Enantioselective Organo-SOMO Cycloadditions: A Catalytic Approach to Complex Pyrrolidines from Aldehydes and Olefins.

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Supporting Information

Contents

1. General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] All aldehydes were purified by silica gel chromatography prior to use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching or by staining using CAM, $KMnO_4$, or *p*-anisaldehyde stains.

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 (400 MHz), Inova 500 (500 MHz), or Bruker 500 (500 MHz), and are internally referenced to residual protio solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity when applicable. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the Princeton University Mass Spectral facility by electrospray ionization, electron ionization, chemical ionization, or fast atom/ion bombardment techniques as indicated. Supercritical fluid chromatography (SFC) was performed on a Berger Minigram equipped with a diode array UV detector (λ = 214–300 nm) using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. High Pressure Liquid chromatography (HPLC) was performed on a Hewlett-Packard 1100 Series chromatograph using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. Optical rotations were measured on a Jasco P-1010 polarimeter with $[a]_D$ values reported in 10^{-1} dg cm^2 g^{-1}; concentration (c) is in g/100 mL.

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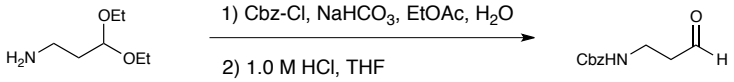
[1] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, **1988**.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518.
[3] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

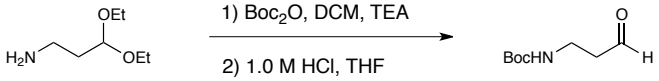
Specific Notes Regarding SOMO Formal Cycloaddition Reactions: Glassware was dried overnight in an oven at 120 °C prior to use. Due to the heterogeneous nature of the reactions, stirring was found to be important for maximum reaction efficiency. Qualitative analysis of reaction progress was monitored by TLC but also conveniently approximated by the color of the mixture resulting from oxidant consumption. The mixture, initially deep blue in color (arising from the oxidizing iron(III) salts), changes to bright red with reaction progress.

2. Substrate Preparation:

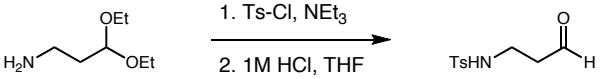


Benzyl (3-oxopropyl)carbamate. To a solution of 3,3-diethoxypropan-1-amine (3.2 mL, 20.0 mmol, 1.0 equiv) in EtOAc (40 mL) was added $NaHCO_3$ (8.4 g, 100 mmol, 5 equiv) and H_2O (40 mL). The mixture was treated with benzyl chloroformate (4.5 mL, 30.0 mmol, 1.5 equiv) and stirred at room temperature for 8 h. The layers were separated and the aqueous was extracted with ethyl acetate (3 x 40 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated to furnish the crude product. To a solution of crude acetal in THF (7 mL) at 0 °C was added an aqueous solution of HCl 1M (3.5 mL). The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was diluted with diethyl ether (25 mL) and washed with saturated solution of $NaHCO_3$ (25 mL) and extracted with diethyl ether (3 x 10 mL). The layers were separated and organics dried over $MgSO_4$, filtered, and concentrated to furnish the crude product. Purification by silica gel chromatography (50% EtOAc/hexanes) afforded the title compound as a white solid (580 mg, 80%). R_f 0.41 (50% EtOAc/hexanes); IR (film) 2952, 2896, 2829, 1695, 1517, 1454, 1243, 1139, 1091, 1023, 776, 737, 696; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H, C**H**O), 7.52 – 7.27 (m, 5H, Ar**H**), 5.15 (t, *J* = 6.5 Hz, 1H, CBz**H**N), 5.08 (s, 2H, ArC**H**$_2$O), 3.54 – 3.40 (m, 2H, CBzHNC**H**$_2$), 2.73 (t, *J* = 5.7 Hz, 2H, CBzHNCH$_2$C**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.3, 156.2, 136.3, 128.5, 128.1, 128.1, 66.7, 44.0, 34.4; HRMS (EI) m/z calculated for $C_{11}H_{13}NNaO_3$ ($[M+Na]^+$)

230.0788, found 230.0788.

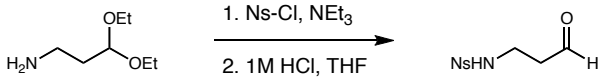


***t*-butyl 3-oxopropylcarbamate.** To a solution of 3,3-diethoxypropan-1-amine (1.6 mL, 10.0 mmol, 1.0 equiv), triethylamine (2.8 mL, 20.0 mmol, 2.0 equiv), 4-(dimethylamino)pyridine (6.1 mg, 0.05 mmol, 0.5 mol%) in DCM (20 mL) at 0 °C was added drop-wise a solution of di-*tert*-butyl dicarbonate (2.5 mL, 11.0 mmol, 1.1 equiv) in DCM (10 mL). The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with H_2O (30 mL) and extracted with diethyl ether (3 x 15 mL). Organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to furnish the crude product. To a solution of the crude acetal in THF (8 mL) at 0 °C was added an aqueous solution of HCl 1M (4.0 mL). The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was diluted with diethyl ether (25 mL) and washed with saturated solution of $NaHCO_3$ (25 mL) and extracted with diethyl ether (3 x 10 mL). The layers were separated and organics dried over $MgSO_4$, filtered, and concentrated to furnish the crude product. Purification by silica gel chromatography (50% EtOAc/hexanes) afforded the title compound as a white solid (492 mg, 71%). R_f 0.42 (50% EtOAc/hexanes); IR (film) 3360, 2978, 1695, 1510, 1392, 1366, 1274, 1250, 1165, 911, 849, 729; ^{1}H NMR (500 MHz, $CDCl_3$) δ δ 9.77 (s, 1H, C**H**O), 4.97 (s, 1H, Boc**H**N), 3.39 (q, *J* = 5.9 Hz, 2H, BocHNC**H**$_2$), 2.68 (t, *J* = 5.7 Hz, 2H, BocHNCH$_2$C**H**$_2$), 1.39 (s, 9H, (C**H**$_3$)$_3$C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.5, 155.8, 79.4, 44.2, 33.9, 28.3; HRMS (EI) m/z calculated for $C_8H_{15}NNaO_3$ ($[M+Na]^+$) 196.0944, found 196.0944.



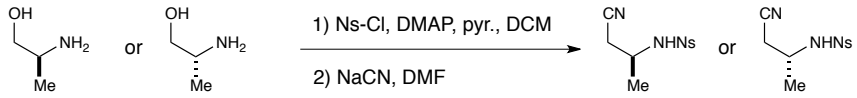
4-Nitro-*N*-(3-oxopropyl)benzenesulfonamide. To a solution of 1-amino-3,3-diethoxyaminopropane (2.43 mL, 15.0 mmol, 1.0 equiv) in CH_2Cl_2 (100 mL) was added NEt_3 (2.4 mL, 18.0 mmol, 1.2 equiv). The solution was cooled to 0 °C and tosyl chloride (2.86 g, 15.0 mmol, 1.0 equiv) was carefully added. The resulting mixture was allowed

to warm to room temperature and treated with saturated aqueous NH_4Cl solution. The layers were separated, organics extracted with CH_2Cl_2, dried over sodium sulfate, and concentrated to a yellow oil. The crude sulfonamide was dissolved in THF (30 mL), treated with 1 M HCl (15 mL), and stirred at room temperature. Upon complete consumption of the acetal as judged by TLC analysis (acetal: R_f 0.60 (50% EtOAc/Hexanes)), EtOAc (100 mL) was added and the layers separated. The organics were washed (H_2O, brine), dried over sodium sulfate, and concentrated. Purification by column chromatography (30% to 50% EtOAc/Hexanes, SiO_2) gave the title compound as a colorless oil (1.60 g, 47%). R_f 0.28 (50% EtOAc/hexanes); IR (film) 3283, 2849, 1717, 1598, 1399, 1321, 1305, 1152, 1089, 1044, 842, 813, 706, 660; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H, C**H**O), 7.75 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.33 (d, *J* = 8.1 Hz, 2H, Ar**H**), 5.27 (t, *J* = 6.2 Hz, 1H, Ts**H**N), 3.21 (q, *J* = 6.2 Hz, 2H, TsHNC**H**$_2$), 2.75 (t, *J* = 6.0 Hz, 2H, TsHNCH$_2$C**H**$_2$), 2.44 (s, 3H, ArC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.9, 143.6, 136.5, 129.7, 126.9, 43.4, 36.7, 21.5; HRMS (EI) m/z calculated for $C_{10}H_{14}NO_3S$ ($[M+H]^+$) 228.0689, found 228.0690.

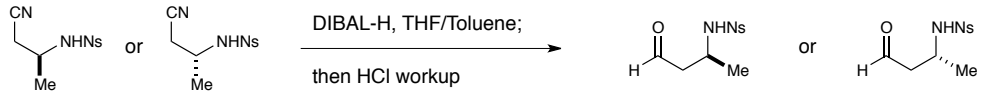


4-Nitro-*N*-(3-oxopropyl)benzenesulfonamide. To a solution of 1-amino-3,3-diethoxyaminopropane (7.36 g, 50.0 mmol, 1.0 equiv) in CH_2Cl_2 (200 mL) was added NEt_3 (8.30 mL, 60.0 mmol, 1.2 equiv). The solution was cooled to 0 °C and nosyl chloride (11.08 g, 50.0 mmol, 1.0 equiv) was carefully added. The resulting mixture was allowed to warm to room temperature and treated with saturated aqueous NH_4Cl solution. The layers were separated, organics extracted with CH_2Cl_2, dried over sodium sulfate, and concentrated to a yellow oil. The crude sulfonamide was dissolved in THF (100 mL), treated with 1 M HCl (50 mL), and stirred at room temperature. Upon complete consumption of the acetal as judged by TLC analysis (acetal: R_f 0.67 (50% EtOAc/Hexanes)), EtOAc (100 mL) was added and the layers separated. The organics were washed (H_2O, brine), dried over sodium sulfate, and concentrated. Purification by column chromatography (30% to 50% EtOAc/Hexanes, SiO_2) gave the title compound as a pale yellow solid (10.5 g, 77%). R_f 0.34 (50% EtOAc/Hexanes); IR (film) 3292, 1721,

1531, 1350, 1265, 1165, 856; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H, C**H**O), 8.38 (d, *J* = 8.9 Hz, 2H, Ar**H**), 8.06 (d, *J* = 8.9 Hz, 2H, Ar**H**), 5.24 (t, *J* = 6.4 Hz, 1H, Ns**H**N), 3.27 (q, *J* = 5.8 Hz, 2H, NsHNC**H**$_2$), 2.75 (t, *J* = 5.8 Hz, 2H, NsHNCH$_2$C**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.7, 150.1, 145.7, 128.2, 124.5, 43.6, 37.0; HRMS (EI) m/z calculated for $C_9H_{11}N_2O_5S$ ([M+H]$^+$) 259.0383, found 259.0381.

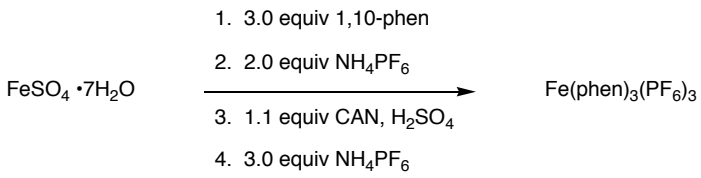


(*R* and *S*)-*N*-(1-cyanopropan-2-yl)-4-nitrobenzenesulfonamide. To a solution of the corresponding enantiomer of 2-amino-propan-1-ol (1.50 g, 20 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) was added pyridine (6.5 mL, 80 mmol, 4.0 equiv). The solution was cooled to 0 °C and 4-dimethylaminopyridine (DMAP) (24 mg, 0.2 mmol, 0.01 equiv) and nosyl chloride (22.62 g, 40 mmol, 2.0 equiv) were carefully added. The resulting mixture was allowed to warm to room temperature and stirred 10 h, then warmed to 40 °C for 30 min to ensure completion. The reaction was rinsed with water (50 mL), the aqueous phase extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic extracts were rinsed three times with 1 M HCl and then sat. aq. $NaHCO_3$ solution, dried over sodium sulfate, and concentrated to yellow solid. The crude sulfonate was dissolved in DMF (50 mL), treated with sodium cyanide (1.81 g, 36 mmol, 1.8 equiv) and stirred at room temperature for 10 h, at which point the sulfonate had been consumed, as judged by TLC analysis. EtOAc (50 mL) and water (50 mL) were added, the mixture was separated, and the aqueous phase was further extracted with EtOAc (4 x 50 mL). The combined organic extracts were washed with brine (4 x 50 mL), dried over magnesium sulfate, and concentrated. Purification by column chromatography (5% EtOAc/DCM, SiO_2) gave the title compounds as pale yellow solids (1.81 g, 34%). IR (film) 3268, 2248, 1527, 1350, 1147, 1056, 853; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.9 Hz, 2H, Ar**H**), 8.06 (d, *J* = 8.9 Hz, 2H, Ar**H**), δ 4.91 (d, *J* = 8.1, 1H Ns**H**N), δ 3.76 (m, 1 H, CH_3C**H**NHNs), δ 2.62 (m, 2 H, CNC**H**$_2$), δ 1.30 (d, *J* = 6.8 Hz, 3 H, C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 147.8, 129.2, 125.4, 117.9, 47.5, 26.5, 20.3; HRMS (EI) m/z calculated for $C_{10}H_{12}N_3O_4S$ ([M+H]$^+$) 270.0549, found 270.0545. The % ee was determined after the next step via reduction to the alcohol.



(*R* and *S*)-4-nitro-*N*-(4-oxobutan-2-yl)benzenesulfonamide. A solution of the corresponding enantiomer of the nitrile (1.35 g, 5.0 mmol, 1.0 equiv) in THF (40 mL) was cooled to -70 °C and treated carefully with a solution of DIBAL-H in toluene (25 mL, 1.0 M, 5 equiv) over 10 min. The reaction was stirred at -70 °C for 1 h at which point consumption of the nitrile was complete, as judged by TLC analysis. The remaining DIBAL-H was quenched by addition, while cold, of acetone (10 mL) and then poured into 1 M HCl (50 mL) at 0 °C. The mixture was warmed to room temperature and then diluted further with water (100 mL) and extracted with ethyl acetate (4 x 50 mL). The combined organic extracts were dried over sodium sulfate, concentrated and purified by column chromatography (30-40% EtOAc/Hex, SiO_2) to yield the title products as pale yellow solids (557 mg, 41%). IR (film) 3286, 1721, 1524, 1347, 1306, 1163, 852; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H, C**H**O), δ 8.38 (d, *J* = 8.9 Hz, 2H, Ar**H**), 8.07 (d, *J* = 8.9 Hz, 2H, Ar**H**), δ 5.16 (d, *J* = 8.7, 1H Ns**H**N), δ 3.82 (m, 1 H, CH_3C**H**NHNs), δ 2.72 (m, 2 H, CHOC**H$_2$**), δ 1.18 (d, *J* = 6.8 Hz, 3 H, C**H$_3$**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2, 150.2, 146.8, 126.4, 124.6, 50.0, 46.0, 21.4; HRMS (EI) m/z calculated for $C_{10}H_{13}N_2O_5S$ ($[M+H]^+$) 273.0545, found 273.05436. Chiral SFC analysis of the corresponding alcohols (IA, 40% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated >99% ee for both samples, t_R (*S* enantiomer) = 2.1 min, t_R (*R* enantiomer) = 2.4 min).

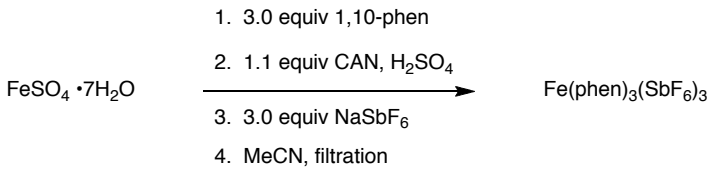
3. Oxidant Preparation



Iron trisphenanthroline trishexafluorophosphate. According to the previously outlined procedure[4], a solution of iron sulfate heptahydrate (12.5 g, 45.0 mmol, 1.0 equiv) in distilled H_2O (200 mL) was added 1,10-phenanthroline (24.3 g, 135.0 mmol, 3.0

[4] Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593-5603.

equiv). After stirring for 2 h, ammonium hexafluorophosphate (14.7 g, 90.0 mmol, 2.0 equiv) was added portionwise. After stirring for 1 h, the thick red suspension was filtered and the resulting solid washed with H_2O (500 mL), taken up in 1 M H_2SO_4 (800 mL), and slowly treated with solid CAN (27.4 g, 50.0 mmol, 1.1 equiv). The resulting deep blue solution was allowed to stir for 15 min and treated with ammonium hexafluorophosphate (22.0 g, 135.0 mmol, 3.0 equiv). A blue solid immediately fell out under a yellow liquor which was collected by filtration, washed with H_2O (500 mL) then Et_2O, and dried under vacuum (0.10 torr) at 95 °C for 8 h to afford the title compound as a deep blue solid which was used without further manipulation (42.2 g, 94%). Anal. calculated for $C_{36}H_{24}F_{18}FeN_6P_3$: C, 41.92; H, 2.35; F, 33.16; Fe, 5.41; N, 8.15; P, 9.01. Found: C, 42.27; H, 2.46; F, 32.64; Fe, 5.81; N, 7.91; P, 7.98.



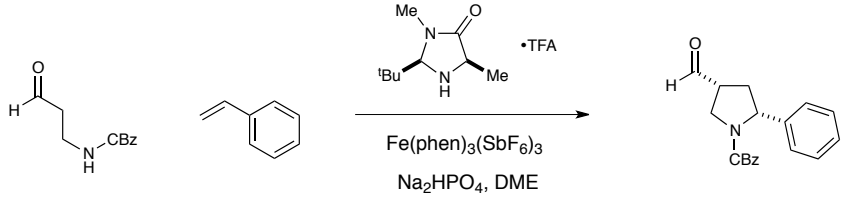
Iron trisphenanthroline trishexafluoroantimonate. To a solution of iron sulfate heptahydrate (13.90 g, 50.0 mmol, 1.0 equiv) in distilled H_2O (400 mL) was added 1,10-phenanthroline (27.0 g, 135.0 mmol, 3.0 equiv). After stirring for 2 h, concentrated sulfuric acid (28 mL) in H_2O (100 mL) was added followed by CAN (30.14 g, 55.0 mmol, 1.1 equiv). The resulting deep blue solution was allowed to stir for 15 min and treated with sodium hexafluoroantimonate (38.8 g, 150.0 mmol, 3.0 equiv). A blue solid immediately fell out under a yellow liquor which was collected by filtration, washed with H_2O (500 mL) then Et_2O, and dried under vacuum (0.10 torr) at 95 °C for 8 h to afford the crude title compound as a deep blue solid. Purification of the title compound was achieved as follows: the solid was dissolved in MeCN (500 mL), filtered through a medium fritted glass funnel, concentrated, and dried under vacuum (0.10 torr) at 95 °C for 8 h. The resulting blue solid was pulverized using a mortar and pestle to afford the title compound as a blue powder (48.4 g, 75%). Anal. calculated for $C_{36}H_{24}F_{18}FeN_6P_3$: C, 33.17; H, 1.86; F, 26.23; Fe, 4.28; N, 6.45; Sb, 28.02. Found: C, 34.45; H, 2.09; F, 22.86; Fe, 4.37; N, 7.24; Sb, 26.90.

4. Experimental Data for Pyrrolidine Products

General procedure. To an oven-dried 2-dram vial containing anhydrous Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt,[5] 14.4 mg, 0.04 mmol, 0.2 equiv), the aldehyde (0.3 mmol, 1.5 equiv), and $Fe(phen)_3(SbF_6)_3$ or $Fe(phen)_3(PF_6)_3$ (0.5 mmol, 2.5 equiv.) under nitrogen at -78 °C was added anhydrous DME (2.7 mL). The mixture was degassed three times by applying vacuum and backfilling with argon while stirring vigorously. The styrene or diene (0.2 mmol, 1.0 equiv.) was added and the reaction allowed to stir at the indicated temperature for 12 h under nitrogen. The reaction mixture was diluted with 50% EtOAc/hexanes, passed through a short plug of silica gel (eluted with EtOAc), and concentrated. Diastereomeric ratios were determined by ^1H NMR analysis of the crude reaction mixtures thus obtained (500 MHz, acetone-d_6, d1=10 s). The crude product was concentrated onto silica gel (1.0 g) and the resulting material was purified by silica gel column chromatography to provide the title compounds. Enantiomeric excess was determined by chiral SFC analysis of the corresponding alcohols. To that end, a fraction of the purified title compound was dissolved in 4:1 (CH_2Cl_2:EtOH) and treated with $NaBH_4$ (2.0 equiv) at 0 °C. Upon complete consumption of the aldehyde as indicated by TLC analysis, the reaction was carefully quenched with 1 M citric acid, the product extracted (CH_2Cl_2), dried over Na_2SO_4, filtered, and concentrated. Purification by silica gel column chromatography afforded the corresponding alcohols.

Experimental Data for Cyclized Products:

Table 1, entry 1:

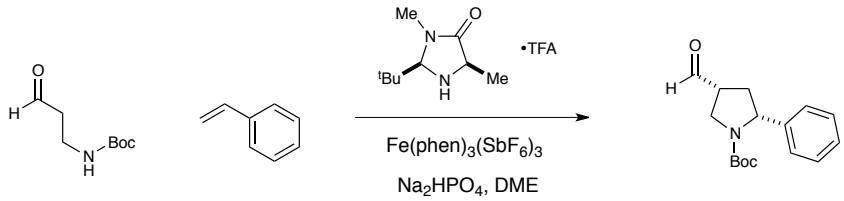


(2*R*,4*R*)-benzyl 4-formyl-2-phenylpyrrolidine-1-carboxylate According to the general procedure, benzyl 3-oxopropylcarbamate (124 mg, 0.60 mmol, 3.0 equiv), styrene (22.9

[5] The imidazolidinone catalyst trifluoroacetic acid salt was recrystallized from iPrOH/Hexanes prior to use.

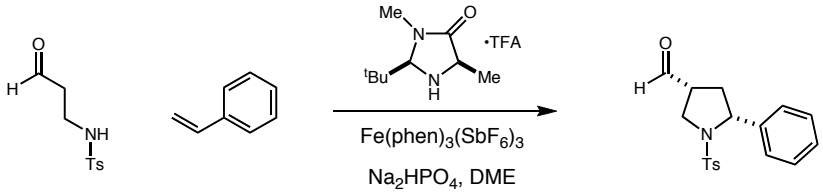
μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-methyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (11.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652.0 mg, 0.5 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 2.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford the crude title compound as a yellow oil after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 1.2:1. The crude residue was purified by column chromatography (30% EtOAc/hexanes) to provide an inseparable mixture of diastereomers of the pyrrolidine as a white solid (41 mg, 66% yield, dr – 1.2:1 *cis*:*trans*, 82% and 80% ee). R_f 0.25 (30% EtOAc/hexanes); **major diastereomer - (2*R*,4*R*)-benzyl 4-formyl-2-phenylpyrrolidine-1-carboxylate:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 – 9.60 (s, 1H, C**H**O), 7.41 – 7.00 (m, overlaps with *trans*-diastereomer, 10H, Ar**H**), 5.18 – 4.78 (m, overlaps with *trans*-diastereomer, 2H, ArOC**H**$_2$), 5.18 – 4.78 (m, overlaps with *trans*-diastereomer, 1H, ArC**H**), 4.08 – 3.67 (m, 2H, CBzNC**H**$_2$), 3.16 – 2.88 (m, 1H, CHOC**H**), 2.69 – 2.42 (m, overlaps with *trans*-diastereomer, 1H, ArCHC**H**$_2$), 2.24 – 1.93 (m, overlaps with *trans*-diastereomer, 1H, ArCHC**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, characteristic signals) δ 200.0, 154.7, 143.0, 136.2, 128.6, 128.6, 128.1, 125.5, 125.3, 66.8, 60.4, 48.1, 46.8, 35.9; **minor diastereomer - (2*S*,4*R*)-benzyl 4-formyl-2-phenylpyrrolidine-1-carboxylate (characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H, C**H**O); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 154.4, 142.0, 136.5, 128.6, 128.4, 128.0, 127.6, 125.3, 67.1, 60.7, 48.8, 46.0, 35.0, 25.2; **for the mixture of diastereomers**: IR (film) 3031, 2949, 1692, 1496, 1449, 1409, 1349, 1259, 1212, 1178, 1115, 1077, 980, 911, 734, 696; HRMS (EI) m/z calculated for $C_{19}H_{20}NO_3$ ($[M+H]^+$) 310.1438, found 310.1438. Chiral SFC analysis (ODH, 5-50% IPA/CO_2, 4.0 mL/min, 220 nm) indicated 82% ee for the major (*cis*) diastereomer, t_R (minor) = 6.5 min, t_R (major) = 7.1 min and 80% ee for the minor (*trans*) diastereomer, t_R (minor) = 6.0 min, t_R (major) = 5.6 min.

Table 1, entry 2:



(2*R*,4*R*)-*t*-butyl 4-formyl-2-phenylpyrrolidine-1-carboxylate. According to the general procedure, *t*-butyl 3-oxopropylcarbamate (104 mg, 0.60 mmol, 3.0 equiv), styrene (22.9 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-methyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (11.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652.0 mg, 0.5 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 2.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford the crude title compound as a yellow oil after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 2:1. The crude residue was purified by column chromatography (50% EtOAc/hexanes) to provide an inseparable mixture of diastereomers of the pyrrolidine as a white solid (37 mg, 62% yield, dr – 1.4:1 *cis*:*trans*, 86% and 84% ee). R_f 0.51 (50% EtOAc/hexanes); **major diastereomer - (2*R*,4*R*)-*t*-butyl 4-formyl-2-phenylpyrrolidine-1-carboxylate:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1H, C**H**O), 7.42 – 7.06 (m, overlaps with *trans*-diastereomer, 5H, Ar**H**), 4.88 – 4.76 (m, 1H, ArC**H**), 4.11 – 3.67 (m, overlaps with *trans*-diastereomer, 2H, BocNC$\mathbf{H}_2$), 3.20 – 3.08 (m, 1H, CHOC**H**), 2.78 – 2.59 (m, 1H, ArCHC$\mathbf{H}_2$), 2.15 – 2.02 (m, 1H, ArCHC$\mathbf{H}_2$), 1.19 (s, 9H, (C$\mathbf{H}_3$)$_3$C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5, 154.2, 143.8, 128.35, 127.0, 125.3, 79.8, 60.6, 48.3, 46.3, 35.9, 28.0; **minor diastereomer - (2*S*,4*R*)-*t*-butyl 4-formyl-2-phenylpyrrolidine-1-carboxylate (characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H, C**H**O); 5.16 – 5.03 (m, 1H, ArC**H**), 3.10 – 3.00 (m, 1H, CHOC**H**), 2.57 – 2.45 (m, 1H, ArCHC$\mathbf{H}_2$), 2.27 – 2.15 (m, 1H, ArCHC$\mathbf{H}_2$), 1.48 (s, 9H, (C$\mathbf{H}_3$)$_3$C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1, 154.0, 142.6, 128.6, 125.5, 125.1, 60.1, 48.8, 46.6, 35.1, 28.4; **for the mixture of diastereomers**: IR (film) 2975, 2929, 2879, 1723, 1683, 1389, 1364, 1251, 1158, 1120, 919, 886, 758, 735, 698; HRMS (EI) m/z calculated for $C_{16}H_{21}NNaO_3$ ($[M+Na]^+$) 298.1414, found 298.1413. Chiral SFC analysis (ODH, 5-50% IPA/CO_2, 4.0 mL/min, 220 nm) indicated 86% ee for the major (*cis*) diastereomer, t_R (minor) = 3.9 min, t_R (major) = 4.2 min and 88% ee for the major (*cis*) diastereomer t_R (minor) = 4.8 min, t_R (major) = 5.3 min.

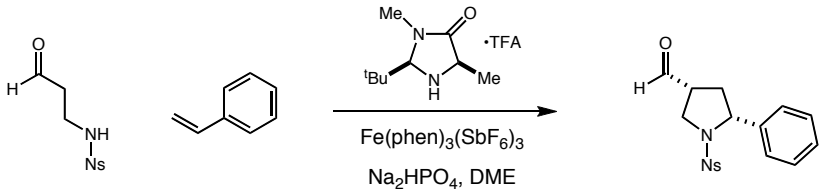
Table 1, entry 3:



(3*R*,5*R*)-5-phenyl-1-tosylpyrrolidine-3-carbaldehyde.

According to the general procedure, 4-methyl-*N*-(3-oxopropyl)benzenesulfonamide (136 mg, 0.60 mmol, 3.0 equiv), styrene (22.9 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-methyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (11.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652.0 mg, 0.5 mmol, 2.5 equiv), and Na_2HPO_4 (56.8 mg, 0.40 mmol, 2.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford the crude title compound as a yellow oil after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 4.1:1. The crude residue was purified by column chromatography (30% EtOAc/hexanes) to provide the (3*R*)-5-phenyl-1-tosylpyrrolidine-3-carbaldehydes as a 4.1:1 mixture of diastereomers as a yellow solid (53 mg, 80% yield). **(3*R*,5*R*)-5-phenyl-1-tosylpyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.4 Hz, 1H, C**H**O), 7.56 – 7.53 (m, 2H, Ar**H**), 7.28 – 7.14 (m, 7H, Ar**H**), 4.74 – 4.69 (m, 1H, ArC**H**), 3.85 (dd, *J* = 11.2, 6.5 Hz, 1H, TsNC**H**$_2$), 3.72 – 3.65 (m, 1H, TsNC**H**$_2$), 2.76 – 2.67 (m, 1H, CHOC**H**), 2.36 (s, 3H, ArC**H**$_3$), 2.18 – 2.09 (m, 2H, ArCHC**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 143.8, 141.0, 134.6, 129.7, 128.5, 127.5, 126.3, 63.1, 49.6, 48.6, 36.8, 21.5. **(3*R*,5*S*)-5-phenyl-1-tosylpyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (d, *J* = 1.4 Hz, 1H, C**H**O), 4.78 (dd, *J* = 7.9, 4.1 Hz, 1H, ArC**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 143.8, 141.5, 134.4, 129.7, 128.5, 127.6, 126.0, 62.8, 49.0, 48.0, 35.9, 21.6. **For the mixture of diastereomers**: R_f 0.35 (30% EtOAc/hexanes); IR (film) 3031, 2922, 1723, 1598, 1494, 1450, 1398, 1344, 1306, 1184, 1155, 1091, 1029, 816, 766, 700, 665; HRMS (EI) m/z calculated for $C_{18}H_{20}NO_3S$ ($[M+H]^+$) 330.1158, found 330.1163; Chiral SFC analysis of the corresponding mixture of alcohols (OJ, 5–50% MeOH/CO_2, 4.0 mL/min, 220 nm) indicated 90% ee for the major (cis) diastereomer (t_R (minor) = 6.0 min, t_R (major) = 5.4 min) and 33% ee for the minor (trans) diastereomer (t_R (minor) = 4.2 min, t_R (major) = 4.4 min).

Table 1, entry 6:

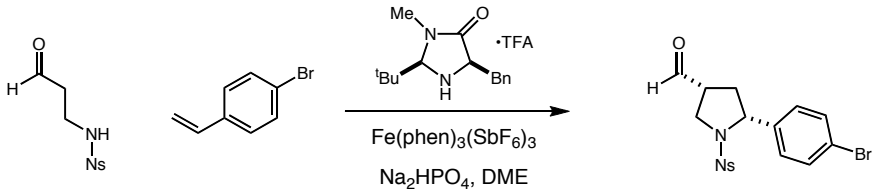


(3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde.

According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), styrene (22.9 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/benzene) to afford the (3*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehydes as a 9.0:1 mixture of diastereomers as a clear viscous syrup (54.2 mg, 77% yield). **(3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H, C**H**O), 8.18 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.68 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.23-7.15 (m, 3H, Ar**H**), 7.10 (d, *J* = 6.8 Hz, 2H, Ar**H**), 4.92 (t, *J* = 7.4 Hz, 1H, ArC**H**), 3.95 (d, *J* = 7.4 Hz, 2H, NC$\mathbf{H}_2$), 3.10 (p, *J* = 7.6 Hz, 1H, C**H**CHO), 2.65 (ddd, *J* = 13.4, 7.6, 7.4 Hz, 1H, CHC$\mathbf{H}_2$CH), 2.25 (dt, *J* = 13.5, 7.4 Hz, 1H, CHC$\mathbf{H}_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 149.8, 144.6, 139.7, 128.7, 128.3, 128.2, 127.0, 124.1, 63.6, 49.7, 48.5, 36.8. **(3*R*,5*S*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H, ArH), 7.95 (d, *J* = 8.8 Hz, 2H, ArH), 4.84 (dd, *J* = 7.3, 5.9 Hz, 1H, ArCH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 149.8, 144.0, 140.5, 128.8, 128.5, 128.1, 126.4, 124.2, 63.3, 49.0, 48.1, 36.2. **For the mixture of distereomers:** R_f 0.33 (20% Et_2O/benzene); IR (film) 1724, 1527, 1348, 1161, 1090, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{17}N_2O_5S$ ($[M+H]^+$) 361.0853, found 361.0849; Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 20% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major (cis)

diastereomer (t_R (minor) = 3.8 min, t_R (major) = 6.0 min) and 34% ee for the minor (trans) diastereomer (t_R (minor) = 4.8 min, t_R (major) = 6.8 min). *When the 5-methyl-substituted catalyst (in place of the benzyl imidazolidinone) is utilized for this reaction with 3.0 equiv. of the aldehyde component, the desired product is formed in 79% yield, 6:1 dr, 90% and 32% ee (for the major and minor diastereomers, respectively) (**Table 1, Entry 4**). When the 5-methyl-substituted catalyst is utilized for this reaction (in place of the benzyl imidazolidinone) with 1.5 equiv. of the aldehyde component, the desired product is formed in 75% yield, 6:1 dr, 90% and 32% ee (for the major and minor diastereomers, respectively) (**Table 1, Entry 5**).*

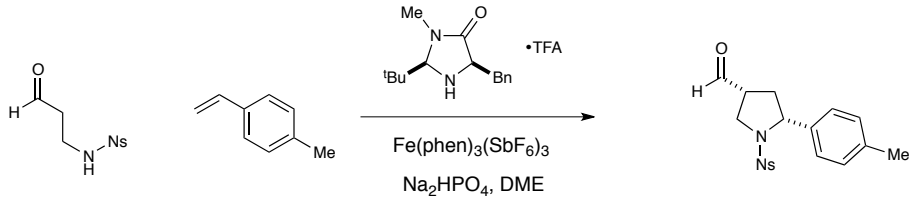
Table 2, entry 1:



(3*R*,5*R*)-5-(4-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 4-bromostyrene (26.2 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 8.8:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/benzene) to afford the (3*R*)-5-(4-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as an 8.4:1 mixture of diastereomers as a clear viscous syrup (63.4 mg, 72% yield). **(3*R*,5*R*)-5-(4-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (s, 1H, C**H**O), 8.27 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.78 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.35 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.00 (d, *J* = 8.3 Hz, 2H, Ar**H**), 4.83 (t, *J* = 7.1 Hz, 1H, ArC**H**), 3.98 (dd, *J* = 10.7, 6.4 Hz, 1H, NC$\mathbf{H}_2$), 3.89-3.77 (m, 1H, NC$\mathbf{H}_2$), 3.10-3.01 (m, 1H, C**H**CHO), 2.58 (dt, *J* = 13.6, 8.2 Hz, 1H, CHC$\mathbf{H}_2$CH), 2.20 (dt, *J* =

13.5, 6.8 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 150.0, 144.0, 139.0, 131.8, 128.5 (2C) 124.3, 122.1, 63.0, 49.5, 48.5, 36.5. **(3*R*,5*S*)-5-(4-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (s, 1H, CHO) 8.32 (d, *J* = 8.6 Hz, 2H, ArH), 7.86 (d, *J* = 8.6 Hz, 2H, ArH), 7.43 (d, *J* = 8.2 Hz, 2H, ArH), 7.12 (d, *J* = 8.2 Hz, 2H, ArH), 4.73 (t, *J* = 6.6 Hz, 1H, ArCH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 150.1, 143.4, 139.8, 131.9, 128.6, 128.0, 124.3, 122.0, 62.7, 48.9, 48.1, 36.1. **For the mixture of distereomers:** R_f 0.25 (20% Et_2O/benzene); IR (film) 1724, 1606, 1527, 1488, 1348, 1309, 1161, 1090, 1010, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{16}BrN_2O_5S$ ($[M+H]^+$) 438.9958, found 438.9948; Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 10% (0.1% Et_2NH/MeOH)/CO_2, 3.0 mL/min, 280 nm) indicated 93% ee for the major (cis) diastereomer (t_R (minor) = 23.5 min, t_R (major) = 43.2 min).

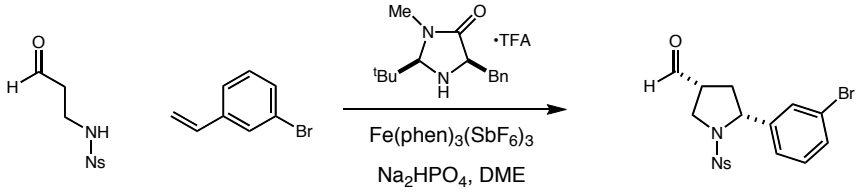
Table 2, entry 2:



(3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-*p*-tolylpyrrolidine-3-carbaldehyde.
According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 4-methylstyrene (26.3 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 6.7:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/benzene) to afford the (3*R*)-1-(4-nitrophenylsulfonyl)-5-*p*-tolylpyrrolidine-3-carbaldehydes as a 6.2:1 mixture of diastereomers as a clear viscous syrup (53.2 mg, 71% yield). **(3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-*p*-tolylpyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (s, 1H, C**H**O), 8.19 (d, *J* = 8.6 Hz, 2H, Ar**H**), 7.69 (d, *J* = 8.6 Hz, 2H,

Ar**H**), 6.99 (d, *J* = 8.0 Hz, 2H, Ar**H**), 6.94 (d, *J* = 8.0 Hz, 2H, Ar**H**), 4.87 (t, *J* = 7.2 Hz, 1H, ArC**H**), 3.97-3.92 (m, 2H, NC$\mathbf{H}_2$), 3.06 (p, *J* = 7.8 Hz, 1H, C**H**CHO), 2.66-2.57 (m, 1H, CHC$\mathbf{H}_2$CH), 2.29 (s, 3H, ArC$\mathbf{H}_3$), 2.25-2.18 (m, 1H, CHC$\mathbf{H}_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 149.8, 144.6, 138.1, 136.6, 129.3, 128.4, 136.9, 124.0, 63.4, 49.6, 48.5, 36.8, 21.1. **minor diastereomer, characteristic signals:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H, ArH), 7.78 (d, *J* = 8.8 Hz, 2H, ArH), 4.79 (dd, *J* = 7.5, 5.7 Hz, 1H, ArCH), 2.31 (s, 3H, $ArCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 149.9, 144.0, 138.0, 137.5, 129.4, 128.5, 126.3, 124.1, 63.0, 49.0, 48.0, 36.2, 21.1. **For the mixture of distereomers:** R_f 0.39 (20% Et_2O/benzene); IR (film) 1724, 1606, 1528, 1350, 1310, 1163, 1092 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{19}N_2O_5S$ ($[M+H]^+$) 375.1006, found 375.1009; Chiral SFC analysis of the corresponding mixture of alcohols (AS-H, 20% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 91% ee for the major (cis) diastereomer (t_R (major) = 3.9 min, t_R (minor) = 6.7 min) and 30% ee for the minor (trans) diastereomer (t_R (major) = 3.5 min, t_R (minor) = 7.1 min).

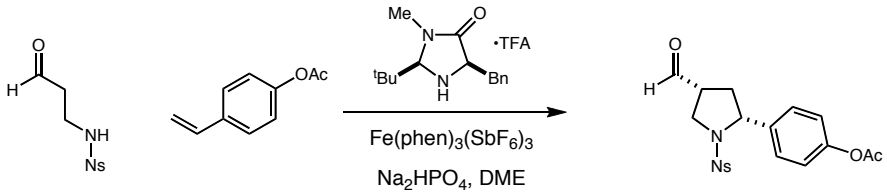
Table 2, entry 3:



(3*R*,5*R*)-5-(3-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 3-bromostyrene (26.0 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 7.5:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/benzene) to afford the (3*R*)-5-(3-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as a 7.6:1 mixture of diastereomers as a clear viscous syrup (63.4 mg, 72% yield). **(3*R*,5*R*)-5-(3-**

bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H, C**H**O), 8.24 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.71 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.34 (d, *J* = 7.7 Hz, 1H, Ar**H**), 7.14 – 7.00 (m, 3H, Ar**H**), 4.86 (t, *J* = 7.4 Hz, 1H, ArC**H**), 4.02 – 3.92 (m, 2H, NC**H**), 3.17 – 3.06 (m, 1H, C**H**CHO), 2.65 (dt, *J* = 13.4, 8.0 Hz, 1H, CHC**H**$_2$CH), 2.27 – 2.14 (m, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 150.0, 144.5, 141.9, 131.2, 130.3, 129.8, 128.2, 125.9, 124.2, 122.8, 63.0, 49.6, 48.6, 36.8. **(3*R*,5*S*)-5-(3-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H, C**H**O), 8.32 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.84 (d, *J* = 8.6 Hz, 2H, Ar**H**), 4.85 – 4.78 (m, 1H, ArC**H**), 4.08 (dd, *J* = 10.8, 5.2 Hz, 1H, NC**H**$_2$), 3.86 (dd, *J* = 10.8, 7.5 Hz, 1H, NC**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 150.0, 143.8, 142.8, 131.2, 130.4,. 128.4, 125.3, 124.3, 122.9, 62.6, 4.9, 48.2, 36.2. **For the mixture of distereomers:** R_f 0.31 (20% Et_2O/benzene); IR (film) 1725, 1528, 1349, 1312, 1162, 1091, 855 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{16}BrN_2O_5S$ ($[M+H]^+$) 438.9958, found 438.9964; Chiral SFC analysis of the corresponding mixture of alcohols (AS-H, 10% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 93% ee for the major (cis) diastereomer (t_R (major) = 10.3 min, t_R (minor) = 12.7 min) and 33% ee for the minor (trans) diastereomer (t_R (major) = 8.4 min, t_R (minor) = 13.3 min).

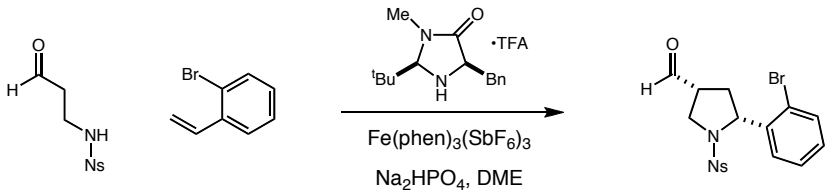
Table 2, entry 4:



4-((2*R*,4*R*)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)phenyl ethanoate. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 4-acetoxystyrene (30.6 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a

diastereomeric ratio of 8.5:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (20% Et_2O/benzene) to afford the 4-((4*R*)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)phenyl ethanoates as an 8.1:1 mixture of diastereomers as a clear viscous syrup (62.0 mg, 74% yield). **4-((2*R*,4*R*)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)phenyl ethanoate:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H, C**H**O), 8.23 (d, *J* = 8.6 Hz, 2H, Ar**H**), 7.67 (d, *J* = 8.6 Hz, 2H, Ar**H**), 7.11 (d, *J* = 8.4 Hz, 2H, Ar**H**), 6.92 (d, *J* = 8.4 Hz, 2H, Ar**H**), 4.94 (t, *J* = 7.5 Hz, 1H, ArC**H**), 4.03 – 3.92 (m, 2H, NC**H**$_2$), 3.19 – 3.11 (m, 1H, C**H**CHO), 2.69 (dt, *J* = 13.5, 8.0 Hz, 1H, CHC**H**$_2$CH), 2.32 (s, 3H, C**H**$_3$CO), 2.29 – 2.20 (m, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 169.3, 150.4, 149.9, 144.6, 137.0, 128.3 (2C), 124.2, 121.9, 63.1, 49.6, 48.5, 36.7, 21.2. **4-((2*S*,4R)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)phenyl ethanoate (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H, C**H**O), 8.30 (d, *J* = 8.6 Hz, 2H, Ar**H**), 7.80 (d, *J* = 8.6 Hz, 2H, Ar**H**), 7.22 (d, *J* = 8.3 Hz, 2H, Ar**H**), 7.01 (d, *J* = 8.4 Hz, 2H, Ar**H**), 4.87 (t, *J* = 6.7 Hz, 1H, ArC**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 169.4, 150.3, 150.0, 143.9, 137.9, 128.4, 127.6, 124.3, 122.0, 62.6, 49.0, 48.0, 36.1, 21.2. **For the mixture of distereomers:** R_f 0.23 (20% Et_2O/benzene); IR (film) 1751, 1724, 1528, 1507, 1349, 1195, 1159, 1090, 1101, 912, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{19}H_{19}N_2O_7S$ ([M+H]$^+$) 419.0908, found 419.0908; Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% EtOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major (cis) diastereomer (t_R (minor) = 7.7 min, t_R (major) = 12.1 min) and 23% ee for the minor (trans) diastereomer (t_R (minor) = 9.0 min, t_R (major) = 11.8 min).

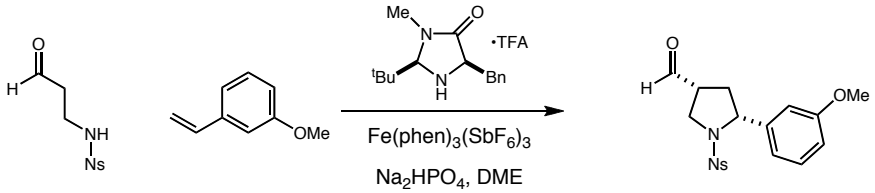
Table 2, entry 5:



(3*R*,5*R*)-5-(2-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde.

According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 2-bromostyrene (25.1 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 3.3:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/benzene) to afford the (3*R*)-5-(2-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as a 3.2:1 mixture of diastereomers as a clear viscous syrup (68.8 mg, 78% yield). **(3*R*,5*R*)-5-(2-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H, C**H**O), 8.28 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.88 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.44 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.19-7.13 (m, 2H, Ar**H**), 7.08-7.02 (m, 1H, Ar**H**), 5.07 (dd, *J* = 8.1, 5.8 Hz, 1H, ArC**H**), 4.07 (dd, *J* = 10.9, 5.8 Hz, 1H, NC$\mathbf{H}_2$), 3.69 (dd, *J* = 10.9, 7.8 Hz, 1H, NC$\mathbf{H}_2$), 2.81-2.78 (m, 1H, C**H**CHO), 2.58 (dt, *J* = 13.5, 8.3 Hz, 1H, CHC$\mathbf{H}_2$CH), 2.16-2.09 (m, 1H, CHC$\mathbf{H}_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 150.3, 142.9, 139.5, 133.1, 129.5, 128.9, 128.3, 127.8, 124.5, 122.0, 63.0, 49.4, 48.9, 35.2. **(3*R*,5*S*)-5-(2-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H, ArH), 7.93 (d, *J* = 8.7 Hz, 2H, ArH), 5.02 (dd, *J* = 7.9, 5.1 Hz, 1H, ArCH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.2, 150.3, 142.7, 140.0, 133.2, 129.5, 128.9, 127.9, 127.8, 125.5, 121.7, 62.8, 48.6, 48.5, 34.9. **For the mixture of distereomers:** R_f 0.31 (20% Et_2O/benzene); IR (film) 1725, 1528, 1349, 1308, 1162, 1090, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{16}BrN_2O_5S$ ($[M+H]^+$) 438.9958, found 438.9962; Chiral SFC analysis of the corresponding mixture of alcohols (AS-H, 20% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 94% ee for the major (cis) diastereomer (t_R (major) = 6.0 min, t_R (minor) = 9.7 min) and 30% ee for the minor (trans) diastereomer (t_R (minor) = 4.3 min, t_R (major) = 8.4 min).

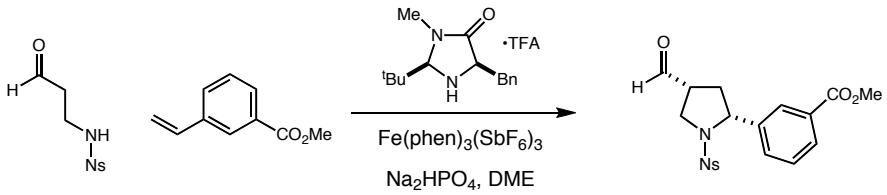
Table 2, entry 6:



(3*R*,5*R*)-5-(3-methoxyphenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 3-vinylanisole (27.6 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (20% Et_2O/benzene) to afford the (3*R*,5*S*)-5-(3-methoxyphenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as an 10:1 mixture of diastereomers as a clear viscous syrup (58.3 mg, 75% yield). **(3*R*,5*R*)-5-(3-methoxyphenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (d, *J* = 0.7 Hz, 1H, C**H**O), 8.22 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.74 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.15 (t, *J* = 7.9 Hz, 1H, Ar**H**), 6.76 (dd, *J* = 8.2, 2.3 Hz, 1H, Ar**H**), 6.69 (d, *J* = 7.6 Hz, 1H, Ar**H**), 6.52 (s, 1H, Ar**H**), 4.92 (t, *J* = 7.2 Hz, 1H, ArC**H**), 3.99 (dd, *J* = 7.3, 1.5 Hz, 2H, NC$\mathbf{H}_2$), 3.71 (s, 3H, OC$\mathbf{H}_3$), 3.18 – 3.06 (m, 1H, C**H**CHO), 2.67 (dt, *J* = 13.3, 8.2 Hz, 1H, CHC$\mathbf{H}_2$CH), 2.26 (dt, *J* = 13.8, 7.1 Hz, 1H, CHC$\mathbf{H}_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 159.7, 149.8, 144.6, 144.2, 129.8, 128.3, 124.0, 119.3, 112.9, 112.8, 63.4, 55.1, 49.6, 48.5, 36.7. **(3*R*,5*S*)-5-(3-methoxyphenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.83 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.25 – 7.18 (m, 1H, Ar**H**), 6.66 (s, 1H, Ar**H**), 4.86 (dd, *J* = 7.6, 5.5 Hz, 1H, ArC**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 144.2, 129.9, 124.1, 118.7, 112.7, 112.6, 63.1, 55.2, 49.0, 48.1, 36.2. **For the mixture of distereomers:** R_f 0.20 (20% Et_2O/benzene); IR (film) 1724, 1604, 1528, 1348, 1263, 1160, 1090, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{19}N_2O_6S$ ($[M+H]^+$) 391.0958, found 391.0942; Chiral SFC analysis of the corresponding mixture of alcohols

(IA, 10% (0.1% Et_2NH/MeOH)/CO_2, 3.0 mL/min, 300 nm) indicated 89% ee for the major (cis) diastereomer (t_R (minor) = 18.5 min, t_R (major) = 21.8 min) and 41% ee for the minor (trans) diastereomer (t_R (minor) = 19.4 min, t_R (major) = 20.5 min).

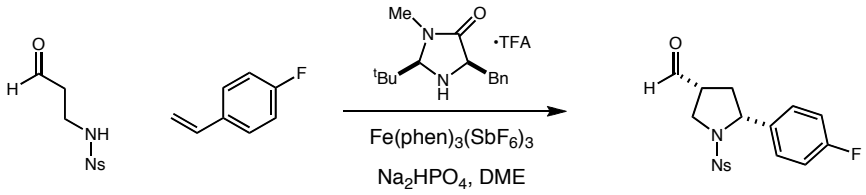
Table 2, entry 7:



Methyl 3-((2*R*,4*R*)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)benzoate. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), methyl 3-vinylbenzoate (29.2 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 5.0:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/benzene) to afford the methyl 3-((4*R*)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)benzoates as a 4.6:1 mixture of diastereomers as a clear viscous syrup (51.0 mg, 61% yield). **Methyl 3-((2*R*,4*R*)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)benzoate:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (d, *J* = 1.0 Hz, 1H, C**H**O), 8.20 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.88 (d, *J* = 7.4 Hz, 1H, Ar**H**), 7.71 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.63 (s, 1H, Ar**H**), 7.39 – 7.29 (m, 2H, Ar**H**), 4.93 (t, *J* = 7.5 Hz, 1H, ArC**H**), 4.00 (d, *J* = 7.4 Hz, 1H, NC**H**$_2$), 3.88 (d, *J* = 7.7 Hz, 1H, Ar**H**), 3.87 (s, 3H, COC**H**$_3$), 3.15 – 3.06 (m, 1H, C**H**CHO), 2.66 (dt, *J* = 13.3, 7.9 Hz, 1H, CHC**H**$_2$CH), 2.22 (dt, *J* = 13.3, 7.7 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 166.3, 144.4, 140.2, 131.6, 130.6, 129.2, 128.3, 127.8, 124.2, 63.3, 52.4, 49.6, 48.7, 36.9. **Methyl 3-((2*R*,4*R*)-4-formyl-1-(4-nitrophenylsulfonyl)pyrrolidin-2-yl)benzoate (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H, C**H**O), 8.25 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.92 (d, *J* = 7.7 Hz, 1H, Ar**H**), 7.79 (d, *J* = 8.8 Hz, 2H, Ar**H**), 4.84 (t, *J* = 6.9 Hz,

1H, Ar**H**), 4.07 (dd, *J* = 10.9, 5.1 Hz, 1H, ArC**H**), 2.58 – 2.49 (m, 1H, CHC**H**$_2$CH), 2.17 – 2.09 (m, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 166.5, 150.0, 143.8, 141.1, 131.2, 130.6, 129.2, 128.9, 128.4, 127.2, 124.2, 62.8, 52.4, 48.9, 48.3, 36.3. **For the mixture of distereomers:** R_f 0.22 (20% Et_2O/benzene); IR (film) 1717, 1606, 1528, 1348, 1287, 1263, 1160, 1088, 855 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{19}H_{19}N_2O_7S$ ([M+H]$^+$) 419.0908, found 419.0895; Chiral SFC analysis of the corresponding mixture of alcohols (OD-H, 35% iPrOH/CO_2, 3.0 mL/min, 300 nm) indicated 89% ee for the major diastereomer (t_R (minor) = 3.6 min, t_R (major) = 7.5 min) and 20% ee for the minor diastereomer (t_R (minor) = 3.2 min, t_R (major) = 4.0 min).

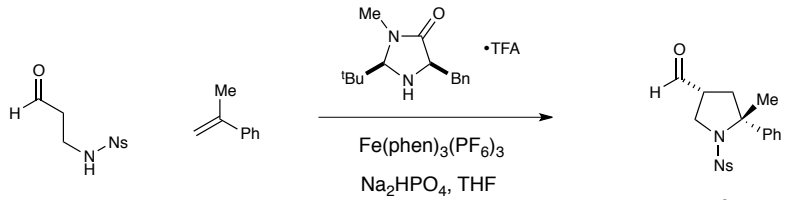
Table 2, entry 8:



(3*R*,5*R*)-5-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 4-fluorostyrene (23.9 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(SbF_6)_3$ (652 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/ benzene) to afford the (3*R*)-5-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as an 9:1 mixture of diastereomers as a clear viscous syrup (61.2 mg, 81% yield). **(3*R*,5*R*)-5-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (s, 1H, C**H**O), 8.25 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.75 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.10 (dd, *J* = 8.5, 5.2 Hz, 2H, Ar**H**), 6.92 (t, *J* = 8.5 Hz, 2H, Ar**H**), 4.88 (t, *J* = 7.2 Hz, 1H, ArC**H**), 3.98 (dd, *J* = 10.7, 6.5 Hz, 1H, NC**H**$_2$), 3.87 (dd, *J* = 10.7, 7.9 Hz, 1H, NC**H**$_2$), 3.05 (p, *J* = 7.3 Hz, 1H, C**H**CHO), 2.59 (dt, *J* = 13.4, 8.1 Hz, 1H, CHC**H**$_2$CH), 2.20 (dt, *J* = 13.4, 7.0 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ

199.0, 163.3, 150.0, 144.3, 135.6, 128.6 (d, J = 8.1 Hz), 128.4, 124.2, 115.6 (d, J = 21.7 Hz), 62.9, 49.5, 48.5, 36.7. **(3*R*,5*S*)-5-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (s, 1H, C**H**O) 8.32 (d, J = 8.8 Hz, 2H, Ar**H**), 7.85 (d, J = 8.8 Hz, 2H, Ar**H**), 4.77 (t, J = 6.5 Hz, 1H, ArC**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 161.4, 150.1, 143.6, 136.5, 128.4, 128.0 (d, J = 8.4 Hz), 124.3, 115.7 (d, J = 21.8 Hz), 62.6, 48.9, 48.1, 36.7. **For the mixture of distereomers:** R_f 0.25 (20% Et_2O/benzene); IR (film) 1724, 1606, 1527, 1488, 1348, 1309, 1161, 1090, 1010, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{17}H_{16}FN_2O_5S$ ($[M+H]^+$) 379.0759, found 379.0751; Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 15% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 91% ee for the major (cis) diastereomer (t_R (minor) = 3.0 min, t_R (major) = 4.8 min) and 53% ee for the minor (trans) diastereomer (t_R (minor) = 3.7 min, t_R (major) = 5.2 min).

Table 2, entry 9:

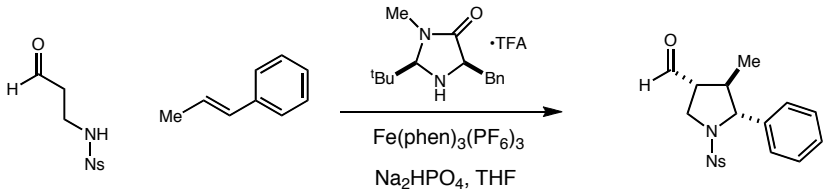


major

(3*R*,5*R*)-5-methyl-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), prop-1-en-2-ylbenzene (26.0 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (618 mg, 0.60 mmol, 3.0 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in THF (2.7 mL) were stirred at -20 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 3:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the title compound as a 3:1 mixture of diastereomers as a white solid (50.0 mg, 67% yield). **(3*R*,5*R*)-5-methyl-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, J = 1.2 Hz, 1H, C**H**O), 8.16 (d, J = 9.0 Hz, 2H,

Ar**H**), 7.55 (d, *J* = 9.0 Hz, 2H, Ar**H**), 7.36 (m, 2H, Ar**H**), 7.19 (m, 3H, Ar**H**), 4.04 (dd, *J* = 10.0, 8.0 Hz, 1H, NC**H**$_2$), 3.95 (dd, *J* = 10.0, 7.6 Hz, 1H, NC**H**$_2$), 3.05 (dqd, *J* = 9.1, 7.9, 1.2 Hz, 1H, C**H**CHO), 2.54 (dd, *J* = 13.2, 9.1 Hz, 1H, CHC**H**$_2$CMePh), 2.38 (dd, *J* = 13.1, 7.9 Hz, 1H, CHC**H**$_2$CMePh), 2.01 (s, 3H, CH$_2$C**CH**$_3$Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 149.6, 146.0, 142.7, 128.4, 128.1, 127.9, 126.7, 124.0, 69.7, 49.2, 48.0, 46.2, 26.6. **(3*R*,5*S*)-5-methyl-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 1.2 Hz 1H, C**H**O) 8.30 (d, *J* = 9.0 Hz, 2H, Ar**H**), 7.88 (d, *J* = 9.0 Hz, 2H, Ar**H**), 2.21 (dd, *J* = 12.7, 9.7 Hz, 1H, CHC**H**$_2$CMePh), 1.89 (s, 3H, CH$_2$C**CH**$_3$-Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 149.8, 146.4, 144.6, 128.7, 128.3, 127.7, 125.6, 124.4, 70.8, 48.9, 47.3, 45.7, 26.8. **For the mixture of distereomers:** R_f 0.25 (20% Et_2O/benzene); IR (film) 2924, 1719, 1531, 1339, 1310, 1153, 1087, 1000, 847 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{19}N_2O_5S$ ([M+H]$^+$) 375.1015, found 375.09816; Chiral SFC analysis of the corresponding mixture of alcohols (IA, 25% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major (cis) diastereomer (t_R (minor) = 3.6 min, t_R (major) = 4.0 min) and 40% ee for the minor (trans) diastereomer (t_R (minor) = 4.4 min, t_R (major) = 4.8 min).

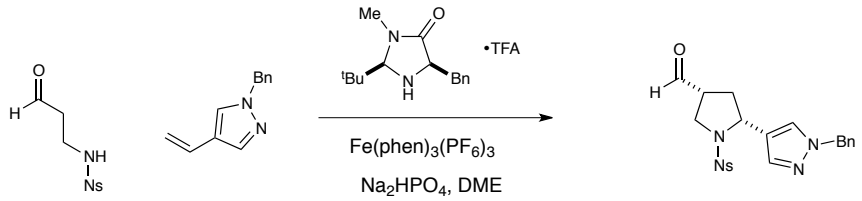
Table 2, entry 10:



(3*R*,4*R*,5*R*)-4-methyl-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), *trans*-prop-1-enylbenzene (26.0 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (618 mg, 0.60 mmol, 3.0 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in THF (2.7 mL) were stirred at -10 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of >20:1.

The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the title compound as a single diastereomer as a clear viscous syrup (37.2 mg, 62% yield). **(3*R*,4*R*,5*R*)-4-methyl-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehyde:** R_f 0.42 (20% Et_2O/benzene); ^1H NMR (500 MHz, $CDCl_3$) δ 9.67 (d, *J* = 0.9 Hz, 1H, C**H**O), 8.29 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.85 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.31-7.27 (m, 3H, Ar**H**), 7.17 (dd, *J* = 6.5, 2.8 Hz, 2H, Ar**H**), 4.39 (d, *J* = 5.3 Hz, 1H, ArC**H**), 4.01 (dd, *J* = 10.7, 6.1 Hz, 1H, NC$\mathbf{H}_2$), 3.75 (dd, *J* = 10.7, 7.1 Hz, 1H, NC$\mathbf{H}_2$), 3.21 (q, *J* = 6.1 Hz, 1H, C**H**CHO), 2.70 – 2.55 (m, 1H), 0.86 (d, *J* = 7.1 Hz, 3H, CHC$\mathbf{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 150.0, 143.9, 138.9, 128.7, 128.6, 128.2, 126.4, 124.1, 70.6, 52.0, 46.8, 45.2, 13.8; IR (film) 2924, 1721, 1528, 1348, 1311, 1168, 1092, 1012, 856 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{19}N_2O_5S$ ($[M+H]^+$) 375.1015, found 375.0998; Chiral SFC analysis of the corresponding alcohol (AD-H, 40% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 96% ee (t_R (major) = 2.1 min, t_R (minor) = 3.6 min).

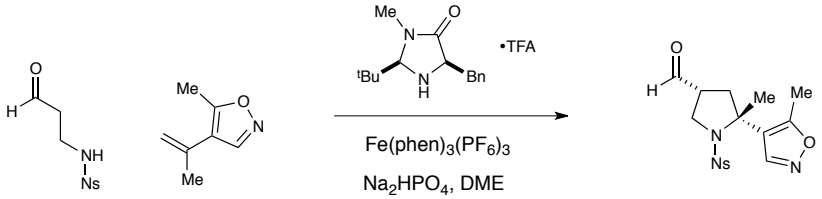
Table 3, entry 1:



(3*R*,5*R*)-5-(1-benzyl-1*H*-pyrazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (51.6 mg, 0.20 mmol, 1.0 equiv), 1-benzyl-4-vinyl-1*H*-pyrazole (36.8 mg, 0.30 mmol, 1.5 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -40 °C for 12 h to afford a colorless syrup after workup. ^1H NMR analysis of the crude mixture indicated a diastereomeric ratio of 3.0:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10 to 20% Et_2O/benzene) to afford the (3*R*)-5-(1-benzyl-1*H*-pyrazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as a 3.0:1 mixture of

diastereomers as a clear viscous syrup (66.0 mg, 75% yield). **(3*R*,5*R*)-5-(1-benzyl-1*H*-pyrazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, Acetone-d_6) δ 9.58 (s, 1H, C**H**O), 8.34 (d, *J* = 8.7 Hz, 2H, Ar**H**), 8.02 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.62 (s, 1H, Ar**H**), 7.44 – 7.20 (m, 6H, Ar**H**), 5.30 (s, 2H, ArC**H**$_2$N), 5.00 (dd, *J* = 7.3, 5.7 Hz,1H, ArC**H**CH$_2$), 3.94 (dd, *J* = 10.8, 6.2 Hz, 1H, NC**H**$_2$CH), 3.79 (dd, *J* = 10.8, 8.0 Hz, 1H, NC**H**$_2$CH), 3.07 (dq, *J* = 7.1 Hz, 1H, C**H**CHO), 2.49 – 2.33 (m, 2H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.1, 151.0, 145.2, 138.7, 138.6, 129.7, 129.6, 129.4, 128.6 (2C), 56.4, 56.2, 50.4, 48.4, 35.8. **(3*R*,5*S*)-5-(1-benzyl-1*H*-pyrazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.30 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.96 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.72 (s, 1H, Ar**H**), 5.03 (dd, *J* = 7.5, 4.3 Hz, 1H, ArC**H**CH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 138.3, 129.4, 128.7 (2C), 125.1, 56.2 (2C), 50.2, 48.0, 35.3. **For the mixture of distereomers:** R_f 0.27 (50% EtOAc/hexanes); IR (film) 1722, 1527, 1348, 1309, 1160, 1091, 1011, 843 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{21}H_{21}N_4O_5S$ ([M+H]$^+$) 441.1227, found 441.1233; Chiral HPLC analysis of the corresponding mixture of alcohols (AD-H to OD-H, 0.1% Et_2NH/EtOH, 0.5 mL/min, 280 nm) indicated 91% ee for the major (cis) diastereomer (t_R (major) = 28.6 min, t_R (minor) = 32.9 min) and 35% ee for the minor (trans) diastereomer (t_R (minor) = 27.4 min, t_R (major) = 37.5 min).

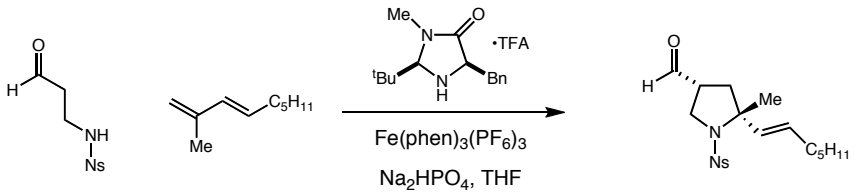
Table 3, entry 2:



(3*R*,5*R*)-5-methyl-5-(5-methylisoxazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (51.7 mg, 0.20 mmol, 1.0 equiv), 5-methyl-4-(prop-1-en-2-yl)isoxazole (38.6 μL, 0.30 mmol, 1.5 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0

equiv) in DME (2.7 mL) were stirred at -20 °C for 12 h to afford a colorless syrup after workup. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (50% EtOAc/hexanes) to afford the (3*R*)-5-methyl-5-(5-methylisoxazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as a 6.2:1 mixture of diastereomers as a clear viscous syrup (42.1 mg, 55% yield). **(3*R*,5*R*)-5-methyl-5-(5-methylisoxazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 0.9 Hz, 1H, C**H**O), 8.29 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.97 (s, 1H, Ar**H**), 7.63 (d, *J* = 8.8 Hz, 2H, Ar**H**), 4.00 (dd, *J* = 9.9, 8.2 Hz, 1H, NC**H**$_2$), 3.81 (dd, *J* = 10.0, 8.0 Hz, 1H, NC**H**$_2$), 3.49– 3.29 (m, 1H, C**H**CHO), 2.42 (dd, *J* = 13.8, 9.3 Hz, 2H, CHC**H**$_2$CH), 2.32 (dd, *J* = 13.4, 7.8 Hz, 1H, CHC**H**$_2$CH), 2.17 (s, 3H, C**H**$_3$), 1.93 (s, 3H, C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 165.5, 150.4, 149.9, 145.6, 127.9, 124.3, 117.2, 63.2, 48.5, 47.3, 43.0, 27.5, 12.8. **(3*R*,5*R*)-5-methyl-5-(5-methylisoxazol-4-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H, C**H**O), 8.35 (d, *J* = 8.8 Hz, 2H, Ar**H**), 8.09 (s, 1H, Ar**H**), 7.87 (d, *J* = 8.8 Hz, 2H, Ar**H**), 3.17 – 2.99 (m, 1H, C**H**CHO), 1.79 (s, 3H, C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 164.0, 150.0, 145.7, 128.3, 124.5, 63.7, 48.4, 47.5, 43.9, 26.9, 12.6. **For the mixture of distereomers:** R_f 0.22 (50% EtOAc/hexanes); IR (film) 1724, 1605, 1528, 1477, 1349, 1306, 1159, 1090, 1003, 855 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{16}H_{18}N_3O_6S$ ($[M+H]^+$) 380.0911, found 380.0907; Chiral SFC analysis of the corresponding mixture of alcohols (IC, 40% iPrOH/CO_2, 3.0 mL/min, 300 nm) indicated 95% ee for the major diastereomer (t_R (minor) = 2.7 min, t_R (major) = 3.2 min) and 92% ee for the minor diastereomer (t_R (minor) = 3.5 min, t_R (major) = 4.7 min).

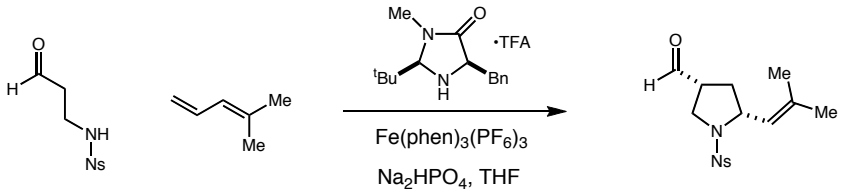
Table 3, entry 3:



(3*R*,5*R*)-5-((*E*)-hept-1-enyl)-5-methyl-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-

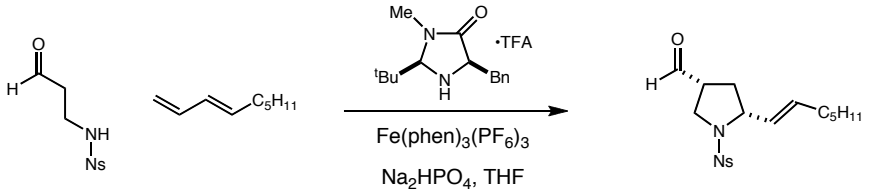
oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), (*E*)-2-methylnona-1,3-diene (36.8 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in THF (2.7 mL) were stirred at -40 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 2.0:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the methyl (3*R*)-5-((*E*)-hept-1-enyl)-5-methyl-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as a 2.0:1 mixture of diastereomers as a clear viscous syrup (66.7 mg, 85% yield). **(3*R*,5*R*)-5-((*E*)-hept-1-enyl)-5-methyl-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (d, *J* = 0.8 Hz, 1H, C**H**O), 8.32 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.97 (d, *J* = 8.8 Hz, 2H, Ar**H**), 5.70 – 5.58 (m, 1H, CH=C**H**CH_2), 5.11 (d, *J* = 15.6 Hz, 1H, C**H**$CHCH_2$), 3.89 – 3.74 (m, 2H, NC**H**$_2$), 3.13 (p, *J* = 7.2 Hz, 1H, C**H**CHO), 2.20-1.82 (m, 4H, CHC**H**$_2$CH, CH=CHC**H**$_2$), 1.61 (s, 3H, N(C)C**H**$_3$), 1.42 – 1.15 (m, 6H, (C**H**$_2$)$_3$$CH_3$), 0.87 (td, *J* = 6.9, 3.3 Hz, 3H, CH_2C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 149.7, 146.8, 132.1, 132.0, 128.6, 124.0, 67.8, 48.2, 47.5, 42.5, 32.3, 31.4, 28.5, 25.8, 22.5, 14.1. **(3*R*,5*S*)-5-((*E*)-hept-1-enyl)-5-methyl-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (d, *J* = 1.2 Hz, 1H, C**H**O), 5.32 (d, *J* = 15.5 Hz, 1H, C**H**=CHCH2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 149.8, 146.5, 132.4, 130.9, 128.6, 124.2, 68.3, 48.2, 47.1, 32.1, 31.4, 28.7, 25.6, 22.5, 14.1. **For the mixture of distereomers:** R_f 0.61 (20% Et_2O/benzene); IR (film) 2925, 2855, 1727, 1528, 1348, 1308, 1160, 1092, 980, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{19}H_{27}N_2O_5S$ ($[M+H]^+$) 395.1635, found 395.1638; Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major diastereomer (t_R (minor) = 3.0 min, t_R (major) = 3.4 min) and 85% ee for the minor diastereomer (t_R (major) = 3.2 min, t_R (minor) = 3.7 min).

Table 3, entry 4:



(3*R*,5*R*)-5-(2-methylprop-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 4-methylpenta-1,3-diene (20.0 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in THF (2.7 mL) were stirred at -30 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 3.6:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the (3*R*)-5-(2-methylprop-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as a 3.7:1 mixture of diastereomers as a clear viscous syrup (52.3 mg, 77c% yield). **(3*R*,5*R*)-5-(2-methylprop-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (d, *J* = 0.8 Hz, 1H, C**H**O), 8.37 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.97 (d, *J* = 8.8 Hz, 2H, Ar**H**), 4.68 – 4.54 (m, 2H, $(CH_3)_2$C=C**H**CH, $(CH_3)_2$C=CHC**H**), 3.82 (dd, *J* = 10.4, 5.9 Hz, 1H, NC**H**$_2$), 3.76 (dd, *J* = 10.3, 7.8 Hz, 1H, NC**H**$_2$), 3.08 (td, *J* = 13.7, 6.2 Hz, 1H, C**H**CHO), 2.50 – 2.39 (m, 1H, CHC**H**$_2$CH), 1.95 (ddd, *J* = 9.6, 6.2, 4.0 Hz, 1H, CHC**H**$_2$CH), 1.74 (s, 3H, (C**H**$_3$)$_2$C=CHCH), 1.58 (s, 3H, (C**H**$_3$)$_2$C=CHCH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 149.9, 145.6, 136.4, 128.6, 124.0, 123.4, 57.8, 49.4, 47.0, 33.9, 25.7, 18.1. **(3*R*,5*S*)-5-(2-methylprop-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H, CHO), 4.91 (d, *J* = 9.4 Hz, 1H, $(CH_3)_2$C=CHCH), 4.48 (dd, *J* = 15.8, 6.8 Hz, 1H, $(CH_3)_2$C=CHCH), 3.93 (dd, *J* = 10.8, 5.0 Hz, 1H, NCH_2), 3.58 (dd, *J* = 10.6, 7.6 Hz, 1H, NCH_2), 1.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 150.0, 144.9, 136.0, 128.6, 124.1, 123.5, 57.7, 48.9, 47.0, 33.6, 25.8, 18.2. **For the mixture of distereomers:** R_f 0.42 (20% Et_2O/benzene); IR (film) 2223, 1724, 1527, 1348, 1309, 1160, 1091, 1011, 855 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{15}H_{19}N_2O_5S$ ($[M+H]^+$) 339.1009, found 339.1004; Chiral SFC analysis of the corresponding mixture of alcohols (AY-H, 6% MeOH/CO_2, 3.0 mL/min, 280 nm) indicated 89% ee for the major diastereomer (t_R (minor) = 5.3 min, t_R (major) = 6.1 min) and 86% ee for the minor diastereomer (t_R (major) = 4.1 min, t_R (minor) = 7.4 min).

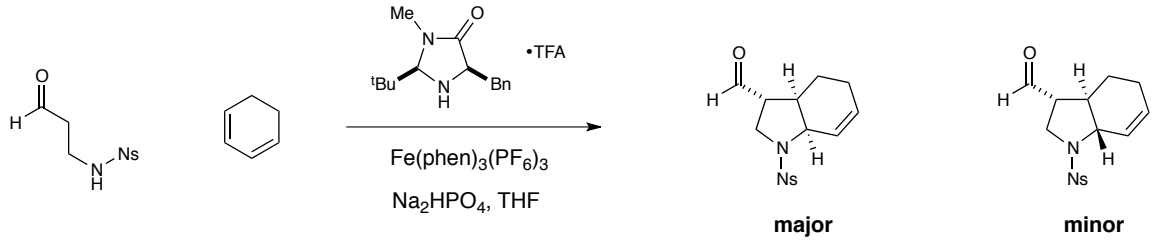
Table 3, entry 5:



(3*R*,5*R*)-5-((*E*)-hept-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), (*E*)-nona-1,3-diene (36.0 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in THF (2.7 mL) were stirred at -20 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 2.8:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the (3*R*)-5-((*E*)-hept-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehydes as a 2.8:1 mixture of diastereomers as a clear viscous syrup (47.2 mg, 62% yield). **(3*R*,5*R*)-5-((*E*)-hept-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (s, 1H, C**H**O), 8.35 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.99 (d, *J* = 8.7 Hz, 2H, Ar**H**), 5.60 (dt, *J* = 15.2, 6.6 Hz, 1H, NCHCH=C**H**CH_2), 5.02 (dd, *J* = 15.2, 7.7 Hz, 1H, NCHC**H**=$CHCH_2$), 4.28 (ddd, *J* = 12.6, 7.6, 6.9 Hz, 1H, NC**H**CH=CH), 3.85 (dd, *J* = 10.6, 5.2 Hz, 1H, NC**H**$_2$), 3.66 (dd, *J* = 10.5, 7.9 Hz, 1H, NC**H**$_2$), 2.96 (ddd, *J* = 13.4, 8.1, 5.5 Hz, 1H, C**H**CHO), 2.31 (dt, *J* = 13.2, 8.2 Hz, 1H, CHC**H**$_2$CH), 2.06 (dt, *J* = 13.2, 5.2 Hz, 1H, CHC**H**$_2$CH), 2.00-1.82 (m, 2H, NCHCH=CHC**H**$_2$), 1.47 – 1.07 (m, 6H, (C**H**$_2$)$_3$$CH_3$), 0.87 (t, *J* = 7.1 Hz, 3H, CH_2C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 150.0, 145.1, 135.0, 128.7, 128.0, 124.2, 61.9, 49.3, 47.3, 33.8, 31.9, 31.4, 28.5, 22.5, 14.1. **(3*R*,5*S*)-5-((*E*)-hept-1-enyl)-1-(4-nitrophenylsulfonyl)pyrrolidine-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (d, *J* = 0.9 Hz, 1H, C**H**O), 5.25 (dd, *J* = 15.2, 7.3 Hz, 1H, NCHC**H**=$CHCH_2$), 4.15 (dd, *J* = 12.6, 7.0 Hz, 1H, NC**H**CH=CH), 3.59 (dd, *J* = 10.7, 7.8 Hz, 1H, NC**H**$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 150.0, 144.3, 134.3, 128.8, 128.1, 124.2, 61.7, 48.8, 47.2, 33.5, 32.0, 29.8, 28.6, 22.5, 14.1. **For the mixture of**

diastereomers: R_f 0.54 (20% Et_2O/benzene); IR (film) 2926, 1725, 1528, 1348, 1309, 1162, 1091, 921, 855 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{25}N_2O_5S$ ($[M+H]^+$) 381.1479, found 381.1464; Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 87% ee for the major diastereomer (t_R (minor) = 3.5 min, t_R (major) = 5.4 min) and 55% ee for the minor diastereomer (t_R (major) = 4.0 min, t_R (minor) = 5.1 min).

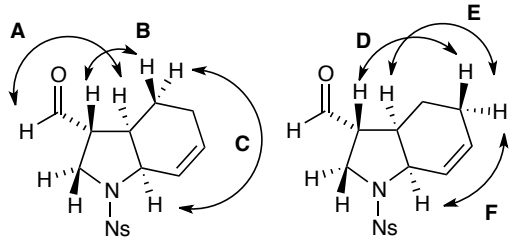
Table 3, entry 6:



(3*R*, 3a*R*, 7a*R*)-1-((4-nitrophenyl)sulfonyl)-2,3,3a,4,5,7a-hexahydro-indole-3-carbaldehyde. According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), 1,3-cyclohexadiene (19.0 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in THF (2.7 mL) were stirred at -40 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 3:2. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the (3*R*)-1-((4-nitrophenyl)sulfonyl)-2,3,3a,4,5,7a-hexahydro-indole-3-carbaldehydes as a 3:2 mixture of diastereomers as a white solid (49.8 mg, 74% yield). **(3*R*, 3a*R*, 7a*R*)-1-((4-nitrophenyl)sulfonyl)-2,3,3a,4,5,7a-hexahydro-indole-3-carbaldehyde:** ^{1}H NMR (500 MHz, acetone) δ 9.50 (s, 1H, C**H**O), 8.50 (d, *J* = 8.6 Hz, 2H, Ar**H**), 8.23 (d, *J* = 8.6 Hz, 2H, Ar**H**), 5.92 (dt, *J*= 3.0, 10.3 Hz, 1H, NCHCH=C**H**CH_2), 5.83 (dd, *J* = 2.5, 10.3 1H, NCHC**H**=$CHCH_2$), 4.23 (d, *J* = 7.6 Hz, 1H, NC**H**CH=CH), 3.71 (m, 2H, NC$\mathbf{H_2}$), 3.09 (td, *J* = 7.7, 8.4 Hz, 1H, CHOC**H**), 2.41 (qd, *J* = 4.0, 7.0, 1H, NCHC**H**(CH)CH_2), 2.10 (m, 1H, CH=CHC$\mathbf{H_2}$), 2.05 (m, 1H, CH=CHC$\mathbf{H_2}$), 1.79 (m, 1H, NCHCH**C**$\mathbf{H_2}$), 1.72 (q, *J* = 5.6, 1H, NCHCH**C**$\mathbf{H_2}$); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 200.5, 149.9, 145.0, 130.4, 129.8, 127.2, 125.3, 58.6, 52.4, 47.2, 38.3, 22.5, 21.4. **(3*R*, 3a*R*, 7a*S*)-1-((4-nitrophenyl)sulfonyl)-2,3,3a,4,5,7a-hexahydro-indole-3-carbaldehyde (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, acetone) δ 9.75 (d, *J* = 0.9 Hz, 1H, C**H**O), 6.09 (dt, *J* = 3.1, 10.5 Hz, 1H, NCHCH=C**H**CH_2), 5.99 (dd, *J* = 10.5, 7.0 Hz, 1H, NC**H**CH=CH), 4.04 (t, *J* = 5.2 Hz, 1H, NC**H**CH=CH), 3.84 (t, *J* = 10.9, 1H, NC$\mathbf{H_2}$), 3.68 (m, 1H, NC$\mathbf{H_2}$), 3.00 (td, *J* = 7.5, 10.0 Hz, 1H, CHOC**H**), 2.82 (m, 1H, NCHC**H**(CH)CH_2), 1.62 (qd, *J* = 4.3, 12.8, NCHCH**C**$\mathbf{H_2}$), 1.39 (m, 1H, NCHCH**C**$\mathbf{H_2}$); ^{13}C NMR (125 MHz, acetone) δ 200.8, 150.0, 145.1, 131.4, 129.9, 126.6, 125.4, 58.5, 53.4, 46.9, 39.2, 24.1, 20.8. **For the mixture of diastereomers:** R_f 0.54 (20% Et_2O/benzene); IR (film) 2928, 1722, 1533, 1347, 1304, 1160, 1108, 1086, 921, 853 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{15}H_{17}N_2O_5S$ ($[M+H]^+$) 337.0858, found 337.0838; Chiral SFC analysis of the corresponding mixture of alcohols (IA, 30% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major diastereomer (t_R (minor) = 2.9 min, t_R (major) = 4.7 min) and 94% ee for the minor diastereomer (t_R (major) = 3.2 min, t_R (minor) = 4.9 min). **Determination of diastereomers**: Two NOESY experiments (500 MHz, d_6-acetone, 295 K) were performed using standard parameters with the following variation: relaxation time: 0.5 μs (short) or 2.0 μs (long).

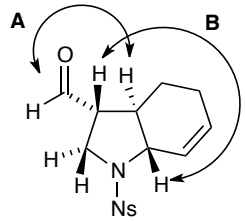
For the major diatereomer:



Indicative interactions observed with the short relaxation time: B: δ 3.09 to 2.41; C: δ 3.09 to 1.72; D: δ 3.09 to 2.17; F: δ 4.23 to 2.05.

Indicative interactions only observed with the long relaxation time: A: δ 9.50 to 2.41; E: δ 2.41 to 2.05.

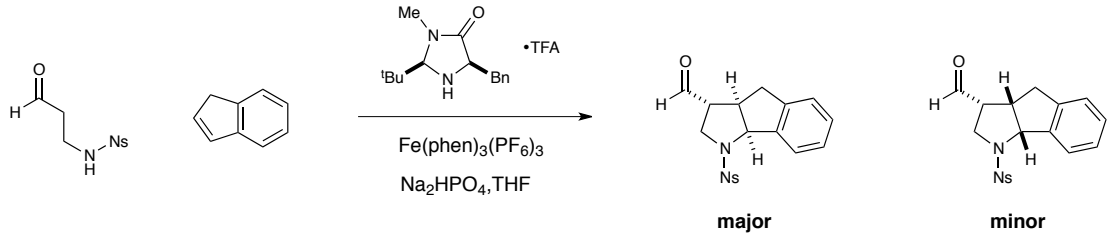
Minor diastereomer:



Indicative interactions observed for the short relaxation time: B: δ 4.04 to 3.00.

Indicative interactions only observed for the long relaxation time: A: δ 9.75 to 2.82.

Equation 2:



(3*R*,3a*R*,8b*S*)-1-((4-nitrophenyl)sulfonyl)-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole-3-carbaldehyde.

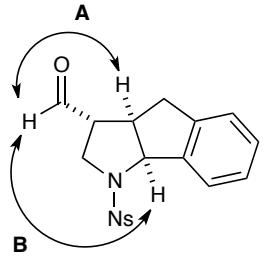
According to the general procedure, 4-nitro-*N*-(3-oxopropyl)benzenesulfonamide (77.4 mg, 0.30 mmol, 1.5 equiv), indene (23.2 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-benzyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (14.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (618 mg, 0.60 mmol, 3.0 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in THF (2.7 mL) were stirred at -40 °C for 12 h to afford a colorless syrup after workup. ^{1}H NMR analysis of the crude mixture indicated a diastereomeric ratio of 9.0:1. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the title compound as a single diastereomer as a clear viscous syrup (55.6 mg, 75% yield). **Indene adduct, major diastereomer:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (d, *J* = 1.0 Hz, 1H, C**H**O), 8.39 (d, *J* = 8.8 Hz, 2H, Ar**H**), 8.06 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.77 (dd, *J* = 5.1, 3.6 Hz, 1H, Ar**H**), 7.33-7.29 (m, 2H, Ar**H**), 7.22 (dd, *J* = 4.9, 3.5 Hz, 1H, Ar**H**), 5.29 (d, *J* = 7.6 Hz, 1H, ArC**H**N), 3.62 (qd, *J* = 11.0, 7.4 Hz, 2H, NC$\mathbf{H}_2$), 3.17 (dd, *J* = 16.4, 7.7 Hz, 1H, ArC$\mathbf{H}_2$CH), 3.04 (ddd, *J* = 15.2, 7.6, 2.3 Hz, 1H, C**H**CHO), 2.92 (dd, *J* = 16.4, 2.1 Hz, 1H, ArC$\mathbf{H}_2$CH), 2.85 (q, *J* = 7.4 Hz, 1H, $ArCH_2C\mathbf{H}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 150.3, 143.6, 140.2 (2C), 129.2, 128.8, 127.9, 126.7, 125.3, 124.6, 69.0, 56.0,

47.9, 43.0, 35.5. **Indene adduct (minor diastereomer, characteristic signals):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H, Ar**H**), 7.95 (d, *J* = 8.8 Hz, 1H, Ar**H**), 5.40 (d, *J* = 7.2 Hz, 1H, ArC**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 141.6, 139.9, 129.5, 128.5, 127.8, 126.7, 124.8, 124.5, 69.3, 53.0, 47.8, 44.5. **For the mixture of distereomers:** R_f 0.51 (20% Et_2O/benzene); IR (film) 2926, 1723, 1528, 1349, 1164, 1109, 1010, 854 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{18}H_{16}N_2O_5S$ ($[M+H]^+$) 373.0853, found 373.0859; Chiral SFC analysis of the corresponding mixture of alcohols (IA, 30% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 85% ee for the major diastereomer (t_R (major) = 3.3 min, t_R (minor) = 5.3 min) and 80% ee for the minor diastereomer (t_R (major) = 3.6 min, t_R (minor) = 4.6 min).

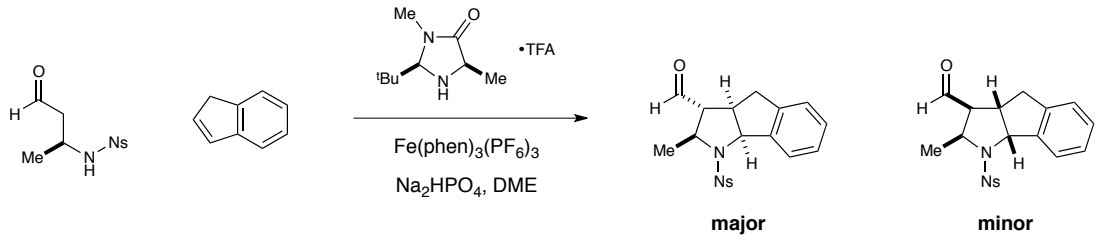
Determination of major diastereomer:

^{1}H NMR NOESY experiment (500 MHz, $CDCl_3$, 295 K) was performed using standard parameters with the following variation: relaxation time: 0.7 μs.

The indicative interactions were A: δ 9.54 to 3.15 and B: δ 9.54 to 5.29.



Equation 3:



(2*S*,3*R*,3a*R*,8b*S*)-2-methyl-1-((4-nitrophenyl)sulfonyl)-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole-3-carbaldehyde.

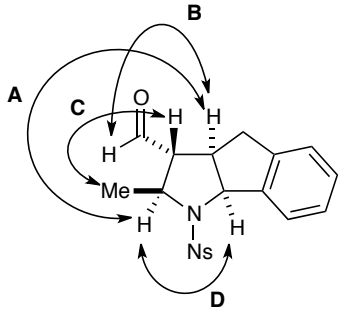
According to the general procedure, (*S*)-4-nitro-*N*-(4-oxobutan-2-yl)benzenesulfonamide (81.6 mg, 0.30 mmol, 1.5 equiv), indene (23.2 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-methyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (11.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.5 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -20 °C for 12 h to afford a

yellow syrup after workup. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford a 19:1 mixture of diastereomers of the title compound as a white solid (50.2 mg, 65% yield). **Indene adduct, major diastereomer:** ^{1}H NMR (500 MHz, d_6-acetone) δ 9.50 (d, *J* = 1.6 Hz, 1H, C**H**O), 8.50 (d, *J* = 8.8 Hz, 2H, Ar**H**), 8.29 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.66 (d, *J* = 7.0 Hz, 1H, Ar**H**), 7.32 (m, 3H, Ar**H**), 5.42 (d, *J* = 7.7 Hz, 1H, ArC**H**N), 4.09 (dq, *J* = 7.7, 6.3 Hz, 1H, CH_3C**H**N), 3.08 (dd, *J* = 16.4, 7.2 Hz, 1H, ArC**H$_2$**), 2.92 (d, *J* = 16.4 Hz, 1H, ArC**H$_2$**), 2.87 (td, *J* = 8.4, 7.9, 6.9 Hz, 1H, ArCH_2C**H**), 2.49 (td, *J* = 8.4, 7.6, 1.6 Hz, 1H, CHOC**H**), 1.26 (d, *J* = 6.3 Hz, 3H, CHC**H$_3$**); ^{13}C NMR (125 MHz, d_6-acetone) δ 199.8, 151.4, 144.2, 143.1, 140.9, 130.1 (2C), 129.5, 128.3, 126.5 (2C), 125.5 (2C), 70.8, 65.0, 58.5, 42.8, 35.8, 23.7. **Indene adduct (minor diastereomer, characteristic signals):** δ^{1}H NMR (500 MHz, d_6-acetone) δ 9.72 (d, *J* = 1.2 Hz, 1H, C**H**O), 8.36 (d, *J* = 8.9 Hz, Ar**H**), 8.16 (d, *J* = 8.9 Hz, 2H, Ar**H**), 7.88 (d, *J* = 7.1 Hz, 1H, Ar**H**), 7.26-7.13 (m, 3H, Ar**H**), 5.58 (d, *J* = 7.6 Hz, 1H, ArC**H**N), 4.48 (p, *J* = 6.8 Hz, 1H, CH_3C**H**N), 3.50 (dtd, *J* = 9.2, 7.4, 1.5 Hz, 1H, ArCH_2C**H**), 3.08 (dd, *J* = 16.5, 7.5 Hz, 1H, ArC**H$_2$**), 2.99 (ddd, *J* = 10.1, 7.4, 1.5 Hz, 1H, CHOC**H**), 2.75 (d, *J* = 16.5 Hz, 1H, ArC**H$_2$**), 1.18 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.78, 149.32, 142.27, 141.89, 129.36 (2C), 128.06, 127.73, 126.27 (2C), 125.20 (2C), 69.37, 59.57, 58.74, 41.22, 17.18.

For the mixture of distereomers: R_f 0.51 (20% Et_2O/benzene); IR (film) 2928, 1721, 1528, 1348, 1310, 1165, 1091, 986, 856 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{19}H_{19}N_2O_5S$ ($[M+H]^+$) 387.1015, found 387.1000; Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 99% ee for the major diastereomer (t_R (major) = 5.7 min, t_R (minor) = 8.8 min) and 99% ee for the minor diastereomer (t_R (major) = 5.3 min, t_R (minor) = 9.2 min).

Determination of diastereomers: Two NOESY experiments (500 MHz, d_6-acetone, 295 K) were performed using standard parameters with the following variation: relaxation time: 0.7 μs (short) or 1.5 μs (long).

For the major diatereomer:



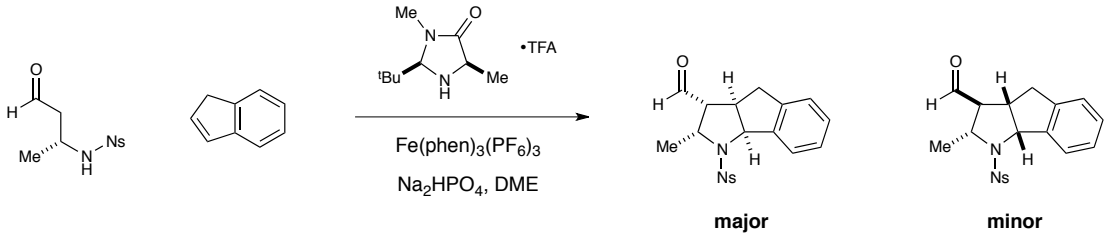
Indicative interactions observed for the short relaxation time: A: δ 4.05 to 2.87, B: δ 9.50 to 2.87, C: δ 2.99 to 1.26.

Indicative interactions only observed for the long relaxation time: D: δ 5.42 to 4.48.

The minor diastereomer was determined by correlation with the products in equation 4.

Equation 4:

(2*R*,3*R*,3a*R*,8b*S*)-2-methyl-1-((4-nitrophenyl)sulfonyl)-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole-3-carbaldehyde.



According to the general procedure, (*R*)-4-nitro-*N*-(4-oxobutan-2-yl)benzenesulfonamide (81.6 mg, 0.30 mmol, 1.5 equiv), indene (23.2 μL, 0.20 mmol, 1.0 equiv), (2*R*,5*R*)-5-methyl-2-*tert*-butyl-3-methylimidazolidin-4-one trifluoroacetic acid salt (11.4 mg, 0.04 mmol, 0.20 equiv), $Fe(phen)_3(PF_6)_3$ (515 mg, 0.50 mmol, 2.5 equiv), and Na_2HPO_4 (28.4 mg, 0.20 mmol, 1.0 equiv) in DME (2.7 mL) were stirred at -20 °C for 12 h to afford a colorless syrup after workup. The crude product was concentrated onto silica gel and purified by silica gel column chromatography (10% Et_2O/benzene) to afford the a mixture of diastereomers of the title compound as a clear viscous syrup (51.0 mg, 66% yield) ^{1}H NMR analysis of the purified compound indicated a diastereomeric ratio of 5:1. **Indene adduct, major diastereomer:** ^{1}H NMR (500 MHz, d_6-acetone) δ 9.72 (d, *J* = 1.2 Hz, 1H, C**H**O), 8.36 (d, *J* = 8.9 Hz, Ar**H**), 8.16 (d, *J* = 8.9 Hz, 2H, Ar**H**), 7.88 (d, *J* =

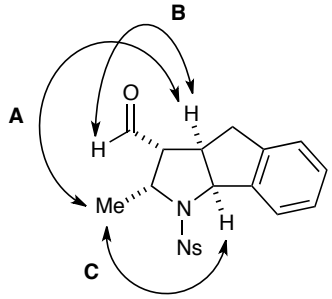
7.1 Hz, 1H, Ar**H**), 7.26-7.13 (m, 3H, Ar**H**), 5.58 (d, *J* = 7.6 Hz, 1H, ArC**H**N), 4.48 (p, *J* = 6.8 Hz, 1H, CH_3C**H**N), 3.50 (dtd, *J* = 9.2, 7.4, 1.5 Hz, 1H, $ArCH_2C$**H**), 3.08 (dd, *J* = 16.5, 7.5 Hz, 1H, ArC$\mathbf{H_2}$), 2.99 (ddd, *J* = 10.1, 7.4, 1.5 Hz, 1H, CHOC**H**), 2.75 (d, *J* = 16.5 Hz, 1H, ArC$\mathbf{H_2}$), 1.18 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, d_6-acetone) δ 200.8, 149.3, 142.3, 141. 9, 129.4, 129.3, 128.1, 127.7, 126.3, 125.2, 69.4, 59.6, 58.7, 41.2, 17.2.

Indene adduct (minor diastereomer): ^{1}H NMR (500 MHz, d_6-acetone) δ 9.50 (d, *J* = 1.6 Hz, 1H, C**H**O), 8.50 (d, *J* = 8.8 Hz, 2H, Ar**H**), 8.29 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.66 (d, *J* = 7.0 Hz, 1H, Ar**H**), 7.32 (m, 3H, Ar**H**), 5.42 (d, *J* = 7.7 Hz, 1H, ArC**H**N), 4.09 (dq, *J* = 7.7, 6.3 Hz, 1H, CH_3C**H**N), 3.08 (dd, *J* = 16.4, 7.2 Hz, 1H, ArC$\mathbf{H_2}$), 2.92 (d, *J* = 16.4 Hz, 1H, ArC$\mathbf{H_2}$), 2.87 (td, *J* = 8.4, 7.9, 6.9 Hz, 1H, $ArCH_2C$**H**), 2.49 (td, *J* = 8.4, 7.6, 1.6 Hz, 1H, CHOC**H**), 1.26 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, d_6-acetone) δ 199.8, 151.4, 144.2, 143.1, 140.9, 130.1, 129.5, 128.3, 126.5, 125.5, 70.8, 65.0, 58.5, 42.8, 35.8, 23.7.

For the mixture of distereomers: R_f 0.51 (20% Et_2O/benzene); IR (film) 2935, 1714, 1527, 1343, 1318, 1156, 1081, 917, 855 cm^{-1}; HRMS (ESI-TOF) m/z calculated for $C_{19}H_{19}N_2O_5S$ ($[M+H]^+$) 387.1015, found 387.1009; Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 99% ee for the major diastereomer (t_R (major) = 9.2 min, t_R (minor) = 5.3 min).. and 99% ee for the minor diastereomer (t_R (major) = 8.8 min, t_R (minor) = 5.7 min).

Determination of diastereomers: Two NOESY experiments (500 MHz, d_6-acetone, 295 K) were performed using standard parameters with the following variation: relaxation time: 0.7 μs (short) or 1.5 μs (long).

For the major diastereomer:

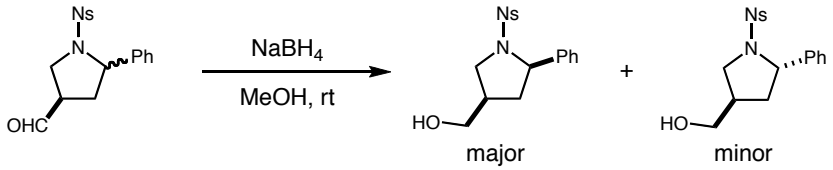


Indicative interactions observed for the short relaxation time: A: δ 3.50 to 1.18, B: δ 9.72 to 3.50.

Indicative interactions only observed for the long relaxation time: C: δ 5.58 to 1.18.

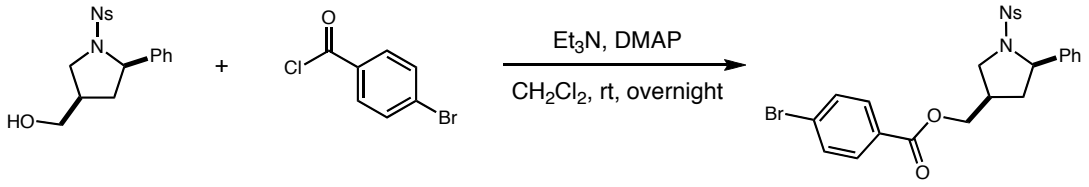
The minor diastereomer was determined by correlation with the products in equation 3.

5. X-Ray Crystallography Data



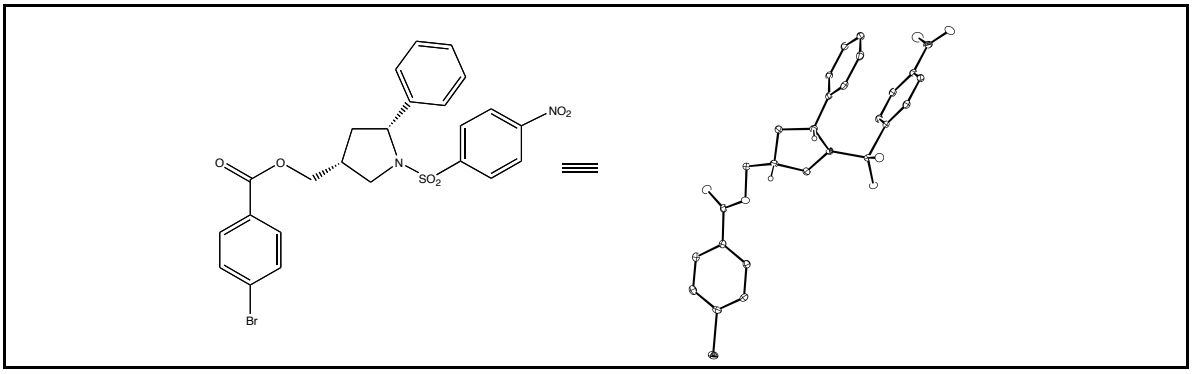
((3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidin-3-yl)methanol and **((3*R*,5*S*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidin-3-yl)methanol** According to the general procedure, (3*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidine-3-carbaldehydes (43 mg, 0.12 mmol, 1.0 equiv) and $NaBH_4$ (23 mg, 0.60 mmol, 5.0 equiv) in MeOH (2.5 mL) was stirred for 30 min to afford the crude alcohols after workup. The crude alcohols were filtered through silica gel (50% EtOAc/hexanes) and concentrated to yield a white solid. Purification of the alcohols by preparative SFC (ADH, 40% EtOH/CO_2, 3.0 mL/min, 220 nm) afforded ((3*R*,5*R*)-5-phenyl-1-nosylpyrrolidin-3-yl)methanol (36.0 mg, 83%) as a white solid and ((3*R*,5*S*)-5-phenyl-1-nosylpyrrolidin-3-yl)methanol (3.8 mg, 17%) as a white solid. R_f 0.29 (50% EtOAc/hexanes); **major diastereomer - ((3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidin-3-yl)methanol:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.78 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.25 – 7.13 (m, 7H, Ar**H**), 4.95 (dd, *J* = 8.1, 4.0 Hz, 1H, NsNC**H**Ar), 3.75 (dd, *J* = 10.0, 7.1 Hz, 1H, HOC**H**$_2$CH), 3.59 (dd, *J* = 10.0, 5.7 Hz, 1H, HOC**H**$_2$CH), 3.54 – 3.45 (m, 2H, NsNC**H**$_2$CH), 2.63 – 2.54 (m, 1H, CHC**H**$_2$CH), 2.08 – 1.92 (m, 1H, CHC**H**$_2$CH), 2.08 – 1.92 (m, 1H, CH$_2$C**H**CH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 144.4, 141.6, 128.5, 128.3, 127.6, 126.3, 124.0, 63.2, 63.1, 51.4, 39.4, 38.0; $[a]_D$ +232.30 (*c* = 0.5, acetone, 26.4 °C) **minor diastereomer - ((3*R*,5*S*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidin-3-yl)methanol:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 2H, Ar**H**), 7.65 (d, *J* = 8.9 Hz, 2H, Ar**H**), 7.25 – 7.13 (m, 5H, Ar**H**), 4.80 (dd, *J* = 9.0, 1.5 Hz, 1H, ArC**H**), 4.03 (dd, *J* = 10.2, 7.6 Hz, 1H, HOC**H**$_2$CH), 3.75 – 3.55 (m, 2H, NsNC**H**Ar), 3.37 (t, *J* = 10.2 Hz, 1H, HOC**H**$_2$CH), 2.52 – 2.42 (m, 1H, CHC**H**$_2$CH), 2.42 – 2.30 (m, 1H, CH$_2$C**H**CH$_2$), 1.76 (ddd, *J* = 12.8, 10.2, 9.0 Hz, 1H, CHC**H**$_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 144.9, 141.0, 128.4, 128.1, 127.7, 126.9, 123.9, 64.3,

63.2, 52.4, 40.9, 39.5; $[a]_D$ +97.69 (*c* = 0.5, acetone, 26.5 °C); **for the mixture of diastereomers**: IR (film) 3410, 3031, 2953, 2921, 1709, 1522, 1495, 1357, 1220, 1154, 1031, 1010, 914, 846, 769, 754, 729, 687, 700, 623; HRMS (EI) m/z calculated for $C_{17}H_{19}N_2O_5S$ ($[M+H]^+$) 363.1009, found 363.1013.



X-ray crystal structure obtained

(3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidin-3-yl 4-bromobenzoate To a solution of ((3*R*,5*R*)-1-(4-nitrophenylsulfonyl)-5-phenylpyrrolidin-3-yl)methanol (12 mg, 0.04 mmol, 1.0 equiv), triethylamine (6.4 mL, 0.05 mmol, 1.2 equiv) and 4-(dimethylamino)pyridine (1.5 mg, 0.012 mmol, 0.3 equiv) in DCM (2.0 mL) at 0 °C was added 4-bromobenzoyl chloride (11.0 g, 0.05 mmol, 1.2 equiv). The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with H_2O (3 mL) and diethyl ether (3 x 5 mL). The layers were separated, organics washed with brine, dried over $MgSO_4$, filtered, and concentrated to furnish the crude product. The crude ester were filtered through silica gel (30% EtOAc/hexanes) and concentrated to yield a white solid and X-ray quality crystals were obtained from 10% CH_2Cl_2/hexanes (slow evaporation technique).



Compound, $C_{24}H_{21}N_2SO_6Br$, crystallizes in the monoclinic space group $P2_1$ (systematic absences 0k0: k=odd) with a=7.3854(8)Å, b=5.7613(6)Å, c=26.815(3)Å,

b=92.526(5)°, V=1139.9(2)Å^3, Z=2, and d_{calc}=1.589 g/cm^3. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation (l=0.71073 Å) at a temperature of 100(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 15 seconds. A total of 2735 frames were collected with a crystal to detector distance of 49.950 mm, rotation widths of 0.5° and exposures of 15 seconds:

scan type	2q	w	f	c	frames
f	-23.00	-13.80	-345.79	32.61	739
w	32.00	16.93	85.96	-51.77	268
w	27.00	-91.31	59.97	48.96	267
w	-23.00	-33.19	-268.05	-98.74	104
w	32.00	-185.37	-258.79	-99.65	68
w	34.50	-48.57	-211.82	97.50	168
w	27.00	-51.59	-36.78	99.23	174
f	29.50	288.30	75.82	39.97	208
f	24.50	68.74	-19.24	-42.87	739

Rotation frames were integrated using SAINT[i], producing a listing of unaveraged F^2 and s(F^2) values which were then passed to the SHELXTL[ii] program package for further processing and structure solution on a Dell Pentium 4 computer. A total of 23418 reflections were measured over the ranges $1.52 \le \theta \le 27.78°$, $-9 \le h \le 9$, $-7 \le k \le 7$, $-35 \le l \le 34$ yielding 5239 unique reflections (Rint = 0.0353). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[iii] (minimum and maximum transmission 0.5786, 0.7456).

The structure was solved by direct methods (SHELXS-97[iv]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[v] All reflections were used during refinement. The weighting scheme used was $w=1/[s^2(F_o^2)+ (0.0265P)^2 + 0.0865P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0230 and wR2=0.0575 for 5090 observed reflections for which $F > 4s(F)$ and R1=0.0239 and wR2=0.0578 and GOF =1.043 for all 5239 unique, non-zero reflections

and 308 variables.[i] The maximum D/s in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.524 and -0.233 e/Å^3.

Table 1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2 and 3 Anisotropic thermal parameters are in Table 4. Tables 5 and 6 list bond distances and bond angles. Figure 1 is an ORTEP[vi] representation of the molecule with 30% probability thermal ellipsoids displayed.

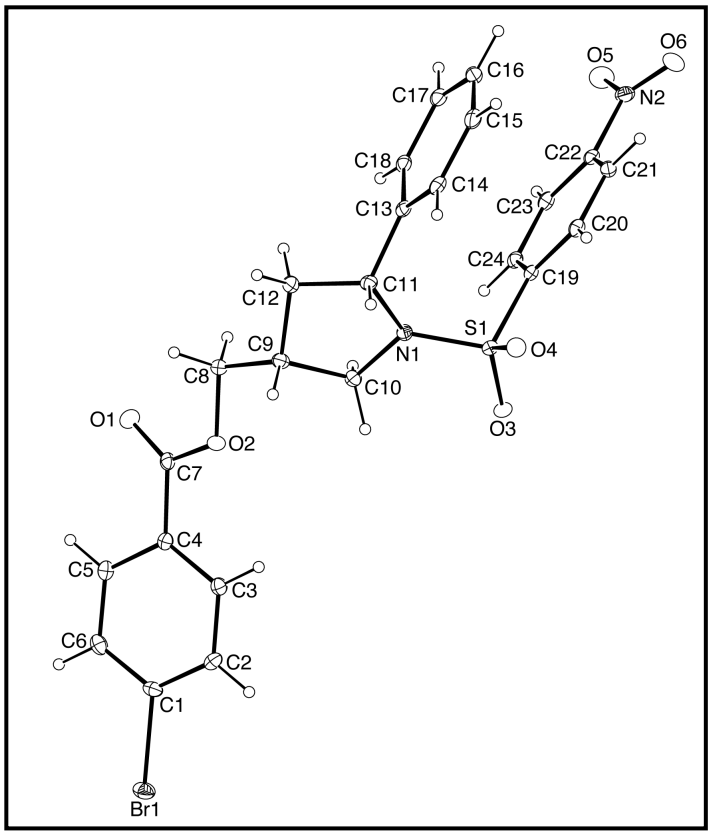


Figure 1. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table 1. Summary of Structure Determination

Empirical formula	$C_{24}H_{21}N_2SO_6Br$
Formula weight	545.40
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1$
Cell constants:	
a	7.3854(8) Å
b	5.7613(6) Å
c	26.815(3) Å
b	92.526(5)°
Volume	1139.9(2) $Å^3$
Z	2
Density (calculated)	1.589 Mg/m^3
Absorption coefficient	1.940 mm^{-1}
F(000)	556
Crystal size	0.45 x 0.22 x 0.02 mm^3
Theta range for data collection	1.52 to 27.78°
Index ranges	-9 £ h £ 9, -7 £ k £ 7, -35 £ l £ 34
Reflections collected	23418
Independent reflections	5239 [R(int) = 0.0353]
Completeness to theta = 27.78°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5786
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5239 / 1 / 308
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0230, wR2 = 0.0575
R indices (all data)	R1 = 0.0239, wR2 = 0.0578
Absolute structure parameter	0.021(5)
Largest diff. peak and hole	0.524 and -0.233 e.$Å^{-3}$

Table 2. Refined Positional Parameters

Atom	x	y	z	U_{eq}, Å^2
C1	0.3172(2)	0.8495(3)	0.44603(6)	0.0178(4)
C2	0.3402(2)	0.6829(3)	0.48306(7)	0.0180(3)
C3	0.2795(2)	0.7303(3)	0.53065(6)	0.0170(4)
C4	0.2003(2)	0.9434(3)	0.54028(6)	0.0150(3)
C5	0.1808(2)	1.1095(3)	0.50261(7)	0.0184(4)
C6	0.2381(2)	1.0626(3)	0.45518(7)	0.0199(4)
C7	0.1273(2)	1.0000(3)	0.58978(6)	0.0164(3)
C8	0.0257(3)	0.8357(3)	0.66474(6)	0.0197(4)
C9	0.0375(2)	0.6018(3)	0.68941(7)	0.0177(3)
C10	0.2338(2)	0.5310(3)	0.70193(6)	0.0172(3)
C11	0.0325(2)	0.3828(3)	0.76642(6)	0.0157(3)
C12	-0.0525(2)	0.5938(3)	0.73965(7)	0.0194(4)
C13	0.0330(2)	0.3912(3)	0.82276(6)	0.0159(3)
C14	-0.0319(2)	0.2031(3)	0.84891(7)	0.0187(3)
C15	-0.0251(3)	0.2021(4)	0.90104(7)	0.0229(4)
C16	0.0463(3)	0.3900(4)	0.92710(7)	0.0231(4)
C17	0.1085(2)	0.5814(3)	0.90117(7)	0.0201(4)
C18	0.1017(2)	0.5814(3)	0.84944(7)	0.0167(3)
C19	0.4621(2)	0.3135(3)	0.82401(6)	0.0147(3)
C20	0.4409(2)	0.1825(3)	0.86658(7)	0.0166(3)
C21	0.5084(2)	0.2668(4)	0.91233(6)	0.0181(3)
C22	0.5917(2)	0.4805(3)	0.91315(6)	0.0176(4)
C23	0.6146(2)	0.6141(3)	0.87101(7)	0.0179(3)
C24	0.5475(2)	0.5283(3)	0.82565(7)	0.0167(3)
N1	0.2192(2)	0.3875(3)	0.74710(5)	0.0179(3)
N2	0.6632(2)	0.5709(3)	0.96170(6)	0.0224(3)
O1	0.0839(2)	1.1904(2)	0.60280(5)	0.0250(3)
O2	0.11127(16)	0.8079(3)	0.61744(4)	0.0204(3)
O3	0.51821(18)	0.2240(2)	0.73145(5)	0.0232(3)
O4	0.29535(19)	-0.0140(2)	0.77539(5)	0.0226(3)
O5	0.71154(19)	0.7734(3)	0.96353(5)	0.0313(3)
O6	0.6693(2)	0.4389(3)	0.99748(5)	0.0296(3)
S1	0.37459(6)	0.20785(7)	0.765593(15)	0.01620(9)
Br1	0.39482(2)	0.78254(4)	0.381293(6)	0.02417(6)

$U_{eq}=^1/_3[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos g+2U_{13}aa^*cc^*\cos b+2U_{23}bb^*cc^*\cos a]$

Table 3. Positional Parameters for Hydrogens

Atom	x	y	z	U_{iso}, Å^2
H2	0.3952	0.5418	0.4764	0.024
H3	0.2920	0.6194	0.5558	0.023
H5	0.1291	1.2526	0.5094	0.024
H6	0.2237	1.1723	0.4299	0.026
H8a	-0.0998	0.8828	0.6594	0.026
H8b	0.0887	0.9518	0.6851	0.026
H9	-0.0192	0.4857	0.6670	0.024
H10a	0.2831	0.4422	0.6750	0.023
H10b	0.3096	0.6659	0.7086	0.023
H11	-0.0298	0.2417	0.7546	0.021
H12a	-0.1827	0.5750	0.7349	0.026
H12b	-0.0278	0.7347	0.7585	0.026
H14	-0.0804	0.0763	0.8315	0.025
H15	-0.0686	0.0749	0.9182	0.031
H16	0.0527	0.3888	0.9618	0.031
H17	0.1547	0.7095	0.9186	0.027
H18	0.1436	0.7098	0.8324	0.022
H20	0.3823	0.0397	0.8646	0.022
H21	0.4975	0.1813	0.9415	0.024
H23	0.6731	0.7570	0.8731	0.024
H24	0.5595	0.6137	0.7965	0.022

Table 4. Refined Thermal Parameters (U's)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0149(8)	0.0259(9)	0.0128(8)	-0.0026(6)	0.0014(6)	-0.0044(6)
C2	0.0159(8)	0.0162(8)	0.0220(9)	-0.0042(7)	0.0022(7)	0.0008(7)
C3	0.0179(8)	0.0161(9)	0.0171(7)	0.0013(6)	0.0000(6)	0.0001(6)
C4	0.0125(8)	0.0144(8)	0.0179(8)	-0.0001(6)	-0.0006(6)	-0.0010(7)
C5	0.0160(8)	0.0175(8)	0.0216(9)	0.0014(7)	-0.0013(7)	0.0009(7)
C6	0.0195(9)	0.0207(9)	0.0193(9)	0.0053(7)	-0.0017(7)	-0.0029(7)
C7	0.0131(8)	0.0185(8)	0.0174(8)	0.0000(7)	-0.0022(6)	0.0018(7)
C8	0.0230(9)	0.0221(11)	0.0142(7)	0.0001(6)	0.0022(6)	0.0063(7)
C9	0.0181(8)	0.0209(9)	0.0142(8)	-0.0015(7)	0.0007(6)	0.0006(7)
C10	0.0191(9)	0.0169(8)	0.0158(8)	0.0018(7)	0.0021(6)	0.0012(7)
C11	0.0122(8)	0.0195(8)	0.0156(8)	-0.0007(7)	0.0034(6)	-0.0005(7)
C12	0.0171(9)	0.0248(9)	0.0165(8)	0.0017(7)	0.0015(7)	0.0040(7)
C13	0.0100(7)	0.0194(8)	0.0185(8)	0.0006(7)	0.0030(6)	0.0024(7)
C14	0.0140(8)	0.0173(8)	0.0250(9)	0.0004(7)	0.0050(7)	0.0035(7)
C15	0.0193(9)	0.0253(9)	0.0250(9)	0.0103(7)	0.0094(7)	0.0070(7)
C16	0.0180(9)	0.0352(10)	0.0163(8)	0.0040(8)	0.0034(7)	0.0089(8)
C17	0.0152(8)	0.0241(9)	0.0211(9)	-0.0033(7)	0.0004(7)	0.0050(7)
C18	0.0135(8)	0.0180(8)	0.0189(8)	0.0019(7)	0.0022(6)	0.0027(7)
C19	0.0120(7)	0.0164(9)	0.0157(7)	-0.0001(7)	0.0013(5)	0.0035(7)
C20	0.0140(8)	0.0152(8)	0.0208(8)	0.0009(7)	0.0024(6)	0.0006(7)
C21	0.0161(7)	0.0232(9)	0.0153(7)	0.0032(8)	0.0030(6)	0.0042(8)
C22	0.0133(8)	0.0233(9)	0.0161(8)	-0.0035(7)	0.0004(6)	0.0054(7)
C23	0.0122(8)	0.0171(8)	0.0244(9)	-0.0005(7)	0.0015(7)	0.0014(7)
C24	0.0145(8)	0.0181(8)	0.0178(8)	0.0024(6)	0.0036(6)	0.0033(7)
N1	0.0142(7)	0.0245(7)	0.0152(7)	0.0039(6)	0.0038(5)	0.0041(6)
N2	0.0175(8)	0.0311(9)	0.0185(8)	-0.0074(7)	0.0009(6)	0.0041(7)
O1	0.0317(7)	0.0183(6)	0.0251(7)	-0.0007(6)	0.0047(5)	0.0061(6)
O2	0.0285(6)	0.0189(7)	0.0139(5)	0.0000(5)	0.0040(5)	0.0050(6)
O3	0.0197(6)	0.0331(9)	0.0172(6)	-0.0007(5)	0.0062(5)	0.0091(6)
O4	0.0273(7)	0.0177(6)	0.0227(7)	-0.0026(5)	-0.0013(5)	0.0006(6)
O5	0.0331(7)	0.0298(7)	0.0306(7)	-0.0103(8)	-0.0031(5)	-0.0041(8)
O6	0.0326(8)	0.0398(9)	0.0161(7)	-0.0010(6)	-0.0013(6)	0.0037(7)
S1	0.0171(2)	0.01713(19)	0.01453(18)	-0.00137(15)	0.00210(15)	0.00346(15)
Br1	0.02036(9)	0.03532(10)	0.01709(8)	-0.00166(8)	0.00391(6)	-0.00282(9)

The form of the anisotropic displacement parameter is:
$\exp[-2p^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table 5. Bond Distance, Å

C1-C2	1.386(3)	C1-C6	1.386(3)	C1-Br1	1.8918(17)
C2-C3	1.398(2)	C3-C4	1.389(2)	C4-C5	1.394(2)
C4-C7	1.491(2)	C5-C6	1.385(3)	C7-O1	1.199(2)
C7-O2	1.341(2)	C8-O2	1.4507(19)	C8-C9	1.502(3)
C9-C10	1.529(3)	C9-C12	1.529(2)	C10-N1	1.474(2)
C11-N1	1.495(2)	C11-C13	1.511(2)	C11-C12	1.532(3)
C13-C14	1.387(3)	C13-C18	1.392(3)	C14-C15	1.397(3)
C15-C16	1.381(3)	C16-C17	1.393(3)	C17-C18	1.386(3)
C19-C20	1.383(2)	C19-C24	1.389(3)	C19-S1	1.7757(16)
C20-C21	1.391(2)	C21-C22	1.376(3)	C22-C23	1.384(3)
C22-N2	1.478(2)	C23-C24	1.384(3)	N1-S1	1.6075(15)
N2-O5	1.220(3)	N2-O6	1.223(2)	O3-S1	1.4345(13)
O4-S1	1.4349(14)				

Table 6. Bond Angles, °

C2-C1-C6	121.72(16)	C2-C1-Br1	118.93(14)	C6-C1-Br1	119.35(13)
C1-C2-C3	119.00(16)	C4-C3-C2	119.79(16)	C3-C4-C5	120.17(17)
C3-C4-C7	122.06(16)	C5-C4-C7	117.73(16)	C6-C5-C4	120.39(17)
C5-C6-C1	118.91(16)	O1-C7-O2	124.27(16)	O1-C7-C4	124.84(17)
O2-C7-C4	110.86(15)	O2-C8-C9	105.48(14)	C8-C9-C10	111.86(16)
C8-C9-C12	113.34(15)	C10-C9-C12	104.09(14)	N1-C10-C9	103.13(14)
N1-C11-C13	112.59(14)	N1-C11-C12	100.86(14)	C13-C11-C12	115.21(15)
C9-C12-C11	104.58(14)	C14-C13-C18	118.77(16)	C14-C13-C11	119.63(16)
C18-C13-C11	121.57(16)	C13-C14-C15	120.73(18)	C16-C15-C14	119.95(18)
C15-C16-C17	119.70(17)	C18-C17-C16	120.09(18)	C17-C18-C13	120.72(17)
C20-C19-C24	121.87(16)	C20-C19-S1	119.39(14)	C24-C19-S1	118.73(13)
C19-C20-C21	119.20(17)	C22-C21-C20	117.98(16)	C21-C22-C23	123.73(16)
C21-C22-N2	118.13(16)	C23-C22-N2	118.14(17)	C22-C23-C24	117.84(17)
C23-C24-C19	119.38(16)	C10-N1-C11	113.38(13)	C10-N1-S1	122.52(12)
C11-N1-S1	122.58(12)	O5-N2-O6	124.19(16)	O5-N2-C22	117.70(16)
O6-N2-C22	118.10(16)	C7-O2-C8	116.41(15)	O3-S1-O4	119.58(8)
O3-S1-N1	107.41(8)	O4-S1-N1	109.81(8)	O3-S1-C19	106.86(8)
O4-S1-C19	106.23(8)	N1-S1-C19	106.17(8)		

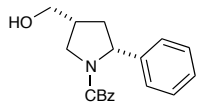
[i]Bruker (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
[ii]Bruker (2009) SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
[iii]Sheldrick, G.M. (2007) SADABS. University of Gottingen, Germany.
[iv]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.
[v]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

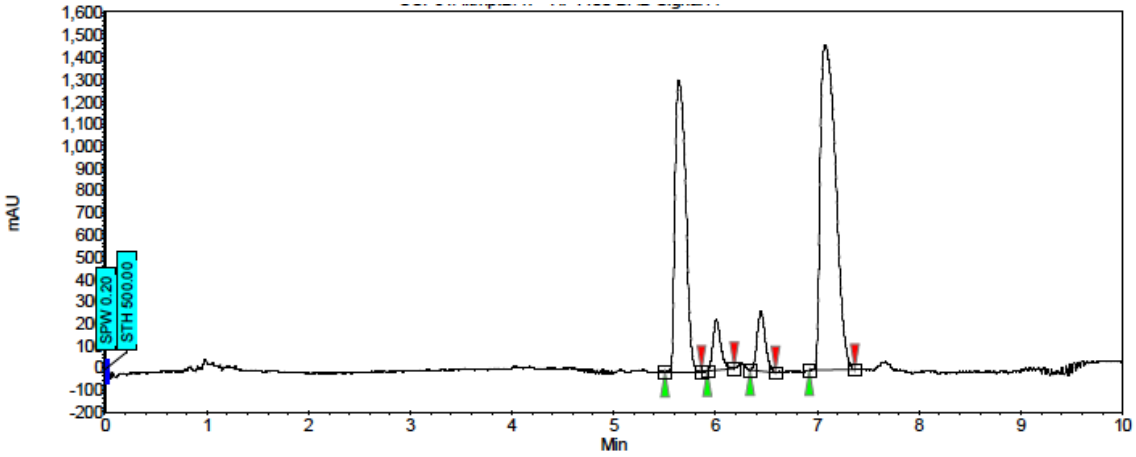
[vi]$R1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$
$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$
where n = the number of reflections and p = the number of parameters refined.

[vii]"ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.

6. SFC and HPLC Traces.

Table 1, Entry 1:





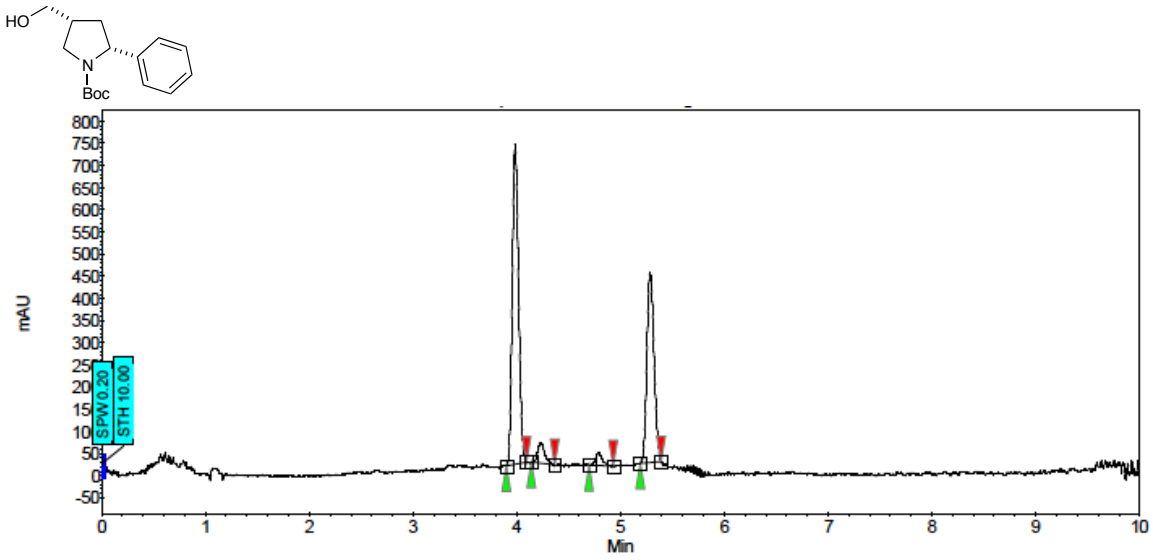
The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.51	5.64	5.86	0.00	34.32	1315.4	159.0	34.319
2	UNKNOWN	5.92	6.01	6.18	0.00	4.39	230.2	20.3	4.391
3	UNKNOWN	6.34	6.45	6.59	0.00	5.47	266.0	25.4	5.475
4	UNKNOWN	6.92	7.08	7.37	0.00	55.82	1465.5	258.6	55.815
Total						100.00	3277.2	463.2	100.000

Chiral SFC analysis (ODH, 5-50% IPA/CO_2, 4.0 mL/min, 220 nm) indicated 82% ee for the major (*cis*) diastereomer, t_R (minor) = 6.5 min, t_R (major) = 7.1 min and 80% ee for the minor (*trans*) diastereomer, t_R (minor) = 6.0 min, t_R (major) = 5.6 min.

Table 1, Entry 2:



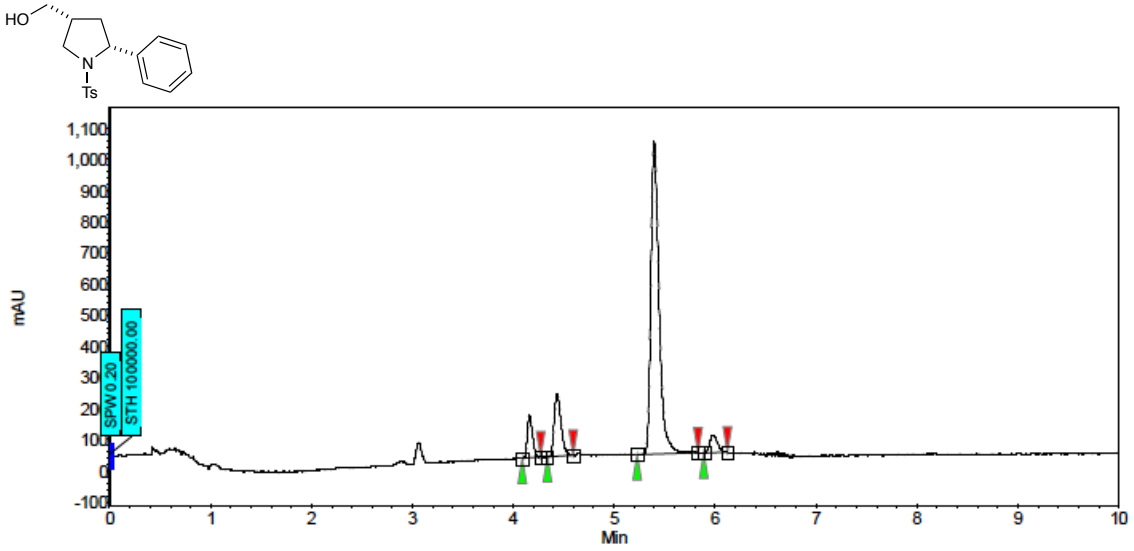
The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.90	3.98	4.09	0.00	55.73	722.9	50.0	55.727
3	UNKNOWN	4.14	4.23	4.36	0.00	3.87	45.9	3.5	3.874
4	UNKNOWN	4.70	4.79	4.93	0.00	2.48	29.3	2.2	2.482
2	UNKNOWN	5.19	5.29	5.39	0.00	37.92	428.4	34.0	37.917
Total						100.00	1226.4	89.7	100.000

Chiral SFC analysis (ODH, 5-50% IPA/CO_2, 4.0 mL/min, 220 nm) indicated 86% ee for the major (*cis*) diastereomer, t_R (minor) = 3.9 min, t_R (major) = 4.2 min and 88% ee for the major (*cis*) diastereomer t_R (minor) = 4.8 min, t_R (major) = 5.3 min.

Table 1, Entry 3:



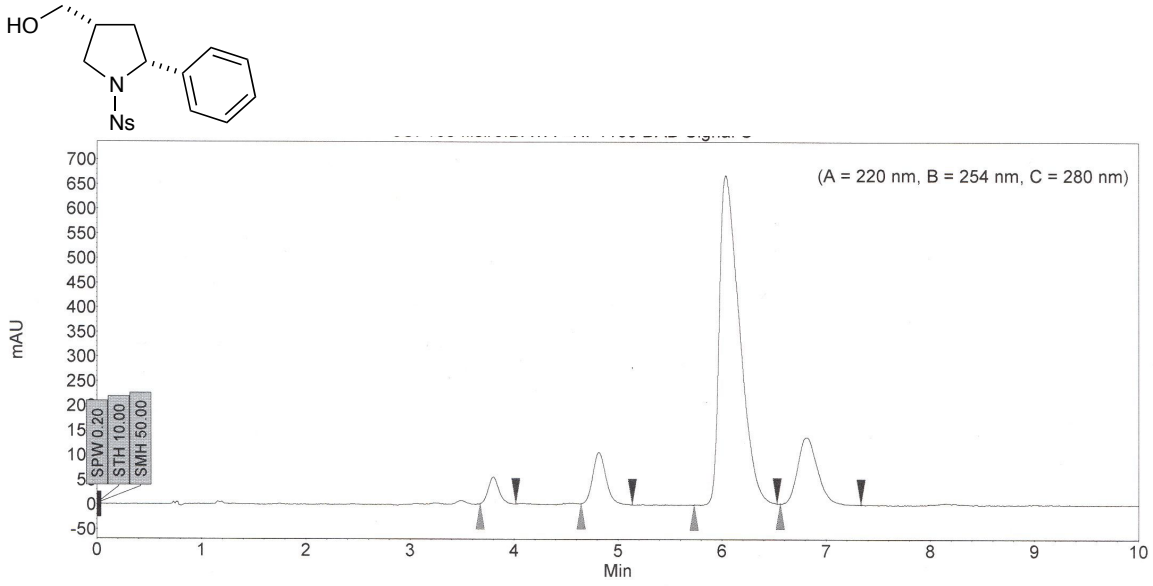
The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.09	4.16	4.27	0.00	6.34	138.4	7.9	6.340
2	UNKNOWN	4.34	4.43	4.59	0.00	12.65	200.2	15.8	12.647
3	UNKNOWN	5.23	5.40	5.83	0.00	76.98	1005.4	95.9	76.976
4	UNKNOWN	5.89	5.98	6.12	0.00	4.04	54.9	5.0	4.037
Total						100.00	1398.9	124.6	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (OJ, 5–50% MeOH/CO_2, 4.0 mL/min, 220 nm) indicated 90% ee for the major (cis) diastereomer (t_R (minor) = 6.0 min, t_R (major) = 5.4 min) and 33% ee for the minor (trans) diastereomer (t_R (minor) = 4.2 min, t_R (major) = 4.4 min).

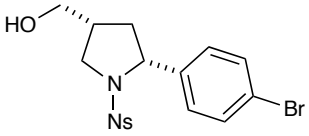
Table 1, Entry 6:

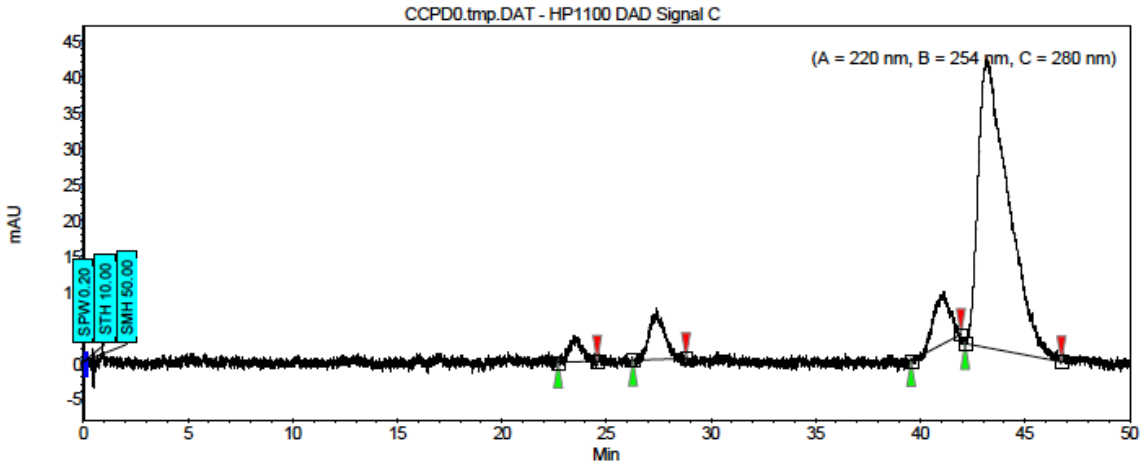


Index	Time	Width	Height	Res. HW	Selectivity	Area	Area
	[Min]	[Min]	[µV]			[µV.Min]	[%]
3	3.80	0.11	54.3	0.00	0.00	6.4	3.209
1	4.82	0.13	104.4	4.95	1.27	15.2	7.588
4	6.04	0.21	667.5	4.20	1.25	149.2	74.429
2	6.82	0.20	135.0	2.24	1.13	29.6	14.774
Total			961.2			200.4	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 20% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major (cis) diastereomer (t_R (minor) = 3.8 min, t_R (major) = 6.0 min) and 34% ee for the minor (trans) diastereomer (t_R (minor) = 4.8 min, t_R (major) = 6.8 min).

Table 2, Entry 1:

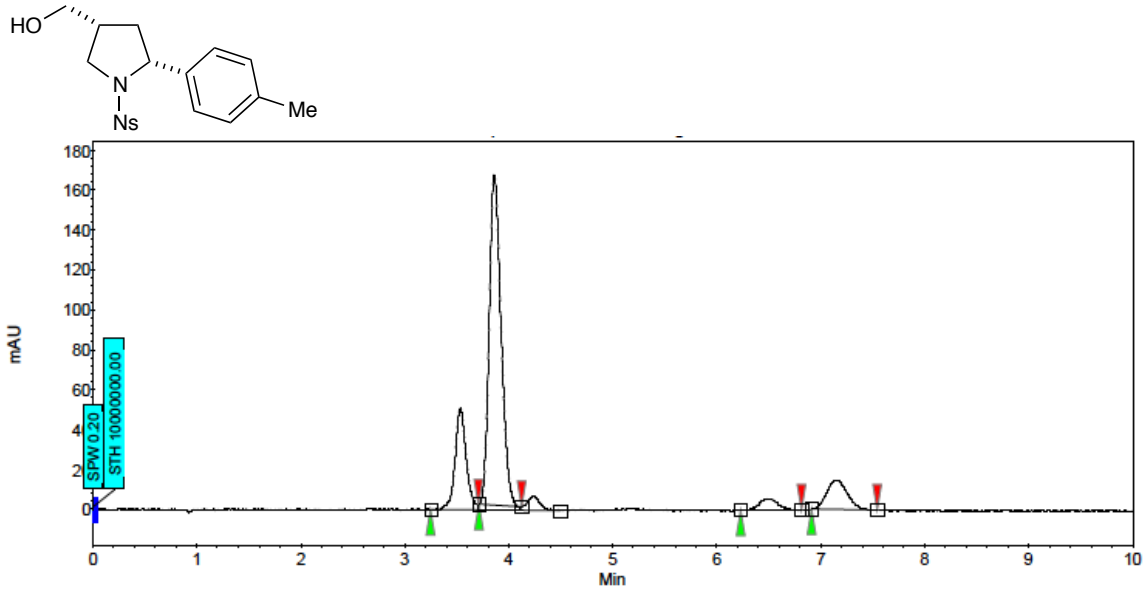




Index	Time	Width	Height	Res. HW	Selectivity	Area	Area
	[Min]	[Min]	[µV]			[µV.Min]	[%]
1	23.51	0.43	3.5	0.00	0.00	2.2	2.737
3	27.37	0.74	7.1	3.90	1.16	5.3	6.597
4	41.09	0.87	7.2	10.05	1.50	6.1	7.526
2	43.20	1.53	40.5	1.04	1.05	67.3	83.140
Total			58.2			81.0	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 10% (0.1% Et_2NH/MeOH)/CO_2, 3.0 mL/min, 280 nm) indicated 93% ee for the major (cis) diastereomer (t_R (minor) = 23.5 min, t_R (major) = 43.2 min).

Table 2, Entry 2:



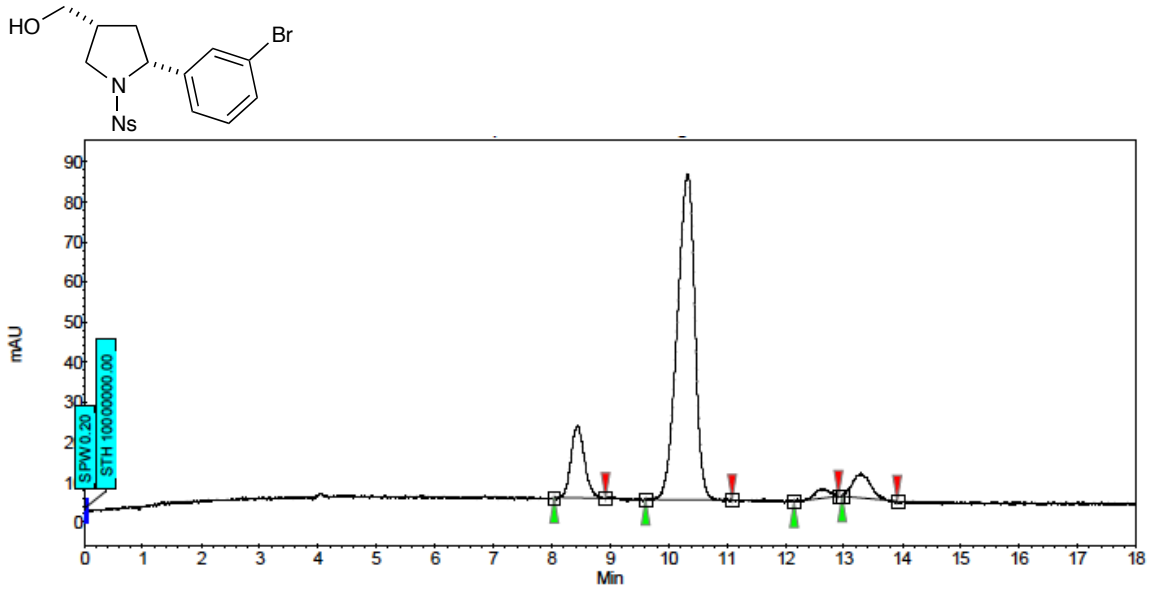
The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	3.24	3.53	3.71	0.00	19.24	50.5	6.3	19.239
3	UNKNOWN	3.71	3.86	4.12	0.00	66.97	165.5	21.9	66.967
4	UNKNOWN	6.23	6.50	6.82	0.00	3.57	5.7	1.2	3.575
1	UNKNOWN	6.91	7.14	7.54	0.00	10.22	14.8	3.3	10.219
Total						100.00	236.6	32.7	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AS-H, 20% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 91% ee for the major (cis) diastereomer (t_R (major) = 3.9 min, t_R (minor) = 6.7 min) and 30% ee for the minor (trans) diastereomer (t_R (major) = 3.5 min, t_R (minor) = 7.1 min).

Table 2, Entry 3:



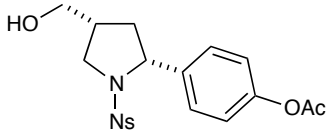
The Chromatogram Noise is 0

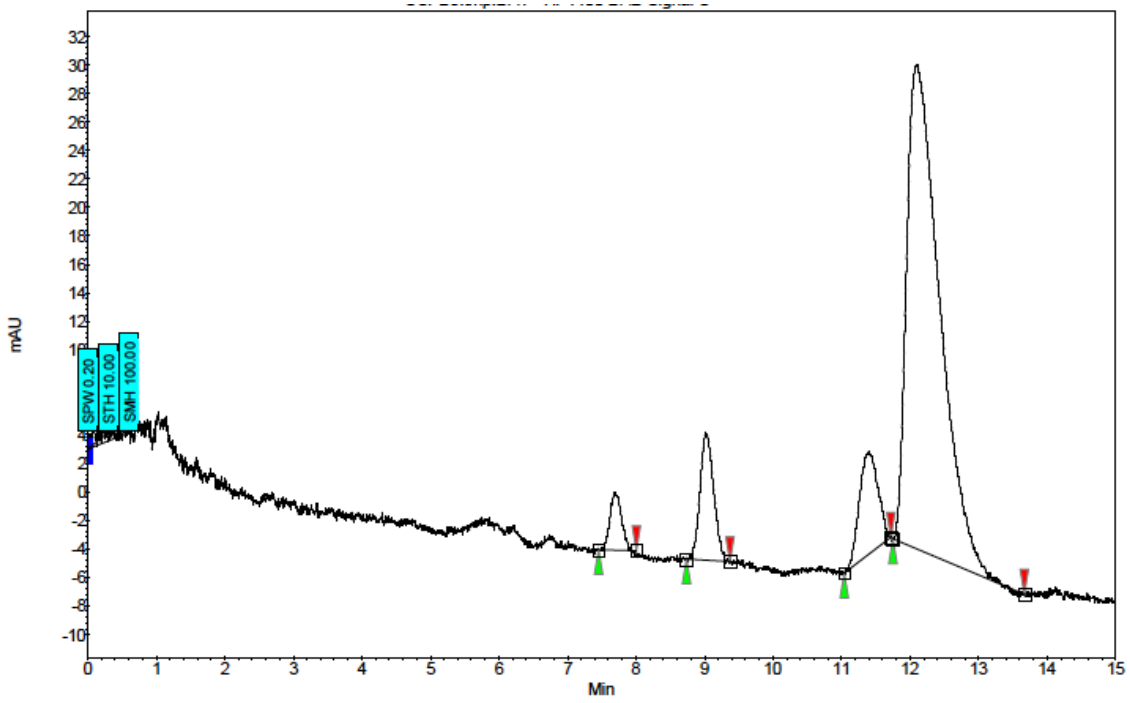
Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	8.04	8.44	8.92	0.00	13.39	18.0	4.8	13.391
2	UNKNOWN	9.61	10.33	11.09	0.00	78.68	81.5	28.3	78.682
3	UNKNOWN	12.15	12.65	12.91	0.00	1.93	2.4	0.7	1.931
4	UNKNOWN	12.97	13.29	13.91	0.00	6.00	6.1	2.2	5.996
Total						100.00	108.0	35.9	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AS-H, 10% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 93% ee for the major (cis) diastereomer (t_R (major) = 10.3 min, t_R (minor) = 12.7 min) and 33% ee for the minor (trans) diastereomer (t_R (major) = 8.4 min, t_R (minor) = 13.3 min).

Table 2, Entry 4:

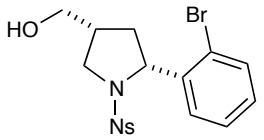


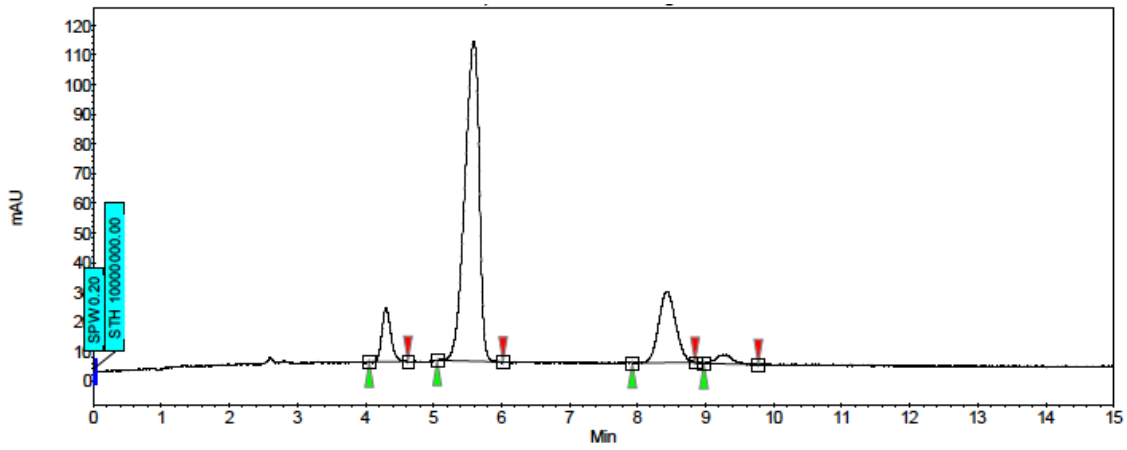


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.45	7.69	8.00	0.00	3.17	4.1	0.8	3.169
2	UNKNOWN	8.74	9.02	9.37	0.00	8.64	8.9	2.1	8.639
3	UNKNOWN	11.04	11.39	11.72	0.00	9.42	7.2	2.3	9.418
4	UNKNOWN	11.75	12.11	13.66	0.00	78.77	34.0	18.9	78.774
Total						100.00	54.3	24.0	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% EtOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major (cis) diastereomer (t_R (minor) = 7.7 min, t_R (major) = 12.1 min) and 23% ee for the minor (trans) diastereomer (t_R (minor) = 9.0 min, t_R (major) = 11.4 min).

Table 2, Entry 5:





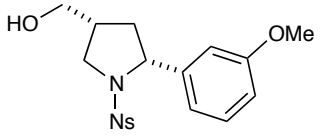
The Chromatogram Noise is 0

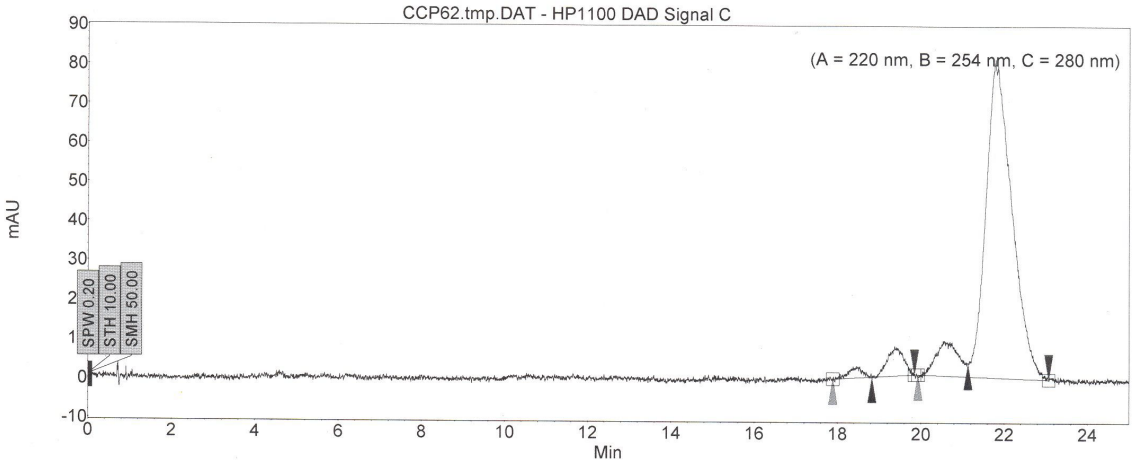
Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
3	UNKNOWN	4.06	4.31	4.62	0.00	7.27	17.9	2.7	7.267
1	UNKNOWN	5.06	5.59	6.03	0.00	71.78	107.8	26.5	71.784
4	UNKNOWN	7.93	8.43	8.85	0.00	18.50	24.0	6.8	18.498
2	UNKNOWN	8.98	9.30	9.78	0.00	2.45	3.0	0.9	2.451
Total						100.00	152.7	36.9	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AS-H, 20% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 94% ee for the major (cis) diastereomer (t_R (major) = 6.0 min, t_R (minor) = 9.7 min) and 30% ee for the minor (trans) diastereomer (t_R (minor) = 4.3 min, t_R (major) = 8.4 min).

Table 2, Entry 6:

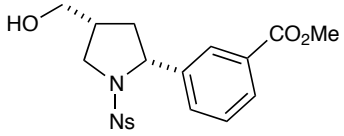


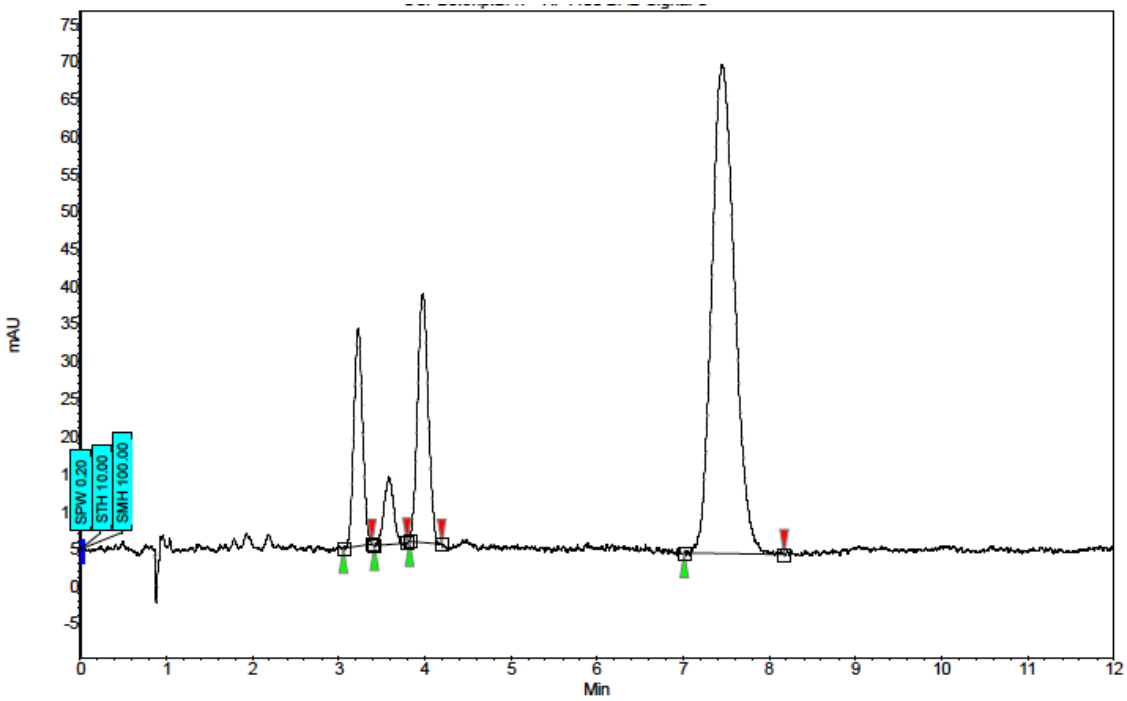


Index	Time	Width	Height	Res. HW	Selectivity	Area	Area
	[Min]	[Min]	[µV]			[µV.Min]	[%]
3	18.45	0.26	3.0	0.00	0.00	1.1	1.580
4	19.37	0.42	7.6	1.59	1.05	3.3	4.842
1	20.53	0.64	8.9	1.29	1.06	5.6	8.175
2	21.78	0.67	80.9	1.13	1.06	58.5	85.403
Total			100.5			68.5	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 10% (0.1% Et_2NH/MeOH)/CO_2, 3.0 mL/min, 300 nm) indicated 89% ee for the major (cis) diastereomer (t_R (minor) = 18.5 min, t_R (major) = 21.8 min) and 41% ee for the minor (trans) diastereomer (t_R (minor) = 19.4 min, t_R (major) = 20.5 min).

Table 2, Entry 7:

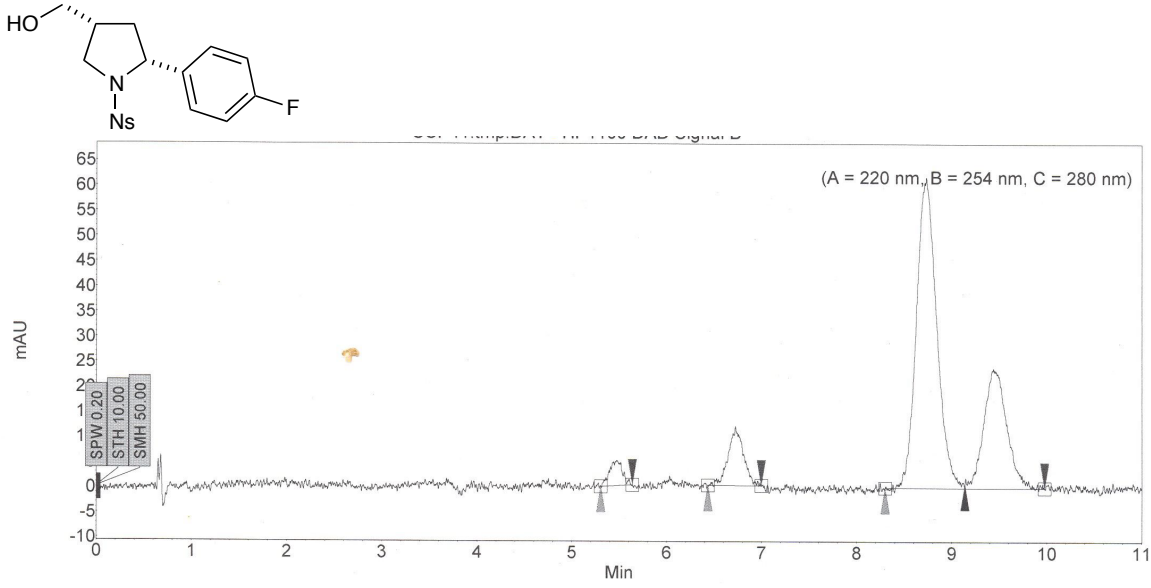




Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
3	UNKNOWN	3.05	3.23	3.39	0.00	11.60	29.1	3.4	11.604
1	UNKNOWN	3.42	3.58	3.79	0.00	3.89	9.0	1.1	3.889
4	UNKNOWN	3.82	3.98	4.19	0.00	16.05	33.3	4.7	16.049
2	UNKNOWN	7.01	7.45	8.17	0.00	68.46	65.2	19.9	68.457
Total						100.00	136.5	29.1	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (OD-H, 35% iPrOH/CO_2, 3.0 mL/min, 300 nm) indicated 89% ee for the major diastereomer (t_R (minor) = 3.6 min, t_R (major) = 7.5 min) and 20% ee for the minor diastereomer (t_R (minor) = 3.2 min, t_R (major) = 4.0 min).

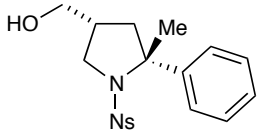
Table 2, Entry 8:

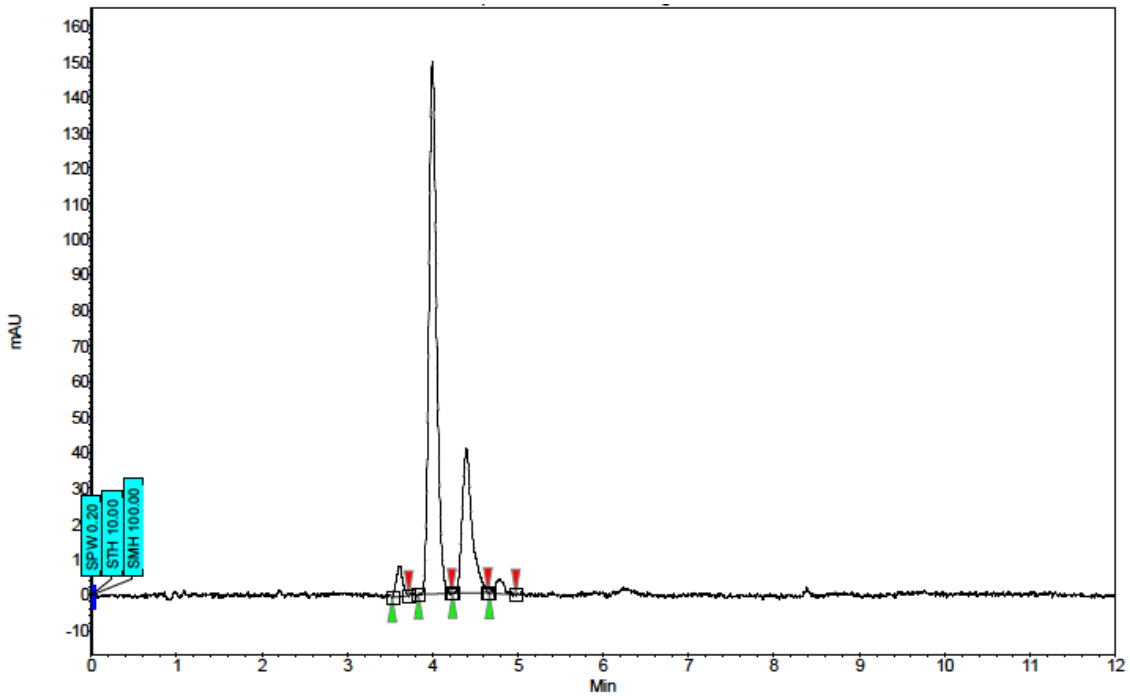


Index	Time	Width	Height	Res. HW	Selectivity	Area	Area
	[Min]	[Min]	[µV]			[µV.Min]	[%]
1	5.48	0.15	4.9	0.00	0.00	0.8	3.151
2	6.72	0.17	11.8	4.64	1.23	2.2	8.735
3	8.73	0.23	61.8	5.96	1.30	15.2	61.245
4	9.44	0.25	23.9	1.73	1.08	6.7	26.869
Total			102.4			24.8	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 15% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 91% ee for the major (cis) diastereomer (t_R (minor) = 3.0 min, t_R (major) = 4.8 min) and 53% ee for the minor (trans) diastereomer (t_R (minor) = 3.7 min, t_R (major) = 5.2 min).

Table 2, Entry 9:

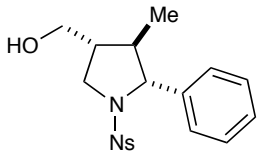


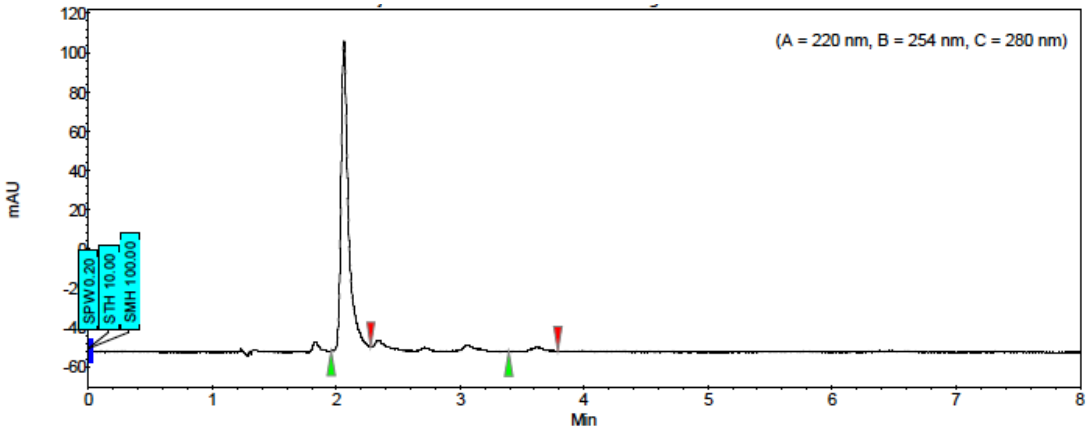


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.52	3.61	3.72	0.00	3.38	8.5	0.8	3.379
2	UNKNOWN	3.83	4.00	4.22	0.00	70.14	149.7	15.8	70.139
3	UNKNOWN	4.24	4.40	4.65	0.00	24.33	40.5	5.5	24.326
4	UNKNOWN	4.66	4.78	4.97	0.00	2.16	4.3	0.5	2.157
Total						100.00	203.0	22.5	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 25% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major (cis) diastereomer (t_R (minor) = 3.6 min, t_R (major) = 4.0 min) and 40% ee for the minor (trans) diastereomer (t_R (minor) = 4.4 min, t_R (major) = 4.8 min).

Table 2, Entry 10:

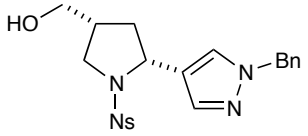


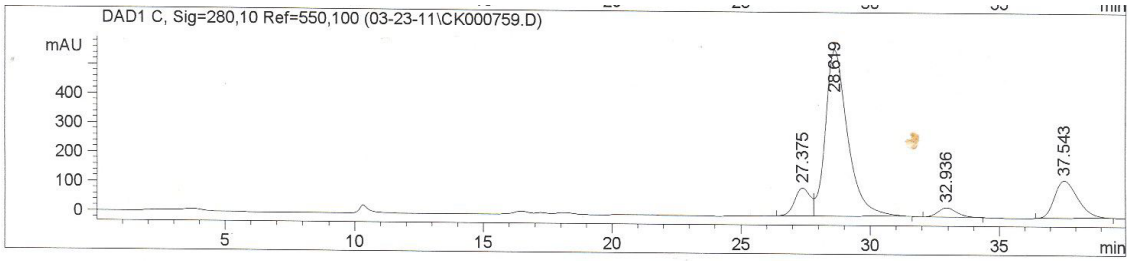


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	1.96	2.06	2.28	0.00	98.27	158.1	11.1	98.269
2	UNKNOWN	3.39	3.62	3.79	0.00	1.73	2.1	0.2	1.731
Total						100.00	160.2	11.3	100.000

Chiral SFC analysis of the corresponding alcohol (AD-H, 40% (0.1% Et_2NH/EtOH)/CO_2, 3.0 mL/min, 300 nm) indicated 96% ee (t_R (major) = 2.1 min, t_R (minor) = 3.6 min).

Table 3, Entry 1:

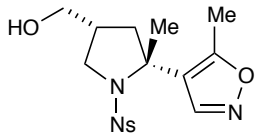


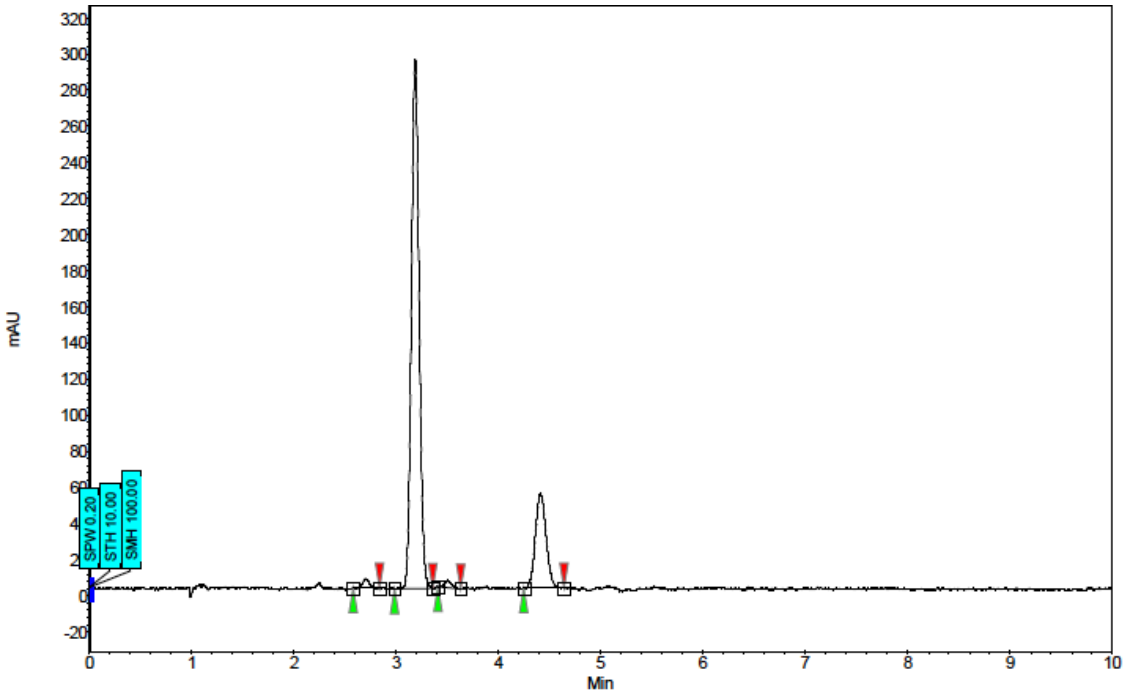


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.375	BV	0.6331	4055.84448	95.95551	8.4515
2	28.619	VB	0.8933	3.39758e4	568.43958	70.7982
3	32.936	PB	0.7247	1672.52490	32.48334	3.4852
4	37.543	BB	0.9528	8285.50977	128.41002	17.2652
Totals :				4.79897e4	825.28844	

Chiral HPLC analysis of the corresponding mixture of alcohols (AD-H to OD-H, 0.1% Et_2NH/EtOH, 0.5 mL/min, 280 nm) indicated 91% ee for the major (cis) diastereomer (t_R (major) = 28.6 min, t_R (minor) = 32.9 min) and 35% ee for the minor (trans) diastereomer (t_R (minor) = 27.4 min, t_R (major) = 37.5 min).

Table 3, Entry 2:

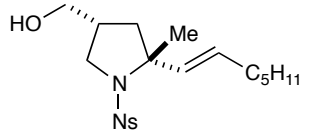


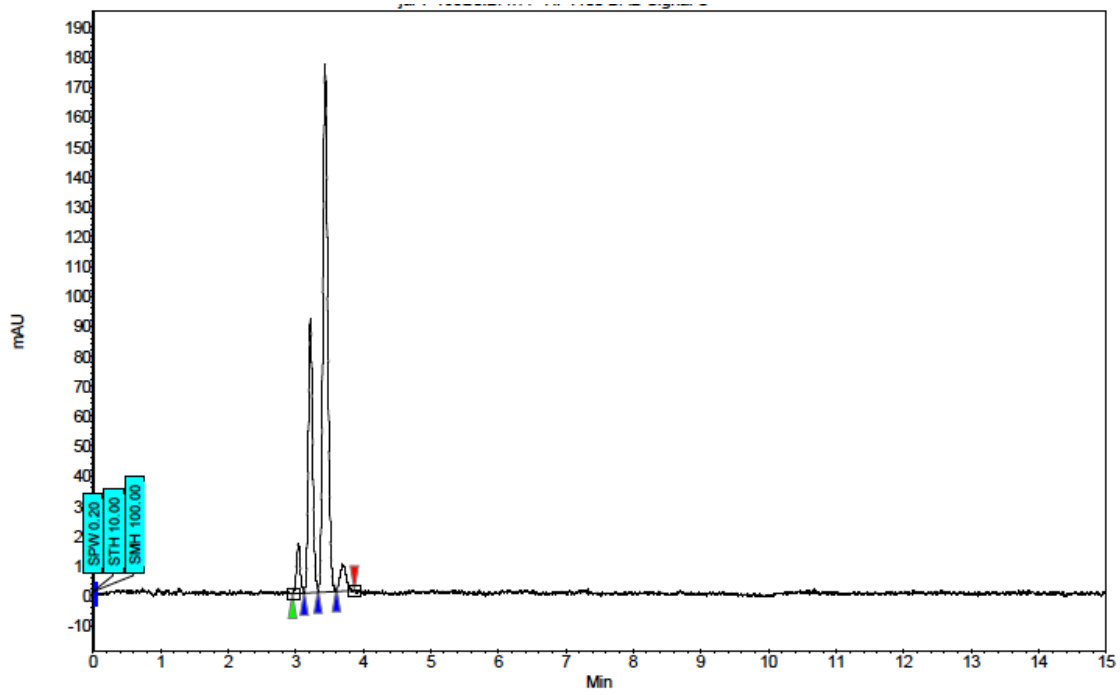


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.58	2.70	2.84	0.00	1.10	5.3	0.4	1.095
2	UNKNOWN	2.98	3.19	3.36	0.00	78.37	293.1	25.5	78.369
3	UNKNOWN	3.41	3.50	3.63	0.00	0.91	4.1	0.3	0.909
4	UNKNOWN	4.25	4.41	4.64	0.00	19.63	52.4	6.4	19.627
Total						100.00	354.9	32.6	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IC, 40% iPrOH/CO_2, 3.0 mL/min, 300 nm) indicated 95% ee for the major diastereomer (t_R (minor) = 2.7 min, t_R (major) = 3.2 min) and 92% ee for the minor diastereomer (t_R (minor) = 3.5 min, t_R (major) = 4.7 min).

Table 3, Entry 3:

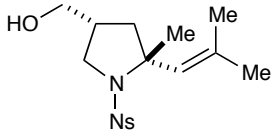


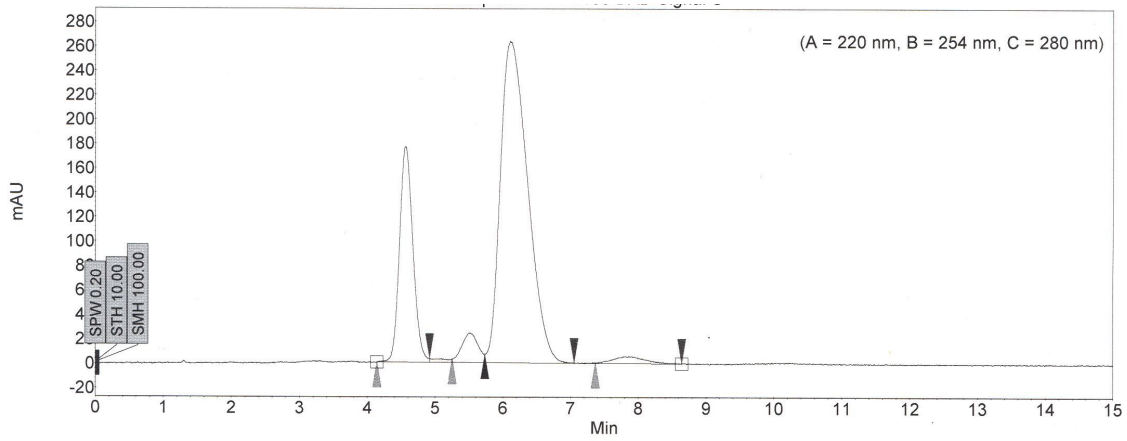


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.95	3.04	3.13	0.00	4.80	16.6	1.1	4.804
2	UNKNOWN	3.13	3.22	3.33	0.00	28.77	91.7	6.7	28.774
3	UNKNOWN	3.33	3.44	3.60	0.00	62.46	176.6	14.5	62.455
4	UNKNOWN	3.60	3.69	3.87	0.00	3.97	8.9	0.9	3.967
Total						100.00	293.8	23.2	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major diastereomer (t_R (minor) = 3.0 min, t_R (major) = 3.4 min) and 85% ee for the minor diastereomer (t_R (major) = 3.2 min, t_R (minor) = 3.7 min).

Table 3, Entry 4:

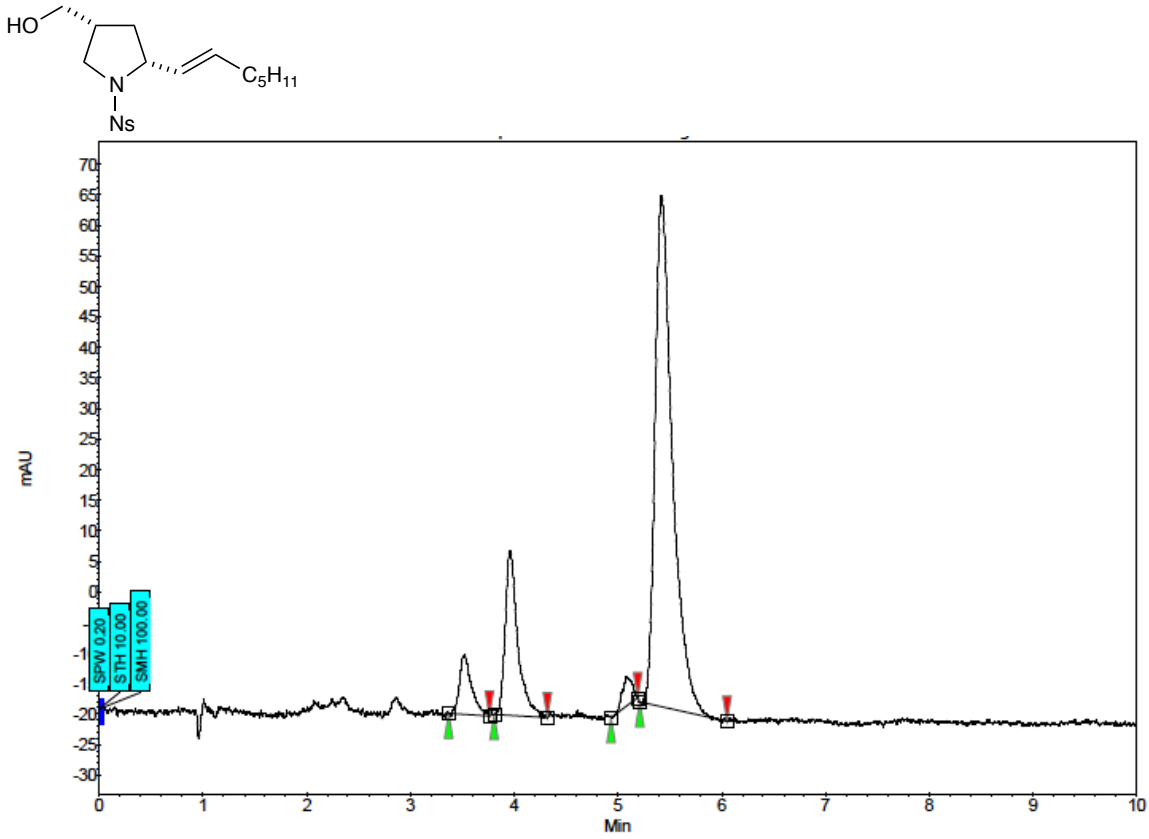




Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.14	4.57	4.92	0.00	23.31	176.6	40.5	23.313
2	UNKNOWN	5.25	5.52	5.73	0.00	3.89	24.3	6.8	3.887
3	UNKNOWN	5.73	6.11	7.05	0.00	70.99	263.7	123.4	70.995
4	UNKNOWN	7.36	7.86	8.64	0.00	1.80	5.9	3.1	1.804
Total						100.00	470.5	173.8	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AY-H, 6% MeOH/CO_2, 3.0 mL/min, 280 nm) indicated 89% ee for the major diastereomer (t_R (minor) = 5.3 min, t_R (major) = 6.1 min) and 86% ee for the minor diastereomer (t_R (major) = 4.1 min, t_R (minor) = 7.4 min).

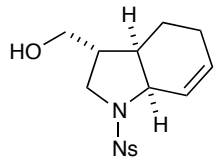
Table 3, Entry 5:

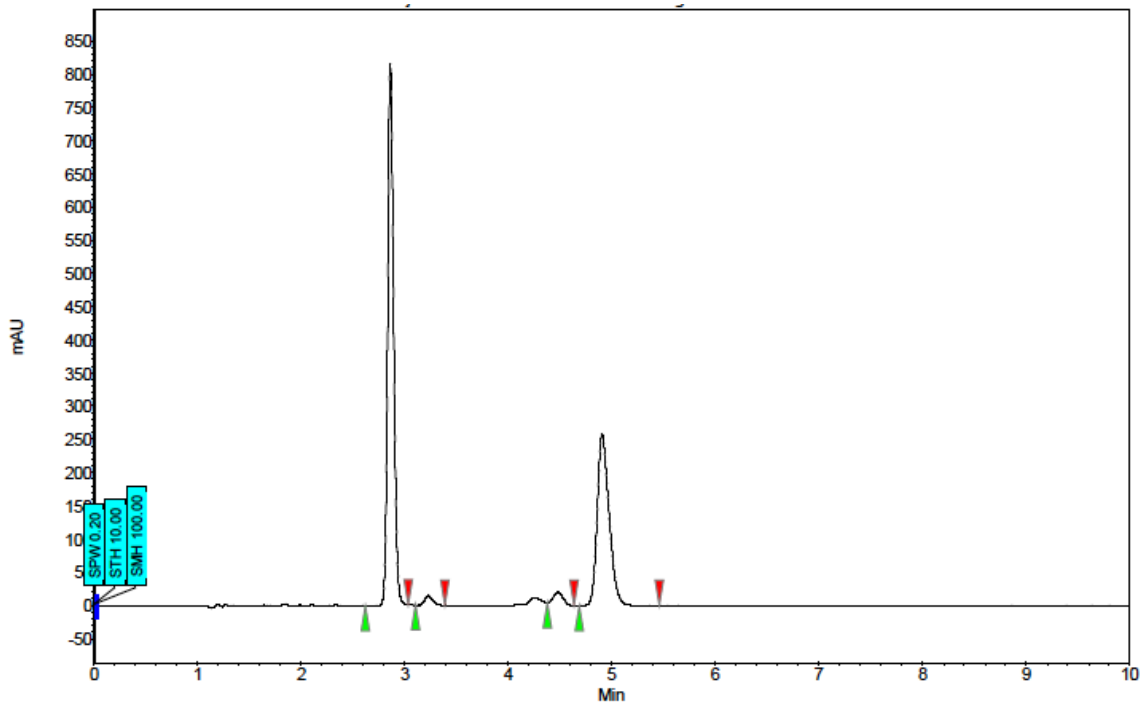


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.37	3.52	3.76	0.00	5.86	9.8	1.3	5.862
2	UNKNOWN	3.81	3.97	4.32	0.00	17.38	26.9	3.8	17.384
3	UNKNOWN	4.93	5.08	5.19	0.00	2.33	4.8	0.5	2.329
4	UNKNOWN	5.21	5.42	6.05	0.00	74.42	83.6	16.2	74.424
Total						100.00	125.1	21.7	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (AD-H, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 87% ee for the major diastereomer (t_R (minor) = 3.5 min, t_R (major) = 5.4 min) and 55% ee for the minor diastereomer (t_R (major) = 4.0 min, t_R (minor) = 5.1 min).

Table 3, Entry 6:

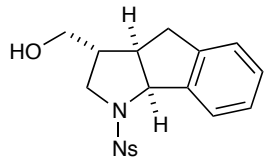


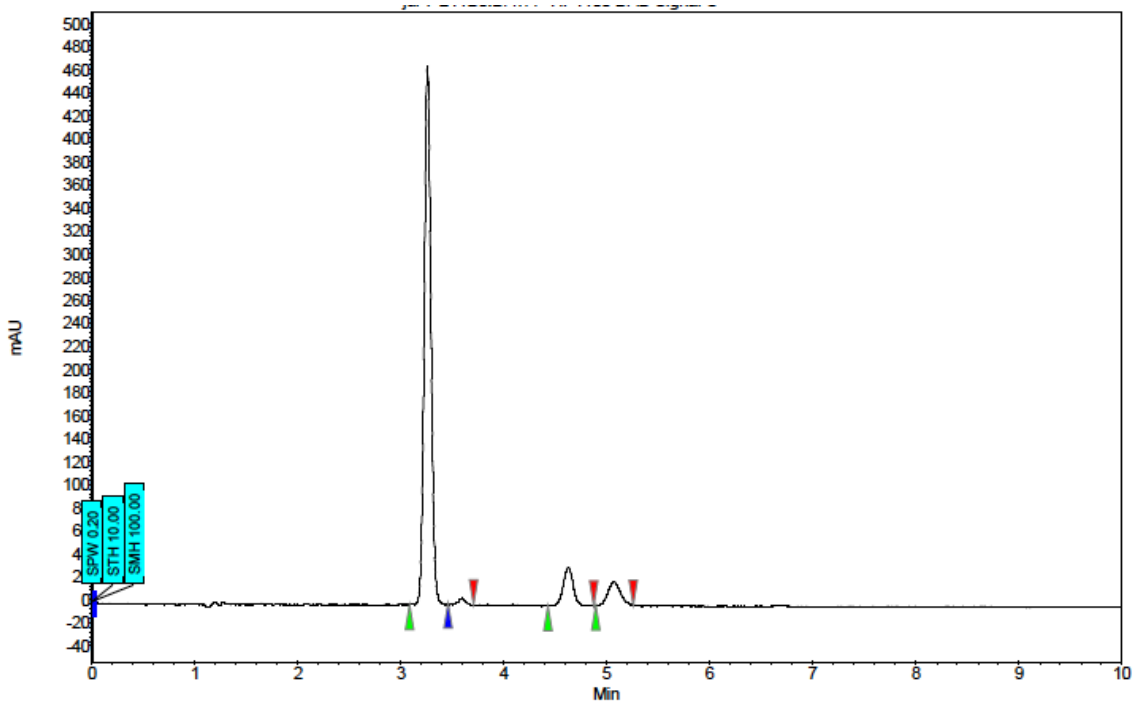


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
3	UNKNOWN	2.62	2.86	3.03	0.00	59.11	815.3	53.7	59.106
2	UNKNOWN	3.11	3.23	3.39	0.00	1.35	14.6	1.2	1.345
4	UNKNOWN	4.38	4.49	4.63	0.00	1.99	18.0	1.8	1.990
1	UNKNOWN	4.69	4.91	5.46	0.00	37.56	258.5	34.1	37.559
Total						100.00	1106.4	90.8	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 30% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 92% ee for the major diastereomer (t_R (minor) = 2.9 min, t_R (major) = 4.7 min) and 94% ee for the minor diastereomer (t_R (major) = 3.2 min, t_R (minor) = 4.9 min).

Equation 2:

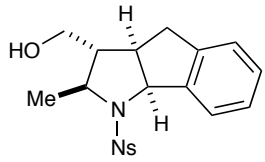


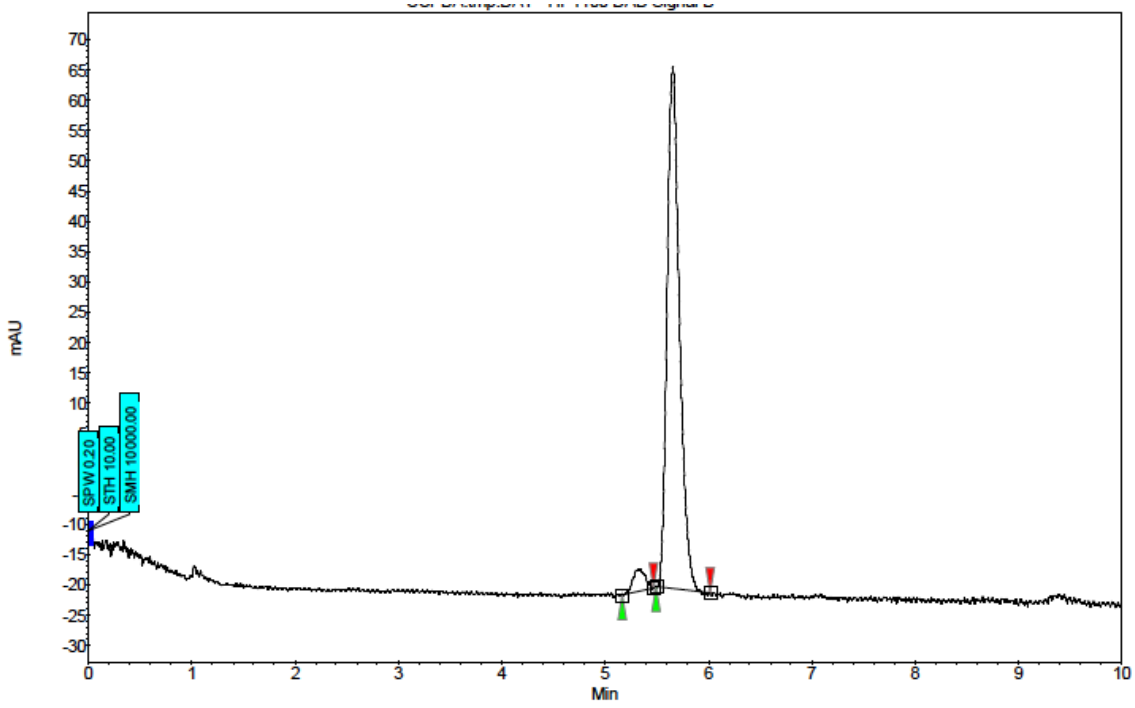


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	3.09	3.26	3.46	0.00	83.16	467.1	34.7	83.157
3	UNKNOWN	3.46	3.60	3.71	0.00	1.15	5.8	0.5	1.145
4	UNKNOWN	4.43	4.62	4.87	0.00	8.95	33.4	3.7	8.945
1	UNKNOWN	4.89	5.06	5.25	0.00	6.75	20.2	2.8	6.752
Total						100.00	526.5	41.7	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 30% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 85% ee for the major diastereomer (t_R (major) = 3.3 min, t_R (minor) = 5.3 min) and 80% ee for the minor diastereomer (t_R (major) = 3.6 min, t_R (minor) = 4.6 min).

Equation 3:

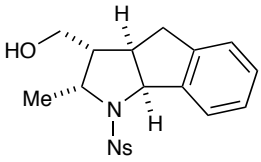


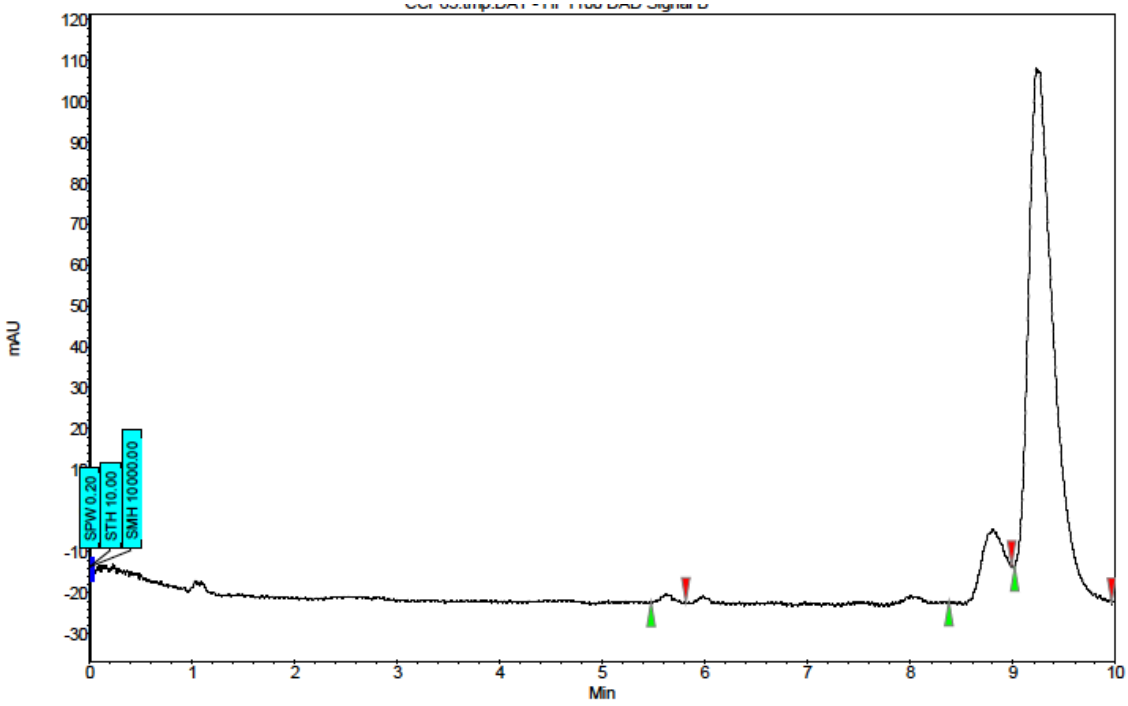


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	5.17	5.33	5.47	0.00	4.10	3.7	0.5	4.103
1	UNKNOWN	5.49	5.66	6.02	0.00	95.90	86.2	12.0	95.897
Total						100.00	89.9	12.5	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 99% ee for the major diastereomer (t_R (major) = 5.7 min, t_R (minor) = 8.8 min) and 99% ee for the minor diastereomer (t_R (major) = 5.3 min, t_R (minor) = 9.2 min).

Equation 4:





Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
3	UNKNOWN	5.47	5.61	5.81	0.00	0.68	2.1	0.2	0.682
1	UNKNOWN	8.38	8.80	8.99	0.00	5.05	11.6	1.8	5.051
2	UNKNOWN	9.02	9.23	9.96	0.00	94.27	123.7	33.4	94.268
Total						100.00	137.4	35.4	100.000

Chiral SFC analysis of the corresponding mixture of alcohols (IA, 20% MeOH/CO_2, 3.0 mL/min, 300 nm) indicated 99% ee for the major diastereomer (t_R (major) = 9.2 min, t_R (minor) = 5.3 min).. and 99% ee for the minor diastereomer (t_R (major) = 8.8 min, t_R (minor) = 5.7 min).