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Supporting Information

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Reactions of Iminium Ions with Michael Acceptors Through a Morita-Baylis-Hillman Type Reaction. Enantiocontrol and Applications in Synthesis

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Experimental procedures, compound characterization, NMR spectra, Chiral HPLC traces, X-ray data and Low-temperature NMR experiment

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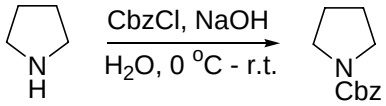
General Procedures: Flash chromatography was performed on silica gel (Merck Silica Gel 60 F_{254} 230-400 mesh). TLC was carried out on aluminium-backed plates (0.2 mm, 60 F_{254}), which were developed using standard visualising agents: UV fluorescence (254 nm), phosphomolybdic acid/Δ and permanganate/Δ. ^{1}H NMR spectra were recorded at 400 MHz on a Delta GX/400 or Eclipse ECP/400 or at 300 MHz on an Eclipse ECP/300 instrument at room temperature unless otherwise specified. Chemical shifts (δ_H) are quoted in parts per million (ppm) and referenced to TMS; coupling constants are quoted in Hz. ^{13}C NMR spectra were recorded at 100 MHz on a Delta GX/400 or Eclipse ECP/400 instrument or at 75 MHz on an Eclipse ECP/300 instrument at room temperature. Chemical shifts (δ_C) are quoted in ppm and referenced to the appropriate residual solvent peak (77.0 ppm for $CDCl_3$ and 39.5 ppm for DMSO-d_6); coupling constants are quoted in Hz. Infrared spectra were recorded using a Perkin Elmer (Spectrum One) FT-IR spectrometer. High resolution mass spectra were obtained using the following instruments: VG Autospec (CI) and a Bruker Daltronics Apex 4e 7.0T FT-MS (ESI). Optical rotations were measured using a Perkin-Elmer 241 MC polarimeter. All chemicals were purchased from Aldrich, Fluka, Lancaster or Acros and used as delivered.

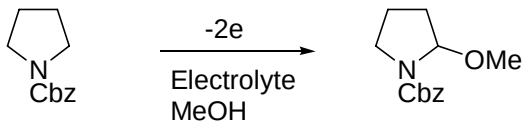
Preparation of aminals:

Benzyl 1-pyrrolidinecarboxylate[1]



To a stirred solution of pyrrolidine (12.9 ml, 150 mmol) and sodium hydroxide (6.00 g, 150 mmol) in water (50 ml) at 0 °C was added dropwise benzyloxycarbonyl chloride (20.8 ml, 150 mmol). The reaction mixture was warmed to room temperature and stirred for 1½ hours. The organics were extracted with CH_2Cl_2 and dried with Na_2SO_4. The solvent was removed and the residue was distilled (~130 °C at 1-2 mm Hg) to yield the desired carbamate as a clear colourless oil (28.1 g, 140 mmol, 94% yield). IR ν_{max} (neat) / cm^{-1} 1697; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.86 (4H, m, $NCH_2CH_2CH_2$), 3.38 (2H, t, J = 6.2 Hz, NCH_2), 3.42 (2H, t, J = 6.2 Hz, NCH_2), 5.14 (2H, s, CH_2Ph), 7.27-7.44 (5H, m, Ar.); [lit.[2] δ = 1.81 (4H, m), 3.33 (4H, m), 5.10 (2H, s), 7.16 (5H, s)].

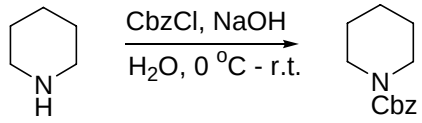
Benzyl 2-methoxy-1-pyrrolidinecarboxylate 1[1]



A solution of benzyl 1-pyrrolidinecarboxylate (12.1 g, 58.9 mmol) and tetraethylammonium *p*-toluenesulfonate (0.49 g, 1.6 mmol) in anhydrous methanol (50

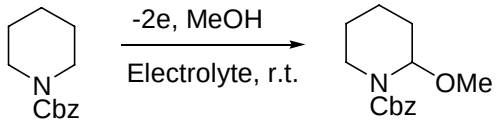
ml) was added to an undivided jacketed cell equipped with two graphite anodes and two graphite cathodes, an exit tube and a magnetic stirrer. Electrical current (~ 0.5 A) was passed through the solution until all starting material (~ 15 hours) was consumed (as determined by GC-MS analysis of the mixture at regular intervals). The solvent was then removed *in vacuo*. The residue was then dissolved in CH_2Cl_2 (150 ml) and washed with brine (50 ml). The brine wash was then re-extracted with CH_2Cl_2 (2 × 50 ml). The combined CH_2Cl_2 layers were then dried with Na_2SO_4 and concentrated *in vacuo*. The residue was then purified by silica gel flash chromatography with CH_2Cl_2 as eluent to give the desired aminal as a clear pale yellow oil (10.8 g, 46.0 mmol, 78 % yield). IR ν_{max} (neat) / cm^{-1} 1700; ^1H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ = 1.70-2.15 (4H, m, $NCH_2CH_2CH_2$), 3.20-3.62 (5H, m, NCH_2 and OCH_3), 5.05-5.30 (3H, m, NCH(OMe) and CH_2Ph), 7.27-7.45 (5H, m, Ar.); [lit.[3] δ = 1.72-2.08 (4H, m), 3.25-3.54 (5H, m), 5.15-5.23 (3H, m), 7.26-7.38 (5H, m)].

Benzyl 1-piperidinecarboxylate



[Using procedure of Shono[1]] Piperidine (13.2 g, 155 mmol) was added to an aqueous solution of NaOH (6.00 g, 150 mmol, and 50 ml of water). At 0 °C, benzyl chloroformate (147 mmol, 20.8 ml) was added over 15 minutes. The reaction was then warmed to room temperature and was stirred for 1.5 h. The mixture was then extracted with CH_2Cl_2 (2 × 200 ml), dried over $MgSO_4$ and evaporated *in vacuo* to give the required carbamate as a yellow oil (24.7 g, 113 mmol, 73% yield). IR ν_{max} (neat) / cm^{-1} 1692; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.42-1.62 (6H, m, $NCH_2CH_2CH_2CH_2$), 3.44 (4H, dd, J = 6.0, 5.0 Hz, CH_2NCH_2), 5.12 (2H, s, CH_2Ph), 7.27-7.40 (5H, m, Ar). [lit.[4] δ = 1.54 (4H), 1.59 (2H), 3.45 (4H, t, J = 5.5 Hz), 5.13 (2H, s), 7.29-7.39 (5H)].

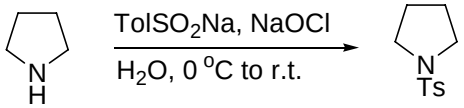
Benzyl 2-methoxy-1-piperidinecarboxylate



[Using the procedure of Shono[1]].A solution of benzyl 1-piperidinecarboxylate (11.5 g, 52.5 mmol), and tetraethylammonium *p*-toluenesulfonate (490 mg, 1.62 mmol) in methanol (50 ml) was added to an undivided jacketed cell equipped with two graphite anodes and two graphite cathodes, an exit tube and a magnetic stirrer. Electrical current (~0.2 A) was passed through the solution until all starting material was consumed (as determined by GC analysis of the mixture at regular intervals). The solvent was then removed *in vacuo*. The residue was the purified by flash chromatography (eluent: CH_2Cl_2/NEt_3; 1: 0.01) to give the required aminal as a yellow oil (9.79 g, 39.3 mmol,

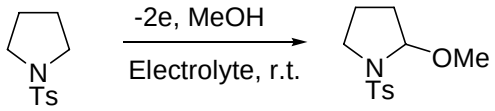
75% yield). IR ν_{max} (neat) / cm^{-1} 1697; ^1H NMR (400 MHz, $CDCl_3$, 1:1 mixture of rotamers) δ = 1.30-2.05 (6H, m, NCH(OMe)$CH_2CH_2CH_2$), 2.87-3.06 (1H, m, NCH_2CH_2), 3.17 (1.5H, br. s, OCH_3), 3.25 (1.5H, br. s, OCH_3), 3.57-3.65 (1H, m, NCH_2CH_2), 5.05-5.20 (2H, m, CH_2Ph), 5.33 (0.5H, br. s, NCH(OMe)), 5.43 (0.5H, br. s, NCH(OMe)), 7.26-7.40 (5H, m, Ar). [lit.[5] 1.25-2.03 (6H, m), 2.98 (1H, q, J = 14.7 Hz), 3.18 (1.5H, s), 3.25 (1.5H, s), 3.98 (1H, t, J = 14.7 Hz), 5.16 (2H, m), 5.34 (0.5H, s), 5.43 (0.5H, s), 7.26-7.60 (5H, m)].

1-(phenylsulfonyl)pyrrolidine[6]



Pyrrolidine (3.33 ml, 40.0 mmol) and sodium *p*-toluenesulfinate (10.0 g, 56.1 mmol) were dissolved in water (60 ml). At 0 °C, a standardised solution (12% w/v) of sodium hypochlorite (30.8 ml 50.0 mmol) was added dropwise over 30 min. The resulting slurry was stirred overnight at room temperature. The suspension was then filtered and washed with water. The resulting white solid was dried *in vacuo* to give the desired sulfonamide (9.61 g, 42.7 mmol, 76% yield). IR ν_{max} (neat) / cm^{-1} 1332, 1159; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.75 (4H, m, $NCH_2CH_2CH_2$), 2.43 (3H, s, Ar-CH_3), 3.23 (4H, m, CH_2N(Ts)CH_2), 7.32 (2H, d, J = 8.5 Hz, Ar), 7.72 (2H, d, J = 8.5 Hz, Ar); [lit.[7] 1.75 (4H, m), 2.43 (3H, s), 3.23 (4H, m), 7.32 (2H, d, J = 8.1 Hz), 7.72 (2H, d, J = 8.1 Hz)].^{13}C NMR (400 MHz, $CDCl_3$) δ = 21.4, 25.1, 47.8, 127.5, 129.5, 134.2, 143.2.

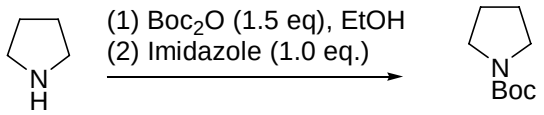
2-methoxy-1-(phenylsulfonyl)pyrrolidine



[Using the procedure of Shono[1]] A solution of 1-(phenylsulfonyl)pyrrolidine (4.00 g, 17.7 mmol), and tetraethylammonium *p*-toluenesulfonate (0.30 g, 1.00 mmol) in 1:1 methanol/acetonitrile (50 ml) was added to an undivided jacketed cell equipped with two graphite anodes and two graphite cathodes, an exit tube and a magnetic stirrer. Electrical current (~0.2 A) was passed through the solution until all starting material was consumed (as determined by GC analysis of the mixture at regular intervals). The solvent was then removed *in vacuo*. The residue was the purified by flash chromatography (eluent: 4:1; EtOAc: pet. ether) to give the required aminal as a clear oil (3.80 g, 14.9 mmol, 85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 1.38 (1H, dddd, J = 13.0, 12.5, 7.5, 5.0 Hz, NCH(OMe)CH_2), 1.76 (1H, ddddd, J = 15.0, 8.0, 7.5, 4.4, 2.5 Hz, NCH(OMe)CH_2CH_2), 1.86 (1H, br. dd, J = 13.0, 7.0 Hz, NCH(OMe)CH_2CH_2), 2.02 (1H, dddd, J = 15.0, 12.5, 9.0, 7.0 Hz, NCH(OMe)CH_2CH_2), 2.42 (3H, s, Ar-CH_3), 3.13 (1H, ddd, J = 19.5, 9.0, 8.0 Hz, NCH_2CH_2), 3.38-3.45 (4H, m, NCH_2CH_2 and NCH(OCH_3)), 5.10 (1H, d, J = 5.0 Hz, NCH(OMe)), 7.31 (2H, d, J = 8.5 Hz, Ar), 7.72 (2H, d, J = 8.5 Hz, Ar); ^{13}C NMR (400

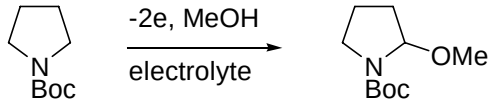
MHz, $CDCl_3$) δ = 21.4, 23.1, 32.5, 47.2, 55.1, 91.6, 127.3, 129.6, 136.0, 143.3. [lit.[8] δ = 21.5, 23.1, 32.6, 47.3, 55.3, 91.7, 127.4, 129.7, 135.9, 143.5].

t-Butyl 1-pyrrolidinecarboxylate[9]



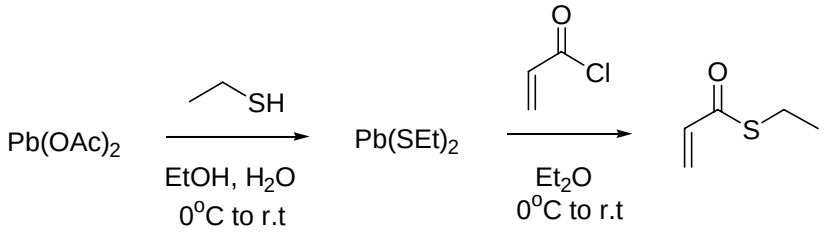
Boc_2O (23.0 g, 105 mmol) was added slowly to a solution of pyrrolidine (5.00 g, 70.4 mmol) in EtOH (200 ml) at room temperature. After 15 minutes, imidazole (4.80 g, 70.4 mmol) was added and the resulting solution was allowed to stir for 15 minutes. $CHCl_3$ (100 ml) was added and the volatiles removed *in vacuo*. The resulting residue was taken up in CH_2Cl_2 (200 ml) and washed with 1% aq. HCl (2 × 100ml). The organic layer was then dried over $MgSO_4$ and the volatiles removed *in vacuo* to give the protected pyrrolidine as a viscous oil (11.4 g, 66.9 mmol, 95% yield). IR ν_{max} (neat) / cm^{-1} 1691; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.46 (9H, s, *t*-Bu), 1.83 (4H, m, CH_2CH_2), 3.31 (4H, m, CH_2N(Boc)CH_2). [lit.[10] 1.46 (9H, s), 1.84 (4H, m), 3.30 (4H, m)].

t-Butyl 2-methoxy-1-pyrrolidinecarboxylate



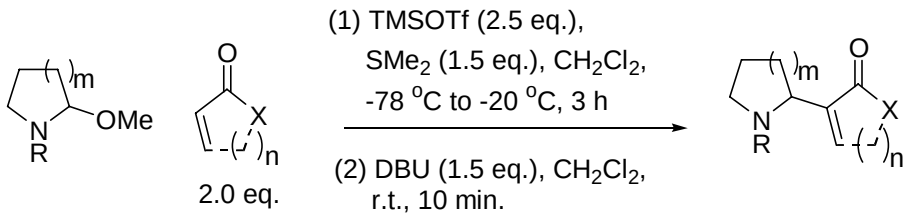
[Using the procedure of Shono[1]] A solution of *t*-butyl 1-pyrrolidinecarboxylate (6.81 g, 39.8 mmol), and tetraethylammonium *p*-toluenesulfonate (490 mg, 1.62 mmol) in methanol (50 ml) was added to an undivided jacketed cell equipped with two graphite anodes and two graphite cathodes, an exit tube and a magnetic stirrer. Electrical current (~0.2 A) was passed through the solution until all starting material was consumed (as determined by GC analysis of the mixture at regular intervals). The solvent was then removed *in vacuo*. The residue was by flash chromatography (eluent: CH_2Cl_2) to give the required aminal as a clear oil (5.59 g, 27.8 mmol, 70% yield). IR ν_{max} (neat) / cm^{-1} 1698; ^1H NMR (400 MHz, $CDCl_3$, 1:1 mixture of rotamers) δ = 1.47 (9H, br. s, *t*-Bu), 1.65-2.10 (4H, m, $NCH_2CH_2CH_2$), 3.20-3.48 (5H, m, NCH_2 and OCH_3), 5.05 (0.5H, br. s, NCH(OMe)), 5.17 (0.5H, br. s, NCH(OMe)). [lit.[11] 1.41 (9H, s), 1.67-2.16 (4H, m), 3.19-3.51 (2H, m), 3.35 (3H, br. s), 5.13 (1H, br. d, *J* = 22 Hz)].

Preparation of *S*-ethyl 2-propenethioate[12]



Lead (II) acetate (63.1 g, 0.16 mol) was dissolved in ethanol (125 ml) and water (175 ml). To this a cooled (0 °C) solution of ethanethiol (23.8 ml, 0.32 mol) in ethanol (75 ml) was added dropwise over 30 minutes. The resulting suspension was then allowed to stir for two hours and the yellow solids were collected by filtration and washed sequentially with water, ethanol and diethyl ether to provide lead (II) ethyl sulfide as a crude yellow solid (44.8 g). A suspension of crude lead (II) ethyl sulfide (8.23 g, ~31.1 mmol) in dry diethyl ether (50 ml) was cooled to 0 °C. Acryloyl chloride (4.60 ml, 56.5 mmol) was then added dropwise over 2 hours at 0 °C. The mixture was then warmed to room temperature and stirred for a further 1 hour. The reaction mixture was then filtered and the residue was washed with diethyl ether (20 ml). Diethyl ether was then distilled from the combined filtrates leaving an oily residue. The product was then distilled off at 64 °C at a pressure of 30 mmHg as a pungent clear liquid (2.68 g, 23.1 mmol, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29 (3H, t, *J* = 7.3 Hz, *CH*$_3$), 2.97 (2H, q, *J* = 7.3 Hz, *CH*$_2$), 5.67 (1H, dd, *J* = 9.7, 1.5 Hz, vinyl *CH*$_2$ *trans*), 6.29 (1H, dd, *J* = 17.2, 1.5 Hz, vinyl *CH*$_2$ *cis*), 6.37 (1H, dd, *J* = 17.2, 9.7 Hz, vinyl *CH*). [lit.[13] δ = 1.24 (3H, t, *J* = 7.2 Hz, *CH*$_3$), 2.92 (2H, q, *J* = 7.2 Hz, *CH*$_2$), 5.62 (1H, dd, AM*X* system), 6.29-6.37 (2H, dq, AM*X* system)].

General Procedure for the synthesis of racemic MBH–type adducts (TMSOTf/SMe_2)

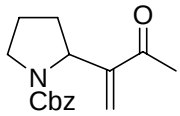


To a solution of aminal (0.21 mmol), alkene (0.43 mmol) and SMe_2 (23 μl, 0.32 mmol) in CH_2Cl_2 (1 ml) at -78 °C was added TMSOTf (96 μl, 0.53 mmol). After stirring the solution for 3 hours, whilst allowing the temperature to rise to -20 °C, the reaction was quenched with sat. aq. $NaHCO_3$ (2 ml) and was allowed to warm to room temperature. Water (25 ml) was added and the resultant mixture was extracted with CH_2Cl_2 (2 × 25 ml). The combined organic layers were then dried with $MgSO_4$ and concentrated *in vacuo*. The resultant oil was taken up in CH_2Cl_2 (1 ml) and DBU (48 μl, 0.32 mmol) was added. After stirring for 10 minutes at room temperature, CH_2Cl_2 (25 ml) was added and the solution was washed with sat. aq. NH_4Cl (3 × 20 ml). The combined aqueous washes

were then extracted with CH_2Cl_2 (25 ml) and the combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo*. The resultant oil was purified by flash chromatography (eluent: 4:2 pet. ether: EtOAc) to give the required adduct.

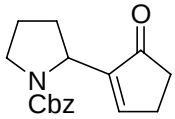
Experimental data for racemic MBH-type adducts

Benzyl 2-(1-acetylvinyl)-1-pyrrolidinecarboxylate 2a



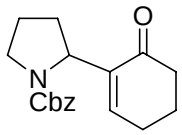
The general procedure was followed on a 0.21 mmol scale to give **2a** as a clear oil (54 mg, 0.20 mmol, 95% yield). IR ν_{max} (neat) / cm^{-1} 1698, 1671; ^1H NMR (400 MHz, $CDCl_3$, 1:1 mixture of rotamers) δ = 1.54-1.69 (1H, m, NCHR*CH*$_2$), 1.69-1.89 (2H, m, NCHRCH$_2$*CH*$_2$), 2.09-2.22 (1H, NCHR*CH*$_2$), 2.29 (1.5H, s, CH_3), 2.35 (1.5H, s, CH_3), 3.44-3.60 (2H, m, N*CH*$_2$), 4.80-4.88 (1H, m, N*CHR*CH$_2$), 5.02 (0.5H, d, *J* = 12.7 Hz, NCO$_2$*CH*$_2$), 5.10 (0.5H, d, *J* = 12.7 Hz, NCO$_2$*CH*$_2$), 5.11 (1H, s, NCO$_2$*CH*$_2$), 5.67 (0.5 H, s, vinyl), 5.68 (0.5H, s, vinyl), 6.01 (0.5H, s, vinyl), 6.07 (0.5H, s, vinyl), 7.20 -7.24 (5H, m, Ar). ^{13}C NMR (75 MHz, DMSO-d_6, 1:1 mixture of rotamers, observed signals) δ = 21.7, 22.6, 26.4, 31.0, 31.9, 46.3, 46.8, 56.1, 56.6, 65.7, 65.7, 124.4, 127.1, 127.3, 127.6, 127.7, 128.3, 128.4, 137.0, 137.2, 147.9, 148.8, 153.5, 153.7, 199.0; HRMS Found: m/z (ESI) 296.1265. $C_{16}H_{19}NO_3Na$ requires 296.1257.

Benzyl 2-(5-oxo-1-cyclopenten-1-yl)-1-pyrrolidinecarboxylate 2b



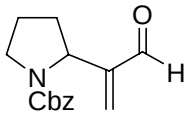
The general procedure was followed on a 0.36 mmol scale to give **2b** as clear oil (98 mg, 0.34 mmol, 96% yield). IR ν_{max} (neat) / cm^{-1} 1689; ^1H NMR (400 MHz, DMSO-d_6, 95 ^oC) δ = 1.62-1.75 (1H, m, NCHR*CH*$_2$), 1.75-1.93 (2H, m, NCH$_2$*CH*$_2$), 1.95-2.20 (1H, m, NCHR*CH*$_2$), 2.25-2.60 (4H, m, C(O)*CH*$_2$*CH*$_2$), 3.40-3.60 (2H, m, N*CH*$_2$CH$_2$), 4.52-4.61 (1H, m, N*CHR*CH$_2$), 4.95-5.07 (1H, m, *CH*$_2$Ph), 5.07-5.18 (1H, m, *CH*$_2$Ph), 7.25-7.42 (6H, m, Ar and C(O)CR*CH*CH$_2$). ^{13}C NMR (100 MHz, DMSO-d_6, 95 ^oC) δ = 22.4, 25.3, 30.5, 34.5, 45.9, 53.1, 65.3, 126.8, 127.1, 127.7, 136.7, 145.9, 153.2, 156.9, 206.4. HRMS Found: m/z (CI) 286.1442. $C_{17}H_{21}NO_3$ $(M+H)^+$ requires 286.1443.

Benzyl 2-(6-oxo-1-cyclohexen-1-yl)-1-pyrrolidinecarboxylate 2c



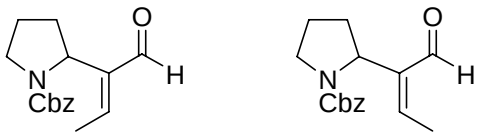
The general procedure was followed on a 0.21 mmol scale to give **2c** as a clear oil (61 mg, 0.20 mmol, 96% yield). IR ν_{max} (neat) / cm^{-1} 1698, 1666. ^1H NMR (400 MHz, DMSO-d_6, 95 ^oC) δ = 1.54 (1H, m, NCHRCH_2), 1.68-1.90 (4H, m, NCH_2CH_2 and $C(O)CH_2CH_2$), 2.00-2.12 (1H, m, NCHRCH_2), 2.20-2.38 (4H, m, $C(O)CH_2CH_2CH_2$), 3.38-3.51 (2H, m, NCH_2CH_2), 4.66 (1H, br. d, J = 8.3 Hz, $NCHRCH_2$), 4.96 (1H, br. d, J = 12.7 Hz, CH_2Ph), 5.09 (1H, br. d, J = 12.7 Hz), 6.56 (1H, app. t, J = 4.2 Hz, =CHR), 7.23-7.40 (5H, m, Ar); ^{13}C NMR (75 MHz, DMSO-d_6, 1:1 mixture of rotamers, observed signals) δ = 21.8, 22.4, 22.6, 25.0, 31.1, 32.0, 38.0, 46.3, 46.8, 55.2, 55.9, 65.5, 65.8, 127.2, 127.4, 127.6, 127.7, 128.3, 128.4, 137.2, 138.3, 139.2, 143.5, 153.5, 153.6, 197.9, 198.1; HRMS Found: m/z (CI) 300.1598. $C_{18}H_{22}NO_3$ $(M+H)^+$ requires 300.1599.

Benzyl 2-(1-formylvinyl)-1-pyrrolidinecarboxylate 2d



The general procedure was followed on a 0.41 mmol scale, with the exception that the treatment with DBU was unnecessary, to give **2d** as a clear oil (90 mg, 85% yield). IR ν_{max} (neat) / cm^{-1} 1683; ^1H NMR (400 MHz, $CDCl_3$, 1:1 mixture of rotamers) 1.62-1.94 (3H, m, NCHRCH_2CH_2), 2.09-2.23 (1H, m, NCHRCH_2), 3.43-3.62 (2H, m, NCH_2), 4.72-4.84 (1H, m, $NCHRCH_2$), 5.04 (0.5H, d, J = 12.5 Hz, NCO_2CH_2), 5.09 (0.5H, d, J = 12.5 Hz, NCO_2CH_2), 5.12 (1H, s, NCO_2CH_2), 5.97 (0.5H, s, vinyl), 6.04 (0.5H, s, vinyl), 6.10 (0.5H, s, vinyl), 6.13 (0.5H, s, vinyl), 7.20-7.39 (5H, m, Ar), 9.56 (0.5H, s, CHO), 9.60 (0.5H, s, CHO); ^{13}C NMR (75 MHz, DMSO-d_6, 1:1 mixture of rotamers) δ = 21.9, 22.8, 30.6, 31.5, 46.3, 46.7, 54.6, 55.2, 65.7, 65.8, 127.1, 127.3, 127.6, 127.7, 128.3, 128.4, 133.5, 133.6, 137.0, 137.1, 149.5, 150.3, 153.5, 153.6, 194.4, 194.5. HRMS Found: m/z (CI) 260.1285 $C_{15}H_{18}NO_3$ $(M+H)^+$ requires 260.1287.

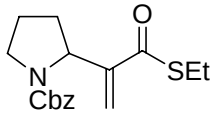
Benzyl 2-[(1*E*)-1-formyl-1-propenyl]-1-pyrrolidinecarboxylate *E*-2e and benzyl 2-[(1*Z*)-1-formyl-1-propenyl]-1-pyrrolidinecarboxylate *Z*-2e



The general procedure was followed on a 0.32 mmol scale, with the exception that the treatment with DBU was unnecessary, to give **2e** (5:1 mixture of E:Z isomers) as a clear

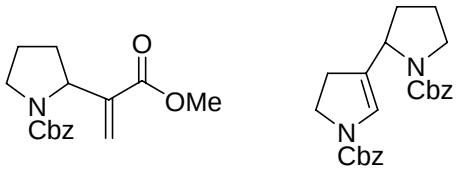
oil (81 mg, 0.30 mmol, 94% yield). IR ν_{max} (neat) / cm^{-1} 1682; ^1H NMR (400 MHz, DMSO-d_6, 90 ^oC, 5:1 mixture of *E* and *Z* isomers) δ = 1.65-1.97 (5.5H, m, NCHR*CH*$_2$ (1H), NCHRCH$_2$*CH*$_2$ (2H), (*E*)-CRR'CH*CH*$_3$ (3 × 0.83H)), 2.00-2.20 (1.5H, m, NCHR*CH*$_2$ (1H), (*Z*)-CRR'CH*CH*$_3$ (3 × 0.17H)), 3.37-3.51 (1H, m, N*CH*$_2$CH$_2$), 3.52-3.62 (1H, m, N*CH*$_2$CH$_2$), 4.60 (0.17H, br. d, *J* = 7.3 Hz, (*Z*)-N*CHR*CH$_2$), 4.69 (0.83H, app. t, *J* = 7.6 Hz, (*E*)-N*CH*RCH$_2$), 4.93-5.10 (2H, m, *CH*$_2$Ph), 6.41 (0.17H, br. q, *J* = 7.8 Hz, (*Z*)-CRR'*CH*CH$_3$), 6.62 (0.83H, br. q, *J* = 6.8 Hz, (E)-CRR'*CH*CH$_3$), 7.23-7.38 (5H, m, Ar), 9.28 (0.83H, br. s, (*E*)-C(O)*H*), 10.09 (0.17H, br. d, *J* = 2.0 Hz, (*Z*)-C(O)*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 5:1 mixture of *E* and *Z* isomers, each displaying 1:1 mixture of rotamers; observed signals) δ = 12.4 (*Z*), 12.7 (*Z*), 14.1 (*E*), 14.3 (*E*), 22.3 (*Z*), 23.1 (*Z*), 24.4 (*E*), 25.0 (*E*), 30.7 (*E*), 31.5 (*Z*), 31.9 (*E*), 32.3 (*Z*), 46.7 (*Z*), 47.0 (*E*), 47.1 (*Z*), 47.4 (*E*), 53.0 (*E*), 53.5 (*E*), 56.1 (*Z*), 57.1 (*Z*), 66.3 (*E*), 66.5 (*Z*), 66.8 (*E*), 66.8 (*Z*), 127.3-128.5 (complex), 136.4-137.1 (complex), 139.7 (*Z*), 140.6 (*Z*), 142.1 (*Z*), 142.1 (*Z*), 143.2 (*E*), 144.1 (*E*), 150.5 (*E*), 151.3 (*E*), 154.5-154.7 (complex), 189.7 (*Z*), 189.8 (*Z*), 193.7 (*E*), 193.8 (*E*). MS m/z (EI): 182 [(M^+- 91), 19%], 138 (65%), 91(100%)]; HRMS (mixture of isomers) found: m/z (CI) 274.1447 $C_{16}H_{20}NO_3$ $(M+H)^+$ requires 274.1443.

Benzyl 2-{1-[(ethylsulfanyl)carbonyl]vinyl}-1-pyrrolidinecarboxylate 2f



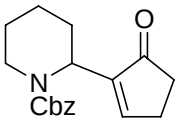
The general procedure was followed on a 0.34 mmol scale to give **2f** as a clear oil (106 mg, 0.33 mmol, 98% yield). IR ν_{max} (neat) / cm^{-1} 1700, 1656. ^1H NMR (400 MHz, $CDCl_3$, mixture of rotamers (11:9) designated major (ma.) and minor (mi.) where possible) δ = 1.27 (1.35H, t, *J* = 7.3 Hz, SCH$_2$*CH*$_3$), 1.28 (1.65H, t, *J* = 7.3 Hz, SCH$_2$*CH*$_3$), 1.75-1.91 (3H, m, NCH$_2$*CH*$_2$*CH*$_2$), 2.07-2.21 (1H, m, NCHR*CH*$_2$), 2.92 (0.9H, q, *J* = 7.3 Hz, S*CH*$_2$CH$_3$), 2.93 (1.1H, q, *J* = 7.3 Hz, S*CH*$_2$CH$_3$), 3.41-3.60 (2H, m, N*CH*$_2$CH$_2$), 4.82-4.90 (1H, m, N*CHR*CH$_2$), 5.07 (0.55H, d, *J* = 12.8 Hz, *CH*$_2$Ph), 5.12 (0.55 H, d, *J* = 12.8 Hz, *CH*$_2$Ph), 5.13 (0.9 H, m, *CH*$_2$Ph), 5.48 (0.55H, s, =*CH*$_2$), 5.51 (0.45H, s, =*CH*$_2$), 6.11 (0.55H, s, =*CH*$_2$), 6.17 (0.45H, s, =*CH*$_2$), 7.25-7.41 (5H, m, Ar); ^{13}C NMR (75 MHz, DMSO-d_6, mixture of rotamers, observed signals) δ = 14.5, 21.7, 22.5, 22.7, 30.8, 31.9, 46.3, 46.7, 57.0, 57.5, 65.8, 65.8, 121.4, 127.0, 127.3, 127.6, 127.7, 128.2, 128.4, 136.9, 137.0, 148.0, 148.9, 153.6, 192.0, 192.1. MS m/z (EI): 258 [(M^+- 61), 17%], 184 (28%), 166 (25%), 122 (48%), 91(100%); HRMS Found: m/z (CI) 320.1317. $C_{17}H_{22}NO_3S$ $(M+H)^+$ requires 320.1320.

Benzyl 2-[1-(methoxycarbonyl)vinyl]-1-pyrrolidinecarboxylate 2g and benzyl 4-{1-[(benzyloxy)carbonyl]-2-pyrrolidinyl}-2,3-dihydro-1*H*- pyrrole-1-carboxylate (aminal dimer)



The general procedure was followed on a 0.37 mmol scale with the exception that the reaction was carried out at -20 ^{o}C for 16 hours to give **2g** as a clear oil (55 mg, 51% yield). Dimer of aminal was also isolated as a clear oil (40 mg, 49% yield). Data for **2g**: IR ν_{max} (neat) / cm^{-1} 1699. ^{1}H NMR (400 MHz, DMSO-d_6, 95 ^{o}C) δ = 1.69 (1H, dddd, J = 12.2, 6.3, 3.9, 2.9 Hz, NCHRCH_2), 1.74-1.88 (2H, m, NCH$_2CH_2$), 2.14 (1H, dddd, J = 12.2, 9.8, 8.3, 7.3 Hz, NCHRCH_2), 3.42-3.52 (2H, m, NCH_2CH$_2$), 3.70 (3H, s, OCH_3), 4.69 (1H, dd, J = 7.8, 2.4 Hz, NCHRCH$_2$), 5.05 (2H, s, CH_2Ph), 5.49 (1H, app. t, J = 1.0 Hz, =CH_2), 6.08 (1H, br. s, =CH_2), 7.25-7.36 (5H, m, Ar). ^{13}C NMR (75 MHz, DMSO-d_6, 1:1 mixture of rotamers, observed signals) δ = 21.5, 22.4, 30.8, 31.7, 46.3, 46.8, 51.8, 54.9, 57.0, 57.5, 65.7, 65.8, 123.3, 123.4, 127.0, 127.3, 127.6, 127.7, 128.2, 128.3, 137.1, 140.3, 141.2, 153.6, 153.7, 165.7, 165.7. HRMS Found: m/z (CI) 290.1383 $C_{16}H_{20}NO_4$ $(M+H)^+$ requires 290.1392. Data for **aminal dimer**: IR ν_{max} (neat) / cm^{-1} 1698. ^{1}H NMR (400 MHz, DMSO-d_6, 95 ^{o}C) δ = 1.72-1.88 (3H, m, NCHRCH_2CH_2), 1.88-2.04 (1H, m, NCHRCH_2CH$_2$), 2.40-2.60 (2H, m, NCHCRCH_2), 3.32-3.45 (2H, m, NCH_2CH$_2$CH$_2$), 3.62-3.80 (2H, m, NCH_2CH$_2$CR), 4.46 (1H, br. d, J = 7.8 Hz, NCHRCH$_2$), 4.95-5.15 (4H, m, 2 × CH_2Ph), 6.28 (1H, br. s, NCRCHCH$_2$), 7.20-7.45 (10H, m, Ar). ^{13}C NMR (75 MHz, DMSO-d_6, complex rotameric mixture, observed signals) δ = 22.9, 23.0, 23.5, 23.6, 28.0, 29.0, 29.3, 30.8, 45.3, 45.5, 46.0, 46.5, 55.0, 55.4, 65.6, 66.0, 66.2, 123.7, 124.3, 124.5, 127.1-128.5 (complex), 136.7, 136.8, 137.1, 151.1, 151.7, 153.7-154.0 (complex). MS m/z (EI): 406 [(M^+), 1%], 315 (11%), 271 (3%), 91(100%). HRMS Found: m/z (ESI) 429.1788 $C_{24}H_{26}N_2O_4Na$ requires 429.1785.

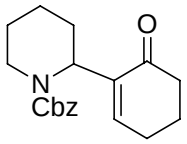
Benzyl 2-(5-oxo-1-cyclopenten-1-yl)-1-piperidinecarboxylate 2h



The general procedure was followed on a 0.23 mmol scale, except that the operating temperature was maintained below -60 ^{o}C, to give **2h** as a clear oil (61 mg, 90% yield). IR ν_{max} (neat) / cm^{-1} 1688. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.25 (1H, app. qt, J = 13.0, 3.7 Hz, NCHRCH$_2CH_2$CH$_2$), 1.47 (1H, app. qdd, J = 13.0, 4.8, 3.3 Hz, NCHRCH$_2$CH$_2CH_2$), 1.54-1.74 (3H, m, NCHR$CH_2CH_2CH_2$), 2.25 (1H, br. d, J = 13.2 Hz, NCHRCH_2), 2.35-2.64 (4H, m, C(O)CH_2CH_2), 2.98 (1H, app. td, J = 13.2, 3.3 Hz, NCH_2CH$_2$), 4.14 (1H, br. d, J = 13.4 Hz, NCH_2CH$_2$), 5.09-5.15 (1H, m, NCHRCH$_2$), 5.11 (1H, d, J = 12.5 Hz, CH_2Ph), 5.15 (1H, d, J = 12.5 Hz, CH_2Ph), 7.24-7.50 (6H, m,

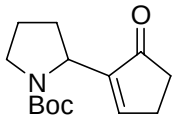
Ar (5H), C(O)CR*CH*R'); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 18.8, 24.8, 26.0, 26.5, 34.7, 40.6, 48.4, 66.1, 127.3, 127.7, 128.3, 137.0, 143.3, 154.8, 159.9, 208.0; HRMS Found: m/z (CI) 300.1592 $C_{18}H_{22}NO_3$ $(M+H)^+$ requires 300.1600.

Benzyl 2-(5-oxo-1-cyclohexen-1-yl)-1-piperidinecarboxylate 2i



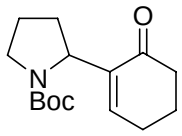
The general procedure was followed on a 0.26 mmol scale, except that the operating temperature was maintained below -60 °C, to give **2q** as a clear oil (61 mg, 75% yield). IR ν_{max} (neat) / cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23-1.36 (1H, m, $NCH_2CH_2CH_2$), 1.44-1.59 (2H, $NCH_2CH_2CH_2$), 1.62-1.80 (2H, m, $NCH_2CH_2CH_2CH_2$), 1.86-2.02 (3H, m, $NCHRCH_2$ and $C(O)CH_2CH_2$), 2.19-2.30 (1H, m, $C(O)CH_2CH_2CH_2$), 2.30-2.49 (3H, m, $C(O)CH_2CH_2CH_2$), 3.04 (1H, ddd, *J* = 13.2, 12.2, 3.9 Hz, NCH_2), 4.13 (1H, m, NCH_2), 5.05 (1H, d, *J* = 12.5 Hz, CH_2Ph), 5.15 (1H, br. s, NCHR), 5.19 (1H, d, *J* = 12.5 Hz, CH_2Ph), 5.60 (1H, app. td, *J* = 4.4, 1.5 Hz, $C(O)CH_2CH_2CH_2CH$R), 7.27-7.39 (5H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.0, 20.7, 24.9, 25.8, 27.7, 38.8, 41.4, 50.9, 66.9, 127.7, 127.8, 128.4, 136.9, 138.4, 144.5, 156.0, 198.6; HRMS Found: m/z (CI) 314.1748 $C_{18}H_{22}NO_3$ $(M+H)^+$ requires 314.1756.

t-Butyl 2-(5-oxo-1-cyclopenten-1-yl)-1-pyrrolidinecarboxylate 2j



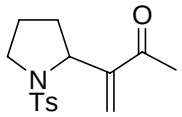
The general procedure was followed on a 0.47 mmol scale to give **2j** as waxy solid (81 mg, 69% yield). IR ν_{max} (neat) / cm^{-1} 1688; ^{1}H NMR (400 MHz, $CDCl_3$, 6:5 mixture of rotamers) δ = 1.32 (4.9H, s, *t*-Bu), 1.41 (4.1H, s, *t*-Bu), 1.63-1.89 (3H, m, $NCH_2CH_2CH_2$), 1.95-2.17 (1H, m, $NCH_2CH_2CH_2$), 2.30-2.46 (2H, m, $C(O)CH_2CH_2$), 2.46-2.64 (2H, m, $C(O)CH_2CH_2$), 3.27-3.53 (2H, m, NCH_2), 4.45-4.62 (1H, m, NCHR), 7.13-7.24 (1H, m, $C(O)CH_2CH_2CH$); ^{13}C NMR (75 MHz, $CDCl_3$, mixture of rotamers, observed signals) δ = 22.9, 23.5, 26.1, 28.3, 30.4, 31.5, 35.3, 35.5, 46.1, 46.6, 53.5, 53.9, 79.1, 146.6, 147.9, 154.1, 156.8, 157.3, 207.9, 208.1; HRMS Found: m/z (CI) 252.1593 $C_{14}H_{22}NO_3$ $(M+H)^+$ requires 252.1600.

t-Butyl 2-(6-oxo-1-cyclohexen-1-yl)-1-pyrrolidinecarboxylate 2k



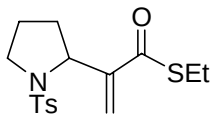
The general procedure was followed on a 0.27 mmol scale to give **2k** as a waxy solid (43 mg, 60% yield). IR ν_{max} (neat) / cm^{-1} 1693, 1668; ^1H NMR (400 MHz, $CDCl_3$, 3:2 mixture of rotamers) δ = 1.36 (5.4H, s, *t*-Bu), 1.46 (3.6H, s, *t*-Bu), 1.55-1.67 (1H, m, NCHR*CH*$_2$), 1.67-1.85 (2H, m, NCH$_2$*CH*$_2$), 1.90-2.05 (2H, m, C(O)CH$_2$*CH*$_2$), 2.05-2.21 (1H, m, NCHR*CH*$_2$), 2.31-2.45 (4H, m, C(O)*CH*$_2$CH$_2$*CH*$_2$), 3.32-3.52 (2H, m, N*CH*$_2$), 4.70 (0.6H, br. d, *J* = 7.6 Hz, N*CH*R), 4.70 (0.4H, br. d, *J* = 8.0 Hz, N*CH*R), 6.56 (0.4H, br. s, C(O)CH$_2$CH$_2$CH$_2$*CH*), 6.61 (0.6H, br. t, *J* = 3.7 Hz, C(O)CH$_2$CH$_2$CH$_2$*CH*); ^{13}C NMR (75 MHz, $CDCl_3$, mixture of rotamers) δ = 22.6, 22.8, 23.0, 23.2, 25.6, 28.4, 28.5, 31.6, 32.6, 38.6, 46.5, 47.0, 55.6, 56.2, 79.0, 79.1, 140.6, 142.8, 154.1, 154.3, 198.7, 198.8; HRMS Found: m/z (CI) 266.1751 $C_{15}H_{24}NO_3$ $(M+H)^+$ requires 266.1756.

3-{1-[(4-methylphenyl)sulfonyl]-2-pyrrolidinyl}-3-buten-2-one 2l



The general procedure was followed on a 0.31 mmol scale, with the exception that the reaction was allowed to warm slowly over 3 hours from -78 ^oC to room temperature to give **2l** as a white solid (80 mg, 90% yield). IR ν_{max} (neat) / cm^{-1} 1660; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.47-1.59 (2H, m, NCHR*CH*$_2$*CH*$_2$), 1.64-1.80 (2H, m, NCHR*CH*$_2$*CH*$_2$), 2.38 (3H, s, C(O)*CH*$_3$), 2.44 (3H, s, Ar-*CH*$_3$), 3.15 (1H, ddd, *J* = 9.8, 8.6, 6.6 Hz, N*CH*$_2$CH$_2$), 3.57 (1H, dddd, *J* = 9.8, 6.8, 3.7, 0.7 Hz, N*CH*$_2$CH$_2$), 4.63 (1H, br. dd, *J* = 8.3, 2.4 Hz, N*CH*RCH$_2$), 6.25 (1H, d, *J* = 0.5 Hz, =*CH*$_2$), 6.29 (1H, d, *J* = 1.5 Hz, =*CH*$_2$), 7.33 (2H, br. d, *J* = 8.3 Hz, Ar), 7.72 (2H, br. d, *J* = 8.3 Hz, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.5, 23.4, 26.4, 32.8, 49.3, 59.0, 126.6, 127.6, 129.7, 134.0, 143.5, 149.2, 198.9; HRMS Found: m/z (CI) 294.1161. $C_{15}H_{20}NO_3S$ $(M+H)^+$ requires 294.1164.

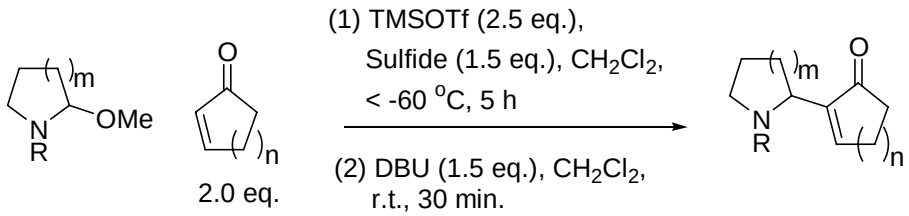
S-ethyl 2-{1-[(4-methylphenyl)sulfonyl]-2-pyrrolidinyl}-2-propene thioate 2m



The general procedure was followed on a 0.26 mmol scale, with the exception that the reaction was allowed to warm slowly over 3 hours from -78 ^oC to room temperature to give **2m** as a white solid (79 mg, 90% yield). IR ν_{max} (neat) / cm^{-1} 1655; ^1H NMR (400

MHz, $CDCl_3$) δ = 1.28 (3H, t, *J* = 7.5 Hz, SCH_2CH_3), 1.55-1.79 (4H, m, $NCHRCH_2CH_2$), 2.43 (3H, s, Ar-CH_3), 2.84-3.00 (2H, m, SCH_2CH_3), 3.17 (1H, dddd, *J* = 9.5, 8.0, 6.0, 1.5 Hz, NCH_2CH_2), 3.55 (1H, dddd, *J* = 9.5, 6.5, 3.0, 3.0 Hz, NCH_2CH_2), 4.67 (1H, br. d, *J* = 7.5 Hz, $NCHRCH_2$), 6.06 (1H, d, *J* = 1.5 Hz, $=CH_2$), 6.31 (1H, s, $=CH_2$), 7.33 (2H, d, *J* = 8.0 Hz, Ar), 7.73 (2H. d, *J* = 8.0 Hz, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.5, 21.5, 23.2, 23.4, 32.5, 49.2, 59.8, 123.6, 127.6, 129.7, 134.5, 143.5, 148.8, 192.8; MS m/z (EI): 289 [(M^+), 2%], 198 (4%), 154 (77%), 122 (36%), 91(100%); HRMS Found: m/z (CI) 340.1031 $C_{16}H_{22}NO_3S_2$ $(M+H)^+$ requires 340.1041.

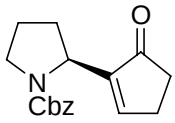
General Procedure for the synthesis of enantiomerically enriched MBH-type adducts



To a solution of aminal (0.21 mmol), alkene (0.43 mmol) and chiral sulfide (23 μl, 0.32 mmol) in CH_2Cl_2 (1 ml) at -78 °C was added TMSOTf (96 μl, 0.53 mmol). After stirring the solution for 5 hours, maintaining the temperature below -60 °C, the reaction was quenched with sat. aq. $NaHCO_3$ (2 ml) and was allowed to warm to room temperature. Water (25 ml) was added and the resultant mixture was extracted with CH_2Cl_2 (2 × 25 ml). The combined organic layers were then dried with $MgSO_4$ and concentrated *in vacuo*. The resultant oil was taken up in CH_2Cl_2 (1 ml) and DBU (48 μl, 0.32 mmol) was added. After stirring for 30 minutes at room temperature, CH_2Cl_2 (25 ml) was added and the solution was washed with sat. aq. NH_4Cl (3 × 20 ml). The combined aqueous washes were then extracted with CH_2Cl_2 (25 ml) and the combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo*. The resultant oil was purified by flash chromatography to give the required adduct.

Asymmetric transformations using Aggarwal's Sulfide 8

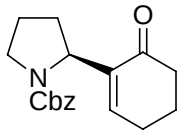
Benzyl (2*S*)-(5-oxo-1-cyclopenten-1-yl)-1-pyrrolidinecarboxylate *S*-2b



The general procedure was followed using Aggarwal's chiral sulfide **8** on a 0.18 mmol scale to give **2b** as clear oil (35 mg, 0.12 mmol, 69% yield). The ^{1}H NMR spectrum matched that obtained previously using racemic sulfide. $[\alpha]^{23}_D$ -90 (*c* 0.6, $CDCl_3$); Chiral

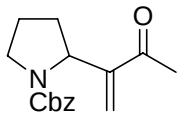
HPLC: Chiracel OD, hexane-*i*-PrOH (90:10) 1.0 ml/min, major 14.1 min, minor 23.0 min, 82% ee.

Benzyl (2*S*)-(6-oxo-1-cyclohexen-1-yl)-1-pyrrolidinecarboxylate *S*-2c



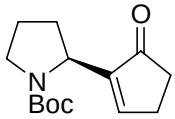
The general procedure was followed using Aggarwal's chiral sulfide **8** on a 0.26 mmol scale to give **2c** as a clear oil (66 mg, 0.22 mmol, 86% yield). The ^{1}H NMR spectrum matched that obtained previously using racemic sulfide. $[\alpha]^{23}_D$ -60 (*c* 0.9, $CDCl_3$); Chiral HPLC: Chiracel OD, hexane-*i*-PrOH (90:10) 1.0 ml/min, major 14.8 min, minor 24.9 min, 80% ee

Benzyl 2-(1-acetylvinyl)-1-pyrrolidinecarboxylate 2a



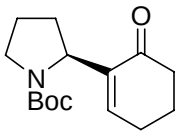
The general procedure was followed using Aggarwal's sulfide on a 0.18 mmol scale to give **2a** as clear oil (38 mg, 0.14 mmol, 78% yield). The ^{1}H NMR spectrum matched that obtained previously using racemic sulfide. Chiral HPLC: Chiracel OD-H, hexane-*i*-PrOH (90:10) 1.0 ml/min, major 12.5 min, minor 8.8 min, 8% ee.

t-Butyl (2*S*)-(5-oxo-1-cyclopenten-1-yl)-1-pyrrolidinecarboxylate *S*-2j



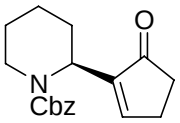
The general procedure was followed using Aggarwal's sulfide **8** on a 0.24 mmol scale to give **2j** as a waxy solid (45 mg, 0.18 mmol, 75% yield). The ^{1}H NMR spectrum matched that obtained previously using racemic sulfide. $[\alpha]^{23}_D$ -70 (*c* 2.1, $CDCl_3$); Chiral HPLC: Chiracel OD, hexane-*i*-PrOH (90:10) 1.0 ml/min, major 7.1 min, minor 8.3 min, 88% ee.

t-Butyl (2*S*)-(6-oxo-1-cyclohexen-1-yl)-1-pyrrolidinecarboxylate *S*-2k



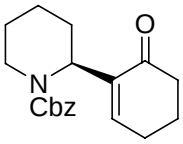
The general procedure was followed using Aggarwal's chiral sulfide **8** on a 0.27 mmol scale to give **2k** as a waxy solid (64 mg, 0.24 mmol, 90% yield). The ^{1}H NMR spectrum matched that obtained previously using racemic sulfide. $[\alpha]^{23}_D$ -73 (*c* 1.1, $CDCl_3$); Chiral HPLC: Chiracel OD, hexane-*i*-PrOH (90:10) 1.0 ml/min, major 6.1 min, minor 10.5 min, 88% ee.

Benzyl (2*S*)-(5-oxo-1-cyclopenten-1-yl)-1-piperidinecarboxylate *S*-2h



The general procedure was followed using Aggarwal's sulfide **8** on a 0.61 mmol scale to give **2h** as clear oil (161 mg, 0.54 mmol, 88% yield). The ^{1}H NMR spectrum matched that obtained previously using racemic sulfide. $[\alpha]^{25}_D$ -45 (*c* 7.3, $CDCl_3$); Chiral HPLC: Chiracel OD-H, hexane-*i*-PrOH (90:10) 1.0 ml/min, major 11.5 min, minor 15.1 min, 94% ee.

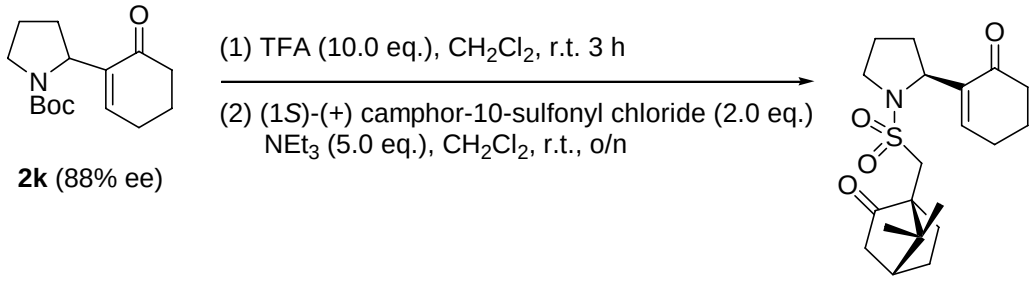
Benzyl (2*S*)-(5-oxo-1-cyclohexen-1-yl)-1-piperidinecarboxylate *S*-2i



The general procedure was followed using Aggarwal's sulfide **8** on a 0.60 mmol scale to give **2i** as white solid (91 mg, 0.29 mmol, 49% yield). The ^{1}H NMR spectrum matched that obtained previously using racemic sulfide. $[\alpha]^{25}_D$ -54 (*c* 2.7, $CDCl_3$); Chiral HPLC: Chiracel OD, hexane-*i*-PrOH (95:5) 1.0 ml/min, major 13.3 min, minor 15.0 min, 99% ee.

Determination of absolute stereochemistry

Preparation of (1*S*,4*R*)-7,7-dimethyl-1-({[(2*S*)-2-(6-oxo-1-cyclohexen-1-yl)pyrrolidinyl]sulfonyl}methyl)bicyclo[2.2.1]heptan-2-one

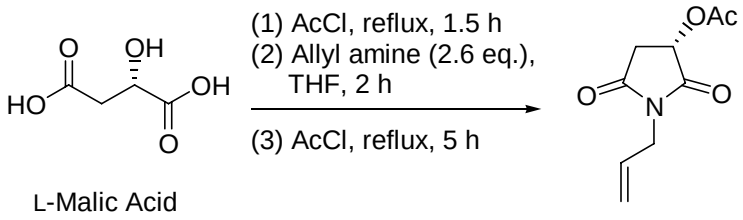


2k (88% ee)

To a solution of MBH-type adduct **2k** (22 mg, 0.08 mmol, 88% ee) in CH_2Cl_2 was added TFA (61 μl, 0.83 mmol). The solution was allowed to stir at room temperature for 3 hours. The volatiles were removed *in vacuo* and the resultant oil was taken up in CH_2Cl_2 and NEt_3 (59 μl, 0.42 mmol) and (1*S*)-(+)-camphor-10-sulfonyl chloride (42 mg, 0.17 mmol) was added. The resulting solution was allowed to stir overnight at room temperature under N_2. Sat. aq. $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2 (25 ml × 2), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (eluent: pet ether/EtOAc 3:2) to give the sulfonamide as a white solid (28 mg, 0.07 mmol, 90% yield, dr = 94:6). The solid was crystallised from hexane/CH_2Cl_2 to give X-ray quality crystals of the major isomer. Data for major diastereomer: IR ν_{max} (neat) / cm^{-1} 1745, 1668; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.92 (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.41 (1H, ddd, *J* = 12.5, 9.3, 3.7 Hz), 1.57 (1H, ddd, *J* = 14.2, 9.3, 4.6 Hz), 1.70-1.79 (1H, m, NCHR*CH*$_2$), 1.79-2.10 (7H, m), 2.18-2.29 (1H, m, NCHR*CH*$_2$), 2.33-2.56 (6H, m), 2.88 (1H, d, *J* = 14.7 Hz, SO_2*CH*$_2$), 3.35 (1H, d, *J* = 14.7 Hz, SO_2*CH*$_2$), 3.46 (1H, app. t, *J* = 8.3 Hz, N*CH*$_2$), 3.54-3.60 (1H, m, N*CH*$_2$), 4.71 (1H, br. d, *J* = 8.1 Hz, NCHR), 7.06 (1H, app. t, *J* = 3.4 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.8, 20.1, 22.7, 23.8, 25.5, 25.7, 26.8, 32.9, 38.5, 42.5, 43.0, 44.4, 47.7, 48.9, 58.4, 58.8, 139.8, 146.0, 198.7, 215.5; HRMS Found: m/z (CI) pending $C_{20}H_{30}NO_4S$ $(M+H)^+$ requires 380.1896.

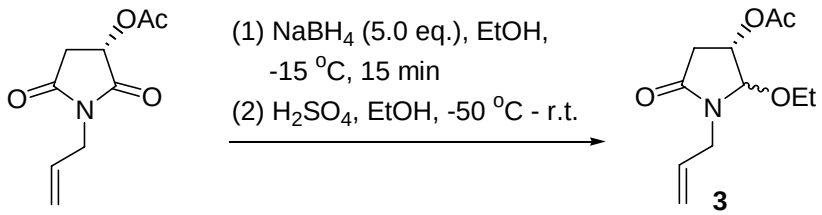
Synthesis of (+)-heliotridine

(3*S*)-1-allyl-2, 5-dioxopyrrolidinyl acetate



L-malic acid (23.8 g, 178 mmol) and acetyl chloride (90.0 ml, 1.27 mol) was refluxed for 1.5 h and then concentrated *in vacuo*. The crude anhydride was dissolved in THF (120 ml) and allylamine (35.0 ml, 470 mmol) was added slowly. After the solution was stirred for 2 h, it was concentrated *in vacuo* and the residue was reluxed in acetyl chloride (90.0 ml, 1.27 mol) for another 5 h. After concentration of the reaction mixture *in vacuo*, the residue was purified by flash chromatography (eluent: pet. ether: EtOAc; gradient 7:3 to 3:2) to give the required imide as a clear oil (33.3 g, 95% yield). $[\alpha]^{23}_{D}$ –31 (*c* 2.5, $CDCl_3$); IR ν_{max} (neat) / cm^{-1} 1790, 1745, 1704. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.17 (3H, s, CH_3), 2.70 (1H, dd, *J* = 18.5, 4.8 Hz, NCO*CH*$_2$), 3.18 (1H, dd, *J* = 18.5, 8.6 Hz, NCO*CH*$_2$), 4.15 (2H, ddd, *J* = 5.9, 1.5, 1.1 Hz, N*CH*$_2$CHCH$_2$), 5.22 (1H, app. dq, *J* = 10.3, 1.5 Hz, NCH$_2$CH*CH*$_2$), 5.27 (1H, app. dq, *J* = 17.2, 1.5 Hz, NCH$_2$CH*CH*$_2$), 5.45 (1H, dd, *J* = 8.6, 4.8 Hz, NCO*CH*(OAc)), 5.80 (1H, ddt, *J* = 17.2, 10.3, 5.9 Hz, NCH$_2$*CH*CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.4, 35.7, 41.1, 67.5, 118.8, 130.1, 169.7, 172.6, 172.9. HRMS Found: m/z (CI) 198.0759 $C_9H_{12}NO_4$ $(M+H)^+$ requires 198.0766.

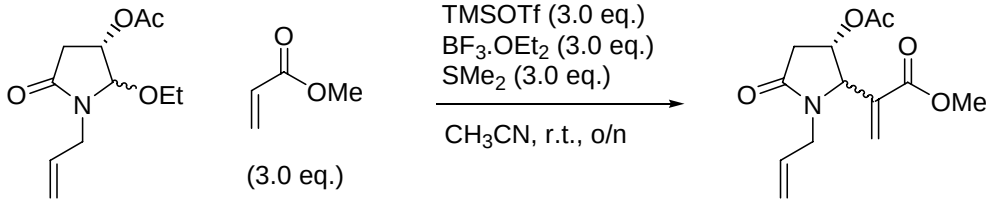
(2*S*, 3*S*)-1-allyl-2-ethoxy-5-oxopyrrolidinyl acetate (*trans*-3) and (2*R*, 3*S*)-1-allyl-2-ethoxy-5-oxopyrrolidinyl acetate (*cis*-3)



To a solution of imide (3.00 g, 15.3 mmol) in EtOH (160 ml) at -15 ^{o}C was added $NaBH_4$ (2.84 g, 76.5 mmol). After the reaction mixture was stirred for 15 min at -15 ^{o}C, it was cooled to -50 ^{o}C, and a 1M solution of H_2SO_4 in EtOH (70 ml) was added over 15 min (the temperature of the reaction mixture was maintained below -25 ^{o}C). After the reaction mixture was stirred for an additional hour at room temperature, it was poured into saturated aqueous $NaHCO_3$ (750 ml). Extraction with CH_2Cl_2 (4 × 150 ml), followed by drying ($MgSO_4$), concentration of the combined organic layers *in vacuo* and flash chromatography (eluent: pet. ether: EtOAc; 7:3) gave ethoxy aminal **3** as a colourless oil

(2.95 g, 85% yield, trans:cis = 85: 15, pure fractions of both epimers were obtained). Data for ***trans*-3**: $[\alpha]^{24}_D$ +7 (*c* 3.4, $CDCl_3$); IR ν_{max} (neat) / cm^{-1} 1739, 1703; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.23 (3H, t, *J* = 7.0 Hz, OCH_2CH_3), 2.08 (3H, s, $OCOCH_3$), 2.36 (1H, d, *J* = 17.9 Hz, $NCOCH_2$), 2.91 (1H, dd, *J* = 17.9, 6.4 Hz, $NCOCH_2$), 3.58 (1H, dq, *J* = 9.5, 7.0 Hz, OCH_2CH_3), 3.61 (1H, br. dd, *J* = 15.7, 7.3 Hz, NCH_2CHCH_2), 3.73 (1H, dq, *J* = 9.5, 7.0 Hz, OCH_2CH_3), 4.29 (1H, app. ddt, *J* = 15.7, 4.8, 1.5 Hz, NCH_2CHCH_2), 4.68 (1H, s, NCH(OEt)), 5.08 (1H, d, *J* = 6.4 Hz, NCH(OEt)CH(OAc)), 5.20 (1H, br. d, *J* = 10.3 Hz, NCH_2CHCH_2), 5.21 (1H, br. d, *J* = 17.2 Hz, NCH_2CHCH_2), 5.76 (1H, dddd, *J* = 17.2, 10.3, 7.3, 4.8 Hz, NCH_2CHCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 15.1, 20.8, 35.7, 42.6, 63.8, 70.7, 92.3, 117.6, 132.3, 170.1, 172.1; HRMS Found: m/z (CI) 228.1234 $C_{11}H_{18}NO_4$ $(M+H)^+$ requires 228.1236. Data for ***cis*-3**: $[\alpha]^{24}_D$ -118 (*c* 2.3, $CDCl_3$); IR ν_{max} (neat) / cm^{-1} 1742, 1706; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.19 (3H, t, *J* = 7.0 Hz, OCH_2CH_3), 2.13 (3H, s $OCOCH_3$), 2.64 (1H, dd, *J* = 16.8, 8.1 Hz, $NCOCH_2$), 2.69 (1H, dd, *J* = 16.8, 8.4 Hz, $NCOCH_2$), 3.54 (1H, dq, *J* = 8.8, 7.0 Hz, OCH_2CH_3), 3.62 (1H, dq, *J* = 8.8, 7.0 Hz, OCH_2CH_3), 3.63 (1H, br. dd, *J* = 15.4, 7.3 Hz, NCH_2CHCH_2), 4.31 (1H, app. ddt, *J* = 15.4, 4.8, 1.5 Hz, NCH_2CHCH_2), 5.02 (1H, d, *J* = 5.3 Hz, NCH(OEt)), 5.18 (1H, ddd, *J* = 8.4, 8.1, 5.3 Hz, NCH(OEt)CH(OAc)), 5.21 (1H, br. d, *J* = 17.5 Hz, NCH_2CHCH_2), 5.22 (1H, br. d, *J* = 9.5 Hz, NCH_2CHCH_2), 5.75 (1H, dddd, *J* = 17.5, 9.5, 7.3, 4.8 Hz, NCH_2CHCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 15.4, 20.6, 34.4, 43.0, 65.6, 67.7, 87.6, 118.1, 132.3, 170.5, 170.5. HRMS Found: m/z (CI) 228.1238 $C_{11}H_{18}NO_4$ $(M+H)^+$ requires 228.1236.

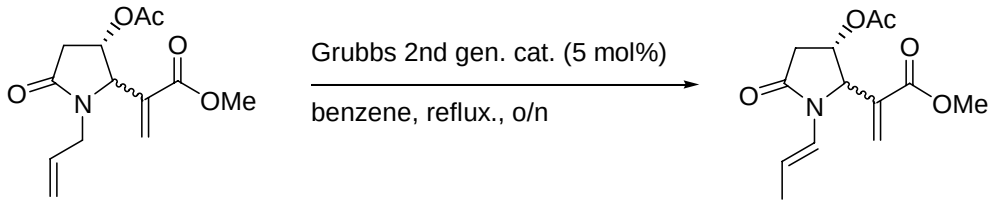
Methyl 2-[(2*R*,3*S*)-3-(acetyloxy)-1-allyl-5-oxopyrrolidinyl]acrylate (*trans*-4) and methyl 2-[(2*S*,3*S*)-3-(acetyloxy)-1-allyl-5-oxopyrrolidinyl]acrylate (*cis*-4)



To a solution of aminal **3** (61 mg, 0.27 mmol) and methyl acrylate (72 μl, 0.81 mmol) in CH_3CN (1 ml) was added TMSOTf (0.15 ml, 0.81 mmol), $BF_3.OEt_2$ (0.10 ml, 0.81 mmol) and SMe_2 (58 μl, 0.81 mmol). The resultant yellow solution was allowed to stir overnight at room temperature under an atmosphere of N_2. The reaction was quenched with sat. aq. $NaHCO_3$ (10 ml) and extracted with CH_2Cl_2 (2×25 ml). The organics were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude oil was purified by column chromatography (eluent: pet. ether/EtOAc 1:1) to give diene **4** as a pale yellow oil (61 mg, 0.23 mmol, 85%, trans:cis = 3.5:1). IR ν_{max} (neat) / cm^{-1} (mixture of isomers) 1742, 1721, 1697; ^1H NMR (400 MHz, $CDCl_3$, ***trans*-4**) δ = 2.10 (3H, s, Ac), 2.40 (1H, dd, *J* = 18.1, 1.2 Hz, $NCOCH_2$), 2.93 (1H, ddd, *J* = 18.1, 6.8, 1.2 Hz, $NCOCH_2$), 3.25 (1H, app. ddq, *J* = 15.4, 7.2, 1.5 Hz, NCH_2), 3.79 (3H, s, OCH_3), 4.45 (1H, app. ddt, *J* = 15.4, 4.4, 1.5 Hz, NCH_2), 4.46 (1H, br. s, NCHCHOAc), 5.14 (1H, app. dt, *J* = 6.8, 1.2 Hz, NCHRCHOAc), 5.16-5.23 (2H, m, NCH_2CHCH_2), 5.67 (1H, br. s,

C*CH*$_2$), 5.71 (1H, dddd, *J* = 17.1, 10.2, 7.2, 4.4 Hz, NCH$_2$*CH*), 6.64 (1H, br. s, C*CH*$_2$); ^{1}H NMR (400 MHz, $CDCl_3$, ***cis*-4**) δ = 1.96 (3H, s, Ac), 2.58 (1H, ddd, *J* = 17.1, 6.8, 1.0 Hz, NCO*CH*$_2$), 2.78 (1H, dd, *J* = 17.1, 8.3 Hz, NCO*CH*$_2$), 3.22 (1H, m, N*CH*$_2$), 3.79 (3H, s, O*CH*$_3$), 4.46 (1H, m, N*CH*$_2$), 4.86 (1H, br. d, *J* = 7.3 Hz, N*CH*CHOAc), 5.09-5.20 (2H, m, NCH$_2$CH*CH*$_2$), 5.56 (1H, ddd, *J* = 8.3, 7.3, 6.8 Hz, NCH*CH*OAc), 5.63-5.74 (1H, m, NCH$_2$*CH*), 5.64 (1H, br. s, C*CH*$_2$), 6.50 (1H, br. s, C*CH*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, ***trans*-4** and ***cis*-4** referred to as major (ma.) and minor (mi.) respectively where possible, observed signals) δ = 20.7 (mi.), 21.4 (ma.), 35.8 (mi.), 36.8 (ma.), 43.0 (ma.), 43.4 (mi.), 52.2 (mi.), 52.3 (ma.), 65.1, 67.2 (ma.), 67.2 (mi.), 70.9 (mi.), 71.5 (ma.), 118.2 (ma.), 119.0 (mi.), 128.0, 131.4 (mi.), 131.6 (ma.), 135.8, 169.9 (mi.), 170.1 (ma.), 172.5; HRMS (mixture of isomers) found: m/z (CI) 268.1185 $C_{13}H_{18}NO_5$ $(M+H)^+$ requires 268.1185.

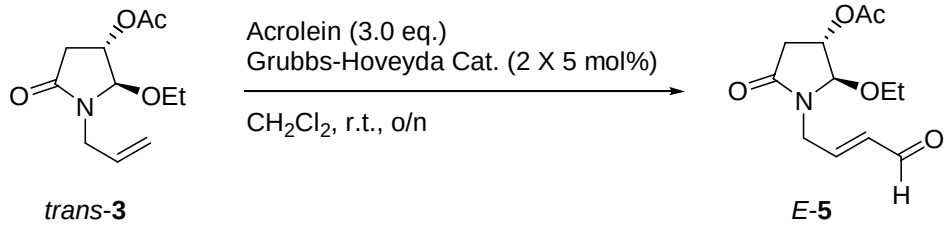
Methyl 2-{(2*R*,3*S*)-3-(acetyloxy)-5-oxo-1-[(1*E*)-1-propenyl] pyrrolidinyl} acrylate and methyl 2-{(2*S*,3*S*)-3-(acetyloxy)-5-oxo-1-[(1*E*)-1-propenyl]pyrrolidinyl}acrylate



4

To a solution of diene **4** (91 mg, 0.34 mmol, trans:cis 3:1) in benzene (35 ml) was added Grubbs 2nd gen. catalyst (14 mg, 0.017 mmol). The solution was allowed to stir at reflux under an atmosphere of N_2 overnight. The solution was concentrated *in vacuo* and purified by column chromatography (eluent: pet. ether/EtOAc 3:2) to give the enamide as a brown oil (46 mg, 0.17 mmol, 50% yield, trans:cis (relationship between substituents on C3 and C4) = 2.3:1, E:Z >95:5) and starting material **4** (40 mg, 0.15 mmol, 44% yield, trans:cis = 4.3:1). IR ν_{max} (neat) / cm^{-1} (mixture of isomers) 1740, 1707; ^{1}H NMR (300 MHz, $CDCl_3$, ***trans*-enamide**) δ = 1.62 (3H, dd, *J* = 6.6, 1.7 Hz, CH*CH*$_3$), 2.02 (3H, s, Ac), 2.35 (1H, d, *J* = 18.3 Hz, NCO*CH*$_2$), 2.78 (1H, dd, *J* = 18.3, 6.0 Hz, NCO*CH*$_2$), 3.76 (3H, s, O*CH*$_3$), 4.70 (1H, br. s, N*CH*CHOAc), 4.77 (1H, dq, *J* = 14.4, 6.6 Hz, NCH*CH*CH$_3$), 5.04 (1H, br. d, *J* = 6.0 Hz, NCH*CH*OAc), 5.50 (1H, br. s, C*CH*$_2$), 6.31 (1H, br. s, C*CH*$_2$), 6.76 (1H, dq, *J* = 14.4, 1.7 Hz, N*CH*CHCH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, ***trans*-enamide**) δ = 15.3, 21.0, 36.7, 52.4, 63.9, 71.4, 109.1, 122.3, 127.0, 134.2, 165.4, 170.0, 170.3. ^{1}H NMR (300 MHz, $CDCl_3$, ***cis*-enamide**) δ = 1.60 (3H, dd, *J* = 6.6, 1.7 Hz, CH*CH*$_3$), 1.91 (3H, s, Ac), 2.51 (1H, dd, *J* = 17.1, 8.3 Hz, NCO*CH*$_2$), 2.75 (1H, dd, *J* = 17.1, 8.6 Hz, NCO*CH*$_2$), 3.73 (3H, s, O*CH*$_3$), 4.77 (1H, dq, *J* = 14.4, 6.6 Hz, NCH*CH*CH$_3$), 5.03 (1H, br. d, *J* = 8.0 Hz, N*CH*CHOAc), 5.52 (1H, app. q, *J* = 8.3 Hz, NCH*CH*OAc), 5.49 (1H, br. s, C*CH*$_2$), 6.36 (1H, br. s, C*CH*$_2$), 6.72 (1H, dq, *J* = 14.4, 1.7 Hz, N*CH*CHCH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, ***cis*-enamide**, observed signals) δ = 15.3, 20.6, 35.5, 52.2, 67.0, 109.6. HRMS (mixture of isomers) found: m/z (CI) 268.1182 $C_{13}H_{18}NO_5$ $(M+H)^+$ requires 268.1185.

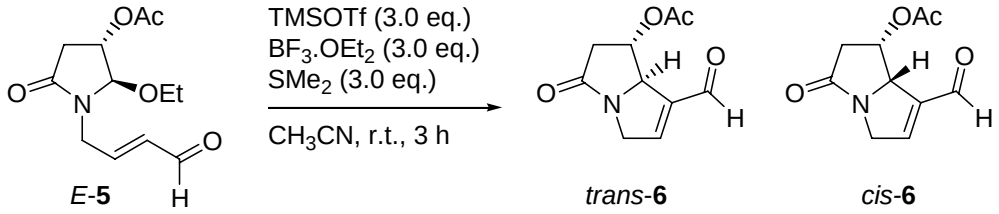
(2*R*,3*S*)-2-ethoxy-5-oxo-1-[(2*E*)-4-oxo-2-butenyl]pyrrolidinyl acetate (*E*- 5)



trans-**3** *E*-**5**

To a solution of aminal *trans*-**3** (262 mg, 1.15 mmol) in CH_2Cl_2 (3.0 ml) was added acrolein (0.25 ml, 3.46 mmol) and Grubbs-Hoveyda catalyst (36 mg, 0.06 mmol). The green solution was allowed to stir under an atmosphere of N_2 for 2 hours at room temperature. To the brown-coloured solution, was added an additional 5 mol% of catalyst (36 mg, 0.06 mmol) and was allowed to stir overnight under N_2 at room temperature. The solution was concentrated *in vacuo* and purified by column chromatography (eluent: pet. ether/EtOAc 3:2) to give aldehyde *E*-**5** as brown oil (220 mg, 0.86 mmol, 74% yield). IR ν_{max} (neat) / cm^{-1} 1740, 1707, 1684; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.21 (3H, dd, *J* = 7.1, 6.8 Hz, OCH_2CH_3), 2.10 (3H, s, Ac), 2.38 (1H, d, *J* = 18.1 Hz, $NCOCH_2$), 2.91 (1H, dd, *J* = 18.1, 6.3 Hz, $NCOCH_2$), 3.54 (1H, dq, *J* = 9.3, 6.8 Hz, OCH_2CH_3), 3.73 (1H, dq, *J* = 9.3, 7.1 Hz, OCH_2CH_3), 4.02 (1H, dddd, *J* = 17.8, 5.4, 1.7, 0.7 Hz, NCH_2), 4.37 (1H, ddd, *J* = 17.8, 4.4, 1.7 Hz, NCH_2), 4.64 (1H, br. s, NCHOEt), 5.10 (1H, br. d, *J* = 6.3 Hz, CHOAc), 6.15 (1H, ddt, *J* = 15.6, 7.7, 1.7 Hz, CHCHO), 6.75 (1H, ddd, *J* = 15.6, 5.4, 4.4, NCH_2CH), 9.56 (1H, d, *J* = 7.7 Hz, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 15.1, 20.9, 31.1, 41.3, 64.1, 70.3, 92.8, 132.8, 150.7, 170.2, 172.5, 192.7. HRMS Found: m/z (CI) 256.1178 $C_{12}H_{18}NO_5$ $(M+H)^+$ requires 256.1185.

(1*S*,7a*R*)-7-formyl-3-oxo-2,3,5,7a-tetrahydro-1*H*-pyrrolizin-1-yl acetate (*trans*-6) and (1*S*,7a*S*)-7-formyl-3-oxo-2,3,5,7a-tetrahydro-1*H*-pyrrolizin-1-yl acetate (*cis*-6)

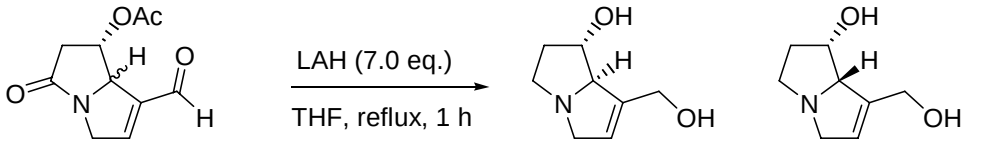


E-**5** *trans*-**6** *cis*-**6**

To a solution of aminal *E*-**5** (220 mg, 0.86 mmol) in CH_3CN (1.5 ml) was added TMSOTf (0.47 ml, 2.59 mmol), $BF_3.OEt_2$ (0.33 ml, 2.59 mmol) and SMe_2 (0.19 ml, 2.59 mmol). The red-brown solution was allowed to stir for 3 hours at room temperature. The solution was quenched with sat. aq. $NaHCO_3$ (10 ml) and the organics extracted with CH_2Cl_2 (2×20 ml), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The oily residue was purified by column chromatography (eluent: 2% MeOH in CH_2Cl_2) to give

bicycle **6** as a waxy solid (102 mg, 0.49 mmol, 57% yield, trans:cis = 3:1). IR ν_{max} (neat) / cm^{-1} (on mixture of isomers) 1738, 1704, 1677; ^{1}H NMR (400 MHz, $CDCl_3$, ***trans*-6**) δ = 2.18 (3H, s, Ac), 2.75 (1H, ddd, *J* = 16.4, 9.5, 1.0 Hz, NCO*CH*$_2$), 2.85 (1H, dd, *J* = 16.4, 8.3 Hz, NCO*CH*$_2$), 3.94 (1H, dddd, *J* = 18.6, 4.4, 1.7, 1.0 Hz, N*CH*$_2$), 4.72 (1H, br. ddd, *J* = 18.6, 4.0, 2.4 Hz, *NCH*$_2$), 4.83 (1H, dddd, *J* = 6.6, 4.4, 4.0, 2.0 Hz, N*CH*R), 5.35 (1H, ddd, *J* = 9.5, 8.3, 6.6 Hz, *CH*(OAc)), 6.94 (1H, app. q, *J* = 2.0, NCH$_2$*CH*), 9.80 (1H, s, *CH*O); ^{13}C NMR (100 MHz, $CDCl_3$, ***trans*-6**) δ = 20.8, 39.6, 50.6, 69.2, 72.5, 144.1, 146.6, 170.0, 174.4, 186.3; ^{1}H NMR (400 MHz, $CDCl_3$, ***cis*-6**) δ = 1.91 (3H, s, Ac), 2.40 (1H, d, *J* = 17.2 Hz, NCO*CH*$_2$), 3.03 (1H, dd, *J* = 17.2, 4.6 Hz, NCO*CH*$_2$), 4.00 (1H, dddd, *J* = 18.6, 4.2, 1.7, 1.0 Hz, N*CH*$_2$), 4.72 (1H, m, N*CH*$_2$), 5.08 (1H, ddd, *J* = 4.4, 4.2, 2.0 Hz, N*CH*R), 5.67 (1H, dd, *J* = 4.6, 4.4 Hz, *CH*(OAc)), 6.97 (1H, app. td, *J* = 2.0, 1.0, NCH$_2$*CH*), 9.80 (1H, s, *CH*O); ^{13}C NMR (100 MHz, $CDCl_3$, ***cis*-6**) δ = 20.7, 41.3, 50.5, 69.1, 72.3, 141.6, 146.5, 169.4, 175.7, 186.4; HRMS (mixture of isomers) found: m/z (CI) 210.0761 $C_{10}H_{12}NO_4$ $(M+H)^+$ requires 210.0766.

(+)-Heliotridine and (-)-retronecine 7

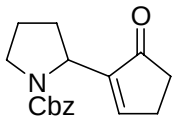


6 (dr = 3:1) (+)-heliotridine (-)-retronecine **7**

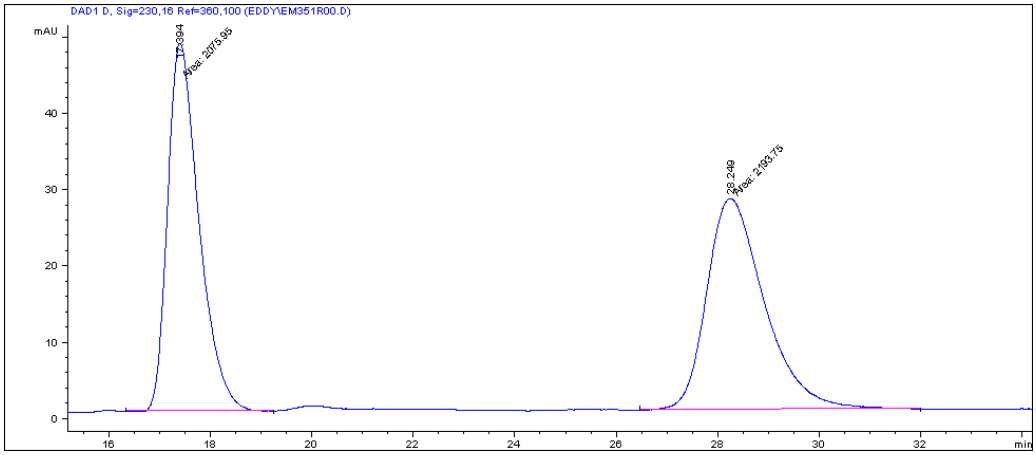
To a solution of aldehyde **6** (100 mg, 0.48 mmol) in dry THF (5 ml) was added $LiAlH_4$ (127 mg, 3.33 mmol). The resultant suspension was heated at reflux for 1 hour. The suspension was then cooled to 0 ^oC and diluted with THF (5 ml). The suspension was then treated with water (100 μl), 1M NaOH (120 ml) and water (100 ml) sequentially. The resultant suspension was then filtered through Celite® and the residue washed with THF (25 ml). The residue was then suspended in 50 ml of MeOH-THF (1:1) and filtered (×2). The combined filtrates were concentrated in vacuo to give a yellow gum. Purification by column chromatography (eluent: 1% NH_4OH in MeOH) provided (+)-heliotridine (28 mg, 0.18 mmol, 38% yield) as a pale yellow waxy solid and (-)-retronecine as an oil (9 mg, 0.06 mmol, 12% yield). Data for **(+)-heliotridine**: $[\alpha]^{24}_D$ +33.8 (*c* 0.59, MeOH) [lit.[14] $[\alpha]^{30}_D$ +32 (*c* 0.22, MeOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.78-2.00 (2H, m, NCH$_2$*CH*$_2$), 2.60 (1H, ddd, *J* = 6.0, 6.2, 11.2 Hz, N*CH*$_2$CH$_2$), 3.24-3.37 (2H, m, N*CH*$_2$CH$_2$ and N*CH*$_2$CH), 3.89 (1H, br. d, *J* = 15.4 Hz, N*CH*$_2$CH), 4.06 (1H, b, N*CH*), 4.08- 4.14 (1H, m,), 4.27 (2H, AB, *J* = 14.5 Hz, *CH*$_2$OH), 4.40 (2H, br. s, OH), 5.52 (1H, br. s, NCH$_2$*CH*). [lit.[14] 1.84-1.90 (1H, m), 1.97-2.03 (1H, m), 2.65 (1H, ddd, *J* = 14.0, 8.0, 6.1 Hz), 3.12 (2H, br. s), 3.29-3.35 (2H, m), 3.68 (1H, dt, *J* = 15.4, 2.0 Hz), 3.97 (1H, br. s), 4.07 (1H, q, *J* = 5.9 Hz), 4.32 (2H, AB q, *J* = 13.4 Hz), 5.53 (1H, d, *J* = 1.5 Hz)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 33.5, 54.1, 59.3, 62.1, 74.7, 80.0, 122.8, 141.3. [lit.[15] 33.8, 54.4, 59.6, 62.4, 75.0, 80.3, 123.0, 141.6]. Data for **(-)-retronecine 7**: ^{1}H NMR (300 MHz, CD_3OD) δ = 1.87-2.00 (2H, m, NCH$_2$*CH*$_2$), 2.78 (1H, ddd, *J* = 11.4, 9.5, 6.6 Hz, N*CH*$_2$CH$_2$), 3.20-3.28 (1H, m, N*CH*$_2$CH$_2$), 3.43 (1H, br. d, *J* = 15.0 Hz, N*CH*$_2$CH), 3.86 (1H, br. d, *J* =15.0 Hz, N*CH*$_2$CH), 4.14-4.27 (3H, m, N*CH* and *CH*$_2$OH),

4.30-4.35 (1H, m, *CH*OH), 5.68-5.71 (1H, m, NCH_2*CH*). [lit.[16] 1.89-1.99 (2H, m), 2.68-2.79 (1H, m), 3.17 (1H, ddd, *J* = 9.1, 6.7, 2.3 Hz), 3.39 (1H, dddd, *J* = 15.1, 5.3, 3.6, 1.8 Hz), 3.81 (1H, dddd, *J* = 8.0, 3.8, 1.8, 1.8 Hz), 4.12-4.33 (3H, m), 4.29-4.33 (1H, m), 5.66-5.68 (1H, m)]; ^{13}C NMR (75 MHz, CD_3OD) δ = 36.7, 54.8, 59.7, 63.0, 71.8, 79.4, 125.5, 139.9 [lit.[16] 36.7, 54.8, 59.7, 63.0, 72.0, 79.4, 125.8, 140.2].

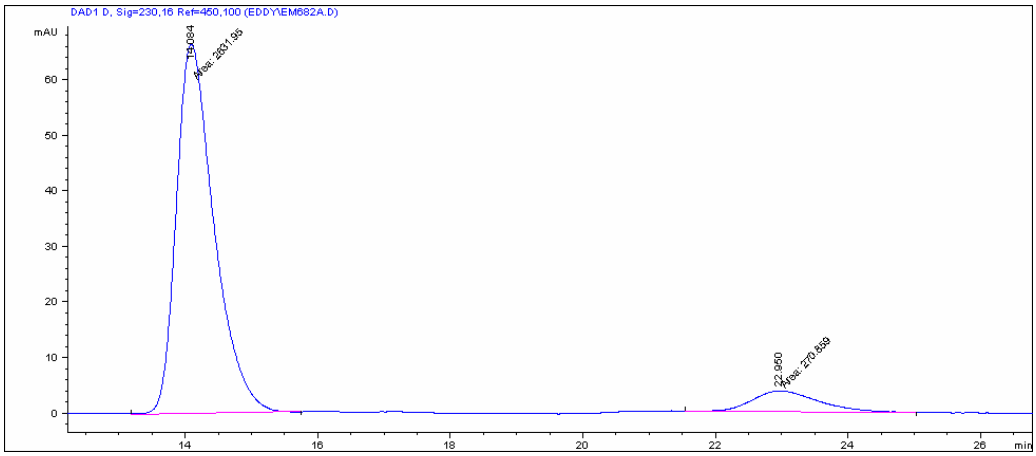
Chiral HPLC traces

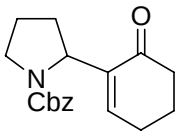


(a) HPLC of racemate **2b**

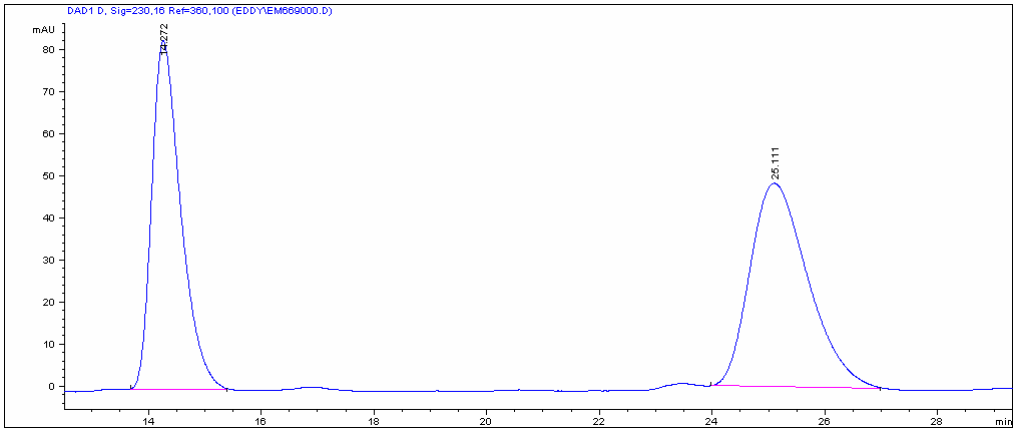


(b) HPLC of enantiomerically enriched product **2b** (from sulfide **8**) 82% ee

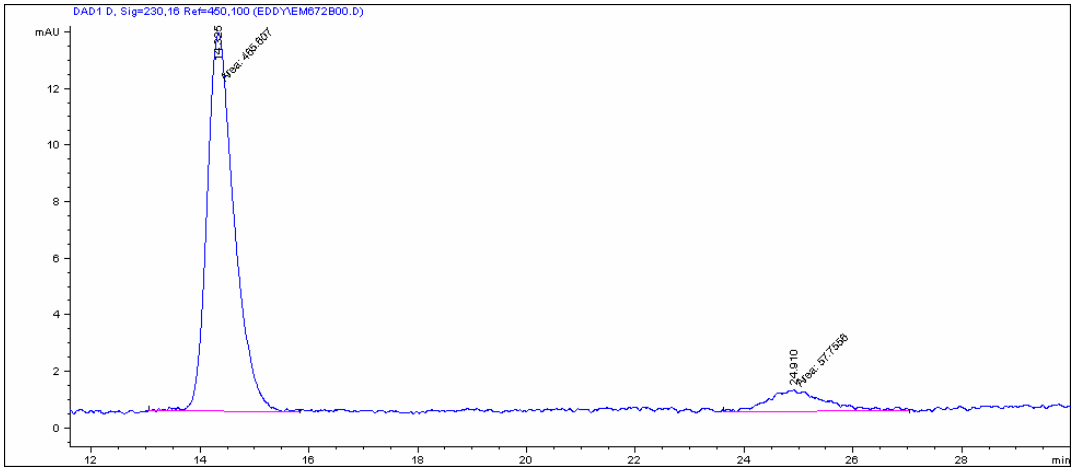


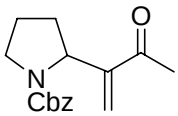


(a) HPLC of racemate **2c**

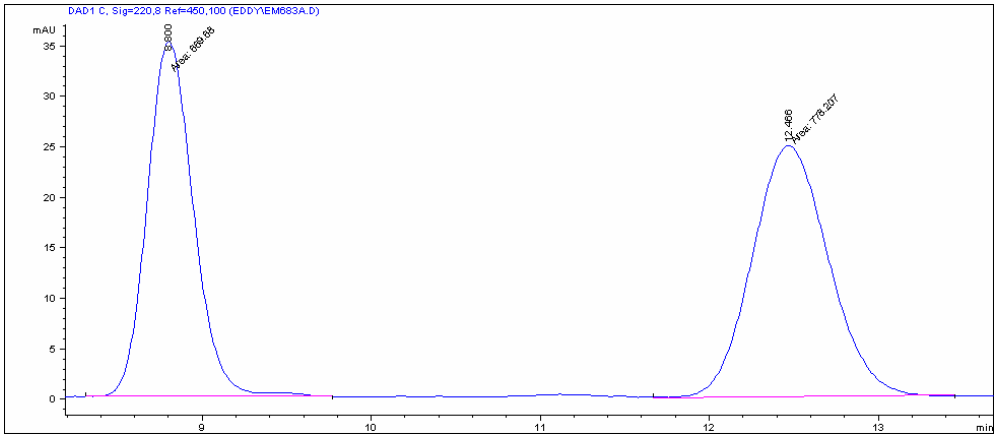


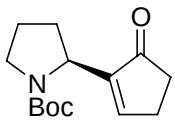
(b) HPLC of enantiomerically enriched product **2c** (from sulfide **8**) 80% ee



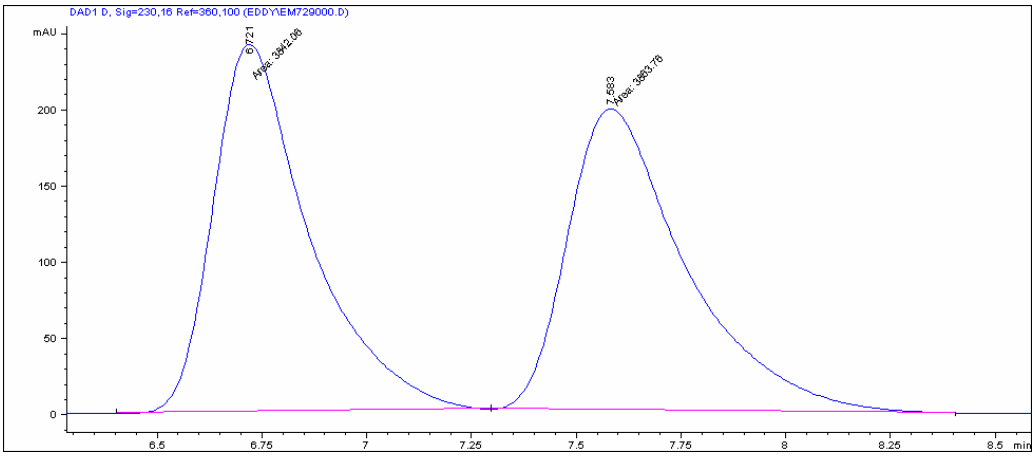


(a) HPLC of enantiomerically enriched product **2a** (from sulfide **8**) 8% ee

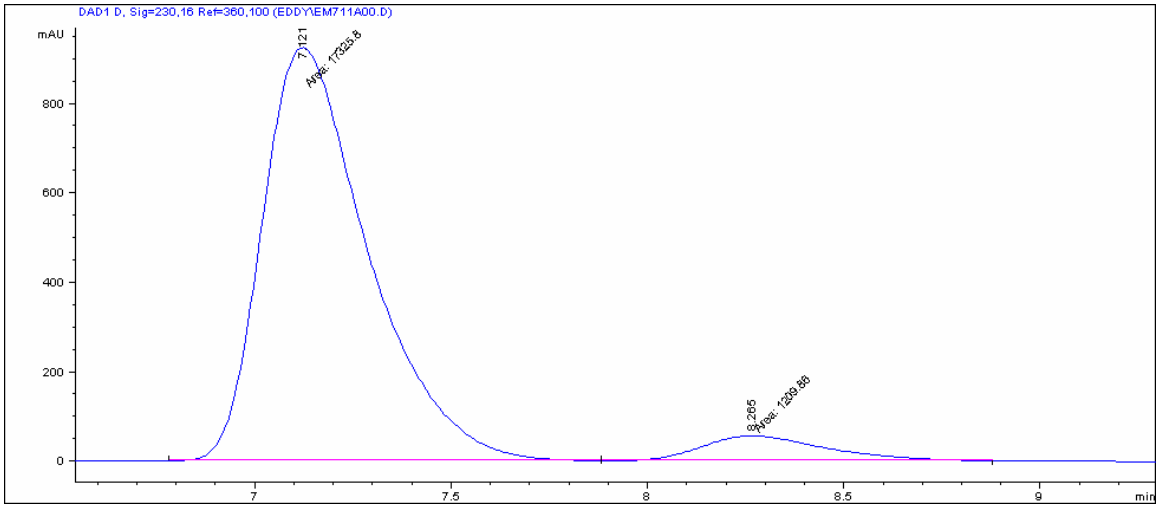


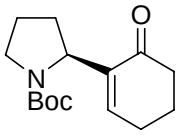


(a) HPLC of racemate **2j**

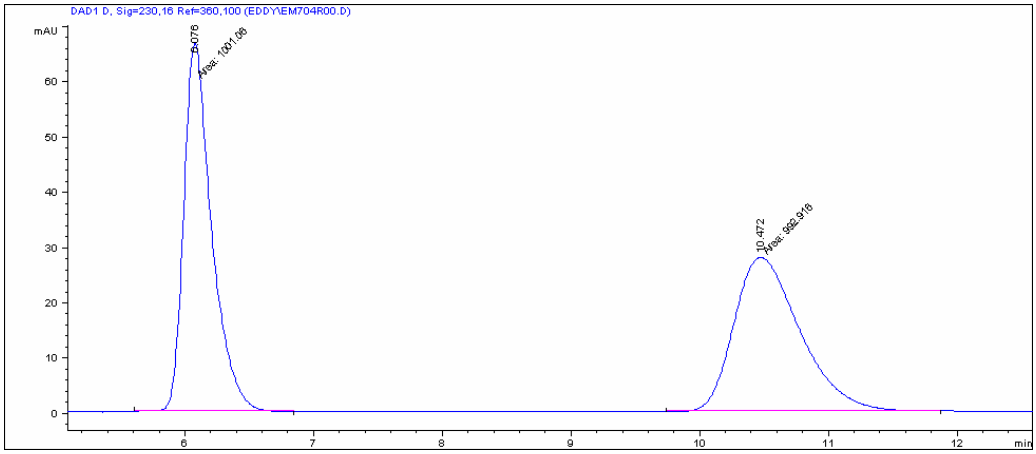


(b) HPLC of enantiomerically enriched product **2j** (from sulfide **8**)

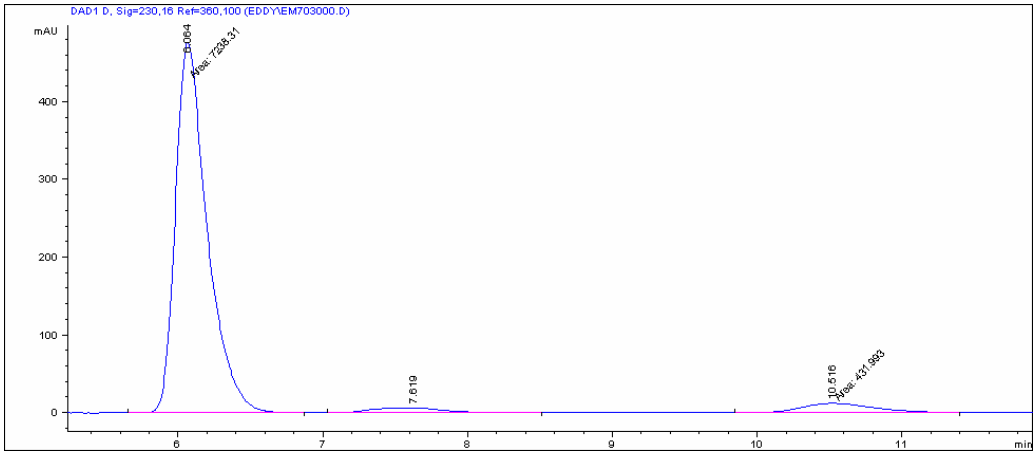


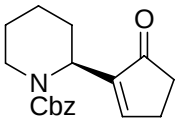


(a) HPLC of racemate **2k**

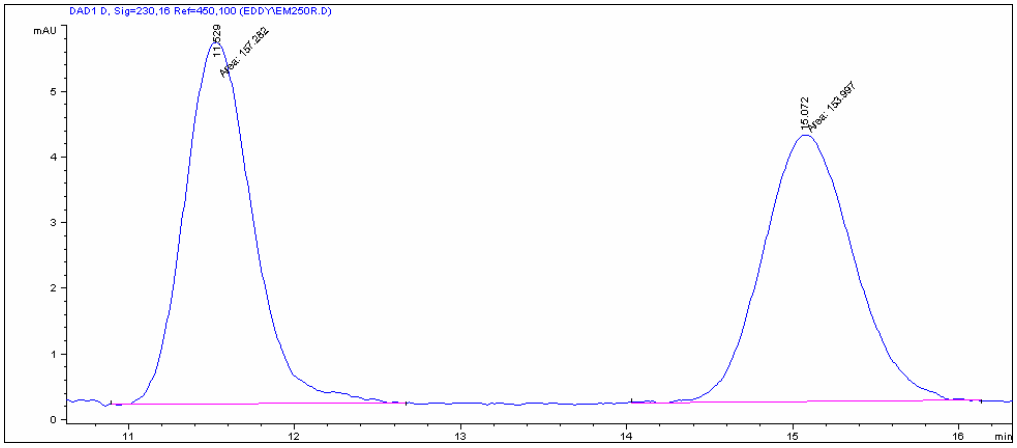


(b) HPLC of enantiomerically enriched product **2k** (from sulfide **8**) 88% ee

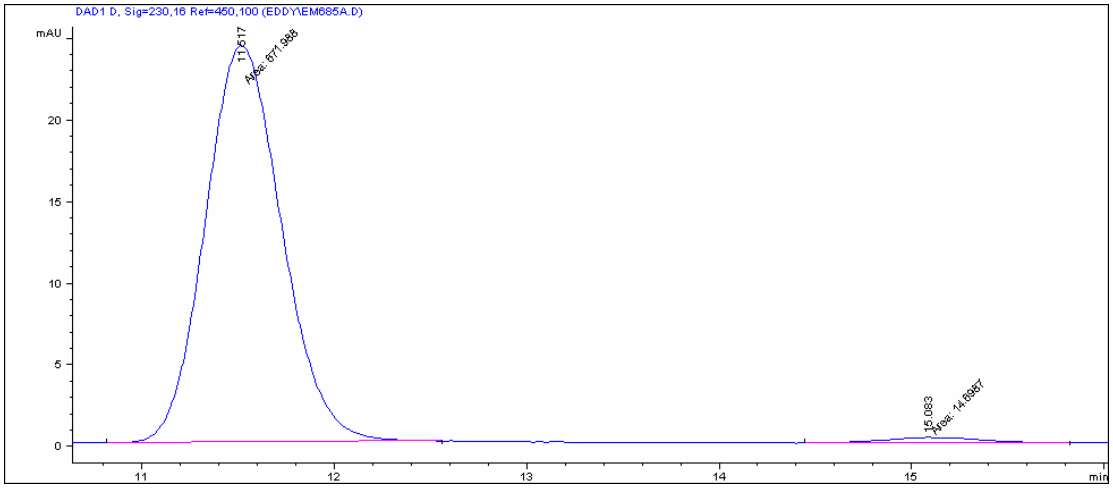


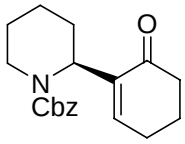


(a) HPLC of racemate **2h**

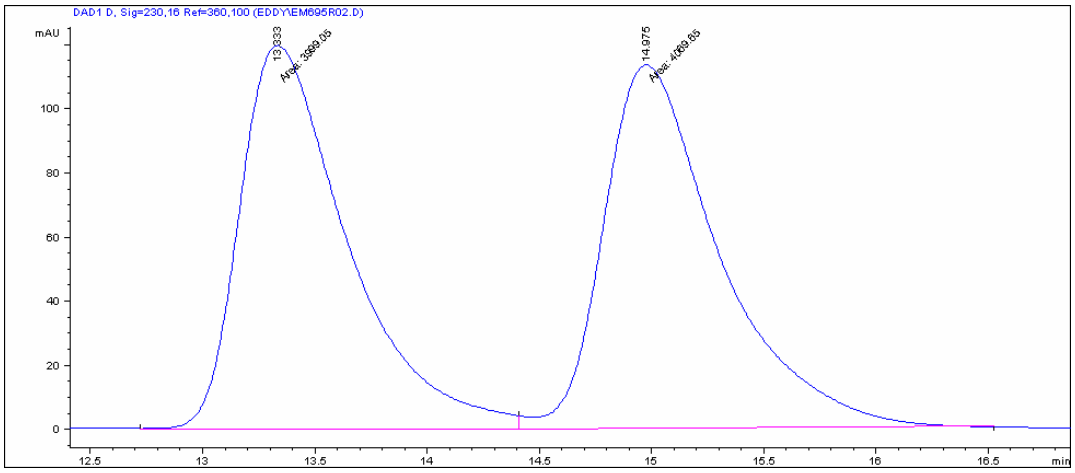


(b) HPLC of enantiomerically enriched product **2h** (from sulfide **8**) 94% ee

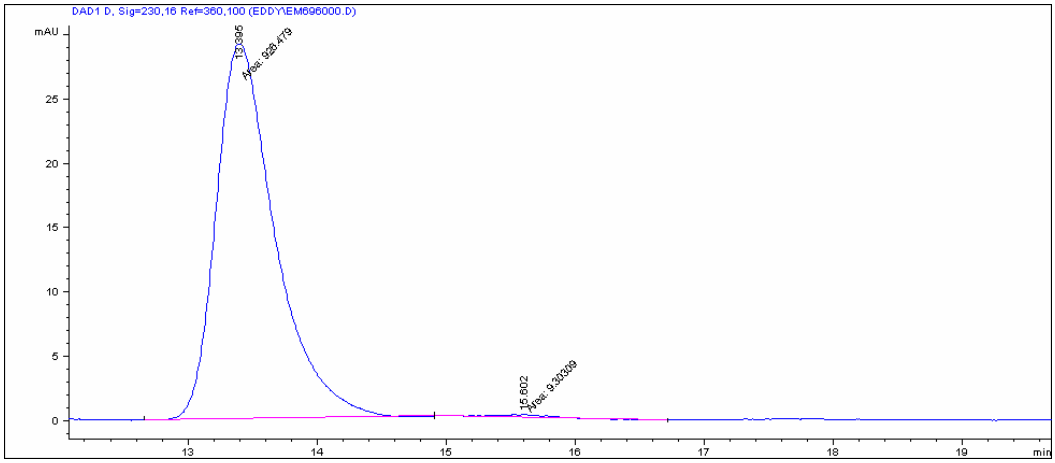




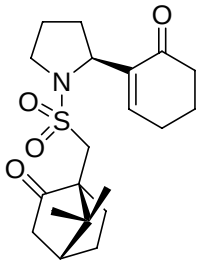
(a) HPLC of racemate **2i**

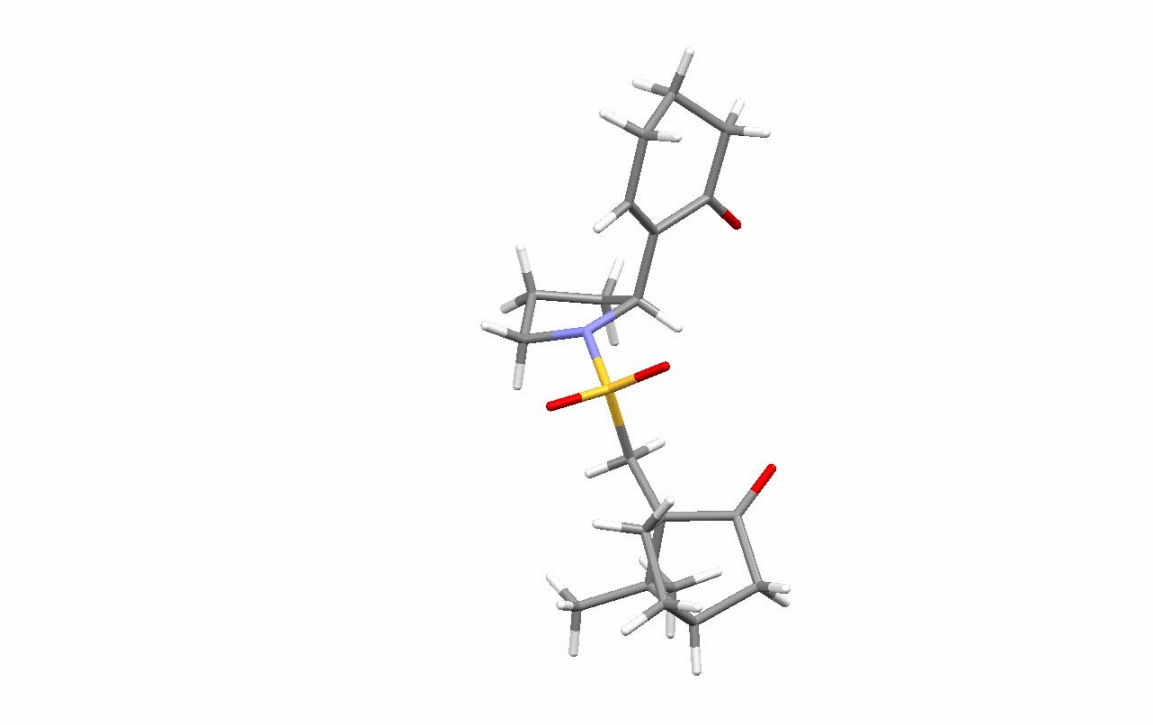


(b) HPLC of enantiomerically enriched product **2i** (from sulfide **8**) 98% ee



X-Ray Structure of Sulfonamide





Structure Report for Sulfonamide

Crystallographic data are presented in the Tables below. A single crystal of **sulfonamide** was coated in perfluoropolyether oil and mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo -K_α radiation (λ = 0.71074 Å).[17] Intensities were integrated[18] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being almost a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[19] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 1).[20] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. The positions of the methyl hydrogen atoms were assigned by a rotating group refinement with fixed, idealised C-H distances. All other hydrogen atoms were constrained to ideal geometries. All hydrogen atoms were assigned isotropic displacement parameters

equal to 1.5 times (methyl hydrogen atoms) or 1.2 times (all other hydrogen atoms) that of their parent atom. Refinement proceeded smoothly to give the residuals shown in Table 1. Complex neutral-atom scattering factors were used.[21]

Table 1. Crystal data and structure refinement for **sulfonamide**.

Identification code	myers-p21	
Empirical formula	C20 H29 N O4 S	
Formula weight	379.50	
Temperature	173 K	
Wavelength	0.71074 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.4144(7) Å	α = 90°
	b = 10.4516(7) Å	β = 105.1160(10)°
	c = 17.2959(11) Å	γ = 90°
Volume	1992.0(2) Å^3	
Z	4	
Density (calculated)	1.265 Mg/m^3	
Absorption coefficient	0.187 mm^{-1}	
F(000)	816	
Crystal size	0.50 x 0.40 x 0.20 mm	
θ range for data collection	1.22 to 25.00°	
Index ranges	-13<=h<=13, -12<=k<=12, -20<=l<=20	
Reflections collected	17805	
Independent reflections	7017 [R_{int} = 0.0477]	
Completeness to θ = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.960 and 0.796	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7017 / 1 / 473	
Goodness-of-fit on F^2	S = 1.010	
R indices [for 5474reflections with $I>2\sigma(I)$]	R_1 = 0.0428, wR_2 = 0.0846	
R indices (for all 7017 data)	R_1 = 0.0666, wR_2 = 0.0938	
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2$,	
	where $P = [\max(F_o^2, 0) + 2F_c^2]/3$	
	a = 0.0435	

Absolute structure (Flack) parameter	0.05(6)
Largest diff. peak and hole	0.216 and -0.266 eÅ^{-3}

Table 2. Bond lengths [Å] and angles [°] for **sulfonamide**.

S(1)-O(2)	1.430(2)
S(1)-O(3)	1.432(2)
S(1)-N(1)	1.616(2)
S(1)-C(11)	1.788(3)
S(2)-O(6)	1.4270(19)
S(2)-O(7)	1.432(2)
S(2)-N(2)	1.625(2)
S(2)-C(31)	1.784(3)
O(1)-C(1)	1.214(4)
O(4)-C(13)	1.207(4)
O(5)-C(22)	1.211(3)
O(8)-C(33)	1.209(4)
N(1)-C(7)	1.480(4)
N(1)-C(10)	1.496(4)
N(2)-C(27)	1.485(4)
N(2)-C(30)	1.485(3)
C(1)-C(6)	1.482(4)
C(1)-C(2)	1.513(4)
C(2)-C(3)	1.513(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.519(5)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.487(4)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.334(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.511(4)

C(7)-C(8)	1.537(4)
C(7)-H(7)	1.0000
C(8)-C(9)	1.505(5)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.516(5)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.521(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.526(4)
C(12)-C(17)	1.562(4)
C(12)-C(18)	1.564(4)
C(13)-C(14)	1.522(5)
C(14)-C(15)	1.527(5)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.531(4)
C(15)-C(18)	1.545(4)
C(15)-H(15)	1.0000
C(16)-C(17)	1.556(5)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(20)	1.523(4)
C(18)-C(19)	1.529(4)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(21)-C(26)	1.327(4)
C(21)-C(22)	1.479(4)
C(21)-C(27)	1.515(4)
C(22)-C(23)	1.501(4)
C(23)-C(24)	1.514(5)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.503(5)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.505(4)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-H(26)	0.9500
C(27)-C(28)	1.522(4)
C(27)-H(27)	1.0000
C(28)-C(29)	1.503(6)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.490(5)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-C(32)	1.515(4)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-C(33)	1.522(4)
C(32)-C(38)	1.559(4)
C(32)-C(37)	1.569(4)
C(33)-C(34)	1.511(4)
C(34)-C(35)	1.526(5)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.535(5)
C(35)-C(38)	1.550(4)

C(35)-H(35)	1.0000
C(36)-C(37)	1.546(4)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-C(39)	1.526(4)
C(38)-C(40)	1.526(4)
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800

O(2)-S(1)-O(3)	119.29(13)
O(2)-S(1)-N(1)	107.08(12)
O(3)-S(1)-N(1)	106.91(13)
O(2)-S(1)-C(11)	108.22(13)
O(3)-S(1)-C(11)	108.87(14)
N(1)-S(1)-C(11)	105.66(13)
O(6)-S(2)-O(7)	118.97(12)
O(6)-S(2)-N(2)	107.48(12)
O(7)-S(2)-N(2)	106.56(12)
O(6)-S(2)-C(31)	109.31(13)
O(7)-S(2)-C(31)	108.03(13)
N(2)-S(2)-C(31)	105.69(13)
C(7)-N(1)-C(10)	110.3(2)
C(7)-N(1)-S(1)	119.91(18)
C(10)-N(1)-S(1)	118.7(2)
C(27)-N(2)-C(30)	111.1(2)
C(27)-N(2)-S(2)	118.98(19)
C(30)-N(2)-S(2)	118.26(19)
O(1)-C(1)-C(6)	120.8(3)
O(1)-C(1)-C(2)	121.7(3)
C(6)-C(1)-C(2)	117.4(3)

C(3)-C(2)-C(1)	112.0(3)
C(3)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2A)	109.2
C(3)-C(2)-H(2B)	109.2
C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
C(2)-C(3)-C(4)	110.6(3)
C(2)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
C(4)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	108.1
C(5)-C(4)-C(3)	110.9(3)
C(5)-C(4)-H(4A)	109.4
C(3)-C(4)-H(4A)	109.4
C(5)-C(4)-H(4B)	109.4
C(3)-C(4)-H(4B)	109.4
H(4A)-C(4)-H(4B)	108.0
C(6)-C(5)-C(4)	125.5(3)
C(6)-C(5)-H(5)	117.2
C(4)-C(5)-H(5)	117.2
C(5)-C(6)-C(1)	119.3(3)
C(5)-C(6)-C(7)	124.7(3)
C(1)-C(6)-C(7)	116.0(3)
N(1)-C(7)-C(6)	111.5(2)
N(1)-C(7)-C(8)	102.7(2)
C(6)-C(7)-C(8)	112.2(2)
N(1)-C(7)-H(7)	110.1
C(6)-C(7)-H(7)	110.1
C(8)-C(7)-H(7)	110.1
C(9)-C(8)-C(7)	102.6(3)
C(9)-C(8)-H(8A)	111.3
C(7)-C(8)-H(8A)	111.3
C(9)-C(8)-H(8B)	111.3
C(7)-C(8)-H(8B)	111.3
H(8A)-C(8)-H(8B)	109.2

C(8)-C(9)-C(10)	104.3(3)
C(8)-C(9)-H(9A)	110.9
C(10)-C(9)-H(9A)	110.9
C(8)-C(9)-H(9B)	110.9
C(10)-C(9)-H(9B)	110.9
H(9A)-C(9)-H(9B)	108.9
N(1)-C(10)-C(9)	103.6(3)
N(1)-C(10)-H(10A)	111.0
C(9)-C(10)-H(10A)	111.0
N(1)-C(10)-H(10B)	111.0
C(9)-C(10)-H(10B)	111.0
H(10A)-C(10)-H(10B)	109.0
C(12)-C(11)-S(1)	118.2(2)
C(12)-C(11)-H(11A)	107.8
S(1)-C(11)-H(11A)	107.8
C(12)-C(11)-H(11B)	107.8
S(1)-C(11)-H(11B)	107.8
H(11A)-C(11)-H(11B)	107.1
C(11)-C(12)-C(13)	111.2(2)
C(11)-C(12)-C(17)	118.8(2)
C(13)-C(12)-C(17)	103.0(3)
C(11)-C(12)-C(18)	119.1(2)
C(13)-C(12)-C(18)	99.5(2)
C(17)-C(12)-C(18)	102.5(2)
O(4)-C(13)-C(14)	126.5(3)
O(4)-C(13)-C(12)	126.7(3)
C(14)-C(13)-C(12)	106.9(3)
C(13)-C(14)-C(15)	101.8(3)
C(13)-C(14)-H(14A)	111.4
C(15)-C(14)-H(14A)	111.4
C(13)-C(14)-H(14B)	111.4
C(15)-C(14)-H(14B)	111.4
H(14A)-C(14)-H(14B)	109.3
C(14)-C(15)-C(16)	106.6(3)
C(14)-C(15)-C(18)	102.5(3)
C(16)-C(15)-C(18)	103.0(2)

C(14)-C(15)-H(15)	114.5
C(16)-C(15)-H(15)	114.5
C(18)-C(15)-H(15)	114.5
C(15)-C(16)-C(17)	103.4(3)
C(15)-C(16)-H(16A)	111.1
C(17)-C(16)-H(16A)	111.1
C(15)-C(16)-H(16B)	111.1
C(17)-C(16)-H(16B)	111.1
H(16A)-C(16)-H(16B)	109.0
C(16)-C(17)-C(12)	103.4(2)
C(16)-C(17)-H(17A)	111.1
C(12)-C(17)-H(17A)	111.1
C(16)-C(17)-H(17B)	111.1
C(12)-C(17)-H(17B)	111.1
H(17A)-C(17)-H(17B)	109.0
C(20)-C(18)-C(19)	109.0(3)
C(20)-C(18)-C(15)	112.8(2)
C(19)-C(18)-C(15)	113.8(2)
C(20)-C(18)-C(12)	114.7(2)
C(19)-C(18)-C(12)	111.9(2)
C(15)-C(18)-C(12)	94.1(2)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(26)-C(21)-C(22)	119.7(3)
C(26)-C(21)-C(27)	124.4(3)
C(22)-C(21)-C(27)	115.7(3)

O(5)-C(22)-C(21)	121.1(3)
O(5)-C(22)-C(23)	120.9(3)
C(21)-C(22)-C(23)	117.9(3)
C(22)-C(23)-C(24)	113.1(3)
C(22)-C(23)-H(23A)	109.0
C(24)-C(23)-H(23A)	109.0
C(22)-C(23)-H(23B)	109.0
C(24)-C(23)-H(23B)	109.0
H(23A)-C(23)-H(23B)	107.8
C(25)-C(24)-C(23)	111.6(3)
C(25)-C(24)-H(24A)	109.3
C(23)-C(24)-H(24A)	109.3
C(25)-C(24)-H(24B)	109.3
C(23)-C(24)-H(24B)	109.3
H(24A)-C(24)-H(24B)	108.0
C(24)-C(25)-C(26)	110.9(3)
C(24)-C(25)-H(25A)	109.5
C(26)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
C(26)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	108.1
C(21)-C(26)-C(25)	124.7(3)
C(21)-C(26)-H(26)	117.7
C(25)-C(26)-H(26)	117.7
N(2)-C(27)-C(21)	111.7(2)
N(2)-C(27)-C(28)	102.3(3)
C(21)-C(27)-C(28)	113.2(2)
N(2)-C(27)-H(27)	109.8
C(21)-C(27)-H(27)	109.8
C(28)-C(27)-H(27)	109.8
C(29)-C(28)-C(27)	103.5(3)
C(29)-C(28)-H(28A)	111.1
C(27)-C(28)-H(28A)	111.1
C(29)-C(28)-H(28B)	111.1
C(27)-C(28)-H(28B)	111.1
H(28A)-C(28)-H(28B)	109.0

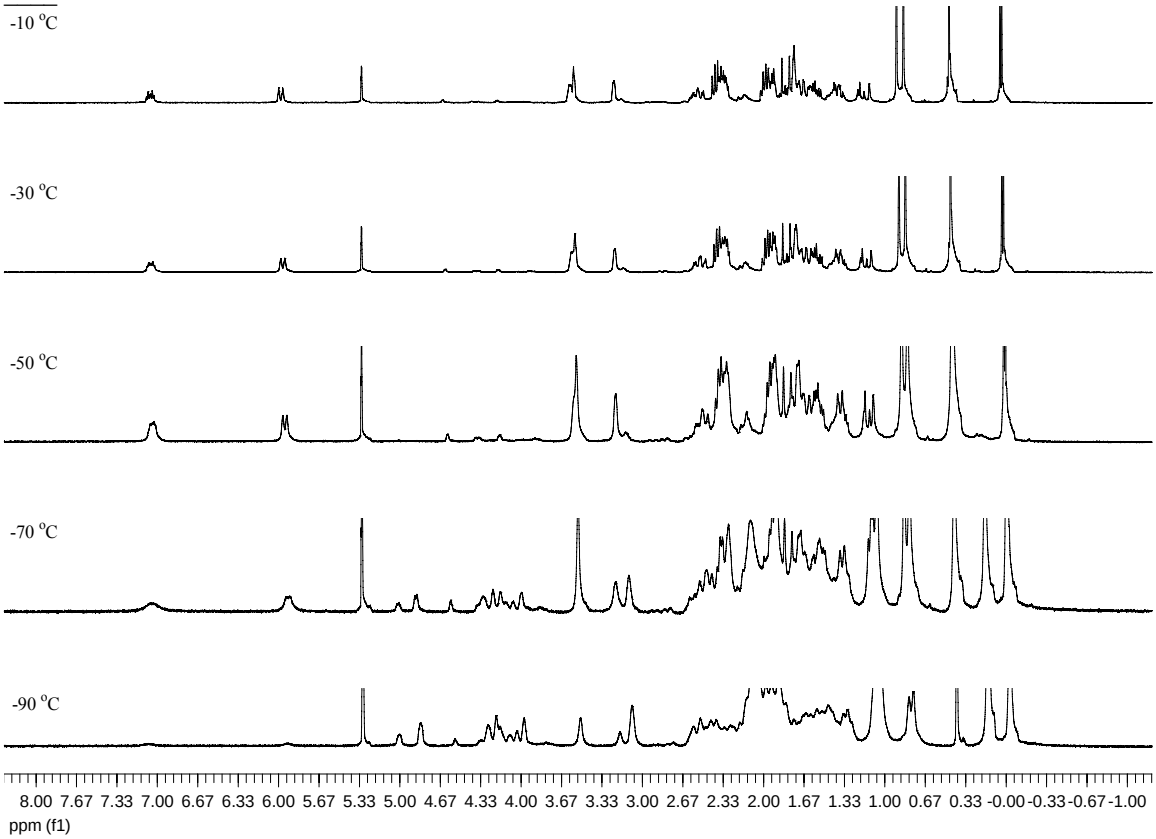
C(30)-C(29)-C(28)	103.8(3)
C(30)-C(29)-H(29A)	111.0
C(28)-C(29)-H(29A)	111.0
C(30)-C(29)-H(29B)	111.0
C(28)-C(29)-H(29B)	111.0
H(29A)-C(29)-H(29B)	109.0
N(2)-C(30)-C(29)	102.5(3)
N(2)-C(30)-H(30A)	111.3
C(29)-C(30)-H(30A)	111.3
N(2)-C(30)-H(30B)	111.3
C(29)-C(30)-H(30B)	111.3
H(30A)-C(30)-H(30B)	109.2
C(32)-C(31)-S(2)	117.4(2)
C(32)-C(31)-H(31A)	108.0
S(2)-C(31)-H(31A)	108.0
C(32)-C(31)-H(31B)	108.0
S(2)-C(31)-H(31B)	108.0
H(31A)-C(31)-H(31B)	107.2
C(31)-C(32)-C(33)	113.7(2)
C(31)-C(32)-C(38)	115.9(2)
C(33)-C(32)-C(38)	99.4(2)
C(31)-C(32)-C(37)	118.9(2)
C(33)-C(32)-C(37)	104.3(2)
C(38)-C(32)-C(37)	102.1(2)
O(8)-C(33)-C(34)	126.1(3)
O(8)-C(33)-C(32)	127.0(3)
C(34)-C(33)-C(32)	106.8(3)
C(33)-C(34)-C(35)	102.0(3)
C(33)-C(34)-H(34A)	111.4
C(35)-C(34)-H(34A)	111.4
C(33)-C(34)-H(34B)	111.4
C(35)-C(34)-H(34B)	111.4
H(34A)-C(34)-H(34B)	109.2
C(34)-C(35)-C(36)	107.3(3)
C(34)-C(35)-C(38)	102.4(2)
C(36)-C(35)-C(38)	102.9(3)

C(34)-C(35)-H(35)	114.3
C(36)-C(35)-H(35)	114.3
C(38)-C(35)-H(35)	114.3
C(35)-C(36)-C(37)	103.1(3)
C(35)-C(36)-H(36A)	111.1
C(37)-C(36)-H(36A)	111.1
C(35)-C(36)-H(36B)	111.1
C(37)-C(36)-H(36B)	111.1
H(36A)-C(36)-H(36B)	109.1
C(36)-C(37)-C(32)	103.7(2)
C(36)-C(37)-H(37A)	111.0
C(32)-C(37)-H(37A)	111.0
C(36)-C(37)-H(37B)	111.0
C(32)-C(37)-H(37B)	111.0
H(37A)-C(37)-H(37B)	109.0
C(39)-C(38)-C(40)	108.1(2)
C(39)-C(38)-C(35)	114.3(2)
C(40)-C(38)-C(35)	113.8(3)
C(39)-C(38)-C(32)	112.6(2)
C(40)-C(38)-C(32)	113.9(2)
C(35)-C(38)-C(32)	93.7(2)
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-H(40A)	109.5
C(38)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5

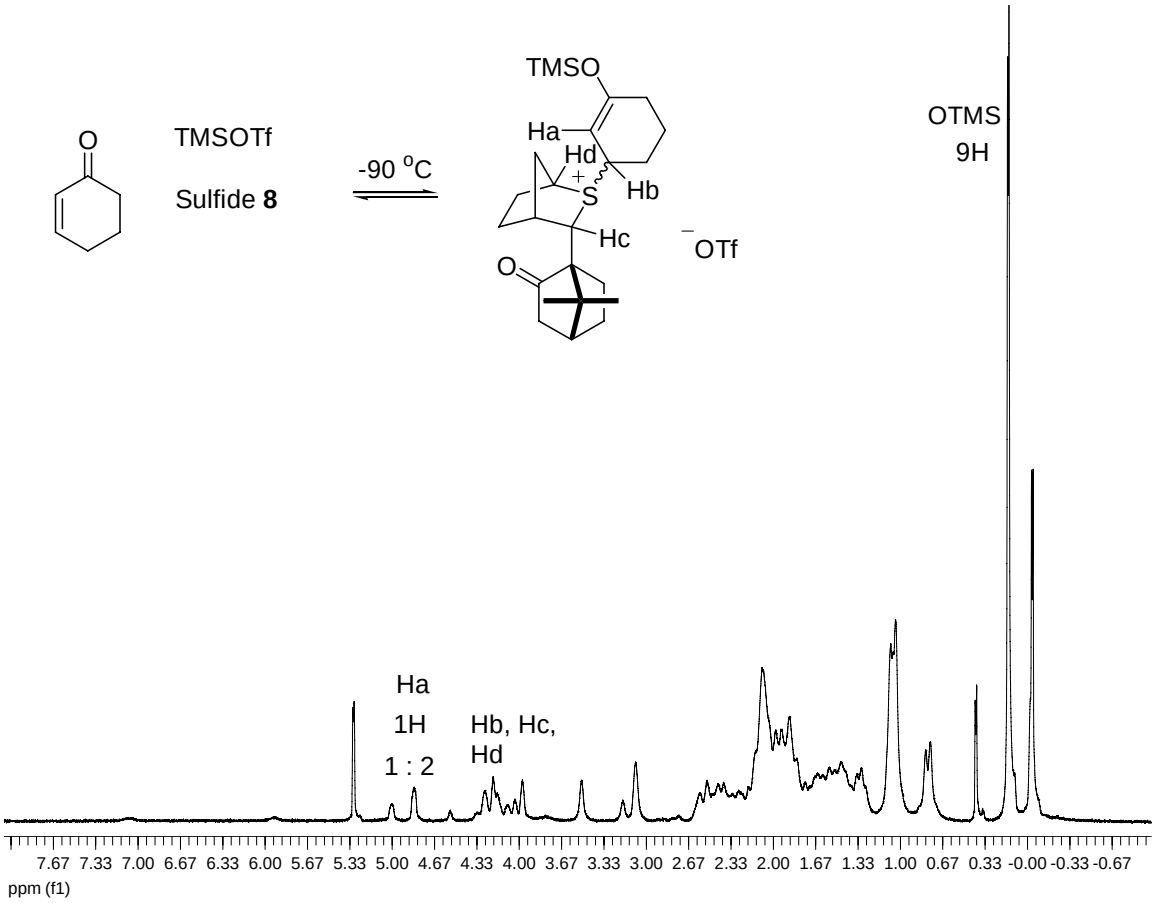
Low-temperature NMR Experiments- Observation of β-sulfonium silyl enol ethers derived from sulfide 8.

Sample preparation

To a dry NMR tube was added sequentially sulphide **8** (13 mg, 0.052 mmol), dry CD_2Cl_2 (0.6 ml), cyclohexenone (~5 μl, 0.052 mmol) and TMSOTf (~9 μl, 0.052 mmol). The sample was sealed with a Young ® valve and placed in a dry-ice acetone bath. Once the NMR probe of an Eclipse ECP/300 instrument was cooled to -10 ^{o}C, the NMR sample was removed from the dry-ice acetone bath and placed into the probe. A ^{1}H NMR spectrum was acquired at that temperature and at lower temperatures in increments of 20 degrees, namely -30, -50, -70 and -90 ^{o}C. The spectra are presented below.



An expansion of the spectrum acquired at -90 ^{o}C is presented below.



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