Supporting Information for

Metal-Free [2+2]-Photocycloaddition of Unactivated Alkenes Enabled by Continuous Flow Processing

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1. Materials and Methods

Unless otherwise stated, all solvents were purchased from Fisher Scientific or Sigma Aldrich and used without further purification. Substrates and reagents were purchased from Alfa Aesar, Fluorochem or Sigma Aldrich and used as received.

Analytical thin-layer chromatography (TLC) was carried out on 250 µm 60-F254 silica gel plates purchased from EMD Millipore, and visualization was affected by staining with either KMnO4, ninhydrin or by fluorescence quenching with ultraviolet light.

^{1}H-NMR spectra were recorded on 400 MHz, 500 MHz and 600 MHz instruments and are reported relative to residual solvent: $CDCl_3$ (δ/ppm 7.26) or TMS (δ/ppm 0) in cases where residual solvent was not clearly visible. ^{13}C-NMR spectra were recorded on the same instruments (101 and 125 MHz) and are reported relative to the corresponding solvent: $CDCl_3$ (δ/ppm 77.16). Data for ^{1}H-NMR are reported as follows: chemical shift (δ/ ppm) (integration, multiplicity, coupling constant (Hz)). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, m = multiplet. Data for ^{13}C-NMR are reported in terms of chemical shift (δ/ ppm) and multiplicity (C, CH, CH_2 or CH_3). COSY, HSQC, HMBC and TOCSY experiments were used in the structural assignment.

IR spectra were obtained by use of a Bruker Platinum spectrometer (neat, ATR sampling) with the intensities of the characteristic signals being reported as weak (w, 71% of tallest signal) .

High-resolution mass spectrometry was performed using the indicated techniques on a micromass LCT orthogonal time-of-flight mass spectrometer with leucine-enkephalin (Tyr-Gly-Phe-Leu) as an internal lock mass.

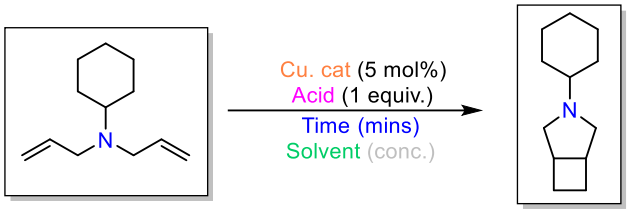
All flow reactions were performed using a Vapourtec E-Series photoflow reactor. The flow reactor was equipped with a medium pressure Hg lamp with different Vapourtec filters used to isolate desired wavelengths. When applicable, a high-power, tuneable LED with two panels (adjustable from 25-50 W each) was used which emitted light with a wavelength of 365 nm. These lamp sources could be swapped out with one another when applicable. The reactor coil had a volume of 10 mL and FEP tubing was used.

2. Optimization of [2+2] cycloaddition and the parameters studied.

2.1 Optimisation of [2+2] cycloaddition.

Table 1: Optimisation experiments ran for the [2+2] photocycloaddition of model substrate 1a.

Flow



Entry	Solvent	Catalyst	Acid	Reaction Time (min)	Conversion Prod.:S.M.
1	Water (0.10 M)	$CuSO_4{\cdot}5H_2O$	H_2SO_4	30	0:100
2	Water (0.10 M)	$CuSO_4{\cdot}5H_2O$	H_2SO_4	90	4:96
3	Water (0.10 M)	$CuSO_4{\cdot}5H_2O$	H_2SO_4	120	7:93
4	Water (0.10 M)	$CuSO_4{\cdot}5H_2O$	H_2SO_4	180	17:83
5	Water (0.10 M)	$CuSO_4{\cdot}5H_2O$ + Acetone 20 mol%	H_2SO_4	45	100:0
6[a]	Water (0.10 M)	$CuSO_4{\cdot}5H_2O$ + Acetone 20 mol%	H_2SO_4	30	100:0
7	Water:Acetone (80:20 0.10 M)	$CuSO_4{\cdot}5H_2O$	H_2SO_4	10	82:18
8	Water:Acetone (80:20 0.10 M)	$CuSO_4{\cdot}5H_2O$	H_2SO_4	20	98:2
9[b]	Water:Acetone (80:20 0.10 M)	$CuSO_4{\cdot}5H_2O$	H_2SO_4	30	100
10[b]	Water:Acetone (80:20 0.10 M)	CuI	H_2SO_4	30	-[a]
11	Water:Acetone (80:20 0.10 M)	CuBr	H_2SO_4	30	-[a]
12	Water:Acetone (80:20 0.10 M)	$CuCl_2.2H_2O$	H_2SO_4	30	79:21
13	Water:Acetone (80:20 0.10 M)	$Cu(CF_3SO_2)_2$	H_2SO_4	30	99:1
14[b]	Water:Acetone (80:20 0.10 M)	-	H_2SO_4	30	100:0
15[b]	Water:Acetone (80:20 0.10 M)	-	-	30	-[c]
16	Water:Acetone (80:20 0.10 M)	-	-	10	-[c]
17	Water:Acetone (80:20 0.10 M)	-	HCl	30	86:14
18	Water:Acetone (80:20 0.10 M)	-	Orthophosphoric Acid	30	99:1
19	Water:Acetone (80:20 0.10 M)	-	Acetic Acid	30	100:0
20	Water:Acetone (90:10 0.10 M)	-	Acetic Acid	30	100:0
21	Water:Acetone (90:10 0.20 M)	-	Acetic Acid	30	100:0
22	**Water:Acetone (90:10 0.25 M)**	**-**	**Acetic Acid**	**30**	**100:0**

[a]Result taken from the "Switch-Off" experiment (See section 2.2); [b]Cu cat. not soluble reaction media and therefore, reaction was not run; [c]Complete degradation.

All optimisation experiments were ran using a Vaportec E-series with a medium pressure Hg lamp and a type-2 filter.

2.2 Switch-Off method for residence time optimisation

Using the model substrate *N,N*-diallylcyclohexanamine (1a) the Switch-Off method[1] was used to obtain the optimal residence time for the [2+2] photocycloaddition reaction.

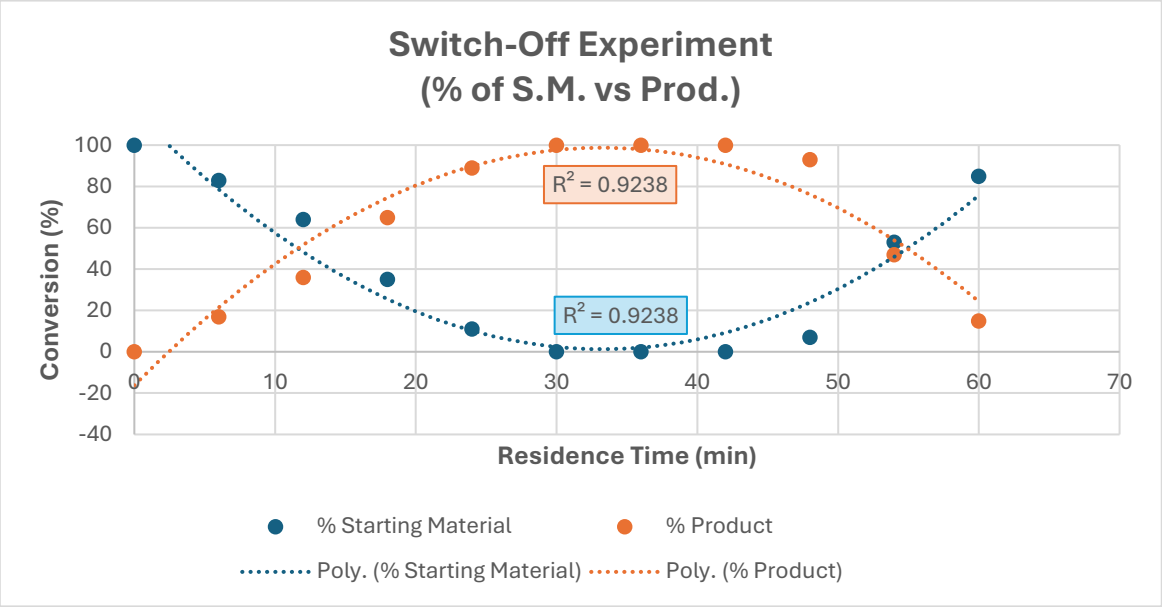


Figure 1: Residence time results for the [2+2] photocycloaddition reaction using the "Switch-Off method".

It was observed that the reaction went to completion after 30 minutes with retrosynthetic activity occurring after ≈45 minutes. This retrosynthetic activity is very clear in the proton NMR with the characteristic alkene peaks reappearing (Figure 2). The results roughly fit a polynomial curve with an order of 2 and an $R^2 = 0.9238$.

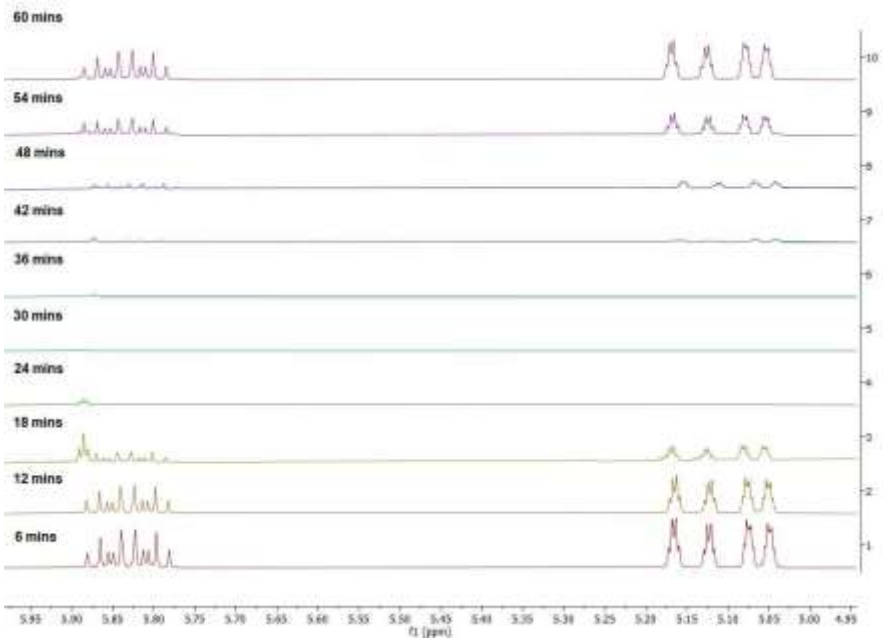
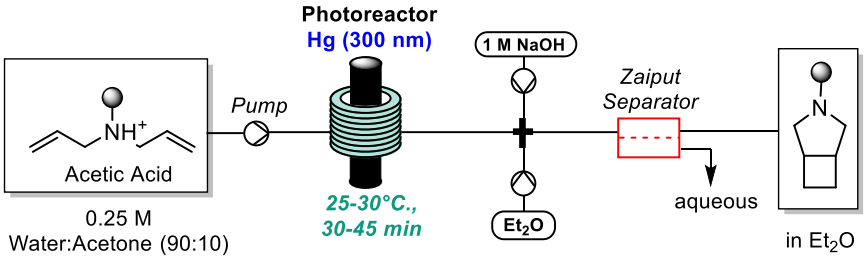


Figure 2: Reappearance of characteristic alkene peaks of 1a in the ^{1}H-NMR samples.

Note: The conversion was obtained by comparing the ^{1}H-NMR integrals of the starting material vs the product. The results from this were used to fill in entry 5 of the optimisation table above with 30 minutes being observed to have full conversion. Due to this reaction being run using acetone in catalytic quantities, the residence time was retested once acetone was used as a co-solvent (entry 6-8) to test if the stoichiometric amounts affected the results.

3. Experimental Procedures

3.1 General Procedure for the [2+2] photocycloaddition



Reactions were carried out using a Vapourtec E-series with a medium pressure Hg lamp (type 2 filter) and a reactor coil of 10mL volume. The zaiput separator (Sep-10) had an OB-900 hydrophobic membrane installed.

Acetic acid (1 equiv.) was added dropwise to a vial containing the diallylamine. The vial was capped and shaken vigorously for one minute followed by addition of the water and acetone (90:10, 0.25 M). The reaction mixture was passed through the flow reactor with a residence time of 30 minutes (0.333 mL/min) using compressed air to control the temperature (25-30 °C). Using a quad-piece mixer, the output of the E-Series was connected with two flow lines coming from a Chemyx Fusion 100 syringe pump containing two syringes (1M NaOH and Et_2O) with the biphasic mixture being separated using a Zaiput separator. The organic product was concentrated *in vacuo* before being sent for ^{1}H-NMR analysis. Where applicable, 1,3,5-trimethoxybenzene was used as an internal standard for q-NMR analysis.

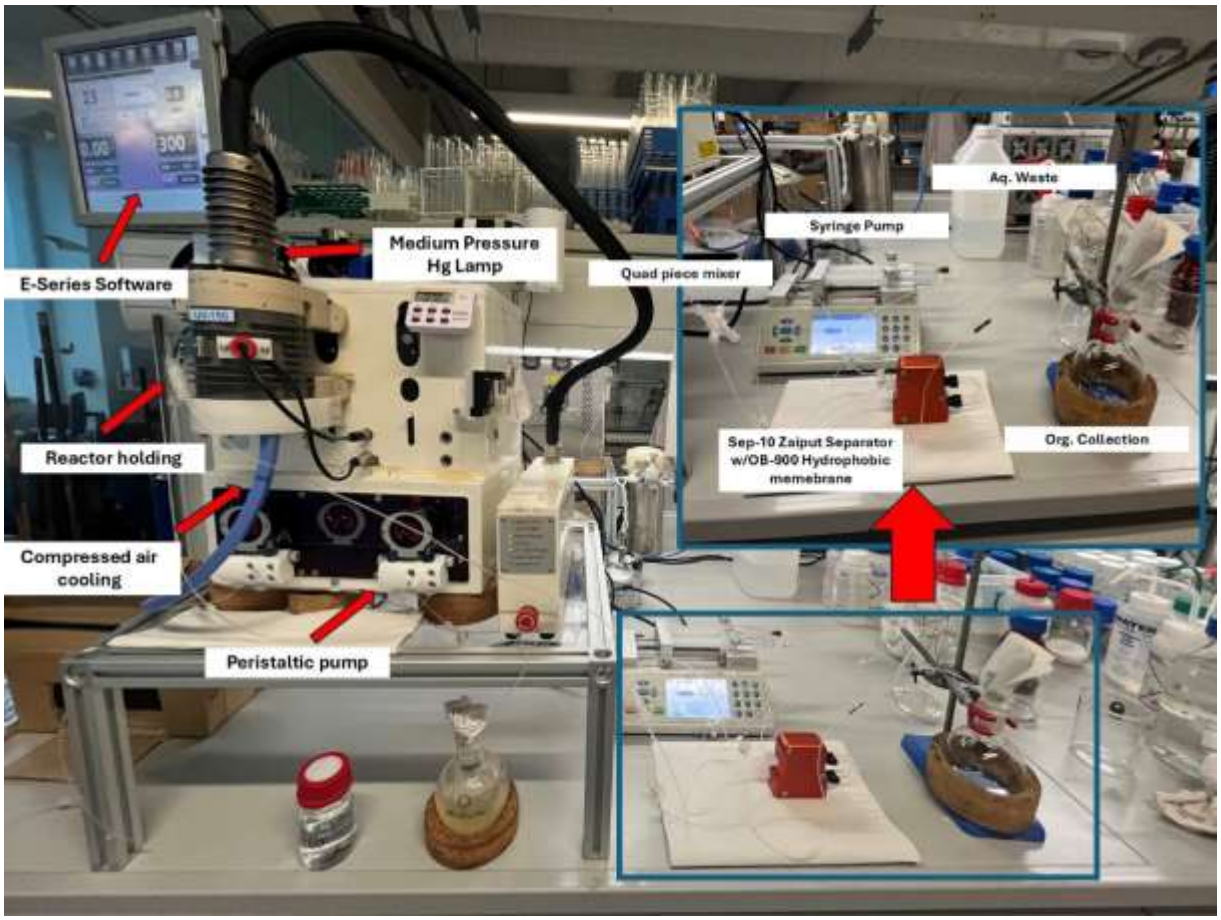
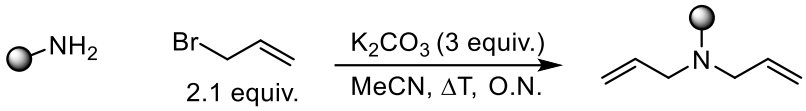


Figure 3. General Set-Up for the [2+2] cycloaddition.

3.2 Synthesis of the diallylamine starting materials.

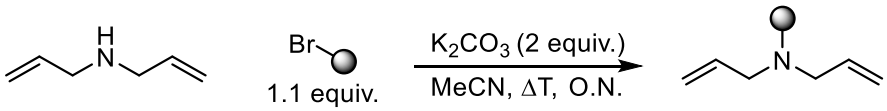
3.2.1 Diallylamine synthesis from allyl bromide



The procedure was followed as described in the literature[2].

A round bottom flask was charged with K_2CO_3 (3 equiv.), MeCN (0.5 M), amine (1 equiv.) and allyl bromide (2.1 equiv.) and the reaction stirred under N_2 at the indicated temperature for the indicated time. Upon completion, the reaction was diluted with Et_2O and filtered, washing with additional Et_2O, then concentrated and purified by flash column chromatography to yield the corresponding diallylamines.

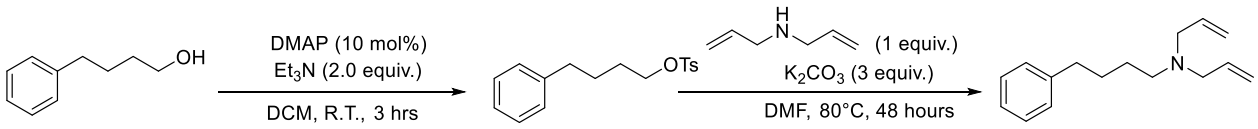
3.2.2 Diallylamine synthesis from alkyl bromo species



The procedure was followed as described in the literature[3].

A round bottom flask was charged with K_2CO_3 (2 equiv.), MeCN (0.5 M), diallylamine (1 equiv.) and the alkyl bromo species (1.1 equiv.) and the reaction stirred overnight. Upon completion, the reaction was diluted with Et_2O and filtered, washing with additional Et_2O, then concentrated and purified by flash column chromatography to yield the corresponding diallylamines.

3.2.3 Synthesis of 3-(4-phenylbutyl)-3-azabicyclo[3.2.0]heptane (**1n**).



3 **1n**

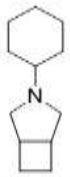
4-phenyl-1-butanol (0.77 mL, 5 mmol) and DMAP (0.06 g, 0.5 mmol) was charged to a round-bottom flask at 0°C containing DCM (15 mL). Following a five-minute stir, triethylamine (1.40 mL, 10 mmol) and tosyl chloride (1.43 g, 7.5 mmol) were charged and the reaction mixture let stir at room temperature for 3 hours. The reaction mixture was quenched with water (15 mL) before being extracted three times with DCM (15 mL). The organic layer was dried with brine (15 mL) and Na_2SO_4 before being concentrated under vacuum to obtain the crude product **3** as a yellow oil. The crude product was purified using column chromatography (80% EtOAc in c-Hex) to obtain the purified **31** as a colourless oil (1.46 g, 4.8 mmol, 96%).

3 (1.24 g, 4.0 mmol), diallylamine (0.51 mL, 4.0 mmol), and K_2CO_3 (1.67 g, 12 mmol) were charged to a round-bottom flask containing DMF (20 mL) and let stir at 80°C for 48 hours. Following the 48 hour stir, the reaction mixture was quenched with water (20 mL) before being extracted three times with EtOAc (20 mL). The organic layer was dried with brine (15 mL) and Na_2SO_4 before being concentrated under vacuum to obtain the crude product **1o**. Using column chromatography (20% EtOAc in c-Hex), **1n** was isolated as a colourless oil (0.19 g, 0.8 mmol, 20%).

4. Characterisation of products

4.1 [2+2] Cycloadduct Species

3-cyclohexyl-3-azabicyclo[3.2.0]heptane (2a): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{12}H_{21}N$
Exact Mass: 179.1674

Yield: 0.19 g (1.08 mmol, 86%)

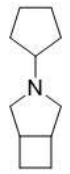
Appearance: Colourless Oil

R_f: 0.29 (60% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{12}H_{22}N^+$ 180.1747; Found 180.1748

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 2.88 (d, *J* = 9.3 Hz, 2H), 2.73 (qd, *J* = 4.5, 1.7 Hz, 2H), 2.10 (dddd, *J* = 11.4, 5.8, 4.4, 2.2 Hz, 4H), 2.03 – 1.94 (m, 1H), 1.94 – 1.87 (m, 2H), 1.80 – 1.74 (m, 2H), 1.74 – 1.67 (m, 2H), 1.57 (d, *J* = 9.9 Hz, 1H), 1.38 – 1.19 (m, 5H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 63.6 (CH), 59.1 (2 x CH_2), 37.0 (2 x CH), 32.3 (2 x CH_2), 26.4 (2 x CH_2), 25.1 (2 x CH_2), 24.7 (CH_2). **IR (neat) ν/cm^{-1}** 2931 (m), 2856 (w), 2775 (w), 1705 (w), 1450 (w), 1230 (w), 921 (w), 1060 (w) 730 (s), 701 (m). Data is consistent with that previously reported[2].

3-cyclopentyl-3-azabicyclo[3.2.0]heptane (2b): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{11}H_{19}N$
Exact Mass: 165.1517

Yield: 0.17 g (1.00 mmol, 80%)

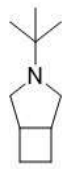
Appearance: Colourless Oil

R_f: 0.31 (10% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{11}H_{20}N^+$ 166.1591; Found 166.1592.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 2.84 (d, *J* = 9.5 Hz, 2H), 2.75 (d, *J* = 7.5 Hz, 2H), 2.39 (s, 1H), 2.17 – 2.08 (m, 4H), 1.85 – 1.70 (m, 6Hi), 1.54 (td, *J* = 6.1, 3.0 Hz, 4H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 67.5 (CH), 61.0 (2 x CH_2), 37.2 (2 x CH), 24.4 (2 x CH_2), 24.0 (2 x CH_2). **IR (neat) ν/cm^{-1}** 2970 (s), 2932 (m), 2883 (m), 1467 (m), 1378 (m), 1307 (w), 11160 (m), 1128 (s), 1108 (s), 950 (s), 817 (m).

3-(tert-butyl)-3-azabicyclo[3.2.0]heptane (2c): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{10}H_{19}N$
Exact Mass: 153.1517

Yield: 0.18 g (1.16 mmol, 93%)

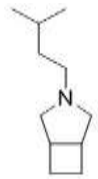
Appearance: Colourless Oil

R_f: 0.14 (20% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}N^+$ 154.1517; Found 154.1519

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 2.74 – 2.62 (m, 4H), 2.40 (ddd, *J* = 9.3, 3.9, 1.5 Hz, 2H), 2.14 – 2.04 (m, 2H), 1.73 – 1.65 (m, 2H), 1.10 (s, 9H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 53.2 (2 x CH_2), 52.0 (C), 37.0 (2 x CH), 26.4 (3 x CH_3), 24.7 (2 x CH_2). **IR (neat) ν/cm^{-1}** 2969 (s), 2934 (w), 2882 (w), 1659 (w), 1466 (w), 1379 (s0, 1304 (m), 1160 (m), 1160 (s), 1129 (m), 951 (s), 817 (m), 731 (m). Data is consistent with that previously reported[2].

3-isopentyl-3-azabicyclo[3.2.0]heptane (2d): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{11}H_{21}N$
Exact Mass: 167.1674

Yield: 0.19 g (1.15 mmol, 92%)

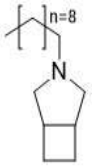
Appearance: Colourless Oil

R_f: 0.23 (20% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{11}H_{22}N^+$ 168.1747; Found 168.1747

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 2.86 – 2.67 (m, 3H), 2.51 – 2.32 (m, 3H), 2.10 (ddd, *J* = 10.5, 6.3, 3.8 Hz, 2H), 1.97 (ddd, *J* = 9.6, 4.0, 1.7 Hz, 2H), 1.76 – 1.66 (m, 2H), 1.66 – 1.57 (m, 1H), 1.51 – 1.39 (m, 2H), 0.92 – 0.87 (m, 6H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 61.6 (2 x CH_2), 55.0 (2 x CH_2), 38.1 (2 x CH_2), 37.3 (2 x CH), 27.0 (CH), 24.5 (2 x CH_2), 22.9 (2 x CH_3). **IR (neat) ν/cm^{-1}** 2954 (s), 2926 (s), 2869 (s), 2792 (w), 1700 (m), 1657 (m), 1466 (s), 1381 (s), 1168 (m), 1118 (m), 770 (w).

3-decyl-3-azabicyclo[3.2.0]heptane (2e): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{16}H_{31}N$
Exact Mass: 237.2457

Yield: 0.07 g (0.28 mmol, 22%)

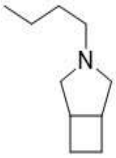
Appearance: Colourless Oil

R_f: 0.23 (15% EtOAc in c-Hex, $KMnO_4$)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{16}H_{32}N^+$ 238.2527; Found 238.2529

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 2.78 (dd, *J* = 38.4, 8.0 Hz, 3H), 2.48 – 2.36 (m, 2H), 2.12 (dt, *J* = 10.5, 6.1 Hz, 2H), 1.99 (dd, *J* = 9.7, 4.6 Hz, 2H), 1.78 – 1.68 (m, 2H), 1.56 (p, *J* = 7.4 Hz, 2H), 1.39 – 1.19 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 61.6 (CH_2), 56.8 (CH_2), 37.4 (2 x CH), 32.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 24.5 (2 x CH_2), 22.8 (CH_2), 14.3 (CH_3)**. IR (neat) ν/cm^{-1}** 2954 (s), 2854 (m), 2771 (w), 1709 (w), 1649 (w), 1465 (m), 1378 (m), 1348 (w), 1179 (w), 731 (m).

3-butyl-3-azabicyclo[3.2.0]heptane (2f): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{10}H_{19}N$
Exact Mass: 153.1517

Yield: 0.15 g (0.96 mmol, 77%)

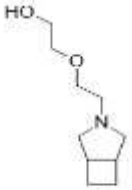
Appearance: Colourless Oil

R_f: 0.21 (20% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}N^+$ 154.1517; Found 154.1519

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 2.82 (d, *J* = 9.4 Hz, 2H), 2.74 (dtq, *J* = 8.1, 3.8, 1.9 Hz, 2H), 2.46 – 2.39 (m, 3H), 2.11 (dq, *J* = 10.2, 6.3 Hz, 3H), 1.99 (ddd, *J* = 9.6, 4.0, 1.6 Hz, 2H), 1.74 – 1.68 (m, 2H), 1.59 – 1.49 (m, 2H), 1.36 (dt, *J* = 14.7, 7.4 Hz, 3H), 1.26 – 1.15 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 4H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 61.4 (CH_2), 56.3 (2 x CH), 37.2 (CH_2), 31.3 (CH_2), 24.4 (2 x CH_2), 21.0 (CH_2), 14.1 (CH_3). **IR (neat) ν/cm^{-1}** 2956 (s), 2928 (s), 2872 (m), 2799 (m), 1669 (s), 1457 (s), 1376 (s), 1245 (m), 1159 (s), 1121 (s), 957 (w), 770 (w), 737 (w).

2-(2-(3-azabicyclo[3.2.0]heptan-3-yl)ethoxy)ethan-1-ol (2g): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{10}H_{19}NO_2$
Exact Mass: 185.1416

Yield: 0.15 g (1.19 mmol, 65%)

Appearance: Colourless Oil

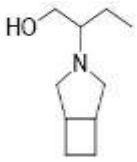
R_f: 0.16 (10% MeOH in DCM, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}NO_2^+$ 186.1489; Found 186.1490

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 3.73 – 3.65 (m, 6H), 3.63 – 3.58 (m, 1H), 2.93 (d, *J* = 9.4 Hz, 2H), 2.79 (dp, *J* = 6.7, 2.4 Hz, 2H), 2.72 (t, *J* = 5.6 Hz, 2H), 2.16 – 2.09 (m, 4H), 1.76 (dq, *J* = 3.8, 2.3 Hz, 2H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 71.9 (CH_2), 69.0 (CH_2), 62.5 (CH_2), 61.3 (2 x CH_2), 55.5 (CH_2), 37.3 (2 x CH),

24.3 (2 x CH_2). **IR (neat) ν/cm^{-1}** 2934 (m), 2867 (m), 2794 (m), 1705 (w), 1467 (s), 1121 (w), 1601 (s), 845 (m) 811 (w).

2-(3-azabicyclo[3.2.0]heptan-3-yl)butan-1-ol (2h): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{10}H_{19}NO$
Exact Mass: 169.1467

Yield: 0.10 g (0.74 mmol, 59%)

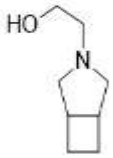
Appearance: Colourless Oil

R_f: 0.05 (30% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}NO^+$ 170.1540; Found 170.1542

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 3.70 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.39 (dd, *J* = 10.3, 7.8 Hz, 1H), 2.83 – 2.69 (m, 3H), 2.68 – 2.59 (m, 2H), 2.52 (dd, *J* = 9.2, 5.7 Hz, 1H), 2.25 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.15 (dd, *J* = 10.0, 5.7 Hz, 2H), 1.64 (dddd, *J* = 21.5, 13.6, 6.7, 4.0 Hz, 3H), 1.36 – 1.25 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 4H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 62.6 (CH), 61.5 (CH_2), 58.7 (2 x CH_2), 52.5 (2 x CH_2), 36.9 (2 x CH), 36.4 (CH_2), 24.7 (2 x CH_2), 24.6 (CH_2), 19.5 (2 x CH_2), 11.5 (CH_3). **IR (neat) ν/cm^{-1}** 3389 (br), 2963 (s), 2932 (s), 2877 (m), 2784 (m), 1711 (w), 1657 (w), 1221 (m), 1049 (s), 854 (w).

2-(3-azabicyclo[3.2.0]heptan-3-yl)ethan-1-ol (2i): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_8H_{15}NO$
Exact Mass: 141.1154

Yield: 0.13 g (0.90 mmol, 72%)

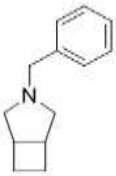
Appearance: Red Oil

R_f: 0.39 (10% MeOH in DCM, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{16}NO^+$ 142.1228; Found 142.1228

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 3.67 (t, *J* = 5.5 Hz, 2H), 2.85 (d, *J* = 9.3 Hz, 2H), 2.82 – 2.75 (m, 2H), 2.70 (t, *J* = 5.5 Hz, 2H), 2.17 – 2.10 (m, 4H), 1.70 (dd, *J* = 6.0, 3.2 Hz, 2H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** δ 60.7 (2 x CH_2), 59.7 (CH_2), 56.5 (CH_2), 37.4 (CH_2), 24.6 (2 x CH_2). **IR (neat) ν/cm^{-1}** 3327 (br), 2936 (s), 2855 (m), 2792 (m), 1175 (m), 1706 (w), 1656 (w), 1056 (s) 886 (m), 834 (w). Data is consistent with that previously reported[2].

3-benzyl-3-azabicyclo[3.2.0]heptane (2j): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{13}H_{17}N$
Exact Mass: 187.1361

Yield: 0.06 g (0.31 mmol, 25%)

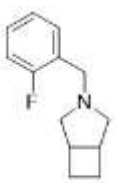
Appearance: Colourless Oil

R_f: 0.32 (10% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{13}H_{18}N^+$ 188.1435; Found 188.1435

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.41 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 3.68 (s, 2H), 2.83 – 2.68 (m, 4H), 2.18 – 2.06 (m, 4H), 1.83 – 1.70 (m, 2H). **^{13}C-NMR (101MHz, $CDCl_3$) δ/ppm** 140.2 (C), 128.8 (2 x CH), 128.2 (2 x CH), 126.7 (CH), 61.0 (2 x CH_2), 59.9 (CH_2), 37.6 (2 x CH), 24.6 (2 x CH_2). **IR (neat) ν/cm^{-1}** 3062 (w) 3029 (w), 2777 (w), 1700 (w), 1416 (m), 966 (w), 1073 (w), 761 (s) 698 (s).

3-(2-fluorobenzyl)-3-azabicyclo[3.2.0]heptane (2k): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{13}H_{16}FN$
Exact Mass: 205.1267

Yield: 0.005 g (0.03 mmol, 2%)

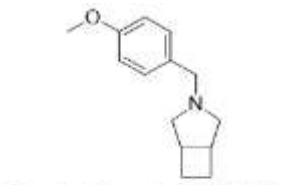
Appearance: Orange Oil

R_f: 0.16 (5% EtOAc in c-Hex, $KMnO_4$)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{13}H_{17}NF^+$ 206.1341; Found 206.1342

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.54 (td, *J* = 7.5, 1.9 Hz, 1H), 7.22 (tdd, *J* = 7.5, 5.1, 1.8 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.78 (s, 2H), 2.80 (d, *J* = 9.3 Hz, 2H), 2.78 – 2.71 (m, 2H), 2.13 (ddd, *J* = 12.6, 9.5, 5.3 Hz, 4H), 1.77 (dhept, *J* = 6.8, 4.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm** 161.2 (C, d, *J* = 245.6 Hz), 131.3 (CH, d, *J* = 4.8 Hz), 128.3 (CH, d, *J* = 8.3 Hz), 126.5 (C, d, *J* = 14.6 Hz), 123.9 (CH, d, *J* = 3.6 Hz), 115.1 (CH, d, *J* = 22.2 Hz), 60.7 (2 x CH_2) 51.8 (d, *J* = 2.4 Hz), 37.6 (2 x CH), 24.5 (2 x CH_2) . **^{19}F-NMR (376 MHz, $CDCl_3$) δ/ppm** -118.63.

3-(4-methoxybenzyl)-3-azabicyclo[3.2.0]heptane (2l): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{14}H_{19}NO$
Exact Mass: 217.1467

Yield: 0.06 g (0.35 mmol, 28%)

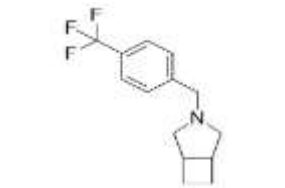
Appearance: Colourless oil

R_f: 0.09 (10% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{13}H_{20}NO^+$ 218.1540 Found 218.1539

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.34 – 7.29 (m, 2H), 6.90 – 6.83 (m, 2H), 3.81 (s, 3H), 3.62 (s, 2H), 2.75 (dd, J = 8.5, 4.5 Hz, 4H), 2.13 – 2.04 (m, 4H), 1.82 – 1.74 (m, 2H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 158.5 (CH), 132.3 (CH), 129.9 (2 x CH), 113.6 (2 x CH_2), 60.85 (2 x CH_2), 59.3 (CH_2), 55.4 (CH_3), 37.55 (2 x CH), 24.54 (2 x CH_2). **IR (neat) ν/cm^{-1}** 3073 (w), 2933 (m), 2776 (m), 1642 (m), 2620 (s), 1464 (w), 1454 (w), 1243 (s), 1170 (m), 1037 (s), 917 (m), 817 (m), 759 (w).

3-(4-(trifluoromethyl) benzyl)-3-azabicyclo[3.2.0]heptane (2m): Synthesised by experimental procedure 3.1.



Chemical Formula: $C_{14}H_{16}F_3N$
Exact Mass: 255.1235

Yield: 0.05 g (0.19 mmol, 15%)

Appearance: Colourless oil

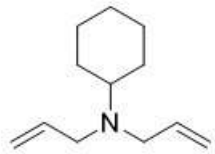
R_f: 0.25 (10% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{14}H_{18}F_3N^+$ 256.1309; Found 256.1308

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.58 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 3.74 (s, 2H), 2.84 – 2.74 (m, 4H), 2.48 (s, 2H), 2.12 (dq, J = 8.7, 5.5 Hz, 4H), 1.82 – 1.75 (m, 2H). **^{13}C-NMR (400 MHz, $CDCl_3$) δ/ppm** 190.4 128.84, 125.17, 125.14, 61.53, 60.90, 59.34, 37.47, 28.32, 26.99, 24.42. **^{19}F-NMR (376 MHz, $CDCl_3$) δ/ppm** -62.33. **IR (neat) ν/cm^{-1}** 2970 (m), 2933 (m), 2781 (w), 1724 (w), 1378 (w), 1324 (s), 1162 (m), 1125 (s), 1066 (m)< 1019 (w), 951 (m), 817 (w).

4.2 Diallylamine Species

***N,N*-diallylcyclohexanamine (1a):** Synthesis by experimental procedure 3.2.1.



Chemical Formula: $C_{12}H_{21}N$
Exact Mass: 179.17

Yield: 1.32 g (7.37 mmol, 74%)

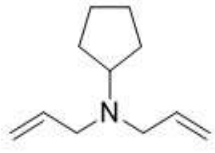
Appearance: Colourless Oil

R_f: 0.57 (30% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{12}H_{22}N^+$ 180.1747; Found 180.1789

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 5.83 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 2H), 5.19 – 5.02 (m, 4H), 3.12 (dt, *J* = 6.3, 1.4 Hz, 4H), 2.59 – 2.46 (m, 1H), 1.77 (dtdd, *J* = 9.8, 6.8, 5.0, 3.0 Hz, 4H), 1.61 (dqd, *J* = 10.7, 3.0, 1.5 Hz, 1H), 1.20 (dtd, *J* = 12.7, 11.1, 9.3 Hz, 4H), 1.08 (ddt, *J* = 12.7, 9.1, 3.3 Hz, 1H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 137.8 (2 x CH), 116.3 (2 x CH_2), 59.2 (2 x CH), 53.1 (CH_2), 29.2 (2 x CH_2), 26.6 (CH_2), 26.3 (2 x CH_2). **IR (neat) ν/cm^{-1}** 3077 (w), 2926 (s), 2853 (m), 2804 (w), 1642 (w), 1162 (m), 1152 (m), 1449 (m), 992 (m), 912 (s). Data is consistent with that previously reported[2].

***N,N*-diallylcyclpentanamine (1b):** Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_{11}H_{19}N$
Exact Mass: 165.1517

Yield: 0.76 g (4.60 mmol, 46%)

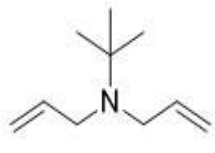
Appearance: Colourless Oil

R_f: 0.61 (60% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{11}H_{19}N^+$ 166.1517; Found 166.1517

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 5.88 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 2H), 5.18 – 5.08 (m, 4H), 3.16 (dt, *J* = 6.5, 1.3 Hz, 4H), 2.99 (tt, *J* = 8.9, 7.3 Hz, 1H), 1.86 – 1.75 (m, 2H), 1.71 – 1.45 (m, 4H), 1.45 – 1.31 (m, 2H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 135.8 (2 x CH), 117.3 (2 x CH_2), 63.1 (CH), 54.3 (2 x CH_2), 30.2 (2 x CH_2), 24.3 (2 x CH_2). Data is consistent with that previously reported[2].

N-allyl-N-(tert-butyl)prop-2-en-1-amine (1c): Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_{10}H_{19}N$
Exact Mass: 153.1517

Yield: 1.18 g (7.70 mmol, 77%)

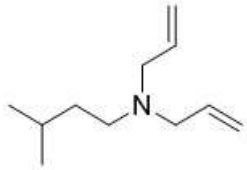
Appearance: Colourless Oil

R_f: 0.23 (20% EtOac in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}N^+$ 154.1591; Found 154.1591

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 5.95 – 5.79 (m, 2H), 5.06 (dd, 4H), 3.20 (d, J = 6.3 Hz, 4H), 1.10 (s, 9H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 138.9 (2 x CH), 115.4 (2 x CH_2), 55.0 (2 x CH_2), 51.7 (CH), 27.8 (3 x CH_3). Data is consistent with that previously reported[2].

***N,N*-diallyl-3-methylbutan-1-amine (1d):** Synthesised by experimental procedure 3.2.2.



Chemical Formula: $C_{11}H_{21}N$
Exact Mass: 167.1674

Yield: 1.19 g (5.02 mmol, 95%)

Appearance: Pale Yellow Oil

R_f: 0.88 (80% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{11}H_{22}N^+$ 168.1747; Found 168.1749

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 5.84 (ddt, J = 16.8, 10.2, 6.5 Hz, 2H), 5.18 – 5.05 (m, 4H), 3.06 (d, J = 6.5 Hz, 4H), 2.47 – 2.33 (m, 2H), 1.54 (dt, J = 13.3, 6.7 Hz, 1H), 1.39 – 1.26 (m, 2H), 0.86 (d, J = 6.7 Hz, 6H). **^{13}C-NMR (500 MHz, $CDCl_3$) δ/ppm** 136.0 (2 x CH), 117.3 (2 x

CH_2), 57.0 (2 x CH_2), 51.6 (CH_2), 36.0 (CH_2), 26.6 (CH), 22.9 (2 x CH_3). **IR (neat) ν/cm^{-1}** 3079 (w), 3008 (w), 2955 (m), 2927 (m), 2794 (m), 1708 (w),1298 (w), 1157 (w), 994 (m), 915 (s).

***N,N*-diallyldecan-1-amine (1e):** Synthesised by experimental procedure 3.2.1.

Chemical Formula: $C_{16}H_{31}N$
Exact Mass: 237.2457

Yield: 0.77g (3.25 mmol, 38%)

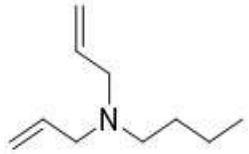
Appearance: Colourless Oil

R_f: 0.36 (30% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{16}H_{31}N^+$ 238.2527; Found; 238.2529

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 5.84 (ddt, J = 16.8, 10.1, 6.5 Hz, 2H), 5.21 – 5.03 (m, 4H), 3.07 (dt, J = 6.5, 1.4 Hz, 4H), 2.43 – 2.34 (m, 2H), 1.48 – 1.38 (m, 2H), 1.25 (m, J = 4.8 Hz, 14H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ/ppm 136.0 (2 x CH), 117.3 (2 x CH_2), 57.0 (2 x CH_2), 53.6 (CH_2), 32.0 (CH_2), 29.8 (2 x CH_2), 29.7 (CH_2), 29.5 (CH_2), 27.6 (CH_2), 27.1 (CH_2), 22.8 (CH_2), 14.2 (CH_3). **IR (neat) ν/cm^{-1}** 3078 (w), 2923 (s), 2854 (m), 2795 (m), 2761 (w), 1643 (w), 1427 (w), 1329 (w), 994 (m), 915 (s).

***N,N*-diallylbutan-1-amine (1f):** Synthesised by experimental procedure 3.2.2.



Chemical Formula: $C_{10}H_{19}N$
Exact Mass: 153.1517

Yield: 1.31 g (8.56 mmol, 66%)

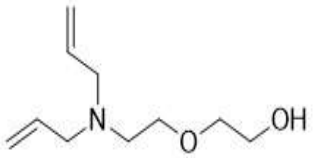
Appearance: Yellow Oil

R_f: 0.24 (20% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}N^+$ 154.1591; Found 154.1590

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 5.85 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 2H), 5.21 – 5.06 (m, 4H), 3.08 (d, *J* = 6.5 Hz, 4H), 2.50 – 2.33 (m, 2H), 1.51 – 1.38 (m, 2H), 1.28 (h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 136.0 (2 x CH), 117.4 (2 x CH_2), 57.0 (2 x CH_2), 53.2 (CH_2), 29.2 (CH_2), 20.8 (CH_2), 14.2 (CH_3). **IR (neat) ν/cm^{-1}** 3084 (w), 2962 (s), 2934 (s), 2875 (m), 1641 (m), 1473 (s), 1427 (m), 993 (m), 948 (s), 859 (s).

2-(2-(diallylamino)ethoxy)ethan-1-ol (1g): Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_{10}H_{19}NO_2$
Exact Mass: 185.1416

Yield: 1.37 g (7.40 mmol, 51%)

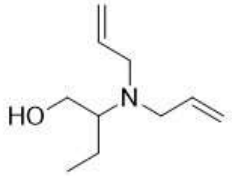
Appearance: Colourless Oil

R_f: 0.33 (10% MeOH in DCM, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}NO_2^+$ 186.1489; Found; 186.1491

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 5.78 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 2H), 5.13 – 5.01 (m, 4H), 3.63 – 3.57 (m, 2H), 3.53 – 3.46 (m, 4H), 3.06 (dt, *J* = 6.7, 1.4 Hz, 4H), 2.57 (t, *J* = 5.6 Hz, 2H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 134.7 (2 x CH), 118.2 (2 x CH_2), 72.6 (CH_2), 68.8 (CH_2), 61.7 (CH_2), 57.2 (2 x CH_2), 52.9 (CH_2). **IR (neat) ν/cm^{-1}** 3375 (br), 3077 (w), 2919 (m), 1643 (w), 1448 (w), 1419 (w), 1532 (w), 1419 (w0, 1122 (s), 1063 (s), 995 (s), 997 (s), 917 (s).

2-(diallylamino)butan-1-ol (1h): Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_{10}H_{19}NO$
Exact Mass: 169.1467

Yield: 1.61 g (9.52 mmol, 95%)

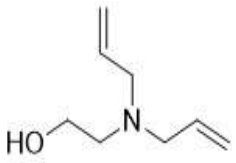
Appearance: Pale Yellow Oil

R_f: 0.33 (20% EtOAc in c-Hex, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{10}H_{20}NO^+$ 170.1540; Found 170.1542

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 5.74 (dddd, *J* = 17.6, 10.1, 7.9, 4.8 Hz, 2H), 5.21 – 4.98 (m, 4H), 3.50 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.29 – 3.17 (m, 4H), 2.91 (dd, *J* = 14.2, 7.9 Hz, 2H), 2.76 (dt, *J* = 10.0, 5.1 Hz, 1H), 1.66 – 1.49 (m, 1H), 1.18 – 1.00 (m, 1H), 0.84 (t, *J* = 7.6 Hz, 3H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 136.8 (2 x CH), 117.1 (2 x CH_2), 61.6 (CH), 60.6 (CH_2), 52.4 (2 x CH_2), 18.5 (CH_2), 11.6 (CH_3). **IR (neat) ν/cm^{-1}** 3406 (br), 3078 (w), 3005 (w), 2964 (w), 2876 (w), 1642 (w), 1416 (m), 1086 (m), 1086 (m), 1051 (m), 992 (s).

2-(diallylamino)ethan-1-ol (1i): Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_8H_{15}NO$
Exact Mass: 141.1154

Yield: 1.20 g (8.50 mmol, 85%)

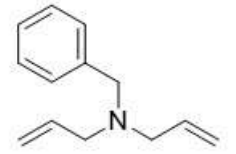
Appearance: Pale Yellow Oil

R_f: 0.19 (10% MeOH in DCM, $KMnO_4$ stain)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_8H_{16}NO^+$ 142.1228; Found 142.1228

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 5.78 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 2H), 5.13 – 5.01 (m, 4H), 3.63 – 3.57 (m, 2H), 3.53 – 3.46 (m, 4H), 3.06 (dt, *J* = 6.7, 1.4 Hz, 4H), 2.57 (t, *J* = 5.6 Hz, 2H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 135.3 (2 x CH), 118.0 (2 x CH_2), 58.5 (CH_2), 56.7 (2 x CH_2), 54.4 (CH_2). **IR (neat) ν/cm^{-1}** 3370 (br), 3077 {w), 3007 (w), 2813 (w), 1623 (w), 1447 (w), 1419 (m), 1048 (s), 995 (s), 916 (s). Data is consistent with that previously reported[2].

***N,N*-diallyl-benzylamine (1j):** Synthesis by experimental procedure 3.2.1.



Chemical Formula: $C_{13}H_{17}N$
Exact Mass: 187.1361

Yield: 1.97 g (10.53 mmol, 99 %)

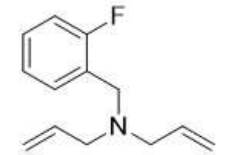
Appearance: Pale Yellow Oil

R_f: 0.53 (20% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{13}H_{18}N^+$ 188.1435; Found 188.1434

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.42 – 7.31 (m, 4H), 7.32 – 7.23 (m, 1H), 5.94 (ddt, J = 16.7, 10.2, 6.3 Hz, 2H), 5.30 – 5.14 (m, 4H), 3.63 (s, 2H), 3.14 (dt, J = 6.3, 1.4 Hz, 4H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 139.5 (2 x CH), 135.9 (2 x CH_2), 128.9 (2 x CH), 128.2 (2 x CH), 126.8 (CH), 117.3 (2 x CH), 57.6 (CH_2), 56.5 (2 x CH_2). **IR (neat) ν/cm^{-1}** 2971 (m), 1700 (w), 1390 (w), 1344 (w), 1249 (w), 993 (w), 884 (w), 731 (s), 698 (s). Data is consistent with that previously reported.[4]

N-allyl-N-(2-fluorobenzyl)prop-2-en-1-amine (1k): Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_{13}H_{16}FN$
Exact Mass: 205.1267

Yield: 1.92 g (9.36 mmol. 91%)

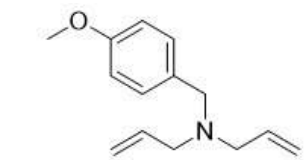
Appearance: Pale Yellow Oil

R_f: 0.76 (20% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{13}H_{17}FN^+$ 206.1267; Found; 206.1267

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.46 (td, J = 7.5, 1.8 Hz, 1H), 7.21 (td, J = 5.5, 2.7 Hz, 1H), 7.11 (td, J = 7.5, 1.2 Hz, 1H), 7.02 (ddd, J = 9.7, 8.2, 1.2 Hz, 1H), 5.90 (dd, J = 17.0, 10.4 Hz, 2H), 5.29 – 5.11 (m, 4H), 3.65 (s, 2H), 3.12 (m, 4H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 161.5 (C, $^{1}J_{C\text{-}F}$= 247.5 Hz), 135.9 (2 x CH), 131.3 (CH, $^{4}J_{C\text{-}F}$= 5.1 Hz), 128.5 (CH, $^{3}J_{C\text{-}F}$= 8.1 Hz), 126.4 ($^{2}J_{C\text{-}F}$= 14.1 Hz), 123.9 (CH, $^{4}J_{C\text{-}F}$= 2.0 Hz), 117.6 (2 x CH_2), 115.3 (CH, $^{2}J_{C\text{-}F}$= 22.2 Hz), 56.7 (2 x CH_2), 50.2 (CH_2) (**$^{3}J_{C\text{-}F}$= 4.04 Hz**).**^{19}F-NMR (376 MHz, $CDCl_3$) δ/ppm** -118.3.

***N,N*-diallyl-(4-methoxybenzyl)-amine (1l):** Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_{14}H_{19}NO$
Exact Mass: 217.1467

Yield: 2.15 g (9.90 mmol, 100%)

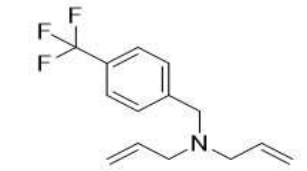
Appearance: Pale Yellow Oil

R_f: 0.20 (10% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{14}H_{20}NO^+$ 218.1540; Found; 218.1539

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.25 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.89 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 2H), 5.24 – 5.11 (m, 4H), 3.80 (s, 3H), 3.53 (s, 2H), 3.07 (d, *J* = 6.4 Hz, 4H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 158.7 (C), 136.1 (2 x CH), 131.4 (C), 130.2 (2 x CH), 117.4 (2 x CH_2), 113.7 (2 x CH), 57.0 (CH_2), 56.4 (2 x CH_2), 55.3 (CH_3). **IR (neat) ν/cm^{-1}** 3075 (w), 2932 (w), 2802 (w), 1642 (m), 1510 (s), 1300 (s), 1170 (m), 10.363 (m), 916 (s), 845 (m), 809 (s).

***N,N*-diallyl-(4-(Trifluoromethyl)benzyl)-amine (1m):** Synthesised by experimental procedure 3.2.1.



Chemical Formula: $C_{14}H_{16}F_3N$
Exact Mass: 255.1235

Yield: 1.92 g (7.53 mmol, 91%)

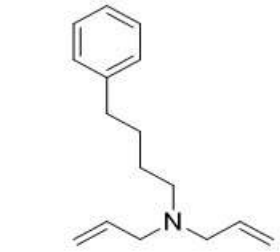
Appearance: Pale Red Oil

R_f: 0.48 (10% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{13}H_{17}FN^+$ 255.1248; Found; 255.1248

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm 7.57 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 5.88 (ddt, J = 16.7, 10.2, 6.3 Hz, 2H), 5.25 – 5.11 (m, 4H), 3.63 (s, 2H), 3.16 – 3.02 (m, 4H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm** 144.2 (CH), 135.7 (2 x CH), 129.0 (2 x CH_2), 129.1 (C, $^2J_{C-F}$= 47.5 Hz), 125.2 (q, 2 x CH, $^3J_{C-F}$ = 1.0 Hz) 123.1 (C, $^1J_{C-F}$ = 277.80 Hz) 117.8 (2 x CH_2), 57.2 (CH_2), 56.7 (2 x CH_2). **^{19}F-NMR (376 MHz, $CDCl_3$) δ/ppm** -62.37. **IR (neat) ν/cm^{-1}** 2810 (w), 1644 (w), 1619 w), 1718 (w), 1322 (s), 1161 (m), 1065 (s), 989 (m), 916 (s), 842 (m). Data is consistent with that previously reported.[5]

***N,N*-diallyl-4-phenylbutan-1-amine (1n)**: Synthesised by experimental procedure D.



Chemical Formula: $C_{16}H_{23}N$
Exact Mass: 229.1830

Yield: 0.19 g (0.8 mmol, 20%).

Appearance: Pale yellow oil

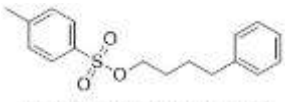
R_f: 0.28 (20% EtOAc in c-Hex)

HR-MS (QTOF) m/z: [M+H] Calcd for $C_{16}H_{24}N^+$ 230.1903; Found 230.1906

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.32 – 7.13 (m, 5H), 5.91 – 5.79 (m, 2H), 5.20 – 5.08 (m, 4H), 3.07 (d, *J* = 6.5 Hz, 4H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.47 – 2.40 (m, 2H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.50 (ddd, *J* = 15.0, 8.6, 6.0 Hz, 2H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 142.74, 135.99, 128.53, 128.38, 125.77, 117.41, 57.01, 53.23, 35.94, 29.41, 26.72.

4.3 Miscellaneous

4-phenylbutyl 4-methylbenzenesulfonate (3): Synthesised by experimental procedure D.



Chemical Formula: $C_{17}H_{20}O_3S$
Exact Mass: 304.1133

Yield: 1.46 g (4.8 mmol, 96%)

Appearance: Pale yellow oi

R_f: 0.79 (80% EtOAc in c-Hex)

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 7.79 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 4.05 (t, *J* = 5.8 Hz, 2H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 1.66 (tt, *J* = 7.9, 3.8 Hz, 4H). **^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm** 144.78, 141.64, 133.23, 129.92, 128.43, 127.94, 125.98, 70.49, 35.14, 28.40, 27.15, 21.70.

4.3 Characterisation of 3-(4-phenylbutyl)-3-azabicyclo[3.2.0]heptane (2n)

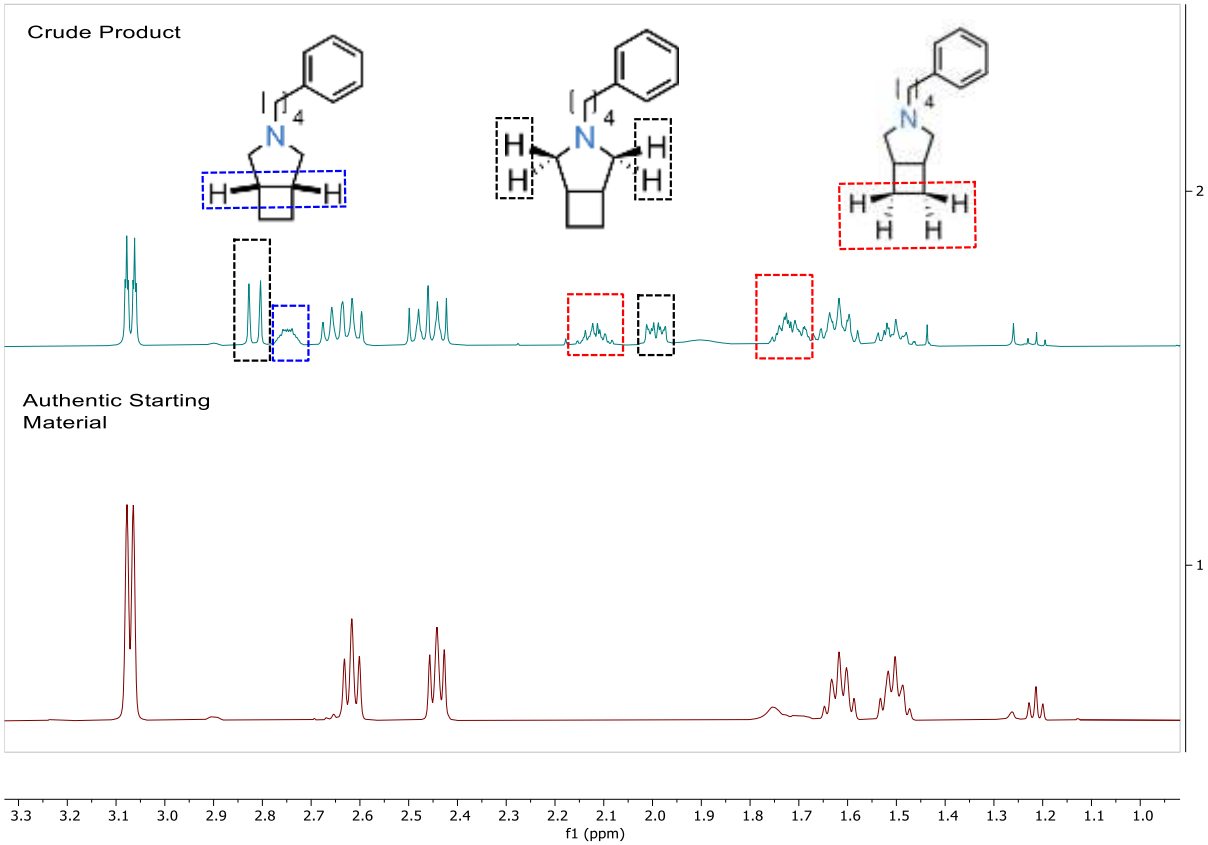


Figure 4. Characteristic diasteretopic protons of the [2+2] cycloadduct present indicating towards the synthesis of the desired product **2n**.

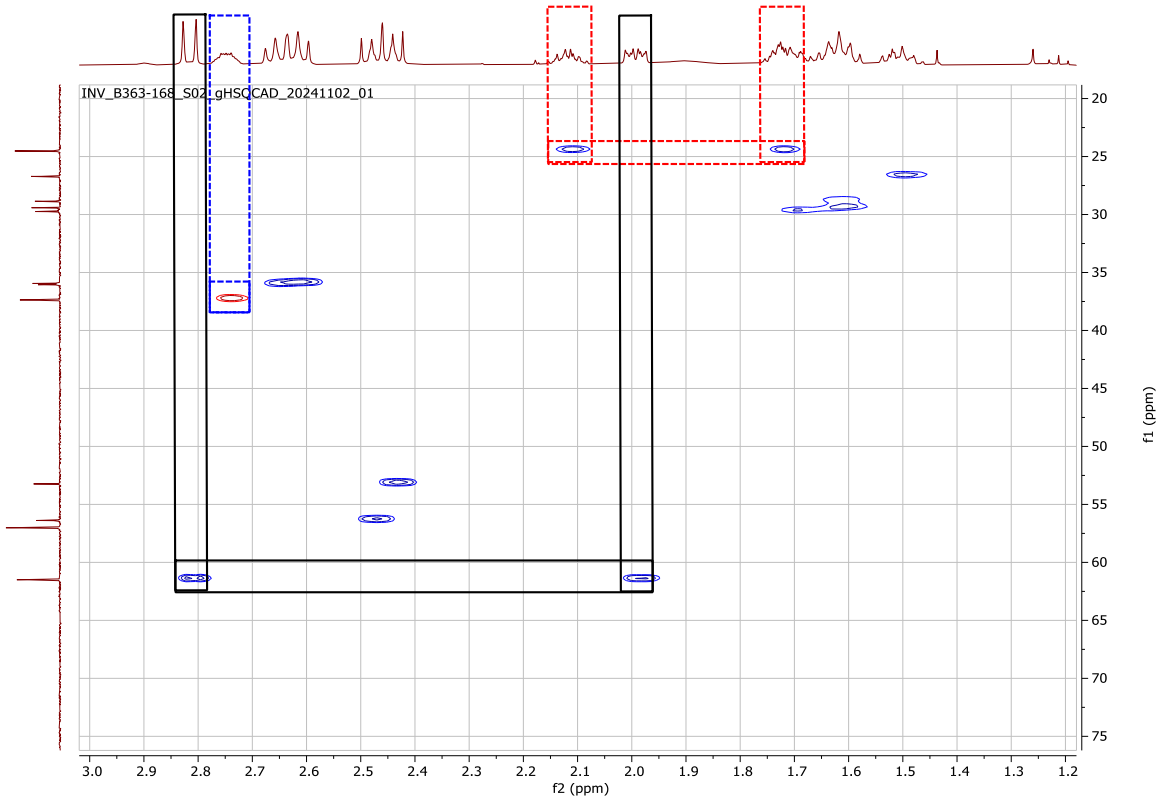


Figure 5. Characteristic diasteretopic protons of the [2+2] cycloadducts present indicating towards the synthesis of the desired product **2n**.

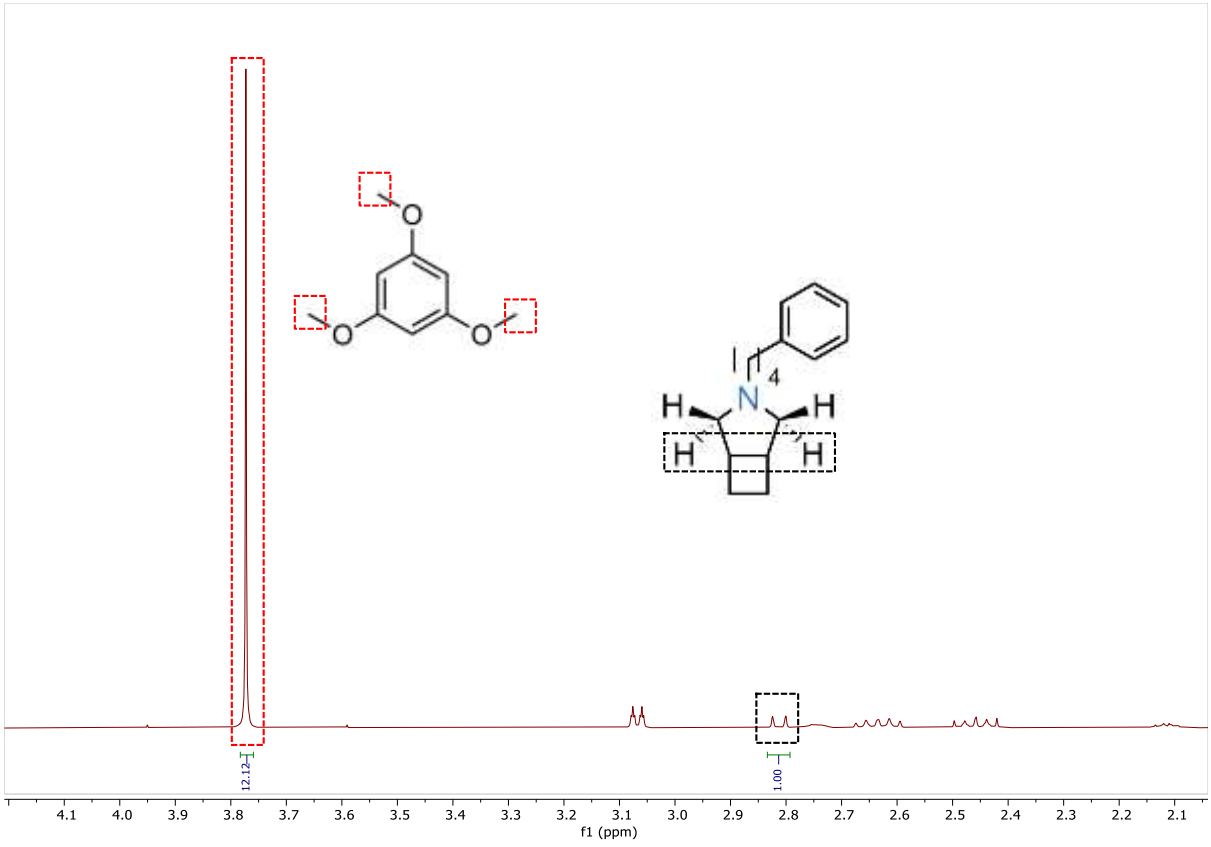


Figure 6. qNMR showing relative integrations of the diastereotopic protons of **2n** and the standard, 1,3,5-trimethoxybenzene.

Equation used for calculating the qNMR:

$$X = \left(\frac{(Product\ integration) \div (No.\ of\ Protons\ in\ Product\ Signal)}{(Internal\ Standard\ Integration) \div (No.\ of\ protons\ in\ Internal\ Standard\ Signal)}\right)$$

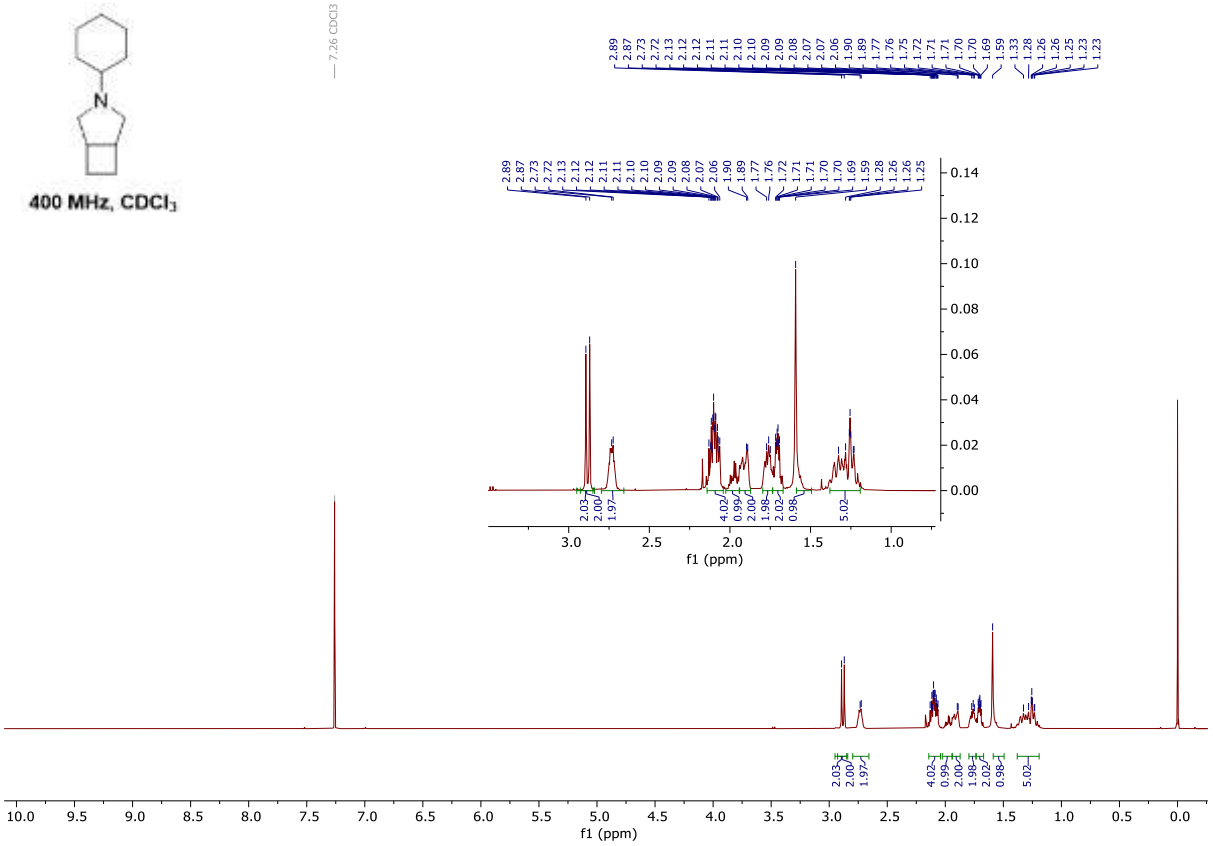
$$y = \left(\frac{(Mass\ of\ internal\ standard\ (mg)) \div (MW\ of\ Internal\ standard\ (\frac{mg}{mmol}))}{(Mass\ of\ Crude\ Material\ NMR\ Sample\ (mg)) \div (Mass\ of\ crude\ Product\ (mg))}\right)$$

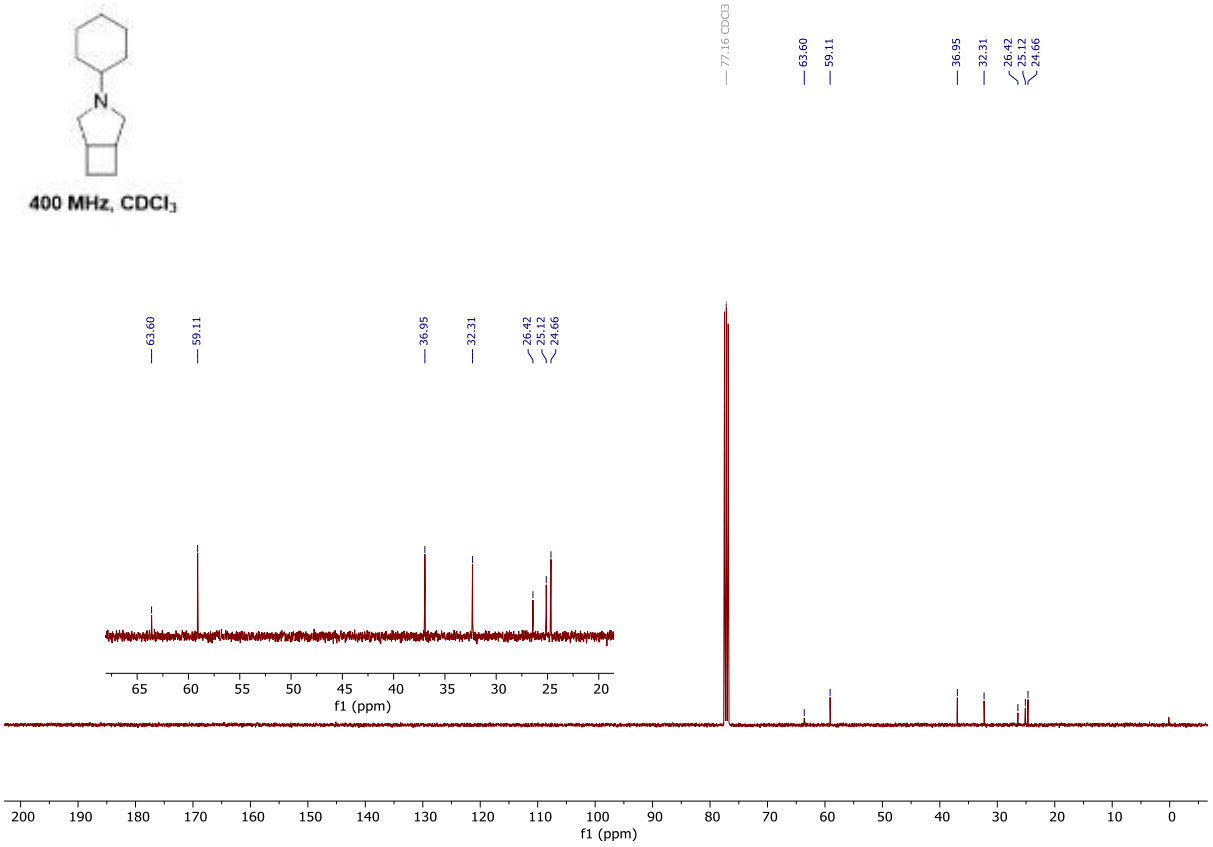
$$\boldsymbol{Yield\ of\ Product}\ (\%) = \big((\boldsymbol{x}) * (\boldsymbol{y})\big) \div \boldsymbol{Starting\ material}\ (\boldsymbol{mmol})\big) \times \mathbf{100}$$

Table 2. qNMR sample measurements for 2n	
Crude mass (mg)	44
NMR sample (mg)	7.4
Standard sample (mg)	5.9
Product integration	1
Number of protons	2
Standard integration	12.12
Number of protons	9
NMR Yield (%)	**20.38**

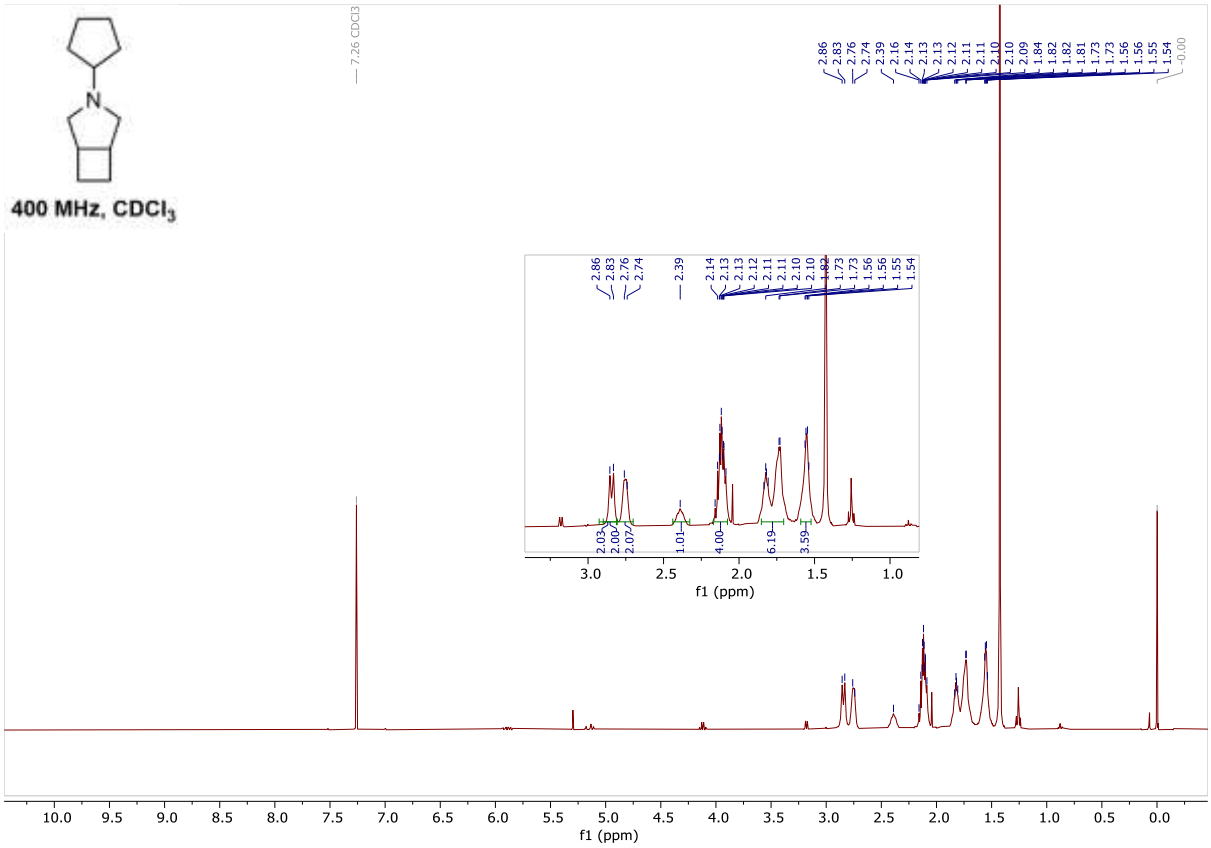
5. Spectroscopic Data

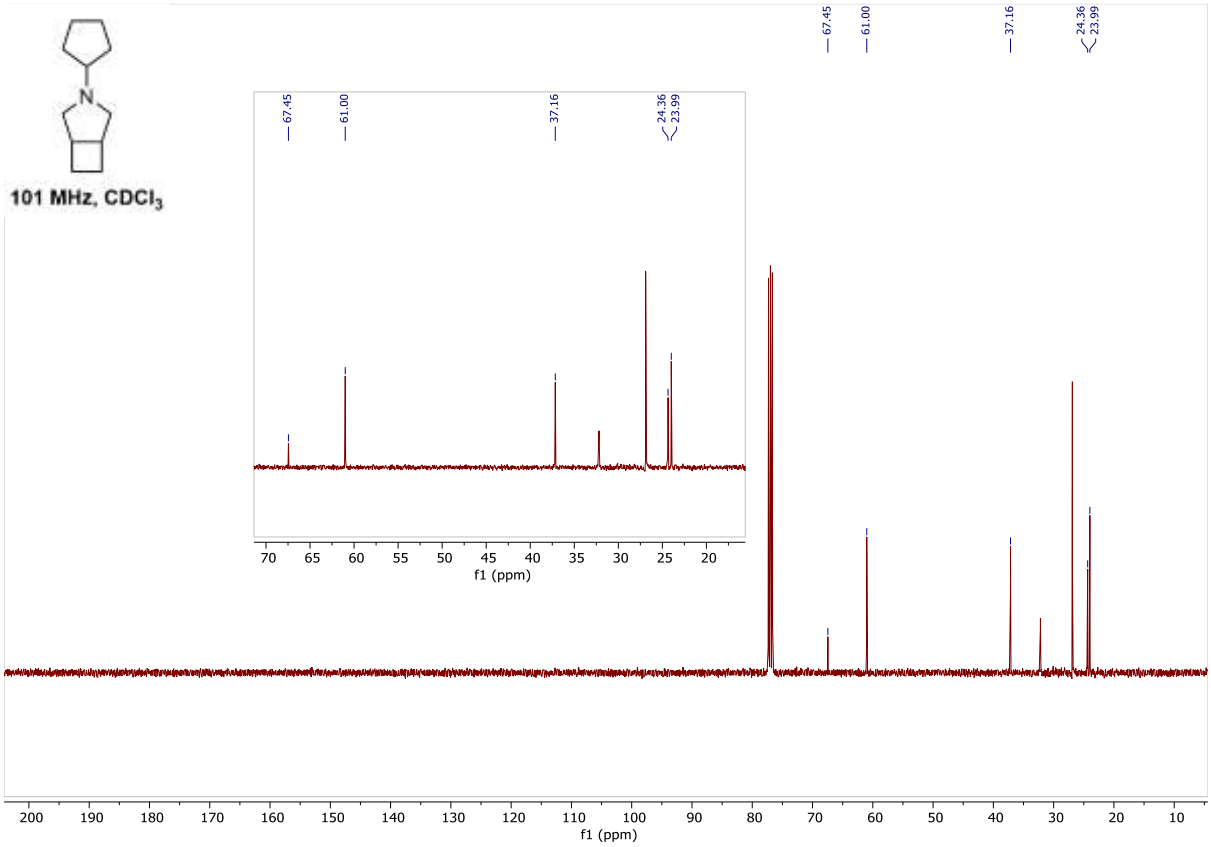
3-cyclohexyl-3-azabicyclo[3.2.0]heptane (2a), 400 MHz, $CDCl_3$



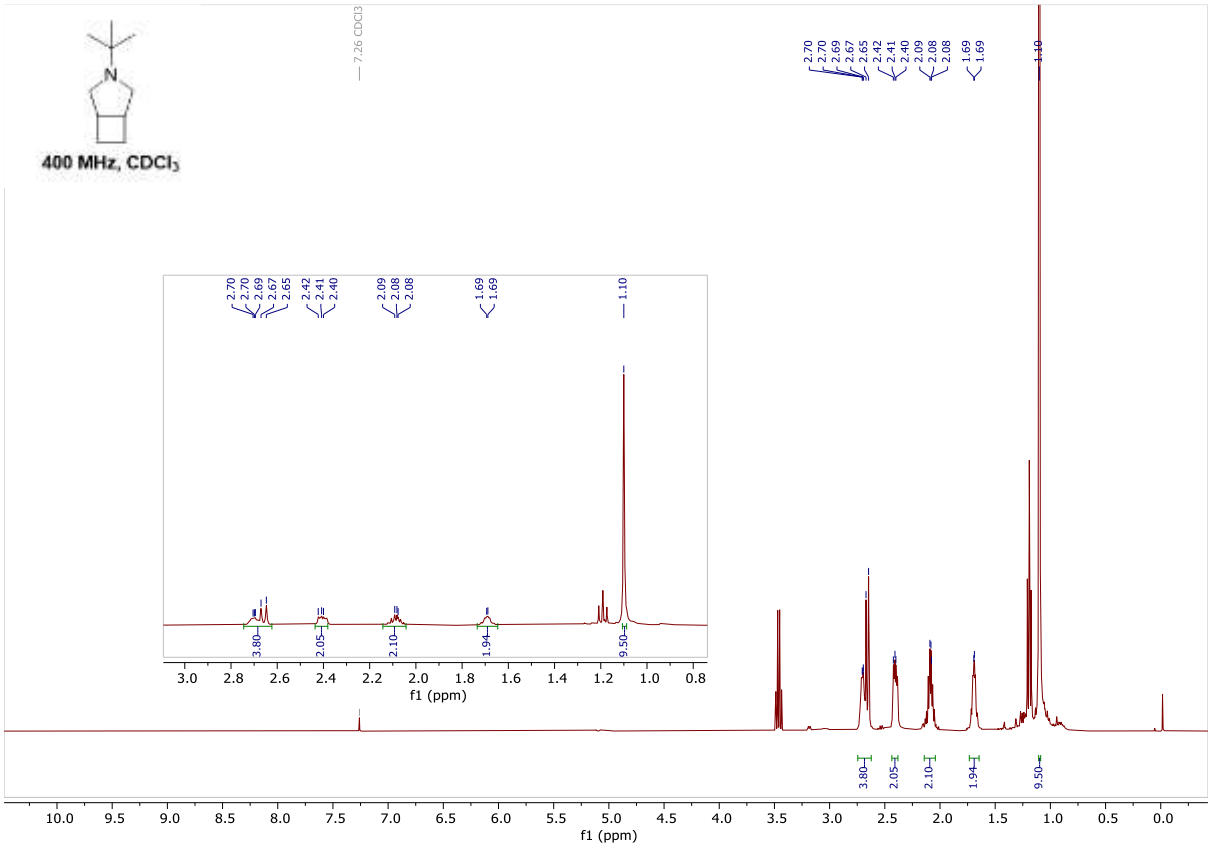


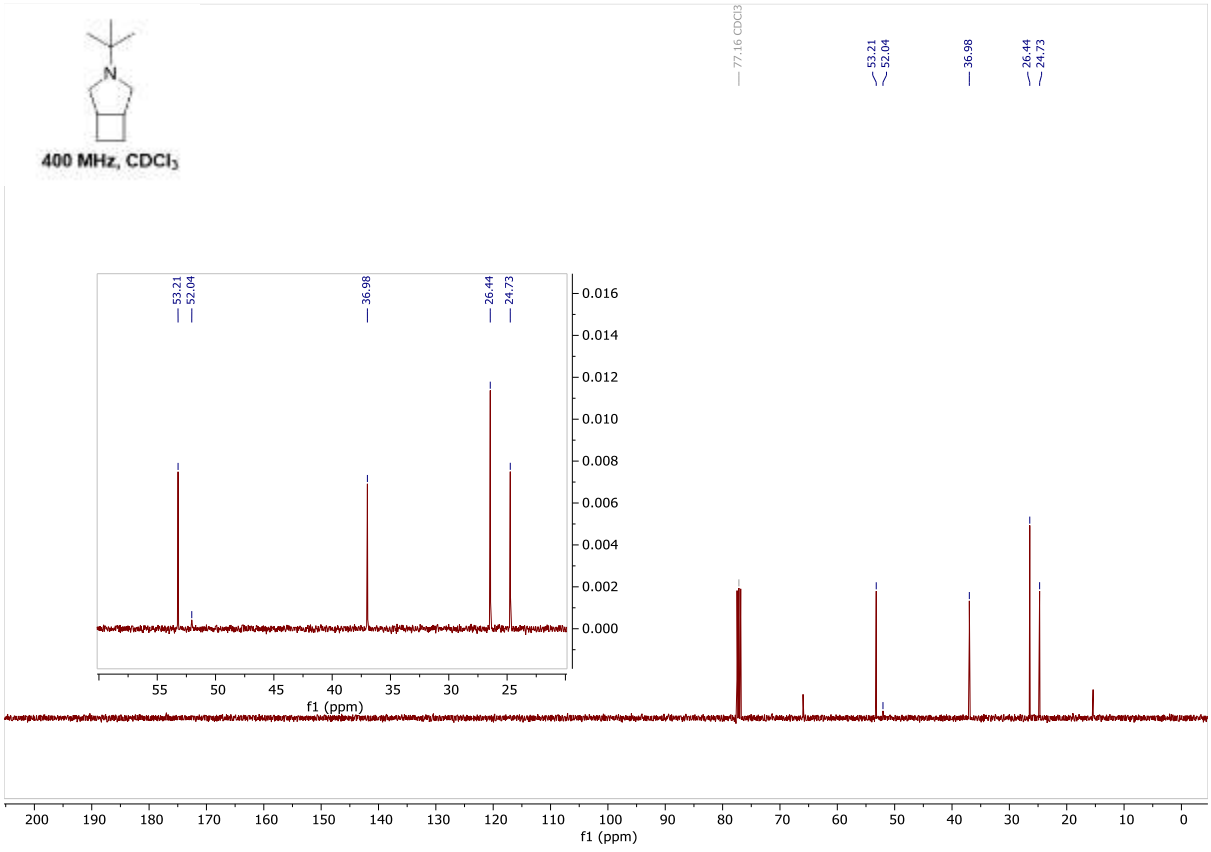
3-cyclopentyl-3-azabicyclo[3.2.0]heptane (2b), 400 MHz, $CDCl_3$



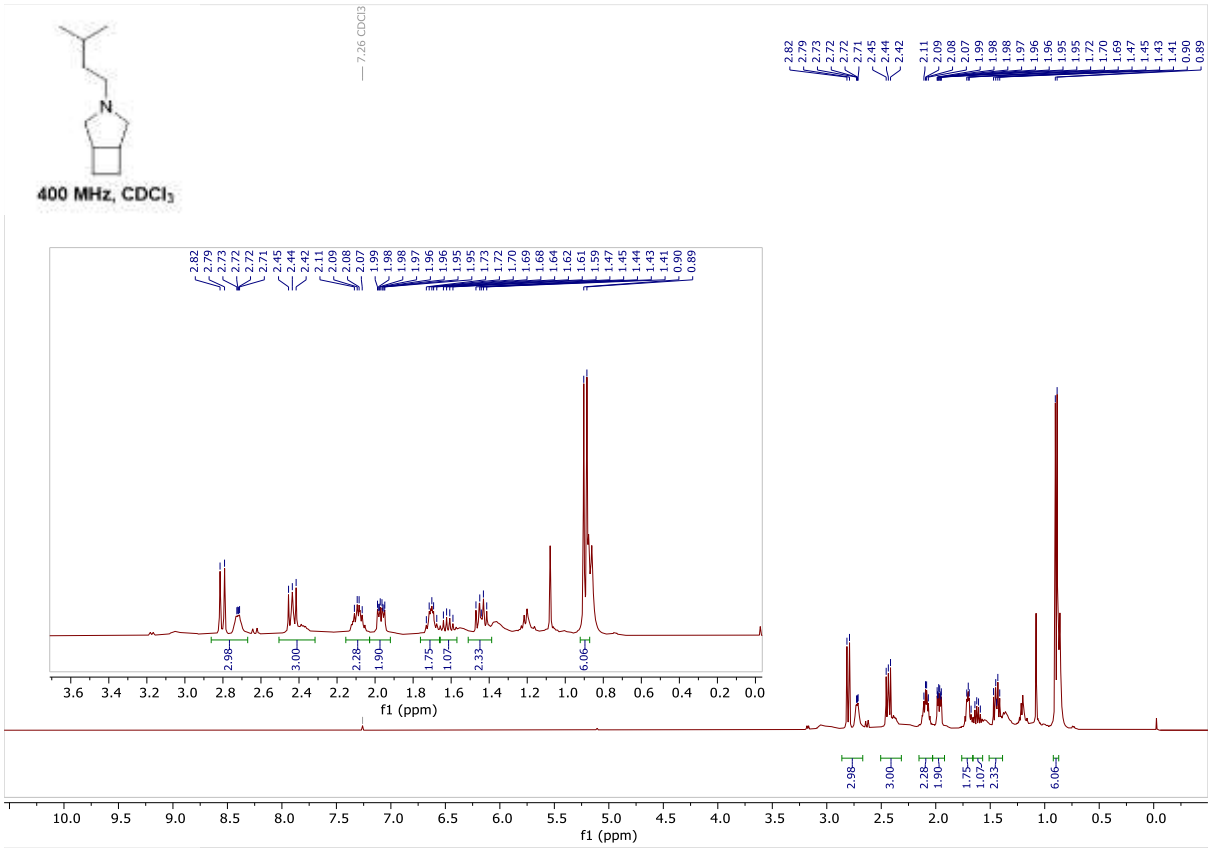


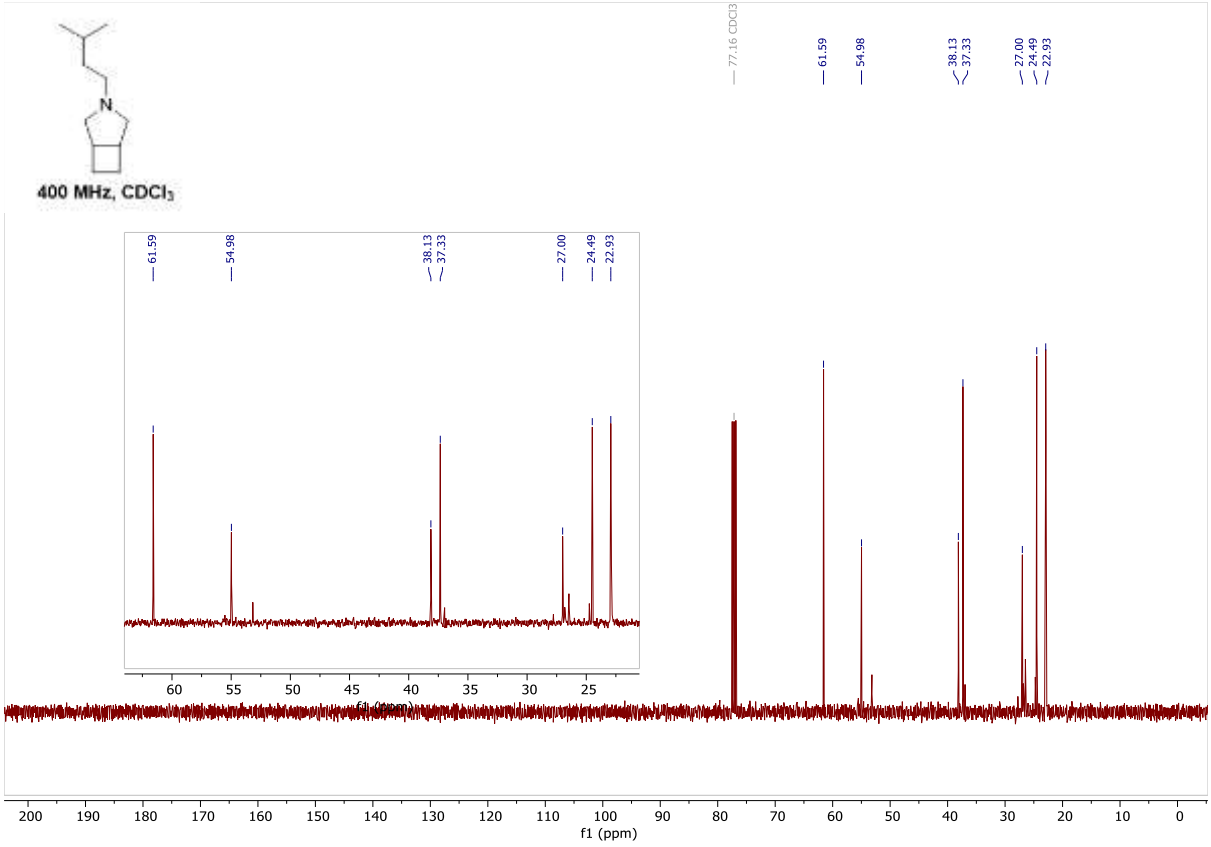
3-(tert-butyl)-3-azabicyclo[3.2.0]heptane (2c), 400 MHZ, $CDCl_3$



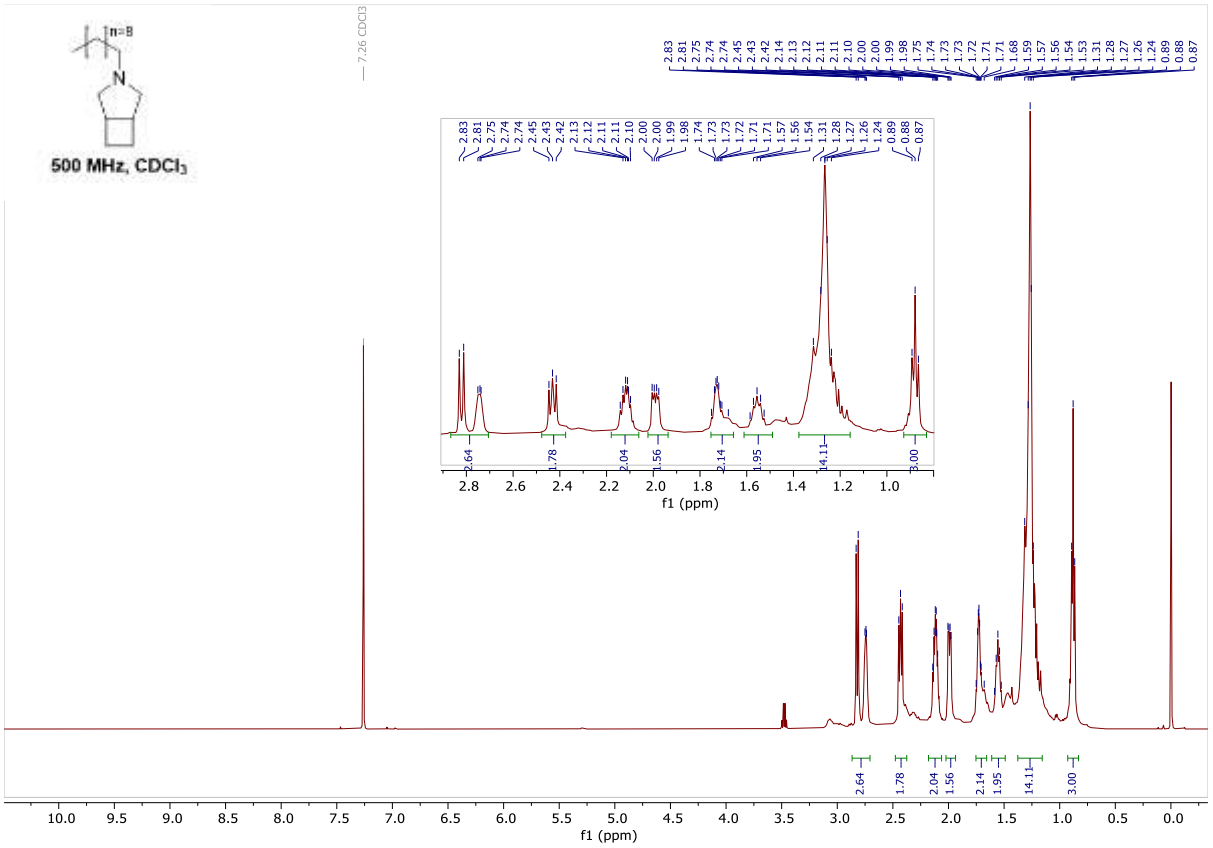


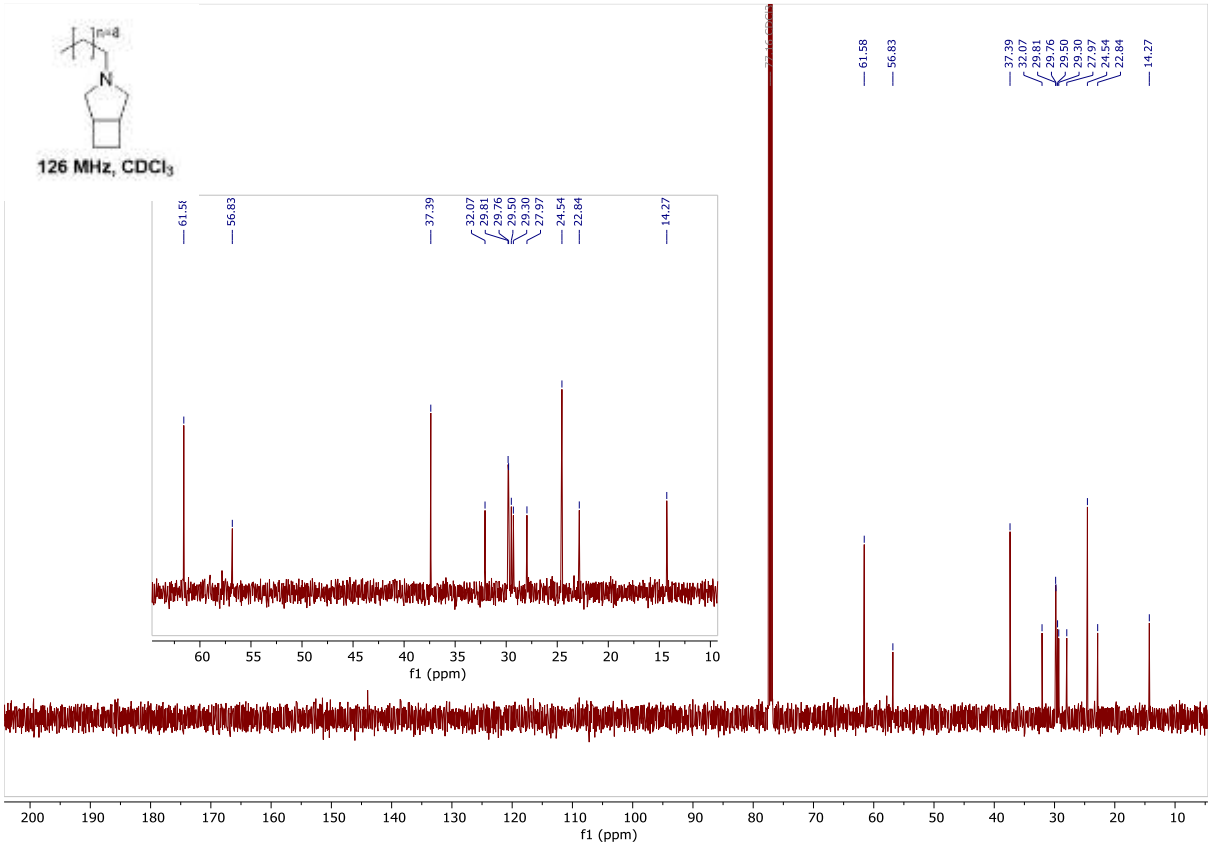
3-isopentyl-3-azabicyclo[3.2.0]heptane (2d), 400 MHz, $CDCl_3$



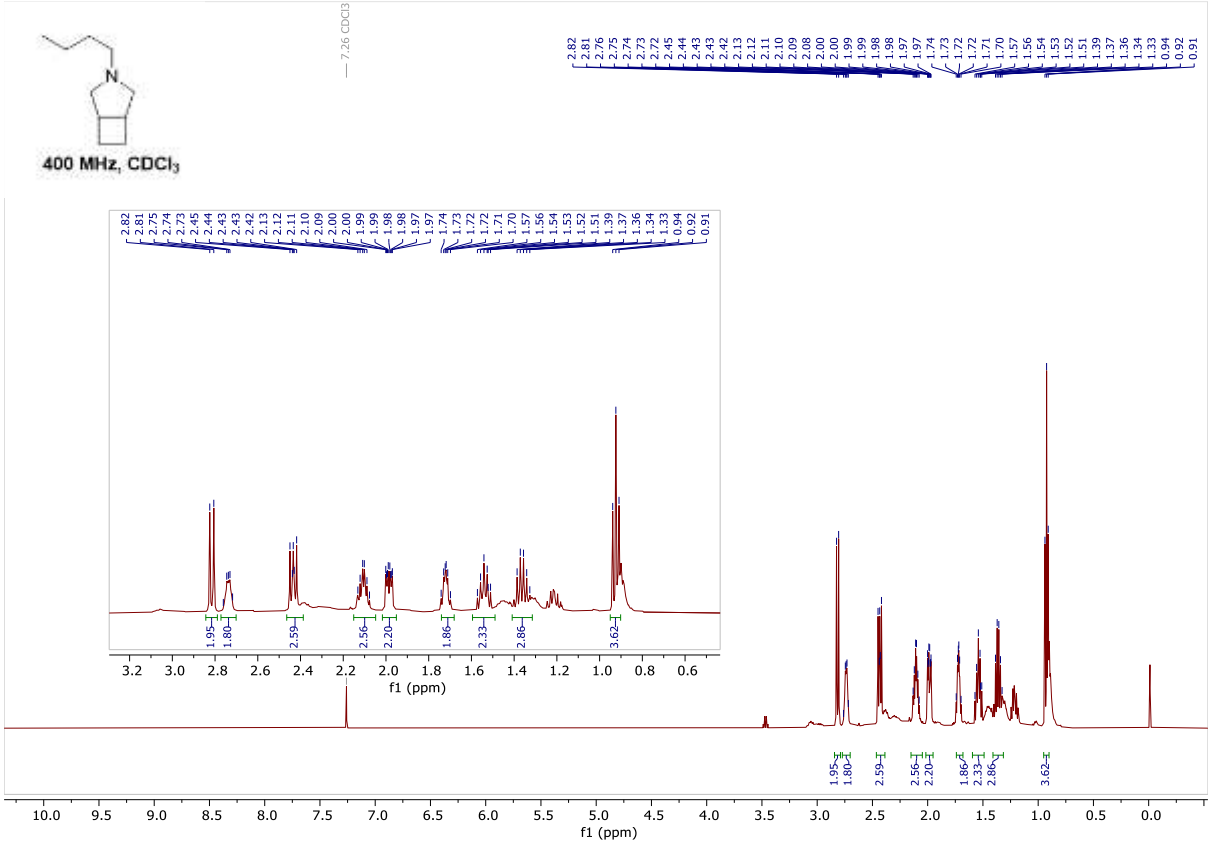


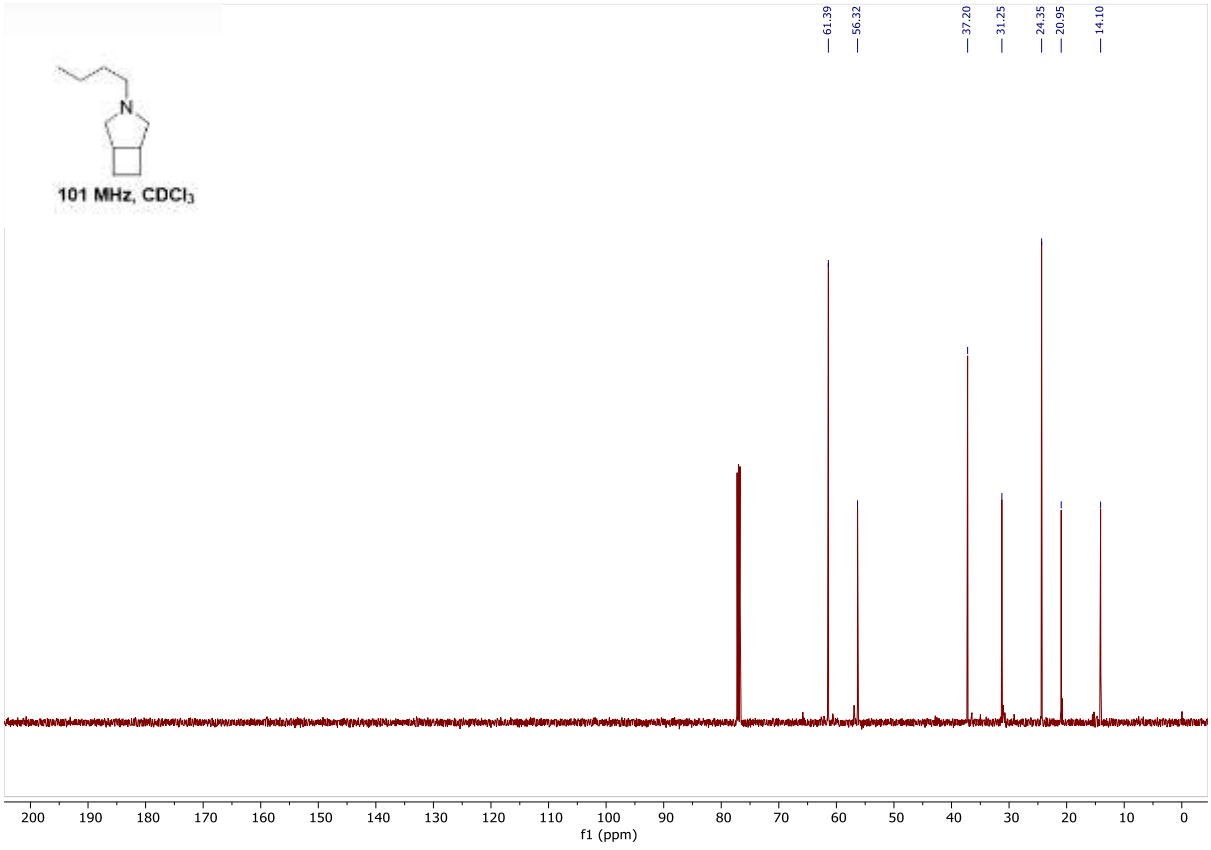
3-decyl-3-azabicyclo[3.2.0]heptane (2e), 500 MHz, $CDCl_3$



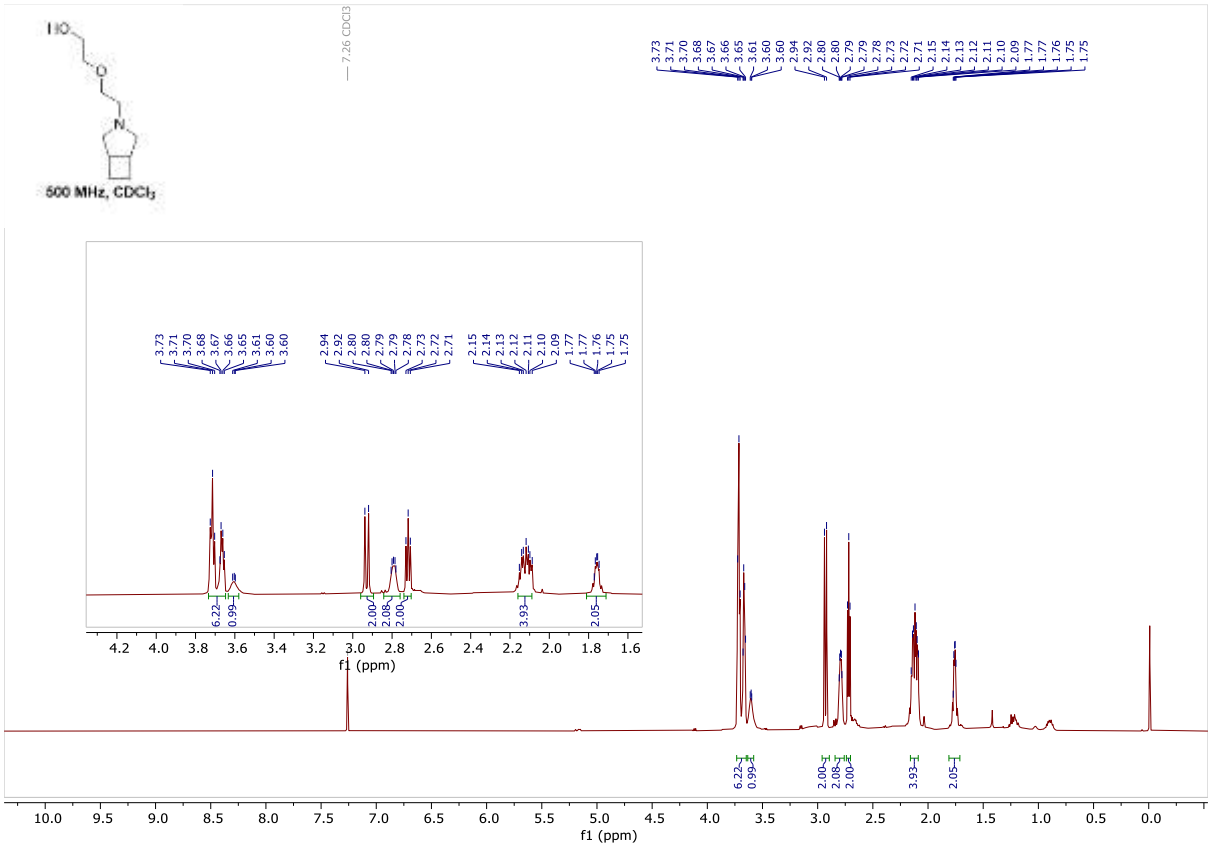


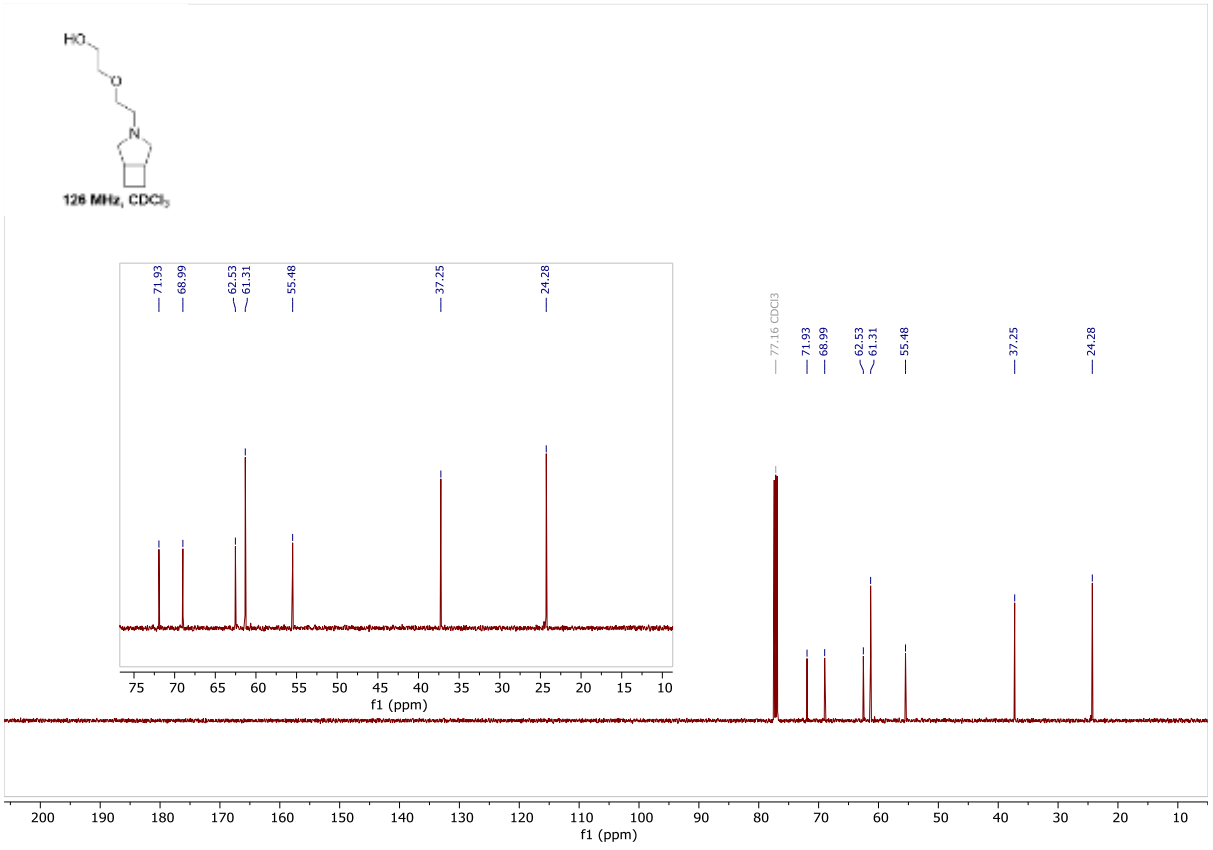
3-butyl-3-azabicyclo[3.2.0]heptane (2f), 500 MHz, $CDCl_3$



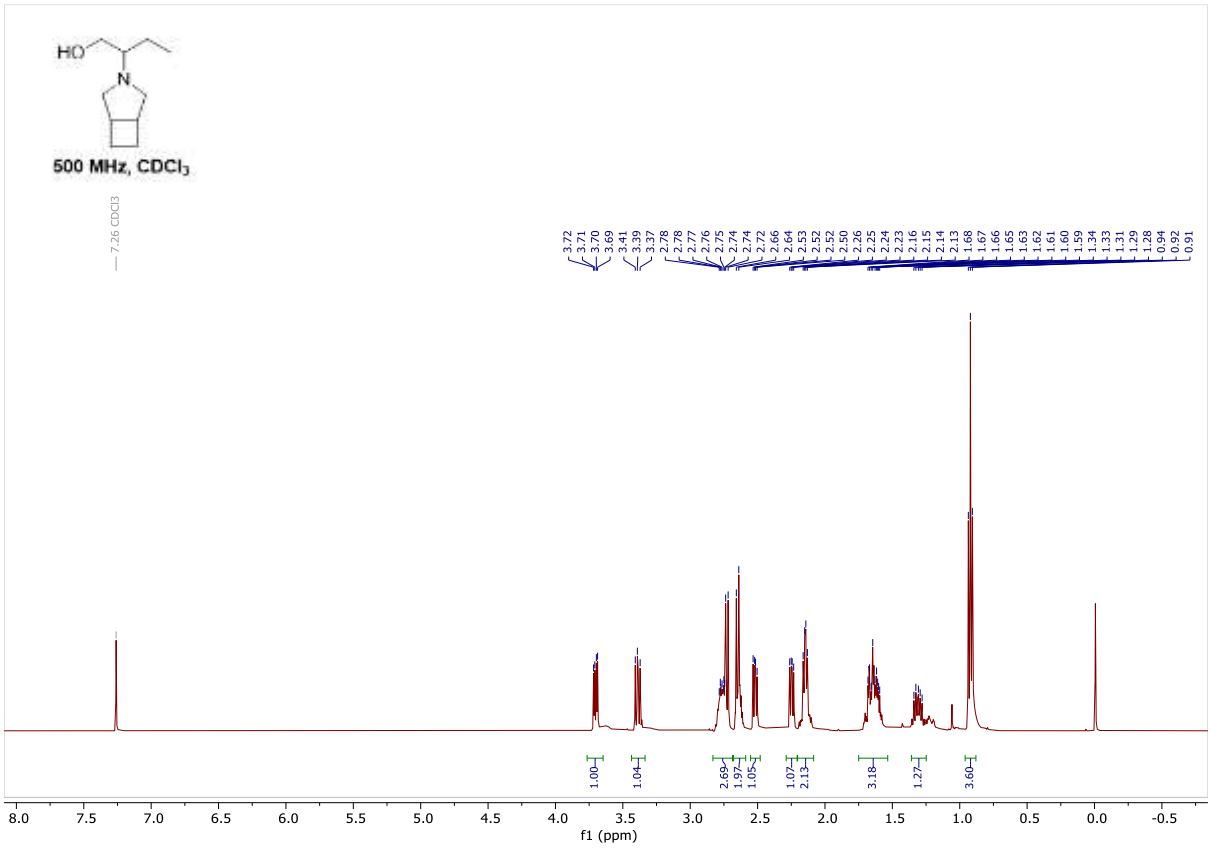


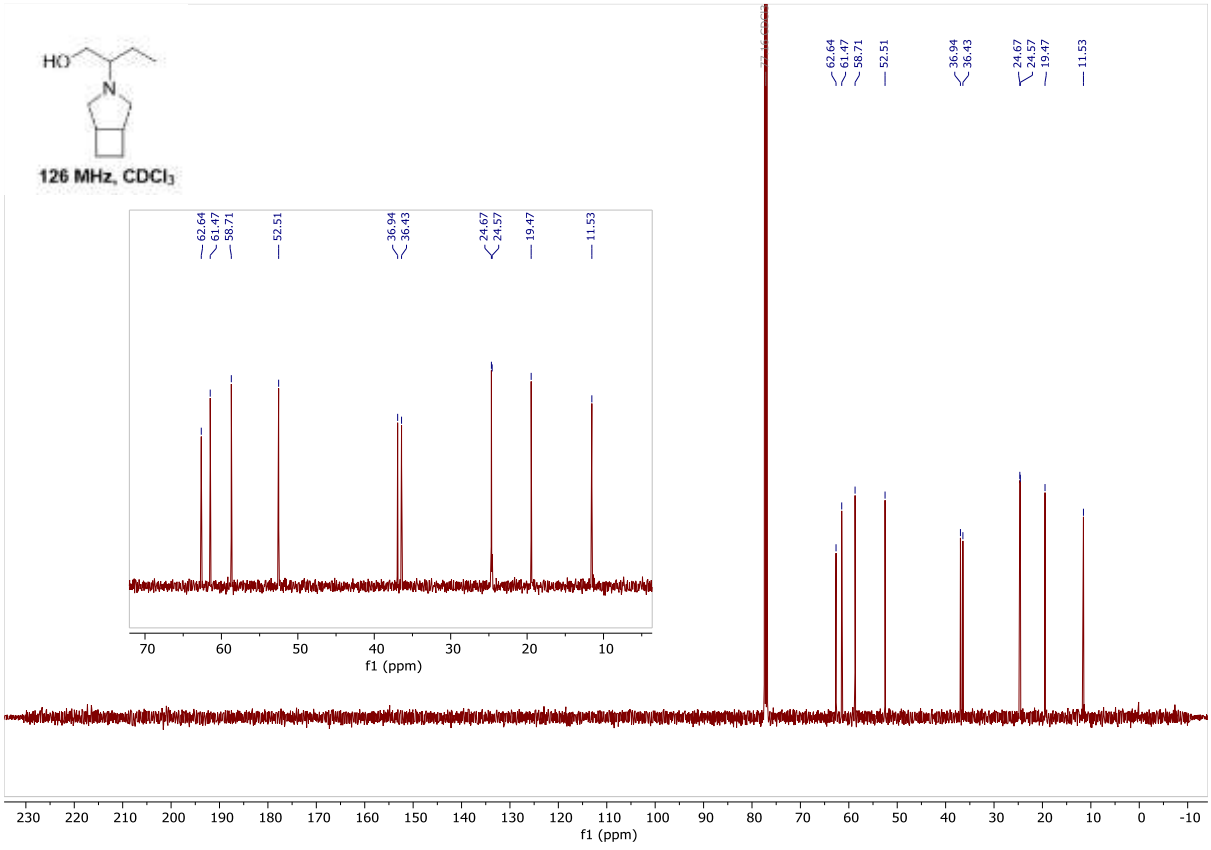
2-(2-(3-azabicyclo[3.2.0]heptan-3-yl)ethoxy)ethan-1-ol (2g), 500 MHz, $CDCl_3$



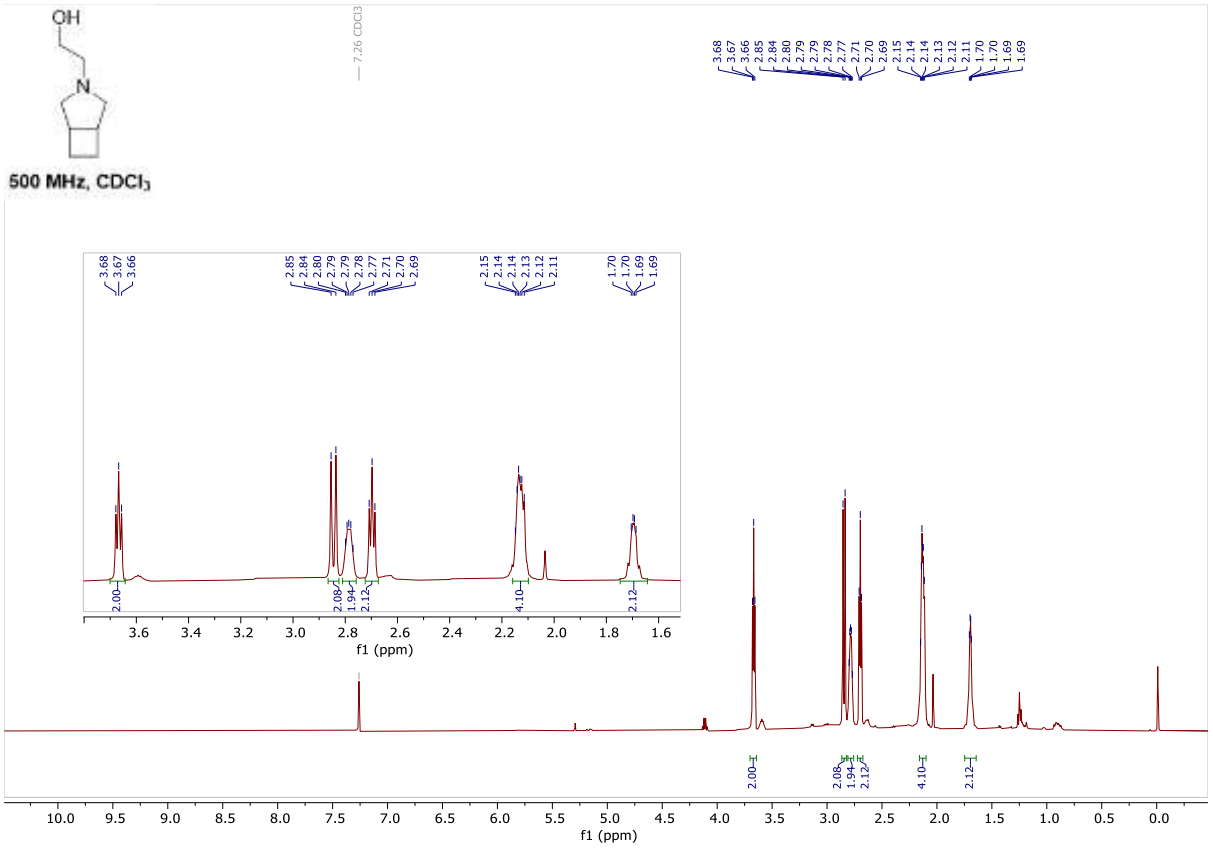


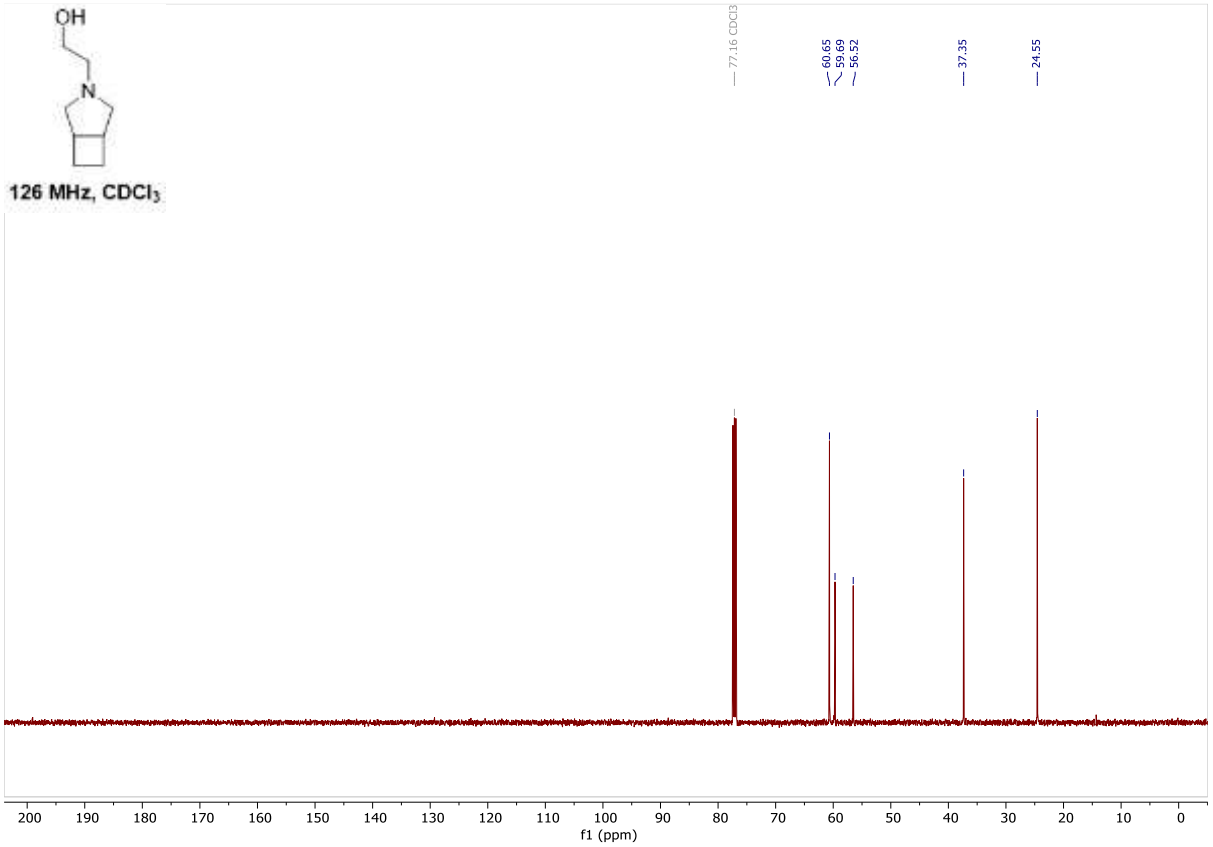
2-(3-azabicyclo[3.2.0]heptan-3-yl)butan-1-ol (2h), 500 MHz, $CDCl_3$



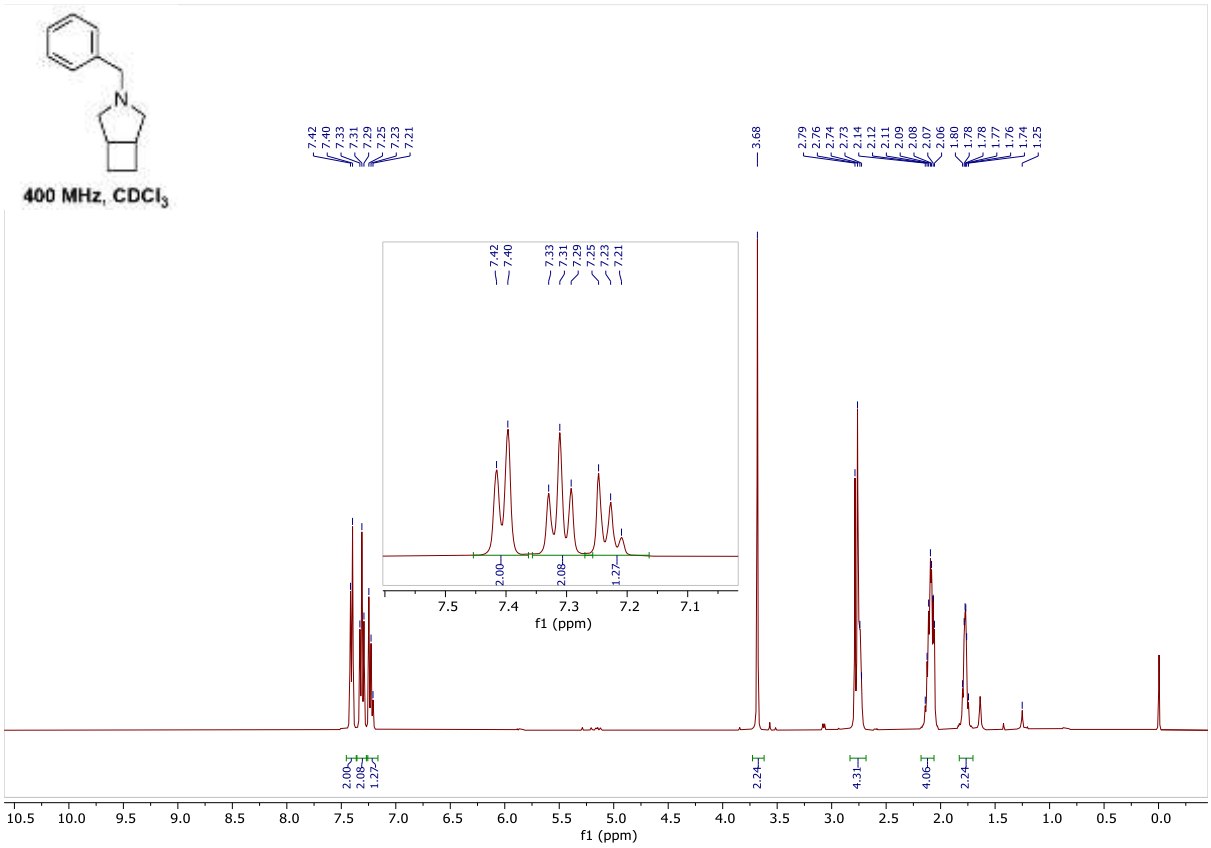


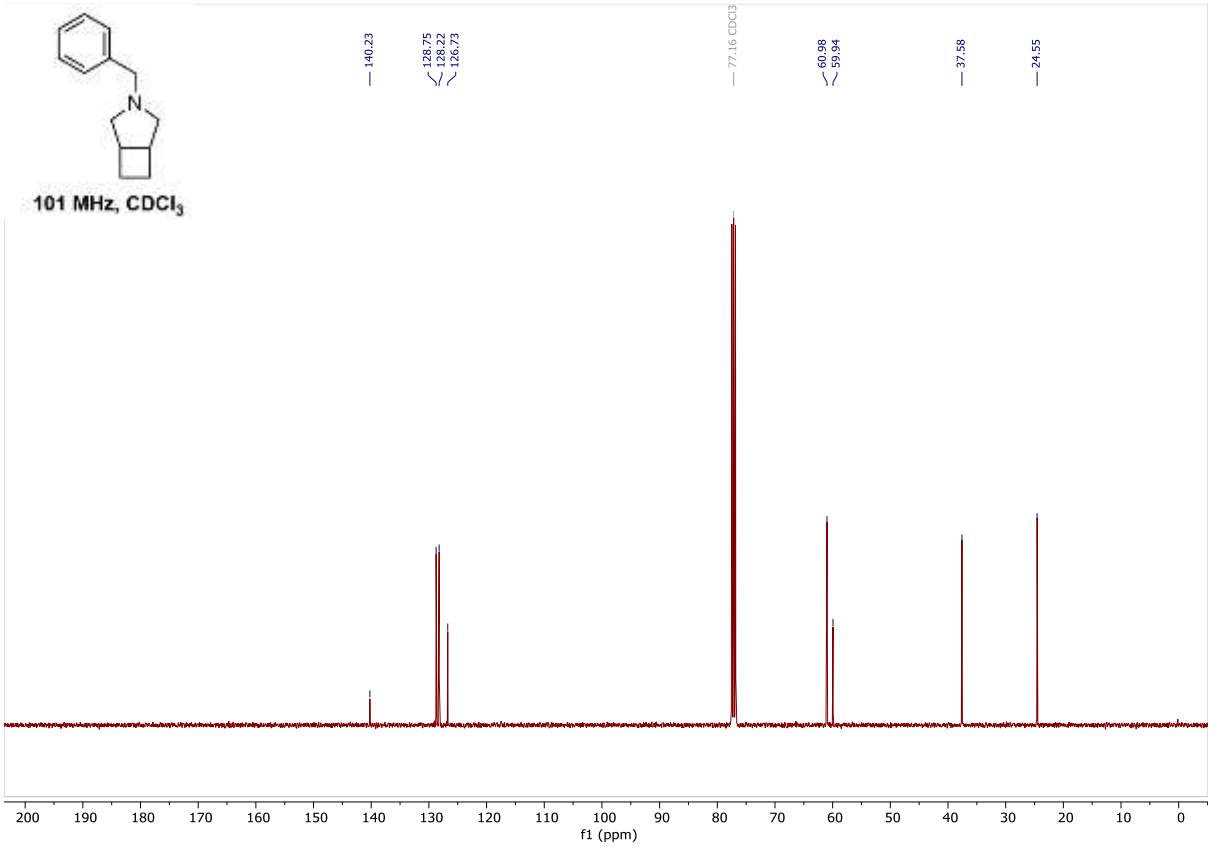
2-(3-azabicyclo[3.2.0]heptan-3-yl)ethan-1-ol (2i), 500 MHz, $CDCl_3$



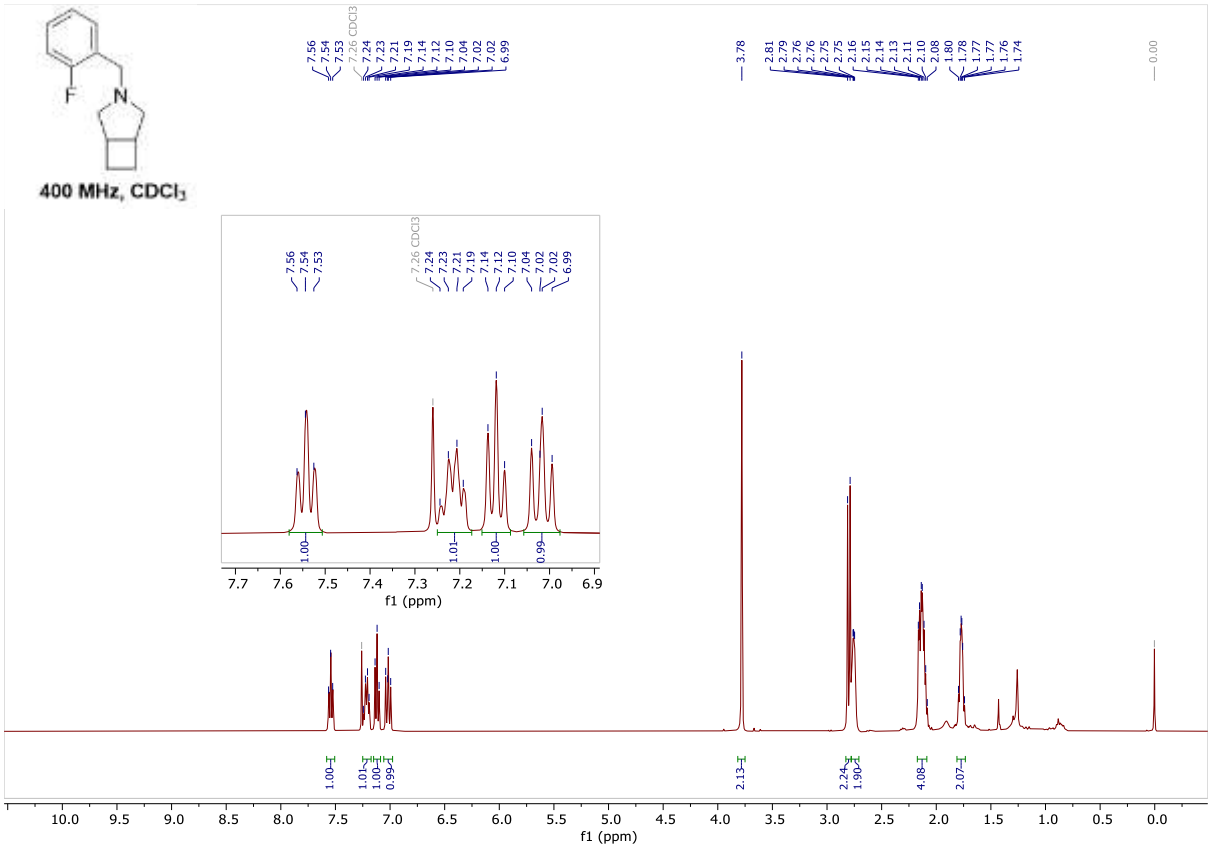


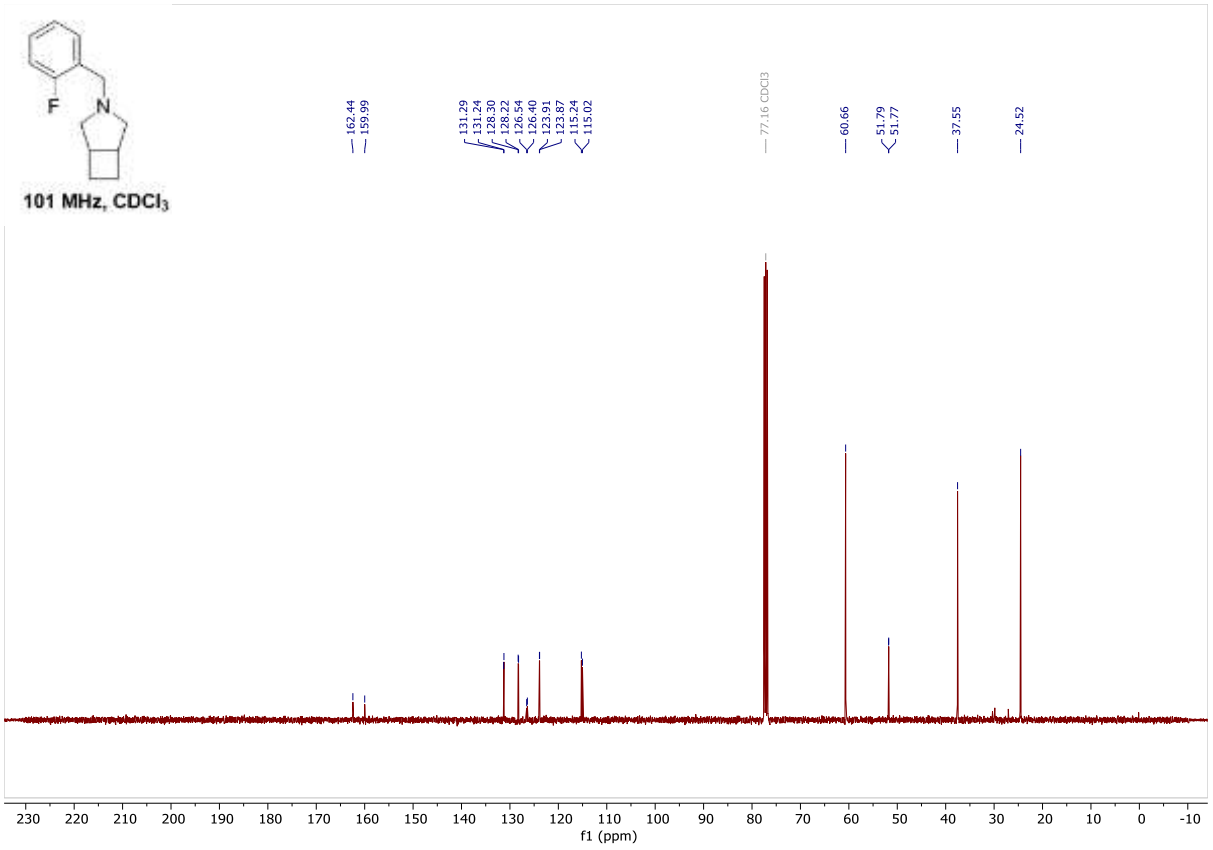
3-benzyl-3-azabicyclo[3.2.0]heptane (2j), 400 MHz, $CDCl_3$



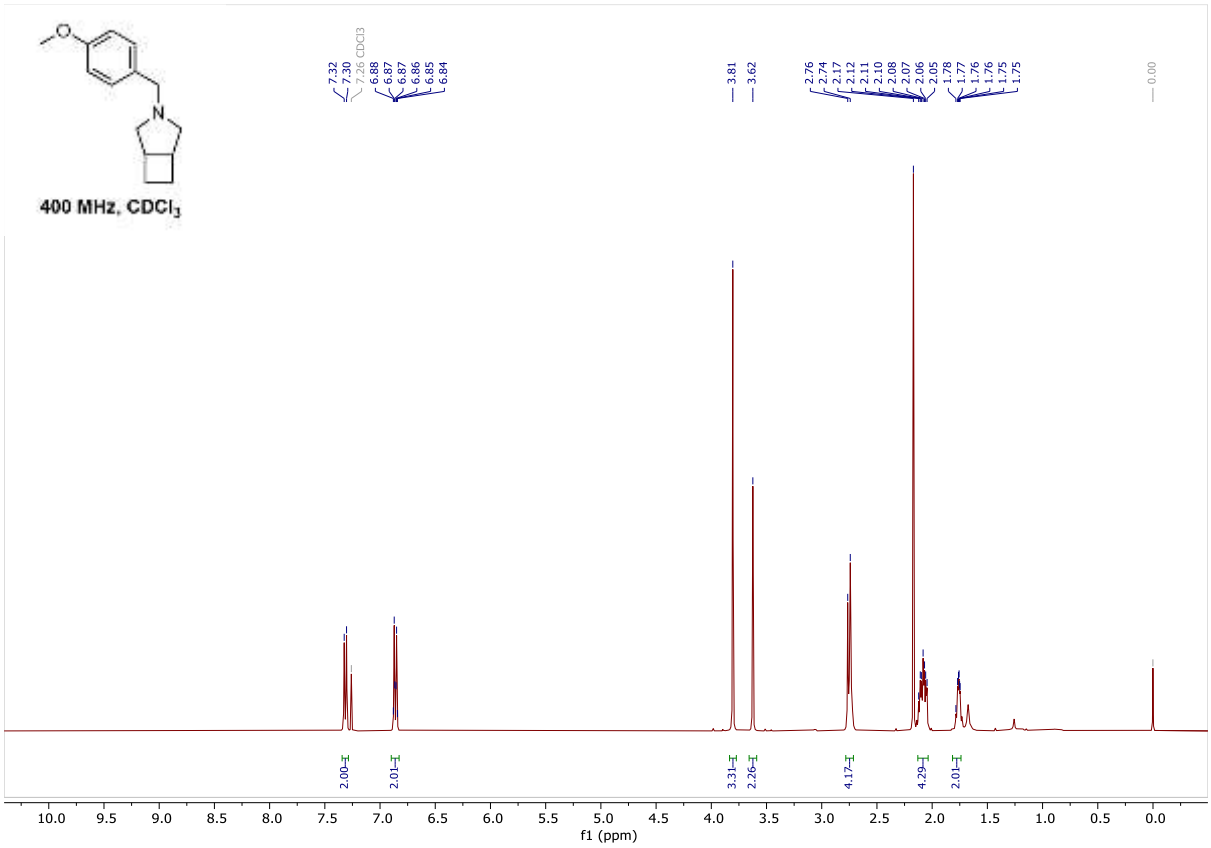


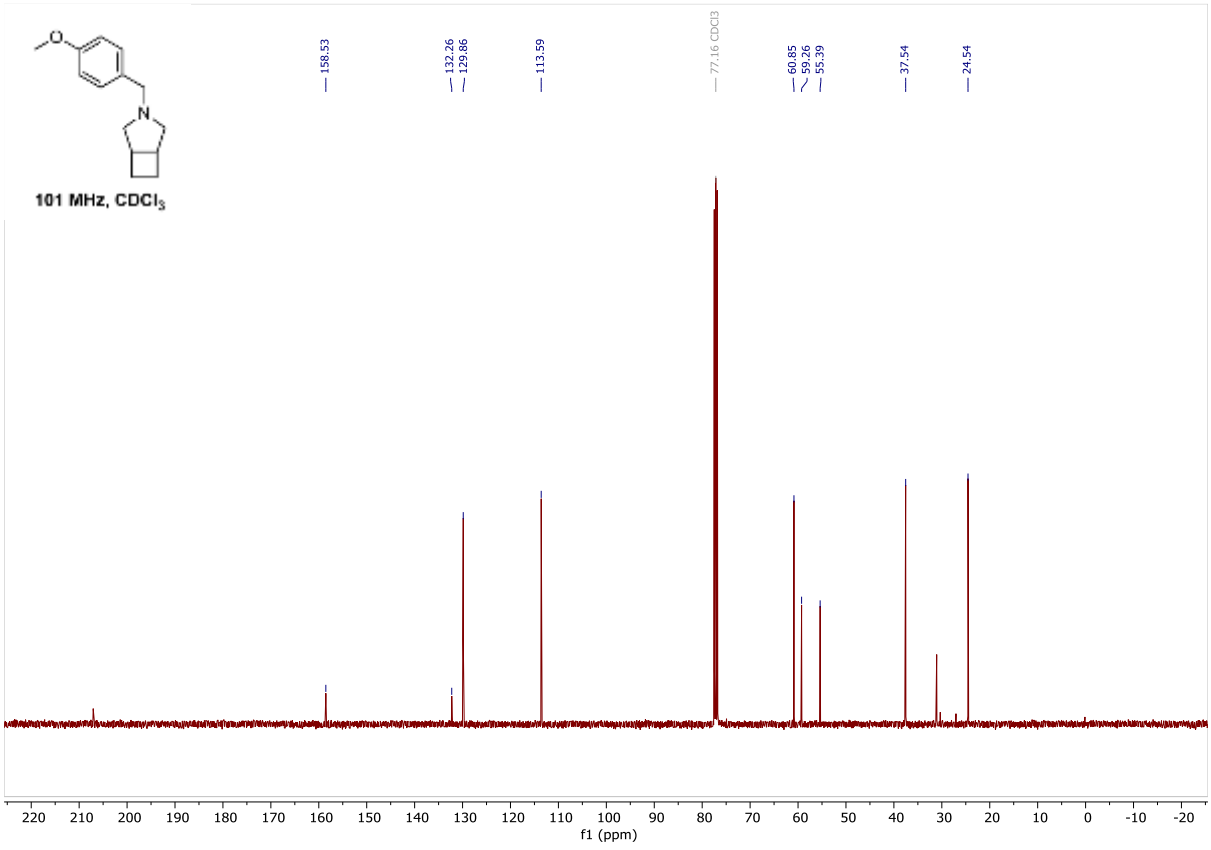
3-(2-fluorobenzyl)-3-azabicyclo[3.2.0]heptane (2k), 400 MHz, $CDCl_3$



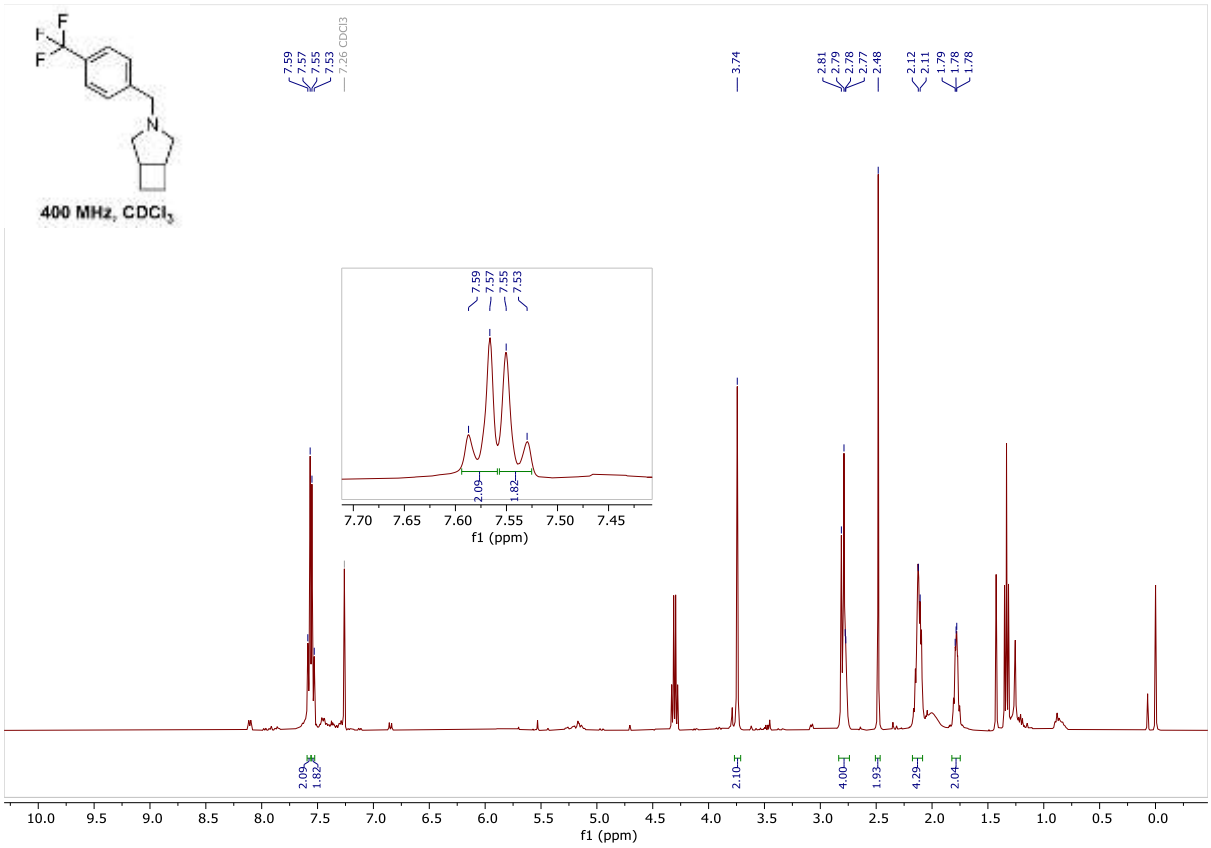


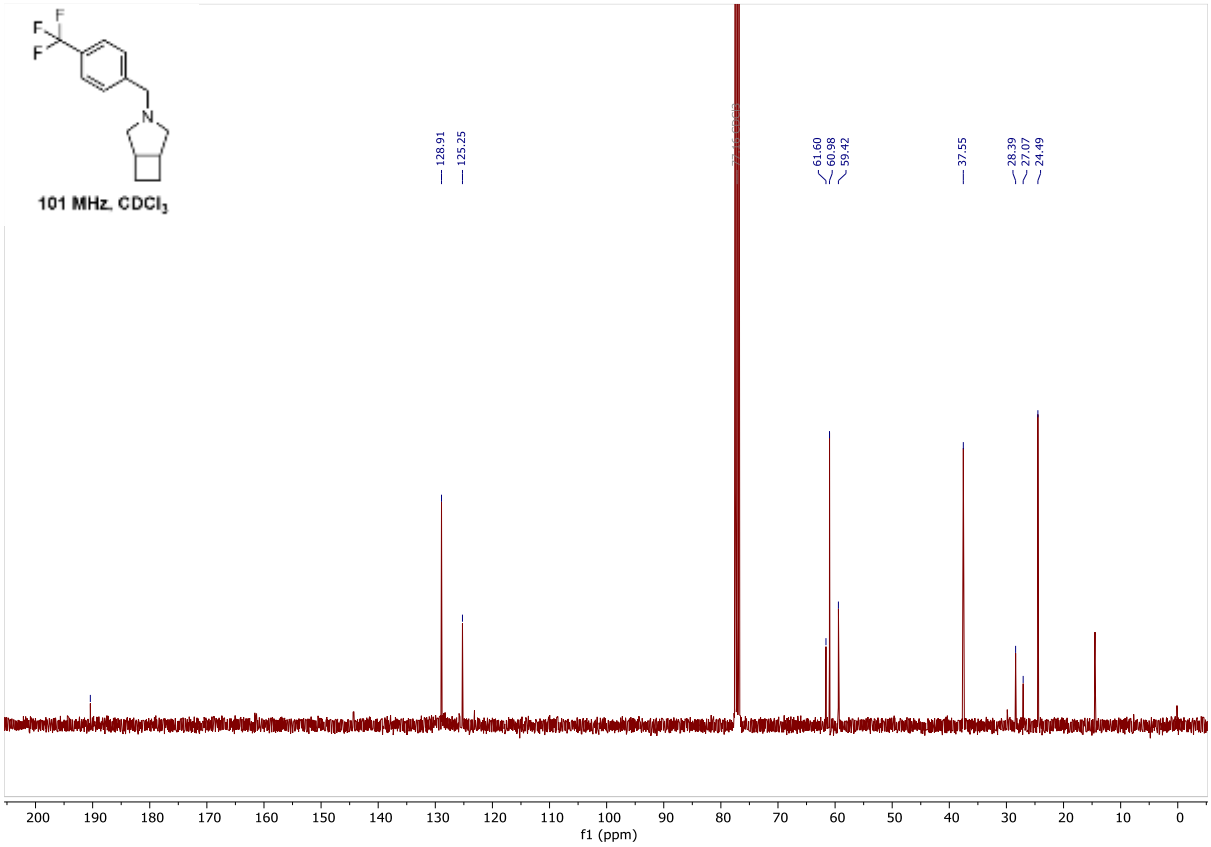
3-(4-methoxybenzyl)-3-azabicyclo[3.2.0]heptane (2l), 400 MHz, $CDCl_3$



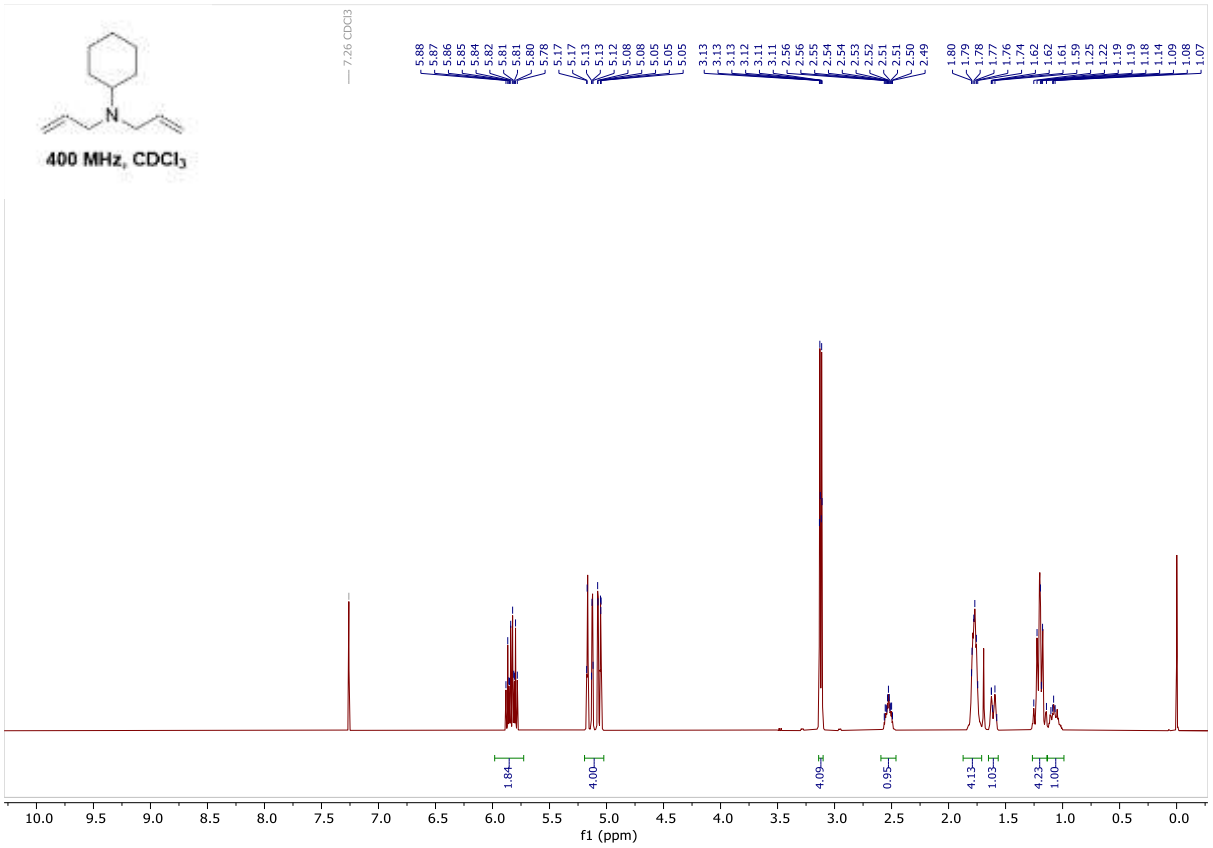


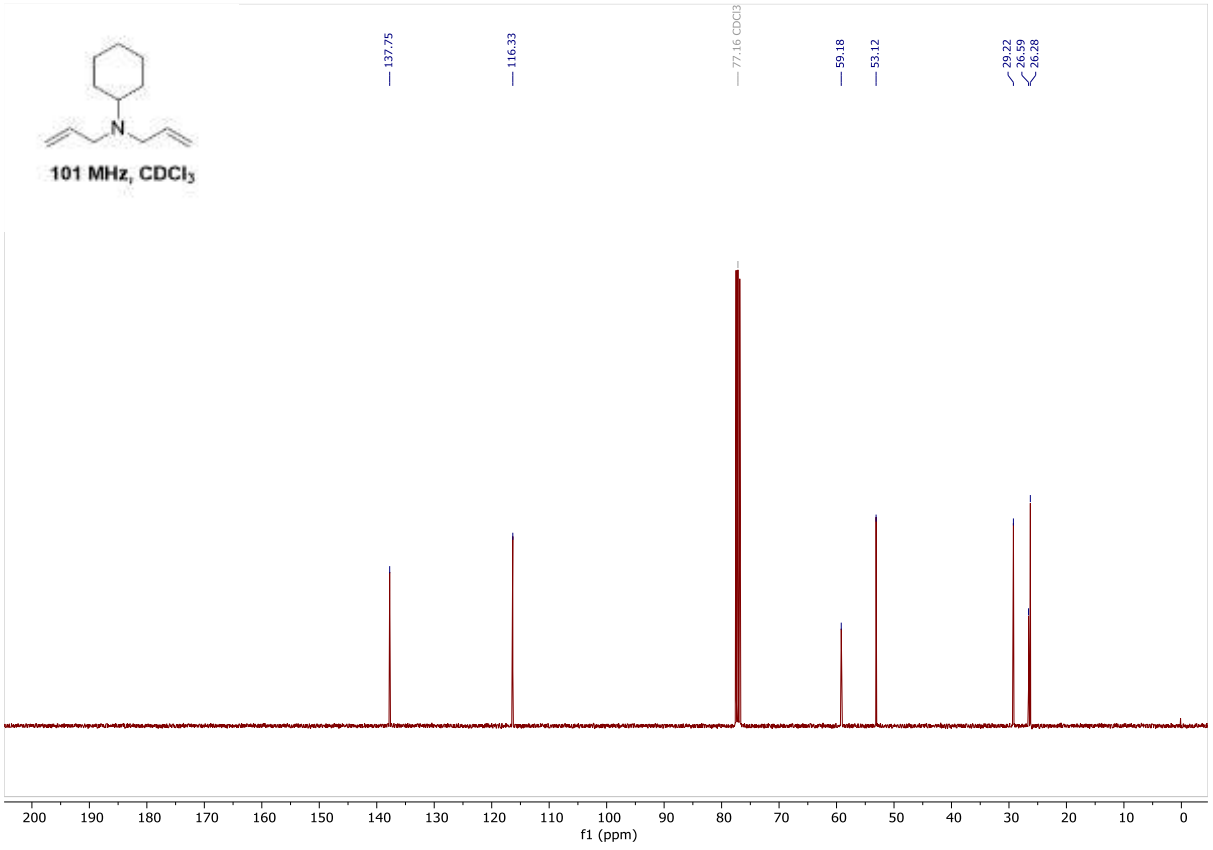
3-(4-(trifluoromethyl) benzyl)-3-azabicyclo[3.2.0]heptane (2m), 400 MHz, $CDCl_3$



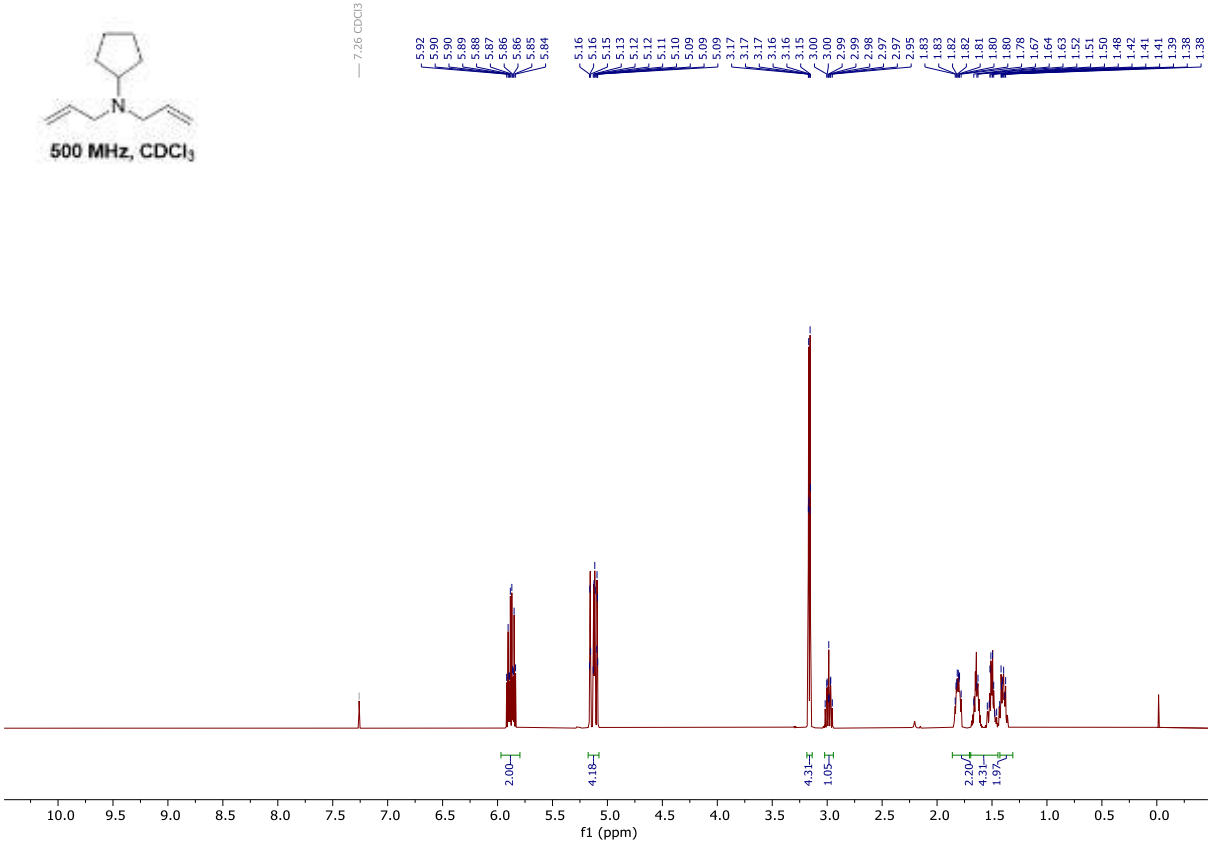


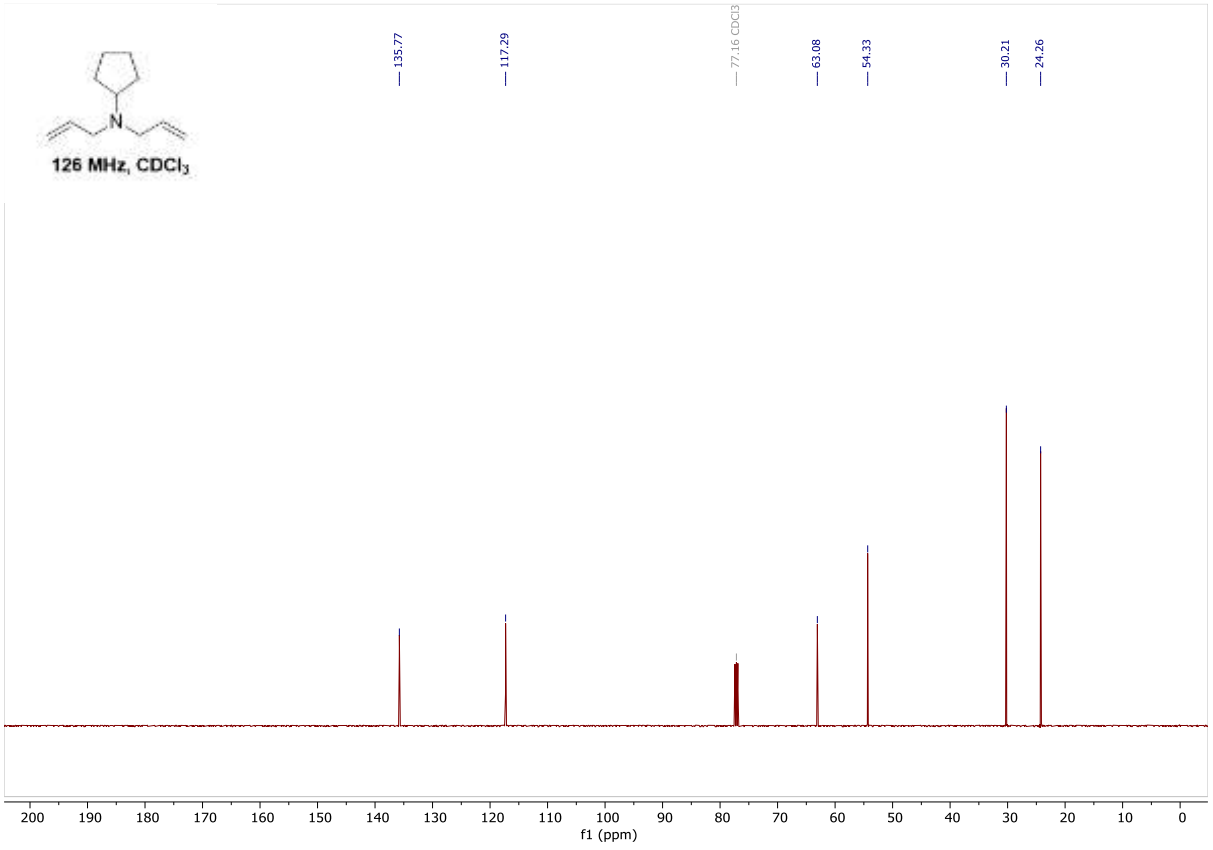
N,N-diallylcyclohexanamine (1a), 400 MHz, $CDCl_3$



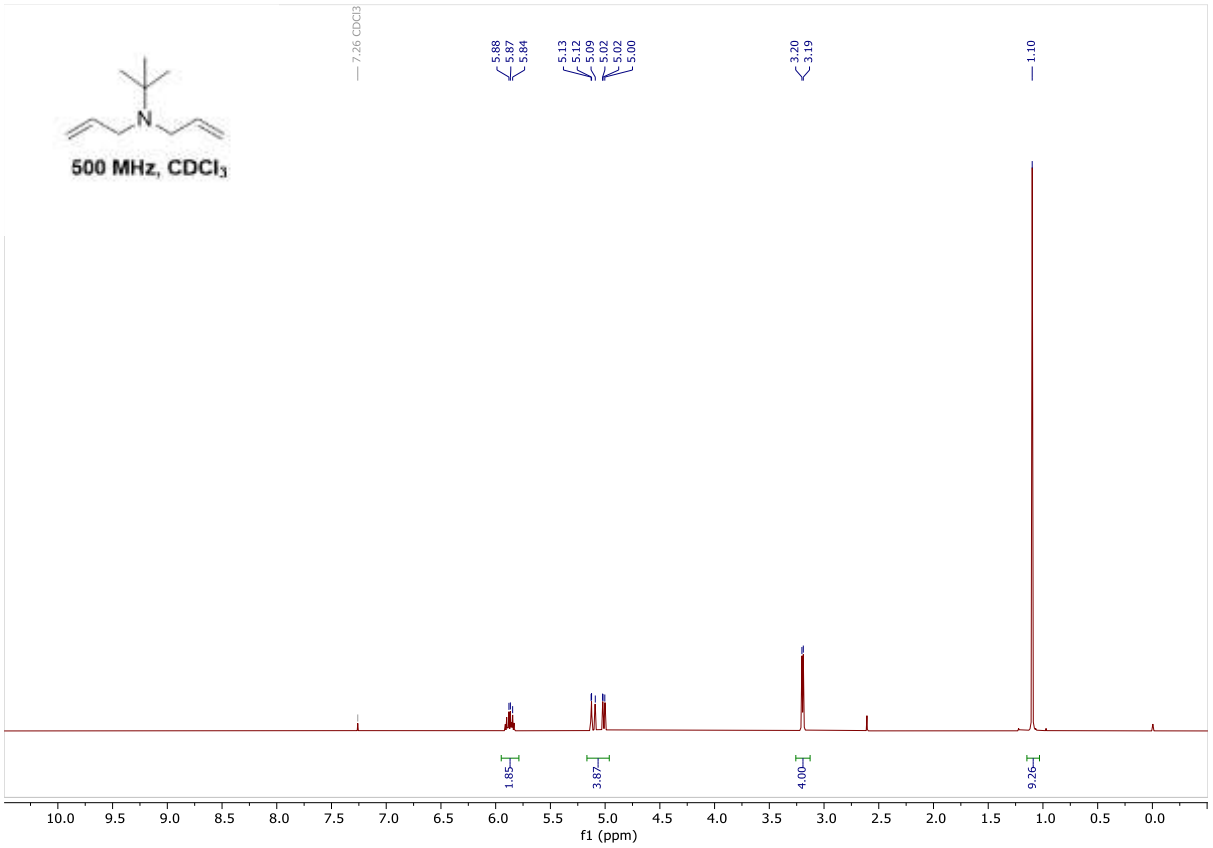


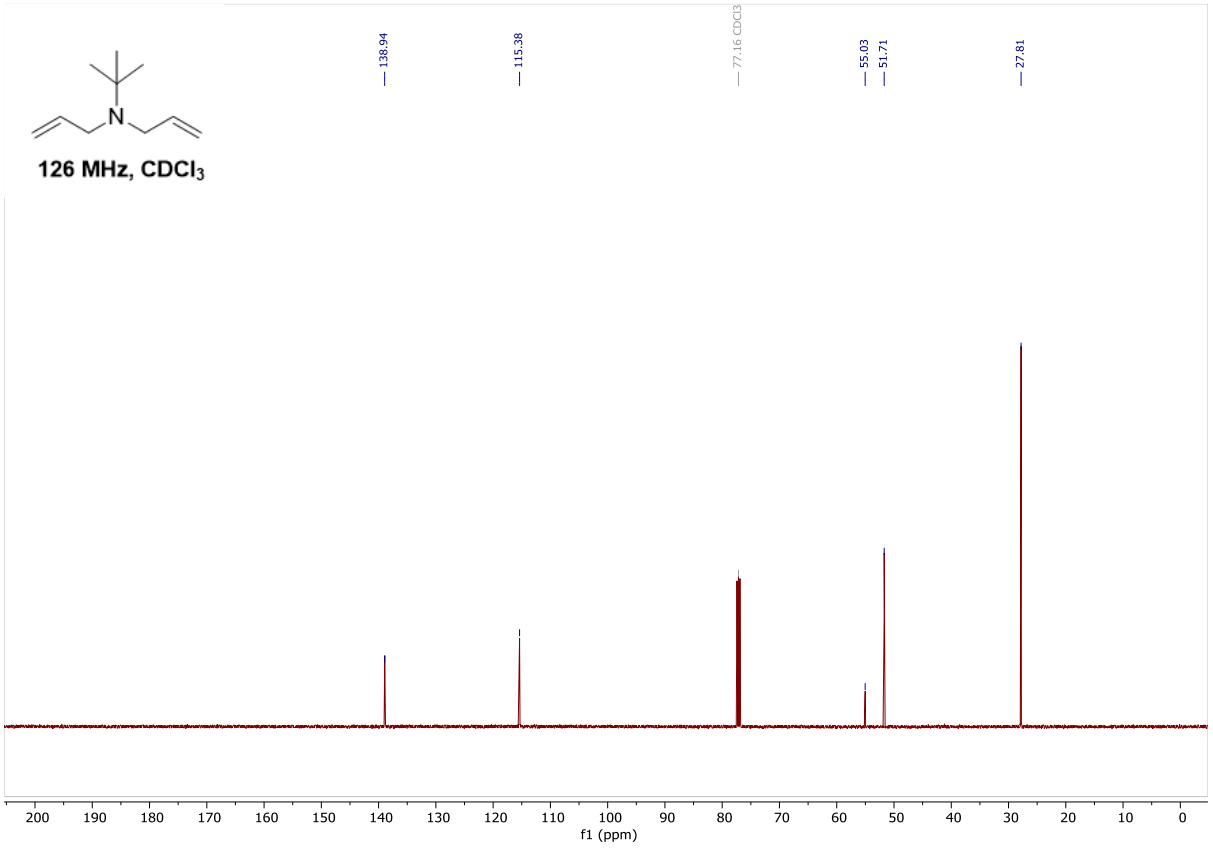
N,N-diallylcyclpentanamine (1b), 500 MHz, $CDCl_3$



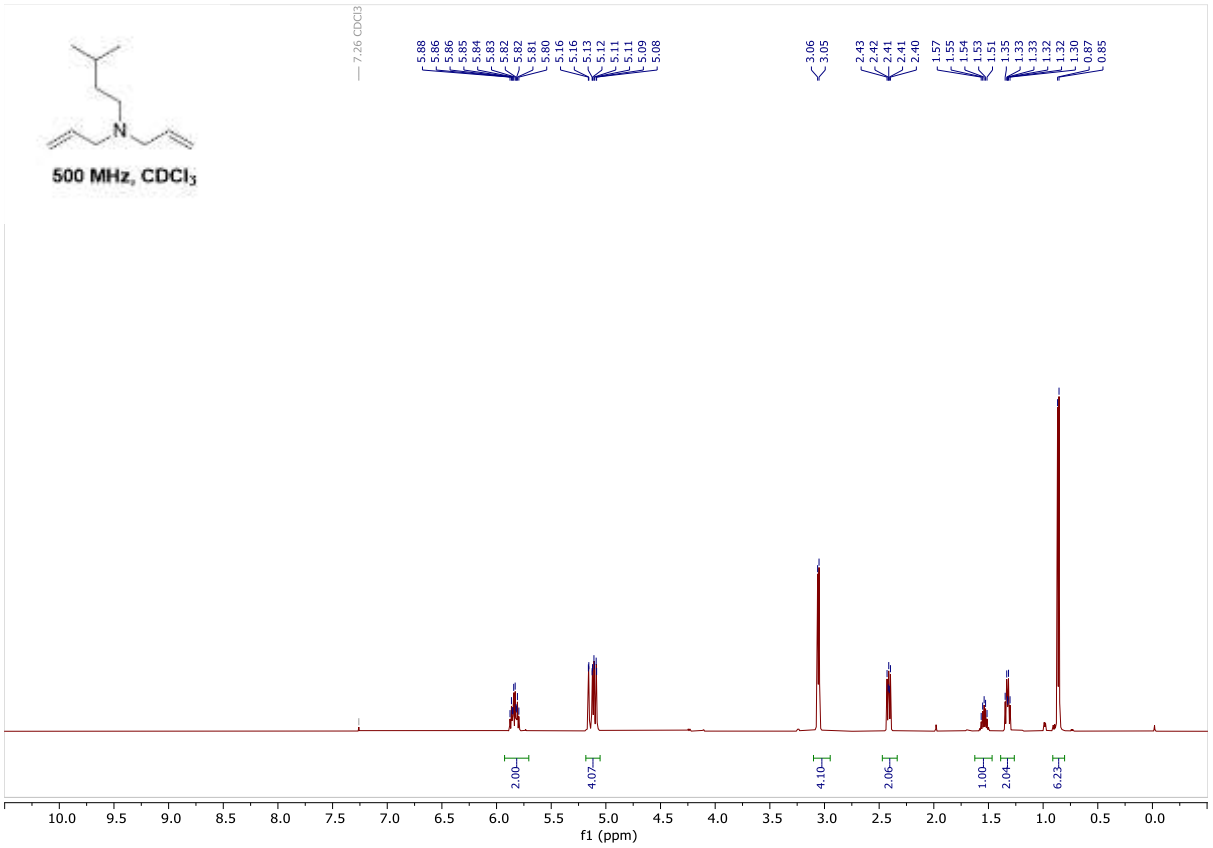


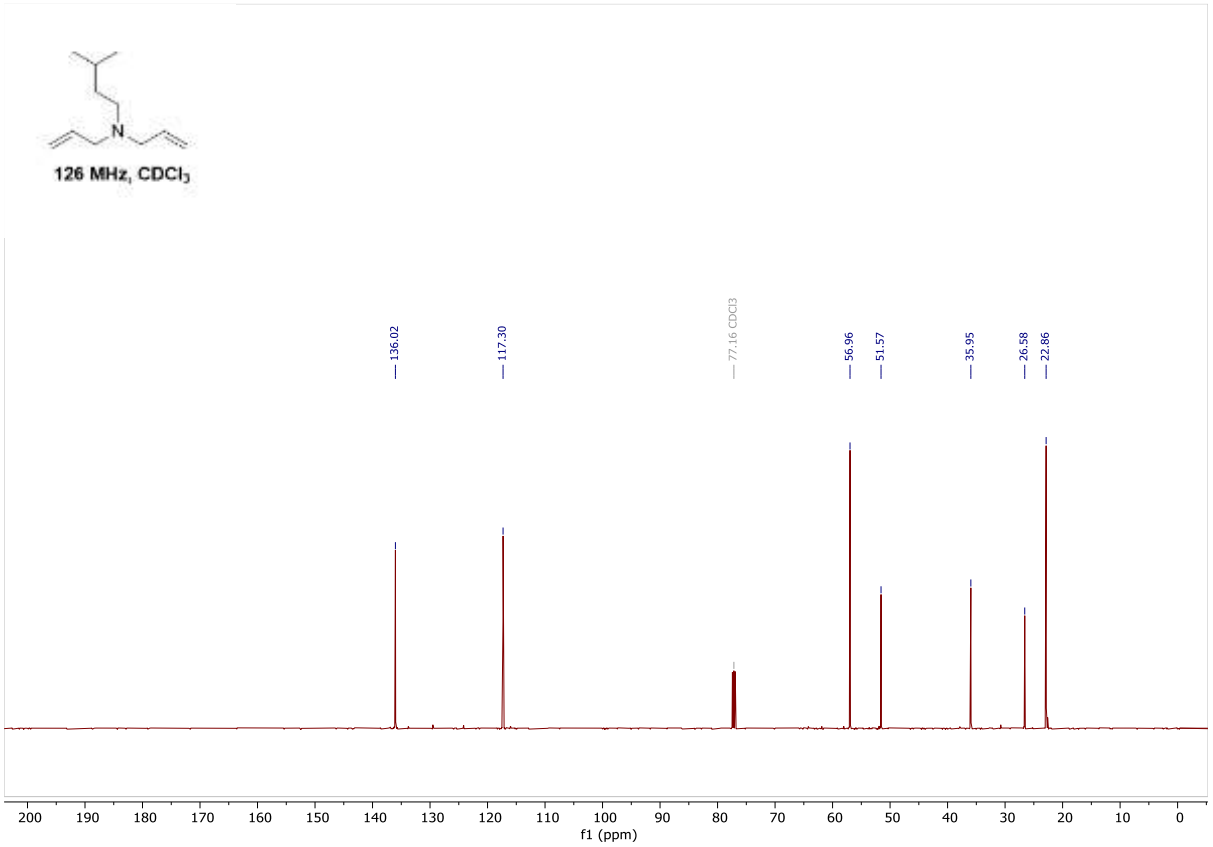
N-allyl-N-(tert-butyl)prop-2-en-1-amine (1c), 500 MHz, $CDCl_3$



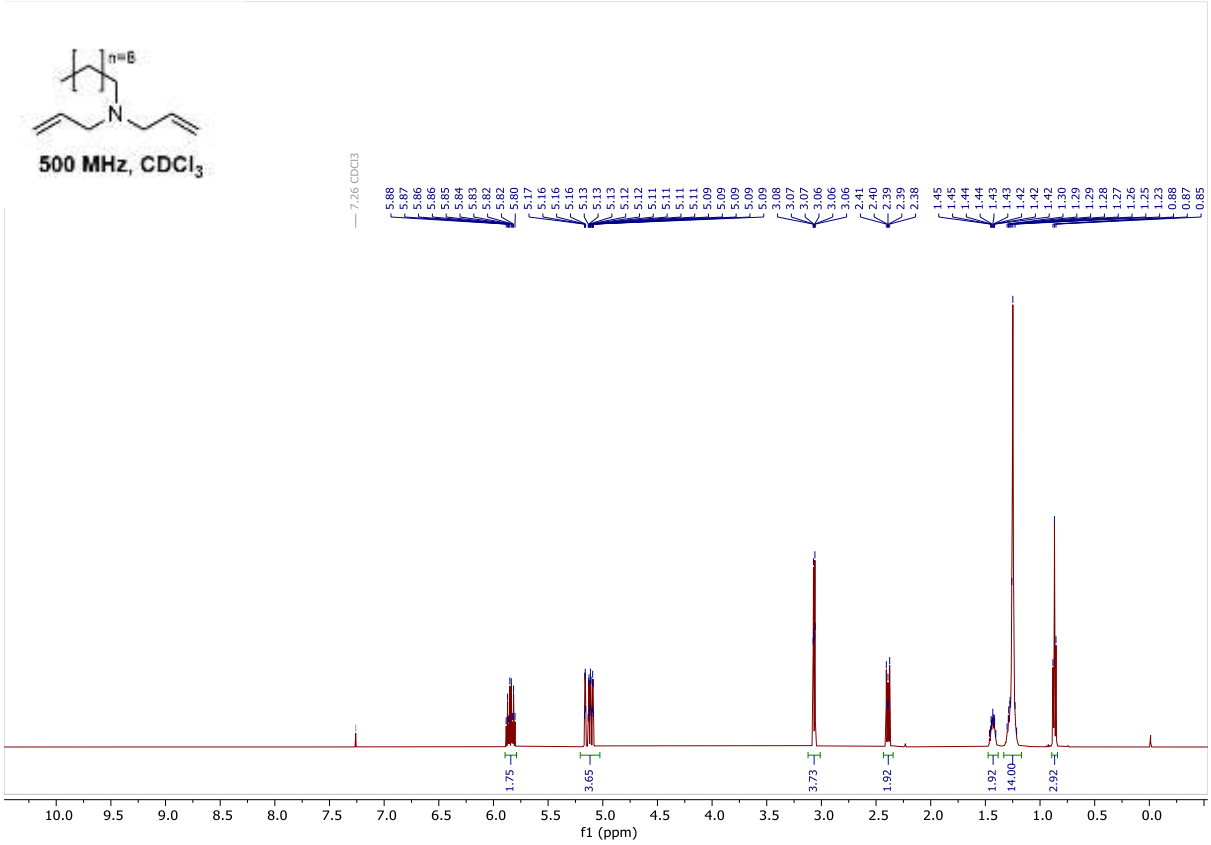


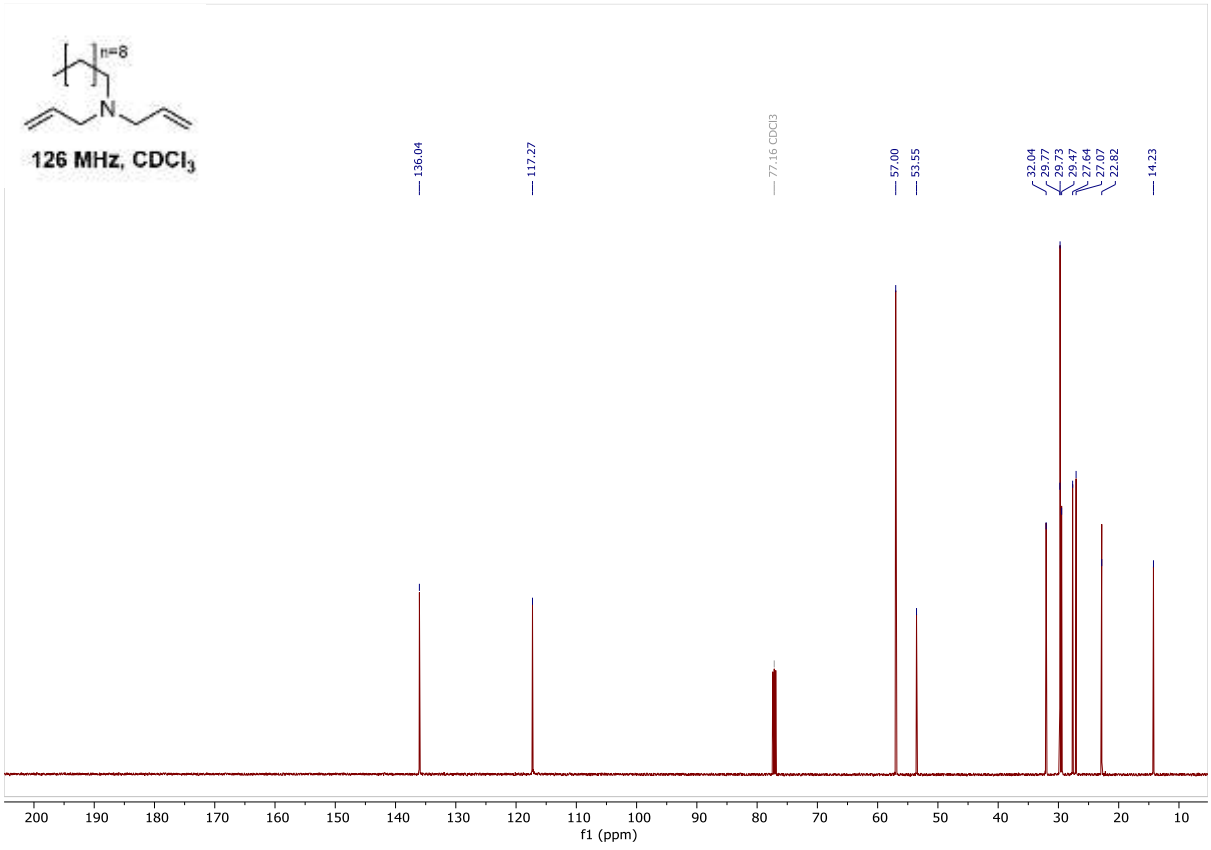
N,N-diallyl-3-methylbutan-1-amine (1d), 500 MHz, $CDCl_3$



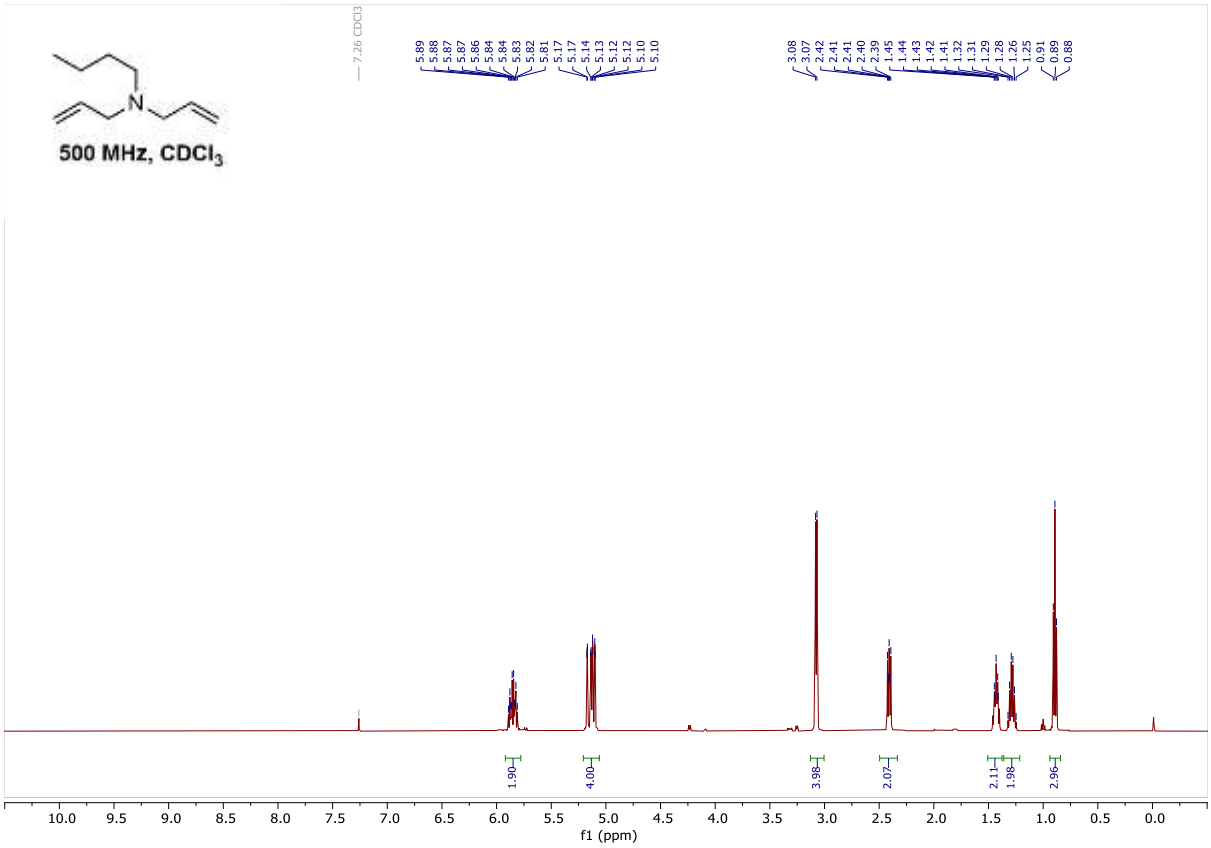


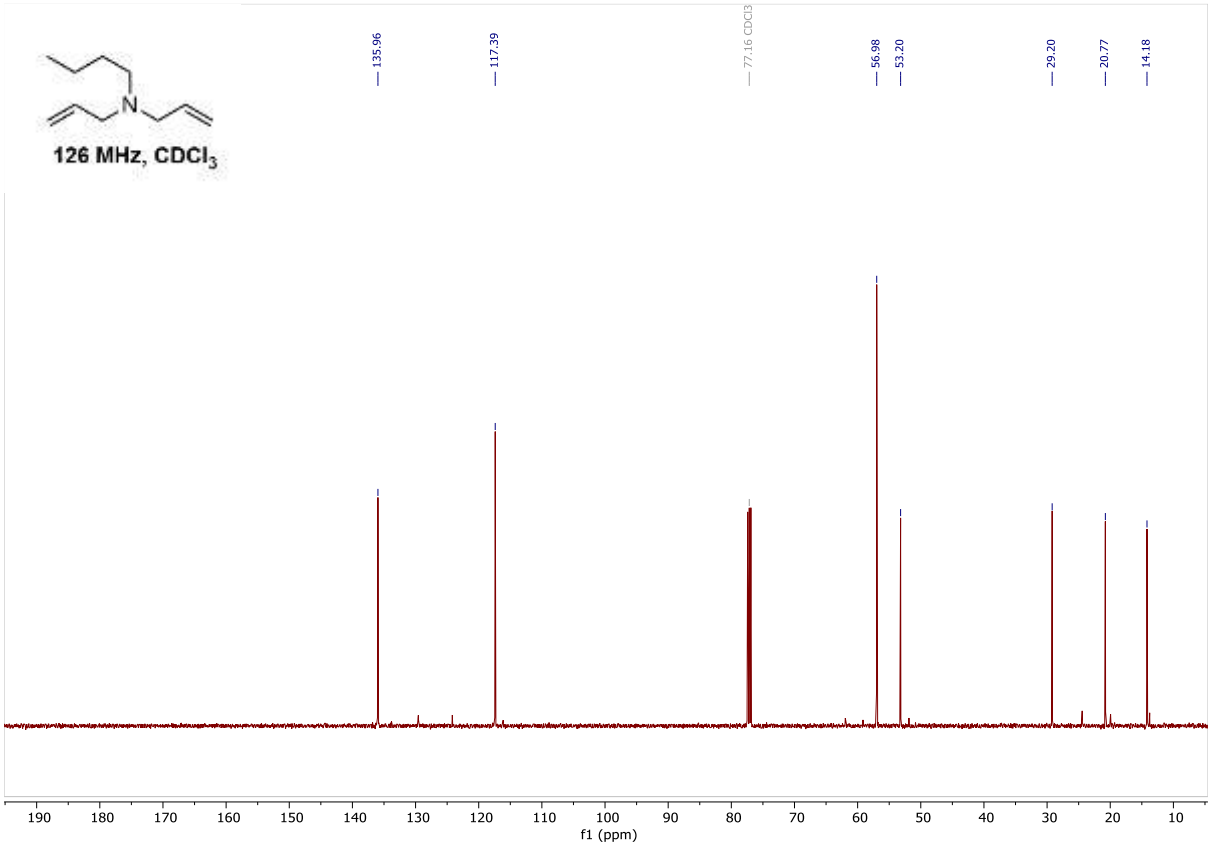
N,N-diallyldecan-1-amine (1e), 500 MHZ, $CDCl_3$



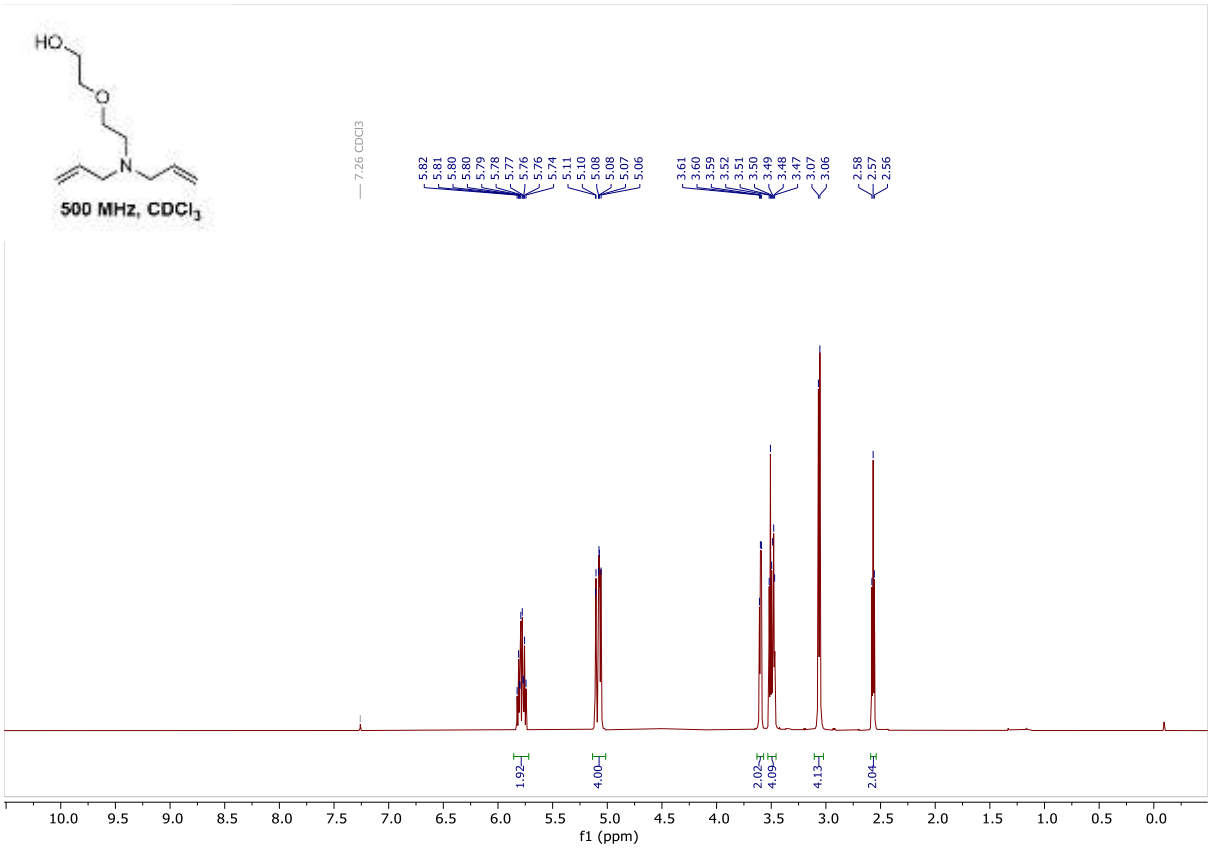


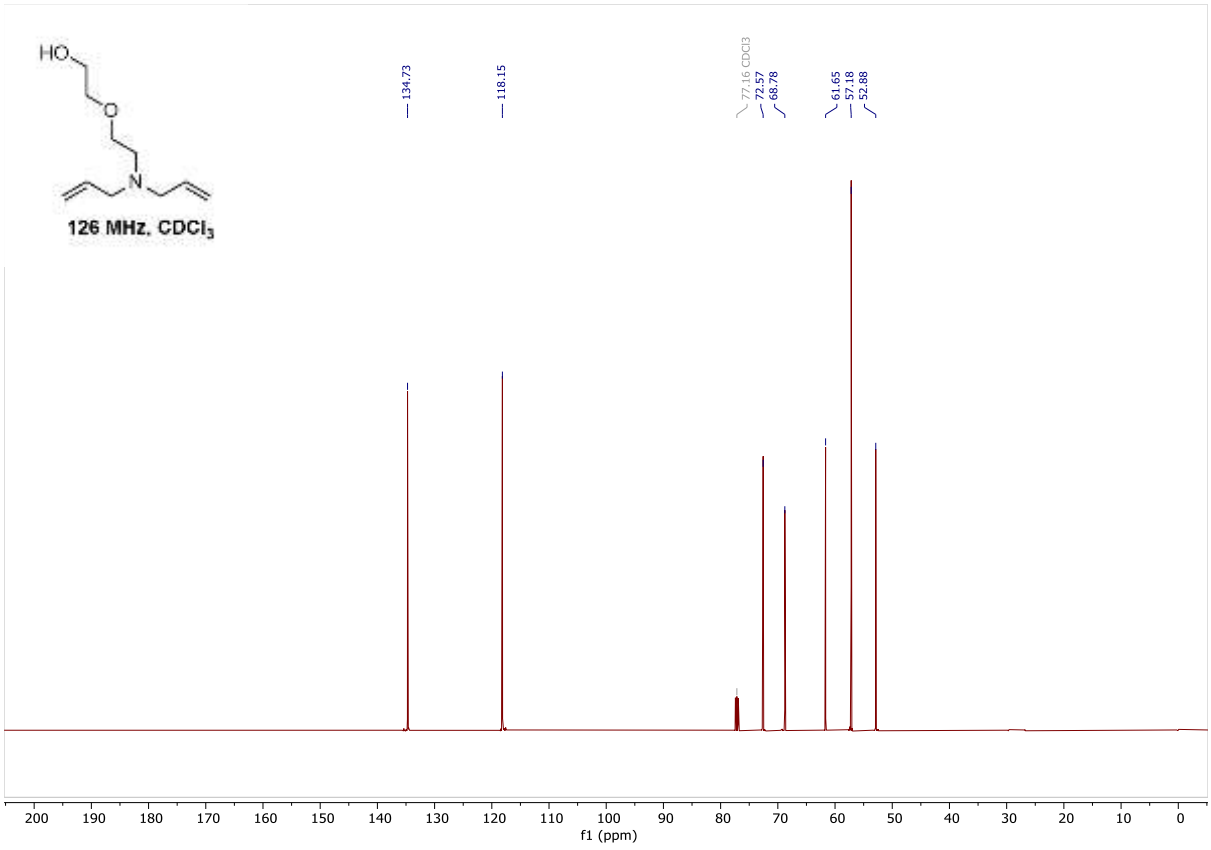
N,N-diallylbutan-1-amine (1f), 500 MHZ, $CDCl_3$



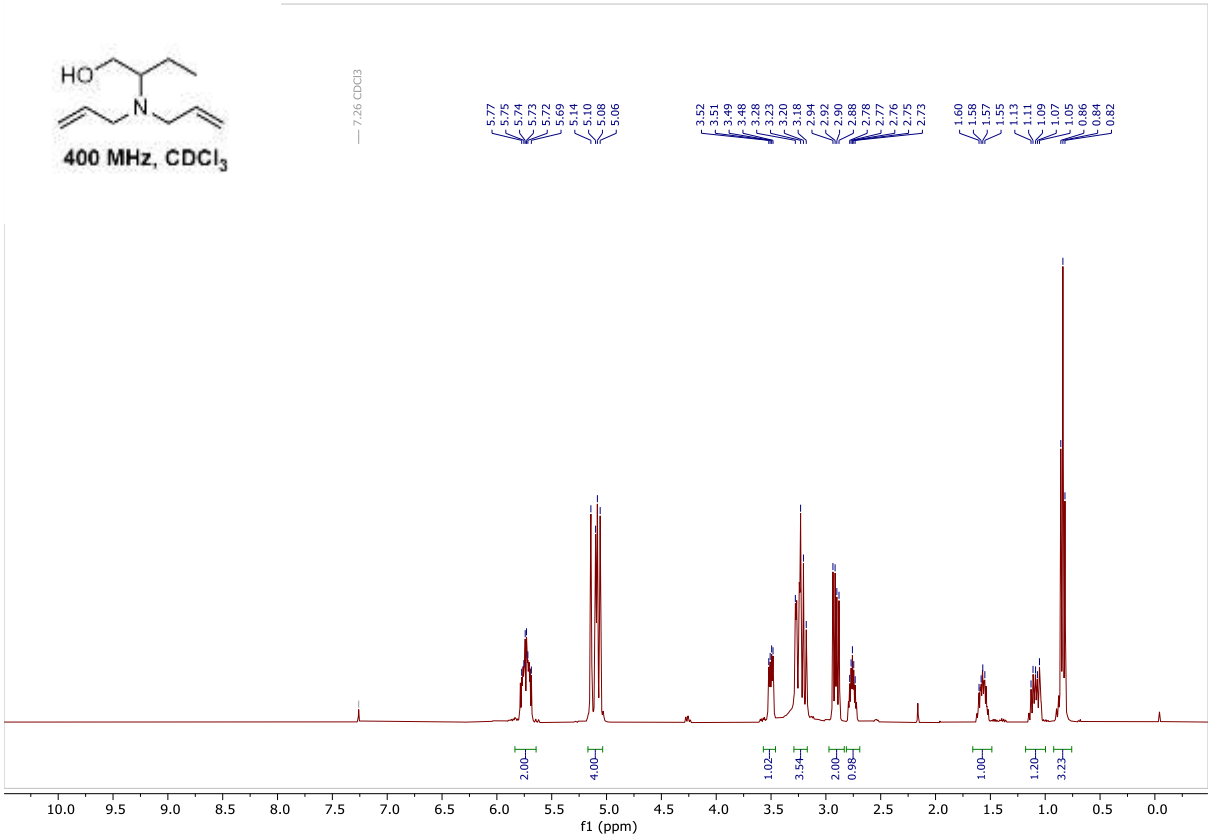


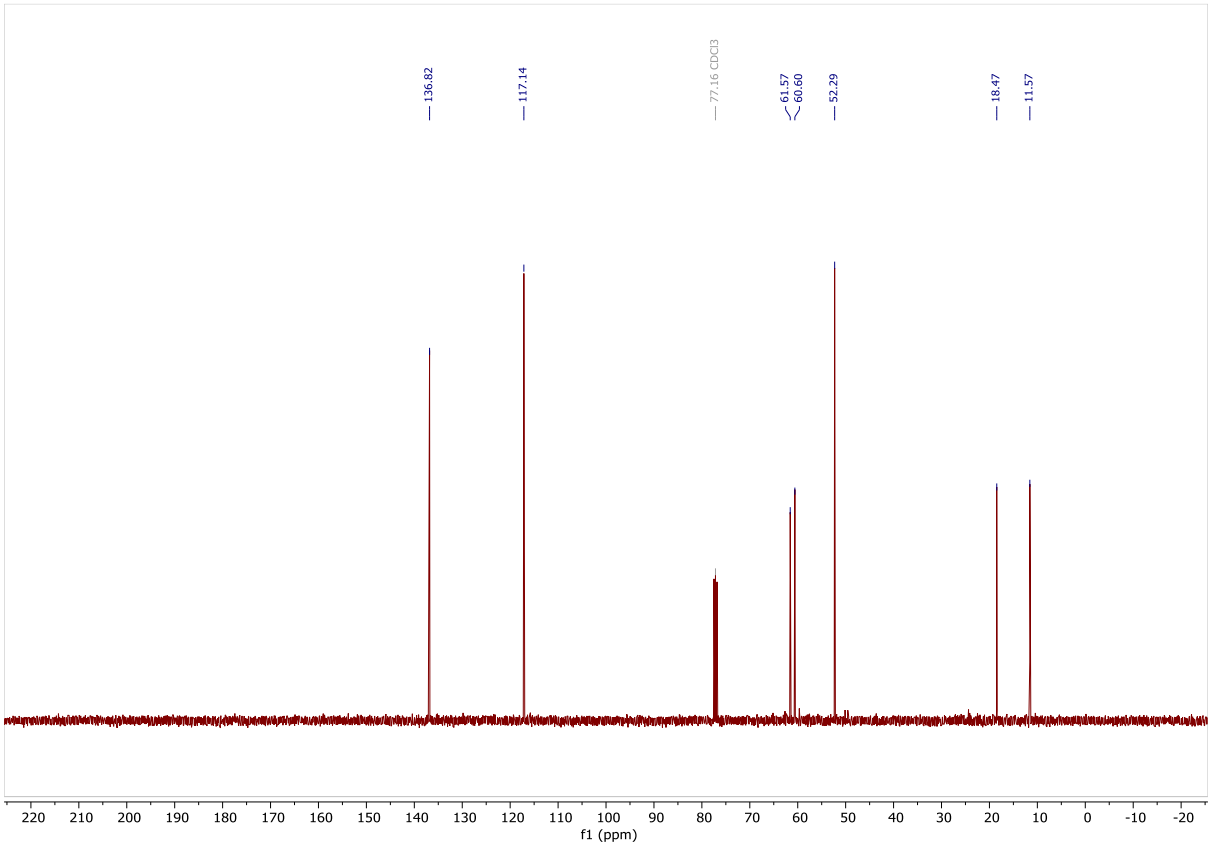
2-(2-(diallylamino)ethoxy)ethan-1-ol (1g), 500 MHz, $CDCl_3$



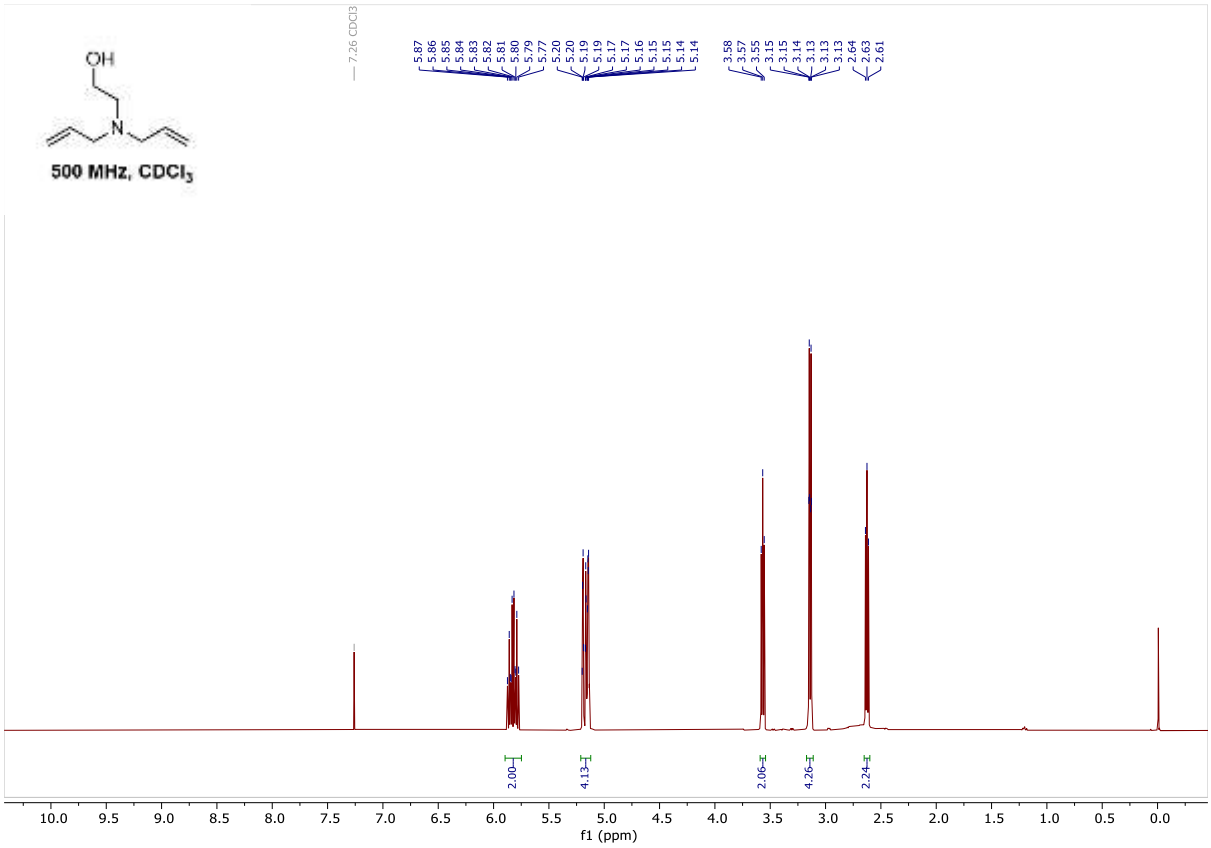


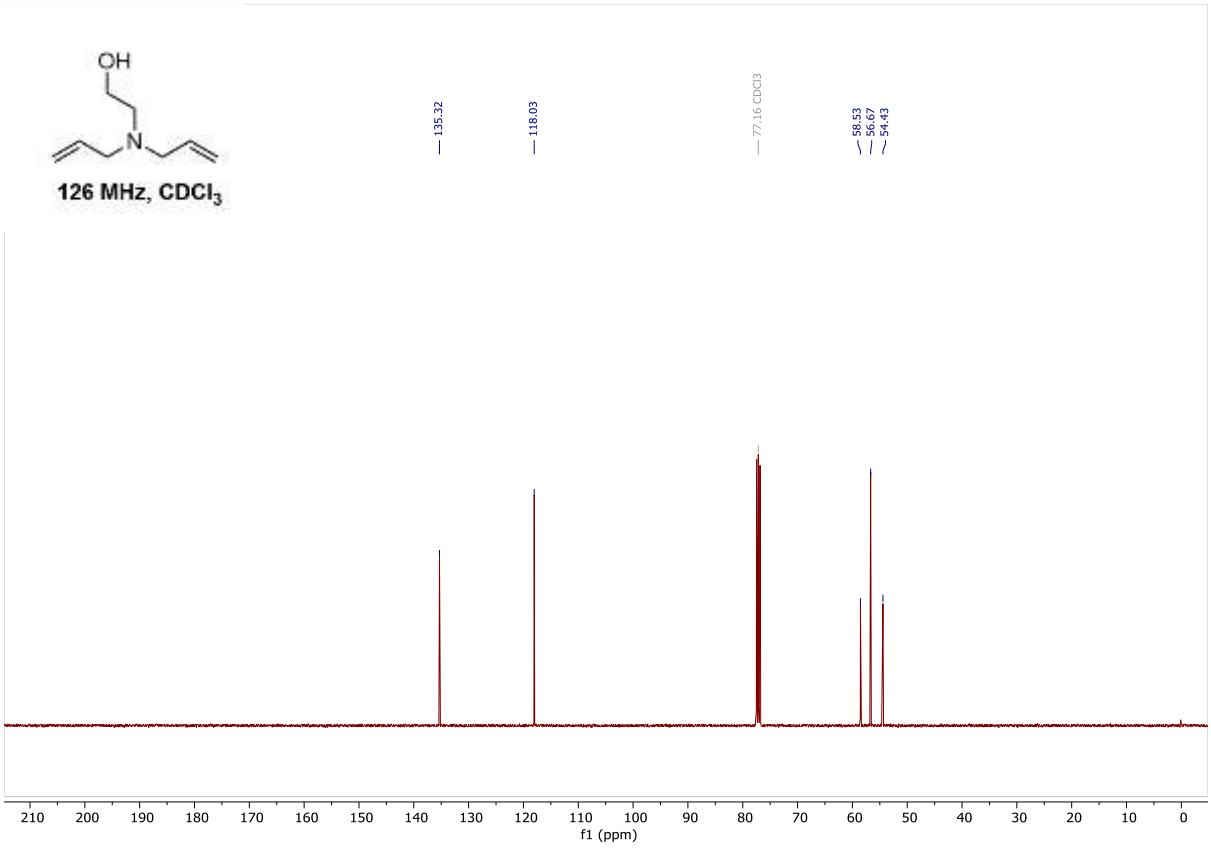
2-(diallylamino)butan-1-ol (1h), 400 MHz, $CDCl_3$



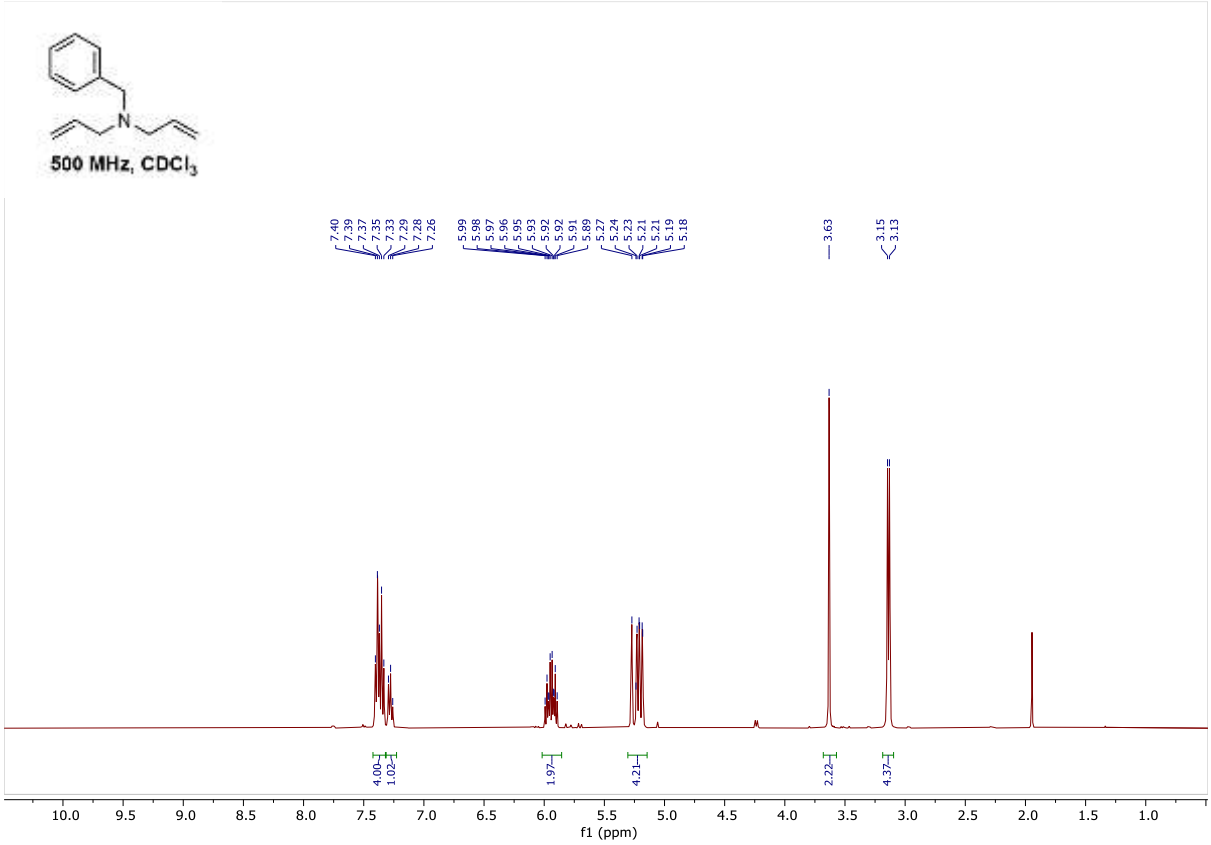


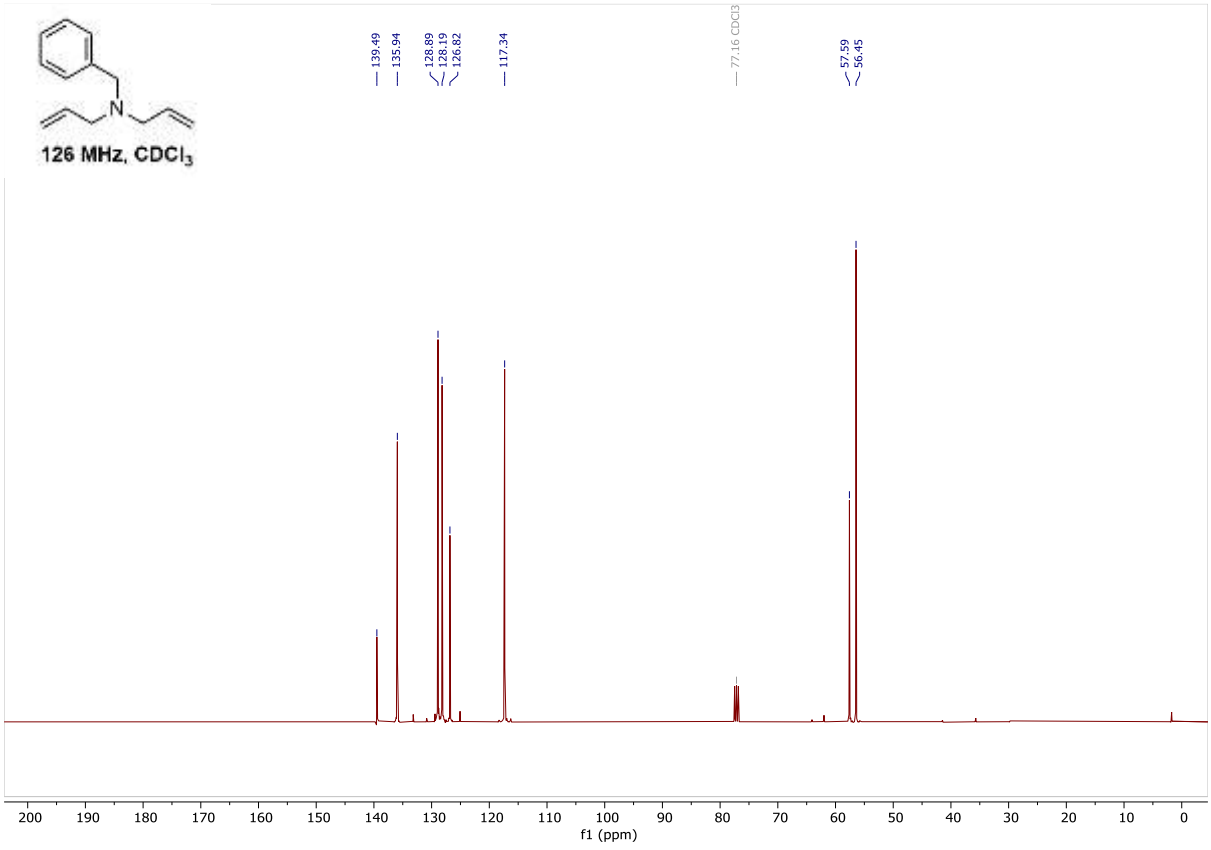
2-(diallylamino)ethan-1-ol (1i), 500 MHZ, $CDCl_3$



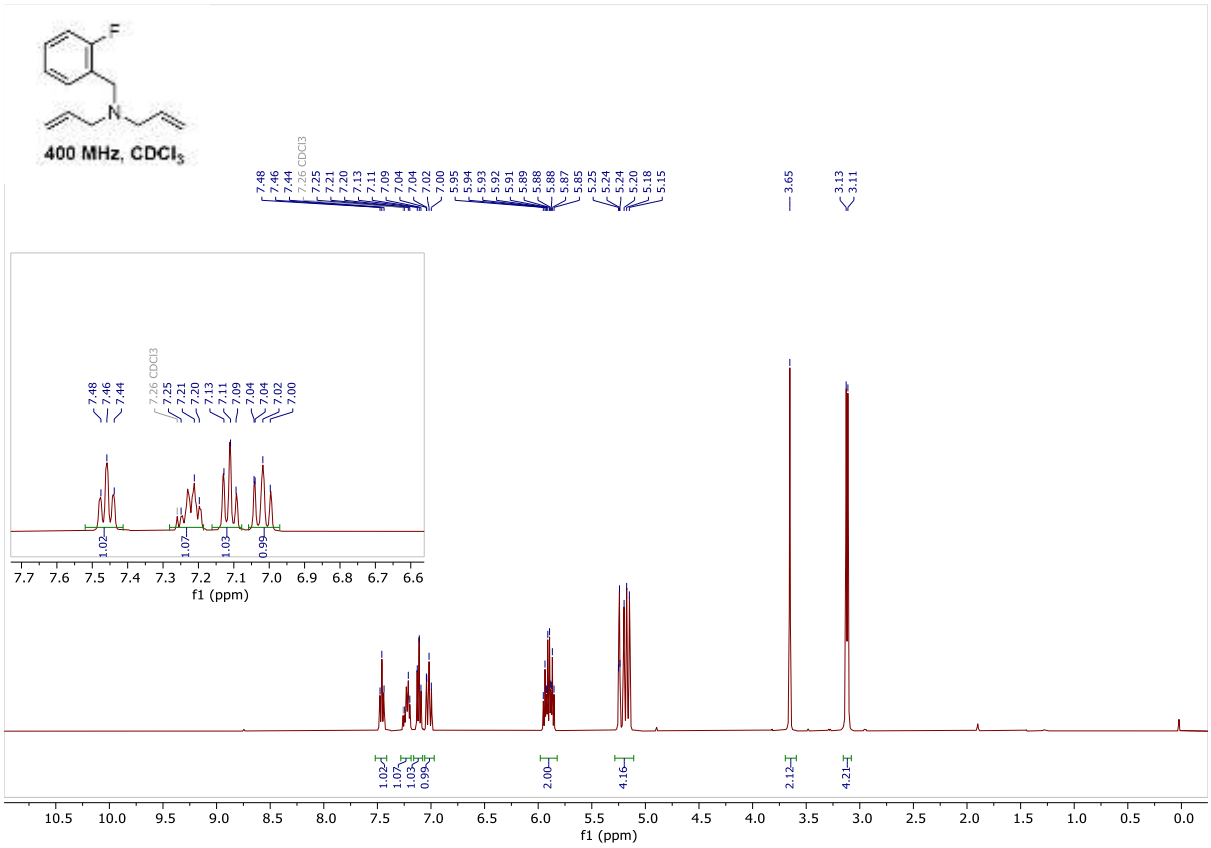


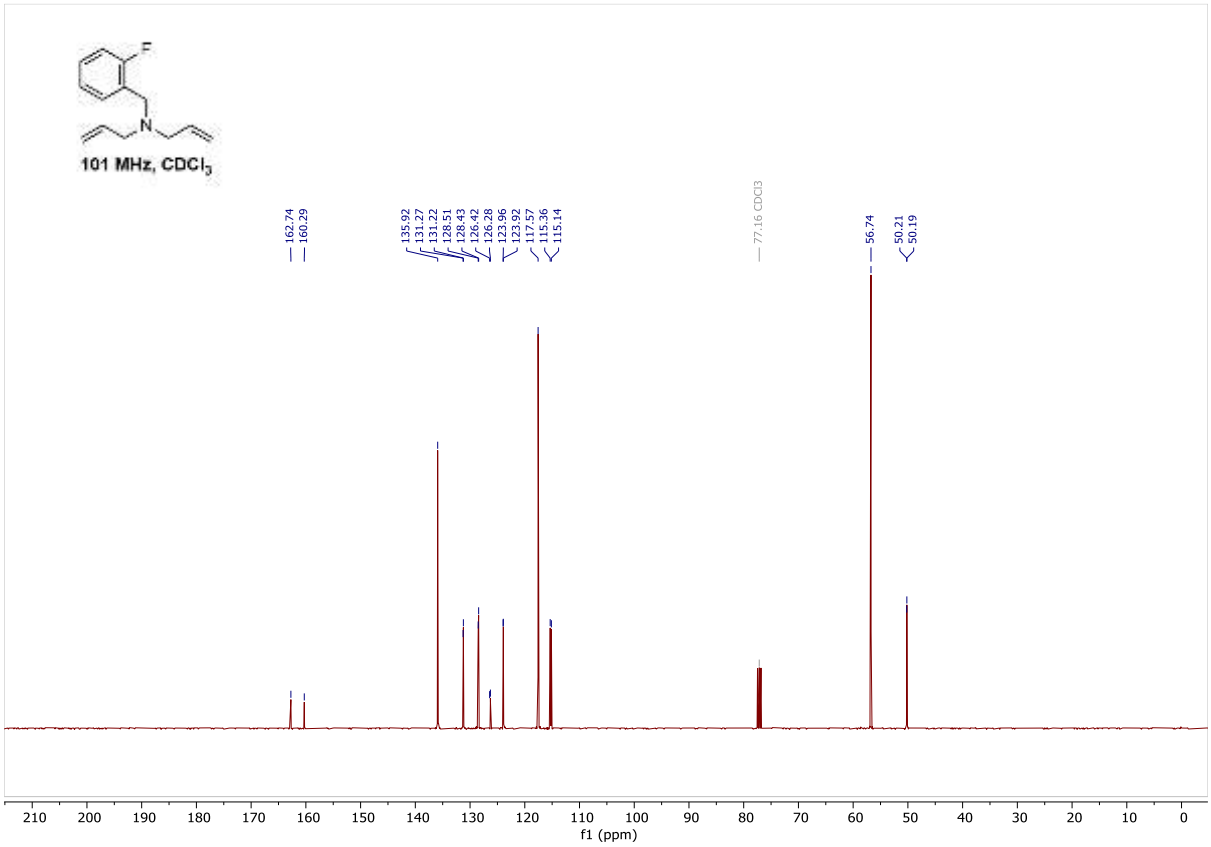
N,N-diallylbenzylamine (1j) 500 MHZ, $CDCl_3$



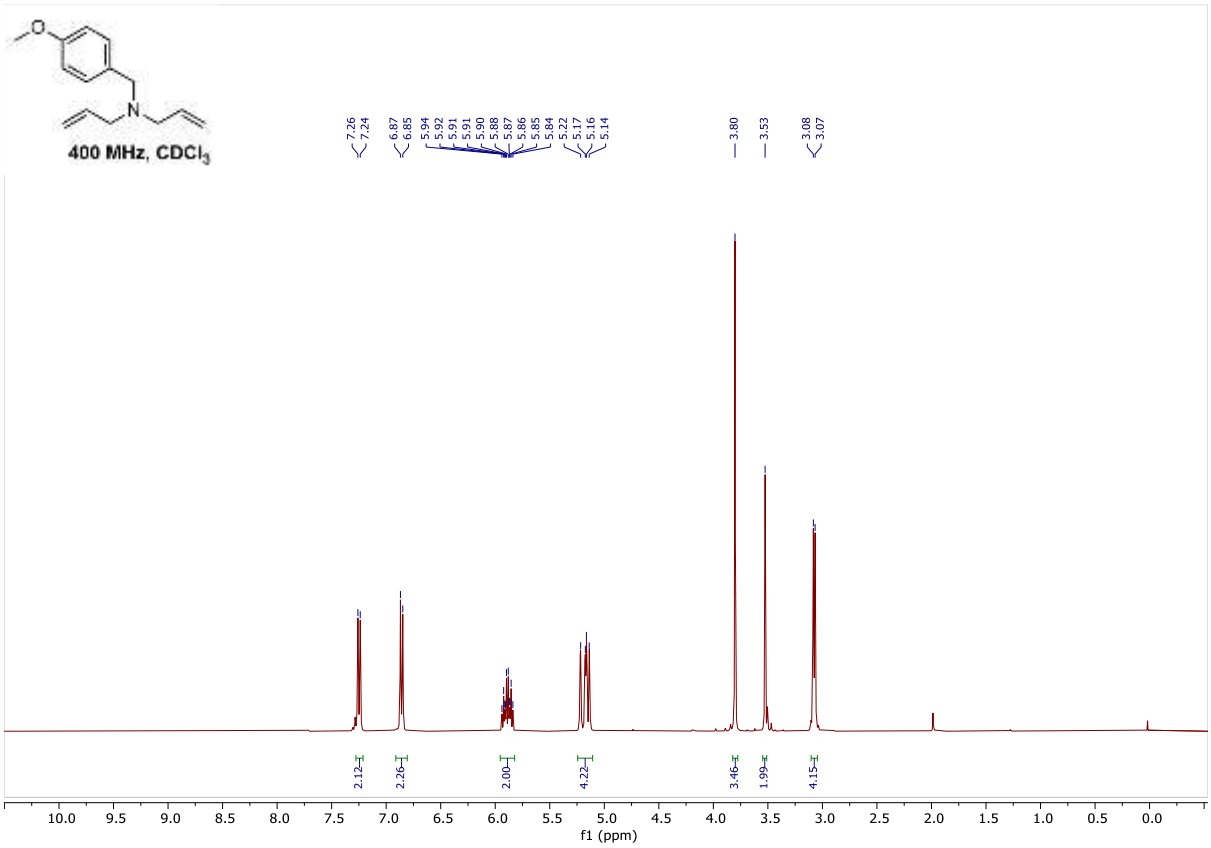


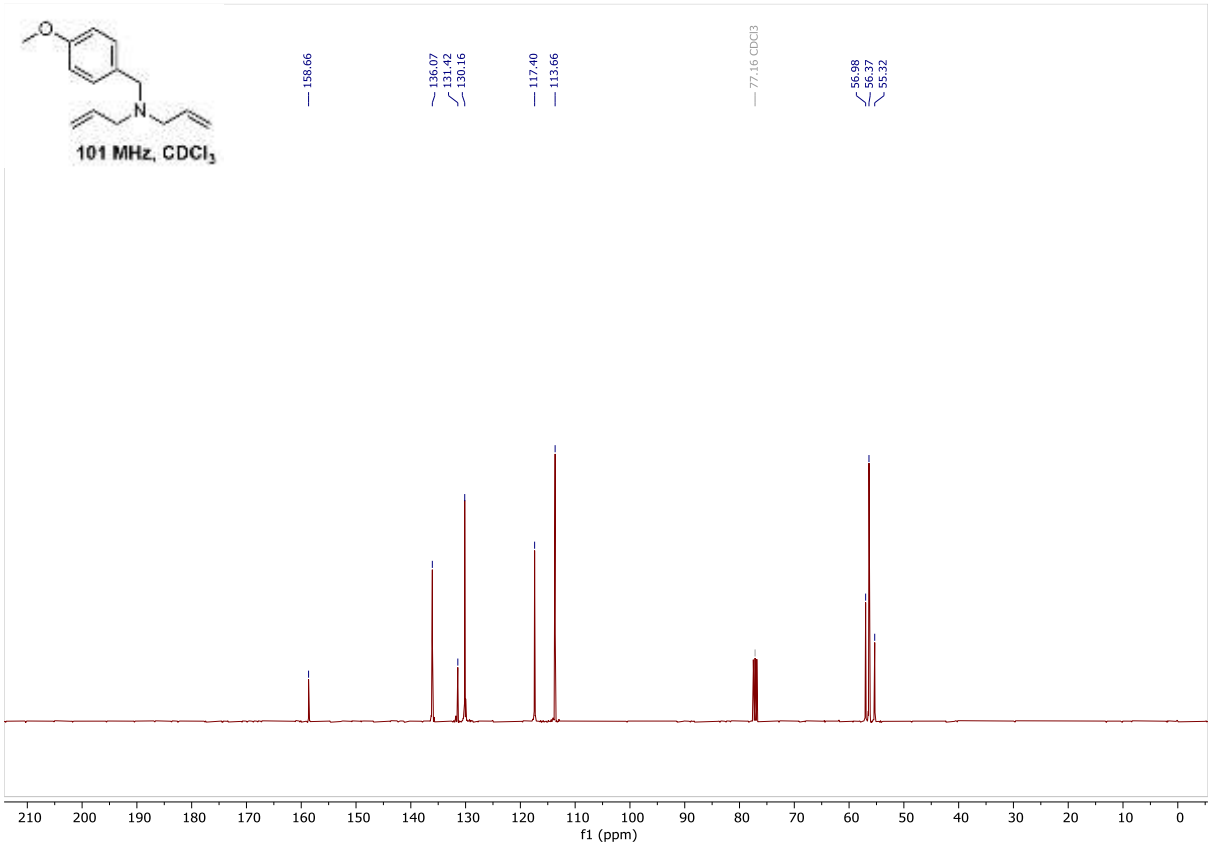
N-allyl-N-(2-fluorobenzyl)prop-2-en-1-amine (1k), 400 MHz, $CDCl_3$



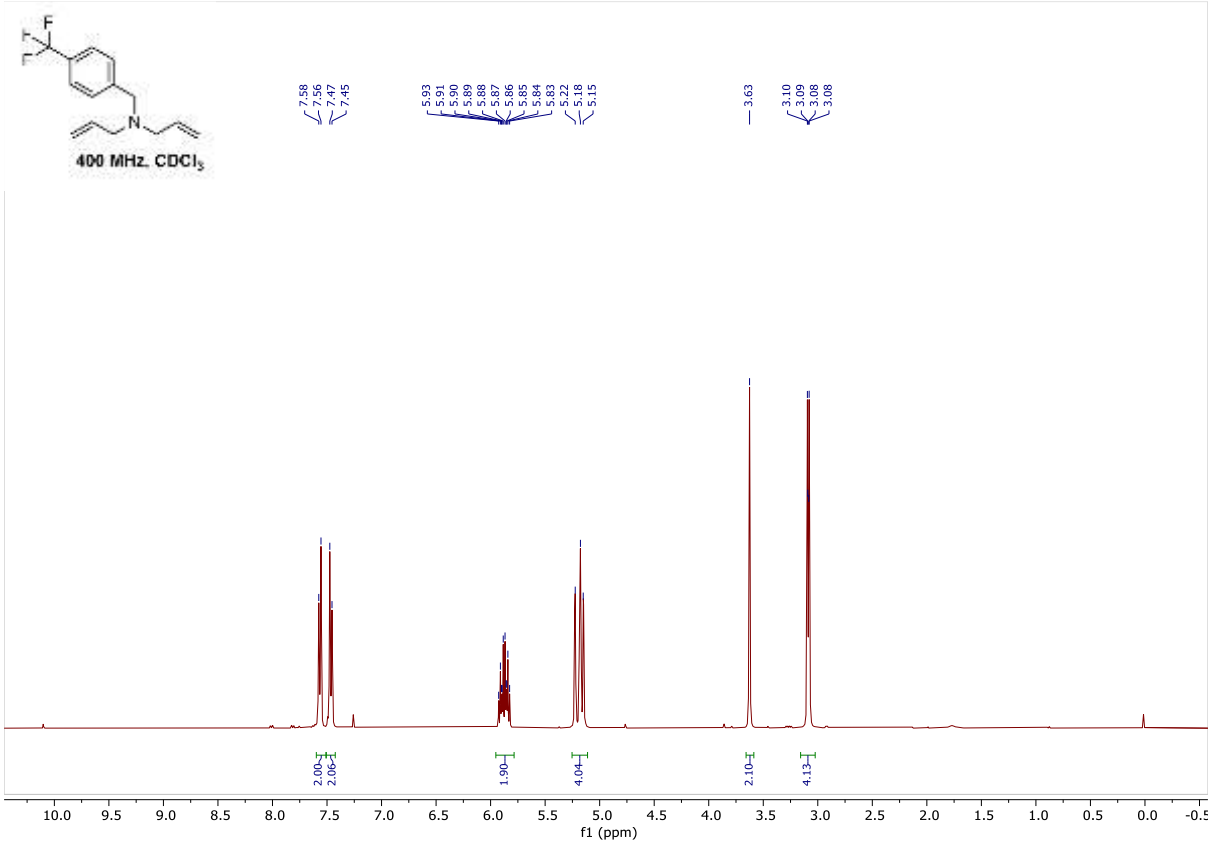


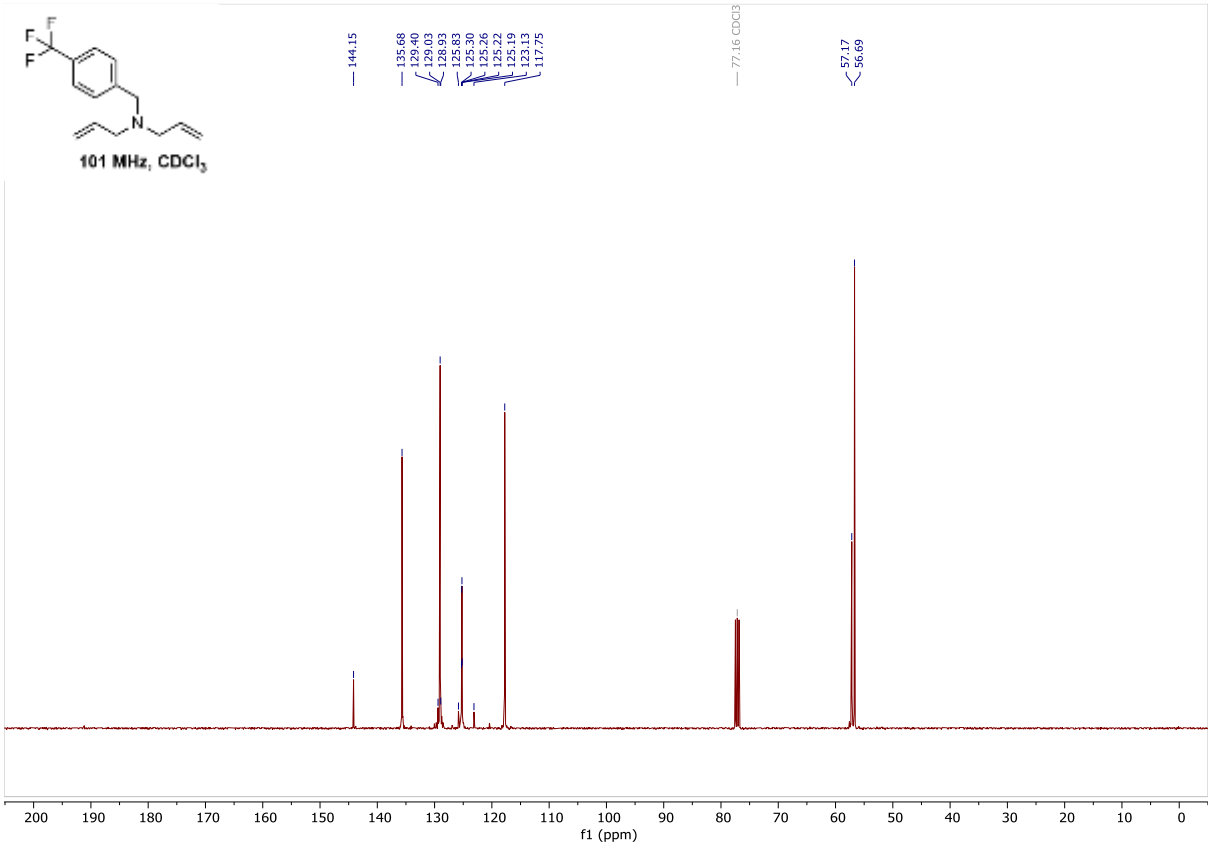
N,N-diallyl-(4-methoxybenzyl)-amine (1l) , 400 MHz, $CDCl_3$

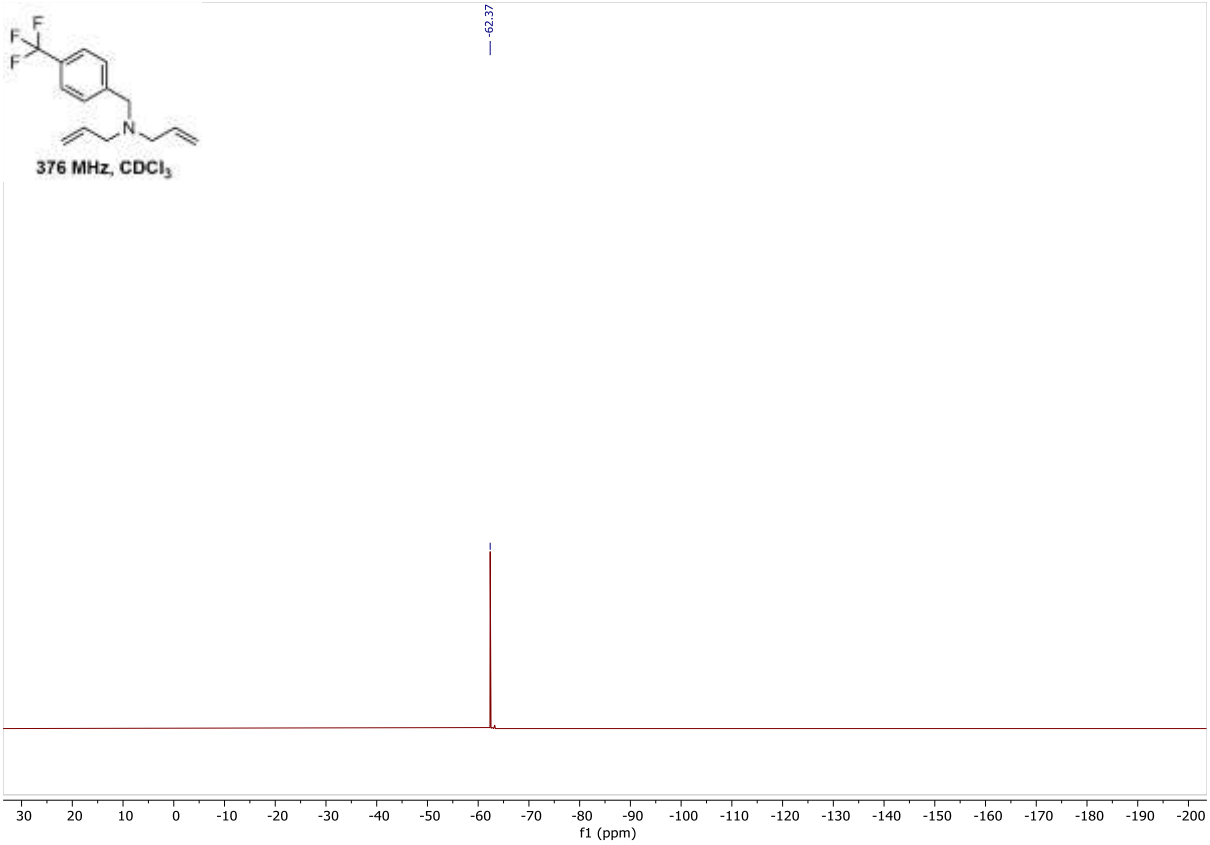




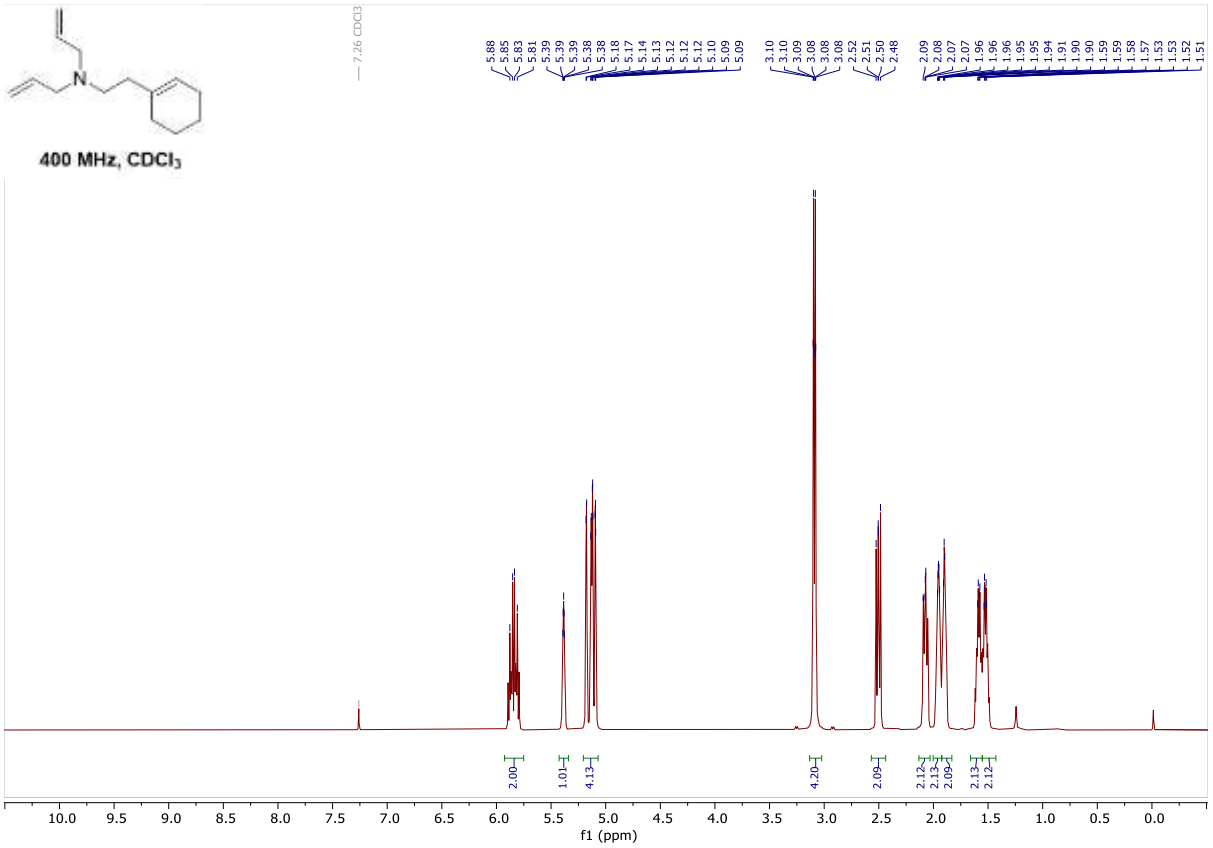
N,N-diallyl-(4-(Trifluoromethyl)benzyl)-amine (1m), 400 MHz, $CDCl_3$

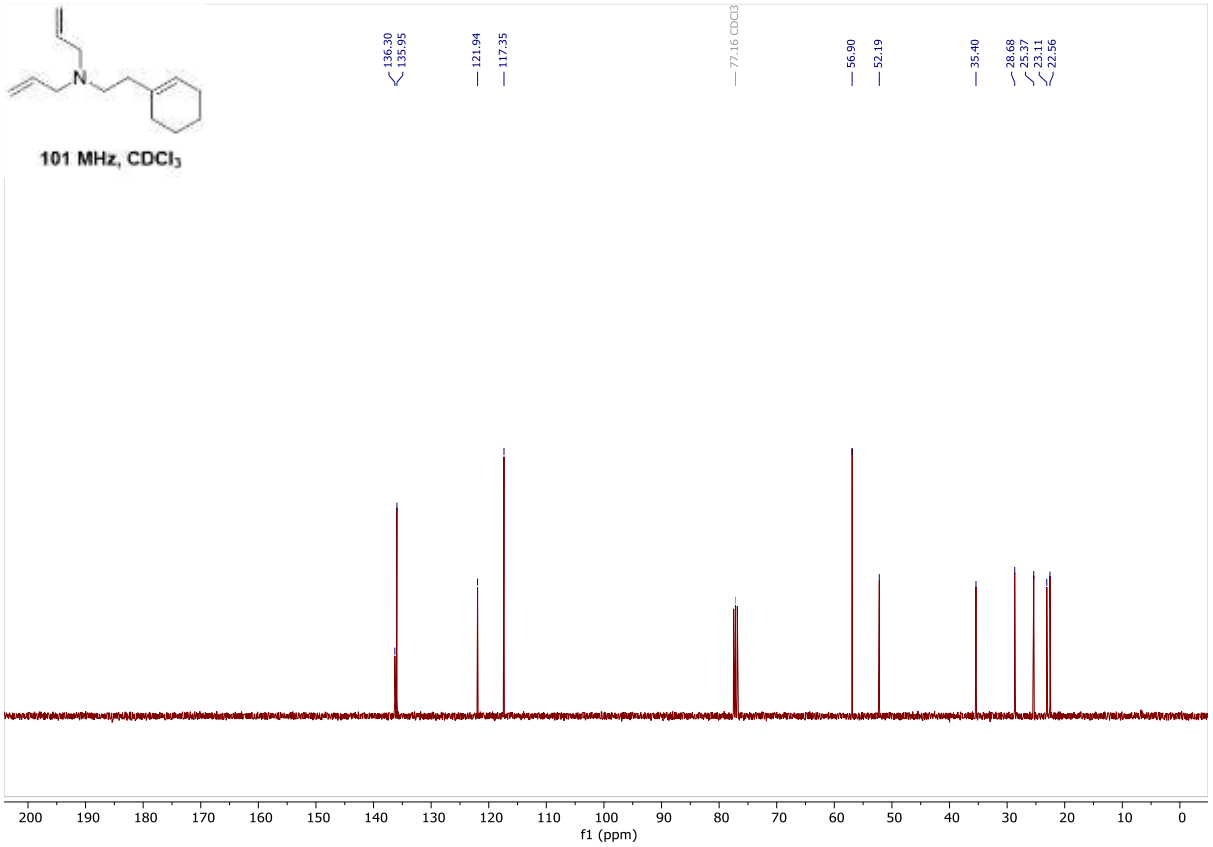





-62.37
376 MHz, CDCl3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

N-allyl-N-(2-(cyclohex-1-en-1-yl)ethyl)prop-2-en-1-amine, 400 MHz, $CDCl_3$





6. References

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3. M. Porel and C. A. Alabi, *J. Am. Chem. Soc.*, 2014, **136**, 13162-13165.
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