Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Rh-Catalyzed Highly Enantioselective Synthesis of 3-Arylbutanoic Acids**

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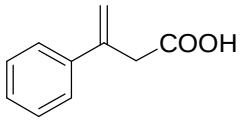
General Remarks. All reactions and manipulations were performed in a nitrogen-filled glovebox or under nitrogen using standard Schlenk techniques unless otherwise noted.

Column chromatography was performed using Sorbent silica gel 60 Å (230×450 mesh). ^{1}H NMR and ^{13}C NMR spectral data were recorded on Bruker DPX-300, CDPX-300, AMX-360, and DRX-400 MHz spectrometers. J values are in Hz. Chemical shifts were reported in ppm upfield to tetramethylsilane with the solvent resonance as the internal standard. MS spectra were recorded on a KRATOS mass spectrometer MS 9/50 for Electrospray (-). Enantiomeric ratios were determined by chiral GC or HPLC analysis.

General Procedure A for the Preparation of 3-Aryl-3-butenoic Acids 1a-1m:

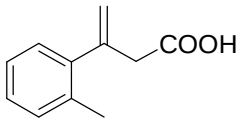
According to literatures[1], with a slight modification, the Grignard reagent was prepared from Mg turning (0.40g, 16.5 mmol) and aryl bromide (15.0 mmol) in 20 mL THF (For better selectivity of halogenated aryl substrates **1g-1k**, aryl bromide solution in THF was added in one portion to Mg turning with cool water bath after initiation). Diketene (1.05g, 12.5 mmol) and $Pd(PPh_3)_4$ (0.375 mmol, 3 mol%) in dry THF 20 mL under nitrogen were added dropwise to a suspension of arylzinc chloride, prepared by adding anhydrous $ZnCl_2$ (2.3 g, 16.8 mmol) in THF 15 mL to aryl magnesium bromide with ice-water cooling and the resulting mixture was stirred for additional 3 h at 0 ^{o}C. The reaction mixture was poured into a cold 2 equiv HCl aq and extracted with ether. The separated organic layer was extracted with 3 equiv NaOH aq. The alkaline extracts was acidified with 6 equiv HCl aq, and then extracted with ether (40 mL × 3). The ether extracts were combined, washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, most of the acids can be purified by recrystallization in hexane to give the corresponding 3-aryl-3-butenoic acids (60-97% isolated yields), which normally are good

enough for asymmetric hydrogenation as substrates. Or the residue was subject to silica gel column chromatography using hexanes-ether (5:1) as eluent for further purification.



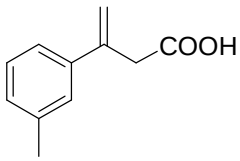
3-Phenyl-3-butenoic Acid (1a):[1]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.60 (s, 2H), 5.32 (s, 1H), 5.65 (s, 1H), 7.32-7.51 (m, 5H), 11.75 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 40.8, 116.7, 125.6, 127.8, 128.4, 139.3, 140.0, 178.1.



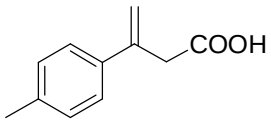
3-(2-Tolyl)-3-butenoic Acid (1b):[1]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 2.34 (s, 3H), 3.41 (s, 2H), 5.15 (d, *J* = 0.7 Hz, 1H), 5.44 (d, *J* = 1.0 Hz, 1H), 7.15-7.20 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 20.1, 43.1, 119.2, 126.0, 127.8, 128.8, 130.7, 135.3, 141.7, 141.9, 177.0.



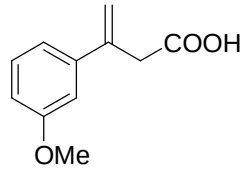
3-(3-Tolyl)-3-butenoic Acid (1c):[2]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 2.35 (s, 3H), 3.54 (s, 2H), 5.24 (s, 1H), 5.57 (s, 1H), 7.10-7.25 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.5, 40.8, 116.6, 122.8, 126.4, 128.4, 128.7, 138.0, 139.3, 140.2, 177.4.



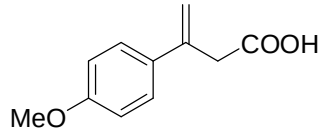
3-(4-Tolyl)-3-butenoic Acid (1d):[1]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 2.35 (s, 3H), 3.53 (s, 2H), 5.21 (s,1H), 5.56 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.1, 40.8, 116.0, 125.5, 129.2, 136.4, 137.8, 139.9, 177.6.



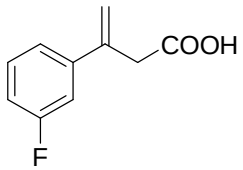
3-(3-Methoxyphenyl)-3-butenoic Acid (1e):

^{1}H NMR ($CDCl_3$, TMS, 360 MHz) d 3.46 (s, 2H), 3.75 (s, 3H), 5.19 (s, 1H), 5.51 (s, 1H), 6.75-7.78 (m, 1H), 6.90-7.16 (m, 2H) 7.18-7.20 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) d 40.9, 55.2, 111.6, 113.3, 117.0, 118.2, 129.4, 140.0, 140.9, 159.6, 177.7; ESI-HRMS Calcd. for $C_{11}H_{11}O_3$ ([M-H]$^-$): 191.0708. Found 191.0693.



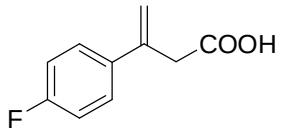
3-(4-Methoxyphenyl)-3-butenoic Acid (1f):[1]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.52 (s, 2H), 3.81 (s, 3H), 5.17 (d, *J* = 0.8 Hz, 1H), 5.44 (d, *J* = 0.6 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.9 Hz, 2H) 11.5 (s, br, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 41.0, 55.2, 113.8, 115.1, 126.8, 131.8, 139.4, 159.4, 177.9.



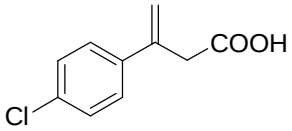
3-(3-Fluorophenyl)-3-butenoic Acid (1g):

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.81 (s, 2H), 5.59 (s, 1H), 5.88 (s, 1H), 7.26-7.59 (m, 4H) 11.86 (s, br, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 40.7, 112.7, 113.0, 114.6, 114.9, 118.0, 121.3, 121.4, 129.9, 130.0, 139.0, 139.1, 141.7, 141.8, 161.3, 164.5, 177.5; ^{19}F NMR ($CDCl_3$, TMS, 282 MHz) d -113.5; ESI-HRMS Calcd. for $C_{10}H_8FO_2$ ($[M-H]^-$) : 179.0508. Found 179.0505.



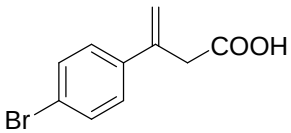
3-(4-Fluorophenyl)-3-butenoic Acid (1h):

^{1}H NMR ($CDCl_3$, TMS, 360 MHz) d 3.53 (s, 2H), 5.24 (s, 1H), 5.52 (s, 1H), 6.99-7.05 (m, 2H), 7.38-7.42 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 41.0, 115.2, 115.5, 116.8, 127.4, 127.5, 135.4, 135.3, 139.1, 160.9, 164.1, 177.7; ^{19}F NMR ($CDCl_3$, TMS, 282 MHz) d -114.7; ESI-HRMS Calcd. for $C_{10}H_8FO_2$ ($[M-H]^-$):179.0508. Found 179.0512.



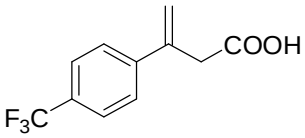
3-(4-Chlorophenyl)-3-butenoic Acid (1i):

^{1}H NMR ($CDCl_3$, TMS, 400 MHz) d 3.52 (s, 2H), 5.28 (s, 1H), 5.56 (s, 1H), 7.29-7.37 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 40.8, 117.5, 127.1, 128.6, 133.8, 137.8, 139.1, 177.4; ESI-HRMS Calcd. for $C_{10}H_8ClO_2$ ($[M-H]^-$): 195.0213. Found 195.0206.



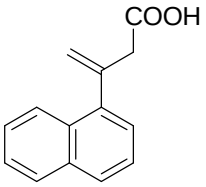
3-(4-Bromophenyl)-3-butenoic Acid (1j):

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.52 (s, 2H), 5.28 (s, 1H), 5.57 (s, 1H), 7.29 (d, *J* = 8.6 Hz, 2H) 7.46 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 40.7, 117.5, 122.0, 127.4, 131.6, 138.3, 139.1, 177.3; ESI-HRMS Calcd. for $C_{10}H_8BrO_2$ ([M-H]$^-$): 238.9708. Found 238.9693.



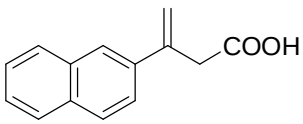
3-(4-Trifluoromethylphenyl)-3-butenoic Acid (1k):

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.57 (s, 2H), 5.38 (s, 1H), 5.64 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 11.86 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 40.67, 118.68, 118.97, 122.29, 125.38, 125.43, 125.48, 125.52, 125.89, 126.11, 129.27, 129.49, 129.70, 130.13, 130.57, 139.17, 143.00, 177.49; ^{19}F NMR ($CDCl_3$, TMS, 282 MHz) d -63.1; ESI-HRMS Calcd. for $C_{10}H_8F_3O_2$ ([M-H]$^-$): 229.0476. Found 229.0471.



3-(1-Naphthy)-3-butenoic Acid 9(1l):[1]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.59 (s, 2H), 5.39 (s, 1H), 5.65 (s, 1H), 7.39-7.54 (m, 4H) 7.80-7.90 (m, 2H) 8.04 (m, 1H), 11.40 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 43.3, 120.3, 125.2, 125.3, 125.4, 125.7, 126.1, 127.8, 128.4, 130.8, 133.7, 139.4, 140.3, 177.5;

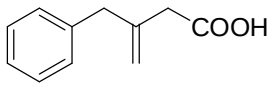


3-(2-Naphthyl)-3-butenoic Acid (1m):

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.70 (s, 2H), 5.40 (s, 1H), 5.77 (s, 1H), 7.49-7.54 (m, 2H) 7.64-7.68 (m, 1H) 7.82-7.88 (m, 4 H)11.74 (s, br, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 40.8, 117.3, 123.8, 124.5, 126.1, 126.2, 127.5, 128.1, 128.3, 132.9, 133.2, 136.5, 139.8, 178.1; ESI-HRMS Calcd. for $C_{14}H_{11}O_2$ ($[M-H]^-$): 211.0759. Found 211.0747.

Typical Procedure B for the Preparation of 3-Benzyl-3-butenoic Acid (1n):[2]

Nickel chloride (0.78 g, 6 mmol) was added to a solution of benzylmagnesium bromide, prepared from a suspension of Mg turning (1.6 g, 66 mol) in 100 mL THF and a solution of benzyl bromide (60 mmol) in 20 mL THF. After gently refluxing for 1 h, the mixture was stirred for 30 min at room temperature. A solution of diketene (3.36g, 40 mmol) in 20 mL THF was gradually added to the mixture at -78°C (dry ice-acetone bath). The reaction mixture was further stirred at -78°C for 3 h. Work-up as described for general procedure A afforded crude title substrate. Further purification was subject to silica gel column chromatography (hexane: ether = 2: 1).

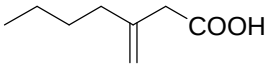


3-Benzyl-3-butenoic Acid (1n):[2]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 3.07 (s, 2H), 3.53 (s, 2H), 5.05 (d, *J* = 1.2 Hz, 1H), 5.09 (d, *J* = 1.2 Hz, 1H), 7.23-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 40.6, 42.6, 116.3, 126.4, 128.5, 129.1, 138.5, 141.2, 177.6.

Typical Procedure C for the Preparation of 3-Methyleneheptanoic Acid (1o):[3]

To a solution of cobalt (II) iodide (4.1 g, 13 mmol) in ether 100 mL was added diketene (10.1 g, 120 mmol) at-78°C. Then ethereal solution of n-butylmagenesium bromide, prepared from a suspension of Mg turning (3.5 g, 145 mmol) in 100 mL ether and a solution of n-butyl bromide (17.9 g, 132 mmol) in 40 mL ether, was slowly dropped and stirring was continued at -78°C for 6 h. Work-up as described for general procedure A afforded crude title substrate. Distillation (bp 78-80 °C/1 mmHg) gave pure product.



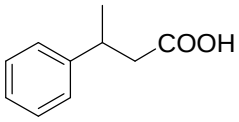
3-Methyleneheptanoic Acid (1o):[3]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 0.94 (t, *J* = 7.1 Hz, 3H), 1.26-1.61 (m, 4H), 2.15-2.43 (m, 2H), 3.11 (s, 2H) 4.98 (s, 2H), 11.32 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 14.1, 22.4, 29.7, 126.44, 35.4, 41.8, 114.2, 142.1, 178.5.

General Procedure D for Asymmetric Hydrogenation of ß,?-Unsaturated Carboxylic Acids 1:

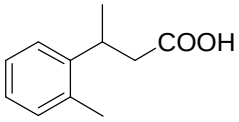
To a solution of $[Rh(nbd)_2]SbF_6$ (182.6 mg, 0.175 mmol) in THF (2 mL) at -20 ^{o}C was added a suspension of (S_p, R_c)-DuanPhos (140 mg, 0.366 mmol) in THF (6 mL). The resulting red solution was allowed to warm to r.t. and stirred for an additional 15 min. The solution was concentrated to about 6 mL. Then 25 mL of Et_2O was added under vigorous stirring, during which orange precipitate was formed. The precipitate was filtered and washed with Et_2O (10 mL × 2) to afford the orange solid complex (198 mg, 67%).[15] The complex was stored in a nitrogen filled glovebox for further usage. The complex (16.3 mg, 0.02 mmol) was dissolved in degassed methanol (100 mL) in a glovebox. 10 mL of the complex solution was divided equally among 10 vials. To each of

the vials, Et_3N (1.01 mg, 0.01 mmol) in 1 mL degassed water was added, followed by ß,?-unsaturated acid substrate (0.2 mmol, S/C = 1000). The resulting solution was then transferred into an autoclave and charged with 3 atm of hydrogen. The hydrogenation was performed at room temperature for 12 h. After carefully releasing the hydrogen, the solvent was removed by evaporation. The residue was dissolved in 20 mL ether and extracted with 3 equiv aq. NaOH (30 mL × 2). The alkaline solution was acidified with 6 equiv aq. HCl, and then extracted with ether (20 mL × 3). The ether extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated by evaporation. The residue was subject to silica gel column chromatography using hexanes-ether (8:1) as eluent for further purification. Enantiomeric excesses were directly determined by chiral GC (Gamma Dex 225 and Beta Dex 325) or HPLC (Chiral OD and OJ-H) under the following conditions.



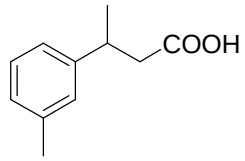
3-Phenylbutanoic Acid (2a):[4]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.36 (d, *J* = 7.0 Hz, 3H), 2.57-2.75 (m, 2H), 3.32 (m, 1H), 7.22-7.38 (m, 5H), 9.96 (s, br,1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.8, 36.1, 42.7, 126.4, 126.7, 128.5, 145.5, 178.7; $[\alpha]^{25}_D$ = + 24.5 (c = 1.0, EtOH) for 97% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm, column temperature: 120 ^{o}C, carrier gas: He, 1 mL/min, t_{major} = 66.3 min, t_{minor} = 69.6 min.



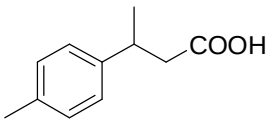
3-(2-Methylphenyl)butanoic Acid (2b):[5]

^{1}H NMR ($CDCl_3$, TMS, 400 MHz) d 1.30 (d, J = 6.9 Hz, 3H), 2.39 (s, 3H), 2.58 (dd, J_1 = 8.6 Hz, J_2 = 15.6 Hz, 1H), 2.70 (dd, J_1 = 6.3 Hz, J_2 = 15.6 Hz, 1H), 3.55 (m, 1H), 7.11-7.20 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) d 19.3, 21.2, 31.1, 41.8, 124.9, 126.2, 126.3, 130.5, 135.2, 143.6, 178.9; $[\alpha]^{25}_D$ = -24.5 (c = 1.0, CH_3Cl) for 98% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm, column temperature: 130^{o}C, carrier gas: He, 1 mL/min, t_{minor} = 57.7 min, t_{major} = 64.9min.



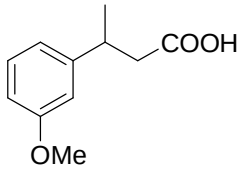
3-(3-Methylphenyl)butanoic Acid (2c):[6]

^{1}H NMR ($CDCl_3$, TMS, 400 MHz) d 1.42 (d, J = 7.0 Hz, 3H), 2.45 (s, 2H), 2.63-2.82 (m, 2H), 3.35 (m, 1H), 7.13-7.33 (m, 4H), 11.49 (s, br,1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.4, 21.8, 36.0, 42.7, 123.6, 127.2, 127.5, 128.4, 138.1, 145.3, 179.0; $[\alpha]^{25}_D$ = +36.8 (c = 1.0, CH_3Cl) for 96% *ee*; Chiral HPLC: Chiralpak OJ-H column, IPA/Hex = 1: 99, 1.0 mL/min, t_{major} = 32.3 min, t_{minor} = 41.3 min.



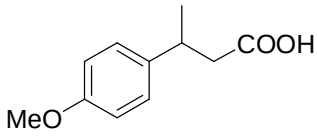
3-(4-Methylphenyl)butanoic Acid (2d):[7]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.14 (d, J = 7.0 Hz, 3H), 2.17 (s, 3H), 2.36-2.53 (m, 2H), 3.08 (m, 1H), 6.96 (s, 4H), 11.04 (s, br,1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.0, 21.9, 35.7, 42.7, 126.5, 129.2, 136.0, 142.4, 179.0; $[\alpha]^{25}_D$ = +33.5 (c = 1.3, CH_3Cl) for 97% *ee*; Chiral GC: Gamma Dex 225, 30 m x 0.25 mm, column temperature: 125 ^{o}C, carrier gas: He, 1 mL/min, t_{major} = 83.5 min, t_{minor} = 85.8 min.



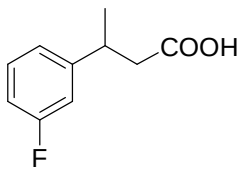
3-(3-Methoxylphenyl)butanoic Acid (2e):[8]

^{1}H NMR (CDCl3, TMS, 300 MHz) d 1.34 (d, *J* = 6.9 Hz, 3H), 2.55-2.74 (m, 2H), 3.28 (m, 1H), 3.83 (s, 3H), 6.77-6.87 (m, 3H), 7.23-7.28 (m, 1H), 9.51 (s, br,1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.7, 36.1, 42.5, 55.1, 111.5, 112.7, 119.0, 129.5, 147.2, 159.6, 178.5; $[\alpha]^{25}_D$ = +37.6 (c = 1.0, CH_3Cl) for 97% *ee*; Chiral HPLC: Chiralpak OJ-H column, IPA/Hex = 5: 95, 1.0 mL/min, t_{major} = 14.1 min, t_{minor} = 23.9 min.



3-(4-Methoxylphenyl)butanoic Acid (2f):[9]

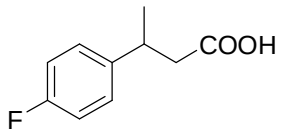
^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.29 (d, *J* = 6.9 Hz, 3H), 2.51-2.67 (m, 2H), 3.24 (m, 1H), 3.79 (s, 3H), 6.86 (d, *J* = 6.7 Hz, 2H), 7.16 (d, *J* = 6.7 Hz, 2H), 10.93 (s, br,1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.9, 35.3, 42.9, 55.2, 113.9, 127.6, 137.6, 158.1, 178.9; $[\alpha]^{25}_D$ = +27.5 (c = 1.0, EtOH) for 94% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm, column temperature: 140^{o}C, carrier gas: He, 1 mL/min, t_{major} = 94.6 min, t_{minor} = 96.1min.



3-(3-Fluorophenyl)butanoic Acid (2g):

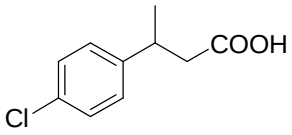
^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.17 (d, *J* = 7.0 Hz, 3H), 2.39-2.56 (m, 2H), 3.14 (dd, J_1 = 7.2 Hz, J_2 = 14.5 Hz, 1H), 6.74-6.81 (m, 2H), 6.86 (d, *J* = 7.7 Hz, 1H), 7.08-

7.16 (m, 1H), 10.75 (s, br,1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.7, 35.8, 35.9, 42.4, 113.2, 113.5, 113.8, 122.3, 122.4, 129.9, 130.1, 147.9, 148.1, 161.3, 164.6, 178.5; ^{19}F NMR ($CDCl_3$, TMS, 282 MHz) d -113.5; ESI-HRMS Calcd. for $C_{10}H_{10}FO_2$ ($[M-H]^-$) :181.0665. Found 181.0647; $[\alpha]^{25}_D$ = +35.8 (c = 1.0, CH_3Cl) for >99% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm, column temperature: 135 ^oC, carrier gas: He, 1 mL/min, t_{major} = 39.8 min, t_{minor} = 41.6 min.



3-(4-Fluorophenyl)butanoic Acid (2h):[10]

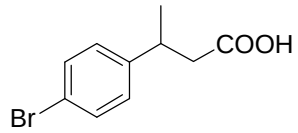
^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.29 (d, *J* = 7.0 Hz, 3H), 2.51-2.66 (m, 2H), 3.25-3.29 (m, 1H), 6.95-7.02 (m, 2H), 7.15-7.20 (m, 2H), 11.05 (s, br,1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.9, 35.5, 42.8, 115.1, 115.4, 128.1, 128.2, 141.0, 141.1 160.0, 163.1, 178.7; ^{19}F NMR ($CDCl_3$, TMS, 282 MHz) d -117.1; $[\alpha]^{25}_D$ = +35.8 (c = 0.7, CH_3Cl) for 95% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm, column temperature: 130 ^oC, carrier gas: He, 1 mL/min, t_{major} = 51.9min, t_{minor} = 54.7 min.



3-(4-Chlorophenyl)butanoic Acid (2i):[11]

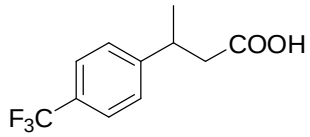
^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.32 (d, *J* = 7.0 Hz, 3H), 2.55-2.70 (m, 2H), 3.29 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H) 11.15 (s, br, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.8, 35.6, 42.4, 128.1, 128.7, 132.2, 143.8, 178.4; $[\alpha]^{25}_D$ = +47.8 (c = 0.8, CH_3Cl) for >99% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm,

column temperature: 135 ^{o}C, carrier gas: He, 1 mL/min, t_{major} = 122.7min, t_{minor} = 133.5 min.



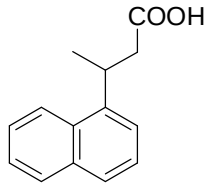
3-(4-Bromophenyl)butanoic Acid (2j):[12]

^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) d 1.28 (d, *J* = 7.0 Hz, 3H), 2.59-2.62 (m, 2H), 3.23 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 22.2, 36.3, 42.5, 120.5, 129.2, 132.1, 145.2, 177.5; $[\alpha]^{25}_{D}$ = +25.9 (c = 0.5, CH_3Cl) for 98% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm, column temperature: 160^{o}C, carrier gas: He, 1 mL/min, t_{major} = 50.209 min, t_{minor} = 52.341 min.



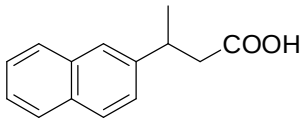
3-(4-Trifluoromethylphenyl)butanoic Acid (2k):[13]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.32 (d, *J* = 7.0 Hz, 3H), 2.56-2.71 (m, 2H), 3.33 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H) 10.78 (s, br, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.72, 36.01, 42.28, 122.39, 125.45, 125.50, 125.55, 125.60, 125.99, 127.12, 128.21, 128.64, 129.07, 129.49, 129.60, 149.40, 149.41, 178.42; ^{19}F NMR ($CDCl_3$, TMS, 282 MHz) d -62.9; $[\alpha]^{25}_{D}$ = +29.1 (c = 1.1, CH_3Cl) for 98% *ee*; Chiral GC: Gamma Dex 225, 30 m × 0.25 mm, column temperature: 135 ^{o}C, carrier gas: He, 1 mL/min, t_{minor}= 47.2 min, t_{major}= 48.9 min.



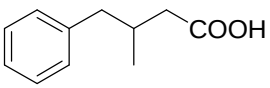
3-(1-Naphthyl)butanoic Acid (2l):[14]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.48 (d, J = 6.9 Hz, 3H), 2.67 (dd, J_1 = 8.4 Hz, J_2 = 15.7 Hz, 1H), 2.92 (dd, J_1 = 5.2 Hz, J_2 = 15.7 Hz, 1H), 4.19 (m, 1H), 7.41-756 (m, 4H), 7.85 (d, J = 7.8 Hz, 1H) 7.86 (d, J = 8.0 Hz, 1H) 8.17 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.1, 30.6, 42.1, 122.3, 122.9, 125.5, 125.6, 126.1, 127.1, 129.0, 131.0, 134.0, 141.3, 178.5; $[\alpha]^{25}_{D}$ = -9.5 (c = 0.6, CH_3Cl) for 98% *ee*; Chiral HPLC: Chiralpak OD column, IPA/Hex = 5: 95, 1.0 mL/min, t_{major} = 10.5 min, t_{minor} = 25.5 min.



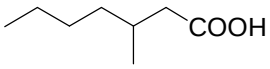
3-(2-Naphthyl)butanoic Acid (2m):[14]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 1.41 (d, J = 6.9 Hz, 3H), 2.63-2.82 (m, 2H), 3.47 (m, 1H), 7.26-7.47 (m, 3H), 7.66 (s, 1H) 7.78-7.82 (m, 3H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 21.9, 36.2, 42.4, 124.9, 125.3, 125.4, 126.0, 127.5, 127.7, 128.2, 132.3, 133.5, 142.8, 178.3; $[\alpha]^{25}_{D}$ = +29.6 (c = 1.0, EtOH) for 97% *ee*; Chiral HPLC: Chiralpak OJ-H column, IPA/Hex = 10: 90, 1.0 mL/min, t_{major} = 32.1 min, t_{minor} = 40.3 min.



3-Methyl-4-phenylbutanoic Acid (2n):[15]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 0.98 (d, J = 6.4 Hz, 3H), 2.16-2.42 (m, 3H), 2.50-2.56 (m, 1H), 2.63-2.67 (m, 1H), 7.16-7.32 (m, 5H) 10.78 (s, br, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 19.5, 32.1, 40.9, 42.9, 126.1, 128.3, 129.2, 140.1, 179.7; $[\alpha]^{25}_{D}$ = +2.9 (c = 1.2, CH_2Cl_2) for 74% *ee*; Chiral HPLC: Chiralpak OD column, IPA/Hex = 1: 99, 1.0 mL/min, t_{major} = 37.4 min, t_{minor} = 58.1 min.



3-Methylheptanoic Acid (2o):[16]

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) d 0.89, (t, J = 6.6 Hz, 3H), 0.96 (d, J = 3.6 Hz, 3H) 1.22-1.33 (m, 6H), 1.94 (m, 1H), 2.35 (dd, J_1 = 5.9 Hz, J_2 = 14.9 Hz, 1H), 2.14 (dd, J_1 = 7.9 Hz, J_2 = 14.9 Hz, 1H), 11.46 (s, br, 1H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) d 14.0, 19.7, 22.7, 29.1, 30.1, 36.3, 41.6, 180.2; $[\alpha]^{25}_{D}$ = +3.5 (c = 0.4, CH_2Cl_2) for 70% *ee*; Chiral GC: Beta Dex 325, 30 m × 0.25 mm, column temperature: 90 ^{o}C, carrier gas: He, 1 mL/min, t_{major} = 62.2 min, t_{minor} = 64.2 min.

Typical Procedure E for Asymmetric Hydrogenation of 3-(2-Naphthyl)-3-butenoic Acid (1m) with Low Catalyst Loading (S/C = 5000):

The Rh-complex **3e** (8.12 mg, 0.01 mmol) was dissolved in degassed methanol (80 mL) in a glovebox. To a suspension of the substrate **1m** (532.5 mg, 2.5 mmol) and Et_3N (12.6 mg, 0.125 mmol) in 4 mL water was added 4 mL of the above complex **3e** methanol solution (0.406 mg, 0.0005 mmol). After further diluted with 8.5 mL degassed water and 8.5 mL degassed methanol, the resulting solution was then transferred into an autoclave and the hydrogenation was performed under 3 atm of initial hydrogen pressure at room

temperature for 24 h (not optimal). After carefully releasing the hydrogen, the solvent was removed by evaporation. The residue was dissolved in 20 mL ether and extracted with 3 equiv NaOH aq (30 mL × 2). The alkaline solution was acidified with 6 equiv HCl aq, and then extracted with ether (40 mL × 3). The ether extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated by evaporation. The enantiomeric excesse was directly determined by chiral HPLC (Chiralpak OJ-H column) under conditions in the general procedure D.

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