

Divergent ring opening and functionalization of N-alkyl aziridines via boryl radical fragmentation

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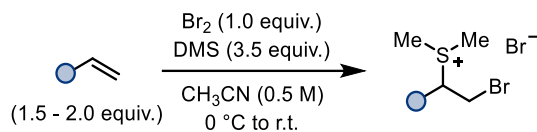
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1 General Experimental Details

All required fine chemicals were used directly without purification unless stated otherwise. All air and moisture sensitive reactions were carried out under Argon atmosphere using standard Schlenk manifold technique. All solvents were bought from Acros as 99.8% purity and degassed by Ar bubbling. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired at various field strengths as indicated and were referenced to CHCl_3 (7.26 and 77.2 ppm for ^1H and ^{13}C respectively) or DMSO (2.50 and 39.5 ppm for ^1H and ^{13}C respectively). ^1H NMR coupling constants are reported in Hertz and refer to apparent multiplicities and not true coupling constants. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, sx = sextet, hp = heptet, n = nonet, m = multiplet, dd = doublet of doublets, etc.), proton and carbon assignment (determined by 2D NOESY NMR experiments) where possible. ^{11}B NMR and ^{19}F NMR spectra were recorded and reported unreferenced. High-resolution mass spectra were obtained using a JEOL JMS-700 spectrometer or a Fissions VG Trio 2000 quadrupole mass spectrometer. Spectra were obtained using electron impact ionization (EI) and chemical ionization (CI) techniques, or positive electrospray (ESI). Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV-light or by dipping the plates in ninhydrin stain followed by heating. Flash column chromatography was performed using Merck Silica Gel 60 (40–63 μm). All mixed solvent eluents are reported as v/v solutions. All the reactions were conducted in CEM 9 mL glass microwave tubes capped with a LABSOLUTE crimp seal with septum (PTFE/butyl) purchased from Th. Geyer. The LEDs used are Kessil PR160L-390 nm.

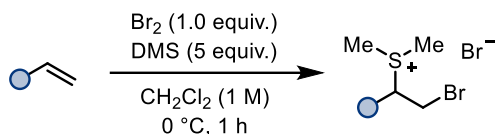
2 General Procedures

General Procedure for the Preparation of the Sulfonium Bromides – GP1a¹



To a round bottom flask equipped with a stirring bar was added Br_2 (1 equiv.) and CH_3CN (0.5 M). The resulting mixture was cooled down at $0\text{ }^\circ\text{C}$ with an ice-water bath and dimethyl sulfide (3.5 equiv.) was added dropwise over 5 min via syringe, leading to the formation of a yellow precipitate. The reaction mixture was stirred for 10 min before adding the corresponding alkene (1.5 or 2.0 equiv.) dropwise over 5 min via syringe. The reaction mixture was then warmed up to room temperature generating a homogeneous solution, followed by the precipitation of the corresponding sulfonium bromide. The reaction mixture was stirred for 30 min before being diluted with Et_2O to ensure full precipitation. The solid precipitate was collected by filtration and washed with Et_2O (x 2) to give the pure sulfonium bromides as solids that were used without any further purification.

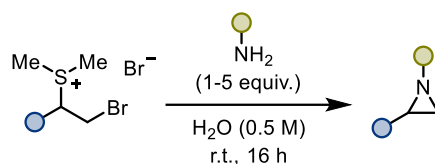
General Procedure for the Preparation of the Sulfonium Bromides – GP1b²



To a round bottom flask equipped with a stirring bar was added the corresponding alkene (1.0 equiv.), dimethyl sulfide (5 equiv.) and CH_2Cl_2 (1 M). The resulting mixture was cooled down at $0\text{ }^\circ\text{C}$ with an ice-water bath and a solution of bromine (Br_2 , 1.0 equiv.) in CH_2Cl_2 (4 M) was slowly added via syringe. The mixture was stirred for 1 h at $0\text{ }^\circ\text{C}$. A fading out of the reaction mixture was observed and a solid precipitated, which was collected by filtration and washed with Et_2O (x 2) to give the pure sulfonium bromides as solids that were used without any further purification.

Note: The stability of the sulfonium bromides greatly depends on the substituents. Some decomposes readily under air and need to be used quickly or stored under inert atmosphere in the fridge or the freezer. Specifically, the sulfonium bromides containing fluoro and/or ortho substituents decompose under air. The sulfonium bromides can be analysed by NMR but they decompose relatively fast (overnight) in D_2O or DMSO.

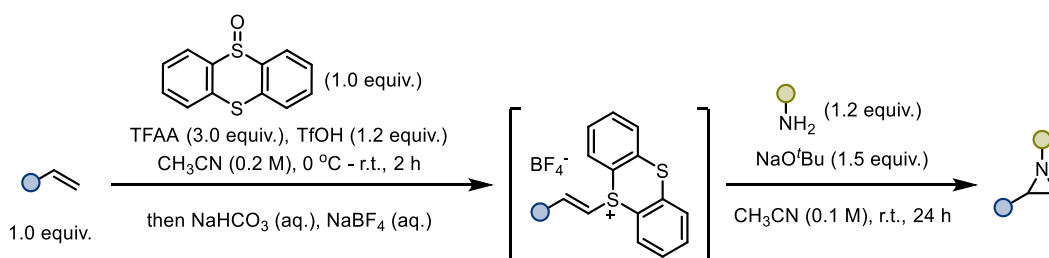
General Procedure for the Preparation of the *N*-Alkyl Aryl Aziridines – GP2³



A round bottom flask equipped with a stirring bar was charged with the corresponding sulfonium bromide (1.0 equiv.), H₂O (0.5 M) and the corresponding amine (1-5 equiv.) were added, and the reaction mixture was stirred for 16 h at room temperature. After complete consumption of starting material, the aqueous phase was extracted with CH₂Cl₂ (x 3). The combined organic layers were dried (MgSO₄) and filtered. Pure *N*-alkyl aziridines were directly obtained by evaporating the solvent and the excess of amine, or via column chromatography on silica gel.

Note: If the excess amine is not volatile, it can be removed by aqueous workup or purified by column chromatography on silica gel.

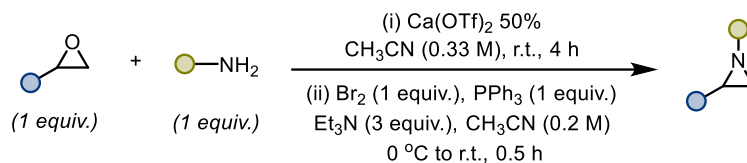
General Procedure for the Preparation of the *N*-Alkyl Alkyl Aziridines – GP3a⁴



Step 1: A Schlenk tube equipped with a magnetic stir bar was charged with the corresponding alkene (1.0 equiv.), thianthrene 5-oxide (1.0 equiv.), and dry CH₃CN (0.2 M). The reaction mixture was cooled down to 0 °C and TFAA (3.0 equiv.) was added dropwise over 2 minutes via syringe, followed by dropwise addition of TfOH (1.2 equiv.) over 2 minutes via syringe. After stirring the lilac mixture at 0 °C for 1 h and then 1 h at room temperature, the mixture was concentrated under reduced pressure, diluted with CH₂Cl₂, and washed with saturated aqueous NaHCO₃ solution, aqueous NaBF₄ solution (x 3, 5 % w/w). The organic layer was dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. The crude thianthrene was directly used for the next step without further purification.

Step 2: To a round bottom flask equipped with a stirring bar was added the corresponding amine (1.2 equiv.), NaOt-Bu (1.5 equiv.), thianthrene (1.0 equiv.) and dry CH₃CN (0.1 M). The reaction mixture was stirred for 24 h at room temperature. After complete consumption of starting material, the reaction mixture was evaporated, and the residue was purified directly by column chromatography on silica gel to afford the product.

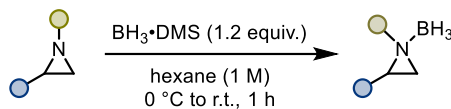
General Procedure for the Preparation of the *N*-Alkyl Alkyl Aziridines – GP3b^{5,6}



Step 1: A round bottom flask equipped with a stirring bar was charged with the corresponding amine (1.0 equiv.), CH₃CN (0.33 M), Ca(OTf)₂ (50 mol%) and the epoxide (1.0 equiv.) in sequence. The resulting mixture was stirred for 4 h at room temperature. Upon completion, water was added, the aqueous layer was extracted and separated with CH₂Cl₂ (x 3). The organic layer was dried (MgSO₄), filtered, and the solvent was removed under reduced pressure. The crude amino alcohol was directly used in the next step without further purification.

Step 2: Br₂ (1.0 equiv.) was added dropwise to an ice-cold solution of PPh₃ (1.0 equiv.) in dry CH₃CN (0.2 M). To this mixture was slowly added the crude amino alcohol (1.0 equiv., the amount depending on first step), followed by the dropwise addition of Et₃N (3.0 equiv.) at 0 °C. The mixture was then stirred at room temperature for 30 min. Et₃N•HBr was filtered off and the solution was concentrated by rotary evaporation and the residue was purified directly by column chromatography on silica gel to give desired aziridine.

General Procedure for the Preparation of the *N*-Alkyl Aziridine Boranes – GP4

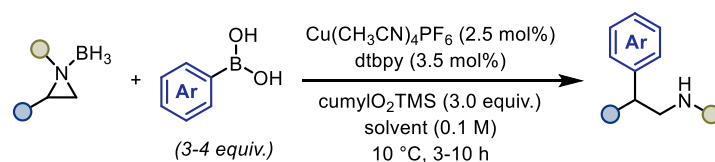


A round bottom flask equipped with a stirring bar was charged with the corresponding alkyl aziridine (1.0 equiv.). *n*-Hexane (1 M) was added, and the reaction mixture was cooled down to 0 °C with an ice bath and BH₃•DMS (1.2 equiv.) was slowly added via syringe. The resulting mixture was slowly warmed up to room temperature and stirred for 1 h at this temperature (a precipitate formed over the course of the reaction). The precipitate was collected by filtration and washed with *n*-hexane (x 2) to give the pure alkyl aziridine boranes as solids that were used without any further purification. If there are no precipitate, the amine boranes were isolated by column chromatography on silica gel.

Note: The filtration is enough in most cases to obtain the pure alkyl aziridine boranes. However, it can also be purified by column chromatography on silica gel or triturated with a mixture of Et₂O/pentane (50% to 100%).

The diastereoselectivity of the BH₃ coordination is discussed in **Section 3.4**.

General Procedure for the Ring Opening-Arylation of Aziridine Boranes – GP5



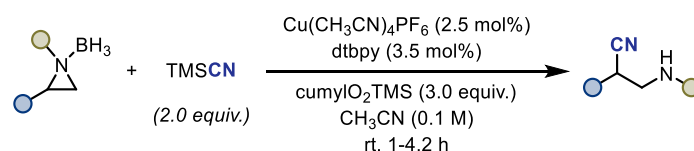
An oven-dried vial equipped with a stirring bar was charged with the corresponding aziridine borane (0.1 mmol, 1.0 equiv.) and the corresponding boronic acid (see **Table S1** for the equivalents). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). The peroxide (0.3 mmol, 3.0 equiv.) and dry and degassed solvent (0.5 mL) was then added to the vial and stirred for around **1 min**. The resulting mixture was cooled down to 10 °C (chiller) and the catalyst solution (0.5 mL of the corresponding dry and degassed solvent, containing Cu(CH₃CN)₄PF₆ (1 mg, 2.5 mol%) and dtbpy (1 mg, 3.5 mol%), pre-stirred for 10 min until fully dissolved) was then added under stirring. The resulting mixture was stirred at 10 °C for 10 h. Upon completion, aqueous NaOH (2 mL, 1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x 3 mL). The combined organic layers were dried (MgSO₄) and filtered. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford the desired products.

Table S1 shows the three conditions that were predominantly used during the Ring Opening-Arylation reactions.

Table S1. Variations used for Ring Opening-Arylation of Aziridine Boranes

General Procedure	solvent	ArB(OH) ₂ equiv.
GP5a	EtOAc	3.0
GP5b	EtOAc:acetone (2:1)	4.0
GP5c	EtOAc:CH ₃ CN (7:3)	4.0
GP5d	EtOAc:PhF (7:3)	4.0

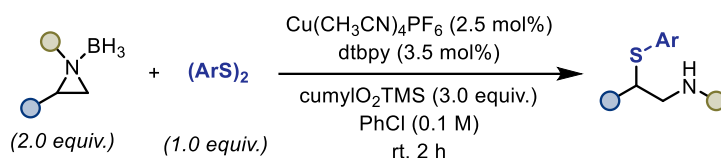
General Procedure for the Ring Opening-Cyanation of Aziridine Boranes – GP6



An oven-dried vial equipped with a stirring bar was charged with the corresponding aziridine borane (0.1 mmol, 1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). The peroxide (0.3 mmol, 3.0 equiv.), TMSCN (0.2 mmol, 2.0 equiv.) and dry and degassed CH₃CN (0.5 mL) was then added to the

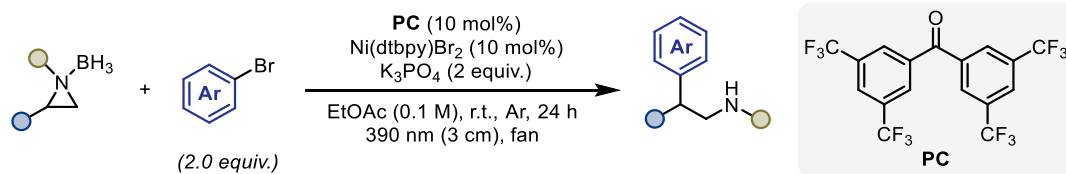
vial and stirred for around **1 min**. The catalyst solution (0.5 mL of dry and degassed CH₃CN, containing Cu(CH₃CN)₄PF₆ (1 mg, 2.5 mol%) and dtbpy (1 mg, 3.5 mol%), pre-stirred for 10 min until fully dissolved) was then added under stirring. The resulting mixture was stirred at room temperature for 2 h. Upon completion, an aqueous solution of NaOH (2 mL, 1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x 3 mL). The combined organic layers were dried (MgSO₄) and filtered. The solvent was evaporated, and the residue was purified by column chromatography on silica gel to afford the desired products.

General Procedure for the Ring Opening-Thiolation of Aziridine Boranes– GP7



An oven-dried vial equipped with a stirring bar was charged with the corresponding aziridine borane (0.2 mmol, 1.0 equiv.) and diaryl disulfide ((ArS)₂, 0.1 mmol, 1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). The peroxide (0.3 mmol, 3.0 equiv.) and dry and degassed PhCl (0.5 mL) was then added to the vial and stirred for around **1 min**. The catalyst solution (0.5 mL of dry and degassed PhCl, containing Cu(CH₃CN)₄PF₆ (1 mg, 2.5 mol%) and dtbpy (1 mg, 3.5 mol%), pre-stirred for 10 min until fully dissolved) was then added under stirring. The resulting mixture was stirred at room temperature for 2 h. Upon completion, aqueous NaOH (2 mL, 1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x 3 mL). The combined organic layers were dried (MgSO₄) and filtered. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford the desired products.

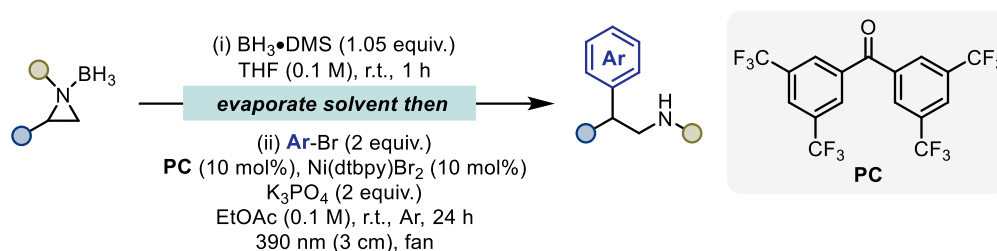
General Procedure for the Nickel Catalyzed Ring Opening-Arylation of Aziridine Boranes – GP8a



An oven-dried microwave vial was charged with aziridine borane (0.1 mmol, 1.0 equiv.), aryl bromides (0.2 mmol, 2.0 equiv.), 3,3',5,5'-tetrakis(trifluoromethyl)benzophenone (5 mg, 10 mol%), Ni(dtbpy)Br₂ (5 mg, 10 mol%) and K₃PO₄ (42 mg, 2.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). Dry and degassed EtOAc (1.0 mL) was then added to the vial and the mixture was stirred for 1

min at room temperature and then was placed 3 cm from the 390 nm purple LEDs (*the reaction temperature was around 35 °C, it's worth noting that distance and temperature have an influence on the reaction yield*). The LEDs were switched on (kessil, 100 W) and the mixture was stirred under irradiation with a fan for 24 hours. Upon completion, aqueous NaOH (2 mL, 1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x 3 mL). The combined organic layers were dried (MgSO₄) and filtered. The solvent was evaporated, and the residue was purified by column chromatography on silica gel to afford the desired products.

General Procedure for the Nickel Catalyzed Ring Opening-Arylation of Aziridine Boranes – GP8b



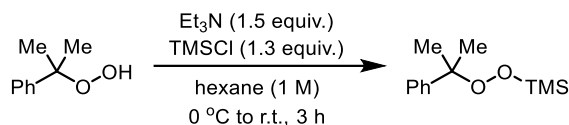
An oven-dried microwave vial equipped with a stirring bar was charged with the aziridine (0.1 mmol, 1.0 equiv.), dry THF (1 mL, 0.1 M) was added, followed by BH₃•DMS (52.5 uL, 1.05 equiv., 2 M in THF). The mixture was stirred for 1 h at r.t. The volatiles were evaporated, and the vial was charged with the aryl bromide (2.0 equiv.), 3,3',5,5'-tetrakis(trifluoromethyl)benzophenone (5 mg, 10 mol%), Ni(dtbpy)Br₂ (5 mg, 10 mol%) and K₃PO₄ (42 mg, 2.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). Dry and degassed EtOAc (1.0 mL) was then added to the vial and the mixture was stirred for **1 min** at room temperature and then was placed 3 cm from the 390 nm purple LEDs (*the reaction temperature was around 35 °C*). The LEDs were switched on (kessil, 100 W) and the mixture was stirred under irradiation with a fan for 24 hours. Upon completion, aqueous NaOH (2 mL, 1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x 3 mL). The combined organic layers were dried (MgSO₄) and filtered. The solvent was evaporated, and the residue was purified by column chromatography on silica gel to afford the desired products.

3 Starting Material Synthesis

Please note that the starting material synthesis is not optimised.

3.1 Peroxides

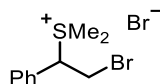
Trimethyl((2-phenylpropan-2-yl)peroxy)silane



A round bottom flask equipped with a stirring bar was charged with Et₃N (10.5 mL, 75.0 mmol, 1.50 equiv.) and hexane (100 mL). CumylO₂H (9.3 mL, 80% technical solution, 50 mmol, 1.0 equiv.) was slowly added. The reaction media was then cooled in an ice-water bath and TMSCl (8.25 mL, 65.0 mmol, 1.30 equiv.) was slowly added. When the addition was completed, the ice-water bath was removed and the reaction was let stirring at room temperature. After 3 h, H₂O (100 mL) was added. The layers were separated and the organic phase was washed with H₂O (100 mL x 4) and brine (100 mL), dried (MgSO₄), filtered and evaporated to give cumylO₂TMS as an oil (10.97 g, 98%) with approx density of 0.94 g/mL. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (2H, d, *J* = 8.4 Hz), 7.33 (2H, t, *J* = 7.7 Hz), 7.24 (1H, t, *J* = 7.9 Hz), 1.58 (6H, s), 0.18 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 145.4, 127.9, 127.0, 125.6, 83.4, 26.5, -1.1. Data in accordance with the literature.⁷

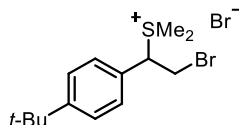
3.2 Sulfonium Bromide Salts

(2-Bromo-1-phenylethyl)dimethylsulfonium Bromide (S1a)



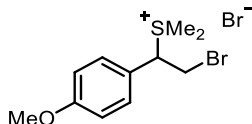
Following **GP1a**, styrene (23 mL, 200 mmol, 2.0 equiv.) gave **S1a** (24.52 g, 75%) as a solid. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) 7.62 – 7.56 (2H, m), 7.56 – 7.50 (3H, m), 5.52 – 5.44 (1H, dd, $J=10.1$, 5.5 Hz), 4.46 – 4.35 (2H, m), 3.00 (3H, s), 2.71 (3H, s); ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 130.4, 130.1, 129.6, 129.3, 58.2, 29.3, 23.9, 22.7. Data in accordance with the literature.⁸

(2-Bromo-1-(4-(*tert*-butyl)phenyl)ethyl)dimethylsulfonium Bromide (S2a)



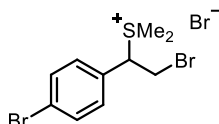
Following **GP1a**, 1-(*tert*-butyl)-4-vinylbenzene (5.49 mL, 30 mmol, 1.5 equiv.) gave **S2a** (4.36 g, 57%) as a solid. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) 7.55 (2H, d, $J = 8.0$ Hz), 7.49 (2H, d, $J = 8.0$ Hz), 5.36 (1H, dd, $J = 10.0$, 5.6 Hz), 4.44 – 4.31 (2H, m), 2.94 (3H, s), 2.67 (3H, s), 1.30 (9H, s); ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$): 153.0, 129.3, 127.0, 126.2, 58.3, 34.6, 30.9, 29.4, 23.8, 22.6.

(2-Bromo-1-(4-methoxyphenyl)ethyl)dimethylsulfonium Bromide (S3a)



Following **GP1a**, 1-methoxy-4-vinylbenzene (4.03 g, 30 mmol, 1.5 equiv.) gave **S3a** (4.27 g, 60%) as a solid. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 7.29 (2H, d, $J = 8.4$ Hz), 6.87 (2H, d, $J = 8.6$ Hz), 4.71 (1H, dd, $J = 7.1$, 4.7 Hz), 3.72 (3H, s), 3.59 (1H, dd, $J = 10.2$, 4.7 Hz), 3.52 (1H, dd, $J = 10.1$, 7.1 Hz), 2.54 (6H, s); ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 158.7, 134.7, 127.5, 113.5, 71.8, 55.1, 40.4 (2C), 40.4.

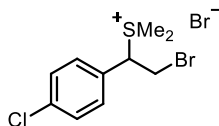
(2-Bromo-1-(4-bromophenyl)ethyl)dimethylsulfonium Bromide (S4a)



Following **GP1b**, 1-bromo-4-vinylbenzene (2.6 mL, 20 mmol, 1.0 equiv.) gave **S4a** (2.90 g, 36%) as a solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.77 (2H, d, $J = 8.3$ Hz), 7.51 (2H, d, $J = 8.5$ Hz), 5.32 (1H, dd, $J = 9.9$, 5.9 Hz), 4.44 – 4.29 (2H, m), 2.92 (3H, s), 2.68 (3H, s); ^{13}C NMR (101

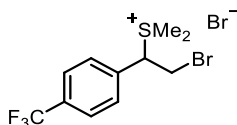
MHz, DMSO-*d*₆) δ 132.4, 131.7, 129.4, 124.2, 57.8, 28.9, 23.9, 22.6. Data in accordance with the literature.¹

(2-Bromo-1-(4-chlorophenyl)ethyl)dimethylsulfonium Bromide (S5a)



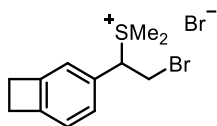
Following **GP1b**, 1-chloro-4-vinylbenzene (3.6 mL, 30 mmol, 1.0 equiv.) gave **S5a** (4.40 g, 41%) as a solid. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.64 (2H, d, *J* = 8.6 Hz), 7.59 (2H, d, *J* = 8.6 Hz), 5.36 (1H, dd, *J* = 10.1, 5.6 Hz), 4.40 (1H, dd, *J* = 10.8, 5.7 Hz), 4.36 (1H, t, *J* = 10.5 Hz), 2.94 (3H, s), 2.69 (3H, s); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 135.3, 131.5, 129.5, 129.0, 57.7, 29.0, 23.9, 22.6.

(2-Bromo-1-(4-(trifluoromethyl)phenyl)ethyl)dimethylsulfonium Bromide (S6a)



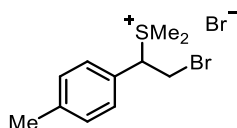
Following **GP1a**, 1-(trifluoromethyl)-4-vinylbenzene (5.16 g, 30 mmol, 1.5 equiv.) gave **S6a** (2.34 g, 30%) as a solid. *Note: This sulfonium bromide salt could not be characterized as it was quickly decomposing. Hence, it was directly used in the second step (see below in section 3.3).*

(1-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-2-bromoethyl)dimethylsulfonium Bromide (S7a)



Following **GP1b**, 3-vinylbicyclo[4.2.0]octa-1(6),2,4-triene (0.5 mL, 3.7 mmol, 1.0 equiv.) gave **S7a** (800 mg, 61%) as a solid. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.32 (1H, d, *J* = 7.4 Hz), 7.28 (1H, s), 7.24 (1H, d, *J* = 7.6 Hz), 5.30 – 5.17 (1H, m), 4.38 (1H, dd, *J* = 10.7, 5.6 Hz), 4.32 (1H, t, *J* = 10.4 Hz), 3.19 (4H, s), 2.91 (3H, s), 2.63 (3H, s); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 148.1, 146.5, 128.8, 128.4, 123.5, 123.4, 59.6, 29.5, 29.3, 29.1, 24.0, 22.7.

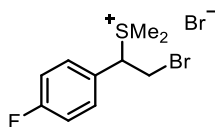
(2-Bromo-1-(*p*-tolyl)ethyl)dimethylsulfonium Bromide (S8a)



Following **GP1b**, 1-methyl-4-vinylbenzene (5.27 mL, 40 mmol, 1.0 equiv.) gave **S8a** (9.0 g, 66%) as a solid. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.47 (2H, d, *J* = 7.5 Hz), 7.36 (2H, d, *J* = 7.8 Hz),

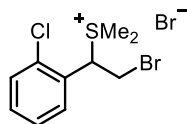
5.58 (1H, dd, $J = 9.2, 5.6$ Hz), 4.38 (1H, dd, $J = 11.0, 5.9$ Hz), 4.25 (1H, t, $J = 10.1$ Hz), 3.11 (3H, s), 2.78 (3H, s), 2.45 (3H, s); ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 140.5, 129.7, 129.0, 126.1, 59.1, 28.7, 24.0, 22.2, 20.8.

(2-Bromo-1-(4-fluorophenyl)ethyl)dimethylsulfonium Bromide (S9a)



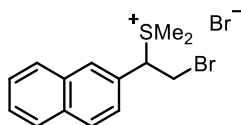
Following **GP1b**, 1-fluoro-4-vinylbenzene (4.77 mL, 40 mmol, 1.0 equiv.) gave **S9a** (9.75 g, 71%) as a solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.66 – 7.57 (2H, m), 7.47 – 7.36 (2H, m), 5.45 – 5.25 (1H, m), 4.54 – 4.26 (2H, m), 2.93 (3H, s), 2.67 (3H, s); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.0 (d, $J = 8.9$ Hz), 126.3 (d, $J = 3.3$ Hz), 116.5 (d, $J = 21.7$ Hz), 57.8, 29.2, 23.9, 22.5; ^{19}F NMR (565 MHz, $\text{DMSO-}d_6$) δ -80.42 (d, $J = 6.2$ Hz).

(2-Bromo-1-(2-chlorophenyl)ethyl)dimethylsulfonium Bromide (S10a)



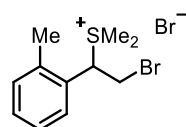
Following **GP1b**, 1-chloro-2-vinylbenzene (5.1 mL, 40 mmol, 1.0 equiv.) gave **S10a** (considered as 60-70%) as a solid. *Note: This sulfonium bromide salt could not be characterized as it was quickly decomposing. Hence, it was directly used in the second step (see below in section 3.3).*

(2-Bromo-1-(naphthalen-2-yl)ethyl)dimethylsulfonium Bromide (S11a)



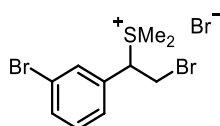
Following **GP1b**, 2-vinylnaphthalene (3.08 g, 20 mmol, 1.0 equiv.) gave **S11a** (4.6 g, 61%) as a solid. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.17 – 8.12 (1H, m), 8.10 (1H, d, $J = 8.5$ Hz), 8.06 – 7.99 (2H, m), 7.68 – 7.59 (3H, m), 5.47 (1H, dd, $J = 8.8, 7.0$ Hz), 4.51 – 4.47 (2H, m), 2.98 (3H, s), 2.70 (3H, s); ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 133.5, 133.6, 130.0, 129.3, 128.3, 127.8, 127.7, 127.4, 127.2, 125.8, 58.9, 29.3, 24.0, 22.8.

(2-Bromo-1-(o-tolyl)ethyl)dimethylsulfonium Bromide (S12a)



Following **GP1a**, 1-methyl-2-vinylbenzene (1.94 mL, 15 mmol, 1.5 equiv.) gave **S12a** (2.15 g, 83%) as a solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.65 – 7.55 (1H, m), 7.44 – 7.32 (3H, m), 5.60 – 5.47 (1H, m), 4.41 – 4.24 (2H, m), 3.14 (3H, s), 2.78 (3H, s), 2.43 (3H, s); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$): 138.5, 131.3, 130.0, 129.6, 127.8 (br s), 127.1, 54.8 (br s), 30.6, 23.5, 23.3, 19.6.

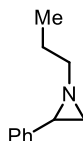
(2-Bromo-1-(3-bromophenyl)ethyl)dimethylsulfonium Bromide (S13a)



Following **GP1b**, 1-bromo-3-vinylbenzene (1.95 mL, 15 mmol, 1.0 equiv.) gave **S13a** (considered as 60-70%) as a solid. *Note: This sulfonium bromide salt could not be characterized as it was quickly decomposing under air. Hence, it was directly used in the second step (see below in section 3.3).*

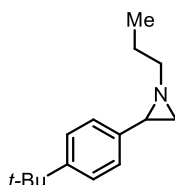
3.3 Aziridines

2-Phenyl-1-propylaziridine (**1**)



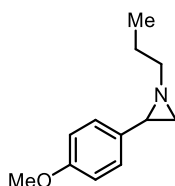
Following **GP2**, **S1a** (1.63 g, 5 mmol, 1.0 equiv.) and propylamine (1.48 g, 25.0 mmol, 5.0 equiv.) gave after purification via column chromatography **1** (734 mg, 91%) as an oil. R_f 0.58 [*n*-pentane:EtOAc (10:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.19 (5H, m), 2.50 (1H, dt, J = 11.5, 7.3 Hz), 2.37 – 2.26 (2H, m), 1.91 (1H, d, J = 3.4 Hz), 1.73 – 1.61 (3H, m), 0.99 (3H, t, J = 7.4 Hz). Data in accordance with the literature.⁹

2-(4-(*tert*-Butyl)phenyl)-1-propylaziridine (**2**)



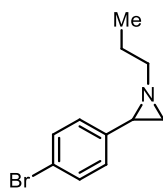
Following **GP2**, **S2a** (4.36 g, 11.4 mmol, 1.0 equiv.) and propylamine (3.37 g, 57.0 mmol, 5.0 equiv.) gave after purification via column chromatography **2** (2.28 g, 92%) as an oil. R_f 0.23 [*n*-pentane:EtOAc (30:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (2H, d, J = 8.3 Hz), 7.22 (2H, d, J = 8.4 Hz), 2.50 (1H, dt, J = 11.6, 7.2 Hz), 2.36 – 2.25 (2H, m), 1.91 (1H, d, J = 3.4 Hz), 1.73 – 1.61 (3H, m), 1.34 (9H, s), 0.99 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 149.8, 137.6, 126.0, 125.3, 63.9, 41.1, 37.7, 34.6, 31.5, 23.2, 12.2. HRMS (ESI) found MH^+ 218.1896, $\text{C}_{15}\text{H}_{24}\text{N}$ requires 218.1903.

2-(4-Methoxyphenyl)-1-propylaziridine (**3**)



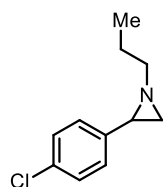
Following **GP2**, **S3a** (4.84 g, 13.6 mmol, 1.0 equiv.) and propylamine (4.02 g, 68.0 mmol, 5.0 equiv.) gave after purification via column chromatography **3** (1.46 g, 56%) as an oil. R_f 0.4 [*n*-pentane:EtOAc (6:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.16 (2H, d, J = 8.6 Hz), 6.83 – 6.81 (2H, d, J = 8.6 Hz), 3.78 (3H, s), 2.46 (1H, dt, J = 11.5, 7.2 Hz), 2.30 – 2.22 (2H, m), 1.85 (1H, d, J = 3.3 Hz), 1.66 – 1.59 (3H, m), 0.95 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 158.8, 132.8, 127.4, 113.9, 63.8, 55.4, 40.9, 37.5, 23.2, 12.1. HRMS (ESI) found MH^+ 192.1375, $\text{C}_{12}\text{H}_{18}\text{NO}$ requires 192.1383.

2-(4-Bromophenyl)-1-propylaziridine (**4**)



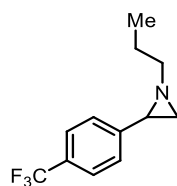
Following **GP2**, **S4a** (2.90 g, 7.2 mmol, 1.0 equiv.) and propylamine (3.0 mL, 36 mmol, 5.0 equiv.) gave **4** (1.57 g, 91%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (2H, d, $J = 8.4$ Hz), 7.12 (2H, d, $J = 8.4$ Hz), 2.46 (1H, dt, $J = 11.5, 7.2$ Hz), 2.36 – 2.19 (2H, m), 1.83 (1H, d, $J = 3.3$ Hz), 1.72 – 1.55 (3H, m), 0.95 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 131.4, 128.0, 120.6, 63.6, 40.7, 38.0, 23.2, 12.1. HRMS (ESI) found MH^+ 240.0384, $\text{C}_{11}\text{H}_{15}\text{BrN}$ requires 240.0382.

2-(4-Chlorophenyl)-1-propylaziridine (**5**)



Following **GP2**, **S5a** (4.40 g, 12.3 mmol, 1.0 equiv.) and propylamine (5.1 mL, 62 mmol, 5.0 equiv.) gave **5** (2.17 g, 90%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 7.25 (2H, d, $J = 8.4$ Hz), 7.17 (2H, d, $J = 8.5$ Hz), 2.46 (1H, dt, $J = 11.5, 7.2$ Hz), 2.35 – 2.22 (2H, m), 1.83 (1H, d, $J = 3.2$ Hz), 1.70 – 1.55 (3H, m), 0.95 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 139.3, 132.5, 128.5, 127.7, 63.6, 40.7, 38.0, 23.2, 12.1. HRMS (ESI) found MH^+ 196.0888, $\text{C}_{11}\text{H}_{15}\text{NCl}$ requires 196.0888.

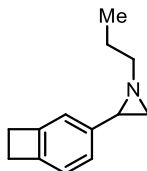
1-Propyl-2-(4-(trifluoromethyl)phenyl)aziridine (**6**)



Following **GP2**, **S6a** (1.89 g, 6.0 mmol, 1.0 equiv.) and propylamine (1.77 g, 30.0 mmol, 5.0 equiv.) gave after purification via column chromatography **6** (1.11 g, 81%) as an oil. R_f 0.55 [n -pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.53 (2H, d, $J = 8.1$ Hz), 7.35 (2H, d, $J = 8.0$ Hz), 2.49 (1H, dt, $J = 11.5, 7.2$ Hz), 2.36 – 2.27 (2H, m), 1.87 (1H, dd, $J = 3.2, 0.8$ Hz), 1.72 (1H, d, $J = 6.5$ Hz), 1.63 (2H, sx, $J = 7.3$ Hz), 0.96 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 145.03, 129.10 (q, $J = 32.3$ Hz), 126.57, 125.31 (q, $J = 3.8$ Hz), 124.5 (q, $J = 271.9$ Hz),

63.5, 40.8, 38.4, 23.1, 12.1; ^{19}F NMR (565 MHz, CDCl_3) δ -62.37. HRMS (ESI) found MH^+ 230.1145, $\text{C}_{12}\text{H}_{15}\text{NF}_3$ requires 230.1151.

2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-1-propylaziridine (7)



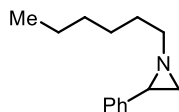
Following **GP2**, **S7a** (800 mg, 2.26 mmol, 1.0 equiv.) and propylamine (900 μL , 11.25 mmol, 5.0 equiv.) gave **7** (360 mg, 95%) as yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.10 (1H, dd, J = 7.4, 1.5 Hz), 6.96 (1H, d, J = 7.6 Hz), 6.94 (1H, s), 3.13 (4H, s), 2.48 (1H, dt, J = 11.5, 7.2 Hz), 2.32 – 2.19 (2H, m), 1.85 (1H, d, J = 3.3 Hz), 1.71 – 1.57 (3H, m), 0.96 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 146.0, 144.4, 139.3, 125.1, 122.4, 120.4, 63.8, 42.0, 37.9, 29.5, 29.4, 23.2, 12.2. HRMS (ESI) found MH^+ 188.1433, $\text{C}_{13}\text{H}_{18}\text{N}$ requires 188.1434.

1-Methyl-2-phenylaziridine (8)



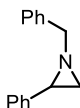
Following **GP2**, **S1a** (3.26 g, 10 mmol, 1 equiv.) and 40% methylamine aqueous solution (4.6 mL, 50 mmol, 5.0 equiv.) gave after purification via column chromatography **8** (821 mg, 54%) as an oil. R_f 0.21 [n -pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.33 – 7.27 (2H, m), 7.25 – 7.19 (3H, m), 2.50 (3H, s), 2.27 (1H, dd, J = 6.5, 3.3 Hz), 1.91 (1H, d, J = 3.4 Hz), 1.63 (1H, d, J = 6.5 Hz). Data in accordance with the literature.¹⁰

1-Hexyl-2-phenylaziridine (9)



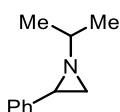
Following **GP2**, **S1a** (4.89 g, 15 mmol, 1.0 equiv.) and n -hexylamine (7.59 g, 75.0 mmol, 5.0 equiv.) gave after purification via column chromatography **9** (2.65 g, 87%) as an oil. R_f 0.72 [n -pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.31 – 7.18 (5H, m), 2.52 – 2.44 (1H, m), 2.36 – 2.27 (2H, m), 1.89 (1H, d, J = 3.3 Hz), 1.67 – 1.57 (3H, m), 1.40 – 1.33 (2H, m), 1.33 – 1.24 (4H, m), 0.88 (3H, t, J = 6.9 Hz). Data in accordance with the literature.⁹

1-Benzyl-2-phenylaziridine (**10**)



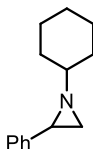
Following **GP2**, **S1a** (4.89 g, 15 mmol, 1.0 equiv.) and benzylamine (8.04 g, 75.0 mmol, 5.0 equiv.) gave after purification via column chromatography **10** (2.64 g, 84%) as an oil. R_f 0.55 [*n*-pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.43 – 7.39 (2H, m), 7.37 – 7.22 (8H, m), 3.73 (1H, d, J = 13.7 Hz), 3.65 (1H, d, J = 13.7 Hz), 2.54 (1H, dd, J = 6.5, 3.4 Hz), 2.02 (1H, d, J = 3.3 Hz), 1.88 (1H, d, J = 6.5 Hz). Data in accordance with the literature.¹⁰

1-Isopropyl-2-phenylaziridine (**11**)



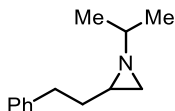
Following **GP2**, **S1a** (1.63 g, 5 mmol, 1.0 equiv.) and isopropylamine (1.48 g, 25.0 mmol, 5.0 equiv.) gave after purification via column chromatography **11** (613 mg, 76%) as an oil. R_f 0.55 [*n*-pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.34 – 7.27 (4H, m), 7.27 – 7.21 (1H, m), 2.37 (1H, dd, J = 6.6, 3.4 Hz), 1.92 (1H, d, J = 3.3 Hz), 1.69 (1H, d, J = 6.6 Hz), 1.64 (1H, hp, J = 6.3 Hz), 1.21 (6H, d, J = 6.3 Hz). Data in accordance with the literature.⁹

1-Cyclohexyl-2-phenylaziridine (**12**)



Following **GP2**, **S1a** (4.89 g, 15 mmol, 1.0 equiv.) and cyclohexylamine (7.44 g, 75.0 mmol, 5.0 equiv.) gave after purification via column chromatography **12** (2.63 g, 87%) as an oil. R_f 0.6 [*n*-pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.27 (4H, m), 7.26 – 7.20 (1H, m), 2.37 (1H, dd, J = 6.6, 3.3 Hz), 1.93 – 1.86 (3H, m), 1.85 – 1.75 (2H, m), 1.69 (1H, d, J = 6.0 Hz), 1.66 – 1.61 (1H, m), 1.50 – 1.41 (2H, m), 1.36 – 1.27 (1H, m), 1.27 – 1.17 (3H, m). Data in accordance with the literature.⁹

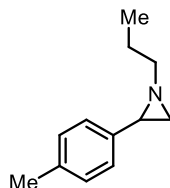
1-Isopropyl-2-phenethylaziridine (**13**)



Following **GP3a**, 4-phenyl-1-butene (1.32 g, 10.0 mmol, 1.0 equiv.) and isopropylamine (709 mg, 12.0 mmol, 1.2 equiv.) gave **13** (571 mg, 30% over two steps) as an oil. R_f 0.26 [*n*-pentane: EtOAc

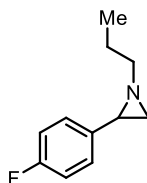
(1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.29 (2H, t, $J = 7.6$ Hz), 7.25 – 7.21 (2H, m), 7.21 – 7.17 (1H, m), 2.86 (1H, ddd, $J = 13.8, 10.1, 5.8$ Hz), 2.73 (1H, ddd, $J = 13.8, 10.0, 6.2$ Hz), 1.81 (1H, dddd, $J = 13.7, 10.0, 6.2, 5.0$ Hz), 1.63 (1H, dddd, $J = 13.6, 10.0, 7.6, 5.8$ Hz), 1.53 (1H, d, $J = 3.4$ Hz), 1.42 – 1.33 (2H, m), 1.25 (1H, d, $J = 6.4$ Hz), 1.17 (3H, d, $J = 6.2$ Hz), 1.14 (3H, d, $J = 6.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 142.1, 128.4, 128.4, 125.8, 60.9, 38.7, 35.2, 34.1, 33.1, 22.5, 21.9. Data in accordance with the literature.⁴

1-Propyl-2-(*p*-tolyl)aziridine (**14**)



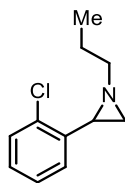
Following **GP2**, **S8a** (9.00 g, 26.4 mmol, 1.0 equiv.) and propylamine (6.5 mL, 135 mmol, 5.0 equiv.) gave **14** (3.1 g, 90%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 7.14 (2H, d, $J = 8.2$ Hz), 7.10 (2H, d, $J = 7.9$ Hz), 2.49 (1H, dt, $J = 11.5, 7.2$ Hz), 2.32 (3H, s), 2.29 – 2.21 (2H, m), 1.87 (1H, dd, $J = 3.4, 0.7$ Hz), 1.68 – 1.58 (3H, m), 0.96 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 137.7, 136.5, 129.1, 126.2, 63.8, 41.2, 37.7, 23.2, 21.2, 12.1. HRMS (ESI) found MH^+ 176.1434, $\text{C}_{12}\text{H}_{18}\text{N}$ requires 176.1434.

2-(4-Fluorophenyl)-1-propylaziridine (**15**)



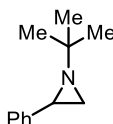
Following **GP2**, **S9a** (9.75 g, 28 mmol, 1.0 equiv.) and propylamine (6.5 mL, 140 mmol, 5.0 equiv.) gave **15** (4.77 g, 95%) as an oil. ^1H NMR (600 MHz, CDCl_3) δ 7.20 (2H, dd, $J = 8.6, 5.6$ Hz), 6.97 (2H, dd, $J = 8.7, 8.3$ Hz), 2.45 (1H, dt, $J = 11.4, 7.2$ Hz), 2.34 – 2.25 (2H, m), 1.84 (1H, d, $J = 3.2$ Hz), 1.68 – 1.58 (3H, m), 0.96 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 162.3 (d, $J = 244.3$ Hz), 136.6 (d, $J = 3.0$ Hz), 128.0 (d, $J = 7.9$ Hz), 115.4 (d, $J = 21.3$ Hz), 63.9, 40.9, 38.0, 23.4, 12.3; ^{19}F NMR (CDCl_3 , 565 MHz) δ –116.39 (tt, $J = 8.6, 4.4$ Hz). HRMS (ESI) found MH^+ 180.1184, $\text{C}_{11}\text{H}_{15}\text{FN}_2$ requires 180.1183.

2-(2-Chlorophenyl)-1-propylaziridine (**16**)



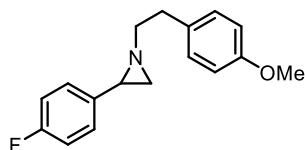
Following **GP2**, **S10a** (8.65 g, 24 mmol, 1.0 equiv.) and propylamine (7.5 mL, 125 mmol, 5.0 equiv.) gave **16** (2.11 g, 27% over two steps) as a light-yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.27 (2H, m), 7.24 – 7.10 (2H, m), 2.65 (1H, dd, J = 6.7, 3.2 Hz), 2.49 (1H, dt, J = 11.8, 7.2 Hz), 2.38 (1H, dt, J = 11.8, 7.0 Hz), 1.81 (1H, d, J = 3.3 Hz), 1.73 (1H, d, J = 6.5 Hz), 1.65 (2H, sx, J = 7.3 Hz), 1.01 – 0.94 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 138.0, 133.8, 128.9, 127.7, 127.5, 126.8, 63.3, 38.8, 37.2, 23.1, 12.0. HRMS (ESI) found MH^+ 196.0889, $\text{C}_{11}\text{H}_{15}\text{ClN}$ requires 196.0888.

1-(*tert*-Butyl)-2-phenylaziridine (**17**)

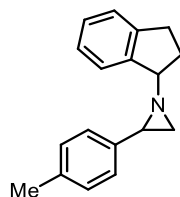


Following **GP2**, **S1a** (4.89 g, 15 mmol, 1.0 equiv.) and *tert*-butylamine (5.49 g, 75.0 mmol, 5.0 equiv.) gave after purification via column chromatography **17** (2.31 g, 88%) as an oil. R_f 0.2 [*n*-pentane:EtOAc (50:1)]. ^1H NMR (600 MHz, CDCl_3): 7.33 – 7.26 (4H, m), 7.23 – 7.17 (1H, m), 2.63 (1H, dd, J = 6.4, 3.0 Hz), 1.89 (1H, dd, J = 6.4, 0.9 Hz), 1.64 (1H, dd, J = 3.1, 0.9 Hz), 1.05 (9H, s). Data in accordance with the literature.¹⁰

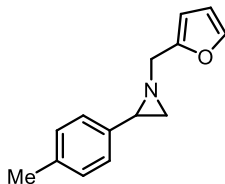
2-(4-Fluorophenyl)-1-(4-methoxyphenethyl)aziridine (**18**)



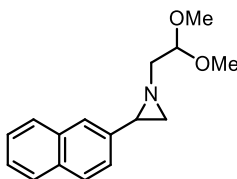
Following **GP2**, **S9a** (4.7 g, 13.65 mmol, 1.0 equiv.) and 2-(4-methoxyphenyl)ethan-1-amine (5.1 mL, 34.5 mmol, 2.5 equiv.) gave after purification via column chromatography **18** (1.84 g, 95%) as a light-yellow oil. R_f 0.39 [*n*-pentane:EtOAc (8:2)]. ^1H NMR (600 MHz, CDCl_3) δ 7.18 – 7.12 (2H, m), 7.09 (2H, d, J = 8.3 Hz), 6.97 (2H, t, J = 8.7 Hz), 6.83 – 6.75 (2H, m), 3.78 (3H, s), 2.86 (2H, t, J = 7.4 Hz), 2.73 (1H, dt, J = 11.5, 7.4 Hz), 2.54 (1H, dt, J = 11.5, 7.4 Hz), 2.23 (1H, dd, J = 6.6, 3.4 Hz), 1.84 (1H, d, J = 3.3 Hz), 1.64 (1H, d, J = 6.5 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 162.1 (d, J = 244.4 Hz), 158.1, 136.2 (d, J = 2.9 Hz), 132.2, 129.9, 127.8 (d, J = 8.1 Hz), 115.2 (d, J = 21.4 Hz), 113.9, 63.6, 55.4, 40.9, 37.9, 35.6; ^{19}F NMR (565 MHz, CDCl_3) δ -116.29. HRMS (ESI) found MH^+ 272.1443, $\text{C}_{17}\text{H}_{19}\text{FNO}$ requires 272.1445.

1-(2,3-dihydro-1H-inden-1-yl)-2-(p-tolyl)aziridine (19)

Following **GP2**, **S8a** (1.02 g, 3 mmol, 1.0 equiv.) and 2,3-dihydro-1H-inden-1-amine (768 μ L, 6 mmol, 2.0 equiv.) gave after purification via column chromatography **19** as mixture of diastereomers (770 mg, 99% yield, the mixture was used directly in the next step) as an oil. d.r. 1:1. R_f 0.74 and 0.87 [*n*-pentane:EtOAc (8:2)]. ^1H NMR (400 MHz, CDCl_3), *signals corresponding to both diastereomers*: δ 7.48 – 7.42 (0.5H, m), 7.31 – 7.14 (5H, m), 7.10 (2.5H, d, J = 8.1 Hz), 3.32 (0.5H, t, J = 7.0 Hz), 3.25 (0.5H, dd, J = 7.0, 4.9 Hz), 3.18 – 3.01 (1H, m), 2.89 – 2.77 (1H, m), 2.71 (0.5H, dd, J = 6.6, 3.3 Hz), 2.57 (0.5H, dd, J = 6.6, 3.4 Hz), 2.42 – 2.26 (4H, m), 2.22 – 2.11 (1H, m), 2.09 (0.5H, d, J = 6.6 Hz), 2.02 (0.5H, d, J = 3.4 Hz), 1.92 (0.5H, d, J = 3.3 Hz), 1.87 (0.5H, d, J = 6.6 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 144.5, 144.2, 144.1, 144.1, 137.4, 137.3, 136.6, 136.5, 129.2, 129.1, 128.0, 127.7, 126.5 (2C), 126.4 (2C), 125.1, 124.8, 124.1 (2C), 74.9, 74.9, 41.2, 39.4, 37.4, 35.2, 33.0, 32.6, 30.8, 30.6, 21.2, 21.2. HRMS (ESI) found MNa^+ 272.1411, $\text{C}_{18}\text{H}_{19}\text{NNa}$ requires 272.1410.

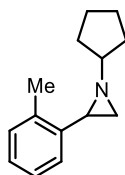
1-(Furan-2-ylmethyl)-2-(p-tolyl)aziridine (20)

Following **GP2**, **S8a** (2.00 g, 5.81 mmol, 1.0 equiv.) and furan-2-ylmethanamine (2.7 mL, 34.5 mmol, 2.5 equiv.) gave **20** (1.30 g, 95%) as a light-yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 7.36 (1H, s), 7.16 – 7.12 (2H, m), 7.10 (2H, d, J = 7.8 Hz), 6.32 – 6.29 (1H, m), 6.23 (1H, d, J = 3.2 Hz), 3.61 (2H, s), 2.51 (1H, dd, J = 6.7, 3.5 Hz), 2.31 (3H, s), 1.99 – 1.93 (1H, m), 1.86 (1H, d, J = 6.2 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 152.8, 142.1, 136.9, 136.7, 129.1, 126.3, 110.3, 107.5, 57.0, 41.1, 37.3, 21.2. HRMS (ESI) found MH^+ 214.1225, $\text{C}_{14}\text{H}_{16}\text{NO}$ requires 214.1226.

1-(2,2-Dimethoxyethyl)-2-(naphthalen-2-yl)aziridine (21)

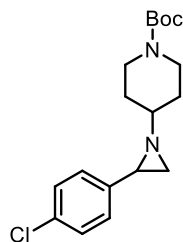
Following **GP2**, **S11a** (1.53 g, 4.1 mmol, 1.0 equiv.) and 2,2-dimethoxyethan-1-amine (2.25 mL, 20 mmol, 5.0 equiv.) gave **21** (1.01 g, 95%) as a light-yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 7.83 – 7.75 (3H, m), 7.74 (1H, t, J = 1.1 Hz), 7.47 – 7.40 (2H, m), 7.36 (1H, dd, J = 8.5, 1.7 Hz), 4.61 (1H, t, J = 5.3 Hz), 3.44 (3H, s), 3.37 (3H, s), 2.76 (1H, dd, J = 12.2, 5.2 Hz), 2.62 (1H, dd, J = 6.5, 3.5 Hz), 2.55 (1H, dd, J = 12.2, 5.4 Hz), 2.05 (1H, d, J = 3.4 Hz), 1.84 (1H, d, J = 6.5 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 137.8, 133.5, 132.8, 128.1, 127.8, 127.8, 126.1, 125.6, 125.1, 124.6, 104.9, 63.1, 54.8, 41.6, 37.6. HRMS (ESI) found MH^+ 258.1488, $\text{C}_{16}\text{H}_{20}\text{NO}_2$ requires 258.1489.

1-Cyclopentyl-2-(*o*-tolyl)aziridine (**22**)

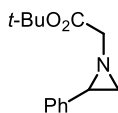


Following **GP2**, **S12a** (1.61 g, 4.75 mmol, 1.0 equiv.) and cyclopentylamine (2.35 mL, 140 mmol, 5.0 equiv.) gave after purification via column chromatography **22** (840 mg, 88%) as a yellow oil. R_f 0.64 [n -pentane:EtOAc (9:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.30 (1H, m), 7.20 – 7.04 (3H, m), 2.42 (1H, dd, J = 6.6, 3.4 Hz), 2.39 (3H, s), 2.11 (1H, p, J = 5.5 Hz), 1.96 – 1.82 (2H, m), 1.82 – 1.66 (6H, m), 1.64 – 1.51 (2H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 138.7, 136.2, 129.5, 126.6, 126.5, 126.1, 72.5, 39.3, 36.1, 33.3, 32.4, 24.6, 24.4, 19.2. HRMS (ESI) found MH^+ 202.1591, $\text{C}_{14}\text{H}_{20}\text{N}$ requires 202.1590.

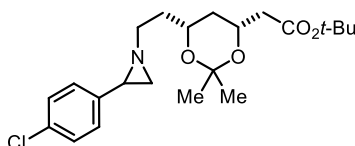
tert-Butyl 4-(2-(4-Chlorophenyl)aziridin-1-yl)piperidine-1-carboxylate (**23**)



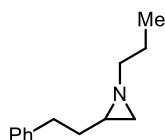
Following **GP2**, **S5a** (1.73 g, 4.8 mmol, 1.0 equiv.) and *tert*-butyl 4-aminopiperidine-1-carboxylate (4.80 g, 24 mmol, 5.0 equiv.) gave after purification via column chromatography **23** (1.44 g, 90%) as a light-yellow oil. R_f 0.65 [n -pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.25 (2H, d, J = 8.4 Hz), 7.19 (2H, d, J = 8.5 Hz), 4.04 – 3.79 (2H, br m), 3.03 – 2.92 (2H, m), 2.36 (1H, dd, J = 6.5, 3.2 Hz), 1.83 (1H, d, J = 3.2 Hz), 1.77 (2H, br m), 1.71 (1H, d, J = 6.5 Hz), 1.62 – 1.52 (3H, m), 1.45 (9H, s); ^{13}C NMR (151 MHz, CDCl_3) δ 154.9, 138.9, 132.5, 128.4, 127.6, 79.4, 66.5, 39.4, 36.6, 31.8 (br s), 31.2 (br s), 28.4. HRMS (ESI) found MH^+ 337.1679, $\text{C}_{18}\text{H}_{26}\text{ClN}_2\text{O}_2$ requires 337.1677.

***tert*-Butyl 2-(2-phenylaziridin-1-yl)acetate (**24**)**

Following **GP2**, **S1a** (1.96 g, 6 mmol, 1.0 equiv.) and *tert*-butyl glycinate (3.15 g, 24.0 mmol, 4.0 equiv.) gave after purification via column chromatography **24** (602 mg, 43%) as an oil. R_f 0.74 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.26 (4H, m), 7.24 – 7.18 (1H, m), 3.20 (1H, d, J = 16.0 Hz), 3.11 (1H, d, J = 15.9 Hz), 2.44 (1H, dd, J = 6.6, 3.5 Hz), 2.04 (1H, d, J = 3.6 Hz), 1.76 (1H, d, J = 6.6 Hz), 1.43 (9H, s); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 139.6, 128.3, 127.0, 126.4, 81.3, 62.7, 41.4, 37.6, 28.1. Data in accordance with the literature.¹¹

***tert*-Butyl 2-((4*R*,6*R*)-6-(2-(2-(4-chlorophenyl)aziridin-1-yl)ethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (**25**)**

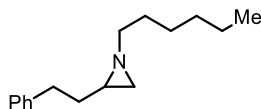
Following **GP2**, **S5a** (1.08 g, 3.00 mmol, 1.0 equiv.) and *tert*-butyl 2-((4*R*,6*R*)-6-(2-aminoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (1.6 mL, 6 mmol, 2.0 equiv.) gave after purification via column chromatography **25** as mixture of diastereomers (1.16 g, 94% yield, the mixture was used directly in the next step) as an oil. d.r. 1:1. R_f 0.45 [*n*-pentane:EtOAc (8:2)]. ^1H NMR (400 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.25 (2H, br d, J = 8.9 Hz), 7.20 – 7.11 (2H, m), 4.29 – 4.15 (1H, m), 4.08 – 3.94 (1H, m), 2.60 – 2.36 (3H, m), 2.34 – 2.23 (2H, m), 1.83 (0.5H, d, J = 3.2 Hz), 1.79 – 1.63 (3.5H, m), 1.61 – 1.54 (1H, m), 1.48 – 1.41 (10.5H, m), 1.38 (1.5H, s), 1.35 (1.5H, s), 1.34 (1.5H, s), 1.23 – 1.12 (1H, m); ^{13}C NMR (101 MHz, CDCl_3 , diastereomers) δ 170.4 (2C), 139.2, 139.2, 132.6, 132.6, 128.5, 128.5, 127.6, 127.6, 98.8, 98.8, 80.7 (2C), 66.9, 66.8, 66.4, 66.3, 57.1, 56.9, 42.9, 42.9, 41.0, 40.3, 38.7, 38.0, 36.9, 36.8, 36.7, 36.7, 30.3, 28.3, 20.0, 19.9. HRMS (ESI) found MH^+ 410.2092, $\text{C}_{22}\text{H}_{33}\text{ClNO}_4$ requires 410.2093.

2-Phenethyl-1-propylaziridine (26**)**

Following **GP3a**, 4-phenyl-1-butene (1.32 g, 10.0 mmol, 1.0 equiv.) and propylamine (709 mg, 12.0 mmol, 1.2 equiv.) gave **26** (291 mg, 15% over two steps) as an oil. R_f 0.29 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.23 – 7.17 (2H, m), 7.15 – 7.08 (3H, m), 2.72 (1H, ddd, J = 13.7, 9.5, 6.1 Hz), 2.64 (1H, ddd, J = 13.8, 9.4, 6.5 Hz), 2.16 (1H, ddd, J = 11.6, 8.5, 6.6 Hz),

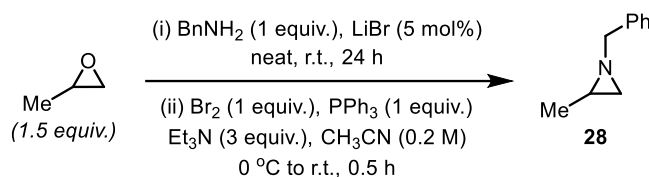
2.04 (1H, ddd, $J = 11.5, 8.3, 5.9$ Hz), 1.70 – 1.55 (2H, m), 1.55 – 1.47 (2H, m), 1.45 (1H, d, $J = 3.5$ Hz), 1.25 – 1.18 (1H, m), 1.13 (1H, d, $J = 6.3$ Hz), 0.86 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 142.1, 128.6, 128.5, 125.9, 63.6, 39.1, 35.0, 34.01, 33.99, 23.2, 12.1. HRMS (ESI) found MH^+ 190.1584, $\text{C}_{13}\text{H}_{20}\text{N}$ requires 190.1590.

1-Hexyl-2-phenethylaziridine (27)



Following **GP3a**, 4-phenyl-1-butene (1.32 g, 10.0 mmol, 1.0 equiv.) and hexylamine (1.21 g, 12.0 mmol, 1.2 equiv.) gave **27** (1.20 g, 52% *over two steps*) as an oil. R_f 0.6 [n -pentane: EtOAc (1:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.12 (5H, m), 2.84 – 2.63 (2H, m), 2.30 – 1.19 (1H, m), 2.16 – 2.04 (1H, m), 1.79 – 1.60 (2H, m), 1.60 – 1.48 (3H, m), 1.40 – 1.20 (7H, m), 1.18 (1H, d, $J = 6.3$ Hz), 0.87 (3H, t, $J = 6.7$ Hz). Data in accordance with the literature.⁴

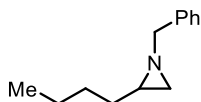
1-Benzyl-2-methylaziridine (28)



Step 1: To a round bottom flask equipped with a stirring bar was added propylene oxide (1.05 mL, 15 mmol, 1.5 equiv.), benzylamine (1.1 mL, 10 mmol, 1.0 equiv.) and LiBr (41 mg, 0.5 mmol, 5 mol%). The mixture was stirred for 24 h at room temperature. The solvent was evaporated to afford crude amino alcohol, that was used directly in the next step.

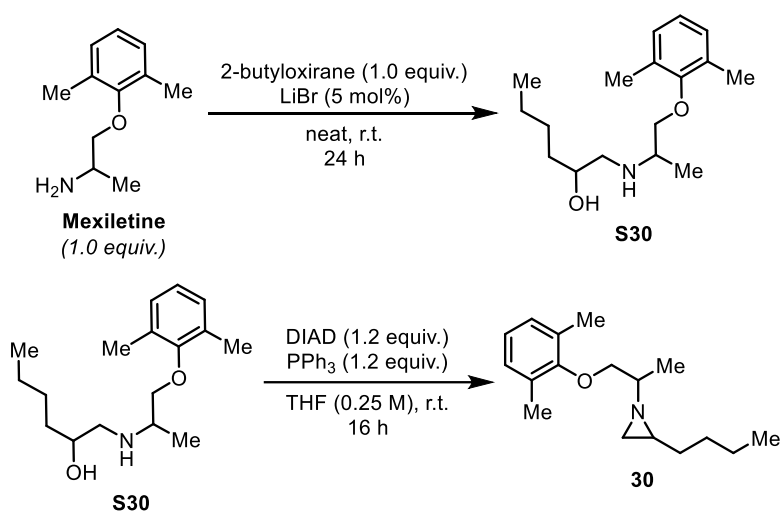
Step 2: An ice-cold solution of bromine (0.51 mL, 10 mmol, 1.0 equiv.) in CH_3CN (6 mL) was added dropwise to an ice-cold solution of triphenylphosphine (2.63 g, 10 mmol, 1.0 equiv.) in CH_3CN (15 mL). To this mixture was slowly added the crude amino alcohol (10 mmol, 1.0 equiv.), followed by the dropwise addition of triethylamine (4.16 mL, 30 mmol, 3.0 equiv.) at 0 °C. The mixture was then stirred at room temperature for 30 min. Triethylamine hydrobromide was filtered off and the solution was concentrated by rotary evaporation and purified directly by column chromatography on silica gel to give **28** (258 mg, 17% *over two steps*) as an oil. R_f 0.38 [n -pentane: EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.30 – 7.23 (4H, m), 7.21 – 7.15 (1H, m), 3.39 (1H, d, $J = 13.6$ Hz), 3.33 (1H, d, $J = 13.6$ Hz), 1.50 (1H, d, $J = 3.5$ Hz), 1.47 – 1.42 (1H, m), 1.31 (1H, d, $J = 6.3$ Hz), 1.14 (3H, d, $J = 5.5$ Hz). Data in accordance with the literature.¹²

1-Benzyl-2-butylaziridine (29)



Following **GP3a**, 1-hexene (1.25 mL, 10 mmol, 1.0 equiv.) and benzylamine (1.30 mL, 12.0 mmol, 1.2 equiv.) gave **29** (700 mg, 37%) as an oil. R_f 0.61 [*n*-pentane: EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.32 (4H, m), 7.31 – 7.25 (1H, m), 3.51 (1H, d, J = 13.2 Hz), 3.36 (1H, d, J = 13.3 Hz), 1.63 (1H, d, J = 3.2 Hz), 1.51 – 1.25 (8H, m), 0.87 (3H, t, J = 7.0 Hz). Data in accordance with the literature.¹²

2-Butyl-1-(1-(2,6-dimethylphenoxy)propan-2-yl)aziridine (30)

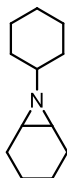


Step 1: A round bottom flask equipped with a stirring bar was charged with Mexiletine (950 mg, 5.3 mmol, 1.0 equiv.), 2-butyloxirane (0.64 mL, 5.3 mmol, 1.0 equiv.) and LiBr (23 mg, 0.26 mmol, 5 mol%). The resulting reaction mixture was stirred at room temperature for 24 h. Upon completion, the mixture was concentrated by rotary evaporation and the residue was purified by column chromatography on silica gel to afford the desired amino alcohol intermediate **S30** as mixture of diastereomers (578 mg, 39%, the mixture was used directly in the next step) as an oil. d.r. 1:1. R_f 0.41 [EtOAc]. ^1H NMR (600 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.00 (2H, d, J = 7.4 Hz), 6.94 – 6.88 (1H, m), 3.72 – 3.64 (2H, m), 3.64 – 3.57 (1H, m), 3.14 – 3.06 (1H, m), 2.92 – 2.83 (1H, m), 2.54 – 2.47 (1H, m), 2.28 (6H, s), 1.52 – 1.41 (3H, m), 1.39 – 1.30 (3H, m), 1.21 (1.5H, d, J = 6.5 Hz), 1.18 (1.5H, d, J = 6.4 Hz), 0.94 – 0.88 (3H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 155.6, 155.5, 130.9, 130.9, 129.1, 129.1, 124.0, 124.0, 76.0, 75.7, 70.3, 70.1, 53.7, 53.2, 53.0, 52.8, 35.1, 34.8, 28.0, 28.0, 23.0, 22.9, 18.0, 17.5, 16.4, 16.4, 14.2; HRMS (ESI) found MH^+ 280.2262, $\text{C}_{17}\text{H}_{30}\text{NO}_2$ requires 280.2271.

Step 2: A round bottom flask equipped with a stirring bar was charged with the amino alcohol (549 mg, 2.1 mmol, 1.0 equiv.) and PPh_3 (0.65 g, 2.52 mmol, 1.2 equiv.). Dry THF (8.4 mL, 0.25

M) was added followed by the dropwise addition of diisopropylazodicarboxylate (DIAD) (0.5 mL, 2.52 mmol, 1.2 equiv.) via syringe. The resulting reaction mixture was stirred at room temperature for 16 h. Upon completion, the mixture was concentrated by rotary evaporation and the residue was purified by column chromatography on silica gel to afford **30** as a single diastereomer (159 mg, 29%) as an oil. R_f 0.69 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.01 (2H, d, $J=7.4$ Hz), 6.92 (1H, t, $J=7.5$ Hz), 3.86 (1H, dd, $J=9.0, 5.5$ Hz), 3.67 (1H, dd, $J=9.0, 6.6$ Hz), 2.28 (6H, s), 1.81 (1H, sx, $J=6.4$ Hz), 1.60 – 1.47 (3H, m), 1.42 – 1.22 (9H, m), 0.87 (3H, t, $J=7.1$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 156.0, 131.0, 129.0, 123.9, 76.2, 65.2, 40.3, 33.1, 31.9, 29.7, 22.7, 17.7, 16.5, 14.1; HRMS (ESI) found MH^+ 262.2158, $\text{C}_{17}\text{H}_{28}\text{NO}$ requires 262.2165.

7-cyclohexyl-7-azabicyclo[4.1.0]heptane (**33**)



Following **GP3b**, 7-oxabicyclo[4.1.0]heptane (491 mg, 5 mmol, 1.0 equiv.) and cyclohexanamine (496 mg, 5.0 mmol, 1.0 equiv.) gave **33** (448 mg, 50% over two steps) as an oil. R_f 0.62 [*n*-pentane:EtOAc (5:1)]. ^1H NMR (600 MHz, CDCl_3) δ 1.80 – 1.68 (8H, m), 1.59 – 1.52 (1H, m), 1.47 – 1.39 (2H, m), 1.37 – 1.26 (4H, m), 1.20 – 1.05 (5H, m), 0.98 (1H, tt, $J=10.8, 3.9$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 69.8, 36.9, 32.5, 26.3, 25.2, 25.0, 20.8. Data in accordance with the literature.¹³

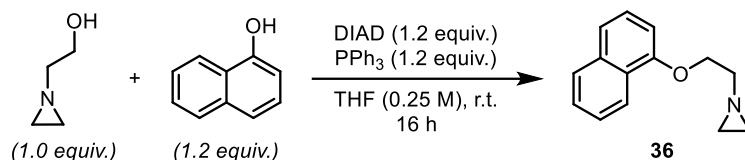
7-Benzyl-7-azabicyclo[4.1.0]heptane (**34**)



A round bottom flask equipped with a stirring bar was charged with (1*R*,2*R*)-2-(benzylamino)cyclohexan-1-ol (0.5 g, 2.4 mmol, 1.0 equiv.) and PPh_3 (0.75 g, 2.9 mmol, 1.2 equiv.). Dry THF (9.6 mL, 0.25 M) was added followed by the dropwise addition of diisopropylazodicarboxylate (DIAD) (0.57 mL, 2.9 mmol, 1.2 equiv.) via syringe. The resulting reaction mixture was stirred at room temperature for 16 h. Upon completion, the mixture was concentrated by rotary evaporation and the residue was purified by column chromatography on silica gel to afford **34** (371 mg, 83%) as an oil. R_f 0.35 [*n*-pentane: EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.34 (2H, m), 7.34 – 7.28 (2H, m), 7.26 – 7.20 (1H, m), 3.47 (2H, s), 1.91

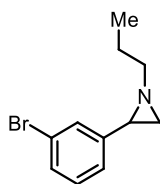
– 1.84 (2H, m), 1.81 – 1.73 (2H, m), 1.65 – 1.60 (2H, m), 1.45 – 1.36 (2H, m), 1.25 – 1.15 (2H, m). Data in accordance with the literature.¹⁴

1-(2-(Naphthalen-1-yloxy)ethyl)aziridine (**36**)



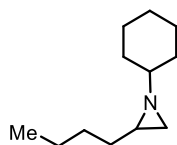
A round bottom flask equipped with a stirring bar was charged with 2-(aziridin-1-yl)ethan-1-ol (261 mg, 3.0 mmol, 1.0 equiv.) and PPh₃ (0.78 g, 3.6 mmol, 1.2 equiv.). Dry THF (12 mL, 0.25 M) was added followed by the dropwise addition of diisopropylazodicarboxylate (0.71 mL, 3.6 mmol, 1.2 equiv.) via syringe. The mixture was stirred at room temperature for 15 min, before adding 1-naphthol (519 mg, 5.0 mmol, 1.2 equiv.) in one portion. The resulting mixture was stirred at room temperature for 16 h. Upon completion, the mixture was concentrated by rotary evaporation and the residue was purified by column chromatography on silica gel to deliver **36** (333 mg, 52%) as an oil. *R*_f 0.16 [EtOAc]. ¹H NMR (600 MHz, CDCl₃) δ 8.32 – 8.27 (1H, m), 7.82 – 7.78 (1H, m), 7.52 – 7.45 (2H, m), 7.47 – 7.41 (1H, m), 7.37 (1H, t, *J* = 7.9 Hz), 6.84 (1H, dd, *J* = 7.5, 1.0 Hz), 4.35 (2H, t, *J* = 5.5 Hz), 2.78 (2H, t, *J* = 5.5 Hz), 1.88 – 1.85 (2H, m), 1.38 – 1.33 (2H, m); ¹³C NMR (151 MHz, CDCl₃) δ 154.8, 134.7, 127.6, 126.5, 126.0, 125.8, 125.3, 122.2, 120.5, 104.8, 68.2, 60.6, 27.5. HRMS (ESI) found MNa⁺ 236.1043, C₁₄H₁₅NONa requires 236.1046.

2-(3-Bromophenyl)-1-propylaziridine (**37**)



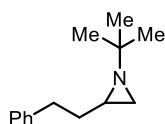
Following **GP2**, **S13a** (3.64 g, 9 mmol, 1.0 equiv.) and propylamine (3.2 mL, 45 mmol, 5.0 equiv.) gave **37** (560 mg, 16% over two steps) as yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 7.41 (1H, t, *J* = 1.8 Hz), 7.35 (1H, ddd, *J* = 7.7, 2.1, 1.3 Hz), 7.20 (1H, dt, *J* = 7.7, 1.5 Hz), 7.16 (1H, t, *J* = 7.7 Hz), 2.47 (1H, dt, *J* = 11.5, 7.2 Hz), 2.32 (1H, dt, *J* = 11.5, 7.1 Hz), 2.25 (1H, dd, *J* = 6.5, 3.2 Hz), 1.87 (1H, dd, *J* = 3.3, 0.7 Hz), 1.69 (1H, d, *J* = 6.6 Hz), 1.65 (2H, sx, *J* = 7.3 Hz), 0.98 (3H, t, *J* = 7.4 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 143.3, 130.0, 129.9, 129.3, 125.1, 122.6, 63.6, 40.7, 38.1, 23.1, 12.1. HRMS (ESI) found MH⁺ 240.0383, C₁₁H₁₅BrN requires 240.0382.

2-Butyl-1-cyclohexylaziridine (**38**)



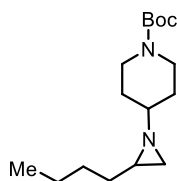
Following **GP3b**, 2-butyloxirane (501 mg, 5 mmol, 1.0 equiv.) and cyclohexanamine (496 mg, 5.0 mmol, 1.0 equiv.) gave **38** (326 mg, 38% over two steps) as an oil. *R_f* 0.48 [*n*-pentane:EtOAc (1:1)]. ¹H NMR (600 MHz, CDCl₃) δ 1.84 – 1.77 (2H, m), 1.77 – 1.69 (2H, m), 1.63 – 1.56 (1H, m), 1.50 – 1.40 (3H, m), 1.40 – 1.08 (11H, m), 0.99 (1H, tt, *J*=10.8, 3.8 Hz), 0.89 (3H, t, *J*=7.2 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 69.2, 38.5, 33.3, 33.2, 32.6, 32.6, 30.2, 26.3, 25.2, 25.2, 22.8, 14.2; HRMS (ESI) found *MH*⁺ 182.1905, C₁₂H₂₄N requires 182.1903.

1-(*tert*-Butyl)-2-phenethylaziridine (**39**)



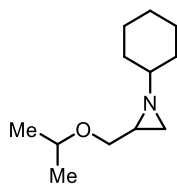
Following **GP3b**, 2-phenethyloxirane (741 mg, 5 mmol, 1.0 equiv.) and *tert*-butylamine (366 mg, 5.0 mmol, 1.0 equiv.) gave **39** (478 mg, 47% over two steps) as an oil. *R_f* 0.36 [*n*-pentane:EtOAc (1:1)]. ¹H NMR (600 MHz, CDCl₃) δ 7.29 (2H, t, *J*=7.6 Hz), 7.23 (2H, d, *J*=6.8 Hz), 7.20 (1H, t, *J*=7.3 Hz), 2.85 (1H, ddd, *J*=14.7, 10.0, 5.0 Hz), 2.70 (1H, ddd, *J*=13.8, 9.7, 6.4 Hz), 1.86 – 1.77 (1H, m), 1.69 – 1.59 (2H, m), 1.51 (1H, d, *J*=6.2 Hz), 1.31 (1H, d, *J*=2.8 Hz), 1.01 (9H, s); ¹³C NMR (151 MHz, CDCl₃) δ 142.2, 128.5, 128.4, 125.8, 52.6, 35.6, 34.4, 32.0, 26.8, 26.8; HRMS (ESI) found *MH*⁺ 204.1742, C₁₂H₂₂N requires 204.1747.

tert-Butyl 4-(2-butyloxiridin-1-yl)piperidine-1-carboxylate (**40**)



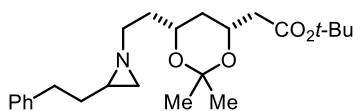
Following **GP3b**, 2-butyloxirane (501 mg, 5 mmol, 1.0 equiv.) and *tert*-butyl 4-aminopiperidine-1-carboxylate (1.00 g, 5.0 mmol, 1.0 equiv.) gave **40** (353 mg, 25% over two steps) as an oil. *R_f* 0.5 [*n*-pentane:EtOAc (1:1)]. ¹H NMR (600 MHz, CDCl₃) δ 4.00 (2H, br s), 2.72 (2H, br s), 1.72 (2H, d, *J*=12.8 Hz), 1.59 – 1.39 (14H, m), 1.38 – 1.28 (4H, m), 1.27 – 1.16 (3H, m), 0.88 (3H, t, *J*=6.9 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 155.0, 79.5, 66.9, 38.7, 33.0, 32.7, 32.1, 31.6, 30.1, 28.6, 22.7, 14.2; HRMS (ESI) found *MH*⁺ 305.2203, C₁₆H₃₀N₂O₂Na requires 305.2200.

1-Cyclohexyl-2-(isopropoxymethyl)aziridine (**41**)



Following **GP3b**, 2-(isopropoxymethyl)oxirane (581 mg, 5 mmol, 1.0 equiv.) and cyclohexanamine (496 mg, 5.0 mmol, 1.0 equiv.) gave **41** (326 mg, 33% over two steps) as an oil. R_f 0.37 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 3.62 (1H, hept, $J=6.1$ Hz), 3.39 (1H, dd, $J=10.5, 5.6$ Hz), 3.30 (1H, dd, $J=10.3, 5.5$ Hz), 1.89 – 1.84 (1H, m), 1.83 – 1.77 (1H, m), 1.76 – 1.70 (2H, m), 1.61 – 1.55 (3H, m), 1.37 – 1.26 (3H, m), 1.09 – 1.04 (10H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 71.7, 70.9, 69.0, 37.7, 33.0, 32.6, 30.8, 26.2, 25.1, 25.0, 22.5, 22.0; HRMS (ESI) found MH^+ 198.1851, $\text{C}_{12}\text{H}_{24}\text{NO}$ requires 198.1852.

tert-Butyl 2-((4*R*,6*R*)-2,2-dimethyl-6-(2-(2-phenethylaziridin-1-yl)ethyl)-1,3-dioxan-4-yl)acetate (**42**)



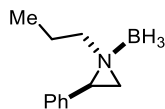
Following **GP3a**, 4-phenyl-1-butene (582 mg, 4.4 mmol, 1.0 equiv.) and *tert*-butyl 2-((4*R*,6*R*)-6-(2-aminoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (2.41 g, 8.8 mmol, 2 equiv.) gave **42** as mixture of diastereomers (604 mg, 34% over two steps, the mixture was used directly in the next step) as an oil. d.r. 1:1. R_f 0.26 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.24 – 7.18 (2H, m), 7.15 – 7.08 (3H, m), 4.22 – 4.13 (1H, m), 3.97 – 3.87 (1H, m), 2.75 – 2.60 (2H, m), 2.38 – 2.09 (4H, m), 1.69 – 1.56 (4H, m), 1.54 – 1.42 (2H, m), 1.39 – 1.34 (12H, m), 1.30 – 1.23 (4H, m), 1.18 – 1.07 (2H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 170.4, 142.0, 128.5, 128.5, 128.5, 125.9, 125.9, 98.8, 67.0, 67.0, 66.4, 57.0, 57.0, 42.9, 39.5, 38.8, 37.0, 36.9, 36.7, 35.0, 34.6, 34.0, 33.9, 33.9, 30.3, 30.3, 28.2, 19.9; HRMS (ESI) found MNa^+ 426.2617, $\text{C}_{23}\text{H}_{28}\text{N}$ requires 426.2615.

Note: Most chemical shift between the two diastereomers in ^1H NMR and ^{13}C NMR are overlapped, the proton and carbon atoms close to the stereocenter are splitting, indicating the presence of a mixture of diastereomers.

3.4 Aziridine-Borane Complexes

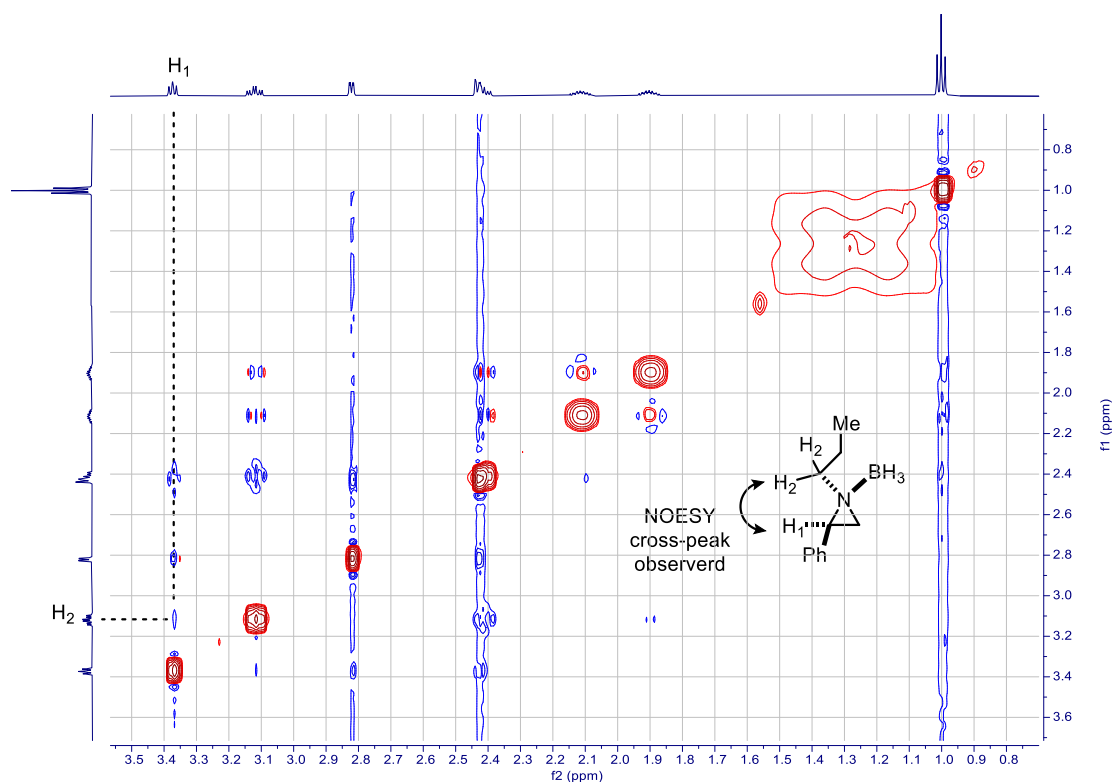
In most cases, *N*-alkyl β -aryl and β -alkyl aziridines coordinate with BH_3 to give almost exclusively the *trans*-diastereomer. In some cases, the *cis*-diastereomer was obtained and it is mentioned in the individual product characterization.

trans-2-Phenyl-1-propylaziridine Borane (**1a**)

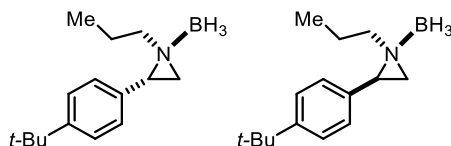


Following **GP4**, but adding $\text{BH}_3\cdot\text{DMS}$ at $-78\text{ }^\circ\text{C}$, **1** (3.22 g, 20.0 mmol, 1.0 equiv.) gave after precipitation and filtration **1a** (2.94 g, 84%) as a solid. ^1H (600 MHz, CDCl_3) δ 7.41 – 7.31 (5H, m), 3.35 (1H, dd, $J = 7.6, 6.2$ Hz), 3.10 (1H, td, $J = 11.5, 4.9$ Hz), 2.80 (1H, dd, $J = 6.2, 1.9$ Hz), 2.45 – 2.34 (2H, m), 2.15 – 2.04 (1H, m), 1.94 – 1.82 (1H, m), 1.57 – 0.92 (6H, m); ^{13}C (101 MHz, $\text{DMSO}-d_6$) δ 131.9, 130.3, 128.2, 127.7, 65.3, 48.2, 40.6, 19.6, 11.1; ^{11}B (128 MHz, $\text{DMSO}-d_6$) δ –15.72. HRMS (ESI) found MNa^+ 198.1425, $\text{C}_{11}\text{H}_{18}\text{BNNa}$ requires 198.1425.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



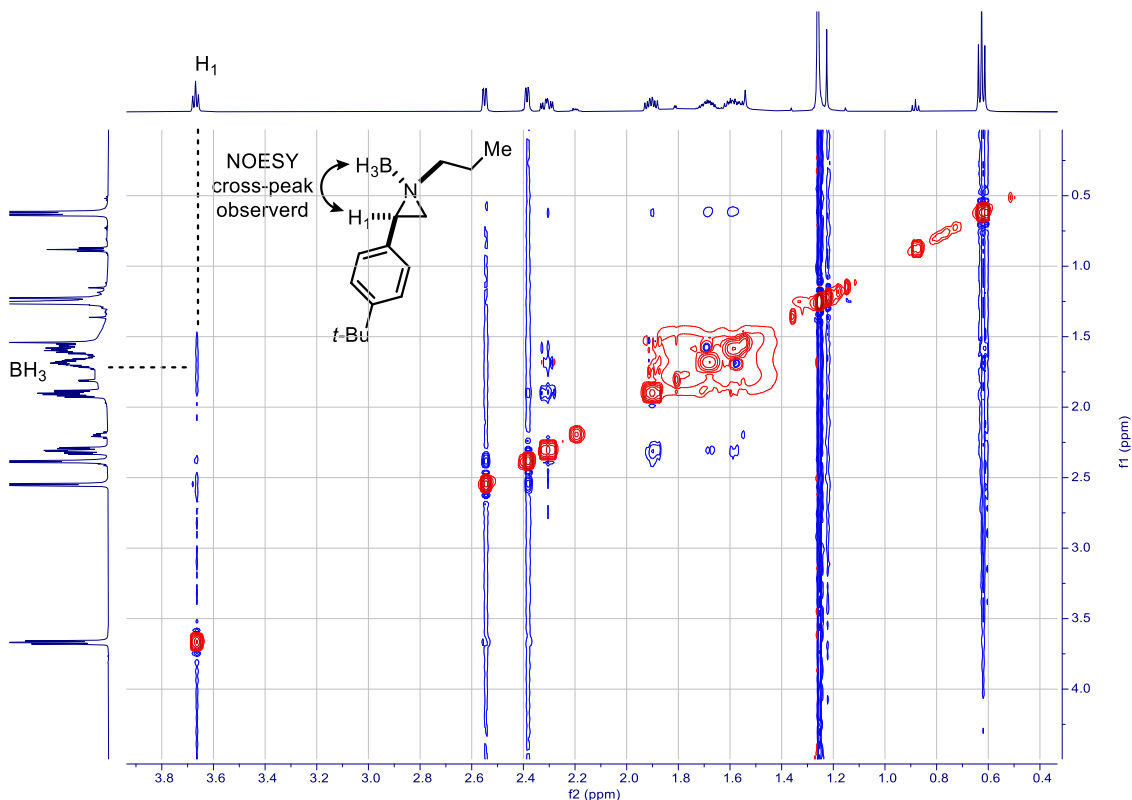
***cis*-2-(4-(*tert*-Butyl)phenyl)-1-propylaziridine Borane (**2a**) and *trans*-2-(4-(*tert*-Butyl)phenyl)-1-propylaziridine Borane (**2a'**)**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C , **2** (1.09 g, 5.0 mmol, 1.0 equiv.) gave after purification via column chromatography **2a** (518 mg, 45%) and **2a'** (379 mg, 33%) as separable mixture of diastereomers. **2a**: **2a'** = 58:42.

Data for **2a** (solid): R_f 0.43 [pentane:EtOAc (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.38 – 7.32 (2H, m), 7.22 – 7.18 (2H, m), 3.67 (1H, t, $J = 6.5$ Hz), 2.55 (1H, dd, $J = 7.0, 1.9$ Hz), 2.39 (1H, dd, $J = 6.2, 1.9$ Hz), 2.31 (1H, ddd, $J = 12.3, 10.7, 4.5$ Hz), 2.09 – 1.38 (6H, m), 1.26 (9H, s), 0.63 (3H, t, $J = 7.5$ Hz); ^{13}C (151 MHz, CDCl_3) δ 152.9, 130.1, 126.9, 125.9, 56.7, 51.0, 39.3, 34.9, 31.3, 19.8, 11.4; ^{11}B (193 MHz, CDCl_3) δ -11.99. HRMS (ESI) found MNa^+ 254.2043, $\text{C}_{15}\text{H}_{26}\text{BNNa}$ requires 254.2051.

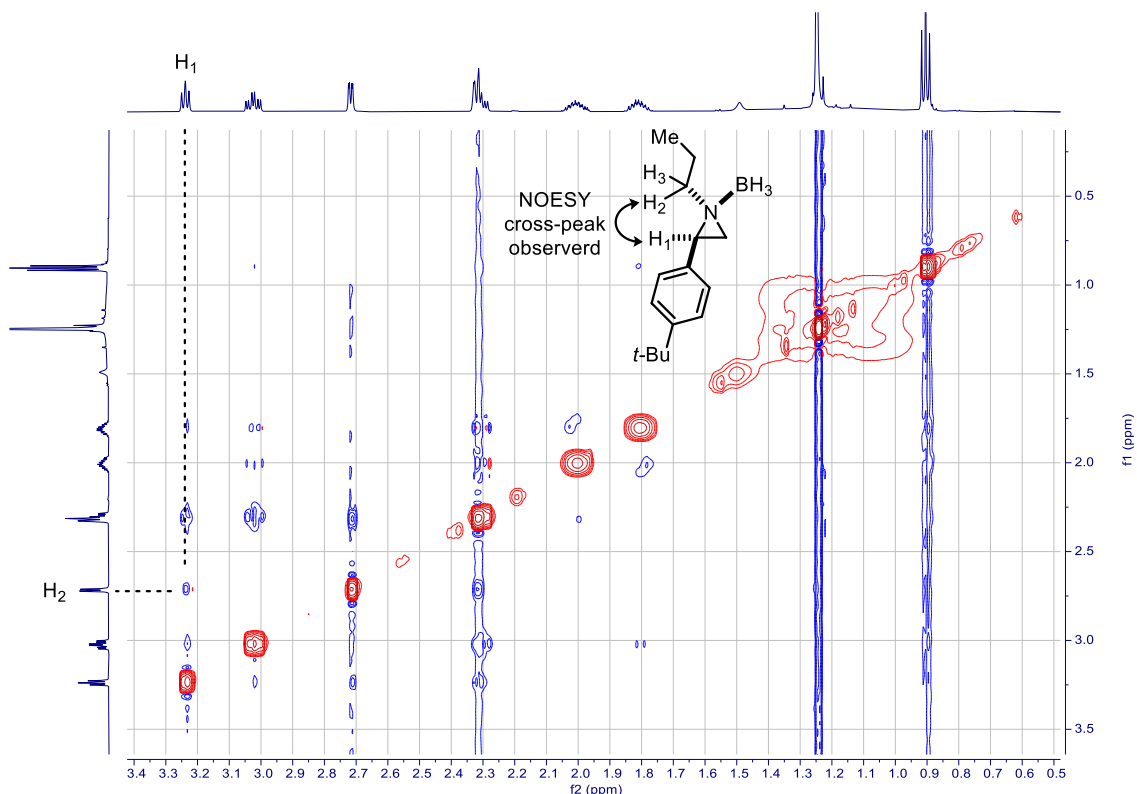
The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



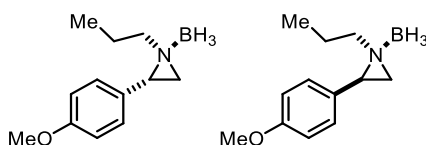
Data for **2a'** (solid): R_f 0.21 [pentane:EtOAc (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.34 – 7.30 (2H, m), 7.22 – 7.17 (2H, m), 3.24 (1H, t, $J = 7.0$ Hz), 3.02 (1H, td, $J = 11.4, 4.9$ Hz), 2.72 (1H, dd, $J = 6.3, 1.9$ Hz), 2.35 – 2.26 (2H, m), 2.07 – 1.95 (1H, m), 1.87 – 1.75 (1H, m), 1.25 (12H, m), 0.90 (3H, t, $J = 7.4$ Hz); ^{13}C (151 MHz, CDCl_3) δ 152.0, 129.9, 128.0, 125.2, 67.1, 49.5, 41.8, 34.8,

31.4, 20.3, 11.5; ^{11}B (193 MHz, CDCl_3) δ -16.43. HRMS (ESI) found MNa^+ 254.2044, $\text{C}_{15}\text{H}_{26}\text{BNNa}$ requires 254.2051.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



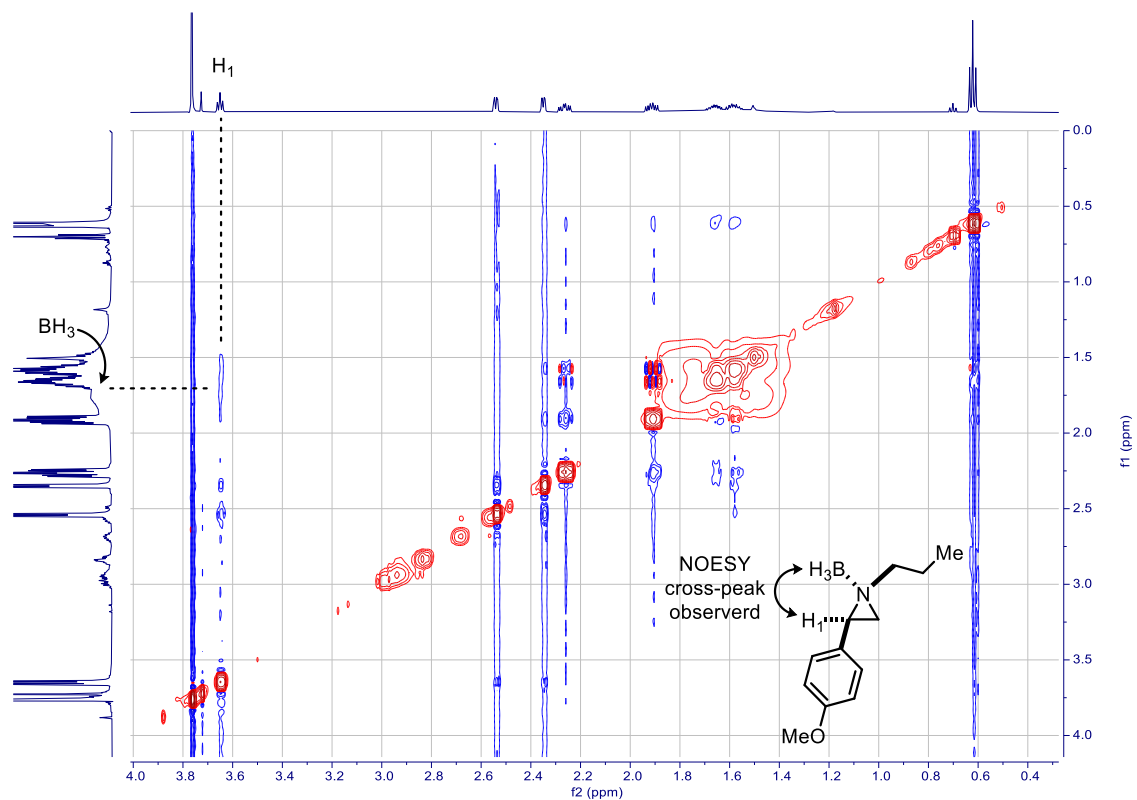
***cis*-2-(4-(*tert*-Butyl)phenyl)-1-propylaziridine Borane (3a) and *trans*-2-(4-(*tert*-Butyl)phenyl)-1-propylaziridine Borane (3a')**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C , **3** (0.96 g, 5.0 mmol, 1.0 equiv.) gave after purification via column chromatography **3a** (297 mg, 29%) and **3a'** (626 mg, 61%) as separable mixture of diastereomers. **3a**: **3a'** = 32:68.

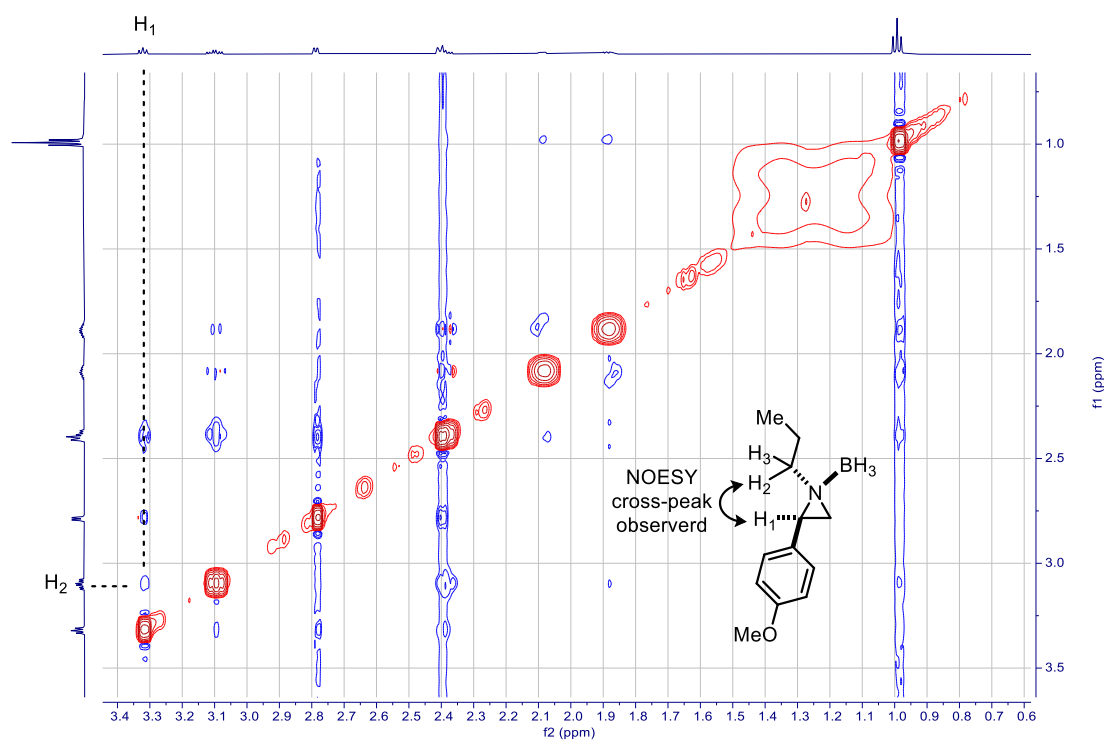
Data for **3a** (oil): R_f 0.6 [*n*-pentane:EtOAc (3:1)]. ^1H (600 MHz, CDCl_3) δ 7.22 – 7.17 (2H, m), 6.88 – 6.83 (2H, m), 3.76 (3H, s), 3.65 (1H, t, J = 6.5 Hz), 2.54 (1H, dd, J = 7.0, 2.0 Hz), 2.35 (1H, dd, J = 6.2, 1.9 Hz), 2.26 (1H, ddd, J = 12.3, 10.8, 4.7 Hz), 1.91 (1H, ddd, J = 12.3, 10.8, 5.8 Hz), 1.84 – 1.39 (5H, m), 0.62 (3H, t, J = 7.5 Hz); ^{13}C (151 MHz, CDCl_3) δ 160.6, 131.7, 121.9, 114.4, 56.6, 55.5, 50.9, 39.4, 19.7, 11.5; ^{11}B (193 MHz, CDCl_3) δ -12.00 (q, J = 103.3 Hz); HRMS (ESI) found MNa^+ 228.1523, $\text{C}_{12}\text{H}_{20}\text{BNONa}$ requires 228.1530.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:

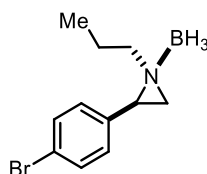


Data for **3a'** (oil): R_f 0.45 [*n*-pentane:EtOAc (3:1)]. ^1H (600 MHz, CDCl_3) δ 7.30 – 7.23 (2H, m), 6.94 – 6.90 (2H, m), 3.83 (3H, s), 3.32 (1H, dd, $J = 7.7, 6.3$ Hz), 3.10 (1H, td, $J = 11.5, 4.9$ Hz), 2.79 (1H, dd, $J = 6.3, 2.0$ Hz), 2.44 – 2.34 (2H, m), 2.15 – 2.02 (1H, m), 1.95 – 1.83 (1H, m), 0.99 (6H, m); ^{13}C (151 MHz, CDCl_3) δ 160.17, 131.51, 122.99, 113.71, 66.97, 55.37, 49.32, 41.46, 20.34, 11.45; ^{11}B (193 MHz, CDCl_3) δ –16.49 (q, $J = 97.8$ Hz); HRMS (ESI) found MNa^+ 228.1529, $\text{C}_{12}\text{H}_{20}\text{BNO}$ requires 228.1530.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



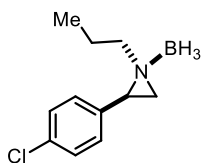
***trans*-2-(4-Bromophenyl)-1-propylaziridine Borane (**4a**)**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **4** (1.57 g, 6.56 mmol, 1.0 equiv.) gave after precipitation and filtration **4a** (1.45 g, 87%) as a solid. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (2H, d, $J = 7.9$ Hz), 7.21 (2H, d, $J = 8.0$ Hz), 3.29 (1H, t, $J = 7.0$ Hz), 3.10 (1H, td, $J = 11.6, 4.9$ Hz), 2.77 (1H, d, $J = 6.2$ Hz), 2.48 – 2.33 (2H, m), 2.17 – 2.01 (1H, m), 1.94 – 1.79 (1H, m), 1.64 – 0.75 (6H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 131.8, 131.5, 130.1, 123.5, 67.1, 48.9, 41.5, 20.4, 11.4; ^{11}B NMR (128 MHz, CDCl_3) δ –16.21; HRMS (ESI) found MNa^+ 276.0533, $\text{C}_{11}\text{H}_{17}\text{NBBNa}$ requires 276.0530.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

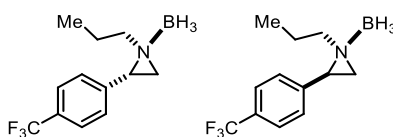
***trans*-2-(4-Chlorophenyl)-1-propylaziridine Borane (5a)**



Following **GP4**, but adding BH₃•DMS at -78 °C and react at r.t. for 4 h, **5** (2.17 g, 11.1 mmol, 1.0 equiv.) gave after precipitation and filtration **5a** (2.08, 87%) as a solid. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.31 (2H, m), 7.27 (2H, dd, *J* = 7.2, 1.7 Hz), 3.31 (1H, t, *J* = 7.0 Hz), 3.10 (1H, td, *J* = 11.3, 4.8 Hz), 2.84 – 2.73 (1H, m), 2.50 – 2.33 (2H, m), 2.18 – 2.00 (1H, m), 1.95 – 1.78 (1H, m), 1.03 – 0.92 (3H, m); ¹³C NMR (101 MHz, CDCl₃) δ 135.2, 131.6, 129.6, 128.6, 67.1, 48.8, 41.5, 20.4, 11.4; ¹¹B NMR (128 MHz, CDCl₃) δ -16.22; HRMS (ESI) found MNa⁺ 232.1037, C₁₁H₁₇NBClNa requires 232.1035.

The relative configuration was determined by ¹H NMR and ¹¹B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

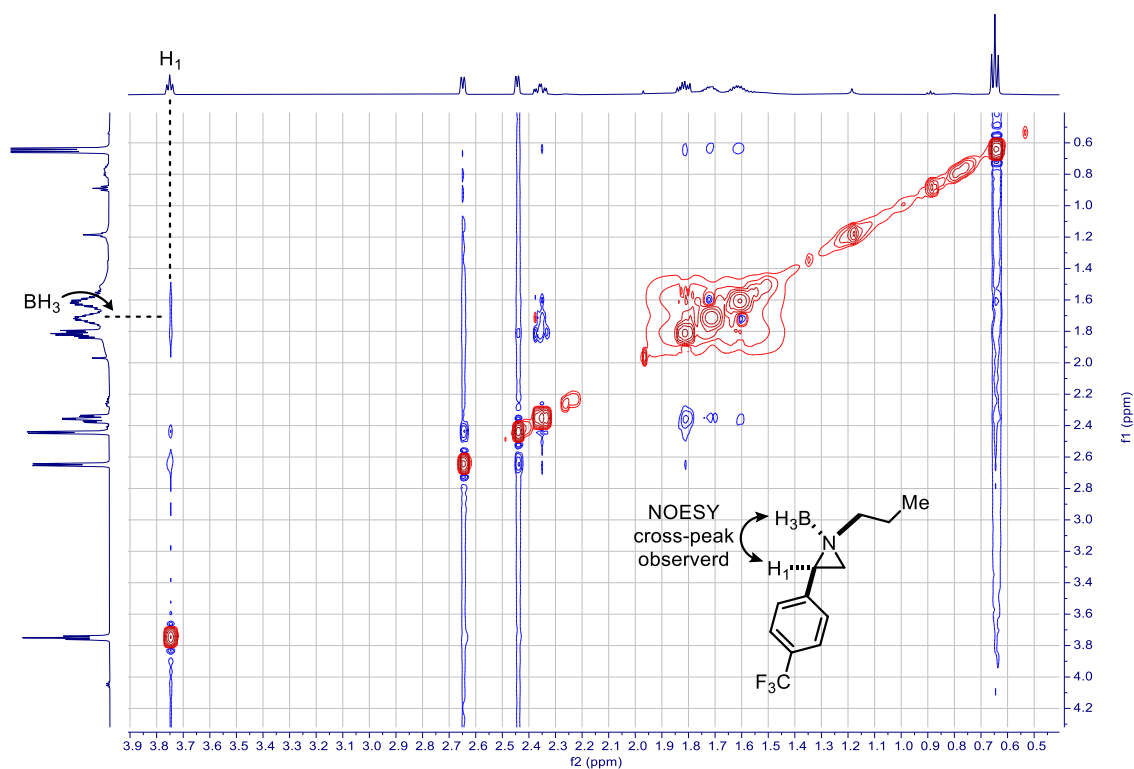
***cis*-1-Propyl-2-(4-(trifluoromethyl)phenyl)aziridine Borane (6a) and *trans*-1-Propyl-2-(4-(trifluoromethyl)phenyl)aziridine Borane (6a')**



Following **GP4**, but adding BH₃•DMS at -78 °C, **6** (917 mg, 4.0 mmol, 1.0 equiv.) gave after purification via column chromatography **6a** (101 mg, 10%) and **6a'** (745 mg, 77%) as separable mixture of diastereomers. **6a**: **6a'** = 11:89.

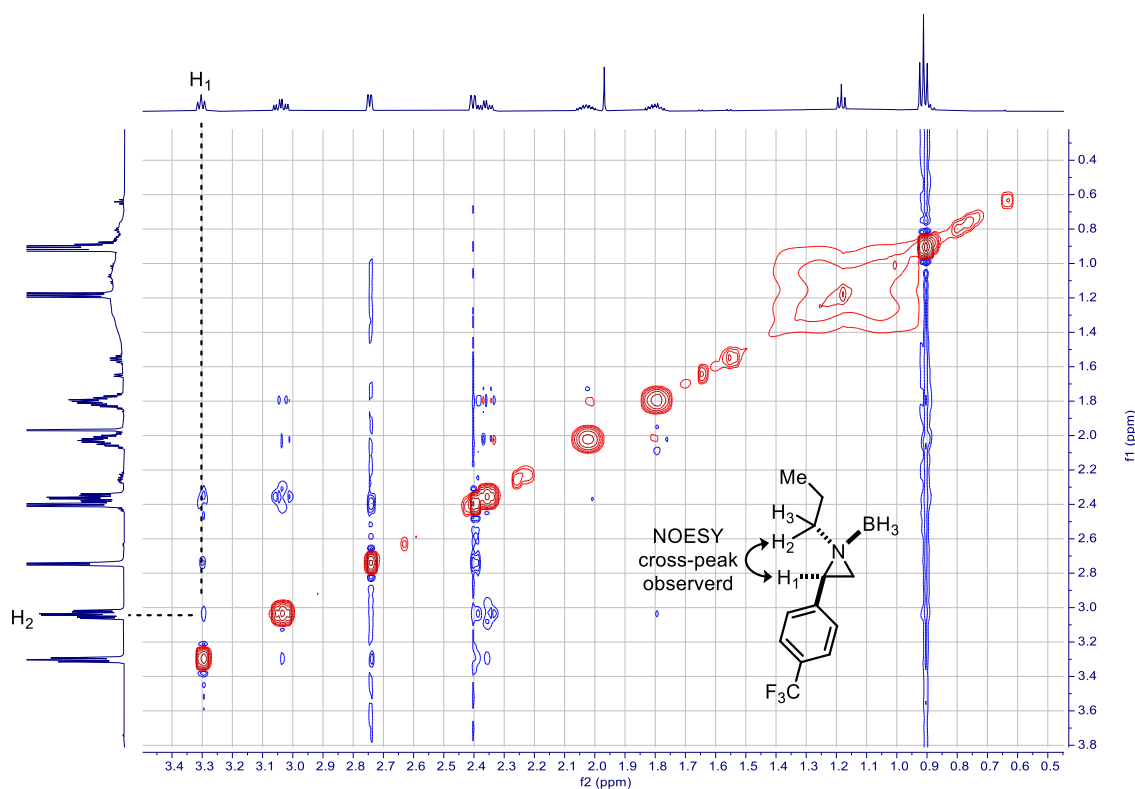
Data for **6a** (solid): ¹H (600 MHz, CDCl₃) δ 7.70 (2H, d, *J* = 7.9 Hz), 7.50 (2H, d, *J* = 8.0 Hz), 3.82 (1H, t, *J* = 6.5 Hz), 2.72 (1H, dd, *J* = 6.8, 2.0 Hz), 2.51 (1H, dd, *J* = 6.2, 2.0 Hz), 2.42 (1H, td, *J* = 11.5, 4.4 Hz), 2.09 – 1.48 (6H, m), 0.71 (3H, t, *J* = 7.4 Hz); ¹³C (151 MHz, CDCl₃) δ 134.1, 132.0 (q, *J* = 32.8 Hz), 130.8, 126.03 (q, *J* = 3.8 Hz), 123.8 (d, *J* = 272.4 Hz), 57.4, 50.5, 39.4, 19.8, 11.3; ¹¹B (193 MHz, CDCl₃) δ -11.46 (q, *J* = 100.7 Hz); ¹⁹F (565 MHz, CDCl₃) δ -62.88; HRMS (ESI) found MNa⁺ 266.1298, C₁₂H₁₇BNF₃Na requires 266.1298.

The relative configuration was determined by a 2D ¹H-¹H NOESY (600 MHz, CDCl₃) experiment:

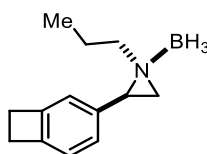


Data for **6a'** (solid): R_f 0.3 [*n*-pentane:EtOAc (6:1)]. ^1H (600 MHz, CDCl_3) δ 7.63 (2H, d, J = 8.1 Hz), 7.46 (2H, d, J = 8.0 Hz), 3.38 (1H, t, J = 6.9 Hz), 3.11 (1H, td, J = 11.5, 4.9 Hz), 2.82 (1H, dd, J = 6.2, 1.9 Hz), 2.50 – 2.40 (2H, m), 2.17 – 2.05 (1H, m), 1.93 – 1.82 (1H, m), 1.52 – 0.90 (6H, m); ^{13}C (151 MHz, CDCl_3) δ 135.0, 131.1 (q, J = 32.6 Hz), 130.6, 125.3 (q, J = 3.7 Hz), 124.1 (d, J = 272.3 Hz), 67.1, 48.7, 41.5, 20.4, 11.4; ^{11}B (193 MHz, CDCl_3) δ –15.88 (q, J = 103.7 Hz); ^{19}F (565 MHz, CDCl_3) δ –62.74; HRMS (ESI) found MNa^+ 266.1294, $\text{C}_{12}\text{H}_{17}\text{BNF}_3\text{Na}$ requires 266.1298.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:

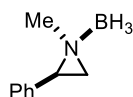


***trans*-2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-1-propylaziridine Borane (**7a**)**



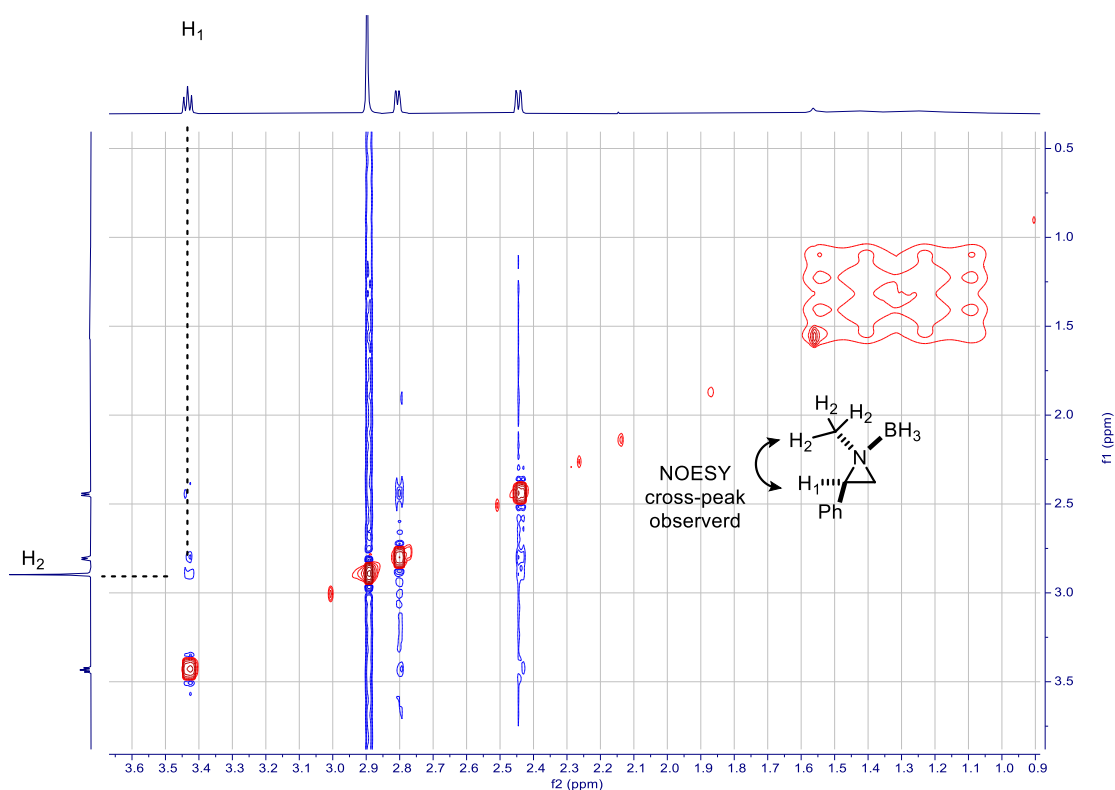
Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **7** (360 mg, 1.92 mmol, 1.0 equiv.) gave after precipitation and filtration **7a** (300 mg, 77%) as a solid. ^1H NMR (600 MHz, CDCl_3) δ 7.15 (1H, d, $J = 7.6$ Hz), 7.05 (1H, d, $J = 7.6$ Hz), 7.02 (1H, s), 3.34 (1H, t, $J = 7.0$ Hz), 3.17 (4H, s), 3.09 (1H, td, $J = 11.6, 4.8$ Hz), 2.79 (1H, dd, $J = 6.0, 2.1$ Hz), 2.43 – 2.33 (2H, m), 2.15 – 2.02 (1H, m), 1.95 – 1.81 (1H, m), 1.45 – 0.90 (6H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 146.9, 145.7, 129.4, 129.0, 124.3, 122.4, 67.1, 50.3, 41.5, 29.7, 29.5, 20.4, 11.5; ^{11}B NMR (192 MHz, CDCl_3) δ –16.45; HRMS (ESI) found MNa^+ 224.1581, $\text{C}_{13}\text{H}_{20}\text{NBNa}$ requires 224.1581. The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

***trans*-1-Methyl-2-phenylaziridine Borane (8a)**

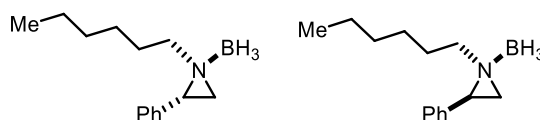


Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at $-78\text{ }^\circ\text{C}$, **8** (666 mg, 5.0 mmol, 1.0 equiv.) gave after precipitation and filtration **8a** (436 mg, 59%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.37 (3H, m), 7.36 – 7.32 (2H, m), 3.41 (1H, dd, $J = 7.6, 6.2$ Hz), 2.87 (3H, s), 2.78 (1H, dd, $J = 6.3, 1.9$ Hz), 2.42 (1H, dd, $J = 7.7, 1.9$ Hz), 1.30 (3H, q, $J = 110.5$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 131.0, 130.2, 129.2, 128.3, 52.6, 50.5, 40.9; ^{11}B (193 MHz, CDCl_3) δ -14.85 (q, $J = 97.4$ Hz). HRMS (ESI) found $\text{MNa}^+ 170.1107$, $\text{C}_9\text{H}_{14}\text{BNNa}$ requires 170.1112.

The relative configuration was determined by a 2D $^1\text{H}/^1\text{H}$ NOESY (600 MHz, CDCl_3) experiment:



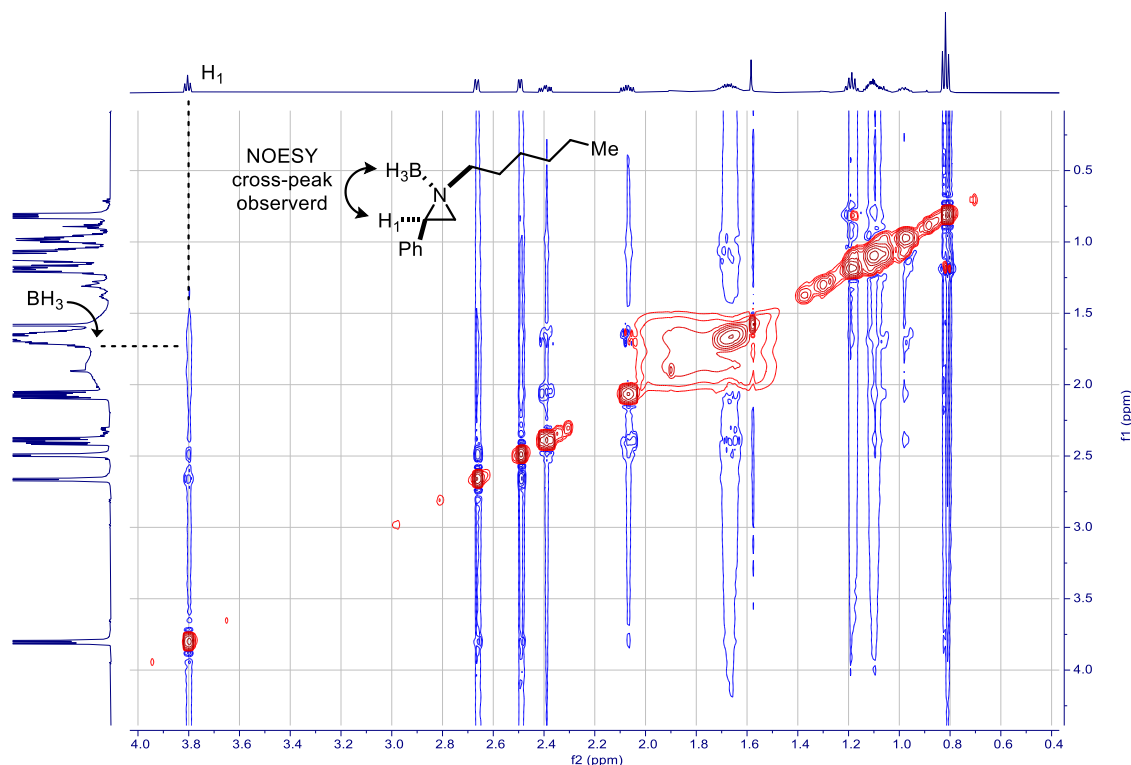
***cis*-1-Hexyl-2-phenylaziridine Borane (**9a**) and *trans*-1-Hexyl-2-phenylaziridine Borane (**9a'**)**



Following **GP4**, but adding BH₃•DMS at -78 °C, **9** (1.02 g, 5.0 mmol, 1.0 equiv.) gave after purification via column chromatography **9a** (597 mg, 55%) and **9a'** (445 mg, 41%) as separable mixture of diastereomers. **9a**: **9a'** = 57:43.

Data for **9a** (colorless oil): R_f 0.5 [pentane:EtOAc (10:1)]. ¹H (400 MHz, CDCl₃) δ 7.45 – 7.39 (3H, m), 7.39 – 7.32 (2H, m), 3.78 (1H, t, *J* = 6.5 Hz), 2.64 (1H, dd, *J* = 7.0, 1.9 Hz), 2.47 (1H, dd, *J* = 6.1, 2.0 Hz), 2.37 (1H, ddd, *J* = 12.2, 10.4, 5.2 Hz), 2.18 – 1.44 (6H, m), 1.23 – 0.91 (6H, m), 0.79 (3H, t, *J* = 7.1 Hz); ¹³C (151 MHz, CDCl₃) δ 130.4, 130.0, 129.7, 129.0, 55.3, 51.3, 39.3, 31.4, 26.6, 26.3, 22.5, 14.0; ¹¹B (193 MHz, CDCl₃) δ -11.75 (q, *J* = 95.9 Hz); HRMS (ESI) found MNa⁺ 240.1889, C₁₄H₂₄BNNa requires 240.1894.

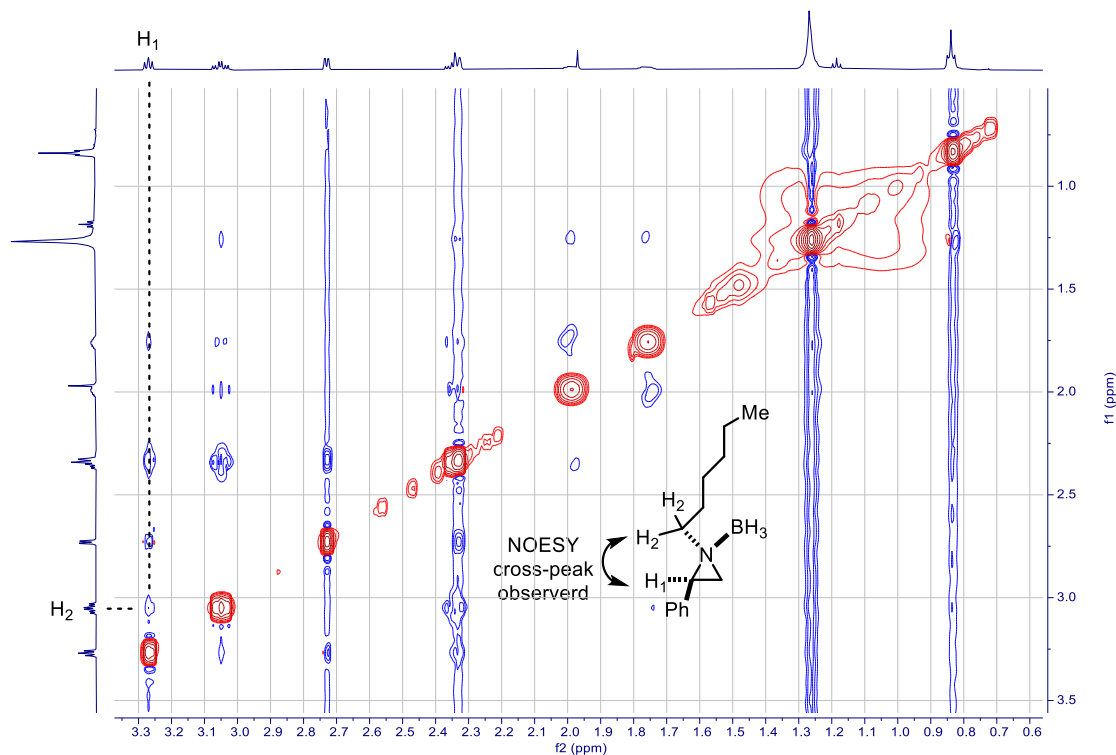
The relative configuration was determined by a 2D ¹H/¹H NOESY (600 MHz, CDCl₃) experiment:



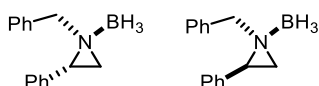
Data for **9a'** (white solid): R_f 0.35 [pentane:EtOAc (10:1)]. ¹H (600 MHz, CDCl₃) δ 7.40 – 7.31 (5H, m), 3.35 (1H, dd, *J* = 7.6, 6.2 Hz), 3.13 (1H, td, *J* = 11.6, 4.9 Hz), 2.81 (1H, dd, *J* = 6.2, 1.9 Hz), 2.46 – 2.38 (2H, m), 2.11 – 2.04 (1H, m), 1.88 – 1.80 (1H, m), 1.67 – 1.01 (9H, m), 0.94 – 0.89 (3H, m); ¹³C (151 MHz, CDCl₃) δ 131.1, 130.2, 129.1, 128.3, 65.6, 49.5, 41.5, 31.7, 27.0,

26.8, 22.7, 14.1; ^{11}B (193 MHz, CDCl_3) δ -16.19 (q, J = 104.3 Hz); HRMS (ESI) found MNa^+ 240.1889, $\text{C}_{14}\text{H}_{24}\text{BNNa}$ requires 240.1894.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



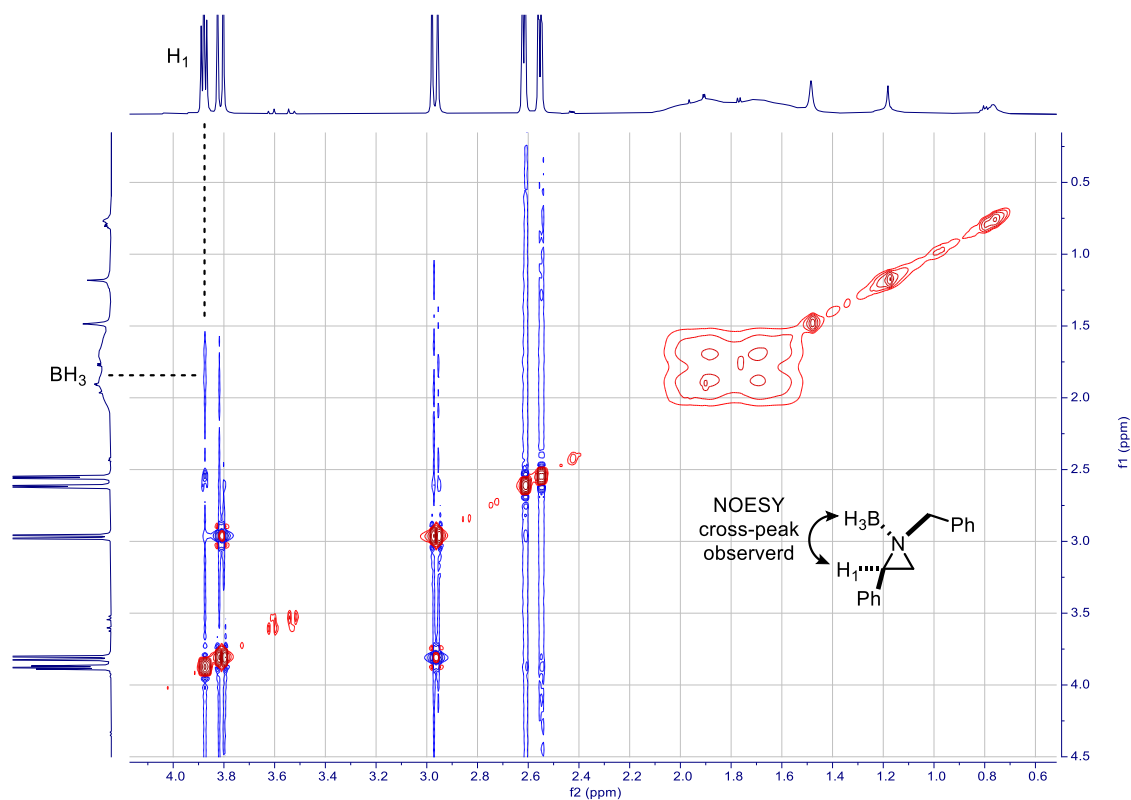
***cis*-1-Benzyl-2-phenylaziridine Borane (**10a**) and *trans*-1-Benzyl-2-phenylaziridine Borane (**10a'**)**



Following **GP4**, but adding $\text{BH}_3\cdot\text{DMS}$ at $-78\text{ }^\circ\text{C}$, **10** (1.05 g, 5.0 mmol, 1.0 equiv.) gave after purification via column chromatography **10a** (63 mg, 6%) and **10a'** (725 mg, 65%) as separable mixture of diastereomers. **10a**: **10a'** = 8:92.

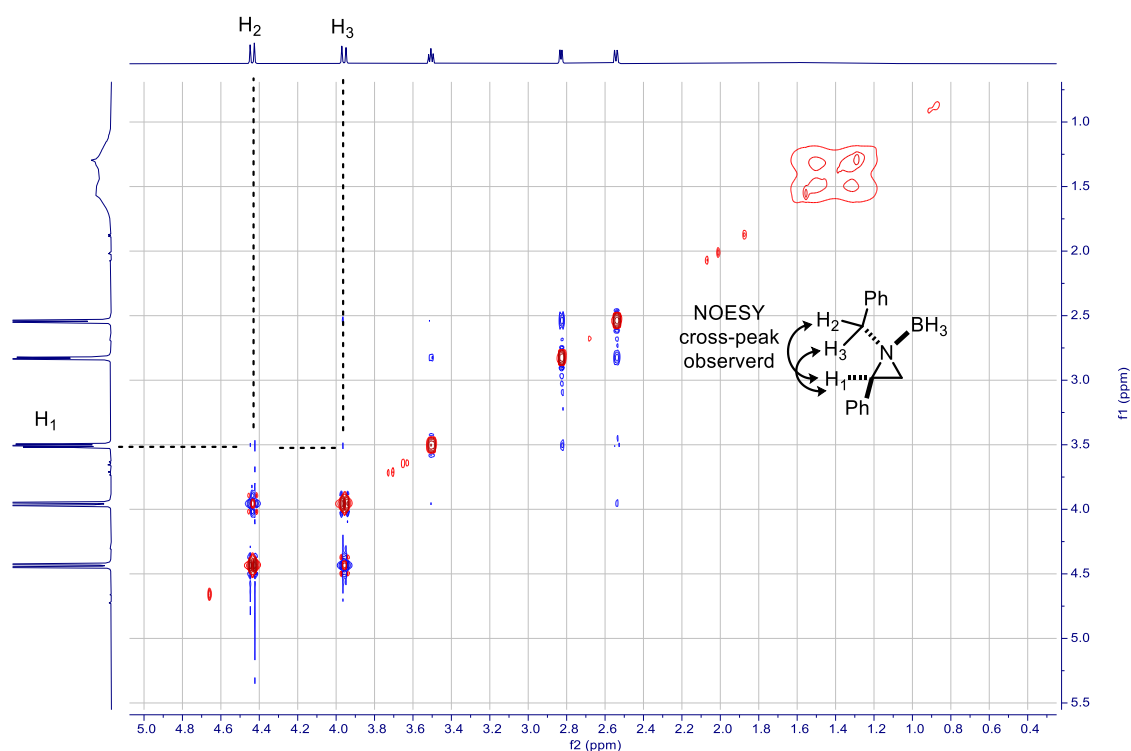
Data for **10a** (white solid): R_f 0.5 [pentane:EtOAc (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.51 – 7.46 (3H, m), 7.43 – 7.38 (2H, m), 7.32 – 7.27 (3H, m), 7.22 – 7.17 (2H, m), 3.96 (1H, t, J = 6.6 Hz), 3.89 (1H, d, J = 13.6 Hz), 3.05 (1H, d, J = 13.6 Hz), 2.70 (1H, dd, J = 6.4, 2.3 Hz), 2.63 (1H, dd, J = 6.9, 2.3 Hz), 1.87 (3H, q, J = 116.0 Hz); ^{13}C (151 MHz, CDCl_3) δ 134.0, 130.6, 130.4, 130.1, 130.0, 129.3, 128.5, 128.4, 57.4, 53.0, 38.1; ^{11}B (193 MHz, CDCl_3) δ -10.18 (q, J = 95.9 Hz); HRMS (ESI) found MNa^+ 246.1424, $\text{C}_{15}\text{H}_{18}\text{BNNa}$ requires 246.1425.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:

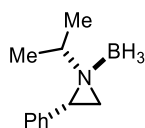


Data for **10a'** (white solid): ^1H (600 MHz, CDCl_3) δ 7.48 – 7.42 (5H, m), 7.36 – 7.30 (3H, m), 7.22 – 7.17 (2H, m), 4.41 (1H, d, $J = 13.1$ Hz), 3.94 (1H, d, $J = 13.1$ Hz), 3.48 (1H, t, $J = 7.0$ Hz), 2.81 (1H, dd, $J = 6.3, 1.9$ Hz), 2.52 (1H, dd, $J = 7.8, 1.9$ Hz), 1.40 (3H, q, $J = 116.0$ Hz); ^{13}C (151 MHz, CDCl_3) δ 132.6, 131.5, 131.0, 130.1, 129.3, 128.9, 128.9, 128.2, 66.1, 46.5 (d, $J = 2.1$ Hz), 39.1 (d, $J = 2.6$ Hz); ^{11}B (193 MHz, CDCl_3) δ –14.50 (q, $J = 97.5$ Hz); HRMS (ESI) found MNa^+ 246.1418, $\text{C}_{15}\text{H}_{18}\text{BNNa}$ requires 246.1425.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:

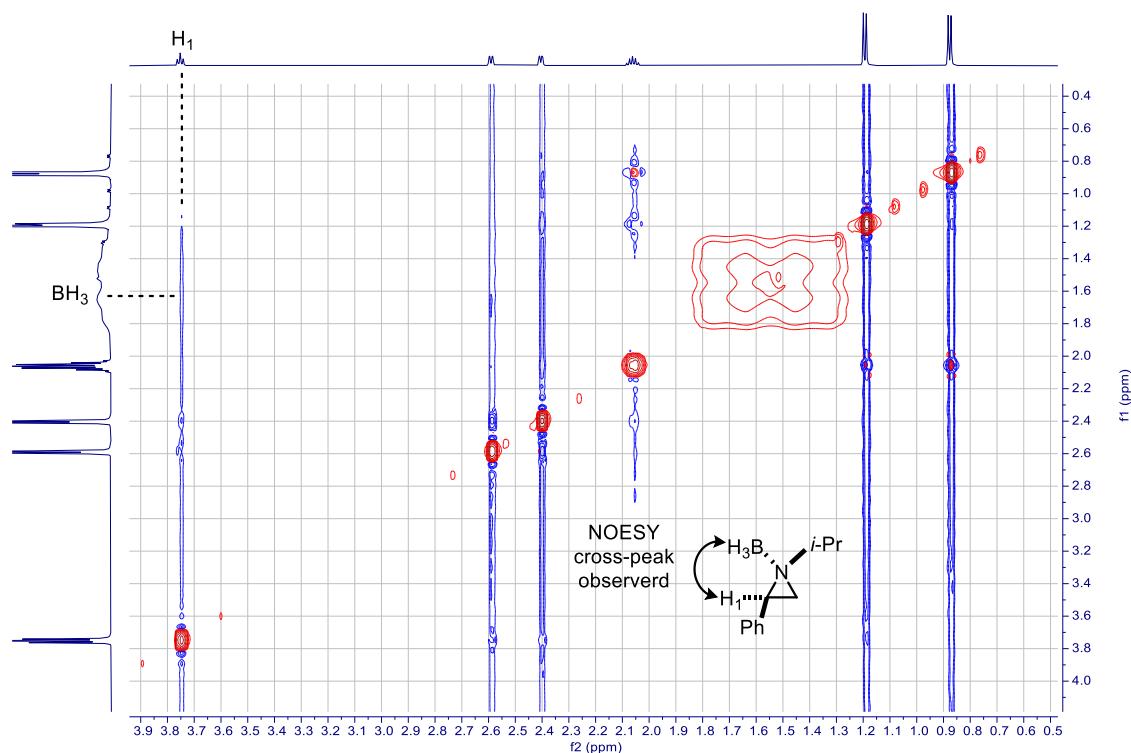


***cis*-1-Isopropyl-2-phenylaziridine Borane (11a)**

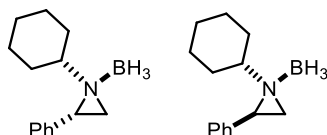


Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C , **11** (806 mg, 5.0 mmol, 1.0 equiv.) gave after purification via column chromatography **11a** (446 mg, 51%) as a white solid. R_f 0.59 [pentane:EtOAc (10:1)] ^1H (600 MHz, CDCl_3) δ 7.44 – 7.38 (5H, m), 3.82 (1H, t, $J = 6.6$ Hz), 2.66 (1H, dd, $J = 6.9, 1.9$ Hz), 2.47 (1H, dd, $J = 6.3, 1.9$ Hz), 2.12 (1H, sx, $J = 6.5$ Hz), 1.62 (1H, q, $J = 111.4$ Hz), 1.26 (3H, d, $J = 6.6$ Hz), 0.95 (3H, d, $J = 6.5$ Hz); ^{13}C (151 MHz, CDCl_3) δ 131.0, 129.7, 129.5, 128.8, 54.4, 52.6, 39.8, 19.5, 18.7; ^{11}B (193 MHz, CDCl_3) δ -15.23 (q, $J = 98.4, 98.0$ Hz); HRMS (ESI) found MNa^+ 198.1422, $\text{C}_{11}\text{H}_{18}\text{BNNa}$ requires 198.1425.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



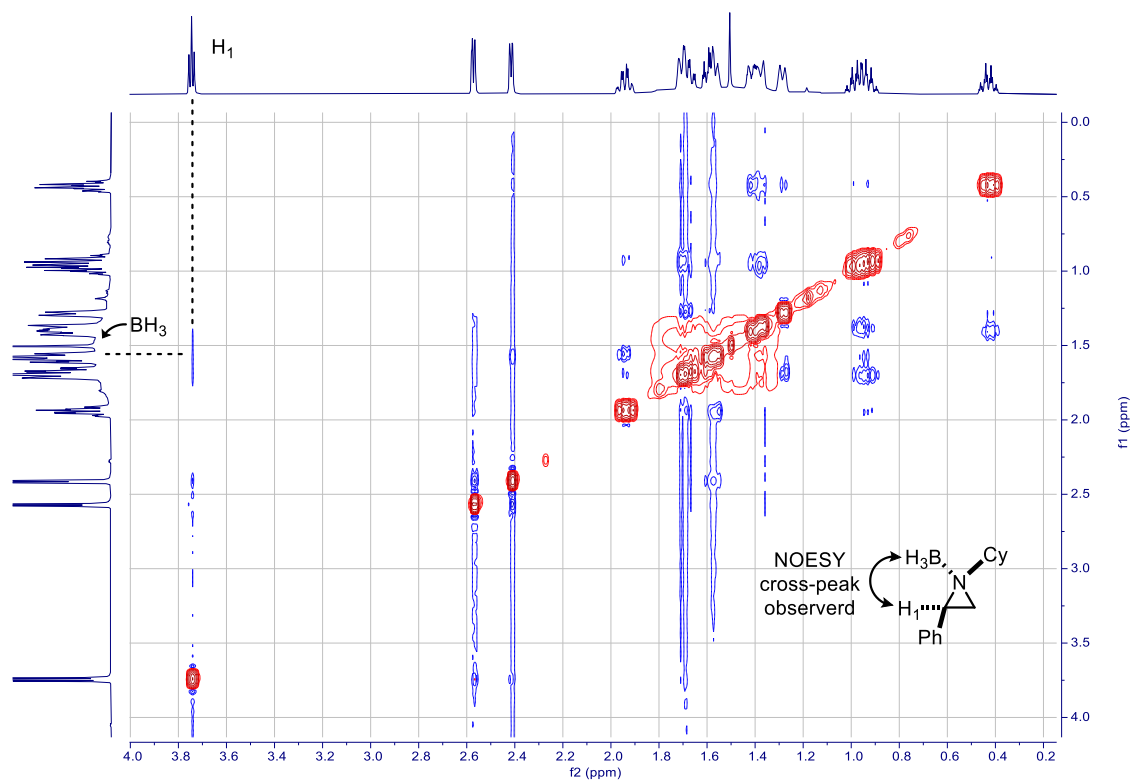
***cis*-1-Cyclohexyl-2-phenylaziridine Borane (**12a**) and *trans*-1-Cyclohexyl-2-phenylaziridine Borane (**12a'**)**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C , **12** (1.07 g, 5.0 mmol, 1.0 equiv.) gave after purification via column chromatography **12a** (194 mg, 18%) and **12a'** (839 mg, 78%) as separable mixture of diastereomers. **12a**: **12a'** = 19:81.

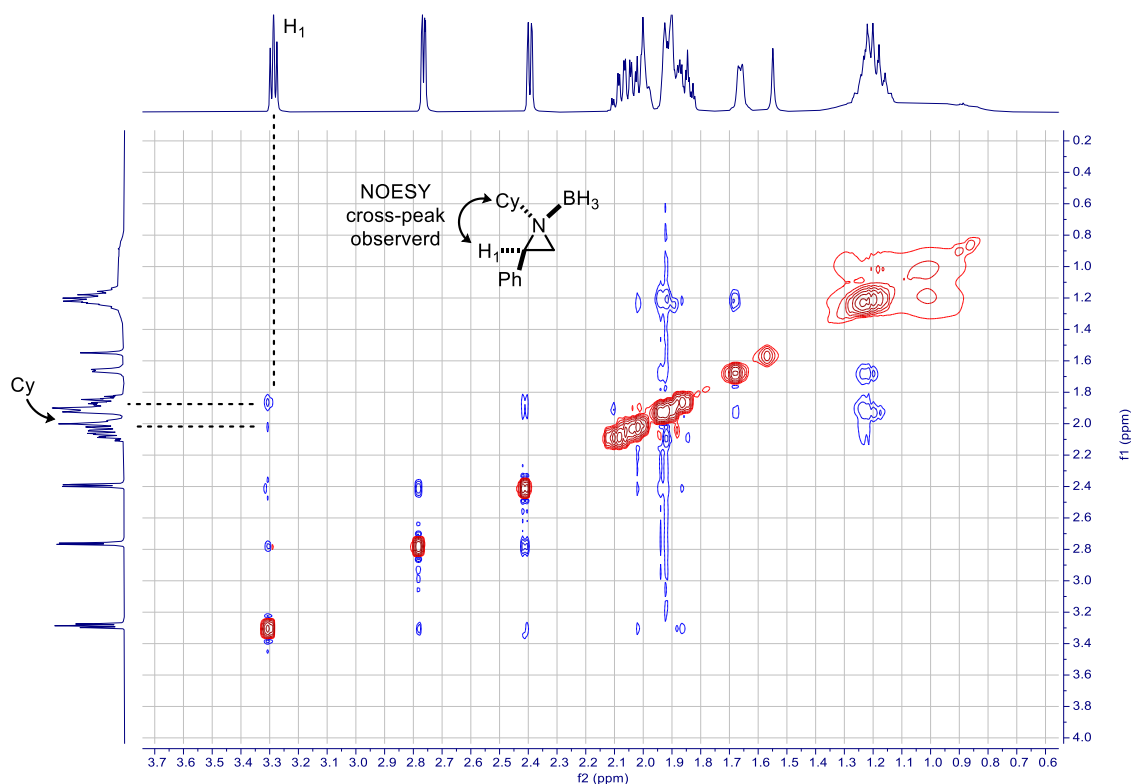
Data for **12a** (white solid): R_f 0.5 [*n*-pentane:EtOAc (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.40 (5H, d, $J = 3.3$ Hz), 3.81 (1H, t, $J = 6.6$ Hz), 2.64 (1H, dd, $J = 6.9, 1.9$ Hz), 2.48 (1H, dd, $J = 6.3, 1.9$ Hz), 2.01 (1H, qd, $J = 11.8, 3.1$ Hz), 1.92 – 1.29 (10H, m), 1.11 – 0.94 (2H, m), 0.50 (1H, qt, $J = 12.8, 3.5$ Hz); ^{13}C (151 MHz, CDCl_3) δ 130.9, 129.7, 129.5, 128.7, 62.6, 52.3, 39.5, 29.4, 29.3, 25.7, 25.4, 25.1; ^{11}B (193 MHz, CDCl_3) δ -14.26 (q, $J = 94.9$ Hz); HRMS (ESI) found MNa^+ 238.1738, $\text{C}_{14}\text{H}_{24}\text{BNNa}$ requires 238.1738.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:

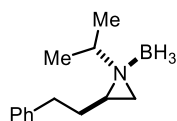


Data for **12a'** (white solid): R_f 0.35 [*n*-pentane:EtOAc (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.40 – 7.30 (5H, m), 3.29 (1H, dd, $J = 7.7, 6.2$ Hz), 2.76 (1H, dd, $J = 6.2, 1.9$ Hz), 2.39 (1H, dd, $J = 7.8, 1.9$ Hz), 2.13 – 1.96 (3H, m), 1.96 – 1.81 (4H, m), 1.69 – 1.64 (1H, m), 1.38 – 0.79 (6H, m); ^{13}C (151 MHz, CDCl_3) δ 131.18, 130.34, 128.88, 128.17, 73.79, 50.70, 40.37, 29.97, 29.32, 25.73(2C), 25.55; ^{11}B (193 MHz, CDCl_3) δ –18.87 (q, $J = 92.5$ Hz). HRMS (ESI) found MNa^+ 238.1731, $\text{C}_{14}\text{H}_{24}\text{BNNa}$ requires 238.1738.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



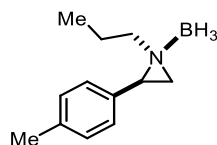
***trans*-1-Isopropyl-2-phenethylaziridine Borane (**13a**)**



Following **GP4**, **13** (511 mg, 2.7 mmol, 1.0 equiv.) gave after purification via column chromatography **13a** (383 mg, 70%) as a solid. R_f 0.54 [*n*-pentane:EtOAc (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.21 – 7.15 (2H, m), 7.15 – 7.12 (2H, m), 7.11 – 7.06 (1H, m), 2.86 (1H, ddd, J = 14.6, 9.6, 5.6 Hz), 2.63 (1H, ddd, J = 13.7, 9.4, 6.8 Hz), 2.32 – 2.23 (1H, m), 2.07 – 1.94 (1H, m), 1.93 – 1.86 (3H, m), 1.82 (1H, hp, J = 6.6 Hz), 1.18 (9H, m); ^{13}C (151 MHz, CDCl_3) δ 140.8, 128.4, 128.3, 126.0, 65.2, 48.1, 42.1, 33.8, 28.8, 19.0, 18.7; ^{11}B (193 MHz, CDCl_3) δ –20.37 (q, J = 99.4 Hz); HRMS (ESI) found MNa^+ 226.1731, $\text{C}_{17}\text{H}_{22}\text{BNNa}$ requires 226.1738.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **12a** and **12a'**.

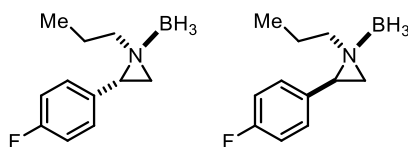
***trans*-1-Propyl-2-(*p*-tolyl)aziridine Borane (**14a**)**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **14** (3.1 g, 14.00 mmol, 1.0 equiv.) gave after precipitation and filtration **14a** (2.31 g, 87%) as a solid. ^1H NMR (600 MHz, CDCl_3) δ 7.22 (2H, d, $J = 8.0$ Hz), 7.18 (2H, d, $J = 7.9$ Hz), 3.32 (1H, t, $J = 6.9$ Hz), 3.10 (1H, td, $J = 11.5, 4.9$ Hz), 2.80 (1H, dd, $J = 6.3, 1.9$ Hz), 2.42 – 2.37 (2H, m), 2.36 (3H, s), 2.14 – 2.03 (1H, m), 1.94 – 1.82 (1H, m), 0.97 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 139.0, 130.1, 129.0, 127.9, 67.1, 49.5, 41.4, 21.5, 20.4, 11.5; ^{11}B NMR (192 MHz, CDCl_3) δ -16.55 ; HRMS (ESI) found MNa^+ 212.1586, $\text{C}_{12}\text{H}_{20}\text{NBNa}$ requires 212.1581.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

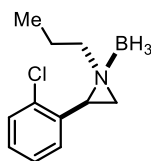
***cis*-2-(4-Fluorophenyl)-1-propylaziridine Borane (**15a**) and *trans*-2-(4-Fluorophenyl)-1-propylaziridine Borane (**15a'**)**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **15** (2.46 g, 13 mmol, 1.0 equiv.) gave after precipitation and filtration **15a** (12%) and **15a'** (77%) as mixture of diastereomers as a solid (2.23 g, 89% total yield; the mixture was used directly in the next step). Mixture of 2 diastereomers, **15a** and **15a'** (Ratio 13:87): ^1H NMR (600 MHz, CDCl_3) δ 7.36 – 7.33 (0.3H, m), 7.33 – 7.28 (2H, m), 7.12 (0.3H, t, $J = 8.5$ Hz), 7.06 (2H, t, $J = 8.6$ Hz), 3.75 (0.15H, t, $J = 6.5$ Hz), 3.32 (1H, t, $J = 6.9$ Hz), 3.10 (1H, td, $J = 11.5, 4.9$ Hz), 2.78 (1H, dd, $J = 6.2, 2.0$ Hz), 2.66 (0.15H, dd, $J = 7.0, 2.0$ Hz), 2.45 – 2.32 (2.3H, m), 2.14 – 2.03 (1H, m), 1.98 – 1.91 (0.15H, m), 1.90 – 1.81 (1H, m), 1.79 – 1.70 (0.15H, m), 1.70 – 1.60 (0.15H, m), 0.98 (3H, t, $J = 7.5$ Hz), 0.70 (0.45H, t, $J = 7.5$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 163.2 (d, $J = 248.4$ Hz) (2C), 132.3 (d, $J = 8.3$ Hz) (**15a**), 132.0 (d, $J = 8.3$ Hz) (**15a'**), 126.9 (d, $J = 3.5$ Hz) (**15a'**), 126.0 (d, $J = 3.2$ Hz) (**15a**), 116.2 (d, $J = 21.6$ Hz) (**15a**), 115.4 (d, $J = 21.5$ Hz) (**15a'**), 67.1 (**15a'**), 57.0 (**15a**), 50.5 (**15a**), 48.8 (**15a'**), 41.6 (**15a'**), 39.5 (**15**), 20.4 (**15a'**), 19.8 (**15a**), 11.4 (2C); ^{19}F NMR (564 MHz, CDCl_3) δ -110.91 (ddd, $J = 13.6, 8.5, 5.1$ Hz) (**15a**), -112.34 (ddd, $J = 13.7, 8.7, 5.1$ Hz) (**15a'**); ^{11}B NMR (192 MHz, CDCl_3) δ -11.79 (**15a**), -16.27 (**15a'**); HRMS (ESI) found MNa^+ 216.1335, $\text{C}_{11}\text{H}_{17}\text{NBFNa}$ requires 216.1330.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

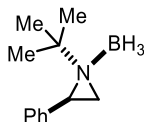
***trans*-2-(2-Chlorophenyl)-1-propylaziridine Borane (16a)**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **16** (2.11 g, 10.79 mmol, 1.0 equiv.) gave after precipitation and filtration **16a** (1.65 g, 73%) as a solid. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (1H, d, $J = 7.9$ Hz), 7.39 – 7.14 (3H, m), 3.47 (1H, t, $J = 7.2$ Hz), 3.07 (1H, dt, $J = 11.6, 7.4$ Hz), 2.78 (1H, d, $J = 6.2$ Hz), 2.67 (1H, dt, $J = 12.0, 8.2$ Hz), 2.48 (1H, d, $J = 7.7$ Hz), 2.19 – 2.01 (1H, m), 2.01 – 1.83 (1H, m), 0.96 (3H, t, $J = 7.5$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 136.8, 131.2, 130.4, 129.7, 129.5, 126.4, 66.6, 48.8, 39.7, 19.8, 11.3; ^{11}B NMR (CDCl_3 , 128 MHz) δ –16.55; HRMS (ESI) found MNa^+ 232.1031, $\text{C}_{11}\text{H}_{17}\text{NBClNa}$ requires 232.1035.

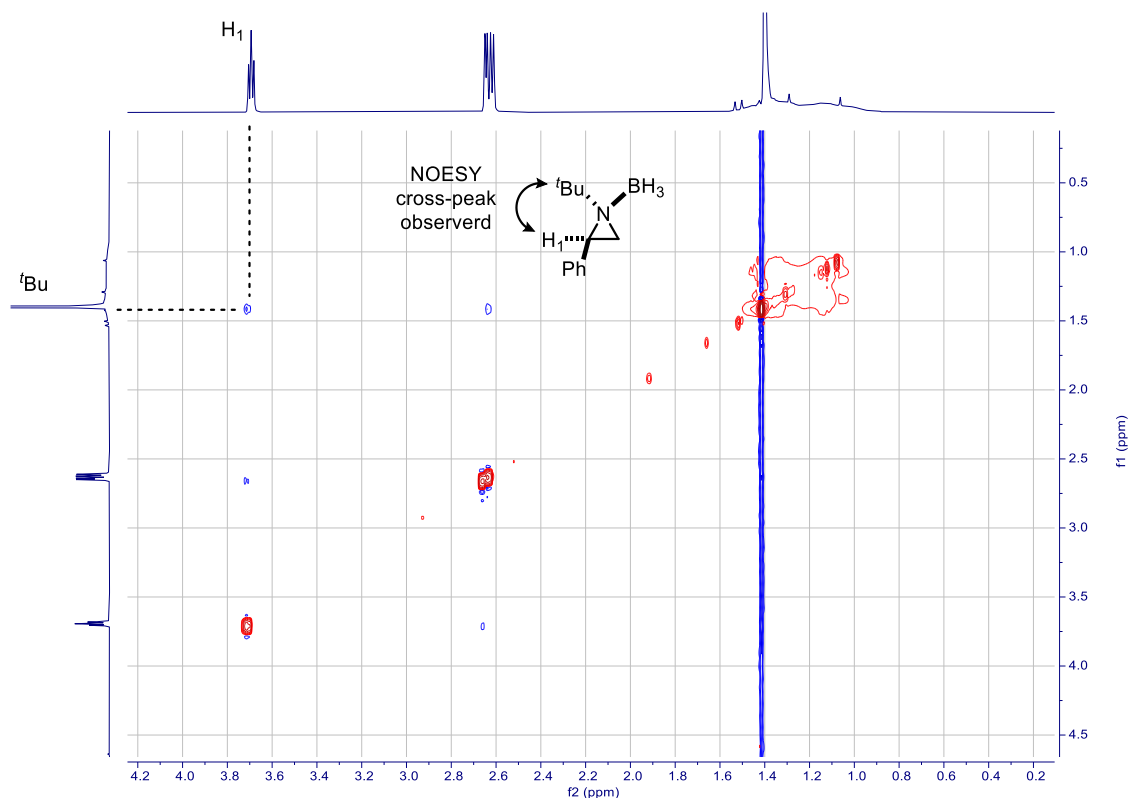
The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

***trans*-1-(*tert*-Butyl)-2-phenylaziridine Borane (17a)**

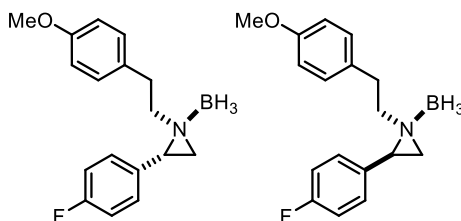


Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C , **17** (876 mg, 5.0 mmol, 1.0 equiv.) gave after precipitation **17a** (520 mg, 55%) as a white solid. ^1H (600 MHz, CDCl_3) δ 7.40 – 7.27 (5H, m), 3.69 (1H, t, $J = 7.2$ Hz), 2.67 – 2.60 (2H, m), 1.56 – 0.91 (12H, m); ^{13}C (151 MHz, CDCl_3) δ 132.2, 130.2, 128.5, 128.1, 60.9, 44.6, 36.1, 26.4; ^{11}B (193 MHz, CDCl_3) δ –16.61 (q, $J = 99.2$ Hz). Data in accordance with the literature.¹⁵

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



***cis*-2-(4-Fluorophenyl)-1-(4-methoxyphenethyl)aziridine Borane (**18a**) and *trans*-2-(4-Fluorophenyl)-1-(4-methoxyphenethyl)aziridine Borane (**18a'**)**



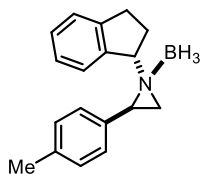
Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **18** (1.84 g, 6.5 mmol, 1.0 equiv.) gave after precipitation and filtration **18a** (12%) and **18a'** (68%) as mixture of diastereomers as a solid (1.48 g, 80% total yield; the mixture was used directly in the next step). Mixture of 2 diastereomers, **18a** and **18a'** (Ratio 15:85): ^1H NMR (600 MHz, CDCl_3) δ 7.34 (0.3H, dd, $J = 8.5, 5.2$ Hz), 7.19 (2H, d, $J = 8.6$ Hz), 7.17 – 7.11 (2.3H, m), 7.03 (2H, t, $J = 8.6$ Hz), 6.88 (2H, d, $J = 8.6$ Hz), 6.83 (0.3H, d, $J = 8.6$ Hz), 6.75 (0.3H, d, $J = 8.6$ Hz), 3.81 (3H, s), 3.75 (0.45H, s), 3.34 (1H, ddd, $J = 11.9, 9.6, 5.3$ Hz), 3.30 – 3.23 (2H, m), 3.12 (1H, ddd, $J = 13.8, 9.6, 6.5$ Hz), 3.02 (0.15H, ddd, $J = 13.6, 10.2, 6.9$ Hz), 2.76 (1H, dd, $J = 6.2, 2.1$ Hz), 2.71 (1H, ddd, $J = 11.8, 9.5, 6.5$ Hz), 2.62 (0.15H, dd, $J = 7.0, 2.2$ Hz), 2.54 (0.15H, ddd, $J = 12.2, 10.2, 4.4$ Hz), 2.37 (1H, dd, $J = 7.7, 2.1$ Hz), 2.35 – 2.29 (0.15H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 163.2 (d, $J = 248.9$ Hz) (**18a'**), 158.7 (**18a'**), 132.3 (d, $J = 8.8$ Hz) (**18a**), 132.1 (d, $J = 8.5$ Hz) (**18a'**), 130.1 (**18a'**), 130.0 (**18a**), 129.8 (**18a'**), 126.6 (d, $J = 2.5$ Hz) (**18a'**), 116.3 (d, $J = 21.8$ Hz) (**18a**), 115.3

(d, $J = 21.5$ Hz) (**18a'**), 114.4 (**18a'**), 114.1 (**18a**), 66.8 (**18a'**), 64.0 (**18a**), 56.9 (**18a'**), 55.5 (**18a**), 50.2 (**18a'**), 49.4 (**18a**), 41.4 (**18a**), 39.8 (**18a'**), 32.4 (**18a**), 31.8 (**18a'**); ^{11}B NMR (192 MHz, CDCl_3) δ -11.72 (**18a**), -16.26 (**18a'**); ^{19}F NMR (564 MHz, CDCl_3) δ -110.62 (tt, $J = 8.4, 5.1$ Hz) (**18a**), -112.21 (tt, $J = 8.4, 5.1$ Hz) (**18a'**); HRMS (ESI) found MNa^+ 308.1599, $\text{C}_{17}\text{H}_{21}\text{NOBFNa}$ requires 308.1592.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

Note: some peaks belonging to the minor diastereomer 18a are missing in ^1H and ^{13}C because either they are overlapping with the peaks of the major diastereomer 18a', or their intensity is low.

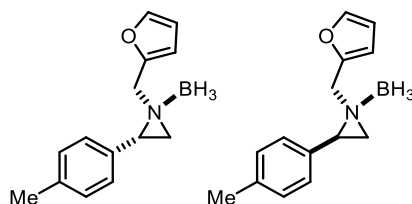
***trans* 1-(2,3-Dihydro-1*H*-inden-1-yl)-2-(*p*-tolyl)aziridine (**19a**)**



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78 °C and react at r.t. for 4 h, **19** (770 mg, 3.0 mmol, 1.0 equiv.) gave after precipitation and filtration **19a** as mixture of diastereomers (680 mg, 86% total yield, the mixture was used directly in the next step) as a solid. d.r. 1:1. ^1H NMR (400 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.52 – 7.40 (1H, m), 7.40 – 7.23 (4H, m), 7.23 – 7.11 (3H, m), 4.49 (0.5H, d, $J = 8.3$ Hz), 4.17 (0.5H, dd, $J = 8.4, 3.9$ Hz), 3.50 (0.5H, t, $J = 7.1$ Hz), 3.34 (0.5H, dt, $J = 17.8, 8.8$ Hz), 3.25 (0.5H, dd, $J = 15.9, 8.0$ Hz), 3.14 (0.5H, t, $J = 7.2$ Hz), 3.00 – 2.83 (2H, m), 2.83 – 2.70 (1H, m), 2.65 (0.5H, d, $J = 7.8$ Hz), 2.57 (0.5H, d, $J = 7.8$ Hz), 2.47 (1H, dq, $J = 16.6, 7.8$ Hz), 2.35 (1.5H, s), 2.35 (1.5H, s); ^{13}C NMR (151 MHz, CDCl_3) δ 147.0, 145.8, 139.0, 138.8, 137.6, 131.0, 130.3, 130.1, 129.9, 129.8, 129.3, 129.1, 128.1, 128.0, 126.8, 126.6, 126.6, 125.8, 125.6, 125.4, 76.6, 74.4, 48.0, 45.1, 39.2, 37.6, 31.2, 31.1, 30.1, 29.6, 21.5, 21.4; ^{11}B NMR (192 MHz, CDCl_3) δ -15.94, -17.69; HRMS (ESI) found MNa^+ 286.1738, $\text{C}_{18}\text{H}_{22}\text{NBNa}$ requires 286.1738.

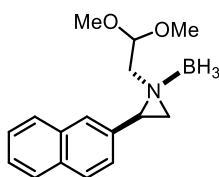
The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **12a** and **12a'**.

***cis*-1-(Furan-2-ylmethyl)-2-(*p*-tolyl)aziridine Borane (**20a**) and *trans*-1-(Furan-2-ylmethyl)-2-(*p*-tolyl)aziridine Borane (**20a'**)**



Following **GP4**, but adding BH₃•DMS at -78 °C and react at r.t. for 4 h, **20** (1.3 g, 5.6 mmol, 1.0 equiv.) gave after precipitation and filtration **20a** (44%) and **20a'** (53%) as mixture of diastereomers as an oil (1.23 g, 97% total yield; the mixture was used directly in the next step). Mixture of 2 diastereomers, **20a** and **20a'** (Ratio 55:45): ¹H NMR (600 MHz, CDCl₃) δ 7.61 (1H, dd, *J* = 1.9, 0.8 Hz), 7.48 (1H, dd, *J* = 1.9, 0.9 Hz), 7.41 (2H, d, *J* = 8.1 Hz), 7.37 (2H, d, *J* = 7.0 Hz), 7.26 (4H, s), 6.63 (1H, d, *J* = 3.3 Hz), 6.54 (1H, dd, *J* = 3.3, 1.9 Hz), 6.44 (1H, dd, *J* = 3.2, 1.8 Hz), 6.41 (1H, d, *J* = 3.3 Hz), 4.45 (1H, d, *J* = 14.3 Hz), 4.10 (1H, d, *J* = 14.3 Hz), 3.99 (1H, t, *J* = 6.7 Hz), 3.81 (1H, d, *J* = 14.4 Hz), 3.66 (1H, dd, *J* = 7.8, 6.4 Hz), 3.17 (1H, d, *J* = 14.4 Hz), 2.97 (1H, dd, *J* = 6.4, 2.4 Hz), 2.86 (1H, dd, *J* = 6.4, 2.0 Hz), 2.73 (1H, dd, *J* = 7.0, 2.4 Hz), 2.67 (1H, dd, *J* = 7.8, 2.0 Hz), 2.50 (3H, s), 2.45 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 148.2, 147.4, 143.8, 142.9, 140.2, 138.9, 130.4, 130.0, 130.0, 129.7, 129.0, 128.7, 127.9, 126.7, 113.0, 111.6, 111.1, 110.7, 57.7, 51.8, 50.1, 46.9, 38.5, 38.4, 21.4, 21.4; ¹¹B NMR (192 MHz, CDCl₃) δ -11.12 (**20**), -15.20 (**20a'**); HRMS (ESI) found MNa⁺ 250.1378, C₁₄H₁₈NOBNa requires 250.1374. The relative configuration was determined by ¹H NMR and ¹¹B NMR shift in analogy with the shift differences observed for **10a** and **10a'**.

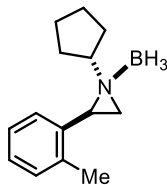
***trans*-1-(2,2-Dimethoxyethyl)-2-(naphthalen-2-yl)aziridine Borane (**21a**)**



Following **GP4**, but adding BH₃•DMS at -78 °C and react at r.t. for 4 h, **21** (1.01 g, 3.93 mmol, 1.0 equiv.) gave after precipitation and filtration **21a** (900 mg, 84%) as a solid. ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.81 (3H, m), 7.79 (1H, s), 7.59 – 7.44 (3H, m), 5.14 (1H, dd, *J* = 7.3, 3.6 Hz), 3.81 (1H, t, *J* = 6.9 Hz), 3.65 (3H, s), 3.52 (3H, s), 3.34 (1H, dd, *J* = 12.4, 3.5 Hz), 2.94 (1H, dd, *J* = 6.6, 2.2 Hz), 2.58 (1H, dd, *J* = 7.7, 2.1 Hz), 2.51 (1H, dd, *J* = 12.4, 7.3 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 133.6, 132.9, 130.0, 128.7, 128.3, 127.9, 127.8, 127.5, 126.8, 126.4, 102.8, 65.7, 56.2, 55.9, 50.5, 41.0; ¹¹B NMR (192 MHz, CDCl₃) δ -15.71; HRMS (ESI) found [M-BH₃]⁺ 258.1488, C₁₆H₂₀NO₂ requires 258.1489.

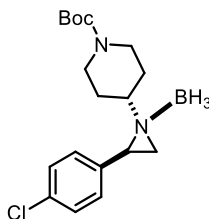
The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

***trans*-1-Cyclopentyl-2-(*o*-tolyl)aziridine Borane (**22a**)**



Following **GP4**, but adding $\text{BH}_3\cdot\text{DMS}$ at $-78\text{ }^\circ\text{C}$ and react at r.t. for 4 h, **22** (840 mg, 4.17 mmol, 1.0 equiv.) gave after precipitation and filtration **22a** (690 mg, 77%) as a solid. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.21 (2H, m), 7.19 (1H, t, $J = 7.4$ Hz), 7.11 (1H, d, $J = 7.6$ Hz), 3.36 (1H, t, $J = 6.9$ Hz), 2.98 (1H, p, $J = 8.1$ Hz), 2.82 (1H, dd, $J = 6.3, 1.8$ Hz), 2.53 – 2.37 (4H, m), 2.28 – 1.99 (3H, m), 1.93 – 1.77 (3H, m), 1.65 – 0.72 (5H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 139.5, 130.4, 130.2, 129.8, 129.2, 125.7, 74.2, 50.0, 38.8, 29.1, 28.7, 24.9, 24.2, 20.4; ^{11}B NMR (128 MHz, CDCl_3) δ –18.56; HRMS (ESI) found MNa^+ 238.1736, $\text{C}_{14}\text{H}_{22}\text{NBNa}$ requires 238.1738. The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **12a** and **12a'**.

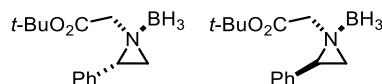
***tert*-Butyl *trans*-4-(2-(4-Chlorophenyl)aziridin-1-yl)piperidine-1-carboxylate Borane (**23a**)**



Following **GP4**, but adding $\text{BH}_3\cdot\text{DMS}$ at $-78\text{ }^\circ\text{C}$ and react at r.t. for 4 h, **23** (1.44 g, 4.27 mmol, 1.0 equiv.) gave after precipitation and filtration **23a** (1.20 g, 80%) as a solid. ^1H NMR (600 MHz, CDCl_3) δ 7.35 (2H, d, $J = 8.4$ Hz), 7.27 – 7.24 (2H, m), 4.53 – 4.04 (2H, br m), 3.31 (1H, t, $J = 7.0$ Hz), 2.80 (1H, dd, $J = 6.2, 2.1$ Hz), 2.65 (2H, br s), 2.48 (1H, dd, $J = 7.8, 2.0$ Hz), 2.30 – 2.15 (2H, m), 2.05 (1H, tt, $J = 11.8, 3.7$ Hz), 1.91 – 1.83 (2H, br m), 1.46 (9H, s); ^{13}C NMR (151 MHz, CDCl_3) δ 154.5, 135.3, 131.6, 129.2, 128.6, 80.2, 71.6, 65.1, 49.9, 40.4, 28.6; ^{11}B NMR (192 MHz, CDCl_3) δ –18.51; HRMS (ESI) found MNa^+ 373.1822, $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_2\text{BClNa}$ requires 373.1825.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **12a** and **12a'**.

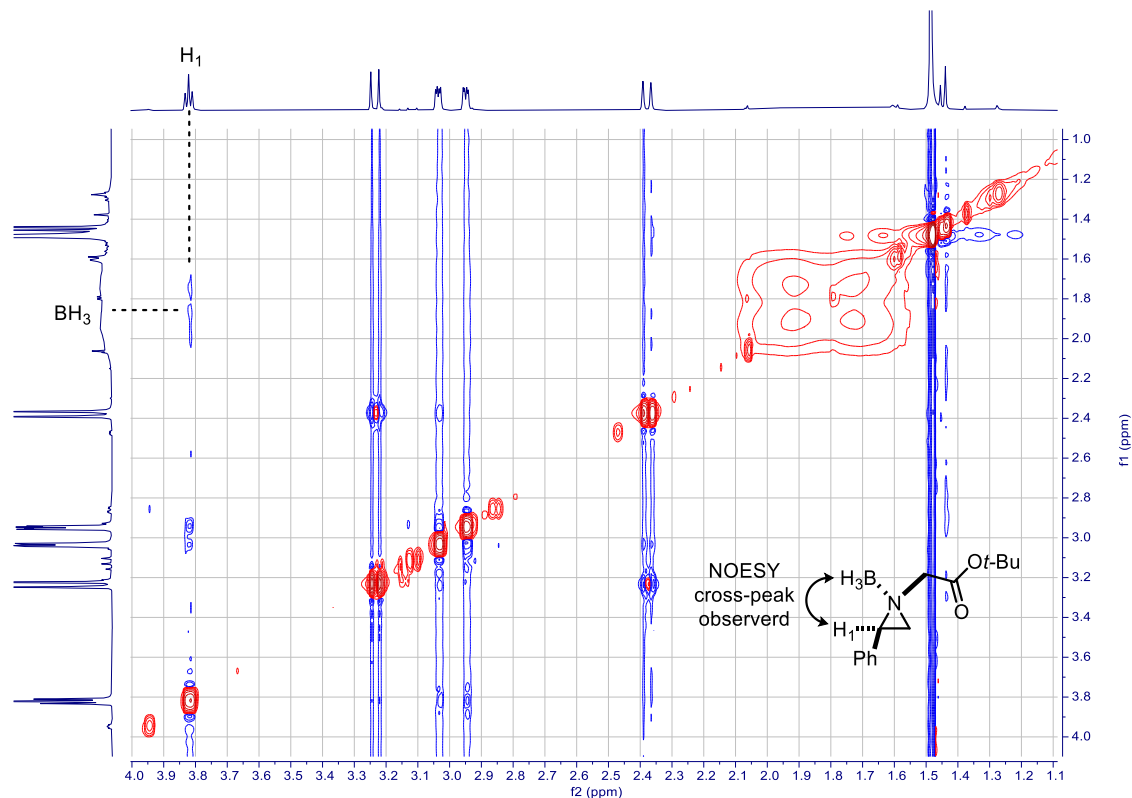
***tert*-Butyl *cis*-2-(2-Phenylaziridin-1-yl)acetate Borane (**24a**) and *tert*-Butyl *trans*-2-(2-Phenylaziridin-1-yl)acetate Borane (**24a'**)**



Following **GP4**, **24** (607 mg, 2.6 mmol, 1.0 equiv.) gave after purification via column chromatography **24a** (122 mg, 19%) and **24a'** (341 mg, 53%) as separable mixture of diastereomers. **24a**: **24a'** = 26:74.

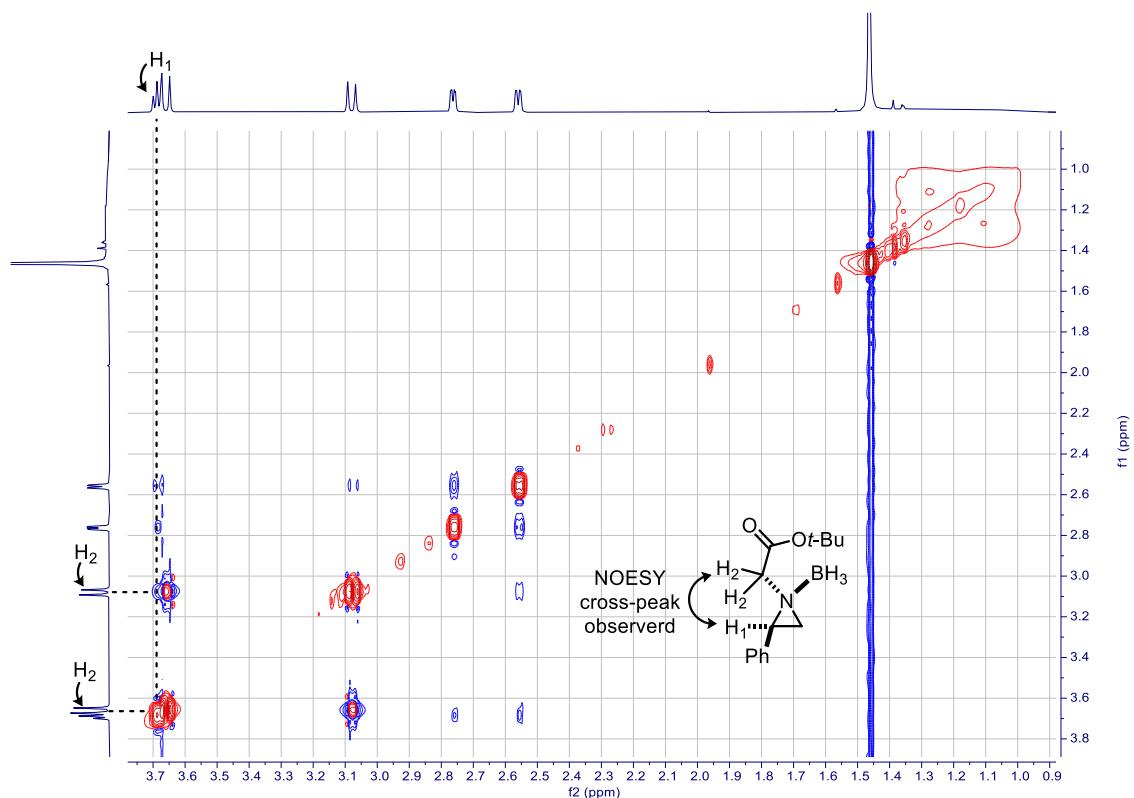
Data for **24a** (solid): ^1H (600 MHz, CDCl_3) δ 7.46 – 7.41 (3H, m), 7.39 – 7.34 (2H, m), 3.80 (1H, t, $J = 6.7$ Hz), 3.21 (1H, d, $J = 15.2$ Hz), 3.01 (1H, dd, $J = 6.7, 3.0$ Hz), 2.93 (1H, dd, $J = 7.0, 2.9$ Hz), 2.36 (1H, d, $J = 15.0$ Hz), 1.46 (9H, s); ^{13}C (151 MHz, CDCl_3) δ 166.5, 130.3, 130.2, 129.8, 129.3, 82.9, 55.7, 50.1, 40.3, 28.1; ^{11}B (193 MHz, CDCl_3) δ –10.74 (q, $J = 103.1$ Hz); HRMS (ESI) found MNa^+ 270.1636, $\text{C}_{14}\text{H}_{22}\text{BNO}_2\text{Na}$ requires 270.1636.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:

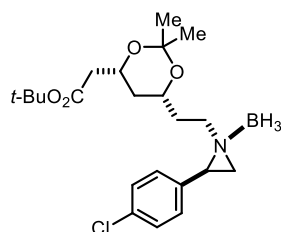


Data for **24a'** (solid): ^1H (600 MHz, CDCl_3) δ 7.53 – 7.48 (2H, m), 7.41 – 7.36 (3H, m), 3.79 – 3.71 (2H, m), 3.16 (1H, d, $J = 14.6$ Hz), 2.84 (1H, dd, $J = 6.7, 2.4$ Hz), 2.64 (1H, dd, $J = 7.8, 2.5$ Hz), 1.54 (12H, m); ^{13}C (151 MHz, CDCl_3) δ 165.9, 130.9, 130.5, 129.2, 128.2, 83.0, 64.5, 50.0, 40.7, 28.2; ^{11}B (193 MHz, CDCl_3) δ –15.28 (q, $J = 87.0$ Hz); HRMS (ESI) found MNa^+ 270.1634, $\text{C}_{14}\text{H}_{22}\text{BNO}_2\text{Na}$ requires 270.1636.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



***tert*-Butyl *trans*-2-((4*R*,6*R*)-6-(2-(2-(4-Chlorophenyl)aziridin-1-yl)ethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (**25a**)**

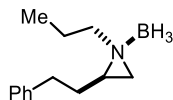


Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **25** (1.16 g, 2.82 mmol, 1.0 equiv.) gave after precipitation and filtration **25a** as mixture of diastereomers (950 mg, 80% total yield, the mixture was used directly in the next step) as a solid. d.r.1.3:1. ^1H NMR (600 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.37 – 7.33 (2.3H, m), 7.30 – 7.24 (2.3H, m), 4.30 – 4.22 (1.15H, m), 4.02 – 3.96 (0.65H, m), 3.96 – 3.89 (0.5H, m), 3.40 – 3.33 (1.15H, m), 3.17 (0.5H, td, $J = 11.0, 6.1$ Hz), 3.09 (0.65H, td, $J = 11.2, 4.8$ Hz), 2.79 (0.5H, dt, $J = 6.2, 1.5$ Hz), 2.77 – 2.69 (1.3H, m), 2.62 (0.5H, td, $J = 11.2, 4.2$ Hz), 2.50 (0.5H, dd, $J = 7.6, 1.9$ Hz), 2.48 – 2.41 (1.8H, m), 2.40 – 2.34 (0.5H, m), 2.34 – 2.31 (0.65H, m), 2.31 – 2.28 (0.5H, m), 2.22 – 2.16 (0.65H, m), 2.04 – 1.96 (0.65H, m), 1.83 – 1.74 (0.5H, m), 1.65 – 1.56 (1.15H, m), 1.45 (10.35H, s), 1.44 (1.5H, s), 1.42 (1.95H, s), 1.35 (1.5H, s), 1.34 (1.95H, s), 1.31 – 1.20 (1.15H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 170.3, 170.2, 135.2, 131.5, 131.5, 129.7, 129.5, 128.6, 128.6, 99.0, 98.9, 80.9, 80.9, 66.6, 66.5, 66.2, 66.2, 61.3, 60.9, 49.7, 48.5, 42.8, 42.7, 42.2, 40.9, 36.7,

36.2, 33.9, 33.4, 30.2, 30.2, 28.2, 20.0, 19.9; ^{11}B NMR (192 MHz, CDCl_3) δ -16.31; HRMS (ESI) found MNa^+ 446.2234, $\text{C}_{22}\text{H}_{35}\text{NO}_4\text{BClNa}$ requires 446.2240.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

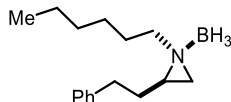
***trans*-2-Phenethyl-1-propylaziridine Borane (26a)**



Following **GP4**, **26** (147 mg, 0.78 mmol, 1.0 equiv.) gave after purification via column chromatography **26a** (124 mg, 78%) as a solid. R_f 0.37 [*n*-pentane:EtOAc (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.33 – 7.27 (2H, m), 7.25 – 7.18 (3H, m), 2.99 – 2.87 (2H, m), 2.76 (1H, ddd, J = 14.0, 9.1, 6.7 Hz), 2.38 – 2.28 (1H, m), 2.15 – 2.05 (4H, m), 2.04 – 2.00 (1H, m), 1.99 – 1.90 (1H, m), 1.86 – 1.33 (4H, m), 0.88 (3H, t, J = 7.4 Hz); ^{13}C (151 MHz, CDCl_3) δ 140.8, 128.6, 128.5, 126.3, 67.0, 46.7, 42.7, 33.8, 29.2, 19.9, 11.3; ^{11}B (193 MHz, CDCl_3) δ -16.71 (q, J = 98.0 Hz); HRMS (ESI) found MNa^+ 226.1734, $\text{C}_{13}\text{H}_{22}\text{BNNa}$ requires 226.1738.

The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

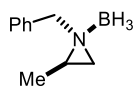
***trans*-1-Hexyl-2-phenethylaziridine Borane (27a)**



Following **GP4**, **27** (1.11 g, 4.8 mmol, 1.0 equiv.) gave after purification via column chromatography **27a** (671 mg, 57%) as an oil. R_f 0.78 [*n*-pentane:EtOAc (6:1)]. ^1H (600 MHz, CDCl_3) δ 7.35 – 7.21 (5H, m), 3.01 – 2.92 (2H, m), 2.82 – 2.74 (1H, m), 2.40 – 2.31 (1H, m), 2.19 – 2.01 (5H, m), 1.98 – 1.88 (1H, m), 1.83 – 1.42 (4H, m), 1.36 – 1.21 (6H, m), 0.91 (3H, t, J = 6.8 Hz); ^{13}C (151 MHz, CDCl_3) δ 140.9, 128.7, 128.6, 126.3, 65.5, 46.6, 42.8, 33.8, 31.6, 29.2, 26.7, 26.6, 22.6, 14.1; ^{11}B (193 MHz, CDCl_3) δ -16.71 (d, J = 103.6 Hz); HRMS (ESI) found MNa^+ 268.2204, $\text{C}_{16}\text{H}_{28}\text{BNNa}$ requires 268.2207.

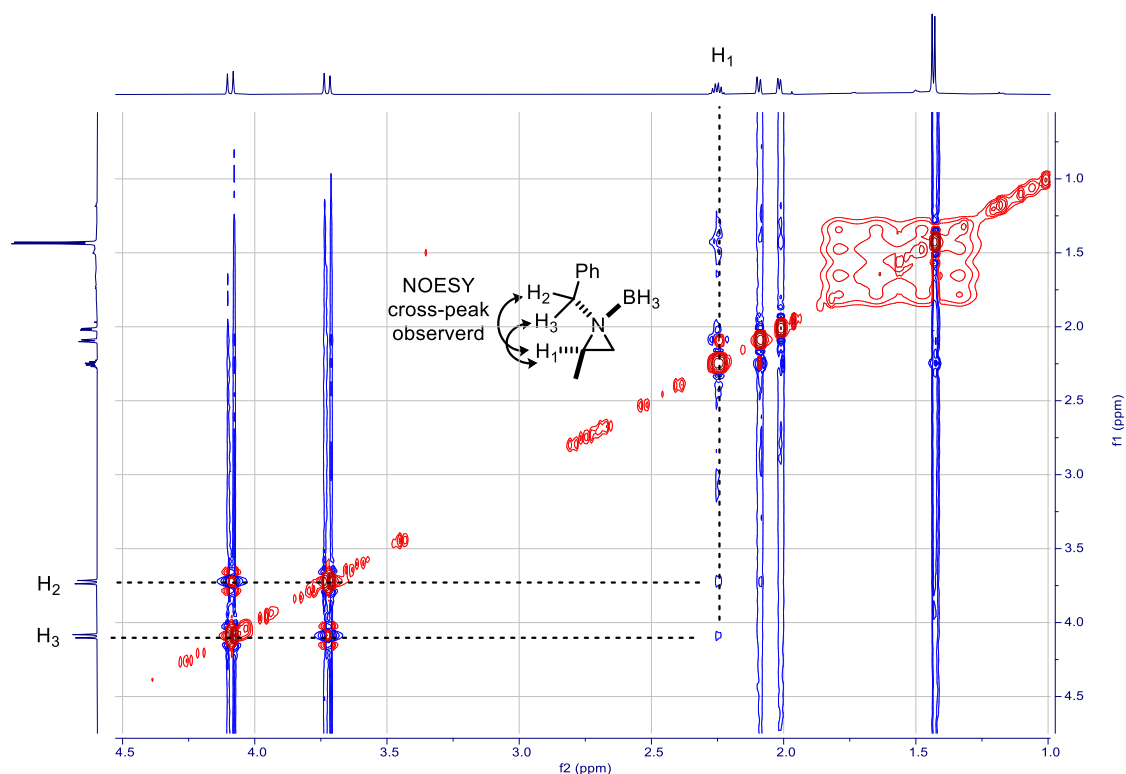
The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

***trans*-1-Benzyl-2-methylaziridine Borane (28a)**

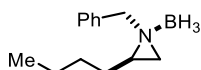


Following **GP4**, **28** (250 mg, 1.7 mmol, 1.0 equiv.) gave after purification via column chromatography **28a** (134 mg, 49%) as a solid. R_f 0.34 [*n*-pentane:EtOAc (3:1)]. ^1H (600 MHz, CDCl_3) δ 7.42 – 7.35 (3H, m), 7.34 – 7.29 (2H, m), 4.16 (1H, d, $J = 13.3$ Hz), 3.80 (1H, d, $J = 13.3$ Hz), 2.37 – 2.28 (1H, m), 2.17 (1H, dd, $J = 7.7, 1.6$ Hz), 2.09 (1H, dd, $J = 6.1, 1.6$ Hz), 1.51 (6H, m); ^{13}C (151 MHz, CDCl_3) δ 132.7, 130.9, 128.9, 128.7, 65.8, 40.7, 40.2, 12.6; ^{11}B (193 MHz, CDCl_3) δ -15.40 (q, $J = 97.8$ Hz); HRMS (ESI) found MNa^+ 184.1270, $\text{C}_{10}\text{H}_{16}\text{BNNa}$ requires 184.1268.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



***trans*-1-Benzyl-2-butylaziridine Borane (29a)**

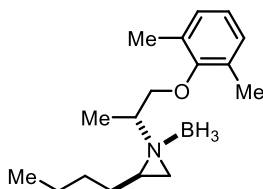


Following **GP4**, **29** (833 mg, 4.4 mmol, 1.0 equiv.) gave after purification via column chromatography **29a** (811 mg, 90%) as a solid. R_f 0.43 [*n*-pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.40 – 7.35 (3H, m), 7.35 – 7.30 (2H, m), 4.19 (1H, d, $J = 13.2$ Hz), 3.74 (1H, d, $J = 13.2$ Hz), 2.20 (1H, p, $J = 6.6$ Hz), 2.16 (1H, d, $J = 7.8$ Hz), 2.11 (1H, d, $J = 6.4$ Hz), 2.04 – 1.95 (1H, m), 1.93 – 1.38 (5H, m), 1.36 – 1.24 (3H, m), 0.88 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (151

MHz, CDCl₃) δ 132.8, 131.2, 129.0, 128.6, 66.2, 44.9, 40.5, 29.7, 26.8, 22.4, 13.9; ¹¹B (193 MHz, CDCl₃) δ -15.15 (q, J = 97.8 Hz); HRMS (ESI) found MNa⁺ 226.1731, C₁₃H₂₂BNNa requires 226.1738.

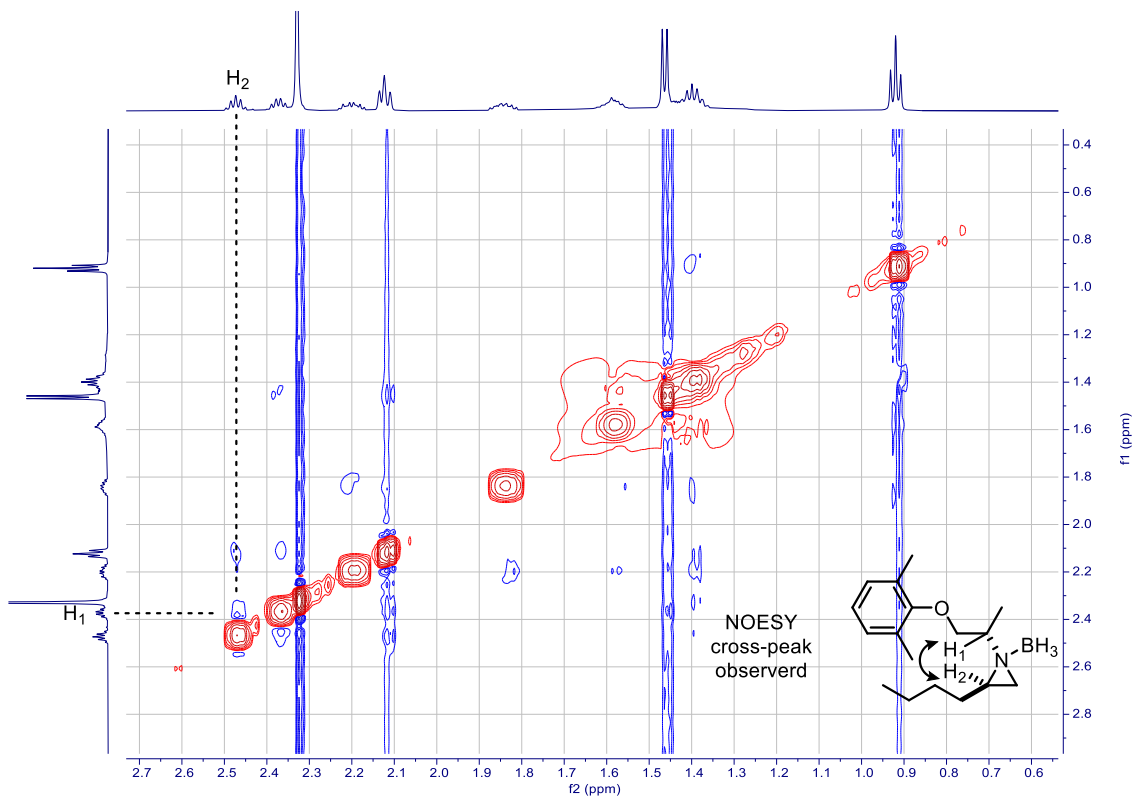
The relative configuration was determined by ¹H NMR and ¹¹B NMR shift in analogy with the shift differences observed for **10a** and **10a'**.

***trans*-2-Butyl-1-(1-(2,6-dimethylphenoxy)propan-2-yl)aziridine Borane (**30a**)**

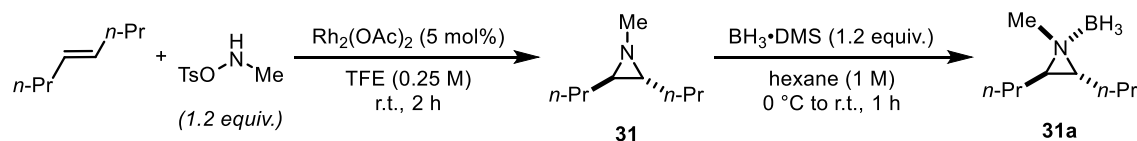


Following **GP4**, **30** (160 mg, 0.61 mmol, 1.0 equiv.) and BH₃•DMS (0.92 mmol, 1.5 equiv.) gave after purification via column chromatography **30a** as a single diastereomer (82 mg, 49%) as an oil. R_f 0.69 [*n*-pentane:EtOAc (1:1)]. ¹H NMR (600 MHz, CDCl₃) δ 7.02 (2H, d, J =7.4 Hz), 6.94 (1H, t, J =7.5 Hz), 4.37 (1H, dd, J =10.0, 7.2 Hz), 3.62 (1H, dd, J =10.0, 5.2 Hz), 2.45 (1H, p, J =6.8 Hz), 2.35 (1H, sx, J =6.7 Hz), 2.31 (6H, s), 2.22 – 2.14 (1H, m), 2.13 – 2.07 (2H, m), 1.87 – 1.78 (1H, m), 1.73 – 1.22 (10H, m), 0.93 – 0.87 (3H, d, J =7.2 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 155.6, 130.9, 129.1, 124.2, 72.9, 69.2, 50.8, 41.4, 29.7, 27.2, 22.5, 16.6, 14.9, 14.0; ¹¹B (193 MHz, CDCl₃) δ -20.01. HRMS could not be obtained for this compound.

The relative configuration was determined by a 2D ¹H-¹H NOESY (600 MHz, CDCl₃) experiment:



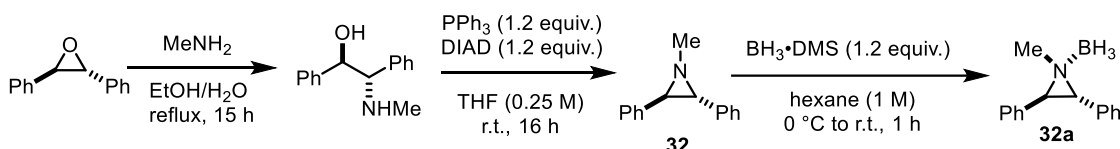
1-Benzyl-2,3-dipropylaziridine Borane (31a)



Step 1: To a round-bottom flask equipped with a magnetic stirring bar were added (*E*)-oct-4-ene (471 μ L, 3.0 mmol, 1.0 equiv.), *N*-methyl-*O*-tosylhydroxylamine (723 mg, 3.6 mmol, 1.2 equiv.), and TFE (12 mL, 0.25 M). To this stirred solution was added $\text{Rh}_2(\text{OAc})_2$ (66 mg, 5 mol %) in one portion. The reaction mixture was stirred at room temperature for 2 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 and washed with a saturated aqueous NaHCO_3 solution (x 2). The aqueous layer was extracted with CH_2Cl_2 (x 2), and the combined organic layers were dried over anhydrous Na_2SO_4 . The solvent was evaporated and purified by column chromatography on silica gel to afford **31**. *Note: the product is volatile, so the crude was used without being completely dried, 47% ^1H NMR yield was obtained.* R_f 0.2 [*n*-pentane: EtOAc (1:1)].

Step 2: Following **GP4**, **31** (1.4 mmol, 1.0 equiv.) gave after purification via column chromatography **31a** (174 mg, 80%) as an oil. R_f 0.59 [*n*-pentane:EtOAc (5:1)]. ^1H NMR (600 MHz, CDCl_3) δ 2.58 (3H, s), 2.18 (1H, q, J = 6.6 Hz), 2.01 – 1.92 (1H, m), 1.86 – 1.28 (11H, m), 0.98 (3H, t, J = 7.3 Hz), 0.96 (3H, t, J = 7.3 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 53.8, 51.8, 44.5, 29.4, 29.0, 20.9, 20.8, 13.9, 13.9; ^{11}B (193 MHz, CDCl_3) δ –14.89 (q, J = 96.2 Hz); HRMS (ESI) found MNa^+ 178.1738, $\text{C}_9\text{H}_{22}\text{BNNa}$ requires 178.1738.

1-Methyl-2,3-diphenylaziridine Borane (32a)



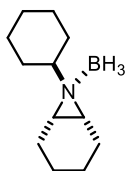
Step 1: Methylamine (33 wt% in EtOH, 20 mL) was added to a solution of *trans*-stilbene oxide (1.96 g, 10 mmol, 1.0 equiv.). Water (0.3 mL) was then added and the solution was stirred at reflux for 15 h. Upon completion, the excess methylamine and EtOH were removed under reduced pressure until crystallization began. The mixture was cooled at 0 $^{\circ}\text{C}$ for 12 h, filtered, and washed with pentane to give erythro-1,2-diphenyl-2-(*N*-methylamino)ethanol as a white solid (1.43 g, 63%). ^1H NMR (600 MHz, CDCl_3) δ 7.33 – 7.25 (6H, m), 7.19 – 7.14 (4H, m), 4.84 (1H, d, J = 5.9 Hz), 3.79 (1H, d, J = 5.9 Hz), 2.30 (3H, s). Data in accordance with the literature.¹⁶

Step 2: A round bottom flask equipped with a stirring bar was charged with erythro-1,2-diphenyl-2-(*N*-methylamino)ethanol (750 mg, 3.3 mmol, 1.0 equiv.) and PPh_3 (0.86 g, 3.9 mmol, 1.2 equiv.). Dry THF (13 mL, 0.25 M) was added followed by the dropwise addition of diisopropylazodicarboxylate (DIAD) (0.65 mL, 3.9 mmol, 1.2 equiv.) via syringe. The resulting

reaction mixture was stirred at room temperature for 16 h. Upon completion, the mixture was concentrated by rotary evaporation and the residue was purified by column chromatography to deliver the crude *trans*-1-methyl-2,3-diphenylaziridine **32** that was directly used in the next step. R_f 0.66 [*n*-pentane:EtOAc (1:1)]. *Note: It can't give pure aziridine by column isolation because of side product from DIAD.*

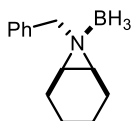
Step 3: Following **GP4** but in THF (1 M), crude *trans*-1-methyl-2,3-diphenylaziridine and $\text{BH}_3 \cdot \text{DMS}$ (6.6 mmol, 2.0 equiv.) gave **32a** (545.1 mg, 74%, overall two steps) as a solid. ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.40 (10H, m), 4.18 (1H, d, $J = 6.5$ Hz), 3.82 (1H, d, $J = 6.5$ Hz), 2.48 (3H, s), 1.48 (3H, q, $J = 121.3$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 131.2, 130.2, 130.02, 129.98, 129.8, 129.19, 129.16, 128.3, 53.4, 53.2, 45.6; ^{11}B (128 MHz, CDCl_3) δ -9.57 – -17.62 (m); HRMS (ESI) found MNa^+ 246.1421, $\text{C}_{15}\text{H}_{18}\text{BNNa}$ requires 246.1425.

***trans*-7-Cyclohexyl-7-azabicyclo[4.1.0]heptane Borane (33a)**



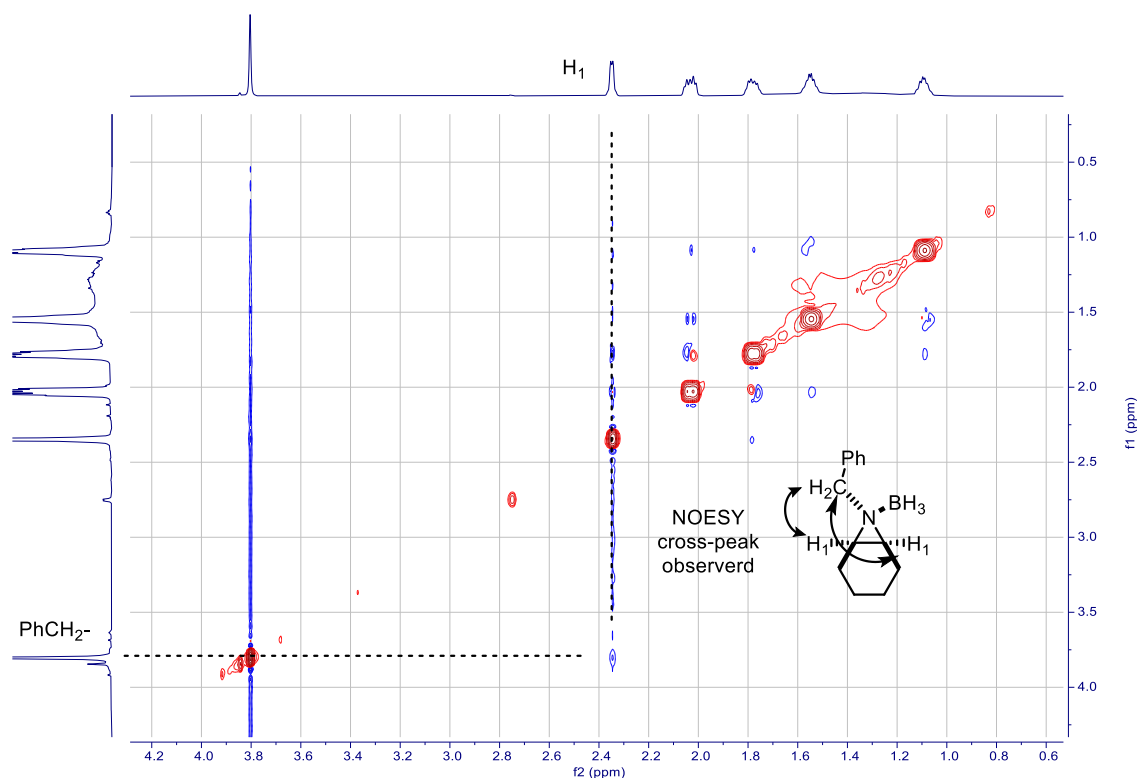
Following **GP4** but in (1 M), **33** (438 mg, 2.4 mmol, 1.0 equiv.) and $\text{BH}_3 \cdot \text{DMS}$ (2.5 mmol, 1.05 equiv.) gave after purification via column chromatography **33a** (367 mg, 78%) as a solid. R_f 0.67 [*n*-pentane:EtOAc (5:1)]. ^1H NMR (400 MHz, CDCl_3) δ 2.21 – 2.10 (4H, m), 2.04 (2H, qd, $J=12.4$, 3.4 Hz), 1.94 – 0.70 (18H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 76.8, 44.1, 29.0, 25.9, 25.7, 19.8, 18.1; ^{11}B (193 MHz, CDCl_3) δ -24.27 (q, $J=96.3$ Hz); HRMS (ESI) found MNa^+ 216.1895, $\text{C}_{12}\text{H}_{24}\text{BNNa}$ requires 216.1894.

***trans*-7-Benzyl-7-azabicyclo[4.1.0]heptane Borane (34a)**

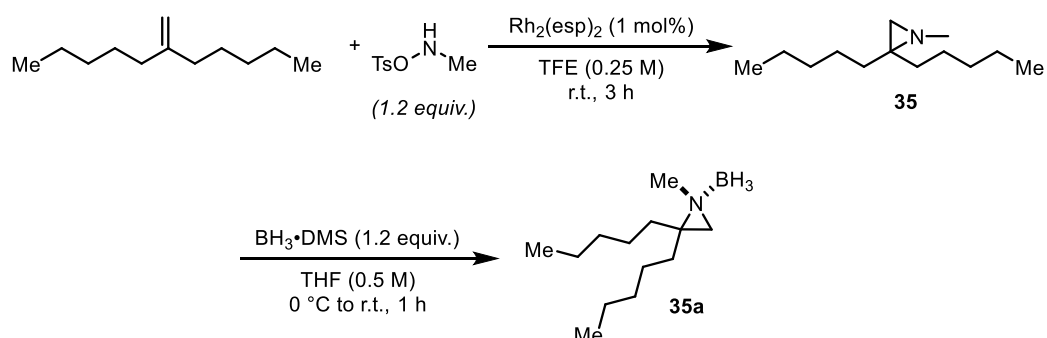


Following **GP4**, **34** (374.6 mg, 2 mmol, 1.0 equiv.) gave **34a** (305.7 mg, 76%) as a solid. R_f 0.22 [*n*-pentane:EtOAc (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.33 – 7.16 (5H, m), 3.80 (2H, s), 2.38 – 2.32 (2H, m), 2.08 – 1.99 (2H, m), 1.84 – 1.71 (2H, m), 1.65 – 1.02 (7H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 133.8, 129.9, 128.2, 128.1, 68.8, 42.1, 19.4, 17.9; ^{11}B (193 MHz, CDCl_3) δ -19.69 (q, $J = 97.4$ Hz); HRMS (ESI) found MNa^+ 224.1574, $\text{C}_{13}\text{H}_{20}\text{BNNa}$ requires 224.1581.

The relative configuration was determined by a 2D ^1H - ^1H NOESY (600 MHz, CDCl_3) experiment:



1-Methyl-2,2-dipentylaziridine borane (**35a**)

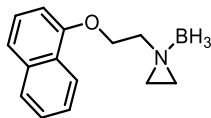


Step 1: A round bottom flask equipped with a stirring bar was charged with *N*-methyl-*O*-tosylhydroxylamine (723 mg, 3.6 mmol, 1.2 equiv.) The flask was evacuated and refilled with Ar (x 3). 6-methyleneundecane (505 mg, 3.0 mmol, 1.0 equiv.) and catalyst solution (12 mL of TFE containing $\text{Rh}_2(\text{esp})_2$ (23 mg, 1 mol %), pre-stirred for 10 min) was then added under stirring. The reaction mixture was stirred at room temperature for 3 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 and washed with a saturated aqueous NaHCO_3 solution (x 2). The aqueous layer was extracted with CH_2Cl_2 (x 2), and the combined organic layers were dried over anhydrous Na_2SO_4 . The solvent was evaporated to afford crude **35** directly for next step. *Note: the product is volatile, so the crude was used without being completely dried.*

Step 2: Following **GP4**, crude **35** and $\text{BH}_3\cdot\text{DMS}$ (3.6 mmol, 1.2 equiv.) in THF (6 mL) gave after purification via column chromatography **35a** (171 mg, 27% over two steps) as an oil. R_f 0.37 [*n*-

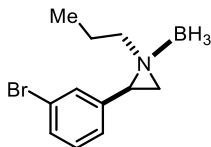
pentane:EtOAc (30:1)]. ^1H NMR (600 MHz, CDCl_3) δ 2.71 (3H, s), 2.19 (1H, d, $J=1.7$ Hz), 2.00 – 1.23 (21H, m), 0.94 – 0.86 (6H, m); ^{13}C (151 MHz, CDCl_3) δ 53.1, 48.5, 45.5, 32.0, 31.8, 30.4, 30.1, 25.8, 25.7, 22.6, 22.6, 14.1, 14.1; ^{11}B (193 MHz, CDCl_3) δ -13.47 (q, $J=98.2$ Hz); HRMS (ESI) found MNa^+ 234.2362, $\text{C}_{13}\text{H}_{30}\text{BNNa}$ requires 234.2364.

1-(2-(Naphthalen-1-yloxy)ethyl)aziridine Borane (36a)



Following **GP4**, **36** (320 mg, 1.5 mmol, 1.0 equiv.) gave after purification via column chromatography **36a** (228 mg, 67%) as a solid. R_f 0.61 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 8.18 – 8.14 (1H, m), 7.85 – 7.80 (1H, m), 7.54 – 7.45 (3H, m), 7.40 (1H, t, $J = 7.9$ Hz), 6.90 – 6.86 (1H, m), 4.63 (2H, t, $J = 5.0$ Hz), 3.17 (2H, t, $J = 5.0$ Hz), 2.45 (2H, d, $J = 5.0$ Hz), 2.38 (2H, d, $J = 4.8$ Hz), 1.67 (3H, q, $J = 130.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 153.9, 134.7, 127.9, 126.6, 126.0, 125.5, 125.5, 121.6, 121.1, 105.2, 64.7, 60.9, 37.1; ^{11}B (193 MHz, CDCl_3) δ -12.81 (q, $J = 99.4$ Hz); HRMS (ESI) found MNa^+ 250.1371, $\text{C}_{14}\text{H}_{18}\text{BNONa}$ requires 250.1374.

trans-2-(3-Bromophenyl)-1-propylaziridine Borane (37a)



Following **GP4**, but adding $\text{BH}_3 \cdot \text{DMS}$ at -78°C and react at r.t. for 4 h, **37** (560 mg, 2.33 mmol, 1.0 equiv.) gave after precipitation and filtration **37a** (490 mg, 86%) as a solid. ^1H NMR (600 MHz, CDCl_3) δ 7.53 (1H, dt, $J = 7.7, 1.6$ Hz), 7.49 (1H, t, $J = 1.8$ Hz), 7.35 – 7.24 (2H, m), 3.33 (1H, t, $J = 6.9$ Hz), 3.12 (1H, td, $J = 11.5, 4.9$ Hz), 2.81 (1H, dd, $J = 6.2, 2.0$ Hz), 2.48 – 2.38 (2H, m), 2.18 – 2.06 (1H, m), 1.97 – 1.80 (1H, m), 1.48 – 0.96 (6H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 133.3, 133.2, 132.2, 129.8, 128.9, 122.3, 67.1, 48.7, 41.4, 20.4, 11.4; ^{11}B NMR (192 MHz, CDCl_3) δ -16.05; HRMS (ESI) found MNa^+ 276.0526, $\text{C}_{11}\text{H}_{17}\text{NBBNa}$ requires 276.0530.

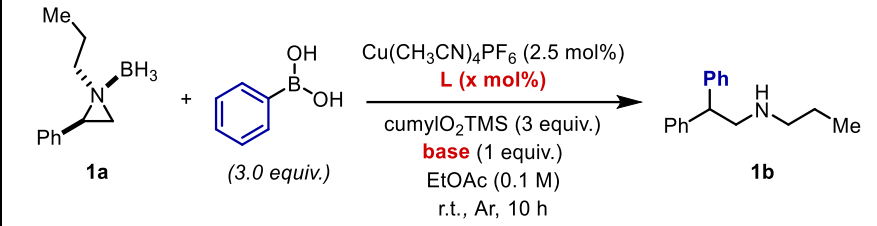
The relative configuration was determined by ^1H NMR and ^{11}B NMR shift in analogy with the shift differences observed for **3a** and **3a'**.

4 Reaction Optimization

4.1 Optimization of the Arylation with Ph-B(OH)₂

An oven-dried vial equipped with a stirring bar was charged with *trans*-aziridine **1a** (0.1 mmol, 1.0 equiv.) and Ph-B(OH)₂ (with the corresponding equivalent stated in the Tables). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). Dry and degassed solvent (0.5 mL) and the oxidant (with the corresponding equivalent stated in the Tables) were then added to the vial and stirred for around **1 min**. If necessary, the resulting mixture was cooled down to the corresponding temperature and the catalyst solution (0.5 mL of the corresponding dry and degassed solvent, containing copper catalyst and ligand with the corresponding loading stated in the Tables, pre-stirred for 10 min until fully dissolved) was then added under stirring. The resulting mixture was stirred at the corresponding temperature for the corresponding amount of time. Upon completion, 1,3,5-trimethoxybenzene (0.066 M in EtOAc, 0.5 mL, 0.033 mmol, 0.33 equiv.) and an aqueous solution of NaOH (2 mL, 1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x 3 mL). The combined organic layers were dried (MgSO₄) and filtered. The solvent was evaporated and analysed by ¹H NMR spectroscopy to determine the NMR yield.

Table S2. Screening of the ligand, ligand equivalent and base.

 Reaction scheme showing the conversion of 1a to 1b using $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (2.5 mol%), ligand L (x mol%), cumylo₂TMS (3 equiv.), base (1 equiv.), EtOAc (0.1 M), r.t., Ar, 10 h.				
entry	ligand (x mol%)	base	1b (%)	1a (%)
1^{a,b}	bathophen (2.7)	KH_2PO_4	36	0
2^{a,b}	L1 (2.7)	KH_2PO_4	26	n.d.
3^{a,b}	L2 (2.7)	KH_2PO_4	30	73
4^{a,b}	L3 (2.7)	KH_2PO_4	n.d.	58
5	bathophen (2.7)	NaHCO_3	47	n.d.
6	bpy (2.7)	NaHCO_3	31	n.d.
7	L4 (2.7)	NaHCO_3	36	n.d.
8	L5 (2.7)	NaHCO_3	32	n.d.
9	L6 (2.7)	NaHCO_3	32	n.d.
10	dtbpy (2.7)	NaHCO_3	47	n.d.
11	L7 (2.7)	NaHCO_3	18	n.d.
12	L8 (2.7)	NaHCO_3	32	n.d.
13	L9 (2.7)	NaHCO_3	17	n.d.
14^c	dtbpy (3.5)	-	61	n.d.
15^{c,d}	phen (3.5)	-	42	n.d.
16^{c,d}	L10 (3.5)	-	36	n.d.
17^c	L11 (3.5)	-	0	0
18^c	L12 (3.5)	-	0	0
19^c	L13 (3.5)	-	0	45
20^c	L14 (3.5)	-	0	64
21^c	L15 (3.5)	-	12	0
22^c	L16 (3.5)	-	0	51
23^c	L17 (3.5)	-	0	46
24^c	L18 (3.5)	-	0	72

^a1.5 equivalents of PhB(OH)₂ was used. ^b8 h. ^cThe reaction was run at 10 °C. ^d12 h.

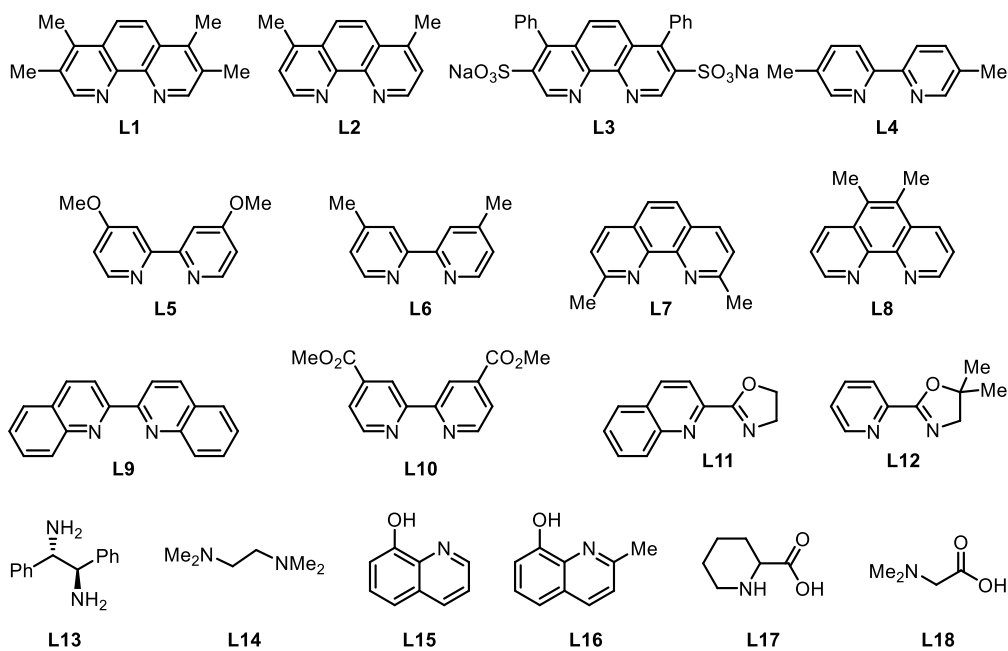


Table S3. Screening of the copper source.

entry	[Cu]	1b (%)	1a (%)
1	CuCl	47	n.d.
2 ^a	CuBr•DME	n.d.	22
3 ^a	Cu(CH ₃ CN) ₄ BF ₄	n.d.	25
4 ^a	Cu(CH ₃ CN) ₄ OTf	n.d.	35
5	CuOAc	43	n.d.
6	Cu(OTf) ₂	54	n.d.
7	[Cu(OTf) ₂] ₂ •PhH	56	n.d.
8	CuBr	47	n.d.
9	CuSO ₄	n.d.	56
10	CuCN	n.d.	28
11	Cu(acac) ₂	53	n.d.
12 ^a	Cu-1	61	n.d.
13 ^a	Cu-2	46	n.d.
14 ^a	Cu-3	53	n.d.
15 ^a	Cu-4	45	n.d.
16	Cu(CH ₃ CN) ₄ PF ₆	61	n.d.

^a12 h.

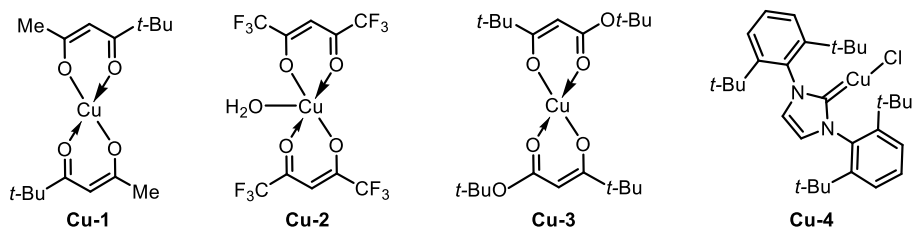


Table S4. Screening of the solvent.

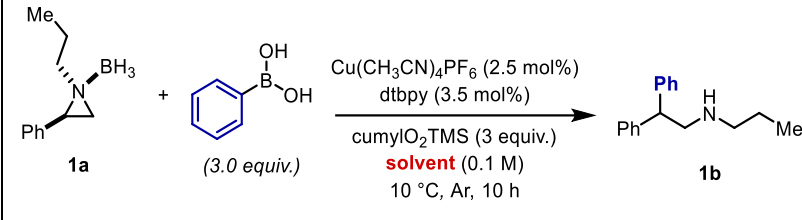
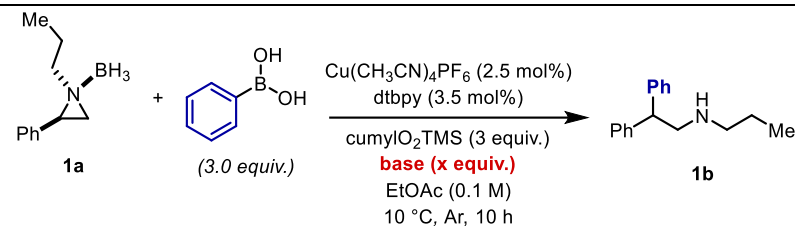
 $\text{1a} + \text{C}_6\text{H}_5\text{B(OH)}_2 \xrightarrow[\text{solvent (0.1 M), 10 } ^\circ\text{C, Ar, 10 h}]{\text{Cu(CH}_3\text{CN)}_4\text{PF}_6 \text{ (2.5 mol\%)}, \text{dtbpy (3.5 mol\%)}, \text{cumylO}_2\text{TMS (3 equiv.)}}$ 1b			
entry	solvent	1b (%)	1a (%)
1	EtOAc	61	n.d.
2	CH ₂ Cl ₂	34	35
3	EtOAc/DMA (4:1)	14	39
4	PhH	5	30
5	EtOMe	58	n.d.
6	PhCl	20	42
7	PhF	16	46
8	EtOAc/CH ₃ CN (19:1)	51	n.d.
9	EtOAc/CH ₃ CN (9:1)	46	n.d.
10	acetone	21	n.d.
11	EtOAc/acetone (2:1)	60	n.d.
12	EtOAc/acetone (9:1)	49	n.d.
13	EtOAc/CH ₂ Cl ₂ (7:3)	n.d.	27
14	EtOAc/PhCF ₃ (7:3)	60	n.d.
15	EtOAc/PhCF ₃ (9:1)	44	n.d.

Table S5. Screening of the base and the base equivalent.

 $\text{1a} + \text{C}_6\text{H}_5\text{B(OH)}_2 \text{ (3.0 equiv.)} \xrightarrow[\text{EtOAc (0.1 M), 10 }^\circ\text{C, Ar, 10 h}]{\text{Cu(CH}_3\text{CN)}_4\text{PF}_6 \text{ (2.5 mol\%), dtbpy (3.5 mol\%), cumylO}_2\text{TMS (3 equiv.), base (x equiv.)}} \text{1b}$			
entry	base (equiv.)	1b (%)	1a (%)
1	-	61	n.d.
2	Li ₂ CO ₃ (1.5)	57	n.d.
3	H ₃ BO ₃ (1.5)	12	24
4	DBN (1.5)	6	56
5	pyridine (1.5)	14	11
6	BTMG (2)	11	58
7	Et ₃ N (1.5)	15	54
8	TMP (1.5)	14	20
9	<i>t</i> -BuOK (1.5)	33	11
10	LiF (1.5)	51	n.d.
11	LiF (3)	51	n.d.
12	BzOK (1.5)	38	12
13	BzOK (3)	36	10
14	LiBr (2)	11	n.d.
15	LiI (2)	11	n.d.
16	LiOt-Bu (2)	n.d.	n.d.
17	LiOH (2)	8	n.d.
18	LiTFA (2)	18	n.d.
19	LiOAc·2H ₂ O (2)	12	10

BTMG = 2-*t*-Bu-1,1,3,3-tetramethylguanidine; TMP = 2,2,6,6-tetramethylpiperidine

Table S6. Screening of the temperature.

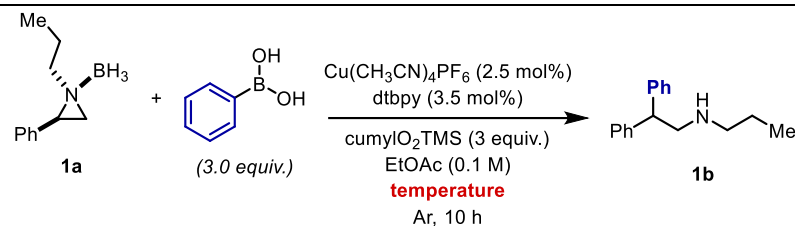
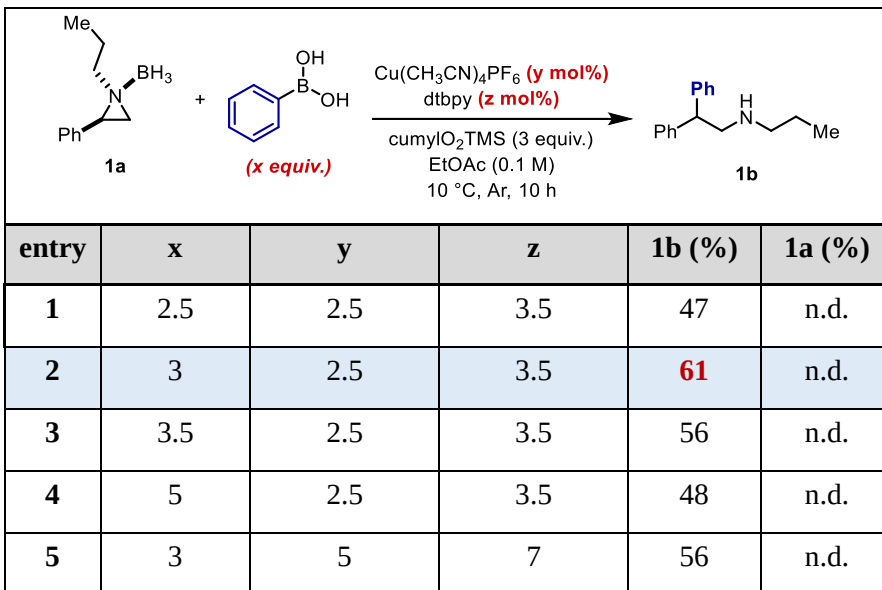
 $\text{1a} + \text{C}_6\text{H}_5\text{B(OH)}_2 \xrightarrow[\text{Ar, 10 h}]{\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 \text{ (2.5 mol\%)}, \text{dtbpy} \text{ (3.5 mol\%)}, \text{cumylO}_2\text{TMS} \text{ (3 equiv.)}, \text{EtOAc} \text{ (0.1 M)}, \text{temperature}}$ 1b			
entry	temperature	1b (%)	1a (%)
1	−10 °C	52	n.d.
2	0 °C	57	n.d.
3	10 °C	61	n.d.
4	r.t.	47	n.d.
5	45 °C	43	n.d.

Table S7. Screening of the oxidant, oxidant equivalent, base and temperature.

entry	oxidant (equiv.)	base (equiv.)	temperature	1b (%)	1a (%)
1	cumylO ₂ TMS (2)	KH ₂ PO ₄ (1.0)	rt	35	28
2	cumylO ₂ TMS (3)	KH ₂ PO ₄ (1.0)	rt	46	n.d.
3	cumylO ₂ TMS (4)	KH ₂ PO ₄ (1.0)	rt	42	n.d.
4	NFSI (3)	KH ₂ PO ₄ (1.0)	rt	n.d.	n.d.
5	(<i>t</i> -BuO) ₂ (3)	KH ₂ PO ₄ (1.0)	rt	n.d.	90
6	(cumylO) ₂ (3)	KH ₂ PO ₄ (1.0)	rt	n.d.	>95
7	cumylO ₂ TES (3)	KH ₂ PO ₄ (1.0)	rt	44	n.d.
8	<i>t</i> -BuO ₂ TMS (3)	KH ₂ PO ₄ (1.0)	rt	30	26
9	cumylO ₂ <i>i</i> -Pr (3)	-	10 °C	n.d.	90
10	cumylO ₂ TBS (3)	-	10 °C	n.d.	74
11	cumylO ₂ TMS (2.5)	-	10 °C	54	n.d.
12	cumylO ₂ TMS (3)	-	10 °C	61	n.d.
13	cumylO ₂ TMS (3.5)	-	10 °C	54	n.d.
14	cumylO ₂ TMS (4)	-	10 °C	49	n.d.
15 ^a	BPO (3)	-	10 °C	<5	33
16 ^a	LPO (3)	-	10 °C	10	36
17 ^a	TBPB (3)	-	10 °C	n.d.	43

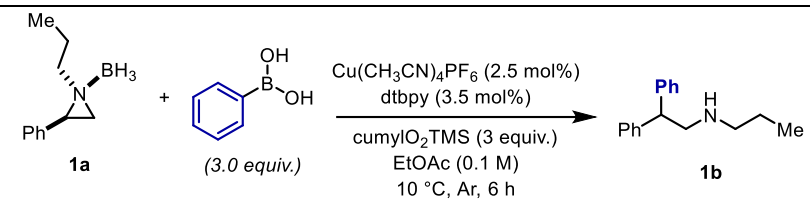
^aThe reaction was run for 16 h. NFSI = *N*-Fluorobenzenesulfonimide; BPO = Benzoyl peroxide;
LPO = Lauroyl peroxide; TBPB = *tert*-Butyl peroxybenzoate

Table S8. Screening of phenylboronic acid equivalent and catalyst/ligand loading.



4.2 Control Reactions

Table S9. Influence of each reagent and time on the reaction outcome.

 Reaction scheme showing the conversion of 1a (a bicyclic amine with a phenyl group and a BH₃ group) to 1b (a secondary amine with a phenyl group and a methyl group). The reaction conditions are: Cu(CH₃CN)₄PF₆ (2.5 mol%), dtbpy (3.5 mol%), cumylO₂TMS (3 equiv.), EtOAc (0.1 M), 10 °C, Ar, 6 h.			
entry	modifications	1b (%)	1a (%)
1	-	55	n.d.
2	no cumylO ₂ TMS	n.d.	85
3 ^a	no Ph-B(OH) ₂	n.d.	12
4	no Cu/dtbpy	n.d.	84
5	no cumylO ₂ TMS, no Ph-B(OH) ₂	n.d.	97
6	no cumylO ₂ TMS, no Cu/dtbpy	n.d.	76
7	no Ph-B(OH) ₂ , no Cu/dtbpy	n.d.	95
8	no Ph-B(OH) ₂ , no Cu/dtbpy, no cumylO ₂ TMS	n.d.	98
9	time = 1 h	15	21
10	time = 2 h	21	10
11	time = 4 h	53	n.d.

4.3 Optimization of the Arylation with Electron-Deficient Boronic Acids

Table S10. Screening of boronic acid equivalent and solvent in the case of boronic acids with electron withdrawing groups.

Reaction scheme: 1a (a chiral borane) + 4-(trifluoromethyl)phenylboronic acid (x equiv.) $\xrightarrow[\text{10 } ^\circ\text{C, Ar, 10 h}]{\text{Cu(CH}_3\text{CN)}_4\text{PF}_6 \text{ (2.5 mol\%)}, \text{dtbbpy (3.5 mol\%)}, \text{cumylO}_2\text{TMS (3 equiv.)}, \text{solvent (0.1 M)}}$ 1h (a chiral amine derivative).				
entry	x	solvent	1h (%)	1a (%)
1	3	EtOAc	19	n.d.
2	3	EtOAc:acetone (2:1)	22	n.d.
3	4	EtOAc:acetone (2:1)	30	n.d.
4	3	EtOAc:PhCF ₃ (7:3)	20	n.d.
5	4	EtOAc:PhCF ₃ (7:3)	23	n.d.
6	5	EtOAc:PhCF ₃ (7:3)	20	n.d.
7	4	EtOAc:MTBE (2:1)	<5	n.d.
8	4	EtOAc:PhF (2:1)	35	n.d.
9	4	EtOAc:DCE (2:1)	17	n.d.
10	4	EtOAc:CH ₃ CN (7:3)	41	n.d.

4.4 Optimization of the Arylation with Electron-Rich Boronic Acids

Table S11. Screening of boronic acid equivalent and solvent in the case of boronic acids with electron rich groups.

Reaction scheme: 1a (a chiral amine) reacts with a 4-fluoro-3-methoxyphenyl boronic acid (x equiv.) in the presence of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (2.5 mol%), dtbbpy (3.5 mol%), cumylO₂TMS (y equiv.), solvent (0.1 M), at 10 °C under Ar for 10 h to yield product 1m.					
entry	x	y	solvent	1m (%)	1a (%)
1	3	3	EtOAc	30	n.d.
2	2	3	EtOAc:acetone (2:1)	20	n.d.
3	3	3	EtOAc:acetone (2:1)	35	n.d.
4 ^a	3	3	EtOAc:acetone (2:1)	30	n.d.
5	4	3	EtOAc:acetone (2:1)	40	n.d.
6	5	3	EtOAc:acetone (2:1)	41	n.d.
7	4	4	EtOAc:acetone (2:1)	35	n.d.
8 ^b	4	3	EtOAc:acetone (2:1)	30	n.d.

^a $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (5 mol%), dtbbpy (7 mol%). ^bBathophen was used instead of dtbbpy.

4.5 Optimization of the Cyanation with TMSCN

Table S12. Screening of the solvent.

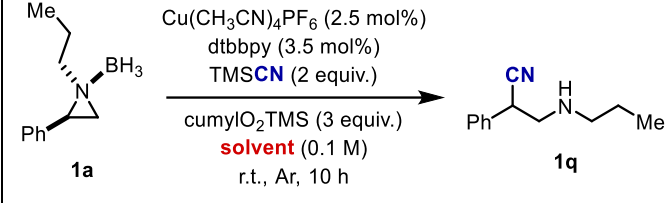
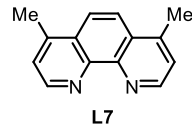
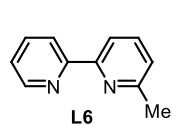
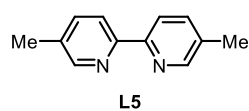
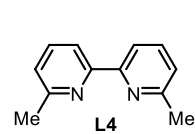
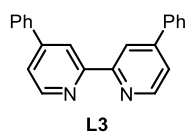
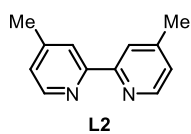
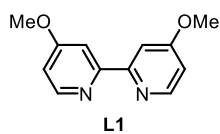
 $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (2.5 mol%) dtbbpy (3.5 mol%) TMSCN (2 equiv.) $\text{cumylO}_2\text{TMS}$ (3 equiv.) solvent (0.1 M) r.t., Ar, 10 h			
entry	solvent	1q (%)	1a (%)
1	EtOAc	48	n.d.
2	acetone	14	n.d.
3	CH ₃ CN	56	n.d.
4	CH ₂ Cl ₂	56	n.d.
5	DCE	52	n.d.
6	PhF	49	n.d.
7	PhCF ₃	51	n.d.
8	MTBE	<5	76

Table S13. Screening of the ligand and ligand equivalent.

entry	ligand	1q (%)	1a (%)
1	bpy (3.5)	49	n.d.
2	L1 (3.5)	53	n.d.
3	L2 (3.5)	30	n.d.
4	dtbbpy (3.5)	56	n.d.
5	L3 (3.5)	41	n.d.
6	L4 (3.5)	31	29
9	L5 (2.7)	n.d.	32
10	L6 (2.7)	38	n.d.
11	phen (3.5)	56	n.d.
12	L7 (3.5)	37	n.d.
13	bathophen (2.7)	54	n.d.
14	L8 (3.5)	30	n.d.
15	L9 (3.5)	50	n.d.
16	L10 (3.5)	38	n.d.
17	L11 (3.5)	10	70
18	L12 (3.5)	16	61
19	L13 (3.5)	n.d.	28



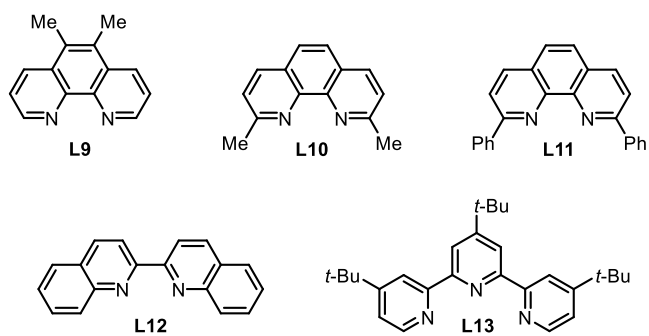


Table S14. Screening of the time.

Reaction scheme showing the conversion of 1a to 1q under the following conditions: $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (2.5 mol%) - dtbbpy (3.5 mol%) - TMS-CN (2 equiv.) - cumylO₂TMS (3 equiv.) - CH₃CN (0.1 M) - r.t., Ar, time			
entry	time	1q (%)	1a (%)
1	1 h	11	56
2	2 h	65	n.d.
3	10 h	56	n.d.
4	20 h	50	n.d.

4.6 Control Reactions for Cyanation and Thioetherification

Table S15. Control reactions for Cyanation.

Reaction scheme for Table S15: 1a (1.0 equiv) reacts with TMS-CN (2.0 equiv) in CH₃CN (0.1 M) at temp., Ar, 2 h to form 1q.			
entry	T (°C)	1q (%)	1a (%)
1	25	n.d.	96
2	80	n.d.	59

Table S16. Control reactions for thioetherification.

Reaction scheme for Table S16: 1a (2.0 equiv) reacts with PhSSPh (1.0 equiv) in PhCl (0.1 M) at temp., Ar, 2 h to form 1r.			
entry	T (°C)	1r (%)	1a (%)
1	25	n.d.	98
2	100	n.d.	9

4.7 Optimization of Photo–Nickel Dual Catalysis

An oven-dried microwave vial was charged with *trans*-aziridine **1a** (0.1 mmol, 1.0 equiv.), methyl 4-bromobenzoate (0.2 mmol, 2.0 equiv.), photocatalyst (with the corresponding equivalent stated in the Tables), nickel catalyst and/or ligand (with the corresponding equivalent stated in the Tables) and K₃PO₄ (42 mg, 2.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). Dry and degassed EtOAc (1.0 mL) was then added to the vial and the mixture was stirred for **1 min** at room temperature and then was placed 4 cm from the 390 nm purple LEDs. The LEDs were switched on (kessil, 100 W) and the mixture was stirred under irradiation with a fan for 16 hours. Upon completion, aqueous NaOH (2 mL, 1 M) was added, the aqueous layer was separated and extracted with EtOAc (3 mL). The aliquot from organic phase was taken for GC analysis.

Table S17. Screening of the nickel catalyst and the ligand.

entry	[Ni]	L	13j (%)	13a (%)	ArBr (%)
1	Ni(dtbpy)Br ₂		82	2	n.d.
2	NiBr ₂ •DME	bpy	3	81	89
3	NiBr ₂ •DME	4,4'-diMe-bpy	1	85	79
4	NiBr ₂ •DME	4,4'-diOMe-bpy	1	68	82
5	NiBr ₂ •DME	phen	n.d.	85	98
6	NiBr ₂ •DME	dtbpy	76	5	2
7	Ni(OAc) ₂ •4H ₂ O	dtbpy	2	77	57
8	Ni(acac) ₂	dtbpy	n.d.	82	93
9	NiCl ₂ •DME	dtbpy	6	71	84
10	Ni(NO ₃) ₂ •6H ₂ O	dtbpy	77	17	6
11	NiCl ₂ •6H ₂ O	dtbpy	1	82	89

Table S18. Screening of the photocatalyst.

<chem>CC1(C)N(B)CC1Cc2ccccc2</chem> + <chem>COC(=O)c1ccc(Br)cc1</chem> 13a (2.0 equiv.) 13j				
PC1 PC2 PC3 PC4 PC5 PC6				
entry	PC	13j (%)	13a (%)	ArBr (%)
1	PC1	82	2	n.d.
2	PC2	19	57	39
3	PC3	9	63	16
4	PC4	25	53	55
5	PC5	30	41	33
6	PC6	1	85	52

Table S19. Screening of the base.

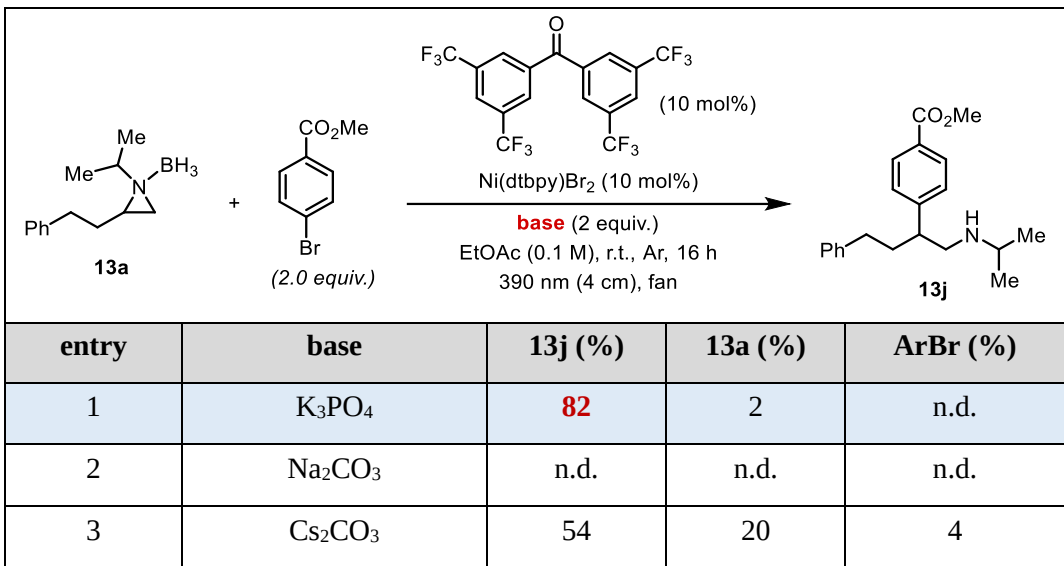


Table S20. Screening of the solvent.

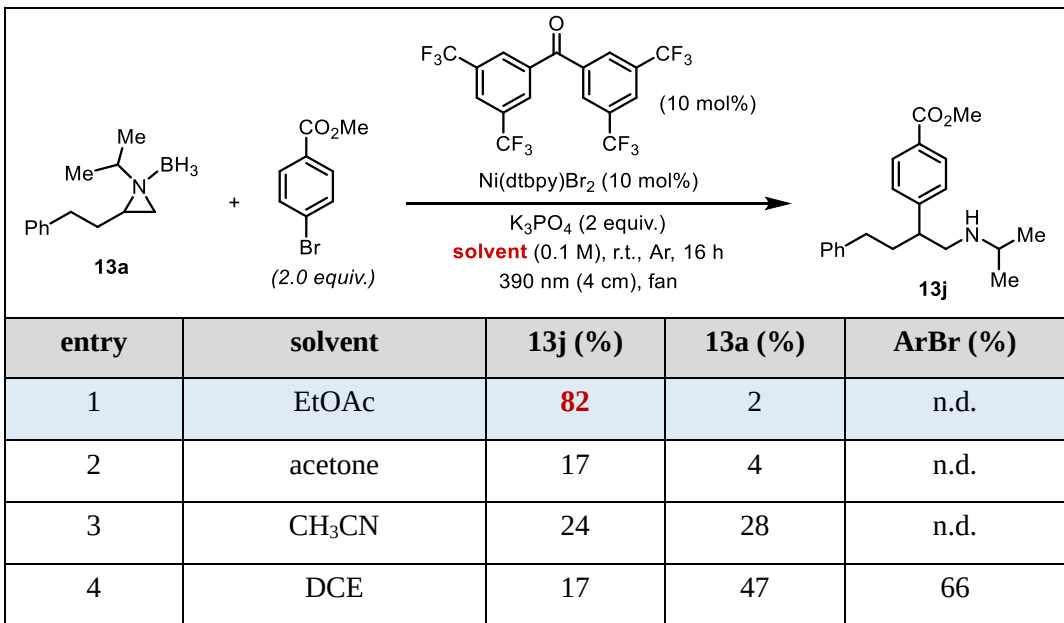


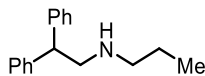
Table S21. Screening of the amount aryl bromide, photocatalyst, nickel catalyst, base and solvent concentration.

entry	ArBr (equiv.)	x	y	z (equiv.)	c	13j (%)	13a (%)	ArBr (%)
1	2.0	5%	10%	2.0	0.1 M	66	15	4
2	2.0	10%	10%	2.0	0.1 M	82	2	n.d.
3	2.0	15%	10%	2.0	0.1 M	69	1	1
4	2.0	20%	10%	2.0	0.1 M	66	13	n.d.
5	2.0	10%	5%	2.0	0.1 M	72	3	n.d.
6	2.0	10%	15%	2.0	0.1 M	54	3	n.d.
7	1.2	10%	10%	2.0	0.1 M	49	21	n.d.
8	1.5	10%	10%	2.0	0.1 M	70	12	n.d.
9	2.5	10%	10%	2.0	0.1 M	84	4	26
10	2.0	10%	10%	1.0	0.1 M	43	32	66
11	2.0	10%	10%	1.5	0.1 M	69	4	10
12	2.0	10%	10%	2.5	0.1 M	73	4	n.d.
13	2.0	10%	10%	1.0	0.2 M	72	5	5

5 Substrate scope

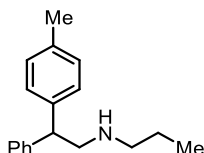
5.1 Ring-Opening–Arylation

N-(2,2-Diphenylethyl)propan-1-amine (**1b**)



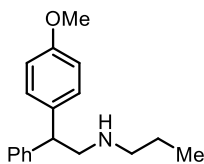
Following **GP5a**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **1b** (61%) as an oil. R_f 0.15 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.31 (4H, t, $J = 7.5$ Hz), 7.28 (4H, d, $J = 6.8$ Hz), 7.21 (2H, t, $J = 7.1$ Hz), 4.23 (1H, t, $J = 7.7$ Hz), 3.25 (2H, d, $J = 7.7$ Hz), 2.62 (2H, t, $J = 7.3$ Hz), 1.46 (2H, sx, $J = 7.3$ Hz), 1.34 (NH, br s), 0.86 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 143.0, 128.7, 128.1, 126.6, 54.5, 51.8, 51.2, 23.0, 11.8. Data in accordance with the literature.¹⁷

N-(2-Phenyl-2-(*p*-tolyl)ethyl)propan-1-amine (**1c**)



Following **GP5a**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and *p*-tolylboronic acid (41 mg, 0.3 mmol, 3.0 equiv.) gave **1c** (73%) as an oil. R_f 0.2 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.29 (2H, t, $J = 7.5$ Hz), 7.25 (2H, dd, $J = 7.2, 1.3$ Hz), 7.21 – 7.17 (1H, tt, $J = 7.2, 1.5$ Hz), 7.15 (2H, d, $J = 8.1$ Hz), 7.11 (2H, d, $J = 7.9$ Hz), 4.17 (1H, t, $J = 7.7$ Hz), 3.21 (2H, d, $J = 7.7$ Hz), 2.63 – 2.57 (2H, m), 2.31 (3H, s), 1.45 (2H, sx, $J = 7.4$ Hz), 0.85 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 143.4, 140.1, 136.2, 129.5, 128.7, 128.1, 128.0, 126.6, 54.7, 51.9, 50.9, 23.2, 21.1, 11.9; HRMS (ESI) found MH^+ 254.1904, $\text{C}_{18}\text{H}_{24}\text{N}$ requires 254.1903.

N-(2-(4-Methoxyphenyl)-2-phenylethyl)propan-1-amine (**1d/3b**)

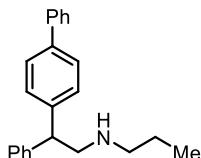


Following **GP5b**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and (4-methoxyphenyl)boronic acid (61 mg, 0.4 mmol, 4.0 equiv.) gave **1d** (50%) as an oil. R_f 0.13 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.29 (2H, t, $J = 7.7$ Hz), 7.25 – 7.22 (2H, d, $J = 7.8$ Hz), 7.22 – 7.19 (1H, t, $J = 7.3$ Hz), 7.17 (2H, d, $J = 8.8$ Hz), 6.85 (2H, d, $J = 8.7$ Hz), 4.17 (1H, t, $J = 7.7$ Hz), 3.78 (3H, s), 3.25 – 3.17 (2H, m), 2.61 (2H, t, $J = 7.3$ Hz), 1.78 (NH, br s), 1.45 (2H, sx, $J = 7.4$ Hz), 0.84 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 158.4, 143.3, 134.9, 129.1,

128.8, 128.0, 126.6, 114.2, 55.4, 54.7, 51.8, 50.3, 23.0, 11.8; HRMS (ESI) found MH^+ 270.1854, $C_{18}H_{24}NO$ requires 270.1852.

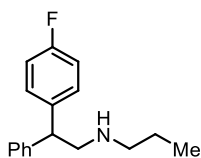
Following **GP5a**, but running the reaction for 5 h, *trans*-aziridine **3a'** (21 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **3b** (33%) as an oil.

***N*-(2-([1,1'-Biphenyl]-4-yl)-2-phenylethyl)propan-1-amine (1e)**



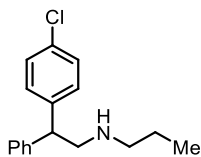
Following **GP5b**, but running the reaction for 6 h, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol) and [1,1'-biphenyl]-4-ylboronic acid (79 mg, 0.4 mmol, 4.0 equiv.) gave **1e** (41%) as a yellow solid. R_f 0.28 [EtOAc]. 1H NMR (600 MHz, $CDCl_3$) δ 7.57 (2H, d, J = 8.3 Hz), 7.54 (2H, d, J = 8.2 Hz), 7.42 (2H, t, J = 7.8 Hz), 7.36 – 7.28 (7H, m), 7.23 (1H, tt, J = 7.8, 1.8 Hz), 4.27 (1H, t, J = 7.7 Hz), 3.29 (2H, d, J = 7.7 Hz), 2.69 – 2.59 (2H, t, J = 7.4 Hz), 1.79 (NH, br s), 1.48 (2H, sx, J = 7.4 Hz), 0.86 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 142.1, 141.0, 139.6, 128.9, 128.9, 128.5, 128.2, 127.5, 127.3, 127.1, 126.8, 54.6, 51.9, 50.9, 23.0, 11.8; HRMS (ESI) found MH^+ 316.2054, $C_{23}H_{26}N$ requires 316.2060.

***N*-(2-(4-Fluorophenyl)-2-phenylethyl)propan-1-amine (1f)**



Following **GP5d**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol) and (4-fluorophenyl)boronic acid (56 mg, 0.4 mmol, 4.0 equiv.) gave **1f** (61%) as an oil. R_f 0.37 [EtOAc]. 1H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.28 (2H, m), 7.25 – 7.18 (5H, m), 7.01 – 6.95 (2H, m), 4.18 (1H, t, J = 7.6 Hz), 3.26 – 3.15 (2H, m), 2.60 (2H, t, J = 7.3 Hz), 1.45 (3H, sx, J = 7.3 Hz), 0.85 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7 (d, J = 244.5 Hz), 142.9, 138.9 (d, J = 3.4 Hz), 129.57 (d, J = 7.9 Hz), 128.9, 128.1, 126.8, 115.6 (d, J = 21.2 Hz), 54.7, 51.9, 50.5, 23.1, 11.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.61 – -116.69 (m). HRMS (ESI) found MH^+ 258.1646, $C_{17}H_{21}FN$ requires 258.1653.

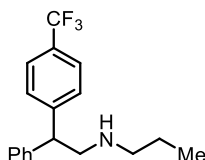
***N*-(2-(4-Chlorophenyl)-2-phenylethyl)propan-1-amine (1g/5b)**



Following **GP5d**, but adding NaHCO₃ (17 mg, 0.2 mmol, 2 equiv.), *trans*-aziridine borane **1a** (18 mg, 0.1 mmol) and (4-chlorophenyl)boronic acid (63 mg, 0.4 mmol, 4.0 equiv.) gave **1g** (59%) as an oil. *R*_f 0.48 [EtOAc]. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.13 (9H, m), 4.19 (1H, t, *J* = 7.6 Hz), 3.33 – 3.10 (2H, m), 2.61 (2H, t, *J* = 7.1 Hz), 1.46 (2H, sx, *J* = 6.9 Hz), 0.86 (3H, t, *J* = 7.3 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 142.6, 141.7, 132.4, 129.5, 128.9, 128.1, 126.9, 54.5, 51.9, 50.7, 23.1, 11.8; HRMS (ESI) found *MH*⁺ 274.1363, C₁₇H₂₁NCl requires 274.1357.

Following **GP5a**, **5a** (42 mg, 0.2 mmol, 1.0 equiv.) and phenylboronic acid (73 mg, 0.6 mmol, 3.0 equiv.) gave **5b** (65%) as an oil.

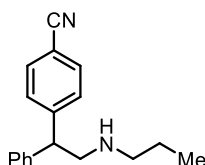
***N*-(2-Phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)propan-1-amine (1h/6b)**



Following **GP5c**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and (4-(trifluoromethyl)phenyl)boronic acid (76 mg, 0.4 mmol, 4.0 equiv.) gave **1h** (41%) as an oil. *R*_f 0.16 [EtOAc]. ¹H NMR (600 MHz, CDCl₃) δ 7.55 (2H, d, *J* = 8.0 Hz), 7.38 (2H, d, *J* = 8.0 Hz), 7.32 (2H, dd, *J* = 8.4, 6.9 Hz), 7.26 – 7.21 (3H, m), 4.27 (1H, t, *J* = 7.6 Hz), 3.31 – 3.22 (2H, m), 2.62 (2H, t, *J* = 7.3 Hz), 1.49 – 1.38 (3H, m), 0.86 (3H, t, *J* = 7.4 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 147.3, 142.0, 128.99, 128.96 (q, *J*_{C-F} = 32.5 Hz), 128.5, 128.1, 127.1, 125.7 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.8 Hz), 54.3, 51.9, 51.2, 23.1, 11.8; ¹⁹F NMR (565 MHz, CDCl₃) δ –62.4; HRMS (ESI) found *MH*⁺ 308.1621, C₁₈H₂₁F₃N requires 308.1621.

Following **GP5a**, but running the reaction for 6 h, *trans*-aziridine **6a'** (24 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **6b** (51%) as an oil.

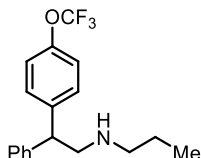
4-(1-Phenyl-2-(propylamino)ethyl)benzonitrile (1i)



Following **GP5c**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and (4-cyanophenyl)boronic acid (60 mg, 0.4 mmol, 4.0 equiv.) gave **1i** (38%) as an oil. *R*_f 0.25 [EtOAc]. ¹H NMR (600 MHz, CDCl₃) δ 7.60 – 7.55 (2H, m), 7.39 – 7.35 (2H, m), 7.34 – 7.30 (2H, m),

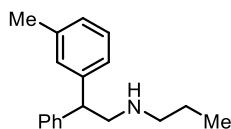
7.26 – 7.20 (3H, m), 4.24 (1H, t, $J = 7.5$ Hz), 3.29 – 3.17 (2H, m), 2.64 – 2.57 (2H, m), 1.53 (NH, br s), 1.45 (2H, sx, $J = 7.4$ Hz), 0.85 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 148.9, 141.5, 132.5, 129.1, 129.0, 128.1, 127.2, 119.0, 110.5, 54.1, 51.9, 51.5, 23.1, 11.8; HRMS (ESI) found MH^+ 265.1692, $\text{C}_{18}\text{H}_{21}\text{N}_2$ requires 265.1699.

***N*-(2-Phenyl-2-(4-(trifluoromethoxy)phenyl)ethyl)propan-1-amine (1j)**



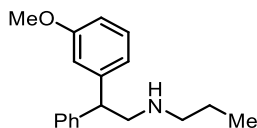
Following **GP5c**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and (4-(trifluoromethoxy)phenyl)boronic acid (82 mg, 0.4 mmol, 4.0 equiv.) gave **1j** (52%) as an oil. R_f 0.35 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.27 – 7.21 (2H, m), 7.21 – 7.17 (2H, m), 7.17 – 7.13 (3H, m), 7.08 – 7.04 (2H, m), 4.14 (1H, t, $J = 7.6$ Hz), 3.21 – 3.11 (2H, m), 2.57 – 2.52 (2H, m), 1.61 (NH, br s), 1.38 (2H, sx, $J = 7.4$ Hz), 0.76 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 148.0, 142.2, 141.8, 129.4, 129.0, 128.1, 127.0, 121.2, 120.6 (q, $J = 256.9$ Hz), 54.4, 51.8, 50.5, 22.9, 11.7; ^{19}F (565 MHz, CDCl_3) δ –57.88; HRMS (EI) found MH^+ 324.1571, $\text{C}_{18}\text{H}_{21}\text{F}_3\text{NO}$ requires 324.1570.

***N*-(2-Phenyl-2-(*m*-tolyl)ethyl)propan-1-amine (1k)**



Following **GP5a**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and *m*-tolylboronic acid (41 mg, 0.3 mmol, 3.0 equiv.) gave **1k** (48%) as an oil. R_f 0.15 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.34 – 7.30 (2H, m), 7.30 – 7.27 (2H, m), 7.24 – 7.19 (2H, m), 7.11 – 7.07 (2H, m), 7.04 (1H, d, $J = 7.5$ Hz), 4.20 (1H, t, $J = 7.7$ Hz), 3.25 (2H, d, $J = 7.7$ Hz), 2.63 (2H, t, $J = 7.3$ Hz), 2.34 (3H, s), 1.53 – 1.43 (3H, m), 0.87 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 143.2, 143.0, 138.3, 129.0, 128.7, 128.6, 128.1, 127.5, 126.6, 125.0, 54.6, 51.9, 51.2, 23.1, 21.6, 11.8; HRMS (EI) found MH^+ 254.1905, $\text{C}_{18}\text{H}_{24}\text{N}$ requires 254.1903.

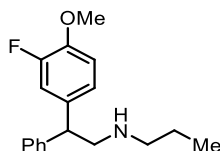
***N*-(2-(3-methoxyphenyl)-2-phenylethyl)propan-1-amine (1l)**



Following **GP5b**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and (3-methoxyphenyl)boronic acid (61 mg, 0.4 mmol, 4.0 equiv.) gave **1l** (51%) as an oil. R_f 0.26

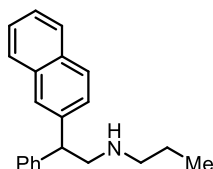
[EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.16 (6H, m), 6.84 (1H, d, J = 7.7 Hz), 6.79 (1H, t, J = 2.2 Hz), 6.73 (1H, dd, J = 8.0, 2.6 Hz), 4.17 (1H, t, J = 7.7 Hz), 3.76 (3H, s), 3.21 (2H, d, J = 7.7 Hz), 2.59 (2H, t, J = 7.3 Hz), 1.58 (NH, br s), 1.44 (2H, sx, J = 7.3 Hz), 0.83 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 159.9, 144.6, 142.9, 129.7, 128.8, 128.1, 126.7, 120.5, 114.3, 111.7, 55.3, 54.6, 51.9, 51.3, 23.1, 11.8. HRMS (ESI) found MH^+ 270.1849, $\text{C}_{18}\text{H}_{24}\text{NO}$ requires 270.1852.

***N*-(2-(3-fluoro-4-methoxyphenyl)-2-phenylethyl)propan-1-amine (1m)**



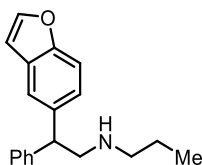
Following **GP5b**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and (3-fluoro-4-methoxyphenyl)boronic acid (68 mg, 0.4 mmol, 4.0 equiv.) gave **1m** (40%) as an oil. R_f 0.35 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.31 (2H, t, J = 7.5 Hz), 7.25 – 7.19 (3H, m), 7.01 – 6.94 (2H, m), 6.92 – 6.86 (1H, m), 4.13 (1H, t, J = 7.6 Hz), 3.85 (3H, s), 3.22 – 3.14 (2H, m), 2.60 (2H, t, J = 7.3 Hz), 1.45 (2H, sx, J = 7.3 Hz), 1.37 (NH, br s), 0.85 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 152.6 (d, J = 245.8 Hz), 146.3 (d, J = 10.9 Hz), 142.8, 136.4 (d, J = 5.8 Hz), 128.9, 128.0, 126.8, 123.7 (d, J = 3.4 Hz), 115.8 (d, J = 18.4 Hz), 113.7 (d, J = 2.3 Hz), 56.5, 54.6, 51.9, 50.4, 23.1, 11.8; ^{19}F NMR (CDCl_3 , 565 MHz) δ –134.80 (dd, J = 12.5, 8.7 Hz). HRMS (ESI) found MH^+ 288.1753, $\text{C}_{18}\text{H}_{23}\text{FNO}$ requires 288.1758.

***N*-(2-(Naphthalen-2-yl)-2-phenylethyl)propan-1-amine (1n)**



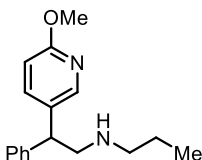
Following **GP5b**, but adding NaHCO_3 (17 mg, 0.2 mmol, 2.0 equiv.), *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and naphthalen-2-ylboronic acid (69 mg, 0.4 mmol, 4.0 equiv.) gave **1n** (34%) as a solid. R_f 0.13 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.83 – 7.75 (3H, m), 7.73 (1H, d, J = 1.8 Hz), 7.48 – 7.41 (2H, m), 7.37 (1H, dd, J = 8.5, 1.8 Hz), 7.32 – 7.29 (4H, m), 7.24 – 7.20 (1H, m), 4.39 (1H, t, J = 7.6 Hz), 3.43 – 3.31 (2H, m), 2.66 (2H, t, J = 7.3 Hz), 1.84 (NH, br s), 1.47 (2H, sx, J = 7.4 Hz), 0.85 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 142.8, 140.3, 133.7, 132.5, 128.8, 128.5, 128.3, 127.9, 127.7, 126.8, 126.8, 126.4, 126.2, 125.8, 54.4, 51.9, 51.2, 23.0, 11.8; HRMS (ESI) found MH^+ 290.1913, $\text{C}_{21}\text{H}_{24}\text{N}$ requires 290.1903.

***N*-(2-(Benzofuran-5-yl)-2-phenylethyl)propan-1-amine (1o)**



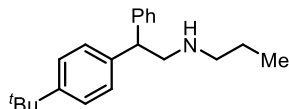
Following **GP5b**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and benzofuran-5-ylboronic acid (49 mg, 0.3 mmol, 3.0 equiv.) gave **1o** (38%) as an oil. R_f 0.25 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.59 (1H, d, J = 2.2 Hz), 7.49 (1H, d, J = 1.8 Hz), 7.43 (1H, d, J = 8.5 Hz), 7.32 – 7.27 (4H, m), 7.23 – 7.17 (2H, m), 6.72 (1H, d, J = 2.2 Hz), 4.32 (1H, t, J = 7.7 Hz), 3.29 (2H, d, J = 7.7 Hz), 2.63 (2H, t, J = 7.3 Hz), 1.46 (2H, sx, J = 7.3 Hz), 0.84 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 154.0, 145.5, 143.4, 137.6, 128.8, 128.1, 127.9, 126.6, 124.7, 120.4, 111.6, 106.7, 54.9, 51.9, 51.0, 23.0, 11.8; HRMS (ESI) found MH^+ 280.1697, $\text{C}_{19}\text{H}_{22}\text{NO}$ requires 280.1696.

***N*-(2-(6-Methoxypyridin-3-yl)-2-phenylethyl)propan-1-amine (1p)**



Following **GP5c**, but running the reaction for 6 h, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and (6-methoxypyridin-3-yl)boronic acid (61 mg, 0.4 mmol, 4.0 equiv.) gave **1p** (38%) as an oil. R_f 0.2 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 8.09 (1H, d, J = 2.5 Hz), 7.43 (1H, dd, J = 8.6, 2.5 Hz), 7.31 (2H, t, J = 7.6 Hz), 7.25 – 7.19 (3H, m), 6.68 (1H, d, J = 8.6 Hz), 4.14 (1H, t, J = 7.6 Hz), 3.91 (3H, s), 3.25 – 3.14 (2H, m), 2.60 (2H, t, J = 7.3 Hz), 1.48 – 1.40 (2H, m), 0.85 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 163.2, 146.1, 142.5, 138.5, 131.3, 128.9, 128.0, 126.9, 111.0, 54.4, 53.5, 51.9, 48.2, 23.2, 11.8. HRMS (ESI) found MH^+ 271.1808, $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}$ requires 271.1805.

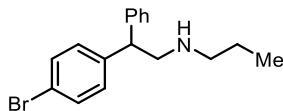
***N*-(2-(4-(*tert*-Butyl)phenyl)-2-phenylethyl)propan-1-amine (2b)**



Following **GP5a**, *trans*-aziridine borane **2a'** (23 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **2b** (54%) as an oil. R_f 0.13 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.35 – 7.27 (6H, m), 7.24 – 7.18 (3H, m), 4.20 (1H, t, J = 7.7 Hz), 3.24 (2H, d, J = 7.7 Hz), 2.65 – 2.60 (2H, t, J = 7.3 Hz), 1.47 (2H, sx, J = 7.4 Hz), 1.31 (9H, s), 0.87 (3H, t, J = 7.4

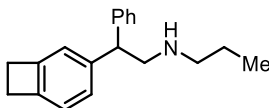
Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 149.3, 143.4, 140.1, 128.7, 128.2, 127.7, 126.6, 125.6, 54.8, 52.0, 50.9, 34.5, 31.5, 23.2, 11.9; HRMS (ESI) found MH^+ 296.2382, $\text{C}_{21}\text{H}_{30}\text{N}$ requires 296.2373.

***N*-(2-(4-Bromophenyl)-2-phenylethyl)propan-1-amine (4b)**



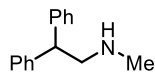
Following **GP5a**, *trans*-aziridine borane **4a** (51 mg, 0.2 mmol, 1.0 equiv.) and phenylboronic acid (73 mg, 0.6 mmol, 3.0 equiv.) gave **4b** (56%) as an oil. R_f 0.48 [EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.38 (2H, m), 7.35 – 7.27 (2H, m), 7.27 – 7.18 (3H, m), 7.18 – 7.09 (2H, m), 4.17 (1H, t, J = 7.6 Hz), 3.28 – 3.14 (2H, m), 2.61 (2H, t, J = 7.3 Hz), 1.45 (2H, sx, J = 7.4 Hz), 0.85 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 142.5, 142.2, 131.8, 129.9, 128.9, 128.0, 126.9, 120.5, 54.4, 51.9, 50.7, 23.1, 11.8; HRMS (ESI) found MH^+ 318.0860, $\text{C}_{17}\text{H}_{21}\text{NBr}$ requires 318.0852.

***N*-(2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-2-phenylethyl)propan-1-amine (7b)**



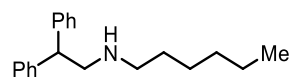
Following **GP5a**, but running the reaction for 5 h, *trans*-aziridine borane **7a** (20 mg, 0.1 mmol) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **7b** (50%) as an oil. R_f 0.30 [EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.24 (4H, m), 7.24 – 7.15 (1H, m), 7.11 (1H, dd, J = 7.5, 1.6 Hz), 7.02 – 6.94 (2H, m), 4.19 (1H, t, J = 7.7 Hz), 3.23 (2H, dd, J = 7.7, 1.6 Hz), 3.13 (4H, s), 2.62 (2H, t, J = 7.3 Hz), 1.47 (2H, sx, J = 7.4 Hz), 0.86 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 146.2, 144.1, 143.6, 141.8, 128.7, 128.1, 126.8, 126.5, 122.8, 122.3, 54.8, 51.9, 51.8, 29.5, 29.4, 23.1, 11.9; HRMS (ESI) found MH^+ 266.1894, $\text{C}_{19}\text{H}_{24}\text{N}$ requires 266.1903.

***N*-Methyl-2,2-diphenylethan-1-amine (8b)**



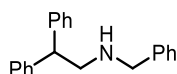
Following **GP5a**, but running the reaction for 5 h, *trans*-aziridine borane **8a** (15 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **8b** (56%) as an oil. R_f 0.27 [CH_2Cl_2 :MeOH (10:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.33 – 7.27 (8H, m), 7.24 – 7.19 (2H, m), 4.50 (1H, t, J = 7.8 Hz), 3.42 (2H, d, J = 7.8 Hz), 2.43 (3H, s); ^{13}C NMR (151 MHz, CDCl_3) δ 141.1, 129.1, 128.1, 127.4, 54.6, 49.1, 34.8. Data in accordance with the literature.¹⁸

***N*-(2,2-Diphenylethyl)hexan-1-amine (9b)**



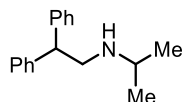
Following **GP5a**, but running the reaction for 6 h, *trans*-aziridine borane **9a'** (22 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **9b** (51%) as an oil. R_f 0.35 [EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.19 (10H, m), 4.23 (1H, t, $J = 7.7$ Hz), 3.26 (2H, d, $J = 7.7$ Hz), 2.65 (2H, t, $J = 7.3$ Hz), 1.62 (NH, br s), 1.48 – 1.39 (2H, m), 1.31 – 1.20 (6H, m), 0.88 (3H, t, $J = 6.8$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 143.1, 128.8, 128.2, 126.7, 54.7, 51.3, 50.0, 31.8, 30.0, 27.1, 22.7, 14.2; HRMS (ESI) found MH^+ 282.2216, $\text{C}_{20}\text{H}_{28}\text{N}$ requires 282.2216.

***N*-Benzyl-2,2-diphenylethan-1-amine (10b)**



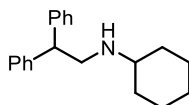
Following **GP5a**, but running the reaction for 5 h, *trans*-aziridine borane **10a'** (22 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **10b** (47%) as an oil. R_f 0.56 [EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.20 (15H, m), 4.25 (1H, t, $J = 7.7$ Hz), 3.85 (2H, s), 3.27 (2H, d, $J = 7.6$ Hz), 1.47 (NH, br s); ^{13}C NMR (101 MHz, CDCl_3) δ 143.0, 140.3, 128.7, 128.5, 128.2, 128.2, 127.1, 126.7, 54.0, 53.9, 51.4; HRMS (ESI) found MH^+ 288.1748, $\text{C}_{21}\text{H}_{22}\text{N}$ requires 288.1747. Data in accordance with the literature.¹⁹

***N*-(2,2-Diphenylethyl)propan-2-amine (11b)**



Following **GP5a**, but running the reaction for 3 h, *cis*-aziridine borane **11a** (18 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **11b** (57%) as an oil. R_f 0.28 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.22 (4H, t, $J = 7.5$ Hz), 7.18 (4H, d, $J = 7.2$ Hz), 7.13 (2H, t, $J = 7.1$), 4.11 (1H, t, $J = 7.7$ Hz), 3.16 (2H, dd, $J = 7.7$), 2.77 (1H, hp, $J = 6.3$), 0.95 (6H, d, $J = 6.2$); ^{13}C NMR (151 MHz, CDCl_3) δ 143.0, 128.8, 128.1, 126.7, 52.2, 51.4, 48.8, 22.9; HRMS (ESI) found MH^+ 240.1748, $\text{C}_{17}\text{H}_{22}\text{N}$ requires 240.1747.

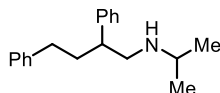
***N*-(2,2-Diphenylethyl)cyclohexanamine (12b)**



Following **GP5a**, *trans*-aziridine borane **12a'** (22 mg, 0.1 mmol, 1.0 equiv.) and phenylboronic acid (37 mg, 0.3 mmol, 3.0 equiv.) gave **12b** (50%) as a solid. R_f 0.58 [EtOAc]. ^1H NMR (600

MHz, CDCl₃) δ 7.30 (4H, t, J = 7.5 Hz), 7.28 – 7.25 (4H, m), 7.23 – 7.17 (2H, m), 4.18 (1H, t, J = 7.7 Hz), 3.26 (2H, d, J = 7.7 Hz), 2.45 (1H, tt, J = 10.5, 3.8 Hz), 1.83 (2H, dd, J = 12.5, 3.8 Hz), 1.69 (2H, dp, J = 10.9, 3.7 Hz), 1.63 – 1.56 (1H, m), 1.29 – 1.18 (3H, m), 1.14 (1H, tt, J = 12.4, 3.5 Hz), 1.03 (2H, tdd, J = 12.7, 10.7, 3.5 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 143.2, 128.7, 128.2, 126.6, 57.0, 51.8, 51.5, 33.6, 26.3, 25.2; HRMS (ESI) found MH⁺ 280.2059, C₂₀H₂₆N requires 280.2060.

***N*-Isopropyl-2,4-diphenylbutan-1-amine (13b)**

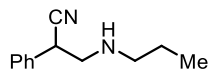


Following **GP5a**, but using Cu(CH₃CN)₄PF₆ (5 mol%) and bathophen (6 mol%) as the ligand, CH₃CN:PhF = 7:3 (0.1 M) as the solvent mixture and react at room temperature for 1.5 h, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) gave **13b** (37%) as an oil. R_f 0.19 [EtOAc]. ¹H NMR (600 MHz, CDCl₃) δ 7.30 – 7.24 (2H, m), 7.20 – 7.12 (5H, m), 7.11 – 7.05 (1H, m), 7.05 – 7.01 (2H, m), 2.81 (1H, dd, J = 10.6, 4.7 Hz), 2.76 – 2.66 (2H, m), 2.62 (1H, hp, J = 6.2 Hz), 2.46 – 2.34 (2H, m), 1.93 (1H, dddd, J = 13.5, 9.7, 7.0, 4.7 Hz), 1.82 (1H, dtd, J = 13.5, 9.4, 5.7 Hz), 0.91 (3H, d, J = 6.3 Hz), 0.87 (3H, d, J = 6.3 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 143.7, 142.5, 128.8, 128.5, 128.4, 128.0, 126.7, 125.8, 53.6, 48.7, 45.9, 36.6, 33.8, 23.1, 22.9; HRMS (ESI) found MH⁺ 268.2055, C₁₉H₂₆N requires 268.2060.

Following **GP8a**, *trans*-aziridine **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and bromobenzene (31 mg, 0.2 mmol, 2.0 equiv.) gave **13b** (54%) as an oil.

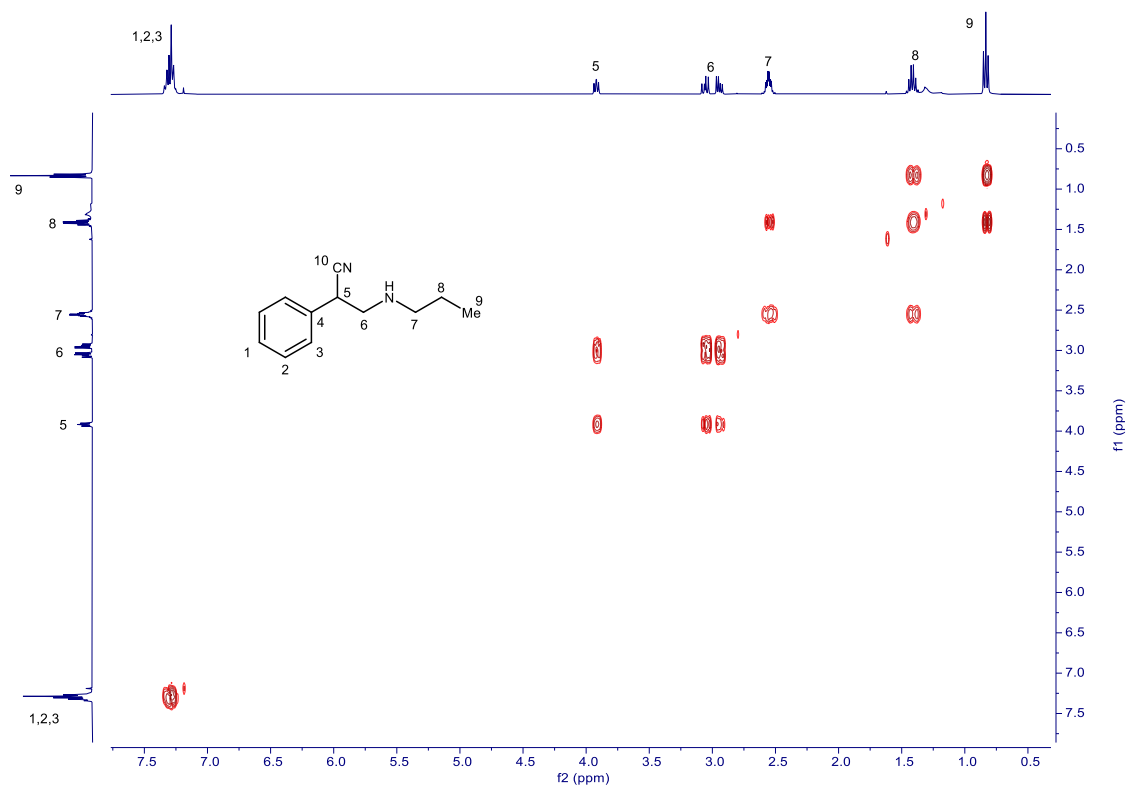
5.2 Ring-Opening–Cyanation

2-Phenyl-3-(propylamino)propanenitrile (**1q**)

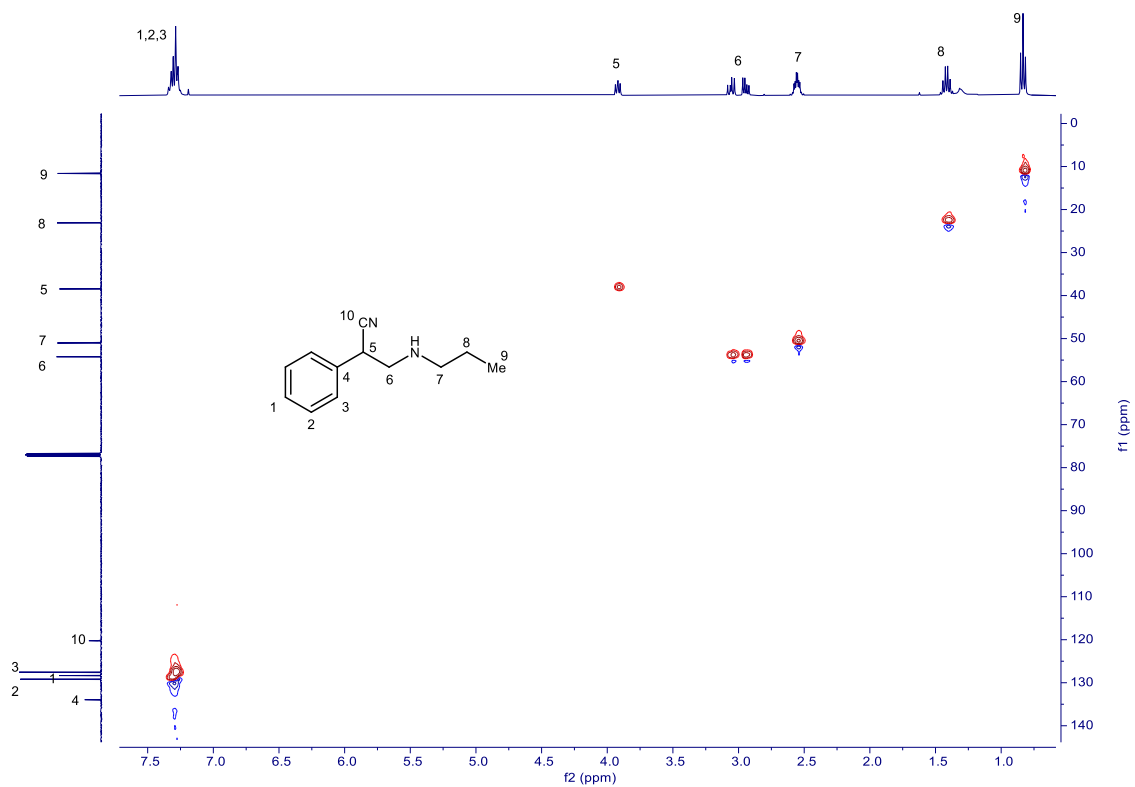


Following **GP6**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) gave **1q** (65%) as a yellow oil. R_f 0.56 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.39 (2H, d, $J = 7.4$ Hz), 7.36 – 7.31 (3H, m), 3.98 (1H, dd, $J = 8.1, 6.3$ Hz), 3.12 (1H, dd, $J = 12.4, 8.1$ Hz), 3.01 (1H, dd, $J = 12.4, 6.3$ Hz), 2.67 – 2.57 (2H, m), 1.48 (2H, sx, $J = 7.3$ Hz), 1.20 (NH, br s), 0.90 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (151 MHz, CDCl_3) δ 134.0, 129.3, 128.4, 127.6, 120.3, 54.3, 51.1, 38.6, 23.2, 11.7; HRMS (ESI) found MH^+ 189.1387, $\text{C}_{12}\text{H}_{17}\text{N}_2$ requires 189.1386.

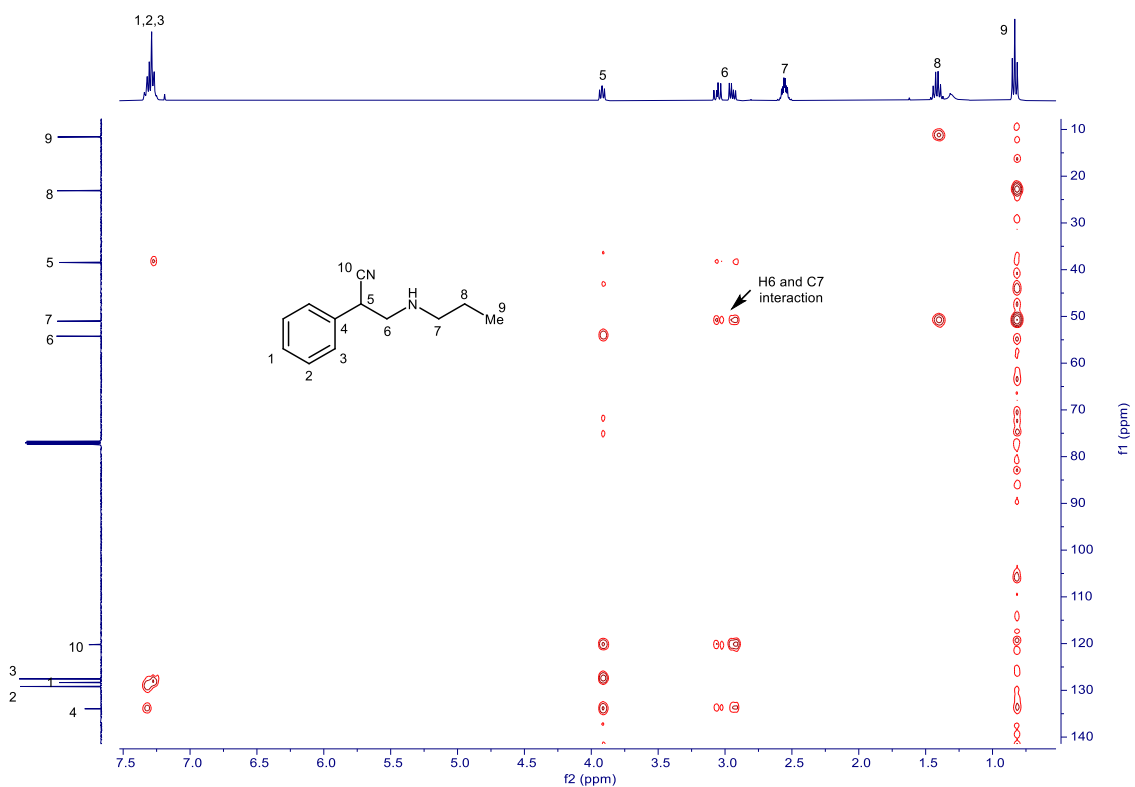
The structure of **1q** was further confirmed by 2D NMR spectroscopy (COSY, HSQC, and HMBC), which also established the regioselectivity of the reaction.



COSY NMR spectrum (600 MHz, CDCl_3 , at rt) of **1q**

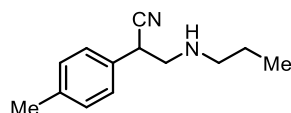


HSQC NMR spectrum (600 MHz, CDCl₃, at rt) of **1q**



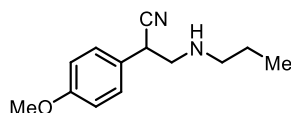
HMBC NMR spectrum (600 MHz, CDCl₃, at rt) of **1q**

3-(Propylamino)-2-(*p*-tolyl)propanenitrile (**14b**)



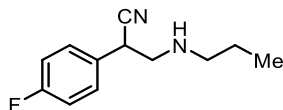
Following **GP6**, *trans*-aziridine borane **14a** (19 mg, 0.1 mmol, 1.0 equiv.) gave **14b** (64%) as a yellow oil. R_f 0.23 [*n*-pentane:EtOAc (8:2)]. ^1H NMR (600 MHz, CDCl_3) δ 7.23 (2H, d, J = 8.1 Hz), 7.19 (2H, d, J = 8.1 Hz), 3.95 (1H, dd, J = 8.1, 6.4 Hz), 3.15 – 3.06 (1H, m), 3.04 – 2.95 (1H, m), 2.68 – 2.56 (2H, m), 2.35 (3H, s), 1.48 (2H, sx, J = 7.4 Hz), 0.90 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 138.3, 131.0, 130.0, 127.5, 120.5, 54.4, 51.1, 38.1, 23.2, 21.2, 11.8; HRMS (ESI) found MH^+ 203.1548, $\text{C}_{13}\text{H}_{19}\text{N}_2$ requires 203.1543.

2-(4-Methoxyphenyl)-3-(propylamino)propanenitrile (**3c**)



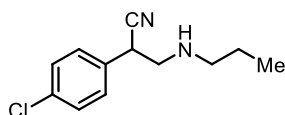
Following **GP6**, *trans*-aziridine borane **3a'** (21 mg, 0.1 mmol, 1.0 equiv.) gave **3c** (55%) as an oil. R_f 0.31 [*n*-pentane:EtOAc (1:1)]. ^1H (400 MHz, CDCl_3) δ 7.26 (2H, d, J = 8.4 Hz), 6.91 (2H, d, J = 8.7 Hz), 3.93 (1H, dd, J = 8.0, 6.5 Hz), 3.81 (3H, s), 3.09 (1H, dd, J = 12.3, 8.0 Hz), 2.97 (1H, dd, J = 12.3, 6.5 Hz), 2.69 – 2.54 (2H, m), 1.47 (2H, sx, J = 7.3 Hz), 1.38 (NH, br s), 0.90 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 159.7, 128.8, 126.0, 120.6, 114.7, 55.5, 54.4, 51.2, 37.7, 23.3, 11.8; HRMS (ESI): found MH^+ 219.1490, $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}$ requires 219.1492.

2-(4-Fluorophenyl)-3-(propylamino)propanenitrile (**15b**)



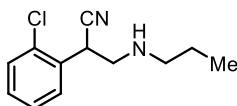
Following **GP6**, *cis*-aziridine borane **15a** and *trans*-aziridine borane **15a'** (Ratio 13:87, 19 mg, 0.1 mmol, 1.0 equiv.) gave **15b** (62%) as a yellow oil. R_f 0.43 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.33 (2H, dd, J = 8.7, 5.1 Hz), 7.08 (2H, t, J = 8.6 Hz), 3.96 (1H, dd, J = 8.0, 6.3 Hz), 3.15 – 3.05 (1H, m), 3.04 – 2.96 (1H, m), 2.67 – 2.56 (2H, m), 1.48 (2H, sx, J = 7.3 Hz), 0.90 (3H, t, J = 7.3 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 162.7 (d, J = 247.3 Hz), 129.9 (d, J = 3.7 Hz), 129.4 (d, J = 8.4 Hz), 120.2, 116.3 (d, J = 21.5 Hz), 54.3, 51.2, 37.9, 23.2, 11.7; ^{19}F NMR (564 MHz, CDCl_3) δ -113.44 (tt, J = 8.2, 5.0 Hz); HRMS (ESI) found MH^+ 207.1300, $\text{C}_{12}\text{H}_{16}\text{N}_2\text{F}$ requires 207.1292.

2-(4-Chlorophenyl)-3-(propylamino)propanenitrile (**5c**)



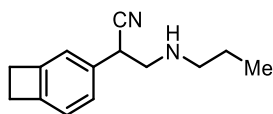
Following **GP6**, but running the reaction for 3 h, *trans*-aziridine borane **5a** (21 mg, 0.1 mmol, 1.0 equiv.) gave **5c** (47%, 9% rsm) as a yellow oil. R_f 0.23 [*n*-pentane:EtOAc (8:2)]. ^1H NMR (600 MHz, CDCl_3) δ 7.37 (2H, d, $J = 8.5$ Hz), 7.29 (2H, d, $J = 8.5$ Hz), 3.96 (1H, dd, $J = 8.0, 6.3$ Hz), 3.10 (1H, dd, $J = 12.4, 8.0$ Hz), 2.99 (1H, dd, $J = 12.5, 6.3$ Hz), 2.61 (2H, qt, $J = 11.5, 7.1$ Hz), 1.48 (2H, sx, $J = 7.3$ Hz), 0.90 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 134.4, 132.5, 129.3, 128.9, 119.8, 54.1, 51.1, 38.0, 23.1, 11.6; HRMS (ESI) found MH^+ 223.0999, $\text{C}_{12}\text{H}_{16}\text{N}_2\text{Cl}$ requires 223.0997.

2-(2-Chlorophenyl)-3-(propylamino)propanenitrile (**16b**)



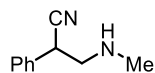
Following **GP6**, *trans*-aziridine borane **16a** (21 mg, 0.1 mmol, 1.0 equiv.) gave **16b** (51%) as a yellow oil. R_f 0.37 [*n*-pentane:EtOAc (8:2)]. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (1H, dd, $J = 7.5, 1.9$ Hz), 7.41 (1H, dd, $J = 7.6, 1.7$ Hz), 7.37 – 7.28 (2H, m), 4.51 (1H, dd, $J = 8.2, 5.6$ Hz), 3.11 – 3.00 (2H, m), 2.72 (1H, dt, $J = 11.4, 7.2$ Hz), 2.62 (1H, dt, $J = 11.4, 7.1$ Hz), 1.51 (2H, sx, $J = 7.3$ Hz), 0.92 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 132.8, 131.8, 130.0, 129.7, 129.3, 127.7, 119.9, 52.4, 50.8, 36.0, 23.2, 11.6; HRMS (ESI) found MH^+ 223.1000, $\text{C}_{12}\text{H}_{16}\text{N}_2\text{Cl}$ requires 223.0997.

2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-3-(propylamino)propanenitrile (**7c**)



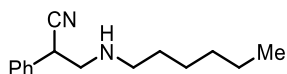
Following **GP6**, but running the reaction for 1 h, *trans*-aziridine borane **7a** (20 mg, 0.1 mmol, 1.0 equiv.) gave **7c** (56%, 13% rsm) as a yellow oil. R_f 0.33 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.17 – 7.13 (1H, m), 7.07 – 7.03 (2H, m), 3.94 (1H, dd, $J = 8.1, 6.5$ Hz), 3.17 (4H, s), 3.10 (1H, dd, $J = 12.3, 8.1$ Hz), 2.98 (1H, dd, $J = 12.3, 6.5$ Hz), 2.67 – 2.57 (2H, m), 1.49 (2H, sx, $J = 7.3$ Hz), 0.91 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 146.9, 146.1, 132.5, 126.4, 123.3, 121.9, 120.7, 54.7, 51.1, 38.9, 29.6, 29.5, 23.2, 11.8; HRMS (ESI) found MH^+ 215.1537, $\text{C}_{14}\text{H}_{19}\text{N}_2$ requires 215.1543.

3-(Methylamino)-2-phenylpropanenitrile (**8c**)



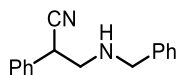
Following **GP6**, *trans*-aziridine borane **8a** (15 mg, 0.1 mmol, 1.0 equiv.) gave **8c** (44%) as a yellow oil. R_f 0.23 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.43 – 7.32 (5H, m), 4.01 (1H, dd, J = 7.9, 6.4 Hz), 3.11 (1H, dd, J = 12.4, 8.0 Hz), 2.99 (1H, dd, J = 12.3, 6.4 Hz), 2.48 (3H, s), 1.33 (NH, br s); ^{13}C NMR (151 MHz, CDCl_3) δ 133.9, 129.3, 128.5, 127.7, 120.23, 56.3, 38.2, 36.0; HRMS (ESI) found MH^+ 161.1071, $\text{C}_{10}\text{H}_{13}\text{N}_2$ requires 161.1073.

3-(Hexylamino)-2-phenylpropanenitrile (**9c**)



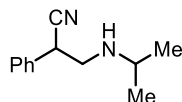
Following **GP6**, *trans*-aziridine borane **9a'** (22 mg, 0.1 mmol, 1.0 equiv.) gave **9c** (56%) as a yellow oil. R_f 0.56 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.43 – 7.30 (5H, m), 3.99 (1H, dd, J = 8.1, 6.4 Hz), 3.13 (1H, dd, J = 12.4, 8.1 Hz), 3.01 (1H, dd, J = 12.4, 6.4 Hz), 2.72 – 2.57 (2H, m), 1.52 (NH, br s), 1.49 – 1.42 (2H, m), 1.31 – 1.23 (6H, m), 0.88 (3H, t, J = 6.7 Hz). ^{13}C NMR (151 MHz, CDCl_3) δ 134.1, 129.3, 128.5, 127.7, 120.4, 54.4, 49.4, 38.6, 31.8, 30.1, 27.0, 22.7, 14.2; HRMS (ESI) found MH^+ 231.1856, $\text{C}_{15}\text{H}_{23}\text{N}_2$ requires 231.1856.

3-(Benzylamino)-2-phenylpropanenitrile (**10c**)



Following **GP6**, *trans*-aziridine borane **10a'** (22 mg, 0.1 mmol, 1.0 equiv.) gave **10c** (63%) as an oil. R_f 0.7 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.11 (10H, m), 3.89 (1H, dd, J = 7.9, 6.3 Hz), 3.76 (2H, s), 3.04 (1H, dd, J = 12.4, 7.9 Hz), 2.95 (1H, dd, J = 12.4, 6.3 Hz), 1.62 (NH, s); ^{13}C NMR (151 MHz, CDCl_3) δ 139.6, 133.9, 129.3, 128.7, 128.5, 128.1, 127.7, 127.4, 120.3, 53.4, 53.3, 38.7; HRMS (ESI) found MH^+ 237.1385, $\text{C}_{16}\text{H}_{17}\text{N}_2$ requires 237.1386.

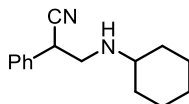
3-(Isopropylamino)-2-phenylpropanenitrile (**11c**)



Following **GP6**, but running the reaction for 2.2 h, *cis*-aziridine borane **11a** (19 mg, 0.1 mmol, 1.0 equiv.) gave **11c** (63%) as an oil. R_f 0.47 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.29 (5H, m), 3.96 (1H, dd, J = 8.2, 6.3 Hz), 3.10 (1H, dd, J = 12.3, 8.3 Hz), 3.01 (1H, dd, J = 12.3, 6.4 Hz), 2.87 (1H, hp, J = 6.3 Hz), 1.51 (NH, br s), 1.05 (6H, d, J = 6.3 Hz); ^{13}C

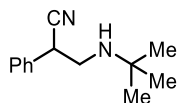
NMR (151 MHz, CDCl₃) δ 134.1, 129.3, 128.5, 127.7, 120.4, 51.9, 48.2, 38.9, 23.1, 22.9; HRMS (ESI) found MH⁺ 189.1386, C₁₂H₁₇N₂ requires 189.1386.

3-(Cyclohexylamino)-2-phenylpropanenitrile (**12c**)



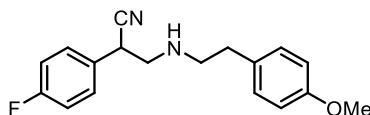
Following **GP6**, but running the reaction for 1.7 h, *trans*-aziridine borane **12a'** (43 mg, 0.2 mmol, 1.0 equiv.) gave **12c** (57%) as an oil. R_f 0.26 [*n*-pentane:EtOAc (3:1)]. ¹H NMR (600 MHz, CDCl₃) δ 7.41 – 7.31 (5H, m), 3.94 (1H, dd, *J* = 8.3, 6.3 Hz), 3.13 (1H, dd, *J* = 12.3, 8.3 Hz), 3.04 (1H, dd, *J* = 12.4, 6.3 Hz), 2.48 (1H, tt, *J* = 10.3, 3.7 Hz), 1.88 – 1.80 (2H, m), 1.75 – 1.69 (2H, m), 1.60 (1H, dt, *J* = 12.7, 3.9 Hz), 1.36 (NH, br s), 1.28 – 1.20 (2H, m), 1.16 (1H, tt, *J* = 12.2, 3.4 Hz), 1.10 – 1.02 (2H, m). ¹³C NMR (151 MHz, CDCl₃) δ 134.2, 129.2, 128.4, 127.7, 120.4, 56.0, 51.5, 39.0, 33.7, 33.5, 26.1, 25.0, 24.9; HRMS (ESI) found MH⁺ 229.1699, C₁₅H₂₁N₂ requires 229.1699.

3-(*tert*-Butylamino)-2-phenylpropanenitrile (**17b**)



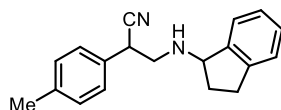
Following **GP6**, but running the reaction for 1.3 h, *trans*-aziridine borane **17a** (20 mg, 0.1 mmol, 1.0 equiv.) gave **17b** (46%) as an oil. R_f 0.55 [*n*-pentane:EtOAc (1:1)]. ¹H NMR (600 MHz, CDCl₃): 7.41 – 7.33 (5H, m), 3.88 (1H, dd, *J* = 8.3, 6.1 Hz), 3.04 (1H, dd, *J* = 11.6, 8.4 Hz), 2.96 (1H, dd, *J* = 11.6, 6.1 Hz), 1.08 (9H, s); ¹³C NMR (151 MHz, CDCl₃): 134.3, 129.2, 128.5, 127.7, 120.5, 50.8, 48.1, 40.1, 29.1; HRMS (ESI) found MH⁺ 203.1534, C₁₃H₁₉N₂ requires 203.1543.

2-(4-Fluorophenyl)-3-((4-methoxyphenethyl)amino)propanenitrile (**18b**)



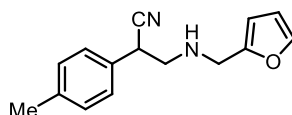
Following **GP6**, *cis*-aziridine borane **18a** and *trans*-aziridine borane **18a'** (Ratio 15:85, 57 mg, 0.2 mmol, 1.0 equiv.) gave **18b** (60%) as yellow oil. R_f 0.25 [*n*-pentane:EtOAc (6:4)]. ¹H NMR (600 MHz, CDCl₃) δ 7.50 – 7.43 (2H, m), 7.30 – 7.21 (4H, m), 7.02 (2H, d, *J* = 8.5 Hz), 4.12 (1H, dd, *J* = 7.6, 6.5 Hz), 3.99 (3H, s), 3.30 (1H, dd, *J* = 12.4, 7.7 Hz), 3.20 (1H, dd, *J* = 12.4, 6.5 Hz), 3.12 – 3.03 (2H, m), 2.91 (2H, t, *J* = 6.6 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 162.6 (d, *J* = 247.8 Hz), 158.3, 131.5, 129.7 (d, *J* = 3.7 Hz), 129.7, 129.4 (d, *J* = 8.3 Hz), 120.1, 116.2 (d, *J* = 22.0 Hz), 114.1, 55.3, 54.1, 50.7, 37.7, 35.4; ¹⁹F NMR (564 MHz, CDCl₃) δ –113.41 (tt, *J* = 8.8, 5.1 Hz); HRMS (ESI) found MH⁺ 299.1549, C₁₈H₂₀FN₂O requires 299.1554.

3-((2,3-Dihydro-1H-inden-1-yl)amino)-2-(*p*-tolyl)propanenitrile (**19b**)



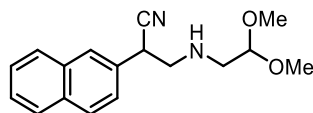
Following **GP6**, *trans*-aziridine borane **19a** (26 mg, 0.1 mmol, 1.0 equiv.) gave as mixture of diastereomers **19b** (54%) as a yellow oil. d.r. 1:1. R_f 0.42 [*n*-pentane:EtOAc (4:1)]. ^1H NMR (600 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.39 – 7.34 (1H, m), 7.34 – 7.29 (3H, m), 7.29 – 7.23 (4H, m), 4.36 (1H, t, J = 6.8 Hz), 4.02 (0.5H, dd, J = 8.2, 5.9 Hz), 3.99 (0.5H, t, J = 7.1 Hz), 3.28 – 3.21 (1H, m), 3.21 – 3.13 (1H, m), 3.07 – 3.00 (1H, m), 2.91 – 2.83 (1H, m), 2.50 – 2.43 (1H, m), 2.42 (3H, s), 1.88 – 1.79 (1H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 144.6, 143.6, 138.4, 138.3, 131.0, 131.0, 130.0, 129.9, 129.9, 129.8, 127.8, 127.8, 127.7, 127.6, 126.5, 126.5, 125.0, 124.9, 124.3, 124.2, 120.6 (2C), 63.2, 63.1, 51.8, 51.7, 39.0, 39.0, 33.7, 33.7, 30.5, 30.4, 21.2 (2C); HRMS (ESI) found MH^+ 277.1698, $\text{C}_{19}\text{H}_{21}\text{N}_2$ requires 277.1699.

3-((Furan-2-ylmethyl)amino)-2-(*p*-tolyl)propanenitrile (**20b**)



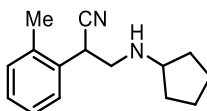
Following **GP6**, *cis*-aziridine borane **20a** and *trans*-aziridine borane **20a'** (Ratio 55:45, 45 mg, 0.2 mmol, 1.0 equiv.) gave **20b** (45%) as yellow oil. R_f 0.42 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.33 (1H, m), 7.21 (2H, d, J = 8.0 Hz), 7.18 (2H, d, J = 8.1 Hz), 6.31 (1H, dd, J = 3.2, 1.8 Hz), 6.17 (1H, d, J = 3.1 Hz), 3.90 (1H, dd, J = 8.0, 6.4 Hz), 3.83 (2H, s), 3.09 (1H, ddd, J = 12.3, 8.1, 0.9 Hz), 2.99 (1H, ddd, J = 12.3, 6.4, 0.9 Hz), 2.35 (3H, s), 2.35 (NH, br s); ^{13}C NMR (151 MHz, CDCl_3) δ 153.2, 142.2, 138.4, 130.8, 130.0, 127.6, 120.4, 110.3, 107.5, 53.3, 45.7, 38.2, 21.2; HRMS (ESI) found MH^+ 241.1328, $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}$ requires 241.1335.

3-((2,2-Dimethoxyethyl)amino)-2-(naphthalen-2-yl)propanenitrile (**21b**)



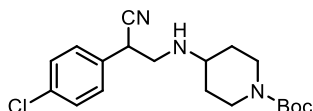
Following **GP6**, *trans*-aziridine borane **21a** (27 mg, 0.1 mmol, 1.0 equiv.) gave **21b** (41%) as a yellow oil. R_f 0.19 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.91 – 7.81 (4H, m), 7.56 7.48 (2H, m), 7.42 (1H, dd, J = 8.5, 1.9 Hz), 4.42 (1H, t, J = 5.3 Hz), 4.14 (1H, dd, J = 8.0, 6.2 Hz), 3.40 – 3.32 (6H, m), 3.24 (1H, dd, J = 12.6, 8.0 Hz), 3.15 (1H, dd, J = 12.6, 6.2 Hz), 2.81 (2H, d, J = 5.3 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 133.4, 133.1, 131.2, 129.3, 128.0, 127.9, 127.0, 126.9, 126.8, 125.0, 120.3, 104.1, 54.4, 54.4, 54.3, 50.8, 39.0; HRMS (ESI) found MNa^+ 307.1416, $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$ requires 307.1417.

3-(Cyclopentylamino)-2-(*o*-tolyl)propanenitrile (**22b**)



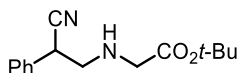
Following **GP6**, but running the reaction for 4.2 h, *trans*-aziridine borane **22a** (22 mg, 0.1 mmol, 1.0 equiv.) gave **22b** (49%) as a yellow oil. R_f 0.53 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.44 (1H, dd, $J = 7.0, 2.1$ Hz), 7.26 – 7.23 (2H, m), 7.22 – 7.18 (1H, m), 4.18 (1H, dd, $J = 9.1, 5.5$ Hz), 3.19 – 3.13 (1H, m), 3.06 (1H, dd, $J = 12.4, 9.2$ Hz), 2.94 (1H, dd, $J = 12.4, 5.5$ Hz), 2.37 (3H, s), 1.89 – 1.78 (2H, m), 1.74 – 1.65 (2H, m), 1.66 – 1.58 (1H, m), 1.57 – 1.51 (2H, m), 1.38 – 1.29 (2H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 135.3, 132.2, 131.0, 128.3, 127.7, 126.9, 120.6, 59.1, 51.7, 35.7, 33.3, 33.0, 24.0, 23.9, 19.2; HRMS (ESI) found MH^+ 229.1691, $\text{C}_{15}\text{H}_{21}\text{N}_2$ requires 229.1699.

tert-Butyl 4-((2-(4-Chlorophenyl)-2-cyanoethyl)amino)piperidine-1-carboxylate (**23b**)



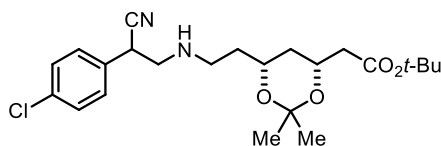
Following **GP6**, but running the reaction for 3 h, *trans*-aziridine borane **23a** (35 mg, 0.1 mmol, 1.0 equiv.) gave **23b** (40%, 7% rsm) as yellow oil. R_f 0.28 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.37 (2H, d, $J = 8.5$ Hz), 7.29 (2H, d, $J = 8.5$ Hz), 3.98 (2H, br s), 3.90 (1H, dd, $J = 7.7, 6.2$ Hz), 3.10 (1H, dd, $J = 12.3, 7.7$ Hz), 3.04 (1H, dd, $J = 12.4, 6.2$ Hz), 2.84 – 2.78 (1H, br m), 2.65 (1H, tt, $J = 10.0, 3.9$ Hz), 1.82 – 1.74 (2H, br m), 1.48 – 1.45 (1H, m), 1.45 (9H, s), 1.22 (2H, br m); ^{13}C NMR (101 MHz, CDCl_3) δ 154.9, 134.6, 132.5, 129.5, 129.1, 119.9, 79.7, 54.4, 51.2, 42.4 (br s), 38.7, 32.6, 32.5, 28.6; HRMS (ESI) found MNa^+ 386.1604, $\text{C}_{19}\text{H}_{26}\text{ClN}_3\text{O}_2\text{Na}$ requires 386.1606.

tert-Butyl (2-cyano-2-phenylethyl)glycinate (**24b**)



Following **GP6**, *trans*-aziridine borane **24a'** (49 mg, 0.2 mmol, 1.0 equiv.) gave **24b** (50%) as an oil. R_f 0.65 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.42 – 7.31 (5H, m), 3.94 (1H, dd, $J = 7.8, 6.2$ Hz), 3.34 (2H, s), 3.13 (1H, dd, $J = 12.2, 7.8$ Hz), 3.06 (1H, dd, $J = 12.2, 6.2$ Hz), 1.76 (NH, br s), 1.45 (9H, s); ^{13}C NMR (151 MHz, CDCl_3) δ 171.3, 133.8, 129.3, 128.5, 127.7, 120.2, 81.7, 53.9, 51.5, 39.1, 28.2; HRMS (ESI) found MNa^+ 283.1417, $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$ requires 283.1417.

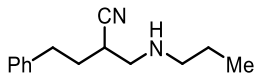
tert-Butyl 2-((4*R*,6*R*)-6-(2-((2-(4-Chlorophenyl)-2-cyanoethyl)amino)ethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (25b)



Following **GP6**, *trans*-aziridine borane **25a** (42 mg, 0.1 mmol, 1.0 equiv.) gave **25b** as mixture of diastereomers (35%) as a yellow oil. d.r. 1:1. R_f 0.13 [*n*-pentane:EtOAc (3:2)]. ^1H NMR (600 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.37 (2H, d, $J = 8.5$ Hz), 7.29 (2H, d, $J = 8.6$ Hz), 4.30 – 4.17 (1H, m), 3.94 – 3.90 (2H, m), 3.15 – 3.04 (1H, m), 2.98 (1H, dd, $J = 12.4, 6.3$ Hz), 2.81 – 2.67 (2H, m), 2.42 (1H, dd, $J = 15.1, 7.0$ Hz), 2.28 (1H, dd, $J = 15.2, 6.1$ Hz), 1.75 (NH, br s), 1.68 – 1.56 (2H, m), 1.44 (9H, s), 1.41 (3H, s), 1.32 (3H, s), 1.27 – 1.14 (2H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 170.4, 134.6, 132.6, 129.5, 129.1, 129.1, 119.9, 98.8, 80.8, 67.9, 67.8, 66.3, 54.6, 54.3, 45.9, 42.8, 38.1, 38.1, 36.7, 36.6, 36.3, 36.3, 30.2, 28.3, 19.9, 19.8; HRMS (ESI) found MH^+ 437.2200, $\text{C}_{23}\text{H}_{34}\text{ClN}_2\text{O}_4$ requires 437.2202.

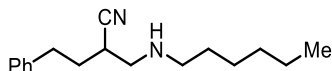
Note: There is no difference in chemical shift between the two diastereomers in ^1H NMR but in ^{13}C NMR, the carbon atoms close to the stereocenter are splitting, indicating the presence of a mixture of diastereomers.

4-Phenyl-2-((propylamino)methyl)butanenitrile (26b)



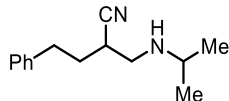
Following **GP6**, *trans*-aziridine borane **26a** (41 mg, 0.2 mmol, 1.0 equiv.) gave **26b** (66%) as an oil. R_f 0.39 [*n*-pentane:EtOAc (1:1)]. ^1H (600 MHz, CDCl_3) δ 7.30 (2H, t, $J = 7.5$ Hz), 7.25 – 7.18 (3H, m), 2.95 – 2.84 (2H, m), 2.80 – 2.66 (3H, m), 2.63 – 2.51 (2H, m), 2.01 – 1.85 (2H, m), 1.48 (2H, sx, $J = 7.3$ Hz), 1.24 (NH, br s), 0.91 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 140.2, 128.8, 128.5, 126.6, 121.6, 51.5, 51.1, 33.3, 32.3, 31.8, 23.3, 11.7; HRMS (ESI) found MH^+ 217.1691, $\text{C}_{14}\text{H}_{21}\text{N}_2$ requires 217.1699.

2-((Hexylamino)methyl)-4-phenylbutanenitrile (27b)

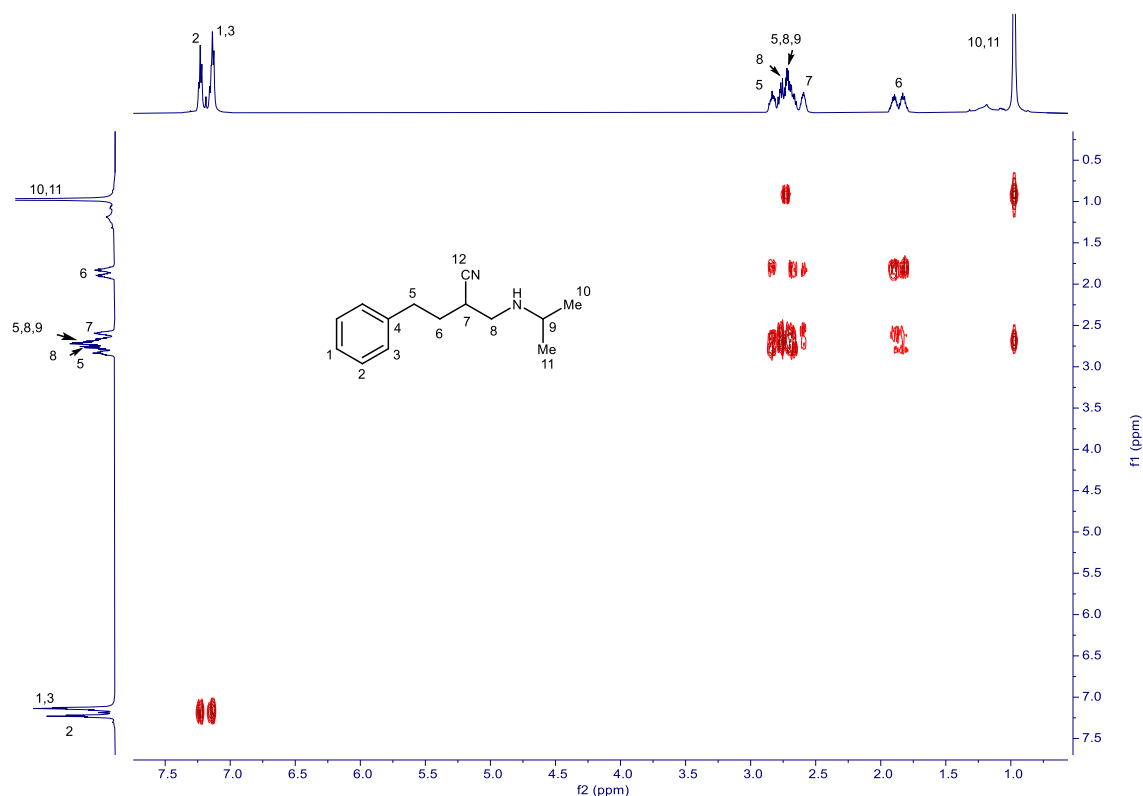


Following **GP6**, *trans*-aziridine borane **27a** (49 mg, 0.2 mmol, 1.0 equiv.) gave **27b** (47%) as an oil. R_f 0.56 [*n*-pentane:EtOAc (1:1)]. ^1H (400 MHz, CDCl_3) δ 7.30 (2H, t, $J = 7.5$ Hz), 7.25 – 7.19 (3H, m), 2.94 – 2.83 (2H, m), 2.80 – 2.65 (3H, m), 2.65 – 2.53 (2H, m), 2.04 – 1.82 (2H, m), 1.49 – 1.39 (2H, m), 1.33 – 1.25 (6H, m), 0.89 (3H, t, $J = 6.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ

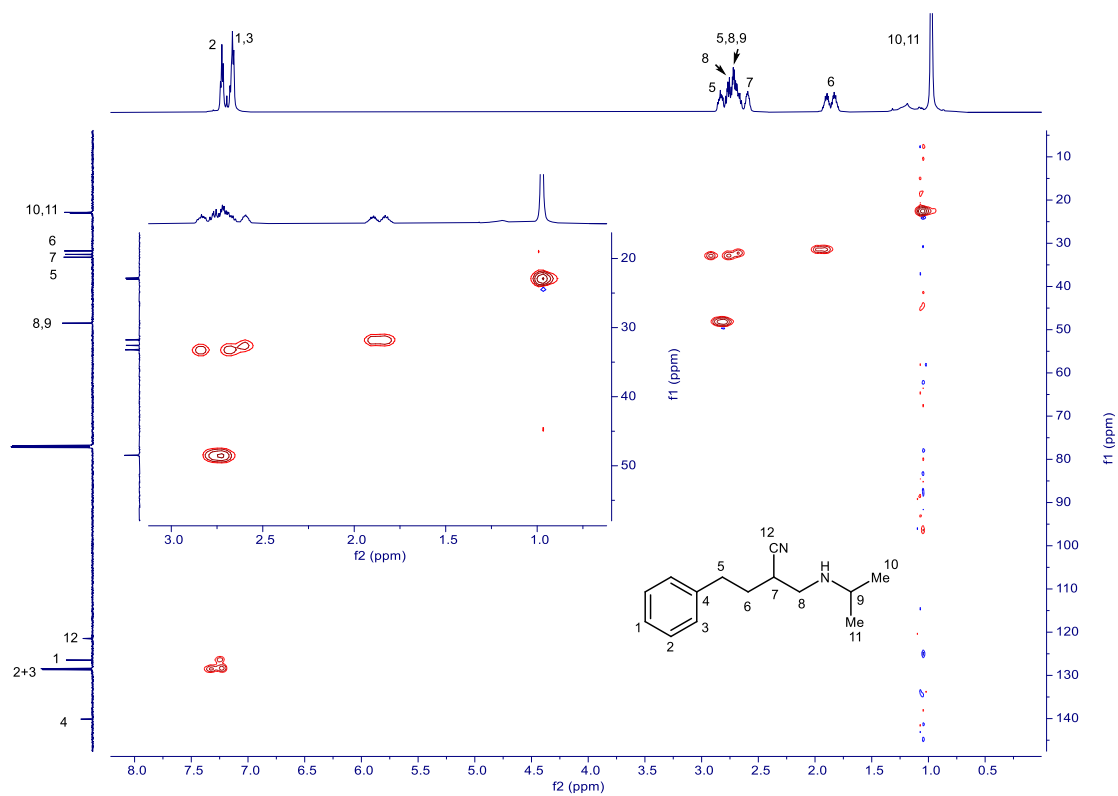
2-((Isopropylamino)methyl)-4-phenylbutanenitrile (13c)



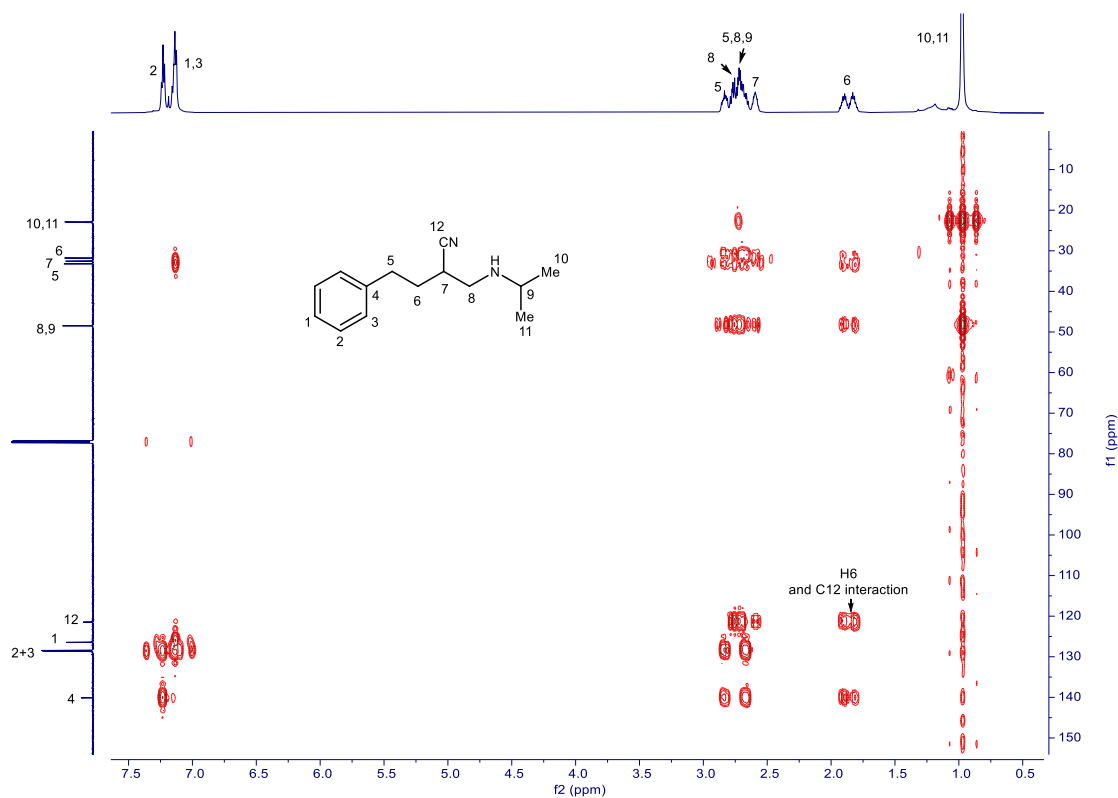
The structure of **13c** was further confirmed by 2D NMR spectroscopy (COSY, HSQC, and HMBC), which also established the regioselectivity of the reaction.



COSY NMR spectrum (600 MHz, CDCl₃, at rt) of **13c**

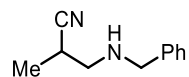


HSQC NMR spectrum (600 MHz, CDCl₃, at rt) of **13c**



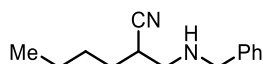
HMBC NMR spectrum (600 MHz, CDCl₃, at rt) of **13c**

3-(Benzylamino)-2-methylpropanenitrile (**28b**)



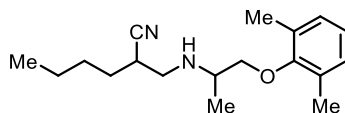
Following **GP6**, *trans*-aziridine borane **28a** (32 mg, 0.2 mmol, 1.0 equiv.) gave **28b** (52%) as an oil. R_f 0.29 [*n*-pentane:EtOAc (5:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.28 – 7.17 (5H, m), 3.81 – 3.73 (2H, m), 2.81 – 2.74 (1H, m), 2.74 – 2.66 (2H, m), 1.56 (NH, br s), 1.23 (3H, d, J = 6.8 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 139.8, 128.6, 128.2, 127.3, 122.4, 53.5, 51.9, 26.9, 15.8; HRMS (ESI) found MH^+ 175.1229, $\text{C}_{11}\text{H}_{15}\text{N}_2$ requires 175.1230.²⁰

2-((Benzylamino)methyl)hexanenitrile (**29b**)



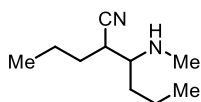
Following **GP6**, *trans*-aziridine borane **29a** (41 mg, 0.2 mmol, 1.0 equiv.) gave **29b** (67%) as an oil. R_f 0.29 [*n*-pentane:EtOAc (5:1)]. ^1H NMR (600 MHz, CDCl_3) 7.36 – 7.30 (4H, m), 7.29 – 7.25 (1H, m), 3.88 – 3.80 (2H, m), 2.86 (1H, dd, J = 12.1, 8.2 Hz), 2.79 (1H, dd, J = 12.2, 5.5 Hz), 2.70 (1H, tt, J = 8.5, 5.5 Hz), 1.67 – 1.55 (2H, m), 1.54 – 1.45 (1H, m), 1.45 – 1.28 (3H, m), 0.92 (3H, t, J = 7.2 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 139.9, 128.7, 128.2, 127.4, 121.8, 53.7, 50.5, 33.1, 29.9, 29.4, 22.4, 13.9; HRMS (ESI) found MH^+ 217.1693, $\text{C}_{14}\text{H}_{21}\text{N}_2$ requires 217.1699.

2-(((1-(2,6-Dimethylphenoxy)propan-2-yl)amino)methyl)hexanenitrile (**30b**)



Following **GP6**, *trans*-aziridine borane **30a** (28 mg, 0.1 mmol, 1.0 equiv.) gave **30b** as mixture of diastereomers (68%) as an oil. d.r. 1:1. R_f 0.33 [*n*-pentane:EtOAc (5:1)]. ^1H NMR (600 MHz, CDCl_3), signals corresponding to both diastereomers: δ 7.01 (2H, d, J =7.4 Hz), 6.95 – 6.89 (1H, m), 3.70 – 3.63 (2H, m), 3.19 – 3.11 (1H, m), 3.01 – 2.88 (2H, m), 2.78 2.68 (1H, m), 2.28 (6H, s), 1.79 (1H, NH), 1.71 – 1.59 (2H, m), 1.59 – 1.49 (1H, m), 1.48 – 1.33 (3H, m), 1.20 – 1.14 (3H, m), 0.96 – 0.90 (3H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 155.6, 155.5, 130.9, 129.1, 124.1, 124.0, 121.8, 121.8, 76.0, 75.9, 53.3, 53.2, 48.8, 48.8, 33.5, 33.4, 29.9, 29.8, 29.4, 29.4, 22.4, 22.4, 17.5, 17.4, 16.5, 16.5, 13.9; HRMS (ESI) found MH^+ 289.2269, $\text{C}_{18}\text{H}_{29}\text{N}_2\text{O}$ requires 289.2274.

3-(Methylamino)-2-propylhexanenitrile (**31b**)

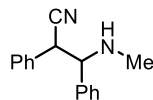


Following **GP6**, **31a** (31 mg, 0.2 mmol, 2.0 equiv.) gave **31b** (49%) as mixture of separable diastereomers. d.r. 1.6:1.

Data for the major diastereomer: (30%), obtained as an oil, R_f 0.47 [*n*-pentane:EtOAc (1:1)]; ^1H NMR (600 MHz, CDCl_3) δ 2.66 (1H, dt, $J = 10.4, 4.4$ Hz), 2.59 – 2.53 (1H, m), 2.45 (3H, s), 1.73 – 1.65 (1H, m), 1.64 – 1.49 (4H, m), 1.46 – 1.35 (3H, m), 0.97 (3H, dt, $J = 7.1$ Hz), 0.95 (3H, d, $J = 7.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 60.4, 36.4, 34.7, 34.6, 30.6, 21.1, 19.6, 14.2, 13.8; HRMS (ESI) found MH^+ 169.1701, $\text{C}_{10}\text{H}_{21}\text{N}_2$ requires 169.1699.

Data for the minor diastereomer: (19%), obtained as an oil, R_f 0.37 [*n*-pentane:EtOAc (1:1)]; ^1H NMR (400 MHz, CDCl_3) δ 2.82 (1H, dt, $J = 9.9, 4.5$ Hz), 2.54 (1H, dt, $J = 8.4, 4.1$ Hz), 2.45 (3H, s), 1.71 – 1.28 (8H, m), 0.98 (3H, t, $J = 7.1$ Hz), 0.95 (3H, t, $J = 6.8$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 60.5, 35.8, 34.0, 33.6, 31.1, 21.2, 19.5, 14.2, 13.8; HRMS (ESI) found MH^+ 169.1699, $\text{C}_{10}\text{H}_{21}\text{N}_2$ requires 169.1699.

3-(Methylamino)-2,3-diphenylpropanenitrile (**32b**)

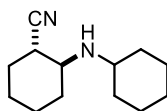


Following **GP6**, **32a** (44.6 mg, 0.2 mmol, 1.0 equiv.) gave **32b** (79%) as mixture of separable diastereomers. d.r. = 1.5:1.

Data for the major diastereomer: (47%), obtained as an oil, R_f 0.63 [*n*-pentane:EtOAc (1:1)]; ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.26 (6H, m), 7.22 – 7.15 (4H, m), 4.01 (1H, d, $J = 6.4$ Hz), 3.90 (1H, d, $J = 6.3$ Hz), 2.27 (3H, s), 1.73 (1H, br s); ^{13}C NMR (151 MHz, CDCl_3) δ 138.7, 133.2, 128.9, 128.6, 128.4, 128.3(8), 128.3(5), 127.8, 119.6, 68.7, 46.3, 34.7; HRMS (ESI) found MH^+ 237.1384, $\text{C}_{16}\text{H}_{17}\text{N}_2$ requires 237.1386.

Data for the minor diastereomer: (32%), obtained as an oil, R_f 0.46 [*n*-pentane:EtOAc (1:1)]; ^1H NMR (600 MHz, CDCl_3) δ 7.36 – 7.30 (6H, m), 7.25 – 7.21 (2H, m), 7.21 – 7.16 (2H, m), 4.11 (1H, d, $J = 7.2$ Hz), 3.88 (1H, d, $J = 7.2$ Hz), 2.27 (3H, s), 1.70 (1H, br s). ^{13}C NMR (151 MHz, CDCl_3) δ 138.3, 133.1, 129.1, 128.6(3), 128.6(0), 128.5(8), 128.5(5), 128.0, 119.3, 68.6, 45.7, 34.6; HRMS (ESI) found MH^+ 237.1382, $\text{C}_{16}\text{H}_{17}\text{N}_2$ requires 237.1386.

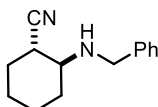
***trans*-2-(Cyclohexylamino)cyclohexane-1-carbonitrile (33b)**



Following **GP6**, *trans*-aziridine borane **33a** (19 mg, 0.1 mmol, 1.0 equiv.) gave **33b** (58%) as an oil. R_f 0.53 [*n*-pentane:EtOAc (1:1)]. ^1H (400 MHz, CDCl_3) δ 2.74 (1H, td, $J=9.8$, 3.9 Hz), 2.58 (1H, tt, $J=10.3$, 3.8 Hz), 2.32 (1H, td, $J=10.4$, 3.7 Hz), 2.16 – 1.98 (2H, m), 1.98 – 1.88 (1H, m), 1.87 – 1.78 (1H, m), 1.78 – 1.66 (4H, m), 1.63 – 1.54 (2H, m), 1.33 – 1.01 (8H, m); ^{13}C (151 MHz, CDCl_3) δ 122.3, 55.0, 54.1, 36.8, 34.9, 33.9, 32.8, 29.0, 26.2, 25.3, 25.1, 24.5, 24.1; HRMS (ESI) found MH^+ 207.1851, $\text{C}_{13}\text{H}_{23}\text{N}_2$ requires 207.1856.

The *trans* configuration was assigned based on the coupling constants observed for peaks at 2.74 ppm (1H, td, $J=9.8$, 3.9 Hz) and 2.32 (1H, td, $J=10.4$, 3.7 Hz).

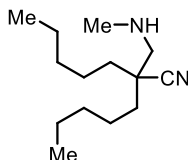
***trans*-2-(Benzylamino)cyclohexane-1-carbonitrile (34b)**



Following **GP6**, *trans*-aziridine borane **34a** (40.2 mg, 0.2 mmol, 1.0 equiv.) gave **34b** (46%) as oil. R_f 0.63 [*n*-pentane:EtOAc (5:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.13 (5H, m), 3.84 (1H, d, $J = 13.1$ Hz), 3.75 (1H, d, $J = 13.1$ Hz), 2.63 (1H, td, $J = 9.7$, 3.8 Hz), 2.33 (1H, ddd, $J = 11.1$, 9.4, 3.8 Hz), 2.06 – 1.95 (2H, m), 1.69 – 1.61 (2H, m), 1.57 – 1.43 (2H, m), 1.22 – 1.10 (2H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 140.2, 128.6, 128.2, 127.3, 122.1, 57.2, 51.1, 35.9, 31.6, 28.8, 24.5, 23.8; HRMS (ESI) found MNa^+ 237.1356, $\text{C}_{14}\text{H}_{18}\text{N}_2\text{Na}$ requires 237.1362.

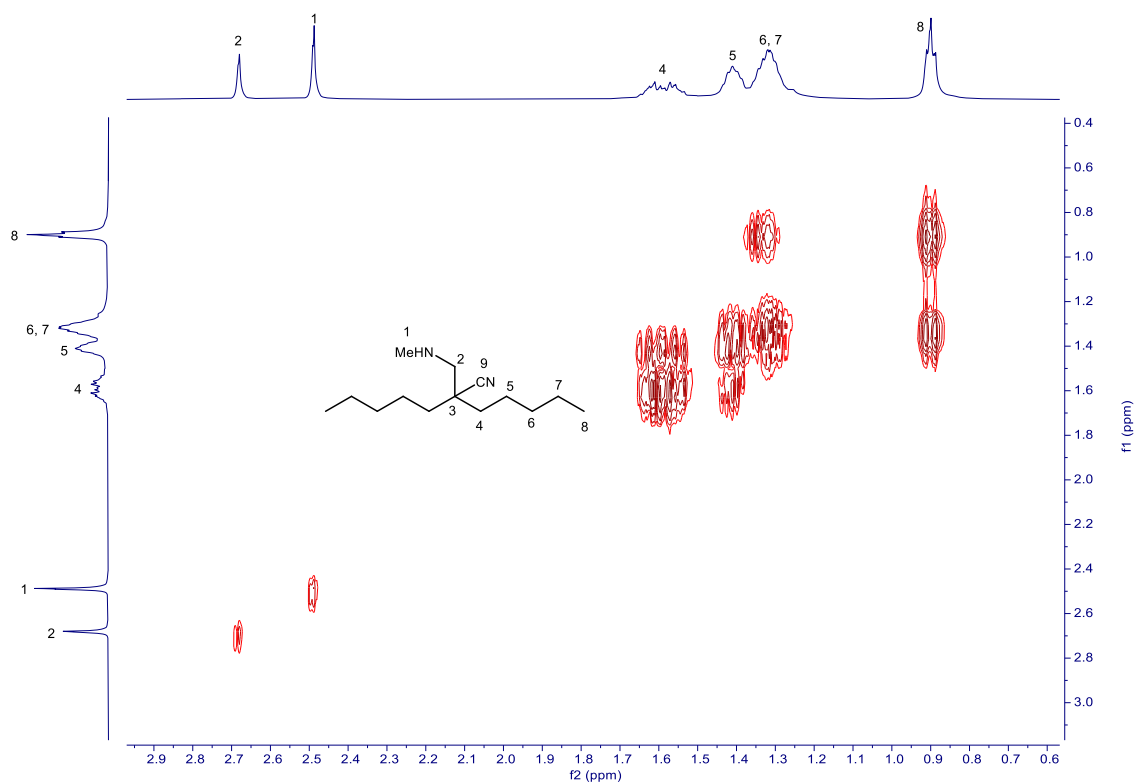
The *trans* configuration was assigned based on the coupling constants observed for peaks at 2.63 (1H, td, $J = 9.7$, 3.8 Hz) and 2.33 (1H, ddd, $J = 11.1$, 9.4, 3.8 Hz).

2-((methylamino)methyl)-2-pentylheptanenitrile (35b)

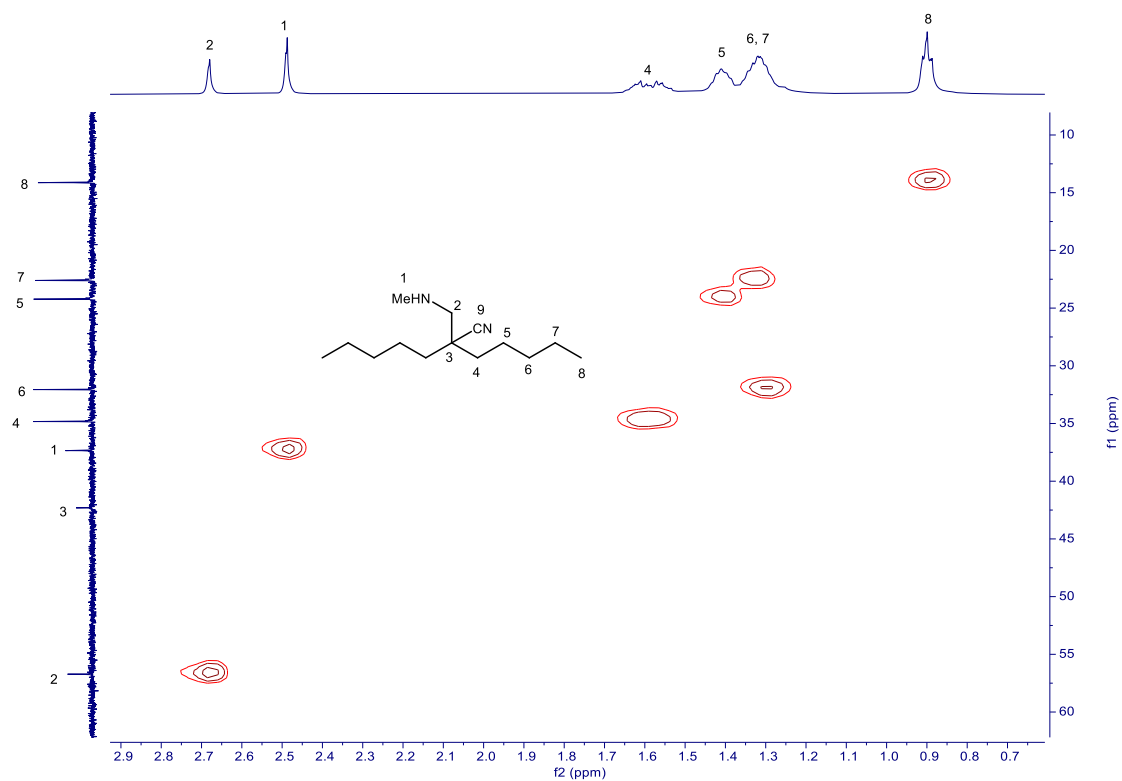


Following **GP6**, **35a** (21.1 mg, 0.1 mmol, 1.0 equiv.) gave **35b** (23%) as an oil. R_f 0.53 [*n*-pentane:EtOAc (1:1)]. ^1H (400 MHz, CDCl_3) δ 2.68 (2H, s), 2.49 (3H, s), 1.65 – 1.51 (4H, m), 1.45 – 1.28 (12H, m), 0.90 (8H, t, $J=6.8$ Hz); ^{13}C (101 MHz, CDCl_3) δ 123.8, 56.7, 42.3, 37.3, 34.8, 32.1, 24.2, 22.6, 14.1; HRMS (ESI) found MH^+ 225.2325, $\text{C}_{14}\text{H}_{29}\text{N}_2$ requires 225.2325.

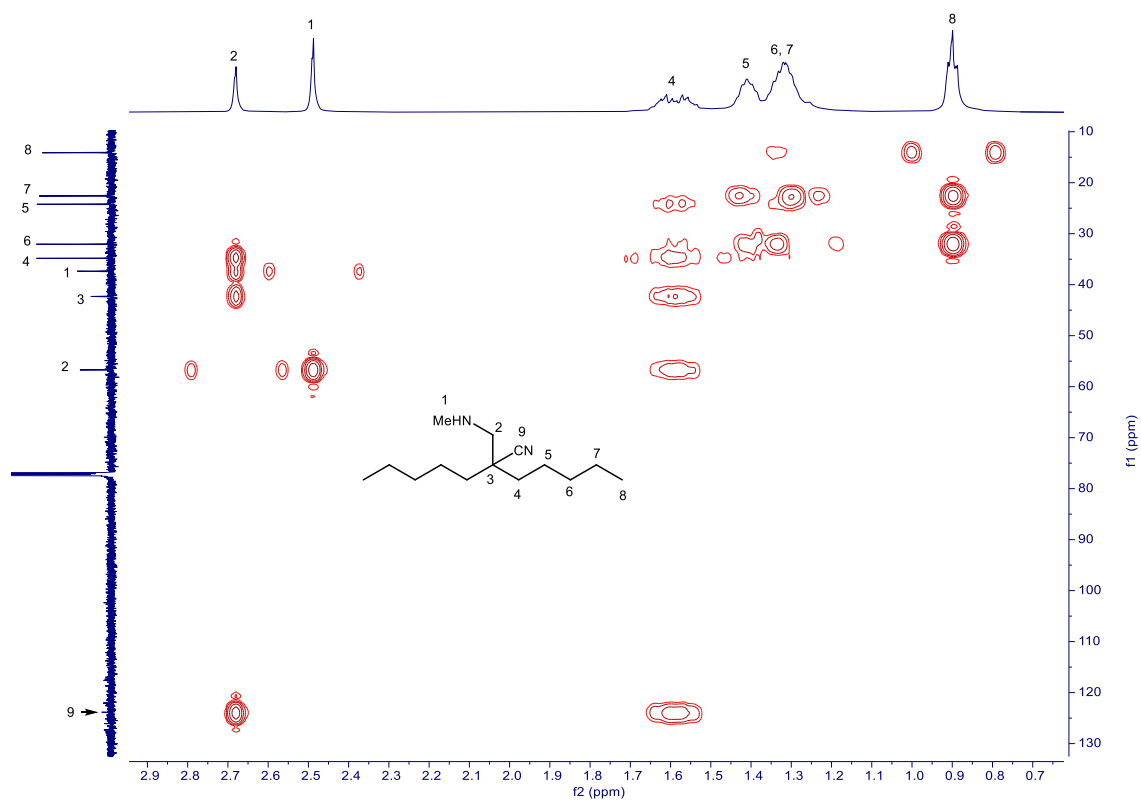
The structure of **35b** was further confirmed by 2D NMR spectroscopy (COSY, HSQC, and HMBC), which also established the regioselectivity of the reaction.



COSY NMR spectrum (600 MHz, CDCl₃, at rt) of **35b**

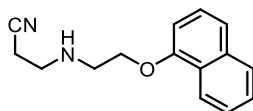


HSQC NMR spectrum (600 MHz, CDCl₃, at rt) of **35b**



HMBC NMR spectrum (600 MHz, CDCl_3 , at rt) of **35b**

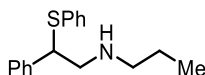
3-((2-(Naphthalen-1-yloxy)ethyl)amino)propanenitrile (**36b**)



Following **GP6**, **36a** (45 mg, 0.2 mmol, 1.0 equiv.) gave **36b** (58%) as an oil. R_f 0.27 [EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 8.28 – 8.21 (1H, m), 7.84 – 7.77 (1H, m), 7.53 – 7.42 (3H, m), 7.37 (1H, t, $J = 7.9$ Hz), 6.83 (1H, d, $J = 7.5$ Hz), 4.26 (2H, t, $J = 5.1$ Hz), 3.19 (2H, t, $J = 5.1$ Hz), 3.07 (2H, t, $J = 6.6$ Hz), 2.56 (2H, t, $J = 6.7$ Hz), 2.01 (NH, br s); ^{13}C NMR (101 MHz, CDCl_3) δ 154.4, 134.6, 127.7, 126.6, 125.9, 125.7, 125.4, 121.9, 120.8, 118.7, 105.0, 67.8, 48.3, 45.2, 19.0; HRMS (ESI) found MNa^+ 263.1152, $\text{C}_{15}\text{H}_{16}\text{N}_2\text{ONa}$ requires 263.1155.

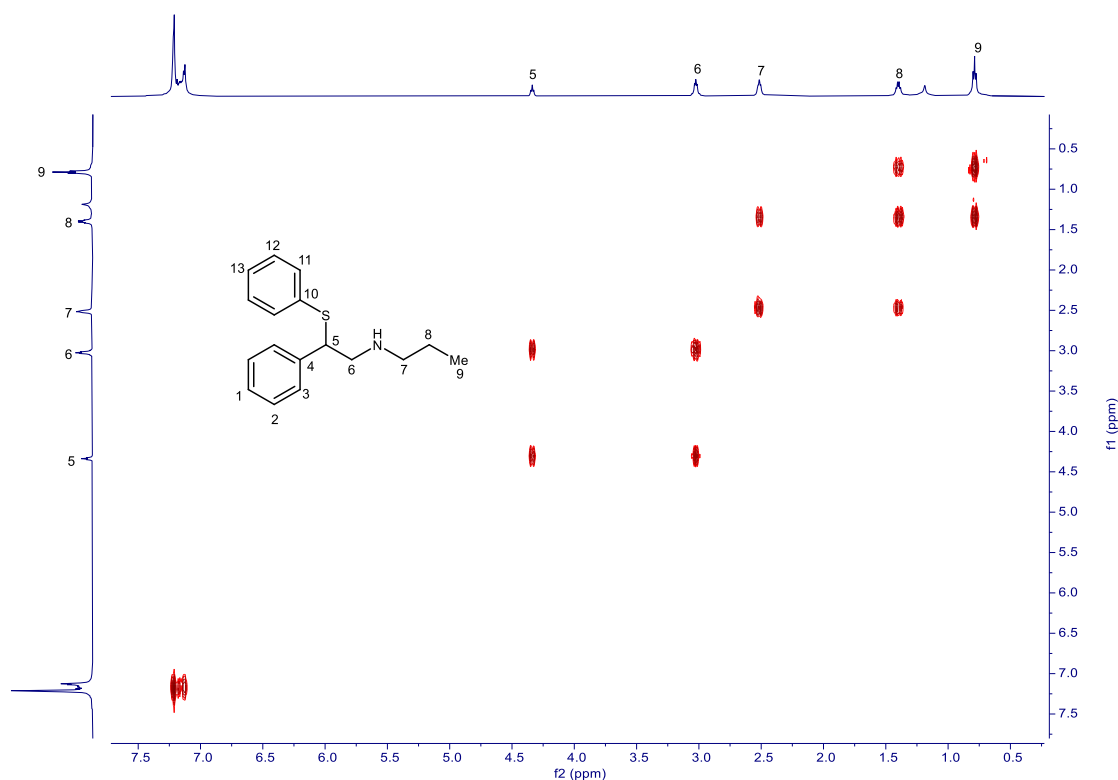
5.3 Ring-Opening–Thioetherification

N-(2-Phenyl-2-(phenylthio)ethyl)propan-1-amine (**1r**)

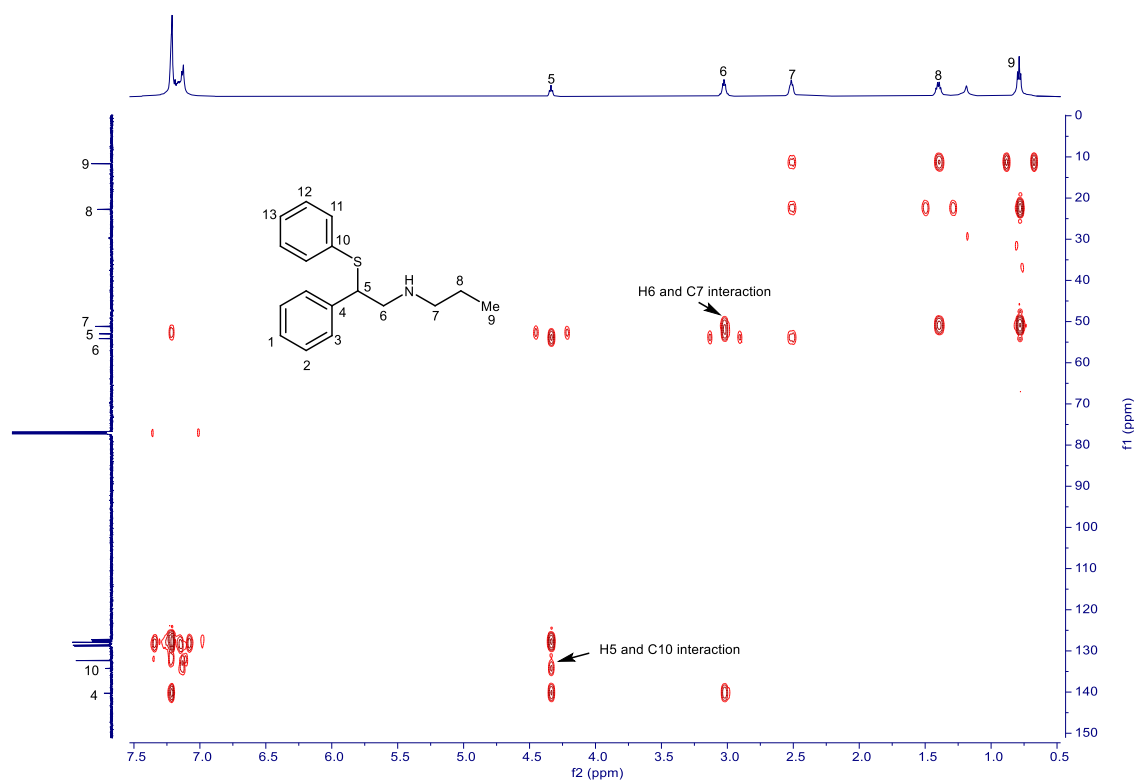
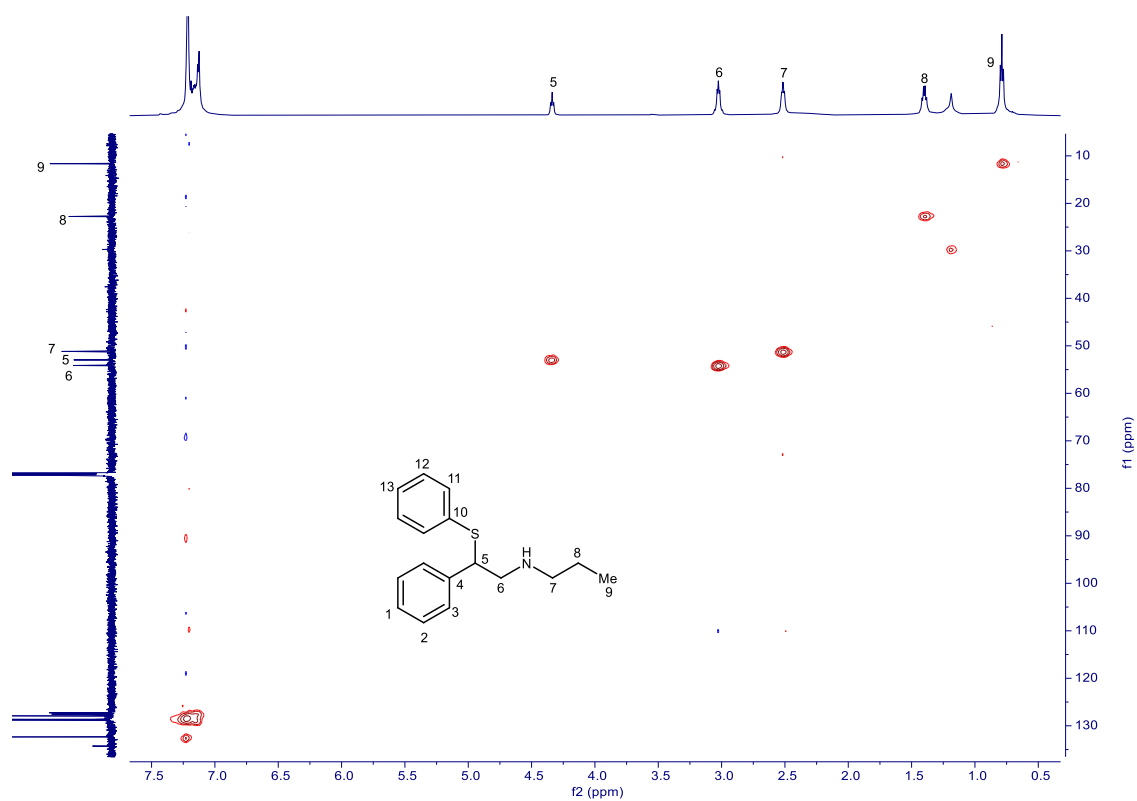


Following **GP7**, *trans*-aziridine borane **1a** (35 mg, 0.2 mmol) and diphenyl disulfide (22 mg, 0.1 mmol) gave **1r** (60%) as an oil. R_f 0.31 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.27 (6H, m), 7.25 – 7.17 (4H, m), 4.38 (1H, t, $J = 7.3$ Hz), 3.15 – 3.03 (2H, m), 2.63 – 2.52 (2H, m), 1.46 (2H, sx, $J = 7.4$ Hz), 0.86 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 140.6, 134.5, 132.4, 128.9, 128.7, 128.0, 127.6, 127.3, 54.5, 53.3, 51.4, 23.1, 11.8; HRMS (ESI) found MH^+ 272.14665, $\text{C}_{17}\text{H}_{22}\text{NS}$ requires 272.14675.

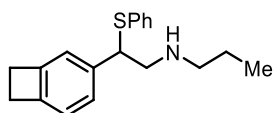
The structure of **1r** was further confirmed by 2D NMR spectroscopy (COSY, HSQC, and HMBC), which also established the regioselectivity of the reaction.



COSY NMR spectrum (600 MHz, CDCl_3 , at rt) of **1r**

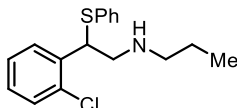


***N*-(2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-2-(phenylthio)ethyl)propan-1-amine (7d)**



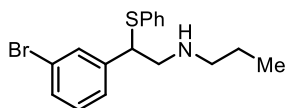
Following **GP7**, *trans*-aziridine borane **7a** (40 mg, 0.2 mmol) and diphenyl disulfide (22 mg, 0.1 mmol) gave **7d** (73%) as an oil. R_f 0.42 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.21 (2H, m), 7.21 – 7.07 (3H, m), 7.04 (1H, dd, J = 7.6, 1.6 Hz), 6.96 (1H, d, J = 1.5 Hz), 6.94 – 6.84 (1H, dd, J = 7.7, 1.0 Hz), 4.27 (1H, t, J = 7.3 Hz), 3.06 (4H, s), 3.02 – 2.90 (2H, m), 2.54 – 2.38 (2H, m), 1.36 (2H, sx, J = 7.3 Hz), 0.78 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 146.24, 145.22, 139.15, 135.15, 131.95, 128.88, 127.05, 126.75, 122.72, 122.04, 55.00, 53.89, 51.46, 29.49, 29.47, 23.20, 11.82; HRMS (ESI) found MH^+ 298.1615, $\text{C}_{19}\text{H}_{24}\text{NS}$ requires 298.1624.

***N*-(2-(2-Chlorophenyl)-2-(phenylthio)ethyl)propan-1-amine (16c)**



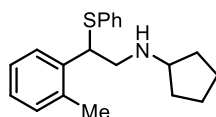
Following **GP7**, *trans*-aziridine borane **16a** (42 mg, 0.2 mmol) and diphenyl disulfide (22 mg, 0.1 mmol) gave **16c** (74%) as an oil. R_f 0.42 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (400 MHz, CDCl_3) δ 7.44 (1H, dd, J = 7.7, 1.9 Hz), 7.35 (1H, dd, J = 7.8, 1.6 Hz), 7.33 – 7.27 (2H, m), 7.25 – 7.13 (5H, m), 4.99 (1H, t, J = 7.1 Hz), 3.18 – 2.95 (2H, m), 2.70 – 2.49 (2H, m), 1.46 (2H, sx, J = 7.3 Hz), 0.88 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 138.2, 134.3, 134.0, 132.1, 129.8, 129.0, 128.9, 128.5, 127.3, 127.2, 53.8, 51.2, 49.0, 23.3, 11.8; HRMS (ESI) found MH^+ 306.1069, $\text{C}_{17}\text{H}_{21}\text{ClNS}$ requires 306.1078.

***N*-(2-(3-Bromophenyl)-2-(phenylthio)ethyl)propan-1-amine (37b)**



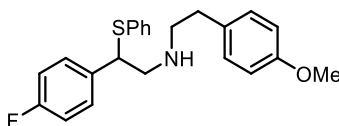
Following **GP7**, *trans*-aziridine borane **37a** (51 mg, 0.2 mmol) and diphenyl disulfide (22 mg, 0.1 mmol) gave **37b** (59%) as an oil. R_f 0.44 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.42 (1H, t, J = 1.9 Hz), 7.36 (1H, ddd, J = 7.8, 2.0, 1.2 Hz), 7.29 – 7.25 (2H, m), 7.25 – 7.20 (3H, m), 7.19 (1H, dt, J = 7.8, 1.5 Hz), 7.14 (1H, t, J = 7.8 Hz), 4.29 (1H, t, J = 7.2 Hz), 3.04 (2H, d, J = 7.2 Hz), 2.57 (2H, t, J = 7.2 Hz), 1.46 (2H, sx, J = 7.4 Hz), 0.88 (3H, t, J = 7.4 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 143.3, 133.9, 132.7, 131.0, 130.7, 130.2, 129.0, 127.6, 126.7, 122.7, 54.3, 53.3, 51.5, 23.2, 11.8; HRMS (ESI) found MH^+ 350.0565, $\text{C}_{17}\text{H}_{21}\text{BrNS}$ requires 350.0573.

***N*-(2-(Phenylthio)-2-(*o*-tolyl)ethyl)cyclopentanamine (22c)**



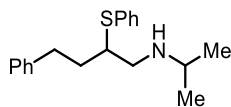
Following **GP7**, *trans*-aziridine borane **22a** (43 mg, 0.2 mmol) and diphenyl disulfide (22 mg, 0.1 mmol) gave **22c** (49%) as an oil. R_f 0.44 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.30 – 7.26 (2H, m), 7.25 – 7.19 (4H, m), 7.17 – 7.12 (3H, m), 4.57 (1H, t, J = 7.3 Hz), 3.16 – 2.99 (3H, m), 2.36 (3H, s), 1.87 – 1.74 (2H, m), 1.70 – 1.60 (2H, m), 1.56 – 1.45 (2H, m), 1.34 – 1.20 (2H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 138.3, 136.6, 134.3, 133.1, 130.7, 128.8, 127.6, 127.3, 126.7, 126.4, 59.6, 52.5, 49.1, 33.3, 24.2, 24.1, 19.6; HRMS (ESI) found MH^+ 312.1771, $\text{C}_{19}\text{H}_{26}\text{NS}$ requires 312.1781.

2-(4-Fluorophenyl)-*N*-(4-methoxyphenethyl)-2-(phenylthio)ethan-1-amine (18c)



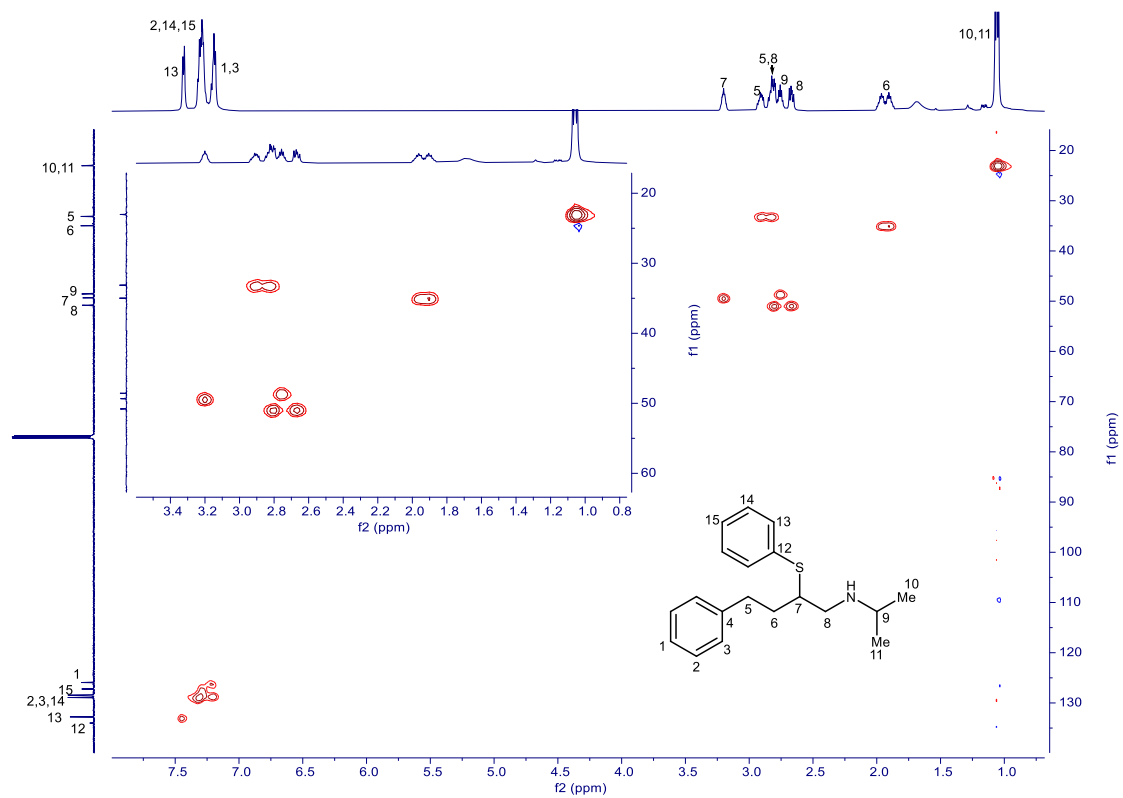
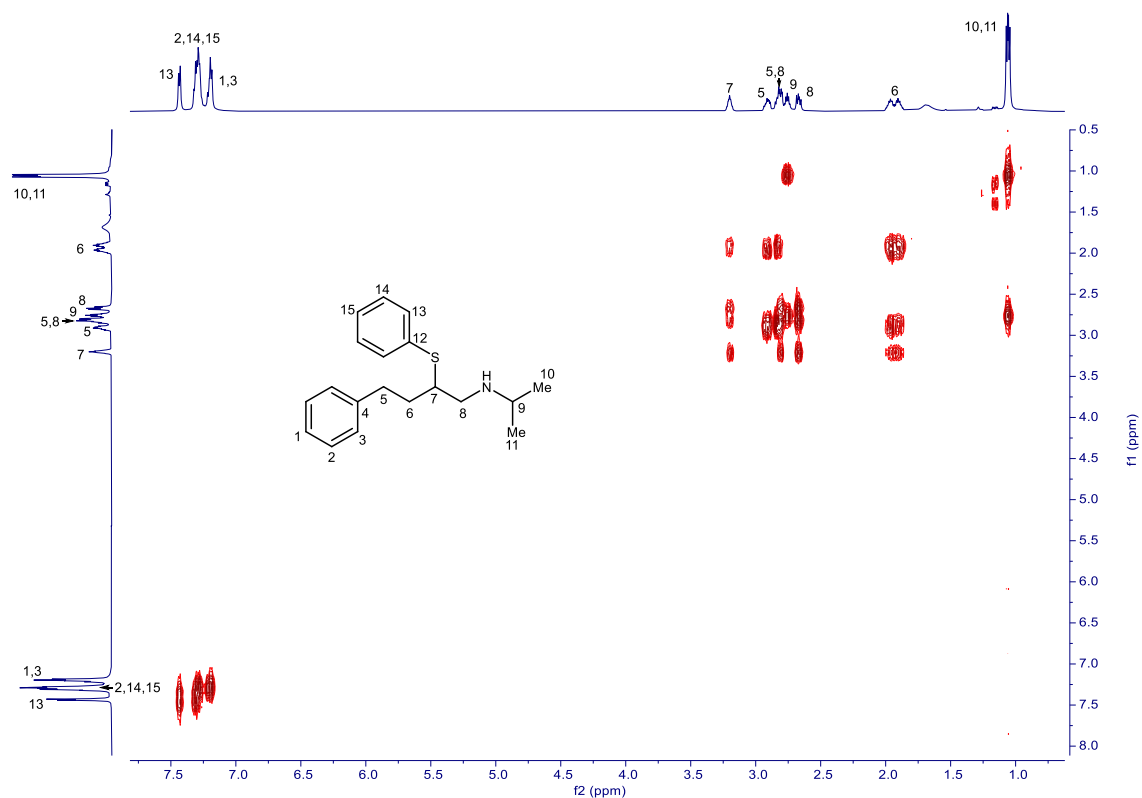
Following **GP7**, *cis*-aziridine borane **18a** and *trans*-aziridine borane **18a'** (Ratio 15:85, 57 mg, 0.2 mmol) and diphenyl disulfide (22 mg, 0.1 mmol) gave **18c** (70%) as an oil. R_f 0.31 [*n*-pentane:EtOAc (6:4)]. ^1H NMR (600 MHz, CDCl_3) δ 7.26 – 7.15 (7H, m), 7.08 – 7.01 (2H, m), 6.97 – 6.89 (2H, m), 6.85 – 6.76 (2H, m), 4.31 (1H, t, J = 7.3 Hz), 3.78 (3H, s), 3.10 – 3.00 (2H, m), 2.88 – 2.79 (2H, m), 2.69 (2H, t, J = 7.1 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 162.1 (d, J = 246.0 Hz), 158.2, 136.3 (d, J = 3.1 Hz), 134.1, 132.7, 131.8, 129.7, 129.5 (d, J = 7.9 Hz), 128.9, 127.5, 115.5 (d, J = 21.5 Hz), 114.0, 55.3, 54.3, 52.7, 51.0, 35.4; ^{19}F NMR (565 MHz, CDCl_3) δ –114.89 (tt, J = 8.6, 5.2 Hz); HRMS (ESI) found MH^+ 382.1637, $\text{C}_{23}\text{H}_{25}\text{FNOS}$ requires 382.1635.

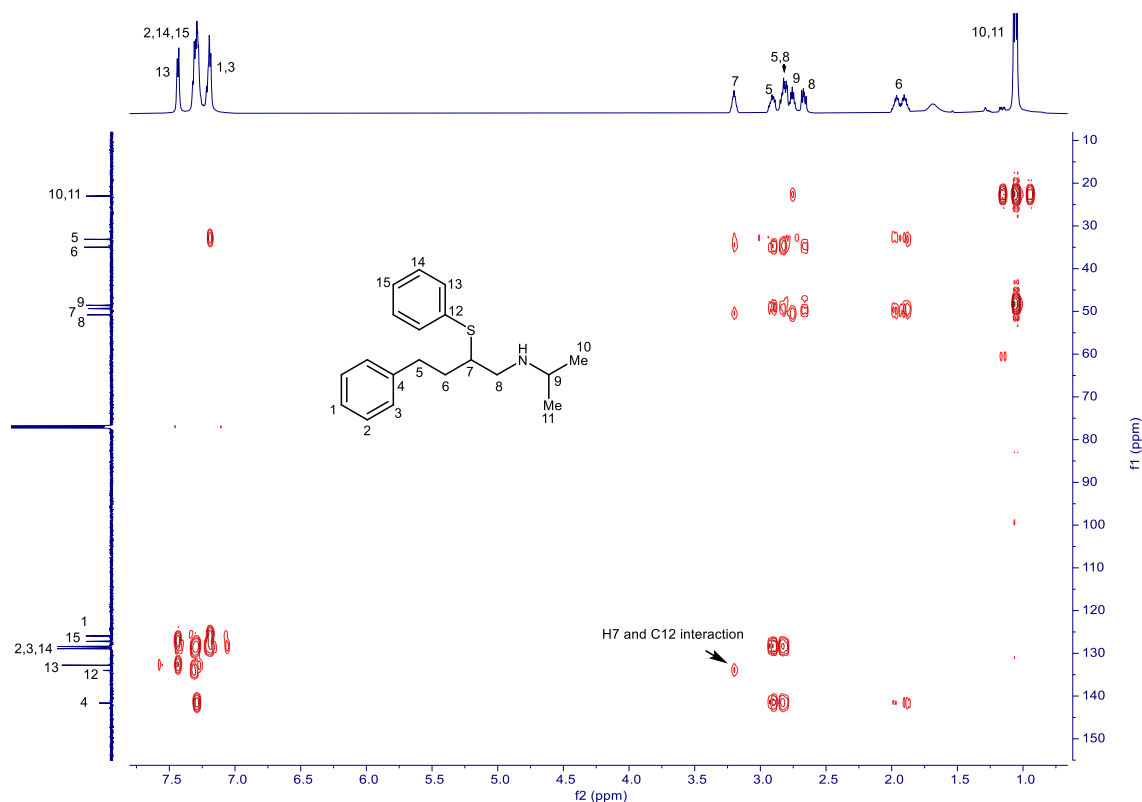
***N*-Isopropyl-4-phenyl-2-(phenylthio)butan-1-amine (13d)**



Following **GP7**, *trans*-aziridine borane **13a** (41 mg, 0.2 mmol, 2 equiv.) and diphenyl disulfide (22 mg, 0.1 mmol) gave **13d** (90%) as an oil. R_f 0.13 [*n*-pentane:EtOAc (1:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.39 (2H, m), 7.35 – 7.24 (5H, m), 7.24 – 7.15 (3H, m), 3.19 (1H, tt, J = 8.0, 5.2 Hz), 2.97 – 2.62 (5H, m), 2.03 – 1.82 (2H, m), 1.54 (NH, br s), 1.06 (3H, d, J = 6.6 Hz), 1.04 (3H, t, J = 6.6 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 141.8, 134.2, 132.9, 129.0, 128.6, 128.5, 127.3, 126.1, 51.0, 49.5, 48.7, 35.1, 33.3, 23.2, 23.1; HRMS (ESI) found MH^+ 300.1774, $\text{C}_{19}\text{H}_{26}\text{NS}$ requires 300.1781.

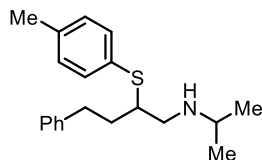
The structure of **13d** was further confirmed by 2D NMR spectroscopy (COSY, HSQC, and HMBC), which also established the regioselectivity of the reaction.





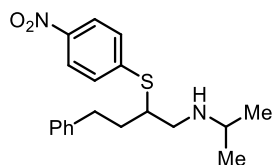
HMBC NMR spectrum (600 MHz, CDCl_3 , at rt) of **13d**

***N*-Isopropyl-4-phenyl-2-(*p*-tolylthio)butan-1-amine (**13e**)**



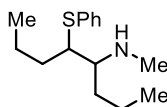
Following **GP7**, *trans*-aziridine borane **13a** (41 mg, 0.2 mmol, 2 equiv.) and *p*-tolyl disulfide (25 mg, 0.1 mmol) gave **13e** (80%) as an oil. R_f 0.32 [EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (2H, d, $J=8.1$ Hz), 7.29 – 7.23 (2H, m), 7.20 – 7.14 (3H, m), 7.10 (2H, d, $J=7.8$ Hz), 3.08 (1H, tt, $J=8.2, 5.2$ Hz), 2.89 (1H, ddd, $J=14.8, 9.2, 6.0$ Hz), 2.84 – 2.69 (3H, m), 2.60 (1H, dd, $J=12.2, 8.1$ Hz), 2.33 (3H, s), 1.96 – 1.79 (2H, m), 1.65 (1H, br s), 1.04 (3H, d, $J=6.6$ Hz), 1.03 (3H, d, $J=6.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 141.9, 137.7, 133.7, 129.9, 129.8, 128.6, 128.5, 126.0, 50.8, 49.8, 48.7, 35.0, 33.3, 23.2, 23.1, 21.2; HRMS (ESI) found MH^+ 314.1939, $\text{C}_{20}\text{H}_{28}\text{NS}$ requires 314.1937.

***N*-Isopropyl-2-((4-nitrophenyl)thio)-4-phenylbutan-1-amine (13f)**



Following **GP7**, *trans*-aziridine borane **13a** (41 mg, 0.2 mmol, 2 equiv.) and 4-nitrophenyl disulfide (31 mg, 0.1 mmol) gave **13f** (64%) as an oil. R_f 0.32 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 8.07 (2H, d, $J=8.9$ Hz), 7.32 (2H, d, $J=8.9$ Hz), 7.29 (2H, t, $J=7.5$ Hz), 7.21 (1H, t, $J=7.4$ Hz), 7.16 (2H, d, $J=7.0$ Hz), 3.41 (1H, tt, $J=7.3, 5.6$ Hz), 2.91 (1H, dd, $J=12.5, 5.2$ Hz), 2.85 – 2.73 (4H, m), 2.10 (1H, ddt, $J=14.7, 8.6, 6.5$ Hz), 1.95 (1H, ddt, $J=14.3, 8.4, 7.1$ Hz), 1.44 (1H, br s), 1.04 (3H, d, $J=6.1$ Hz), 1.03 (3H, d, $J=6.1$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 146.7, 145.6, 141.1, 128.7, 128.6, 128.4, 126.4, 124.0, 50.8, 48.9, 47.9, 35.0, 33.1, 23.2; HRMS (ESI) found MH^+ 345.1632, $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ requires 345.1631.

***N*-methyl-5-(phenylthio)octan-4-amine (31c)**

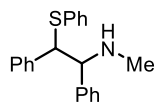


Following **GP7**, *trans*-aziridine borane **31a** (31 mg, 0.2 mmol, 2.0 equiv.) and diphenyl disulfide (22 mg, 0.1 mmol) gave **31c** (90%, dr = 1.4:1) as an oil.

Data for the major diastereomer: (53%), obtained as an oil, R_f 0.27 [*n*-pentane:EtOAc (2:3)]; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (2H, d, $J = 7.0$ Hz), 7.32–7.26 (3H, m), 7.21 (1H, t, $J = 7.3$ Hz), 3.40–3.31 (1H, m), 2.49 (1H, td, $J = 6.3, 2.9$ Hz), 2.36 (3H, s), 1.71–1.49 (4H, m), 1.49–1.36 (3H, m), 1.39–1.25 (2H, m), 0.96–0.84 (6H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 136.5, 131.9, 129.0, 126.8, 62.0, 53.4, 34.9, 33.4, 33.1, 21.4, 20.1, 14.4, 14.1; HRMS (ESI) found MH^+ 252.1781, $\text{C}_{15}\text{H}_{26}\text{NS}$ requires 252.1781.

Data for the minor diastereomer: (37%), obtained as an oil, R_f 0.17 [*n*-pentane:EtOAc (2:3)]; ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.37 (2H, m), 7.31–7.23 (2H, m), 7.22–7.16 (1H, m), 3.22 (1H, dt, $J = 8.8, 4.1$ Hz), 2.53 (1H, dt, $J = 6.7, 4.3$ Hz), 2.39 (3H, s), 1.77–1.59 (3H, m), 1.45–1.29 (5H, m), 0.93–0.87 (6H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 131.4, 129.0, 126.5, 62.7, 52.9, 35.0, 33.3, 33.1, 21.2, 20.0, 14.4, 14.2; HRMS (ESI) found MH^+ 252.1782, $\text{C}_{15}\text{H}_{26}\text{NS}$ requires 252.1781.

***N*-methyl-1,2-diphenyl-2-(phenylthio)ethan-1-amine (32c)**

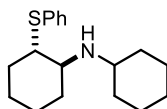


Following **GP7**, *trans*-aziridine borane **32a** (45 mg, 0.2 mmol, 2.0 equiv.) and diphenyl disulfide (22 mg, 0.1 mmol) gave **32c** (84%, dr = 1.15:1).

Data for the major diastomer: (45%), obtained as an oil, R_f 0.28 [*n*-pentane:EtOAc (8:2)]; ^1H NMR (400 MHz, CDCl_3) δ 7.25–7.19 (2H, m), 7.21–7.04 (11H, m), 7.03–6.98 (2H, m), 4.35 (1H, d, J = 8.8 Hz), 3.89 (1H, d, J = 8.9 Hz), 2.30 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 140.2, 135.7, 134.9, 132.2, 128.9, 128.8, 128.4, 128.1, 128.0, 127.4, 127.2, 127.0, 69.8, 61.6, 34.7; HRMS (ESI) found MH^+ 320.1468, $\text{C}_{21}\text{H}_{22}\text{NS}$ requires 320.1468.

Data for the minor diastomer: (39%), obtained as an oil, R_f 0.20 [*n*-pentane:EtOAc (8:2)]; ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.27 (3H, m), 7.24–7.18 (7H, m), 7.15–7.08 (5H, m), 4.44 (1H, d, J = 7.2 Hz), 3.95 (1H, d, J = 7.3 Hz), 2.18 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 139.2, 136.1, 135.0, 132.3, 129.1, 128.7, 128.4, 128.4, 128.3, 127.9, 127.6, 127.1, 69.3, 60.7, 34.6; HRMS (ESI) found MH^+ 320.1470, $\text{C}_{21}\text{H}_{22}\text{NS}$ requires 320.1468.

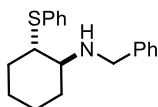
***trans*-N-cyclohexyl-2-(phenylthio)cyclohexan-1-amine (33c)**



Following **GP7**, *trans*-aziridine borane **33a** (39 mg, 0.2 mmol, 2 equiv.) and diphenyl disulfide (22 mg, 0.1 mmol) gave **33c** (92%) as an oil. R_f 0.55 [EtOAc]. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (2H, d, J = 7.2 Hz), 7.34 – 7.22 (3H, m), 2.97 (1H, td, J = 10.7, 4.0 Hz), 2.64 – 2.49 (2H, m), 2.15 – 2.06 (2H, m), 2.04 – 1.95 (1H, m), 1.93 – 1.84 (1H, m), 1.80 – 1.66 (4H, m), 1.65 – 1.58 (1H, m), 1.50 – 1.39 (1H, m), 1.34 – 1.13 (5H, m), 1.12 – 0.99 (1H, m); ^{13}C (151 MHz, CDCl_3) δ 134.4, 132.9, 129.0, 127.2, 57.0, 54.0, 53.7, 35.4, 33.8, 33.4, 33.1, 26.3, 26.2, 25.5, 25.3, 24.6; HRMS (ESI) found MH^+ 290.1938, $\text{C}_{10}\text{H}_{21}\text{N}_2$ requires 290.1937.

The *trans* configuration was assigned based on the coupling constants observed for peak at 2.97 (1H, td, J = 10.7, 4.0 Hz).

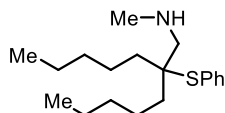
***N*-benzyl-2-(phenylthio)cyclohexan-1-amine (34c)**



Following **GP7**, *trans*-aziridine borane **34a** (40 mg, 0.2 mmol, 2.0 equiv.) and diphenyl disulfide (22 mg, 0.1 mmol) gave **34c** (20%, dr > 10:1) as an oil, R_f 0.34 [*n*-pentane:EtOAc (3:2)]; ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.26 (5H, m), 7.21–7.15 (5H, m), 3.85 (1H, d, J = 13.1 Hz), 3.65 (1H, d, J = 13.1 Hz), 2.87 (1H, ddd, J = 11.5, 9.9, 4.0 Hz), 2.36 (1H, td, J = 9.8, 4.1 Hz), 2.18–2.08 (1H, m), 2.05–1.96 (1H, m), 1.68–1.56 (2H, m), 1.39–1.26 (1H, m), 1.23–1.06 (3H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 140.6, 133.9, 133.4, 128.9, 128.6, 128.4, 127.4, 127.1, 59.2, 53.9, 51.0, 33.6, 32.3, 26.4, 24.5; HRMS (ESI) found MH^+ 298.1624, $\text{C}_{10}\text{H}_{21}\text{N}_2$ requires 298.1619.

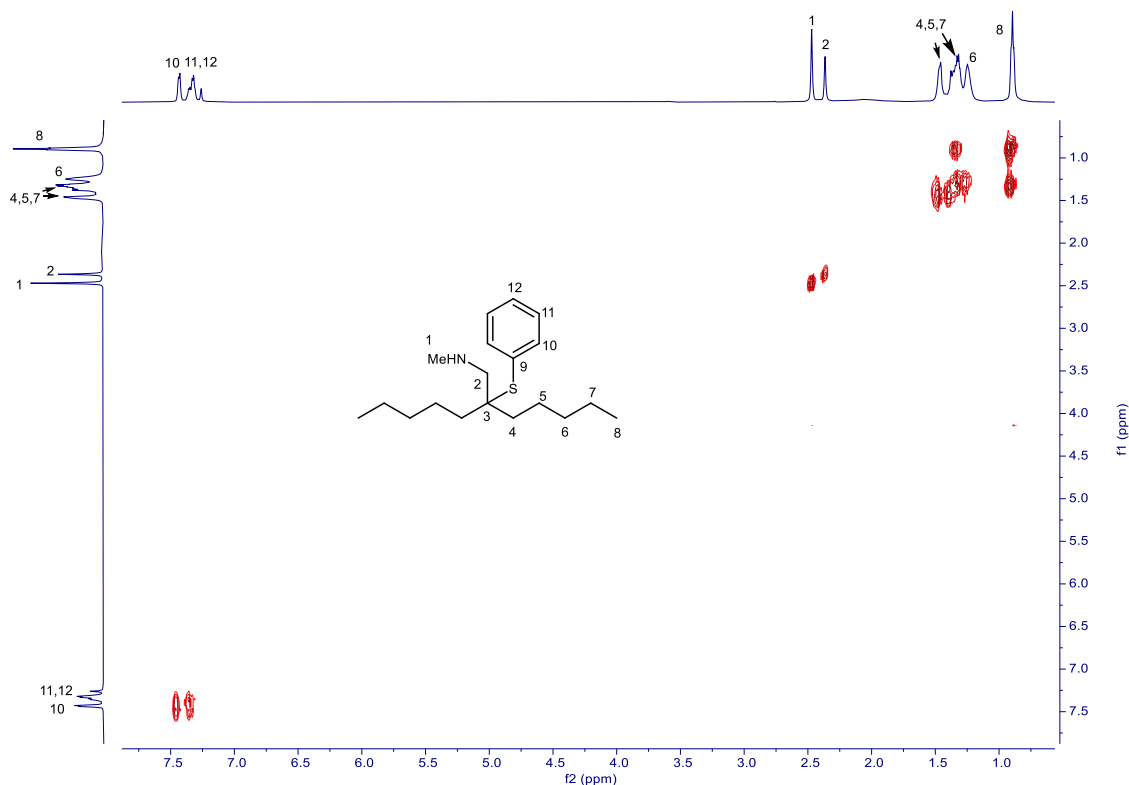
The *trans* configuration was assigned based on the coupling constants observed for peak at 2.87 (1H, ddd, $J = 11.5, 9.9, 4.0$ Hz).

2-Butyl-*N*-methyl-2-(phenylthio)heptan-1-amine (**35c**)

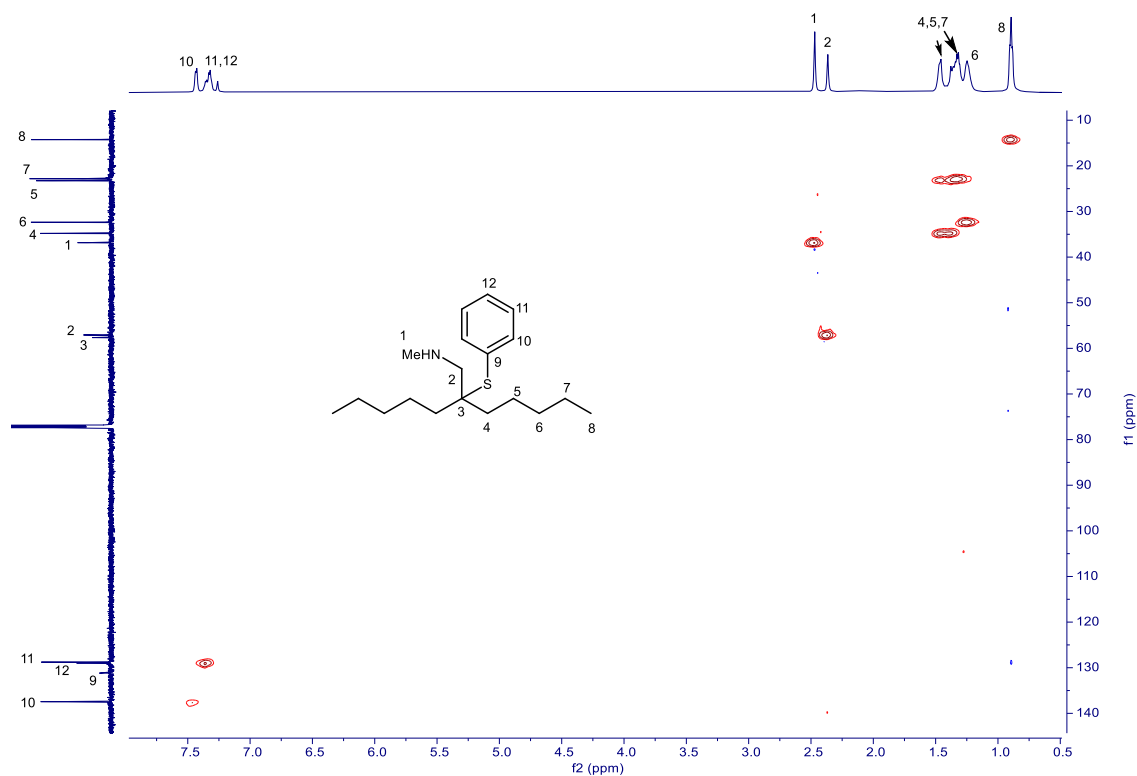


Following **GP7**, **35a** (42 mg, 0.2 mmol, 2 equiv.) and diphenyl disulfide (22 mg, 0.1 mmol) gave **35c** (59%) as an oil. R_f 0.55 [EtOAc]. ^1H (600 MHz, CDCl_3) δ 7.43 (2H, d, $J=7.2$ Hz), 7.38 – 7.28 (3H, m), 2.47 (3H, s), 2.37 (2H, s), 1.54 – 1.43 (4H, m), 1.39 – 1.27 (8H, m), 1.27 – 1.20 (4H, m), 0.89 (6H, t, $J=7.1$ Hz); ^{13}C (151 MHz, CDCl_3) δ 137.4, 131.2, 129.0, 128.8, 57.6, 57.1, 36.8, 34.8, 32.4, 23.3, 22.8, 14.3; HRMS (ESI) found MH^+ 308.2407, $\text{C}_{19}\text{H}_{34}\text{NS}$ requires 308.2407.

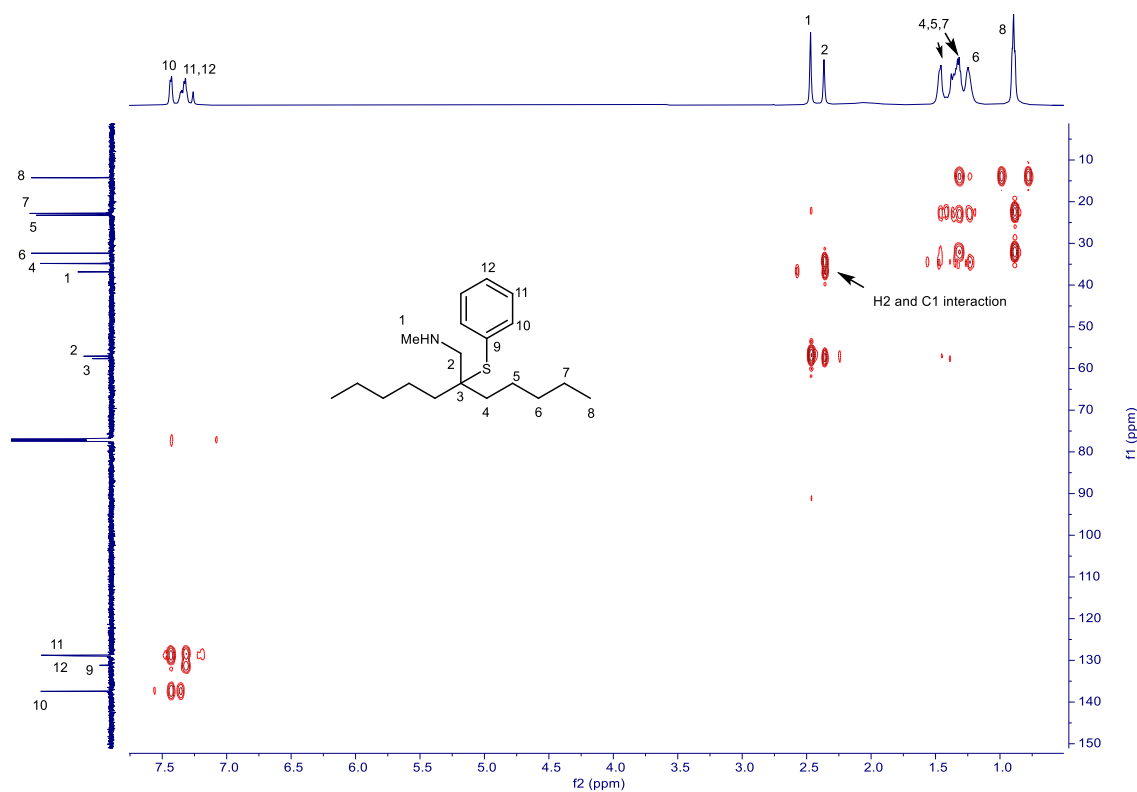
The structure of **1r** was further confirmed by 2D NMR spectroscopy (COSY, HSQC, and HMBC), which also established the regioselectivity of the reaction.



COSY NMR spectrum (600 MHz, CDCl_3 , at rt) of **35c**

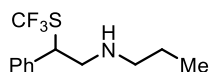


HSQC NMR spectrum (600 MHz, CDCl₃, at rt) of **35c**



HMBC NMR spectrum (600 MHz, CDCl₃, at rt) of **35c**

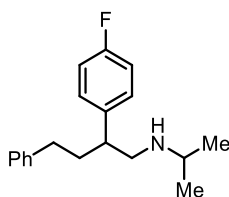
***N*-(2-Phenyl-2-((trifluoromethyl)thio)ethyl)propan-1-amine (1s)**



Following **GP7**, but using AgSCF₃ instead of diaryl disulfide and adding NaHCO₃ (17 mg, 0.2 mmol, 2 equiv.), *trans*-aziridine borane **1a** (35 mg, 0.2 mmol) and AgSCF₃ (21 mg, 0.1 mmol) gave **1s** (40%) as an oil. R_f 0.56 [*n*-pentane:EtOAc (1:1)]. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.26 (m, 5H), 4.52 (t, *J* = 7.1 Hz, 1H), 3.13 (d, *J* = 7.1 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.54 (br s, NH), 1.45 (sx, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 139.2, 130.8 (q, *J* = 308.5 Hz), 129.1, 128.3, 127.7, 54.6, 51.2, 49.4, 23.1, 11.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.72; HRMS (ESI) found MH⁺ 264.1030, C₁₂H₁₇F₃NS requires 264.1028.

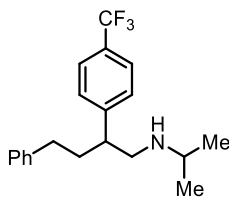
5.4 Ring-Opening–Arylation via Dual Photo–Ni-Catalysis

2-(4-Fluorophenyl)-*N*-isopropyl-4-phenylbutan-1-amine (**13g**)



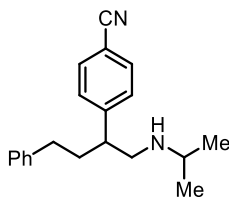
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 1-bromo-4-fluorobenzene (22.0 μ L, 0.2 mmol, 2.0 equiv.) gave **13g** (50%) as an oil. R_f 0.22 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 7.26 (2H, t, $J = 7.4$ Hz), 7.23 – 7.14 (3H, m), 7.11 (2H, d, $J = 7.1$ Hz), 7.05 (2H, t, $J = 8.7$ Hz), 2.90 (1H, dd, $J = 11.2, 5.3$ Hz), 2.84 (1H, hept, $J = 6.0$ Hz), 2.78 – 2.72 (2H, m), 2.52 – 2.43 (2H, m), 2.07 – 2.01 (1H, m), 1.90 – 1.83 (1H, m), 1.03 (3H, d, $J = 6.3$ Hz), 1.00 (3H, d, $J = 6.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 161.8 (d, $J = 243.7$ Hz), 142.1, 139.0 (d, $J = 9.5$ Hz), 129.4 (d, $J = 7.3$ Hz), 128.4, 128.4, 125.9, 115.7 (d, $J = 20.7$ Hz), 53.3, 48.8, 44.9, 36.5, 33.6, 22.7, 22.6; ^{19}F NMR (564 MHz, CDCl_3) δ –116.4; HRMS (ESI) found MH^+ 286.1961, $\text{C}_{19}\text{H}_{25}\text{FN}$ requires 286.1965.

N-Isopropyl-4-phenyl-2-(4-(trifluoromethyl)phenyl)butan-1-amine (**13h**)



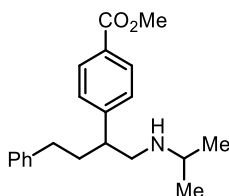
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 1-bromo-4-(trifluoromethyl)benzene (28.0 μ L, 0.2 mmol, 2.0 equiv.) gave **13h** (61%) as an oil. R_f 0.22 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 7.62 (2H, d, $J = 8.2$ Hz), 7.36 (2H, d, $J = 8.2$ Hz), 7.26 (2H, t, $J = 6.0$ Hz), 7.17 (1H, t, $J = 7.4$ Hz), 7.10 (2H, d, $J = 6.9$ Hz), 2.97 – 2.93 (2H, m), 2.85 – 2.81 (1H, m), 2.77 (1H, hept, $J = 6.2$ Hz), 2.47 (2H, t, $J = 6.9$ Hz), 2.14 – 2.09 (1H, m), 1.95 – 1.89 (1H, m), 1.05 (3H, d, $J = 6.3$ Hz), 1.03 (3H, d, $J = 6.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 147.6, 141.8, 129.2 (q, $J = 31.1$ Hz), 128.5, 128.5, 128.4, 126.0, 125.8 (q, $J = 3.7$ Hz), 124.4 (q, $J = 271.8$ Hz), 52.7, 49.0, 45.5, 36.1, 33.6, 22.5, 22.3; ^{19}F NMR (564 MHz, CDCl_3) δ –62.4; HRMS (ESI) found MH^+ 336.1926, $\text{C}_{20}\text{H}_{25}\text{F}_3\text{N}$ requires 336.1934.

4-(1-(Isopropylamino)-4-phenylbutan-2-yl)benzonitrile (**13i**)



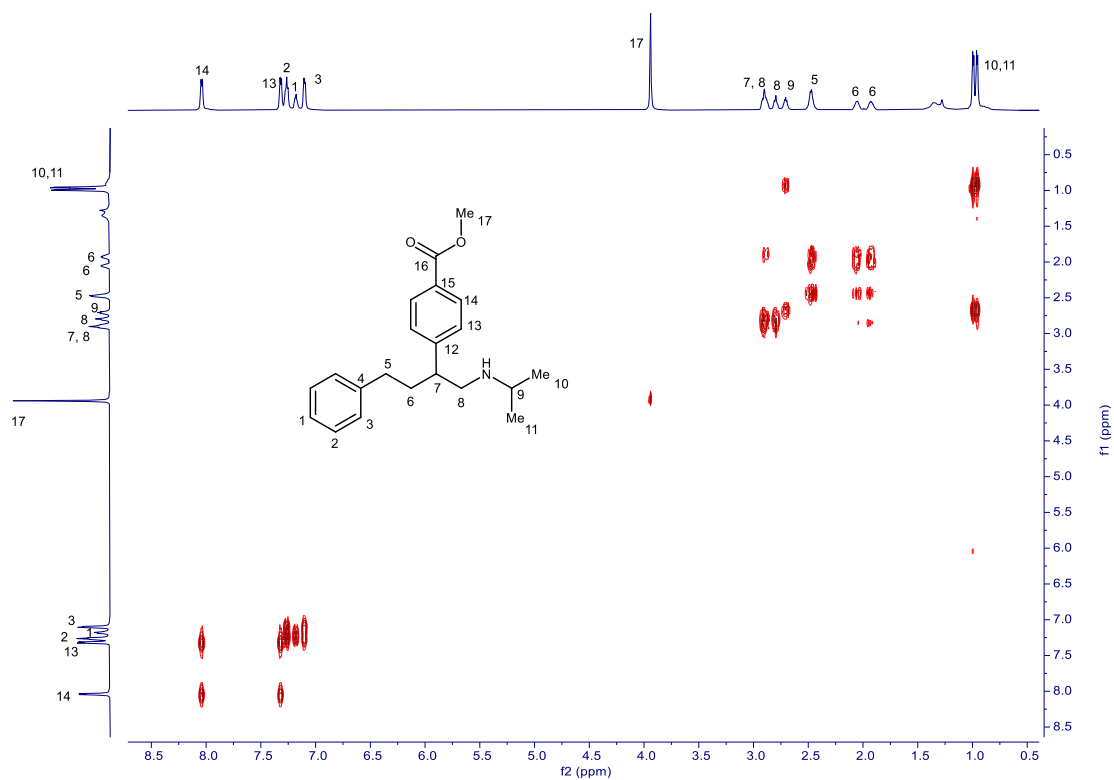
Following **GP8b**, **1331d** (19 mg, 0.1 mmol, 1.0 equiv.) and 4-bromobenzonitrile (36 mg, 0.2 mmol, 2.0 equiv.) gave **13i** (66% over two steps) as an oil. R_f 0.14 [EtOAc]. ^1H (600 MHz, CDCl_3) δ 7.65 – 7.61 (2H, m), 7.35 – 7.30 (2H, m), 7.27 – 7.22 (2H, m), 7.19 – 7.15 (1H, m), 7.09 – 7.05 (2H, m), 2.91 – 2.81 (2H, m), 2.80 – 2.73 (1H, m), 2.68 (1H, hp, $J=6.3$ Hz), 2.50 – 2.39 (2H, m), 2.10 – 2.01 (1H, m), 1.93 – 1.83 (1H, m), 0.98 (1H, d, $J=6.2$ Hz), 0.95 (1H, d, $J=6.2$ Hz); ^{13}C (151 MHz, CDCl_3) δ 149.7, 141.6, 132.6, 128.8, 128.5, 128.4, 126.1, 119.1, 110.6, 53.1, 48.7, 46.3, 36.0, 33.6, 23.0, 22.9. HRMS (ESI) found MH^+ 293.2013, $\text{C}_{20}\text{H}_{25}\text{N}_2$ requires 293.2012.

Methyl 4-(1-(Isopropylamino)-4-phenylbutan-2-yl)benzoate (**13j**)

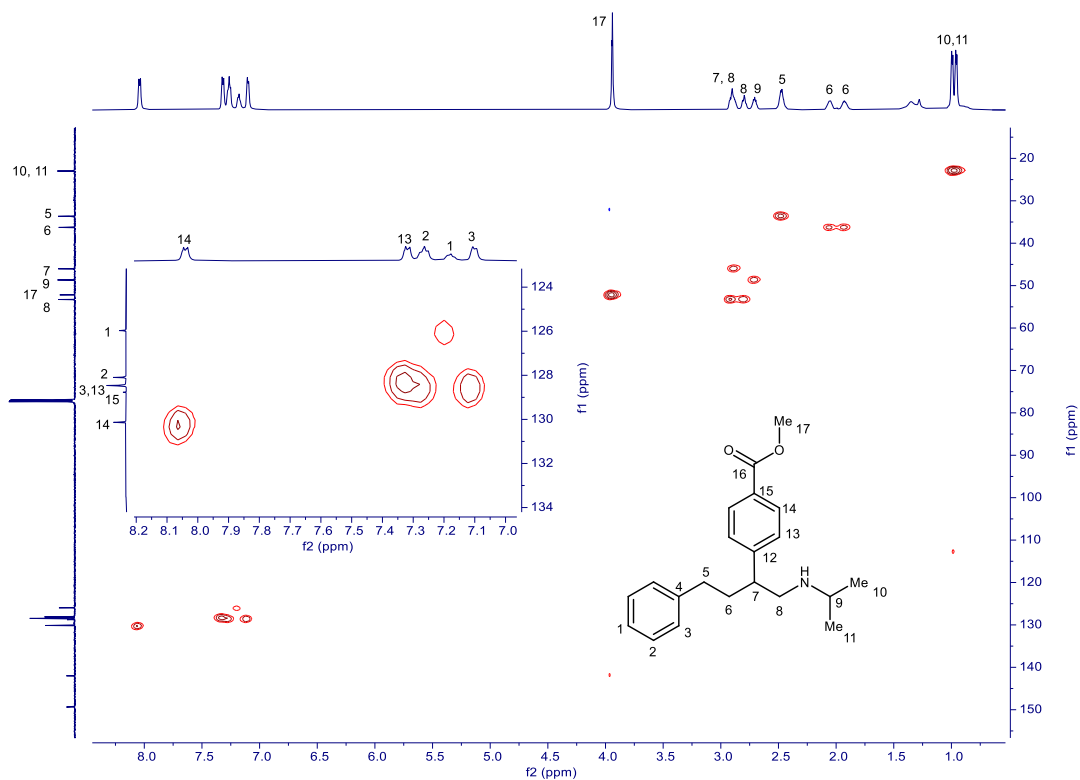


Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **13j** (82%) as an oil. R_f 0.18 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 8.04 (2H, dd, $J=7.9, 2.8$ Hz), 7.32 (2H, dd, $J=7.9, 2.8$ Hz), 7.27 (2H, t, $J=8.0$ Hz), 7.18 (1H, t, $J=7.7$ Hz), 7.10 (2H, d, $J=7.5$ Hz), 3.94 (3H, s), 2.94 – 2.85 (2H, m), 2.83 – 2.76 (1H, m), 2.74 – 2.68 (1H, m), 2.53 – 2.42 (2H, m), 2.09 – 2.02 (1H, m), 1.96 – 1.89 (1H, m), 1.02 – 0.92 (6H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 149.4, 142.0, 130.1, 128.8, 128.5, 128.1, 126.0, 53.3, 52.2, 48.7, 46.1, 36.3, 33.7, 23.0, 22.9; HRMS (ESI) found MH^+ 326.2102, $\text{C}_{21}\text{H}_{28}\text{NO}_2$ requires 326.2115.

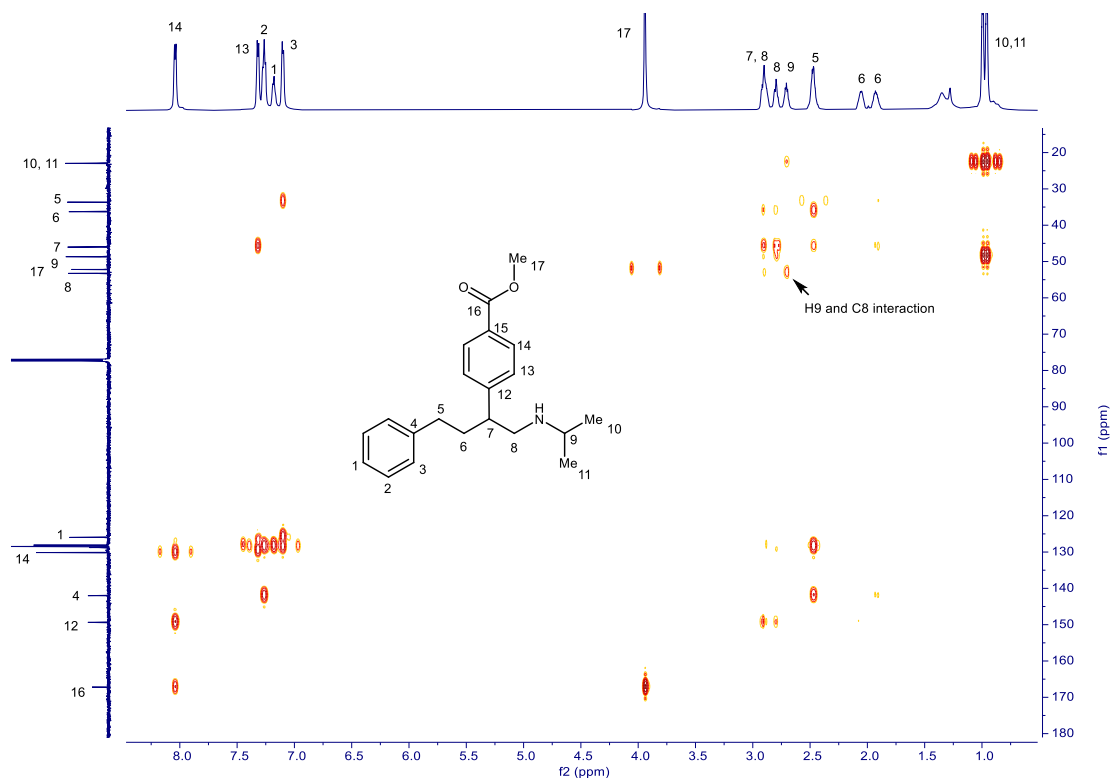
The structure of **13j** was further confirmed by 2D NMR spectroscopy (COSY, HSQC, and HMBC), which also established the regioselectivity of the reaction.



COSY NMR spectrum (600 MHz, CDCl₃, at rt) of **13j**

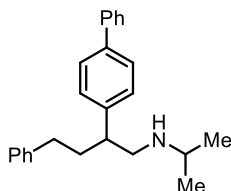


HSQC NMR spectrum (600 MHz, CDCl₃, at rt) of **13j**



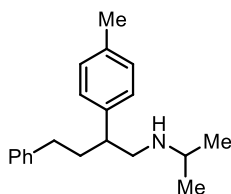
HMBC NMR spectrum (600 MHz, CDCl₃, at rt) of **13j**

2-([1,1'-biphenyl]-4-yl)-N-isopropyl-4-phenylbutan-1-amine (13k**)**



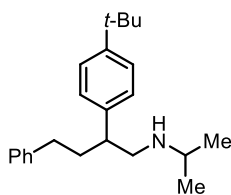
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 4-bromo-1,1'-biphenyl (47 mg, 0.2 mmol, 2.0 equiv.) gave **13k** (51%) as an oil. *R*_f 0.32 [DCM:MeOH (15:1)]. ¹H NMR (600 MHz, CDCl₃) δ 7.58 – 7.47 (4H, m), 7.37 (2H, t, *J*=7.4 Hz), 7.31 – 7.14 (5H, m), 7.11 – 7.01 (3H, m), 2.96 – 2.81 (2H, m), 2.79 – 2.66 (2H, m), 2.50 – 2.38 (2H, m), 1.99 (1H, dtd, *J*=14.0, 10.2, 5.1 Hz), 1.91 – 1.82 (1H, m), 0.96 (3H, d, *J*=6.3 Hz), 0.94 (3H, d, *J*=6.3 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 142.3, 142.3, 141.0, 139.7, 128.9, 128.5, 128.4, 128.4, 127.6, 127.3, 127.1, 125.9, 53.1, 48.9, 45.2, 36.4, 33.7, 22.6, 22.4; HRMS (ESI) found *MH*⁺ 344.2372, C₂₅H₃₀N requires 344.2373.

***N*-isopropyl-4-phenyl-2-(*p*-tolyl)butan-1-amine (13l)**



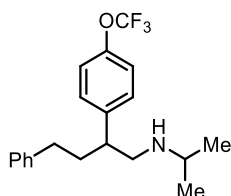
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 1-bromo-4-methylbenzene (43 mg, 0.25 mmol, 2.5 equiv.) gave **13l** (51%) as an oil. R_f 0.31 [DCM:MeOH (15:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (2H, t, 7.7 Hz), 7.21 – 7.05 (7H, m), 2.94 (1H, dd, $J=10.6, 5.0$ Hz), 2.86 (1H, tt, $J=9.5, 4.6$ Hz), 2.82 – 2.71 (2H, m), 2.56 – 2.43 (2H, m), 2.37 (3H, s), 2.12 – 1.99 (1H, m), 1.96 – 1.82 (1H, m), 1.11 – 0.97 (6H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 142.4, 140.0, 136.4, 129.6, 128.5, 128.4, 127.9, 125.8, 53.0, 48.9, 45.0, 36.5, 33.7, 22.5, 22.3, 21.2; HRMS (ESI) found MH^+ 282.2214, $\text{C}_{20}\text{H}_{28}\text{N}$ requires 282.2216.

2-(4-(*tert*-butyl)phenyl)-*N*-isopropyl-4-phenylbutan-1-amine (13m)



Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 1-bromo-4-(*tert*-butyl)benzene (35 mg, 0.2 mmol, 2.0 equiv.) gave **13m** (58%) as an oil. R_f 0.46 [DCM:MeOH (10:1)]. ^1H (600 MHz, CDCl_3) δ 7.3 (1H, d, $J=8.4$ Hz), 7.19 – 7.14 (2H, m), 7.11 – 6.97 (5H, m), 2.85 (1H, dd, $J=11.2, 5.5$ Hz), 2.78 (1H, tt, $J=9.9, 5.1$ Hz), 2.73 – 2.82 (2H, m), 2.47 – 2.35 (2H, m), 2.00 – 1.91 (1H, m), 1.82 (1H, dtd, $J=13.2, 9.3, 6.1$ Hz), 1.25 (9H, s), 0.96 (3H, d, $J=6.3$ Hz), 0.94 (3H, d, $J=6.3$ Hz); ^{13}C (151 MHz, CDCl_3) δ 149.6, 142.5, 139.9, 128.5, 128.4, 127.6, 125.8, 125.7, 52.9, 48.9, 44.8, 36.4, 34.6, 33.8, 31.5, 22.5, 22.2; HRMS (ESI) found MH^+ 324.2677, $\text{C}_{23}\text{H}_{34}\text{N}$ requires 324.2686.

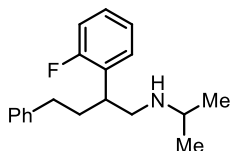
***N*-isopropyl-4-phenyl-2-(4-(trifluoromethoxy)phenyl)butan-1-amine (13o)**



Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 1-bromo-4-(trifluoromethoxy)benzene (48 mg, 0.2 mmol, 2.0 equiv.) gave **13o** (76%) as an oil. R_f 0.32 [DCM:MeOH (15:1)]. ^1H NMR (600 MHz, CDCl_3) δ 7.29 – 7.22 (4H, m), 7.21 – 7.12 (3H, m),

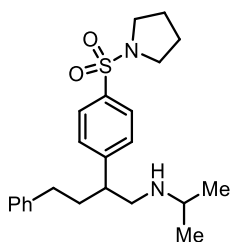
7.09 (2H, d, $J=7.4$ Hz), 2.90 (1H, dd, $J=11.1, 5.3$ Hz), 2.88 – 2.81 (1H, m), 2.81 – 2.70 (2H, m), 2.54 – 2.41 (2H, m), 2.09 – 2.01 (1H, m), 1.87 (1H, dtd, $J=14.7, 9.3, 5.7$ Hz), 1.01 (3H, d, $J=6.2$ Hz), 0.98 (3H, d, $J=6.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 148.1, 142.2, 142.0, 129.2, 128.5, 128.5, 126.0, 121.3, 120.7 (q, $J=257.0$ Hz), 53.2, 48.9, 45.1, 36.3, 33.6, 22.7, 22.6; ^{19}F NMR (564 MHz, CDCl_3) δ -57.84; HRMS (ESI) found MH^+ 352.1881, $\text{C}_{20}\text{H}_{25}\text{F}_3\text{NO}$ requires 352.1883.

2-(2-Fluorophenyl)-*N*-isopropyl-4-phenylbutan-1-amine (13p)



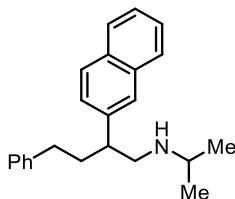
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 1-bromo-2-fluorobenzene (21.8 μL , 0.2 mmol, 2.0 equiv.) gave **13p** (44%) as an oil. R_f 0.22 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 7.27 – 7.22 (4H, m), 7.18 – 7.12 (4H, m), 7.07 (1H, t, $J = 9.0$ Hz), 3.22 – 3.17 (1H, m), 2.92 – 2.85 (2H, m), 2.75 (1H, hept, $J = 6.3$ Hz), 2.52 (2H, t, $J = 6.6$ Hz), 2.09 – 2.03 (1H, m), 2.00 – 1.93 (1H, m), 1.00 (3H, d, $J = 6.7$ Hz), 0.99 (3H, d, $J = 6.7$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 161.6 (d, $J = 244.7$ Hz), 142.2, 129.9 (d, $J = 14.5$ Hz), 129.2 (d, $J = 5.0$ Hz), 128.5, 128.4, 128.2 (d, $J = 8.3$ Hz), 125.9, 124.5 (d, $J = 3.6$ Hz), 115.8 (d, $J = 23.1$ Hz), 51.7, 48.7, 39.2, 35.2, 33.8, 22.6, 22.5; ^{19}F NMR (564 MHz, CDCl_3) δ -117.5; HRMS (ESI) found MH^+ 286.1961, $\text{C}_{19}\text{H}_{25}\text{FN}$ requires 286.1965.

N-Isopropyl-4-phenyl-2-(4-(pyrrolidin-1-ylsulfonyl)phenyl)butan-1-amine (13q)



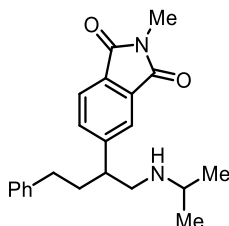
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 1-((4-bromophenyl)sulfonyl)pyrrolidine (58 mg, 0.2 mmol, 2.0 equiv.) gave **13q** (62%) as a syrup. R_f 0.22 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 7.81 (2H, d, $J = 7.9$ Hz), 7.39 (2H, d, $J = 7.9$ Hz), 7.26 (2H, t, $J = 7.5$ Hz), 7.17 (2H, t, $J = 7.4$ Hz), 7.10 (2H, d, $J = 7.5$ Hz), 3.30 – 3.27 (4H, m), 2.95 – 2.91 (2H, m), 2.84 – 2.80 (1H, m), 2.73 (1H, hept, $J = 6.2$ Hz), 2.48 (2H, t, $J = 7.9$ Hz), 2.13 – 2.07 (1H, m), 1.96 – 1.89 (1H, m), 1.79 – 1.77 (4H, m), 1.02 (3H, d, $J = 6.3$ Hz), 0.99 (3H, d, $J = 6.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 149.0, 141.7, 135.6, 128.7, 128.5, 128.4, 128.0, 126.1, 52.9, 48.9, 48.1, 45.8, 36.0, 33.7, 25.4, 22.8, 22.6; HRMS (ESI) found MH^+ 401.2247, $\text{C}_{23}\text{H}_{33}\text{N}_2\text{O}_2\text{S}$ requires 401.2257.

***N*-Isopropyl-2-(naphthalen-2-yl)-4-phenylbutan-1-amine (13r)**



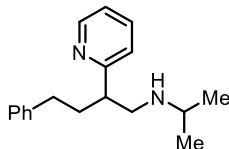
Following **GP8b**, **13** (19 mg, 0.1 mmol, 1.0 equiv.) and 2-bromonaphthalene (41 mg, 0.2 mmol, 2.0 equiv.) gave **13r** (45% over two steps) as an oil. R_f 0.14 [EtOAc]. ^1H (600 MHz, CDCl_3) δ 7.88 – 7.81 (3H, m), 7.68 (1H, d, $J=1.7$ Hz), 7.52 – 7.44 (2H, m), 7.39 (1H, dd, $J=8.5, 1.7$ Hz), 7.28 – 7.22 (2H, m), 7.19 – 7.13 (1H, m), 7.13 – 7.08 (2H, m), 3.03 – 2.93 (2H, m), 2.90 – 2.83 (1H, m), 2.71 (1H, hp, $J=6.2$ Hz), 2.54 – 2.45 (2H, m), 2.13 – 1.96 (2H, m), 0.98 (3H, d, $J=6.2$ Hz), 0.93 (3H, d, $J=6.2$ Hz); ^{13}C (151 MHz, CDCl_3) δ 142.4, 141.0, 133.7, 132.7, 128.7, 128.5, 128.4, 127.8, 127.3, 126.2, 125.9, 125.6, 125.6, 53.4, 48.7, 46.1, 36.5, 33.8, 23.0, 22.9. HRMS (ESI) found MH^+ 318.2212, $\text{C}_{23}\text{H}_{28}\text{N}$ requires 318.2216.

5-(1-(Isopropylamino)-4-phenylbutan-2-yl)-2-methylisoindoline-1,3-dione (13s)



Following **GP8b**, **13** (19 mg, 0.1 mmol, 1.0 equiv.) and 5-bromo-2-methylisoindoline-1,3-dione (48 mg, 0.2 mmol, 2.0 equiv.) gave **13s** (50% over two steps) as an oil R_f 0.14 [EtOAc]. ^1H (600 MHz, CDCl_3) δ 7.73 (1H, d, $J=7.6$ Hz), 7.65 (1H, s), 7.46 (1H, dd, $J=7.6, 1.5$ Hz), 7.20 – 7.15 (2H, m), 7.09 (1H, t, $J=7.4$ Hz), 7.00 (2H, d, $J=7.5$ Hz), 3.11 (3H, s), 2.91 – 2.81 (2H, m), 2.74 (1H, dd, $J=11.2, 8.3$ Hz), 2.62 (1H, hp, $J=6.2$ Hz), 2.43 – 2.35 (2H, m), 2.07 – 1.98 (1H, m), 1.91 – 1.81 (1H, m), 0.90 (3H, d, $J=6.2$ Hz), 0.87 (3H, d, $J=6.2$ Hz); ^{13}C (151 MHz, CDCl_3) δ 168.8, 168.5, 151.5, 141.5, 134.1, 133.1, 130.8, 128.6, 128.4, 126.1, 123.6, 122.3, 53.2, 48.8, 46.6, 36.1, 33.6, 24.1, 23.0, 22.9. HRMS (ESI) found MH^+ 351.2064, $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_2$ requires 351.2067.

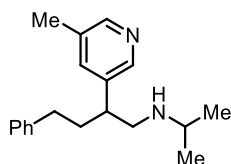
***N*-Isopropyl-4-phenyl-2-(pyridin-2-yl)butan-1-amine (13t)**



Following **GP8a**, but using 3,3',5,5'-tetrakis(trifluoromethyl)benzophenone (20 mol%) and heteroaryl bromide (3 equiv.), *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 2-

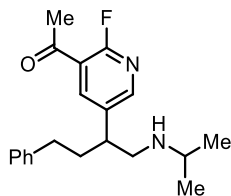
bromopyridine (28.7 μ L, 0.3 mmol, 3.0 equiv.) gave **13t** (45%) as an oil. R_f 0.14 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 8.60 (1H, d, J = 4.8 Hz), 7.63 (2H, t, J = 7.7 Hz), 7.24 (2H, t, J = 7.5 Hz), 7.16 – 7.11 (5H, m), 3.08 – 3.01 (2H, m), 2.96 – 2.91 (1H, m), 2.80 (1H, hept, J = 6.3 Hz), 2.49 (2H, t, J = 8.0 Hz), 2.14 – 2.00 (2H, m), 1.04 (3H, d, J = 6.3 Hz), 1.02 (3H, d, J = 6.3 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 163.1, 149.7, 142.2, 136.6, 128.5, 128.4, 125.9, 123.9, 121.8, 51.6, 49.0, 46.8, 35.3, 33.6, 22.5, 22.5; HRMS (ESI) found MH^+ 269.2009, $\text{C}_{18}\text{H}_{25}\text{N}_2$ requires 269.2012.

N-Isopropyl-2-(5-methylpyridin-3-yl)-4-phenylbutan-1-amine (13u)



Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 3-bromo-5-methylpyridine (23.1 μ L, 0.2 mmol, 2.0 equiv.) gave **13u** (60%) as an oil. R_f 0.21 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 8.24 (1H, s), 8.15 (1H, s), 7.26 (1H, s), 7.14 (2H, t, J = 7.5 Hz), 7.06 (1H, t, J = 7.4 Hz), 6.99 (2H, d, J = 7.6 Hz), 2.85 – 2.71 (4H, m), 2.37 (2H, t, J = 8.0 Hz), 2.24 (3H, s), 1.99 – 1.94 (1H, m), 1.83 – 1.77 (1H, m), 0.96 (3H, d, J = 6.2 Hz), 0.93 (3H, d, J = 6.2 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 148.8, 147.1, 141.7, 138.1, 136.0, 133.3, 128.5, 128.4, 126.0, 52.8, 49.1, 43.0, 36.0, 33.6, 29.8, 22.4, 18.6; HRMS (ESI) found MH^+ 283.2165, $\text{C}_{19}\text{H}_{27}\text{N}_2$ requires 283.2169.

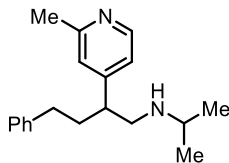
1-(2-Fluoro-5-(1-(isopropylamino)-4-phenylbutan-2-yl)pyridin-3-yl)ethanone (13v)



Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 3-acetyl-5-bromo-2-fluoropyridine (47 mg, 0.2 mmol, 2.0 equiv.) gave **13v** (43%) as an oil. R_f 0.22 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 8.22 (1H, s), 8.19 (1H, dd, J = 9.0, 2.6 Hz), 7.26 (2H, t, J = 8.4 Hz), 7.18 (1H, t, J = 7.3 Hz), 7.08 (2H, d, J = 7.5 Hz), 2.93 – 2.86 (2H, m), 2.81 (1H, dd, J = 10.8, 7.6 Hz), 2.75 – 2.68 (4H, m), 2.54 – 2.45 (2H, m), 2.16 – 2.10 (1H, m), 1.95 – 1.88 (1H, m), 1.01 (3H, d, J = 6.2 Hz), 0.99 (3H, d, J = 6.3 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 194.9, 160.9 (d, J = 243.2 Hz), 151.7 (d, J = 14.9 Hz), 141.3, 140.5 (d, J = 2.5 Hz), 138.0, 128.6, 128.4, 126.2, 119.8 (d, J = 28.7 Hz), 52.7, 48.9, 42.6, 35.6, 33.5, 31.2, 31.1,

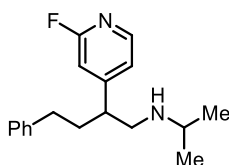
22.8; ^{19}F NMR (564 MHz, CDCl_3) δ -65.4; HRMS (ESI) found MH^+ 329.2021, $\text{C}_{20}\text{H}_{26}\text{FN}_2\text{O}$ requires 329.2024.

***N*-Isopropyl-2-(2-methylpyridin-4-yl)-4-phenylbutan-1-amine (13w)**



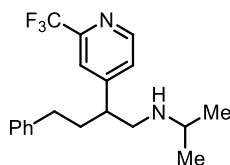
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 4-bromo-2-methylpyridine (23.7 μL , 0.2 mmol, 2.0 equiv.) gave **13w** (60%) as an oil. R_f 0.13 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 8.44 (1H, d, J = 5.1 Hz), 7.26 (3H, t, J = 7.5 Hz), 7.17 (1H, t, J = 7.4 Hz), 7.10 (2H, d, J = 7.5 Hz), 7.03 (1H, s), 6.98 (1H, d, J = 5.1 Hz), 2.92 – 2.88 (1H, m), 2.83 – 2.73 (3H, m), 2.56 (3H, s), 2.48 (2H, t, J = 8.2 Hz), 2.08 – 2.02 (1H, m), 1.92 – 1.86 (1H, m), 1.03 (3H, d, J = 6.3 Hz), 1.01 (3H, d, J = 6.2 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 158.8, 153.1, 149.5, 141.7, 128.5, 128.4, 126.0, 123.1, 120.4, 52.6, 48.9, 45.3, 35.6, 33.6, 24.6, 22.7, 22.6; HRMS (ESI) found MH^+ 283.2165, $\text{C}_{19}\text{H}_{27}\text{N}_2$ requires 283.2169.

2-(2-Fluoropyridin-4-yl)-*N*-isopropyl-4-phenylbutan-1-amine (13x)



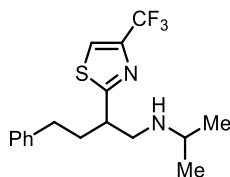
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 4-bromo-2-fluoropyridine (20.5 μL , 0.2 mmol, 2.0 equiv.) gave **13x** (50%) as an oil. R_f 0.28 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 8.17 (1H, d, J = 5.1 Hz), 7.26 (2H, t, J = 7.5 Hz), 7.18 (1H, t, J = 7.4 Hz), 7.09 (2H, d, J = 7.5 Hz), 7.05 (1H, d, J = 5.1 Hz), 6.79 (1H, s), 2.89 – 2.77 (3H, m), 2.71 (1H, hept, J = 5.3 Hz), 2.53 – 2.44 (2H, m), 2.09 – 2.03 (1H, m), 1.92 – 1.86 (1H, m), 1.00 (3H, d, J = 6.3 Hz), 0.98 (3H, d, J = 6.2 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 164.4 (d, J = 239.0 Hz), 159.5 (d, J = 7.8 Hz), 147.9 (d, J = 15.6 Hz), 141.4, 128.6, 128.4, 126.2, 121.1 (d, J = 4.1 Hz), 108.9 (d, J = 37.2 Hz), 52.6, 48.8, 45.7, 35.5, 33.5, 22.9, 22.9; ^{19}F NMR (564 MHz, CDCl_3) δ -68.3; HRMS (ESI) found MH^+ 287.1914, $\text{C}_{18}\text{H}_{24}\text{FN}_2$ requires 287.1918.

***N*-Isopropyl-4-phenyl-2-(2-(trifluoromethyl)pyridin-4-yl)butan-1-amine (13y)**



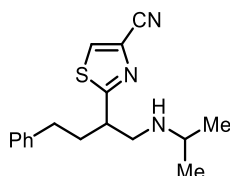
Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 4-bromo-2-(trifluoromethyl)pyridine (26.5 μ L, 0.2 mmol, 2.0 equiv.) gave **13y** (58%) as an oil. R_f 0.22 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 8.66 (1H, d, J = 5.1 Hz), 7.53 (1H, s), 7.34 (1H, d, J = 3.5 Hz), 7.26 (2H, t, J = 7.6 Hz), 7.18 (1H, t, J = 7.4 Hz), 7.08 (2H, d, J = 7.1 Hz), 2.91 – 2.81 (3H, m), 2.71 (1H, hept, J = 6.2 Hz), 2.53 – 2.45 (2H, m), 2.14 – 2.09 (1H, m), 1.96 – 1.89 (1H, m), 1.00 (3H, d, J = 6.2 Hz), 0.98 (3H, d, J = 6.2 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 155.5, 150.2, 148.7 (q, J = 34.3 Hz), 141.2, 128.6, 128.4, 126.3, 126.2, 121.8 (q, J = 273.9 Hz), 120.9, 52.4, 48.8, 45.9, 35.3, 33.5, 22.9, 22.9; ^{19}F NMR (564 MHz, CDCl_3) δ –67.9; HRMS (ESI) found MH^+ 337.1881, $\text{C}_{19}\text{H}_{24}\text{F}_3\text{N}_2$ requires 337.1886.

***N*-Isopropyl-4-phenyl-2-(4-(trifluoromethyl)thiazol-2-yl)butan-1-amine (13z)**



Following **GP8a**, *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 2-bromo-4-(trifluoromethyl)thiazole (24.4 μ L, 0.2 mmol, 2.0 equiv.) gave **13z** (46%) as an oil. R_f 0.30 [$\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_3$ 15:1:0.01]. ^1H NMR (600 MHz, CDCl_3) δ 7.65 (1H, s), 7.27 (2H, t, J = 7.5 Hz), 7.18 – 7.14 (3H, m), 3.31 (1H, p, J = 6.8 Hz), 3.01 – 2.93 (2H, m), 2.77 (1H, hept, J = 6.3 Hz), 2.63 (2H, t, J = 7.9 Hz), 2.16 – 2.06 (2H, m), 1.03 (3H, d, J = 6.0 Hz), 1.02 (3H, d, J = 6.1 Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 176.3, 144.2 (q, J = 36.2 Hz), 141.4, 128.6, 128.5, 126.2, 120.7 (q, J = 270.5 Hz), 120.5 (q, J = 3.0 Hz), 51.3, 48.9, 44.4, 35.7, 33.4, 22.9, 22.8; ^{19}F NMR (564 MHz, CDCl_3) δ –63.8; HRMS (ESI) found MH^+ 343.1459, $\text{C}_{17}\text{H}_{22}\text{F}_3\text{N}_2\text{S}$ requires 343.1450.

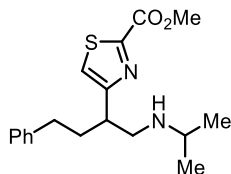
2-(1-(Isopropylamino)-4-phenylbutan-2-yl)thiazole-4-carbonitrile (13ab)



Following **GP8a**, but using 3,3',5,5'-tetrakis(trifluoromethyl)benzophenone (20 mol%) and heteroaryl bromide (3 equiv.), *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and 2-bromo-4-cyanothiazole (57 mg, 0.3 mmol, 3.0 equiv.) gave **13ab** (43%) as an oil. R_f 0.29

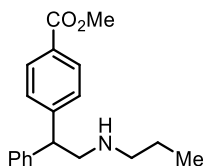
[CH₂Cl₂/MeOH/NH₃ 15:1:0.01]. ¹H NMR (600 MHz, CDCl₃) δ 7.89 (1H, s), 7.27-7.24 (2H, m), 7.18 (1H, t, *J* = 7.4 Hz), 7.14 (2H, d, *J* = 7.4 Hz), 3.28 – 3.23 (1H, m), 2.97 – 2.90 (2H, m), 2.74 (1H, hept, *J* = 6.0 Hz), 2.61 (2H, t, *J* = 7.9 Hz), 2.15 – 2.03 (2H, m), 1.08 (3H, d, *J* = 5.5 Hz), 1.01 (3H, d, *J* = 5.6 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 175.8, 141.2, 130.4, 128.6, 128.5, 126.3, 126.1, 114.5, 51.1, 49.0, 44.4, 35.5, 33.4, 23.0, 22.9; HRMS (ESI) found MH⁺ 300.1535, C₁₇H₂₂N₃S requires 300.1529.

Methyl 4-(1-(isopropylamino)-4-phenylbutan-2-yl)thiazole-2-carboxylate (**13ac**)



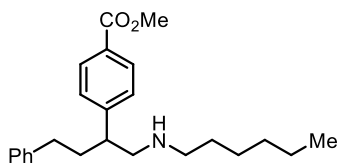
Following **GP8a**, but using 3,3',5,5'-tetrakis(trifluoromethyl)benzophenone (20 mol%) and heteroaryl bromide (3 equiv.), *trans*-aziridine borane **13a** (20 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromothiazole-2-carboxylate (67 mg, 0.3 mmol, 3.0 equiv.) gave **13ac** (33%) as an oil. *R_f* 0.39 [CH₂Cl₂/MeOH/NH₃ 15:1:0.01; double run]. ¹H NMR (600 MHz, CDCl₃) δ 7.36 (1H, s), 7.24 (2H, t, *J* = 7.6 Hz), 7.15 (1H, t, *J* = 7.4 Hz), 7.11 (2H, d, *J* = 7.5 Hz), 4.01 (3H, s), 3.28 – 3.23 (1H, m), 3.06 (1H, t, *J* = 10.2 Hz), 3.00 (1H, dd, *J* = 12.1, 5.4 Hz), 2.83 (1H, hept, *J* = 6.0 Hz), 2.55 – 2.48 (2H, m), 2.17 – 2.05 (2H, m), 1.08 (3H, d, *J* = 6.3 Hz), 1.06 (3H, d, *J* = 6.2 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 161.0, 160.6, 157.9, 141.7, 128.5, 128.5, 126.0, 121.7, 53.3, 50.8, 49.3, 41.6, 34.6, 33.5, 22.2, 22.1; HRMS (ESI) found MH⁺ 333.1639, C₁₈H₂₅N₂O₂S requires 333.1631.

Methyl 4-(1-phenyl-2-(propylamino)ethyl)benzoate (**1t**)



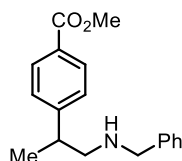
Following **GP8a**, *trans*-aziridine borane **1a** (18 mg, 0.1 mmol, 1.0 equiv.) and 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **1t** (19%) as an oil. *R_f* 0.31 [EtOAc]. ¹H NMR (600 MHz, CDCl₃) δ 7.97 (2H, d, *J* = 8.3 Hz), 7.35 – 7.29 (4H, m), 7.25 – 7.20 (3H, m), 4.26 (1H, t, *J* = 7.6 Hz), 3.89 (3H, s), 3.29 – 3.22 (2H, m), 2.61 (2H, t, *J* = 7.3 Hz), 1.45 (2H, sx, *J* = 7.4 Hz), 0.84 (3H, t, *J* = 7.4 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 167.1, 148.5, 142.2, 130.1, 128.9, 128.6, 128.2, 128.2, 127.0, 54.3, 52.2, 51.9, 51.4, 23.1, 11.8; HRMS (ESI) found MH⁺ 298.1795, C₁₉H₂₄NO₂ requires 298.1802.

Methyl 4-(1-(Hexylamino)-4-phenylbutan-2-yl)benzoate (27c)



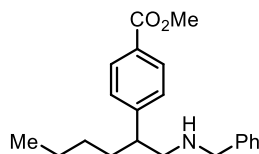
Following **GP8a**, *trans*-aziridine borane **27a** (25 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **27c** (65%) as an oil. R_f 0.49 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 8.02 (2H, d, $J=8.3$ Hz), 7.29 (2H, d, $J=8.2$ Hz), 7.24 (2H, t, $J=7.6$ Hz), 7.16 (1H, t, $J=7.4$ Hz), 7.08 (2H, d, $J=6.8$ Hz), 3.92 (3H, s), 2.93 – 2.84 (2H, m), 2.81 (1H, dd, $J=11.4, 8.8$ Hz), 2.57 – 2.41 (4H, m), 2.03 (1H, dddd, $J=14.3, 9.7, 7.1, 4.7$ Hz), 1.91 (1H, dtd, $J=13.6, 9.4, 5.7$ Hz), 1.41 – 1.30 (2H, m), 1.28 – 1.17 (6H, m), 0.85 (3H, t, $J=7.1$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 149.4, 142.0, 130.1, 128.7, 128.5, 128.1, 125.9, 55.8, 52.1, 50.1, 45.9, 36.1, 33.6, 31.8, 30.0, 27.0, 22.7, 14.1; HRMS (ESI) found MH^+ 368.2578, $\text{C}_{24}\text{H}_{34}\text{NO}_2$ requires 368.2584.

Methyl 4-(1-(Benzylamino)propan-2-yl)benzoate (28c)



Following **GP8a**, *trans*-aziridine borane **28a** (16 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **28c** (47%) as an oil. R_f 0.29 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.90 (2H, d, $J=8.3$ Hz), 7.25 – 7.13 (7H, m), 3.83 (3H, s), 3.70 (1H, d, $J=13.4$ Hz), 3.65 (1H, d, $J=13.4$ Hz), 2.95 (1H, h, $J=7.0$ Hz), 2.75 – 2.72 (2H, dd, $J=7.2, 1.3$ Hz), 1.44 (1H, br s), 1.19 (3H, d, $J=6.9$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 151.1, 140.3, 130.0, 128.5, 128.1, 127.4, 127.1, 56.1, 53.9, 52.1, 40.4, 20.0; HRMS (ESI) found MH^+ 284.1642, $\text{C}_{18}\text{H}_{22}\text{NO}_2$ requires 284.1645.

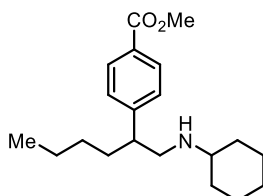
Methyl 4-(1-(Benzylamino)hexan-2-yl)benzoate (29c)



Following **GP8a**, *trans*-aziridine borane **29a** (20 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **29c** (46%) as an oil. R_f 0.20 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.98 (2H, d, $J=8.3$ Hz), 7.28 (2H, t, $J=7.5$ Hz), 7.26 – 7.17 (5H, m), 3.91 (3H, s), 3.76 (1H, d, $J=13.4$ Hz), 3.69 (1H, d, $J=13.4$ Hz), 2.90 – 2.77 (3H, m), 1.67 (1H, ddt, $J=13.4, 10.4, 5.2$ Hz), 1.57 – 1.51 (1H, m), 1.47 (1H, s), 1.32 – 1.05 (4H, m), 0.81 (3H, t,

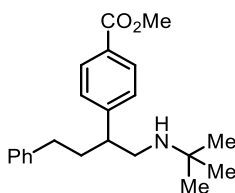
$J=7.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 149.9, 140.3, 130.0, 128.5, 128.5, 128.1, 128.0, 127.0, 55.0, 54.0, 52.1, 46.5, 34.2, 29.7, 22.8, 14.1; HRMS (ESI) found MH^+ 326.2108, $\text{C}_{21}\text{H}_{28}\text{NO}_2$ requires 326.2115.

Methyl 4-(1-(Cyclohexylamino)hexan-2-yl)benzoate (38b)



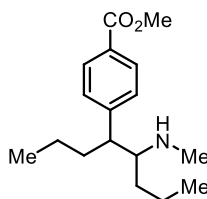
Following **GP8b**, **38** (18 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **38b** (57% over two steps) as an oil. R_f 0.19 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 8.00 (2H, d, $J=8.0$ Hz), 7.29 (2H, d, $J=7.7$ Hz), 3.93 (3H, s), 2.93 (1H, dd, $J=10.3$, 4.0 Hz), 2.88 – 2.77 (2H, m), 2.40 – 2.30 (1H, m), 1.83 (1H, d, $J=12.8$ Hz), 1.78 – 1.64 (4H, m), 1.62 – 1.53 (2H, m), 1.29 – 1.10 (7H, m), 1.04 – 0.93 (2H, m), 0.84 (3H, t, $J=7.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 167.3, 150.1, 130.0, 128.5, 128.0, 56.9, 52.8, 52.1, 46.6, 34.5, 33.7, 33.6, 29.7, 26.3, 25.2, 25.1, 22.8, 14.1; HRMS (ESI) found MH^+ 318.2426, $\text{C}_{20}\text{H}_{32}\text{NO}_2$ requires 318.2428.

Methyl 4-(1-(tert-Butylamino)-4-phenylbutan-2-yl)benzoate (39b)



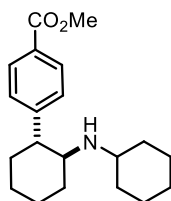
Following **GP8b**, **39** (20 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **39b** (48% over two steps) as an oil. R_f 0.14 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 8.02 (2H, d, $J=8.3$ Hz), 7.30 (2H, d, $J=8.2$ Hz), 7.24 (2H, t, $J=7.7$ Hz), 7.16 (1H, t, $J=7.6$ Hz), 7.08 (2H, d, $J=7.2$ Hz), 3.92 (3H, s), 2.86 – 2.75 (3H, m), 2.51 – 2.40 (2H, m), 2.10 – 2.02 (1H, m), 1.95 – 1.86 (1H, m), 0.99 (9H, s); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 149.5, 142.1, 130.1, 128.8, 128.5, 128.1, 126.0, 52.2, 50.3, 48.5, 46.6, 36.5, 33.7, 29.0; HRMS (ESI) found MH^+ 340.2266, $\text{C}_{22}\text{H}_{30}\text{NO}_2$ requires 340.2271.

Methyl 4-(5-(Methylamino)octan-4-yl)benzoate (**31d**)



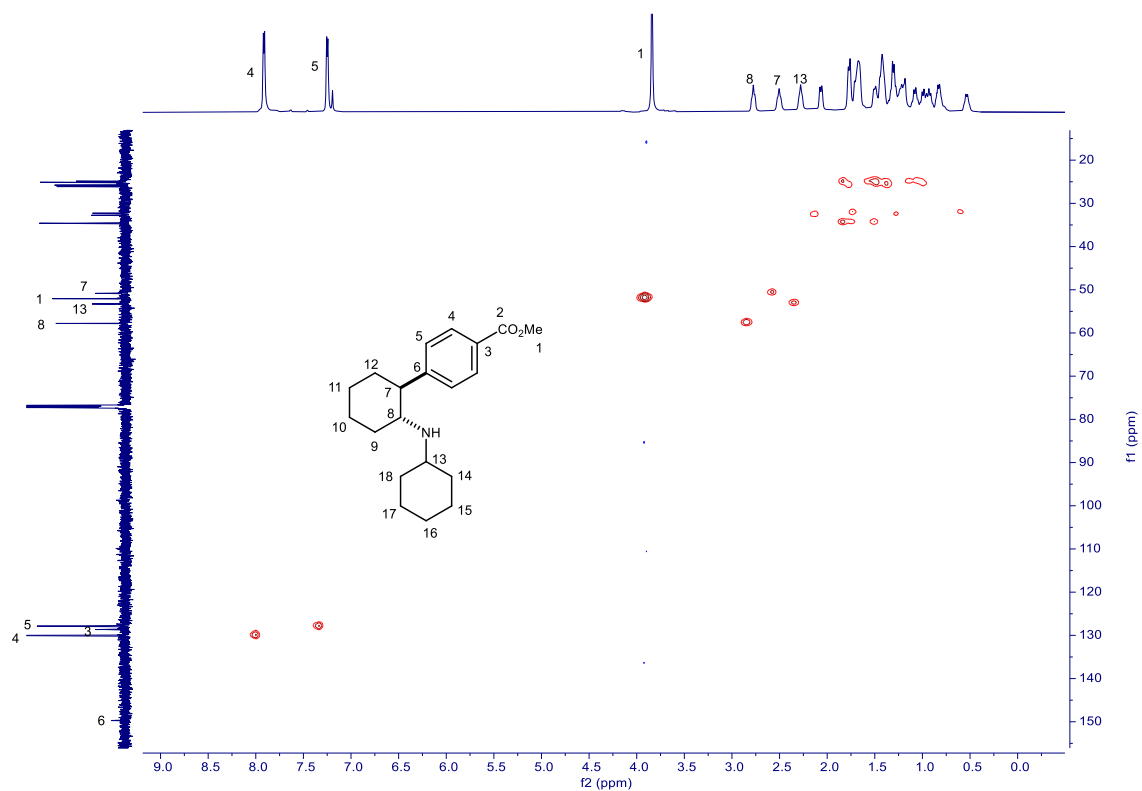
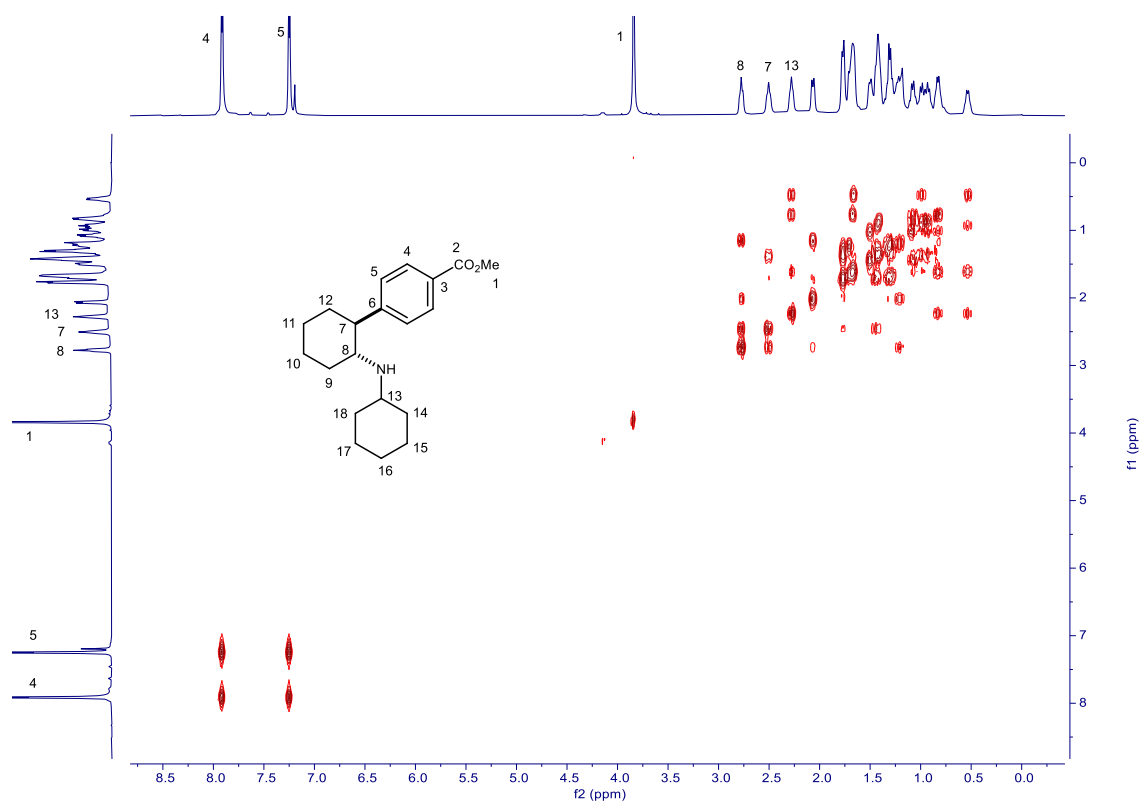
Following **GP8a**, but using 3,3',5,5'-tetrakis(trifluoromethyl)benzophenone (20 mol%) and running the reaction for 16 h, **31a** (16 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **31d** as mixture of diastereomers (41%) as an oil. d.r. 1.7:1. R_f 0.11 [EtOAc]. ^1H NMR (400 MHz, CDCl_3), signals corresponding to both diastereomers: δ 8.00 – 7.88 (2H, m), 7.31 – 7.14 (2H, m), 3.88 (3H, s), 2.82 – 2.67 (1H, m), 2.59 – 2.48 (1H, m), 2.39 (1.1H, s), 2.28 (1.9H, s), 1.83 – 1.54 (2H, m), 1.31 – 0.99 (6H, m), 0.92 – 0.72 (6H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 167.3, 167.3, 149.4, 149.2, 129.7, 129.6, 128.9, 128.8, 128.4, 128.2, 64.0, 63.8, 52.1, 52.1, 48.9, 48.5, 34.5, 33.8, 33.8, 33.7, 33.3, 33.0, 21.1, 21.0, 19.3, 18.9, 14.5, 14.3, 14.3, 14.2; HRMS (ESI) found MH^+ 278.2108, $\text{C}_{17}\text{H}_{28}\text{NO}_2$ requires 278.2115.

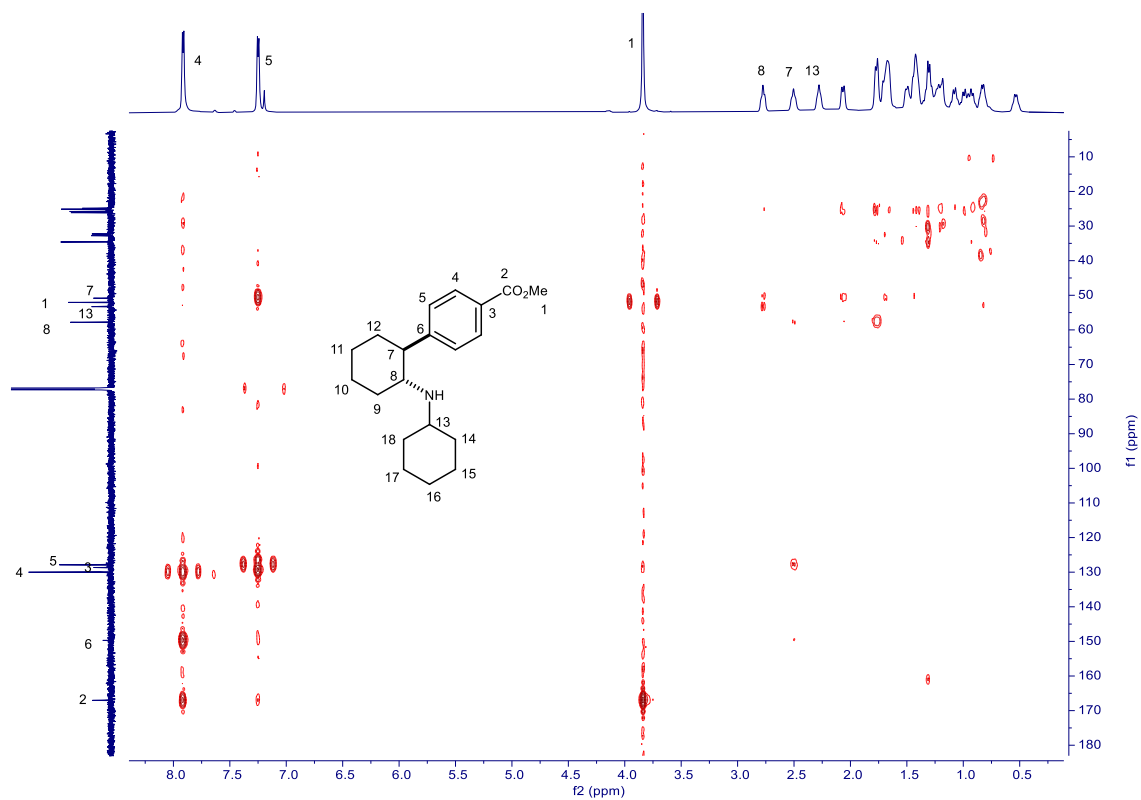
trans-Methyl 4-(2-(cyclohexylamino)cyclohexyl)benzoate (**33d**)



Following **GP8a** but using 3,3',5,5'-tetrakis(trifluoromethyl)benzophenone (20 mol%), *trans*-aziridine borane **33a** (19 mg, 0.1 mmol, 1.0 equiv.) and 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **33d** (55%) as an oil. R_f 0.28 [DCM:MeOH (15:1)]. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (2H, d, $J=7.9$ Hz), 7.31 (2H, d, $J=7.9$ Hz), 3.90 (3H, s), 2.84 (1H, td, $J=10.5$, 3.7 Hz), 2.63 – 2.51 (1H, m), 2.40 – 2.29 (1H, m), 2.18 – 2.08 (1H, m), 1.90 – 1.69 (5H, m), 1.62 – 1.43 (4H, m), 1.42 – 1.22 (4H, m), 1.20 – 0.79 (4H, m), 0.59 (1H, q, $J=11.6$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 149.8, 130.1, 128.8, 128.0, 57.9, 53.4, 52.2, 51.0, 34.7, 32.9, 32.4, 26.2, 25.9, 25.3, 25.2, 25.0; HRMS (ESI) found MH^+ 316.2265, $\text{C}_{20}\text{H}_{30}\text{NO}_2$ requires 316.2271.

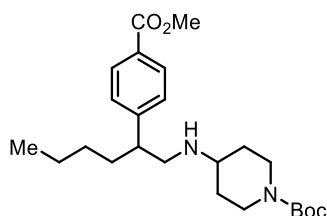
The key ^1H and ^{13}C chemical shifts were further assigned using 2D NMR. The *trans* configuration was assigned based on the coupling constants observed for H-8 (^1H NMR: δ , 2.84, td, $J = 10.5$, 3.7 Hz, 1H).





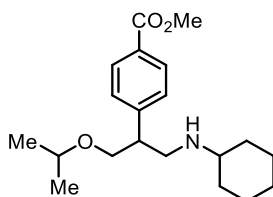
HMBC NMR spectrum (600 MHz, CDCl₃, at rt) of **33d**

***tert*-Butyl 4-((2-(4-(Methoxycarbonyl)phenyl)hexyl)amino)piperidine-1-carboxylate (**40b**)**



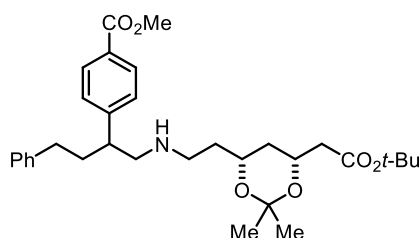
Following **GP8b**, **40** (28 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **40b** (58% over two steps) as an oil. *R_f* 0.25 [EtOAc]. ¹H NMR (600 MHz, CDCl₃) δ 7.98 (2H, d, *J*=8.3 Hz), 7.25 (2H, d, *J*=8.3 Hz), 4.06 – 3.82 (5H, m), 2.94 – 2.85 (1H, m), 2.83 – 2.67 (4H, m), 2.50 (1H, tt, *J*=10.2, 3.8 Hz), 1.79 – 1.63 (3H, m), 1.61 – 1.49 (1H, m), 1.42 (9H, s), 1.30 – 1.07 (6H, m), 0.81 (3H, t, *J*=7.3 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 167.2, 154.9, 149.8, 130.0, 128.6, 127.9, 79.5, 55.0, 52.6, 52.2, 46.7, 34.3, 29.7, 28.6, 22.8, 14.1; HRMS (ESI) found *MH*⁺ 419.2896, C₂₄H₃₉N₂O₄ requires 419.2904.

Methyl 4-(1-(Cyclohexylamino)-3-isopropoxypropan-2-yl)benzoate (41b**)**



Following **GP8b**, **41** (20 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **41b** (47% *over two steps*) as an oil. R_f 0.16 [EtOAc]. ^1H NMR (600 MHz, CDCl_3) δ 7.97 (2H, d, $J=8.3$ Hz), 7.31 (2H, d, $J=8.2$ Hz), 3.90 (3H, s), 3.63 – 3.55 (2H, m), 3.50 (1H, hp, $J=6.0$ Hz), 3.14 – 3.03 (2H, m), 2.88 (1H, dd, $J=11.3, 7.4$ Hz), 2.37 (1H, tt, $J=10.5, 3.7$ Hz), 1.83 – 1.75 (2H, m), 1.71 – 1.64 (2H, m), 1.57 (1H, dt, $J=13.3, 3.7$ Hz), 1.49 (1H, br s), 1.27 – 1.15 (2H, m), 1.15 – 1.07 (7H, m), 1.06 – 0.93 (2H, m); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 147.7, 129.9, 128.7, 128.2, 72.0, 71.5, 56.9, 52.1, 49.9, 46.7, 33.6, 33.5, 26.3, 25.2, 25.1, 22.1; HRMS (ESI) found MH^+ 334.2381, $\text{C}_{20}\text{H}_{32}\text{NO}_3$ requires 334.2377.

Methyl 4-(1-((2-((4*R*,6*R*)-6-(2-(*tert*-Butoxy)-2-oxoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl)amino)-4-phenylbutan-2-yl)benzoate (42b)



Following **GP8b**, **42** (40 mg, 0.1 mmol, 1.0 equiv.) and methyl 4-bromobenzoate (43 mg, 0.2 mmol, 2.0 equiv.) gave **42b** as mixture of diastereomers (37% *over two steps*) as an oil. d.r. 1:1. R_f 0.13 [EtOAc]. ^1H NMR (400 MHz, CDCl_3), *signals corresponding to both diastereomers*: δ 7.94 (2H, d, $J=8.0$ Hz), 7.26 – 7.13 (4H, m), 7.08 (1H, t, $J=7.3$ Hz), 7.00 (2H, d, $J=7.4$ Hz), 4.17 – 4.05 (1H, m), 3.85 (3H, s), 3.79 – 3.68 (1H, m), 2.86 – 2.71 (3H, m), 2.61 – 2.47 (2H, m), 2.43 – 2.27 (3H, m), 2.23 – 2.14 (1H, m), 2.01 – 1.89 (1H, m), 1.87 – 1.75 (1H, m), 1.53 – 1.33 (12H, s), 1.26 – 1.14 (6H, m), 1.13 – 1.00 (1H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 170.4, 167.1, 149.4, 149.4, 142.0, 130.1, 128.7, 128.5, 128.5, 128.1, 126.0, 98.7, 98.7, 68.0, 67.5, 66.3, 55.9, 55.9, 52.2, 46.5, 46.0, 46.0, 42.8, 42.8, 36.7, 36.6, 36.5, 36.4, 36.2, 36.0, 33.6, 30.1, 30.1, 28.2, 19.7, 19.7; HRMS (ESI) found MH^+ 540.3312, $\text{C}_{32}\text{H}_{46}\text{NO}_6$ requires 540.3320.

6 Scope of Other Nucleophiles

We attempted to engage other nucleophiles under various reaction conditions. While we did not succeed in obtaining high yields, the results below demonstrate proof-of-principle results that additional ring-opening functionalisations could be further developed.

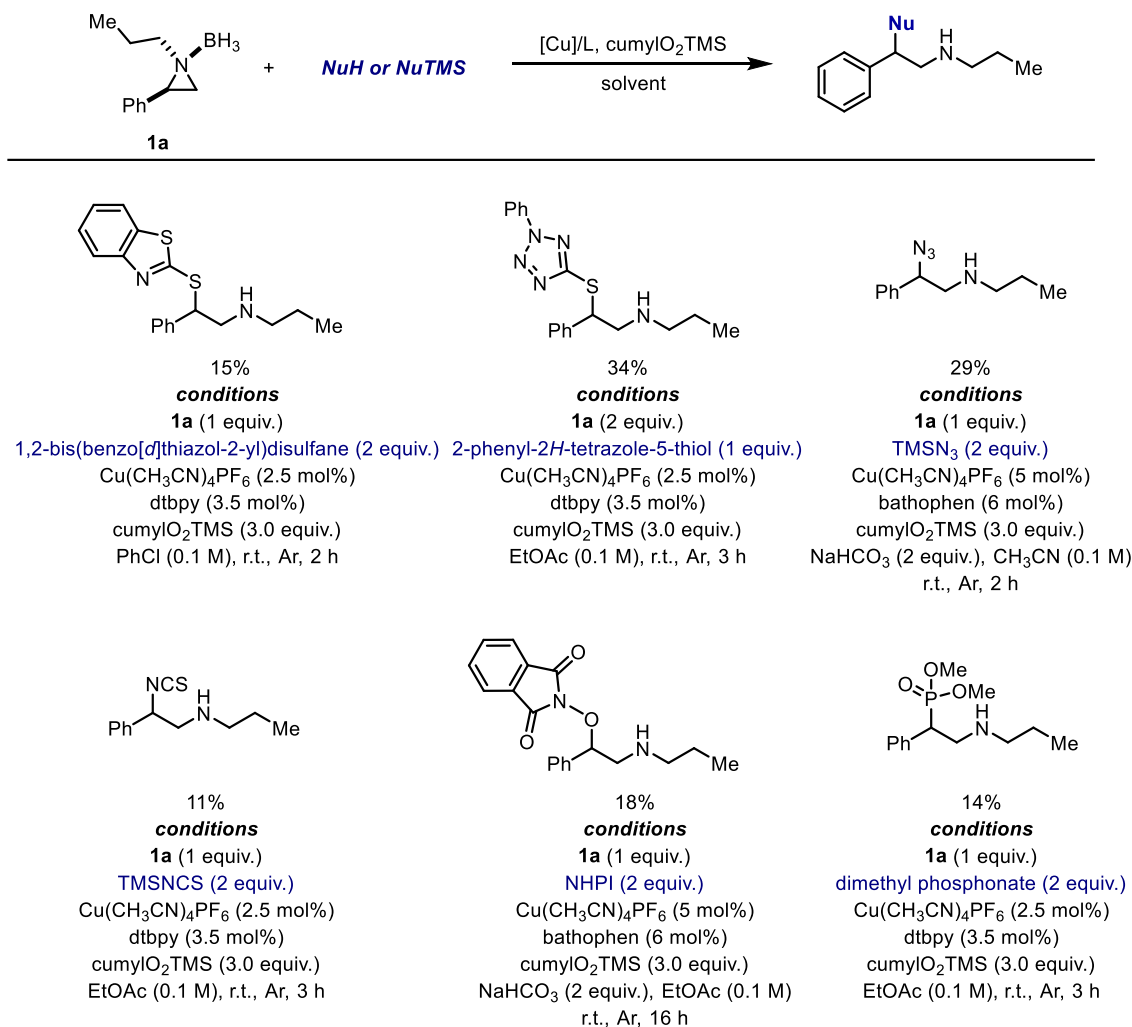


Figure S1. Scope of other nucleophiles. All reported yields are NMR yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

7 Comparison of Arylation of *cis* and *trans* Aziridine Boranes

The *cis* and *trans* aziridine boranes **12a** and **12a'** were engaged separately under the optimised conditions (**GP5a**).

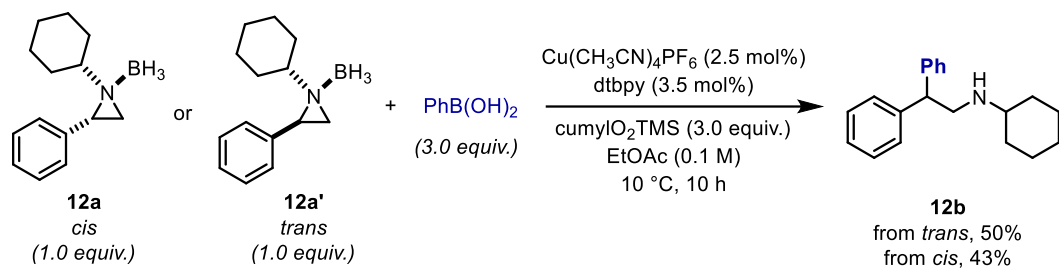
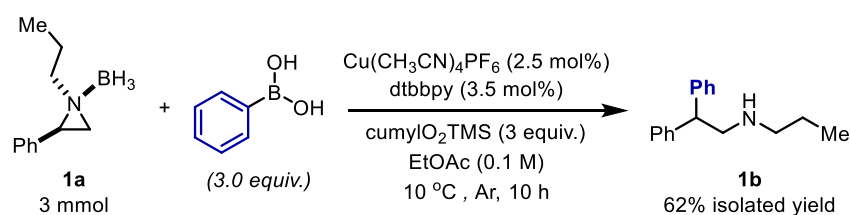
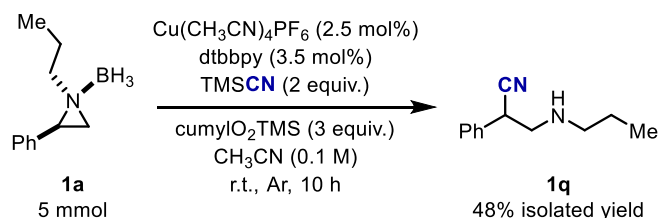


Figure S2.

8 Scale-up Experiments



An oven-dried vial equipped with a stirring bar was charged with the *trans*-2-phenyl-1-propylaziridine borane **1a** (3 mmol, 1.0 equiv.) and phenylboronic acid (9 mmol, 3.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). The peroxide (9 mmol, 3.0 equiv.) and dry and degassed solvent (15 mL) was then added to the vial and stirred for around **1 min**. The resulting mixture was cooled down to 10 °C and the catalyst solution (15 mL of the corresponding dry and degassed solvent, containing $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (27 mg, 2.5 mol%) and dtbbpy (30 mg, 3.5 mol%), pre-stirred for 10 min until fully dissolved) was then added under stirring. The resulting mixture was stirred at 10 °C for 10 h. Upon completion, aqueous NaOH (1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x). The combined organic layers were dried (MgSO_4) and filtered. The solvent was evaporated and purified by column chromatography on silica gel to afford the desired product **1b** in 62% yield (1.86 mmol, 450 mg).



An oven-dried vial equipped with a stirring bar was charged with the *trans*-2-phenyl-1-propylaziridine borane **1a** (5 mmol, 1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with Ar (x 3). The peroxide (9 mmol, 3.0 equiv.), TMSCN (10 mmol, 2.0 equiv.) and dry and degassed CH_3CN (25 mL) was then added to the vial and stirred for around **1 min**. The catalyst solution (25 mL of dry and degassed CH_3CN , containing $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (45 mg, 2.5 mol%) and dtbbpy (50 mg, 3.5 mol%), pre-stirred for 10 min until fully dissolved) was then added under stirring. The resulting mixture was stirred at room temperature for 2 h. Upon completion, an aqueous solution of NaOH (1 M) was added, the aqueous layer was separated and extracted with EtOAc (2 x). The combined organic layers were dried (MgSO_4) and filtered. The solvent was evaporated and purified by column chromatography on silica gel to afford the desired product **1q** in 48% yield (2.4 mmol, 450 mg).

9 Cyclic Voltammetry Studies

Cyclic voltammetry (CV) experiments were conducted using a conventional three-electrode cell equipped with a platinum working electrode (1 mm diameter), an Ag/AgCl reference electrode (3.0 M KCl), and a platinum wire counter electrode. Measurements of the substrates (20 mM) were performed in CH₃CN containing *n*-Bu₄NPF₆ (0.1 M) as the supporting electrolyte at a scan rate of 100 mV s⁻¹. Ferrocene (Cp₂Fe, 20 mM) was dissolved in CH₃CN with *n*-Bu₄NPF₆ (0.1 M) and measured under identical conditions. The half-wave potential of the Fc⁺/Fc redox couple was determined to be 0.43 V vs. Ag/AgCl (3.0 M KCl).

Cyclic voltammetry (CV) experiments were performed on *N*-alkyl β-aryl and β-alkyl aziridines (**1** and **13**), as well as their corresponding borane complexes (**1a** and **13a**). As shown in **Figure S3**, both *N*-alkyl β-aryl and β-alkyl aziridines exhibit relatively high oxidative potentials. The oxidation potential of the *N*-alkyl β-alkyl aziridine **13** (*E*_p = 1.82 V) is lower than that of the *N*-alkyl β-aryl aziridine **1** (*E*_p = 2.04 V). Upon coordination with borane, the oxidation potentials of both aziridines decrease significantly (*E*_p = 1.56 V for **1a** and 1.06 V for **13a**). In contrast, both the aziridines and their borane complexes display highly negative reduction potentials, and no obvious reductive peaks were observed within the accessible potential window.

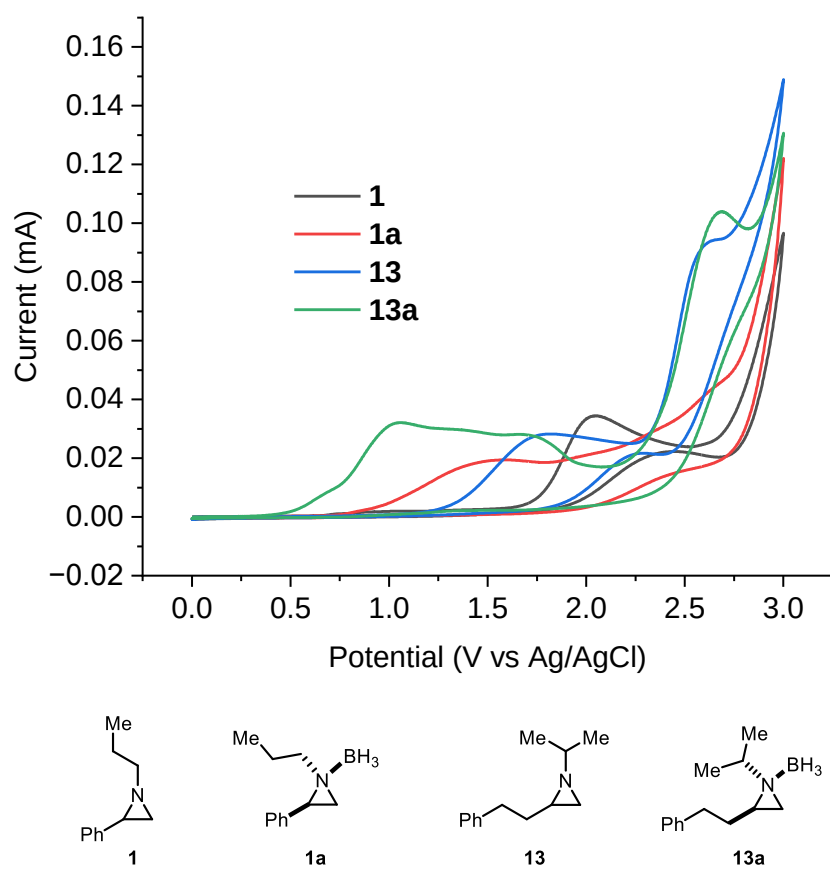


Figure S3. Cyclic voltammogram (positive current) of model aziridine and aziridine boranes in CH_3CN . A scan rate of 100 mV/s was used for all CV experiments.

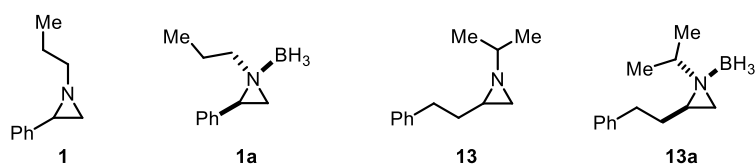
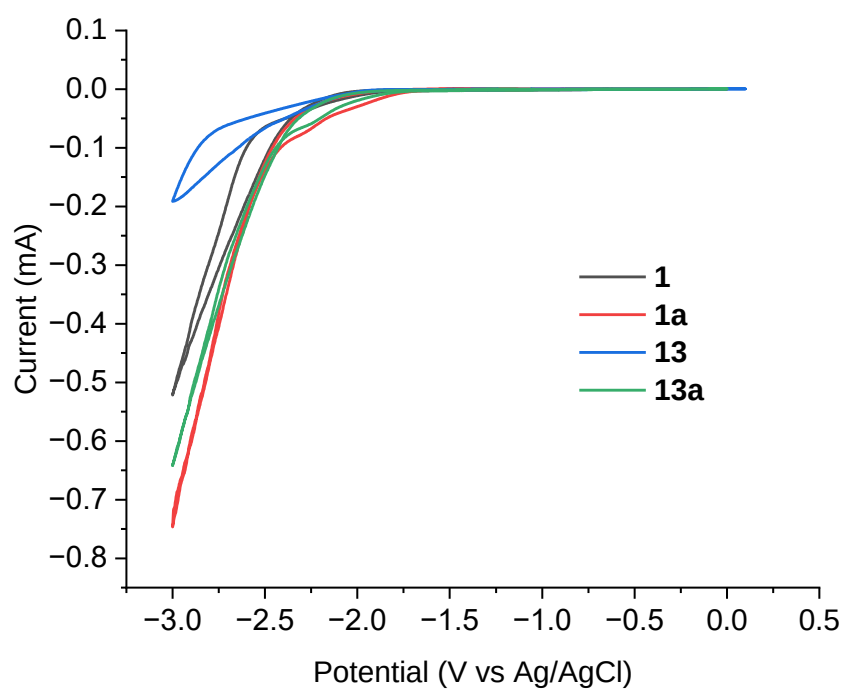


Figure S4. Cyclic voltammogram (negative current) of model aziridine and aziridine boranes in CH_3CN . A scan rate of 100 mV/s was used for all CV experiments.

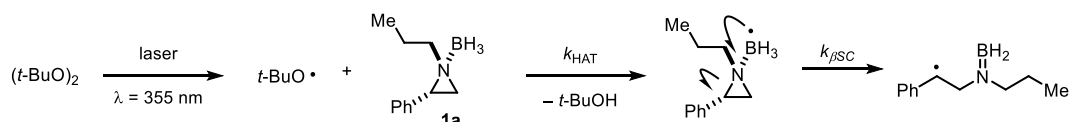
10 Laser Flash Photolysis Studies

General Remarks

Laser Flash Photolysis (LFP) experiments were carried out with a laser spectrometer using the third harmonic (355 nm) of a Q-switched Nd:YAG laser, delivering 8 ns pulses. The laser energy was adjusted to 10 mJ/pulse. A 3.5 mL Suprasil quartz cell (10 mm × 10 mm) was used in all experiments. Argon saturated EtOAc–(*t*-BuO)₂ (3:1) or CH₃CN–(*t*-BuO)₂ (3:1) solutions were employed. Boryl-radicals have been generated by hydrogen atom transfer (HAT) from the pertinent amine borane precursor with *t*-BuO•.

Transient Absorption Spectroscopy Studies

To provide direct evidence regarding the formation of radical species we performed transient absorption spectroscopy (TAS) studies. The whole process can be described according to **Scheme 1**. According to our computational data, the ring-opening of the boryl radical arising from **1a** is barrierless. Indeed, when TAS studies using a solution of **1a** in EtOAc–(*t*-BuO)₂ (or CH₃CN) at 25 °C or –10 °C, provided only a signal at $\lambda \approx 300$ nm, which match the known absorption profile of benzylic radicals.²¹ No boryl radical absorption was detected. Overall, these studies clearly confirms that the process goes via the formation of a benzylic radical and it is in line with the fast ring-opening of the aziridine-ligated boryl radical.



Scheme 1.

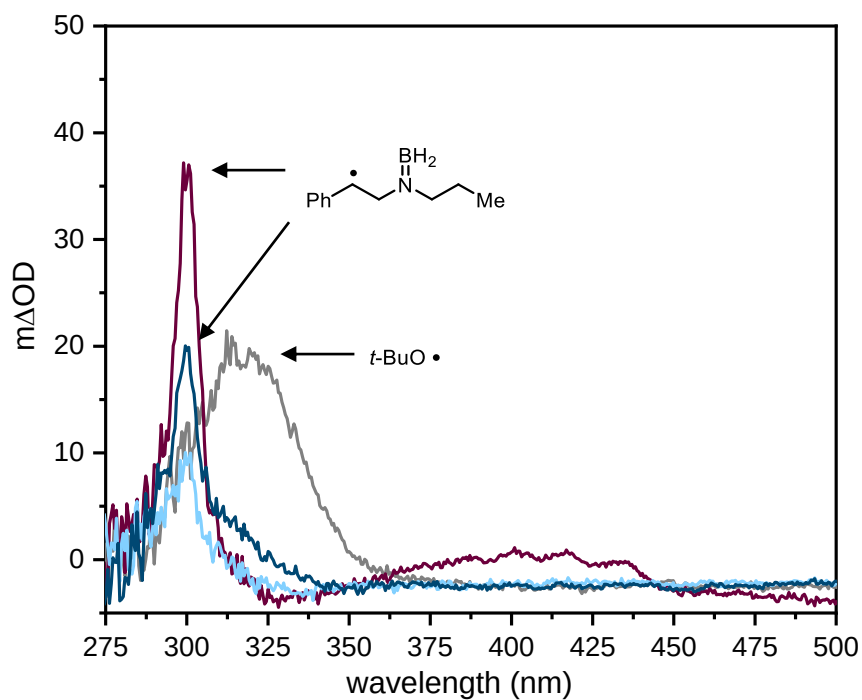
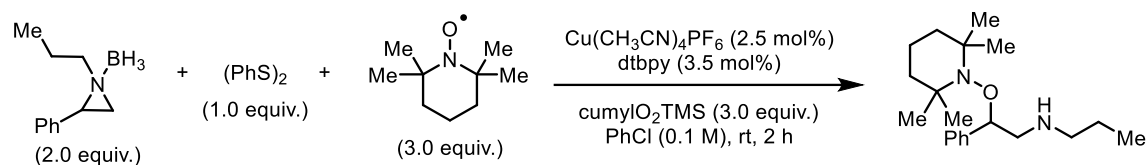


Figure S5. Transient Absorption Spectroscopy observed 200 ns after 355 nm LFP of **1a** in EtOAc-(*t*-BuO)₂ 3:1 at 25°C (red), CH₃CN-(*t*-BuO)₂ 3:1 at 25°C (dark blue), CH₃CN-(*t*-BuO)₂ 3:1 at -10°C (light blue) and of the blank solution EtOAc-(*t*-BuO)₂ 3:1 without **1a** at 25°C (grey).

11 Radical Trapping Experiment

N-(2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)propan-1-amine (S14)



Following **GP7**, *trans*-aziridine **1a** (31 mg, 0.2 mmol, 2.0 equiv.), diphenyl disulfide (22 mg, 0.1 mmol) and TEMPO (47 mg, 0.3 mmol, 3.0 equiv.) gave **S14** as an oil (30%). R_f 0.26 [*n*-pentane:EtOAc (1:1)]; ^1H NMR (400 MHz, CDCl_3) δ 7.39–7.27 (5H, m), 5.03 (1H, br s), 3.28 (1H, dd, J = 12.1, 6.6 Hz), 2.98 (1H, dd, J = 11.2, 6.5 Hz), 2.59 (2H, t, J = 7.3 Hz), 1.61–1.47 (5H, m), 1.41–1.31 (6H, m), 1.19 (3H, br s), 1.04 (3H, br s), 0.88 (3H, t, J = 7.3 Hz), 0.81 (3H, br s); ^{13}C NMR (151 MHz, CDCl_3) δ 141.3, 128.4, 127.9, 127.7, 84.0, 60.4, 54.9, 51.3, 49.6, 40.6, 34.4, 34.1, 29.8, 27.1, 22.7, 20.6, 17.3, 11.8; HRMS (ESI) found MH^+ 319.2742, $\text{C}_{20}\text{H}_{35}\text{ON}_2$ requires 319.2744.

Table S22. Control experiments for radical trapping.

entry	deviation	S14 (%)	1a	1
1	without Cu & dtbpy	—	99	—
2	1 instead of 1a	—	—	—*
3	without $(\text{PhS})_2$	30	89	

*full decomposition of the starting amine **1**

12 Computational Studies

12.1 General Information

The computational work was carried out in the framework of density functional theory (DFT)^{22,23} using the ORCA (version 5.0.4)²⁴ software package. For all critical points, geometry optimizations and harmonic vibrational frequencies, the Minnesota hybrid functional (U)M06-2X²⁵ was employed in combination with the def2-TZVP^{26,27} basis set. This level of theory was applied to these studies as this functional and basis set have been used in literature to describe boryl radical processes effectively.²⁸⁻³¹ The self-consistent field (SCF) convergence was controlled by the 'TightSCF' keyword, and the integration grids were set with the 'defgrid3' keyword to increase numerical precision. Moreover, the default settings of this version of ORCA included the def2/J auxiliary basis set²⁷ and the RIJCOSX approximation in all calculations. All potential-energy minima were ensured to present only all-real vibrational frequencies. The transition state guess was determined by completing a scan of the breaking bond of interest and the optimized structure displayed only one imaginary frequency corresponding to the reaction normal mode. Intrinsic reaction coordinate (IRC) calculations were performed to confirm the connection between reactants and products through the corresponding transition states.

More accurate single-point electronic energies were calculated at the (U)M06-2X/def2-QZVP level of theory.²⁵⁻²⁷ For the single point calculations (SPC), the solvent effects of EtOAc were included using the SMD solvation model.³² The same level of theory was applied to determine the energy gap between orbitals and the Mayer bond order using *Gaussian 16*³³ and its implemented NBO 3.1 program.³⁴

The thermodynamic data was obtained with the python script *OTHERM.py*,³⁵ where the thermodynamic contributions from the vibrational analysis were combined with the SPC calculations. The final thermodynamic values were corrected for the conditions at 298.15 K and with a concentration of 1.0 mol L⁻¹. All Cartesian coordinates of the geometries and their corresponding energies can be found in the Supplementary Material file.

12.2 Thermodynamics

Thermodynamic data and the SOMO- σ^* orbital energy gap in EtOAc give an insight into the regioselectivity of the ring-opening step for the *N*-Me-aziridine-ligated boryl radical bearing either a β -Me or a β -Ph substituent (**Figure S6**). For the β -Me substituted species:

Trans. The secondary radical is the preferred thermodynamic and kinetic product, although showing a larger orbital gap between SOMO and the σ^* of the breaking C–N bond. The energetics result in the reaction being regioselective thanks to the strain release between the substituents.

Cis. As in the *trans*-conformation, the SOMO- σ^* energy gap is lower for the formation of the primary radical. Moreover, the primary and secondary radical products present a similar activation free energy ($\Delta\Delta G^\ddagger = 0.7$ kcal mol⁻¹), with the more hindered position being favored thermodynamically ($\Delta\Delta G^0 > 3$ kcal mol⁻¹). Hence, due to the promiscuous parameters, a less regioselective reaction is likely to occur, leading to a mixture of both products.

The trends mentioned generally agree with the observation of Roberts³⁶ with *N*-H-aziridine-ligated boryl radical processes, with the *trans*-conformer leading to a more regioselective ring opening than the *cis*-species.

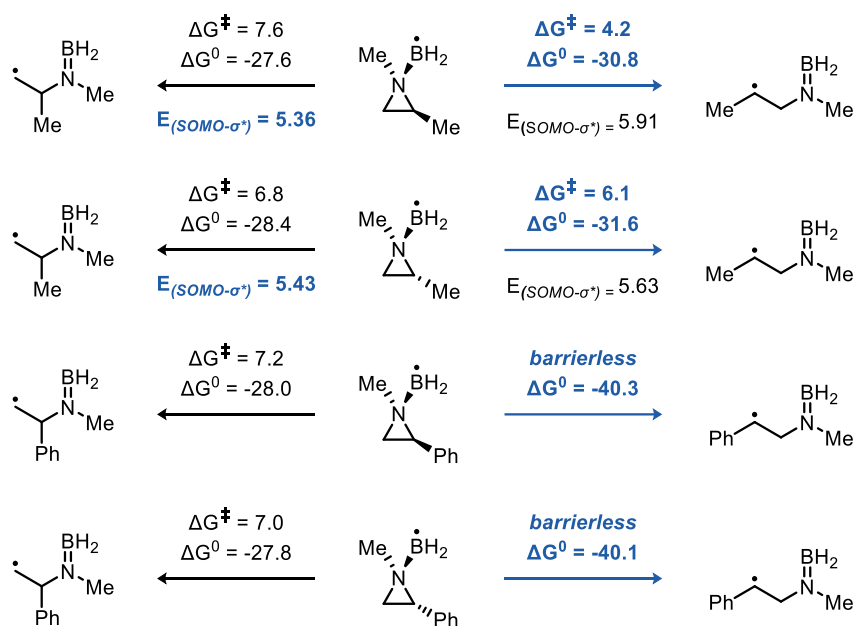


Figure S6. Gibbs free energy change at the transition state ($\Delta G^\ddagger$), Gibbs free energy change of the ring-opening (ΔG^0) in kcal mol⁻¹, followed by the energy gap of the SOMO and the σ^* of the breaking C–N bond in eV. (U)M06-2X/def2-QZVP(SMD,EtOAc)/(U)M06-2X/def2-TZVP

The β -Ph *N*-Me-aziridine-ligated boryl radical favors the benzyl radical regardless of the conformation of the initial ring, suggesting that the stability of the radical product trumps the conformation of the initial species (**Figure S7**). Energy scans of the breaking C–N bond for all

species were employed to locate the transition state geometry guess. In the case of the β -Ph substituent with the ring-opening towards the formation of the benzyl radical, both *trans*- and *cis*-conformations resulted in a small electronic energy difference of $\Delta E \approx 1$ kcal mol⁻¹ (**Figure S7**). However, transition state optimizations initiated from the scan maximum did not converge to a first-order saddle point and instead relaxed directly toward products, therefore deeming the reaction “barrierless”.

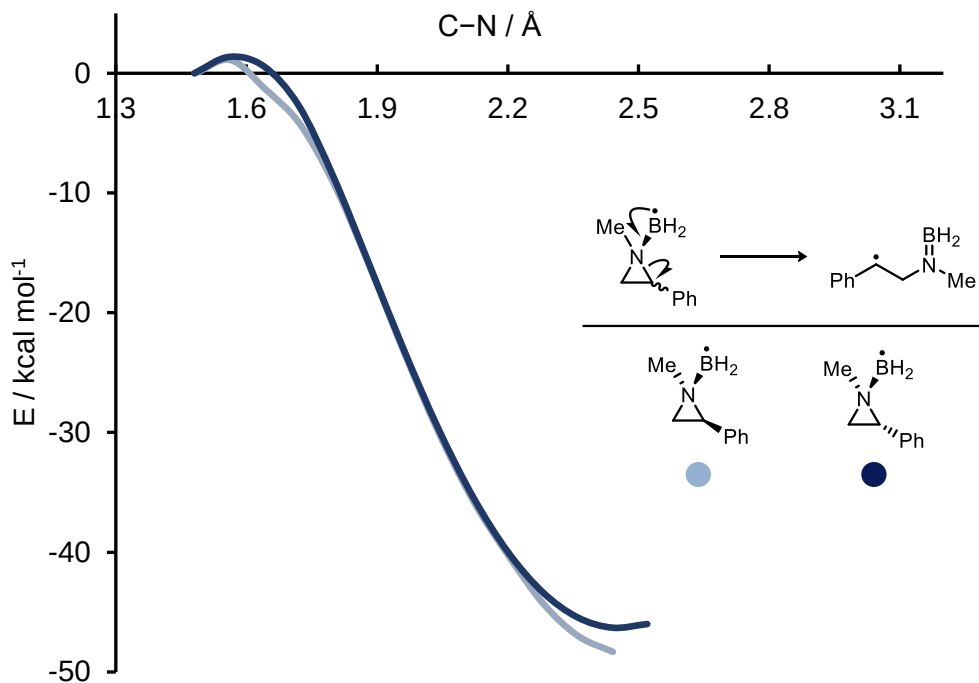
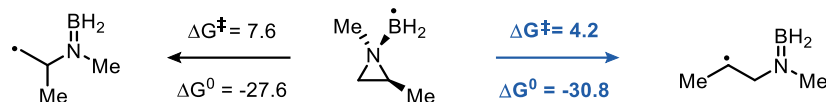


Figure S7. Energy scan of breaking the C–N bond for both conformations (*cis* and *trans*) of the *N*-Me-aziridine-ligated boryl radical, bearing a β -Ph substituent, ring opening step to yield the benzyl radical product. (U)M06-2X/def2-TZVP

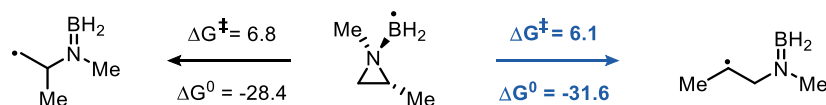
12.3 Chemical Properties Across the Potential Energy Surface

Table S23. Data of the *trans*-*N*-Me-aziridine-ligated boryl radical, and its two possible radical products, bearing a β -methyl substituent in EtOAc.



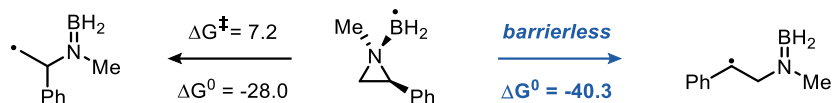
R	Species	B–N (Å)	Mayer BO B–N	C–N (Å)	Mayer BO C–N	Spin Density (C)	Spin Density (B)	E _{SOMO-σ*} (eV)
1°	SM	1.57	0.70	1.46	0.89	-0.05	1.01	-
Radical	TS	1.49	0.90	1.71	0.66	0.24	0.88	5.36
Formation	P	1.39	1.32	2.44	-	1.01	0.00	-
2°	SM	1.57	0.70	1.49	0.87	0.06	1.01	-
Radical	TS	1.50	0.87	1.68	0.67	0.22	0.89	5.91
Formation	P	1.39	1.31	2.47	-	1.02	0.00	-

Table S24. Data of the *cis*-*N*-Me-aziridine-ligated boryl radical, and its two possible radical products, bearing a β -methyl substituent in EtOAc.



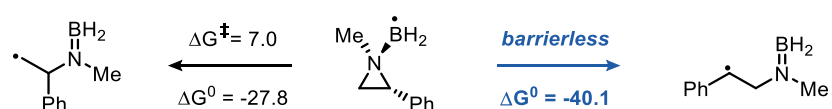
R	Species	B–N (Å)	Mayer BO B–N	C–N (Å)	Mayer BO C–N	Spin Density (C)	Spin Density (B)	E _{SOMO-σ*} (eV)
1°	SM	1.57	0.70	1.48	0.87	0.00	1.05	-
Radical	TS	1.49	0.90	1.70	0.67	0.23	0.90	5.43
Formation	P	1.39	1.32	2.44	-	1.01	0.00	-
2°	SM	1.57	0.70	1.47	0.88	-0.05	1.05	-
Radical	TS	1.49	0.86	1.72	0.90	0.20	0.92	5.63
Formation	P	1.39	1.31	2.47	-	1.02	0.00	-

Table S25. Data of the *trans*-*N*-Me-aziridine-ligated boryl radical, and its two possible radical products, bearing a β -Ph substituent in EtOAc.



R	Species	B–N (Å)	Mayer BO B–N	C–N (Å)	Mayer BO C–N	Spin Density (C)	Spin Density (B)
1°	SM	1.57	0.69	1.48	0.87	-0.02	0.96
Radical	TS	1.49	0.89	1.71	0.66	0.21	0.85
Formation	P	1.39	1.32	2.45	-	0.97	0.00
2°	SM	1.57	0.69	1.48	0.86	0.04	0.96
Radical	TS	-	-	-	-	-	-
Formation	P	1.39	1.30	2.48	-	0.89	0.00

Table S26. Data of the *cis*-*N*-Me-aziridine-ligated boryl radical, and its two possible radical products, bearing a β -Ph substituent in EtOAc



R	Species	B–N (Å)	Mayer BO B–N	C–N (Å)	Mayer BO C–N	Spin Density (C)	Spin Density (B)
1°	SM	1.57	0.72	1.48	0.88	-0.01	1.00
Radical	TS	1.48	0.91	1.71	0.65	0.23	0.84
Formation	P	1.39	1.32	2.45	-	0.97	0.00
2°	SM	1.57	0.72	1.48	0.86	0.01	1.00
Radical	TS	-	-	-	-	-	-
Formation	P	1.39	1.30	2.48	-	0.89	0.00

12.4 Visual Representation of Orbital Overlap at the Transition State

For the β -Me-substituted borylated aziridines, visual representations of the single occupied molecular orbital (SOMO) and the σ^* of the breaking C–N bond at the transition state geometry are displayed below. The energies (eV) of the orbitals were used to determine the energy gap to predict the regioselectivity of the ring-opening step, as previously described by Roberts³⁶ using similar motifs.

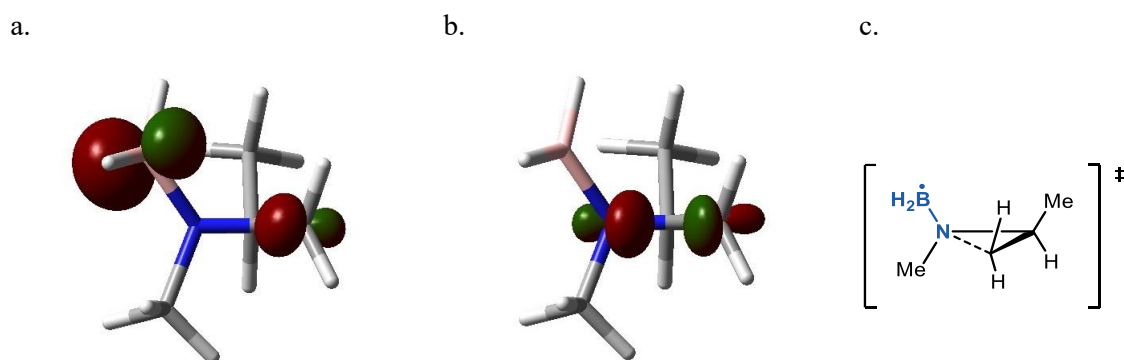


Figure S8. SOMO (a) and σ^* orbital of the C–N bond (b) of the *trans*-*N*-Me-aziridine-ligated boryl radical at the transition state (c) to form the primary radical as product in EtOAc.

Grey = carbon; white = hydrogen; blue = nitrogen; pink = boron.

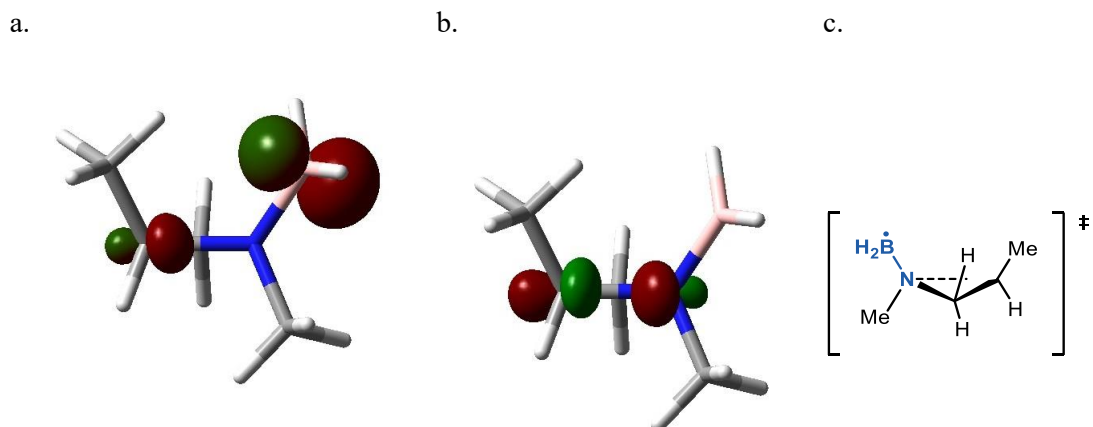


Figure S9. SOMO (a) and σ^* orbital of the C–N bond (b) of the *trans*-*N*-Me-aziridine-ligated boryl radical at the transition state (c) to form the secondary radical as product in EtOAc. Grey = carbon; white = hydrogen; blue = nitrogen; pink = boron.

13 Literature Review of Ring-Opening Reactions of *N*-alkyl aziridines

13.1 Background

In the context of aziridine ring-opening chemistry, most studies rely on the use of electron-withdrawing *N*-activating protecting groups (mainly sulfonamide, see **Figure S12**) to activate the C–N bond.

While *N*-alkyl aziridines retain considerable ring strain, their inherent reactivity is low unless activated upon either protonation with strong Brønsted acids or coordination with Lewis acids (**Figure S12**). As a result, ring-opening reactions involving *N*-alkyl aziridines are less common and often restricted by the range of compatible nucleophiles. In particular, while methods for ring-opening and divergent cross-couplings have been developed for *N*-Ts-aziridines, to the best of our knowledge, *N*-alkyl aziridines cannot be engaged.

Below, we have summarized the state-of-the-art in ring-opening functionalization reactions of *N*-alkyl aziridines.

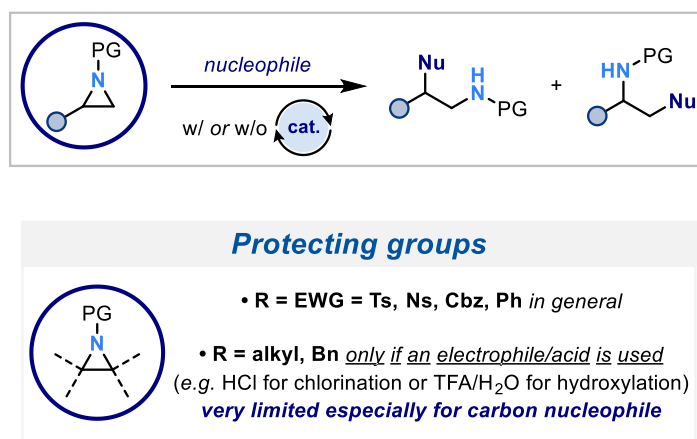


Figure S12. General aziridine ring-opening transformations scheme and commonly used protecting groups.

13.2 Nucleophilic Ring Opening³⁷⁻³⁹

Thiols can be used, and they lead often to nucleophilic attack at either the benzylic or at the least substituted position (**Figure S13**)⁴⁰⁻⁴². These approaches are often rationalised on the basis of the basic aziridine N-atom undergoing deprotonation or H-bonding interaction with the thiol that synergistically activates the aziridine electrophile and the thiol nucleophile. The same reactivity featuring substitution at the least substituted site has been reported via the use of Brønsted/Lewis acids (**Figure S13**).^{43,44} Please note that the latter is the opposite selectivity developed in our work.

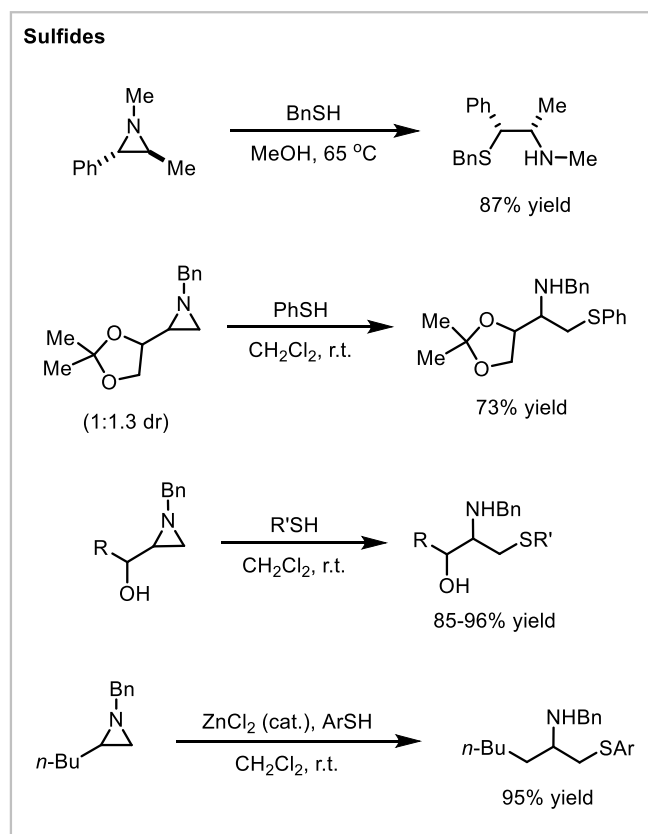


Figure S13. Summary of thioetherification ring-opening transformations involving *N*-alkyl aziridines.

Similarly to thiols, trimethylsilyl azide (TMSN_3) is able to directly open *N*-alkyl aziridines with various alkyl and aryl substituents (**Figure S14**), displaying a comparatively broad substrate scope and high yields.⁴⁵ Also in this case, β -alkyl aziridines undergo ring-opening at the least substituted side.

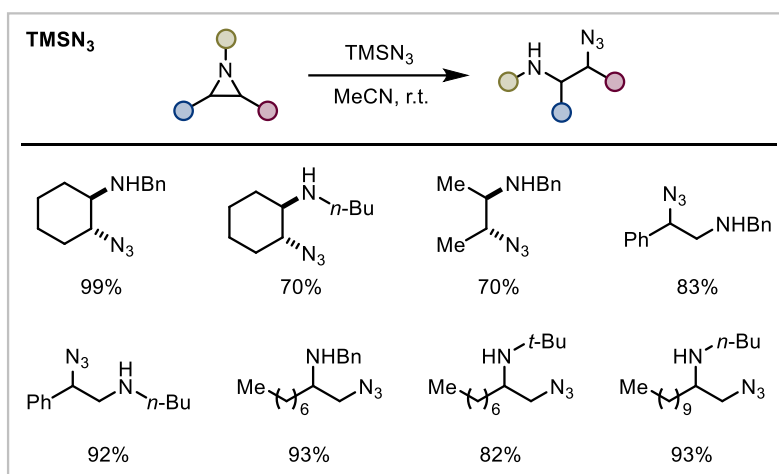


Figure S14. Summary of azidation ring-opening transformations involving *N*-alkyl aziridines.

HF-pyridine⁴⁶, TFA in a H₂O–acetone solvent mixture, and AcOH⁴⁷ can function as both Brønsted acids and nucleophiles to promote aziridine ring opening reactions (**Figure S15**). Similar methodologies have been reported with HBr and HI.^{37,38} In this case, the ring-opening selectivity is less general and depends on both the nucleophile and the aziridine structure.

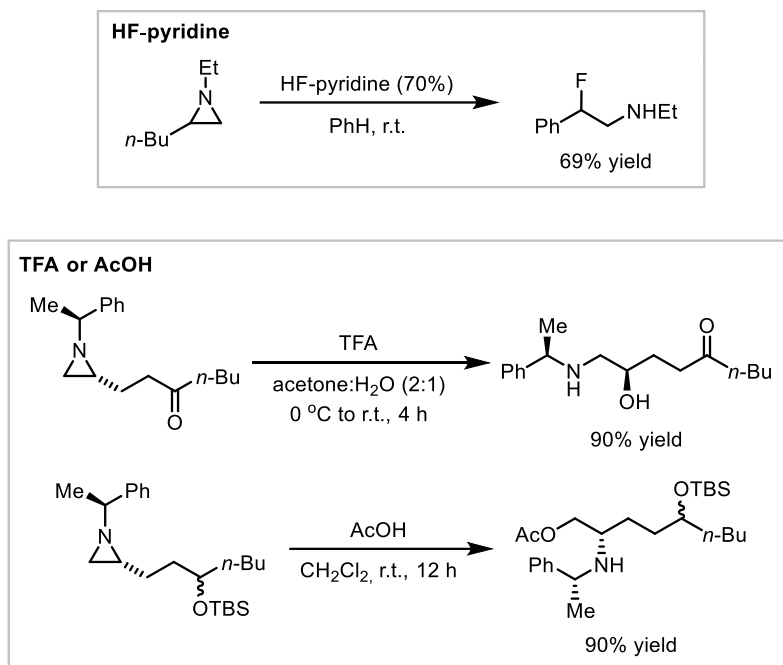


Figure S15. Summary of fluorination, hydroxylation and acetoxylation ring-opening transformations involving *N*-alkyl aziridines.

The use of cyanide as the nucleophile is well established for *N*-Ns-aziridines,⁴⁸⁻⁵¹ while the use of *N*-alkyl aziridine requires the use of strong Lewis acids (e.g. Et₂AlCN) or forcing conditions (microwave).⁵²⁻⁵⁴

Another mode of activation relies on N-quaternarization using either benzyl or methyl halides. These electrophiles can readily react with the nucleophilic nitrogen of *N*-alkyl aziridines to form highly electrophilic aziridinium intermediates, which can subsequently undergo efficient nucleophilic ring opening by a nucleophile present in the reaction medium (often the leaving group derived from the electrophile used) (**Figure S16**).^{39,55-58} However, this strategy is limited to the formation of tertiary alkyl amines, and in the case of β -substituted *N*-alkyl aziridines, regioselectivity during the ring opening of the corresponding aziridinium intermediate can become a major issue. Overall, these two limitations curtail the broader applicability of this approach.

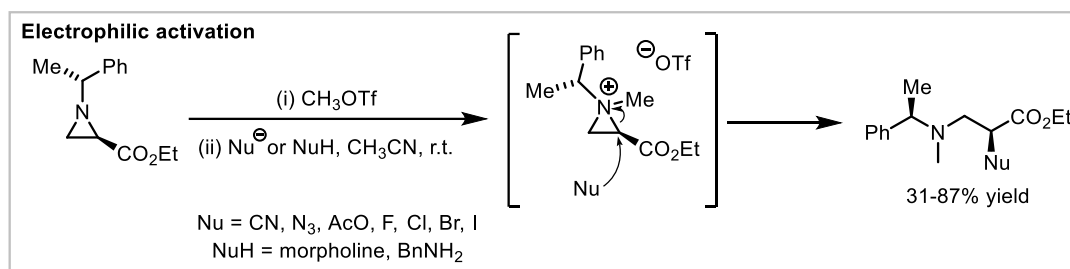


Figure S16. Summary of ring-opening transformations involving electrophilic activation.

The only example involving a carbon nucleophile was reported by Baldwin *et al.*⁵⁹ but required a β -ester substituent and the use of a higher order butylcuprate or *n*-BuMgCl in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. However, the process led to a mixture of ring-opening products in low yield (**Figure S17**).

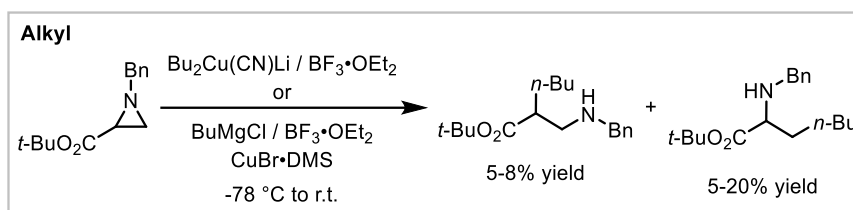


Figure S17. Summary of ring-opening transformations involving *N*-alkyl aziridines with cyanide anions.

Overall, reported ring-opening reactions of *N*-alkyl aziridines remain largely limited to strong nucleophiles and often suffer from poor generality. Consequently, general, mild, and broadly applicable catalytic systems for the ring opening of *N*-alkyl aziridines are still scarce, underscoring a clear opportunity for further methodological development.

13.3 Metal-Catalysed Ring Opening⁶⁰

To our knowledge, only two documented approaches exist in the literature for the ring-opening of *N*-alkyl aziridines. The first method requires extremely forcing conditions and relies on a directing group to achieve the transformation (depicted in the top section of **Figure S18**). The second approach involves a specific reactivity pattern, where carbon monoxide is inserted into *N*-alkyl aziridines to produce a range of β -lactam products (illustrated in the bottom section of **Figure S18**).^{61,62}

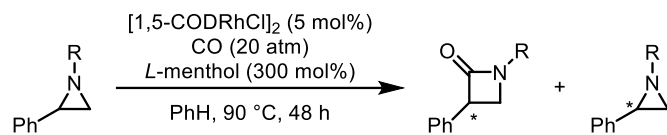
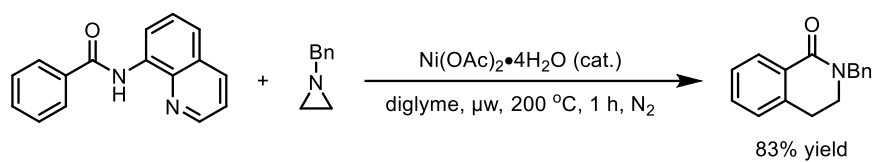
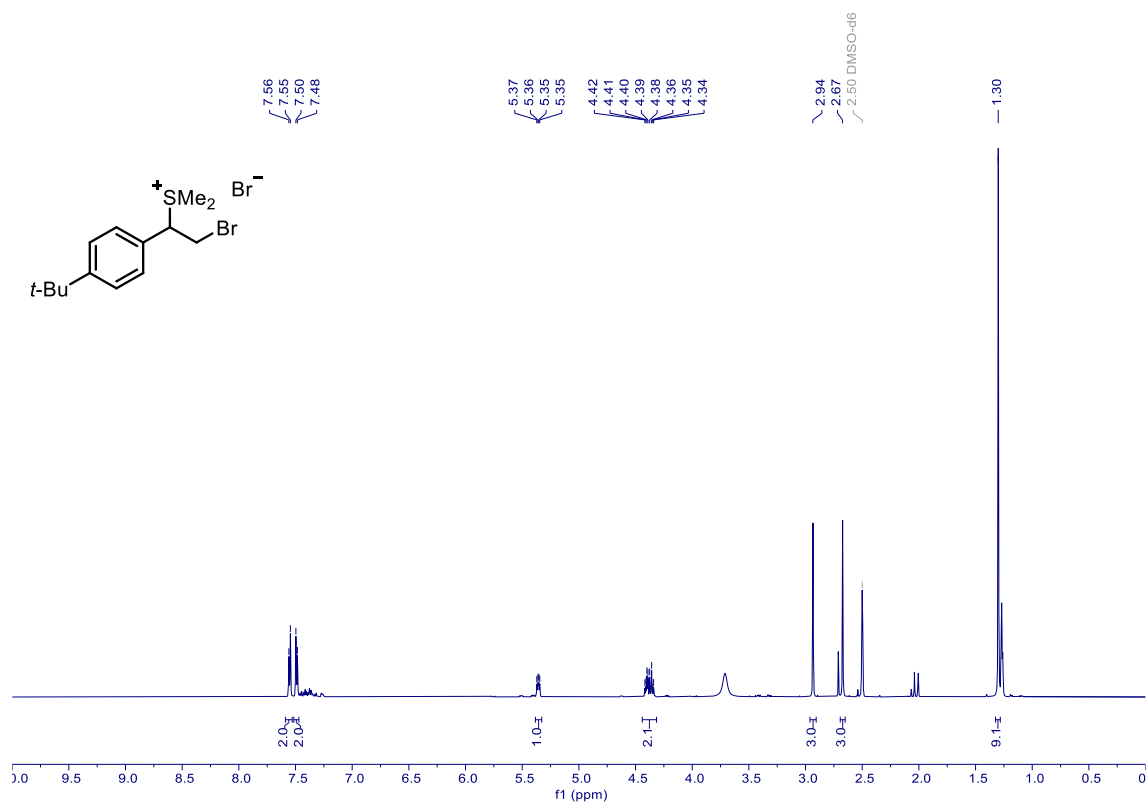


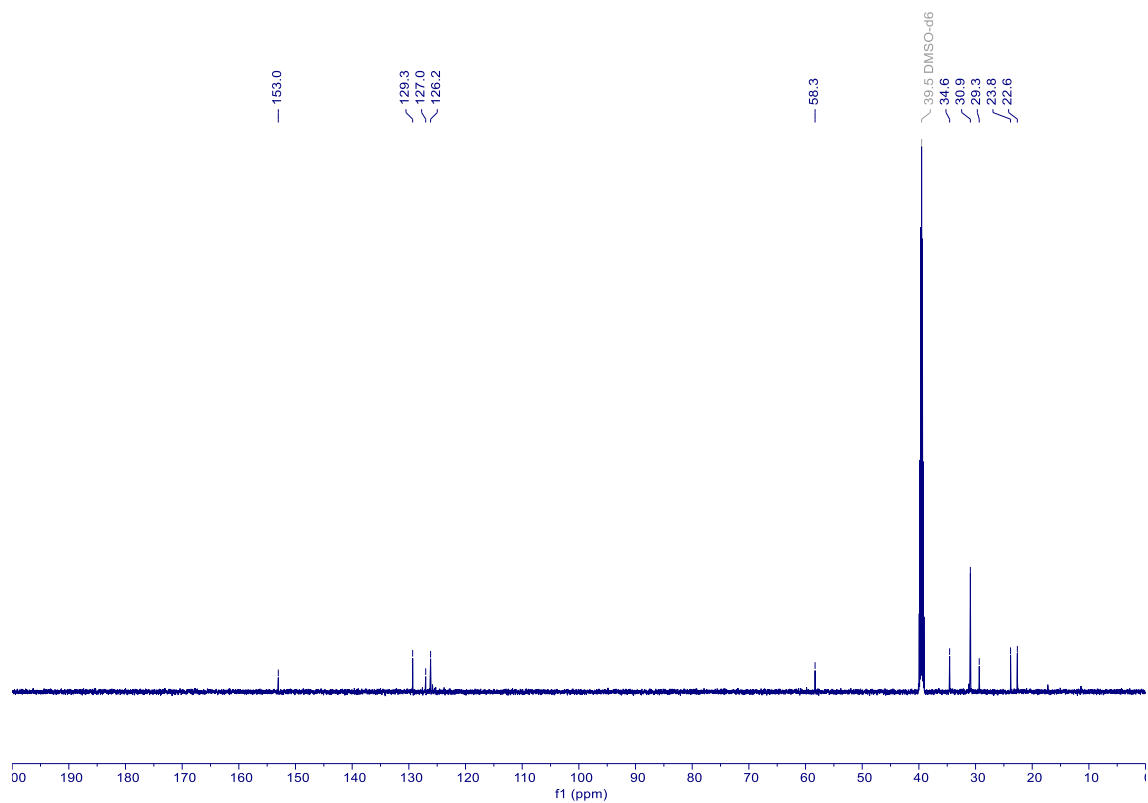
Figure S18. Summary of metal-catalysed ring opening reaction of *N*-alkyl aziridines.

14 NMR Spectra

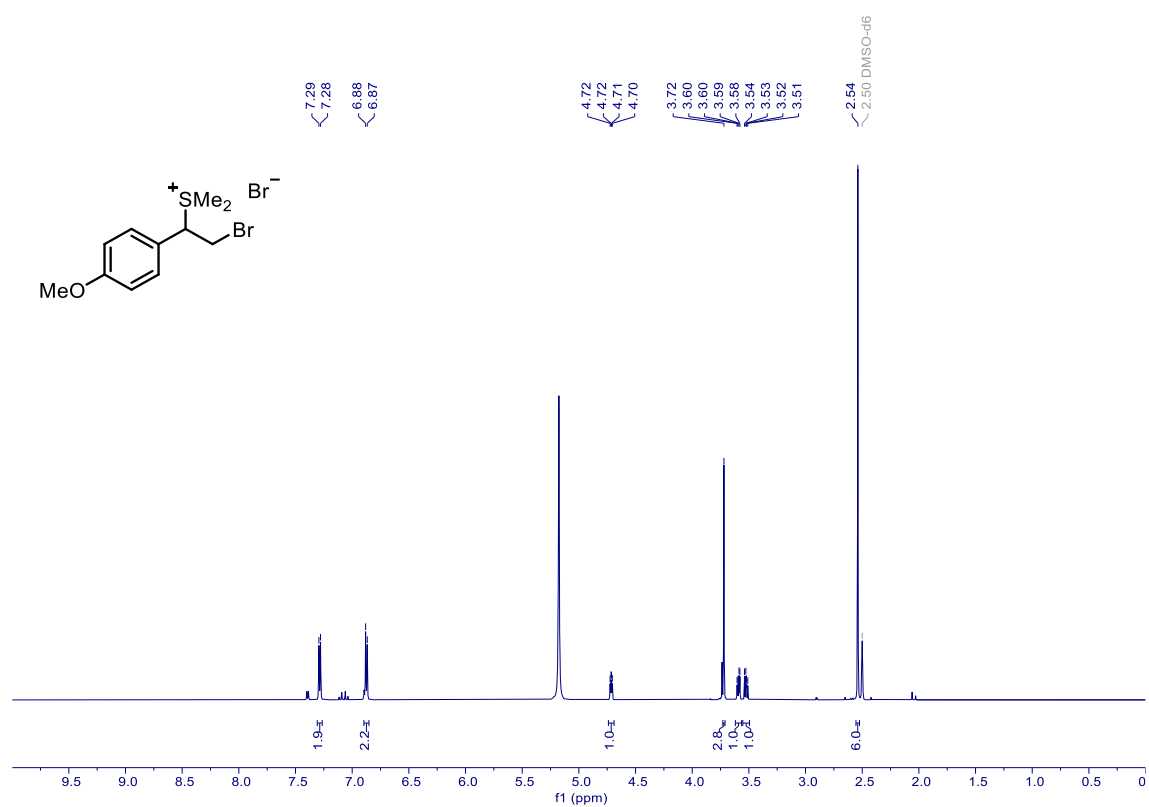
S2a – ^1H NMR (600 MHz, CDCl_3)



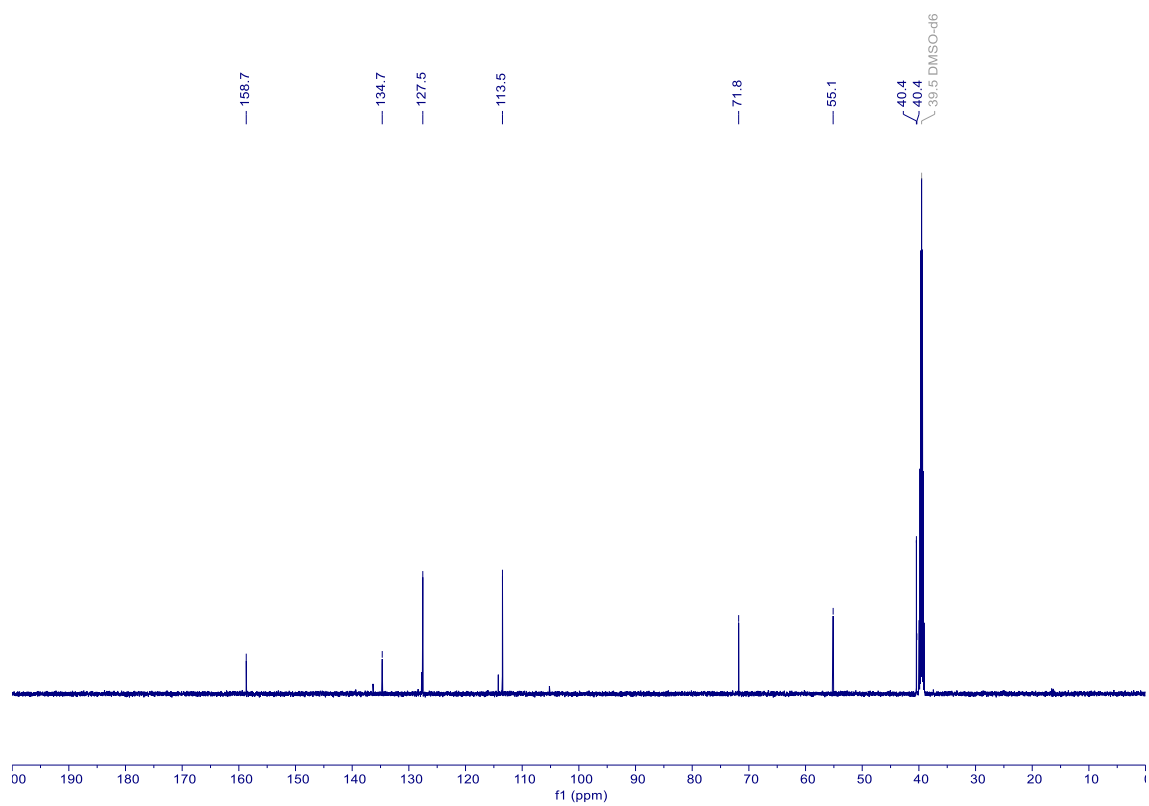
S2a – ^{13}C NMR (151 MHz, CDCl_3)



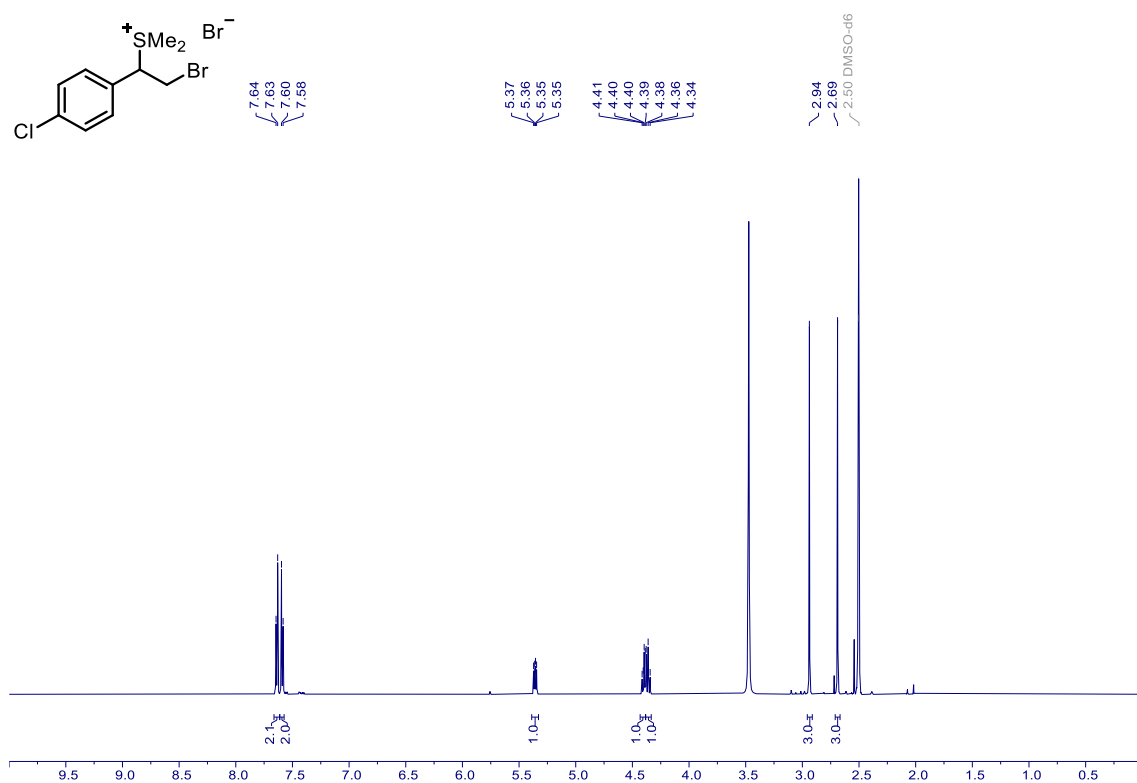
S3a – ^1H NMR (600 MHz, $\text{DMSO-}d_6$)



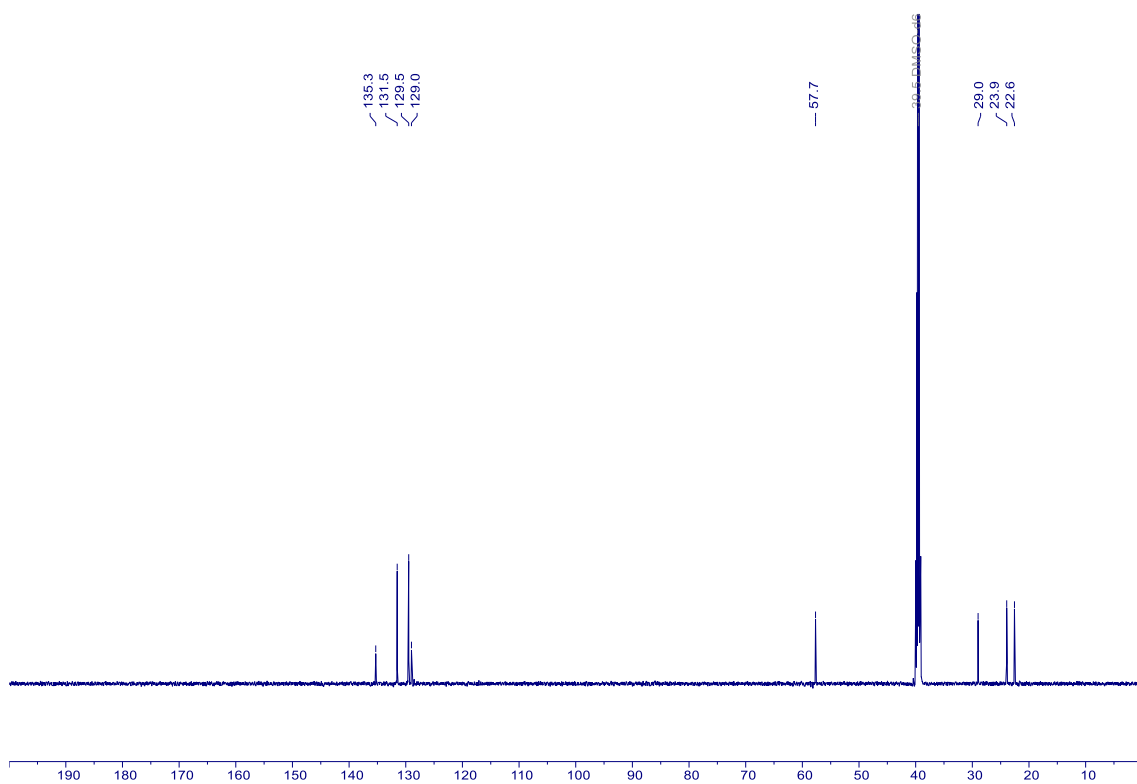
S3a – ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$)



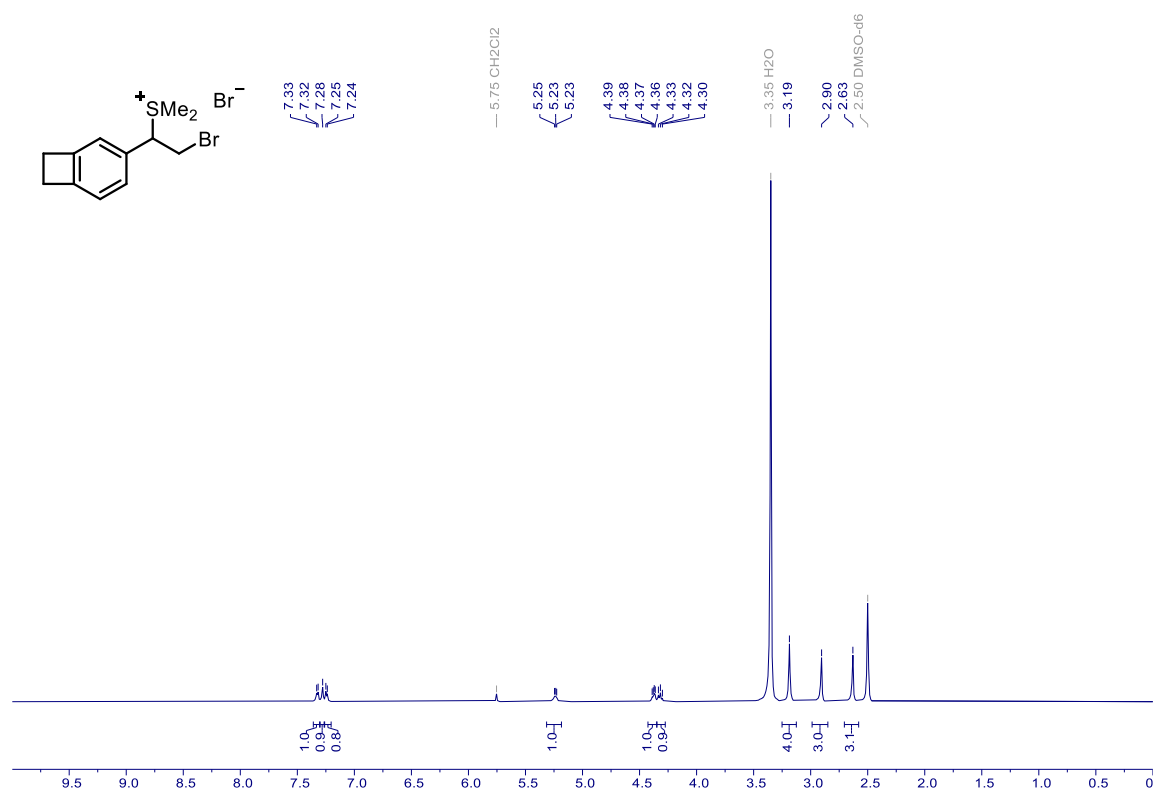
S5a – ^1H NMR (600 MHz, $\text{DMSO-}d_6$)



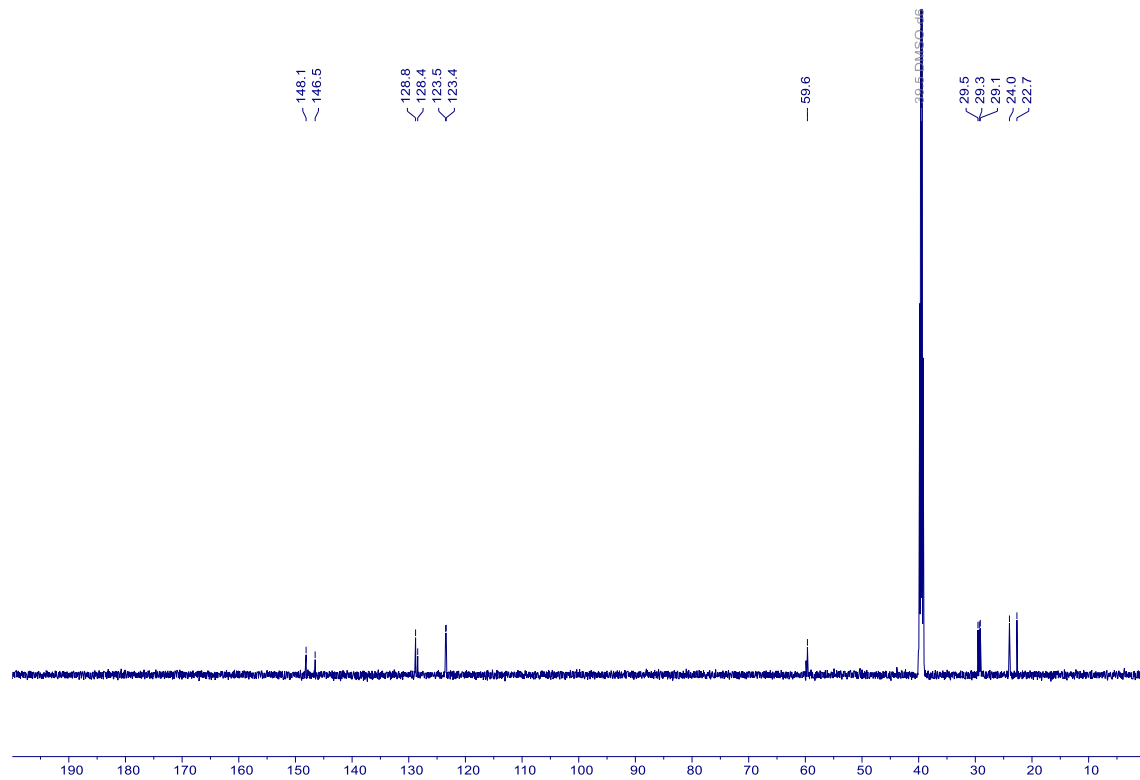
S5a – ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$)



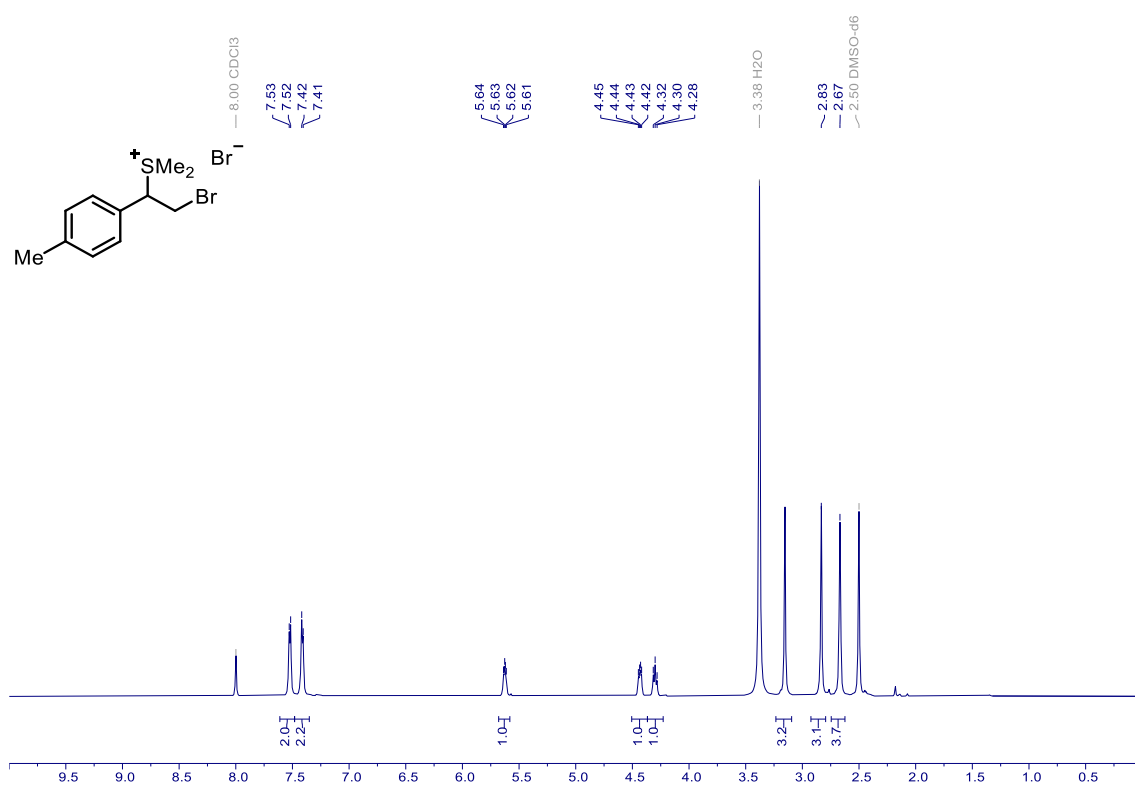
S7a – ^1H NMR (600 MHz, $\text{DMSO-}d_6$)



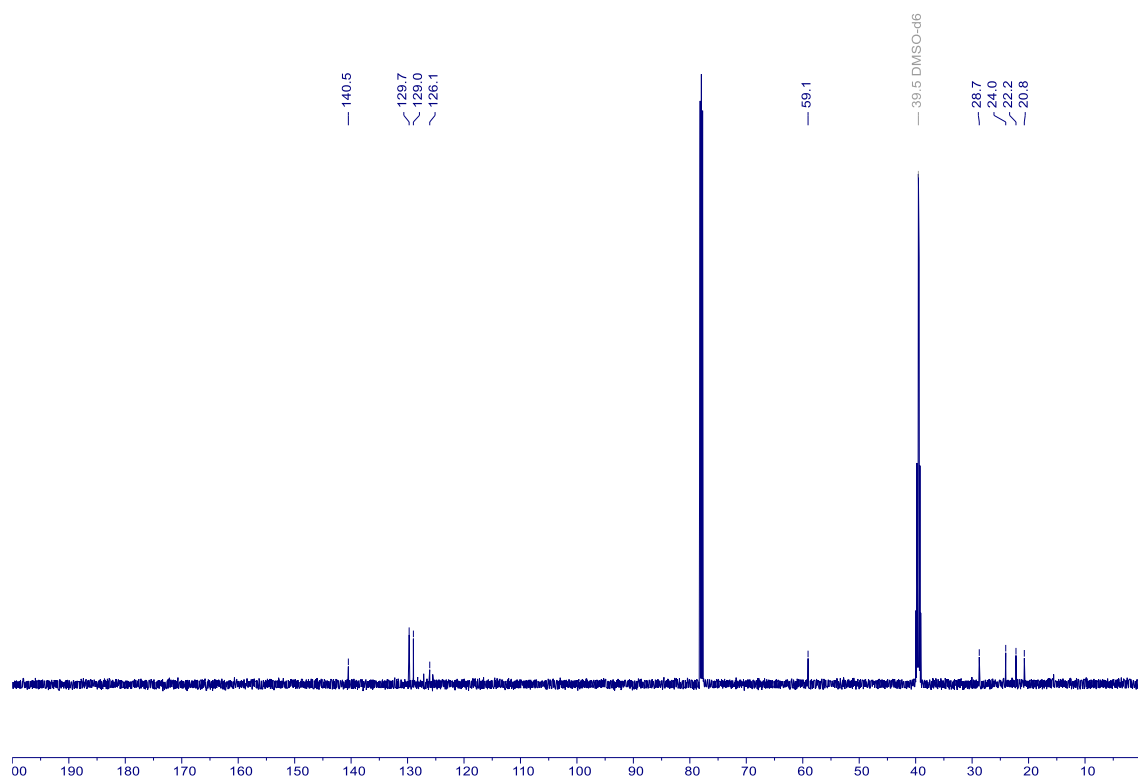
S7a – ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$)



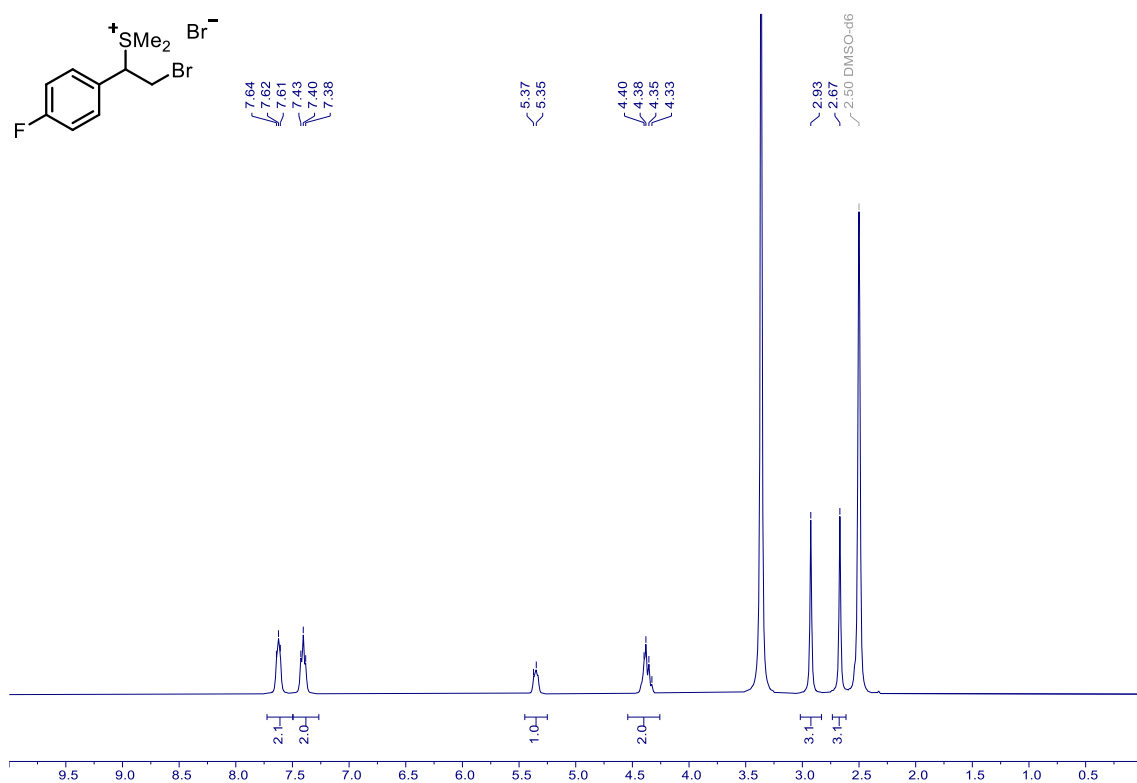
S8a – ^1H NMR (600 MHz, $\text{DMSO}-d_6$)



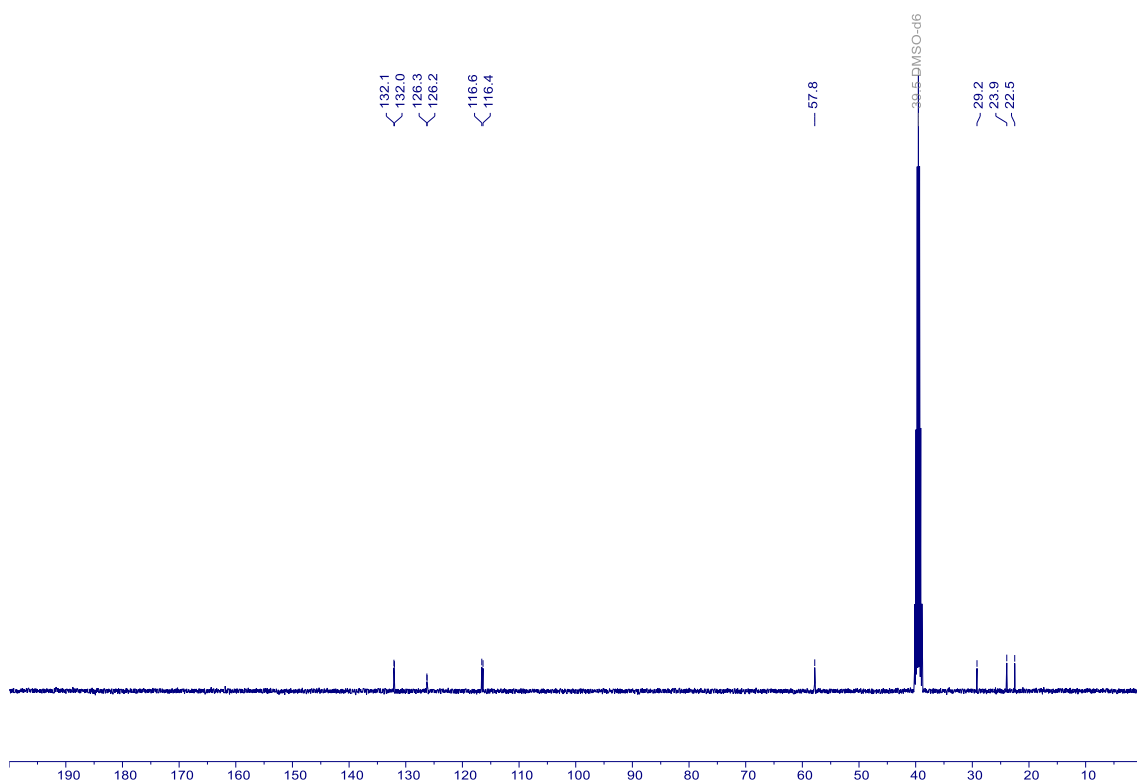
S8a – ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$)



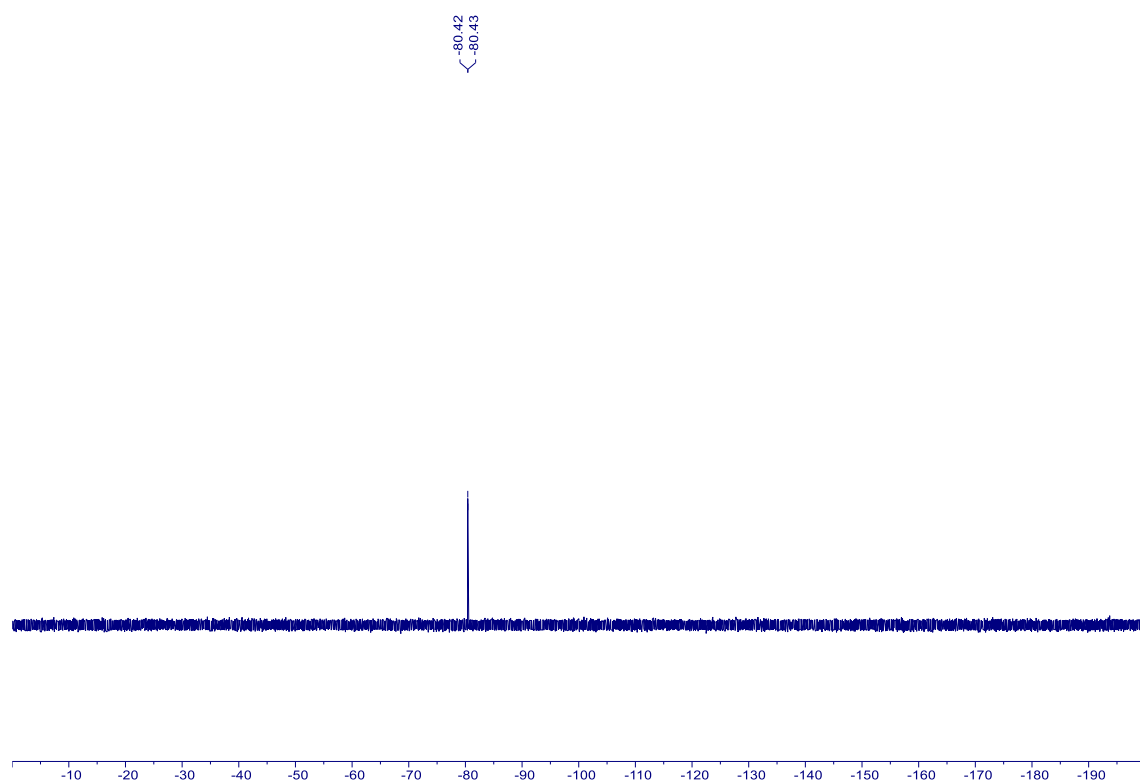
S9a – ^1H NMR (400 MHz, CDCl_3)



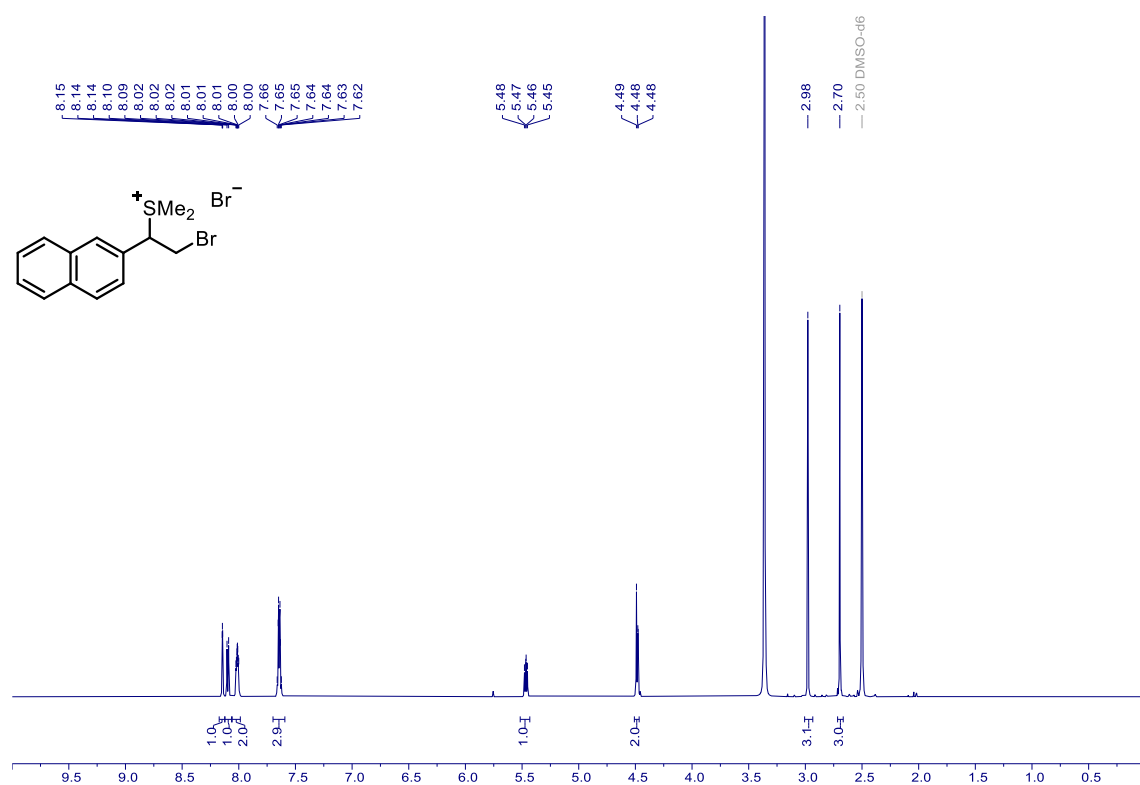
S9a – ^{13}C NMR (101 MHz, CDCl_3)



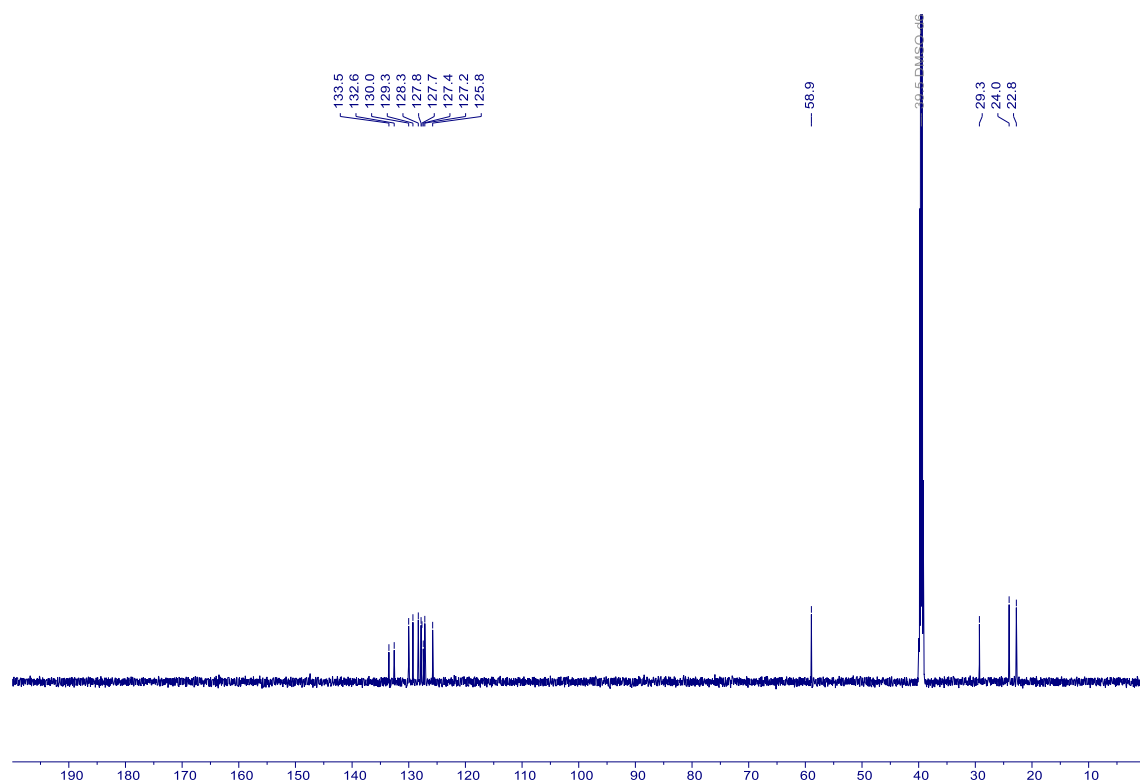
S9a – ^{19}F NMR (565 MHz, CDCl_3)



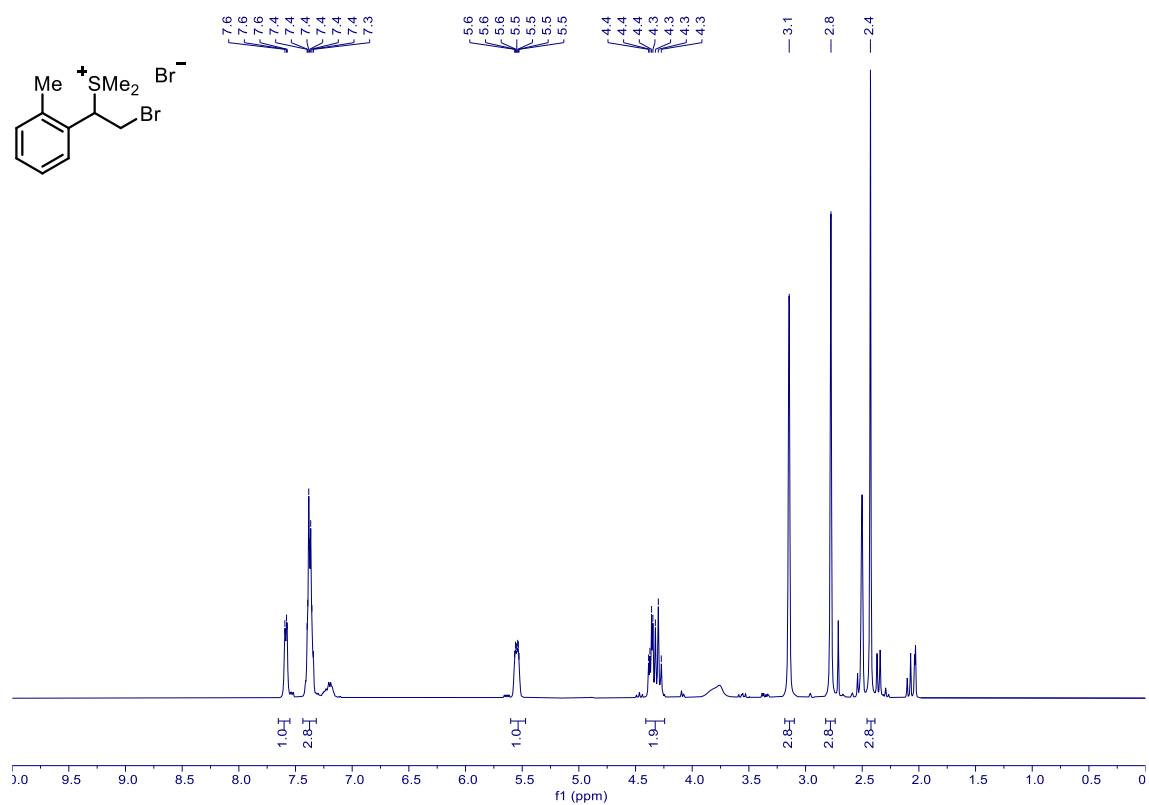
S11a – ^1H NMR (600 MHz, CDCl_3)



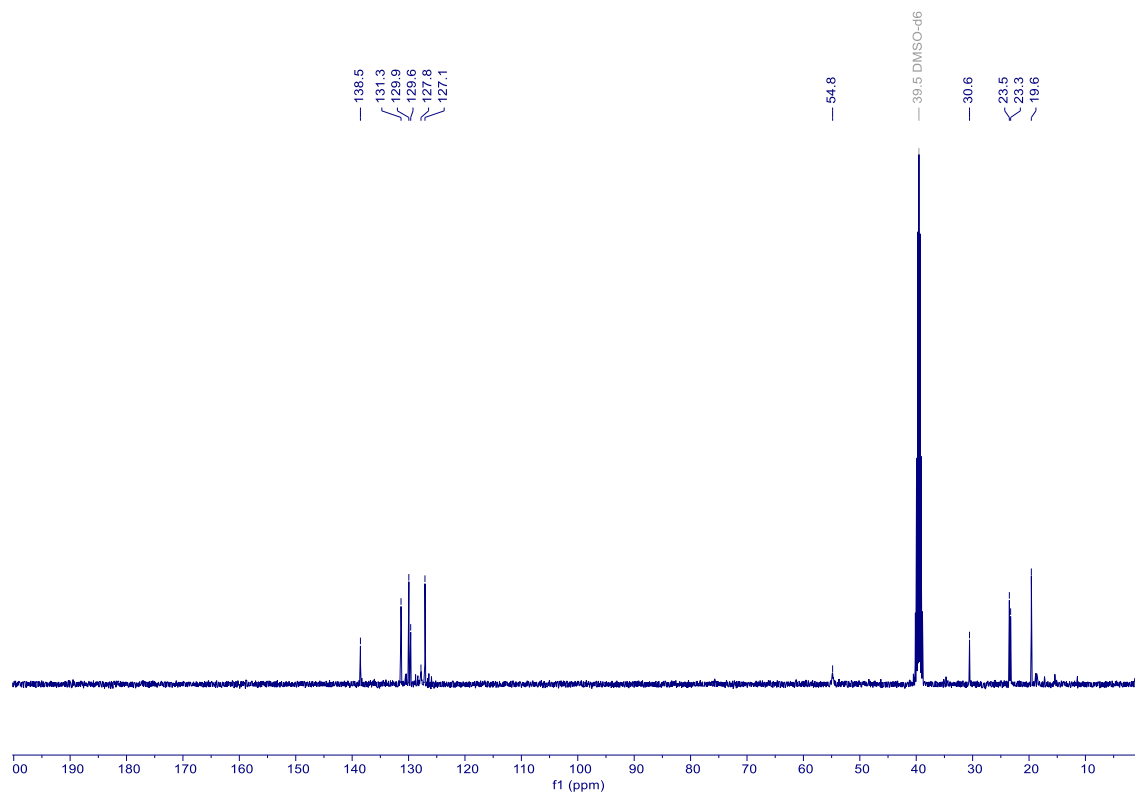
S11a – ^{13}C NMR (151 MHz, CDCl_3)



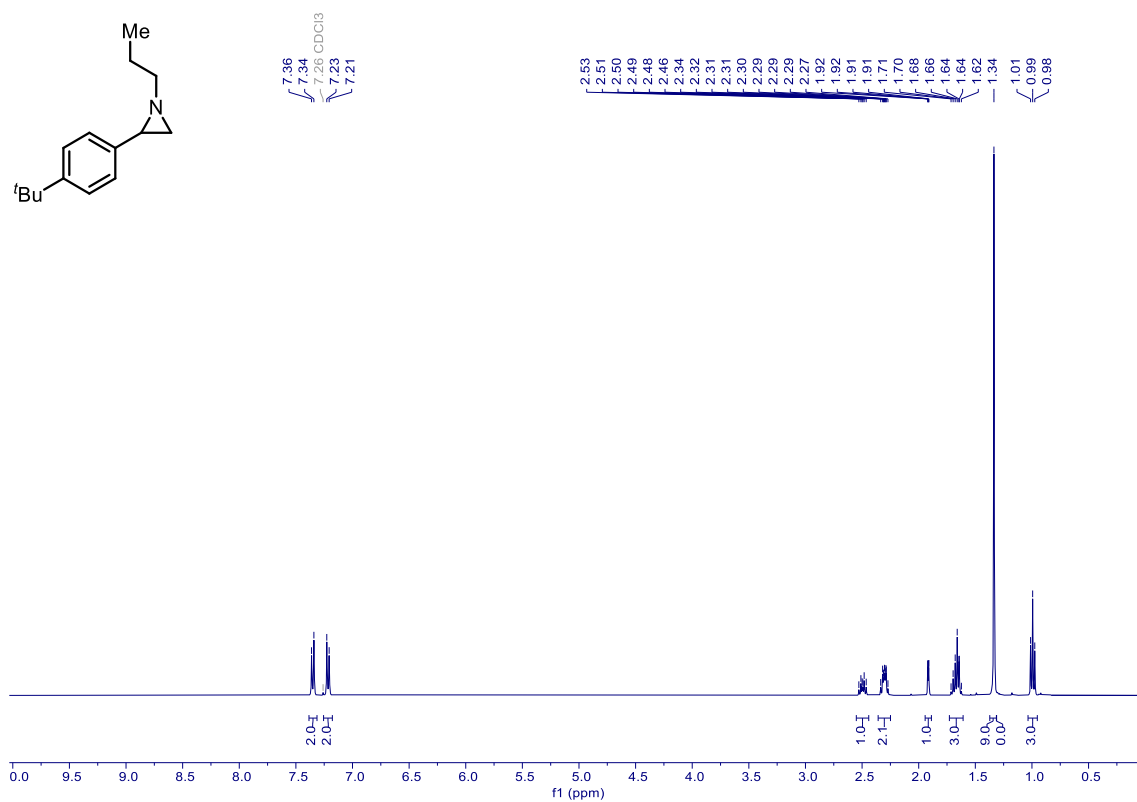
S12a – ^1H NMR (400 MHz, $\text{DMSO-}d_6$)



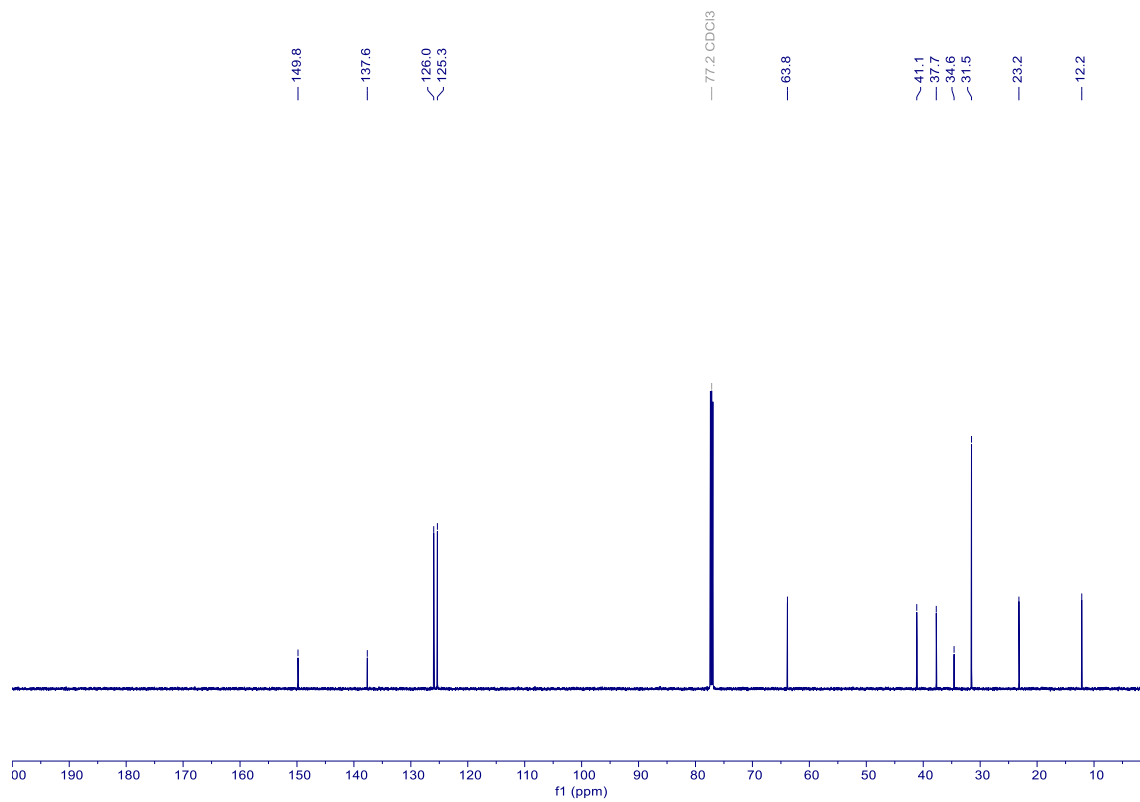
S12a – ^{13}C NMR (101 MHz, CDCl_3)



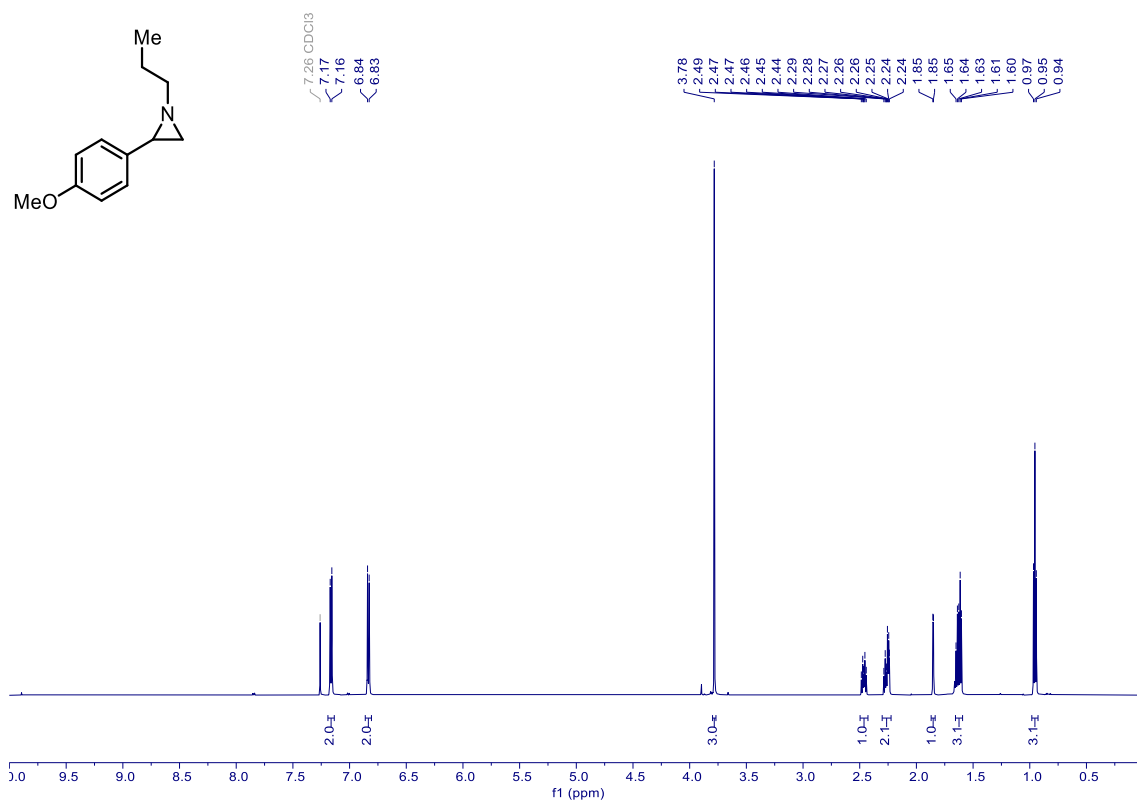
2 – ^1H NMR (400 MHz, CDCl_3)



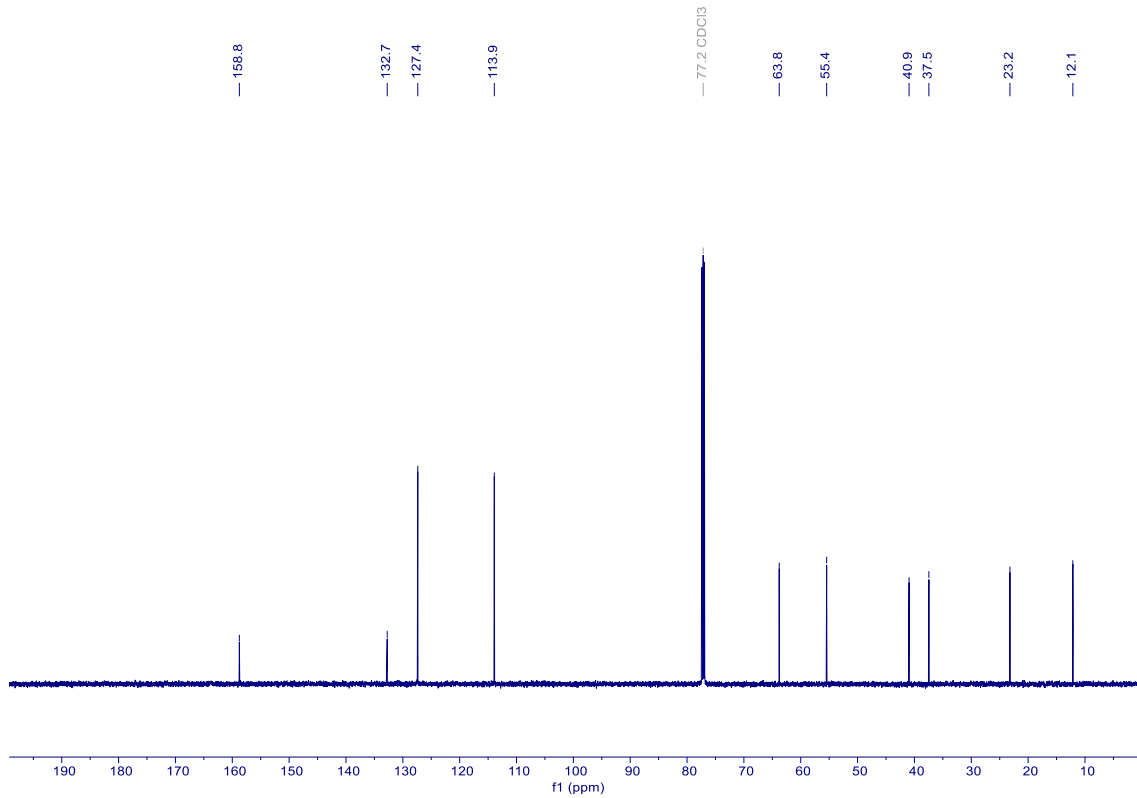
2 – ^{13}C NMR (151 MHz, CDCl_3)



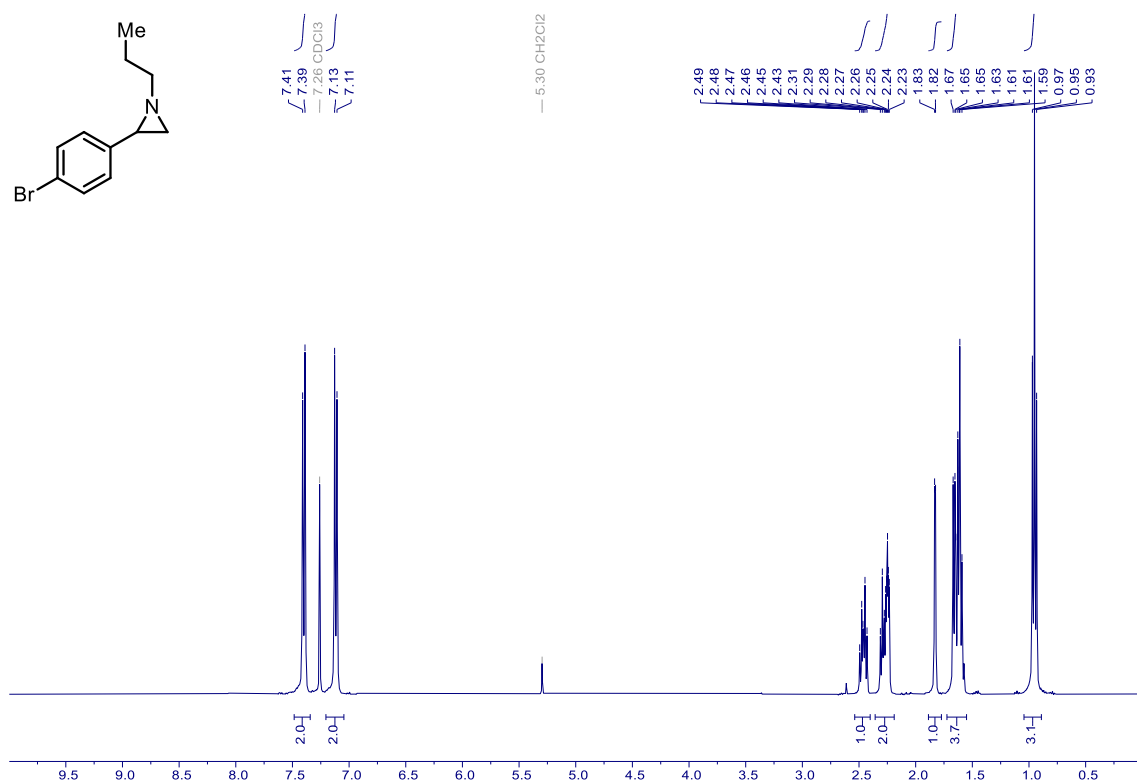
3 – ^1H NMR (600 MHz, CDCl_3)



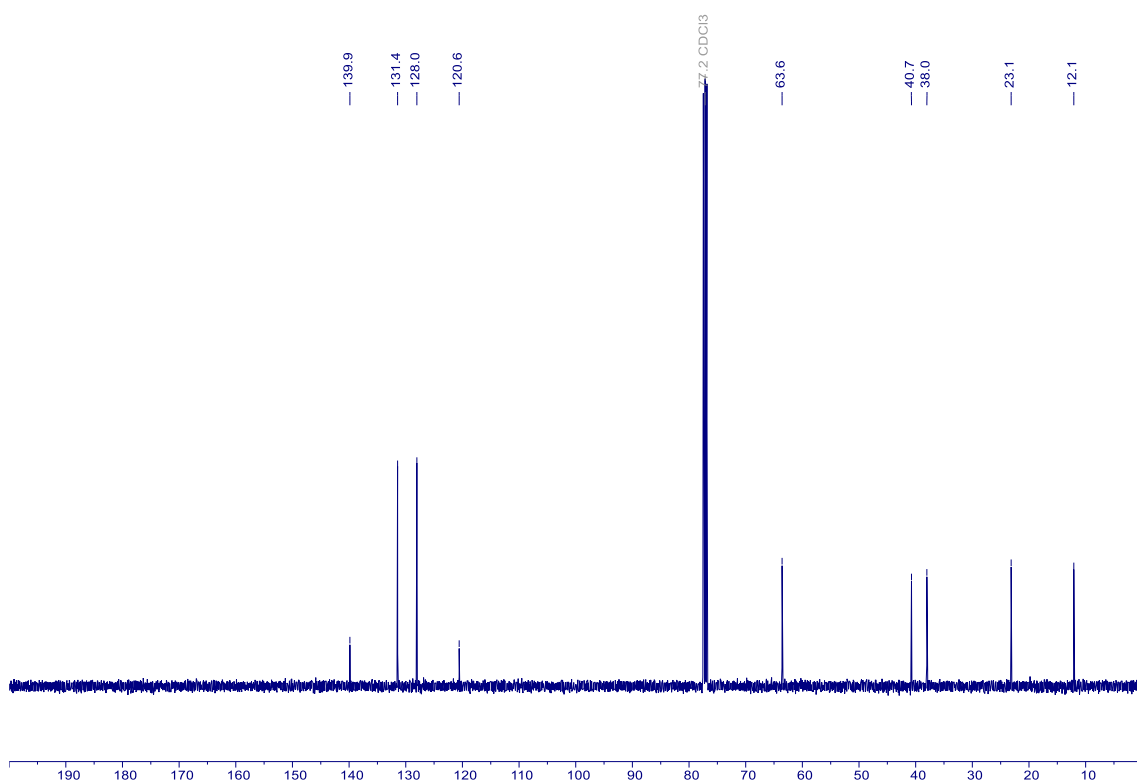
3 – ^{13}C NMR (151 MHz, CDCl_3)



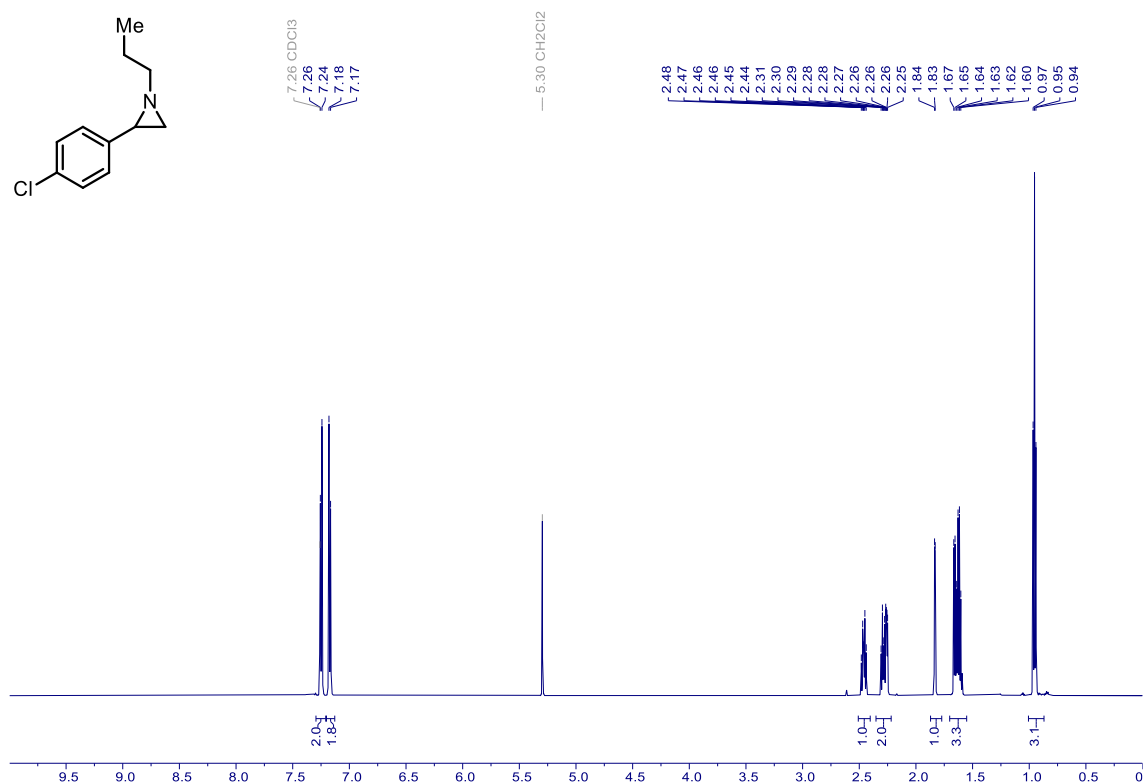
4 – ^1H NMR (400 MHz, CDCl_3)



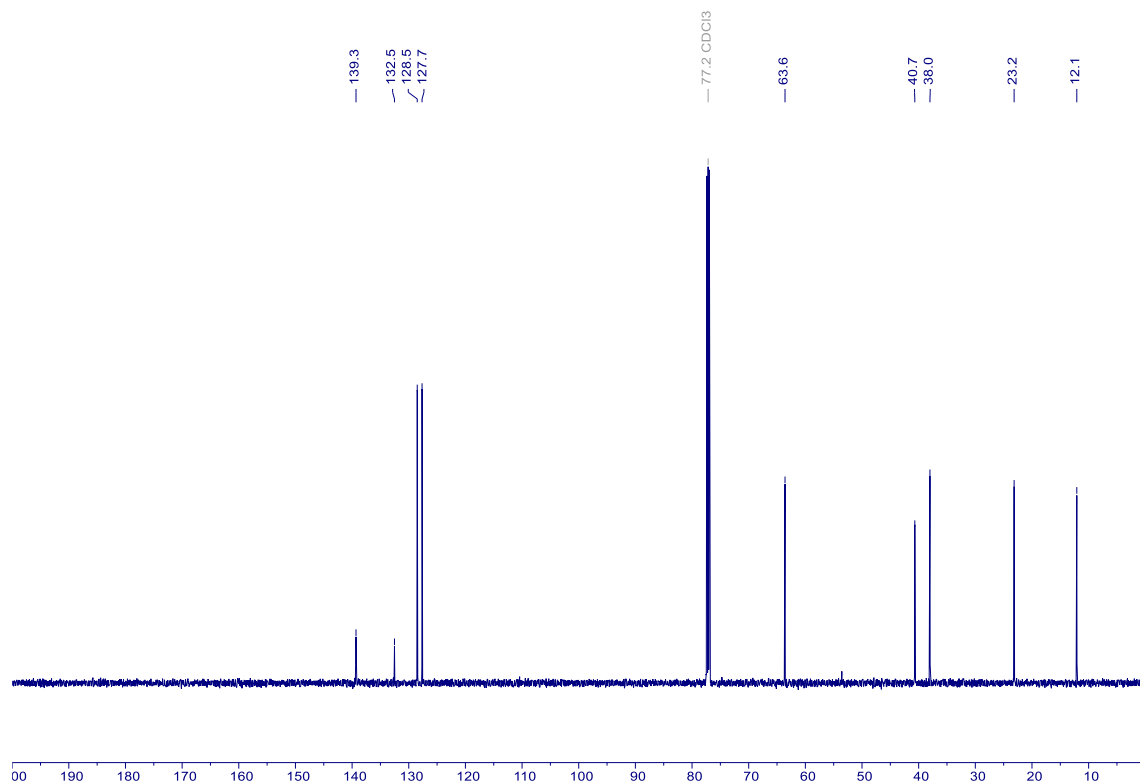
4 – ^{13}C NMR (151 MHz, CDCl_3)



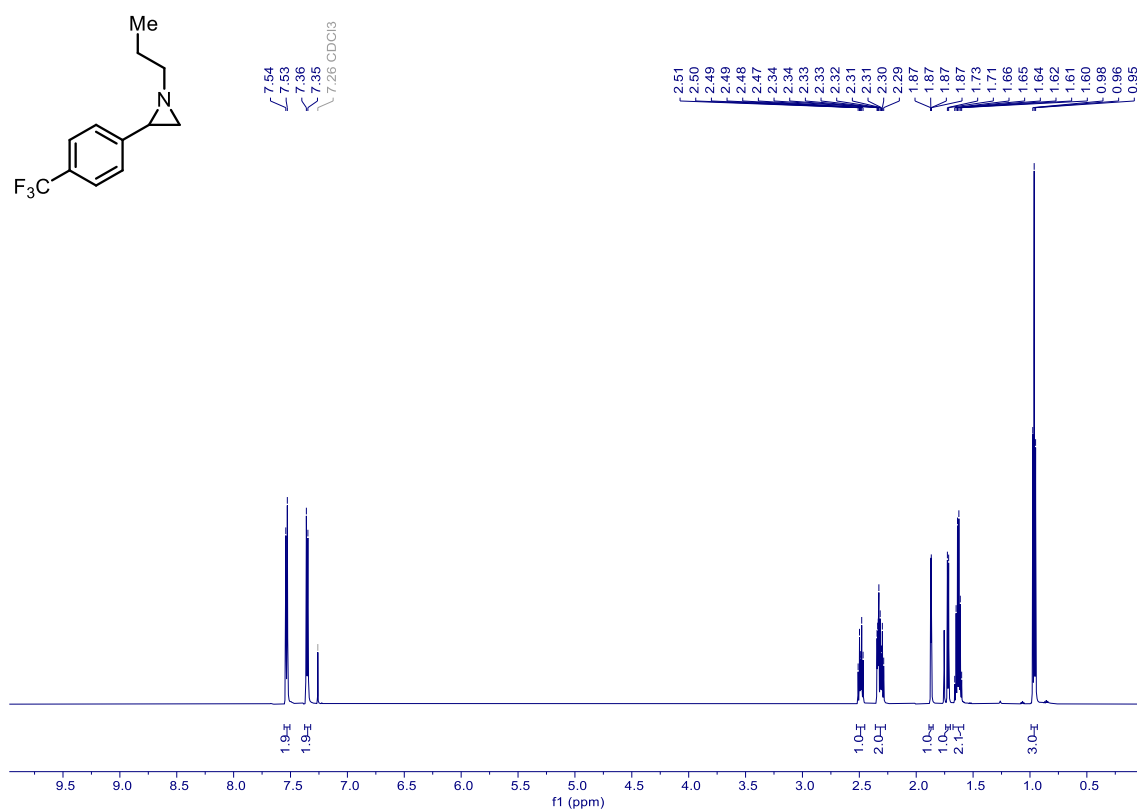
5 – ^1H NMR (600 MHz, CDCl_3)



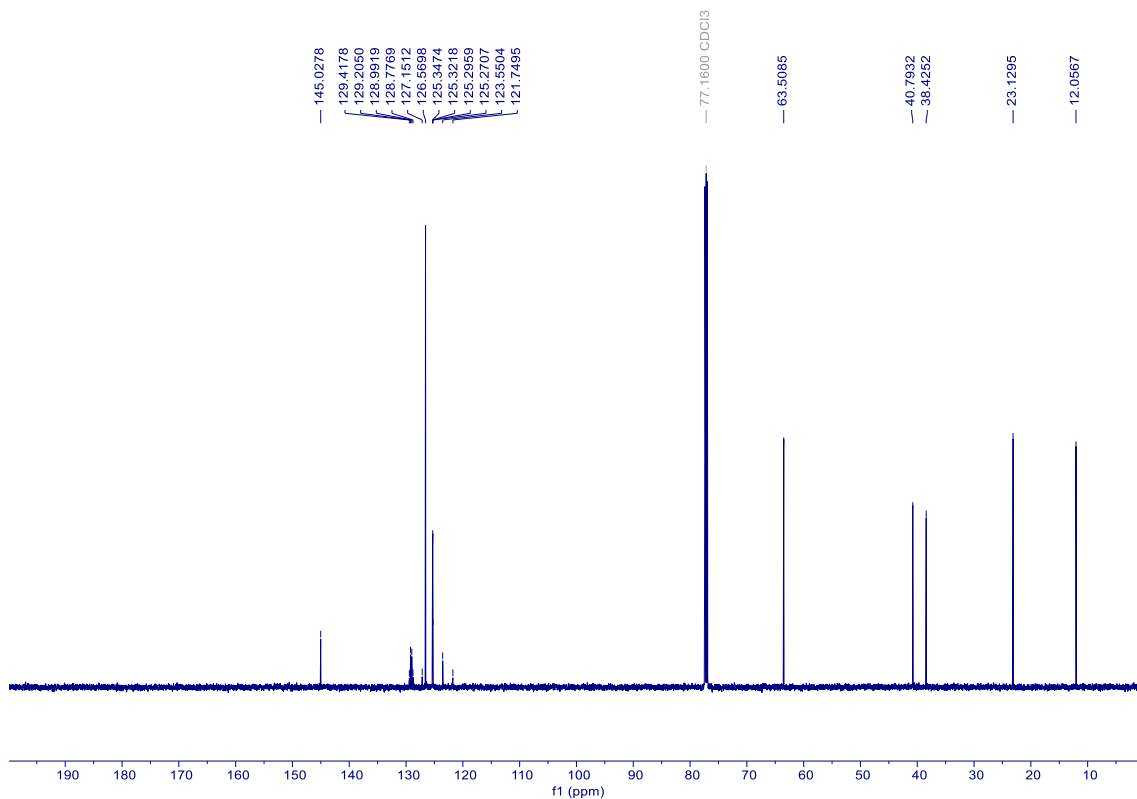
5 – ^{13}C NMR (151 MHz, CDCl_3)



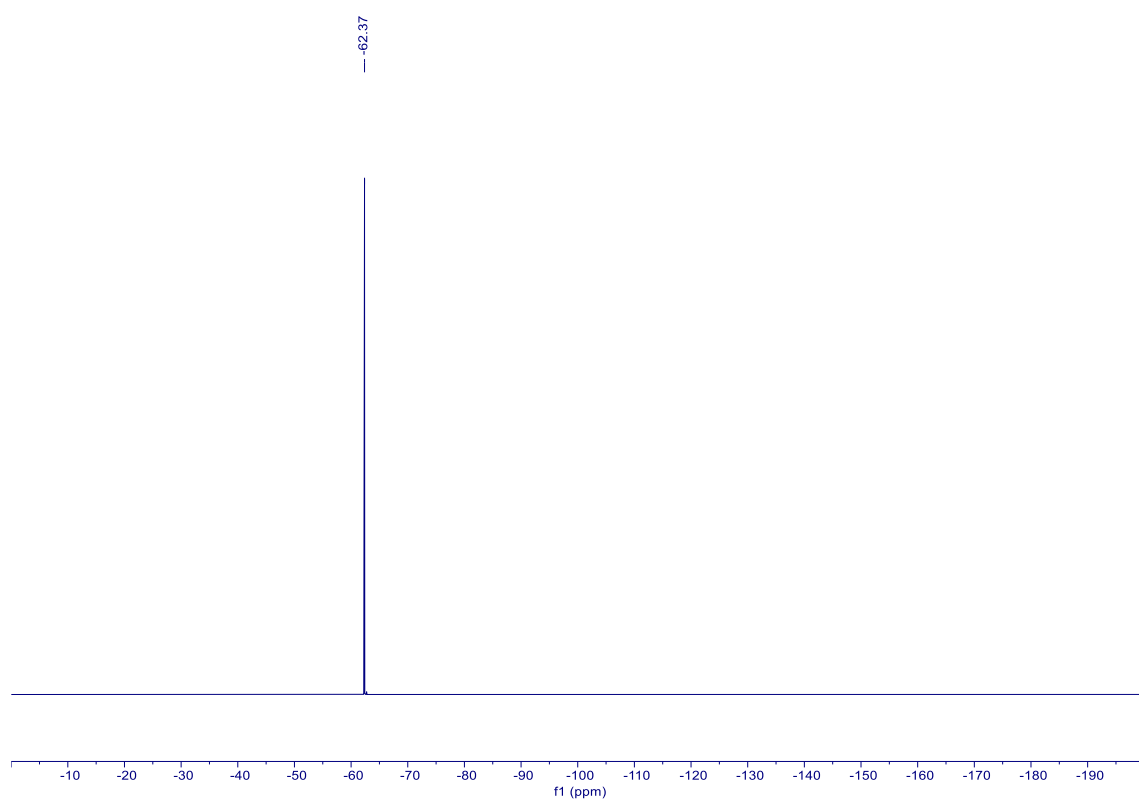
6 – ^1H NMR (600 MHz, CDCl_3)



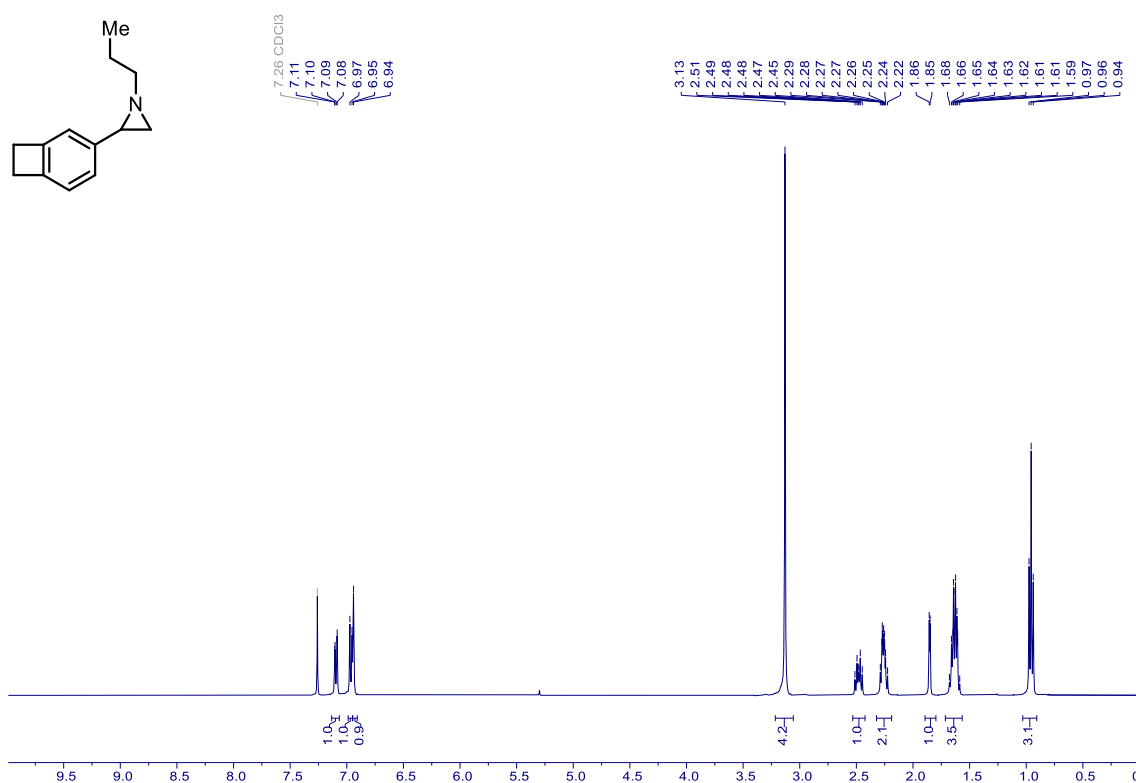
6 – ^{13}C NMR (151 MHz, CDCl_3)



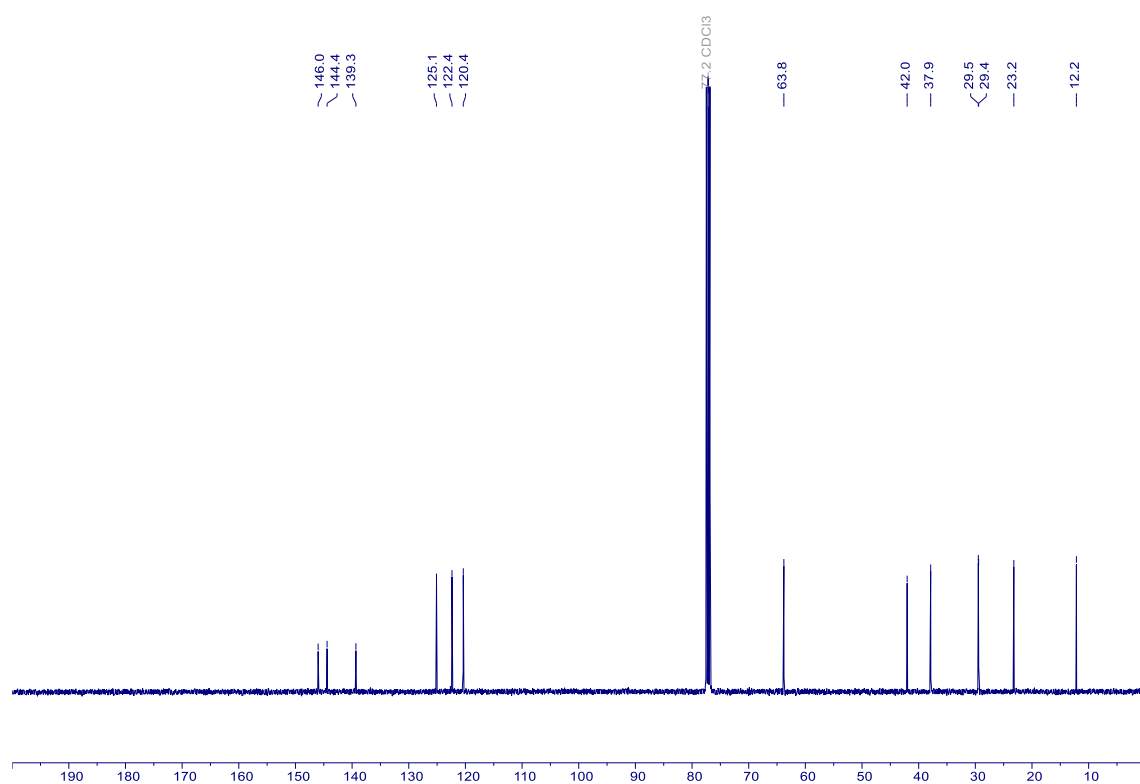
6 – ^{19}F NMR (565 MHz, CDCl_3)



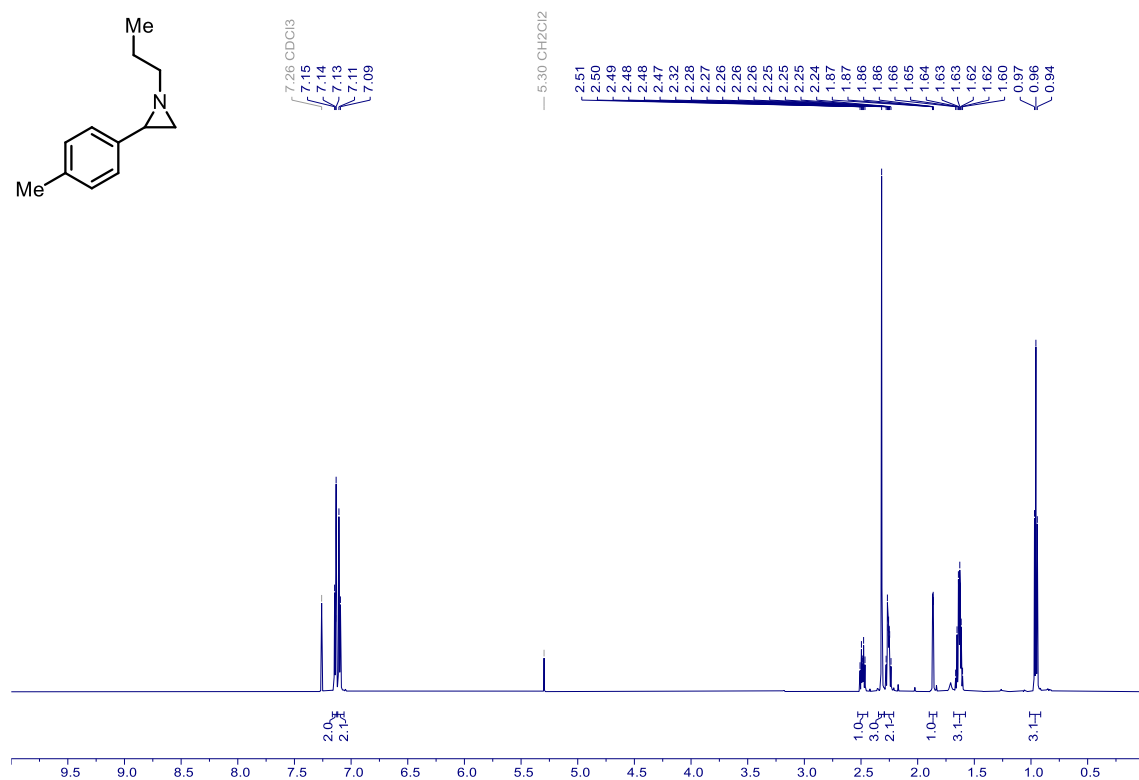
7 – ^1H NMR (400 MHz, CDCl_3)



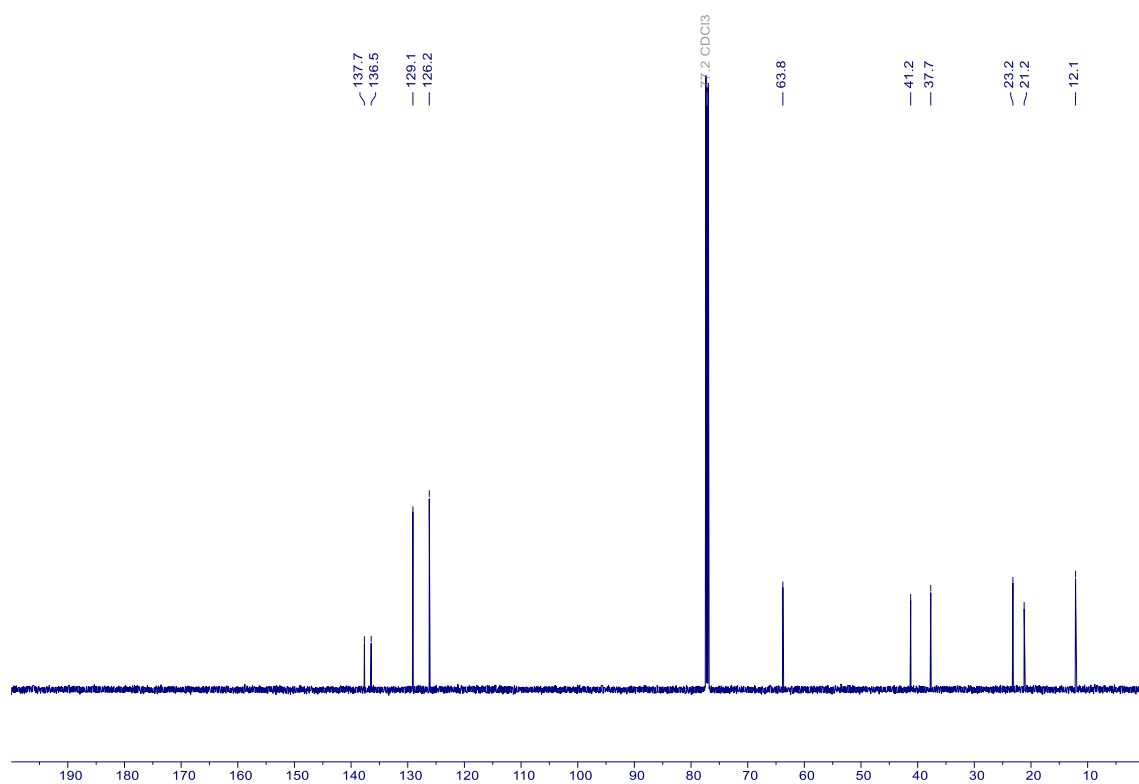
7 – ^{13}C NMR (101 MHz, CDCl_3)



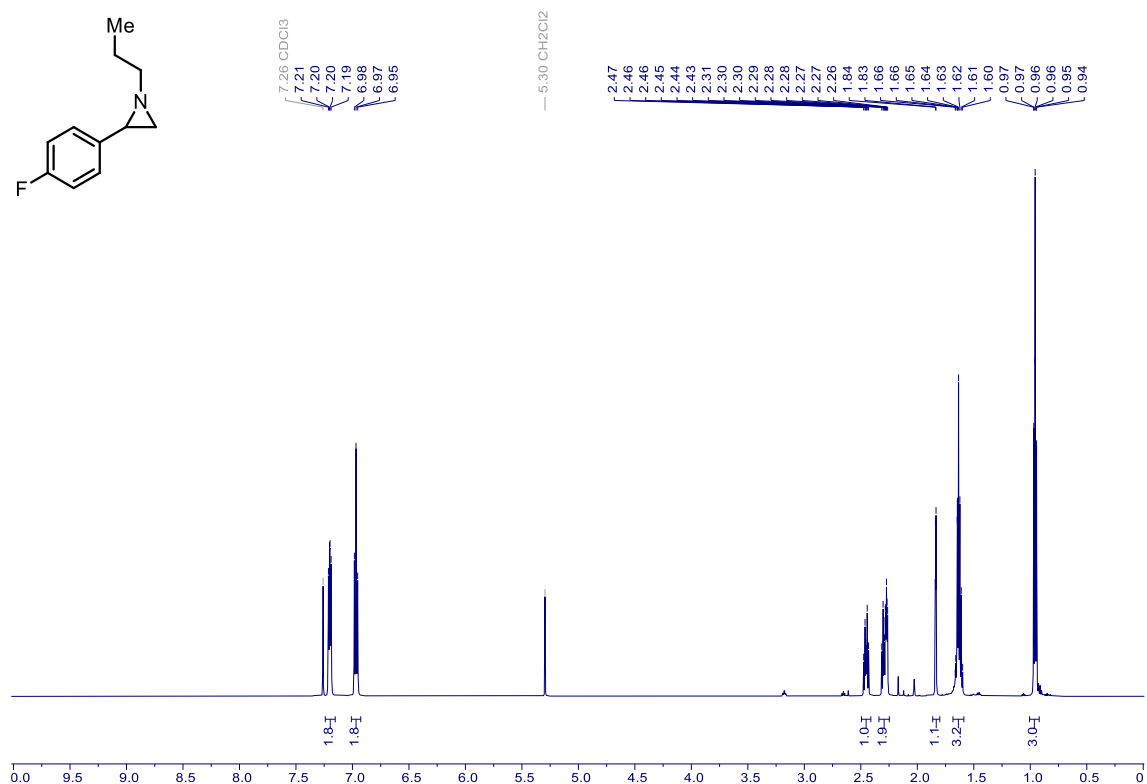
14 – ^1H NMR (600 MHz, CDCl_3)



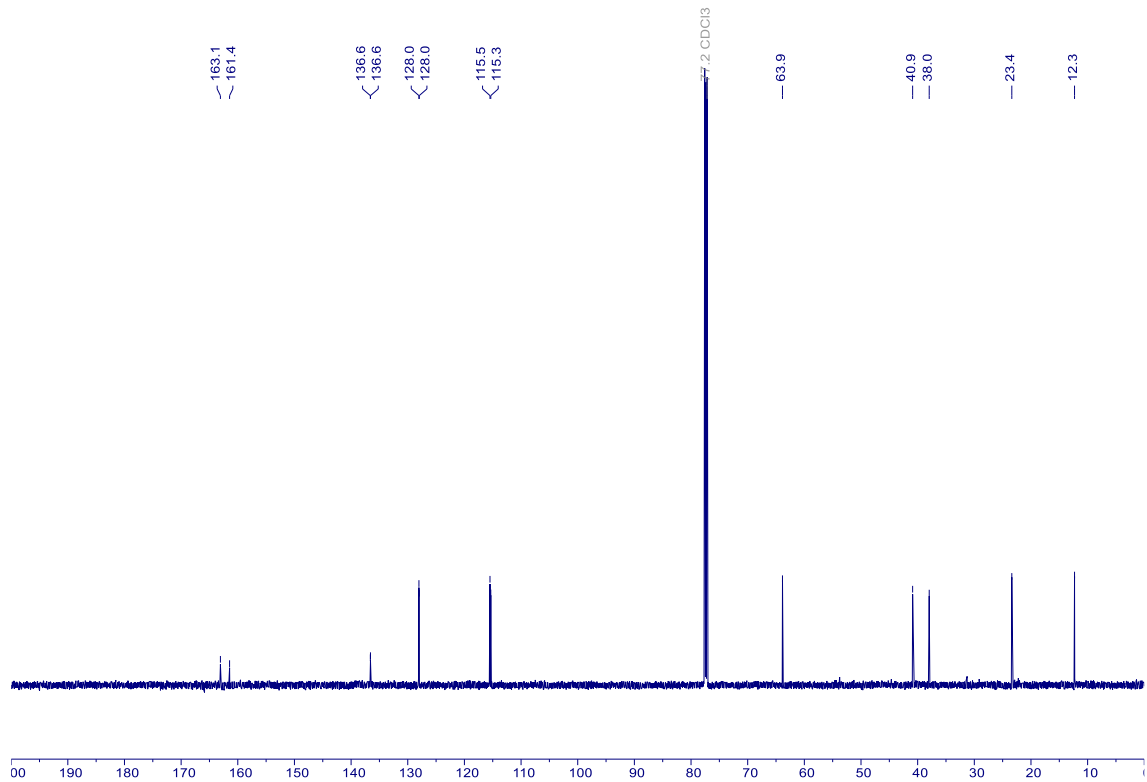
14 – ^{13}C NMR (151 MHz, CDCl_3)



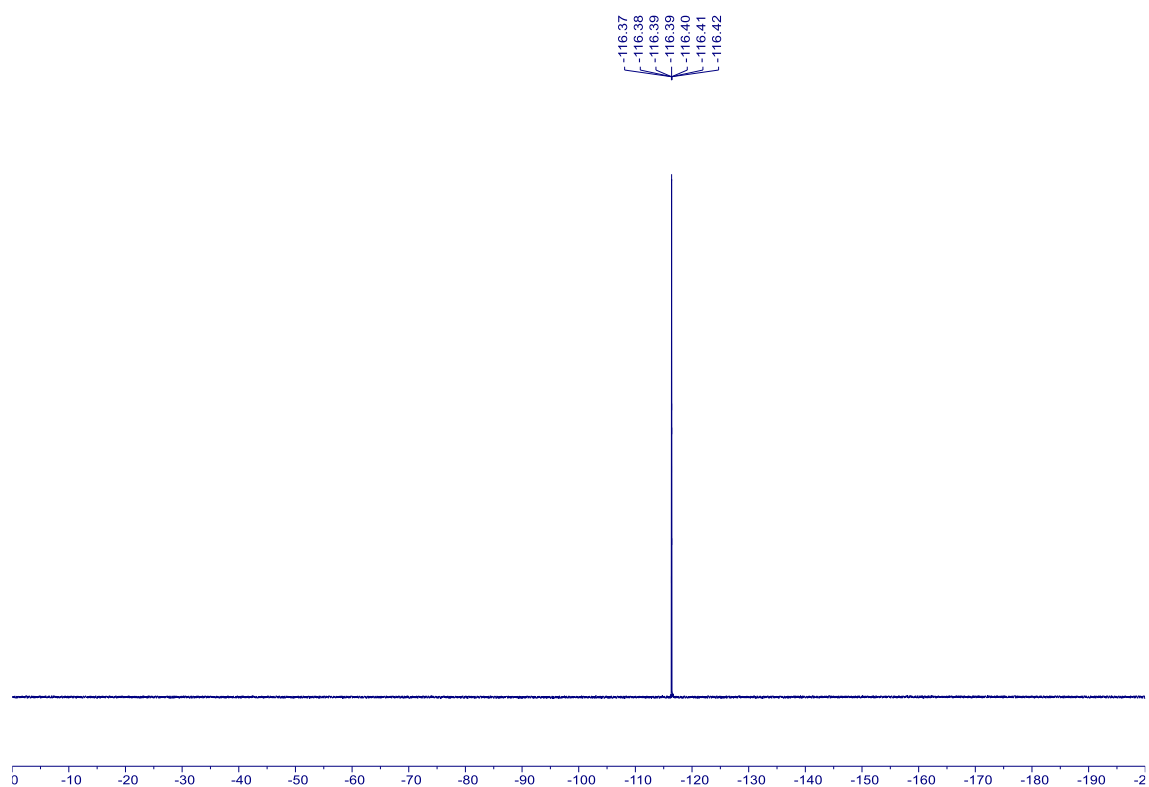
15 – ^1H NMR (600 MHz, CDCl_3)



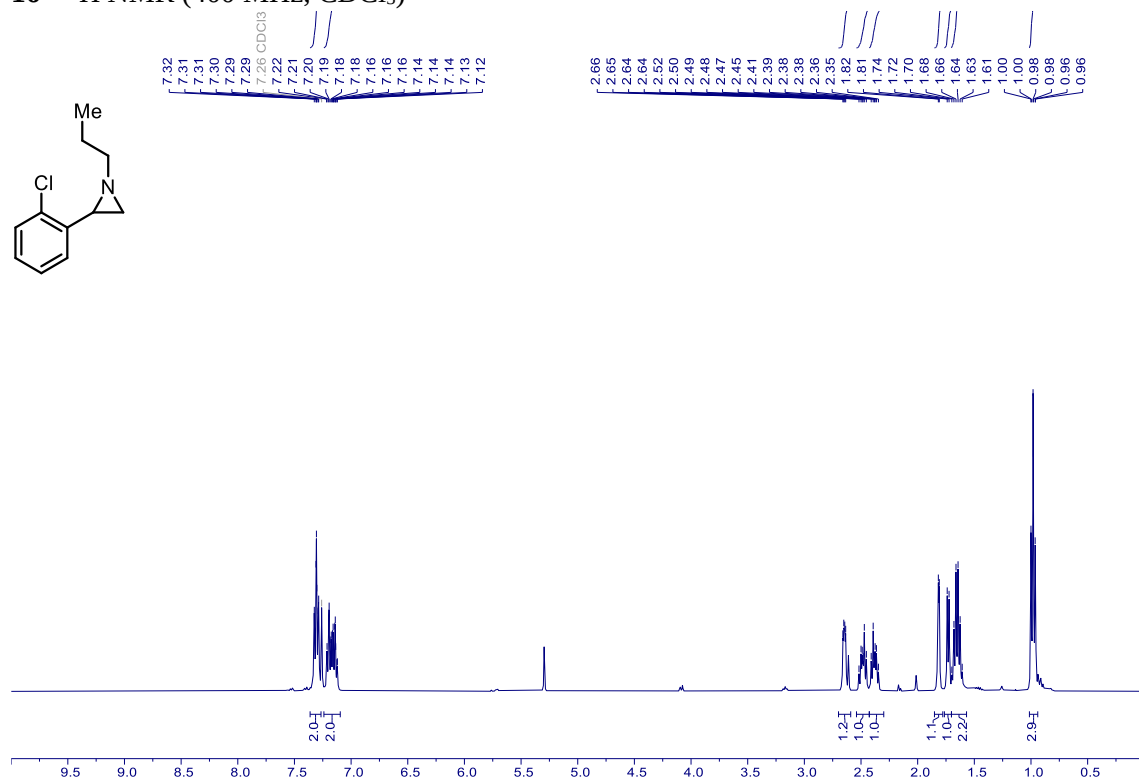
15 – ^{13}C NMR (151 MHz, CDCl_3)



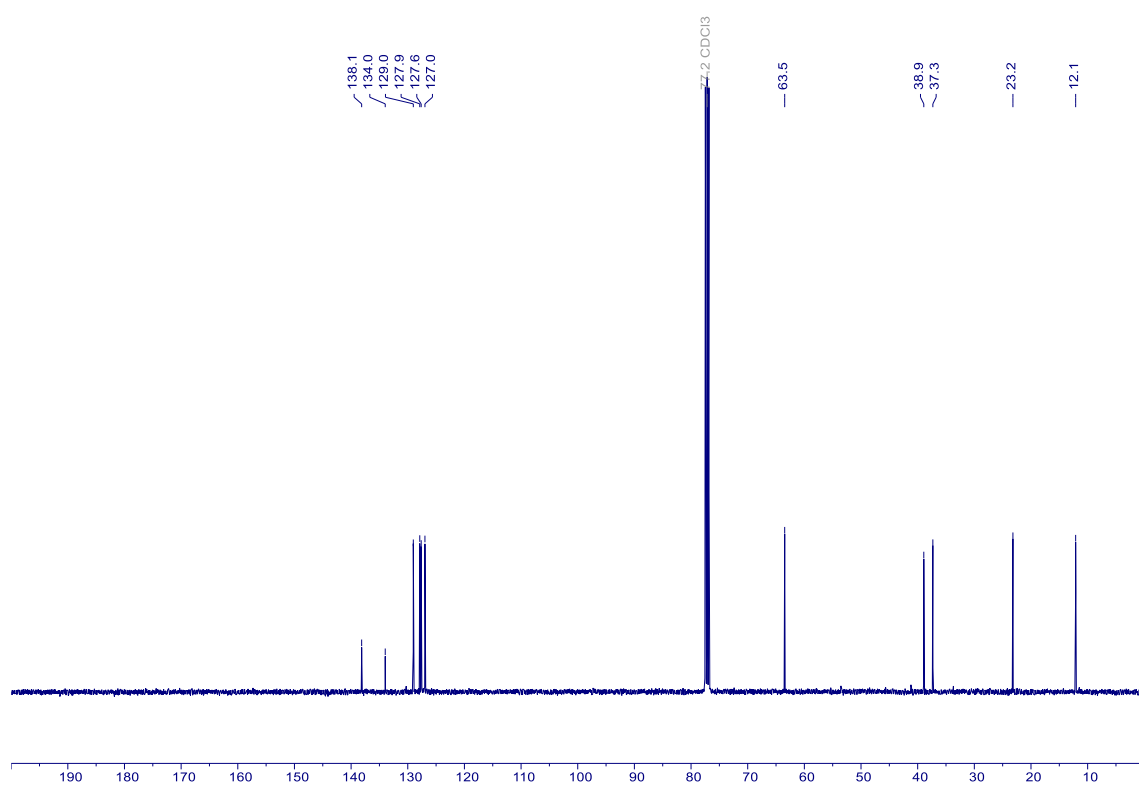
15 – ^{19}F NMR (565 MHz, CDCl_3)



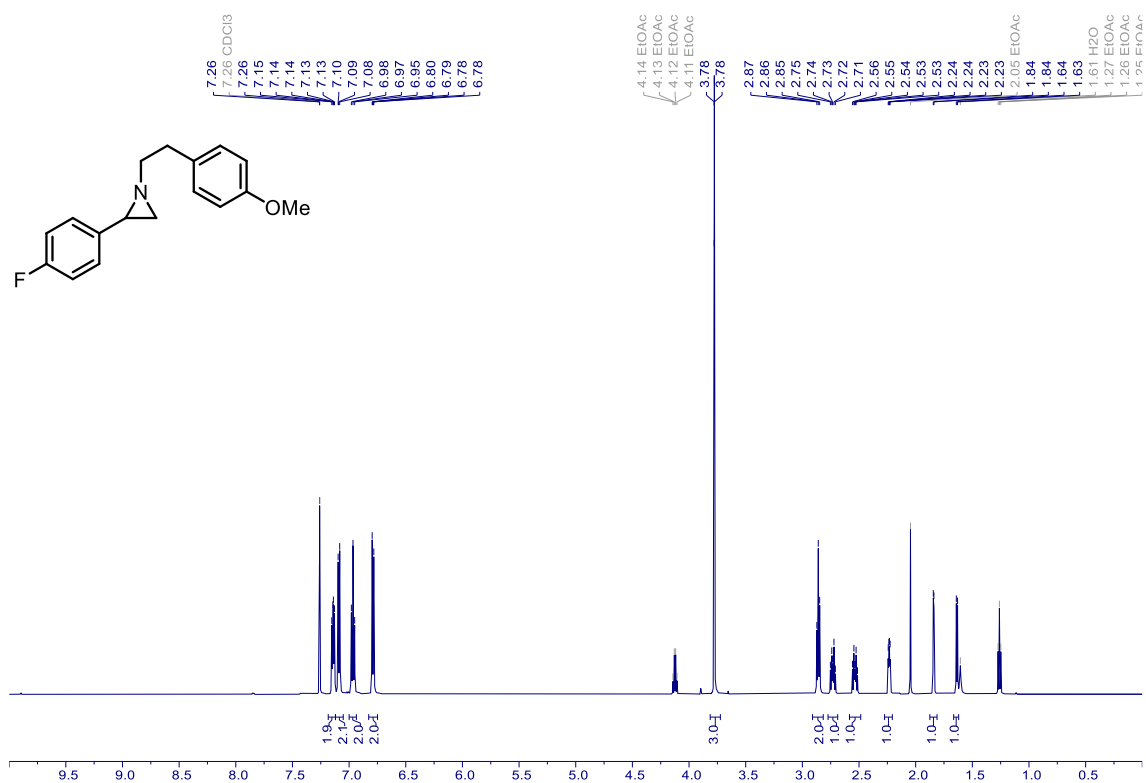
16 – ^1H NMR (400 MHz, CDCl_3)



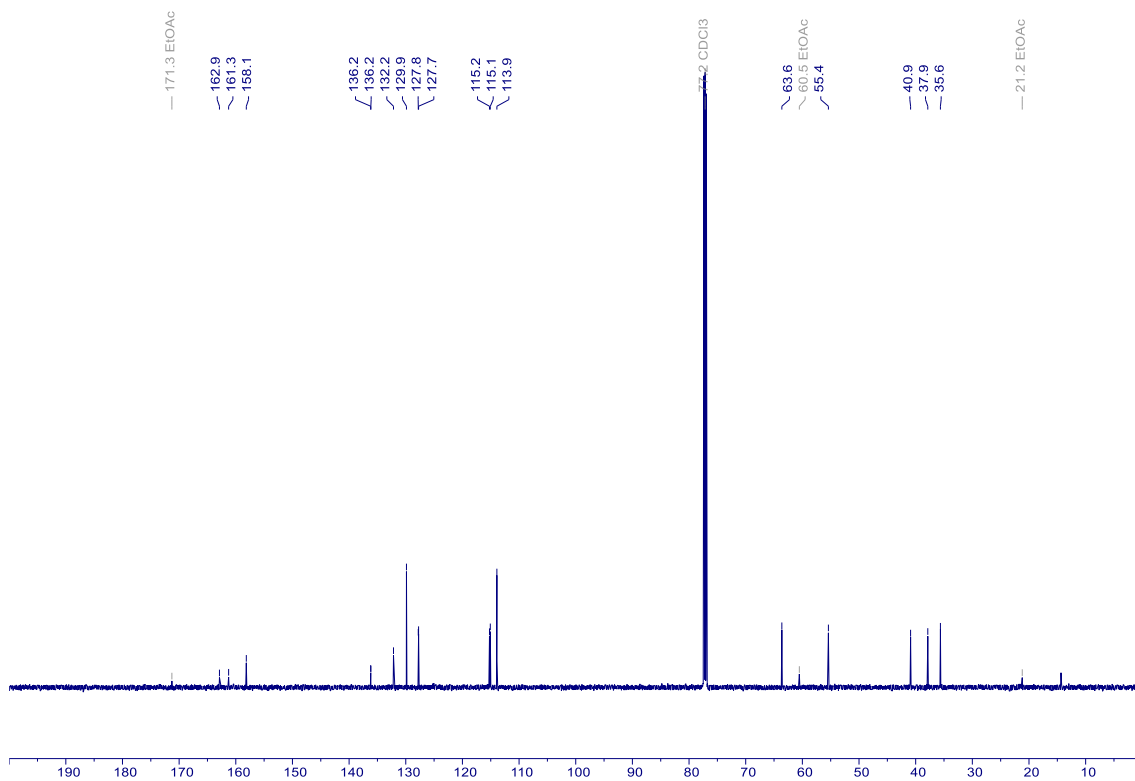
16 – ^{13}C NMR (101 MHz, CDCl_3)



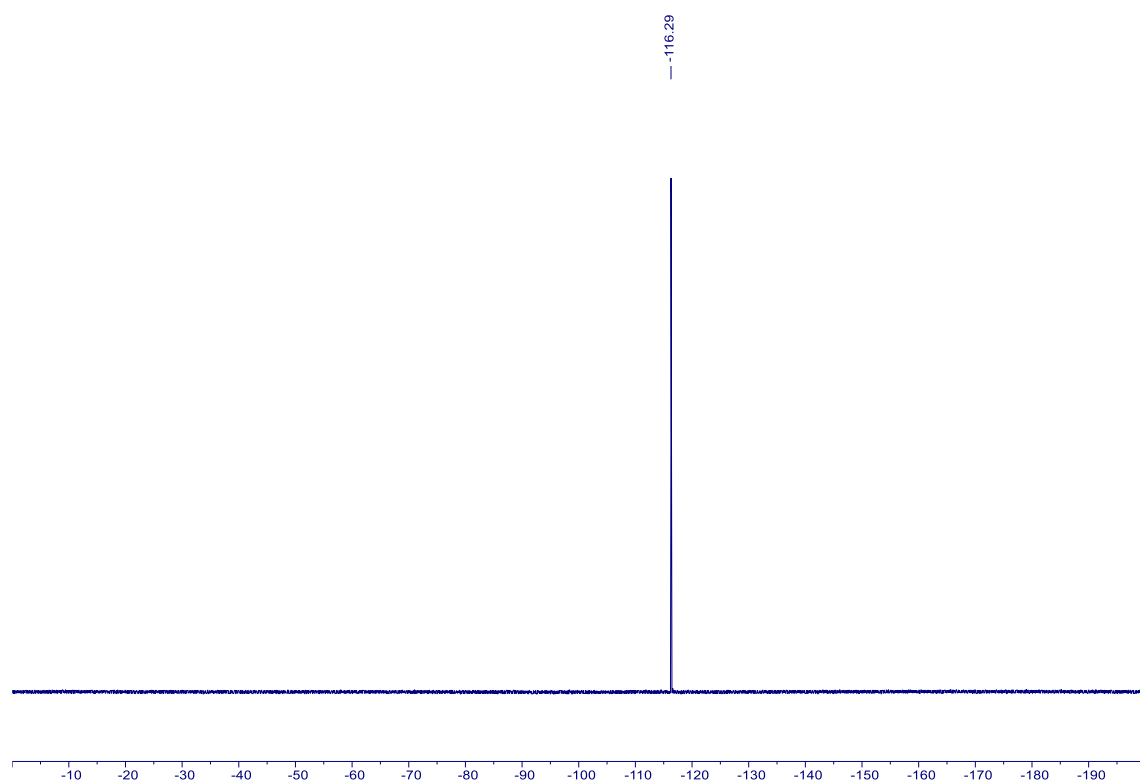
18 – ^1H NMR (600 MHz, CDCl_3)



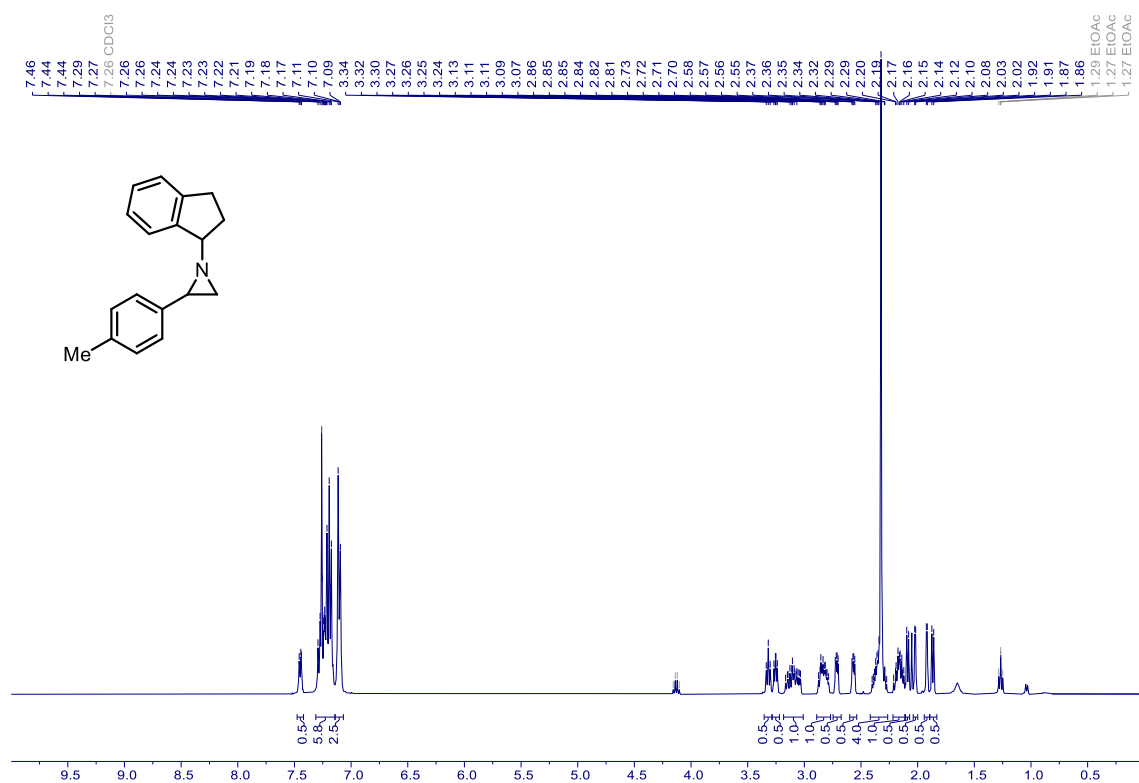
18 – ^{13}C NMR (151 MHz, CDCl_3)



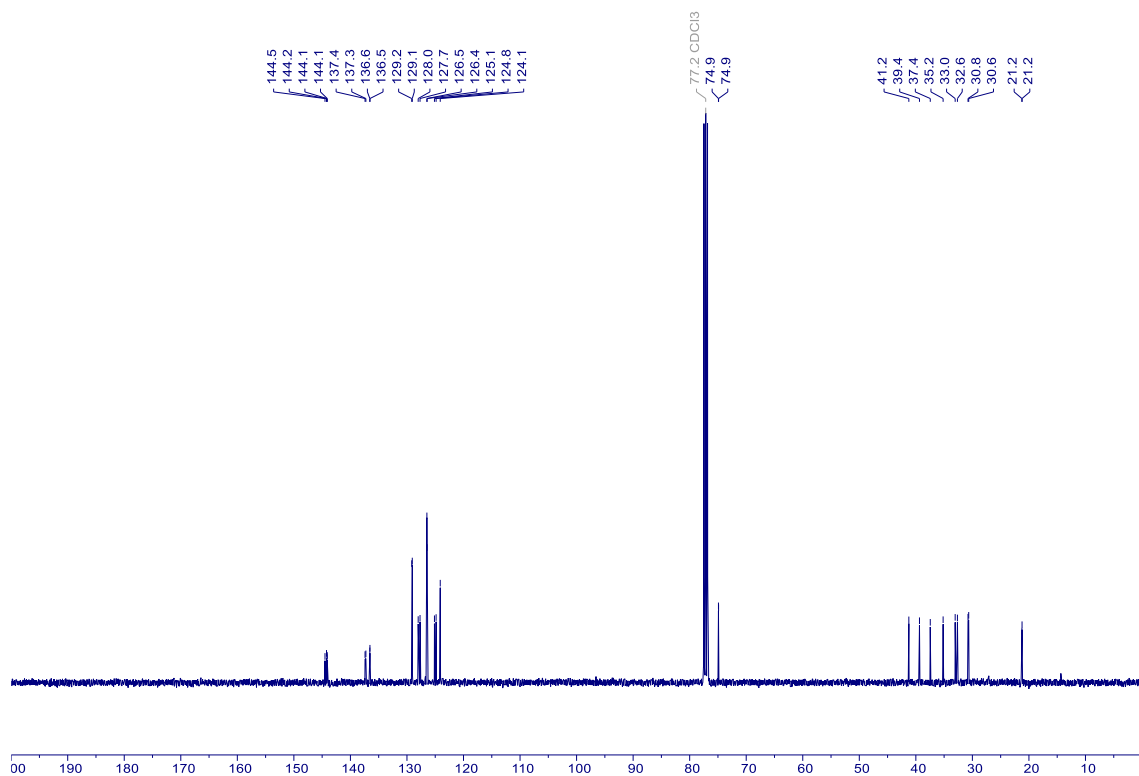
18 – ^{19}F NMR (565 MHz, CDCl_3)



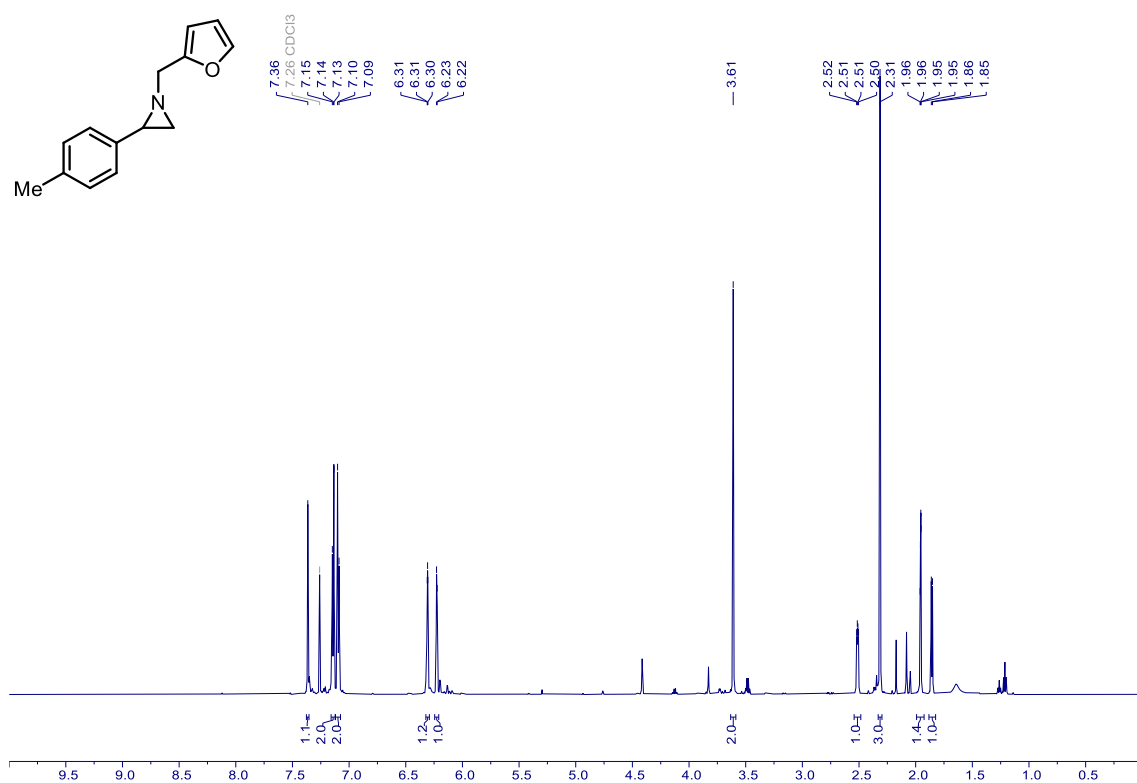
19 – ^1H NMR (400 MHz, CDCl_3)



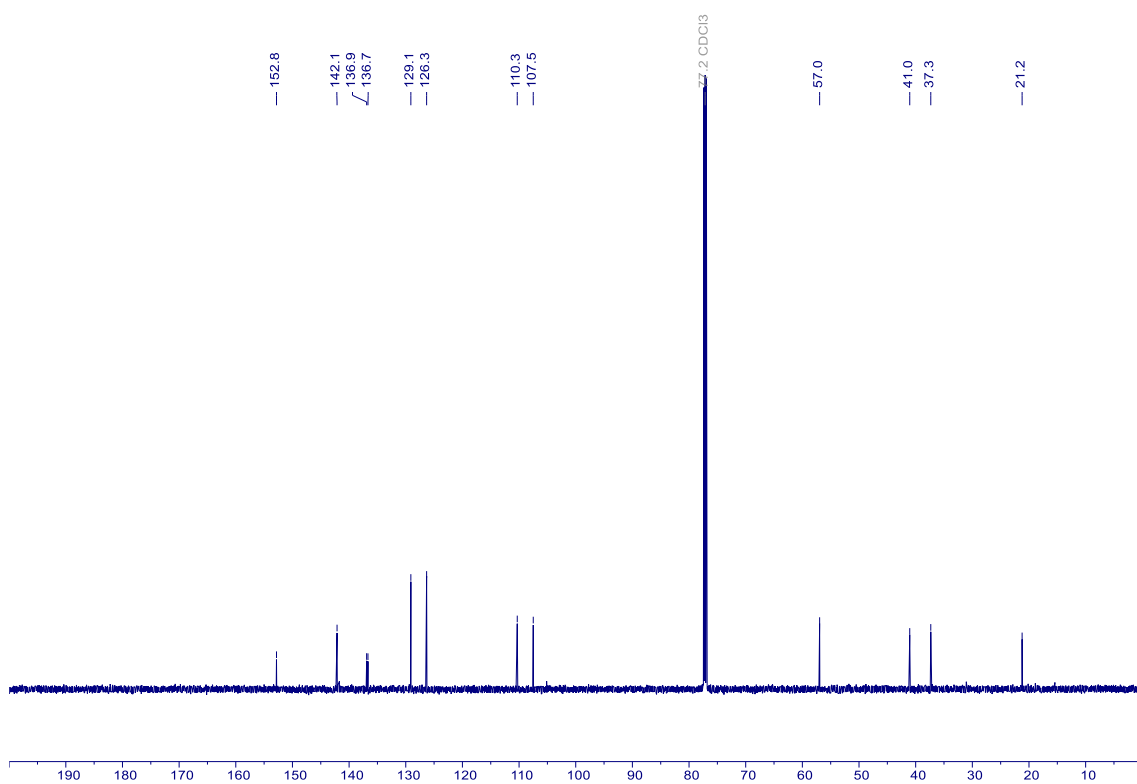
19 – ^{13}C NMR (101 MHz, CDCl_3)



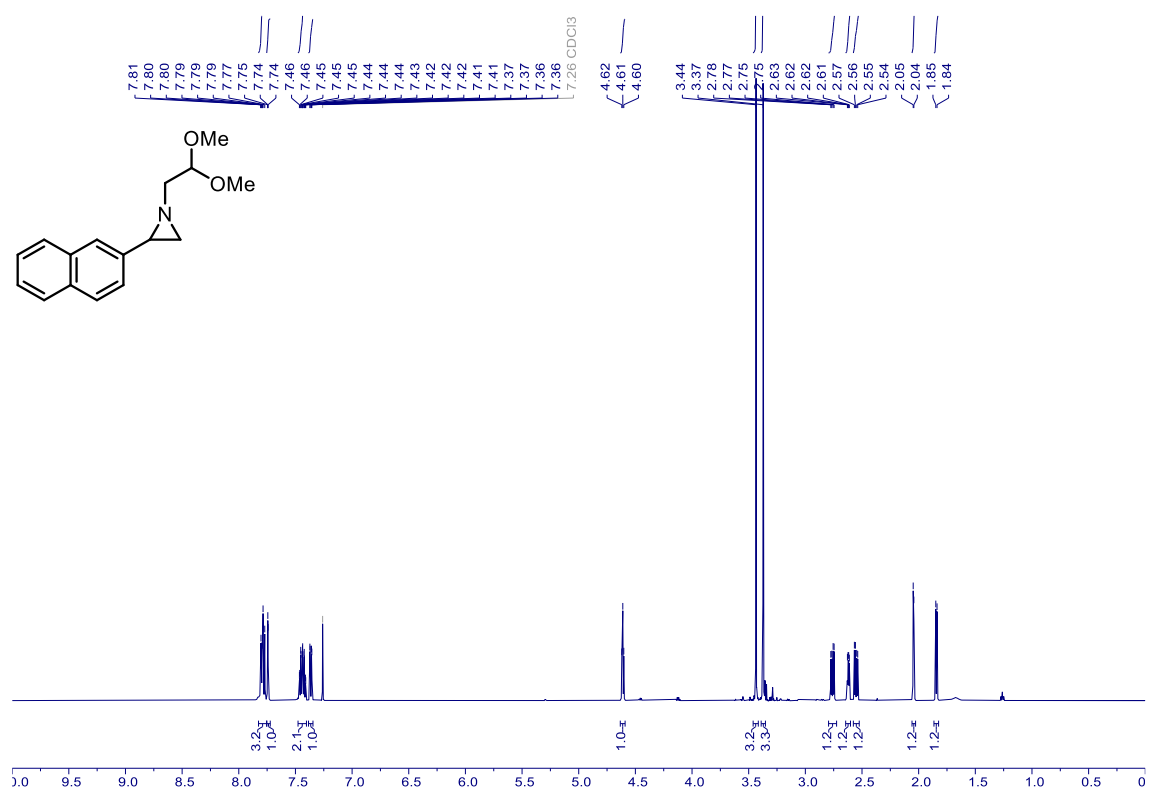
20 – ^1H NMR (600 MHz, CDCl_3)



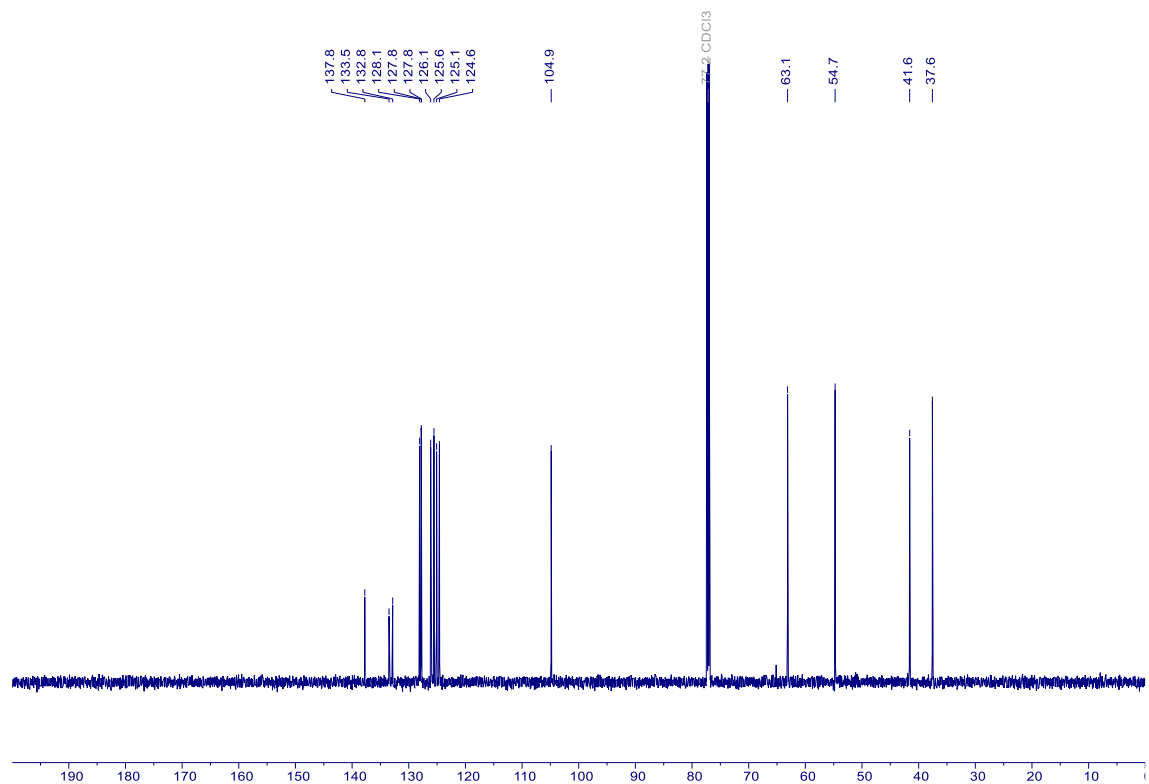
20 – ^{13}C NMR (151 MHz, CDCl_3)



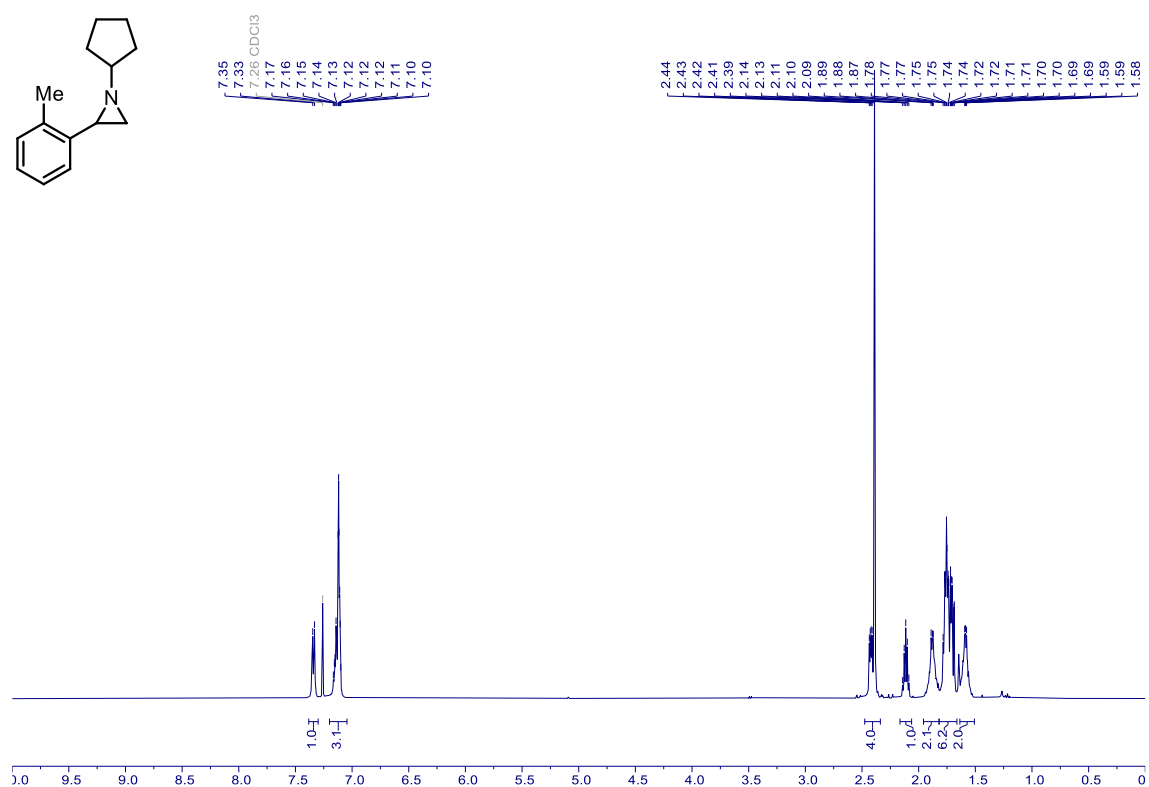
21 – ^1H NMR (600 MHz, CDCl_3)



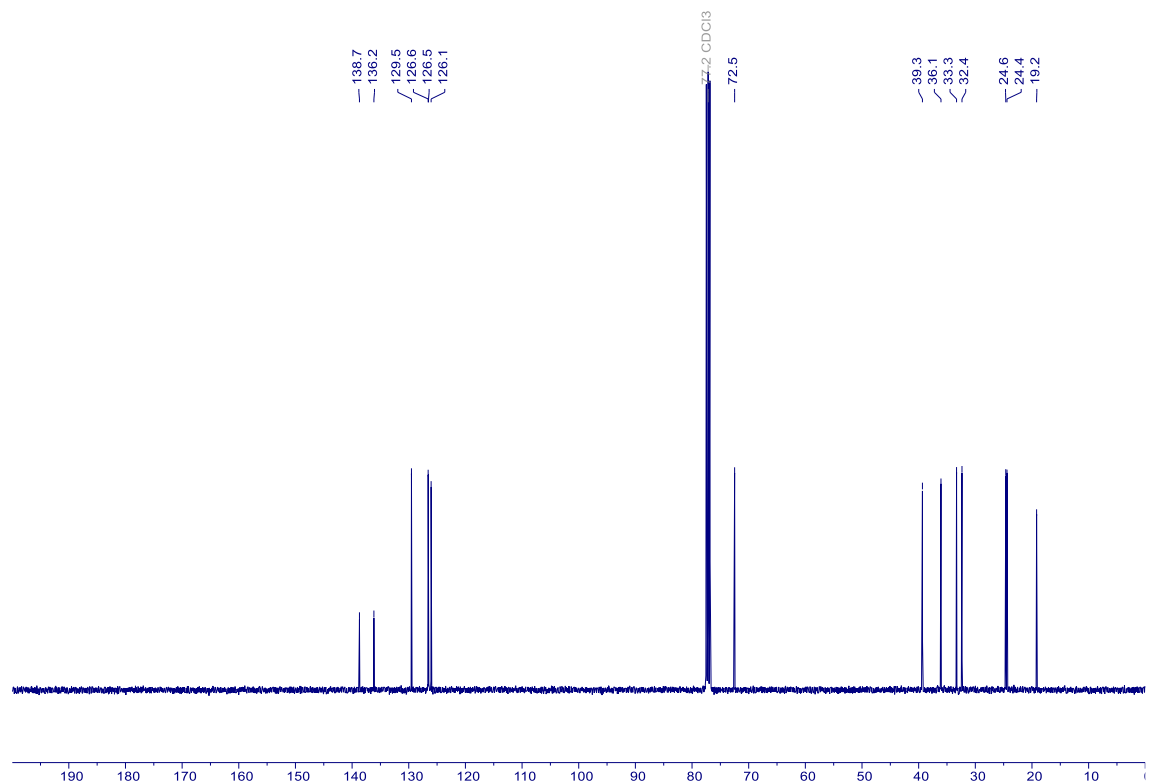
21 – ^{13}C NMR (151 MHz, CDCl_3)



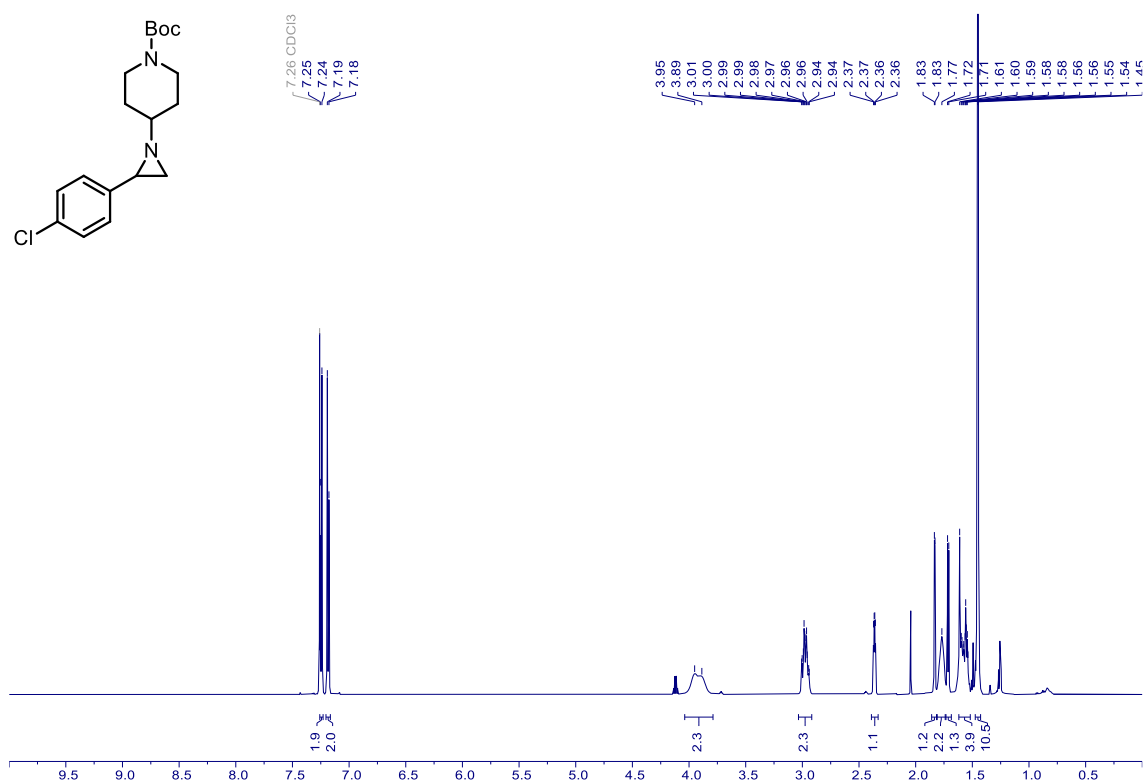
22 – ^1H NMR (400 MHz, CDCl_3)



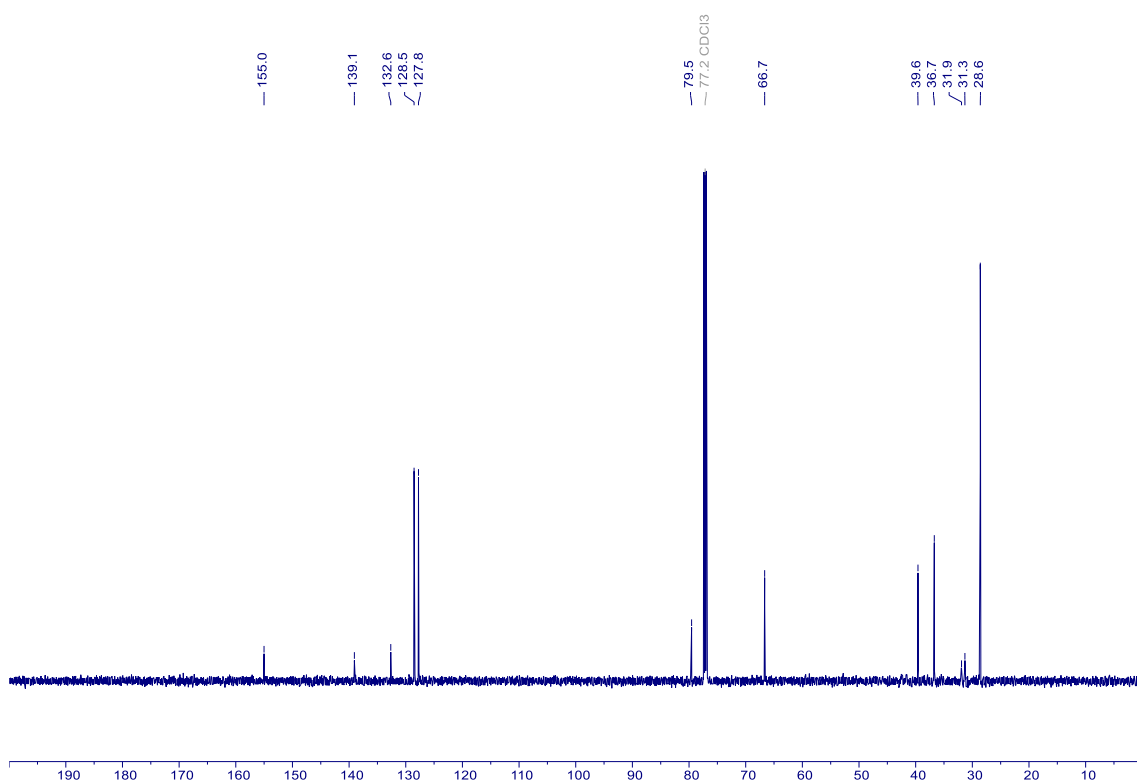
22 – ^{13}C NMR (101 MHz, CDCl_3)



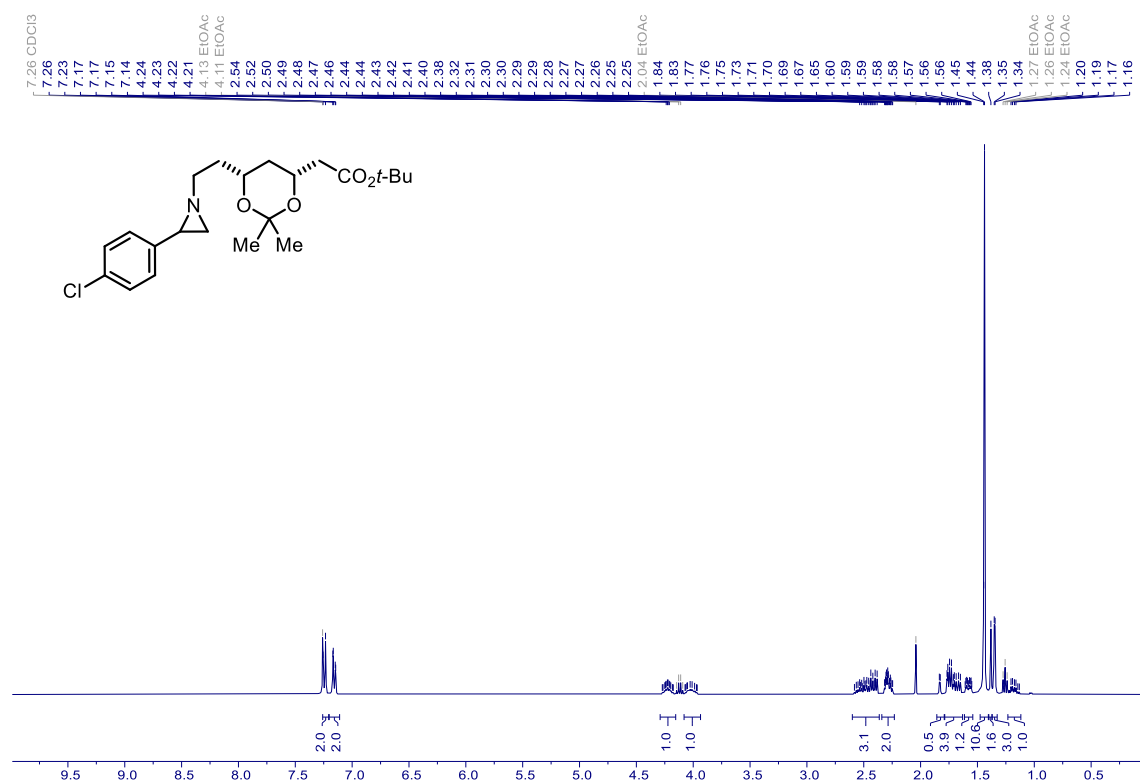
23 – ^1H NMR (600 MHz, CDCl_3)



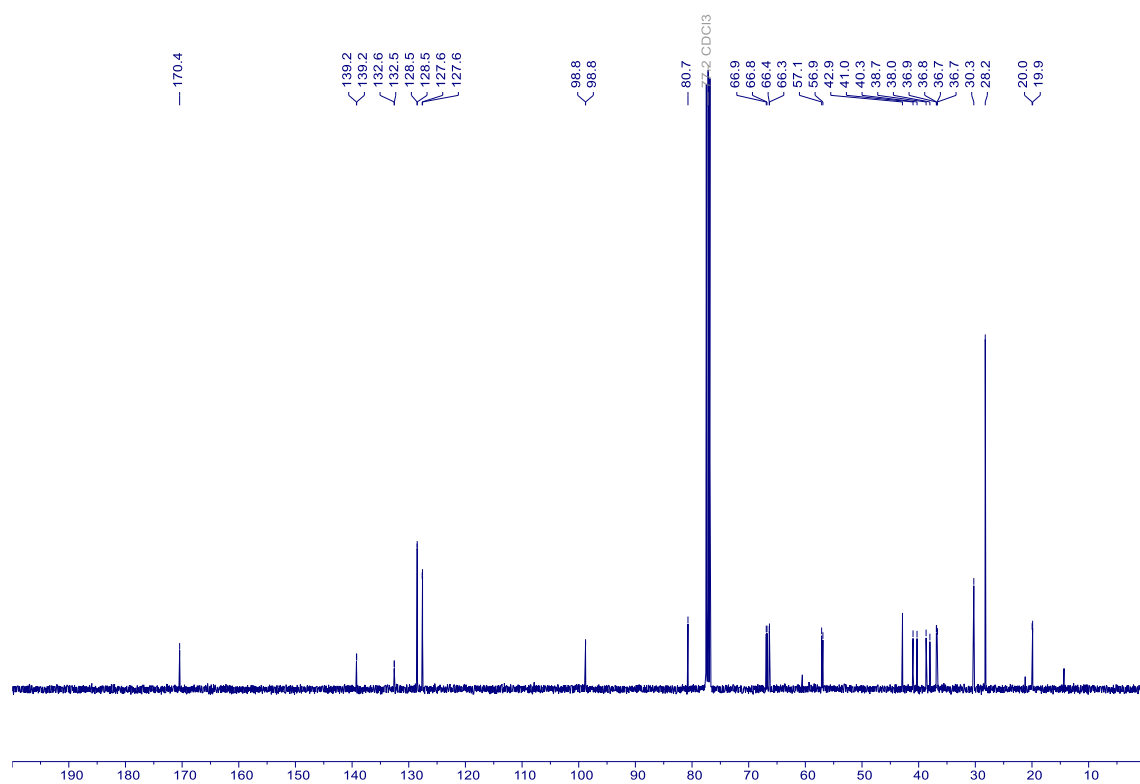
23 – ^{13}C NMR (151 MHz, CDCl_3)



25 – ^1H NMR (400 MHz, CDCl_3)



25 – ^{13}C NMR (101 MHz, CDCl_3)

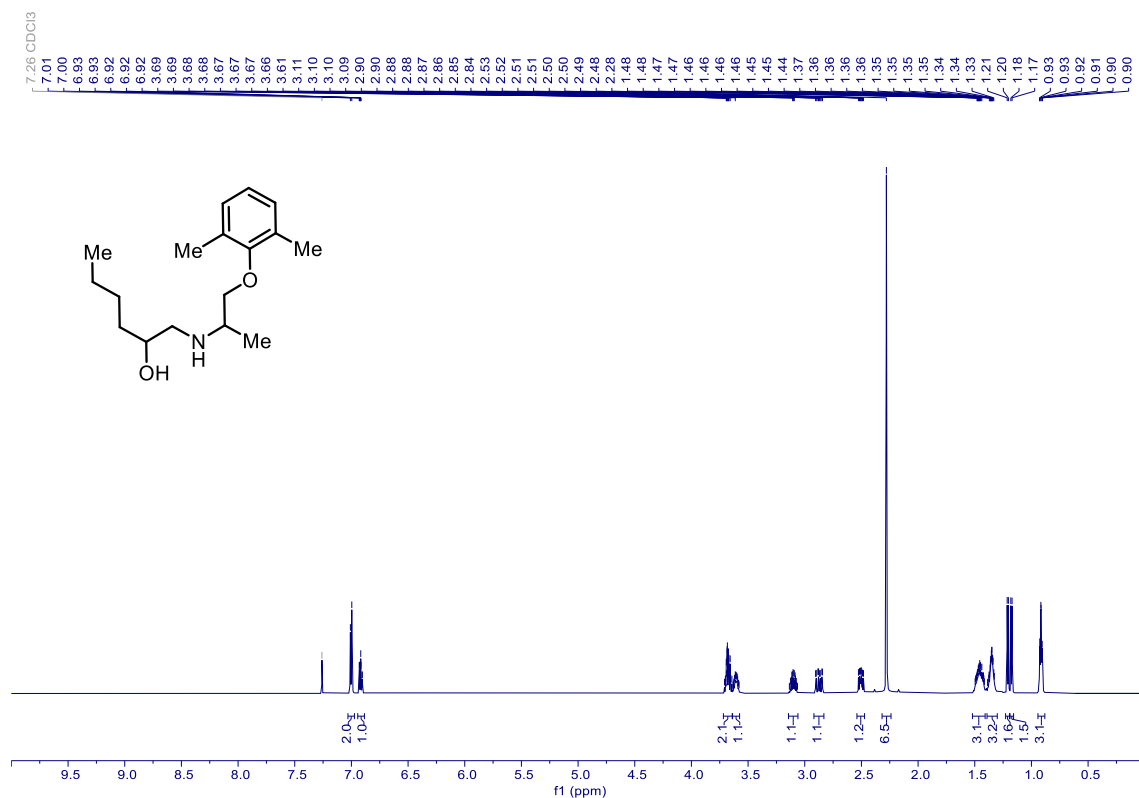


CCN(CC1CC2=CC=CC=C2C1)CC3

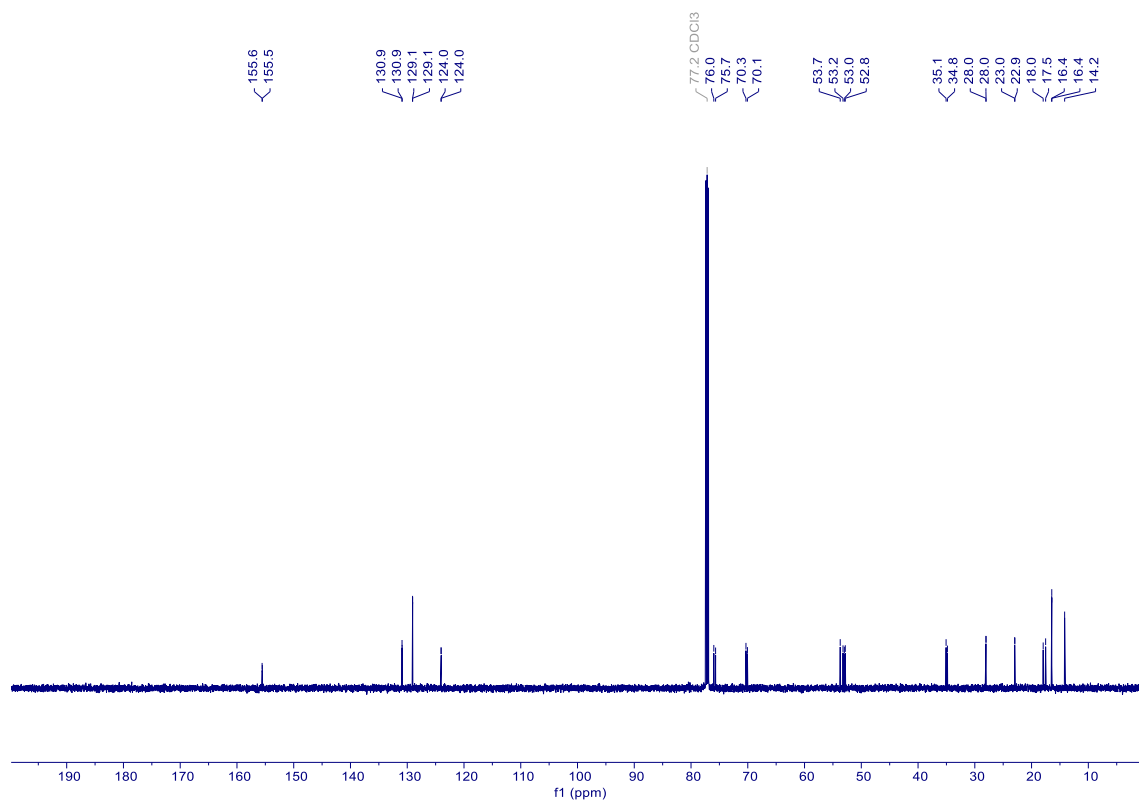
142.1
128.6
128.5
125.9
77.2 CDCl₃
63.6
39.1
35.0
34.0
34.0
23.2
12.1

f1 (ppm)

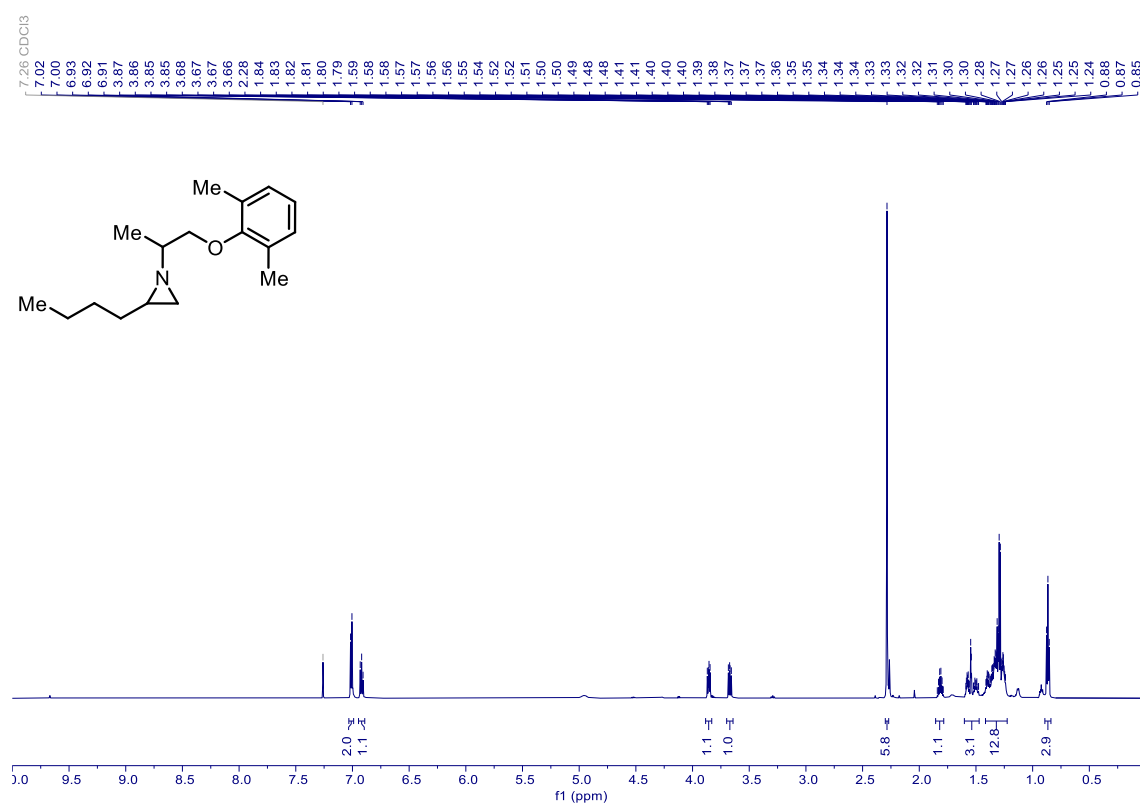
S30 – ^1H NMR (600 MHz, CDCl_3)



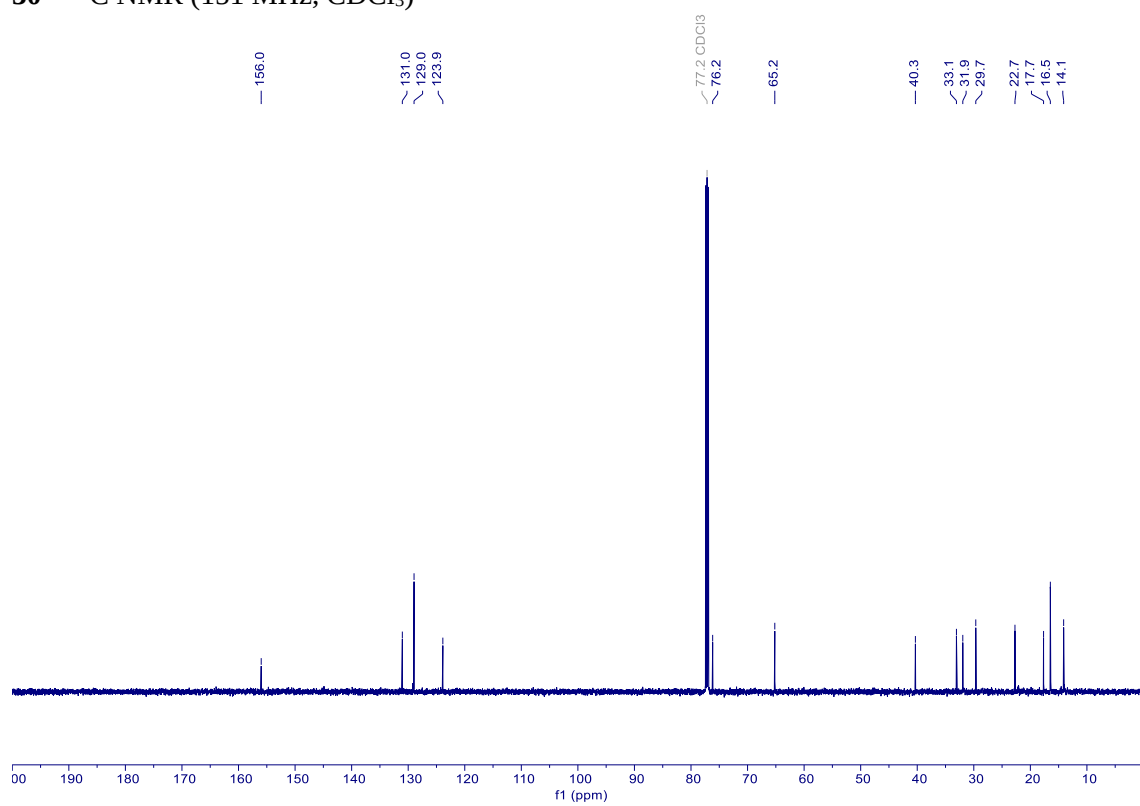
S30 – ^{13}C NMR (151 MHz, CDCl_3)



30 – ^1H NMR (600 MHz, CDCl_3)



30 – ^{13}C NMR (151 MHz, CDCl_3)



Chemical structure: CCNCCOc1cccc2ccccc12

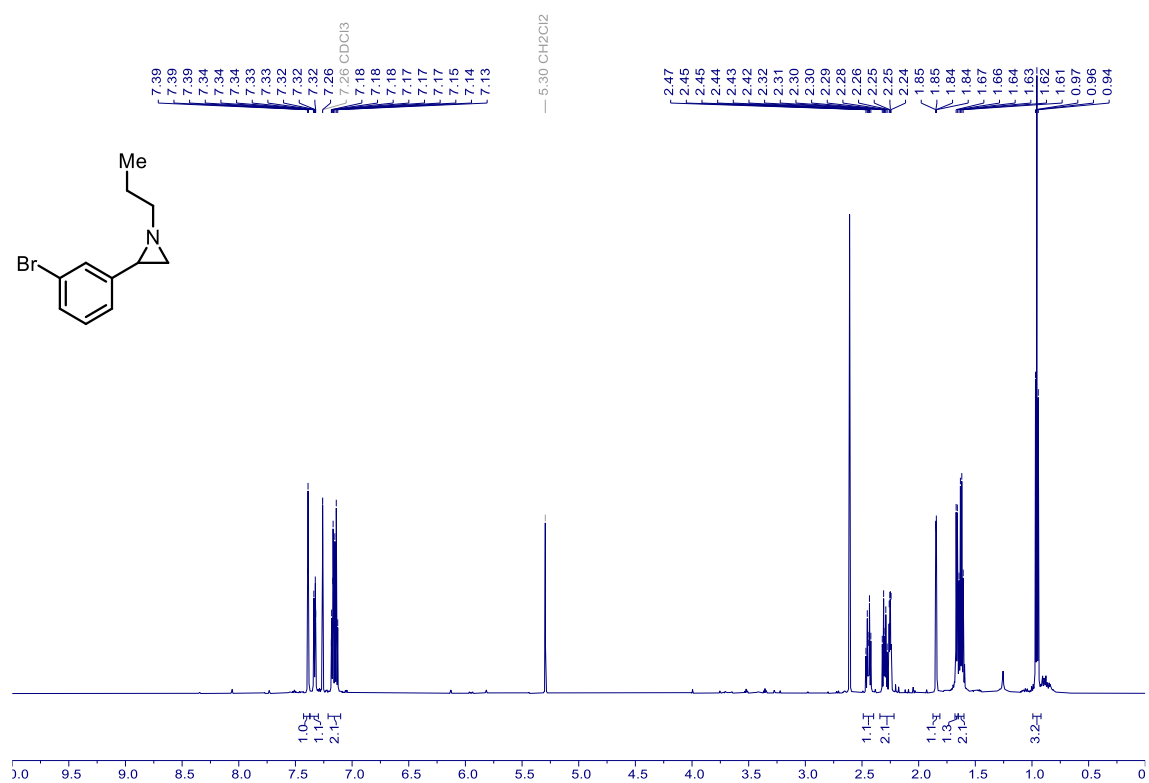
¹H NMR spectrum (CDCl₃) showing peaks and integration values:

Chemical Shift (ppm)	Integration
8.30, 8.30, 8.30, 8.29, 8.28, 7.81, 7.80, 7.79, 7.79	0.9±
7.50, 7.50, 7.49, 7.49, 7.49, 7.49, 7.48, 7.48, 7.48, 7.47, 7.47, 7.47, 7.46, 7.46, 7.44, 7.44, 7.43, 7.42, 7.39, 7.37, 7.36, 7.26	0.9±, 0.9±, 0.9±, 0.9±
4.34, 4.35, 4.63, 4.65, 4.65, 4.726 (CDCl ₃)	2.0±
2.79, 2.78, 2.77	2.0±
1.87, 1.87, 1.86	2.3±
1.36, 1.36, 1.36	2.2±

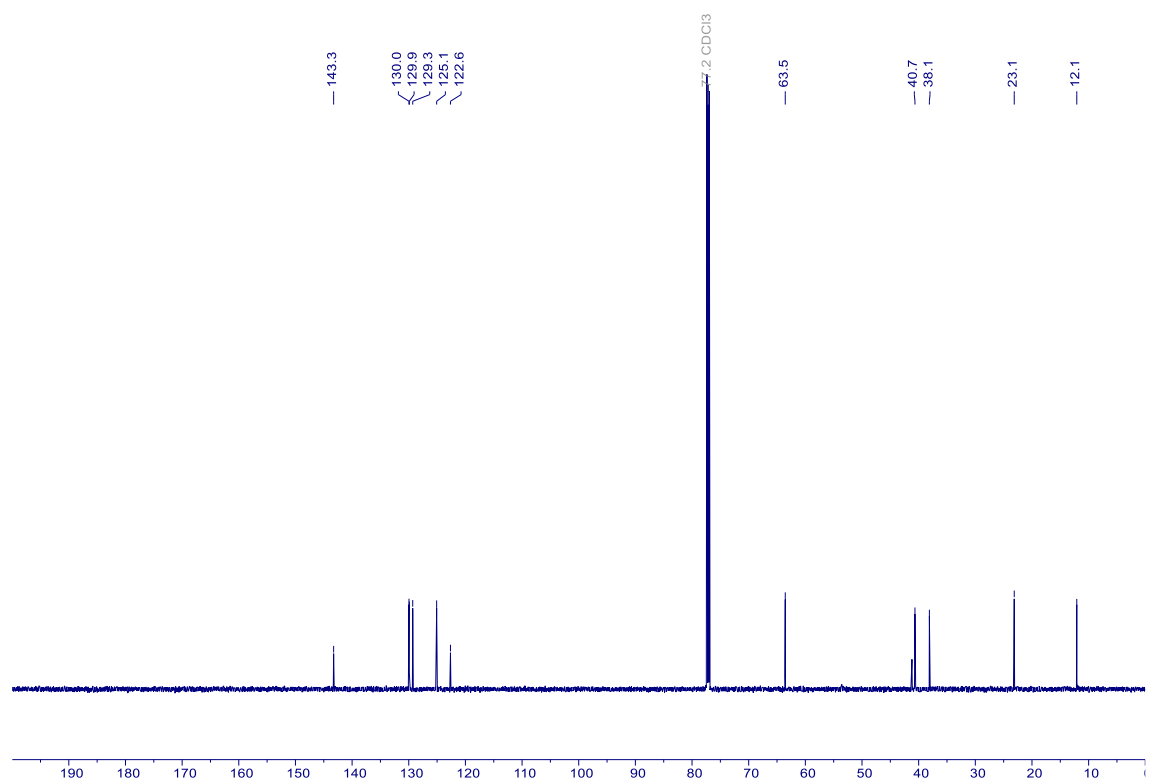
13C NMR spectrum (CDCl₃) of compound 10. The x-axis is labeled 'f1 (ppm)' and ranges from 0 to 200. The spectrum shows several peaks:

- 154.8
- 134.7
- 127.6
- 126.5
- 126.0
- 125.8
- 125.3
- 122.2
- 120.5
- 104.8
- 77.2 CDCl₃
- 68.2
- 60.6
- 27.5

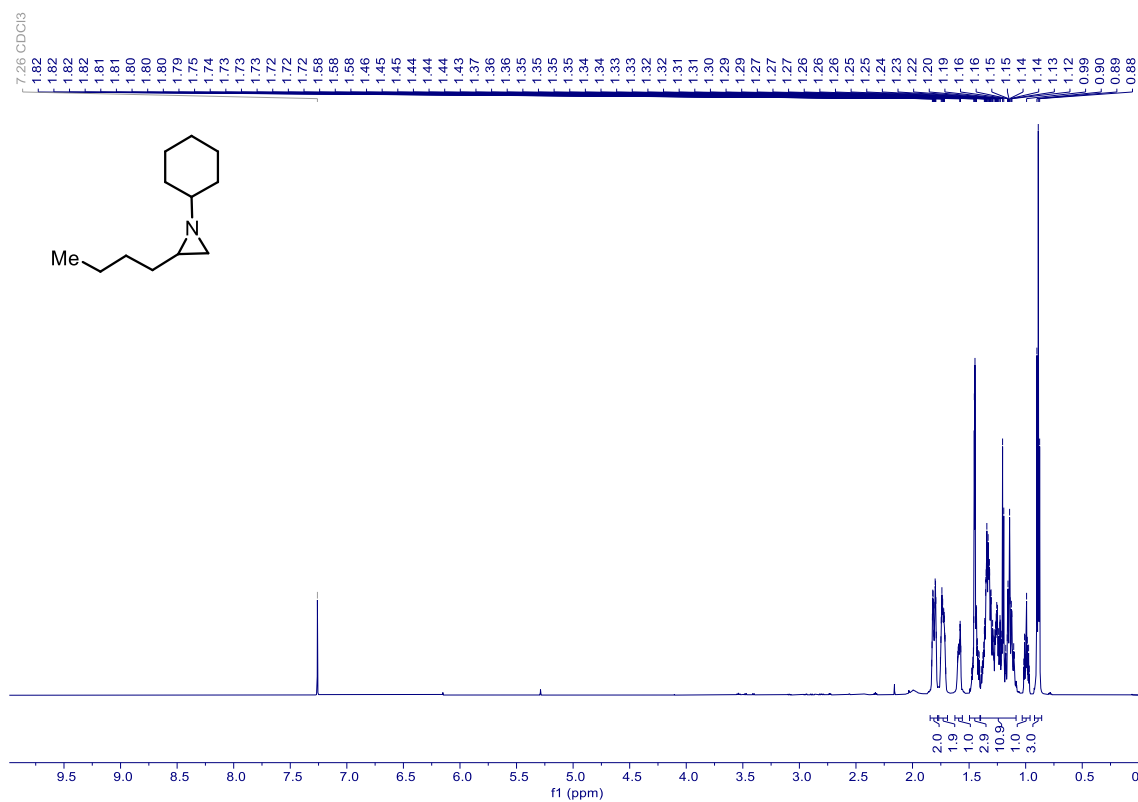
37 – ^1H NMR (600 MHz, CDCl_3)



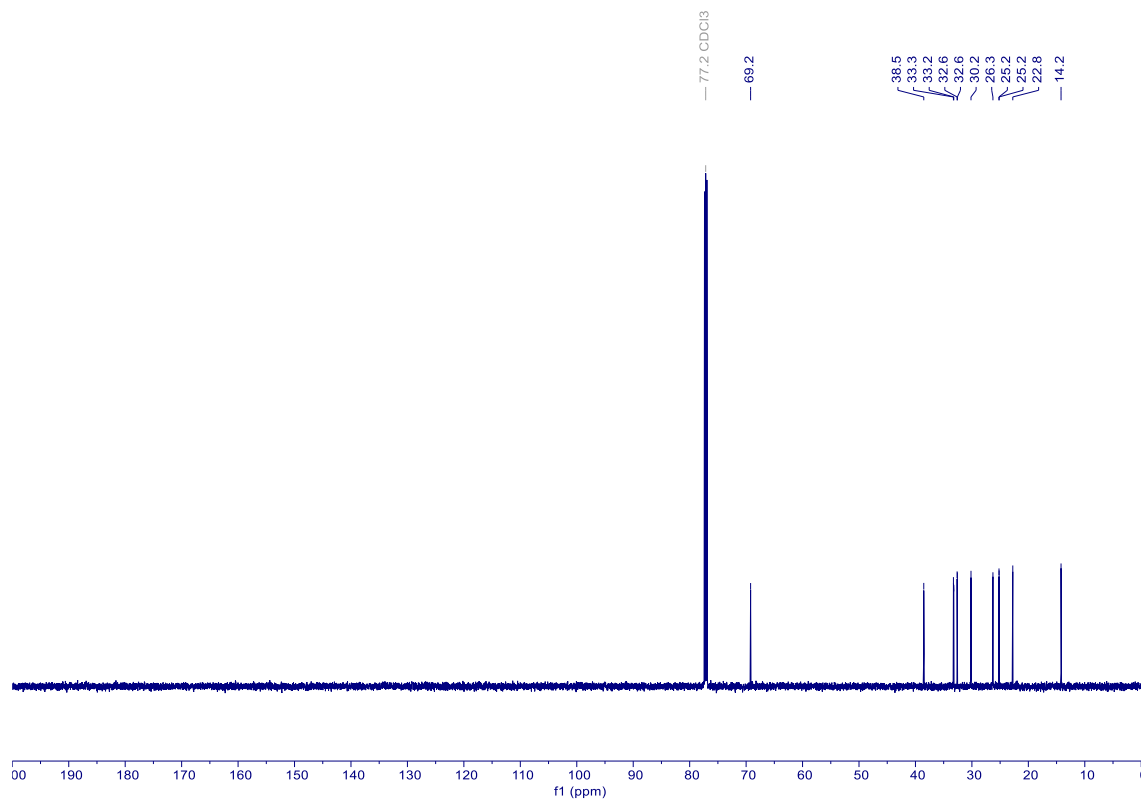
37 – ^{13}C NMR (151 MHz, CDCl_3)



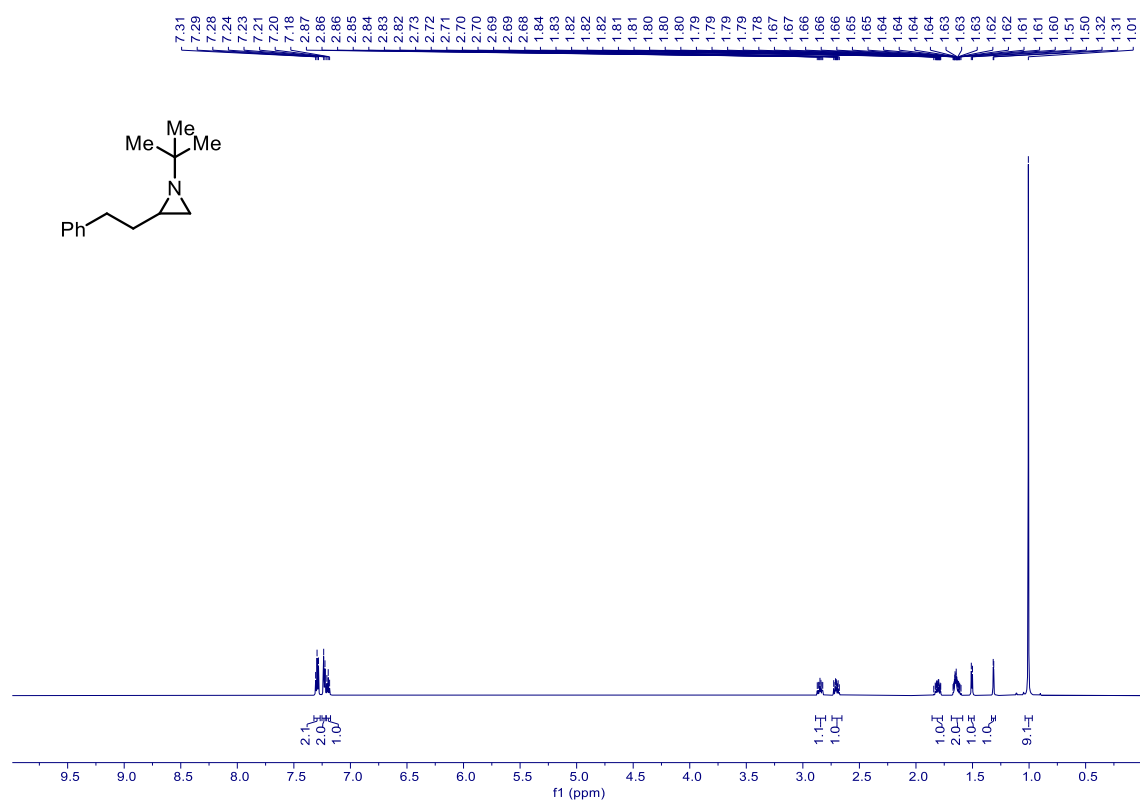
38 – ^1H NMR (600 MHz, CDCl_3)



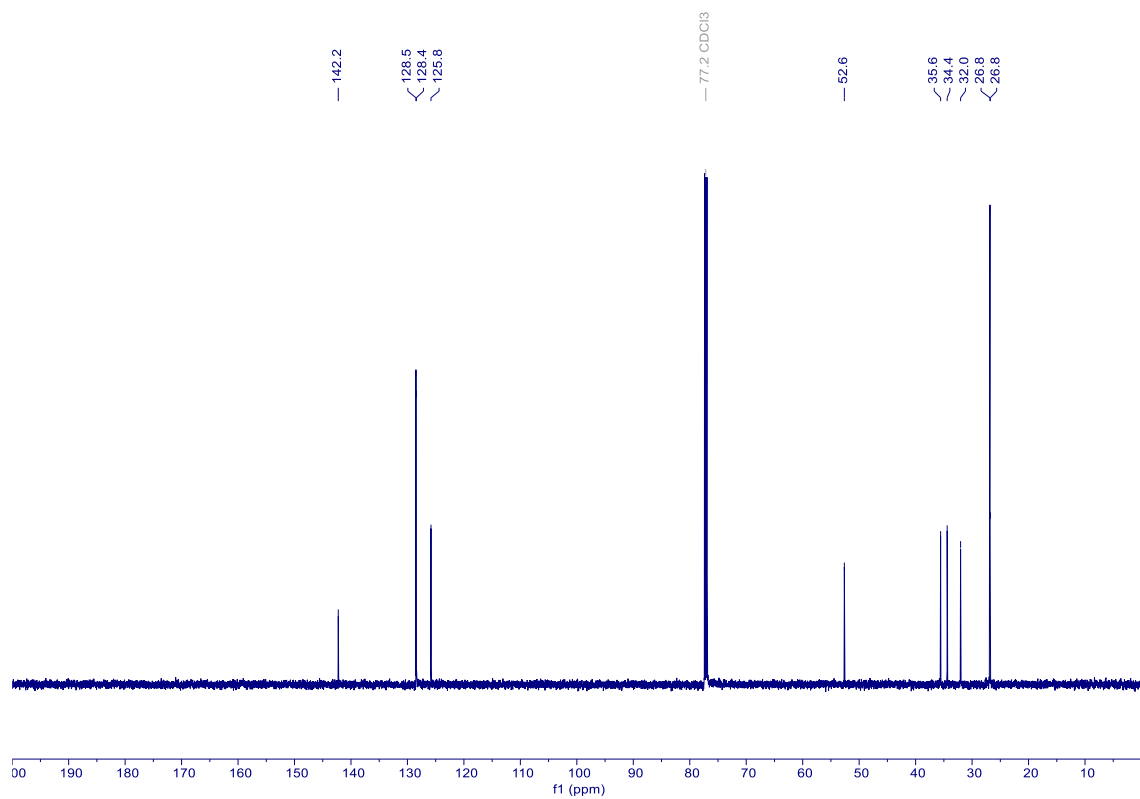
38 – ^{13}C NMR (151 MHz, CDCl_3)



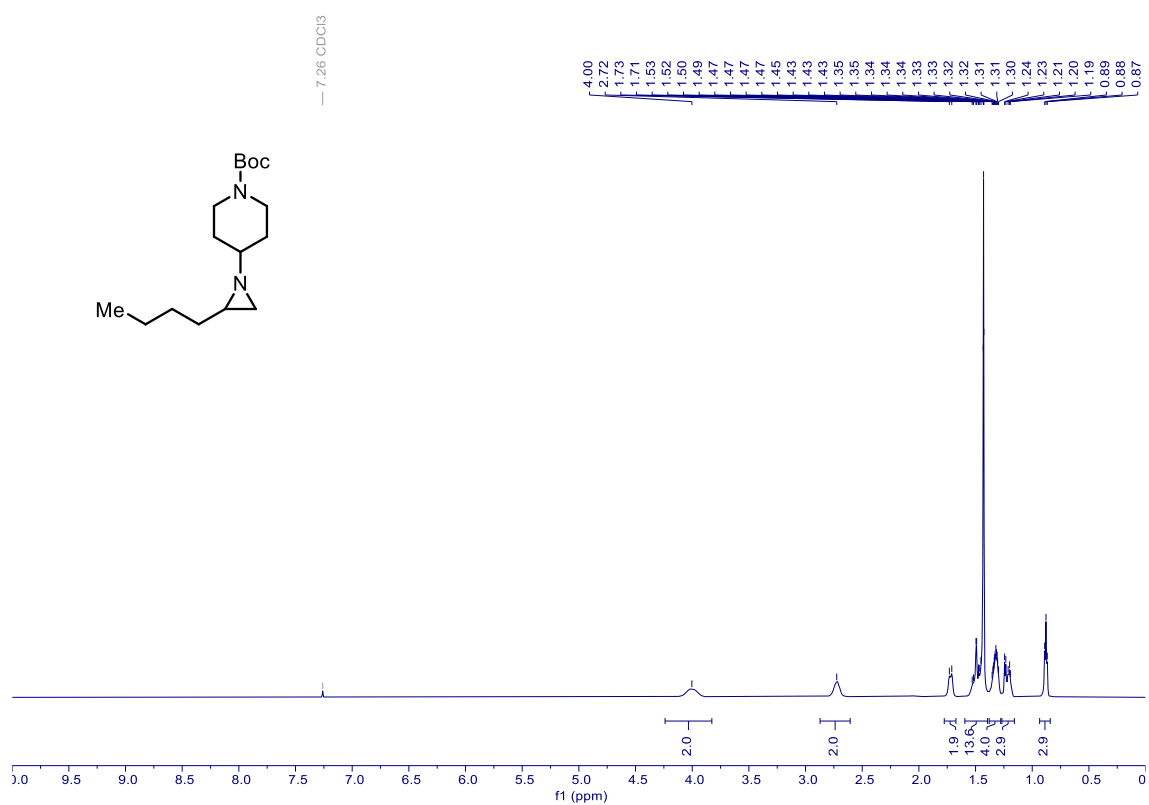
39 – ^1H NMR (600 MHz, CDCl_3)



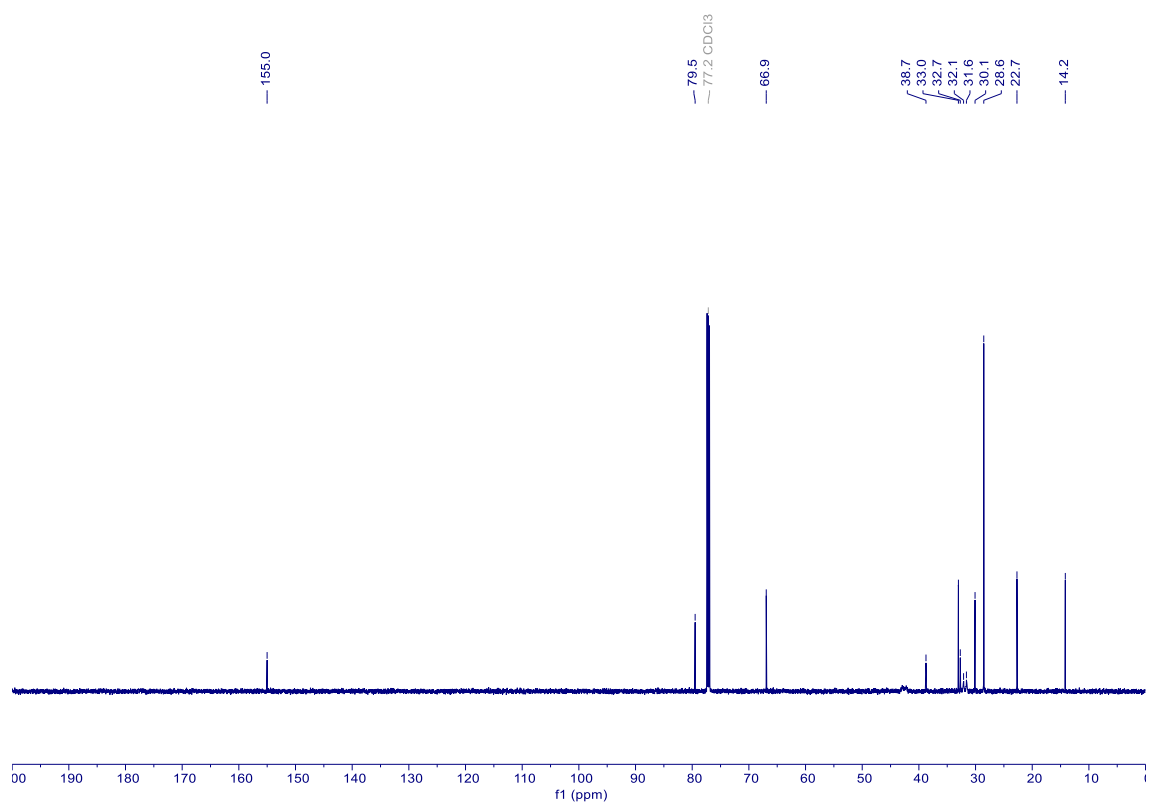
39 – ^{13}C NMR (151 MHz, CDCl_3)



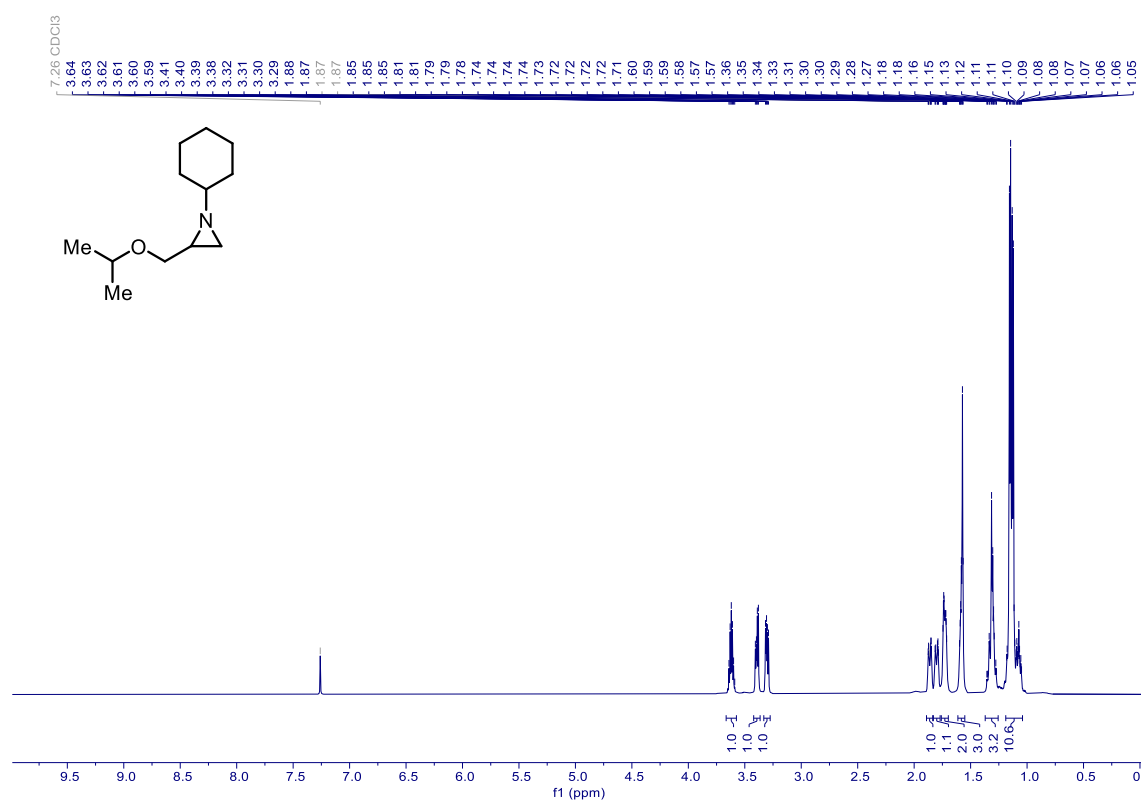
40 – ^1H NMR (600 MHz, CDCl_3)



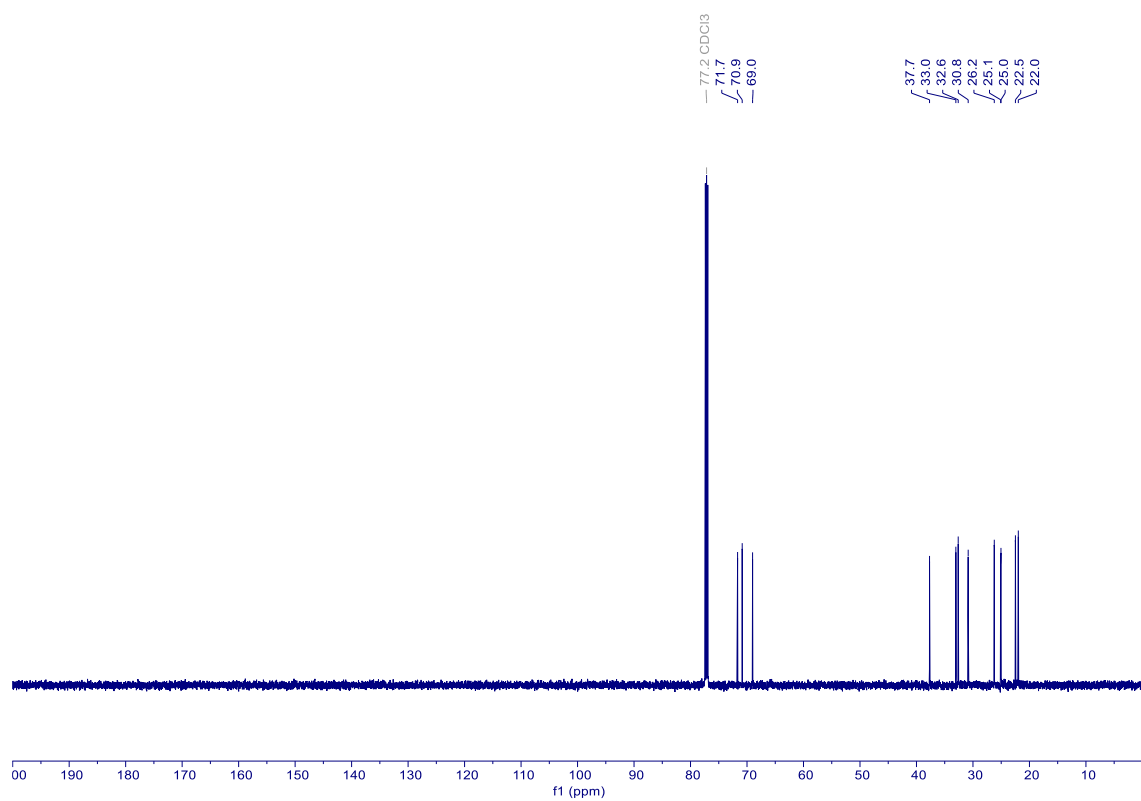
40 – ^{13}C NMR (151 MHz, CDCl_3)



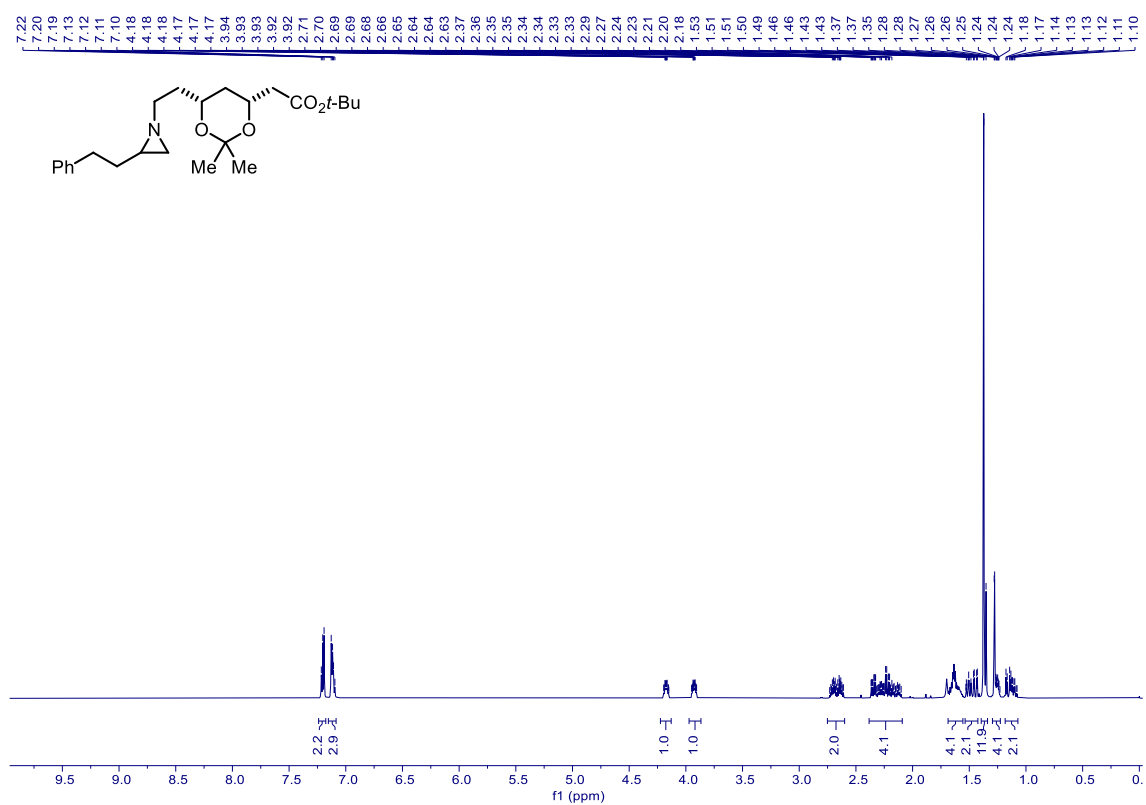
41 – ^1H NMR (600 MHz, CDCl_3)



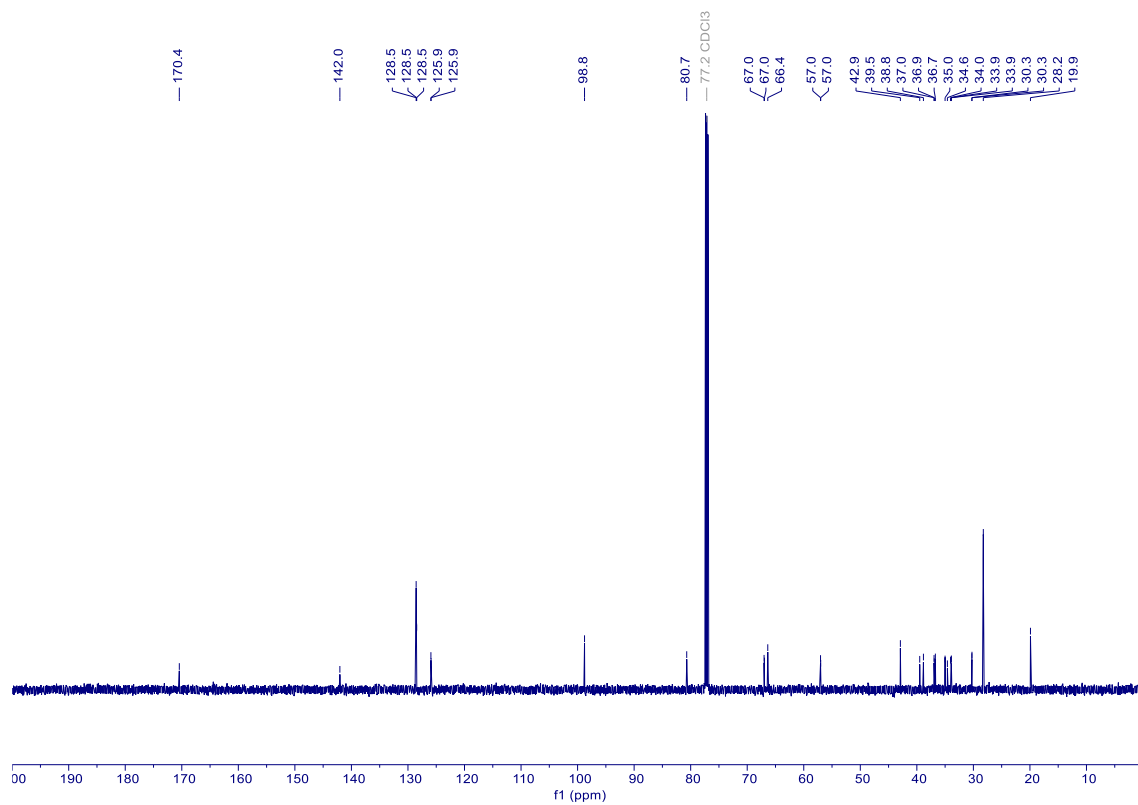
41 – ^{13}C NMR (151 MHz, CDCl_3)



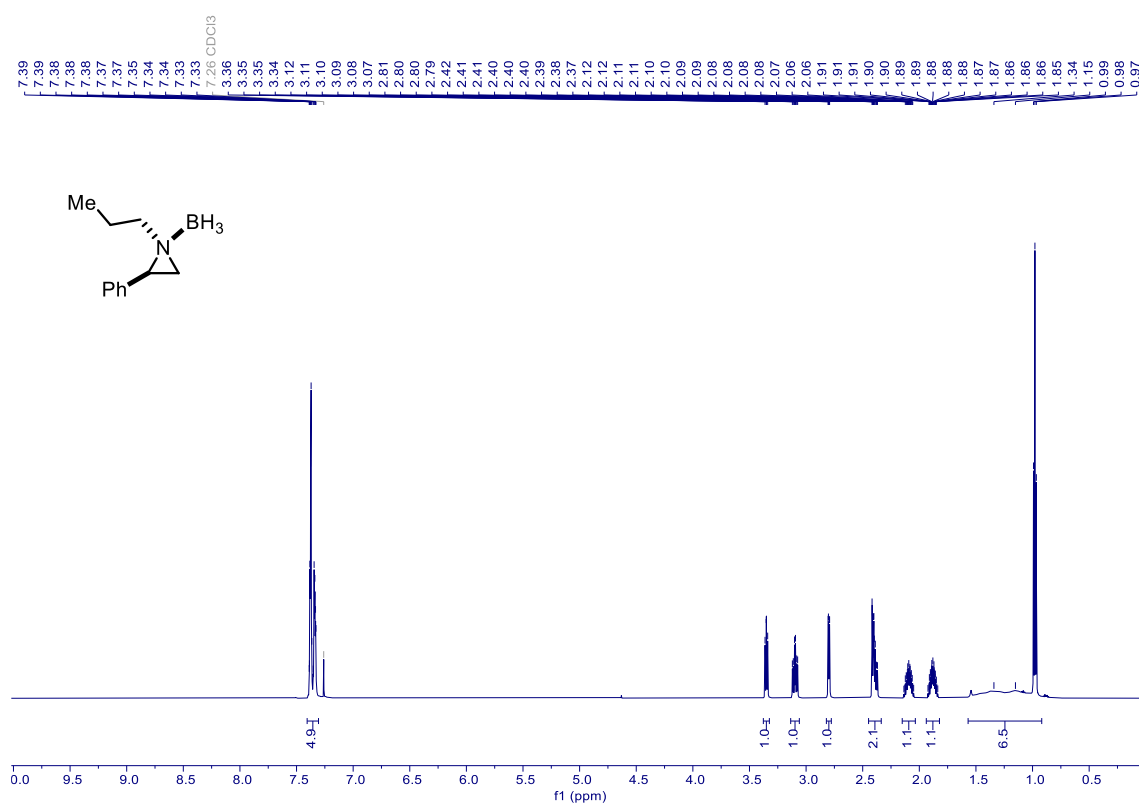
42 – ^1H NMR (600 MHz, CDCl_3)



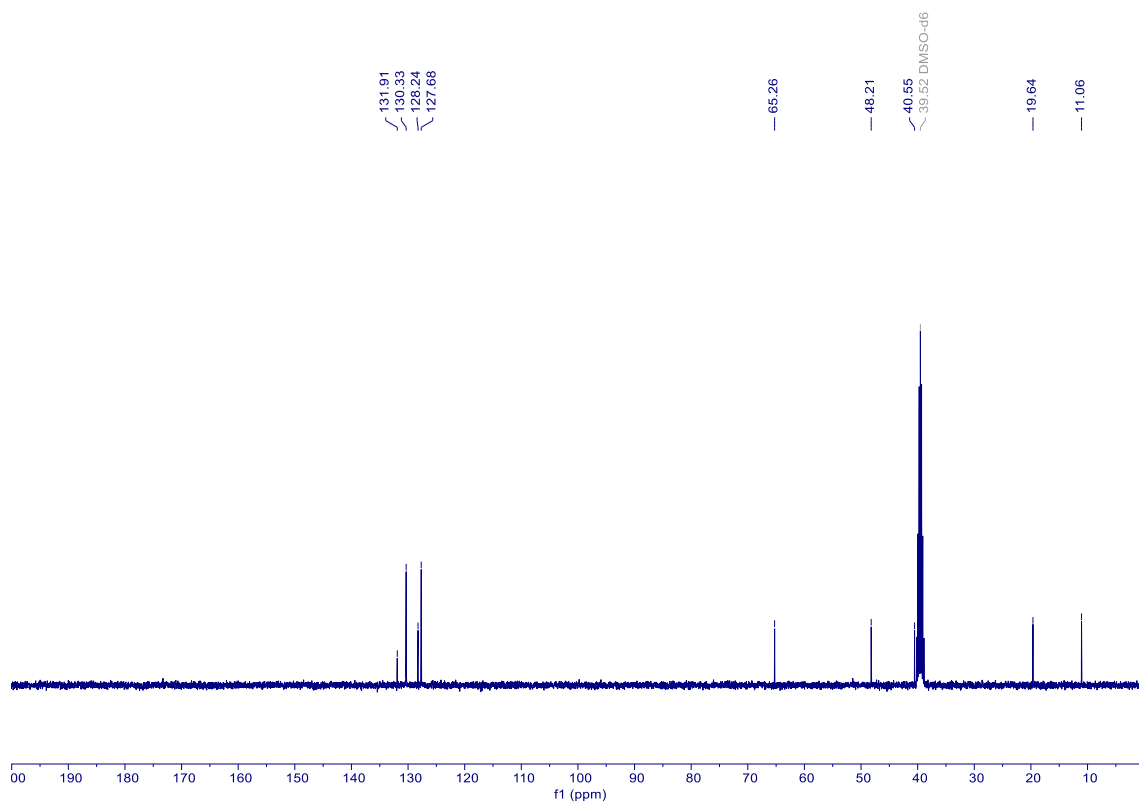
42 – ^{13}C NMR (151 MHz, CDCl_3)



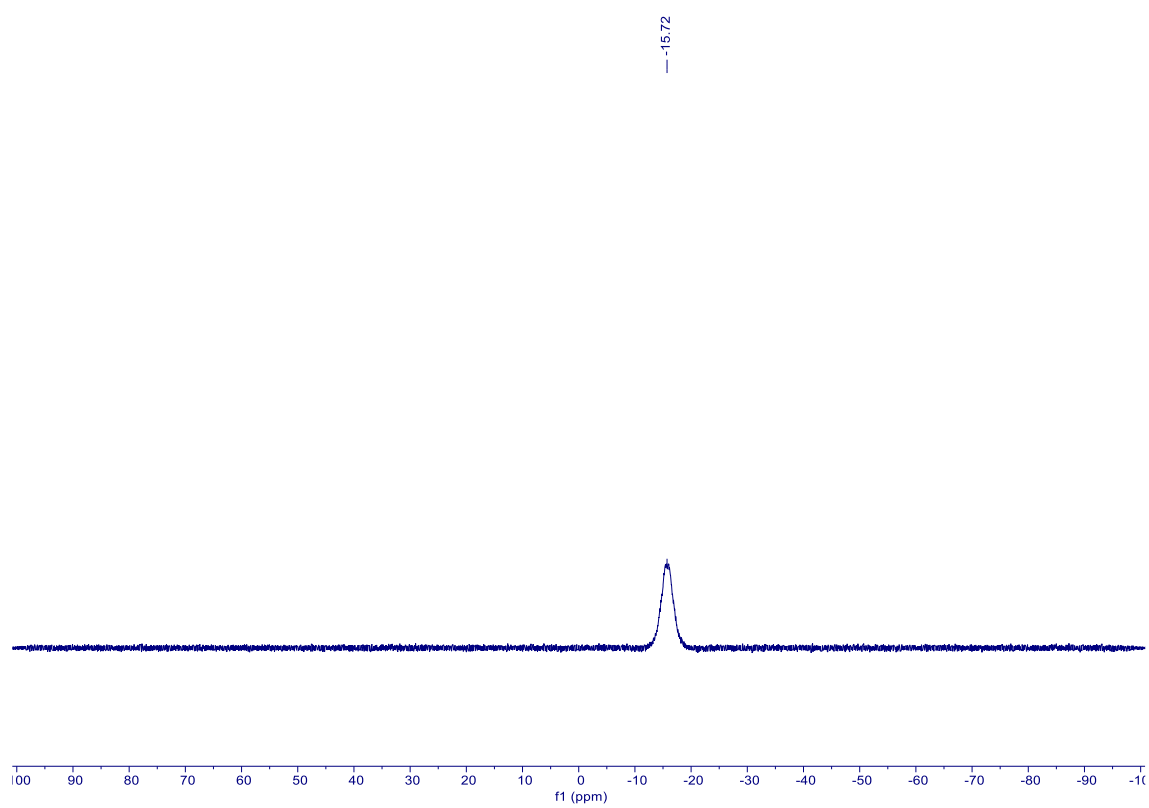
1a – ^1H NMR (600 MHz, CDCl_3)



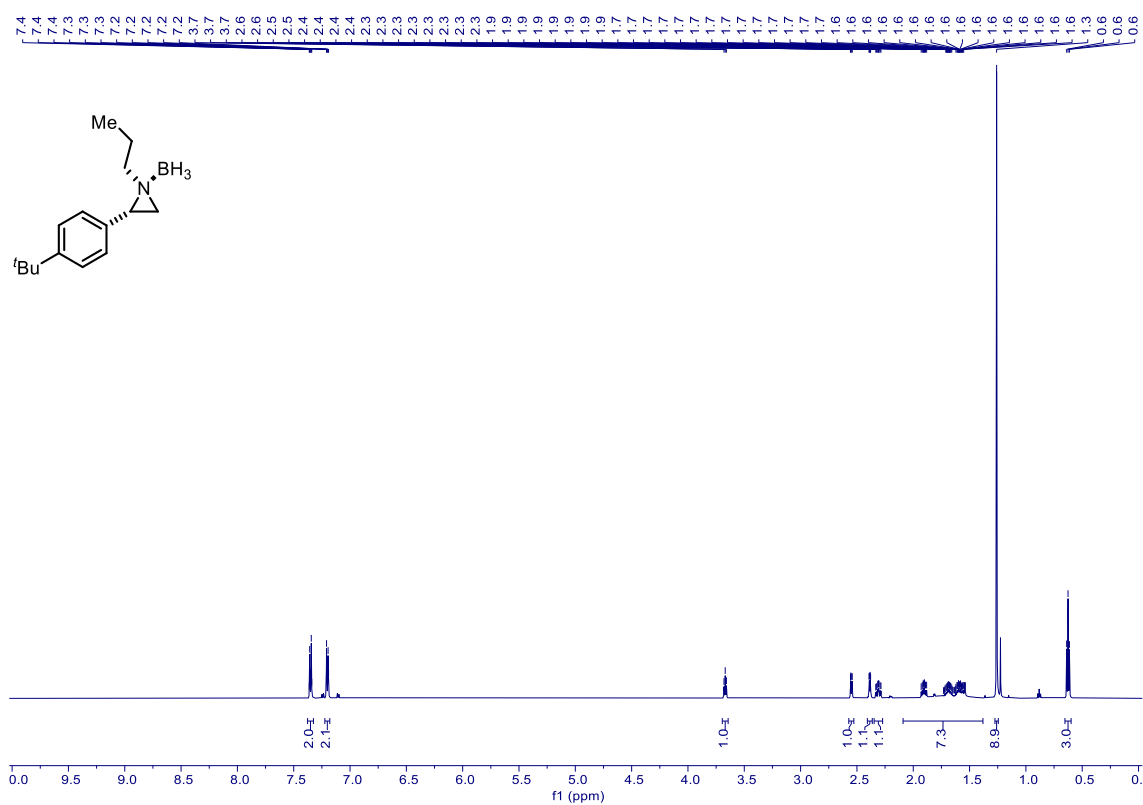
1a – ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$)



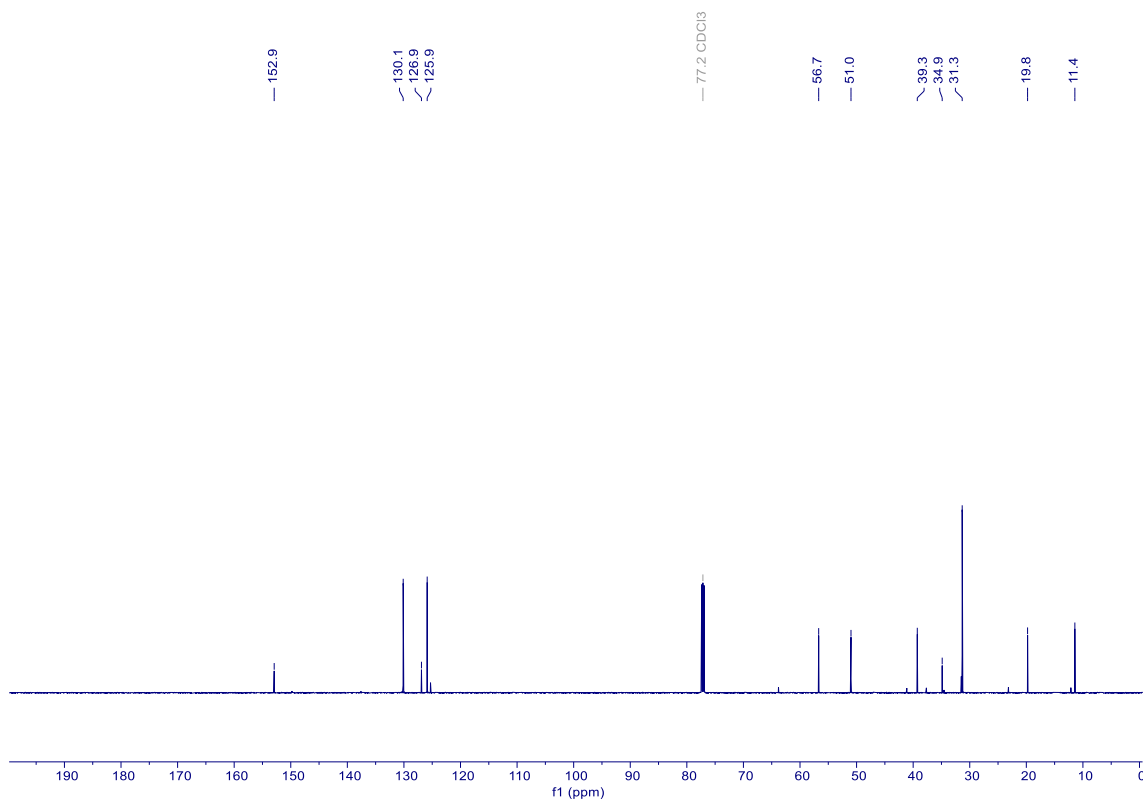
1a – ^{11}B NMR (128 MHz, $\text{DMSO-}d_6$)



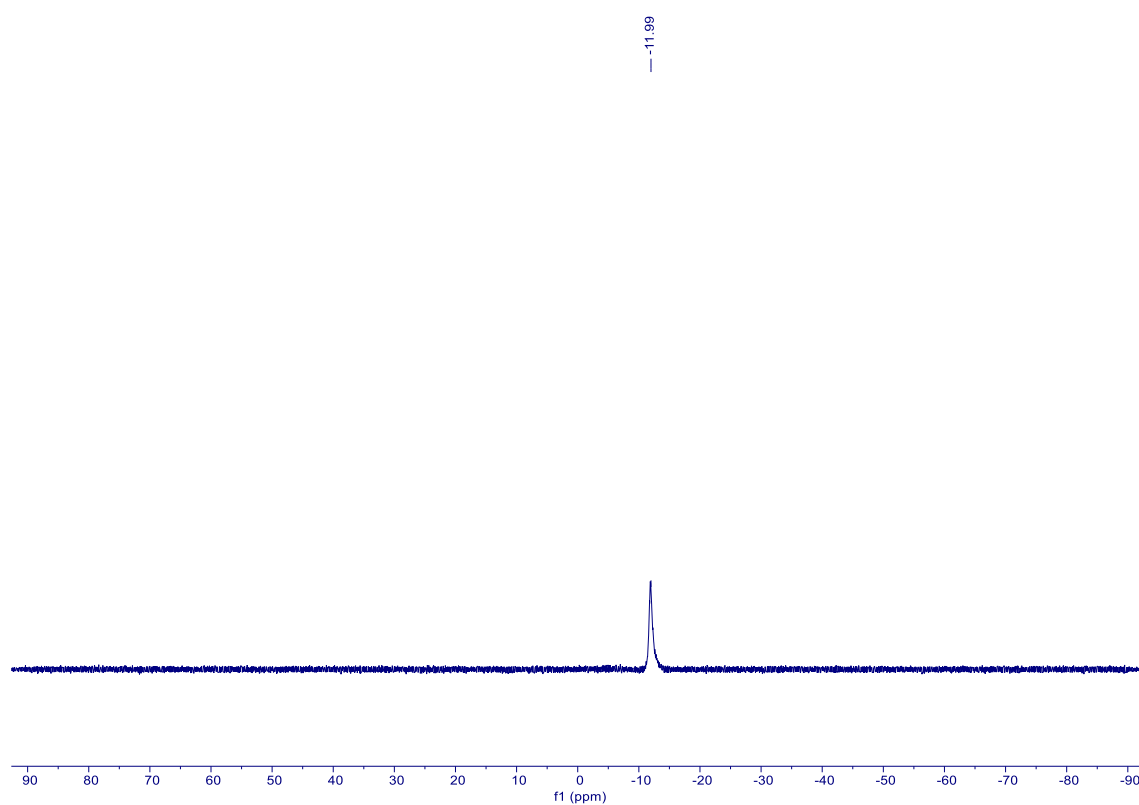
2a – ^1H NMR (600 MHz, CDCl_3)



2a – ^{13}C NMR (151 MHz, CDCl_3)



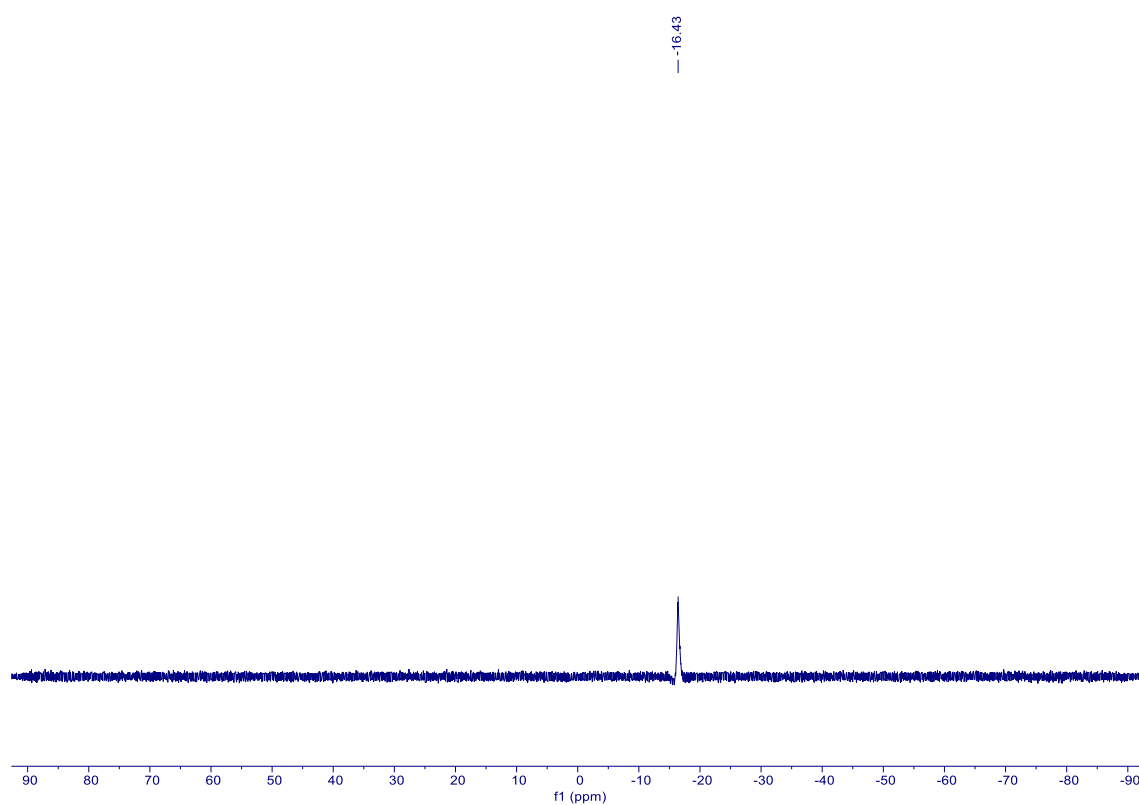
2a – ^{11}B NMR (193 MHz, CDCl_3)



[illegible]

13C NMR spectrum (CDCl₃) of compound 10. The x-axis is labeled 'f1 (ppm)' and ranges from 0 to 190. The spectrum shows several peaks: a small peak at 152.0 ppm, a cluster of peaks between 125 and 130 ppm (labeled 129.9, 128.0, 125.2), a large peak at 77.2 ppm (labeled 77.2 CDCl₃), and several peaks in the aliphatic region (labeled 67.1, 49.5, 41.5, 34.8, 31.4, 20.3, 11.5).

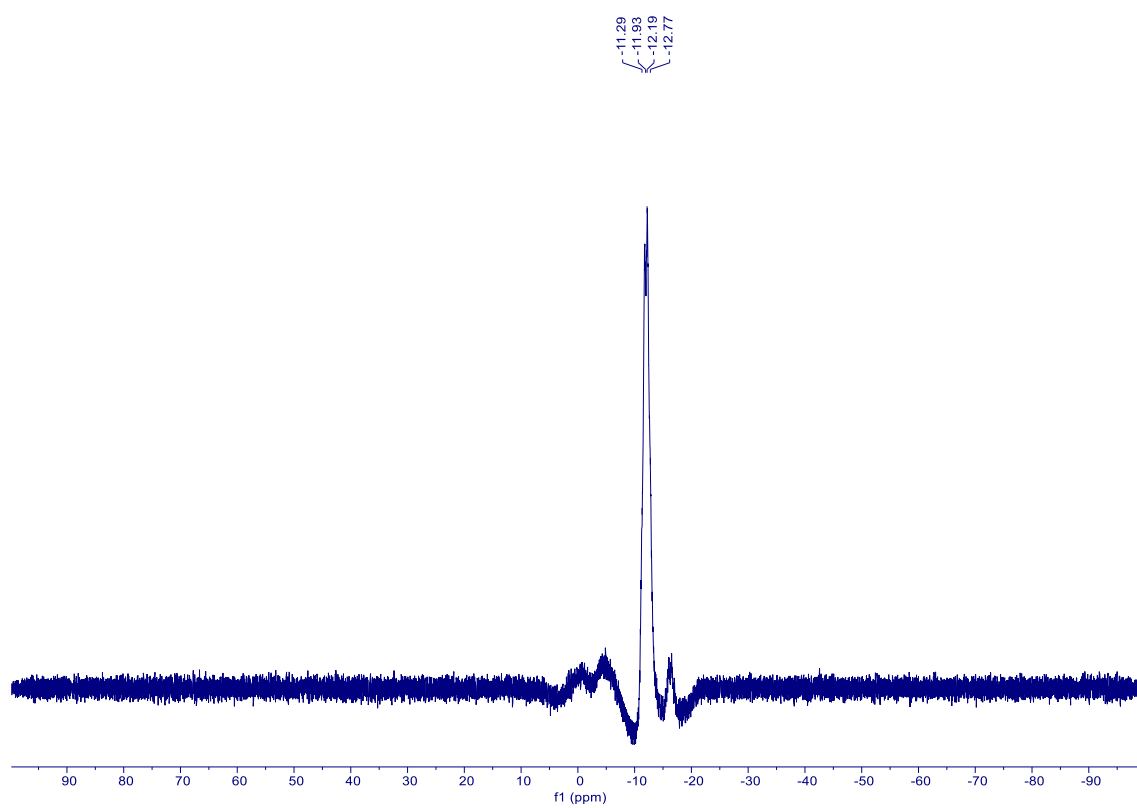
2a' – ^{11}B NMR (193 MHz, CDCl_3)



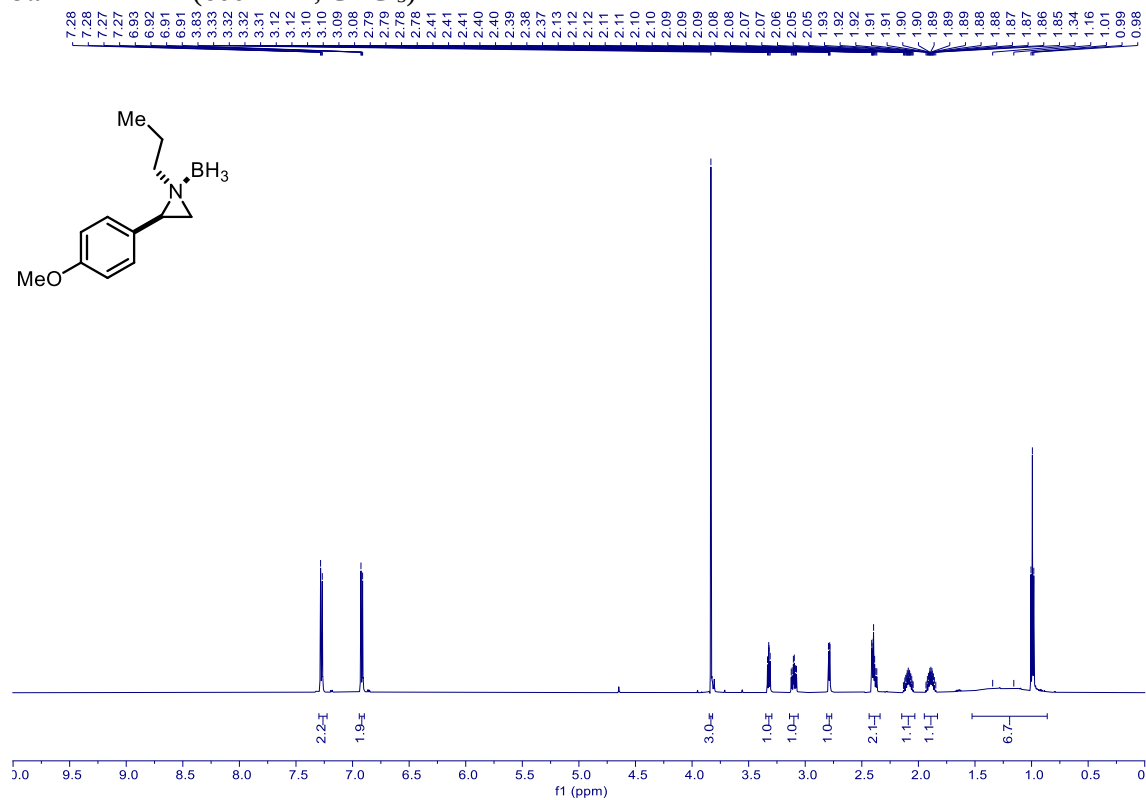
[illegible]

160.6
131.7
121.9
114.4
77.2 CDCl₃
56.6
55.5
50.9
39.4
19.7
11.5

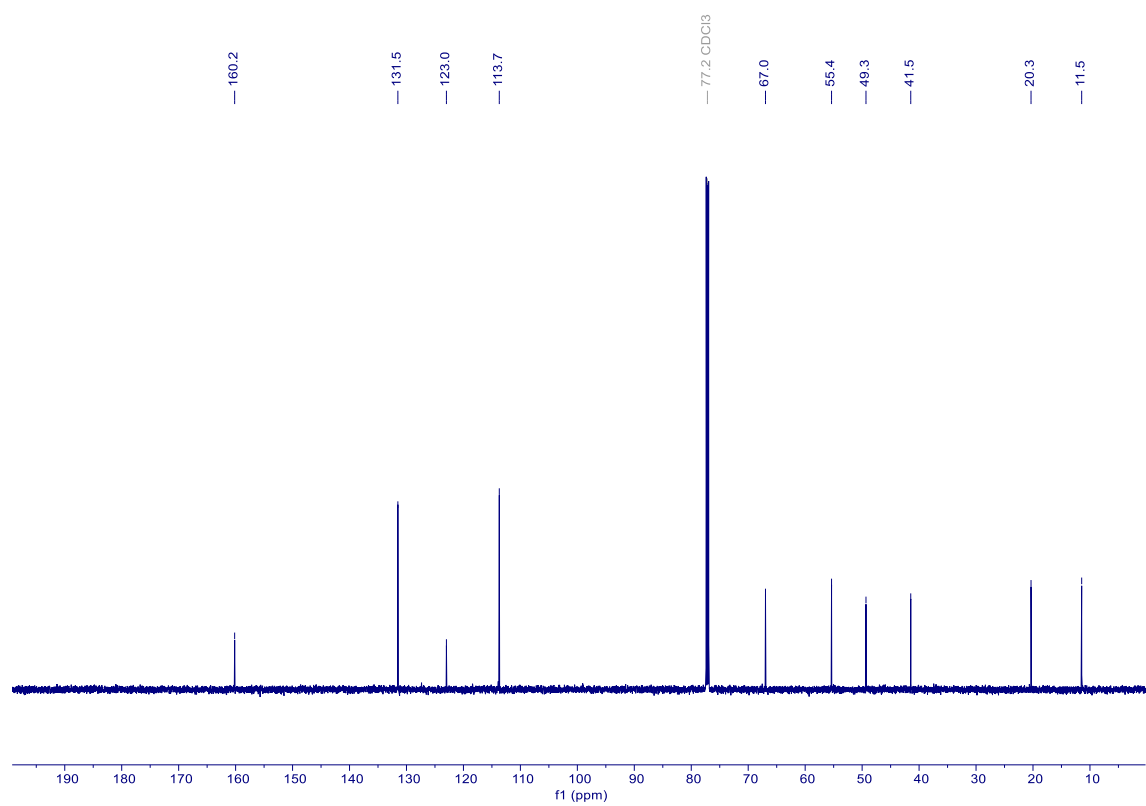
3a – ^{11}B NMR (193 MHz, CDCl_3)



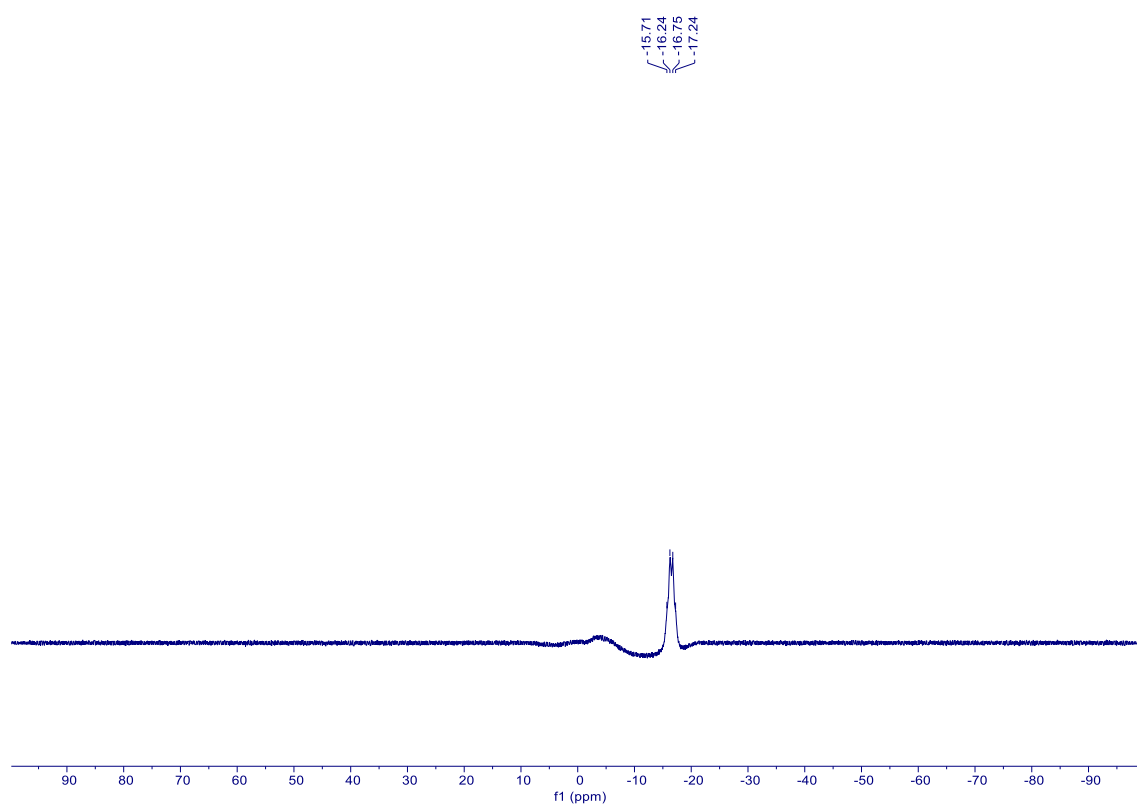
3a' – ^1H NMR (600 MHz, CDCl_3)



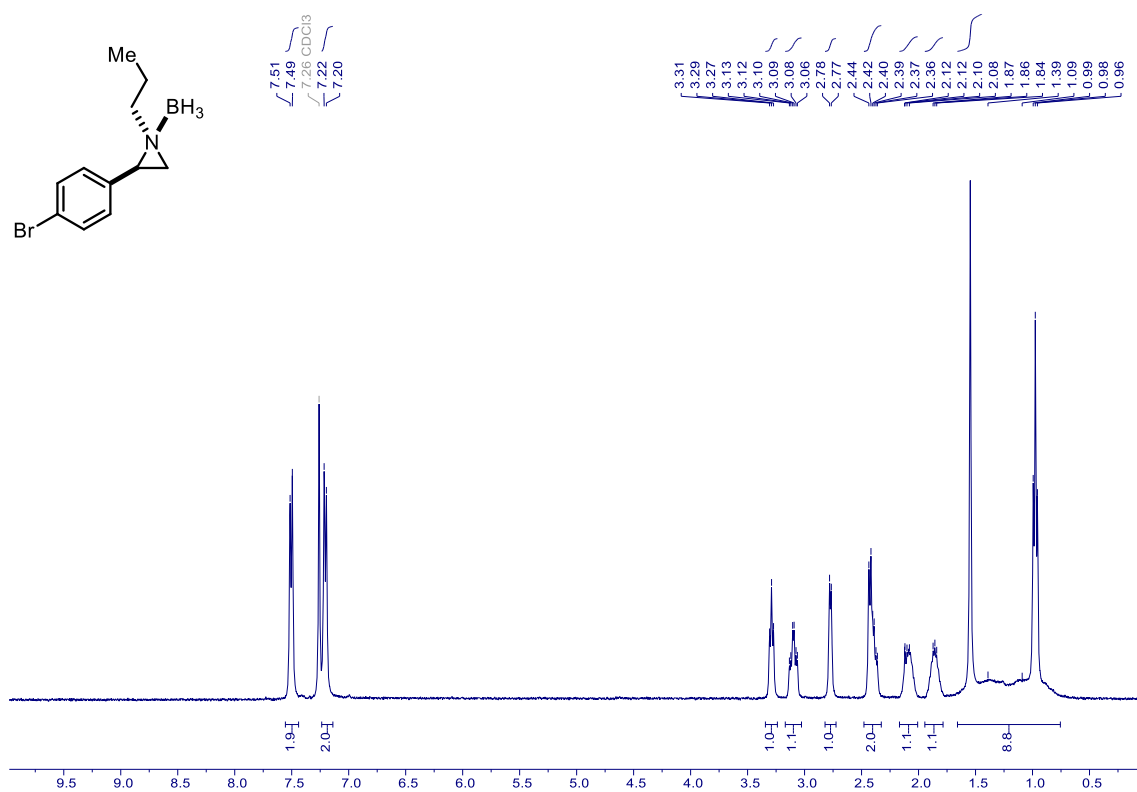
3a' – ^{13}C NMR (151 MHz, CDCl_3)



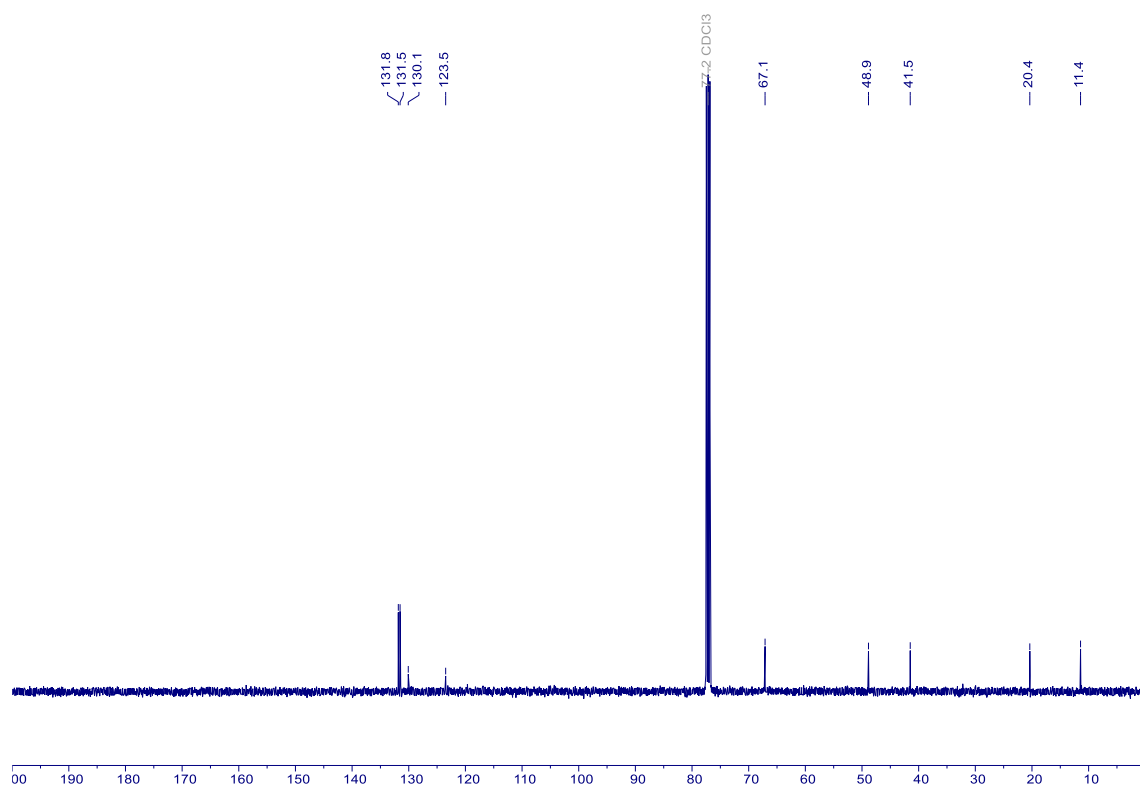
3a' – ^{11}B NMR (193 MHz, CDCl_3)



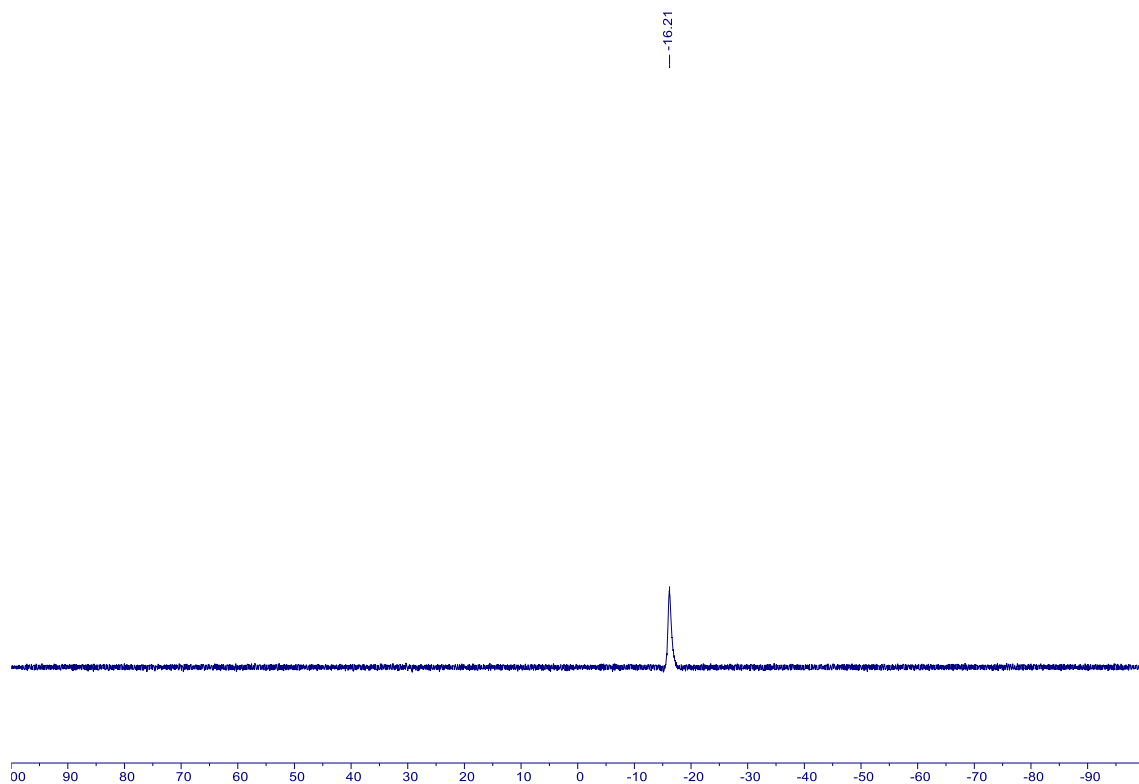
4a – ^1H NMR (400 MHz, CDCl_3)



4a – ^{13}C NMR (101 MHz, CDCl_3)

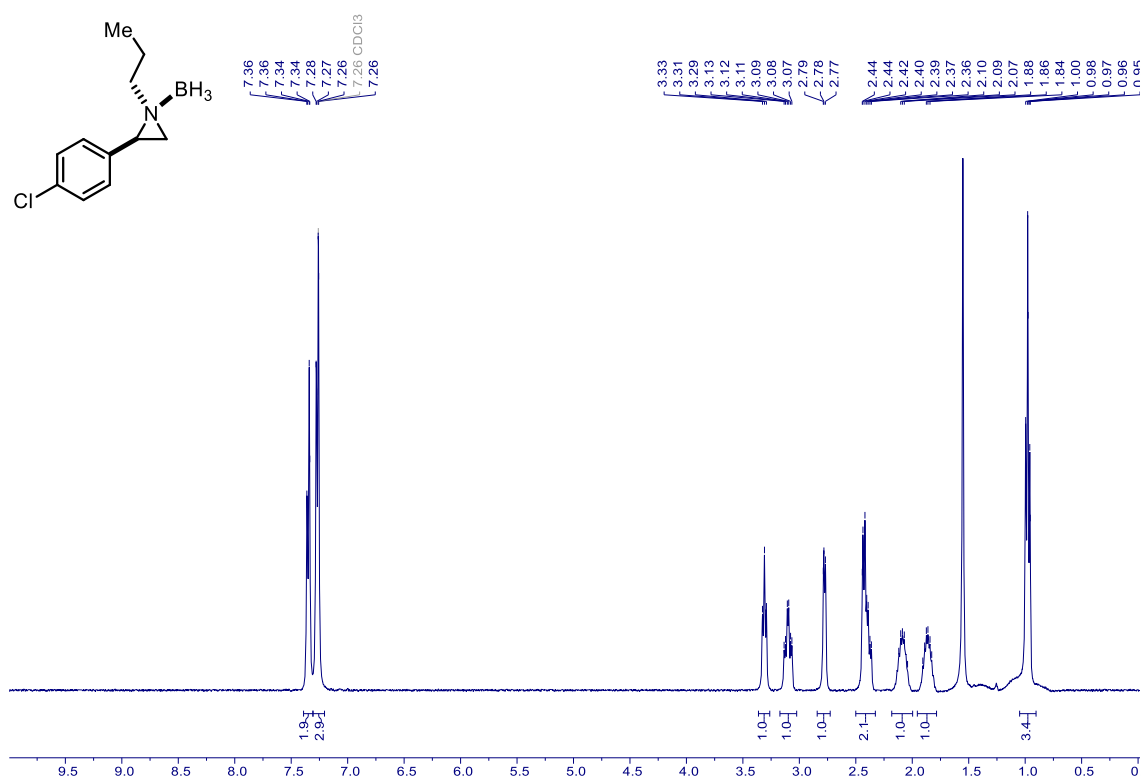


4a – ^{11}B NMR (128 MHz, CDCl_3)

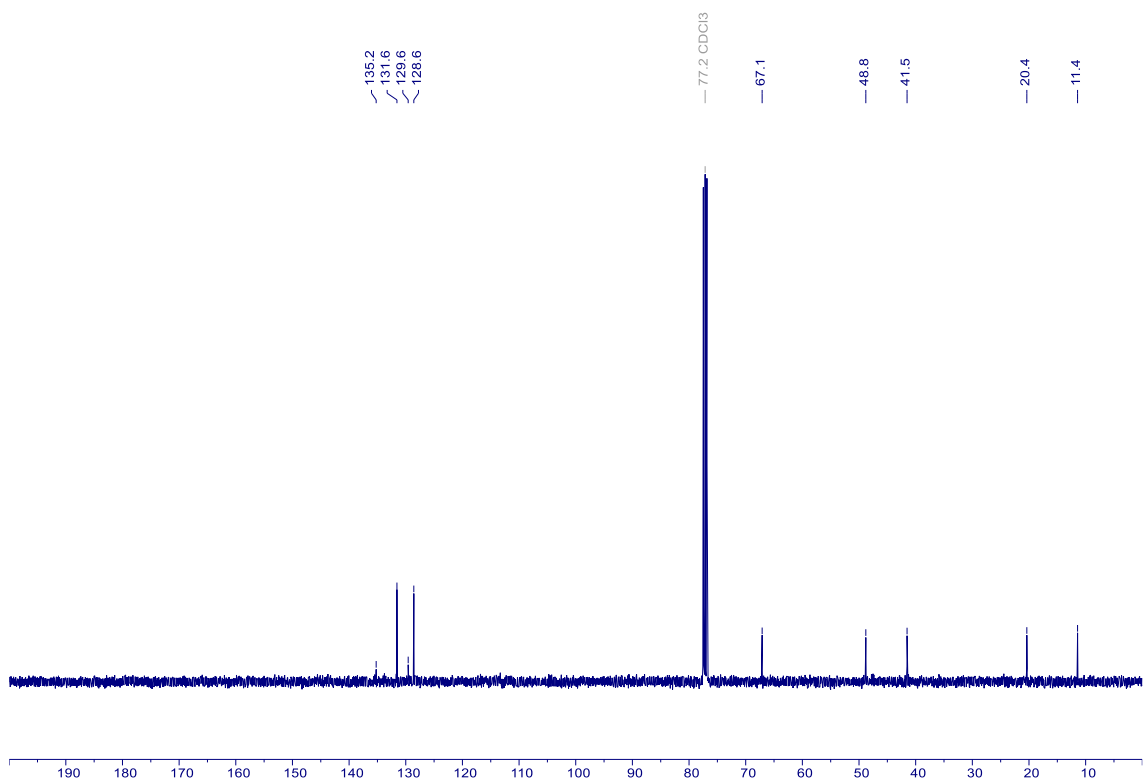


S204

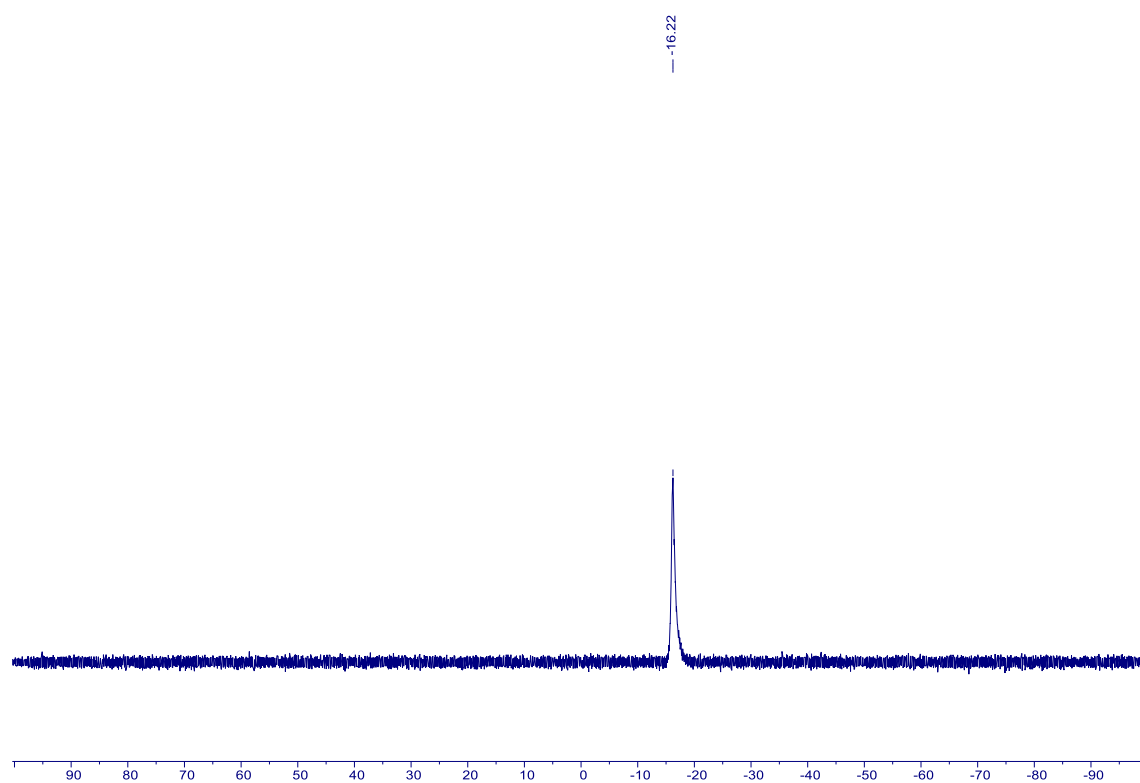
5a – ^1H NMR (400 MHz, CDCl_3)



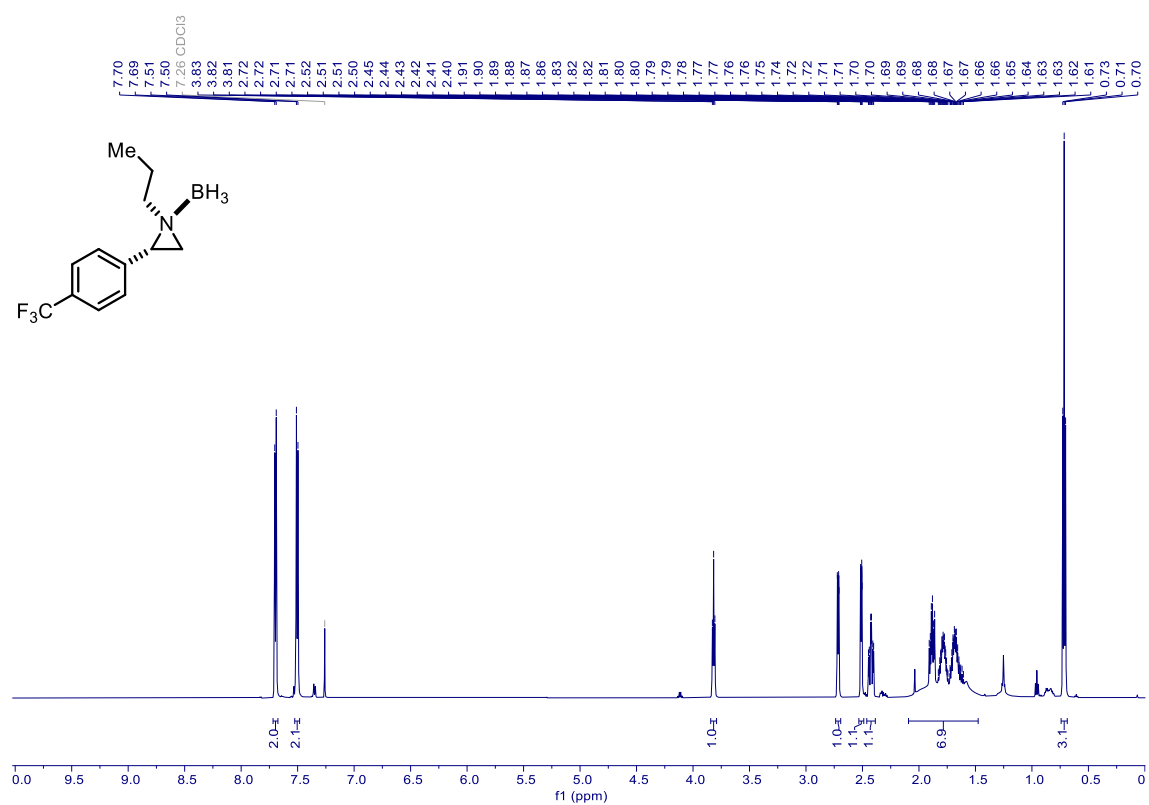
5a – ^{13}C NMR (101 MHz, CDCl_3)



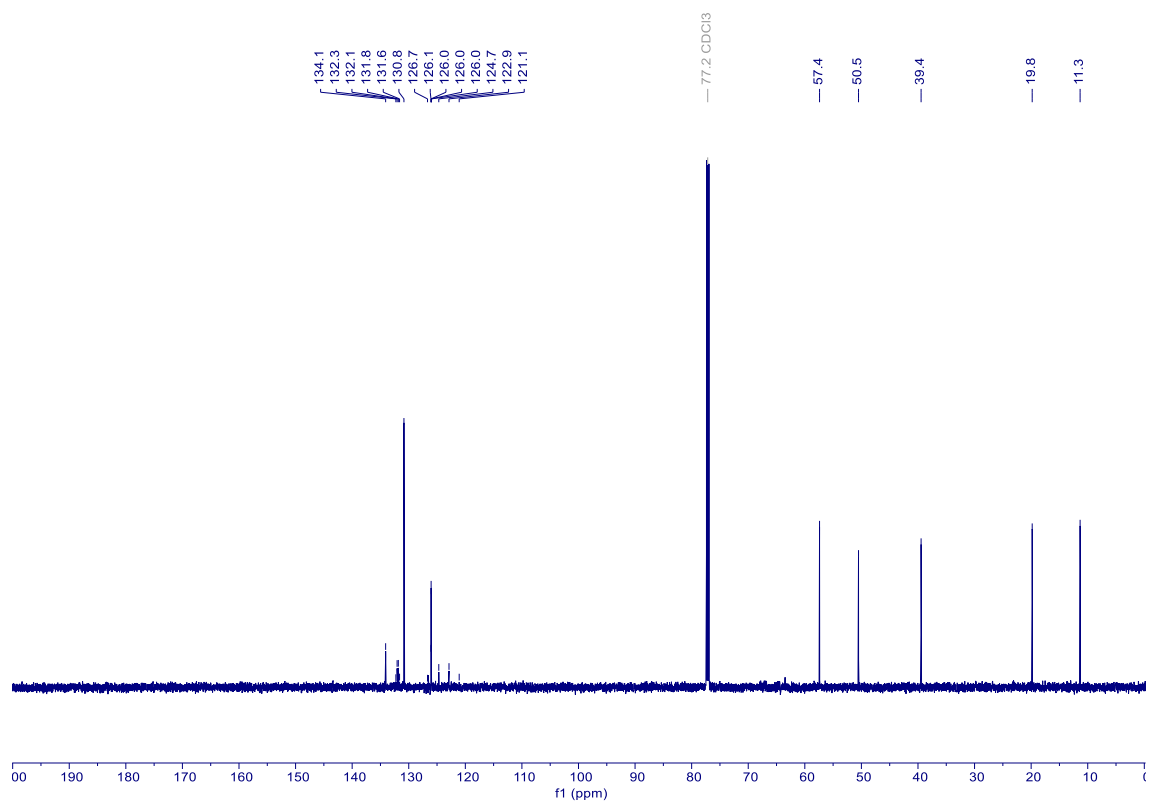
5a – ^{11}B NMR (128 MHz, CDCl_3)



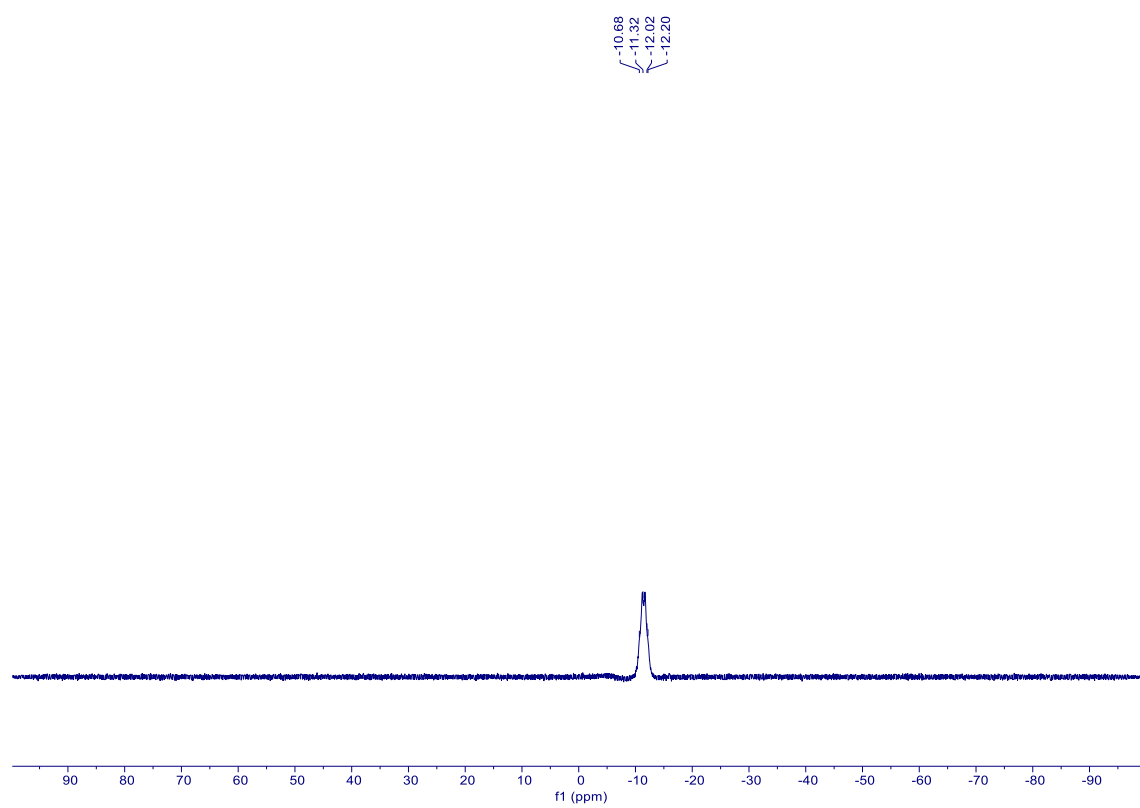
6a – ^1H NMR (600 MHz, CDCl_3)



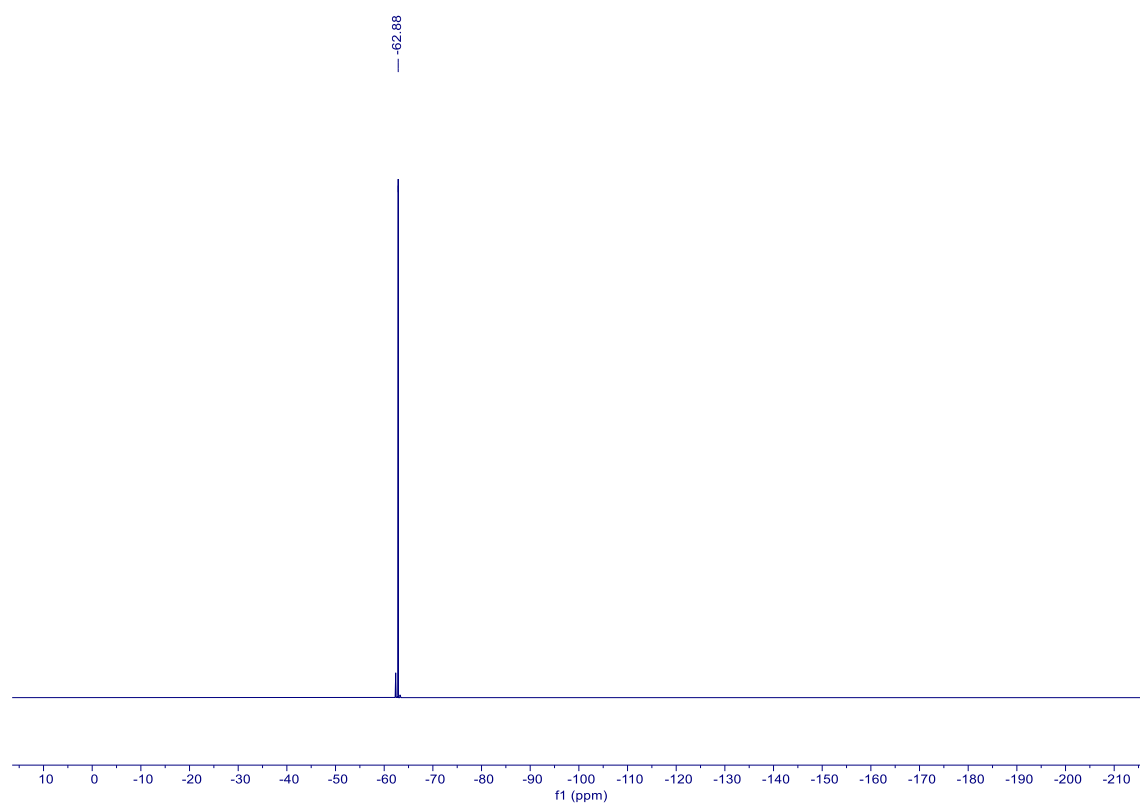
6a – ^{13}C NMR (151 MHz, CDCl_3)



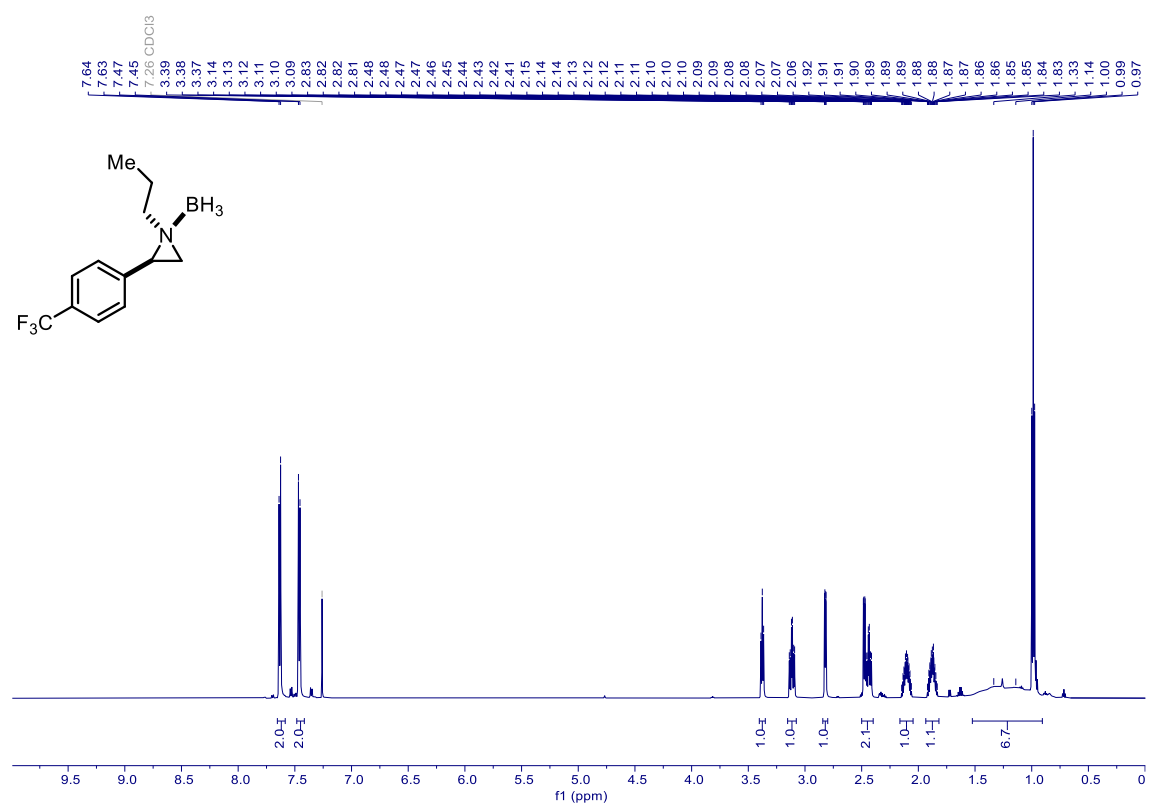
6a – ^{11}B NMR (193 MHz, CDCl_3)



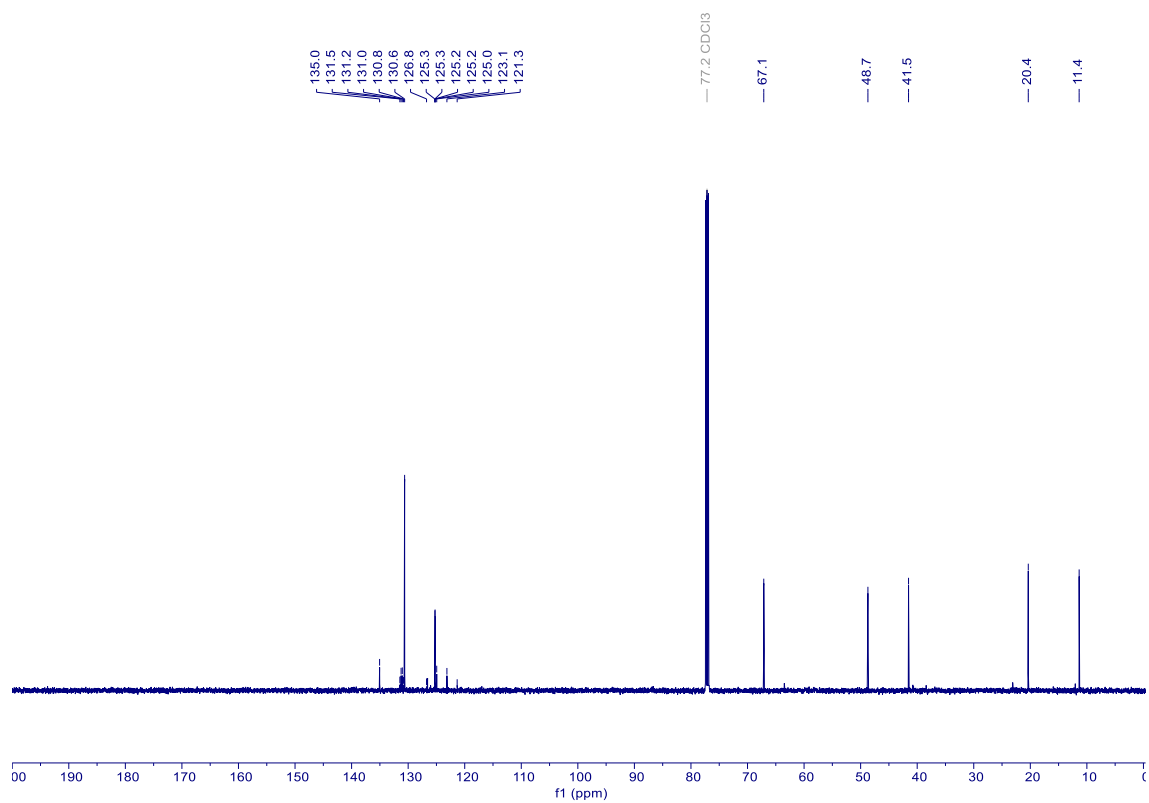
6a – ^{19}F NMR (565 MHz, CDCl_3)



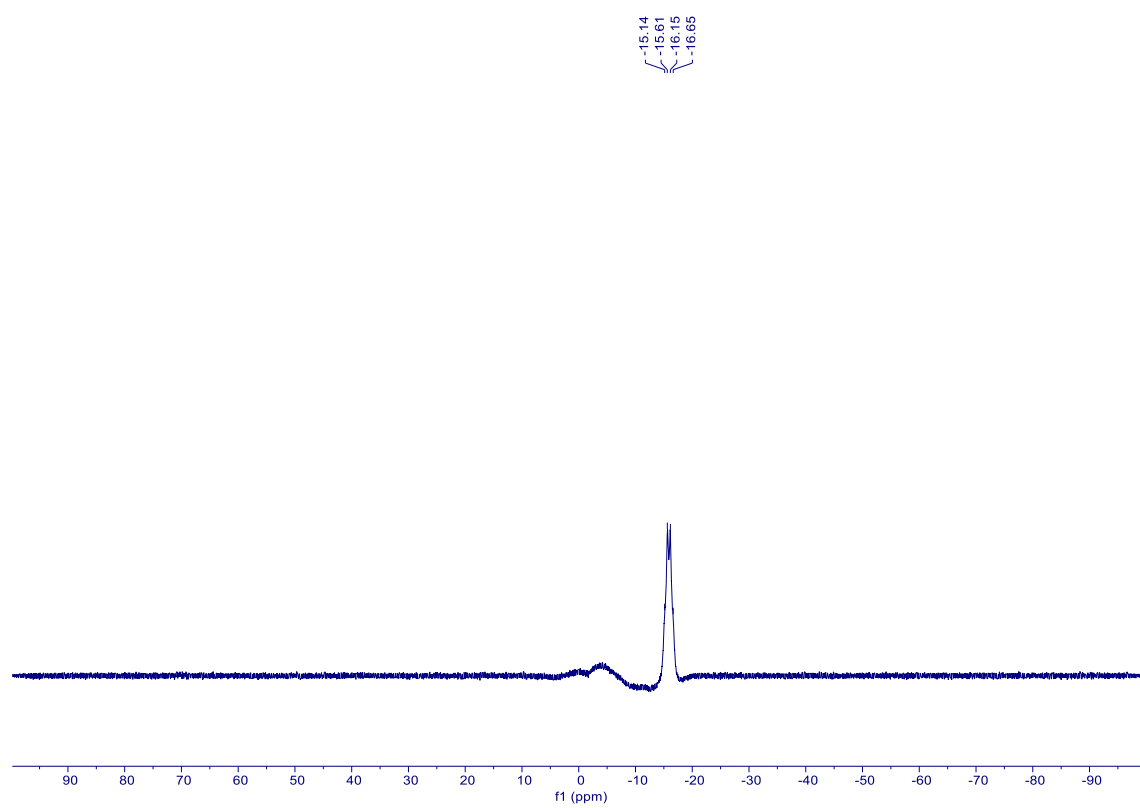
6a' – ^1H NMR (600 MHz, CDCl_3)



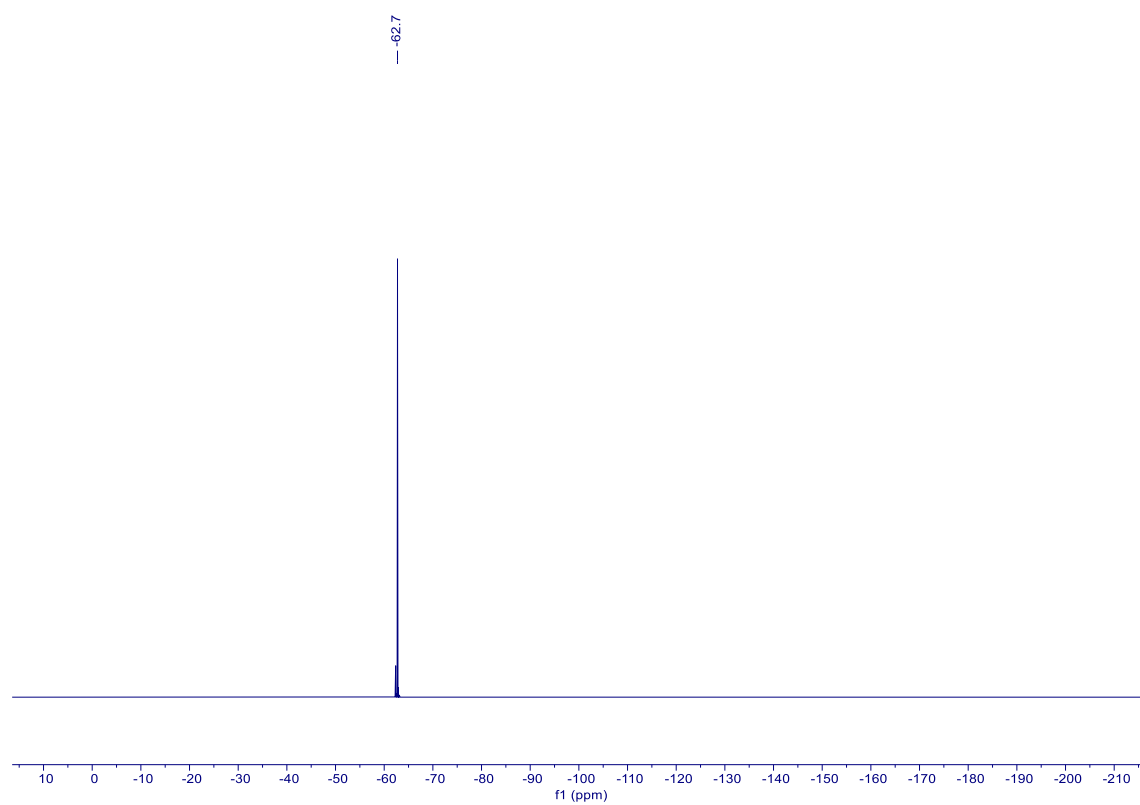
6a' – ^{13}C NMR (151 MHz, CDCl_3)



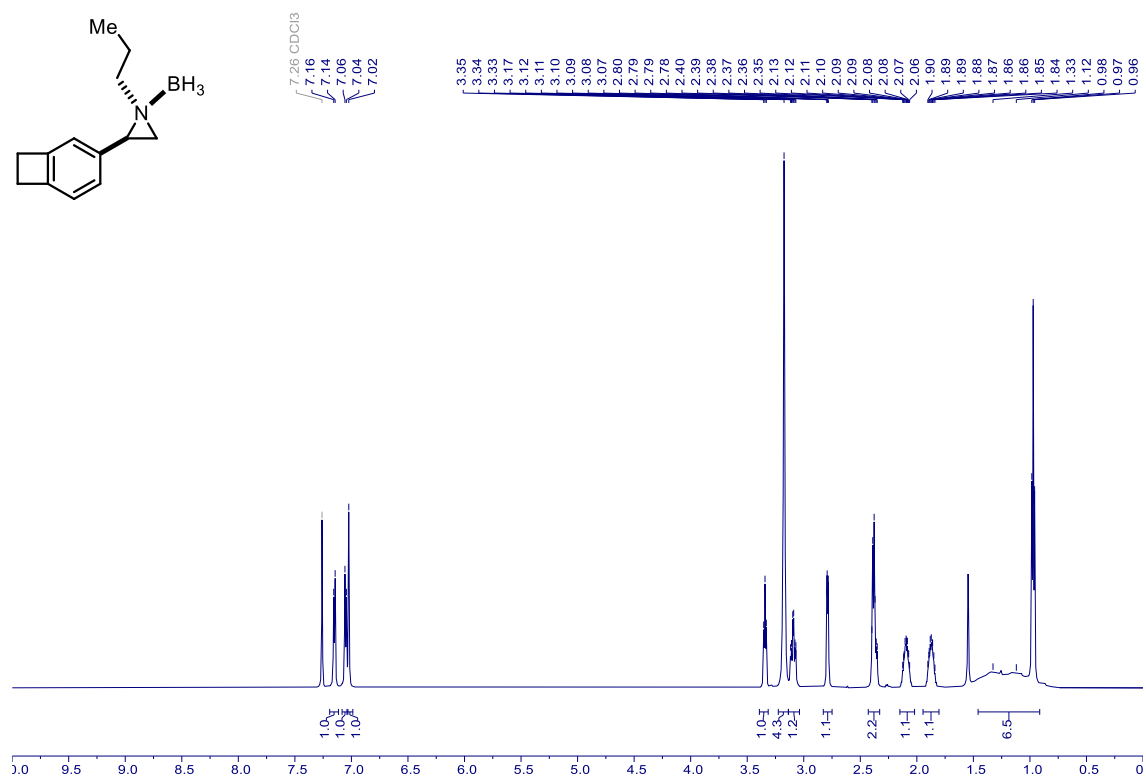
6a' – ^{11}B NMR (193 MHz, CDCl_3)



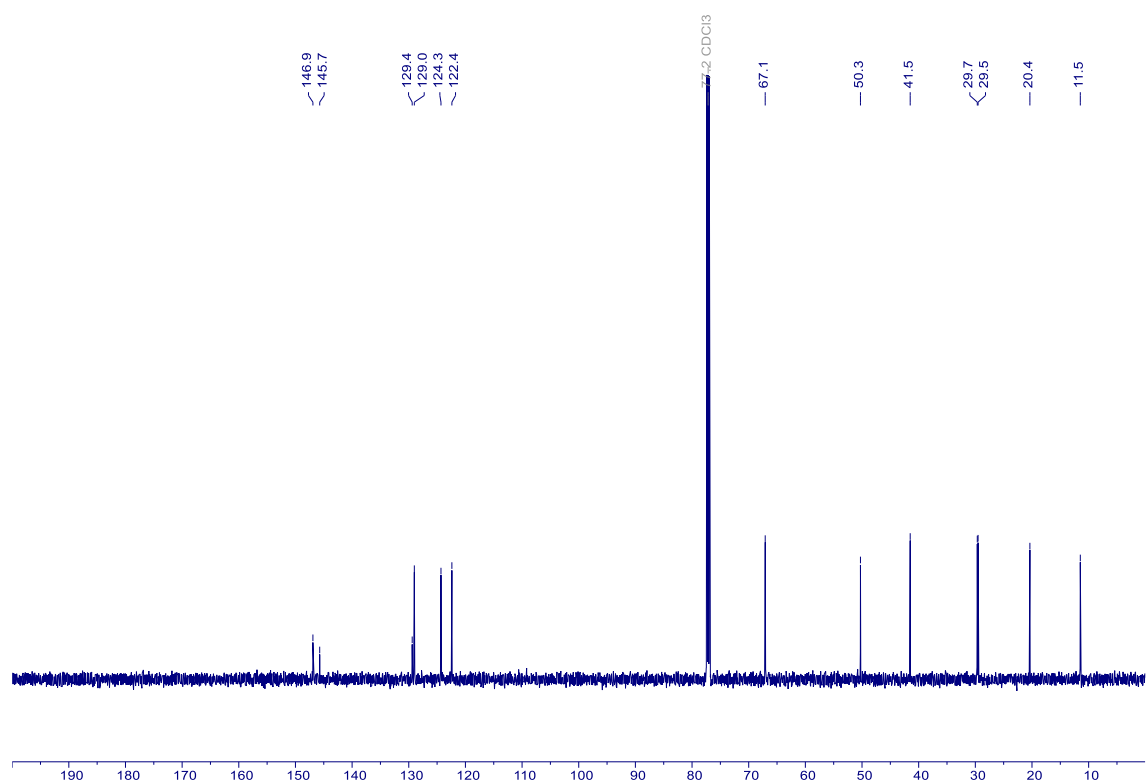
6a' – ^{19}F NMR (565 MHz, CDCl_3)



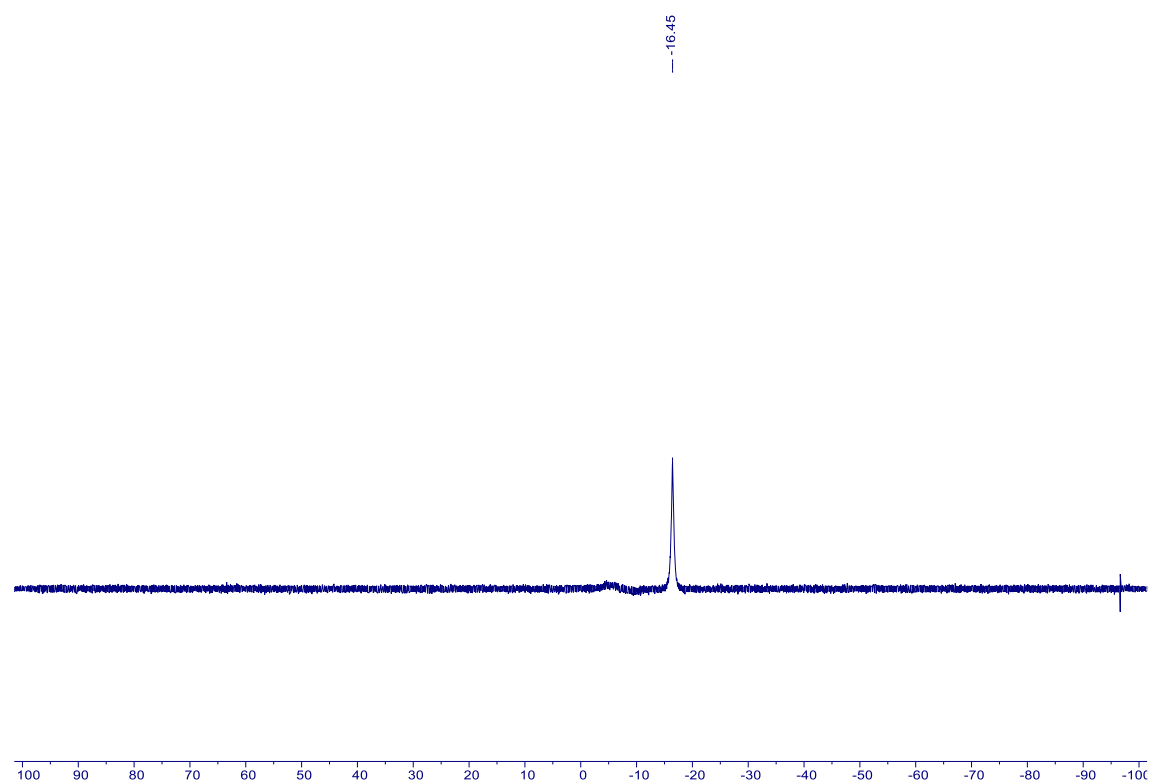
7a – ^1H NMR (600 MHz, CDCl_3)



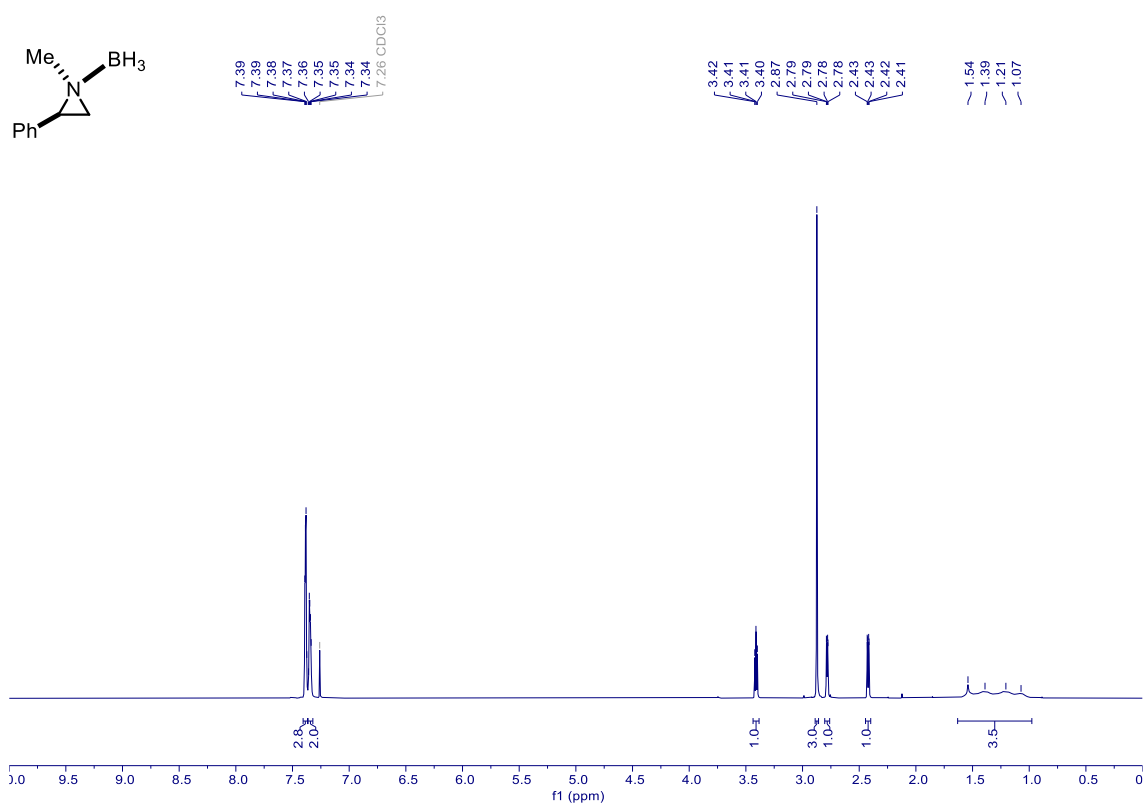
7a – ^{13}C NMR (151 MHz, CDCl_3)



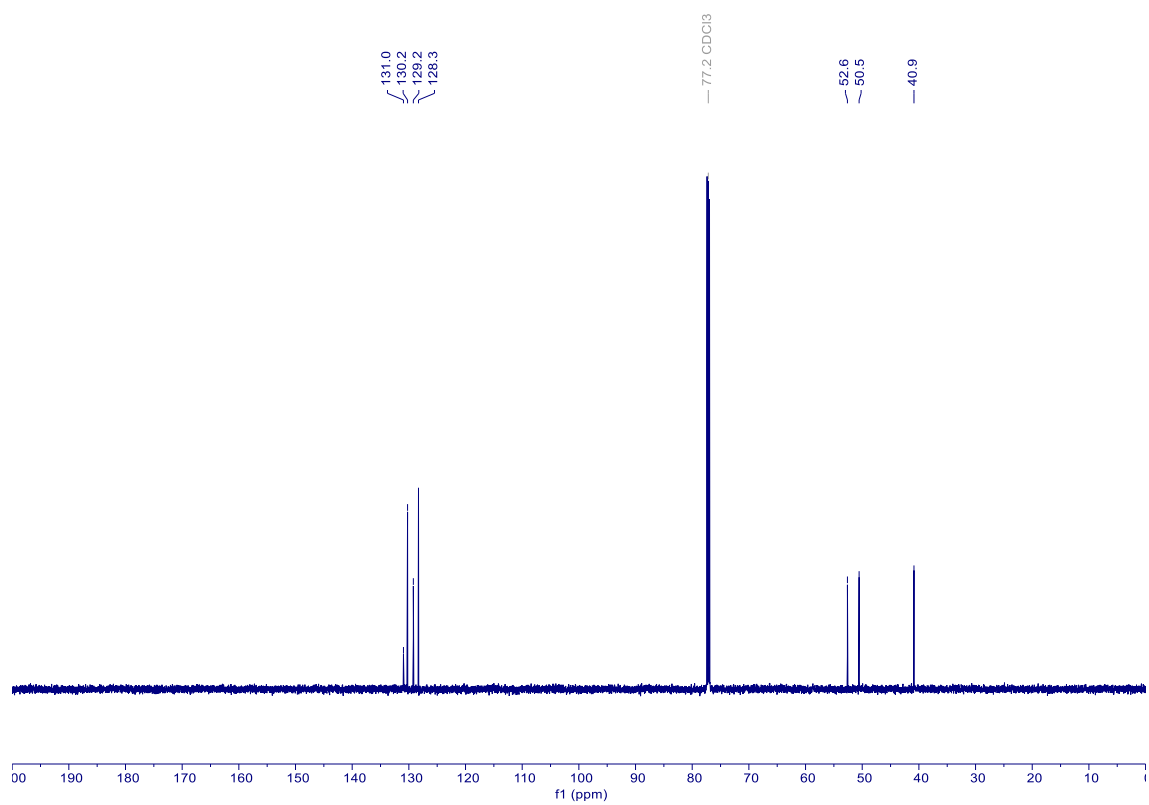
7a – ^{11}B NMR (192 MHz, CDCl_3)



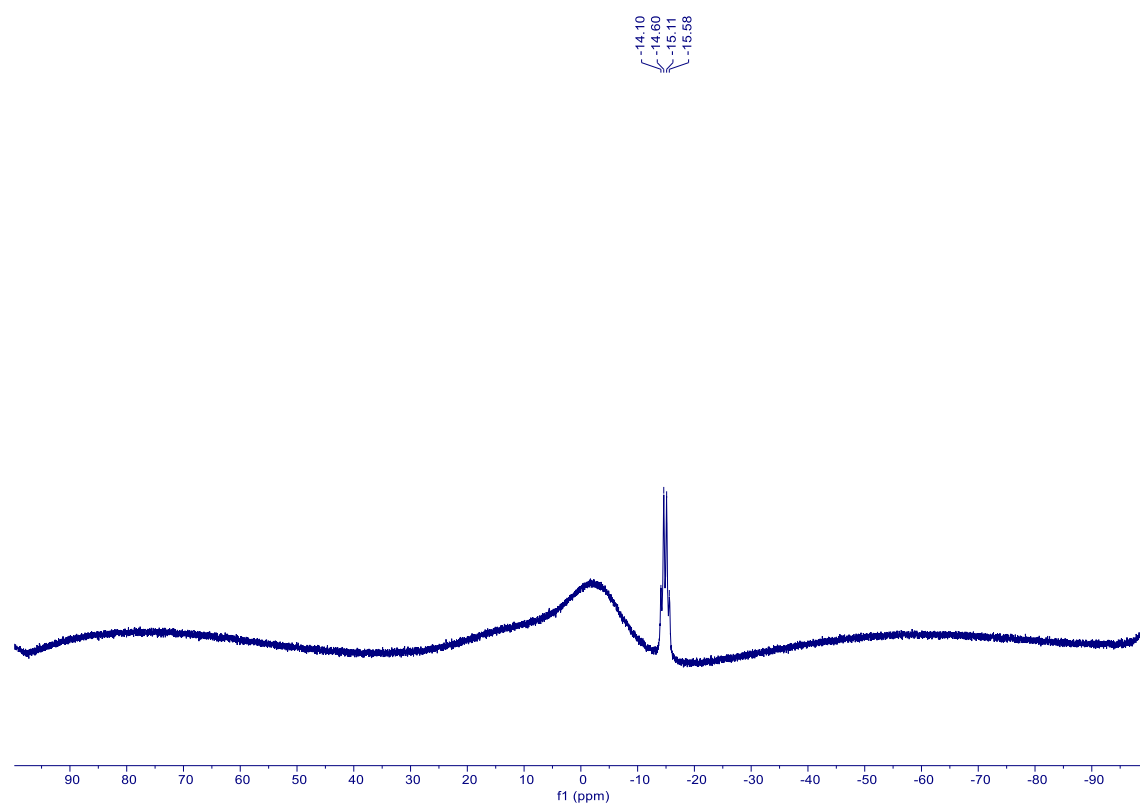
8a – ^1H NMR (600 MHz, CDCl_3)



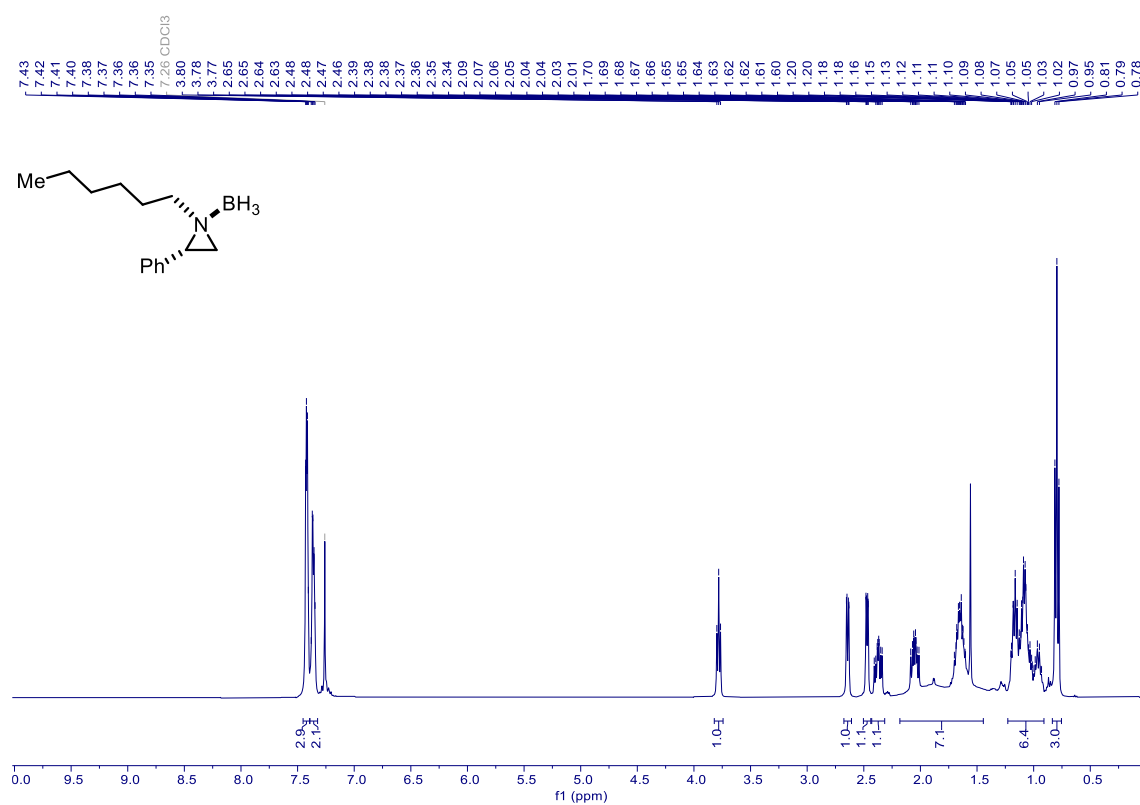
8a – ^{13}C NMR (151 MHz, CDCl_3)



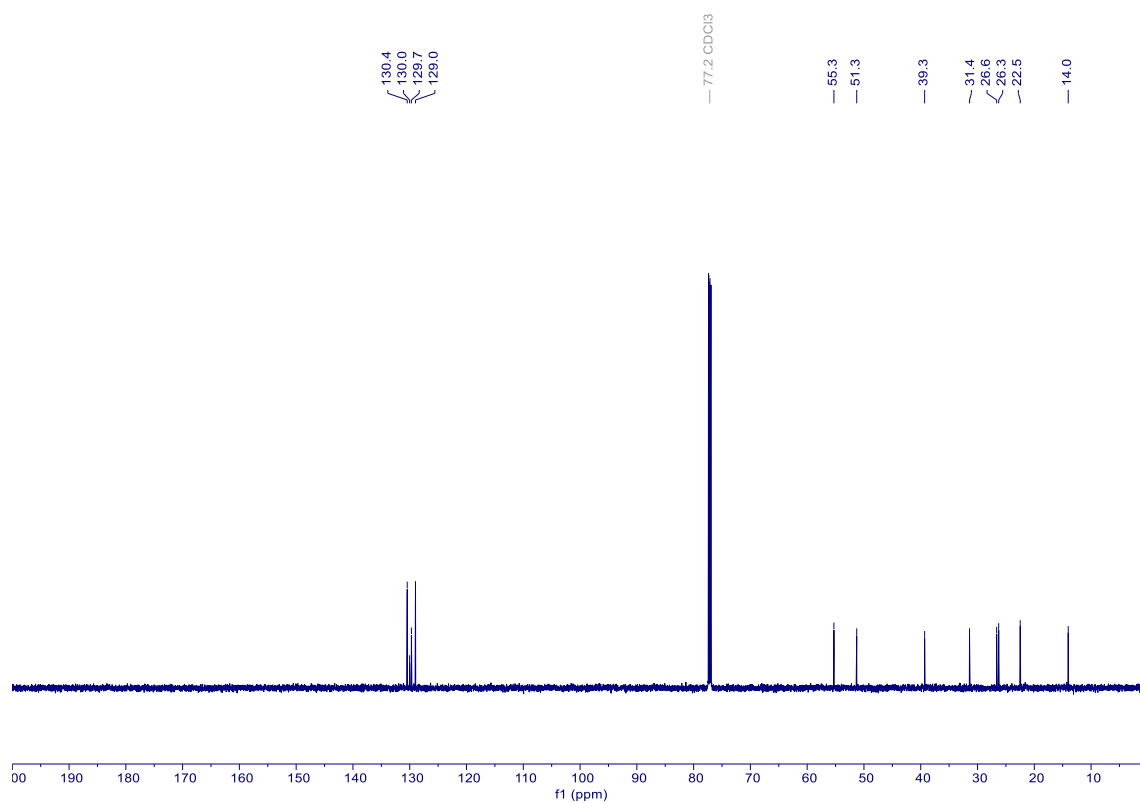
8a – ^{11}B NMR (193 MHz, CDCl_3)



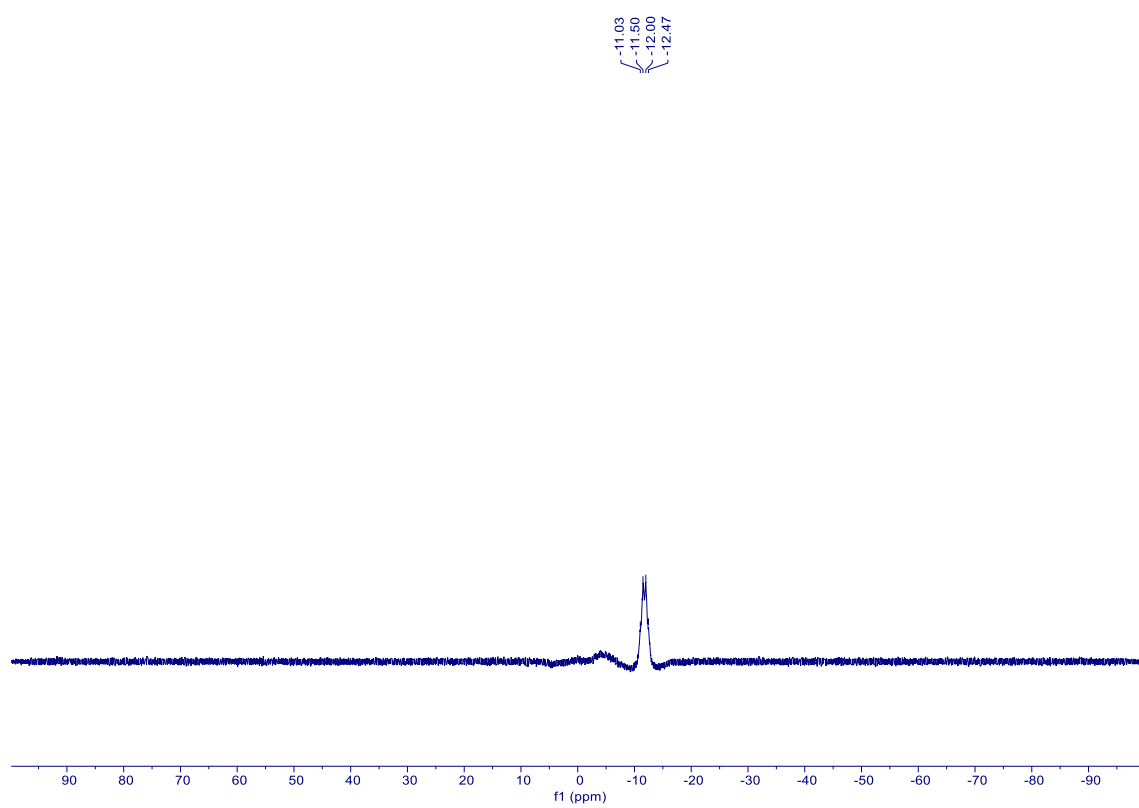
9a – ^1H NMR (400 MHz, CDCl_3)



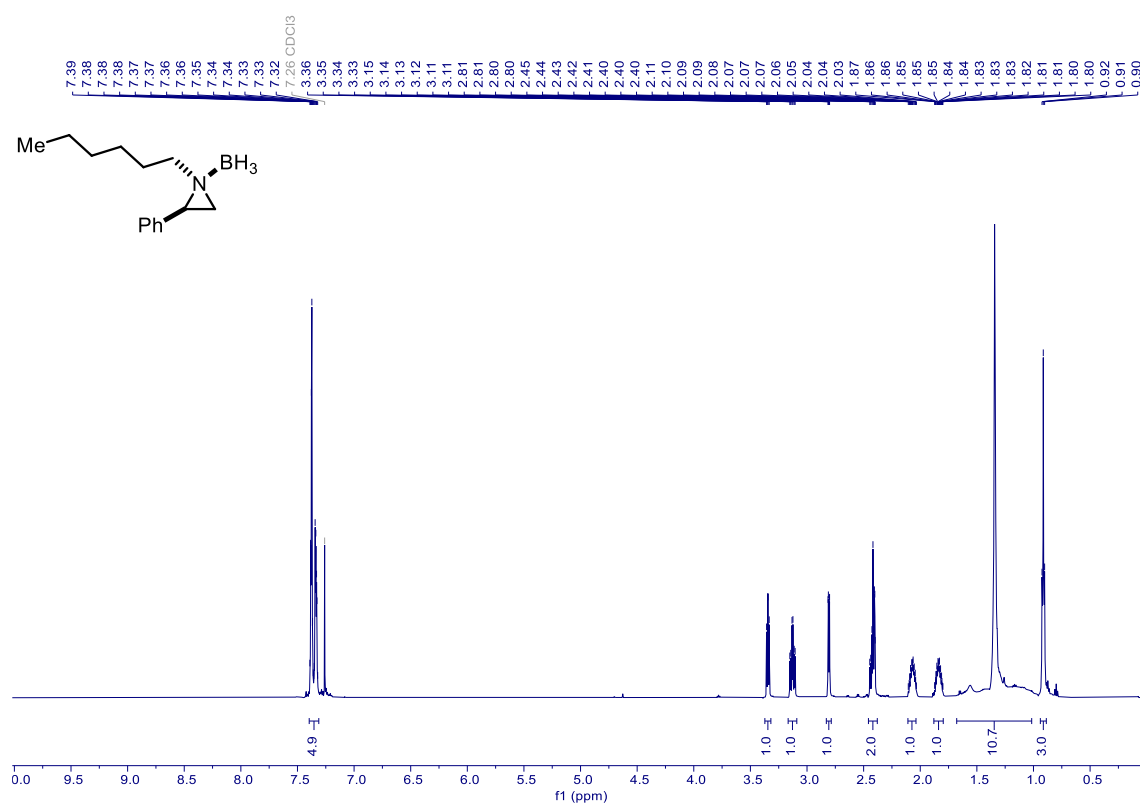
9a – ^{13}C NMR (151 MHz, CDCl_3)



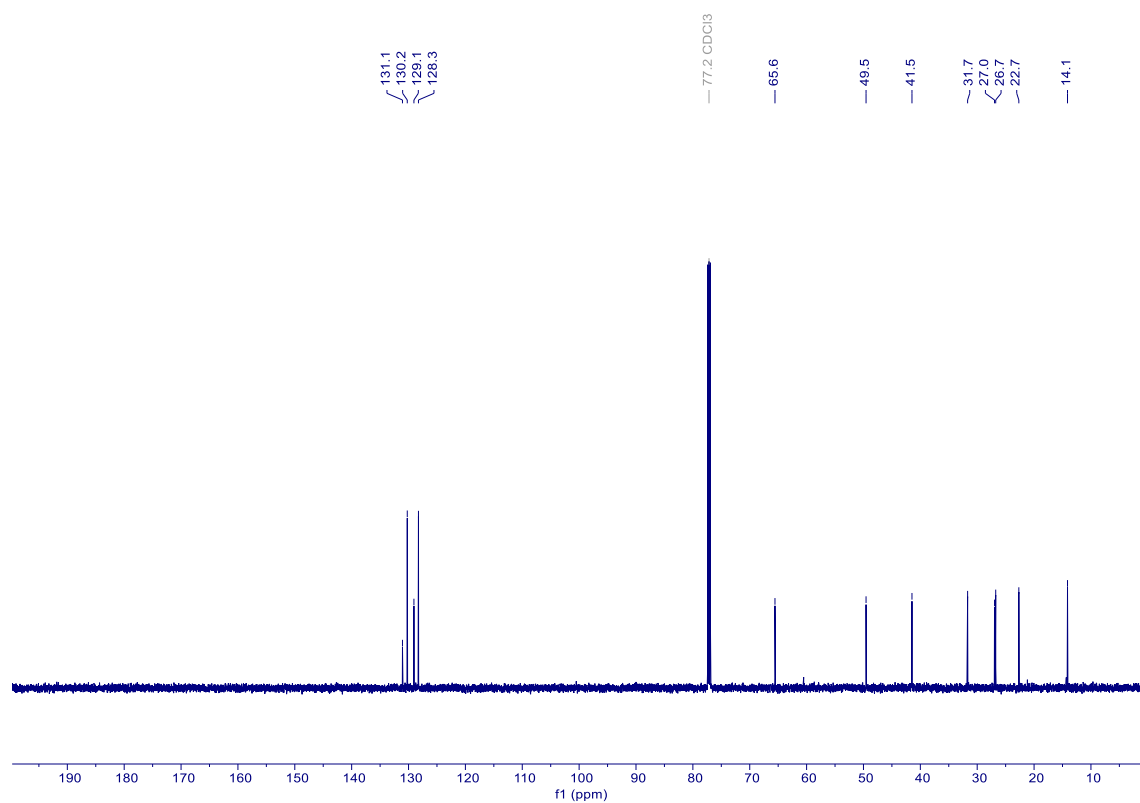
9a – ^{11}B NMR (193 MHz, CDCl_3)



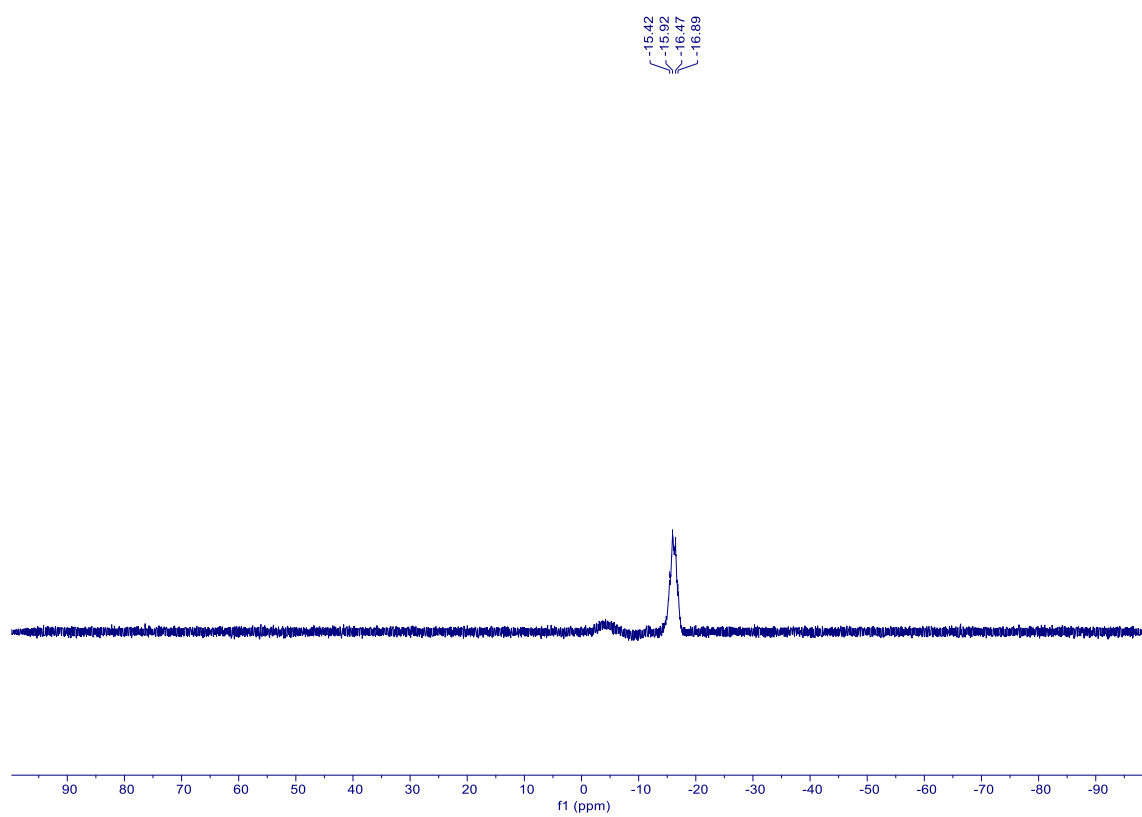
9a' – ^1H NMR (600 MHz, CDCl_3)



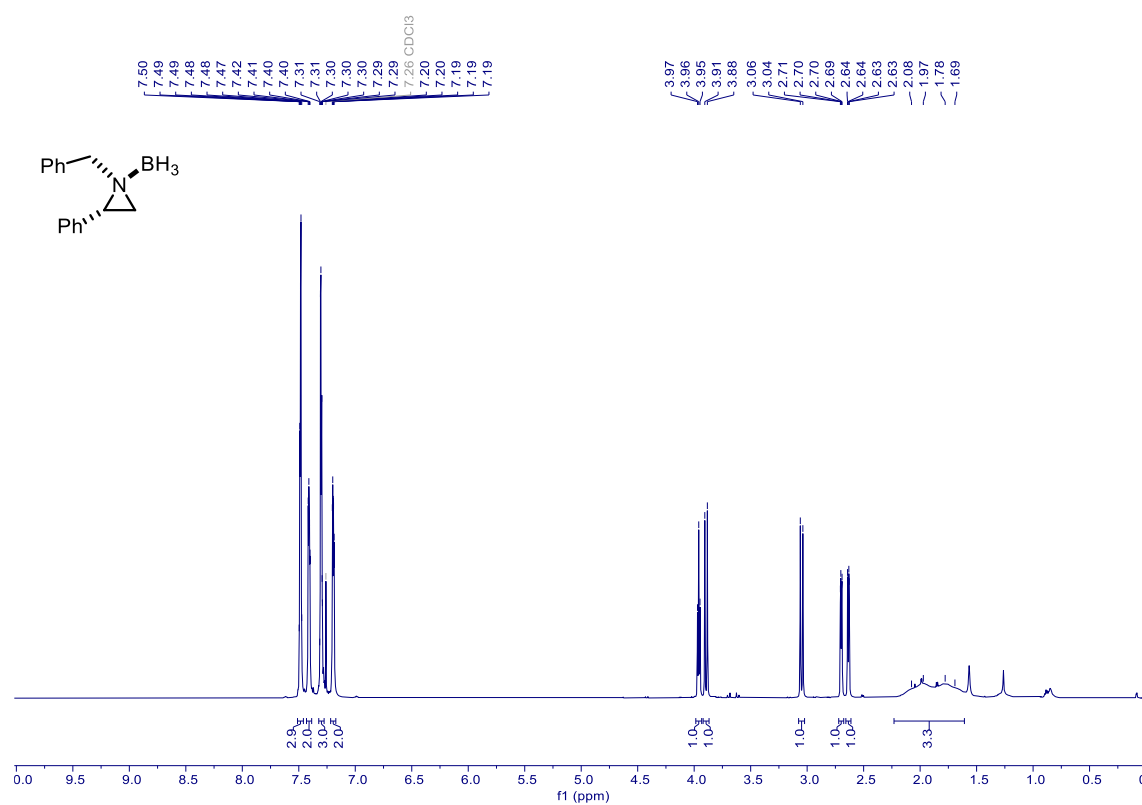
9a' – ^{13}C NMR (151 MHz, CDCl_3)



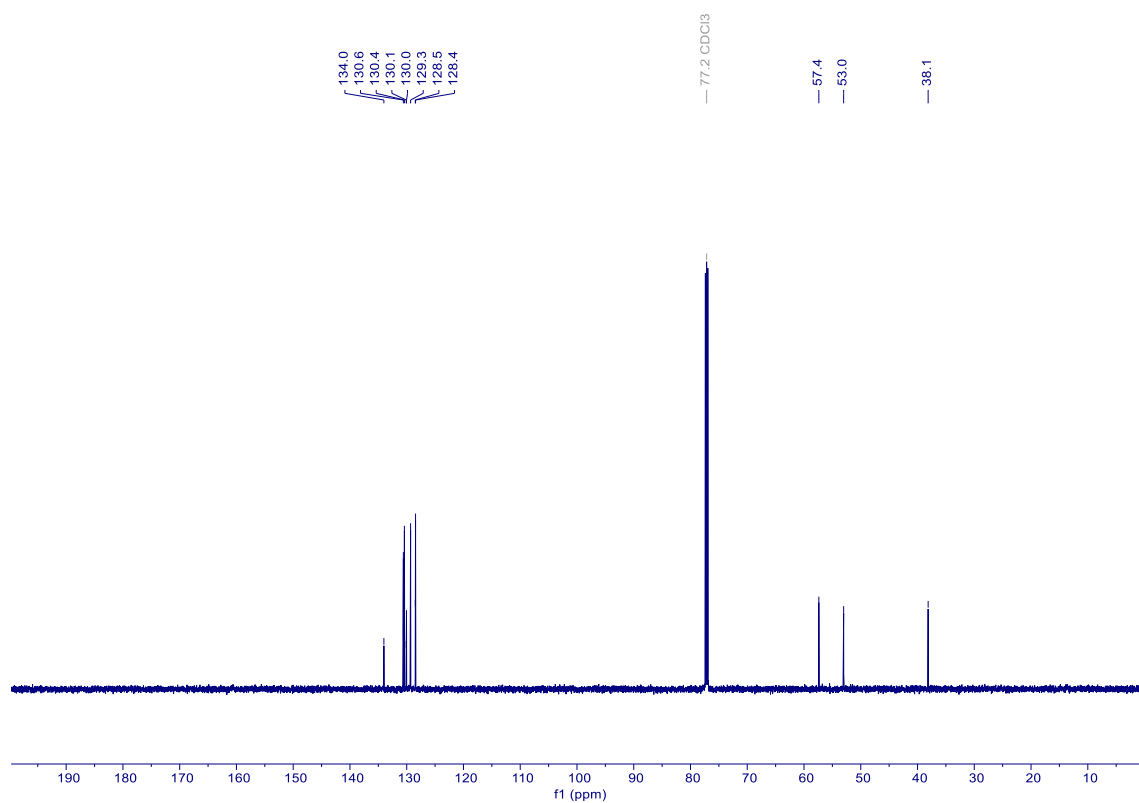
9a' – ^{11}B NMR (193 MHz, CDCl_3)



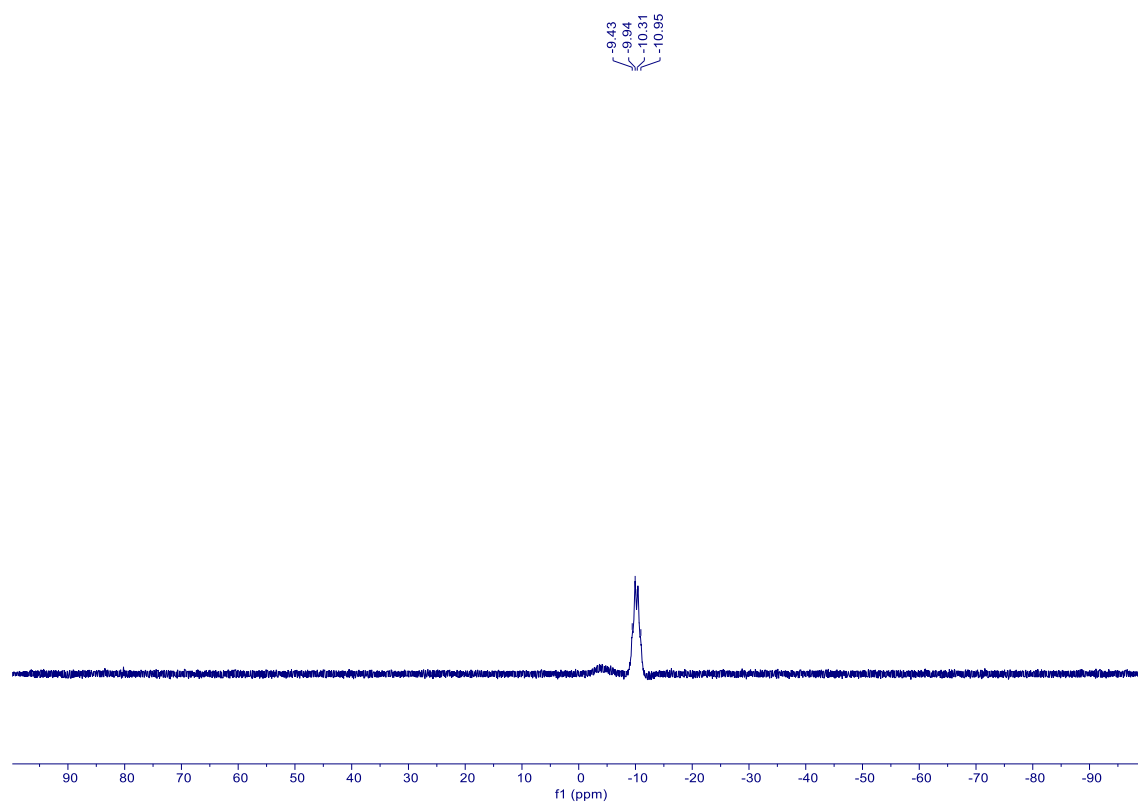
10a – ^1H NMR (600 MHz, CDCl_3)



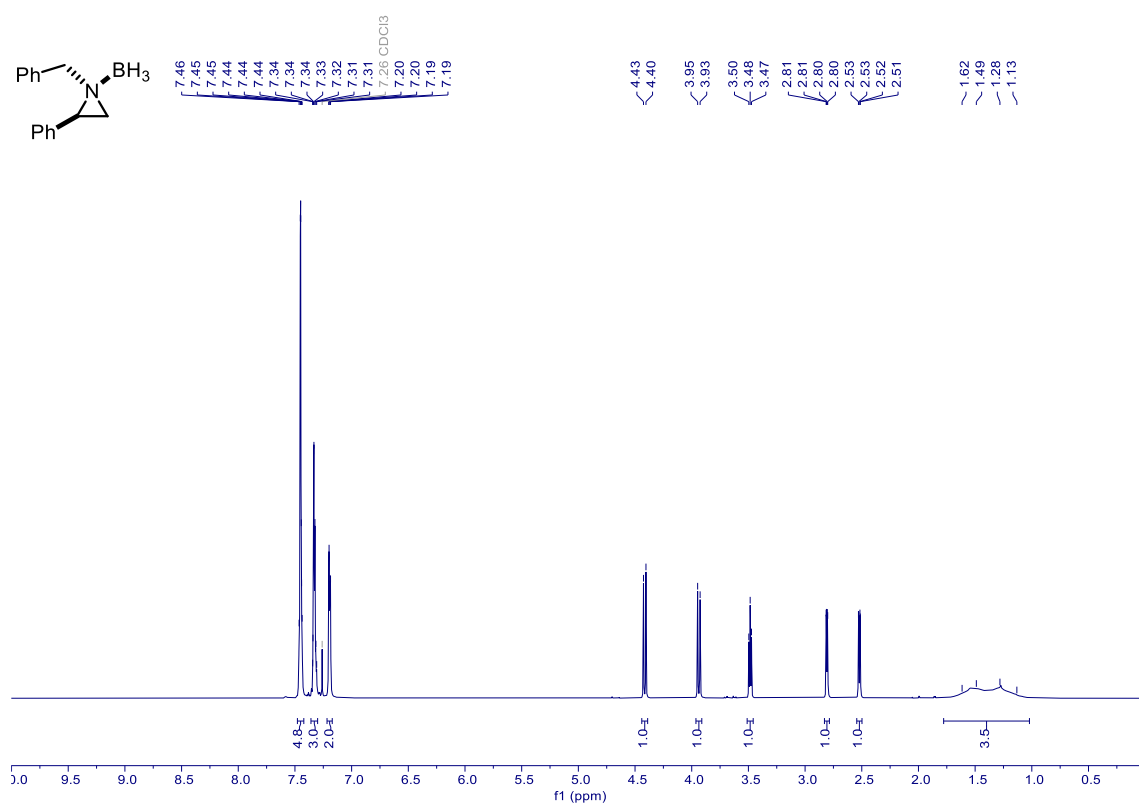
10a – ^{13}C NMR (151 MHz, CDCl_3)



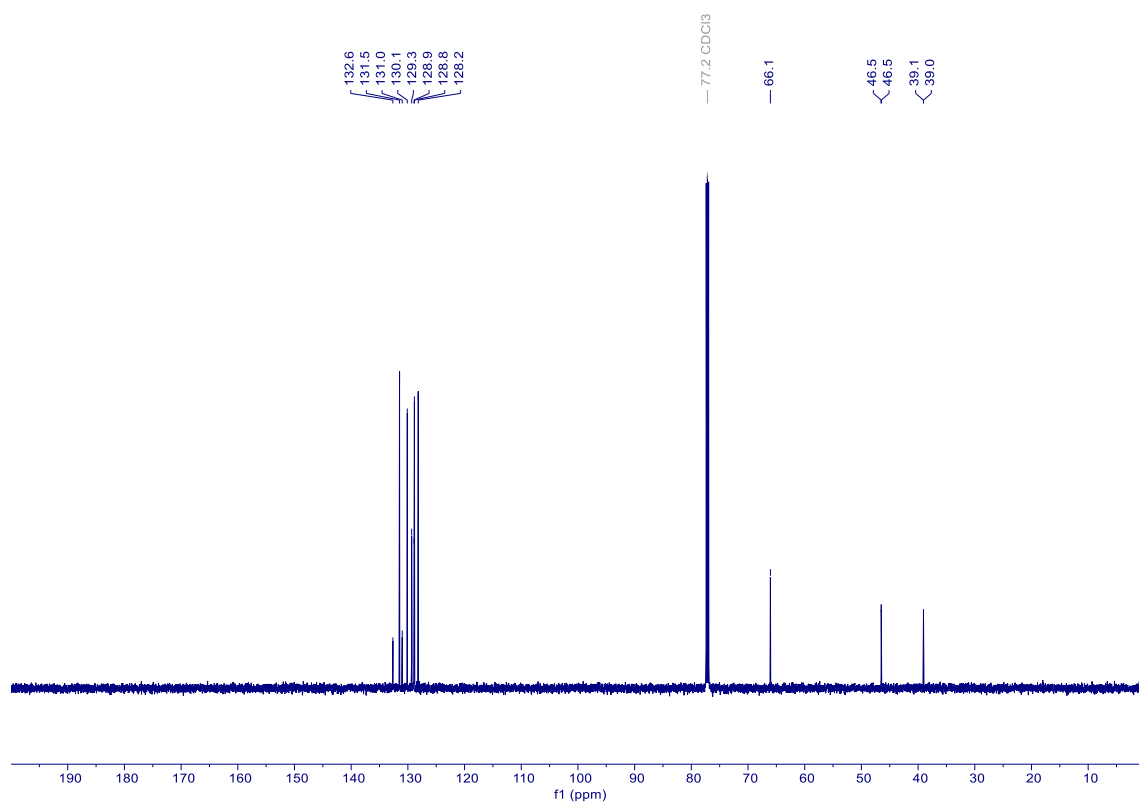
10a – ^{11}B NMR (193 MHz, CDCl_3)



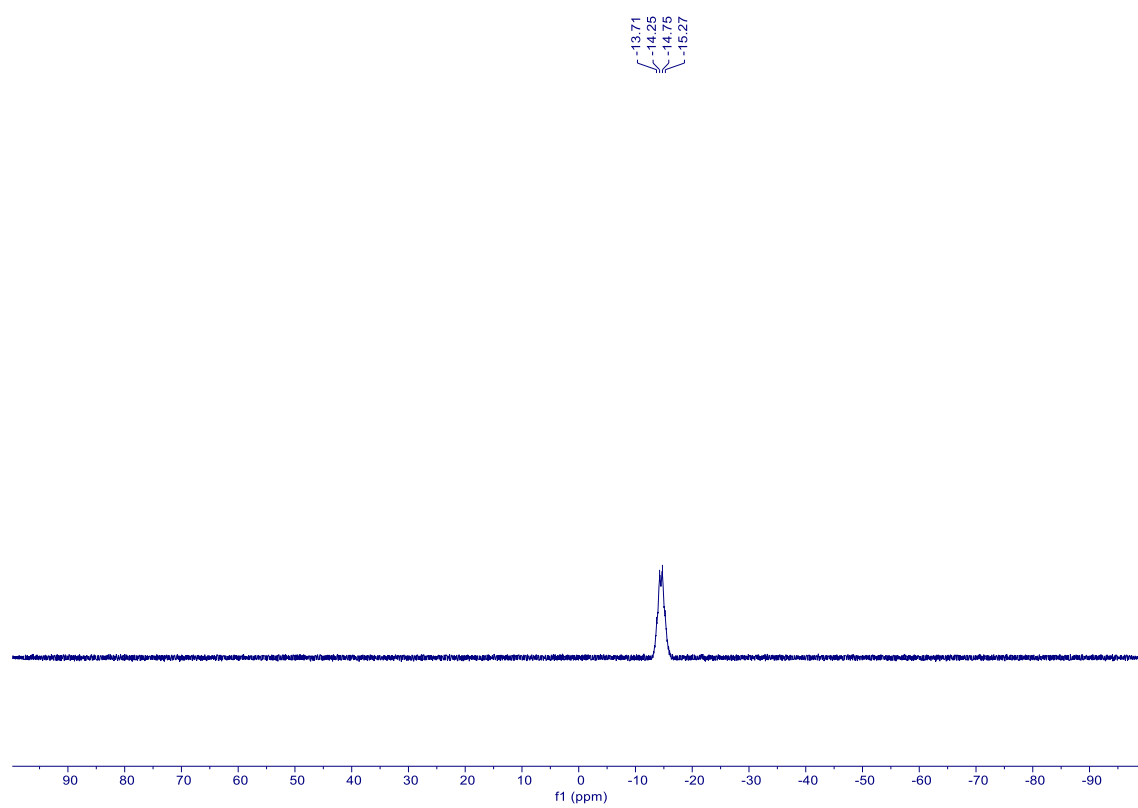
10a' – ^1H NMR (600 MHz, CDCl_3)



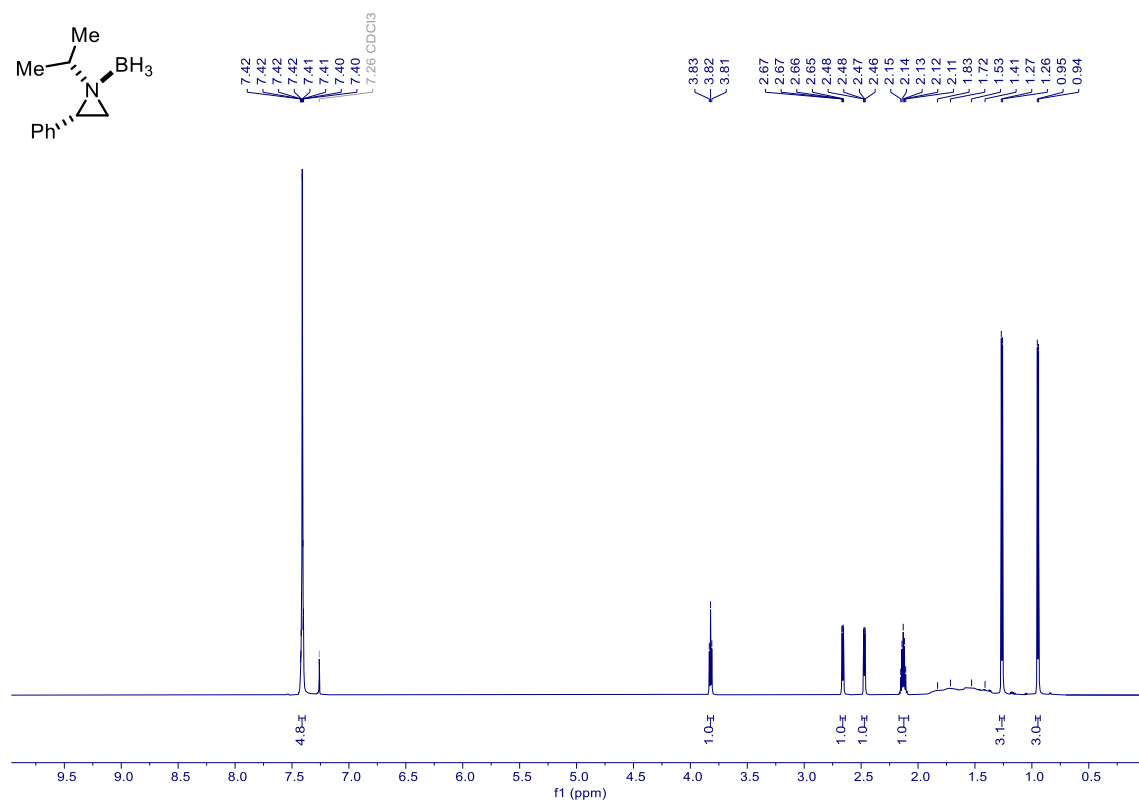
10a' – ^{13}C NMR (151 MHz, CDCl_3)



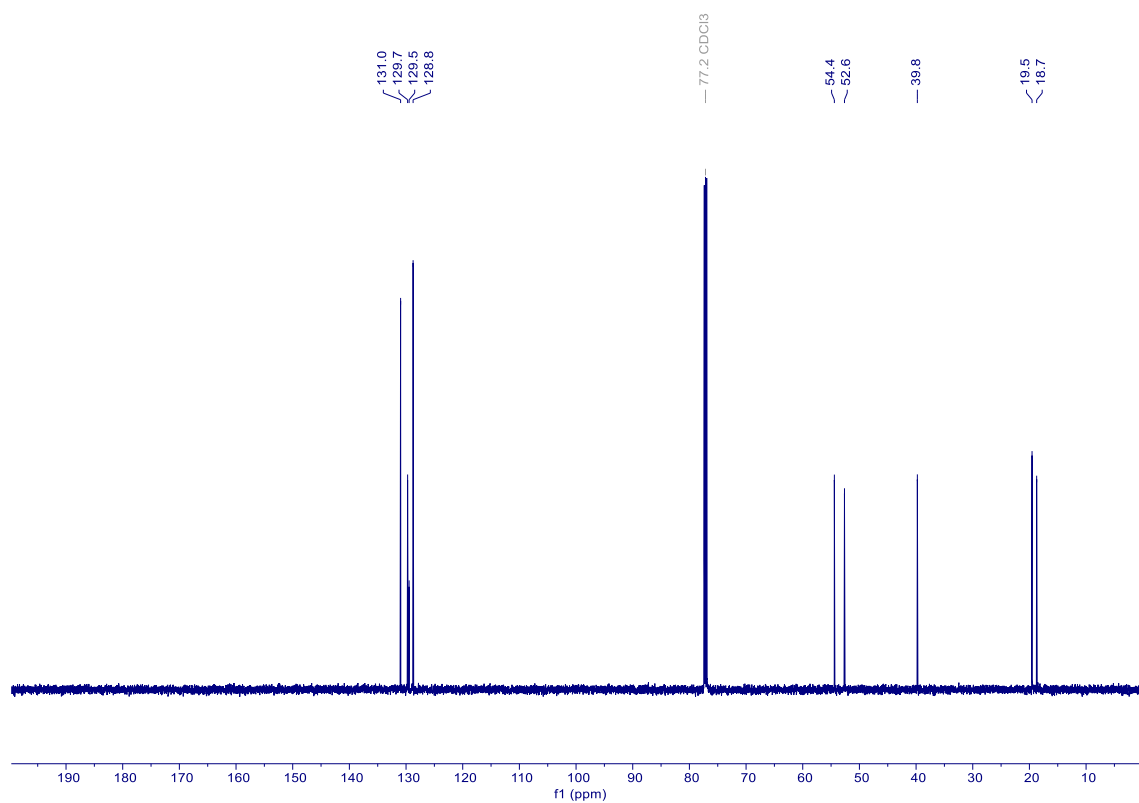
10a' – ^{11}B NMR (193 MHz, CDCl_3)



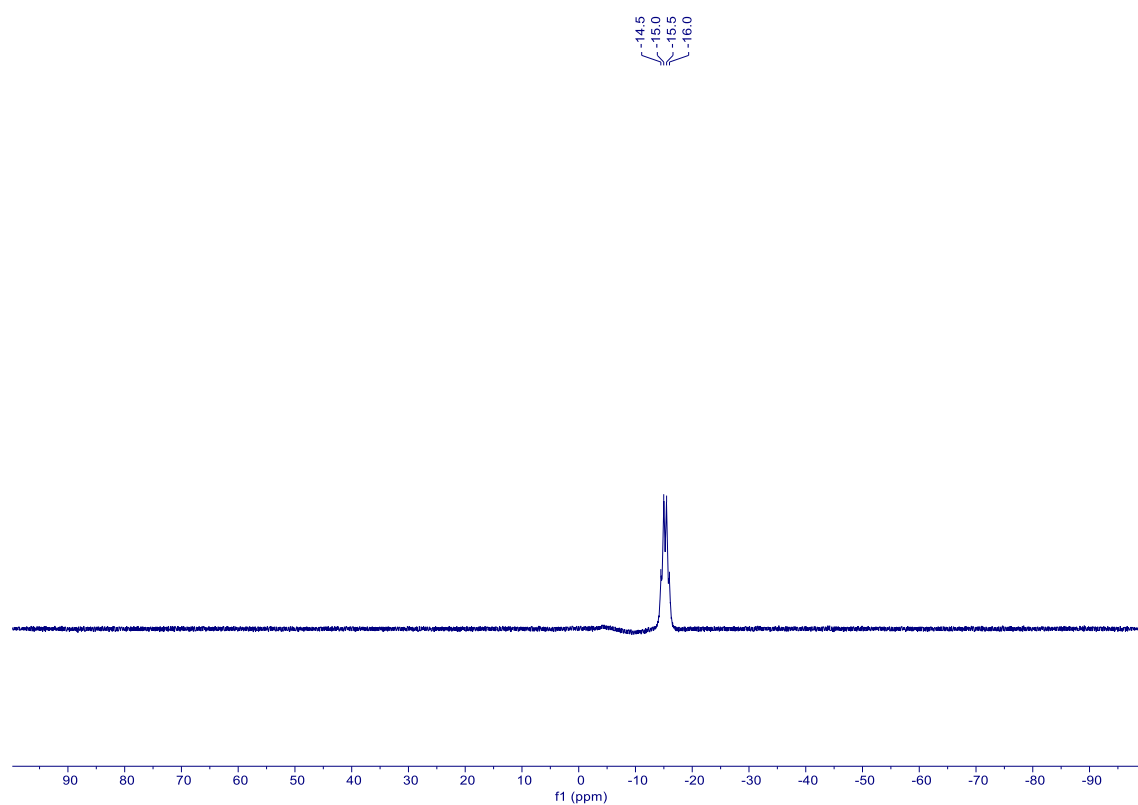
11a – ^1H NMR (600 MHz, CDCl_3)



11a – ^{13}C NMR (151 MHz, CDCl_3)



11a – ^{11}B NMR (193 MHz, CDCl_3)



Chemical structure: C[C@H]1CC(B1)C2=CC=CC=C2C3CCCCC3

¹H NMR spectrum (CDCl₃) showing peaks from 0.49 to 7.42 ppm. The spectrum includes integration values and a list of peak positions (ppm) on the right side.

Integration values (from left to right): 4.9, 1.0, 1.0, 1.1, 1.1, 1.1, 1.1, 2.2, 1.1.

Peak positions (ppm) (from left to right): 7.42, 7.42, 7.42, 7.41, 7.41, 7.40, 7.40, 7.39, 7.26 (CDCl₃), 3.83, 3.81, 3.80, 2.65, 2.65, 2.64, 2.63, 2.49, 2.48, 2.48, 2.48, 2.03, 2.02, 2.00, 2.00, 1.79, 1.78, 1.78, 1.78, 1.77, 1.77, 1.76, 1.76, 1.75, 1.74, 1.74, 1.68, 1.68, 1.67, 1.66, 1.66, 1.65, 1.65, 1.64, 1.63, 1.63, 1.62, 1.62, 1.50, 1.49, 1.49, 1.49, 1.48, 1.47, 1.47, 1.46, 1.45, 1.45, 1.45, 1.44, 1.43, 1.43, 1.37, 1.37, 1.34, 1.06, 1.04, 1.03, 1.02, 1.01, 0.99, 0.51, 0.49.

130.9
129.7
129.5
128.7

77.2 CDCl₃

62.6

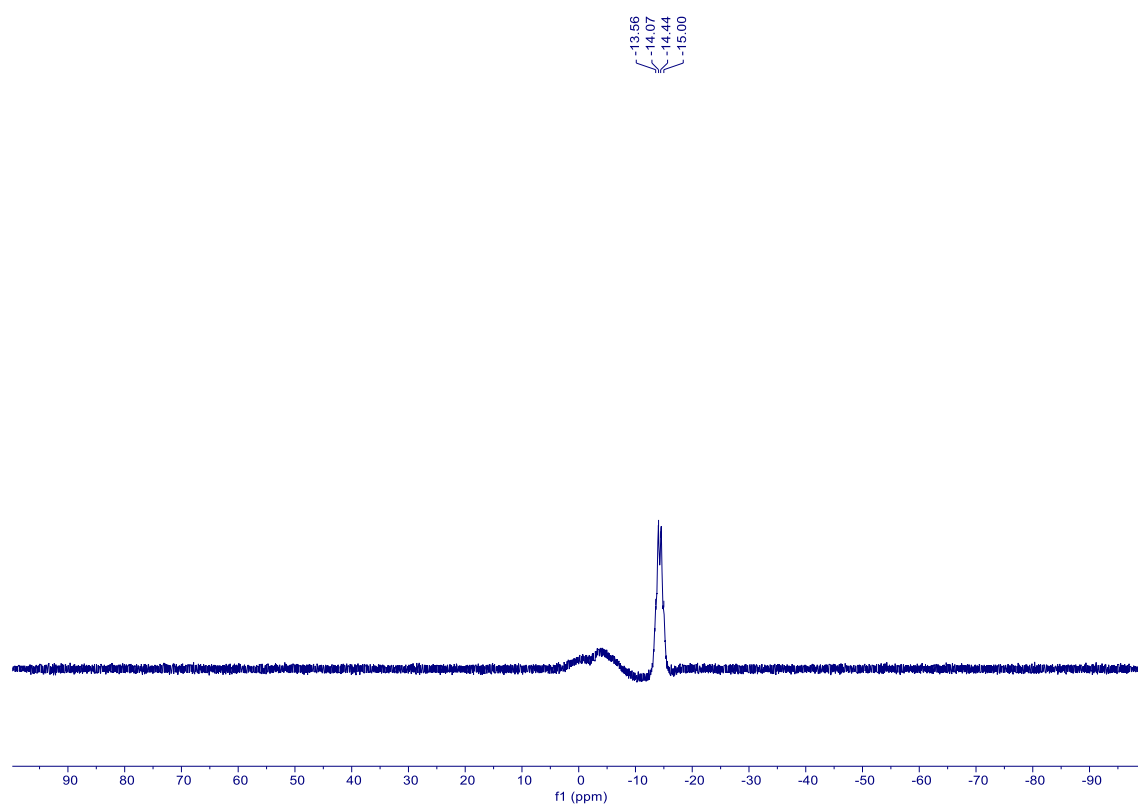
52.3

39.4

29.4
29.3
25.7
25.4
25.1

f1 (ppm)

12a – ^{11}B NMR (193 MHz, CDCl_3)



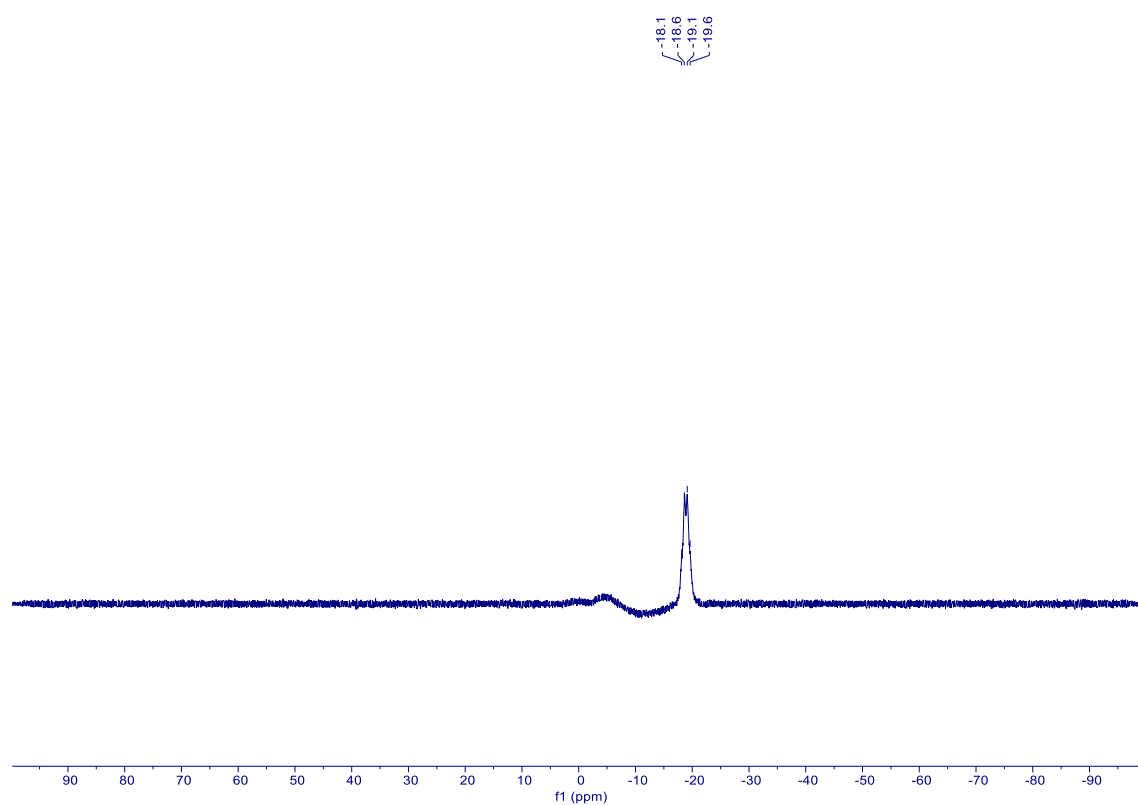
Chemical structure: C1CCC(CC1)N[C@H](C)[C@@H](O)C2=CC=CC=C2

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 10 ppm. The x-axis is labeled f1 (ppm). The y-axis represents intensity. Integration values are shown below the peaks.

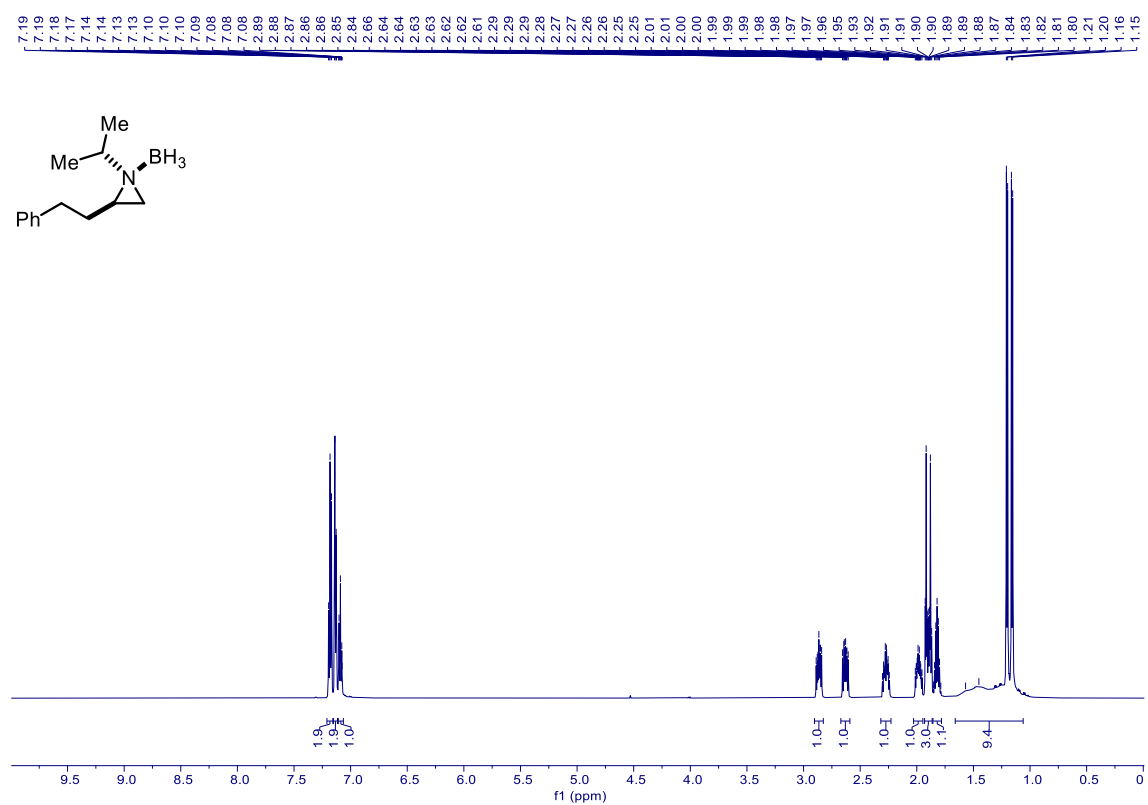
Chemical Shift (ppm)	Integration
7.37	4.91
7.36	
7.35	
7.34	
7.33	
7.32	
7.30	
7.29	
7.27	
7.17	
7.16	
7.15	
7.14	
7.13	
7.12	
7.11	
7.10	
7.09	
7.08	
7.07	
7.06	
7.05	
7.04	
7.03	
7.02	
7.01	
7.00	
6.99	
6.98	
6.97	
6.96	
6.95	
6.94	
6.93	
6.92	
6.91	
6.90	
6.89	
6.88	
6.87	
6.86	
6.85	
6.84	
6.83	
6.82	
6.81	
6.80	
6.79	
6.78	
6.77	
6.76	
6.75	
6.74	
6.73	
6.72	
6.71	
6.70	
6.69	
6.68	
6.67	
6.66	
6.65	
6.64	
6.63	
6.62	
6.61	
6.60	
6.59	
6.58	
6.57	
6.56	
6.55	
6.54	
6.53	
6.52	
6.51	
6.50	
6.49	
6.48	
6.47	
6.46	
6.45	
6.44	
6.43	
6.42	
6.41	
6.40	
6.39	
6.38	
6.37	
6.36	
6.35	
6.34	
6.33	
6.32	
6.31	
6.30	
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6.26	
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6.23	
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6.21	
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6.18	
6.17	
6.16	
6.15	
6.14	
6.13	
6.12	
6.11	
6.10	
6.09	
6.08	
6.07	
6.06	
6.05	
6.04	
6.03	
6.02	
6.01	
6.00	
5.99	
5.98	
5.97	
5.96	
5.95	
5.94	
5.93	
5.92	
5.91	
5.90	
5.89	
5.88	
5.87	
5.86	
5.85	
5.84	
5.83	
5.82	
5.81	
5.80	
5.79	
5.78	
5.77	
5.76	
5.75	
5.74	
5.73	
5.72	
5.71	
5.70	
5.69	
5.68	
5.67	
5.66	
5.65	
5.64	
5.63	
5.62	
5.61	
5.60	
5.59	
5.58	
5.57	
5.56	
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5.54	
5.53	
5.52	
5.51	
5.50	
5.49	
5.48	
5.47	
5.46	
5.45	
5.44	
5.43	
5.42	
5.41	
5.40	
5.39	
5.38	
5.37	
5.36	
5.35	
5.34	
5.33	
5.32	
5.31	
5.30	
5.29	
5.28	
5.27	
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5.24	
5.23	
5.22	
5.21	
5.20	
5.19	
5.18	
5.17	
5.16	
5.15	
5.14	
5.13	
5.12	
5.11	
5.10	
5.09	
5.08	
5.07	
5.06	
5.05	
5.04	
5.03	
5.02	
5.01	
5.00	
4.99	
4.98	

¹³C NMR spectrum (CDCl₃) of 1,3-bis(4-methoxyphenyl)propan-2-one. The spectrum shows peaks at the following chemical shifts (ppm): 131.2, 130.3, 128.9, 128.2, 77.2 (CDCl₃), 73.8, 50.7, 40.4, 30.0, 29.3, 25.7, and 25.5.

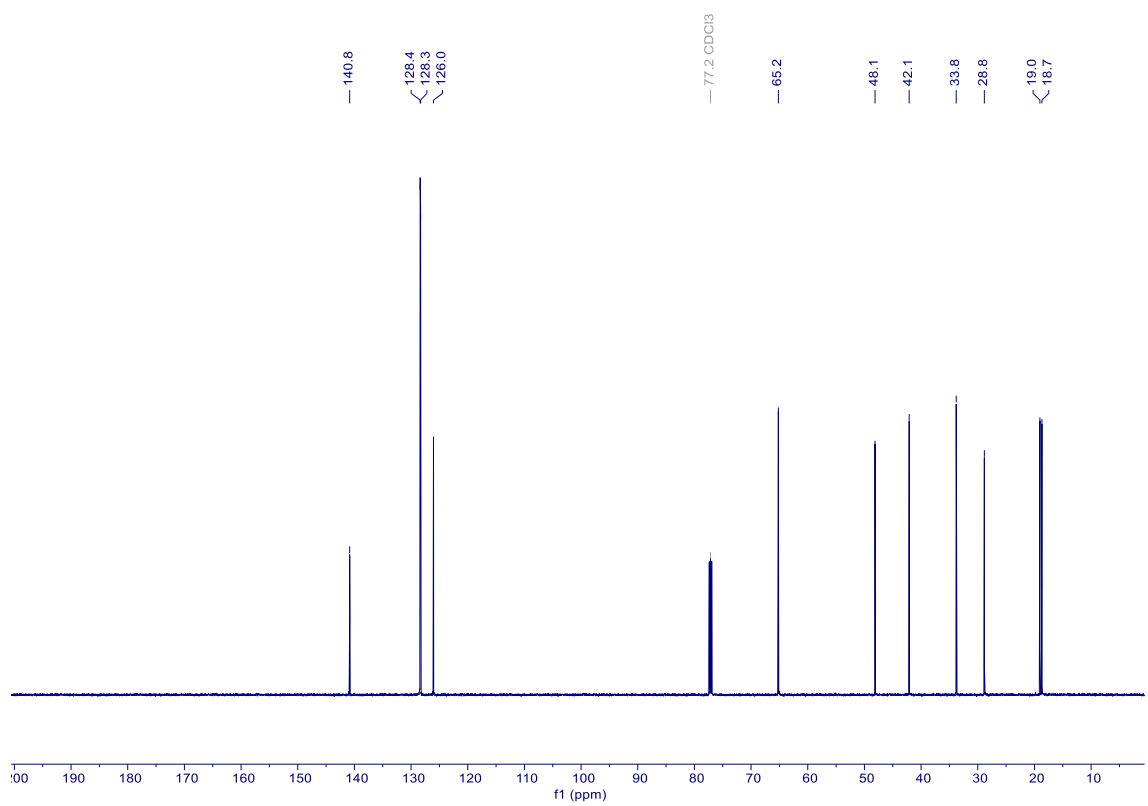
12a' – ^{11}B NMR (193 MHz, CDCl_3)



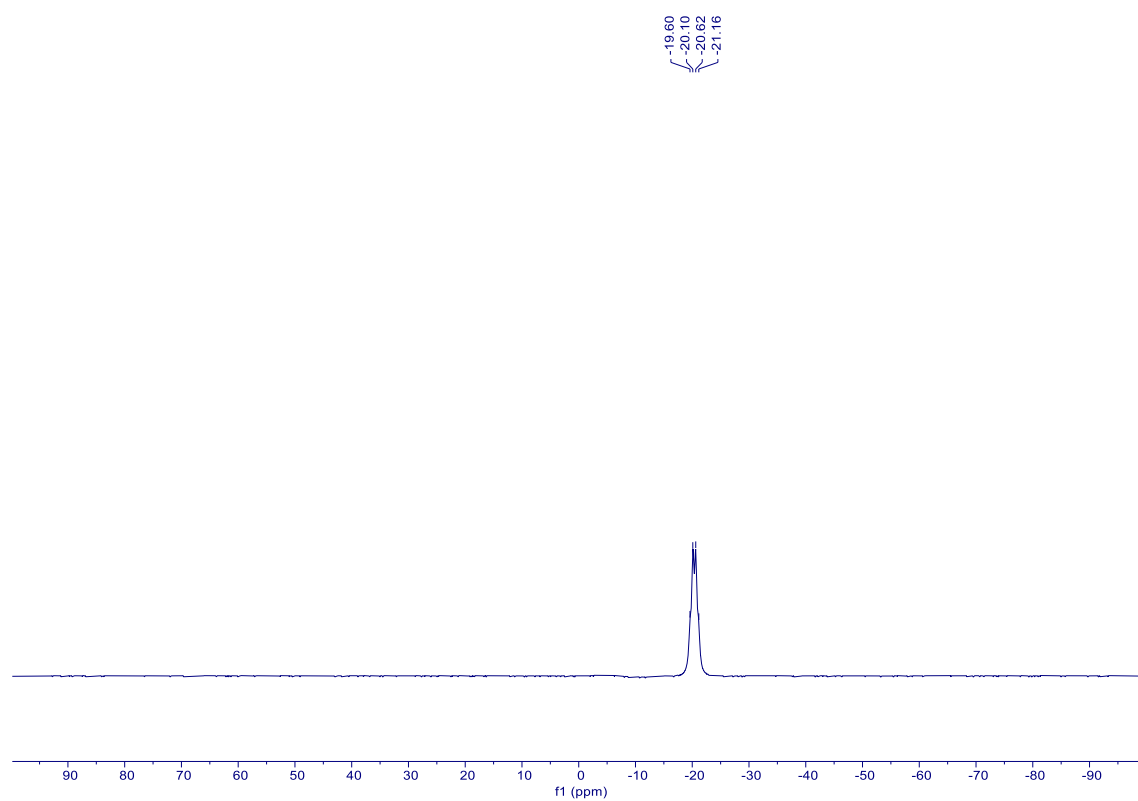
13a – ^1H NMR (600 MHz, CDCl_3)



13a – ^{13}C NMR (151 MHz, CDCl_3)



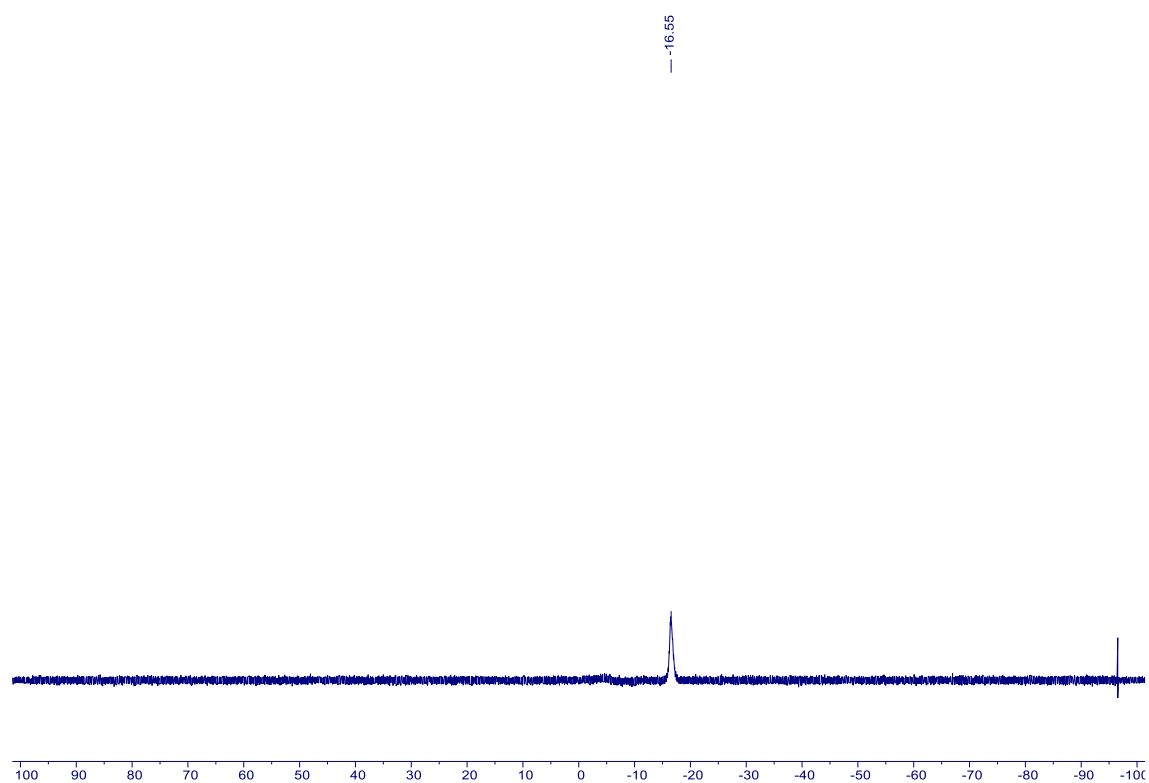
13a – ^{11}B NMR (193 MHz, CDCl_3)



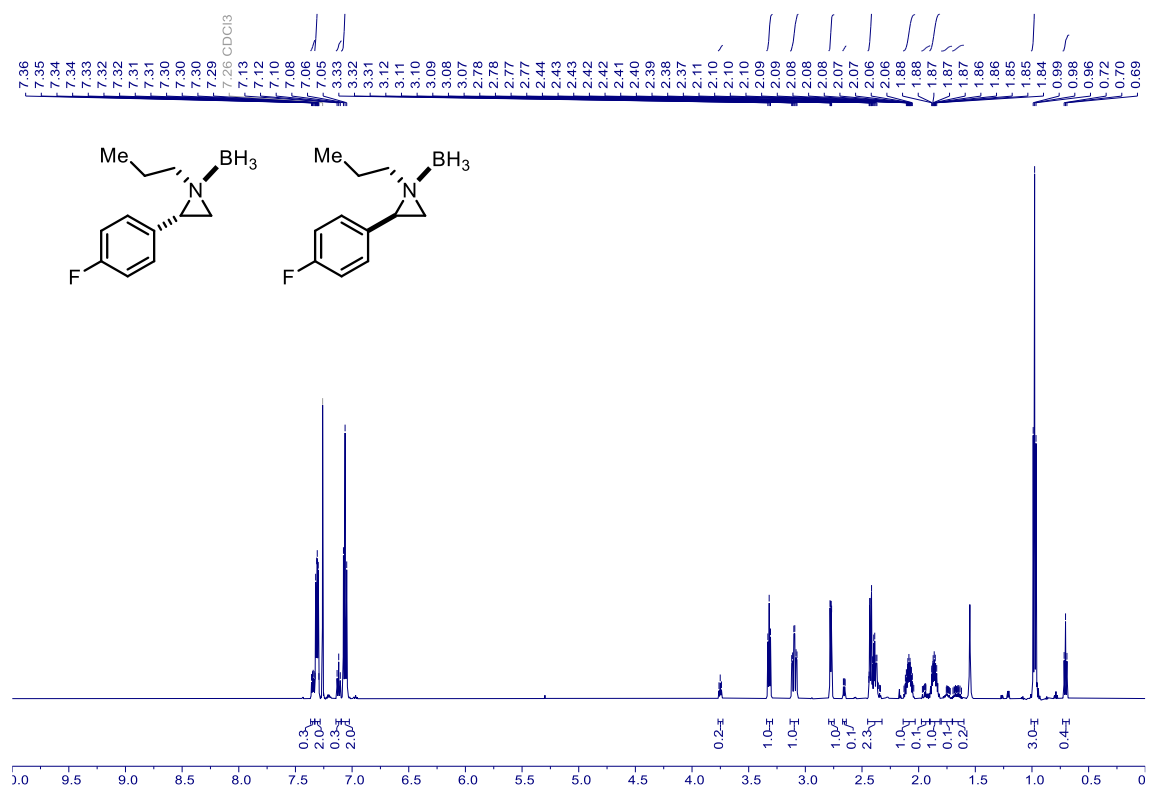
[illegible]

139.0
130.1
129.0
127.9
77.2 CDCl₃
67.1
49.4
41.4
21.5
20.4
11.5

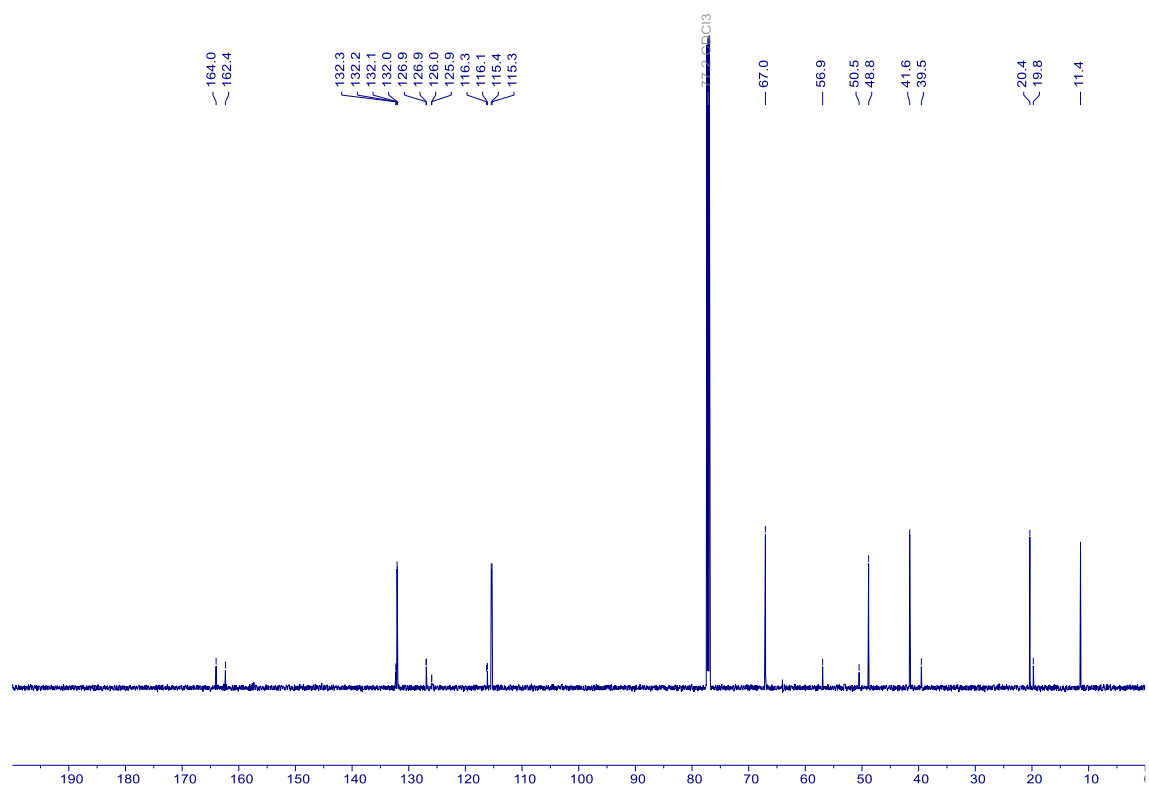
14a – ^{11}B NMR (192 MHz, CDCl_3)



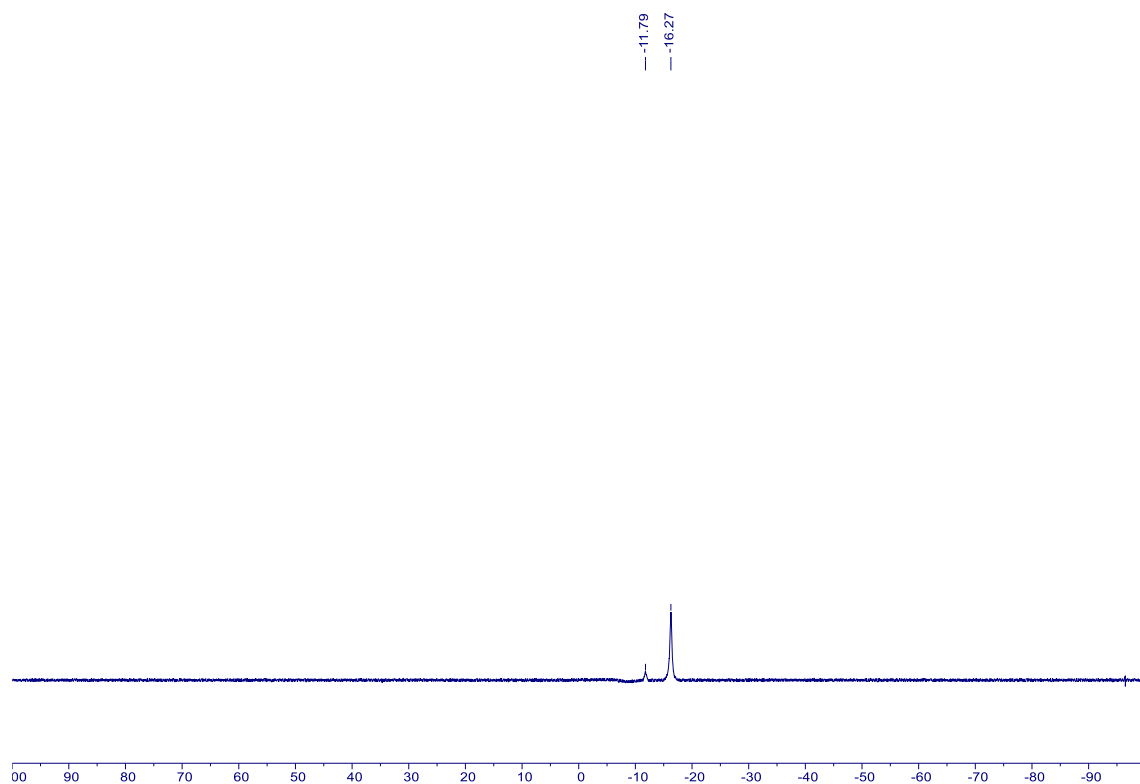
15a and 15a' – ^1H NMR (600 MHz, CDCl_3)



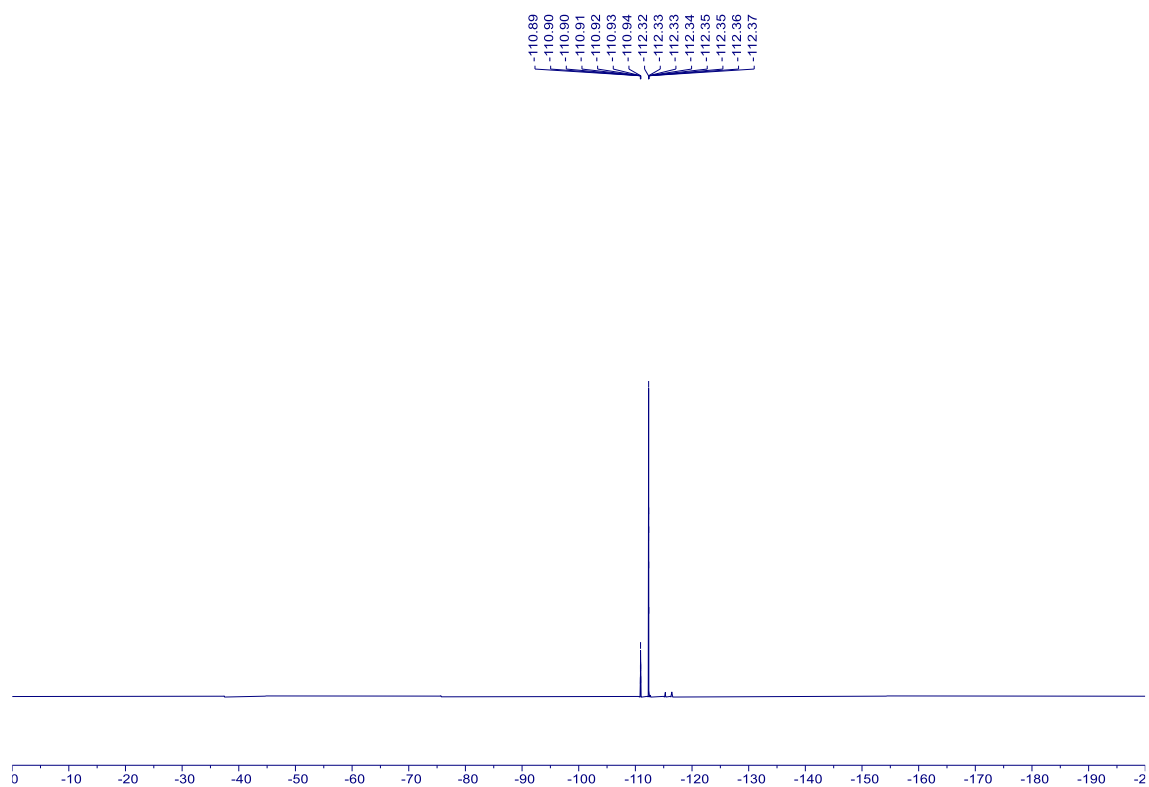
15a and 15a' – ^{13}C NMR (151 MHz, CDCl_3)



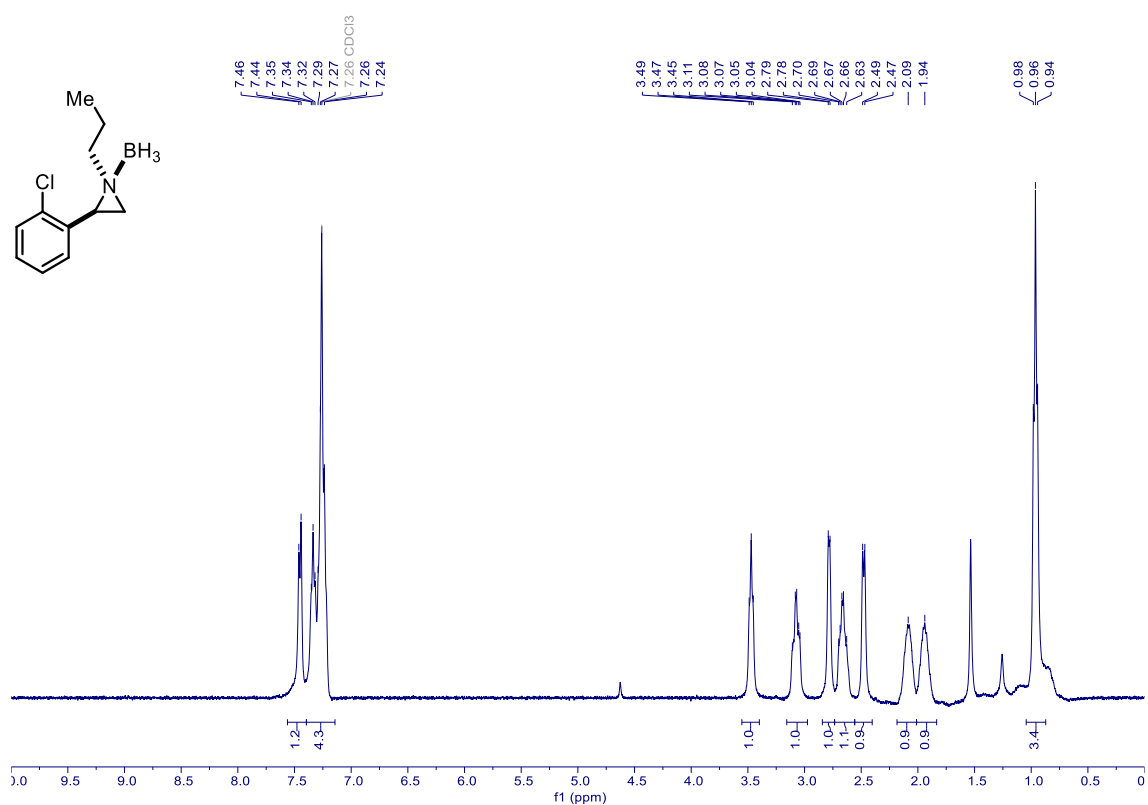
15a and 15a' – ^{11}B NMR (192 MHz, CDCl_3)



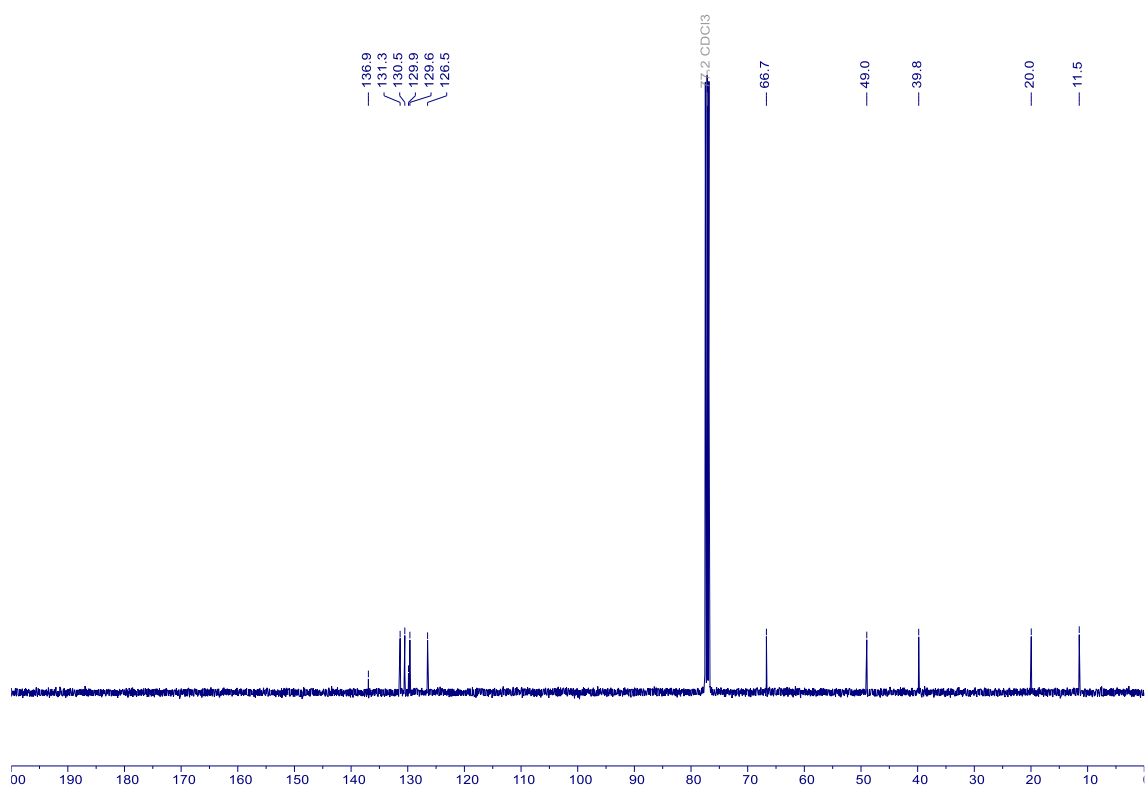
15a and 15a' – ^{19}F NMR (564 MHz, CDCl_3)



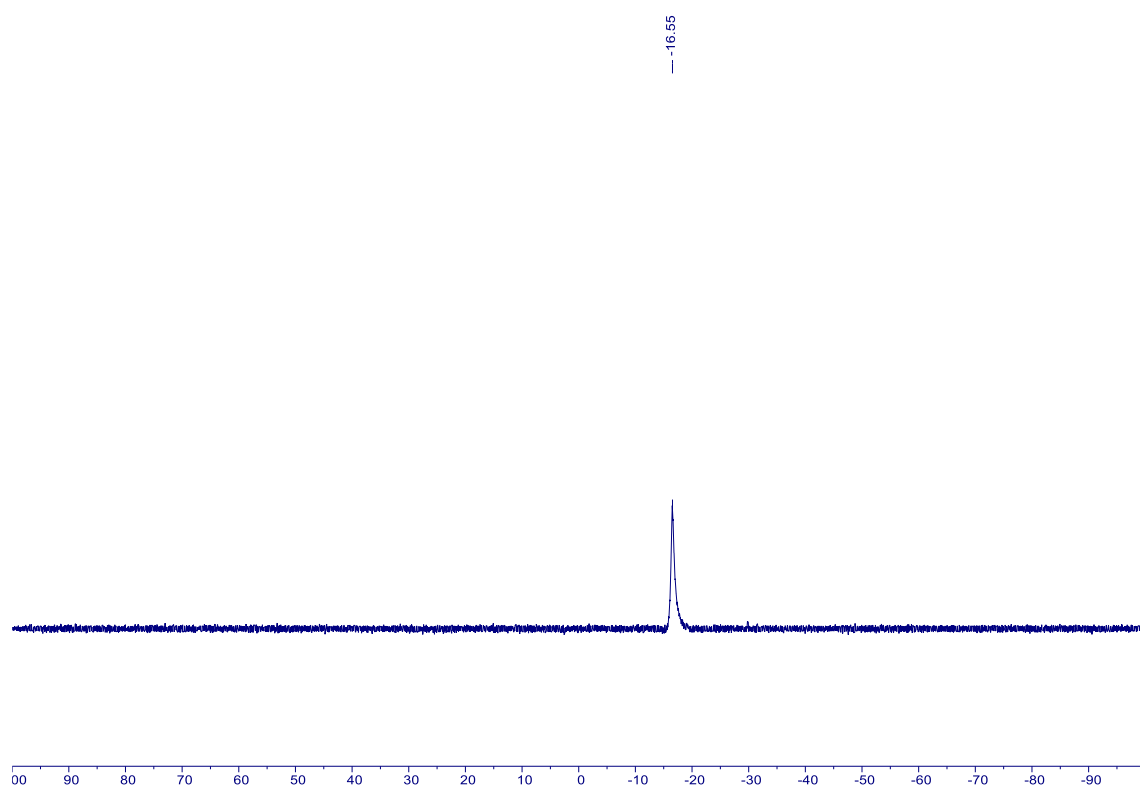
16a – ^1H NMR (400 MHz, CDCl_3)



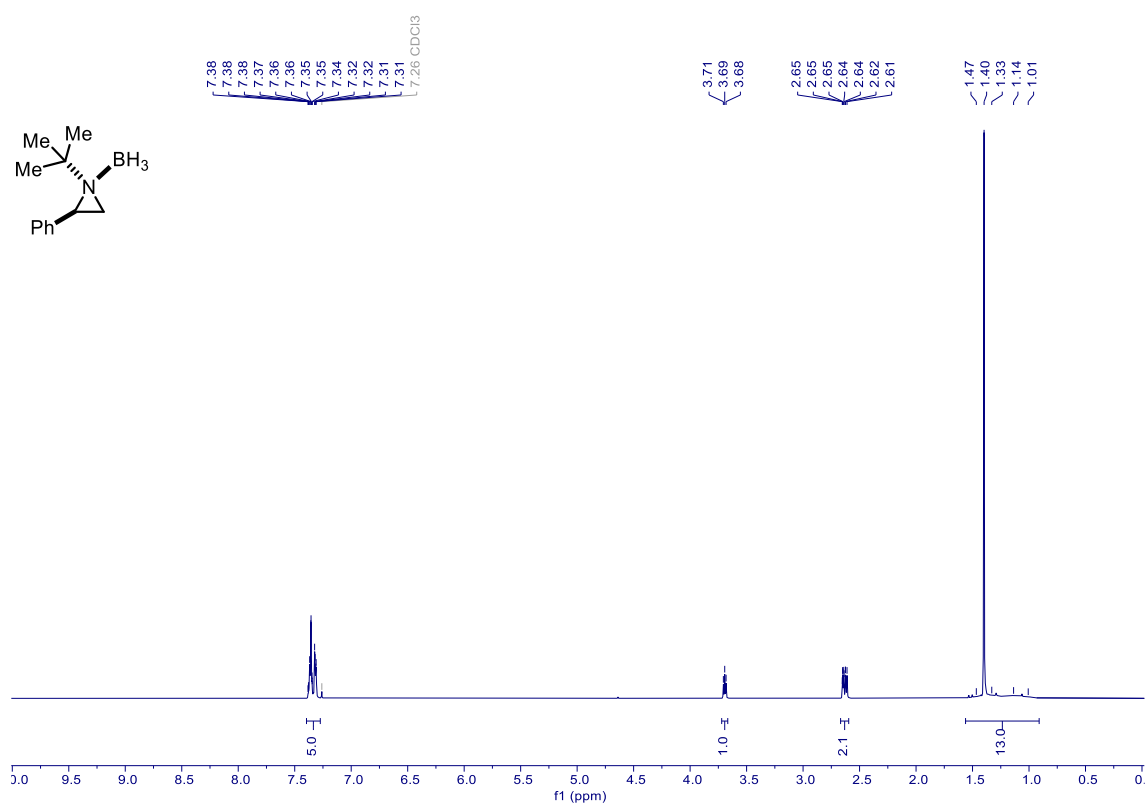
16a – ^{13}C NMR (101 MHz, CDCl_3)



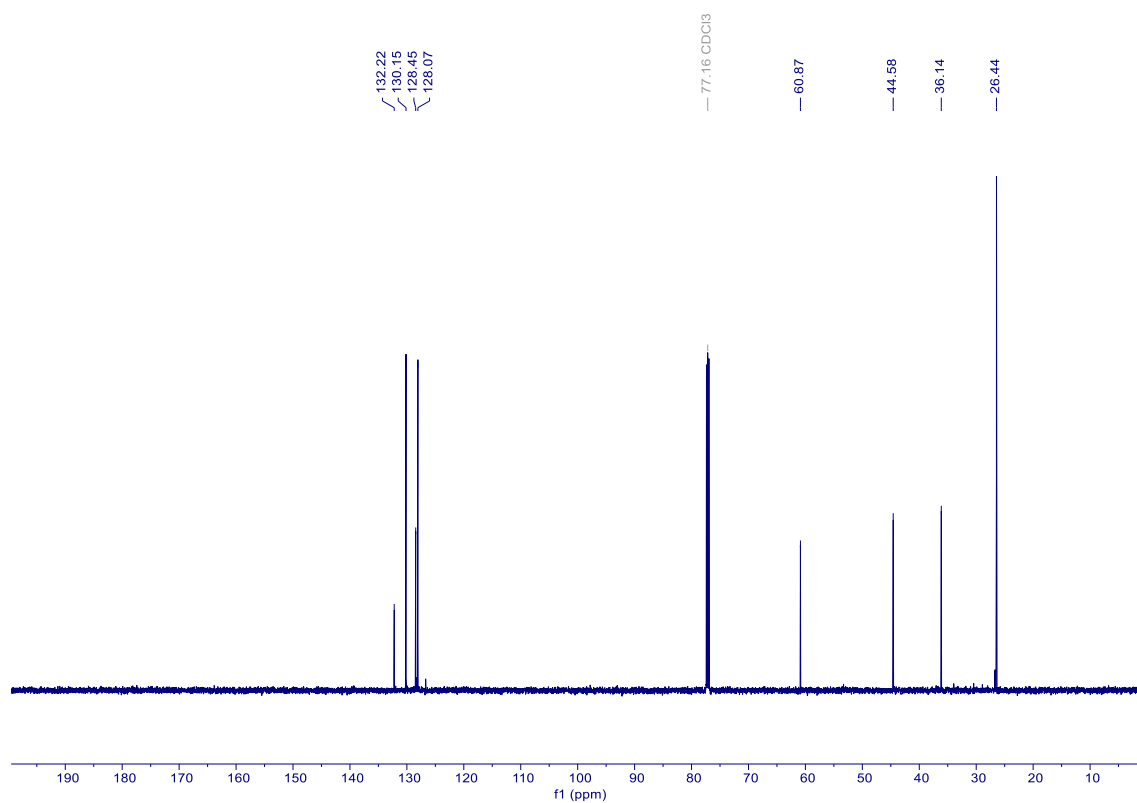
16a – ^{11}B NMR (128 MHz, CDCl_3)



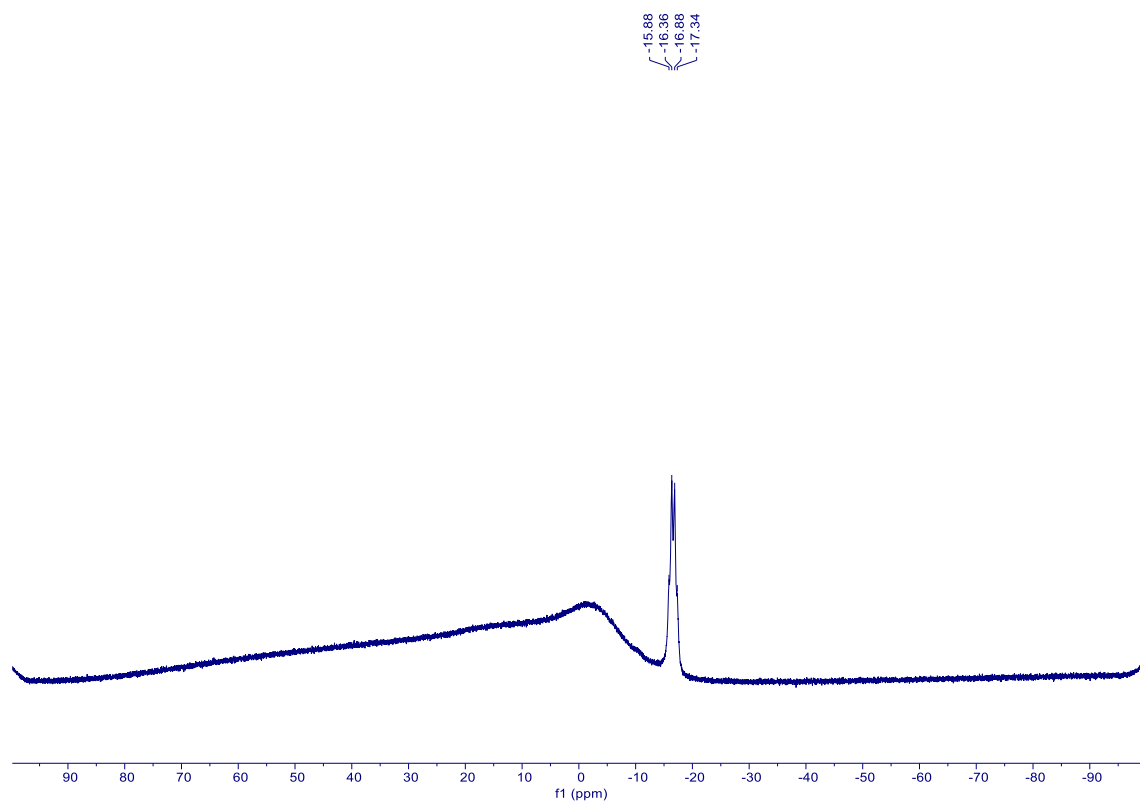
17a – ^1H NMR (600 MHz, CDCl_3)



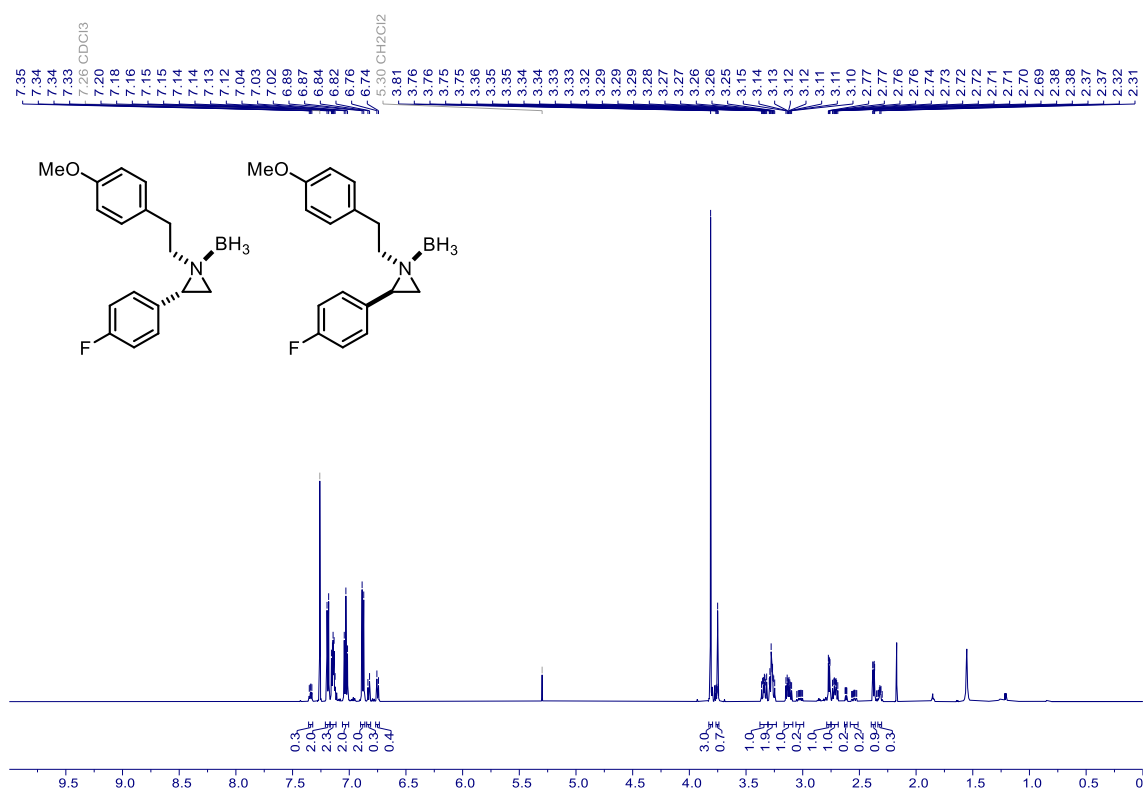
17a – ^{13}C NMR (151 MHz, CDCl_3)



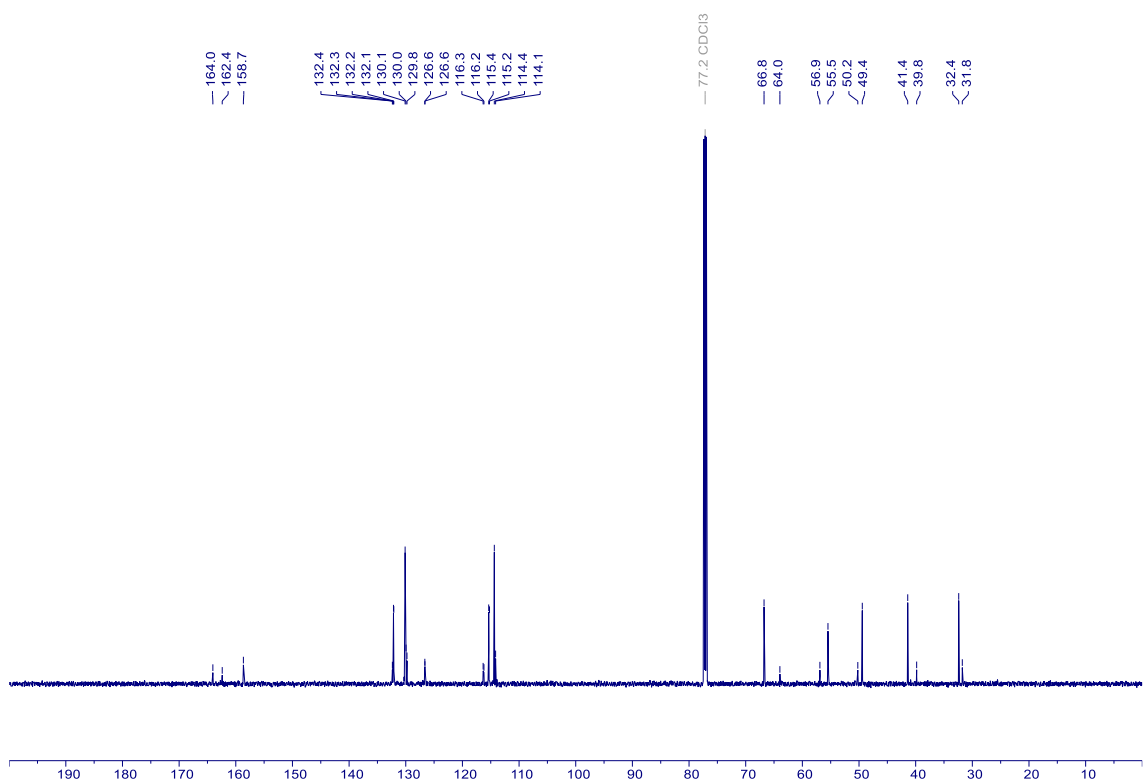
17a – ^{11}B NMR (193 MHz, CDCl_3)



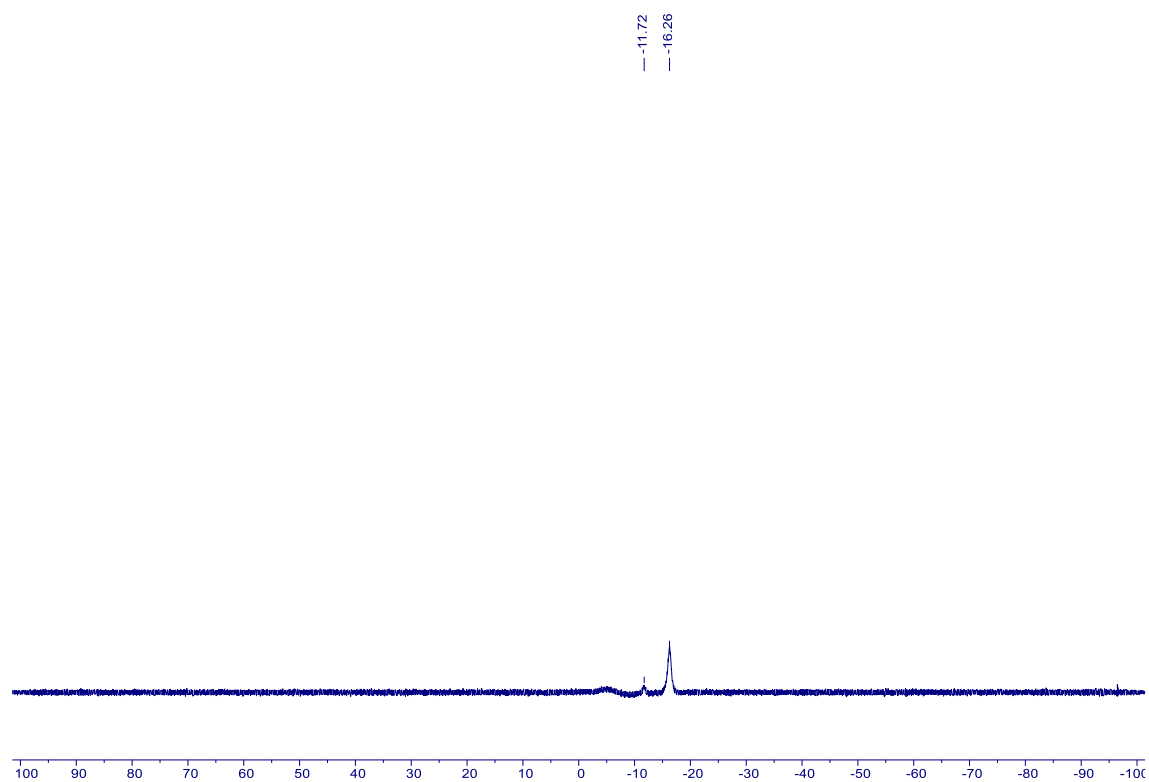
18a and 18a' – ^1H NMR (600 MHz, CDCl_3)



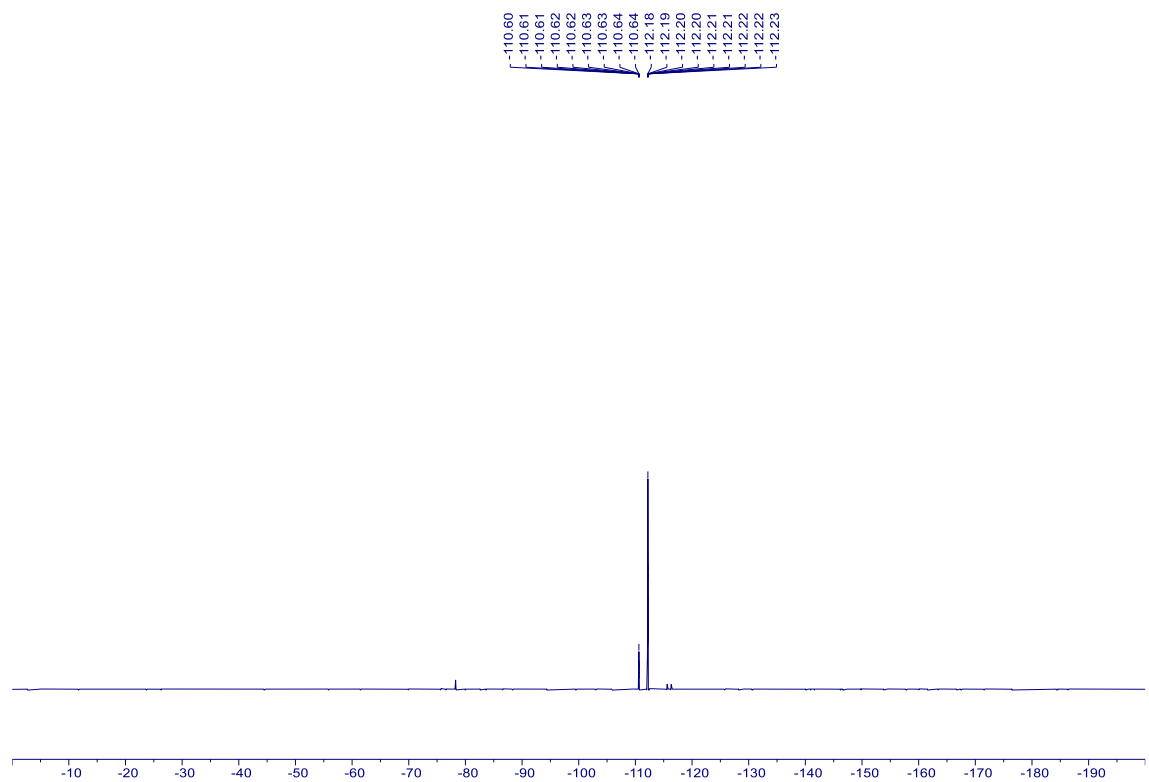
18a and 18a' – ^{13}C NMR (151 MHz, CDCl_3)



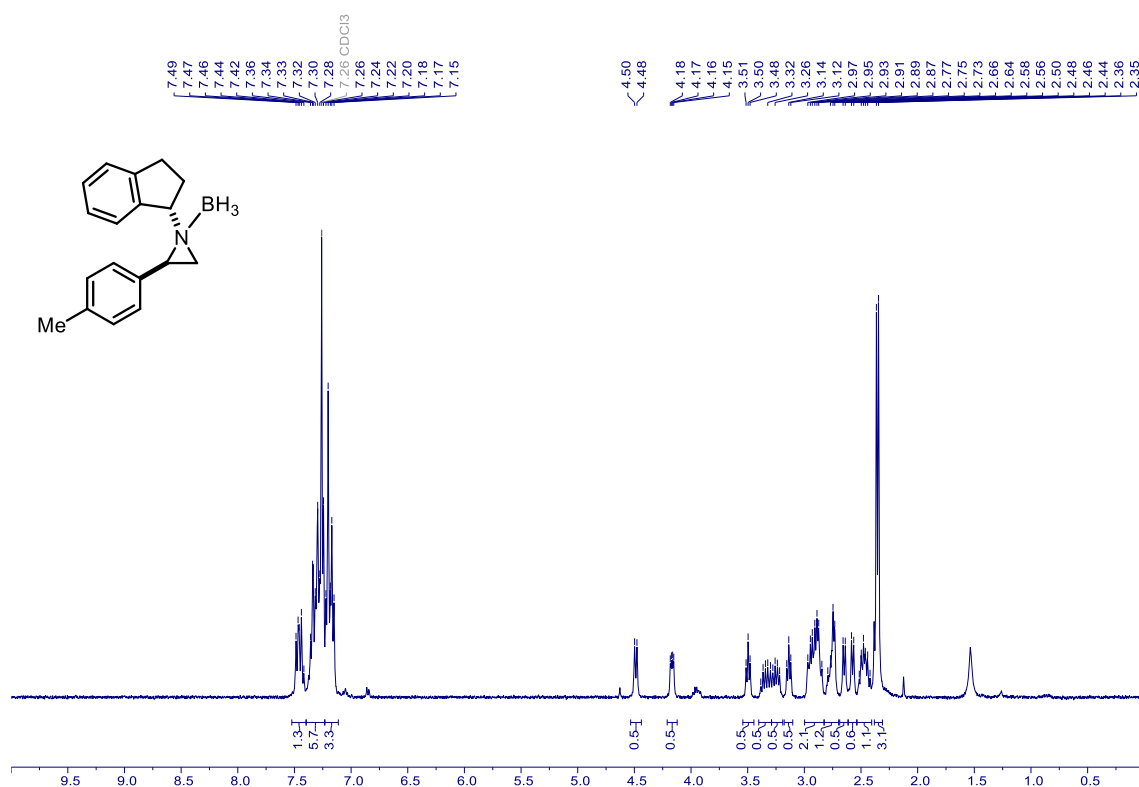
18a and 18a' – ^{11}B NMR (192 MHz, CDCl_3)



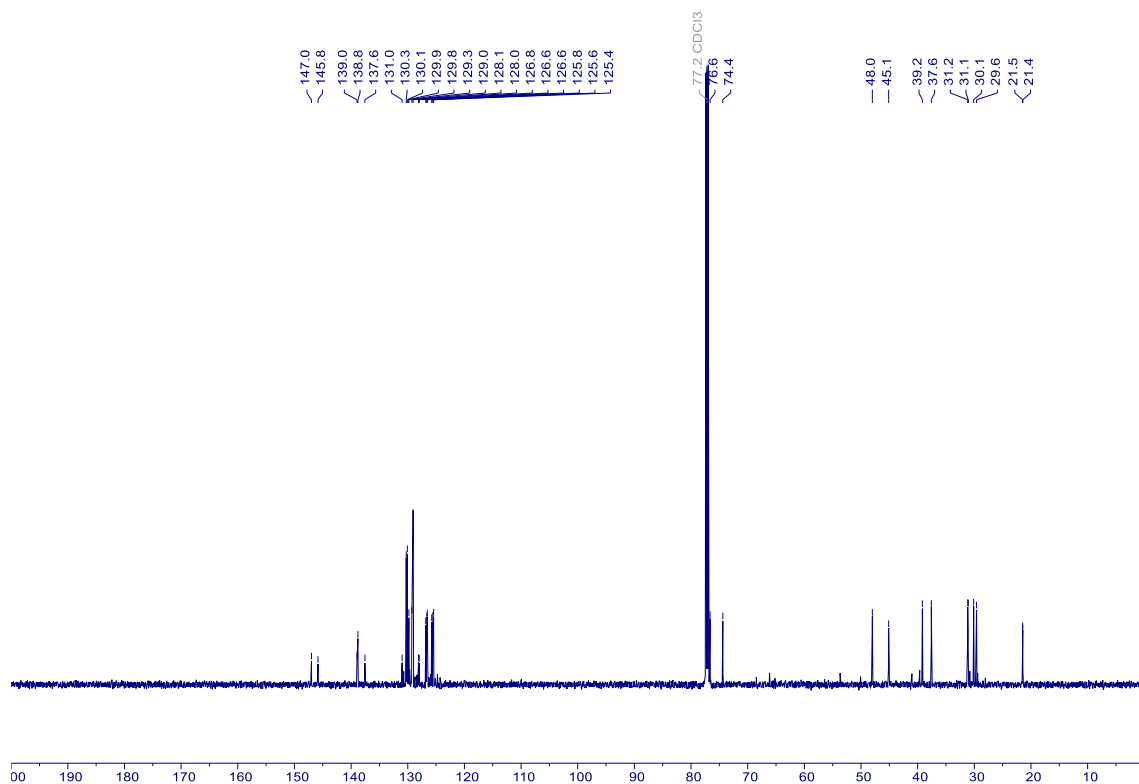
18a and 18a' – ^{19}F NMR (564 MHz, CDCl_3)



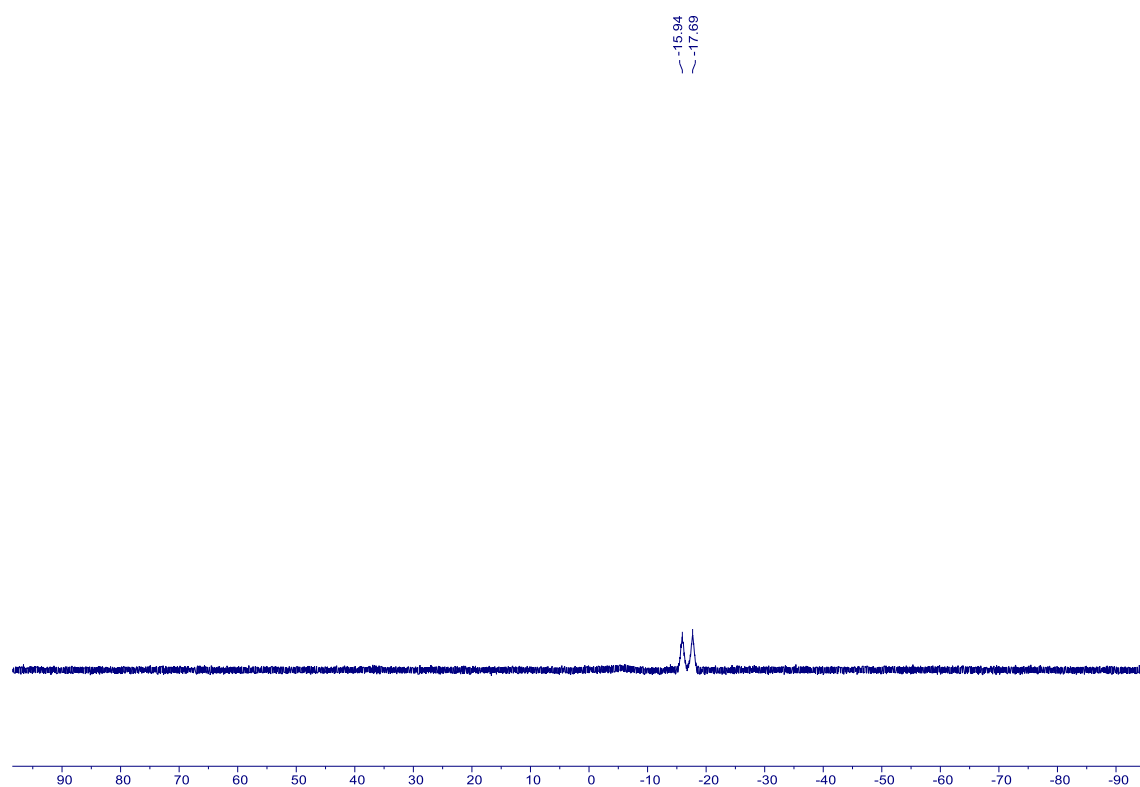
19a – ^1H NMR (400 MHz, CDCl_3)



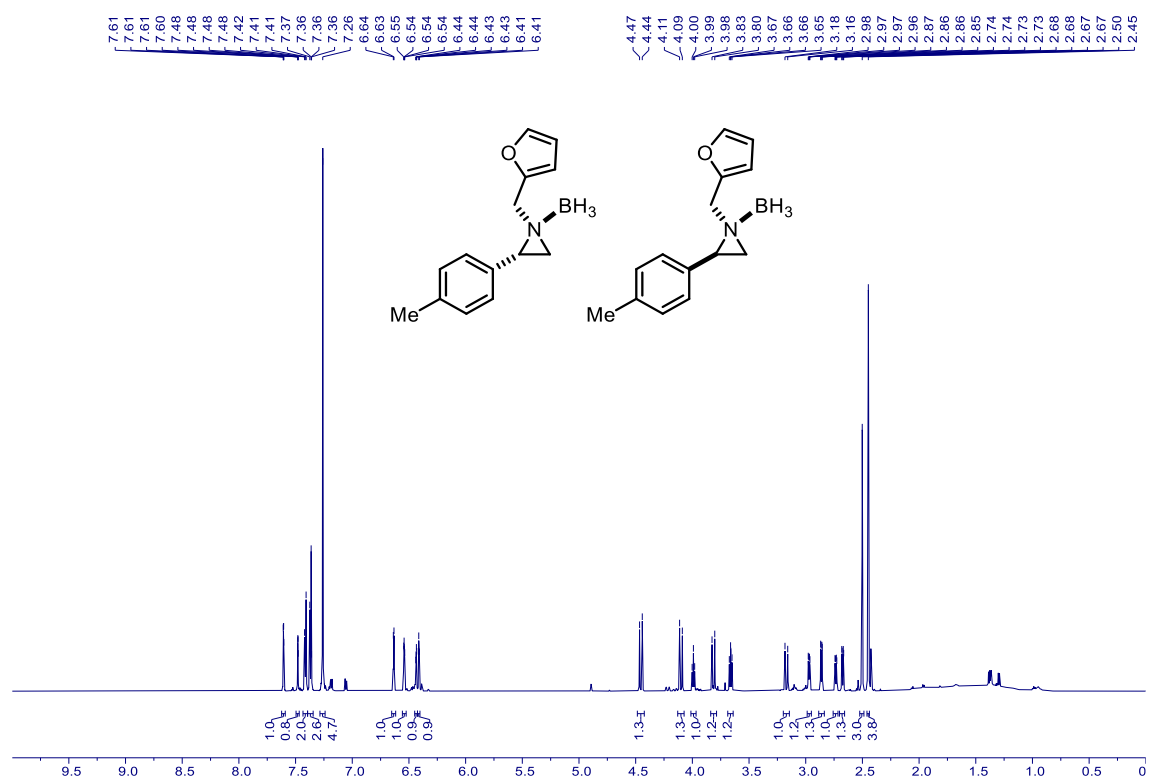
19a – ^{13}C NMR (151 MHz, CDCl_3)



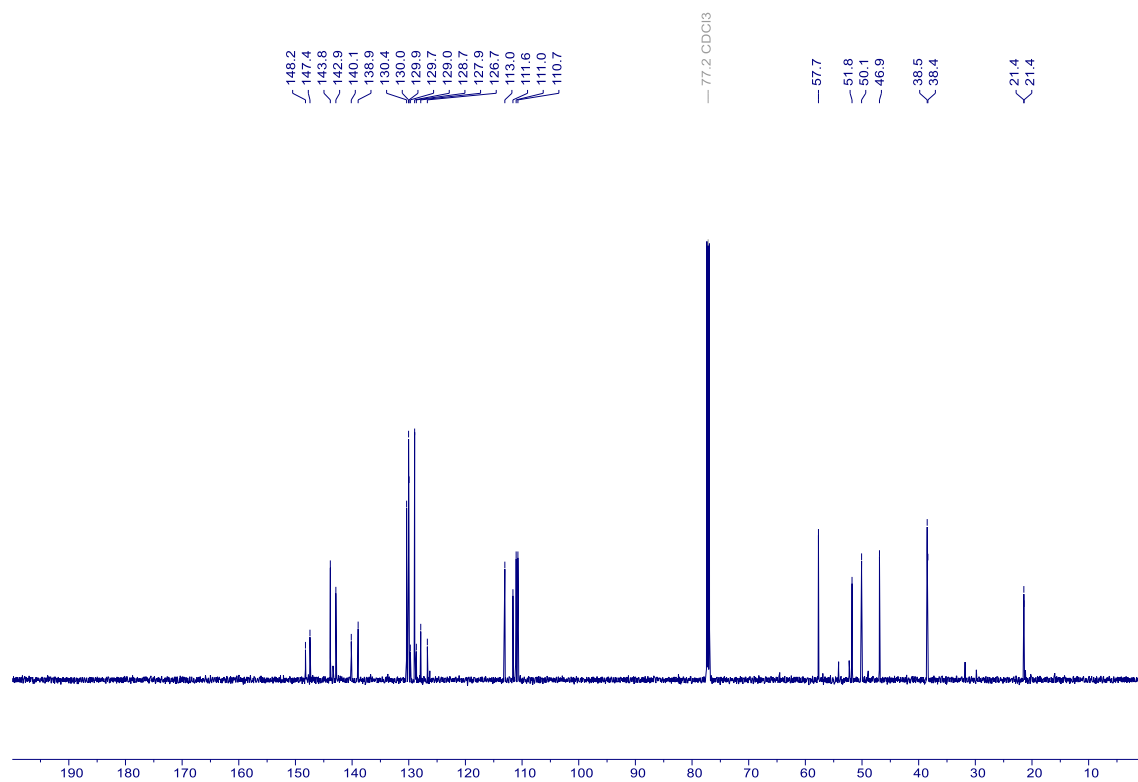
19a – ^{11}B NMR (192 MHz, CDCl_3)



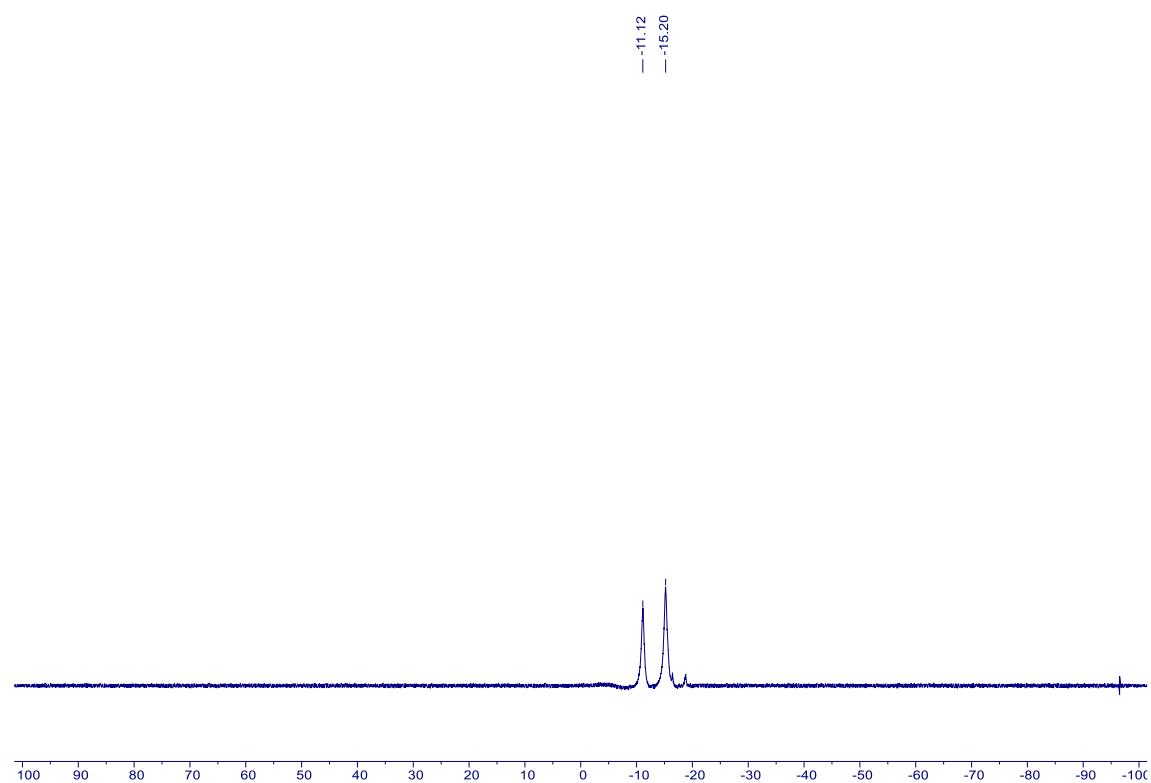
20a and 20a' – ^1H NMR (600 MHz, CDCl_3)



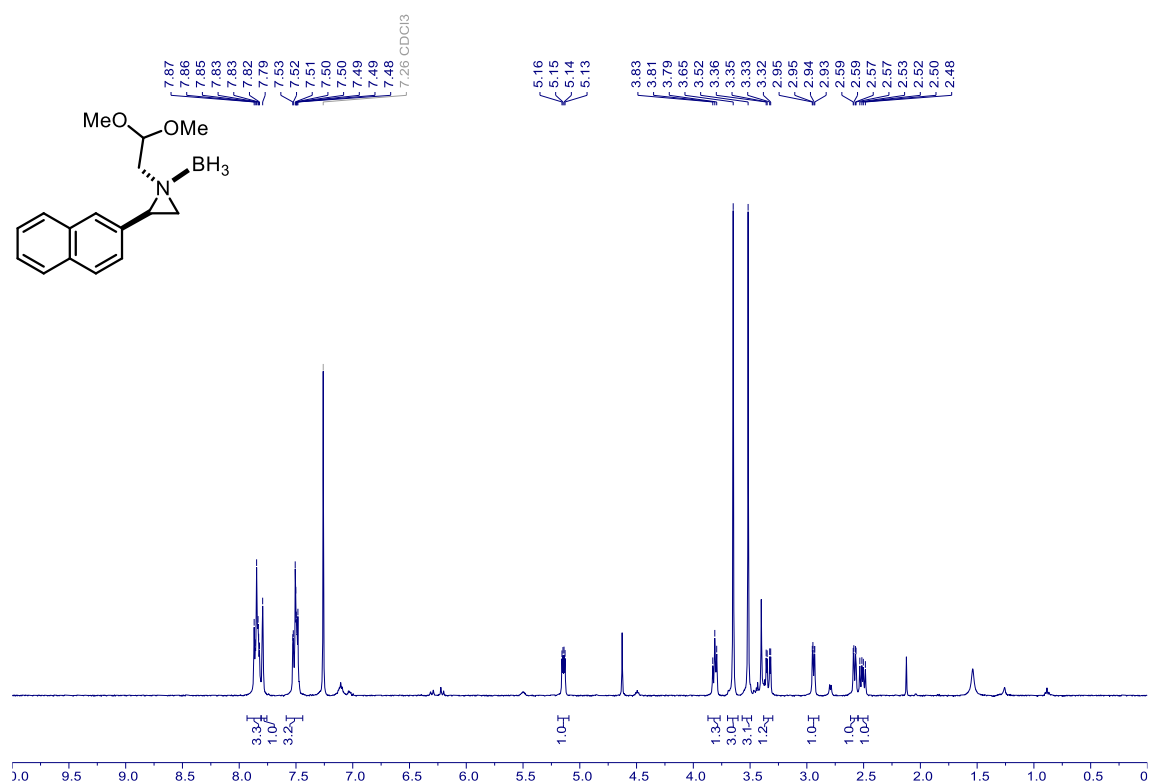
20a and 20a' – ^{13}C NMR (151 MHz, CDCl_3)



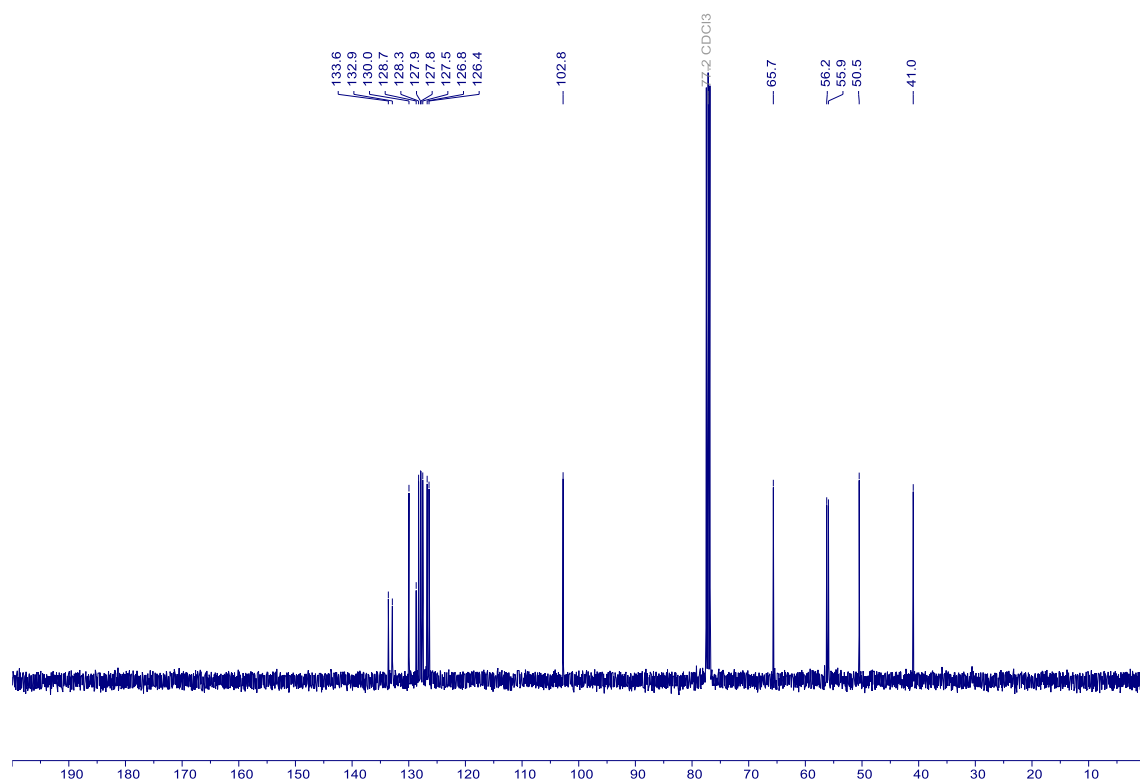
20a and 20a' – ^{11}B NMR (192 MHz, CDCl_3)



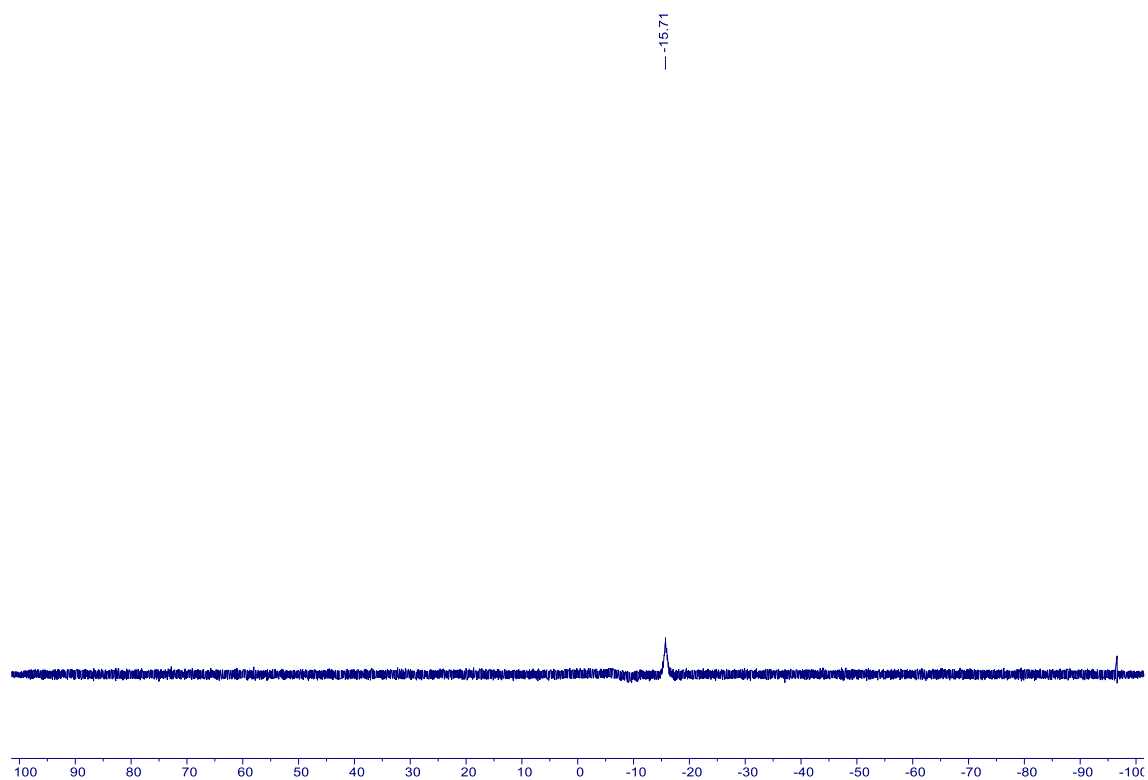
21a – ^1H NMR (400 MHz, CDCl_3)



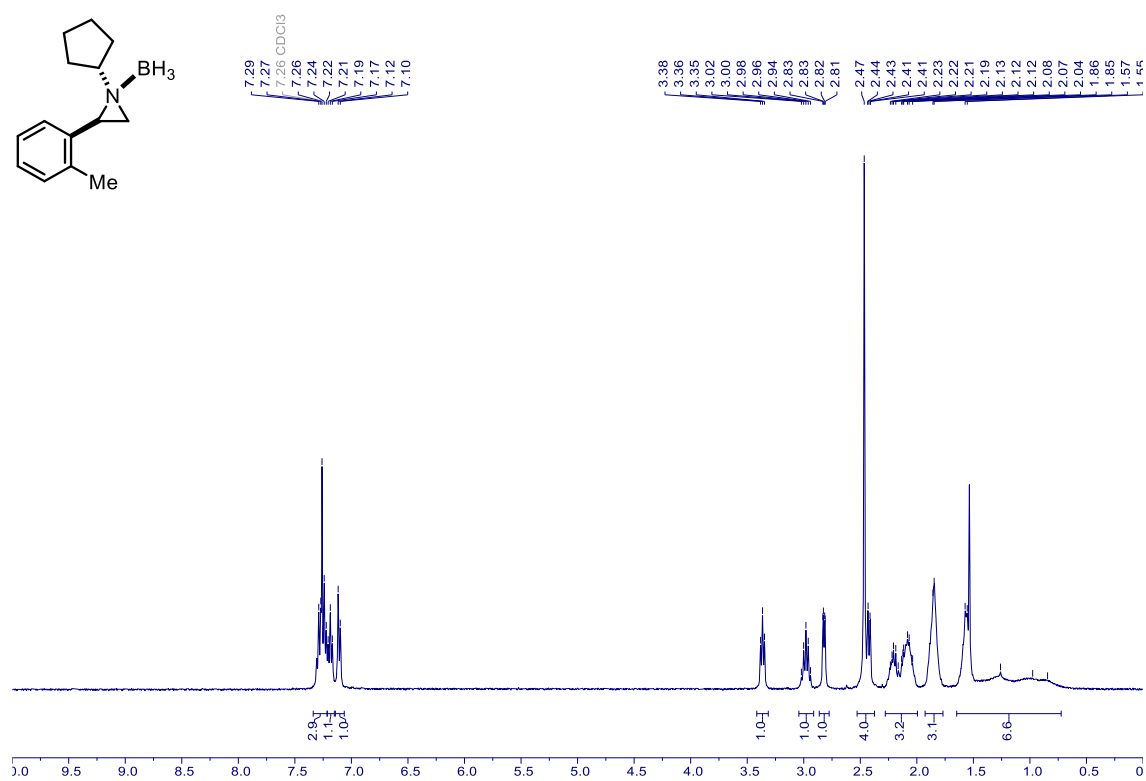
21a – ^{13}C NMR (101 MHz, CDCl_3)



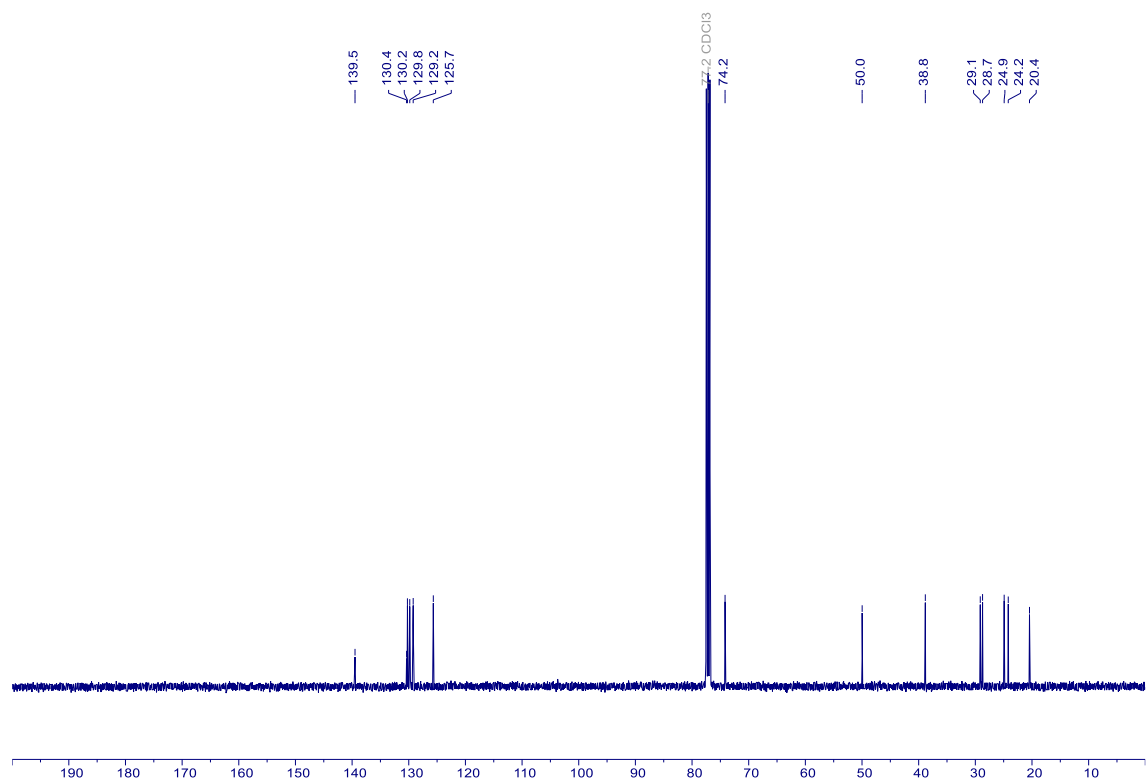
21a – ^{11}B NMR (192 MHz, CDCl_3)



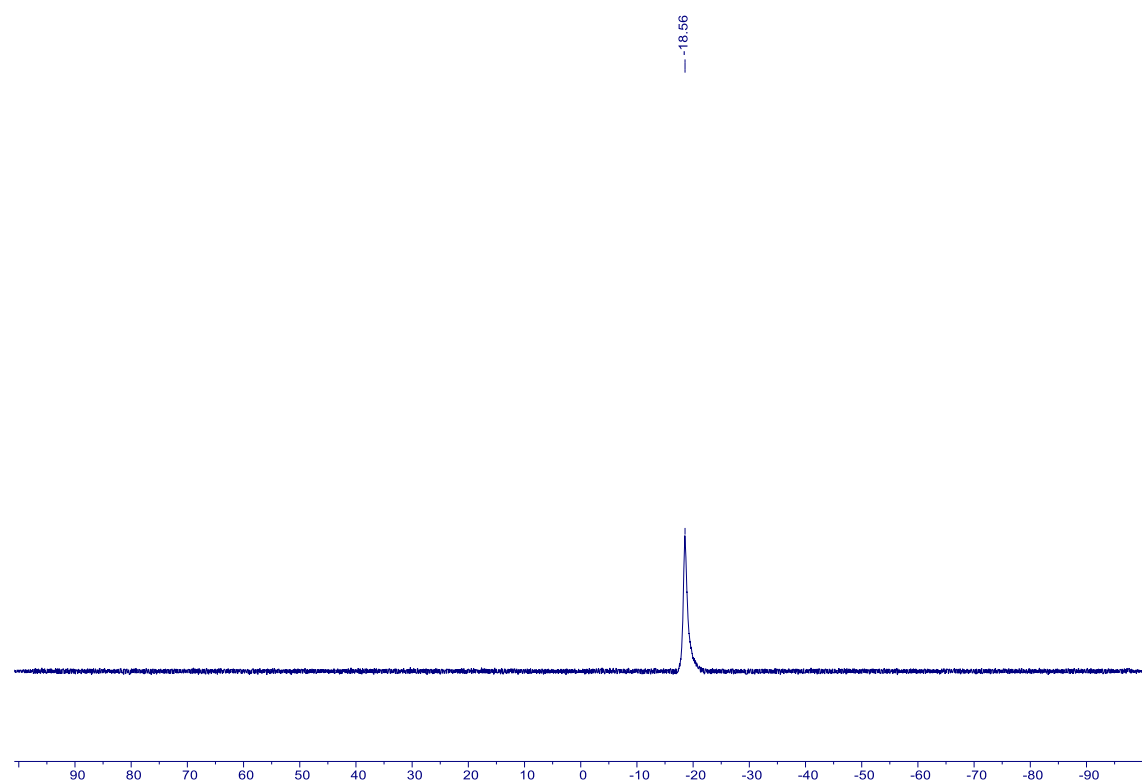
22a – ^1H NMR (600 MHz, CDCl_3)



22a – ^{13}C NMR (101 MHz, CDCl_3)



22a – ^{11}B NMR (128 MHz, CDCl_3)



Chemical structure: (S)-1-(4-chlorophenyl)-2-((tert-butoxycarbonyl)amino)aziridine

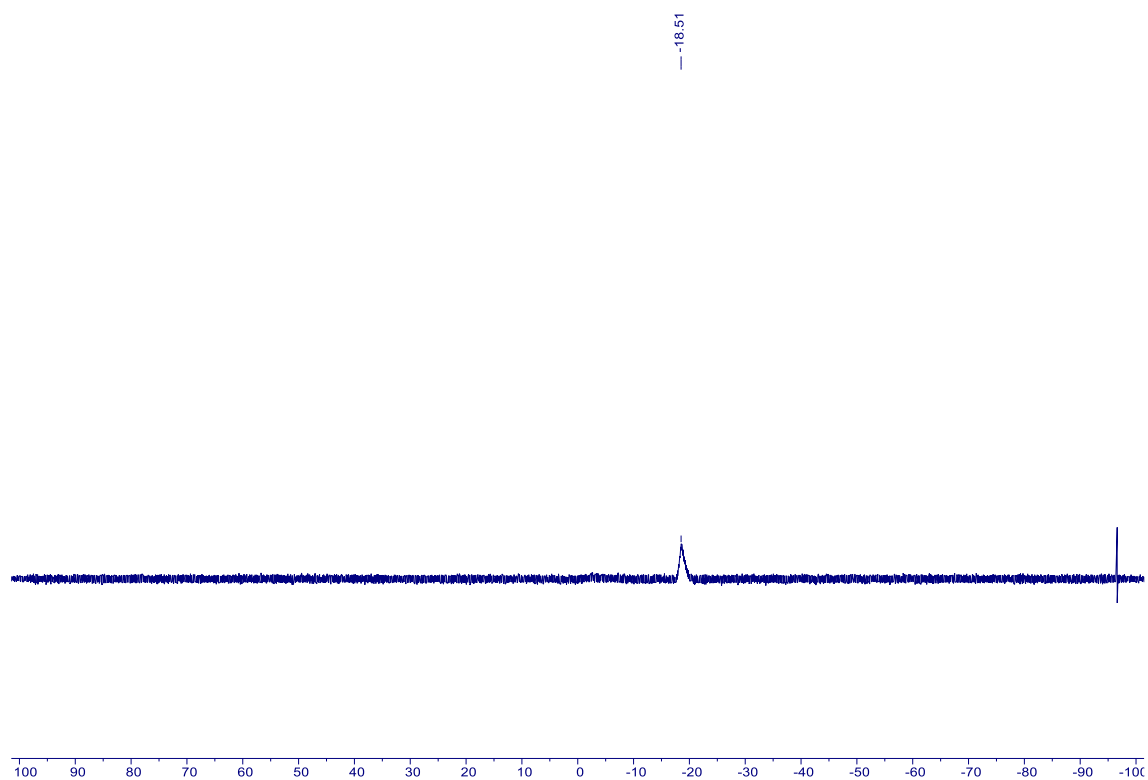
¹H NMR spectrum (CDCl₃) showing peaks and integration values:

Chemical Shift (ppm)	Integration
7.36, 7.34, 7.26, 7.24	2.0, 3.1
4.33, 4.25, 4.23, 3.32, 3.31, 3.30, 3.30, 2.80, 2.80, 2.79, 2.79, 2.49, 2.48, 2.47, 2.47, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.23, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 1.88, 1.86, 1.46	2.2, 1.1, 1.1, 1.2, 1.1, 1.1, 10.2

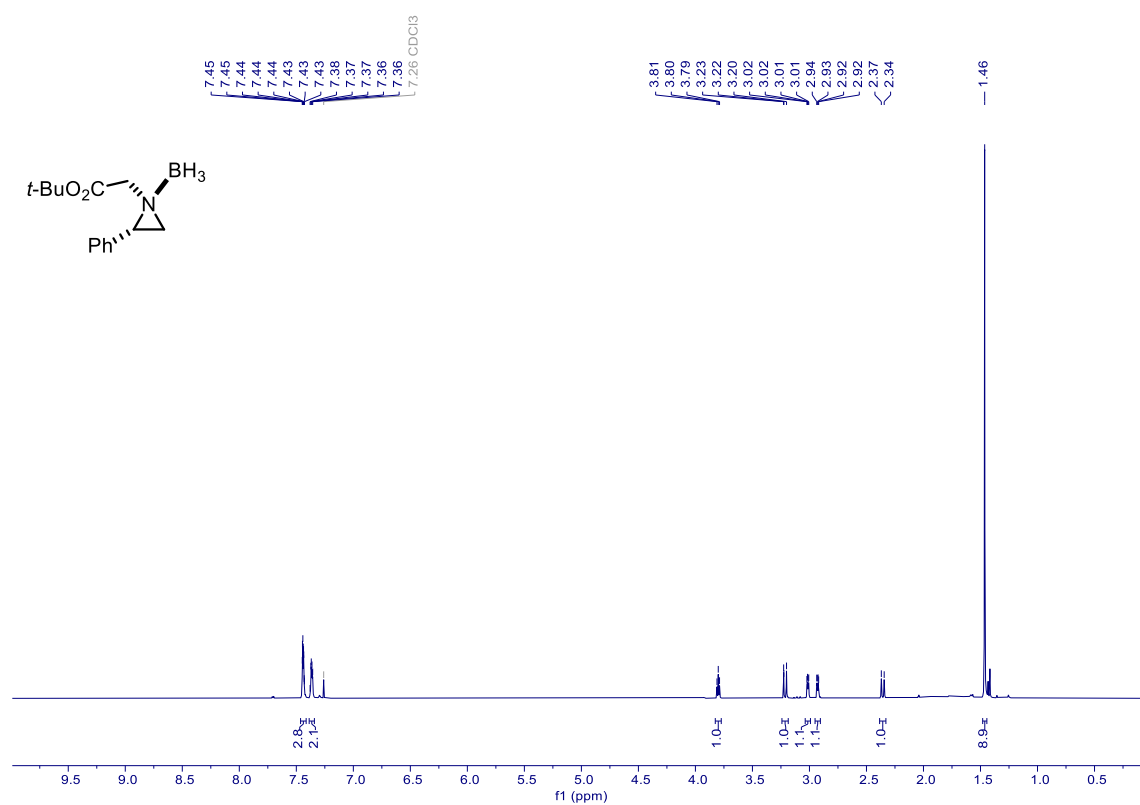
¹³C NMR spectrum of compound 10 in CDCl₃. The x-axis represents chemical shift in ppm, ranging from 10 to 190. The spectrum shows several peaks:

- 154.5
- 135.3
- 131.6
- 128.2
- 128.6
- 80.2
- 77.2 CDCl₃
- 71.6
- 65.1
- 49.9
- 40.4
- 28.5

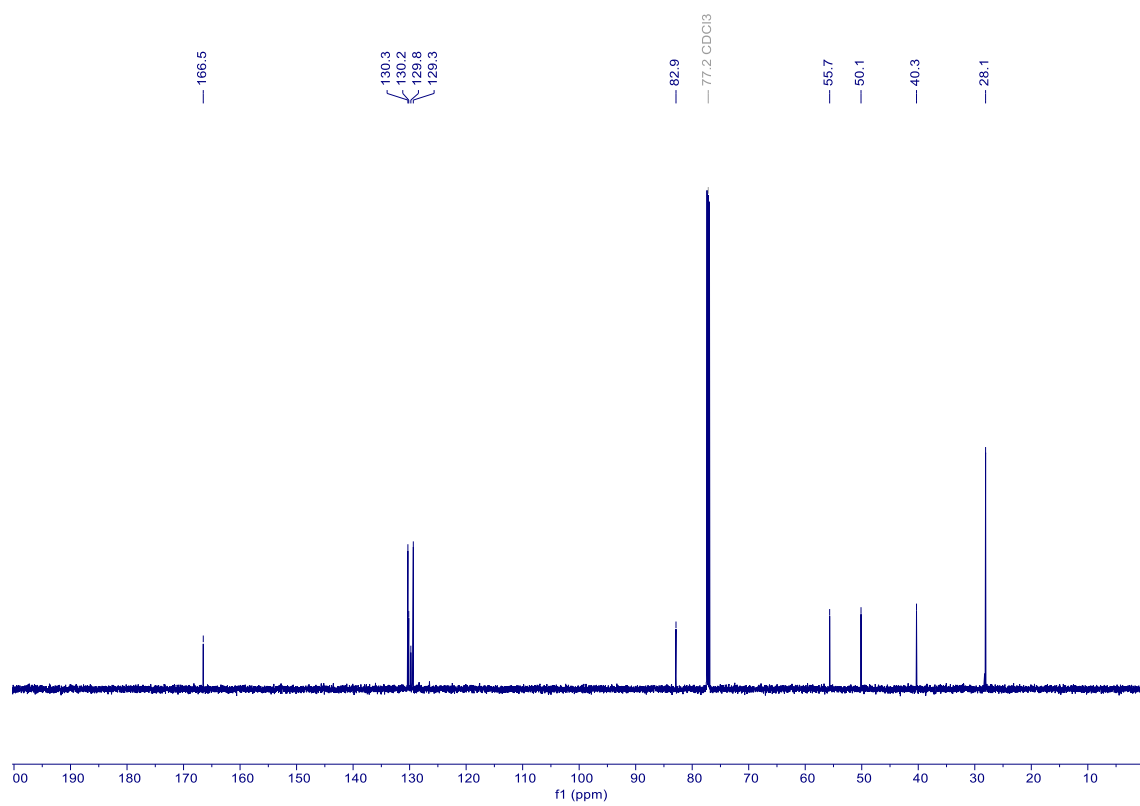
23a – ^{11}B NMR (192 MHz, CDCl_3)



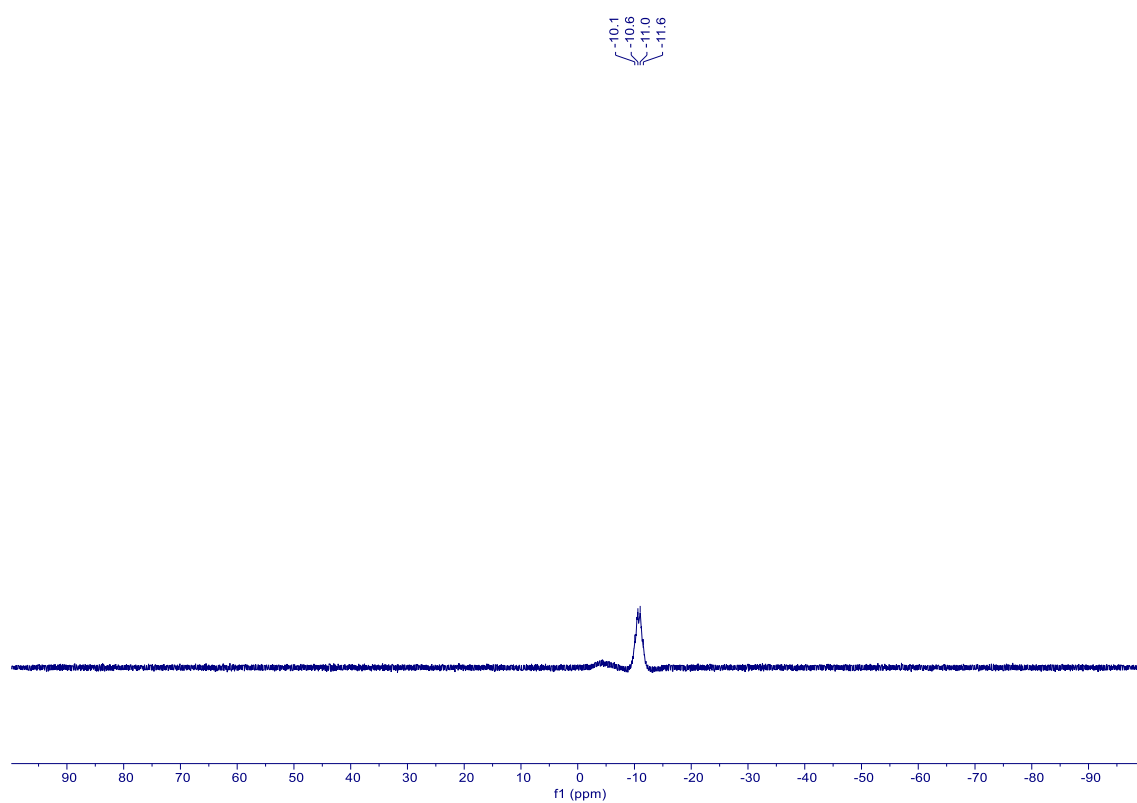
24a – ^1H NMR (600 MHz, CDCl_3)



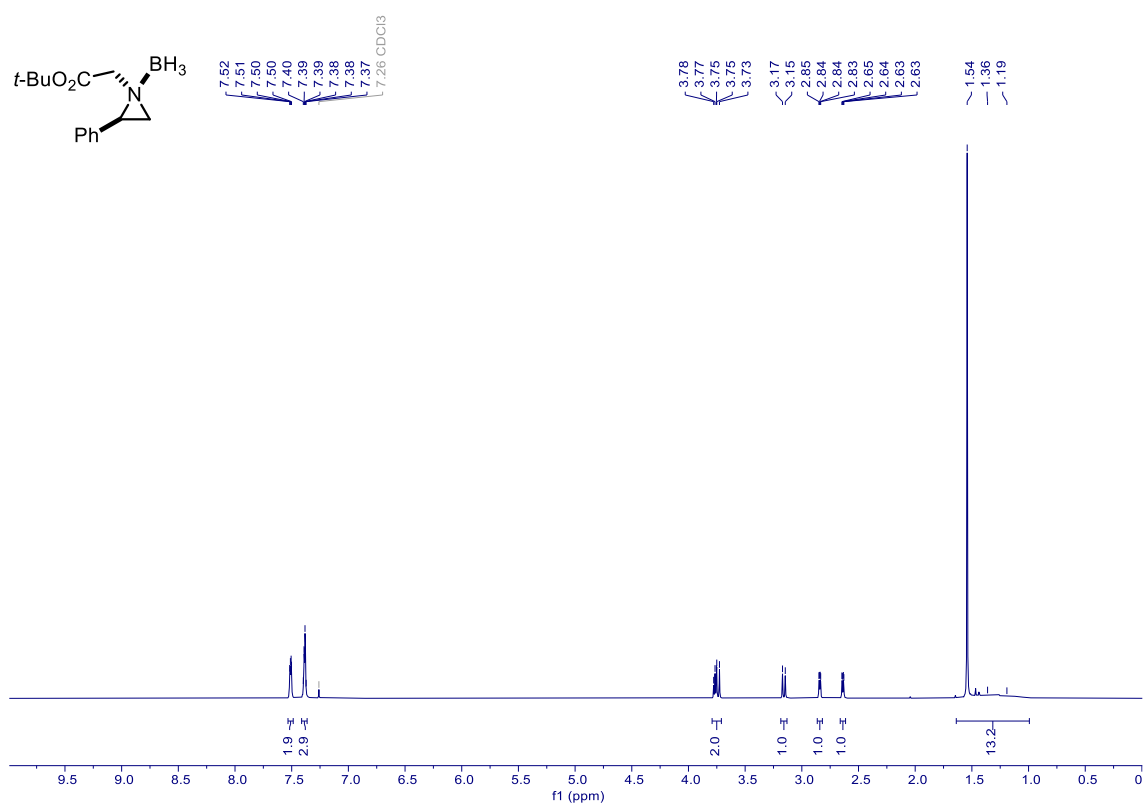
24a – ^{13}C NMR (151 MHz, CDCl_3)



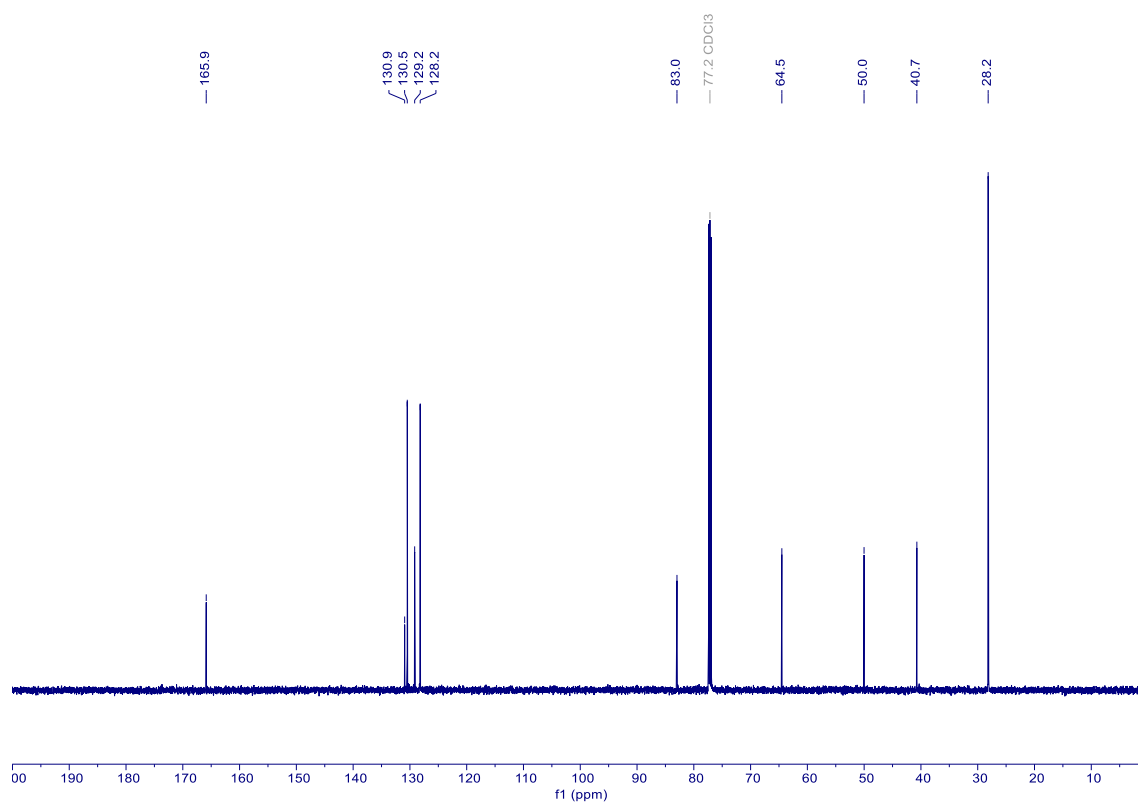
24a – ^{11}B NMR (193 MHz, CDCl_3)



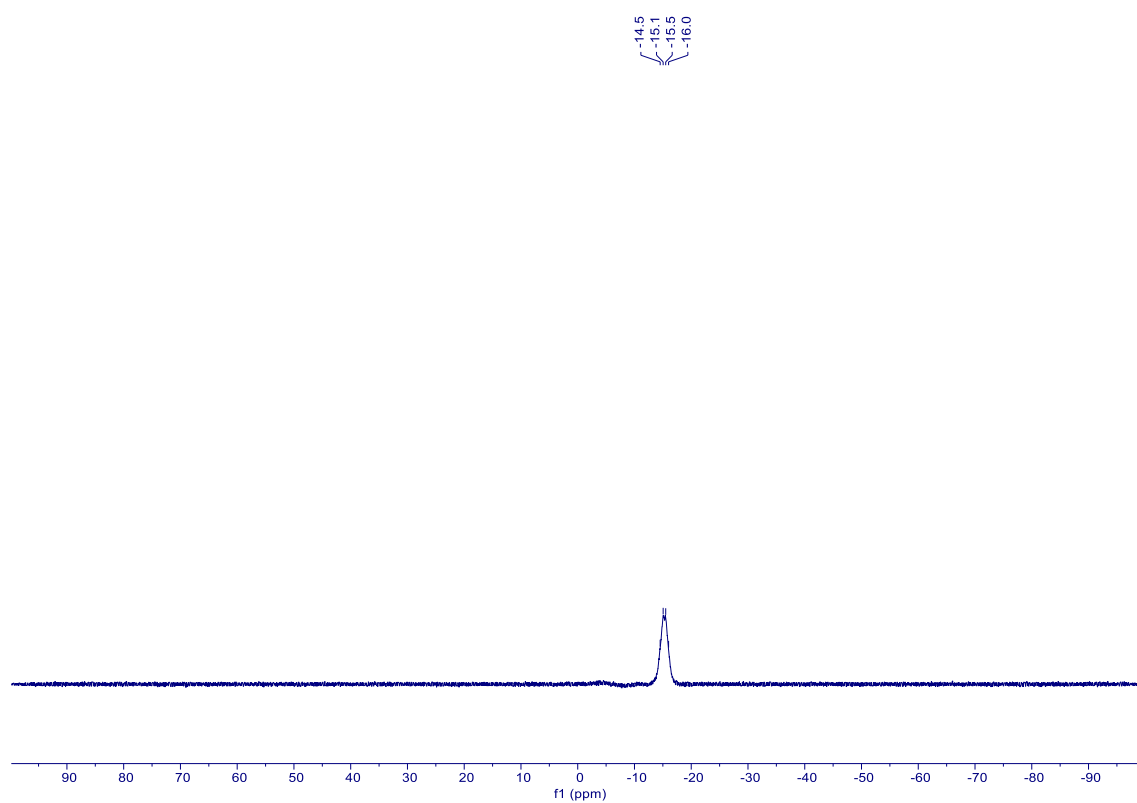
24a' – ^1H NMR (600 MHz, CDCl_3)



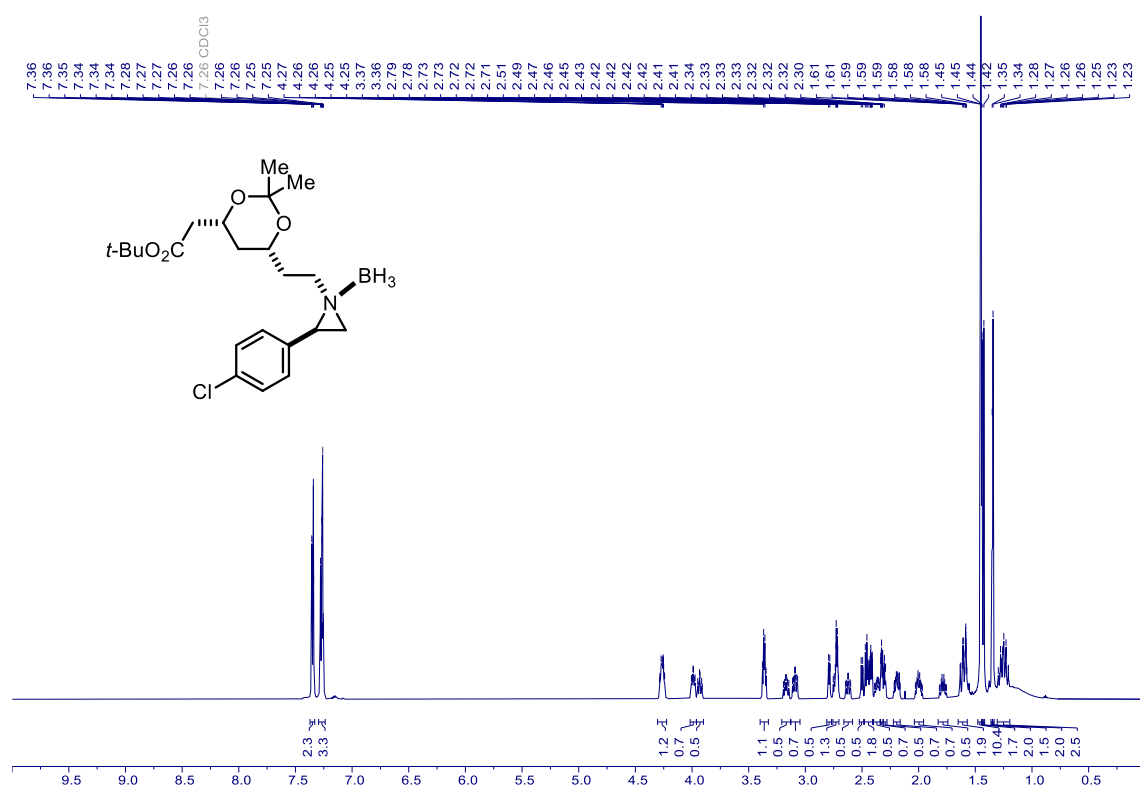
24a' – ^{13}C NMR (151 MHz, CDCl_3)



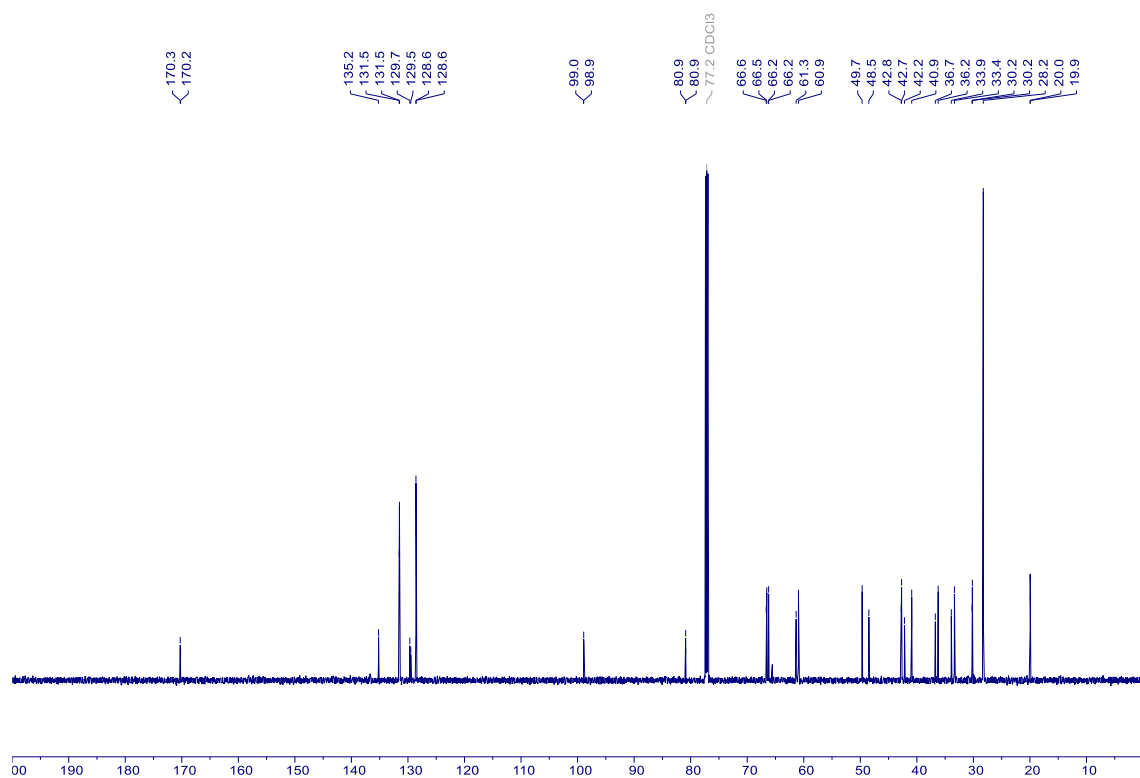
24a' – ^{11}B NMR (193 MHz, CDCl_3)



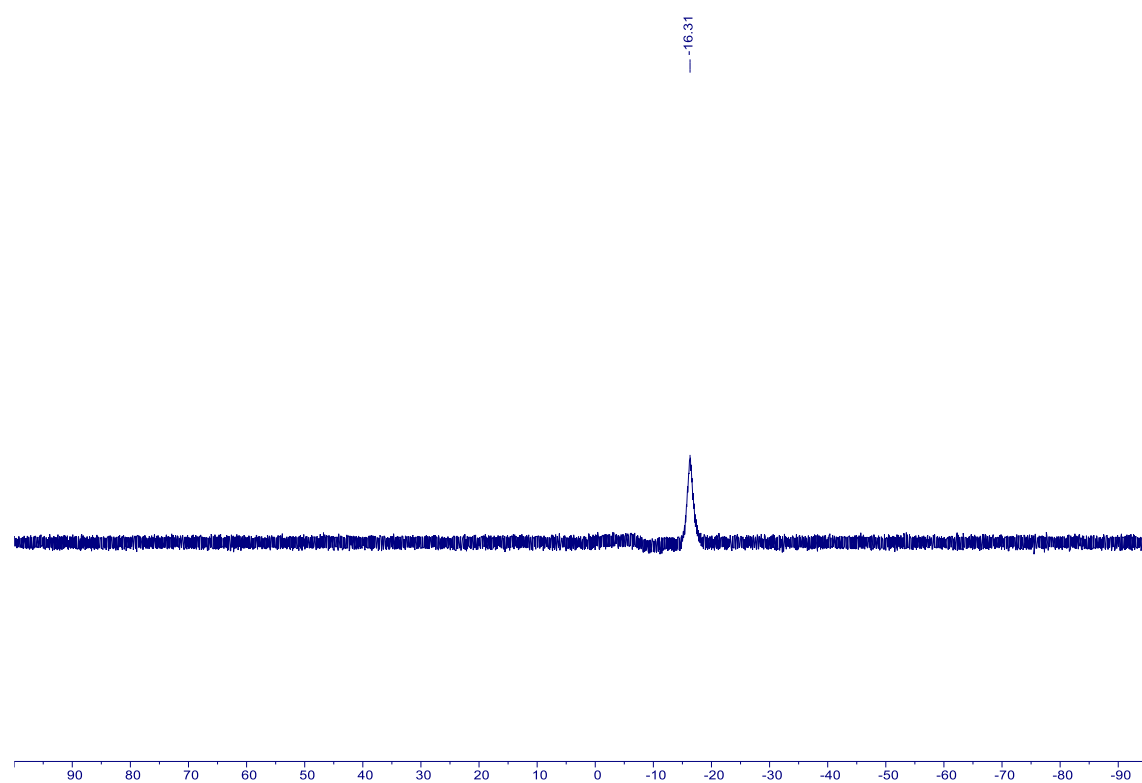
25a – ^1H NMR (600 MHz, CDCl_3)



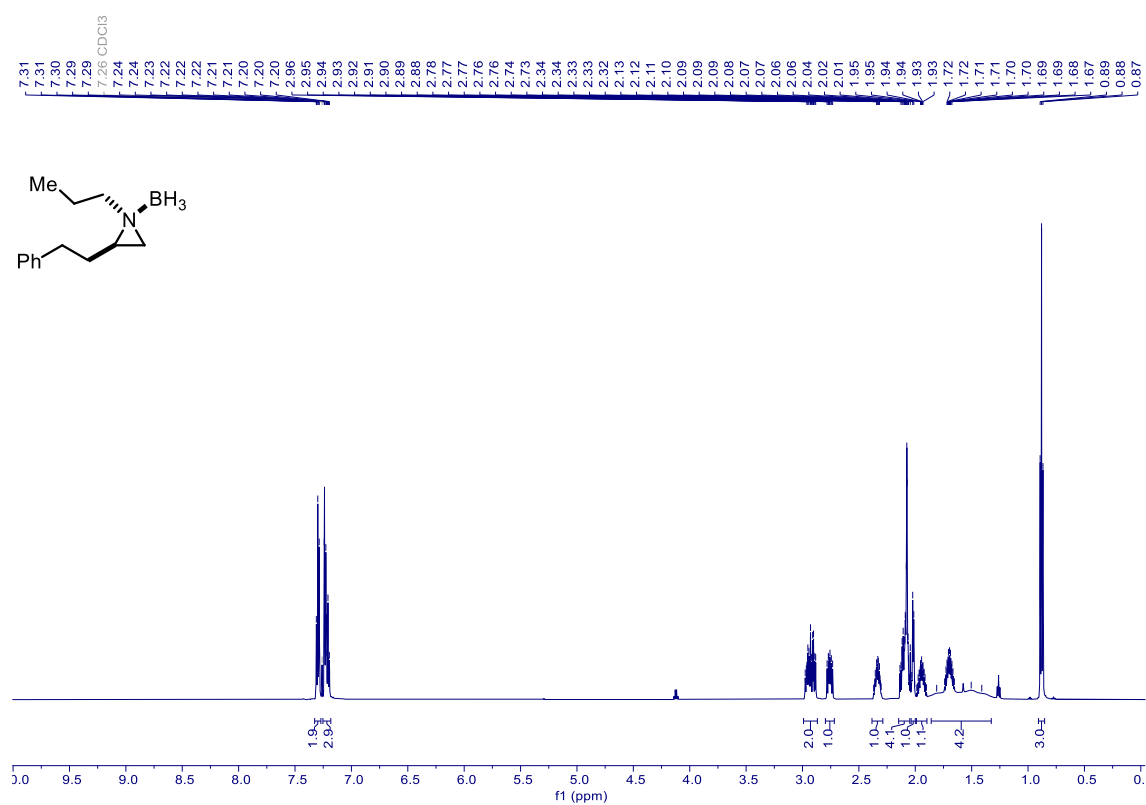
25a – ^{13}C NMR (151 MHz, CDCl_3)



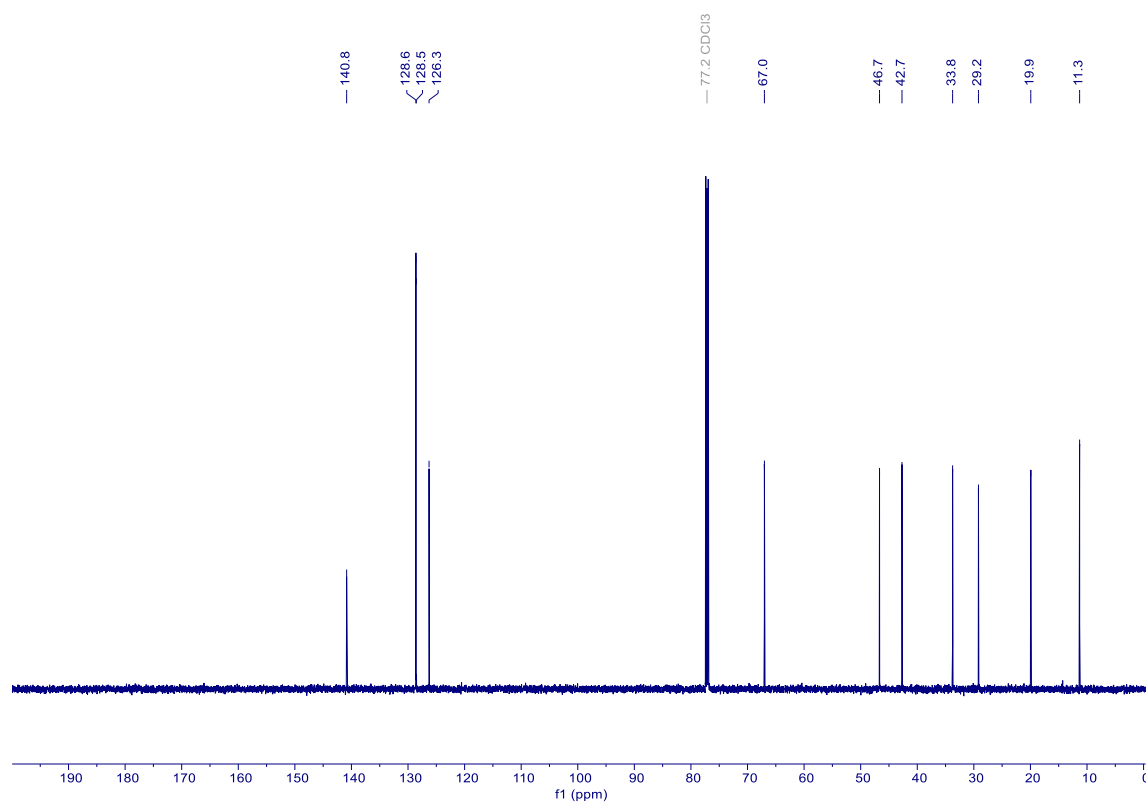
25a – ^{11}B NMR (192 MHz, CDCl_3)



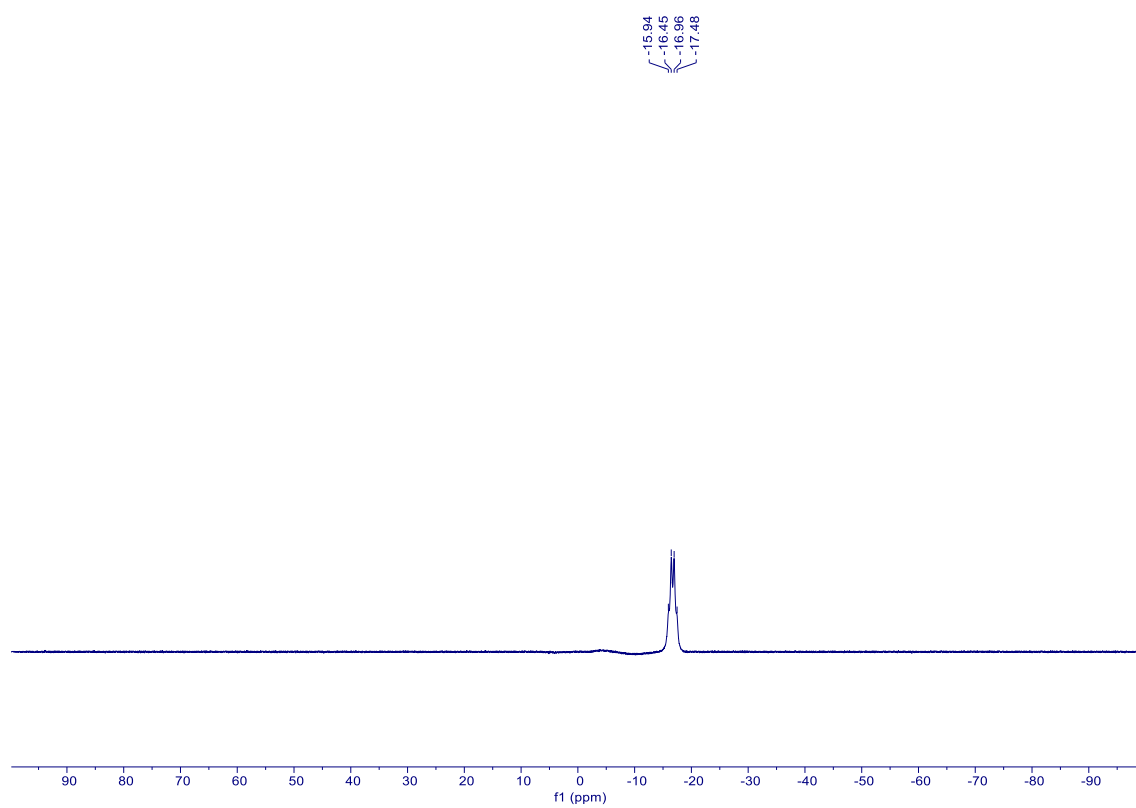
26a – ^1H NMR (600 MHz, CDCl_3)



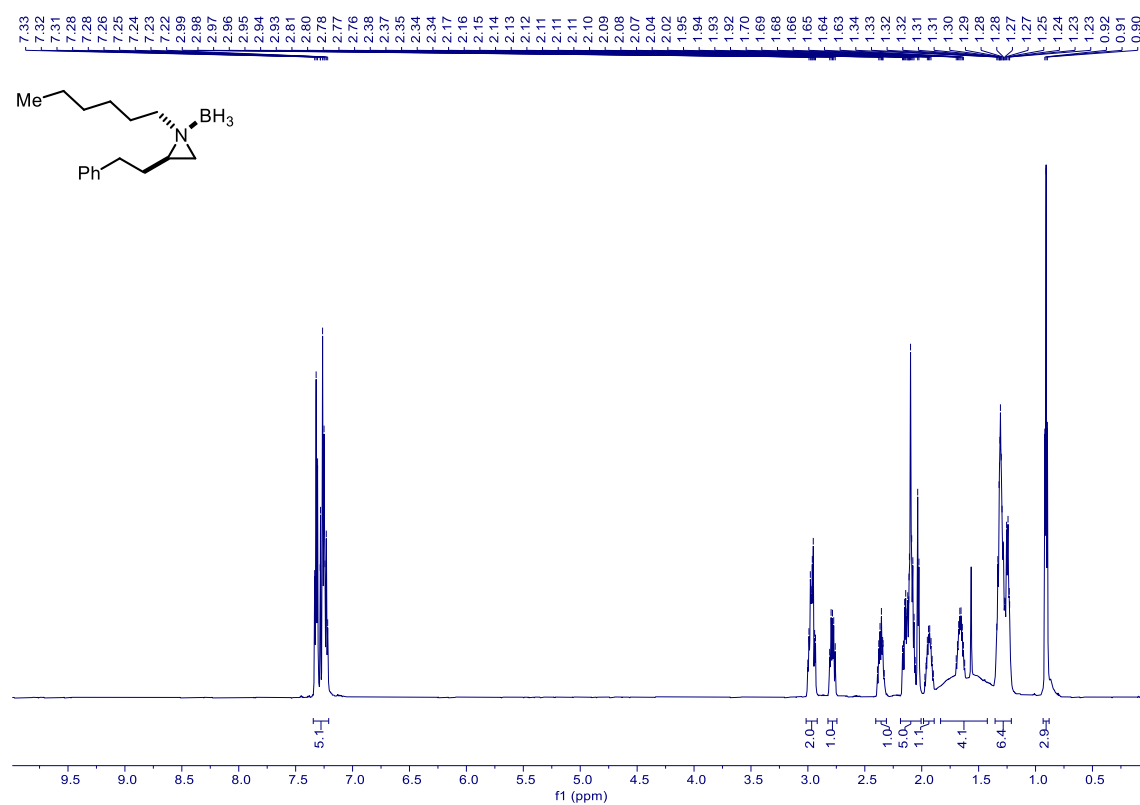
26a – ^{13}C NMR (151 MHz, CDCl_3)



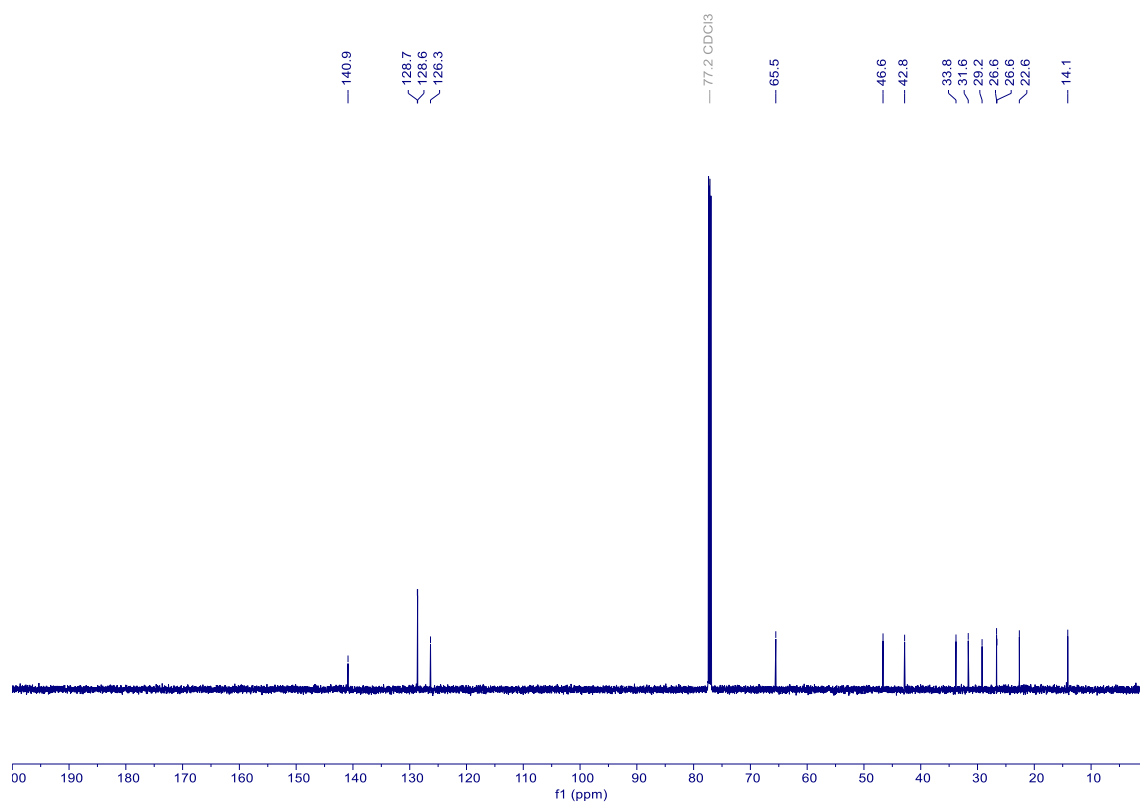
26a – ^{11}B NMR (193 MHz, CDCl_3)



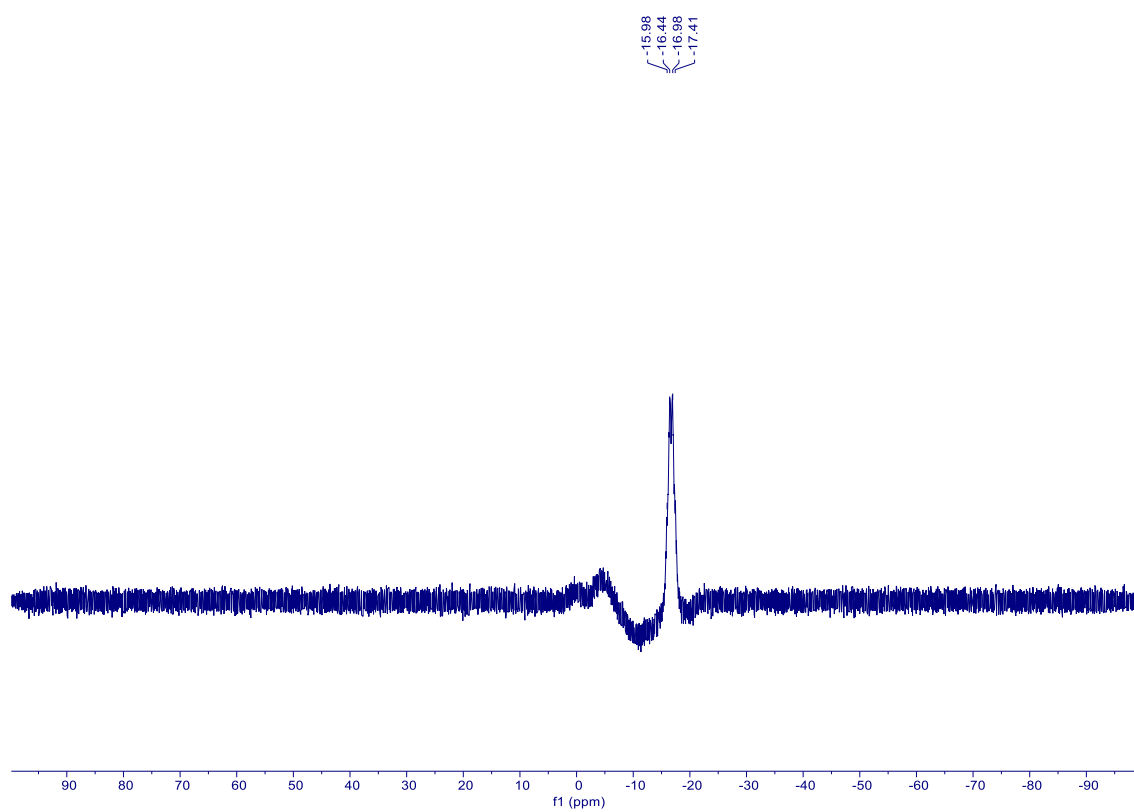
27a – ^1H NMR (600 MHz, CDCl_3)



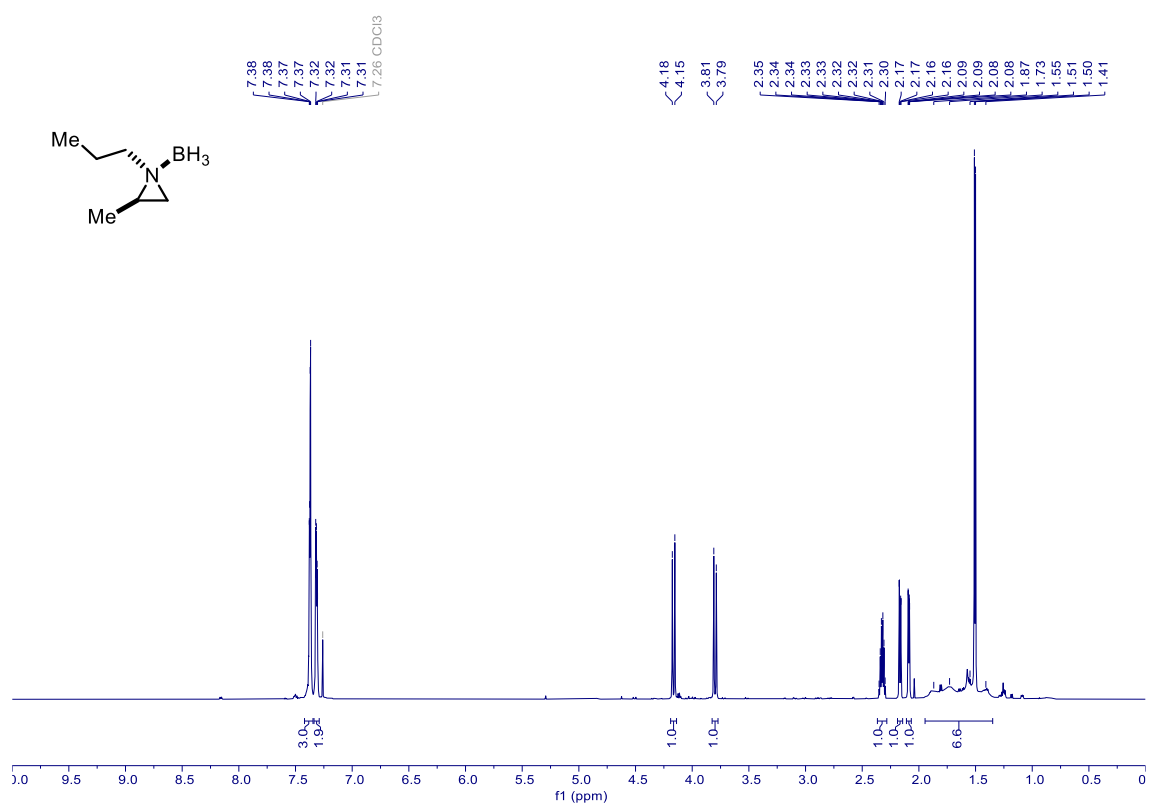
27a – ^{13}C NMR (151 MHz, CDCl_3)



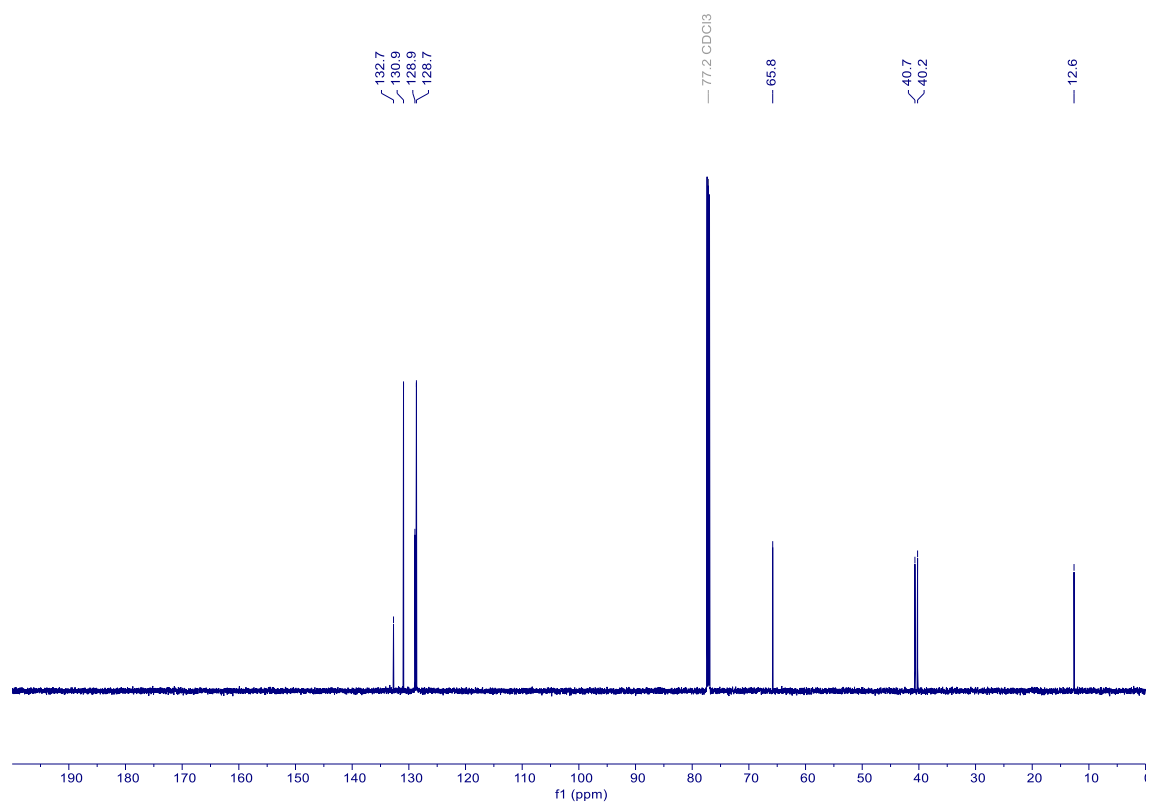
27a – ^{11}B NMR (193 MHz, CDCl_3)



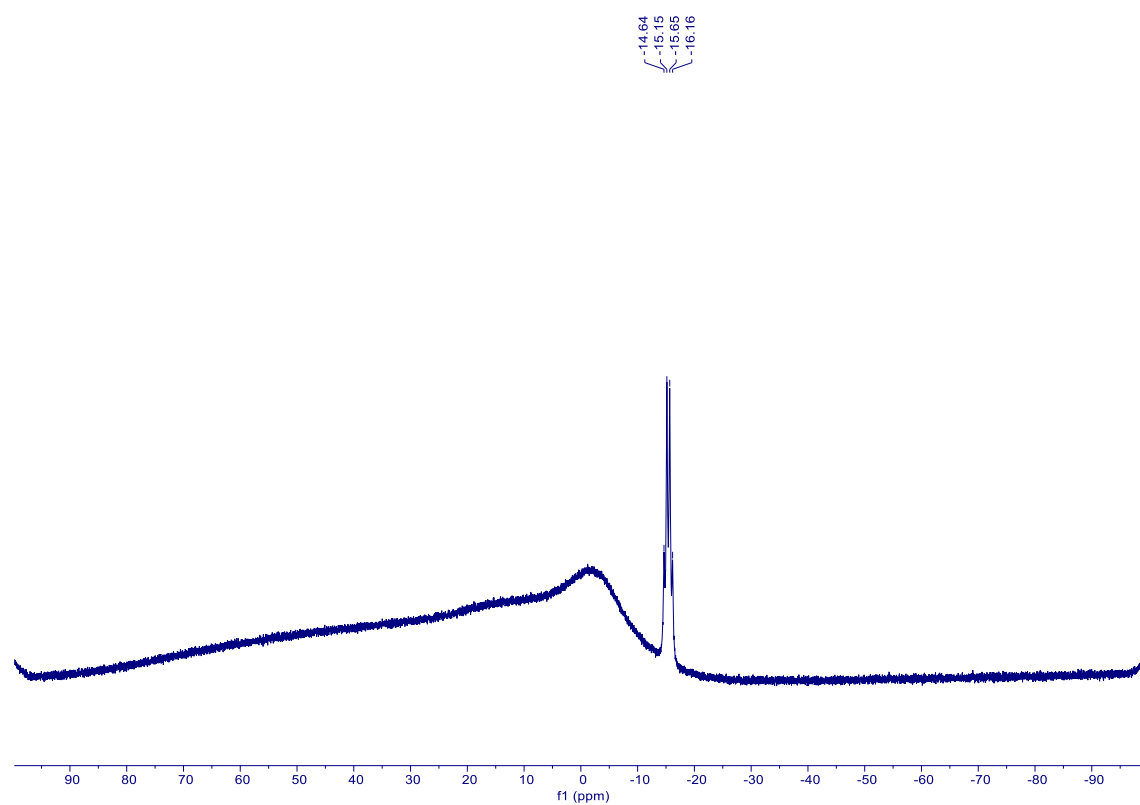
28a – ^1H NMR (600 MHz, CDCl_3)



28a – ^{13}C NMR (151 MHz, CDCl_3)



28a – ^{11}B NMR (193 MHz, CDCl_3)



Chemical structure: CC[C@H](C1CCCN1)[C@H](C2=CC=CC=C2)C3=CC=CC=C3

¹H NMR spectrum (CDCl₃) showing peaks from 0.87 to 7.38 ppm. Integration values are provided below the peaks: 29.4, 20.4, 1.0, 1.0, 1.0, 1.1, 5.3, 3.1, and 3.0.

132.8
131.2
129.0
128.6

77.2 CDCl3

66.2

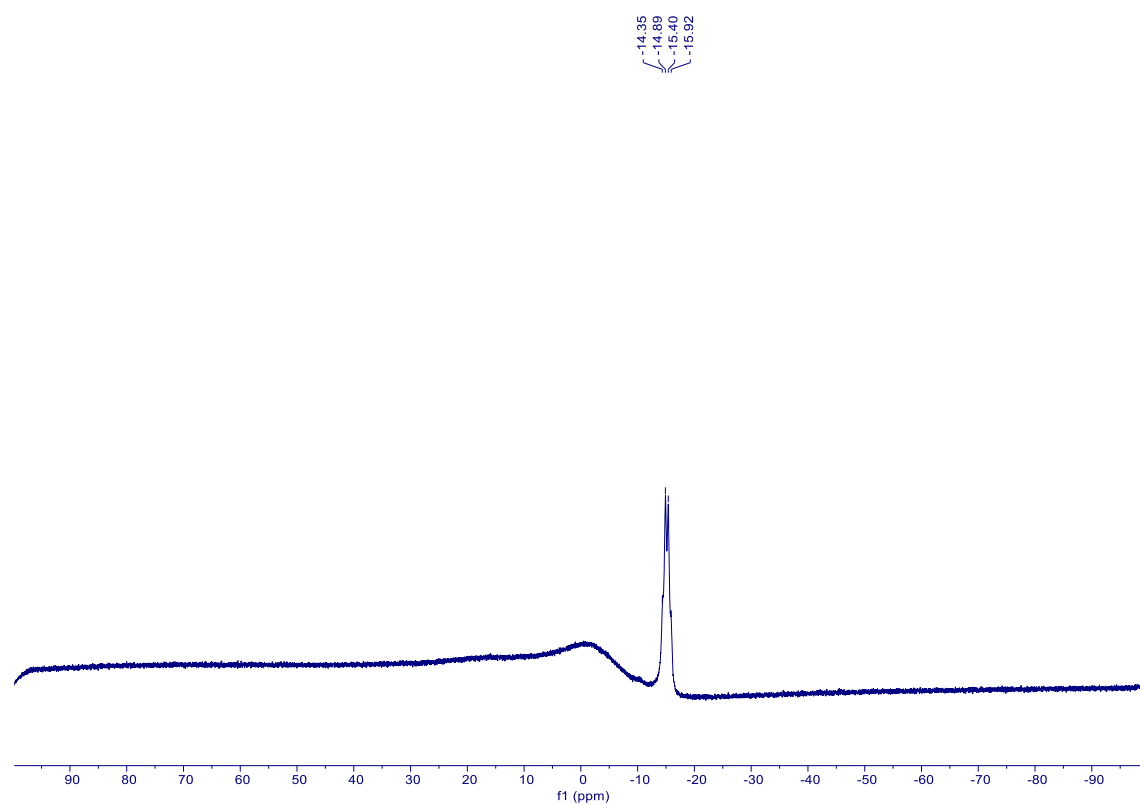
44.9
40.5

29.7
26.8
22.4

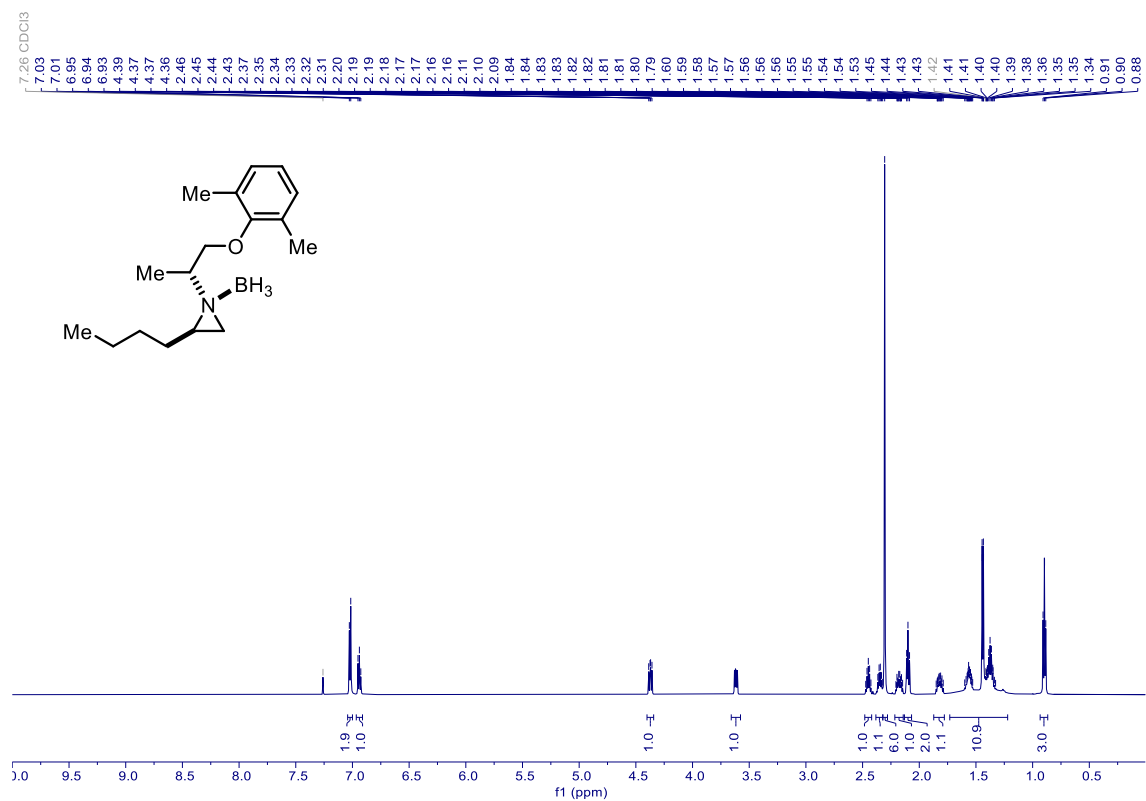
13.9

f1 (ppm)

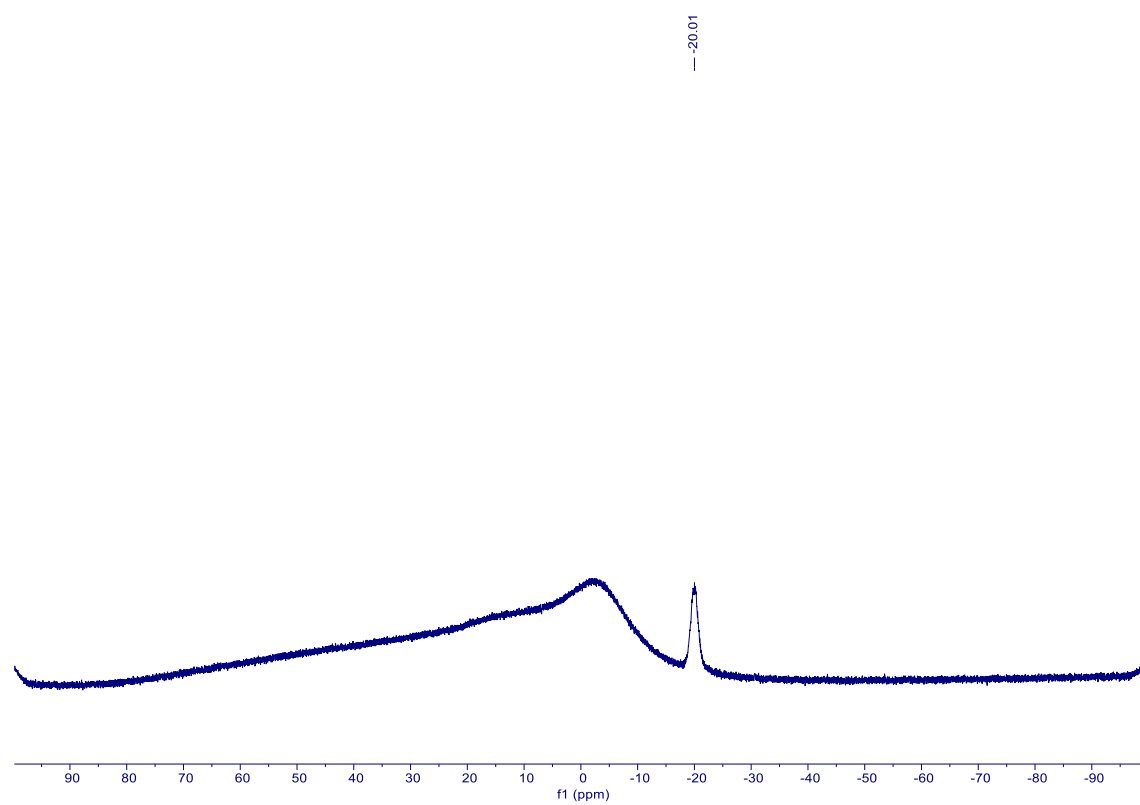
29a – ^{11}B NMR (193 MHz, CDCl_3)



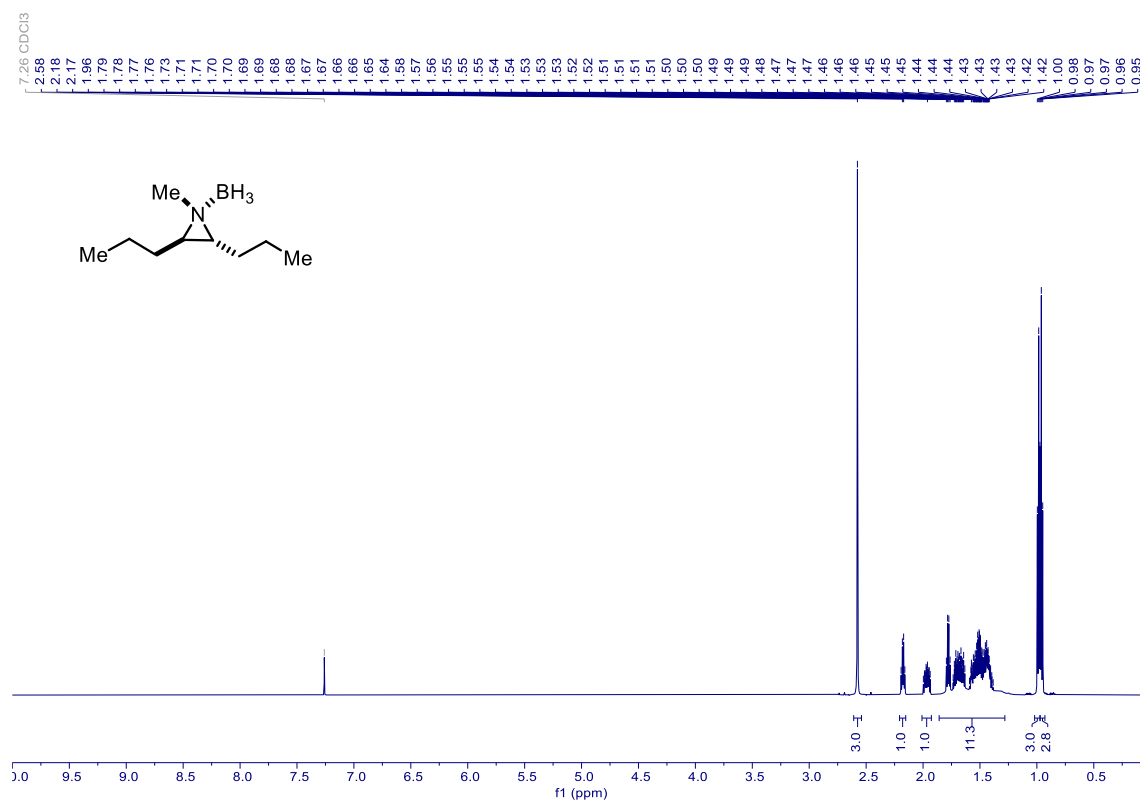
30a – ^1H NMR (600 MHz, CDCl_3)



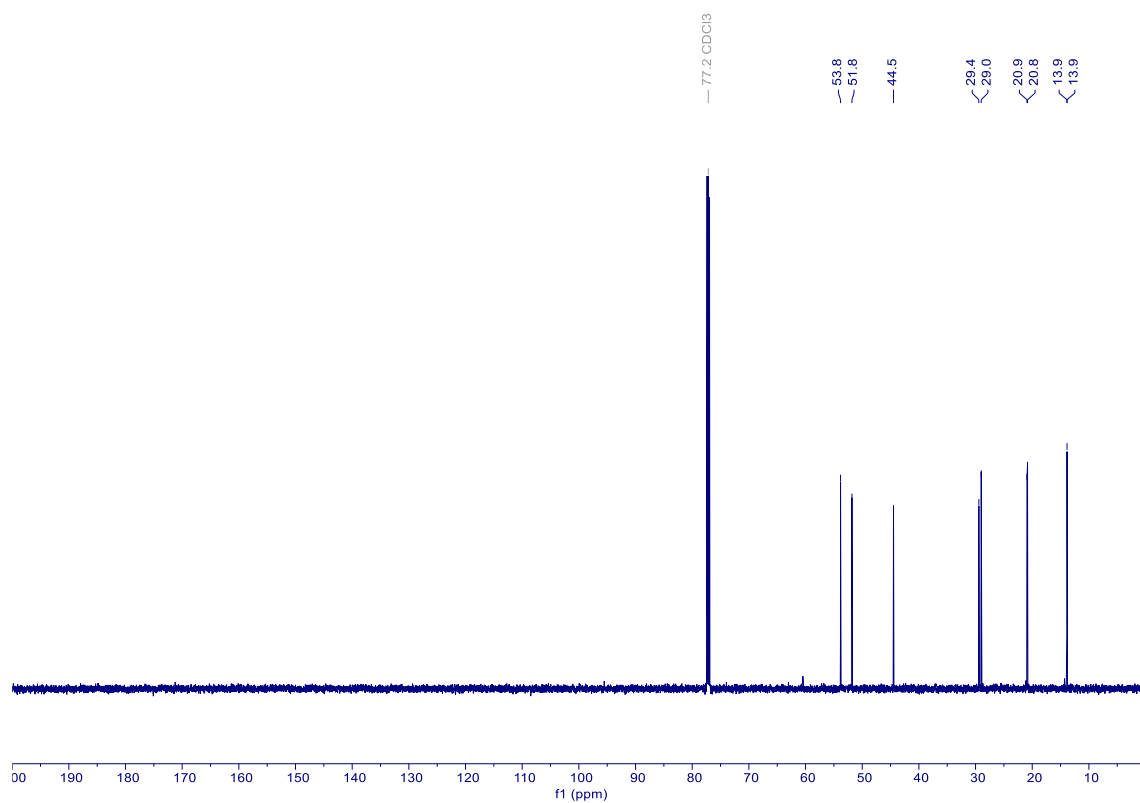
30a – ^{11}B NMR (193 MHz, CDCl_3)



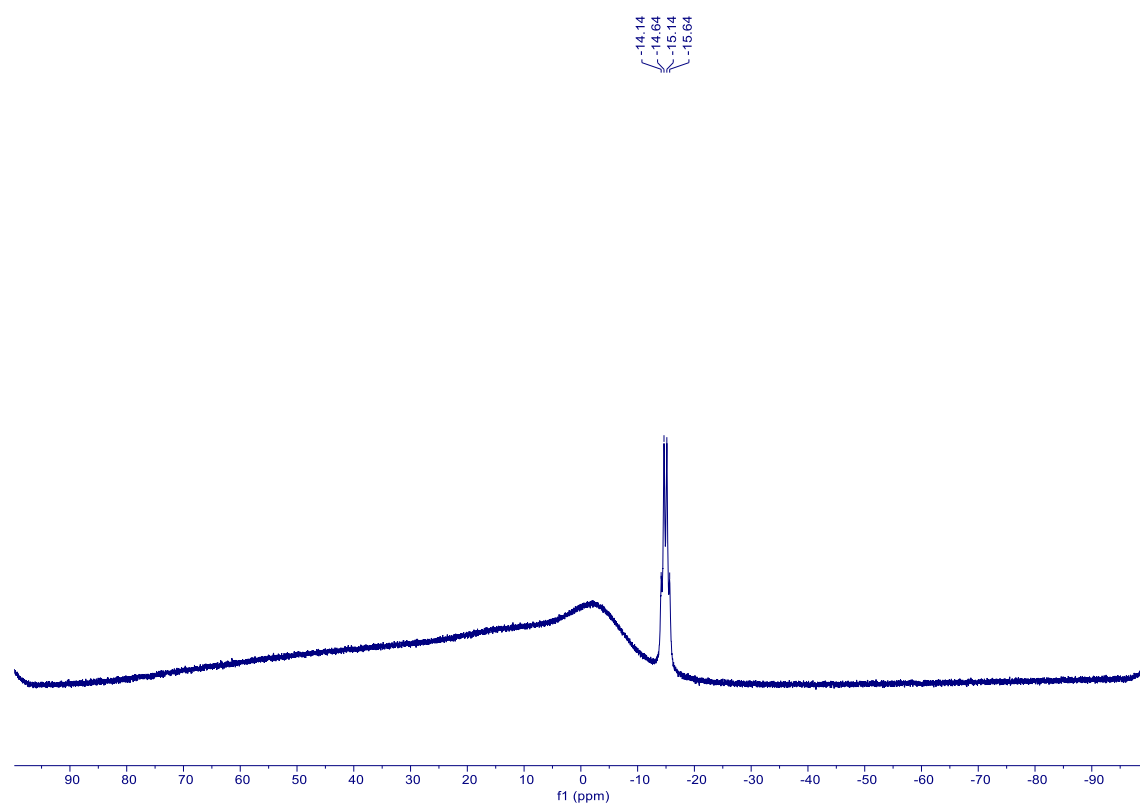
31a – ^1H NMR (600 MHz, CDCl_3)



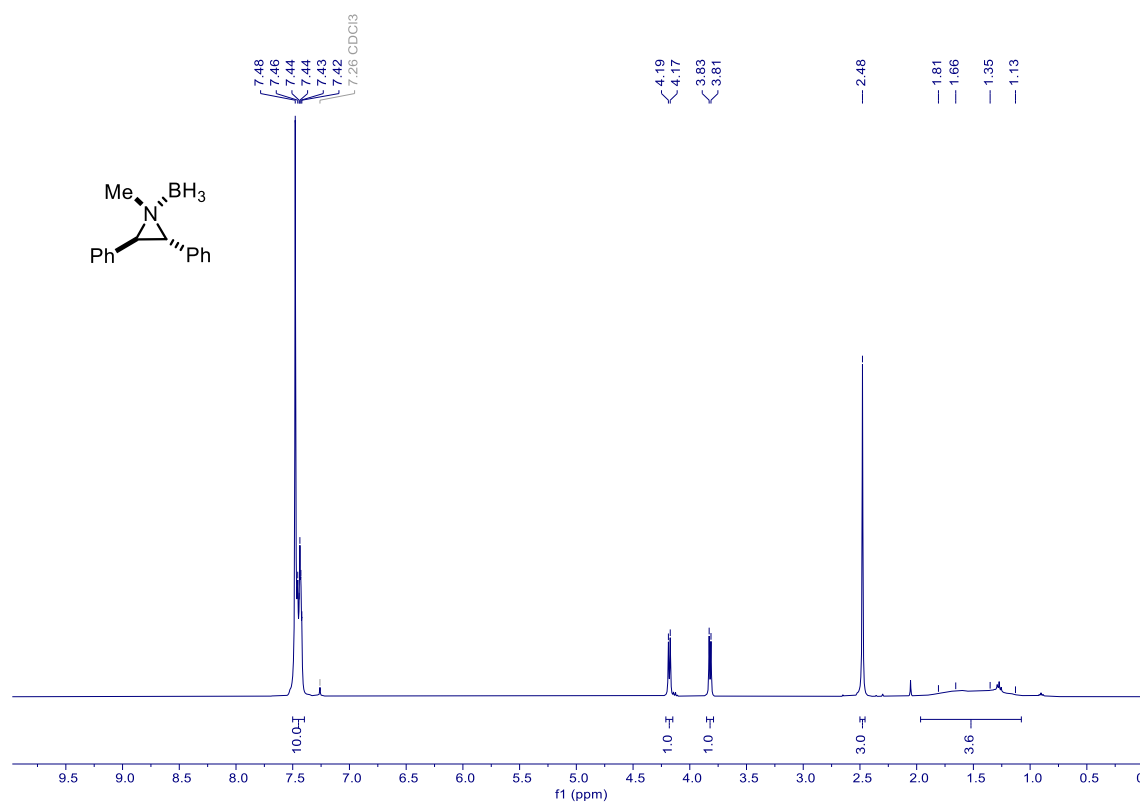
31a – ^{13}C NMR (151 MHz, CDCl_3)



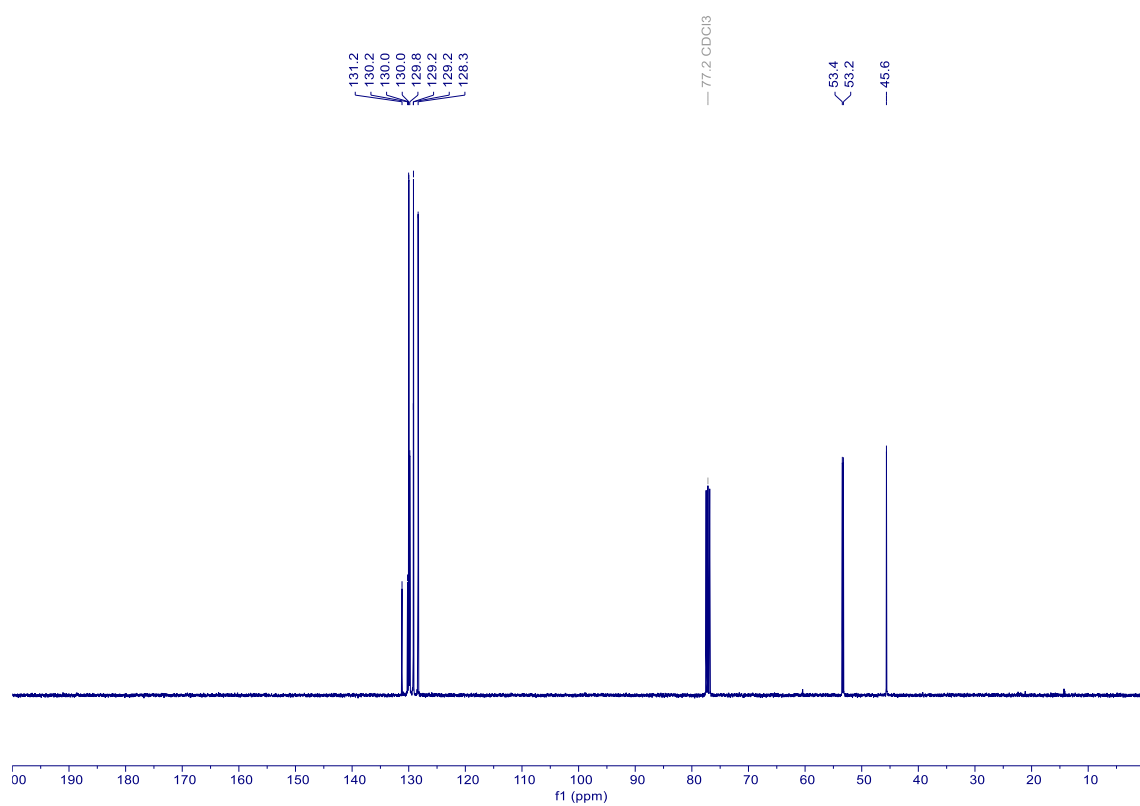
31a – ^{11}B NMR (193 MHz, CDCl_3)



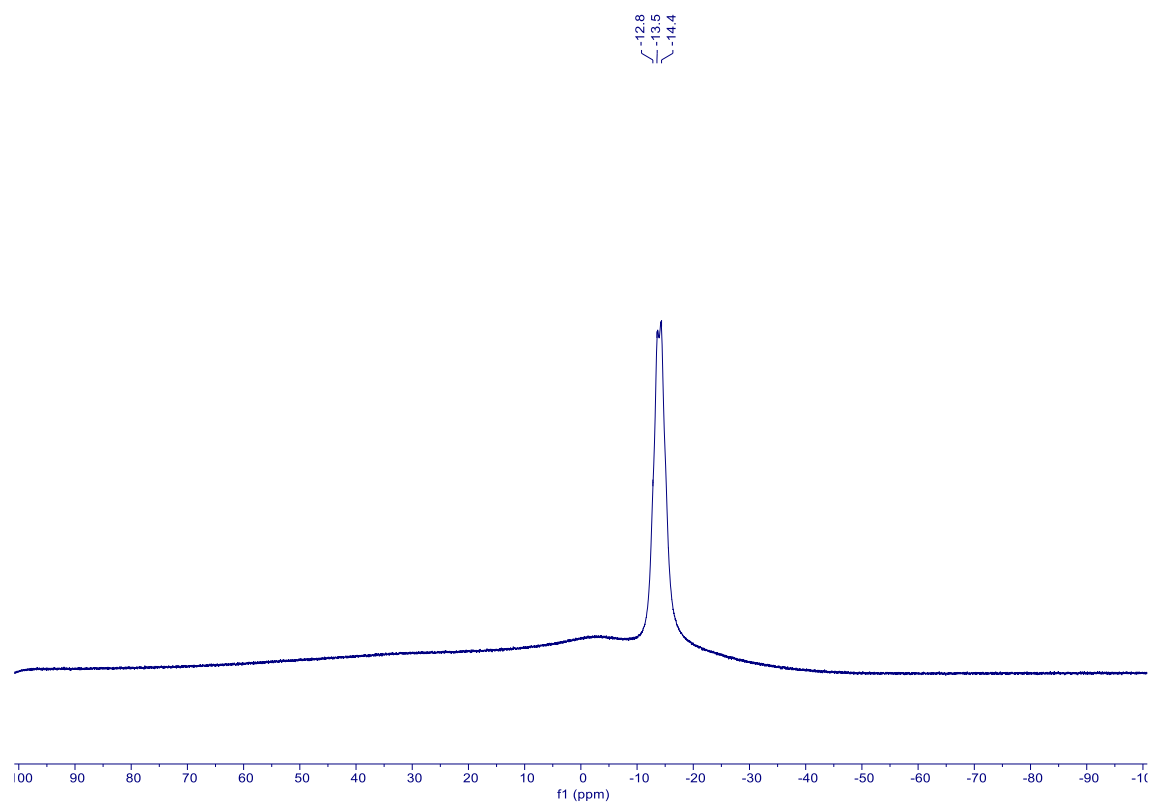
32a – ^1H NMR (400 MHz, CDCl_3)



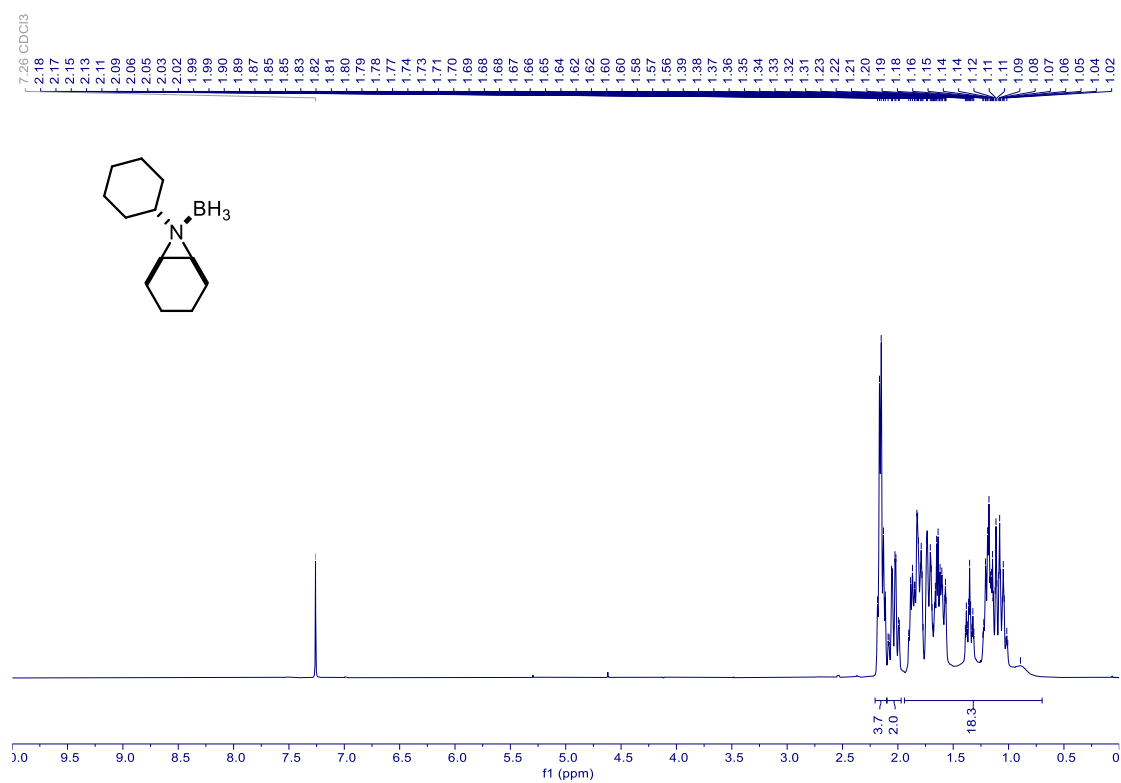
32a – ^{13}C NMR (101 MHz, CDCl_3)



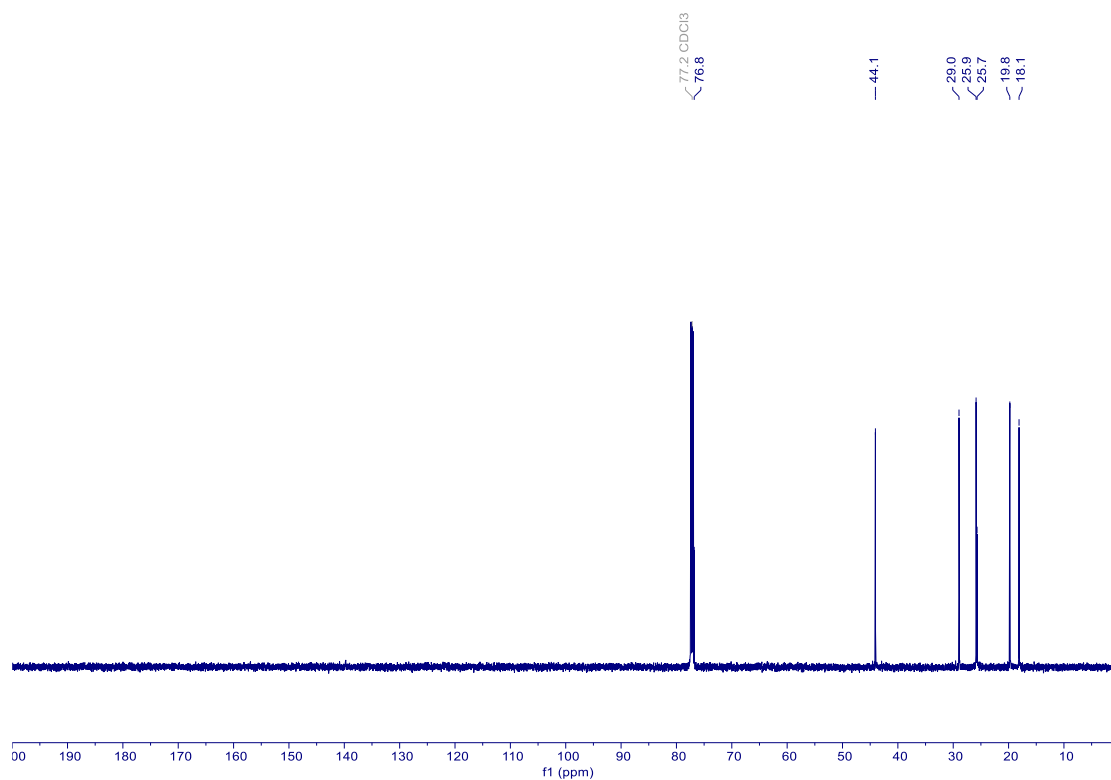
32a – ^{11}B NMR (128 MHz, CDCl_3)



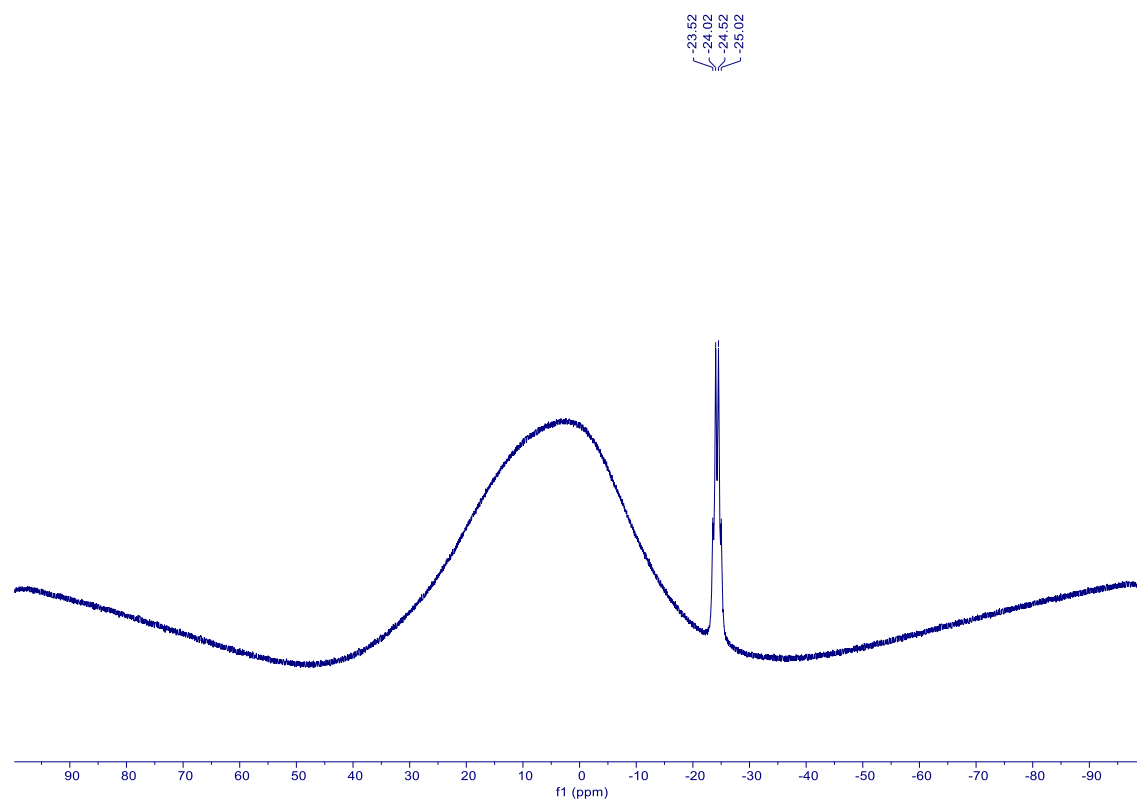
33a – ^1H NMR (400 MHz, CDCl_3)



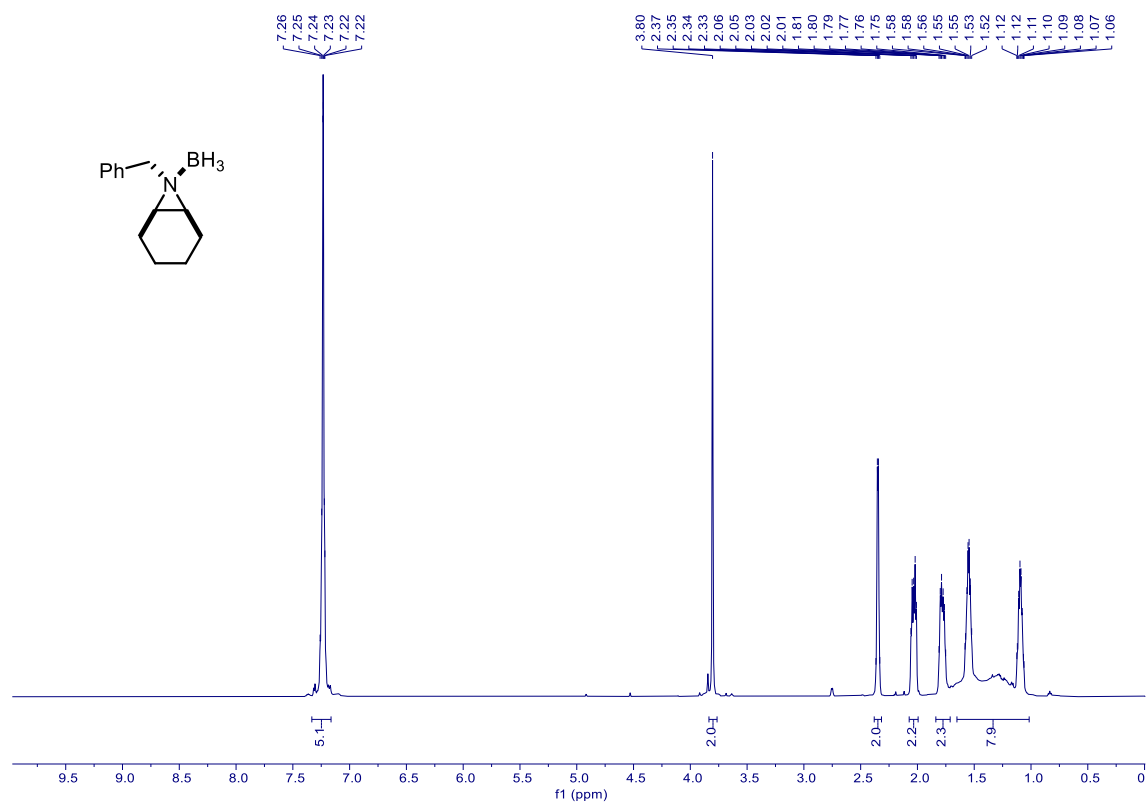
33a – ^{13}C NMR (151 MHz, CDCl_3)



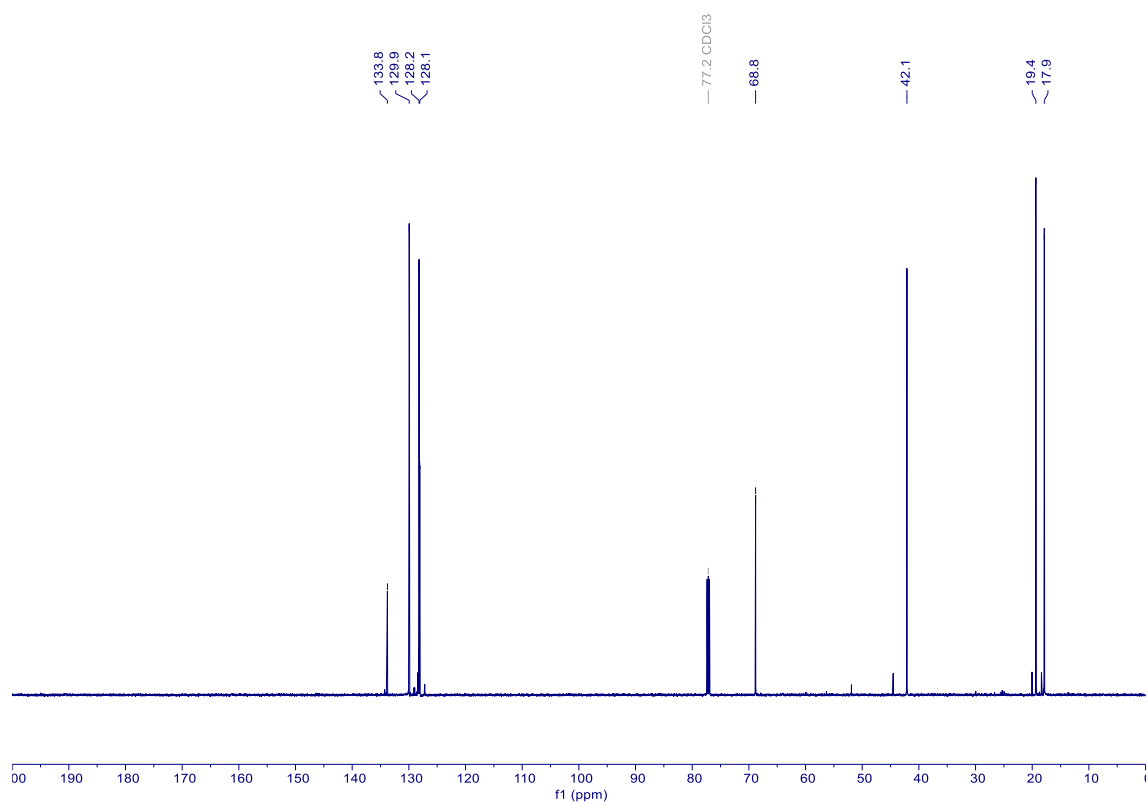
33a – ^{11}B NMR (193 MHz, CDCl_3)



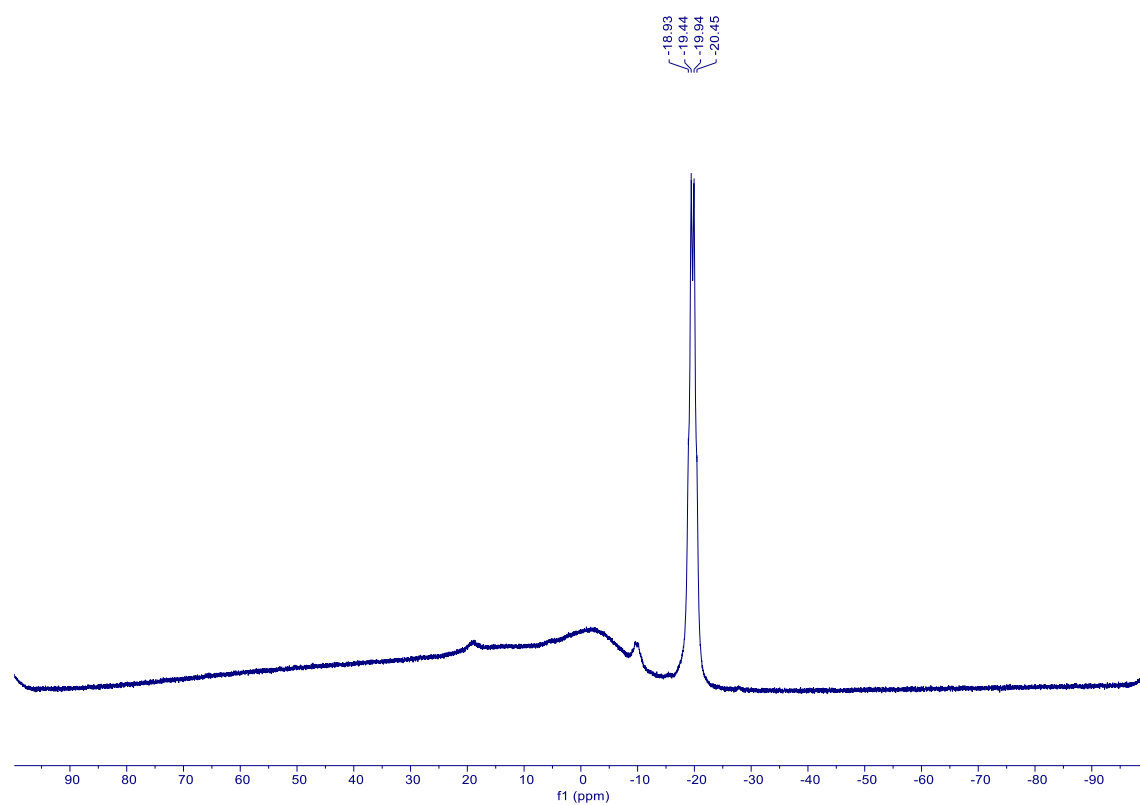
34a – ^1H NMR (600 MHz, CDCl_3)



34a – ^{13}C NMR (151 MHz, CDCl_3)



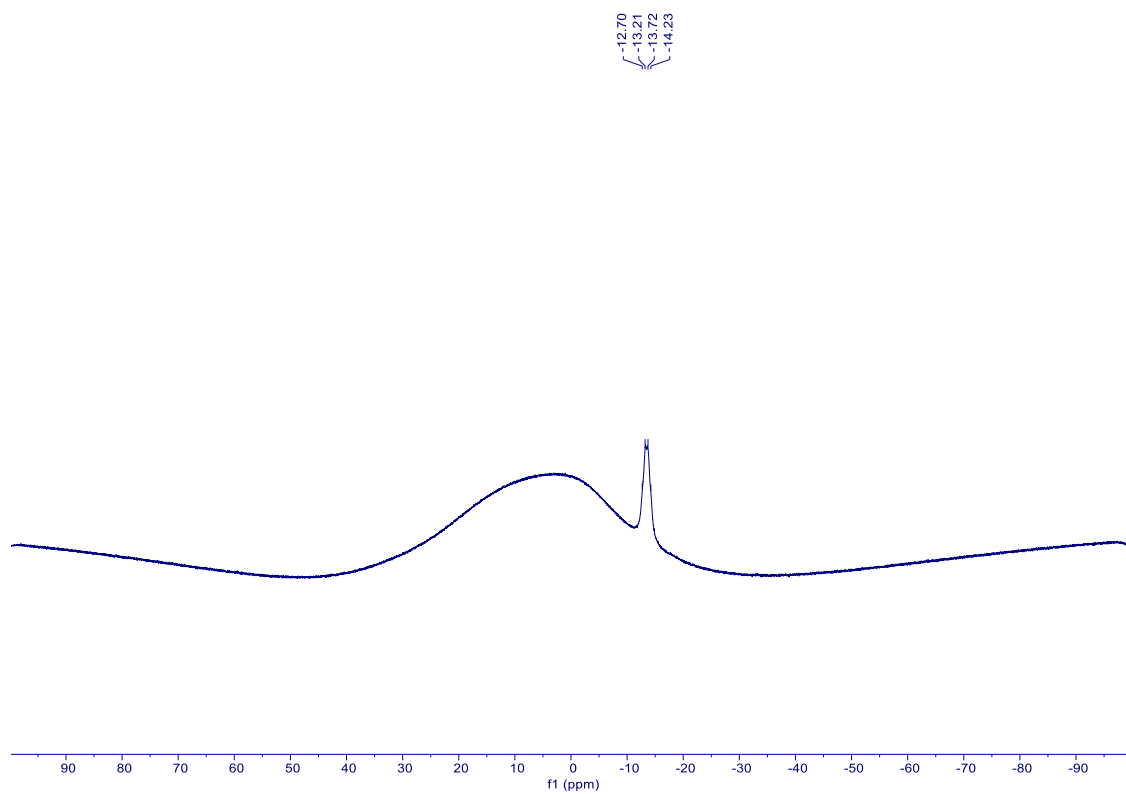
34a – ^{11}B NMR (193 MHz, CDCl_3)



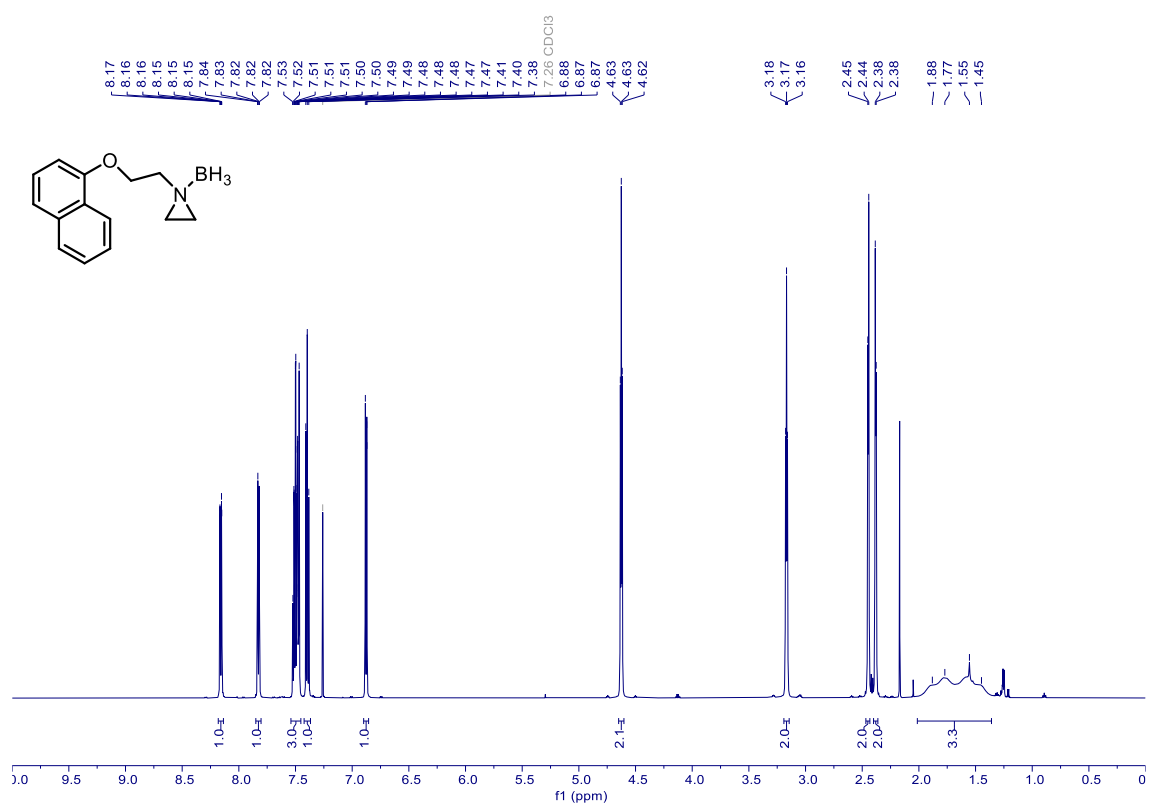
Chemical structure of (1S,2S)-1,2-dimethyl-2-((S)-methylboran-1-yl)butane is shown. The ¹H NMR spectrum (CDCl₃) displays peaks at 7.26 ppm (s, 1H), 1.41 ppm (d, 2H), 1.34 ppm (d, 2H), 1.33 ppm (d, 2H), 1.32 ppm (d, 2H), 1.31 ppm (d, 2H), 1.30 ppm (d, 2H), 1.29 ppm (d, 2H), 1.28 ppm (d, 2H), 1.26 ppm (d, 2H), 1.25 ppm (d, 2H), 1.24 ppm (d, 2H), 1.23 ppm (d, 2H), 1.22 ppm (d, 2H), 1.21 ppm (d, 2H), 1.20 ppm (d, 2H), 1.19 ppm (d, 2H), 1.18 ppm (d, 2H), 1.17 ppm (d, 2H), 1.16 ppm (d, 2H), 1.15 ppm (d, 2H), 1.14 ppm (d, 2H), 1.13 ppm (d, 2H), 1.12 ppm (d, 2H), 1.11 ppm (d, 2H), 1.10 ppm (d, 2H), 1.09 ppm (d, 2H), 1.08 ppm (d, 2H), 1.07 ppm (d, 2H), 1.06 ppm (d, 2H), 1.05 ppm (d, 2H), 1.04 ppm (d, 2H), 1.03 ppm (d, 2H), 1.02 ppm (d, 2H), 1.01 ppm (d, 2H), 1.00 ppm (d, 2H), 0.99 ppm (d, 2H), 0.98 ppm (d, 2H), 0.97 ppm (d, 2H), 0.96 ppm (d, 2H), 0.95 ppm (d, 2H), 0.94 ppm (d, 2H), 0.93 ppm (d, 2H), 0.92 ppm (d, 2H), 0.91 ppm (d, 2H), 0.90 ppm (d, 2H), 0.89 ppm (d, 2H), 0.88 ppm (d, 2H), 0.87 ppm (d, 2H), 0.86 ppm (d, 2H), 0.85 ppm (d, 2H), 0.84 ppm (d, 2H), 0.83 ppm (d, 2H), 0.82 ppm (d, 2H), 0.81 ppm (d, 2H), 0.80 ppm (d, 2H), 0.79 ppm (d, 2H), 0.78 ppm (d, 2H), 0.77 ppm (d, 2H), 0.76 ppm (d, 2H), 0.75 ppm (d, 2H), 0.74 ppm (d, 2H), 0.73 ppm (d, 2H), 0.72 ppm (d, 2H), 0.71 ppm (d, 2H), 0.70 ppm (d, 2H), 0.69 ppm (d, 2H), 0.68 ppm (d, 2H), 0.67 ppm (d, 2H), 0.66 ppm (d, 2H), 0.65 ppm (d, 2H), 0.64 ppm (d, 2H), 0.63 ppm (d, 2H), 0.62 ppm (d, 2H), 0.61 ppm (d, 2H), 0.60 ppm (d, 2H), 0.59 ppm (d, 2H), 0.58 ppm (d, 2H), 0.57 ppm (d, 2H), 0.56 ppm (d, 2H), 0.55 ppm (d, 2H), 0.54 ppm (d, 2H), 0.53 ppm (d, 2H), 0.52 ppm (d, 2H), 0.51 ppm (d, 2H), 0.50 ppm (d, 2H), 0.49 ppm (d, 2H), 0.48 ppm (d, 2H), 0.47 ppm (d, 2H), 0.46 ppm (d, 2H), 0.45 ppm (d, 2H), 0.44 ppm (d, 2H), 0.43 ppm (d, 2H), 0.42 ppm (d, 2H), 0.41 ppm (d, 2H), 0.40 ppm (d, 2H), 0.39 ppm (d, 2H), 0.38 ppm (d, 2H), 0.37 ppm (d, 2H), 0.36 ppm (d, 2H), 0.35 ppm (d, 2H), 0.34 ppm (d, 2H), 0.33 ppm (d, 2H), 0.32 ppm (d, 2H), 0.31 ppm (d, 2H), 0.30 ppm (d, 2H), 0.29 ppm (d, 2H), 0.28 ppm (d, 2H), 0.27 ppm (d, 2H), 0.26 ppm (d, 2H), 0.25 ppm (d, 2H), 0.24 ppm (d, 2H), 0.23 ppm (d, 2H), 0.22 ppm (d, 2H), 0.21 ppm (d, 2H), 0.20 ppm (d, 2H), 0.19 ppm (d, 2H), 0.18 ppm (d, 2H), 0.17 ppm (d, 2H), 0.16 ppm (d, 2H), 0.15 ppm (d, 2H), 0.14 ppm (d, 2H), 0.13 ppm (d, 2H), 0.12 ppm (d, 2H), 0.11 ppm (d, 2H), 0.10 ppm (d, 2H), 0.09 ppm (d, 2H), 0.08 ppm (d, 2H), 0.07 ppm (d, 2H), 0.06 ppm (d, 2H), 0.05 ppm (d, 2H), 0.04 ppm (d, 2H), 0.03 ppm (d, 2H), 0.02 ppm (d, 2H), 0.01 ppm (d, 2H), 0.00 ppm (d, 2H).

13C NMR spectrum of compound 1. The x-axis is labeled 'f1 (ppm)' and ranges from 0 to 200. The spectrum shows a solvent peak at 77.2 ppm (CDCl3) and several aliphatic peaks. The peaks are labeled with their chemical shifts: 53.1, 48.5, 45.5, 32.0, 31.8, 30.4, 30.1, 25.8, 25.7, 22.6, 22.6, 14.1, and 14.1. The peaks at 14.1 ppm are the most intense.

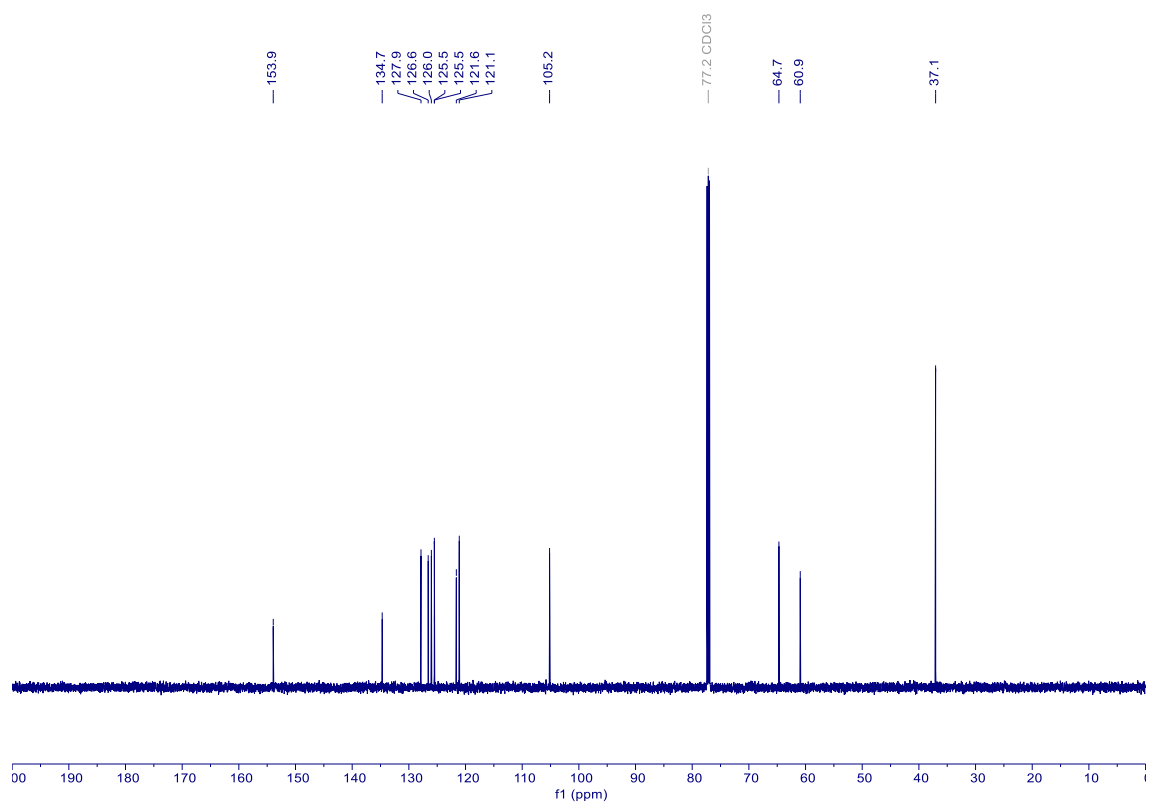
35a – ^{11}B NMR (193 MHz, CDCl_3)



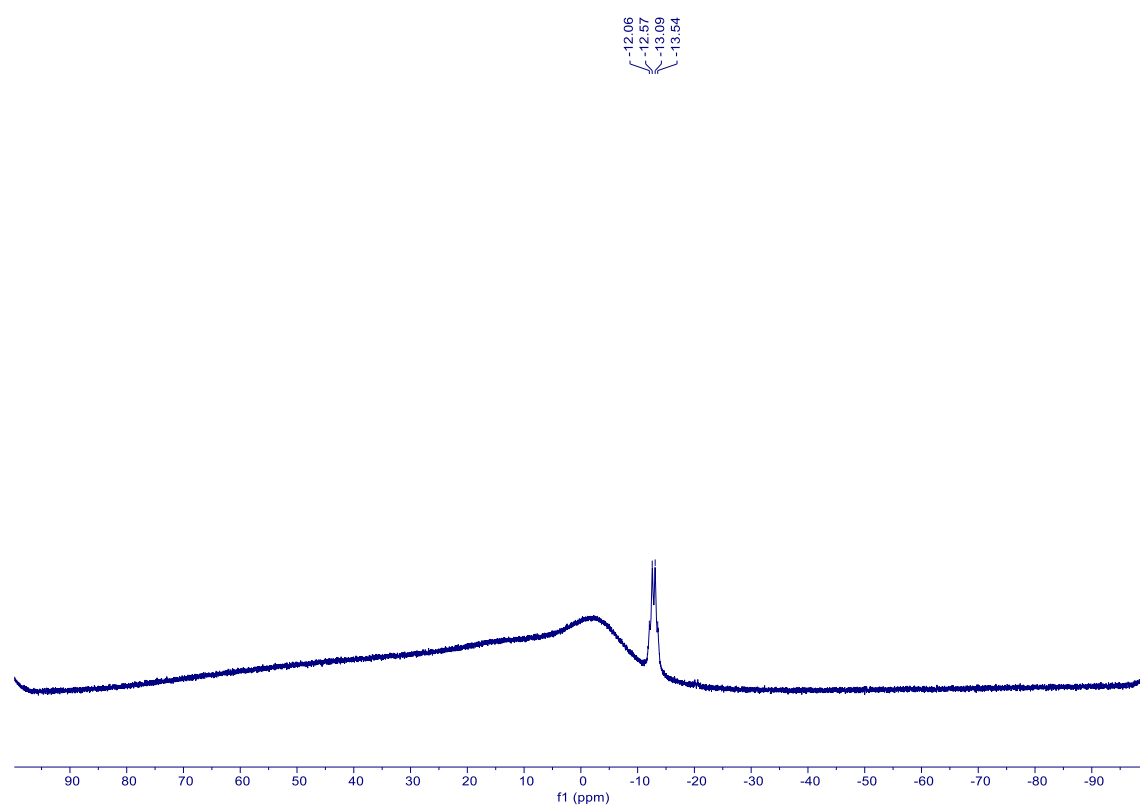
36a – ^1H NMR (600 MHz, CDCl_3)



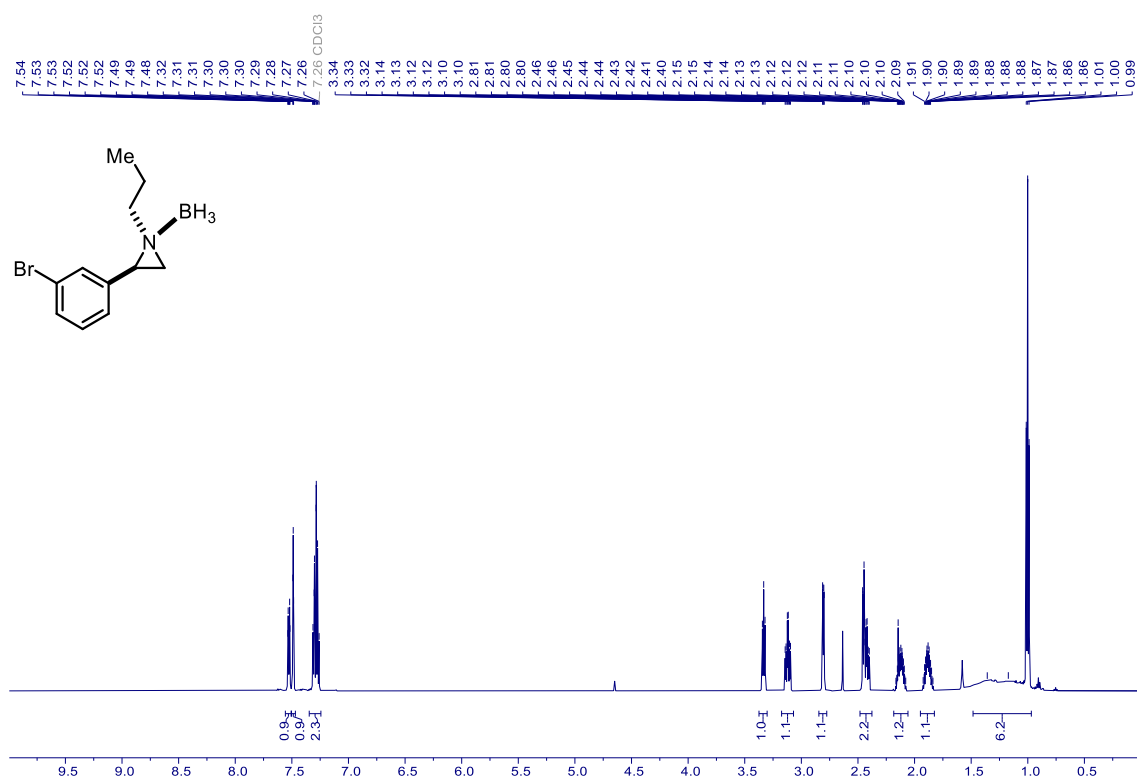
36a – ^{13}C NMR (151 MHz, CDCl_3)



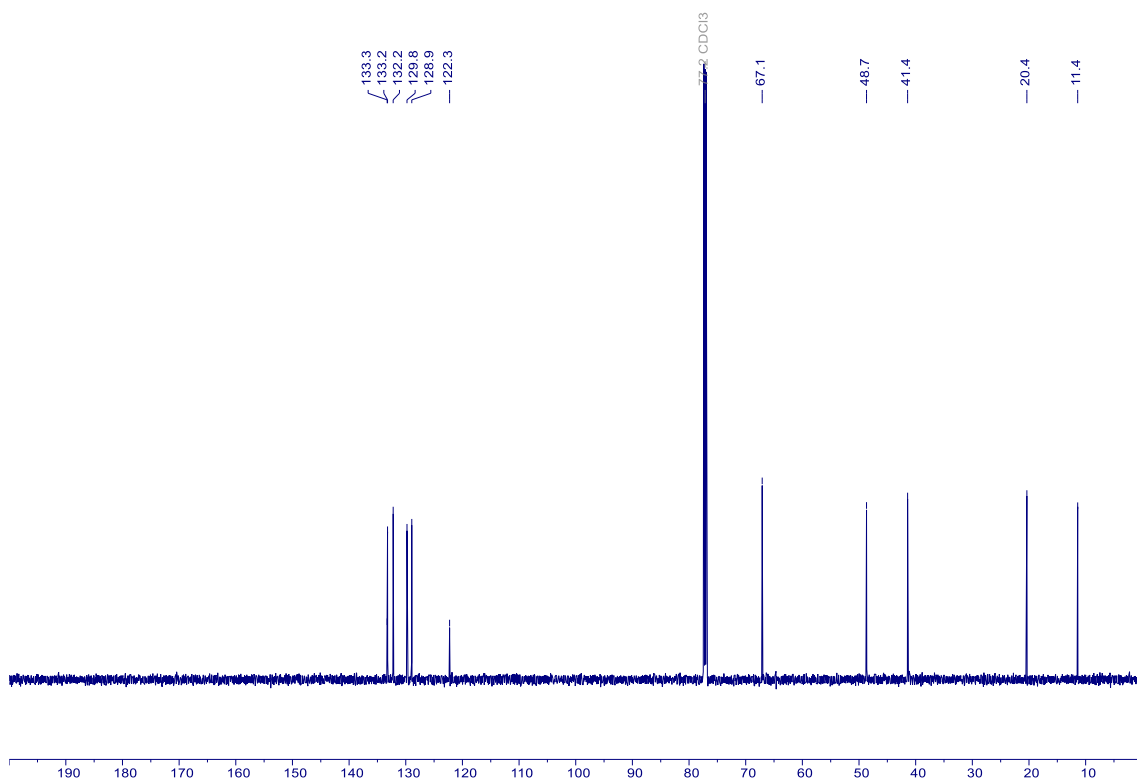
36a – ^{11}B NMR (193 MHz, CDCl_3)



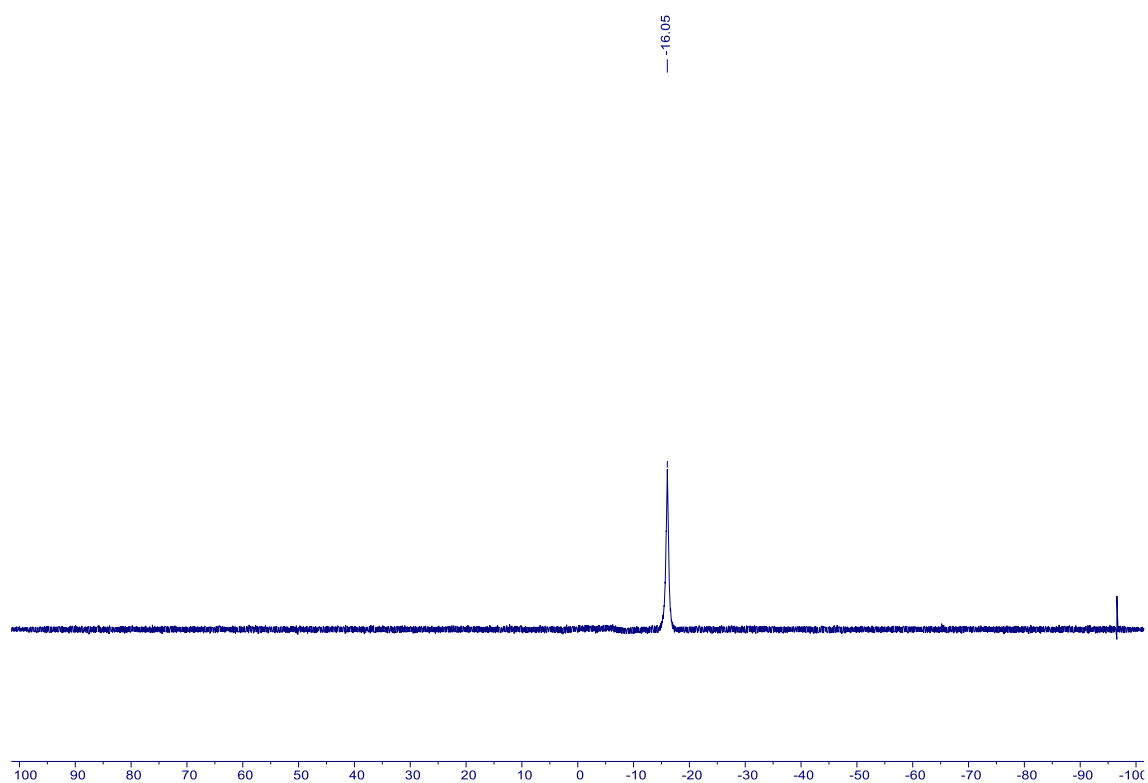
37a – ^1H NMR (600 MHz, CDCl_3)



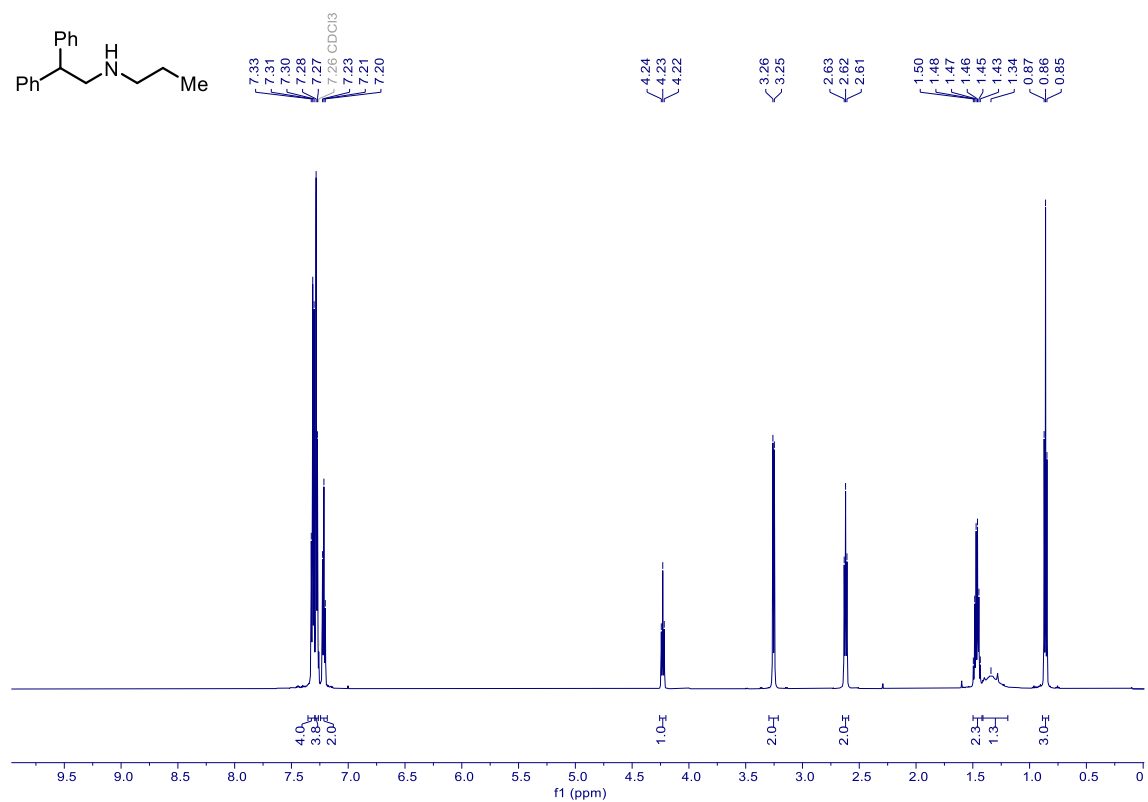
37a – ^{13}C NMR (151 MHz, CDCl_3)



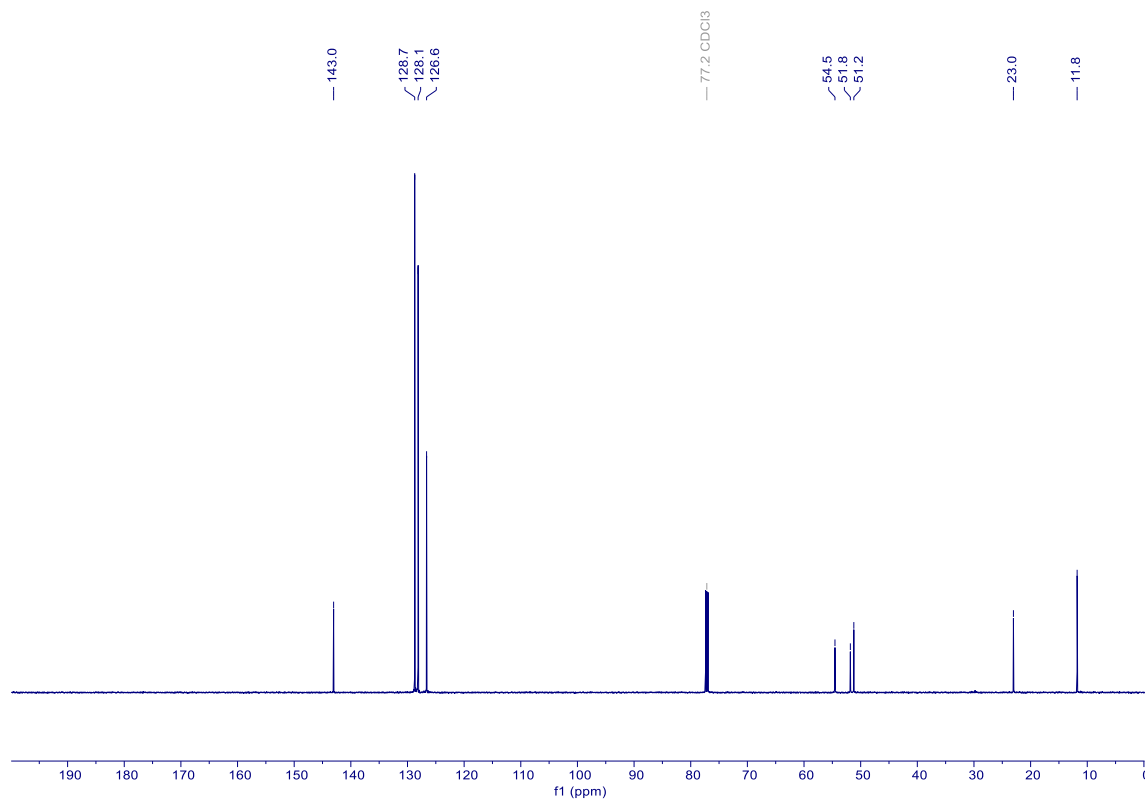
37a – ^{11}B NMR (192 MHz, CDCl_3)



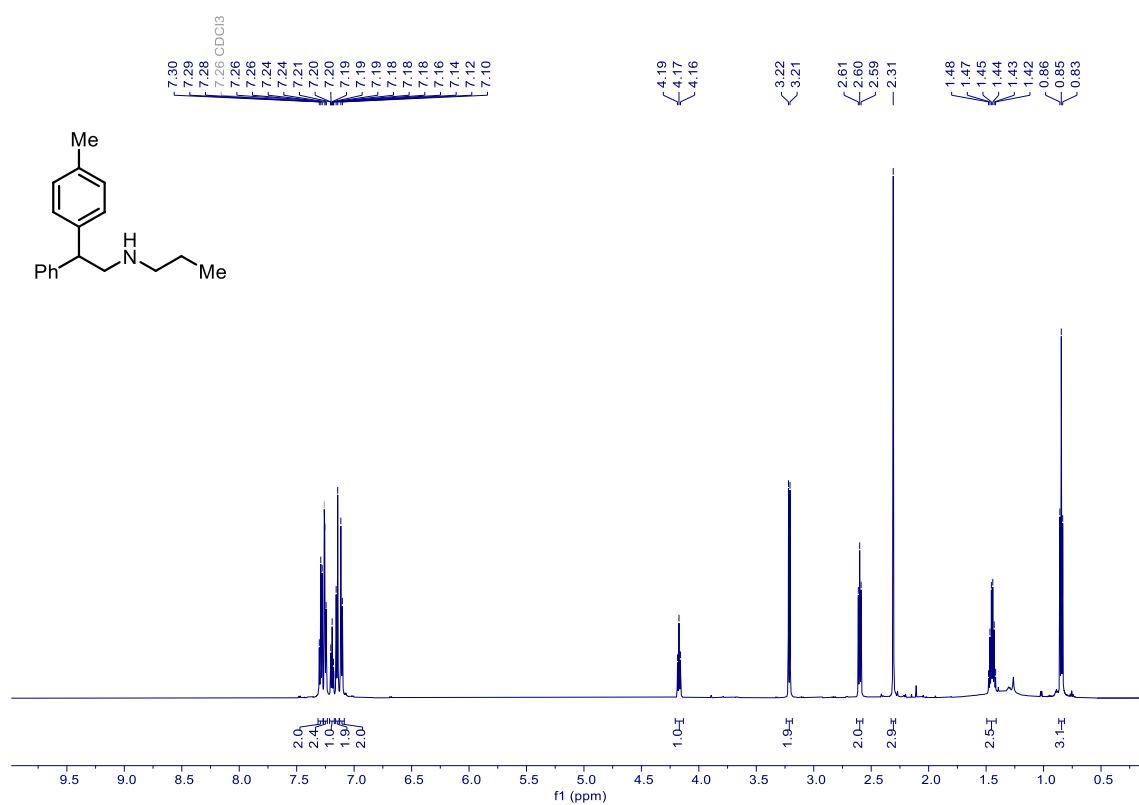
1b – ^1H NMR (600 MHz, CDCl_3)



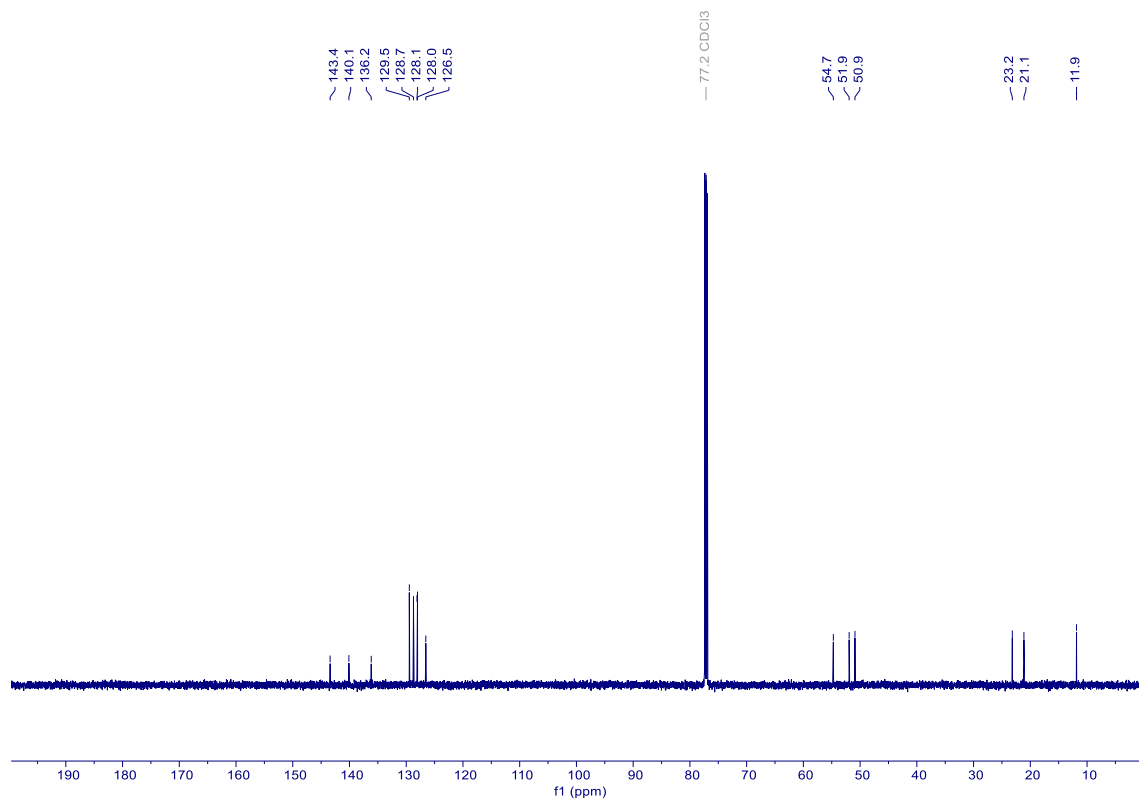
1b – ^{13}C NMR (151 MHz, CDCl_3)



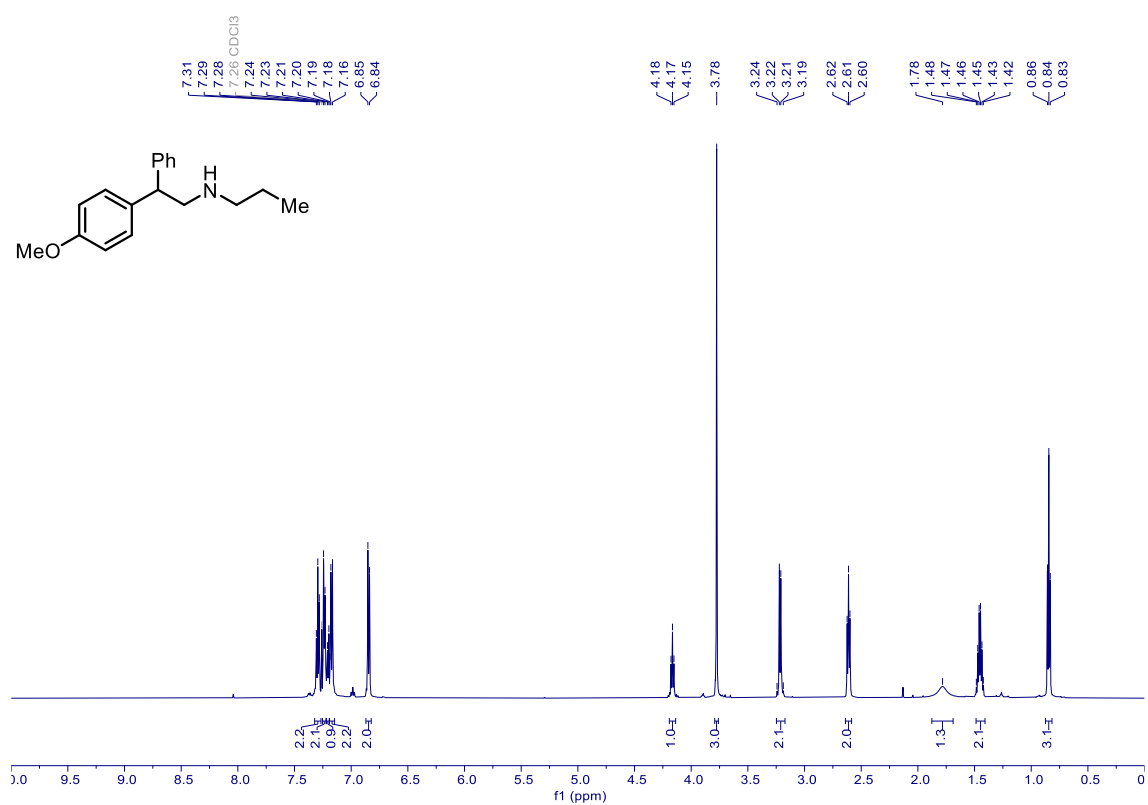
1c – ^1H NMR (600 MHz, CDCl_3)



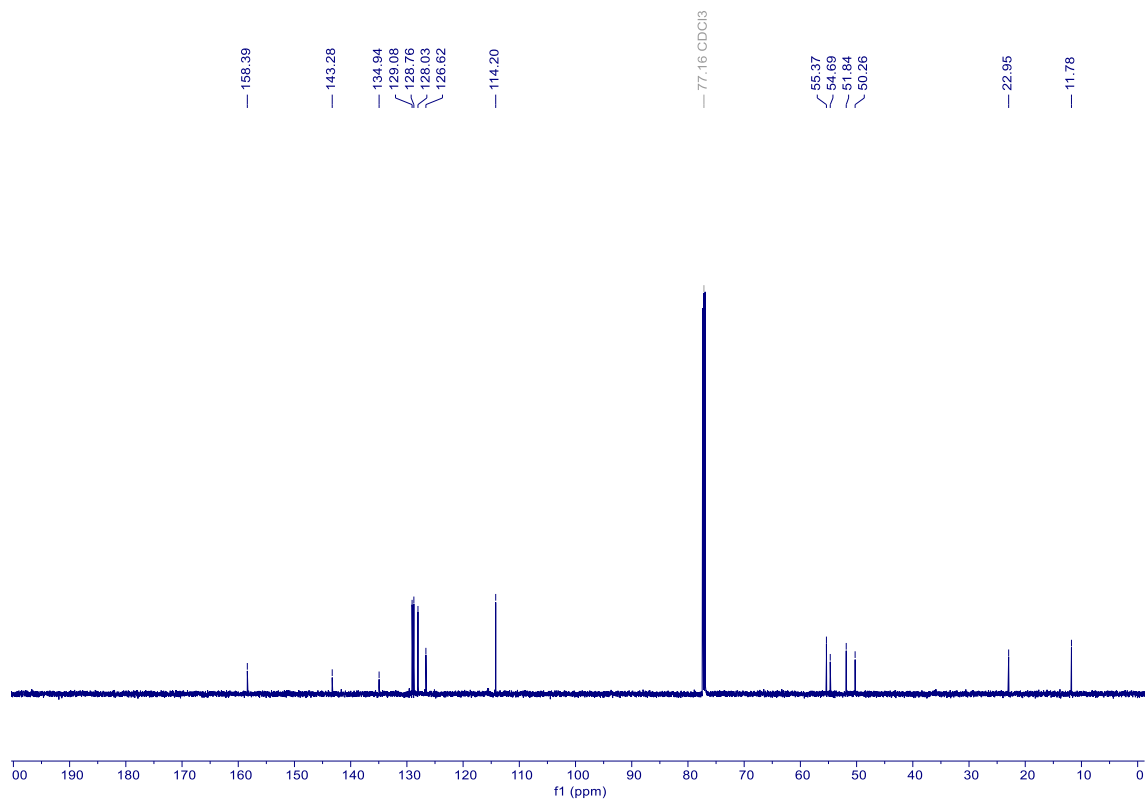
1c – ^{13}C NMR (151 MHz, CDCl_3)



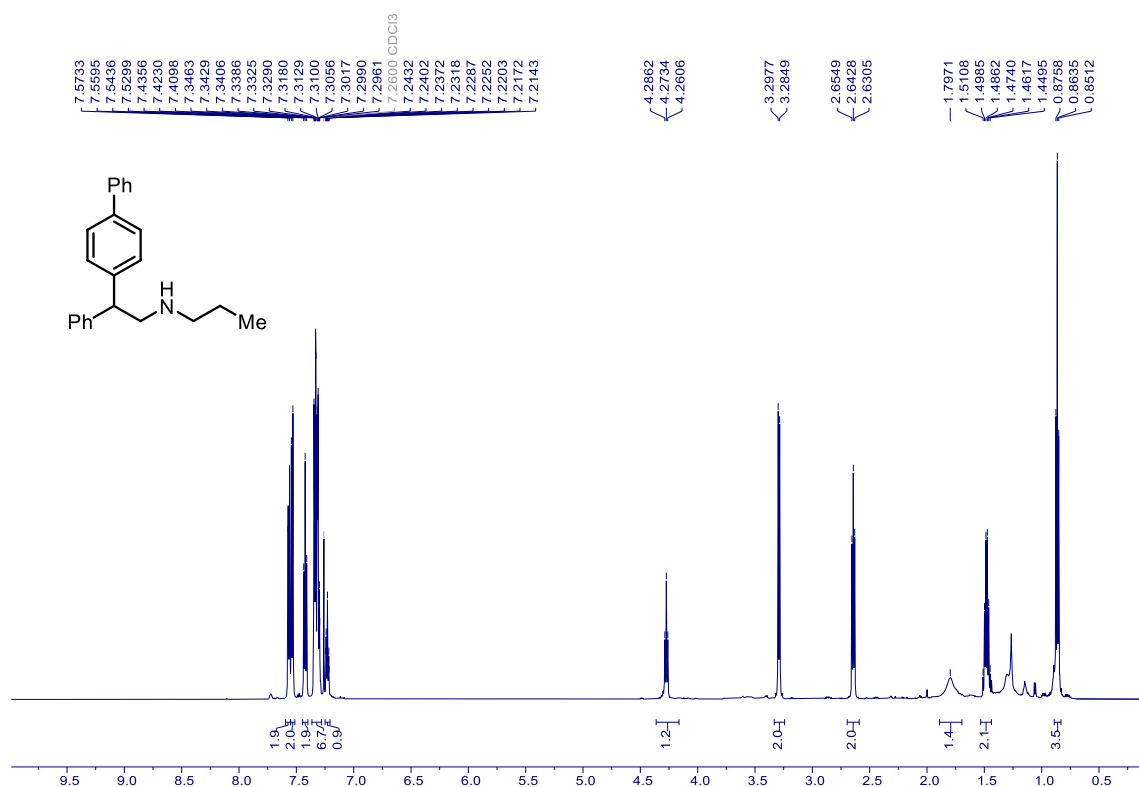
1d/3b – ^1H NMR (600 MHz, CDCl_3)



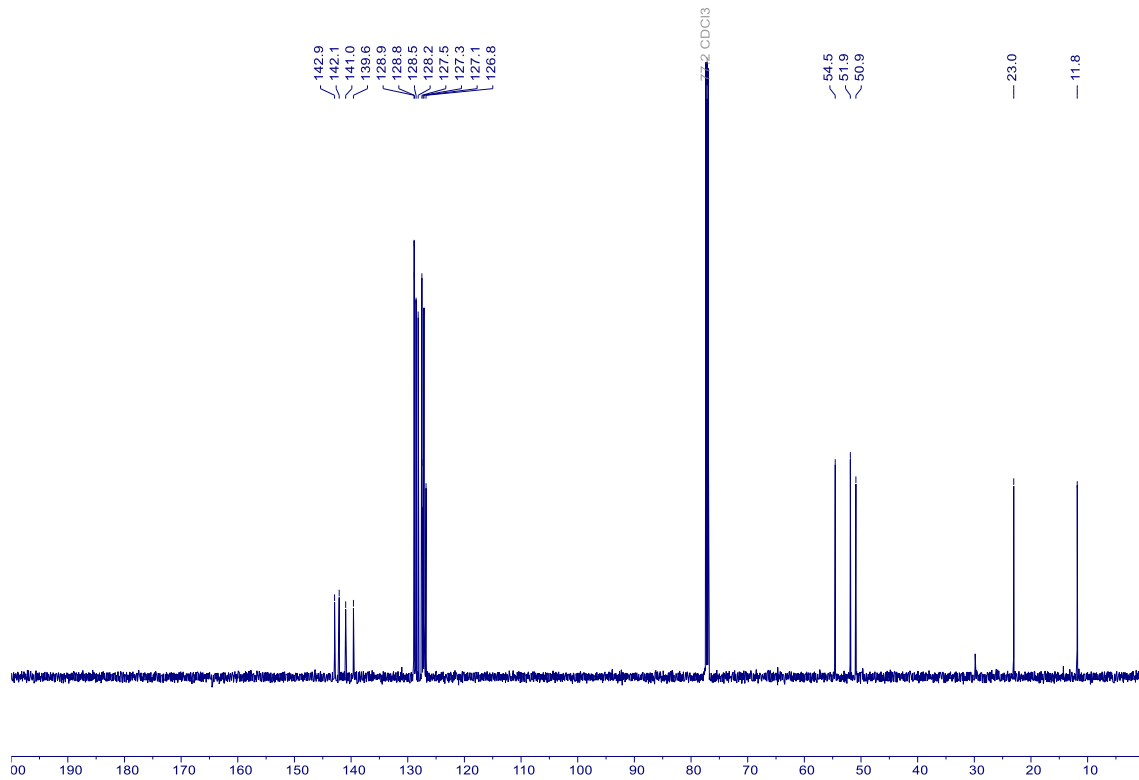
1d/3b – ^{13}C NMR (151 MHz, CDCl_3)



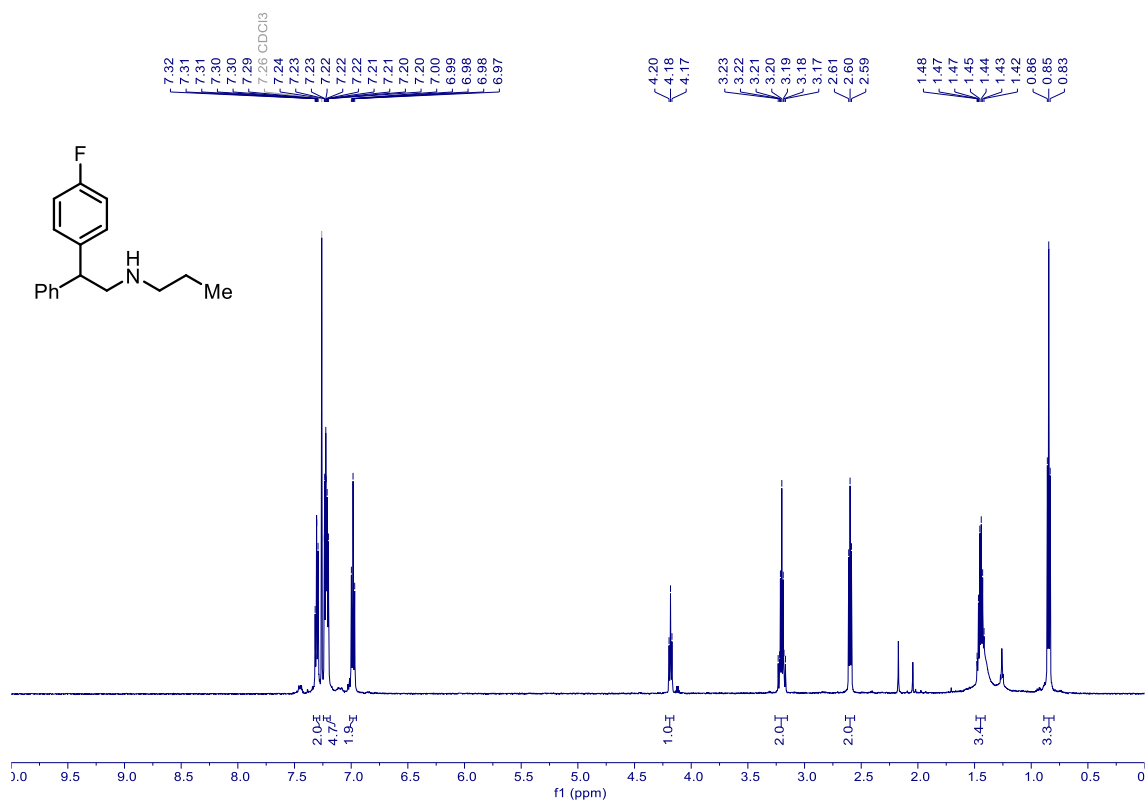
1e – ^1H NMR (600 MHz, CDCl_3)



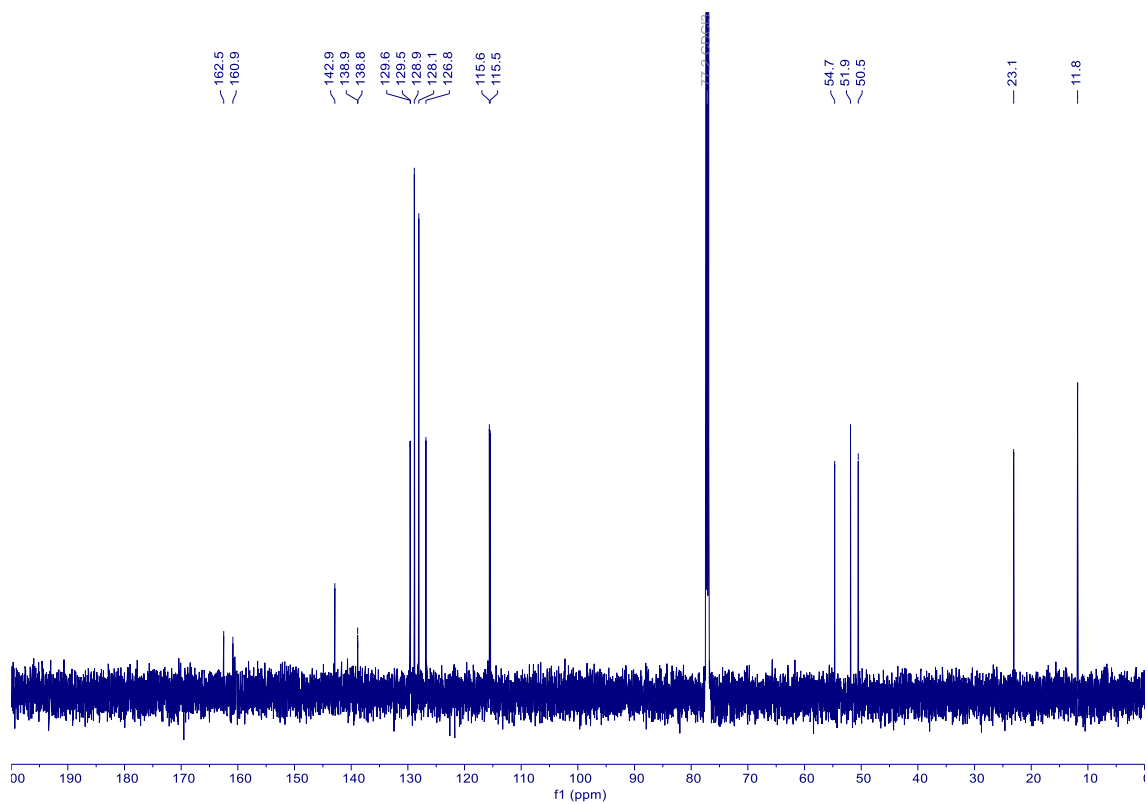
1e – ^{13}C NMR (151 MHz, CDCl_3)



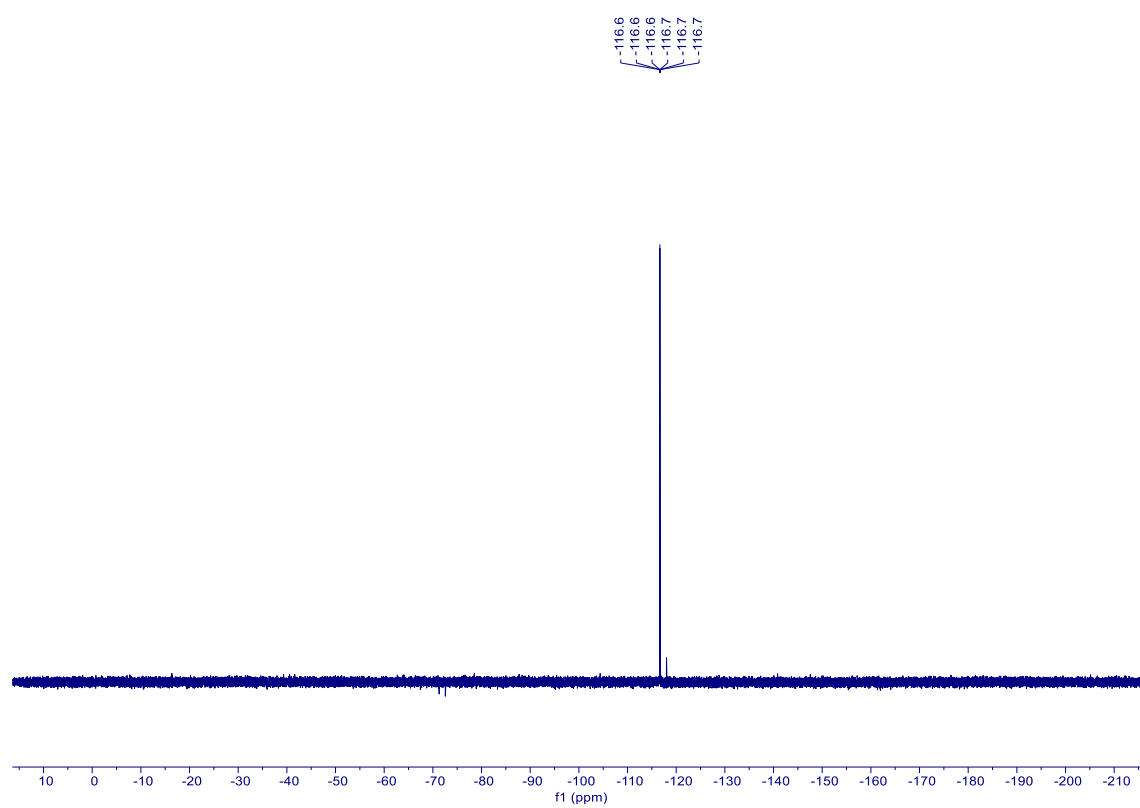
1f – ^1H NMR (600 MHz, CDCl_3)



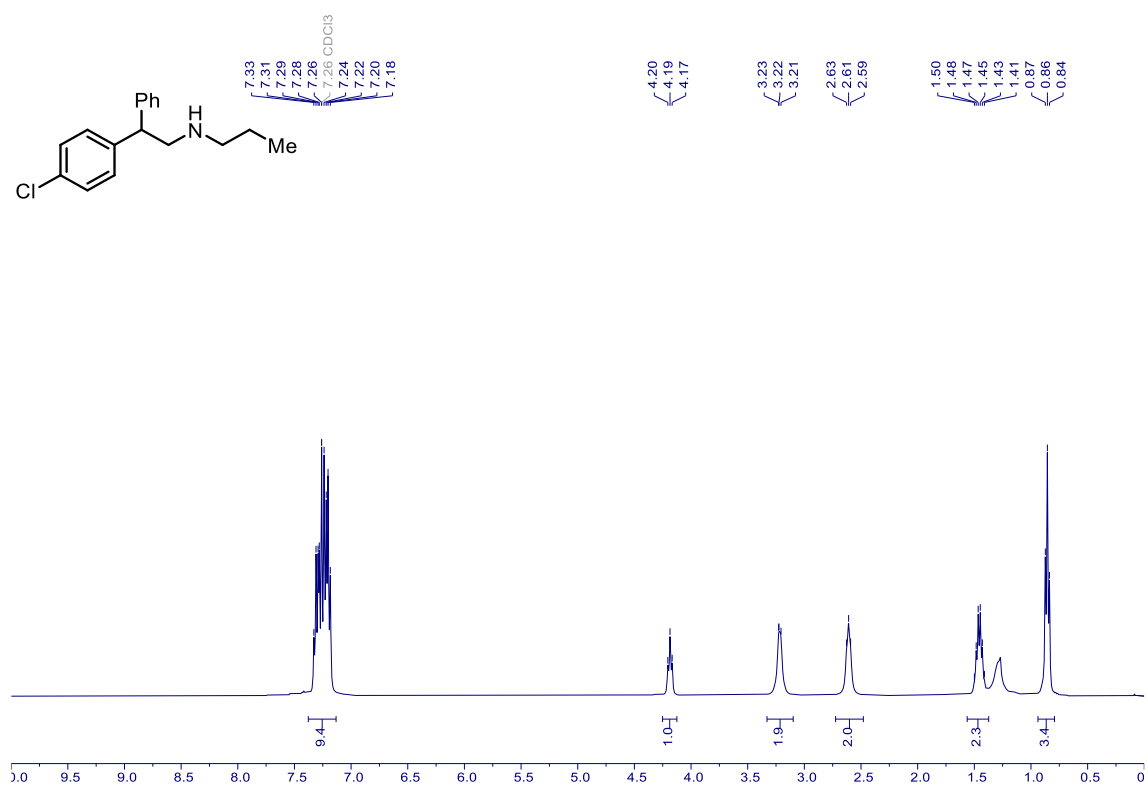
1f – ^{13}C NMR (151 MHz, CDCl_3)



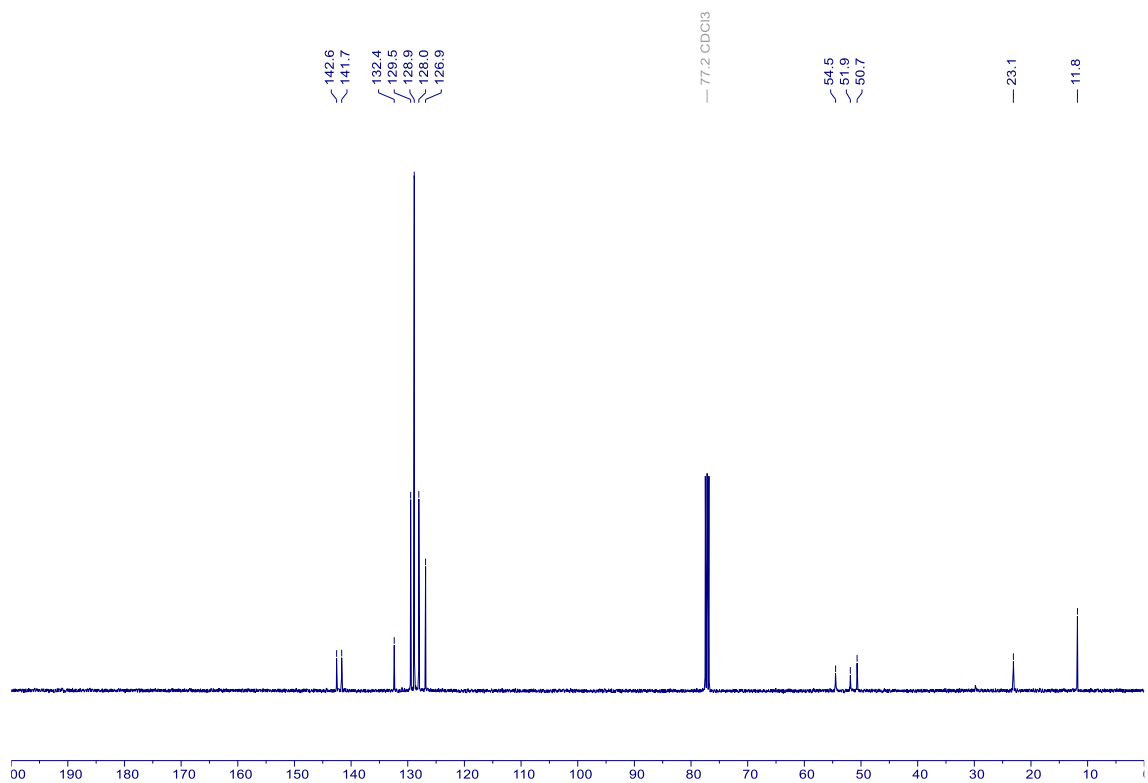
1f – ^{19}F NMR (565 MHz, CDCl_3)



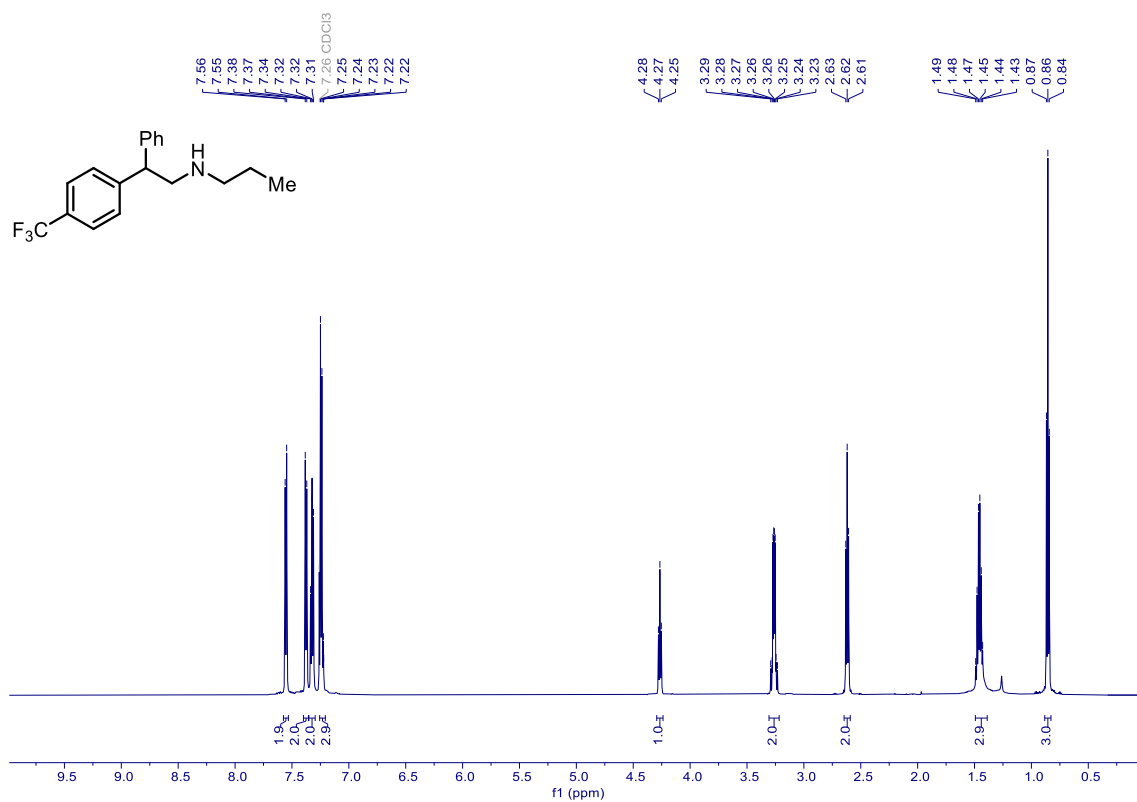
1g/5b – ^1H NMR (400 MHz, CDCl_3)



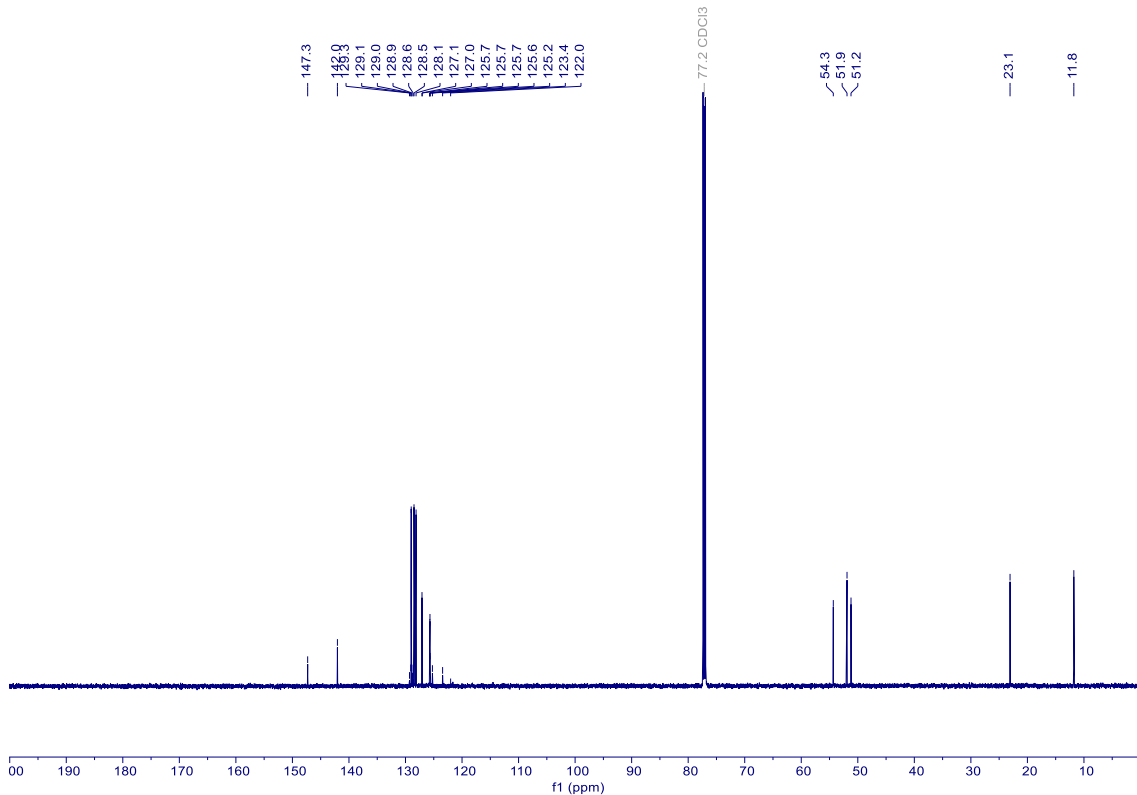
1g/5b – ^{13}C NMR (101 MHz, CDCl_3)



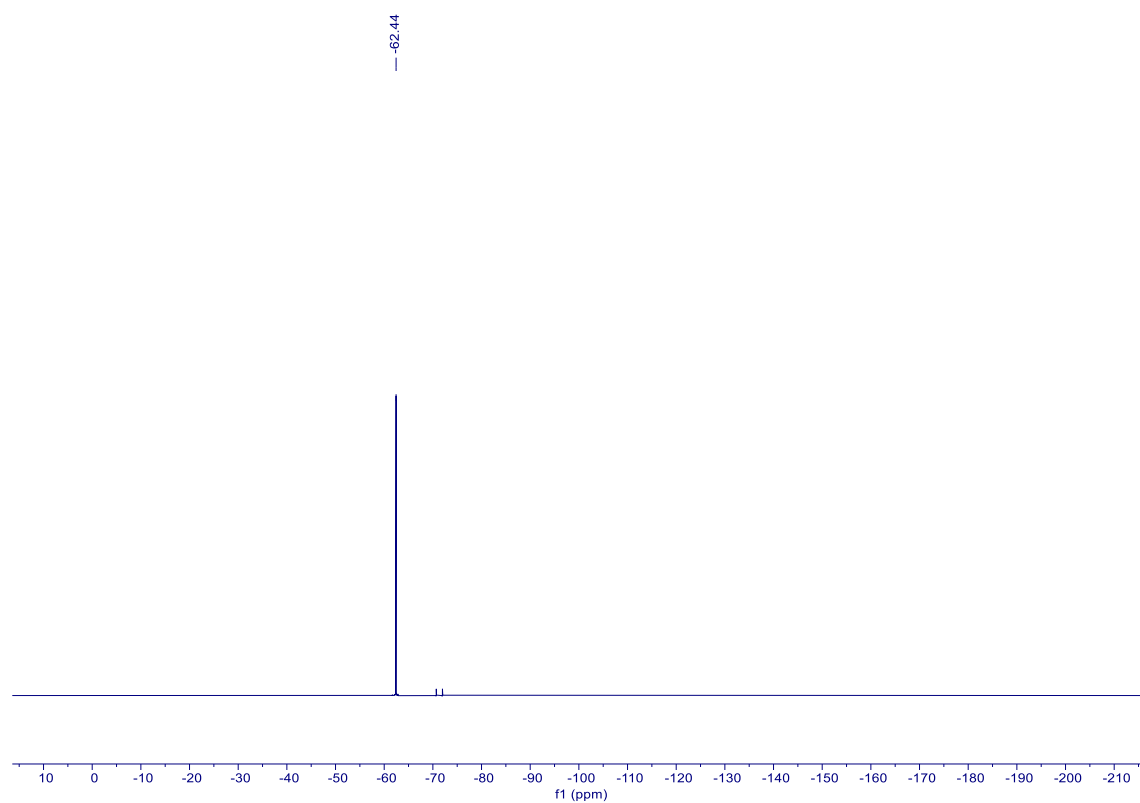
1h/6b – ^1H NMR (600 MHz, CDCl_3)



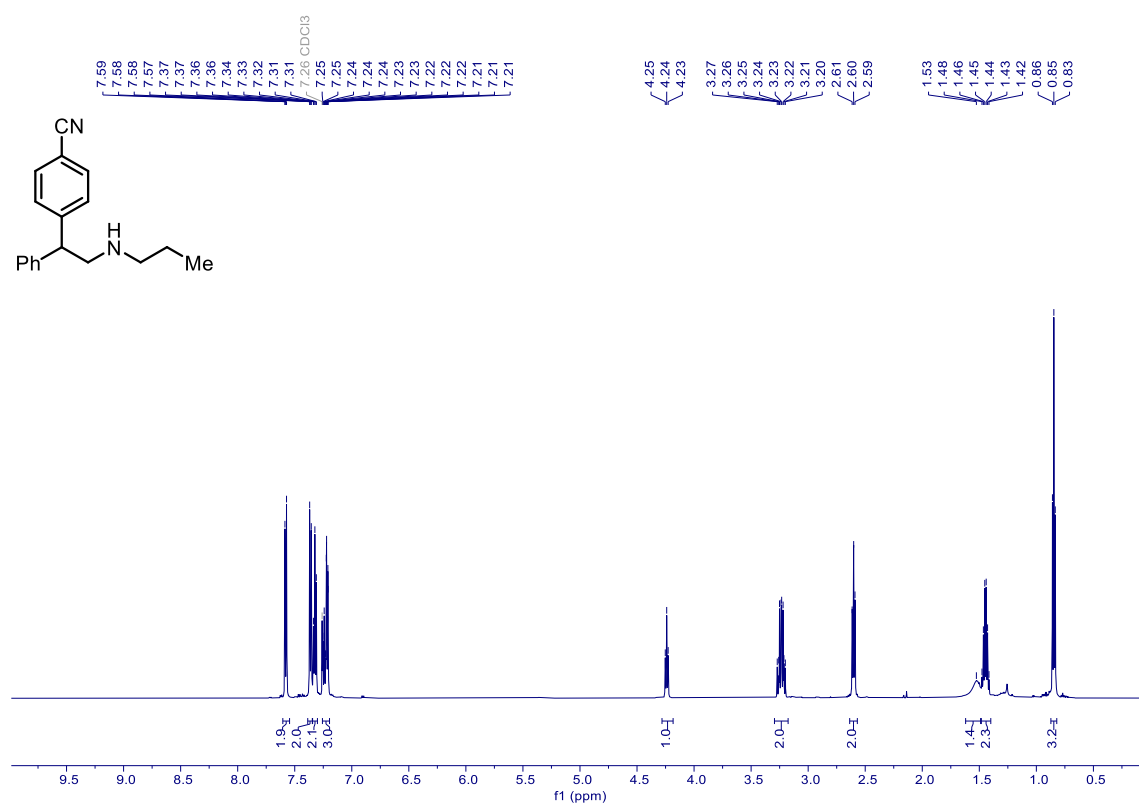
1h/6b – ^{13}C NMR (151 MHz, CDCl_3)



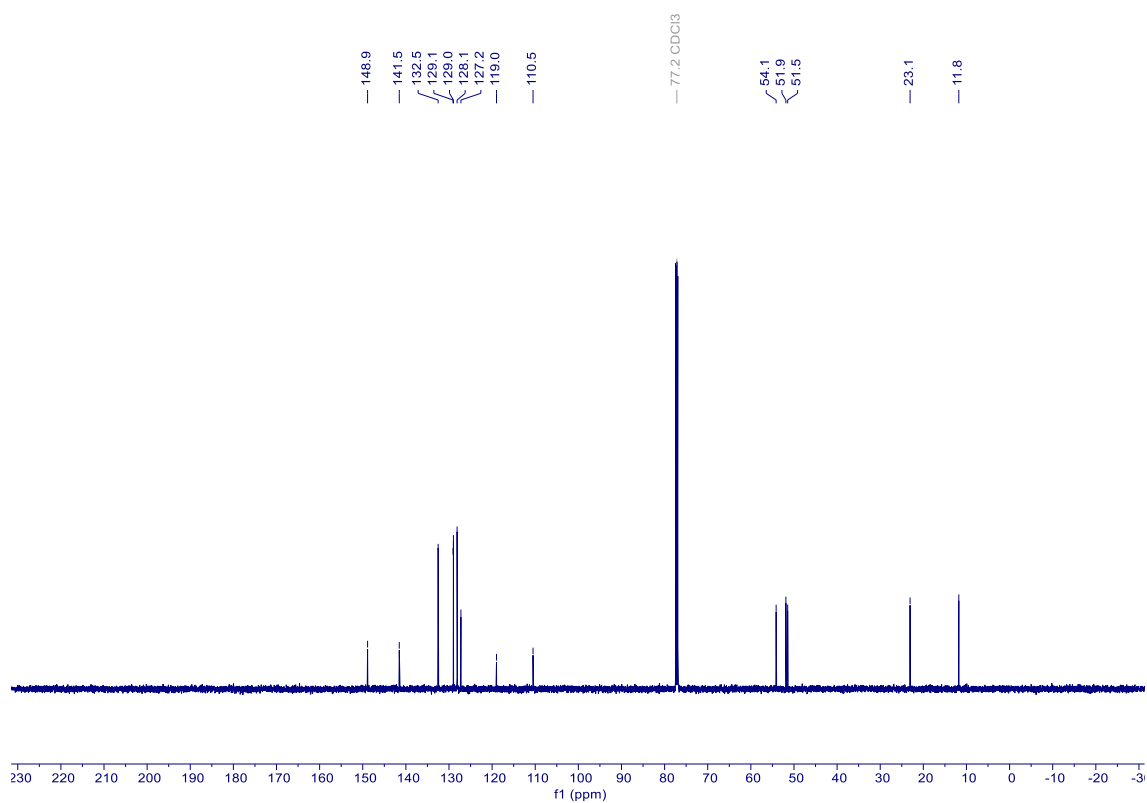
1h/6b – ^{19}F NMR (565 MHz, CDCl_3)



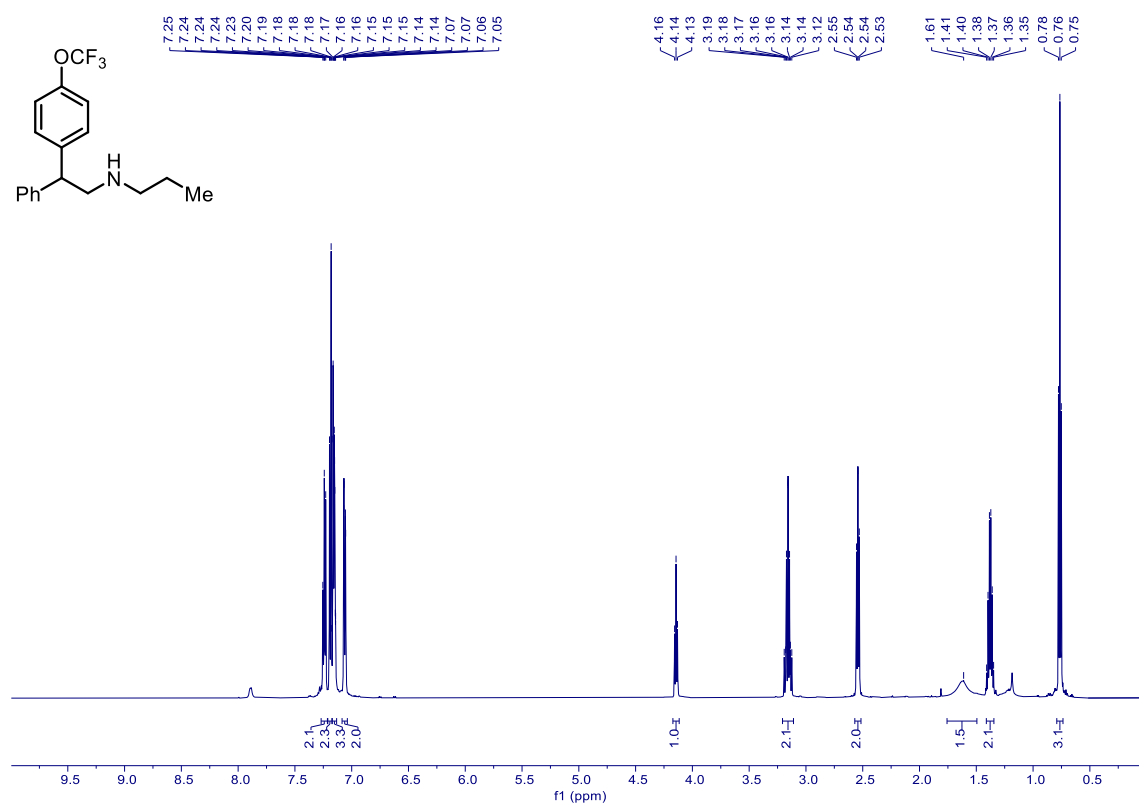
1i – ^1H NMR (600 MHz, CDCl_3)



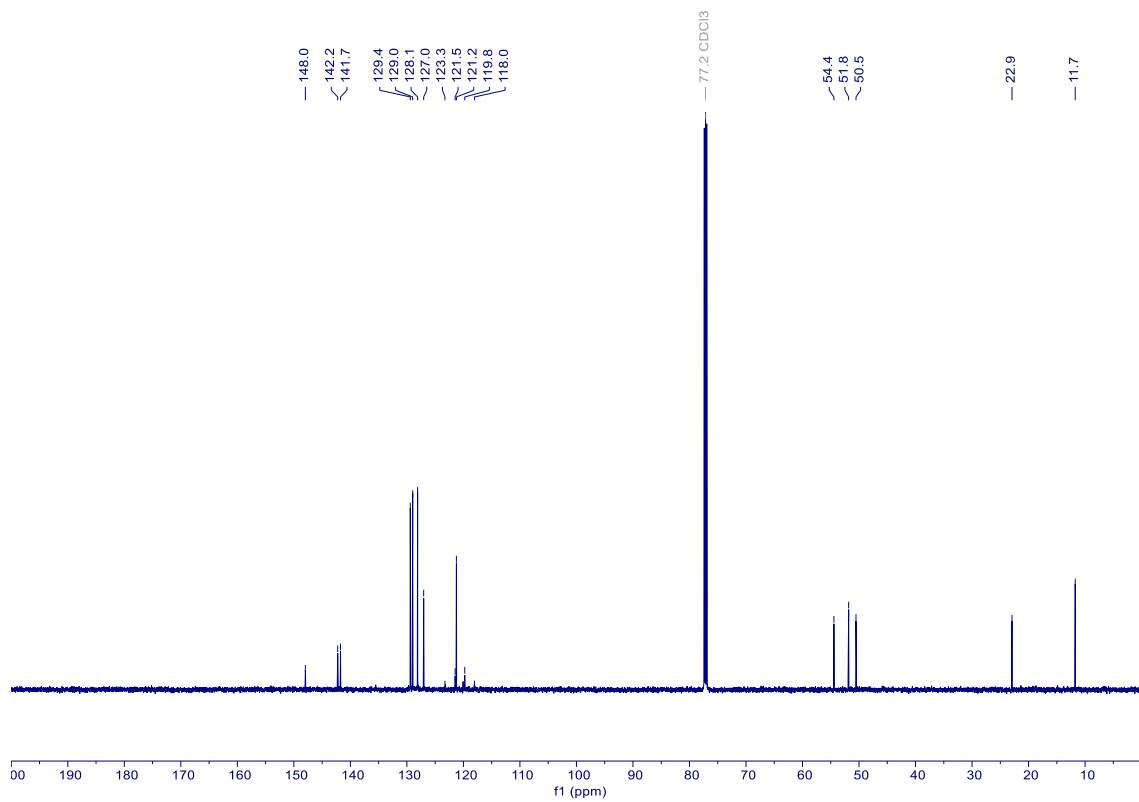
1i – ^{13}C NMR (151 MHz, CDCl_3)



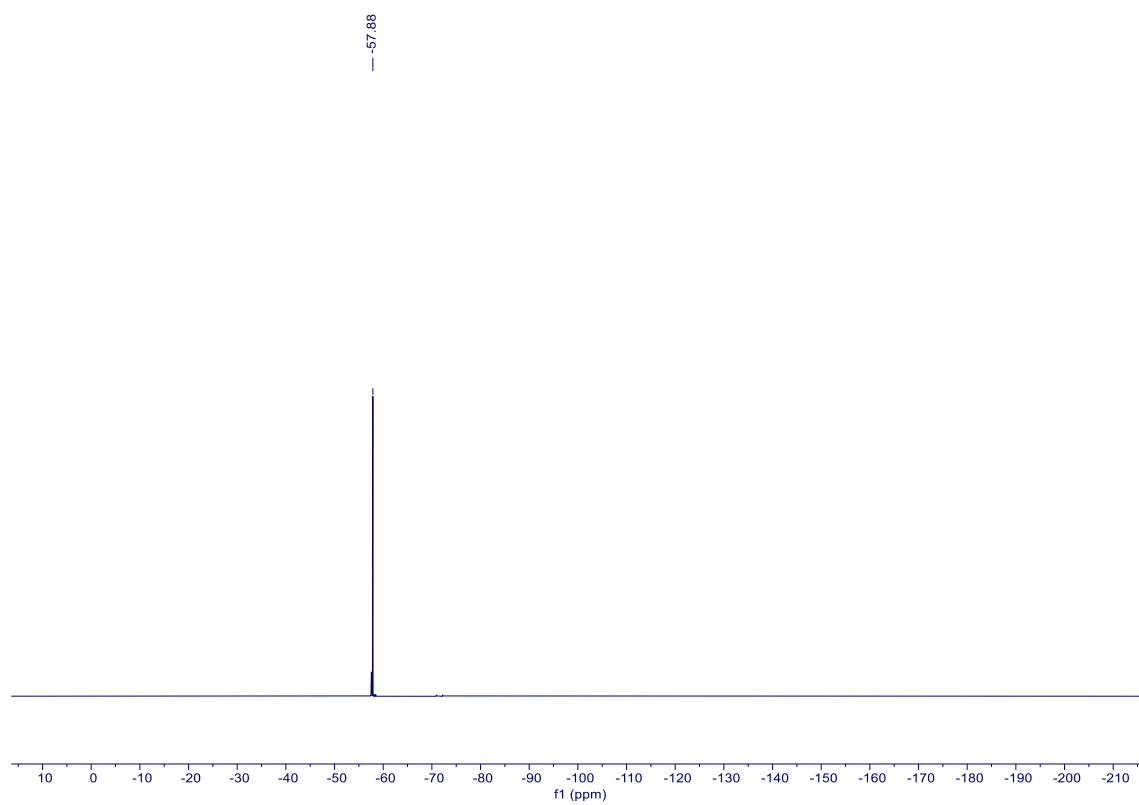
1j – ^1H NMR (600 MHz, CDCl_3)



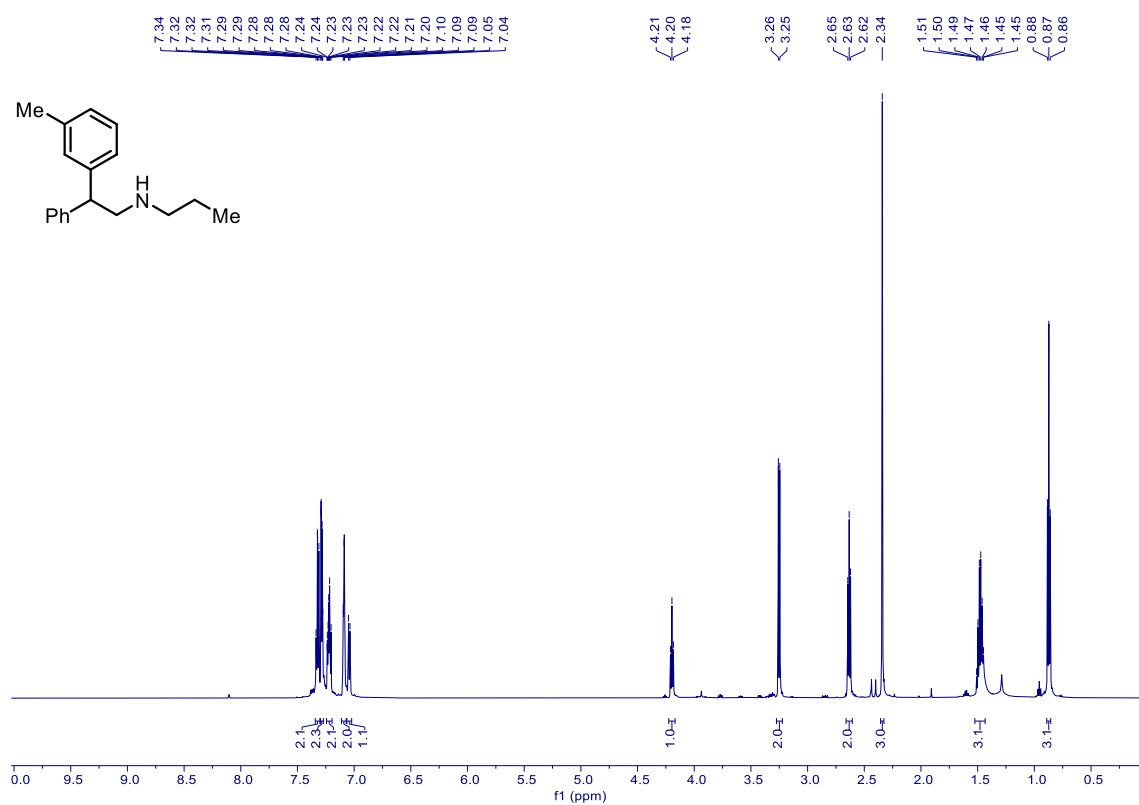
1j – ^{13}C NMR (151 MHz, CDCl_3)



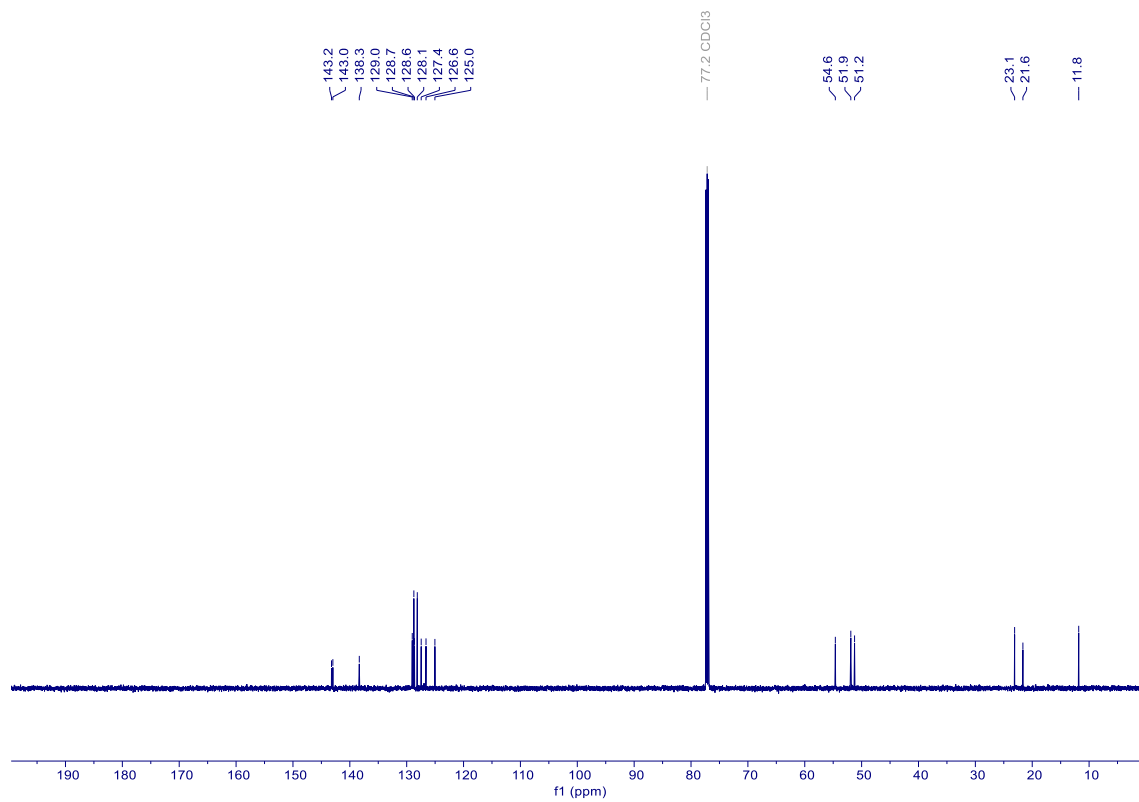
1j – ^{19}F NMR (565 MHz, CDCl_3)



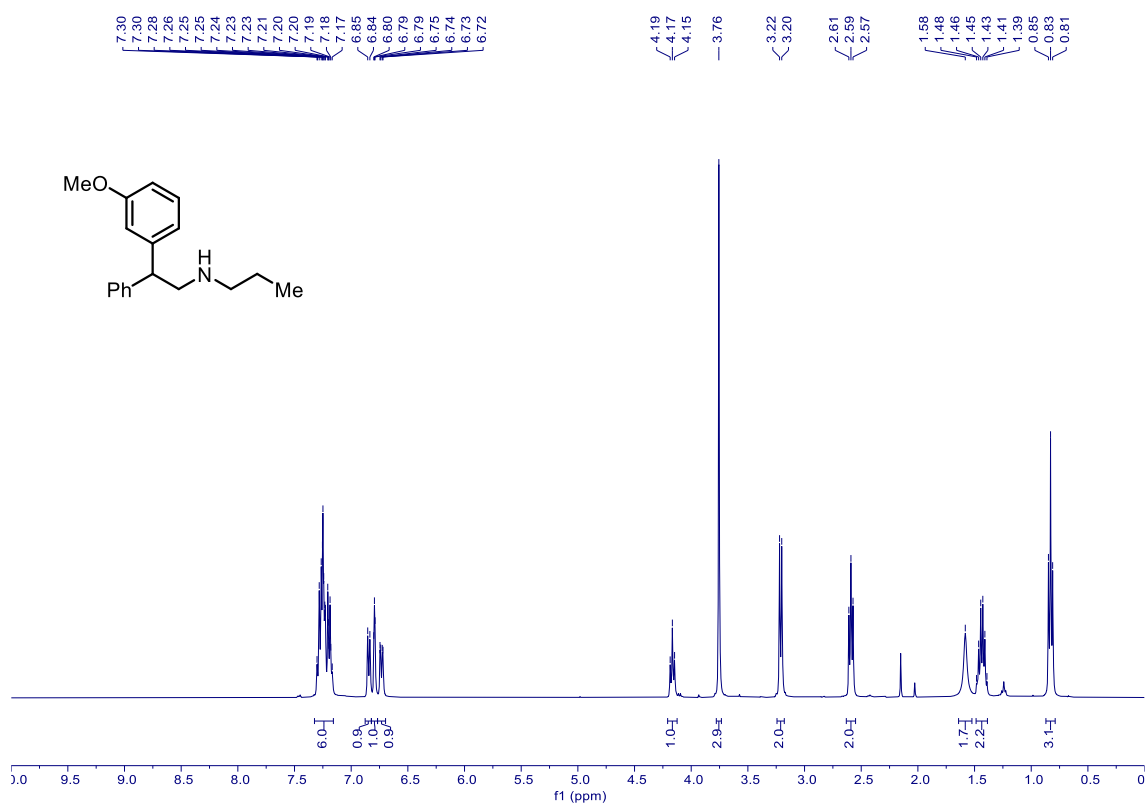
1k – ^1H NMR (600 MHz, CDCl_3)



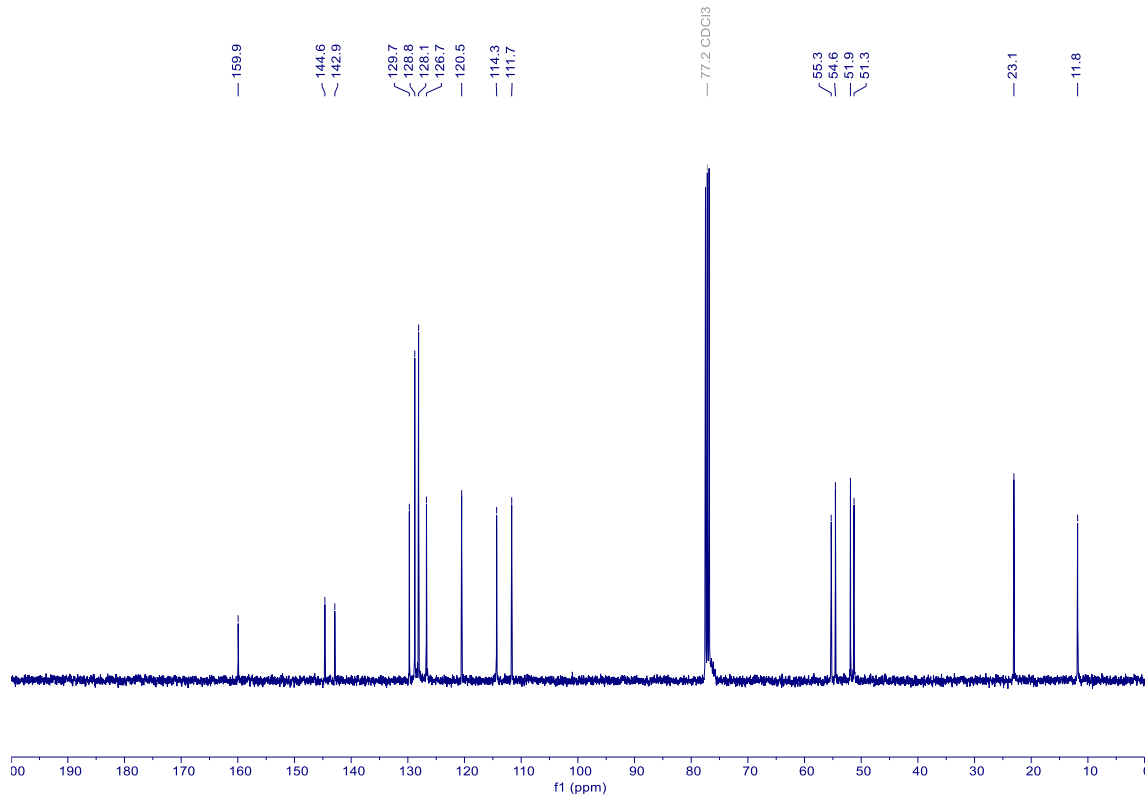
1k – ^{13}C NMR (151 MHz, CDCl_3)



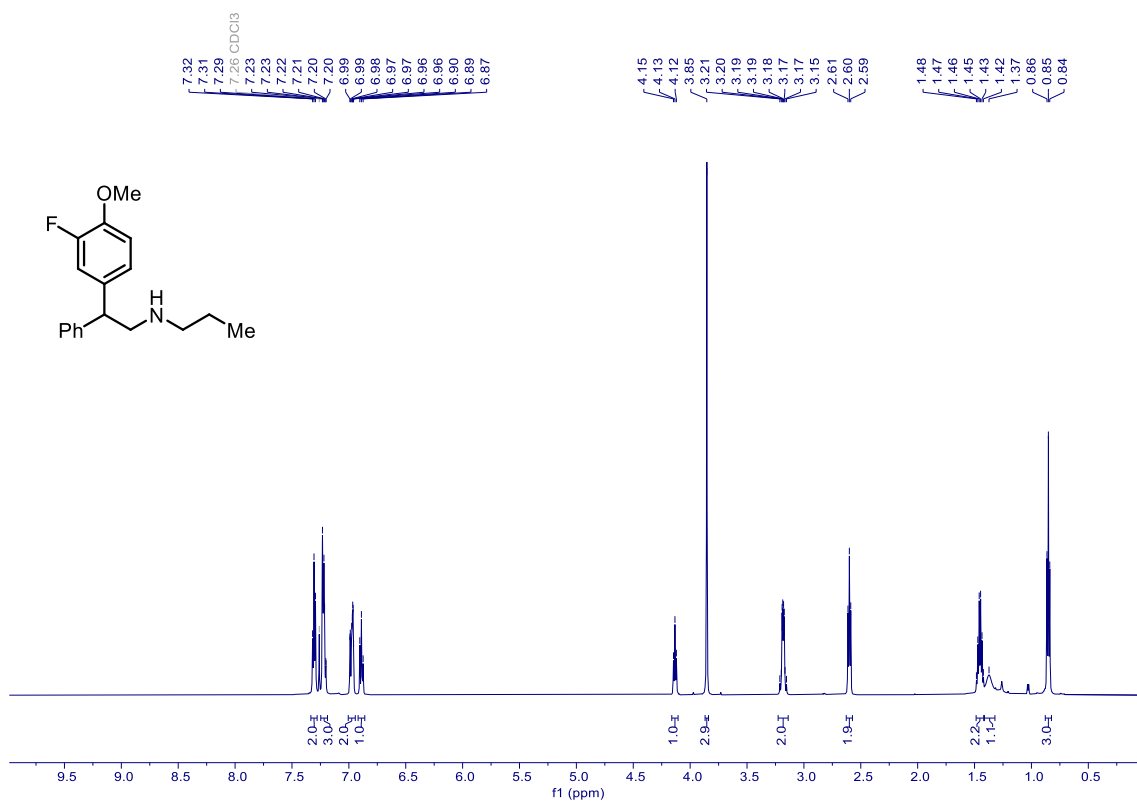
11 – ^1H NMR (400 MHz, CDCl_3)



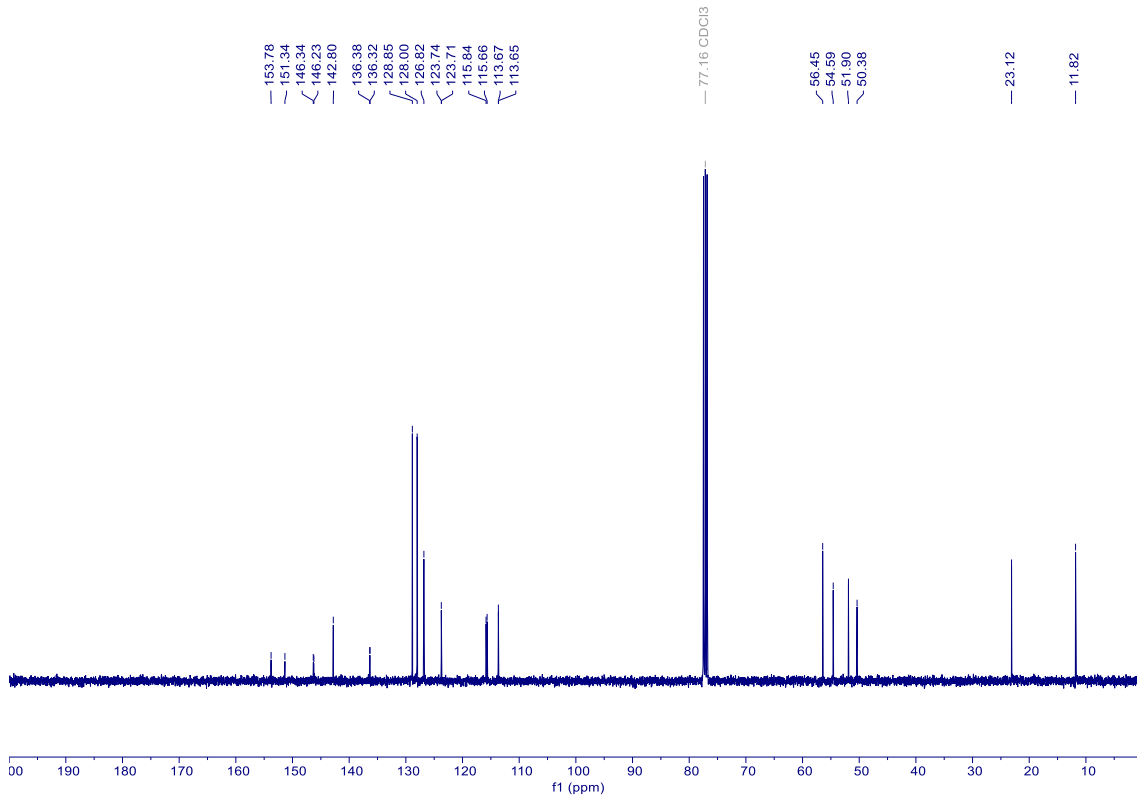
11 – ^{13}C NMR (101 MHz, CDCl_3)



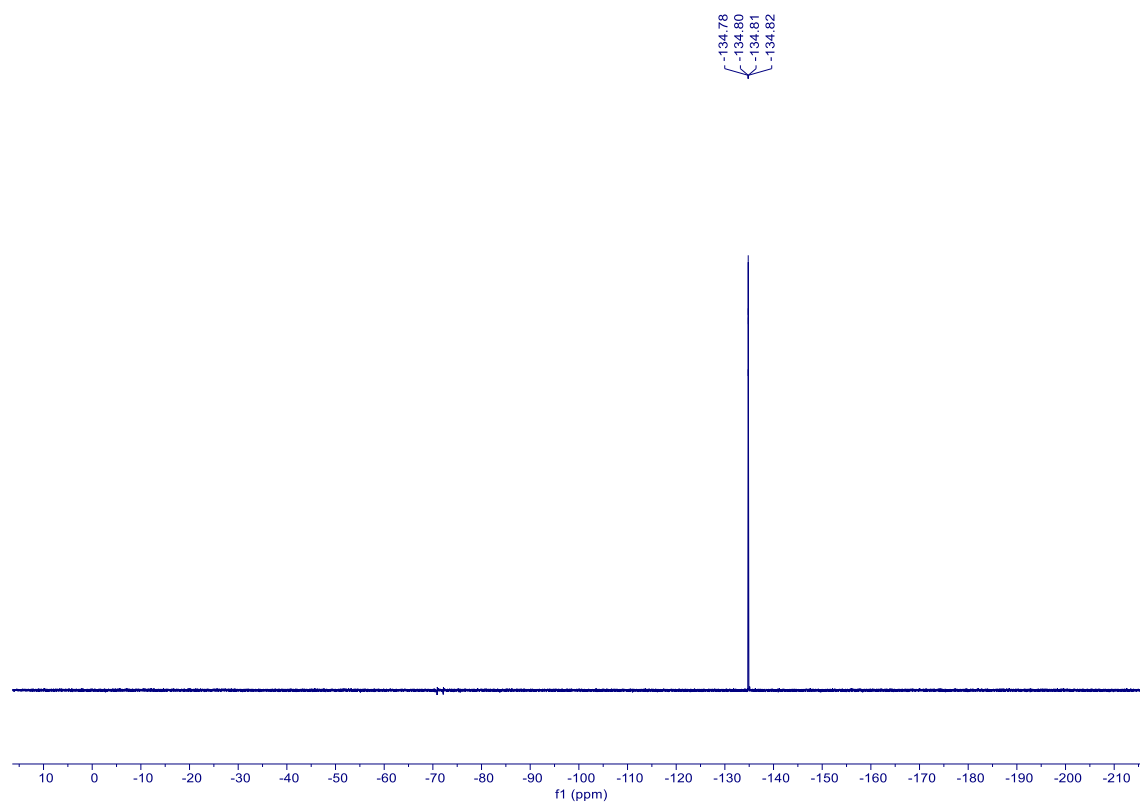
1m – ^1H NMR (600 MHz, CDCl_3)



1m – ^{13}C NMR (101 MHz, CDCl_3)



1m – ^{19}F NMR (565 MHz, CDCl_3)



CCNCCc1ccccc1

¹H NMR spectrum (CDCl₃) of N-propylbenzylamine. The spectrum shows aromatic protons (7.21-7.81 ppm), a triplet for the benzylic CH₂ (2.91 ppm), a quartet for the propyl CH₂ (1.61 ppm), and a triplet for the propyl methyl (0.91 ppm). Integration values are provided below the peaks.

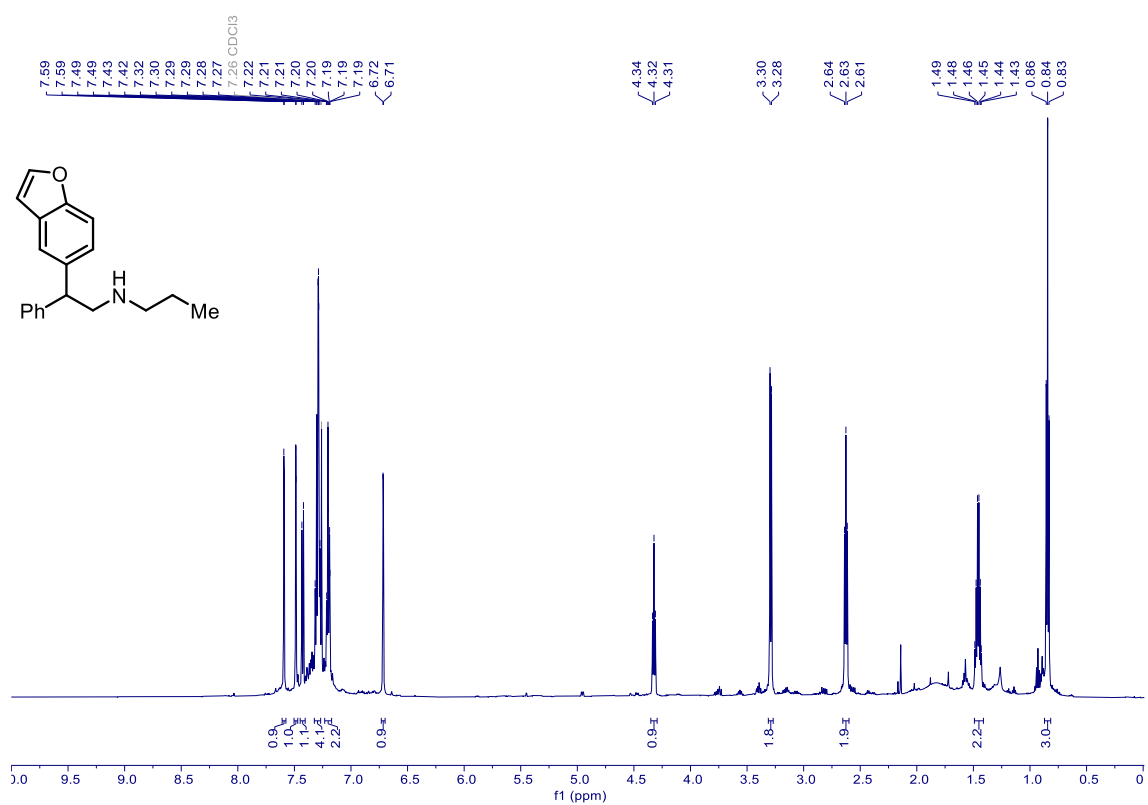
Chemical Shift (ppm)	Integration
7.81	3.1
7.80	1.0
7.79	2.1
7.78	1.0
7.77	3.9
7.73	1.0
7.73	1.0
7.48	1.0
7.47	1.0
7.46	1.0
7.46	1.0
7.45	1.0
7.45	1.0
7.45	1.0
7.44	1.0
7.44	1.0
7.43	1.0
7.42	1.0
7.39	1.0
7.37	1.0
7.36	1.0
7.34	1.0
7.30	1.0
7.28	1.0
7.23	1.0
7.22	1.0
7.21	1.0
7.21	1.0
4.40	1.0
4.39	1.0
4.38	1.0
3.41	2.1
3.39	2.1
3.39	2.1
3.37	2.1
3.36	2.1
3.35	2.1
3.34	2.1
3.33	2.1
2.67	2.0
2.66	2.0
2.64	2.0
1.84	1.5
1.50	1.5
1.49	1.5
1.47	1.5
1.46	1.5
1.45	1.5
1.44	1.5
0.86	3.3
0.85	3.3
0.84	3.3

142.8
140.3
133.7
132.5
128.8
128.5
128.2
127.9
127.7
126.8
126.4
126.2
125.8
77.2
54.4
51.9
51.2
22.9
11.8

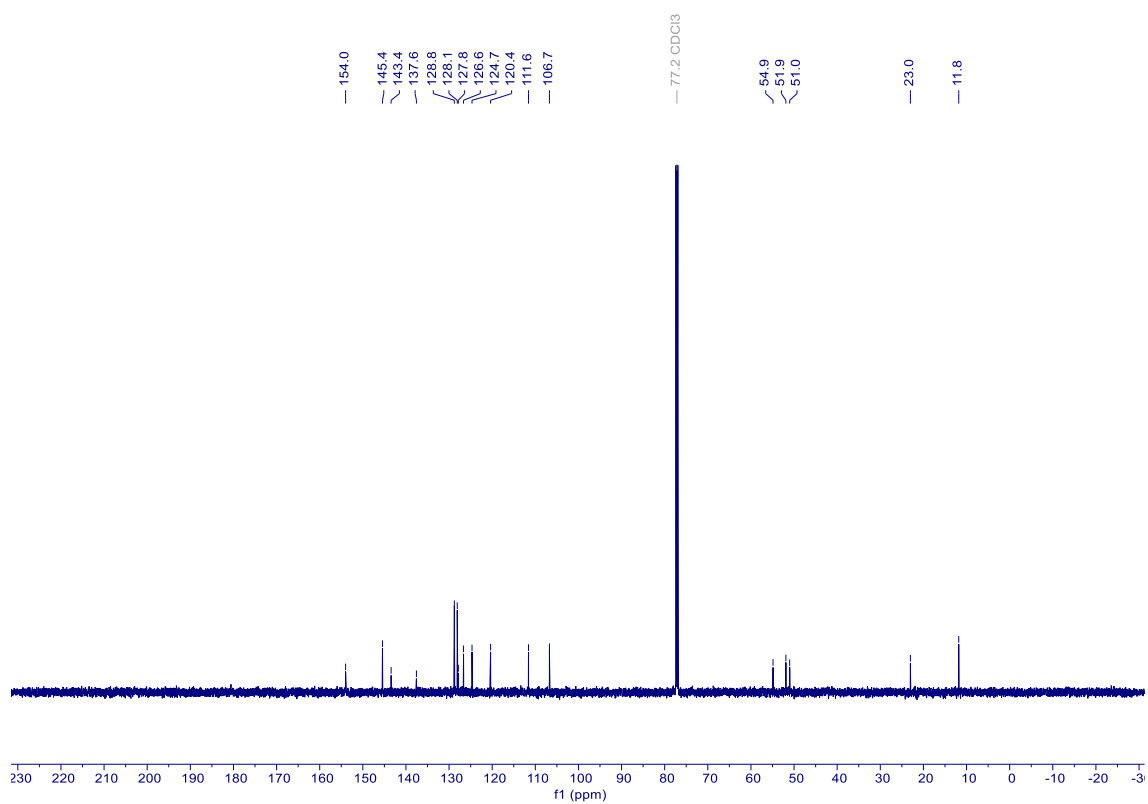
CDCl₃

f1 (ppm)

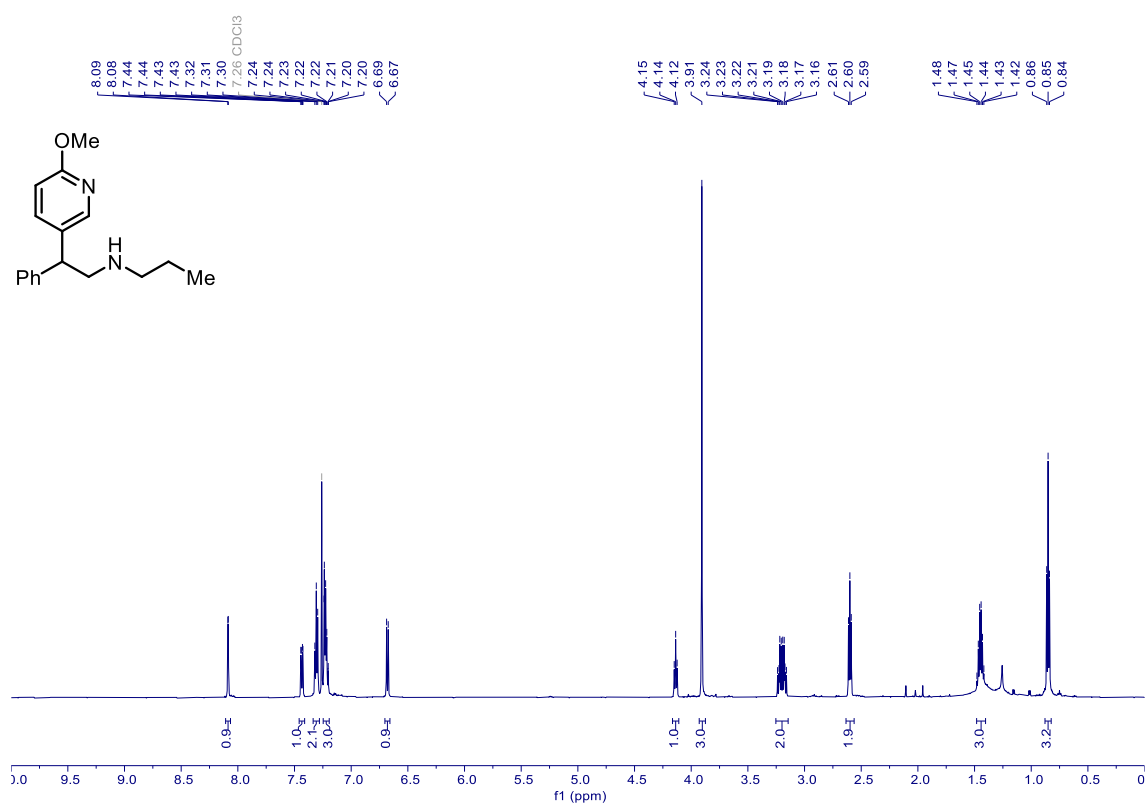
1o – ^1H NMR (600 MHz, CDCl_3)



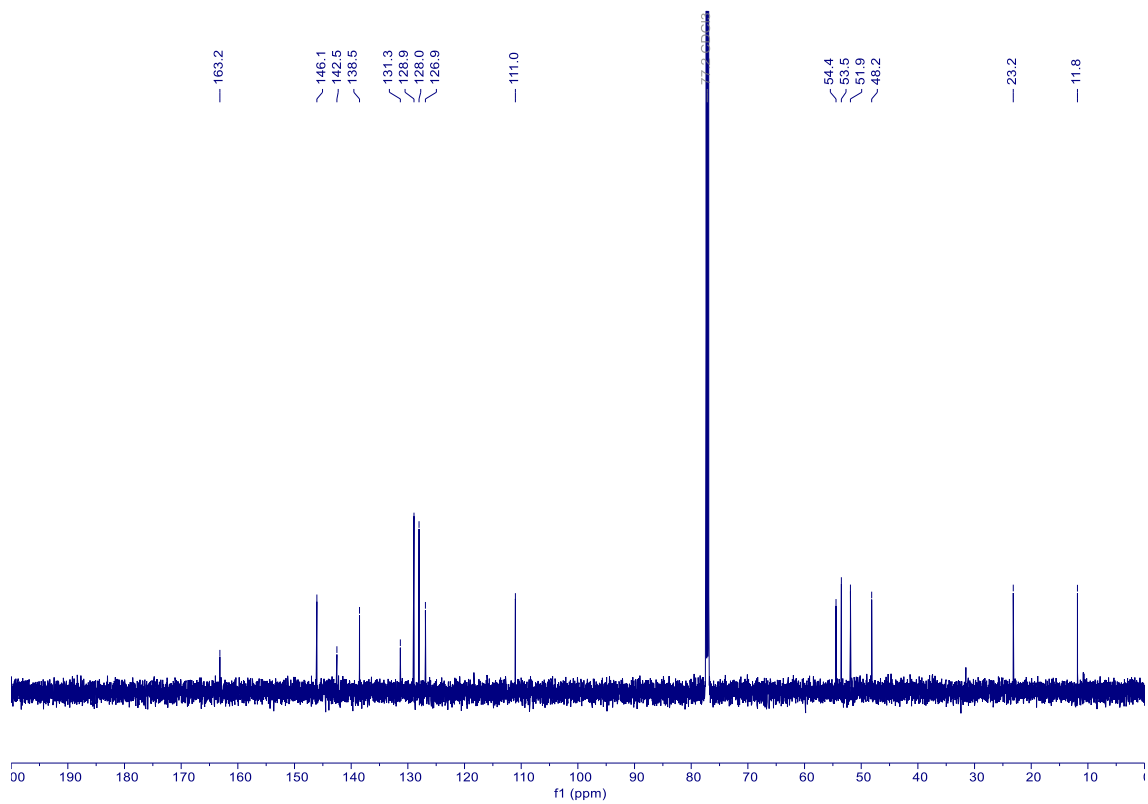
1o – ^{13}C NMR (151 MHz, CDCl_3)



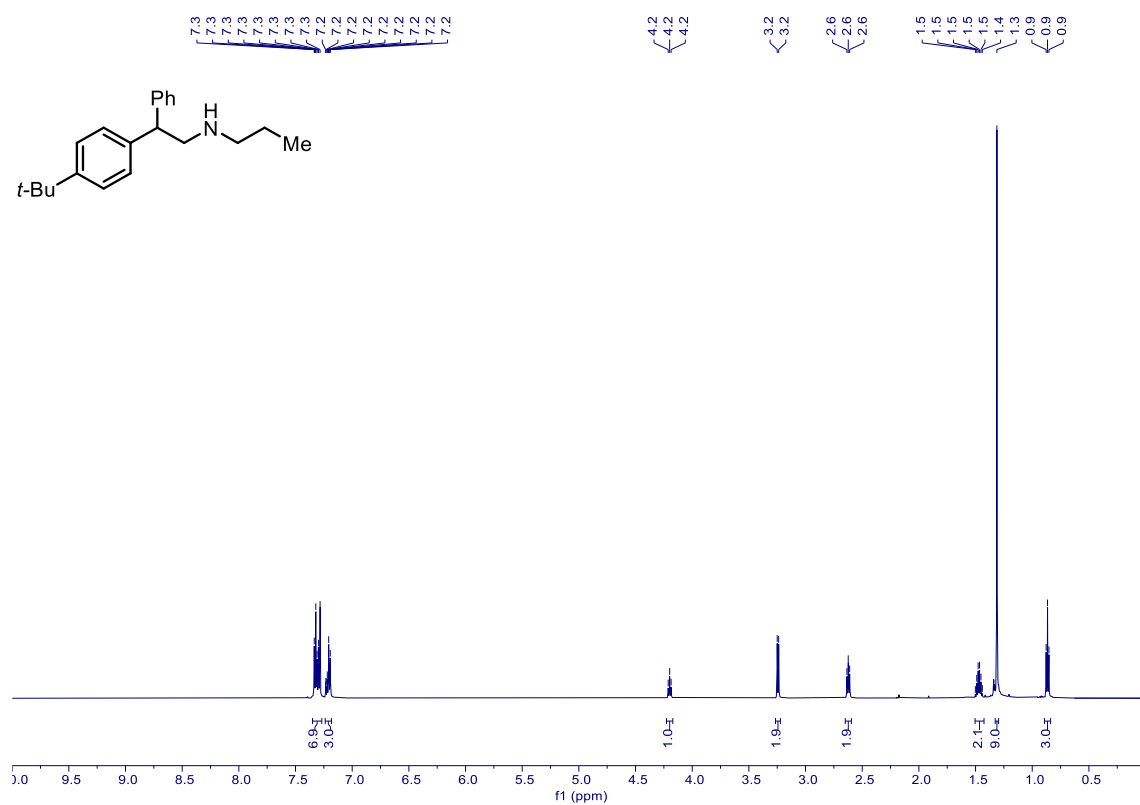
1p – ^1H NMR (600 MHz, CDCl_3)



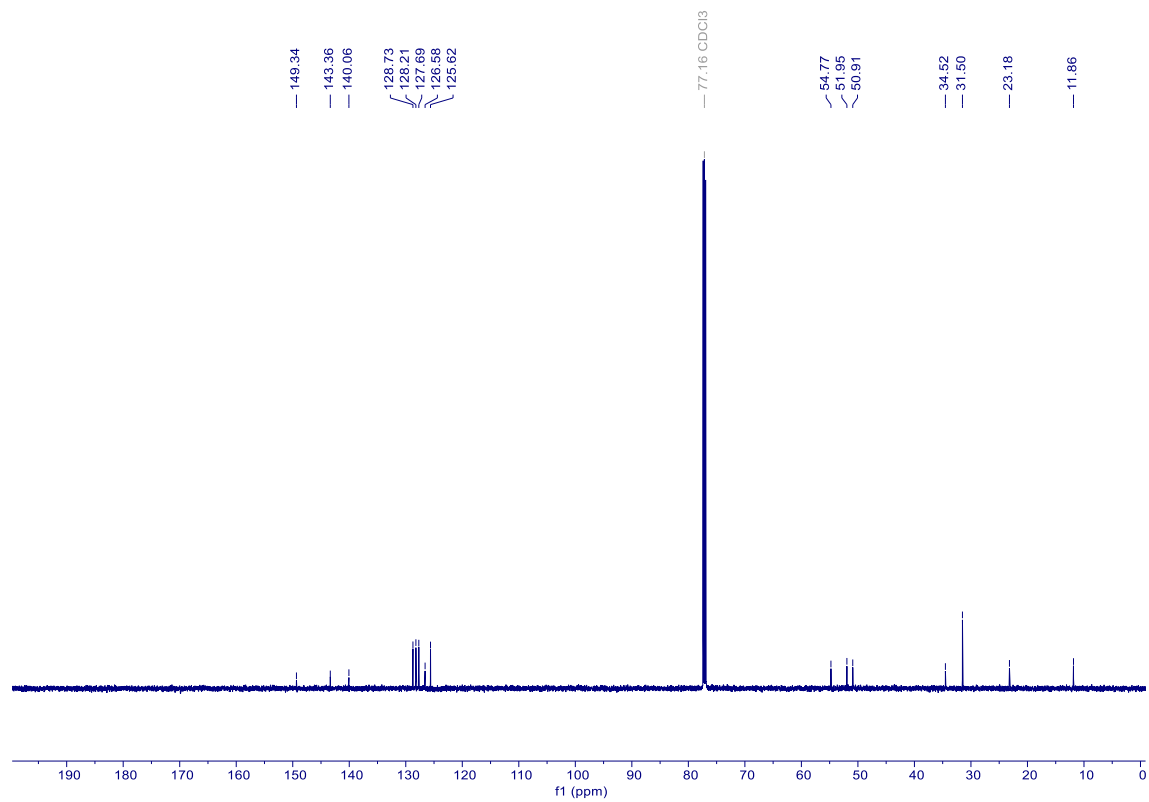
1p – ^{13}C NMR (151 MHz, CDCl_3)



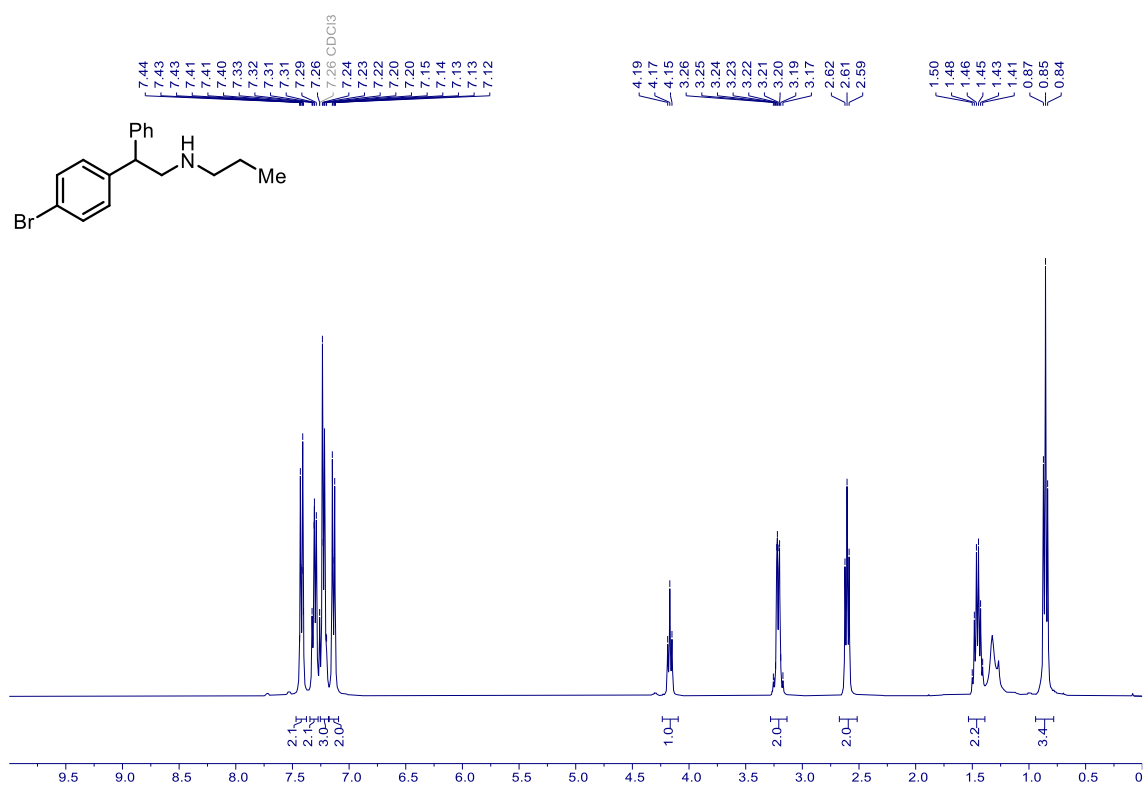
2b – ^1H NMR (600 MHz, CDCl_3)



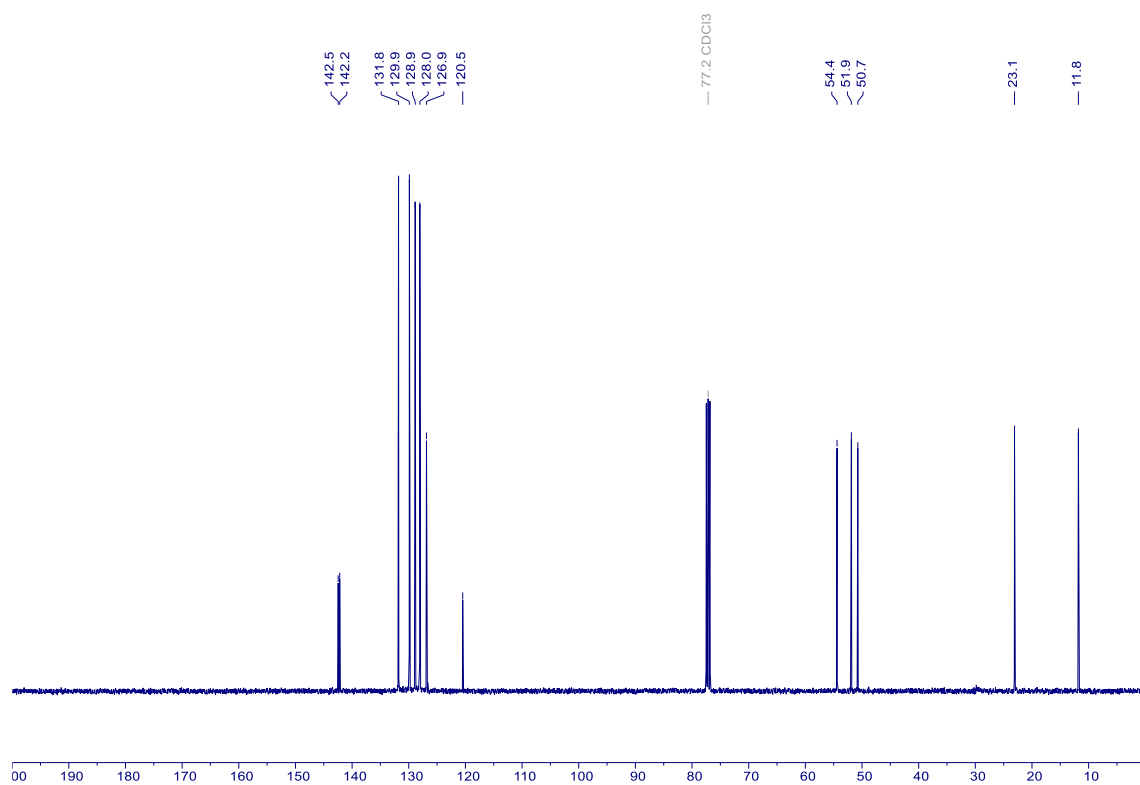
2b – ^{13}C NMR (151 MHz, CDCl_3)



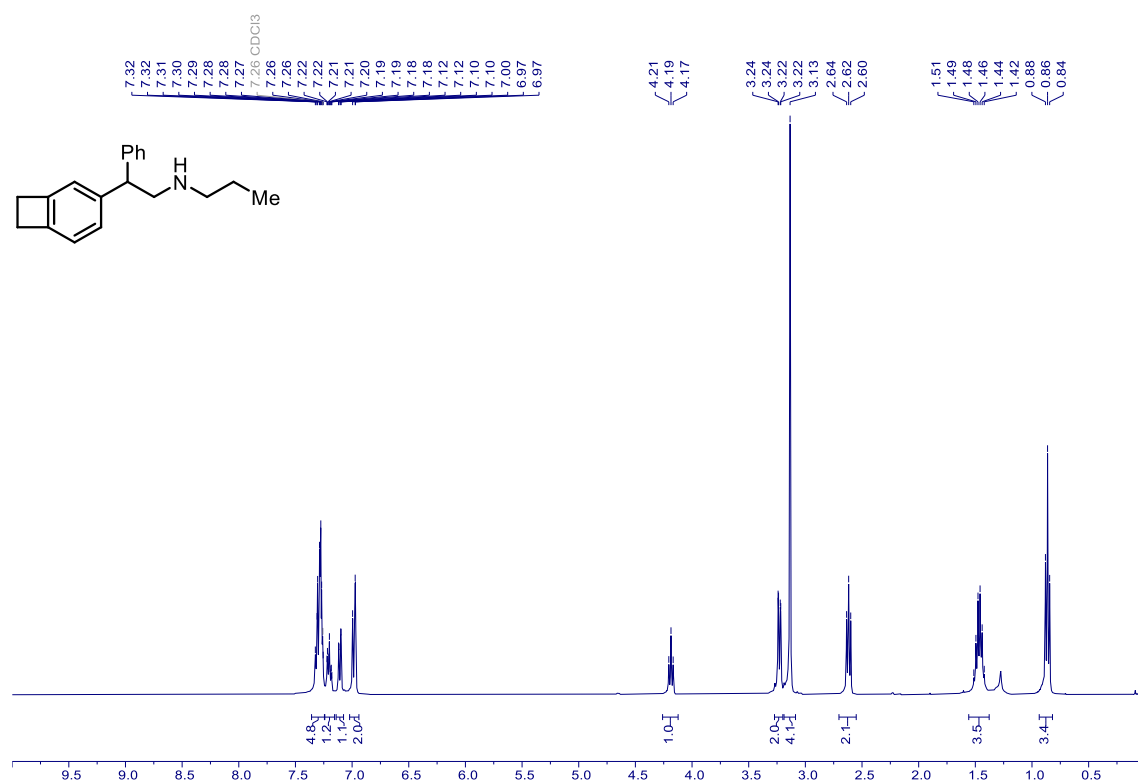
4b – ^1H NMR (400 MHz, CDCl_3)



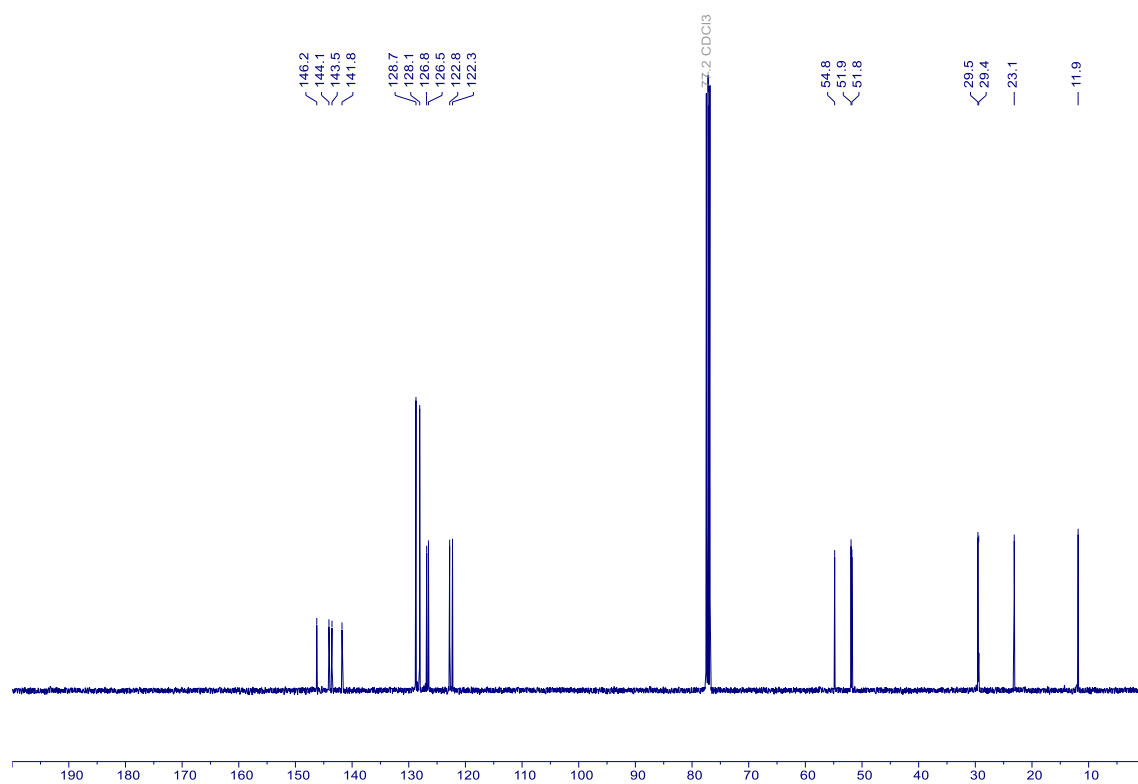
4b – ^{13}C NMR (101 MHz, CDCl_3)



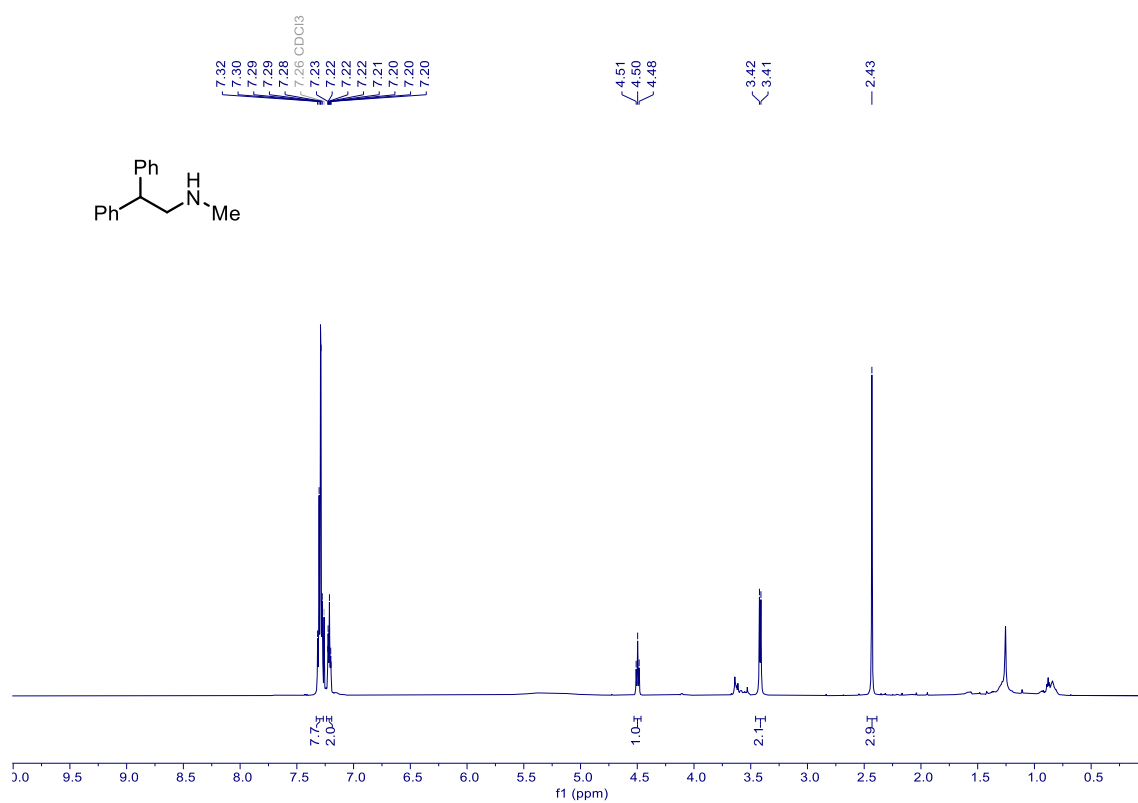
7b – ^1H NMR (400 MHz, CDCl_3)



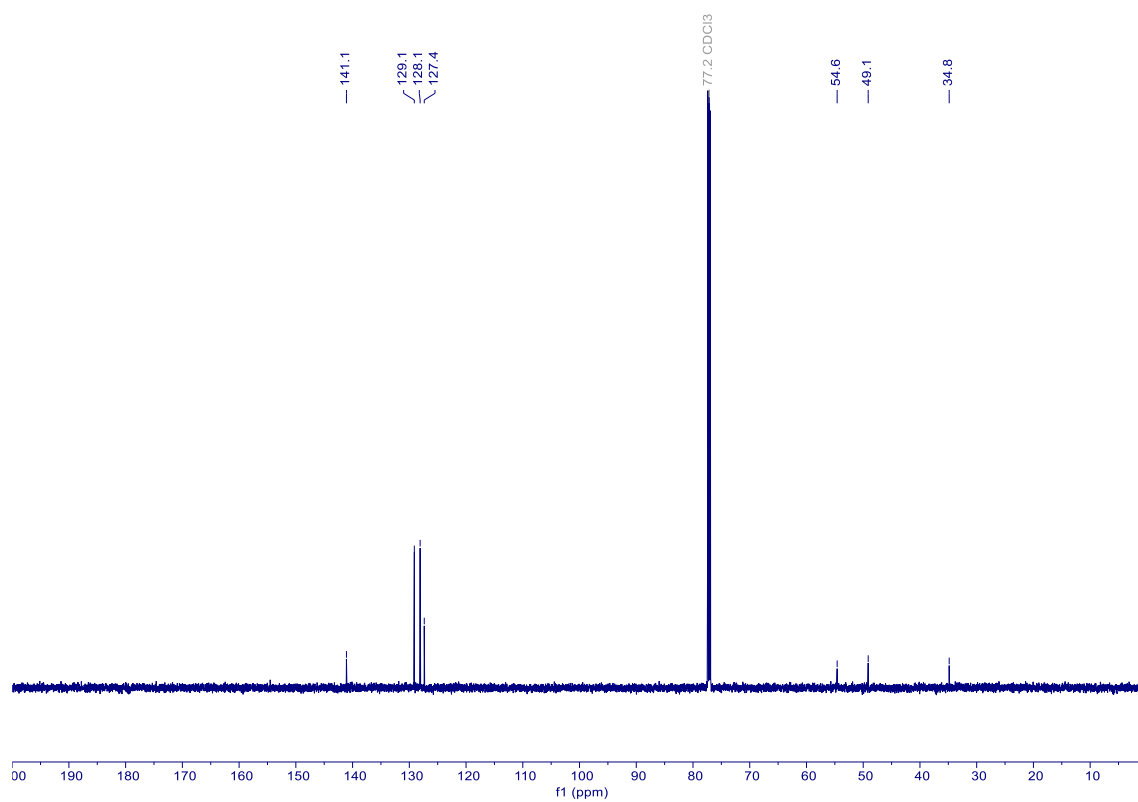
7b – ^{13}C NMR (151 MHz, CDCl_3)



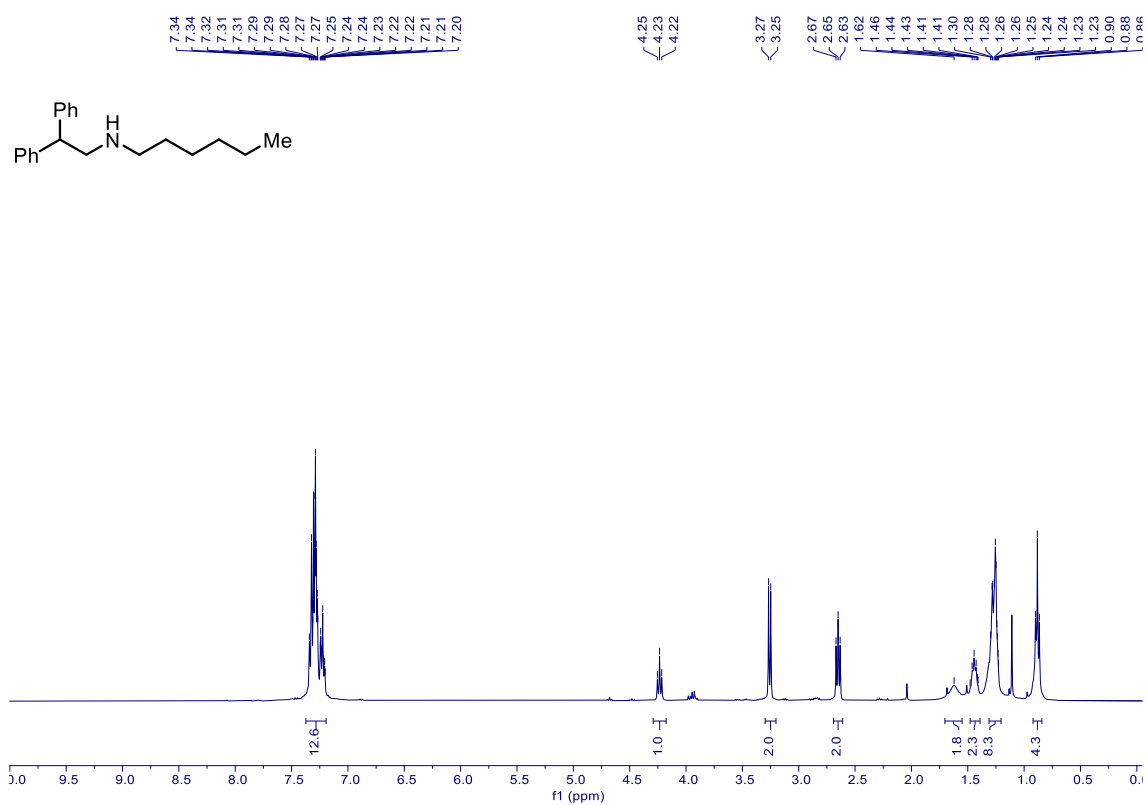
8b – ^1H NMR (600 MHz, CDCl_3)



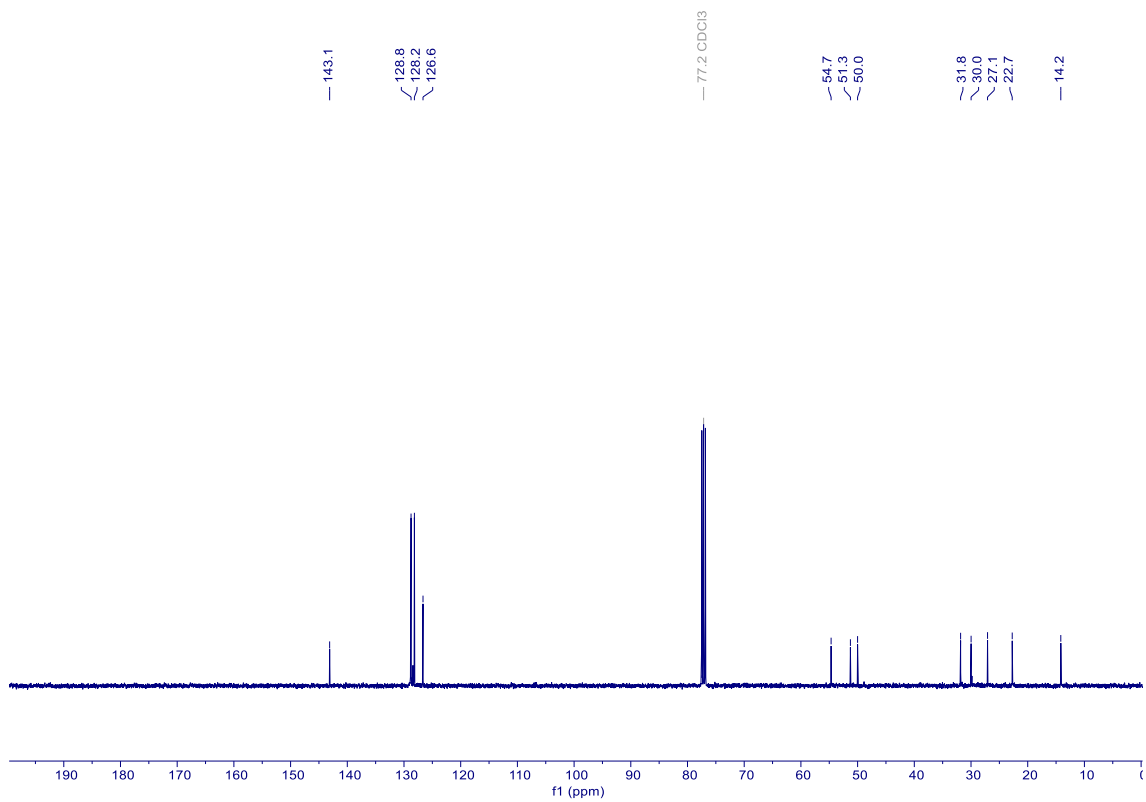
8b – ^{13}C NMR (151 MHz, CDCl_3)



9b – ^1H NMR (400 MHz, CDCl_3)



9b – ^{13}C NMR (101 MHz, CDCl_3)

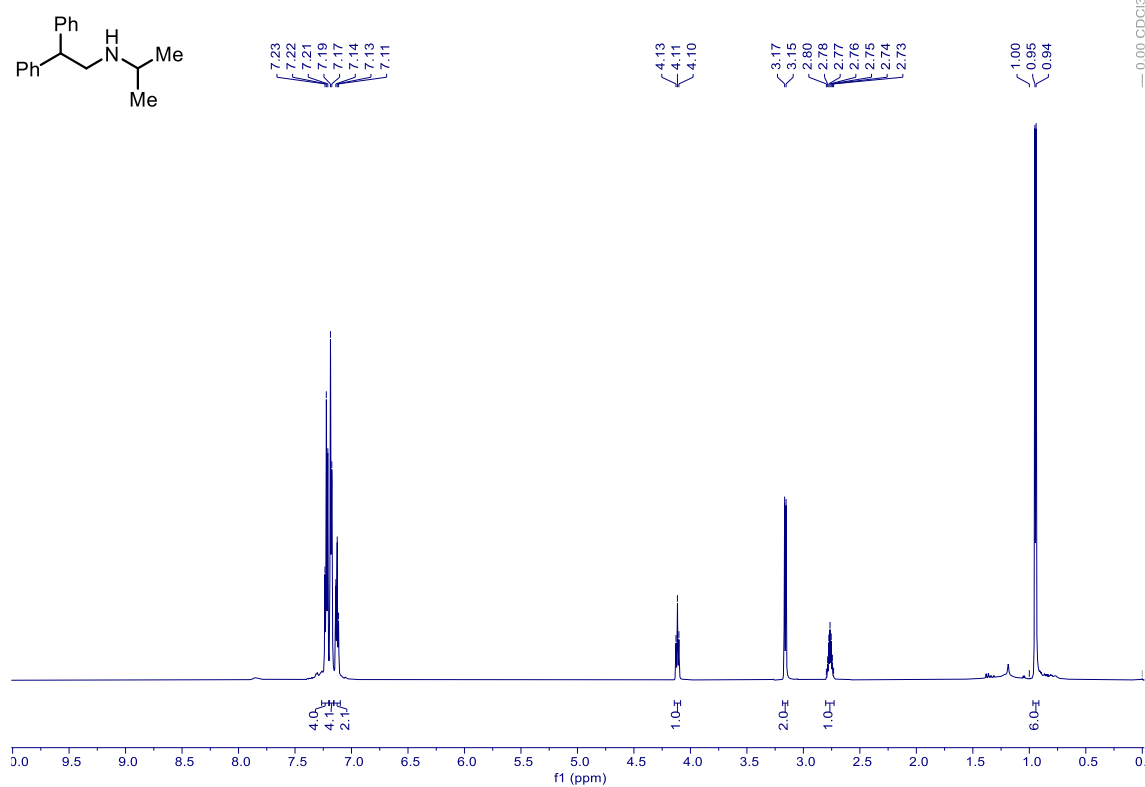


c1ccccc1C(Cc2ccccc2)NCC3=CC=CC=C3

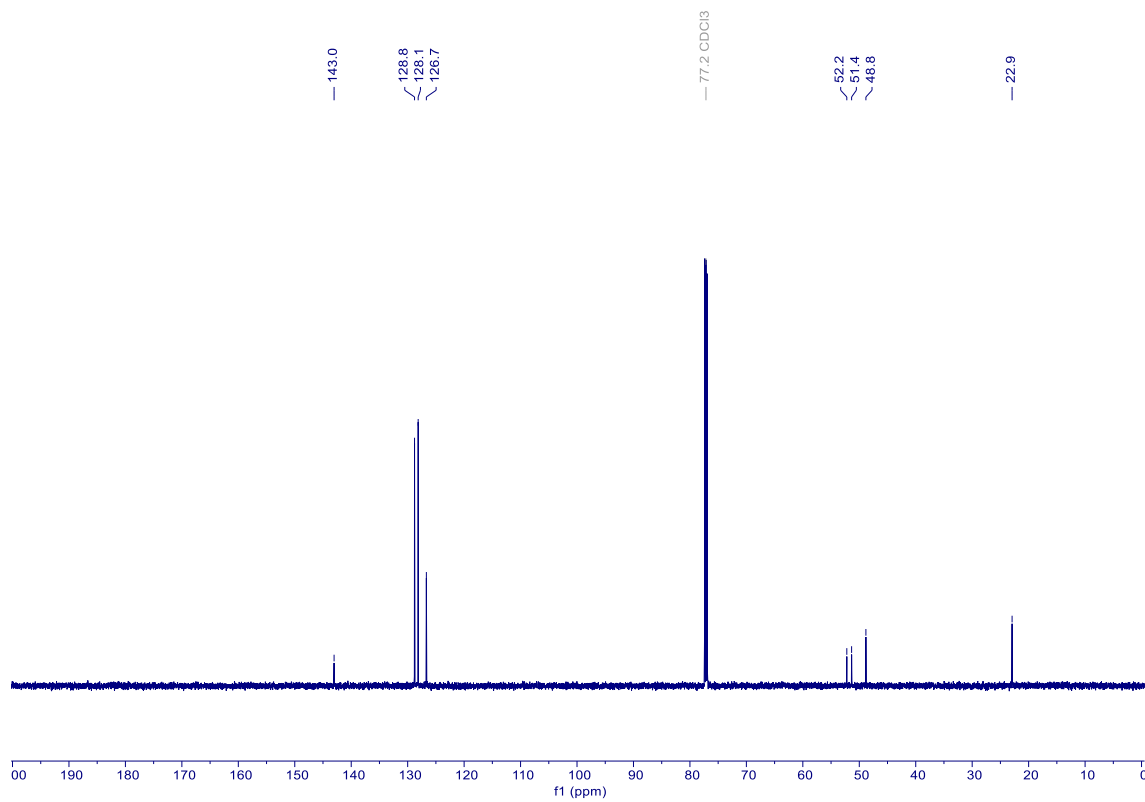
¹H NMR spectrum (400 MHz, CDCl₃) of N-(1,1-diphenylethyl)ethan-1-amine. The spectrum shows peaks at 7.2-7.3 ppm (15.8H), 4.3-4.4 ppm (1.0H), 3.8 ppm (2.0H), 3.3 ppm (2.0H), and 1.5 ppm (1.4H).

143.0
140.3
128.7
128.5
128.2
128.2
127.1
126.7
77.2 CDCl₃
54.0
53.9
51.4

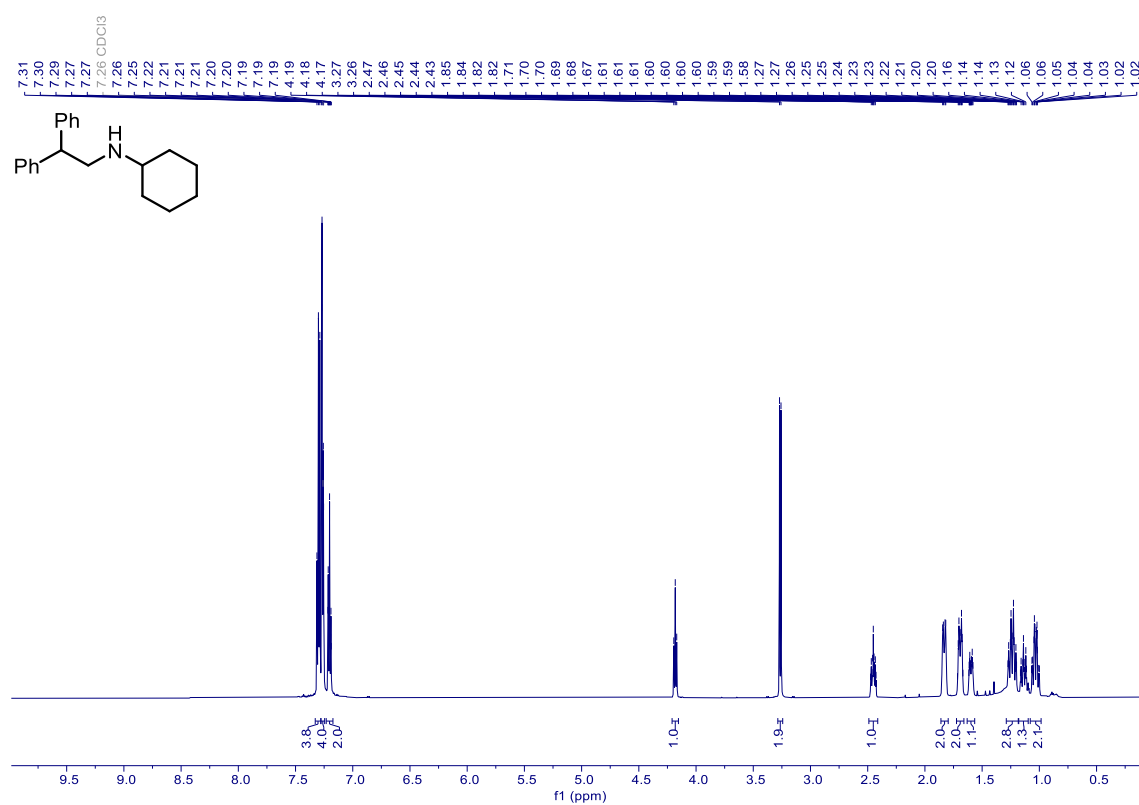
11b – ^1H NMR (600 MHz, CDCl_3)



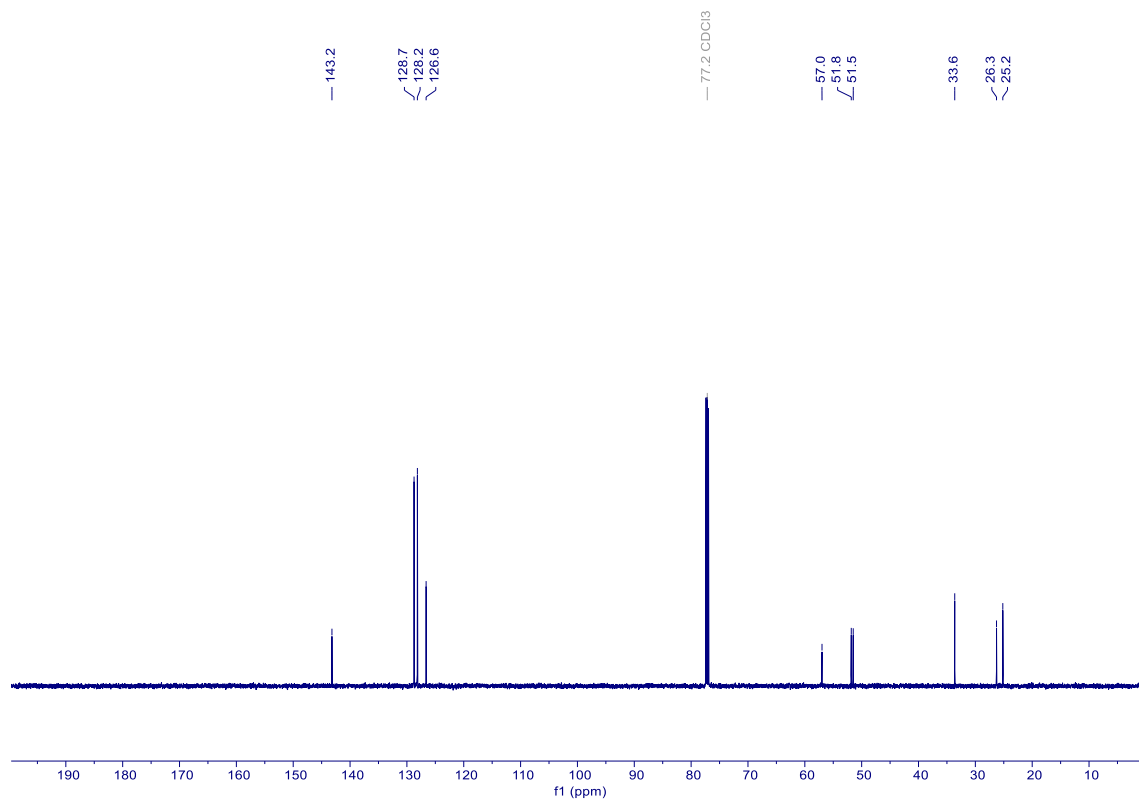
11b – ^{13}C NMR (151 MHz, CDCl_3)



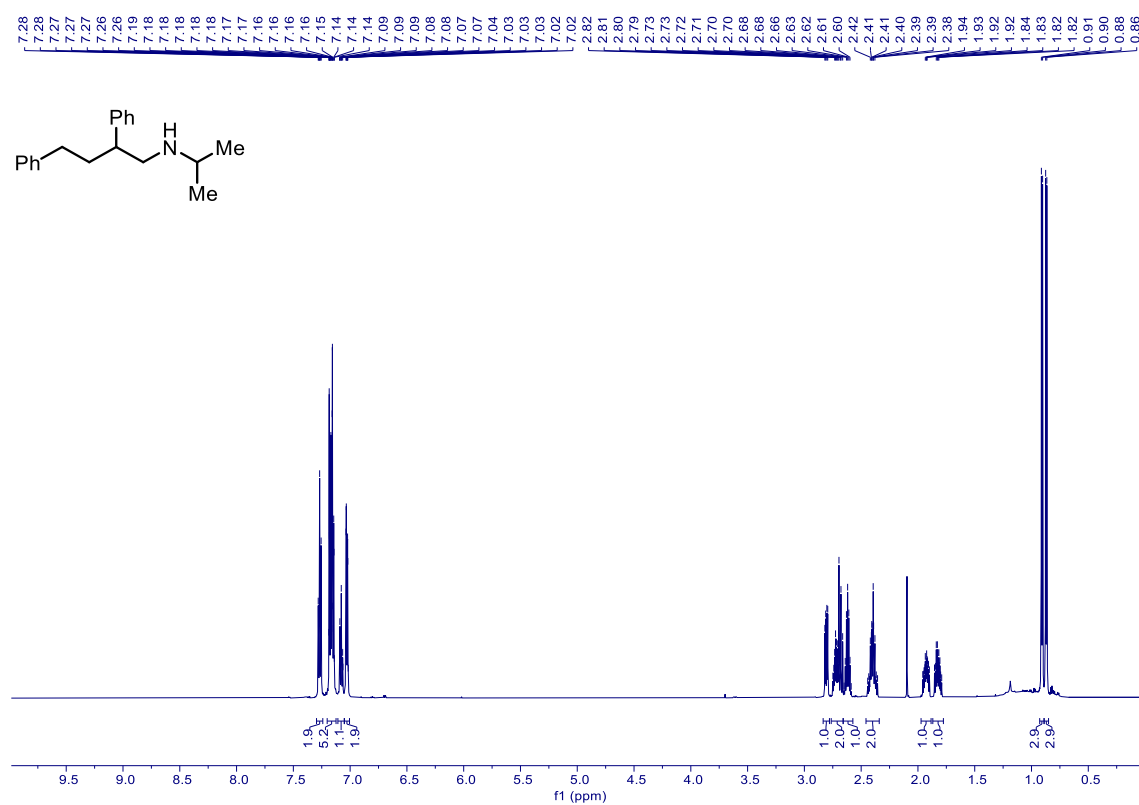
12b – ^1H NMR (600 MHz, CDCl_3)



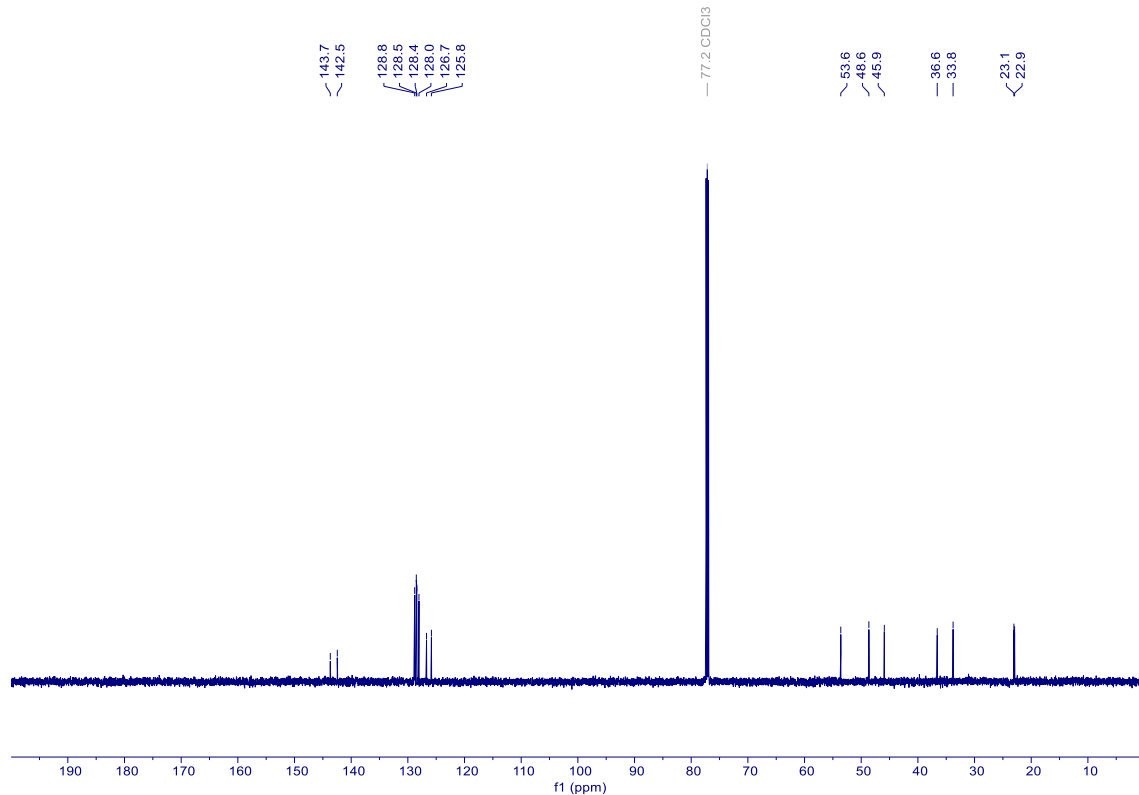
12b – ^{13}C NMR (151 MHz, CDCl_3)



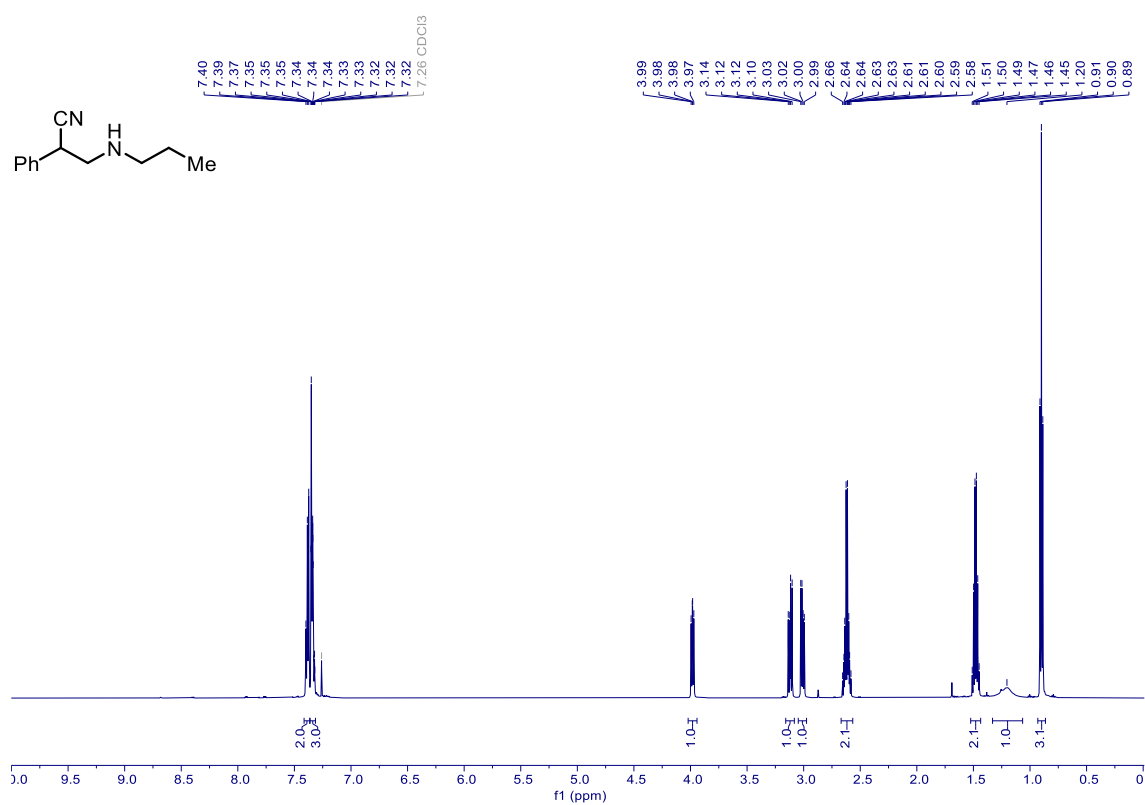
13b – ^1H NMR (600 MHz, CDCl_3)



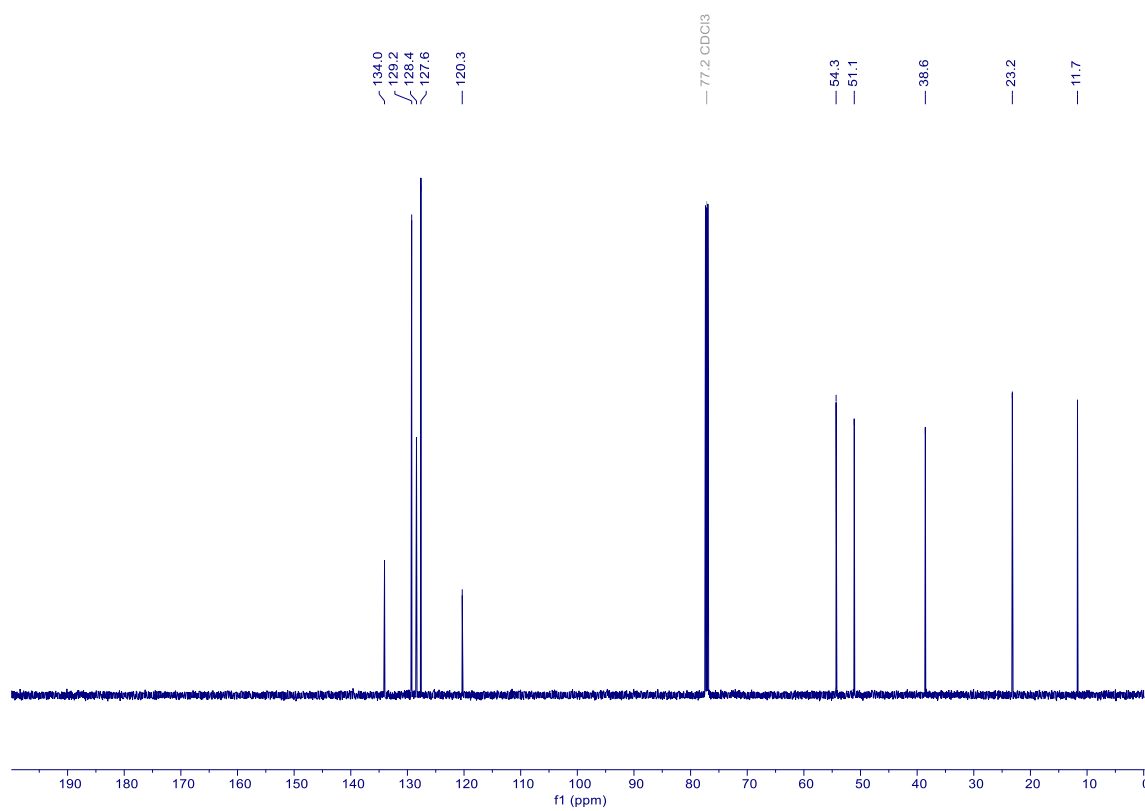
13b – ^{13}C NMR (151 MHz, CDCl_3)



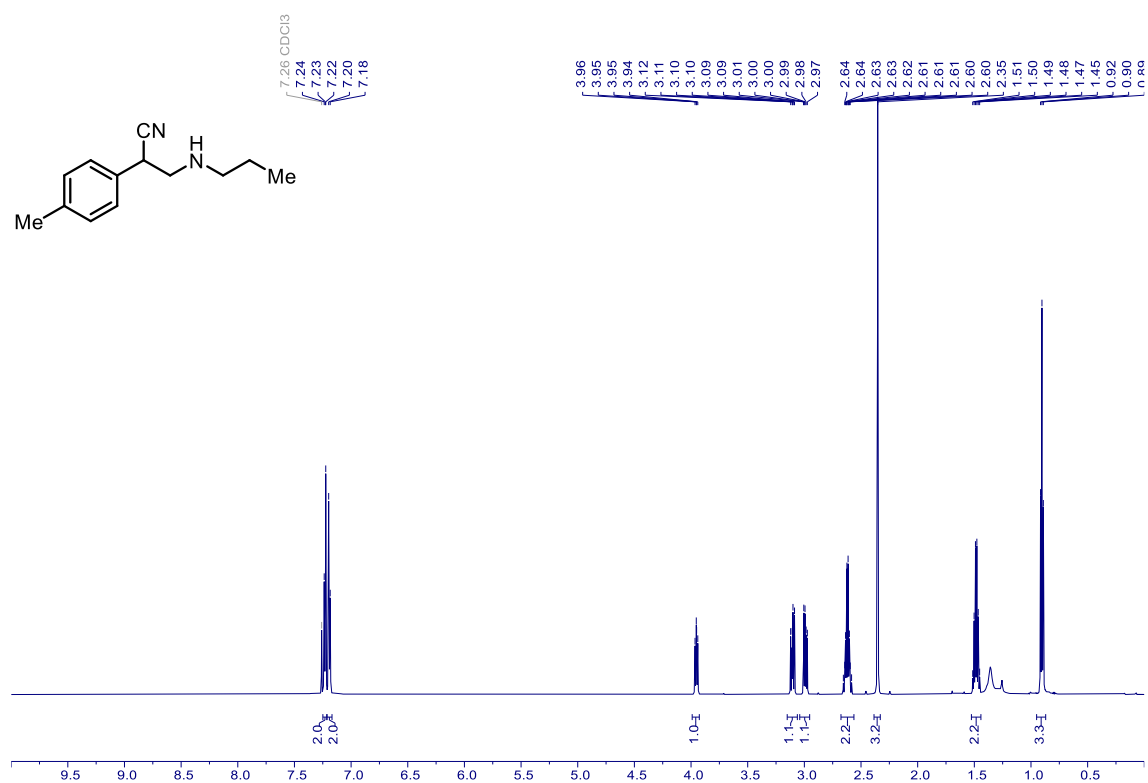
1q – ^1H NMR (600 MHz, CDCl_3)



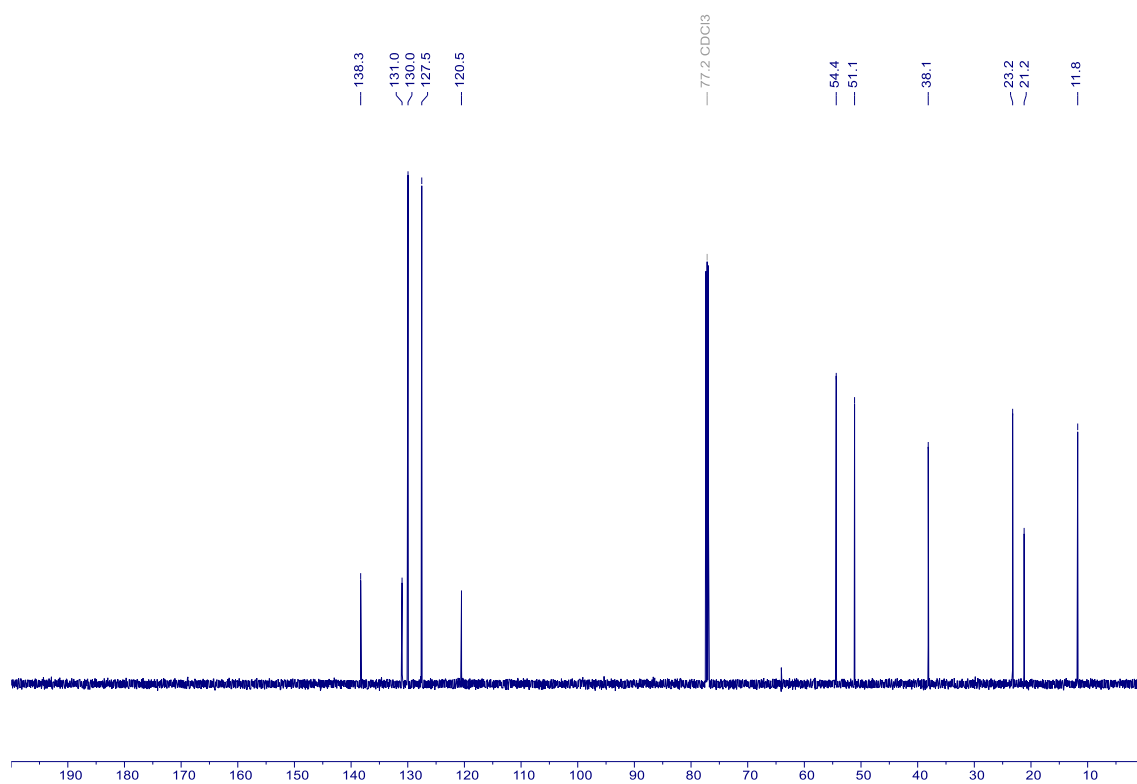
1q – ^{13}C NMR (151 MHz, CDCl_3)



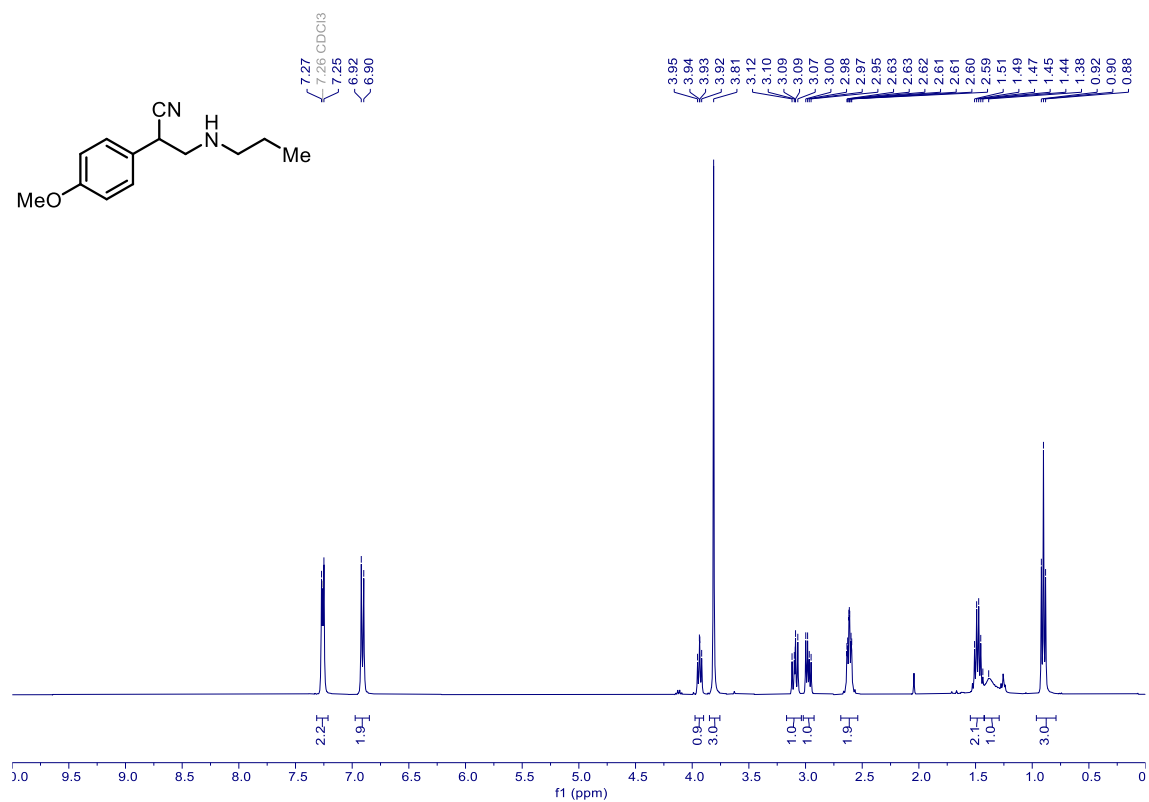
14b – ^1H NMR (600 MHz, CDCl_3)



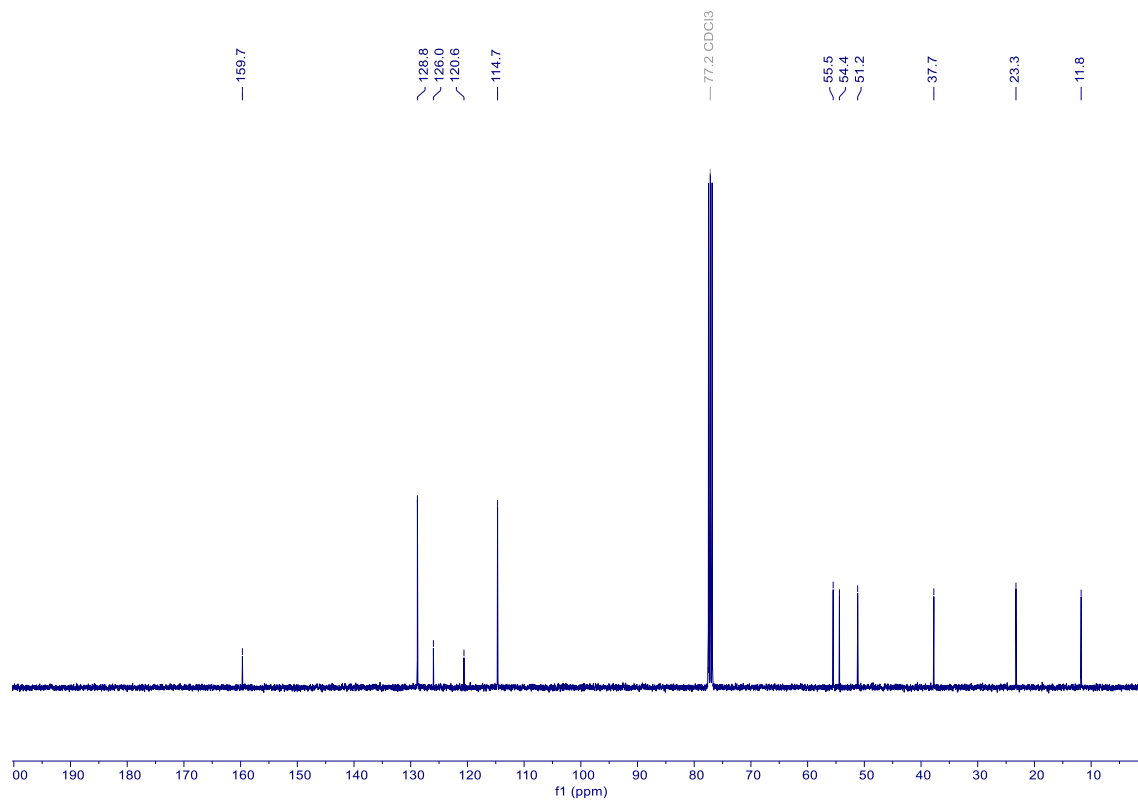
14b – ^{13}C NMR (151 MHz, CDCl_3)



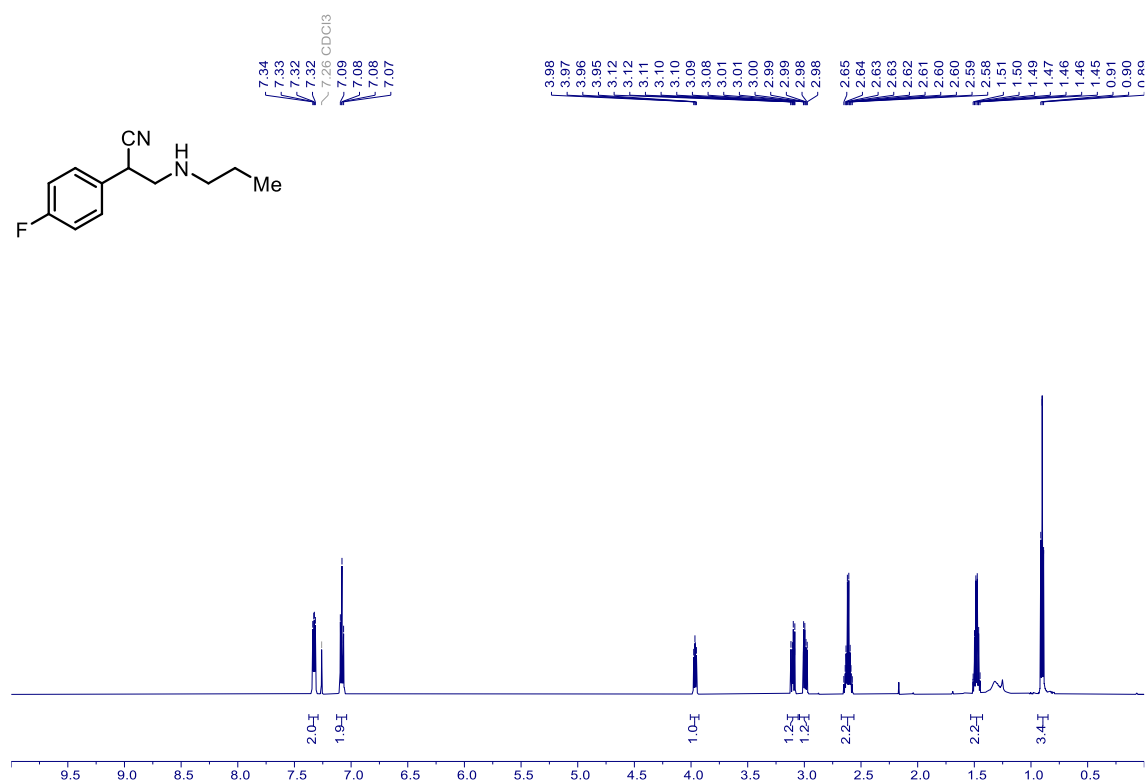
3c – ^1H NMR (400 MHz, CDCl_3)



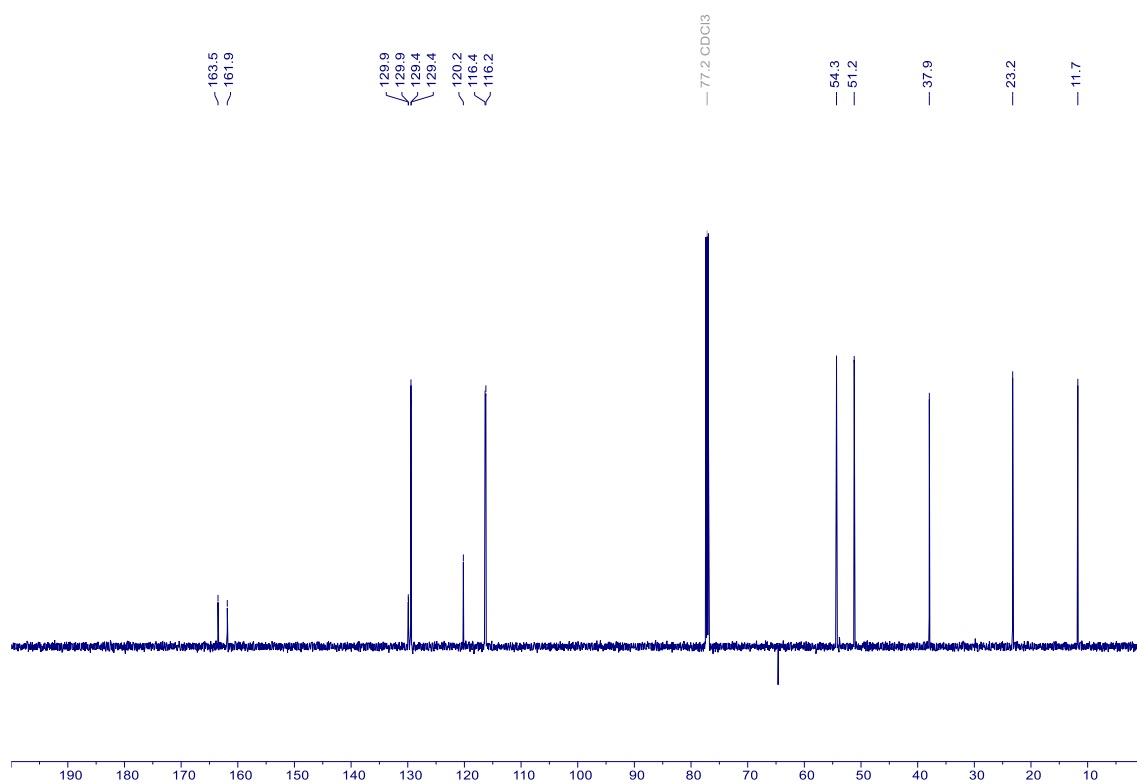
3c – ^{13}C NMR (101 MHz, CDCl_3)



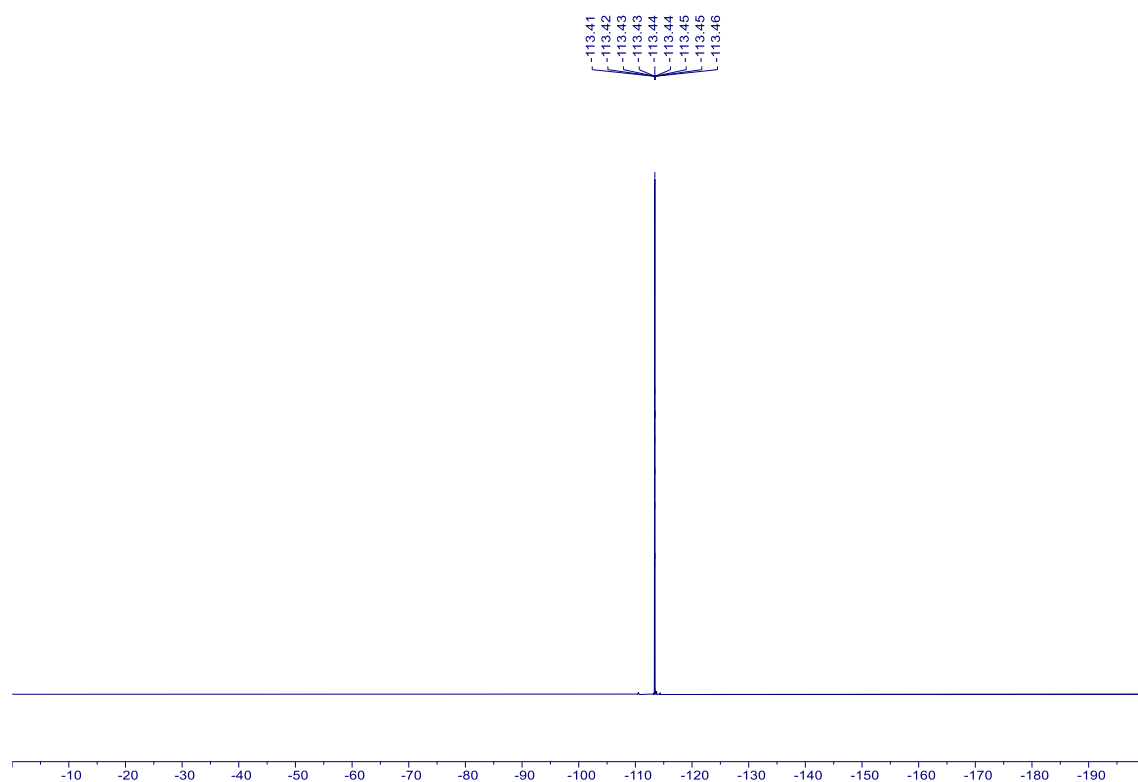
15b – ^1H NMR (600 MHz, CDCl_3)



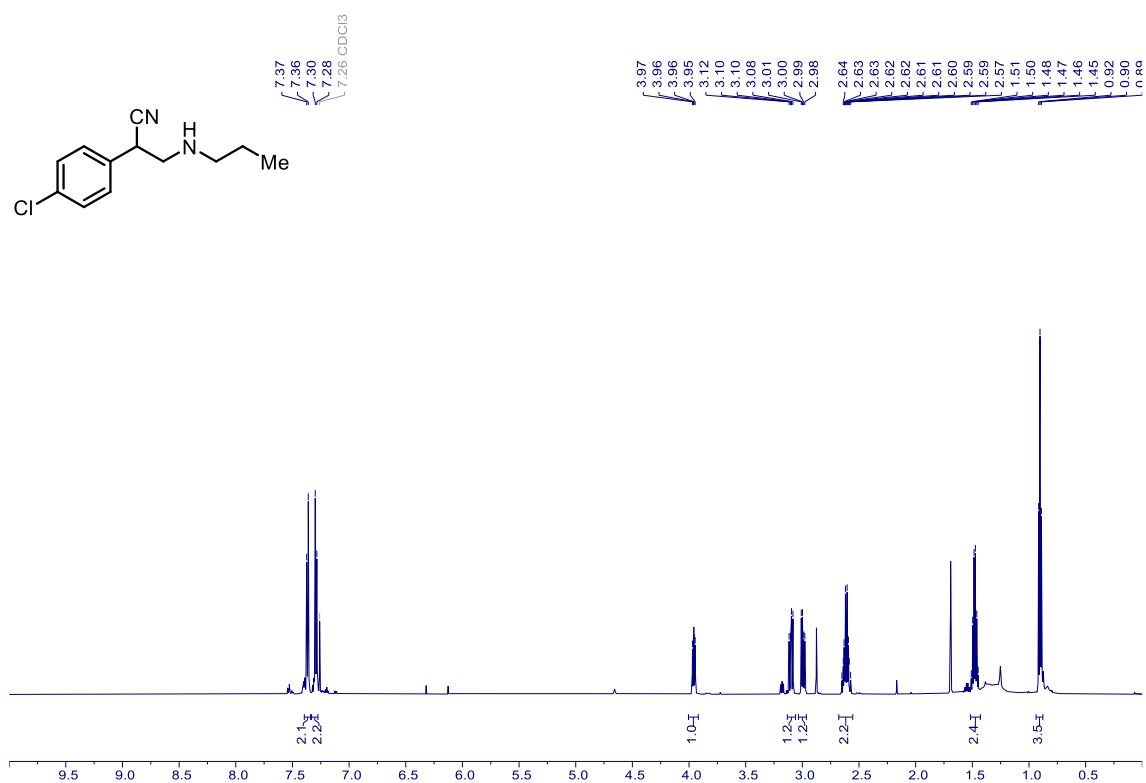
15b – ^{13}C NMR (151 MHz, CDCl_3)



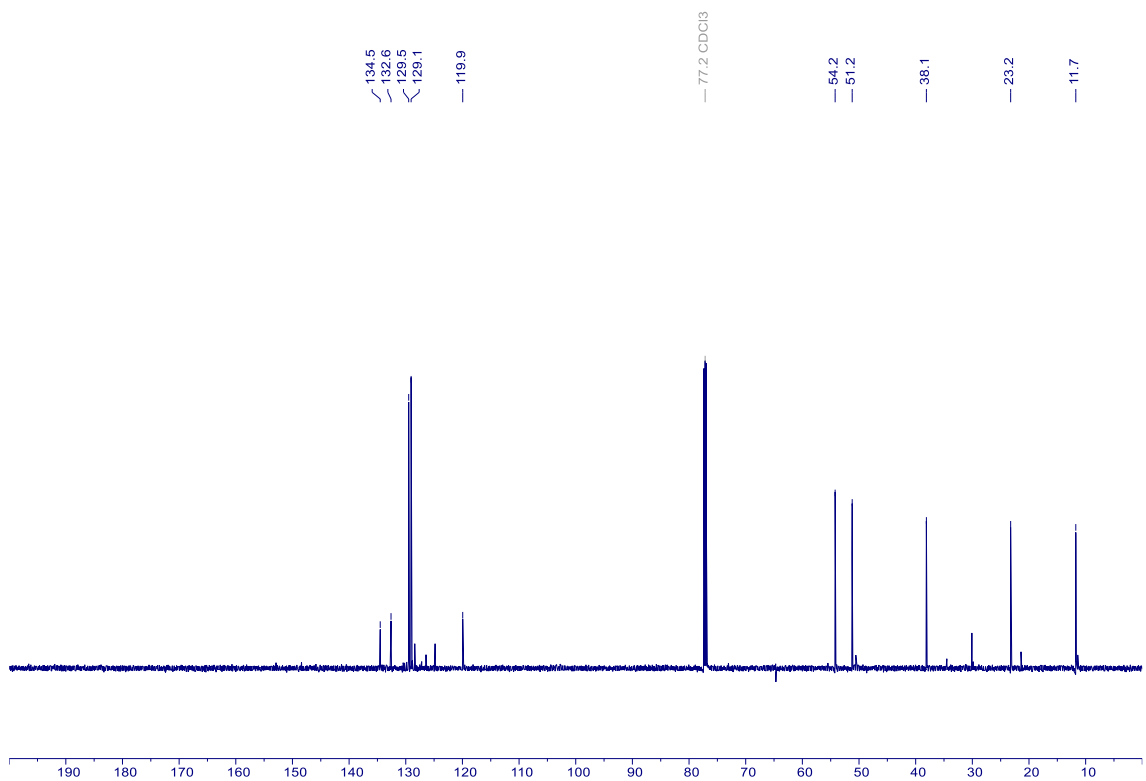
15b – ^{19}F NMR (564 MHz, CDCl_3)



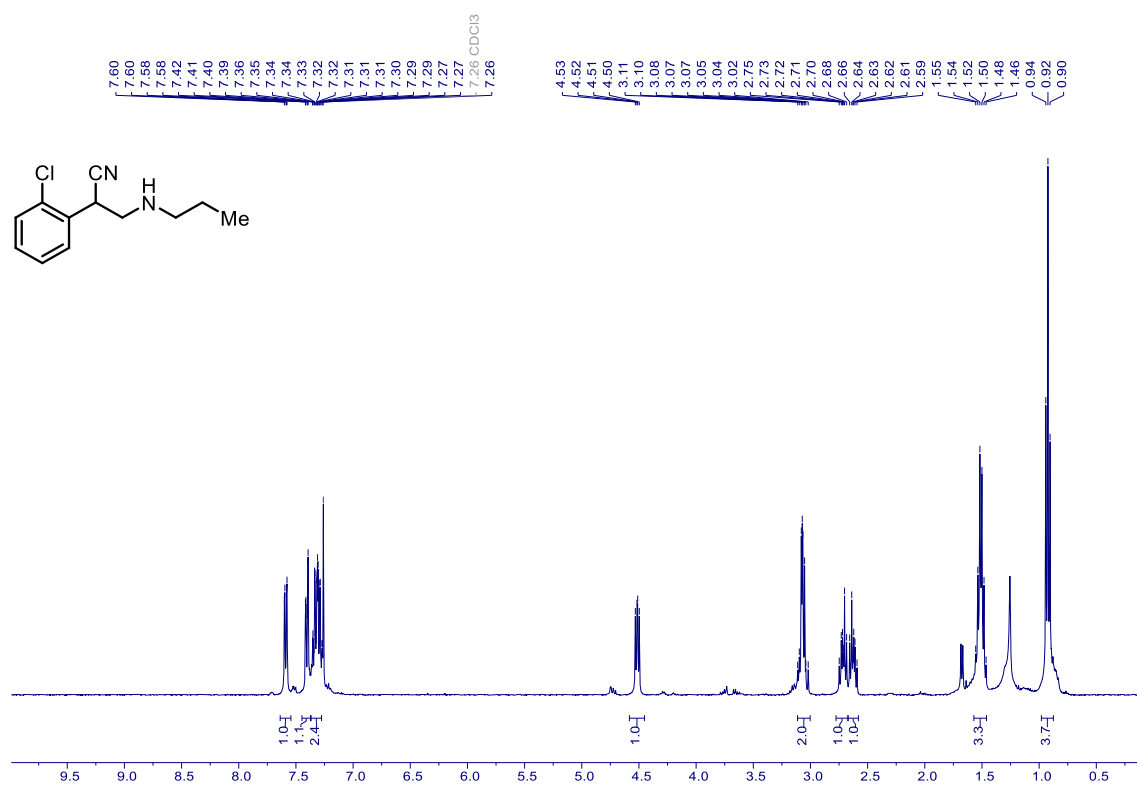
5c – ^1H NMR (600 MHz, CDCl_3)



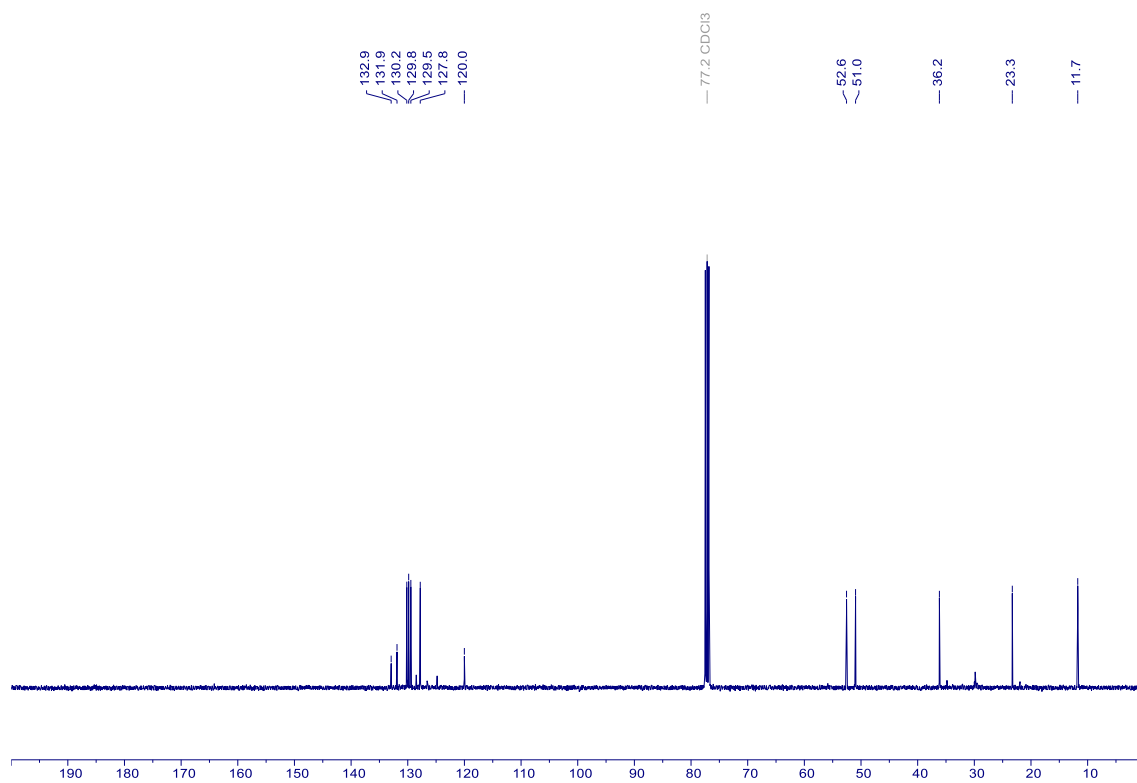
5c – ^{13}C NMR (151 MHz, CDCl_3)



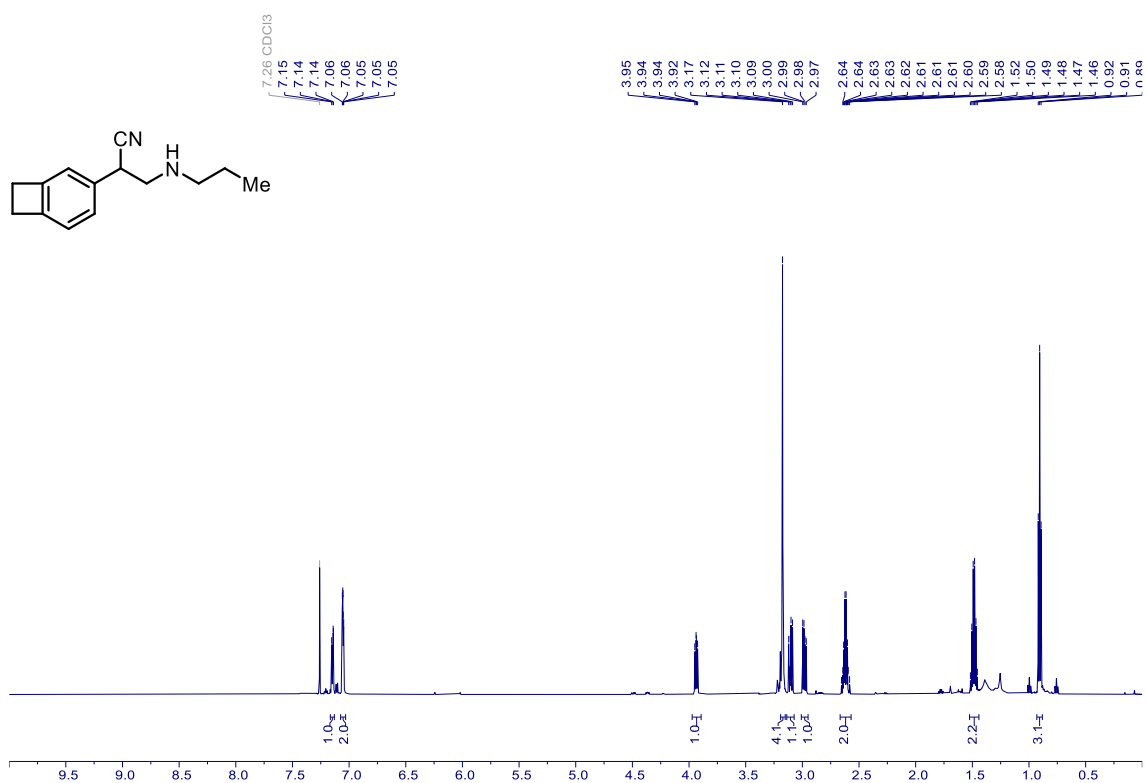
16b – ^1H NMR (400 MHz, CDCl_3)



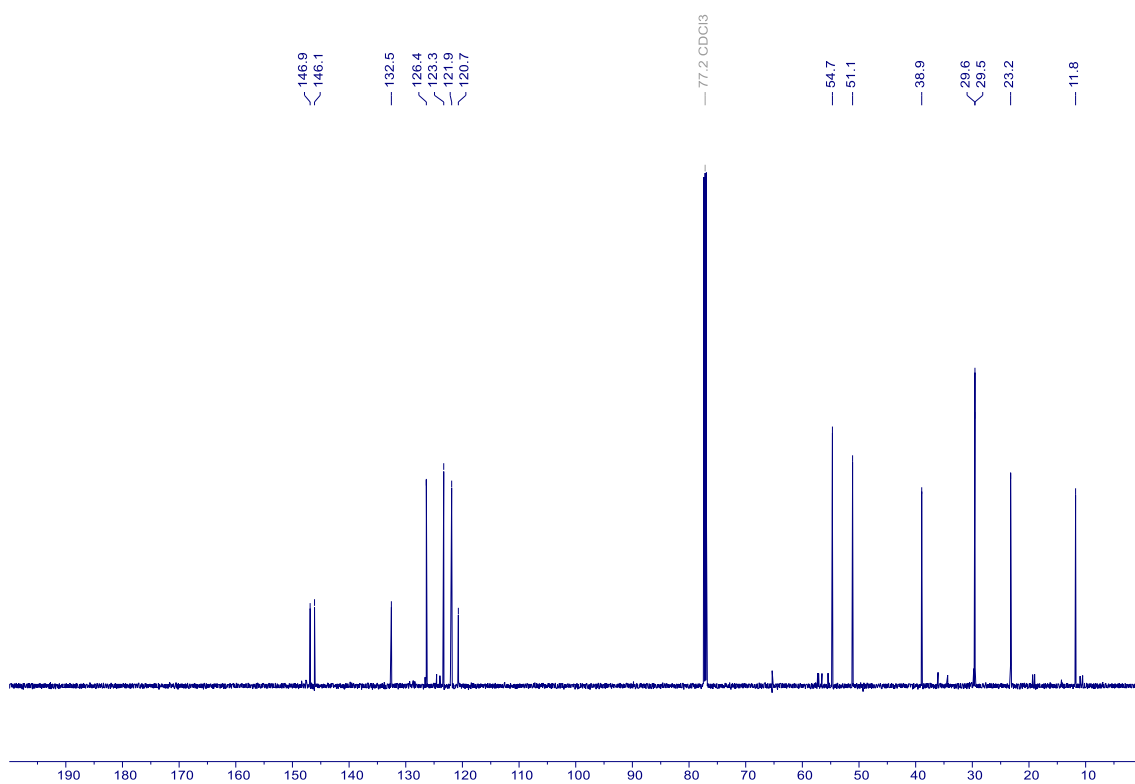
16b – ^{13}C NMR (101 MHz, CDCl_3)



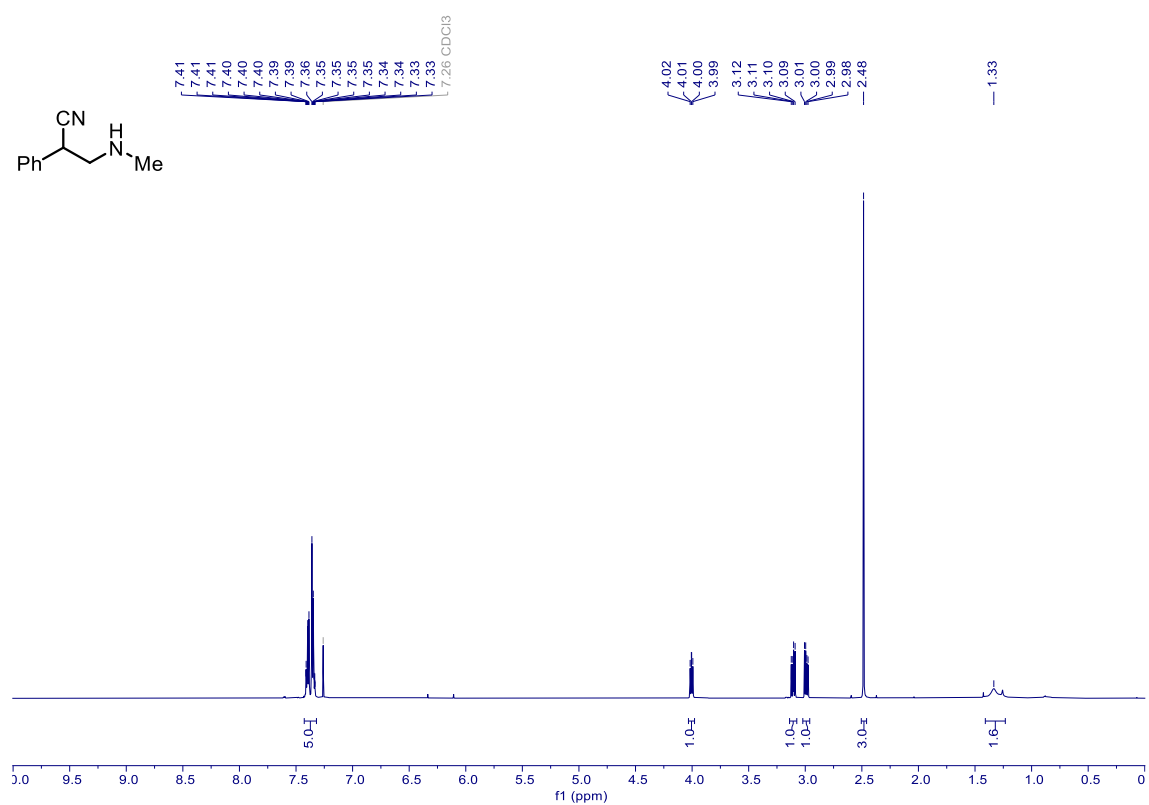
7c – ^1H NMR (600 MHz, CDCl_3)



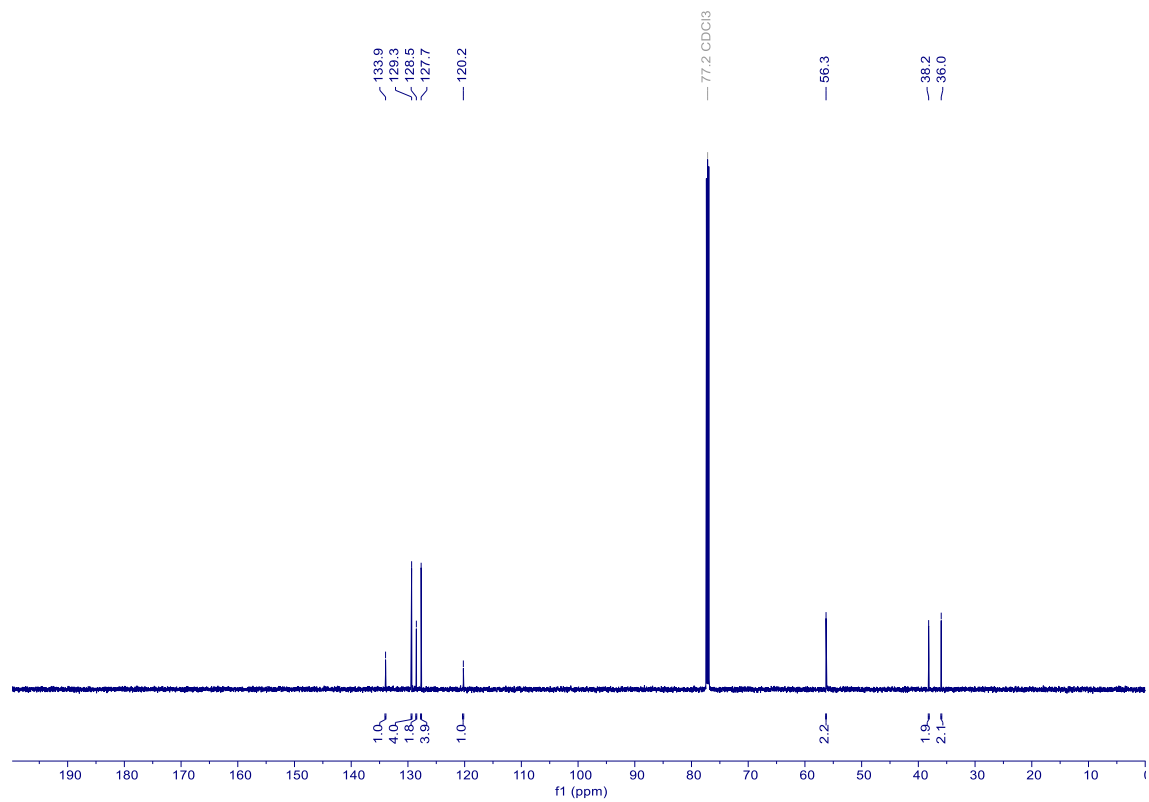
7c – ^{13}C NMR (151 MHz, CDCl_3)



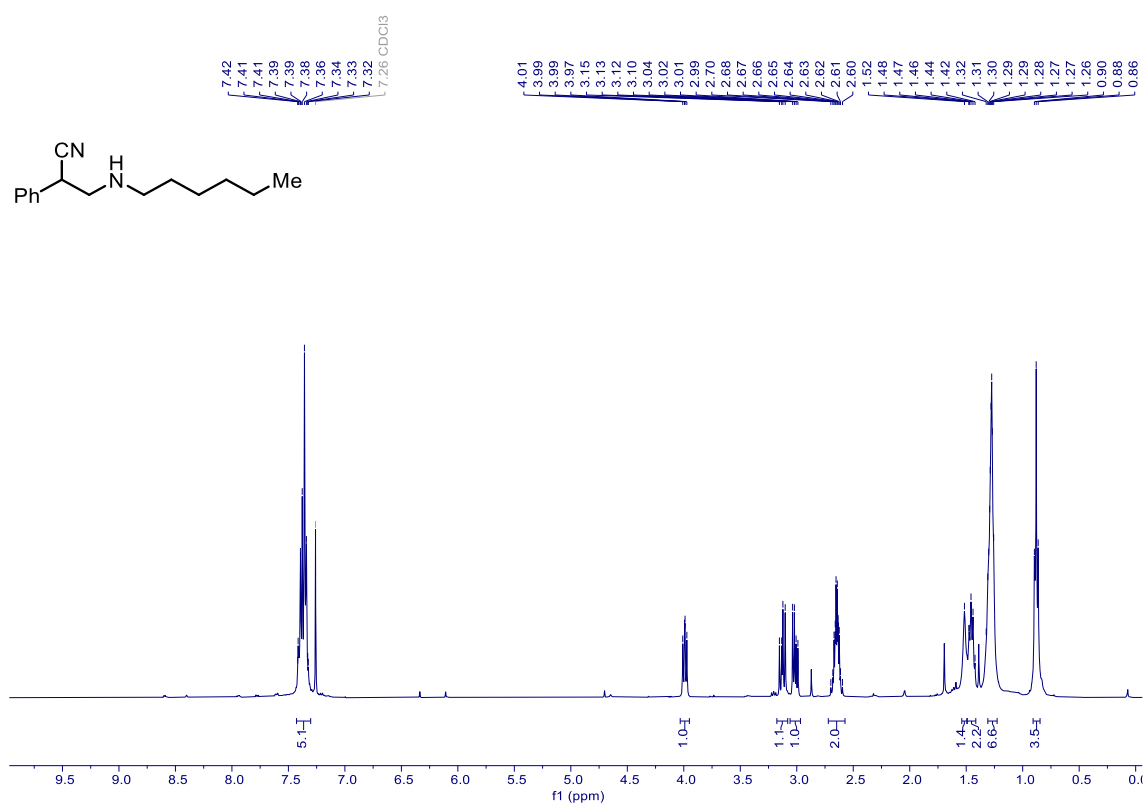
8c – ^1H NMR (600 MHz, CDCl_3)



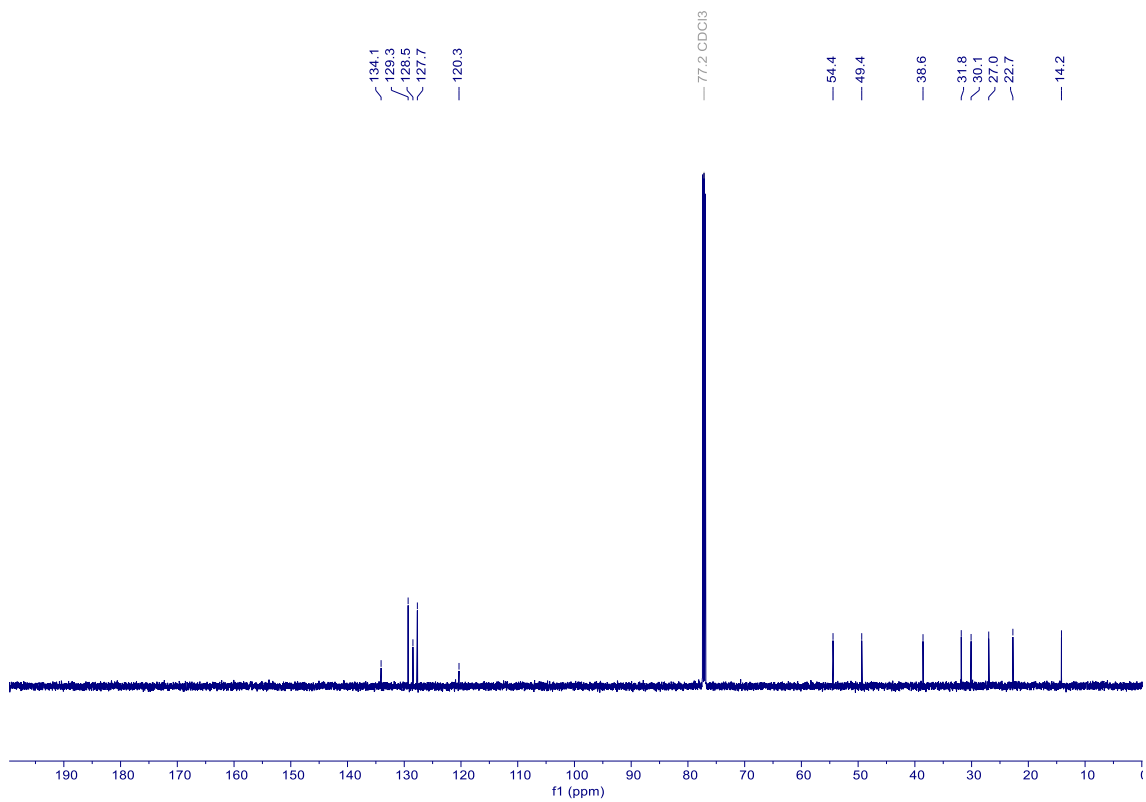
8c – ^{13}C NMR (151 MHz, CDCl_3)



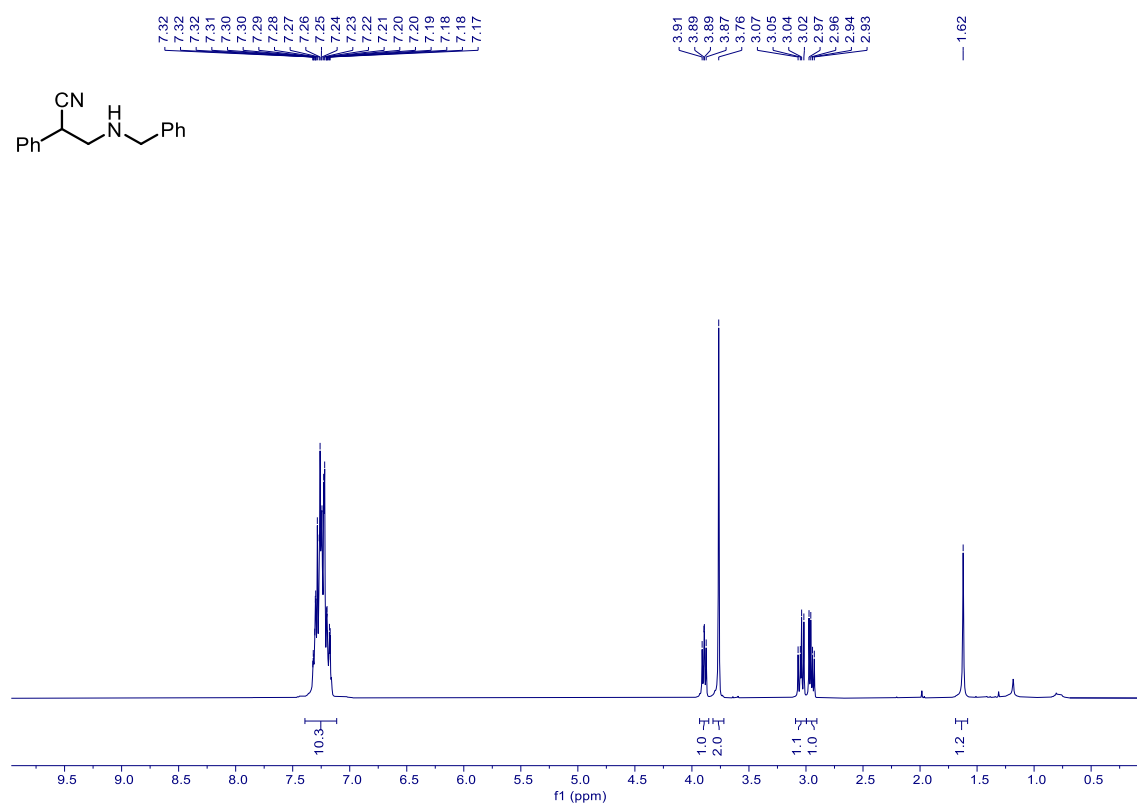
9c – ^1H NMR (600 MHz, CDCl_3)



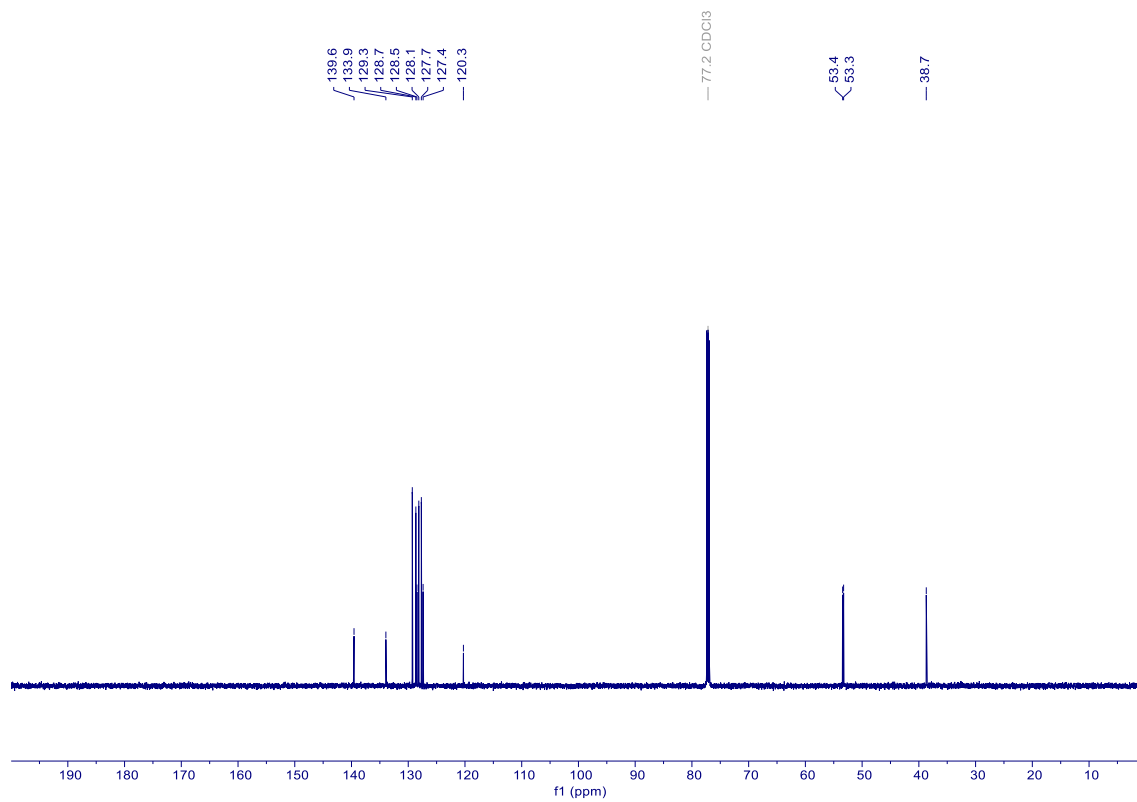
9c – ^{13}C NMR (151 MHz, CDCl_3)



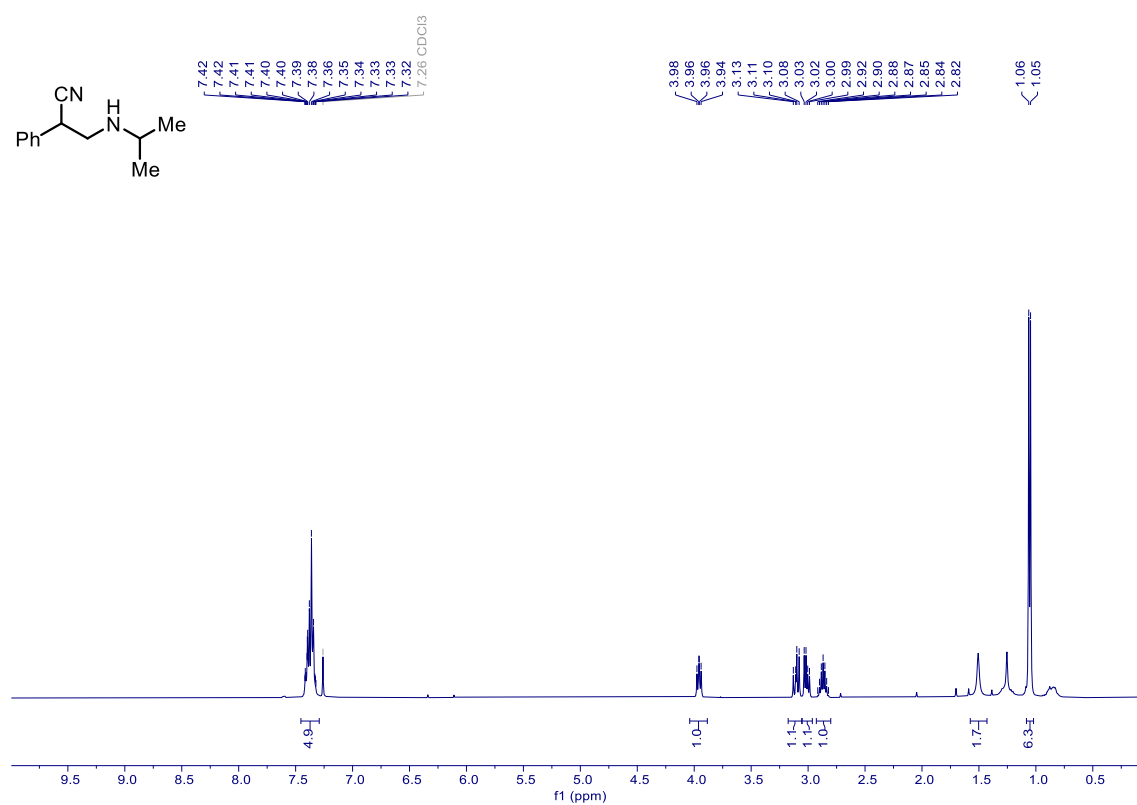
10c – ^1H NMR (400 MHz, CDCl_3)



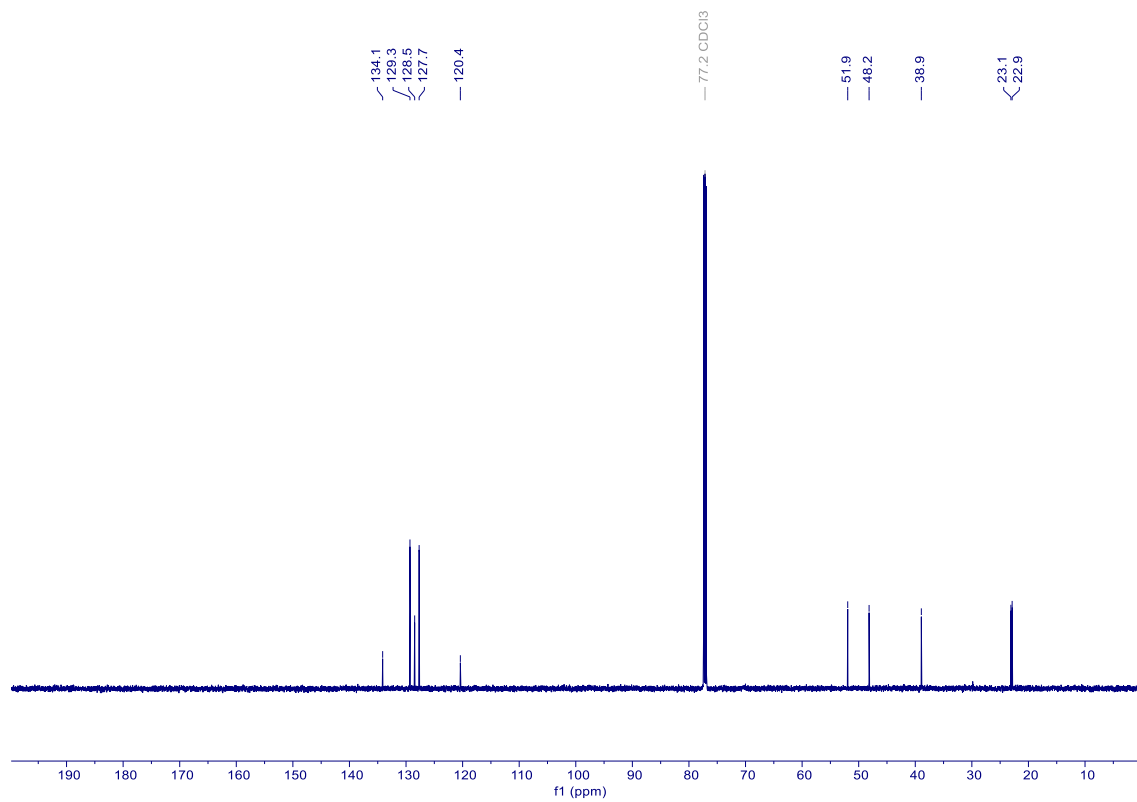
10c – ^{13}C NMR (151 MHz, CDCl_3)



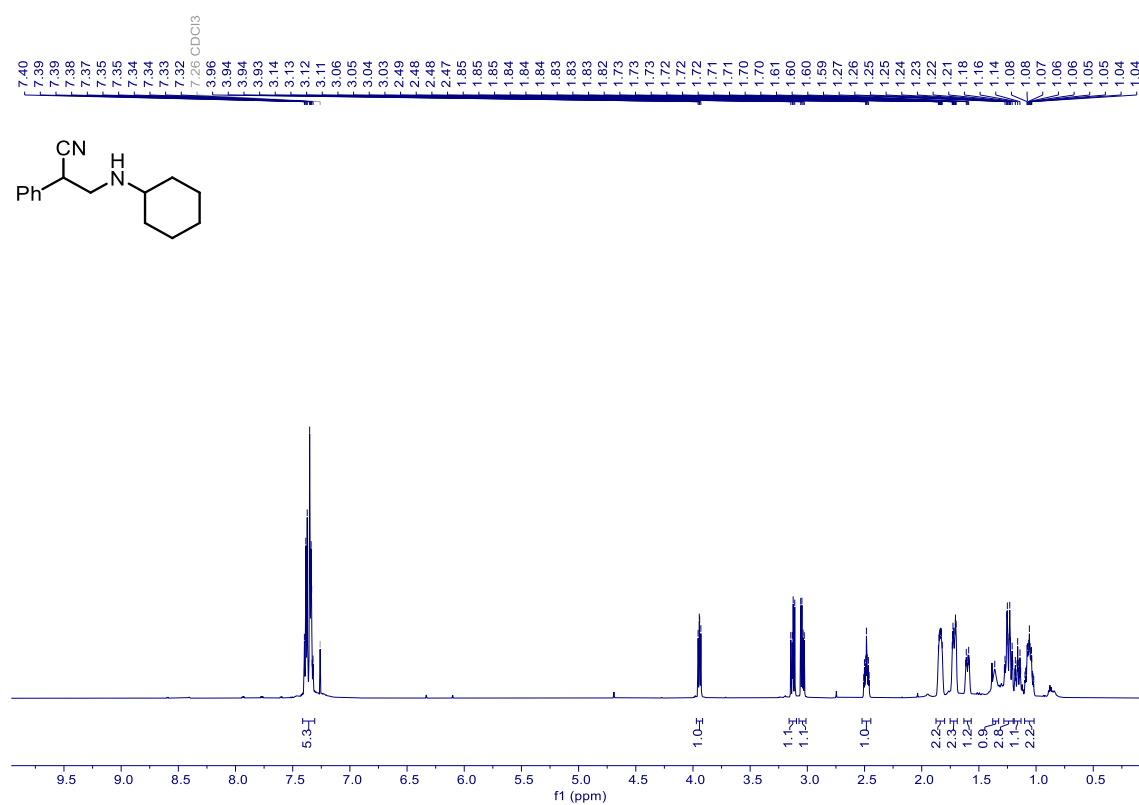
11c – ^1H NMR (400 MHz, CDCl_3)



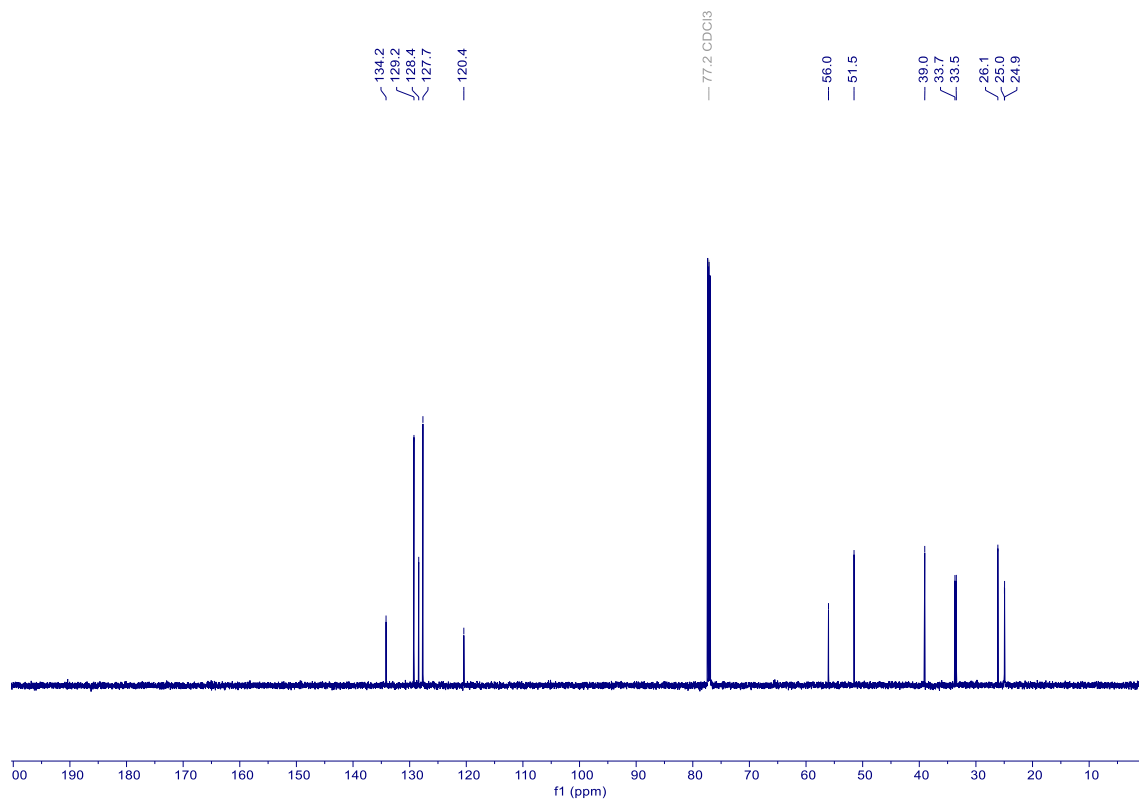
11c – ^{13}C NMR (151 MHz, CDCl_3)



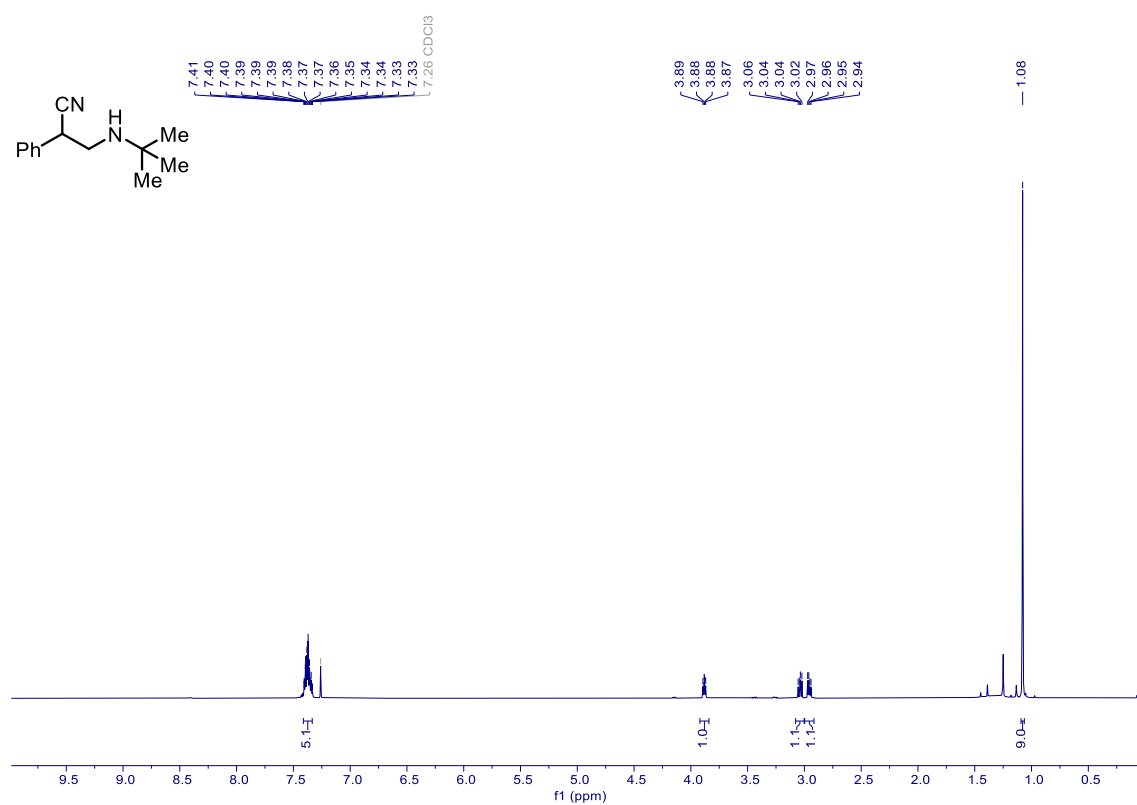
12c – ^1H NMR (600 MHz, CDCl_3)



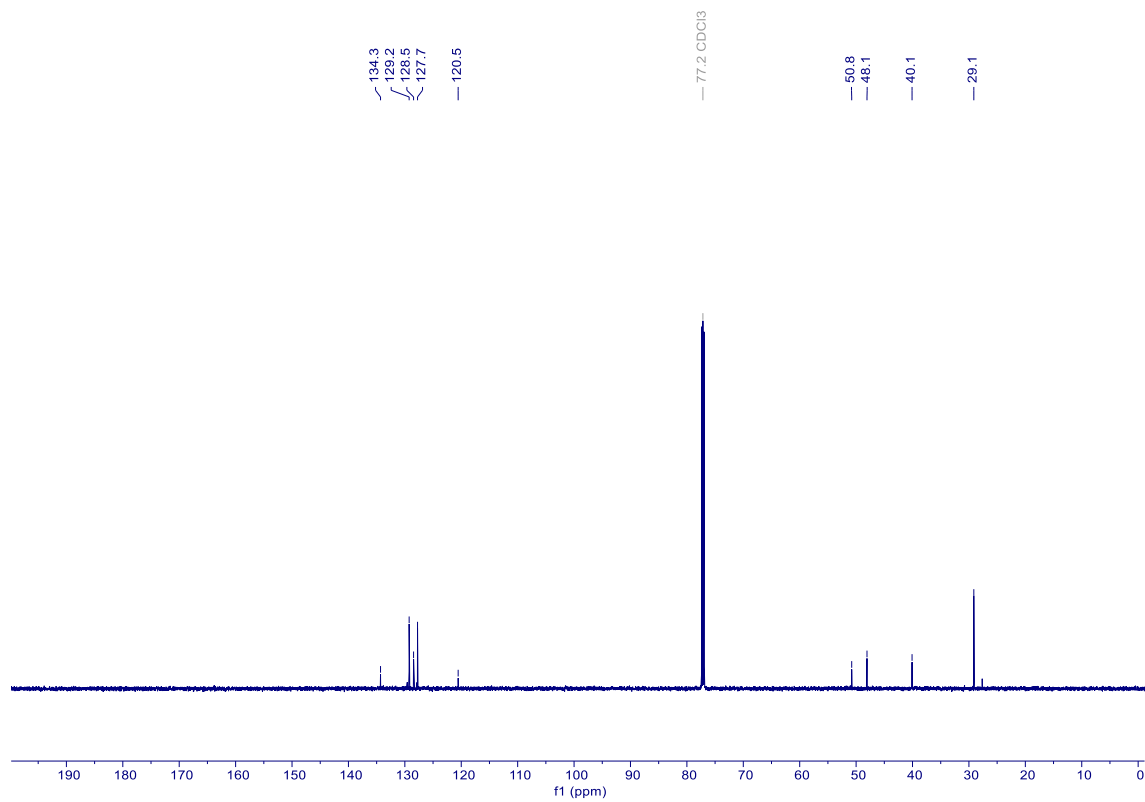
12c – ^{13}C NMR (151 MHz, CDCl_3)



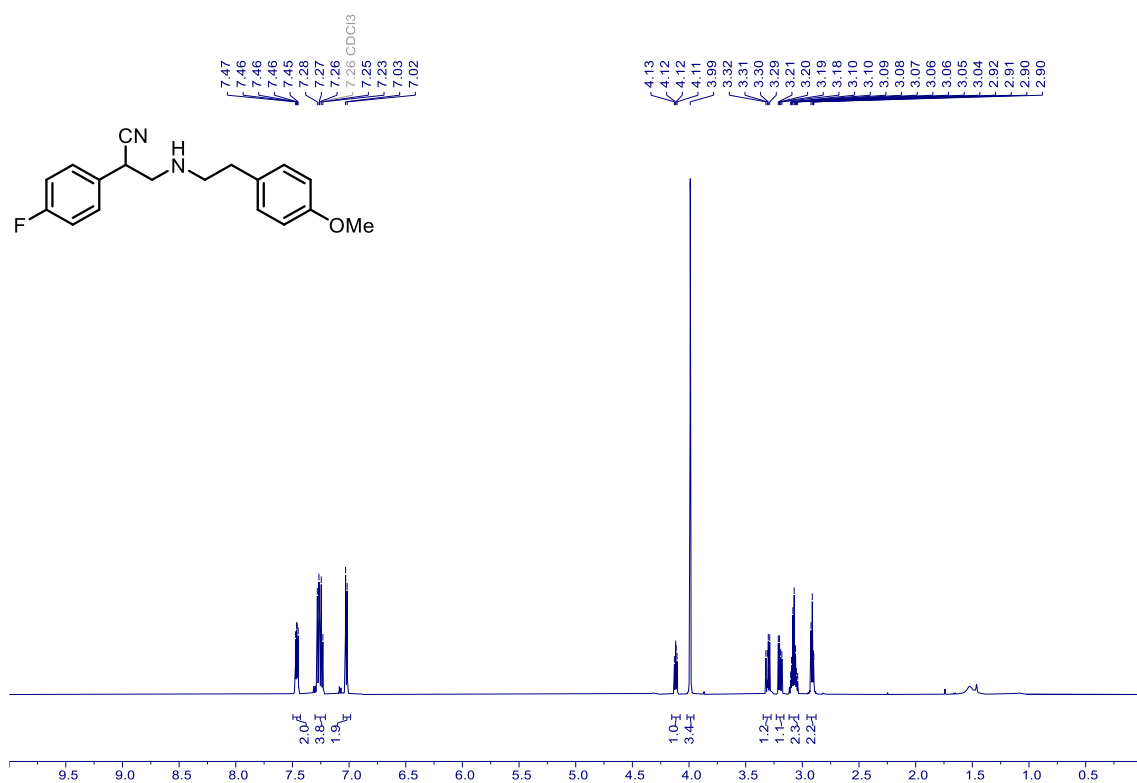
17b – ^1H NMR (600 MHz, CDCl_3)



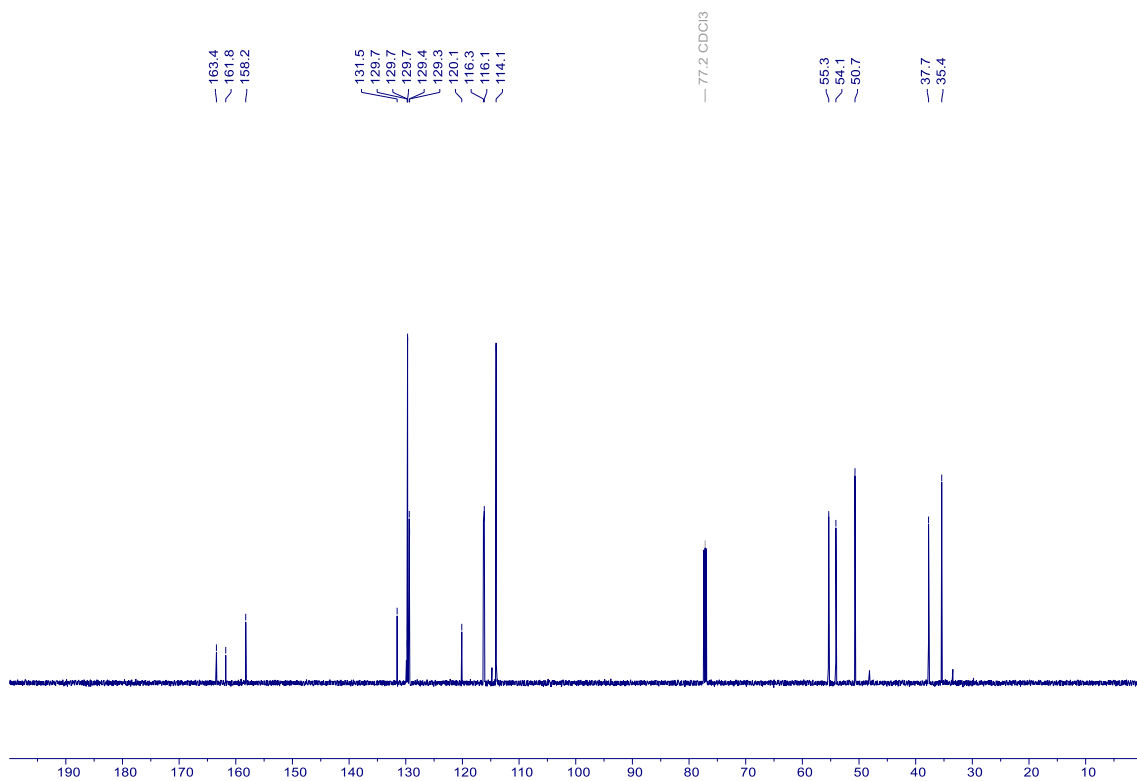
17b – ^{13}C NMR (151 MHz, CDCl_3)



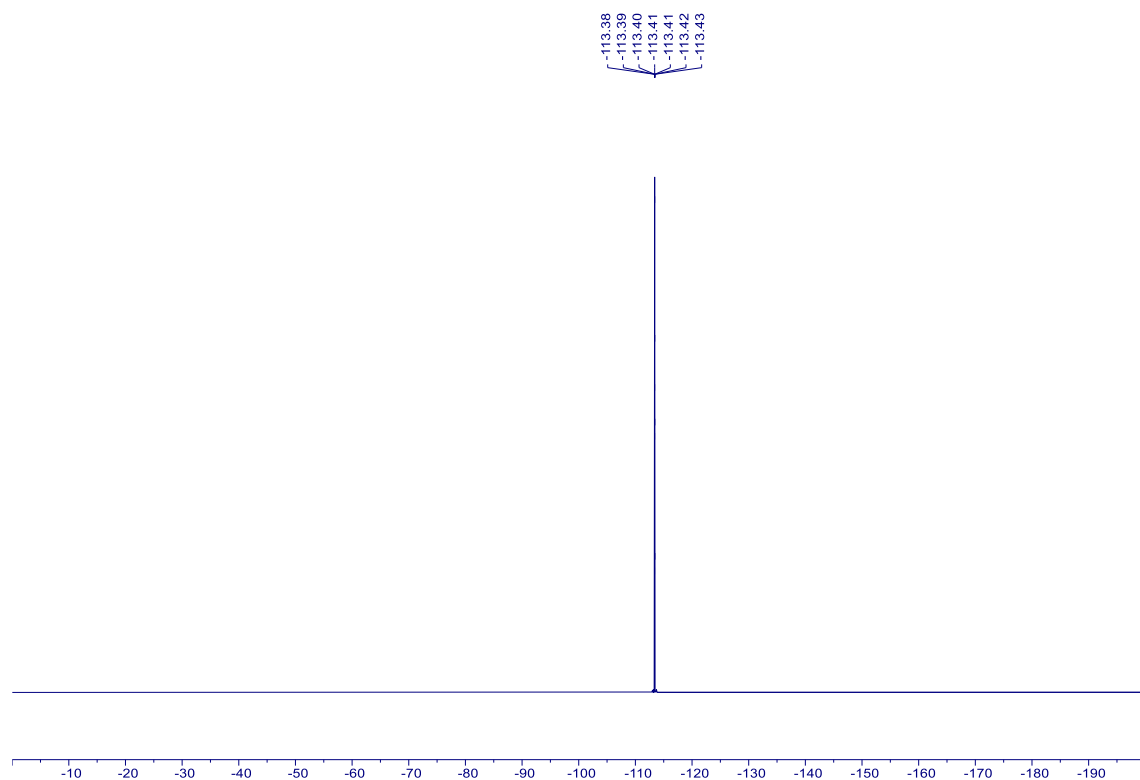
18b – ^1H NMR (600 MHz, CDCl_3)



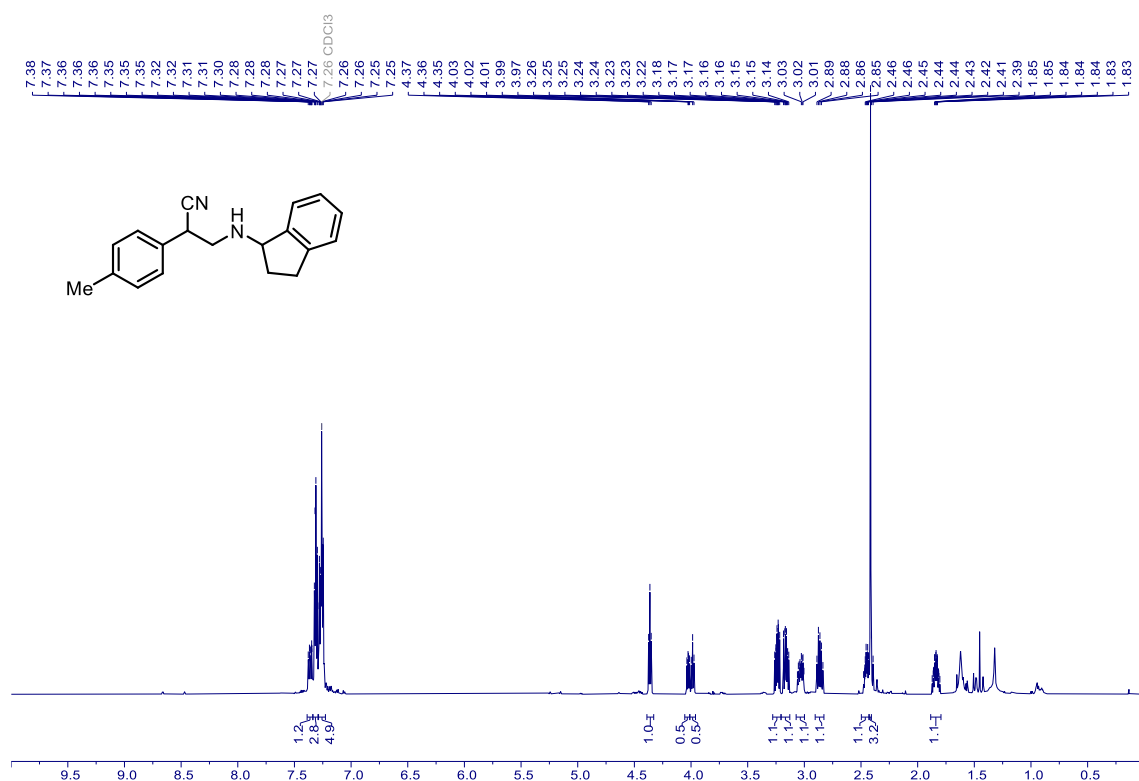
18b – ^{13}C NMR (151 MHz, CDCl_3)



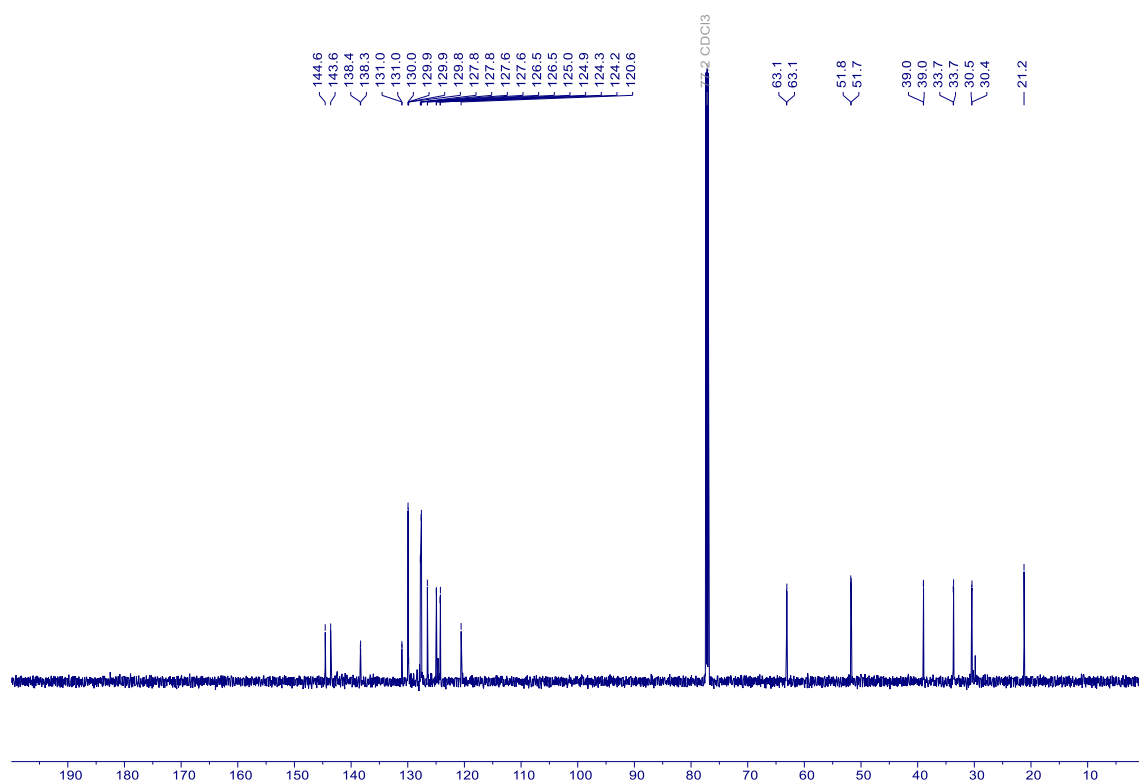
18b – ^{19}F NMR (564 MHz, CDCl_3)



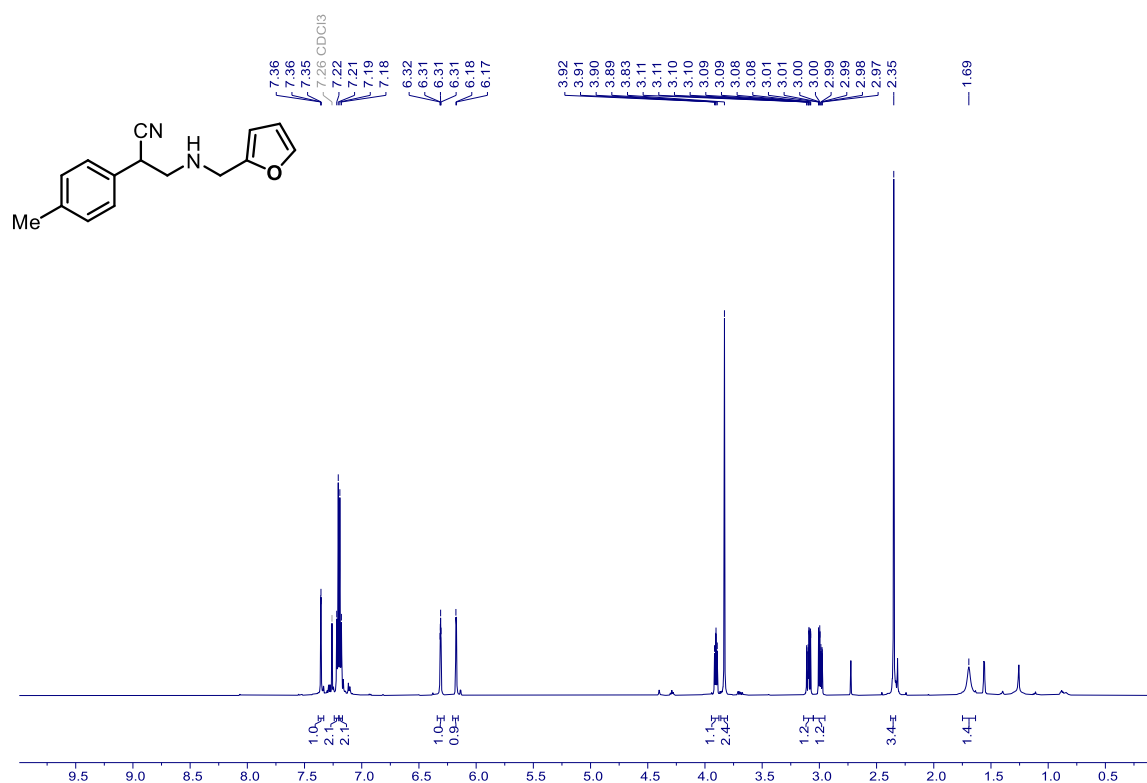
19b – ^1H NMR (600 MHz, CDCl_3)



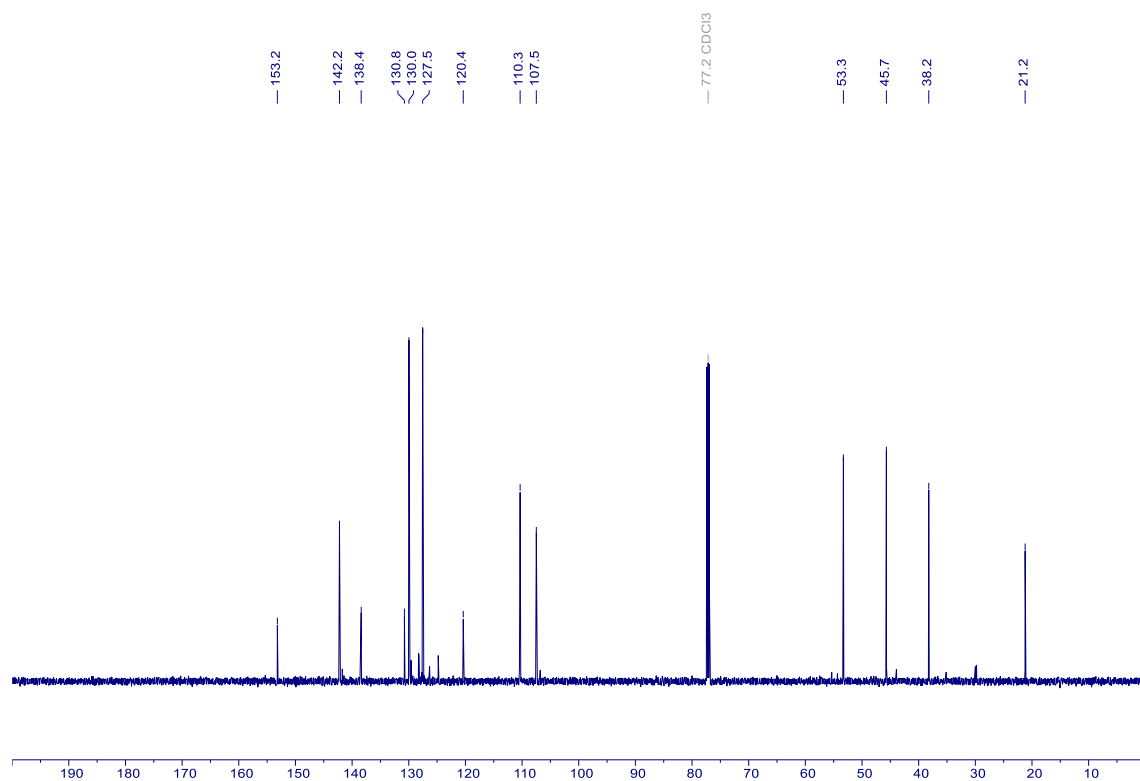
19b – ^{13}C NMR (151 MHz, CDCl_3)



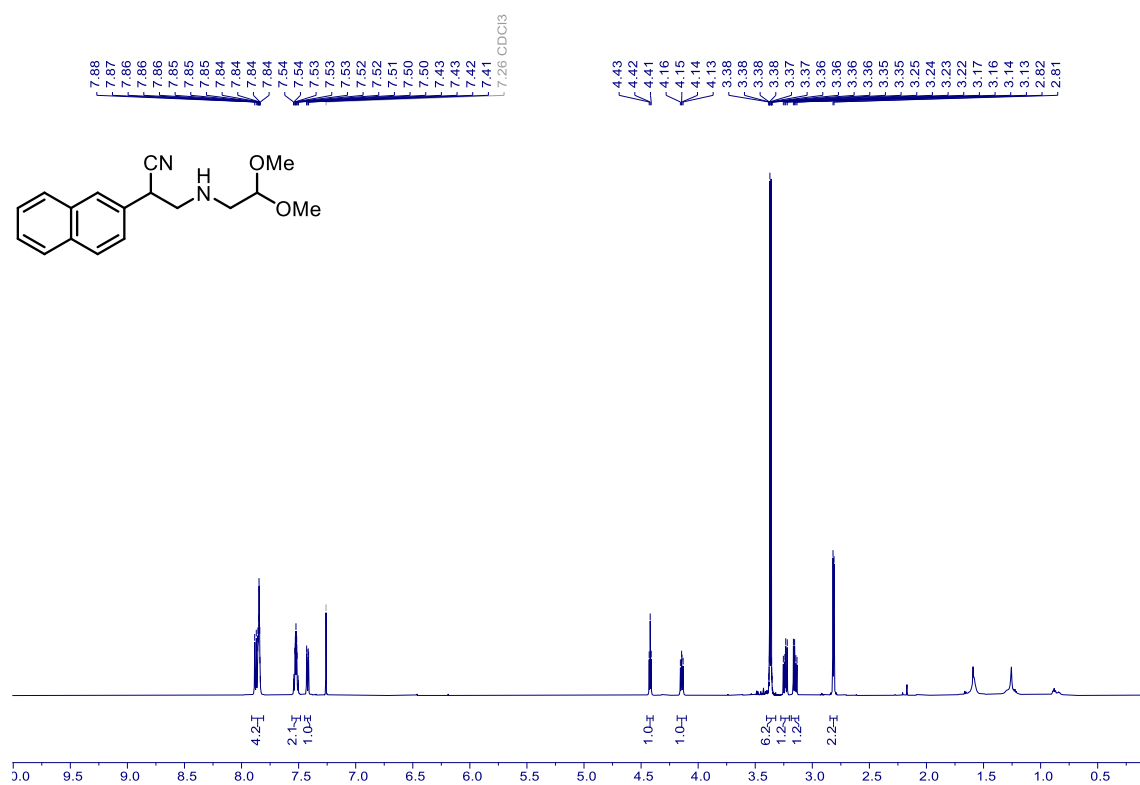
20b – ^1H NMR (600 MHz, CDCl_3)



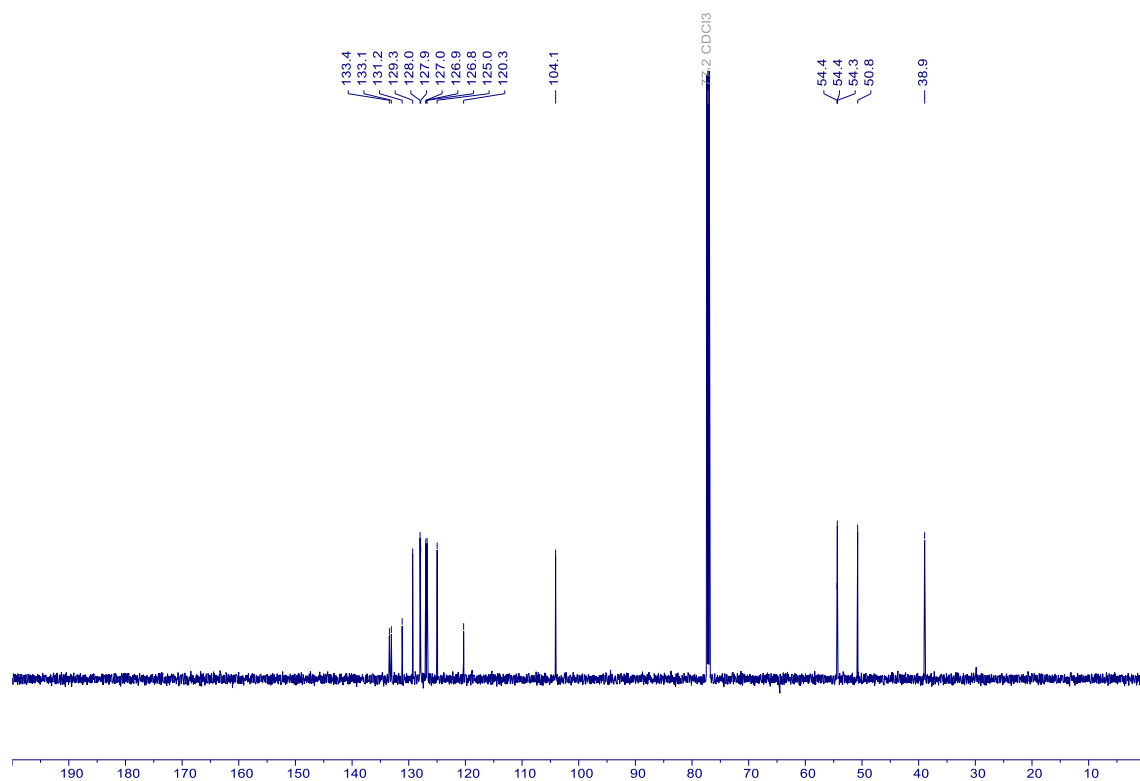
20b – ^{13}C NMR (151 MHz, CDCl_3)



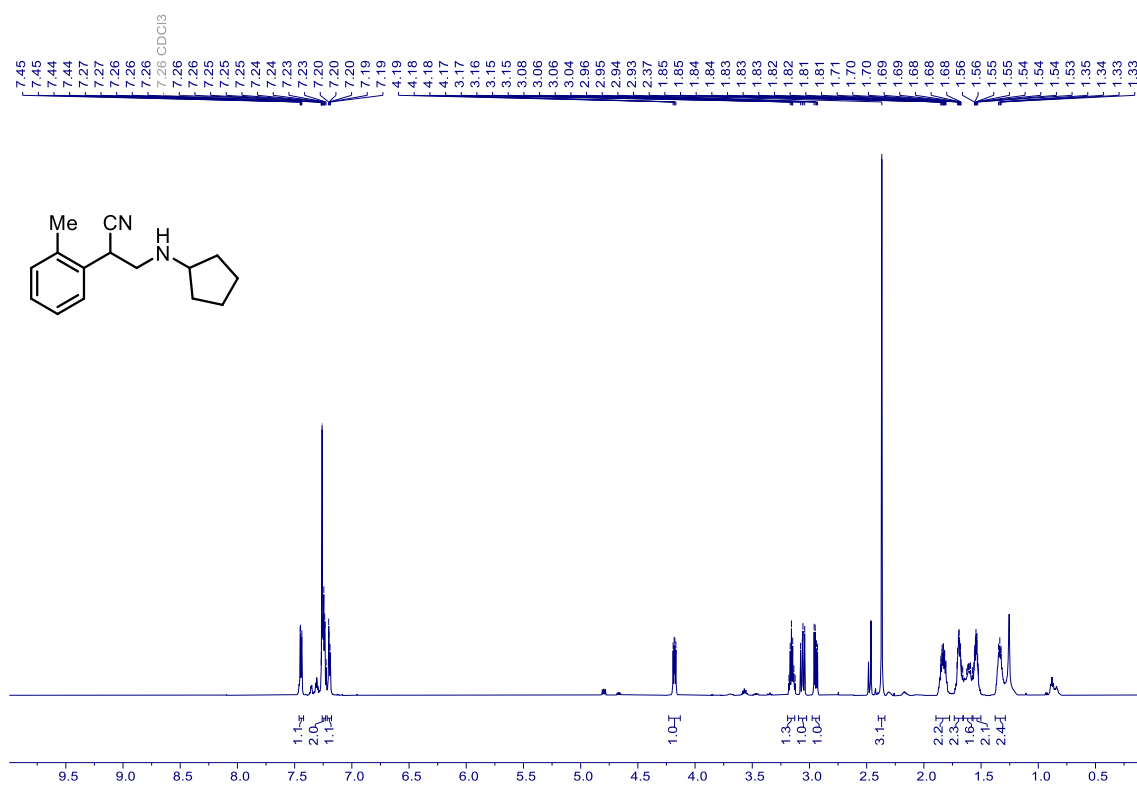
21b – ^1H NMR (600 MHz, CDCl_3)



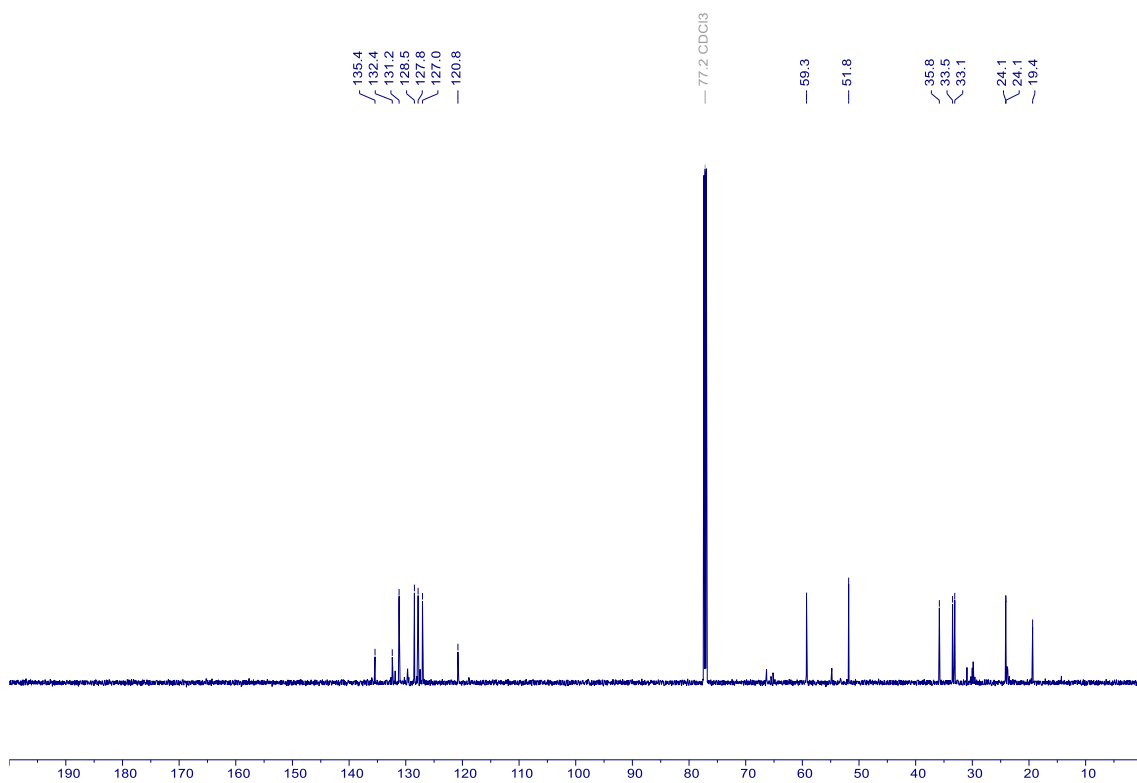
21b – ^{13}C NMR (151 MHz, CDCl_3)



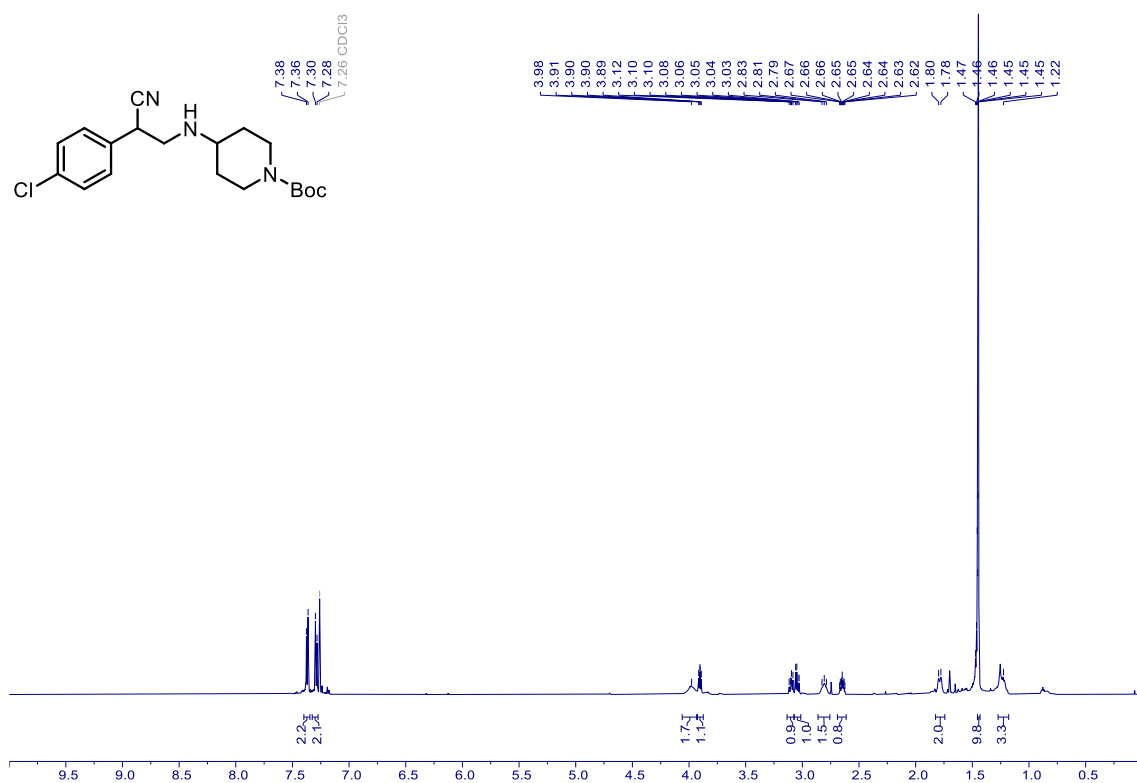
22b – ^1H NMR (600 MHz, CDCl_3)



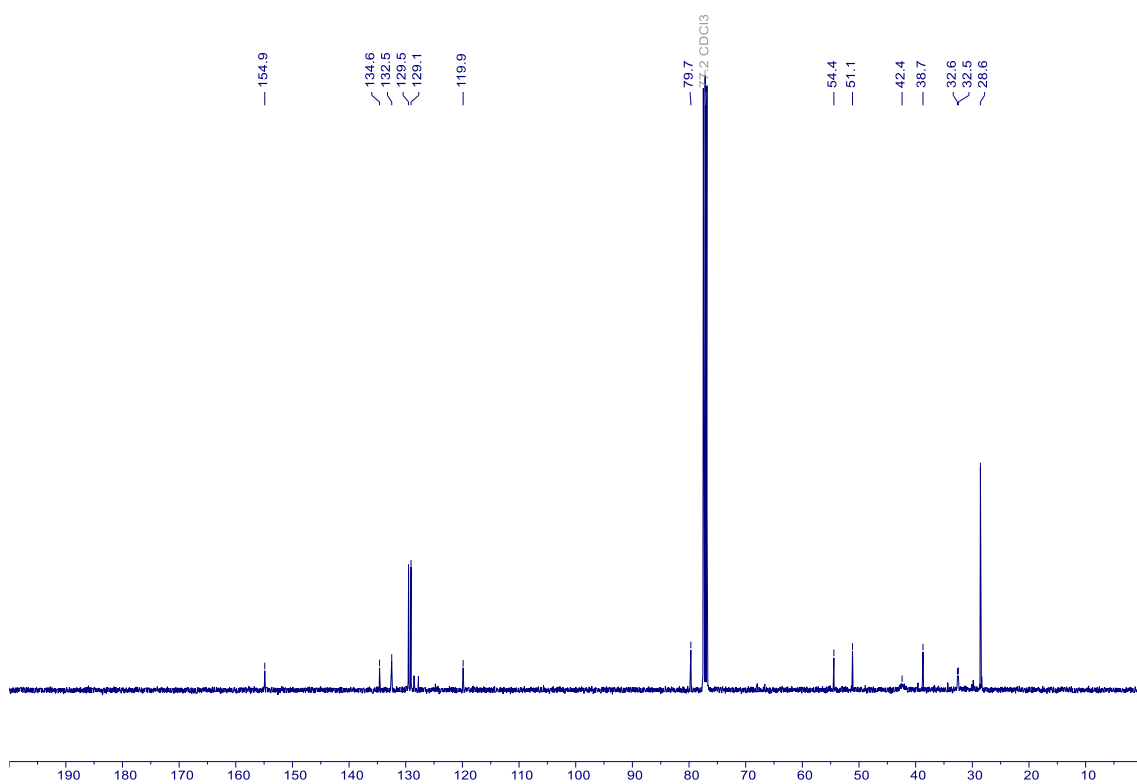
22b – ^{13}C NMR (151 MHz, CDCl_3)



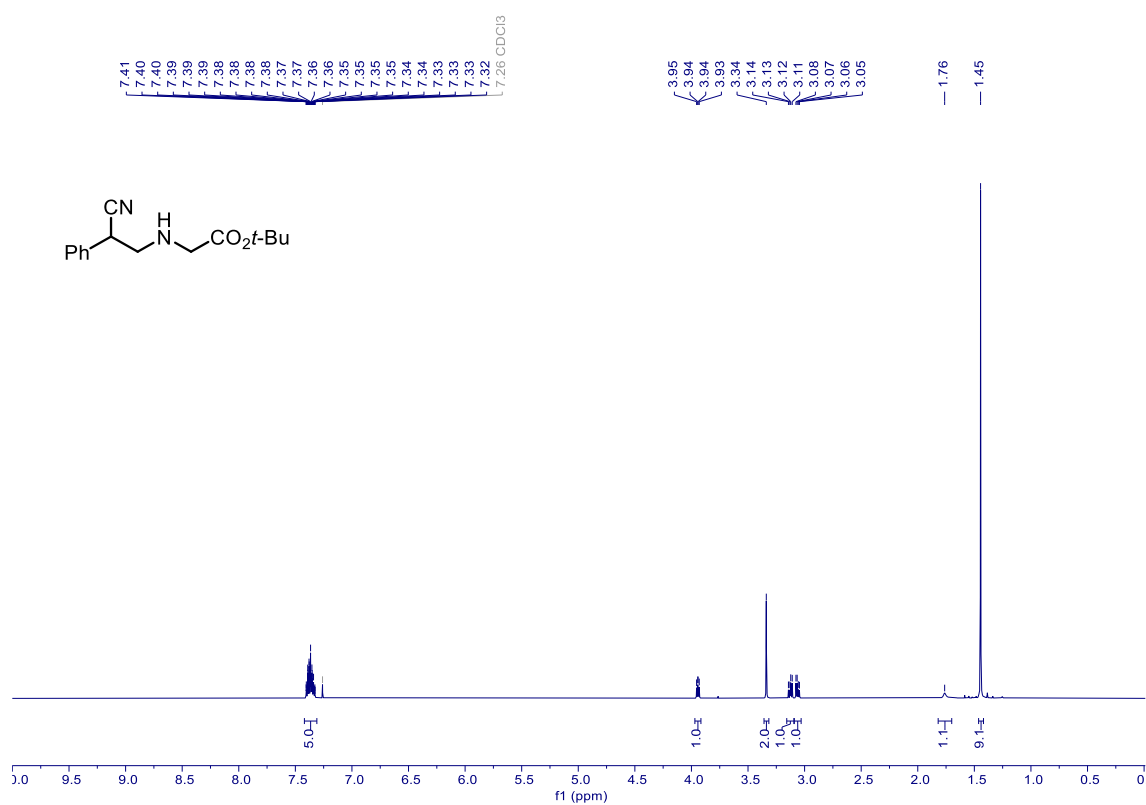
23b – ^1H NMR (600 MHz, CDCl_3)



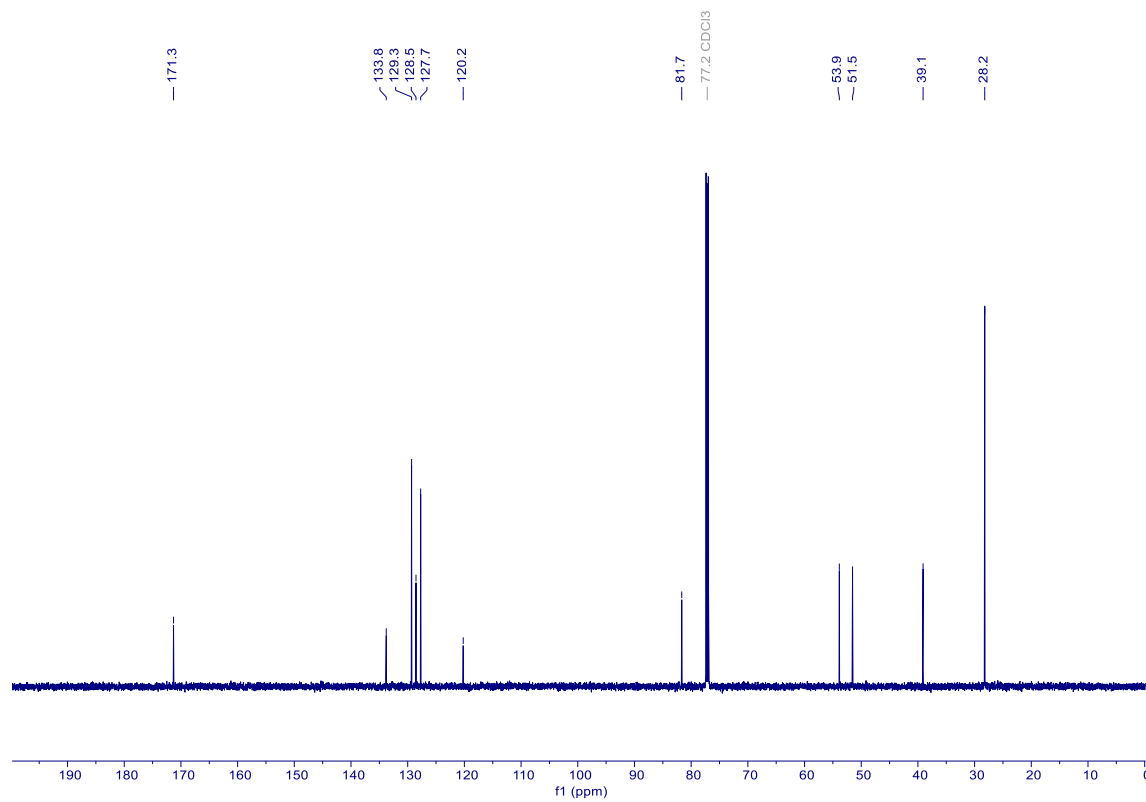
23b – ^{13}C NMR (101 MHz, CDCl_3)



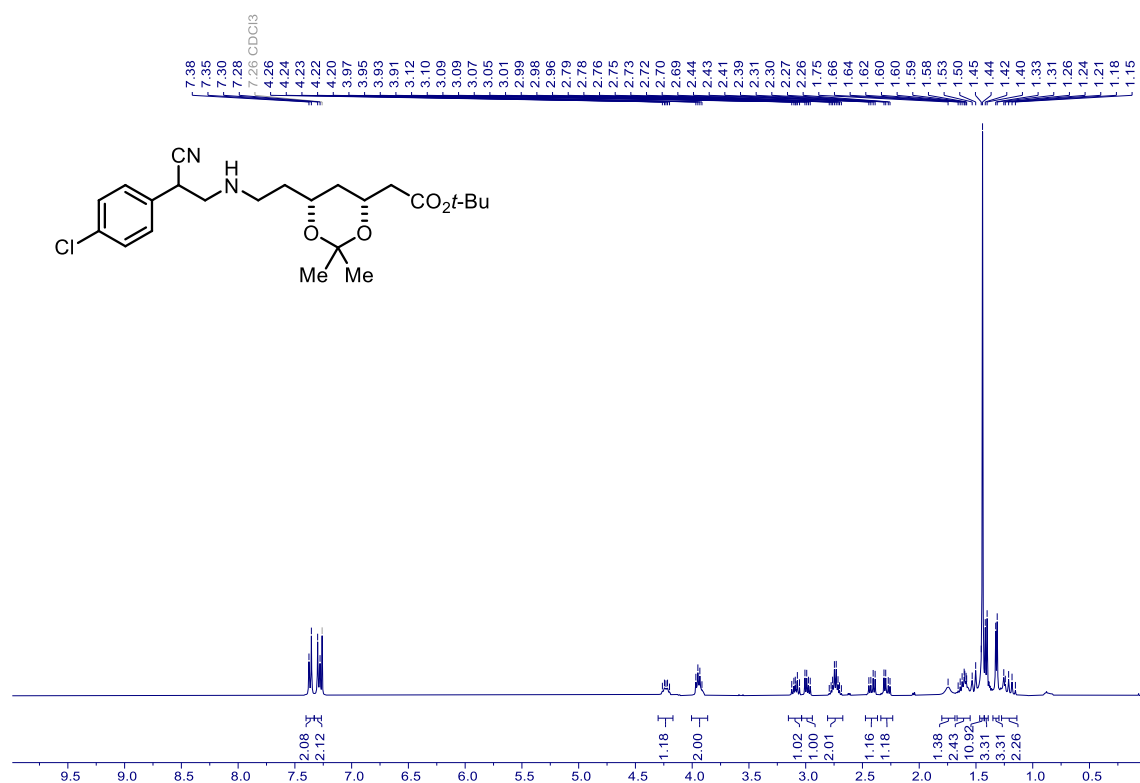
24b – ^1H NMR (600 MHz, CDCl_3)



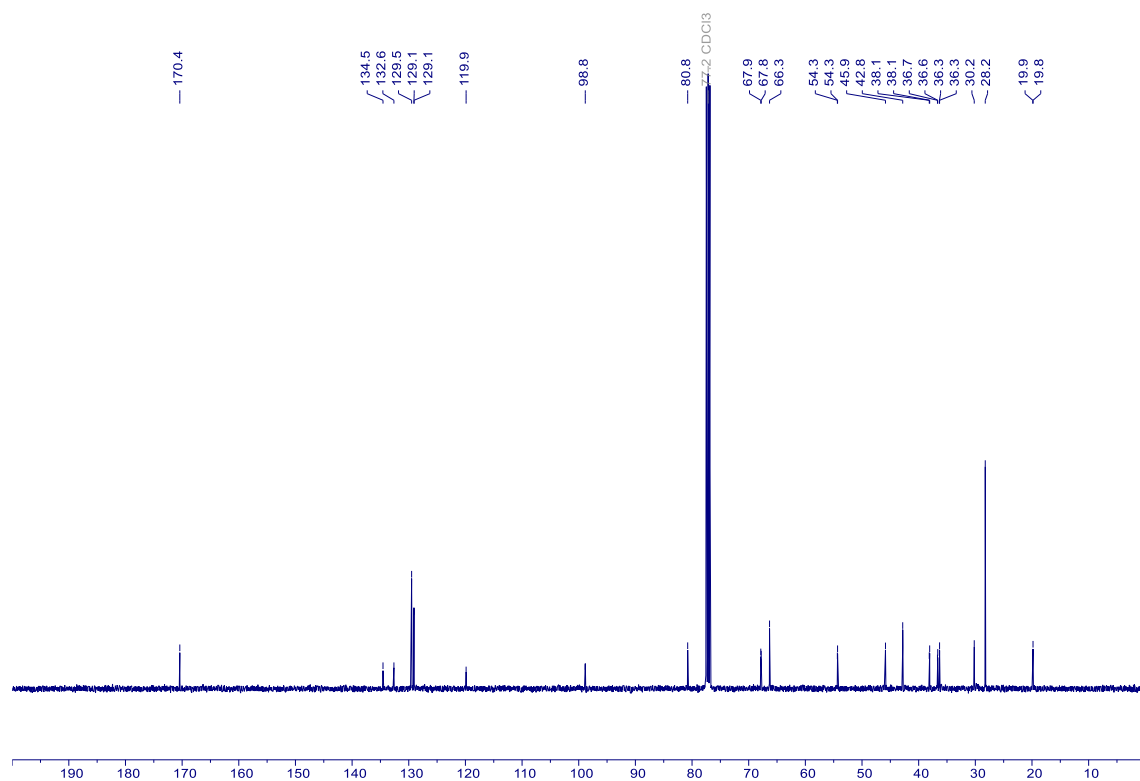
24b – ^{13}C NMR (151 MHz, CDCl_3)



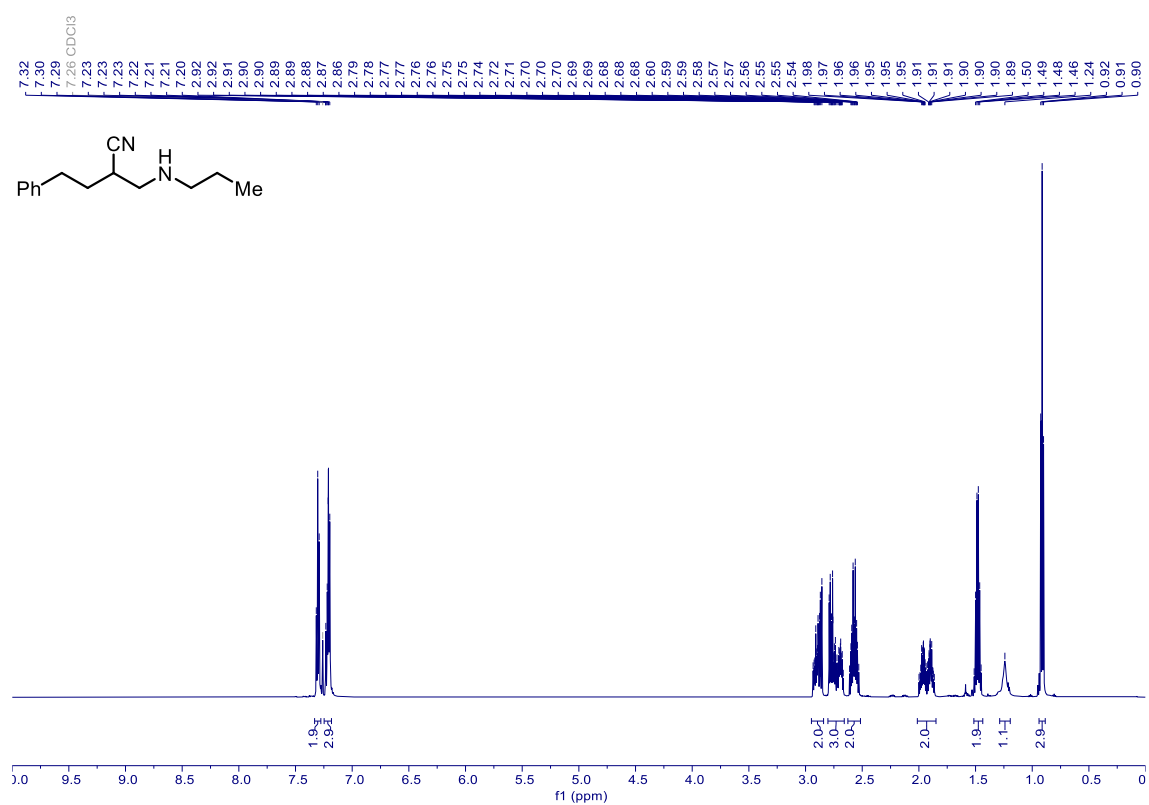
25b – ^1H NMR (600 MHz, CDCl_3)



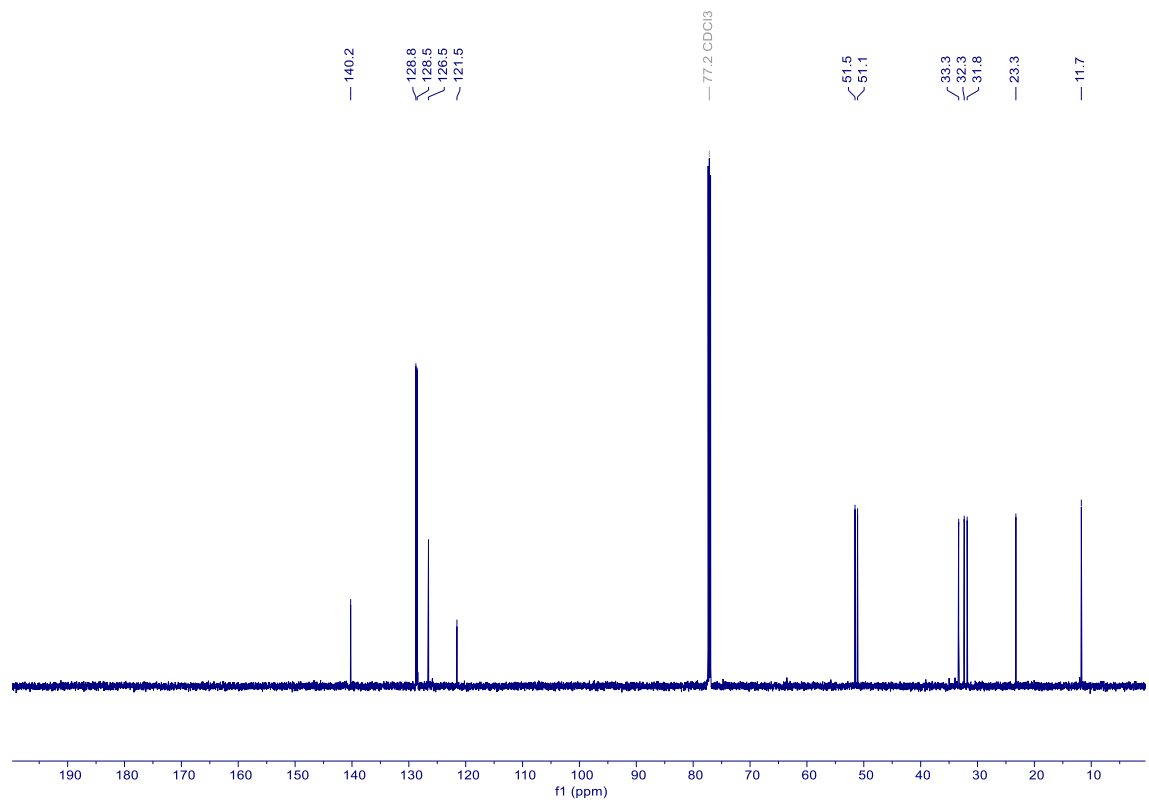
25b – ^{13}C NMR (151 MHz, CDCl_3)



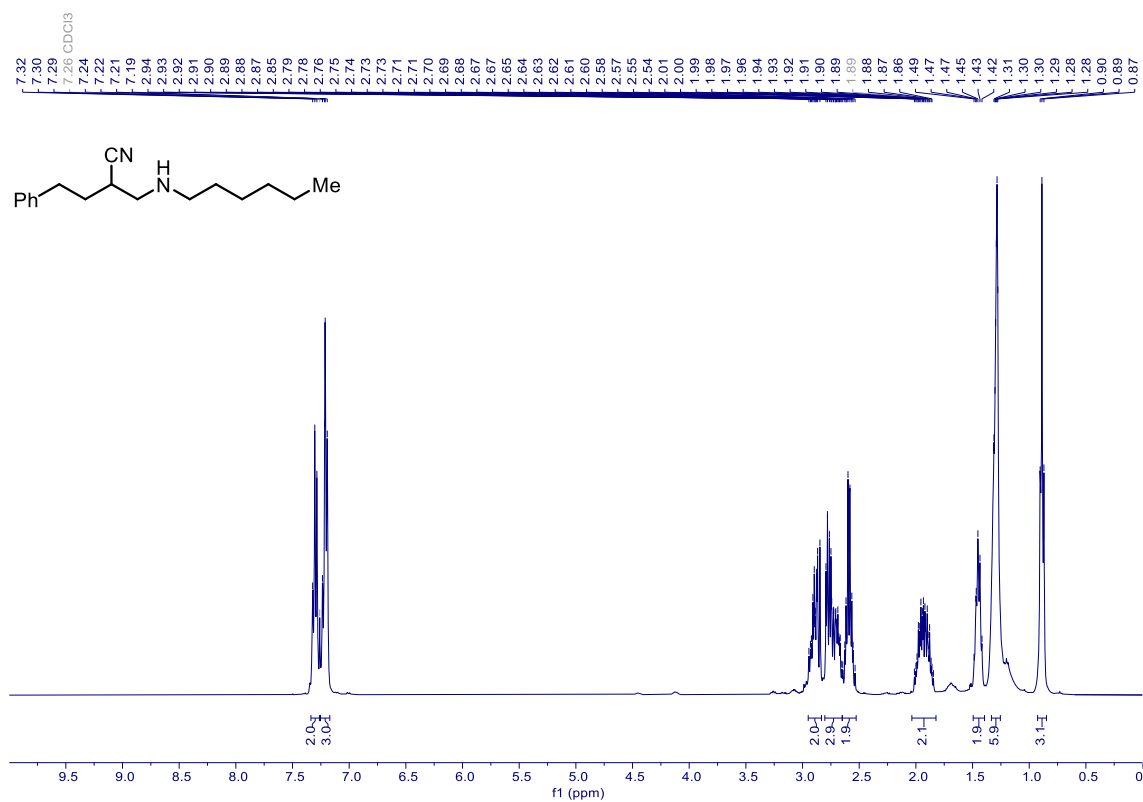
26b – ^1H NMR (600 MHz, CDCl_3)



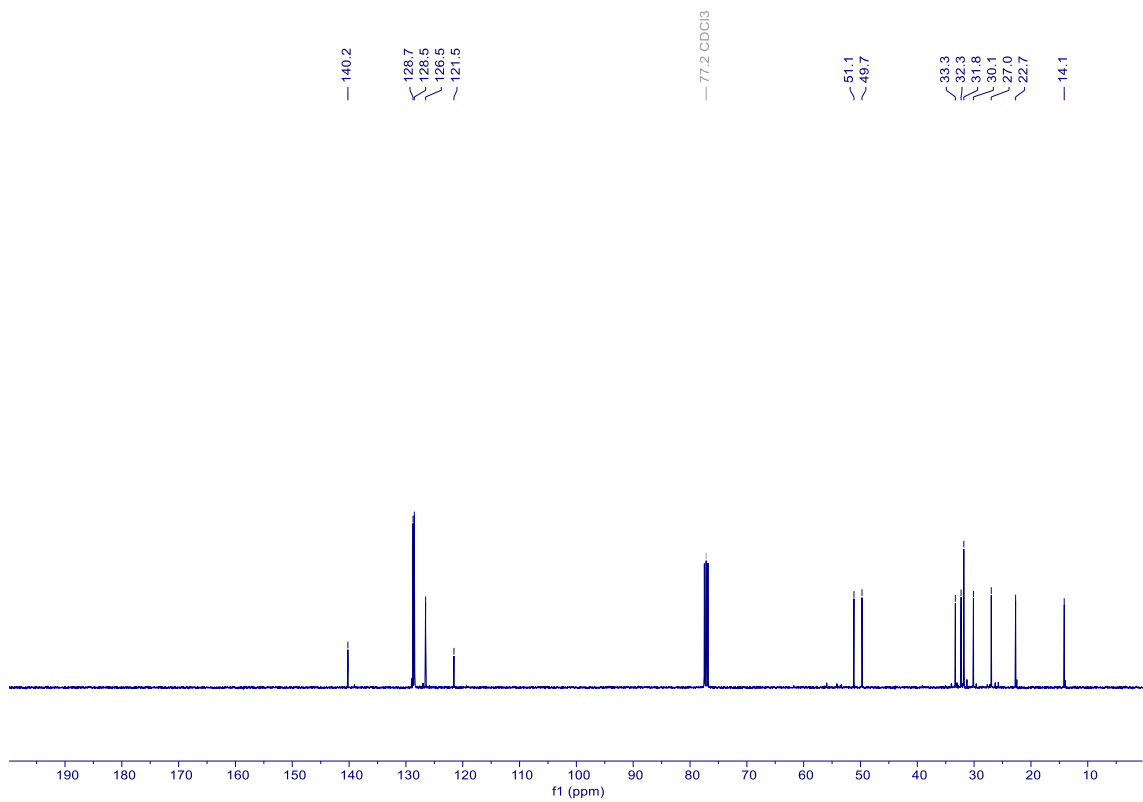
26b – ^{13}C NMR (151 MHz, CDCl_3)



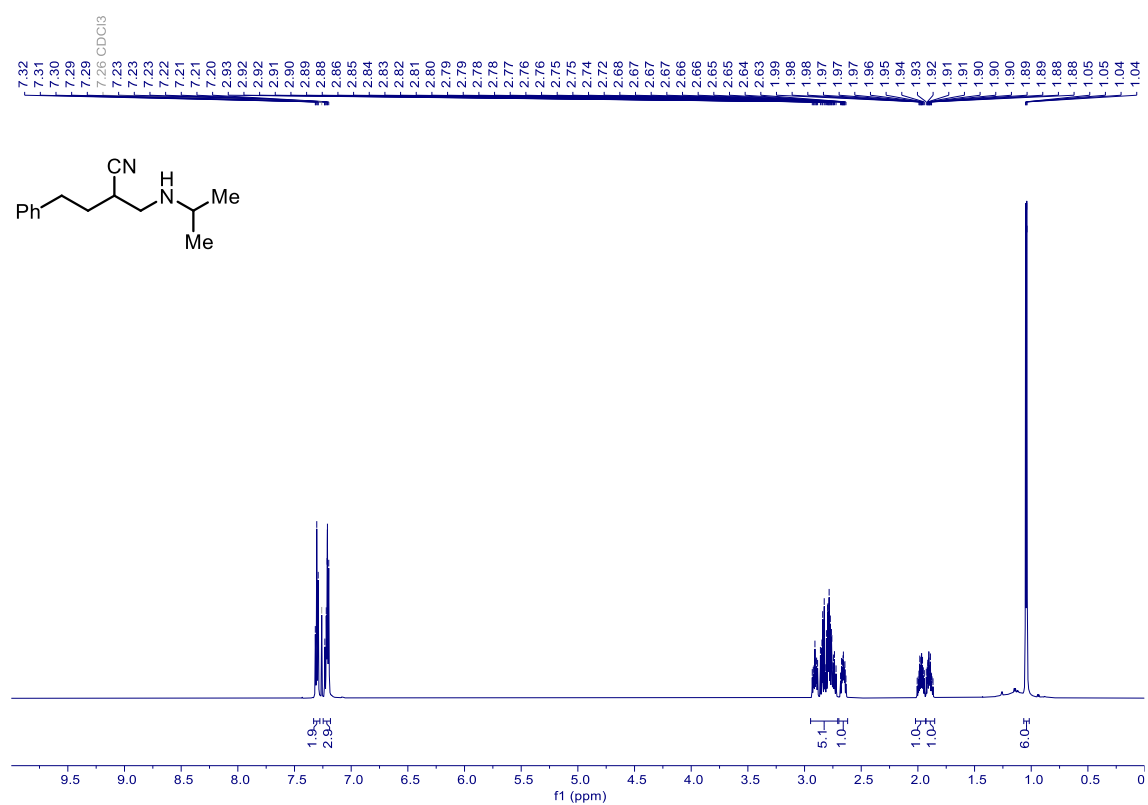
27b – ^1H NMR (400 MHz, CDCl_3)



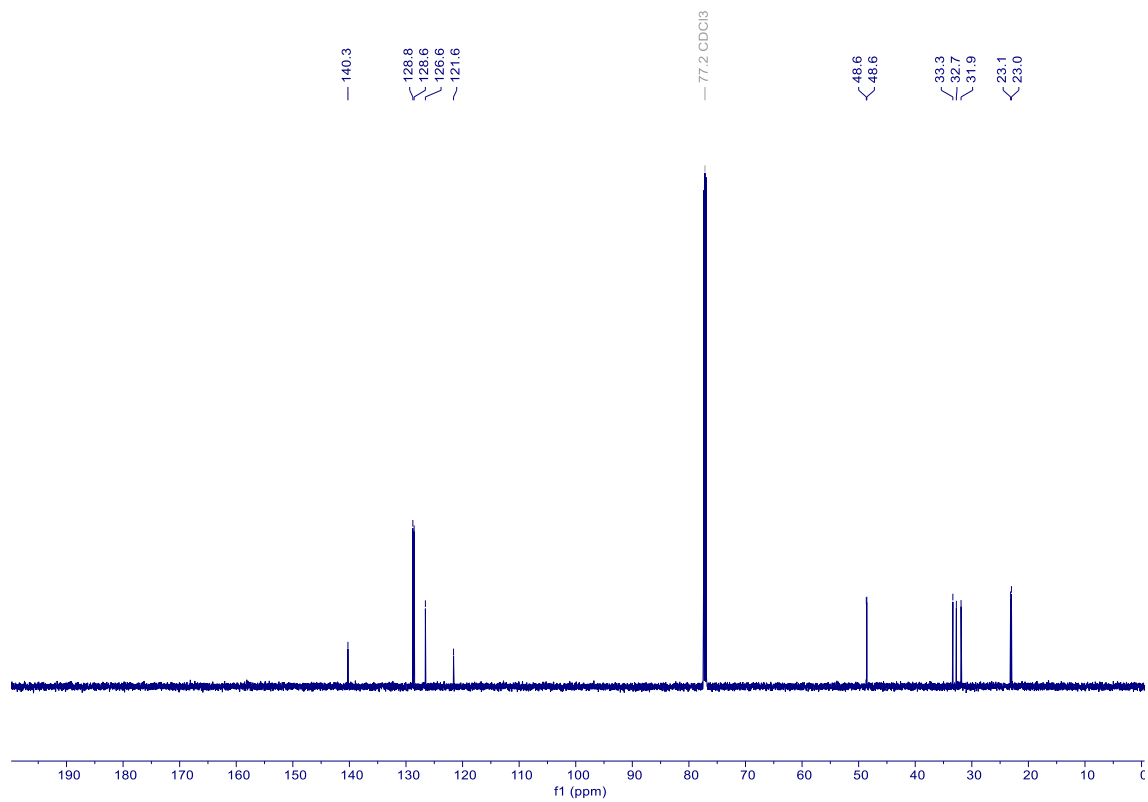
27b – ^{13}C NMR (101 MHz, CDCl_3)



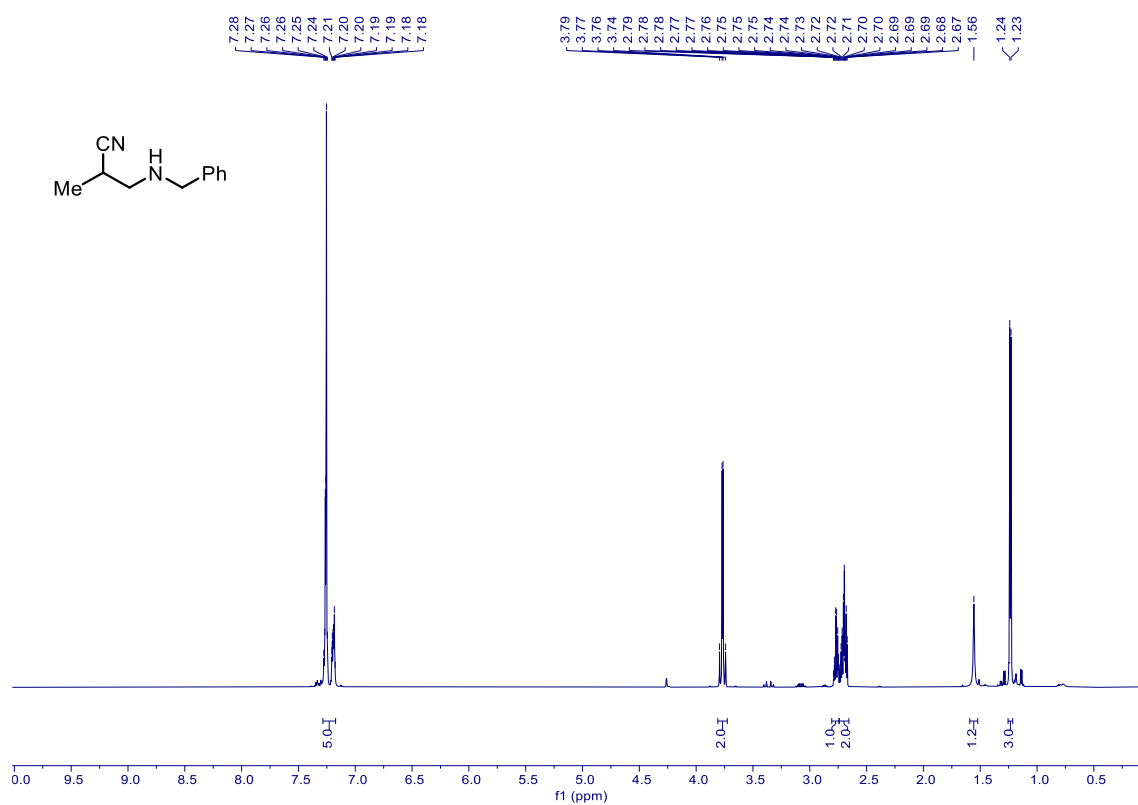
13c – ^1H NMR (600 MHz, CDCl_3)



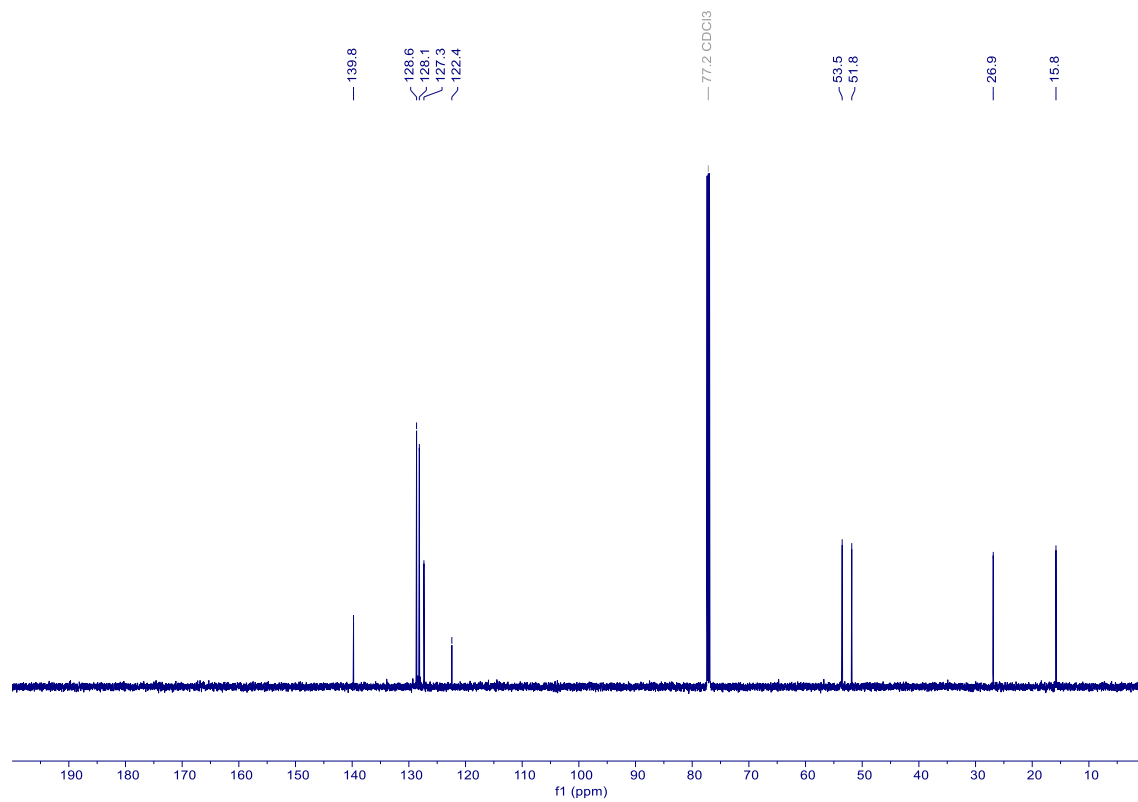
13c – ^{13}C NMR (151 MHz, CDCl_3)



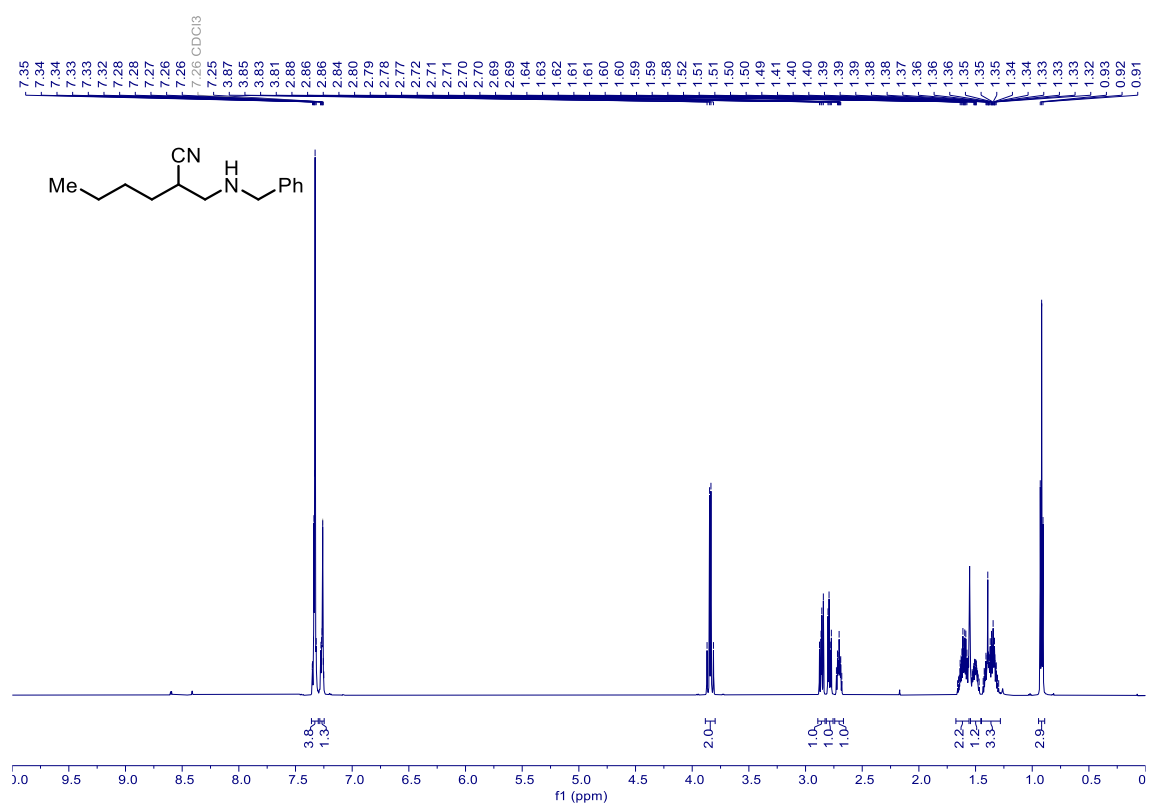
28b – ^1H NMR (600 MHz, CDCl_3)



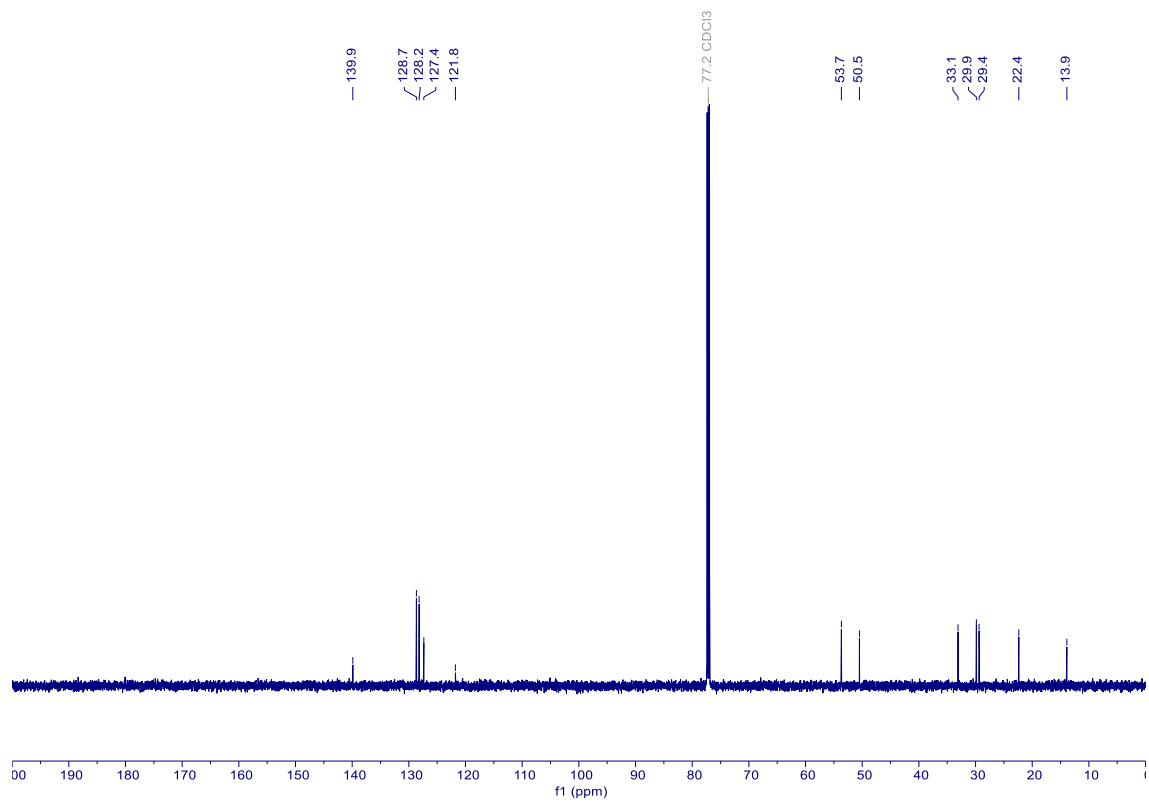
28b – ^{13}C NMR (151 MHz, CDCl_3)



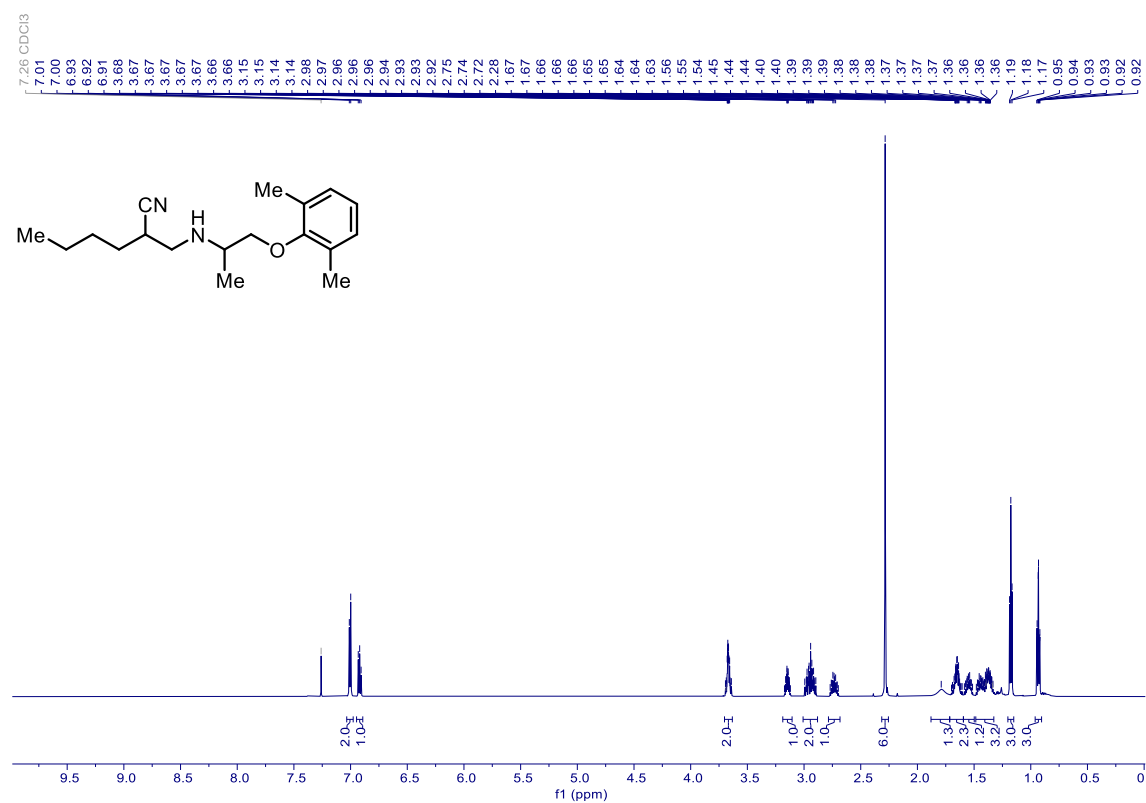
29b – ^1H NMR (600 MHz, CDCl_3)



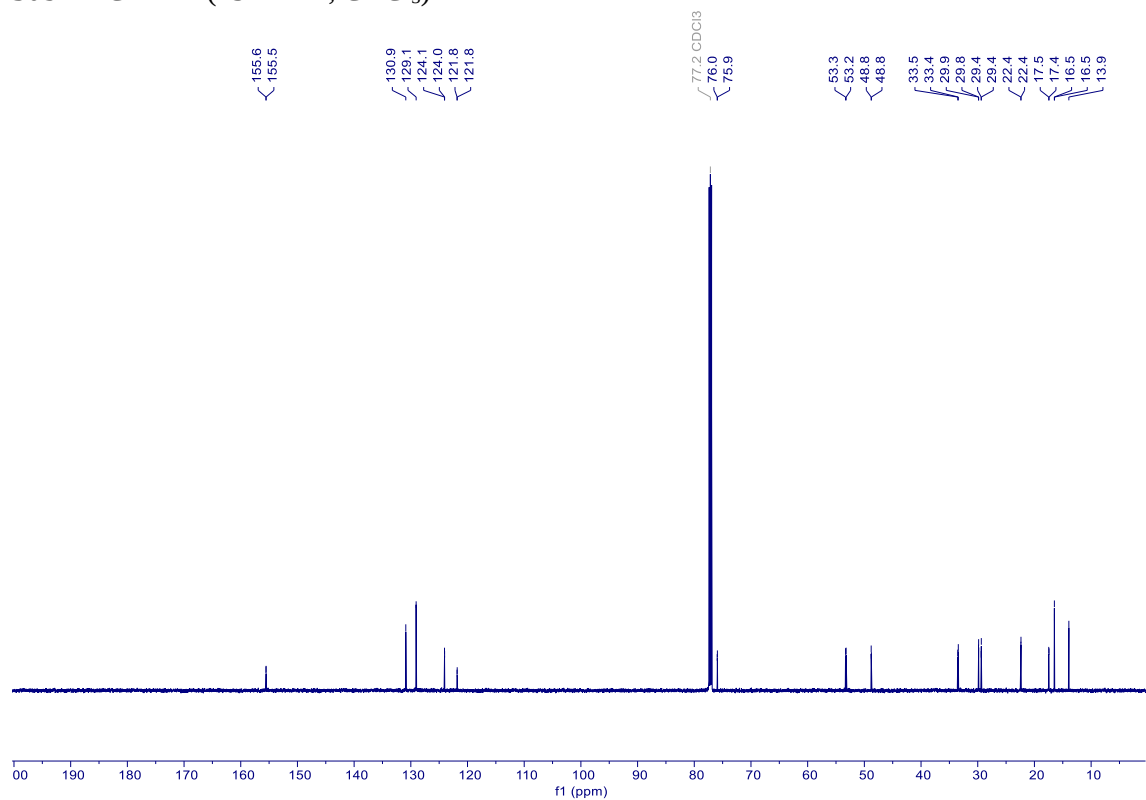
29b – ^{13}C NMR (151 MHz, CDCl_3)



30b – ^1H NMR (600 MHz, CDCl_3)



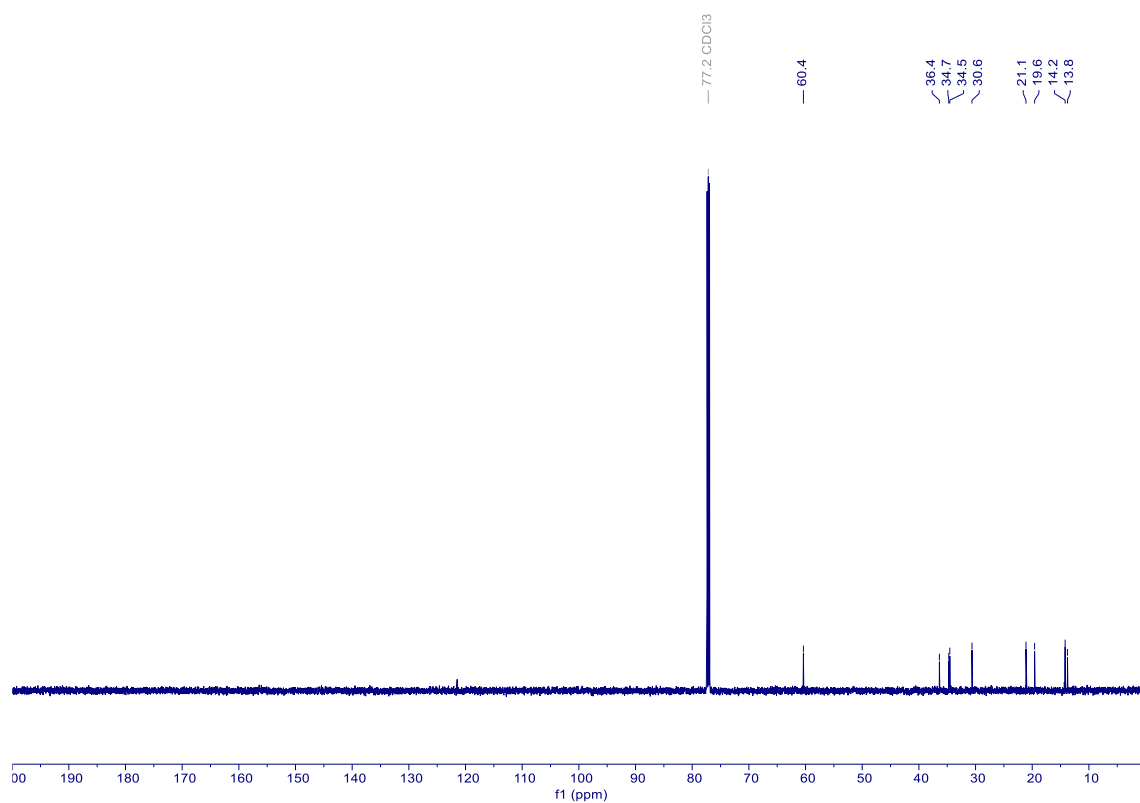
30b – ^{13}C NMR (151 MHz, CDCl_3)



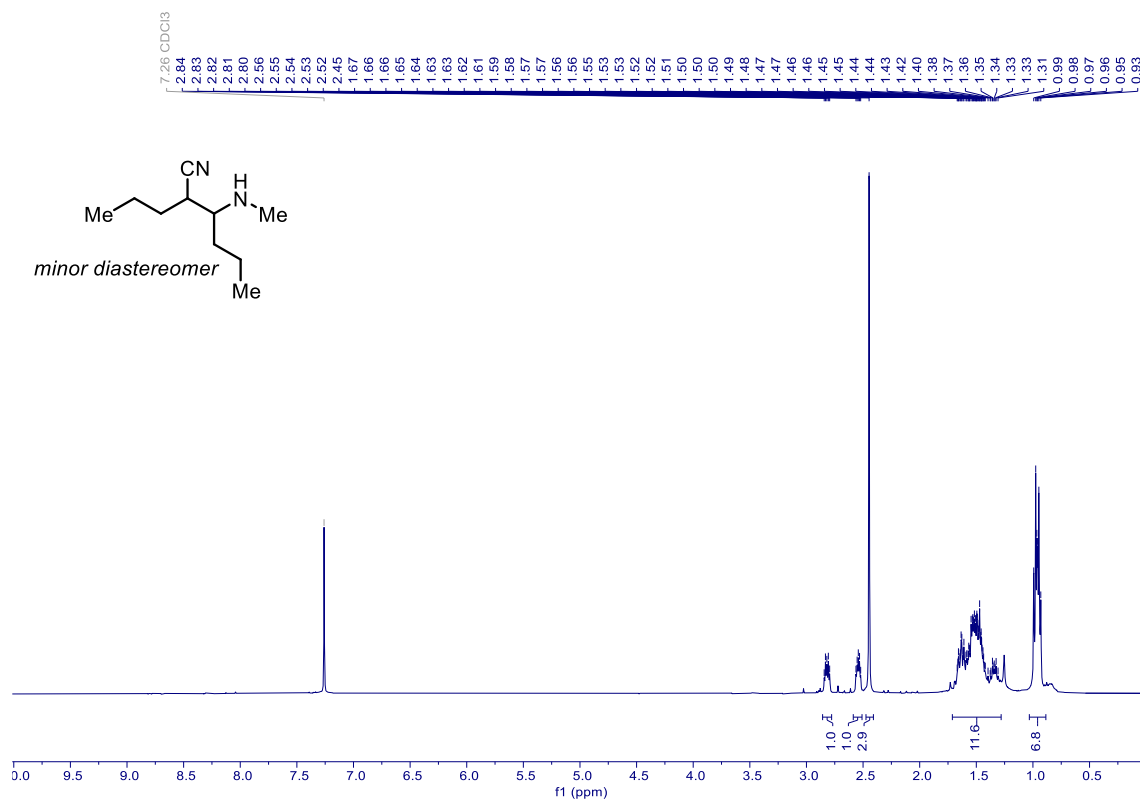
31b (*major diastereomer*) – ^1H NMR (600 MHz, CDCl_3)



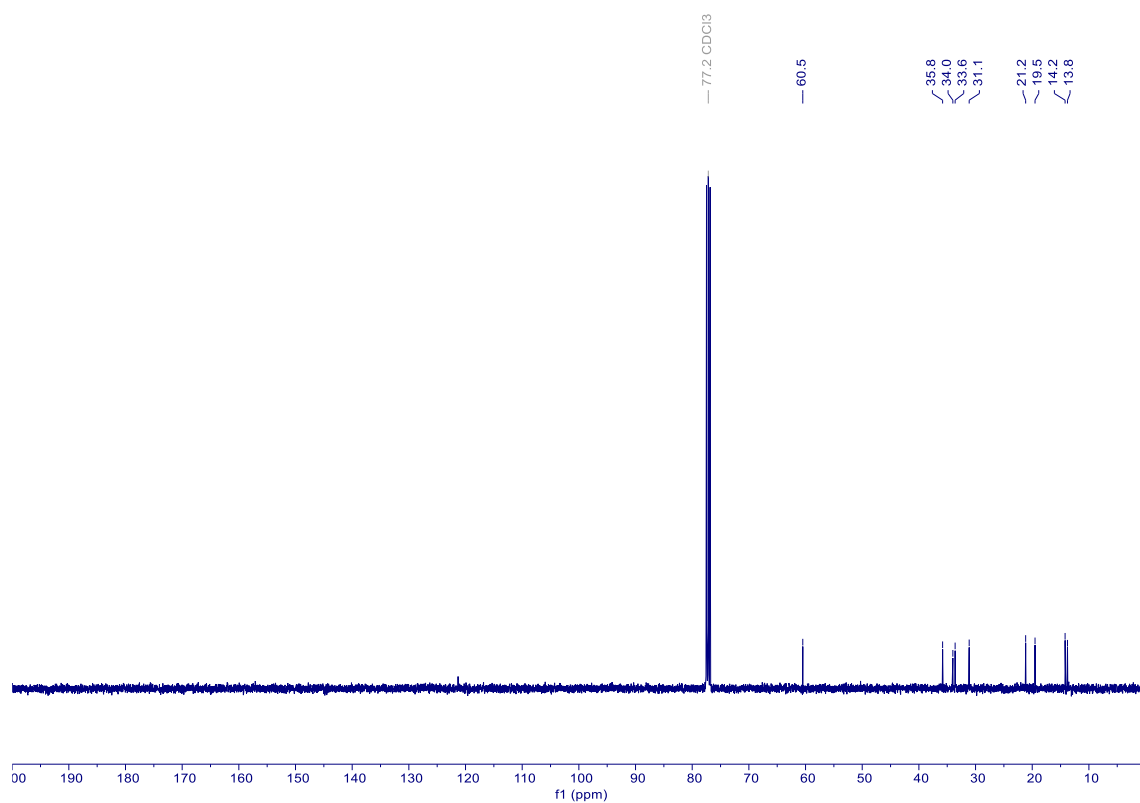
31b (*major diastereomer*) – ^{13}C NMR (151 MHz, CDCl_3)



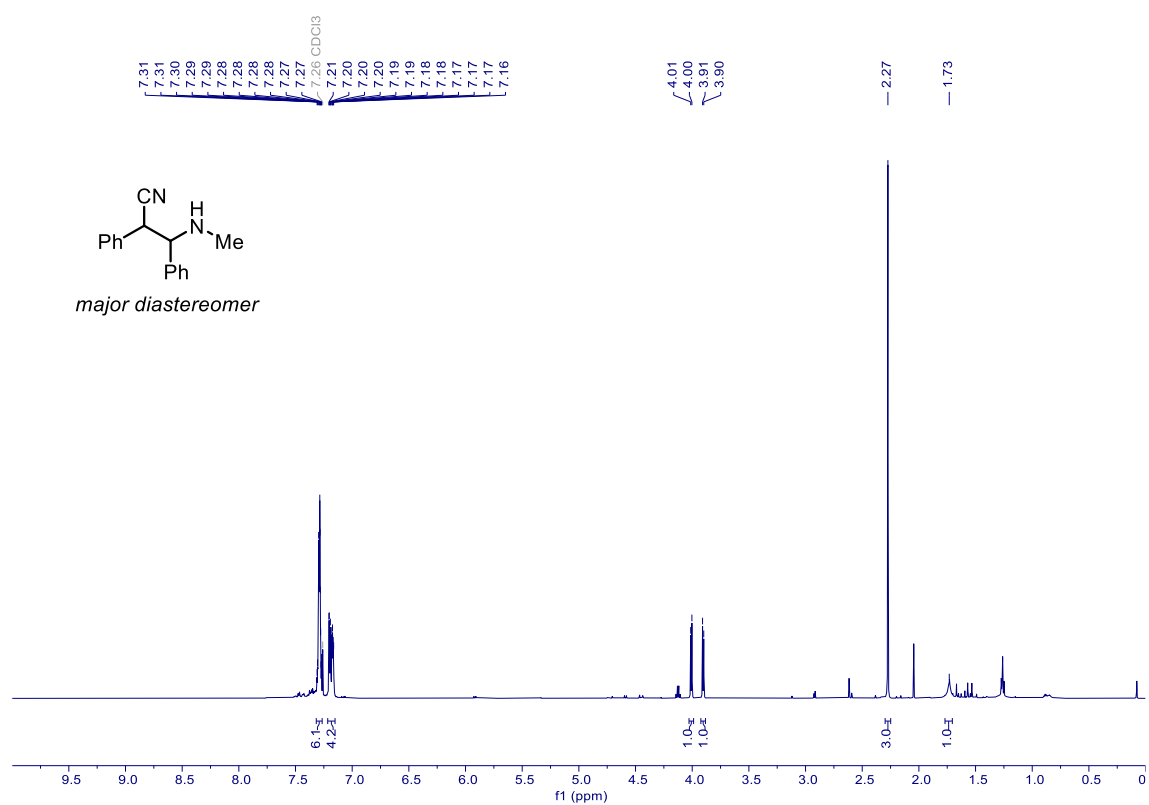
31b (minor diastereomer) – ^1H NMR (400 MHz, CDCl_3)



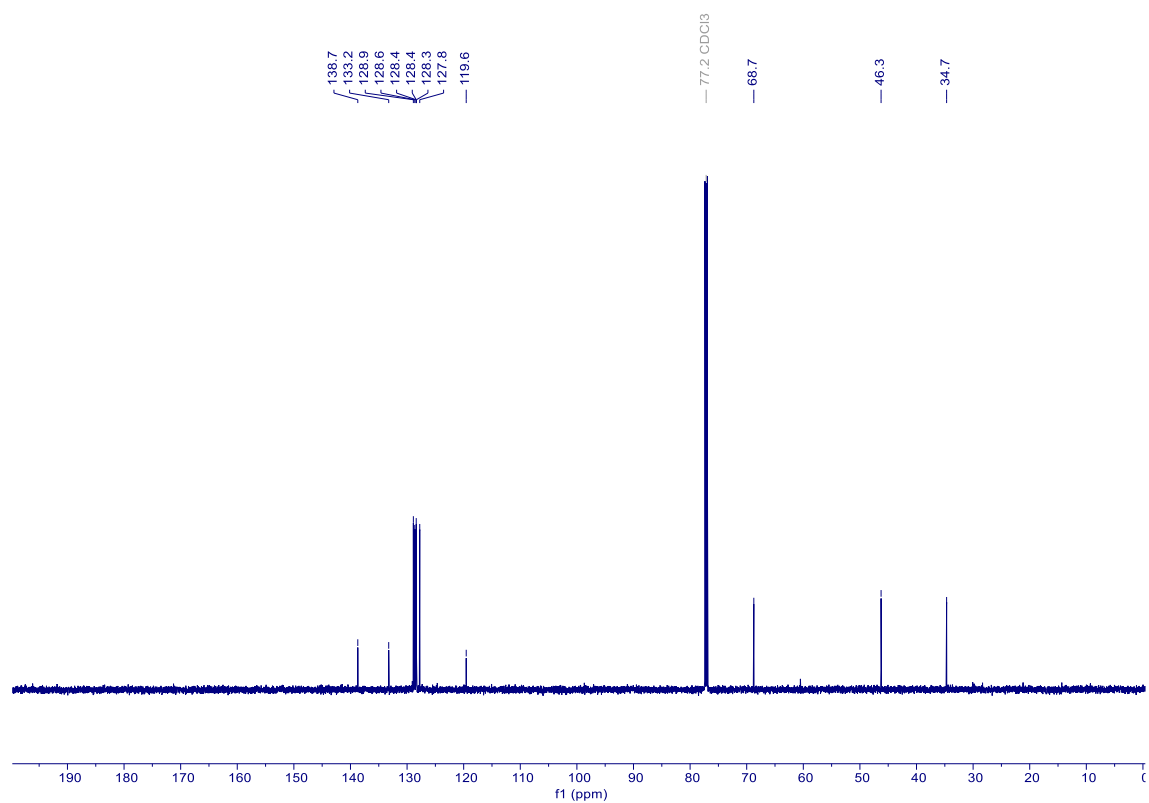
31b (minor diastereomer) – ^{13}C NMR (101 MHz, CDCl_3)



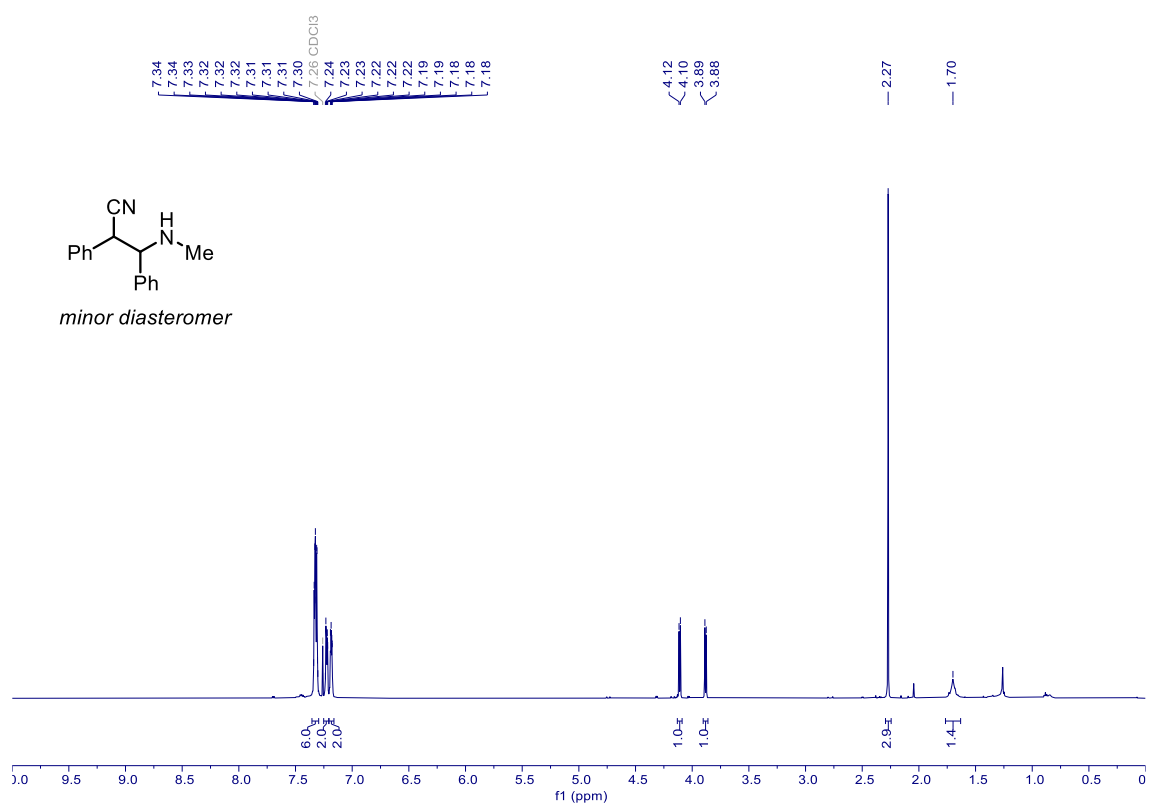
32b (*major diastereomer*) – ^1H NMR (600 MHz, CDCl_3)



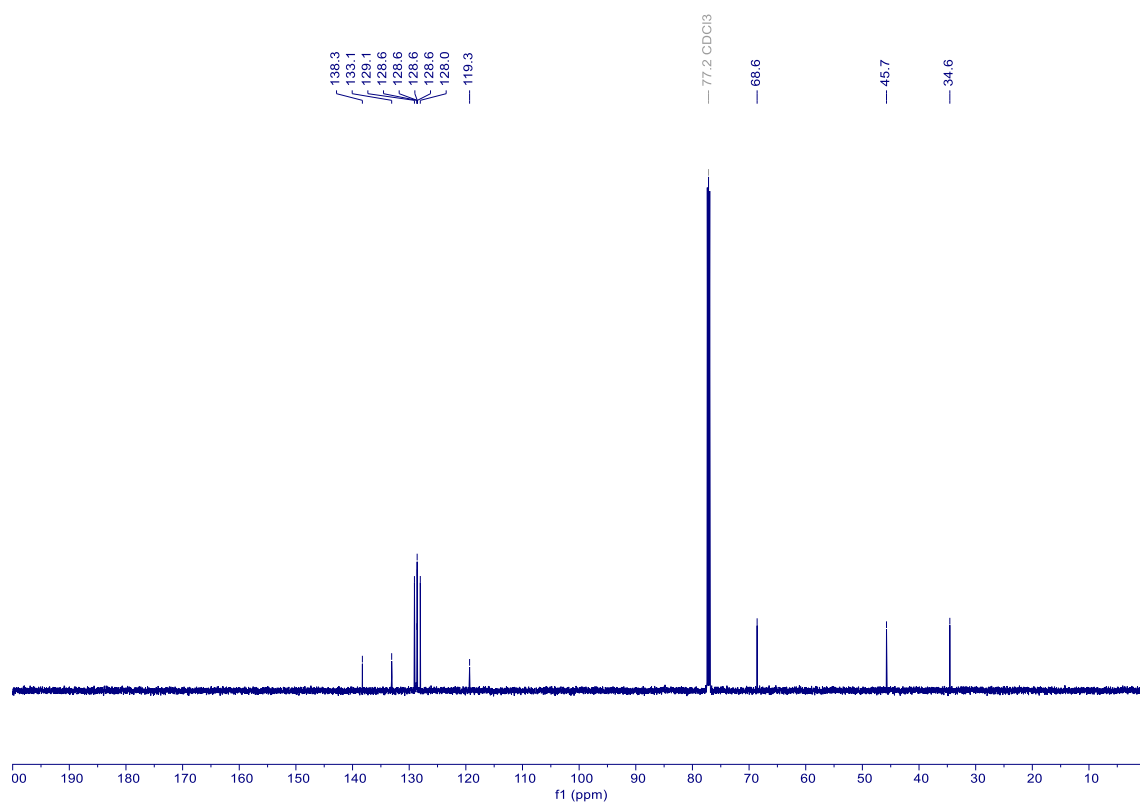
32b (*major diastereomer*) – ^{13}C NMR (151 MHz, CDCl_3)



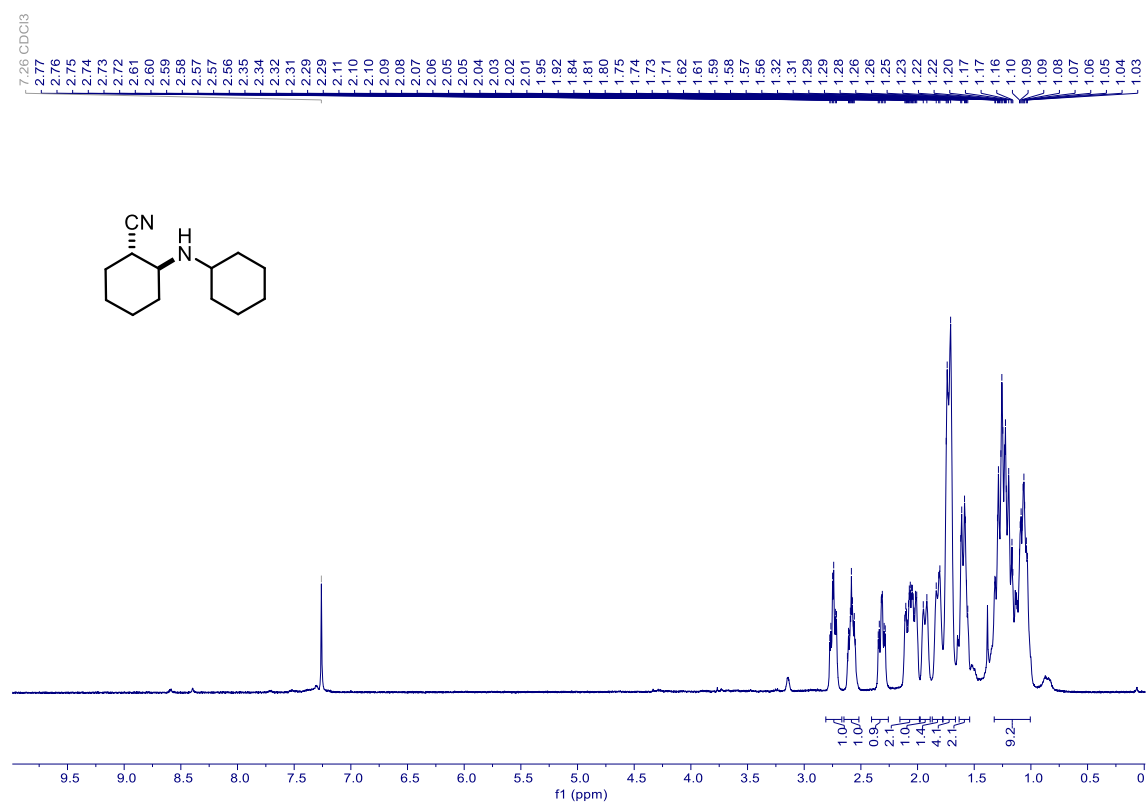
32b (minor diastereomer) – ^1H NMR (600 MHz, CDCl_3)



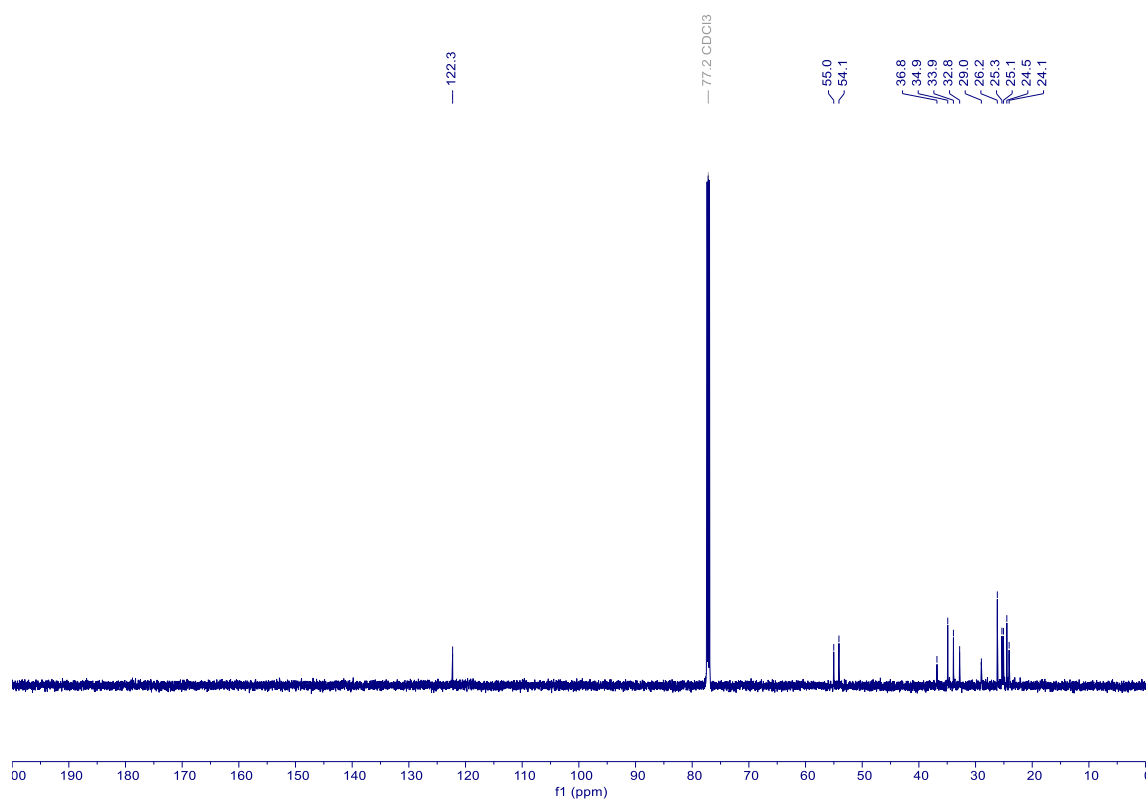
32b (minor diastereomer) – ^{13}C NMR (151 MHz, CDCl_3)



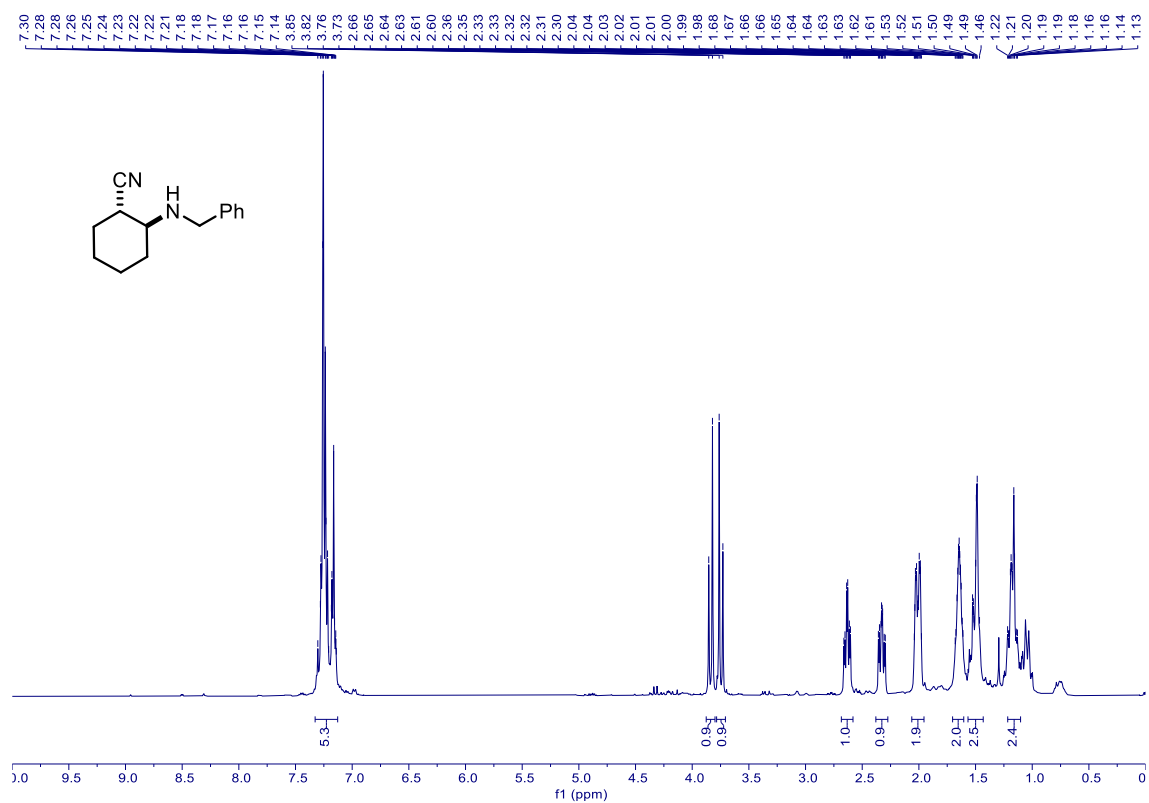
33b – ^1H NMR (400 MHz, CDCl_3)



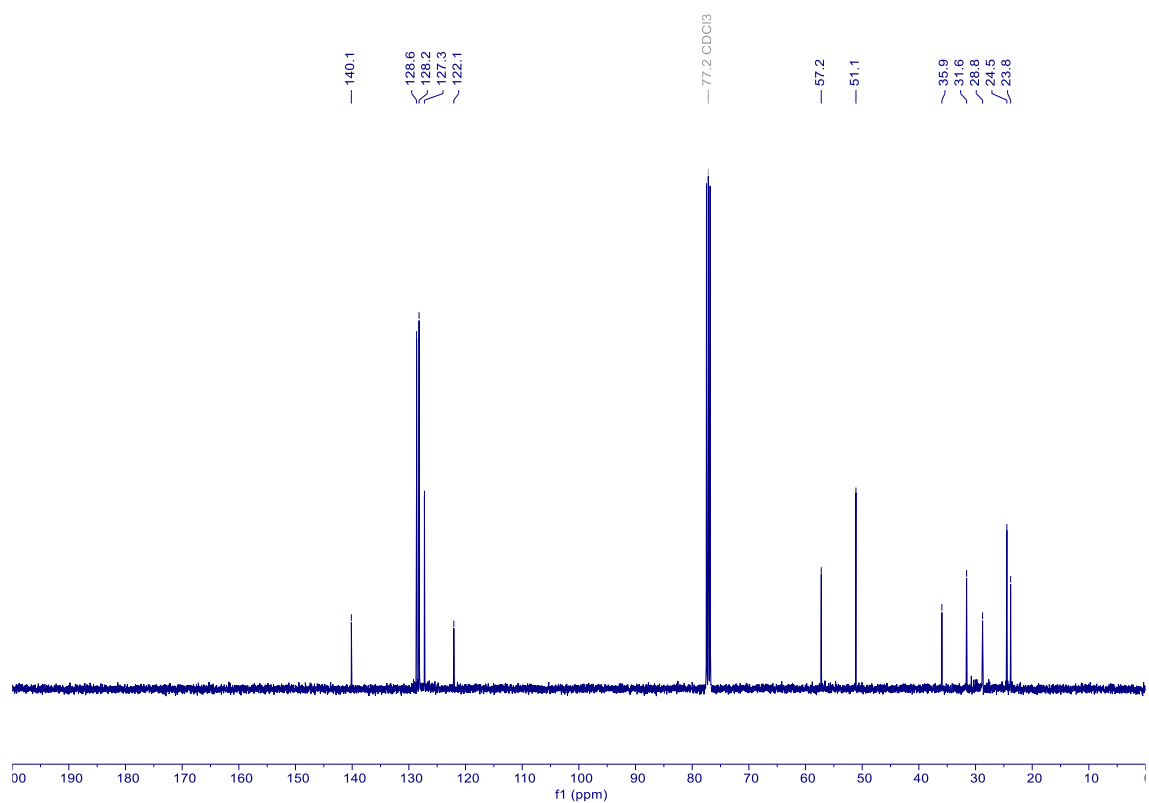
33b – ^{13}C NMR (151 MHz, CDCl_3)



34b – ^1H NMR (400 MHz, CDCl_3)



34b – ^{13}C NMR (101 MHz, CDCl_3)



Chemical structure of the compound is shown above the spectrum. The spectrum displays peaks corresponding to the structure, with the following chemical shifts (ppm) labeled on the right side:

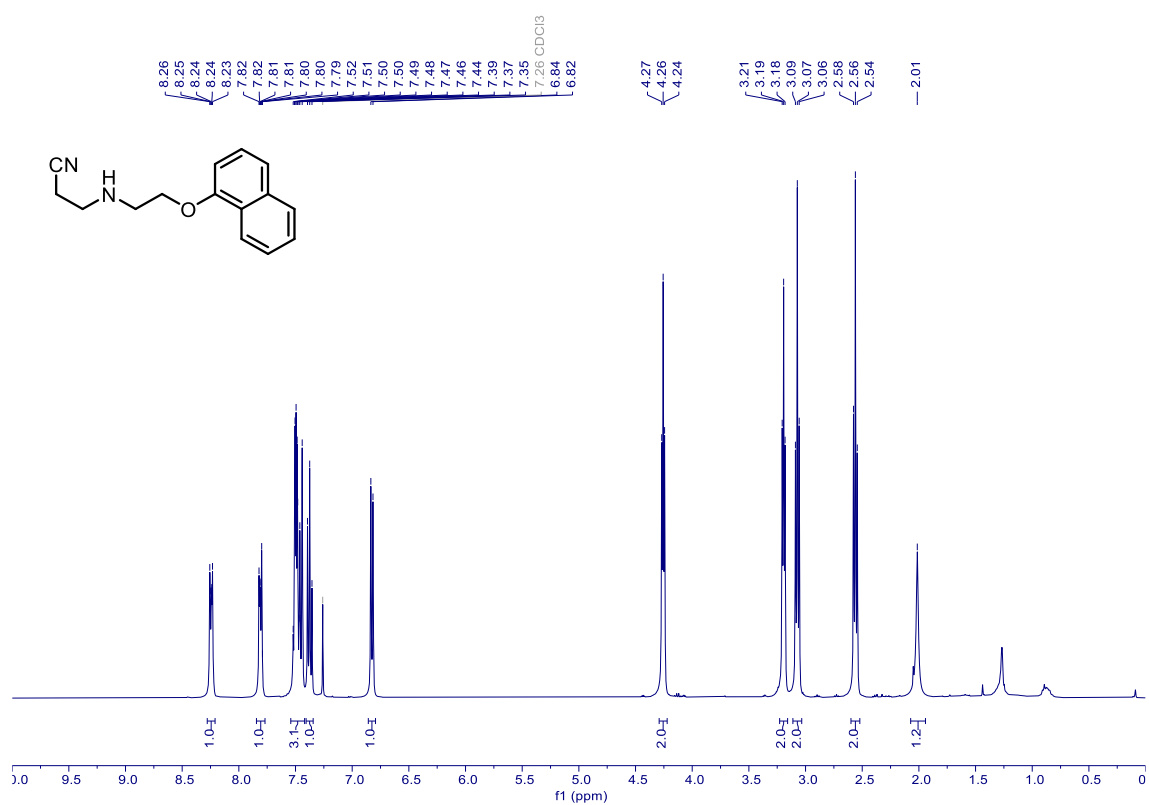
2.68, 2.44, 1.84, 1.64, 1.63, 1.62, 1.61, 1.59, 1.59, 1.57, 1.56, 1.55, 1.54, 1.54, 1.45, 1.43, 1.42, 1.41, 1.41, 1.40, 1.39, 1.39, 1.37, 1.36, 1.35, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.28, 1.27, 0.92, 0.90, 0.88

Integration values are provided below the baseline: 2.0, 3.0, 4.6, 15.0, and 7.6.

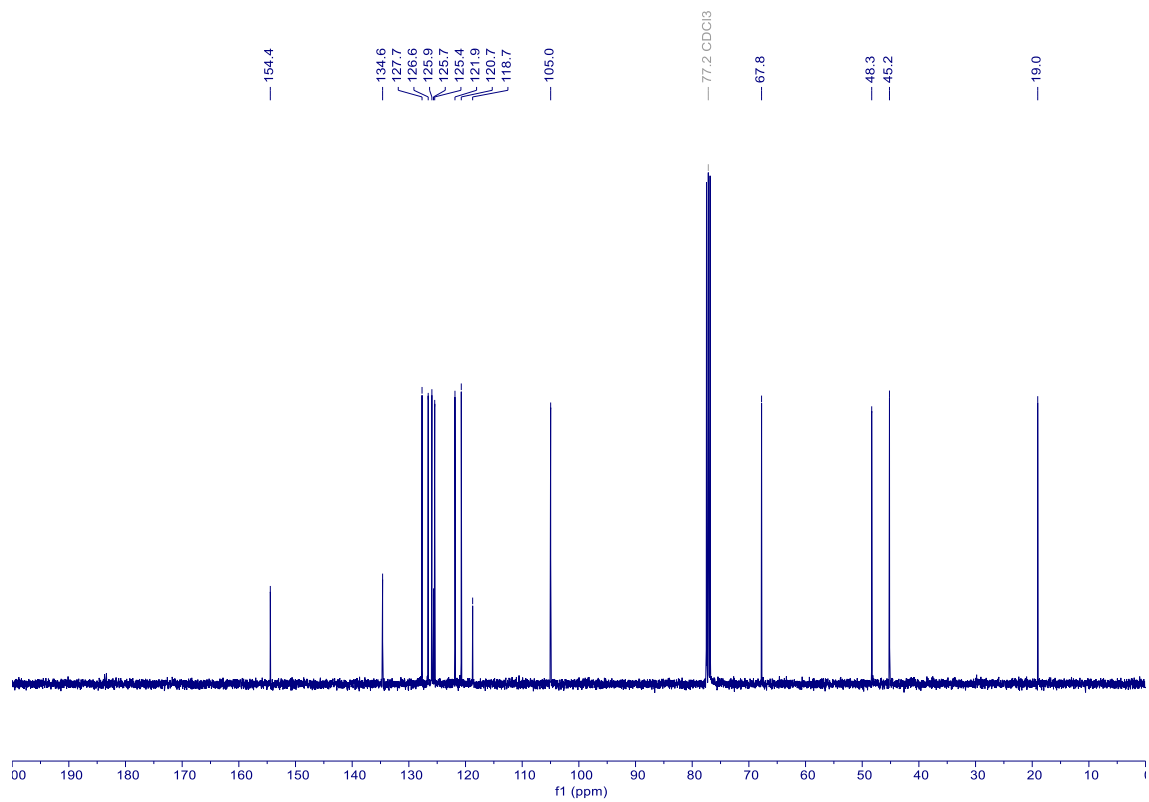
123.8
77.2 CDCl₃
56.7
42.3
34.3
34.8
32.1
24.2
22.6
14.1

f1 (ppm)

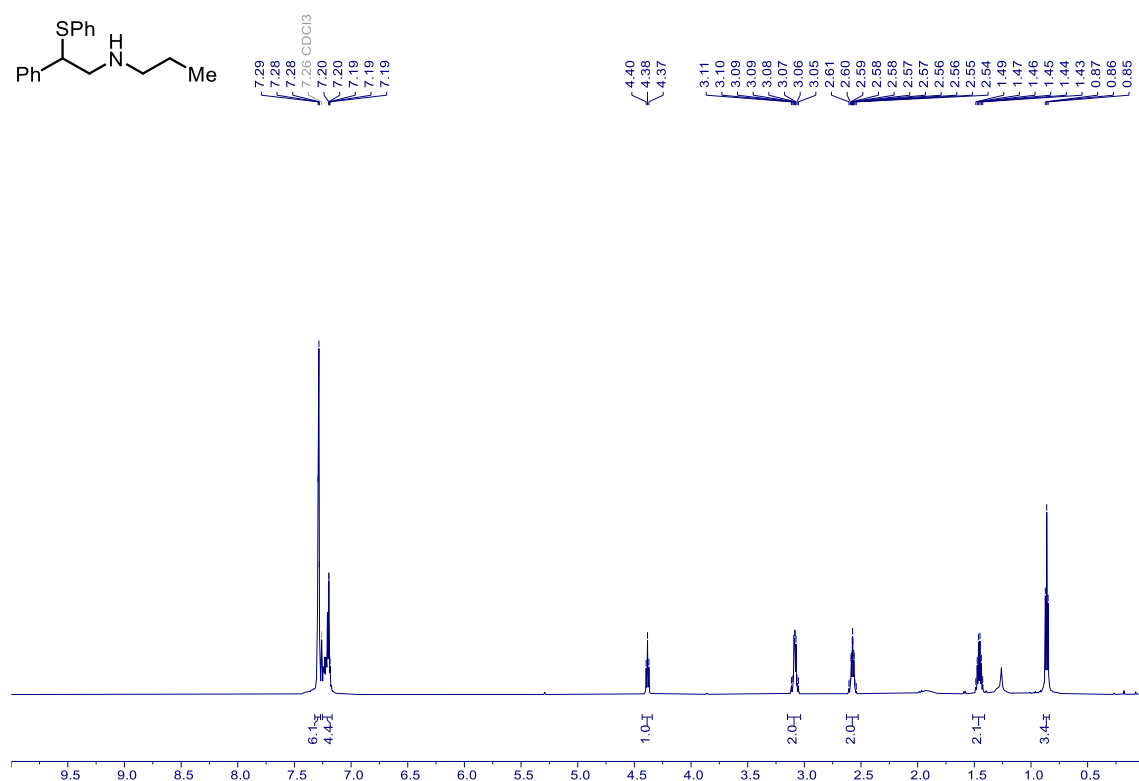
36b – ^1H NMR (400 MHz, CDCl_3)



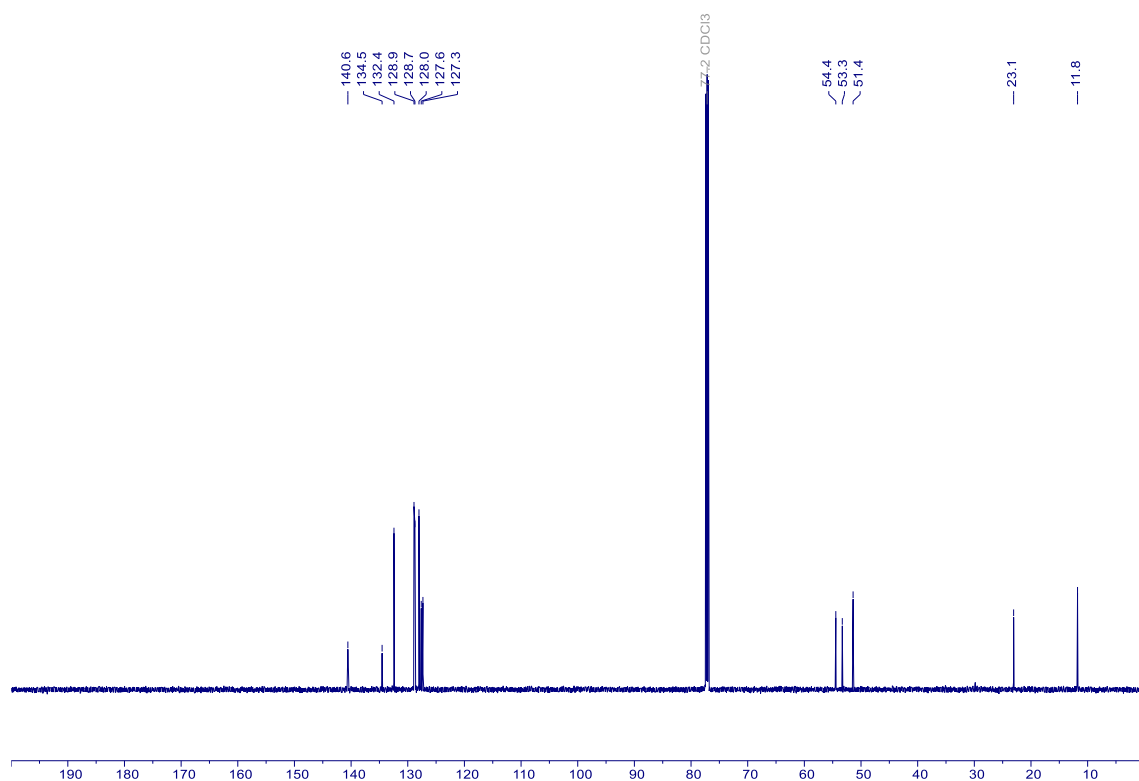
36b – ^{13}C NMR (101 MHz, CDCl_3)



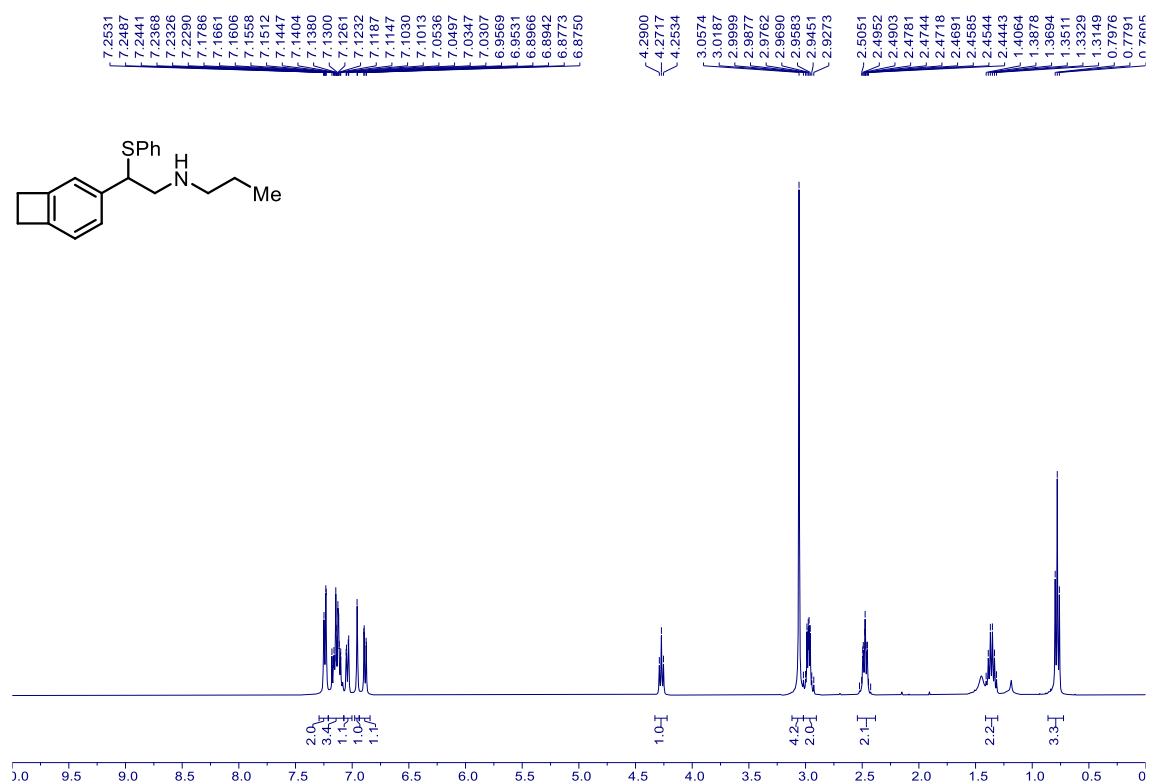
1r – ^1H NMR (600 MHz, CDCl_3)



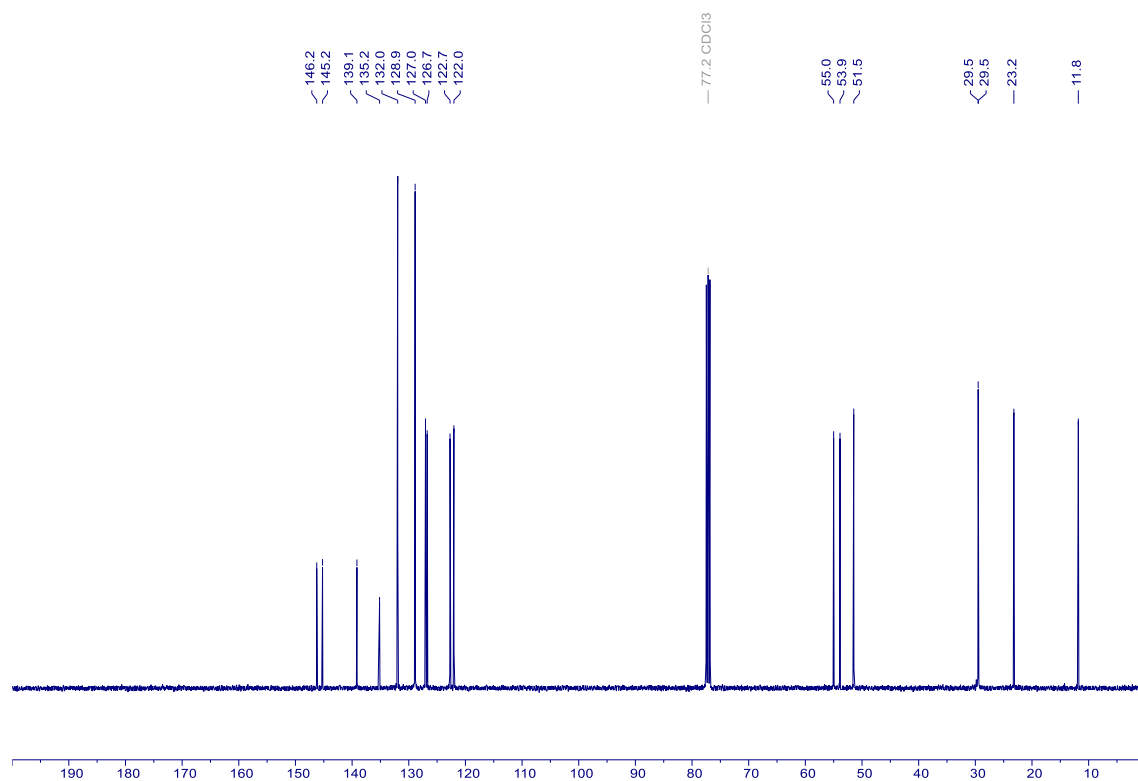
1r – ^{13}C NMR (151 MHz, CDCl_3)



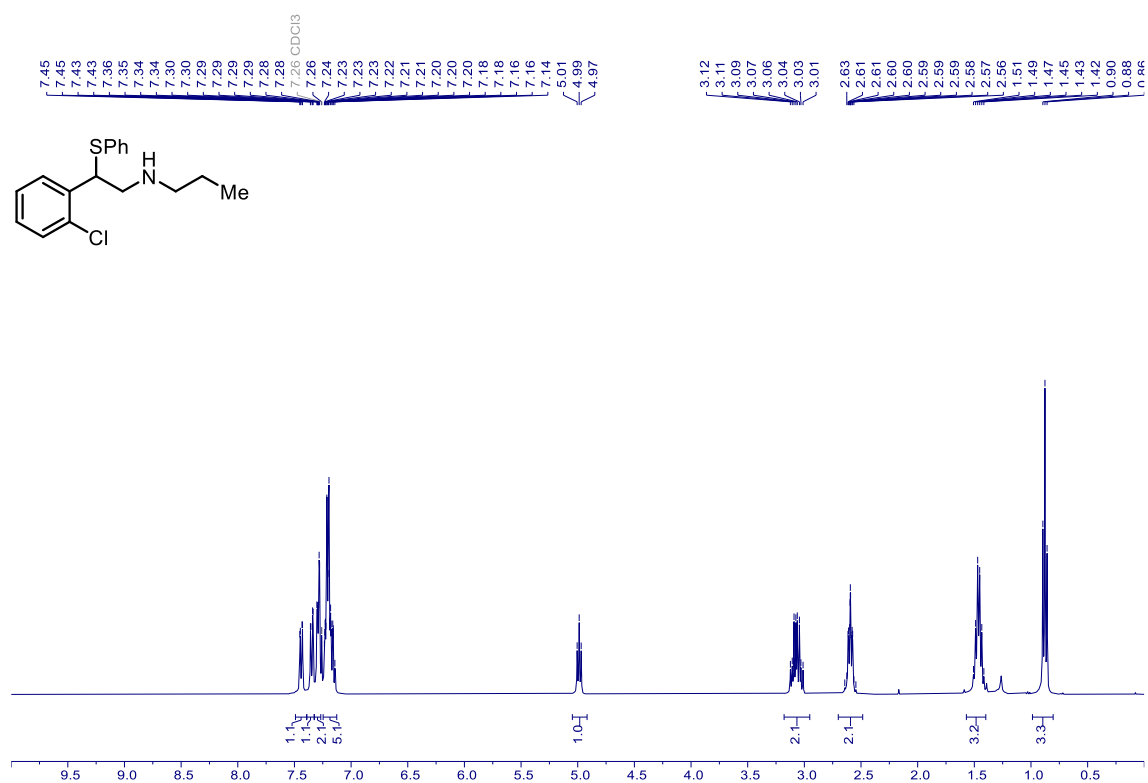
7d – ^1H NMR (400 MHz, CDCl_3)



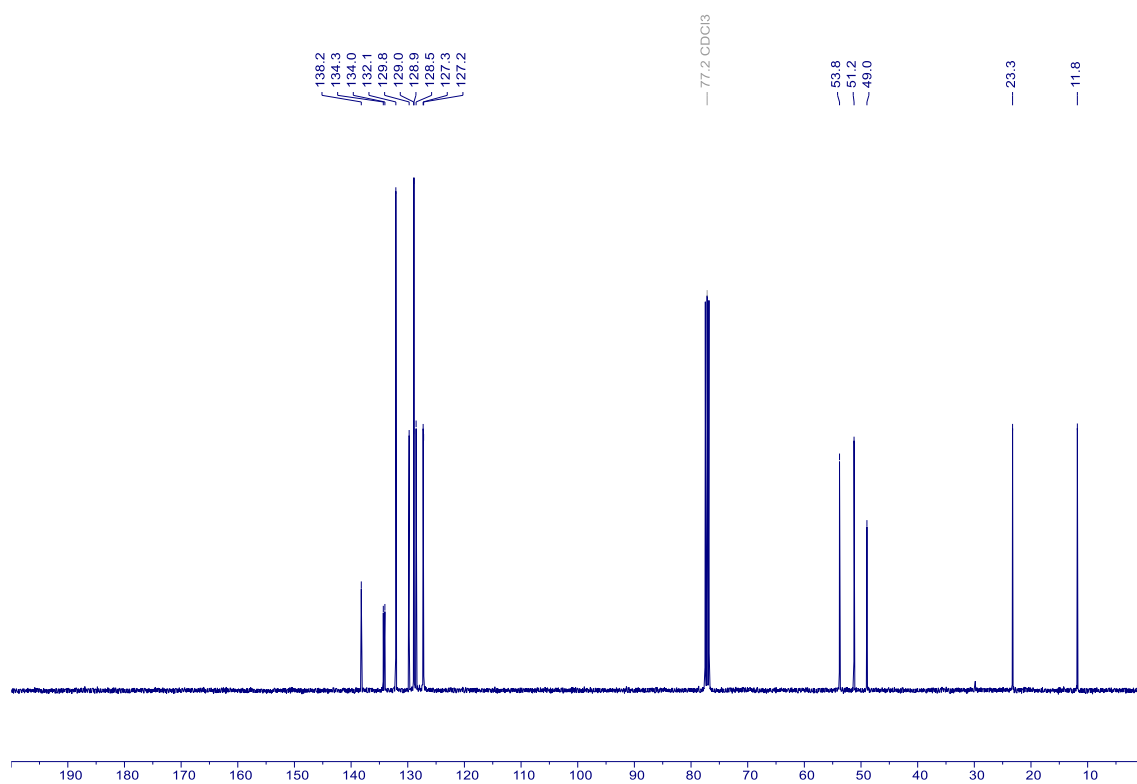
7d – ^{13}C NMR (101 MHz, CDCl_3)



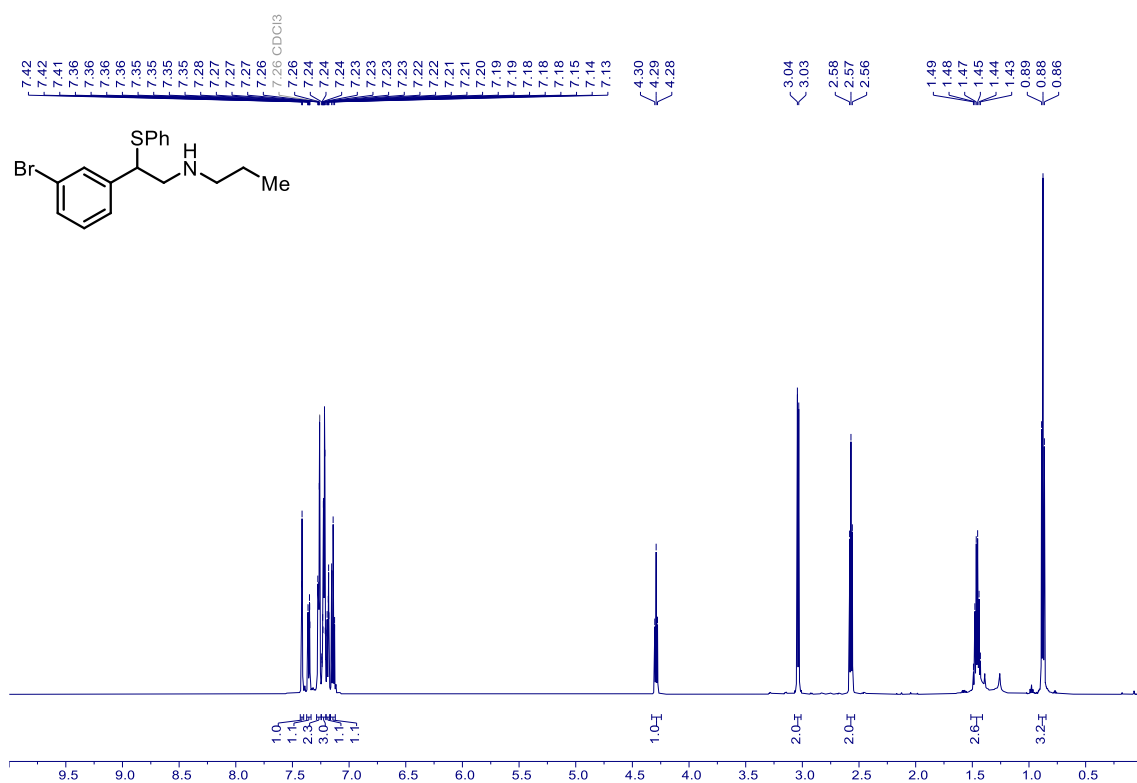
16c – ^1H NMR (400 MHz, CDCl_3)



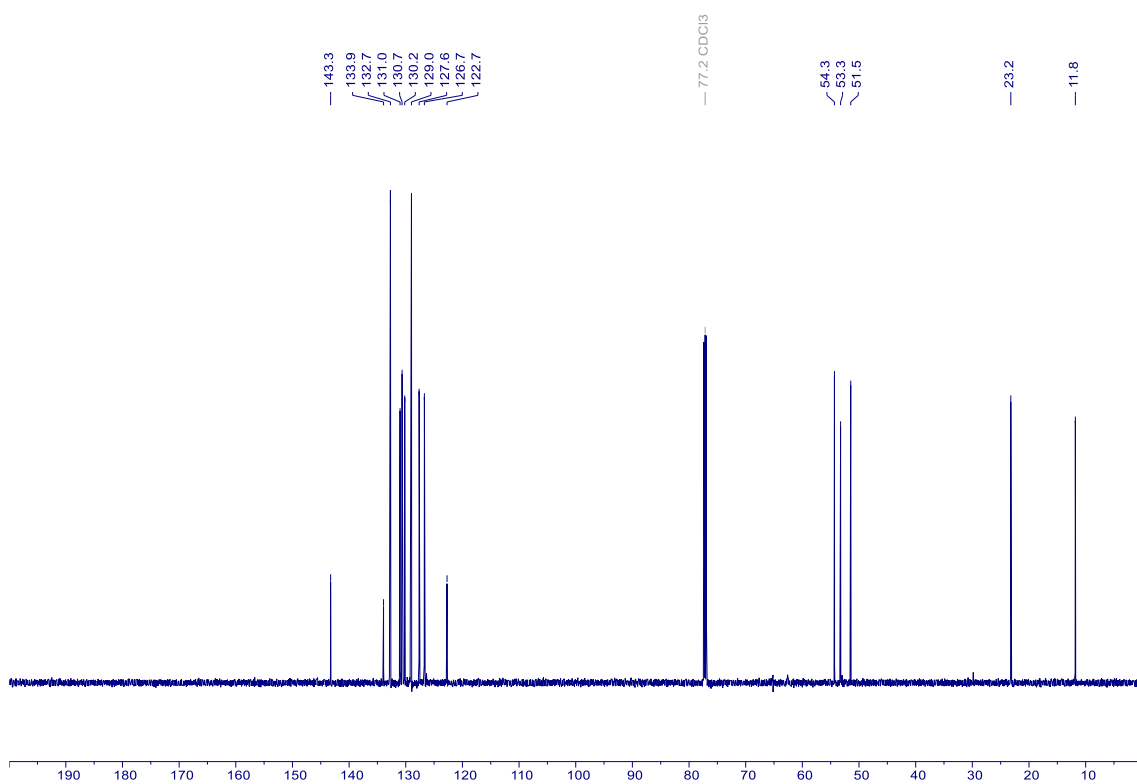
16c – ^{13}C NMR (101 MHz, CDCl_3)



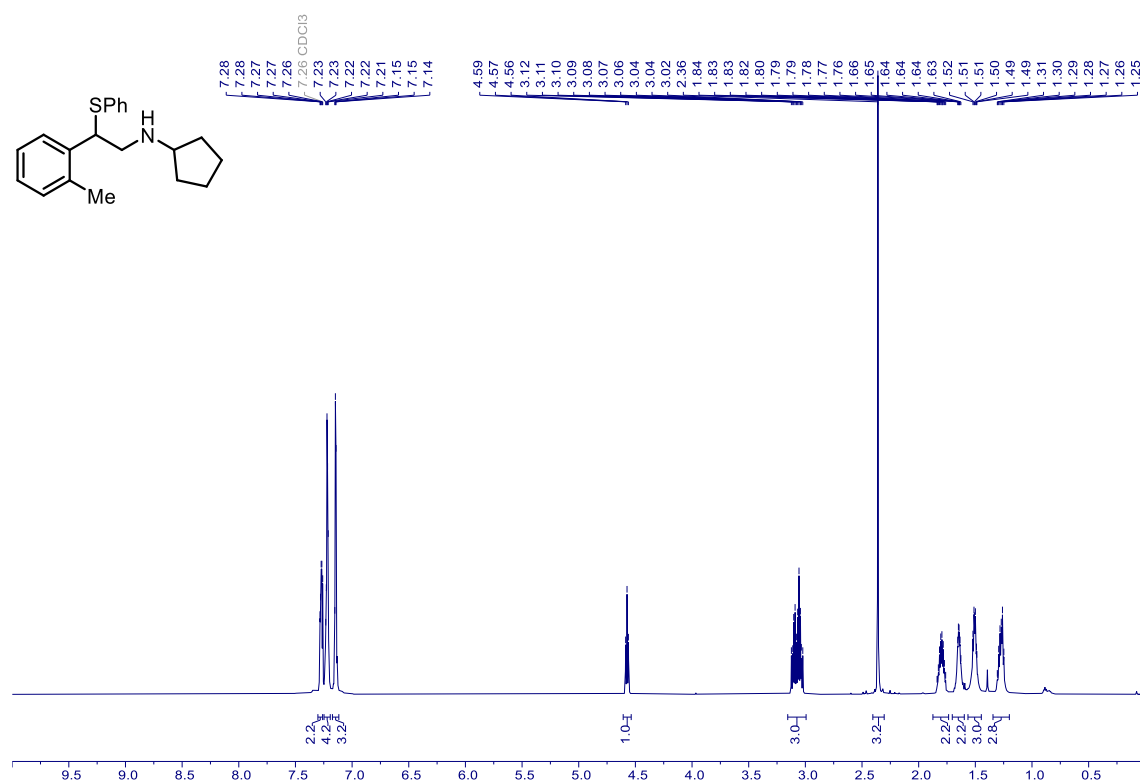
33b – ^1H NMR (600 MHz, CDCl_3)



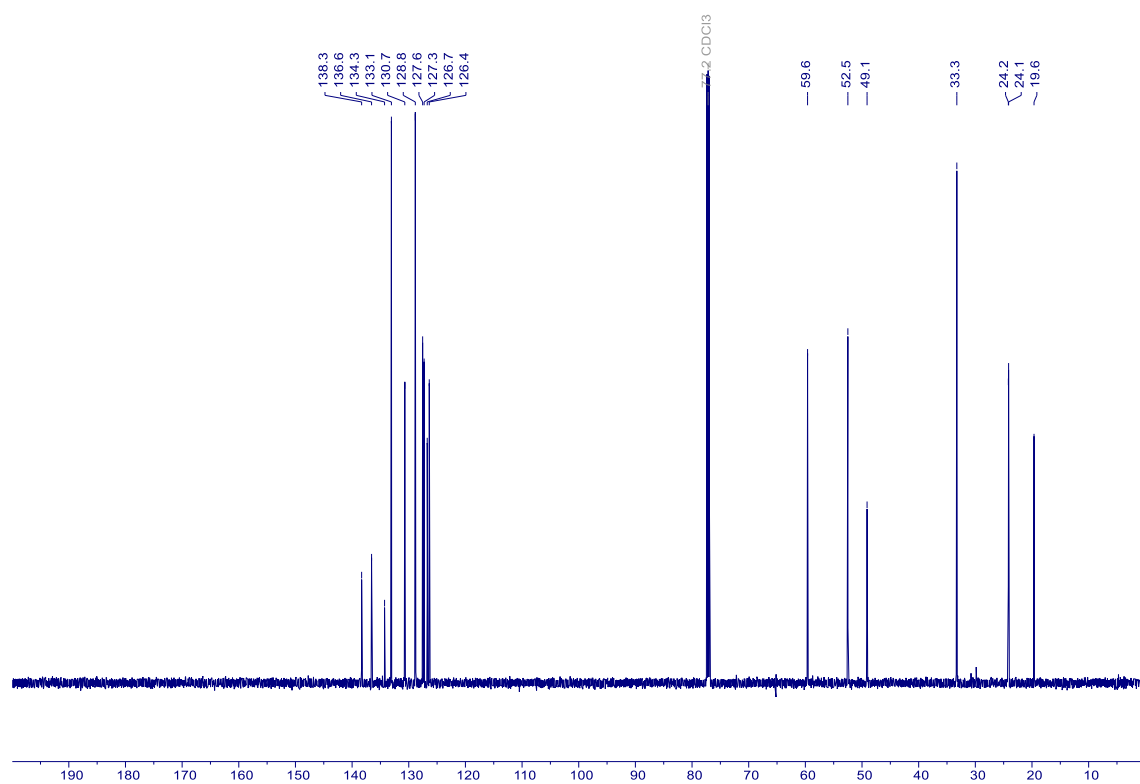
33b – ^{13}C NMR (151 MHz, CDCl_3)



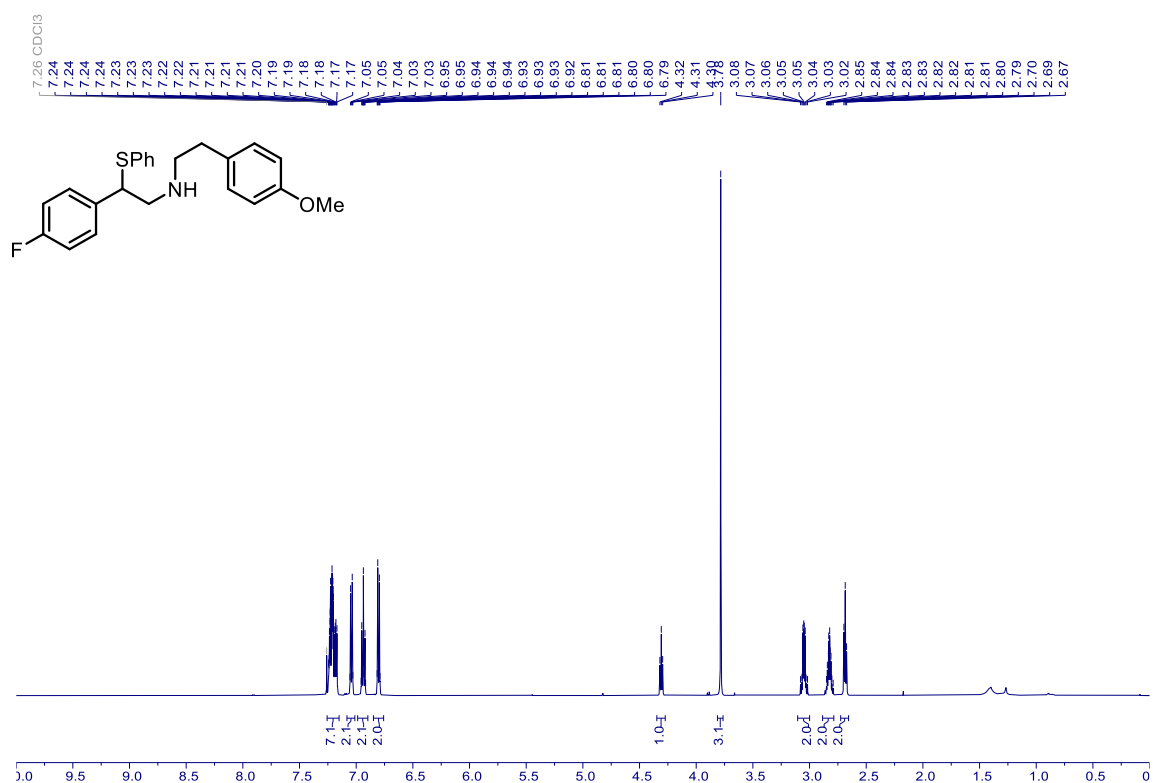
22c – ^1H NMR (600 MHz, CDCl_3)



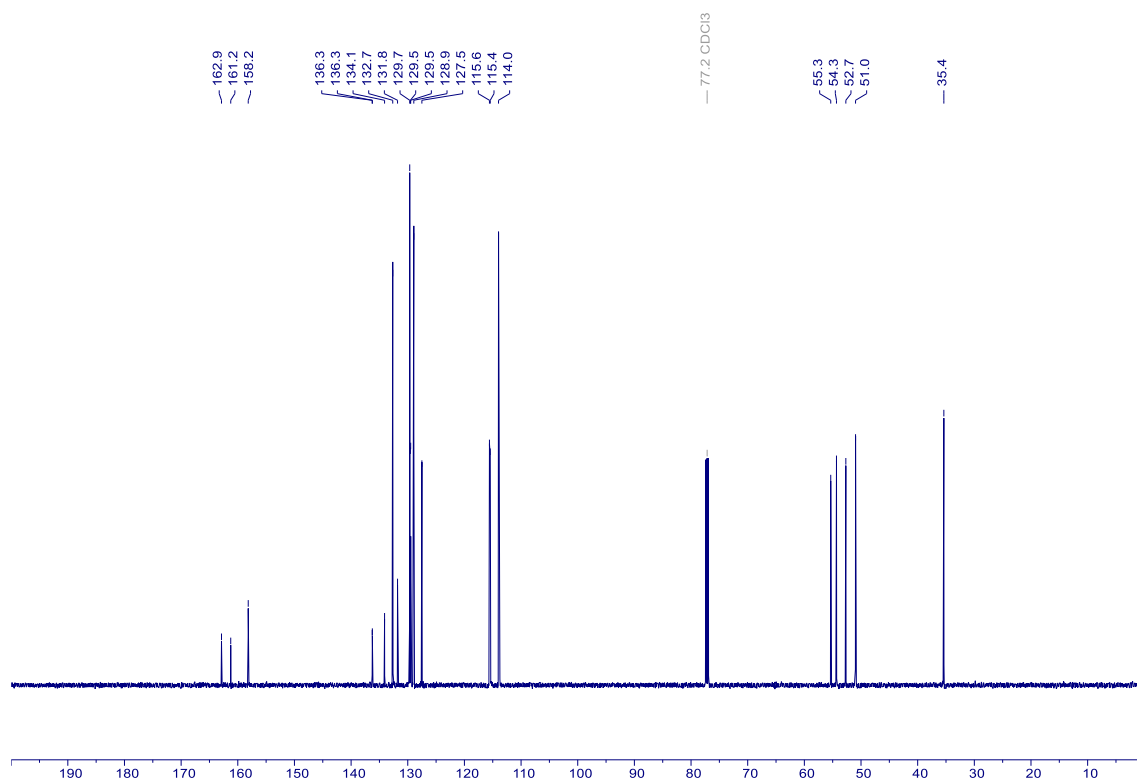
22c – ^{13}C NMR (151 MHz, CDCl_3)



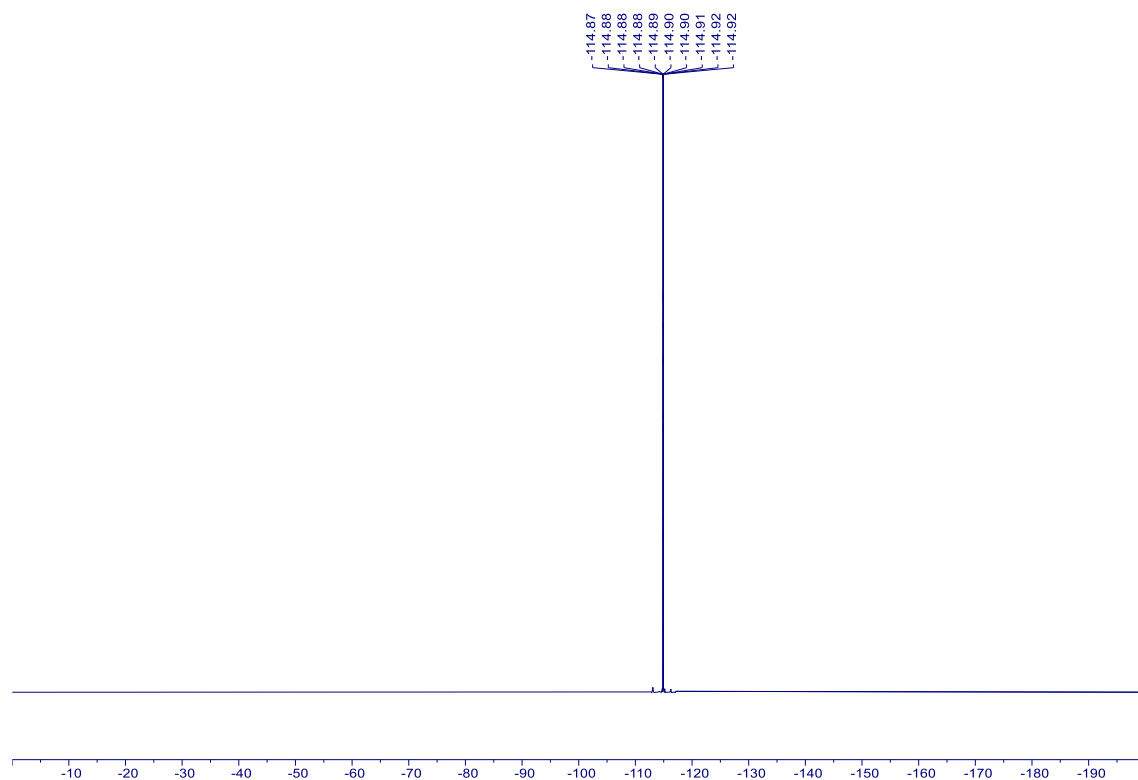
18c – ^1H NMR (600 MHz, CDCl_3)



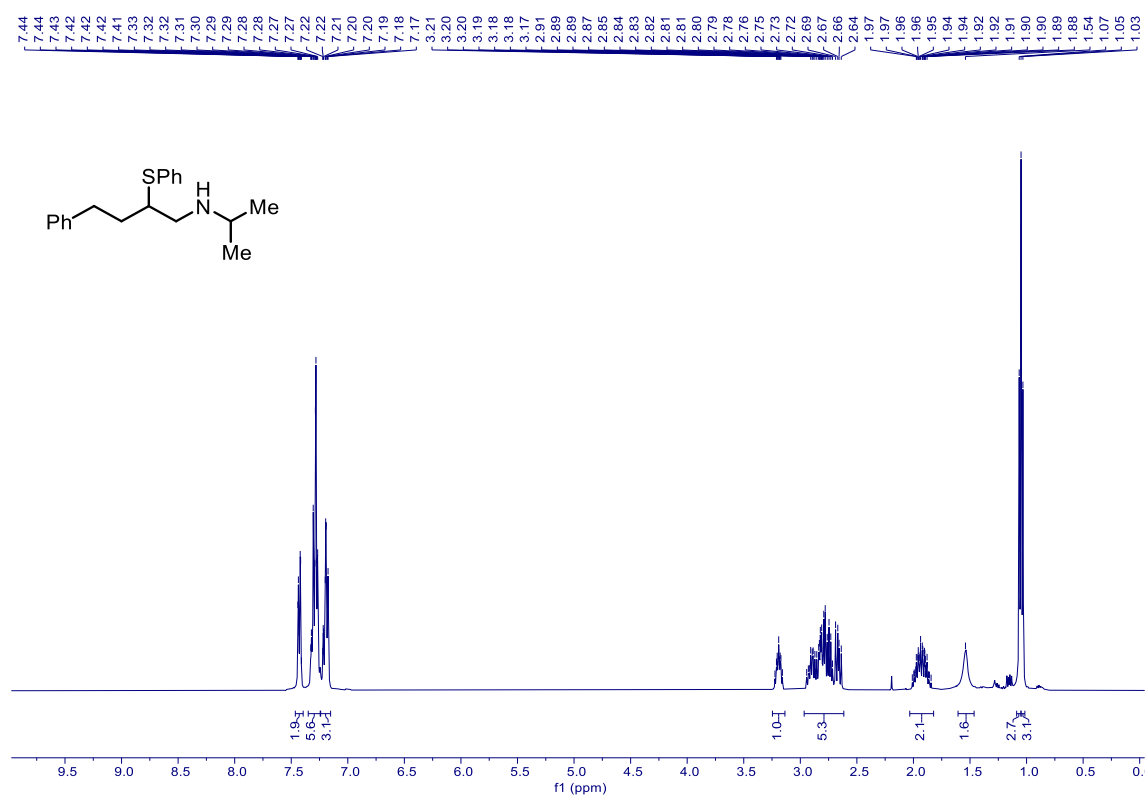
18c – ^{13}C NMR (151 MHz, CDCl_3)



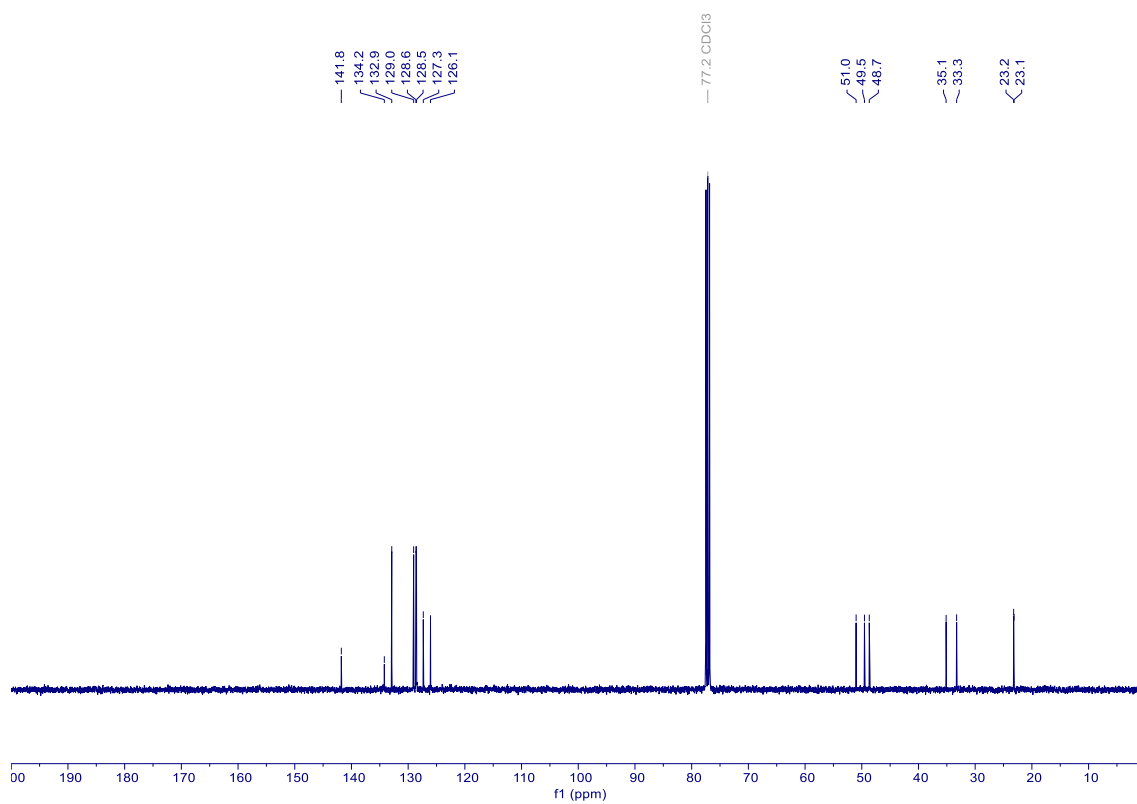
18c – ^{19}F NMR (565 MHz, CDCl_3)



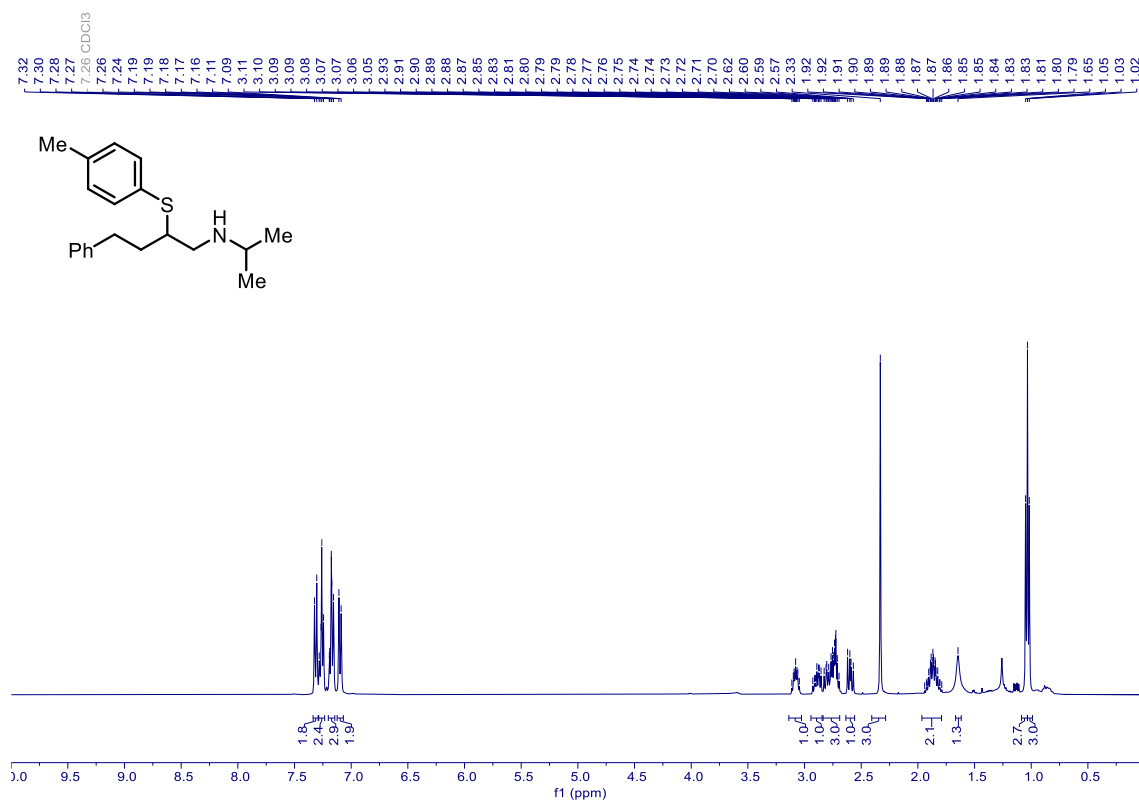
13d – ^1H NMR (400 MHz, CDCl_3)



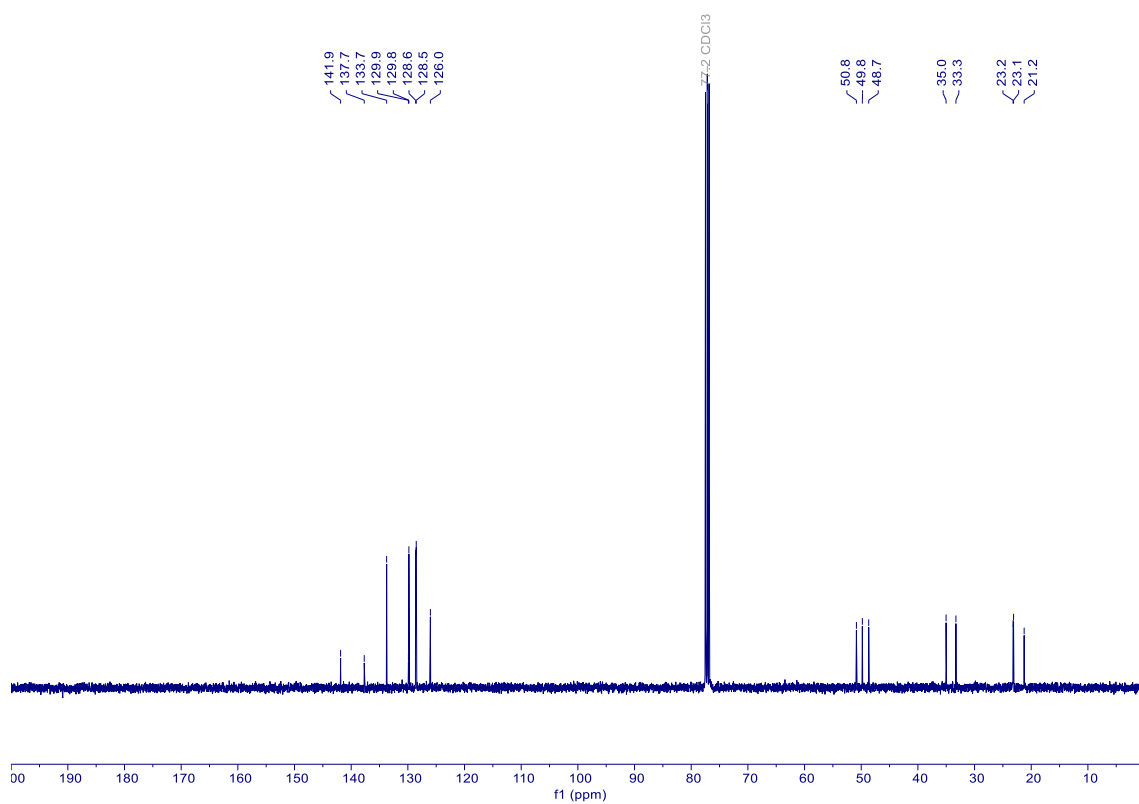
13d – ^{13}C NMR (101 MHz, CDCl_3)



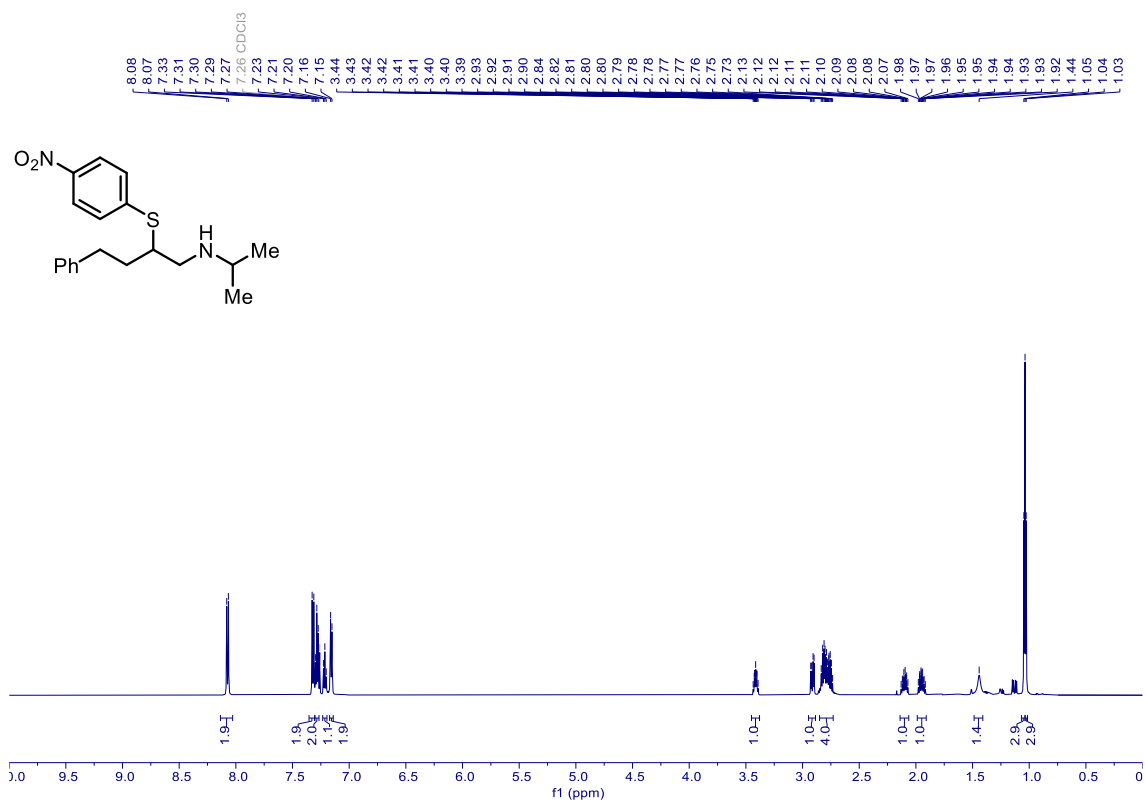
13e – ^1H NMR (400 MHz, CDCl_3)



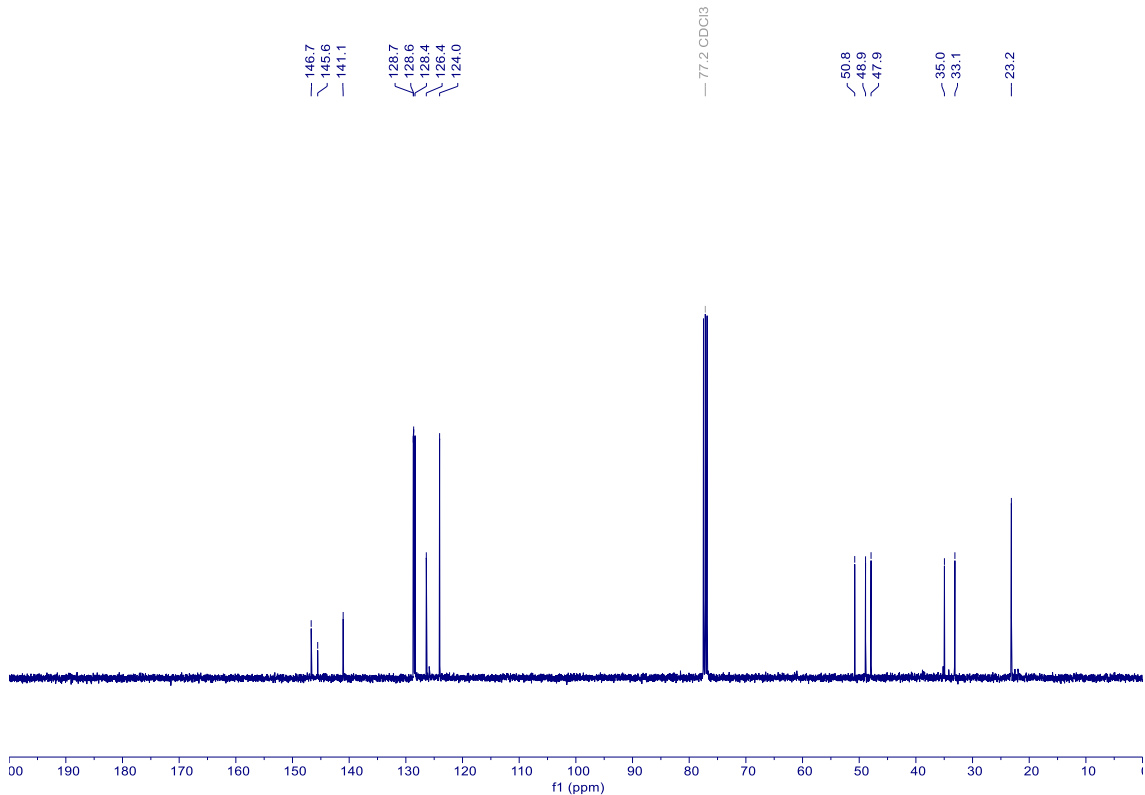
13e – ^{13}C NMR (101 MHz, CDCl_3)



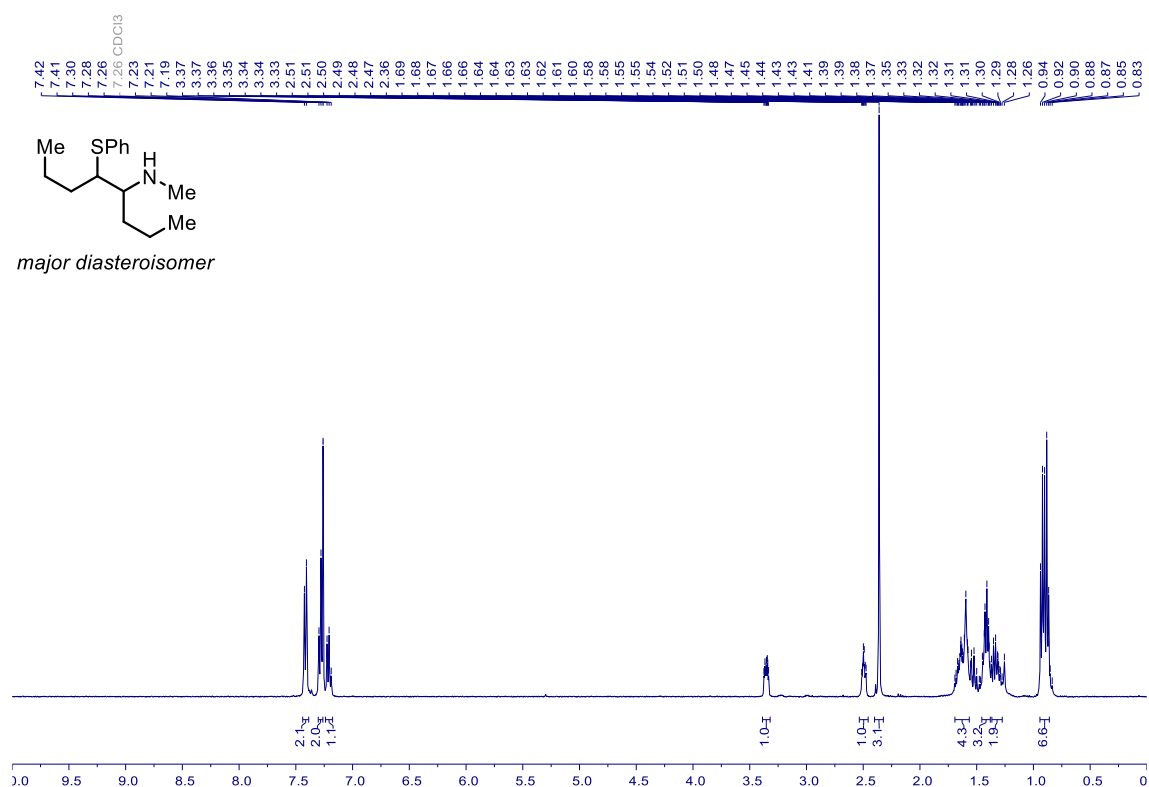
13f – ^1H NMR (600 MHz, CDCl_3)



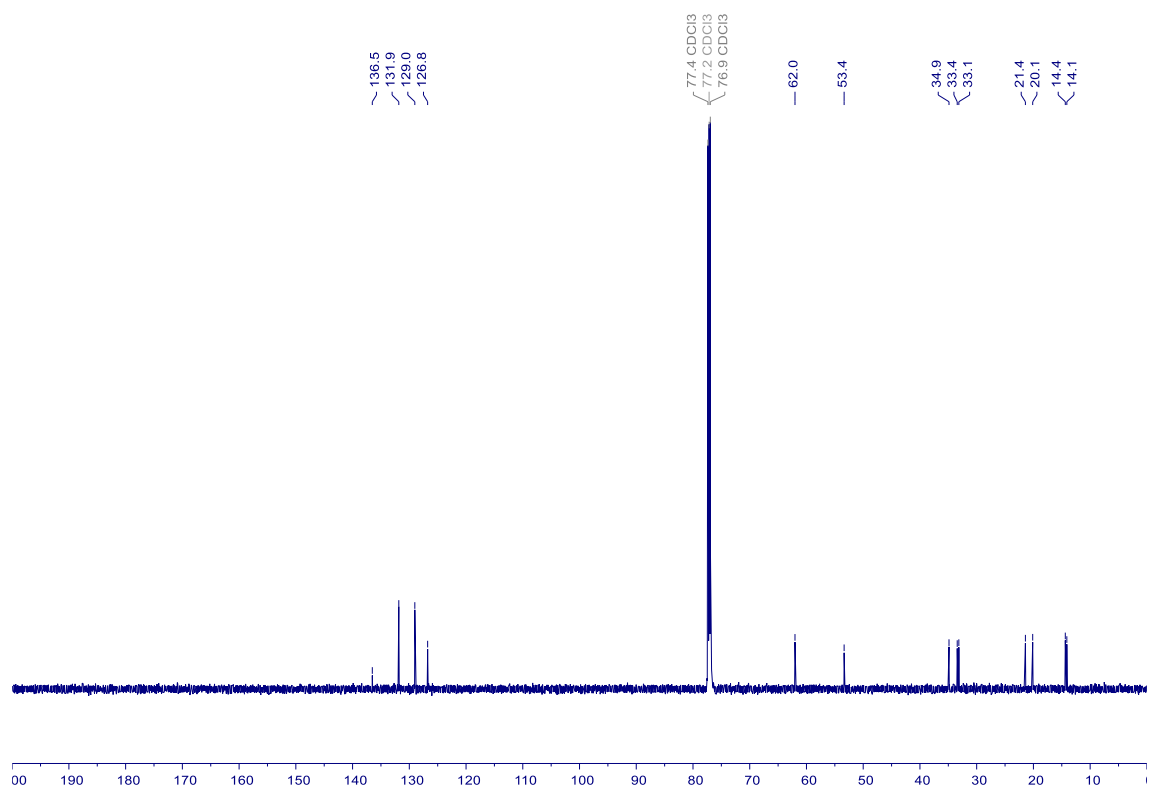
13f – ^{13}C NMR (101 MHz, CDCl_3)



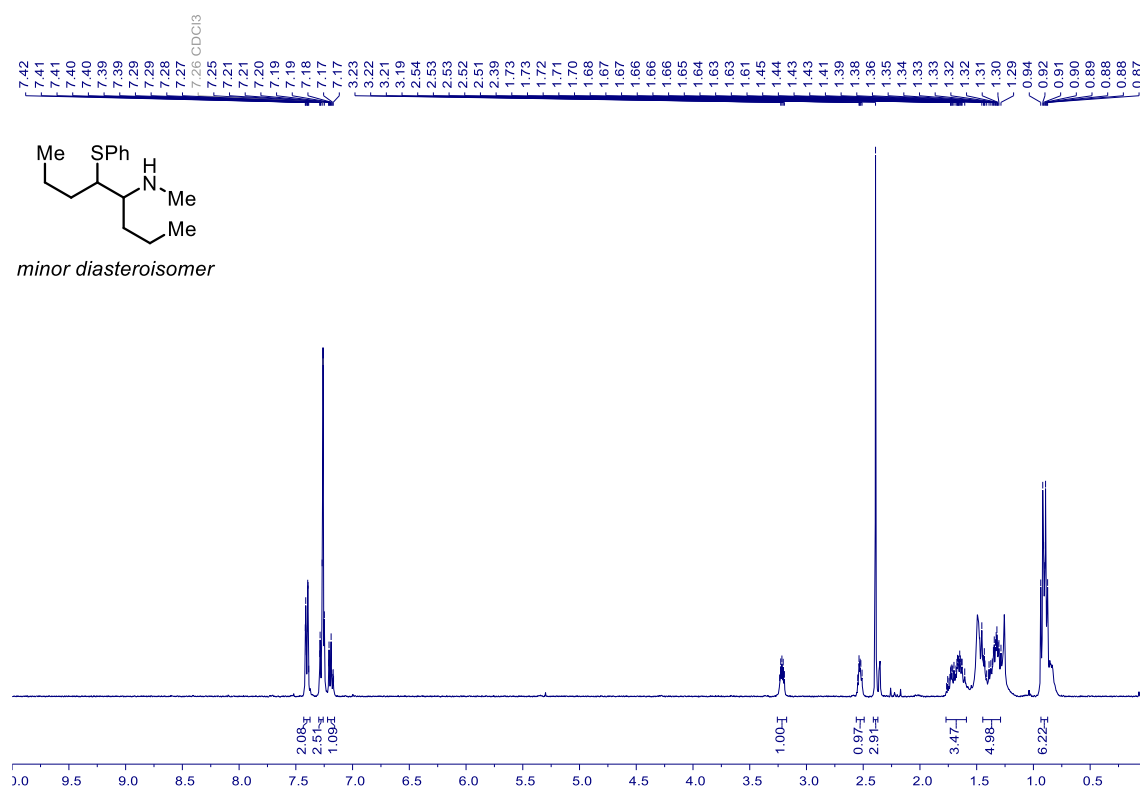
31c (major diastereoisomer) – ^1H NMR (400 MHz, CDCl_3)



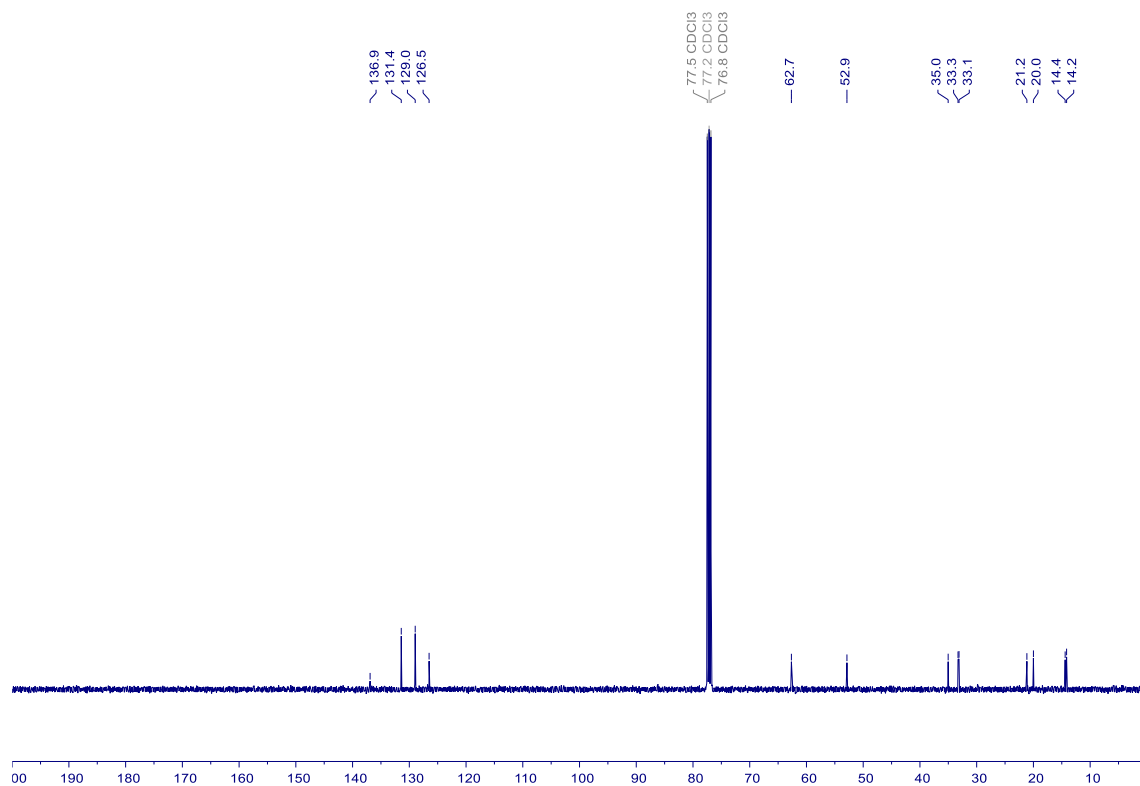
31c (major diastereoisomer) – ^{13}C NMR (101 MHz, CDCl_3)



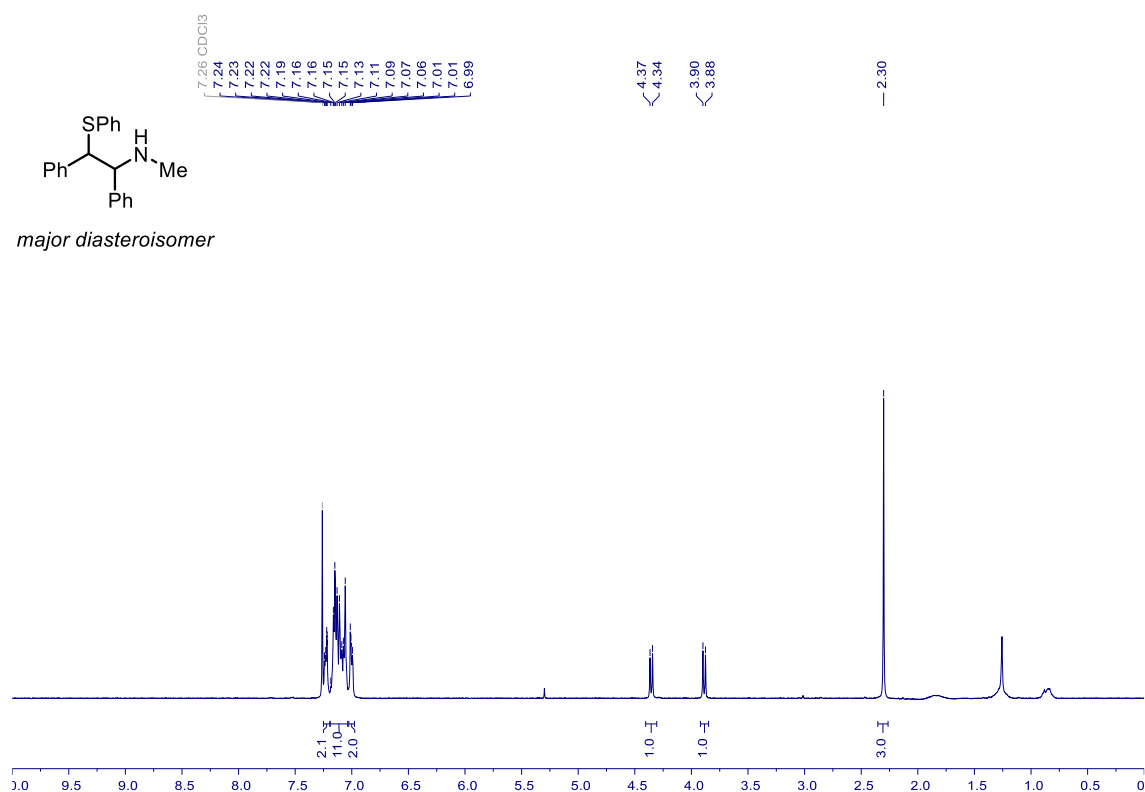
31c (minor diastereoisomer) – ^1H NMR (400 MHz, CDCl_3)



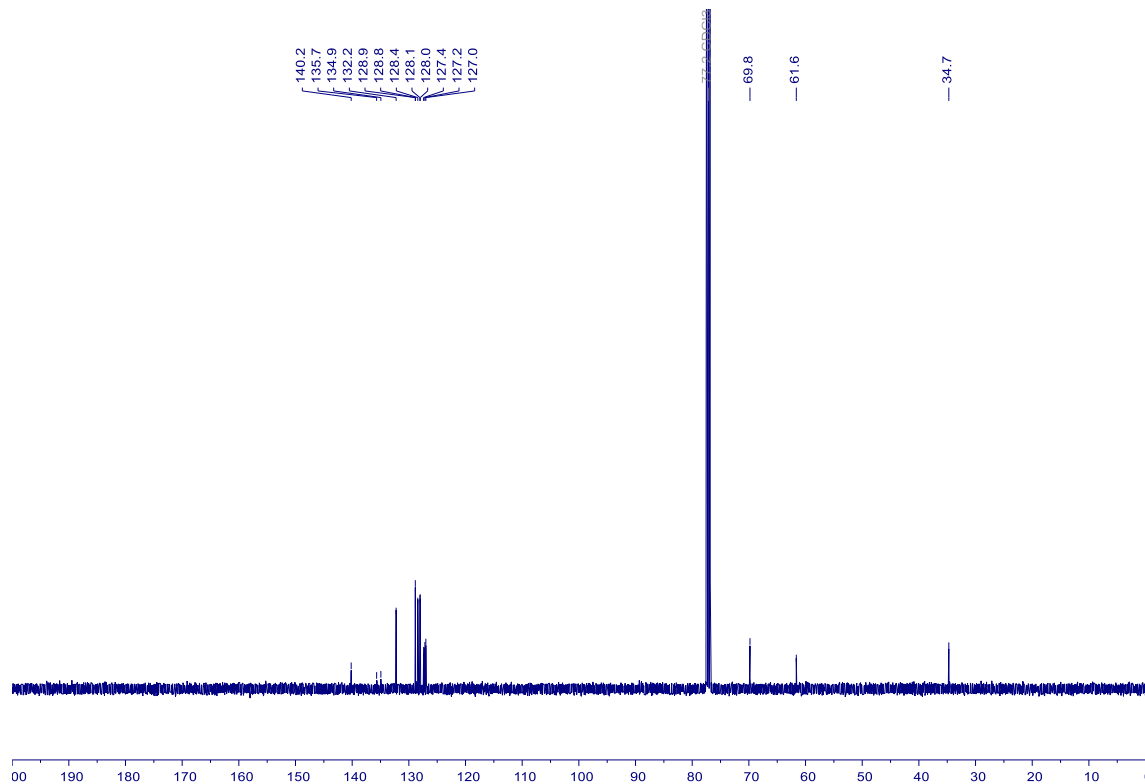
31c (minor diastereoisomer) – ^{13}C NMR (101 MHz, CDCl_3)



32c (major diastereomer) – ^1H NMR (400 MHz, CDCl_3)



32c (major diastereomer) – ^{13}C NMR (101 MHz, CDCl_3)



CN(Cc1ccccc1)C(c2ccccc2)Sc3ccccc3

minor diastereoisomer

Chemical structure of the minor diastereoisomer: CN(Cc1ccccc1)C(c2ccccc2)Sc3ccccc3

minor diastereoisomer

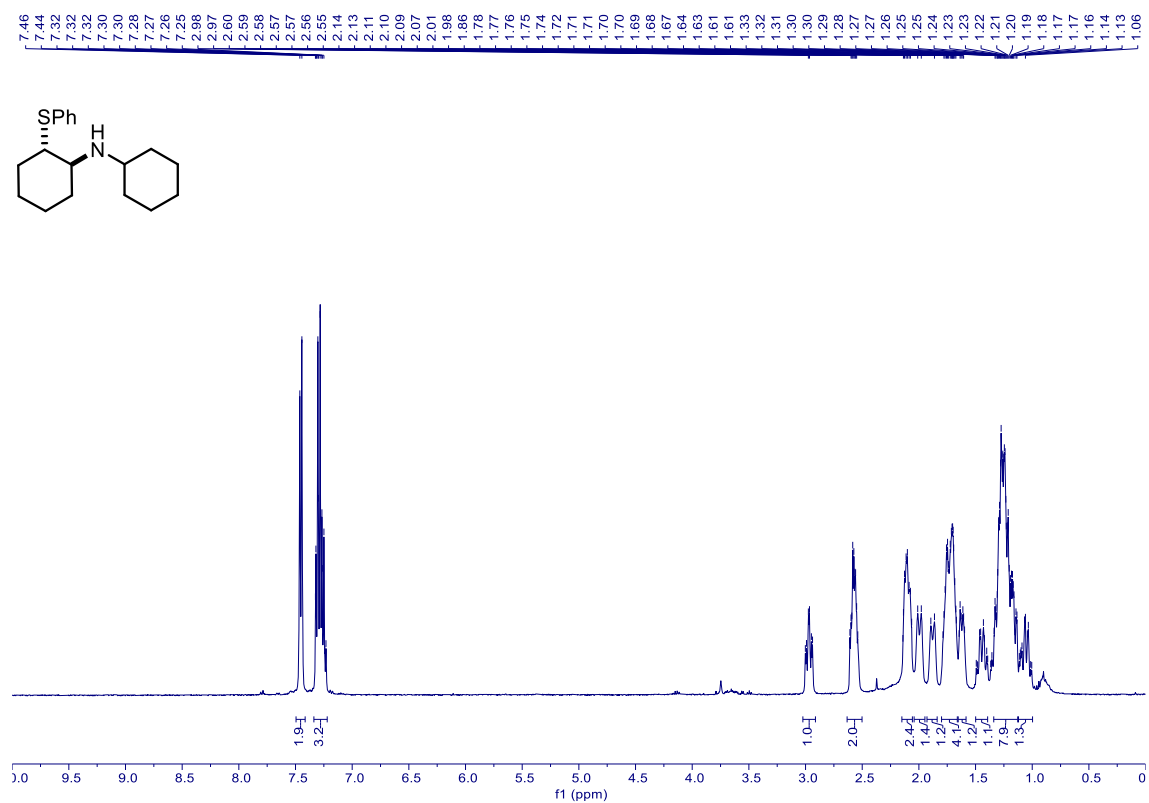
¹H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
7.29, 7.28, 7.26, 7.21, 7.19, 7.14, 7.12, 7.11, 7.10	2.8, 7.2, 5.4
4.45, 4.43	1.0
3.96, 3.94	1.0
2.18	3.1

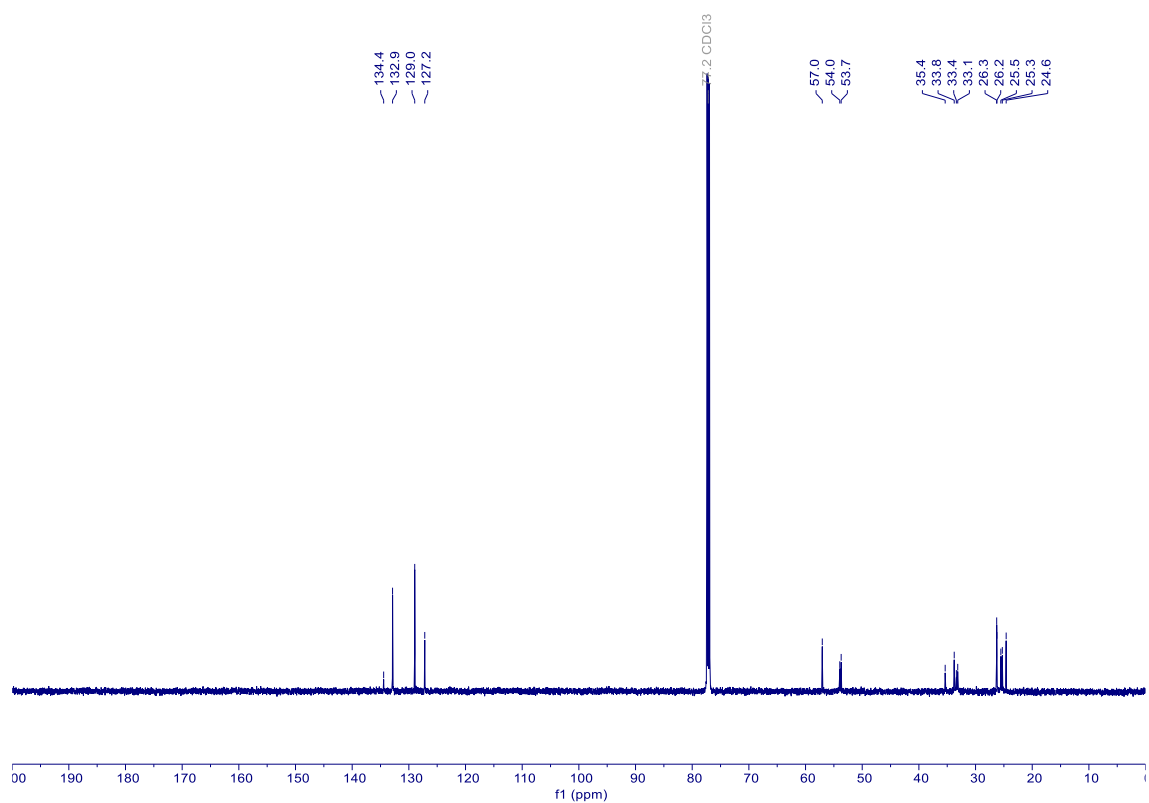
130.2
136.1
135.0
132.3
129.1
128.7
128.4
128.3
127.9
127.6
127.1

69.3
60.7
34.6

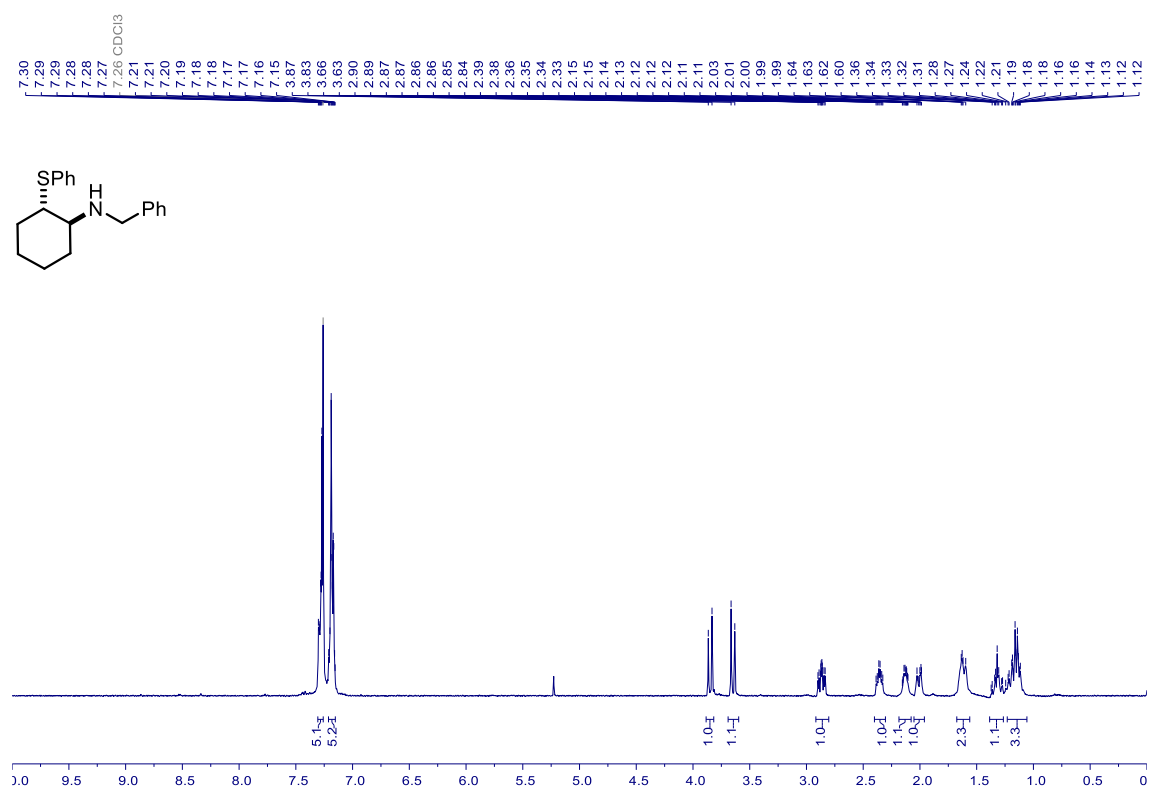
33c – ^1H NMR (400 MHz, CDCl_3)



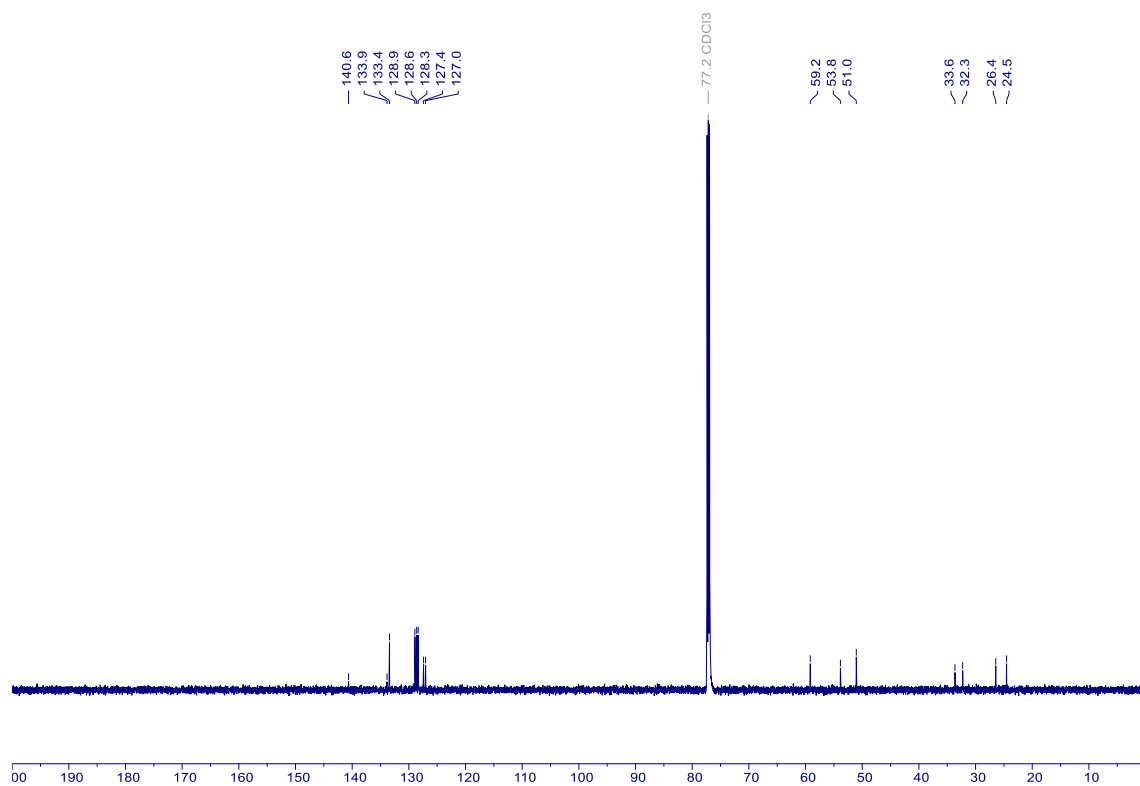
33c – ^{13}C NMR (151 MHz, CDCl_3)



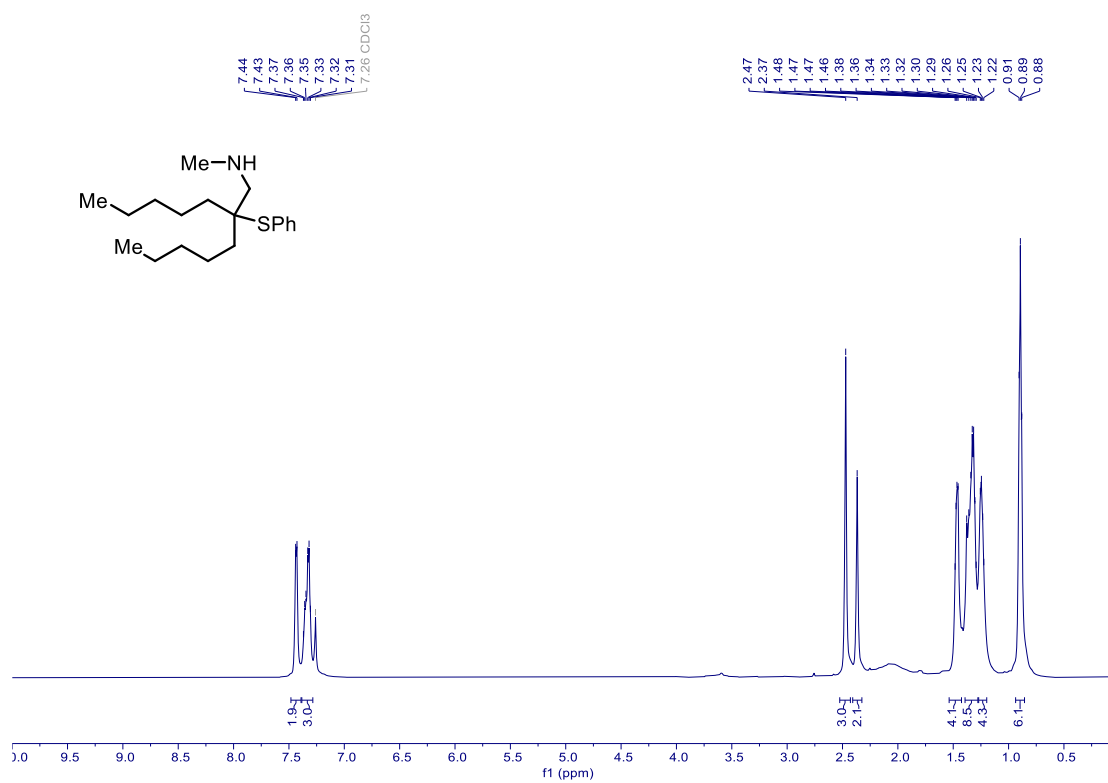
34c – ^1H NMR (400 MHz, CDCl_3)



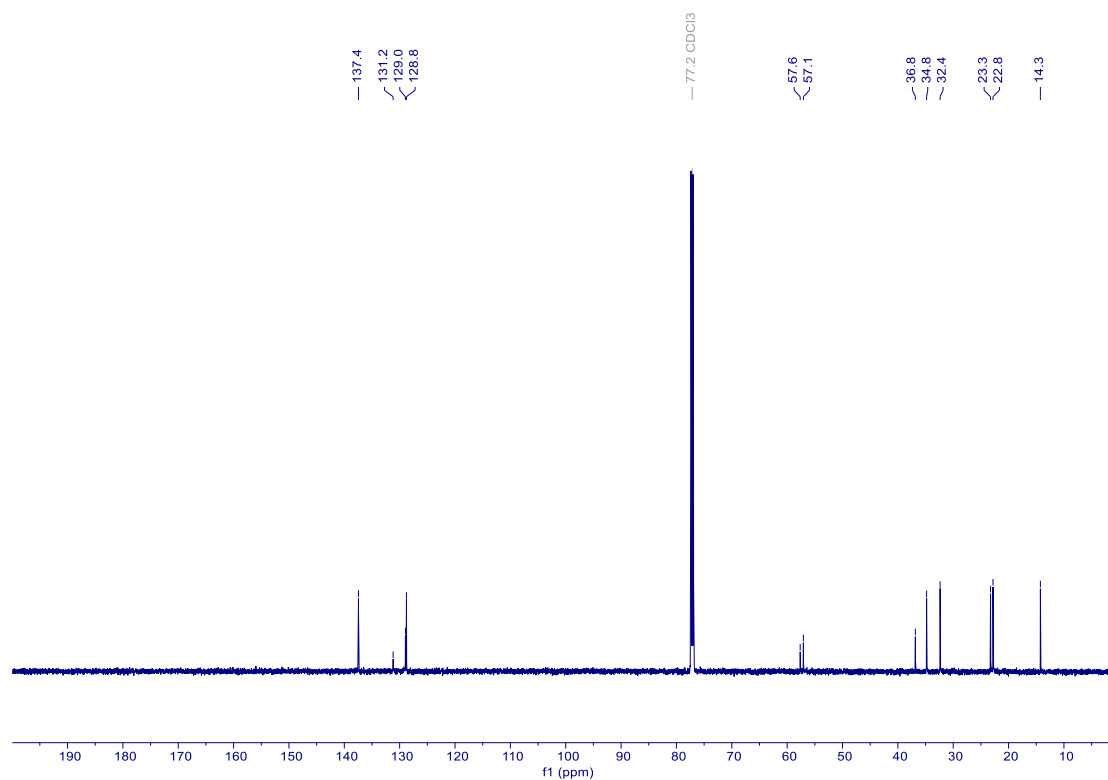
34c – ^{13}C NMR (101 MHz, CDCl_3)



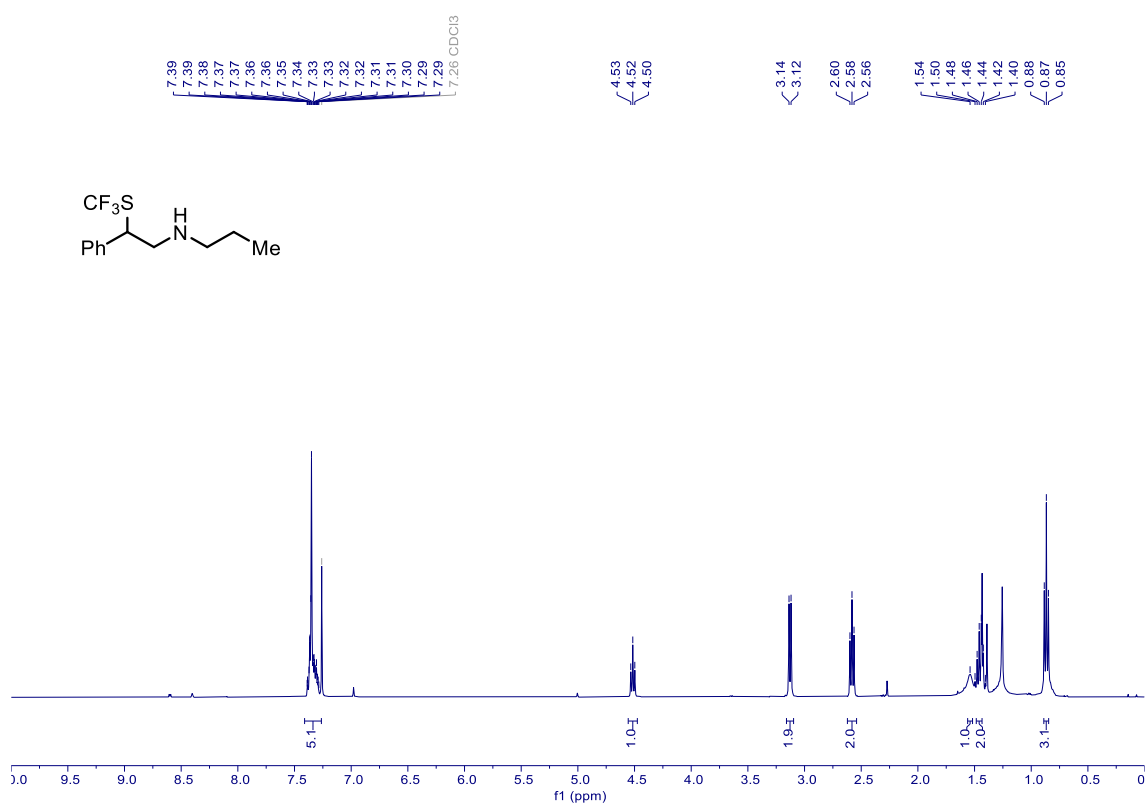
35c – ^1H NMR (600 MHz, CDCl_3)



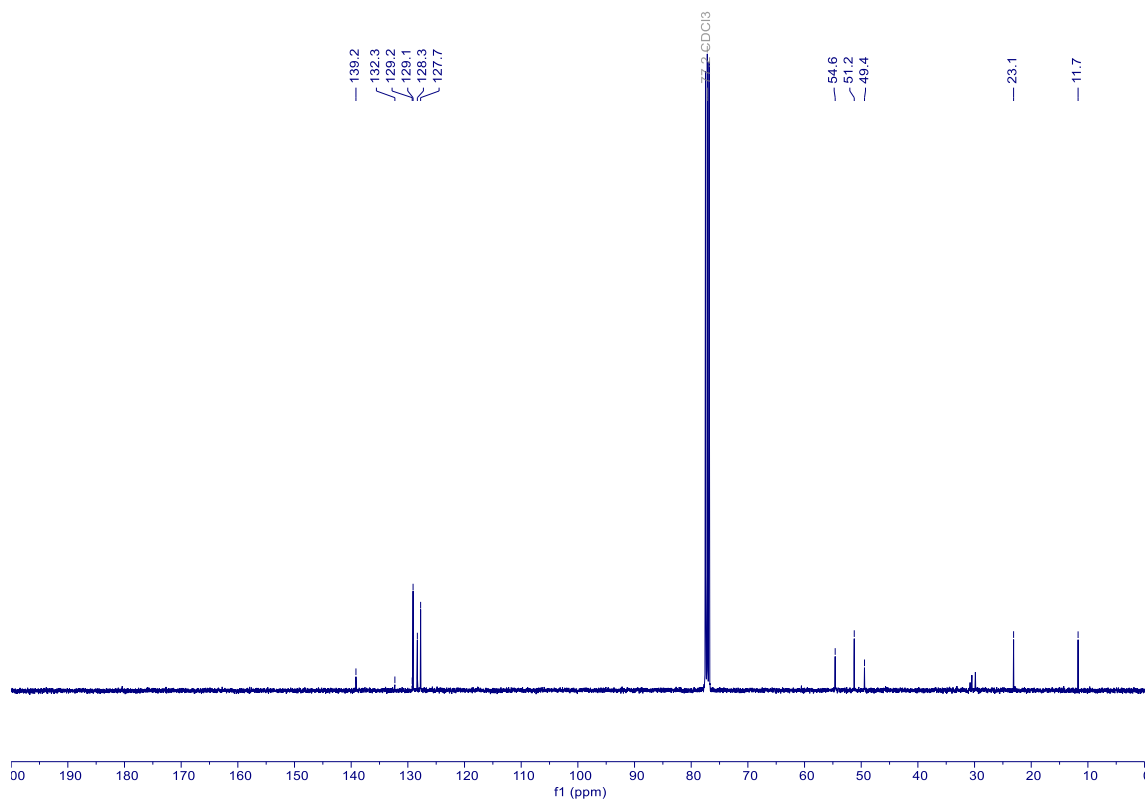
35c – ^{13}C NMR (151 MHz, CDCl_3)



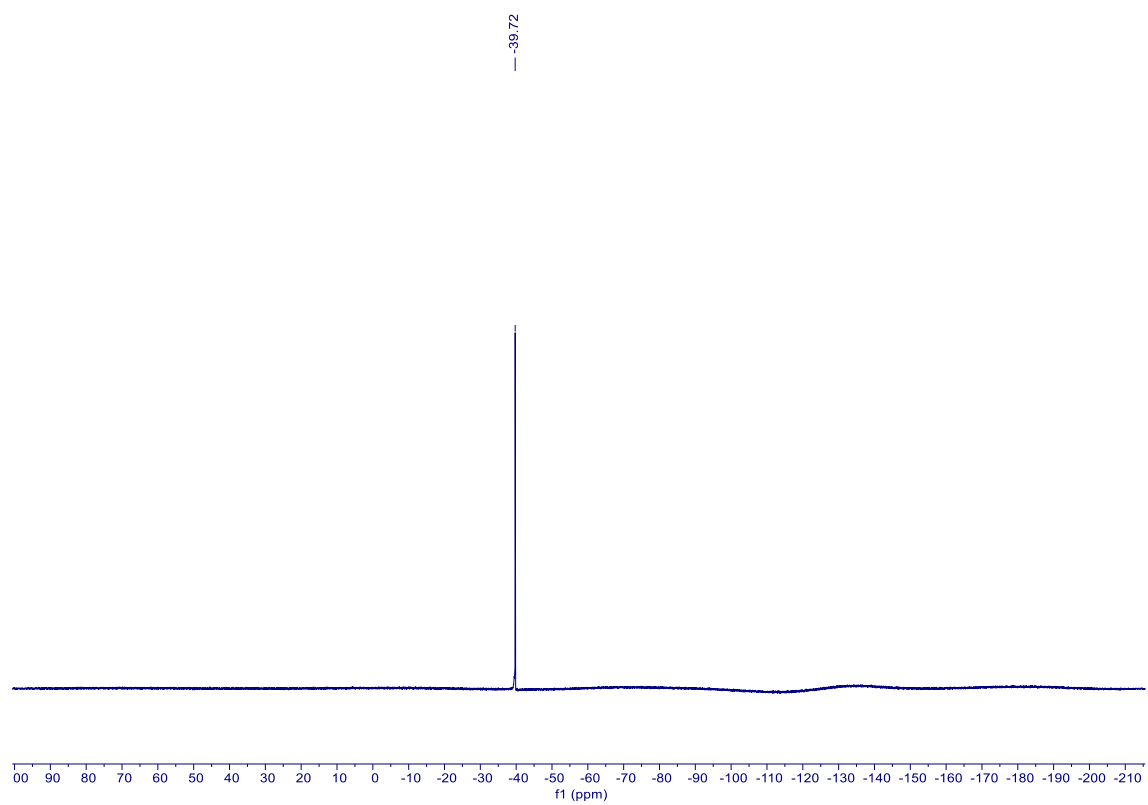
1s – ^1H NMR (400 MHz, CDCl_3)



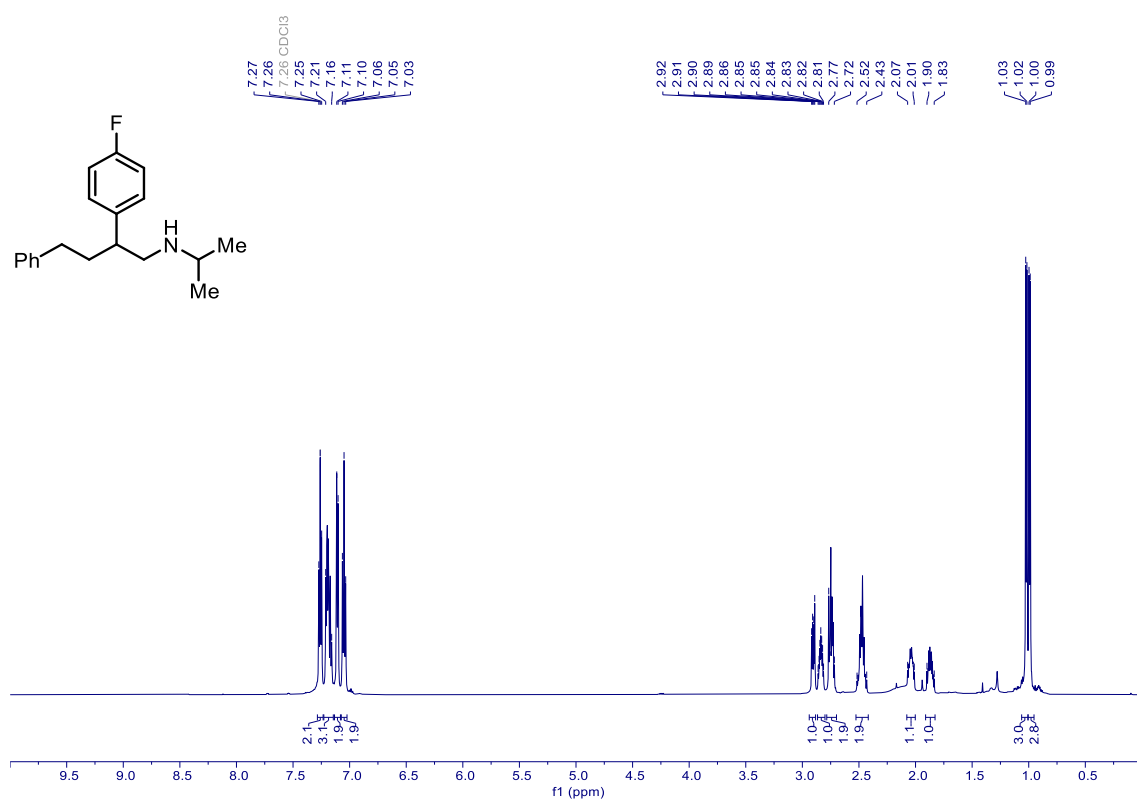
1s – ^{13}C NMR (101 MHz, CDCl_3)



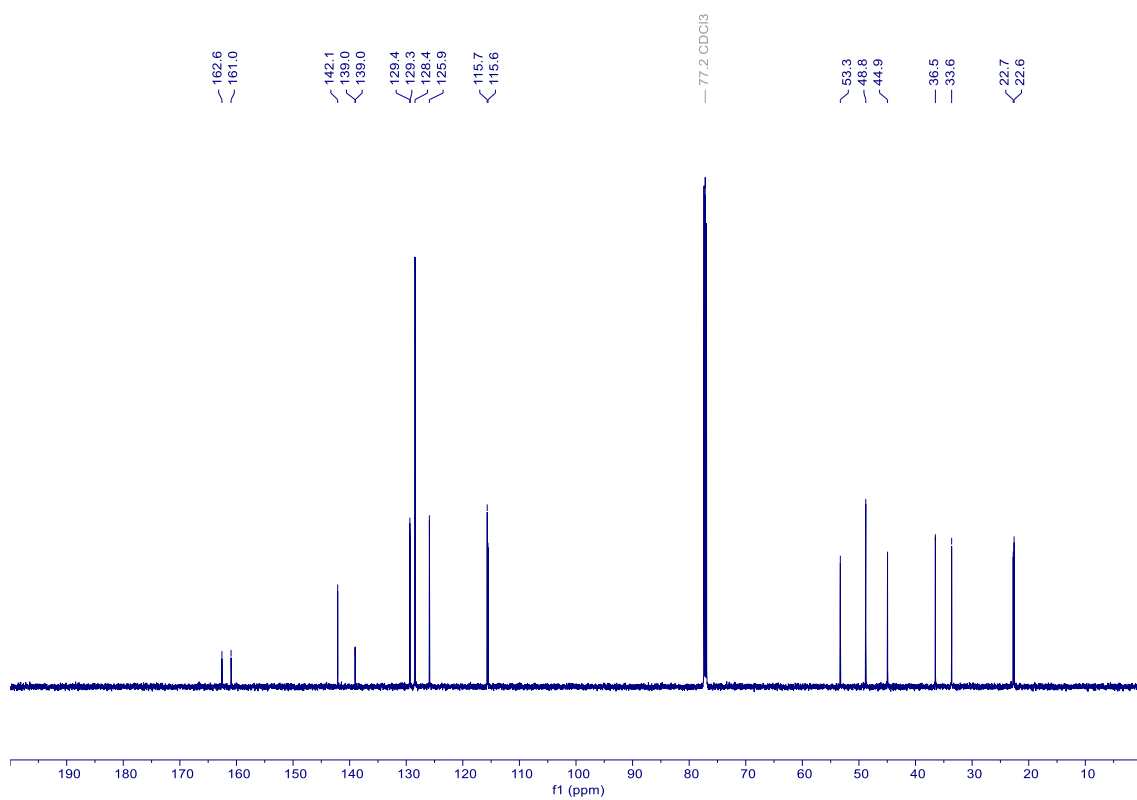
1s – ^{19}F NMR (376 MHz, CDCl_3)



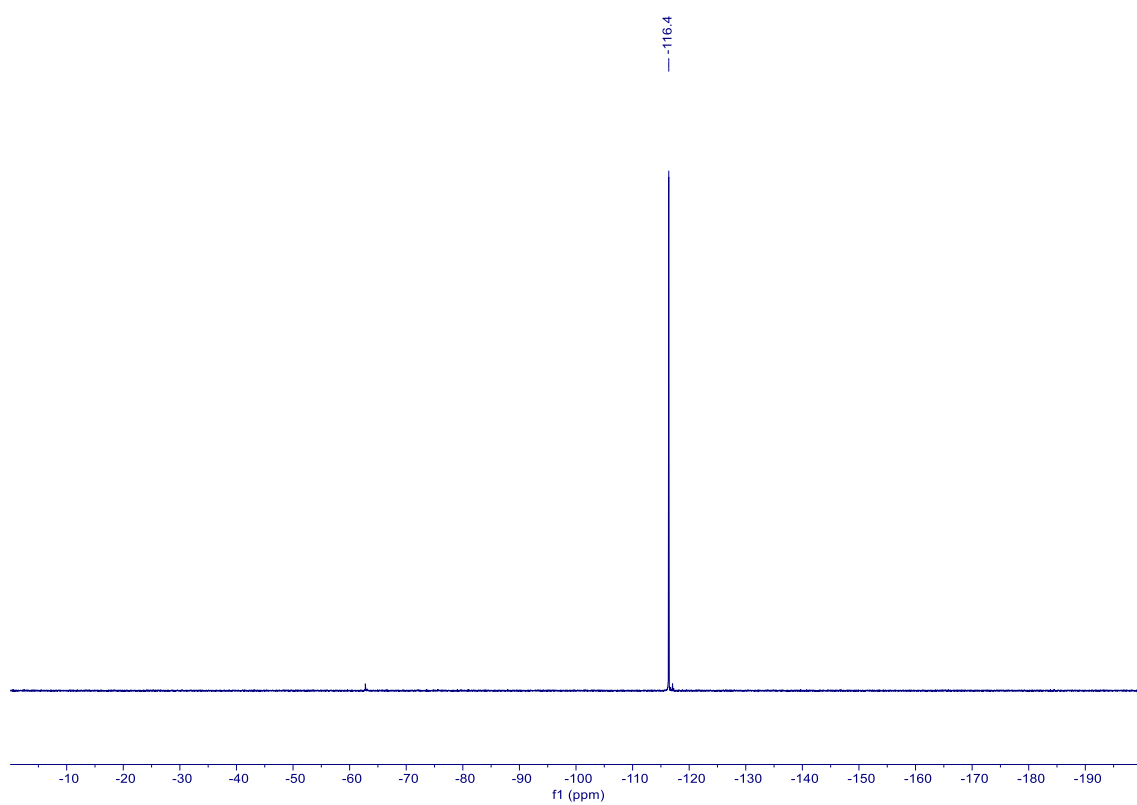
13g – ^1H NMR (600 MHz, CDCl_3)



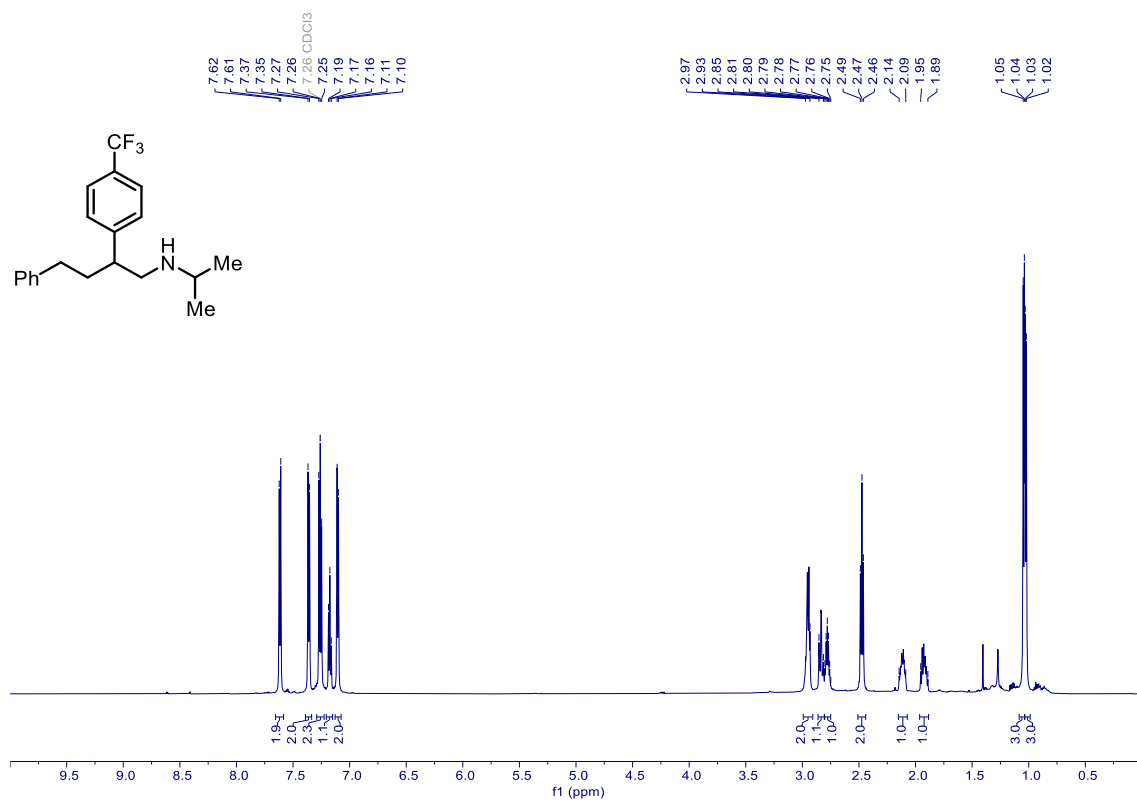
13g – ^{13}C NMR (151 MHz, CDCl_3)



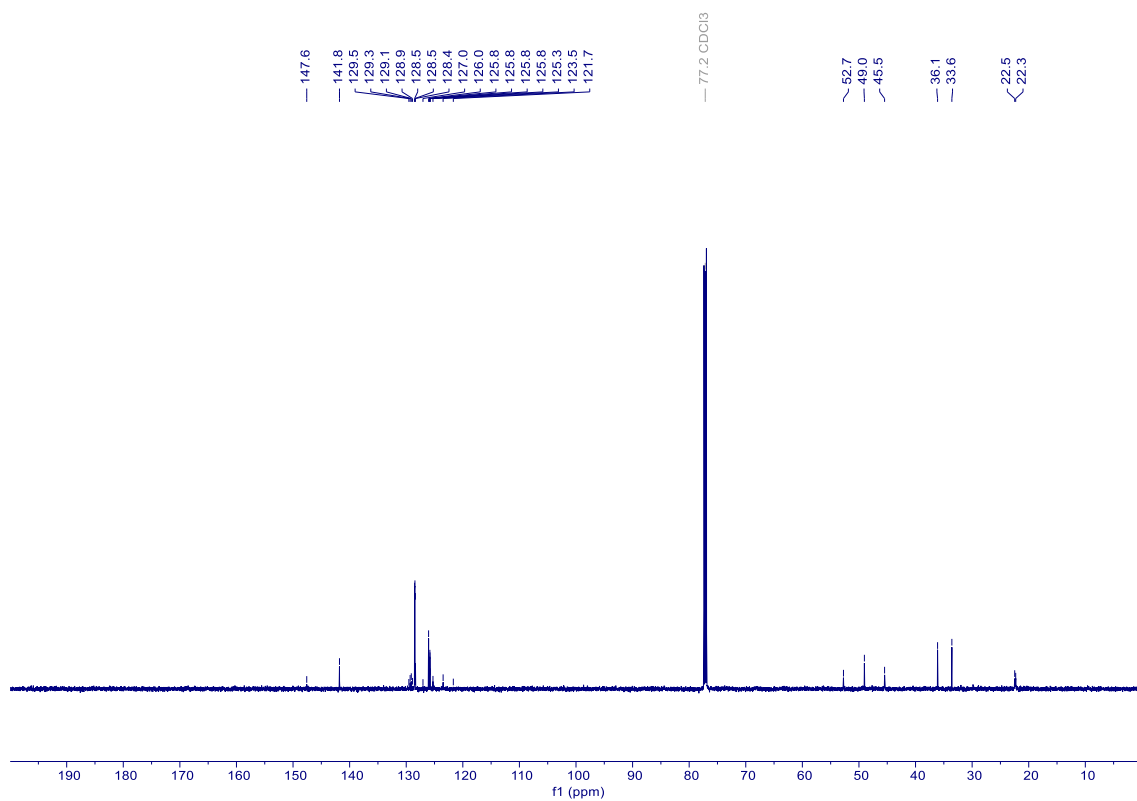
13g – ^{19}F NMR (564 MHz, CDCl_3)



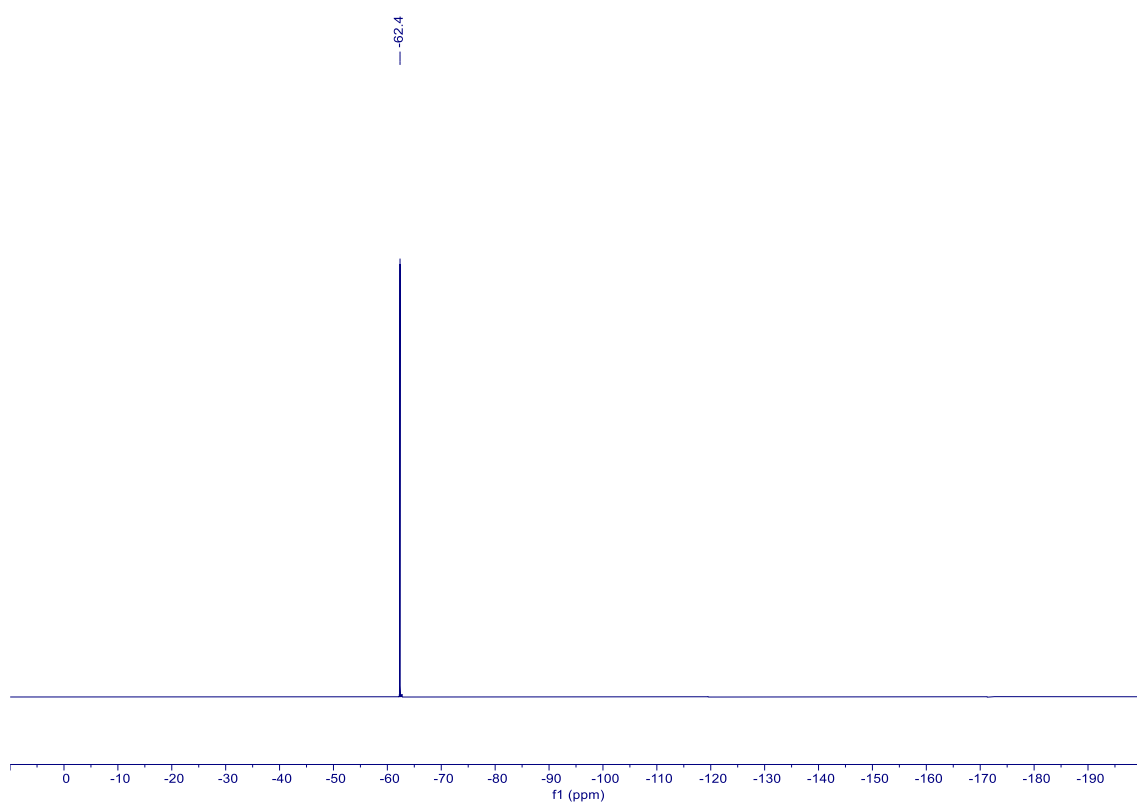
13h – ^1H NMR (600 MHz, CDCl_3)



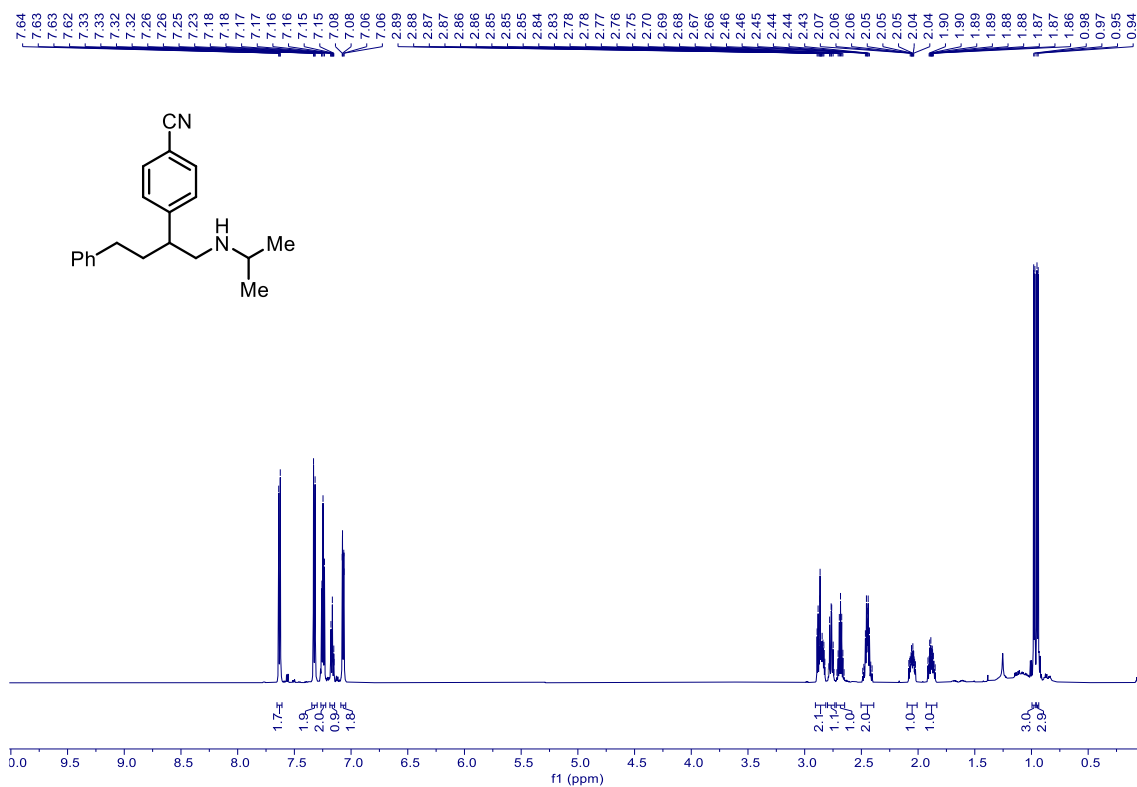
13h – ^{13}C NMR (151 MHz, CDCl_3)



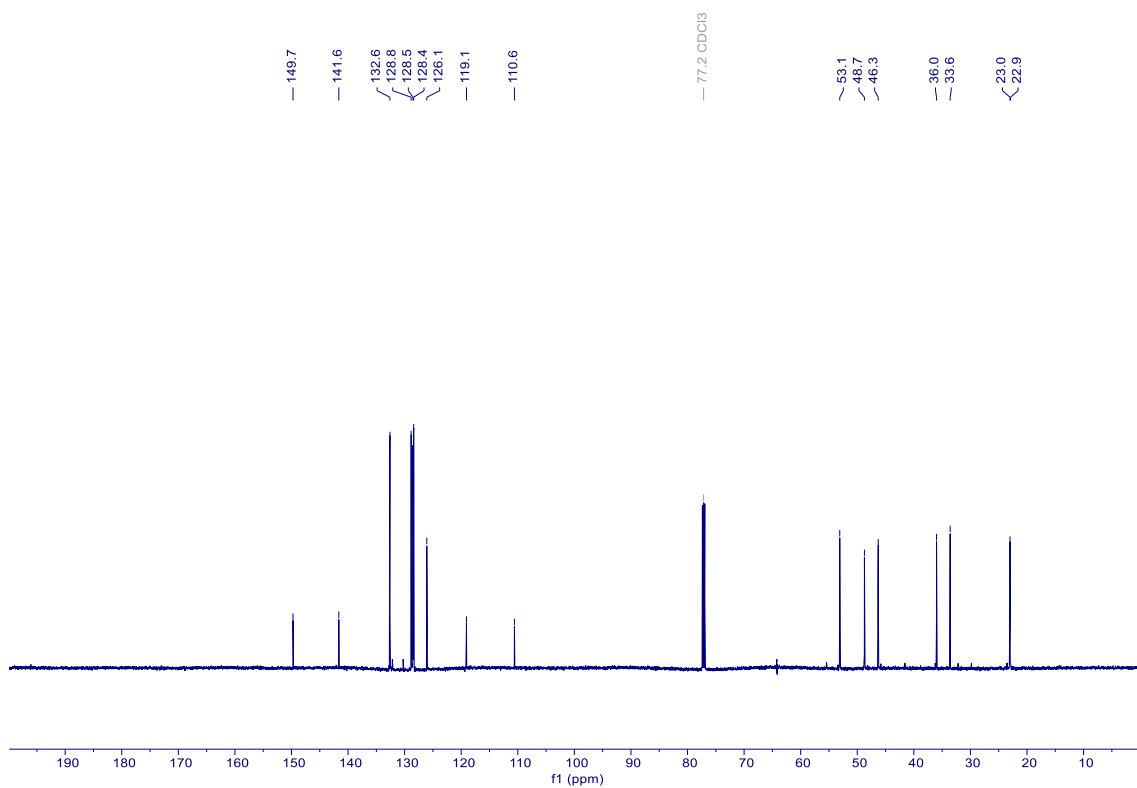
13h – ^{19}F NMR (564 MHz, CDCl_3)



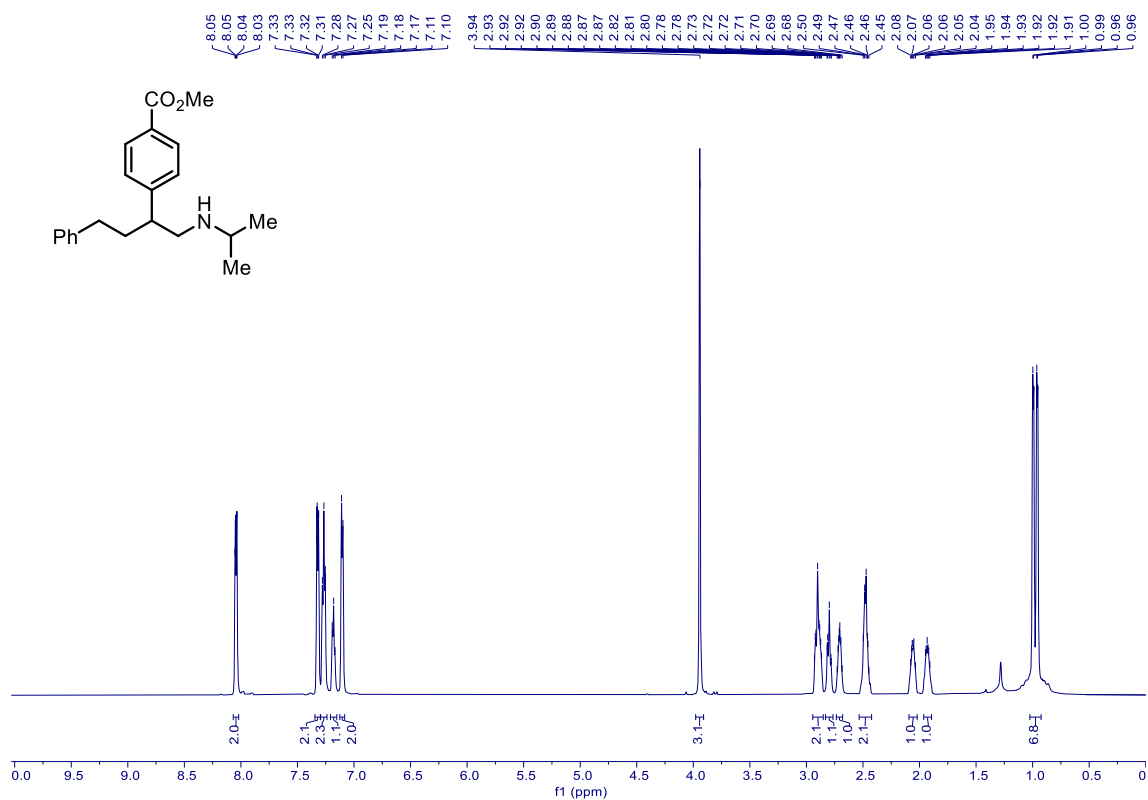
13i – ^1H NMR (600 MHz, CDCl_3)



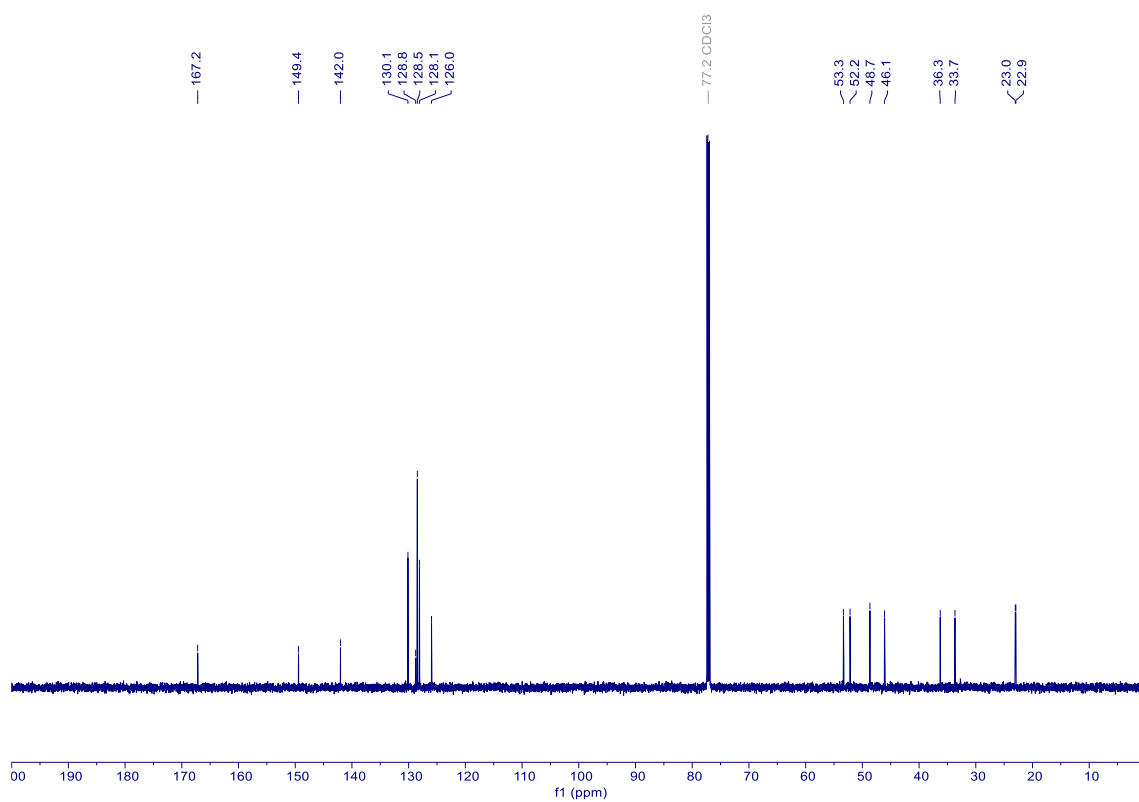
13i – ^{13}C NMR (151 MHz, CDCl_3)



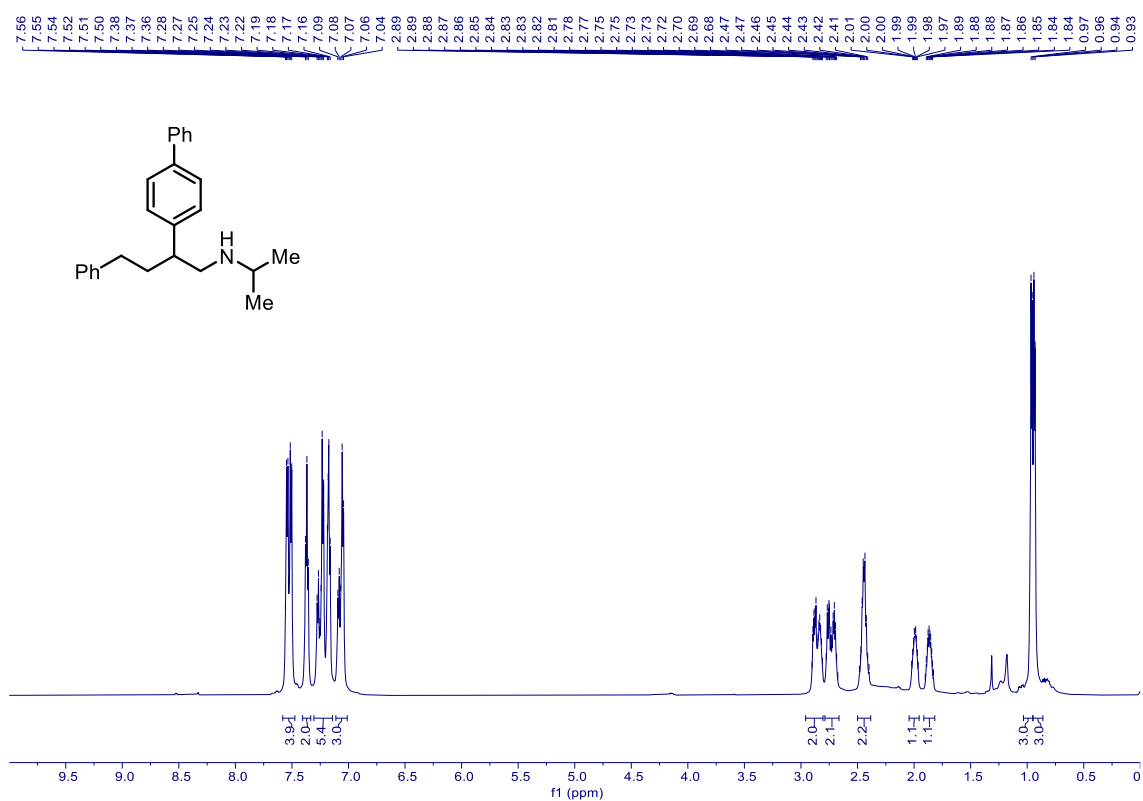
13j – ^1H NMR (600 MHz, CDCl_3)



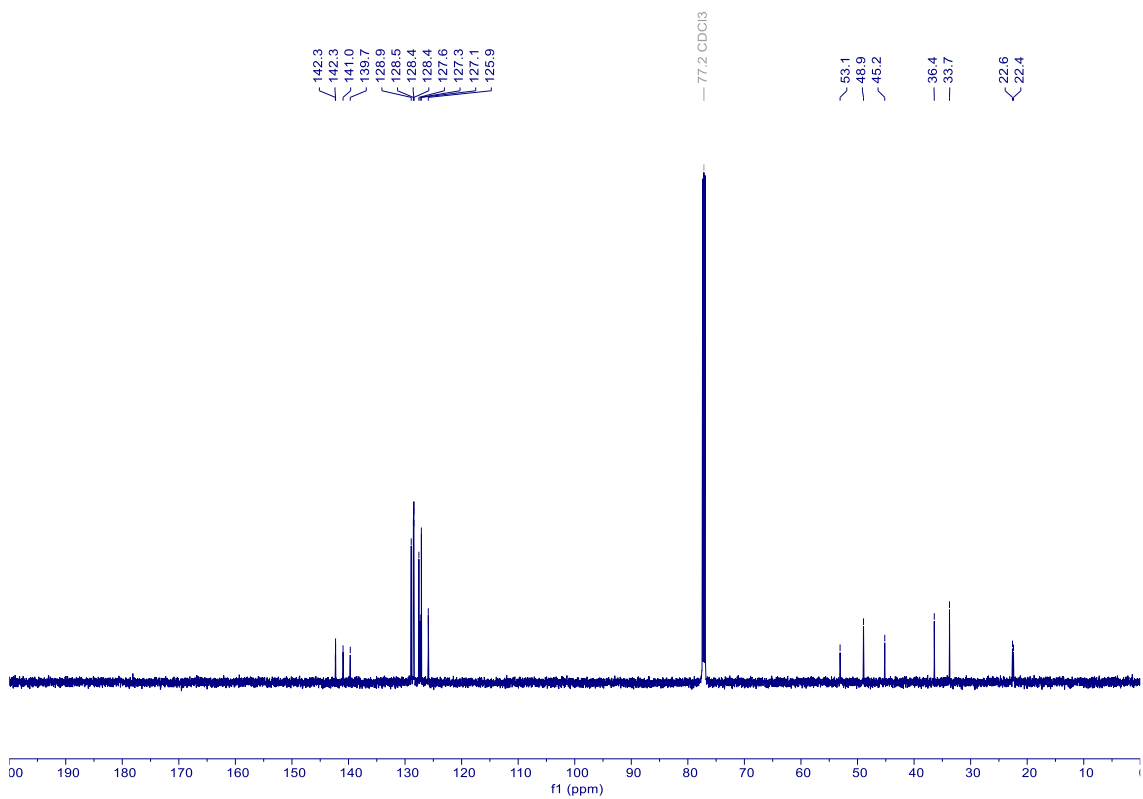
13j – ^{13}C NMR (151 MHz, CDCl_3)



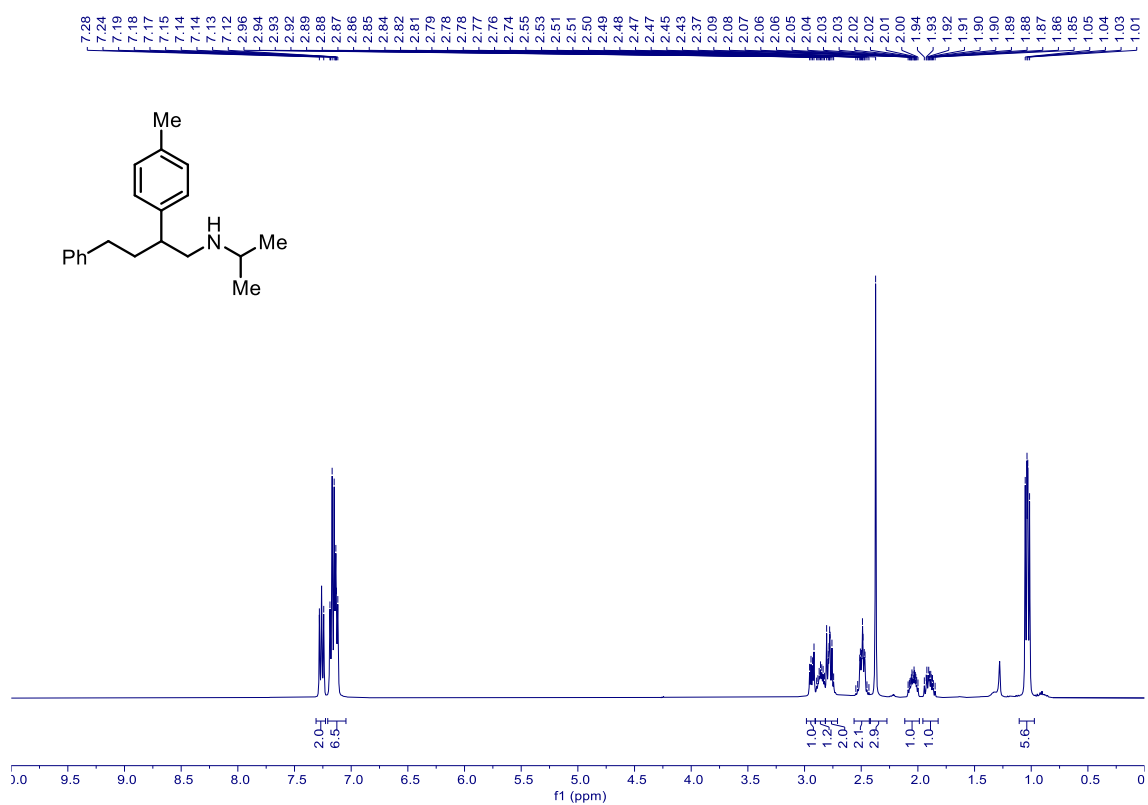
13k – ^1H NMR (600 MHz, CDCl_3)



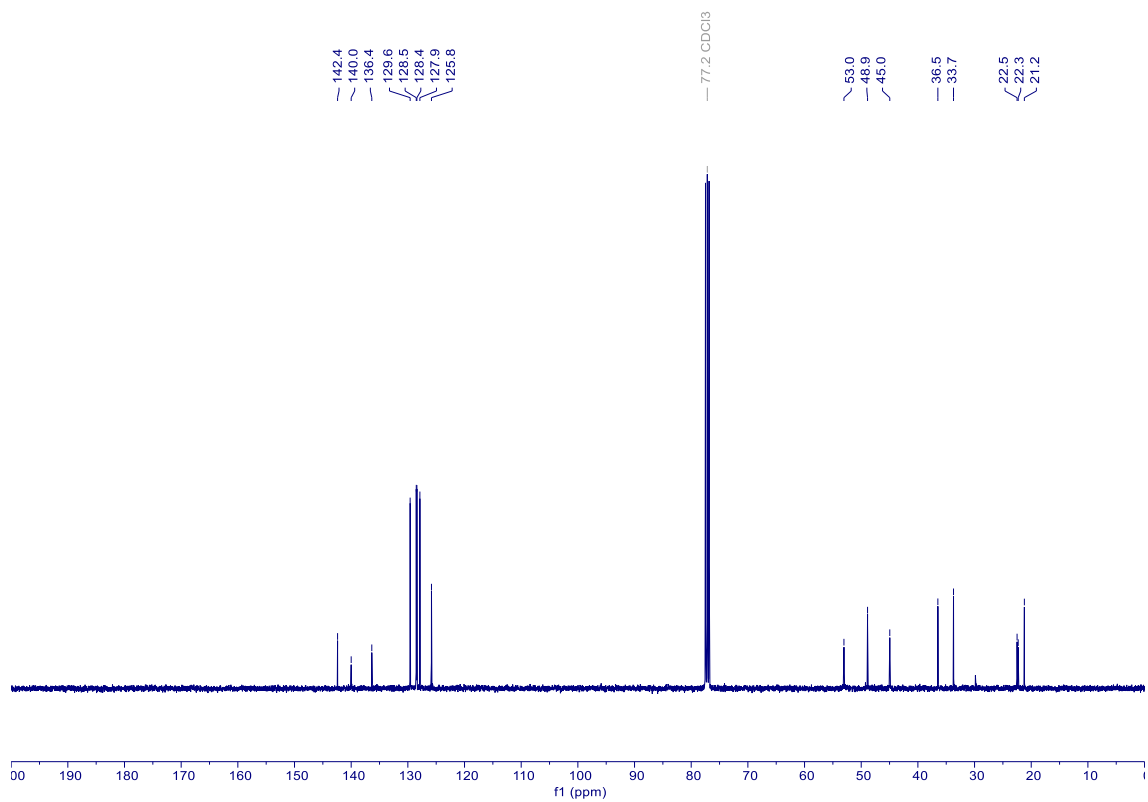
13k – ^{13}C NMR (151 MHz, CDCl_3)



13I – ^1H NMR (400 MHz, CDCl_3)



13I – ^{13}C NMR (101 MHz, CDCl_3)



CC(C)NCC(Cc1ccc(cc1)C(C)(C)C)CCc2ccccc2

7.28
7.26
7.18
7.17
7.16
7.15
7.08
7.07
7.05
7.04
2.86
2.85
2.84
2.83
2.80
2.79
2.78
2.76
2.75
2.72
2.71
2.70
2.69
2.68
2.45
2.44
2.43
2.42
2.41
2.40
2.39
2.38
2.37
1.99
1.98
1.98
1.97
1.97
1.96
1.95
1.95
1.95
1.94
1.94
1.93
1.85
1.84
1.83
1.83
1.82
1.82
1.81
1.80
1.80
1.79
1.79
1.25
0.97
0.95
0.95
0.93

1.93
2.14
4.81
1.01
1.01
2.01
1.01
1.01
9.12
2.71
3.01

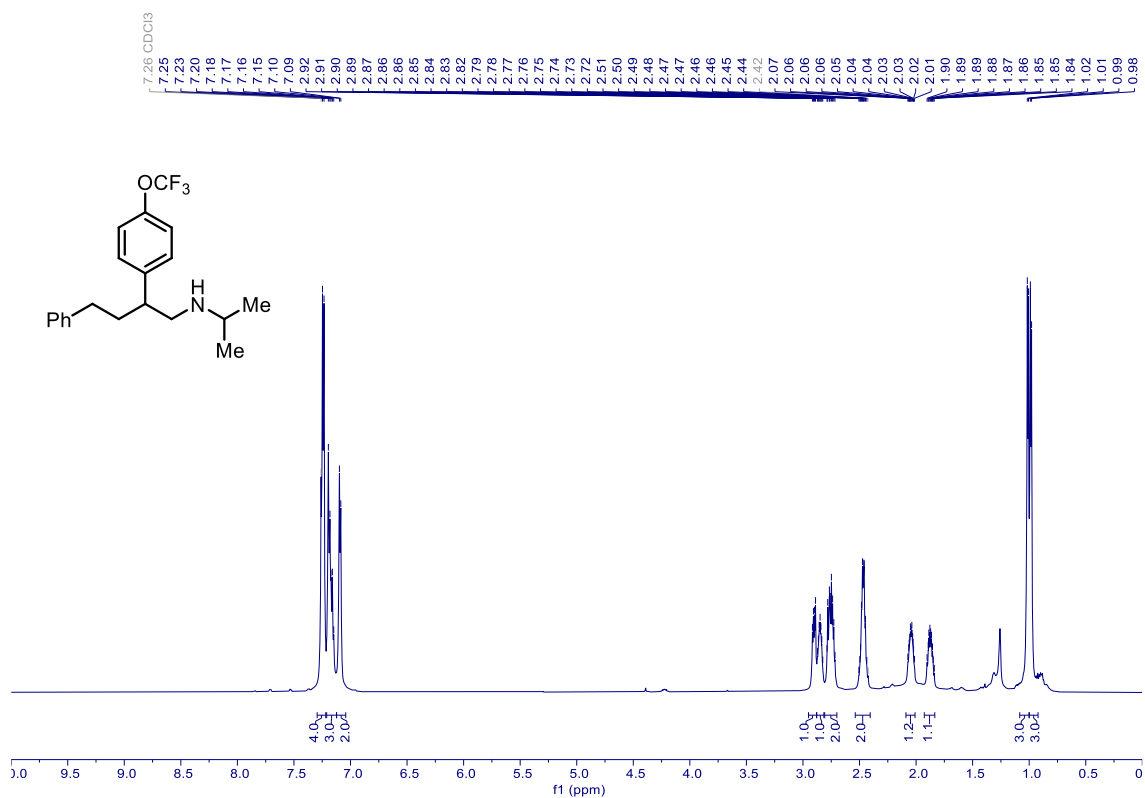
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

f1 (ppm)

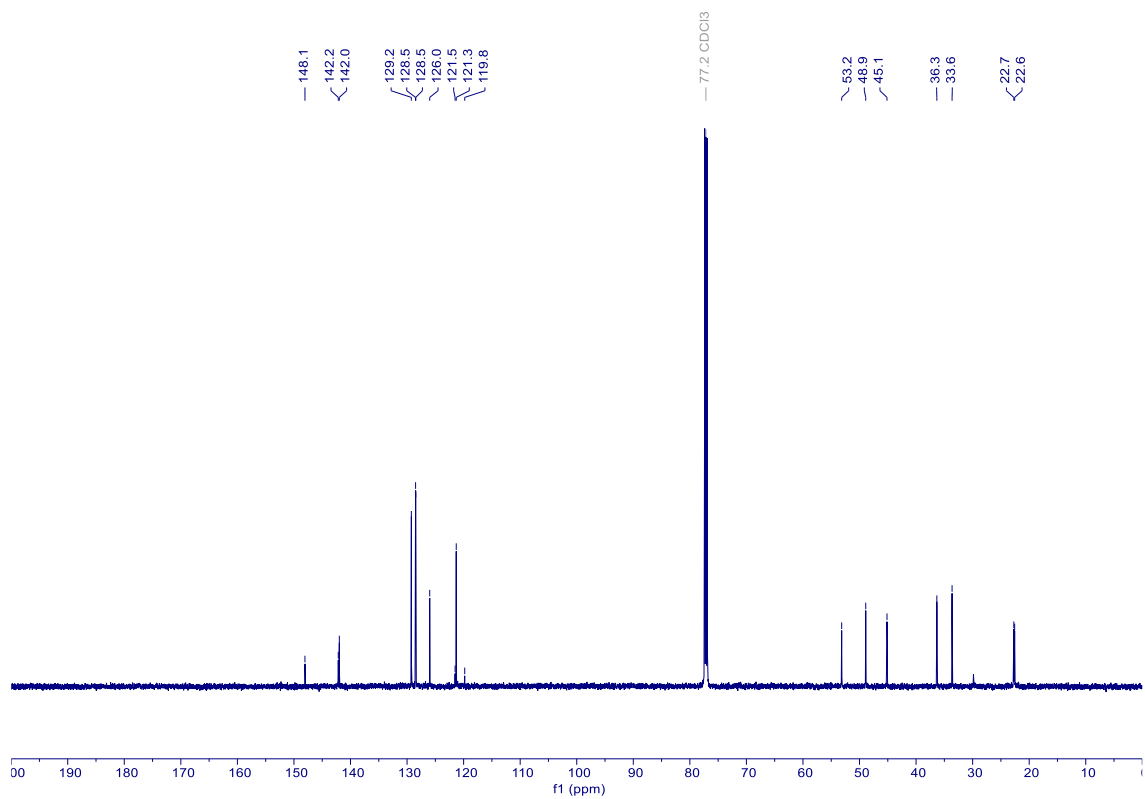
149.6
142.5
139.9
128.5
128.4
127.6
125.8
125.7
77.2 CDCl₃
52.9
48.9
44.8
36.4
34.6
33.8
31.5
22.5
22.2

f1 (ppm)

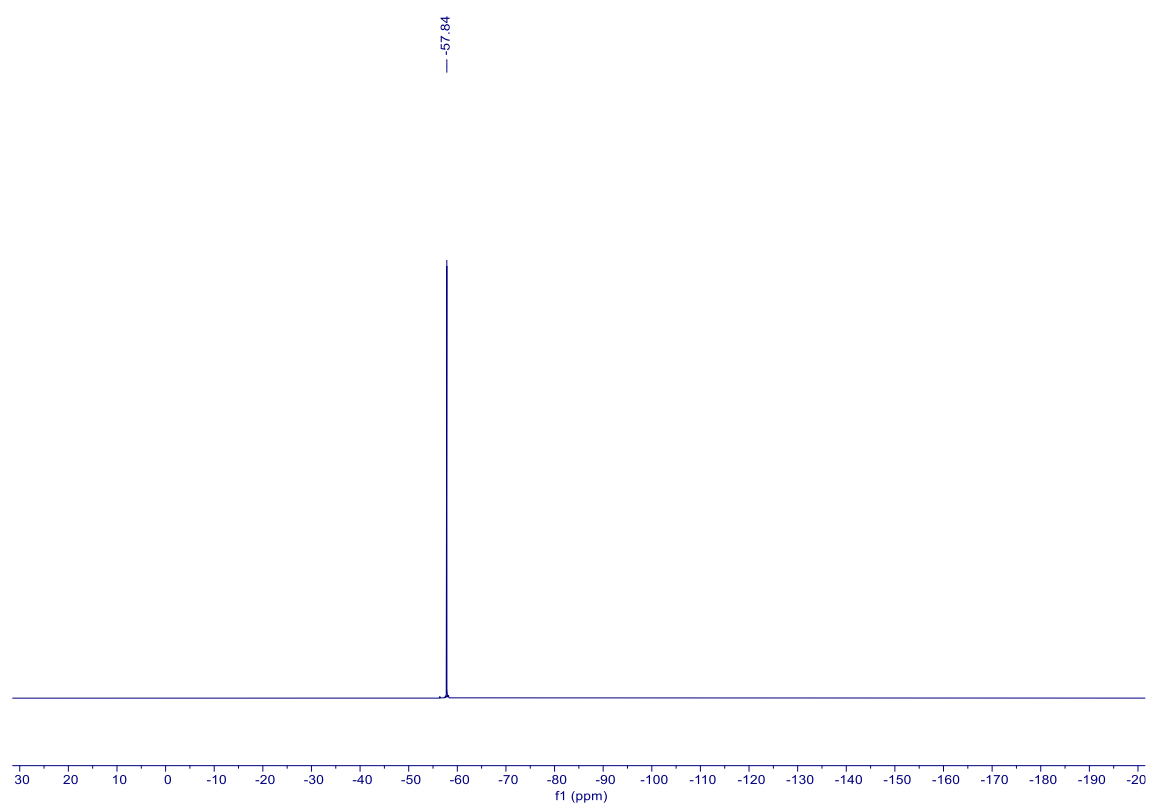
13o – ^1H NMR (600 MHz, CDCl_3)



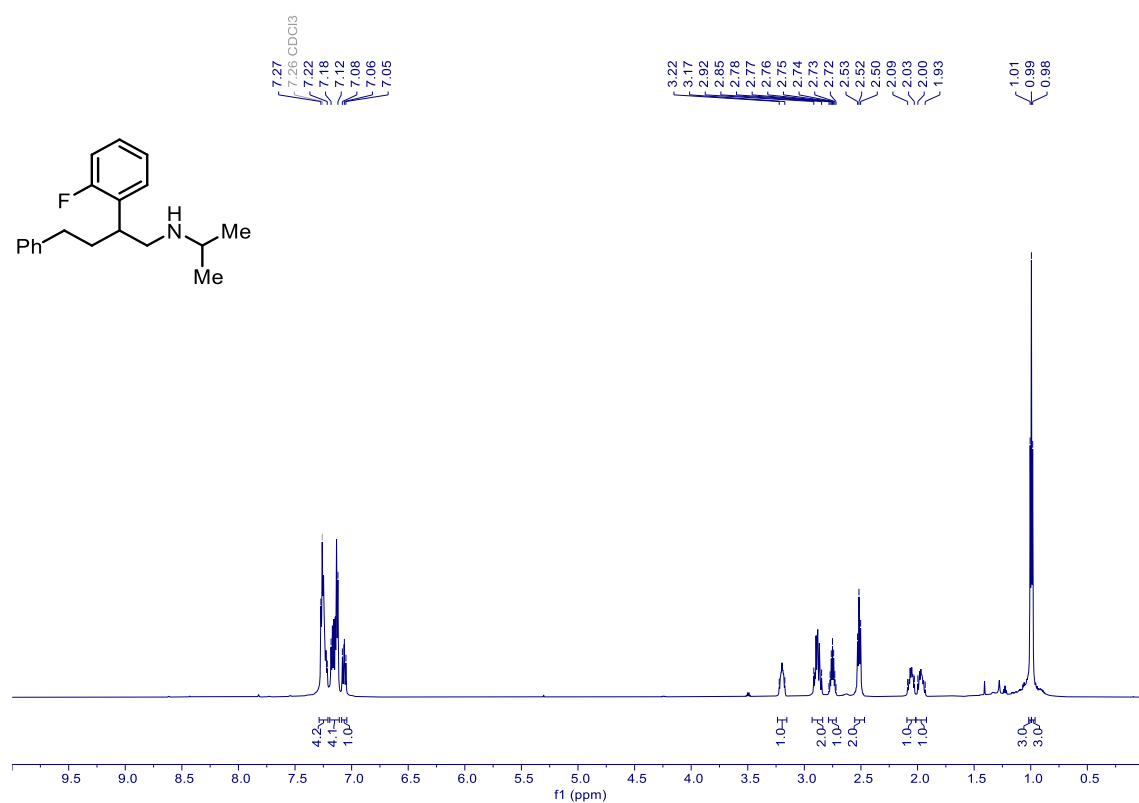
13o – ^{13}C NMR (151 MHz, CDCl_3)



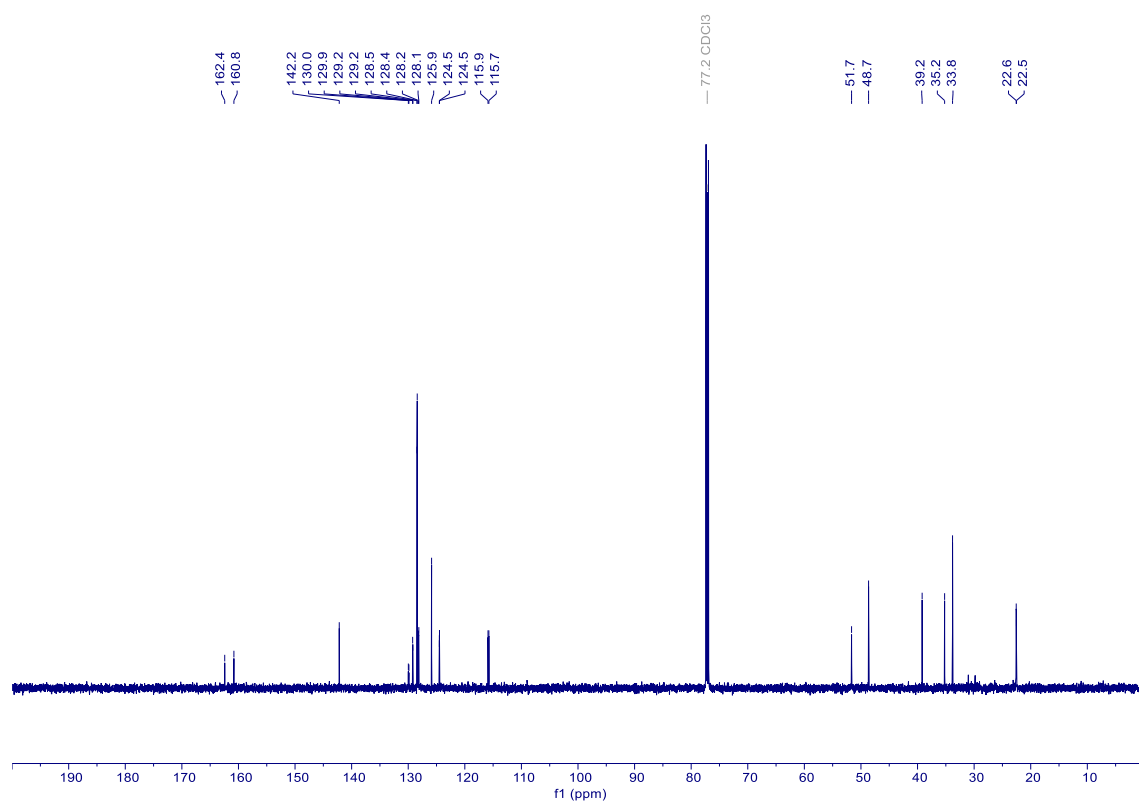
13o – ^{19}F NMR (564 MHz, CDCl_3)



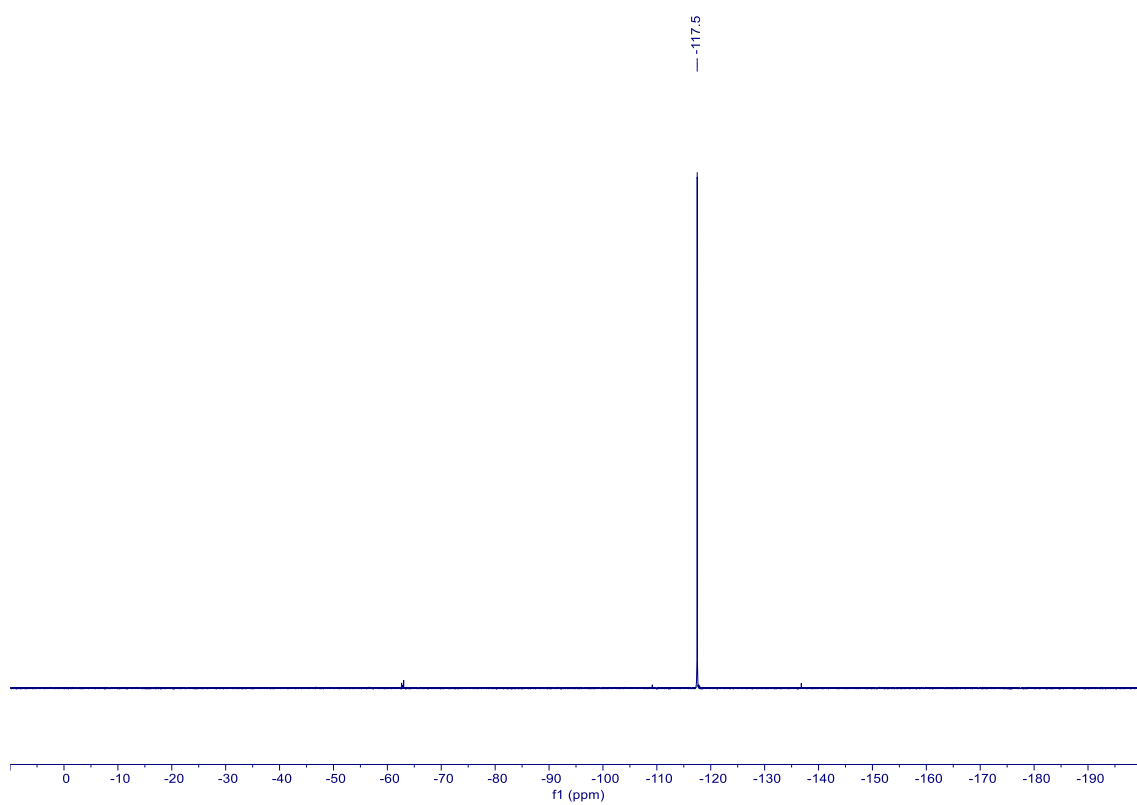
13p – ^1H NMR (600 MHz, CDCl_3)



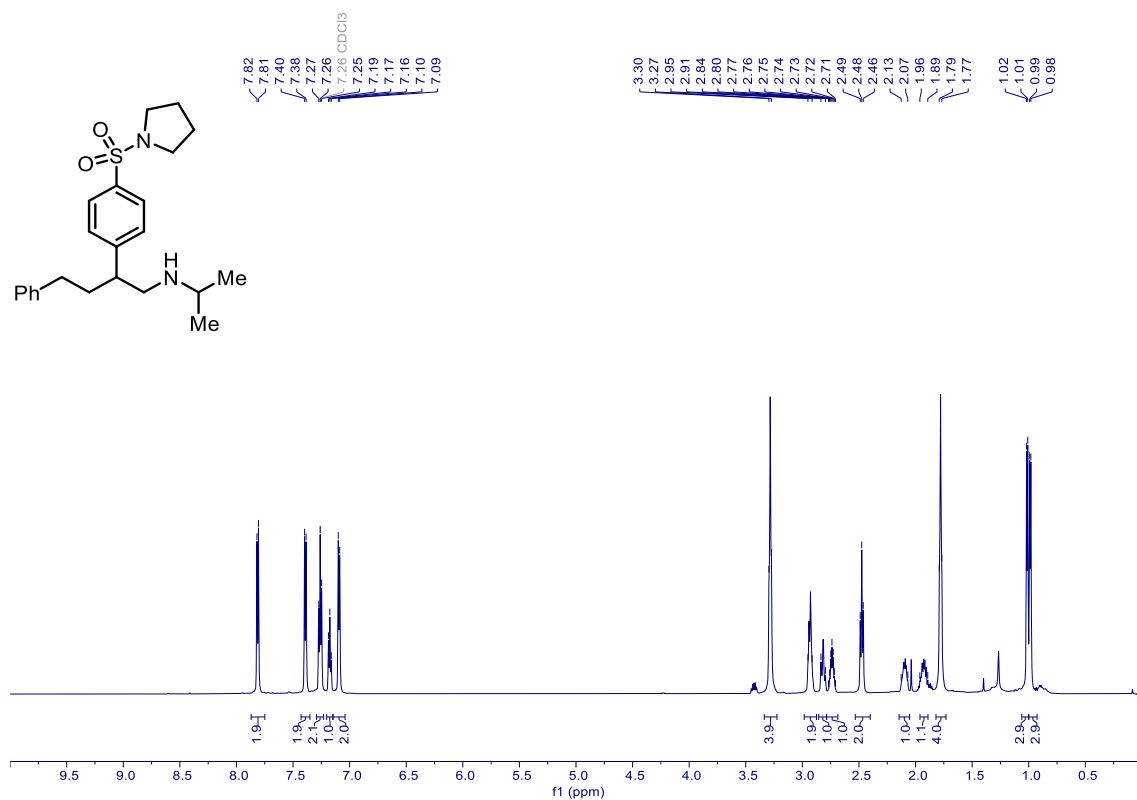
13p – ^{13}C NMR (151 MHz, CDCl_3)



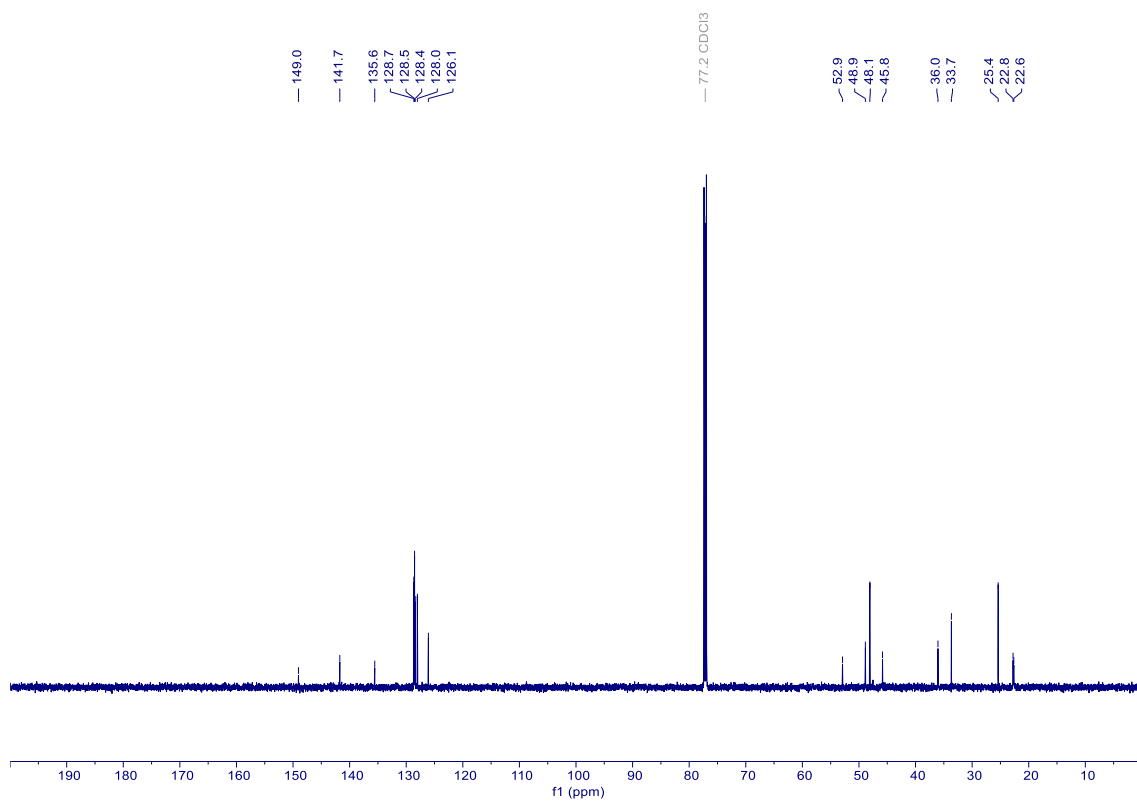
13p – ^{19}F NMR (564 MHz, CDCl_3)



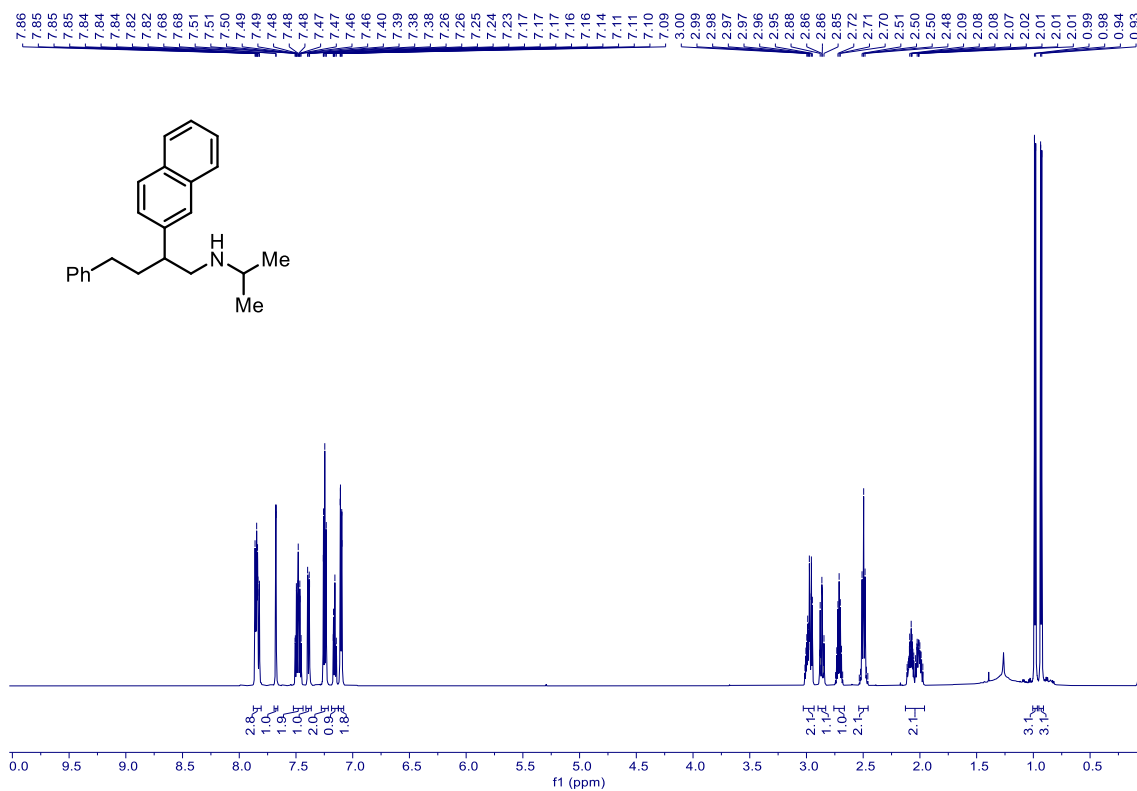
13q – ^1H NMR (600 MHz, CDCl_3)



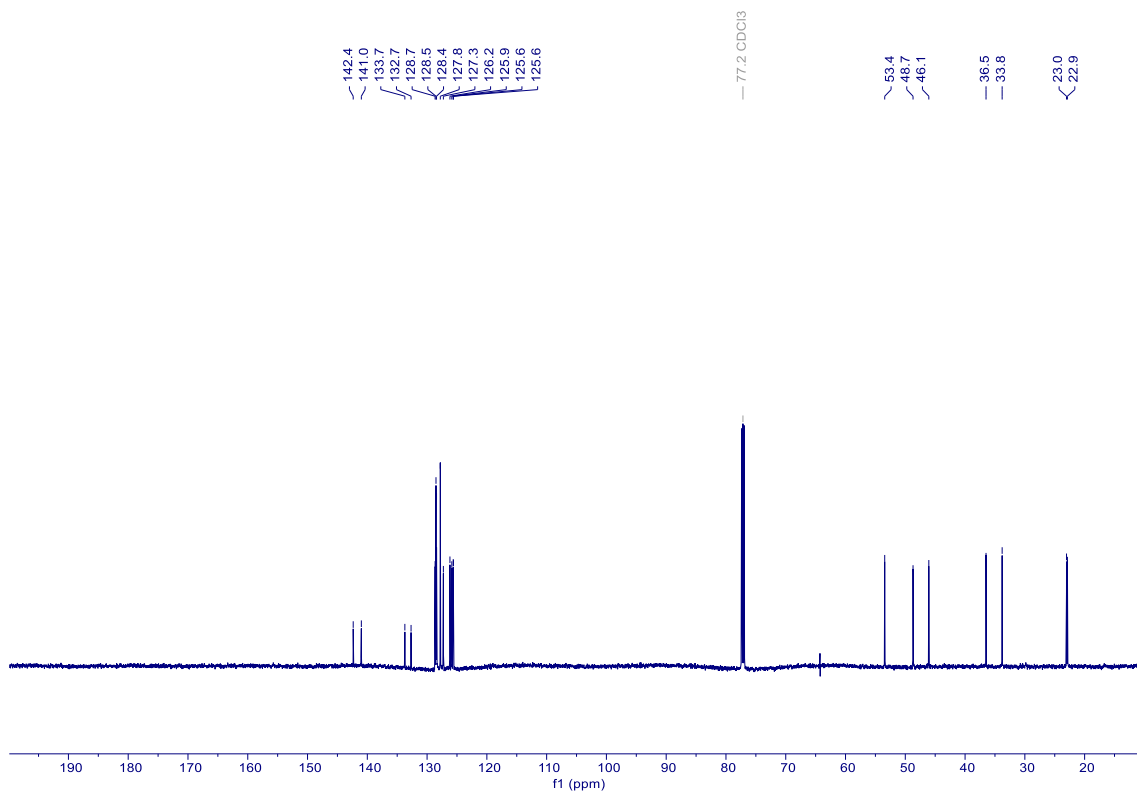
13q – ^{13}C NMR (151 MHz, CDCl_3)



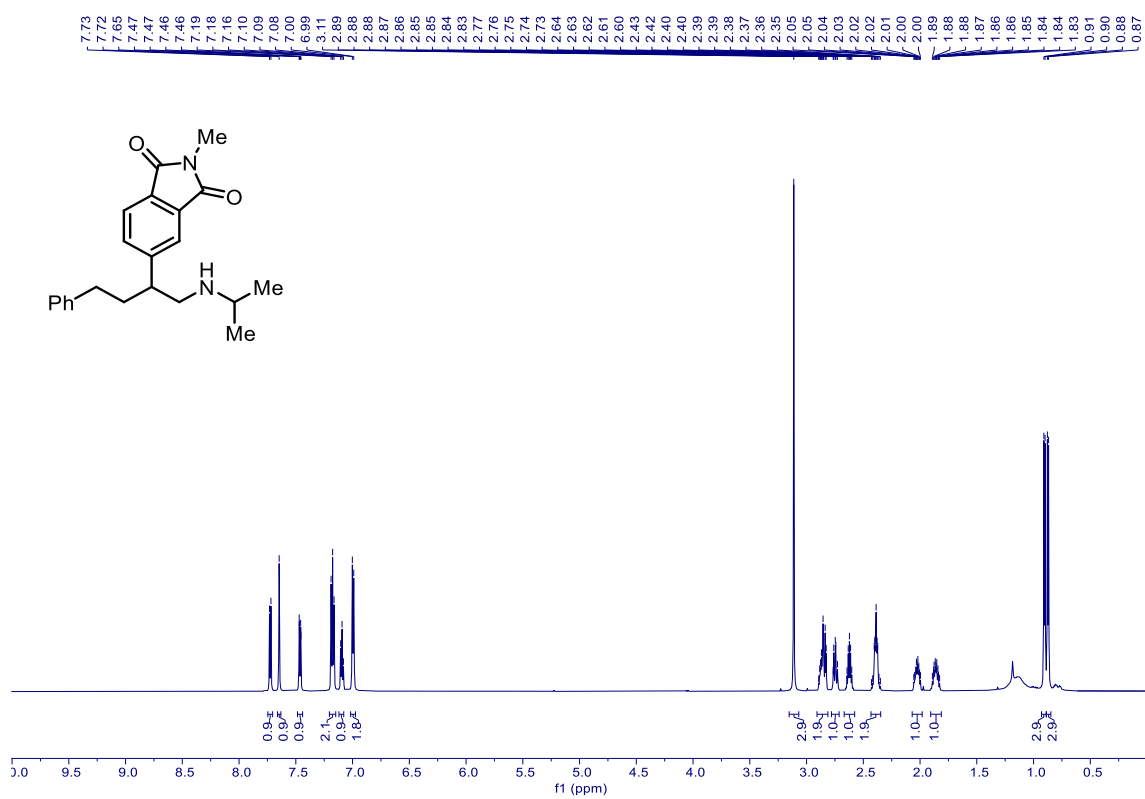
13r – ^1H NMR (600 MHz, CDCl_3)



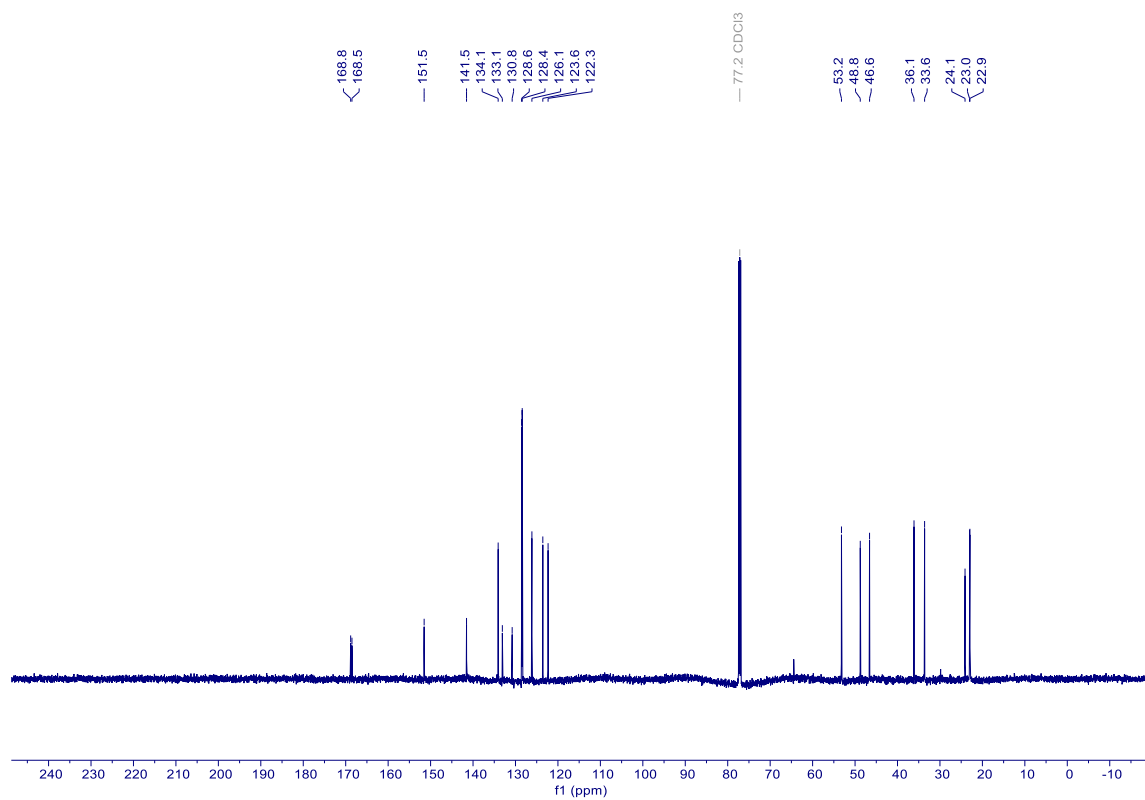
13r – ^{13}C NMR (151 MHz, CDCl_3)



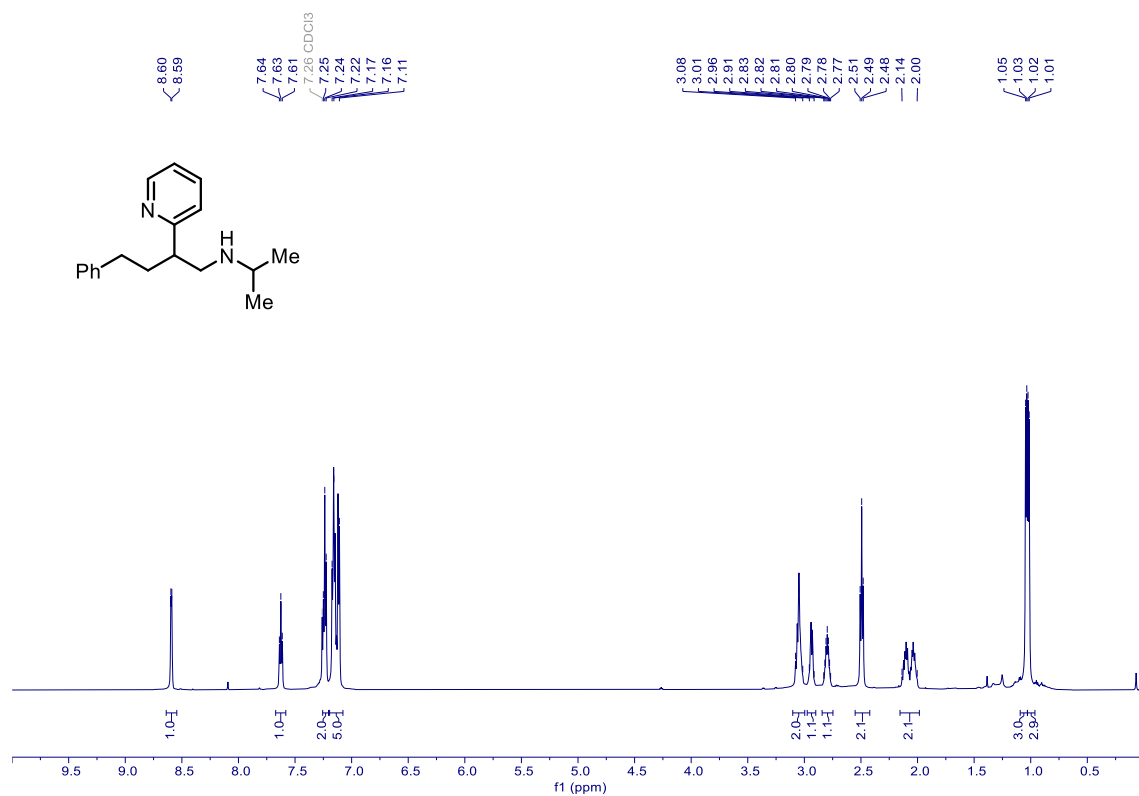
13s – ^1H NMR (600 MHz, CDCl_3)



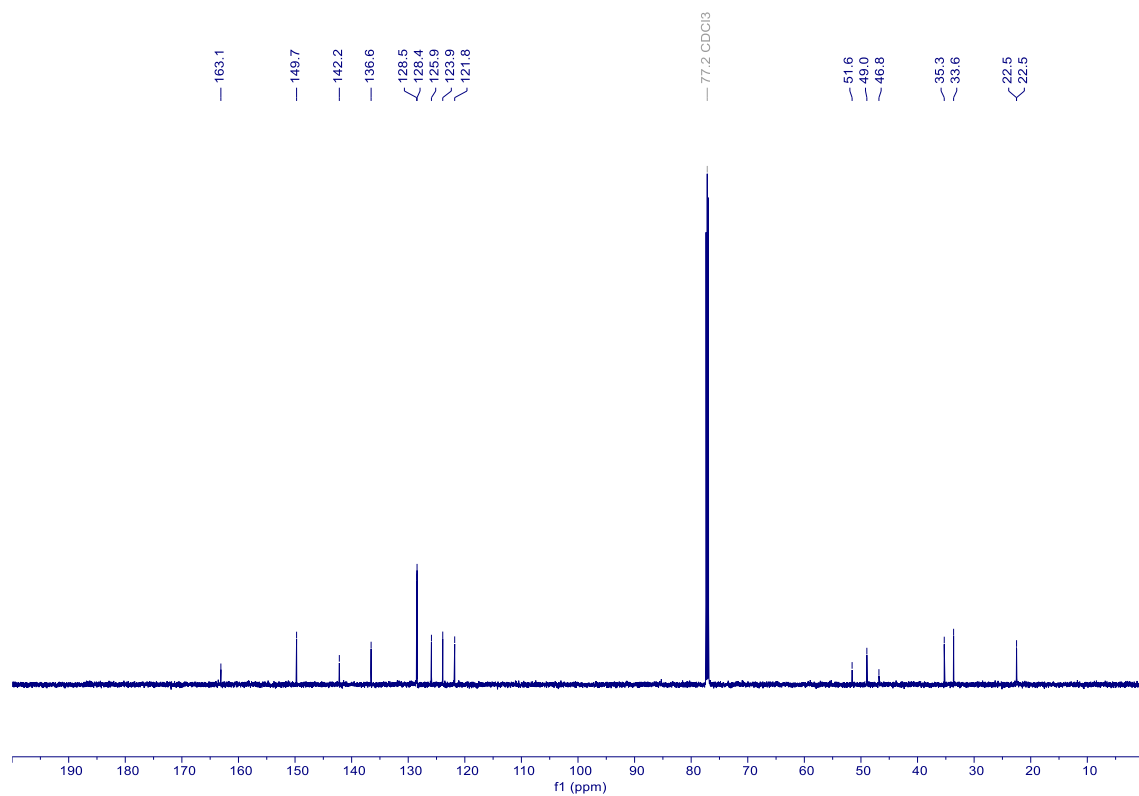
13s – ^{13}C NMR (151 MHz, CDCl_3)



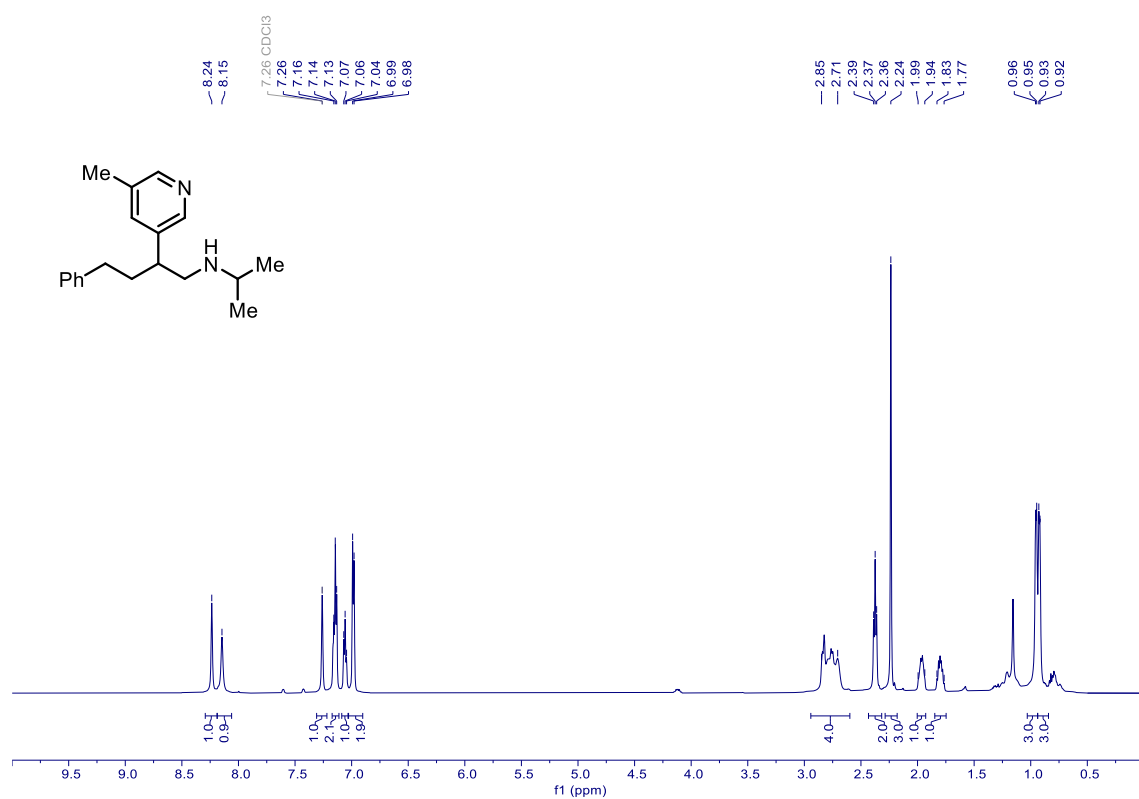
13t – ^1H NMR (600 MHz, CDCl_3)



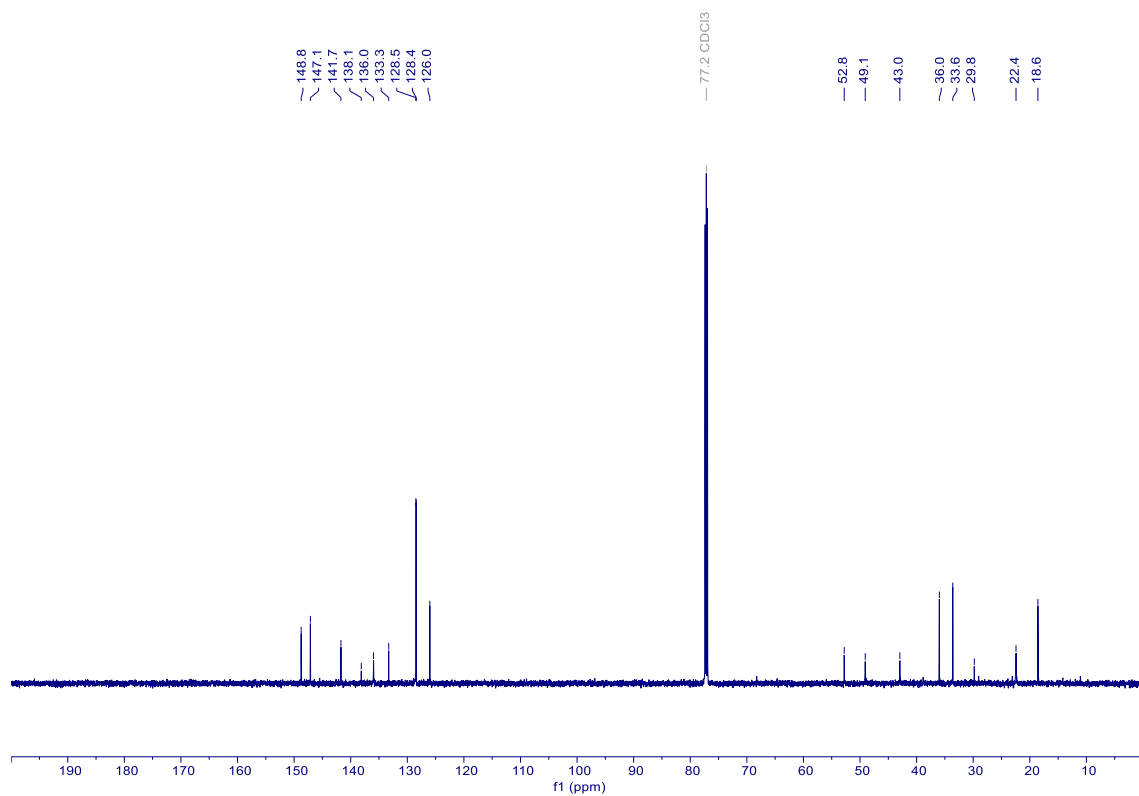
13t – ^{13}C NMR (151 MHz, CDCl_3)



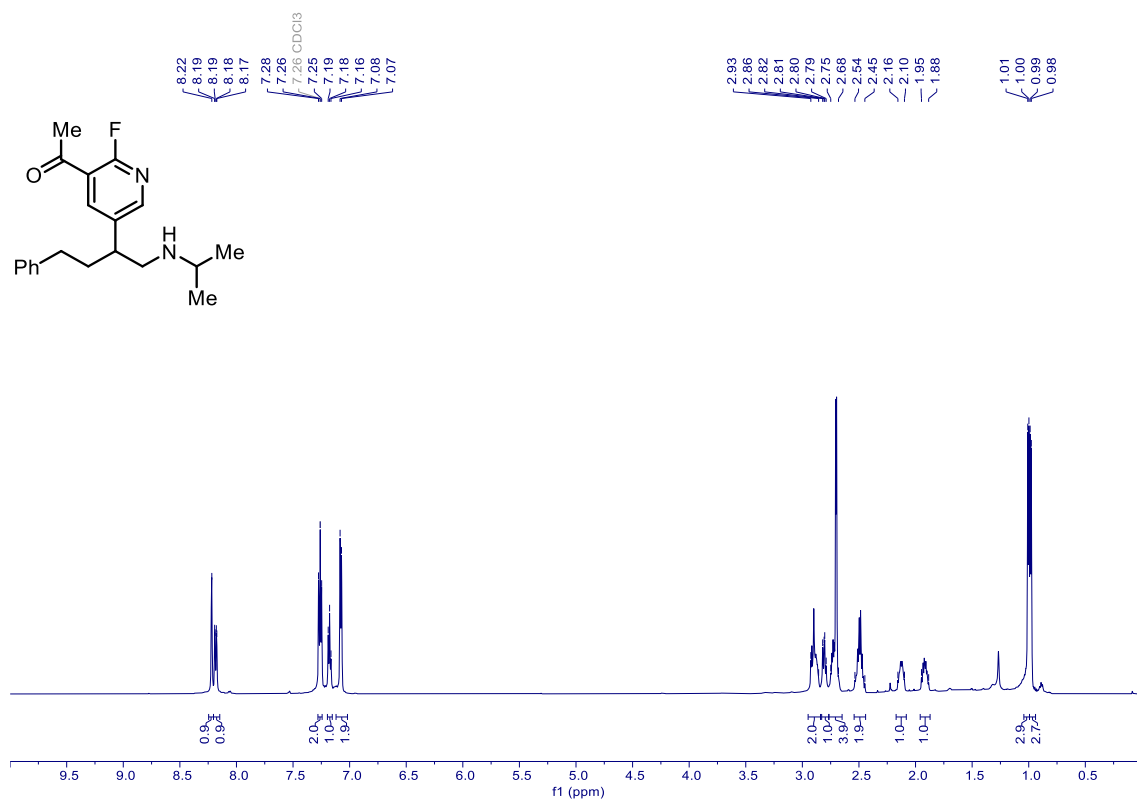
13u – ^1H NMR (600 MHz, CDCl_3)



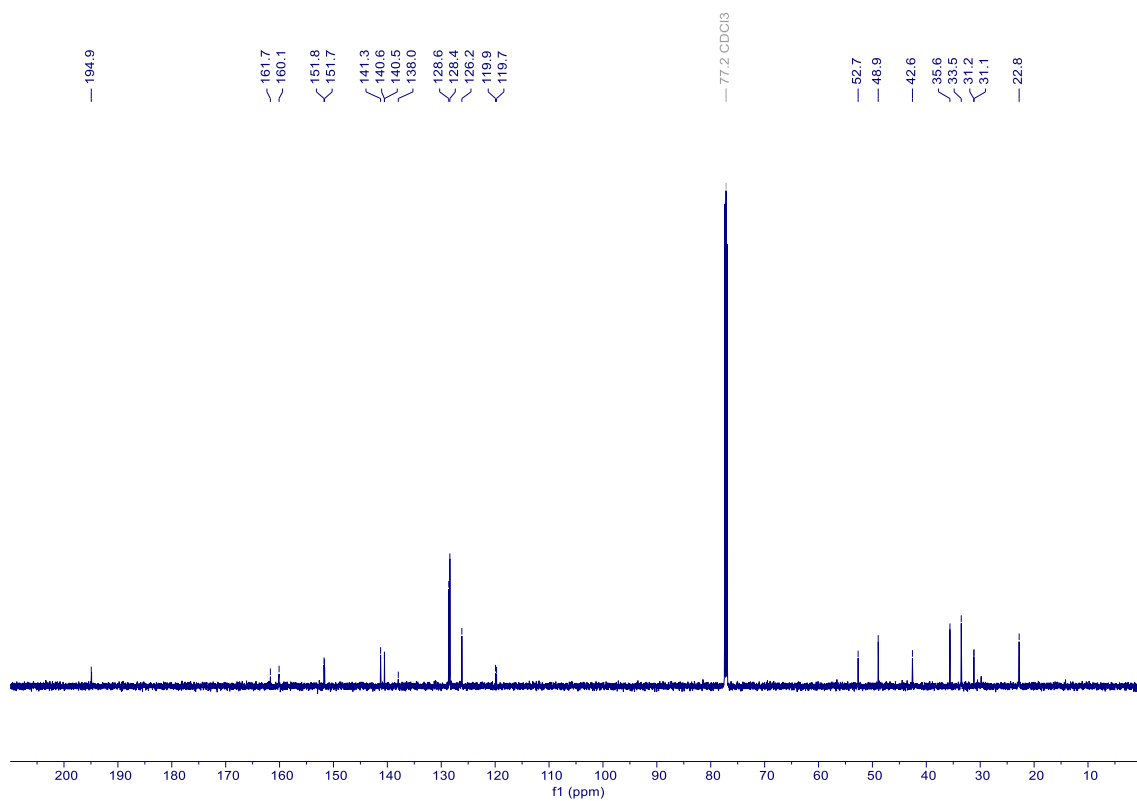
13u – ^{13}C NMR (151 MHz, CDCl_3)



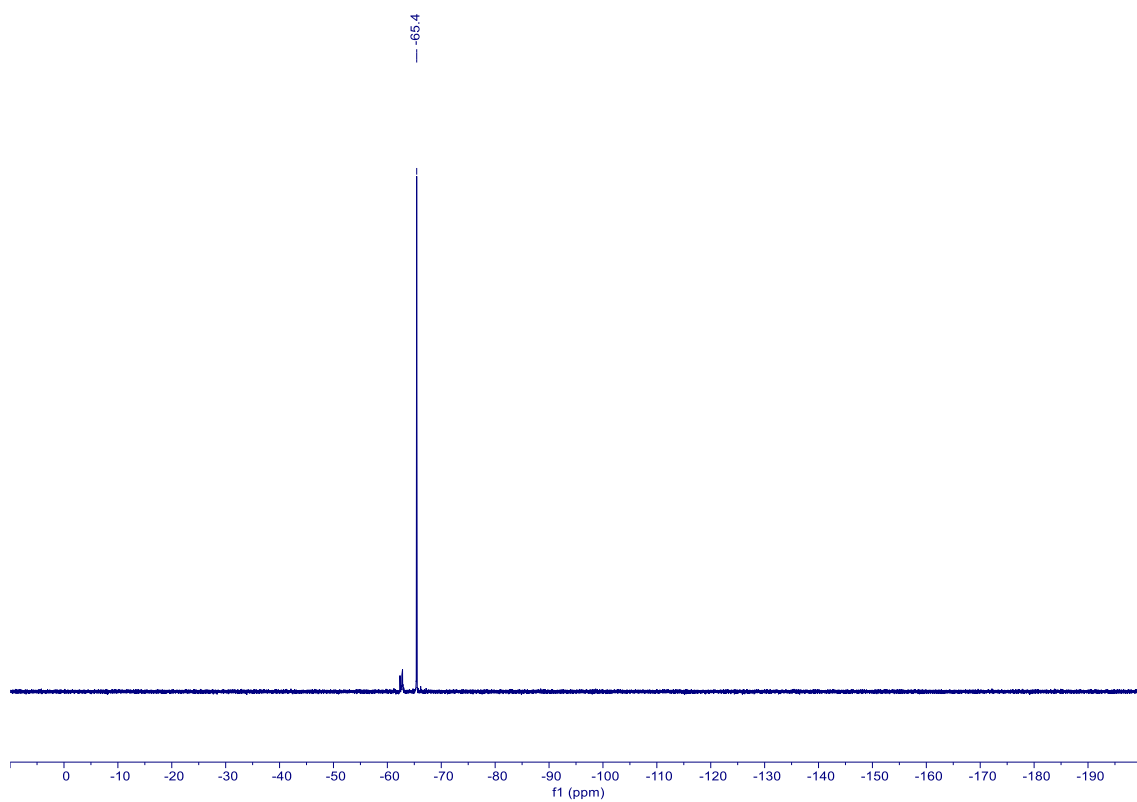
13v – ^1H NMR (600 MHz, CDCl_3)



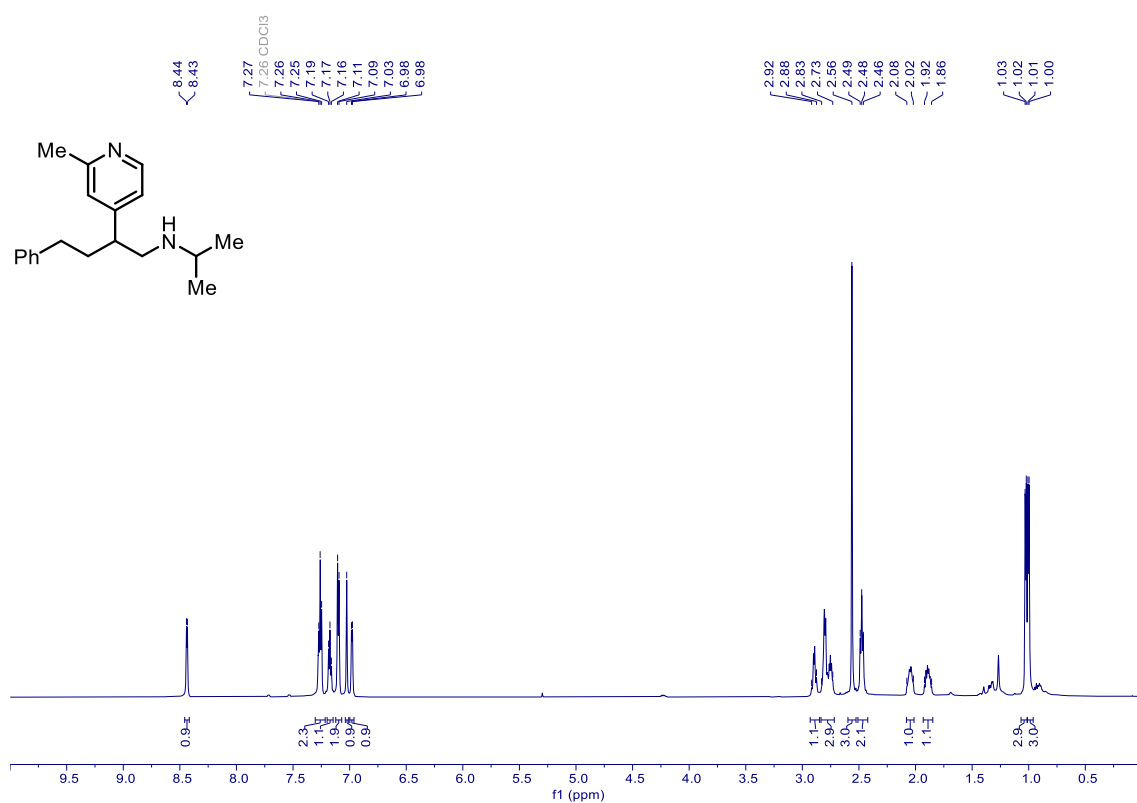
13v – ^{13}C NMR (151 MHz, CDCl_3)



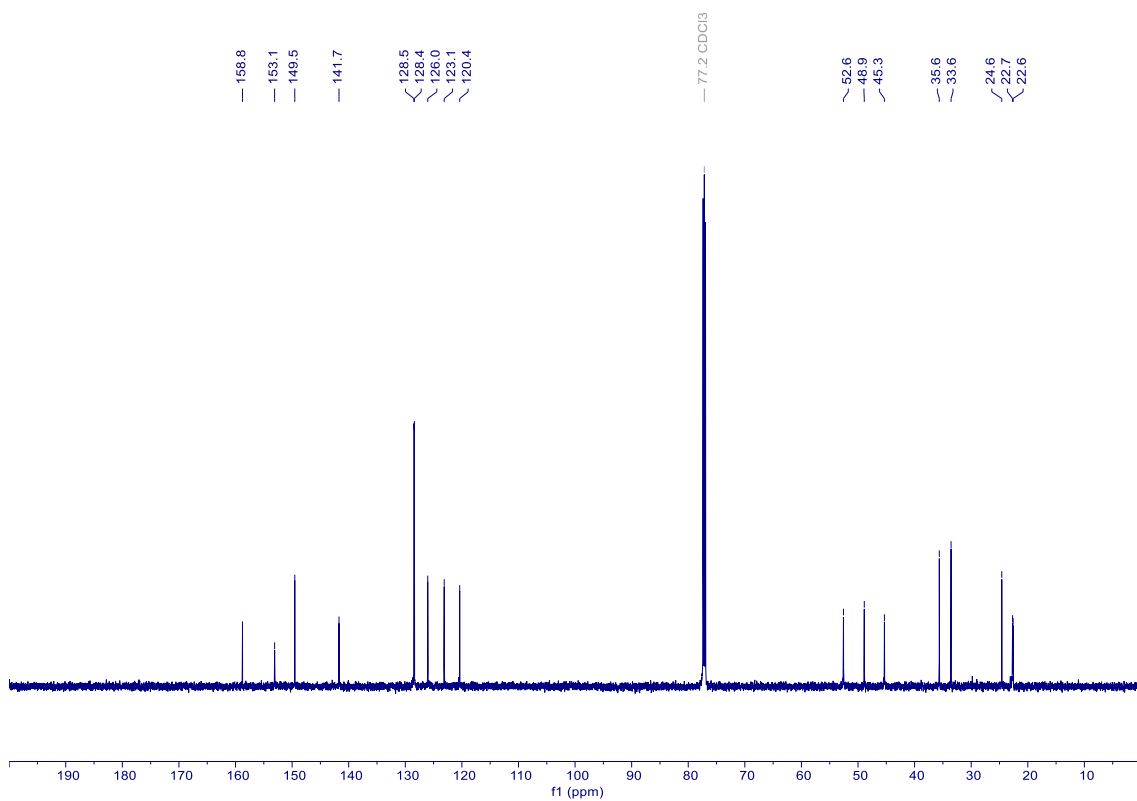
13v – ^{19}F NMR (564 MHz, CDCl_3)



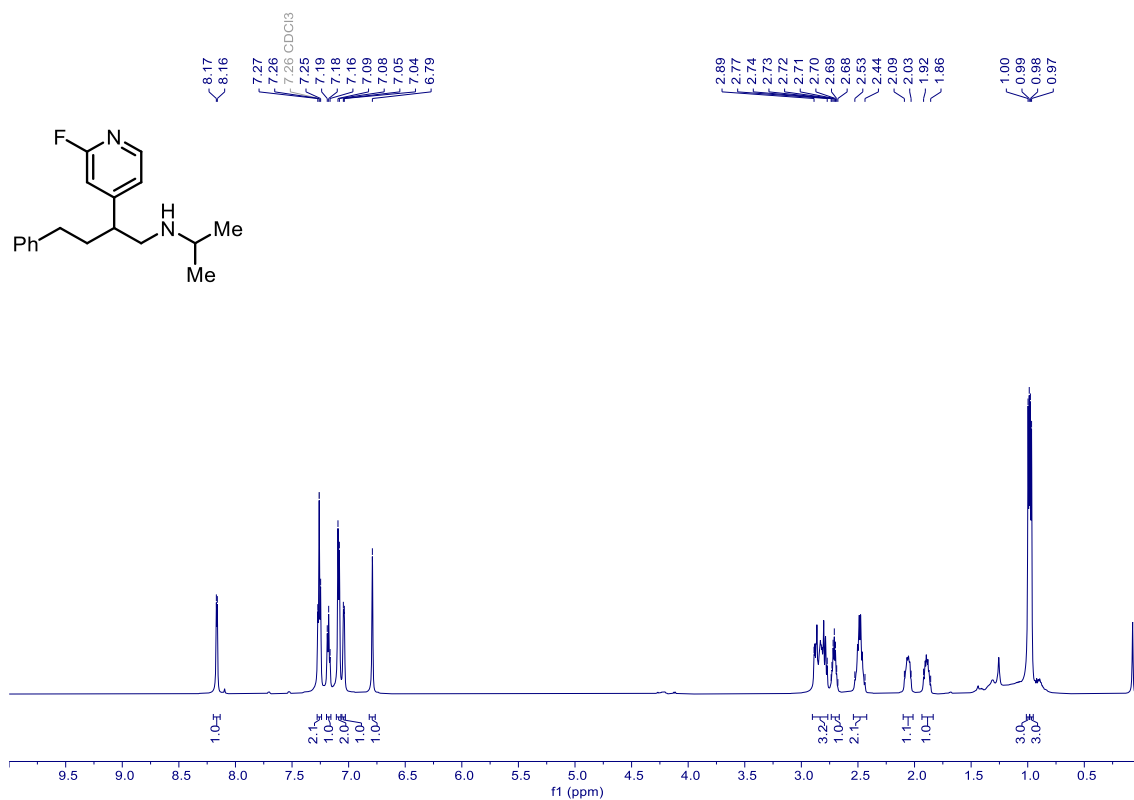
13w – ^1H NMR (600 MHz, CDCl_3)



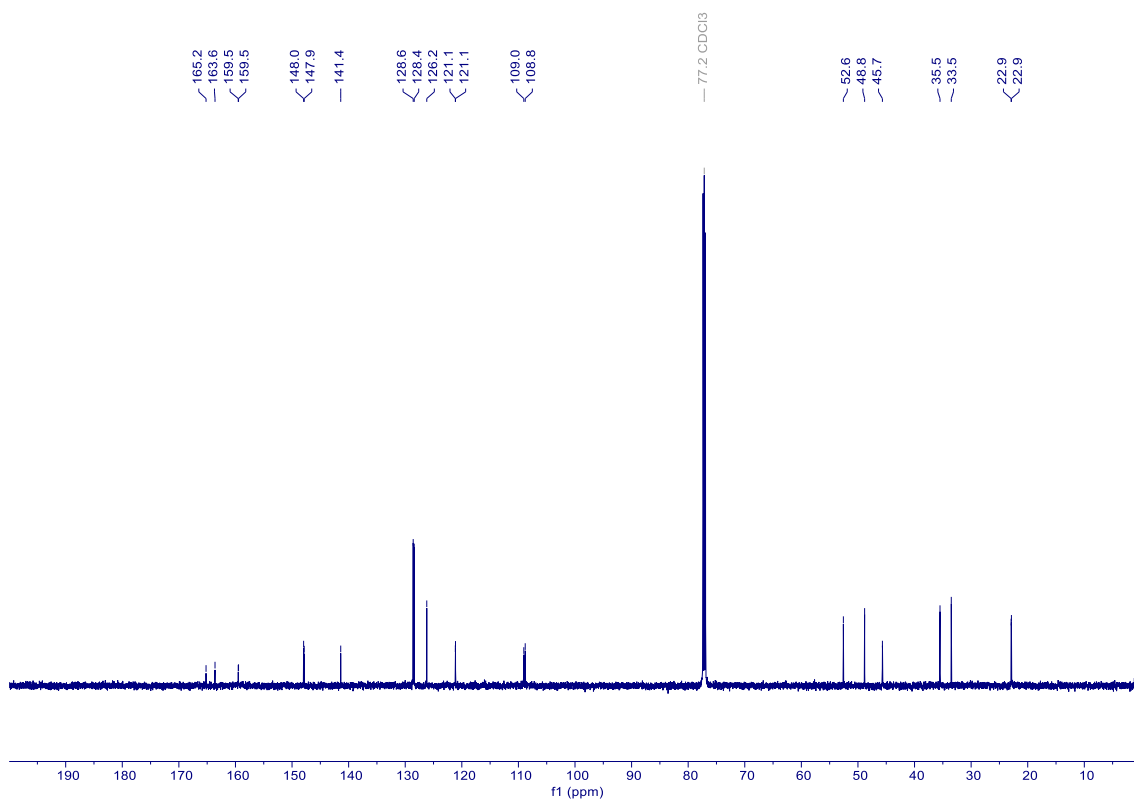
13w – ^{13}C NMR (151 MHz, CDCl_3)



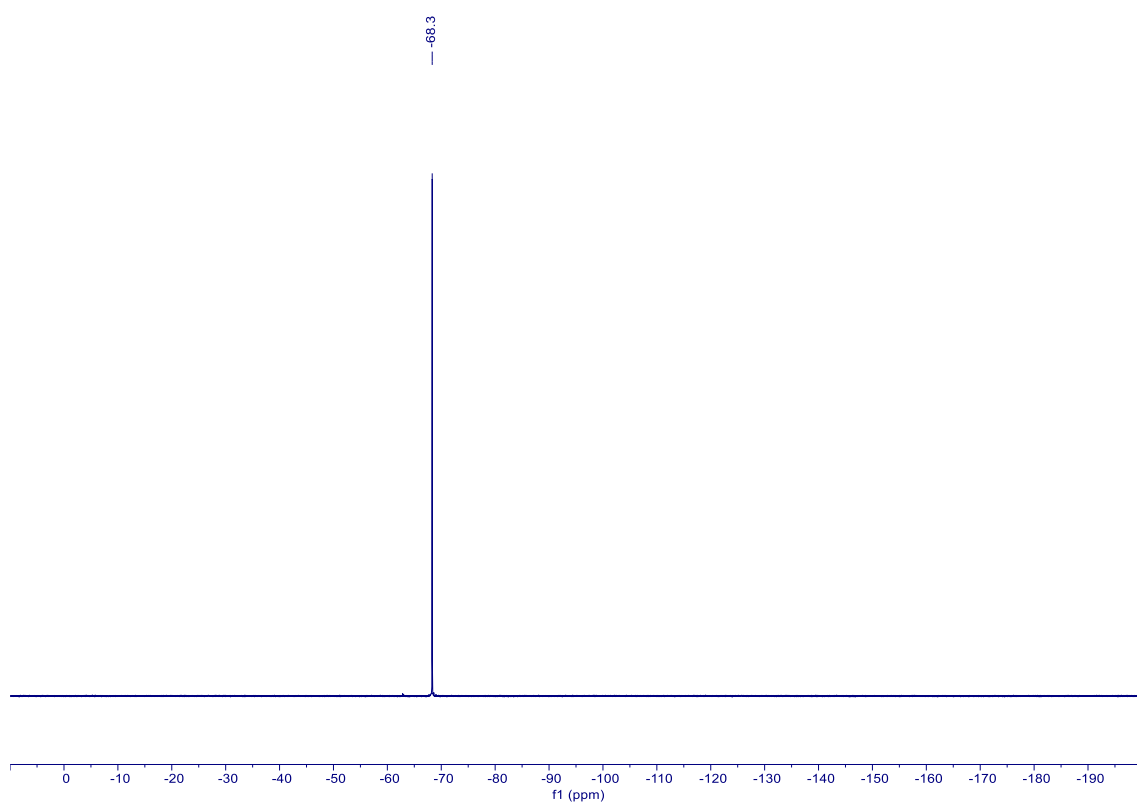
13x – ^1H NMR (600 MHz, CDCl_3)



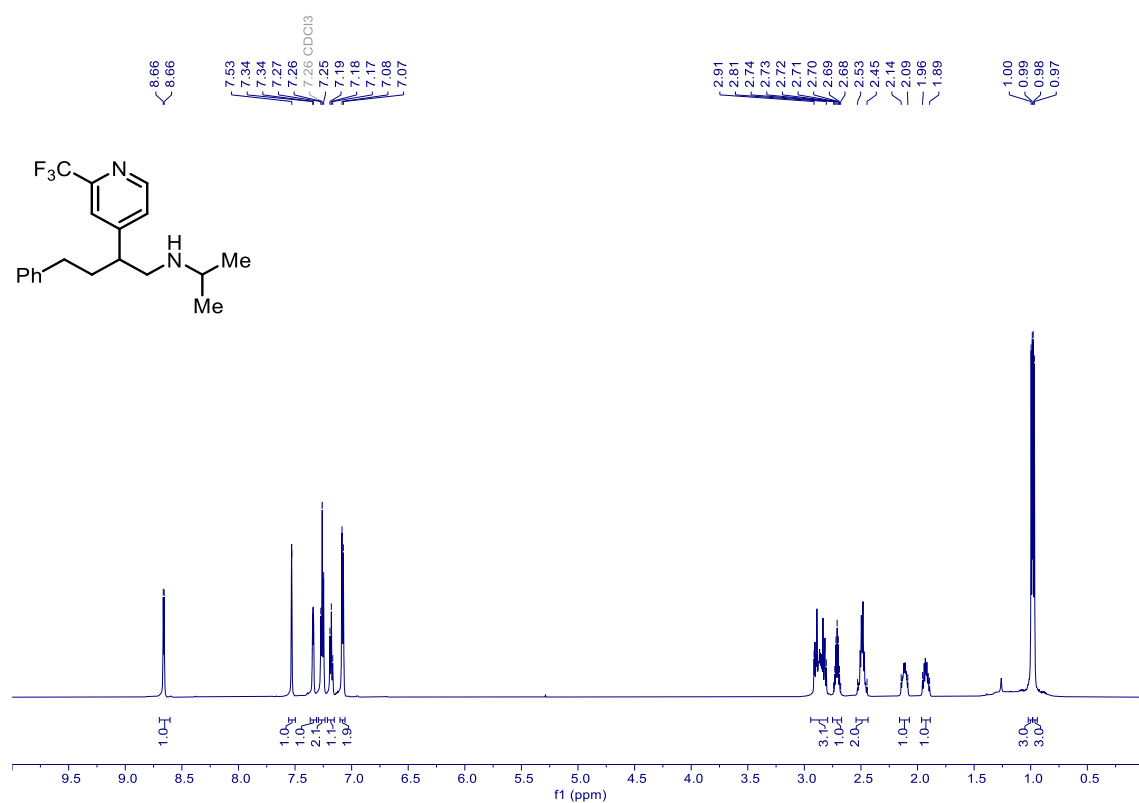
13x – ^{13}C NMR (151 MHz, CDCl_3)



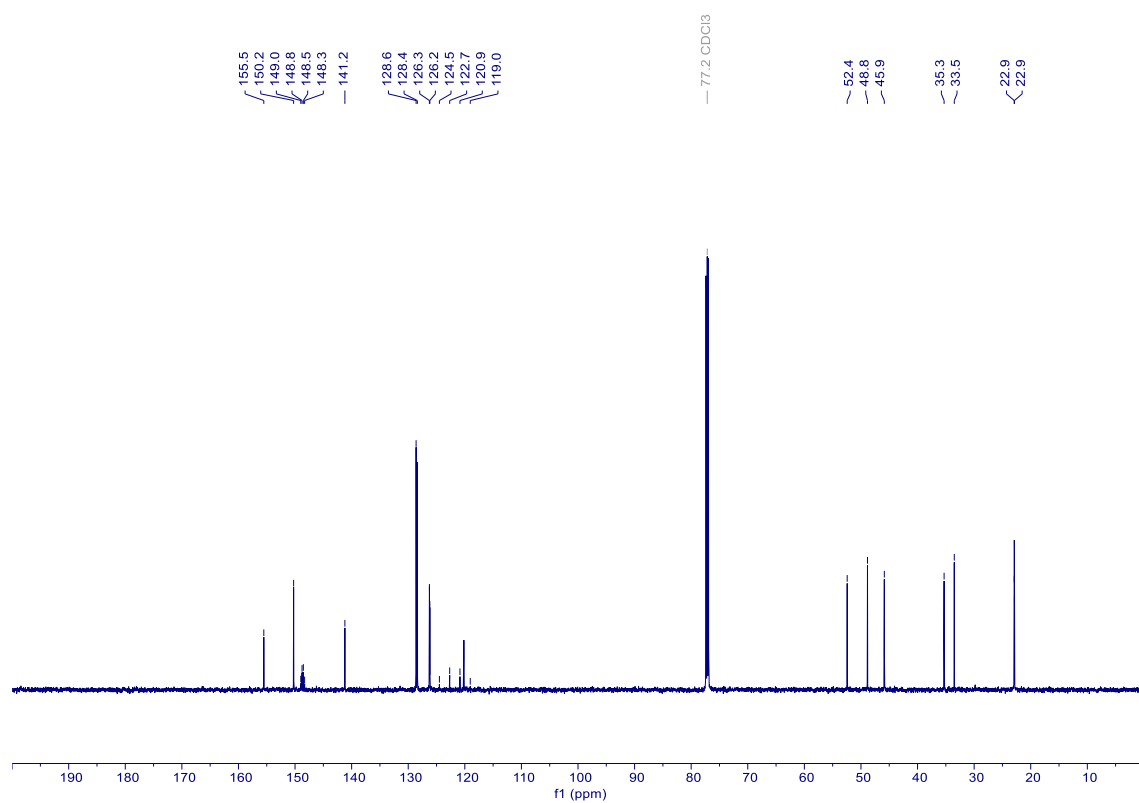
13x – ^{19}F NMR (564 MHz, CDCl_3)



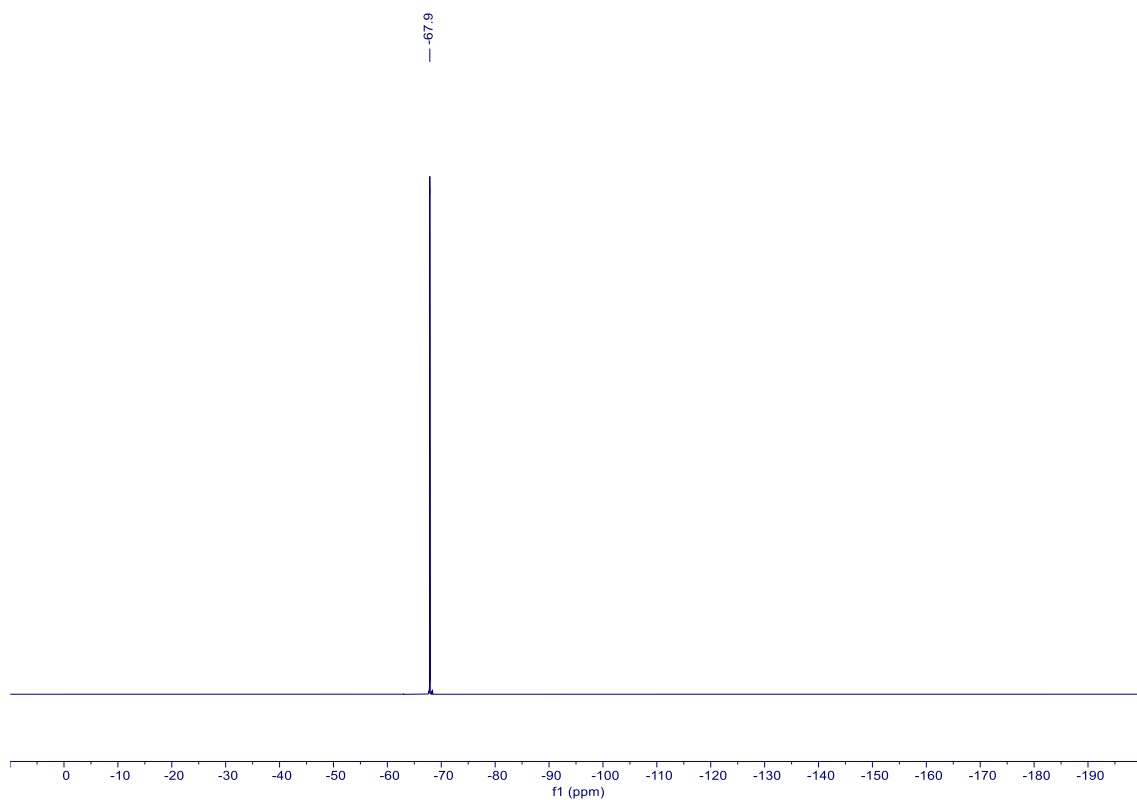
13y – ^1H NMR (600 MHz, CDCl_3)



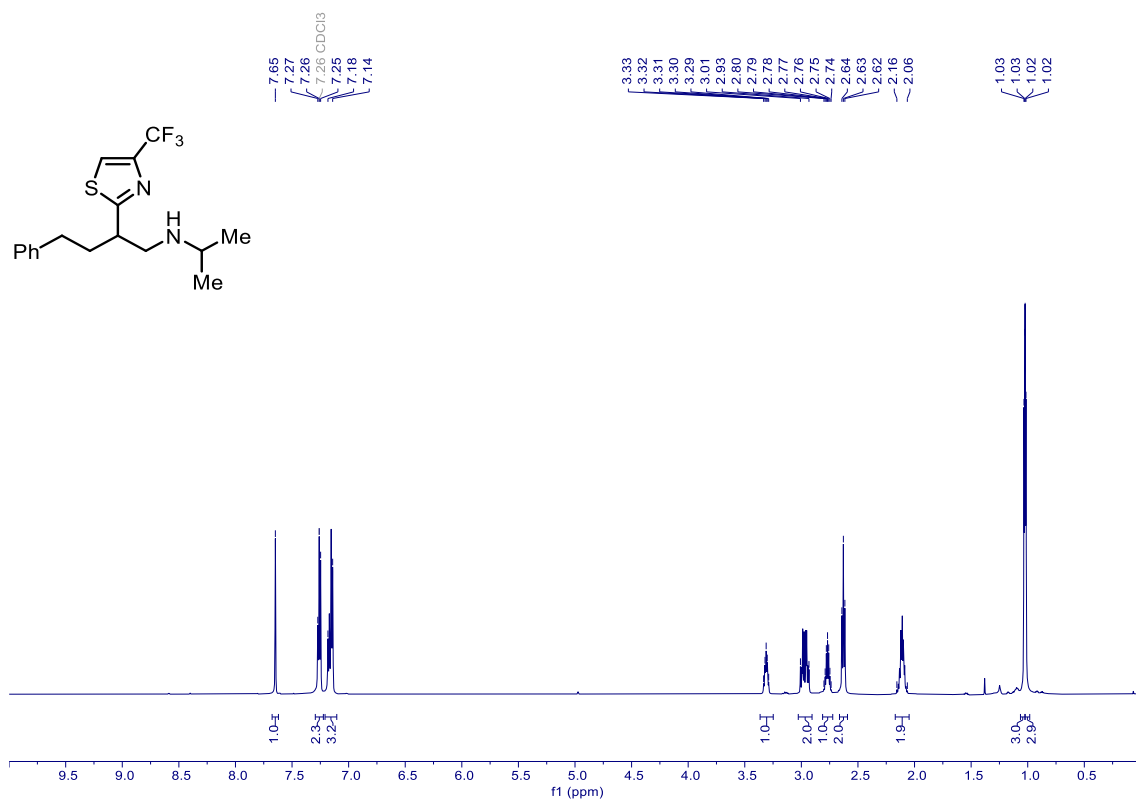
13y – ^{13}C NMR (151 MHz, CDCl_3)



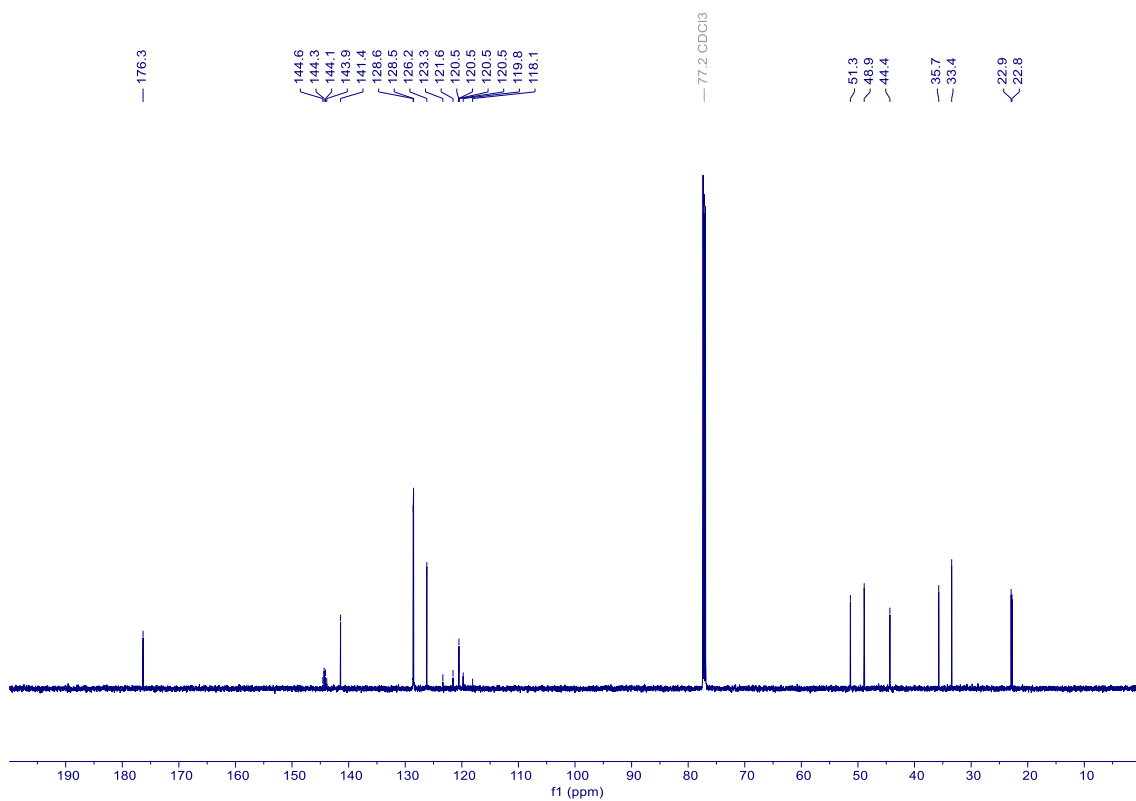
13y – ^{19}F NMR (564 MHz, CDCl_3)



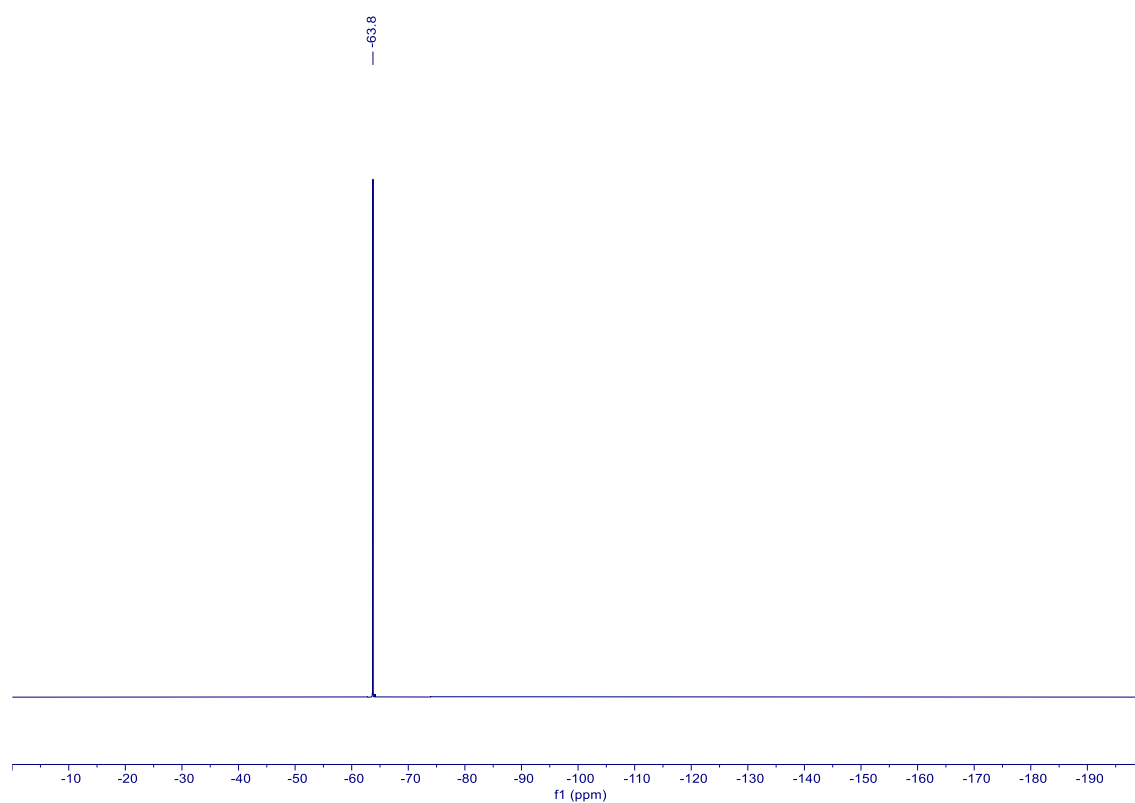
13z – ^1H NMR (600 MHz, CDCl_3)



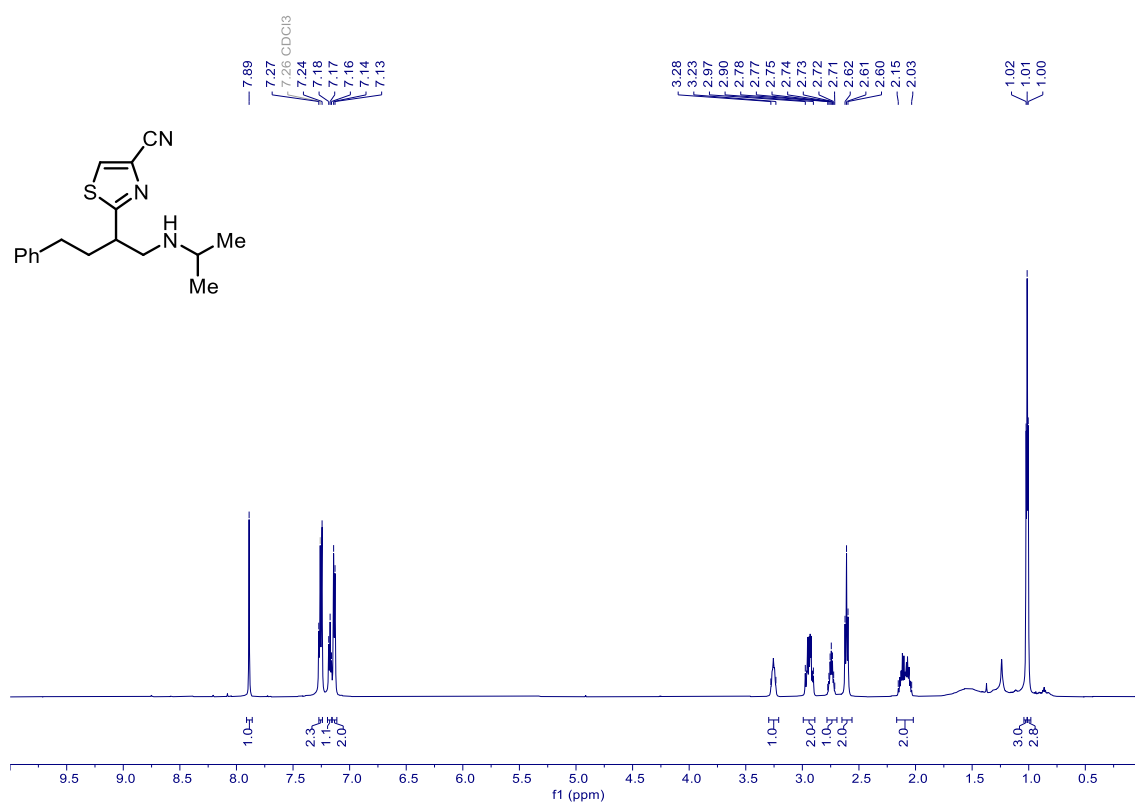
13z – ^{13}C NMR (151 MHz, CDCl_3)



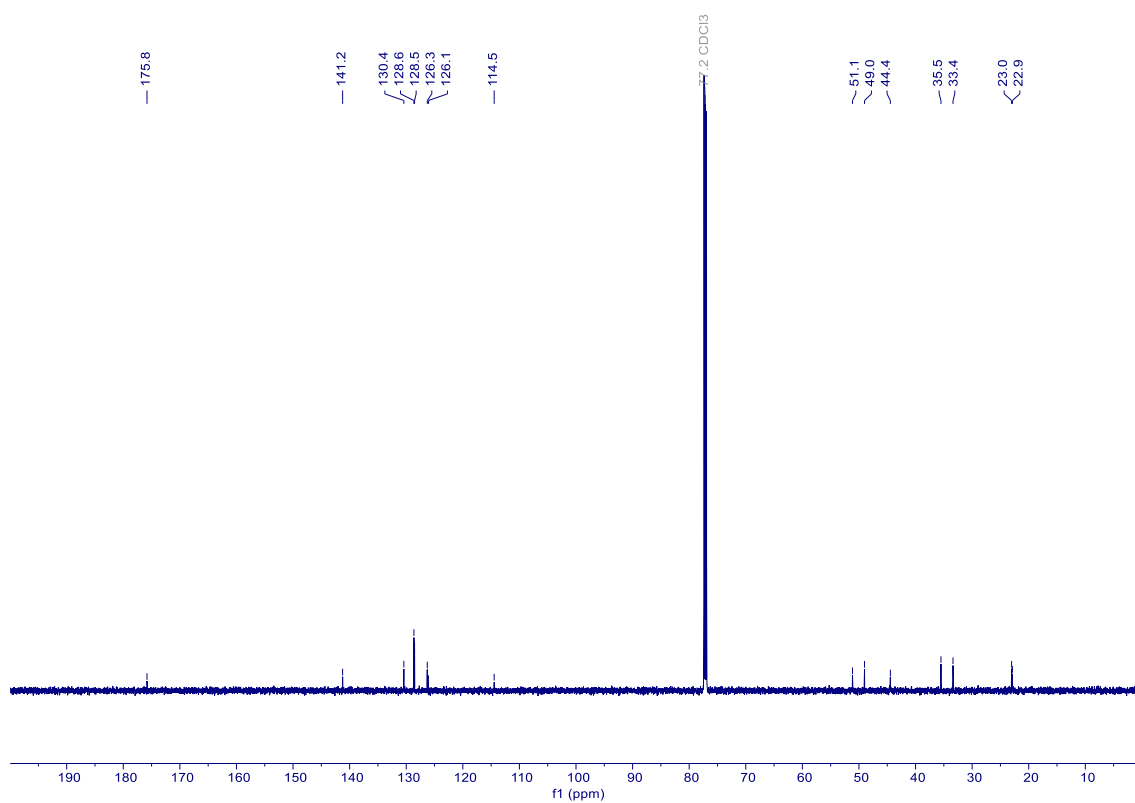
13z – ^{19}F NMR (564 MHz, CDCl_3)



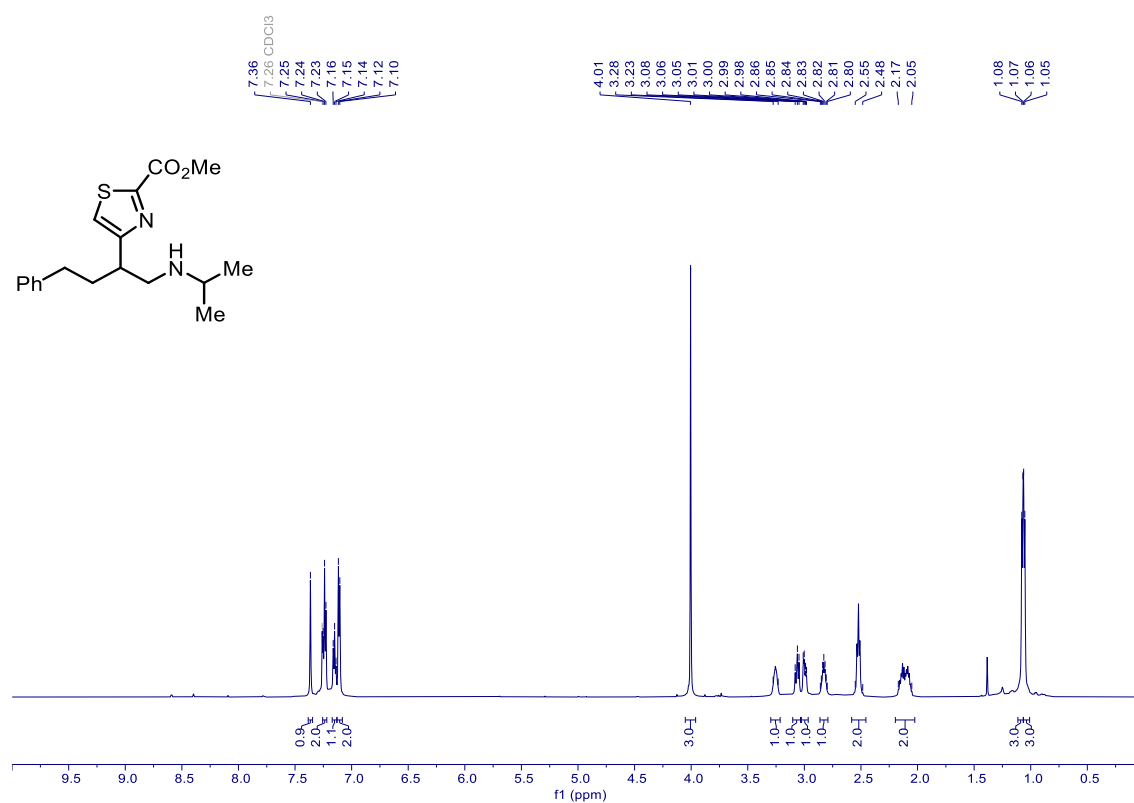
13ab – ^1H NMR (600 MHz, CDCl_3)



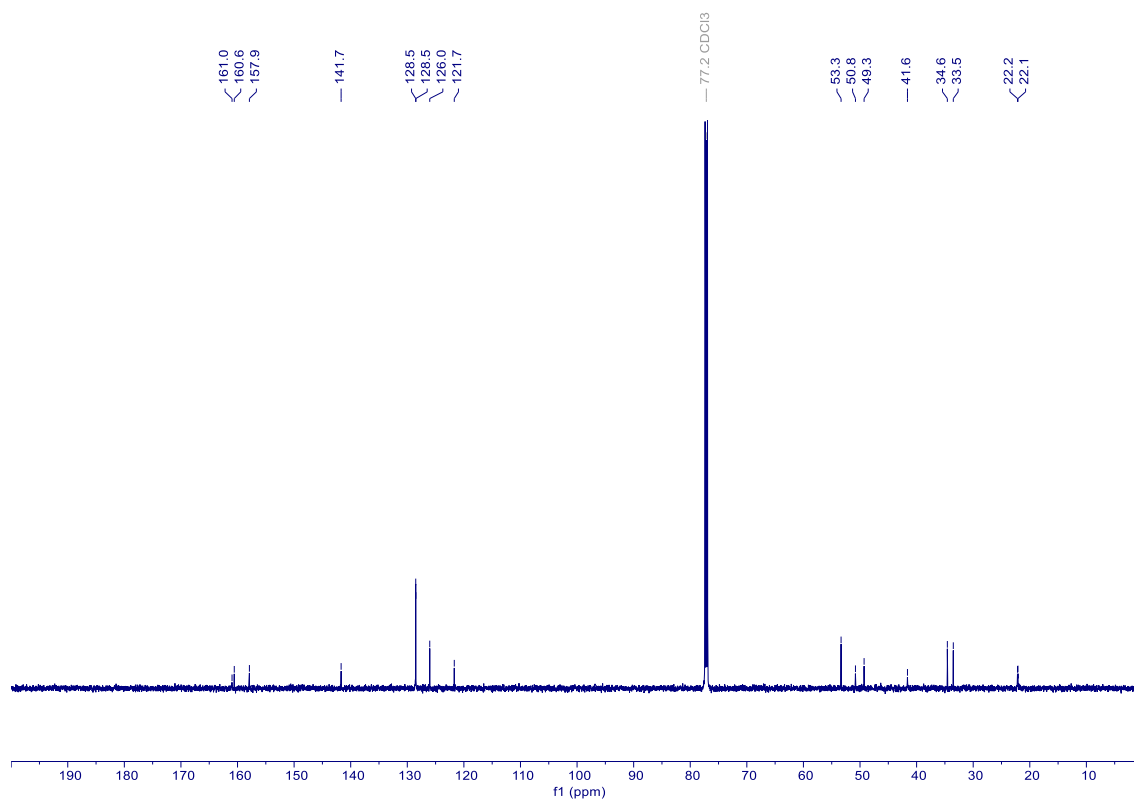
13ab – ^{13}C NMR (151 MHz, CDCl_3)



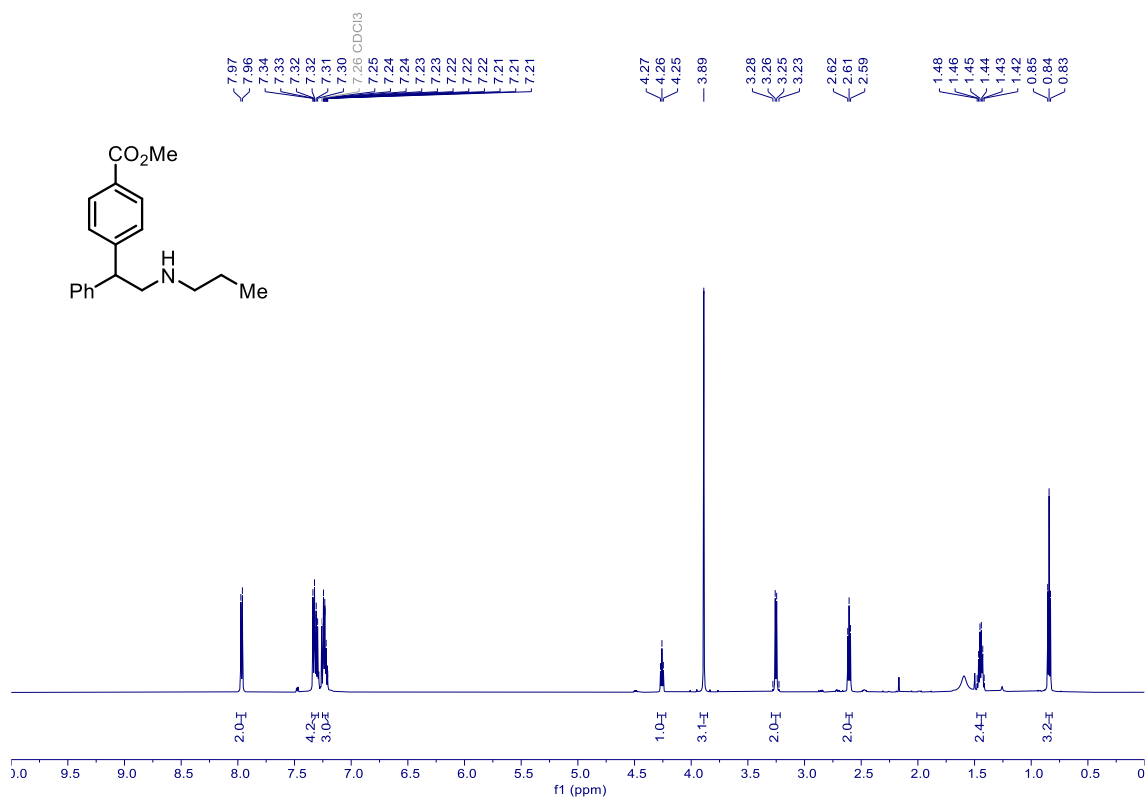
13ac – ^1H NMR (600 MHz, CDCl_3)



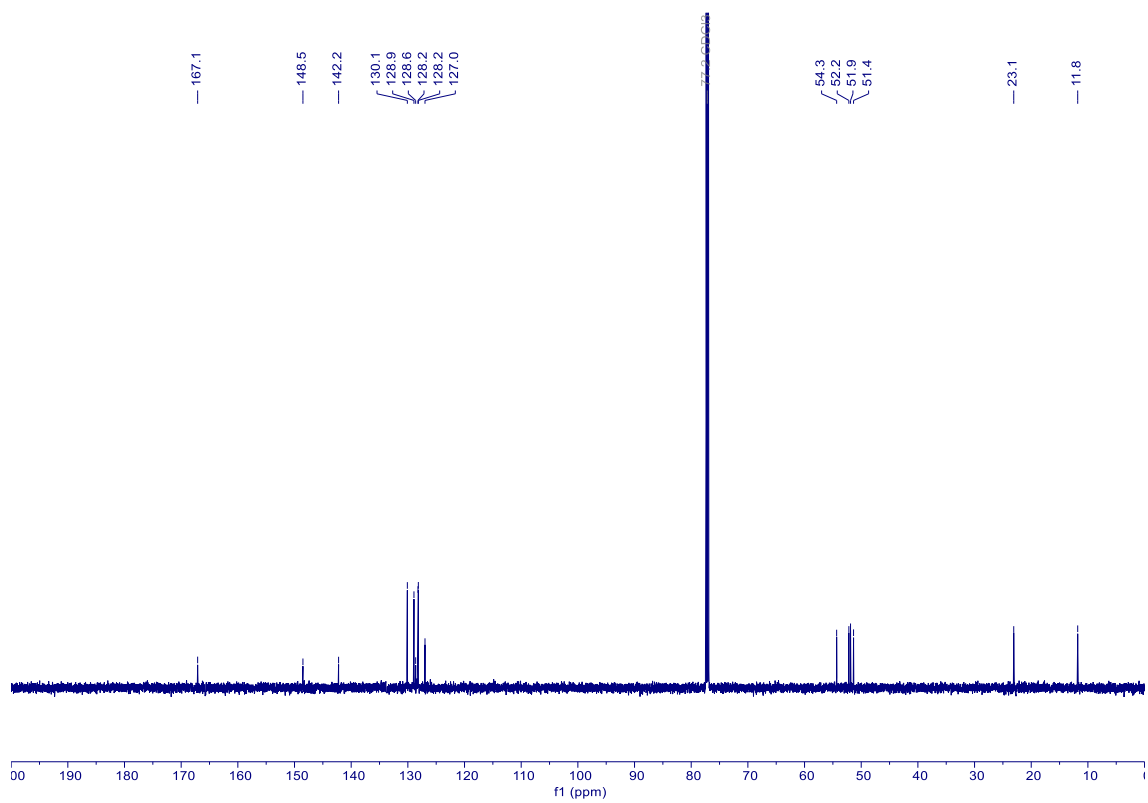
13ac – ^{13}C NMR (151 MHz, CDCl_3)



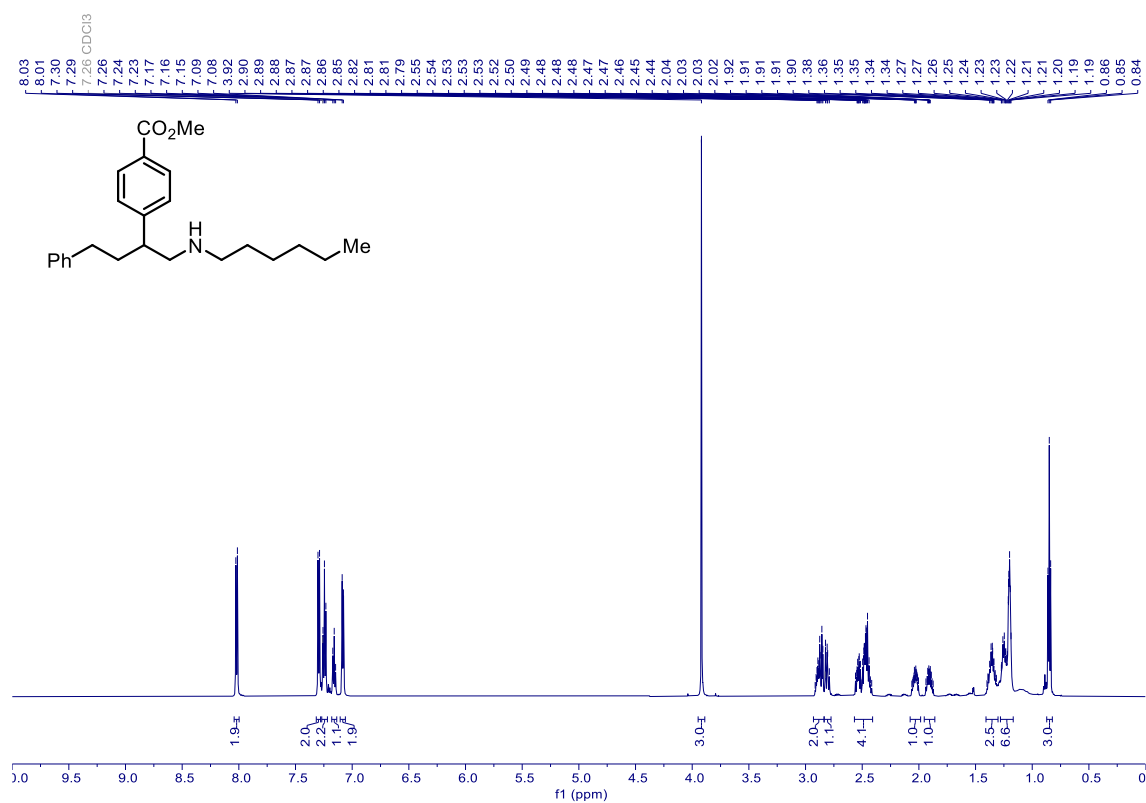
1t – ^1H NMR (600 MHz, CDCl_3)



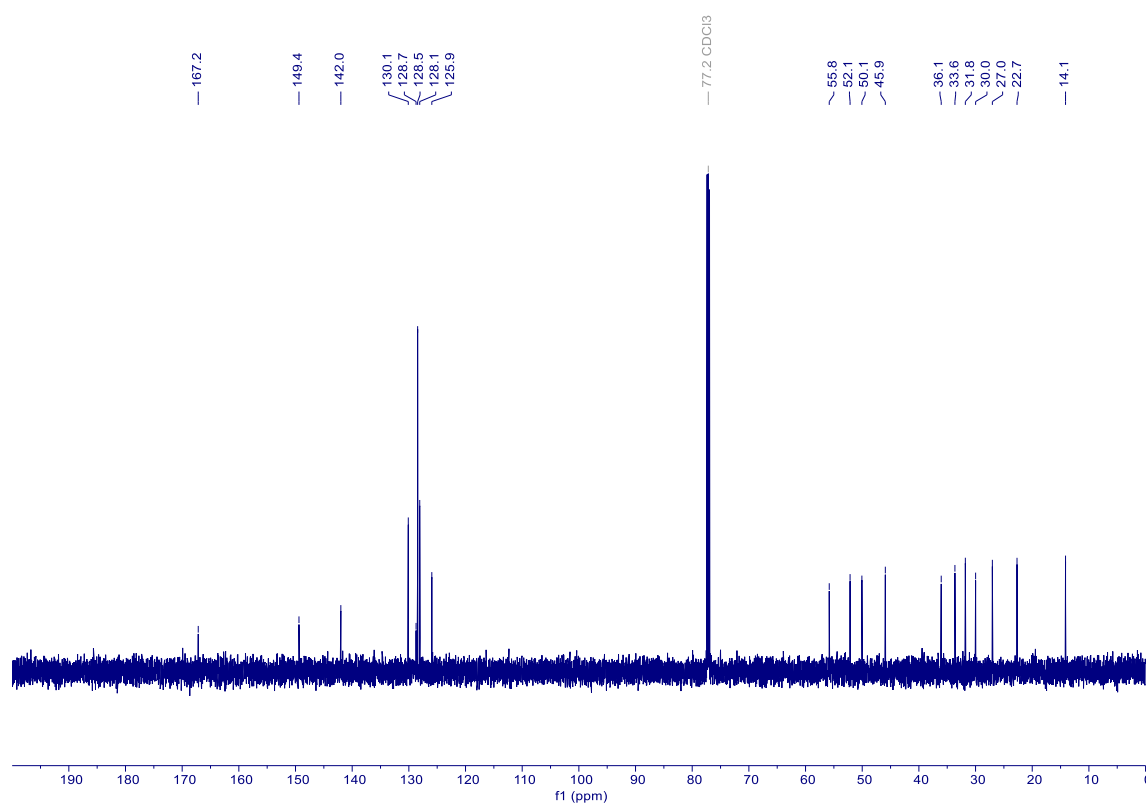
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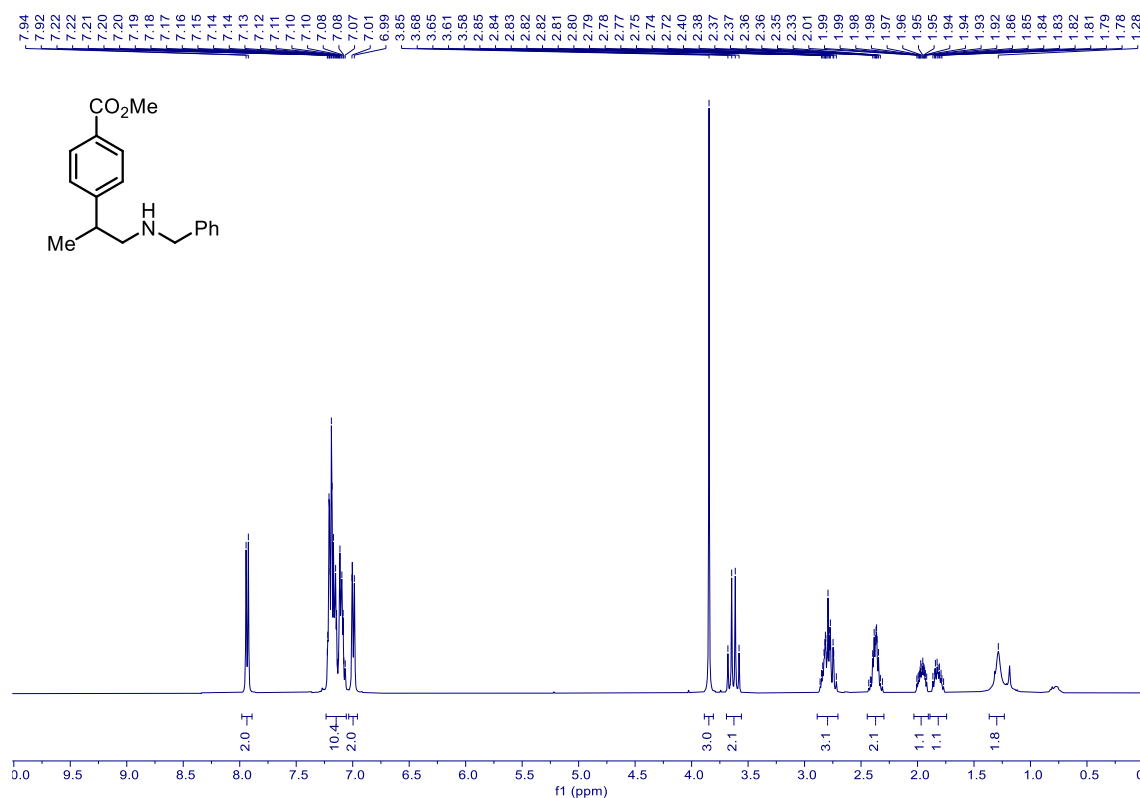
27c – ^1H NMR (600 MHz, CDCl_3)



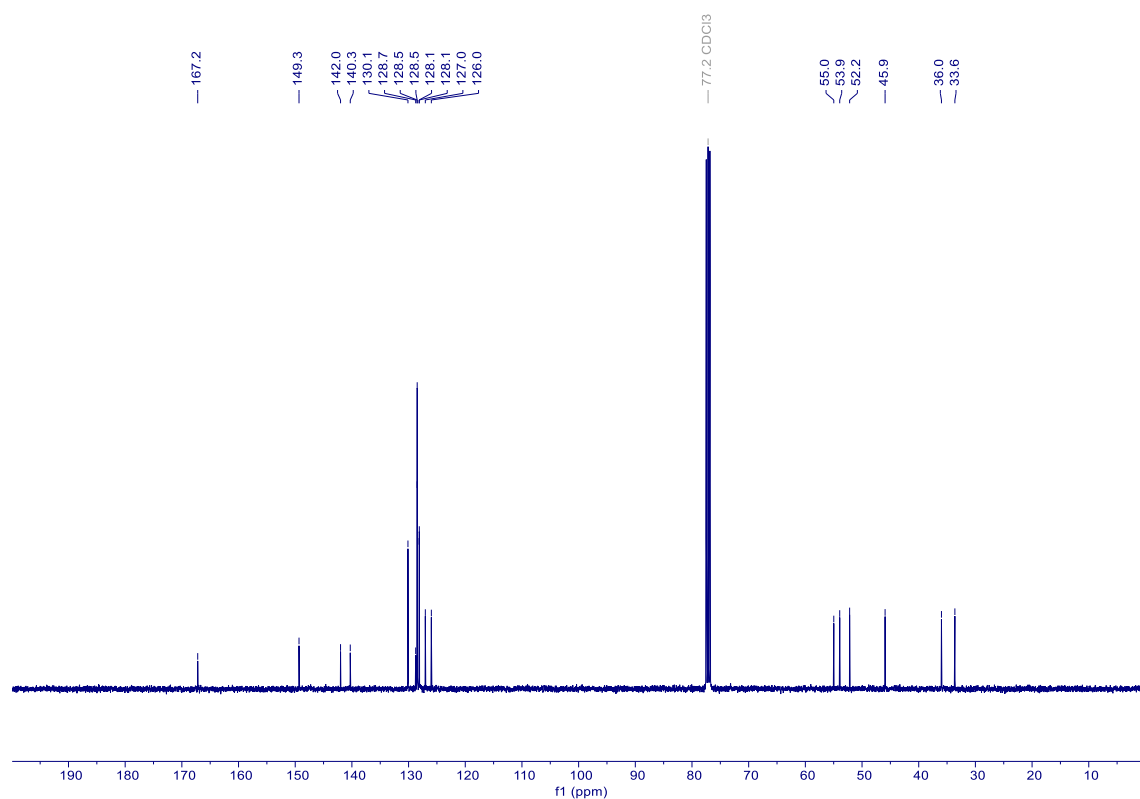
27c – ^{13}C NMR (151 MHz, CDCl_3)



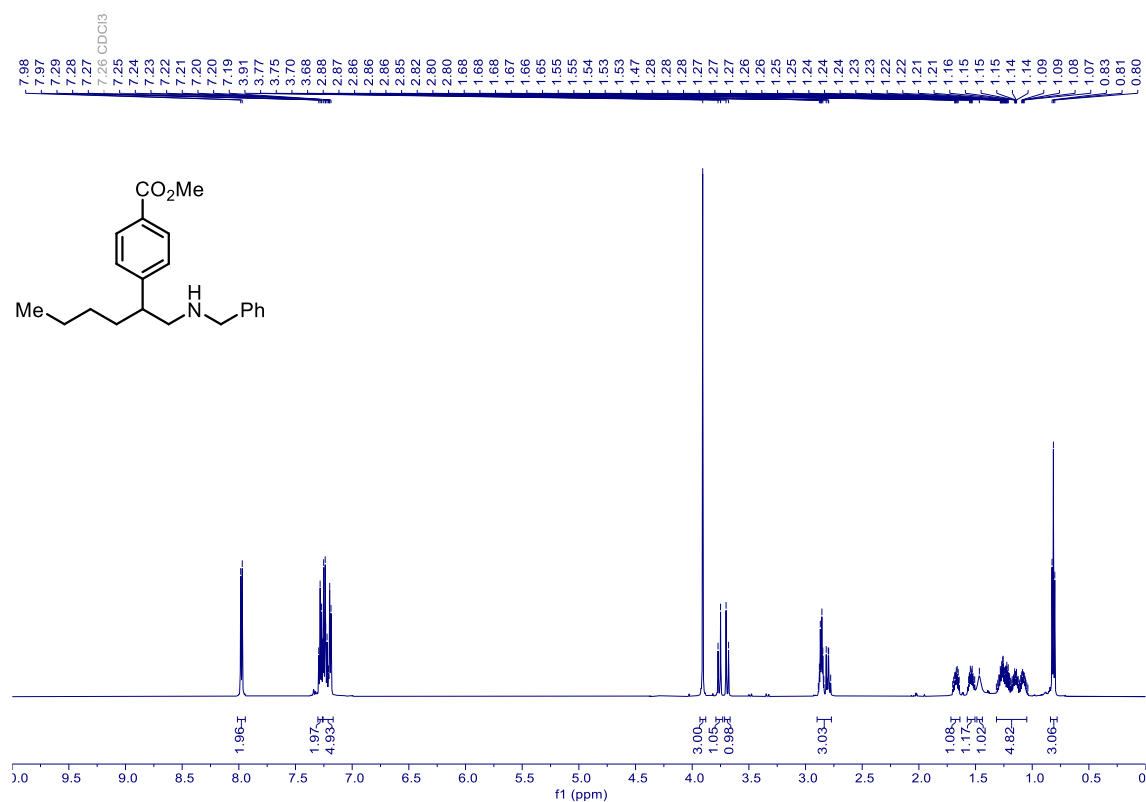
28c – ^1H NMR (600 MHz, CDCl_3)



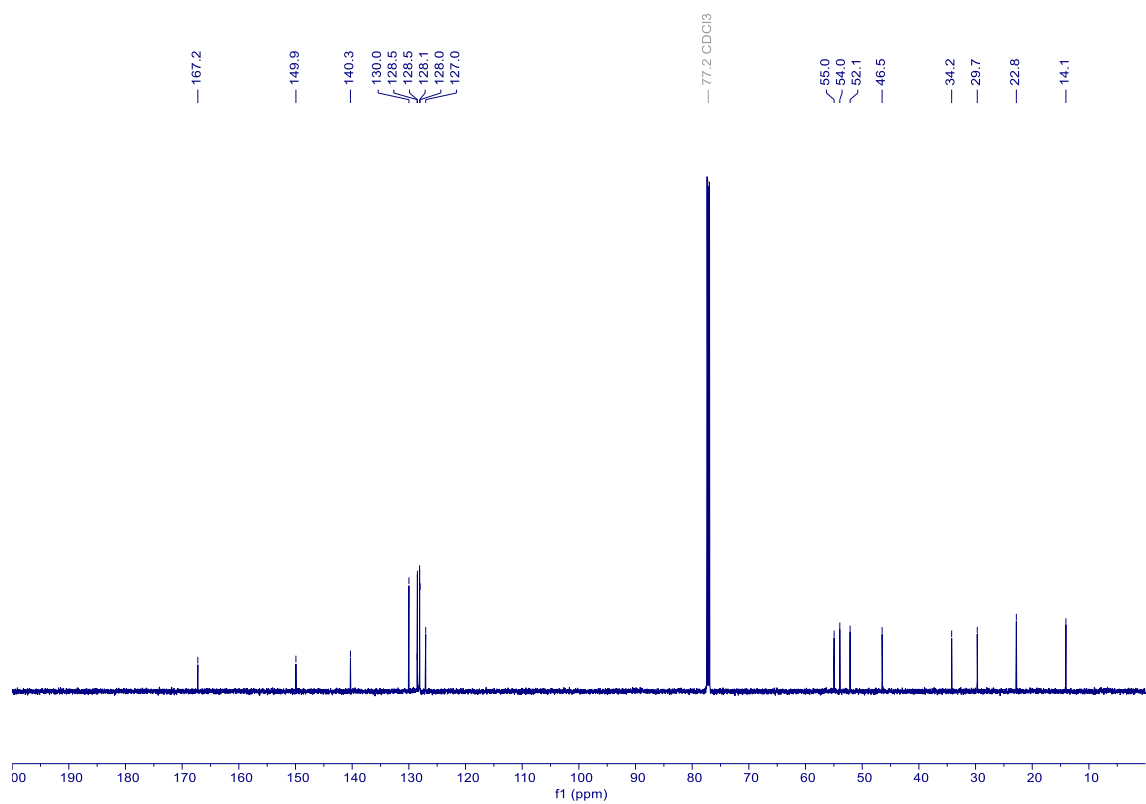
28c – ^{13}C NMR (151 MHz, CDCl_3)



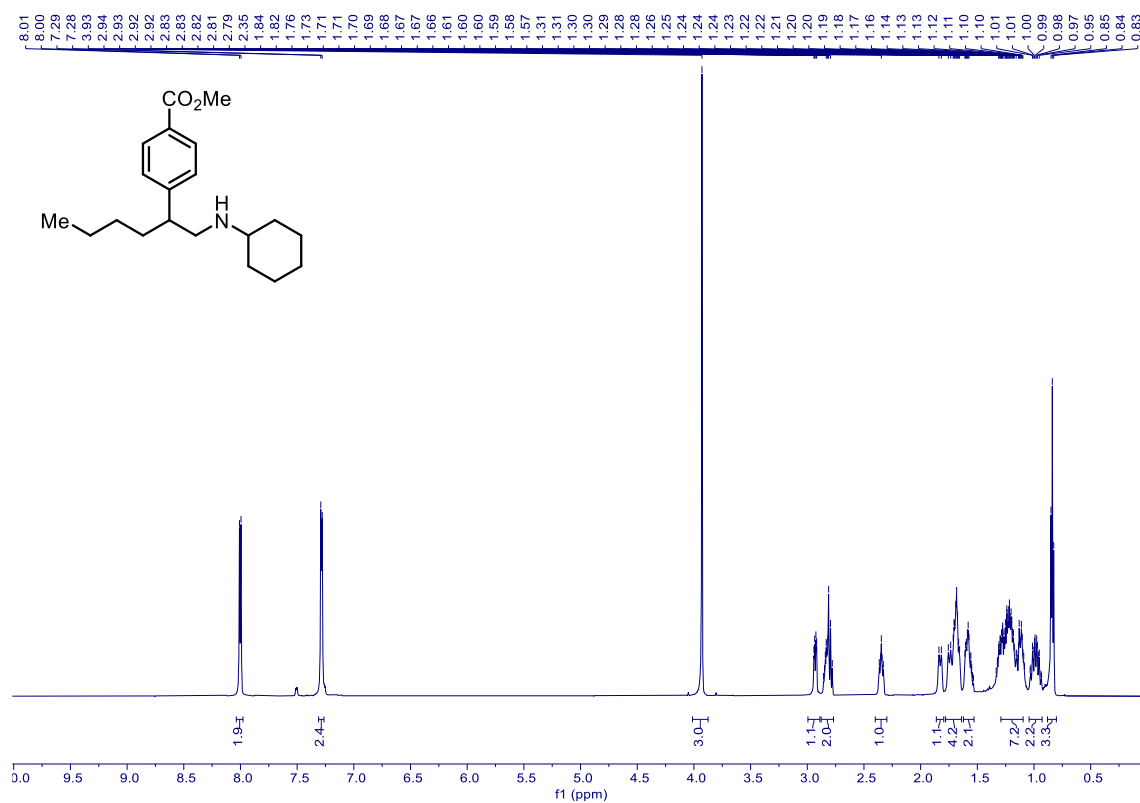
29c – ^1H NMR (600 MHz, CDCl_3)



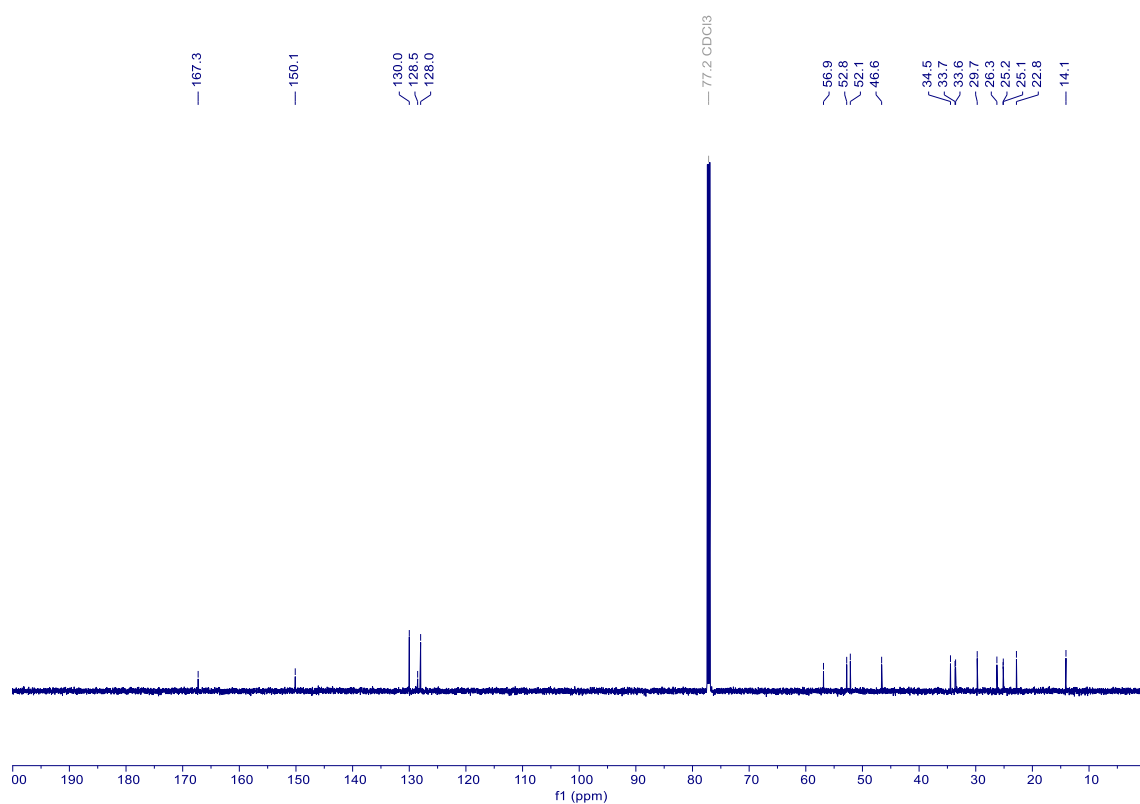
29c – ^{13}C NMR (151 MHz, CDCl_3)



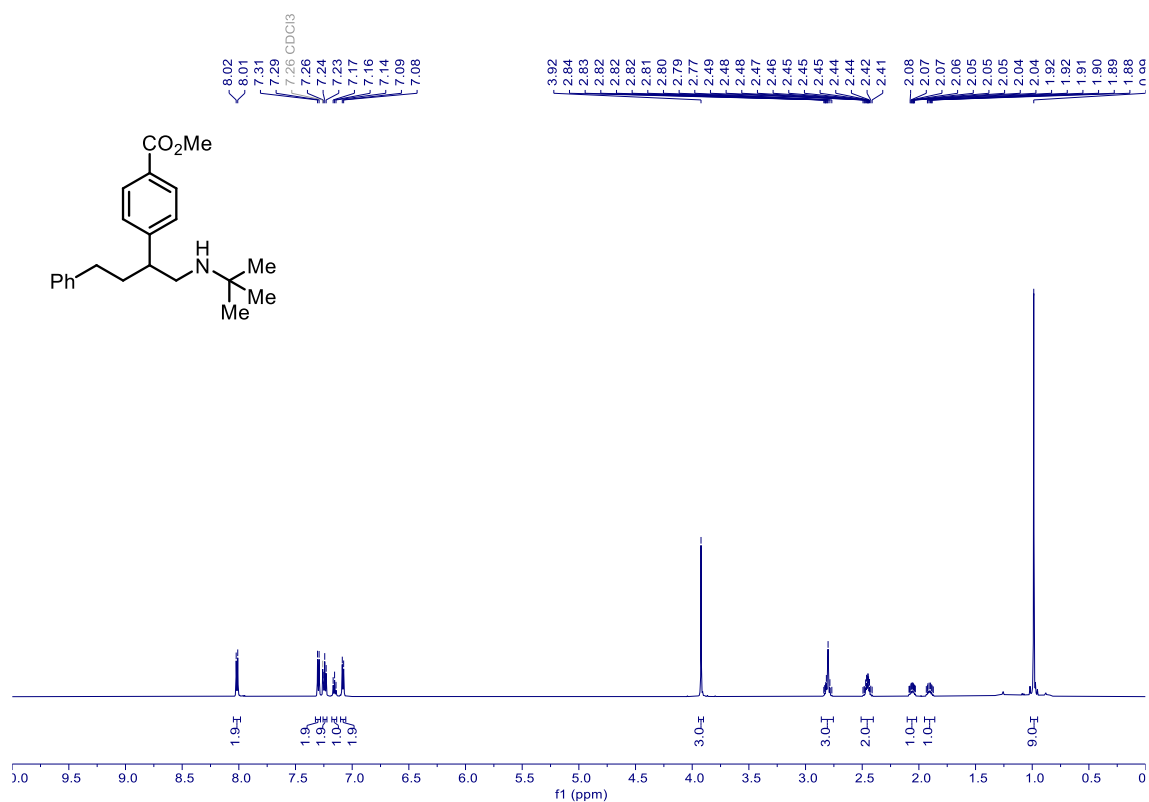
38b – ^1H NMR (600 MHz, CDCl_3)



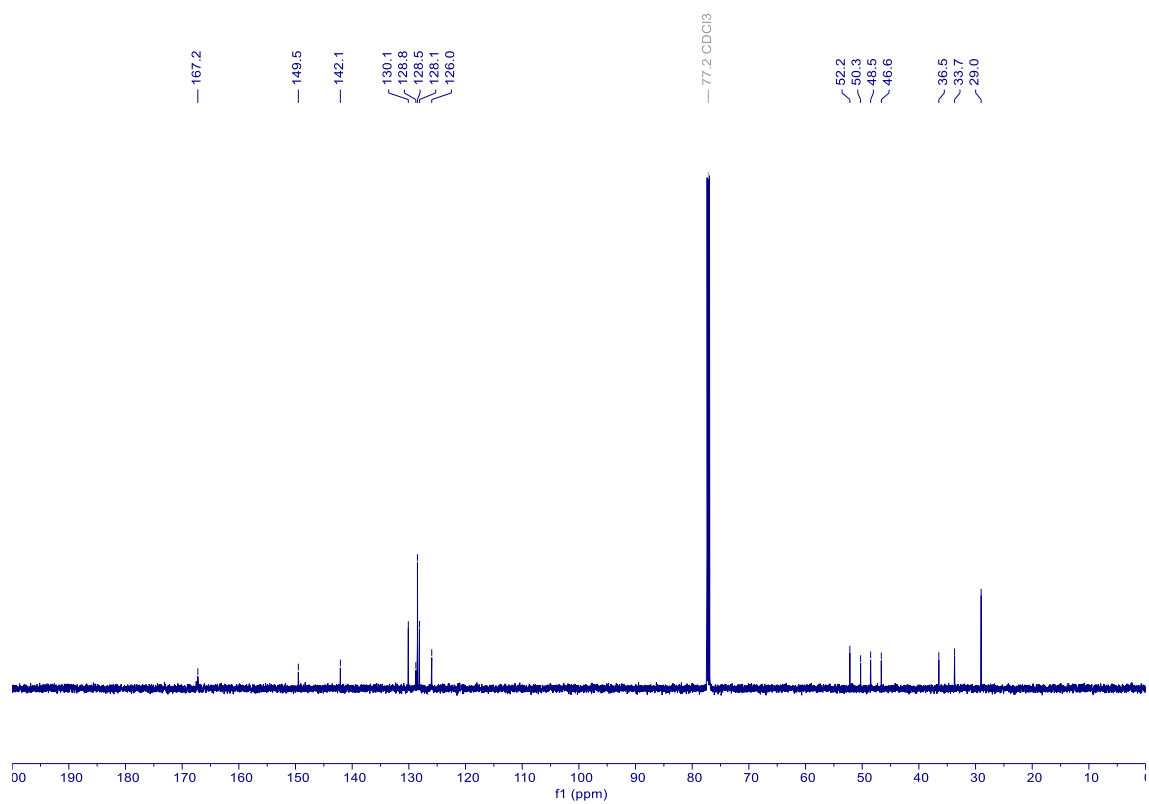
38b – ^{13}C NMR (151 MHz, CDCl_3)



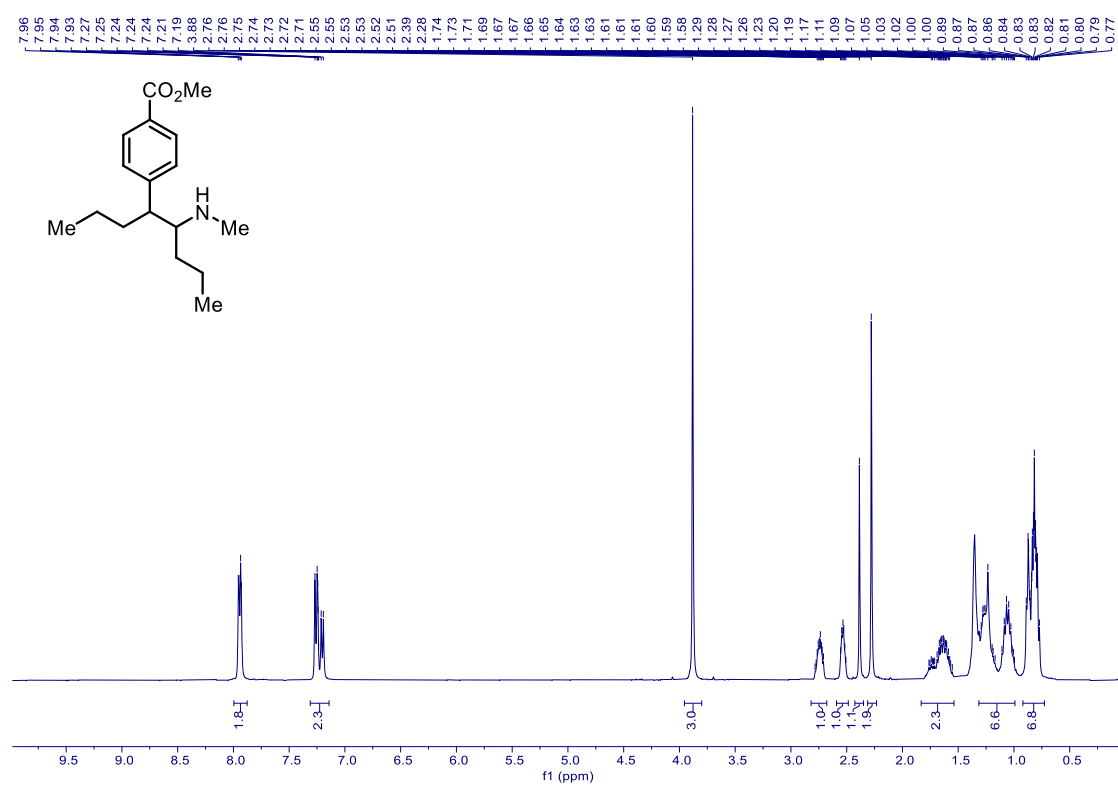
39b – ^1H NMR (600 MHz, CDCl_3)



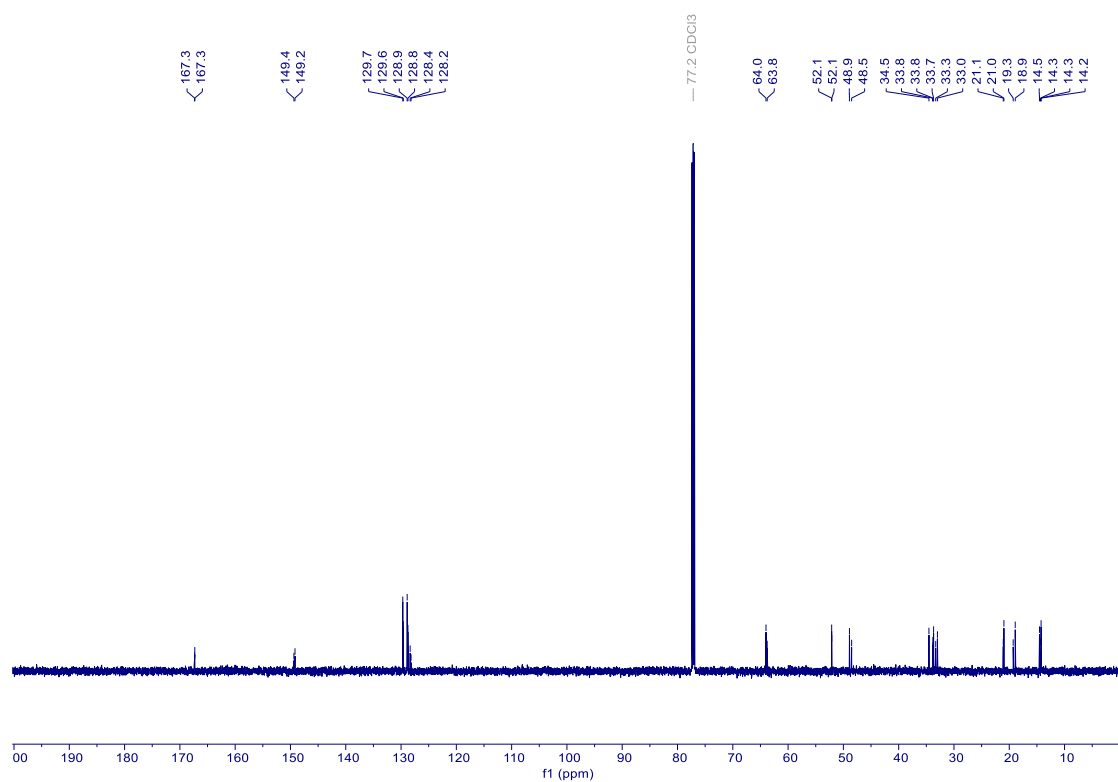
39b – ^{13}C NMR (151 MHz, CDCl_3)



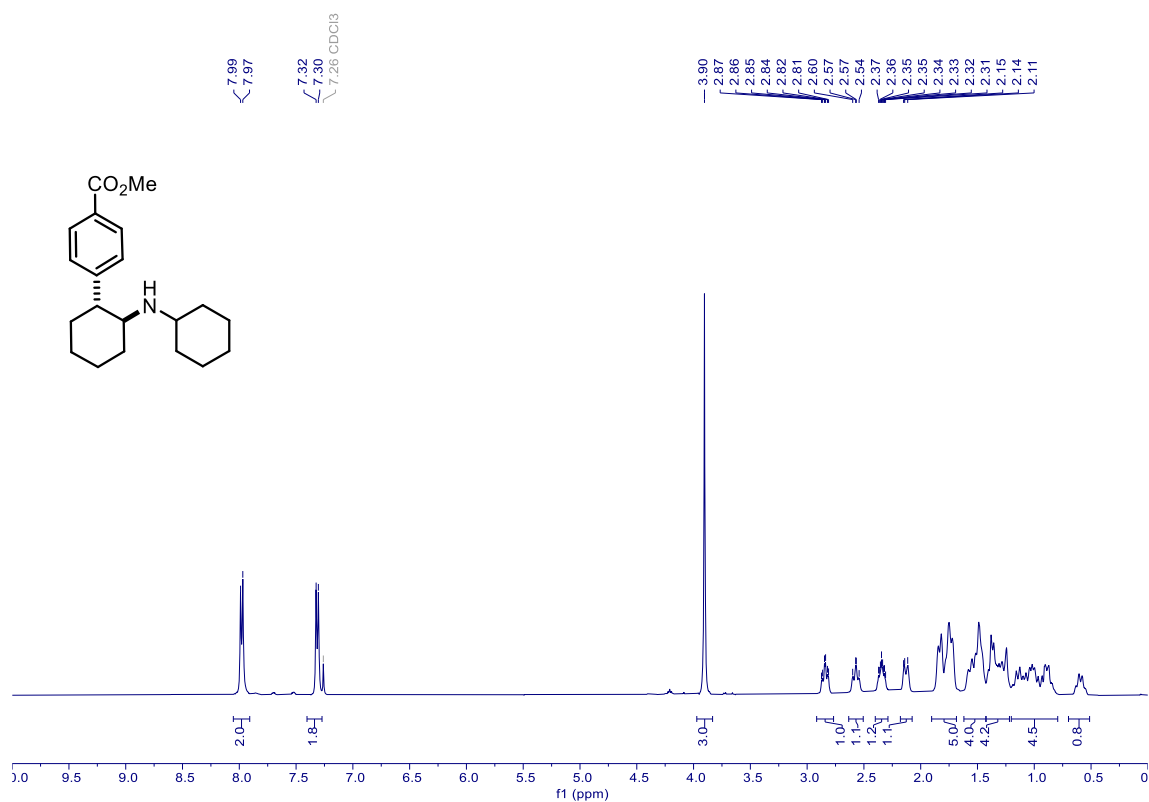
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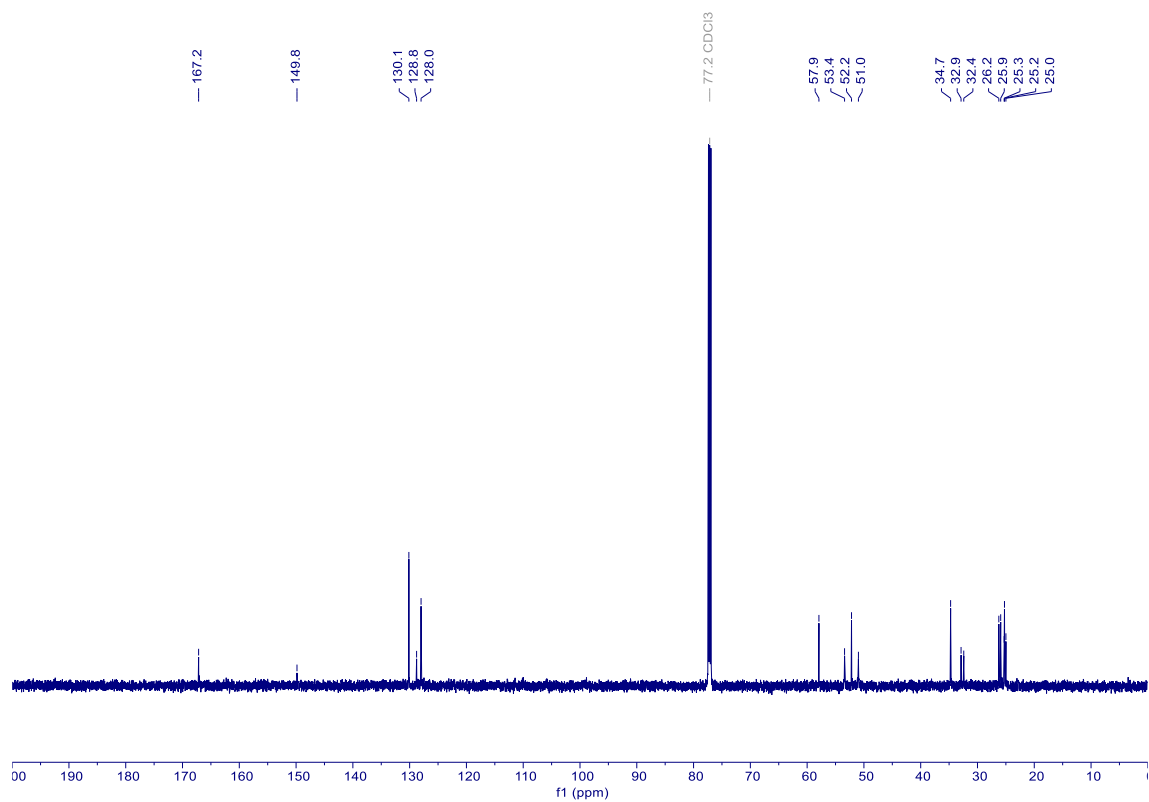
31d – ^{13}C NMR (151 MHz, CDCl_3)



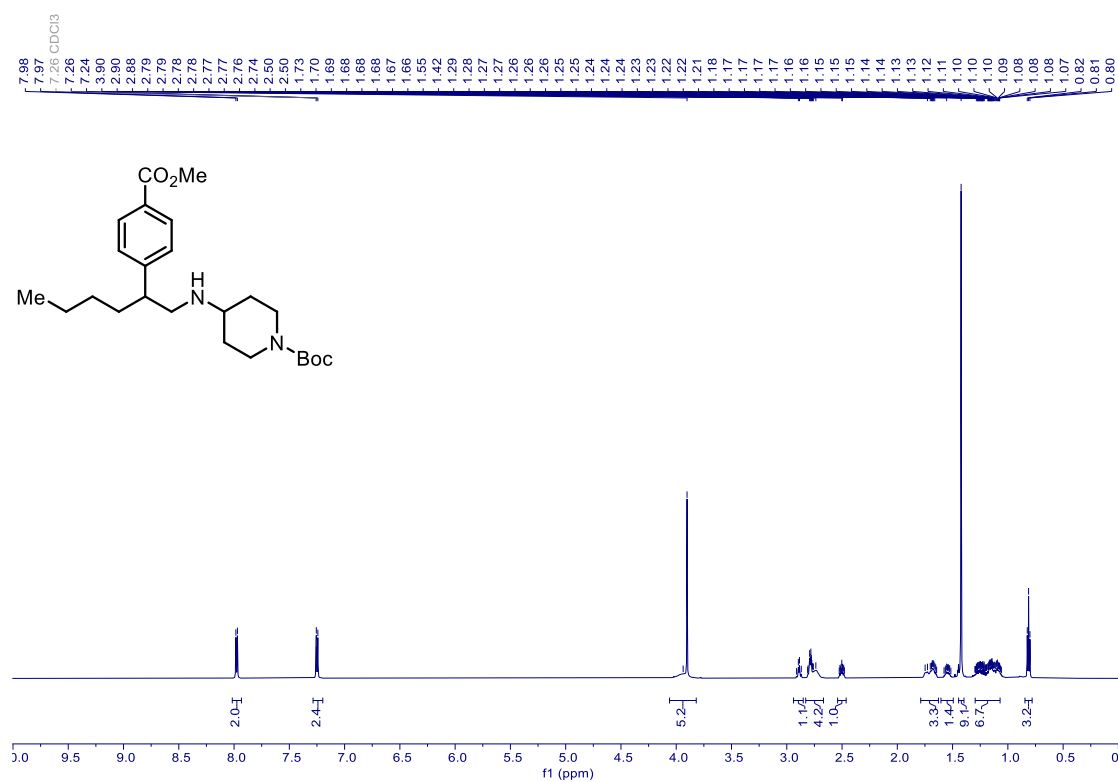
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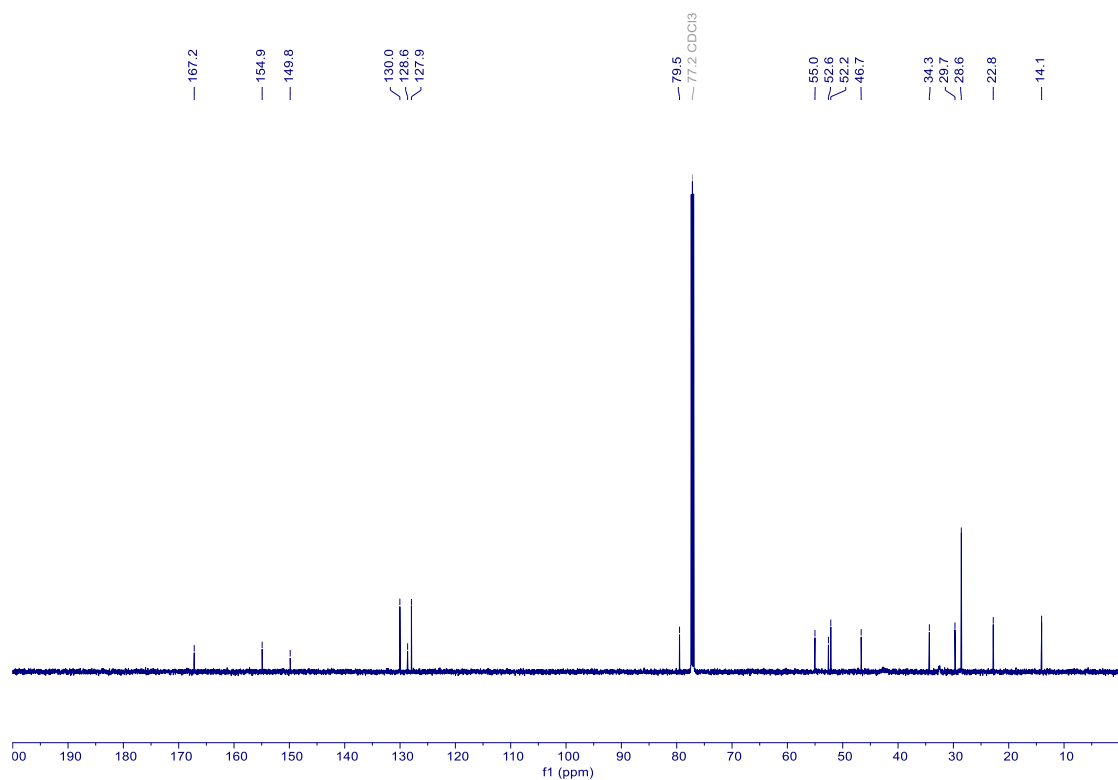
33d – ^{13}C NMR (151 MHz, CDCl_3)



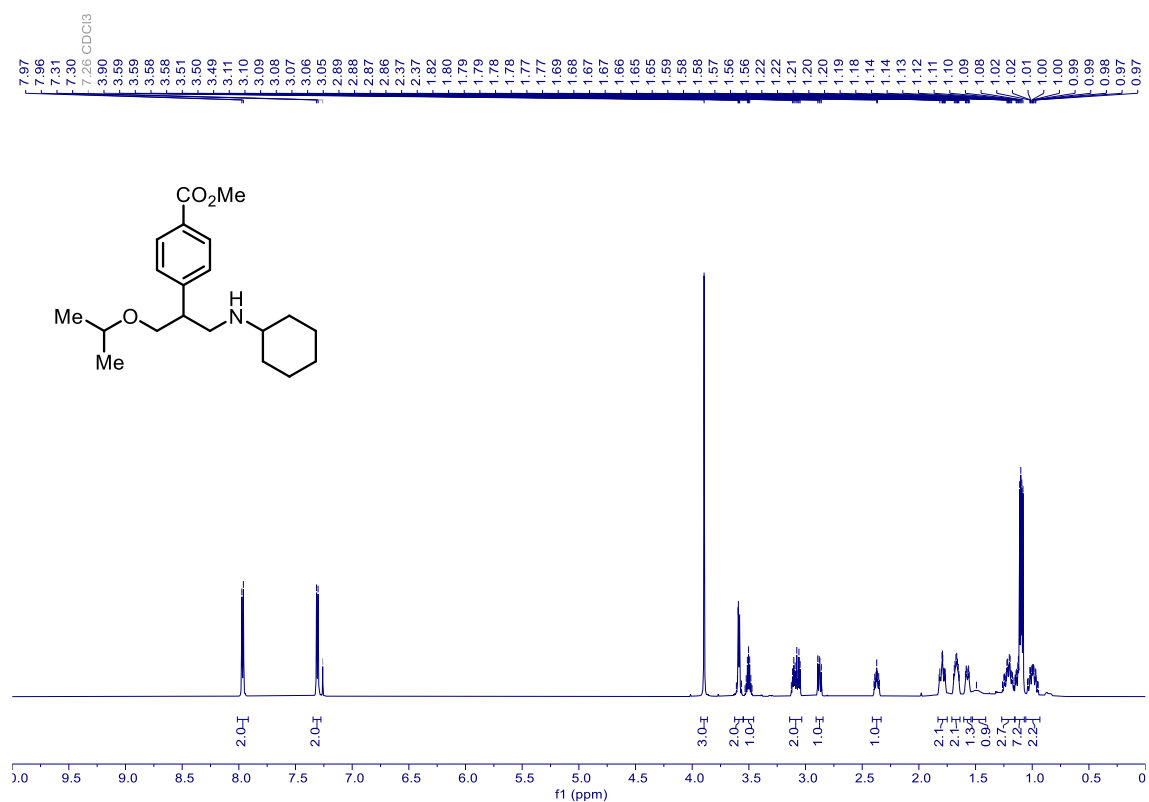
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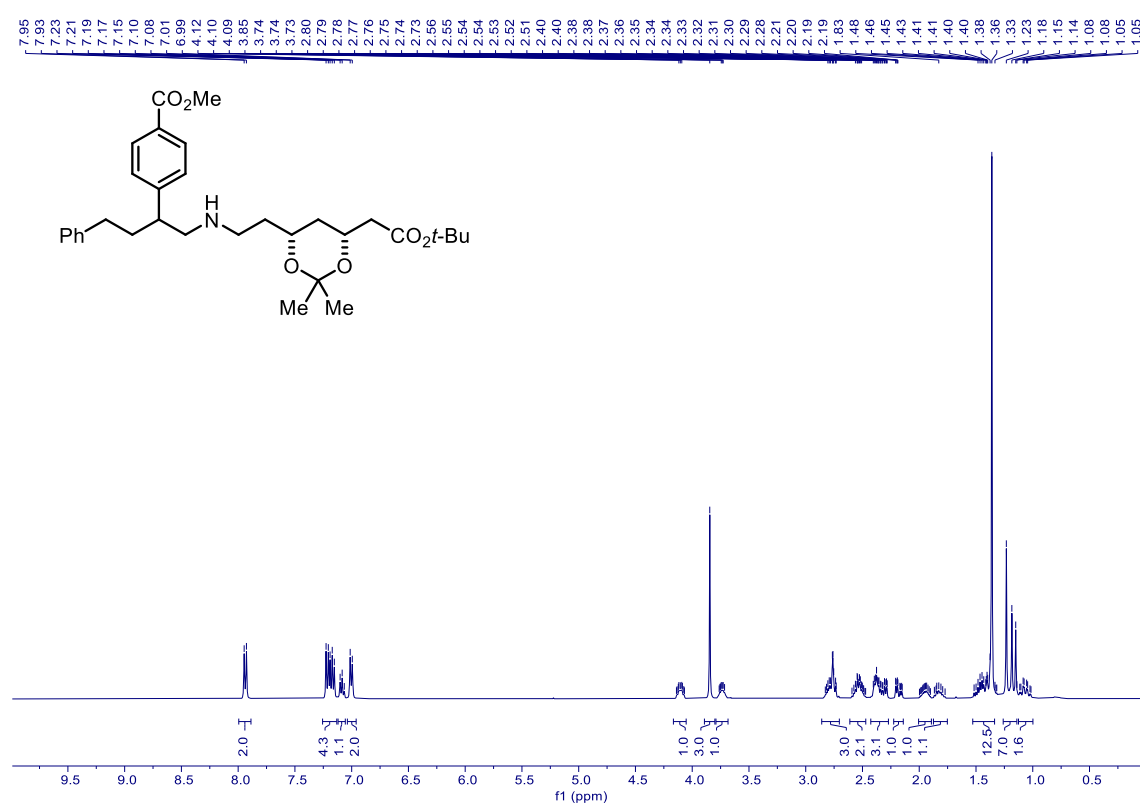
40b – ^{13}C NMR (151 MHz, CDCl_3)



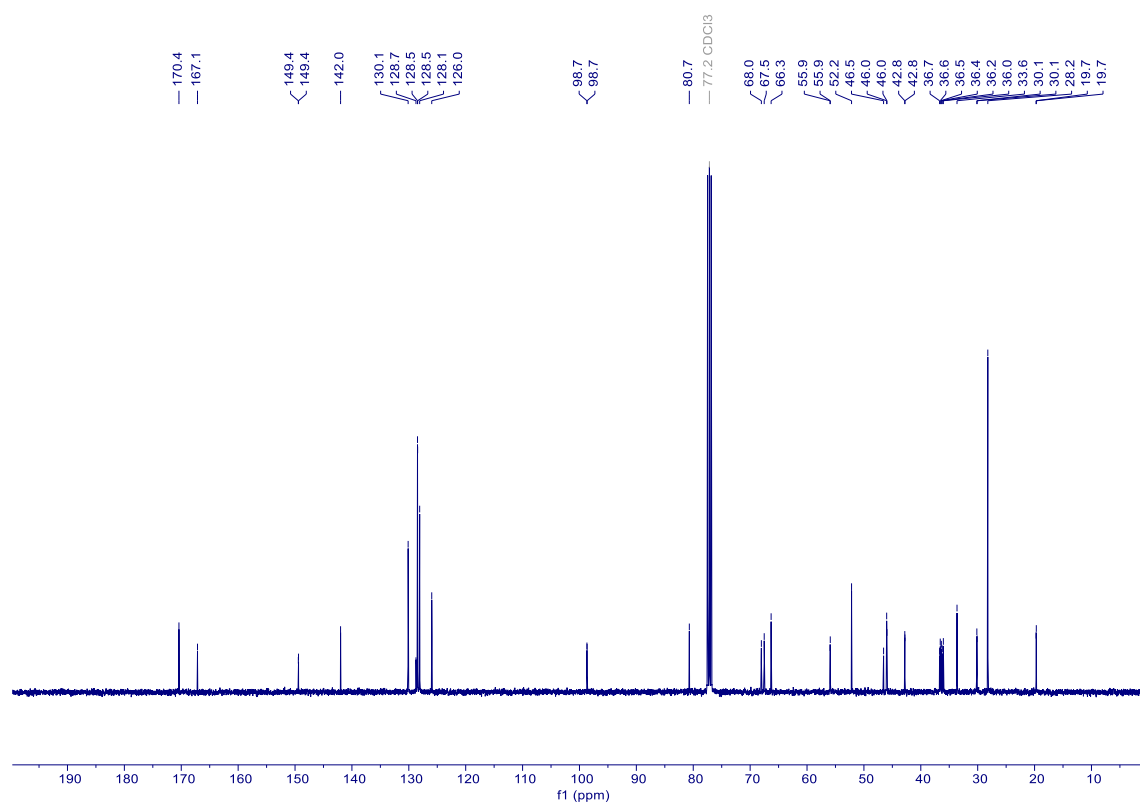
41b – ^1H NMR (600 MHz, CDCl_3)



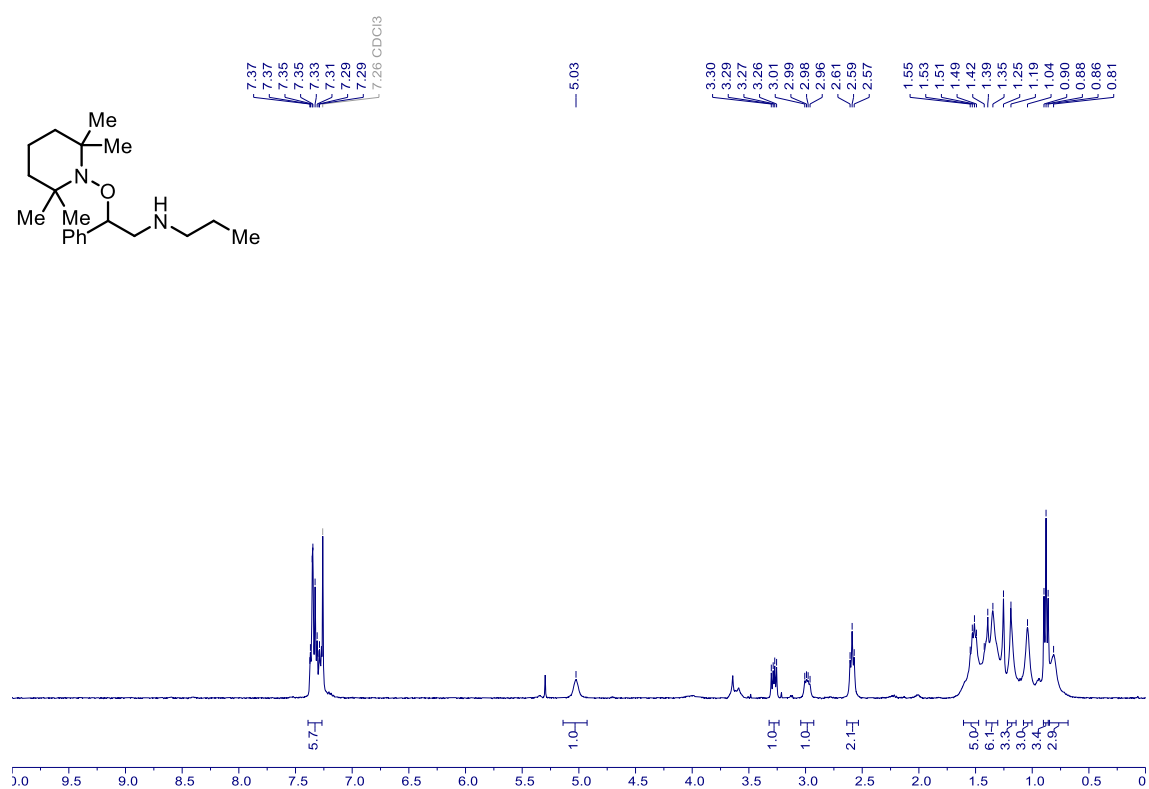
42b – ^1H NMR (400 MHz, CDCl_3)



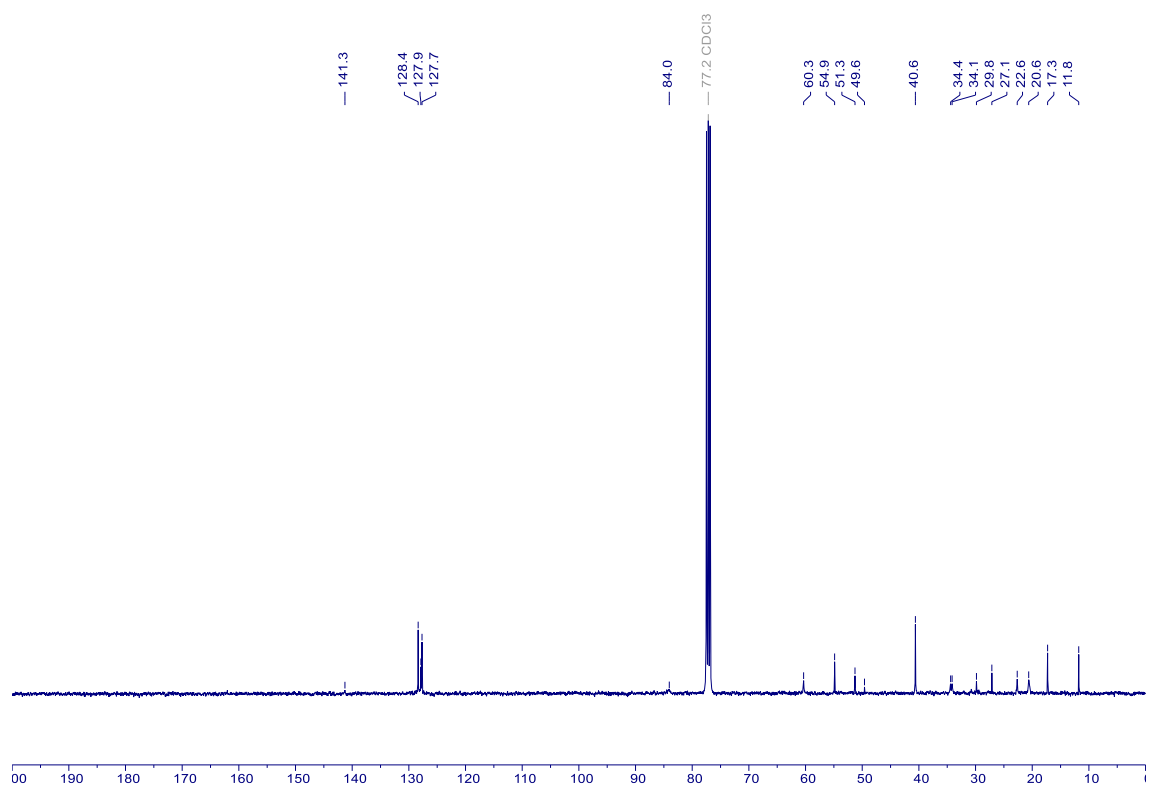
42b – ^{13}C NMR (101 MHz, CDCl_3)



S14 – ^1H NMR (400 MHz, CDCl_3)



S14 – ^{13}C NMR (101 MHz, CDCl_3)



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