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Supporting Information

New Highly Asymmetric Henry Reaction Catalyzed by Cu(II) and a C_1-Symmetric Amino Pyridine Ligand, and Its Application to the Synthesis of Miconazole.

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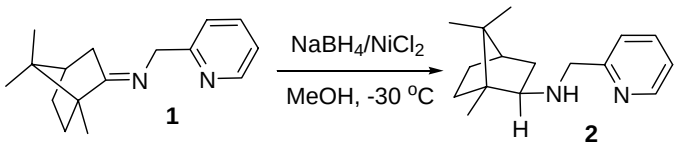
General methods: Commercial reagents were used as purchased. Reagent quality absolute EtOH without additional drying was used for all enantioselective reactions which were carried out in test tubes stopped with a septum. No special precautions were observed for air or moisture exclusion. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm. Diastereomerically pure samples of compounds **10**-**12** were obtained by HPLC. Specific optical rotations were recorded on a Perkin-Elmer 241 polarimeter using sodium light (D line 589 nm). NMR spectra were recorded on Bruker Avance spectrometers in the deuterated solvents as stated, using residual non-deuterated solvent as internal standard and $CFCl_3$ as internal standard for ^{19}F NMR. *J* values are given in Hz. The carbon type was determined by DEPT experiments. Mass spectra were recorded on a Fisons Instruments VG Autospec GC 8000 series. Mass spectra (EI) were run at 70 eV. Mass spectra (FAB) were carried out at 30 kV in a MNBA matrix. Chiral HPLC analyses were performed in a Hitachi Elite Lachrom instrument equipped with a Hitachi UV diode-array L-4500 detector using chiral stationary columns from Daicel. Retention times are given in min. Diastereomerically pure samples of compounds **10**-**12** were obtained by HPLC. For the stereochemical notation of these compounds, i. e. (1*S*, 2*R*), 1 always refers to the C-OH carbon and 2 always refers to the C-NO_2 carbon.

Synthesis of amino pyridine ligands

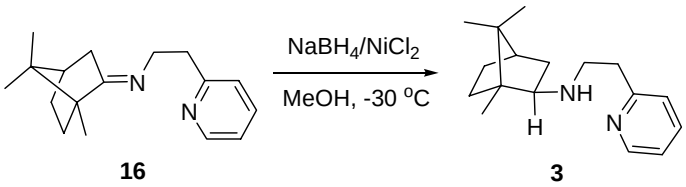
Compound 2:



Sodium borohydride (1.59 g, 4.13 mmol) was added portionwise to a solution of imino pyridine **1**[1] (1.00 g, 4.13 mmol) and $NiCl_2$ (1.09 g, 8.26 mmol) in MeOH (60 mL) at -30 ºC under nitrogen atmosphere over a 1 h period. After 2h, the solvent was evaporated under reduced pressure. Column chromatography eluting with EtOAc afforded 624 mg (62 %) of amino pyridine **2**: an oil; $[\alpha]_D^{25}$ = -80.6 (*c* = 1.01 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.51 (dd, *J* = 4.8, 0.6 Hz, 1H), 7.61 (td, *J* = 7.5, 1.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.12 (ddd, *J* = 7.5, 5.1, 0.6 Hz, 1H), 3.88 (d, *J* = 14.4 Hz, 1H), 3.78 (d, *J* = 14.4 Hz, 1H), 2.62-2.57 (m, 1H), 2.53 (br s, 1H), 1.70-1.42 (m, 5H), 1.07 (s, 3H), 1.03 (d, *J* = 8.4 Hz, 2H), 0.92 (s, 3H), 0.80 ppm (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.4 (s), 149.0 (d), 136.3 (d), 122.2 (d), 121.7 (d), 66.4 (d), 53.9 (t), 48.4 (s), 46.7 (s), 45.2 (d), 38.5 (t), 36.8 (t), 27.3 (t), 20.5 (q), 20.5 (q),

12.2 ppm (q); MS (EI) *m/z* (%): 244 (M^+, 0.8), 152 (100), 135 (29), 95 (41), 93 (92); HRMS calcd for $C_{16}H_{24}N_2$ (M^+): 244.1939, found: 244.1936.

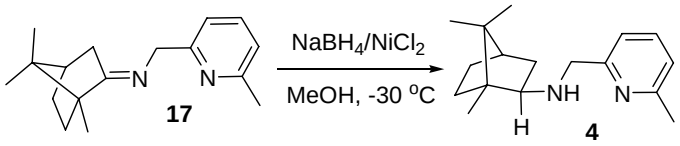
Compound 3



16 **3**

Following the same procedure as for the synthesis of compound **2**, from compound **16**[1] (100 mg, 0.39 mmol) was obtained compound **3** (60.8 mg, 60%): $[\alpha]_D^{25}$ = -70.3 (*c* = 1.02 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (dq, *J* = 4.8, 0.9 Hz, 1H), 7.57 (td, *J* = 7.5, 1.8 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.09 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H), 2.99-2.84 (m, 4H), 2.56 (t, *J* = 6.6 Hz, 1H), 1.69-1.41 (m, 5H), 1.09-0.98 (m, 2H), 0.94 (s, 3H), 0.82 (s, 3H), 0.77 ppm (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.7 (s), 149.1 (d), 136.2 (d), 123.3 (d), 121.1 (d), 66.5 (d), 48.4 (s), 48.3 (t), 46.6 (s), 45.2 (d), 38.7 (t), 38.5 (t), 36.9 (t), 27.3 (t), 20.5 (q), 20.3 (q), 12.1 ppm (q); MS (EI) *m/z* (%): 258 (M^+, 23.2), 187 (63), 152 (100), 149 (61), 106 (85), 95 (91), 93 (88); HRMS calcd for $C_{17}H_{26}N_2$ (M^+): 258.2096, found: 258.2104 .

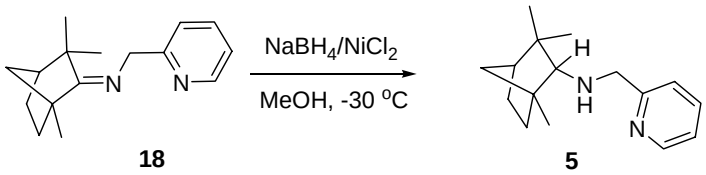
Compound 4



17 **4**

Following the same procedure as for the synthesis of compound **2**, from compound **17**[1] (100 mg, 0.39 mmol) was obtained compound **4** (73 mg, 72 %): $[\alpha]_D^{25}$ = -66.0 (*c* = 1.01 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 3.88 (d, *J* = 14.4 Hz, 1H), 3.81 (d, *J* = 14.4 Hz, 1H), 2.67-2.63 (m, 1H), 2.52 (s, 3H), 1.71-1.48 (m, 5H), 1.09 (s, 3H), 1.07-1.04 (m, 2H), 0.95 (s, 3H), 0.82 ppm (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.1 (s), 157.6 (s), 136.7 (d), 121.4 (d), 119.0 (d), 66.5 (d), 53.7 (t), 48.5 (s), 46.8 (s), 45.2 (d), 38.3 (t), 36.8 (t), 27.3 (t), 24.4 (q), 20.5 (q), 20.5 (q), 12.2 ppm (q); MS (EI) *m/z* (%): 258 (M^+, 0.4), 152 (58), 107 (100), 95 (34); HRMS calcd for $C_{17}H_{26}N_2$ (M^+): 258.2096, found: 258.2097.

Compound 5

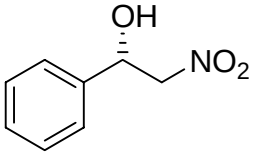


18 **5**

Following the same procedure as for the synthesis of compound **2**, from compound **18**[1] (200 mg, 0.83 mmol) was obtained compound **5** (201 mg, 99 %): $[\alpha]_D^{25}$ = +49.4 (*c* = 1.11 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 4.8 Hz, 1H), 7.64 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42 (d, *J* = 7.8, 1H), 7.14 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.01 (d, *J* = 14.4 Hz, 1H), 3.87 (d, *J* = 14.4 Hz, 1H), 2.37 (br s, 1H), 2.34 (d, *J* = 1.8 Hz, 1H), 1.73-1.33 (m, 5H), 1.11 (s, 3H), 1.08-1.03 (m, 2H), 1.01 (s, 3H), 1.00 ppm (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.4 (s), 149.0 (d), 136.3 (d), 122.2 (d), 121.8 (d), 73.3 (d), 55.4 (t), 49.1 (s), 48.9 (d), 42.8 (t), 39.3 (s), 32.3 (q), 26.5 (t), 26.2 (t), 21.0 (q), 20.5 ppm (q); MS (EI) m/z (%): 244 (M^+, 0.8), 175 (28), 152 (100), 121 (60), 93 (100); HRMS calcd for $C_{16}H_{24}N_2$ (M^+): 244.1939, found: 244.1938.

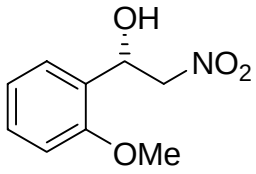
General procedure for the catalytic enantioselective Henry Reaction: Compound **2** (6.7 mg, 0.025 mmol) dissolved in absolute EtOH (2 mL) was added to $Cu(OAc)_2 \cdot H_2O$ (5.0 mg, 0.025 mmol) placed in a test tube. The test tube was stopped with a septum, and the solution was stirred for 1h to give a blue solution. The aldehyde (0.5 mmol) was added and the tube was introduced in a bath at the reaction temperature. After 5 min, the nitroalkane (5 mmol) was added followed by DIPEA (87.1 μL, 0.5 mmol). After the indicated time, the solvent was removed under reduced pressure and the product was isolated by column chromatography.

(*S*)-(+)-2-Nitro-1-phenylethanol (8a) [1]



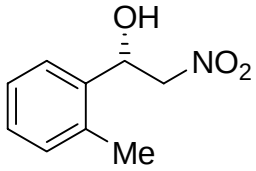
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (98%, Table 1, entry 1) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 15.8, minor enantiomer (*R*) t_r = 13.5; $[\alpha]_D^{25}$ = +51.3 (*c* = 0.76 in CH_2Cl_2, 98% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.40 (m, 5H), 5.47 (dd, *J* = 9.3, 3.6 Hz, 1H), 4.62 (dd, *J* = 13.8, 9.3 Hz, 1H), 4.52 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.77 (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.0 (s), 129.0 (d), 128.9 (s), 125.9 (d), 81.1 (t), 70.9 (d).

(*S*)-(+)-1-(2-Methoxyphenyl)-2-nitroethanol (8b)[1]



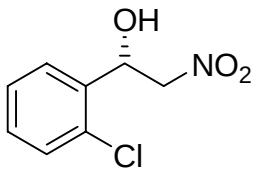
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (98%, Table 1, entry 5) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 13.3, minor enantiomer (*R*) t_r = 11.5; $[\alpha]_D^{25}$ = +49.2 (*c* = 1.13 in CH_2Cl_2, 98% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.04-6.99 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.63 (dd, *J* = 9.0, 3.3 Hz, 1H), 4.65 (dd, *J* = 13.2, 3.3 Hz, 1H), 4.57 (dd, *J* = 13.2, 9.0 Hz, 1H), 3.88 (s, 3H), 2.87 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.9 (s), 129.7 (d), 127.1 (d), 125.9 (s), 121.0 (d), 110.5 (d), 79.8 (t), 67.7 (d), 55.3 ppm (q).

(*S*)-(+)-2-Nitro-1-*o*-tolylethanol (8c)[1]



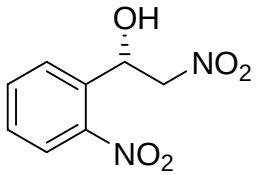
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (98%, Table 1, entry 6) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 15.0, minor enantiomer (*R*) t_r = 10.4; $[\alpha]_D^{25}$ = +49.7 (*c* = 1.13 in CH_2Cl_2, 98% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.46 (m, 1H), 7.25-7.22 (m, 2H), 7.17-7.15 (m, 1H), 5.64 (dd, *J* = 9.6, 2.7 Hz, 1H), 4.51 (dd, *J* = 13.5, 9.6 Hz, 1H), 4.39 (dd, *J* = 13.5, 2.7 Hz, 1H), 2.79 (br s, 1H), 2.35 ppm (s , 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.2 (s), 134.4 (s), 130.8 (d), 128.7 (d), 126.7 (d), 125.6 (d), 80.2 (t), 67.9 (d), 18.8 ppm (q).

(*S*)-(+)-1-(2-Chlorophenyl)-2-nitroethanol (8d)[1]



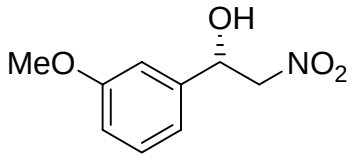
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (96%, Table 1, entry 7) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 95:5, 0.5 mL/min, major enantiomer (*S*) t_r = 27.8, minor enantiomer (*R*) t_r = 26.5; $[\alpha]_D^{25}$ = +60.3 (*c* = 1.02 in CH_2Cl_2, 96% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.40-7.27 (m, 3H), 5.85 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.68 (dd, *J* = 13.5, 2.4 Hz, 1H), 4.45 (dd, *J* = 13.5, 9.6 Hz, 1H), 2.88 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 135.4 (s), 131.5 (s), 129.9 (d), 129.7 (d), 127.6 (d), 127.5 (d), 79.3 (t), 67.8 ppm (d).

(*S*)-(−)-2-Nitro-1-(2-nitrophenyl)ethanol (8e)[1]



Purified by flash chromatography hexane:ether (80:20). Enantiomeric excess (86%, Table 1, entry 8) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 0.8 mL/min, major enantiomer (*S*) t_r = 19.8, minor enantiomer (*R*) t_r = 18.0; $[\alpha]_D^{25}$ = −203.1 (*c* = 0.51 in CH_2Cl_2, 86% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.95 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.75 (td, *J* = 7.8, 1.2 Hz, 1H), 7.55 (td, *J* = 7.8, 1.2 Hz, 1H) 6.04 (dd, *J* = 9.3, 2.4 Hz, 1H), 4.86 (dd, *J* = 13.8, 2.4 Hz, 1H), 4.55 (dd, *J* = 13.8, 9.3 Hz, 1H), 3.28 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.1 (s), 134.3 (d), 134.0 (s), 129.7 (d), 128.7 (d), 125.0 (d), 80.0 (t), 66.7 ppm (d).

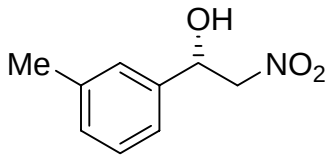
(*S*)-(+)-1-(3-Metoxyphenyl)-2-nitroethanol (8f)[1]



Purified by flash chromatography hexane:ether (82:18). Enantiomeric excess (98%, Table 1, entry 9) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 27.9, minor enantiomer (*R*) t_r = 21.6; $[\alpha]_D^{25}$ = +41.3 (*c* = 0.64 in CH_2Cl_2, 98% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 8.1, 1H), 6.96 (m, 2H), 6.89 (dd, *J* = 8.1, 2.4 Hz, 1H), 5.44 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.60 (dd, *J* = 13.2, 9.3 Hz, 1H), 4.51 (dd, *J* = 13.2, 3.3 Hz, 1H), 3.82 (s, 3H), 2.59

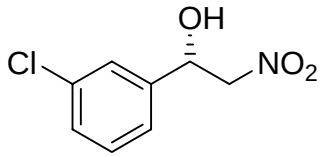
ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.0 (s), 139.7 (s), 130.0 (d), 118.0 (d), 114.3 (d), 111.4 (d), 81.1 (t), 70.8 (d), 55.3 ppm (t).

(*S*)-(+)-2-Nitro-1-*m*-tolylethanol (8g)[1]



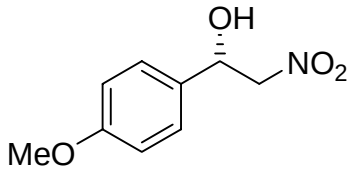
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (98%, Table 1, entry 10) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 13.1, minor enantiomer (*S*) t_r = 11.5; $[\alpha]_D^{25}$ = +41.9 (*c* = 0.54 in CH_2Cl_2, 98% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.5 Hz, 1H), 7.12-7.08 (m, 3H), 5.32 (dd, *J* = 9.3, 3.0 Hz, 1H), 4.50 (dd, *J* = 13.2, 9.3 Hz, 1H), 4.40 (dd, *J* = 13.2, 3.0 Hz, 1H), 2.79 (br s, 1H), 2.29 ppm (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.8 (s), 138.0 (s), 129.6 (d), 128.8 (d), 126.5 (d), 122.9 (d), 81.2 (t), 71.0 (d), 21.3 ppm (q).

(*S*)-(+)-1-(3-Chlorophenyl)-2-nitroethanol (8h)[1]



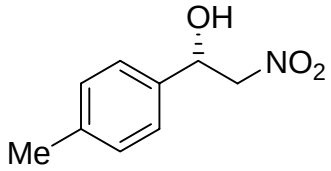
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (97%, Table 1, entry 11) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 16.1, minor enantiomer (*R*) t_r = 13.1; $[\alpha]_D^{25}$ = +40.2 (*c* = 0.80 in CH_2Cl_2, 97% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 1H), 7.35-7.26 (m, 3H), 5.44 (dd, *J* = 9.3, 3.6 Hz, 1H), 4.58 (dd, *J* = 13.5, 9.3 Hz, 1H), 4.50 (dd, *J* = 13.5, 3.6 Hz, 1H), 3.01 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.0 (s), 134.9 (s), 130.3 (d), 129.1 (d), 126.2 (d), 124.0 (d), 80.9 (t), 70.2 ppm (d).

(*S*)-(+)-1-(4-Metoxyphenyl)-2-nitroethanol (8i)[1]



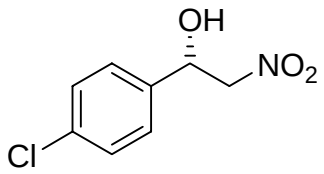
Purified by flash chromatography hexane:ether (82:18). Enantiomeric excess (98%, Table 1, entry 12) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 25.3, minor enantiomer (*R*) t_r = 19.6; $[\alpha]_D^{25}$ = +43.5 (*c* = 0.95 in CH_2Cl_2, 98% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.7, 2H), 6.92 (d, *J* = 8.7, 2H), 5.41 (dd, *J* = 9.3, 3.0 Hz, 1H), 4.60 (dd, *J* = 13.2, 9.3 Hz, 1H), 4.47 (dd, *J* = 13.2, 3.0 Hz, 1H), 3.81 (s, 3H), 2.35 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.9 (s), 130.2 (s), 127.2 (d), 114.3 (d), 81.2 (t), 70.6 (d), 55.3 ppm (q).

(*S*)-(+)-2-Nitro-1-*p*-tolylethanol (8j)[1]



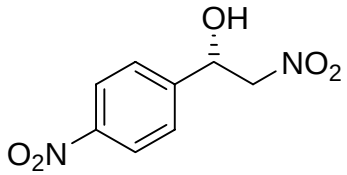
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (98%, Table 1, entry 13) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 16.2, minor enantiomer (*R*) t_r = 12.9; $[\alpha]_D^{25}$ = +47.0 (*c* = 1.00 in CH_2Cl_2, 98% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 5.46 (dd, *J* = 9.3, 3.0 Hz, 1H), 4.64 (dd, *J* = 13.2, 9.3 Hz, 1H), 4.52 (dd, *J* = 13.2, 3.0 Hz, 1H), 2.82 (br s, 1H), 2.41 ppm (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.9 (s), 135.1 (s), 129.6 (d), 125.8 (d), 81.2 (t), 70.8 (d), 21.1 ppm (q).

(*S*)-(+)-1-(4-Chlorophenyl)-2-nitroethanol (8k)[1]



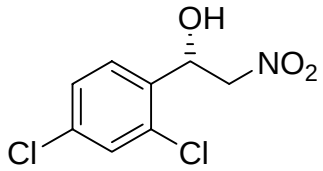
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (97%, Table 1, entry 14) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 16.4, minor enantiomer (*R*) t_r = 13.1; $[\alpha]_D^{25}$ = +35.2 (*c* = 1.12 in CH_2Cl_2, 97% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.31 (m, 4H), 5.43 (dd, *J* = 9.0, 3.3 Hz, 1H), 4.56 (dd, *J* = 13.2, 9.0 Hz, 1H), 4.47 (dd, *J* = 13.2, 3.3 Hz, 1H), 3.11 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.5 (s), 134.7 (s), 129.2 (d), 127.3 (d), 80.9 (t), 70.2 ppm (d).

(*S*)-(+)-1-(4-Nitrophenyl)-2-nitroethanol (8l)[1]



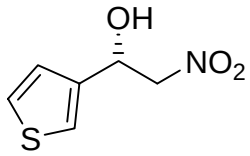
Purified by flash chromatography hexane:ether (80:20). Enantiomeric excess (86%, Table 1, entry 15) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 33.3, minor enantiomer (*R*) t_r = 26.6; $[\alpha]_D^{25}$ = +25.1 (*c* = 0.53 in CH_2Cl_2, 86% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 5.61 (dd, *J* = 7.5, 4.5 Hz, 1H), 4.61-4.58 (m, 2H), 3.30 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 148.0 (s), 145.0 (s), 126.9 (d), 124.1 (d), 80.6 (t), 69.9 ppm (d).

(*S*)-(+)-1-(2,4-Dichlorophenyl)-2-nitroethanol (8m)[2]



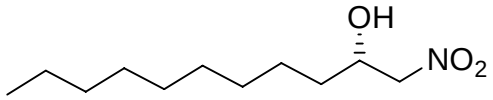
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (89%, Table 1, entry 16) was determined by HPLC (Chiralpak AD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 10.0, minor enantiomer (*R*) t_r = 8.4; $[\alpha]_D^{25}$ = +54.3 (*c* = 1.08 in CH_2Cl_2, 89% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.80 (d, *J* = 9.3 Hz, 1H), 4.65 (dd, *J* = 13.5, 2.4 Hz, 1H), 4.42 (dd, *J* = 13.5, 9.3 Hz, 1H), 3.11 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 135.2 (s), 134.1 (s), 132.0 (s), 129.5 (d), 128.6 (d), 128.0 (d), 79.0 (t), 67.4 ppm (d).

(*S*)-(+)-2-Nitro-1-(thiophen-3-yl)ethanol (8n)



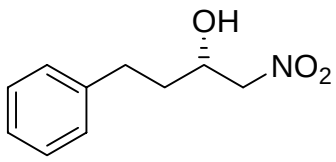
Purified by flash chromatography hexane:ether (85:15). Enantiomeric excess (98%, Table 1, entry 17) was determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 17.3, minor enantiomer (*R*) t_r = 15.0; $[\alpha]_D^{25}$ = +50.0 (*c* = 1.02 in CH_2Cl_2, 98%), absolute stereochemistry assigned by analogy to other compounds in this work; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.36 (m, 2H), 7.09 (dd, *J* = 4.8, 1.2 Hz, 1H), 5.56 (dd, *J* = 9.0, 3.3 Hz, 1H), 4.65 (dd, *J* = 13.5, 9.0 Hz, 1H), 4.57 (dd, *J* = 13.5, 3.3 Hz, 1H), 2.87 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 139.3 (s), 127.2 (d), 125.0 (d), 122.6 (d), 80.5 (t), 67.3 ppm (d); MS (EI) *m/z* (%): 173 (M^+, 15), 126 (100), 113 (42), 85 (59); HRMS 173.0141 (M^+), $C_6H_7NO_3S$ required 173.0147.

(*S*)-(+)-1-Nitroundecan-2-ol (8o)



Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (92%, Table 1, entry 18) was determined by HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, major enantiomer (*S*) t_r = 17.0, minor enantiomer (*R*) t_r = 11.1; $[\alpha]_D^{25}$ = +4.3 (*c* = 0.98 in CH_2Cl_2, 92% ee), absolute stereochemistry assigned by analogy to other compounds in this work; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47-4.27 (m, 2H), 2.52 (br s, 1H), 1.60-1.47 (m, 4H), 1.26 (m, 13H), 0.88 ppm (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 80.6 (t), 68.7 (d), 33.7 (t), 31.8 (t), 29.4 (t), 29.4 (t), 29.3 (t), 29.2 (t), 25.1 (t), 22.6 (t), 14.1 ppm (q).

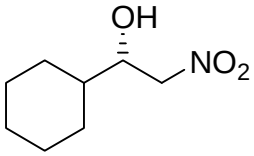
(*S*)-(−)-1-Nitro-4-phenylbutan-2-ol (8p)[1]



Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (94%, Table 1, entry 19) was determined by HPLC (Chiralpak AD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 14.6, minor enantiomer (*R*) t_r = 11.6; $[\alpha]_D^{25}$ = -14.3 (*c* = 0.97 in CH_2Cl_2, 94% ee), absolute

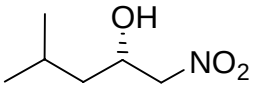
stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.10 (m, 5H), 4.33-4.30 (m, 2H), 4.26-4.20 (m, 1H), 2.83-260 (m, 3H), 1.80-1.69 ppm (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.6 (s), 128.6 (d), 128.4 (d), 126.3 (d), 80.5 (t), 67.7 (d), 35.1 (t), 31.3 ppm (t).

(*S*)-(+)-1-Cyclohexyl-2-nitroethanol (8q)[1]



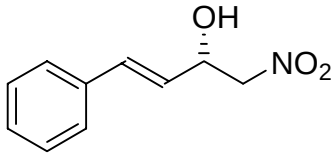
Purified by flash chromatography hexane:ether (88:12). The enantiomeric excess (90%, Table 1, entry 20) was determined by HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 0.7 mL/min, major enantiomer (*S*) t_r = 23.4, minor enantiomer (*R*) t_r = 21.7; $[\alpha]_D^{25}$ = +16.9 (*c* = 0.89 in CH_2Cl_2, 90% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.48 (dd, *J* = 12.9, 3.3 Hz, 1H), 4.41 (dd, *J* = 12.9, 8.7 Hz, 1H), 4.11-4.05 (m, 1H), 2.68 (br s, 1H), 1.84-1.75 (m, 3H), 1.70-1.58 (m, 2H), 1.50-1.37 (m, 1H), 1.28-1.05 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 79.3 (t), 72.8 (d), 41.3 (d), 28.8 (t), 27.9 (t), 26.0 (t), 25.8 (t), 25.7 ppm (t).

(*S*)-(−)-4-Methyl-1-nitropentan-2-ol (8r)[1]



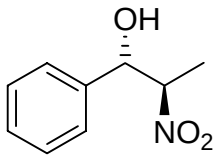
Purified by flash chromatography hexane:ether (88:12). Enantiomeric excess (91%, Table 1, entry 21) was determined by HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, major enantiomer (*S*) t_r = 16.1, minor enantiomer (*R*) t_r = 11.4; $[\alpha]_D^{25}$ = -2.3 (*c* = 0.38 in CH_2Cl_2, 91% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.43-4.33 (m, 3H), 2.41 (br s, 1H), 1.87-1.78 (m, 1H), 1.53-1.45 (m, 1H), 1.26-1.17 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.94 ppm (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 81.0 (t), 66.9 (d), 42.4 (t), 24.3 (d), 23.1 (q), 21.7 ppm (q).

(*S*,*E*)-(+)-1-Nitro-4-phenylbut-3-en-2-ol (8s)[3]



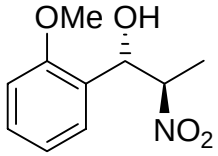
Purified by flash chromatography hexane:ether (80:20). Enantiomeric excess (96%, Table 1, entry 22) was determined by HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, major enantiomer (*S*) t_r = 36.9, minor enantiomer (*R*) t_r = 35.5; $[\alpha]_D^{25}$ = +11.8 (*c* = 0.64 in CH_2Cl_2, 96% ee), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.25 (m, 5H), 6.78 (dd, *J* = 15.9, 1.2 Hz, 1H), 6.14 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.04 (qd, *J* = 6.3, 1.2 Hz, 1H), 4.54-4.45 (m, 2H), 2.53 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 135.5 (s), 133.6 (d), 129.7 (d), 128.5 (d), 126.7 (d), 124.9 (d), 79.8 (t), 69.6 ppm (d).

2-Nitro-1-phenylpropan-1-ol (10a)[4-8]



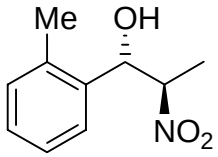
Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 80:20, Table 2, entry 1) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, $anti_{major}$(1*S*,2*R*) t_r = 13.7, $anti_{minor}$(1*R*,2*S*) t_r = 15.0, syn_{major}(1*S*,2*S*) t_r = 18.6, syn_{minor}(1*R*,2*R*) t_r = 21.1, absolute stereochemistry of both diastereomers assigned by comparison of the retention times in HPLC with literature data; *anti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = +1.1 (*c* = 0.65 in CH_2Cl_2, 95% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.33 (m, 5H), 5.40 (d, *J* = 3.6 Hz, 1H), 4.75-4.66 (m, 1H), 2.77 (br s, 1H), 1.50 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.4 (s), 128.7 (d), 128.5 (d), 125.9 (d), 87.4 (d), 73.9 (d), 12.0 ppm (q); s*yn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +47.2 (*c* = 0.31 in CH_2Cl_2, 91% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.33 (m, 5H), 5.03 (d, *J* = 9.0 Hz, 1H), 4.82-4.75 (m, 1H), 2.77 (br s, 1H), 1.32 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.3 (s), 129.2 (d), 129.0 (d), 126.9 (d), 88.4 (d), 76.3 (d), 16.5 ppm (q).

1-(2-Methoxyphenyl)-2-nitropropan-1-ol (10b)[9]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 82:18, Table 2, entry 5) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, *anti*$_{major}$(1*S*,2*R*) t_r = 14.0, *anti*$_{minor}$(1*R*,2*S*) t_r = 17.7, *syn*$_{major}$(1*S*,2*S*) t_r = 24.7, *syn*$_{minor}$(1*R*,2*R*) t_r = 26.3, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; *anti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = +0.9 (*c* = 0.90 in CH_2Cl_2, 95% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 7.5, 1.5 Hz,1H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.53 (d, *J* = 3.6 Hz, 1H), 4.94-4.86 (m, 1H), 3.87 (s, 3H), 3.11 (br s, 1H), 1.47 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.7 (s), 129.4 (d), 127.6 (d), 126.2 (s), 120.9 (d), 110.3 (d), 85.0 (d), 70.7 (d), 55.3 (q), 12.5 ppm (q); *syn isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = +37.8 (*c* = 0.17 in CH_2Cl_2, 94% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (dd, *J* = 7.5, 1.5 Hz,1H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.13 (d, *J* = 9.0 Hz, 1H), 5.05-4.95 (m, 1H), 3.89 (s, 3H), 3.33 (br s, 1H), 1.33 ppm (d, *J* = 6.9 Hz, 3H): ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.7 (s), 130.0 (d), 129.0 (d), 125.8 (s), 121.2 (d), 110.9 (d), 87.6 (d), 74.2 (d), 55.4 (q), 16.6 ppm (q); MS (EI) *m/z* (%): 211 (M^+, 0.1), 197 (33), 150 (30), 137 (100), 135 (86), 107(67), 91 (48), 77 (47).

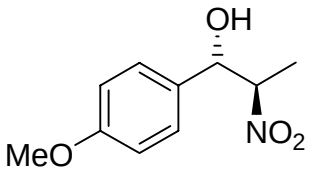
2-nitro-1-*o*-tolylpropan-1-ol (10c)[5,10]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 79:21, Table 2, entry 6) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, *anti*$_{major}$(1*S*,2*R*) t_r = 11.0, *anti*$_{minor}$(1*R*,2*S*) t_r = 12.2, *syn*$_{major}$(1*S*,2*S*) t_r = 15.0, *syn*$_{minor}$(1*R*,2*R*) t_r = 18.4, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; *anti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -9.7 (*c* = 0.90 in CH_2Cl_2, 91% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 1H), 7.30-7.16 (m, 3H), 5.64 (d, *J* = 3.0 Hz, 1H), 4.64 (dq, *J* = 6.6, 3.6 Hz, 1H), 2.38 (s, 3H), 2.38 (br s, 1H), 1.52 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C

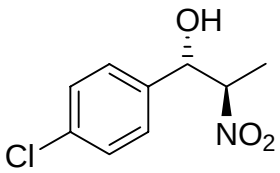
NMR (75.5 MHz, $CDCl_3$): δ = 136.6 (s), 134.3 (s), 130.7 (d), 128.3 (d), 126.4 (d), 125.9 (d), 85.3 (d), 70.8 (d), 18.8 (q), 11.4 ppm (q); *syn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +22.7 (*c* = 0.33 in CH_2Cl_2, 91% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.38 (m, 1H), 7.30-7.16 (m, 3H), 5.38 (d, *J* = 9.3 Hz, 1H), 4.89-4.84 (m, 1H), 2.45 (s, 3H), 2.38 (br s, 1H), 1.33 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.5 (s), 135.8 (s), 131.0 (d), 128.7 (d), 126.8 (d), 126.5 (d), 88.8 (d), 72.1 (d), 19.5 (q), 16.0 ppm (q); MS (EI) *m/z* (%): 195 (M^+, 5), 121 (100), 91 (61).

1-(4-Methoxyphenyl)-2-nitropropan-1-ol (10i)[11,12]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 66:34, Table 2, entry 7) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 90:10, 1 mL/min, $anti_{major}$(1*S*,2*R*) t_r = 11.7, $anti_{minor}$(1*R*,2*S*) t_r = 13.0, syn_{major} (1*S*,2*S*) t_r = 16.3, syn_{minor}(1*R*,2*R*) t_r = 18.8, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -3.6 (*c* = 0.66 in CH_2Cl_2, 91% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.7 Hz, 2H), 6.90 (m, 2H), 5.30 (d, *J* = 3.9 Hz, 1H), 4.72-4.63 (m, 1H), 3.81 (s, 3H), 2.64 (br s, 1H), 1.52 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.6 (s), 130.5 (s), 127.2 (d), 114.1 (d), 87.5 (d), 73.7 (d), 55.3 (q), 12.4 ppm (q); s*yn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +38.2 (*c* = 0.57 in CH_2Cl_2, 85% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.7 Hz, 2H), 6.90 (m, 2H), 4.98 (d, *J* = 9.3 Hz, 1H), 4.79-4.72 (m, 1H), 3.82 (s, 3H), 2.64 (br s, 1H), 1.30 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.1 (s), 130.4 (s), 128.1 (d), 114.3 (d), 88.5 (d), 75.9 (d), 55.6 (q), 16.4 ppm (q); MS (EI) *m/z* (%): 211 (M^+, 21), 137 (100), 135 (44), 77 (21).

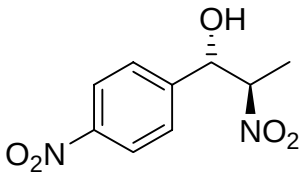
1-(4-Chlorophenyl)-2-nitropropan-1-ol (10k)[8,13]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 81:19, Table 2, entry 8) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC

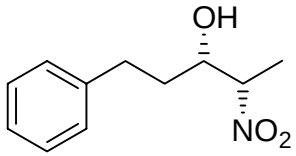
(Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, a*nti*$_{major}$(1*S*,2*R*) t_r = 15.0, *anti*$_{minor}$(1*R*,2*S*) t_r = 16.4, *syn*$_{major}$(1*S*,2*S*) t_r = 24.0, *syn*$_{minor}$(1*R*,2*R*) t_r = 21.9, absolute stereochemistry of both diastereomers assigned by comparison of the retention times in HPLC with literature data and by analogy to other compounds in this work; *anti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = +3.7 (*c* = 1.13 in CH_2Cl_2, 95% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.30 (m, 4H), 5.38 (d, *J* = 3.6 Hz, 1H), 4.72-4.62 (m, 1H), 2.87 (br s, 1H), 1.49 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.8 (s), 134.4 (s), 128.9 (d), 127.3 (d), 87.2 (d), 73.2 (d), 12.0 ppm (q); s*yn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +33.1 (*c* = 0.26 in CH_2Cl_2, ee 84%), Lit.[13] $[\alpha]_D^{25}$ = -15.8 (*c* = 1 in $CHCl_3$, for the 1*R* enantiomer, 71% ee, mixture of diastereomers); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.30 (m, 4H), 5.02 (d, *J* = 9.0 Hz, 1H), 4.77-4.70 (m, 1H), 2.87 (br s, 1H), 1.33 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.7 (s), 135.1 (s), 129.2 (d), 128.2 (d), 88.1 (d), 75.5 (d), 16.3 ppm (q).

2-Nitro-1-(4-nitrophenyl)propan-1-ol (10l)[11,12,14,15]



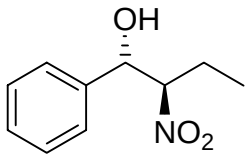
Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 80:20, Table 2, entry 9) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H + Chiralpak AD-H), hexane:*i*-PrOH 80:20, 1 mL/min, *anti*$_{major}$(1*S*,2*R*) t_r=17.5, *anti*$_{minor}$(1*R*,2*S*) t_r=16.1, *syn*$_{major}$(1*S*,2*S*) t_r = 22.7, *syn*$_{minor}$(1*R*,2*R*) t_r = 20.1, absolute stereochemistry of both diastereomers assigned by comparison of the retention times in HPLC with literature data and by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -0.37 (*c* = 0.57 in CH_2Cl_2, 92% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 5.56 (br s, 1H), 4.75-4.67 (m, 1H), 2.98 (br s, 1H), 1.49 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.8 (s), 145.6 (s), 127.0 (d), 123.9 (d), 86.8 (d), 72.9 (d), 11.8 ppm (q); *syn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +19.6 (*c* = 0.17 in CH_2Cl_2, 63% ee), Lit.[14] $[\alpha]_D^{25}$ = +20.8 (*c* = 0.36 in CH_2Cl_2, 91% ee, mixture of diastereomers); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 5.19 (d, *J* = 8.7 Hz, 1H), 4.79-4.72 (m, 1H), 2.90 (br s, 1H), 1.40 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 148.2 (s), 145.3 (s), 127.9 (d), 124.0 (d), 87.8 (d), 75.0 (d), 16.1 ppm (q).

4-Nitro-1-phenylpentan-3-ol (10p)[8,16-18]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 47:53, Table 2, entry 10) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, *syn*$_{major}$(1*S*,2*S*) t_r = 21.3, *syn*$_{minor}$(1*R*,2*R*) t_r = 19.4, *anti*$_{major}$(1*S*,2*R*) t_r = 15.2, *anti*$_{minor}$(1*R*,2*S*) t_r = 15.2, absolute stereochemistry of both diastereomers assigned by comparison of the retention times in HPLC with literature data; s*yn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = -19.5 (*c* = 0.67 in CH_2Cl_2, 80% ee), $[\alpha]_D^{25}$ = -28.8 (*c* = 0.61 in EtOH, 80% ee), Lit.[17] $[\alpha]_D^{24}$ = -43.7 (*c* = 1.06 in EtOH, 97% ee), Lit.[16] $[\alpha]_D^{25}$ = +29.0 (*c* = 0.96 in EtOH, for the 1*R*,2*R* enantiomer, 83% ee, mixture of diastereomers); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33-7.18 (m, 5H), 4.54 (quint, *J* = 6.9 Hz, 1H), 3.93-3.86 (m, 1H), 2.79-2.65 (m, 2H), 2.29 (br s, 1H), 1.90-1.76 (m, 2H), 1.53 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.8 (s), 128.6 (d), 128.4 (d), 126.2 (d), 87.7 (d), 72.1 (d), 34.7 (t), 31.4 (t), 16.2 ppm (q); a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -16.1 (*c* = 0.59 in CH_2Cl_2, 77% ee), $[\alpha]_D^{25}$ = -23.5 (*c* = 0.47 in EtOH, 77% ee), Lit.[17] $[\alpha]_D^{24}$ = -18.4 (*c* = 1.04 in EtOH, 49% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33-7.18 (m, 5H), 4.48 (qd, *J* = 6.9, 3.0 Hz, 1H), 4.21-4.15 (dt, *J* = 9.3, 3.6 Hz, 1H), 2.94-2.83 (m, 2H), 2.29 (br s, 1H), 1.90-1.76 (m, 2H), 1.55 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.8 (s), 128.6 (d), 128.4 (d), 126.2 (d), 86.3 (d), 71.1 (d), 34.6 (t), 31.9 (t), 12.5 ppm (q); MS (EI) *m/z* (%): 209 (M^+, 0.1), 105 (49), 91 (100), 57 (39).

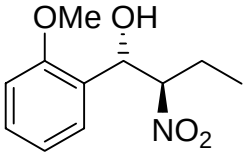
2-Nitro-1-phenylbutan-1-ol (11a)[6,7,8,19]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 71:29, Table 2, entry 11) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H + Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, *anti*$_{major}$(1*S*,2*R*) t_r = 26.8, *anti*$_{minor}$(1*R*,2*S*) t_r = 22.5, *syn*$_{major}$(1*S*,2*S*) t_r = 31.1, *syn*$_{minor}$(1*R*,2*R*) t_r = 28.6, absolute stereochemistry of the *anti* diastereomer assigned by comparison of the retention times in HPLC with literature data and that of the *syn* isomer assigned by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -9.7 (*c* = 1.01 in CH_2Cl_2, 94% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.35 (m, 5H), 5.19 (d, *J* = 4.8 Hz, 1H),

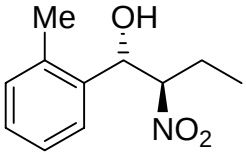
4.61-4.55 (m, 1H), 2.62 (br s, 1H), 2.23-2.09 (m, 1H), 1.98-1.80 (m, 1H), 0.94 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.5 (s), 129.1 (d), 128.7 (d), 126.2 (d), 94.6 (d), 74.2 (d), 21.3 (t), 10.3 ppm (q); *syn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +36.8 (*c* = 0.54 in CH_2Cl_2, 92% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.35 (m, 5H), 5.04 (d, *J* = 9.0 Hz, 1H), 4.66-4.60 (m, 1H), 2.62 (br s, 1H), 1.98-1.80 (m, 1H), 1.49-1.35 (m, 1H), 0.88 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 138.6 (s), 130.1 (d), 129.0 (d), 126.8 (d), 95.2 (d), 75.5 (d), 23.9 (t), 10.0 ppm (q).

1-(2-Methoxyphenyl)-2-nitrobutan-1-ol (11b)



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 70:30, Table 2, entry 12) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H + Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, a*nti*$_{major}$(1*S*,2*R*) t_r = 21.2, *anti*$_{minor}$(1*R*,2*S*) t_r = 23.5, *syn*$_{major}$(1*S*,2*S*) t_r = 35.0, *syn*$_{minor}$(1*R*,2*R*) t_r = 33.3, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -17.6 (*c* = 0.84 in CH_2Cl_2, 93% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 2H), 7.02-6.89 (m, 2H), 5.24 (t, *J* = 5.7 Hz, 1H), 4.81-4.75 (m, 1H), 3.89 (s, 3H), 3.31 (d, *J* = 6.3 Hz), 2.23-2.09 (m, 1H), 1.99-1.86 (m, 1H), 0.93 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.1 (s), 129.6 (d), 128.3 (d), 125.9 (s), 121.0 (d), 110.6 (d), 92.5 (d), 72.1 (d), 55.4 (q), 21.7 (t), 10.4 ppm (q); s*yn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +24.0 (*c* = 0.48 in CH_2Cl_2, 95% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 2H), 7.02-6.89 (m, 2H), 5.13 (t, *J* = 9.0 Hz, 1H), 4.88-4.83 (m, 1H), 3.90 (s, 3H), 3.27 (d, *J* = 6.3 Hz), 1.99-1.86 (m, 1H), 1.59-1.43 (m, 1H), 0.88 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.7 (s), 130.0 (d), 128.9 (d), 126.1 (s), 121.2 (d), 110.9 (d), 94.4 (d), 73.4 (d), 55.4 (q), 24.1 (t), 10.2 ppm (q); MS (EI) *m/z* (%): 225 (M^+, 26), 137 (100), 107 (32), 77 (18).

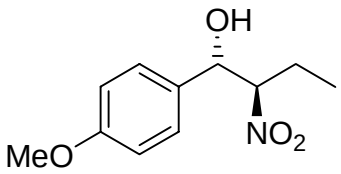
2-Nitro-1-*o*-tolylbutan-1-ol (11c)



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 75:25, Table 2, entry 13) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC

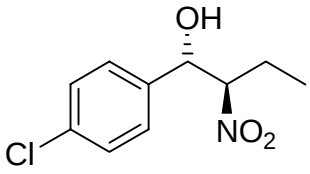
(Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, a*nti*$_{major}$(1*S*,2*R*) t_r = 9.9, *anti*$_{minor}$(1*R*,2*S*) t_r = 11.0, *syn*$_{major}$(1*S*,2*S*) t_r = 13.8, *syn*$_{minor}$(1*R*,2*R*) t_r = 16.0, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; *anti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = +0.2 (*c* = 1.02 in CH_2Cl_2, 89% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 1H), 7.29-7.16 (m, 3H), 5.42 (d, *J* = 3.9 Hz, 1H), 4.58-4.52 (m, 1H), 2.37 (s, 3H), 2.25-2.19 (m, 1H), 1.91-1.82 (m, 1H), 0.93 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.6 (s), 134.8 (s), 130.8 (d), 128.5 (s), 126.4 (d), 126.0 (d), 92.9 (d), 71.0 (d), 20.6 (t), 18.9 (q), 10.4 ppm (q), s*yn isomer* (1*S*,2*S*) : $[\alpha]_D^{25}$ = +34.1 (*c* = 0.40 in CH_2Cl_2, 90% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41-7.38 (m, 1H), 7.29-7.16 (m, 3H), 5.36 (d, *J* = 9.3 Hz, 1H), 4.73-4.65 (m, 1H), 2.44 (s, 3H), 1.91-1.82 (m, 1H), 1.45-1.32 (m, 1H), 0.87 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.9 (s), 135.8 (s), 131.0 (d), 128.8 (s), 126.9 (d), 126.5 (d), 95.7 (d), 71.6 (d), 23.4 (t), 19.5 (q), 10.3 ppm (q); MS (EI) *m/z* (%): 209 (M^+, 5), 121 (100), 119 (37), 93 (43), 91 (47).

1-(4-Methoxyphenyl)-2-nitrobutan-1-ol (11i)[20]



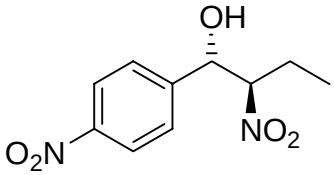
Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 61:39, Table 2, entry 14) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, a*nti*$_{major}$(1*S*,2*R*) t_r = 20.3, *anti*$_{minor}$(1*R*,2*S*) t_r = 21.0, *syn*$_{major}$(1*S*,2*S*) t_r = 31.0, *syn*$_{minor}$(1*R*,2*R*) t_r = 28.6, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -10.5 (*c* = 0.68 in CH_2Cl_2, 89% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 6.93-6.88 (m, 2H), 5.10 (d, *J* = 5.4 Hz, 1H), 4.58-4.52 (m, 1H), 3.80 (s, 3H), 2.22-2.04 (m, 1H), 2.00-1.88 (m, 1H), 0.95 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.8 (s), 130.7 (s), 127.5 (d), 114.1 (d), 94.8 (d), 74.0 (d), 55.2 (q), 21.8 (t), 10.3 ppm (q); s*yn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +45.8 (*c* = 0.56 in CH_2Cl_2, 93% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 6.93-6.88 (m, 2H), 4.98 (d, *J* = 9.0 Hz, 1H), 4.63-4.57 (m, 1H), 3.82 (s, 3H), 1.85-1.75 (m, 1H), 1.47-1.33 (m, 1H), 0.86 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.1 (s), 130.7 (s), 128.1 (d), 114.3 (d), 95.3 (d), 75.1 (d), 55.3 (q), 23.9 (t), 10.0 ppm (q); MS (EI) *m/z* (%): 225 (M^+, 12), 137 (100), 135 (31).

1-(4-Chlorophenyl)-2-nitrobutan-1-ol (11k)[21]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 65:35, Table 2, entry 15) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, a*nti*$_{major}$(1*S*,2*R*) t_r = 12.4, *anti*$_{minor}$(1*R*,2*S*) t_r = 13.3, *syn*$_{major}$(1*S*,2*S*) t_r = 21.6, *syn*$_{minor}$(1*R*,2*R*) t_r = 17.8, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -9.2 (*c* = 0.79 in CH_2Cl_2, 91% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.30 (m, 4H), 5.17 (d, *J* = 4.8 Hz, 1H), 4.56-4.50 (m, 1H), 2.70 (br s), 2.23-2.01 (m, 1H), 1.94-1.78 (m, 1H), 0.94 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.0 (s), 134.5 (s), 129.2 (d), 127.6 (d), 94.5 (d), 73.5 (d), 21.3 (t), 10.3 ppm (q); *syn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +66.5 (*c* = 0.26 in CH_2Cl_2, 87% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.30 (m, 4H), 5.03 (d, *J* = 8.7 Hz, 1H), 4.61-4.55 (m, 1H), 2.70 (br s, 1H), 2.23-2.01 (m, 1H), 1.50-1.21 (m, 1H), 0.89 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.1 (s), 135.0 (s), 129.4 (d), 128.2 (d), 95.0 (d), 74.7 (d), 23.8 (t), 10.0 ppm (q); MS (EI) *m/z* (%): 229 (M^+, 2), 182 (30), 141 (100), 77 (40).

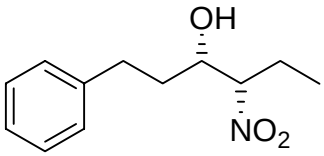
2-Nitro-1-(4-nitrophenyl)butan-1-ol (11l)[20,22]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 74:26, Table 2, entry 16) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 90:10, 1 mL/min, a*nti* t_r = 12.8, *syn*$_{major}$ (1*S*,2*S*) t_r = 29.2, *syn*$_{minor}$(1*R*,2*R*) t_r = 19.1 and (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, *anti*$_{major}$(1*S*,2*R*) t_r = 13.1, *Anti*$_{minor}$(1*R*,2*S*) t_r = 12.2, *syn* t_r = 16.0, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -19.9 (*c* = 0.89 in CH_2Cl_2, 91% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28-8.23 (m, 2H), 7.61-7.57 (m, 2H), 5.33 (d, *J* = 4.5 Hz, 1H), 4.61-4.54 (m, 1H), 2.94 (br s, 1H), 2.26-2.13 (m, 1H), 1.84-1.75 (m, 1H), 0.94 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.9 (s), 145.5 (s), 127.2 (d), 123.9 (d), 94.1 (d), 73.2 (d), 21.2 (t), 10.3

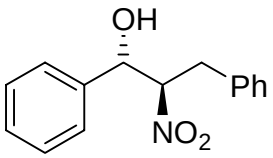
ppm (q); s*yn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = +40.9 (*c* = 0.36 in CH_2Cl_2, 75% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28-8.23 (m, 2H), 7.61-7.57 (m, 2H), 5.18 (d, *J* = 8.1 Hz, 1H), 4.65-4.59 (m, 1H), 2.94 (br s, 1H), 2.01-1.89 (m, 1H), 1.56-1.43 (m, 1H), 0.92 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 148.2 (s), 145.6 (s), 127.8 (d), 124.1 (d), 94.5 (d), 74.3 (d), 23.8 (t), 10.0 ppm (q); MS (EI) *m/z* (%): 240 (M^+, 0.1), 193 (34), 152 (66), 151 (100), 150 (91), 77 (74).

4-Nitro-1-phenylhexan-3-ol (11p)[17,18]



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 39:61, Table 2, entry 17) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min, s*yn*$_{major}$(1*S*,2*S*) t_r = 18.9, *syn*$_{minor}$(1*R*,2*R*) t_r = 18.0, *anti*$_{major}$(1*S*,2*R*) t_r = 12.7, *anti*$_{minor}$(1*R*,2*S*) t_r = 13.4, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; *syn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = -22.8 (*c* = 0.66 in CH_2Cl_2, 80% ee), Lit[17] $[\alpha]_D^{24}$ = -28.6 (*c* = 1.2 in $CHCl_3$, 95% ee) ; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32-7.18 (m, 5H), 4.42-4.33 (m, 1H), 3.92-3.86 (m, 1H), 2.98-2.80 (m, 1H), 2.78-2.64 (m, 1H), 2.40 (br s, 1H), 2.12-1.95 (m, 1H), 1.92-1.69 (m, 3H), 0.95 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.8 (s), 128.6 (d), 128.4 (d), 126.2 (d), 94.3 (d), 71.0 (d), 35.2 (t), 31.5 (t), 23.8 (t), 10.1 ppm (q); a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = -17.4 (*c* = 0.56 in CH_2Cl_2, 80% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32-7.18 (m, 5H), 4.42-4.33 (m, 1H), 4.04-3.99 (m, 1H), 2.98-2.80 (m, 1H), 2.78-2.64 (m, 1H), 2.40 (br s, 1H), 2.12-1.95 (m, 1H), 1.92-1.69 (m, 3H), 0.97 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.7 (s), 128.5 (d), 128.4 (d), 126.2 (d), 93.8 (d), 71.3 (d), 34.7 (t), 31.7 (t), 21.5 (t), 10.5 ppm (q).

2-Nitro-1,3-diphenylpropan-1-ol (12)



Purified by flash chromatography hexane:ether (88:12). Diastereomeric ratios (*anti/syn*, 68:32, Table 2, entry 18) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, a*nti*$_{major}$(1*S*,2*R*) t_r = 14.9, *anti*$_{minor}$(1*R*,2*S*) t_r = 10.1,

syn$_{major}$(1*S*,2*S*) t_r = 12.7, *syn*$_{minor}$(1*R*,2*R*) t_r = 11.1, absolute stereochemistry of both diastereomers assigned by analogy to other compounds in this work; a*nti isomer* (1*S*,2*R*): $[\alpha]_D^{25}$ = +27.0 (*c* = 1.04 in CH_2Cl_2, 83% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33-7.28 (m, 5H), 7.17-7.13 (m, 3H), 6.99-6.97 (m, 2H), 5.17 (d, *J* = 5.1 Hz, 1H), 4.85-4.79 (m, 1H), 3.31 (dd, *J* = 15.0, 11.1 Hz, 1H), 3.10 (dd, *J* = 14.7, 3.0 Hz, 1H), 2.48 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.2 (s), 135.6 (s), 128.8 (d), 128.8 (d), 128.7 (d), 128.7 (d) 127.2 (d), 126.1 (d), 94.4 (d), 74.3 (d), 33.9 ppm (t); *syn isomer* (1*S*,2*S*): $[\alpha]_D^{25}$ = -14.9 (*c* = 0.79 in CH_2Cl_2, 54% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.10 (m, 8H), 7.03 (dd, *J* = 7.8, 2.4 Hz, 2H), 5.09 (d, *J* = 8.4 Hz, 1H), 4.95 (ddd, *J* = 10.8, 8.4, 3.9 Hz, 1H), 3.13 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.77 ppm (dd, *J* = 14.4, 3.9 Hz, 1H), 2.48 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.4 (s), 134.8 (s), 129.4 (d), 129.2 (d), 128.8 (d), 128.6 (d), 127.5 (d), 126.8 (d), 94.9 (d), 75.4 (d), 36.7 ppm (t); MS (EI) *m/z* (%): 257 (M^+, 0.1), 210 (55), 105 (69), 91 (100), 77 (67).

Computational Methods.

Density functional theory calculations have been carried out using the B3LYP exchange–correlation functionals, together with the standard 6-31G* basis sets.[23] Unrestricted calculations (UB3LYP) were used due to the radical nature of the complex. All calculations were carried out with the Gaussian 03 suite of programs.[24]

Total Energy and Cartesian coordinates of the complex **2**-$Cu(OAc)_2$

```
E(UB+HF-LYP) =  -2831.01285924  au
S**2   =   0.7519

Cu         0.000000000000      0.000000000000      0.000000000000
C          0.000000000000      0.000000000000      2.860478360000
C          2.180073690157      0.000000000000      2.045661298722
C          0.457752569230      0.145608819941      4.171052067065
C          2.708843396818      0.133934103293      3.323613729238
H          2.795401796138     -0.059277118249      1.153845080658
C          1.828805730268      0.211590504446      4.404756287685
H         -0.253666030627      0.206622637970      4.989220150279
H          3.783392618578      0.183221475726      3.464308982004
H          2.206388132232      0.325504137977      5.416985315000
N          0.855236921747     -0.062823482647      1.825642979274
N         -1.709960579869      0.100676096428      1.097512433403
C         -1.471500735574     -0.147551318640      2.527635883674
H         -1.770445725615     -1.166953078840      2.777780333326
H         -2.058563229650      0.524213227610      3.168140600162
H         -1.758743620419      1.135365973235      0.946120567926
C         -2.946375166032     -0.416360549770      0.427497288821
C         -3.357087873803     -1.942584008553      0.488425177281
C         -4.269252046748      0.321844389871      0.800840600323
C         -4.076299166110     -2.124038408455     -0.887018974541
C         -4.610211864113     -1.982586271322      1.459976513551
C         -5.324009034752     -0.803209492050      0.734545339431
H         -4.214859156523      0.764267828725      1.801000394636
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H	-4.478472242083	1.143359106450	0.108654420294
C	-5.389930816518	-1.294532488123	-0.734408401542
H	-3.445057270973	-1.781911597683	-1.712464034299
H	-4.284703937084	-3.181460946089	-1.075297575944
H	-6.295701875664	-0.515880605311	1.151375679079
H	-5.438029553110	-0.453638570406	-1.434697765691
H	-6.278563213164	-1.908208688194	-0.913908007553
H	-2.714592391234	-0.191649314983	-0.614969457854
C	-4.348825107296	-1.725967706154	2.955572152078
H	-3.681608735466	-2.489606966516	3.375388887995
H	-3.922159455268	-0.748135434098	3.176316755681
H	-5.292953138824	-1.790653499919	3.510440523080
C	-5.395690865199	-3.311606207113	1.410505167301
H	-4.814947623271	-4.120327460282	1.870505103228
H	-6.324711451221	-3.214826882790	1.985560792115
H	-5.669342228190	-3.636889530175	0.405733570190
C	-2.251810112927	-2.971040326541	0.706472572711
H	-1.448366881440	-2.854082158826	-0.026177119787
H	-1.802165456673	-2.913851378577	1.705090799854
H	-2.657578783500	-3.984403500535	0.600038562130
O	1.725878830334	-0.319842007359	-0.914511980912
O	-0.613510388498	1.292460406517	-1.323713260334
C	-1.191022863250	2.396773931039	-0.993888472474
C	1.343327417517	-1.410296034220	-1.480948103408
O	-1.645287337115	2.673103248283	0.138247131685
O	0.206858416751	-1.888774772137	-1.249780135078
C	2.292643786306	-2.074961408003	-2.452606662481
H	2.293156821930	-1.510258702427	-3.392127353296
H	3.314143237784	-2.060442226955	-2.061360738374
H	1.978163467388	-3.100397918492	-2.656520940258
C	-1.306895148506	3.414870766015	-2.120155169869
H	-0.304840889229	3.716937119699	-2.443896746255
H	-1.798221707761	2.957857419547	-2.985524735783
H	-1.867050346689	4.292331533930	-1.791480472878

Literature

[1] G. Blay, E. Climent, I. Fernández, V. Hernández-Olmos, J. R. Pedro, *Tetrahedron: Asymmetry* **2007**, *18*, 1603-1612, and references cited therein.

[2] Y. Kogami, T. Nakajima, T. Ikeno, T. Yamada, *Synthesis* **2004**, 1947-1950.

[3] M. Bandini, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, C. Ventrici, *Chem. Commun.* **2007**, 616-618.

[4] T. Purkarthofer, K. Gruber, M. Gruber-Khadjawi, K. Waich, W. Skrank, D. Mink, H. Griengl, *Angew. Chem. Int. Ed*. **2006**, *45*, 3454-3456.

[5] M. Terada, H. Ube, S. Yokoyama, H. Shimizu, (Takasago International Corporation, Japan). PCT Int. Appl., **2005**, PIXXD2 WO 2005077908 A1 20050825 [*Chem. Abs.* **2005**, 143, 229737].

[6] K. Maruoka, T. Ooi, PCT Int. Appl., 2004, PIXXD2 WO2004076459 A1 20040910 [*Chem. Abs.* **2004**, 141, 260392].

[7] T. Ooi, K. Doda, K. Maruoka, *J. Am. Chem. Soc.* **2003**, *125*, 2054-2055.

[8] D. Uraguchi, S. Sakaki, T. Ooi, *J. Am. Chem. Soc.* **2007**, *129*, 12392-12393.

[9] K. Bayley, *Tetrahedron* **1972**, *28*, 3981-3986, racemic.

[10] A. Solladie-Cavallo, G. Lapitajs, P. Buchert, A. Klein, S. Colonna, A. Manfredi, *J. Org. Chem.* **1987**, *330*, 357-363, racemic.

[11] S. E. Denmark, B. S. Kesler, Y.C. Moon, *J. Org. Chem.* **1992**, *57*, 4912-24, racemic.

[12] N. Hirata, M. Hayashi, *Synth. Commun.* **2007**, *37*, 1653-1657, racemic.

[13] J. C. Borah, J. Boruwa, B. Kalita, A. K. Hazarika, N. C. Barua, *Indian J. Chem.* **2005**, *44B*, 1961-1965.

[14] Y. Xiong, F. Wang, X. Huang, Y. Wen, X. Feng, *Chem. Eur. J.* **2007**, *13*, 829-833.

[15] R. Ballini, G. Bosica, E. Marcantoni, P. Vita, G. Bartoli, *J. Org. Chem.* **2000**, *65*, 5854-5857, racemic.

[16] Y. Sohtome, Y. Hashimoto, K. Nagasawa, *Eur. J. Org. Chem.* **2006**, 2894-2897.

[17] H. Sasai, T. Tokunaga, S. Watanabe, T. Suzuki, N. Itoh, M. Shibasaki, *J. Org. Chem.* **1995**, *60*, 7388-7389.

[18] M. Shibazaki, H. Sasai, Jpn. Kokai Tokkyo Koho, **1997**, JKXXAF JP 09253502 A 19970930 Heisei. [*Chem. Abs.* **1997**, 127, 346210].

[19] D. Seebach, A. K. Beck, T. Mukhopadhyay, E. Thomas. *Helv. Chim. Acta* **1982**, *65*, 1101-1133.

[20] A. G. M. Barrett, C. Robyr, C. D. Spilling, *J. Org. Chem.* **1989**, *54*, 1233-1234, racemic.

[21] U. V. Desai, D. M. Pore, R. B. Mane, S. B. Solabannar, P. P. Wadgaonkar, *Synth. Commun.* **2004**, 34, 19-24, racemic.

[22] A. J. Parratt, D. J. Adams, A. A. Clifford, C. M. Rayner, *Chem. Commun.* **2004**, 2720-2721, racemic

[23] (a) A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648–5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785-789.

[24] M. J. Frisch, *et al*., GAUSSIAN 03 (Revision C.02), Gaussian, Inc., Wallingford, CT, 2004.