

Supporting Information

Rigid and concave, 2,4-*cis*-azetidine derivatives: A platform for asymmetric catalysis

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General apparatus and equipment

Reagents were used as purchased from commercial suppliers without further purification. Anhydrous solvents were dispensed from a solvent purification system (SPS), monitored by Karl-Fisher titrations for water levels. Proton NMR spectra were recorded at 300 MHz on a Bruker AVIII300 NMR spectrometer or at 400 MHz on a Bruker AVIII400 NMR spectrometer. All ¹³C NMR spectra are proton decoupled and recorded at 101 MHz on a Bruker AVIII400 NMR spectrometer or at 75.5 MHz on a Bruker AVIII300 NMR spectrometer, ¹⁹F NMR spectra are proton decoupled and recorded at 282 MHz on a Bruker AVIII300 NMR spectrometer. The PENDANT technique ((+) = CH and CH₃ and (-) = C and CH₂) and two-dimensional NMR spectroscopy were used to confirm assignments in some cases. Proton NMR chemical shifts are reported in ppm relative to TMS (δ 0.00) or residual solvent signals, ¹³C NMR shifts relative to chloroform (δ 77.36). Coupling constants *J* are given in Hertz (Hz). Melting points were carried out in triplicate and

an average of the values taken and reported as a range using StuartTM digital melting point apparatus (SMP10). Infrared spectra were recorded on a PerkinElmer 100 FT-IR spectrometer at room temperature. Optical rotations were recorded on a polar 2001 Automatic Polarimeter, measurements of each sample were recorded three times and the average used. The majority of column chromatography was carried out using a Combiflash Rf 200i (silica 4-12 g column), column traces were recorded at two wavelengths (254 nm and 280 nm) and ELS. However, amino azetidines **1** were typically purified by manual flash column chromatography, occasionally requiring repeat purifications in order to obtain analytically pure material. Enantiomeric excess (% *e.e.*) of products **6** were determined by HPLC (Shimadzu LC2010) using OD (Eurocel 01, 5 μ m) and amylose-1 (Lux[®] 5 μ m) column. All calculations were performed in Gaussian09. Minima and transition states were confirmed by computation of second-derivatives.

Experimental

General procedures

General procedure A: Preparation of N-tert butyl sulfinylamides S1

Pyridinium *p*-toluenesulfonate (0.05 equiv.) was added to a suspension of aldehyde (3.00 equiv.), (*R*)-*tert*-butylsulfinamide (1.00 equiv.) and anhydrous magnesium sulfate (5.00 equiv.) in dichloromethane (100 mL). The mixture was stirred for 24 hours and monitored by TLC. After the reaction was judged complete by TLC, magnesium sulfate was removed by filtration and the volatiles removed *in vacuo*. The crude material thus obtained was purified by column chromatography using a *Combiflash Rf 200i*.

General procedure B: Preparation of homoallyl sulfonamides S2

Allyl bromide (3.00 equiv.) was added to a suspension of activated zinc powder (3.00 equiv.) in anhydrous tetrahydrofuran (30 mL) at 0 °C and stirred for five minutes. Indium(III) triflate (1.30 equiv.) and (*E*)-*N-tert* butyl sulfinylamides **S1** (1.00 equiv.) were added and the mixture was stirred for 16 hours at room temperature. The reaction mixture was quenched by addition of saturated aqueous sodium bicarbonate solution, extracted with ethyl acetate (3 x 30 mL), washed with water (3 x 20 mL), dried over anhydrous magnesium sulfate, filtered and the volatile components were removed *in vacuo*. This material was purified by column chromatography using a *Combiflash Rf 200i*.

General procedure C: Preparation of primary homoallyl amines S3

Sulfinamides (**S2**) were added to the solution of hydrochloric acid (4.00 M in dioxane) and stirred for 16 hours at room temperature. The reaction mixture was quenched with water, extracted with dichloromethane (3 x 30 mL), washed with water (3 x 20 mL) and dried over magnesium sulfate and the volatile compounds were removed *in vacuo*.

General procedure D: Preparation of secondary homoallyl amines S4

To primary amines **S3** aldehydes (1.10 equiv.) were added in methanol and the reaction mixture was heated at reflux for 16 hours. The reaction mixture was allowed to cool to room temperature and excess sodium borohydride was added

to the reaction mixture which was stirred for a further three hours. The reaction mixture was quenched with distilled water and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with water (3 x 20 mL), dried over anhydrous magnesium sulfate and volatile components were removed *in vacuo*. This material was purified by column chromatography using a *Combiflash Rf 200i*.

*General procedure E: Cyclisation and derivatization of homoallylamines **S3** to synthesise azetidine derivatives **1***

Sodium hydrogen carbonate (5.00 equiv.) and iodine (3.00 equiv.) were added to a solution of homoallylamines **S3** (1.00 equiv.) in acetonitrile and the mixture was stirred at ≤ 20 °C for 16 hours. The reaction solution was quenched and washed with saturated aqueous sodium thiosulfate solution (2 x 10 mL), extracted with ethyl acetate (3 x 30 mL), washed with water (3 x 20 mL), dried over anhydrous magnesium sulfate, filtrated and the volatiles were removed *in vacuo*. The iodoazetidine thus formed (and confirmed by ^1H NMR spectroscopy) were not further manipulated and taken immediately on to the next step where they were stirred at room temperature for 48 hours in neat amine. Unreacted amines were removed *in vacuo* and the crude material was purified by flash column chromatography on silica.

General procedure F: Preparation of racemic Henry reaction adducts

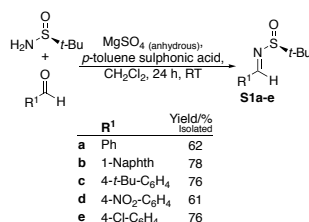
In order to identify analytical HPLC for enantiomeric excess determination of asymmetric catalyst mediated Henry reaction adducts, corresponding racemates were required to determine conditions for enantiomer separation/resolution by analytical HPLC using a chiral stationary phase. Aqueous sodium hydroxide solution (10 M, 1.00 equiv.) was added very slowly to a solution of aldehyde (1.00 equiv.) and nitromethane (1.00 equiv.) in ethanol. The reaction mixture was stirred at room temperature for 10 minutes then acetic acid (1.00 equiv.) was added and the mixture stirred for a further five minutes. Diethyl ether was added to the reaction mixture and the resulting precipitate was removed by filtration. The organic extracts were washed with water, dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*, the material obtained was purified by column chromatography using a *Combiflash Rf 200i*.

General procedure G: Standard conditions for the asymmetric Henry deploying azetidines as ligands

Amino azetidine ligands **1a-o** (0.025 mmol) and metal salt (0.025 mmol) were stirred at room temperature for 1 hour in solvent (1.00 mL). Aldehydes **5a-j** (0.50 mmol) and excess nitromethane (5 mmol) were added and the resulting mixture was stirred at a defined temperature for a specified amount of time. After the reaction was judged completed, as determined by TLC, the reaction was quenched by addition of saturated aqueous ammonium chloride solution (1 x 5 mL), extracted with diethyl ether (3 x 10 mL), washed with water (3 x 10 mL), dried over anhydrous magnesium sulfate, filtered and the volatiles were removed *in vacuo*. Conversion was determined by ^1H NMR spectroscopy and the residues were purified by a silica gel chromatography using a *Combiflash Rf 200i* to afford the nitroaldol products **6a-j**. The enantiomeric excess was determined by analytical HPLC using a chiral stationary phase.

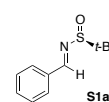
Synthesis

An Ellman auxiliary¹ route is used to deliver single enantiomer amines for cyclisation to azetidines according to a route previously described by us.² The first step is the synthesis of sulfinamides **S1a-e**, Scheme S 1, followed by allylation Scheme S 2 to **S2a-e**, auxiliary removal to **S3a-e** and reductive amination to **S4a-j** Scheme S 3. Subsequent iodine mediated cyclisation and direct iodine displacement by amines to give products **S5a-o** Scheme S 4

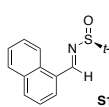


Scheme S 1. General procedure A leading to products **S1a-e**.

Synthesis of (*S*, *E*)-*N*-benzylidene-2-methylpropane-2-sulfinamide, **S1a**.

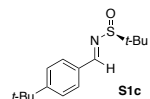
 Prepared using *General Procedure A* with (*S*)-*tert*-butanesulfinamide (2.00 g, 1.00 equiv., 16.5 mmol), benzaldehyde (5.25 g, 3.00 equiv., 49.5 mmol), pyridinium *p*-toluenesulfonate (207 mg, 0.05 equiv., 0.83 mmol), magnesium sulfate (9.93 g, 5.00 equiv., 82.5 mmol) and dichloromethane (100 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-20% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.³ Colourless oil (2.15 g, 10.3 mmol, 62%). TLC (EtOAc/*n*-hexane = 10:90 v/v, visualised by UV 254 nm): *R*_f = 0.29; ¹H NMR (300 MHz, CDCl₃): δ 8.60 (1H, s, CH=N), 7.82 (2H, dd, *J* 7.9 & 1.5, ArH), 7.56-7.45 (3H, m, ArH), 1.27 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 162.8 (CH, (+), CH=N), 134.1 (C, (-), Ar), 132.4 (CH, (+), Ar), 129.4 (CH, (+), Ar), 129.0 (CH, (+), Ar), 57.8 (C, (-), *t*-Bu), 22.6 (CH₃, (+), *t*-Bu); IR (neat) *v*_{max} = 3062 (w), 3026 (w), 2981 (m), 2930 (w), 1606 (s), 1450 (s), 1364 (m), 1084 (s) cm⁻¹ [lit (CHCl₃):^{3a} 2964, 1608, 1574, 1451, 1364, 1171, 1077 cm⁻¹]; MS TOF AP+ (*m/z*): 210.1 [M+H]⁺.

Synthesis of (*S*, *E*)-2-methyl-*N*-(naphthalen-1-ylmethylene)propane-2-sulfinamide, **S1b**.

 Prepared using *General Procedure A* with (*S*)-*tert*-butanesulfinamide (1.00 g, 1.00 equiv., 8.25 mmol), 1-naphthaldehyde (2.87 g, 3.00 equiv., 24.8 mmol), pyridinium *p*-toluenesulfonate (104 mg, 0.05 equiv., 0.41 mmol), magnesium sulfate (4.97 g, 5.00 equiv., 41.3 mmol) and dichloromethane (50 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-20% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.⁴ Yellow oil (1.67 g, 6.44 mmol, 78%). TLC (EtOAc/*n*-hexane = 5:95 v/v, visualised with KMnO₄): *R*_f = 0.15; ¹H NMR (300 MHz, CDCl₃): δ 9.16 (1H, s, CH=N), 9.04 (1H, d, *J* 8.6, ArH), 8.04 (2H, dd, *J* 7.1 & 8.2, ArH), 7.93 (1H, d, *J* 8.7, ArH), 7.68-7.55 (3H, m, ArH), 1.33 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 162.5 (CH, (+), CH=N), 133.9 (C, (-), Ar), 133.3 (CH, (+), Ar), 132.1 (CH, (+), Ar), 131.3 (C, (-), Ar), 129.4 (C, (-), Ar), 128.9 (CH, (+), Ar), 128.1 (CH, (+), Ar), 126.5 (CH, (+), Ar), 125.3 (CH, (+), Ar), 124.4 (CH, (+), Ar), 57.7 (C, (-), *t*-Bu), 22.7 (CH₃, (+), *t*-Bu); IR (neat) *v*_{max} = 3056 (w), 2960 (m), 1581 (s), 1511 (m), 1363 (m),

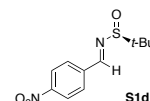
1175 (m), 1078 (s) cm^{-1} [lit⁴ (*R* isomer, KBr): 3054, 2965, 1579, 1512, 1364, 1178, 1073 cm^{-1}]; MS TOF ES+ (*m/z*): 282.1 [M+Na]⁺.

Synthesis of (S, E)-N-(4-(tert-butyl)benzylidene)-2-methylpropane-2-sulfinamide, S1c.



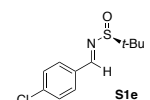
Prepared using *General Procedure A* with (*S*)-tert-butanethioamide (1.00 g, 1.00 equiv., 8.25 mmol), 4-*tert*-butylbenzaldehyde (4.01 g, 3.00 equiv., 24.8 mmol), pyridinium *p*-toluenesulfonate (104 mg, 0.50 equiv., 0.41 mmol), magnesium sulfate (4.97 g, 5.00 equiv., 41.3 mmol) and dichloromethane (50.0 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-20% EtOAc/*n*-hexane). White crystalline solid (1.67 g, 6.29 mmol, 76%). mp: 76-78 °C; TLC (EtOAc:*n*-hexane = 5:95 v/v, visualised with KMnO_4): R_f = 0.29; δ 8.57 (1H, s, CH=N), 7.80 (2H, d, *J* 8.4 Hz, ArH), 7.51 (2H, d, *J* 8.4 Hz, ArH), 1.35 (9H, s, *t*-Bu), 1.26 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl_3): δ 162.5 (CH, (+), CH=N), 156.2 (C, (-), Ar), 131.6 (C, (-), Ar), 129.3 (CH, (+), Ar), 126.0 (CH, (+), Ar), 57.7 (C, (-), *t*-Bu), 35.2 (C, (-), *t*-Bu), 31.1 (CH₃, (+), *t*-Bu), 22.6 (CH₃, (+), *t*-Bu); IR (solid) ν_{max} = 2961 (m), 2905 (m), 2869 (m), 1594 (s), 1561 (s), 1475 (m), 1411 (w), 1364 (s), 1084 (s) cm^{-1} ; MS TOF ES+ (*m/z*): 288.2 [M+Na]⁺.

Synthesis of (S, E)-2-Methyl-N-(4-nitrobenzylidene)propane-2-sulfinamide, S1d.



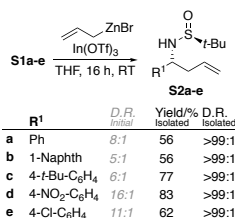
Prepared using *General Procedure A* with (*S*)-tert-butanethioamide (1.00 g, 1.00 equiv., 8.25 mmol), 4-nitrobenzaldehyde (3.74 g, 3.00 equiv., 24.8 mmol), pyridinium *p*-toluenesulfonate (104 mg, 0.05 equiv., 0.41 mmol), magnesium sulfate (4.97 g, 5.00 equiv., 41.3 mmol) and dichloromethane (50.0 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-5% Et₂O/ CH_2Cl_2). The characterisation reported is consistent with that given the literature.⁵ Pale yellow solid (1.29 g, 5.07 mmol, 61%). mp: 139-140 °C [lit:⁵ 140-142 °C]; TLC (Et₂O: CH_2Cl_2 = 2:98 v/v, visualised with KMnO_4): R_f = 0.46; ¹H NMR (300 MHz, CDCl_3): δ 8.68 (1H, s, CH=N), 8.35 (2H, d, *J* 8.8, ArH), 8.03 (2H, d, *J* 8.9, ArH), 1.30 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl_3): δ 160.7 (CH, (+), CH=N), 149.9 (C, (-), Ar), 138.9 (C, (-), Ar), 130.1 (CH, (+), Ar), 124.2 (CH, (+), Ar), 58.5 (C, (-), *t*-Bu), 22.7 (CH₃, (+), *t*-Bu); IR (Solid) ν_{max} = 3109 (w), 2949 (w), 1587 (m), 1516 (s), 1472 (m), 1341 (s), 1175 (m), 1084 (s), 857 (m), 834 (m), 732 (m), 688 (m), 661 (m) cm^{-1} [lit⁵ (CHCl_3): 3009, 2985, 2337, 1616, 1527, 1348, 1074 cm^{-1}]; MS TOF AP+ (*m/z*): 255.1 [M+H]⁺.

Synthesis of (S, E)-N-(4-chlorobenzylidene)-2-methylpropane-2-sulfinamide, S1e.



Prepared using *General Procedure A* with (*S*)-tert-butanethioamide (1.00 g, 1.00 equiv., 8.25 mmol), 4-chlorobenzaldehyde (3.48 g, 3.00 equiv., 24.8 mmol), pyridinium *p*-toluenesulfonate (104 mg, 0.0500 equiv., 0.413 mmol) magnesium sulfate (4.97 g, 5.00 equiv., 41.3 mmol) and dichloromethane (50.0 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-20% EtOAc/*n*-hexane). Data reported is in accordance with that found in the literature.⁶ White crystalline solid (1.53 g, 6.28 mmol, 76%). mp: 39-41 °C [lit:⁶ 37-38 °C]; TLC (EtOAc:*n*-hexane = 10:90 v/v, visualised by UV 254 nm): R_f = 0.29; ¹H NMR (300 MHz, CDCl_3): δ 8.55 (1H, s,

CH=N), 7.80 (2H, d, *J* 8.6, *ArH*), 7.46 (2H, d, *J* 8.5, *ArH*), 1.27 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 161.5 (CH, (+), CH=N), 138.7 (C, (-), *Ar*), 132.5 (C, (-), *Ar*), 130.6 (CH, (+), *Ar*), 129.3 (CH, (+), *Ar*), 58.0 (C, (-), *t*-Bu), 22.6 (CH₃, (+), *t*-Bu); IR (solid) $\nu_{\max}$ = 2961 (m), 1592 (s), 1566 (s), 1489 (m), 1404 (m), 1363 (m), 1083 (s) cm⁻¹; MS TOF ES+ (*m/z*): 266.05 [M+Na]⁺.



Scheme S 2. General procedure B, the conversion of **S1a-e** into **S2a-e**.

Synthesis of (S)-2-methyl-N-((R)-1-phenylbut-3-en-1-yl)propane-2-sulfinamide, S2a.

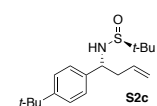
Prepared using *General Procedure B* with (*S*, *E*)-*N*-benzylidene-2-methylpropane-2-sulfinamide **S1a** (600 mg, 1.00 equiv., 2.87 mmol), allyl bromide (0.50 mL, 2.0 equiv., 5.73 mmol), zinc powder (469 mg, 2.50 equiv., 7.17 mmol), indium(III) trifluoromethanesulfonate (2.09 g, 1.30 equiv., 3.73 mmol), anhydrous tetrahydrofuran (30 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-40% EtOAc/petroleum ether). Data reported is in accord with that found in the literature.⁷ White solid (407 mg, 1.62 mmol, 56%). mp: 68-70 °C; dr = >99:1 (crude dr = 8:1); TLC (EtOAc:petroleum ether = 30:70 v/v, visualised with KMnO₄): R_f = 0.28; ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.25 (5H, m, *ArH*), 5.80-5.67 (1H, m, CH₂CHCH₂), 5.22-5.15 (2H, m, CH₂CHCH₂), 4.50-4.44 (1H, m, PhCHNH), 3.68 (1H, br s, NH), 2.65-2.56 (1H, m, CHCH₂CH), 2.52-2.42 (1H, m, CHCH₂CH), 1.19 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 141.7 (C, (-), *Ar*), 134.2 (CH, (+), CH₂CHCH₂), 128.5 (CH, (+), *Ar*), 127.7 (CH, (+), *Ar*), 127.5 (CH, (+), *Ar*), 119.3 (CH₂, (-), CH₂CHCH₂), 57.0 (CH, (+), CHCH₂CH), 55.6 (C, (-), *t*-Bu), 43.5 (CH₂, (-), CHCH₂CH), 22.6 (CH₃, (+), *t*-Bu); IR (Solid) $\nu_{\max}$ = 3337 (w), 3209 (m), 3085 (w), 3058 (w), 3030 (w), 2957 (m), 2907 (m), 2908 (m), 2869 (m), 1644 (m), 1451 (s), 1348 (m), 1292 (s), 1139 (m), 1115 (m), 1050 (s), 906 (m), 958 (m), 917 (s), 777 (s), 755 (s), 696 (s) cm⁻¹ [lit.⁷ (film) 3033, 2927, 2869, 2235, 1640, 1456, 1058, 911, 734, 701 cm⁻¹]; MS TOF ES+ (*m/z*): 274.1 [M+Na]⁺.

Synthesis of (S)-2-methyl-N-((R)-1-(naphthalen-1-yl)but-3-en-1-yl)propane-2-sulfinamide, S2b.

Prepared using *General Procedure B* with (*S*, *E*)-2-methyl-*N*-(naphthalen-1-ylmethylene)propane-2-sulfinamide **S1b** (600 mg, 1.00 equiv., 2.31 mmol), allyl bromide (0.40 mL, 4.6 mmol), zinc powder (378 mg, 2.50 equiv., 5.78 mmol), indium(III) trifluoromethanesulfonate (1.69 g, 1.30 equiv., 3.01 mmol), anhydrous tetrahydrofuran (30.0 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-40% EtOAc/petroleum ether). ¹H and ¹³C NMR spectroscopy, optical rotation, IR and mass spectra reported are consistent with that found in the literature.⁸ Pale yellow sticky oil (389 mg, 1.29 mmol, 56%). dr = >99:1 (crude compound dr = 5:1); TLC (EtOAc:pet ether = 30:70 v/v, visualised by UV 254 nm): R_f = 0.33; ¹H NMR (400 MHz, CDCl₃): δ 8.19 (1H, d, *J* 8.4, *ArH*),

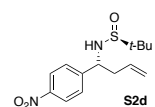
7.88 (1H, d, *J* 9.4, *ArH*), 7.79 (1H, d, *J* 6.1, *ArH*), 7.59-7.44 (4H, m, *ArH*), 5.84-5.74 (1H, m, CH₂CHCH₂), 5.33-5.29 (1H, m, CH₂CHCH₂), 5.26-5.18 (2H, m, CHNH), 3.82 (1H, s, *NH*), 2.88-2.80 (1H, m, CHCH₂CH), 2.71-2.63 (1H, m, CHCH₂CH), 1.22 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): 137.2 (C, (-), *Ar*), 134.3 (CH, (+), CH₂CHCH₂), 134.0 (C, (-), *Ar*), 131.0 (C, (-), *Ar*), 129.0 (CH, (+), *Ar*), 128.2 (CH, (+), *Ar*), 126.2 (CH, (+), *Ar*), 125.6 (CH, (+), *Ar*), 125.2 (CH, (+), *Ar*), 125.0 (CH, (+), *Ar*), 123.2 (CH, (+), *Ar*), 119.4 (CH₂, (-), CH₂CHCH₂), 55.8 (C, (-), *t*-Bu), 53.5 (CH, (+), CHCH₂CH), 42.3 (CH₂, (-), CHCH₂CH), 22.7 (CH₃, (+), *t*-Bu); IR (neat) $\nu_{\max}$ = 3207 (m), 2958 (m), 2929 (m), 2868 (w), 1639 (w), 1600 (w), 1518 (w), 1364 (m), 1169 (m), 1059 (s), 917 (m), 778 (s) cm⁻¹ [lit (film):⁸ 3281, 3209, 2957, 2923, 2866, 1639, 1597, 1511, 1364, 1169, 1063, 920, 779, 751 cm⁻¹]; MS TOF ES+ (*m/z*): 324.1 [M+Na]⁺.

Synthesis of (S)-N-((R)-1-(4-(tert-butyl)phenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide, S2c.



Prepared using *General Procedure B* with (*R, E*)-*N*-(4-(*tert*-butyl)benzylidene)-2-methylpropane-2-sulfinamide **S1c** (600 mg, 1.00 equiv., 2.31 mmol), allyl bromide (0.391 mL, 2.00 equiv., 4.52 mmol), zinc powder (370 mg, 2.50 equiv., 5.65 mmol), indium(III) trifluoromethanesulfonate (1.65 g, 1.30 equiv., 2.94 mmol), anhydrous tetrahydrofuran (30 mL). Purified by flash column chromatography (silica gel 40-63 μ m, 30 % EtOAc/petroleum ether). Colourless oil (533 mg, 1.73 mmol, 77%), dr = >99:1 (crude compound dr = 6:1); TLC (EtOAc:petroleum ether = 30:70 v/v, visualised with KMnO₄): *R_f* = 0.31; ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.22 (4H, m, *ArH*), 5.75-5.71 (1H, m, CH₂CHCH₂), 5.22-5.16 (2H, m, CH₂CHCH₂), 4.47-4.43 (1H, m, PhCHNH), 3.67 (1H, s, *NH*), 2.62-2.45 (2H, m, CHCH₂CH), 1.32 (9H, s, *t*-Bu), 1.20 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 150.4 (C, (-), *Ar*), 138.6 (C, (-), *Ar*), 134.4 (CH, (+), CH₂CHCH₂), 127.0 (CH, (+), *Ar*), 125.3 (CH, (+), *Ar*), 119.2 (CH₂, (-), CH₂CHCH₂), 56.7 (CH, (+), CHCH₂CH), 55.7 (C, (-), *t*-Bu), 43.5 (CH₂, (-), CHCH₂CH), 34.5 (C, (-), *t*-Bu), 31.4 (CH₃, (+), *t*-Bu), 22.7 (CH₃, (+), *t*-Bu); IR (neat) $\nu_{\max}$ = 3440 (w), 3207 (w), 3078 (w), 2959 (s), 2906 (m), 2868 (m), 1640 (w), 1510 (m), 1474 (m), 1363 (m), 1269 (m), 1110 (m), 1053 (s), 995 (m), 913 (m), 831 (s) cm⁻¹; MS TOF ES+ (*m/z*): 330.2 [M+Na]⁺; HRMS (*m/z*): [M+Na]⁺ calcd. for C₁₈H₂₉NONaS⁺, 330.1862; found, 330.1864.

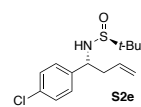
Synthesis of (R)-2-methyl-N-((S)-1-(4-nitrophenyl)but-3-en-1-yl)propane-2-sulfinamide, S2d.

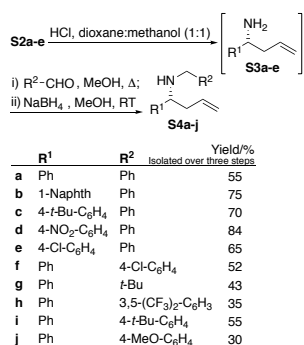


Prepared using *General Procedure B* with (*R, E*)-2-methyl-*N*-(4-nitrobenzylidene)propane-2-sulfinamide **S1d** (1.00 g, 1.00 equiv., 3.93 mmol), allyl bromide (0.681 mL, 2.00 equiv., 7.86 mmol), zinc powder (643 mg, 2.50 equiv., 9.83 mmol), indium(III) trifluoromethanesulfonate (2.87 g, 1.30 equiv., 5.11 mmol), anhydrous tetrahydrofuran (30 mL). Purified using a *Combiflash Rf 200i* (silica 12 g column, 0-70% EtOAc/petroleum ether). Pale yellow crystalline solid (968 mg, 3.27 mmol, 83%). mp: 112-113 °C; dr = >99:1 (crude product dr = 16:1); TLC (EtOAc:petroleum ether = 50:50 v/v, visualised with KMnO₄): *R_f* = 0.36; ¹H NMR (300 MHz, CDCl₃): δ 8.22 (2H, d, *J* 8.8 Hz, *ArH*), 7.51 (2H, d, *J* 8.7 Hz, *ArH*), 5.72-5.64 (1H, m, CH₂CHCH₂), 5.23-5.16 (2H, m, CH₂CHCH₂), 4.63-4.58 (1H, m, PhCHNH), 3.76 (1H, s, *NH*), 2.63-2.46 (2H, m, CHCH₂CH), 1.22 (9H, s, *t*-Bu); ¹³C NMR (101

MHz, PENDANT, CDCl₃): δ 149.3 (C, (-), Ar), 147.5 (C, (-), Ar), 133.0 (CH, (+), CH₂CHCH₂), 128.4 (CH, (+), Ar), 123.8 (CH, (+), Ar), 120.3 (CH₂, (-), CH₂CHCH₂), 56.4 (CH, (+), CHCH₂CH), 56.0 (C, (-), *t*Bu), 43.1 (CH₂, (-), CHCH₂CH), 22.5 (CH₃, (+), *t*Bu); IR (solid) $\nu_{\max}$ = 3206 (w), 3079 (w), 2962 (w), 2933 (w), 2867 (w), 1641 (w), 1601 (m), 1519 (s), 1474 (w), 1344 (s), 1052 (s), 1014 (m), 919 (m), 854 (s) cm⁻¹; MS TOF ES⁺ (*m/z*): 319.11 [M+Na]⁺; HRMS (*m/z*): [M+Na]⁺ calcd. for C₁₄H₂₀N₂O₃NaS⁺, 319.1087; found, 319.1093

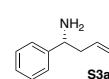
Synthesis of (R)-2-methyl-N-((S)-1-(4-nitrophenyl)but-3-en-1-yl)propane-2-sulfonamide, S2e.

 Prepared using *General Procedure B* with (*R*, *E*)-2-methyl-*N*-(4-nitrobenzylidene) propane-2-sulfonamide **S1e** (1.00 g, 1.00 equiv., 3.93 mmol), allyl bromide (0.68 mL, 2.00 equiv., 7.86 mmol), zinc powder (643 mg, 2.50 equiv., 9.83 mmol), indium(III) trifluoromethanesulfonate (2.87 g, 1.30 equiv., 5.11 mmol), anhydrous tetrahydrofuran (30 mL). *Purified using* a Combiflash Rf200i (silica 12 g column, 0-70% EtOAc/petroleum ether. Pale yellow crystalline solid (968 mg, 3.27 mmol, 83%). Mp: 112-113 °C; dr = >99:1 (crude product dr = 16:1); TLC (EtOAc:petroleum ether = 50:50 v/v, visualised with KMnO₄): R_f = 0.36; ¹H NMR (300 MHz, CDCl₃): δ 8.22 (2H, d, *J* 8.8, ArH), 7.51 (2H, d, *J* 8.7, ArH), 5.72-5.64 (1H, m, CH₂CHCH₂), 5.23-5.16 (2H, m, CH₂CHCH₂), 4.63-4.58 (1H, m, PhCHNH), 3.76 (1H, s, NH), 2.63-2.46 (2H, m, CHCH₂CH), 1.22 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 149.3 (C, (-), Ar), 147.5 (C, (-), Ar), 133.0 (CH, (+), CH₂CHCH₂), 128.4 (CH, (+), Ar), 123.8 (CH, (+), Ar), 120.3 (CH₂, (-), CH₂CHCH₂), 56.4 (CH, (+), CHCH₂CH), 56.0 (C, (-), *t*-Bu), 43.1 (CH₂, (-), CHCH₂CH), 22.5 (CH₃, (+), *t*-Bu); IR (solid) $\nu_{\max}$ = 3206 (w), 3079 (w), 2962 (w), 2933 (w), 2867 (w), 1641 (w), 1601 (m), 1519 (s), 1474 (w), 1344 (s), 1052 (s), 1014 (m), 919 (m), 854 (s) cm⁻¹; MS TOF ES⁺ (*m/z*): 319.11 [M+Na]⁺; HRMS (*m/z*): [M+Na]⁺ calcd. for C₁₄H₂₀N₂O₃NaS⁺, 319.1087; found, 319.1093



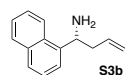
Scheme S 3. General procedure C, the conversion of **S2a-e** into secondary homoallyl amines **S4a-j**, via amines **S3a-e**.

Synthesis of (R)-1-phenylbut-3-en-1-amine S3a.

 Prepared using *General Procedure C* with (*S*)-2-methyl-*N*-((*R*)-1-phenylbut-3-en-1-yl)propane-2-sulfonamide **S2a** (407 mg, 1.62 mmol) and hydrochloric acid (4 M in dioxane, 4 mL). The characterisation reported is consistent with that given in the literature.^{7,9} Colourless liquid (151 mg, 1.03 mmol, 63%). ¹H NMR (300 MHz, CDCl₃): δ 7.34-7.23 (5H, m, ArH), 5.77-5.69 (1H, m, CH₂CHCH₂), 5.16-5.06 (2H, m, CH₂CHCH₂), 4.00 (1H, dd, *J* 8.1, 5.3, CHN), 2.46-2.35 (2H, m, CHCH₂CH), 1.55 (2H, br s, NH₂); ¹³C NMR (101 MHz, PENDANT,

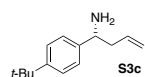
CDCl₃): δ 145.9 (C, (-), Ar), 135.5 (CH, (+), CH₂CHCH₂), 128.4 (CH, (+), Ar), 127.0 (CH, (+), Ar), 126.3 (CH, (+), Ar), 117.7 (CH₂, (-), CH₂CHCH₂), 55.4 (CH, (+), PhCHNH₂), 44.2 (CH₂, (-), CHCH₂CH); IR (neat) $\nu_{\max}$ = 3371 (w, NH), 3070 (w), 3028 (w), 2977 (w), 2908 (w), 2850 (w), 1639 (m), 1603 (m), 1493 (m), 1453 (m), 1336 (w), 1069 (w), 1028 (w), 997 (m), 913 (s), 839 (m), 757 (s), 698 (s) cm⁻¹ [lit (film):⁹ 3379 (NH), 3065, 3026, 1639, 1492 cm⁻¹]; MS TOF ES+ (m/z): 131.1 [M-NH₂]⁺.

Synthesis of (R)-1-(naphthalen-1-yl)but-3-en-1-amine S3b.



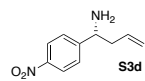
Prepared using *General Procedure C* with (*R*)-2-methyl-*N*-((*S*)-1-(naphthalen-1-yl)but-3-en-1-yl)propane-2-sulfonamide **S2b** (389 mg, 1.26 mmol) and hydrochloric acid (4 M in dioxane, 3.9 mL). Pale yellow oil (212 mg, 1.07 mmol, 85%). ¹H NMR (400 MHz, CDCl₃): δ 8.12 (1H, dd, *J* 8.6 & 1.3, Ar*H*), 7.86 (1H, dd, *J* 7.9 & 1.6, Ar*H*), 7.74 (1H, dt, *J* 8.2 & 1.1, Ar*H*), 7.64 (1H, dt, *J* 7.2 & 0.9, Ar*H*), 7.53-7.44 (3H, m, Ar*H*), 5.85 (1H, dddd, *J* 16.8, 10.1, 7.8 & 6.3, CH₂CHCH₂), 5.21-5.11 (2H, m, CH₂CHCH₂), 4.84 (1H, dd, *J* 8.5 & 4.2, CHN), 2.68-2.42 (2H, m, CHCH₂CH), 1.63 (2H, br s, NH₂); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 141.5 (C, (-), Ar), 135.7 (CH, (+), CH₂CHCH₂), 133.9 (C, (-), Ar), 130.8 (C, (-), Ar), 129.1 (CH, (+), Ar), 127.4 (CH, (+), Ar), 126.0 (CH, (+), Ar), 125.6 (CH, (+), Ar), 125.5 (CH, (+), Ar), 122.9 (CH, (+), Ar), 122.5 (CH, (+), Ar), 117.8 (CH₂, (-), CH₂CHCH₂), 50.3 (CH, (+), PhCHNH₂), 43.2 (CH₂, (-), CHCH₂CH); IR (neat) $\nu_{\max}$ = 3360 (w, NH), 3059 (w), 2975 (w), 2921 (w), 2860 (w), 1638 (m, HC=C), 1597 (m), 1509 (m), 1436 (w), 1395 (w), 1258 (w), 1166 (w), 1065 (w), 996 (m), 914 (s), 860 (m), 798 (s), 775 (s) cm⁻¹; MS TOF AP+ (m/z): 198.1 [M+H]⁺; HRMS (m/z): [M+H]⁺ calcd. for C₁₄H₁₆N⁺, 198.1277; found, 198.1282.

Synthesis of (R)-1-(4-(tert-butyl)phenyl)but-3-en-1-amine S3c.



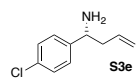
Prepared using *General Procedure C* with (*R*)-*N*-((*S*)-1-(4-(*tert*-butyl)phenyl)but-3-en-1-yl)-2-methylpropane-2-sulfonamide **S2c** (533 mg, 1.73 mmol) and hydrochloric acid (4 M in dioxane, 5.3 mL). Colourless oil (296 mg, 1.46 mmol, 84%). ¹H NMR (400 MHz, CDCl₃): δ 7.35 (2H, d, *J* 8.4, Ar*H*), 7.27 (2H, d, *J* 8.3, Ar*H*), 5.76 (1H, dddd, *J* 17.1, 10.2, 8.0 & 6.2, CH₂CHCH₂), 5.21-4.98 (2H, m, CH₂CHCH₂), 3.97 (1H, dd, *J* 8.2 & 5.2, CHN), 2.50-2.35 (2H, m, CH₂CHCH₂), 1.98 (2H, br s, NH₂), 1.32 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 149.9 (C, (-), Ar), 142.5 (C, (-), Ar), 135.5 (CH, (+), CH₂CHCH₂), 126.0 (CH, (+), Ar), 125.3 (CH, (+), Ar), 117.6 (CH₂, (-), CH₂CHCH₂), 55.0 (CH₂, (-), CHN), 43.9 (CH₂, (-), CHCH₂CH), 34.5 (C, (-), *t*-Bu), 31.4 (CH₃, (+), *t*-Bu); IR (neat) $\nu_{\max}$ = 3304 (w, NH), 3077 (w), 2961 (s), 2904 (m), 2868 (w), 1640 (m, HC=C), 1582 (m), 1510 (m), 1462 (s), 1435 (w), 1410 (w), 1362 (m), 1269 (m), 1203 (w), 1110 (m), 997 (m), 913 (s), 829 (s) cm⁻¹; MS TOF ES+ (m/z): 204.19 [M+H]⁺; HRMS (m/z): [M+H]⁺ calcd. for C₁₄H₂₂N⁺, 204.1747; found, 204.1754.

Synthesis of (R)-1-(4-nitrophenyl)but-3-en-1-amine **S3d**.



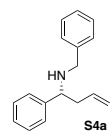
Prepared using *General Procedure C* with (R)-2-methyl-N-((S)-1-(4-nitrophenyl)but-3-en-1-yl)propane-2-sulfonamide **S2d** (650 mg, 2.19 mmol) and hydrochloric acid (4 M in dioxane, 5 mL). The characterisation reported is consistent with that in the literature.¹⁰ Pale yellow oil (386 mg, 2.01 mmol, 92% yield).; ¹H NMR (400 MHz, CDCl₃): δ 8.19 (2H, d, *J* 8.8, Ar*H*), 7.53 (2H, d, *J* 8.8, Ar*H*), 5.88-5.55 (1H, m, CH₂CHCH₂), 5.22-5.05 (2H, m, CH₂CHCH₂), 4.15 (1H, dd, *J* 8.0, 5.2 Hz, CHN), 2.57-2.29 (2H, m, CHCH₂CH), 1.60 (2H, br s, NH₂); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 153.3 (C, (-), Ar), 147.0 (C, (-), Ar), 134.3 (CH, (+), CH₂CHCH₂), 127.3 (CH, (+), Ar), 123.7 (CH, (+), Ar), 118.7 (CH₂, (-), CH₂CHCH₂), 54.9 (CH, (+), PhCHNH₂), 44.1 (CH₂, (-), CHCH₂CH); IR (neat) ν_{max} = 3376 (w, NH), 3077 (w), 2980 (w), 2926 (w), 2854 (w), 1640 (m, HC=C), 1600 (m), 1513 (s), 1437 (w), 1342 (s), 1180 (w), 1108 (m), 998 (m), 917 (s), 852 (s), 752 (s), 699 (s) cm⁻¹; MS TOF AP- (*m/z*): 191.07 [M-H]⁻.

Synthesis of (R)-1-(4-chlorophenyl)but-3-en-1-amine **S3e**.



Prepared using *General Procedure C* with (R)-N-((S)-1-(4-chlorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfonamide **S2e** (436 mg, 1.53 mmol) and hydrochloric acid (4 M in dioxane, 4.4 mL). The characterisation reported is consistent with that given the literature.⁹ Colourless oil (189 mg, 1.04 mmol, 68%). ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.27 (4H, m, Ar*H*), 5.76-5.65 (1H, m, CH₂CHCH₂), 5.15-5.07 (2H, m, CH₂CHCH₂), 3.99 (1H, dd, *J* 7.9 & 5.4, CHN), 2.45-2.30 (2H, m, CHCH₂CH), 1.53 (2H, br s, NH₂); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 144.3 (C, (-), Ar), 135.0 (CH, (+), CH₂CHCH₂), 132.5 (C, (-), Ar), 128.5 (CH, (+), Ar), 127.8 (CH, (+), Ar), 118.0 (CH₂, (-), CH₂CHCH₂), 54.8 (CH, (+), PhCHNH₂), 44.2 (CH₂, (-), CHCH₂CH); IR (neat) ν_{max} = 3375 (w, NH), 3077 (w), 2978 (w), 2907 (w), 2844 (w), 1640 (m, HC=C), 1593 (m), 1491 (s), 1090 (s), 1013 (s), 915 (s), 822 (s) cm⁻¹ [lit (film):⁹ 3375 (NH), 3076, 1640 (HC=C), 1091 cm⁻¹]; MS TOF AP+ (*m/z*): 165.0 [M-NH₂]⁺.

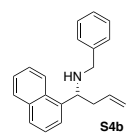
Synthesis of (R)-N-benzyl-1-phenylbut-3-en-1-amine **S4a**.



Prepared using *General Procedure D* with (S)-1-phenylbut-3-en-1-amine **S3a** (151 mg, 1.00 equiv., 1.03 mmol), benzaldehyde (109 mg, 1.00 equiv., 1.03 mmol), sodium borohydride (77.6 mg, 2.00 equiv., 2.05 mmol) and methanol (20 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation (¹H, ¹³C NMR spectroscopy, and optical rotation value) reported is consistent with that given the literature.¹¹ Colourless oil (216 mg, 0.910 mmol, 88% yield over two steps). TLC (EtOAc:*n*-hexane= 10:90 v/v, visualised with KMnO₄): R_f = 0.30; ¹H NMR (300 MHz, CDCl₃): δ 7.38-7.23 (10H, m, Ar*H*), 5.78-5.63 (1H, m, CH₂CHCH₂), 5.11-5.01 (2H, m, CH₂CHCH₂), 3.71-3.67 (1H, m, CHCH₂CH), 3.67 (1H, d, *J* = 13.3, PhCH*H*N), 3.52 (1H, d, *J* 13.3 Hz, PhCH*H*N), 2.46-2.35 (2H, m, CHCH₂CH), 1.75 (br s, 1H, NH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 143.9 (C, (-), Ar), 140.7 (C, (-), Ar), 135.5 (CH, (+), CH₂CHCH₂), 128.4 (CH, (+), Ar), 128.3 (CH, (+), Ar), 128.1 (CH, (+), Ar), 127.3 (CH, (+), Ar), 127.1 (CH, (+), Ar), 126.8 (CH, (+), Ar), 117.6 (CH₂,

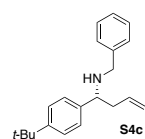
(-), CH₂CHCH₂), 61.6 (CH, (+), PhCHNH), 51.5 (CH₂, (-), NHCH₂Ph), 43.2 (CH₂, (-), CHCH₂CH); IR (neat) $\nu_{\max}$ = 3328 (w), 3063 (w), 2978 (w), 2908 (w), 2834 (w), 1639 (w), 1603 (w), 1493 (m), 1453 (s), 1356 (w), 1307 (w), 1198 (w), 1115 (m), 1071 (m), 1028 (m), 995 (m), 914 (s), 824 (w), 757 (s), 732 (s), 696 (s) cm⁻¹; MS TOF ES+ (*m/z*): 238.2 [M+H]⁺.

Synthesis of (R)-N-benzyl-1-(naphthalen-1-yl)but-3-en-1-amine S4b.



Prepared using *General Procedure D* with (*R*)-1-(naphthalen-1-yl)but-3-en-1-amine **S3b** (212 mg, 1.00 equiv., 1.07 mmol), benzaldehyde (114 mg, 1.00 equiv., 1.07 mmol), sodium borohydride (81.3 mg, 2.00 equiv., 2.15 mmol) and methanol (20 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.¹² Pale yellow oil (272 mg, 0.946 mmol, 88% yield over two steps). TLC (EtOAc:*n*-hexane = 10:90 v/v, visualised with KMnO₄): *R_f* = 0.32; ¹H NMR (400 MHz, CDCl₃): δ 8.22-8.15 (1H, m, *ArH*), 7.93-7.84 (1H, m, *ArH*), 7.84-7.74 (2H, m, *ArH*), 7.55-7.43 (3H, m, *ArH*), 7.37-7.19 (5H, m, *ArH*), 5.86-5.80 (1H, m, CH₂CHCH₂), 5.17-5.02 (2H, m, CH₂CHCH₂), 4.59 (1H, dd, *J* 8.4 & 4.6, CHCH₂CH), 3.75 (1H, d, *J* 13.2, NHCHH), 3.58 (1H, d, *J* 13.2, NHCHH), 2.69-2.43 (2H, m, CHCH₂CH), 1.77 (1H, br s, NH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 140.7 (C, (-), Ar), 139.1 (C, (-), Ar), 135.6 (CH, (+), CH₂CHCH₂), 134.1 (C, (-), Ar), 131.7 (C, (-), Ar), 129.0 (CH, (+), Ar), 128.4 (CH, (+), Ar), 128.2 (CH, (+), Ar), 127.4 (CH, (+), Ar), 126.9 (CH, (+), Ar), 125.7 (CH, (+), Ar), 125.3 (CH, (+), Ar), 123.9 (CH, (+), Ar), 123.0 (CH, (+), Ar), 117.7 (CH₂, (-), CH₂CHCH₂), 57.1 (CH, (+), CHNH), 51.7 (CH₂, (-), NHCH₂), 42.2 (CH₂, (-), naphthCHCH₂) IR (neat) $\nu_{\max}$ = 3324 (w), 3061 (m), 2909 (w), 2831 (w), 1638 (m), 1596 (m), 1453 (m), 1393 (m), 1167 (w), 1075 (w), 1028 (m), 994 (m), 912 (s), 799 (s), 776 (s) cm⁻¹ [lit¹² (CHCl₃): 3437, 3062, 2928, 2856, 1638, 1597, 1456, 1394, 1167, 1106, 1028, 997, 917, 800, 778 cm⁻¹]; MS TOF ES+ (*m/z*): 288.2 [M+H]⁺.

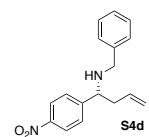
Synthesis of (R)-N-benzyl-1-(4-(tert-butyl)phenyl)but-3-en-1-amine S4c.



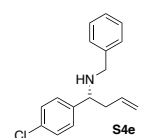
Prepared using *General Procedure D* with (*S*)-1-(4-(*tert*-butyl)phenyl)but-3-en-1-amine **S3c** (296 mg, 1.00 equiv., 1.46 mmol), benzaldehyde (154 mg, 1.00 equiv., 1.46 mmol), sodium borohydride (110 mg, 2.00 equiv., 2.91 mmol) and methanol (20 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). Colourless oil (356 mg, 1.21 mmol, 83% yield over two steps). TLC (EtOAc:*n*-hexane = 5:95 v/v, visualised with KMnO₄): *R_f* = 0.32; ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.21 (9H, m, *ArH*), 5.77-5.67 (1H, m, CH₂CHCH₂), 5.11-5.03 (2H, m, CH₂CHCH₂), 3.67 (1H, t, *J* 6.5, CHCH₂CH), 3.69 (1H, d, *J* 13.2, NHCH₂Ph), 3.53 (1H, d, *J* 13.3, NHCH₂Ph), 2.47-2.35 (2H, m, CHCH₂CH), 1.88 (1H, br s, NH), 1.33 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 149.8 (C, (-), Ar), 140.7 (C, (-), Ar), 135.7 (CH, (+), CH₂CHCH₂), 128.3 (CH, (+), Ar), 128.2 (CH, (+), Ar), 126.9 (CH, (+), Ar), 126.8 (CH, (+), Ar), 125.3 (CH, (+), Ar), 117.5 (CH₂, (-), CH₂CHCH₂), 61.2 (CH, (+), PhCHNH), 51.5 (CH₂, (-), NHCH₂Ph), 43.1 (CH₂, (-), PhCHCH₂), 34.5 (C, (-), *t*-Bu), 31.5 (CH₃, (+), *t*-Bu); IR (neat) $\nu_{\max}$ = 3334 (w), 3063 (w), 3028 (w), 2962 (s), 2904 (m), 2867 (m), 2833 (w), 1640 (w), 1603 (m), 1508 (w), 1495 (w), 1457 (m), 1363 (m), 1269 (m), 1203 (w), 1109 (m), 1017 (m), 995 (m), 914

(s), 830 (s), 731 (s), 697 (s) cm^{-1} ; MS TOF ES+ (m/z): 294.2 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{28}\text{N}^+$, 294.2216; found, 294.2220.

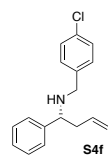
Synthesis of (R)-N-benzyl-1-(4-nitrophenyl)but-3-en-1-amine S4d.

 Prepared using *General Procedure D* with (S)-1-(4-nitrophenyl)but-3-en-1-amine **S3d** (386 mg, 1.00 equiv., 2.01 mmol), benzaldehyde (213 mg, 1.00 equiv., 2.01 mmol), sodium borohydride (152 mg, 2.00 equiv., 4.02 mmol) and methanol (20.0 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.¹¹ Pale yellow oil (515 mg, 1.82 mmol, 91% yield over two steps). TLC (EtOAc:*n*-hexane = 5:95 v/v, visualised with KMnO_4): R_f = 0.18; ^1H NMR (400 MHz, CDCl_3): δ 8.20 (2H, d, J 8.8, ArH), 7.55 (2H, d, J 8.6, ArH), 7.34-7.22 (5H, m, ArH), 5.68-5.63 (1H, m, CH_2CHCH_2), 5.09-5.05 (2H, m, CH_2CHCH_2), 3.82 (1H, dd, J 7.9 & 5.6, CHCH_2CH), 3.65 (1H, d, J 13.3, NHCHH), 3.52 (1H, d, J 13.4, NHCHH), 2.45-2.32 (2H, m, CHCH_2CH), 1.81 (1H, br s, NH); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 151.9 (C, (-), Ar), 147.2 (C, (-), Ar), 140.0 (C, (-), Ar), 134.3 (CH, (+), CH_2CHCH_2), 128.5 (CH, (+), Ar), 128.2 (CH, (+), Ar), 128.0 (CH, (+), Ar), 127.1 (CH, (+), Ar), 123.7 (CH, (+), Ar), 118.6 (CH_2 , (-), CH_2CHCH_2), 61.2 (CH, (+), CHNH), 51.6 (CH_2 , (-), NHCH_2), 43.0 (CH_2 , (-), CHCH_2CH); IR (neat) ν_{max} = 3334 (w), 3061 (w), 3027 (w), 2927 (w), 2837 (w), 1640 (w), 1600 (w), 1516 (s), 1454 (m), 1342 (w), 1197 (w), 1108 (s), 995 (s), 918 (s), 854 (s), 823 (m), 736 (s), 697 (s) cm^{-1} [lit¹¹ (CHCl_3): 3335, 3078, 3029, 2924, 2849, 1640, 1599, 1520, 1455, 1347, 1315, 1109, 1014, 996, 920, 856, 824, 754, 700 cm^{-1}]; MS TOF ES+ (m/z): 283.2 $[\text{M}+\text{H}]^+$.

Synthesis of (R)-N-benzyl-1-(4-chlorophenyl)but-3-en-1-amine S4e.

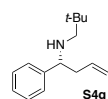
 Prepared using *General Procedure D* with (S)-1-(4-chlorophenyl)but-3-en-1-amine **S3e** (189 mg, 1.00 equiv., 1.04 mmol), benzaldehyde (110 mg, 1.00 equiv., 1.04 mmol), sodium borohydride (79.1 mg, 2.00 equiv., 2.08 mmol) and methanol (20 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.¹² Colourless oil (268 mg, 0.986 mmol, 95% yield over two steps). TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised with KMnO_4): R_f = 0.55; ^1H NMR (300 MHz, CDCl_3): δ 7.34-7.21 (9H, m, ArH), 5.74-5.60 (1H, m, CH_2CHCH_2), 5.09-5.03 (2H, m, CH_2CHCH_2), 3.69-3.63 (2H, m, CHCH_2CH & NHCHH), 3.49 (1H, d, J 13.3, NHCHH), 2.39-2.33 (2H, m, CHCH_2CH), 1.73 (1H, br s, NH); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 142.4 (C, (-), Ar), 140.4 (C, (-), Ar), 135.0 (CH, (+), CH_2CHCH_2), 132.6 (C, (-), Ar), 128.7 (CH, (+), Ar), 128.6 (CH, (+), Ar), 128.4 (CH, (+), Ar), 128.1 (CH, (+), Ar), 127.0 (CH, (+), Ar), 118.0 (CH_2 , (-), CH_2CHCH_2), 61.0 (CH, (+), PhCHNH), 51.4 (CH_2 , (-), NHCH_2Ph), 43.1 (CH_2 , (-), CHCH_2CH); IR (neat) ν_{max} = 3335 (w), 3064 (w), 2979 (w), 2909 (w), 2832 (w), 1639 (m), 1598 (w), 1491 (s), 1454 (s), 1343 (w), 1090 (s), 1014 (s), 916 (s), 824 (s), 697 (s) cm^{-1} [lit¹² (CHCl_3): 3396, 3077, 2931, 2844, 1646, 1460, 1046, 917, 765 cm^{-1}]; MS TOF ES+ (m/z): 272.1 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{17}\text{H}_{19}\text{N}^{35}\text{Cl}^+$, 272.1201; found, 272.1205.

Synthesis of (R)-N-(4-chlorobenzyl)-1-phenylbut-3-en-1-amine **S4f**.



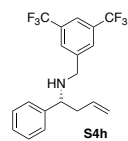
Prepared using *General Procedure D* with (S)-1-phenylbut-3-en-1-amine **S3a** (150 mg, 1.02 mmol), 4-chlorobenzaldehyde (143 mg, 1.02 mmol), sodium borohydride (77.1 mg, 2.04 mmol) and methanol (20 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). Colourless oil (230 mg, 0.846 mmol, 83% yield over two steps). TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised with KMnO₄): R_f = 0.57; ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.17 (9H, m, ArH), 5.77-5.63 (1H, m, CH₂CHCH₂), 5.11-5.02 (2H, m, CH₂CHCH₂), 3.68 (1H, t, J 7.6, CHCH₂CH), 3.66 (1H, d, J 14.6, NHCH₂), 3.49 (1H, d, J 13.5, NHCH₂), 2.48-2.32 (2H, m, CHCH₂CH), 1.68 (1H, br s, NH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 143.6 (C, (-), Ar), 139.1 (C, (-), Ar), 135.4 (CH, (+), CH₂CHCH₂), 132.5 (C, (-), Ar), 129.5 (CH, (+), Ar), 128.5 (CH, (+), Ar), 127.3 (CH, (+), Ar), 127.2 (CH, (+), Ar), 117.7 (CH₂, (-), CH₂CHCH₂), 61.6 (CH, (+), CHNH), 50.7 (CH₂, (-), NHCH₂), 43.1 (CH₂, (-), CHCH₂); IR (neat) $\nu_{\max}$ = 3328 (w), 3063 (w), 3027 (w), 2978 (w), 2912 (w), 2834 (w), 1639 (m), 1599 (w), 1490 (s), 1453 (s), 1407 (w), 1356 (w), 1197 (w), 1090 (s), 1015 (s), 995 (m), 915 (s), 804 (s), 700 (s) cm⁻¹; MS TOF ES+ (m/z): 272.1 [M+H]⁺; HRMS (m/z): [M+H]⁺ calcd. for C₁₇H₁₉N³⁵Cl⁺, 272.1201; found, 272.1204.

Synthesis of (R)-N-neopentyl-1-phenylbut-3-en-1-amine **S4g**.



Prepared using *General Procedure D* with (S)-1-phenylbut-3-en-1-amine **S3a** (150 mg, 1.00 equiv., 1.02 mmol), trimethylacetaldehyde (87.8 mg, 1.00 equiv., 1.02 mmol), sodium borohydride (77.1 mg, 2.00 equiv., 2.04 mmol) and methanol (20 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). Colourless oil (150 mg, 0.690 mmol, 68% yield over two steps). TLC (EtOAc:*n*-hexane = 15:85 v/v, visualised with KMnO₄): R_f = 0.48; ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.20 (5H, m, ArH), 5.81-5.70 (1H, m, CH₂CHCH₂), 5.11-5.03 (2H, m, CH₂CHCH₂), 3.58 (1H, dd, J 8.1 & 5.6, CHCH₂CH), 2.44-2.29 (2H, m, CHCH₂CH), 2.17 (2H, q, J 9.6, NHCH₂*t*-Bu), 1.38 (1H, br s, NH), 0.87 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 144.8 (C, (-), Ar), 135.9 (CH, (+), CH₂CHCH₂), 128.2 (CH, (+), Ar), 127.2 (CH, (+), Ar), 126.7 (CH, (+), Ar), 117.2 (CH₂, (-), CH₂CHCH₂), 63.1 (CH, (+), CHNH), 60.0 (CH₂, (-), NHCH₂*t*-Bu), 43.5 (CH₂, (-), PhCHCH₂), 31.6 (C, (-), *t*-Bu), 27.8 (CH₃, (+), *t*-Bu); IR (neat) $\nu_{\max}$ = 3349 (w), 3075 (w), 3027 (w), 2952 (s), 2906 (m), 2866 (m), 2798 (w), 1639 (m), 1602 (m), 1474 (m), 1454 (m), 1395 (w), 1362 (m), 1283 (w), 1189 (w), 1122 (m), 1069 (w), 994 (m), 915 (s), 755 (s), 699 (s) cm⁻¹; MS TOF ES+ (m/z): 218.2 [M+H]⁺; HRMS (m/z): [M+H]⁺ calcd. for C₁₅H₂₄N⁺, 218.1903; found, 218.1910.

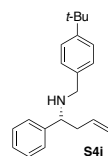
Synthesis of (R)-N-(3,5-bis(trifluoromethyl)benzyl)-1-phenylbut-3-en-1-amine **S4h**.



Prepared using *General Procedure D* with (S)-1-phenylbut-3-en-1-amine **S3a** (150 mg, 1.00 equiv., 1.02 mmol), 3,5-bis(trifluoromethyl)benzaldehyde (247 mg, 1.00 equiv., 1.02 mmol), sodium borohydride (77.1 mg, 2.00 equiv., 2.04 mmol) and methanol (20 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). Colourless oil (250 mg, 0.670 mmol, 56% yield over two steps). TLC (EtOAc:*n*-hexane = 10:90 v/v, visualised with KMnO₄): R_f = 0.45. ¹H NMR (300 MHz, CDCl₃): δ 7.72 (3H, s, ArH), 7.38-7.23

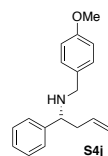
(5H, m, *ArH*), 5.81-5.67 (1H, m, CH_2CHCH_2), 5.15-5.06 (2H, m, CH_2CHCH_2), 3.78-3.63 (3H, m, CHCH_2CH & NHCH_2), 2.51-2.36 (2H, m, CHCH_2CH), 1.82 (1H, br s, *NH*); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 143.4 (C, (-), *Ar*), 143.2 (C, (-), *Ar*), 135.2 (CH, (+), CH_2CHCH_2), 131.4 (C, (-), q, $^3J_{\text{C-F}} = 33.2$, *Ar*), 128.6 (CH, (+), *Ar*), 128.2 (CH, (+), *Ar*), 127.4 (CH, (+), *Ar*), 127.2 (CH, (+), *Ar*), 123.5 (C, q, $^1J_{\text{C-F}} = 272.1$, CF_3), 120.8 (CH, (+), q, $^2J_{\text{C-F}} = 3.4$, *Ar*), 117.9 (CH_2 , (-), CH_2CHCH_2), 62.1 (CH, (+), PhCHNH), 50.6 (CH_2 , (-), NHCH_2), 43.0 (CH_2 , (-), PhCHCH_2). ^{19}F NMR (282 MHz, CDCl_3): δ -62.8 (s); IR (neat) $\nu_{\text{max}} = 3343$ (w), 3082 (w), 3030 (w), 2983 (w), 2918 (w), 2838 (w), 2801 (w), 1641 (w), 1623 (w), 1493 (w), 1455 (w), 1355 (w), 1383 (w), 1275 (s), 1168 (s), 1125 (s), 1028 (w), 996 (w), 918 (m), 891 (m), 843 (m), 760 (m), 732 (w), 700 (s), 681 (s) cm^{-1} ; MS TOF ES+ (m/z): 374.1 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{19}\text{H}_{18}\text{NF}_6$, 374.1338; found, 374.1344.

Synthesis of (R)-N-(4-(tert-butyl)benzyl)-1-phenylbut-3-en-1-amine S4i.



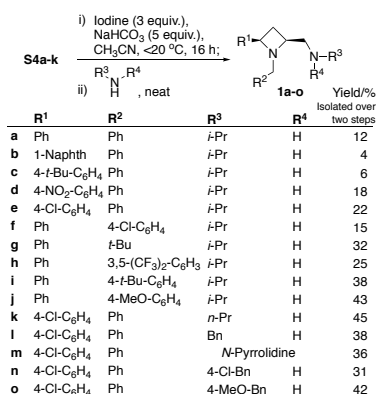
Prepared using *General Procedure D* with (*S*)-1-phenylbut-3-en-1-amine **S3a** (150 mg, 1.00 equiv., 1.02 mmol), 4-*tert*-butylbenzaldehyde (165 mg, 1.00equiv., 1.00 mmol), sodium borohydride (77.1 mg, 2.00 equiv., 2.04 mmol) and methanol (20 mL). Purified using a *CombiFlash Rf 200i* (silica 4 g column, 0-30% ethyl acetate/*n*-hexane). Colourless oil (259 mg, 0.883 mmol, 87% yield over two steps). TLC (EtOAc:*n*-hexane = 15:85 v/v, visualised with KMnO_4): $R_f = 0.42$; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.23 (7H, m, *ArH*), 7.19 (2H, d, J 8.2, *ArH*), 5.77-5.66 (1H, m, CH_2CHCH_2), 5.10-5.02 (2H, m, CH_2CHCH_2), 3.71 (1H, dd, J 7.7 & 6.0, CHCH_2CH), 3.63 (1H, d, J 13.1, NHCH_2Ph), 3.50 (1H, d, J 13.2, NHCH_2Ph), 2.47-2.35 (2H, m, CHCH_2CH), 1.69 (1H, br s, *NH*), 1.31 (9H, s, *t*-Bu); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 149.7 (C, (-), *Ar*), 144.0 (C, (-), *Ar*), 137.7 (C, (-), *Ar*), 135.6 (CH, (+), CH_2CHCH_2), 128.4 (CH, (+), *Ar*), 127.8 (CH, (+), *Ar*), 127.3 (CH, (+), *Ar*), 127.0 (CH, (+), *Ar*), 125.3 (CH, (+), *Ar*), 117.5 (CH_2 , (-), CH_2CHCH_2), 61.8 (CH, (+), PhCHNH), 51.1 (CH_2 , (-), NHCH_2), 43.2 (CH_2 , (-), PhCHCH_2), 34.5 (C, (-), *t*-Bu), 31.4 (CH_3 , (+), *t*-Bu); IR (neat) $\nu_{\text{max}} = 3334$ (w), 3061 (w), 3026 (w), 2962 (m), 2095 (w), 2868 (w), 2832 (w), 1640 (w), 1603 (w), 1513 (m), 1492 (m), 1453 (s), 1363 (m), 1269 (m), 1202 (w), 1111 (m), 1015 (w), 995 (w), 915 (m), 831 (m), 758 (s) cm^{-1} ; MS TOF ES+ (m/z): 294.2 $[\text{M}+\text{H}]^+$, 316.2 $[\text{M}+\text{Na}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{28}\text{N}^+$, 294.2216; found, 294.2224.

Synthesis of (R)-N-(4-methoxybenzyl)-1-phenylbut-3-en-1-amine S4j.



Prepared using *General Procedure D* with (*S*)-1-phenylbut-3-en-1-amine **S3a** (0.150 g, 1.00 equiv., 1.02 mmol), 4-methoxybenzaldehyde (139 mg, 1.00 equiv., 1.02 mmol), sodium borohydride (77.1 mg, 2.00 equiv., 2.04 mmol) and methanol (20 mL). Purified using a *CombiFlash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that in the literature.¹² Colourless oil (178 mg, 0.485 mmol, 48% yield over two steps). TLC (EtOAc:*n*-hexane = 10:90 v/v, visualised with KMnO_4): $R_f = 0.23$; ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.15 (7H, m, *ArH*), 6.84 (2H, d, J 8.7, *ArH*), 5.74-5.63 (1H, m, CH_2CHCH_2), 5.10-5.01 (2H, m, CH_2CHCH_2), 3.79 (3H, s, OMe), 3.68 (1H, t, J 7.6, CHCH_2CH), 3.61 (1H, d, J 13.0, NHCH_2H), 3.45 (1H, d, J 13.0, NHCH_2H), 2.47-2.32 (2H, m, CHCH_2CH), 1.69 (1H, br s, *NH*); ^{13}C NMR (101 MHz, PENDANT,

CDCl₃): δ 158.5 (C, (-), Ar), 143.9 (C, (-), Ar), 135.5 (CH, (+), CH₂CHCH₂), 132.8 (C, (-), Ar), 129.3 (CH, (+), Ar), 128.4 (CH, (+), Ar), 127.3 (CH, (+), Ar), 127.0 (CH, (+), Ar), 117.5 (CH₂, (-), CH₂CHCH₂), 113.7 (CH, (+), Ar), 61.5 (CH, (+), PhCHNH), 55.3 (CH₃, (+), OMe), 50.8 (CH₂, (-), NHCH₂), 43.1 (CH₂, (-), PhCHCH₂); IR (neat) $\nu_{\max}$ = 3325 (w), 3063 (w), 3027 (w), 3001 (w), 2936 (w), 2907 (w), 2834 (w), 1639 (w), 1611 (m), 1585 (w), 1510 (s), 1453 (m), 1355 (w), 1301 (m), 1244 (s), 1173 (m), 1105 (m), 1035 (s), 995 (m), 915 (s), 817 (s), 775 (s) cm⁻¹; MS TOF ES⁺ (m/z): 268.2 [M+H]⁺.

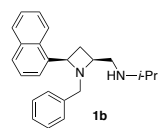


Scheme S 4. General procedure D, two-step conversion of homoallyl amines **S4a-j** into azetidine derivatives **1a-o**.

Synthesis of N-(((2S,4R)-1-benzyl-4-phenylazetidin-2-yl)methyl)propan-2-amine **1a.**

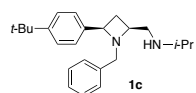
Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-phenylbut-3-en-1-amine (216 mg, 1.00 equiv., 0.910 mmol), iodine (693 mg, 3.00 equiv., 2.73 mmol), NaHCO₃ (382 mg, 5.00 equiv., 4.55 mmol), acetonitrile (30 mL) and isopropyl amine (269 mg, 5.00 equiv., 4.55 mmol). Purified by flash column chromatography (silica gel 40-63 μ m, 0-100% EtOAc/*n*-hexane) and further triturated with 70% EtOAc/*n*-hexane (v/v). White powder (33.0 mg, 0.112 mmol, 12% yield over two steps). [α]_D²¹ +9.2 (*c* 1.00, CH₂Cl₂); mp: 153-154 °C; TLC (MeOH:EtOAc =10:90 v/v, visualised with KMnO₄); ¹H NMR (300 MHz, CDCl₃): 7.48-7.30 (10H, m, ArH), 4.23 (1H, t, *J* 8.2, PhCHCH₂), 3.90 (1H, d, *J* 12.4, PhCHHN), 3.87-3.78 (1H, m, NCHCH₂NH), 3.53 (1H, d, *J* 12.4, PhCHHN), 2.99 (1H, dd, *J* 12.6 & 3.7, NCHCHH), 2.69-2.57 (2H, m, NHCH(CH₃)₂ & PhCHCHH), 2.49-2.40 (2H, m, & PhCHCHH & NCHCHH), 1.26 (3H, d, *J* 6.5, Me), 1.19 (3H, d, *J* 6.6, Me); ¹³C NMR (101 MHz, CDCl₃): δ 140.9 (C, (-), Ar), 138.2 (C, (-), Ar), 129.6 (CH, (+), Ar), 129.5 (CH, (+), Ar), 128.8 (CH, (+), Ar), 128.5 (CH, (+), Ar), 128.1 (CH, (+), Ar), 127.0 (CH, (+), Ar), 65.8 (CH, (+), PhCHCH₂), 60.5 (CH₂, (-), PhCH₂N), 58.1 (CH, (+), NCHCH₂), 52.2 (CH, (+), CH(CH₃)₂), 47.8 (CH₂, (-), CHCH₂NH), 30.2 (CH₂, (-), CHCH₂CH), 19.8 (CH₃, (+), Me), 18.1 (CH₃, (+), Me); IR (powder) $\nu_{\max}$ = 2954 (s), 2798 (s), 2477 (w), 1604 (w), 1569 (w), 1494 (m), 1454 (m), 1396 (m), 1364 (w), 1308 (w), 1212 (w), 1153 (m), 1007 (m), 753 (s), 697 (s) cm⁻¹; MS TOF EI⁺ (m/z): 294.2 [M]⁺; HRMS (m/z): [M]⁺ calcd. for C₂₀H₂₆N₂⁺, 294.2091; found, 294.2094

Synthesis of N-(((2S,4R)-1-benzyl-4-(naphthalen-1-yl)azetidin-2-yl)methyl) propan-2-amine **1b**.



Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(naphthalen-1-yl)but-3-en-1-amine (272 mg, 1.00 equiv., 0.946 mmol), iodine (721 mg, 3.00 equiv., 2.84 mmol), NaHCO₃ (398 mg, 5.00 equiv., 4.73 mmol), acetonitrile (30 mL) and isopropyl amine (0.405 mL, 5.00 equiv., 4.73 mmol). Purified by flash column chromatography (silica gel 40-63 μm, 0-20% MeOH/EtOAc (v/v)) and further triturated with 70% EtOAc/*n*-hexane (v/v). White powder (13.0 mg, 0.0377 mmol, 4% yield over two steps); [α]_D²¹ +33.3 (*c* 1.00, CH₂Cl₂); mp: 169-172 °C; TLC (100% EtOAc, visualised with KMnO₄): R_f = 0.47; ¹H NMR (400 MHz, DMSO d₆): δ: 9.25-9.0 (1H (measured 1.8H), br s), 8.28 (1H, d, *J* 7.9, Ar*H*), 7.96 (1H, d, *J* 7.7, Ar*H*), 7.84 (1H, d, *J* 8.1, Ar*H*), 7.69 (1H, d, *J* 7.0, Ar*H*), 7.60-7.44 (8H, m, Ar*H*), 4.68 (1H, t, *J* 7.0, ArCHCH₂), 4.21 (2H, app br s, PhCHHN & NCHCH₂NH), 3.87-3.83 (1H, m, NCHCH), 3.53 (1H, t, *J* 8.3, ArCHHN), 2.84-2.77 (2H, m, NHCH(CH₃)₂ & CHCHHCH), 2.03-1.96 (1H, m, CHCHHCH), 1.24-1.20 (1H, m, CH), 1.04 (3H, d, *J* 6.5, CH₃), 0.94 (3H, d, *J* 6.5, CH₃); ¹³C NMR (101 MHz, DMSO d₆): δ 134.1 (CH, Ar), 132.6 (CH, Ar), 131.2 (CH, Ar), 130.4 (CH, Ar), 129.5 (CH, Ar), 129.3 (CH, Ar), 128.8 (C, Ar), 127.7 (C, Ar), 126.5 (CH, Ar), 126.2 (CH, Ar), 126.1 (CH, Ar), 124.5 (C, Ar), 123.6 (CH, Ar), 59.4 (CH, naphth CHCH₂), 54.8 (CH, NCHCH₂), 49.7 (CH₂, PhCH₂N), 49.2 (CH₂, NCHCH₂NH), 48.5 (CH, NHCH(CH₃)₂), 37.9 (CH₂, CHCH₂CH), 22.3 (CH₃, Me), 15.0 (CH₃, Me), *one quaternary carbon not observed*; IR (neat) ν_{max} = 2963 (s), 2933 (s), 2803 (s), 2720 (m), 1594 (m), 1564 (s), 1516 (w), 1498 (w), 1459 (s), 1437 (s), 1393 (m), 1369 (m), 1333 (m), 1267 (w), 1246 (w), 1123 (m), 1090 (m), 1033 (m), 1006 (m) 922 (w) cm⁻¹; MS TOF ES⁺ (*m/z*): 345.23 [M+H]⁺; HRMS (*m/z*): [M+H]⁺ calcd. for C₂₄H₂₉N₂⁺, 345.2325; found, 345.2334.

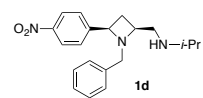
Synthesis of N-(((2S,4R)-1-Benzyl-4-(4-(*tert*-butyl)phenyl)azetidin-2-yl)methyl) propan-2-amine **1c**.



Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-(*tert*-butyl)phenyl)but-3-en-1-amine (356 mg, 1.0 equiv., 1.21 mmol), iodine (924 mg, 3.0 equiv., 3.64 mmol), NaHCO₃ (510 mg, 5.0 equiv., 6.07 mmol), acetonitrile (15 mL) and isopropyl amine (0.52 mL, 5.0 equiv., 6.1 mmol). Purified by flash column chromatography (silica gel 40-63 μm 100% EtOAc) and washed with 70% EtOAc/*n*-hexane (v/v). White powder (25.4 mg, 0.0725 mmol, 6% yield over two steps). [α]_D²¹ +9.8 (*c* 1.00, CH₂Cl₂); mp: 137-139 °C; TLC (100%EtOAc, visualised with KMnO₄): R_f = 0.23; ¹H NMR (300 MHz, CDCl₃): δ 7.50-7.20 (9H, m, Ar*H*), 4.22 (1H, t, *J* 8.2, PhCHCH₂), 3.93 (1H, d, *J* 12.3, PhCHHN), 3.80-3.74 (1H, m, NCHCH₂NH), 3.50 (1H, d, *J* 12.3, PhCHHN), 3.05 (1H, dd, *J* 12.5 & 3.5, CHCHHNNH), 2.64-2.43 (3H, m, NHCH(CH₃)₂, CHCHHCH & CHCHHNNH), 2.33 (1H, dd, *J* 12.5 & 4.2, CHCHHCH), 1.34 (9H, s, *t*-Bu), 1.27 (3H, d, *J* 6.6, Me), 1.19 (3H, d, *J* 6.5, Me); ¹³C NMR: (101 MHz, PENDANT, CDCl₃): δ 151.0 (C, (-), Ar), 138.2 (C, (-), Ar), 137.9 (C, (-), Ar), 129.6 (CH, (+), Ar), 129.4 (CH, (+), Ar), 128.4 (CH, (+), Ar), 126.7 (CH, (+), Ar), 125.6 (CH, (+), Ar), 65.6 (CH, (+), PhCHCH₂), 60.5 (CH₂, (-), PhCH₂N), 58.1 (CH, (+), NCHCH₂), 50.4 (CH, (+), CH(CH₃)₂), 47.7 (CH₂, (-), CHCH₂NH), 34.6 (C, (-), *t*-Bu), 31.4 (CH₃, (+), *t*-Bu), 30.4 (CH₂, (-), CHCH₂CH), 19.8 (CH₃, (+), Me), 18.1 (CH₃, (+), Me); IR (neat) ν_{max} =

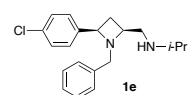
3020 (m), 2958 (s), 2868 (s), 2708 (s), 1570 (w), 1510 (w), 1454 (m), 1393 (m), 1362 (m), 1306 (m), 1269 (s), 1207 (w), 1152 (m), 1110 (m), 1017 (m), 924 (w), 831 (s), 736 (s), 702 (s) cm^{-1} ; MS TOF EI+ (m/z): 350.3 $[\text{M}]^+$; HRMS (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{24}\text{H}_{34}\text{N}_2^+$, 350.2717; found, 350.2725.

Synthesis of N-(((2S,4R)-1-benzyl-4-(4-nitrophenyl)azetidin-2-yl)methyl) propan-2-amine 1d.



Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-nitrophenyl)but-3-en-1-amine (515 mg, 1.0 equiv., 1.82 mmol), iodine (1.39 g, 3.0 equiv., 5.5 mmol), NaHCO_3 (770 mg, 5.0 equiv., 9.12 mmol), acetonitrile (30 mL) and isopropyl amine (0.75 mL, 5.0 equiv., 9.1 mmol). Purified by flash column chromatography (silica gel 40-63 μm , 100% EtOAc). Colourless crystalline solid (113 mg, 0.333 mmol, 18% yield over two steps). TLC (100% EtOAc, visualised with KMnO_4): R_f = 0.21; $[\alpha]_{\text{D}}^{21} +11.1$ (c 1.00, CH_2Cl_2); mp: 155-157 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 8.21 (2H, d, J 8.7, ArH), 7.63 (2H, d, J 8.7, ArH), 7.42-7.31 (5H, m, ArH), 4.28 (1H, t, J 8.2, PhCHCH $_2$), 3.96-3.89 (1H, m, NCHCH $_2$ NH), 3.84 (1H, d, J 12.3, PhCHHN), 3.61 (1H, d, J 12.2, PhCHHN), 3.04-2.94 (1H, m, NHCH(CH $_3$) $_2$), 2.89 (1H, dd, J 12.7 & 3.8, CHCHHNH), 2.77 (1H, dt, J 11. & 7.6, NCHCHH), 2.61 (1H, dd, J 12.7 & 5.4, CHCHHNH), 2.35 (1H, dt, J 11.2 & 8.6, NCHCHH), 1.29 (3H, d, J 6.6, Me), 1.21 (3H, d, J 6.6, Me); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 148.6 (C, (-), Ar), 147.5 (C, (-), Ar), 137.3 (C, (-), Ar), 129.7 (CH, (+), Ar), 129.4 (CH, (+), Ar), 128.5 (CH, (+), Ar), 127.7 (CH, (+), Ar), 123.9 (CH, (+), Ar), 64.8 (CH, (+), PhCHCH $_2$), 60.9 (CH $_2$, (-), PhCH $_2$ N), 58.1 (CH, (+), NCHCH $_2$), 52.0 (CH, (+), CH(CH $_3$) $_2$), 47.6 (CH $_2$, (-), CHCH $_2$ NH), 31.5 (CH $_2$, (-), CHCH $_2$ CH), 19.3 (CH $_3$, (+), Me), 18.2 (CH $_3$, (+), Me); IR (neat) ν_{max} = 3030 (m), 2939 (s), 2787 (s), 2705 (m), 1600 (m), 1516 (s), 1454 (m), 1393 (m), 1343 (s), 1289 (w), 1269 (w), 1245 (w), 1212 (w), 1151 (w), 1108 (m), 1070 (w), 844 (m), 978 (w), 921 (w), 854 (s), 782 (w), 733 (s), 798 (s) cm^{-1} ; MS TOF ES+ (m/z): 340.2 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{26}\text{N}_3\text{O}_2^+$, 340.2020; found, 340.2029.

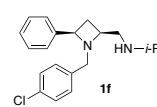
Synthesis of N-(((2R,4S)-1-Benzyl-4-(4-chlorophenyl)azetidin-2-yl)methyl) propan-2-amine 1e.



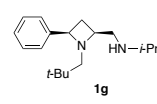
Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-chlorophenyl)but-3-en-1-amine (268 mg, 1.00 equiv., 0.99 mmol), iodine (751 mg, 3.00 equiv., 2.96 mmol), NaHCO_3 (414 mg, 5.00 equiv., 4.93 mmol), acetonitrile (30 mL) and isopropyl amine (0.425 mL, 5.00 equiv., 4.93 mmol). Purified by flash column chromatography (silica gel 40-63 μm , 100% EtOAc). White powder (71.0 mg, 22% yield over two steps). TLC (MeOH:EtOAc =10:90 v/v, visualised with KMnO_4): R_f = 0.49; $[\alpha]_{\text{D}}^{21} +4.4$ (c 1.00, CH_2Cl_2); mp: 160-162 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.33 (9H, m, ArH), 4.16 (1H, t, J 8.2, PhCHCH $_2$), 3.84 (1H, d, J 12.4, PhCHHN), 3.86-3.80 (1H, m, NCHCH $_2$ NH), 3.52 (1H, d, J 12.3, PhCHHN), 2.92 (1H, dd, J 12.6 & 3.5, NCHCHH), 2.80-2.71 (1H, m, NHCH(CH $_3$) $_2$), 2.67-2.61 (1H, m, CHCHHCH), 2.48 (1H, dd, J 12.6 & 5.0, NCHCHH), 2.43-2.36 (1H, m, CHCHHCH), 1.27 (3H, d, J 6.7, Me), 1.19 (3H, d, J 6.6, Me); ^{13}C NMR (101 MHz, CDCl_3): δ 139.5 (C, (-), Ar), 137.8 (C, (-), Ar), 133.7 (C, (-), Ar), 129.6 (CH, (+), Ar), 129.4 (CH, (+), Ar), 128.9 (CH, (+), Ar), 128.5 (CH, (+), Ar), 128.5 (CH, (+), Ar), 65.2 (CH, (+), PhCHCH $_2$), 60.5 (CH $_2$, (-), PhCH $_2$ N), 58.1 (CH, (+), NCHCH $_2$), 52.2 (CH, (+), CH(CH $_3$) $_2$), 47.7 (CH $_2$, (-), CHCH $_2$ NH), 30.8 (CH $_2$, (-), CHCH $_2$ CH), 19.6 (CH $_3$, (+), Me), 18.1

(CH₃, (+), Me); IR (neat) $\nu_{\max}$ = 2934 (s), 2791 (s), 2705 (m), 1597 (m), 1572 (m), 1490 (s), 1454 (s), 1393 (s), 1294 (w), 1275 (w), 1245 (w), 1212 (w), 1153 (s), 1088 (s), 1013 (s), 979 (w), 943 (w), 922 (w), 823 (s), 785 (s), 742 (s), 703 (s) cm⁻¹; MS TOF ES+ (m/z): 329.2 [M+H]⁺; HRMS (m/z): [M+H]⁺ calcd. for C₂₀H₂₆N₂³⁵Cl⁺, 329.1779; found, 329.1786.

Synthesis of N-(((2S,4R)-1-(4-Chlorobenzyl)-4-phenylazetidin-2-yl)methyl)propan-2-amine 1f.

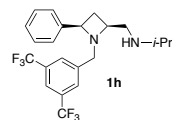
 Prepared using *General Procedure E* with (*R*)-*N*-(4-chlorobenzyl)-1-phenylbut-3-en-1-amine (150 mg, 1.0 equiv., 0.55 mmol), iodine (420 mg, 3.0 equiv., 1.7 mmol), NaHCO₃ (232 mg, 5.0 equiv., 2.8 mmol), acetonitrile (30 mL) and isopropyl amine (0.23 mL, 5.0 equiv., 2.8 mmol). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-100% EtOAc/*n*-hexane (v/v)). White powder (28 mg, 0.09 mmol, 15% yield over two steps). TLC (MeOH: CH₂Cl₂ = 2:98 v/v, visualised with KMnO₄): R_f = 0.23; [α]_D²¹ +7.3 (c 1.00, CH₂Cl₂); mp: 164-166 °C; ¹H NMR (400 MHz, CDCl₃): 7.42-7.27 (9H, m, ArH), 4.14 (1H, t, *J* 8.2, PhCHCH₂), 3.88-3.82 (2H, m, NCHCH₂NH & PhCHHN), 3.58 (1H, d, *J* 12.7, PhCHHN), 3.08 (1H, hept, NHCH(CH₃)₂), 2.87 (1H, dd, *J* 12.6 & 3.5, CHCHHNH), 2.76-2.64 (2H, m, NCHCHH & CHCHHNH), 2.26 (1H, dt, *J* 11.2 & 8.6, NCHCHH), 1.34 (3H, d, *J* 6.6, Me), 1.29 (3H, d, *J* 6.6, Me); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 141.2 (C, (-), Ar), 136.3 (C, (-), Ar), 134.0 (C, (-), Ar), 131.1 (CH, (+), Ar), 129.2 (CH, (+), Ar), 128.6 (CH, (+), Ar), 127.9 (CH, (+), Ar), 126.8 (CH, (+), Ar), 65.7 (CH, (+), PhCHCH₂), 59.8 (CH₂, (-), PhCH₂N), 57.9 (CH, (+), NCHCH₂), 52.0 (CH, (+), CH(CH₃)₂), 47.8 (CH₂, (-), CHCH₂NH), 31.9 (CH₂, (-), CHCH₂CH), 19.3 (CH₃, (+), Me), 18.4 (CH₃, (+), Me); IR (neat) $\nu_{\max}$ = 3026 (m), 2958 (s), 2818 (m), 1598 (w), 1571 (w), 1492 (m), 1458 (w), 1433 (w), 1406 (w), 1309 (w), 1245 (s), 1213 (w), 1154 (m), 1090 (m), 1015 (m), 954 (w), 843 (m), 809 (m), 751 (s), 689 (s) cm⁻¹; MS TOF ES+ (m/z): 329.2 [M+H]⁺; HRMS (m/z): [M+H]⁺ calcd. for C₂₀H₂₆N₂Cl⁺, 329.1779; found, 329.1787;

Synthesis of N-(((2S,4R)-1-neopentyl-4-phenylazetidin-2-yl)methyl)propan-2-amine 1g.

 Prepared using *General Procedure E* with (*R*)-*N*-neopentyl-1-phenylbut-3-en-1-amine (150 mg, 1.0 equiv., 0.69 mmol), iodine (525 mg, 3.0 equiv., 2.1 mmol), NaHCO₃ (289 mg, 5.0 equiv., 3.5 mmol), acetonitrile (10 mL) and isopropyl amine (203 mg, 5.0 equiv., 3.5 mmol). Pale brown powder (61.0 mg, 0.22 mmol, 32% yield over two steps). [α]_D²¹ +30.5 (c 1.00, CH₂Cl₂); TLC (5% MeOH/DCM, visualised with KMnO₄): R_f = 0.23; ¹H NMR (300 MHz, CDCl₃): δ 7.46-7.22 (5H, m, ArH), 3.94 (1H, t, *J* 8.1, CHCH₂CH), 3.68-3.60 (1H, m, NCHCH₂N), 3.57-3.45 (1H, m, NHCH(CH₃)₂), 3.26 (1H, dd, *J* 12.5 & 2.4, NCHCHH), 3.01 (1H, dd, *J* 12.5 & 7.7, NCHCHH), 2.74-2.68 (1H, m, CHCHHCH), 2.45 (2H, s, *t*-BuCHHN), 2.22-2.12 (1H, m, CHCHHCH), 1.55 (6H, d, *J* 6.5, Me), 0.63 (9H, s, *t*-Bu); ¹³C NMR (75.5 MHz, CDCl₃): δ 143.2 (C, Ar), 128.4 (CH, Ar), 127.6 (CH, Ar), 127.4 (CH, Ar), 72.6 (CH, PhCHCH₂), 70.1 (CH, NCHCH₂), 58.7 (CH₂, *t*-BuCH₂N), 51.8 (CH, CH(CH₃)₂), 47.9 (CH₂, CHCH₂NH), 31.5 (CH₂, CHCH₂CH), 29.7 (C, *t*-Bu), 28.4 (CH₃, *t*-Bu), 19.8 (CH₃, Me), 19.2 (CH₃, Me); IR (neat) $\nu_{\max}$ = 2951 (s), 2867 (s), 1639 (m), 1601 (m), 1567 (m), 1460 (s), 1394 (s), 1363 (s), 1318 (m), 1252

(w), 1207 (w), 1157 (m), 1073 (m), 1026 (m), 917 (m), 758 (s), 732 (s), 700 (s) cm^{-1} ; MS TOF ES+ (m/z): 275.3 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{18}\text{H}_{31}\text{N}_2^+$, 275.2483; found, 275.4529;

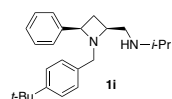
Synthesis of N-(((2S,4R)-1-(3,5-bis(trifluoromethyl)benzyl)-4-phenylazetidin-2-yl)methyl)propan-2-amine 1h.



Prepared using *General Procedure E* with (*R*)-*N*-(3,5-bis(trifluoromethyl)benzyl)-1-phenylbut-3-en-1-amine (150 mg, 1.0 equiv., 0.4 mmol), iodine (306 mg, 3.0 equiv., 1.2 mmol), NaHCO_3 (169 mg, 5.0 equiv., 2.0 mmol), acetonitrile (20 mL) and isopropyl amine (0.172 mL, 5.00 equiv., 2.0 mmol).

Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-100% EtOAc/*n*-hexane) and triturated with Et_2O (2 mL). White powder (58 mg, 0.14 mmol, 34% yield over two steps). TLC (MeOH: EtOAc = 2:98 v/v, visualised with KMnO_4): R_f = 0.33; $[\alpha]_{\text{D}}^{21}$ +9.6 (c 1.00, CH_2Cl_2); mp: 159-162 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.63 (3H, dd, J 17.6 and 1.8, ArH), 7.23-7.15 (5H, m, ArH), 4.09-3.95 (3H, m, PhCHCH₂, NCHCH₂NH & PhCHHN), 3.78 (1H, d, J 13.5, PhCHHN), 3.54-3.44 (1H, m, NHCH(CH₃)₂), 3.09 (1H, dd, J 12.7 & 3.3, NCHCHH), 3.01 (1H, dt, J 12.7 & 7.8, NCHCHH), 2.87 (1H, dt, J 11.1 & 7.5, CHCHHCH), 2.22 (1H, dt, J 11.1 & 8.5, CHCHHCH), 1.50 (3H, d, J 5.0, Me), 1.48 (3H, d, J 5.0, Me); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 140.9 (C, Ar), 140.0 (C, Ar), 131.4 (C, q, $^3J_{\text{C-F}}$ = 33.9 Hz, Ar), 129.2 (CH, Ar), 128.4 (CH, Ar), 127.9 (CH, Ar), 126.8 (CH, Ar), 122.9 (C, q, $^1J_{\text{C-F}}$ = 212 Hz, CF₃), 121.2 (CH, q, $^2J_{\text{C-F}}$ = 3.3 Hz, Ar), 67.0 (CH, PhCHCH₂), 60.4 (CH₂, CH₂N), 57.9 (CH, NCHCH₂), 51.8 (CH, CH(CH₃)₂), 47.8 (CH₂, CHCH₂NH), 33.8 (CH₂, CHCH₂CH), 19.0 (CH₃, Me), 18.7 (CH₃, Me); ^{19}F NMR (282 MHz, CDCl_3): δ 62.8 (s, CF₃); IR (neat) ν_{max} = 2959 (s), 2837 (s), 2801 (s), 1579 (w), 1459 (w), 1383 (m), 1349 (m), 1278 (s), 1173 (m), 1130 (s), 896 (w), 843 (w), 754 (m), 700 (s) cm^{-1} ; MS TOF ES+ (m/z): 431.2 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{F}_6^+$, 431.1916; found, 431.1918.

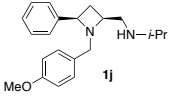
Synthesis of N-(((2S,4R)-1-(4-(tert-butyl)benzyl)-4-phenylazetidin-2-yl)methyl)propan-2-amine 1i.



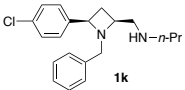
Prepared using *General Procedure E* with (*R*)-*N*-(4-(*tert*-butyl)benzyl)-1-phenylbut-3-en-1-amine (150 mg, 1.0 equiv., 0.51 mmol), iodine (389 mg, 3.0 equiv., 1.5 mmol), NaHCO_3 (215 mg, 5.0 equiv., 2.6 mmol), acetonitrile (10 mL) and isopropyl amine (1 mL, 5.0 equiv., 2.6 mmol). Purified by flash column chromatography (silica gel 40-63 μm , 0-5% MeOH/EtOAc). Pale brown oil (68.1 mg, 0.19 mmol, 38% yield over two steps). $[\alpha]_{\text{D}}^{21}$ +87.9 (c 1.00, CH_2Cl_2); TLC (100% EtOAc, visualised with KMnO_4): R_f = 0.47; ^1H NMR (300 MHz, CDCl_3): δ 7.48-7.29 (9H, m ArH), 4.23 (1H, t, J 8.2, PhCHCH₂), 3.87-3.74 (2H, m, NCHCH₂NH & PhCHHN), 3.49 (1H, d, J 12.3, PhCHHN), 3.04 (1H, dd, J 12.5 & 3.2, CHCHHNH), 2.65-2.34 (4H, m, NHCH(CH₃)₂, NCHCH₂ & CHCHHNH), 1.29 (9H, s, *t*-Bu), 1.24 (3H, d, J 6.6, Me), 1.16 (3H, d, J 6.6, Me); ^{13}C NMR (75.5 MHz, CDCl_3): δ 151.8 (C, Ar), 140.8 (C, Ar), 135.1 (C, Ar), 129.3 (CH, Ar), 128.8 (CH, Ar), 128.1 (CH, Ar), 127.0 (CH, Ar), 126.3 (CH, Ar), 65.8 (CH, PhCHCH₂), 59.9 (CH₂, PhCH₂N), 58.3 (CH, NCHCH₂), 52.2 (CH, CH(CH₃)₂), 47.3 (CH₂, CHCH₂NH), 34.7 (C, *t*-Bu), 31.3 (CH₃, *t*-Bu), 30.0 (CH₂, CHCH₂CH), 19.9 (CH₃, Me), 17.9 (CH₃, Me); IR (neat) ν_{max} = 3020 (m), 2958 (s), 2871 (s), 2793 (s), 2708 (s), 1600 (w), 1570 (w), 1511 (w), 1492 (w), 1453 (w), 1393 (m), 1362 (m), 1307 (w), 1269 (m), 1245 (w), 1215 (w), 1152 (m), 1109 (m), 1017 (m), 979 (w),

927 (w), 858 (w), 841 (w), 812 (w), 782 (w), 755 (m), 734 (s), 699 (s) cm^{-1} ; MS TOF EI+ (m/z): 351.4 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{35}\text{N}_2$, 351.2795; found, 351.2798

Synthesis of N-(((2S,4R)-1-(4-methoxybenzyl)-4-phenylazetidin-2-yl)methyl) propan-2-amine 1j.

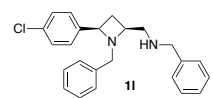
 Prepared using *General Procedure E* with (*R*)-*N*-(4-methoxybenzyl)-1-phenylbut-3-en-1-amine (150 mg, 1.0 equiv., 0.56 mmol), iodine (311 mg, 3.0 equiv., 1.7 mmol), NaHCO_3 (170 mg, 5.0 equiv., 2.0 mmol), acetonitrile (10 mL) and isopropyl amine (0.167 mL, 5.0 equiv., 2.0 mmol). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-100% EtOAc/*n*-hexane and 0-10% MeOH/ CH_2Cl_2). Pale brown oil (78.3 mmol, 0.241 mmol, 43% yield over two steps). $[\alpha]_{\text{D}}^{21} +48.0$ (c 1.00, CH_2Cl_2); TLC (10% MeOH/EtOAc, visualised with KMnO_4): $R_f = 0.42$; ^1H NMR (300 MHz, CDCl_3): δ 7.44-7.29 (7H, m, ArH), 6.94 (2H, d, J 8.6, ArH), 4.20 (1H, t, J 8.3, PhCHCH_2), 3.85-3.80 (5H, m, NCHCH_2NH , PhCHHN & OMe), 3.47 (1H, d, J 12.4, PhCHHN), 2.94 (1H, dd, J 12.5 & 4.6, CHCHHNH), 2.82-2.75 (1H, m, $\text{NHCH}(\text{CH}_3)_2$), 2.69-2.62 (1H, m, NCHCHH), 2.56 (1H, dd, J 12.5 & 4.3, CHCHHNH), 2.30 (1H, dt, J 11.3 & 8.6, NCHCHH), 1.27 (3H, d, J 6.5, Me), 1.21 (3H, d, J 6.5, Me); ^{13}C NMR (101 MHz, CDCl_3): δ 159.7 (C, (-), Ar), 141.2 (C, (-), Ar), 130.9 (CH, (+), Ar), 130.0 (C, (-), Ar), 128.7 (CH, (+), Ar), 128.0 (CH, (+), Ar), 126.8 (CH, (+), Ar), 114.8 (CH, (+), Ar), 65.4 (CH, (+), PhCHCH_2), 59.8 (CH_2 , (-), PhCH_2N), 57.7 (CH, (+), NCHCH_2), 55.5 (CH_3 , (+), OMe), 52.1 (CH, (+), $\text{CH}(\text{CH}_3)_2$), 48.5 (CH_2 , (-), NCHCH_2NH), 30.3 (CH_2 , (-), CHCH_2CH), 19.7 (CH_3 , (+), Me), 18.2 (CH_3 , (+), Me); IR (neat) $\nu_{\text{max}} = 2936$ (m), 2833 (m), 2781 (m), 2705 (m), 1610 (s), 1584 (m), 1511 (s), 1454 (m), 1393 (m), 1354 (w), 1302 (m), 1246 (s), 1175 (m), 1155 (m), 1109 (w), 1030 (s), 852 (m), 822 (m), 788 (w), 749 (s), 734 (s), 699 (s) cm^{-1} ; MS TOF ES+ (m/z): 325.2 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}^+$, 325.2274; found, 325.2282.

Synthesis of N-(((2S,4R)-1-Benzyl-4-(4-chlorophenyl)azetidin-2-yl)methyl) propan-1-amine 1k.

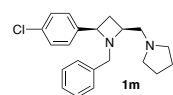
 Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-chlorophenyl)but-3-en-1-amine (150 mg, 1.0 equiv., 0.6 mmol), iodine (420 mg, 3.0 equiv., 1.7 mmol), NaHCO_3 (232 mg, 5.0 equiv., 2.8 mmol), acetonitrile (15 mL) and *n*-propyl amine (163 mg, 5.0 equiv., 2.8 mmol). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-100% EtOAc/*n*-hexane) and washed with Et_2O (2 mL). Pale brown powder (82.0 mg, 45% yield over two steps). mp: 161-163 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{21} +13.2$ (c 1.00, CH_2Cl_2); TLC (100% EtOAc, visualised with KMnO_4): $R_f = 0.24$; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.34 (9H, m, ArH), 4.17 (1H, t, J 8.2, PhCHCH_2), 3.87 (1H, d, J 12.2, PhCHHN), 3.72-3.66 (1H, m, NCHCH_2NH), 3.49 (1H, d, J 12.2, PhCHHN), 3.04 (1H, dd, J 12.8 & 2.6, CHCHHNH), 2.64-2.56 (2H, m, NCHCHH & *n*-propyl), 2.47-2.42 (1H, m, NCHCHH), 2.26 (1H, dd, J 12.8 & 5.1, CHCHHNH), 2.19-2.12 (1H, m, *n*-propyl), 1.72-1.55 (2H, m, *n*-propyl), 0.86 (3H, t, J 7.4, *n*-propyl); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 139.3 (C, (-), Ar), 137.6 (C, (-), Ar), 133.7 (C, (-), Ar), 129.5 (CH, (+), Ar), 129.4 (CH, (+), Ar), 128.9 (CH, (+), Ar), 128.4₂ (CH, (+), Ar), 128.3₈ (CH, (+), Ar), 65.3 (CH, (+), PhCHCH_2), 60.5 (CH_2 , (-), PhCH_2N), 58.0 (CH, (+), NCHCH_2), 49.9 (CH_2 , (-), *n*-propyl), 49.5 (CH_2 , (-), CHCH_2N), 30.5 (CH_2 , (-), CHCH_2CH), 19.4 (CH_2 , (-), *n*-propyl), 11.0 (CH_3 , (+), *n*-propyl); IR (neat) $\nu_{\text{max}} = 2953$ (s), 2884 (m), 2851 (m), 2801

(s), 1573 (m), 1492 (s), 1455 (m), 1440 (m), 1407 (m), 1363 (m), 1295 (w), 1265 (s), 1208 (m), 1157 (m), 1089 (s), 1043 (w), 1015 (s), 968 (w), 922 (w), 821 (s), 779 (w), 734 (s), 701 (s) cm^{-1} ; MS TOF ES+ (m/z): 329.2 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{26}\text{N}_2^{35}\text{Cl}^+$, 329.1779⁺; found, 329.1786.

Synthesis of N-benzyl-1-((2R, 4S)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine 1l.

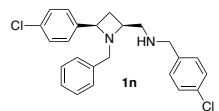
 Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-chlorophenyl)but-3-en-1-amine (1.50 g, 1.0 equiv., 5.5 mmol), iodine (4.20 g, 3.0 equiv., 16.6 mmol), NaHCO_3 (2.32 g, 5.0 equiv., 27.6 mmol), acetonitrile (15 mL) and benzylamine (2.96 mL, 5.0 equiv., 27.6 mmol). Purified using a *Combiflash 200i* (silica 12 g column, 0-50% EtOAc/*n*-hexane and 0-5% MeOH/DCM). Pale yellow oil (782 mg, 2.1 mmol, 38% yield over two steps). $[\alpha]_{\text{D}}^{21} +47.1$ (c 1.00, CH_2Cl_2); TLC (30% EtOAc/Hexane, visualised with KMnO_4): R_f = 0.26; ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.18 (14H, m, ArH), 3.94 (1H, t, J 8.1, PhCHCH_2), 3.75 (1H, d, J 12.8, PhCHHN), 3.58 (2H, d, J 2.1, PhCH_2N), 3.51 (1H, d, J 12.8, PhCHHN), 3.32-3.26 (1H, m, NCHCH_2NH), 2.50 (1H, dd, J 12.1 & 4.4, CHCHHNH), 2.43-2.35 (2H, m, NCHCHH & CHCHHNH), 1.92 (1H, dt, J 10. & 8.6, CHCHHNH), 1.43 (1H, br s, NH); ^{13}C NMR (101 MHz, CDCl_3): δ 142.1 (C, Ar), 140.6 (C, Ar), 138.6 (C, Ar), 132.6 (C, Ar), 129.1 (CH, Ar), 128.2 (CH, Ar), 128.2₈ (CH, Ar), 128.2₃ (CH, Ar), 128.1 (CH, Ar), 127.9 (CH, Ar), 127.2 (CH, Ar), 126.7 (CH, Ar), 64.6 (CH, PhCHCH_2), 62.6 (CH, (+), NCHCH_2), 61.5 (CH_2 , PhCH_2N), 54.1 (CH_2 , PhCH_2N), 53.6 (CH_2 , NCHCH_2NH), 31.1 (CH_2 , CHCH_2CH); IR (neat) ν_{max} = 3315 (w), 3083 (w), 3062 (w), 3027 (w), 3000 (w), 2816 (m), 1598 (w), 1490 (s), 1453 (s), 1411 (w), 1382 (w), 1354 (w), 1292 (w), 1236 (w), 1206 (w), 1155 (w), 1087 (s), 1057 (w), 1028 (w), 1013 (s), 939 (w), 909 (w), 822 (s), 792 (w), 734 (s), 696 (s) cm^{-1} ; MS TOF ES+ (m/z): 377.2 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{26}\text{N}_2^{35}\text{Cl}^+$, 377.1779⁺; found, 377.1776

Synthesis of 1-(((2S,4R)-1-Benzyl-4-(4-chlorophenyl)azetidin-2-yl)methyl) pyrrolidine 1m.

 Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-chlorophenyl)but-3-en-1-amine (150 mg, 1.00 equiv., 0.552 mmol), iodine (420 mg, 3.0 equiv., 1.7 mmol), NaHCO_3 (232 mg, 5.0 equiv., 2.8 mmol), acetonitrile (10 mL) and pyrrolidine (169 mg, 5.0 equiv., 2.8 mmol). Pale brown powder (67 mg, 0.20 mmol, 36% yield over two steps). $[\alpha]_{\text{D}}^{21} +52.7$ (c 1.00, CH_2Cl_2); mp: 157-159 °C; TLC (5% MeOH/DCM, visualised with KMnO_4): R_f = 0.24; ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.24 (9H, m, ArH), 4.10 (1H, t, J 8.1, CHCH_2CH), 3.85-3.77 (2H, m, NCHCH_2N & PhCHHN), 3.57 (1H, d, J 12.4, PhCHHN), 3.21 (4H, br s, pyrrolidine), 2.91-2.80 (2H, m, CHCHHN & CHCHHCH), 2.62 (1H, dd, J 12.8 & 2.8, CHCHHN), 2.07 (4H, br s, pyrrolidine), 1.96 (1H, dt, J 10.7 & 8.4, CHCHHCH); ^{13}C NMR (75.5 MHz, PENDANT, CDCl_3): δ 140.5 (C, (-), Ar), 137.1 (C, (-), Ar), 133.2 (C, (-), Ar), 129.7 (CH, (+), Ar), 128.6₄ (CH, (+), Ar), 128.5₆ (CH, (+), Ar), 127.9 (CH, (+), Ar), 127.8 (CH, (+), Ar), 65.1 (CH, (+), PhCHCH_2), 60.9 (CH_2 , (-), PhCH_2N), 59.7 (CH, (-), NCHCH_2), 57.2 (CH_2 , (+), CHCH_2N), 54.4 (CH_2 , (-), pyrrolidine), 35.4 (CH_2 , (-), CHCH_2CH), 23.2 (CH_2 , (-), pyrrolidine); IR (neat) ν_{max} = 3027 (m), 2883 (m), 2824 (m), 2676 (m), 2605 (w), 2475 (w), 1598 (w), 1490 (s), 1453 (s), 1396 (m), 1354 (m), 1272 (w), 1213 (w),

1157 (m), 1087 (s), 1013 (s), 939 (w), 912 (w), 821 (s), 780 (w), 733 (s), 703 (s) cm^{-1} ; MS TOF ES+ (m/z): 341.18 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{26}\text{N}_2^{35}\text{Cl}^+$, 341.1779; found, 341.1786;

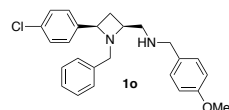
Synthesis of 1-((2R, 4S)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)-N-(4-chlorobenzyl)methanamine 1n.



Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-chlorophenyl)but-3-en-1-amine (250 mg, 1.0 equiv., 0.92 mmol), iodine (702 mg, 3.0 equiv., 2.8 mmol), NaHCO_3 (387 mg, 5.0 equiv., 4.6 mmol), acetonitrile (15 mL) and 4-chlorobenzylamine (653 mg, 5.0 equiv., 4.6 mmol).

Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-100% EtOAc/*n*-hexane and 0-5% MeOH/DCM). Pale yellow oil (118 mg, 0.287 mmol, 31% yield over two steps). $[\alpha]_{\text{D}}^{21} +59.1$ (c 1.00, CH_2Cl_2); TLC (50% EtOAc/*n*-hexane, visualised with KMnO_4): $R_f = 0.50$; ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.09 (13H, m, ArH), 3.96 (1H, t, J 8.1, PhCHCH_2), 3.76 (1H, d, J 12.8, PhCHHN), 3.54-3.47 (3H, m, PhCHHN & CH_2NHCH_2), 3.31-3.24 (1H, m, NCHCH_2NH), 2.45 (1H, dd, J 12.1 & 4.4, CHCHHNH), 2.41-2.36 (1H, m, NCHCHH), 2.32 (1H, dd, J 12.1 & 4.5, CHCHHNH), 1.97-1.90 (1H, m, CHCHHCH), 1.55 (1H, br s, NH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 142.0 (C, Ar), 139.0 (C, Ar), 138.6 (C, Ar), 132.7 (C, Ar), 132.3 (C, Ar), 129.3 (CH, Ar), 129.1 (CH, Ar), 128.3 (CH, Ar), 128.3 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 127.2 (CH, Ar), 64.6 (CH, PhCHCH_2), 62.6 (CH, NCHCH_2), 61.5 (CH_2 , PhCH_2N), 53.4 (CH_2 , PhCH_2N), 53.3 (CH_2 , NCHCH_2NH), 31.0 (CH_2 , CHCH_2CH); IR (neat) $\nu_{\text{max}} = 3086$ (w), 3065 (w), 3029 (w), 2831 (m), 1597 (w), 1490 (s), 1454 (m), 1407 (m), 1381 (w), 1292 (w), 1234 (w), 1165 (w), 1088 (s), 1060 (m), 1014 (s), 940 (w), 821 (s), 742 (m), 702 (s) cm^{-1} ; MS TOF ES+ (m/z): 411.14 $[\text{M}+\text{H}]^+$; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{Cl}_2^+$, 411.1389; found, 411.1396;

Synthesis of 1-((2R, 4S)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)-N-(4-methoxybenzyl)methanamine 1o.

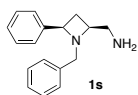


Prepared using *General Procedure E* with (*R*)-*N*-benzyl-1-(4-chlorophenyl)but-3-en-1-amine (250 mg, 1.0 equiv., 0.92 mmol), iodine (702 mg, 3.0 equiv., 2.8 mmol), NaHCO_3 (387 mg, 5.0 equiv., 4.6 mmol), acetonitrile (15 mL) and 4-methoxybenzylamine (632 mg, 5.0 equiv., 4.6 mmol). Purified using a

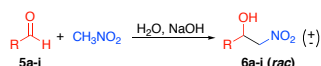
Combiflash Rf 200i (silica 4 g column, 0-100% EtOAc/*n*-hexane and 0-5% MeOH/DCM). Pale yellow oil (156 mg, 0.38 mmol, 42% yield over two steps). $[\alpha]_{\text{D}}^{21} +81.6$ (c 1.00, CH_2Cl_2); TLC (50% EtOAc/hexane, visualised with KMnO_4): $R_f = 0.26$; ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.09 (11H, m, ArH), 6.83 (2H, d, J 8.7, ArH), 3.94 (1H, t, J 8.2, PhCHCH_2), 3.80 (3H, s, OMe), 3.75 (1H, d, J 12.8, PhCHHN), 3.53-3.48 (3H, m, PhCH_2N & CH_2NHCH_2), 3.33-3.24 (1H, m, NCHCH_2NH), 2.49 (1H, dd, J 12.1 & 4.5, CHCHHNH), 2.44-2.33 (2H, m, CHCHHNH & NCHCHH), 1.90 (1H, dt, J 10.2 & 8.8, CHCHHCH), 1.43 (1H, br s, NH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 158.5 (C, Ar), 142.1 (C, Ar), 138.6 (C, Ar), 132.6 (C, Ar), 129.1 (CH, Ar), 128.7 (CH, Ar), 128.3 (C, Ar), 128.3 (CH, Ar), 128.2 (CH, Ar), 128.2 (CH, Ar), 127.2 (CH, Ar), 113.6 (CH, Ar), 64.6 (CH, PhCHCH_2), 62.6 (CH, (+), NCHCH_2), 61.5 (CH_2 , PhCH_2N), 55.3 (CH_2 , PhCH_2N), 53.5 (CH_2 , NCHCH_2NH), 31.2 (CH_2 , CHCH_2CH); IR (neat) $\nu_{\text{max}} = 3089$ (w), 3065 (w), 3029 (w), 2996 (w), 2830 (m), 1611 (m), 1585 (m), 1511 (s), 1490 (s), 1454 (s), 1384 (w), 1357 (w), 1300 (m), 1245 (s), 1173 (m), 1088 (m), 1035 (s), 1016 (s), 943 (w), 821 (s), 742 (m), 701 (s)

cm⁻¹; MS TOF ES+ (*m/z*): 407.19 [M+H]⁺; HRMS (*m/z*): [M+H]⁺ calcd. for C₂₅H₂₈N₂OCl⁺, 407.1885; found, 407.1893.

Synthesis of ((2S,4R)-1-benzyl-4-phenylazetidin-2-yl)methanamine, 1s.

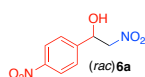


Caesium carbonate (0.87 mmol, 283 mg) and iodine (0.29 mmol, 74 mg), were added to *N*-benzyl-1-((2*S*,4*R*)-1-benzyl-4-phenylazetidin-2-yl)methanamine **1r** (0.29 mmol, 100 mg),¹³ in CH₃CN (15 mL) and stirred at room temperature until starting azetidine was completely consumed (TLC). Subsequent treatment with HCl (3 M, aqueous) at 60 °C (1 h) followed by neutralisation with NaOH (2 M, aqueous), extraction into dichloromethane, drying over magnesium sulfate, filtration and evaporation to dryness *in vacuo* afforded a yellow oil, 73 mg, >99%. [α]_D²⁰ = +107.8 (*c* 1.4, CHCl₃). All other characterisation matched that reported for the racemate.¹⁴ IR 3061, 3027, 2019, 2851, 1601, 1493, 1454, 1353, 1303, 1209, 1157; ¹H NMR (δ ; 300 MHz, CDCl₃); 1.22 (2H, br, NH₂), 1.76 (1H, aptq, obs *J* = 8.7, PhCHCHH), 2.26-2.35 (3H, m, PhCHCHH and NCHCH₂NH₂), 3.07-3.15 (1H, m, NCHCH₂NH₂), 3.59 (2H, ABq, *J*_{AB} = 12.9, NCH₂Ph), 3.95 (1H, aptt, obs *J* = 8.1, PhCHCH₂), 7.12-7.40 (10H, m, PhH); ¹³C NMR (δ ; 100 MHz, CDCl₃), 29.79 (CH₂), 45.60 (CH₂), 61.45 (CH₂), 64.59 (CH), 64.89 (CH), 126.70 (CH), 127.05 (CH), 127.08 (CH), 128.17 (CH), 128.21 (CH), 129.12 (CH), 138.97 (C), 143.56 (C). High-resolution MS calcd. for [M+H]⁺ formula C₁₇H₂₁N₂⁺: 253.1699; found: 253.1717.



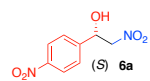
Scheme S 5. Conversion of aldehydes **5a-j** into the corresponding racemic nitromethane Henry reaction adducts **6a-j**.

Synthesis of (rac)-1-(4-nitrophenyl)-2-nitroethanol (rac)-6a.



Prepared using *General Procedure F* with 4-nitrobenzaldehyde (0.30 g, 2.0 mmol), nitromethane (0.11 mL, 2.0 mmol), sodium hydroxide aqueous solution (10 M, 0.2 mL, 2.0 mmol) and acetic acid (0.11 mL, 2.0 mmol) and ethanol (3 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation (¹H and ¹³C NMR spectroscopy, IR and mass spectra) reported is consistent with that given the literature (racemic product).¹⁵ Pale yellow crystalline solid (0.33 g, 1.5 mmol, 77% yield). mp: 92-94 °C; TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): R_f = 0.34; ¹H NMR (300 MHz, CDCl₃): δ 8.30 (2H, d, *J* 8.8 Hz, ArH), 7.65 (2H, d, *J* 8.5 Hz, ArH), 5.66-5.61 (1H, m, CHOH), 4.63-4.60 (2H, m, CH₂NO₂), 3.16 (1H, br s, OH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 148.2 (C, (-), Ar), 144.9 (C, (-), Ar), 126.9 (CH, (+), Ar), 124.2 (CH, (+), Ar), 80.6 (CH₂, (-), CH₂NO₂), 70.0 (CH, (+), CHOH); IR (solid) ν_{max} = 3520 (broad, m), 3115 (w), 3083 (w), 2921 (w) 1553 (s), 1518 (s), 1348 (s), 1083 (m), 857 (m) cm⁻¹ [lit.¹⁵ (racemic, film): 3458, 3113, 3082, 2984, 2931, 1527, 1348, 1085, 857 cm⁻¹]; MS Scan AP+ (*m/z*): 213.3 [M+H]⁺;

Synthesis of (S)-1-(4-nitrophenyl)-2-nitroethanol (**S**)-**6a**.



Prepared using *General Procedure G* with 4-nitrobenzaldehyde (75.6 mg, 1.0 equiv., 0.5 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.¹⁶ Pale yellow solid (85.7 mg, 0.429 mmol, 86% yield); 91% *e.e.* was determined by HPLC using a chiral stationary phase (Eurocel 01, 5 μm, OD, 6.5 % IPA/*n*-hexane, 0.5 mL/min, UV 254 nm), minor enantiomer (*R*) *t*_r = 37.0 min, major enantiomer (*S*) *t*_r = 44.9 min; [α]_D²¹ +19.9 (*c* 1.00, CH₂Cl₂); mp: 87-89 °C; TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): *R*_f = 0.20; ¹H NMR (300 MHz, CDCl₃): δ 8.27 (2H, d, *J* 8.8 Hz, *ArH*), 7.63 (2H, d, *J* 9.0 Hz, *ArH*), 5.62 (1H, dd, *J* 7.8, 4.5 Hz, *CHOH*), 4.76-4.52 (2H, m, CH₂NO₂), 3.19 (1H, br s, *OH*); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 148.2 (C, (-), *Ar*), 144.9 (C, (-), *Ar*), 127.0 (CH, (+), *Ar*), 124.2 (CH, (+), *Ar*), 80.6 (CH₂, (-), CH₂NO₂), 70.0 (CH, (+), *CHOH*); IR (solid) *ν*_{max} = 3484 (broad, m), 3116 (w), 3083 (w), 2913 (w), 1546 (s), 1509 (s), 1347 (s), 1076 (s), 860 (s) cm⁻¹; MS TOF AP+ (*m/z*): 213.1 [M+H]⁺. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit.^{16b} [α]_D²¹-31.6 (*c* 1.05, CH₂Cl₂, 78% *e.e.*, (*R*)-isomer)], [lit.^{16a} [α]_D²⁵+36.1 (*c* 0.98, CH₂Cl₂, 95% *e.e.*, (*S*)-isomer)].

Synthesis of (rac)-1-phenyl-2-nitroethanol (**rac**)-**6b**.



Prepared using *General Procedure F* with benzaldehyde (0.300 g, 2.83 mmol), nitromethane (0.15 mL, 2.8 mmol), sodium hydroxide aqueous solution (10 M, 0.28 mL, 2.8 mmol), acetic acid (0.16 mL, 2.8 mmol) and ethanol (3 mL). Purified by flash column chromatography (silica gel 40-63 μm, 15-20 % EtOAc/*n*-hexane). The characterisation (¹H and ¹³C NMR spectroscopy, IR and mass spectra) reported is consistent with that given the literature (racemic product).¹⁵ Colourless oil (0.366 g, 2.2 mmol, 77% yield). TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): *R*_f = 0.47; ¹H NMR (300 MHz, CDCl₃): δ 7.41-7.34 (5H, m, *ArH*), 5.46 (1H, dd, *J* 9.4 & 3.2, *CHOH*), 4.61 (1H, dd, *J* 13.3 & 9.4, CHHNO₂), 4.51 (1H, dd, *J* 13.3 & 3.2, CHHNO₂), 2.88 (1H, br s, *OH*); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 138.1 (C, (-), *Ar*), 129.1 (CH, (+), *Ar*), 129.0 (CH, (+), *Ar*), 126.0 (CH, (+), *Ar*), 81.2 (CH₂, (-), CH₂NO₂), 71.0 (CH, (+), CHCH₂); IR (neat) *ν*_{max} = 3432 (broad, m), 3065 (w), 3033 (w), 2921 (w), 1548 (s), 1495 (m), 1453 (m), 1417 (m), 1377 (s), 1288 (m), 1192 (m), 1065 (m), 894 (m), 764 (m), 698 (s), 522 (m) cm⁻¹ [lit.¹⁵ (racemic, film): 3442, 3065, 3033, 2922, 1556, 1495, 1454, 1419, 1378 cm⁻¹]; MS TOF EI+ (*m/z*): 167.07 [M]⁺.

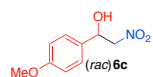
Synthesis of (S)-1-phenyl-2-nitroethanol (**S**)-**6b**.



Prepared using *General Procedure G* with benzaldehyde (53.1 mg, 1.0 equiv., 0.50 mmol), nitromethane (0.27 mL, 10.0 equiv., 5.0 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified

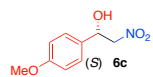
using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.^{16a, 17} Colourless oil (68.0 mg, 0.407 mmol, 81% yield); 95% *e.e.* was determined by HPLC using a chiral stationary phase (Eurocel 01, 5 μ m, OD, 6.0 % IPA/*n*-hexane, 0.5 mL/min, UV 230 nm), minor enantiomer (*R*) t_r = 20.9 min, major enantiomer (*S*) t_r = 25.0 min); $[\alpha]_D^{21}$ +26.8 (*c* 1.00, CH₂Cl₂); TLC (EtOAc:*n*-hexane= 20:80 v/v, visualised with KMnO₄): R_f = 0.31; ¹H NMR (300 MHz, CDCl₃): δ 7.42-7.35 (5H, m, ArH), 5.47 (1H, dd, *J* 9.5 & 3.0, CHOH), 4.62 (1H, dd, *J* 13.4 & 9.6, CHHNO₂), 4.52 (1H, dd, *J* 13. & 3.1, CHHNO₂), 2.79 (1H, br s, OH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 138.1 (C, (-), Ar), 129.1 (CH, (+), Ar), 129.0 (CH, (+), Ar), 125.9 (CH, (+), Ar), 81.2 (CH₂, (-), CH₂NO₂), 71.0 (CH, (+), CHCH₂); IR (neat) ν_{max} = 3431 (broad, m), 3068 (w), 3033 (w), 2921 (w), 1547 (s) 1495 (m), 1454 (m), 1418 (m), 1377 (s), 1288 (m), 1193 (m), 1065 (m), 894 (m), 763 (m), 698 (s) cm⁻¹; MS TOF AP- (*m/z*): 166.0 [M-H]⁻. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit:¹⁷ $[\alpha]_D^{20}$ -42.6 (*c* 1.0, CH₂Cl₂, 94% *e.e.*, (*R*)-isomer)], [lit:^{16a} $[\alpha]_D^{25}$ +40.2 (*c* 0.96, CH₂Cl₂), 98% *e.e.*, (*S*)-isomer].

Synthesis of (rac)-1-(4-methoxyphenyl)-2-nitroethanol (**rac**)-6c.



Prepared using *General Procedure F* with 4-methoxybenzaldehyde (0.300 g, 2.2 mmol), nitromethane (0.12 mL, 2.2 mmol), sodium hydroxide aqueous solution (10 M, 0.22 mL, 2.2 mmol) and acetic acid (0.13 mL, 2.2 mmol) and ethanol (3 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation (¹H and ¹³C NMR spectroscopy, IR and mass spectra) reported is consistent with that given the literature (racemic product).¹⁵ Colourless oil (0.334 g, 1.69 mmol, 77% yield); TLC (EtOAc:*n*-hexane= 20:80 v/v, visualised by UV 254 nm): R_f = 0.19; ¹H NMR (300 MHz, CDCl₃): δ 7.33 (2H, d, *J* 8.7 Hz, ArH), 6.94 (2H, d, *J* 8.6, ArH), 5.42 (1H, dd, *J* 9.2 & 2.2, CHOH), 4.62 (1H, dd, *J* 13.1 & 9.6, CHCHHNO₂), 4.49 (1H, dd, *J* 13.2 & 3.2, CHCHHNO₂), 3.83 (3H, s, OMe), 2.85 (1H, br s, OH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 160.0 (C, (-), Ar), 130.2 (C, (-), Ar), 127.3 (CH, (+), Ar), 114.4 (CH, (+), Ar), 81.2 (CH₂, (-), CHCH₂NO₂), 70.7 (CH, (+), PhCHCH₂), 55.4 (CH₃, (+), OMe); IR (neat) ν_{max} = 3457 (broad, m), 2969 (w), 2926 (w), 2840 (w), 1709 (w), 1549 (s), 1377 (m), 1245 (s), 1027 (s) cm⁻¹ [lit:¹⁵ (racemic, film): 3452, 3005, 2960, 2839, 2036, 1895, 1553, 1379, 1250, 1030 cm⁻¹]; MS Scan AP+ (*m/z*): 197.3 [M]⁺.

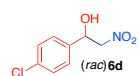
Synthesis of (S)-1-(4-methoxyphenyl)-2-nitroethanol (**S**)-6c.



Prepared using *General Procedure G* with 4-methoxybenzaldehyde (68.1 mg, 1.0 equiv., 0.50 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.^{16a, 17} Colourless oil (73.0 mg, 0.37 mmol, 74% yield); 93% *e.e.* was determined by HPLC with a chiral stationary phase (Eurocel 01, 5 μ m, OD, 6.0% IPA/*n*-hexane, 0.5 mL/min, UV 220 nm), minor enantiomer (*R*) t_r = 26.1 min, major enantiomer (*S*) t_r = 30.7 min); $[\alpha]_D^{21}$ +24.5 (*c* 1.00, CH₂Cl₂); TLC

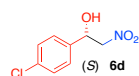
(EtOAc:*n*-hexane= 20:80 v/v, visualised with KMnO₄): *R_f* = 0.21; ¹H NMR (400 MHz, CDCl₃): δ 7.32 (2H, d, *J* 8.4, *ArH*), 6.92 (2H, d, *J* 8.8, *ArH*), 5.41 (1H, dd, *J* 9.6 & 3.1, *CHOH*), 4.60 (1H, dd, *J* 13.3 & 9.4, *CHCHHNO*₂), 4.48 (1H, dd, *J* 13.3 & 3.1, *CHCHHNO*₂), 2.77 (1H, br s, *OH*); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 160.1 (C, (-), *Ar*), 130.2 (C, (-), *Ar*), 127.3 (CH, (+), *Ar*), 114.4 (CH, (+), *Ar*), 81.3 (CH₂, (-), *CHCH₂NO*₂), 70.7 (CH, (+), *CHCH₂*), 55.4 (CH₃, (+), *OMe*); IR (neat) *v*_{max} 3452 (broad, m), 2969 (w), 2925 (w), 2840 (w), 1677 (w), 1549 (s), 1377 (m), 1245 (s), 1026 (s) cm⁻¹; MS TOF AP- (*m/z*): 196.0 [M-H]⁻. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit.¹⁷ [α]_D²⁰ -31.9 (*c* 1.00, CH₂Cl₂, 94% *e.e.*, (*R*)-isomer)], [lit.^{16a} [α]_D²⁵ +28.4 (*c* 1.76, CH₂Cl₂), 95% *e.e.*, (*S*)-isomer].

Synthesis of (rac)-1-(4-chlorophenyl)-2-nitroethanol (**rac**)-6d.



Prepared using *General Procedure F* with 4-chlorobenzaldehyde (0.30 g, 2.1 mmol), nitromethane (0.12 mL, 2.1 mmol), sodium hydroxide aqueous solution (10 M, 0.21 mL, 2.1 mmol) and acetic acid (0.13 mL, 2.13 mmol) and ethanol (3 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature (*S* isomer).¹⁸ Colourless oil (0.261 g, 1.29 mmol, 61% yield). TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): *R_f* = 0.35; ¹H NMR (300 MHz, CDCl₃): δ 7.40-7.33 (4H, m, *ArH*), 5.45 (1H, dt, *J* 9.1 & 5.9, *CHOH*), 4.58 (1H, dd, *J* 13.4 & 9.2, *CHHNO*₂), 4.48 (1H, dd, *J* 13.4 & 3.4, *CHHNO*₂), 2.94 (1H, br s, *OH*); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 136.5 (C, (-), *Ar*), 134.9 (C, (-), *Ar*), 129.3 (CH, (+), *Ar*), 127.3 (CH, (+), *Ar*), 81.0 (CH₂, (-), *CH₂NO*₂), 70.3 (CH, (+), *CHOH*); IR (neat) *v*_{max} = 3470 (broad, m), 2921 (w), 1594 (m), 1549 (s), 1491 (s), 1411 (m), 1377 (s), 1339 (s), 1294 (m), 1207 (m), 1191 (m), 1085 (s), 1014 (s), 895 (m), 823 (s), 739 (s), 660 (m), 524 (s) cm⁻¹ [lit.¹⁸ ((*S*)-isomer, KBr): 3436, 2922, 1596, 1557, 1493, 1414, 1379, 1209, 1191, 1089, 1014, 896, 829, 740, 661, 528 cm⁻¹]; MS TOF EI+ (*m/z*): 201.04 [M]⁺.

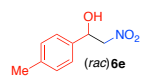
Synthesis of (*S*)-1-(4-chlorophenyl)-2-nitroethanol (**S**)-6d.



Prepared using *General Procedure G* with 4-chlorobenzaldehyde (70.3 mg, 1.0 equiv., 0.50 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.^{16a, 17} Colourless oil (70 mg, 0.347 mmol, 69% yield); 95% *e.e.* was determined by HPLC using a chiral stationary phase (Eurocel 01, 5 μm, OD, 6.0 % IPA/*n*-hexane, 0.5 mL/min, UV 220 nm), minor enantiomer (*R*) *t_r* = 20.1 min, major enantiomer (*S*) *t_r* = 23.8 min; [α]_D²¹ +26.9 (*c* 1.00, CH₂Cl₂); TLC (EtOAc:*n*-hexane= 20:80 v/v, visualised with KMnO₄): *R_f* = 0.26; ¹H NMR (300 MHz, CDCl₃): δ 7.40-7.33 (4H, m, *ArH*), 5.45 (1H, dd, *J* 9.2 & 3.3, *CHOH*), 4.60-4.47 (2H, m, *CHCH₂NO*₂), 2.98 (1H, br s, *OH*); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 136.5 (C, (-), *Ar*), 134.9 (C, (-), *Ar*), 129.3 (CH, (+), *Ar*), 127.3 (CH, (+), *Ar*), 81.0 (CH₂, (-), *CH₂NO*₂), 70.3 (CH, (+), *CHOH*); IR (neat) *v*_{max} = 3467 (broad, m), 2921 (w), 1597 (m), 1549 (s),

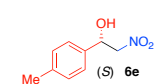
1492 (s), 1413 (m), 1377 (s), 1343 (m), 1289 (m), 1209 (m), 1192 (m), 1084 (s), 1014 (s), 895 (m), 825 (s), 739 (s), 660 (m) cm^{-1} ; MS TOF AP- (m/z): 200.0 $[\text{M}-\text{H}]^-$. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit¹⁷ $[\alpha]_{\text{D}}^{20}$ -38.1 (c 1.00, CH_2Cl_2), 92% *e.e.*, (*R*)-isomer], [lit^{16a} $[\alpha]_{\text{D}}^{25}$ +19.9 (c 1.00, CH_2Cl_2), 98% *e.e.*, (*S*)-isomer)].

Synthesis of (rac)-1-(4-methylphenyl)-2-nitroethanol (**(rac)-6e**).



Prepared using *General Procedure F* with *p*-tolualdehyde (0.30 g, 2.5 mmol), nitromethane (0.13 mL, 2.5 mmol), Sodium hydroxide aqueous solution (10 M, 0.25 mL, 2.5 mmol) and acetic acid (0.14 mL, 2.5 mmol) and ethanol (3 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature (*S* isomer).¹⁸ Colourless solid (0.391 g, 2.16 mmol, 86%). TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): R_f = 0.40; ¹H NMR (300 MHz, CDCl_3): δ 7.28 (2H, d, J 8.1, ArH), 7.20 (2H, d, J 8.0, ArH), 5.36 (1H, dd, J 9.4 & 3.2, CHOH), 4.59 (1H, dd, J 13.2 & 9.5, CHHNO₂), 4.48 (1H, dd, J 13.2 & 3.0, CHHNO₂), 2.85 (1H, br s, OH), 2.36 (3H, s, Me); ¹³C NMR (101 MHz, PENDANT, CDCl_3): δ 139.0 (C, (-), Ar), 135.2 (C, (-), Ar), 129.7 (CH, (+), Ar), 125.9 (CH, (+), Ar), 81.3 (CH₂, (-), CH₂NO₂), 70.9 (CH, (+), CHOH), 21.2 (CH₃, (+), Me); IR (neat) ν_{max} = 3540 (w), 3439 (w), 3028 (w), 2922 (w), 1549 (s), 1417 (m), 1376 (s), 1337 (s), 1206 (m), 1076 (m), 1040 (m), 894 (w), 816 (s), 693 (m) cm^{-1} [lit¹⁸ ((*S*)-isomer, KBr): 3539, 3421, 3028, 2922, 1557, 1418, 1378, 1340, 1205, 1078, 1041, 895, 819, 692 cm^{-1}]; MS Scan AP- (m/z): 181.2 $[\text{M}]^-$.

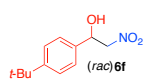
Synthesis of (*S*)-1-(4-methylphenyl)-2-nitroethanol (**(S)-6e**).



Prepared using *General Procedure G* with *p*-tolualdehyde (60.1 mg, 1.0 equiv., 0.5 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*,4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.^{16a, 19} Colourless oil (65 mg, 0.359 mmol, 72% yield); 93% *e.e.* was determined by HPLC with a chiral stationary phase (Eurocel 01, 5 μm , OD, 6.0% IPA/*n*-hexane, 0.5 mL/min, UV 210 nm), minor enantiomer (*R*) t_r = 20.6 min, major enantiomer (*S*) t_r = 24.3 min; $[\alpha]_{\text{D}}^{21}$ +35.1 (c 1.00, CH_2Cl_2); mp: 55-57 °C; TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): R_f = 0.25; ¹H NMR (300 MHz, CDCl_3): δ 7.28 (2H, d, J 8.1, ArH), 7.21 (2H, d, J 7.9, ArH), 5.41 (1H, dd, J 9.6, 3.1 Hz, CHOH), 4.59 (1H, dd, J 13.2 & 9.6, CHHNO₂), 4.48 (1H, dd, J 13.2 & 3.0, CHHNO₂), 2.74 (1H, br s, OH), 2.36 (3H, s, Me); ¹³C NMR (101 MHz, PENDANT, CDCl_3): δ 139.0 (C, (-), Ar), 135.2 (C, (-), Ar), 129.7 (CH, (+), Ar), 125.9 (CH, (+), Ar), 81.3 (CH₂, (-), CHCH₂NO₂), 70.9 (CH, (+), PhCHCH₂), 21.2 (CH₃, (+), Me); IR (solid) ν_{max} = 3550 (broad, m), 3040 (w), 2956 (m), 1552 (s), 1419 (m), 1381 (s), 1339 (m), 1216 (m), 1077 (s), 1030 (m), 902 (m), 829 (s), 667 (s) cm^{-1} ; MS TOF AP- (m/z): 180.1 $[\text{M}-\text{H}]^-$. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following

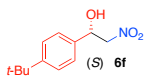
literature values: [lit:¹⁹ $[\alpha]_{\text{D}}^{25}$ -26.8 (*c* 4.60, CH₂Cl₂, 93% *e.e.*, (*R*)-isomer)], [lit:^{16a} $[\alpha]_{\text{D}}^{25}$ +24.8 (*c* 1.10, CH₂Cl₂), 98% *e.e.*, (*S*)-isomer].

Synthesis of (rac)-1-(4-tert-butylphenyl)-2-nitroethanol (rac)-6f



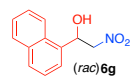
Prepared using *General Procedure F* with 4-*tert*-buthylbenzaldehyde (0.30 g, 1.9 mmol), nitromethane (0.1 mL, 1.9 mmol), sodium hydroxide aqueous solution (10 M, 0.19 mL, 1.9 mmol) and acetic acid (0.1 mL, 1.9 mmol) and ethanol (3 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation (¹H and ¹³C NMR spectroscopy, IR and mass spectra) reported is consistent with that given the literature (*R* isomer).²⁰ White crystalline solid (0.342 g, 1.53 mmol, 83%). mp: 80-82 °C [lit:²⁰ (*R*-isomer) 70-72 °C ((*R*)-isomer)]; TLC (EtOAc: *n*-hexane= 20:80 *v/v*, visualized by UV 254 nm): *R_f* = 0.50; ¹H NMR (300 MHz, CDCl₃): δ 7.42 (2H, d, *J* 8.4 Hz, *ArH*), 7.33 (2H, d, *J* 8.3 Hz, *ArH*), 5.43 (1H, dd, *J* 9.5, 2.2 Hz, PhCHCH₂), 4.65-4.47 (2H, m, CH₂NO₂), 2.79 (1H, br, s, OH), 1.32 (9H, s, *t*Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 152.2 (C, (-), Ar), 135.1 (CH, (-), Ar), 126.0 (CH, (+), Ar), 125.7 (CH, (+), Ar), 81.2 (CH₂, (-), CHCH₂NO₂), 70.9 (CH, (+), PhCHCH₂), 34.7 (C, (-), *t*Bu), 31.3 (CH₃, (+), *t*Bu); IR (solid) ν_{max} = 3516 (broad, m), 2953 (m), 2901 (m), 2867 (m), 1552 (s), 1510 (m), 1417 (m), 1383 (s), 1266 (m), 1218 (m), 1106 (m), 1076 (s), 897 (m), 828 (s), 748 (m) cm⁻¹ [lit:²⁰ (thin film (*R*)-isomer) 3546, 2963, 2360, 1555, 1378, 1219, 1078, 836, 772 cm⁻¹]; MS TOF ES+ (*m/z*): 246.3 [M+Na]⁺; HRMS (*m/z*): [M+Na]⁺ calcd. for C₁₂H₁₇NO₃Na, 246.1106; found, 246.1107.

Synthesis of (S)-1-(4-tert-butylphenyl)-2-nitroethanol (S)-6f



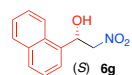
Prepared using *General Procedure G* with 4-*tert*-buthylbenzaldehyde (81.1 mg, 1.0 equiv., 0.5 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.²⁰⁻²¹ White solid (85.7 mg, 0.384 mmol, 77% yield); 93% *e.e.* was HPLC using a chiral stationary phase (Eurocel 01, 5 μm, OD, 6.0% IPA/*n*-hexane, 0.5 mL/min, UV 220 nm), minor enantiomer (*R*) *t_r* = 17.1 min, major enantiomer (*S*) *t_r* = 20.9 min); $[\alpha]_{\text{D}}^{21}$ +23.9 (*c* 1.00, CHCl₃); mp: 68-70 °C; TLC (EtOAc:*n*-hexane= 20:80 *v/v*, visualised with KMnO₄): *R_f* = 0.40; ¹H NMR (300 MHz, CDCl₃): δ 7.42 (2H, d, *J* 8.4, *ArH*), 7.33 (2H, d, *J* 8.3, *ArH*), 5.44 (1H, dd, *J* 9.6 & 3.0, CHOH), 4.62 (1H, dd, *J* 13.3 & 9.7, CHCHHNO₂), 4.51 (1H, dd, *J* 13.3 & 3.0, CHCHHNO₂), 2.73 (1H, br, s, OH), 1.32 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 152.2 (C, (-), Ar), 135.1 (CH, (-), Ar), 126.0 (CH, (+), Ar), 125.7 (CH, (+), Ar), 81.2 (CH₂, (-), CHCH₂NO₂), 70.9 (CH, (+), PhCHCH₂), 34.7 (C, (-), *t*-Bu), 31.3 (CH₃, (+), *t*-Bu); IR (solid) ν_{max} = 3550 (broad, m), 2955 (m), 2901 (m), 2867 (m), 1553 (s), 1510 (m), 1420 (m), 1385 (s), 1266 (m), 1216 (m), 1107 (m), 1076 (s), 902 (s), 829 (s), 749 (m), 667 (s) cm⁻¹; MS TOF AP- (*m/z*): 222.1 [M-H]⁻. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit:²⁰ $[\alpha]_{\text{D}}^{21}$ -31.35 (*c* 0.7, CHCl₃, 92% *e.e.*, (*R*)-isomer)], [lit:²¹ $[\alpha]_{\text{D}}^{25}$ +38.3 (*c* 1.00, CHCl₃, 99% *e.e.*, (*S*)-isomer)].

Synthesis of (rac)-1-(1-naphthyl)-2-nitroethanol (**(rac)-6g**)



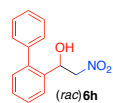
Prepared using *General Procedure F* with 1-naphthaldehyde (0.30 g, 1.9 mmol), nitromethane (0.10 mL, 1.92 mmol), sodium hydroxide aqueous solution (10 M, 0.19 mL, 1.9 mmol) and acetic acid (0.11 mL, 1.9 mmol) and ethanol (3 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature (*S* isomer).¹⁸ Yellow oil (0.324 g, 78% yield); TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): R_f = 0.47; ¹H NMR (300 MHz, CDCl₃): δ 8.04 (1H, d, *J* 8.7, Ar*H*), 7.93-7.85 (2H, m, Ar*H*), 7.77 (1H, d, *J* 7.2, Ar*H*), 7.63-7.50 (3H, m, Ar*H*), 6.28 (1H, dd, *J* 8.1 & 3.8, CHOH), 4.69-4.66 (2H, m, CH₂NO₂), 2.88 (1H, br s, OH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 133.8 (C, (-), Ar), 133.5 (C, (-), Ar), 129.6 (C, (-), Ar), 129.4 (CH, (+), Ar), 129.3 (CH, (+), Ar), 127.1 (CH, (+), Ar), 126.1 (CH, (+), Ar), 125.5 (CH, (+), Ar), 123.9 (CH, (+), Ar), 121.8 (CH, (+), Ar), 80.8 (CH₂, (-), CH₂NO₂), 68.3 (CH, (+), CHOH); IR (neat) $\nu_{\max}$ = 3512 (broad, m), 3056 (w), 2918 (w), 1598 (w), 1549 (s), 1508 (s), 1377 (s), 1334 (s), 1202 (m), 1165 (m), 1096 (m), 1047 (m), 896 (m), 802 (s), 773 (s), 696 (m), 623 (m) cm⁻¹ [lit:¹⁸ ((*S*)-isomer, KBr): 3543, 3060, 3930, 1554, 1513, 1378, 1201, 1166, 1098, 1052, 897, 804, 776, 697, 624 cm⁻¹]; MS TOF ES- (*m/z*): 216.1 [M-H]⁻.

Synthesis of (*S*)-1-(1-naphthyl)-2-nitroethanol (**(S)-6g**)



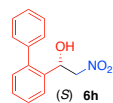
Prepared using *General Procedure G* with 1-naphthaldehyde (78.1 mg, 1.0 equiv., 0.5 mmol), nitromethane (0.27 mL, 10 equiv., 5 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.¹⁶ Yellow oil (93.0 mg, 0.428 mmol, 86% yield); 93% *e.e.* was determined by HPLC with a chiral stationary phase (Eurocel 01, 5 μ m, OD, 6.0 % IPA/*n*-hexane, 0.5 mL/min, UV 254 nm), minor enantiomer (*R*) t_r = 23.1 min, major enantiomer (*S*) t_r = 34.7 min; $[\alpha]_D^{21}$ +18.3 (*c* 1.00, CH₂Cl₂); TLC (EtOAc:*n*-hexane= 20:80 v/v, visualised by UV 254 nm): R_f = 0.33; ¹H NMR (400 MHz, CDCl₃): δ 8.03-7.93 (1H, m, Ar*H*), 7.89 (2H, ddt, *J* 20.9, 8.2 & 0.9, Ar*H*), 7.77 (1H, dt, *J* 7.2 & 1.0, Ar*H*), 7.60 (1H, m, Ar*H*), 7.60-7.47 (2H, m, Ar*H*), 6.27 (1H, dt, *J* 8.5 & 3.1, CHOH), 4.69-4.66 (2H, m, CH₂NO₂), 2.82-2.90 (1H, br s, OH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 133.8 (C, (-), Ar), 133.5 (C, (-), Ar), 129.6 (C, (-), Ar), 129.5 (CH, (+), Ar), 129.4 (CH, (+), Ar), 127.1 (CH, (+), Ar), 126.1 (CH, (+), Ar), 125.5 (CH, (+), Ar), 123.9 (CH, (+), Ar), 121.8 (CH, (+), Ar), 80.8 (CH₂, (-), CH₂NO₂), 68.4 (CH, (+), CHOH); IR (neat) $\nu_{\max}$ = 3527 (broad, m), 3058 (w), 2921 (w), 1598 (w), 1547 (s), 1511 (s), 1376 (s), 1331 (m), 1201 (m), 1166 (m), 1097 (m), 1047 (m), 895 (m), 803 (s), 773 (s), 696 (m) cm⁻¹; MS TOF AP+ (*m/z*): 217.1 [M]⁺. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit:^{16b} $[\alpha]_D^{23}$ -24.9 (*c* 1.08, CH₂Cl₂, 87% *e.e.*, (*R*)-isomer)], [lit:^{16a} $[\alpha]_D^{25}$ +26.0 (*c* 1.06, CH₂Cl₂, 98% *e.e.*, (*S*)-isomer)].

Synthesis of (rac)-1-(biphenyl-2-yl)-2-nitroethanol (**(rac)-6h**).



Prepared using *General Procedure F* with biphenyl-2-carboxaldehyde (0.10 g, 0.55 mmol), nitromethane (0.03 mL, 0.6 mmol), sodium hydroxide aqueous solution (10 M, 0.06 mL, 0.6 mmol) and acetic acid (0.03 mL, 0.5 mmol) and ethanol (2mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature (single enantiomer product).¹⁸ Colourless oil (0.112 g, 0.460 mmol, 84% yield); TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): R_f = 0.43; ¹H NMR (300 MHz, CDCl₃): δ 7.65 (1H, dd, J 7.5, 1.7 Hz, ArH), 7.50-7.35 (5H, m, ArH), 7.32-7.24 (3H, m, ArH), 5.58 (1H, dd, J 9.6 & 2.7, CHOH), 4.50 (1H, dd, J 13.5 & 9.6, CHCHHNO₂), 4.34 (1H, dd, J 13.5 & 2.7), 2.80 (1H, br s, OH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 140.9 (C, (-), Ar), 139.8 (C, (-), Ar), 135.4 (C, (-), Ar), 130.5 (CH, (+), Ar), 128.9 (CH, (+), Ar), 128.8 (CH, (+), Ar), 128.7 (CH, (+), Ar), 128.3 (CH, (+), Ar), 127.9 (CH, (+), Ar), 126.1 (CH, (+), Ar), 80.3 (CH₂, (-), CHCH₂NO₂), 67.6 (CH, (+), PhCHOH); IR (neat) $\nu_{\max}$ = 3479 (broad, m), 3060 (w), 3026 (w), 1708 (w), 1596 (w), 1550 (s), 1477(s), 1376 (s), 1281 (m), 1188 (m), 1068 (s), 1009 (m), 893 (m), 763 (s), 702 (s), 607 (s) cm⁻¹ [lit:¹⁸ ((S)-isomer, KBr): 3544, 3060, 3026, 1683, 1596, 1556, 1478, 1377, 1340, 1282, 1188, 1069, 1009, 894, 764, 704, 608 cm⁻¹]; MS TOF AP- (m/z): 243.1 [M]⁺.

Synthesis of (S)-1-(biphenyl-2-yl)-2-nitroethanol (**(S)-6h**).



Prepared using *General Procedure G* with biphenyl-2-carboxaldehyde (91.1 mg, 1.0 equiv., 0.50 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.03 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.03 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.¹⁸ Colourless oil (68.0 mg, 56% yield); 87% *e.e.* was determined by HPLC with a chiral stationary phase (Eurocel 01, 5 μ m, OD, 3.0 % IPA/*n*-hexane, 0.5 mL/min, UV 220 nm), minor enantiomer (*R*) t_r = 17.5 min, major enantiomer (*S*) t_r = 20.3 min); [α]_D²¹ +9.1 (c 1.00, CH₂Cl₂); TLC (EtOAc:*n*-hexane= 20:80 v/v, visualised by UV 254 nm): R_f = 0.32; ¹H NMR (300 MHz, CDCl₃): δ 7.66-7.28 (9H, m, ArH), 5.58 (1H, dd, J 9.6, 2.7 Hz, CHOH), 4.51 (1H, dd, J 13.6, 9.6, CHCHHNO₂), 4.35 (1H, dd, J 13.6, 2.7, CHCHHNO₂), 2.75 (1H, br s, OH); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 140.9 (C, (-), Ar), 139.8 (C, (-), Ar), 135.4 (C, (-), Ar), 130.5 (CH, (+), Ar), 128.9 (CH, (+), Ar), 128.8 (CH, (+), Ar), 128.7 (CH, (+), Ar), 128.3 (CH, (+), Ar), 127.9 (CH, (+), Ar), 126.1 (CH, (+), Ar), 80.3 (CH₂, (-), CHCH₂NO₂), 67.6 (CH, (+), PhCHOH); IR (neat) $\nu_{\max}$ = 3540 (broad, m), 3060 (w), 3026 (w), 1710 (w), 1597 (w), 1549 (s), 1478 (m), 1376 (s), 1280 (m), 1188 (m), 1068 (s), 1009 (m), 893 (m), 763 (s), 702 (s) cm⁻¹; MS TOF AP- (m/z): 242.1 [M-H]⁺. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit:¹⁸ [α]_D²⁰ +23.0 (c 1.00, CH₂Cl₂, 90% *e.e.*, (*S*)-isomer)].

Synthesis of (rac)-1-cyclohexyl-2-nitroethanol (**(rac)-6i**).



Prepared using *General Procedure F* with cyclohexanecarboxaldehyde (0.30 g, 2.7 mmol), nitromethane (0.15 mL, 2.7 mmol), Sodium hydroxide aqueous solution (10 M, 0.27 mL, 2.7 mmol) and acetic acid (0.15 mL, 2.7 mmol) and ethanol (3 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation (^1H and ^{13}C NMR spectroscopy, IR and mass spectra) reported is consistent with that given the literature (racemic product).¹⁵ Colourless oil (0.36 g, 2.1 mmol, 78% yield). TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised by UV 254 nm): R_f = 0.34; ^1H NMR (300 MHz, CDCl_3): δ 4.51 (1H, dd, J 13.1 & 3.2, CHCHHNO_2), 4.43 (1H, dd, J 13. & 8.6, CHCHHNO_2), 4.14-4.08 (1H, m, CHOH), 2.62 (1H, br s, OH), 1.86-1.78 (3H, m, Cy), 1.72-1.66 (2H, m, Cy), 1.55-1.43 (1H, m, Cy), 1.33-1.05 (5H, m, Cy); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 79.3 (CH_2 , (-), CHCH_2NO_2), 72.9 (CH , (+), CHOH), 41.4 (CH , (+), Cy), 28.8 (CH_2 , (-), Cy), 28.0 (CH_2 , (-), Cy), 26.1 (CH_2 , (-), Cy), 25.9 (CH_2 , (-), Cy), 25.8 (CH_2 , (-), Cy); IR (neat) ν_{max} = 3454 (broad, m), 2925 (s), 2853 (m), 1551 (s), 1450 (m), 1423 (w), 1382 (m), 1066 (m), 1203 (m), 1046 (m), 894 (m), 651 (m) cm^{-1} [lit:¹⁵ (racemic, film): 3450, 2925, 2855, 1557, 1450, 1424, 1376 cm^{-1}]; MS Scan AP+ (m/z): 174.3 $[\text{M}+\text{H}]^+$.

Synthesis of (S)-1-cyclohexyl-2-nitroethanol (**(S)-6i**).



Prepared using *General Procedure G* with cyclohexanecarboxaldehyde (56.1 mg, 1.0 equiv., 0.5 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). The characterisation reported is consistent with that given the literature.¹⁶ Colourless oil (74.0 mg, 0.271 mmol., 54% yield); >99% *e.e.* was determined by chiral HPLC (Eurocel 01, 5 μm , OD, 6.0 % IPA/*n*-hexane, 0.5 mL/min, UV 210 nm), (major enantiomer (*S*) t_r = 40.3 min); $[\alpha]_{\text{D}}^{21}$ +5.2 (c 1.00, CH_2Cl_2); TLC (EtOAc:*n*-hexane= 20:80 v/v, visualised with KMnO_4): R_f = 0.49; ^1H NMR (400 MHz, CDCl_3): δ 4.49 (1H, dd, J 13.1 & 3.0, CHCHHNO_2), 4.43 (1H, dd, J 13.1 & 8.9, CHCHHNO_2), 4.12-4.08 (1H, m, CHOH), 2.68 (1H, br s, OH), 1.86-1.77 (3H, m, Cy), 1.72-1.65 (2H, m, Cy), 1.52-1.43 (1H, m, Cy), 1.32-1.04 (5H, m, Cy); ^{13}C NMR (101 MHz, PENDANT, CDCl_3): δ 79.3 (CH_2 , (-), CHCH_2NO_2), 72.9 (CH , (+), CHOH), 41.4 (CH , (+), Cy), 28.8 (CH_2 , (-), Cy), 28.0 (CH_2 , (-), Cy), 26.1 (CH_2 , (-), Cy), 25.9 (CH_2 , (-), Cy), 25.8 (CH_2 , (-), Cy); IR (neat) ν_{max} = 3411 (broad, m), 2926 (s), 2854 (m), 1550 (s), 1450 (m), 1424 (w), 1384 (m), 1202 (m), 1066 (m), 1045 (m), 894 (m) cm^{-1} ; MS TOF AP- (m/z): 172.1 $[\text{M}-\text{H}]^-$. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit^{16b} $[\alpha]_{\text{D}}^{21}$ -21.6 (c 1.33, CHCl_3 , 93% *e.e.*, (*R*) isomer)], [lit^{16a} $[\alpha]_{\text{D}}^{25}$ +18.0 (c 1.02, CH_2Cl_2), 93% *e.e.*, (*S*) isomer].

Synthesis of (rac)-3,3-dimethyl-1-nitrobutan-2-ol (**(rac)-6j**).



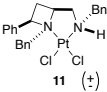
Prepared using *General Procedure F* with trimethylacetaldehyde (0.20 g, 2.3 mmol), nitromethane (0.13 mL, 2.3 mmol), sodium hydroxide aqueous solution (10 M, 0.23 mL, 2.3 mmol) and acetic acid (0.13 mL, 2.3 mmol) and ethanol (2 mL). The characterisation (^1H and ^{13}C NMR spectroscopy, IR and mass spectra) reported is

consistent with that given the literature (racemic product).¹⁵ Colourless oil (0.263 g, 1.79 mmol, 77% yield). TLC (EtOAc: hexane = 20:80 v/v, visualised with KMnO₄): R_f = 0.42; ¹H NMR (300 MHz, CDCl₃): δ 4.53 (1H, dd, J 13.0 & 2.2, 1H), 4.37 (1H, dd, J 13.0 & 10.1, CHHNO₂), 4.07-4.01 (1H, m, CHOH), 2.38-2.42 (1H, br s, OH), 0.98 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 78.3 (CH₂, (-), CHCH₂NO₂), 76.2 (CH, (+), CHCH₂), 34.3 (C, (-), *t*-Bu), 25.6 (CH₃, (+), *t*-Bu); IR (neat) $\nu_{\max}$ = 3479 (broad, m), 2962 (m), 2875 (m), 1551 (s) 1480 (m), 1382 (m), 1348 (m), 1191 (m), 1085 (s), 1007 (m), 924 (m), 881 (m), 791 (w), 699 (s) cm⁻¹ [lit:¹⁵ (racemic, film): 3554, 2963, 2874, 1560, 1480, 1382, 1347 cm⁻¹]; MS TOF AP+ (m/z): 148.1 [M+H]⁺.

Synthesis of (S)-3,3-dimethyl-1-nitrobutan-2-ol (**S**)-**6j**.

 Prepared using *General Procedure G* with trimethylacetaldehyde (43.1 mg, 1.0 equiv., 0.5 mmol), nitromethane (0.27 mL, 10 equiv., 5.0 mmol), Cu(OAc)₂·H₂O (4.99 mg, 5 mol%, 0.025 mmol), *N*-benzyl-1-((2*R*, 4*S*)-1-benzyl-4-(4-chlorophenyl)azetidin-2-yl)methanamine (9.42 mg, 5 mol%, 0.025 mmol) and ethanol (1 mL). Purified using a *Combiflash Rf 200i* (silica 4 g column, 0-30% EtOAc/*n*-hexane). Colourless oil (45.0 mg, 61% yield); >99% *e.e.* was determined by HPLC with a chiral stationary phase (Eurocel 01, 5 μ m, OD, 0.8 % IPA/*n*-hexane, 0.8 mL/min, UV 210 nm), minor enantiomer (*R*) t_r = 14.2 min, major enantiomer (*S*) t_r = 15.3 min; [α]_D²¹ +20.9 (*c* 1.00, CH₂Cl₂); TLC (EtOAc:*n*-hexane = 20:80 v/v, visualised with KMnO₄): R_f = 0.47; ¹H NMR (400 MHz, CDCl₃): δ 4.76-4.12 (2H, m, CHCH₂NO₂), 4.04 (1H, dq, J 10.2 & 2.1, CHOH), 2.40 (1H, br s, OH), 0.98 (9H, s, *t*-Bu); ¹³C NMR (101 MHz, PENDANT, CDCl₃): δ 78.3 (CH₂, (-), CHCH₂NO₂), 76.2 (CH, (+), CHCH₂), 34.3 (C, (-), *t*-Bu), 25.6 (CH₃, (+), *t*-Bu); IR (neat) $\nu_{\max}$ = 3500 (broad, m), 2963 (m), 2875 (m), 1551 (s) 1480 (m), 1382 (m), 1348 (m), 1191 (m), 1084 (s), 1007 (m), 923 (m), 880 (m), 791 (w), 699 (s) cm⁻¹; MS TOF AP- (m/z): 146.1 [M-H]⁻. The absolute configuration was assigned as (*S*) by comparison of the optical rotation with the following literature values: [lit:^{16b} [α]_D²¹ -35.9 (*c* 1.01, CH₂Cl₂, 94% *e.e.*, (*R*)-isomer)], [lit [α]_D²⁵ +33.02 (*c* 3.71, CH₂Cl₂, 92% *e.e.*, (*S*)-isomer)].

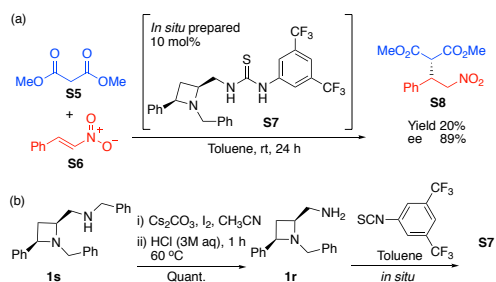
Synthesis of (rac)-N-benzyl-1-((cis)-1-benzyl-4-phenylazetidin-2-yl)methanamine platinum(II)chloride (**rac**)-**7**.

 Under nitrogen atmosphere, K₂PtCl₄ (0.26 mmol, 110 mg) was added to a solution of methanol and *rac*-**1r** (0.29 mol, 100 mg). The mixture was stirred for 16 hours at 60 °C after which the solvent was removed *in vacuo* and crystallisation from CH₃CN:Et₂O afforded a small number of yellow crystals, suitable for analysis by XRD, see later. M/z : (ES⁺) [M-Cl]⁺ 572.4, [M-2Cl]⁺ 536.1.

Preliminary organocatalysis experiment

To further exemplify the potential of the 2,4-*cis*-substituted azetidine structure as a platform for asymmetric catalysis a preliminary organocatalysis experiment was conducted.²² Menguy and Couty had already demonstrated an *in situ* preparation of amino azetidine thiourea derivatives and applied this scaffold to catalytic asymmetric Michael additions of diethyl malonate to nitrovinyl Michael acceptors.²³

To give a preliminary indication of the stereinduction capability of 2,4-*cis*-substituted azetidines in organocatalysis the Menguy and Couty protocol was attempted. An *in situ* prepared thiourea catalyst **S7** was able to deliver product **S8** in 89% e.e. albeit in only 20% yield (**Scheme S 6a**).²⁴ Catalyst **S7** was prepared according to the Menguy and Couty procedure from homochiral azetidine derivative **1s** which was accessed from **1r** by the same method, previously reported by Feula and Fossey.^{14,25}



Scheme S 6. Preliminary experiment which demonstrates the *in situ* generation and use of a thiourea derivative **S7** as a promising organocatalyst for Michael-type reactions of malonates with nitroalkenes.

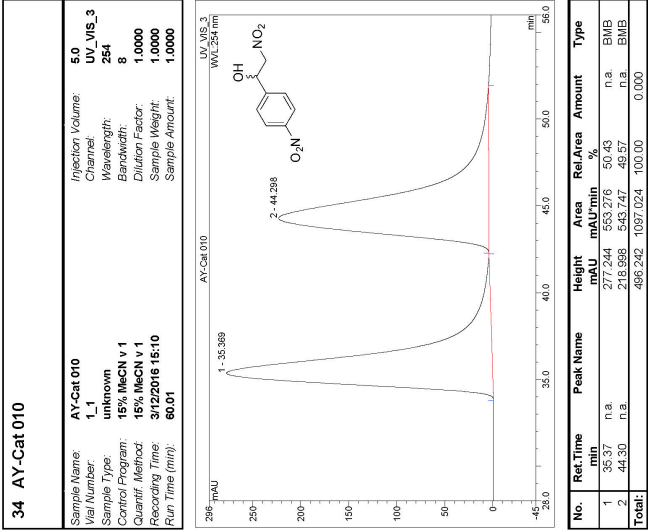
This single, un-optimised, attempt to prepare **S8** under control of an organocatalytic azetidine derivative (**Scheme S 6a**) demonstrates the plural capacity for the azetidine scaffold to engender asymmetry across a range of reaction manifolds. Exploration of the organocatalytic potential of *cis*-disubstituted azetidine scaffold will be the subject of further study emerging from the laboratories of this team.

Synthesis of (S)-dimethyl 2-(2-nitro-1-phenylethyl)malonate **S8**.

S8 1-Isothiocyanato-3,5-bis(trifluoromethyl)benzene (0.04 mmol, 11 mg) was stirred with (2*S*,4*R*)-**1r** (0.04 mmol, 10 mg) for 30 minutes in dry toluene under argon atmosphere after which (E)-(2-nitrovinyl)benzene (0.40 mmol, 59 mg) and dimethyl malonate (0.80 mmol, 106 mg) were added and the mixture was stirred at rt temperature for 48 hours. Toluene was removed *in vacuo* and the product was purified by flash chromatography (silica, hexane:ethyl acetate 7:3). Yield = 23 mg, 20%. [α]_D²⁵ = +5.5 (*c* 1.0, CHCl₃). Absolute stereochemistry (*S*) and *e.e.* were assigned by comparison of the specific optical rotation with the literature ([α]_D²⁵ = +5.9; 96% *e.e.*).²⁴ ¹H NMR (δ ; 300 MHz, CDCl₃); 3.49 (3H, s, OCH₃), 3.70 (3H, s, OCH₃), 3.80 (1H, d, *J* 9.0, MeO(O)CCH), 4.14-4.22 (1H, m, PhCHCH₂NO₂), 4.80-4.90 (2H, m, CH₂NO₂), 7.14-7.29 (5H, m, PhH); ¹³C NMR (δ ; 100 MHz, CDCl₃), 45.34 (CH), 53.69 (CH₃), 54.01 (CH₃), 56.46 (CH), 79.41 (CH₂), 129.92 (CH), 130.11 (CH), 130.39 (CH), 138.69 (C), 169.65 (C), 170.12 (C). M/z: (EI⁺) 281 [M]⁺.

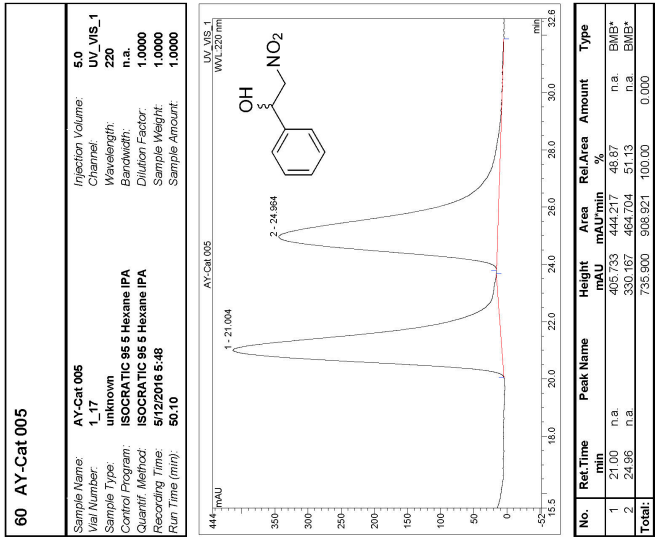
HPLC Traces

HPLC Trace (rac)-6a



HPLC Trace (rac)-6b

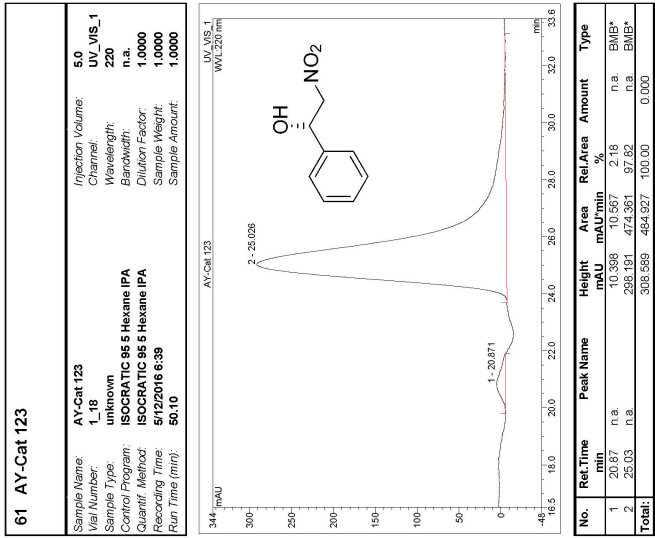
Operator:Shimadzu Timebase:LC_System2 Sequence:ISOCRATIC 95 5 Hexane IPA 11/12/2016 11:26 PM Page 1-1



Chromatogram (a) Diarray 1995-2005
Version 6.80 SR15 Build 4656 (2-6-2003)

HPLC Trace (S)-6b

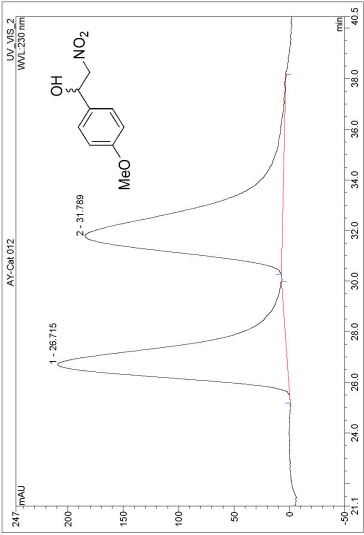
Operator:Shimadzu Timebase:LC_System2 Sequence:ISOCRATIC 95 5 Hexane IPA 11/12/2016 11:28 PM Page 1-1



Chromatogram (a) Diarray 1995-2005
Version 6.80 SR15 Build 4656 (2-6-2003)

HPLC Trace (rac)-6c

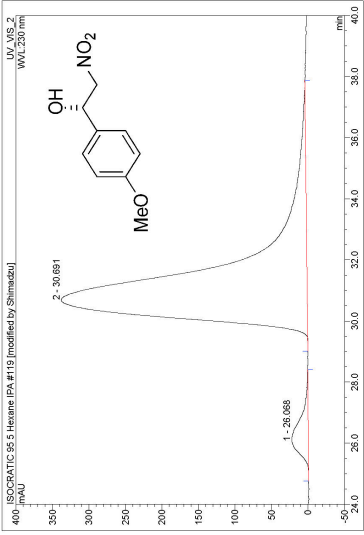
93 AY-Cat 012	
Sample Name:	AY-Cat 012
Vial Number:	1_11
Injection Volume:	5.0
Sample Type:	unknown
Control Program:	ISOCRATIC 95 5 Hexane IPA
Wavelength:	230
Bandwidth:	n.a.
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Dilution Factor:	1.0000
Recording Time:	6/12/2016 14:03
Sample Weight:	1.0000
Run Time (min):	50.10
Sample Amount:	1.0000



No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.72	n.a.	207.279	292.962	46.20	n.a. BMB*
2	31.79	n.a.	178.121	341.236	53.80	n.a. BMB*
Total:			385.401	634.228	100.00	0.000

HPLC Trace (S)-6c

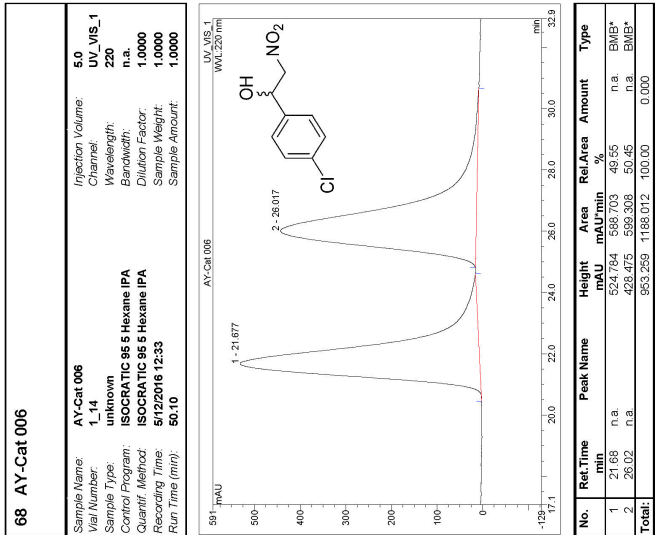
119 AY-Cat 111	
Sample Name:	AY-Cat 111
Vial Number:	1_20
Injection Volume:	5.0
Sample Type:	unknown
Control Program:	ISOCRATIC 95 5 Hexane IPA
Wavelength:	230
Bandwidth:	n.a.
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Dilution Factor:	1.0000
Recording Time:	11/12/2016 22:35
Sample Weight:	1.0000
Run Time (min):	50.10
Sample Amount:	1.0000



No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.07	n.a.	22.410	27.895	4.47	n.a. BMB*
2	30.09	n.a.	336.771	596.000	95.53	n.a. BMB*
Total:			359.181	623.895	100.00	0.000

HPLC Trace (rac)-6d

Operator:Shimadzu Timebase:LC_System2 Sequence:ISOCRATIC 95 5 Hexane IPA 11/12/2016 11:30 PM Page 1-1

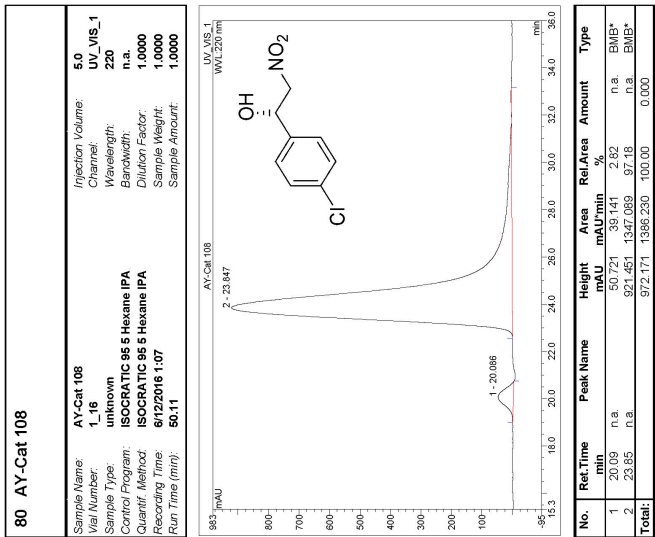


Chromatlab (c) Dionex 1998-2005
Version 6.80 SR15 Build 4656 (2-6-2003)

DEFAULT/Integration

HPLC Trace (S)-6d

Operator:Shimadzu Timebase:LC_System2 Sequence:ISOCRATIC 95 5 Hexane IPA 11/12/2016 11:34 PM Page 1-1

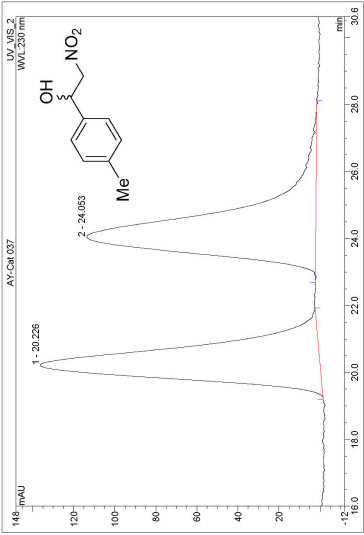


Chromatlab (c) Dionex 1998-2005
Version 6.80 SR15 Build 4656 (2-6-2003)

DEFAULT/Integration

HPLC Trace (rac)-6e

90 AY-Cat 037	
Sample Name:	AY-Cat 037
Vial Number:	1 5
Injection Volume:	5.0
Channel:	UV_VIS_2
Sample Type:	unknown
Wavelength:	230
Control Program:	ISOCRATIC 95 5 Hexane IPA
Bandwidth:	n.a.
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Dilution Factor:	1.0000
Recording Time:	6/12/2016 11:32
Sample Weight:	1.0000
Run Time (min):	50.10
Sample Amount:	1.0000

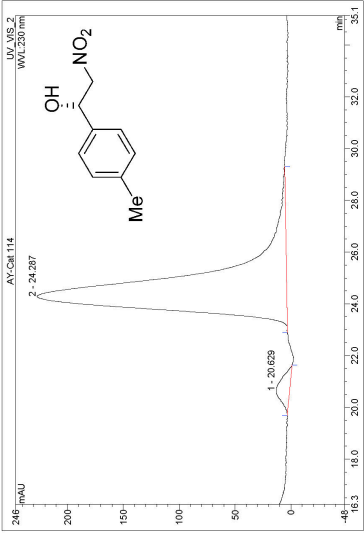


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.23	n.a.	136.175	137.915	48.39	n.a.	BMB*
2	24.05	n.a.	111.520	147.096	51.61	n.a.	BMB*
Total:			247.696	285.011	100.00	0.000	

DEFAULT Integration

HPLC Trace (S)-6e

92 AY-Cat 114	
Sample Name:	AY-Cat 114
Vial Number:	1 7
Injection Volume:	5.0
Channel:	UV_VIS_2
Sample Type:	unknown
Wavelength:	230
Control Program:	ISOCRATIC 95 5 Hexane IPA
Bandwidth:	n.a.
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Dilution Factor:	1.0000
Recording Time:	6/12/2016 13:13
Sample Weight:	1.0000
Run Time (min):	50.10
Sample Amount:	1.0000

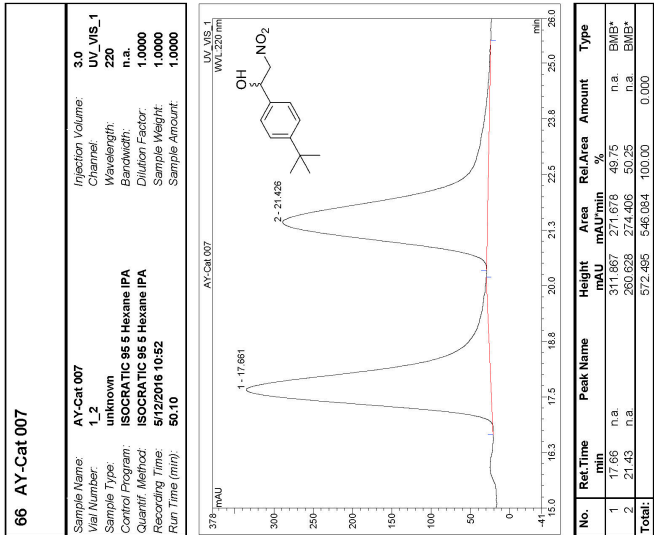


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.63	n.a.	12.016	12.469	3.67	n.a.	BMB*
2	24.29	n.a.	223.448	309.626	96.13	n.a.	BMB*
Total:			235.464	322.096	100.00	0.000	

DEFAULT Integration

HPLC Trace (rac)-6f

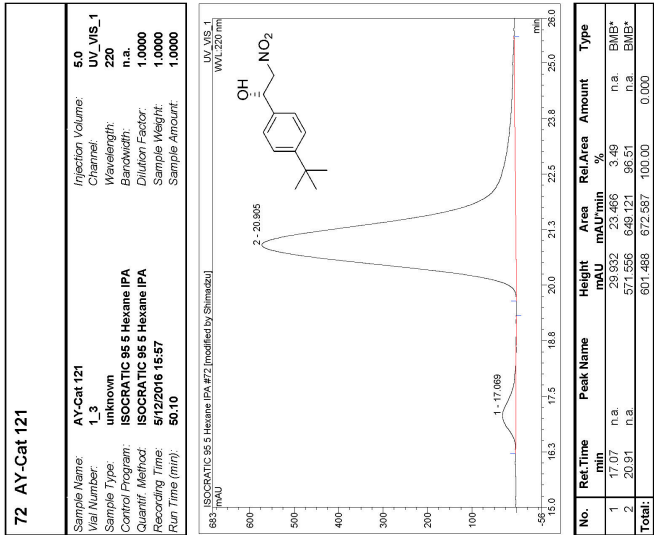
Operator Shimadzu Timebase.LC_System2 Sequence: ISOCRATIC 95 5 Hexane IPA 28/1/2017 9:08 PM Page 1-1



Chromatogram (a) Diode: 1995-2005 Version 6.80 SR15 Build 4656 (2-6-2003) DEFAULT/Integration

HPLC Trace (S)-6f

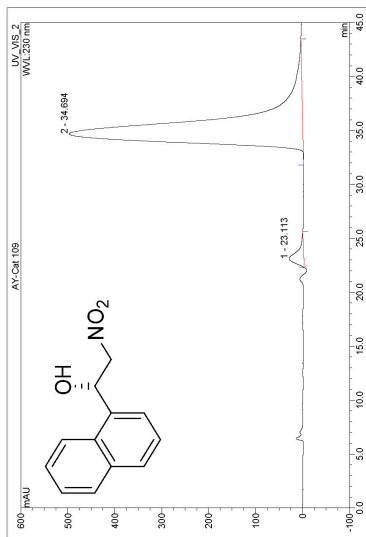
Operator Shimadzu Timebase.LC_System2 Sequence: ISOCRATIC 95 5 Hexane IPA 28/1/2017 9:19 PM Page 1-1



Chromatogram (a) Diode: 1995-2005 Version 6.80 SR15 Build 4656 (2-6-2003) DEFAULT/Integration

HPLC Trace (S)-6g

39 AY-Cat 109		Injection Volume:	5.0
Sample Name:	AY-Cat 109	Channel:	UV_VIS_2
Vial Number:	15	Wavelength:	230
Sample Type:	unknown	Bandwidth:	8
Control Program:	15% MeCN v1	Dilution Factor:	1.0000
Quantif. Method:	15% MeCN v1	Sample Weight:	1.0000
Recording Time:	31/2/2016 21:00	Sample Amount:	1.0000
Run Time (min):	45.01		

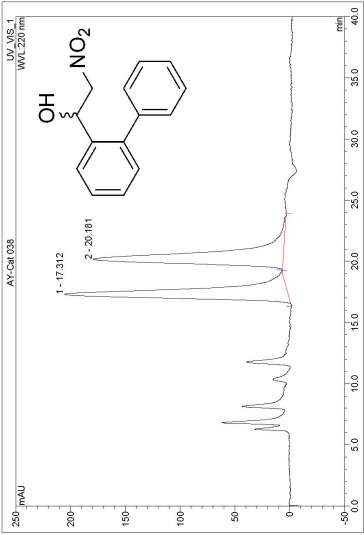


No.	Ret.Time	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.11	n.a.	31.190	38.363	3.34	n.a.	BMB*
2	34.69	n.a.	487.834	1111.088	96.66	n.a.	BMB*
Total:			529.024	1149.451	100.00	0.000	

HPLC Trace (rac)-6h

Operator:Shimadzu Timebase:LC_System2 Sequence:ISOCRATIC 95 5 Hexane IPA 11/12/2016 6:17 PM Page 1-1

117 AY-Cat 038	
Sample Name:	AY-Cat 038
Vial Number:	1_11
Sample Type:	unknown
Control Program:	ISOCRATIC 95 5 Hexane IPA
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Recording Time:	11/12/2016 14:49
Run Time (min):	40.10
Injection Volume:	4.0
Channel:	UV_VIS_1
Wavelength:	220
Bandwidth:	n.a.
Dilution Factor:	1.0000
Sample Weight:	1.0000
Sample Amount:	1.0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.31	n.a.	204.003	167.974	49.57	n.a.	BMB*
2	20.18	n.a.	173.277	170.889	50.43	n.a.	BMB*
Total:			377.281	338.862	100.00	0.000	

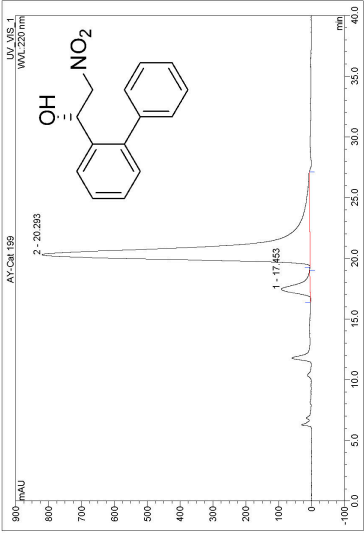
Chromatogram (a) Diode: 1995-2005 Version 6.80 SR15 Build 4656 (2-6-2003)

DEFAULT/Integration

HPLC Trace (S)-6h

Operator:Shimadzu Timebase:LC_System2 Sequence:ISOCRATIC 95 5 Hexane IPA 11/12/2016 6:19 PM Page 1-1

118 AY-Cat 199	
Sample Name:	AY-Cat 199
Vial Number:	1_12
Sample Type:	unknown
Control Program:	ISOCRATIC 95 5 Hexane IPA
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Recording Time:	11/12/2016 15:29
Run Time (min):	40.10
Injection Volume:	4.0
Channel:	UV_VIS_1
Wavelength:	220
Bandwidth:	n.a.
Dilution Factor:	1.0000
Sample Weight:	1.0000
Sample Amount:	1.0000



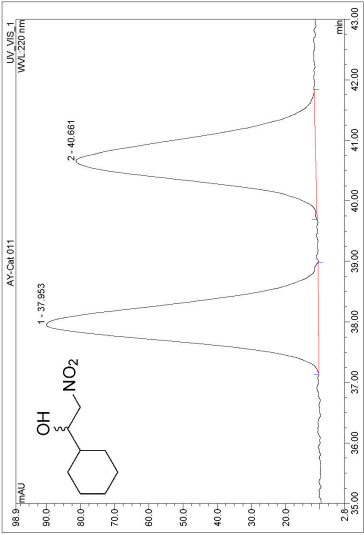
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.45	n.a.	87.555	69.369	6.79	n.a.	BMB*
2	20.29	n.a.	815.309	951.710	93.21	n.a.	BMB*
Total:			902.864	1021.080	100.00	0.000	

Chromatogram (a) Diode: 1995-2005 Version 6.80 SR15 Build 4656 (2-6-2003)

DEFAULT/Integration

HPLC Trace (rac)-6i

125 AY-Cat 011				
Sample Name:	AY-Cat 011	Injection Volume:	5.0	UV_VIS_1
Vial Number:	1, 2	Channel:		
Sample Type:	unknown	Wavelength:	220	
Control Program:	ISOCRATIC 95 5 Hexane IPA	Bandwidth:	n.a.	
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA	Dilution Factor:	1.0000	
Recording Time:	14/12/2016 12:54	Sample Weight:	1.0000	
Run Time (min):	50.10	Sample Amount:	1.0000	

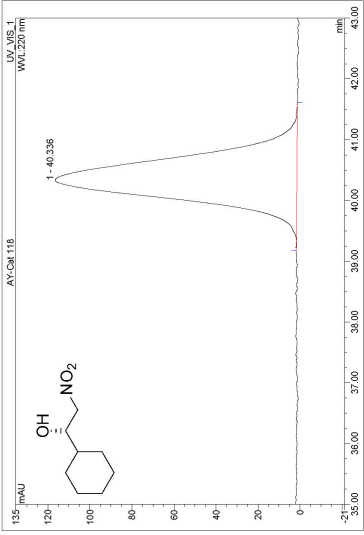


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	37.95	n.a.	79.594	54.886	50.27	n.a.	BMB*
2	40.66	n.a.	70.083	54.406	49.73	n.a.	BMB*
Total:			149.676	109.392	100.00	0.000	

DEFAULT Integration

HPLC Trace (S)-6i

134 AY-Cat 118				
Sample Name:	AY-Cat 118	Injection Volume:	5.0	UV_VIS_1
Vial Number:	1, 4	Channel:		
Sample Type:	unknown	Wavelength:	220	
Control Program:	ISOCRATIC 95 5 Hexane IPA	Bandwidth:	n.a.	
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA	Dilution Factor:	1.0000	
Recording Time:	15/12/2016 16:46	Sample Weight:	1.0000	
Run Time (min):	52.46	Sample Amount:	1.0000	



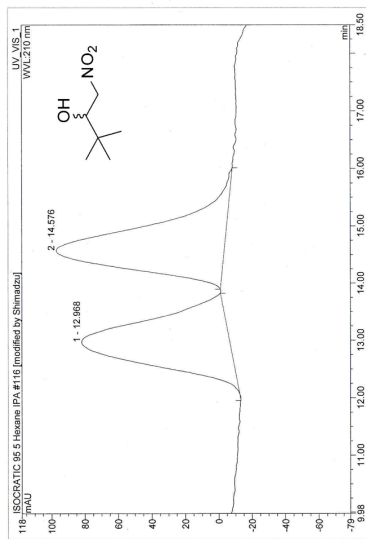
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	40.34	n.a.	115.062	84.429	100.00	n.a.	BMB*
Total:			115.062	84.429	100.00	0.000	

DEFAULT Integration

HPLC Trace (rac)-6j

Operator: Shimadzu Timebase: LC_System2 Sequence: ISOCRATIC 95 5 Hexane IPA 12/10/2017 7:25 PM Page 1-1

116 AY-Cat 032	
Sample Name:	AY-Cat 032
Vial Number:	1.2
Injection Volume:	5.0
Channel:	UV_VIS_1
Wavelength:	210
Bandwidth:	n.a.
Control Program:	ISOCRATIC 95 5 Hexane IPA
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Dilution Factor:	1.0000
Recording Time:	11/12/2016 19:39
Sample Weight:	1.0000
Run Time (min):	40.10
Sample Amount:	1.0000



No.	Ret. Time min	Peak Name	Height mAU	Area mAU*min	Rel. Area %	Amount	Type
1	12.97	n.a.	88.463	75.196	48.15	n.a.	BMB*
2	14.59	n.a.	100.389	80.966	51.85	n.a.	BMB*
Total:			188.852	156.162	100.00	0.000	

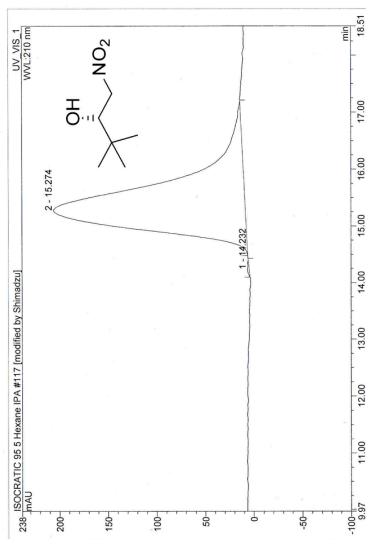
Chromatogram (c) Dionex 1986-2008
Version 6.00 SR15 Build 4656 (243203)

DEFAULT Integration

HPLC Trace (S)-6j

Operator: Shimadzu Timebase: LC_System2 Sequence: ISOCRATIC 95 5 Hexane IPA 12/10/2017 7:29 PM Page 1-1

117 AY-Cat 116	
Sample Name:	AY-Cat 116
Vial Number:	1.4
Injection Volume:	5.0
Channel:	UV_VIS_1
Wavelength:	210
Bandwidth:	n.a.
Control Program:	ISOCRATIC 95 5 Hexane IPA
Quantif. Method:	ISOCRATIC 95 5 Hexane IPA
Dilution Factor:	1.0000
Recording Time:	11/12/2016 20:20
Sample Weight:	1.0000
Run Time (min):	26.51
Sample Amount:	1.0000



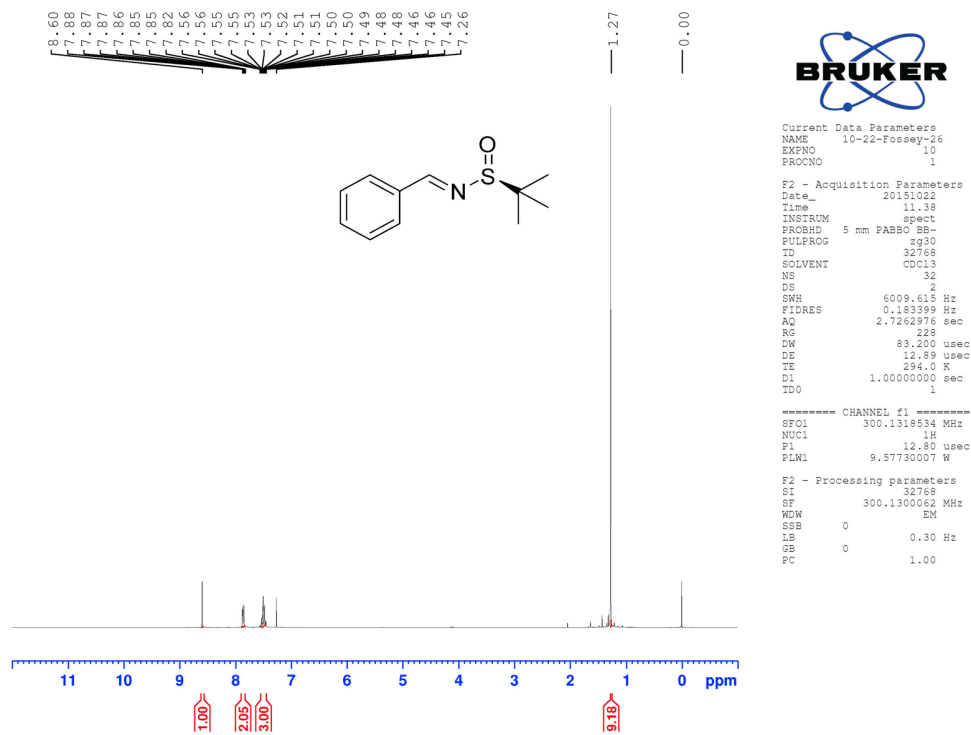
No.	Ret. Time min	Peak Name	Height mAU	Area mAU*min	Rel. Area %	Amount	Type
1	14.23	n.a.	1.679	0.313	0.18	n.a.	BMB*
2	15.27	n.a.	187.191	172.132	99.82	n.a.	BMB*
Total:			188.870	172.445	100.00	0.000	

Chromatogram (c) Dionex 1986-2008
Version 6.00 SR15 Build 4656 (243203)

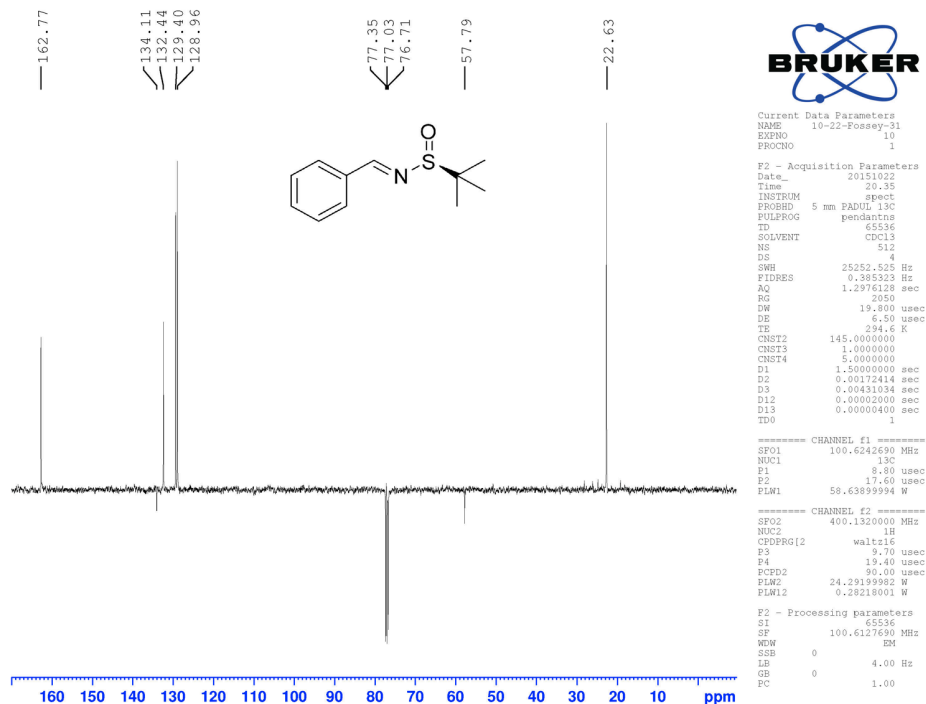
DEFAULT Integration

NMR Spectrums

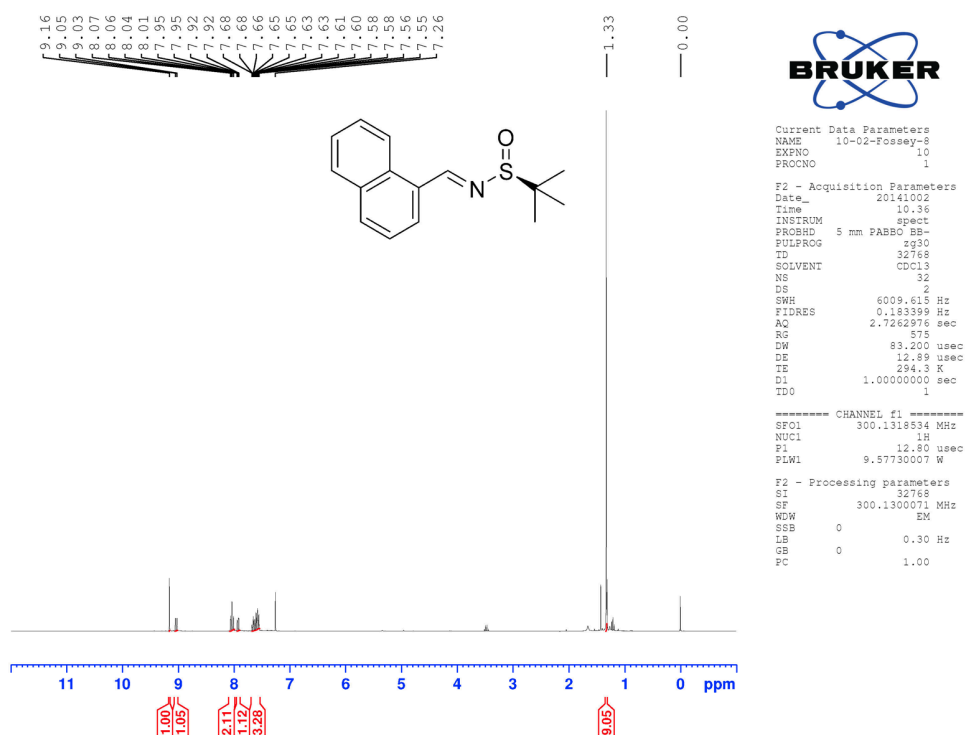
Proton NMR Spectrum of **S1a**



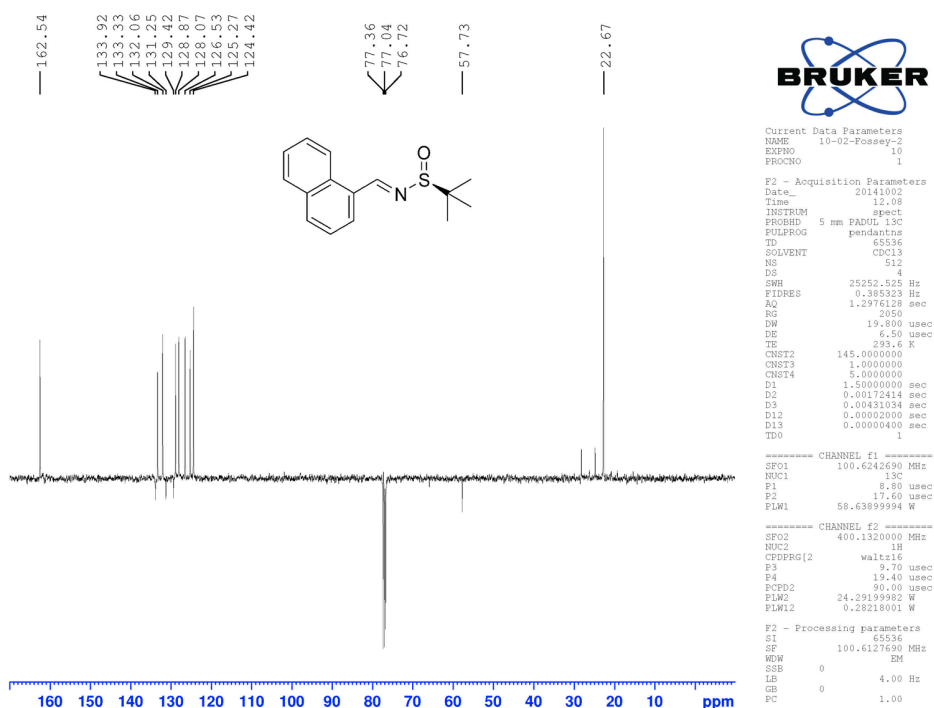
Carbon NMR Spectrum of **S1a**



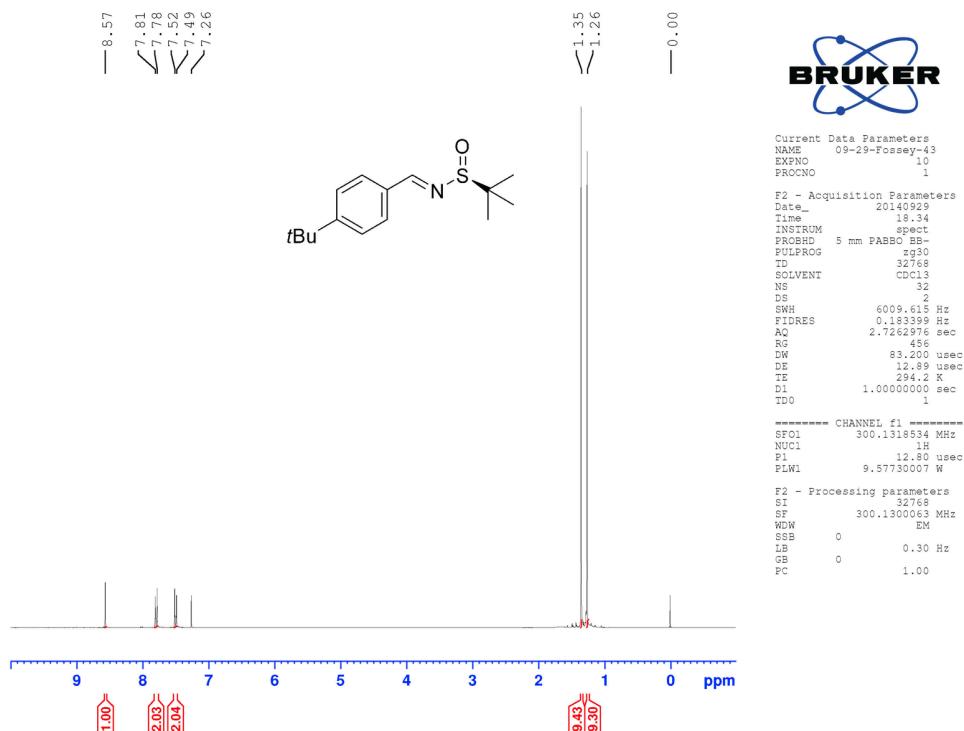
Proton NMR Spectrum of S1b



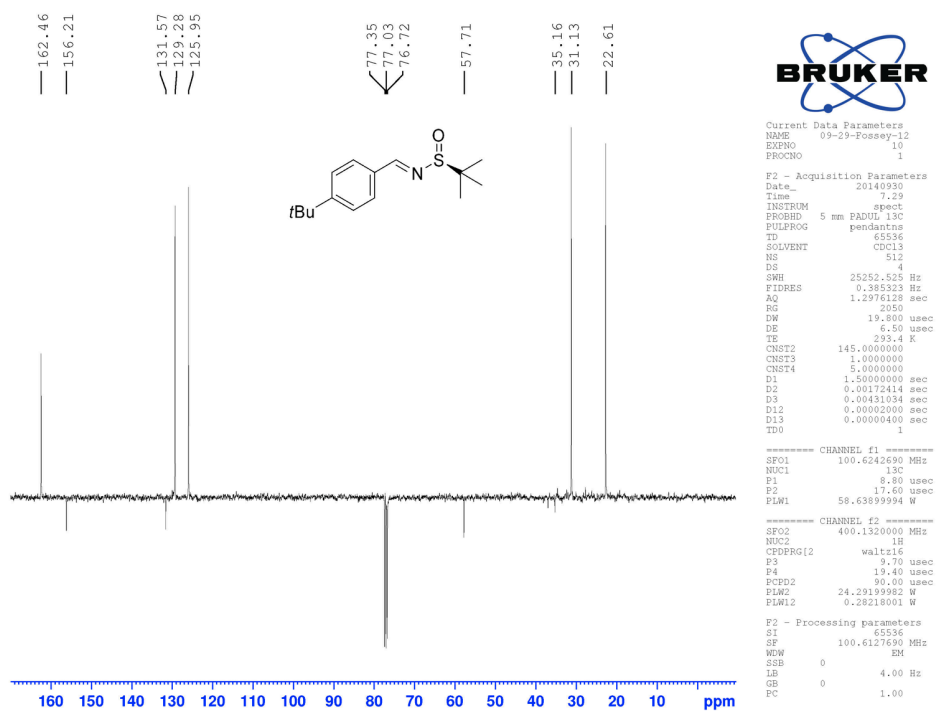
Carbon NMR Spectrum of S1b



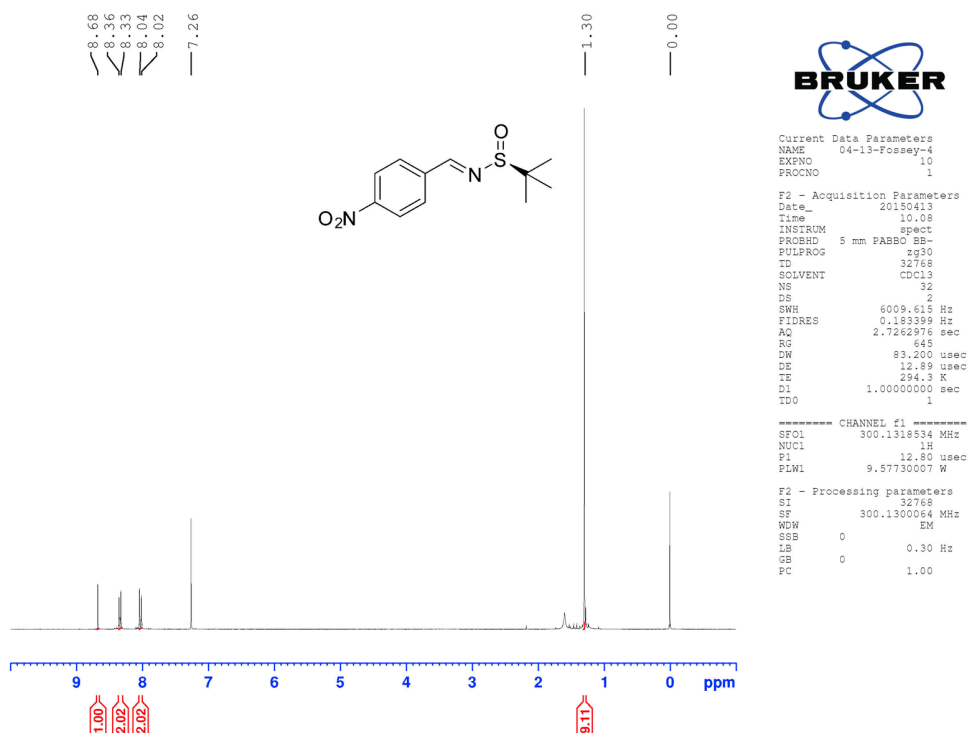
Proton NMR Spectrum of **S1c**



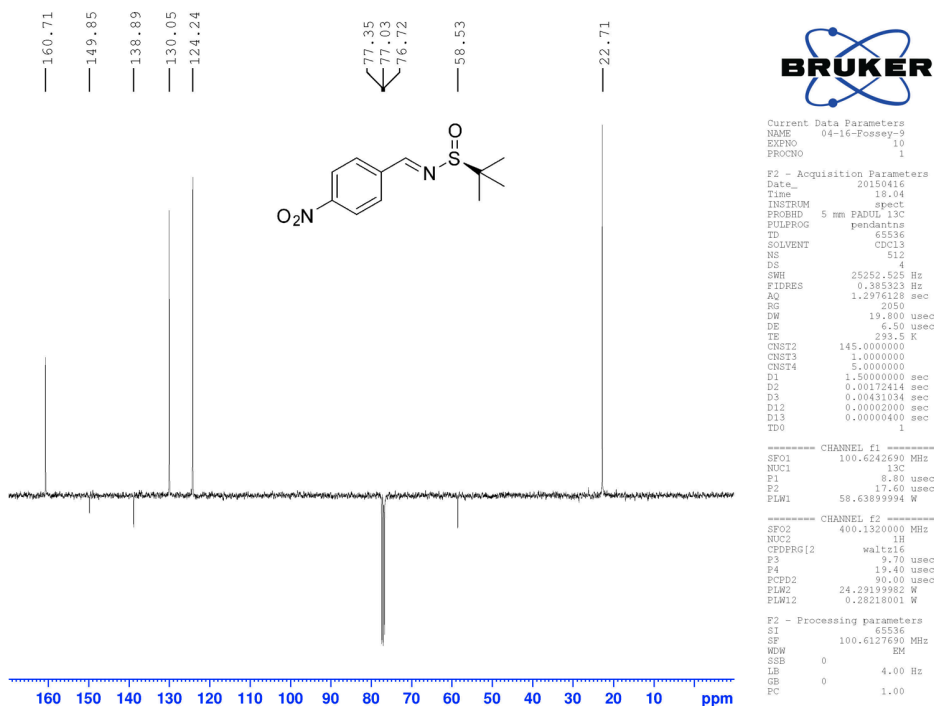
Carbon NMR Spectrum of **S1c**



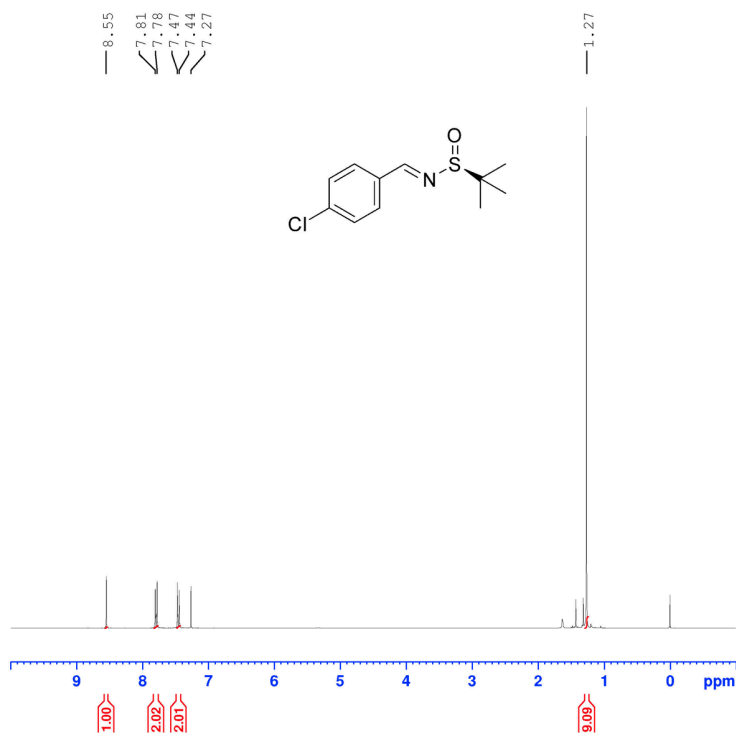
Proton NMR Spectrum of S1d



Carbon NMR Spectrum of S1d



Proton NMR Spectrum of **S1e**



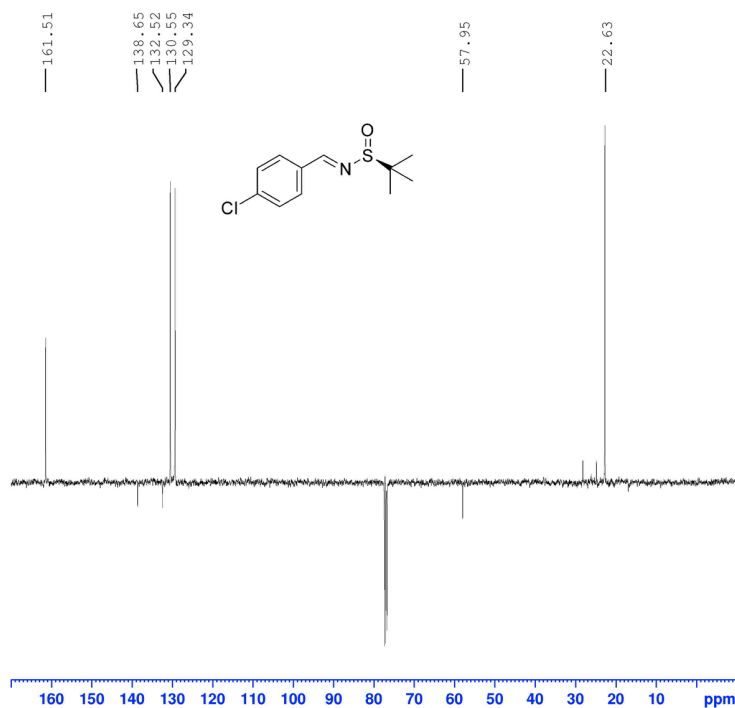
Current Data Parameters
NAME 09-29-Fossey-42
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140929
Time 18.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 724
DW 83.200 usec
DE 12.89 usec
TE 294.1 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SF01 300.1318534 MHz
NUC1 1H
P1 12.80 usec
PLW1 9.57730007 W

F2 - Processing parameters
SI 32768
SF 300.1300056 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of **S1e**



Current Data Parameters
NAME 09-29-Fossey-11
EXPNO 10
PROCNO 1

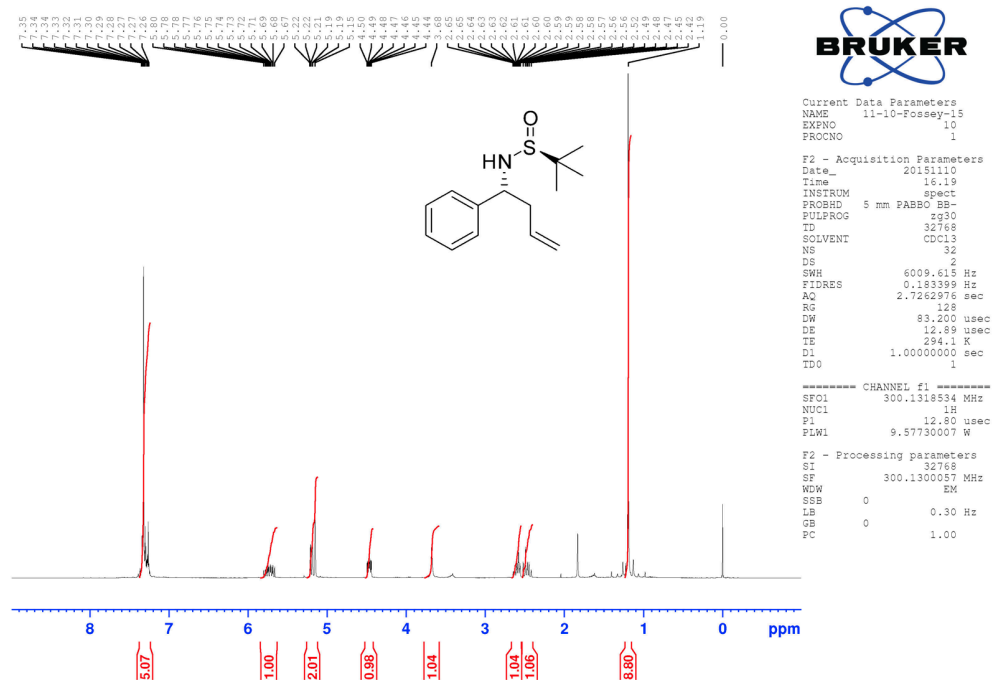
F2 - Acquisition Parameters
Date_ 20140930
Time 7.00
INSTRUM spect
PROBHD 5 mm PABBO 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.505 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.5 K
CNST2 145.000000
CNST3 1.0000000
CNST4 5.0000000
D1 1.50000000 sec
D2 0.00172414 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1

===== CHANNEL f1 =====
SF01 100.6242690 MHz
NUC1 13C
P1 8.80 usec
F2 17.60 usec
PLW1 58.63899994 W

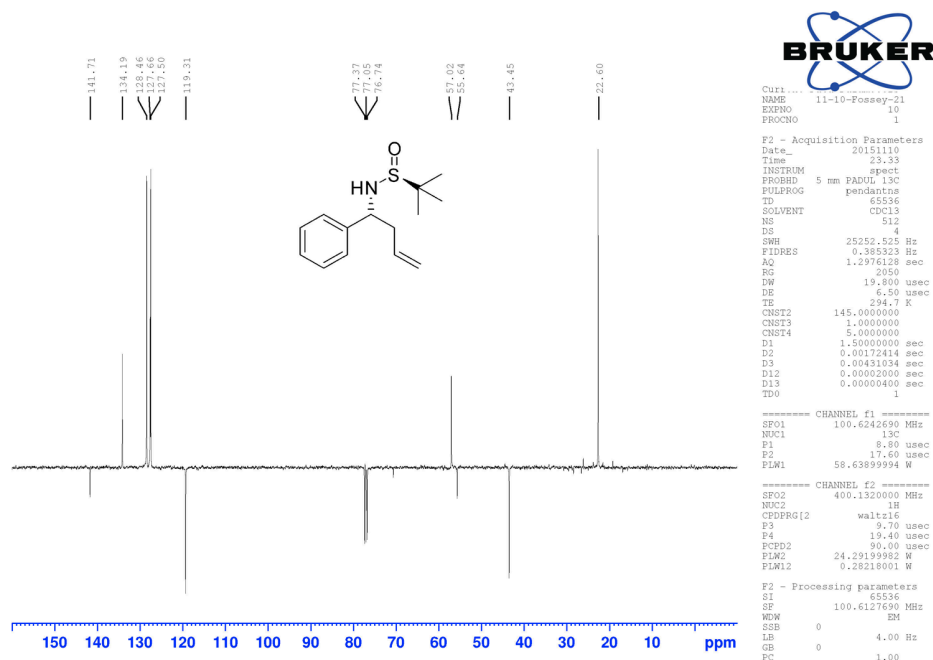
===== CHANNEL f2 =====
SF02 400.1320000 MHz
NUC2 1H
PCPDPRG2 waltz16
P3 9.70 usec
P4 19.40 usec
PCPD2 90.00 usec
PLW2 24.29199982 W
PLW12 0.28218001 W

F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

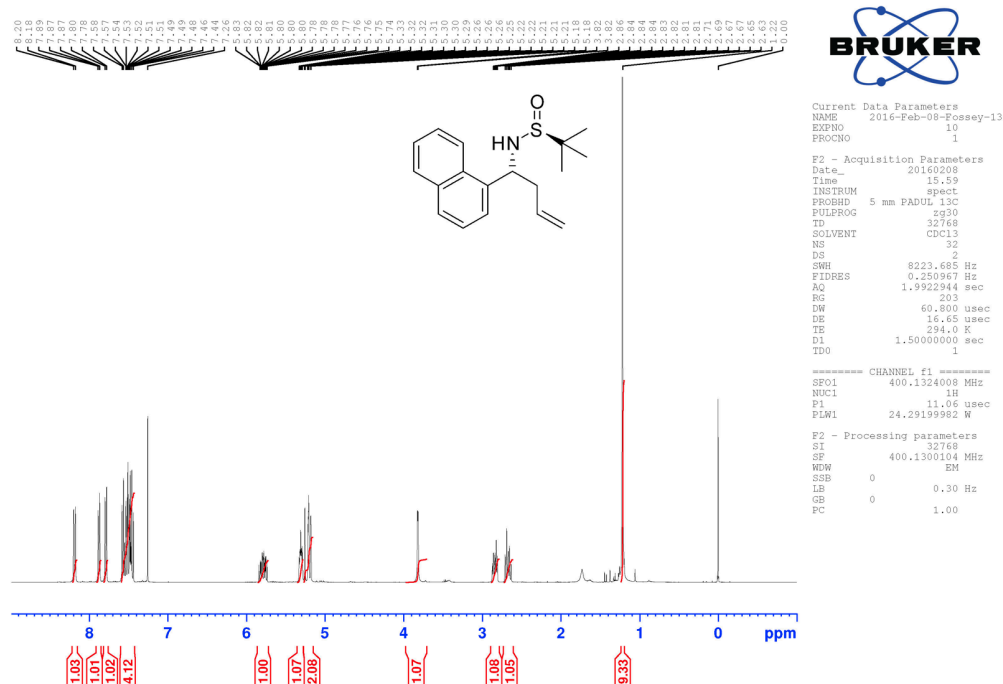
Proton NMR Spectrum of S2a



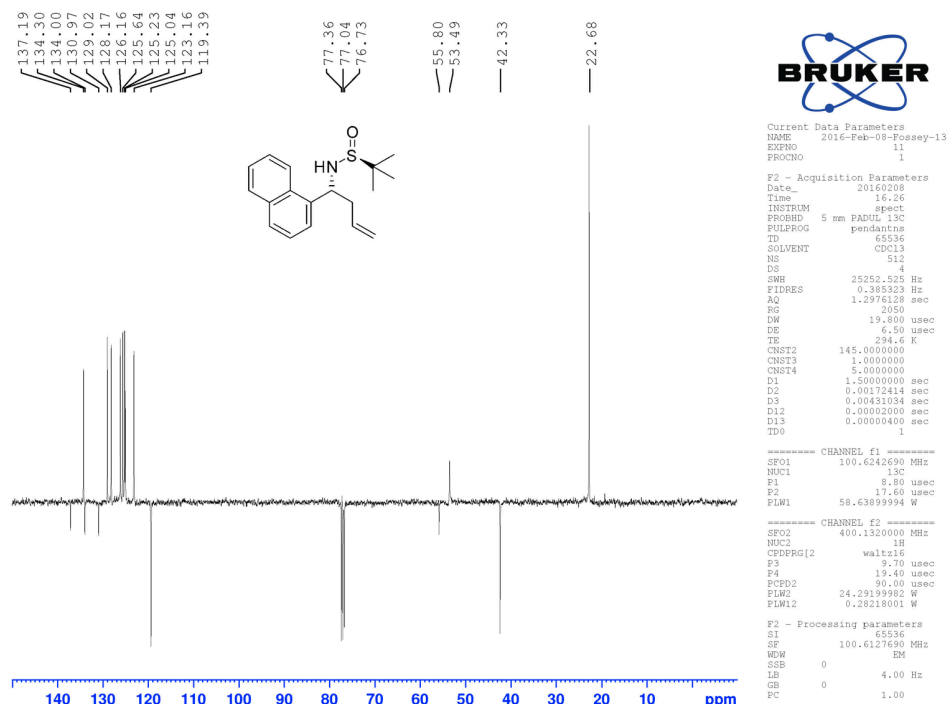
Carbon NMR Spectrum of S2a



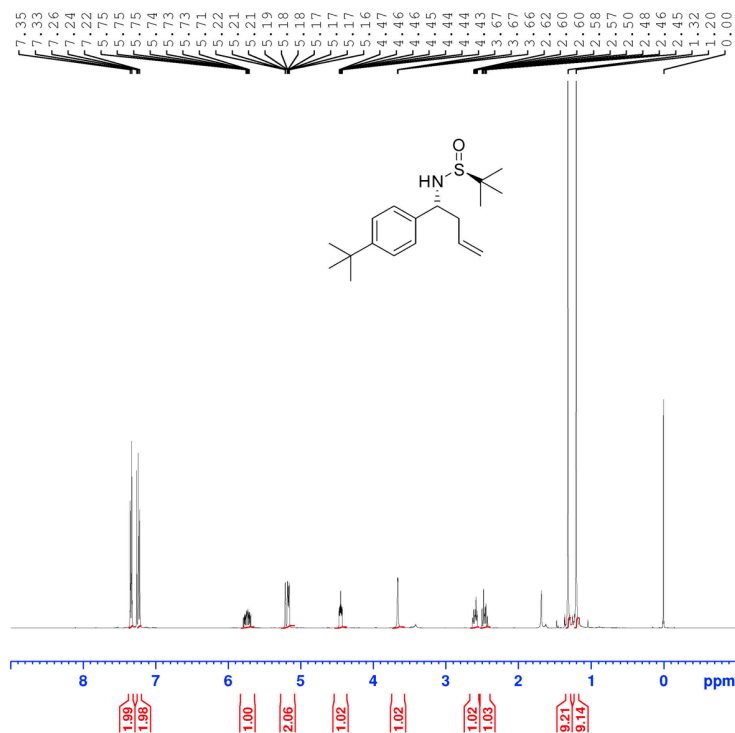
Proton NMR Spectrum of S2b



Carbon NMR Spectrum of S2b



Proton NMR Spectrum of S2c



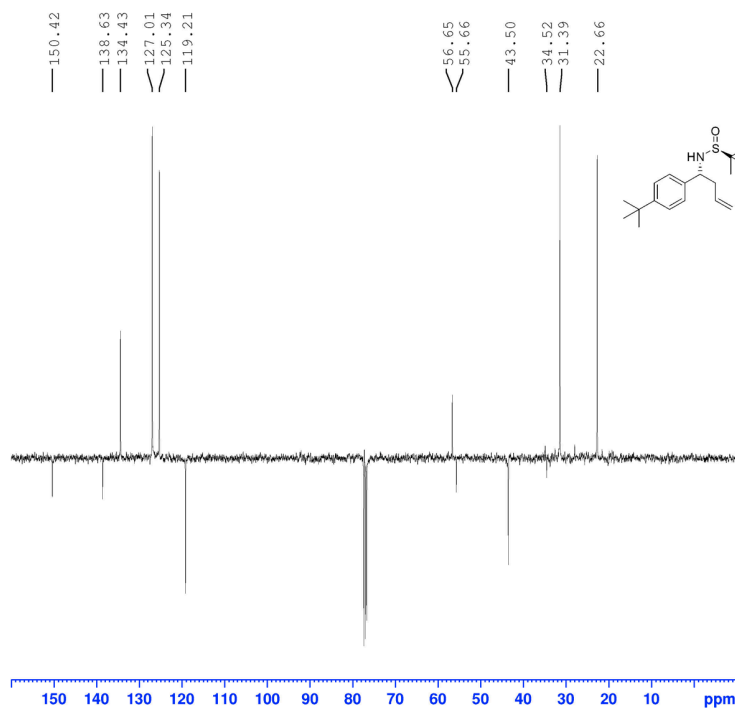
Current Data Parameters
NAME 12-05-Fossey-5
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151205
Time 16.23
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250987 Hz
AQ 1.9922944 sec
RG 256
DW 60.800 usec
DE 16.99 usec
TE 294.2 K
D1 1.5000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 9.50 usec
PLW1 24.29199982 W

F2 - Processing parameters
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of S2c



Current Data Parameters
NAME 12-05-Fossey-5
EXPNO 11
PROCNO 1

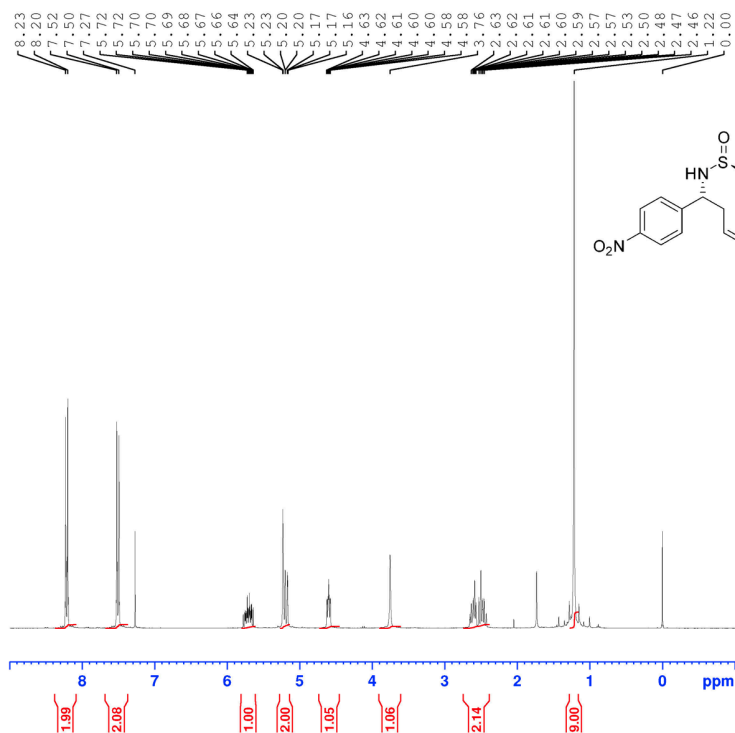
F2 - Acquisition Parameters
Date_ 20151205
Time 16.50
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG pendultra
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 294.6 K
CHST2 145.0000000
CHST3 1.0000000
CHST4 5.0000000
D1 1.5000000 sec
D2 0.00172414 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1

===== CHANNEL f1 =====
SFO1 100.6242690 MHz
NUC1 13C
P1 8.80 usec
P2 17.60 usec
PLW1 58.63899994 W

===== CHANNEL f2 =====
SFO2 400.1320000 MHz
NUC2 1H
CPDPRG2 waltz16
P3 9.70 usec
P4 19.40 usec
PCPD2 90.00 usec
PLW2 24.29199982 W
PLW12 0.28218001 W

F2 - Processing parameters
SI 65536
SF 100.6127530 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

Proton NMR Spectrum of **S2d**



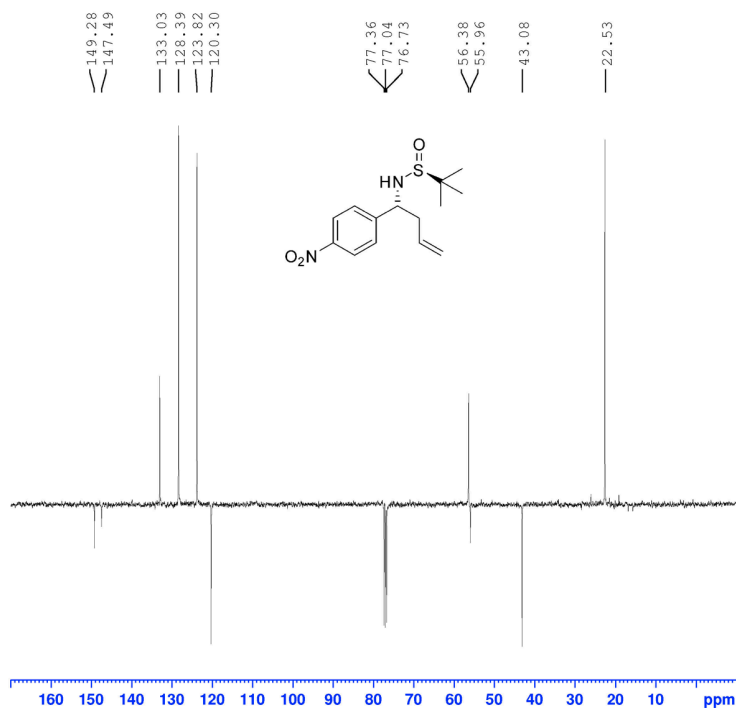
Current Data Parameters
NAME 07-03-Fossey-34
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150703
Time 14.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 181
DW 83.200 usec
DE 12.89 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 300.1318534 MHz
NUC1 1H
P1 12.80 usec
PLW1 9.57730007 W

F2 - Processing parameters
SI 32768
SF 300.1300038 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of **S2d**



Current Data Parameters
NAME 07-03-Fossey-7
EXPNO 10
PROCNO 1

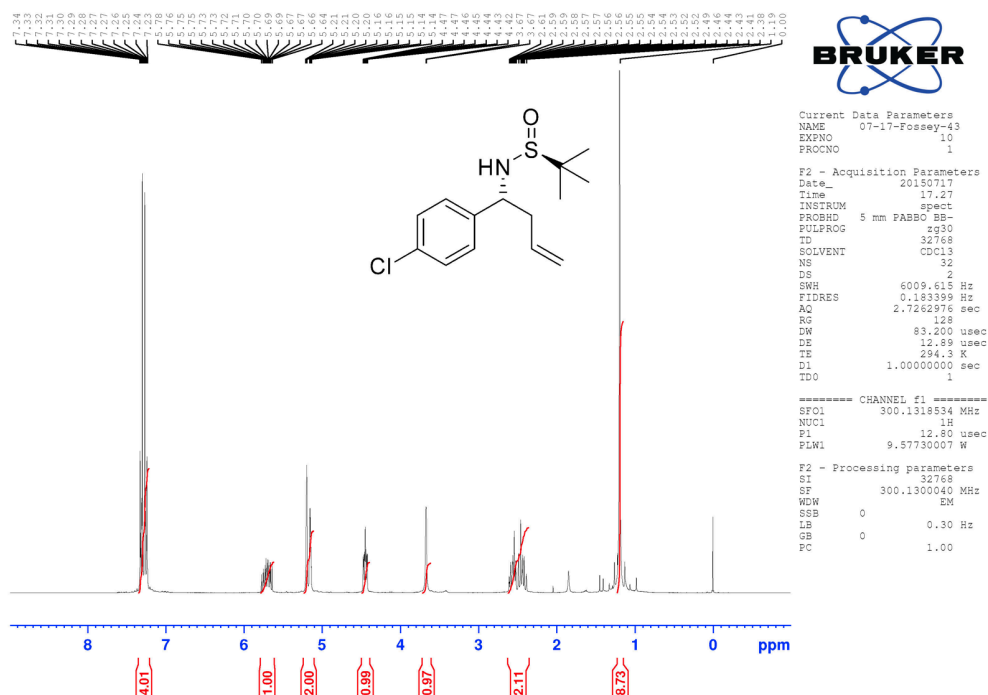
F2 - Acquisition Parameters
Date_ 20150703
Time 15.50
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG pendantns
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.525 Hz
FIDRES 0.365223 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 293.7 K
CNST2 145.0000000
CNST3 1.0000000
CNST4 5.0000000
D1 1.50000000 sec
D2 0.00172414 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1

===== CHANNEL f1 =====
SFO1 100.6242690 MHz
NUC1 13C
P1 8.60 usec
P2 17.60 usec
PLW1 58.63899994 W

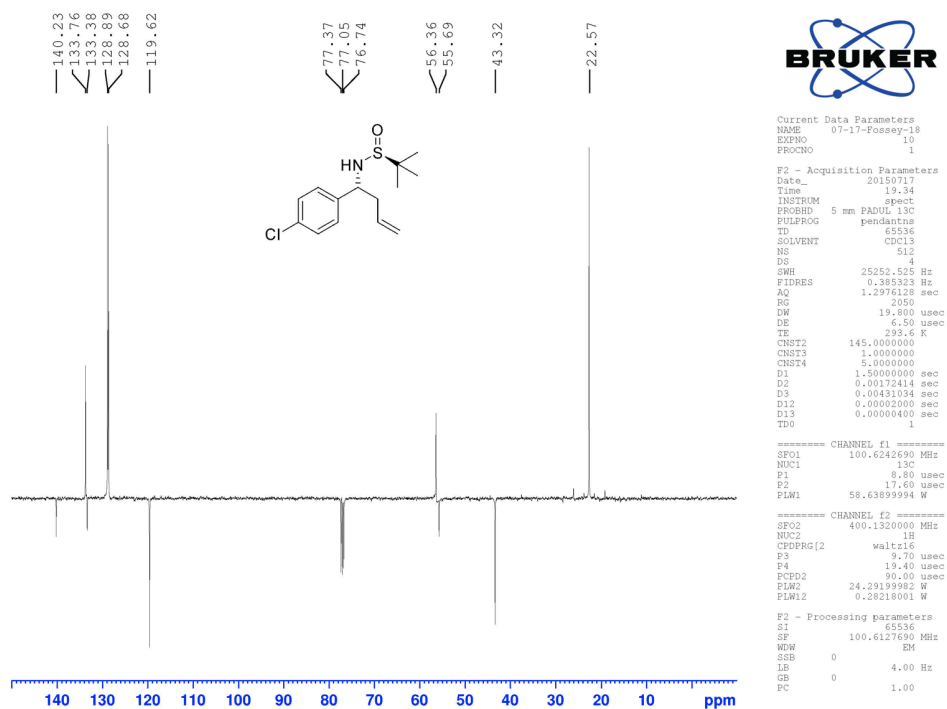
===== CHANNEL f2 =====
SFO2 400.1320000 MHz
NUC2 1H
CPDPRG2 waltz16
P3 9.70 usec
P4 19.40 usec
PCPD2 90.00 usec
PLW2 24.29199982 W
PLW12 0.28218001 W

F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

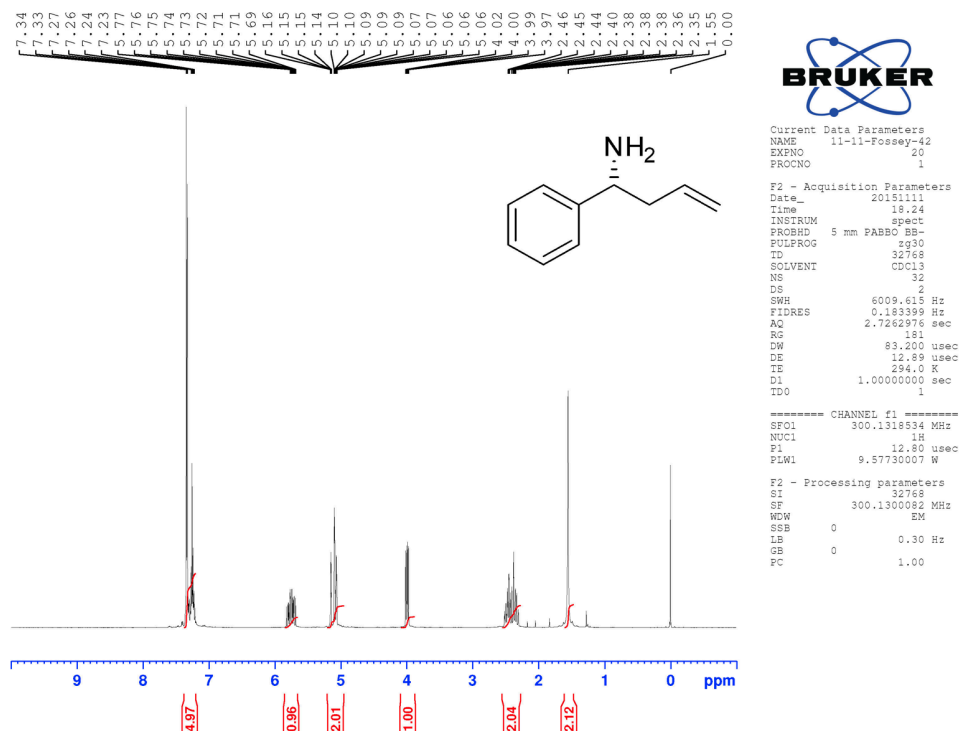
Proton NMR Spectrum of S2e



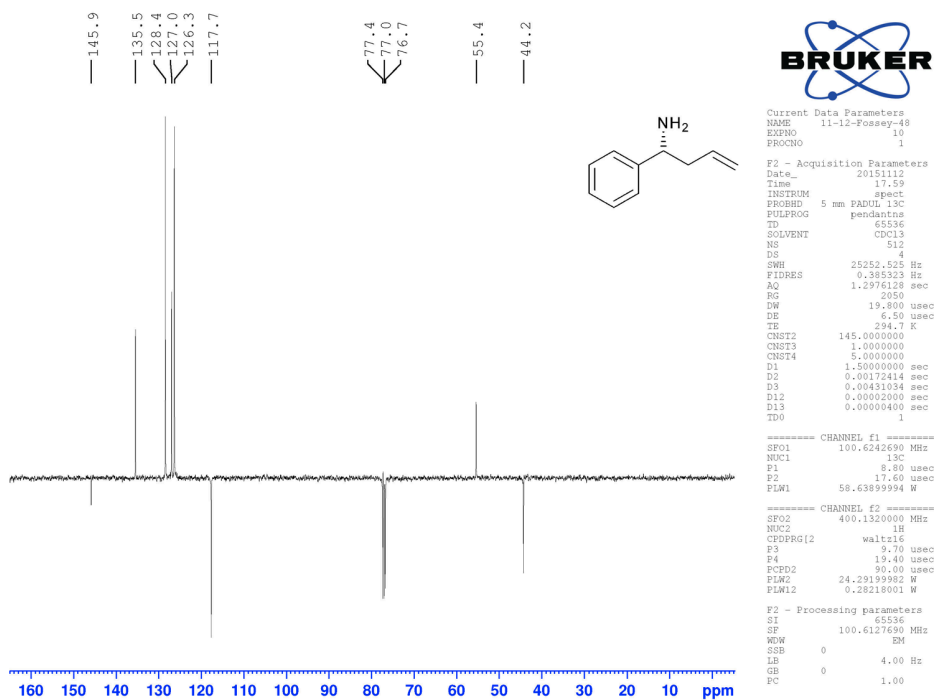
Carbon NMR Spectrum of S2e



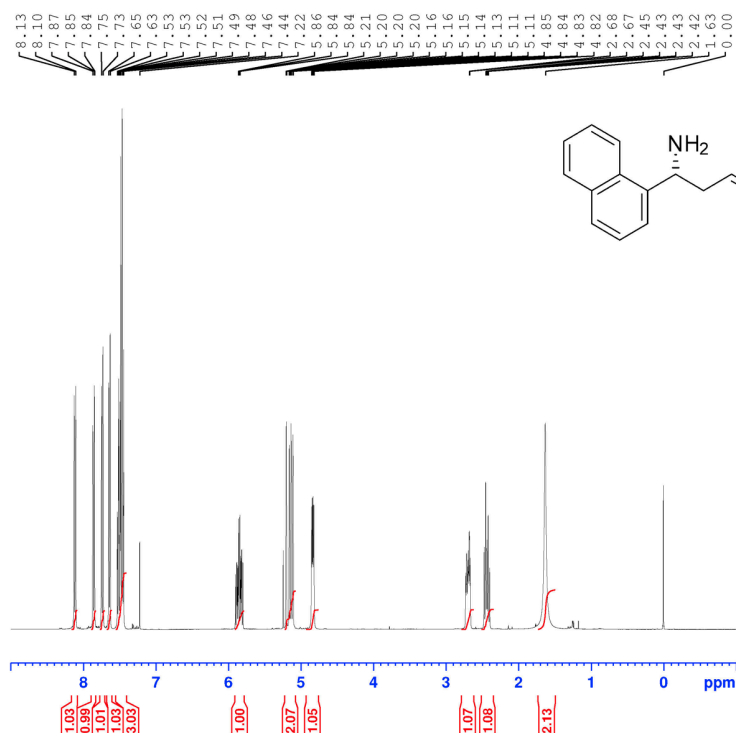
Proton NMR Spectrum of S3a



Carbon NMR Spectrum of S3a



Proton NMR Spectrum of **S3b**



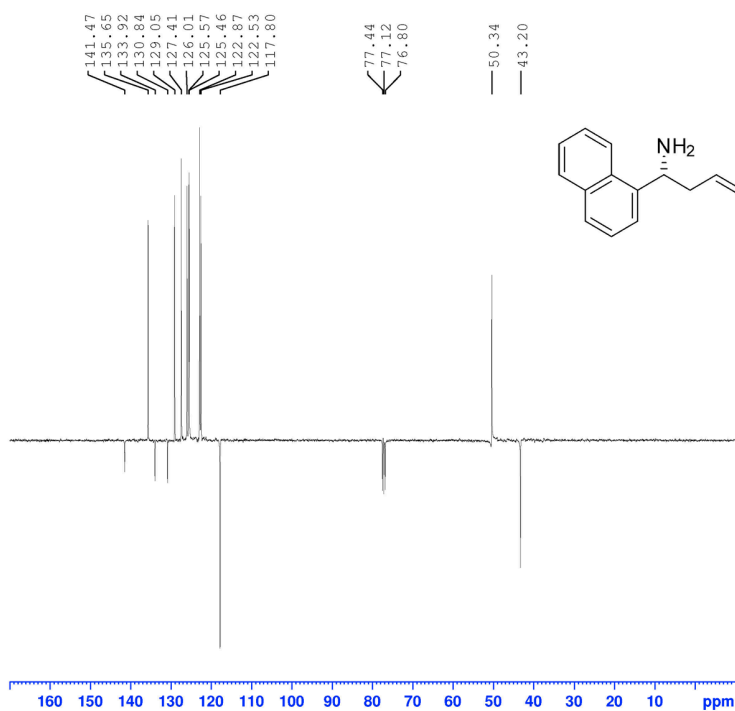
Current Data Parameters
 NAME 2016-Feb-09-Possey-26
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160209
 Time 16.09
 INSTRUM spect
 PROBHD 5 mm PADUL 13C
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.250967 Hz
 AQ 1.9922944 sec
 RG 64
 DW 60.800 usec
 DE 16.65 usec
 TE 294.0 K
 D1 1.50000000 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 400.1324008 MHz
 NUC1 1H
 P1 11.06 usec
 PLW1 24.29199982 W

F2 - Processing parameters
 SI 32768
 SF 400.1300244 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Carbon NMR Spectrum of **S3b**



Current Data Parameters
 NAME 2016-Feb-09-Possey-26
 EXPNO 11
 PROCNO 1

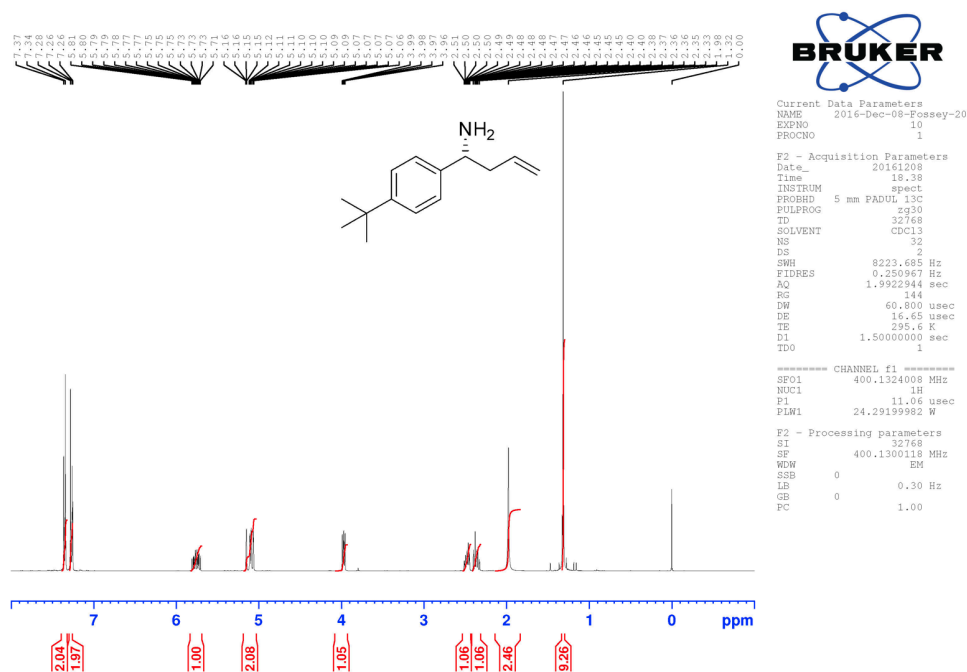
F2 - Acquisition Parameters
 Date_ 20160209
 Time 16.35
 INSTRUM spect
 PROBHD 5 mm PADUL 13C
 PULPROG pendantis
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SWH 25252.525 Hz
 FIDRES 0.385323 Hz
 AQ 1.2976128 sec
 RG 2050
 DW 19.800 usec
 DE 6.50 usec
 TE 294.6 K
 CNST2 145.0000000
 CNST3 1.0000000
 CNST4 5.0000000
 D1 1.50000000 sec
 D2 0.00172414 sec
 D3 0.00431034 sec
 D12 0.00002000 sec
 D13 0.00000400 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 100.6242690 MHz
 NUC1 13C
 P1 8.80 usec
 P2 17.60 usec
 PLW1 58.63899994 W

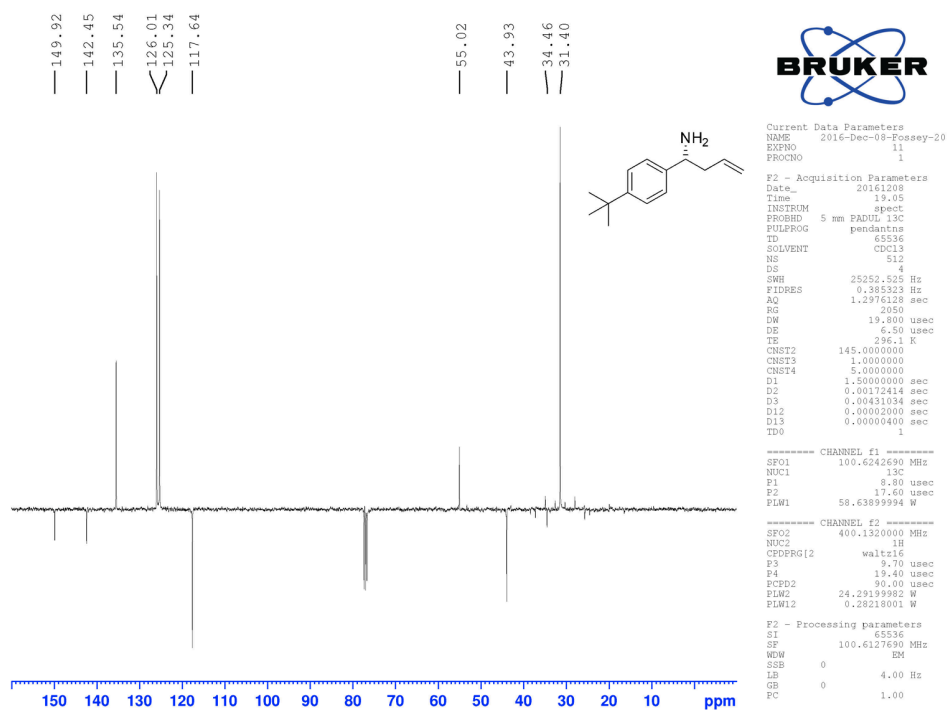
===== CHANNEL f2 =====
 SFO2 400.1320000 MHz
 NUC2 1H
 CPDPRG2 waltz16
 P3 9.70 usec
 P4 19.40 usec
 FCR02 50.00 usec
 PLW2 24.29199982 W
 PLW12 0.28218001 W

F2 - Processing parameters
 SI 65536
 SF 100.6107690 MHz
 WDW EM
 SSB 0
 LB 4.00 Hz
 GB 0
 PC 1.00

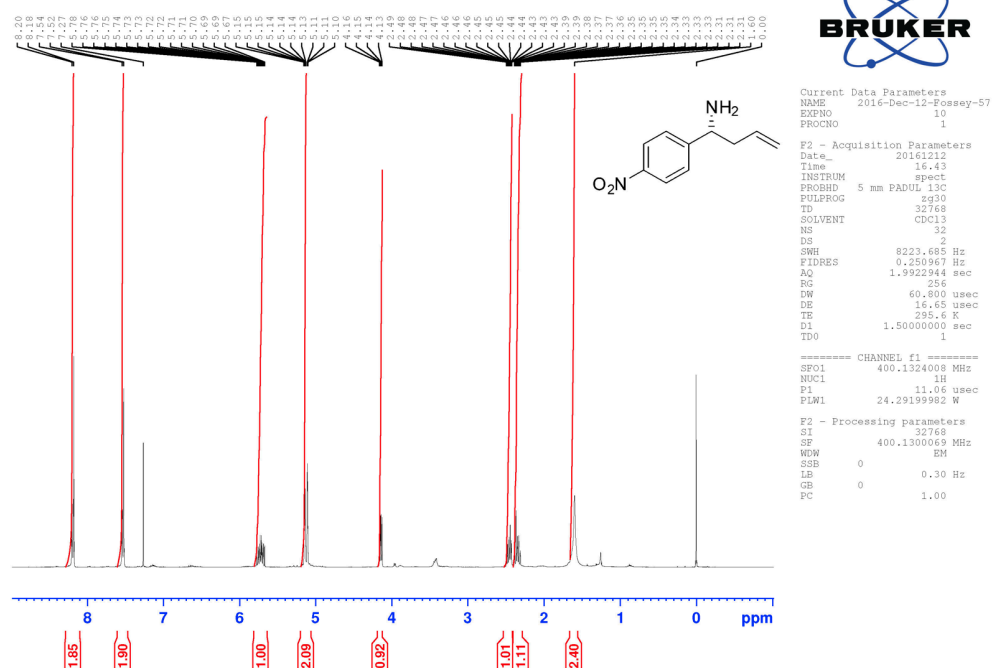
Proton NMR Spectrum of S3c



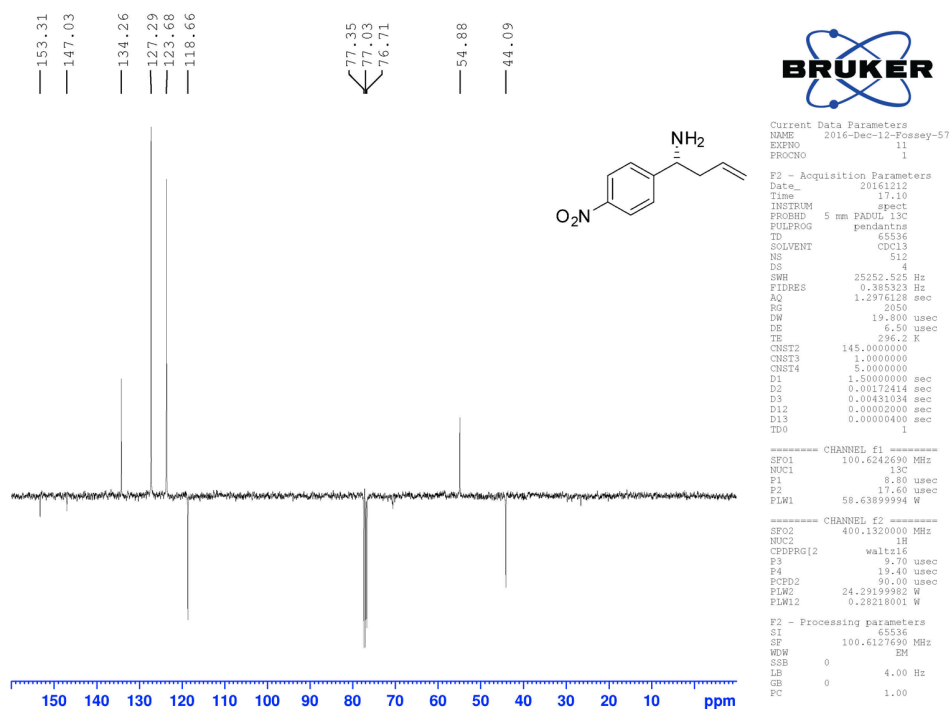
Carbon NMR Spectrum of S3c



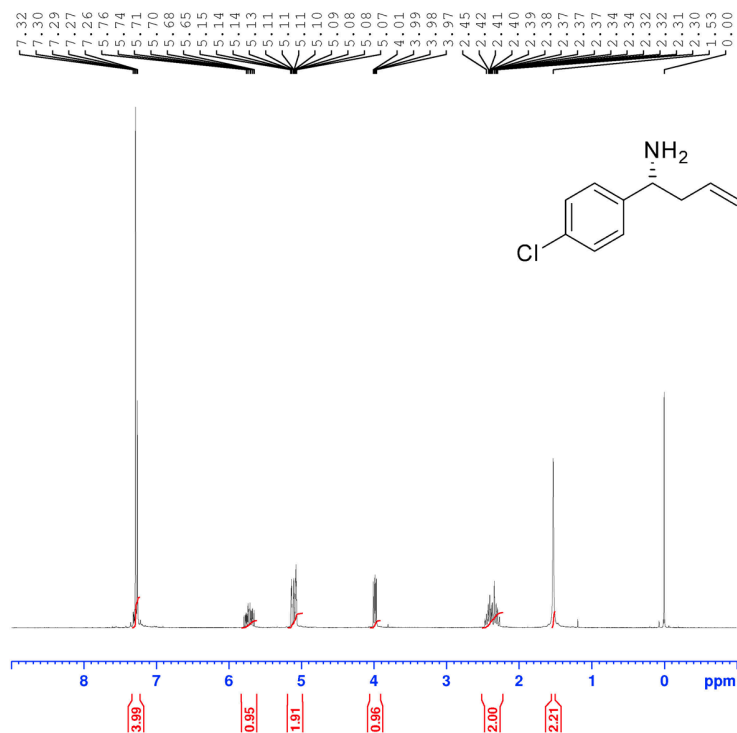
Proton NMR Spectrum of S3d



Carbon NMR Spectrum of S3d



Proton NMR Spectrum of **S3e**



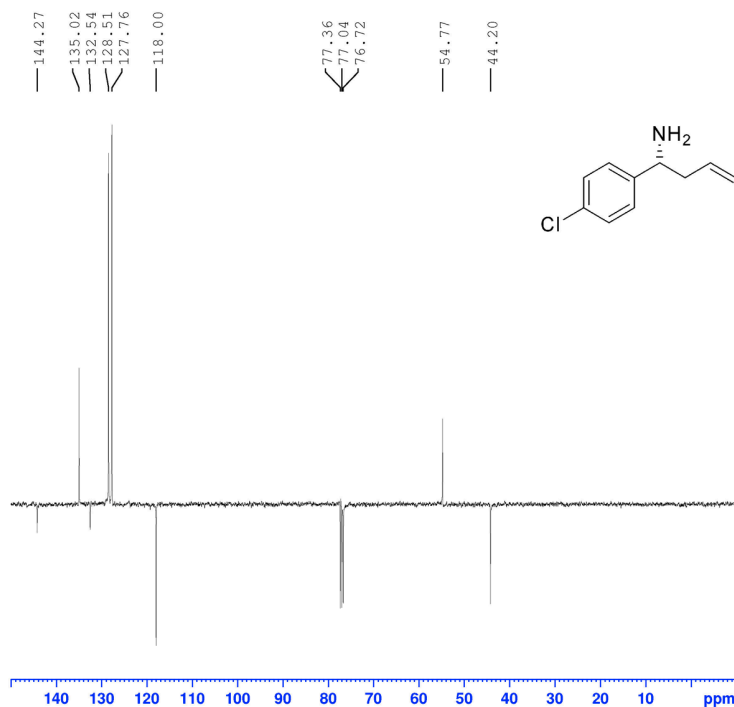
Current Data Parameters
NAME 06-15-Fossey-9
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150615
Time 10.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
SOLVENT CDCl3
NS 32
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 512
DW 83.200 usec
DE 12.89 usec
TE 294.3 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 300.1318534 MHz
NUC1 1H
P1 12.80 usec
PLW1 9.57730007 W

F2 - Processing parameters
SI 32768
SF 300.1300069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of **S3e**



Current Data Parameters
NAME 2016-Apr-15-Fossey-5
EXPNO 10
PROCNO 1

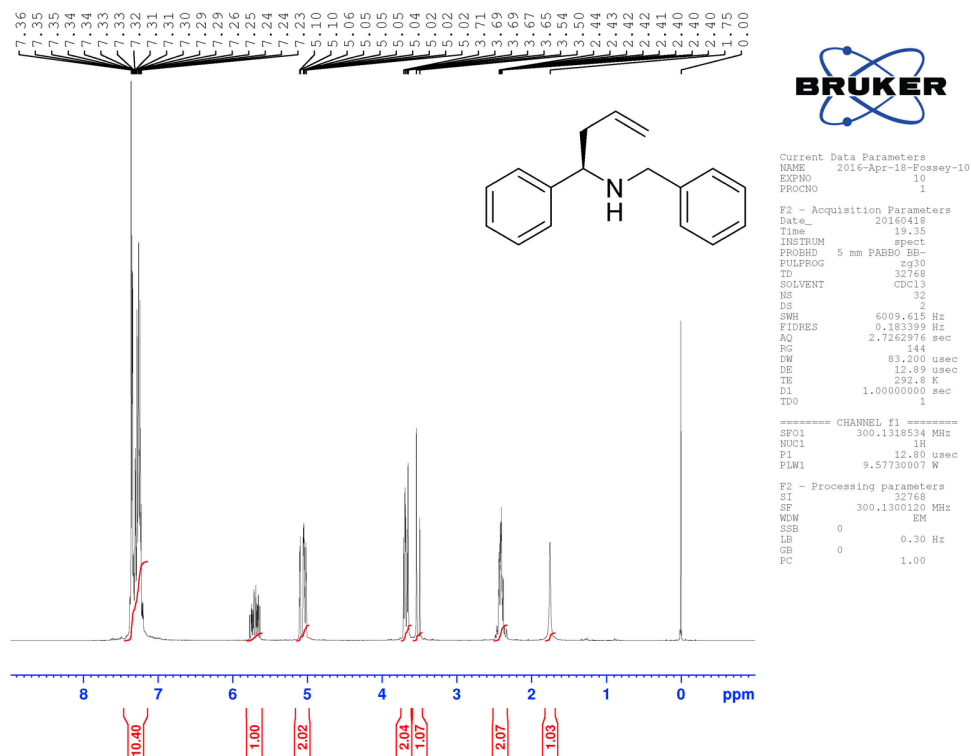
F2 - Acquisition Parameters
Date_ 20160415
Time 12.01
INSTRUM spect
PROBHD 5 mm PABBO 13C
PULPROG pendantas
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 294.5 K
CNS1 145.000000
CNS2 1.0000000
CNS3 5.0000000
CNS4 1.5000000 sec
D1 0.00172414 sec
D2 0.00431034 sec
D3 0.00002000 sec
D12 0.00000400 sec
D13 0.00000400 sec
TD0 1

===== CHANNEL f1 =====
SFO1 100.6242690 MHz
NUC1 13C
P1 8.80 usec
P2 17.60 usec
PLW1 58.63899994 W

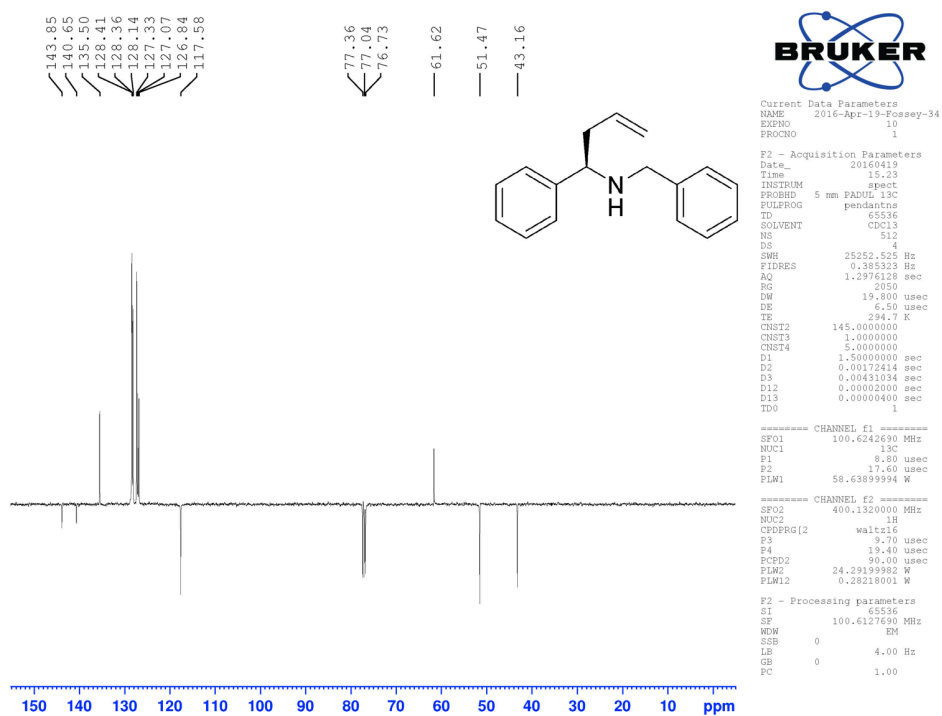
===== CHANNEL f2 =====
SFO2 400.1320000 MHz
NUC2 1H
PULPROG2 waltz16
P3 9.70 usec
P4 19.40 usec
PCPD2 90.00 usec
PLW2 24.29199982 W
PLW12 0.26218001 W

F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

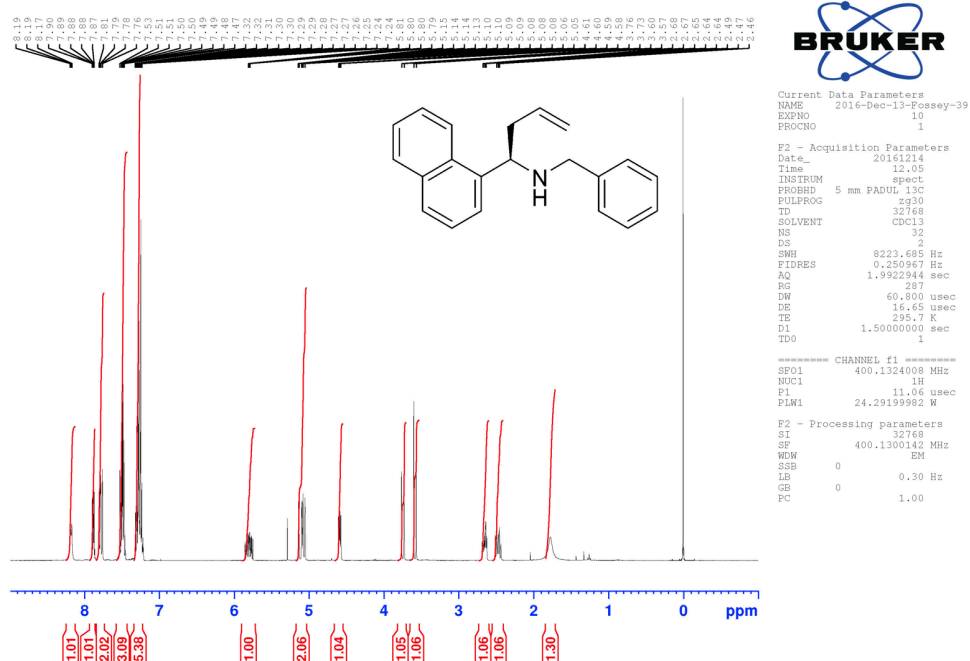
Proton NMR Spectrum of S4a



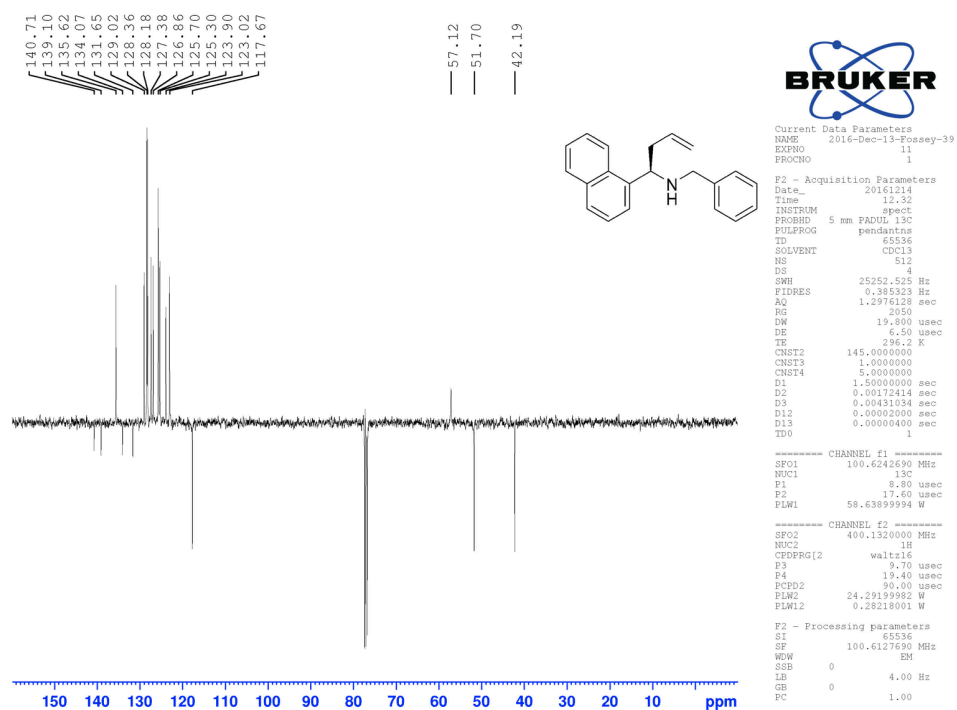
Carbon NMR Spectrum of S4a



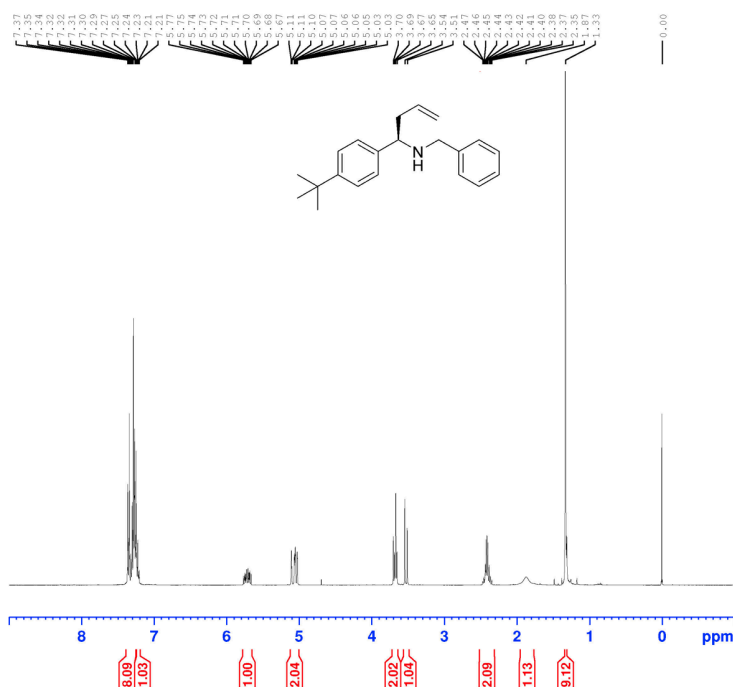
Proton NMR Spectrum of S4b



Carbon NMR Spectrum of S4b



Proton NMR Spectrum of S4c



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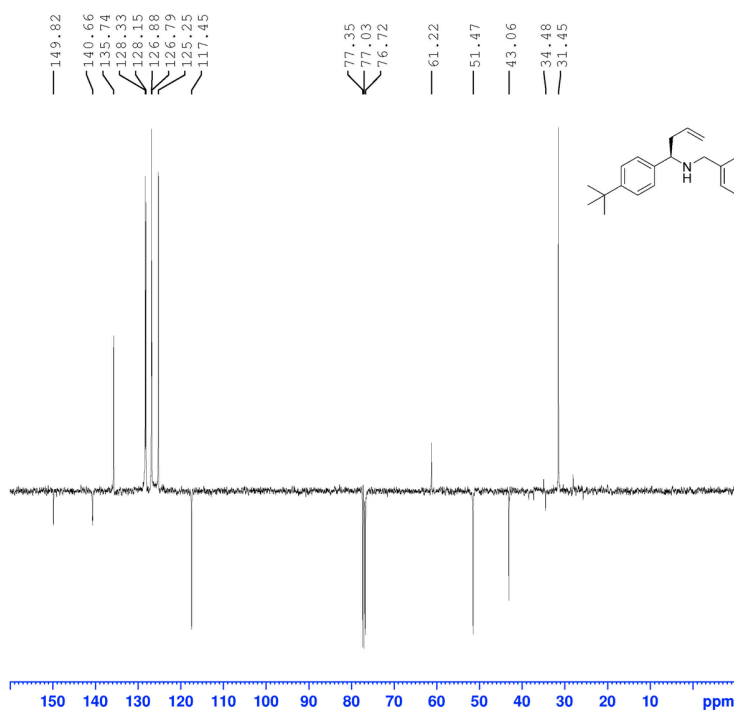
Current Data Parameters
NAME 12-05-Posey-6
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151205
Time 16.57
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 203
DM 60.800 usec
DE 16.98 usec
TE 294.2 K
D1 1.50000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 9.50 usec
PLW1 24.29199982 W

F2 - Processing parameters
SI 32768
SF 400.1300138 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of S4c



BRUKER

Current Data Parameters
NAME 12-05-Posey-6
EXPNO 11
PROCNO 1

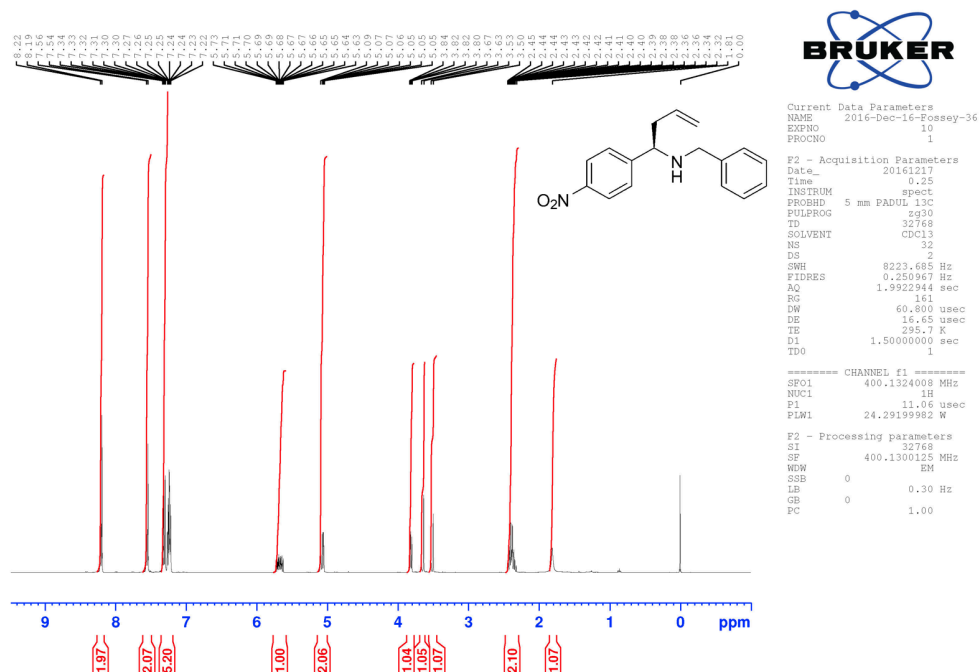
F2 - Acquisition Parameters
Date_ 20151205
Time 17.33
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG pendantus
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.535 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DM 19.800 usec
DE 6.50 usec
TE 294.7 K
D1 145.0000000 sec
D2 0.00172414 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1

===== CHANNEL f1 =====
SFO1 100.6242690 MHz
NUC1 13C
P1 8.80 usec
P2 17.60 usec
PLW1 58.63899994 W

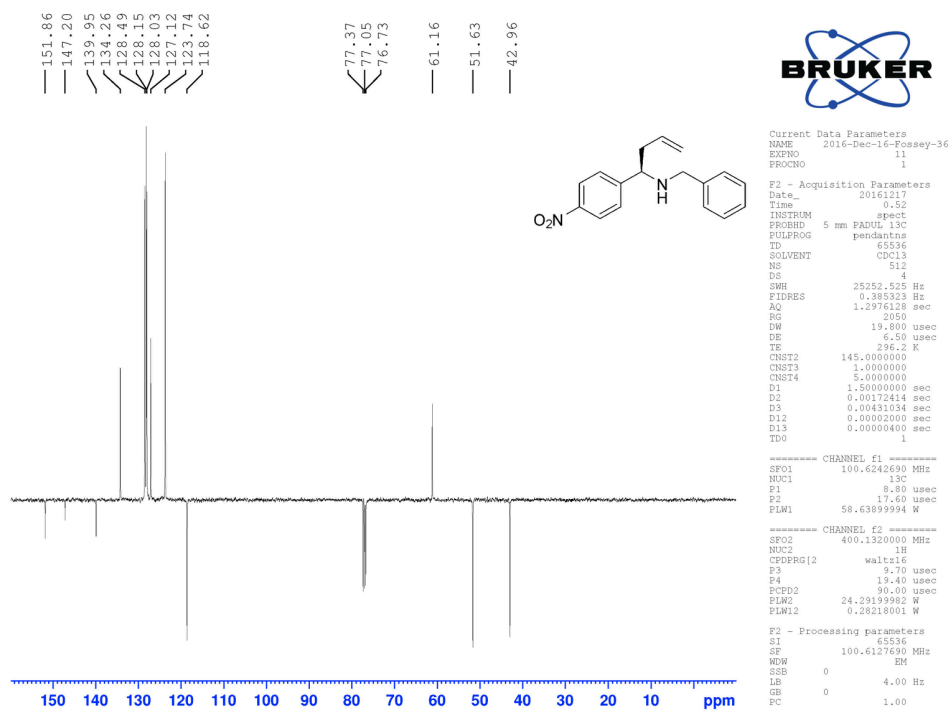
===== CHANNEL f2 =====
SFO2 400.1320000 MHz
NUC2 1H
CFPRG2 waltz16
P3 9.70 usec
P4 19.40 usec
PTD2 90.00 usec
PLW2 24.29199982 W
PLW12 0.28218001 W

F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

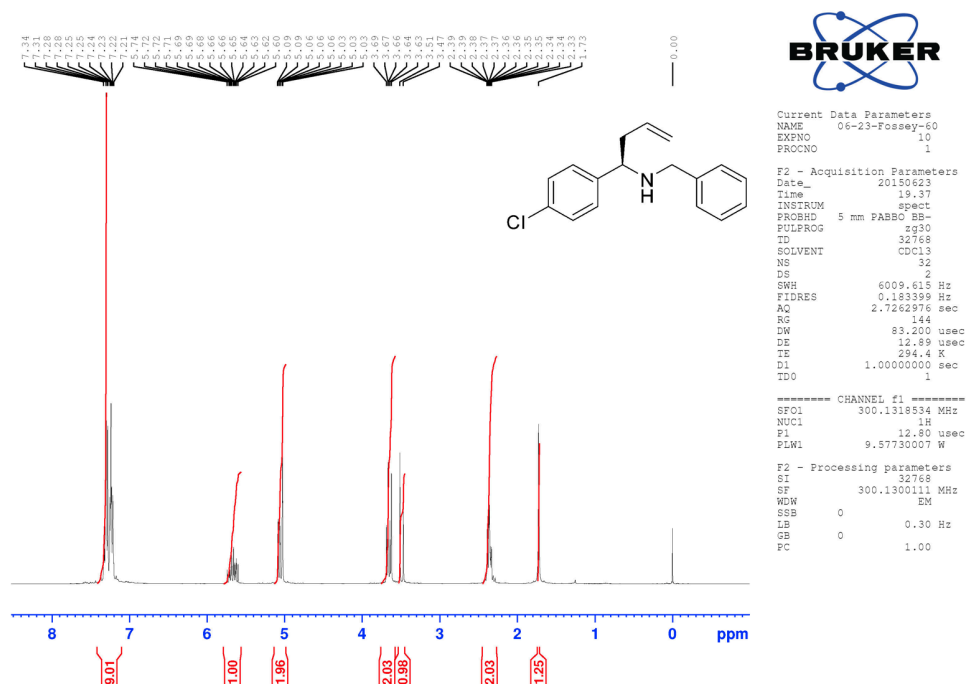
Proton NMR Spectrum of S4d



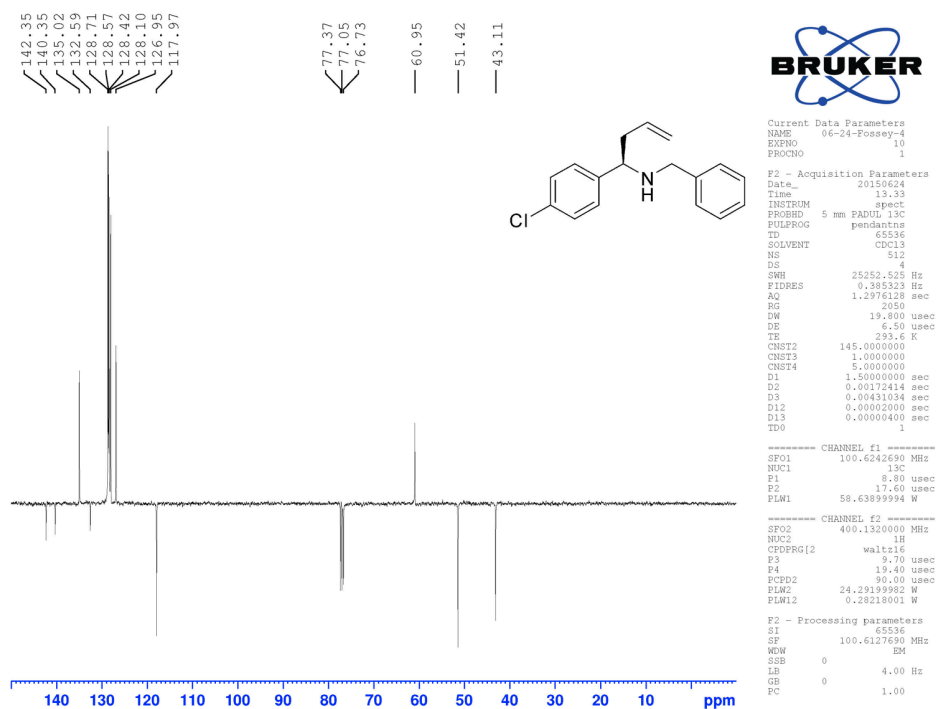
Carbon NMR Spectrum of S4d



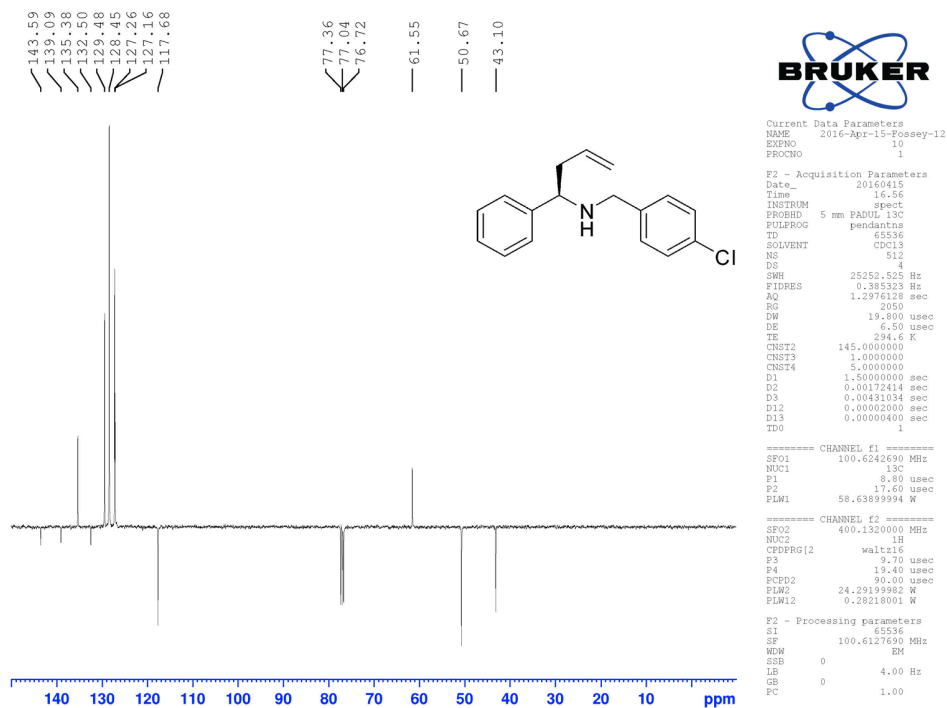
Proton NMR Spectrum of **S4e**



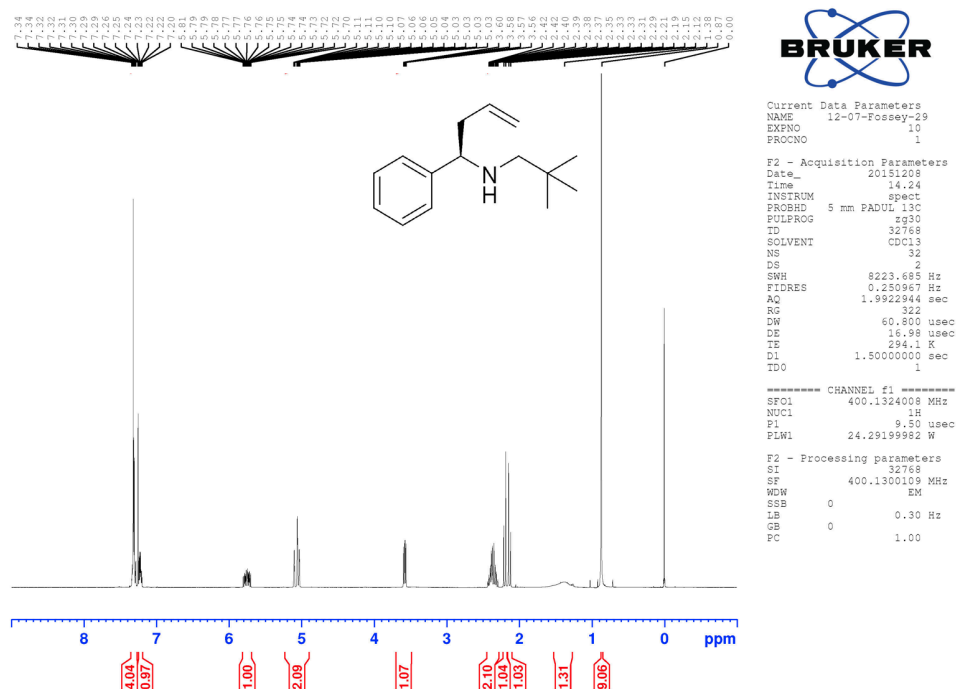
Carbon NMR Spectrum of **S4e**



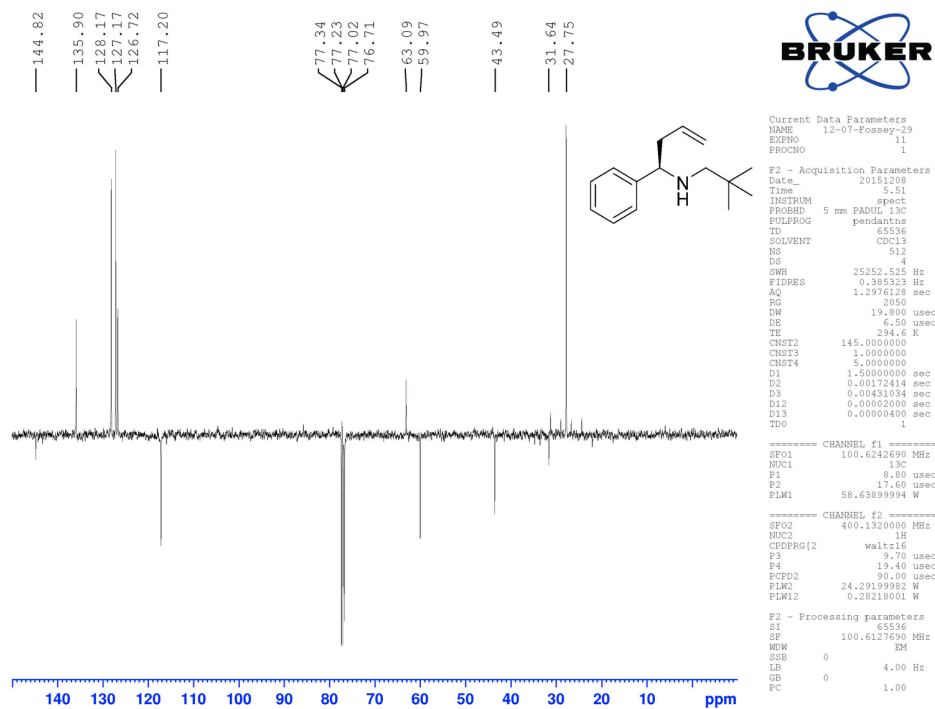
Carbon NMR Spectrum of S4f



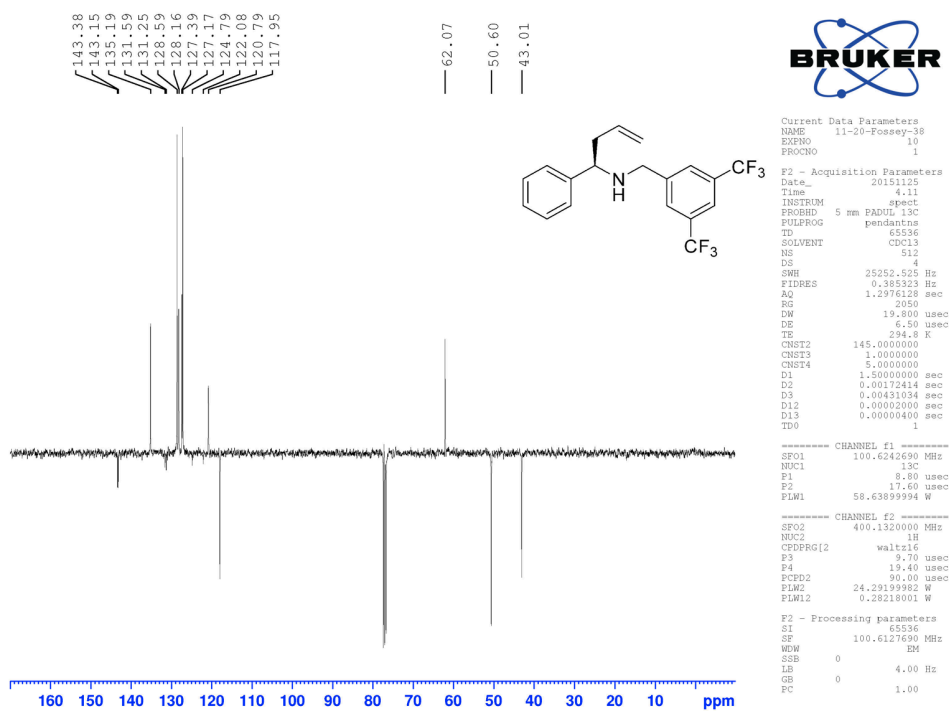
Proton NMR Spectrum of S4g



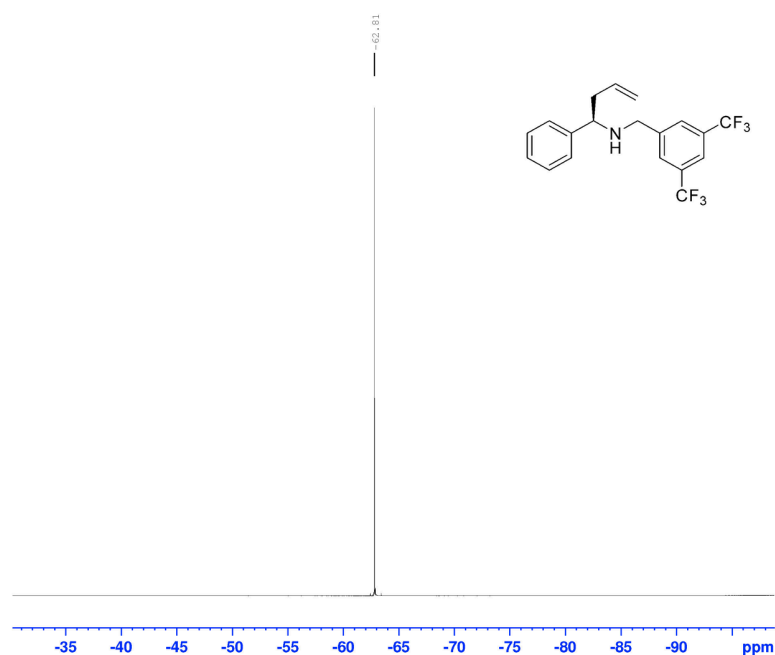
Carbon NMR Spectrum of S4g



Carbon NMR Spectrum of S4h



Fluorine NMR Spectrum of **S4b**



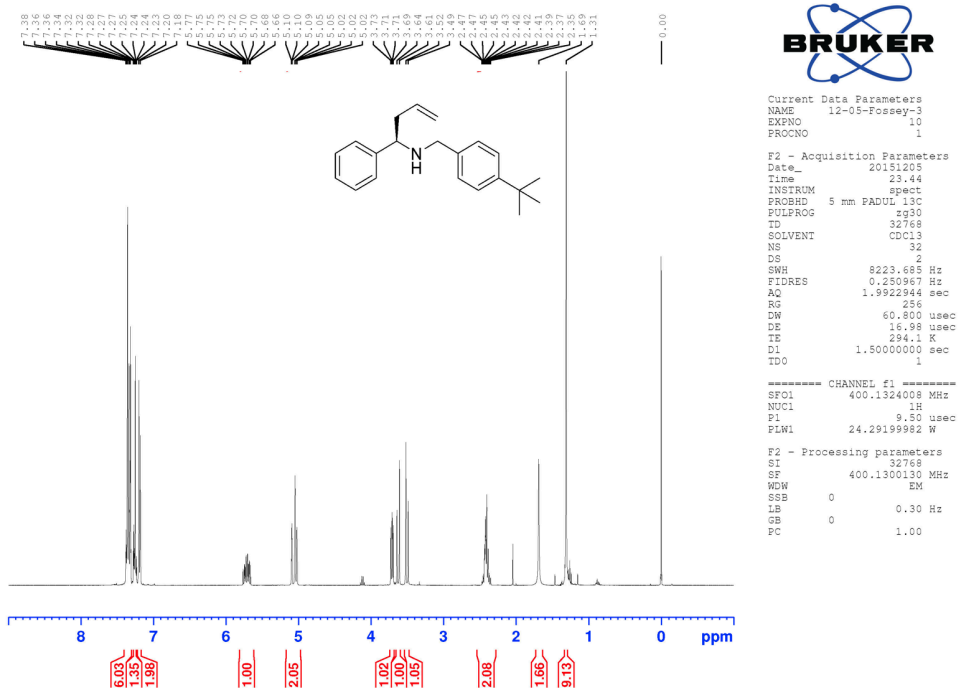
Current Data Parameters
 Date_ 2017-01-09
 NAME 2017-Jan-09-Fessey-51
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20170109
 Time 15.19
 INSTRUM spect
 FPROBHD 5 mm PABBO HB-
 PULPROG zg
 TD 131072
 SOLVENT CDCl3
 NS 32
 DS 4
 SWH 66964.289 Hz
 FIDRES 0.510897 Hz
 AQ 0.9786710 sec
 RG 322
 DW 7.467 usec
 DE 7.27 usec
 TE 294.2 K
 D1 3.00000000 sec
 TD0 1

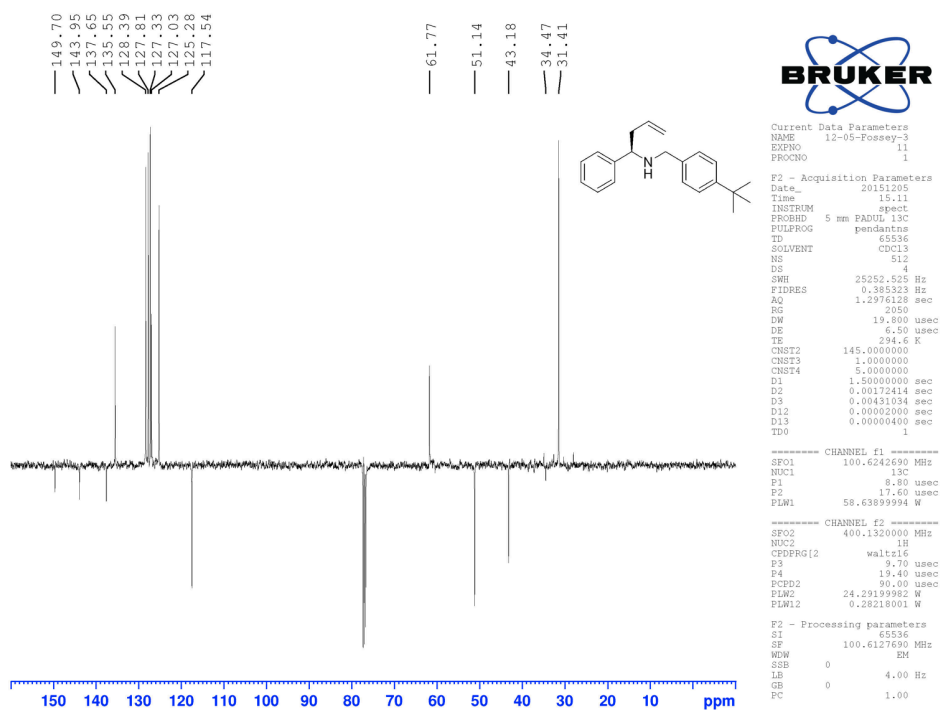
===== CHANNEL f1 =====
 SF01 282.3623550 MHz
 NUC1 19F
 P1 8.70 usec
 PLW1 30.58200073 W

F2 - Processing parameters
 SI 131072
 SF 282.4043550 MHz
 WDW EM
 SSB 0
 LB 0.50 Hz
 GB 0
 PC 1.00

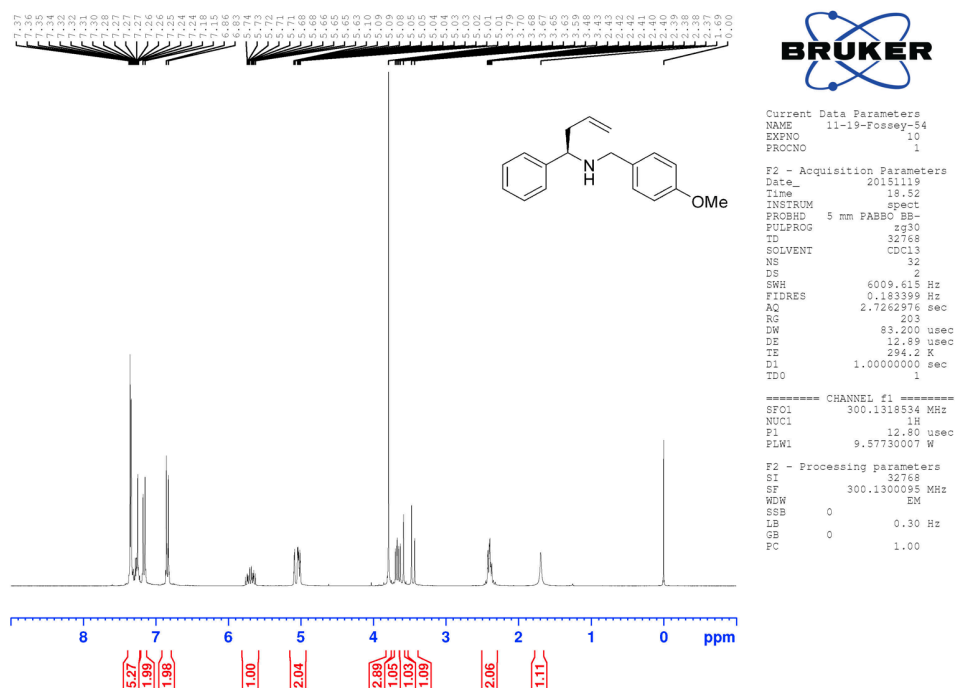
Proton NMR Spectrum of **S4i**



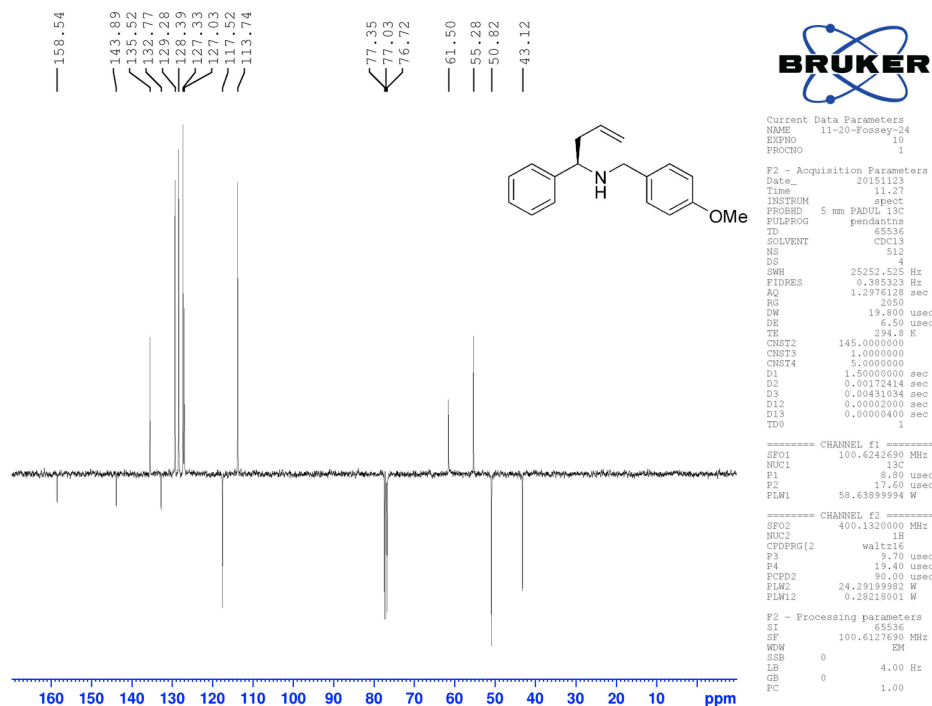
Carbon NMR Spectrum of **S4i**



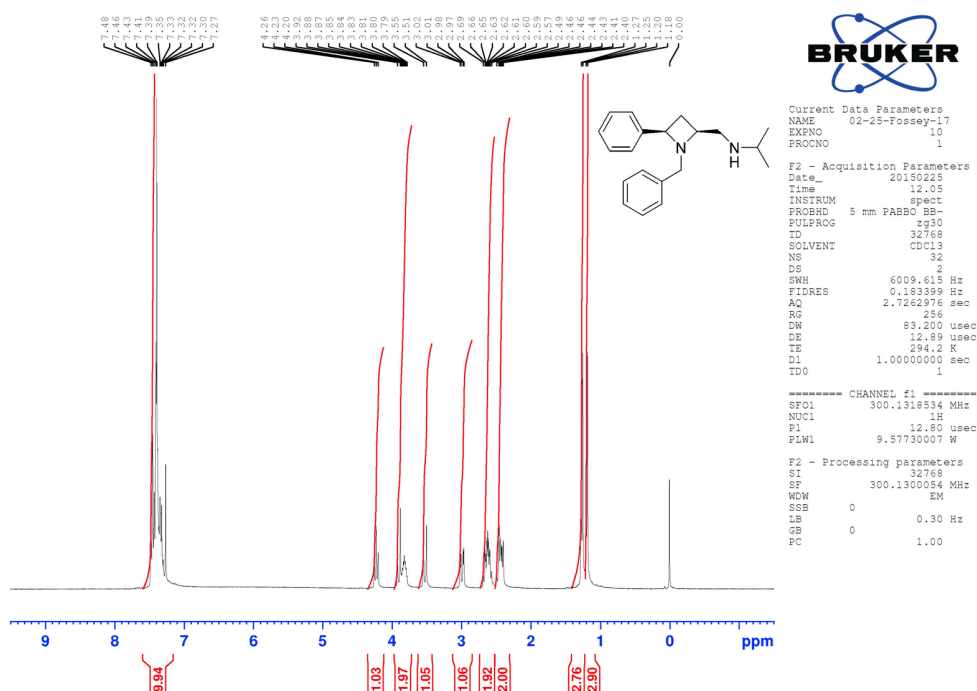
Proton NMR Spectrum of S4j



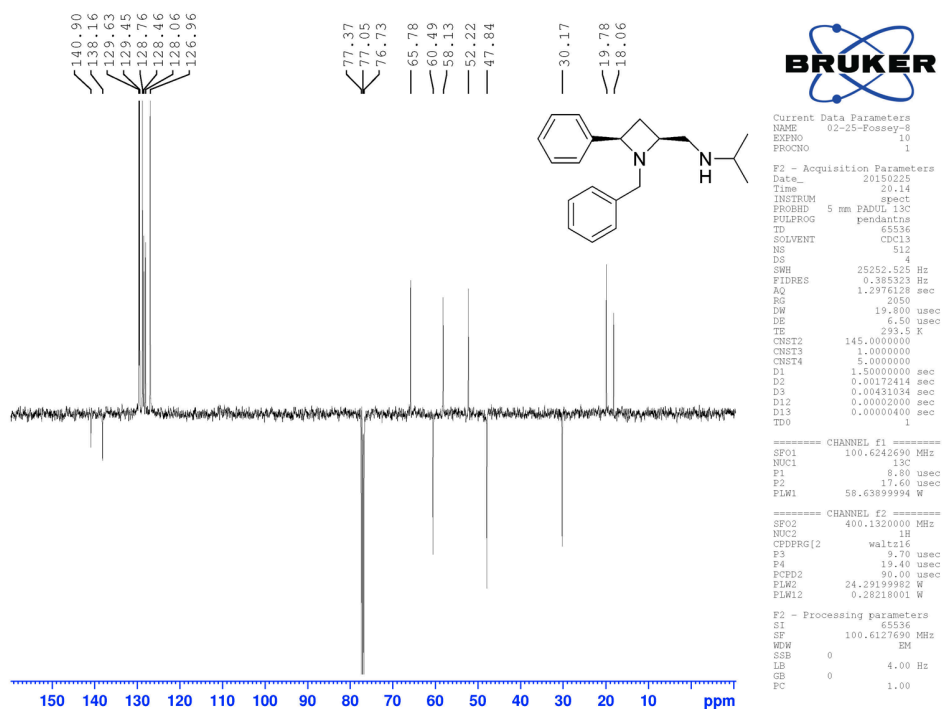
Carbon NMR Spectrum of S4j



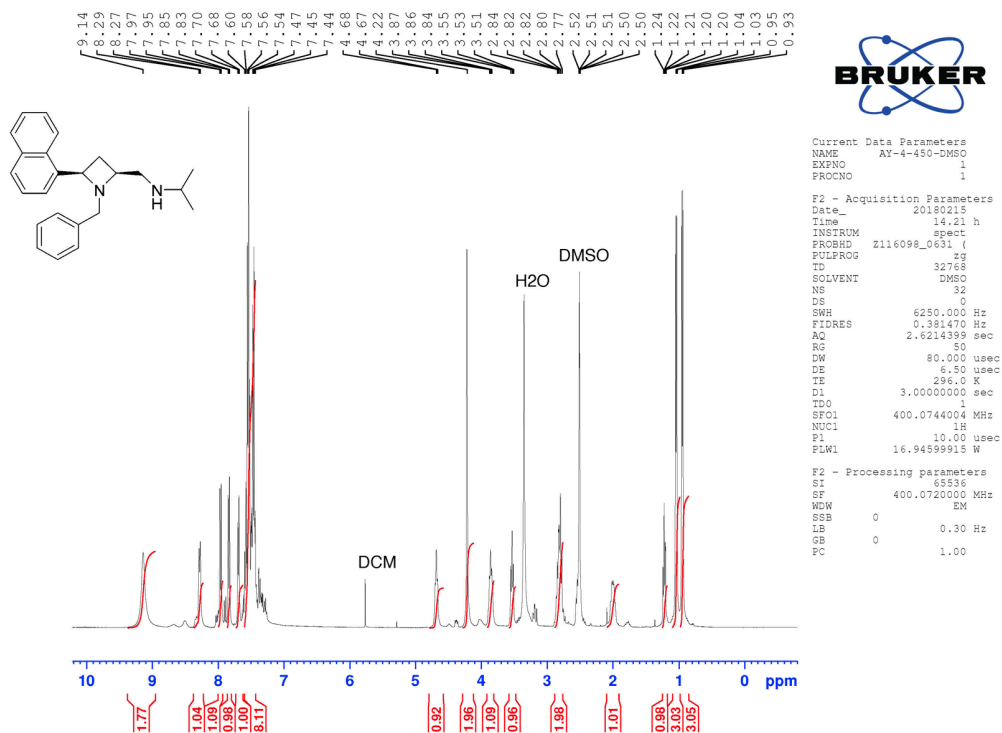
Proton NMR Spectrum of 1a



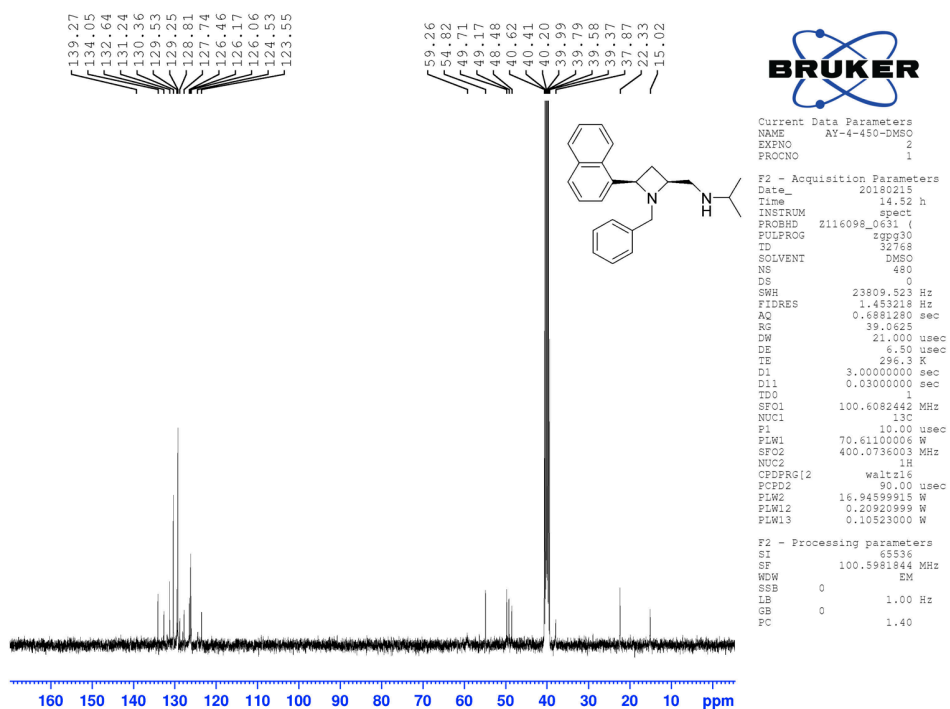
Carbon NMR Spectrum of 1a



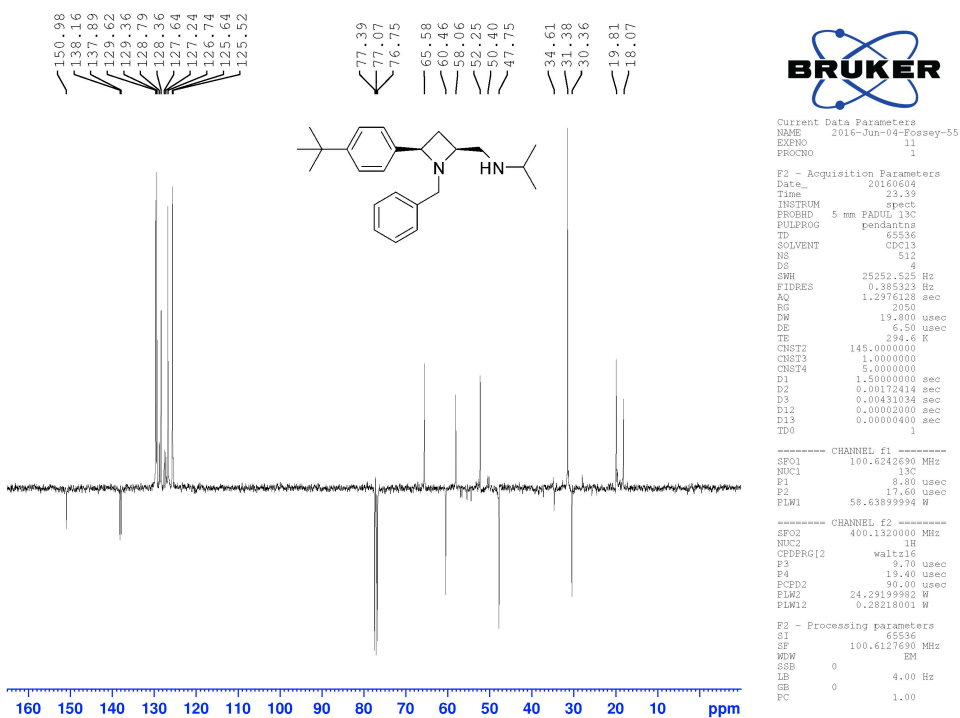
Proton NMR Spectrum of **1b**



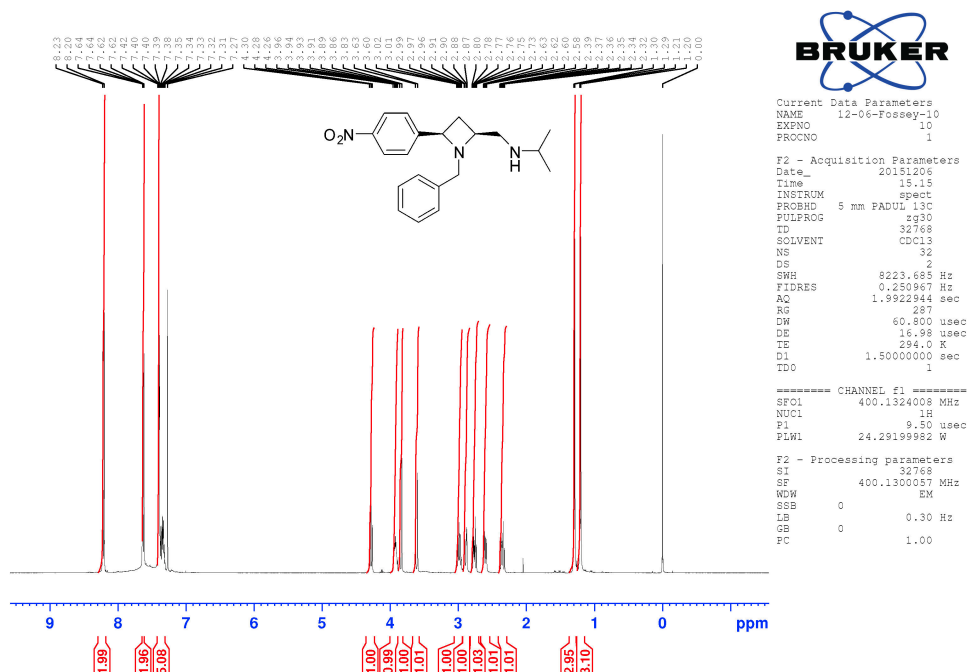
Carbon NMR Spectrum of **1b**



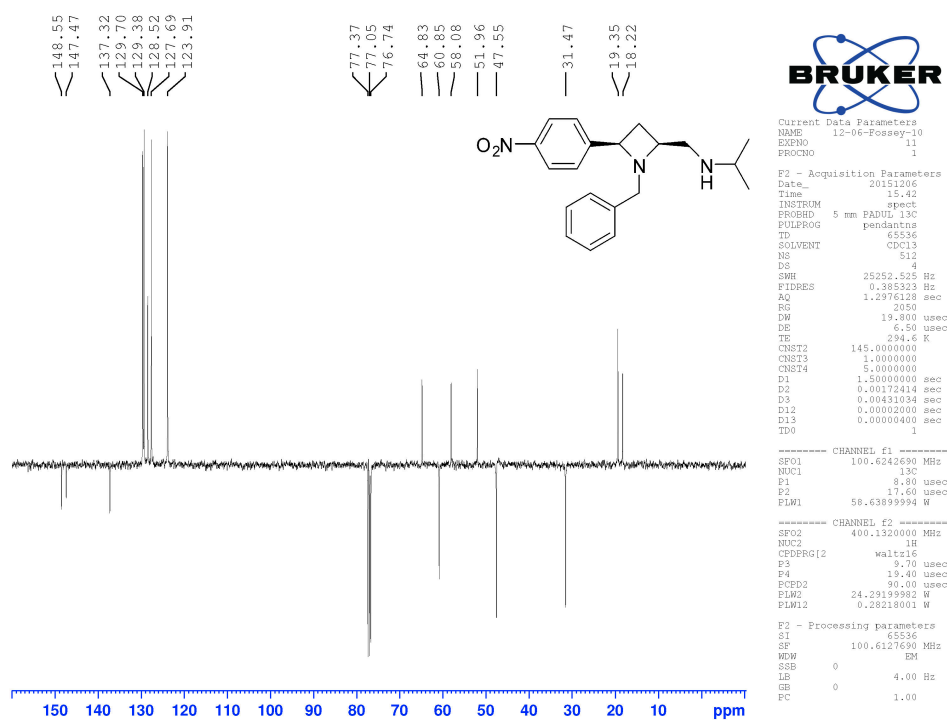
Carbon NMR Spectrum of 1c



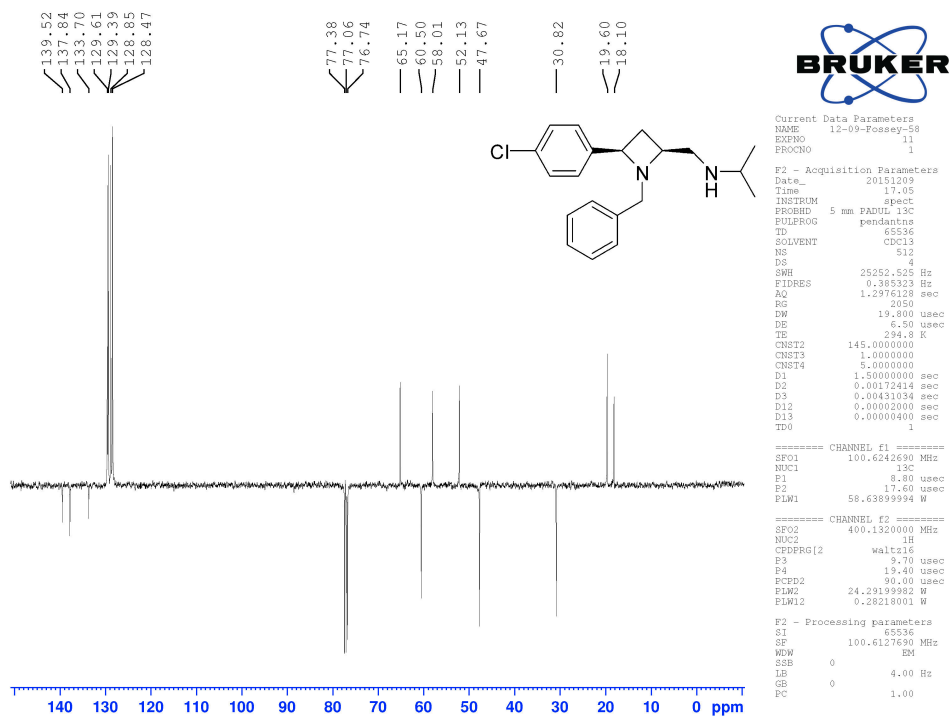
Proton NMR Spectrum of 1d



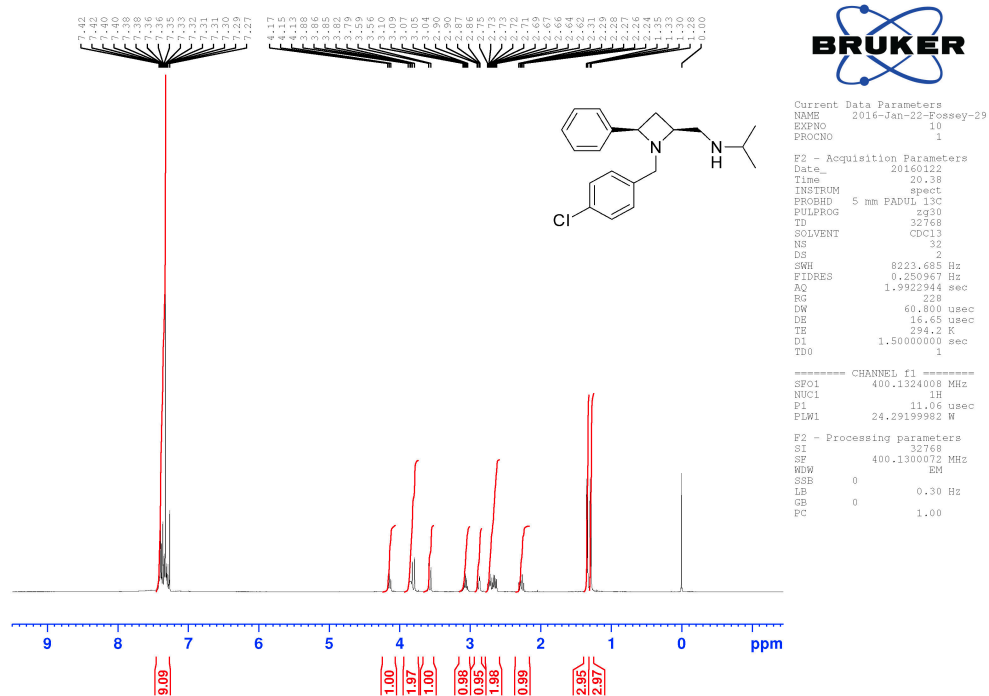
Carbon NMR Spectrum of 1d



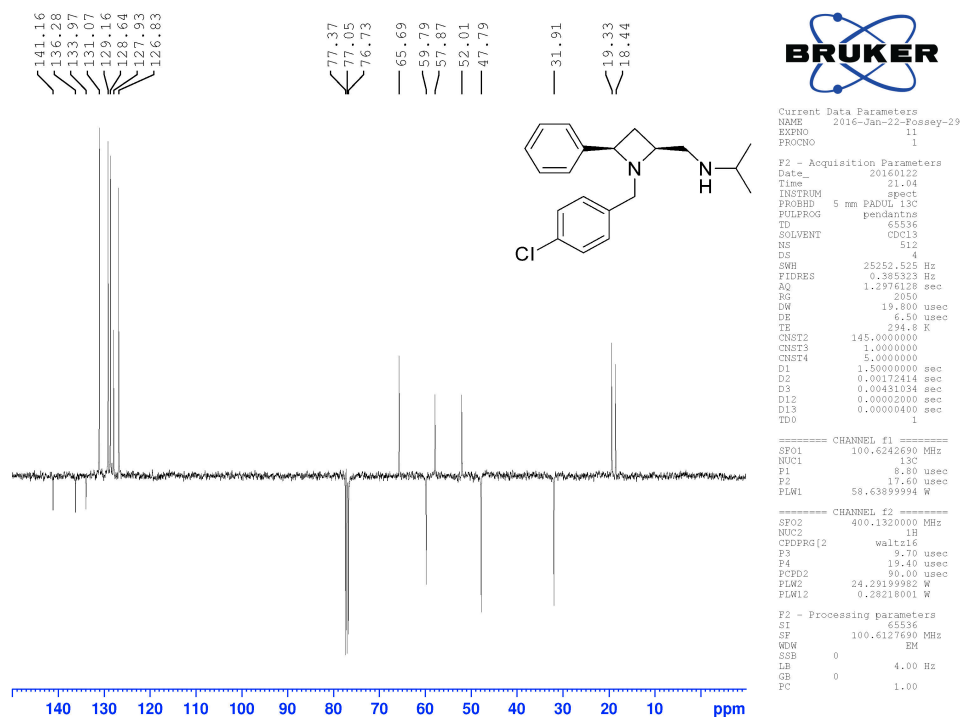
Carbon NMR Spectrum of 1e



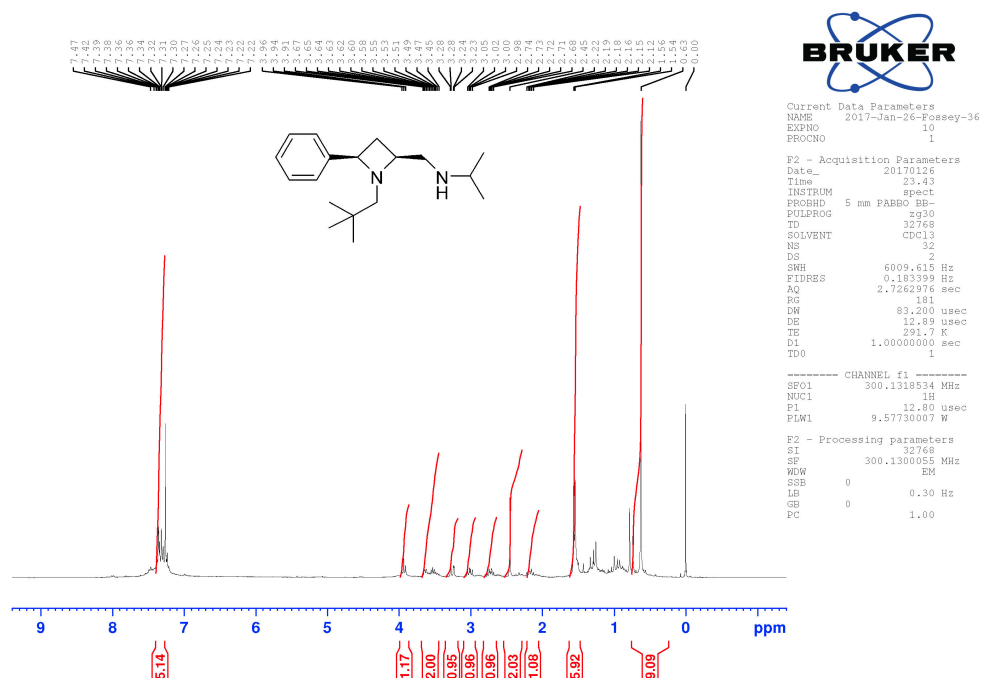
Proton NMR Spectrum of 1f



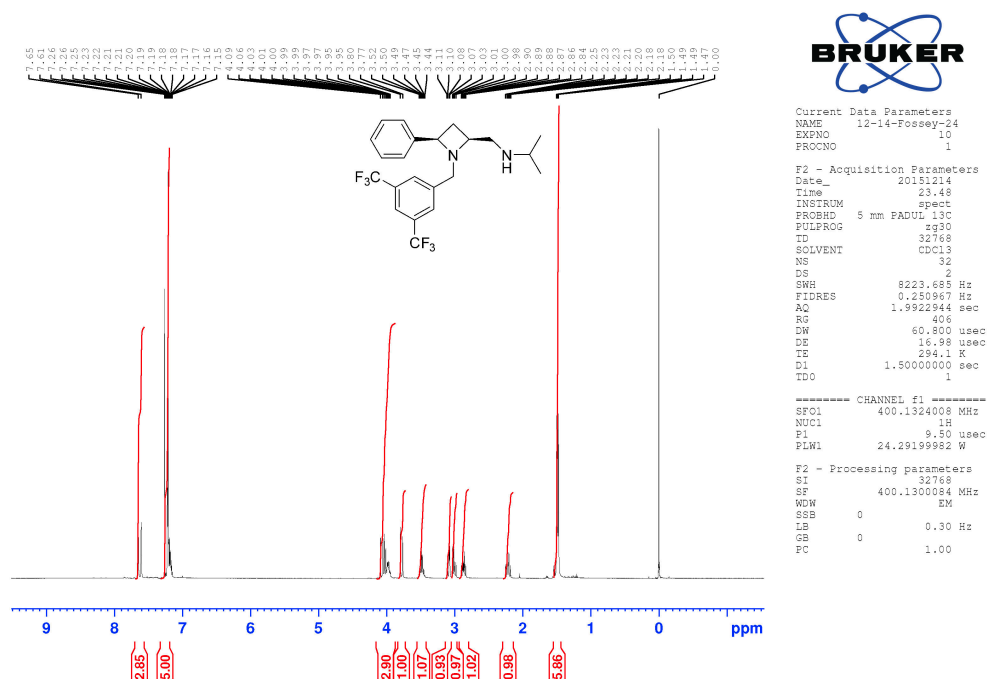
Carbon NMR Spectrum of 1f



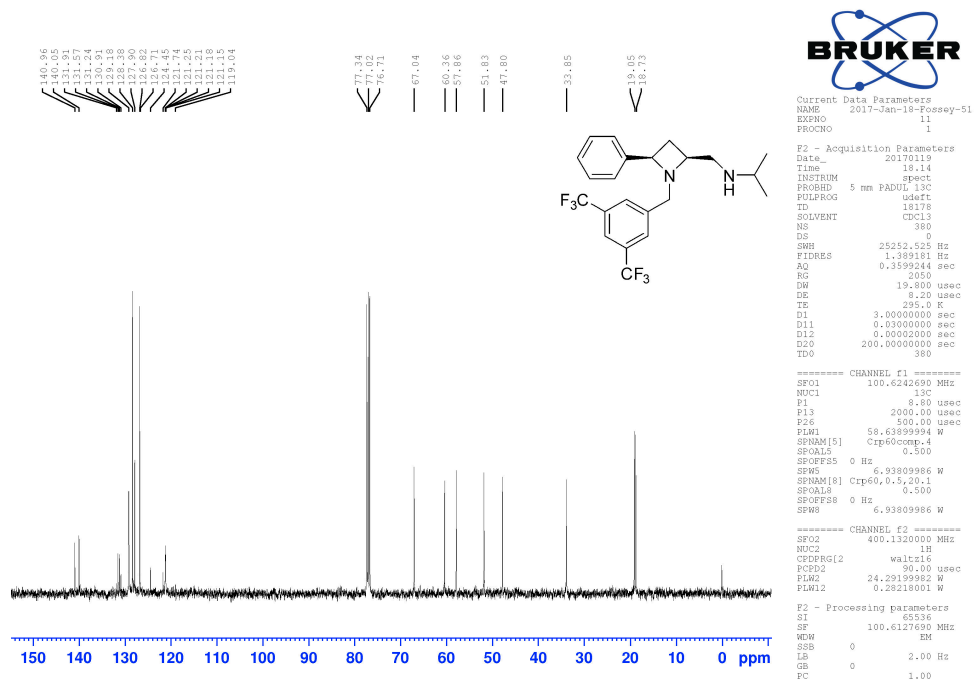
Proton NMR Spectrum of 1g



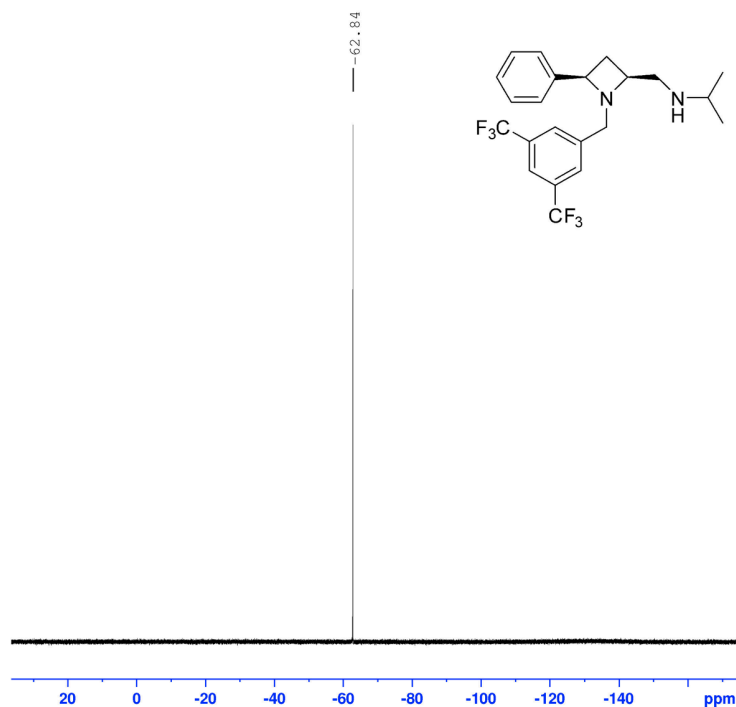
Proton NMR Spectrum of 1b



Carbon NMR Spectrum of 1b



Fluorine NMR Spectrum of **1b**



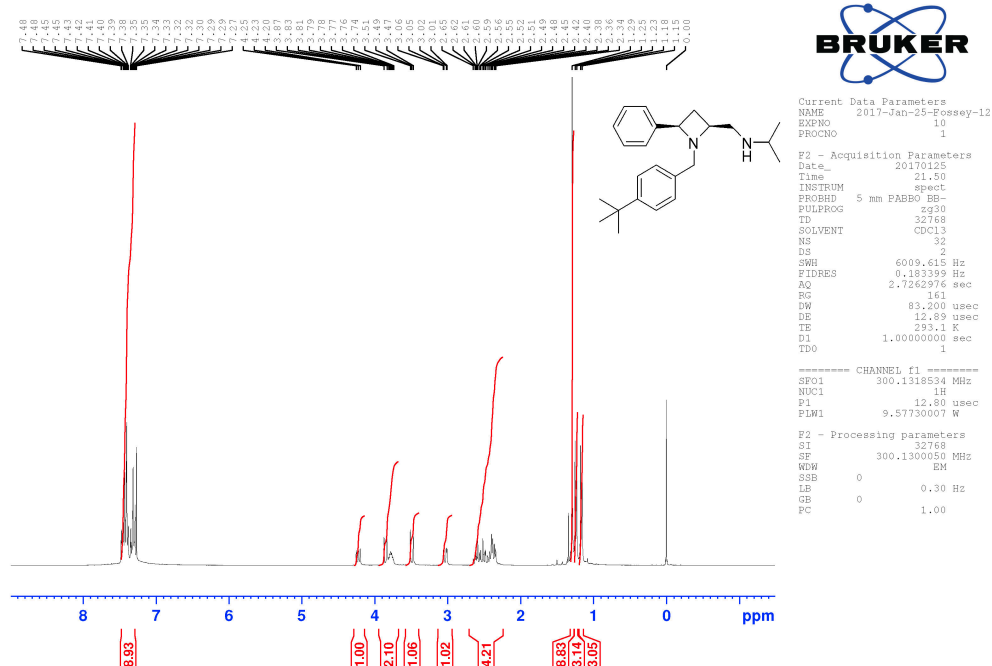
Current Data Parameters
 NAME 2018-Feb-07-Fossey-46
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20180207
 Time 10.04
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg
 TD 131072
 SOLVENT CDCl3
 NS 32
 DS 4
 SWH 66964.289 Hz
 FIDRES 0.510897 Hz
 AQ 0.9786710 sec
 RG 2050
 DW 7.467 usec
 DE 7.27 usec
 TE 292.6 K
 D1 3.0000000 sec
 TD0 1

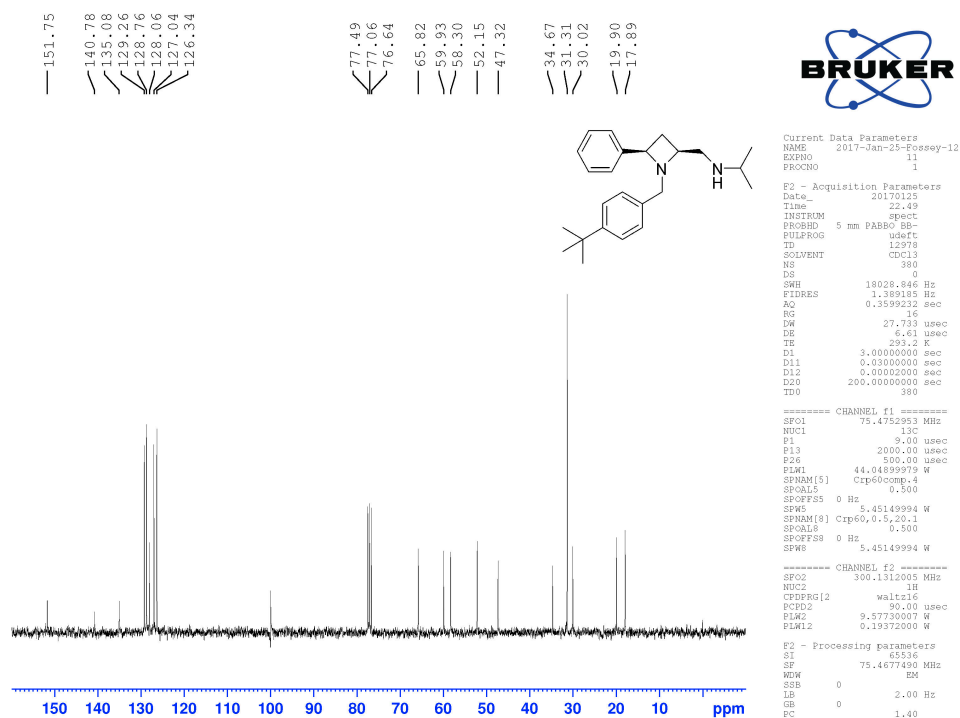
===== CHANNEL f1 =====
 SFO1 282.3623550 MHz
 NUC1 19F
 P1 8.70 usec
 PLW1 30.58200073 W

F2 - Processing parameters
 SI 131072
 SF 282.4043550 MHz
 WDW EM
 SSB 0
 LB 0.50 Hz
 GB 0
 PC 1.00

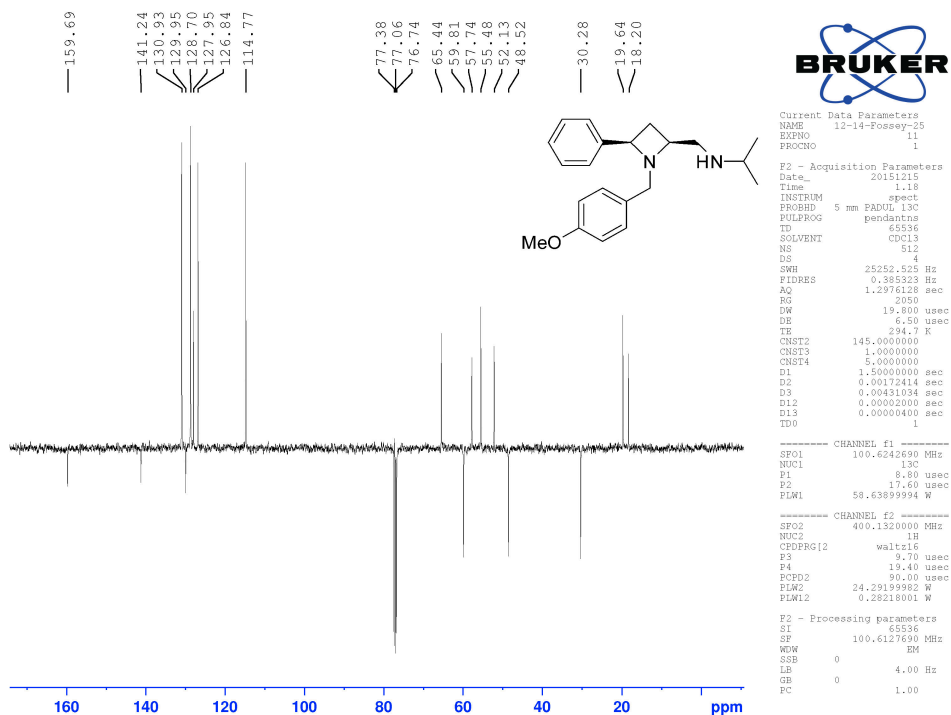
Proton NMR Spectrum of **1i**



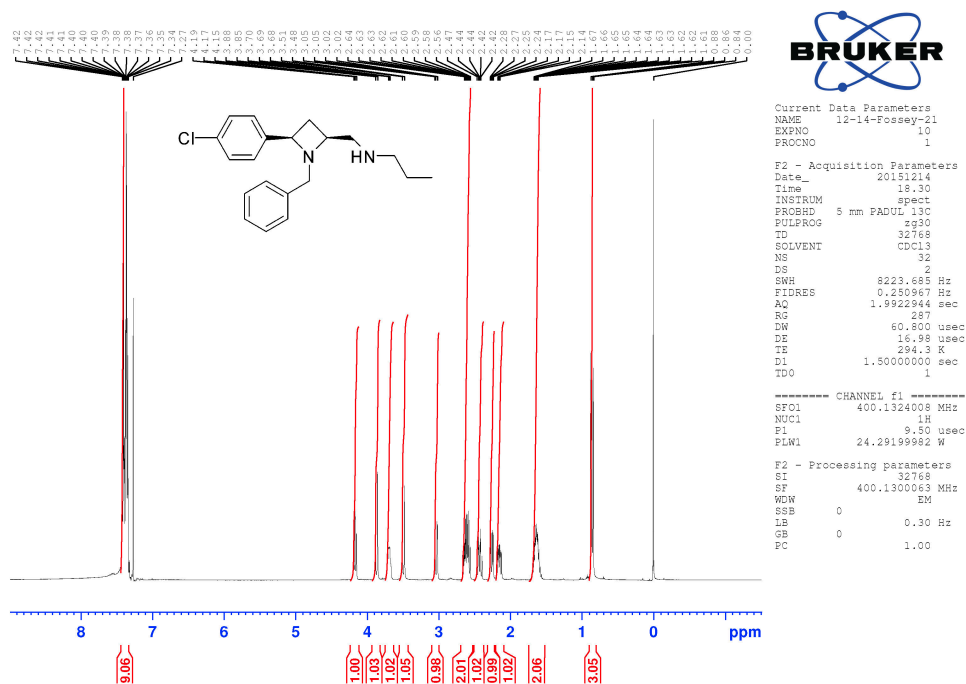
Carbon NMR Spectrum of **1i**



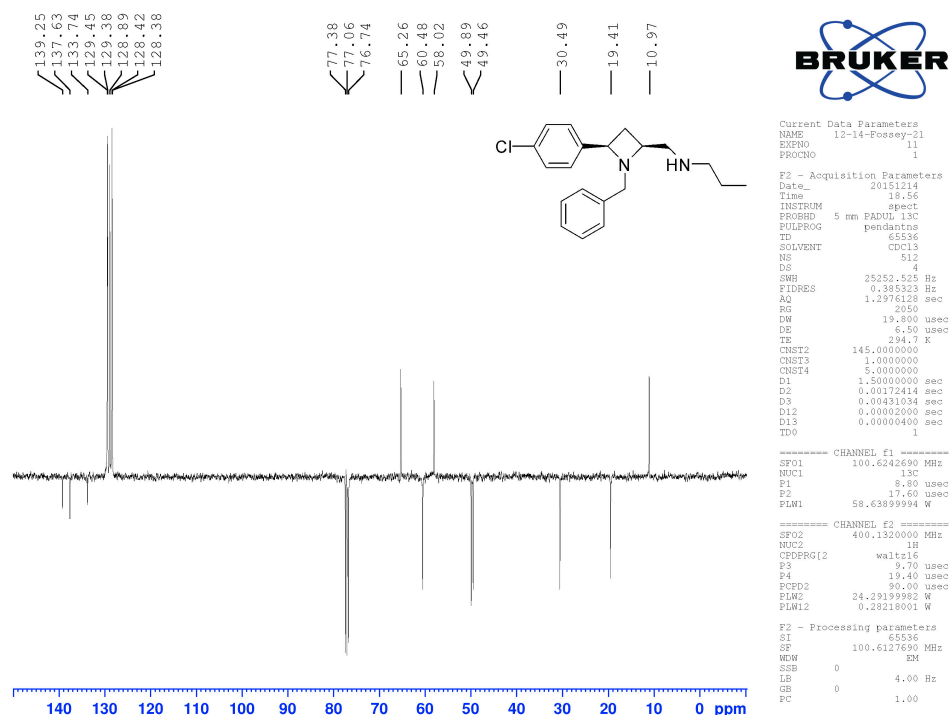
Carbon NMR Spectrum of 1j



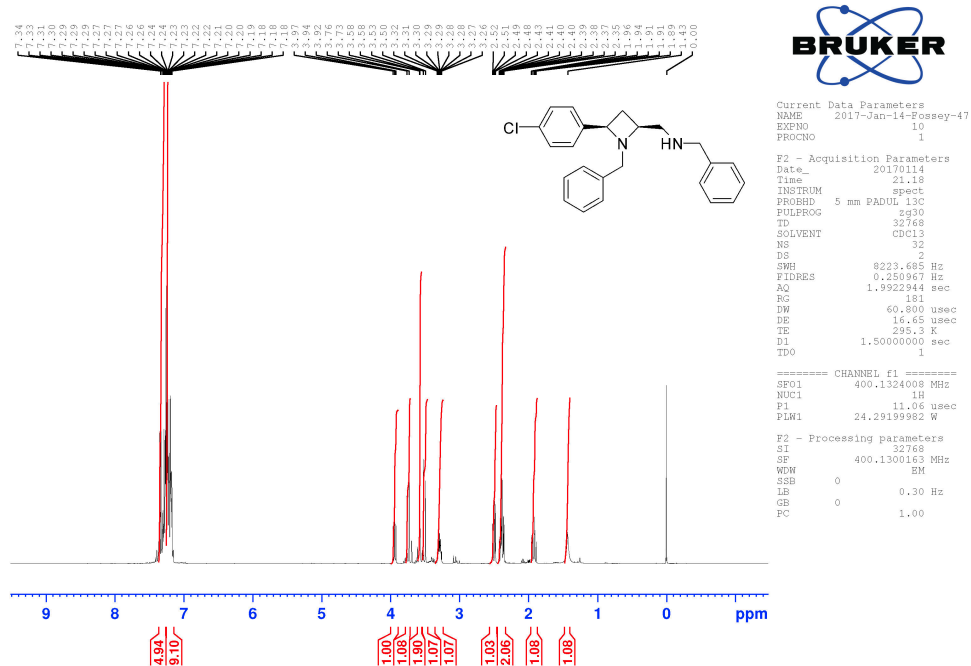
Proton NMR Spectrum of **1k**



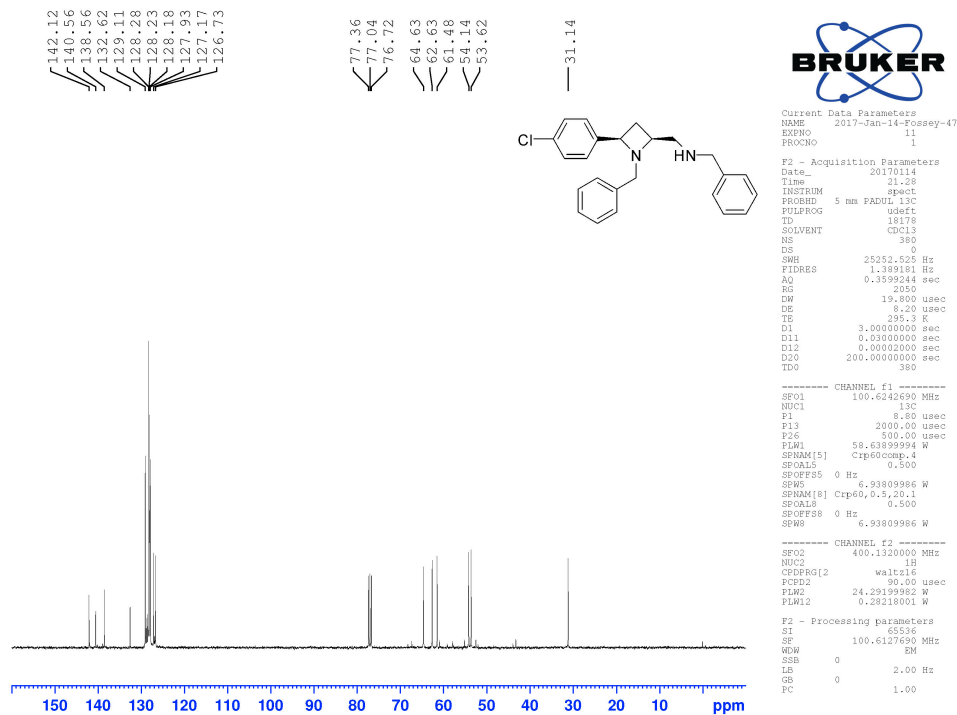
Carbon NMR Spectrum of **1k**



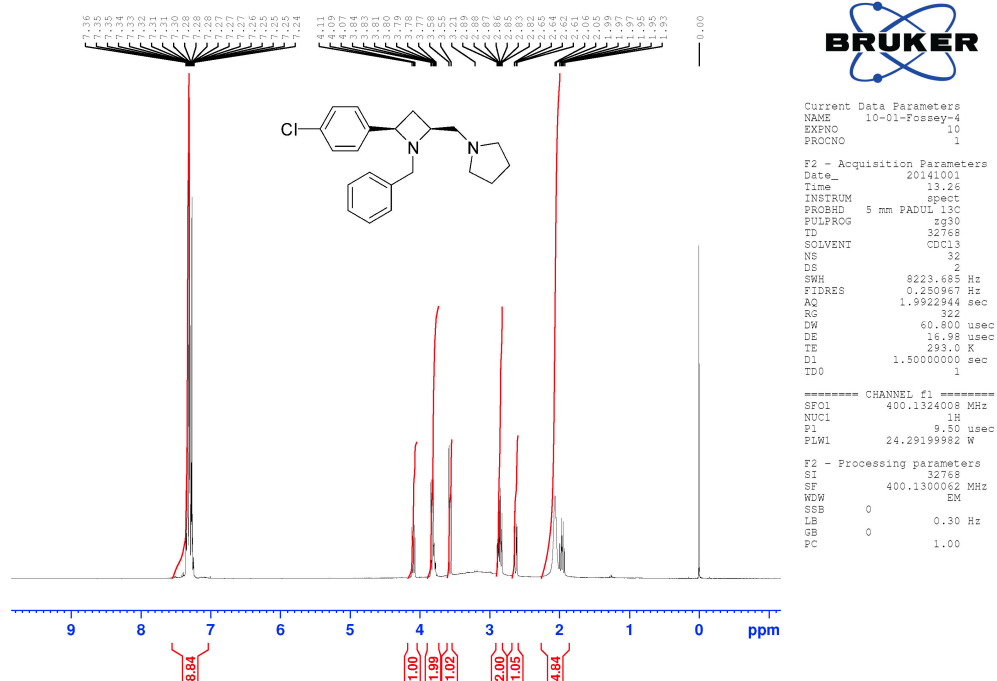
Proton NMR Spectrum of **11**



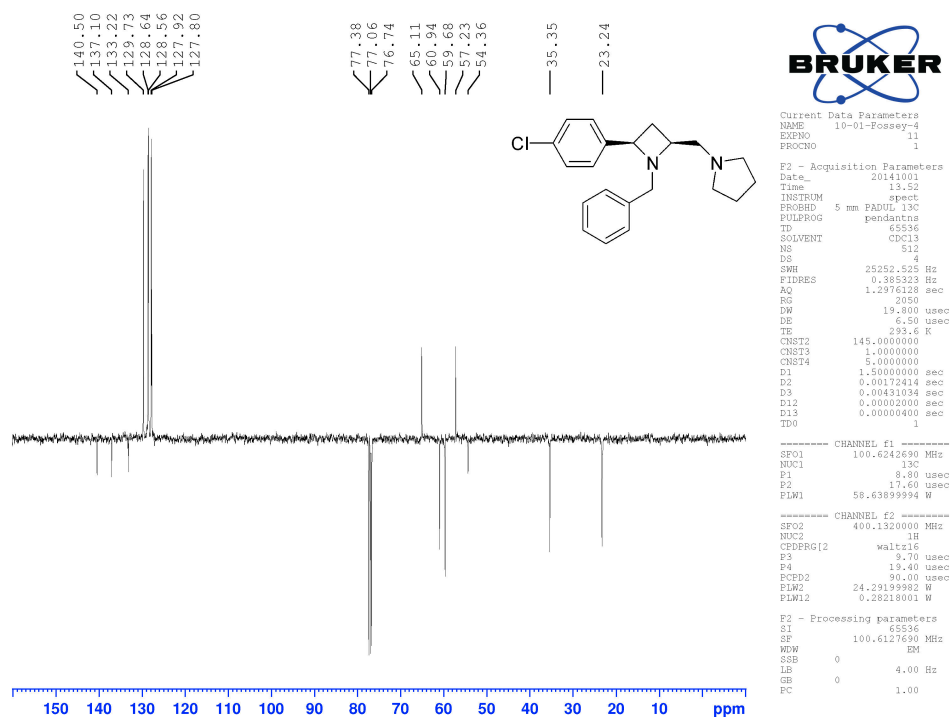
Carbon NMR Spectrum of **11**



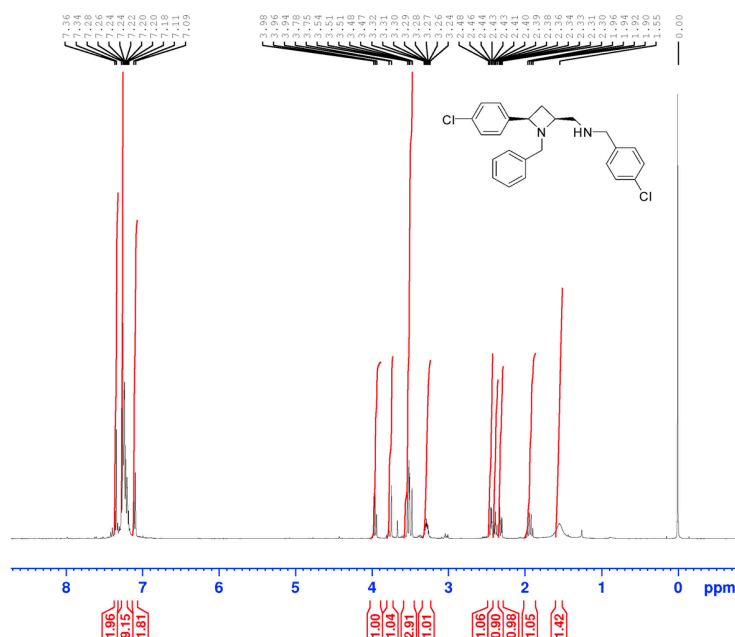
Proton NMR Spectrum of 1m



Carbon NMR Spectrum of 1m



Proton NMR Spectrum of **1n**

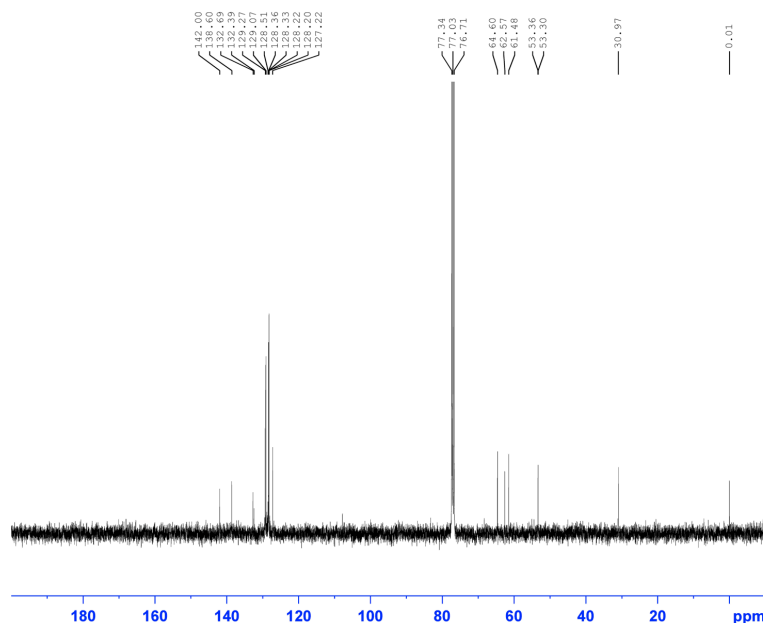


Current Data Parameters
NAME YZ-AY4-403
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180207
Time 9.50 h
INSTRUM spect
PROBHD z116098_0631 (4
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6250.000 Hz
FIDRES 0.381470 Hz
AQ 2.6214399 sec
RG 80
CW 80.000 usec
DE 6.50 usec
TE 296.5 K
D1 3.0000000 sec
TD0 1
SF01 400.0744004 MHz
NUC1 1H
P1 10.00 usec
PLW1 16.94599915 W

F2 - Processing parameters
SI 65536
SF 400.0720099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of **1n**

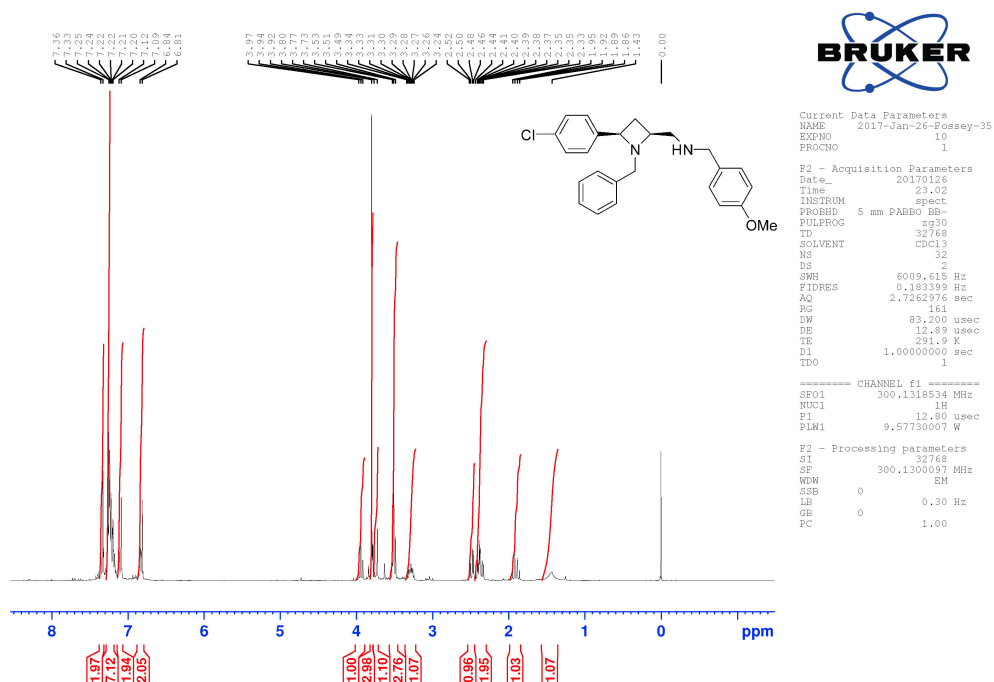


Current Data Parameters
NAME AY4-443
EXPNO 2
PROCNO 1

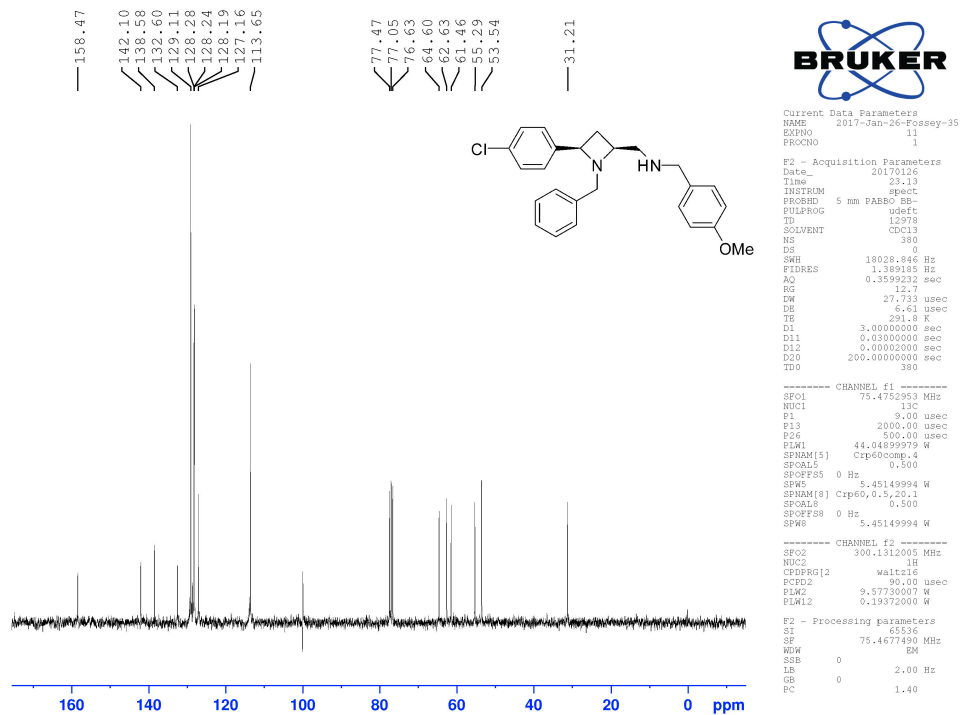
F2 - Acquisition Parameters
Date_ 20180214
Time 12.33 h
INSTRUM spect
PROBHD z116098_0631 (4
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1024
DS 0
SWH 23809.523 Hz
FIDRES 1.453218 Hz
AQ 0.6881280 sec
RG 39.0625
CW 21.000 usec
DE 6.50 usec
TE 296.4 K
D1 3.0000000 sec
D11 0.03000000 sec
TD0 1
SF01 100.6082442 MHz
NUC1 13C
P1 10.00 usec
PLW1 70.61100006 W
SF02 400.0736003 MHz
NUC2 1H
CTDPRG12 waltz16
PCPD2 90.00 usec
PLW2 16.94599915 W
PLW12 0.20920999 W
PLW13 0.10523000 W

F2 - Processing parameters
SI 65536
SF 100.5981844 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

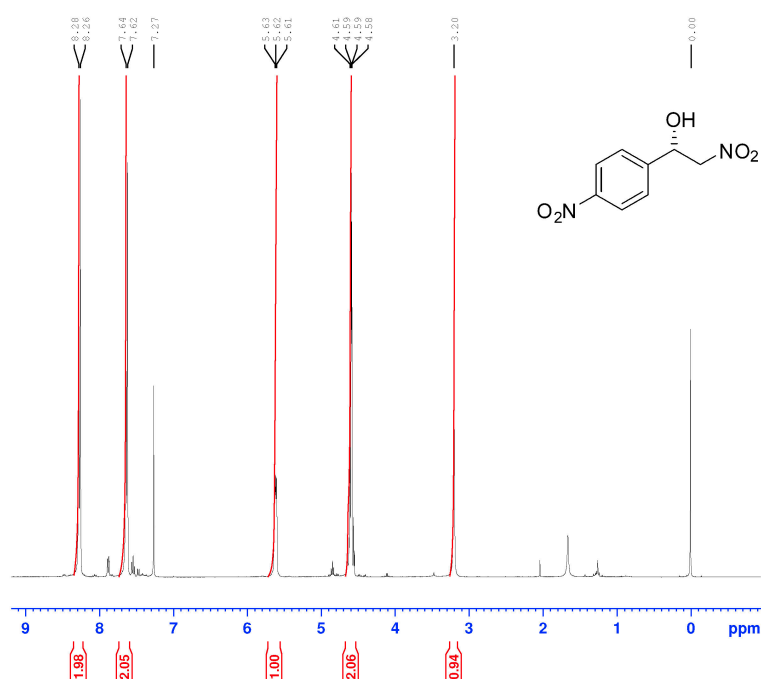
Proton NMR Spectrum of **1o**



Carbon NMR Spectrum of **1o**



Proton NMR Spectrum of (rac)-6a



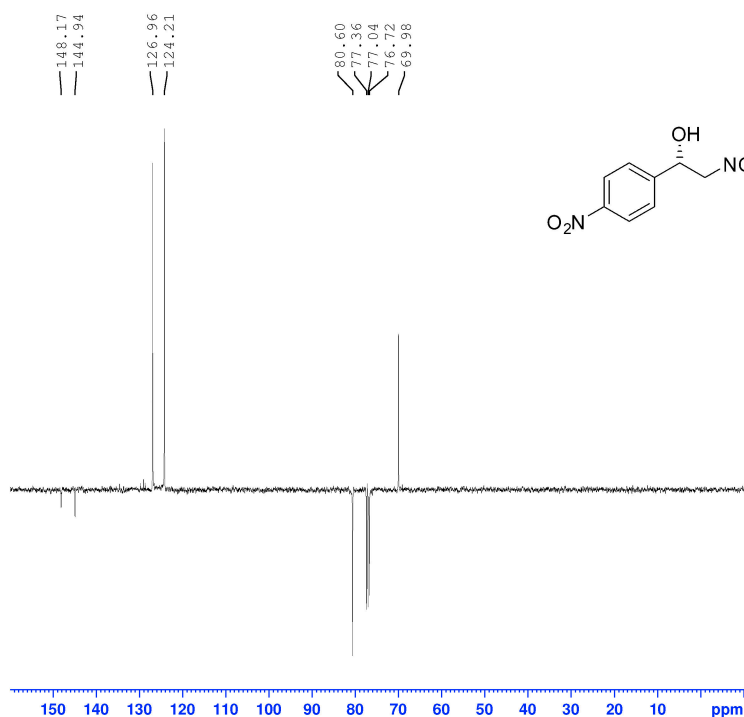
Current Data Parameters
NAME 2016-Dec-04-Possey-13
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161204
Time 21.28
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 287
DW 60.800 usec
DE 16.65 usec
TE 295.2 K
D1 1.50000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 11.06 usec
PLW1 24.29199982 W

F2 - Processing parameters
SI 32768
SF 400.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of (rac)-6a



Current Data Parameters
NAME 2016-Dec-04-Possey-13
EXPNO 11
PROCNO 1

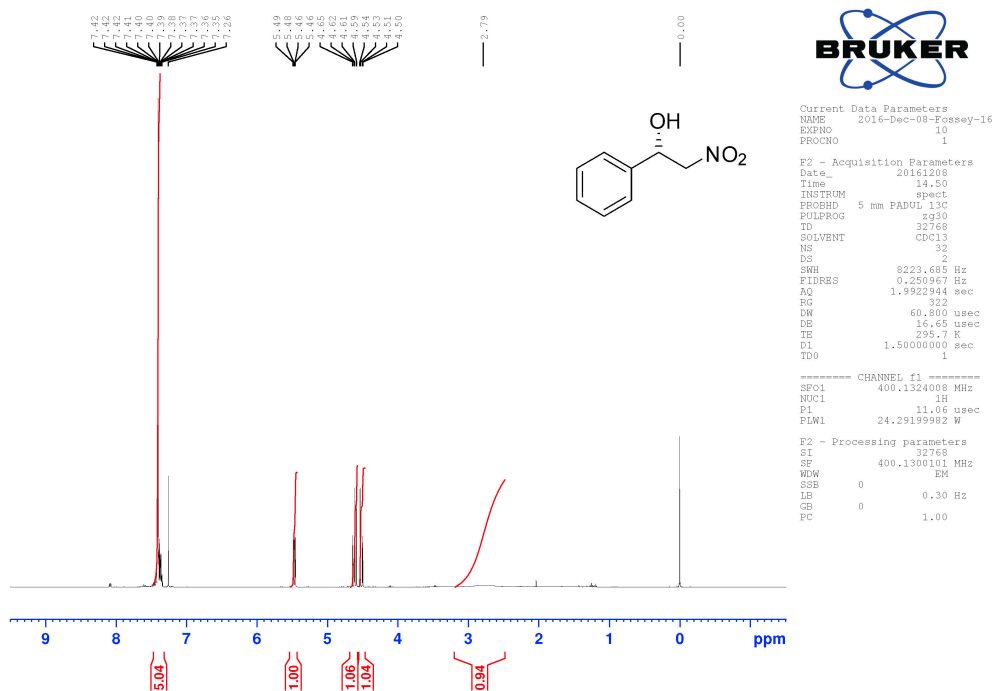
F2 - Acquisition Parameters
Date_ 20161204
Time 21.55
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG pendantns
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 296.5 K
CNST2 145.000000
CNST3 1.0000000
CNST4 5.0000000
D1 1.50000000 sec
D2 0.00172414 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1

===== CHANNEL f1 =====
SFO1 100.6242690 MHz
NUC1 13C
P1 8.80 usec
P2 17.60 usec
PLW1 58.63899994 W

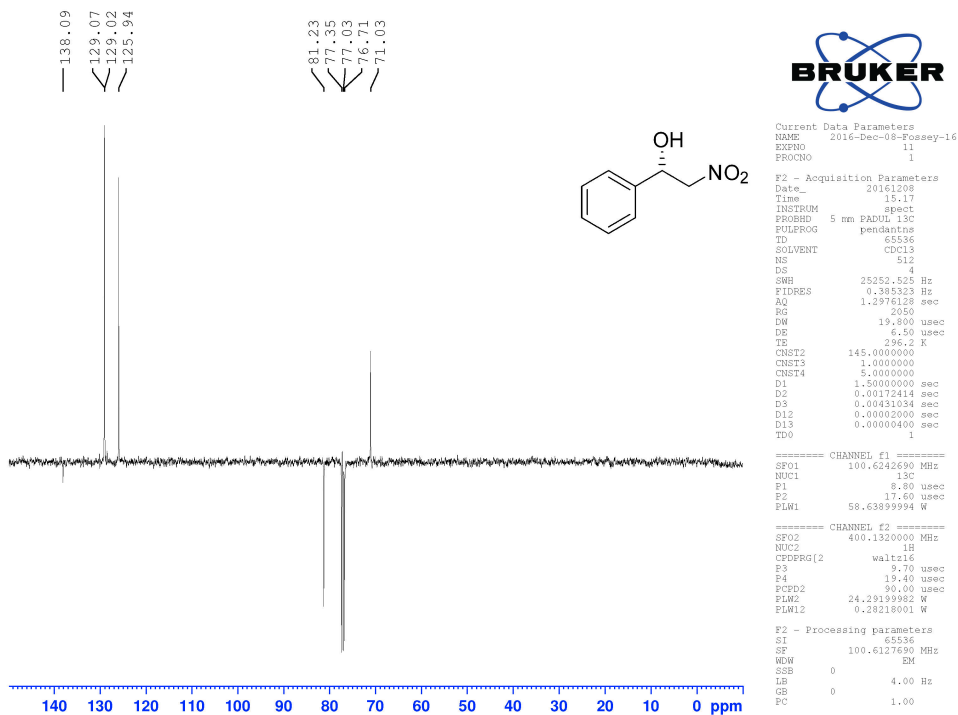
===== CHANNEL f2 =====
SFO2 400.1320000 MHz
NUC2 1H
CHPRG2 waltz16
P3 9.70 usec
P4 19.40 usec
PCTD2 90.00 usec
PLW2 24.29199982 W
PLW12 0.28218001 W

F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

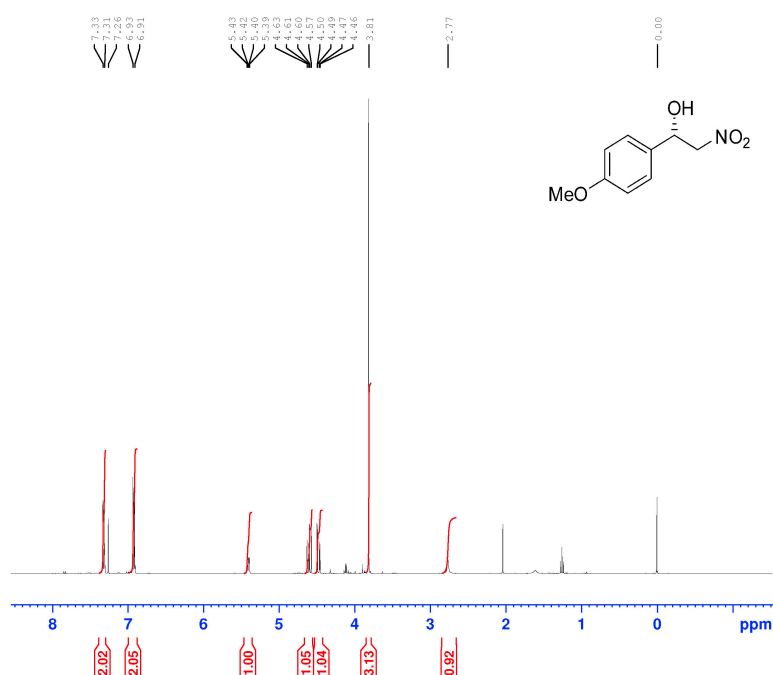
Proton NMR Spectrum of (rac)-6b



Carbon NMR Spectrum of (rac)-6b



Proton NMR Spectrum of (rac)-6c



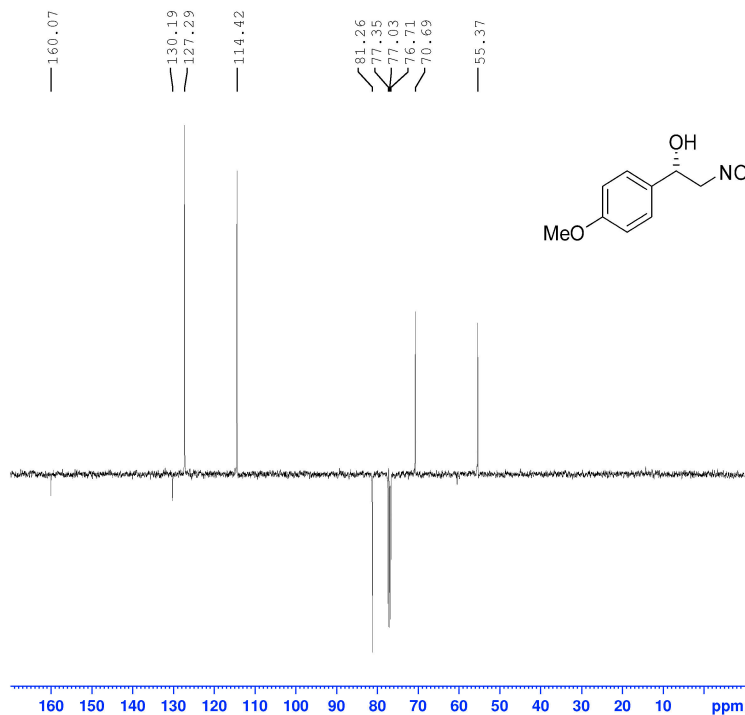
Current Data Parameters
NAME 2016-Dec-08-Fossey-21
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161208
Time 19.11
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 287
DW 60.800 usec
DE 16.65 usec
TE 295.7 K
D1 1.50000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 11.06 usec
PLW1 24.29199982 W

F2 - Processing parameters
SI 32768
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of (rac)-6c



Current Data Parameters
NAME 2016-Dec-08-Fossey-21
EXPNO 11
PROCNO 1

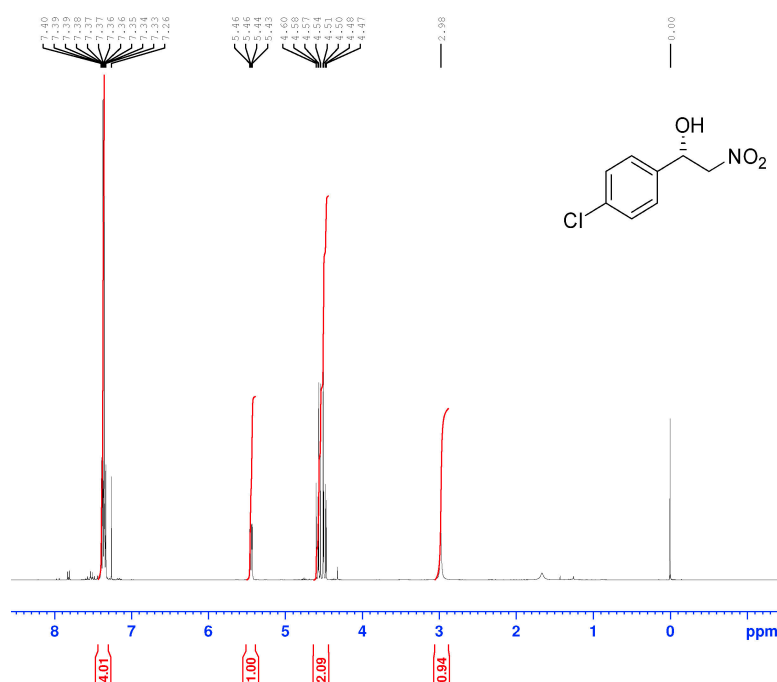
F2 - Acquisition Parameters
Date_ 20161208
Time 19.38
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 296.1 K
CNST2 145.000000
CNST3 1.0000000
CNST4 5.0000000
D1 1.50000000 sec
D2 0.00172414 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1

===== CHANNEL f1 =====
SFO1 100.6242690 MHz
NUC1 13C
P1 8.80 usec
P2 7.60 usec
PLW1 58.63899994 W

===== CHANNEL f2 =====
SFO2 400.1320000 MHz
NUC2 1H
CPCPRG2 waltz16
P3 9.70 usec
P4 19.40 usec
PCPD2 90.00 usec
PLW2 24.29199982 W
PLW12 0.28218001 W

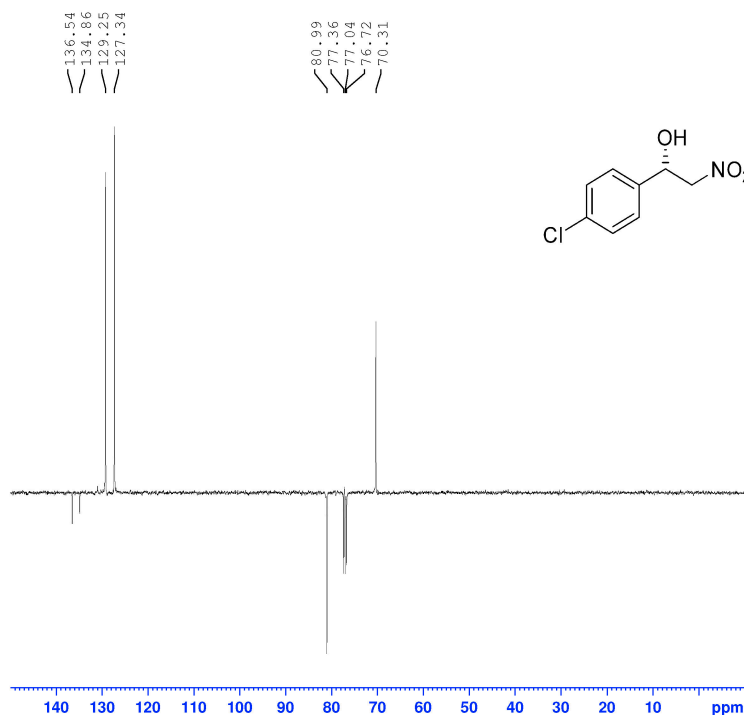
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

Proton NMR Spectrum of (rac)-6d



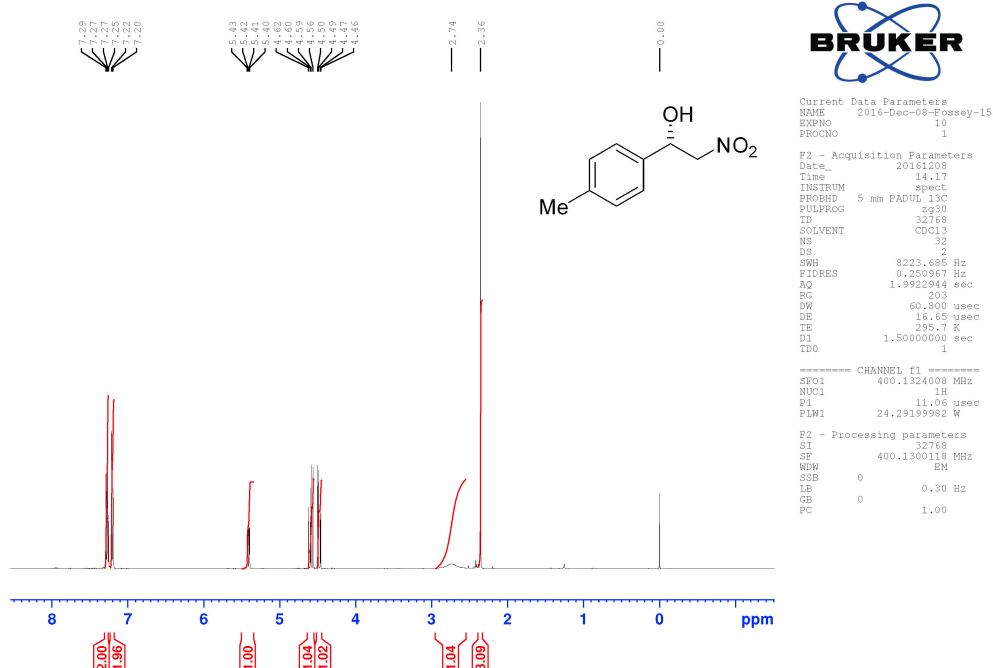
Current Data Parameters
NAME 2016-Dec-12-Fossey-2
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161212
Time 22.23
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.350967 Hz
AQ 1.9922944 sec
RG 228
DW 60.800 usec
DE 16.65 usec
TE 295.9 K
D1 1.50000000 sec
TD0 1
----- CHANNEL f1 -----
SFO1 400.1324008 MHz
NUC1 1H
P1 11.06 usec
PLW1 24.29199982 W
F2 - Processing parameters
SI 32768
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbon NMR Spectrum of (rac)-6d

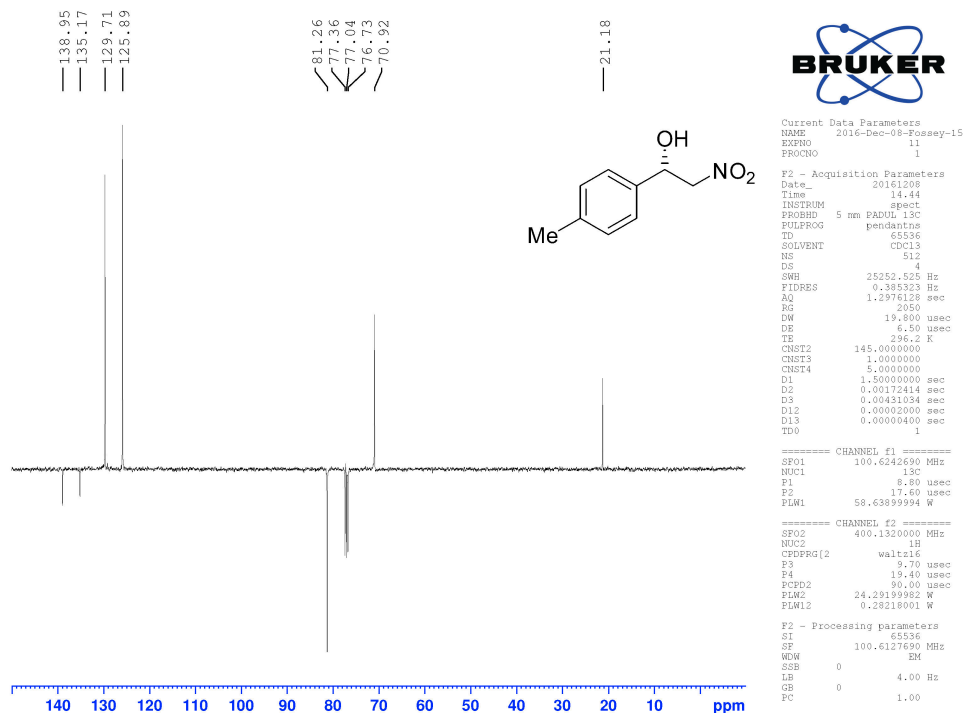


Current Data Parameters
NAME 2016-Dec-12-Fossey-2
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161212
Time 22.50
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG pendantns
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 296.2 K
CNST2 145.0000000
CNST3 1.0000000
CNST4 5.0000000
D1 1.50000000 sec
D2 0.0017244 sec
D3 0.00431034 sec
D12 0.00002000 sec
D13 0.00000400 sec
TD0 1
----- CHANNEL f1 -----
SFO1 100.6242690 MHz
NUC1 13C
P1 8.80 usec
P2 17.60 usec
PLW1 58.6389994 W
----- CHANNEL f2 -----
SFO2 400.1320000 MHz
NUC2 1H
CPDPRG2 waltz16
P3 9.70 usec
P4 19.40 usec
PCPD2 30.00 usec
PLW2 24.29199982 W
PLW12 0.28218001 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

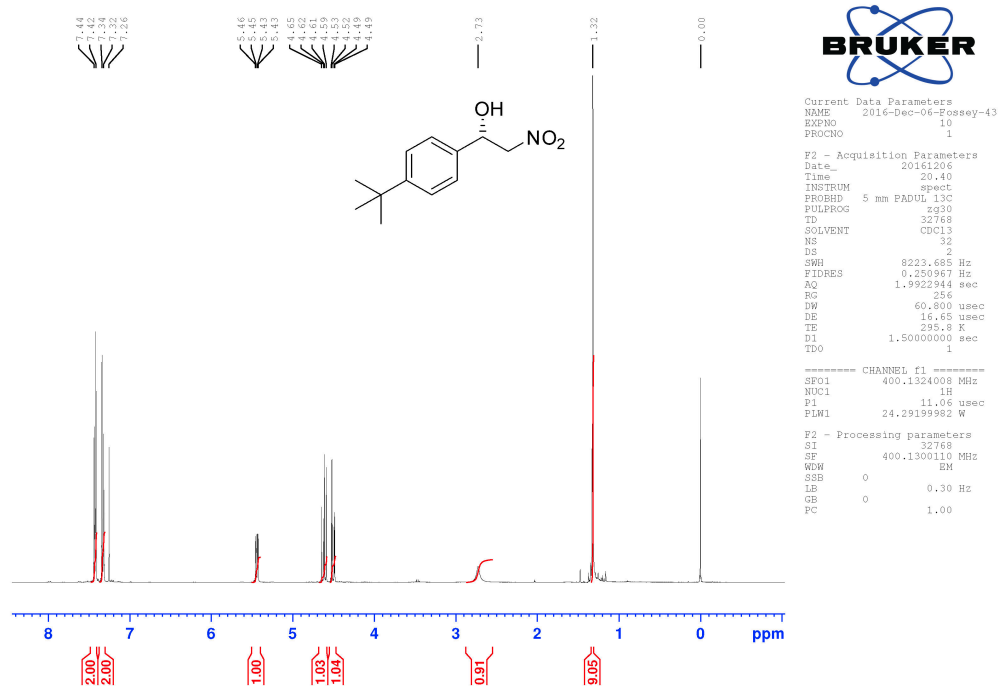
Proton NMR Spectrum of (rac)-6e



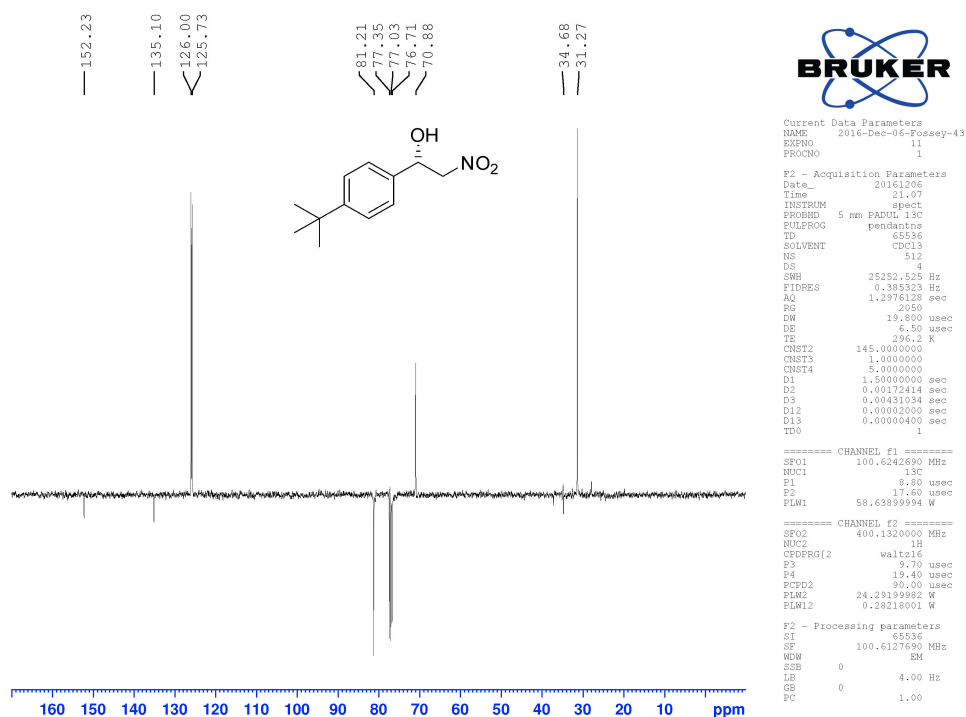
Carbon NMR Spectrum of (rac)-6e



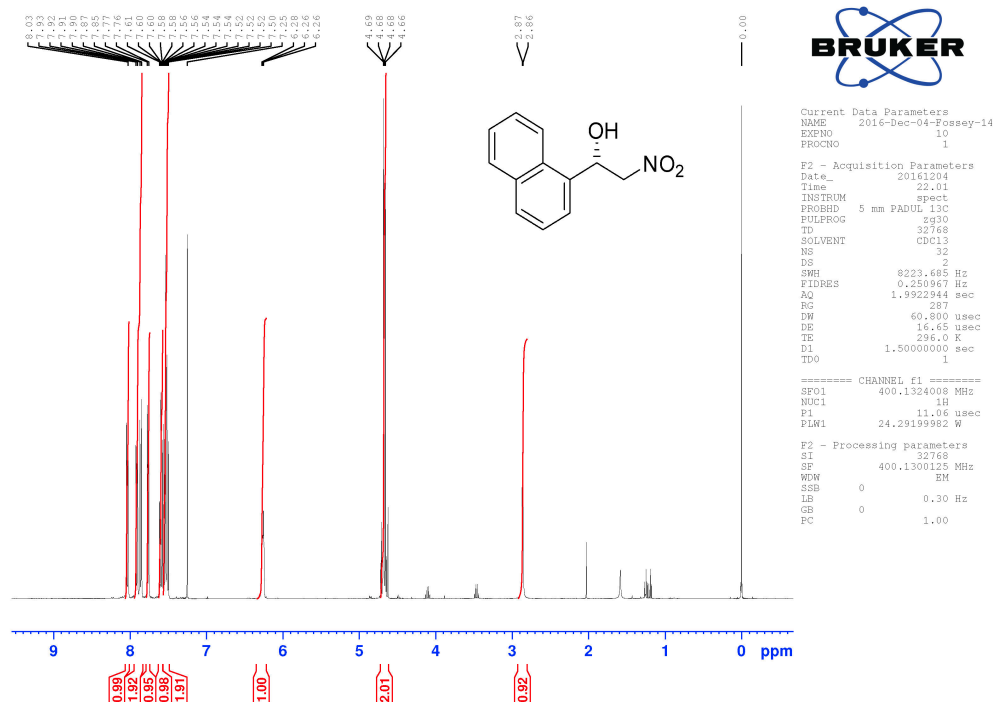
Proton NMR Spectrum of (rac)-6f



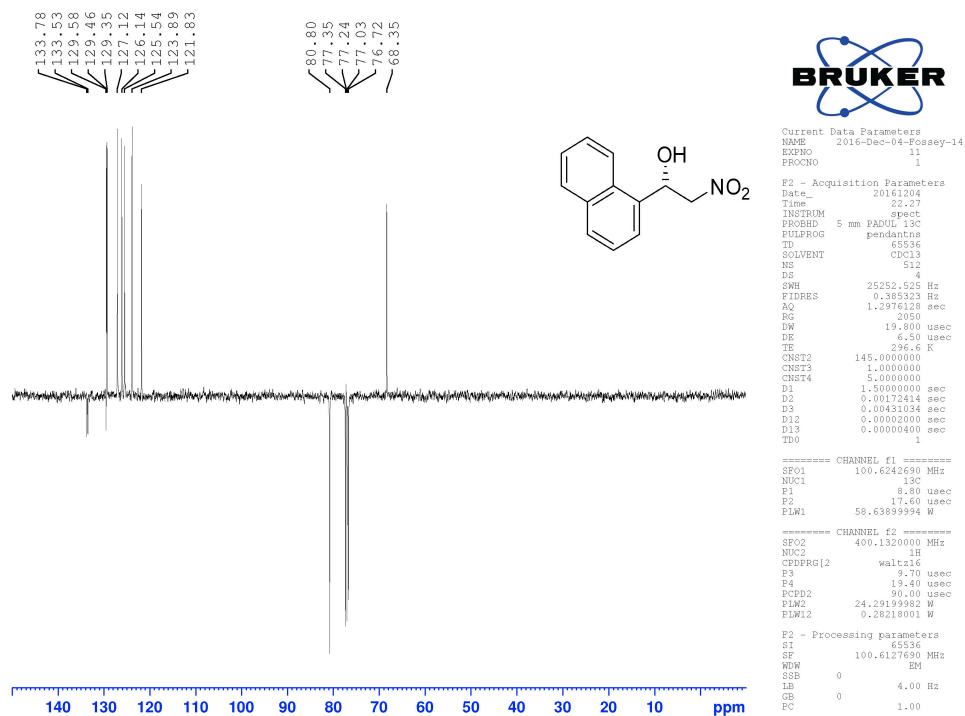
Carbon NMR Spectrum of (rac)-6f



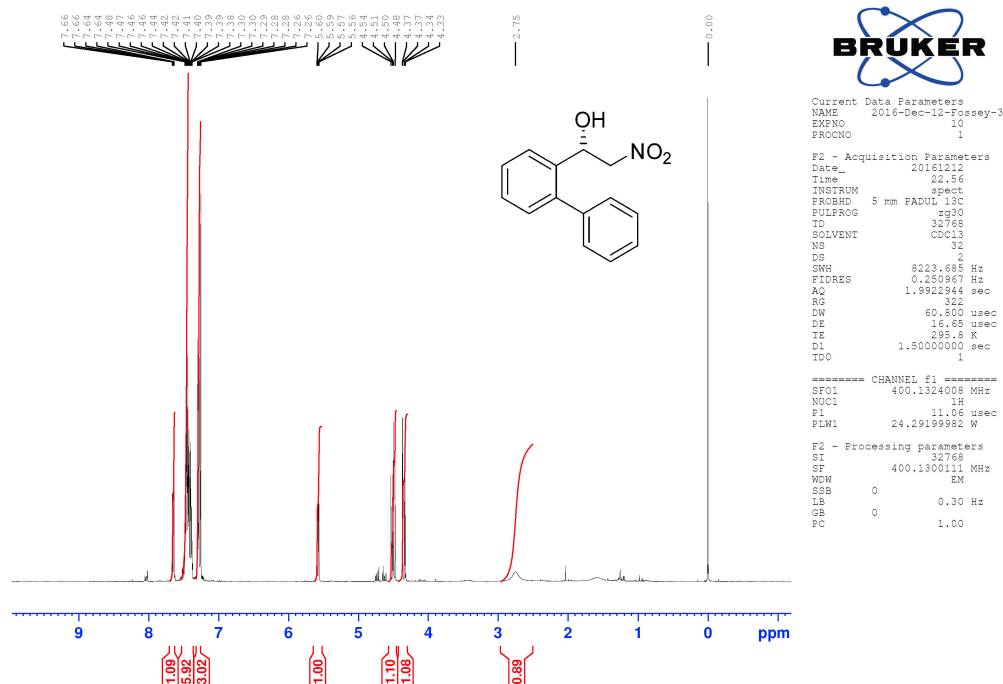
Proton NMR Spectrum of (rac)-6g



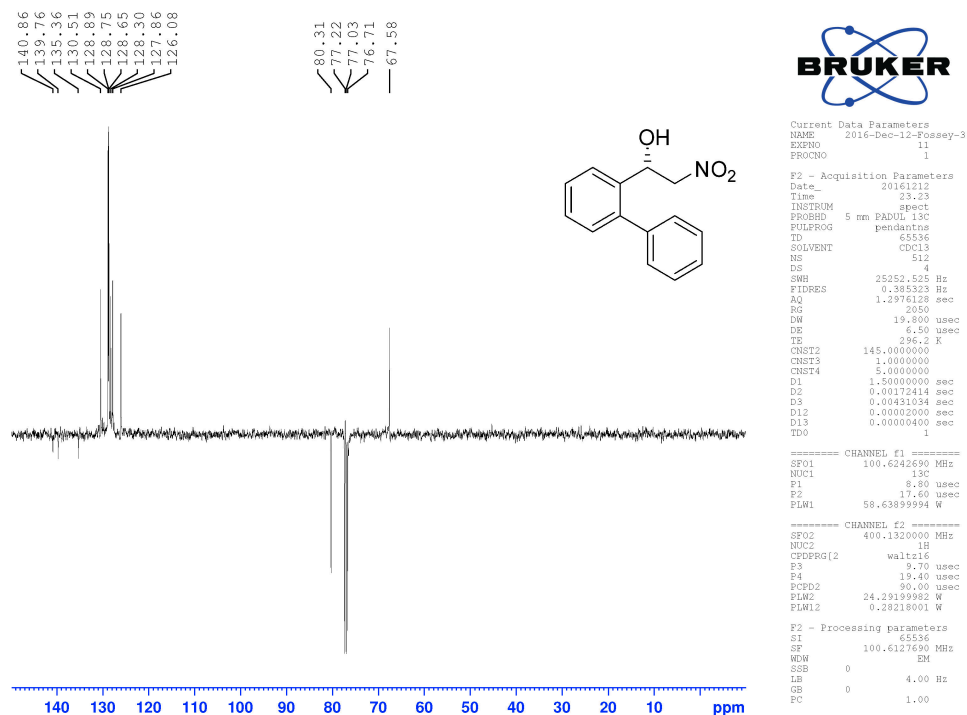
Carbon NMR Spectrum of (rac)-6g



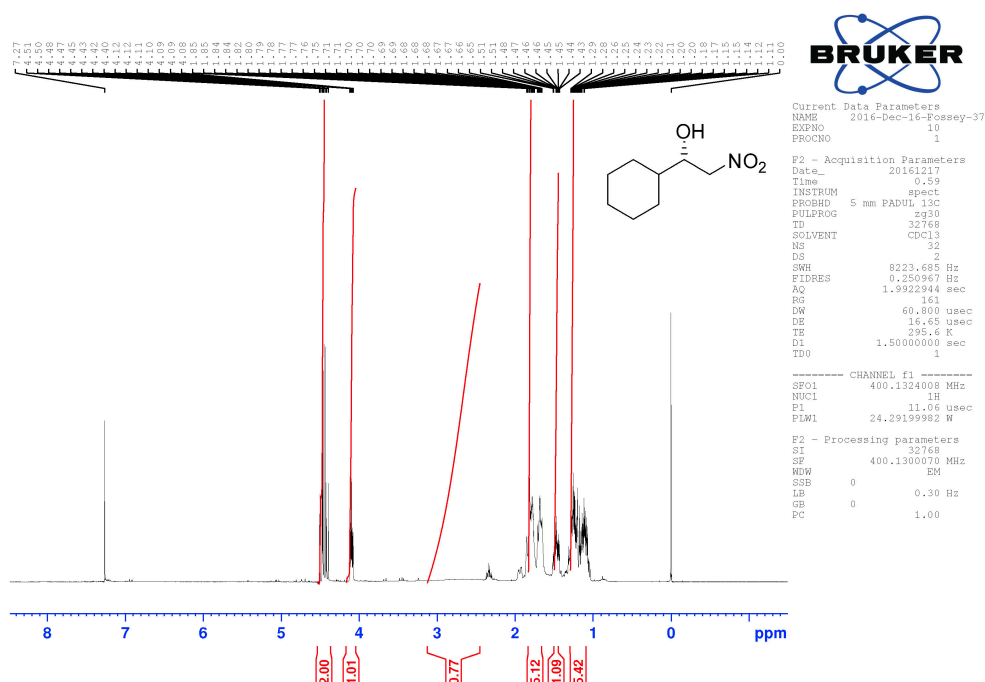
Proton NMR Spectrum of (rac)-6h



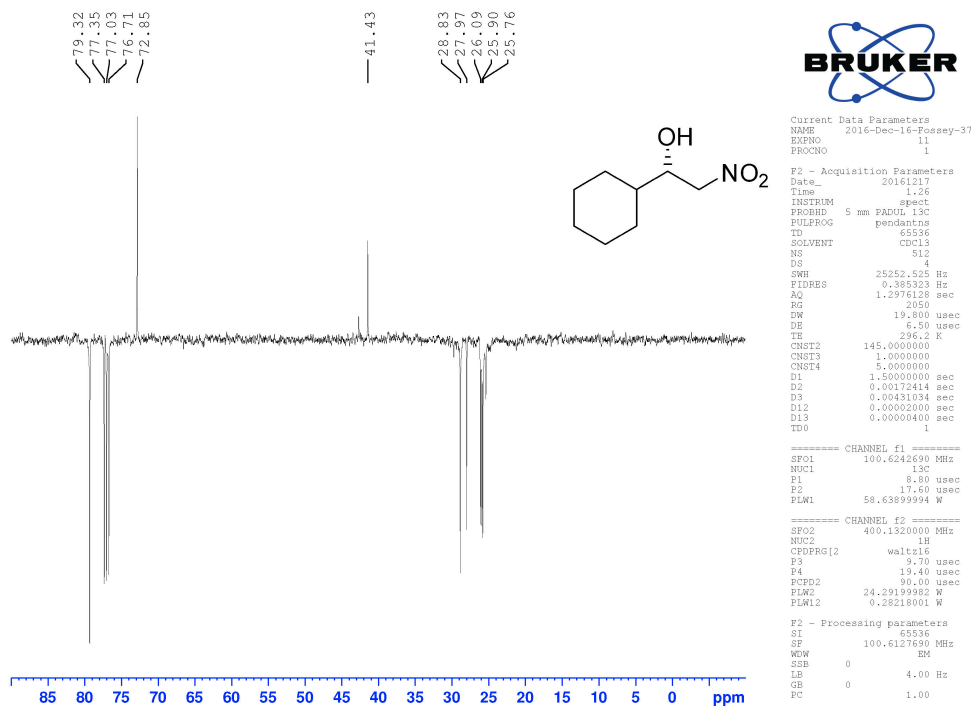
Carbon NMR Spectrum of (rac)-6h



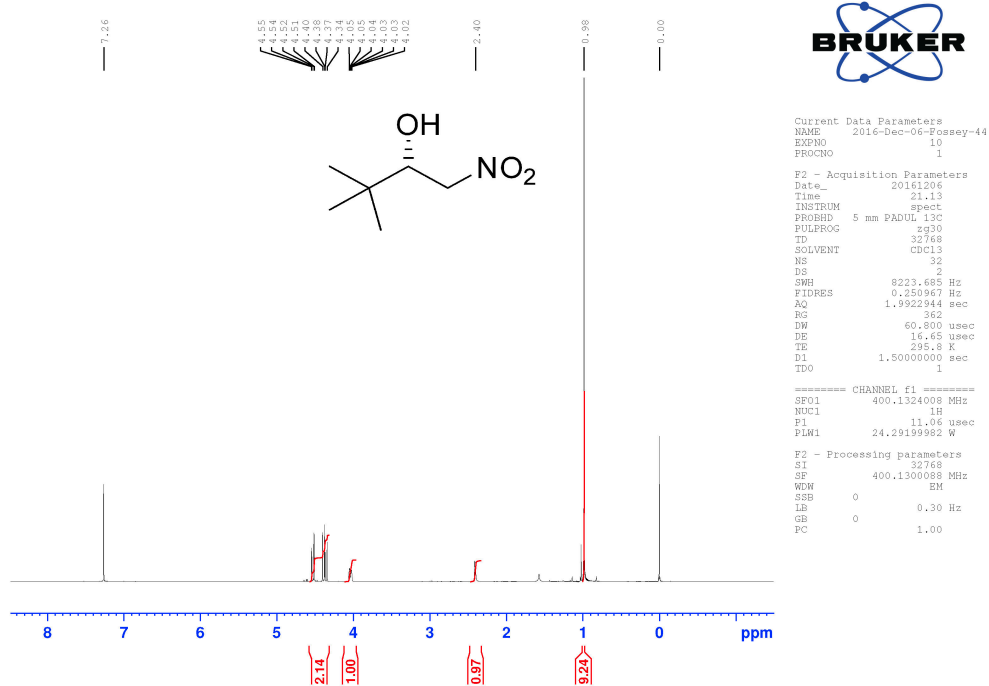
Proton NMR Spectrum of (rac)-6i



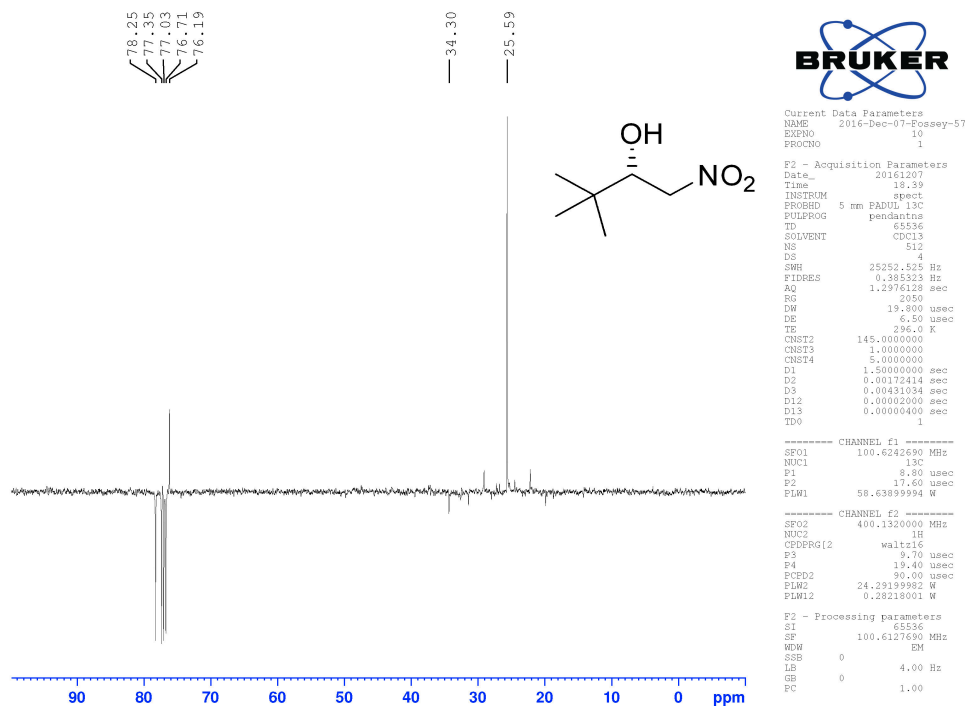
Carbon NMR Spectrum of (rac)-6i



Proton NMR Spectrum of (rac)-6j



Carbon NMR Spectrum of (rac)-6j



Computational data tables

This section includes the geometry of all structures reported in the main text. In addition, where alternative conformations have been explored and found to be higher in energy, those structures are included here. Where complexes of alternative ligand geometries led to dissociation from the metal, they were high in energy and were terminated before completion and are therefore not included.

Acetate anion

SCF energy= -228.401395147
Zero-point correction= 0.049059
Thermal correction to Energy= 0.053465
Thermal correction to Enthalpy= 0.054409
Thermal correction to Gibbs Free Energy= 0.021712
SCF energy+Solvation free energy= -228.492104536

Coordinates:

8 -0.693327 1.15978 -0.000879
6 -0.21917 0.001691 0.003895
8 -0.802185 -1.10401 -0.000955
6 1.3479 -0.05345 0.001292
1 1.72047 -1.07832 0.094554
1 1.74344 0.559525 0.820039
1 1.72783 0.383199 -0.931049

Benzaldehyde

SCF energy= -345.419894224
Zero-point correction= 0.111324
Thermal correction to Energy= 0.117589
Thermal correction to Enthalpy= 0.118533
Thermal correction to Gibbs Free Energy= 0.080818
SCF energy+Solvation free energy= -345.424933960

Coordinates:

6 -1.73279 -1.05617 0.000023
6 -0.361093 -1.29039 0.000012
6 0.528747 -0.216803 -0.00002
6 0.050211 1.09602 -0.000033
6 -1.31819 1.32903 -0.000012
6 -2.20815 0.25307 0.000013
1 -2.42858 -1.8891 0.000042
1 0.024576 -2.30768 0.000022
1 0.768526 1.91049 -0.000058
1 -1.69755 2.34606 -0.000019
1 -3.27817 0.438064 0.000028
6 1.98984 -0.470579 -0.000045
1 2.27908 -1.54279 -0.000262
8 2.83007 0.397482 0.000077

Nitromethane anion

SCF energy= -244.301524468

Zero-point correction= 0.036834
 Thermal correction to Energy= 0.040701
 Thermal correction to Enthalpy= 0.041645
 Thermal correction to Gibbs Free Energy= 0.010915
 SCF energy+Solvation free energy= -244.390635638

Coordinates:

6 -1.28536 -1.6e-05 0.000004
 1 -1.78911 0.953148 0.000065
 1 -1.78908 -0.953192 -0.000043
 7 0.046699 0.0 -0.000024
 8 0.68523 -1.10136 0.000013
 8 0.685199 1.10137 0.000002

Free Product 6b

SCF energy= -589.751417985
 Zero-point correction= 0.152302
 Thermal correction to Energy= 0.162524
 Thermal correction to Enthalpy= 0.163468
 Thermal correction to Gibbs Free Energy= 0.115151

Coordinates:

6 3.04121 -1.01636 0.326127
 6 1.69422 -1.16513 0.006065
 6 0.907717 -0.056499 -0.29918
 6 1.49886 1.20816 -0.293045
 6 2.84686 1.36565 0.022633
 6 3.6236 0.250775 0.337548
 1 3.64649 -1.8892 0.563815
 1 1.18569 -2.12546 -0.041346
 1 0.895726 2.07895 -0.552067
 1 3.2959 2.35693 0.019695
 1 4.67663 0.370305 0.581897
 6 -0.586049 -0.323276 -0.642301
 1 -0.829359 0.392425 -1.48327
 6 -1.3666 0.374092 0.599802
 1 -1.18373 -0.21774 1.49503
 1 -1.12303 1.43046 0.72232
 7 -2.79864 0.301254 0.30613
 8 -3.25874 1.13852 -0.466506
 8 -3.44913 -0.612177 0.786441
 8 -0.908717 -1.56759 -0.794294

Cu[IpC-(OAc)₂]

SCF energy= -1230.37463809
 Zero-point correction= 0.395809
 Thermal correction to Energy= 0.420540
 Thermal correction to Enthalpy= 0.421484
 Thermal correction to Gibbs Free Energy= 0.340814
 SCF energy+Solvation free energy= =
 SCF energy+Solvation free energy= =
 SCF energy+Solvation free energy= =
 SCF energy+Solvation free energy= =

SCF energy+Solvation free energy= =
SCF energy+Solvation free energy= =

Coordinates:

6 -1.41423 -2.5272 0.330615
1 -0.792093 -2.76275 1.20004
6 -0.508246 -2.32516 -0.89946
7 -2.15752 -1.30974 0.664631
1 -2.82522 -1.01661 -0.061399
7 -0.222381 -0.91116 -1.27692
29 -0.815472 0.274155 0.635542
8 -1.8809 1.6422 -0.184083
8 0.536724 1.48323 1.61086
1 -0.911655 -2.86261 -1.76981
6 -3.07967 1.53523 -0.644839
8 -3.73007 0.485797 -0.738538
6 -3.67967 2.84971 -1.11004
1 -3.03805 3.28708 -1.87998
1 -3.70405 3.55238 -0.272921
1 -4.68459 2.69491 -1.50174
6 -0.979846 -0.393605 -2.41381
1 -2.03961 -0.328464 -2.15311
1 -0.859484 -1.04269 -3.29555
1 -0.627793 0.611474 -2.66202
6 -2.88036 -1.41495 1.93555
1 -3.48887 -0.516406 2.06168
1 -2.15881 -1.48506 2.75526
1 -3.5359 -2.29482 1.96062
1 -2.10069 -3.36939 0.168056
6 1.00585 -2.57117 -0.741697
6 1.19382 -1.27096 -1.5472
1 1.3278 -2.44623 0.294424
1 1.4092 -3.48815 -1.17217
1 1.31227 -1.50265 -2.61852
6 2.24875 -0.282334 -1.12816
6 3.55508 -0.730461 -0.908621
6 1.96517 1.07494 -0.986426
6 4.56183 0.164129 -0.560798
1 3.7806 -1.78974 -1.0117
6 2.96893 1.97046 -0.619984
1 0.952673 1.44378 -1.13419
6 4.26902 1.52044 -0.413922
1 5.57222 -0.197564 -0.395215
1 2.7237 3.01906 -0.486206
1 5.05034 2.21891 -0.130697
6 1.10991 0.432573 2.00645
8 0.56646 -0.695205 1.75206
6 2.44319 0.482003 2.69135
1 2.51192 -0.300364 3.44892
1 2.61166 1.4668 3.12698
1 3.20767 0.29481 1.92807

Cu[1pC-(OAc)(O₂NCH₂)] – lowest energy conformation

SCF energy= -1246.27584727
Zero-point correction= 0.383170
Thermal correction to Energy= 0.406548
Thermal correction to Enthalpy= 0.407493
Thermal correction to Gibbs Free Energy= 0.329897
SCF energy+Solvation free energy= -1246.28830458

Coordinates:

6 1.36606 -2.51984 -0.408913
1 0.713633 -2.71835 -1.26638
6 0.503721 -2.34895 0.85684
7 2.11413 -1.30097 -0.724627
1 2.79712 -1.03149 -0.003446
7 0.230248 -0.943632 1.26956
29 0.786443 0.291312 -0.631599
8 1.87926 1.63218 0.200315
8 -0.557266 1.52543 -1.5142
1 0.938978 -2.90505 1.69949
6 3.08446 1.50185 0.63593
8 3.72724 0.444614 0.689601
6 3.70227 2.79408 1.13944
1 3.61047 3.56825 0.374057
1 4.74789 2.63944 1.4044
1 3.145 3.1368 2.01648
6 1.00704 -0.455737 2.40557
1 2.06331 -0.39253 2.12981
1 0.895757 -1.12133 3.27637
1 0.666929 0.546828 2.67936
6 2.81131 -1.37599 -2.01183
1 3.42072 -0.476483 -2.12592
1 2.07327 -1.4206 -2.81859
1 3.46233 -2.25753 -2.07288
1 2.04438 -3.3773 -0.299474
6 -1.01377 -2.59563 0.738333
6 -1.18758 -1.29527 1.54653
1 -1.36309 -2.47393 -0.289359
1 -1.40451 -3.51323 1.17905
1 -1.30634 -1.52206 2.61859
6 -2.23271 -0.299884 1.11729
6 -3.51919 -0.747855 0.804119
6 -1.95275 1.06366 1.04649
6 -4.51099 0.152502 0.430997
1 -3.74074 -1.81197 0.850739
6 -2.94089 1.96576 0.656805
1 -0.951436 1.42989 1.26127
6 -4.22175 1.51456 0.353989
1 -5.50656 -0.208364 0.190434
1 -2.69807 3.02083 0.579789
1 -4.99144 2.21868 0.052376
8 -0.612382 -0.643176 -1.72968
6 -2.39484 0.574691 -2.49311
1 -2.86782 -0.346771 -2.79193

1 -2.82847 1.55557 -2.60122
7 -1.23372 0.497825 -1.94576

Cu[1pC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1246.26960401
Zero-point correction= 0.383875
Thermal correction to Energy= 0.407899
Thermal correction to Enthalpy= 0.408843
Thermal correction to Gibbs Free Energy= 0.330061
SCF energy+Solvation free energy= -1246.28444419

Coordinates:

6 1.13227 -2.34399 -1.26628
1 0.519674 -2.01215 -2.1075
6 0.215216 -2.60344 -0.054257
7 2.09694 -1.27464 -0.995084
7 -0.019766 -1.44739 0.86116
29 0.918899 0.35594 -0.29981
8 2.0712 0.996688 1.11647
8 -0.278671 1.96376 -0.637229
1 0.561047 -3.47303 0.523008
6 3.06649 1.53438 0.488864
8 3.22008 1.43821 -0.734714
6 4.04614 2.30133 1.35305
1 4.33165 1.69964 2.21945
1 3.55296 3.20245 1.72905
1 4.92591 2.58216 0.774451
6 0.614815 -1.49434 2.17781
1 1.64596 -1.1418 2.12406
1 0.574045 -2.5083 2.60717
1 0.078073 -0.813894 2.84495
1 1.63887 -3.27621 -1.55467
6 -1.29699 -2.66792 -0.349558
6 -1.47707 -1.74854 0.870671
1 -1.54906 -2.14963 -1.27805
1 -1.77343 -3.64781 -0.308133
1 -1.71962 -2.34479 1.76522
6 -2.41675 -0.575748 0.774521
6 -3.67615 -0.75088 0.194338
6 -2.07092 0.675255 1.28225
6 -4.57827 0.305549 0.128473
1 -3.94946 -1.72376 -0.208848
6 -2.96718 1.73889 1.20255
1 -1.08572 0.839268 1.71088
6 -4.22371 1.55602 0.632773
1 -5.55417 0.156209 -0.323678
1 -2.67095 2.71321 1.5781
1 -4.92258 2.38501 0.574547
8 -0.42189 0.105207 -1.77028
6 -1.99997 1.72398 -2.1252
1 -2.47053 1.07256 -2.8437
1 -2.35656 2.70377 -1.85235
7 -0.938947 1.29503 -1.53745

1 2.42706 -0.86722 -1.86957
6 3.26316 -1.70531 -0.21837
1 3.93224 -0.853054 -0.098516
1 3.79453 -2.52408 -0.720897
1 2.94222 -2.05398 0.76536

Cu[1pC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1246.24344268
Zero-point correction= 0.383450
Thermal correction to Energy= 0.407915
Thermal correction to Enthalpy= 0.408859
Thermal correction to Gibbs Free Energy= 0.326021
SCF energy+Solvation free energy= =
SCF energy+Solvation free energy= =

Coordinates:

6 -0.808244 1.45652 -1.18966
7 -1.2024 1.62193 0.220163
29 1.90222 -0.025516 0.00109
8 1.4325 -1.74821 0.793651
8 2.69328 1.04618 1.52327
6 2.52044 -2.36274 0.479255
8 3.39115 -1.81539 -0.22226
6 2.68665 -3.77056 0.999003
1 1.81393 -4.36931 0.725913
1 2.73379 -3.74144 2.091
1 3.59654 -4.21843 0.600955
6 -0.773504 0.73611 1.2796
1 0.263624 0.956135 1.56005
1 -0.868887 -0.340157 1.05879
1 -1.3824 0.939896 2.16597
6 -2.19011 2.03104 -1.58058
6 -2.63529 1.76801 -0.126186
1 -2.14671 3.09682 -1.8073
1 -2.73573 1.51742 -2.37452
8 2.48359 1.79829 -0.511317
6 3.45433 3.15674 1.05626
1 3.5744 3.91077 0.29526
1 3.76485 3.25806 2.08373
7 2.90257 2.04734 0.712118
1 -3.0811 2.63185 0.38325
6 -3.51994 0.563909 0.140724
6 -4.12697 0.459376 1.39704
6 -3.72862 -0.469132 -0.777084
6 -4.90242 -0.644879 1.73554
1 -3.98986 1.26239 2.11795
6 -4.50659 -1.57649 -0.445615
1 -3.29473 -0.41608 -1.77131
6 -5.09245 -1.67052 0.812944
1 -5.36166 -0.703202 2.71757
1 -4.65817 -2.36422 -1.17726
1 -5.6982 -2.53331 1.07113
6 -0.558934 0.032284 -1.71043

1 -0.995263 -0.073601 -2.71606
1 -1.03487 -0.715846 -1.06767
7 0.878188 -0.303448 -1.77801
1 0.056299 2.08082 -1.45537
6 1.09157 -1.65185 -2.32947
1 2.16209 -1.84427 -2.40645
1 0.609785 -1.76005 -3.30879
1 0.660183 -2.37115 -1.62966
1 1.33532 0.382211 -2.38339

Cu[1pC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1246.24383978
Zero-point correction= 0.383476
Thermal correction to Energy= 0.407923
Thermal correction to Enthalpy= 0.408867
Thermal correction to Gibbs Free Energy= 0.326315
SCF energy+Solvation free energy= -1246.25866679

Coordinates:

6 -0.756846 1.41262 -1.13013
7 -1.1827 1.52951 0.277092
29 1.88615 -0.108338 0.150997
8 1.50968 -1.88049 0.869296
8 2.74533 0.843685 1.69543
6 2.39086 -2.55927 0.220677
8 3.08991 -2.04 -0.669367
6 2.54949 -4.0121 0.604409
1 1.57064 -4.47148 0.755393
1 3.08765 -4.06162 1.55573
1 3.11715 -4.54682 -0.156735
6 -0.799597 0.596332 1.31242
1 0.219732 0.808833 1.66064
1 -0.871497 -0.469556 1.03673
1 -1.45412 0.749517 2.176
6 -2.1167 2.02823 -1.53238
6 -2.60212 1.73101 -0.097169
1 -2.04915 3.09866 -1.72921
1 -2.65395 1.54682 -2.35204
8 2.45774 1.74617 -0.265649
6 3.45822 2.99824 1.3718
1 3.53941 3.81289 0.670326
1 3.79995 3.02369 2.39405
7 2.91301 1.9102 0.957501
1 -3.03057 2.59332 0.429722
6 -3.53727 0.553356 0.110911
6 -4.17467 0.431967 1.35068
6 -3.77263 -0.436473 -0.847451
6 -5.00403 -0.64796 1.63501
1 -4.02017 1.2043 2.10102
6 -4.60472 -1.51907 -0.570487
1 -3.31795 -0.366229 -1.83124
6 -5.21945 -1.63139 0.672808
1 -5.48583 -0.719659 2.60527

1 -4.77565 -2.2736 -1.3323
 1 -5.86767 -2.4749 0.888361
 6 -0.53167 0.000605 -1.68866
 1 -0.868302 -0.033065 -2.73655
 1 -1.12137 -0.728989 -1.12575
 7 0.882466 -0.420834 -1.62413
 1 0.938092 -1.43685 -1.68879
 6 1.71025 0.141567 -2.70611
 1 1.27333 -0.076546 -3.68844
 1 2.70621 -0.300394 -2.63501
 1 1.79497 1.22222 -2.57722
 1 0.125101 2.02814 -1.34771

Cu[1pC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1246.26804547
 Zero-point correction= 0.384330
 Thermal correction to Energy= 0.408119
 Thermal correction to Enthalpy= 0.409063
 Thermal correction to Gibbs Free Energy= 0.330818
 SCF energy+Solvation free energy= =
 SCF energy+Solvation free energy= =
 SCF energy+Solvation free energy= =
 SCF energy+Solvation free energy= =

Coordinates:

6 1.50853 -2.50187 0.135786
 1 0.884913 -2.90719 -0.66738
 6 0.611395 -2.08087 1.31549
 7 2.22398 -1.35356 -0.424683
 1 2.86097 -0.900956 0.238589
 7 0.292907 -0.627548 1.39988
 29 0.850522 0.167448 -0.729901
 8 1.69528 1.79286 -0.144466
 8 -0.557608 1.10147 -1.89348
 1 1.03762 -2.42247 2.27004
 8 3.62666 0.822724 0.428376
 6 3.23652 2.98779 0.963326
 1 2.54701 3.81272 0.896641
 1 4.21473 3.03789 1.41256
 6 1.05521 0.139985 2.3818
 1 2.11317 0.148993 2.10169
 1 0.949685 -0.292012 3.3893
 1 0.70155 1.17447 2.39508
 6 2.97418 -1.67697 -1.64186
 1 3.55376 -0.796568 -1.9271
 1 2.26938 -1.92941 -2.44008
 1 3.65678 -2.52269 -1.48857
 1 2.21311 -3.28542 0.44676
 6 -0.89685 -2.38816 1.23248
 6 -1.10874 -0.957165 1.76398
 1 -1.23115 -2.48196 0.196516
 1 -1.27313 -3.2091 1.8436
 1 -1.20655 -0.97296 2.8622

6 -2.19755 -0.102211 1.1739
 6 -3.4944 -0.620194 1.09346
 6 -1.95657 1.19807 0.73438
 6 -4.53473 0.150918 0.586607
 1 -3.68539 -1.63687 1.43061
 6 -2.99582 1.96627 0.210117
 1 -0.951307 1.61344 0.768895
 6 -4.28562 1.44928 0.141113
 1 -5.53706 -0.262837 0.529554
 1 -2.78616 2.96717 -0.153248
 1 -5.09328 2.05011 -0.265367
 6 -1.08861 -0.028344 -2.06752
 8 -0.48261 -1.06239 -1.62519
 6 -2.43795 -0.168477 -2.70625
 1 -2.46564 -1.05568 -3.34132
 1 -2.68758 0.728261 -3.27294
 1 -3.16939 -0.297775 -1.8998
 7 2.88756 1.85815 0.427391

Cu[1pC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1246.26725131
 Zero-point correction= 0.383840
 Thermal correction to Energy= 0.407856
 Thermal correction to Enthalpy= 0.408801
 Thermal correction to Gibbs Free Energy= 0.329848
 SCF energy+Solvation free energy= -1246.28161774

Coordinates:

6 1.2313 -2.26758 -1.33289
 1 0.653587 -1.91512 -2.18969
 6 0.261209 -2.56104 -0.172384
 7 2.17824 -1.20133 -0.9966
 7 -0.021778 -1.44184 0.776549
 29 1.01328 0.418436 -0.285883
 8 2.11725 0.888391 1.26459
 8 -0.271959 2.01635 -0.502587
 1 0.577618 -3.45128 0.390786
 8 3.10403 1.51313 -0.600176
 6 4.01915 2.11683 1.40029
 1 3.91252 2.07405 2.47145
 1 4.80979 2.63223 0.880217
 6 0.567896 -1.53983 2.11229
 1 1.60538 -1.20314 2.10522
 1 0.498817 -2.56713 2.50508
 1 0.016421 -0.875253 2.78373
 1 1.75484 -3.19045 -1.62086
 6 -1.2356 -2.61668 -0.536113
 6 -1.46935 -1.78601 0.735768
 1 -1.45016 -2.03264 -1.43453
 1 -1.70628 -3.59885 -0.587293
 1 -1.70321 -2.45395 1.58139
 6 -2.45781 -0.651468 0.711557
 6 -3.73057 -0.869369 0.174692

6 -2.15327 0.596425 1.25129
 6 -4.68567 0.142085 0.184756
 1 -3.9712 -1.83979 -0.254426
 6 -3.10431 1.61534 1.24951
 1 -1.15906 0.794259 1.64261
 6 -4.3731 1.38947 0.724723
 1 -5.6701 -0.038984 -0.236146
 1 -2.84113 2.58945 1.64926
 1 -5.1131 2.18391 0.72493
 6 -0.803918 1.38178 -1.45096
 8 -0.293997 0.263903 -1.80763
 6 -2.05297 1.87223 -2.12174
 1 -1.97843 1.73034 -3.20181
 1 -2.23357 2.91878 -1.87745
 1 -2.88771 1.26575 -1.7516
 7 3.11347 1.53572 0.678395
 6 3.32181 -1.63395 -0.188597
 1 2.96779 -2.02778 0.766077
 1 3.96337 -0.771298 -0.003774
 1 3.89473 -2.41958 -0.698284
 1 2.53318 -0.76959 -1.84932

Cu[1pC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1246.24231877
 Zero-point correction= 0.383133
 Thermal correction to Energy= 0.407535
 Thermal correction to Enthalpy= 0.408480
 Thermal correction to Gibbs Free Energy= 0.326071
 SCF energy+Solvation free energy= =
 SCF energy+Solvation free energy= =

Coordinates:

6 -0.737081 1.37174 -1.20203
 7 -1.13237 1.56855 0.205526
 29 1.92557 -0.100655 0.027075
 8 1.38074 -1.76503 0.924572
 8 2.67979 1.14411 1.49309
 8 3.31474 -1.83065 -0.111272
 6 2.59505 -3.68802 1.00829
 1 1.8128 -4.10853 1.61864
 1 3.4992 -4.20093 0.723934
 6 -0.764299 0.664506 1.27305
 1 0.273699 0.840435 1.5807
 1 -0.899616 -0.406614 1.04819
 1 -1.38419 0.892183 2.14572
 6 -2.08476 2.01072 -1.60912
 6 -2.55342 1.78887 -0.15509
 1 -1.98559 3.06985 -1.84925
 1 -2.65067 1.51508 -2.40042
 6 2.8921 1.97884 0.573733
 8 2.55402 1.67197 -0.62083
 6 3.54823 3.30158 0.845026

1 4.5669 3.27344 0.447359
 1 3.58101 3.49653 1.91628
 1 3.00742 4.09329 0.322923
 7 2.45713 -2.46549 0.61298
 1 -2.95453 2.6815 0.341512
 6 -3.50557 0.638256 0.115559
 6 -4.13943 0.58422 1.36159
 6 -3.75151 -0.396447 -0.791113
 6 -4.97652 -0.473875 1.70144
 1 -3.97421 1.39021 2.0733
 6 -4.59066 -1.45744 -0.45832
 1 -3.29822 -0.380711 -1.77784
 6 -5.20219 -1.50274 0.79061
 1 -5.45573 -0.493028 2.67548
 1 -4.76919 -2.24754 -1.18137
 1 -5.85525 -2.33 1.0499
 6 -0.551621 -0.068503 -1.70037
 1 -0.967799 -0.166807 -2.71527
 1 -1.08442 -0.779812 -1.0609
 7 0.866504 -0.47795 -1.7199
 1 0.158822 1.94924 -1.46803
 1 1.36397 0.134485 -2.37002
 6 1.02363 -1.87773 -2.14892
 1 2.08617 -2.1221 -2.1877
 1 0.550899 -2.05053 -3.12338
 1 0.552101 -2.51354 -1.39561

Cu[1pC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1246.24111109
 Zero-point correction= 0.383228
 Thermal correction to Energy= 0.407685
 Thermal correction to Enthalpy= 0.408629
 Thermal correction to Gibbs Free Energy= 0.326587
 SCF energy+Solvation free energy= -1246.25533406

Coordinates:

6 -0.724164 1.31229 -1.14158
 7 -1.146 1.45059 0.266725
 29 1.90083 -0.168406 0.13235
 8 1.45957 -1.91695 0.926561
 8 2.67793 0.942176 1.66791
 8 3.17997 -1.93542 -0.439234
 6 2.67188 -3.83271 0.729227
 1 2.00738 -4.2786 1.45085
 1 3.5086 -4.33143 0.268101
 6 -0.811634 0.497427 1.30172
 1 0.211898 0.663602 1.66179
 1 -0.927065 -0.562995 1.02042
 1 -1.46641 0.675522 2.16028
 6 -2.05802 1.97792 -1.54852
 6 -2.55567 1.71221 -0.111253
 1 -1.94774 3.04298 -1.7551
 1 -2.61408 1.51116 -2.36416

6 2.83021 1.87619 0.833378
 8 2.46543 1.6776 -0.373946
 6 3.43574 3.19235 1.22489
 1 4.40281 3.29775 0.725333
 1 3.57085 3.24315 2.3045
 1 2.79225 4.00419 0.878709
 7 2.46358 -2.59967 0.402903
 1 -2.94574 2.59589 0.409842
 6 -3.54133 0.577667 0.102611
 6 -4.19701 0.497125 1.33605
 6 -3.8049 -0.413979 -0.846342
 6 -5.07169 -0.545995 1.62328
 1 -4.02066 1.27191 2.07908
 6 -4.68171 -1.45972 -0.566358
 1 -3.3371 -0.37416 -1.82563
 6 -5.31445 -1.53233 0.670778
 1 -5.56754 -0.586131 2.5883
 1 -4.87313 -2.21635 -1.3212
 1 -5.99814 -2.34685 0.888208
 6 -0.546503 -0.110727 -1.68722
 1 -0.879425 -0.143981 -2.73615
 1 -1.1626 -0.815036 -1.12102
 7 0.853676 -0.574313 -1.60896
 1 0.873449 -1.59363 -1.59552
 6 1.68566 -0.108789 -2.7314
 1 1.24349 -0.392695 -3.69439
 1 2.67618 -0.557845 -2.63063
 1 1.78642 0.976881 -2.67941
 1 0.18167 1.89135 -1.3609

TS-IpC-II – lowest energy conformation

SCF energy= -1591.69252316
 Zero-point correction= 0.496793
 Thermal correction to Energy= 0.527769
 Thermal correction to Enthalpy= 0.528714
 Thermal correction to Gibbs Free Energy= 0.432821
 SCF energy+Solvation free energy= -1591.70766979

Coordinates:

6 3.12232 -1.38501 -1.24864
 1 2.36015 -1.48797 -2.03075
 6 2.73998 -2.24114 -0.045305
 7 3.12635 0.026917 -0.864983
 1 3.76095 0.235013 -0.086515
 7 1.64793 -1.63142 0.781382
 29 1.29106 0.383339 -0.038505
 8 1.75407 2.25309 0.46335
 6 -0.741334 2.16822 -1.81775
 7 -0.714729 0.858653 -2.07346
 8 0.423819 0.232667 -1.9505
 8 -1.73612 0.205691 -2.3297
 1 3.61375 -2.4689 0.579734
 6 2.84476 2.45676 1.11887

8 3.68392 1.5882 1.39504
 6 3.0612 3.89596 1.55385
 1 4.01965 4.00254 2.06098
 1 2.25043 4.19713 2.22324
 1 3.02176 4.55226 0.680166
 6 2.02698 -1.20984 2.13926
 1 2.69611 -0.343053 2.09844
 1 2.52548 -2.0279 2.68031
 1 1.11497 -0.930028 2.6754
 6 3.40988 0.937608 -1.98134
 1 3.38759 1.96171 -1.60368
 1 2.62186 0.820722 -2.72839
 1 4.08848 -1.70377 -1.66437
 6 1.85125 -3.46399 -0.328622
 6 0.897678 -2.93675 0.764552
 1 1.3997 -3.42912 -1.32322
 1 2.28343 -4.4493 -0.154086
 1 1.09244 -3.4504 1.71606
 6 -1.08649 1.68171 0.526442
 8 -0.525465 0.571052 0.679236
 1 0.213916 2.66156 -1.71111
 1 -1.66145 2.67899 -2.054
 6 -0.579974 -2.94006 0.499421
 6 -1.42925 -3.63248 1.36472
 6 -1.11024 -2.33554 -0.642854
 6 -2.78895 -3.74354 1.08598
 1 -1.02037 -4.09669 2.25943
 6 -2.46857 -2.44957 -0.924558
 1 -0.484005 -1.7452 -1.30842
 6 -3.30801 -3.15943 -0.066457
 1 -3.4378 -4.28897 1.76452
 1 -2.86073 -1.95315 -1.80621
 1 -4.36672 -3.25072 -0.292149
 6 -2.55134 1.77772 0.487328
 6 -3.17267 3.0294 0.542851
 6 -3.31411 0.612612 0.382654
 6 -4.55722 3.11537 0.499948
 1 -2.56452 3.92876 0.613577
 6 -4.70057 0.704057 0.336498
 1 -2.80585 -0.344243 0.341758
 6 -5.32052 1.95047 0.394475
 1 -5.04526 4.08364 0.547519
 1 -5.29659 -0.199733 0.253178
 1 -6.40365 2.01904 0.357353
 1 -0.501634 2.60078 0.648472
 1 4.3895 0.730325 -2.4284

Product arising from TS-1pC-II – lowest energy conformation

SCF energy=	-1591.71873258
Zero-point correction=	0.500883
Thermal correction to Energy=	0.531389
Thermal correction to Enthalpy=	0.532333
Thermal correction to Gibbs Free Energy=	0.438749

Coordinates:

6 3.03866 -1.89242 -0.762397
1 2.33675 -2.2693 -1.51571
6 2.58521 -2.33017 0.630692
7 3.03203 -0.432422 -0.859384
1 3.69076 -0.014808 -0.190044
7 1.44696 -1.4975 1.12939
29 1.32302 0.348098 0.004467
8 2.09595 2.20216 -0.103615
6 -0.762332 2.39382 -1.00446
7 -0.831014 1.24337 -1.93427
8 0.200054 0.575555 -2.08059
8 -1.87987 0.978482 -2.47187
1 3.42405 -2.32164 1.3361
6 3.1287 2.32567 0.651013
8 3.70647 1.37726 1.21082
6 3.63274 3.7454 0.833615
1 4.55099 3.75451 1.41998
1 2.86283 4.33334 1.34152
1 3.80136 4.20494 -0.143741
6 1.65169 -0.904584 2.46291
1 2.44902 -0.156683 2.40595
1 1.92118 -1.67668 3.19889
1 0.719177 -0.41364 2.75181
6 3.3054 0.073065 -2.20963
1 3.2481 1.16297 -2.18399
1 2.53508 -0.296943 -2.89138
1 4.02517 -2.31758 -0.995895
6 1.70669 -3.59554 0.66672
6 0.542972 -2.69913 1.1711
1 1.53015 -4.05306 -0.309775
1 2.02159 -4.36339 1.37429
1 0.276597 -2.92199 2.21021
6 -1.04691 1.88047 0.455512
8 -0.341826 0.75384 0.765204
1 0.254761 2.77735 -1.06812
1 -1.51415 3.10805 -1.33738
6 -0.709913 -2.64113 0.343976
6 -1.9052 -3.15107 0.851458
6 -0.69588 -2.11848 -0.949817
6 -3.06524 -3.13905 0.07805
1 -1.93189 -3.5535 1.8612
6 -1.85552 -2.07577 -1.71519
1 0.220228 -1.70767 -1.36383
6 -3.04439 -2.59309 -1.20191
1 -3.98869 -3.53925 0.485991
1 -1.83049 -1.61481 -2.69667
1 -3.95332 -2.55661 -1.79401
6 -2.54659 1.66735 0.620133
6 -3.41214 2.75702 0.726985
6 -3.06795 0.376833 0.641981
6 -4.78391 2.56201 0.848539
1 -3.00739 3.76833 0.724571

6 -4.44167 0.179166 0.761306
1 -2.37803 -0.458146 0.578979
6 -5.30296 1.26819 0.864392
1 -5.44798 3.41696 0.93616
1 -4.83655 -0.8332 0.77429
1 -6.3734 1.11269 0.961355
1 -0.75584 2.75461 1.07049
1 4.29164 -0.243608 -2.57036

TS-IpC-I – lowest energy conformation

SCF energy= -1591.69250351
Zero-point correction= 0.497680
Thermal correction to Energy= 0.528136
Thermal correction to Enthalpy= 0.529080
Thermal correction to Gibbs Free Energy= 0.435249
SCF energy+Solvation free energy= -1591.70610939

Coordinates:

6 -1.54062 -1.95537 -2.15991
1 -1.30576 -1.10544 -2.80563
6 -2.70469 -1.57505 -1.22632
7 -0.320307 -2.25892 -1.41028
1 -0.410571 -3.11426 -0.841589
7 -2.32271 -1.08015 0.131479
29 -0.01405 -0.826781 0.028807
8 0.774695 -2.06212 1.31025
6 0.528032 2.57563 -0.881356
7 0.567319 1.41237 -1.55752
8 1.54034 1.04971 -2.22371
8 -0.415691 0.589406 -1.3537
1 -3.41407 -2.40849 -1.12807
6 0.677772 -3.34385 1.397
8 -0.00068 -4.07406 0.662027
6 1.47913 -3.94899 2.53619
1 1.40288 -5.0359 2.52102
1 1.10085 -3.56134 3.48626
1 2.52439 -3.63954 2.45425
6 -2.57436 -2.02537 1.21912
1 -1.9514 -2.91399 1.07969
1 -3.63382 -2.32641 1.24836
1 -2.31016 -1.56721 2.17681
6 0.861293 -2.3693 -2.27585
1 1.71058 -2.68671 -1.66449
1 1.07918 -1.38612 -2.70437
1 -1.8237 -2.80414 -2.79709
6 -3.42225 -0.241488 -1.50901
6 -3.3078 0.03581 -0.00068
1 -2.7959 0.435276 -2.0944
1 -4.42758 -0.297111 -1.92784
1 -4.23928 -0.250299 0.513716
6 1.30861 1.64573 0.939003
8 0.53135 0.690371 1.19132
1 1.26242 3.30612 -1.19002

1 -0.442618 2.85294 -0.492709
 6 -2.8868 1.40685 0.460924
 6 -2.15428 1.57713 1.6346
 6 -3.27378 2.53547 -0.264668
 6 -1.80549 2.85258 2.0717
 1 -1.82287 0.710256 2.19682
 6 -2.93661 3.81353 0.17478
 1 -3.84076 2.41442 -1.18448
 6 -2.19858 3.97545 1.34576
 1 -1.22615 2.96535 2.98371
 1 -3.24391 4.68124 -0.400975
 1 -1.93088 4.97005 1.68923
 6 2.70466 1.42261 0.483694
 6 3.54748 2.51152 0.242535
 6 3.18562 0.121467 0.321192
 6 4.85224 2.30658 -0.180369
 1 3.16829 3.52189 0.382517
 6 4.49637 -0.081115 -0.105087
 1 2.55314 -0.723832 0.584151
 6 5.32574 1.0056 -0.361613
 1 5.5028 3.15428 -0.370879
 1 4.87306 -1.09189 -0.227699
 1 6.34636 0.843389 -0.694537
 1 1.11482 2.6037 1.44613
 1 0.707695 -3.10179 -3.07828

Product arising from TS-1pC-I – lowest energy conformation

SCF energy=	-1591.71980564
Zero-point correction=	0.500228
Thermal correction to Energy=	0.530850
Thermal correction to Enthalpy=	0.531794
Thermal correction to Gibbs Free Energy=	0.437280

Coordinates:

6 -2.91354 -2.25758 -0.312533
 1 -3.3721 -1.47971 -0.935309
 6 -2.8877 -1.79695 1.14861
 7 -1.55271 -2.44463 -0.820035
 1 -1.05094 -3.17414 -0.301834
 7 -1.74001 -0.882714 1.42113
 29 -0.366132 -0.856578 -0.220454
 8 1.24821 -1.72188 -1.06548
 6 1.42318 1.19824 -1.66416
 7 0.075968 1.35809 -2.26618
 8 -0.712529 0.412931 -2.17645
 8 -0.203683 2.40906 -2.79765
 1 -2.88864 -2.65409 1.83197
 6 1.58183 -2.73333 -0.347673
 8 0.864534 -3.21093 0.550804
 6 2.95068 -3.31623 -0.6353
 1 3.0851 -4.26499 -0.1162
 1 3.70282 -2.59725 -0.292936

1 3.08667 -3.44352 -1.71187
 6 -0.836416 -1.28371 2.51043
 1 -0.27288 -2.17218 2.2118
 1 -1.40032 -1.48538 3.43328
 1 -0.137255 -0.457507 2.66844
 6 -1.49944 -2.731 -2.25861
 1 -0.452649 -2.83408 -2.54874
 1 -1.92612 -1.88367 -2.80207
 1 -3.52407 -3.165 -0.422747
 6 -3.88773 -0.678201 1.50954
 6 -2.67262 0.231809 1.81643
 1 -4.51182 -0.343954 0.67751
 1 -4.52306 -0.879425 2.37257
 1 -2.56992 0.420922 2.89106
 6 1.35474 1.44606 -0.119429
 8 0.412241 0.693624 0.512048
 1 1.72985 0.169283 -1.85375
 1 2.0605 1.92846 -2.16012
 6 -2.48518 1.51961 1.06857
 6 -1.96352 2.63289 1.72487
 6 -2.7645 1.60737 -0.295181
 6 -1.71963 3.81455 1.03118
 1 -1.72895 2.56739 2.78438
 6 -2.52262 2.78436 -0.994619
 1 -3.15211 0.744097 -0.832305
 6 -1.99611 3.89078 -0.331248
 1 -1.30555 4.67191 1.553
 1 -2.71611 2.82793 -2.06074
 1 -1.79583 4.80612 -0.879315
 1 -2.054 -3.64234 -2.51404
 6 2.77865 1.19358 0.375358
 6 3.06295 0.040936 1.1062
 6 3.81189 2.08574 0.084458
 6 4.36466 -0.220295 1.52855
 1 2.24847 -0.63437 1.35158
 6 5.11349 1.82688 0.504242
 1 3.59363 2.99906 -0.467098
 6 5.39396 0.668045 1.22489
 1 4.57538 -1.1194 2.10123
 1 5.90754 2.53142 0.27493
 1 6.40779 0.463772 1.5557
 1 1.12749 2.52234 0.006667

*Cu[**IqC**-(OAc)₂] – lowest energy conformation*

SCF energy= -1461.33379042
 Zero-point correction= 0.478461
 Thermal correction to Energy= 0.507431
 Thermal correction to Enthalpy= 0.508375
 Thermal correction to Gibbs Free Energy= 0.416922
 SCF energy+Solvation free energy= -1461.34705552

Coordinates:

6 -0.239081 -2.09796 1.94142
1 0.13604 -1.44437 2.73587
6 0.945059 -2.51757 1.04881
7 -1.23965 -1.32279 1.20463
1 -1.71854 -1.86289 0.4655
7 1.10269 -1.78815 -0.243337
29 -0.278392 0.092096 0.024135
8 -1.29415 -0.064003 -1.59937
8 0.574218 1.95544 -0.273144
1 0.920981 -3.59984 0.856941
6 -2.25823 -0.879612 -1.84579
8 -2.53699 -1.89616 -1.19053
6 -3.08747 -0.512627 -3.06208
1 -2.43557 -0.394682 -3.93163
1 -3.56721 0.452974 -2.87725
1 -3.84228 -1.27532 -3.2539
6 0.662815 -2.51803 -1.43137
1 1.16882 -3.49431 -1.49993
1 -0.418722 -2.66979 -1.39142
6 -2.25326 -0.705024 2.0841
1 -2.9118 -1.47318 2.51213
1 -1.71443 -0.222365 2.90726
1 -0.690824 -2.9798 2.41584
6 2.35593 -2.05544 1.46234
6 2.5732 -1.74041 -0.028131
1 2.3208 -1.14007 2.05723
1 3.01237 -2.79626 1.91997
1 3.03848 -2.6043 -0.530982
6 3.30542 -0.485582 -0.419622
6 4.5294 -0.201833 0.194484
6 2.82535 0.374551 -1.4054
6 5.26669 0.917562 -0.177135
1 4.90563 -0.86768 0.968167
6 3.55548 1.50636 -1.7679
1 1.86332 0.186401 -1.87581
6 4.77884 1.77618 -1.16252
1 6.21699 1.12416 0.305852
1 3.1551 2.18013 -2.51856
1 5.347 2.6559 -1.44838
6 1.14284 1.80784 0.84098
8 0.839314 0.793948 1.55859
6 2.20678 2.75649 1.30939
1 2.08193 2.96888 2.37312
1 2.18718 3.67378 0.721291
1 3.17403 2.26041 1.16965
1 0.894435 -1.93471 -2.32651
6 -3.04242 0.323067 1.3123
6 -2.55321 1.62854 1.21064
6 -4.1941 -0.031698 0.609671
6 -3.19466 2.56315 0.403042
1 -1.65381 1.90398 1.75935
6 -4.84342 0.904914 -0.189582
1 -4.56459 -1.0514 0.665331
6 -4.34169 2.20085 -0.29798

1 -2.79416 3.56809 0.317938
1 -5.73561 0.619162 -0.738533
1 -4.84421 2.92677 -0.92991

Cu[1qC-(OAc)₂] – higher energy conformation

SCF energy= -1461.33324018
Zero-point correction= 0.477998
Thermal correction to Energy= 0.506973
Thermal correction to Enthalpy= 0.507917
Thermal correction to Gibbs Free Energy= 0.417339
SCF energy+Solvation free energy= -1461.34645880

Coordinates:

6 1.01459 -0.447442 -2.44254
1 0.849724 0.634342 -2.41345
6 -0.342746 -1.17512 -2.46094
7 1.76933 -0.797727 -1.23829
1 1.94698 -1.80363 -1.13745
7 -0.865875 -1.6095 -1.13081
29 0.461419 -0.417391 0.363761
8 1.02199 -1.80406 1.57081
8 -0.367278 0.871847 1.74438
1 -0.307229 -2.03927 -3.14015
6 1.86183 -2.75697 1.35216
8 2.40258 -3.01751 0.268967
6 2.16404 -3.60347 2.57626
1 1.23244 -4.0229 2.9657
1 2.58429 -2.96842 3.3609
1 2.8612 -4.40273 2.32627
6 -0.745709 -3.03492 -0.833762
1 -1.19786 -3.6451 -1.63176
1 0.30745 -3.30668 -0.720394
6 3.06693 -0.103452 -1.09794
1 3.66354 -0.721354 -0.419988
1 3.58304 -0.059191 -2.0675
1 1.58613 -0.686298 -3.3506
6 -1.6176 -0.335336 -2.67646
6 -2.22534 -1.14468 -1.51423
1 -1.46625 0.709716 -2.39922
1 -2.10704 -0.418826 -3.6473
1 -2.80268 -1.99786 -1.90645
6 -3.03489 -0.432051 -0.463887
6 -4.04425 0.447815 -0.864726
6 -2.82286 -0.64588 0.896864
6 -4.83357 1.09752 0.078344
1 -4.20843 0.625647 -1.92531
6 -3.60223 0.016291 1.84425
1 -2.02505 -1.30546 1.23051
6 -4.61285 0.882691 1.43889
1 -5.61479 1.77782 -0.247347
1 -3.40429 -0.140452 2.89968
1 -5.22019 1.3963 2.17775
6 -0.6292 1.64741 0.783285

8 -0.270534 1.31128 -0.392618
 6 -1.39987 2.91719 0.993875
 1 -1.04342 3.6877 0.308172
 1 -1.31624 3.24528 2.03033
 1 -2.45213 2.70693 0.770416
 1 -1.25472 -3.25279 0.109601
 6 2.87495 1.27946 -0.526857
 6 2.73007 2.39213 -1.35567
 6 2.72959 1.43657 0.854072
 6 2.41329 3.63616 -0.818559
 1 2.85553 2.27865 -2.43039
 6 2.4073 2.67766 1.39468
 1 2.83792 0.572435 1.50937
 6 2.24145 3.7782 0.556578
 1 2.2948 4.49377 -1.47381
 1 2.27319 2.779 2.46701
 1 1.98716 4.74723 0.975572

Cu[1qC-(OAc)₂] – higher energy conformation

SCF energy= -1461.33100338
 Zero-point correction= 0.478233
 Thermal correction to Energy= 0.507418
 Thermal correction to Enthalpy= 0.508362
 Thermal correction to Gibbs Free Energy= 0.416040
 SCF energy+Solvation free energy= -1461.34374548

Coordinates:

6 -1.24761 1.36465 0.706732
 1 -0.924967 2.08921 -0.048594
 6 -0.132073 1.18573 1.75189
 7 -1.50518 0.107016 -0.000587
 1 -1.83586 -0.650965 0.61219
 7 0.771393 0.012606 1.55606
 29 0.315249 -0.641194 -0.633376
 8 -0.004832 -2.51991 -0.38292
 8 1.85275 -0.759433 -1.98938
 1 -0.55347 1.15662 2.7671
 6 -1.0499 -3.0923 0.104586
 8 -2.00525 -2.52002 0.650062
 6 -1.03927 -4.60523 -0.015931
 1 -0.171288 -5.00313 0.517223
 1 -0.928666 -4.88469 -1.06687
 1 -1.95611 -5.02805 0.393771
 6 0.519765 -1.13099 2.43032
 1 0.533059 -0.829161 3.4895
 1 -0.452306 -1.57315 2.19372
 6 -2.47065 0.227754 -1.10869
 1 -2.04874 0.920596 -1.84589
 1 -2.53823 -0.76475 -1.56797
 1 -2.16036 1.74723 1.17958
 6 1.09068 2.1203 1.67598
 6 1.9406 0.858169 1.91414
 1 1.2363 2.5111 0.666322

1 1.15844 2.91577 2.41868
 1 2.15566 0.742497 2.98913
 6 3.20881 0.668251 1.12619
 6 4.12737 1.7206 1.06326
 6 3.51249 -0.535025 0.492357
 6 5.33277 1.57009 0.385845
 1 3.89287 2.66411 1.55139
 6 4.71275 -0.682401 -0.202091
 1 2.80326 -1.35912 0.510975
 6 5.62808 0.364398 -0.250553
 1 6.03799 2.39486 0.347128
 1 4.92128 -1.61764 -0.711599
 1 6.56417 0.2469 -0.787592
 6 1.8694 0.501707 -2.00501
 8 0.967303 1.1335 -1.35873
 6 2.95797 1.26181 -2.70293
 1 2.54053 2.13029 -3.21614
 1 3.49164 0.614501 -3.39843
 1 3.65493 1.61831 -1.93588
 1 1.28775 -1.89235 2.26872
 6 -3.83745 0.686638 -0.657306
 6 -4.61076 -0.151766 0.152558
 6 -4.32609 1.94538 -1.00201
 6 -5.85667 0.269529 0.605771
 1 -4.22628 -1.13527 0.420012
 6 -5.57595 2.36658 -0.551555
 1 -3.72402 2.5987 -1.62935
 6 -6.34169 1.52879 0.253518
 1 -6.45444 -0.386658 1.23092
 1 -5.94903 3.34769 -0.829011
 1 -7.31532 1.85474 0.606052

Cu[1qC-(OAc)(O₂NCH₂)] – lowest energy conformation

SCF energy= -1477.23514498
 Zero-point correction= 0.466178
 Thermal correction to Energy= 0.494438
 Thermal correction to Enthalpy= 0.495382
 Thermal correction to Gibbs Free Energy= 0.406121

Coordinates:

6 -0.202837 -2.1486 1.89052
 1 0.190181 -1.51377 2.69245
 6 0.96487 -2.56614 0.974435
 7 -1.20316 -1.34802 1.18161
 1 -1.69637 -1.86821 0.437892
 7 1.10829 -1.81102 -0.302752
 29 -0.241708 0.081504 0.015594
 8 -1.27097 -0.034152 -1.60315
 8 0.577085 1.92974 -0.24251
 1 0.926052 -3.64439 0.764445
 6 -2.2458 -0.83588 -1.8523
 8 -2.5265 -1.8616 -1.21236
 6 -3.08882 -0.437194 -3.049

1 -3.57558 0.516983 -2.82633
 1 -3.83973 -1.19918 -3.25815
 1 -2.44712 -0.2835 -3.92039
 6 0.662151 -2.51691 -1.50163
 1 -0.418651 -2.67297 -1.45461
 1 1.17139 -3.48934 -1.59776
 1 0.881337 -1.91273 -2.38601
 6 -2.19857 -0.736009 2.08512
 1 -0.658388 -3.03264 2.35734
 6 2.38378 -2.12113 1.38043
 6 2.57988 -1.74283 -0.098547
 1 2.361 -1.23247 2.01537
 1 3.04656 -2.88099 1.7957
 1 3.06134 -2.57095 -0.643743
 6 3.26909 -0.447893 -0.435935
 6 4.44097 -0.106259 0.24465
 6 2.79069 0.400465 -1.43297
 6 5.13026 1.05931 -0.071218
 1 4.81446 -0.76235 1.02802
 6 3.47144 1.57747 -1.74002
 1 1.86678 0.165337 -1.95547
 6 4.64486 1.9055 -1.06744
 1 6.04106 1.31131 0.46356
 1 3.07291 2.24023 -2.50168
 1 5.17682 2.81978 -1.31268
 8 0.875781 0.732008 1.55572
 6 2.13962 2.62186 1.27978
 1 2.62616 2.40629 2.21722
 1 2.37598 3.45562 0.638677
 7 1.22956 1.80552 0.87821
 1 -2.85553 -1.50544 2.51359
 1 -1.64346 -0.267932 2.90601
 6 -2.99389 0.307393 1.34037
 6 -4.16523 -0.029693 0.661971
 6 -2.49509 1.6093 1.24062
 6 -4.82652 0.921218 -0.110072
 1 -4.54326 -1.04679 0.715858
 6 -3.14885 2.55818 0.460034
 1 -1.57531 1.86956 1.76261
 6 -4.3171 2.21452 -0.21483
 1 -5.73417 0.648932 -0.640128
 1 -2.74056 3.56002 0.375369
 1 -4.82977 2.95248 -0.824301

Cu[1qC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1477.23224607
 Zero-point correction= 0.466099
 Thermal correction to Energy= 0.494502
 Thermal correction to Enthalpy= 0.495446
 Thermal correction to Gibbs Free Energy= 0.405128

Coordinates:

6 1.23377 1.37233 -0.696812

1 0.889166 2.0886 0.057918
6 0.143773 1.19223 -1.76879
7 1.48419 0.110713 0.005737
1 1.81614 -0.645301 -0.608753
7 -0.76365 0.022852 -1.58274
29 -0.342656 -0.634305 0.621979
8 -0.025579 -2.51473 0.371527
8 -1.87676 -0.766472 1.93085
1 0.590477 1.15789 -2.77278
6 1.01981 -3.08739 -0.11363
8 1.98111 -2.51525 -0.649273
6 1.00299 -4.60134 -0.004606
1 0.884259 -4.88858 1.04336
1 1.92099 -5.02453 -0.411366
1 0.137223 -4.9919 -0.546776
6 -0.512298 -1.11623 -2.46128
1 0.458361 -1.56108 -2.22336
1 -0.522267 -0.811531 -3.51993
1 -1.2812 -1.87763 -2.30471
6 2.44153 0.221495 1.1218
1 2.49912 -0.773353 1.57736
1 2.01739 0.913051 1.85891
1 2.15375 1.76764 -1.14462
6 -1.07608 2.13272 -1.71952
6 -1.93463 0.871412 -1.93018
1 -1.22299 2.5516 -0.721527
1 -1.13686 2.90997 -2.4819
1 -2.17439 0.743434 -2.99828
6 -3.18132 0.6932 -1.10507
6 -4.05187 1.77412 -0.942066
6 -3.50512 -0.532281 -0.525508
6 -5.23088 1.63164 -0.218572
1 -3.80046 2.73471 -1.38671
6 -4.67864 -0.673144 0.212918
1 -2.82672 -1.3772 -0.616764
6 -5.54664 0.404314 0.362625
1 -5.90005 2.4789 -0.101875
1 -4.90311 -1.62748 0.678896
1 -6.46321 0.291968 0.934006
8 -0.994284 1.13185 1.32288
6 -2.92341 1.17165 2.55566
1 -2.90587 2.24839 2.50651
1 -3.69 0.587799 3.03865
7 -1.97061 0.534315 1.97342
6 3.81441 0.674224 0.683037
6 4.30826 1.92829 1.03737
6 4.58857 -0.164881 -0.125313
6 5.56379 2.34418 0.597862
1 3.70571 2.58211 1.66373
6 5.84019 0.251113 -0.567585
1 4.20002 -1.14465 -0.400428
6 6.33023 1.50572 -0.205867
1 5.94076 3.3216 0.882916
1 6.43843 -0.405656 -1.19167

1 7.30828 1.82744 -0.549943

Cu[1qC-(OAc)(O₂NCH₂)] – higher energy conformation

SCF energy= -1477.23386363

Zero-point correction= 0.465329

Thermal correction to Energy= 0.493755

Thermal correction to Enthalpy= 0.494699

Thermal correction to Gibbs Free Energy= 0.404916

Coordinates:

6 1.07747 -0.356924 -2.4029
1 0.912733 0.724225 -2.33966
6 -0.277857 -1.08343 -2.50311
7 1.78583 -0.75561 -1.18572
1 1.95063 -1.76716 -1.1144
7 -0.843067 -1.57328 -1.2116
29 0.423282 -0.444577 0.382494
8 0.951357 -1.88053 1.54749
8 -0.427644 0.741737 1.7917
1 -0.215256 -1.91597 -3.21849
6 1.7859 -2.83267 1.30849
8 2.35844 -3.0464 0.23124
6 2.02995 -3.75045 2.49333
1 2.3499 -3.15976 3.35538
1 2.78048 -4.50124 2.2475
1 1.0902 -4.23874 2.76747
6 -0.74773 -3.01198 -0.981391
1 0.299509 -3.30097 -0.855743
1 -1.18612 -3.5787 -1.81841
1 -1.28246 -3.26968 -0.062658
6 3.08566 -0.08289 -0.979425
1 3.63424 -0.707855 -0.267752
1 1.68368 -0.55753 -3.29779
6 -1.54386 -0.232138 -2.72668
6 -2.18639 -1.06547 -1.60076
1 -1.39767 0.805856 -2.42159
1 -2.00915 -0.289995 -3.71121
1 -2.77945 -1.89195 -2.02468
6 -2.98639 -0.360782 -0.537035
6 -3.91031 0.617732 -0.912707
6 -2.84688 -0.679217 0.812426
6 -4.6853 1.26492 0.043652
1 -4.01835 0.875526 -1.96408
6 -3.61027 -0.019787 1.77398
1 -2.11527 -1.41922 1.12859
6 -4.53468 0.94781 1.39277
1 -5.39949 2.02347 -0.2629
1 -3.46719 -0.259007 2.82301
1 -5.13011 1.45901 2.14318
8 -0.318984 1.29089 -0.315028
6 -1.44941 2.67303 1.11345
1 -1.67395 3.31638 0.278262
1 -1.78207 2.83415 2.126

7 -0.757427 1.61381 0.878982
 1 3.65434 -0.055136 -1.91981
 6 2.88853 1.30807 -0.43116
 6 2.87293 2.42167 -1.26937
 6 2.60492 1.47513 0.92749
 6 2.55119 3.68005 -0.766226
 1 3.1043 2.29937 -2.32543
 6 2.27008 2.72719 1.4314
 1 2.62085 0.61169 1.59253
 6 2.23888 3.83172 0.581799
 1 2.53711 4.54036 -1.42833
 1 2.02613 2.83587 2.48355
 1 1.9761 4.81018 0.972244

TS-1qC-I – lowest energy conformation

SCF energy= -1822.64883257
 Zero-point correction= 0.579388
 Thermal correction to Energy= 0.614680
 Thermal correction to Enthalpy= 0.615624
 Thermal correction to Gibbs Free Energy= 0.507147
 SCF energy+Solvation free energy= -1822.66286994

Coordinates:

6 1.65548 1.88281 0.831946
 1 1.27719 1.55253 1.80337
 6 0.699406 2.93532 0.239961
 7 1.72242 0.693109 -0.02065
 1 2.17289 0.889579 -0.927998
 7 -0.311711 2.43221 -0.740663
 29 -0.155622 0.124754 -0.605116
 8 0.432932 -0.52814 -2.34817
 6 -2.57903 -0.915292 1.79168
 7 -1.24444 -0.740866 1.82098
 8 -0.453662 -1.62128 2.17058
 8 -0.793797 0.35934 1.30173
 1 1.26449 3.7634 -0.210052
 6 1.51279 -0.307944 -3.0124
 8 2.42448 0.46693 -2.68559
 6 1.60922 -1.08308 -4.31455
 1 2.57963 -0.923562 -4.7839
 1 0.812518 -0.751937 -4.98686
 1 1.44816 -2.14688 -4.12215
 6 -0.03369 2.76975 -2.13608
 1 0.888373 2.27259 -2.45369
 1 0.077645 3.85765 -2.26985
 1 -0.849756 2.41623 -2.77307
 6 2.4202 -0.448065 0.606403
 1 2.37052 -1.27369 -0.11463
 1 1.84369 -0.744186 1.48993
 1 2.65347 2.31211 0.980721
 6 -0.438142 3.4448 1.14457
 6 -1.36762 3.24432 -0.064332
 1 -0.659224 2.73528 1.94511

1 -0.345653 4.45742 1.53828
 1 -1.49497 4.19175 -0.612507
 6 -2.53029 -1.59402 -0.287685
 8 -1.94119 -0.684576 -0.926319
 1 -2.9423 -1.74972 2.3745
 1 -3.15678 -0.01374 1.63589
 6 -2.71497 2.60528 0.151297
 6 -3.30492 1.81628 -0.834758
 6 -3.41247 2.83802 1.33845
 6 -4.56531 1.2586 -0.633845
 1 -2.7681 1.60549 -1.75388
 6 -4.67832 2.29262 1.53853
 1 -2.96051 3.44914 2.11586
 6 -5.25759 1.49708 0.5515
 1 -5.0044 0.636045 -1.40819
 1 -5.20779 2.48374 2.46695
 1 -6.24246 1.06654 0.705186
 6 3.85881 -0.144446 0.953124
 6 4.28821 -0.118826 2.27904
 6 4.77083 0.144091 -0.06762
 6 5.61363 0.182762 2.58775
 1 3.57908 -0.339943 3.07325
 6 6.09245 0.449251 0.2399
 1 4.43485 0.129138 -1.10375
 6 6.51693 0.46756 1.5685
 1 5.93819 0.196077 3.62381
 1 6.79545 0.66863 -0.558
 1 7.54993 0.702603 1.80615
 1 -3.63088 -1.56669 -0.268085
 6 -1.90901 -2.92448 -0.063413
 6 -2.61169 -3.9279 0.610783
 6 -0.625001 -3.18183 -0.547889
 6 -2.02937 -5.16964 0.819318
 1 -3.61674 -3.7256 0.976167
 6 -0.041881 -4.42894 -0.335191
 1 -0.111118 -2.4266 -1.13809
 6 -0.737704 -5.41844 0.35126
 1 -2.57643 -5.94596 1.34474
 1 0.955334 -4.62887 -0.71509
 1 -0.281053 -6.38965 0.515243

TS-1qC-I – higher energy conformation

SCF energy= -1822.63332074
 Zero-point correction= 0.580155
 Thermal correction to Energy= 0.614923
 Thermal correction to Enthalpy= 0.615867
 Thermal correction to Gibbs Free Energy= 0.511851
 SCF energy+Solvation free energy= -1822.65053262

Coordinates:

6 1.77085 -1.87624 1.61478
 1 2.06113 -0.889952 1.99762
 6 2.7199 -2.29637 0.506771

7 0.42221 -1.74635 1.06818
1 0.121109 -2.63633 0.666528
7 2.6818 -1.29571 -0.615825
29 0.735249 -0.41291 -0.645658
8 0.495604 -0.428236 -2.61295
6 -0.488535 2.87066 0.32684
7 0.63199 2.1995 0.004812
8 0.993951 1.23052 0.761668
8 1.16466 2.34903 -1.11333
1 2.48549 -3.30873 0.156491
6 -0.122749 -1.53257 -2.82165
8 -0.246857 -2.41961 -1.95544
6 -0.698649 -1.71866 -4.21133
1 -1.46195 -0.955049 -4.38565
1 -1.13662 -2.71095 -4.31689
1 0.08648 -1.56879 -4.95691
6 2.89725 -1.9593 -1.91666
1 2.03622 -2.59366 -2.13064
1 3.81079 -2.56998 -1.89683
1 2.97931 -1.19366 -2.68976
1 1.82384 -2.59684 2.44589
6 4.19286 -1.97621 0.788641
6 4.01879 -0.732837 -0.11272
1 4.45734 -1.81217 1.83394
1 4.88535 -2.70427 0.363514
1 4.71642 -0.703596 -0.955399
6 -1.56242 1.33798 -0.858926
8 -1.14814 0.231922 -0.427614
1 -0.856542 2.72819 1.33196
1 -0.67024 3.7775 -0.231491
6 3.98051 0.637049 0.513946
6 3.85545 1.73447 -0.337731
6 4.08195 0.860567 1.88783
6 3.80287 3.0267 0.169558
1 3.75394 1.57318 -1.4078
6 4.03315 2.15363 2.40028
1 4.19994 0.032079 2.57906
6 3.8875 3.23957 1.54246
1 3.67168 3.86182 -0.510541
1 4.10923 2.31055 3.47187
1 3.8436 4.24796 1.94246
6 -2.95432 1.77049 -0.572028
6 -3.48705 2.87474 -1.24156
6 -3.73998 1.06141 0.339154
6 -4.79797 3.27054 -1.00157
1 -2.86964 3.41871 -1.95354
6 -5.05035 1.45962 0.577411
1 -3.31789 0.199231 0.844657
6 -5.58069 2.56273 -0.089922
1 -5.21186 4.12658 -1.52542
1 -5.65832 0.899697 1.28188
1 -6.60565 2.86944 0.095953
1 -1.06353 1.78621 -1.73353
6 -0.55277 -1.28465 2.06801

1 -0.253844 -1.63597 3.06763
 1 -0.508004 -0.188709 2.07266
 6 -1.96768 -1.74433 1.8029
 6 -2.9025 -1.60205 2.83287
 6 -2.38795 -2.25065 0.571134
 6 -4.23798 -1.9382 2.63716
 1 -2.57963 -1.21045 3.7953
 6 -3.72443 -2.60028 0.381451
 1 -1.69904 -2.33014 -0.266831
 6 -4.65356 -2.4406 1.40488
 1 -4.95172 -1.81344 3.44598
 1 -4.03985 -2.98327 -0.584144
 1 -5.69442 -2.7051 1.24534

TS-1qC-I – higher energy conformation

SCF energy= -1822.65206163
 Zero-point correction= 0.581055
 Thermal correction to Energy= 0.615389
 Thermal correction to Enthalpy= 0.616334
 Thermal correction to Gibbs Free Energy= 0.515059
 SCF energy+Solvation free energy= -1822.66579683

Coordinates:

6 -0.325971 2.85498 1.6437
 1 -0.6483 2.22482 2.47764
 6 -1.53108 3.1271 0.728869
 7 0.75254 2.1225 0.970746
 1 1.21305 2.69027 0.241347
 7 -1.68105 2.22926 -0.453095
 29 -0.046413 0.594042 -0.148507
 8 1.25457 0.719158 -1.58502
 6 -1.80714 -2.10922 1.35312
 7 -0.855255 -1.24659 1.76086
 8 0.23994 -1.61194 2.1999
 8 -1.06106 0.007279 1.5122
 1 -1.54756 4.17662 0.403251
 6 2.0271 1.70328 -1.88887
 8 1.92631 2.86181 -1.45756
 6 3.1335 1.34348 -2.86171
 1 3.73775 2.22025 -3.09468
 1 2.70037 0.927516 -3.77535
 1 3.75822 0.568601 -2.40728
 6 -1.33996 2.83971 -1.73838
 1 -0.28024 3.11092 -1.74059
 1 -1.94938 3.73852 -1.92666
 1 -1.50852 2.11993 -2.54448
 6 1.7426 1.63515 1.95624
 1 1.2442 0.859989 2.54885
 1 2.01838 2.46205 2.6279
 1 0.055942 3.79621 2.0619
 6 -2.90483 2.66401 1.24776
 6 -3.14184 2.10031 -0.160847
 1 -2.79714 1.86677 1.98751

1 -3.5947 3.42991 1.60346
 1 -3.68732 2.83446 -0.776357
 6 -1.05121 -2.15471 -0.661076
 8 -0.916006 -0.953895 -1.01711
 1 -1.70005 -3.11525 1.73272
 1 -2.77267 -1.66347 1.15344
 6 -3.78919 0.74908 -0.317368
 6 -3.56049 -0.020801 -1.45862
 6 -4.67992 0.27719 0.647959
 6 -4.19906 -1.24576 -1.62517
 1 -2.85743 0.325236 -2.20867
 6 -5.32815 -0.946358 0.48131
 1 -4.87169 0.869336 1.53912
 6 -5.08445 -1.71383 -0.654556
 1 -4.00456 -1.8346 -2.51708
 1 -6.01903 -1.29949 1.24085
 1 -5.5852 -2.66805 -0.787195
 6 2.98218 1.07895 1.30175
 6 3.91212 1.94002 0.710442
 6 3.2289 -0.294154 1.30736
 6 5.07386 1.4375 0.135629
 1 3.71901 3.00967 0.69146
 6 4.40621 -0.794987 0.751755
 1 2.50076 -0.967764 1.75369
 6 5.32812 0.066298 0.164883
 1 5.78566 2.11586 -0.324763
 1 4.60586 -1.86103 0.794745
 1 6.24565 -0.325925 -0.263587
 6 0.124131 -3.04345 -0.46794
 6 -0.060716 -4.39056 -0.141108
 6 1.41023 -2.5509 -0.697669
 6 1.0299 -5.23931 -0.023652
 1 -1.06841 -4.76993 0.017917
 6 2.50141 -3.4117 -0.5942
 1 1.54873 -1.51706 -1.01016
 6 2.31655 -4.7472 -0.251181
 1 0.882124 -6.2835 0.233298
 1 3.49738 -3.03524 -0.802924
 1 3.17123 -5.41257 -0.174417
 1 -1.98659 -2.66061 -0.947516

TS-1qC-I – higher energy conformation

SCF energy= -1822.63095462
 Zero-point correction= 0.579383
 Thermal correction to Energy= 0.614252
 Thermal correction to Enthalpy= 0.615196
 Thermal correction to Gibbs Free Energy= 0.510706
 SCF energy+Solvation free energy= -1822.64604153

Coordinates:

6 0.473519 1.75071 1.74998
 1 -0.201316 0.995011 2.16594
 6 -0.284527 2.64113 0.783802

7 1.59641 1.0623 1.10274
1 2.07869 1.72826 0.475711
7 -1.09136 1.92864 -0.232781
29 1.06644 -0.382638 -0.243985
8 2.22944 0.214337 -1.64037
6 -1.01276 -2.13967 1.03113
8 -0.170575 -1.18264 1.1115
6 -0.160109 -3.75294 -0.005245
1 0.144056 -4.52246 0.692686
1 -0.886624 -3.96826 -0.774973
7 0.862084 -2.94853 -0.404103
8 1.8821 -2.83166 0.279359
8 0.617331 -2.08335 -1.31296
1 0.389966 3.3837 0.331913
6 2.79187 1.36589 -1.79254
8 2.53784 2.38409 -1.13442
6 3.84852 1.39525 -2.87783
1 4.19704 2.41503 -3.04162
1 3.44802 0.970978 -3.8014
1 4.68307 0.763557 -2.55773
6 -0.699201 2.03755 -1.62937
1 0.175514 1.42186 -1.85554
1 -0.464017 3.07595 -1.91733
1 -1.53632 1.68717 -2.24506
6 2.55297 0.47723 2.06944
1 2.08739 -0.410851 2.51157
1 2.72831 1.20478 2.87563
1 0.849798 2.37526 2.57576
6 -1.5682 3.25552 1.37173
6 -2.28864 2.738 0.107313
1 -1.89977 2.75437 2.28569
1 -1.57873 4.33483 1.52453
1 -2.42758 3.55346 -0.620486
1 -1.13424 -2.74613 1.94031
6 -3.57563 1.97496 0.259609
6 -3.64669 0.896179 1.14666
6 -4.70812 2.32017 -0.475032
6 -4.8298 0.187742 1.30557
1 -2.74929 0.592805 1.68297
6 -5.8976 1.60757 -0.324343
1 -4.65924 3.15506 -1.17045
6 -5.9605 0.543836 0.569144
1 -4.86688 -0.658636 1.98458
1 -6.77236 1.88609 -0.904201
1 -6.88422 -0.015098 0.686516
6 -2.23763 -2.04496 0.187028
6 -3.29944 -2.91964 0.438114
6 -2.34078 -1.1132 -0.845272
6 -4.45275 -2.86437 -0.333908
1 -3.21392 -3.64725 1.24341
6 -3.49307 -1.06391 -1.62411
1 -1.54035 -0.400159 -1.00386
6 -4.54827 -1.93557 -1.37104
1 -5.27736 -3.53993 -0.128053

1 -3.57845 -0.324297 -2.41445
1 -5.4516 -1.88376 -1.97104
6 3.85455 0.1311 1.38754
6 4.65392 1.15421 0.867389
6 4.26362 -1.1931 1.24404
6 5.83575 0.85373 0.200008
1 4.34177 2.19102 0.968898
6 5.44982 -1.49561 0.577773
1 3.64312 -1.99097 1.63857
6 6.23482 -0.47481 0.052709
1 6.44528 1.65556 -0.205654
1 5.75351 -2.53152 0.465126
1 7.1569 -0.710192 -0.469984

TS-1qC-II – lowest energy conformation

SCF energy= -1822.64937938
Zero-point correction= 0.579558
Thermal correction to Energy= 0.614846
Thermal correction to Enthalpy= 0.615790
Thermal correction to Gibbs Free Energy= 0.509297
SCF energy+Solvation free energy= -1822.66467018

Coordinates:

6 -2.27949 -1.67103 0.360738
1 -1.72364 -1.73116 1.30477
6 -1.56304 -2.48562 -0.712107
7 -2.27524 -0.259574 -0.031398
1 -2.71408 -0.097278 -0.946767
7 -0.36623 -1.78235 -1.27819
29 -0.338239 0.242498 -0.399213
8 -0.811777 2.03686 -1.14346
6 1.12496 2.20588 1.75058
7 1.1016 0.896492 2.01601
8 0.047878 0.217133 1.65702
8 2.0722 0.295025 2.49341
1 -2.25077 -2.77834 -1.5169
6 -1.7974 2.18917 -1.95527
8 -2.57634 1.29233 -2.31634
6 -1.97555 3.60401 -2.4789
1 -2.85265 3.66595 -3.12245
1 -1.08271 3.89735 -3.03816
1 -2.07472 4.29576 -1.63795
6 -0.470845 -1.3705 -2.6859
1 -1.20494 -0.563684 -2.79455
1 -0.770068 -2.21624 -3.323
1 0.508598 -1.00651 -3.01064
6 -2.91964 0.642142 0.945927
1 -2.6962 1.66264 0.617244
1 -2.42302 0.488355 1.90831
1 -3.29592 -2.04908 0.531393
6 -0.664186 -3.63534 -0.227895
6 0.464051 -3.02159 -1.08514
1 -0.449506 -3.57715 0.842068

1 -0.965545 -4.65 -0.48812
 1 0.533382 -3.54083 -2.05104
 6 1.99444 1.73099 -0.435482
 8 1.57141 0.573692 -0.673854
 1 0.188795 2.65374 1.45021
 1 1.94241 2.76096 2.18356
 6 1.83745 -2.90243 -0.490486
 6 2.91716 -3.51209 -1.13235
 6 2.04058 -2.26787 0.737817
 6 4.18121 -3.5139 -0.548784
 1 2.76441 -3.99873 -2.09304
 6 3.30236 -2.27403 1.32492
 1 1.23175 -1.73881 1.23805
 6 4.37188 -2.90378 0.688186
 1 5.01112 -3.99571 -1.05658
 1 3.44028 -1.75866 2.26964
 1 5.35405 -2.91103 1.15242
 6 3.40773 1.94453 -0.094443
 6 3.93381 3.23913 -0.038226
 6 4.21672 0.839493 0.177112
 6 5.27017 3.42666 0.28721
 1 3.28985 4.09088 -0.246924
 6 5.55351 1.03237 0.505895
 1 3.78187 -0.151869 0.119128
 6 6.079 2.32156 0.561411
 1 5.68545 4.42853 0.329508
 1 6.18403 0.175128 0.721392
 1 7.1235 2.47103 0.818067
 1 1.38174 2.59477 -0.716759
 6 -4.41036 0.419908 1.03328
 6 -4.99578 -0.137425 2.16952
 6 -5.21762 0.748564 -0.061209
 6 -6.37065 -0.361201 2.21904
 1 -4.37121 -0.394128 3.02202
 6 -6.589 0.522576 -0.013765
 1 -4.75903 1.18066 -0.950143
 6 -7.16838 -0.031547 1.12745
 1 -6.81641 -0.792658 3.11001
 1 -7.20853 0.783881 -0.866135
 1 -8.23952 -0.204208 1.16459

TS-1qC-II – higher energy conformation

SCF energy= -1822.63008073
 Zero-point correction= 0.580359
 Thermal correction to Energy= 0.614456
 Thermal correction to Enthalpy= 0.615400
 Thermal correction to Gibbs Free Energy= 0.512534
 SCF energy+Solvation free energy= -1822.64668351

Coordinates:

6 2.46488 1.30917 -1.60975
 1 2.51342 0.244786 -1.87177
 6 3.29416 1.55933 -0.360488

7 1.06071 1.62823 -1.3852
1 0.981274 2.59664 -1.05659
7 2.77882 0.749539 0.799535
29 0.572012 0.564135 0.552388
8 0.196139 2.01899 1.77603
6 -1.15351 -2.4726 -0.193448
7 0.057605 -2.00526 0.261165
8 0.693505 -1.19956 -0.505106
8 0.334412 -2.06564 1.45029
1 3.33025 2.62687 -0.124047
6 0.400627 3.25888 1.5212
8 1.02051 3.70064 0.540565
6 -0.169965 4.21242 2.55689
1 -1.24967 4.05768 2.63348
1 0.045011 5.24595 2.28641
1 0.258196 3.9827 3.5368
6 3.03723 1.45536 2.07146
1 2.53422 2.41833 2.05541
1 4.11353 1.62492 2.21651
1 2.65184 0.856576 2.90026
6 0.256267 1.36782 -2.57637
1 0.460665 0.333863 -2.88042
1 0.571517 2.0146 -3.41253
1 2.90272 1.88107 -2.44489
6 4.614 0.775333 -0.363158
6 3.9268 -0.246002 0.571002
1 4.96378 0.418781 -1.33361
1 5.43433 1.29923 0.130272
1 4.45272 -0.384859 1.52044
6 -2.02214 -0.739298 0.100921
8 -1.31988 -0.018101 0.898542
1 -1.18735 -2.62512 -1.265
1 -1.58053 -3.2255 0.457587
6 3.58046 -1.61907 0.051019
6 3.12051 -2.56417 0.970775
6 3.74241 -2.00839 -1.27939
6 2.78476 -3.85103 0.567197
1 2.99632 -2.27749 2.01178
6 3.41231 -3.29746 -1.68885
1 4.12964 -1.31117 -2.01528
6 2.92362 -4.21995 -0.768646
1 2.40747 -4.56164 1.29591
1 3.54194 -3.58046 -2.72896
1 2.66494 -5.22502 -1.08744
6 -3.36936 -1.18458 0.577732
6 -4.32057 -1.64051 -0.336555
6 -3.67655 -1.14027 1.93743
6 -5.57288 -2.05501 0.105024
1 -4.07682 -1.65235 -1.39739
6 -4.92928 -1.55648 2.37785
1 -2.92543 -0.764792 2.62514
6 -5.87772 -2.01529 1.46485
1 -6.31266 -2.40496 -0.608713
1 -5.16994 -1.51978 3.43612

1 -6.85484 -2.33769 1.81143
1 -1.98408 -0.496744 -0.971286
6 -1.22892 1.51147 -2.34193
6 -1.74715 2.22066 -1.25985
6 -2.11206 0.878811 -3.22367
6 -3.12359 2.25892 -1.03876
1 -1.08291 2.72848 -0.566723
6 -3.48512 0.929221 -3.01293
1 -1.71319 0.325612 -4.07163
6 -3.99445 1.6092 -1.90624
1 -3.50918 2.78466 -0.170952
1 -4.15793 0.42511 -3.70073
1 -5.06364 1.6248 -1.71981

TS-1qC-II – higher energy conformation

SCF energy= -1822.64970786
Zero-point correction= 0.579576
Thermal correction to Energy= 0.614552
Thermal correction to Enthalpy= 0.615496
Thermal correction to Gibbs Free Energy= 0.510563
SCF energy+Solvation free energy= -1822.66537161

Coordinates:

6 -1.4664 -2.94153 0.9192
1 -0.808982 -2.71892 1.76982
6 -0.630801 -3.484 -0.234464
7 -2.11373 -1.67607 0.555824
1 -2.70904 -1.76122 -0.2835
7 0.148015 -2.41076 -0.922016
29 -0.632295 -0.467094 -0.193595
8 -1.76924 0.674779 -1.3675
6 0.09368 2.40481 1.17406
7 0.536521 1.29283 1.77389
8 -0.211773 0.225442 1.71929
8 1.65734 1.21244 2.28684
1 -1.25002 -4.04312 -0.946915
6 -2.80511 0.212057 -1.9669
8 -3.17574 -0.975322 -1.94727
6 -3.58861 1.23589 -2.76843
1 -2.98479 1.56293 -3.62071
1 -3.78739 2.10949 -2.14312
1 -4.52359 0.805456 -3.12795
6 -0.153629 -2.23952 -2.35105
1 -1.18674 -1.89889 -2.47155
1 -0.019117 -3.18672 -2.89508
1 0.528403 -1.48824 -2.75924
6 -2.8919 -1.13121 1.68986
1 -2.1828 -0.943823 2.50087
1 -3.60982 -1.89435 2.02532
1 -2.19856 -3.69161 1.25119
6 0.673442 -4.19523 0.173295
6 1.43329 -3.15309 -0.685036
1 0.896408 -4.11666 1.24031

1 0.783726 -5.23177 -0.146118
 1 1.76308 -3.59716 -1.63282
 6 0.976869 1.69809 -0.883205
 8 0.991709 0.446443 -0.787161
 1 -0.945312 2.41277 0.875553
 1 0.667082 3.29817 1.36719
 6 2.59184 -2.4262 -0.061766
 6 3.86756 -2.59633 -0.604108
 6 2.44163 -1.65254 1.09198
 6 4.98304 -2.02732 0.005216
 1 3.98894 -3.18665 -1.50964
 6 3.55514 -1.08349 1.70359
 1 1.45842 -1.45241 1.51365
 6 4.82801 -1.27824 1.16823
 1 5.96799 -2.17067 -0.428589
 1 3.40943 -0.462081 2.57992
 1 5.69408 -0.834336 1.65051
 6 2.23944 2.44896 -0.791683
 6 2.28988 3.801 -1.14456
 6 3.38637 1.79212 -0.339066
 6 3.48855 4.49505 -1.04896
 1 1.38719 4.3008 -1.48975
 6 4.58305 2.49278 -0.242058
 1 3.32048 0.74207 -0.074528
 6 4.63508 3.8398 -0.595089
 1 3.53427 5.54344 -1.32625
 1 5.47545 1.9851 0.111281
 1 5.57152 4.38433 -0.518862
 1 0.092067 2.19301 -1.30242
 6 -3.61837 0.141821 1.33742
 6 -4.73686 0.114324 0.500913
 6 -3.18413 1.36146 1.8561
 6 -5.39987 1.2932 0.174781
 1 -5.07908 -0.830067 0.085178
 6 -3.85005 2.54225 1.53491
 1 -2.30911 1.377 2.49972
 6 -4.95728 2.51016 0.691778
 1 -6.26375 1.26249 -0.482233
 1 -3.50237 3.48577 1.94542
 1 -5.4787 3.42884 0.440405

TS-1qC-II – higher energy conformation

SCF energy= -1822.64664357
 Zero-point correction= 0.580510
 Thermal correction to Energy= 0.615218
 Thermal correction to Enthalpy= 0.616162
 Thermal correction to Gibbs Free Energy= 0.512117
 SCF energy+Solvation free energy= -1822.66277014

Coordinates:

6 -0.627407 -0.237837 -2.60161
 1 0.175038 -0.968062 -2.46094
 6 -0.026655 1.18006 -2.67007

7 -1.54579 -0.390159 -1.4695
1 -2.37435 0.219966 -1.54943
7 -0.109722 1.9907 -1.42231
29 -0.639453 0.381411 0.254794
8 -2.13476 1.35316 0.965238
6 2.12323 -0.677234 0.336367
8 0.999895 -0.704677 -0.250881
6 1.8396 -1.23757 2.425
1 2.11427 -2.27507 2.55114
1 2.37548 -0.440015 2.9199
7 0.526054 -1.01642 2.22088
8 -0.215859 -1.92319 1.82587
8 0.118282 0.203609 2.17695
1 -0.468896 1.7428 -3.50433
6 -3.32346 1.48577 0.47925
8 -3.65461 1.28644 -0.696023
6 -4.35184 1.95232 1.49264
1 -4.38832 1.23296 2.31489
1 -5.33321 2.03895 1.02642
1 -4.04277 2.91495 1.91017
6 -1.11915 3.04795 -1.42478
1 -2.11523 2.60765 -1.49709
1 -0.957187 3.73832 -2.26812
1 -1.06278 3.61122 -0.489043
6 -1.99672 -1.79085 -1.28449
1 -1.20109 -2.33008 -0.756372
1 -2.13962 -2.26303 -2.26711
1 -1.13878 -0.47628 -3.54447
6 1.50947 1.32633 -2.65042
6 1.28544 2.45282 -1.62035
1 1.99982 0.453338 -2.21413
1 1.99162 1.60471 -3.58803
1 1.28622 3.43365 -2.12238
6 2.14188 2.50844 -0.384855
6 3.52961 2.39299 -0.500016
6 1.57121 2.63038 0.882635
6 4.33411 2.38354 0.635696
1 3.97877 2.28565 -1.4848
6 2.37445 2.60822 2.02222
1 0.491775 2.70799 0.995255
6 3.75613 2.48201 1.90254
1 5.4112 2.2866 0.533625
1 1.90923 2.67091 3.0008
1 4.38174 2.46357 2.78969
6 3.15298 -1.67923 -0.029805
6 4.48662 -1.45057 0.316643
6 2.79982 -2.83185 -0.734605
6 5.46545 -2.37079 -0.039678
1 4.74529 -0.544816 0.861596
6 3.7804 -3.75317 -1.08488
1 1.75663 -2.98787 -0.992619
6 5.11198 -3.52398 -0.739541
1 6.5029 -2.1909 0.224361
1 3.50921 -4.65182 -1.63009

1 5.87557 -4.24397 -1.0176
 1 2.49034 0.268633 0.744754
 6 -3.2958 -1.81708 -0.517103
 6 -4.50582 -1.82704 -1.21178
 6 -3.30833 -1.73657 0.876954
 6 -5.71579 -1.74699 -0.531151
 1 -4.49824 -1.88336 -2.29818
 6 -4.52041 -1.6552 1.55876
 1 -2.37121 -1.72829 1.42719
 6 -5.72416 -1.65524 0.858254
 1 -6.6498 -1.75011 -1.08441
 1 -4.52119 -1.59025 2.643
 1 -6.66661 -1.58815 1.39353

Product arising from TS-1qC-I

SCF energy= -1822.67015161
 Zero-point correction= 0.582813
 Thermal correction to Energy= 0.617775
 Thermal correction to Enthalpy= 0.618719
 Thermal correction to Gibbs Free Energy= 0.513020

Coordinates:

6 1.07589 1.78376 1.13976
 1 0.830042 1.1957 2.02882
 6 -0.125259 2.66648 0.754101
 7 1.38892 0.842192 0.058787
 1 1.78666 1.33095 -0.763405
 7 -0.969367 2.16036 -0.370126
 29 -0.28309 0.010946 -0.801072
 8 0.561179 -0.060236 -2.60599
 6 -2.6059 -1.85679 0.800905
 7 -1.82498 -0.990225 1.7391
 8 -2.20268 -0.909378 2.8819
 8 -0.838303 -0.378522 1.32293
 1 0.20366 3.69075 0.529359
 6 1.58093 0.556423 -3.07148
 8 2.23013 1.44595 -2.48815
 6 1.99126 0.130943 -4.47159
 1 2.87007 0.685506 -4.79999
 1 1.15957 0.300906 -5.16049
 1 2.19986 -0.942728 -4.47588
 6 -0.754121 2.83572 -1.65207
 1 0.271528 2.65629 -1.9904
 1 -0.921185 3.92026 -1.55879
 1 -1.43633 2.43199 -2.40503
 6 2.34026 -0.220849 0.440995
 1 2.49885 -0.828534 -0.457586
 1 1.85569 -0.862603 1.18825
 1 1.94857 2.40197 1.38016
 6 -1.36305 2.66878 1.67252
 6 -2.19638 2.54919 0.384164
 1 -1.41535 1.76944 2.29157
 1 -1.52506 3.55718 2.28365

1 -2.5165 3.54934 0.049501
 6 -1.85327 -2.19928 -0.490793
 8 -1.72895 -1.09953 -1.30502
 1 -2.91769 -2.70742 1.40894
 1 -3.4816 -1.25158 0.551504
 6 -3.37853 1.61715 0.335383
 6 -3.78939 1.04116 -0.869393
 6 -4.12315 1.37478 1.49167
 6 -4.94386 0.265165 -0.921819
 1 -3.19426 1.17396 -1.76691
 6 -5.27555 0.591759 1.44349
 1 -3.80147 1.80161 2.4384
 6 -5.69508 0.04564 0.232155
 1 -5.24607 -0.180529 -1.86421
 1 -5.84215 0.410231 2.35143
 1 -6.59526 -0.559911 0.190841
 6 3.65596 0.312409 0.958288
 6 4.05986 0.081217 2.27181
 6 4.47045 1.07639 0.114875
 6 5.26626 0.596619 2.74319
 1 3.42605 -0.510068 2.92868
 6 5.67142 1.5956 0.586743
 1 4.15188 1.26138 -0.910559
 6 6.07288 1.35526 1.90083
 1 5.57232 0.407032 3.76759
 1 6.29935 2.18704 -0.072657
 1 7.0125 1.75879 2.26547
 1 -2.51689 -2.94305 -0.974236
 6 -0.515235 -2.90794 -0.229078
 6 -0.177581 -3.53742 0.972375
 6 0.421335 -2.89844 -1.26854
 6 1.07003 -4.13751 1.1354
 1 -0.87887 -3.56443 1.80376
 6 1.6647 -3.50578 -1.10835
 1 0.167376 -2.38337 -2.19085
 6 1.99614 -4.12295 0.095672
 1 1.31743 -4.61441 2.0792
 1 2.37928 -3.48842 -1.92671
 1 2.96846 -4.58825 0.224735

Product arising from TS-1qC-II

SCF energy=	-1822.67503821
Zero-point correction=	0.582702
Thermal correction to Energy=	0.617719
Thermal correction to Enthalpy=	0.618663
Thermal correction to Gibbs Free Energy=	0.512696

Coordinates:

6 -2.27459 -1.72075 -0.258227
 1 -1.78361 -2.16325 0.617422
 6 -1.52997 -2.11517 -1.5328
 7 -2.2185 -0.266213 -0.102585
 1 -2.65392 0.206546 -0.908676

7 -0.279247 -1.31325 -1.71618
29 -0.322 0.449239 -0.460776
8 -1.0123 2.34385 -0.465977
6 1.52721 2.29723 1.15243
7 1.33336 1.07955 1.97244
8 0.27513 0.456699 1.81406
8 2.21423 0.718912 2.71522
1 -2.18638 -2.03012 -2.40683
6 -1.91961 2.59971 -1.33713
8 -2.50915 1.74336 -2.02272
6 -2.27251 4.0681 -1.48973
1 -3.03285 4.20242 -2.25853
1 -1.37256 4.63208 -1.74835
1 -2.6358 4.4549 -0.533331
6 -0.17821 -0.614122 -3.00856
1 -0.948483 0.164006 -3.06006
1 -0.312098 -1.31364 -3.847
1 0.807956 -0.145893 -3.05885
6 -2.85106 0.243159 1.12881
1 -2.6082 1.30988 1.17724
1 -2.36684 -0.243344 1.98238
1 -3.30715 -2.09371 -0.281114
6 -0.711592 -3.41747 -1.45803
6 0.564882 -2.55631 -1.65706
1 -0.758969 -3.92527 -0.491722
1 -0.900725 -4.13757 -2.25477
1 1.03167 -2.73043 -2.63299
6 2.13904 1.87363 -0.234207
8 1.48794 0.810646 -0.790263
1 0.537678 2.72616 1.00212
1 2.19934 2.94706 1.71109
6 1.61593 -2.62197 -0.585333
6 2.87342 -3.15081 -0.874011
6 1.33871 -2.2127 0.720503
6 3.83595 -3.27563 0.126942
1 3.10383 -3.46428 -1.8893
6 2.30306 -2.3093 1.717
1 0.369629 -1.78691 0.965501
6 3.55425 -2.84974 1.42157
1 4.8106 -3.69129 -0.111321
1 2.08205 -1.94148 2.71318
1 4.31076 -2.92439 2.1965
6 3.62499 1.59199 -0.050198
6 4.53359 2.63848 0.115695
6 4.08386 0.277924 -0.015747
6 5.88474 2.37691 0.31962
1 4.18122 3.66847 0.076829
6 5.43576 0.013797 0.190468
1 3.36763 -0.522711 -0.1657
6 6.33911 1.05963 0.359561
1 6.58453 3.1984 0.441779
1 5.78115 -1.01618 0.217358
1 7.39337 0.852735 0.517821
1 2.03601 2.80265 -0.828508

6 -4.34539 0.019714 1.14971
 6 -4.94271 -0.78828 2.11575
 6 -5.14485 0.612723 0.166457
 6 -6.32056 -0.999245 2.11001
 1 -4.32482 -1.25302 2.88062
 6 -6.51879 0.398149 0.156072
 1 -4.68315 1.24246 -0.593785
 6 -7.10987 -0.407118 1.12945
 1 -6.77438 -1.62851 2.86951
 1 -7.13136 0.863678 -0.609945
 1 -8.18293 -0.571002 1.1217

Model complex with N-Bn on azetidine nitrogen

SCF energy= -1461.32752570
 Zero-point correction= 0.478616
 Thermal correction to Energy= 0.506956
 Thermal correction to Enthalpy= 0.507900
 Thermal correction to Gibbs Free Energy= 0.418655
 SCF energy+Solvation free energy= -1461.34087427

Coordinates:

6 -0.399342 1.27222 2.4622
 1 0.524828 1.08083 3.01716
 6 -0.891727 -0.049179 1.84007
 7 -0.075534 2.27653 1.44683
 1 -0.886017 2.59236 0.898002
 7 -0.591122 -0.248869 0.390432
 29 1.07835 1.36346 -0.005834
 8 0.378135 2.19606 -1.58751
 8 2.90829 0.78908 -0.753325
 1 -1.9618 -0.195624 2.03092
 6 -0.592701 3.03974 -1.67057
 8 -1.35124 3.3654 -0.747212
 6 -0.782224 3.63194 -3.05507
 1 -1.01321 2.82885 -3.76081
 1 0.150945 4.09484 -3.38571
 1 -1.58883 4.36462 -3.04841
 6 -1.6679 0.032656 -0.58779
 1 -1.86321 1.1095 -0.548444
 1 -1.25705 -0.178527 -1.58111
 6 0.584637 3.4588 2.00879
 1 0.69883 4.20159 1.21595
 1 1.57115 3.17295 2.38655
 1 0.002752 3.89989 2.82824
 1 -1.14228 1.66405 3.17059
 6 -0.09833 -1.33122 2.15915
 6 -0.236436 -1.66784 0.66313
 1 0.937546 -1.11074 2.42458
 1 -0.548078 -2.02856 2.86674
 1 -1.11348 -2.31345 0.514688
 6 0.940705 -2.24932 -0.071827
 6 1.5693 -3.37663 0.468044
 6 1.40082 -1.73327 -1.28196

6 2.63451 -3.97992 -0.190624
 1 1.21629 -3.78124 1.41417
 6 2.47967 -2.32809 -1.93728
 1 0.942762 -0.844756 -1.71047
 6 3.09353 -3.45438 -1.39919
 1 3.11164 -4.85476 0.240689
 1 2.84157 -1.89734 -2.86537
 1 3.93091 -3.91751 -1.91174
 6 3.16024 0.306098 0.383617
 8 2.32857 0.507445 1.33224
 6 4.36472 -0.555741 0.617705
 1 4.78645 -0.358751 1.60493
 1 5.10654 -0.397701 -0.164893
 1 4.02939 -1.59914 0.587176
 6 -2.95798 -0.728675 -0.387529
 6 -3.99132 -0.182747 0.37913
 6 -3.14635 -1.98975 -0.962599
 6 -5.17406 -0.886676 0.588621
 1 -3.87026 0.813234 0.800296
 6 -4.32698 -2.69773 -0.756719
 1 -2.3597 -2.41334 -1.5844
 6 -5.34162 -2.14873 0.024069
 1 -5.96797 -0.446107 1.1838
 1 -4.45806 -3.67471 -1.21157
 1 -6.2645 -2.69773 0.183049

Model complex with N-Bn on azetidine nitrogen

SCF energy= -1461.33022122
 Zero-point correction= 0.478794
 Thermal correction to Energy= 0.507911
 Thermal correction to Enthalpy= 0.508855
 Thermal correction to Gibbs Free Energy= 0.417285
 SCF energy+Solvation free energy= -1461.34384869

Coordinates:

6 1.69443 2.14616 -1.80294
 1 1.231 3.02891 -1.35182
 6 0.598112 1.19402 -2.29924
 7 2.51456 1.52339 -0.765628
 1 3.00453 0.673512 -1.08145
 7 0.125169 0.134627 -1.34506
 29 1.23641 0.772462 0.647565
 8 2.43732 -0.615352 1.2756
 8 -0.107236 0.793669 2.16189
 1 0.900833 0.72015 -3.24331
 6 3.41437 -1.17119 0.64228
 8 3.77609 -0.905422 -0.51191
 6 4.11108 -2.27245 1.41951
 1 3.4598 -3.15311 1.4318
 1 4.26759 -1.96418 2.45503
 1 5.05601 -2.53473 0.944015
 6 0.588227 -1.22643 -1.7028
 1 0.464145 -1.37184 -2.78942

1 1.66003 -1.2848 -1.47668
6 3.50075 2.43744 -0.18175
1 4.10946 1.87961 0.533551
1 2.97932 3.24586 0.339639
1 4.15584 2.87027 -0.948022
1 2.31373 2.47984 -2.64739
6 -0.826071 1.76191 -2.37558
6 -1.29022 0.442926 -1.73671
1 -0.958827 2.60076 -1.68721
1 -1.21713 2.00537 -3.36414
1 -1.59989 -0.266551 -2.52012
6 -2.37755 0.518666 -0.693165
6 -3.44898 1.38516 -0.937028
6 -2.40534 -0.277313 0.451999
6 -4.53345 1.44491 -0.066731
1 -3.43727 2.01616 -1.82296
6 -3.48657 -0.21144 1.32909
1 -1.57532 -0.934907 0.679171
6 -4.55625 0.640565 1.07126
1 -5.35671 2.12144 -0.275633
1 -3.48355 -0.832597 2.21955
1 -5.39819 0.686014 1.75516
6 -0.547508 1.89257 1.71646
8 0.038992 2.42644 0.718614
6 -1.74972 2.55804 2.31746
1 -1.49789 3.58589 2.5909
1 -2.10067 2.00355 3.18705
1 -2.53648 2.59153 1.5566
6 -0.178429 -2.30365 -0.975885
6 -1.27028 -2.91985 -1.5914
6 0.150493 -2.66545 0.334743
6 -2.03725 -3.8607 -0.908837
1 -1.52329 -2.66216 -2.61745
6 -0.613148 -3.60844 1.01684
1 0.982228 -2.17972 0.837604
6 -1.71152 -4.20416 0.399923
1 -2.88673 -4.32498 -1.39995
1 -0.351441 -3.87246 2.03693
1 -2.30748 -4.93672 0.935505

Single crystal X-ray diffraction data

CDCC Deposition Numbers

CCDC 1824096-1824097

XRD Data tables for compound (2*S*, 4*R*)-1*d*

The dataset was measured on an Agilent SuperNova diffractometer using an Atlas detector. The data collection was driven and processed and an absorption correction was applied using CrysAlisPro.²⁶ The structure was solved using ShelXS² and refined by a full-matrix least-squares procedure on F² in ShelXL.²⁷ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Reports were produced using OLEX2.²⁸

Table 1 Crystal data and structure refinement for (2*S*, 4*R*)-1*d*.

Identification code	(2 <i>S</i> , 4 <i>R</i>)-1 <i>d</i>
Empirical formula	C ₂₀ H ₂₆ IN ₃ O ₂
Formula weight	467.34
Temperature/K	99.9(4)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	8.26967(7)
b/Å	7.63280(6)
c/Å	16.69601(11)
α /°	90
β /°	96.4510(7)
γ /°	90
Volume/Å ³	1047.191(14)
Z	2
ρ_{calc}/cm^3	1.482
μ/mm^{-1}	12.155
F(000)	472.0
Crystal size/mm ³	0.3448 × 0.1981 × 0.0956
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	5.326 to 148.828
Index ranges	-9 ≤ h ≤ 10, -9 ≤ k ≤ 9, -20 ≤ l ≤ 20
Reflections collected	19506
Independent reflections	4208 [R_{int} = 0.0237, R_{sigma} = 0.0151]
Data/restraints/parameters	4208/1/237
Goodness-of-fit on F ²	1.068
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0151, wR_2 = 0.0386
Final R indexes [all data]	R_1 = 0.0153, wR_2 = 0.0388
Largest diff. peak/hole / e Å ⁻³	0.21/-0.58
Flack parameter	-0.017(2)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (2*S*, 4*R*)-1*d*. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C ⁽¹⁾	7564(3)	7308(5)	2586.1(14)	17.6(5)
C ⁽²⁾	6873(3)	7786(4)	1702.8(15)	21.0(6)
C ⁽³⁾	5228(3)	8067(3)	2038.6(15)	18.1(5)
C ⁽⁴⁾	3721(3)	7251(4)	1605.6(14)	18.7(6)
C ⁽⁵⁾	8689(3)	5772(3)	2701.3(14)	16.6(5)
C ⁽⁶⁾	10354(3)	6050(3)	2895.0(16)	19.7(5)
C ⁽⁷⁾	11458(4)	4680(4)	2930.5(17)	21.0(6)
C ⁽⁸⁾	10856(3)	3003(3)	2779.2(15)	19.3(5)
C ⁽⁹⁾	9208(3)	2674(5)	2598.6(14)	22.8(5)
C ⁽¹⁰⁾	8125(4)	4059(4)	2561.2(16)	21.3(5)
C ⁽¹¹⁾	5482(3)	7673(6)	3552.9(14)	22.8(6)
C ⁽¹²⁾	6410(3)	6583(5)	4205.6(15)	24.5(6)
C ⁽¹³⁾	7722(3)	7286(7)	4691.6(15)	32.3(8)
C ⁽¹⁴⁾	8657(4)	6232(6)	5247(2)	44.8(10)
C ⁽¹⁵⁾	8277(5)	4489(7)	5321(2)	46.9(10)
C ⁽¹⁶⁾	6953(5)	3775(5)	4849(2)	41.0(8)
C ⁽¹⁷⁾	6027(4)	4824(5)	4289.8(16)	30.5(7)
C ⁽¹⁸⁾	1708(3)	7414(6)	348.4(13)	20.7(5)
C ⁽¹⁹⁾	1550(4)	8070(5)	-513.2(17)	33.3(8)
C ⁽²⁰⁾	357(4)	8130(5)	793.1(18)	33.5(8)
N ⁽¹⁾	5856(3)	7045(3)	2766.5(12)	17.5(5)
N ⁽²⁾	3340(3)	7967(3)	768.5(12)	17.0(5)
N ⁽³⁾	12020(3)	1548(3)	2807.6(14)	24.9(5)
O ⁽¹⁾	13452(3)	1837(3)	3041.3(14)	31.2(5)
O ⁽²⁾	11490(3)	87(3)	2593.6(15)	33.7(5)
I ⁽¹⁾	3796.0(2)	2507.5(3)	739.2(2)	19.92(5)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (2*S*, 4*R*)-1*d*. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C ⁽¹⁾	15(1)	18.3(15)	19.1(9)	-0.9(11)	0.2(8)	-1.8(12)
C ⁽²⁾	17.6(11)	26.1(19)	19.6(10)	3.4(10)	2.8(8)	3.9(11)
C ⁽³⁾	17.5(12)	18.5(12)	18.3(11)	0.3(8)	2.0(9)	3.3(9)
C ⁽⁴⁾	21.4(12)	17.2(16)	17.3(10)	0.8(10)	0.8(8)	1.9(11)
C ⁽⁵⁾	17.4(12)	18.9(12)	13.3(10)	0.2(9)	0.5(9)	1.2(10)
C ⁽⁶⁾	21.5(14)	15.7(12)	21.5(12)	-0.4(9)	0.6(10)	-1.2(10)
C ⁽⁷⁾	18.5(14)	19.4(14)	24.5(14)	0.3(11)	-1.2(11)	0.8(11)
C ⁽⁸⁾	22.6(13)	18.3(14)	17.1(11)	0.9(8)	2.8(9)	4.3(10)
C ⁽⁹⁾	28.1(12)	15.6(15)	24.5(10)	-1.1(13)	2.0(9)	-2.8(14)
C ⁽¹⁰⁾	19.5(14)	21.4(14)	22.7(12)	-0.8(10)	1(1)	-1.9(11)
C ⁽¹¹⁾	21.5(11)	28.5(16)	18.5(10)	-3.8(13)	2.8(8)	3.6(14)
C ⁽¹²⁾	20.7(14)	38.4(18)	15.0(12)	-1.2(11)	4.9(10)	4.3(12)
C ⁽¹³⁾	26.2(13)	51(2)	19.1(10)	-5.4(15)	0.6(9)	1.0(17)
C ⁽¹⁴⁾	28.3(18)	85(3)	19.8(14)	0.7(16)	-2.8(13)	5.2(19)
C ⁽¹⁵⁾	36(2)	82(3)	22.6(15)	18.2(16)	5.2(13)	20(2)

C ⁽¹⁶⁾	41(2)	54(2)	30.1(15)	17.5(15)	11.0(14)	11.4(17)
C ⁽¹⁷⁾	28.7(17)	40(2)	22.9(14)	5.7(11)	4.3(12)	4.3(13)
C ⁽¹⁸⁾	17.4(11)	21.4(12)	22(1)	-2.1(15)	-3.6(8)	-2.7(15)
C ⁽¹⁹⁾	18.5(13)	61(2)	19.5(12)	1.0(12)	-1(1)	-0.9(13)
C ⁽²⁰⁾	15.1(13)	60(2)	24.5(13)	0.4(12)	0.4(11)	-1.2(13)
N ⁽¹⁾	14.7(10)	21.9(13)	15.7(9)	0.7(7)	0.5(7)	3.5(8)
N ⁽²⁾	14(1)	19.8(13)	17.0(9)	-1.0(7)	1.0(7)	1.3(8)
N ⁽³⁾	32.2(15)	20.2(13)	23.4(11)	1.5(9)	7.1(10)	7.1(11)
O ⁽¹⁾	23.9(11)	28.9(10)	40.2(12)	-0.5(9)	0.7(9)	9.3(8)
O ⁽²⁾	43.1(14)	16.8(11)	41.6(13)	-4(1)	6.8(11)	4.1(10)
I ⁽¹⁾	19.74(8)	19.04(8)	21.14(7)	-0.65(8)	2.99(5)	-0.04(9)

Table 4 Bond Lengths for (2*S*, 4*R*)-1d .

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C ⁽¹⁾	C ⁽²⁾	1.564(3)	C ⁽¹¹⁾	C ⁽¹²⁾	1.510(4)
C ⁽¹⁾	C ⁽⁵⁾	1.496(4)	C ⁽¹¹⁾	N ⁽¹⁾	1.463(3)
C ⁽¹⁾	N ⁽¹⁾	1.491(3)	C ⁽¹²⁾	C ⁽¹³⁾	1.388(4)
C ⁽²⁾	C ⁽³⁾	1.543(3)	C ⁽¹²⁾	C ⁽¹⁷⁾	1.391(5)
C ⁽³⁾	C ⁽⁴⁾	1.504(4)	C ⁽¹³⁾	C ⁽¹⁴⁾	1.394(5)
C ⁽³⁾	N ⁽¹⁾	1.488(3)	C ⁽¹⁴⁾	C ⁽¹⁵⁾	1.376(7)
C ⁽⁴⁾	N ⁽²⁾	1.501(3)	C ⁽¹⁵⁾	C ⁽¹⁶⁾	1.386(6)
C ⁽⁵⁾	C ⁽⁶⁾	1.394(4)	C ⁽¹⁶⁾	C ⁽¹⁷⁾	1.392(4)
C ⁽⁵⁾	C ⁽¹⁰⁾	1.399(4)	C ⁽¹⁸⁾	C ⁽¹⁹⁾	1.515(4)
C ⁽⁶⁾	C ⁽⁷⁾	1.385(4)	C ⁽¹⁸⁾	C ⁽²⁰⁾	1.511(4)
C ⁽⁷⁾	C ⁽⁸⁾	1.386(4)	C ⁽¹⁸⁾	N ⁽²⁾	1.510(3)
C ⁽⁸⁾	C ⁽⁹⁾	1.385(4)	N ⁽³⁾	O ⁽¹⁾	1.224(3)
C ⁽⁸⁾	N ⁽³⁾	1.468(3)	N ⁽³⁾	O ⁽²⁾	1.236(3)
C ⁽⁹⁾	C ⁽¹⁰⁾	1.383(5)			

Table 5 Bond Angles for (2*S*, 4*R*)-1d .

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C ⁽⁵⁾	C ⁽¹⁾	C ⁽²⁾	117.4(2)	C ⁽¹³⁾	C ⁽¹²⁾	C ⁽¹¹⁾	120.6(3)
N ⁽¹⁾	C ⁽¹⁾	C ⁽²⁾	88.17(17)	C ⁽¹³⁾	C ⁽¹²⁾	C ⁽¹⁷⁾	119.1(3)
N ⁽¹⁾	C ⁽¹⁾	C ⁽⁵⁾	117.3(3)	C ⁽¹⁷⁾	C ⁽¹²⁾	C ⁽¹¹⁾	120.1(3)
C ⁽³⁾	C ⁽²⁾	C ⁽¹⁾	86.17(18)	C ⁽¹²⁾	C ⁽¹³⁾	C ⁽¹⁴⁾	120.3(4)
C ⁽⁴⁾	C ⁽³⁾	C ⁽²⁾	119.0(2)	C ⁽¹⁵⁾	C ⁽¹⁴⁾	C ⁽¹³⁾	120.2(4)
N ⁽¹⁾	C ⁽³⁾	C ⁽²⁾	89.04(19)	C ⁽¹⁴⁾	C ⁽¹⁵⁾	C ⁽¹⁶⁾	120.1(3)
N ⁽¹⁾	C ⁽³⁾	C ⁽⁴⁾	111.7(2)	C ⁽¹⁵⁾	C ⁽¹⁶⁾	C ⁽¹⁷⁾	119.7(4)
N ⁽²⁾	C ⁽⁴⁾	C ⁽³⁾	111.9(2)	C ⁽¹²⁾	C ⁽¹⁷⁾	C ⁽¹⁶⁾	120.6(3)
C ⁽⁶⁾	C ⁽⁵⁾	C ⁽¹⁾	119.6(2)	C ⁽²⁰⁾	C ⁽¹⁸⁾	C ⁽¹⁹⁾	111.0(3)
C ⁽⁶⁾	C ⁽⁵⁾	C ⁽¹⁰⁾	118.9(2)	N ⁽²⁾	C ⁽¹⁸⁾	C ⁽¹⁹⁾	109.0(2)
C ⁽¹⁰⁾	C ⁽⁵⁾	C ⁽¹⁾	121.3(2)	N ⁽²⁾	C ⁽¹⁸⁾	C ⁽²⁰⁾	110.0(2)
C ⁽⁷⁾	C ⁽⁶⁾	C ⁽⁵⁾	121.6(3)	C ⁽³⁾	N ⁽¹⁾	C ⁽¹⁾	90.89(19)
C ⁽⁶⁾	C ⁽⁷⁾	C ⁽⁸⁾	117.8(3)	C ⁽¹¹⁾	N ⁽¹⁾	C ⁽¹⁾	116.0(2)
C ⁽⁷⁾	C ⁽⁸⁾	N ⁽³⁾	118.1(2)	C ⁽¹¹⁾	N ⁽¹⁾	C ⁽³⁾	118.2(2)
C ⁽⁹⁾	C ⁽⁸⁾	C ⁽⁷⁾	122.1(3)	C ⁽⁴⁾	N ⁽²⁾	C ⁽¹⁸⁾	114.4(2)

C ⁽⁹⁾	C ⁽⁸⁾	N ⁽³⁾	119.7(3)	O ⁽¹⁾	N ⁽³⁾	C ⁽⁸⁾	118.8(2)
C ⁽¹⁰⁾	C ⁽⁹⁾	C ⁽⁸⁾	119.2(3)	O ⁽¹⁾	N ⁽³⁾	O ⁽²⁾	123.6(3)
C ⁽⁹⁾	C ⁽¹⁰⁾	C ⁽⁵⁾	120.3(3)	O ⁽²⁾	N ⁽³⁾	C ⁽⁸⁾	117.6(3)
N ⁽¹⁾	C ⁽¹¹⁾	C ⁽¹²⁾	109.0(3)				

Table 6 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (2*S*, 4*R*)-1d.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H ⁽¹⁾	8056	8361	2875	21
H ^(2A)	7344	8862	1493	25
H ^(2B)	6879	6804	1316	25
H ⁽³⁾	5052	9326	2170	22
H ^(4A)	3874	5967	1576	22
H ^(4B)	2789	7474	1915	22
H ⁽⁶⁾	10739	7207	3005	24
H ⁽⁷⁾	12592	4883	3054	25
H ⁽⁹⁾	8826	1510	2502	27
H ⁽¹⁰⁾	6992	3847	2440	26
H ^(11A)	4298	7576	3589	27
H ^(11B)	5797	8920	3622	27
H ⁽¹³⁾	7984	8491	4646	39
H ⁽¹⁴⁾	9558	6719	5575	54
H ⁽¹⁵⁾	8924	3772	5696	56
H ⁽¹⁶⁾	6680	2577	4906	49
H ⁽¹⁷⁾	5125	4333	3963	37
H ⁽¹⁸⁾	1647	6106	344	25
H ^(19A)	1680	9346	-515	50
H ^(19B)	474	7759	-783	50
H ^(19C)	2394	7529	-799	50
H ^(20A)	420	7597	1330	50
H ^(20B)	-697	7852	491	50
H ^(20C)	473	9403	847	50
H ^(2C)	4130	7615	466	20
H ^(2D)	3371	9158	793	20

Experimental

Single crystals of C₂₀H₂₆IN₃O₂ [(2*S*, 4*R*)-1d] mounted on a **SuperNova, Dual, Cu at zero, Atlas** diffractometer. The crystal was kept at 99.9(4) K during data collection. Using Olex2,²⁸ the structure was solved with the ShelXS²⁷ structure solution program using Patterson Method and refined with the ShelXL²⁹ refinement package using Least Squares minimisation.

Crystal structure determination of [(2*S*, 4*R*)-1d]

Crystal Data for C₂₀H₂₆IN₃O₂ (*M* = 467.34 g/mol): monoclinic, space group P2₁ (no. 4), *a* = 8.26967(7) Å, *b* = 7.63280(6) Å, *c* = 16.69601(11) Å, β = 96.4510(7)°, *V* = 1047.191(14) Å³, *Z* = 2, *T* = 99.9(4) K, $\mu(\text{CuK}\alpha)$ = 12.155 mm⁻¹, *D*_{calc} = 1.482 g/cm³, 19506 reflections measured (5.326° ≤ 2 θ ≤ 148.828°), 4208 unique (*R*_{int} = 0.0237, *R*_{sigma} = 0.0151) which were used in all calculations. The final *R*₁ was 0.0151 (*I* > 2 σ (*I*)) and *wR*₂ was 0.0388 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All N(H,H) groups

At 1.5 times of:

All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates:

C1(H1), C3(H3), C18(H18)

2.b Secondary CH2 refined with riding coordinates:

C2(H2A,H2B), C4(H4A,H4B), C11(H11A,H11B), N2(H2C,H2D)

2.c Aromatic/amide H refined with riding coordinates:

C6(H6), C7(H7), C9(H9), C10(H10), C13(H13), C14(H14), C15(H15), C16(H16),

C17(H17)

2.d Idealised Me refined as rotating group:

C19(H19A,H19B,H19C), C20(H20A,H20B,H20C)

This report has been created with Olex2, compiled on 2017.08.10 svn.r3458 for OlexSys. Please [let us know](#) if there are any errors or if you would like to have additional features.

XRD Data tables for (rac)-7

7: The dataset was measured by the EPSRC UK National Crystallography Service³⁰ on a Bruker-Nonius Roper CCD diffractometer at the window of a Bruker-Nonius FR591 rotating anode. The data collection was driven by COLLECT³¹ and processed by DENZO³² and an absorption correction was applied using SADABS³³. The structure was solved in Sir2004,³⁴ and was refined by a full-matrix least-squares procedure on F^2 in SHELXL-97.²⁷ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bonded to N(2), N(102), N(202) and N(302) (one per crystallographically-independent platinum complex) were located in the electron density and their positions refined subject to suitable distance restraints, (N-H = 0.91 (2) Å and Pd ... H = 2.48 (4) Å and C(104)-H(12C) = C(112)-H(12C) = 1.92 (4) Å). The isotropic thermal parameters (U_{iso}) of these hydrogen atoms were set at 1.2 times the equivalent isotropic thermal parameter (U_{eq}) of the parent nitrogen atom. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. The structure contains four crystallographically-independent platinum complexes with one acetonitrile molecule per platinum complex.

Table 1. Crystal data and structure refinement for **(rac)-7**.

Identification code	(rac)-7 , 2010src0915	
Empirical formula	C ₂₄ H ₂₆ Cl ₂ N ₂ Pt, C ₂ H ₃ N	
Formula weight	649.51	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)	
Unit cell dimensions	a = 10.6958(2) Å	$\alpha = 90^\circ$.
	b = 10.4600(2) Å	$\beta = 93.9630(10)^\circ$.
	c = 43.9267(10) Å	$\chi = 90^\circ$.
Volume	4902.68(17) Å ³	
Z, Z'	8, 4	
Density (calculated)	1.760 Mg/m ³	
Absorption coefficient	5.961 mm ⁻¹	
F(000)	2544	
Crystal size	0.16 x 0.12 x 0.10 mm ³	
Theta range for data collection	2.92 to 25.03°.	

Index ranges	-12<=h<=12, -12<=k<=12, -52<=l<=52
Reflections collected	44832
Independent reflections	16268 [R(int) = 0.1064]
Completeness to theta = 25.03°	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5871 and 0.4489
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	16268 / 277 / 1165
Goodness-of-fit on F ²	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0623, wR2 = 0.0856
R indices (all data)	R1 = 0.0871, wR2 = 0.0908
Absolute structure parameter	0.041(7)
Largest diff. peak and hole	1.236 and -1.882 e.Å ⁻³

Notes:

The structure contains four crystallographically-independent platinum complexes with one acetonitrile molecule per platinum complex.

The hydrogen atoms bonded to N(2), N(102), N(202) and N(302) (one per crystallographically-independent platinum complex) were located in the electron density and their positions refined subject to suitable distance restraints, (N-H = 0.91 (2) Å and Pd ... H = 2.48 (4) Å and C(104)-H(12C) = C(112)-H(12C) = 1.92 (4) Å). The isotropic thermal parameters (U_{iso}) of these hydrogen atoms were set at 1.2 times the equivalent isotropic thermal parameter (U_{eq}) of the parent nitrogen atom. All remaining hydrogen atoms were fixed as riding models. The hydrogen bonding is detailed in Table 7, of this section.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*rac*)-7. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(1)	4373(10)	1349(10)	4311(2)	24(2)
C(2)	4417(10)	2692(10)	4176(2)	27(2)
C(3)	3934(9)	2097(9)	3869(2)	22(2)
C(4)	4454(8)	2506(10)	3573(2)	21(2)
C(5)	3592(9)	-336(10)	3927(2)	23(2)
C(6)	3359(9)	-760(10)	3599(3)	24(2)
C(7)	2369(11)	-234(11)	3425(3)	38(3)
C(8)	2076(12)	-718(13)	3140(3)	45(3)
C(9)	2752(13)	-1712(13)	3016(3)	47(3)
C(10)	3747(12)	-2219(12)	3197(3)	42(3)
C(11)	4045(10)	-1746(10)	3489(3)	28(3)
C(12)	6385(10)	2546(10)	3294(2)	26(2)
C(13)	5763(10)	1802(10)	3029(2)	29(2)
C(14)	5900(11)	505(11)	2994(2)	38(3)
C(15)	5379(13)	-131(12)	2743(3)	50(3)
C(16)	4645(11)	482(14)	2522(3)	47(3)
C(17)	4538(14)	1797(13)	2549(3)	60(4)
C(18)	5077(11)	2434(12)	2803(2)	45(3)
C(19)	5241(9)	865(9)	4566(2)	20(2)
C(20)	5029(9)	-339(9)	4688(2)	21(2)
C(21)	5781(10)	-815(10)	4933(2)	28(2)
C(22)	6736(11)	-71(11)	5062(3)	32(3)
C(23)	6952(10)	1112(12)	4950(3)	35(3)
C(24)	6217(9)	1582(11)	4697(2)	29(3)
N(1)	4432(7)	792(8)	3982(2)	24(2)
N(2)	5836(7)	2299(9)	3598(2)	22(2)
Cl(1)	6644(2)	-1248(2)	4098(1)	22(1)

Cl(2)	8233(2)	506(3)	3661(1)	23(1)
Pt(1)	6231(1)	612(1)	3828(1)	18(1)
C(101)	8463(9)	1280(11)	684(2)	23(2)
C(102)	7203(9)	1239(12)	828(2)	23(2)
C(103)	7907(9)	1661(10)	1127(2)	20(2)
C(104)	7656(10)	1083(11)	1427(3)	24(3)
C(105)	10241(9)	2079(10)	1043(3)	24(3)
C(106)	10727(10)	2330(12)	1369(2)	26(3)
C(107)	10204(10)	3265(12)	1541(3)	31(3)
C(108)	10681(12)	3548(13)	1831(3)	46(4)
C(109)	11707(14)	2872(13)	1948(3)	48(4)
C(110)	12296(13)	1988(12)	1785(3)	42(3)
C(111)	11791(11)	1662(11)	1497(3)	30(3)
C(112)	7735(9)	-922(10)	1724(3)	26(3)
C(113)	8519(11)	-301(11)	1983(3)	35(3)
C(114)	9816(10)	-463(13)	2007(3)	33(3)
C(115)	10502(13)	72(13)	2252(3)	47(4)
C(116)	9906(14)	759(14)	2473(3)	50(3)
C(117)	8646(14)	898(13)	2456(3)	52(4)
C(118)	7936(12)	348(13)	2204(3)	46(3)
C(119)	8776(9)	454(11)	425(2)	24(2)
C(120)	9948(10)	538(13)	311(2)	31(2)
C(121)	10247(13)	-155(13)	53(3)	44(3)
C(122)	9379(13)	-889(12)	-95(3)	42(3)
C(123)	8158(14)	-979(11)	9(3)	43(3)
C(124)	7889(12)	-328(10)	271(3)	32(3)
N(101)	9140(7)	1207(9)	1007(2)	19(2)
N(102)	7885(8)	-311(8)	1416(2)	23(2)
Cl(11)	11247(2)	-933(2)	925(1)	24(1)
Cl(12)	9695(2)	-2689(3)	1372(1)	25(1)
Pt(11)	9460(1)	-628(1)	1182(1)	18(1)
C(201)	10235(9)	6385(9)	4329(2)	21(2)
C(202)	10125(9)	7742(9)	4193(2)	22(2)
C(203)	10465(9)	7148(9)	3887(2)	20(2)
C(204)	9800(9)	7546(10)	3593(2)	25(2)
C(205)	10859(10)	4721(10)	3951(2)	26(3)
C(206)	10967(9)	4322(12)	3628(3)	27(3)
C(207)	10290(10)	3250(10)	3506(3)	27(3)
C(208)	10498(12)	2819(11)	3215(3)	38(3)
C(209)	11370(12)	3405(11)	3043(3)	38(3)
C(210)	12030(11)	4483(13)	3157(3)	41(3)
C(211)	11818(10)	4906(11)	3454(3)	29(3)
C(212)	7764(9)	7516(10)	3288(2)	24(2)
C(213)	8259(9)	6793(11)	3033(2)	26(2)
C(214)	8107(10)	5459(12)	3012(3)	34(3)
C(215)	8533(14)	4787(13)	2770(3)	50(4)
C(216)	9143(13)	5462(18)	2543(3)	59(4)
C(217)	9278(15)	6752(17)	2556(3)	65(4)
C(218)	8825(10)	7419(12)	2801(3)	36(3)
C(219)	9506(8)	5875(9)	4575(2)	20(2)
C(220)	9776(9)	4686(10)	4706(2)	26(2)
C(221)	9156(10)	4170(11)	4944(3)	31(3)
C(222)	8256(11)	4937(13)	5070(3)	39(3)
C(223)	7985(10)	6138(13)	4956(2)	33(3)
C(224)	8584(10)	6617(11)	4709(2)	29(3)
N(201)	10011(7)	5842(7)	4002(2)	19(2)
N(202)	8438(7)	7286(9)	3601(2)	21(2)

Cl(21)	7889(2)	3754(2)	4099(1)	22(1)
Cl(22)	6077(2)	5499(3)	3654(1)	23(1)
Pt(21)	8162(1)	5625(1)	3833(1)	17(1)
C(301)	3462(9)	5499(12)	688(2)	21(2)
C(302)	2201(8)	5561(14)	834(2)	26(2)
C(303)	2923(9)	5114(10)	1134(2)	21(2)
C(304)	2658(8)	5689(11)	1430(2)	17(2)
C(305)	5271(9)	4732(10)	1048(3)	26(3)
C(306)	5777(9)	4509(11)	1373(2)	22(2)
C(307)	6754(10)	5227(12)	1503(3)	36(3)
C(308)	7255(14)	5001(13)	1789(3)	50(4)
C(309)	6758(14)	3980(13)	1967(3)	50(4)
C(310)	5765(13)	3288(14)	1840(3)	47(4)
C(311)	5274(12)	3518(12)	1535(3)	38(3)
C(312)	2719(10)	7685(11)	1731(2)	26(3)
C(313)	3536(9)	7139(10)	1986(2)	21(2)
C(314)	4823(10)	7403(13)	2031(3)	35(3)
C(315)	5571(12)	6879(12)	2274(3)	39(3)
C(316)	5066(12)	6087(13)	2477(3)	46(3)
C(317)	3815(12)	5783(14)	2432(3)	47(3)
C(318)	3067(11)	6317(14)	2195(3)	40(3)
C(319)	3806(10)	6380(10)	435(2)	24(3)
C(320)	4997(11)	6275(12)	318(2)	32(3)
C(321)	5268(12)	6945(12)	63(3)	36(3)
C(322)	4336(14)	7717(12)	-91(3)	46(4)
C(323)	3178(13)	7787(12)	16(3)	41(3)
C(324)	2891(12)	7112(10)	276(3)	33(3)
N(301)	4155(7)	5613(10)	1010(2)	20(1)
N(302)	2888(8)	7111(9)	1424(2)	24(2)
Cl(31)	6230(2)	7767(2)	924(1)	23(1)
Cl(32)	4663(2)	9527(2)	1372(1)	25(1)
Pt(31)	4451(1)	7448(1)	1187(1)	18(1)
C(401)	3472(11)	1302(14)	642(3)	31(3)
N(401)	3093(11)	2284(11)	690(3)	52(3)
C(402)	3953(11)	74(12)	576(3)	33(3)
C(501)	4321(11)	6358(11)	4315(2)	28(3)
C(502)	5562(9)	6008(10)	4441(3)	29(3)
N(501)	3349(10)	6666(11)	4220(3)	52(3)
C(601)	8457(10)	5490(13)	639(2)	25(2)
C(602)	8921(11)	6786(10)	583(3)	32(3)
N(601)	8061(10)	4483(11)	681(3)	49(3)
C(701)	300(10)	1384(10)	4311(3)	26(2)
C(702)	-849(9)	1030(10)	4449(3)	28(3)
N(701)	1207(9)	1620(10)	4211(3)	47(3)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (*rac*)-7.

C(1)-C(19)	1.495(15)
C(1)-C(2)	1.526(15)
C(1)-N(1)	1.564(12)
C(1)-H(1)	1.0000
C(2)-C(3)	1.545(15)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.511(13)
C(3)-N(1)	1.535(13)

C(3)-H(3)	1.0000
C(4)-N(2)	1.491(12)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-N(1)	1.492(13)
C(5)-C(6)	1.513(15)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(11)	1.373(15)
C(6)-C(7)	1.377(16)
C(7)-C(8)	1.367(18)
C(7)-H(7)	0.9500
C(8)-C(9)	1.397(18)
C(8)-H(8)	0.9500
C(9)-C(10)	1.387(18)
C(9)-H(9)	0.9500
C(10)-C(11)	1.391(16)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-C(13)	1.515(15)
C(12)-N(2)	1.517(13)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(18)	1.363(12)
C(13)-C(14)	1.374(13)
C(14)-C(15)	1.374(13)
C(14)-H(14)	0.9500
C(15)-C(16)	1.365(14)
C(15)-H(15)	0.9500
C(16)-C(17)	1.385(14)
C(16)-H(16)	0.9500
C(17)-C(18)	1.390(14)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(24)	1.378(14)
C(19)-C(20)	1.392(13)
C(20)-C(21)	1.392(15)
C(20)-H(20)	0.9500
C(21)-C(22)	1.375(16)
C(21)-H(21)	0.9500
C(22)-C(23)	1.359(16)
C(22)-H(22)	0.9500
C(23)-C(24)	1.403(16)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
N(1)-Pt(1)	2.092(7)
N(2)-Pt(1)	2.062(9)
N(2)-H(2C)	0.92(2)
Cl(1)-Pt(1)	2.306(2)
Cl(2)-Pt(1)	2.314(2)
C(101)-C(119)	1.486(15)
C(101)-C(102)	1.529(14)
C(101)-N(101)	1.547(13)
C(101)-H(101)	1.0000
C(102)-C(103)	1.532(14)
C(102)-H(10A)	0.9900
C(102)-H(10B)	0.9900

C(103)-C(104)	1.492(15)
C(103)-N(101)	1.530(12)
C(103)-H(103)	1.0000
C(104)-N(102)	1.479(14)
C(104)-H(10C)	0.9900
C(104)-H(10D)	0.9900
C(105)-N(101)	1.490(13)
C(105)-C(106)	1.512(15)
C(105)-H(10E)	0.9900
C(105)-H(10F)	0.9900
C(106)-C(107)	1.378(16)
C(106)-C(111)	1.419(16)
C(107)-C(108)	1.374(18)
C(107)-H(107)	0.9500
C(108)-C(109)	1.38(2)
C(108)-H(108)	0.9500
C(109)-C(110)	1.352(18)
C(109)-H(109)	0.9500
C(110)-C(111)	1.383(17)
C(110)-H(110)	0.9500
C(111)-H(111)	0.9500
C(112)-C(113)	1.511(17)
C(112)-N(102)	1.516(14)
C(112)-H(11A)	0.9900
C(112)-H(11B)	0.9900
C(113)-C(118)	1.369(16)
C(113)-C(114)	1.394(16)
C(114)-C(115)	1.379(17)
C(114)-H(114)	0.9500
C(115)-C(116)	1.395(18)
C(115)-H(115)	0.9500
C(116)-C(117)	1.352(18)
C(116)-H(116)	0.9500
C(117)-C(118)	1.419(19)
C(117)-H(117)	0.9500
C(118)-H(118)	0.9500
C(119)-C(120)	1.385(13)
C(119)-C(124)	1.392(16)
C(120)-C(121)	1.398(18)
C(120)-H(120)	0.9500
C(121)-C(122)	1.339(19)
C(121)-H(121)	0.9500
C(122)-C(123)	1.416(19)
C(122)-H(122)	0.9500
C(123)-C(124)	1.382(16)
C(123)-H(123)	0.9500
C(124)-H(124)	0.9500
N(101)-Pt(11)	2.088(9)
N(102)-Pt(11)	2.060(9)
N(102)-H(12C)	0.901(18)
Cl(11)-Pt(11)	2.309(2)
Cl(12)-Pt(11)	2.319(3)
C(201)-C(219)	1.476(13)
C(201)-C(202)	1.541(14)
C(201)-N(201)	1.549(12)
C(201)-H(201)	1.0000
C(202)-C(203)	1.547(14)

C(202)-H(20A)	0.9900
C(202)-H(20B)	0.9900
C(203)-C(204)	1.491(14)
C(203)-N(201)	1.545(11)
C(203)-H(203)	1.0000
C(204)-N(202)	1.484(12)
C(204)-H(20C)	0.9900
C(204)-H(20D)	0.9900
C(205)-C(206)	1.493(15)
C(205)-N(201)	1.508(12)
C(205)-H(20E)	0.9900
C(205)-H(20F)	0.9900
C(206)-C(211)	1.372(14)
C(206)-C(207)	1.419(16)
C(207)-C(208)	1.388(15)
C(207)-H(207)	0.9500
C(208)-C(209)	1.383(16)
C(208)-H(208)	0.9500
C(209)-C(210)	1.403(17)
C(209)-H(209)	0.9500
C(210)-C(211)	1.409(16)
C(210)-H(210)	0.9500
C(211)-H(211)	0.9500
C(212)-C(213)	1.480(14)
C(212)-N(202)	1.526(13)
C(212)-H(21A)	0.9900
C(212)-H(21B)	0.9900
C(213)-C(218)	1.383(14)
C(213)-C(214)	1.406(16)
C(214)-C(215)	1.377(15)
C(214)-H(214)	0.9500
C(215)-C(216)	1.420(19)
C(215)-H(215)	0.9500
C(216)-C(217)	1.36(2)
C(216)-H(216)	0.9500
C(217)-C(218)	1.397(18)
C(217)-H(217)	0.9500
C(218)-H(218)	0.9500
C(219)-C(220)	1.391(14)
C(219)-C(224)	1.413(13)
C(220)-C(221)	1.389(15)
C(220)-H(220)	0.9500
C(221)-C(222)	1.396(16)
C(221)-H(221)	0.9500
C(222)-C(223)	1.375(17)
C(222)-H(222)	0.9500
C(223)-C(224)	1.393(15)
C(223)-H(223)	0.9500
C(224)-H(224)	0.9500
N(201)-Pt(21)	2.075(8)
N(202)-Pt(21)	2.047(9)
N(202)-H(22C)	0.91(2)
Cl(21)-Pt(21)	2.308(2)
Cl(22)-Pt(21)	2.317(2)
C(301)-C(319)	1.508(15)
C(301)-C(302)	1.532(12)
C(301)-N(301)	1.554(12)

C(301)-H(301)	1.0000
C(302)-C(303)	1.556(14)
C(302)-H(30A)	0.9900
C(302)-H(30B)	0.9900
C(303)-C(304)	1.476(13)
C(303)-N(301)	1.552(12)
C(303)-H(303)	1.0000
C(304)-N(302)	1.508(14)
C(304)-H(30C)	0.9900
C(304)-H(30D)	0.9900
C(305)-N(301)	1.508(13)
C(305)-C(306)	1.512(15)
C(305)-H(30E)	0.9900
C(305)-H(30F)	0.9900
C(306)-C(307)	1.377(16)
C(306)-C(311)	1.387(16)
C(307)-C(308)	1.352(18)
C(307)-H(307)	0.9500
C(308)-C(309)	1.448(19)
C(308)-H(308)	0.9500
C(309)-C(310)	1.37(2)
C(309)-H(309)	0.9500
C(310)-C(311)	1.426(18)
C(310)-H(310)	0.9500
C(311)-H(311)	0.9500
C(312)-C(313)	1.489(15)
C(312)-N(302)	1.496(13)
C(312)-H(31A)	0.9900
C(312)-H(31B)	0.9900
C(313)-C(318)	1.376(15)
C(313)-C(314)	1.404(15)
C(314)-C(315)	1.401(17)
C(314)-H(314)	0.9500
C(315)-C(316)	1.357(17)
C(315)-H(315)	0.9500
C(316)-C(317)	1.376(17)
C(316)-H(316)	0.9500
C(317)-C(318)	1.386(17)
C(317)-H(317)	0.9500
C(318)-H(318)	0.9500
C(319)-C(324)	1.393(16)
C(319)-C(320)	1.411(15)
C(320)-C(321)	1.369(16)
C(320)-H(320)	0.9500
C(321)-C(322)	1.417(19)
C(321)-H(321)	0.9500
C(322)-C(323)	1.356(18)
C(322)-H(322)	0.9500
C(323)-C(324)	1.395(16)
C(323)-H(323)	0.9500
C(324)-H(324)	0.9500
N(301)-Pt(31)	2.087(10)
N(302)-Pt(31)	2.061(9)
N(302)-H(32C)	0.91(2)
Cl(31)-Pt(31)	2.317(2)
Cl(32)-Pt(31)	2.327(3)
C(401)-N(401)	1.130(16)

C(401)-C(402)	1.420(17)
C(402)-H(40A)	0.9800
C(402)-H(40B)	0.9800
C(402)-H(40C)	0.9800
C(501)-N(501)	1.140(14)
C(501)-C(502)	1.450(16)
C(502)-H(50A)	0.9800
C(502)-H(50B)	0.9800
C(502)-H(50C)	0.9800
C(601)-N(601)	1.154(16)
C(601)-C(602)	1.470(16)
C(602)-H(60A)	0.9800
C(602)-H(60B)	0.9800
C(602)-H(60C)	0.9800
C(701)-N(701)	1.121(13)
C(701)-C(702)	1.455(14)
C(702)-H(70A)	0.9800
C(702)-H(70B)	0.9800
C(702)-H(70C)	0.9800
C(19)-C(1)-C(2)	124.6(9)
C(19)-C(1)-N(1)	120.3(8)
C(2)-C(1)-N(1)	88.9(7)
C(19)-C(1)-H(1)	107.0
C(2)-C(1)-H(1)	107.0
N(1)-C(1)-H(1)	107.0
C(1)-C(2)-C(3)	87.1(8)
C(1)-C(2)-H(2A)	114.1
C(3)-C(2)-H(2A)	114.1
C(1)-C(2)-H(2B)	114.1
C(3)-C(2)-H(2B)	114.1
H(2A)-C(2)-H(2B)	111.3
C(4)-C(3)-N(1)	112.9(8)
C(4)-C(3)-C(2)	121.2(8)
N(1)-C(3)-C(2)	89.3(8)
C(4)-C(3)-H(3)	110.5
N(1)-C(3)-H(3)	110.5
C(2)-C(3)-H(3)	110.5
N(2)-C(4)-C(3)	108.4(8)
N(2)-C(4)-H(4A)	110.0
C(3)-C(4)-H(4A)	110.0
N(2)-C(4)-H(4B)	110.0
C(3)-C(4)-H(4B)	110.0
H(4A)-C(4)-H(4B)	108.4
N(1)-C(5)-C(6)	116.3(8)
N(1)-C(5)-H(5A)	108.2
C(6)-C(5)-H(5A)	108.2
N(1)-C(5)-H(5B)	108.2
C(6)-C(5)-H(5B)	108.2
H(5A)-C(5)-H(5B)	107.4
C(11)-C(6)-C(7)	120.9(11)
C(11)-C(6)-C(5)	120.0(10)
C(7)-C(6)-C(5)	118.8(10)
C(8)-C(7)-C(6)	118.6(12)
C(8)-C(7)-H(7)	120.7
C(6)-C(7)-H(7)	120.7
C(7)-C(8)-C(9)	122.6(12)
C(7)-C(8)-H(8)	118.7

C(9)-C(8)-H(8)	118.7
C(10)-C(9)-C(8)	117.3(12)
C(10)-C(9)-H(9)	121.3
C(8)-C(9)-H(9)	121.3
C(9)-C(10)-C(11)	120.6(12)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7
C(6)-C(11)-C(10)	119.8(11)
C(6)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(13)-C(12)-N(2)	114.4(8)
C(13)-C(12)-H(12A)	108.7
N(2)-C(12)-H(12A)	108.7
C(13)-C(12)-H(12B)	108.7
N(2)-C(12)-H(12B)	108.7
H(12A)-C(12)-H(12B)	107.6
C(18)-C(13)-C(14)	117.0(11)
C(18)-C(13)-C(12)	119.8(10)
C(14)-C(13)-C(12)	123.2(9)
C(15)-C(14)-C(13)	121.8(11)
C(15)-C(14)-H(14)	119.1
C(13)-C(14)-H(14)	119.1
C(16)-C(15)-C(14)	121.7(12)
C(16)-C(15)-H(15)	119.2
C(14)-C(15)-H(15)	119.2
C(15)-C(16)-C(17)	116.8(12)
C(15)-C(16)-H(16)	121.6
C(17)-C(16)-H(16)	121.6
C(16)-C(17)-C(18)	120.9(12)
C(16)-C(17)-H(17)	119.6
C(18)-C(17)-H(17)	119.6
C(13)-C(18)-C(17)	121.6(12)
C(13)-C(18)-H(18)	119.2
C(17)-C(18)-H(18)	119.2
C(24)-C(19)-C(20)	118.1(10)
C(24)-C(19)-C(1)	122.8(9)
C(20)-C(19)-C(1)	119.0(9)
C(21)-C(20)-C(19)	121.3(10)
C(21)-C(20)-H(20)	119.4
C(19)-C(20)-H(20)	119.4
C(22)-C(21)-C(20)	119.4(10)
C(22)-C(21)-H(21)	120.3
C(20)-C(21)-H(21)	120.3
C(23)-C(22)-C(21)	120.3(12)
C(23)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(22)-C(23)-C(24)	120.5(12)
C(22)-C(23)-H(23)	119.8
C(24)-C(23)-H(23)	119.8
C(19)-C(24)-C(23)	120.4(11)
C(19)-C(24)-H(24)	119.8
C(23)-C(24)-H(24)	119.8
C(5)-N(1)-C(3)	117.3(8)
C(5)-N(1)-C(1)	112.4(7)
C(3)-N(1)-C(1)	86.1(7)
C(5)-N(1)-Pt(1)	115.7(6)
C(3)-N(1)-Pt(1)	106.4(5)

C(1)-N(1)-Pt(1)	115.4(6)
C(4)-N(2)-C(12)	110.6(8)
C(4)-N(2)-Pt(1)	109.3(6)
C(12)-N(2)-Pt(1)	119.8(6)
C(4)-N(2)-H(2C)	118(6)
C(12)-N(2)-H(2C)	94(6)
Pt(1)-N(2)-H(2C)	105(3)
N(2)-Pt(1)-N(1)	85.4(3)
N(2)-Pt(1)-Cl(1)	178.1(2)
N(1)-Pt(1)-Cl(1)	93.3(2)
N(2)-Pt(1)-Cl(2)	92.8(2)
N(1)-Pt(1)-Cl(2)	177.5(3)
Cl(1)-Pt(1)-Cl(2)	88.56(9)
C(119)-C(101)-C(102)	123.6(10)
C(119)-C(101)-N(101)	123.9(8)
C(102)-C(101)-N(101)	89.4(7)
C(119)-C(101)-H(101)	105.9
C(102)-C(101)-H(101)	105.9
N(101)-C(101)-H(101)	105.9
C(101)-C(102)-C(103)	87.2(8)
C(101)-C(102)-H(10A)	114.1
C(103)-C(102)-H(10A)	114.1
C(101)-C(102)-H(10B)	114.1
C(103)-C(102)-H(10B)	114.1
H(10A)-C(102)-H(10B)	111.3
C(104)-C(103)-N(101)	113.1(8)
C(104)-C(103)-C(102)	122.2(9)
N(101)-C(103)-C(102)	90.0(7)
C(104)-C(103)-H(103)	110.0
N(101)-C(103)-H(103)	110.0
C(102)-C(103)-H(103)	110.0
N(102)-C(104)-C(103)	109.2(9)
N(102)-C(104)-H(10C)	109.8
C(103)-C(104)-H(10C)	109.8
N(102)-C(104)-H(10D)	109.8
C(103)-C(104)-H(10D)	109.8
H(10C)-C(104)-H(10D)	108.3
N(101)-C(105)-C(106)	115.1(8)
N(101)-C(105)-H(10E)	108.5
C(106)-C(105)-H(10E)	108.5
N(101)-C(105)-H(10F)	108.5
C(106)-C(105)-H(10F)	108.5
H(10E)-C(105)-H(10F)	107.5
C(107)-C(106)-C(111)	118.5(11)
C(107)-C(106)-C(105)	121.1(10)
C(111)-C(106)-C(105)	120.3(10)
C(108)-C(107)-C(106)	121.5(12)
C(108)-C(107)-H(107)	119.2
C(106)-C(107)-H(107)	119.2
C(107)-C(108)-C(109)	118.2(12)
C(107)-C(108)-H(108)	120.9
C(109)-C(108)-H(108)	120.9
C(110)-C(109)-C(108)	122.8(13)
C(110)-C(109)-H(109)	118.6
C(108)-C(109)-H(109)	118.6
C(109)-C(110)-C(111)	119.1(14)
C(109)-C(110)-H(110)	120.4

C(111)-C(110)-H(110)	120.4
C(110)-C(111)-C(106)	119.6(12)
C(110)-C(111)-H(111)	120.2
C(106)-C(111)-H(111)	120.2
C(113)-C(112)-N(102)	113.8(8)
C(113)-C(112)-H(11A)	108.8
N(102)-C(112)-H(11A)	108.8
C(113)-C(112)-H(11B)	108.8
N(102)-C(112)-H(11B)	108.8
H(11A)-C(112)-H(11B)	107.7
C(118)-C(113)-C(114)	120.4(12)
C(118)-C(113)-C(112)	119.3(11)
C(114)-C(113)-C(112)	120.2(10)
C(115)-C(114)-C(113)	118.9(12)
C(115)-C(114)-H(114)	120.5
C(113)-C(114)-H(114)	120.5
C(114)-C(115)-C(116)	120.5(12)
C(114)-C(115)-H(115)	119.8
C(116)-C(115)-H(115)	119.8
C(117)-C(116)-C(115)	121.2(13)
C(117)-C(116)-H(116)	119.4
C(115)-C(116)-H(116)	119.4
C(116)-C(117)-C(118)	118.6(12)
C(116)-C(117)-H(117)	120.7
C(118)-C(117)-H(117)	120.7
C(113)-C(118)-C(117)	120.5(12)
C(113)-C(118)-H(118)	119.8
C(117)-C(118)-H(118)	119.8
C(120)-C(119)-C(124)	117.7(11)
C(120)-C(119)-C(101)	119.9(11)
C(124)-C(119)-C(101)	122.1(9)
C(119)-C(120)-C(121)	121.5(12)
C(119)-C(120)-H(120)	119.2
C(121)-C(120)-H(120)	119.2
C(122)-C(121)-C(120)	120.1(12)
C(122)-C(121)-H(121)	119.9
C(120)-C(121)-H(121)	119.9
C(121)-C(122)-C(123)	120.2(12)
C(121)-C(122)-H(122)	119.9
C(123)-C(122)-H(122)	119.9
C(124)-C(123)-C(122)	119.1(12)
C(124)-C(123)-H(123)	120.4
C(122)-C(123)-H(123)	120.4
C(123)-C(124)-C(119)	121.2(11)
C(123)-C(124)-H(124)	119.4
C(119)-C(124)-H(124)	119.4
C(105)-N(101)-C(103)	117.9(8)
C(105)-N(101)-C(101)	112.6(8)
C(103)-N(101)-C(101)	86.6(7)
C(105)-N(101)-Pt(11)	114.5(6)
C(103)-N(101)-Pt(11)	106.3(6)
C(101)-N(101)-Pt(11)	116.0(7)
C(104)-N(102)-C(112)	110.9(9)
C(104)-N(102)-Pt(11)	108.6(7)
C(112)-N(102)-Pt(11)	121.2(7)
C(104)-N(102)-H(12C)	108(3)
C(112)-N(102)-H(12C)	103(3)

Pt(11)-N(102)-H(12C)	104(3)
N(102)-Pt(11)-N(101)	85.3(3)
N(102)-Pt(11)-Cl(11)	178.5(3)
N(101)-Pt(11)-Cl(11)	93.8(2)
N(102)-Pt(11)-Cl(12)	92.5(3)
N(101)-Pt(11)-Cl(12)	176.7(2)
Cl(11)-Pt(11)-Cl(12)	88.56(9)
C(219)-C(201)-C(202)	125.9(8)
C(219)-C(201)-N(201)	119.5(8)
C(202)-C(201)-N(201)	88.6(7)
C(219)-C(201)-H(201)	106.9
C(202)-C(201)-H(201)	106.9
N(201)-C(201)-H(201)	106.9
C(201)-C(202)-C(203)	87.2(7)
C(201)-C(202)-H(20A)	114.1
C(203)-C(202)-H(20A)	114.1
C(201)-C(202)-H(20B)	114.1
C(203)-C(202)-H(20B)	114.1
H(20A)-C(202)-H(20B)	111.3
C(204)-C(203)-N(201)	112.8(8)
C(204)-C(203)-C(202)	121.0(8)
N(201)-C(203)-C(202)	88.5(7)
C(204)-C(203)-H(203)	110.9
N(201)-C(203)-H(203)	110.9
C(202)-C(203)-H(203)	110.9
N(202)-C(204)-C(203)	109.8(8)
N(202)-C(204)-H(20C)	109.7
C(203)-C(204)-H(20C)	109.7
N(202)-C(204)-H(20D)	109.7
C(203)-C(204)-H(20D)	109.7
H(20C)-C(204)-H(20D)	108.2
C(206)-C(205)-N(201)	116.4(9)
C(206)-C(205)-H(20E)	108.2
N(201)-C(205)-H(20E)	108.2
C(206)-C(205)-H(20F)	108.2
N(201)-C(205)-H(20F)	108.2
H(20E)-C(205)-H(20F)	107.4
C(211)-C(206)-C(207)	118.9(11)
C(211)-C(206)-C(205)	120.3(11)
C(207)-C(206)-C(205)	120.5(10)
C(208)-C(207)-C(206)	119.5(10)
C(208)-C(207)-H(207)	120.2
C(206)-C(207)-H(207)	120.2
C(209)-C(208)-C(207)	121.1(11)
C(209)-C(208)-H(208)	119.4
C(207)-C(208)-H(208)	119.4
C(208)-C(209)-C(210)	120.2(10)
C(208)-C(209)-H(209)	119.9
C(210)-C(209)-H(209)	119.9
C(209)-C(210)-C(211)	118.2(10)
C(209)-C(210)-H(210)	120.9
C(211)-C(210)-H(210)	120.9
C(206)-C(211)-C(210)	122.1(11)
C(206)-C(211)-H(211)	119.0
C(210)-C(211)-H(211)	119.0
C(213)-C(212)-N(202)	115.5(8)
C(213)-C(212)-H(21A)	108.4

N(202)-C(212)-H(21A)	108.4
C(213)-C(212)-H(21B)	108.4
N(202)-C(212)-H(21B)	108.4
H(21A)-C(212)-H(21B)	107.5
C(218)-C(213)-C(214)	118.5(11)
C(218)-C(213)-C(212)	120.8(10)
C(214)-C(213)-C(212)	120.6(9)
C(215)-C(214)-C(213)	120.8(11)
C(215)-C(214)-H(214)	119.6
C(213)-C(214)-H(214)	119.6
C(214)-C(215)-C(216)	118.8(13)
C(214)-C(215)-H(215)	120.6
C(216)-C(215)-H(215)	120.6
C(217)-C(216)-C(215)	121.0(13)
C(217)-C(216)-H(216)	119.5
C(215)-C(216)-H(216)	119.5
C(216)-C(217)-C(218)	119.3(13)
C(216)-C(217)-H(217)	120.4
C(218)-C(217)-H(217)	120.4
C(213)-C(218)-C(217)	121.5(13)
C(213)-C(218)-H(218)	119.3
C(217)-C(218)-H(218)	119.3
C(220)-C(219)-C(224)	116.8(9)
C(220)-C(219)-C(201)	121.3(9)
C(224)-C(219)-C(201)	121.6(9)
C(221)-C(220)-C(219)	124.2(10)
C(221)-C(220)-H(220)	117.9
C(219)-C(220)-H(220)	117.9
C(220)-C(221)-C(222)	117.0(11)
C(220)-C(221)-H(221)	121.5
C(222)-C(221)-H(221)	121.5
C(223)-C(222)-C(221)	121.0(11)
C(223)-C(222)-H(222)	119.5
C(221)-C(222)-H(222)	119.5
C(222)-C(223)-C(224)	121.0(11)
C(222)-C(223)-H(223)	119.5
C(224)-C(223)-H(223)	119.5
C(223)-C(224)-C(219)	119.9(10)
C(223)-C(224)-H(224)	120.1
C(219)-C(224)-H(224)	120.1
C(205)-N(201)-C(203)	115.7(7)
C(205)-N(201)-C(201)	111.4(7)
C(203)-N(201)-C(201)	86.9(7)
C(205)-N(201)-Pt(21)	115.5(6)
C(203)-N(201)-Pt(21)	107.1(6)
C(201)-N(201)-Pt(21)	117.0(5)
C(204)-N(202)-C(212)	110.7(8)
C(204)-N(202)-Pt(21)	110.0(6)
C(212)-N(202)-Pt(21)	120.5(7)
C(204)-N(202)-H(22C)	106(6)
C(212)-N(202)-H(22C)	99(6)
Pt(21)-N(202)-H(22C)	110(3)
N(202)-Pt(21)-N(201)	85.3(3)
N(202)-Pt(21)-Cl(21)	178.9(3)
N(201)-Pt(21)-Cl(21)	93.6(2)
N(202)-Pt(21)-Cl(22)	92.7(2)
N(201)-Pt(21)-Cl(22)	176.7(2)

Cl(21)-Pt(21)-Cl(22)	88.37(9)
C(319)-C(301)-C(302)	123.2(10)
C(319)-C(301)-N(301)	119.8(9)
C(302)-C(301)-N(301)	89.8(7)
C(319)-C(301)-H(301)	107.4
C(302)-C(301)-H(301)	107.4
N(301)-C(301)-H(301)	107.4
C(301)-C(302)-C(303)	86.7(7)
C(301)-C(302)-H(30A)	114.2
C(303)-C(302)-H(30A)	114.2
C(301)-C(302)-H(30B)	114.2
C(303)-C(302)-H(30B)	114.2
H(30A)-C(302)-H(30B)	111.4
C(304)-C(303)-N(301)	113.1(8)
C(304)-C(303)-C(302)	120.7(9)
N(301)-C(303)-C(302)	89.0(7)
C(304)-C(303)-H(303)	110.7
N(301)-C(303)-H(303)	110.7
C(302)-C(303)-H(303)	110.7
C(303)-C(304)-N(302)	110.2(8)
C(303)-C(304)-H(30C)	109.6
N(302)-C(304)-H(30C)	109.6
C(303)-C(304)-H(30D)	109.6
N(302)-C(304)-H(30D)	109.6
H(30C)-C(304)-H(30D)	108.1
N(301)-C(305)-C(306)	115.3(8)
N(301)-C(305)-H(30E)	108.5
C(306)-C(305)-H(30E)	108.5
N(301)-C(305)-H(30F)	108.5
C(306)-C(305)-H(30F)	108.5
H(30E)-C(305)-H(30F)	107.5
C(307)-C(306)-C(311)	120.4(11)
C(307)-C(306)-C(305)	121.2(10)
C(311)-C(306)-C(305)	118.3(11)
C(308)-C(307)-C(306)	121.9(12)
C(308)-C(307)-H(307)	119.0
C(306)-C(307)-H(307)	119.0
C(307)-C(308)-C(309)	119.7(14)
C(307)-C(308)-H(308)	120.2
C(309)-C(308)-H(308)	120.2
C(310)-C(309)-C(308)	118.2(13)
C(310)-C(309)-H(309)	120.9
C(308)-C(309)-H(309)	120.9
C(309)-C(310)-C(311)	121.1(13)
C(309)-C(310)-H(310)	119.4
C(311)-C(310)-H(310)	119.4
C(306)-C(311)-C(310)	118.5(13)
C(306)-C(311)-H(311)	120.7
C(310)-C(311)-H(311)	120.7
C(313)-C(312)-N(302)	115.1(8)
C(313)-C(312)-H(31A)	108.5
N(302)-C(312)-H(31A)	108.5
C(313)-C(312)-H(31B)	108.5
N(302)-C(312)-H(31B)	108.5
H(31A)-C(312)-H(31B)	107.5
C(318)-C(313)-C(314)	115.5(11)
C(318)-C(313)-C(312)	121.3(9)

C(314)-C(313)-C(312)	123.2(10)
C(315)-C(314)-C(313)	122.1(11)
C(315)-C(314)-H(314)	118.9
C(313)-C(314)-H(314)	118.9
C(316)-C(315)-C(314)	120.5(12)
C(316)-C(315)-H(315)	119.8
C(314)-C(315)-H(315)	119.8
C(315)-C(316)-C(317)	118.3(12)
C(315)-C(316)-H(316)	120.8
C(317)-C(316)-H(316)	120.8
C(316)-C(317)-C(318)	121.4(12)
C(316)-C(317)-H(317)	119.3
C(318)-C(317)-H(317)	119.3
C(313)-C(318)-C(317)	122.2(11)
C(313)-C(318)-H(318)	118.9
C(317)-C(318)-H(318)	118.9
C(324)-C(319)-C(320)	118.6(11)
C(324)-C(319)-C(301)	120.5(10)
C(320)-C(319)-C(301)	119.6(10)
C(321)-C(320)-C(319)	120.4(12)
C(321)-C(320)-H(320)	119.8
C(319)-C(320)-H(320)	119.8
C(320)-C(321)-C(322)	120.0(11)
C(320)-C(321)-H(321)	120.0
C(322)-C(321)-H(321)	120.0
C(323)-C(322)-C(321)	119.6(12)
C(323)-C(322)-H(322)	120.2
C(321)-C(322)-H(322)	120.2
C(322)-C(323)-C(324)	120.9(13)
C(322)-C(323)-H(323)	119.5
C(324)-C(323)-H(323)	119.5
C(319)-C(324)-C(323)	120.2(11)
C(319)-C(324)-H(324)	119.9
C(323)-C(324)-H(324)	119.9
C(305)-N(301)-C(303)	116.2(8)
C(305)-N(301)-C(301)	112.2(8)
C(303)-N(301)-C(301)	86.0(7)
C(305)-N(301)-Pt(31)	115.0(6)
C(303)-N(301)-Pt(31)	106.8(6)
C(301)-N(301)-Pt(31)	117.4(7)
C(312)-N(302)-C(304)	110.5(8)
C(312)-N(302)-Pt(31)	122.6(7)
C(304)-N(302)-Pt(31)	108.4(6)
C(312)-N(302)-H(32C)	109(6)
C(304)-N(302)-H(32C)	98(7)
Pt(31)-N(302)-H(32C)	105(3)
N(302)-Pt(31)-N(301)	85.6(3)
N(302)-Pt(31)-Cl(31)	178.3(3)
N(301)-Pt(31)-Cl(31)	93.2(2)
N(302)-Pt(31)-Cl(32)	92.6(3)
N(301)-Pt(31)-Cl(32)	176.6(2)
Cl(31)-Pt(31)-Cl(32)	88.62(9)
N(401)-C(401)-C(402)	179.0(13)
C(401)-C(402)-H(40A)	109.5
C(401)-C(402)-H(40B)	109.5
H(40A)-C(402)-H(40B)	109.5
C(401)-C(402)-H(40C)	109.5

H(40A)-C(402)-H(40C)	109.5
H(40B)-C(402)-H(40C)	109.5
N(501)-C(501)-C(502)	178.0(14)
C(501)-C(502)-H(50A)	109.5
C(501)-C(502)-H(50B)	109.5
H(50A)-C(502)-H(50B)	109.5
C(501)-C(502)-H(50C)	109.5
H(50A)-C(502)-H(50C)	109.5
H(50B)-C(502)-H(50C)	109.5
N(601)-C(601)-C(602)	178.1(13)
C(601)-C(602)-H(60A)	109.5
C(601)-C(602)-H(60B)	109.5
H(60A)-C(602)-H(60B)	109.5
C(601)-C(602)-H(60C)	109.5
H(60A)-C(602)-H(60C)	109.5
H(60B)-C(602)-H(60C)	109.5
N(701)-C(701)-C(702)	177.4(12)
C(701)-C(702)-H(70A)	109.5
C(701)-C(702)-H(70B)	109.5
H(70A)-C(702)-H(70B)	109.5
C(701)-C(702)-H(70C)	109.5
H(70A)-C(702)-H(70C)	109.5
H(70B)-C(702)-H(70C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*rac*)-**7**. The anisotropic displacement factor exponent takes the form: $-2 \sum [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	24(4)	28(4)	21(4)	-6(3)	9(4)	-4(4)
C(2)	23(4)	29(4)	29(5)	-5(3)	7(4)	0(4)
C(3)	20(4)	20(4)	27(4)	0(3)	6(4)	-1(4)
C(4)	20(5)	21(5)	23(6)	-1(5)	-1(4)	0(5)
C(5)	23(5)	37(6)	10(5)	-5(4)	8(4)	-8(5)
C(6)	18(5)	21(5)	31(6)	1(5)	-4(5)	-8(5)
C(7)	36(7)	29(6)	47(8)	7(6)	-8(6)	2(5)
C(8)	39(7)	50(8)	44(8)	13(7)	-20(6)	-4(7)
C(9)	55(8)	57(9)	29(7)	-1(6)	-6(7)	-19(7)
C(10)	43(7)	41(7)	40(8)	-9(6)	-7(6)	-4(6)
C(11)	26(6)	28(6)	29(6)	-4(5)	0(5)	-14(5)
C(12)	35(6)	13(5)	32(6)	0(5)	11(5)	-2(5)
C(13)	29(6)	32(5)	28(6)	10(5)	6(4)	10(5)
C(14)	67(7)	22(5)	22(5)	9(5)	-5(5)	4(6)
C(15)	78(9)	48(7)	24(6)	-2(5)	11(6)	0(6)
C(16)	51(6)	68(6)	23(5)	-12(5)	3(4)	5(6)
C(17)	71(9)	82(7)	26(7)	-3(6)	-18(6)	35(8)
C(18)	69(8)	43(6)	23(6)	9(5)	2(5)	24(6)
C(19)	21(5)	21(6)	20(5)	-2(4)	8(4)	10(4)
C(20)	16(5)	23(5)	26(6)	-8(5)	12(4)	4(4)
C(21)	33(6)	25(6)	25(6)	-4(5)	3(5)	1(5)
C(22)	32(5)	46(6)	20(5)	6(5)	15(5)	1(5)
C(23)	17(5)	56(8)	29(7)	-3(6)	-4(5)	-5(5)
C(24)	23(6)	43(7)	23(6)	-5(5)	16(5)	-2(5)
N(1)	26(4)	22(4)	23(4)	1(3)	2(3)	1(4)

N(2)	16(4)	29(5)	21(5)	-5(4)	-1(4)	-4(4)
Cl(1)	23(1)	21(1)	23(1)	3(1)	4(1)	5(1)
Cl(2)	17(1)	24(1)	30(1)	-5(1)	9(1)	1(1)
Pt(1)	15(1)	17(1)	21(1)	-1(1)	2(1)	0(1)
C(101)	20(4)	24(4)	23(4)	0(4)	-4(3)	5(4)
C(102)	18(3)	26(4)	25(5)	2(4)	-4(3)	2(4)
C(103)	18(4)	20(4)	23(4)	4(4)	-3(3)	6(4)
C(104)	21(5)	29(6)	22(6)	-5(5)	4(5)	2(5)
C(105)	16(5)	20(6)	37(7)	2(5)	16(5)	6(4)
C(106)	31(6)	30(6)	19(6)	8(5)	1(5)	-13(6)
C(107)	23(6)	40(7)	29(7)	-9(6)	6(5)	1(5)
C(108)	41(8)	44(8)	55(9)	-21(7)	17(7)	1(7)
C(109)	66(9)	57(9)	23(7)	-16(7)	7(7)	-18(8)
C(110)	49(8)	40(7)	35(8)	2(6)	-4(6)	-22(6)
C(111)	33(7)	28(6)	28(7)	12(5)	2(5)	-7(5)
C(112)	18(5)	23(6)	36(7)	11(5)	4(5)	-1(5)
C(113)	37(7)	37(7)	31(7)	3(6)	6(6)	2(6)
C(114)	21(6)	51(8)	25(6)	-4(6)	2(5)	7(6)
C(115)	38(7)	54(8)	46(9)	1(7)	-19(6)	-5(7)
C(116)	84(7)	43(8)	22(6)	-6(7)	-5(6)	-4(8)
C(117)	79(6)	50(8)	29(6)	-8(5)	12(5)	11(6)
C(118)	54(7)	60(10)	27(6)	-1(6)	13(5)	21(7)
C(119)	24(5)	20(6)	28(6)	12(6)	8(4)	8(5)
C(120)	41(6)	32(6)	22(5)	0(7)	6(5)	7(7)
C(121)	43(8)	44(8)	44(9)	9(7)	4(7)	-1(7)
C(122)	71(9)	36(8)	21(7)	4(6)	12(7)	14(7)
C(123)	76(10)	28(7)	23(7)	-2(6)	1(6)	-11(7)
C(124)	45(7)	29(7)	22(6)	-5(5)	-2(5)	-1(6)
N(101)	15(3)	22(4)	19(4)	-4(4)	1(3)	-1(3)
N(102)	27(5)	18(5)	22(5)	-11(4)	-2(4)	-10(4)
Cl(11)	21(1)	25(2)	28(2)	2(1)	9(1)	6(1)
Cl(12)	21(1)	22(1)	31(2)	5(1)	1(1)	2(1)
Pt(11)	16(1)	20(1)	20(1)	0(1)	2(1)	0(1)
C(201)	15(4)	24(4)	22(4)	-1(3)	-5(4)	-3(4)
C(202)	13(4)	20(4)	32(5)	-4(3)	-2(4)	1(4)
C(203)	18(4)	13(4)	30(4)	3(3)	4(4)	1(4)
C(204)	32(6)	14(5)	30(6)	8(5)	4(5)	2(5)
C(205)	26(6)	28(6)	23(6)	-6(5)	-8(5)	16(5)
C(206)	20(5)	32(6)	30(6)	5(6)	6(5)	2(5)
C(207)	31(6)	25(6)	23(6)	2(5)	-2(5)	4(5)
C(208)	56(8)	30(6)	26(6)	-11(5)	-4(6)	-2(6)
C(209)	52(8)	45(7)	20(6)	-10(6)	11(6)	0(6)
C(210)	43(7)	57(8)	24(6)	14(6)	18(6)	-8(7)
C(211)	25(6)	34(6)	30(6)	6(5)	6(5)	-7(5)
C(212)	19(5)	18(5)	35(6)	6(5)	-2(5)	7(5)
C(213)	11(5)	43(7)	24(6)	0(5)	-3(4)	-6(5)
C(214)	39(6)	32(7)	32(6)	-3(6)	5(5)	0(6)
C(215)	85(10)	42(7)	24(7)	-3(6)	13(7)	16(7)
C(216)	70(9)	88(8)	19(6)	-7(8)	0(6)	28(10)
C(217)	73(10)	100(9)	26(7)	19(7)	29(7)	13(9)
C(218)	41(6)	39(6)	29(6)	18(5)	3(5)	-2(6)
C(219)	15(5)	25(7)	18(5)	-1(4)	-2(4)	5(4)
C(220)	18(5)	41(7)	19(6)	-6(5)	-6(4)	-3(5)
C(221)	34(6)	29(6)	28(6)	-2(5)	-7(5)	-11(5)
C(222)	22(6)	64(8)	30(7)	3(6)	-2(5)	0(6)
C(223)	25(6)	58(8)	17(6)	0(6)	4(5)	9(6)
C(224)	29(6)	33(6)	25(6)	1(5)	-4(5)	1(5)

N(201)	23(4)	19(4)	17(4)	3(3)	2(3)	-2(3)
N(202)	13(4)	29(5)	22(5)	-4(4)	9(3)	9(4)
Cl(21)	21(1)	20(1)	26(1)	2(1)	0(1)	-4(1)
Cl(22)	15(1)	25(1)	30(1)	-3(1)	-2(1)	0(1)
Pt(21)	15(1)	17(1)	20(1)	-2(1)	1(1)	0(1)
C(301)	28(4)	16(4)	20(3)	-6(4)	4(3)	4(4)
C(302)	24(3)	25(4)	27(4)	0(5)	-2(3)	-2(5)
C(303)	21(4)	21(4)	22(4)	2(3)	2(3)	-5(4)
C(304)	17(4)	9(4)	27(4)	4(4)	4(3)	6(4)
C(305)	20(5)	24(6)	34(7)	-7(5)	-7(5)	6(5)
C(306)	11(5)	30(6)	25(6)	3(5)	3(4)	10(5)
C(307)	27(6)	48(9)	31(7)	14(6)	-4(5)	7(6)
C(308)	56(9)	39(7)	51(10)	-1(7)	-17(7)	9(7)
C(309)	69(10)	53(9)	26(7)	-5(7)	-3(7)	12(8)
C(310)	45(8)	56(9)	40(8)	15(7)	13(7)	14(7)
C(311)	40(7)	37(7)	37(8)	9(6)	5(6)	19(6)
C(312)	26(6)	31(7)	23(6)	-6(5)	15(5)	3(5)
C(313)	16(5)	29(6)	20(6)	-9(5)	5(4)	1(5)
C(314)	29(6)	45(7)	32(7)	14(7)	-1(5)	1(6)
C(315)	33(7)	52(8)	30(7)	-6(6)	-3(6)	9(6)
C(316)	53(6)	45(8)	38(8)	6(6)	-9(6)	15(6)
C(317)	65(7)	58(9)	19(6)	13(6)	4(5)	-7(7)
C(318)	33(6)	67(8)	21(6)	4(6)	9(5)	-4(6)
C(319)	36(6)	23(6)	13(5)	-2(5)	-7(5)	-2(5)
C(320)	36(5)	47(6)	15(5)	-7(5)	9(4)	-4(5)
C(321)	46(8)	41(7)	20(7)	-11(6)	7(6)	-19(6)
C(322)	81(10)	28(7)	34(8)	1(6)	31(8)	-21(7)
C(323)	64(9)	34(7)	25(7)	-1(6)	-7(6)	8(7)
C(324)	48(7)	33(7)	18(6)	-2(5)	0(5)	-8(6)
N(301)	23(3)	15(3)	22(3)	-2(4)	4(3)	-2(4)
N(302)	18(4)	30(6)	24(5)	-5(4)	-7(4)	6(4)
Cl(31)	20(1)	26(2)	26(1)	-4(1)	10(1)	-4(1)
Cl(32)	24(1)	22(1)	30(2)	-5(1)	1(1)	-2(1)
Pt(31)	16(1)	19(1)	20(1)	-1(1)	1(1)	0(1)
C(401)	30(7)	36(7)	28(7)	5(6)	2(5)	-9(6)
N(401)	60(7)	35(7)	66(9)	-1(7)	27(7)	-7(6)
C(402)	36(7)	41(7)	24(7)	17(6)	8(5)	1(6)
C(501)	39(7)	32(6)	13(5)	9(5)	-1(5)	-9(6)
C(502)	31(6)	30(6)	28(6)	6(5)	12(5)	4(5)
N(501)	30(6)	65(8)	58(8)	26(6)	-6(6)	-8(6)
C(601)	38(6)	21(6)	16(5)	-1(6)	10(4)	5(6)
C(602)	36(7)	27(6)	34(7)	2(6)	10(6)	-3(5)
N(601)	55(7)	36(6)	61(8)	-4(6)	37(6)	14(6)
C(701)	25(6)	23(6)	31(6)	3(5)	4(5)	1(5)
C(702)	29(6)	29(6)	28(6)	0(5)	8(5)	-2(5)
N(701)	20(5)	63(7)	59(8)	24(6)	7(5)	14(5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*rac*)-7.

	x	y	z	U(eq)
H(1)	3500	1210	4372	29
H(2A)	5271	3058	4177	32
H(2B)	3827	3302	4262	32

H(3)	2997	2096	3849	27
H(4A)	4064	1998	3401	25
H(4B)	4266	3420	3533	25
H(5A)	2773	-134	4008	28
H(5B)	3956	-1064	4047	28
H(7)	1900	452	3501	45
H(8)	1384	-366	3021	55
H(9)	2540	-2027	2816	57
H(10)	4228	-2895	3120	51
H(11)	4721	-2105	3612	33
H(12A)	6317	3470	3248	31
H(12B)	7288	2325	3313	31
H(14)	6367	36	3148	45
H(15)	5534	-1020	2722	60
H(16)	4228	29	2357	57
H(17)	4089	2268	2393	72
H(18)	4966	3332	2820	54
H(20)	4358	-845	4601	25
H(21)	5637	-1646	5010	33
H(22)	7246	-385	5232	38
H(23)	7606	1625	5042	42
H(24)	6394	2399	4616	35
H(2C)	6320(70)	2910(40)	3699(16)	26
H(101)	8567	2180	614	27
H(10A)	6830	374	836	28
H(10B)	6585	1871	743	28
H(103)	7902	2614	1143	24
H(10C)	8213	1474	1591	28
H(10D)	6777	1247	1473	28
H(10E)	10010	2907	945	28
H(10F)	10929	1709	931	28
H(107)	9497	3725	1456	37
H(108)	10312	4193	1948	55
H(109)	12015	3032	2153	58
H(110)	13047	1597	1867	50
H(111)	12154	994	1386	36
H(11A)	6842	-878	1769	31
H(11B)	7968	-1836	1714	31
H(114)	10220	-935	1858	39
H(115)	11387	-28	2271	57
H(116)	10394	1137	2638	60
H(117)	8245	1353	2609	62
H(118)	7049	430	2189	56
H(120)	10563	1080	409	38
H(121)	11067	-106	-16	52
H(122)	9582	-1351	-271	51
H(123)	7534	-1480	-99	51
H(124)	7083	-416	347	39
H(12C)	7260(30)	-670(40)	1297(8)	27
H(201)	11140	6244	4393	25
H(20A)	10757	8352	4282	27
H(20B)	9271	8107	4188	27
H(203)	11393	7145	3871	24
H(20C)	9936	8469	3559	30
H(20D)	10139	7068	3422	30
H(20E)	11708	4933	4041	32
H(20F)	10555	3981	4065	32

H(207)	9697	2831	3623	32
H(208)	10035	2110	3133	45
H(209)	11522	3078	2847	46
H(210)	12604	4915	3037	49
H(211)	12278	5619	3536	35
H(21A)	6868	7293	3299	29
H(21B)	7807	8440	3241	29
H(214)	7705	5017	3167	41
H(215)	8421	3888	2756	60
H(216)	9462	5004	2378	71
H(217)	9676	7196	2401	78
H(218)	8907	8323	2809	43
H(220)	10426	4196	4626	32
H(221)	9335	3333	5019	37
H(222)	7825	4626	5237	47
H(223)	7379	6648	5048	40
H(224)	8374	7441	4630	35
H(22C)	8120(90)	7960(30)	3702(15)	25
H(301)	3574	4602	616	25
H(30A)	1571	4941	748	31
H(30B)	1844	6432	843	31
H(303)	2931	4160	1149	26
H(30C)	3203	5294	1595	21
H(30D)	1775	5523	1472	21
H(30E)	5952	5090	932	32
H(30F)	5034	3895	955	32
H(307)	7085	5901	1388	43
H(308)	7931	5510	1872	60
H(309)	7110	3794	2167	60
H(310)	5398	2644	1958	56
H(311)	4616	3004	1445	46
H(31A)	2883	8615	1720	31
H(31B)	1834	7574	1778	31
H(314)	5198	7955	1891	43
H(315)	6439	7081	2297	46
H(316)	5563	5750	2646	55
H(317)	3457	5195	2566	57
H(318)	2200	6109	2176	48
H(320)	5615	5737	417	39
H(321)	6080	6892	-11	43
H(322)	4522	8184	-268	56
H(323)	2554	8302	-88	50
H(324)	2069	7152	344	40
H(32C)	2230(30)	7330(100)	1293(12)	29
H(40A)	4072	12	357	50
H(40B)	3361	-584	633	50
H(40C)	4759	-52	692	50
H(50A)	6029	5606	4283	44
H(50B)	5489	5405	4610	44
H(50C)	6007	6776	4517	44
H(60A)	8209	7360	537	47
H(60B)	9450	6768	409	47
H(60C)	9413	7094	764	47
H(70A)	-1438	652	4293	43
H(70B)	-1226	1794	4534	43
H(70C)	-658	407	4612	43

Table 6. Torsion angles [°] for (*rac*)-7.

C(19)-C(1)-C(2)-C(3)	148.7(9)
N(1)-C(1)-C(2)-C(3)	21.7(7)
C(1)-C(2)-C(3)-C(4)	-138.8(9)
C(1)-C(2)-C(3)-N(1)	-22.2(7)
N(1)-C(3)-C(4)-N(2)	-46.9(11)
C(2)-C(3)-C(4)-N(2)	57.1(12)
N(1)-C(5)-C(6)-C(11)	97.3(11)
N(1)-C(5)-C(6)-C(7)	-89.4(12)
C(11)-C(6)-C(7)-C(8)	0.4(17)
C(5)-C(6)-C(7)-C(8)	-172.9(10)
C(6)-C(7)-C(8)-C(9)	-1.1(18)
C(7)-C(8)-C(9)-C(10)	0.9(18)
C(8)-C(9)-C(10)-C(11)	0.0(18)
C(7)-C(6)-C(11)-C(10)	0.5(16)
C(5)-C(6)-C(11)-C(10)	173.7(10)
C(9)-C(10)-C(11)-C(6)	-0.7(17)
N(2)-C(12)-C(13)-C(18)	112.0(11)
N(2)-C(12)-C(13)-C(14)	-71.3(13)
C(18)-C(13)-C(14)-C(15)	0.4(18)
C(12)-C(13)-C(14)-C(15)	-176.4(11)
C(13)-C(14)-C(15)-C(16)	-3(2)
C(14)-C(15)-C(16)-C(17)	5(2)
C(15)-C(16)-C(17)-C(18)	-5(2)
C(14)-C(13)-C(18)-C(17)	0.2(18)
C(12)-C(13)-C(18)-C(17)	177.1(12)
C(16)-C(17)-C(18)-C(13)	2(2)
C(2)-C(1)-C(19)-C(24)	-3.2(14)
N(1)-C(1)-C(19)-C(24)	109.0(10)
C(2)-C(1)-C(19)-C(20)	173.9(8)
N(1)-C(1)-C(19)-C(20)	-73.9(11)
C(24)-C(19)-C(20)-C(21)	-0.4(13)
C(1)-C(19)-C(20)-C(21)	-177.6(9)
C(19)-C(20)-C(21)-C(22)	1.5(14)
C(20)-C(21)-C(22)-C(23)	-0.8(15)
C(21)-C(22)-C(23)-C(24)	-0.9(15)
C(20)-C(19)-C(24)-C(23)	-1.4(13)
C(1)-C(19)-C(24)-C(23)	175.8(9)
C(22)-C(23)-C(24)-C(19)	2.0(15)
C(6)-C(5)-N(1)-C(3)	69.4(11)
C(6)-C(5)-N(1)-C(1)	166.8(9)
C(6)-C(5)-N(1)-Pt(1)	-57.6(11)
C(4)-C(3)-N(1)-C(5)	-101.3(10)
C(2)-C(3)-N(1)-C(5)	134.8(7)
C(4)-C(3)-N(1)-C(1)	145.5(8)
C(2)-C(3)-N(1)-C(1)	21.6(7)
C(4)-C(3)-N(1)-Pt(1)	30.1(9)
C(2)-C(3)-N(1)-Pt(1)	-93.8(6)
C(19)-C(1)-N(1)-C(5)	89.8(10)
C(2)-C(1)-N(1)-C(5)	-139.9(8)
C(19)-C(1)-N(1)-C(3)	-152.2(9)
C(2)-C(1)-N(1)-C(3)	-21.9(7)
C(19)-C(1)-N(1)-Pt(1)	-45.9(10)
C(2)-C(1)-N(1)-Pt(1)	84.4(7)
C(3)-C(4)-N(2)-C(12)	173.3(8)

C(3)-C(4)-N(2)-Pt(1)	39.4(9)
C(13)-C(12)-N(2)-C(4)	-53.4(11)
C(13)-C(12)-N(2)-Pt(1)	75.0(10)
C(4)-N(2)-Pt(1)-N(1)	-18.6(7)
C(12)-N(2)-Pt(1)-N(1)	-147.6(7)
C(4)-N(2)-Pt(1)-Cl(2)	163.0(6)
C(12)-N(2)-Pt(1)-Cl(2)	34.0(7)
C(5)-N(1)-Pt(1)-N(2)	126.4(7)
C(3)-N(1)-Pt(1)-N(2)	-5.9(6)
C(1)-N(1)-Pt(1)-N(2)	-99.4(7)
C(5)-N(1)-Pt(1)-Cl(1)	-54.9(7)
C(3)-N(1)-Pt(1)-Cl(1)	172.8(6)
C(1)-N(1)-Pt(1)-Cl(1)	79.3(6)
C(119)-C(101)-C(102)-C(103)	150.9(10)
N(101)-C(101)-C(102)-C(103)	19.5(8)
C(101)-C(102)-C(103)-C(104)	-137.3(10)
C(101)-C(102)-C(103)-N(101)	-19.7(8)
N(101)-C(103)-C(104)-N(102)	-46.8(12)
C(102)-C(103)-C(104)-N(102)	58.7(13)
N(101)-C(105)-C(106)-C(107)	-84.5(12)
N(101)-C(105)-C(106)-C(111)	99.8(11)
C(111)-C(106)-C(107)-C(108)	-0.7(17)
C(105)-C(106)-C(107)-C(108)	-176.4(11)
C(106)-C(107)-C(108)-C(109)	0.2(18)
C(107)-C(108)-C(109)-C(110)	3.2(19)
C(108)-C(109)-C(110)-C(111)	-5.8(19)
C(109)-C(110)-C(111)-C(106)	5.1(16)
C(107)-C(106)-C(111)-C(110)	-2.0(15)
C(105)-C(106)-C(111)-C(110)	173.8(10)
N(102)-C(112)-C(113)-C(118)	112.7(12)
N(102)-C(112)-C(113)-C(114)	-71.7(14)
C(118)-C(113)-C(114)-C(115)	-1.9(19)
C(112)-C(113)-C(114)-C(115)	-177.5(11)
C(113)-C(114)-C(115)-C(116)	0(2)
C(114)-C(115)-C(116)-C(117)	1(2)
C(115)-C(116)-C(117)-C(118)	-1(2)
C(114)-C(113)-C(118)-C(117)	2(2)
C(112)-C(113)-C(118)-C(117)	177.6(11)
C(116)-C(117)-C(118)-C(113)	0(2)
C(102)-C(101)-C(119)-C(120)	-179.0(11)
N(101)-C(101)-C(119)-C(120)	-63.5(15)
C(102)-C(101)-C(119)-C(124)	7.2(17)
N(101)-C(101)-C(119)-C(124)	122.7(11)
C(124)-C(119)-C(120)-C(121)	-1.3(18)
C(101)-C(119)-C(120)-C(121)	-175.4(11)
C(119)-C(120)-C(121)-C(122)	2.3(19)
C(120)-C(121)-C(122)-C(123)	-0.7(19)
C(121)-C(122)-C(123)-C(124)	-1.8(19)
C(122)-C(123)-C(124)-C(119)	2.8(18)
C(120)-C(119)-C(124)-C(123)	-1.2(17)
C(101)-C(119)-C(124)-C(123)	172.7(11)
C(106)-C(105)-N(101)-C(103)	65.5(12)
C(106)-C(105)-N(101)-C(101)	164.0(9)
C(106)-C(105)-N(101)-Pt(11)	-60.6(10)
C(104)-C(103)-N(101)-C(105)	-101.3(11)
C(102)-C(103)-N(101)-C(105)	133.3(9)
C(104)-C(103)-N(101)-C(101)	144.8(9)

C(102)-C(103)-N(101)-C(101)	19.5(8)
C(104)-C(103)-N(101)-Pt(11)	28.8(10)
C(102)-C(103)-N(101)-Pt(11)	-96.6(7)
C(119)-C(101)-N(101)-C(105)	90.4(12)
C(102)-C(101)-N(101)-C(105)	-138.4(8)
C(119)-C(101)-N(101)-C(103)	-150.8(11)
C(102)-C(101)-N(101)-C(103)	-19.5(8)
C(119)-C(101)-N(101)-Pt(11)	-44.3(12)
C(102)-C(101)-N(101)-Pt(11)	87.0(8)
C(103)-C(104)-N(102)-C(112)	175.8(8)
C(103)-C(104)-N(102)-Pt(11)	40.2(10)
C(113)-C(112)-N(102)-C(104)	-53.5(12)
C(113)-C(112)-N(102)-Pt(11)	75.6(10)
C(104)-N(102)-Pt(11)-N(101)	-19.6(8)
C(112)-N(102)-Pt(11)-N(101)	-149.7(7)
C(104)-N(102)-Pt(11)-Cl(12)	162.8(7)
C(112)-N(102)-Pt(11)-Cl(12)	32.7(7)
C(105)-N(101)-Pt(11)-N(102)	127.4(7)
C(103)-N(101)-Pt(11)-N(102)	-4.6(6)
C(101)-N(101)-Pt(11)-N(102)	-98.8(6)
C(105)-N(101)-Pt(11)-Cl(11)	-51.5(6)
C(103)-N(101)-Pt(11)-Cl(11)	176.6(6)
C(101)-N(101)-Pt(11)-Cl(11)	82.3(6)
C(219)-C(201)-C(202)-C(203)	-148.3(10)
N(201)-C(201)-C(202)-C(203)	-22.2(7)
C(201)-C(202)-C(203)-C(204)	138.1(9)
C(201)-C(202)-C(203)-N(201)	22.2(7)
N(201)-C(203)-C(204)-N(202)	43.3(11)
C(202)-C(203)-C(204)-N(202)	-59.4(12)
N(201)-C(205)-C(206)-C(211)	85.6(12)
N(201)-C(205)-C(206)-C(207)	-101.0(12)
C(211)-C(206)-C(207)-C(208)	-0.1(16)
C(205)-C(206)-C(207)-C(208)	-173.6(10)
C(206)-C(207)-C(208)-C(209)	1.0(17)
C(207)-C(208)-C(209)-C(210)	-2.3(19)
C(208)-C(209)-C(210)-C(211)	2.7(18)
C(207)-C(206)-C(211)-C(210)	0.6(17)
C(205)-C(206)-C(211)-C(210)	174.2(11)
C(209)-C(210)-C(211)-C(206)	-1.9(18)
N(202)-C(212)-C(213)-C(218)	-113.7(11)
N(202)-C(212)-C(213)-C(214)	69.5(13)
C(218)-C(213)-C(214)-C(215)	1.2(17)
C(212)-C(213)-C(214)-C(215)	178.1(11)
C(213)-C(214)-C(215)-C(216)	0.6(19)
C(214)-C(215)-C(216)-C(217)	-2(2)
C(215)-C(216)-C(217)-C(218)	1(2)
C(214)-C(213)-C(218)-C(217)	-2.1(17)
C(212)-C(213)-C(218)-C(217)	-178.9(12)
C(216)-C(217)-C(218)-C(213)	1(2)
C(202)-C(201)-C(219)-C(220)	-172.5(9)
N(201)-C(201)-C(219)-C(220)	75.5(12)
C(202)-C(201)-C(219)-C(224)	1.4(15)
N(201)-C(201)-C(219)-C(224)	-110.6(11)
C(224)-C(219)-C(220)-C(221)	3.5(15)
C(201)-C(219)-C(220)-C(221)	177.7(9)
C(219)-C(220)-C(221)-C(222)	-3.8(16)
C(220)-C(221)-C(222)-C(223)	1.4(16)

C(221)-C(222)-C(223)-C(224)	1.0(17)
C(222)-C(223)-C(224)-C(219)	-1.3(16)
C(220)-C(219)-C(224)-C(223)	-0.9(15)
C(201)-C(219)-C(224)-C(223)	-175.0(10)
C(206)-C(205)-N(201)-C(203)	-68.1(12)
C(206)-C(205)-N(201)-C(201)	-165.2(9)
C(206)-C(205)-N(201)-Pt(21)	58.2(11)
C(204)-C(203)-N(201)-C(205)	102.4(9)
C(202)-C(203)-N(201)-C(205)	-134.4(8)
C(204)-C(203)-N(201)-C(201)	-145.3(8)
C(202)-C(203)-N(201)-C(201)	-22.1(7)
C(204)-C(203)-N(201)-Pt(21)	-28.0(8)
C(202)-C(203)-N(201)-Pt(21)	95.2(6)
C(219)-C(201)-N(201)-C(205)	-90.0(10)
C(202)-C(201)-N(201)-C(205)	138.6(8)
C(219)-C(201)-N(201)-C(203)	153.5(9)
C(202)-C(201)-N(201)-C(203)	22.2(7)
C(219)-C(201)-N(201)-Pt(21)	45.9(10)
C(202)-C(201)-N(201)-Pt(21)	-85.4(6)
C(203)-C(204)-N(202)-C(212)	-172.4(8)
C(203)-C(204)-N(202)-Pt(21)	-36.7(10)
C(213)-C(212)-N(202)-C(204)	55.4(12)
C(213)-C(212)-N(202)-Pt(21)	-74.9(9)
C(204)-N(202)-Pt(21)-N(201)	16.9(7)
C(212)-N(202)-Pt(21)-N(201)	147.6(7)
C(204)-N(202)-Pt(21)-Cl(22)	-165.7(6)
C(212)-N(202)-Pt(21)-Cl(22)	-35.0(6)
C(205)-N(201)-Pt(21)-N(202)	-124.8(7)
C(203)-N(201)-Pt(21)-N(202)	5.7(5)
C(201)-N(201)-Pt(21)-N(202)	101.1(6)
C(205)-N(201)-Pt(21)-Cl(21)	55.2(6)
C(203)-N(201)-Pt(21)-Cl(21)	-174.3(5)
C(201)-N(201)-Pt(21)-Cl(21)	-78.9(6)
C(319)-C(301)-C(302)-C(303)	-148.1(10)
N(301)-C(301)-C(302)-C(303)	-21.8(8)
C(301)-C(302)-C(303)-C(304)	138.3(10)
C(301)-C(302)-C(303)-N(301)	21.8(8)
N(301)-C(303)-C(304)-N(302)	44.4(11)
C(302)-C(303)-C(304)-N(302)	-59.0(11)
N(301)-C(305)-C(306)-C(307)	-94.7(12)
N(301)-C(305)-C(306)-C(311)	88.4(12)
C(311)-C(306)-C(307)-C(308)	0.0(18)
C(305)-C(306)-C(307)-C(308)	-176.9(11)
C(306)-C(307)-C(308)-C(309)	-0.2(19)
C(307)-C(308)-C(309)-C(310)	-1.4(19)
C(308)-C(309)-C(310)-C(311)	3.3(19)
C(307)-C(306)-C(311)-C(310)	1.8(16)
C(305)-C(306)-C(311)-C(310)	178.8(10)
C(309)-C(310)-C(311)-C(306)	-3.5(18)
N(302)-C(312)-C(313)-C(318)	-105.0(12)
N(302)-C(312)-C(313)-C(314)	74.2(14)
C(318)-C(313)-C(314)-C(315)	-0.9(18)
C(312)-C(313)-C(314)-C(315)	179.8(11)
C(313)-C(314)-C(315)-C(316)	0(2)
C(314)-C(315)-C(316)-C(317)	2(2)
C(315)-C(316)-C(317)-C(318)	-3(2)
C(314)-C(313)-C(318)-C(317)	-0.3(18)

C(312)-C(313)-C(318)-C(317)	179.0(12)
C(316)-C(317)-C(318)-C(313)	2(2)
C(302)-C(301)-C(319)-C(324)	-14.0(16)
N(301)-C(301)-C(319)-C(324)	-125.8(10)
C(302)-C(301)-C(319)-C(320)	178.8(11)
N(301)-C(301)-C(319)-C(320)	67.0(14)
C(324)-C(319)-C(320)-C(321)	4.0(17)
C(301)-C(319)-C(320)-C(321)	171.4(10)
C(319)-C(320)-C(321)-C(322)	-2.0(17)
C(320)-C(321)-C(322)-C(323)	-0.1(18)
C(321)-C(322)-C(323)-C(324)	0.2(19)
C(320)-C(319)-C(324)-C(323)	-3.8(16)
C(301)-C(319)-C(324)-C(323)	-171.1(10)
C(322)-C(323)-C(324)-C(319)	1.8(18)
C(306)-C(305)-N(301)-C(303)	-67.1(11)
C(306)-C(305)-N(301)-C(301)	-163.8(9)
C(306)-C(305)-N(301)-Pt(31)	58.7(10)
C(304)-C(303)-N(301)-C(305)	102.5(10)
C(302)-C(303)-N(301)-C(305)	-134.3(9)
C(304)-C(303)-N(301)-C(301)	-144.7(9)
C(302)-C(303)-N(301)-C(301)	-21.5(8)
C(304)-C(303)-N(301)-Pt(31)	-27.3(9)
C(302)-C(303)-N(301)-Pt(31)	95.9(7)
C(319)-C(301)-N(301)-C(305)	-92.5(11)
C(302)-C(301)-N(301)-C(305)	138.5(9)
C(319)-C(301)-N(301)-C(303)	150.9(9)
C(302)-C(301)-N(301)-C(303)	21.8(9)
C(319)-C(301)-N(301)-Pt(31)	44.0(10)
C(302)-C(301)-N(301)-Pt(31)	-85.0(8)
C(313)-C(312)-N(302)-C(304)	57.8(11)
C(313)-C(312)-N(302)-Pt(31)	-72.0(11)
C(303)-C(304)-N(302)-C(312)	-175.5(8)
C(303)-C(304)-N(302)-Pt(31)	-38.5(9)
C(312)-N(302)-Pt(31)-N(301)	149.1(8)
C(304)-N(302)-Pt(31)-N(301)	18.4(6)
C(312)-N(302)-Pt(31)-Cl(32)	-33.8(8)
C(304)-N(302)-Pt(31)-Cl(32)	-164.5(6)
C(305)-N(301)-Pt(31)-N(302)	-126.4(7)
C(303)-N(301)-Pt(31)-N(302)	4.1(6)
C(301)-N(301)-Pt(31)-N(302)	98.4(6)
C(305)-N(301)-Pt(31)-Cl(31)	52.5(6)
C(303)-N(301)-Pt(31)-Cl(31)	-177.1(6)
C(301)-N(301)-Pt(31)-Cl(31)	-82.8(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for (*rac*)-**7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2C)...Cl(21)	0.92(2)	2.50(3)	3.363(9)	156(4)
N(2)-H(2C)...Cl(22)	0.92(2)	2.73(4)	3.365(10)	127(4)
N(102)-H(12C)...Cl(31)#1	0.901(18)	2.52(2)	3.365(9)	157(4)
N(102)-H(12C)...Cl(32)#1	0.901(18)	2.83(3)	3.443(9)	127(3)
N(202)-H(22C)...Cl(1)#2	0.91(2)	2.57(4)	3.375(8)	148(5)
N(202)-H(22C)...Cl(2)#2	0.91(2)	2.68(4)	3.387(10)	136(4)
N(302)-H(32C)...Cl(11)#3	0.91(2)	2.60(5)	3.398(10)	146(7)

N(302)-H(32C)...Cl(12)#3 0.91(2) 2.75(4) 3.413(9) 130(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 x,y+1,z #3 x-1,y+1,z

References

1. (a) J. A. Ellman, T. D. Owens and T. P. Tang, *Acc. Chem. Res.*, 2002, **35**, 984-995; (b) M. T. Robak, M. A. Herbage and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 3600-3740.
2. (a) A. Feula, L. Male and J. S. Fossey, *Org. Lett.*, 2010, **12**, 5044-5047; (b) A. Feula, S. S. Dhillon, R. Byravan, M. Sangha, R. Ebanks, M. A. Hama Salih, N. Spencer, L. Male, I. Magyary, W.-P. Deng, F. Müller and J. S. Fossey, *Org. Biomol. Chem.*, 2013, **11**, 5083-5093.
3. (a) T. Moragas, I. Churcher, W. Lewis and R. A. Stockman, *Org. Lett.*, 2014, **16**, 6290-6293; (b) J. L. G. Ruano, I. Fernandez, M. D. Catalina and A. A. Cruz, *Tetrahedron-Asymmetr.*, 1996, **7**, 3407-3414.
4. N. Plobeck and D. Powell, *Tetrahedron Asymmetr.*, 2002, **13**, 303-310.
5. T. Moragas, I. Churcher, W. Lewis and R. A. Stockman, *Org. Lett.*, 2014, **16**, 6290-6293.
6. D. A. Petrone, H. Yoon, H. Weinstabl and M. Lautens, *Angew. Chem., Int. Ed.*, 2014, **53**, 7908-7912.
7. X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979-4982.
8. X.-W. Sun, M. Liu, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2008, **10**, 1259-1262.
9. R. Almansa, J. F. Collados, D. Guijarro and M. Yus, *Tetrahedron Asymmetr.*, 2010, **21**, 1421-1431.
10. (a) M. Sugiura, K. Hirano and S. Kobayashi, *J. Am. Chem. Soc.*, 2004, **126**, 7182-7183; (b) M. Sugiura, C. Mori and S. Kobayashi, *J. Am. Chem. Soc.*, 2006, **128**, 11038-11039; (c) P. V. Ramachandran and T. E. Burghardt, *Chem.-Eur. J.*, 2005, **11**, 4387-4395.
11. R. A. Fernandes and J. L. Nallasivam, *Org. Biomol. Chem.*, 2012, **10**, 7789-7800.
12. R. A. Fernandes and D. A. Chaudhari, *Eur. J. Org. Chem.*, 2012, **2012**, 1945-1952.
13. Synthesised in a previous study.
14. A. Feula and J. S. Fossey, *RSC Adv.*, 2013, **3**, 5370-5373.
15. F. K. MacDonald, K. M. M. Carneiro and I. R. Pottie, *Tetrahedron Lett.*, 2011, **52**, 891-893.
16. (a) G. Lai, F. Guo, Y. Zheng, Y. Fang, H. Song, K. Xu, S. Wang, Z. Zha and Z. Wang, *Chem. Eur. Jour.*, 2011, **17**, 1114-1117; (b) D. A. Evans, D. Seidel, M. Rueping, H. W. Lam, J. T. Shaw and C. W. Downey, *J. Am. Chem. Soc.*, 2003, **125**, 12692-12693.
17. B. V. Subba Reddy and J. George, *Tetrahedron Asymmetr.*, 2011, **22**, 1169-1175.
18. R. Boobalan, G.-H. Lee and C. Chen, *Adv. Synth. Catal.*, 2012, **354**, 2511-2520.
19. J.-L. Li, L. Liu, Y.-N. Pei and H.-J. Zhu, *Tetrahedron*, 2014, **70**, 9077-9083.
20. H. Vázquez-Villa, S. Reber, M. A. Ariger and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2011, **50**, 8979-8981.
21. O. Soltani, M. A. Ariger, H. Vázquez-Villa and E. M. Carreira, *Org. Lett.*, 2010, **12**, 2893-2895.
22. (a) M. S. Taylor and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, 2006, **45**, 1520-1543; (b) X. H. Yu and W. Wang, *Chem.-Asian J.*, 2008, **3**, 516-532.
23. L. Menguy and F. Couty, *Tetrahedron-Asymmetr.*, 2010, **21**, 2385-2389.
24. L. Zhang, M.-M. Lee, S.-M. Lee, J. Lee, M. Cheng, B.-S. Jeong, H.-g. Park and S.-s. Jew, *Adv. Synth. Catal.*, 2009, **351**, 3063-3066.
25. These preliminary findings are by no means complete, and should be seen only as indicative of the organocatalytic potential, full details will be reported in due course, once comprehensive studies are concluded.
26. CrysAlisPro, 2013, **Version 1.171.36.28**, Agilent Technologies.
27. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **A64**, 112-122.
28. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
29. G. M. Sheldrick, *Acta Crystallogr A*, 2015, **71**, 3-8.
30. S. J. Coles and P. A. Gale, *Chem. Sci.*, 2012, **3**, 683-689.
31. R. W. W. Hooft, *COLLECT Data Collection Software*, 1998, ed. Nonius, B.V., Delft, The Netherlands.
32. Z. Otwinowski and W. Minor, eds. C. W. Carter and R. M. Sweet, Academic Press, New York, 1997, vol. 276, pp. 307-326.
33. G. M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
34. M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Casciaro, L. De Caro, G. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381-388.

