10%).

TLC (hexane): *R_f* = 0.93.

Boiling point: 48-51°C, 0.08 mbar.

¹H-NMR (400.1 MHz, CDCl₃, 300 K): *d* = 1.21 (t, *J* = 7.3 Hz, 3H, CH₂CH₃), 2.44 (s, 3H, CCH₃), 2.60 (q, *J* = 7.3 Hz, 2H, CH₂CH₃), 5.12 (s, 1H, C=CH₂), 5.35 (s, 1H, C=CH₂), 7.22 (d, *J* = 7.3 Hz, Ar-H), 7.41 (d, *J* = 7.3 Hz, Ar-H) ppm.

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 300 K): *d* = 13.5 (CH₃), 21.5 (CH₃), 28.6 (CH₂), 110.2 (C=CH₂), 126.4 (Ar-CH), 129.1 (Ar-CH), 137.4 (Ar-C), 139.1 (Ar-C), 150.7 (C=CH₂) ppm.

IR (NaCl): $\tilde{\nu}$ = 3083m, 3024m, 2967s, 2928s, 2867m, 1900w, 1789w, 1627s, 1567w, 1512s, 1456s, 1375m, 1295m, 1261w, 1187w, 1118m, 1044m, 1019m, 891s, 824s, 732w cm⁻¹.

MS (EI): *m/z* (%) = 146 (M⁺, 99), 131 (100), 117 (54), 105 (7), 91 (34), 77 (6).

HRMS calculated for C₁₁H₁₄: $m/z = 146.1096$. Found: 146.1094.

R_f (GC, Restek Rtx-1701, 60 kPa He) = 4.9 min.

2-(4-Trifluoromethylphenyl)-1-butene (7c)

4-Trifluoromethylpropiophenone (3.0 g, 14.8 mmol) was treated as above to furnish the title compound as a colorless liquid (1.61g, 8.05 mmol, 54%).

TLC (hexane:EtOAc 90:10): $R_f = 0.94$.

Boiling point: 46-48°C, 0.1 mbar.

¹H-NMR (400.1 MHz, CDCl₃, 300 K): δ = 1.11 (t, $J = 7.3$ Hz, 3H, CH₂CH₃), 2.53 (q, $J = 7.3$ Hz, 2H, CH₂CH₃), 5.16 (s, 1H, C=CH₂), 5.34 (s, 1H, C=CH₂), 7.50 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.58 (d, $J = 8.3$ Hz, 2H, Ar-H) ppm.

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 300 K): δ = 13.2 (CH₃), 28.4 (CH₂), 113.3 (C=CH₂), 125.0 (q, $J = 272$ Hz, CF₃), 125.2 (q, $J = 3.8$ Hz, CCF₃), 129.5 (Ar-CH), 145.6 (Ar-C), 149.4 (C=CH₂) ppm.

¹⁹F-NMR (376.5 MHz, CDCl₃, 300 K): δ = -63.4 ppm.

IR (NaCl): $\tilde{\nu}$ = 3090w, 2972, 2939, 2884s, 1920w, 1803w, 1618m, 1573w, 1461w, 1406m, 1329s, 1167s, 1125s, 1069m, 1015m, 956w, 904m, 846s, 800w, 719w cm⁻¹.

MS (EI): m/z (%) = 200 (M⁺, 100), 185 (60), 171 (21), 165 (27), 151 (21), 131 (57), 116 (14), 91 (8).

HRMS calculated for C₁₁H₁₁F₃: $m/z = 200.0813$. Found: 200.0809.

R_f (GC, Restek Rtx-1701, 60 kPa He) = 7.5 min.

2-(4-Chlorophenyl)-1-butene (7d)

4-Chloropropiophenone (3.0 g, 18.1 mmol) was treated as above to furnish the title compound as a colorless liquid (1.36g, 8.2 mmol, 46%).

TLC (hexane): $R_f = 0.90$.

Boiling point: 58-59°C, 0.08 mbar.

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3 , 300 K): $\delta = 1.12$ (t, $J = 7.3$ Hz, 3H, CH_2CH_3), 2.51 (q, $J = 7.3$ Hz, 2H, CH_2CH_3), 5.12 (s, 1H, $\text{C}=\text{CH}_2$), 5.31 (s, 1H, $\text{C}=\text{CH}_2$), 7.26 - 7.37 (m, 4H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 300 K): $\delta = 13.3$ (CH_3), 28.4 (CH_2), 111.9 ($\text{C}=\underline{\text{C}}\text{H}_2$), 127.8 (Ar-CH), 128.8 (Ar-CH), 133.5 (Ar-C), 140.4 (Ar-C), 149.3 ($\underline{\text{C}}=\text{CH}_2$) ppm.

IR (NaCl): $\tilde{\nu} = 3085\text{m}$, 3040m, 2969s, 2935s, 2878m, 1898w, 1798w, 1691m, 1627m, 1592m, 1491s, 1461m, 1396m, 1294w, 1218w, 1094s, 1011s, 951w, 898s, 839s, 797w, 757w, 735w cm^{-1} .

MS (EI): m/z (%) = 166 (M^+ , 100), 151 (48), 137 (46), 131 (81), 115 (35), 101 (21), 91 (15), 77 (8).

HRMS calculated for $\text{C}_{10}\text{H}_{11}^{35}\text{Cl}$: $m/z = 166.0549$. Found: 166.0551.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 10.9 min.

2-(4-Bromophenyl)-1-butene (7e)

4-Bromopropiophenone (3.0 g, 14.1 mmol) was treated as above to furnish the title compound as a colorless liquid (1.99g, 9.5 mmol, 67%).

TLC (hexane:EtOAc 90:10) : $R_f = 0.68$.

Boiling point: 53-57°C, 0.08 mbar.

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3 , 300 K): $\delta = 1.12$ (t, $J = 7.3$ Hz, 3H, CH_2CH_3), 2.51 (q, $J = 7.3$ Hz, 2H, CH_2CH_3), 5.11 (s, 1H, $\text{C}=\text{CH}_2$), 5.31 (s, 1H, $\text{C}=\text{CH}_2$), 7.30 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.47 (d, $J = 8.3$ Hz, 2H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 300 K): $\delta = 13.3$ (CH_3), 28.4 (CH_2), 112.0 ($\text{C}=\underline{\text{C}}\text{H}_2$), 121.6 (Ar-CH), 128.1 (Ar-CH), 131.8 (Ar-C), 140.8 (Ar-C), 149.3 ($\underline{\text{C}}=\text{CH}_2$) ppm.

IR (NaCl): $\tilde{\nu} = 3084\text{m}$, 2967s, 2933s, 2878m, 1998w, 1800w, 1627s, 1587w, 1488s, 1462m, 1392m, 1293w, 1183w, 1108w, 1074s, 1008s, 897s, 831s, 735m cm^{-1} .

MS (EI): m/z (%) = 210 (M^+ , 88), 181 (29), 131 (69), 116 (100), 102 (50), 91 (27), 77 (13).

HRMS calculated for $C_{10}H_{11}^{79}Br$: m/z = 210.0044. Found: 210.0047.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 13.0 min.

2-(3-Chlorophenyl)-1-butene (7f)

3-Chloropropiophenone (3.0g, 18.1 mmol) was treated as above to furnish the title compound as a colorless liquid (2.02 g, 12.2 mmol, 67%).

TLC (hexane:EtOAc 90:10) : R_f = 0.94.

Boiling point: 58-61°C, 0.08 mbar.

1H -NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 1.12 (t, J = 7.3 Hz, 3H, CH_2CH_3), 2.51 (q, J = 7.3 Hz, 2H, CH_2CH_3), 5.12 (s, 1H, $C=CH_2$), 5.31 (s, 1H, $C=CH_2$), 7.26 - 7.30 (m, 3H, Ar-H), 7.47 (s, 1H, Ar-H) ppm.

$^{13}C\{^1H\}$ -NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 13.3 (CH_3), 28.4 (CH_2), 112.5 ($C=CH_2$), 124.6 (Ar-CH), 126.7 (Ar-CH), 127.7 (Ar-CH), 129.9 (Ar-CH), 134.6 (Ar-C), 143.9 (Ar-C), 149.3 ($C=CH_2$) ppm.

IR (NaCl): $\tilde{\nu}$ = 3083m, 2969s, 2935m, 2878m, 1937w, 1867w, 1802w, 1671w, 1628m, 1592s, 1563s, 1473s, 1411m, 1291m, 1258m, 1128m, 1083s, 1000w, 891s, 787s, 720m, 677m cm^{-1} .

MS (EI): m/z (%) = 166 (M^+ , 96), 151 (31), 137 (20), 131 (100), 115 (37), 101 (16), 91 (23), 77 (8).

HRMS calculated for $C_{10}H_{11}^{35}Cl$: m/z = 166.0549. Found: 166.0548.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 10.8 min.

2-(3-Bromophenyl)-1-butene (7g)

3-Bromopropiophenone (3.0 g, 18.1 mmol) was treated as above to furnish the title compound as a colorless liquid (2.02 g, 9.6 mmol, 53%).

TLC (hexane:EtOAc 90:10) : R_f = 0.87.

Boiling point: 56-58°C, 0.08 mbar.

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3 , 300 K): δ = 1.12 (t, J = 7.3 Hz, 3H, CH_2CH_3), 2.49 (q, J = 7.3 Hz, 2H, CH_2CH_3), 5.11 (s, 1H, $\text{C}=\text{CH}_2$), 5.29 (s, 1H, $\text{C}=\text{CH}_2$), 7.20 (t, J = 7.8 Hz, 1H, Ar-H), 7.34 (d, J = 7.8 Hz, 1H, Ar-H), 7.41 (d, J = 7.8 Hz, 1H, Ar-H), 7.47 (s, 1H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 300 K): δ = 13.3 (CH_3), 28.4 (CH_2), 112.5 ($\text{C}=\text{CH}_2$), 122.9 (Ar-CH), 125.1 (Ar-CH), 129.6 (Ar-CH), 130.2 (Ar-CH), 130.6 (Ar-C), 144.2 (Ar-C), 149.2 ($\text{C}=\text{CH}_2$) ppm.

IR (NaCl): $\tilde{\nu}$ = 3082m, 2968s, 2934m, 2878m, 1937w, 1868w, 1802w, 1692m, 1628m, 1590s, 1559s, 1471s, 1409m, 1290m, 1257m, 1212w, 1169w, 1125w, 1074w, 996m, 896s, 786s, 719m, 664m cm^{-1} .

MS (EI): m/z (%) = 210 (M^+ , 85), 181 (12), 156 (11), 131 (100), 116 (92), 102 (43), 91 (40), 77 (14).

HRMS calculated for $\text{C}_{10}\text{H}_{11}^{79}\text{Br}$: m/z = 210.0044. Found: 210.0048.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 12.7 min.

All hydrogenations were performed according to the procedure "Screening conditions for catalytic hydrogenations at elevated pressure" specified in the paper.

2-(4-Methoxyphenyl)-butane (8a)

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3 , 300 K): δ = 0.86 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.26 (d, J = 7.0 Hz, 3H, CHCH_3), 1.61 (quin, J = 7.3 Hz, 2H, CH_2), 2.59 (sext, J = 7.1 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 6.88 (d, J = 8.6 Hz, 2H, Ar-H), 7.15 (d, J = 8.6 Hz, 2H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 300 K): δ = 12.2 (CH_3), 22.0 (CH_3), 31.3 (CH_2), 40.8 (CH), 55.1 (OCH_3), 113.6 (Ar-CH), 127.8 (Ar-CH), 139.7 (Ar-C), 157.6 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 2959s, 2927s, 2872m, 2835m, 1877w, 1612m, 1583w, 1512s, 1459m, 1374w, 1300m, 1247s, 1179m, 1108w, 1038m, 957w, 829m, 681w cm^{-1} .

MS (EI): m/z (%) = 164 (M^+ , 19), 149 (5), 135 (100), 105 (9), 91 (7), 77 (5).

Anal. calculated for $C_{11}H_{16}O$: C 80.44; H 9.82; O 9.74. Found: C 80.44; H 9.68; O, 9.36.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 11.9 min.

Chiral CG (γ -CD, TFA, 30 m, 70 kPa H_2 , 60 °C for 30 min, 5 K/min to 100 °C, 20 K/min to 180 °C, for 10 min). R_t (S) = 37.4 min; R_t (R) = 37.6 min.

$[\alpha]_D^{23} = +27$ (c = 1.0, $CHCl_3$).

2-(4-Methylphenyl)-butane (8b)

1H -NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 0.83 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.23 (d, J = 6.8 Hz, 3H, $CHCH_3$), 1.59 (quin, J = 7.6 Hz, 2H, CH_2), 2.33 (s, 3H, CCH_3), 2.57 (sext, J = 7.1 Hz, 1H, CH), 7.10 (m, 4H, Ar-H) ppm.

$^{13}C\{^1H\}$ -NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 12.6 (CH_3), 21.3 (CH_3), 22.3 (CH_3), 31.5 (CH_2), 41.6 (CH), 127.3 (Ar-CH), 129.3 (Ar-CH), 135.5 (Ar-C), 145.0 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 3015m, 2981s, 2924s, 2872s, 1893w, 1789w, 1513s, 1456s, 1376m, 1308w, 1111w, 1018w, 958w, 815s cm^{-1} .

MS (EI): m/z (%) = 148 (M^+ , 34), 133 (5), 119 (100), 105 (14), 91 (17), 77 (6).

Anal. calculated for $C_{11}H_{16}$: C 89.12; H 10.88. Found: C 89.02; H 10.78.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 7.8 min.

Chiral CG (γ -CD, TFA, 30 m, 70 kPa H_2 , 50 °C for 40 min, 20 K/min to 180 °C for 10 min).

R_t (+) = 28.0 min; R_t (-) = 31.3 min.

$[\alpha]_D^{23} = +25$ (c = 2.0, $CHCl_3$).

2-(4-Trifluoromethylphenyl)-butane (8c)

$^1\text{H-NMR}$ (500.1 MHz, CDCl_3 , 300 K): δ = 0.83 (t, J = 7.5 Hz, 3H, CH_2CH_3), 1.24 (d, J = 6.8 Hz, 3H, CHCH_3), 1.62 (dq, J = 7.6, 1.0 Hz, 2H, CH_2), 2.57 (sext, J = 7.0 Hz, 1H, CH), 7.28 (d, J = 8.0 Hz, 2H, Ar-H), 7.54 (s, J = 8.0 Hz, 2H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz, CDCl_3 , 300 K): δ = 12.1 (CH_3), 21.6 (CH_3), 31.0 (CH_2), 41.6 (CH), 125.0 (q, J = 272 Hz, CF_3), 125.2 (q, J = 3.8 Hz, CCF_3), 127.4 (Ar-CH), 151.7 (Ar-C) ppm.

$^{19}\text{F-NMR}$ (376.5 MHz, CDCl_3 , 300 K): δ = -63.4 ppm.

IR (NaCl): $\tilde{\nu}$ = 2966s, 2930m, 2877m, 1916w, 1619m, 1459m, 1419m, 1378w, 1327s, 1164s, 1126s, 1071s, 1017m, 957w, 839m, 721w cm^{-1} .

MS (EI): m/z (%) = 202 (M^+ , 32), 183 (7), 173 (100), 159 (22), 133 (18), 103 (4).

Anal. calculated for $\text{C}_{11}\text{H}_{13}\text{F}_3$: C 65.34; H 6.48. Found: C 65.31; H 6.66.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 6.8 min.

Chiral CG (γ -CD, TFA, 30 m, 100 kPa H_2 , 60 °C for 20 min, 20 K/min to 180 °C for 10 min).

R_t (+) = 9.4 min; R_t (-) = 10.5 min.

$[\alpha]_D^{23}$ = +15 (c = 2.0, CHCl_3).

2-(4-Chlorophenyl)-butane (8d)

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3 , 300 K): δ = 0.81 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.22 (d, J = 6.8 Hz, 3H, CHCH_3), 1.55 (dq, J = 7.6, 3.0 Hz, 2H, CH_2), 2.58 (sext, J = 7.1 Hz, 1H, CH), 7.11 (m, 2H, Ar-H), 7.25 (m, 2H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 300 K): δ = 12.5 (CH_3), 22.2 (CH_3), 31.4 (CH_2), 41.5 (CH), 128.7 (Ar-CH), 131.6 (Ar-C), 146.4 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 3029w, 2963s, 2926s, 2874s, 1893w, 1774w, 1647w, 1596w, 1491s, 1459s, 1409m, 1377m, 1179w, 1094s, 1013m, 959w, 826s, 759w, 718w cm^{-1} .

MS (EI): m/z (%) = 168 (M^+ , 34), 139 (100), 125 (17), 103 (41), 77 (15).

Anal. calculated for C₁₀H₁₃Cl: C 71.21; H 7.77. Found: C 71.26; H 7.80.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 10.1 min.

Chiral CG (γ-CD, TFA, 30 m, 100 kPa H₂, 60 °C for 30 min, 0.5 K/min to 70 °C, 20.0 K/min to 180 °C for 10 min). *R_t* (+) = 32.9 min; *R_t* (-) = 37.1 min.

$[\alpha]_D^{23} = +22$ (c = 2.0, CHCl₃).

2-(4-Bromophenyl)-butane (8e)

¹H-NMR (400.1 MHz, CDCl₃, 300 K): *d* = 0.82 (t, *J* = 7.3 Hz, 3H, CH₂CH₃), 1.22 (d, *J* = 6.8 Hz, 3H, CHCH₃), 1.59 (dquin, *J* = 7.6, 2.8 Hz, 2H, CH₂), 2.56 (sext, *J* = 7.1 Hz, 1H, CH), 7.06 (d, 2H, Ar-H), 7.40 (d, 2H, Ar-H) ppm.

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 300 K): *d* = 12.5 (CH₃), 22.1 (CH₃), 31.4 (CH₂), 41.5 (CH), 119.7 (Ar-C), 129.2 (Ar-CH), 131.6 (Ar-CH), 146.9 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 3025w, 2962s, 2925s, 2873s, 1893w, 1645w, 1590w, 1488s, 1459m, 1405m, 1377w, 1074m, 1009m, 958w, 823s, 752w, 715w cm⁻¹.

MS (EI): *m/z* (%) = 212 (M⁺, 34), 183 (100), 169 (9), 104 (68), 91 (6), 77 (15).

Anal. calculated for C₁₀H₁₃Br: C 56.36; H 6.15. Found: C 56.28; H 6.13.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 12.1 min.

Chiral CG (γ-CD, TFA, 30 m, 100 kPa H₂, 60 °C for 30 min, 1.0 K/min to 90 °C, 20.0 K/min to 180 °C for 10 min). *R_t* (+) = 50.1 min; *R_t* (-) = 52.6 min.

$[\alpha]_D^{23} = +20$ (c = 2.0, CHCl₃).

2-(3-Chlorophenyl)-butane (8f)

¹H-NMR (400.1 MHz, CDCl₃, 300 K): *d* = 0.84 (t, *J* = 7.3 Hz, 3H, CH₂CH₃), 1.23 (d, *J* = 6.8 Hz, 3H, CHCH₃), 1.59 (quin, *J* = 7.6 Hz, 2H, CH₂), 2.58 (sext, *J* = 7.1 Hz, 1H, CH), 7.08 (m, 1H, Ar-H), 7.21 (m, 3H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 300 K): δ = 12.5 (CH_3), 22.0 (CH_3), 31.3 (CH_2), 41.9 (CH), 125.7 (Ar-CH), 126.8 (Ar-CH), 127.5 (Ar-CH), 129.8 (Ar-CH), 134.4 (Ar-C), 150.1 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 3062w, 2963s, 2927s, 2874m, 1934w, 1862w, 1757w, 1595m, 1573m, 1462m, 1429m, 1378w, 1342w, 1205w, 1147w, 1082m, 1000w, 960w, 878m, 780s, 695m cm^{-1} .

MS (EI): m/z (%) = 168 (M^+ , 27), 139 (100), 125 (11), 103 (37), 91 (3), 77 (12).

Anal. calculated for $\text{C}_{10}\text{H}_{13}\text{Cl}$: C 71.21; H 7.77. Found: C 71.29 H 7.86.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 9.9 min.

Chiral CG (Hydrodex β -3P, 25 m, 60 kPa H_2 , 90 °C for 30 min, 20 K/min to 180 °C for 10 min).

R_t (-) = 19.0 min; R_t (+) = 19.7 min.

$[\alpha]_D^{23} = +22$ (c = 2.0, CHCl_3).

2-(3-Bromophenyl)-butane (8g)

^1H -NMR (400.1 MHz, CDCl_3 , 300 K): δ = 0.82 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.22 (d, J = 6.8 Hz, 3H, CHCH_3), 1.58 (quin, J = 7.6 Hz, 2H, CH_2), 2.57 (sext, J = 7.1 Hz, 1H, CH), 7.11 (m, 2H, Ar-H), 7.31 (m, 2H, Ar-H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 300 K): δ = 12.5 (CH_3), 22.0 (CH_3), 31.4 (CH_2), 41.9 (CH), 122.7 (Ar-C), 126.1 (Ar-CH), 129.2 (Ar-CH), 130.2 (Ar-CH), 130.5 (Ar-CH), 150.4 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 3060w, 2962s, 2926s, 2873m, 1935w, 1864w, 1692w, 1592m, 1567m, 1459m, 1426m, 1377w, 1342w, 1296w, 1205w, 1072m, 997w, 960w, 879w, 779s, 695m cm^{-1} .

MS (EI): m/z (%) = 212 (M^+ , 33), 183 (100), 169 (10), 133 (6), 117 (5), 104 (83), 91 (9), 77 (21).

Anal. calculated for $\text{C}_{10}\text{H}_{13}\text{Br}$: C 56.36; H 6.15. Found: C 56.47; H 6.17.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 11.8 min.

Chiral CG (Hydrodex β -3P, 25 m, 60 kPa H₂, 90 °C for 40 min, 20 K/min to 180 °C for 10 min).

R_t (-) = 33.3 min; R_t (-) = 34.3 min.

$[\alpha]_D^{23} = +19$ ($c = 2.0$, CHCl₃).

2-(4-Chlorophenyl)-prop-2-en-1-ol (9)^[3]

¹H-NMR (400.1 MHz, CDCl₃, 300 K): δ = 1.65 (br s, 1H, OH), 4.51 (m, 2H, CH₂OH), 5.36 (m, 1H, C=CH₂), 5.46 (m, 1H, C=CH), 7.31 (d, $J = 8.9$ Hz, 2H, Ar-H), 7.38 (d, $J = 8.9$ Hz, 2H, Ar-H) ppm.

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 300 K): δ = 65.4 (CH₂), 113.7 (C=CH₂), 127.8 (Ar-CH), 129.1 (Ar-CH), 134.2 (Ar-C), 137.3 (Ar-C), 146.6 (C=CH₂) ppm.

IR (NaCl): $\tilde{\nu}$ = 3585m, 3337s, 3091m, 2877m, 2361m, 1899w, 1633w, 1594w, 1562w, 1493w, 1396m, 1309w, 1227w, 1092s, 1040s, 1015s, 909s, 833s, 765w, 739w cm⁻¹.

MS (EI): m/z (%) = 168 (M⁺, 100), 137 (78), 125 (54), 115 (26), 112 (29), 101 (61), 91 (33).

Anal. calculated for C₉H₉ClO: C 64.11; H 5.38. Found: C 63.97; H 5.47.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 17.3 min.

2-(4-Chlorophenyl)-propan-1-ol (10)

¹H-NMR (500.1 MHz, CDCl₃, 300 K): δ = 1.24 (d, $J = 7.0$ Hz, 3H, CHCH₃), 1.58 (br s, 1H, OH), 2.91 (sext, $J = 6.5$ Hz, 1H, CH), 3.66 (q, $J = 11.5$ Hz, 1H, CH₂), 3.67 (q, $J = 7.5$ Hz, 1H, CH₂), 7.17 (dt, $J = 7.5$ Hz, 2.5 Hz, 2H, Ar-H), 7.29 (dt, $J = 7.5$ Hz, 2.5 Hz, 2H, Ar-H) ppm.

¹³C{¹H}-NMR (125.8 MHz, CDCl₃, 300 K): δ = 17.6 (CH₃), 41.9 (CH), 68.5 (CH₂), 128.7 (Ar-CH), 128.9 (Ar-CH), 132.3 (Ar-C), 142.2 (Ar-C) ppm.

IR (NaCl): $\tilde{\nu}$ = 3352s, 3046m, 2963s, 2928s, 2876s, 1896w, 1716w, 1647w, 1596w, 1491s, 1461s, 1409s, 1265m, 1231m, 1185m, 1092s, 1040s, 1015s, 976m, 938w, 891w, 825s, 788w, 766w, 719w cm⁻¹.

MS (EI): m/z (%) = 170 (M⁺, 19), 139 (100), 103 (53), 91 (3).

Anal. calculated for C₉H₁₁ClO: C 63.35; H 6.50; O 9.38. Found: C 63.60; H 6.73; O 9.65.

R_t (GC, Restek Rtx-1701, 60 kPa He) = 16.2 min.

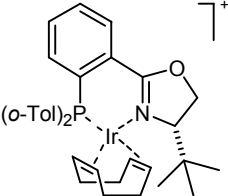
Chiral HPLC (Daicel Chiralcel OD-H, heptane/Isopropanol 99.8:0.2, 0.8 mL/min, 40 °C):

R_t (-) = 43.0 min; R_t (+) = 46.1 min; R_t (SM) = 69.0 min.

$[\alpha]_D^{23} = +7.2$ (c = 1.7, CHCl₃, ee = 86%).

2. Additional Results from Ir-catalyzed Hydrogenation Reactions

Table S1: Hydrogenation of substrates **7a-g** with catalyst **Ir-1** using three different reaction conditions.

| Entry | Complex ^[a] | Substrate | <i>p</i> [bar] | <i>T</i> [°C] | Time [min] | Conv. ^[b] [%] | ee ^[c] [%] |
|-------|--|-----------|-------------------|---------------|---------------|-----------------------------|--------------------------|
| 1 |  Ir-1 | 7a | 50 | 25 | 60 | >99 | rac |
| 2 | | 7a | 1 | 25 | 30 | >99 | 61 |
| 3 | | 7a | 1 | 0 | 60 | >99 | 18 |
| 4 | | 7b | 50 | 25 | 60 | >99 | rac |
| 5 | | 7b | 1 | 25 | 30 | >99 | 46 |
| 6 | | 7b | 1 | 0 | 60 | >99 | 6 |
| 7 | | 7c | 50 | 25 | 60 | >99 | 7 |
| 8 | | 7c | 1 | 25 | 30 | >99 | 40 |
| 9 | | 7c | 1 | 0 | 60 | >99 | 9 |
| 10 | | 7d | 50 | 25 | 60 | >99 | 4 |
| 11 | | 7d | 1 | 25 | 60 | >99 | 47 |
| 12 | | 7d | 1 | 0 | 60 | >99 | 11 |
| 13 | | 7e | 50 | 25 | 60 | >99 | 6 |
| 14 | | 7e | 1 | 25 | 60 | >99 | 51 |
| 15 | | 7e | 1 | 0 | 60 | >99 | 12 |
| 16 | | 7f | 50 | 25 | 60 | >99 | 12 |
| 17 | | 7f | 1 | 25 | 30 | >99 | 55 |
| 18 | | 7f | 1 | 0 | 60 | >99 | 16 |
| 19 | | 7g | 50 | 25 | 60 | >99 | 11 |
| 20 | | 7g | 1 | 25 | 60 | >99 | 55 |
| 21 | | 7g | 1 | 0 | 60 | >99 | 14 |

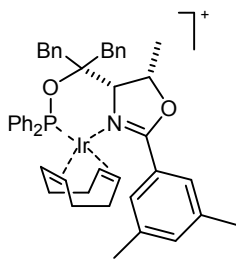
a) 1 mol% of Ir-complex **Ir-1**. Anion: BARF⁻.

b) Determined by GC.

c) Determined by HPLC (see refs. [5b,5c]).

Table S2: Hydrogenation of substrates **7a-g** with catalyst **Ir-4** using three different reaction conditions.

| Entry | Complex ^[a] | Substrate | <i>p</i> [bar] | <i>T</i> [°C] | Time [min] | Conv. ^[b] [%] | ee ^[c] [%] |
|-------|------------------------|-----------|-------------------|---------------|---------------|-----------------------------|--------------------------|
| 1 | | 7a | 50 | 25 | 60 | >99 | 66 |
| 2 | | 7a | 1 | 25 | 30 | >99 | 86 |
| 3 | | 7a | 1 | 0 | 30 | >99 | 86 |
| 4 | | 7b | 50 | 25 | 60 | >99 | 67 |
| 5 | | 7b | 1 | 25 | 30 | >99 | 84 |
| 6 | | 7b | 1 | 0 | 30 | >99 | 81 |
| 7 | | 7c | 50 | 25 | 60 | >99 | 35 |
| 8 | | 7c | 1 | 25 | 30 | >99 | 50 |
| 9 | | 7c | 1 | 0 | 30 | >99 | 53 |
| 10 | | 7d | 50 | 25 | 60 | >99 | 47 |
| 11 | | 7d | 1 | 25 | 30 | >99 | 63 |
| 12 | | 7d | 1 | 0 | 30 | >99 | 59 |
| 13 | | 7e | 50 | 25 | 60 | >99 | 48 |
| 14 | | 7e | 1 | 25 | 30 | >99 | 60 |
| 15 | | 7e | 1 | 0 | 30 | >99 | 57 |
| 16 | | 7f | 50 | 25 | 60 | >99 | 53 |
| 17 | | 7f | 1 | 25 | 30 | >99 | 70 |
| 18 | | 7f | 1 | 0 | 30 | 97 | 68 |
| 19 | | 7g | 50 | 25 | 60 | >99 | 56 |
| 20 | | 7g | 1 | 25 | 30 | >99 | 71 |
| 21 | | 7g | 1 | 0 | 30 | >99 | 68 |

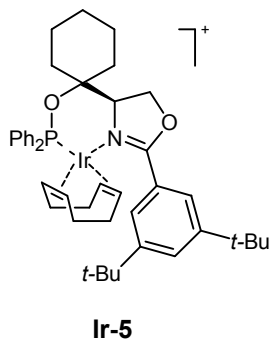
**Ir-4**a) 1 mol% of Ir-complex **Ir-4**. Anion: BAR_F^- .

b) Determined by GC.

c) Determined by HPLC (see refs. [5b,5c]).

Table S3: Hydrogenation of substrates **7a-g** with catalyst **Ir-5** using three different reaction conditions.

| Entry | Complex ^[a] | Substrate | <i>p</i> [bar] | <i>T</i> [°C] | Time [min] | Conv. ^[b] [%] | ee ^[c] [%] |
|-------|------------------------|-----------|-------------------|---------------|---------------|-----------------------------|--------------------------|
| 1 | | 7a | 50 | 25 | 60 | >99 | 61 |
| 2 | | 7a | 1 | 25 | 30 | >99 | 90 |
| 3 | | 7a | 1 | 0 | 30 | >99 | 78 |
| 4 | | 7b | 50 | 25 | 60 | >99 | 49 |
| 5 | | 7b | 1 | 25 | 30 | >99 | 89 |
| 6 | | 7b | 1 | 0 | 30 | >99 | 82 |
| 7 | | 7c | 50 | 25 | 60 | >99 | 26 |
| 8 | | 7c | 1 | 25 | 30 | >99 | 63 |
| 9 | | 7c | 1 | 0 | 30 | >99 | 59 |
| 10 | | 7d | 50 | 25 | 60 | >99 | 34 |
| 11 | | 7d | 1 | 25 | 30 | >99 | 77 |
| 12 | | 7d | 1 | 0 | 30 | >99 | 66 |
| 13 | | 7e | 50 | 25 | 60 | >99 | 38 |
| 14 | | 7e | 1 | 25 | 30 | >99 | 77 |
| 15 | | 7e | 1 | 0 | 30 | >99 | 66 |
| 16 | | 7f | 50 | 25 | 60 | >99 | 40 |
| 17 | | 7f | 1 | 25 | 30 | >99 | 79 |
| 18 | | 7f | 1 | 0 | 30 | >99 | 72 |
| 19 | | 7g | 50 | 25 | 60 | >99 | 41 |
| 20 | | 7g | 1 | 25 | 30 | >99 | 78 |
| 21 | | 7g | 1 | 0 | 30 | >99 | 73 |

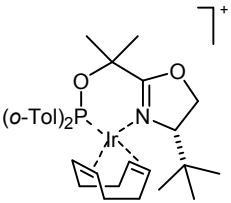


a) 1 mol% of Ir-complex **Ir-5**. Anion: BARF⁻.

b) Determined by GC.

c) Determined by HPLC (see refs. [5b,5c]).

Table S4: Hydrogenation of substrates **7a-g** with catalyst **Ir-6** using three different reaction conditions.

| Entry | Complex ^[a] | Substrate | <i>p</i> [bar] | <i>T</i> [°C] | Time [min] | Conv. ^[b] [%] | ee ^[c] [%] |
|-------|---|-----------|-------------------|---------------|---------------|-----------------------------|--------------------------|
| 1 |  | 7a | 50 | 25 | 60 | >99 | 51 |
| 2 | | 7a | 1 | 25 | 30 | >99 | 76 |
| 3 | | 7a | 1 | 0 | 30 | >99 | 62 |
| 4 | | 7b | 50 | 25 | 60 | >99 | 53 |
| 5 | | 7b | 1 | 25 | 30 | >99 | 77 |
| 6 | | 7b | 1 | 0 | 60 | >99 | 64 |
| 7 | | 7c | 50 | 25 | 60 | >99 | 42 |
| 8 | | 7c | 1 | 25 | 60 | >99 | 57 |
| 9 | | 7c | 1 | 0 | 30 | >99 | 53 |
| 10 | | 7d | 50 | 25 | 60 | >99 | 46 |
| 11 | | 7d | 1 | 25 | 30 | >99 | 68 |
| 12 | | 7d | 1 | 0 | 60 | >99 | 56 |
| 13 | | 7e | 50 | 25 | 60 | >99 | 45 |
| 14 | | 7e | 1 | 25 | 30 | >99 | 67 |
| 15 | | 7e | 1 | 0 | 60 | >99 | 56 |
| 16 | | 7f | 50 | 25 | 60 | >99 | 46 |
| 17 | | 7f | 1 | 25 | 30 | >99 | 69 |
| 18 | | 7f | 1 | 0 | 30 | >99 | 64 |
| 19 | | 7g | 50 | 25 | 60 | >99 | 47 |
| 20 | | 7g | 1 | 25 | 30 | >99 | 71 |
| 21 | | 7g | 1 | 0 | 30 | >99 | 60 |

a) 1 mol% of Ir-complex **Ir-6**. Anion: BARF^- .

b) Determined by GC.

c) Determined by HPLC (see ref. [5b,5c]).

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