Supporting Methods

General Considerations

Unless otherwise noted, tetrahydrofuran (THF) and toluene were purchased from J. T. Baker in CYCLE-TAINER solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF) or through neutral alumina and copper (II) oxide (for toluene) (1, 2). Starting materials for substrate synthesis were purchased from commercial sources and used as is. Ethyl *trans*-β-methylcinnamate, PMHS (polymethylhydrosiloxane), *t*-BuOH, and N,N'-dimethylethylene diamine were purchased from Aldrich and used as is.

Yields refer to isolated yields of compounds of greater than 95% purity as estimated by capillary GC and ^{1}H NMR. Yields reported in this section refer to a single experiment, while those reported in the tables are the average of two or more runs.

All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, in addition to elemental analysis (Atlantic Microlabs) or HRMS. Nuclear Magnetic Resonance spectra were recorded on a Varian Mercury 300 or a Varian Unity 300 instrument. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 (liquids and solids were measured neat on a DiComp probe). All ^{1}H NMR experiments are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^{1}H decoupling. Melting points (uncorrected) were obtained on a Mel-Temp capillary melting point apparatus. Optical rotations were taken on a Jasco Model-1010 Polarimeter at 23°C. Gas Chromatographic analyses were performed on a Hewlett-Packard 6890 gas chromatography instrument with an FID detector by using 25m × 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. Chiral High Performance Liquid Chromatography analyses were performed on a Hewlett-Packard 1100 system with an HP 1100 Diode Array Detector, using the columns and

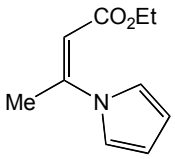
wavelengths mentioned in *Asymmetric Conjugate Reduction of Dehydro-β-Amino Acid Derivatives*. Separation conditions were determined from racemic material that was obtained via hydrogenation over Pd/C of the dehydro-β-amino acid derivatives.

Synthesis of Dehydro-β-Amino Acid Derivatives

General Procedure A. An oven-dried Schlenk flask with Teflon-coated magnetic stir bar was allowed to cool to room temperature under nitrogen, and then charged with copper (I) iodide (0.10 mmol), potassium phosphate (1.5 mmol), and (if a solid) the nitrogen nucleophile (1.5 mmol). The flask was then capped with a rubber septum, evacuated, backfilled with nitrogen; this process was repeated one time. Toluene (0.50 ml) was added, followed by the diamine (0.20 mmol), (if a liquid) the nitrogen nucleophile (1.5 mmol), and the vinyl iodide (1.0 mmol) as a solution in toluene (0.50 ml). The septum was then replaced with a Teflon screw cap under a positive pressure of nitrogen and the flask was sealed and placed in a 65°C oil bath with stirring for the time indicated. On complete conversion of the vinyl iodide (as judged by gas chromatography), the reaction mixture was allowed to cool to room temperature. The reaction solution was partitioned between water and ethyl acetate, the phases were separated, and the aqueous phase was extracted 3 additional times with ethyl acetate. The combined organic layers were then dried over magnesium sulfate, filtered, and the solvent removed with the aid of a rotary evaporator. The crude residue was then purified by flash chromatography on silica gel to give the desired compound.

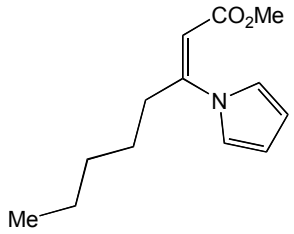
General Procedure B. A flame-dried 25-ml round-bottom flask containing a Teflon-coated magnetic stir bar was allowed to cool to room temperature under nitrogen, then charged with copper (I) iodide (0.50 mmol), potassium phosphate (7.5 mmol), and (if a solid) the nitrogen nucleophile (7.5 mmol). The flask was then capped with a rubber septum, evacuated, backfilled with nitrogen; this process was repeated one time. Toluene (2.5 ml) was added, followed by the diamine (1.0 mmol), (if a liquid) the nitrogen nucleophile (7.5 mmol), and the vinyl iodide (5.0 mmol) as a solution in toluene (2.5 ml). The flask was then placed in a 65°C oil bath with stirring for the time indicated. On

complete conversion of the vinyl iodide (as judged by gas chromatography), the reaction mixture was allowed to cool to room temperature. The reaction solution was partitioned between water and ethyl acetate, the phases were separated, and the aqueous phase was extracted 3 additional times with ethyl acetate. The combined organic layers were then dried over magnesium sulfate, filtered, and the solvent removed with the aid of a rotary evaporator. The crude residue was then purified by flash chromatography on silica gel to give the desired compound.



3-Pyrrol-1-yl-but-2-enoic acid ethyl ester

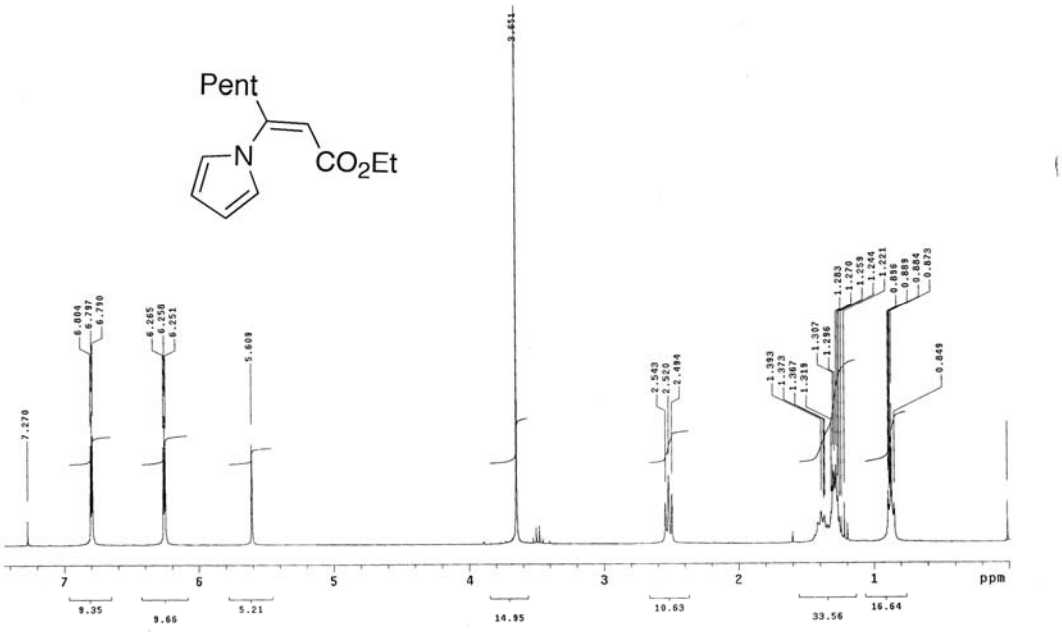
General procedure B was followed and the reaction mixture was allowed to stir for 15 h. Flash chromatography on silica gel eluting with 5:95 ethyl acetate:hexane gave 627 mg (70%) of the title compound as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.93 (t, J = 2 Hz, 2H), 6.25 (t, J = 2 Hz, 2H), 5.55 (q, J = 1 Hz, 1H), 4.13 (q, J = 7 Hz, 2H), 2.27 (d, J = 1 Hz, 3H), 1.22 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.1, 147.6, 121.3, 110.0, 107.5, 60.4, 24.4, 14.3; IR (cm^{-1}): 2358, 1715, 1644, 1482, 1273, 1187, 1082, 1050; Anal. calc for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31. Found: C, 66.83; H, 7.25.

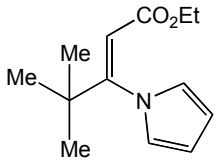


3-Pyrrol-1-yl-oct-2-enoic acid methyl ester

General procedure B was followed using 0.05 eq of copper (I) iodide and 0.20 eq of N,N'-dimethylethylene diamine and the reaction mixture was allowed to stir for 15 h. Flash chromatography on silica gel eluting with 3:7 dichloromethane:hexane gave 690

mg (63%) of the title compound as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.80 (t, *J* = 2 Hz, 2H), 6.26 (t, *J* = 2 Hz, 2H), 5.61 (s, 1H), 3.65 (s, 3H), 2.52 (m, 2H), 1.29 (m, 6H), 0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.5, 152.9, 121.1, 109.9, 108.3, 51.5, 37.7, 31.2, 26.8, 22.5, 14.1; IR (cm^{-1}): 2952, 2929, 1719, 1638, 1480, 1436, 1246, 1171, 1067, 723; HRMS calc: 221.1410; Found: 221.1406.

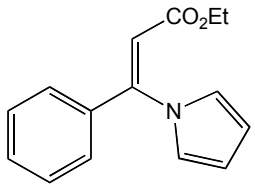




4,4-Dimethyl-3-pyrrol-1-yl-pent-2-enoic acid ethyl ester

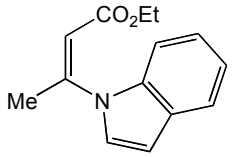
General procedure B was followed using 1.0 mmol (0.10 eq) of copper (I) iodide and 2.0 mmol (0.20 eq) of N,N'-dimethylethylene diamine, and the reaction mixture was allowed to stir for 48 h. Flash chromatography on silica gel eluting with 5:95 ethyl acetate:hexane gave 850 mg (77%) of the title compound as an orange oil. ^{1}H NMR (300

MHz, $CDCl_3$) δ: 6.55 (t, *J* = 2 Hz, 2H), 6.23 (t, *J* = 2 Hz, 2H), 6.05 (s, 1H), 3.99 (q, *J* = 7 Hz, 2H), 1.18 (s, 9H), 1.10 (t, *J* = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 161.3, 122.4, 116.4, 108.2, 60.6, 38.3, 28.7, 14.2; IR (cm^{-1}): 2973, 1708, 1648, 1484, 1347, 1266, 1169, 1040; Anal. calc for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65. Found: C, 70.45; H, 8.60.



3-Phenyl-3-pyrrol-1-yl-acrylic acid ethyl ester

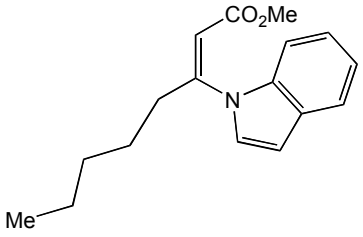
General procedure B was followed but on double the scale, with 0.50 mmol (0.05 eq) of copper (I) iodide and 2.0 mmol (0.20 eq) of N,N'-dimethylethylene diamine. The reaction mixture was allowed to stir for 36 h. Flash chromatography on silica gel eluting with 5:95 ethyl acetate:hexane gave 1.3 g (54%) of the title compound as an orange solid. MP: 44-46°C; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.33 (m, 5H), 6.73 (t, *J* = 2 Hz, 2H), 6.30 (t, *J* = 2 Hz, 2H), 6.01 (s, 1H), 4.16 (q, *J* = 7 Hz, 2H), 1.24 (t, *J* = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 150.8, 137.3, 131.0, 128.8, 123.2, 109.9, 109.7, 99.9, 60.6, 14.4; IR (cm^{-1}): 1719, 1627, 1480, 1275, 1150, 1088, 1071, 773, 729, 692; Anal. calc for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27. Found: C, 74.80; H, 6.28.



3-Indol-1-yl-but-2-enoic acid ethyl ester

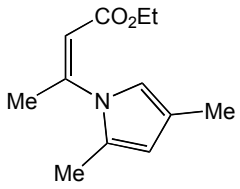
General procedure A was followed on a 1.5 mmol scale using 0.075 mmol (0.05 eq) of copper (I) iodide and 0.30 mmol (0.20 eq) of N,N'-dimethylethylene diamine. The reaction mixture was allowed to stir for 14 h, and after flash chromatography on silica gel eluting with 3:7 dichloromethane:hexane gave 205 mg (60%) of the title compound as a light purple oil. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.60 (m, 1H), 7.19 (m, 4H), 6.62 (m, 1H),

5.92 (q, J = 1 Hz, 1H), 3.89 (q, J = 7 Hz, 2H), 2.34 (d, J = 1 Hz, 3H), 0.87 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.6, 147.3, 135.9, 129.3, 127.0, 122.5, 121.2, 120.7, 113.5, 111.3, 104.4, 60.4, 24.1, 13.9; IR (cm^{-1}): 2983, 1719, 1648, 1459, 1358, 1229, 1181, 1131, 1046, 739; Anal. calc for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59. Found: C, 73.19; H, 6.54.



3-Indol-1-yl-oct-2-enoic acid methyl ester

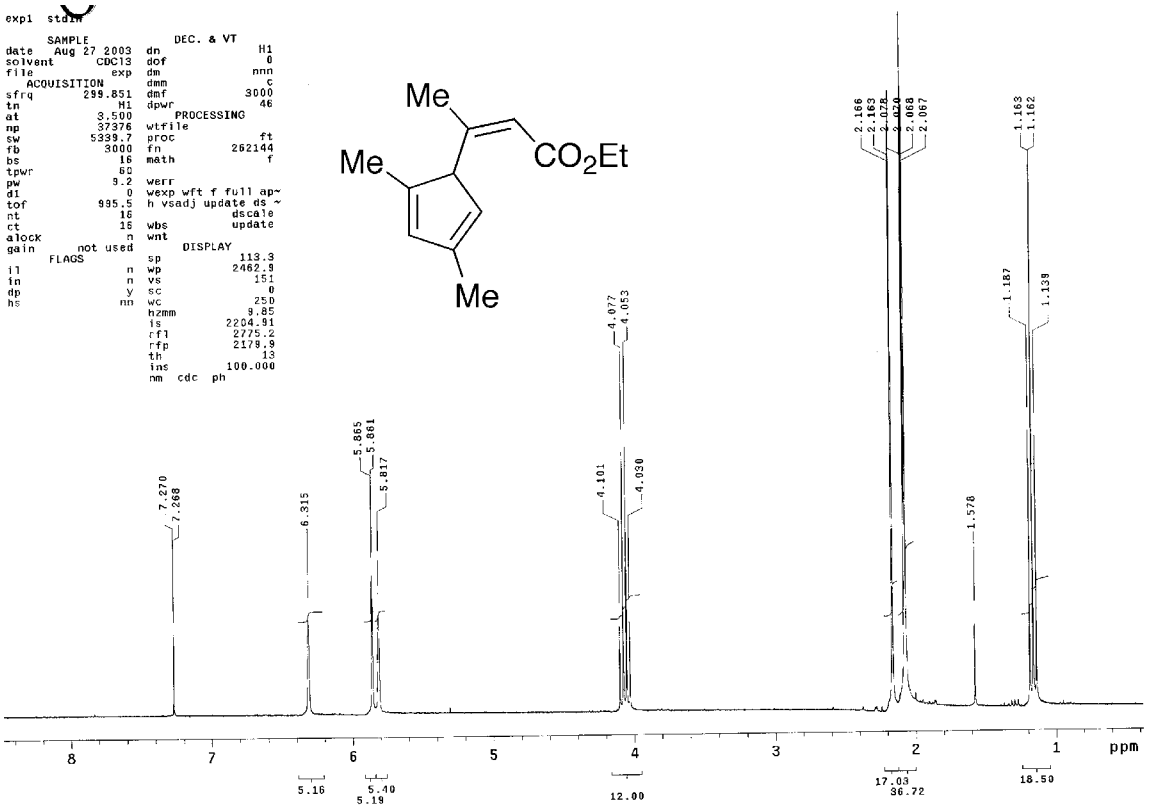
General procedure B was followed on a 8.0 mmol scale using 0.40 mmol (0.050 eq) of copper (I) iodide and 1.6 mmol (0.20 eq) of N,N'-dimethylethylene diamine. The reaction mixture was allowed to stir for 15 h, and after flash chromatography on silica gel eluting with 3:7 dichloromethane:hexane gave 1.5 g (69%) of the title compound as a light pink oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.63 (m, 1H), 7.17 (m, 4H), 6.61 (m, 1H), 5.97 (s, 1H), 3.45 (s, 3H), 2.65 (m, 2H), 1.23 (m, 6H), 0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 152.2, 136.1, 127.2, 122.5, 121.3, 120.6, 113.2, 111.0, 104.2, 99.9, 51.6, 37.5, 31.3, 26.7, 22.4, 14.1; IR (cm^{-1}): 2952, 2931, 1719, 1708, 1648, 1455, 1436, 1281, 1223, 1210, 1173, 1133, 764, 739; Anal. calc for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80. Found: C, 75.24; H, 7.79.

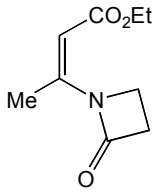


3-(2,4-Dimethyl-pyrrol-1-yl)-but-2-enoic acid ethyl ester

General procedure A was followed on a 2.0 mmol scale using 0.40 mmol (0.20 eq) of copper (I) iodide and 0.80 mmol (0.40 eq) of N,N'-dimethylethylene diamine. The

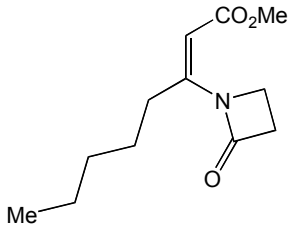
reaction mixture was allowed to stir for 17 h, and after flash chromatography on silica gel eluting with 1:1 dichloromethane:hexane gave 170 mg (40%) of the title compound as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.32 (s, 1H), 5.86 (q, J = 1 Hz, 1H), 5.82 (s, 1H), 4.06 (q, J = 7 Hz, 2H), 2.16 (d, J = 1 Hz, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.16 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.4, 149.1, 128.9, 119.5, 116.5, 115.4, 110.1, 60.4, 25.3, 14.2, 12.3, 12.1; IR (cm^{-1}): 2979, 2929, 1719, 1708, 1656, 1414, 1221, 1140, 1044, 783; HRMS calc: 207.1254; Found: 207.1248.





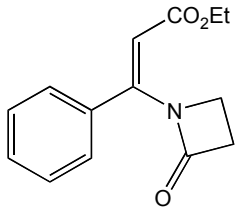
3-(2-Oxo-azetidin-1-yl)-but-2-enoic acid ethyl ester

General procedure B was followed using 1.0 mmol (0.20 eq) of copper (I) iodide and 2.0 mmol (0.40 eq) of N,N'-dimethylethylene diamine. The reaction mixture was allowed to stir for 3 h, and after flash chromatography on silica gel eluting with 1:3 ethyl acetate:hexane gave 600 mg (66%) of the title compound as a white solid. MP: 48-50°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.93 (m, 1H), 4.11 (q, *J* = 7 Hz, 2H), 3.89 (t, *J* = 5 Hz, 2H), 3.01 (t, *J* = 5 Hz, 2H), 2.27 (d, *J* = 1 Hz, 3H), 1.27 (t, *J* = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.2, 165.0, 146.9, 99.7, 59.9, 43.6, 37.1, 22.4, 14.5; IR (cm^{-1}): 1764, 1702, 1621, 1264, 1196, 1140, 725; Anal. calc for $C_9H_{13}NO_3$: C, 59.00; H, 7.15. Found: C, 59.17; H, 7.18.



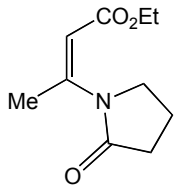
3-(2-Oxo-azetidin-1-yl)-oct-2-enoic acid methyl ester

General procedure B was followed on a 7.0 mmol scale using 0.35 mmol (0.050 eq) of copper (I) iodide and 1.4 mmol (0.20 eq) of N,N'-dimethylethylene diamine. The reaction mixture was allowed to stir for 24 h, and after flash chromatography on silica get eluting with 1:3 ethyl acetate:hexane gave 1.25 g (79%) of the title compound as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.00 (m, 1H), 3.85 (t, *J* = 5 Hz, 2H), 3.67 (s, 3H), 3.01 (t, *J* = 5 Hz, 2H), 2.56 (m, 2H), 1.54 (m, 2H), 1.29 (m, 4H), 0.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.6, 165.6, 151.4, 99.5, 51.3, 43.3, 36.9, 34.9, 31.4, 28.4, 22.6, 14.2; IR (cm^{-1}): 2952, 1764, 1708, 1611, 1407, 1254, 1183, 1123, 820; Anal. calc for $C_{12}H_{19}NO_3$: C, 63.98; H, 8.50. Found: C, 63.61; H, 8.50.



3-(2-Oxo-azetidin-1-yl)-3-phenyl-acrylic acid ethyl ester

General procedure B was followed on a 10 mmol scale using 0.50 mmol (0.050 eq) of copper (I) iodide and 2.0 mmol (0.20 eq) of N,N'-dimethylethylene diamine. The reaction mixture was allowed to stir for 23 h, and after flash chromatography on silica gel eluting with 1:3 ethyl acetate:hexane gave 1.65 g (67%) of the title compound as a red oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.43 (m, 5H), 5.68 (s, 1H), 4.22 (q, J = 7 Hz, 2H), 3.72 (t, J = 5 Hz, 2H), 3.15 (t, J = 5 Hz, 2H), 1.31 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.0, 165.0, 146.1, 134.7, 130.6, 128.9, 128.3, 108.9, 60.5, 42.1, 37.2, 14.5; IR (cm^{-1}): 2977, 1764, 1702, 1609, 1383, 1275, 1152, 1109, 1027, 781, 696; Anal. calc for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16. Found: C, 68.51; H, 6.23



3-(2-Oxo-pyrrolidin-1-yl)-but-2-enoic acid ethyl ester

General procedure A was followed on a 2.0 mmol scale using 0.20 mmol (0.10 eq) of copper (I) iodide and 0.40 mmol (0.2 eq) of N,N'-dimethylethylene diamine. The reaction mixture was allowed to stir for 19 h, and after flash chromatography on silica gel eluting with 1 :3 ethyl acetate:hexane gave 250 mg (64%) of light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.69 (q, J = 1 Hz, 1H), 4.12 (q, J = 7 Hz, 2H), 3.64 (t, J = 7 Hz, 2H), 2.45 (t, J = 7 Hz, 2H), 2.11 (quint, J = 7 Hz, 2H), 2.03 (d, J = 1 Hz, 3H), 1.25 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.1, 164.7, 147.0, 114.4, 60.2, 48.4, 31.8, 21.7, 19.1, 14.4; IR (cm^{-1}): 2981, 1719, 1702, 1638, 1401, 1264, 1175, 1129, 1050, 845; Anal. calc for $C_{10}H_{15}NO_3$: C, 60.90; H, 7.67. Found: C, 59.7; H, 7.69.

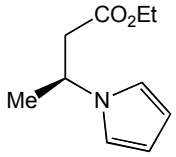
Asymmetric Conjugate Reduction of Dehydro-β-Amino Acid Derivatives

General Procedure. A 1 dram vial equipped with a Teflon-coated magnetic stir bar was charged with copper (II) acetate monohydrate (0.05 eq), and S-BINAP (0.05 eq). The vial

was capped with a screw-on top with a Teflon center, through which a glass pipette filled with calcium sulfate was inserted. THF was then added to the vial via syringe and this was allowed to stir for [dsim]5 min. Then PMHS (4.0 eq) was added to the vial and this was again allowed to stir for 5 min. Finally, a solution of the substrate (0.33 molar in the total volume of THF) and t-BuOH (4.0 eq) in THF was added to the vial and allowed to stir for the time indicated. On complete conversion of the starting material as judged by gas chromatography or thin layer chromatography, the reaction was worked up in one of two ways:

Work-Up A. The reaction mixture was diluted with ethyl acetate, and then partitioned between water and ethyl acetate. The phases were separated and the aqueous was extracted three times with ethyl acetate. The combined organic layers were dried over magnesium sulfate, filtered, and the solvent removed with the aid of a rotary evaporator. The crude residue was then purified by flash chromatography over silica gel.

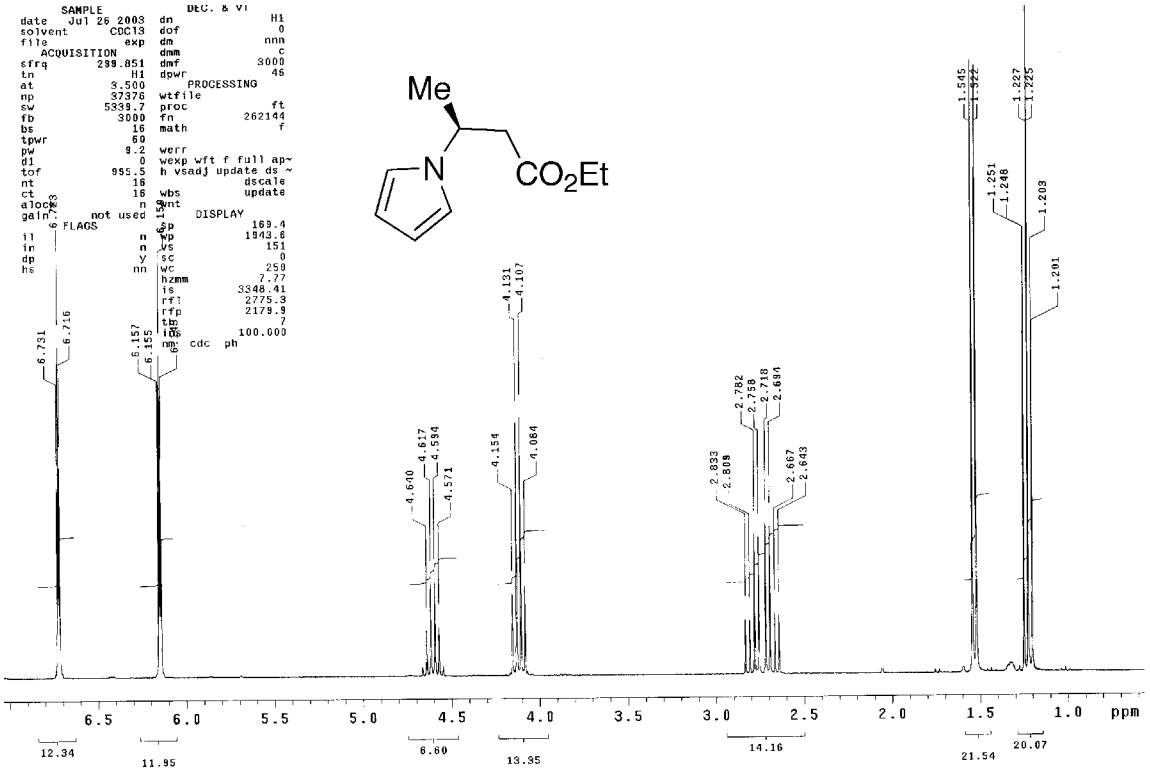
Work-Up B. The reaction mixture was loaded directly onto a silica gel column and purified by flash chromatography.

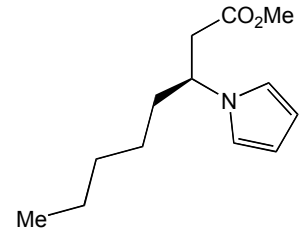


3-Pyrrol-1-yl-butyric acid ethyl ester

The general procedure was followed and the reaction was allowed to stir for 1 h. Work-up A, eluting with 5:95 ethyl acetate:hexane gave 80 mg (88%) of the title compound as a colorless oil. Chiral HPLC analysis [Daicel Chiralpak OD column (0.46 cmØ × 25 cm), 0.7 ml/min, 5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 8.32 min (major), 9.81 min (minor)] showed 81% enantiomeric excess (ee). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.72 (t, J = 2 Hz, 2H), 6.15 (t, J = 2 Hz, 2H), 4.60 (sext, J = 7 Hz, 1H), 4.12 (q, J = 7 Hz, 2H), 2.74 (ABX, dd, J = 15 Hz, 7 Hz, 2H), 1.53 (d, J = 7 Hz, 3H), 1.22 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.9, 118.6, 108.2, 60.9, 52.0, 43.4, 21.9, 14.3; IR (cm^{-1}):

2979, 1735, 1181, 1167, 1088, 1034, 721; HRMS calc: 181.1097; Found: 181.1090. α_D (589 nm, 0.45 g/100 ml $CHCl_3$) = -17.5.

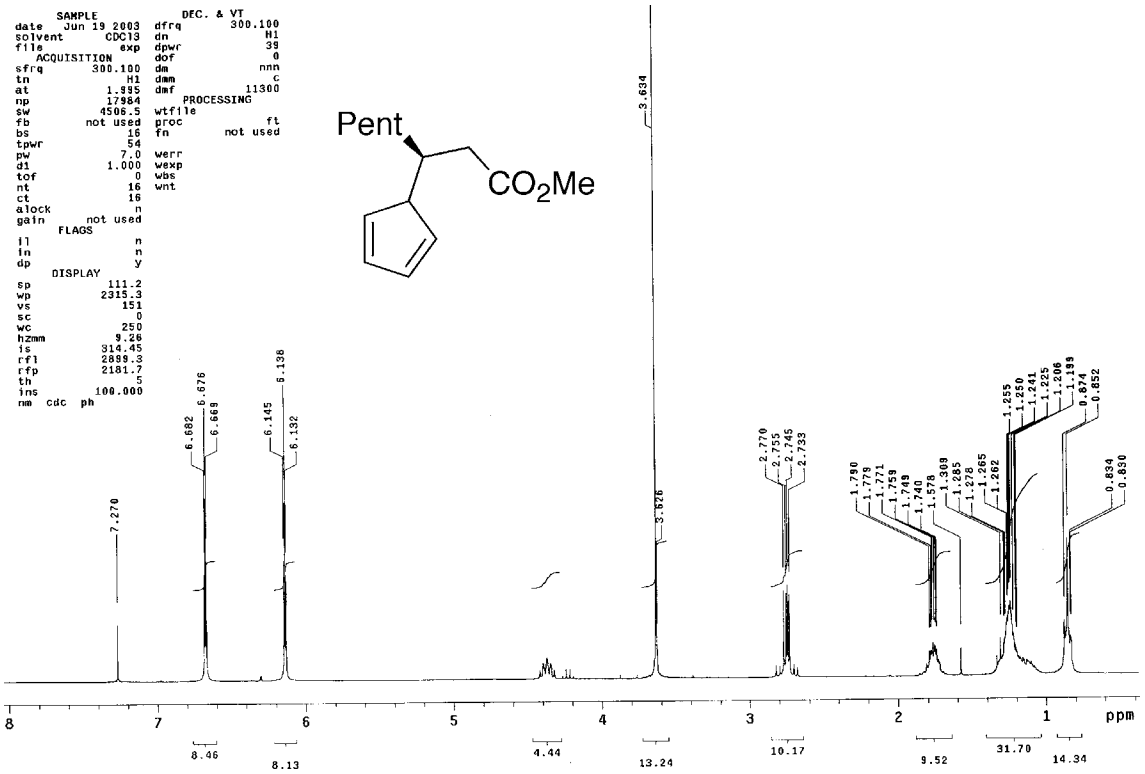


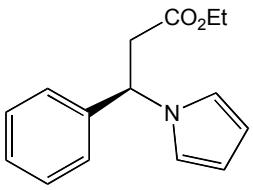


3-Pyrrol-1-yl-octanoic acid methyl ester

The general procedure was followed and the reaction was allowed to stir for 1 h. Work-up A, eluting with 1:9 ethyl acetate:hexane gave 57 mg (85%) of the title compound as a colorless oil. Chiral HPLC analysis (Daicel Chiralpak OD column (0.46 cmØ x 25 cm), 0.7 ml/min, 5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 7.24 min (major), 9.66 min (minor)) showed 87% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.68 (t, *J* = 2 Hz, 2H), 6.14 (t, *J* = 2 Hz, 2H), 4.38 (m, 1H), 3.63 (s, 3H), 2.75 (m, 2H), 1.77 (m,

2H), 1.23 (m, 6H), 0.84 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5, 119.0, 108.1, 56.8, 52.1, 41.9, 36.1, 31.5, 25.9, 22.6, 14.2; IR (cm^{-1}): 2956, 2931, 1737, 1490, 1262, 1246, 1165, 1090, 1069, 719; HRMS calc: 223.1561; Found: 223.1573. α_D (589 nm, 0.11 g/100 ml $CHCl_3$) = -12.0.

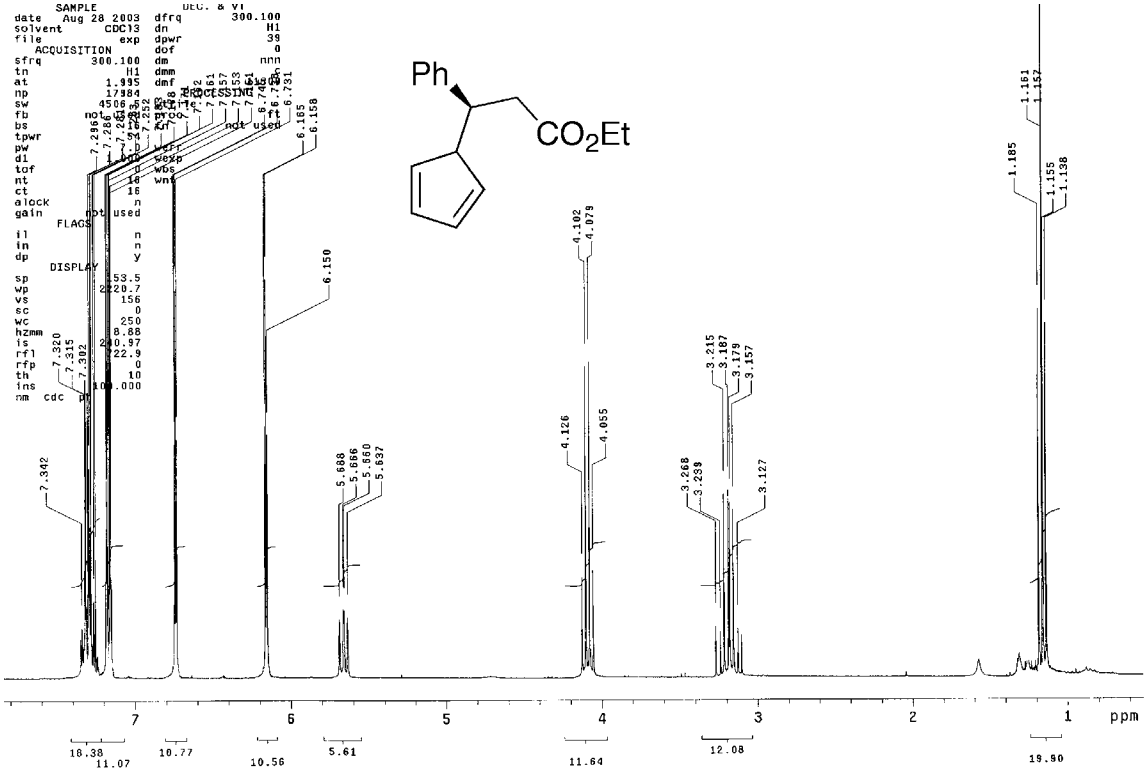


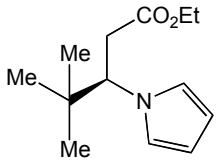


3-Phenyl-3-pyrrol-1-yl-propionic acid ethyl ester

The general procedure was followed using 10 eq of PMHS and the reaction was allowed to stir for 20 h. Work-up B, eluting with 5:95 ethyl acetate:hexane gave 105 mg (87%) of the title compound as a yellow oil. Chiral HPLC analysis (Daicel Chiralpak OJ column (0.46 cmØ × 25 cm), 0.7 ml/min, 3% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 31.84 min (major), 35.30 min (minor)) showed 83% ee. ^{1}H NMR (300 MHz,

$CDCl_3$) δ: 7.25 (m, 3H), 7.16 (m, 2H), 6.74 (t, *J* = 2 Hz, 2H), 6.15 (t, *J* = 2 Hz, 2H), 5.66 (m, 1H), 4.09 (q, *J* = 7 Hz, 2H), 3.18 (ABX, dd, *J* = 15 Hz, 7 Hz, 2H) 1.16 (t, *J* = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.4, 140.7, 128.9, 128.2, 126.5, 119.8, 108.6, 61.2, 59.5, 41.3, 14.2; IR (cm^{-1}): 2979, 1737, 1490, 1372, 1264, 1156, 1084, 1021, 721; HRMS calc: 243.1254; Found: 243.1252. α_D (589 nm, 0.10 g/100 ml $CHCl_3$) = -6.5.

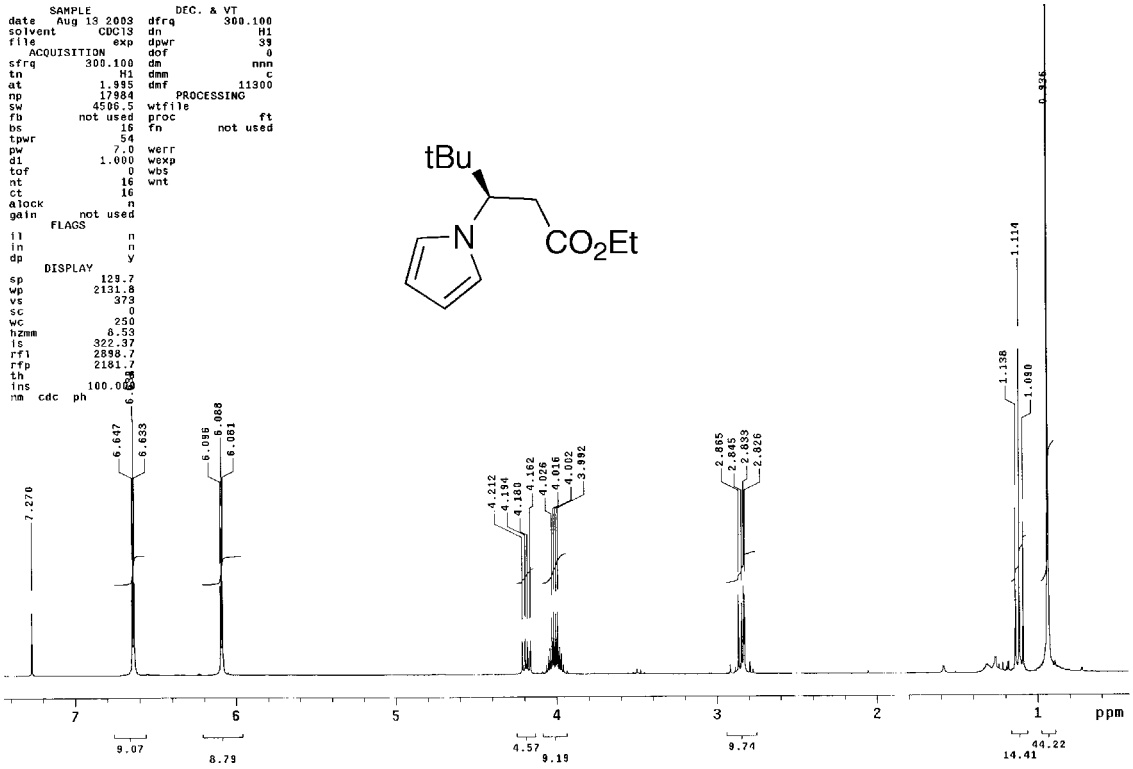


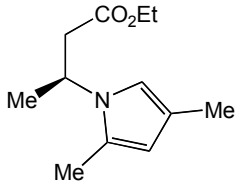


4,4-Dimethyl-3-pyrrol-1-yl-pentanoic acid ethyl ester

The general procedure was followed using 10 mol % catalyst and 10 eq of PMHS, and the reaction was allowed to stir for 22 h. Work-up A, eluting with 5:95 ethyl acetate:hexane gave 92 mg (83%) of the title compound as a yellow oil. Chiral HPLC analysis (Daicel Chiralpak AD-H column (0.46 cmØ × 25 cm), 0.5 ml/min, 1% *i*-

PrOH/Hexane, 254 nm, 280 nm, retention times: 12.99 min (major), 13.98 min (minor)) showed 86% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.64 (t, J = 2 Hz, 2H), 6.09 (t, J = 2 Hz, 2H), 4.18 (m, 1H), 4.02 (m, 2H), 2.84 (m, 2H), 1.14 (m, 3H), 0.94 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5, 120.9, 107.2, 65.8, 60.9, 36.1, 35.6, 27.2, 14.2; IR (cm^{-1}): 2966, 1737, 1370, 1299, 1248, 1152, 1094, 1030, 721; HRMS calc: 223.1567; Found: 223.1568. α_D (589 nm, 0.50 g/100 ml $CHCl_3$) = -9.4.

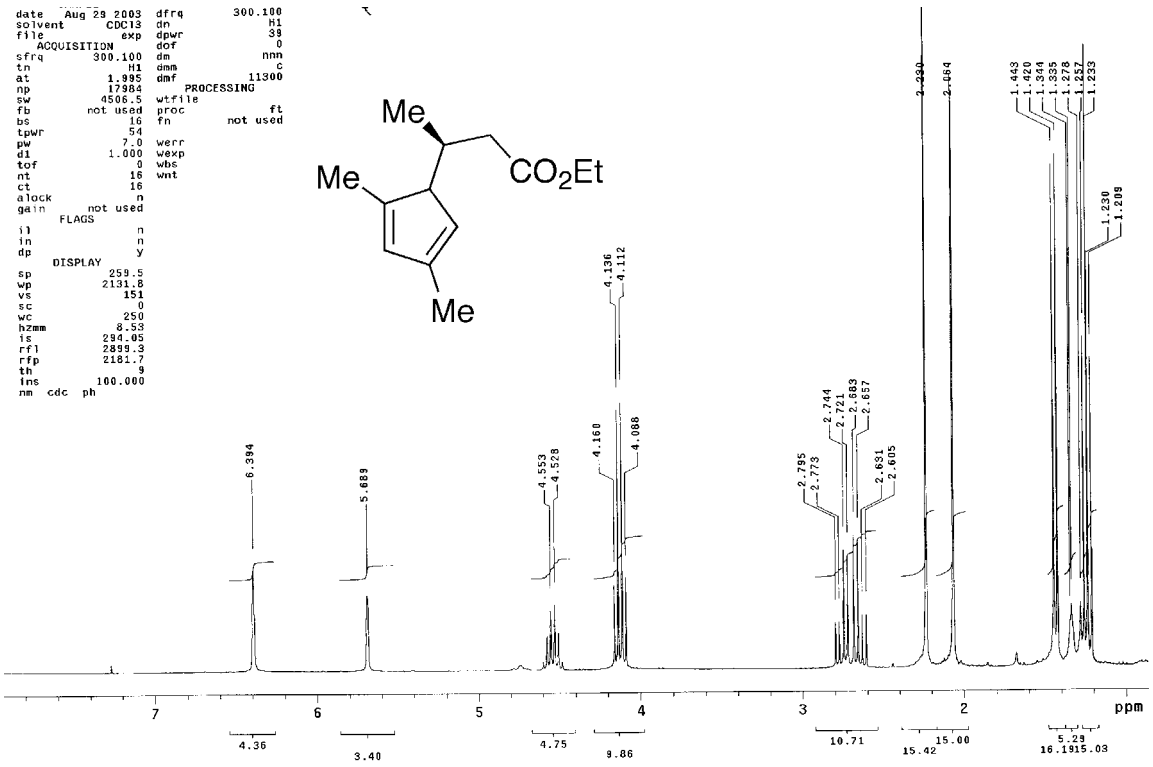


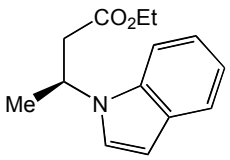


3-(2,4-Dimethyl-pyrrol-1-yl)-butyric acid ethyl ester

The general procedure was followed using 10 eq of PMHS and the reaction was allowed to stir for 24 h. Work-up B, eluting with 1:9 ethyl acetate:hexane gave 52 mg (83%) of the title compound as a colorless oil. Chiral HPLC analysis (Daicel Chiralpak

OD column (0.46 cmØ × 25 cm), 0.6 ml/min, 4% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 8.11 min (major), 9.34 min (minor)) showed 86% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.39 (s, 1H), 5.69 (s, 1H), 4.54 (sx, J = 7 Hz, 1H), 4.12 (q, J = 7 Hz, 2H), 2.70 (ABX, ddd, J = 15 Hz, 7 Hz, 2H), 2.23 (s, 3H), 2.06 (s, 3H), 1.43 (d, J = 7 Hz, 3H), 1.23 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.0, 128.2, 118.2, 113.2, 108.0, 60.8, 47.8, 42.8, 22.0, 14.3, 12.2, 12.1; IR (cm^{-1}): 2981, 1725, 1376, 1096, 1081, 1038, 904, 731; HRMS calc: 209.1410; Found: 209.1415. α_D (589 nm, 0.10 g/100 ml $CHCl_3$) = -2.3.

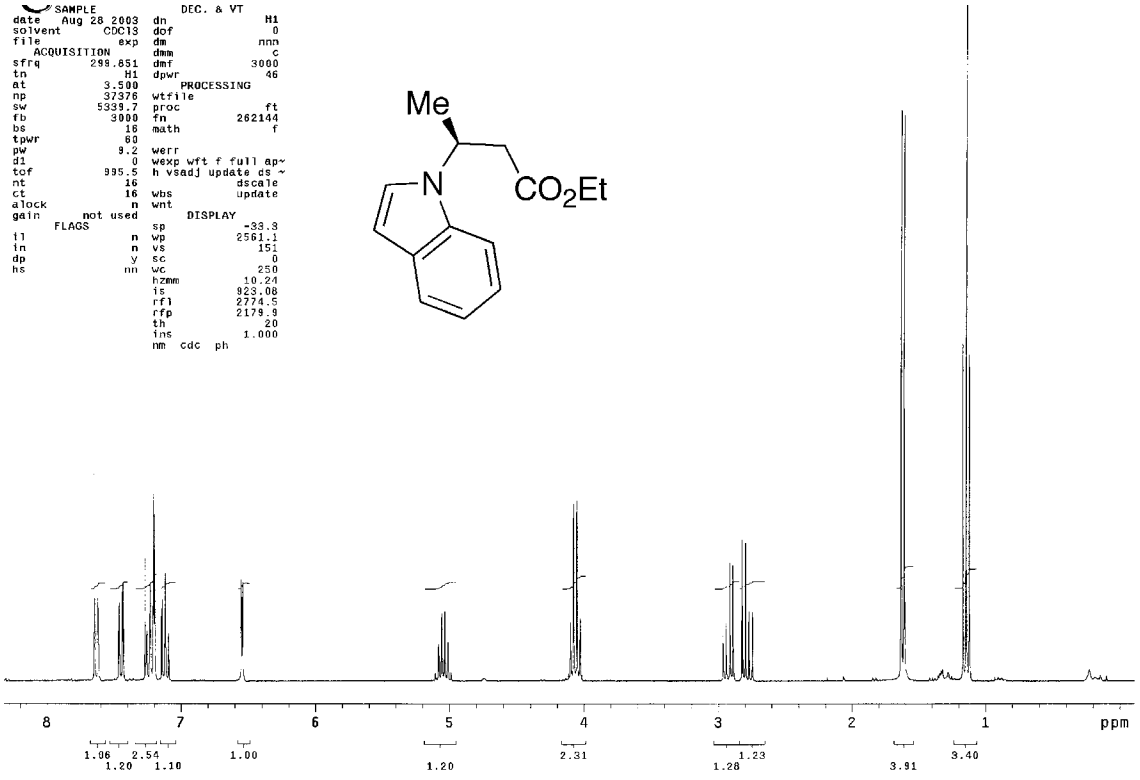


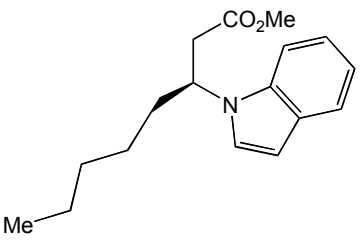


3-Indol-1-yl-butyric acid ethyl ester

The general procedure was followed and the reaction was allowed to stir for 1.25 h. Work-up B, eluting with 1:9 ethyl acetate:hexane gave 111 mg (96%) of the title

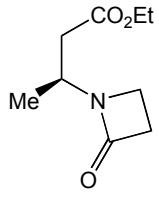
compound as a colorless oil. Chiral HPLC analysis (Daicel Chiralpak OD column (0.46 cmØ × 25 cm), 0.7 ml/min, 5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 13.3 min (major), 21.66 min (minor)) showed 90% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64 (m, 1H), 7.43 (m, 1H), 7.21 (m, 2H), 7.11 (m, 1H), 6.54 (m, 1H), 5.04 (sext, J = 7 Hz, 1H), 4.06 (q, J = 7 Hz, 2H), 2.84 (ABX, ddd, J = 15 Hz, 7 Hz, 2H), 1.64 (d, J = 7 Hz, 3H), 1.15 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.9, 135.7, 128.7, 124.1, 121.7, 121.2, 119.7, 109.7, 102.2, 60.9, 48.5, 42.2, 21.0, 14.2; IR (cm^{-1}): 2956, 1750, 1397, 1245, 1206, 1169, 1011; HRMS calc: 231.1254; Found: 231.1257. α_D (589 nm, 0.11 g/100 ml $CHCl_3$) = +16.8.





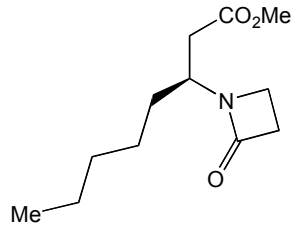
3-Indol-1-yl-octanoic acid methyl ester

The general procedure was followed 10 mol % catalyst and 10 eq of PMHS, and the reaction was allowed to stir for 23 h. Work-up B, eluting with 1:9 ethyl acetate:hexane gave 110 mg, 96% of the title compound as a colorless oil. Chiral HPLC analysis (Daicel Chiralpak OD column (0.46 cmØ × 25 cm), 0.7 ml/min, 5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 10.17 min (major), 20.77 min (minor)) showed 85% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.62 (m, 1H), 7.44 (m, 1H), 7.18 (m, 3H), 6.53 (m, 1H), 4.84 (m, 1H), 3.54 (s, 3H), 2.84 (m, 2H), 1.92 (m, 2H), 1.21 (m, 6H), 0.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5, 136.3, 128.6, 124.5, 121.7, 121.1, 119.6, 109.8, 102.4, 53.2, 52.0, 40.9, 35.3, 31.5, 25.9, 22.6, 14.1; IR (cm^{-1}): 2931, 1737, 1459, 1306, 1194, 1167, 737; Anal. calc for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48. Found: C, 74.67; H, 8.43. α_D (589 nm, 0.10 g/100 ml $CHCl_3$) = -2.2.



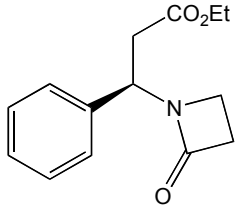
3-(2-Oxo-azetidin-1-yl)-butyric acid ethyl ester

The general procedure was used with 10 mol % catalyst and 8 eq of PMHS, and the reaction was allowed to stir for 24 h. Work-up A, eluting with 1:3 ethyl acetate:hexane gave 80 mg (86%) of the title compound as a light yellow oil. Chiral HPLC analysis (Daicel Chiralpak OD column (0.46 cmØ × 25 cm), 0.7 ml/min, 5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 24.29 min (minor), 26.25 min (major)) showed 84% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.14 (m, 3H), 3.23 (m, 2H), 2.85 (t, J = 4 Hz, 2H), 2.55 (ABX, ddd, J = 15 Hz, 7 Hz, 2H), 1.24 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.8, 166.9, 60.8, 45.2, 39.6, 36.5, 35.7, 18.4, 14.2; IR (cm^{-1}): 2977, 1750, 1719, 1393, 1374, 1246, 1206, 1183, 1028; Anal. calc for $C_9H_{15}NO_3$: C, 58.36; H, 8.16. Found: C, 58.5; H, 7.89. α_D (589 nm, 0.10 g/100 ml $CHCl_3$) = -8.3.



3-(2-Oxo-azetidin-1-yl)-octanoic acid methyl ester

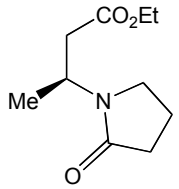
The general procedure was followed using 10 mol % catalyst with 10 eq of PMHS, and the reaction was allowed to stir for 24 h. Work-up B, eluting with 1:1 ethyl acetate:hexane gave 110 mg (98%) of the title compound as a colorless oil. Chiral HPLC analysis (Daicel Chiralpak OD column (0.46 cmØ × 25 cm), 0.6 ml/min, 2% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 42.55 min (minor), 44.24 min (major)) showed 94% ee ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.02 (m, 1H), 3.65 (s, 3H), 3.24 (m, 2H), 2.87 (m, 2H), 2.55 (ABX, ddd, J = 15 Hz, 7 Hz, 2H), 1.57 (m, 2H), 1.23 (m, 6H), 0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.6, 167.6, 52.1, 49.7, 38.1, 36.9, 35.9, 32.7, 31.5, 26.1, 22.6, 14.1; IR (cm^{-1}): 2979, 1737, 1727, 1461, 1306, 1289, 1179, 1038, 1025, 737; Anal. calc for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31. Found: C, 63.44; H, 9.33. α_D (589 nm, 0.10 g/100 ml $CHCl_3$) = +8.3.



3-(2-Oxo-azetidin-1-yl)-3-phenyl-propionic acid ethyl ester

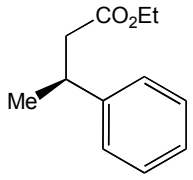
The general protocol was followed using 10 eq of PMHS and the reaction was allowed to stir for 24 h. Work-up B, eluting with 1:9 ethyl acetate:hexane gave 118 mg (96%) of the title compound as a yellow oil. Chiral HPLC analysis (Daicel Chiralpak OD column (0.46 cmØ × 25 cm), 0.7 ml/min, 5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 33.50 min (minor), 34.75 min (major)) showed 99% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32 (m, 5H), 5.07 (m, 1H), 4.13 (q, J = 7 Hz, 2H), 3.24 (m, 2H), 3.11 (m, 1H), 2.86 (m, 3H), 1.22 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.7, 167.4, 138.7,

129.1, 128.3, 127.2, 61.1, 54.5, 38.4, 37.7, 36.2, 14.3; IR (cm^{-1}): 2979, 1752, 1719, 1389, 1245, 1165, 1030, 700; Anal. calc for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93. Found: C, 67.71; H, 6.91. α_D (589 nm, 0.10 g/100 ml $CHCl_3$) = -16.3.



3-(2-Oxo-pyrrolidin-1-yl)-butyric acid ethyl ester

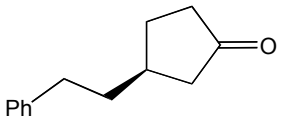
The general procedure was followed using 10 mol % catalyst with 10 eq of PMHS and the reaction was allowed to stir for 9 h. Work-up B, eluting with ethyl acetate gave 56 mg (92%) of the title compound as a yellow oil. Chiral HPLC analysis (Daicel Chiralpak OD column (0.46 cmØ × 25 cm), 0.7 ml/min, 5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 28.35 min (minor), 29.57 min (major)) showed 81% ee. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.54 (sext, J = 7 Hz, 1H), 4.07 (q, J = 7 Hz, 2H), 3.32 (m, 2H), 2.50 (ABX, ddd, J = 15 Hz, 7 Hz, 2H), 2.32 (m, 2H), 1.96 (m, 2H), 1.19 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.5, 170.8, 60.6, 44.4, 42.6, 39.0, 31.4, 18.1, 17.9, 14.1; IR (cm^{-1}): 2979, 1729, 1686, 1422, 1285, 1177, 1094, 1042, 1028; Anal. calc for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60. Found: C, 60.44; H, 8.58. α_D (589 nm, 0.11 g/100 ml $CHCl_3$) = -1.6.



3-Phenyl-butyric acid ethyl ester

The general procedure was followed and the reaction was allowed to stir for 3 h. Work-up A, eluting with 5:95 ethyl acetate:hexane gave 62 mg (85%) of the title compound as a colorless oil. Chiral HPLC analysis (Daicel Chiralpak OB column (0.46 cmØ × 25 cm), 0.5 ml/min, 0.5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times:

20.32 min (minor), 21.64 min (major)) showed 92% ee. Spectral data were the same as those previously reported (3).



3-Phenethyl-cyclopentanone

The general procedure was followed and the reaction was allowed to stir for 1 h. Work-up A, eluting with 1:10 ethyl acetate:hexane gave 47 mg (82%) of the title compound as a colorless oil. Chiral HPLC analysis [Daicel Chiralpak OB column (0.46 cmØ × 25 cm), 0.5 ml/min, 0.5% *i*-PrOH/Hexane, 254 nm, 280 nm, retention times: 6.49 min (minor), 7.34 min (major)] showed 92% ee. Spectral data were the same as those previously reported (4).

1. Pangborn, A. B., Giardello, M. A., Grubbs, R. H., Rosen, R. K. & Timmers, F. J. (1996) *Organometallics* **15,** 1518–1520.
2. Alaimo, P. J., Peters, D. W., Arnold, J. & Bergman, R. G. (2001) *J. Chem. Ed.* **78,** 64.
3. Appela, D. H., Moritani, Y., Shintani, R., Ferreira, E. M. & Buchwald, S. L. (1999) *J. Am. Chem. Soc.* **121,** 9473–9474.
4. Gadwood, R. C., Mallick, I. M. & DeWinter, A. J. (1987) *J. Org. Chem.* **52,** 774–782.