

SUPPORTING INFORMATION:

**Amine-boranes as dual-purpose reagents for direct amidation of
carboxylic acids**

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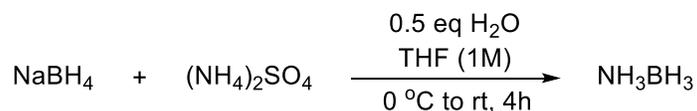
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Experimental Section

General Information:

Unless otherwise noted, all manipulations were carried out under open air conditions. ^{11}B , ^{19}F , ^{13}C , and ^1H NMR spectra were recorded at room temperature, on a Varian INOVA 300 MHz NMR spectrophotometer. Chemical shifts (δ values) are reported in parts per million relative to $\text{BF}_3\cdot\text{Et}_2\text{O}$ for ^{11}B NMR. Data are reported as: δ value, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, h=hextet, m=multiplet, br=broad) and integration. All solvents for routine isolation of products were reagent-grade. Sodium borohydride (powder, purity >99% by hydride estimation¹) was purchased in bulk from Dow Chemical Co. (Rohm and Haas). Ammonium sulfate (ACS reagent >99.0%, Fisher Chemical), was powdered prior to use. Tetrahydrofuran (THF, ACS reagent >99.0% containing 0.004% water and 0.025% BHT) was purchased from Sigma-Aldrich. All amines and carboxylic acids were purchased from commercial sources and used without further purification.

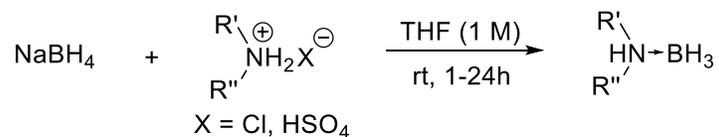
Preparation of ammonia-borane² (procedure i-a):



Scheme S1. Reaction equation for the preparation of ammonia-borane.

Sodium borohydride (18.91 g, 500 mmol, 1 eq.) and powdered ammonia sulfate (66.07 g, 500 mmol, 1 eq.) were transferred to a dry 2 L round bottom flask containing a large magnetic stir bar. The flask was then cooled in an ice-water bath followed by the addition of 495 mL of reagent-grade tetrahydrofuran. With vigorous stirring 4.5 mL of water was then added dropwise over a period of 5 minutes to limit frothing. Once all water is added the flask is moved to room temperature and stirred vigorously. The reaction is monitored using ^{11}B NMR until completion (~4 h) as judged by the absence of sodium borohydride peaks in the ^{11}B NMR. (Prior to running the ^{11}B NMR experiments, a drop of dimethyl sulfoxide is added to the aliquot to solubilize any sodium borohydride present.) Once complete the reaction mixture is filtered through celite and the filter cake thoroughly rinsed with tetrahydrofuran. The combined filtrates are condensed via rotary evaporation following by drying *in vacuo* for 12 h.

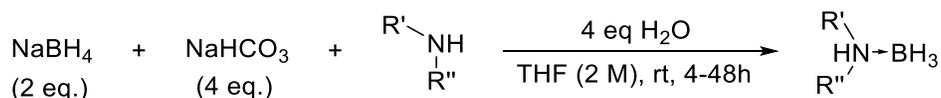
Preparation of amine boranes via salt metathesis³ (procedure i-b):



Scheme S2. Reaction equation for the preparation of amine-boranes from ammonium salts.

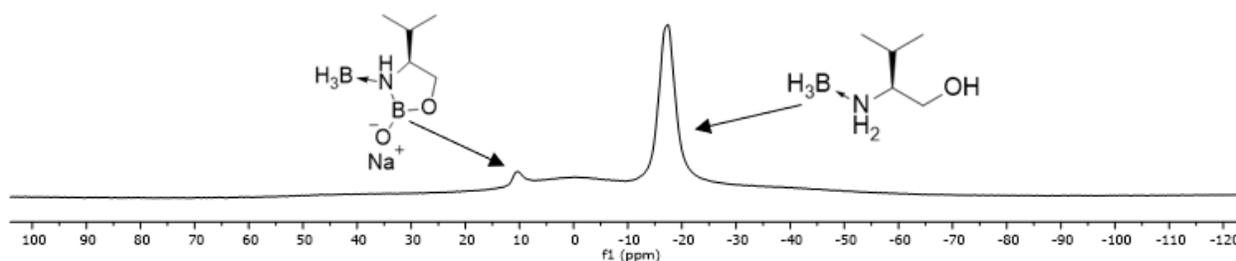
Sodium borohydride (0.76 g, 20 mmol) and the appropriate ammonium salt (20 mmol) were transferred to a 100 mL dry round bottom flask, charged with a magnetic stir-bar. This was followed by addition of reagent-grade tetrahydrofuran (20.0 mL) at rt. Reaction progress was monitored by ^{11}B NMR spectroscopy (Note: A drop of anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment to solubilized NaBH_4). Upon completion of the reaction (1-24 h, as determined by ^{11}B NMR), the reaction contents were filtered through sodium sulfate and celite and the solid residue washed with THF. Removal of the solvent in vacuo from the filtrate yielded the corresponding amine-borane. No further purification was necessary in the examples (**1b-d**, **p**, **r**) presented here.

Preparation of amine boranes via sodium bicarbonate⁴ (procedure ii):



Scheme S3. Reaction equation for the preparation of amine-boranes from free amines.

Sodium borohydride (1.51 g, 2 eq., 40 mmol) and powdered sodium bicarbonate (6.72 g, 4 eq., 80 mmol) were transferred to a 100 mL dry round bottom flask, charged with a magnetic stir-bar. The corresponding amine (1 eq., 20 mmol) was charged into the reaction flask followed by addition of reagent-grade tetrahydrofuran (20 mL) at rt. Under vigorous stirring, water (0.36 mL, 4 eq., 80 mmol) was added drop-wise to prevent excessive frothing. Reaction progress was monitored by ^{11}B NMR spectroscopy (Note: A drop of anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment to solubilize NaBH_4). Upon completion of the reaction (4-48 h, as determined by ^{11}B NMR), the reaction contents were filtered through sodium sulfate and celite and the solid residue washed with THF. Removal of the solvent in vacuo from the filtrate yielded the corresponding amine-borane (**1e-o**, **q**, **s**). Residual solvent was removed by placing under high-vacuum for ~12 h. In the case of valinol-borane (**1s**) additional work-up, detailed below, was necessary to break-up the partial formation of an intermediate amine-borane borate.

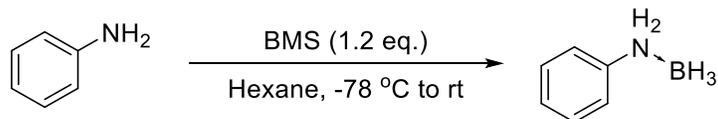


^{11}B NMR (96 MHz, Chloroform-*d*) of crude valinol-borane prior to basic work-up.

Valinol-borane work-up: The crude amine-borane material obtained after celite filtration was placed in a 100 mL round bottom flask and dissolved in diethyl ether (20 mL). The solution was brought to 0 °C. Then a dilute NaOH solution (20 mL, 0.05 M) was added slowly to the amine-borane solution. The mixture was moved to rt and stirred vigorously for 3 hours. After completion

the volatiles were removed via rotary evaporation, and the remaining aqueous fraction was extracted with chloroform (3 x 50 mL). The organic extracts were dried over MgSO₄, filtered through cotton and condensed via rotary evaporation. Residual solvent was removed by placing under high-vacuum for ~12 h.

Preparation of aniline borane via Lewis-base exchange⁵ (procedure iii):

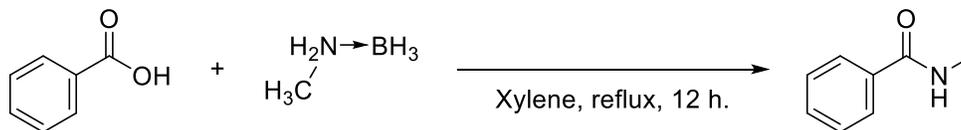


Scheme S4. Reaction equation for the preparation of aniline-borane from aniline and BMS.

Anhydrous hexanes (25 mL, 1 M w.r.t. amine) was transferred to a 100 mL dry round bottom flask, charged with a magnetic stir-bar. The flask was sealed with a rubber septum and borane-dimethylsulfide (BMS) (3.3 mL, 1.2 eq., 30 mmol) was added via syringe at rt. After BMS addition the solution was brought to -78 °C. Then at -78 °C aniline (2.3 mL, 1 eq., 25 mmol) was added via syringe. The frozen mixture was stirred and gradually brought to rt whereupon a white precipitate formed. The mixture was stirred at rt for 1 hour, then the solvent was removed using a cotton plugged plastic pipette. The white solid was washed with hexanes (6 x 10 mL) each time removing the solvent using a cotton plugged plastic pipette. Residual solvent was removed by placing under high-vacuum for ~12 h.

Optimization of amide synthesis:

Optimization of Reagent Equivalents



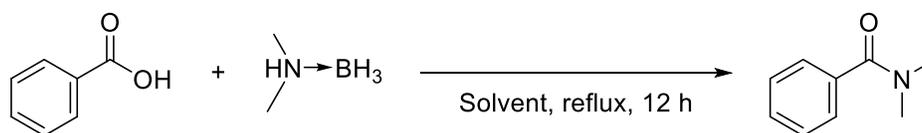
Scheme S5. Reaction equation for the study of required acid equivalents.

In a 25 ml round bottom flask containing a magnetic stir bar was weighed methylamine-borane (0.090 g, 2 mmol, 1 eq.) followed by benzoic acid (1, 2, 3, or 4 eq). Xylenes was then added to the flask, (1 M with respect to benzoic acid). A reflux condenser was attached to the flask and the reaction mixture was brought to reflux. After 12 hours the reaction mixture was diluted with methanol (50 mL) and condensed via rotary evaporation. The crude mixture was diluted with ethyl acetate (15 mL) and transferred to a separatory funnel. The mixture was washed with cold 3M sodium hydroxide solution (3 x 10 mL), then washed with brine (1 x 15 mL). The organic layer was dried with sodium sulfate, filtered through cotton, and condensed via rotary evaporation. Residual solvent was removed by placing under high-vacuum for ~12 h. Results of the study are summarized below in Table S1.

Benzoic Acid	Methylamine-Borane	N-Methyl Benzamide Yield
1 eq.	1 eq.	49% (12 h)
2eq.	1 eq.	78% (12 h)
3 eq.	1 eq.	90% (12 h)
4 eq.	1 eq.	89% (12 h)

Table S1. Summary of results of the reagent equivalency study.

Optimization of Reaction Conditions



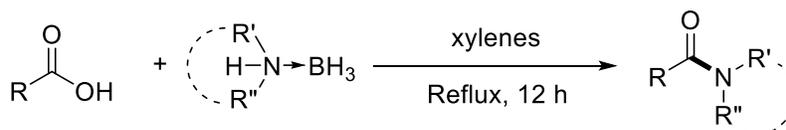
Scheme S6. Reaction equation for the study of optimal reaction conditions.

In a 25 ml round bottom flask containing a magnetic stir bar was weighed dimethylamine-borane (0.118 g, 2 mmol, 1 eq.) followed by benzoic acid (0.733 g, 6 mmol, 3 eq.). The tested solvent was then added to the flask, (6 mL, 1 M with respect to benzoic acid). A reflux condenser was attached to the flask and the reaction mixture was brought to reflux. After 12 hours the reaction mixture was condensed via rotary evaporation (diluted with methanol (50 mL) in the reactions utilizing xylenes and toluene). The crude mixture was diluted with ethyl acetate (15 mL) and transferred to a separatory funnel. The mixture was washed with cold 3M sodium hydroxide solution (3 x 10 mL), then washed with brine (1 x 15 mL). The organic layer was dried with sodium sulfate, filtered through cotton, and condensed via rotary evaporation. Residual solvent was removed by placing under high-vacuum for ~12 h. Results of the study are summarized below in Table S2.

Solvent (reflux)	Benzoic Acid	(Dimethylamine-Borane	Yield
Xylenes	3 eq.	1 eq.	99%
Xylenes + 3 eq. H ₂ O	3 eq.	1 eq.	89%
Toluene	3 eq.	1 eq.	27%
Toluene + 3 eq. H ₂ O	3 eq.	1 eq.	26%
Cyclohexane	3 eq.	1 eq.	Trace
Ethanol	3 eq.	1 eq.	NR
Tetrahydrofuran	3 eq.	1 eq.	NR

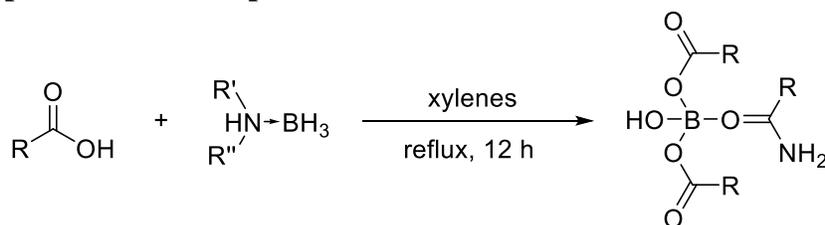
Table S2. Summary of results of the reaction conditions study.

Preparation of amides:



Scheme S7. Reaction equation for the preparation of amide products.

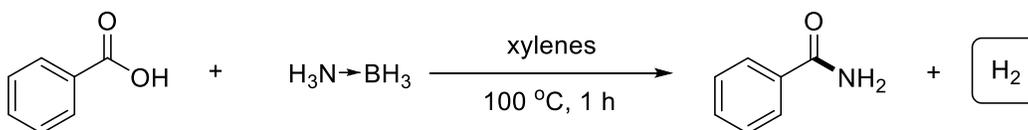
Preparation of post-reaction complex :



Scheme S9. Reaction equation for the preparation of post-reaction complex.

In a 100 ml round bottom flask containing a magnetic stir bar was weighed amine-borane (10 mmol, 1 eq.) followed by carboxylic acid (30 mmol, 3 eq). Xylenes was then added to the flask, (30 mL, 1 M with respect to carboxylic acid). A reflux condenser was attached to the flask and the reaction mixture was brought to reflux and monitored by TLC. After completion the reaction mixture was first allowed to cool to room temperature, then placed in a 0 °C freezer overnight. The precipitated solid was collected by filtration through a Büchner funnel and rinsed with cold hexanes. The solid material was transferred to a dry 100 mL round bottom flask, sealed, and residual solvent was removed by placing under high-vacuum for ~12 h.

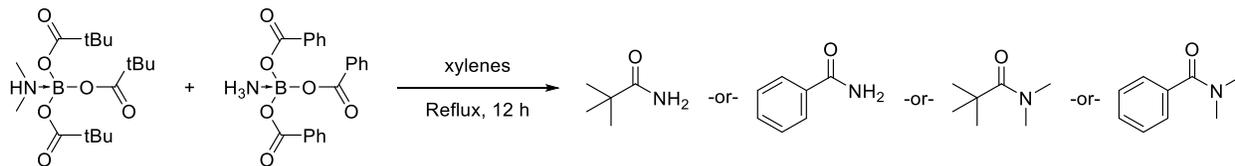
Amidation monitored by hydride analysis:



Scheme S10. Reaction equation for the preparation of post-reaction complex.

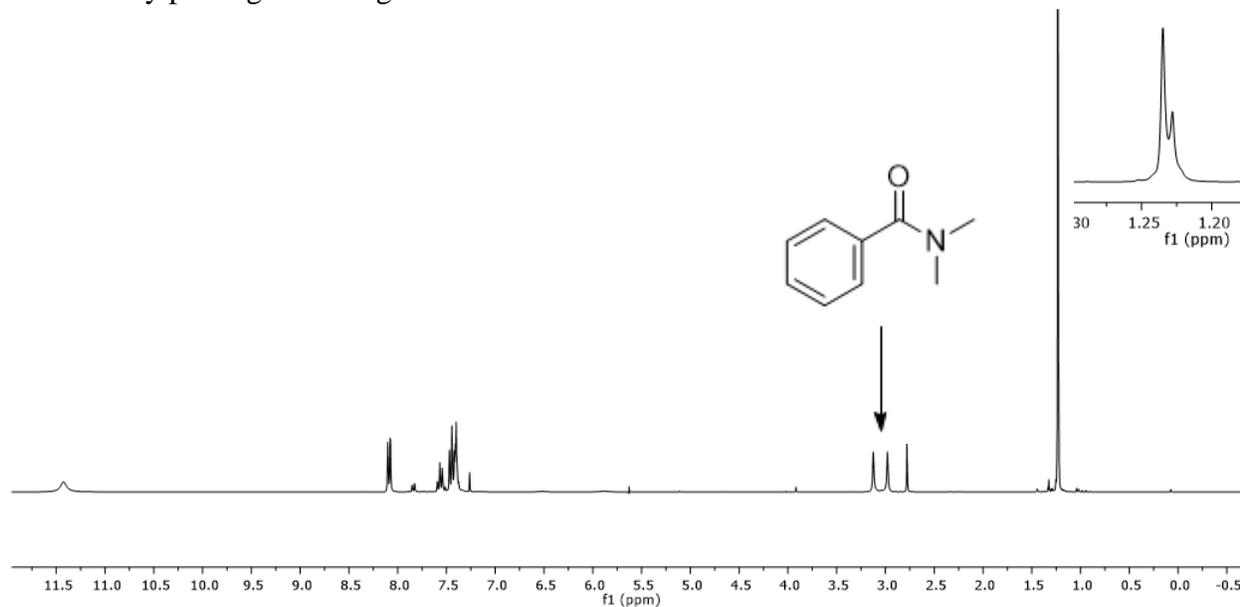
In a 25 ml round bottom flask containing a magnetic stir bar was weighed ammonia-borane (2 mmol, 1 eq., 0.0617 g) followed by benzoic acid (6 mmol, 3 eq, 0.7327 g). Xylenes was then added to the flask, (6 mL, 1 M with respect to carboxylic acid). A reflux condenser was attached to the flask, sealed with vacuum grease and Teflon tape. A barbed tygon hose adaptor was attached to the top of the reflux condenser and sealed with vacuum grease and Teflon tape. An analytical gas buret was connect to the barbed adaptor of the reaction apparatus using tygon tubing. The reaction mixture was then brought to 100 °C and the amount of gas being evolved was monitored. After completion (~1 hour) the reaction mixture was diluted with methanol (50mL) and condensed via rotary evaporation. The crude mixture was diluted with ethyl acetate (15mL) and transferred to a separatory funnel. The mixture was washed with cold 3M sodium hydroxide solution (3 x 10 mL), then washed with brine (1 x 15 mL). The organic layer was dried with sodium sulfate, filtered through cotton, and condensed via rotary evaporation. Residual solvent was removed by placing under high-vacuum for ~12 h.

Cross reaction of triacyloxyborane-amine complexes:



Scheme S11. Reaction equation for the cross reaction of amine-triacyloxyborane complexes.

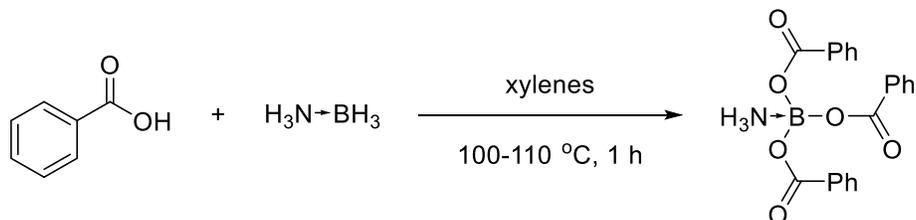
In a 50 ml round bottom flask containing a magnetic stir bar was weighed triacyloxyborane-amine **4aa** (2 mmol, 1 eq., 0.7823 g) followed by triacyloxyborane-amine **4cd** (2 mmol, 1 eq., 0.7327 g). Xylenes was then added to the flask, (4 mL, 0.5 M w.r.t. either complex). A reflux condenser was attached to the flask and a reflux condenser were sealed with rubber septa. The reaction mixture was then brought to reflux and allowed to react for 12 hours. After completion the reaction mixture was diluted with methanol (50mL) and condensed via rotary evaporation. Residual solvent was removed by placing under high-vacuum for ~12 h.



¹H NMR (300 MHz, Chloroform-*d*) cross reaction of amine-triacyloxyborane complexes.

Crystallographic information for 4aa

Preparation of triacyloxyborane-amine complex 4aa sample for crystallographic analysis:



Scheme S12. Reaction equation for the preparation of the ammonia-tribenzyloxyborane complex.

In a 100 ml round bottom flask containing a magnetic stir bar was weighed ammonia-borane (10 mmol, 1 eq., 0.3087 g) followed by benzoic acid (30 mmol, 3 eq, 3.6636 g). Xylenes was then added to the flask, (30 mL, 1 M w.r.t. carboxylic acid). The reaction mixture was heated to 100-110 °C and stirred for 1 hour. After completion the reaction mixture was first allowed to cool to room temperature, turning off the stir plate and oil bath and leaving the flask in the bath to slowly equilibrate to r.t. Once completely cooled to r.t. the flask was sealed and placed in a 0 °C freezer overnight. A sample of the precipitated solid was removed from the flask and placed into a 20 mL vial with a portion of the xylenes supernatant, this sample was subjected to x-ray crystallographic analysis. The crystallographic structure is shown below, see the attached CIF file for full structural details.

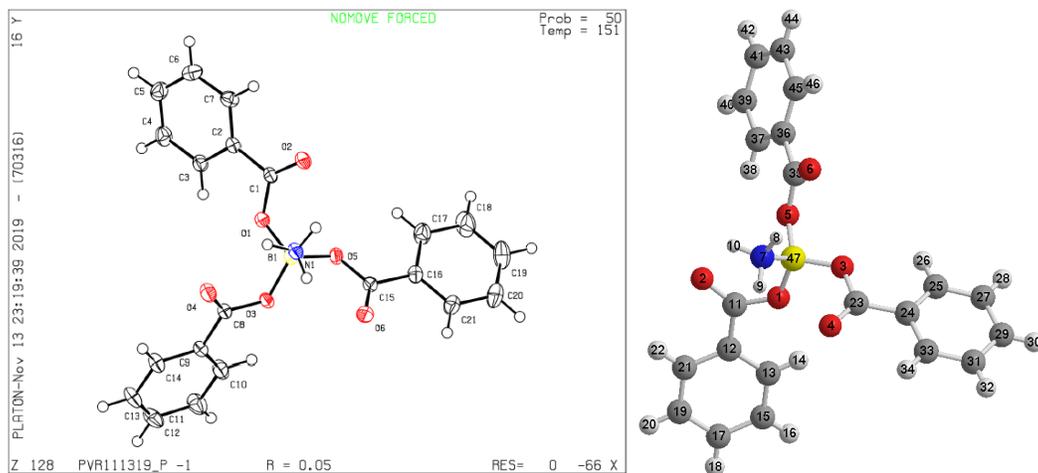
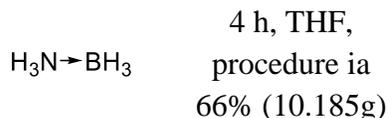


Figure S1. Crystal structure of the ammonia-tribenzyloxyborane complex.

Characterization of ammonia-borane and amine-boranes:

Ammonia-borane (1a):

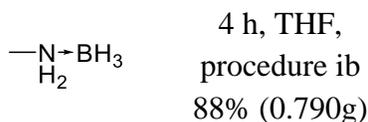


White solid.

$^1\text{H NMR}$ (300 MHz, Tetrahydrofuran-*d*8) δ 4.26 – 3.69 (m, 3H), 2.08 – 0.80 (m, 3H). $^{11}\text{B NMR}$ (96 MHz, Tetrahydrofuran-*d*8) δ -22.04 (q, $J = 95.6$ Hz).

Characterization is in agreement with previous reports for this compound.²

Methylamine-borane (1b):

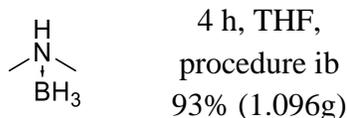


White solid.

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 3.78 (s, 2H), 2.54 (t, $J = 6.3$ Hz, 3H), 1.49 (q, $J = 91.9$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 34.7. $^{11}\text{B NMR}$ (96 MHz, Chloroform-*d*) δ -18.78 (q, $J = 96.1$ Hz).

Characterization is in agreement with previous reports for this compound.⁶

Dimethylamine-borane (1c):

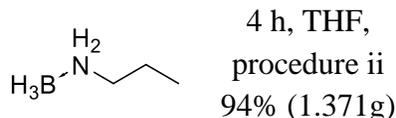


White solid.

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 4.30 (s, 1H), 2.46 (d, $J = 5.8$ Hz, 6H), 1.42 (dd, $J = 188.2$, 91.9 Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 44.4. $^{11}\text{B NMR}$ (96 MHz, Chloroform-*d*) δ -14.76 (q, $J = 95.5$ Hz).

Characterization is in agreement with previous reports for this compound.⁷

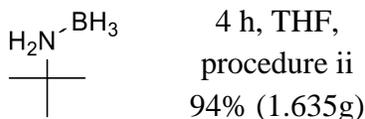
Propylamine-borane (1d):



White solid.

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 3.81 (s, 2H), 2.74 (p, $J = 7.2$ Hz, 2H), 1.62 (h, $J = 7.4$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 50.5, 22.4, 11.1. $^{11}\text{B NMR}$ (96 MHz, Chloroform-*d*) δ -19.84 (q, $J = 95.4$ Hz).

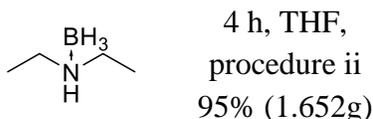
Characterization is in agreement with previous reports for this compound.⁴

Tert-butylamine-borane (1e):

White solid.

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 3.76 (s, 2H), 1.27 (s, 9H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 53.2, 28.0. $^{11}\text{B NMR}$ (96 MHz, Chloroform-*d*) δ -23.25 (q, $J = 95.7$ Hz).

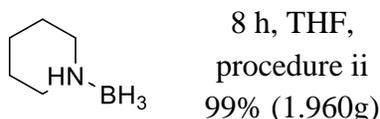
Characterization is in agreement with previous reports for this compound.⁴

Diethylamine-borane (1f):

Colorless liquid.

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 3.58 (s, 1H), 2.72 (qd, $J = 7.3, 5.6$ Hz, 4H), 1.16 (t, $J = 7.3$ Hz, 6H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 48.8, 11.6. $^{11}\text{B NMR}$ (96 MHz, Chloroform-*d*) δ -17.44 (q, $J = 95.9, 95.4$ Hz).

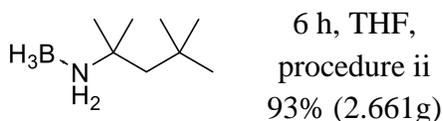
Characterization is in agreement with previous reports for this compound.⁴

Piperidine-borane (1g):

White solid.

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 3.75 (s, 1H), 3.32 – 3.13 (m, 2H), 2.47 (tdd, $J = 13.5, 11.3, 2.7$ Hz, 2H), 1.79 – 1.73 (m, 2H), 1.63 – 1.23 (m, 4H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 53.4, 25.4, 22.6. $^{11}\text{B NMR}$ (96 MHz, Chloroform-*d*) δ -15.55 (q, $J = 95.4$ Hz).

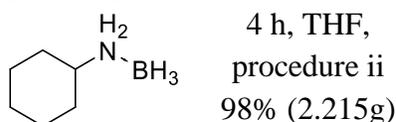
Characterization is in agreement with previous reports for this compound.⁴

Tert-octylamine-borane (1h):

White solid.

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 3.70 (s, 2H), 1.62 (s, 2H), 1.33 (s, 6H), 1.03 (s, 9H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 57.0, 52.4, 31.5, 27.5. $^{11}\text{B NMR}$ (96 MHz, Chloroform-*d*) δ -23.46 (q, $J = 96.4$ Hz).

Cyclohexylamine-borane (**1i**):

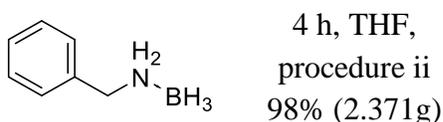


White solid.

¹H NMR (300 MHz, Chloroform-*d*) δ 4.03 – 3.25 (m, 2H), 2.68 (ttt, $J = 10.2, 6.4, 3.8$ Hz, 1H), 2.12 (dt, $J = 12.4, 3.7$ Hz, 2H), 1.75 (dq, $J = 12.3, 3.7, 3.2$ Hz, 2H), 1.62 (dt, $J = 12.3, 3.7$ Hz, 1H), 1.37 – 1.10 (m, 5H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 57.0, 32.4, 25.4, 24.6. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ -20.90 (q, $J = 96.5, 95.8$ Hz).

Characterization is in agreement with previous reports for this compound.⁴

Benzylamine-borane (**1j**):

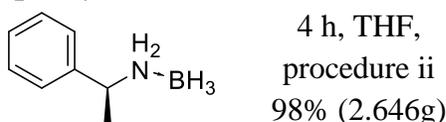


White solid.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.32 (tdd, $J = 7.3, 4.9, 1.9$ Hz, 5H), 4.22 (s, 2H), 3.98 – 3.81 (m, 2H), 2.45 – 0.93 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 135.9, 129.1, 128.6, 128.4, 53.0. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ -19.76 (q, $J = 102.1$ Hz).

Characterization is in agreement with previous reports for this compound.⁴

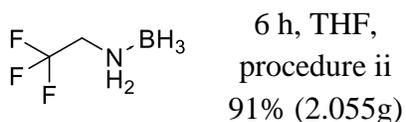
1-phenylethan-1-amine-borane (**1k**):



White solid.

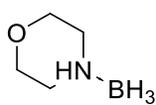
¹H NMR (300 MHz, Chloroform-*d*) δ 7.50 – 7.20 (m, 5H), 3.96 (dq, $J = 9.7, 6.6, 3.1$ Hz, 3H), 1.62 (d, $J = 6.6$ Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 141.4, 129.1, 128.5, 126.2, 58.6, 19.9. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ -20.04 (q, $J = 100.1, 98.4$ Hz).

2,2,2-trifluoroethylamine-borane (**1l**):



White solid.

¹H NMR (300 MHz, Chloroform-*d*/ DMSO-*d*6) δ 6.02 (d, $J = 11.3$ Hz, 2H), 3.15 (dq, $J = 15.2, 9.6$ Hz, 2H), 1.32 (d, $J = 70.1$ Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*/ DMSO-*d*6) δ 129.0 (q, $J = 278.1$ Hz), 53.4 (q, $J = 32.6$ Hz). **¹¹B NMR** (96 MHz, Chloroform-*d*/ DMSO-*d*6) δ -17.76 (q, $J = 98.0$ Hz). **¹⁹F NMR** (282 MHz, Chloroform-*d*/ DMSO-*d*6) δ -70.00.

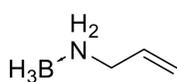
Morpholine-borane (1m):

8 h, THF,
 procedure ii
 97% (1.959g)

White solid.

¹H NMR (300 MHz, Chloroform-*d*) δ 4.40 (s, 1H), 3.91 (dd, *J* = 12.7, 3.6 Hz, 2H), 3.55 (td, *J* = 12.3, 2.3 Hz, 2H), 3.12 – 2.96 (m, 2H), 2.75 (dtd, *J* = 13.9, 11.5, 3.6 Hz, 2H), 1.44 (d, *J* = 115.8 Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 65.8, 52.0. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ -15.48 (q, *J* = 96.5 Hz).

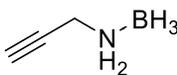
Characterization is in agreement with previous reports for this compound.⁴

Allylamine-borane (1n):

4 h, THF,
 procedure ii
 94% (1.333g)

Colorless oil.

¹H NMR (300 MHz, Chloroform-*d*) δ 5.88 (ddt, *J* = 16.8, 10.4, 6.3 Hz, 1H), 5.34 – 5.13 (m, 2H), 4.08 (s, 2H), 3.28 (tdd, *J* = 7.8, 5.8, 1.3 Hz, 2H), 1.88 - 0.91 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 132.4, 119.3, 50.8. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ -19.90 (q, *J* = 95.2, 94.0 Hz). Characterization is in agreement with previous reports for this compound.⁴

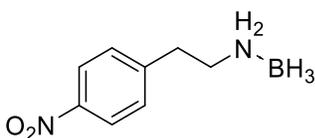
Propargylamine-borane (1o):

4 h, THF,
 procedure ii
 90% (1.240g)

White solid.

¹H NMR (300 MHz, DMSO-*d*6) δ 5.70 (s, 2H), 3.30 (d, *J* = 29.1 Hz, 1H), 3.15 (t, *J* = 6.9 Hz, 2H), 1.24 (d, *J* = 103.9 Hz, 3H). **¹³C NMR** (75 MHz, DMSO-*d*6) δ 80.1, 76.0, 36.7. **¹¹B NMR** (96 MHz, DMSO-*d*6) δ -18.85 (q, *J* = 119.7 Hz).

Characterization is in agreement with previous reports for this compound.⁴

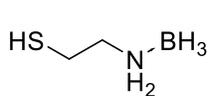
2-(4-nitrophenyl)ethan-1-amine-borane (1p):

16 h, THF,
 procedure ib
 85% (3.060g)

Orange solid.

¹H NMR (300 MHz, DMSO-*d*6) δ 8.24 – 7.94 (m, 2H), 7.44 (d, *J* = 1.8 Hz, 2H), 5.33 (s, 2H), 2.93 (dd, *J* = 9.5, 6.4 Hz, 2H), 2.78 – 2.58 (m, 2H), 1.32 (s, 3H). **¹³C NMR** (75 MHz, DMSO-*d*6) δ 152.1, 151.2, 134.9, 128.6, 53.5, 39.2. **¹¹B NMR** (96 MHz, DMSO-*d*6) δ -19.80 (q, *J* = 112.2 Hz).

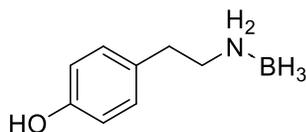
Characterization is in agreement with previous reports for this compound.⁴

2-aminoethane-1-thiol-borane (1q):

4 h, THF,
 procedure ii
 71% (1.292g)

Pale yellow solid.

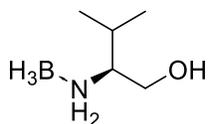
¹H NMR (300 MHz, DMSO-*d*6) δ 4.52 (s, 2H), 2.55 – 2.11 (m, 5H), 0.79 (m, 3H). **¹³C NMR** (75 MHz, DMSO-*d*6) δ 51.9, 40.3. **¹¹B NMR** (96 MHz, DMSO-*d*6) δ -19.92 (q, *J* = 95.0, 94.3 Hz).

Tyramine-borane (1r):

24 h, THF,
 procedure ib
 93% (2.809g)

White solid.

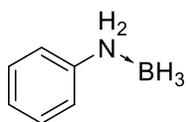
¹H NMR (300 MHz, DMSO-*d*6) δ 6.91 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 7.9 Hz, 2H), 5.21 (s, 2H), 2.65 (dd, *J* = 9.9, 4.9 Hz, 2H), 2.60 – 2.51 (m, 2H), 2.51 – 2.43 (m, 1H), 1.25 (s, 3H). **¹³C NMR** (75 MHz, DMSO-*d*6) δ 156.7, 129.1, 127.8, 115.5, 49.8, 33.5. **¹¹B NMR** (96 MHz, DMSO-*d*6) δ -20.55 (q, *J* = 95.3 Hz).

Valinol-borane (1s):

16 h, THF,
 procedure ii
 87% (2.036g)

Colorless oil.

¹H NMR (300 MHz, Chloroform-*d*) δ 4.17 (s, 1H), 4.01 (d, *J* = 11.7 Hz, 1H), 3.73 – 3.66 (m, 1H), 2.65 – 2.55 (m, 1H), 2.48 (s, 2H), 2.10 (dp, *J* = 13.9, 6.9 Hz, 1H), 0.98 (dd, *J* = 21.5, 6.8 Hz, 6H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 63.99, 58.75, 27.47, 19.53, 18.06. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ -21.27 (q, *J* = 98.1, 96.2 Hz).

Aniline-borane (1t):

1 h, hexane,
 procedure iii
 88% (2.824 g)

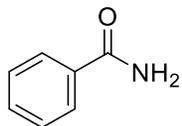
White solid.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.80 – 6.89 (m, 5H), 5.44 (s, 2H), 2.55 – 1.27 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*/ DMSO-*d*6) δ 147.92, 133.58, 130.41, 127.01. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ -16.17 (q, *J* = 99.2, 97.3 Hz).

Characterization is in agreement with previous reports for this compound.⁵

Characterization of amide products:

Benzamide (3aa):



12 h, xylene, reflux
91% (220mg)

White solid, Melting point: 128-130°C (Meltemp),

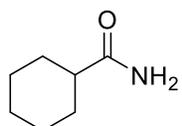
R_f = 0.31 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, DMSO-*d*₆) δ 7.96 (s, 1H), 7.90 – 7.81 (m, 2H), 7.55 – 7.39 (m, 3H), 7.36 (s, 1H). **¹³C NMR** (75 MHz, DMSO-*d*₆) δ 172.9, 139.3, 136.3, 133.3, 132.5.

HRMS (ESI) *m/z*: [M+H] calculated for C₇H₈NO 122.0606, found 122.0609.

Characterization is in agreement with previous reports for this compound.^{8, 9, 16}

Cyclohexanecarboxamide (3ab):



12 h, xylene, reflux
81% (206mg)

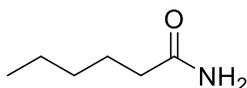
White solid, Melting point: 185-187°C (Meltemp),

R_f = 0.32 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, DMSO-*d*₆) δ 5.54 (d, *J* = 37.5 Hz, 2H), 2.14 (tt, *J* = 11.6, 3.5 Hz, 1H), 1.90 (dq, *J* = 12.4, 3.1, 1.7 Hz, 2H), 1.79 (ddt, *J* = 12.2, 6.8, 2.7 Hz, 2H), 1.67 (dddd, *J* = 10.5, 5.3, 3.2, 1.9 Hz, 1H), 1.42 (qd, *J* = 12.0, 2.5 Hz, 2H), 1.35 – 1.16 (m, 3H). **¹³C NMR** (75 MHz, DMSO-*d*₆) δ 182.4, 48.9, 34.5, 30.8, 30.6. **HRMS** (ESI) *m/z*: [M+H] calculated for C₇H₁₄NO 128.1075, found 128.1076.

Characterization is in agreement with previous reports for this compound.⁹

Hexanamide (3ac):



12 h, xylene, reflux
90% (207mg)

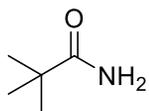
White solid, Melting point: 101-102°C (Meltemp),

R_f = 0.17 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 5.94 (d, *J* = 145.1 Hz, 2H), 2.22 – 2.13 (m, 2H), 1.60 (dq, *J* = 12.1, 7.3 Hz, 2H), 1.28 (pd, *J* = 7.2, 4.5 Hz, 4H), 0.97 – 0.72 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 176.1, 36.0, 31.5, 25.3, 22.5, 14.0. **HRMS** (ESI) *m/z*: [M+H] calculated for C₆H₁₄NO 116.1075, found 116.1083.

Characterization is in agreement with previous reports for this compound.¹⁰

Pivalamide (3ad):



2 h, xylene, reflux
83% (168mg)

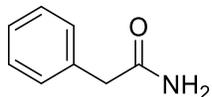
White solid, Melting point: 154-156°C (Meltemp),

R_f = 0.32 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, DMSO-*d*₆) δ 6.85 (d, *J* = 90.1 Hz, 2H), 1.05 (s, 9H). **¹³C NMR** (75 MHz, DMSO-*d*₆) δ 184.8, 43.1, 32.7. **HRMS** (ESI) *m/z*: [M+H] calculated for C₅H₁₂NO 102.0919, found 102.0915.

Characterization is in agreement with previous reports for this compound.¹⁰

2-phenylacetamide (3ae):



12 h, xylene, reflux
77% (208mg)

White solid, Melting point: 156-158°C (Meltemp),

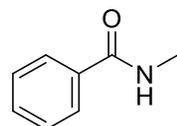
R_f = 0.26 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, DMSO-*d*₆) δ 7.64 – 7.09 (m, 5H), 5.66 (d, *J* = 137.8 Hz, 2H), 3.57 (s, 2H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ 177.5, 141.5, 134.2, 133.3, 131.4, 47.6. **HRMS** (ESI) *m/z*: [M+H] calculated for C₈H₁₀NO 136.0762, found 136.0762.

Characterization is in agreement with previous reports for this compound.^{9, 10}

N-methylbenzamide (3ba):



12 h, xylene, reflux
90% (243mg)

White solid, Melting point: 79-81°C (Meltemp),

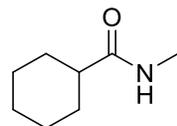
R_f = 0.38 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.90 – 7.68 (m, 2H), 7.53 – 7.30 (m, 3H), 6.73 (s, 1H), 2.95 (d, *J* = 4.8 Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 168.3, 134.5, 131.2, 128.4, 126.8, 26.9.

HRMS (ESI) *m/z*: [M+H] calculated for C₈H₁₀NO 136.0762, found 136.0770.

Characterization is in agreement with previous reports for this compound.^{10, 16, 17}

N-methylcyclohexanecarboxamide (3bb):



12 h, xylene, reflux
74% (209mg)

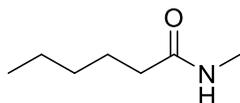
White solid, Melting point: 111-113°C (Meltemp),

R_f = 0.77 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 6.05 (s, 1H), 2.73 (d, *J* = 4.8 Hz, 3H), 2.05 (tt, *J* = 11.8, 3.4 Hz, 1H), 1.89 – 1.53 (m, 5H), 1.38 (tt, *J* = 12.1, 6.0 Hz, 2H), 1.31 – 1.04 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 176.8, 45.5, 29.7, 26.2, 25.8. **HRMS** (ESI) *m/z*: [M+H] calculated for C₈H₁₆NO 142.1232, found 142.1231.

Characterization is in agreement with previous reports for this compound.¹¹

N-methylhexanamide (3bc):



12 h, xylene, reflux
84% (217mg)

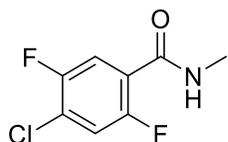
Slightly yellow liquid

R_f = 0.78 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 6.00 (s, 1H), 2.75 (d, *J* = 4.8 Hz, 3H), 2.21 – 2.06 (m, 2H), 1.67 – 1.52 (m, 2H), 1.30 – 1.21 (m, 4H), 0.93 – 0.79 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 173.9, 36.7, 31.6, 26.3, 25.6, 22.5, 14.0. **HRMS** (ESI) *m/z*: [M+H] calculated for C₇H₁₆NO 130.1232, found 130.1229.

Characterization is in agreement with previous reports for this compound.¹⁰

4-chloro-2,5-difluoro-N-methylbenzamide (3bf):



12 h, xylene, reflux
83% (341mg)

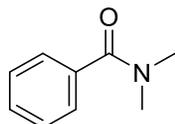
White solid, Melting point: 128-130°C (Meltemp),

R_f = 0.50 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 9.3, 6.6 Hz, 1H), 7.16 (dd, *J* = 10.5, 5.7 Hz, 1H), 6.81 (s, 1H), 2.97 (dd, *J* = 4.8, 1.1 Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 161.7, 156.6 (d, *J* = 61.3 Hz), 153.3 (d, *J* = 61.6 Hz), 125.0 (dd, *J* = 20.5, 11.9 Hz), 121.1 (dd, *J* = 14.3, 6.1 Hz), 118.6 (dd, *J* = 25.7, 3.6 Hz), 118.0, 27.0. **¹⁹F NMR** (282 MHz, Chloroform-*d*) δ -119.00, -120.91. **HRMS** (ESI) *m/z*: [M+H] calculated for C₈H₇ClF₂NO 206.0184, found 206.0189.

Characterization is in agreement with previous reports for this compound.¹²

N,N-dimethylbenzamide (3ca):



12 h, xylene, reflux
99% (295mg)

White solid, Melting point: 41-43°C (Meltemp),

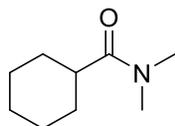
R_f = 0.41 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.31 (q, *J* = 4.8, 4.4 Hz, 5H), 2.94 (d, *J* = 42.2 Hz, 6H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 171.3, 136.2, 129.3, 128.2, 126.9, 39.6, 35.3.

HRMS (ESI) *m/z*: [M+H] calculated for C₉H₁₂NO 150.0919, found 150.0914.

Characterization is in agreement with previous reports for this compound.^{13, 14, 19}

N,N-dimethylcyclohexanecarboxamide (3cb):



12 h, xylene, reflux
92% (286mg)

Clear, colorless liquid

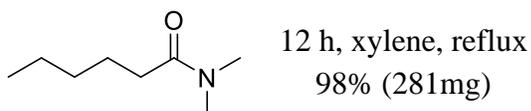
R_f = 0.30 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 3.05 – 2.89 (m, 6H), 2.47 (tt, *J* = 11.4, 3.4 Hz, 1H), 1.82 – 1.64 (m, 5H), 1.48 (qd, *J* = 11.7, 3.1 Hz, 2H), 1.32 – 1.18 (m, 3H). **¹³C NMR** (75 MHz,

Chloroform-*d*) δ 175.9, 40.7, 37.1, 35.5, 29.2, 25.9. **HRMS** (ESI) m/z : [M+H] calculated for C₉H₁₈NO 156.1388, found 156.1388.

Characterization is in agreement with previous reports for this compound.¹⁴

N,N-dimethylhexanamide (3cc):



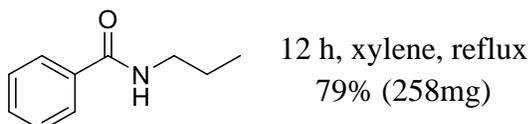
Slightly yellow liquid

R_f = 0.33 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 2.98 – 2.83 (m, 6H), 2.23 (dd, J = 8.6, 6.7 Hz, 2H), 1.64 – 1.49 (m, 2H), 1.25 (tt, J = 10.2, 4.4 Hz, 4H), 0.90 – 0.75 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 173.0, 37.3, 35.3, 33.4, 31.7, 24.9, 22.6, 14.0. **HRMS** (ESI) m/z : [M+H] calculated for C₈H₁₈NO 144.1388, found 144.1396.

Characterization is in agreement with previous reports for this compound.¹⁵

N-propylbenzamide (3da):



White solid, Melting point: 82-84°C (Meltemp),

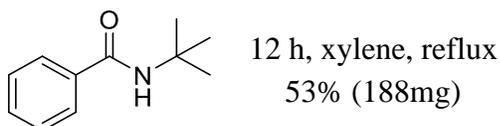
R_f = 0.49 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.84 – 7.68 (m, 2H), 7.47 – 7.38 (m, 1H), 7.38 – 7.29 (m, 2H), 6.84 (s, 1H), 3.43 – 3.25 (m, 2H), 1.58 (h, J = 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 167.6, 134.7, 131.1, 128.3, 126.9, 41.8, 23.0, 11.6.

HRMS (ESI) m/z : [M+H] calculated for C₁₀H₁₄NO 164.1075, found 164.1076.

Characterization is in agreement with previous reports for this compound.¹⁶

N-(tert-butyl)benzamide (3ea):



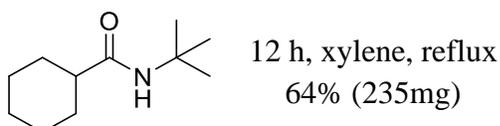
White solid, Melting point: 132-135°C (Meltemp),

R_f = 0.80 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.76 – 7.65 (m, 2H), 7.48 – 7.33 (m, 3H), 5.98 (s, 1H), 1.46 (s, 9H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 166.8, 135.8, 131.0, 128.4, 126.6, 51.7, 29.0. **HRMS** (ESI) m/z : [M+Na] calculated for C₁₁H₁₅NONa 200.1051, found 200.1057.

Characterization is in agreement with previous reports for this compound.^{17, 19}

N-(tert-butyl)cyclohexanecarboxamide (3eb):



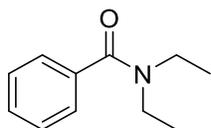
White solid, Melting point: 160-162°C (Meltemp),

R_f = 0.67 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 5.37 (s, 1H), 1.89 (tt, *J* = 11.7, 3.4 Hz, 1H), 1.71 (tdd, *J* = 11.5, 5.4, 2.7 Hz, 4H), 1.63 – 1.51 (m, 1H), 1.44 – 1.29 (m, 2H), 1.25 (s, 9H), 1.22 – 1.08 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 175.4, 50.7, 46.2, 29.8, 28.9, 25.8. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₁H₂₂NO 184.1701, found 184.1696.

Characterization is in agreement with previous reports for this compound.¹⁸

N,N-diethylbenzamide (3fa):



12 h, xylene, reflux
91% (323mg)

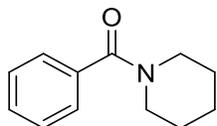
Slightly yellow liquid

R_f = 0.47 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.30 (s, 5H), 3.53 – 3.08 (m, 4H), 1.33 – 0.79 (m, 6H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 171.1, 137.1, 129.0, 128.3, 126.1, 41.3 (d, *J* = 304.7 Hz), 13.7 (d, *J* = 97.2 Hz). **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₁H₁₆NO 178.1232, found 178.1230.

Characterization is in agreement with previous reports for this compound.¹⁹

Phenyl(piperidin-1-yl)methanone (3ga):



12 h, xylene, reflux
84% (318mg)

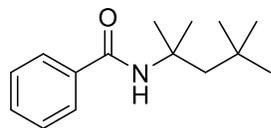
White solid, Melting point: 47-48°C (Meltemp)

R_f = 0.46 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.34 (s, 5H), 3.48 (d, *J* = 112.1 Hz, 4H), 1.63 (s, 4H), 1.48 (s, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 170.1, 136.4, 129.2, 128.3, 126.7, 48.8, 43.1, 26.6, 25.7, 24.7. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₂H₁₆NO 190.1232, found 190.1232.

Characterization is in agreement with previous reports for this compound.^{19, 21}

N-(2,4,4-trimethylpentan-2-yl)benzamide (3ha):



12 h, xylene, reflux
72% (336mg)

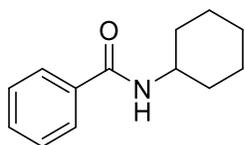
White solid, Melting point: 69-70°C (Meltemp)

R_f = 0.70 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.74 – 7.65 (m, 2H), 7.46 – 7.36 (m, 3H), 5.98 (s, 1H), 1.86 (s, 2H), 1.52 (s, 6H), 1.04 (s, 9H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 166.5, 136.1, 130.9, 128.4, 126.5, 55.6, 51.7, 31.8, 31.7, 29.4. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₅H₂₄NO 234.1858, found 234.1855.

Characterization is in agreement with previous reports for this compound.²⁰

N-cyclohexylbenzamide (3ia):



12 h, xylene, reflux
89% (362mg)

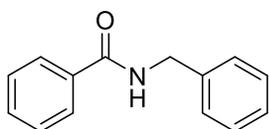
White solid, Melting point: 148-150°C (Meltemp)

R_f = 0.64 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 7.2, 1.7 Hz, 2H), 7.51 – 7.29 (m, 3H), 6.35 (d, *J* = 8.2 Hz, 1H), 4.04 – 3.79 (m, 1H), 1.96 (dt, *J* = 11.6, 3.9 Hz, 2H), 1.71 (dq, *J* = 12.7, 3.7 Hz, 2H), 1.60 (dt, *J* = 12.5, 3.7 Hz, 1H), 1.46 – 1.01 (m, 5H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 166.5, 135.0, 131.0, 128.3, 126.8, 48.8, 33.2, 25.6, 25.1. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₃H₁₈NO⁺ 204.1388, found 204.1382

Characterization is in agreement with previous reports for this compound.²¹

N-benzylbenzamide (3ja):



12 h, xylene, reflux
87% (368mg)

White solid, Melting point: 103-105°C (Meltemp)

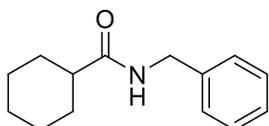
R_f = 0.55 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.75 (m, 2H), 7.53 – 7.45 (m, 1H), 7.44 – 7.36 (m, 2H), 7.36 – 7.23 (m, 5H), 6.73 (s, 1H), 4.61 (d, *J* = 5.7 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 138.3, 134.3, 131.4, 128.6, 128.4, 127.7, 127.3, 127.0, 43.9.

HRMS (ESI) *m/z*: [M+H] calculated for C₁₄H₁₄NO 212.1075, found 212.1071.

Characterization is in agreement with previous reports for this compound.^{16, 19, 21, 23}

N-benzylcyclohexanecarboxamide (3jb):



12 h, xylene, reflux
93% (404mg)

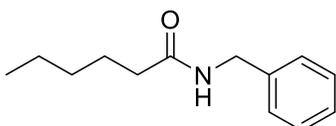
White solid, Melting point: 113-114°C (Meltemp)

R_f = 0.52 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.01 (m, 5H), 6.55 (t, *J* = 5.9 Hz, 1H), 4.33 (d, *J* = 5.8 Hz, 2H), 2.11 (tt, *J* = 11.8, 3.5 Hz, 1H), 1.97 – 1.56 (m, 5H), 1.56 – 1.33 (m, 2H), 1.21 (tdd, *J* = 18.1, 12.4, 6.1 Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 176.2, 138.7, 128.4, 127.4, 127.1, 45.4, 43.2, 29.8, 25.8. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₄H₂₀NO 218.1545, found 218.1544.

Characterization is in agreement with previous reports for this compound.^{22, 23}

N-benzylhexanamide (3jc):



12 h, xylene, reflux
84% (345mg)

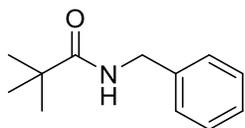
White solid, Melting point: 51-53°C (Meltemp)

R_f = 0.63 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.44 – 7.15 (m, 5H), 6.29 (s, 1H), 4.37 (d, *J* = 5.7 Hz, 2H), 2.27 – 2.09 (m, 2H), 1.73 – 1.51 (m, 2H), 1.44 – 1.15 (m, 4H), 1.02 – 0.79 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 173.1, 138.4, 128.5, 127.6, 127.3, 43.5, 36.7, 31.6, 25.6, 22.2, 14.1. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₃H₂₀NO 206.1545, found 206.1545.

Characterization is in agreement with previous reports for this compound.²³

N-benzylpivalamide (3jd):



12 h, xylene, reflux
88% (337mg)

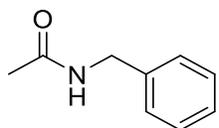
White solid, Melting point: 81-82°C (Meltemp)

R_f = 0.69 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.35 – 7.15 (m, 5H), 6.35 (s, 1H), 4.36 (d, *J* = 5.8 Hz, 2H), 1.19 (s, 9H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 178.2, 138.8, 128.5, 127.4, 127.1, 43.5, 38.7, 27.7. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₂H₁₈NO 192.1388, found 192.1383.

Characterization is in agreement with previous reports for this compound.²³

N-benzylacetamide (3jg):



12 h, xylene, reflux
74% [3 eq.] (221mg)
78% [5 eq.] (233mg)

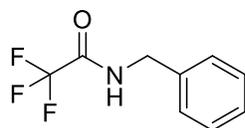
White solid, Melting point: 62-64°C (Meltemp)

R_f = 0.30 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.15 (m, 5H), 6.29 (s, 1H), 4.36 (d, *J* = 5.7 Hz, 2H), 1.96 (s, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 170.0, 138.2, 128.6, 127.7, 127.4, 43.7, 23.3. **HRMS** (ESI) *m/z*: [M+H] calculated for C₉H₁₂NO 150.0919, found 150.0918.

Characterization is in agreement with previous reports for this compound.²⁴

N-benzyl-2,2,2-trifluoroacetamide (3jh):



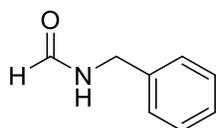
12 h, xylene, reflux
41% [3 eq.] (167mg)
63% [5 eq.] (256mg)

White solid, Melting point: 71-73°C (Meltemp)

R_f = 0.55 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 3H), 7.31 – 7.15 (m, 3H), 4.47 (d, *J* = 5.9 Hz, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 157.3 (q, *J* = 36.9 Hz), 135.9, 128.8, 128.1, 127.8, 115.9 (q, *J* = 286.9 Hz), 43.9. **¹⁹F NMR** (282 MHz, Chloroform-*d*) δ -77.28. **HRMS** (ESI) *m/z*: [M+H] calculated for C₉H₉F₃NO 204.0636, found 204.0635.

Characterization is in agreement with previous reports for this compound.²⁵

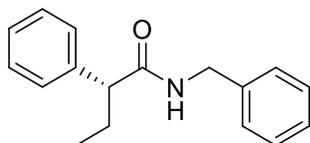
N-benzylformamide (3ji):

12 h, xylene, reflux
62% (167 mg)

White solid, Melting point: 59-61°C (Meltemp),
R_f = 0.16 in hexanes:ethyl acetate 50:50 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 8.09 (s, 0.87 H), 7.99 (d, *J* = 11.9 Hz, 0.13H), 7.40 – 7.12 (m, 5H), 6.88 (s, 0.85 H), 6.46 (s, 0.15 H), 4.35 (d, *J* = 6.0 Hz, 1.75 H), 4.28 (d, *J* = 6.5 Hz, 0.33 H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 164.8 (minor), 161.3 (major), 137.6 (major), 137.5 (minor), 128.8 (minor), 128.6 (major), 127.8 (minor), 127.6 (major), 127.4 (major), 126.9 (minor), 45.7 (minor), 42.1 (major). **HRMS** (ESI) *m/z*: [M+H] calculated for C₈H₁₀NO 136.0762, found 136.0761.

Characterization is in agreement with previous reports for this compound.²⁶

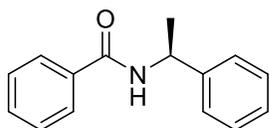
(R)-N-benzyl-2-phenylbutanamide (3jj):

12 h, xylene, reflux
89% (425 mg)

White solid, Melting point: 73-76°C (Meltemp),
R_f = 0.23 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.35 – 7.22 (m, 8H), 7.14 (dd, *J* = 7.4, 1.9 Hz, 2H), 5.97 (d, *J* = 5.9 Hz, 1H), 4.52 – 4.24 (m, 2H), 3.29 (t, *J* = 7.6 Hz, 1H), 2.36 – 2.12 (m, 1H), 1.92 – 1.73 (m, 1H), 1.02 – 0.83 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 139.9, 138.3, 128.7, 128.5, 127.9, 127.4, 127.2, 127.1, 55.3, 43.6, 26.5, 12.6. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₇H₂₀NO 254.1545, found 254.1548.

Characterization is in agreement with previous reports for this compound.²⁷

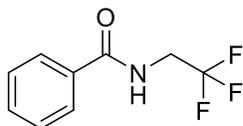
(S)-N-(1-phenylethyl)benzamide (3ka):

12 h, xylene, reflux
96% (433 mg)

White solid, Melting point: 121-124°C (Meltemp),
R_f = 0.66 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.90 – 7.74 (m, 2H), 7.48 – 7.17 (m, 9H), 5.31 (p, *J* = 7.0 Hz, 1H), 1.64 – 1.47 (m, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 166.7, 143.4, 134.5, 131.3, 128.5, 128.4, 127.2, 126.2, 49.3, 21.9. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₅H₁₆NO 226.1232, found 226.1227.

Characterization is in agreement with previous reports for this compound.²¹

N-(2,2,2-trifluoroethyl)benzamide (3la):

12 h, xylene, reflux
95% (386mg)

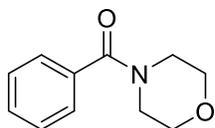
White solid, Melting point: 114-116°C (Meltemp),

R_f = 0.62 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.90 – 7.72 (m, 2H), 7.60 – 7.52 (m, 1H), 7.47 (tq, *J* = 6.6, 1.2 Hz, 2H), 6.39 (s, 1H), 4.14 (qdd, *J* = 9.1, 6.5, 0.8 Hz, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 167.8, 133.1, 132.1, 128.6, 127.1, 41.1 (q, *J* = 34.6, 34.0 Hz). **¹⁹F NMR** (282 MHz, Chloroform-*d*) δ -73.82. **HRMS** (ESI) *m/z*: [M+H] calculated for C₉H₉F₃NO 204.0636, found 204.0644.

Characterization is in agreement with previous reports for this compound.²⁸

Morpholino(phenyl)methanone (3ma):



12 h, xylene, reflux
97% (371mg)

White solid, Melting point: 70-73°C (Meltemp),

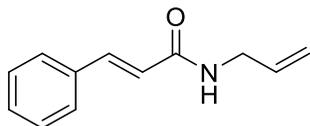
R_f = 0.41 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.36 (s, 5H), 3.55 (d, *J* = 79.9 Hz, 8H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 170.2, 135.2, 129.8, 128.5, 127.0, 66.9, 48.4, 42.5.

HRMS (ESI) *m/z*: [M+H] calculated for C₁₁H₁₄NO₂ 192.1025, found 192.1032.

Characterization is in agreement with previous reports for this compound.^{19, 21}

N-allylcinnamamide (3nk):



12 h, xylene, reflux
73% (273mg)

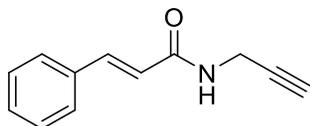
White solid, Melting point: 87-89°C (Meltemp),

R_f = 0.44 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 15.7 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.33 – 7.24 (m, 3H), 7.10 (t, *J* = 5.8 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 5.98 – 5.80 (m, 1H), 5.30 – 5.17 (m, 1H), 5.11 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.06 – 3.93 (m, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 166.2, 140.7, 134.8, 134.0, 129.5, 128.7, 127.7, 120.9, 116.3, 42.3. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₂H₁₄NO 188.1075, found 188.1074.

Characterization is in agreement with previous reports for this compound.²⁹

N-(prop-2-yn-1-yl)cinnamamide (3ok):



12 h, xylene, reflux
81% (300mg)

White solid, Melting point: 103-106°C (Meltemp),

R_f = 0.48 in hexanes:ethyl acetate 30:70 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 15.6 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.38 (dt, *J* = 4.8, 2.9 Hz, 3H), 6.39 (d, *J* = 15.6 Hz, 1H), 5.78 (s, 1H), 4.20 (dd, *J* = 5.3, 2.6 Hz, 2H), 2.27 (t, *J* = 2.5 Hz, 1H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 165.6, 141.7, 134.5, 129.8, 128.7, 127.8, 119.9, 71.7, 29.6. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₂H₁₂NO 186.0919, found 186.0905.

Characterization is in agreement with previous reports for this compound.³⁰

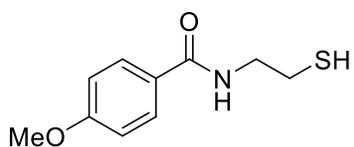
N-(4-nitrophenethyl)benzamide (3pa):

12 h, xylene, reflux
92% (497mg)

White solid, Melting point: 162-164°C (Meltemp),

R_f = 0.43 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.79 – 7.65 (m, 2H), 7.53 – 7.46 (m, 1H), 7.44 – 7.34 (m, 4H), 6.44 (s, 1H), 3.73 (q, *J* = 6.7 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 167.5, 146.8, 146.6, 134.1, 131.6, 129.6, 128.6, 126.7, 123.8, 40.9, 35.8. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₅H₁₅N₂O₃ 271.1083, found 271.1079.

N-(2-mercaptoethyl)-4-methoxybenzamide (3qi):

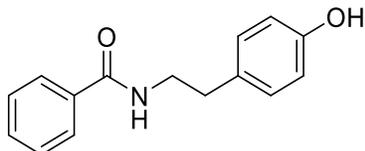
12 h, xylene, reflux
87% (368mg)

Pale yellow solid, Melting point: 87-90°C (Meltemp),

R_f = 0.28 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.87 – 7.73 (m, 2H), 7.01 (d, *J* = 6.3 Hz, 1H), 6.95 – 6.82 (m, 2H), 3.83 (s, 3H), 3.77 (q, *J* = 6.2 Hz, 2H), 2.96 (t, *J* = 6.4 Hz, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 167.2, 162.1, 128.8, 126.3, 113.7, 55.5, 39.3, 38.2.

HRMS (ESI) *m/z*: [M+H] calculated for C₁₀H₁₄NO₂S 212.0745, found 212.0753.

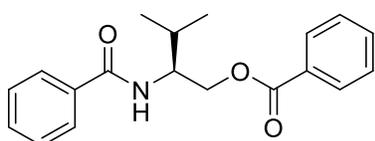
N-(4-hydroxyphenethyl)benzamide (3ra):

12 h, xylene, reflux
90% (433mg)

White solid, Melting point: 162-164°C (Meltemp),

R_f = 0.39 in hexanes:ethyl acetate 20:80 (UV, I₂)

¹H NMR (300 MHz, DMSO-*d*₆) δ 9.17 (s, 1H), 8.50 (d, *J* = 5.7 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.45 (dt, *J* = 13.9, 6.7 Hz, 3H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 3.39 (q, *J* = 6.7 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H). **¹³C NMR** (75 MHz, DMSO-*d*₆) δ 171.2, 160.7, 139.8, 136.1, 134.6, 133.3, 132.2, 120.3, 46.6, 39.6. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₅H₁₆NO₂ 242.1181, found 242.1181.

(S)-2-benzamido-3-methylbutyl benzoate (3sa):

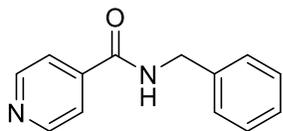
12 h, xylene, reflux
50% (311 mg)

White solid, Melting point: 76-81°C (Meltemp),

R_f = 0.37 in hexanes:ethyl acetate 50:50 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 8.15 – 7.92 (m, 2H), 7.88 – 7.69 (m, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.28 (m, 5H), 6.56 (d, *J* = 8.8 Hz, 1H), 4.54 (dd, *J* = 11.3, 6.8 Hz, 1H), 4.48 – 4.26 (m, 2H), 2.21 – 1.91 (m, *J* = 6.8 Hz, 1H), 1.05 (dd, *J* = 6.8, 3.6 Hz, 6H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 167.42, 166.68, 134.58, 133.07, 131.31, 129.66, 129.53, 128.45, 128.34, 126.83, 65.18, 54.14, 30.04, 19.53, 18.97. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₉H₂₂NO₃ 312.3890, found 312.3879.

N-benzylisonicotinamide (3jm):



12 h, xylene, reflux
79% (336 mg)

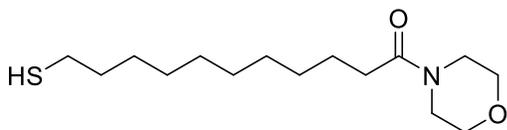
White solid, Melting point: 85-87°C (Meltemp),

R_f = 0.10 in hexanes:ethyl acetate 50:50 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 5.1 Hz, 2H), 7.65 – 7.55 (m, 2H), 7.38 – 7.25 (m, 5H), 7.25 – 7.13 (m, 1H), 4.58 (d, *J* = 5.7 Hz, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 165.34, 150.17, 141.45, 137.44, 128.74, 127.79, 127.71, 121.01, 44.26. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₃H₁₃N₂O 213.1028, found 213.1024.

Characterization is in agreement with previous reports for this compound.³¹

11-mercapto-1-morpholinoundecan-1-one (3mn):



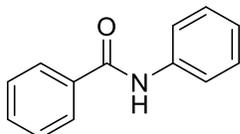
12 h, xylene, reflux
68% (391 mg)

Clear, colorless oil

R_f = 0.17 in hexanes:ethyl acetate 50:50 (I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 3.70 – 3.60 (m, 4H), 3.58 (d, *J* = 4.7 Hz, 2H), 3.43 (t, *J* = 4.7 Hz, 2H), 2.48 (q, *J* = 7.4 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.57 (h, *J* = 7.4, 6.8 Hz, 4H), 1.36 – 1.20 (m, 13H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 171.67, 66.96, 66.69, 46.09, 41.90, 34.10, 33.20, 29.52, 29.47, 29.11, 28.43, 25.32, 24.75. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₅H₃₀NO₂S 288.1997, found 288.1990.

N-phenylbenzamide (3ta):



12 h, xylene, reflux
95% (375 mg)

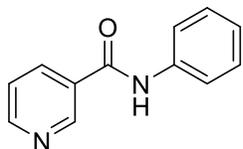
White solid, Melting point: 163-165°C (Meltemp),

R_f = 0.57 in hexanes:ethyl acetate 50:50 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.86 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.69 – 7.61 (m, 2H), 7.60 – 7.51 (m, 1H), 7.47 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.16 (td, *J* = 7.4, 1.3 Hz, 1H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 166.12, 138.62, 135.12, 131.26, 128.52, 128.15, 127.46, 123.85, 120.48. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₃H₁₂NO 198.0919, found 198.0911.

Characterization is in agreement with previous reports for this compound.³²

N-phenylnicotinamide (3to):



12 h, xylene, reflux
55% (218 mg)

White solid, Melting point: 122-124°C (Meltemp),

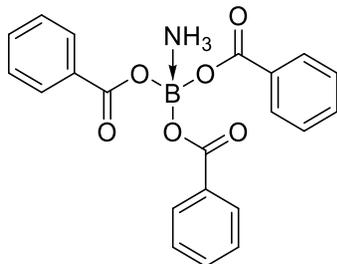
R_f = 0.10 in hexanes:ethyl acetate 50:50 (UV, I₂)

¹H NMR (300 MHz, Chloroform-*d*) δ 9.05 (d, *J* = 2.3 Hz, 1H), 8.69 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.55 (s, 1H), 8.16 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.43 – 7.30 (m, 3H), 7.21 – 7.12 (m, 1H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 163.97, 152.17, 147.82, 137.45, 135.40, 130.79, 129.04, 124.97, 123.61, 120.55. **HRMS** (ESI) *m/z*: [M+H] calculated for C₁₂H₁₁N₂O 199.0871, found 199.0859.

Characterization is in agreement with previous reports for this compound.³³

Characterization of mechanistic intermediates:

Ammonia-tribenzyloxyborane (4aa)



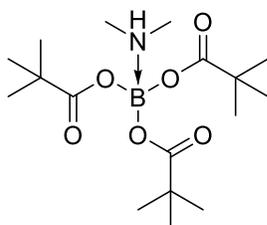
1 h, xylene, 100 °C
~99% (3.87 g)

White solid, Melting point: 137-143°C (Meltemp),

R_f = 0.42 in hexanes:ethyl acetate 50:50 (UV)

¹H NMR (300 MHz, DMSO-*d*₆) δ 7.97 (dd, *J* = 22.9, 7.4 Hz, 6H), 7.49 (td, *J* = 20.9, 17.7, 7.6 Hz, 9H), 6.47 (s, 3H). **¹³C NMR** (75 MHz, DMSO-*d*₆) δ 168.46, 165.7, 132.8, 131.7, 129.8, 129.4, 128.6, 128.4. **¹¹B NMR** (96 MHz, DMSO-*d*₆) δ 1.02 (s).

Dimethylamine-tripivaloxyborane (4cd)



4 h, xylene, 100 °C
~98% (3.50 g)

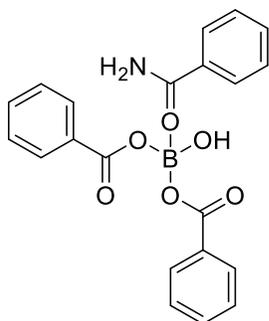
White solid, Melting point: 79-82°C (Meltemp),

R_f = 0.52 in hexanes:ethyl acetate 50:50 (Ceric Ammonium Molybdate)

¹H NMR (300 MHz, DMSO-*d*₆) δ 2.42 (s, 6H), 2.36 (s, 1H), 1.16 – 0.96 (m, 27H). **¹³C NMR** (75 MHz, DMSO-*d*₆) δ 180.7, 176.8, 38.4, 37.1, 34.9, 28.0, 27.5. **¹¹B NMR** (96 MHz, Chloroform-*d*) δ 0.65 (s).

Benzamide-dibenzyloxyboric anhydride (**complex V**)

(*Compound Identity is tentatively assigned*)



12 h, xylene, reflux

White solid

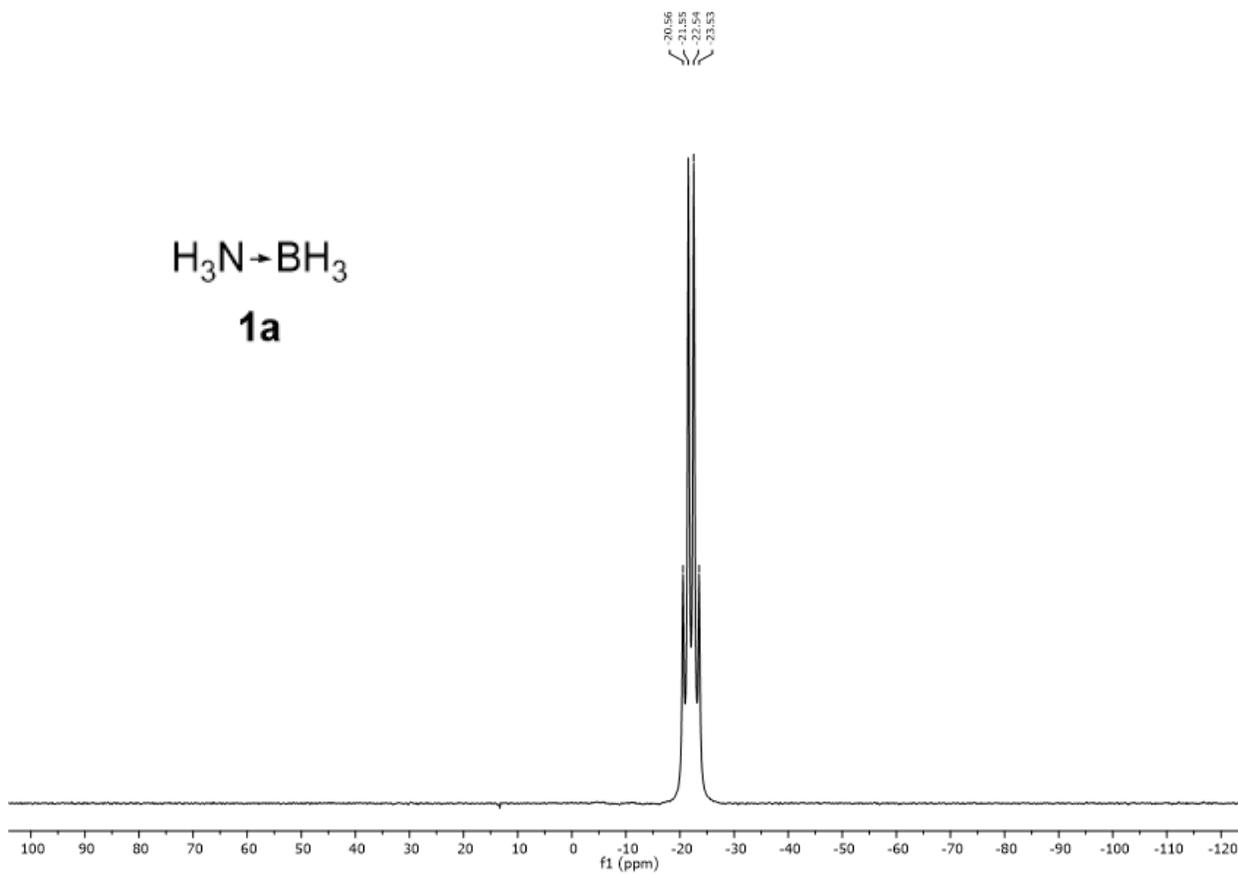
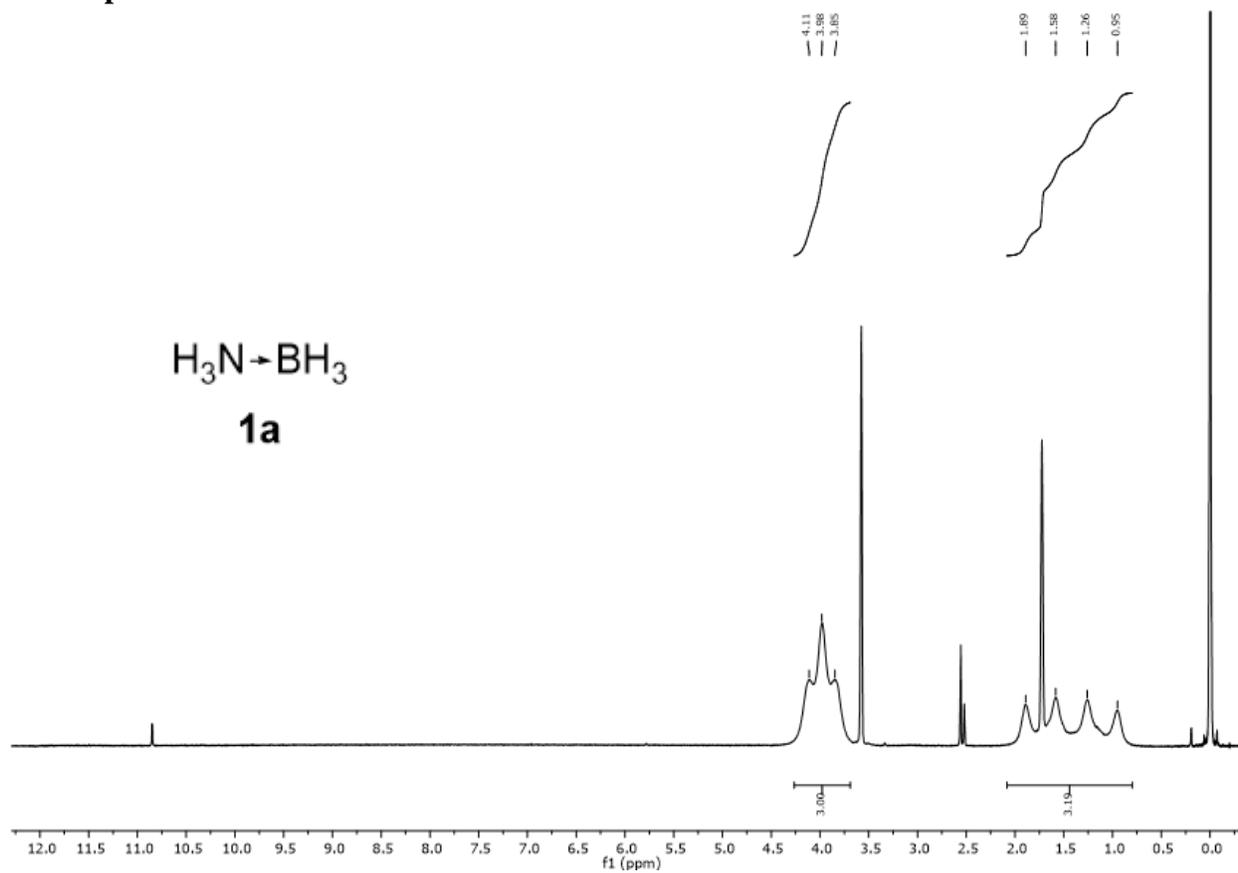
R_f = decomp. in hexanes:ethyl acetate 50:50 (UV, I₂)

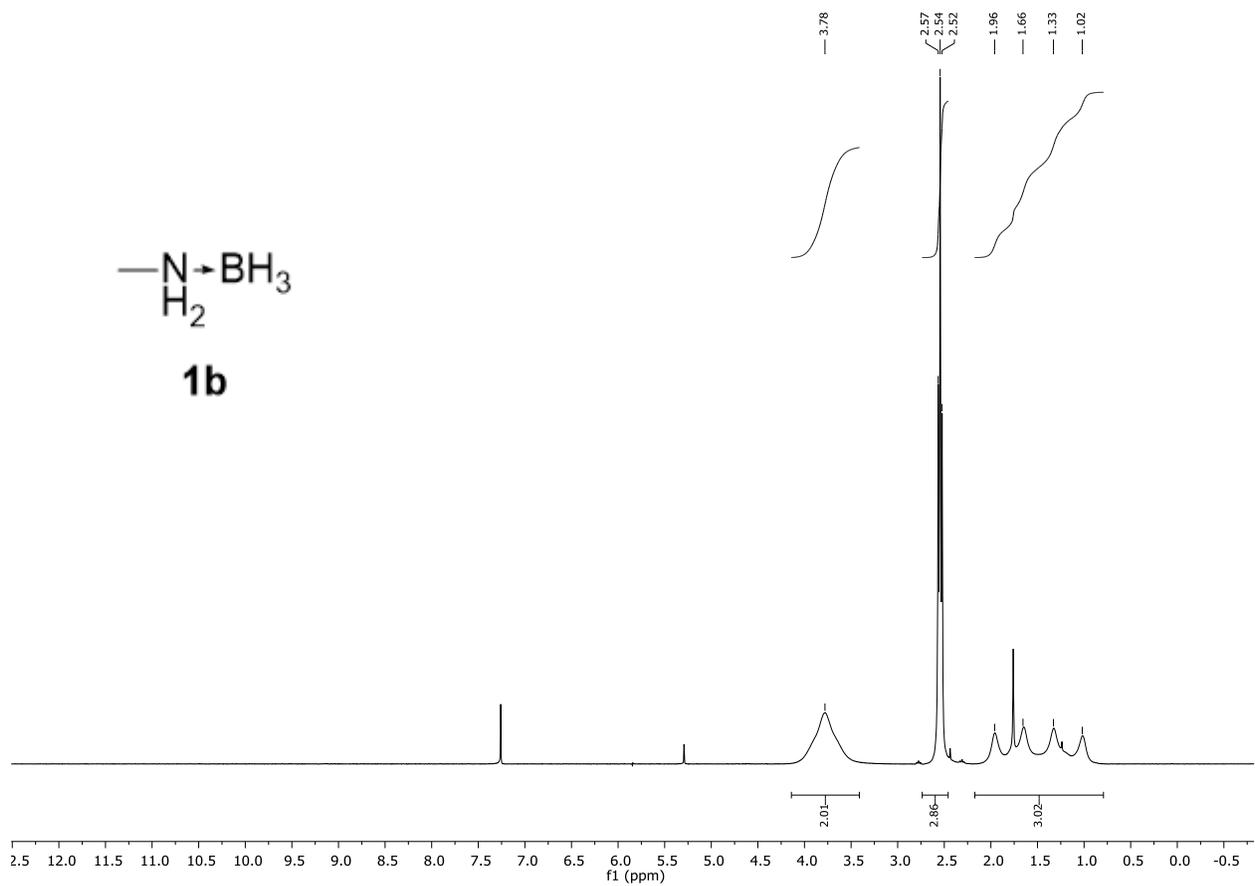
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.95 (s, 1H), 7.95 – 7.90 (m, 2H), 7.91 – 7.79 (m, 3H), 7.63 – 7.55 (m, 1H), 7.55 – 7.39 (m, 6H), 7.34 (s, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.2, 167.7, 134.6, 133.2, 131.6, 131.1, 129.6, 128.9, 128.5, 127.8. ¹¹B NMR (96 MHz, Chloroform-*d*) δ 1.86.

References:

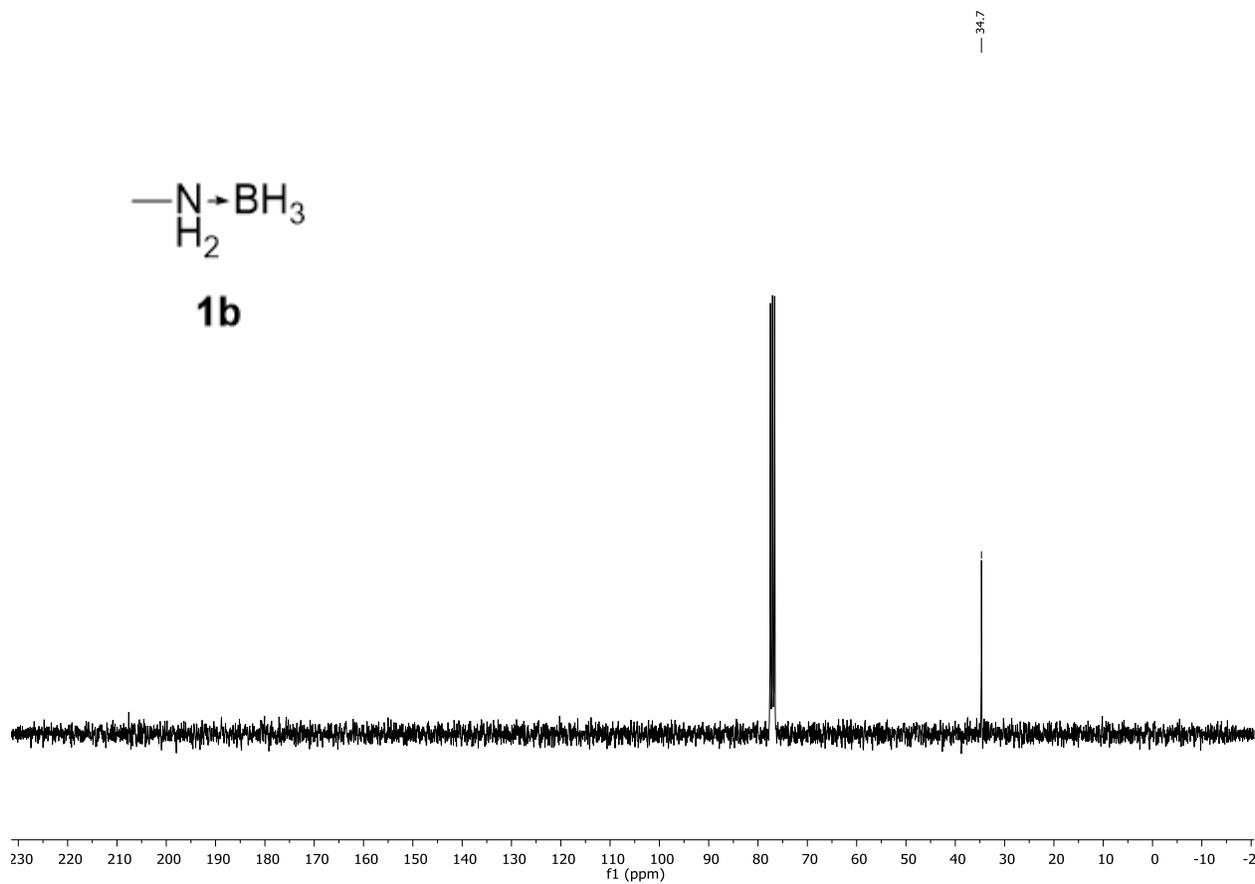
- ¹ Brown, H. C. *Organic Syntheses Via Boranes*, Wiley: New York, **1975**, Chapter 9.
- ² Ramachandran P. V.; Kulkarni A S, *Int. J. Hydrogen Energy* **2017**, *42*, 1451.
- ³ Noth, H.; Beyer, H. *Chem. Ber.* **1960**, *93*, 931.
- ⁴ Ramachandran, P. V.; Kulkarni, A. S.; Zhao, Y.; Mei, J., *Chem. Comm.* **2016**, *52*, 11885.
- ⁵ Helten, H.; Robertson, A. P. M.; Staubitz, A.; Vance, J. R.; Haddow, M. F.; Manners, I., *Chem. Eur. J.* **2012**, *18*, 4665.
- ⁶ Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I., *J. Am. Chem. Soc.* **2003**, *125*, 9424.
- ⁷ Ortmann, R.; Schlitzer, M., *Synthesis* **2009**, *10*, 1757.
- ⁸ Zhang, C.; Li, Z.; Chen, J.; Qi, S.; Fang, Y.; Zhang, S.; Ren, C.; Lu, F.; Liang, Z.; Jiang, S.; Jia, X.; Yu, S.; Zhang, G., *J. Org. Chem.* **2020**, *85*, 7728.
- ⁹ Chen, J.; Xia, Y.; Lee, S., *Org. Lett.* **2020**, *22*, 3504.
- ¹⁰ Chhatwal, A. R.; Lomax, H. V.; Blacker, A. J.; Williams, J. M. J.; Marce, P., *Chem. Sci.* **2020**, *11*, 5808.
- ¹¹ Chen, Y.; Murray, P. R. D.; Davies, A. T.; Willis, M. C., *J. Am. Chem. Soc.* **2018**, *140*, 8781.
- ¹² Tao, Y.; Widlicka, D. W.; Hill, P. D.; Couturier, M.; Young, G. R., *Org. Process Res. Dev.* **2012**, *16*, 1805.
- ¹³ Cheng, H.; Pu, M.; Kundu, G.; Schoenebeck, F., *Org. Lett.* **2020**, *22*, 331.
- ¹⁴ Hanada, S.; Tsutsumi, E.; Motoyama, Y.; Nagashima, H., *J. Am. Chem. Soc.* **2009**, *131*, 15032.
- ¹⁵ Guo, L.; Liu, Y.; Yao, W.; Leng, X.; Huang, Z., *Org. Lett.* **2013**, *15*, 1144.
- ¹⁶ Peng, H.; Ma, J.; Luo, W.; Zhang, G.; Yin, B., *Green Chem.* **2019**, *21*, 2252.
- ¹⁷ Yi, X.; Lei, S.; Liu, W.; Che, F.; Yu, C.; Liu, X.; Wang, Z.; Zhou, X.; Zhang, Y., *Org. Lett.* **2020**, *22*, 4583.
- ¹⁸ Michiyuki, T.; Osaka, I.; Komeyama, K., *Chem. Commun.* **2020**, *56*, 1247.
- ¹⁹ Shi, T.; Zhang, Z.; Yang, Y.; Yang, Z.; He, W.; Liu, C.; Fang, Z.; Guo, K., *Tetrahedron* **2020**, *76*, 131044.
- ²⁰ Alender, J.; Morgan, P.; Timberlake, J., *J. Org. Chem.* **1983**, *48*, 755.
- ²¹ Irving, C. D.; Floreancig, J. T.; Laulhe, S., *ACS Omega* **2020**, *5*, 15734.
- ²² Torres, G. M.; Liu, Y.; Arndtsen, B. A., *Science*, **2020**, *368*, 318.
- ²³ Yoshii, T.; Tsuzuki, S.; Sakurai, S.; Sakamoto, R.; Jiang, J.; Hatanaka, M.; Matsumoto, A.; Maruoka, K., *Chem. Sci.* **2020**, *11*, 5772.
- ²⁴ Luecke, M.-P.; Kostenko, A.; Wang, Y.; Yao, S.; Driess, M., *Angew. Chem., Int. Ed.*, **2019**, *58*, 12940.
- ²⁵ Sharley, D. D. S.; Williams, J. M. J., *Chem. Commun.* **2017**, *53*, 2020.
- ²⁶ Suchy, M.; Elmehriki, A. A. H.; Hudson, R. H. E. *Org. Lett.* **2011**, *13*, 3952.
- ²⁷ Ishihara, K.; Lu, Y., *Chem. Sci.* **2016**, *7*, 1276.
- ²⁸ Nemchik, A.; Badescu, V.; Phanstiel, O., *Tetrahedron* **2003**, *59*, 4315.
- ²⁹ Li, J.; Oost, R.; Maryasin, B.; Gonzalez, L.; Maulide, N., *Nat. Commun.* **2019**, *10*.
- ³⁰ Herszman, J. D.; Berger, M.; Waldvoel, S. R., *Org. Lett.* **2019**, *21*, 7893.
- ³¹ Krause, T.; Baader, S.; Erb, B.; Gooßen, L. J., *Nat. Commun.* **2016**, *7*.
- ³² Li, G.; Ji, C.; Hong, X.; Szostak, M., *J. Am. Chem. Soc.* **2019**, *141*, 11161.
- ³³ Li, G.; Szostak, M., *Nat. Commun.* **2018**, *9*.

NMR spectra of ammonia-borane and amine-boranes:

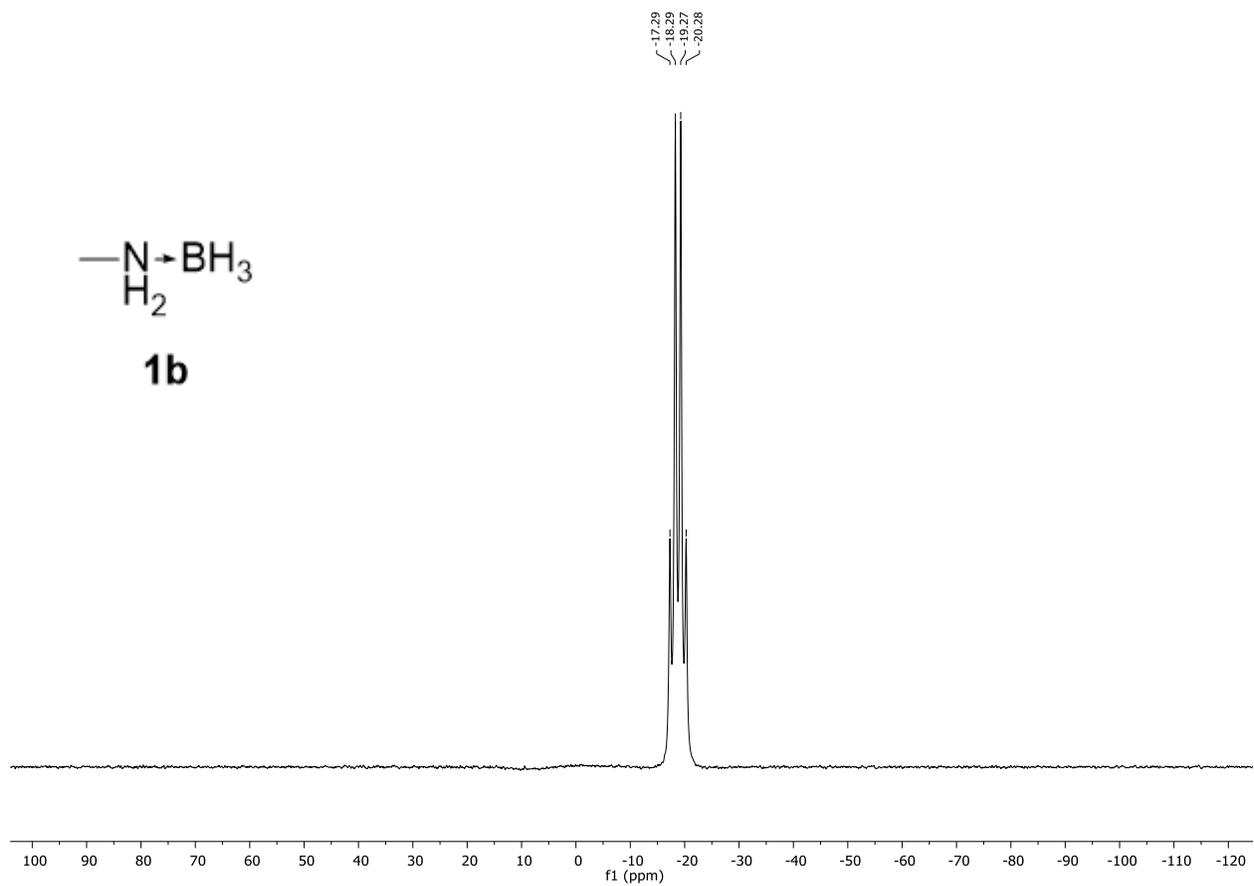




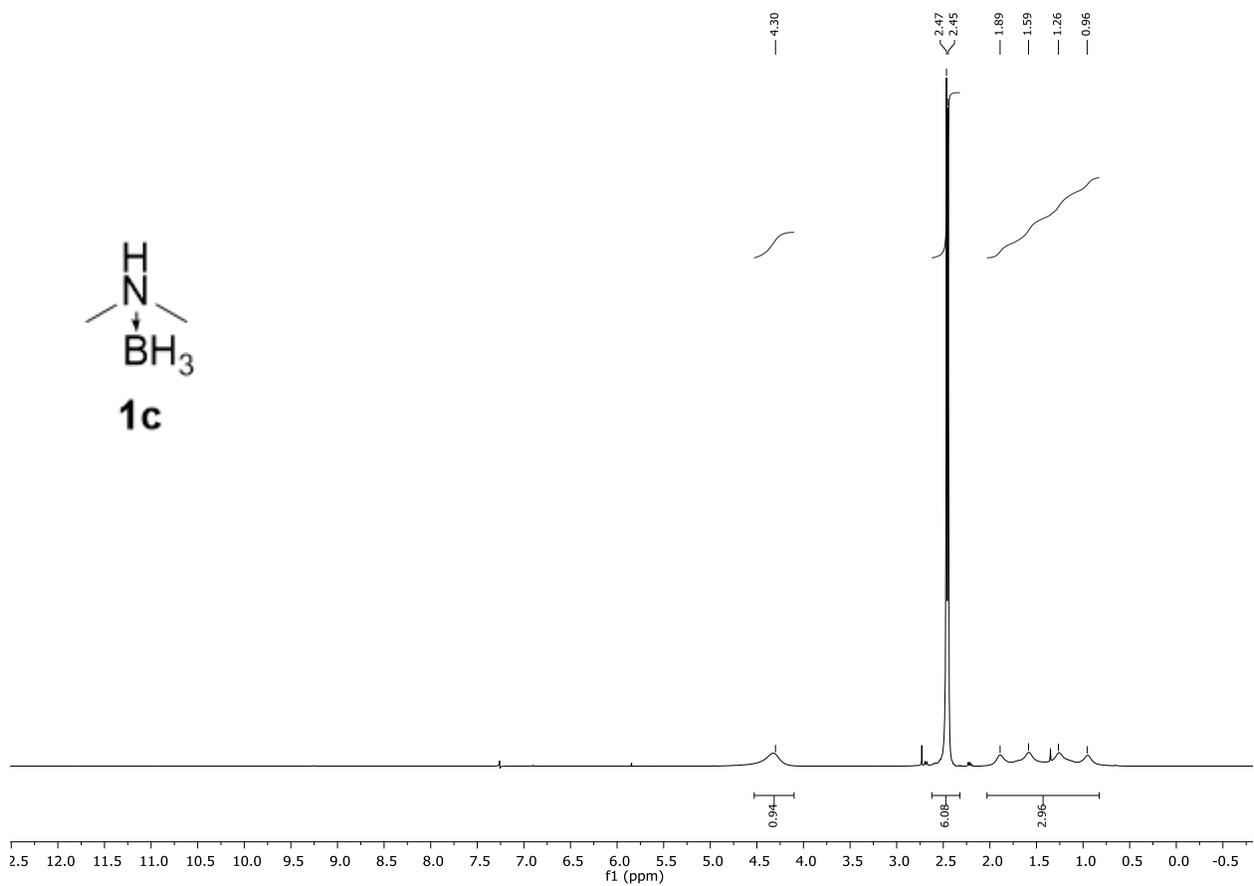
^1H NMR (300 MHz, Chloroform-*d*) methylamine-borane (**1b**)



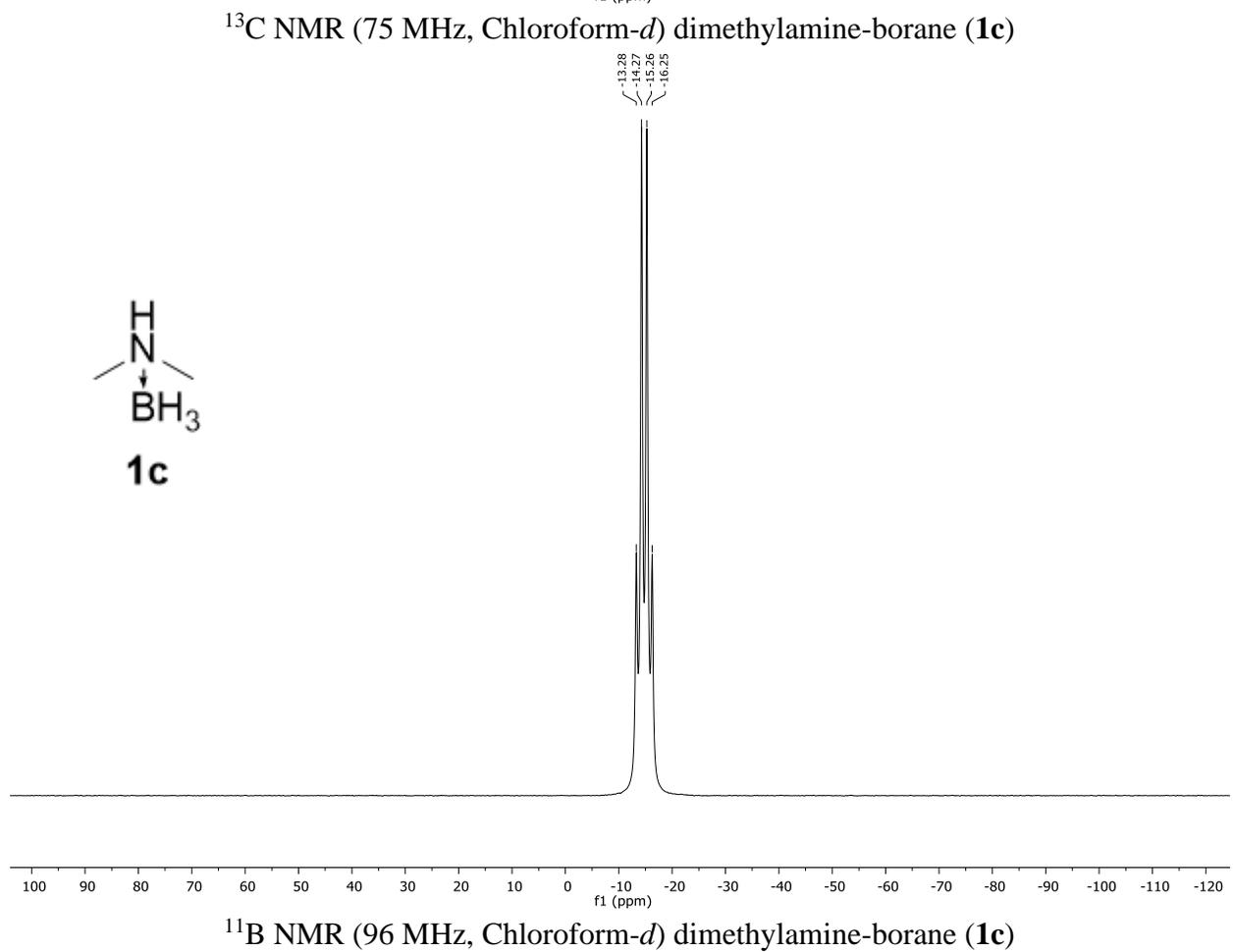
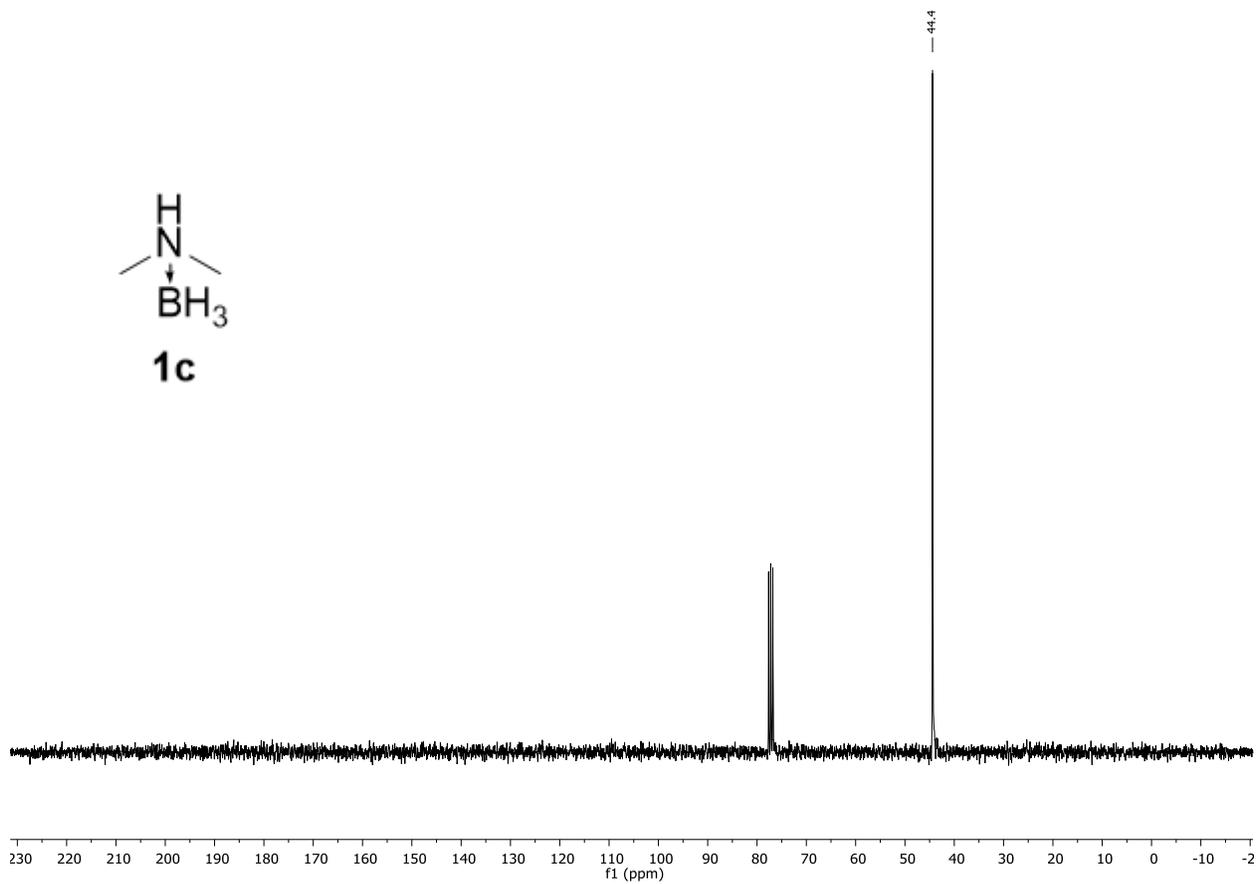
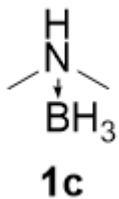
^{13}C NMR (75 MHz, Chloroform-*d*) methylamine-borane (**1b**)

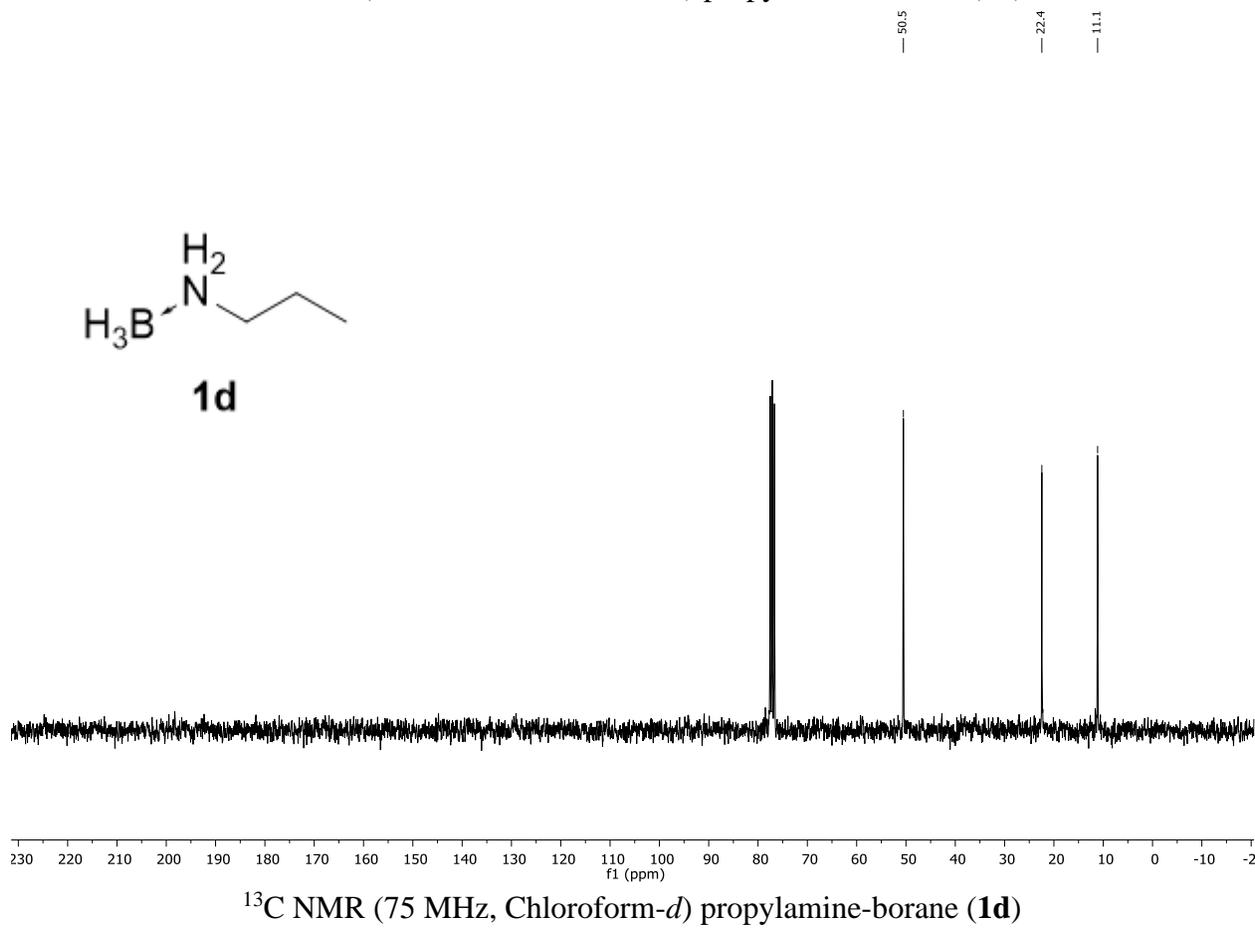
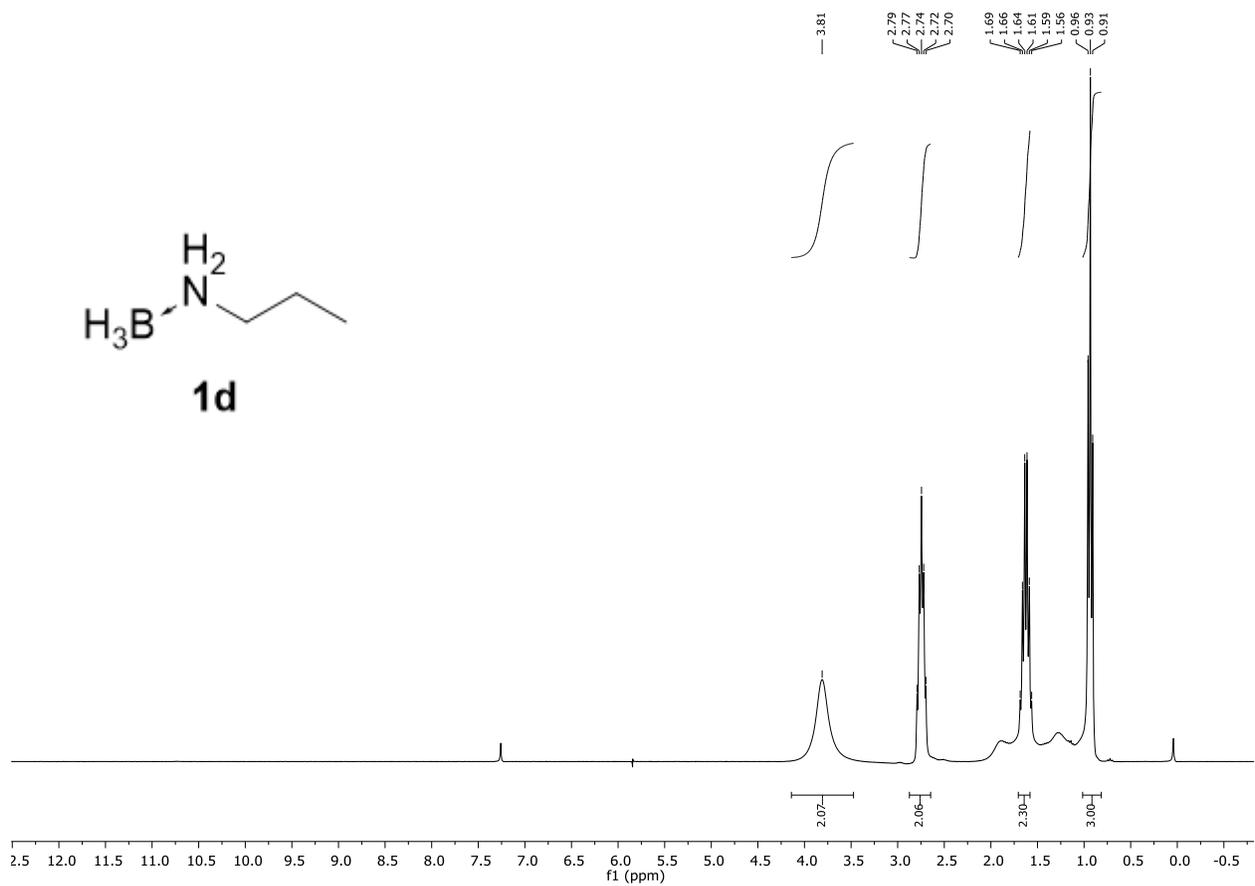


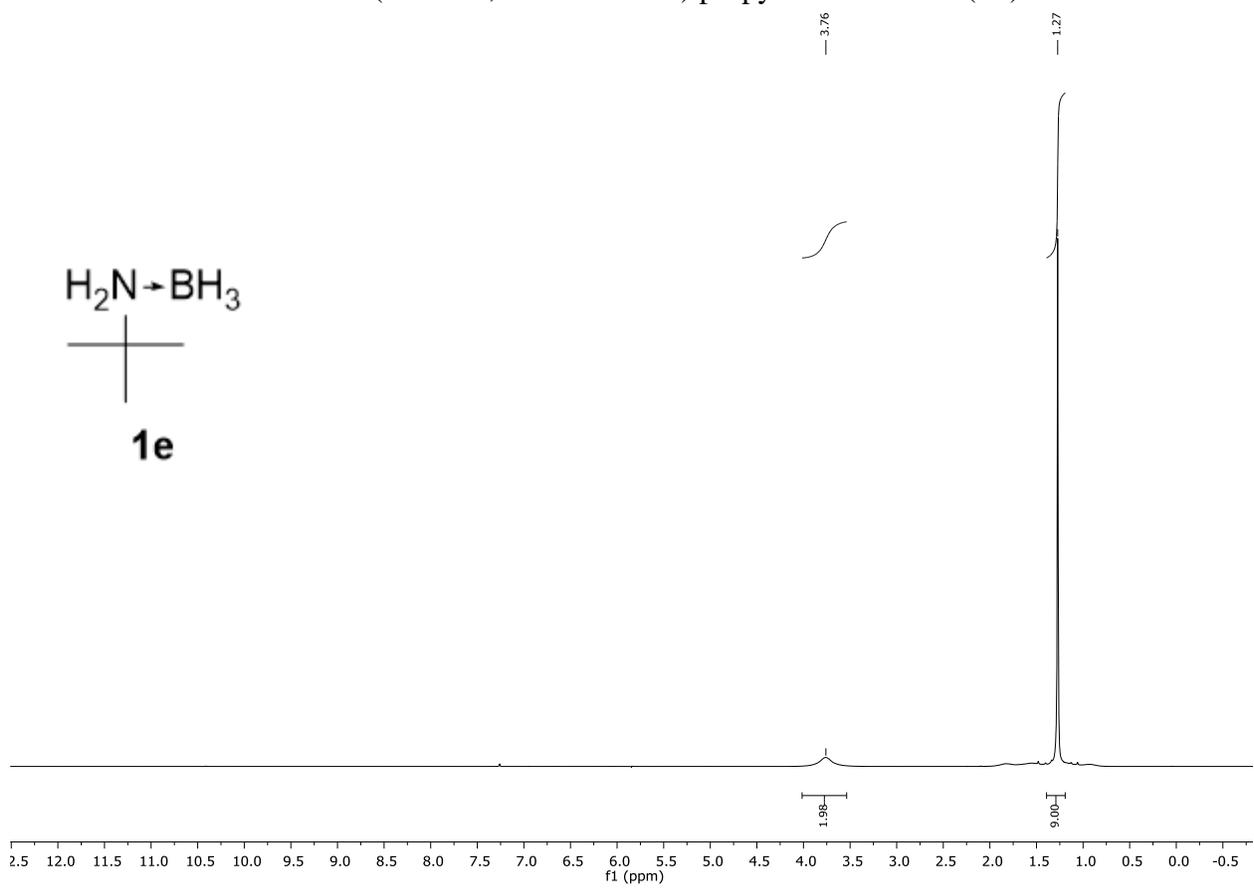
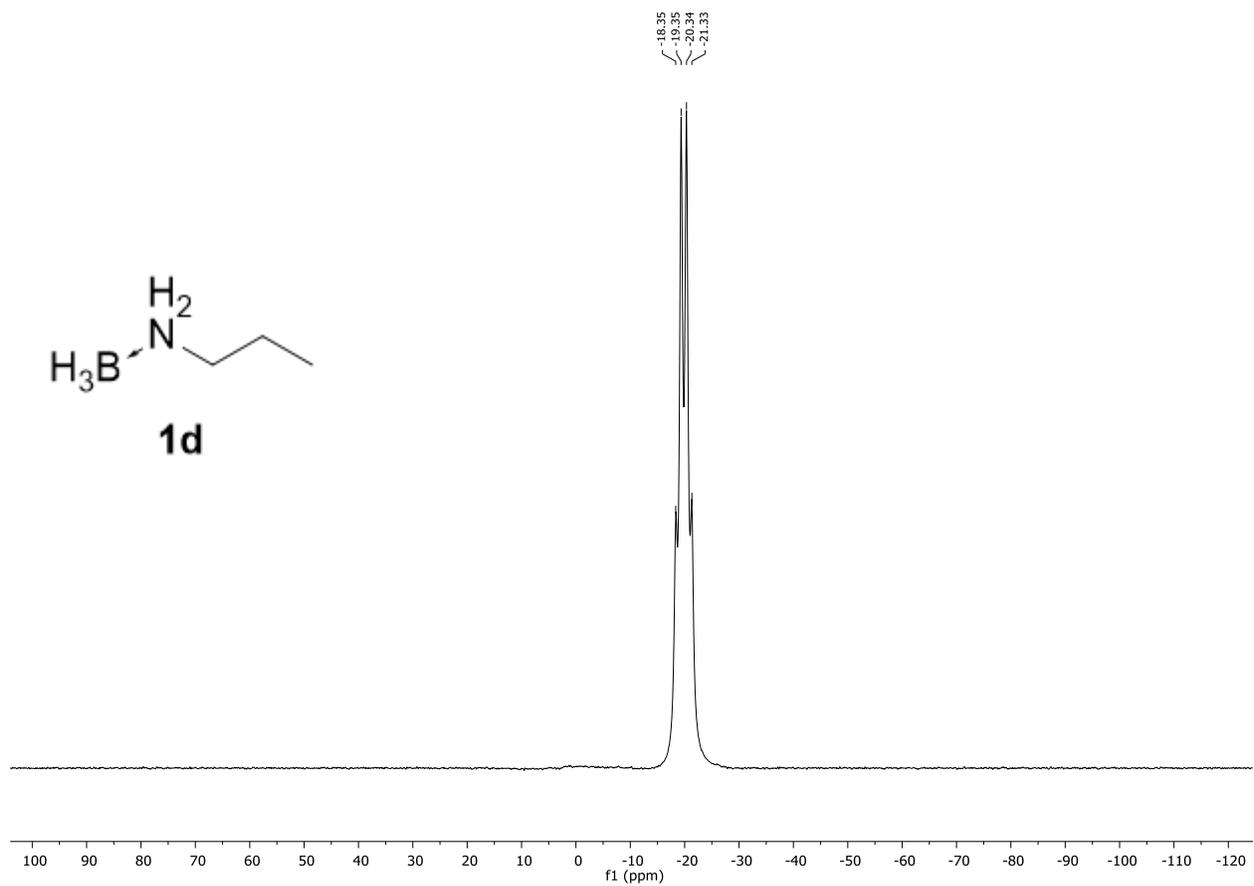
^{11}B NMR (96 MHz, Chloroform-*d*) methyamine-borane (**1b**)

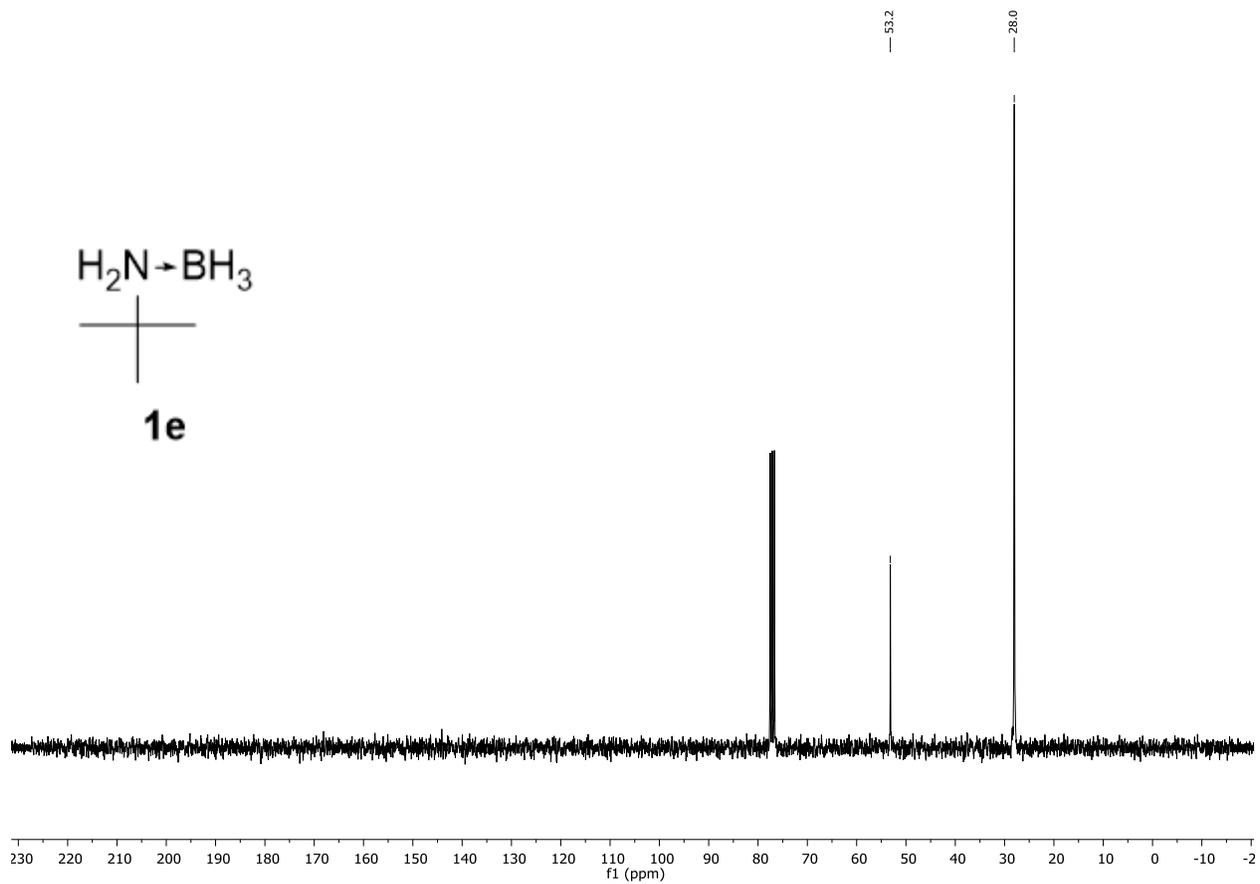


^1H NMR (300 MHz, Chloroform-*d*) dimethylamine-borane (**1c**)

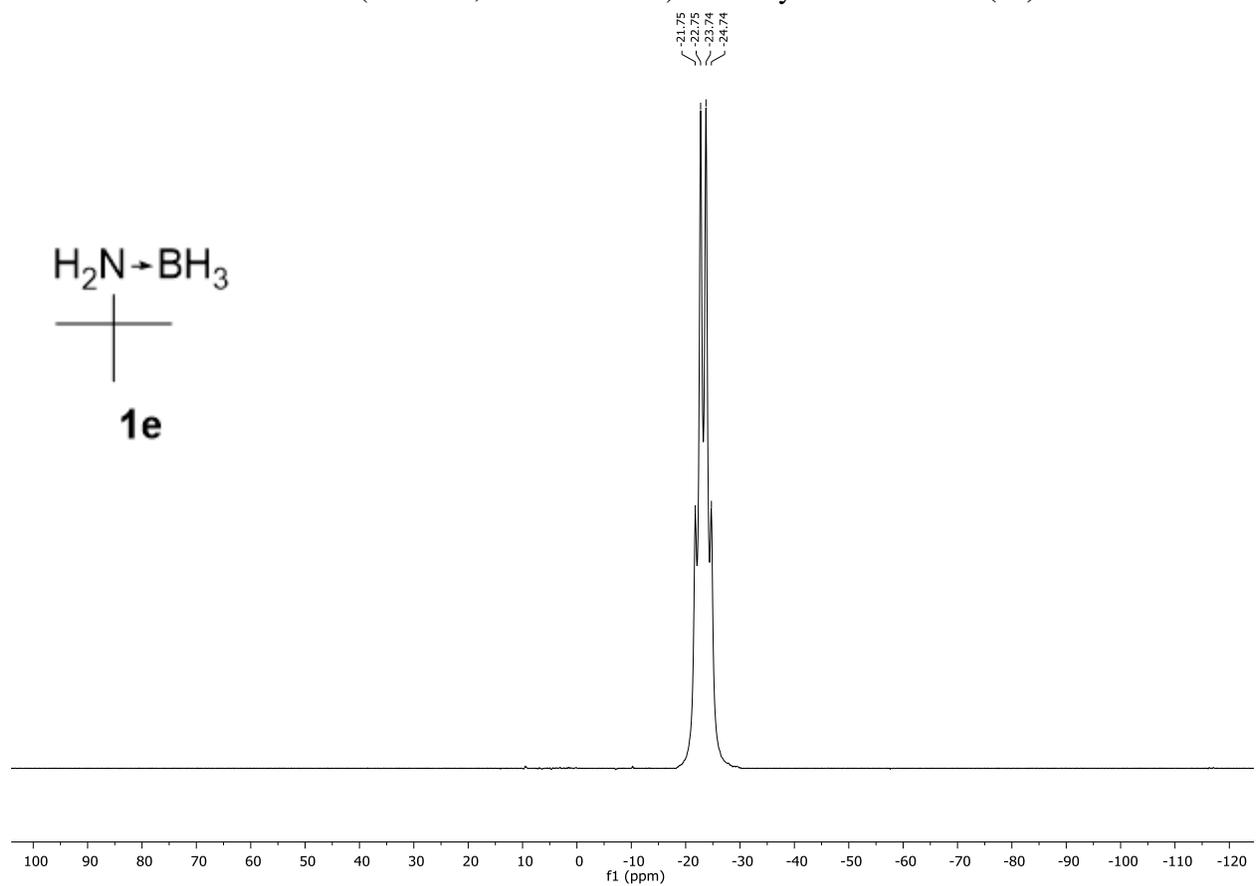




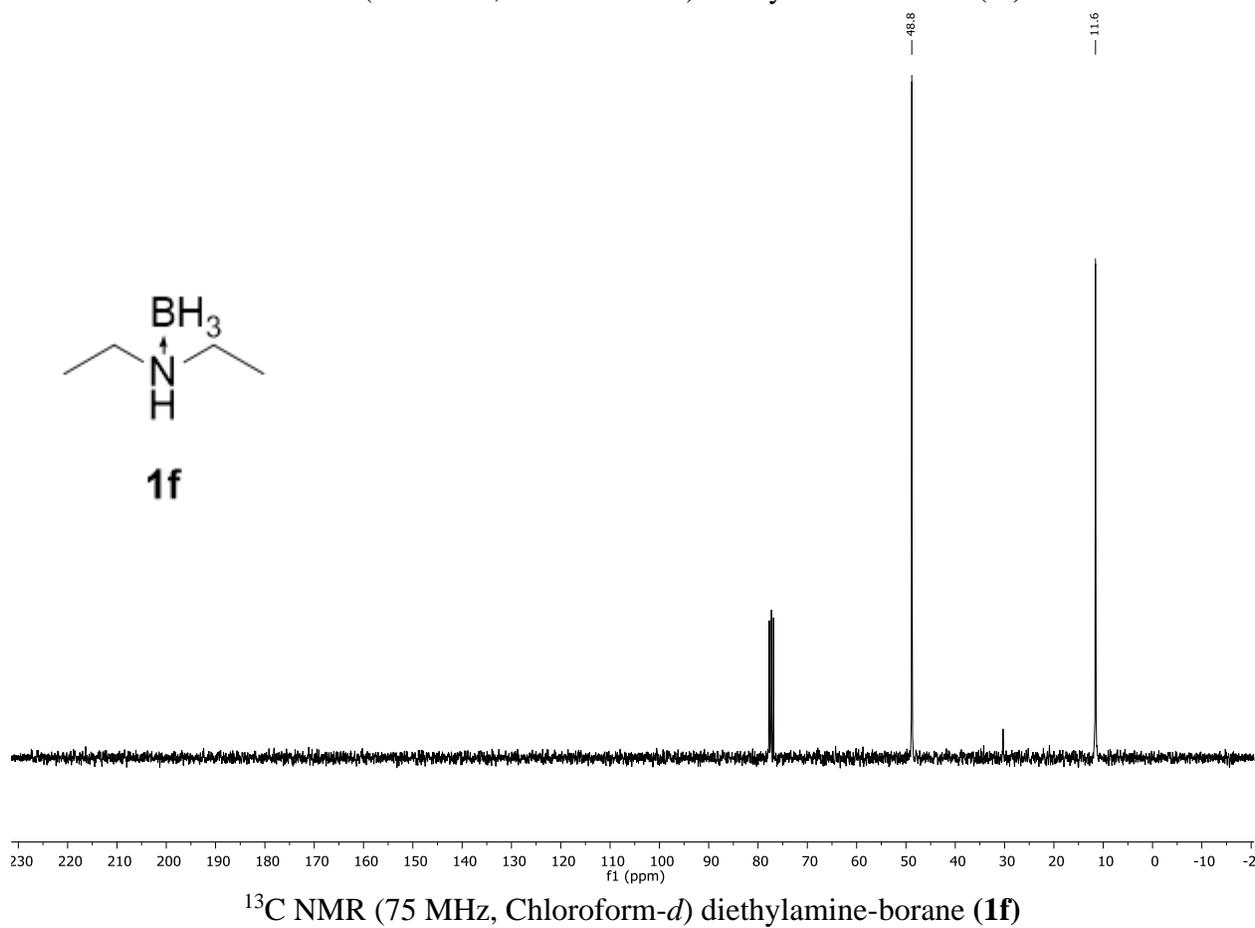
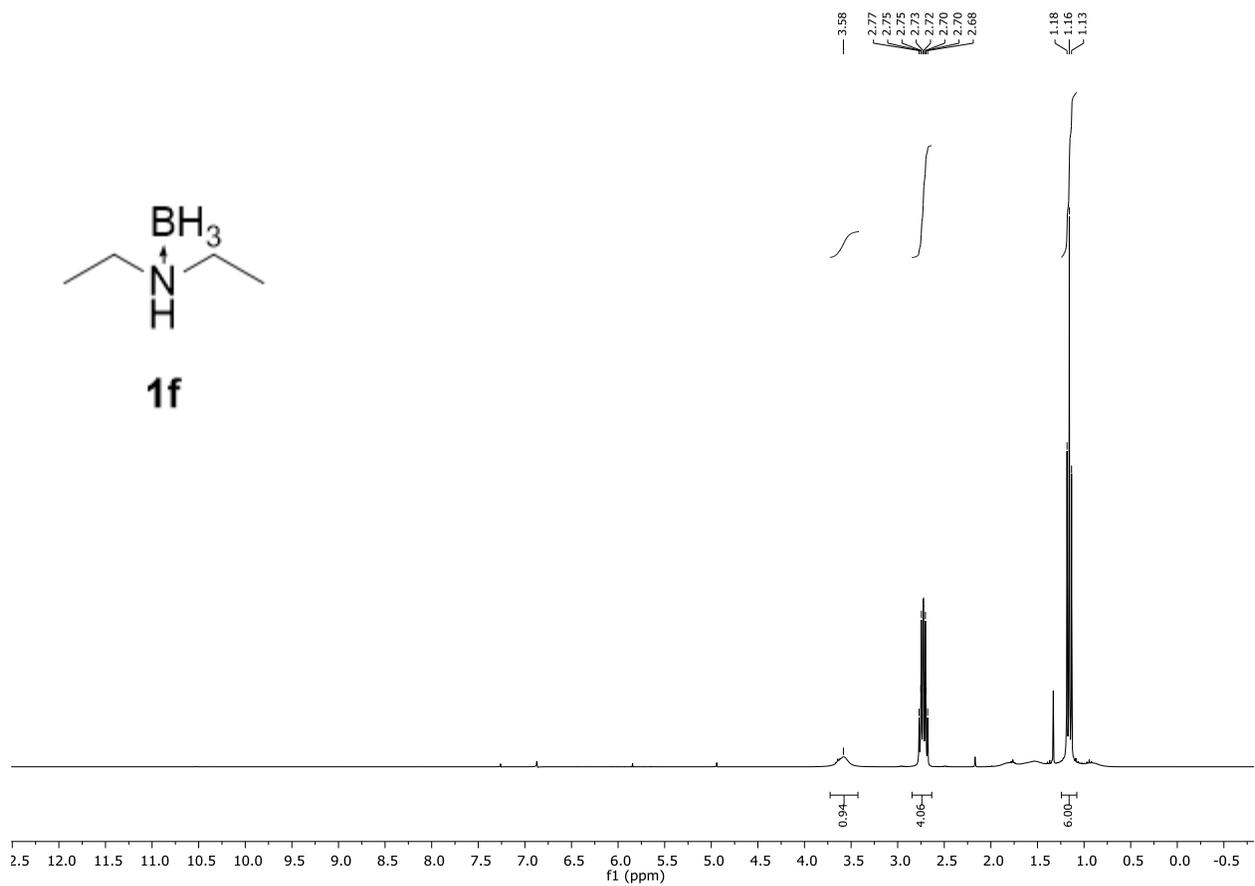


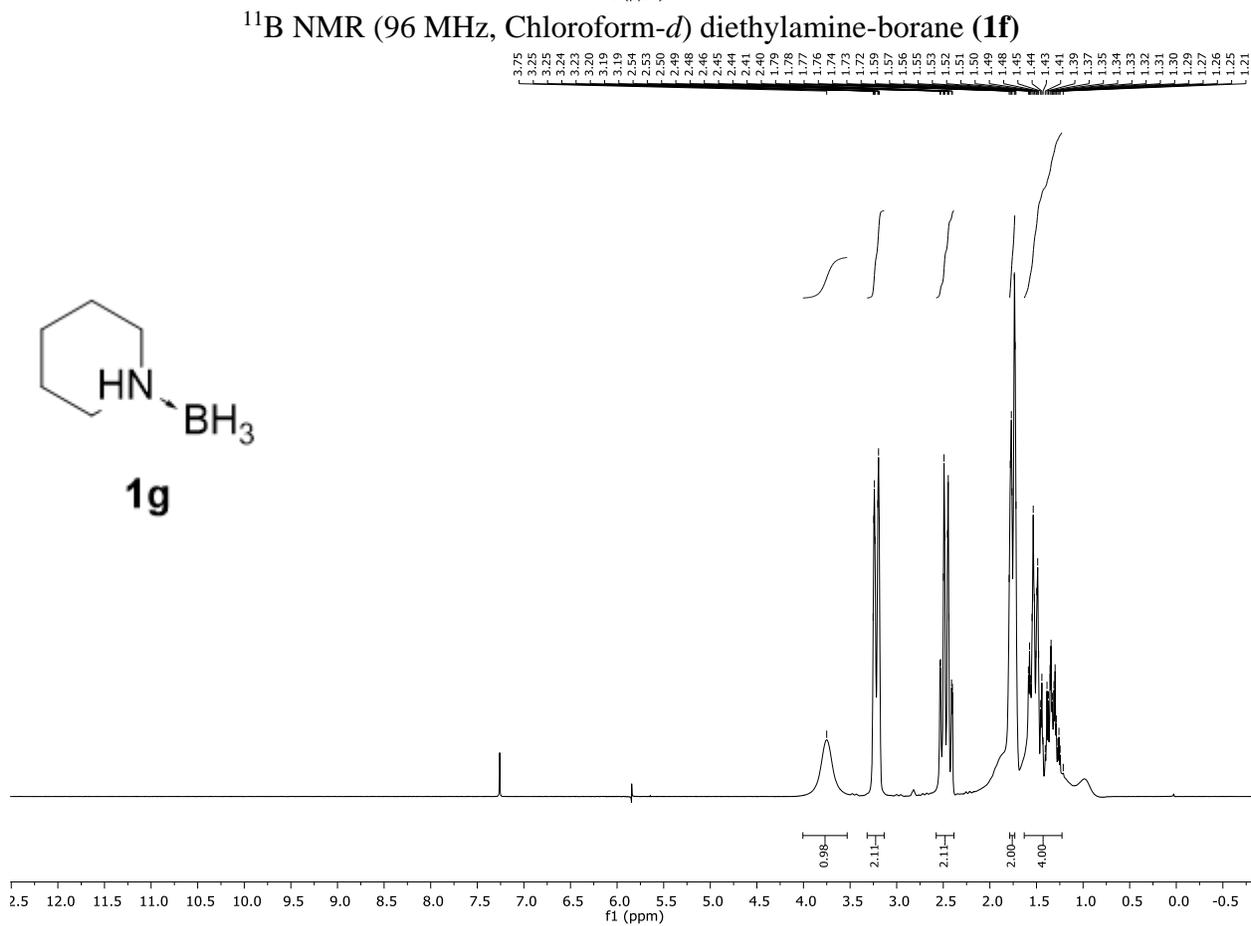
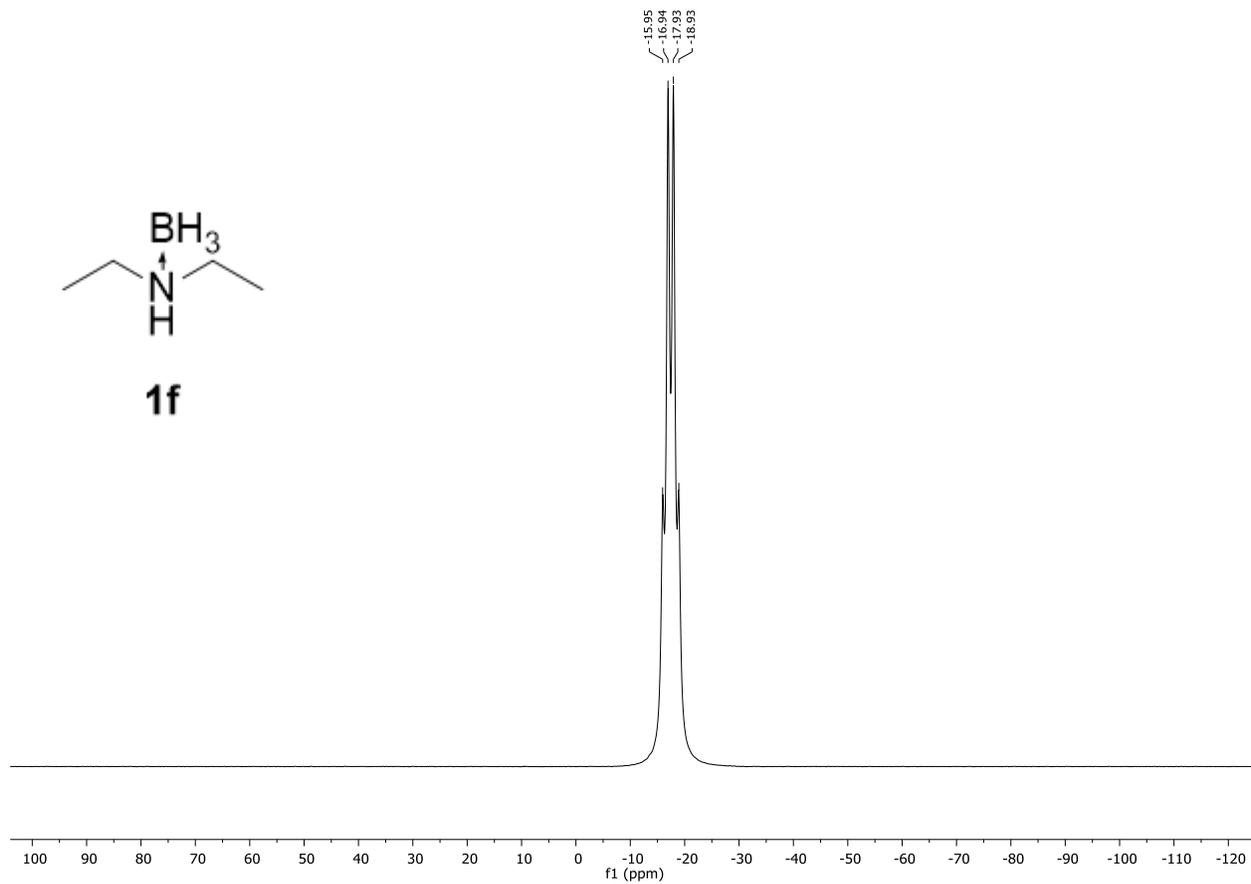


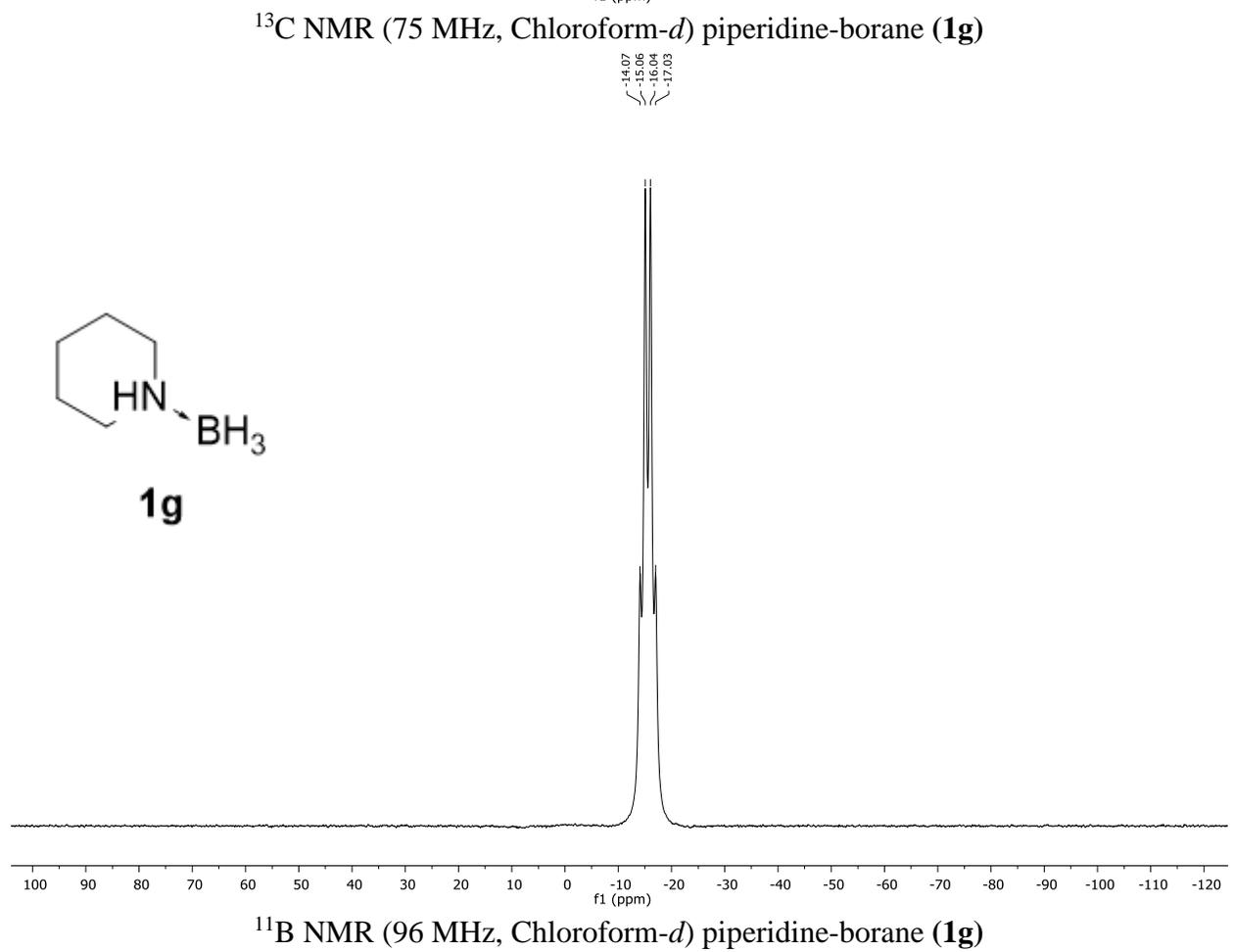
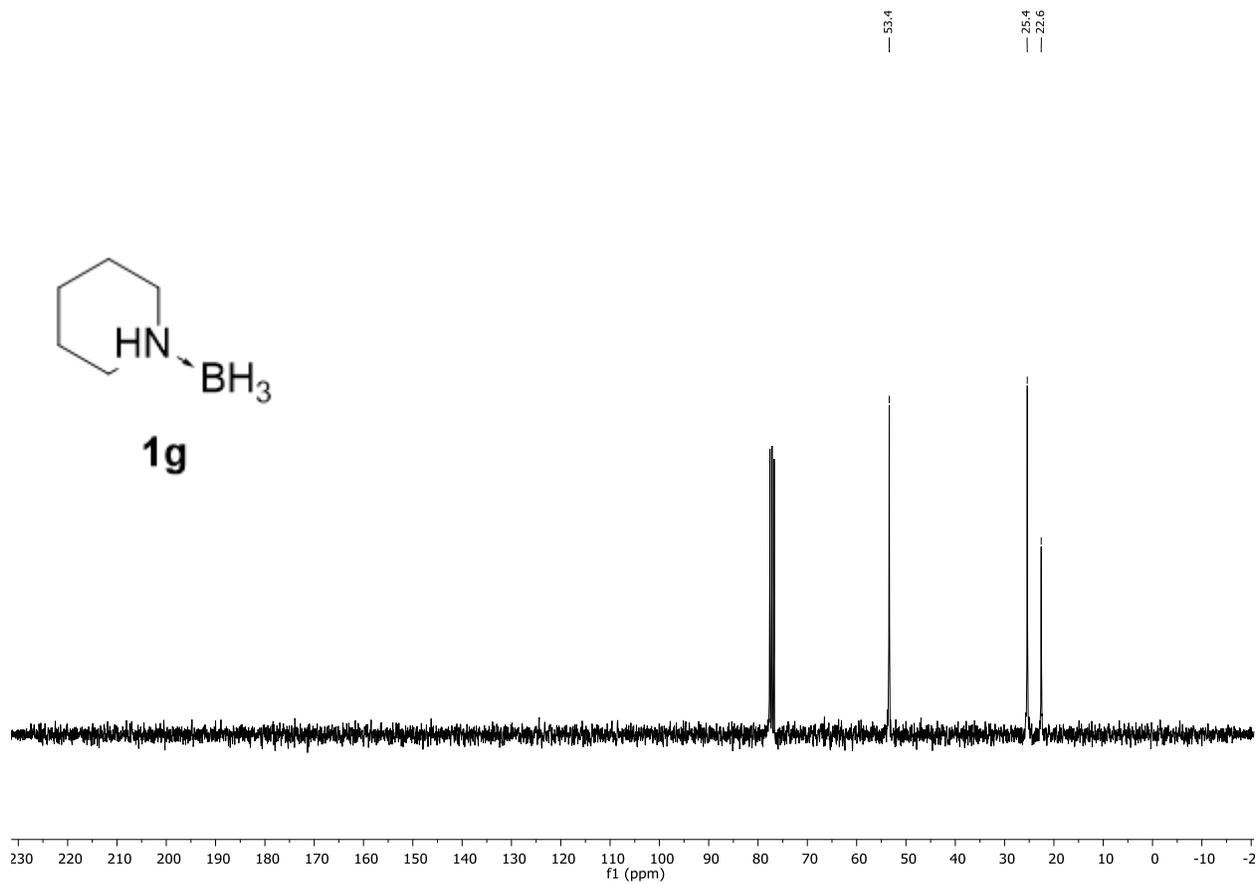
^{13}C NMR (75 MHz, Chloroform-*d*) tert-butylamine-borane (**1e**)

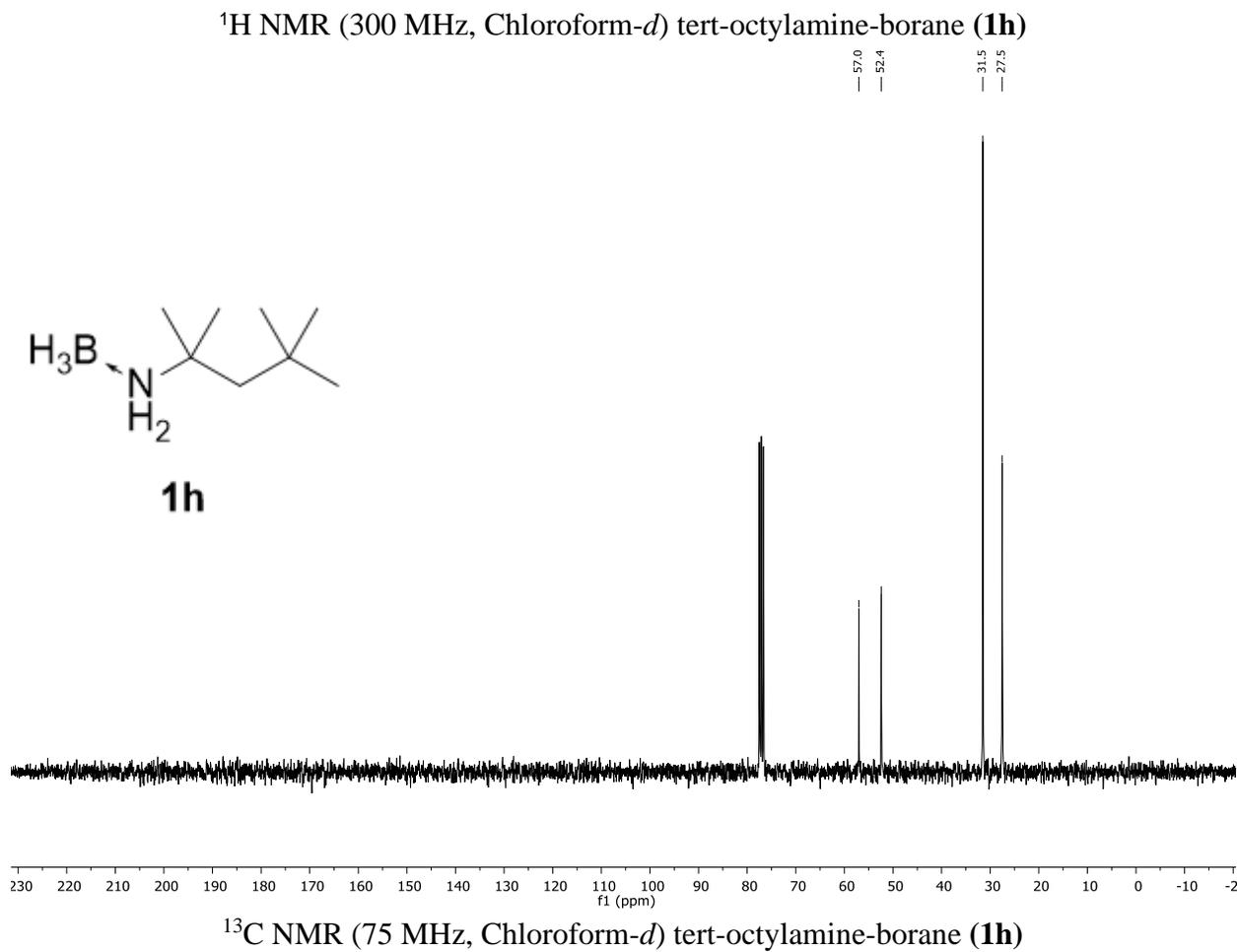
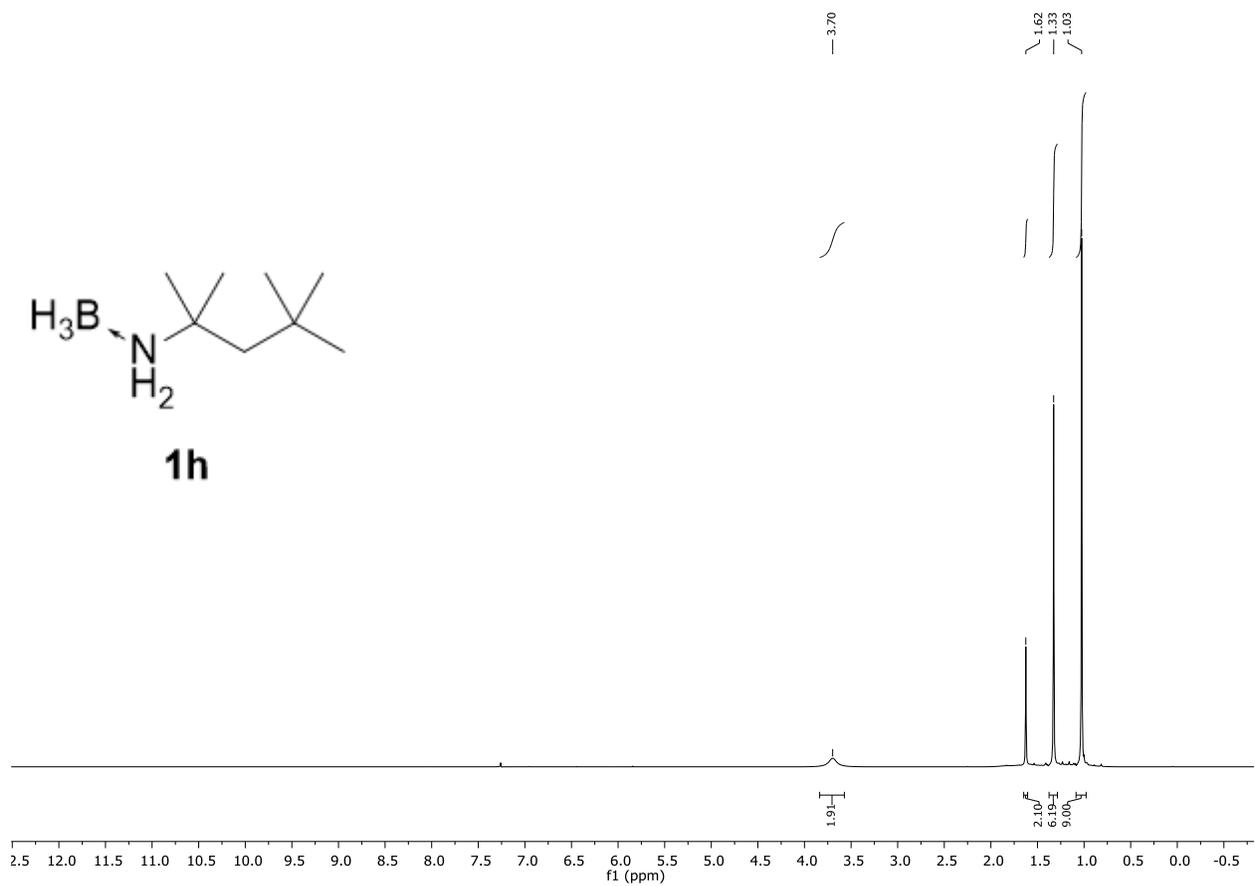


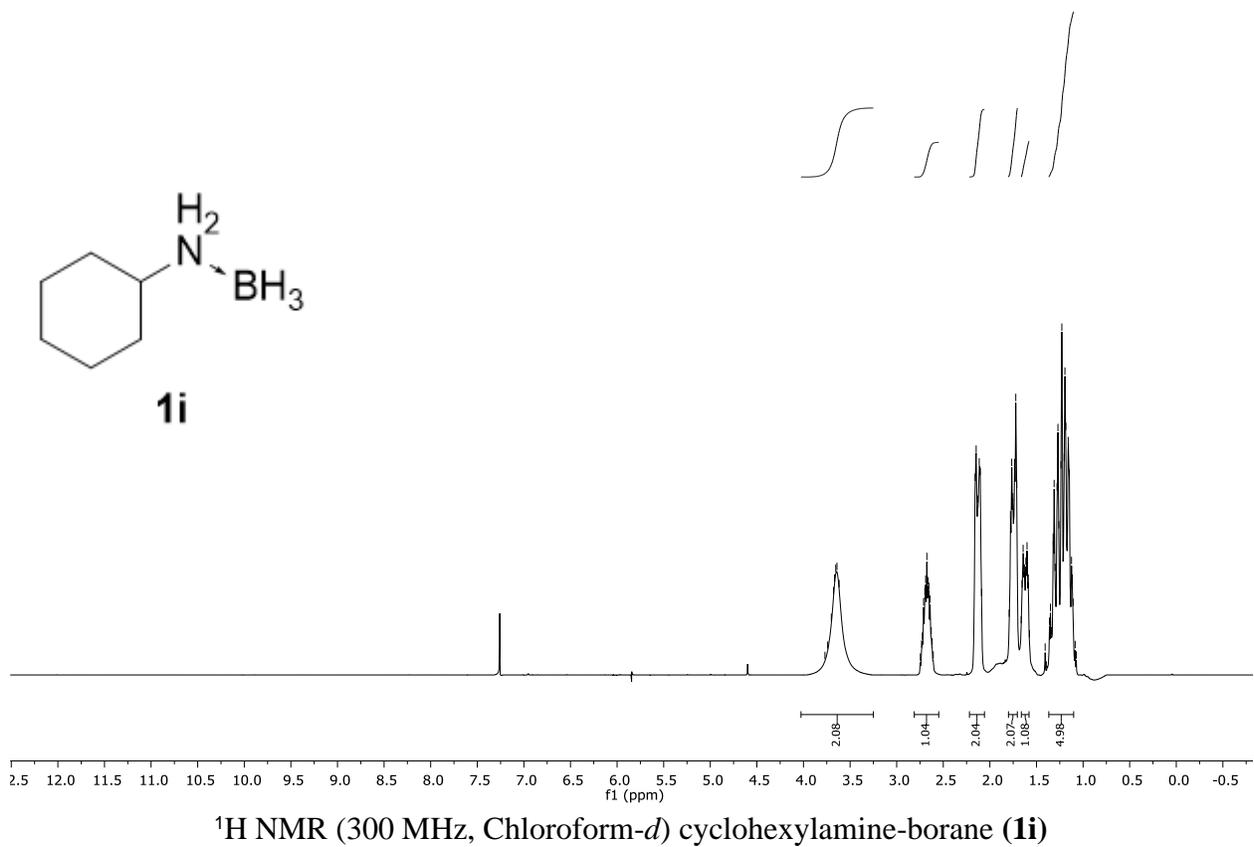
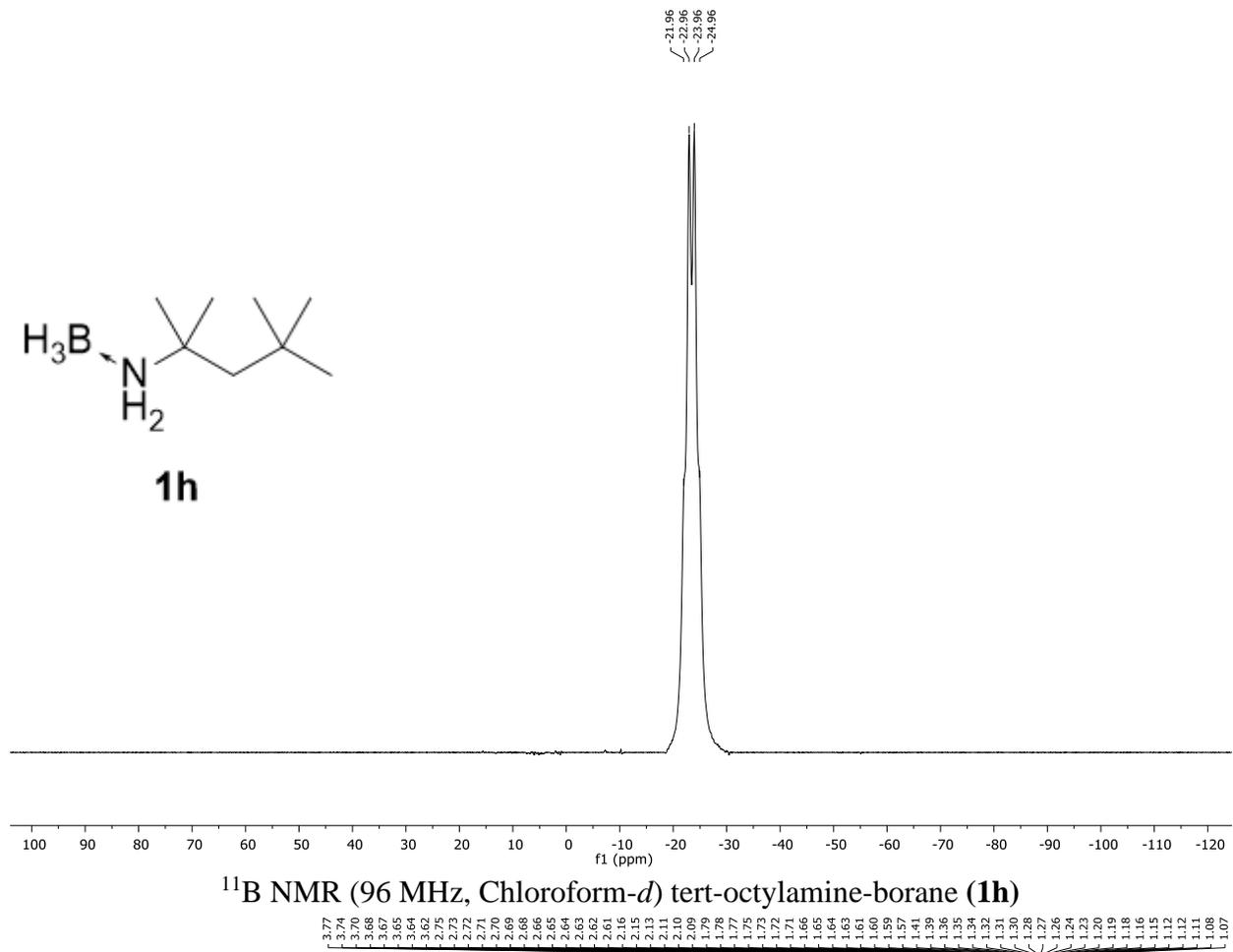
^{11}B NMR (96 MHz, Chloroform-*d*) tert-butylamine-borane (**1e**)

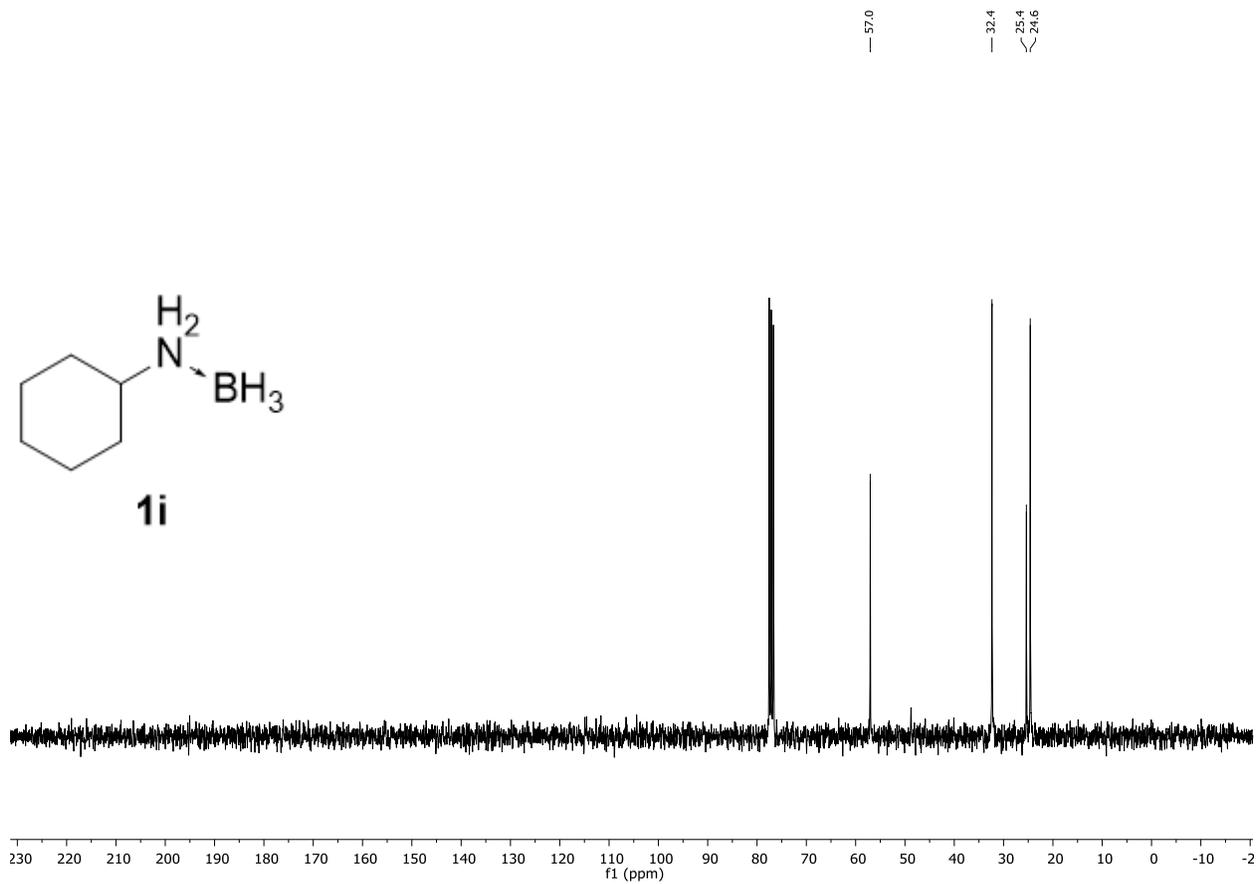




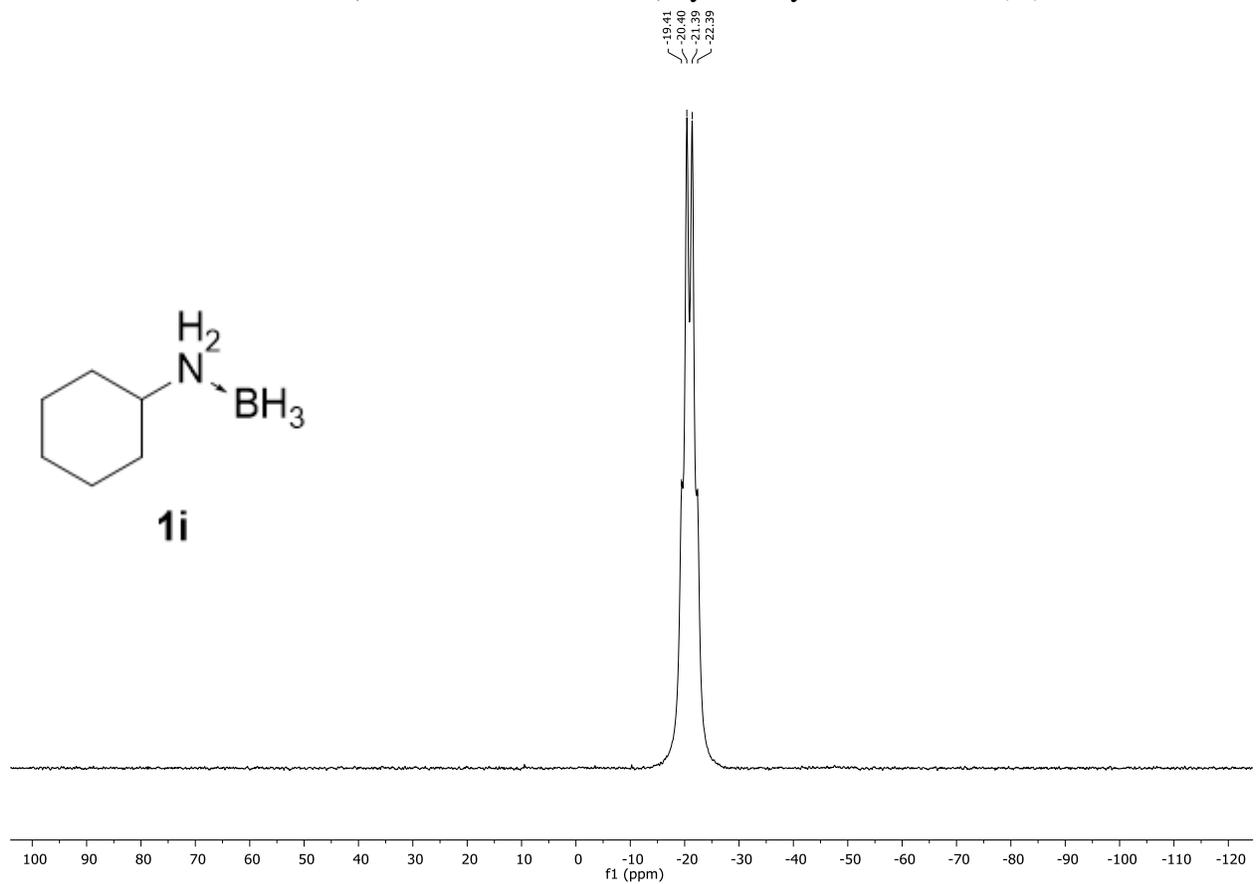




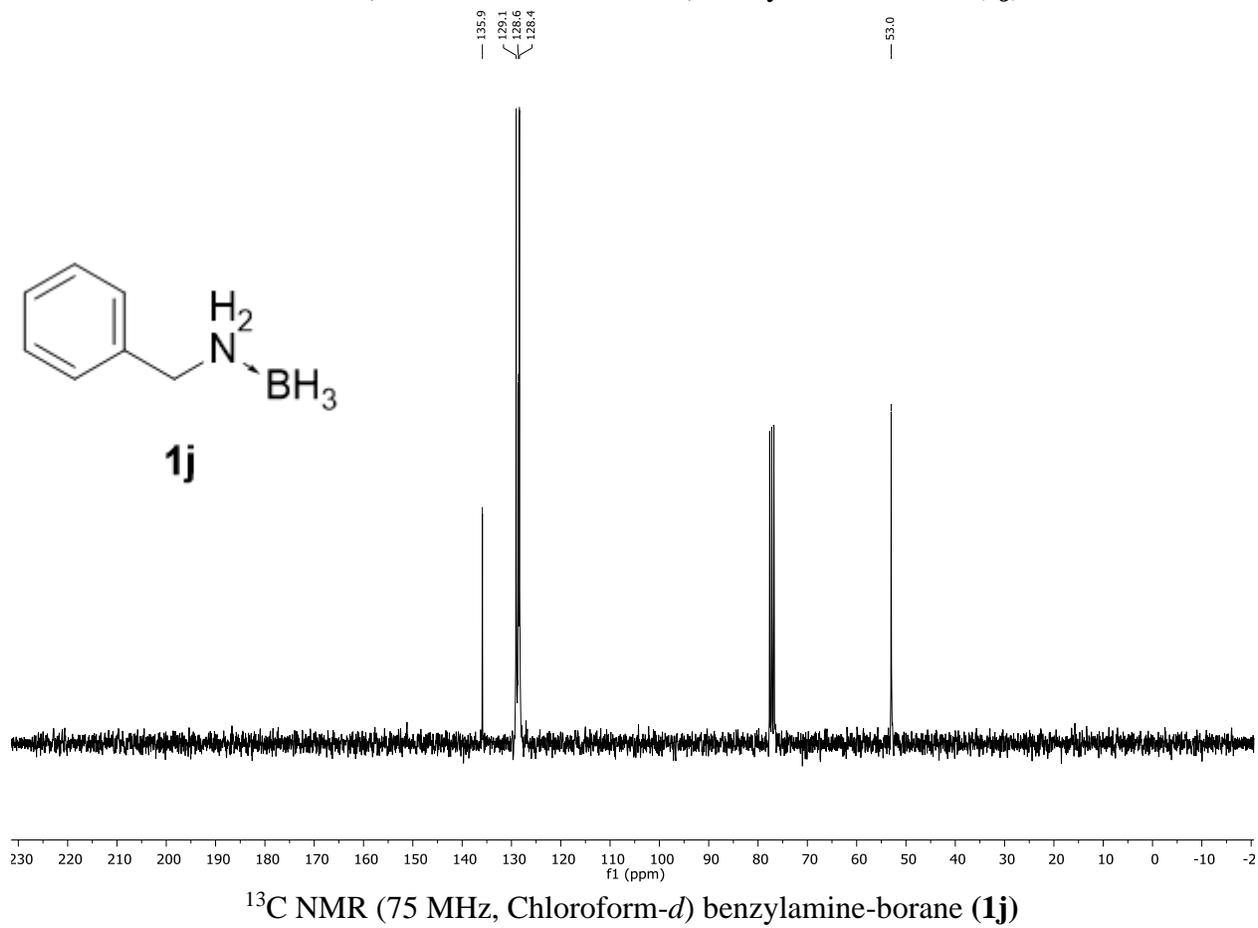
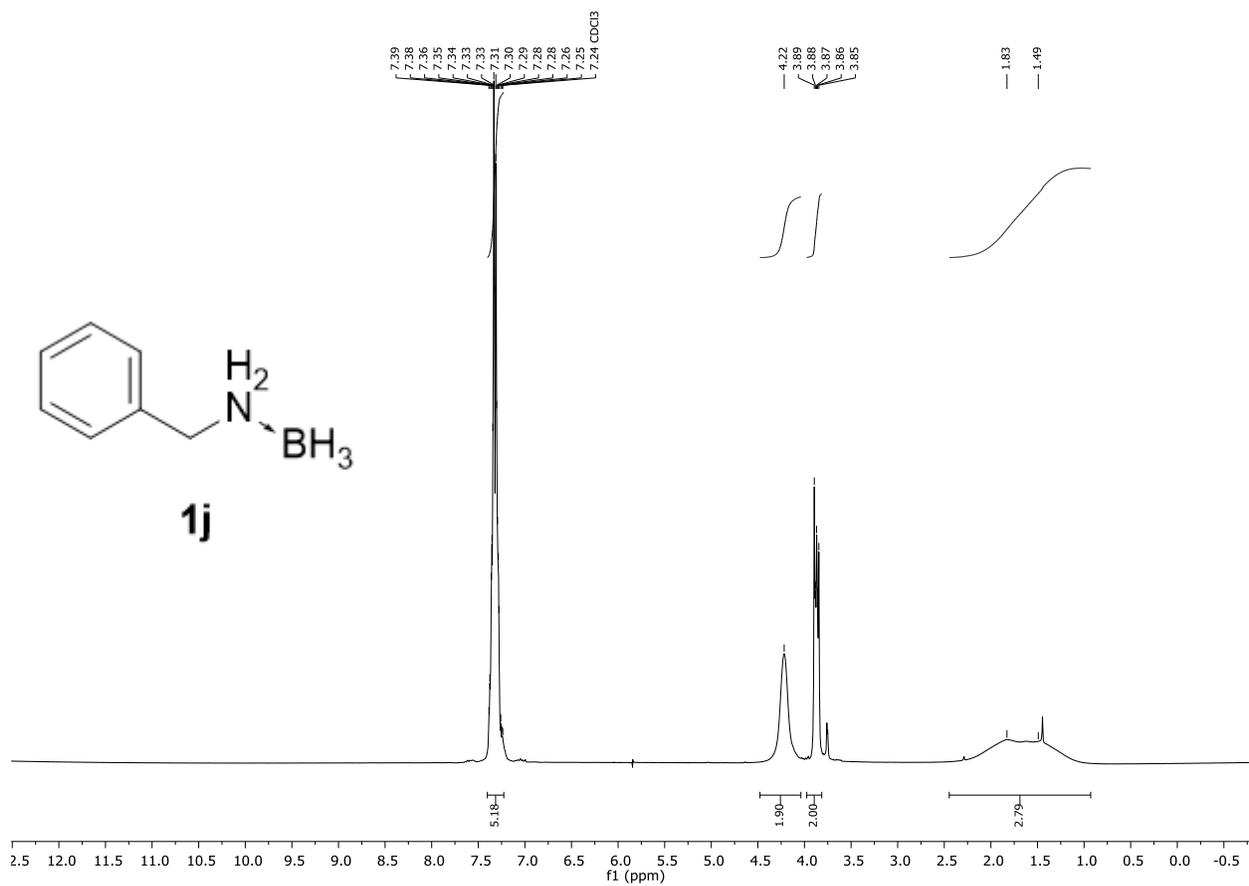


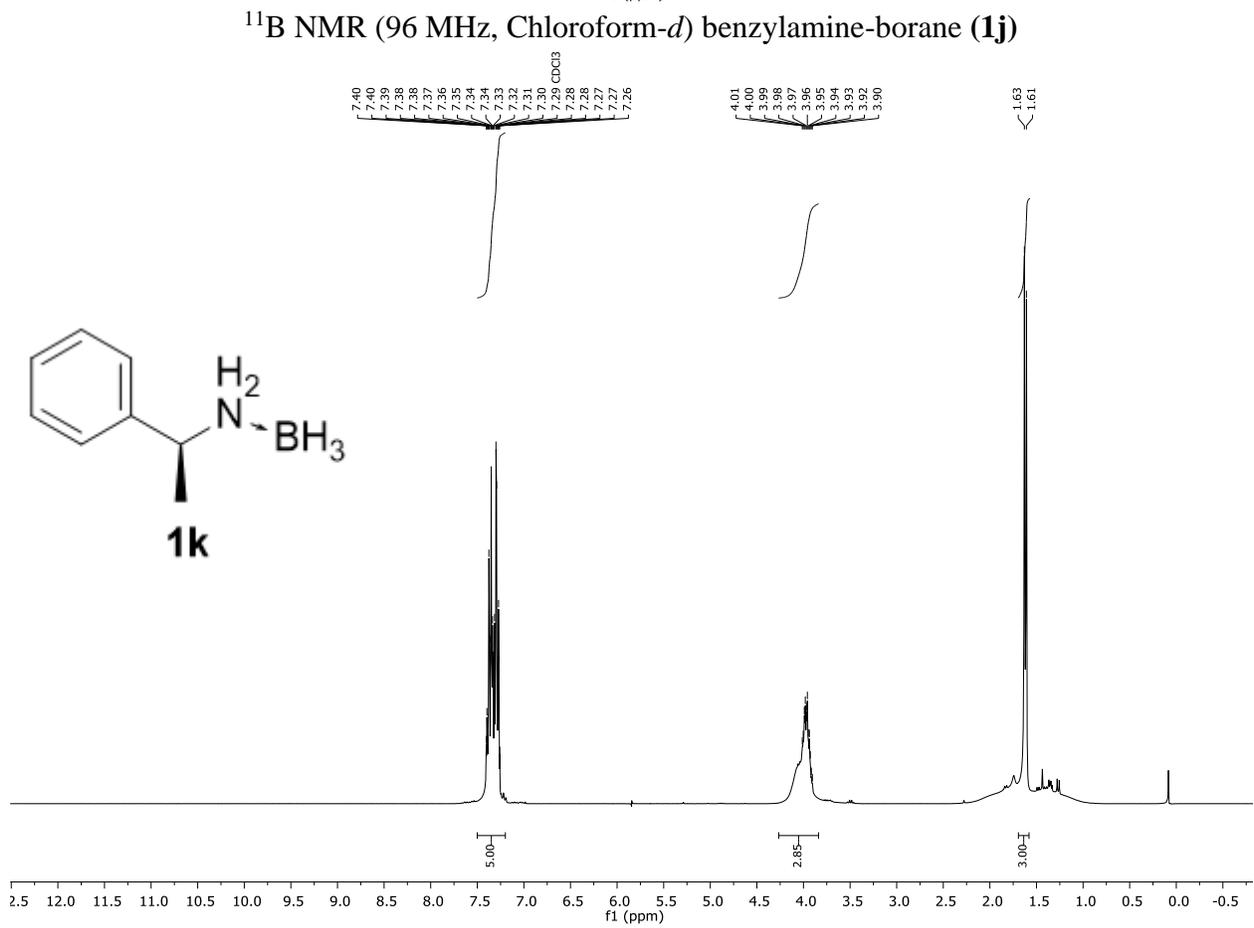
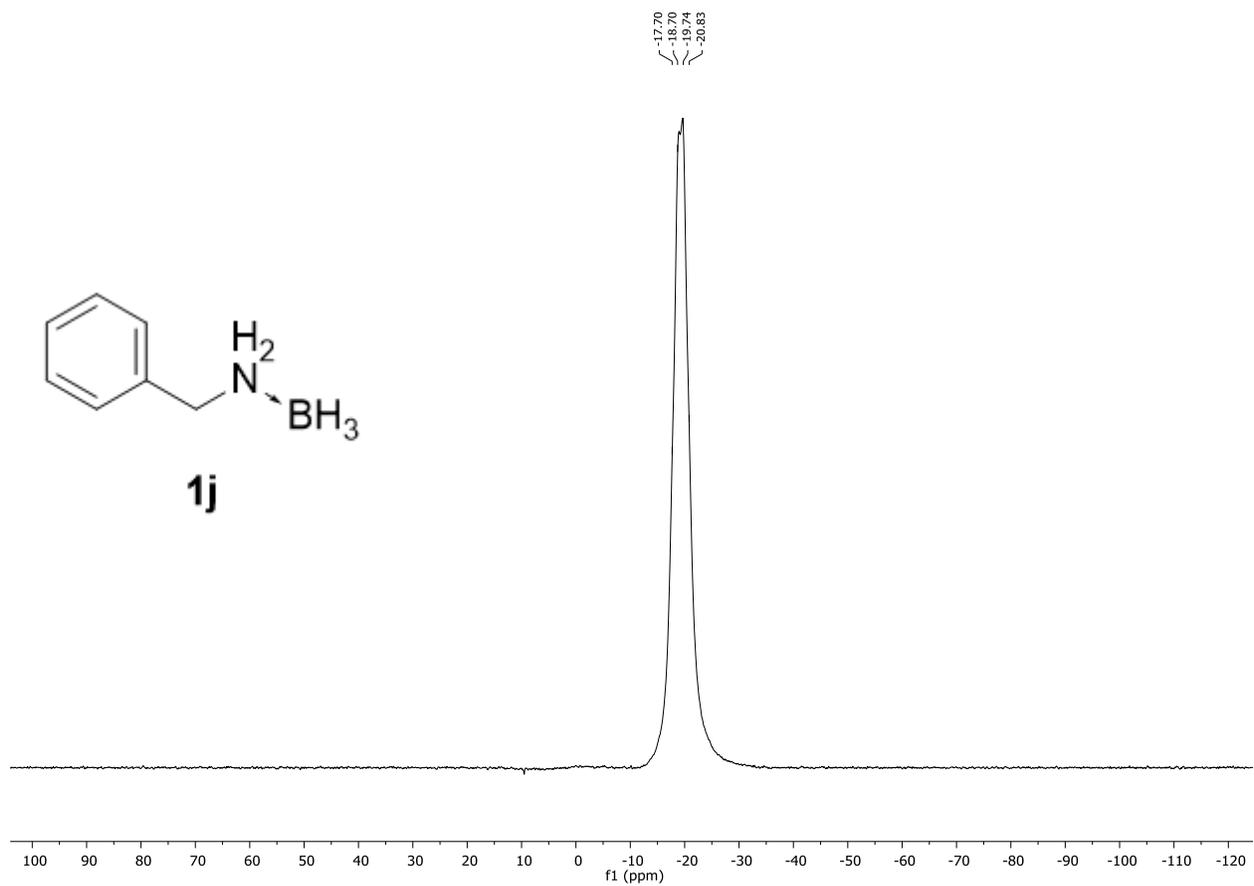


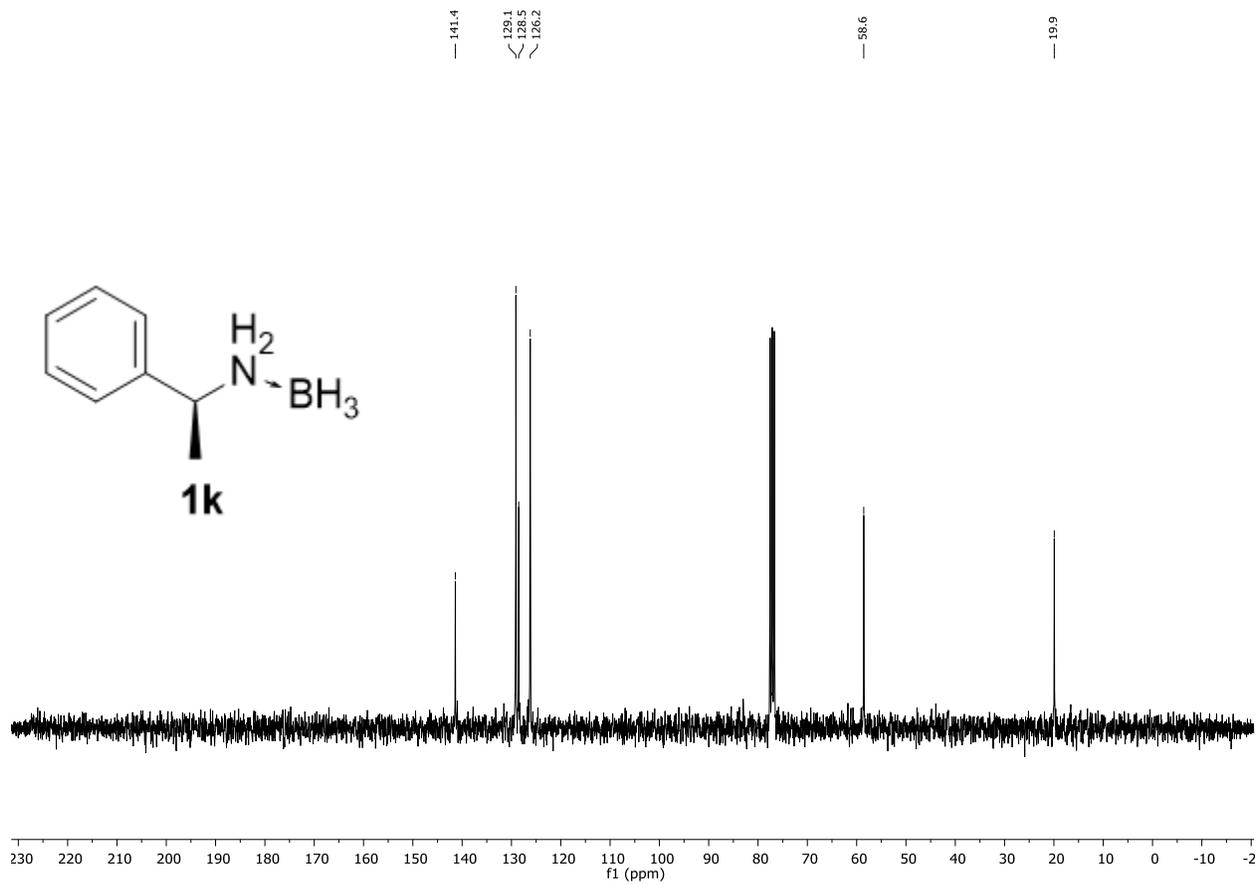
^{13}C NMR (75 MHz, Chloroform-*d*) cyclohexylamine-borane (**1i**)



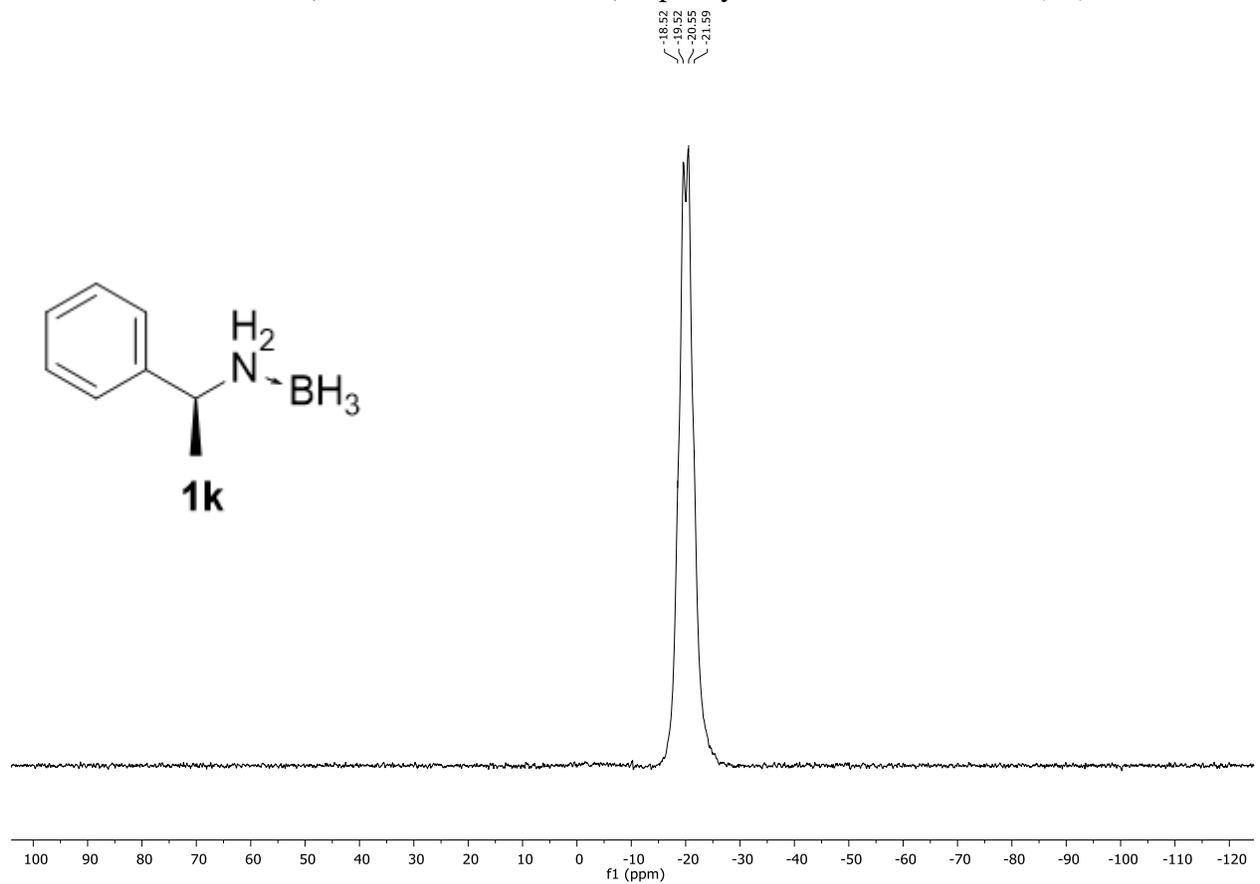
^{11}B NMR (96 MHz, Chloroform-*d*) cyclohexylamine-borane (**1i**)



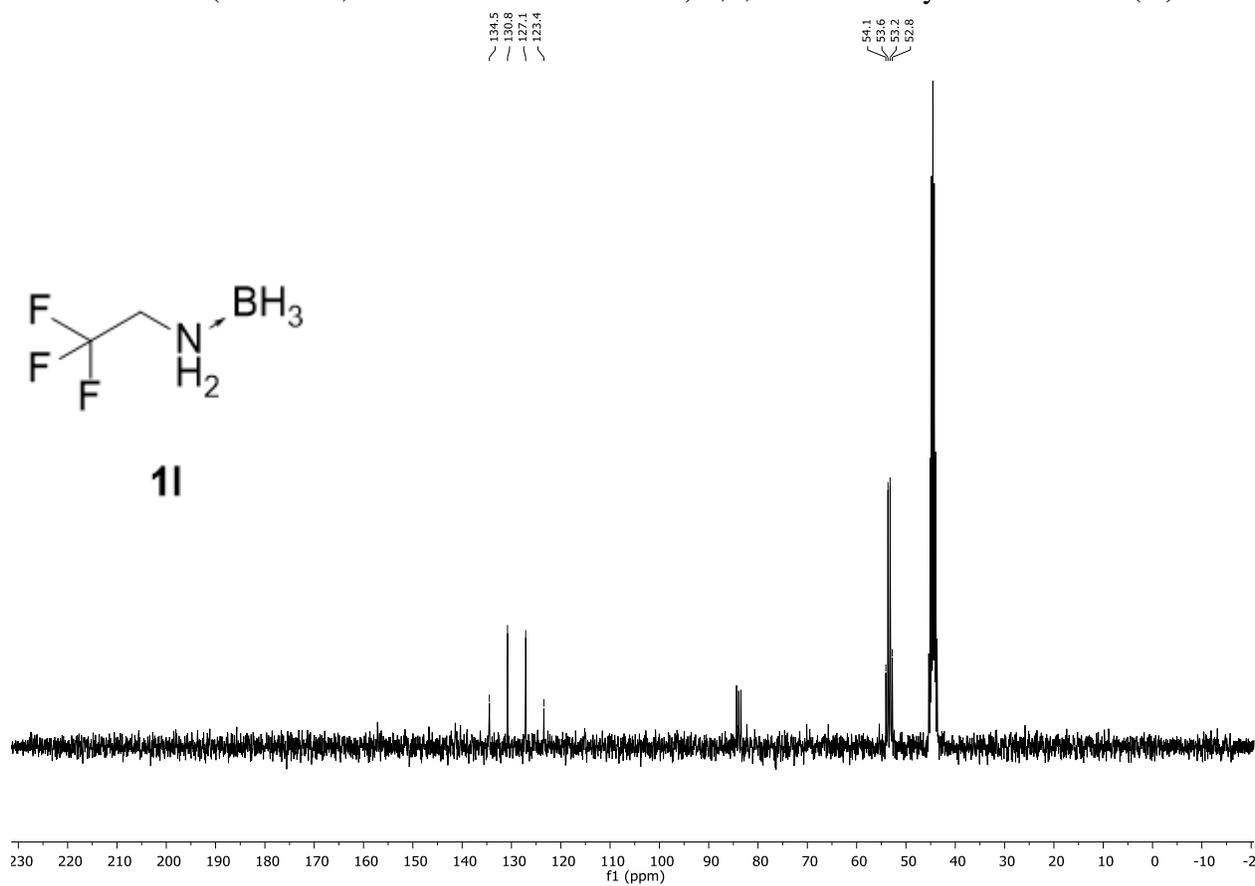
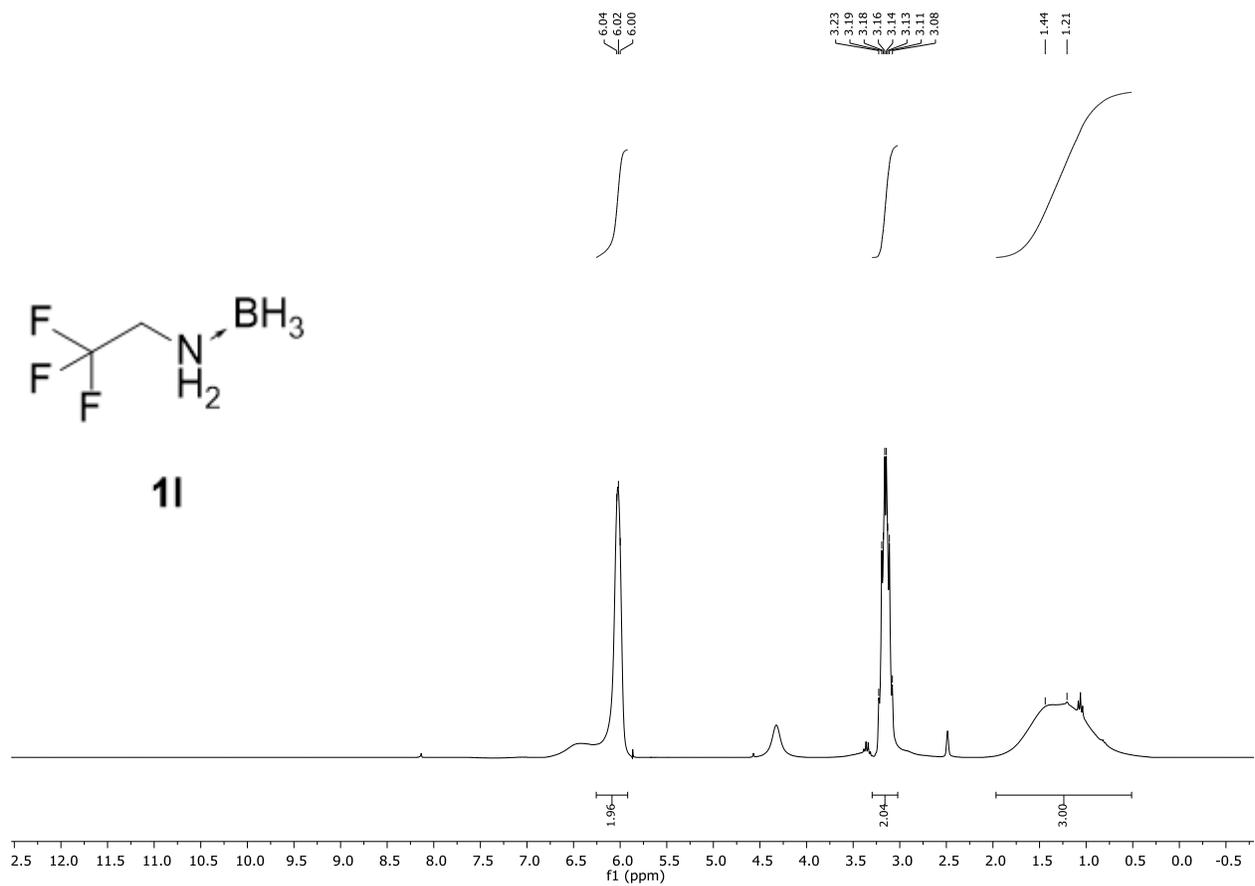




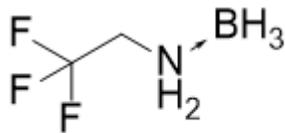
¹³C NMR (75 MHz, Chloroform-*d*) 1-phenylethan-1-amine-borane (**1k**)



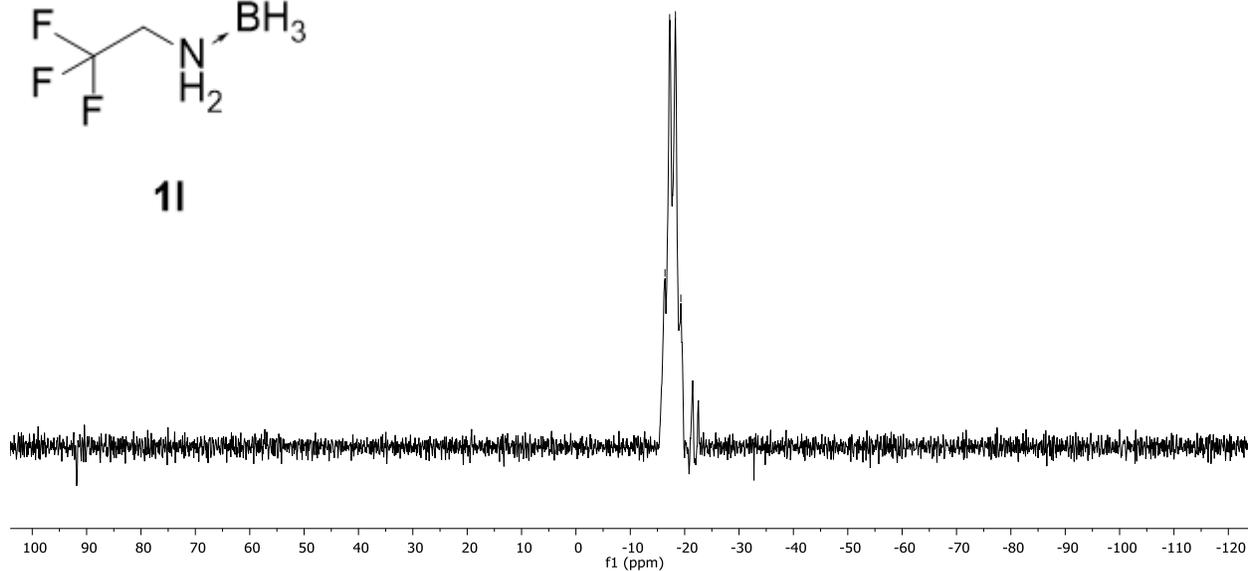
¹¹B NMR (96 MHz, Chloroform-*d*) 1-phenylethan-1-amine-borane (**1k**)



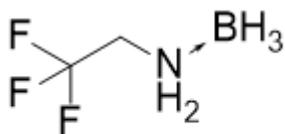
16.38
-17.24
-18.54
-19.29



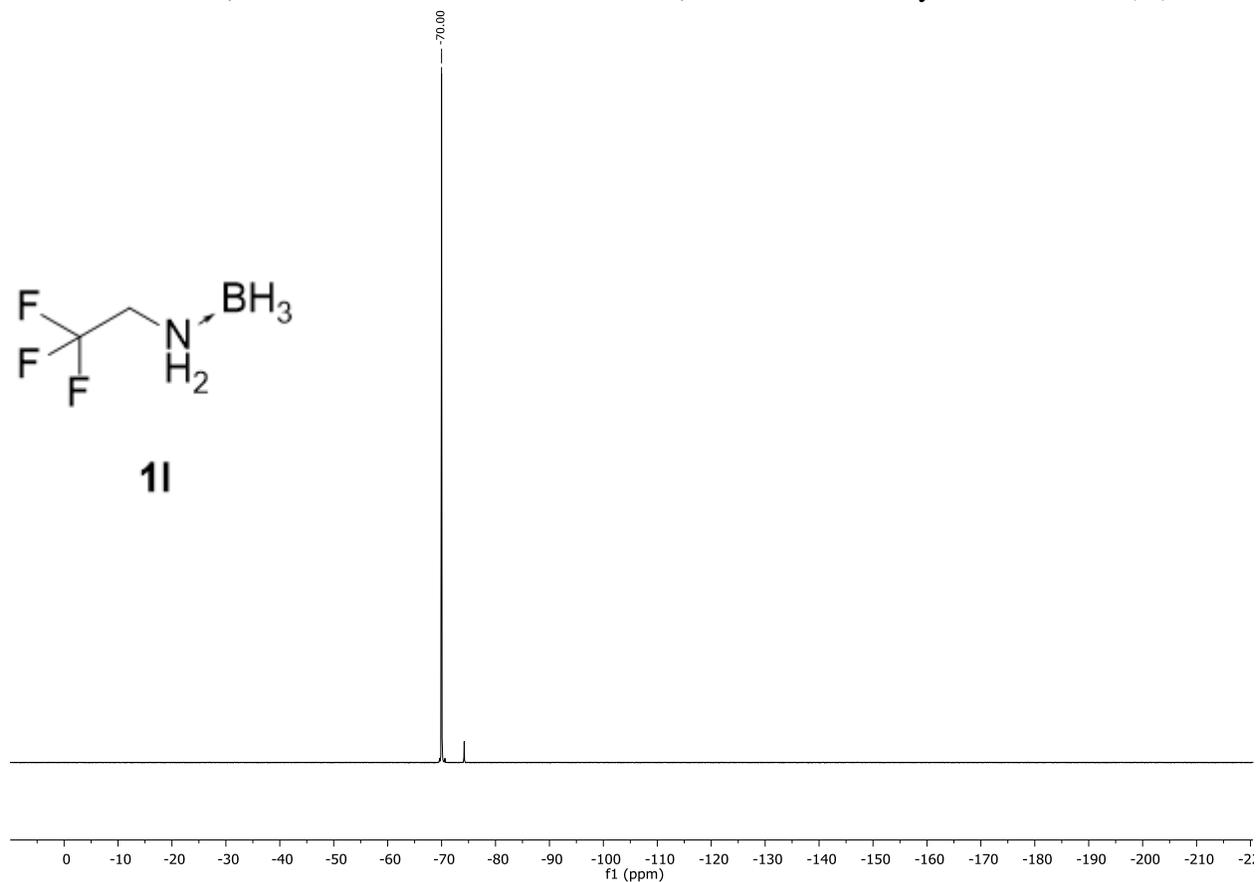
11



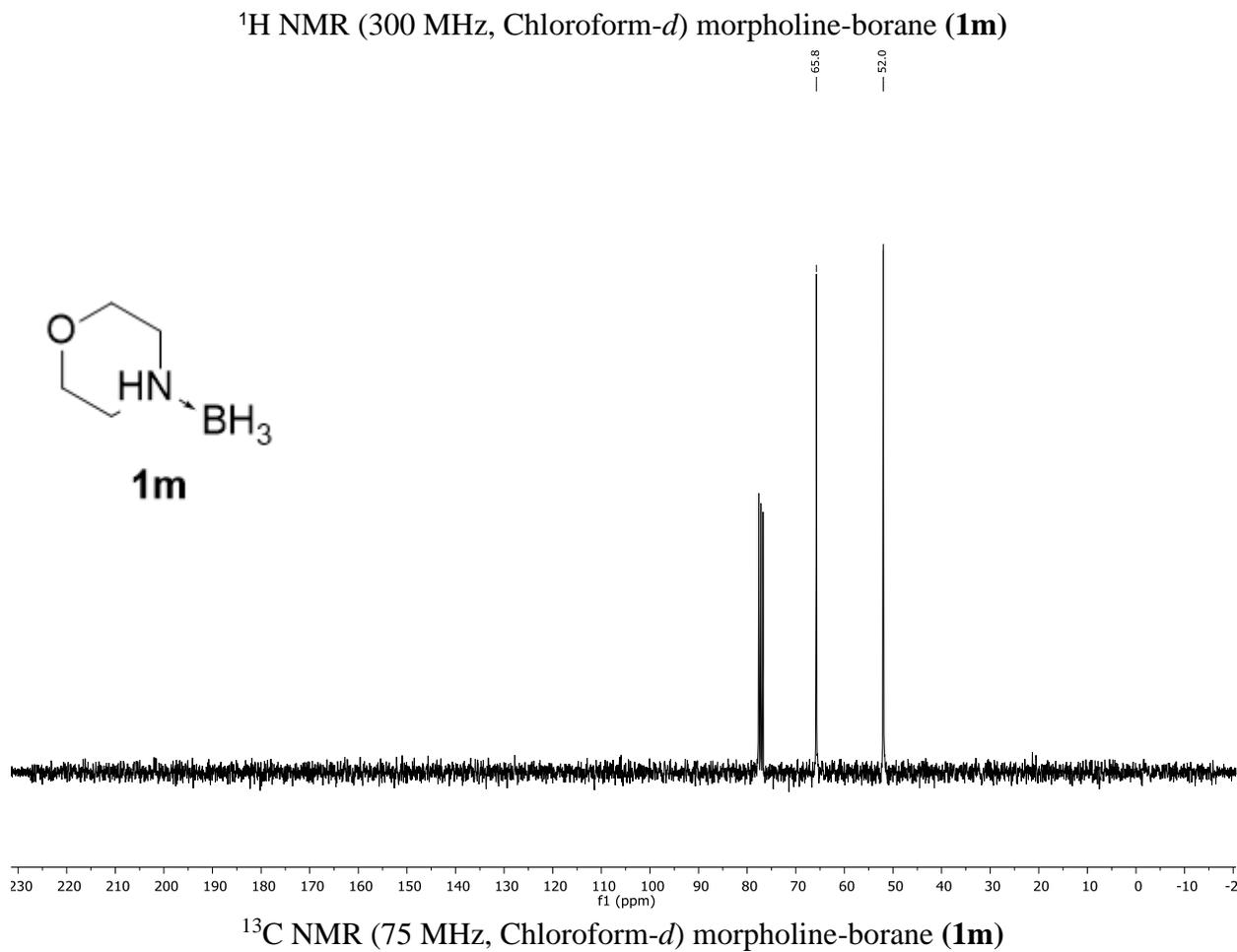
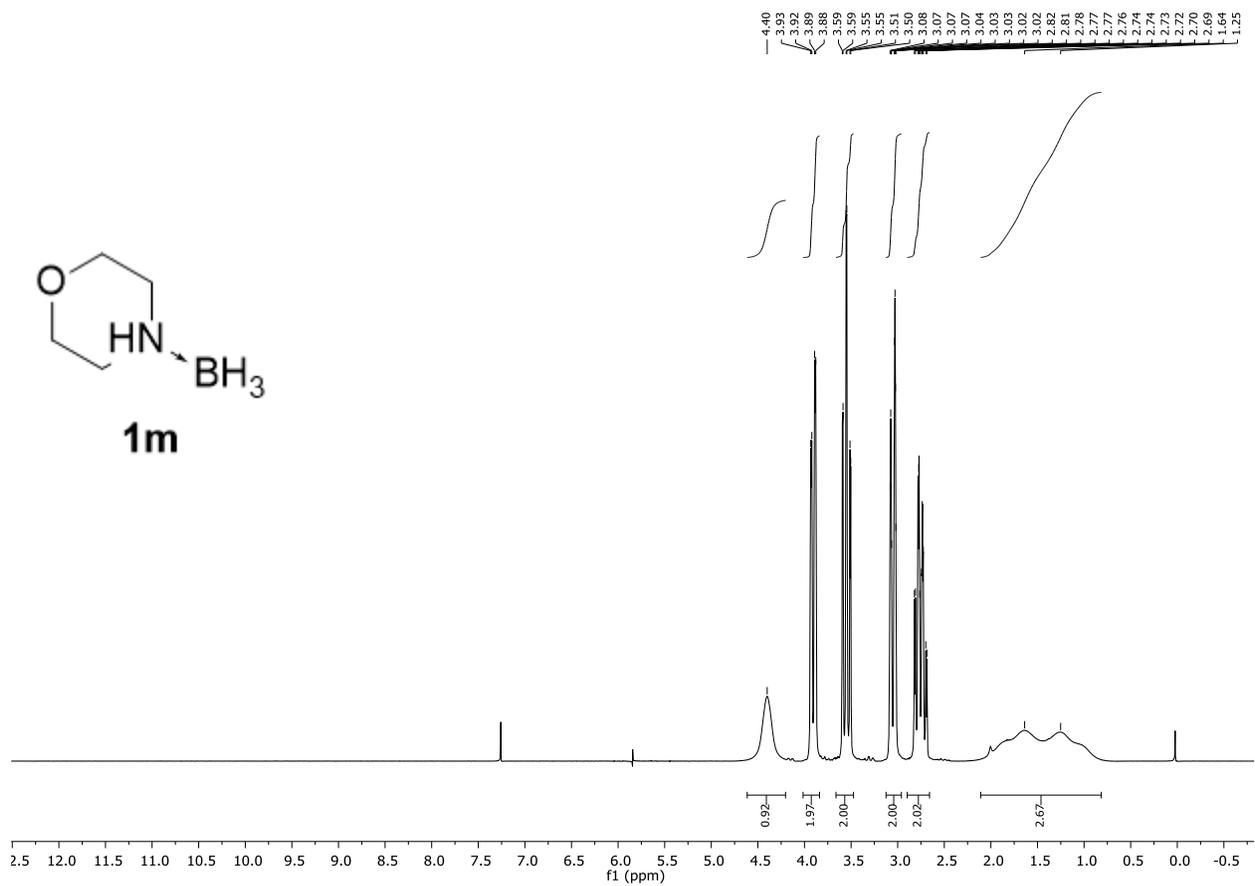
¹¹B NMR (96 MHz, Chloroform-*d*/ DMSO-*d*₆) 2,2,2-trifluoroethylamine-borane (**11**)

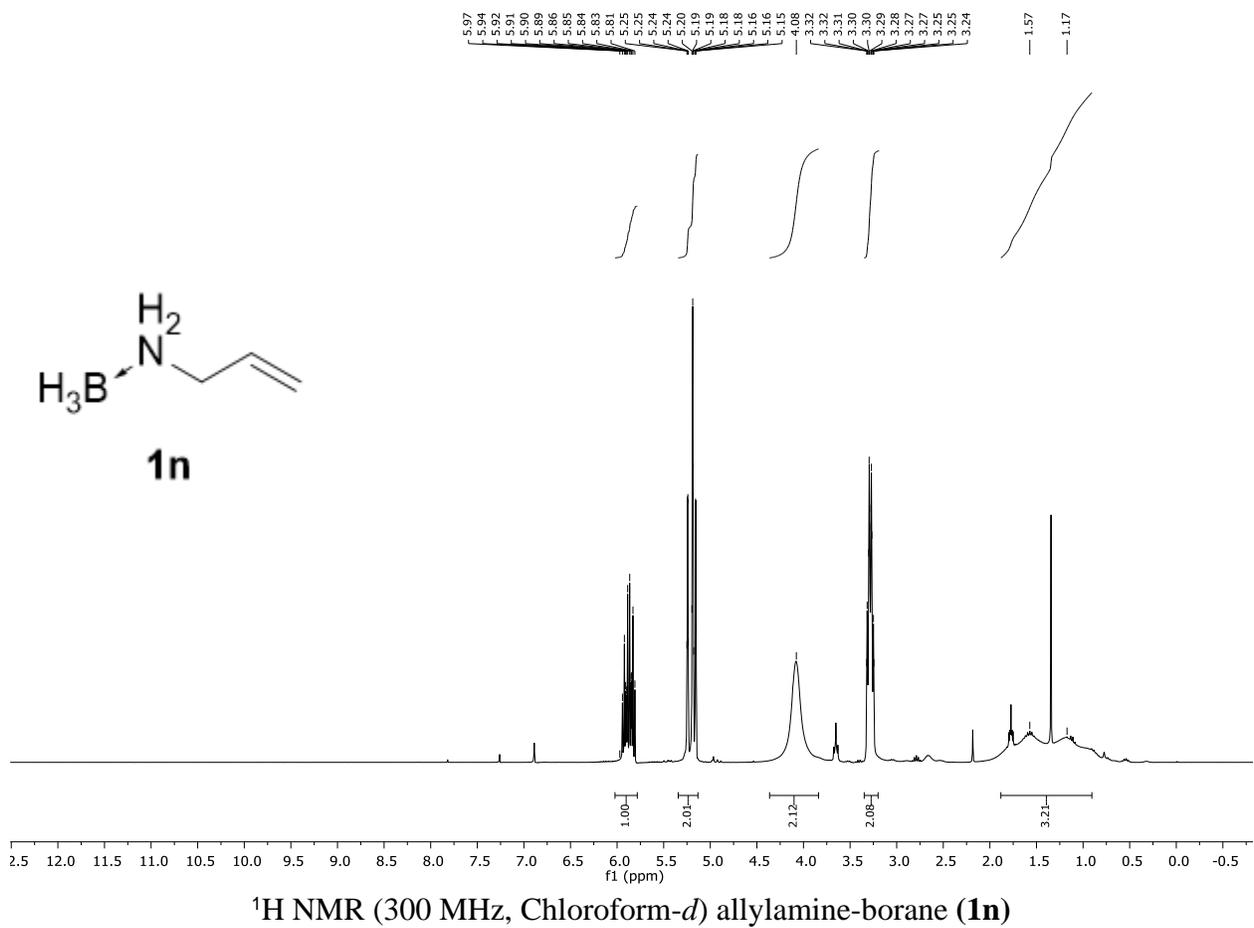
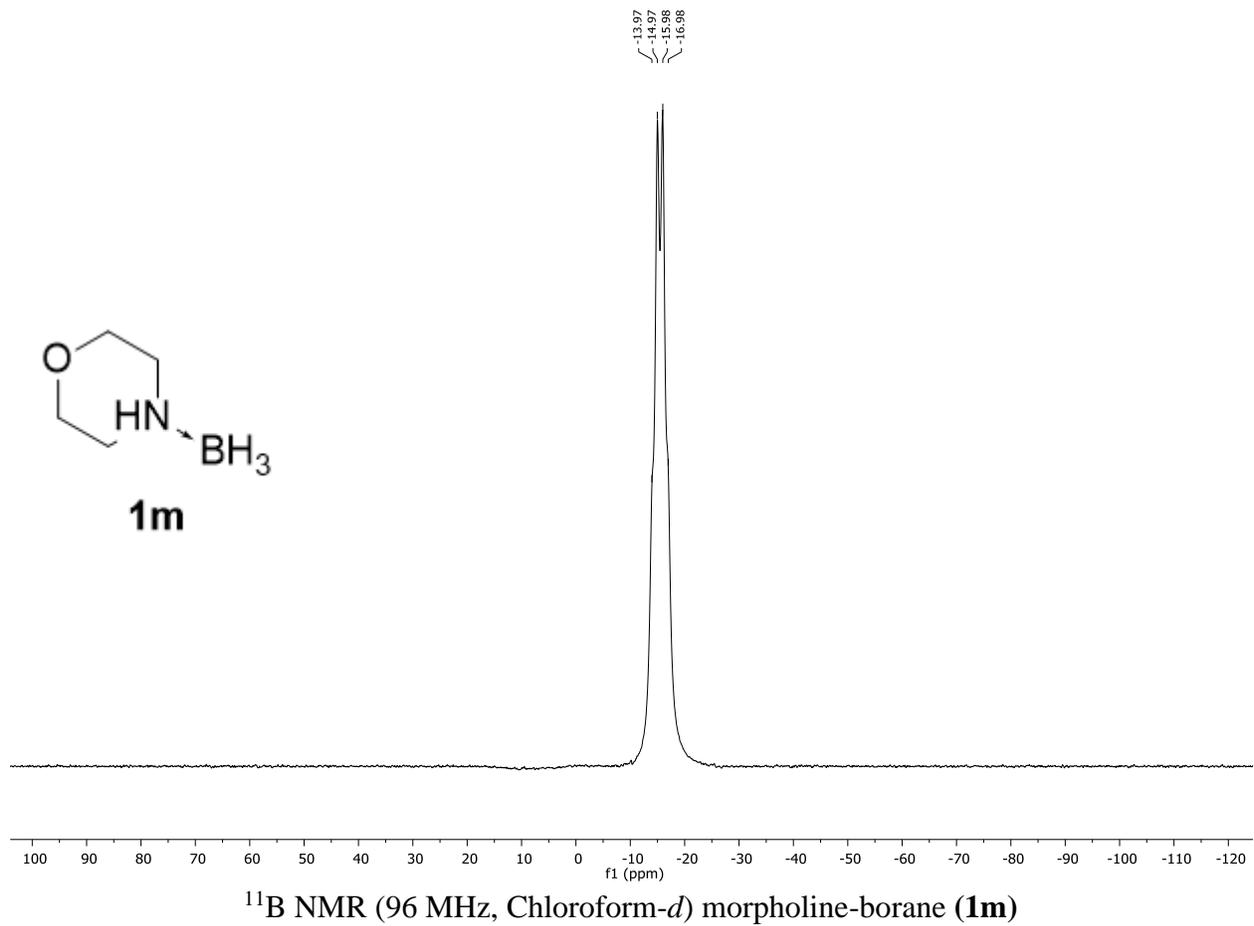


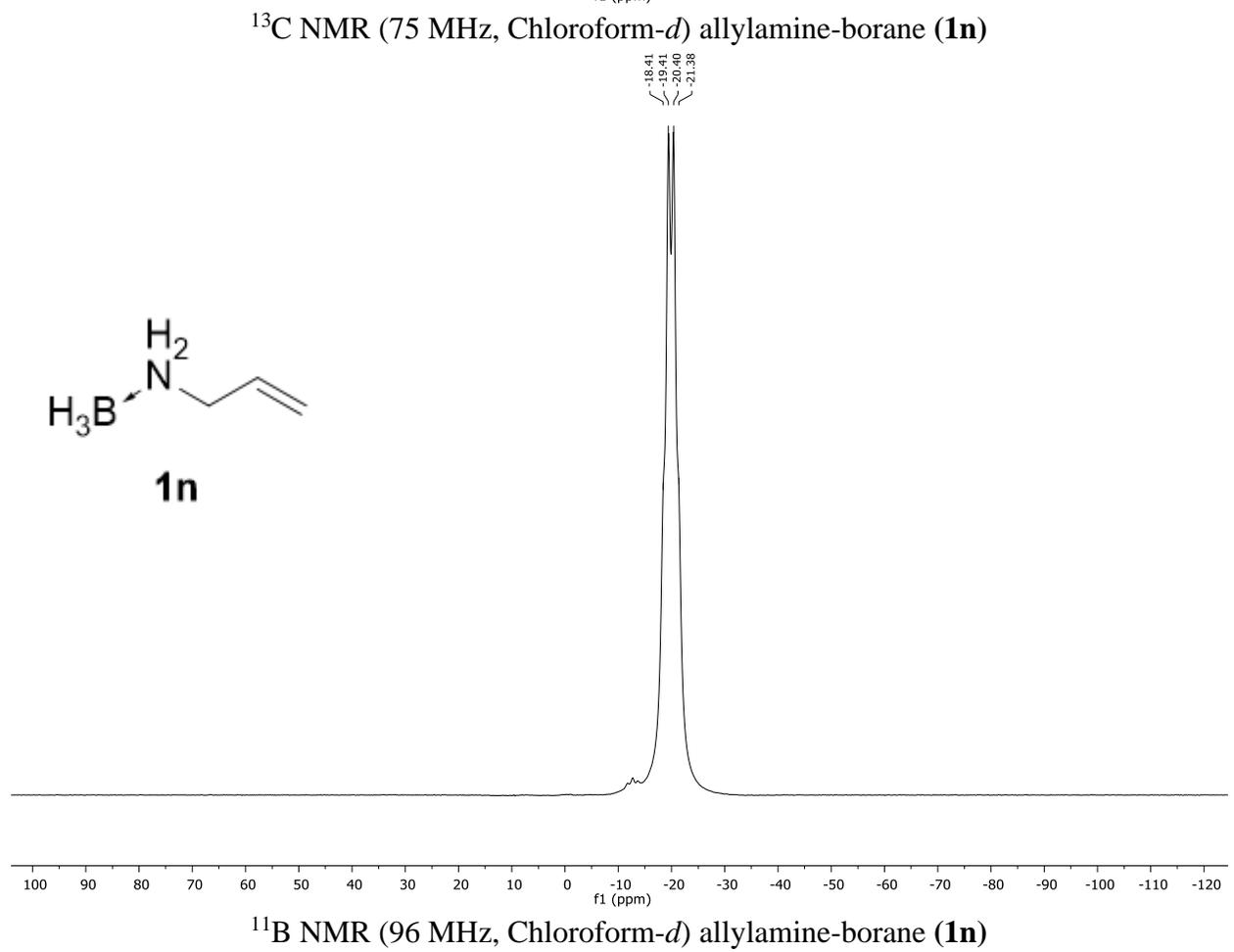
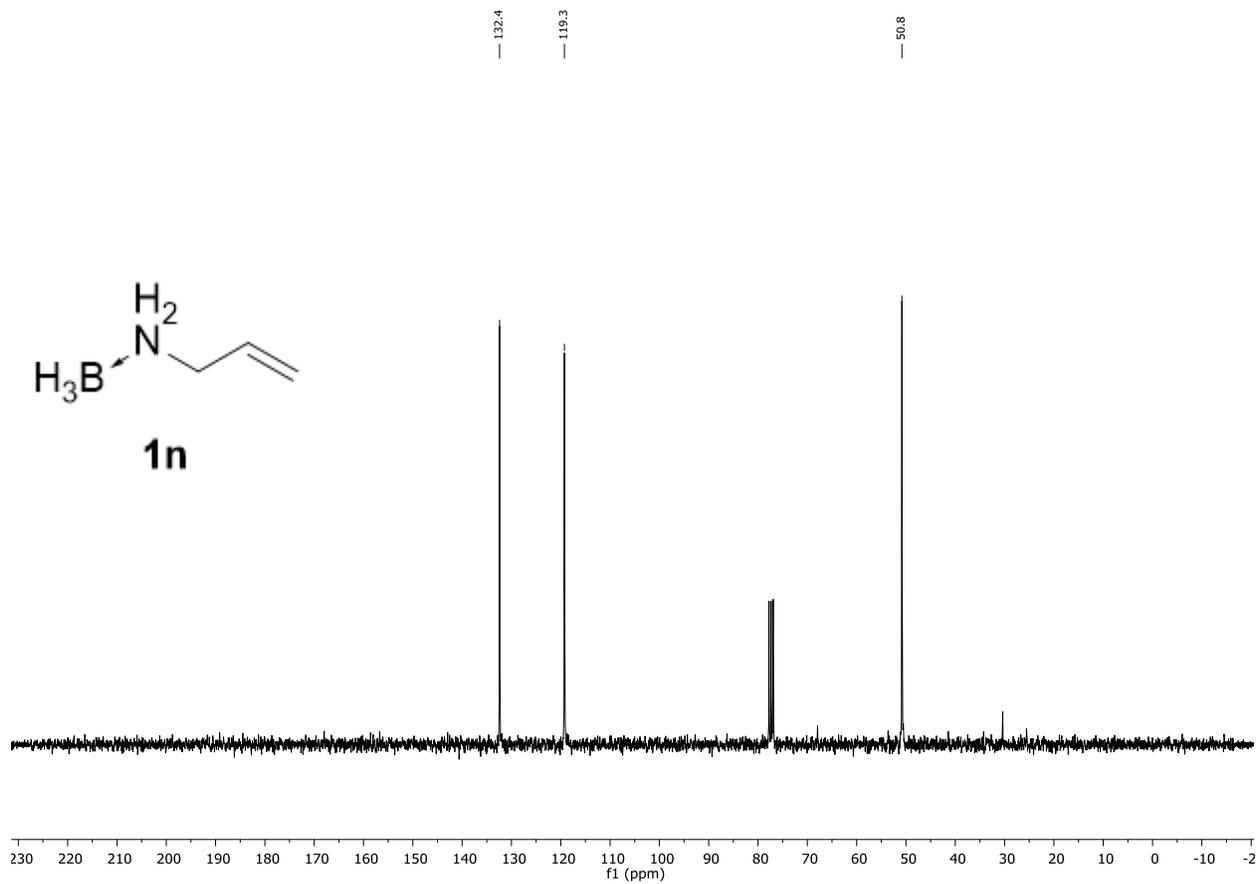
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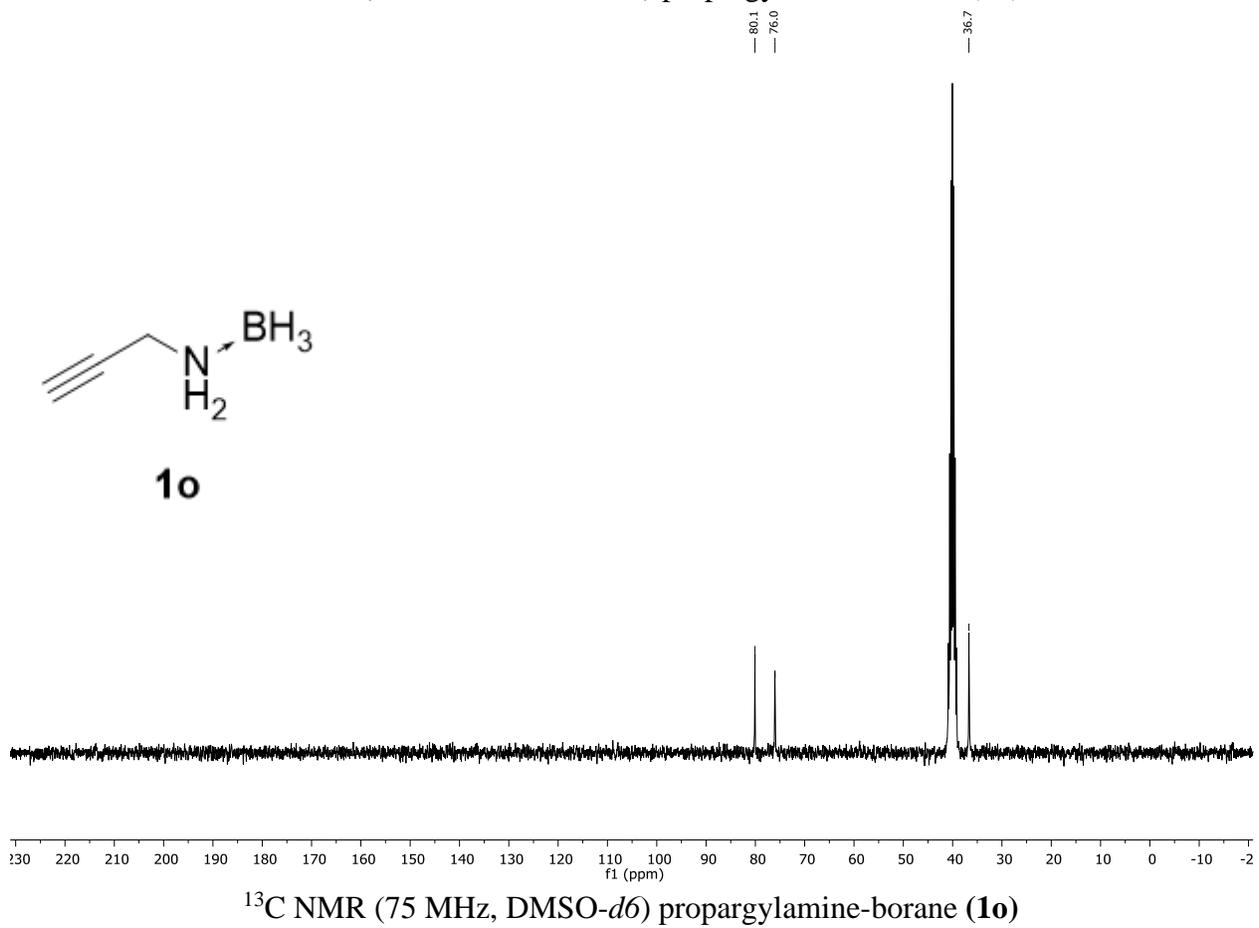
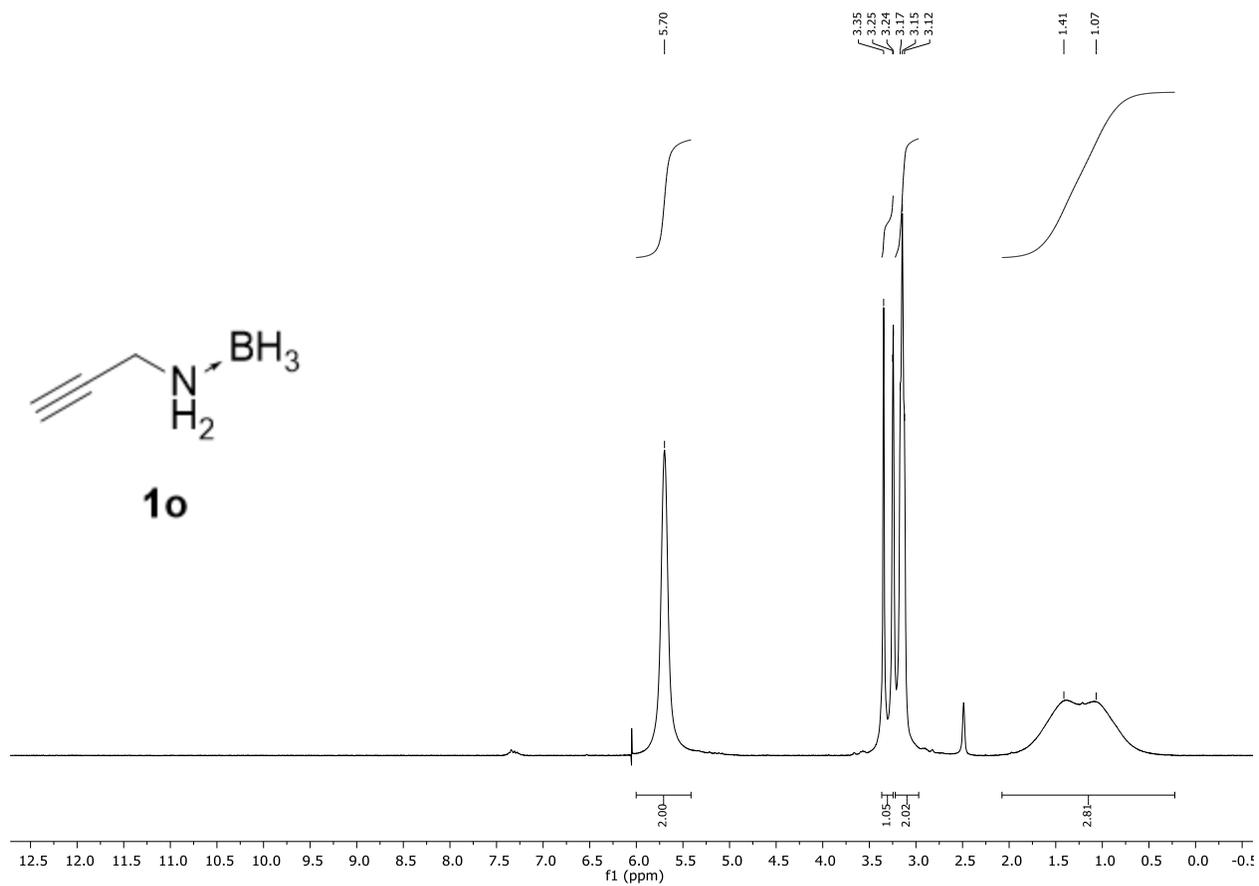


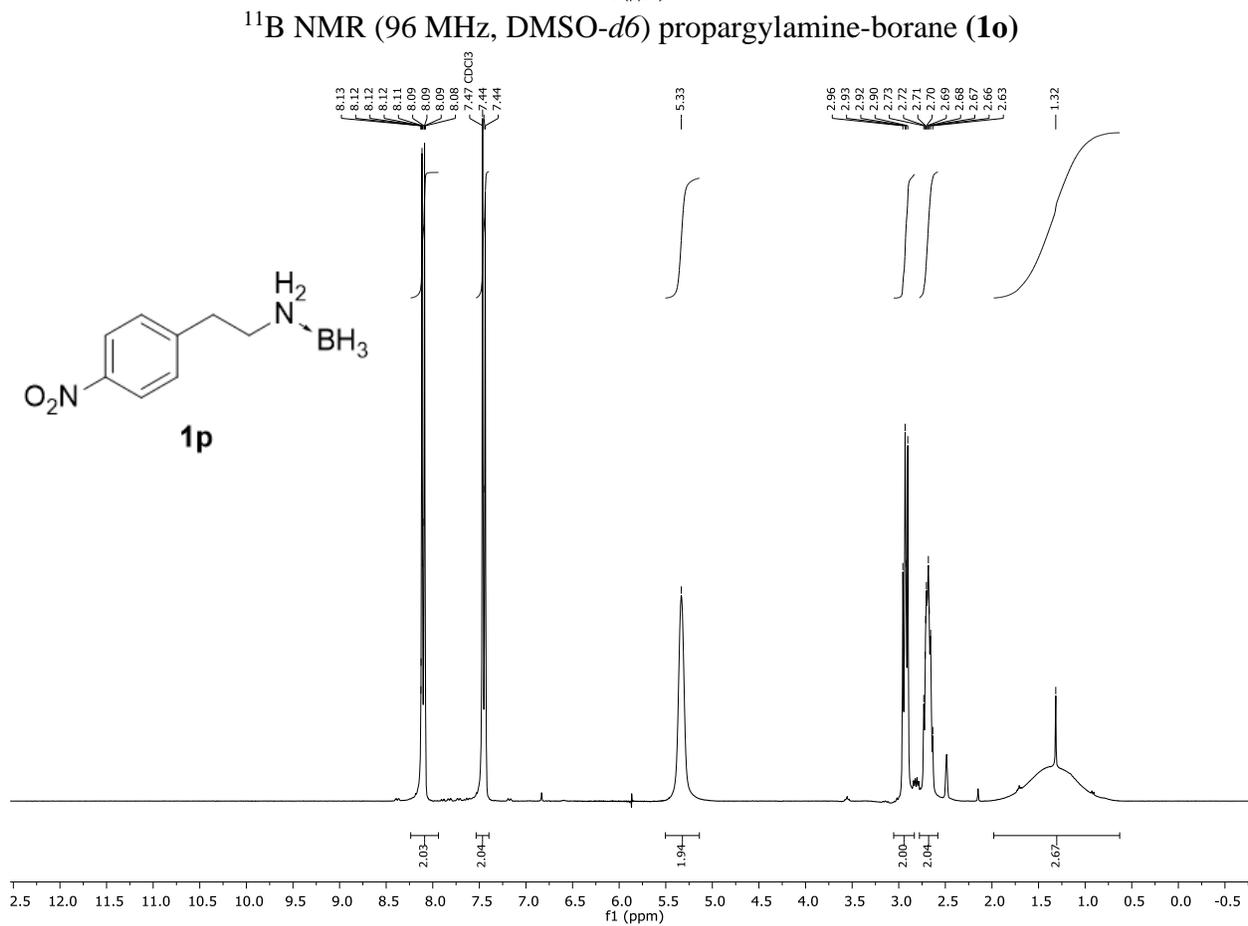
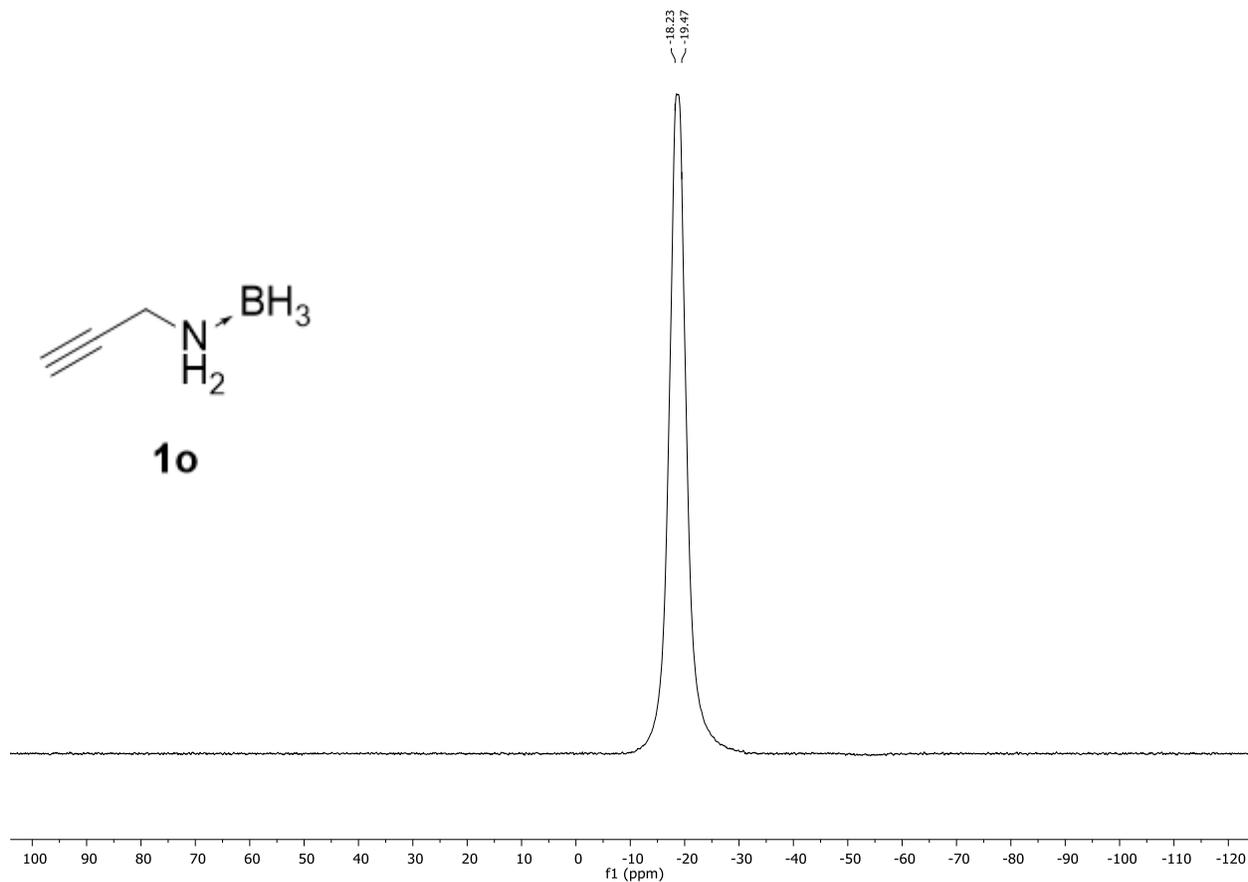
¹⁹F NMR (282 MHz, Chloroform-*d*/ DMSO-*d*₆) 2,2,2-trifluoroethylamine-borane (**11**)

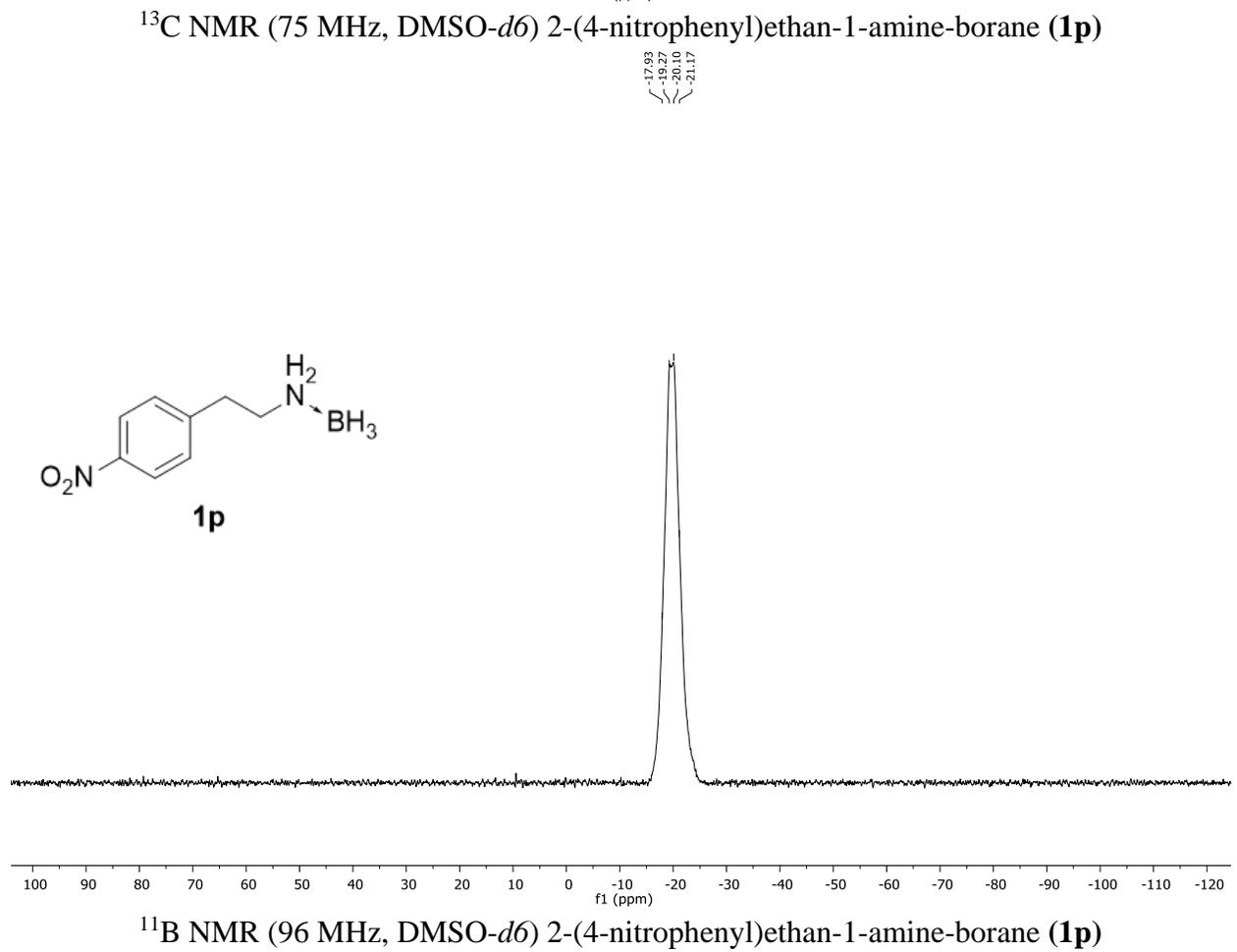
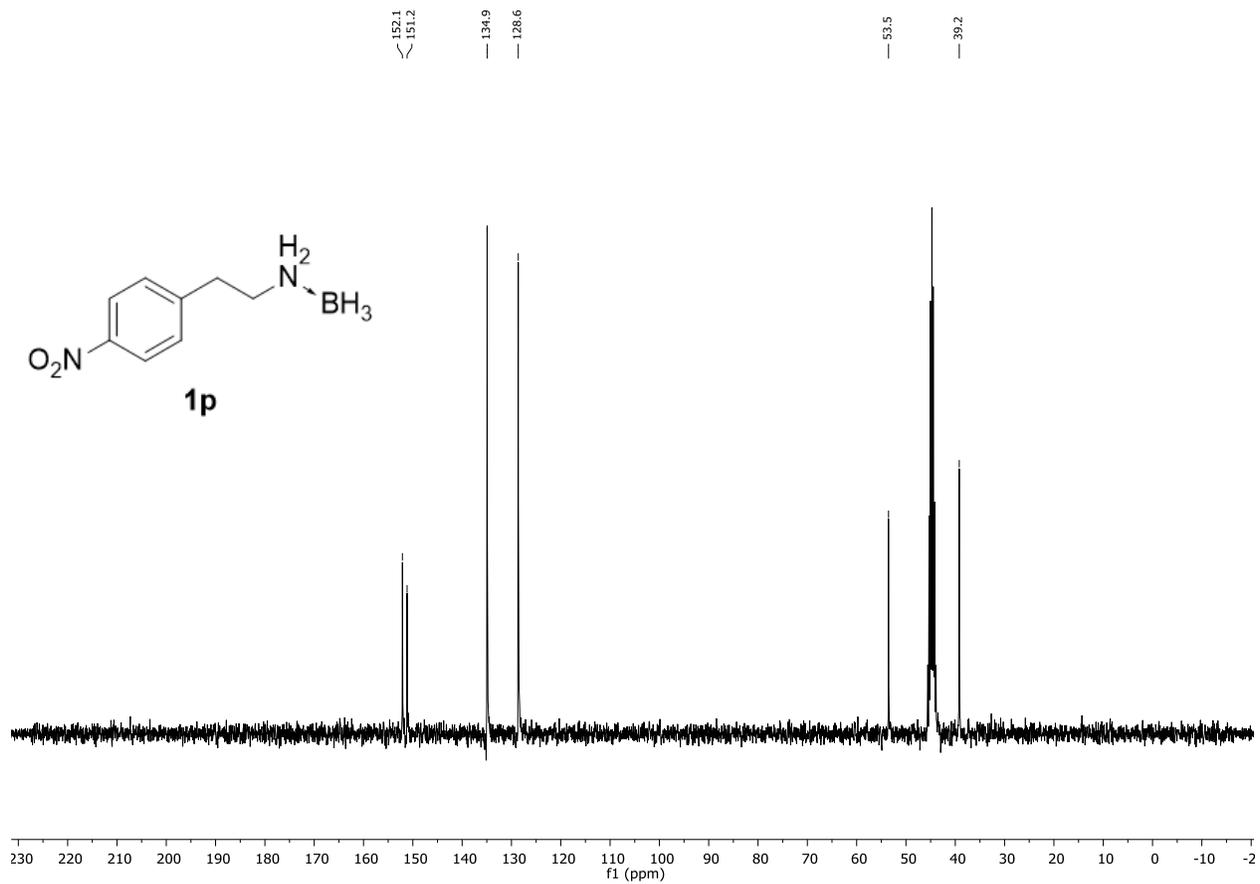


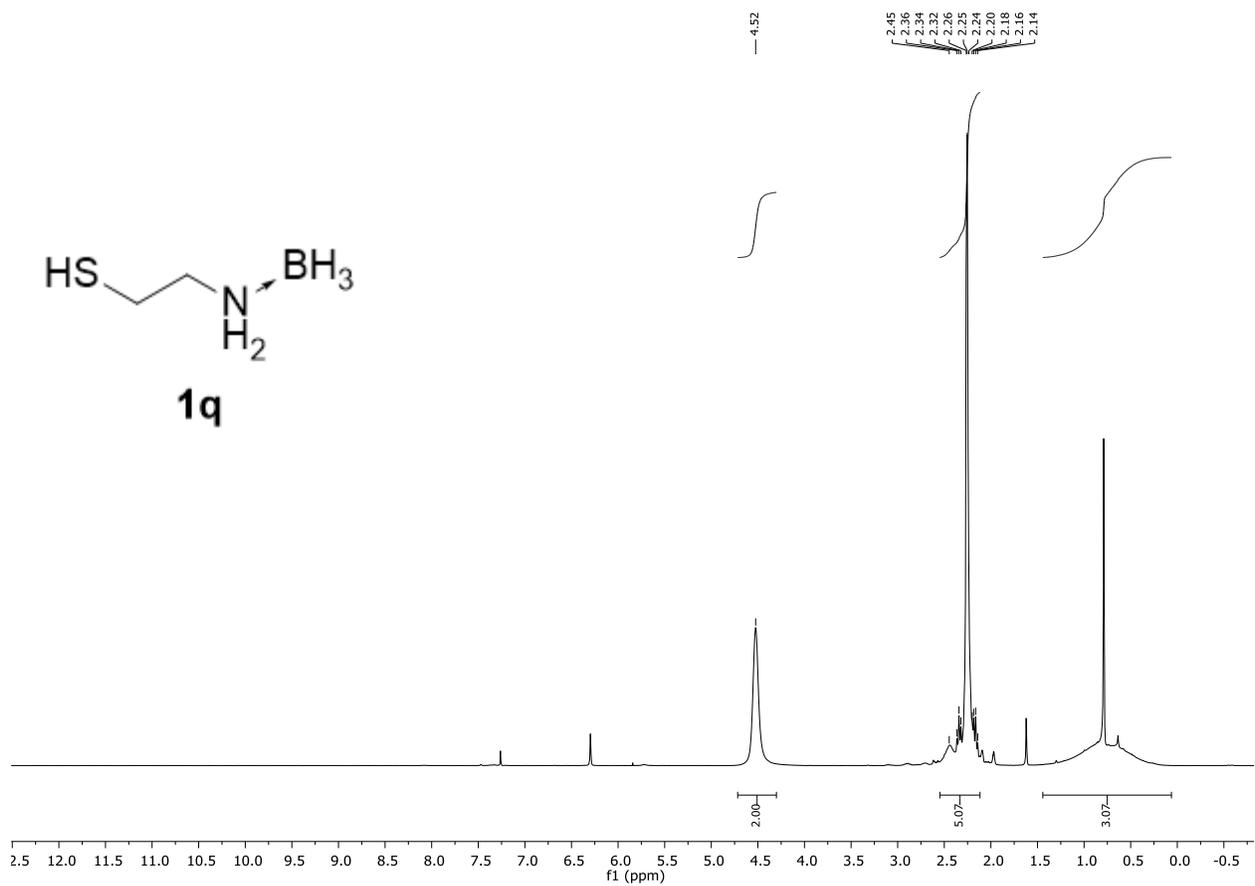




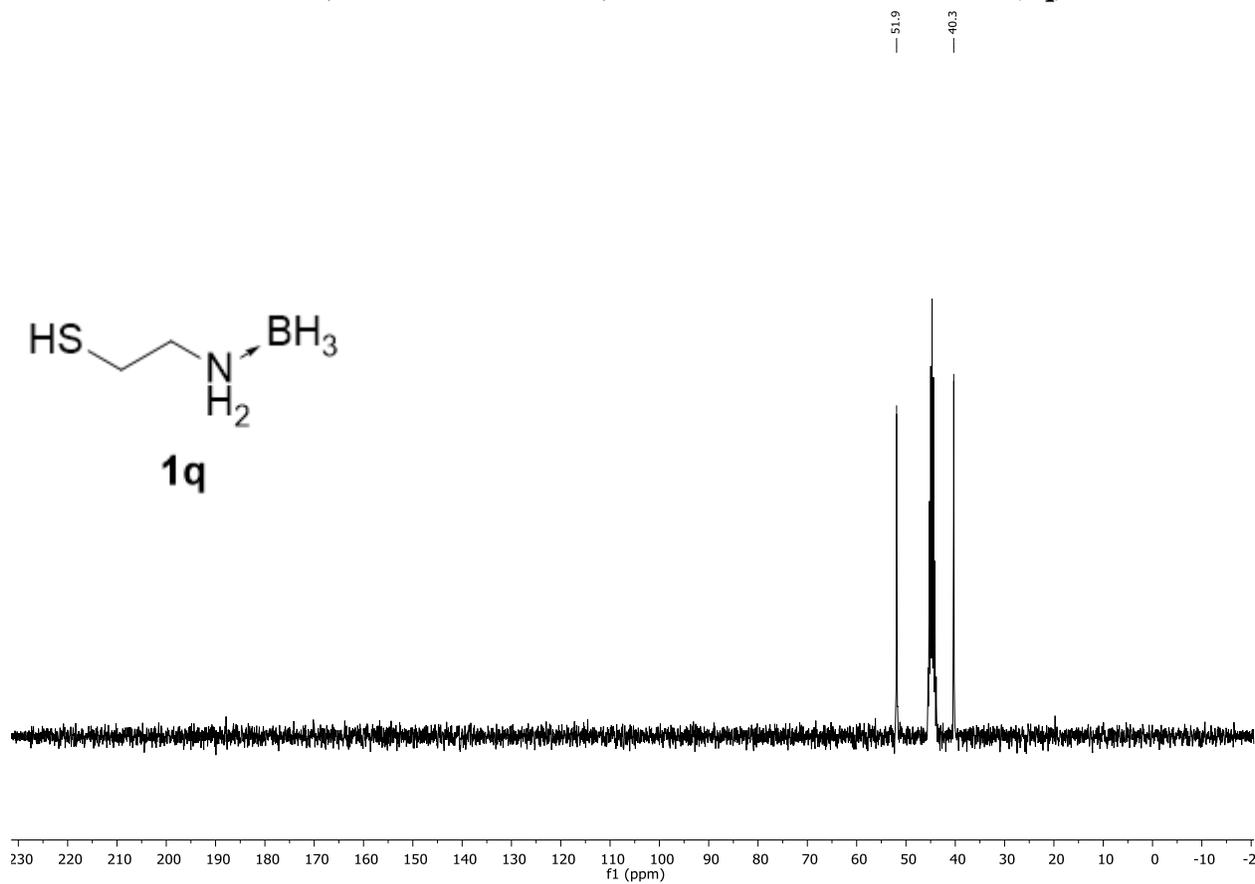




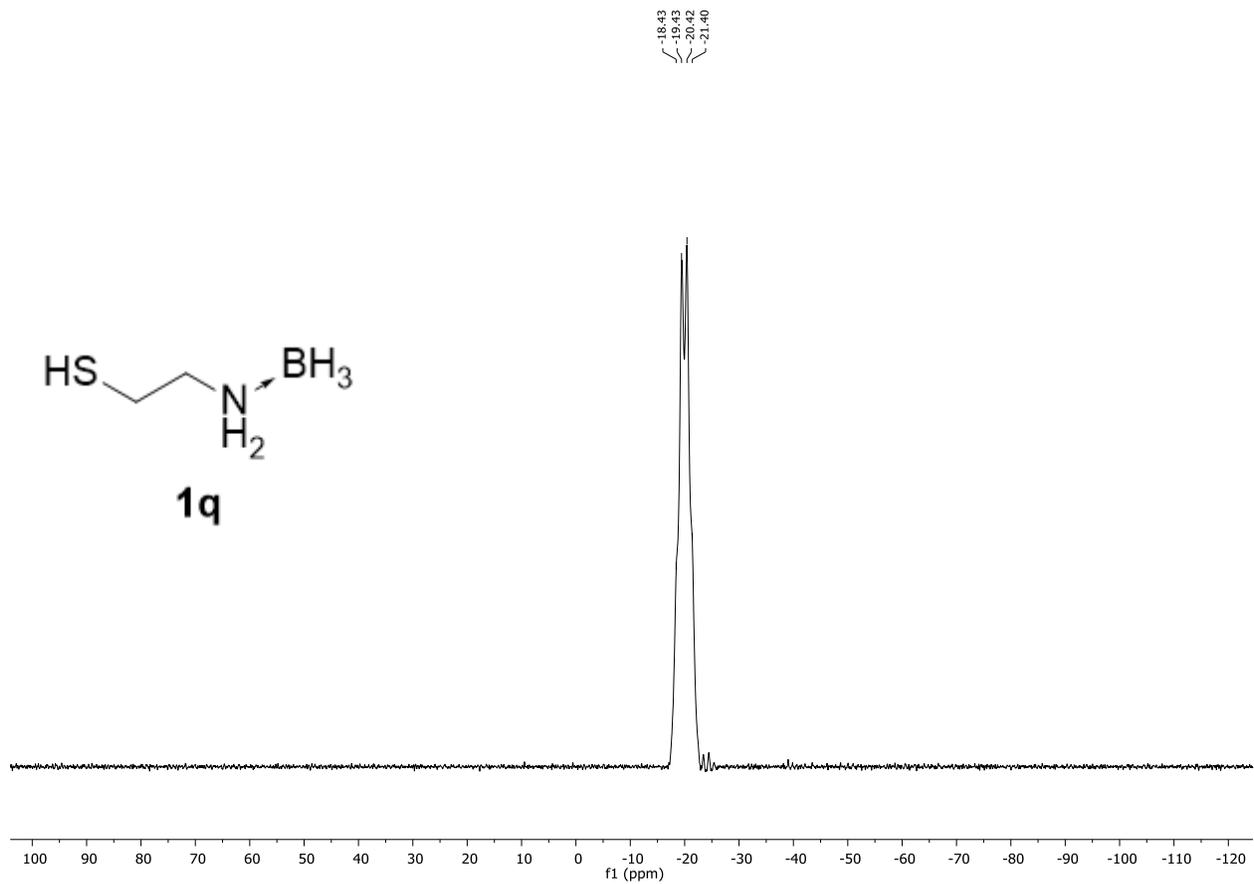




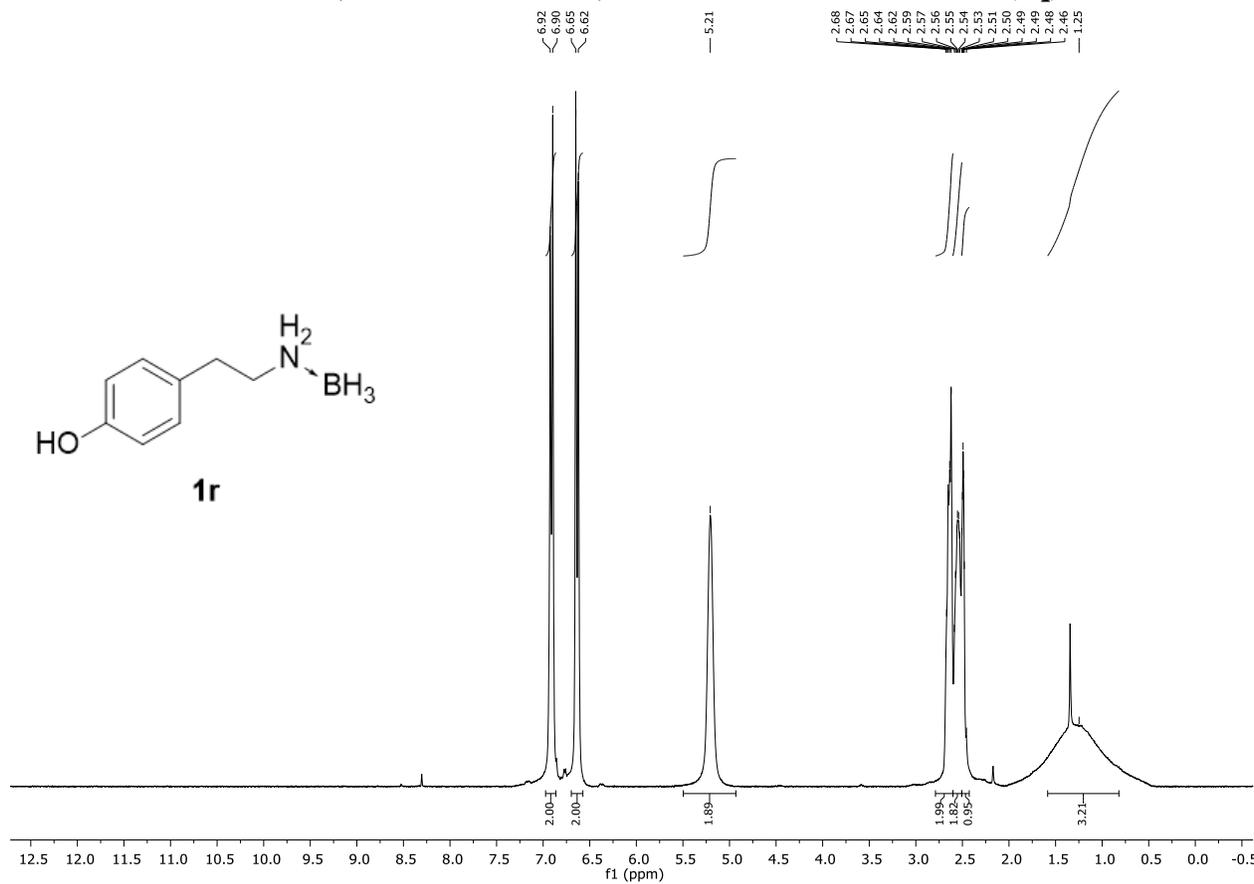
^1H NMR (300 MHz, DMSO- d_6) 2-aminoethane-1-thiol-borane (**1q**)



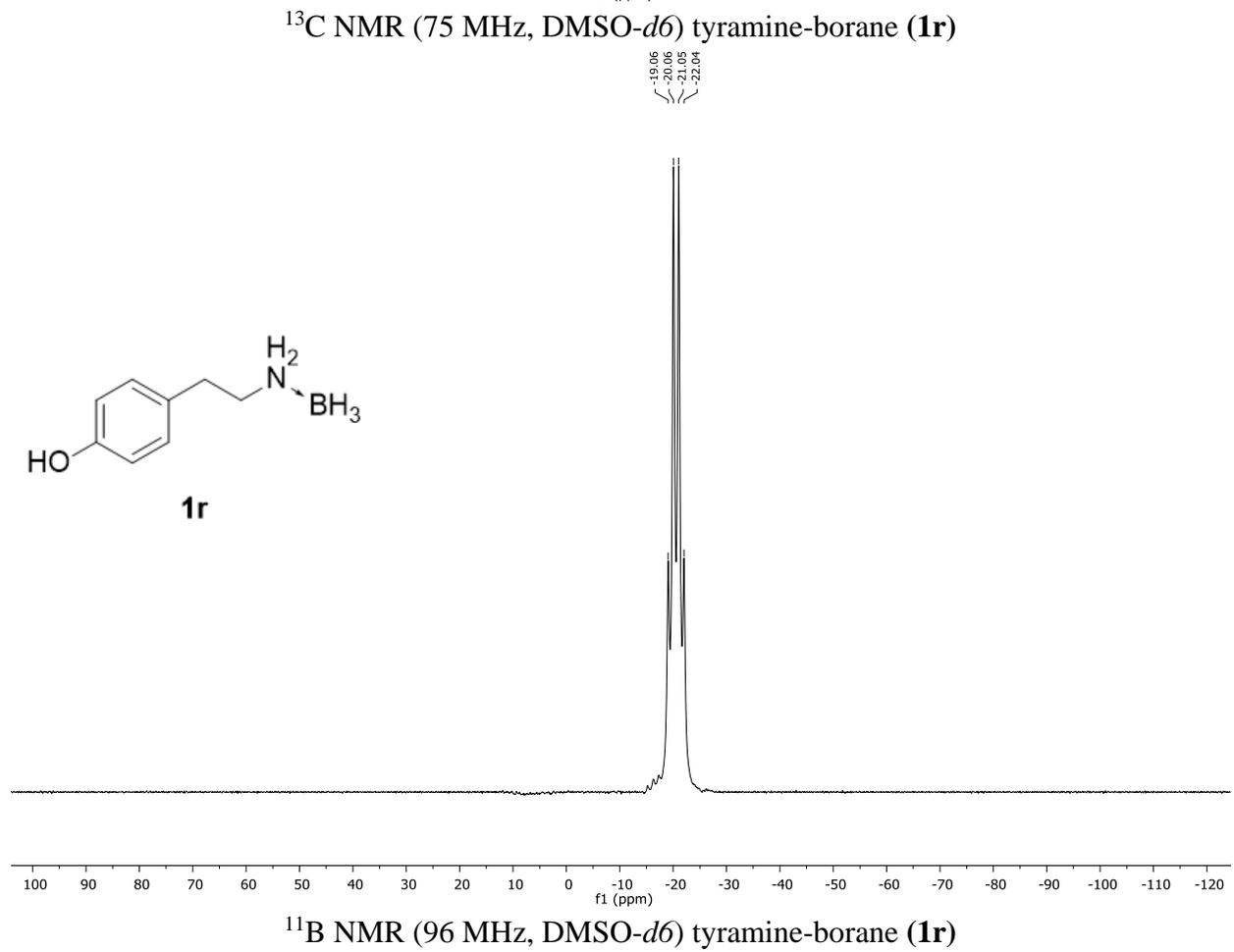
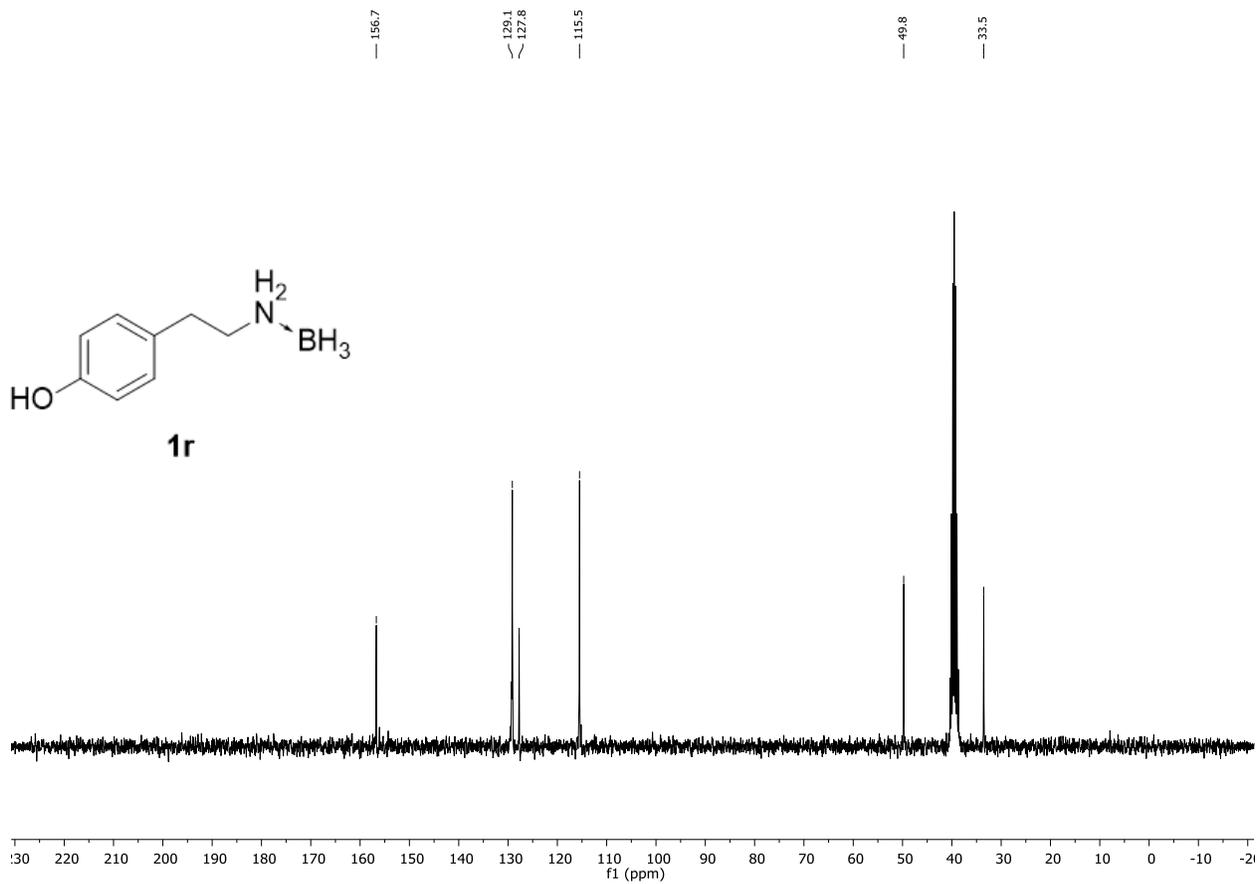
^{13}C NMR (75 MHz, DMSO- d_6) 2-aminoethane-1-thiol-borane (**1q**)

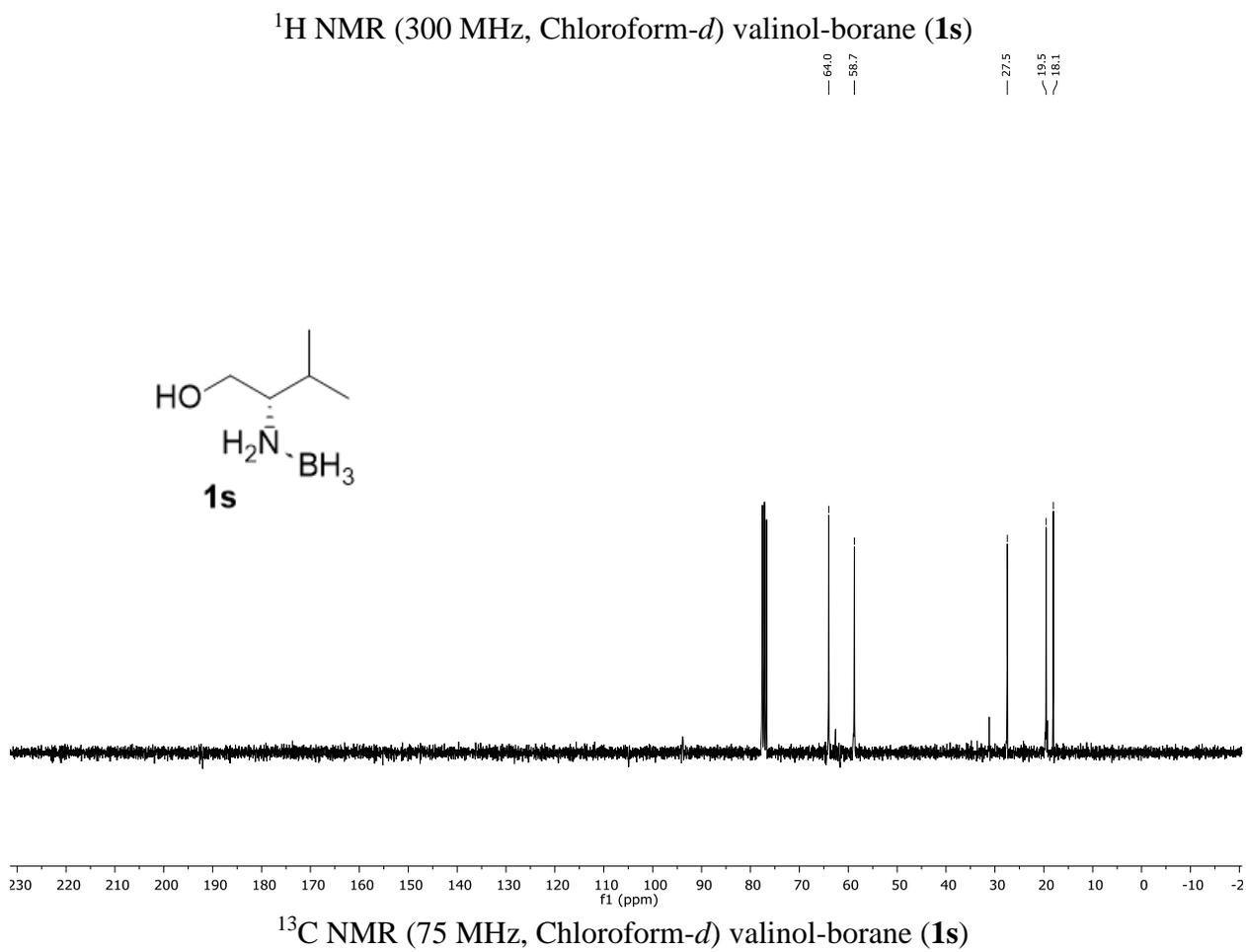
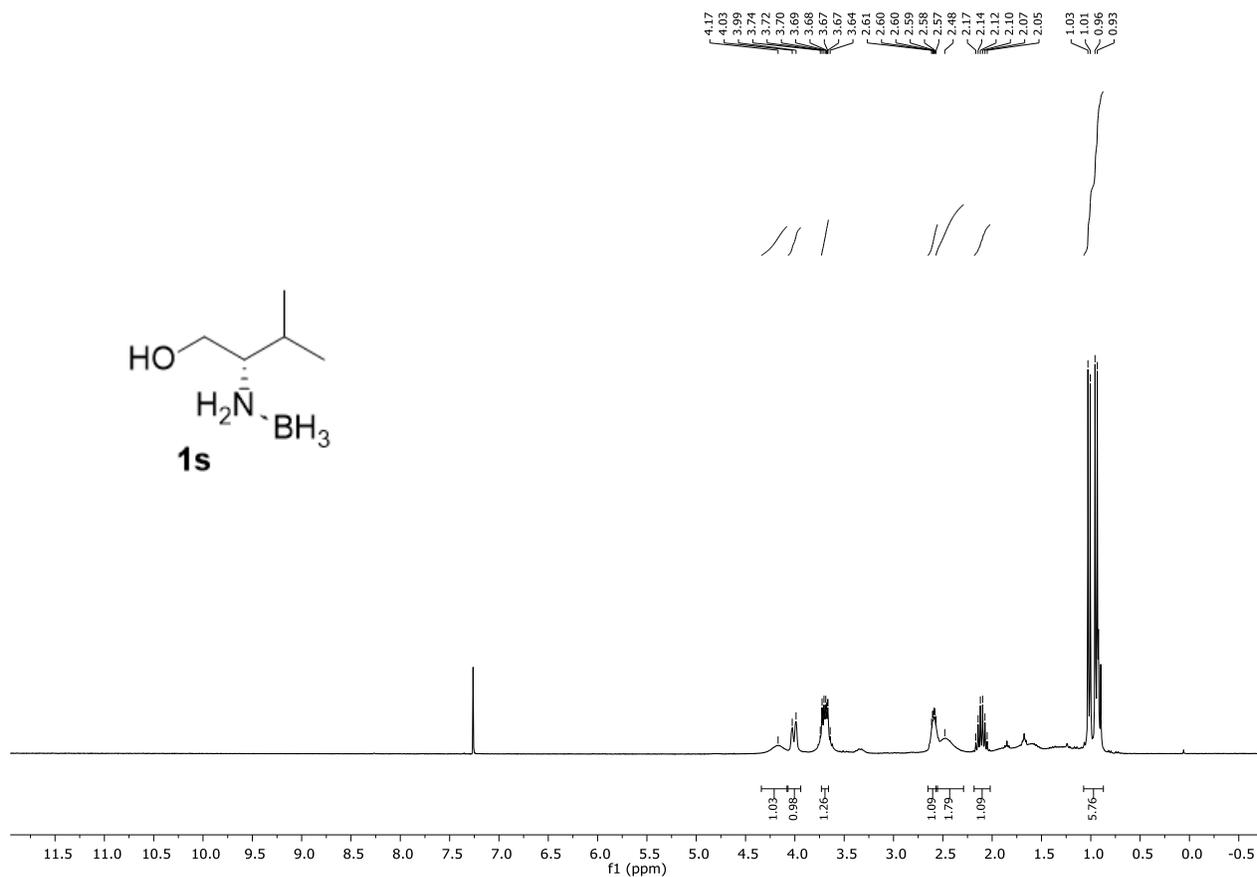


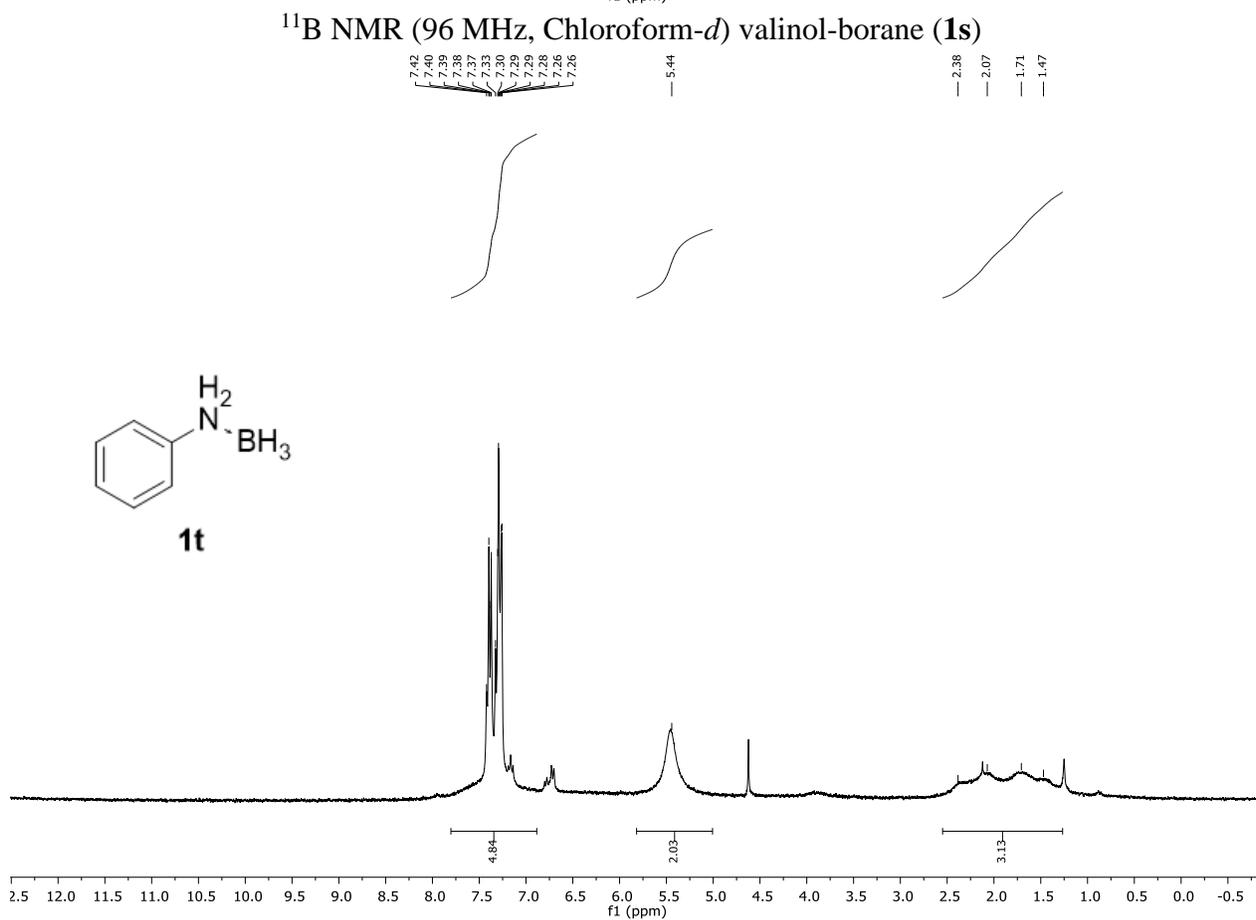
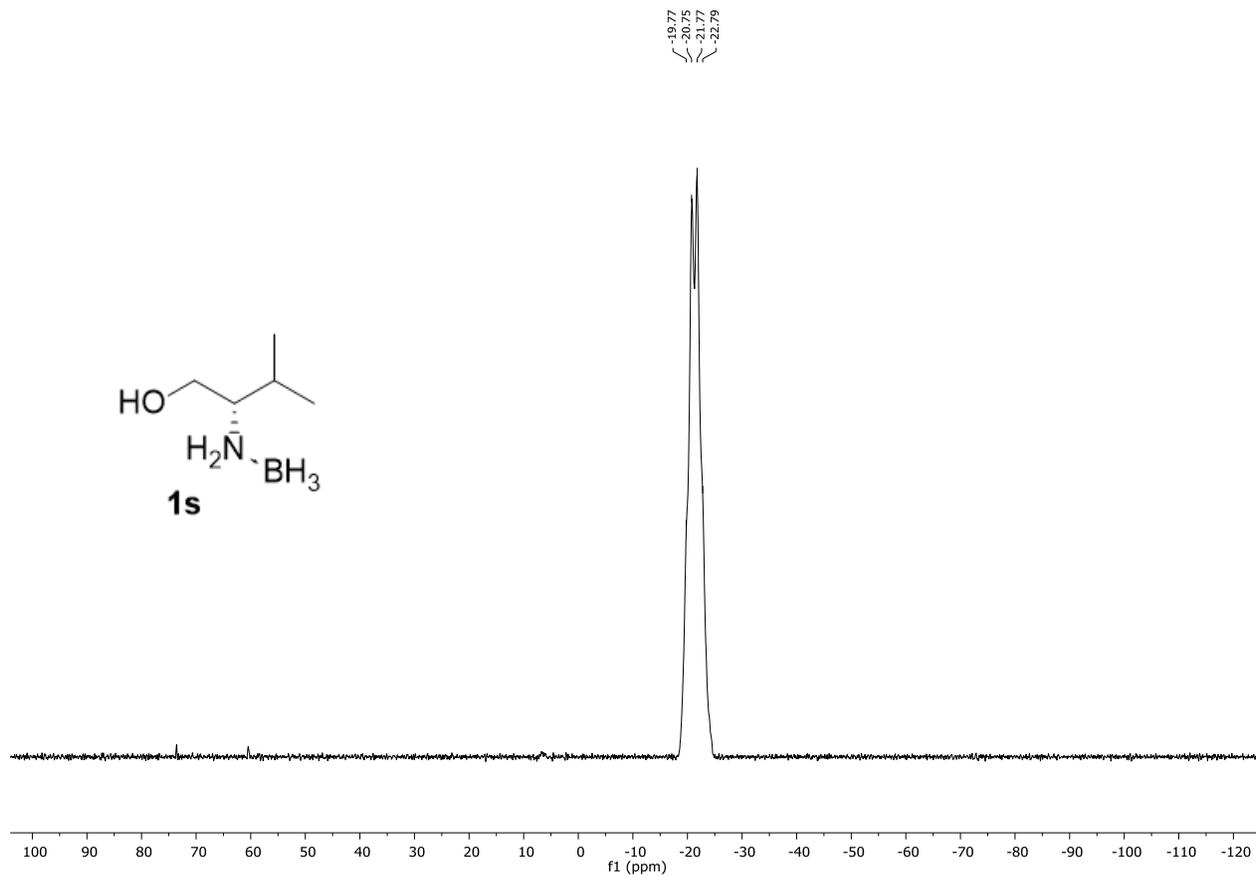
^{11}B NMR (96 MHz, DMSO-*d*₆) 2-aminoethane-1-thiol-borane (**1q**)

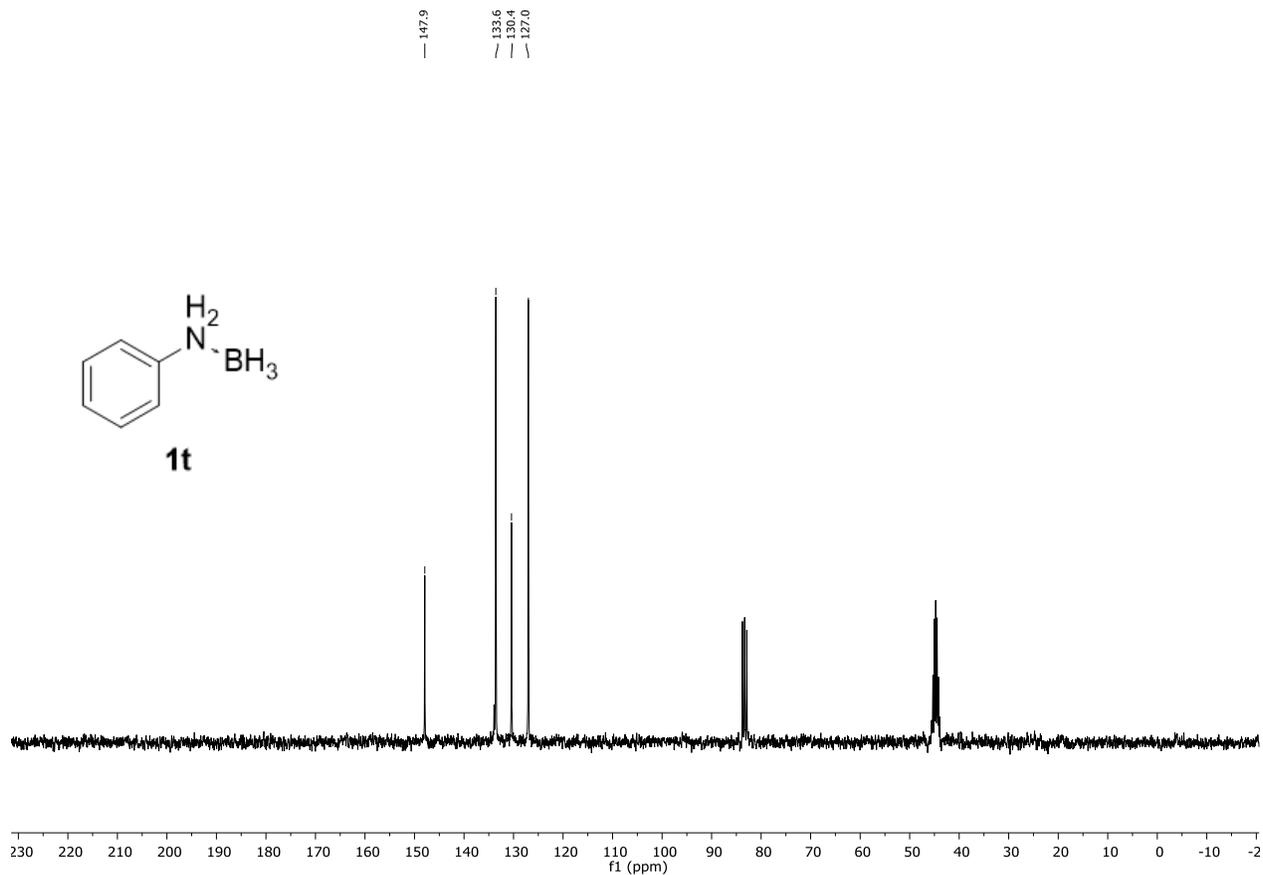


^1H NMR (300 MHz, DMSO-*d*₆) tyramine-borane (**1r**)

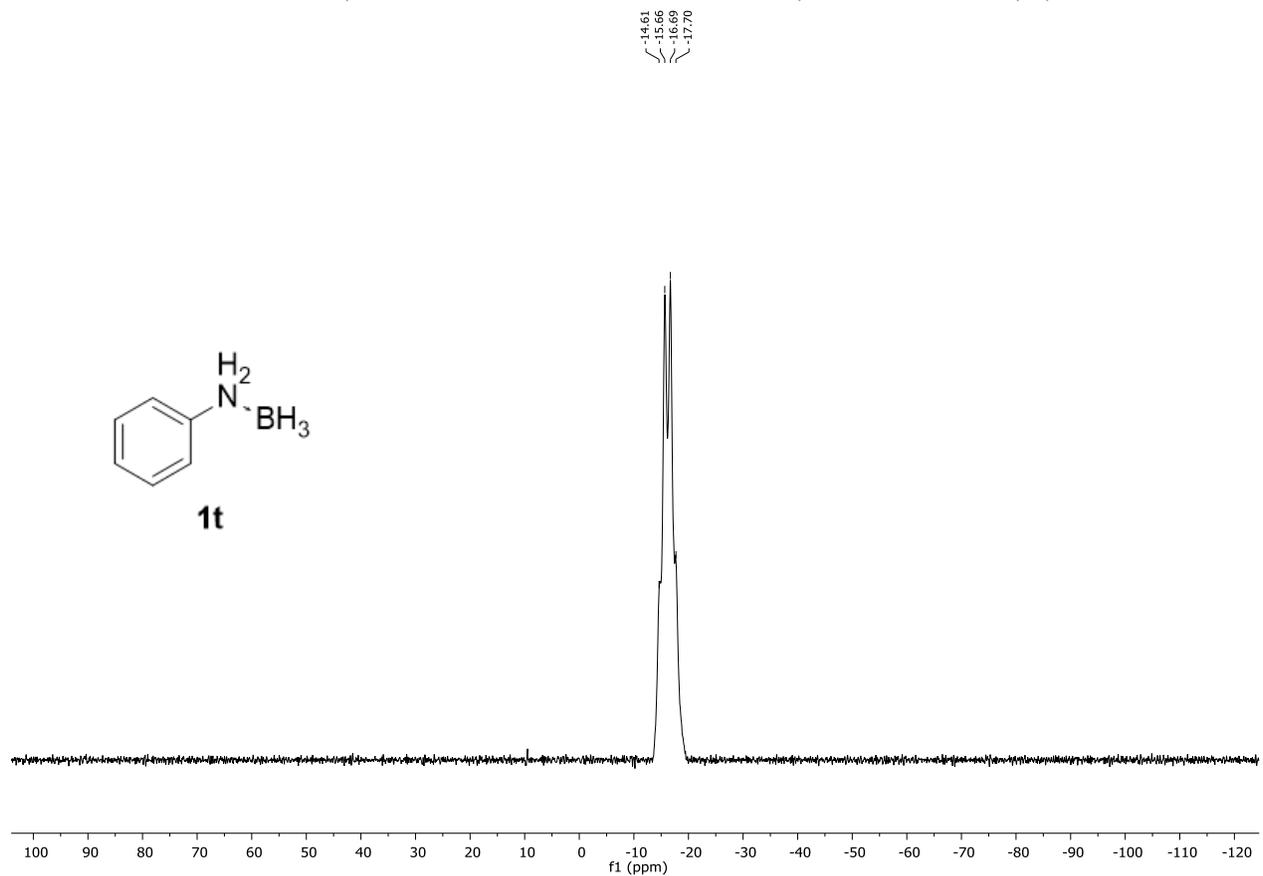






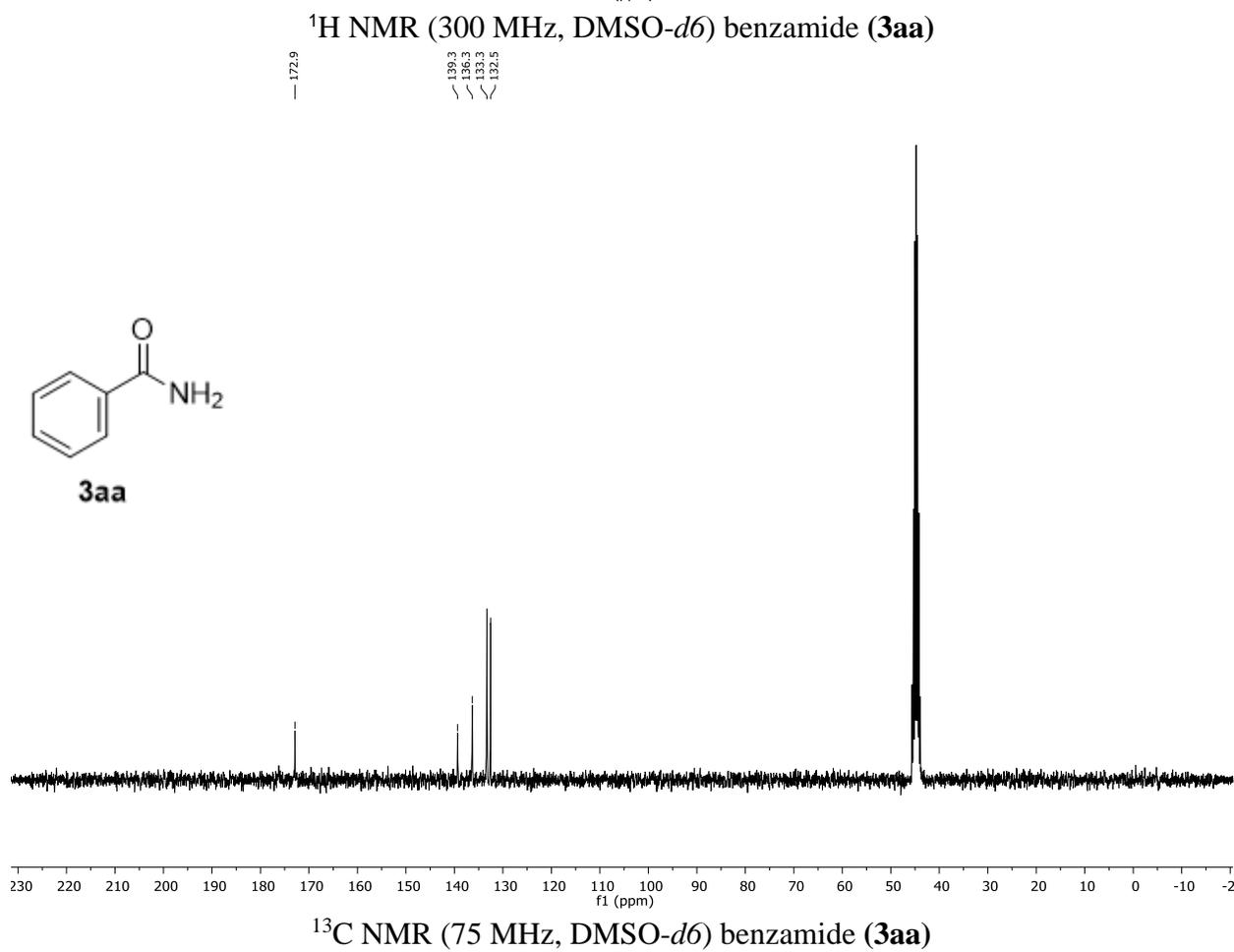
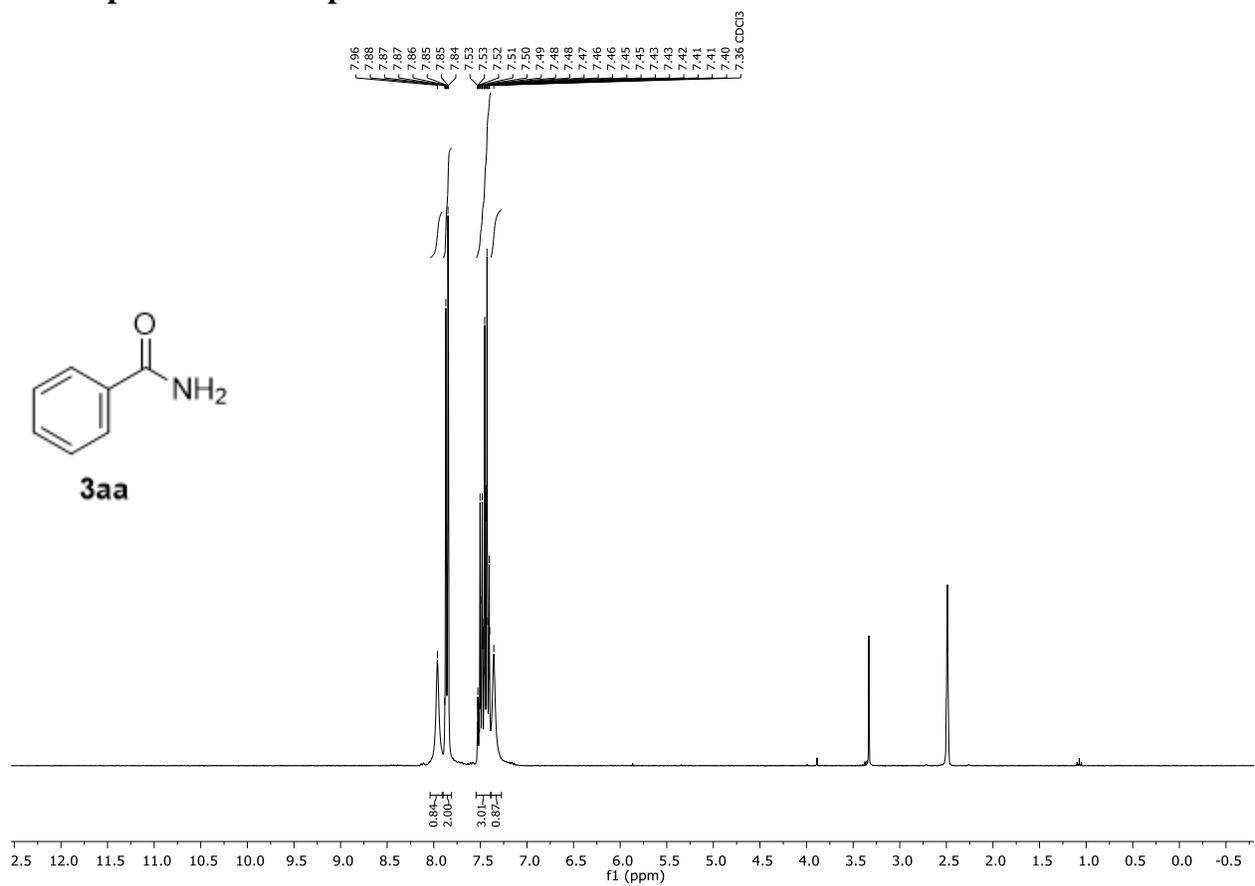


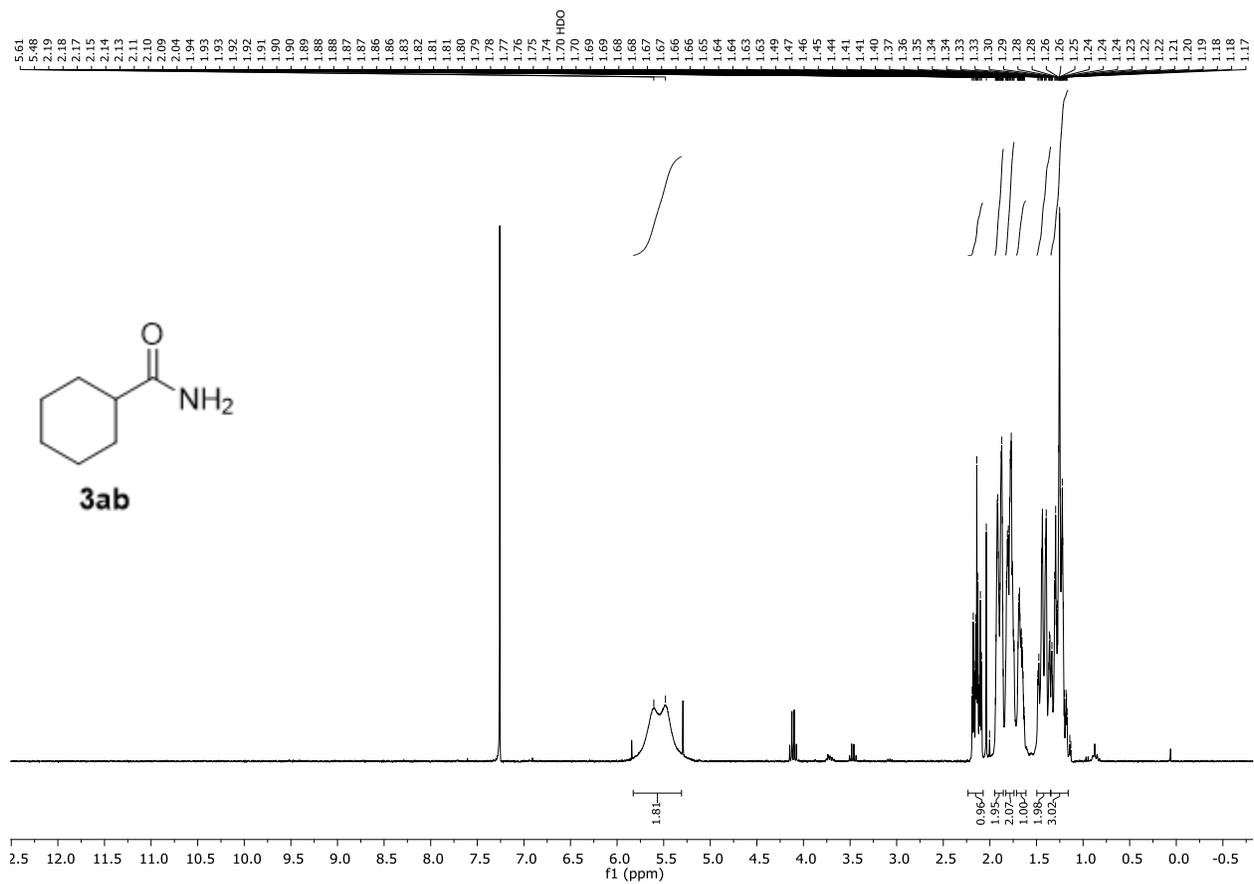
^{13}C NMR (75 MHz, Chloroform-*d*/ DMSO-*d*₆) aniline-borane (**1t**)



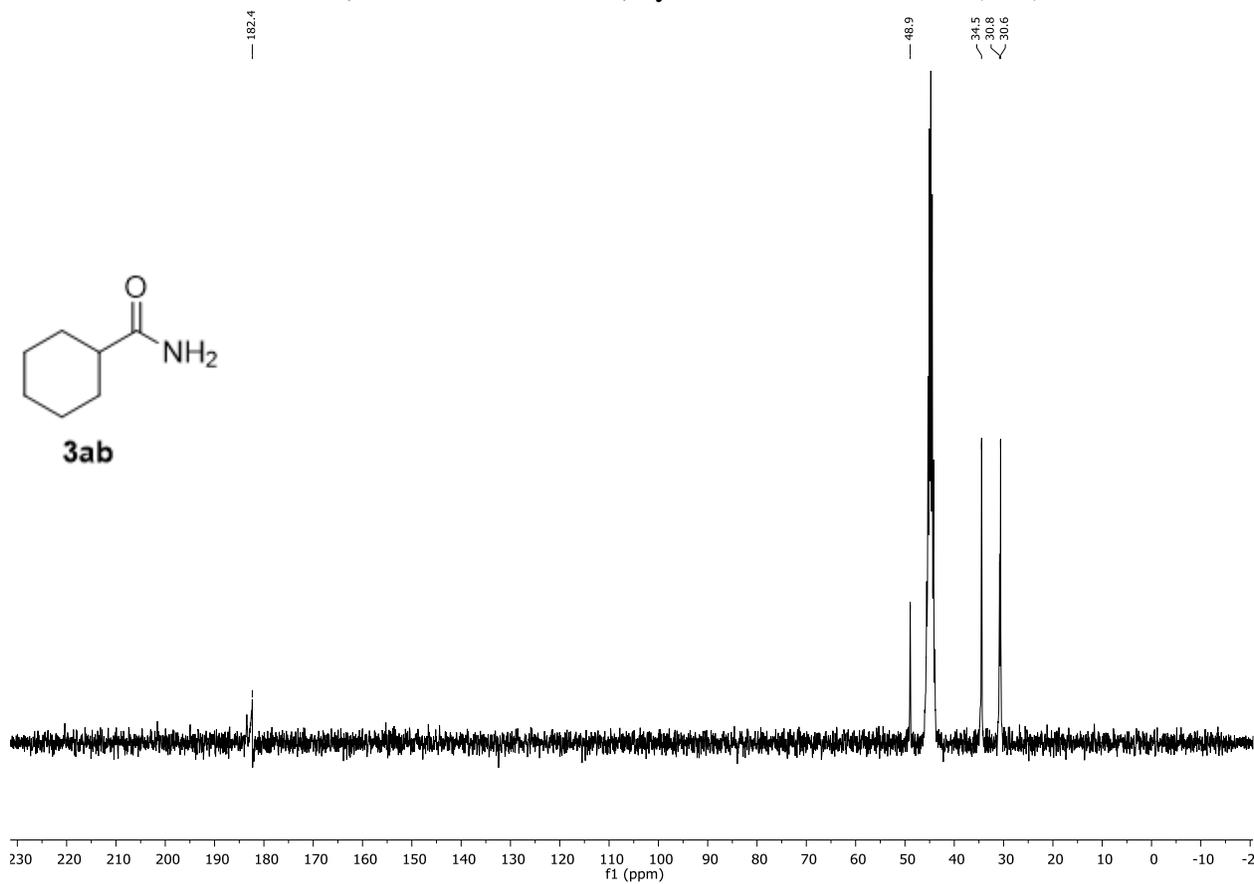
^{11}B NMR (96 MHz, Chloroform-*d*) aniline-borane (**1t**)

NMR spectra of amide products:

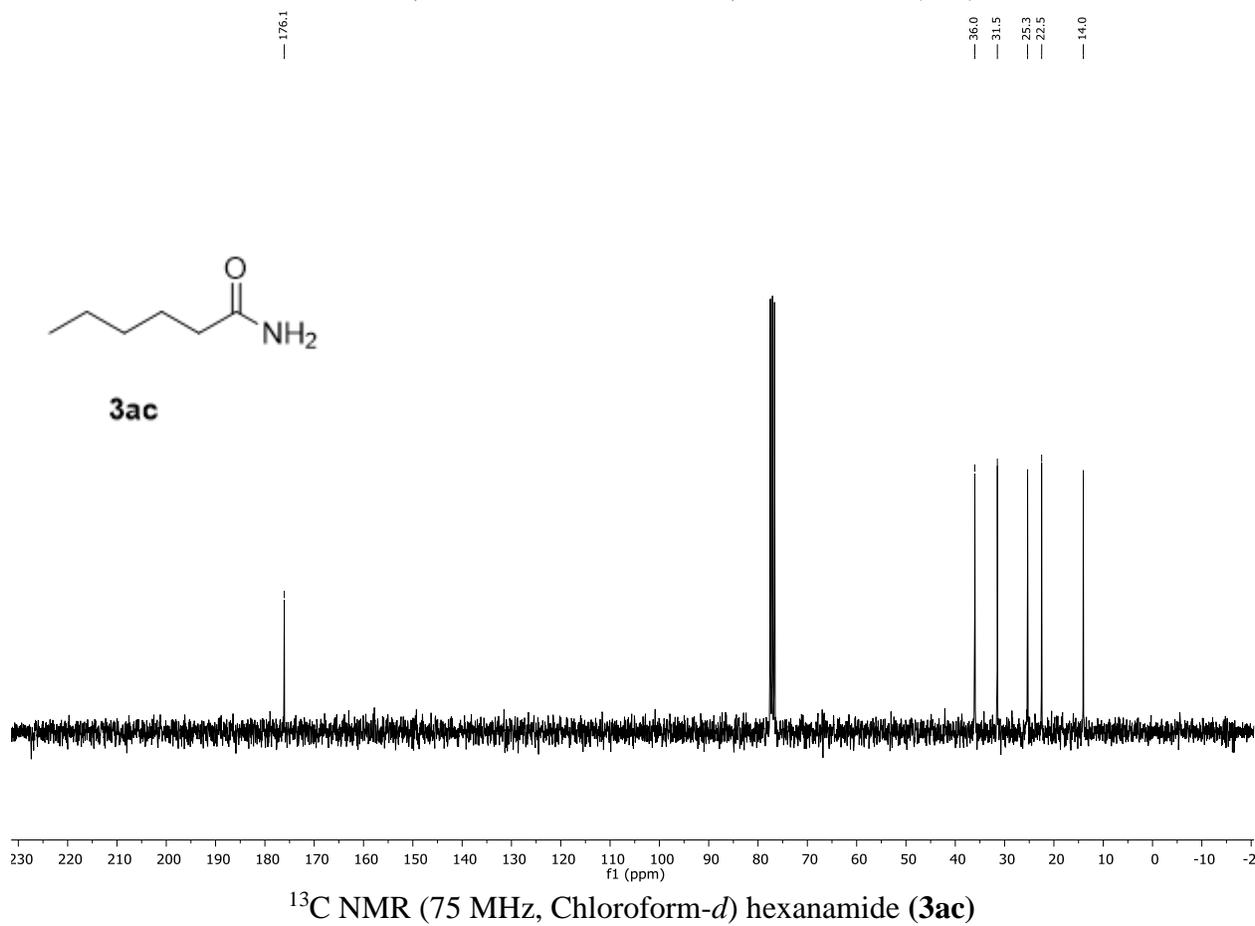
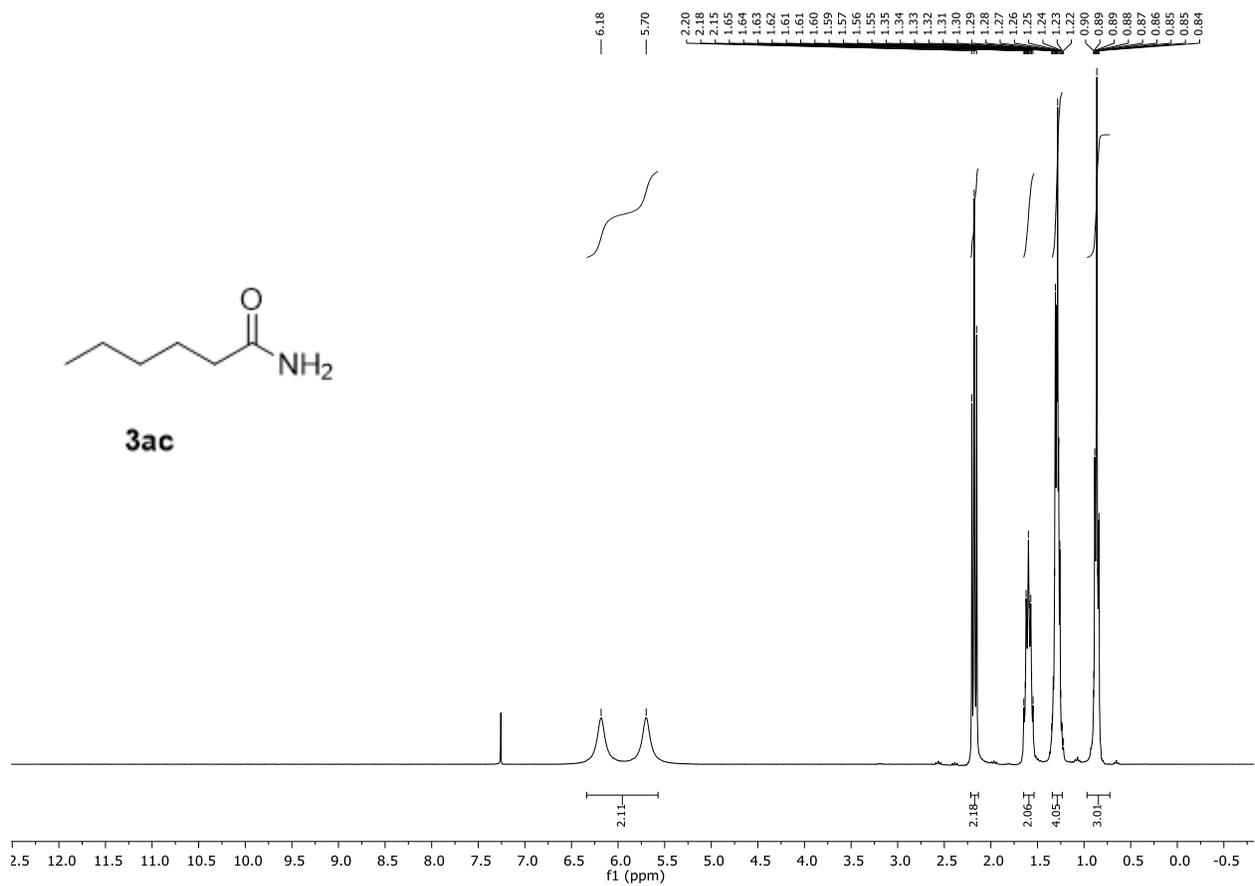


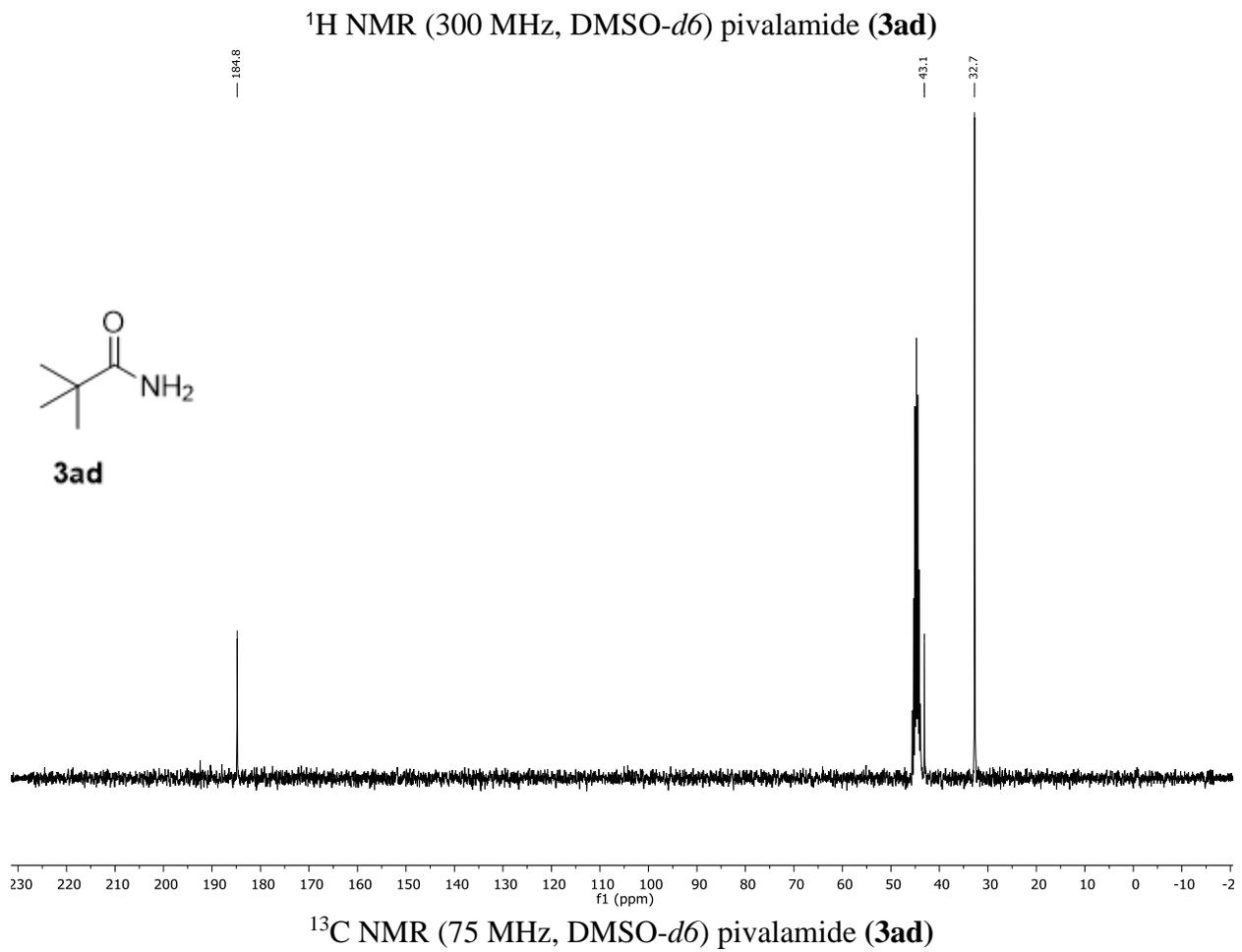
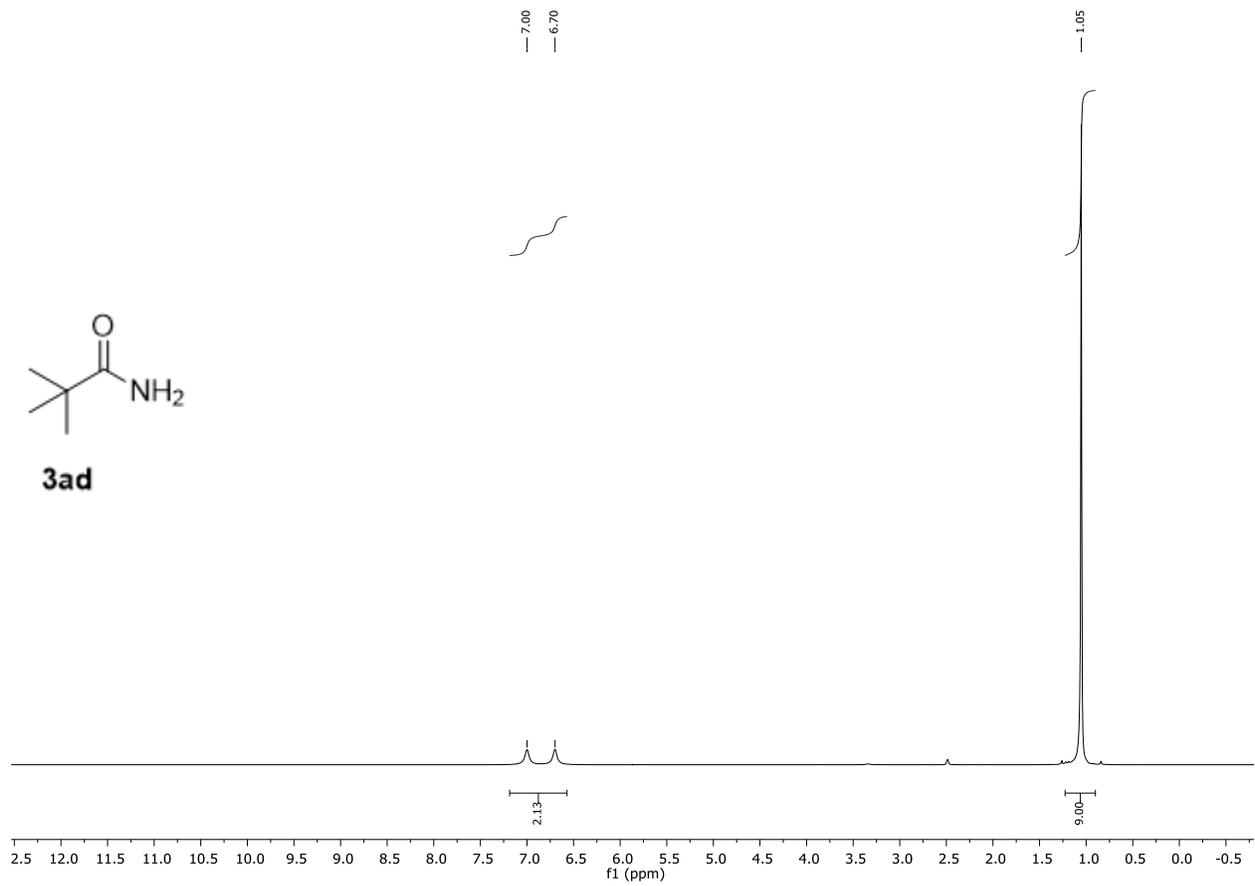


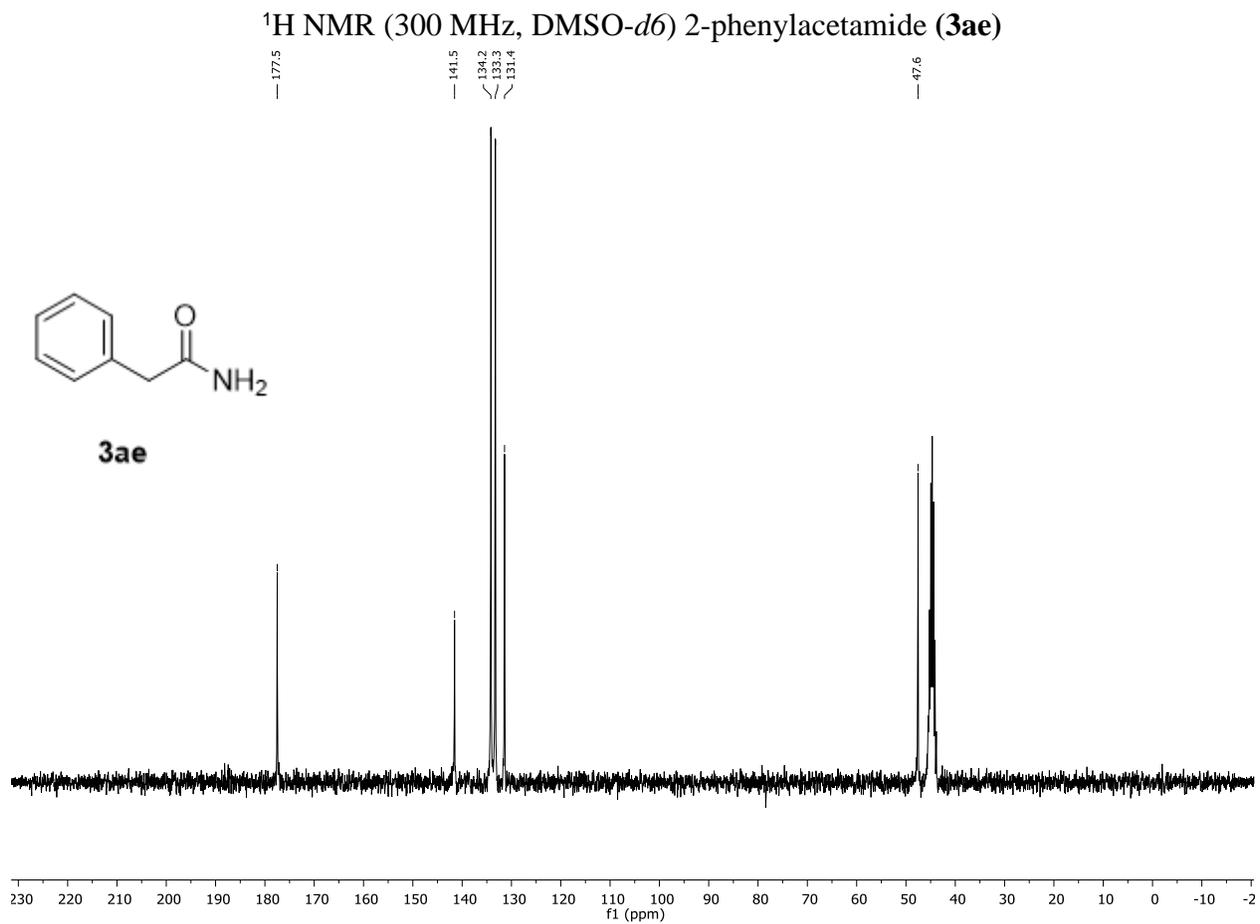
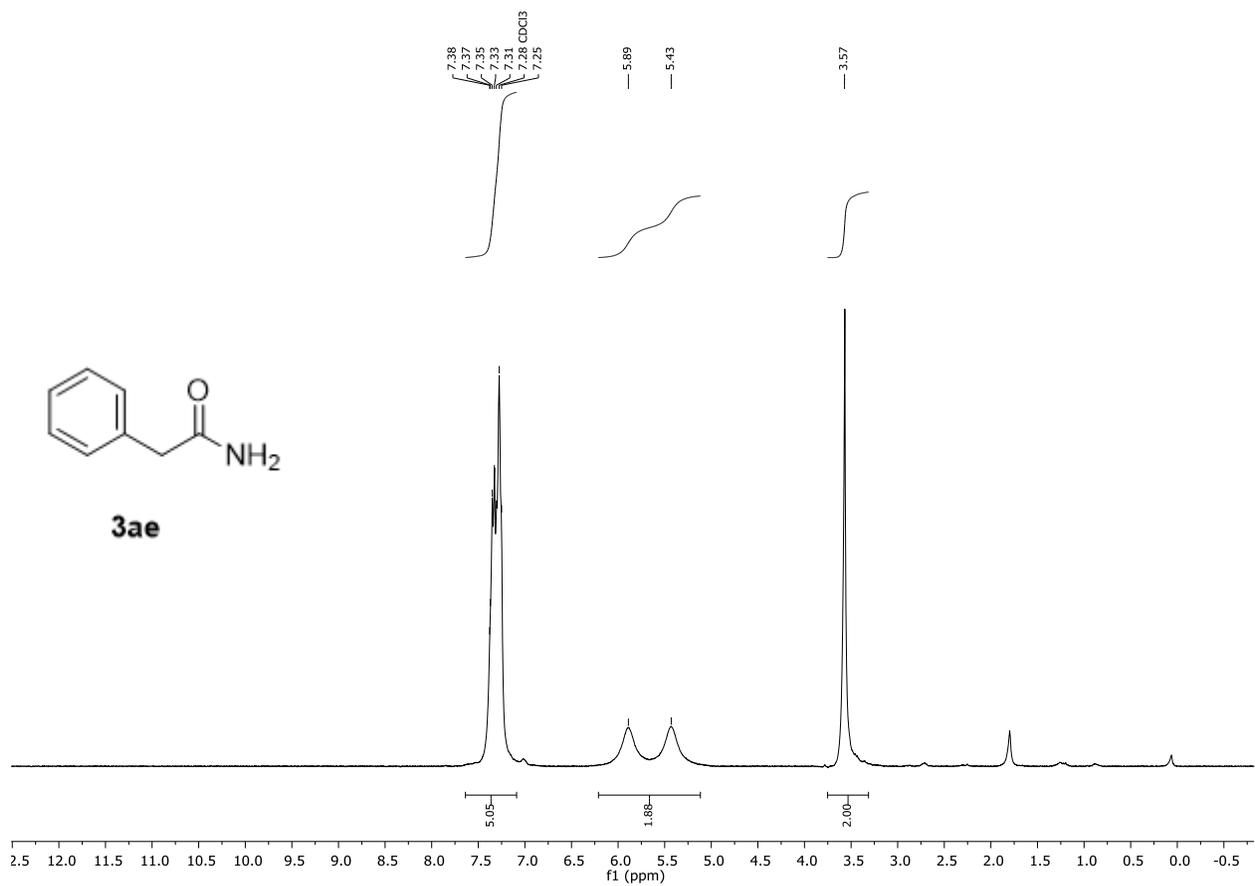
¹H NMR (300 MHz, DMSO-*d*₆) cyclohexanecarboxamide (**3ab**)

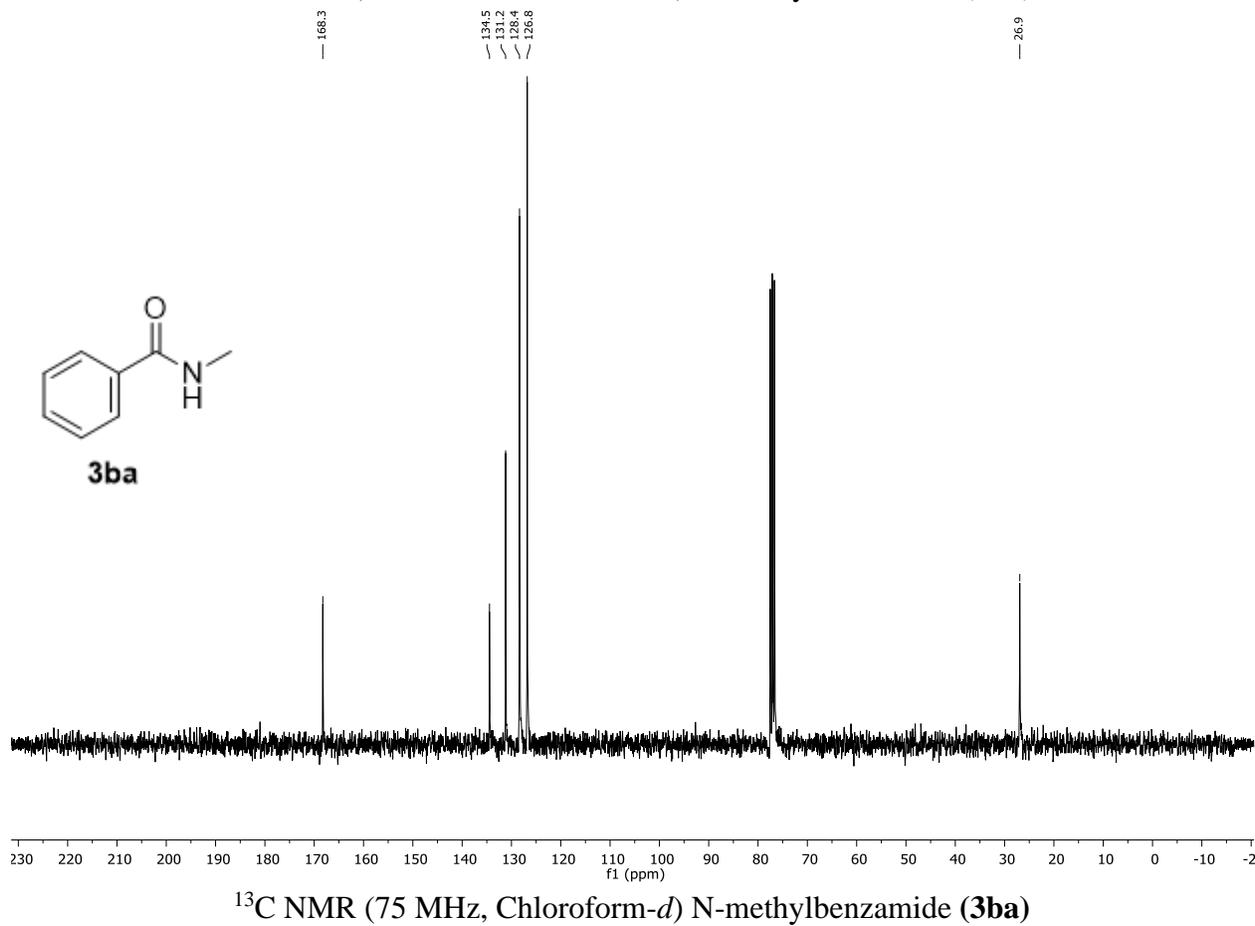
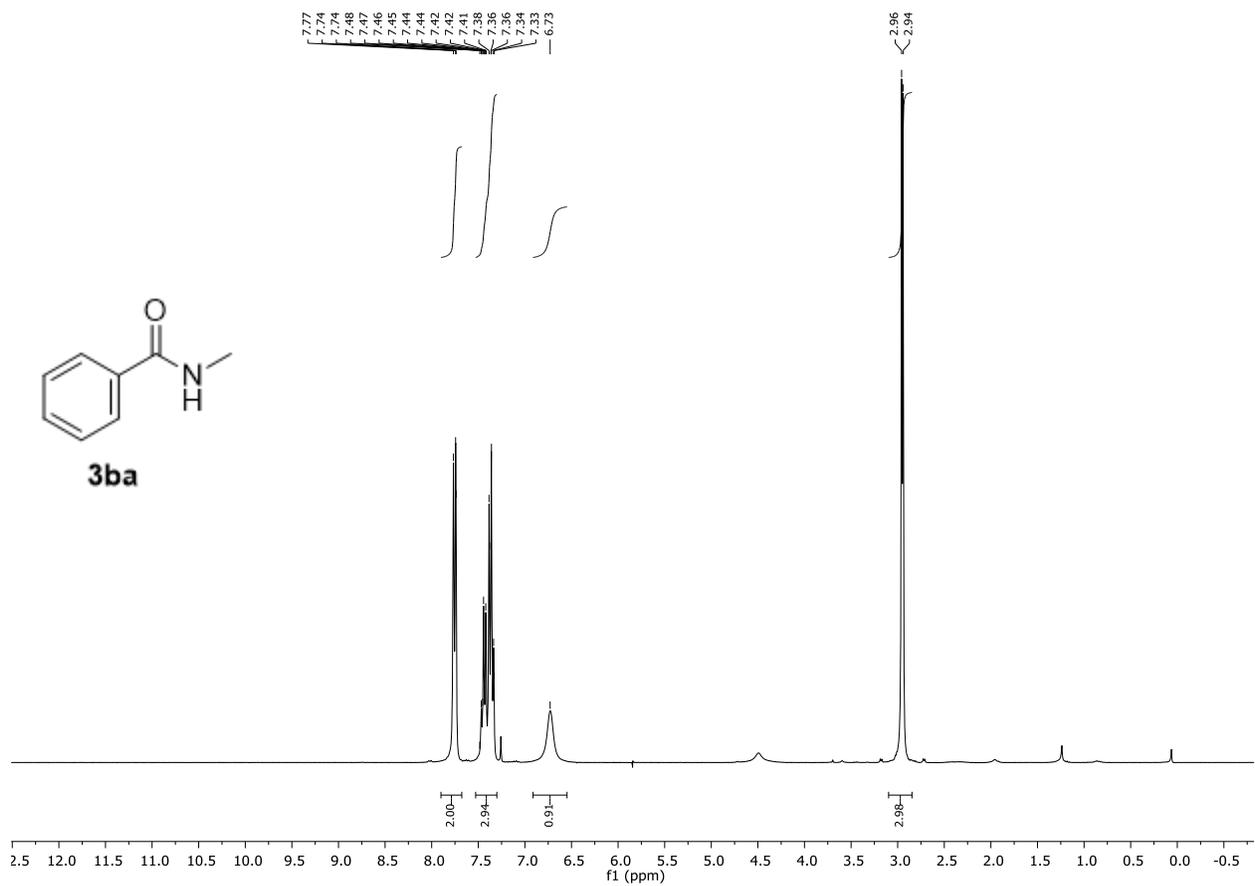


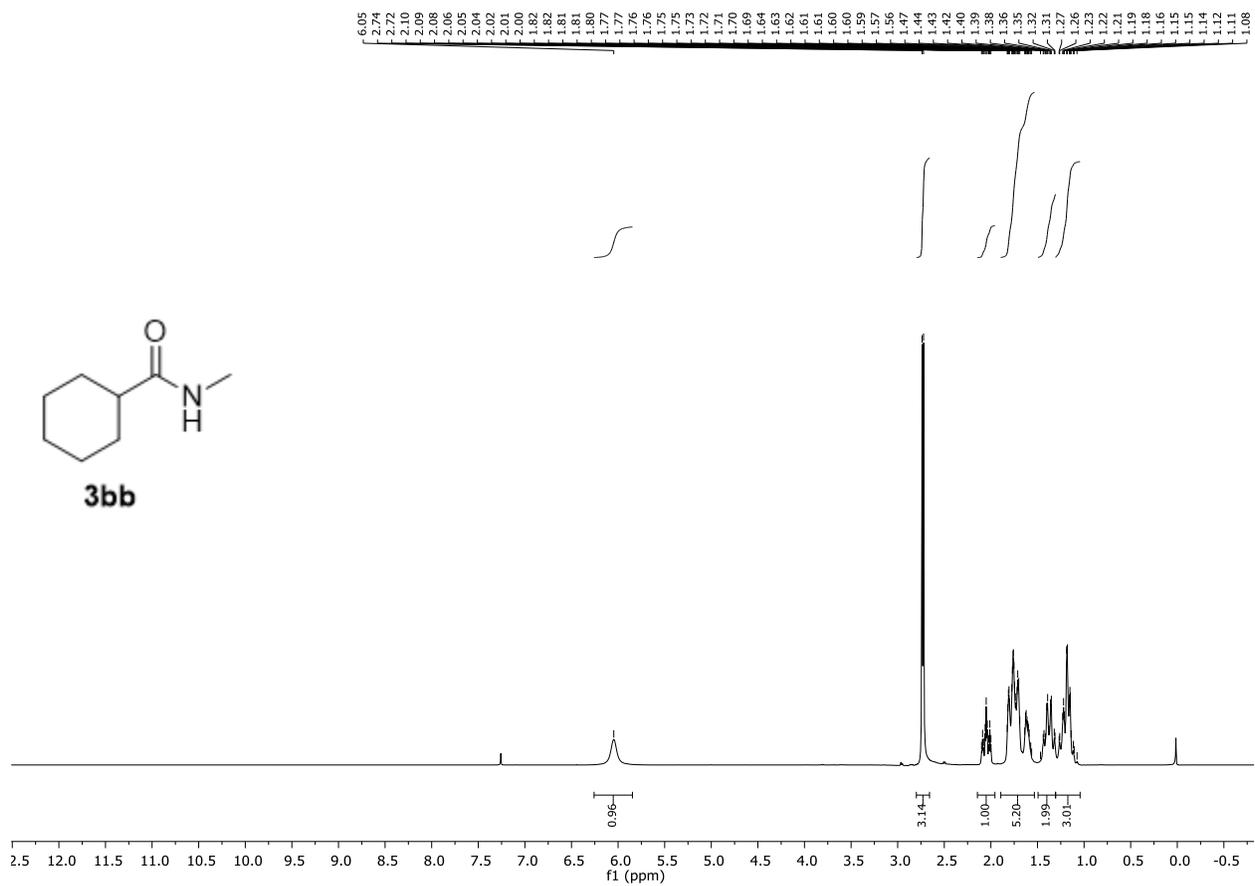
¹³C NMR (75 MHz, DMSO-*d*₆) cyclohexanecarboxamide (**3ab**)



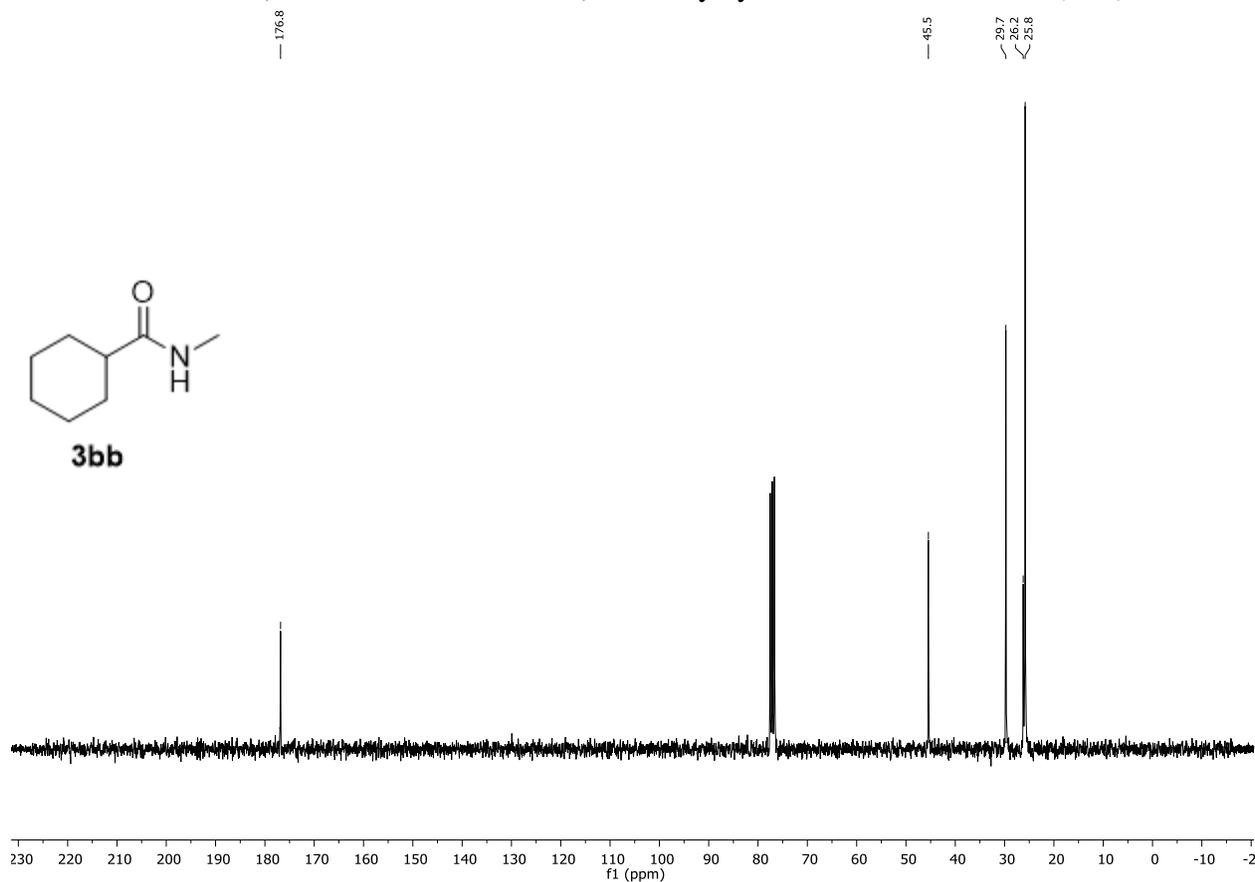




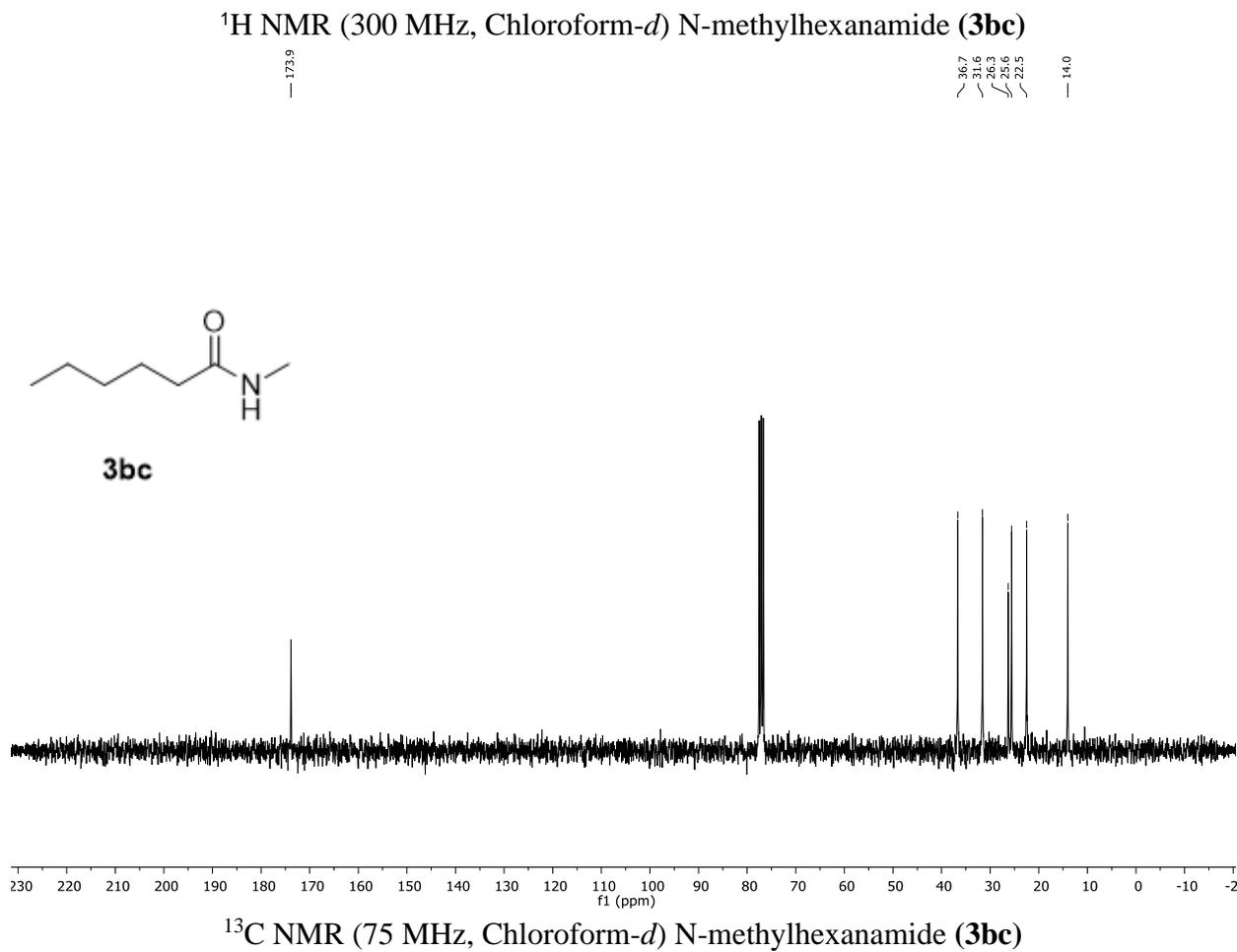
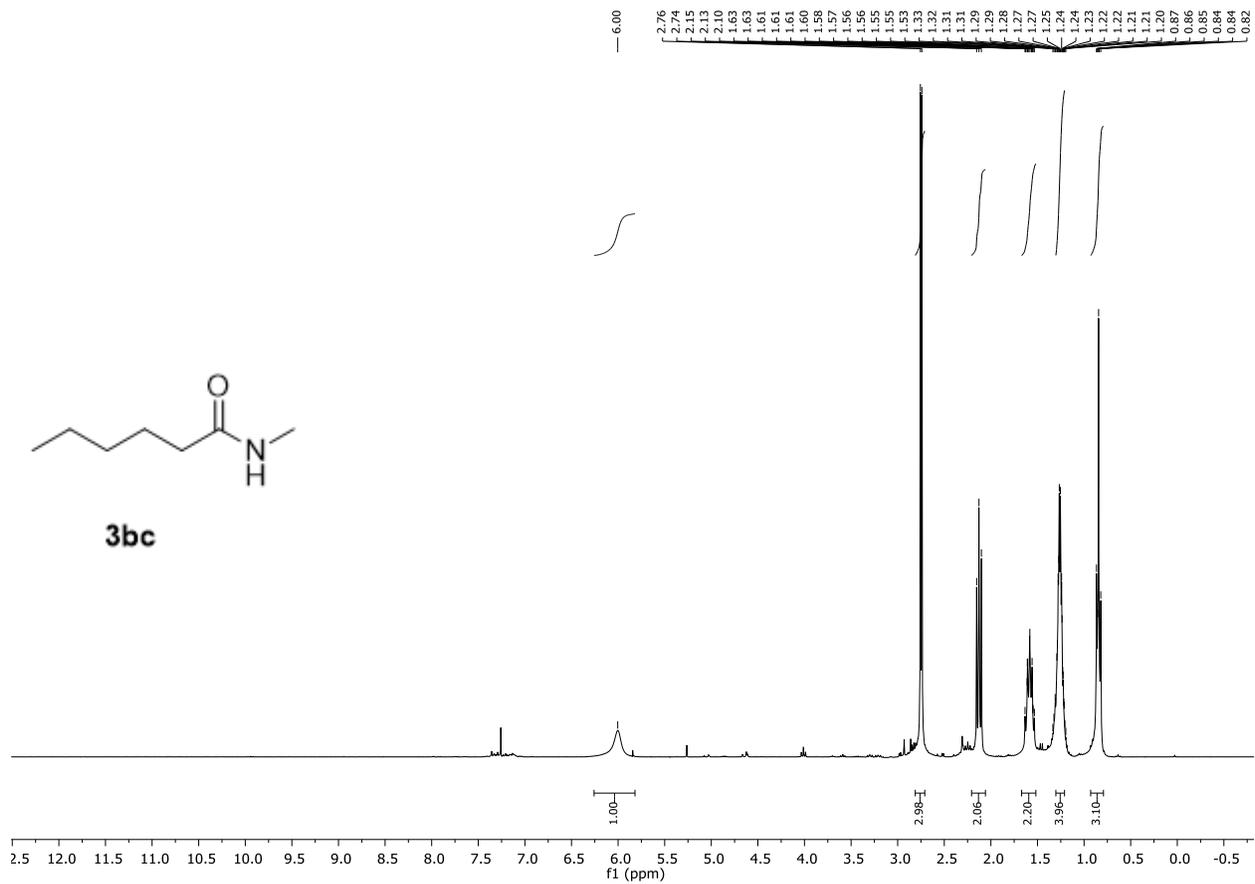


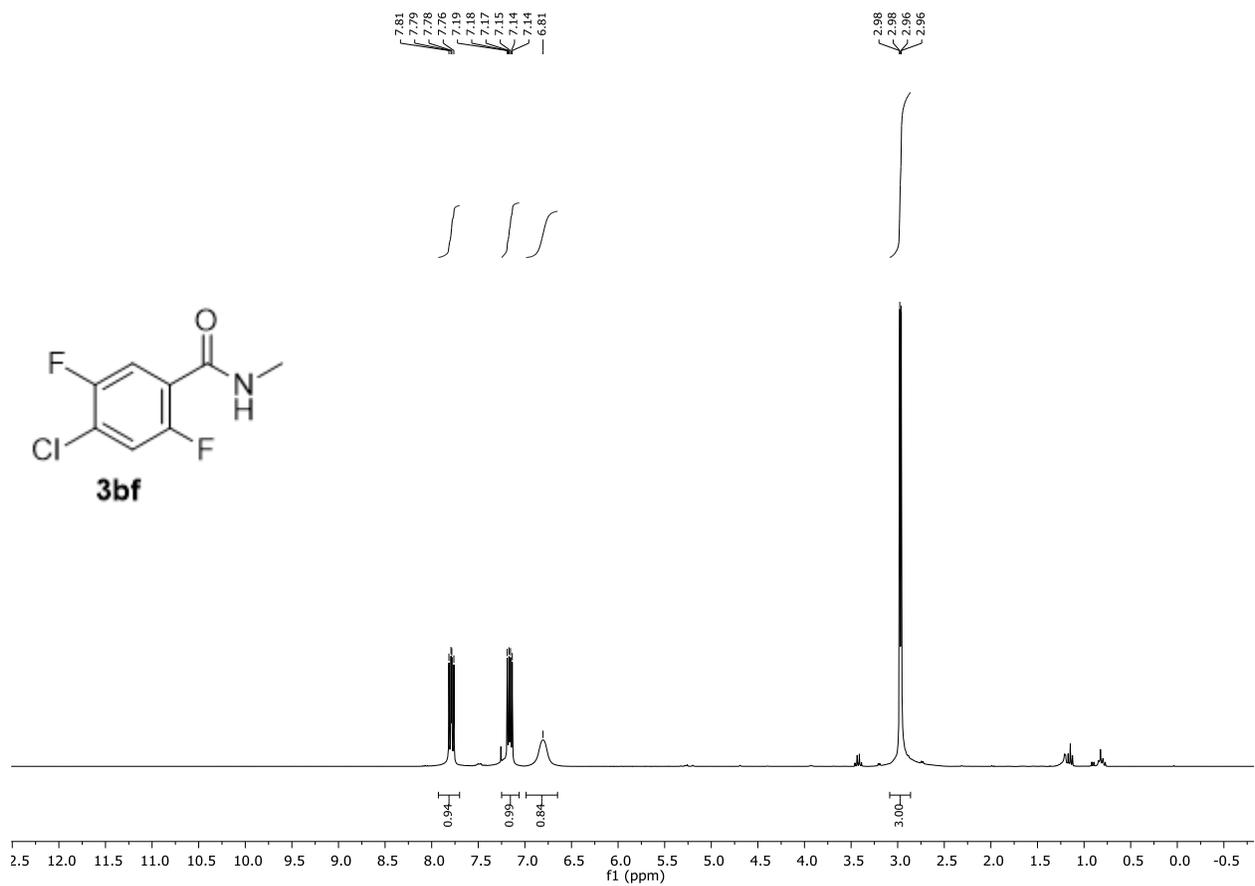


¹H NMR (300 MHz, Chloroform-*d*) N-methylcyclohexanecarboxamide (**3bb**)

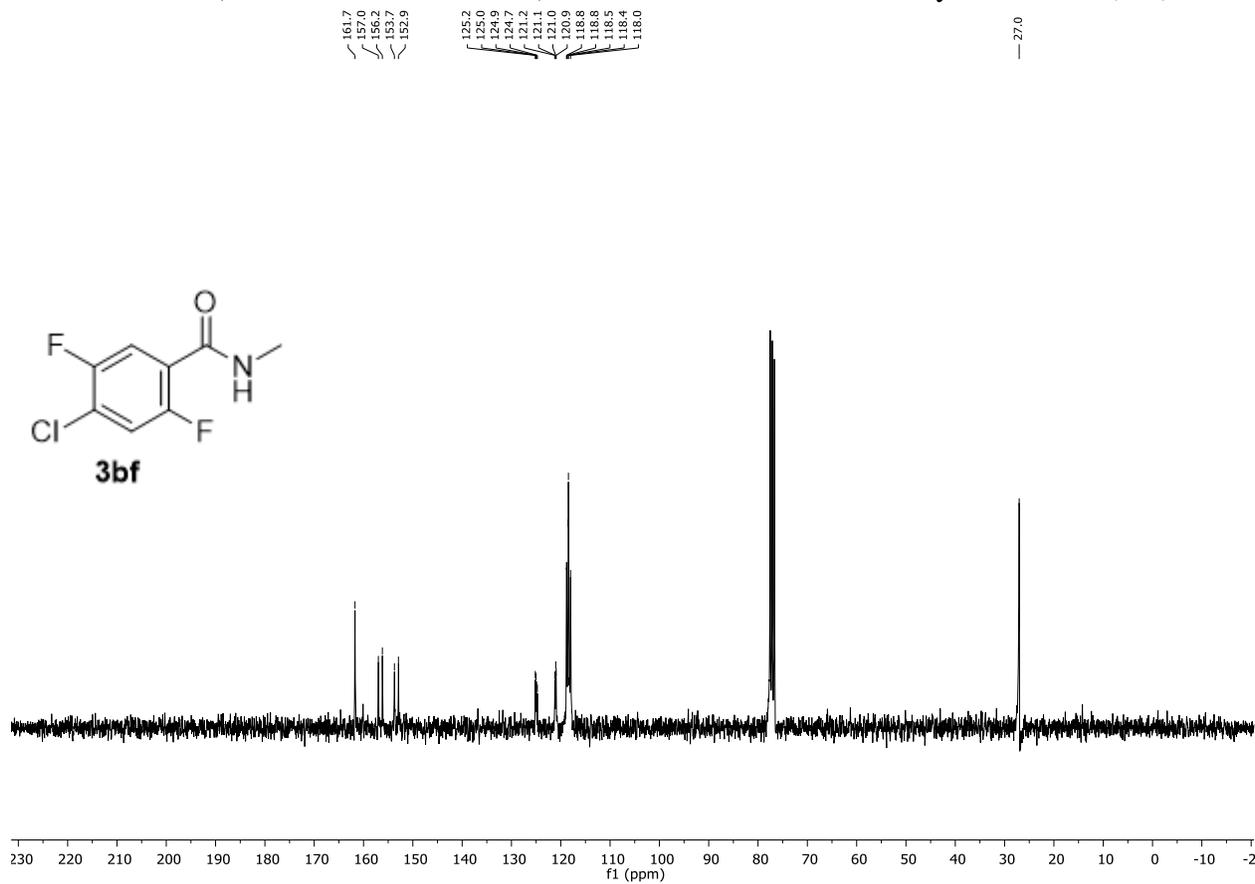


¹³C NMR (75 MHz, Chloroform-*d*) N-methylcyclohexanecarboxamide (**3bb**)

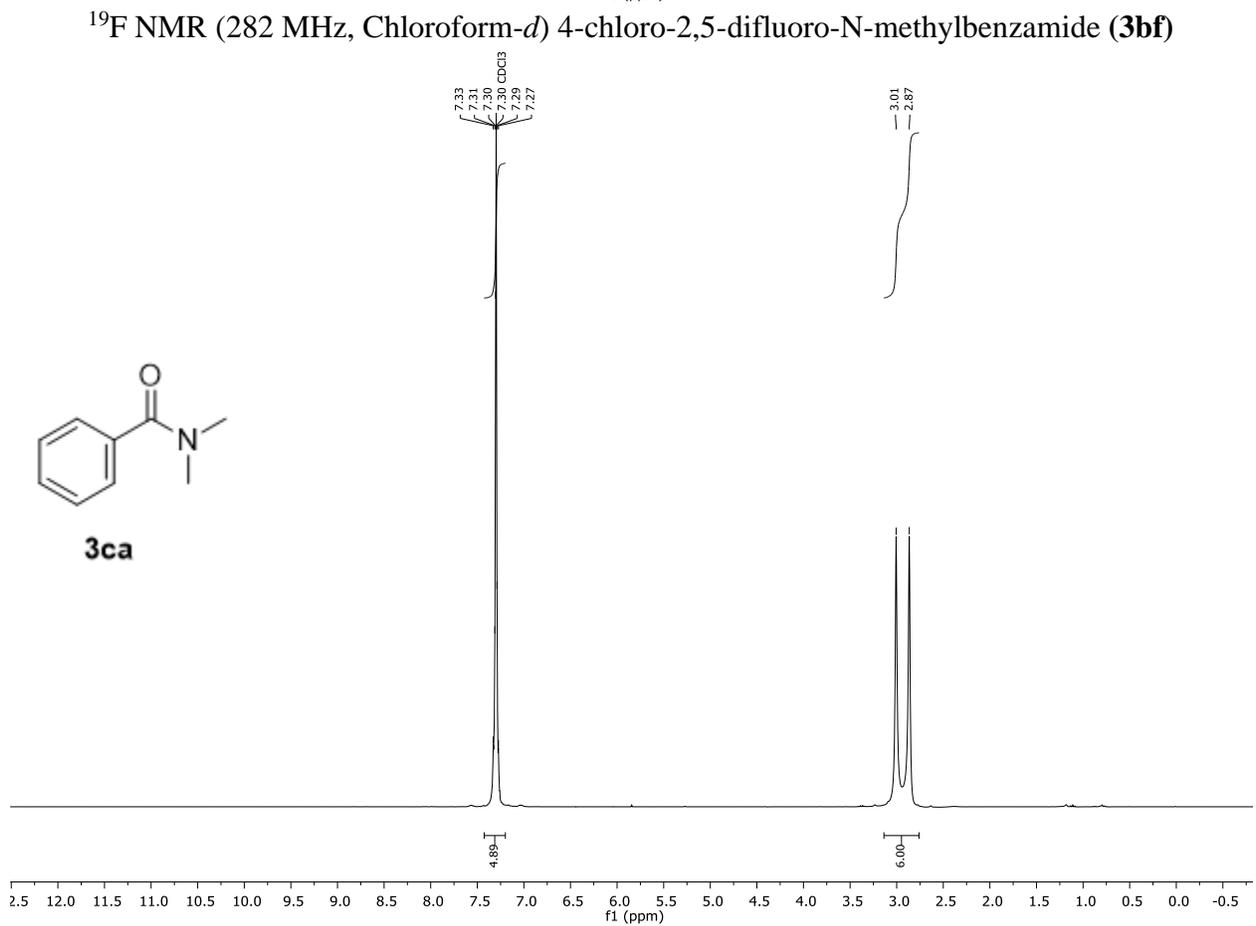
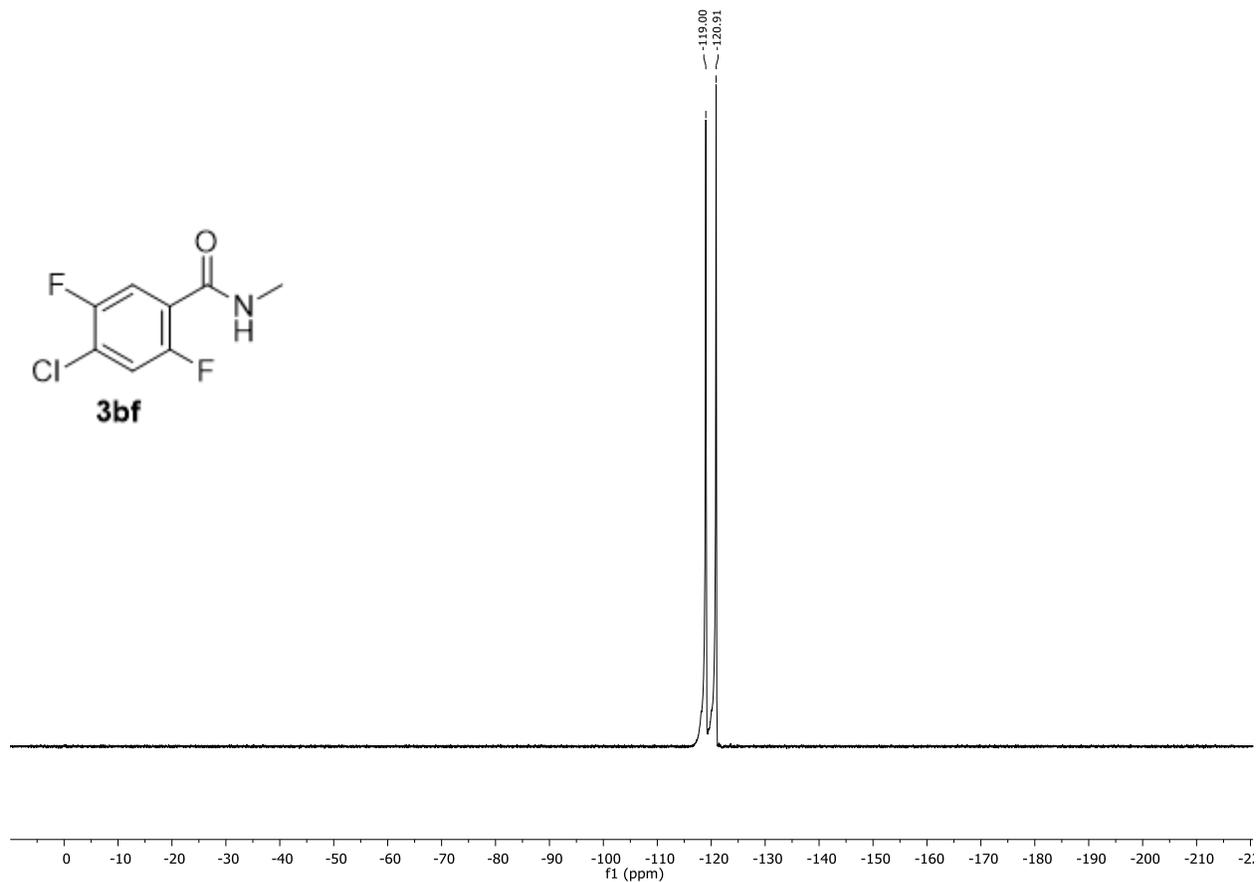


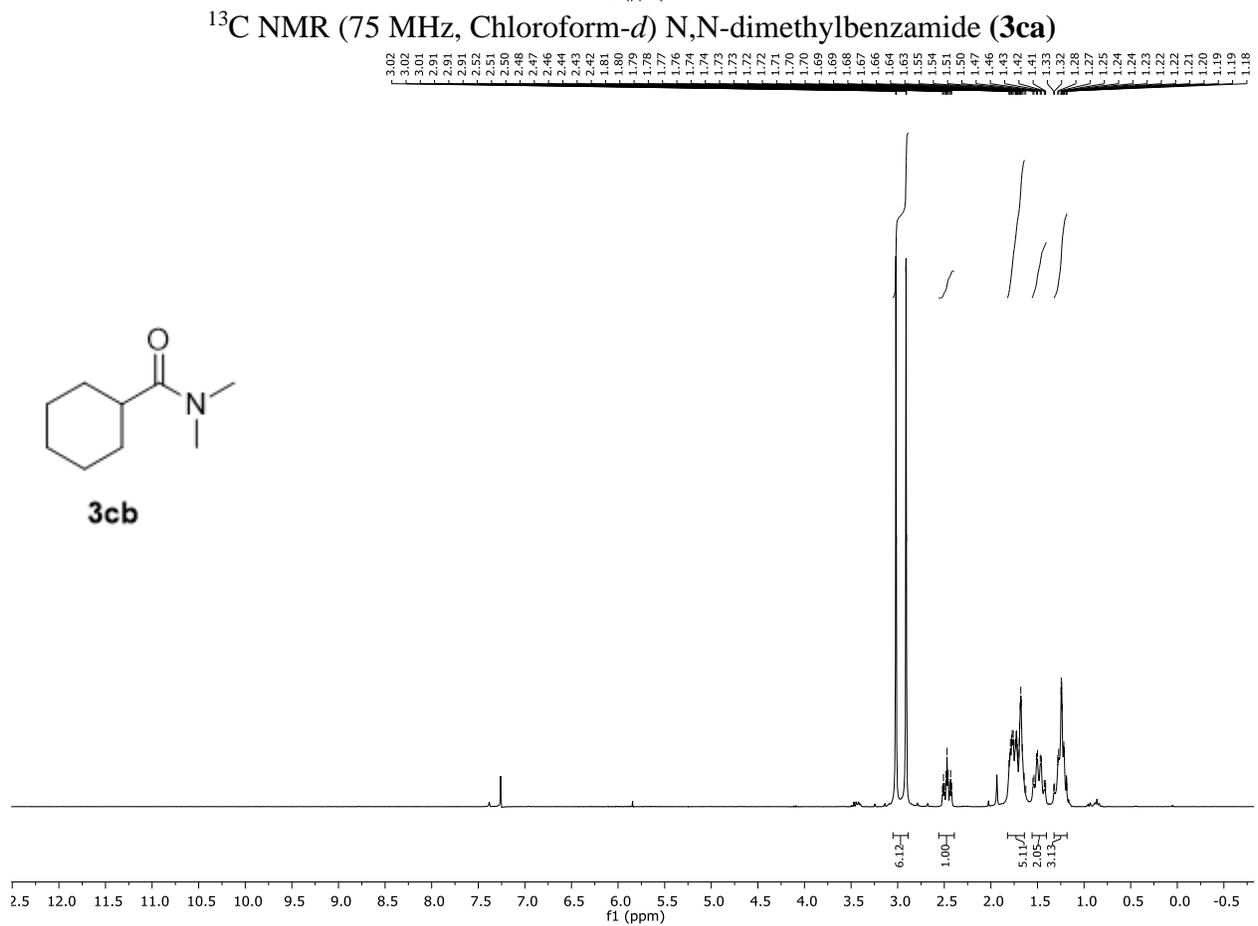
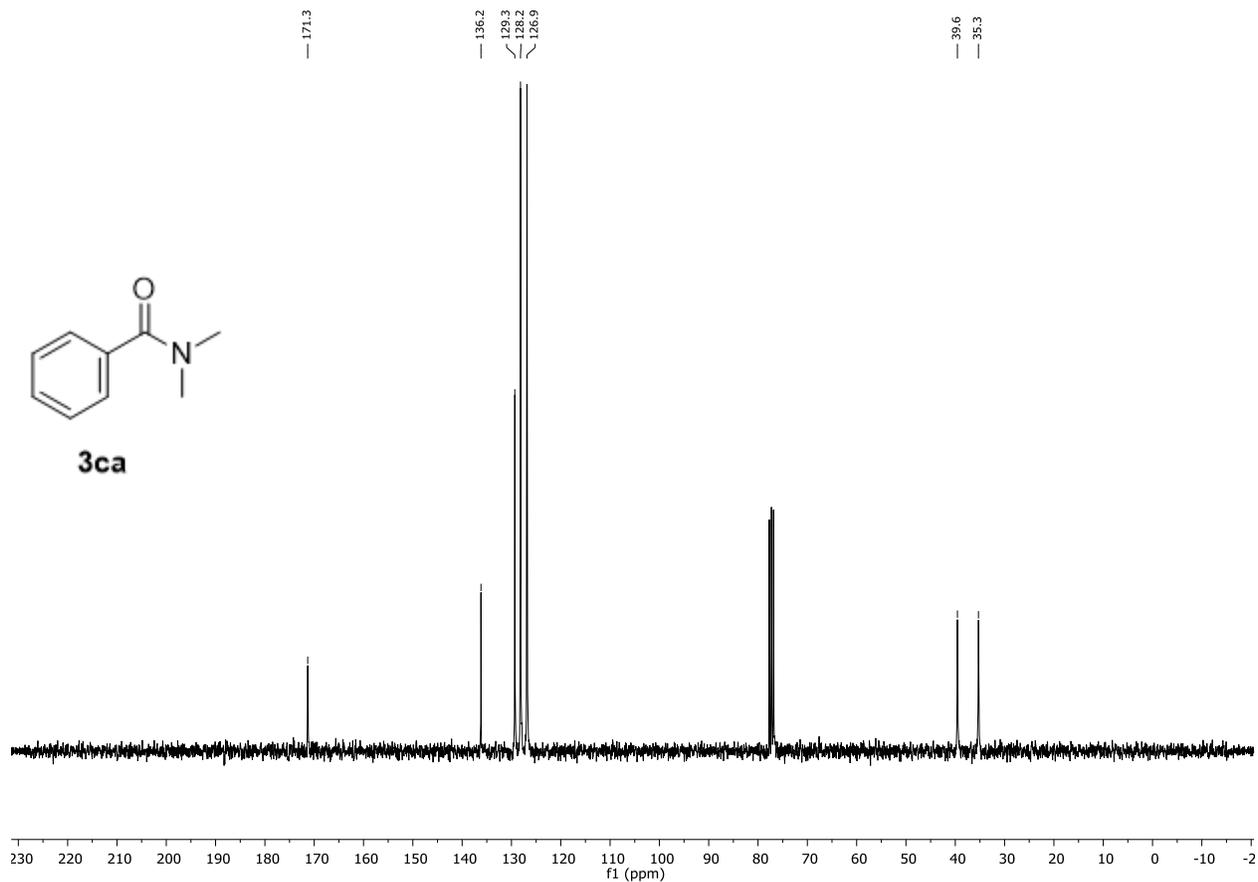


¹H NMR (300 MHz, Chloroform-*d*) 4-chloro-2,5-difluoro-N-methylbenzamide (**3bf**)



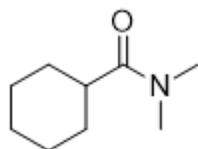
¹³C NMR (75 MHz, Chloroform-*d*) 4-chloro-2,5-difluoro-N-methylbenzamide (**3bf**)



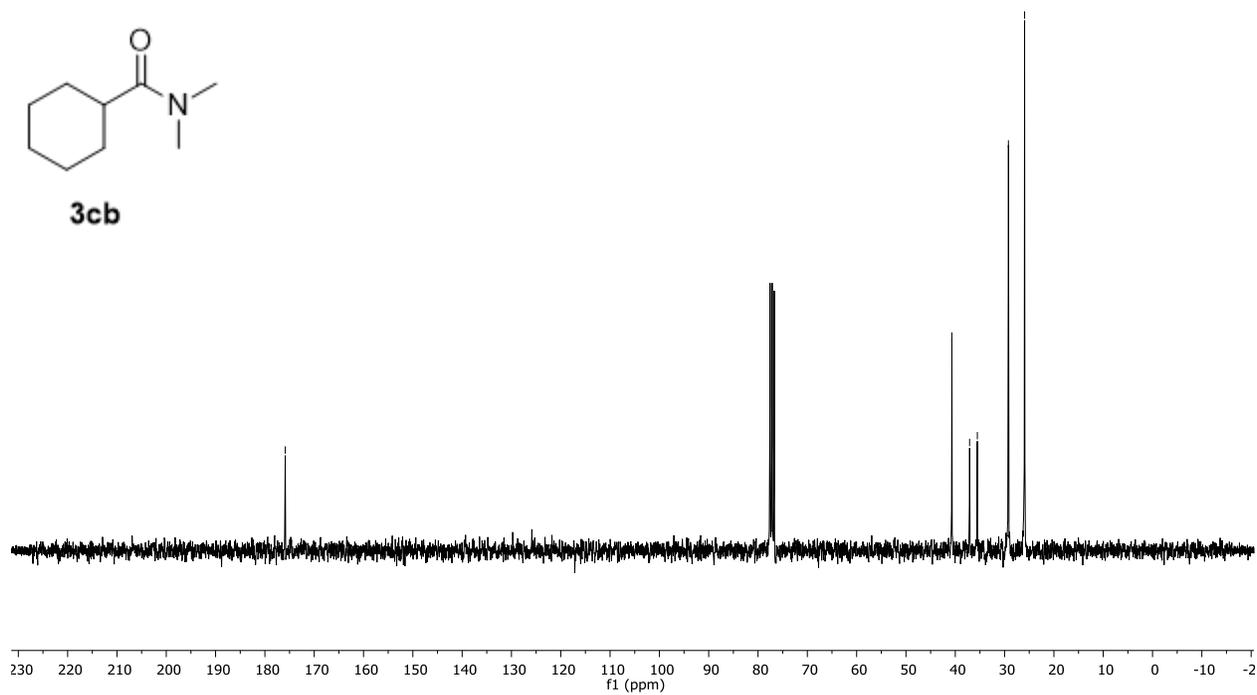


— 175.9

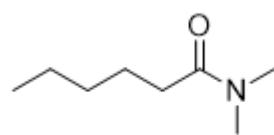
— 40.7
— 37.1
— 35.5
— 29.2
— 25.9



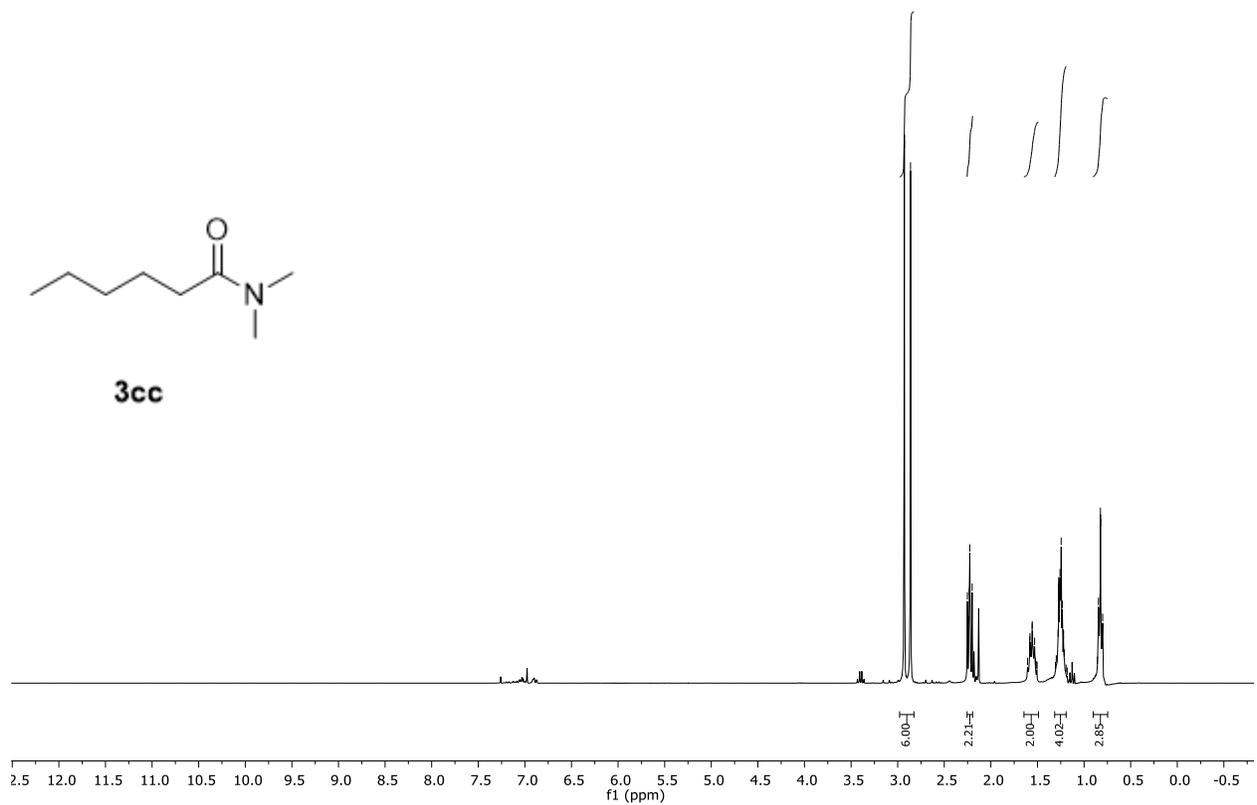
3cb



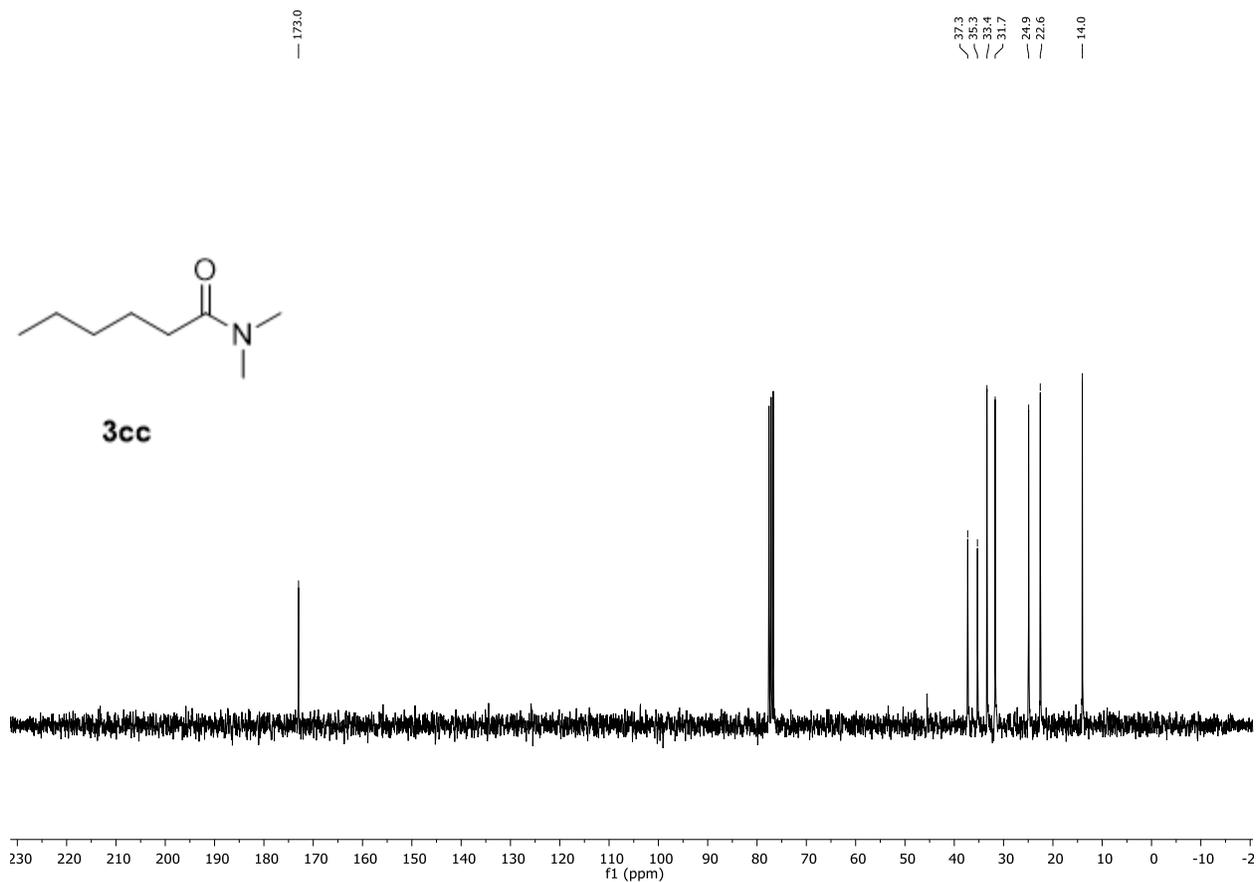
¹³C NMR (75 MHz, Chloroform-*d*) N,N-dimethylcyclohexanecarboxamide (**3cb**)



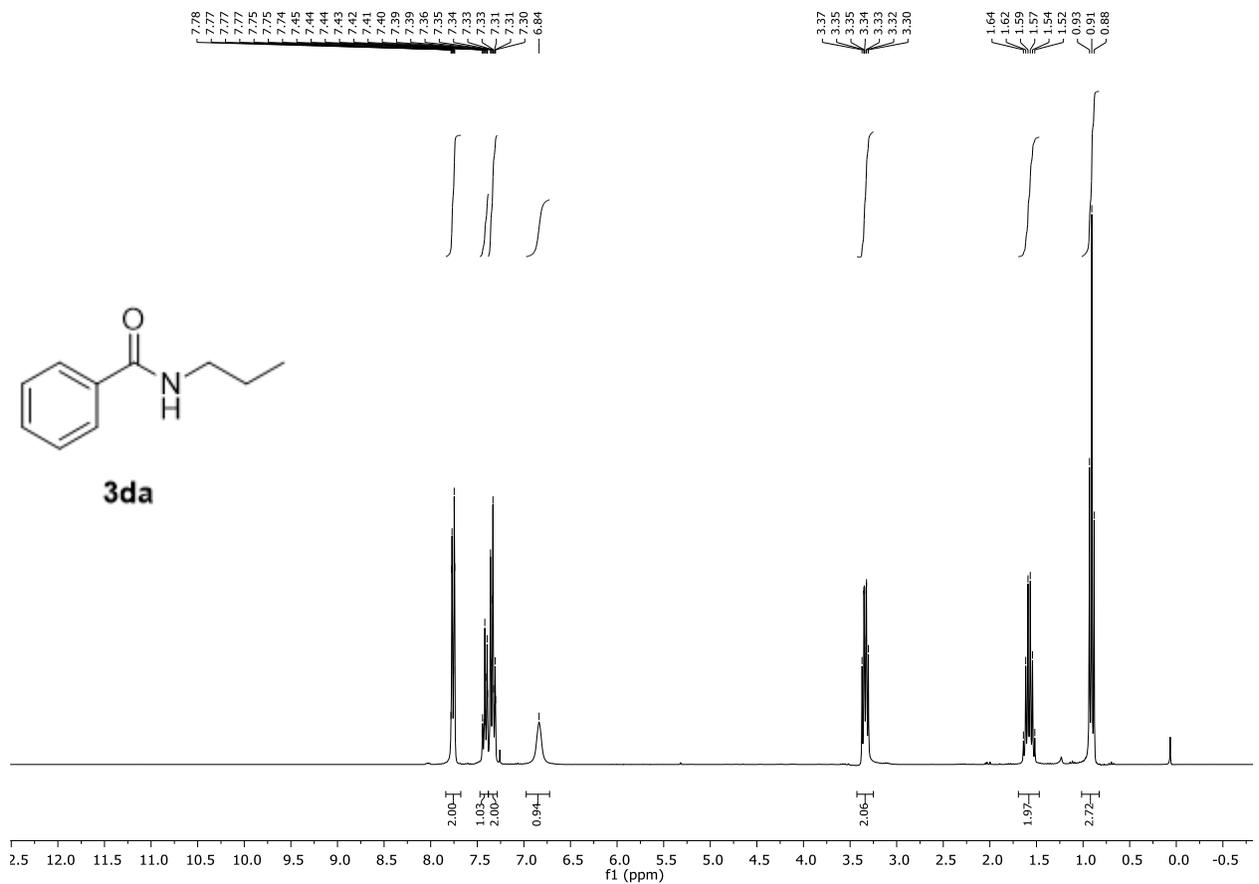
3cc



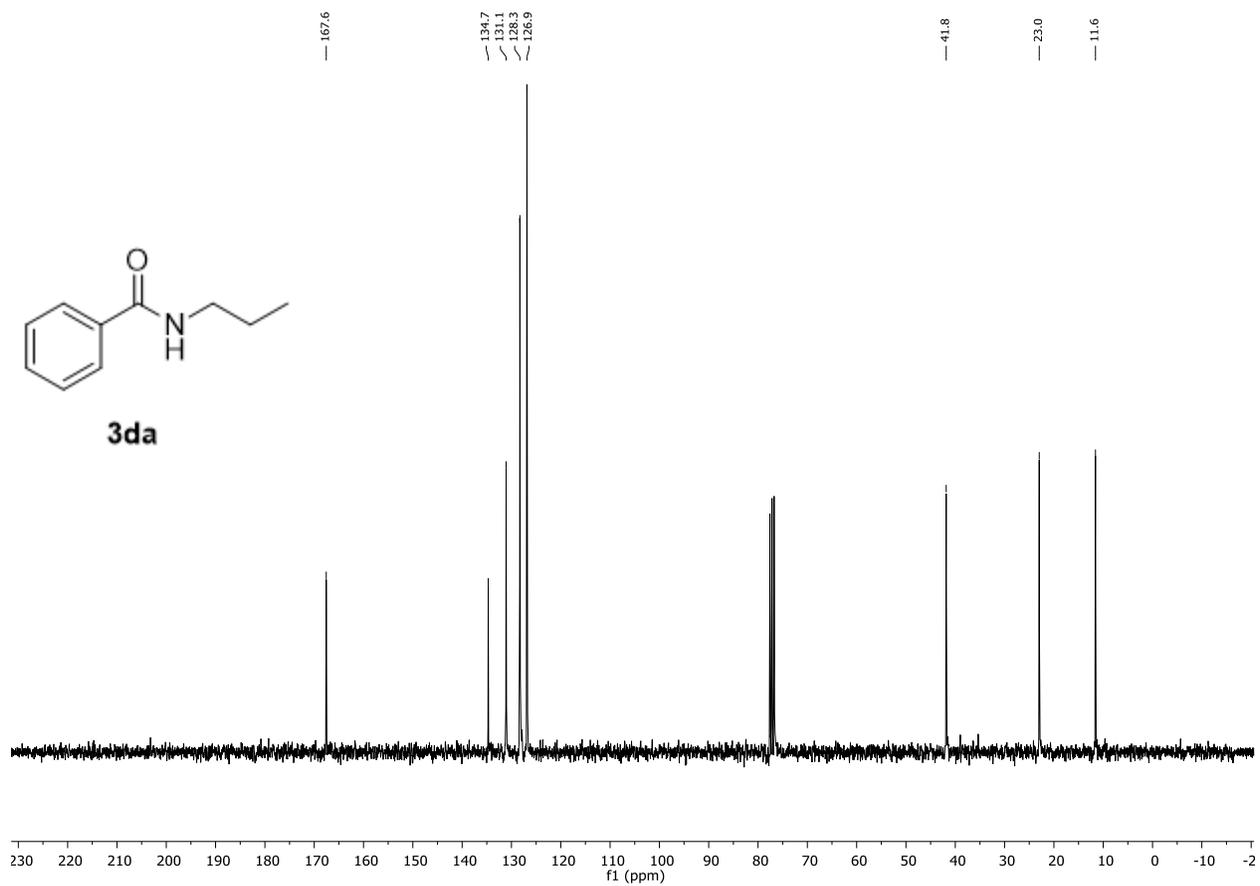
¹H NMR (300 MHz, Chloroform-*d*) N,N-dimethylhexanamide (**3cc**)



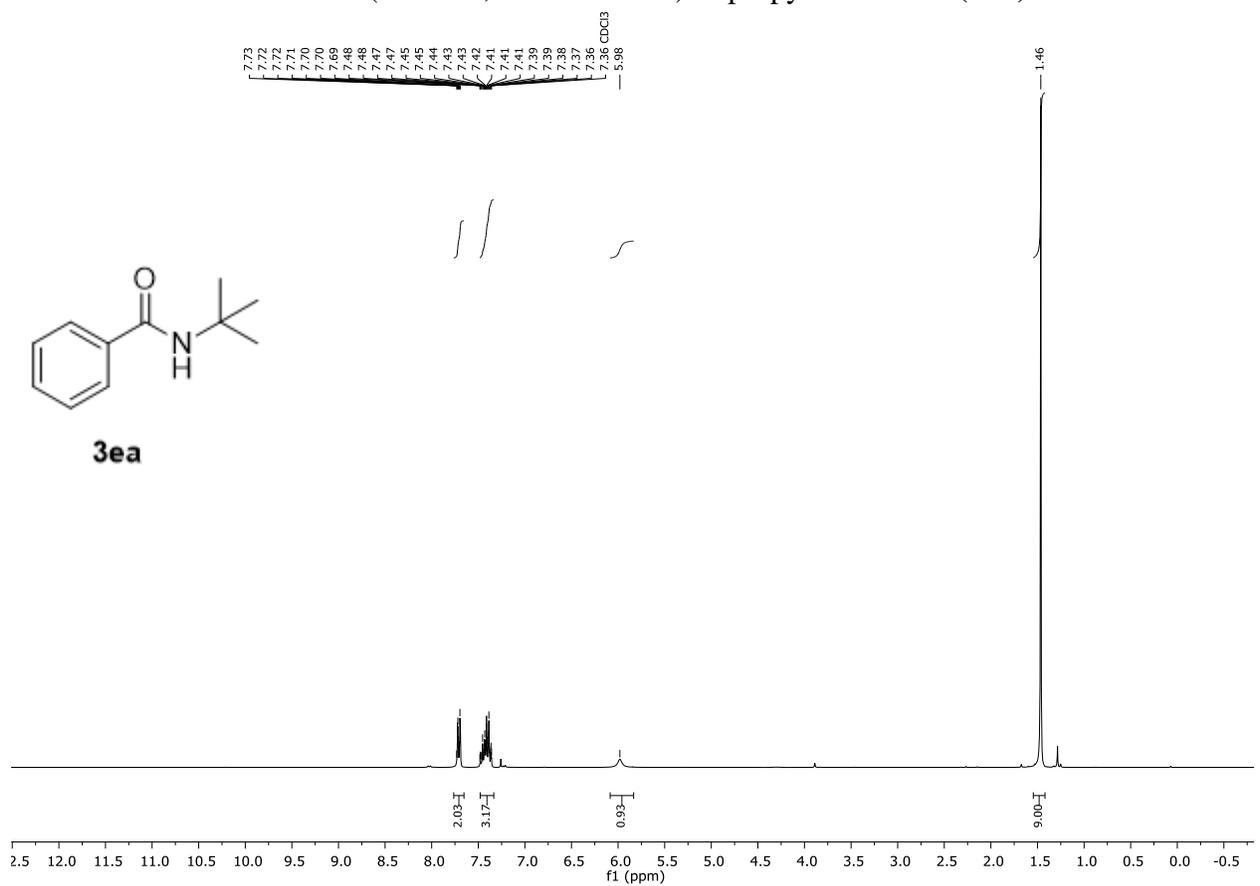
¹³C NMR (75 MHz, Chloroform-*d*) N,N-dimethylhexanamide (**3cc**)



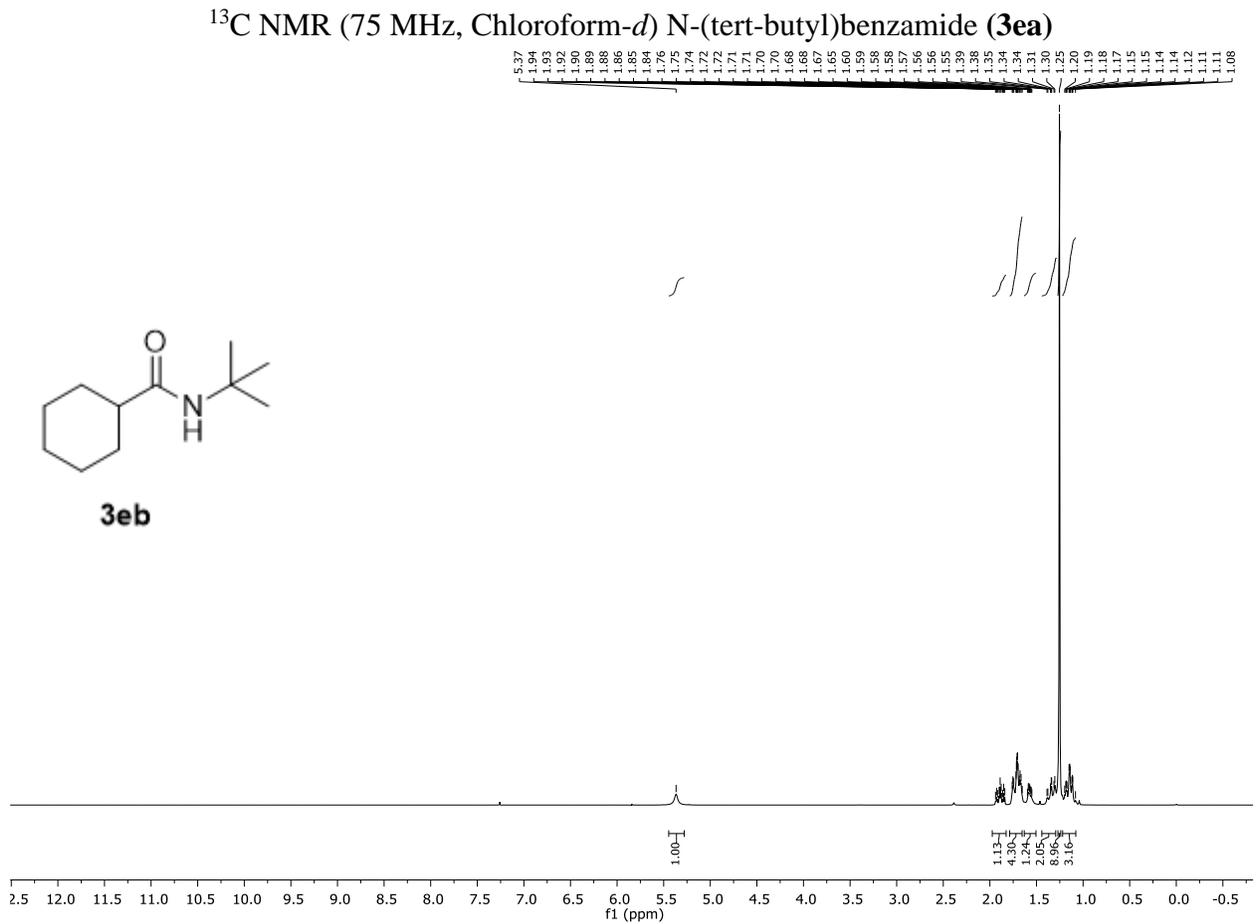
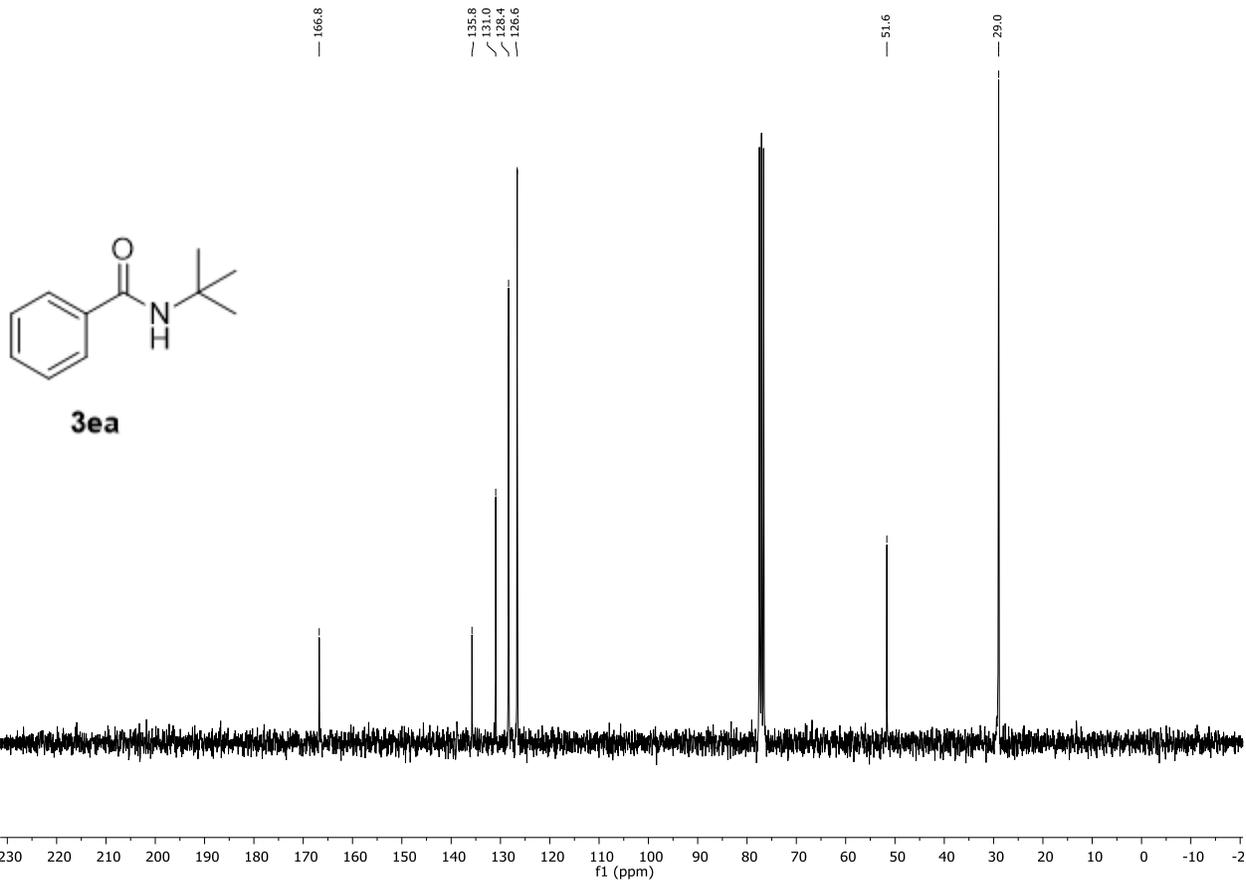
¹H NMR (300 MHz, Chloroform-*d*) N-propylbenzamide (**3da**)

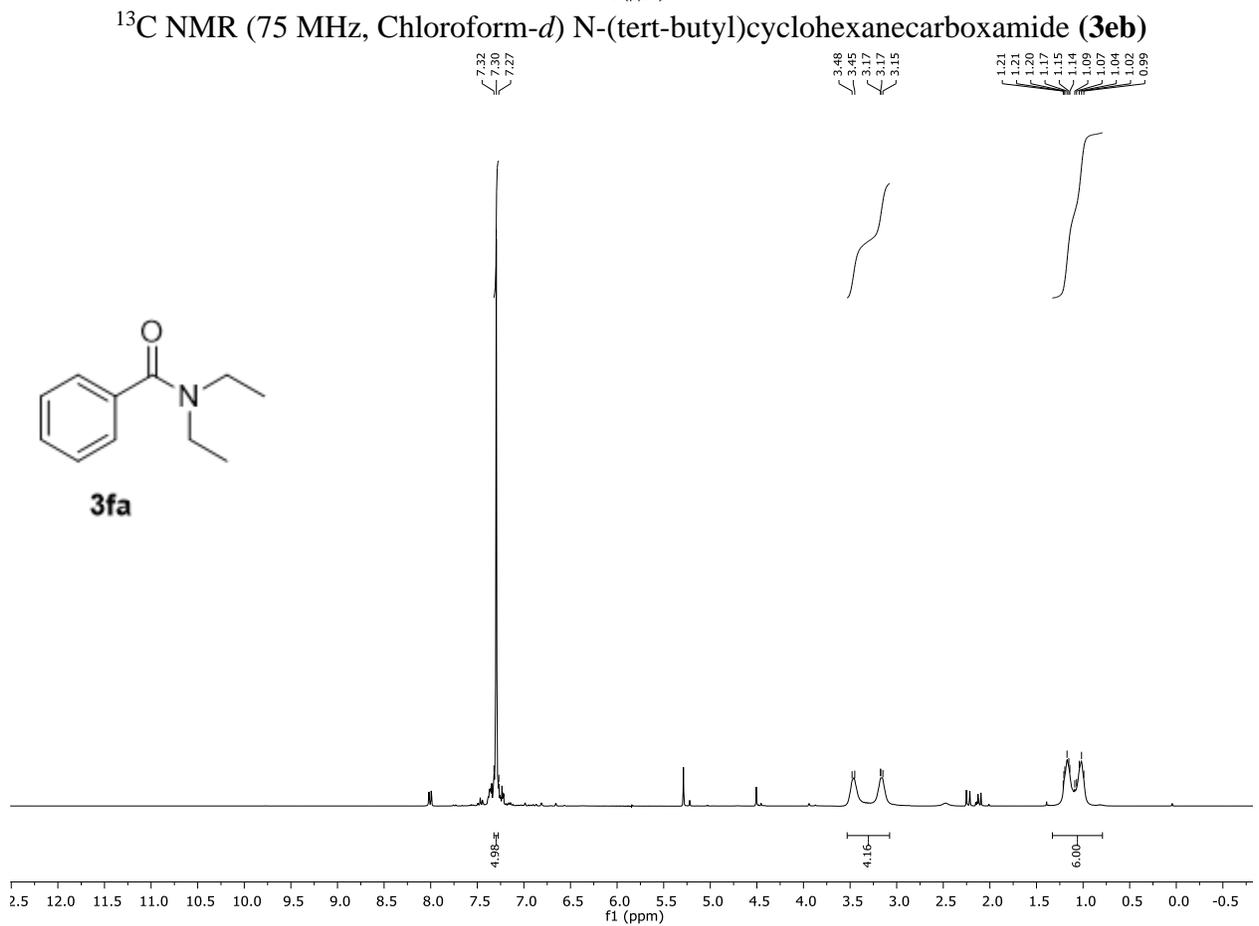
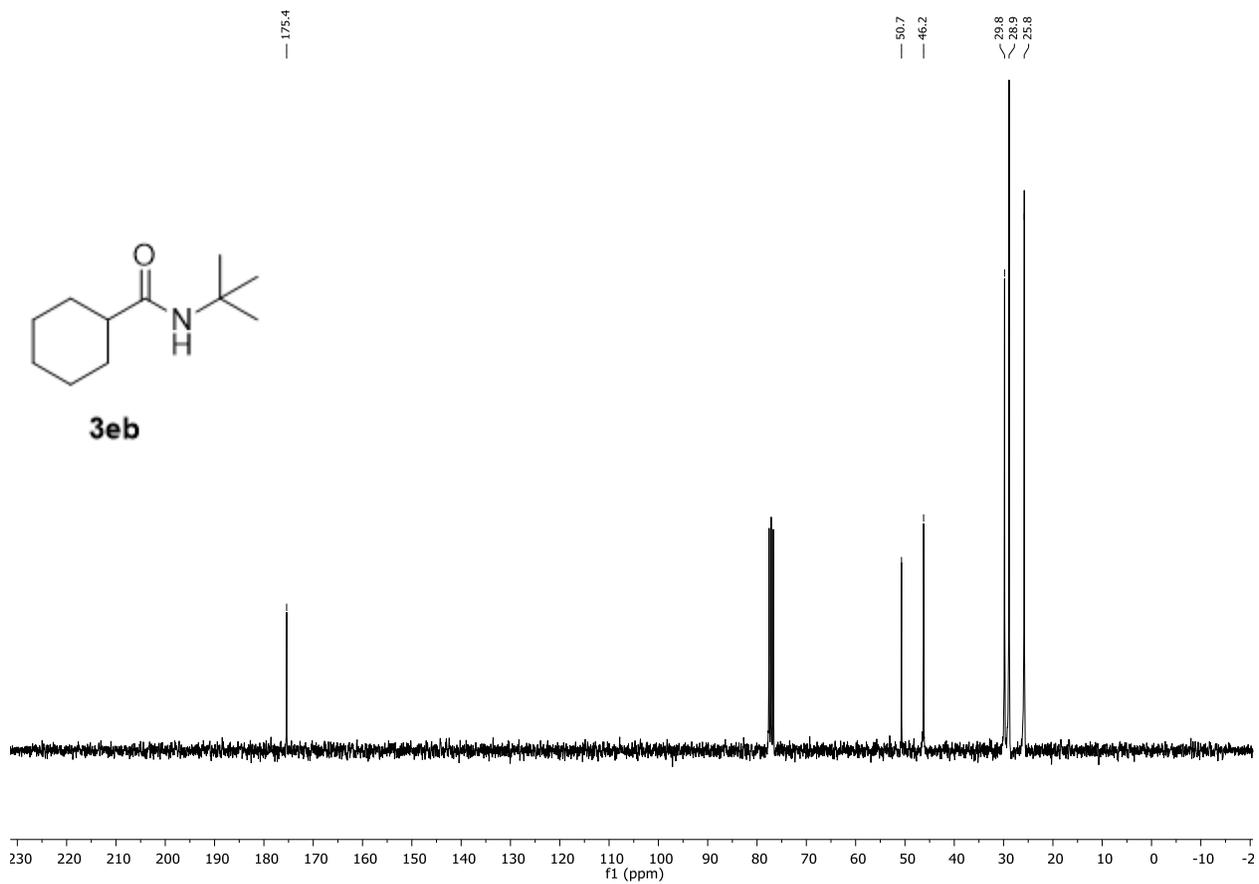


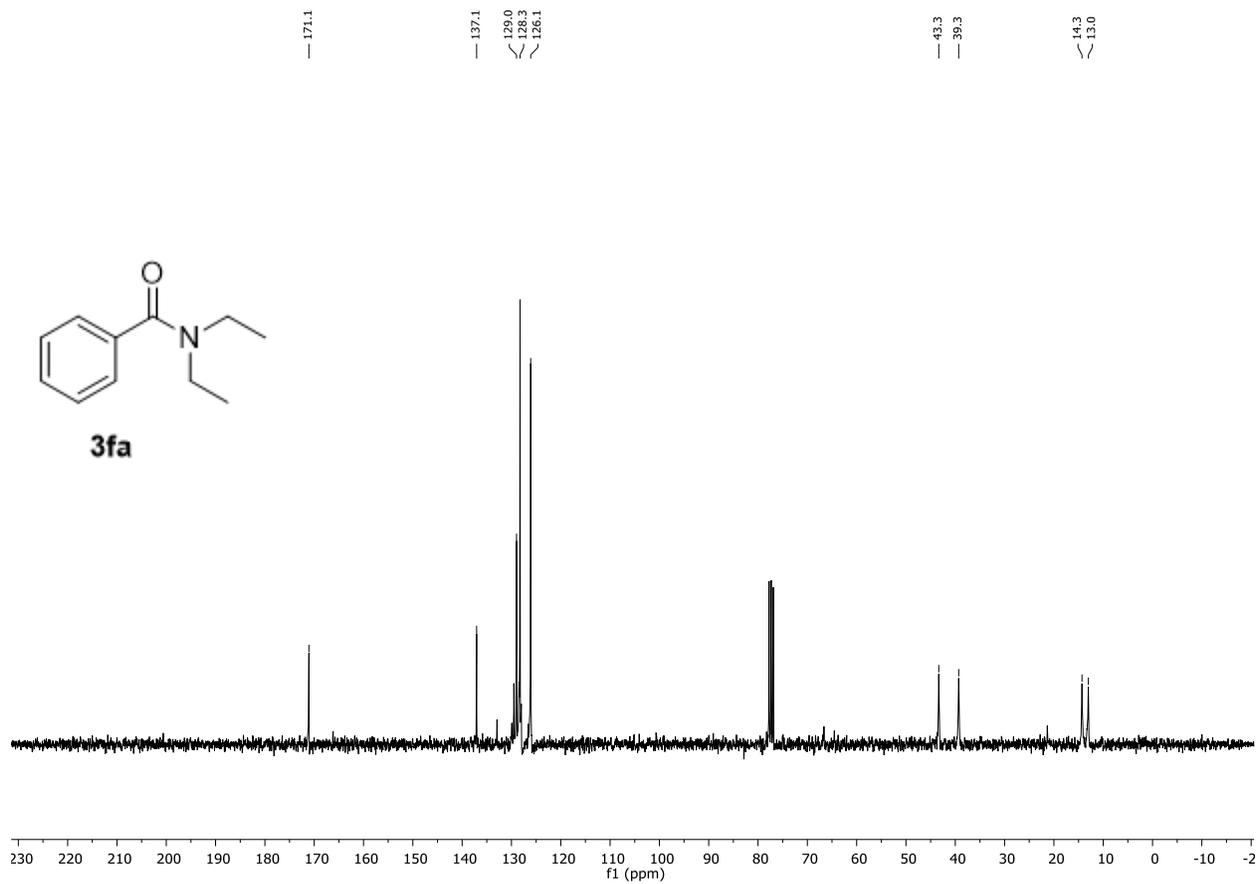
^{13}C NMR (75 MHz, Chloroform-*d*) N-propylbenzamide (**3da**)



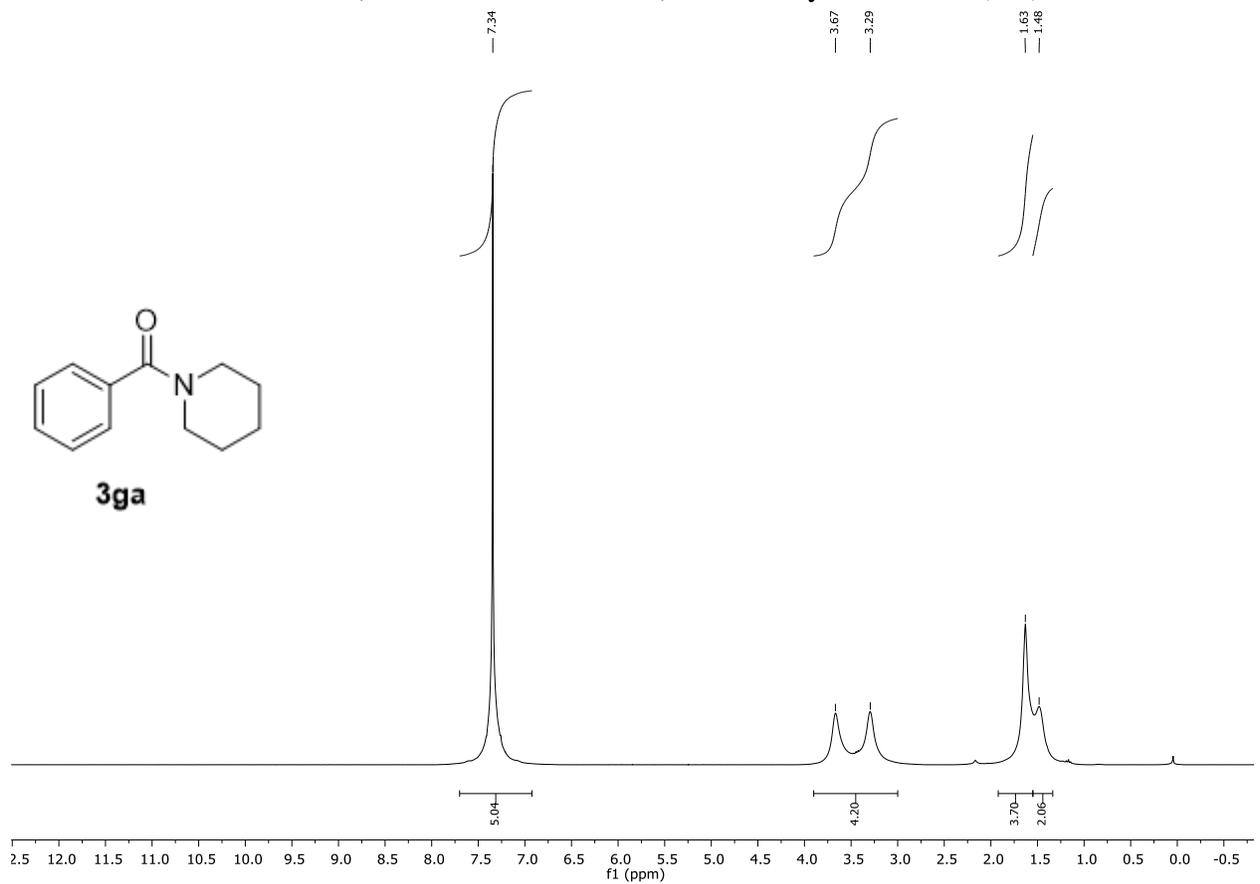
^1H NMR (300 MHz, Chloroform-*d*) N-(tert-butyl)benzamide (**3ea**)



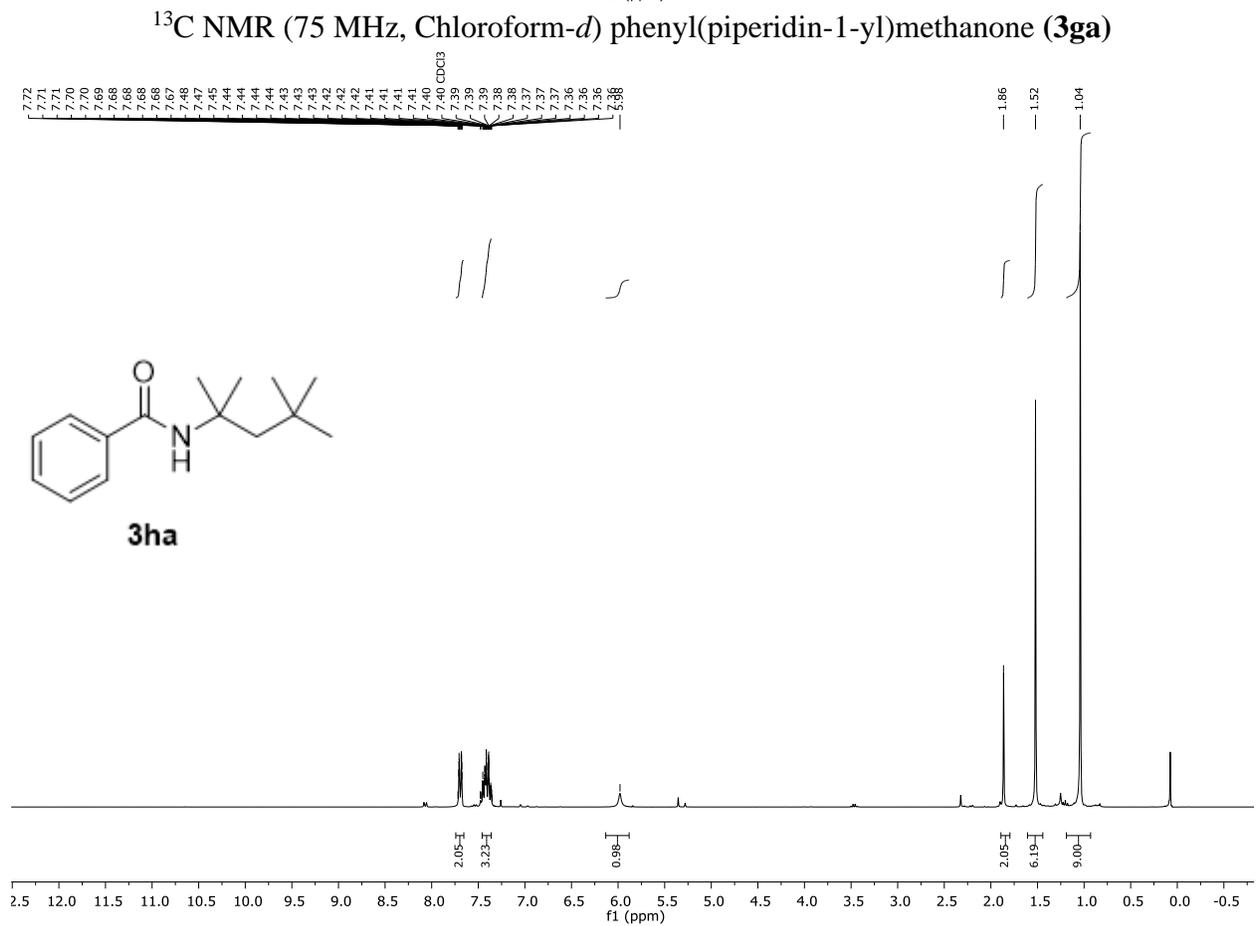
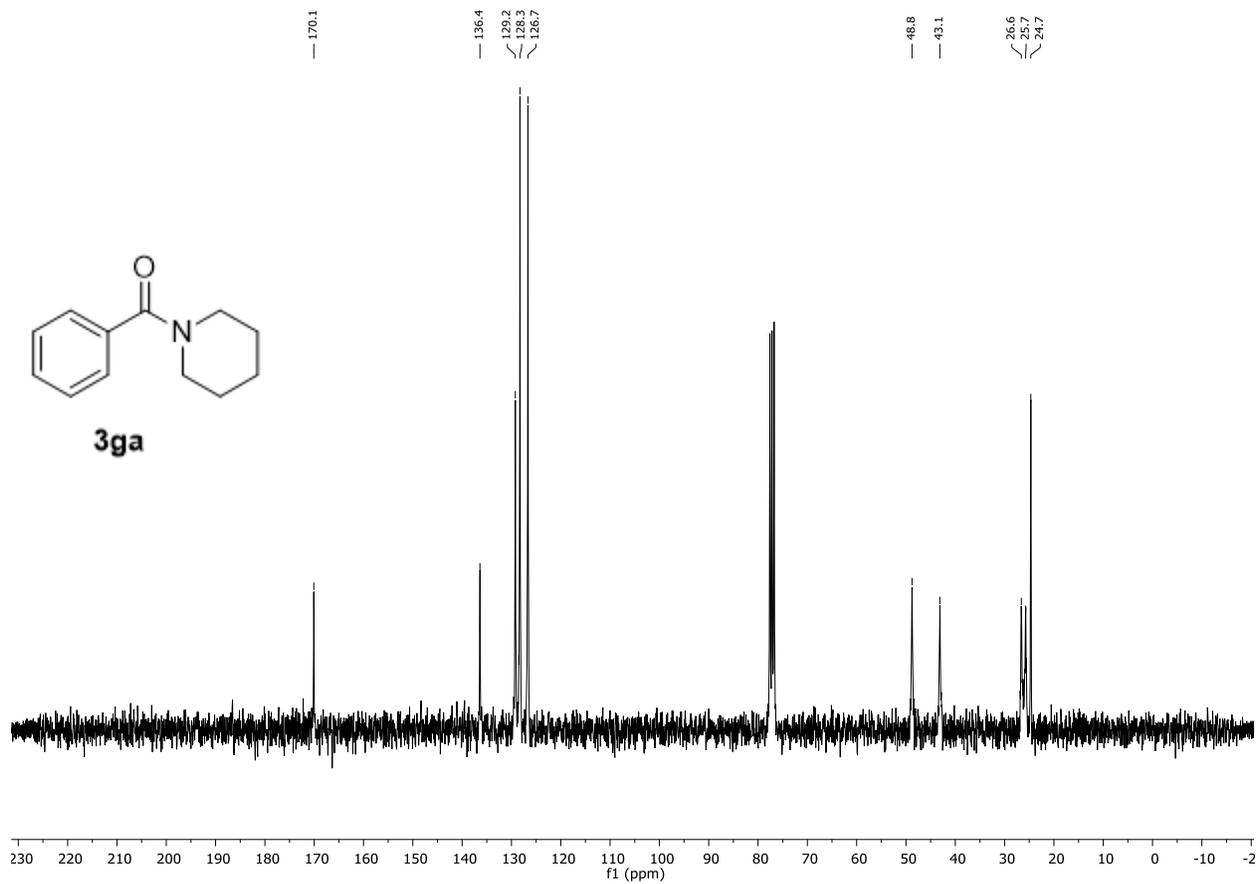


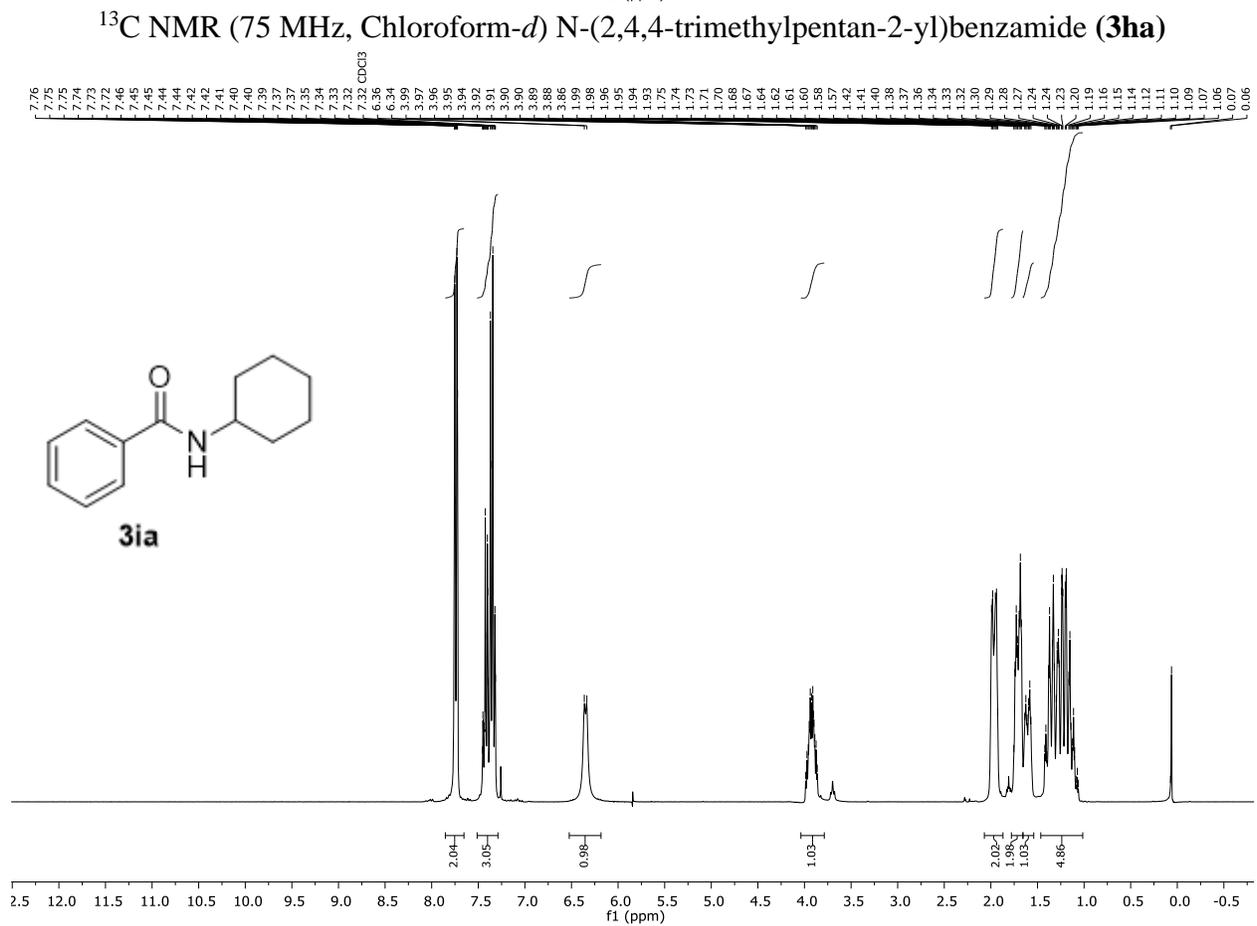
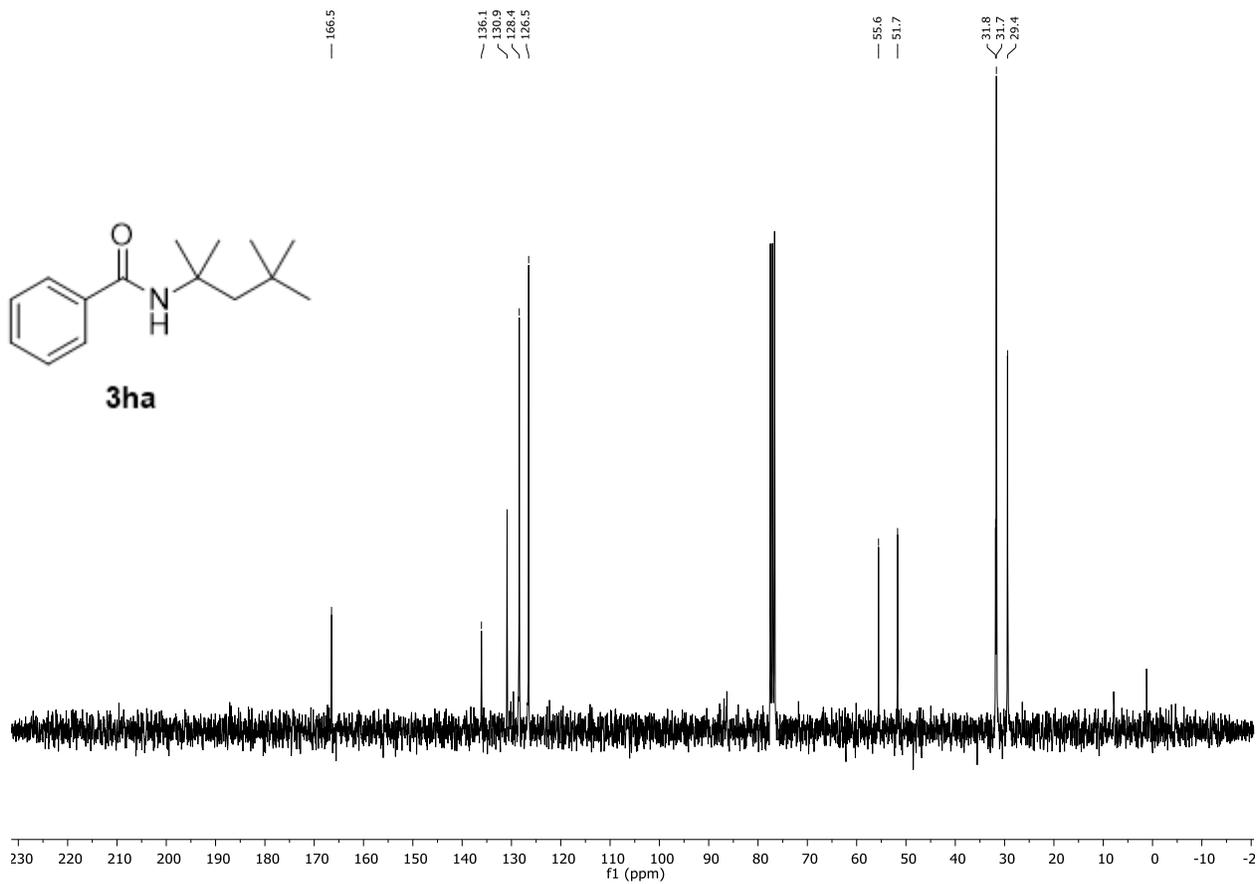


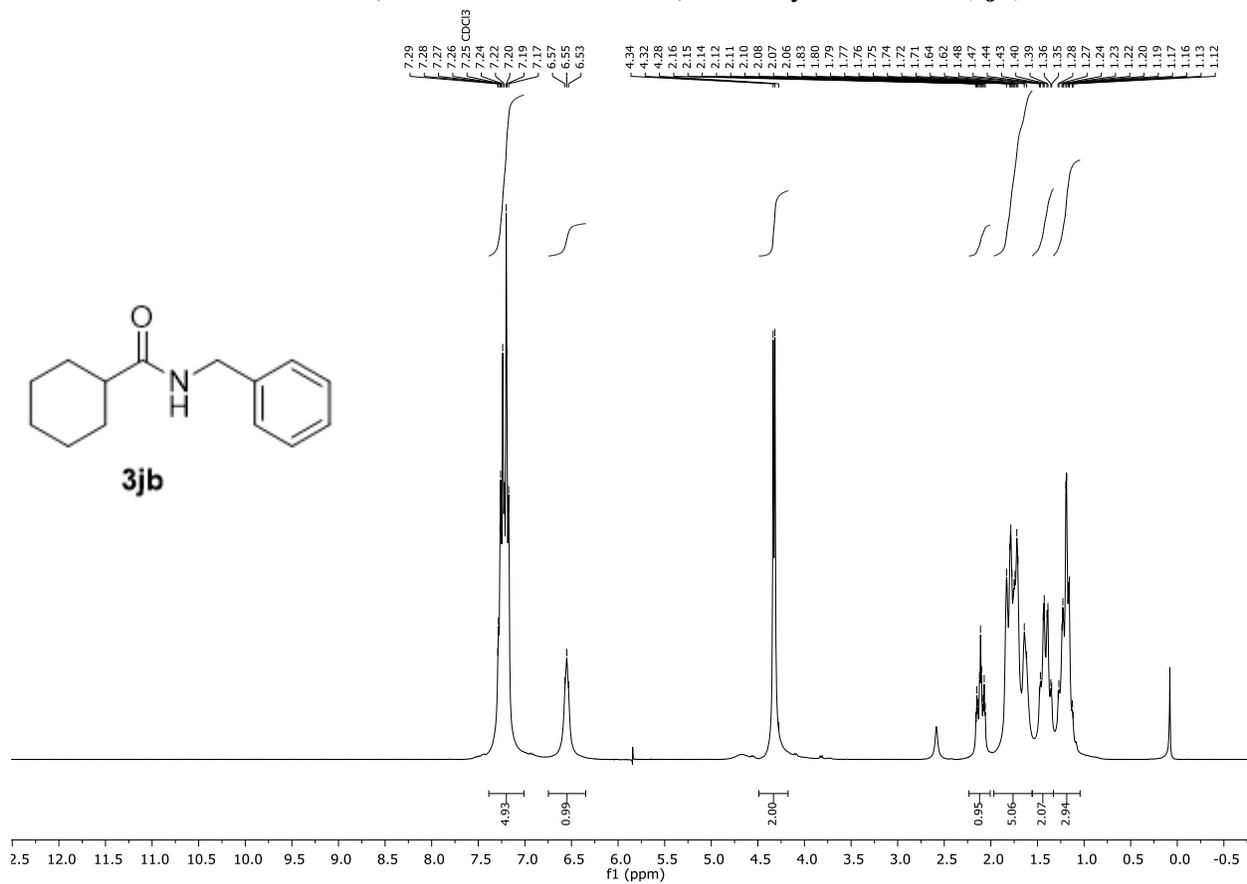
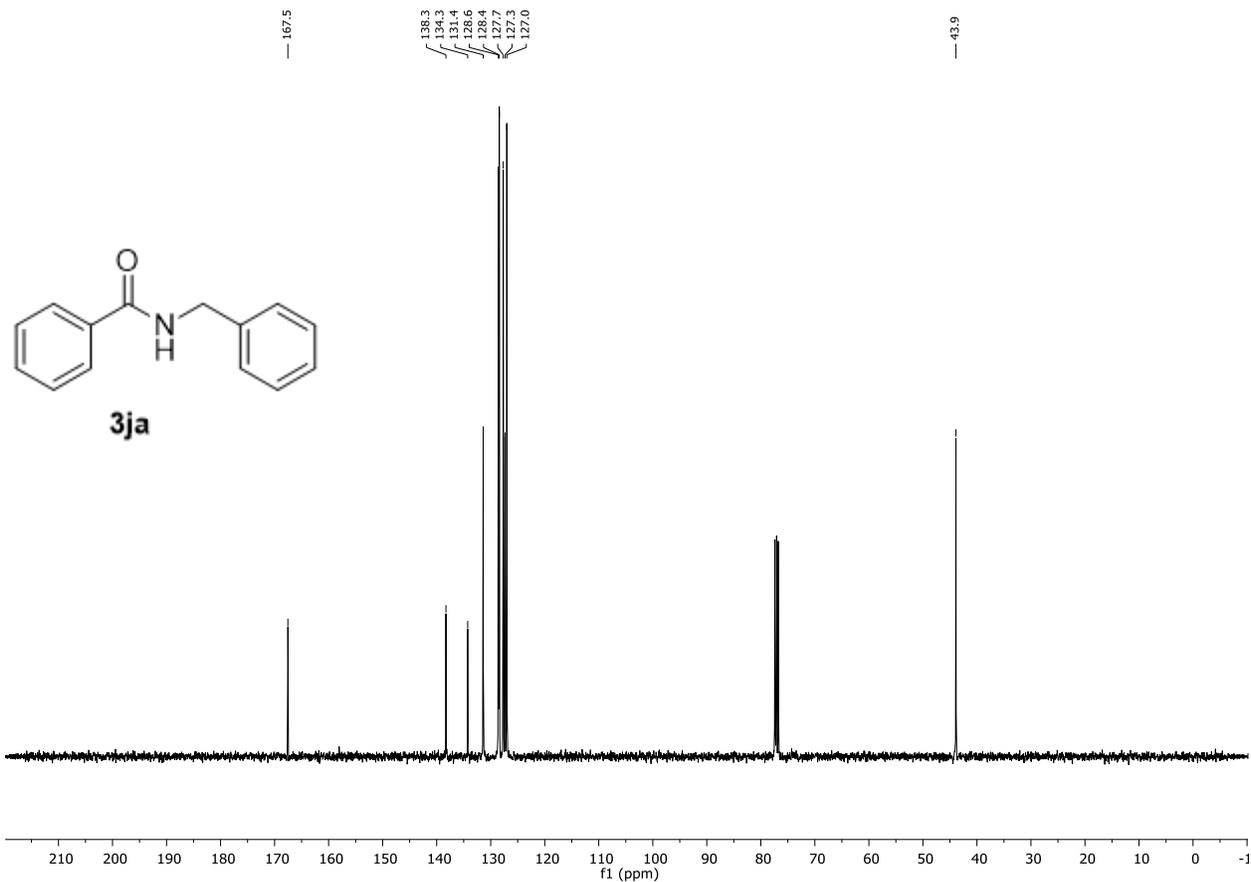
^{13}C NMR (75 MHz, Chloroform-*d*) N,N-diethylbenzamide (**3fa**)

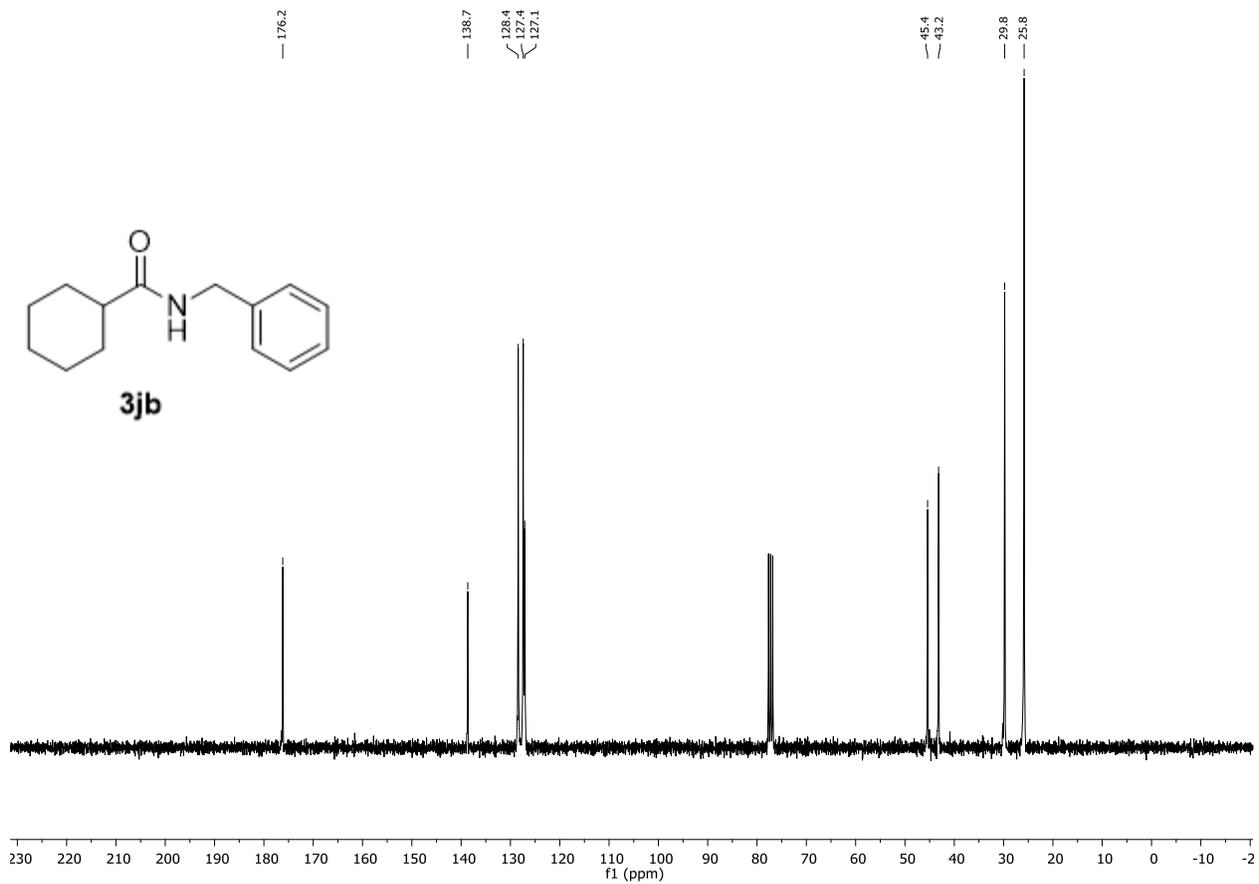


^1H NMR (300 MHz, Chloroform-*d*) phenyl(piperidin-1-yl)methanone (**3ga**)

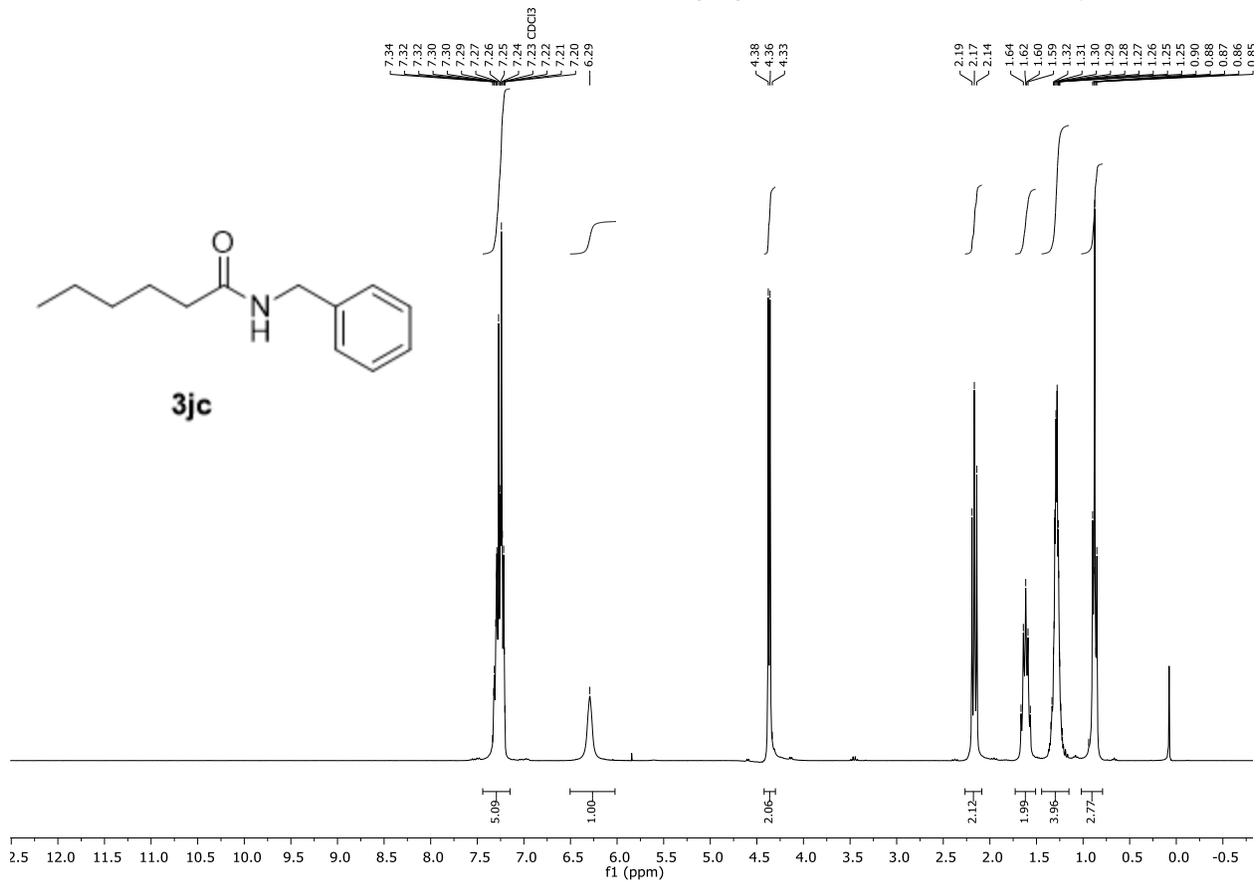




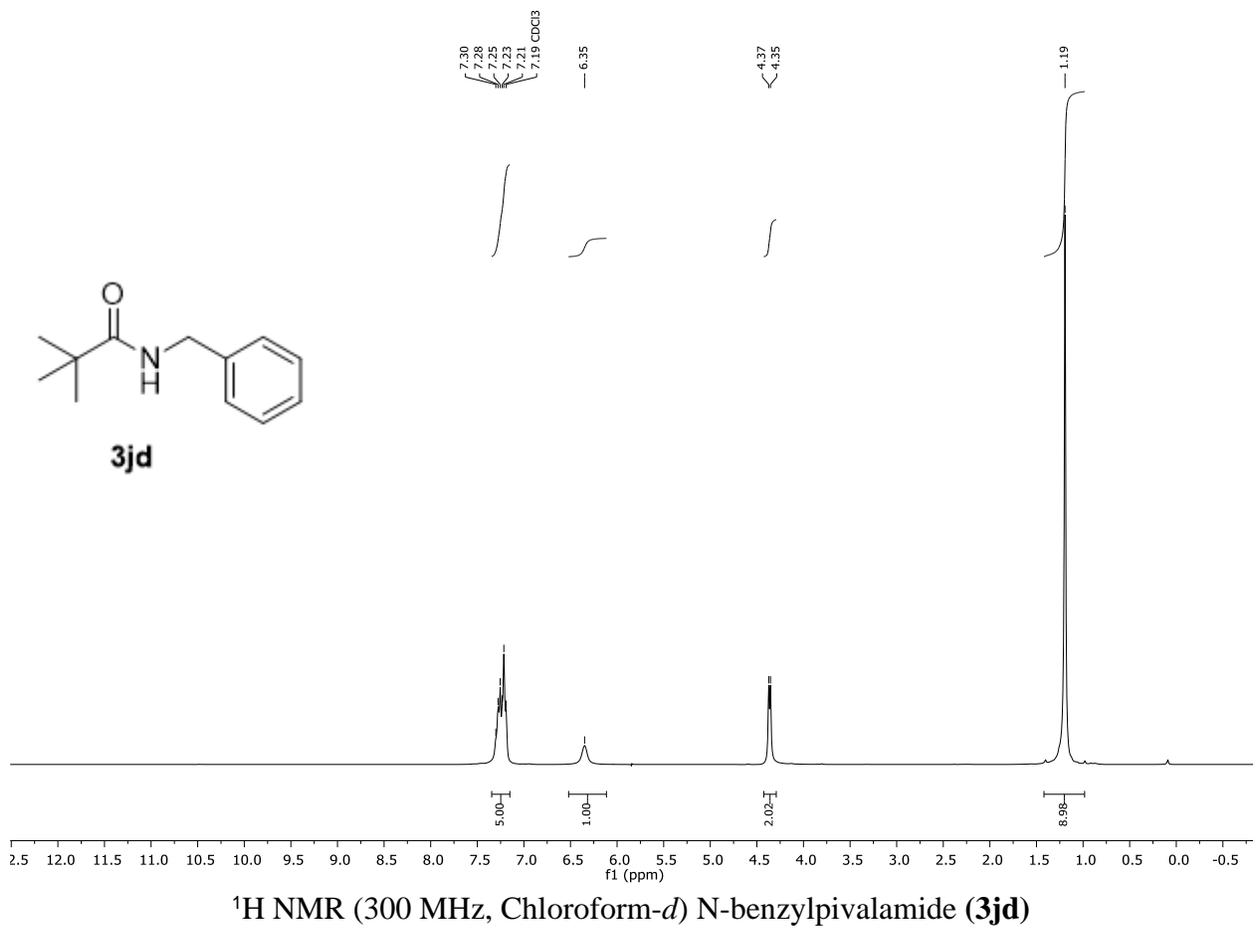
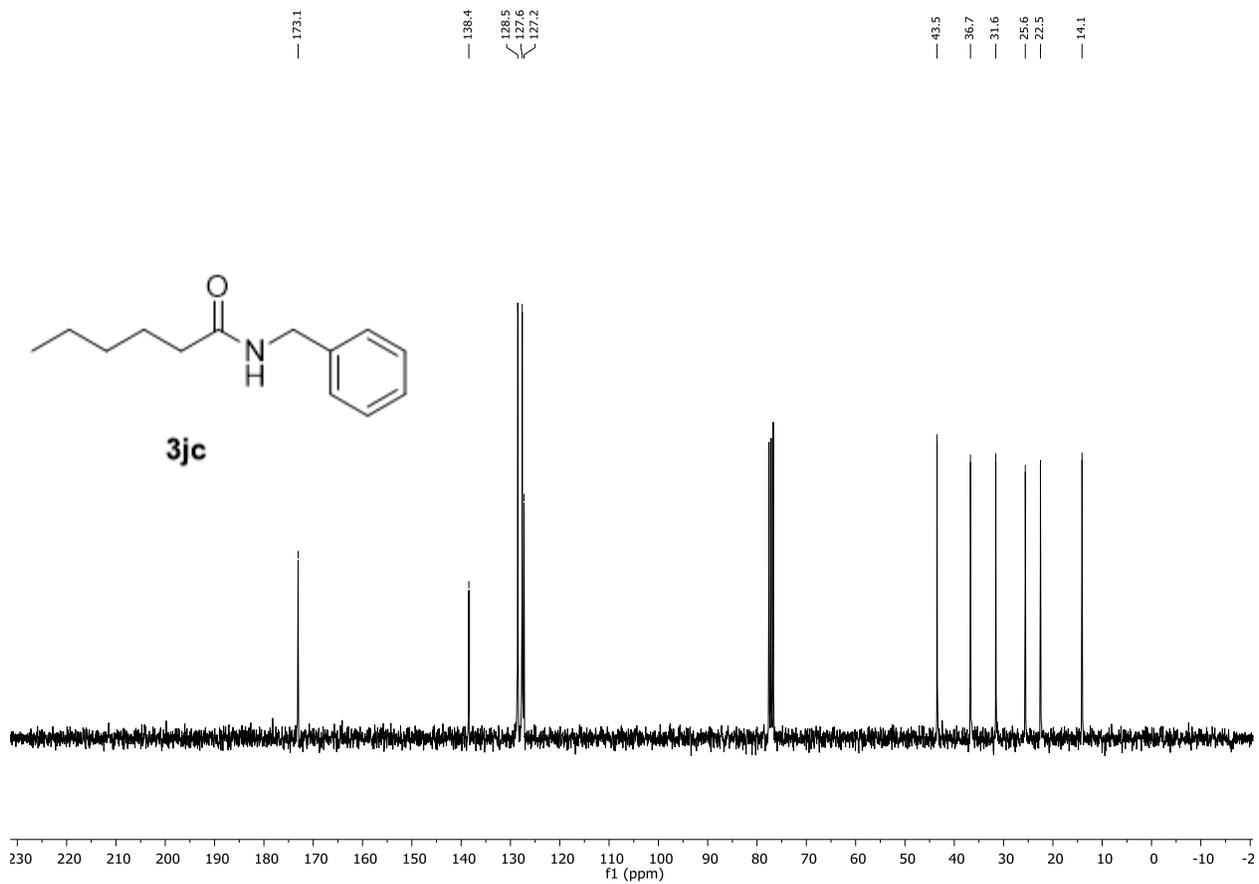


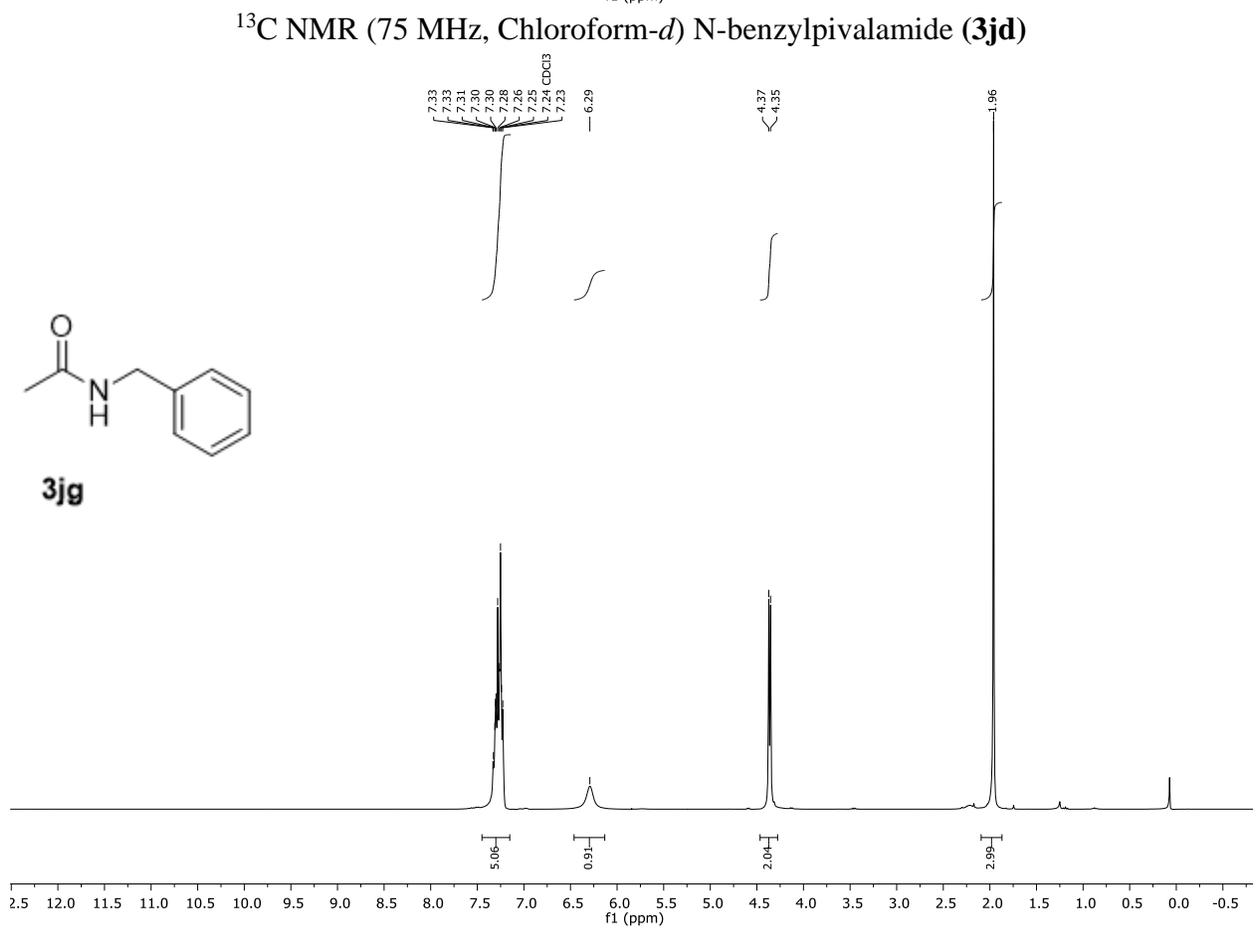
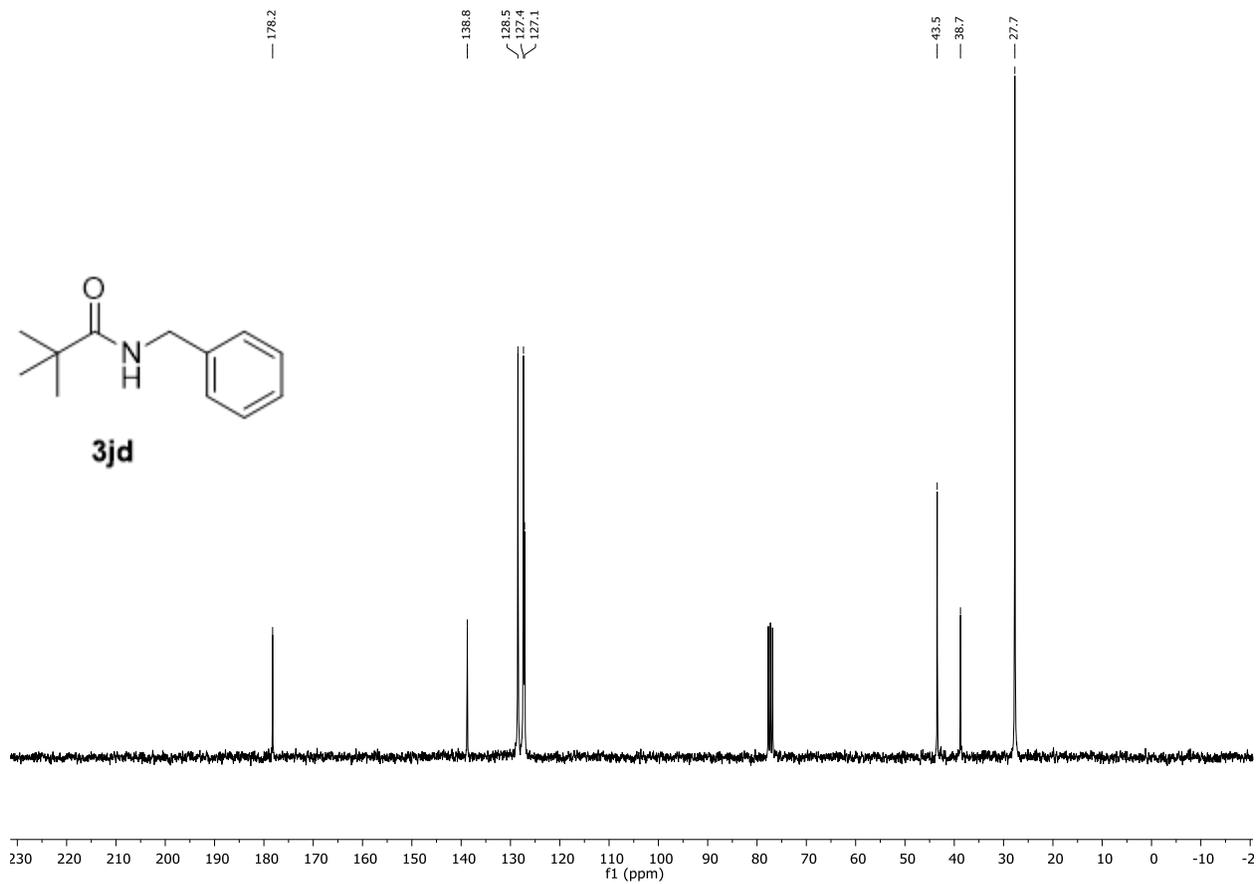


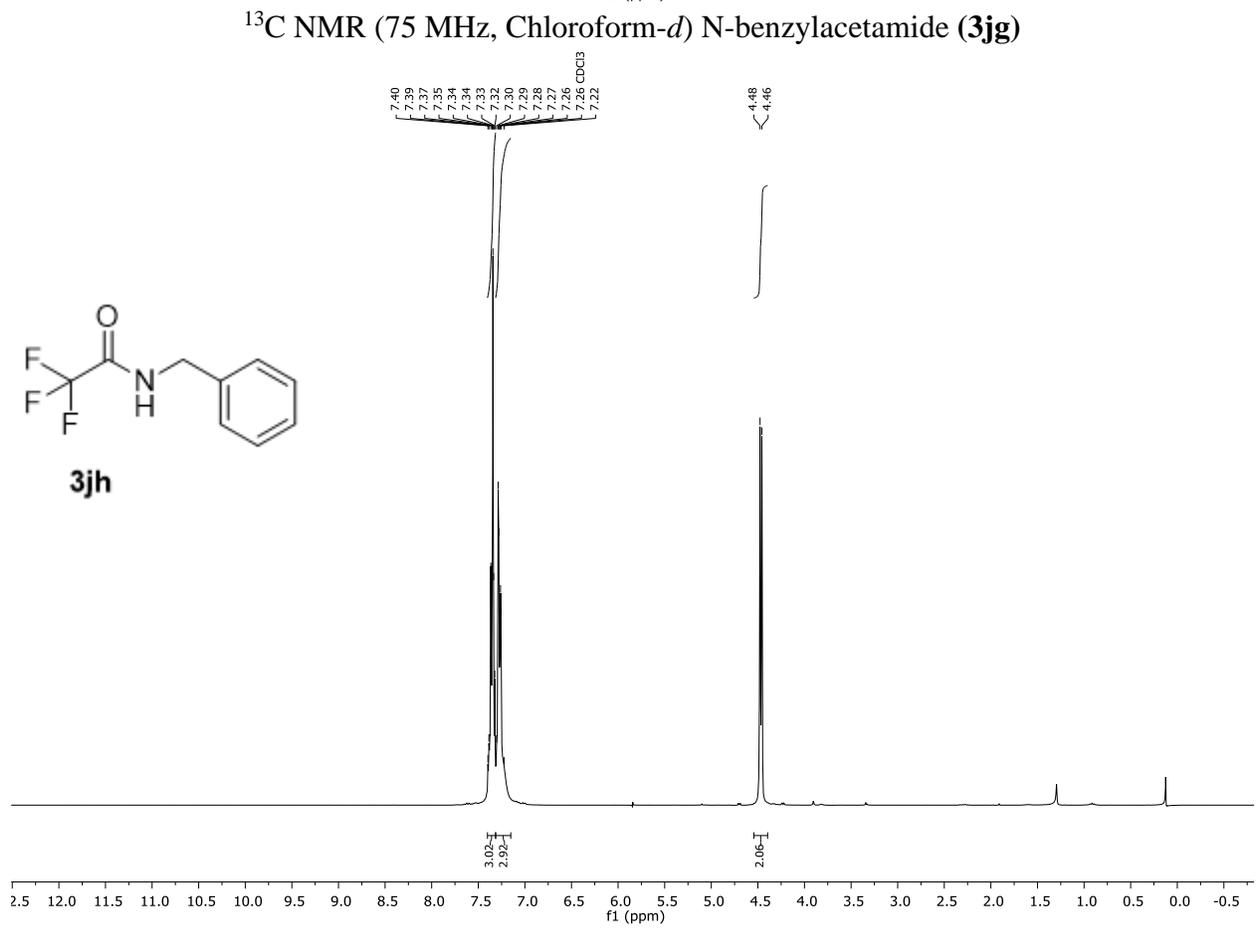
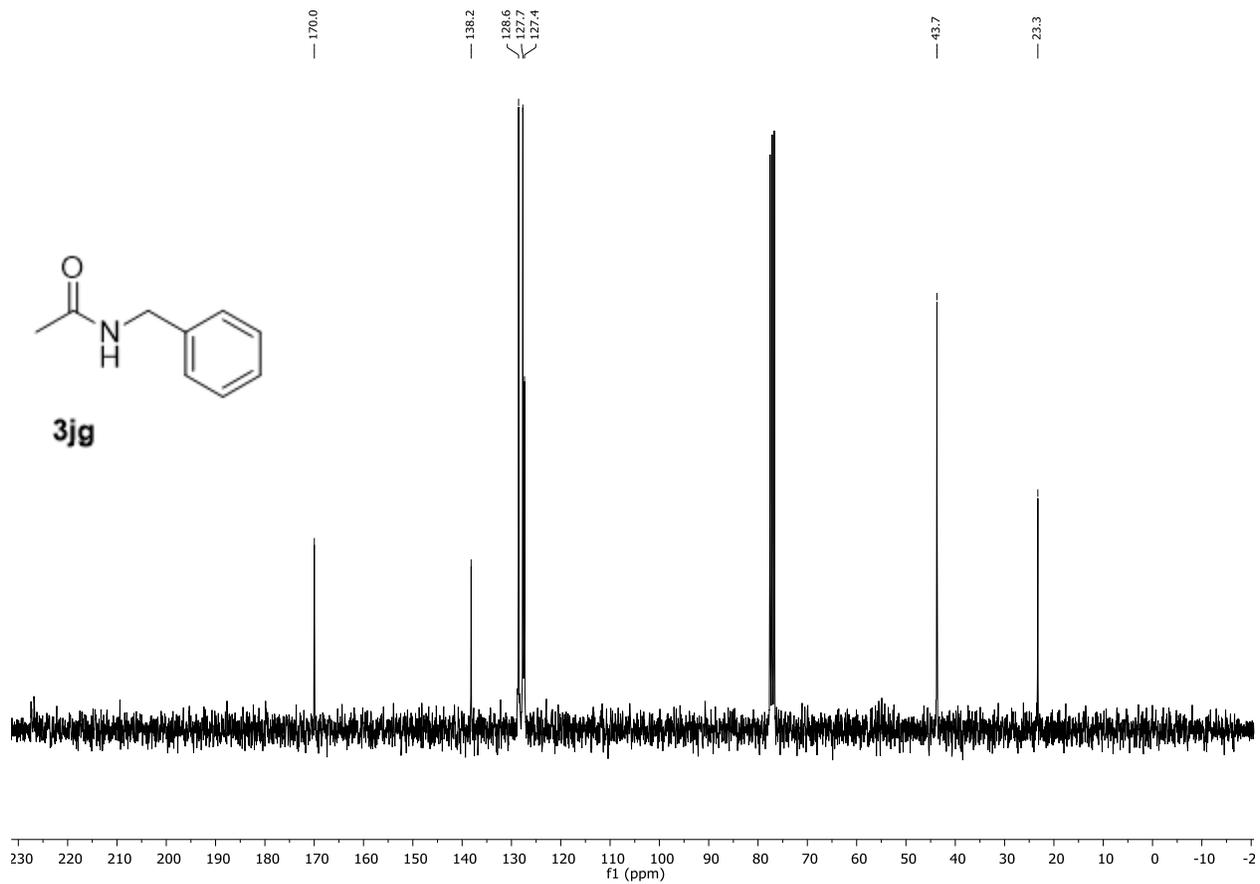
^{13}C NMR (75 MHz, Chloroform-*d*) N-benzylcyclohexanecarboxamide (**3jb**)

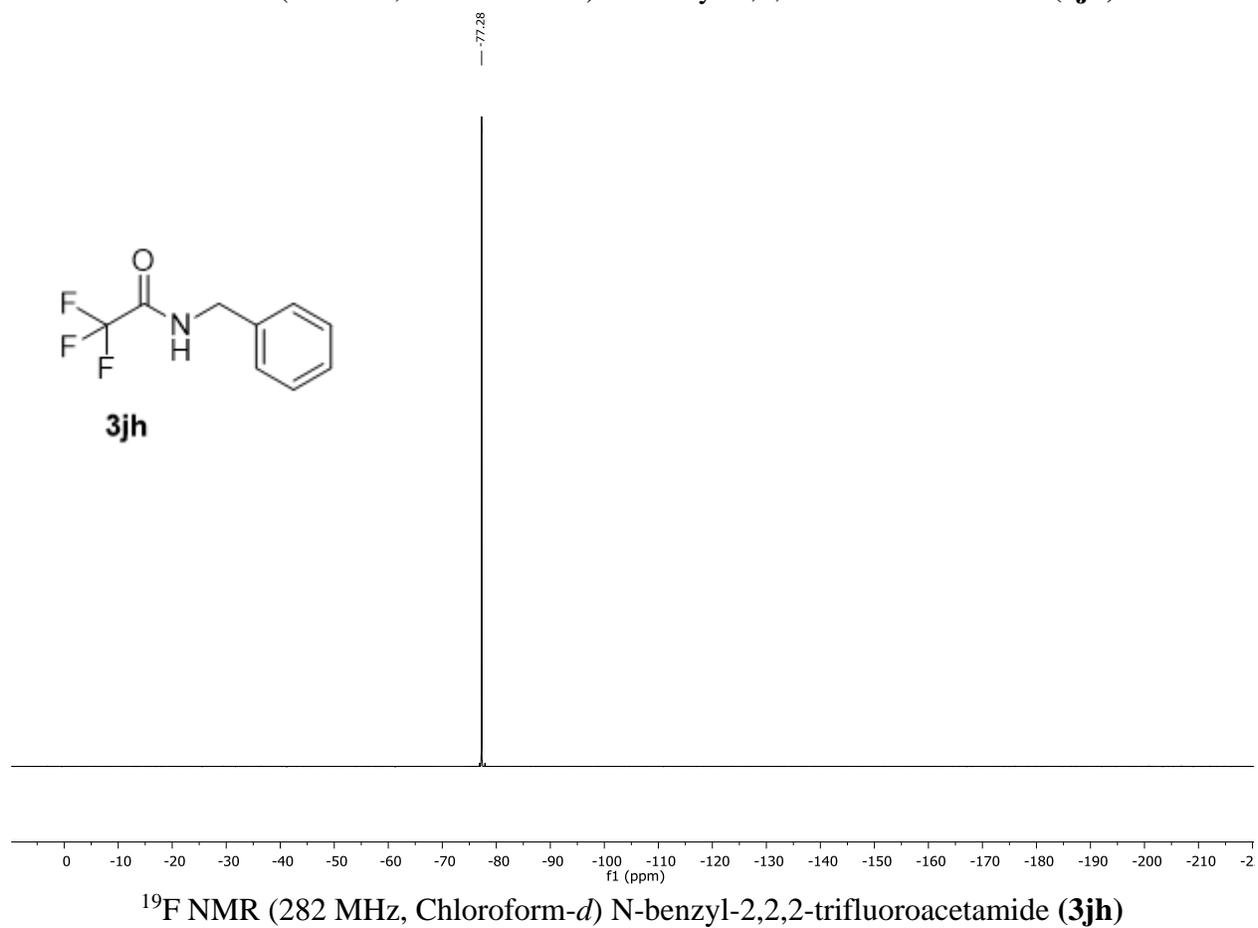
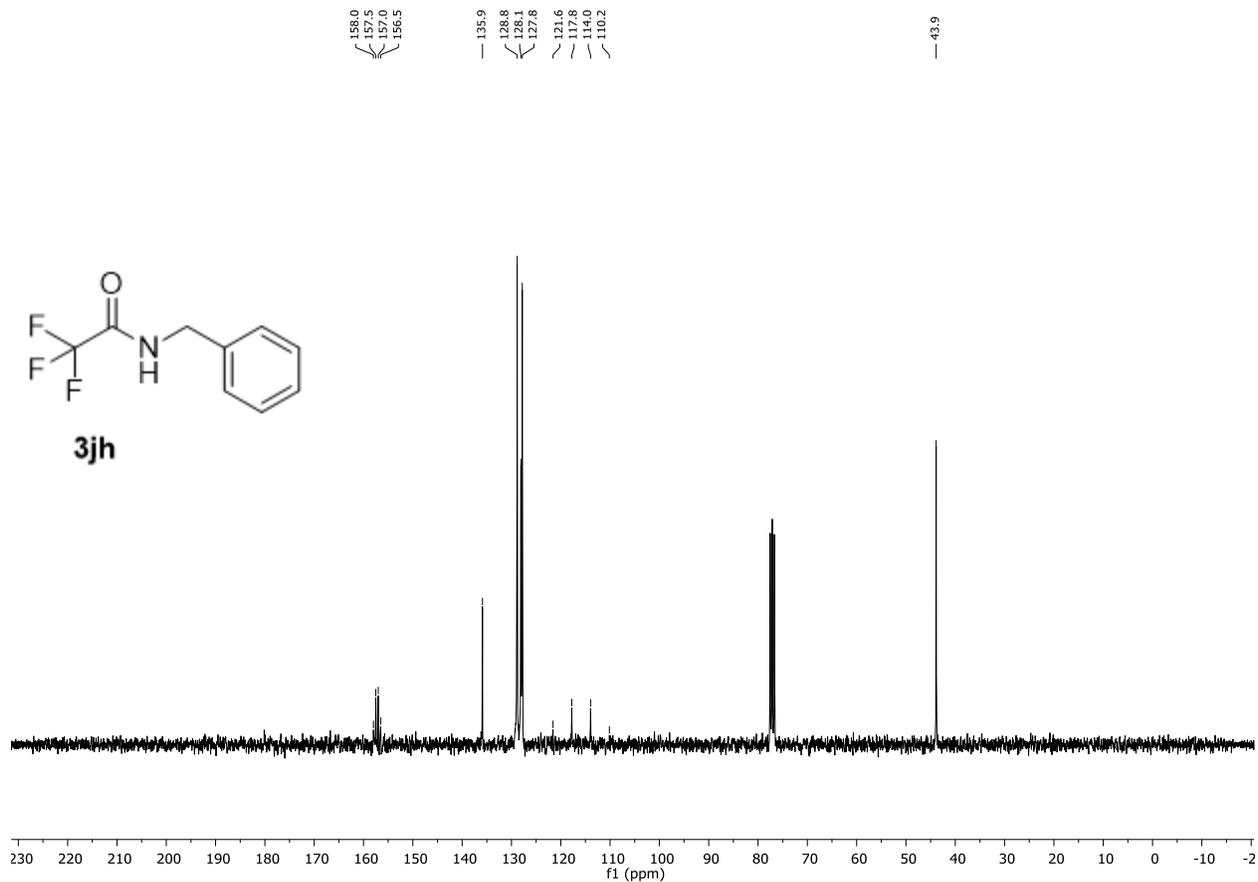


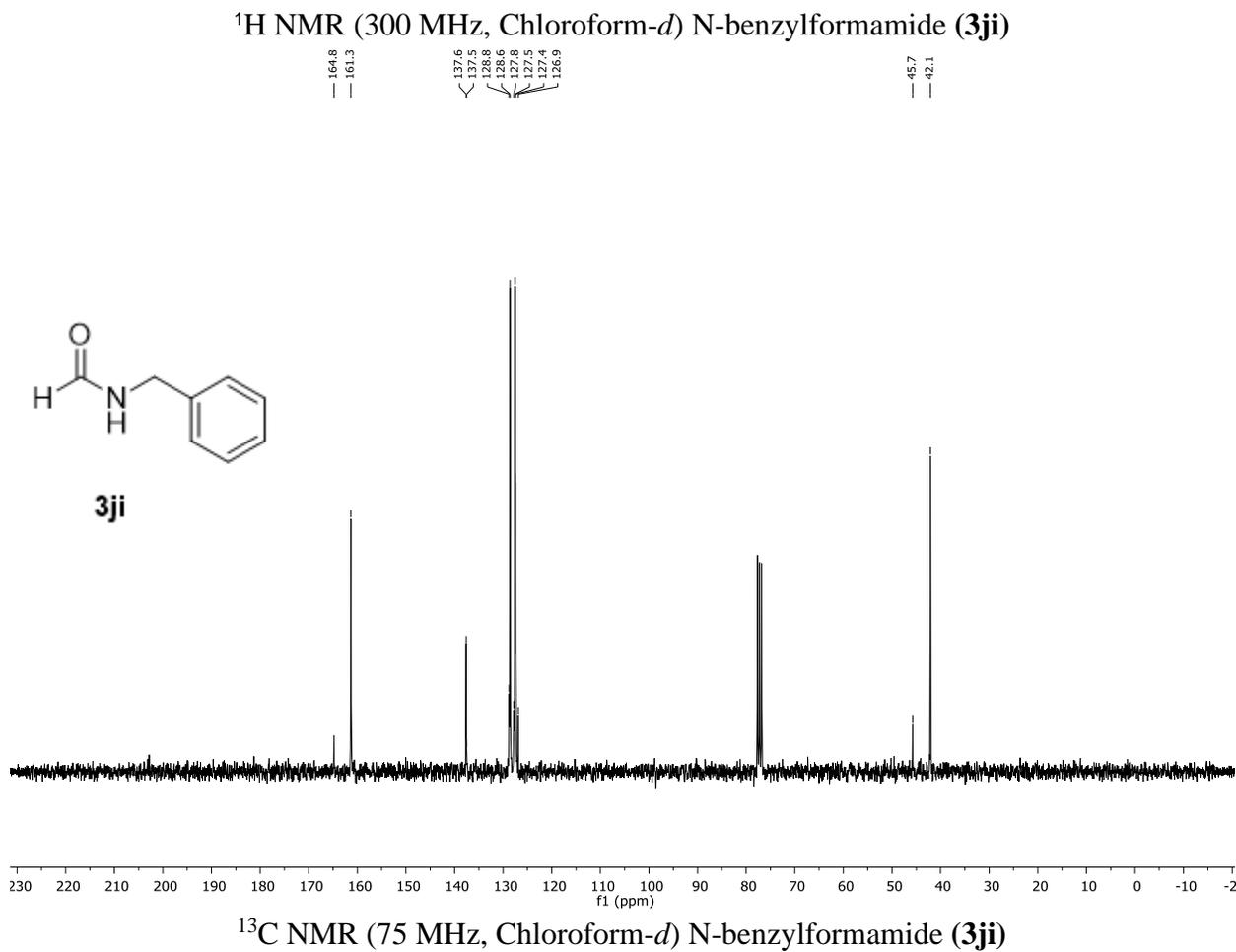
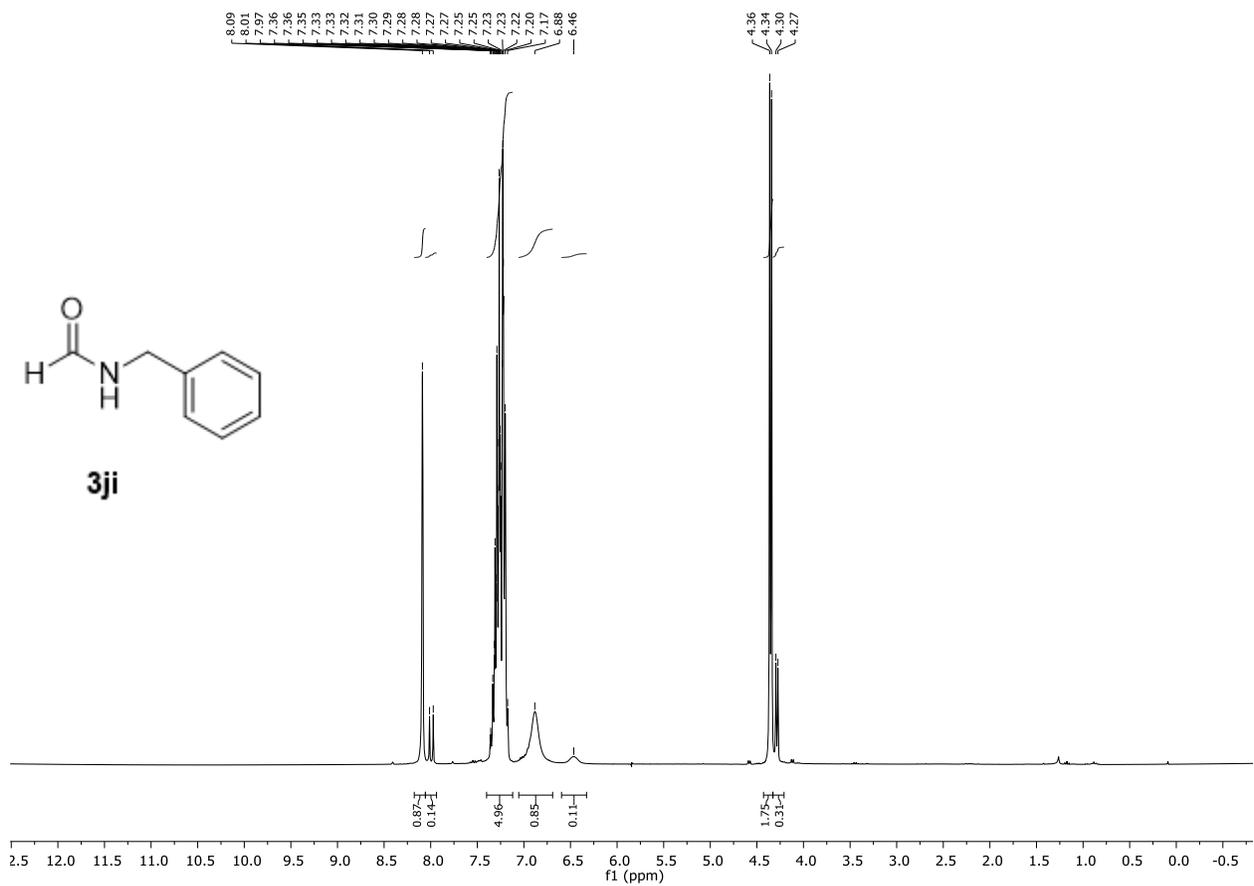
^1H NMR (300 MHz, Chloroform-*d*) N-benzylhexanamide (**3jc**)

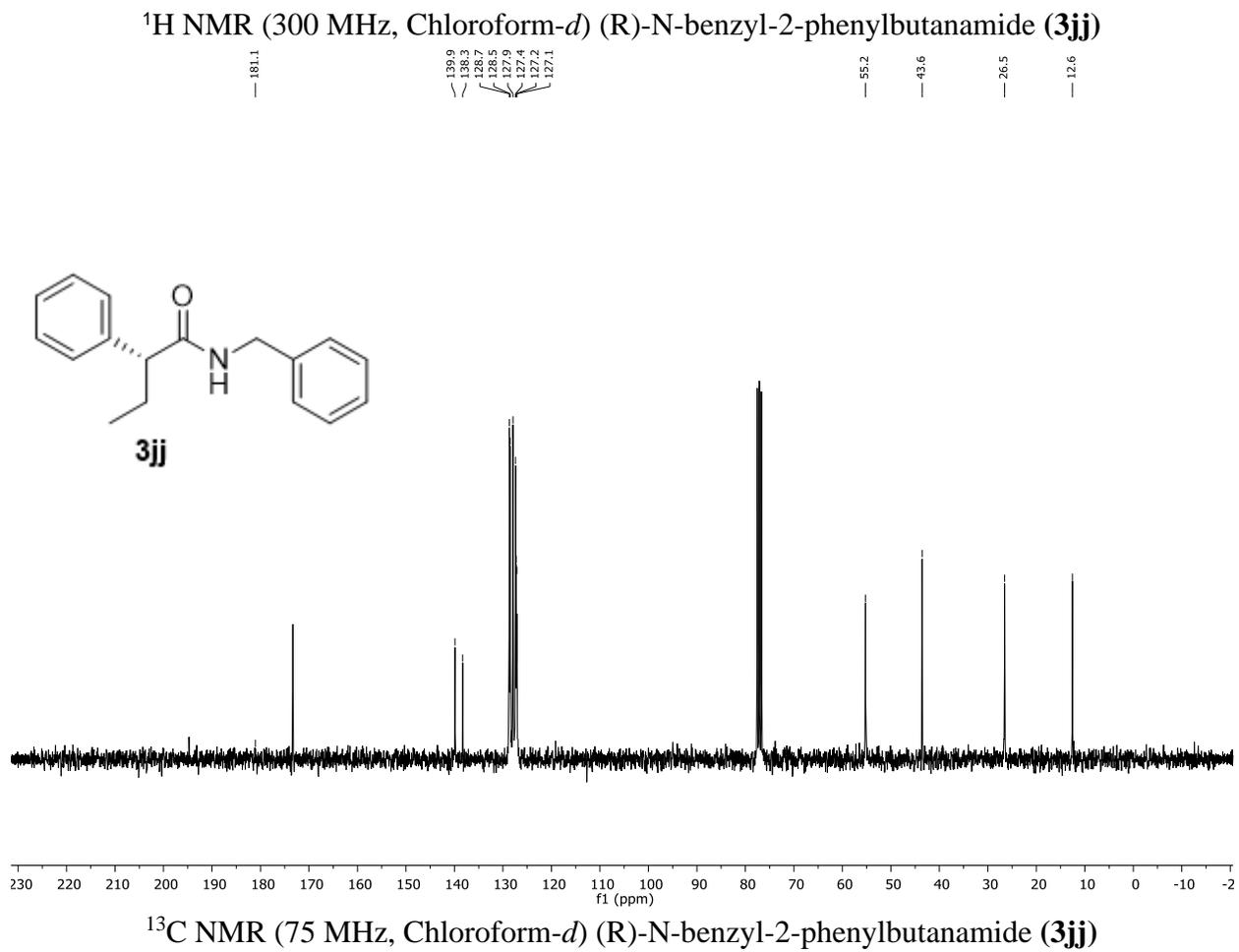
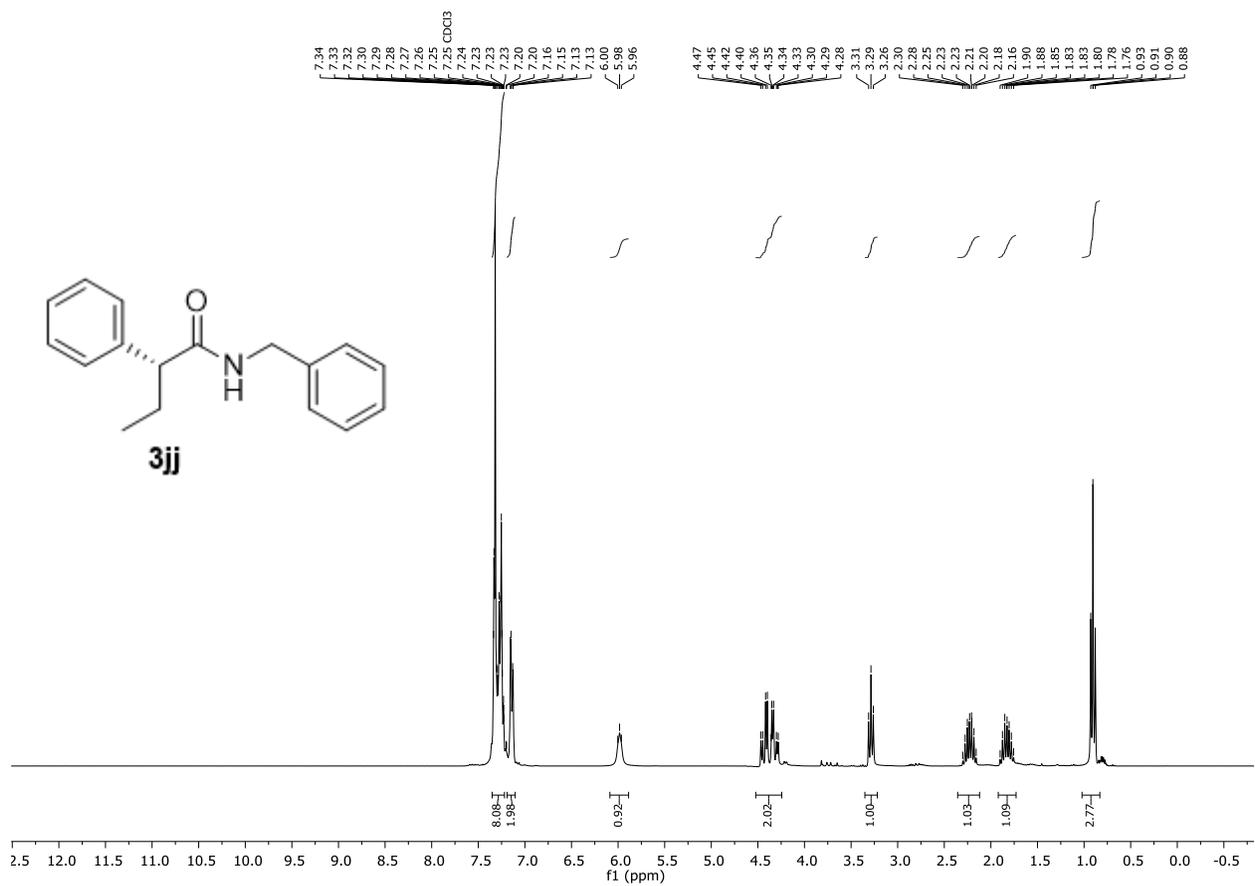


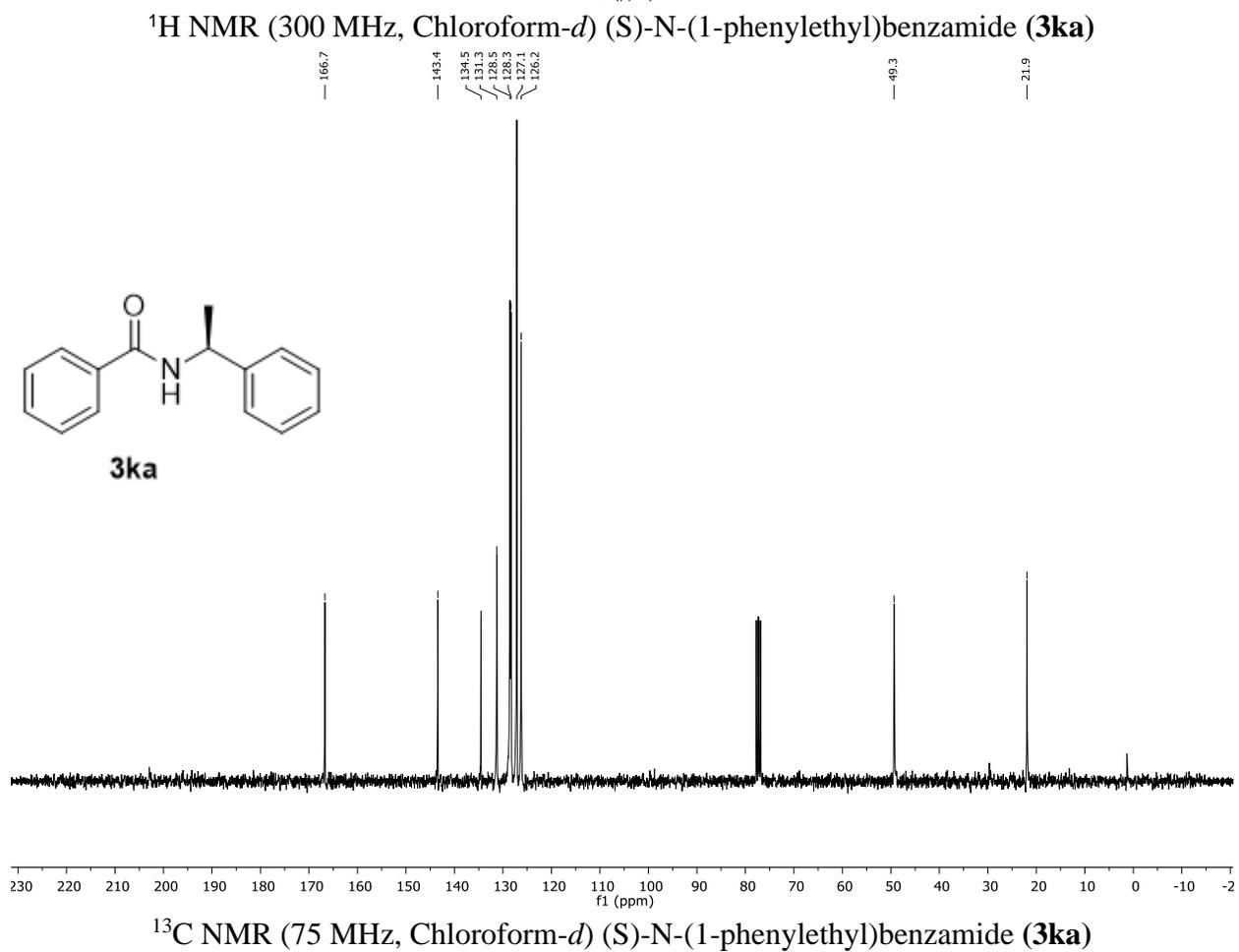
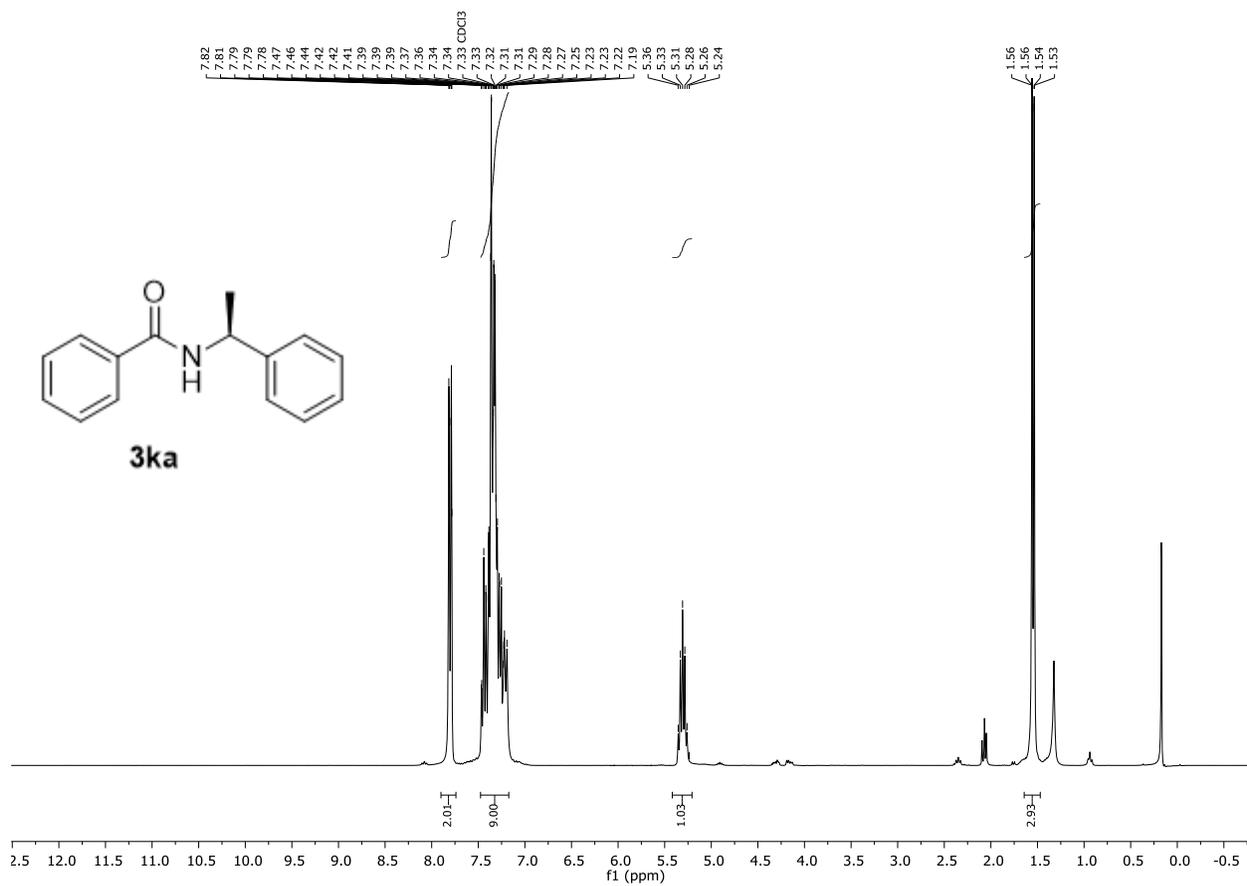


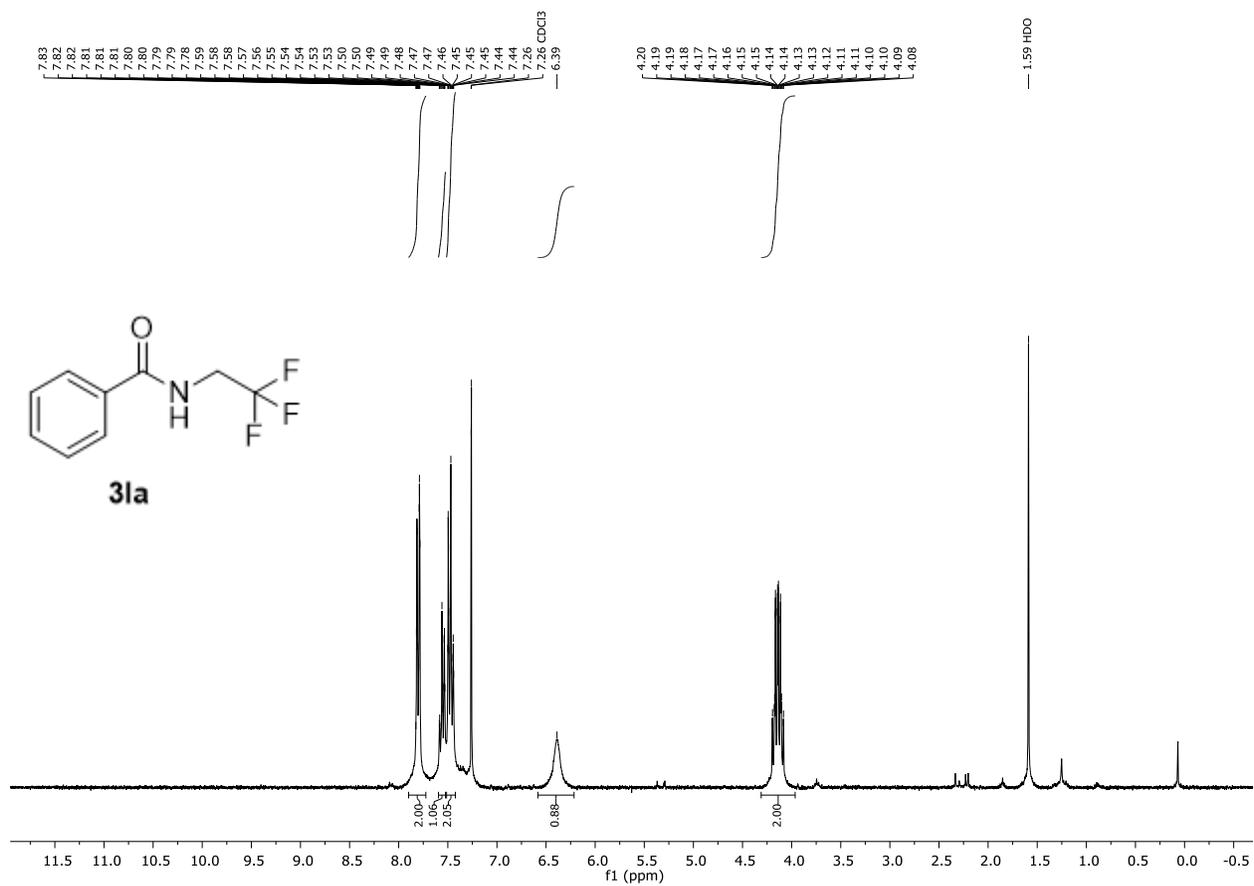




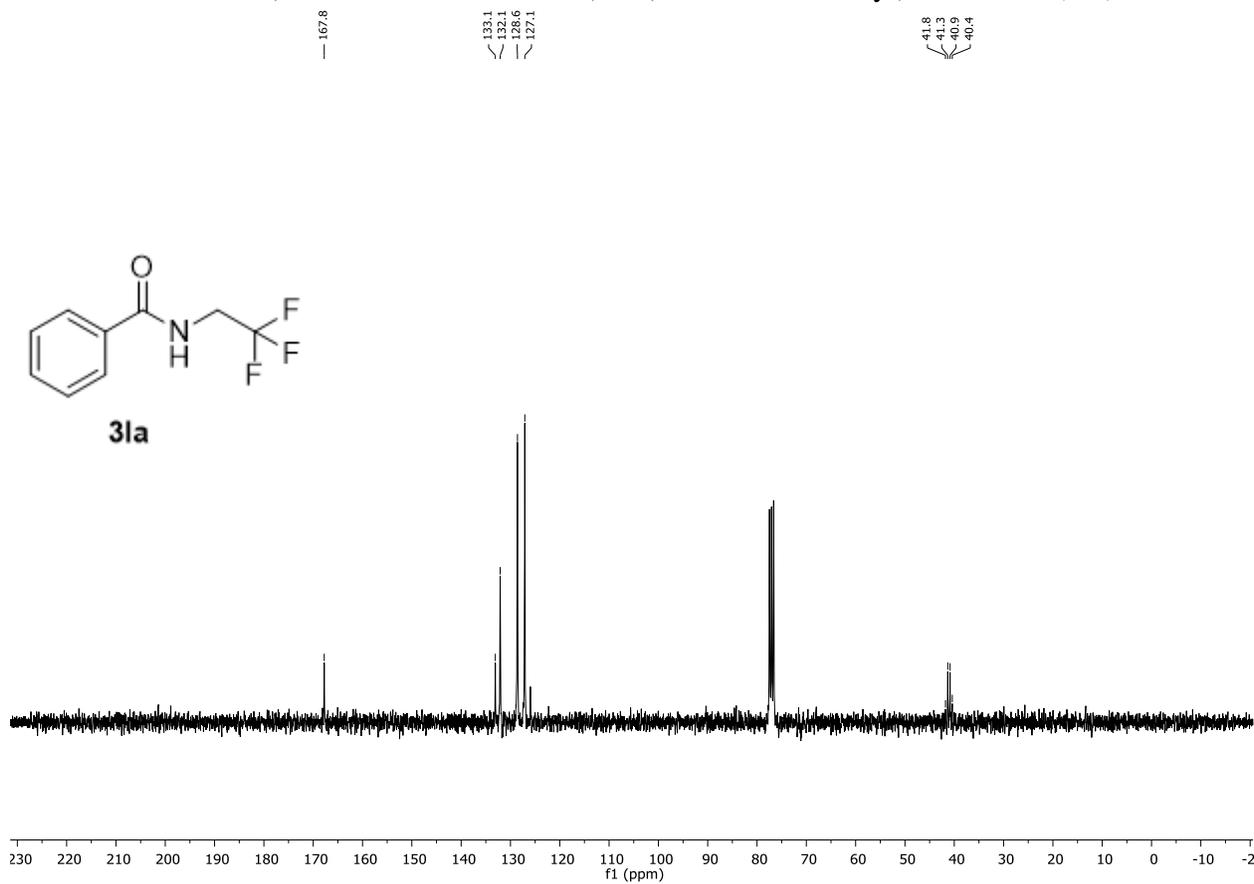




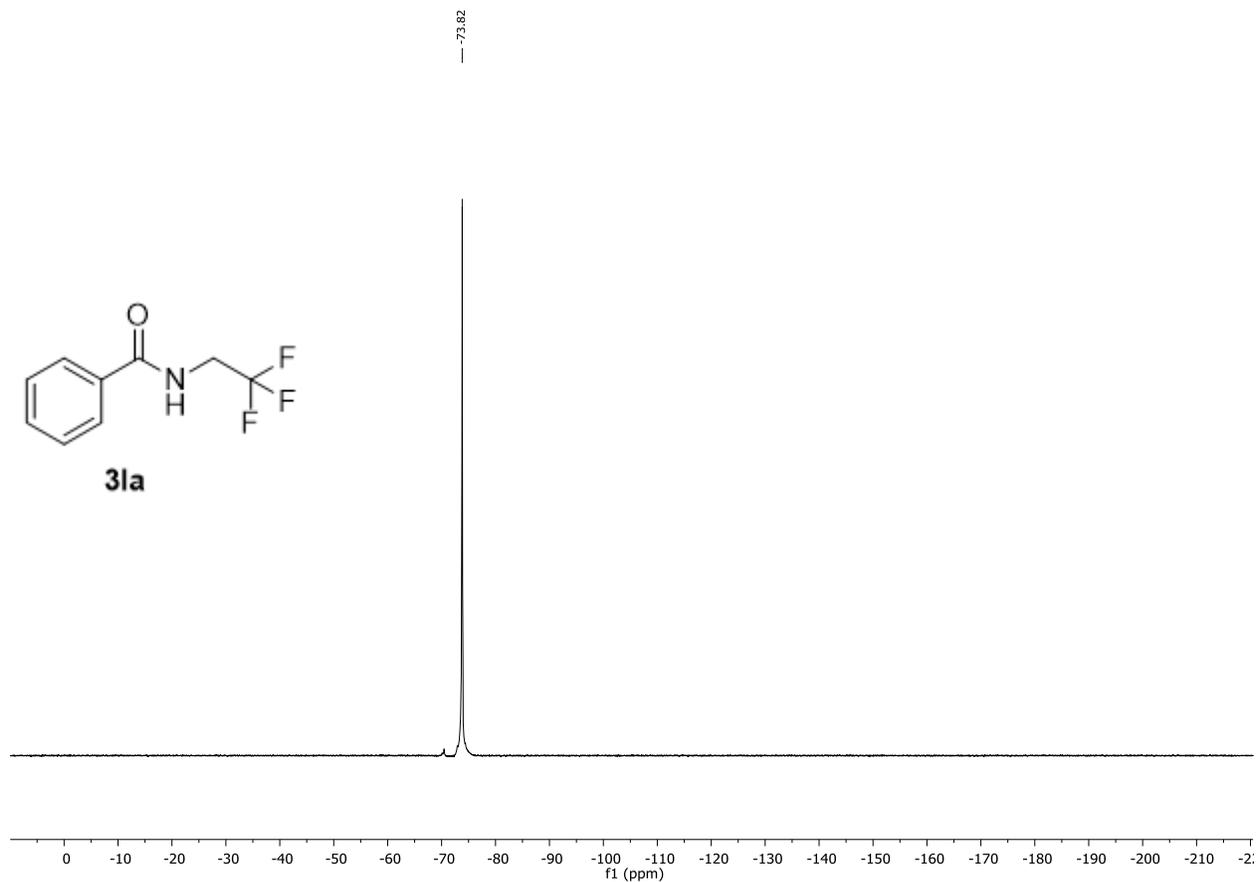




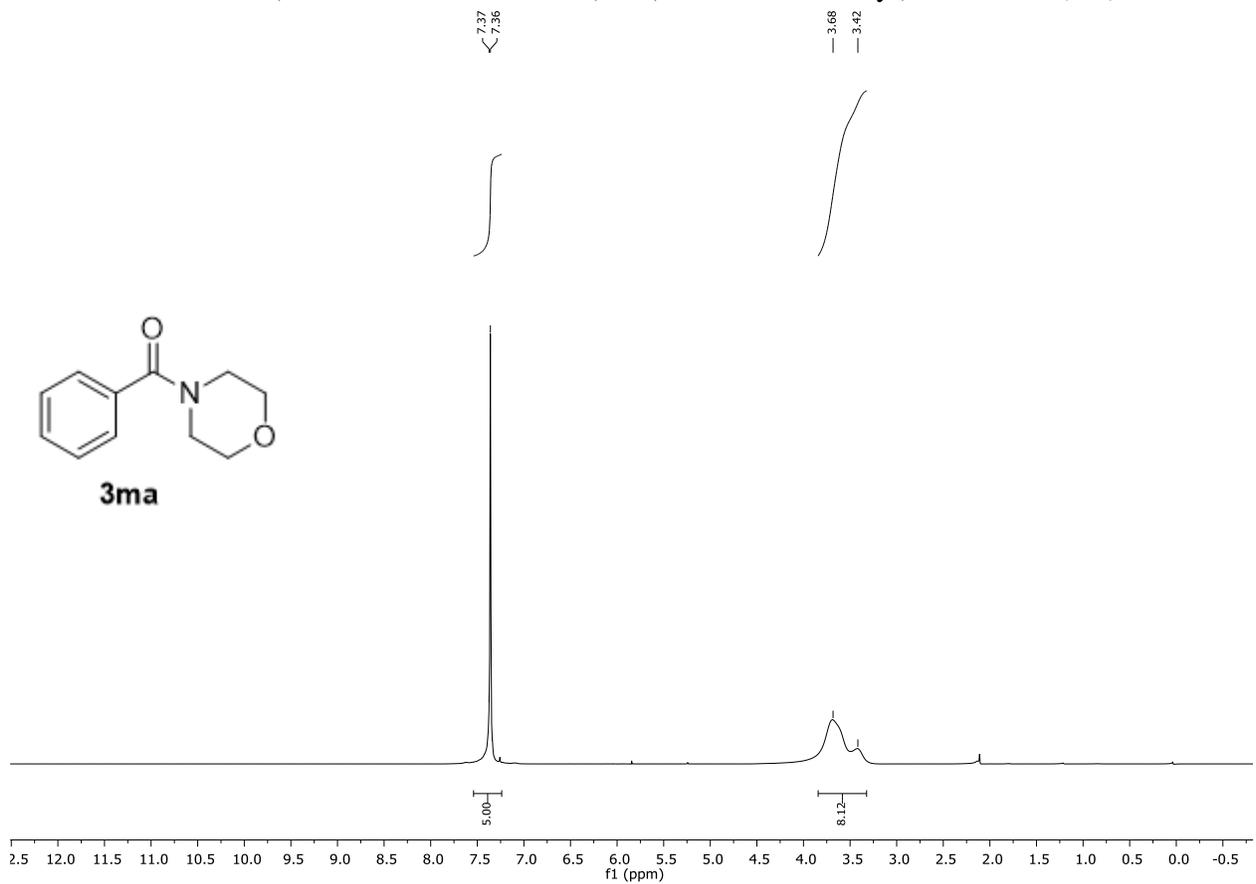
¹H NMR (300 MHz, Chloroform-*d*) N-(2,2,2-trifluoroethyl)benzamide (**3la**)



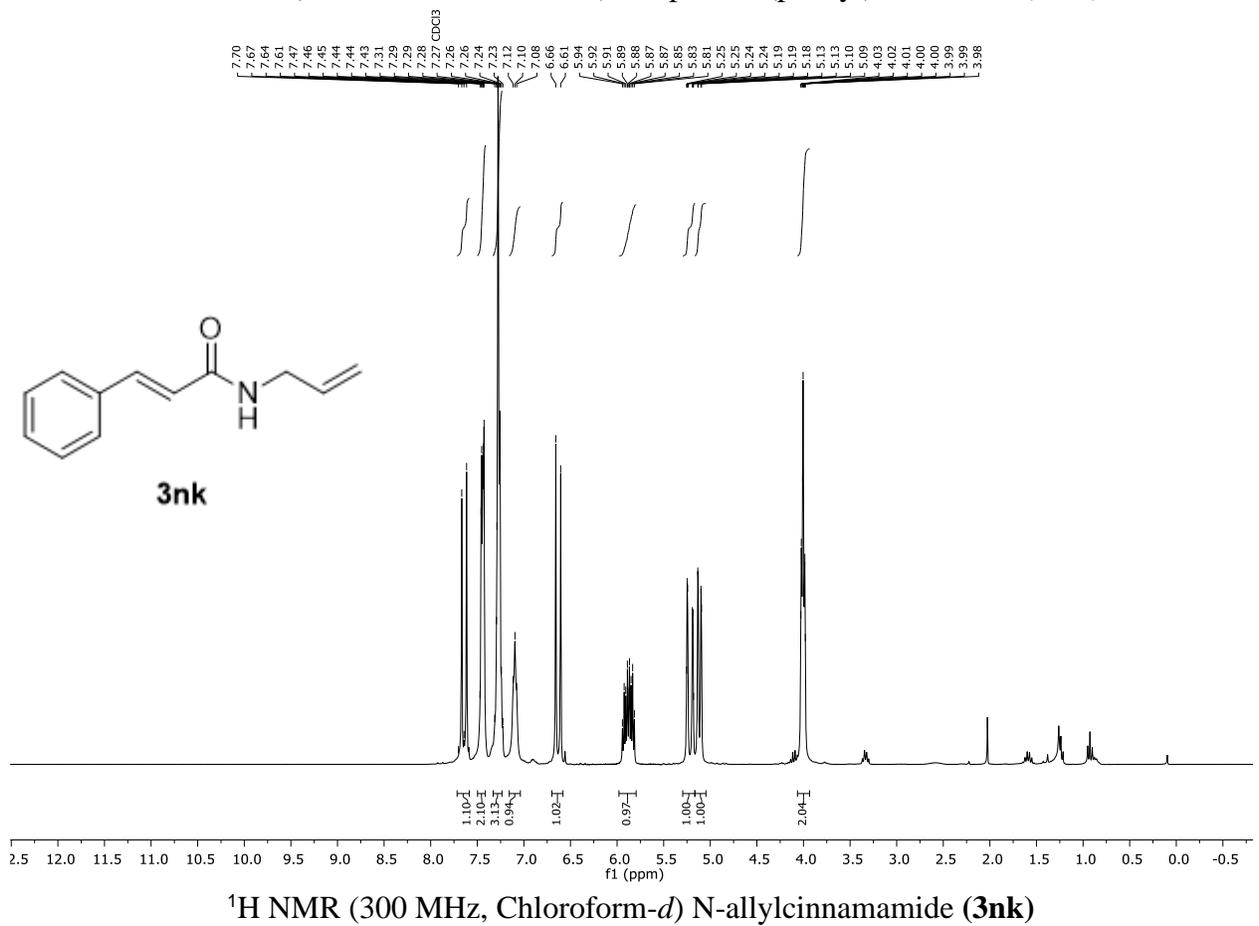
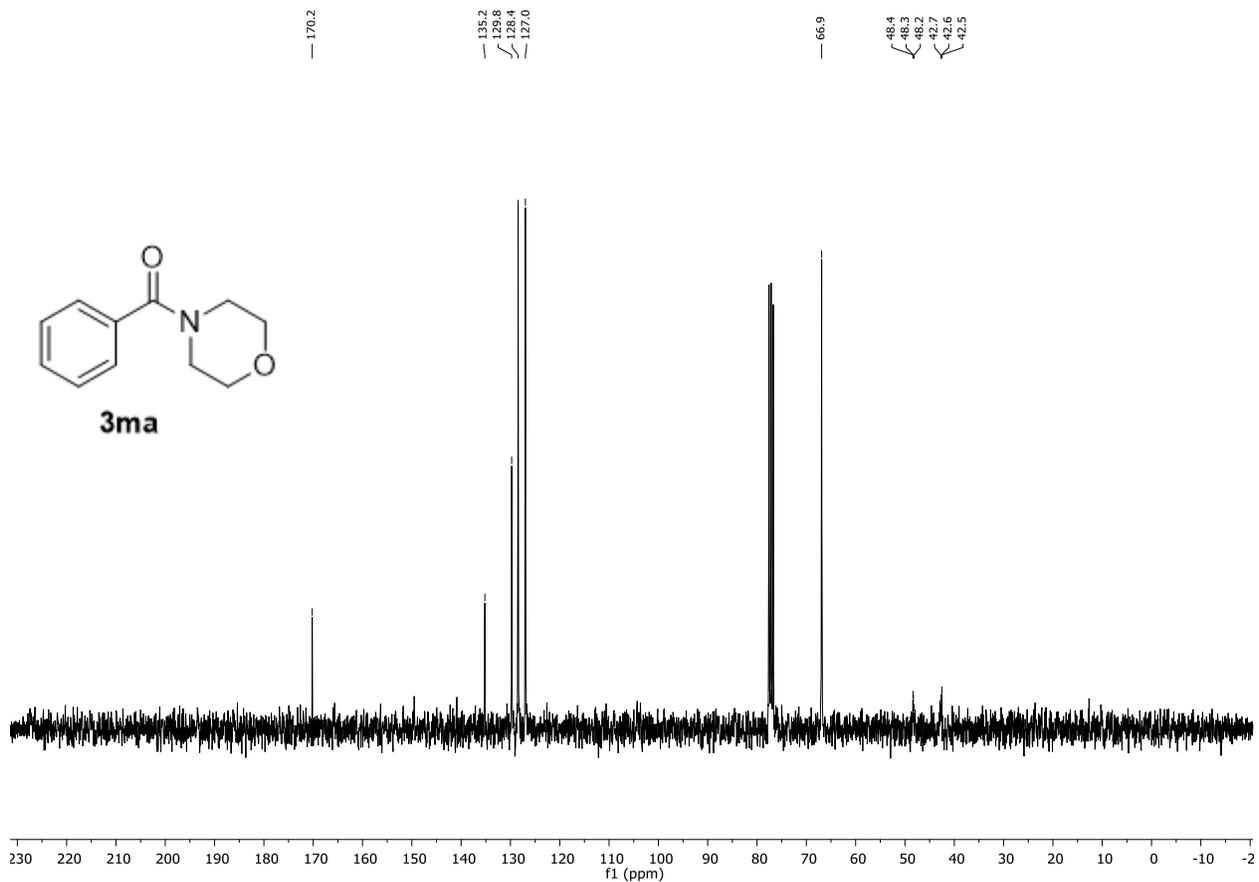
¹³C NMR (75 MHz, Chloroform-*d*) N-(2,2,2-trifluoroethyl)benzamide (**3la**)

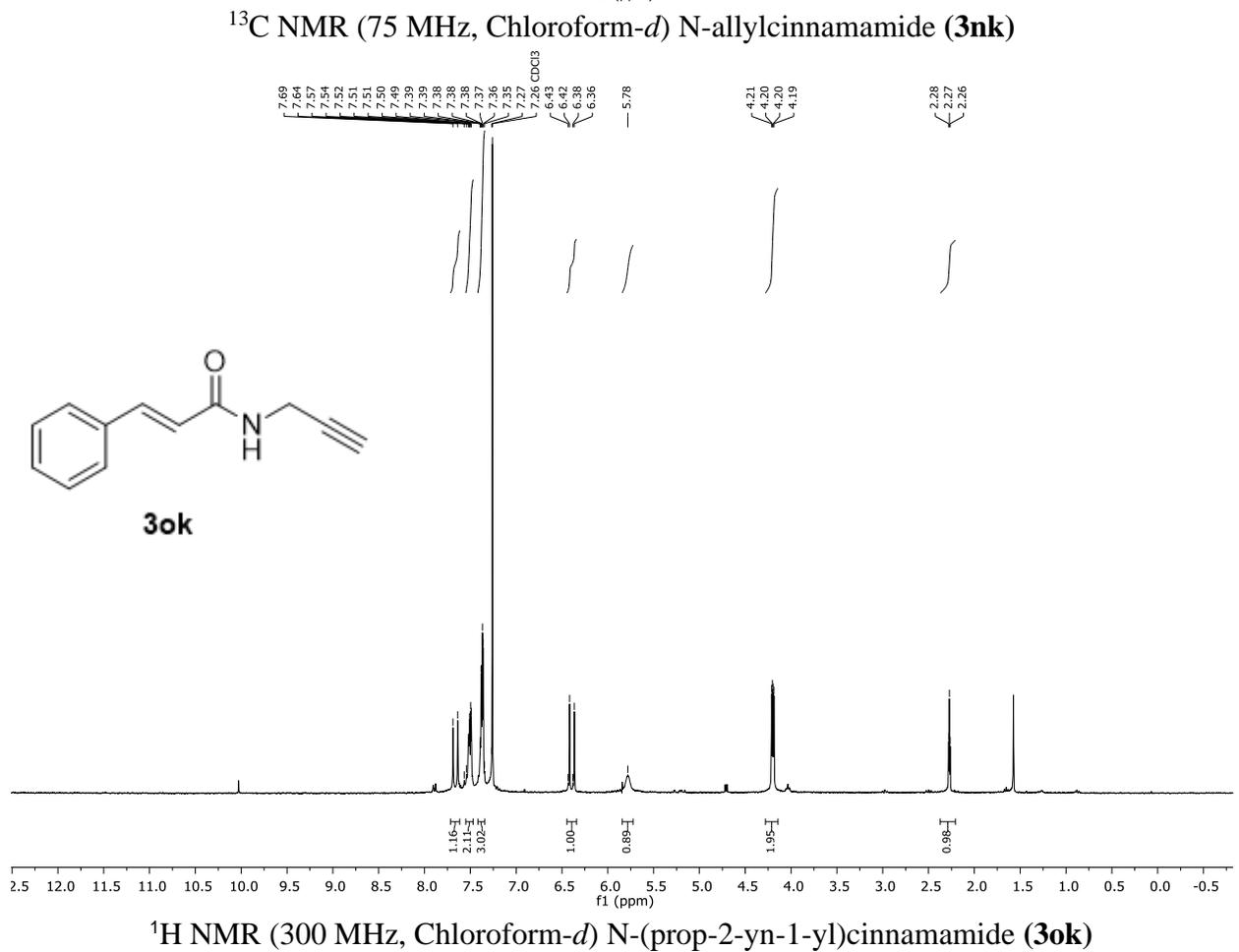
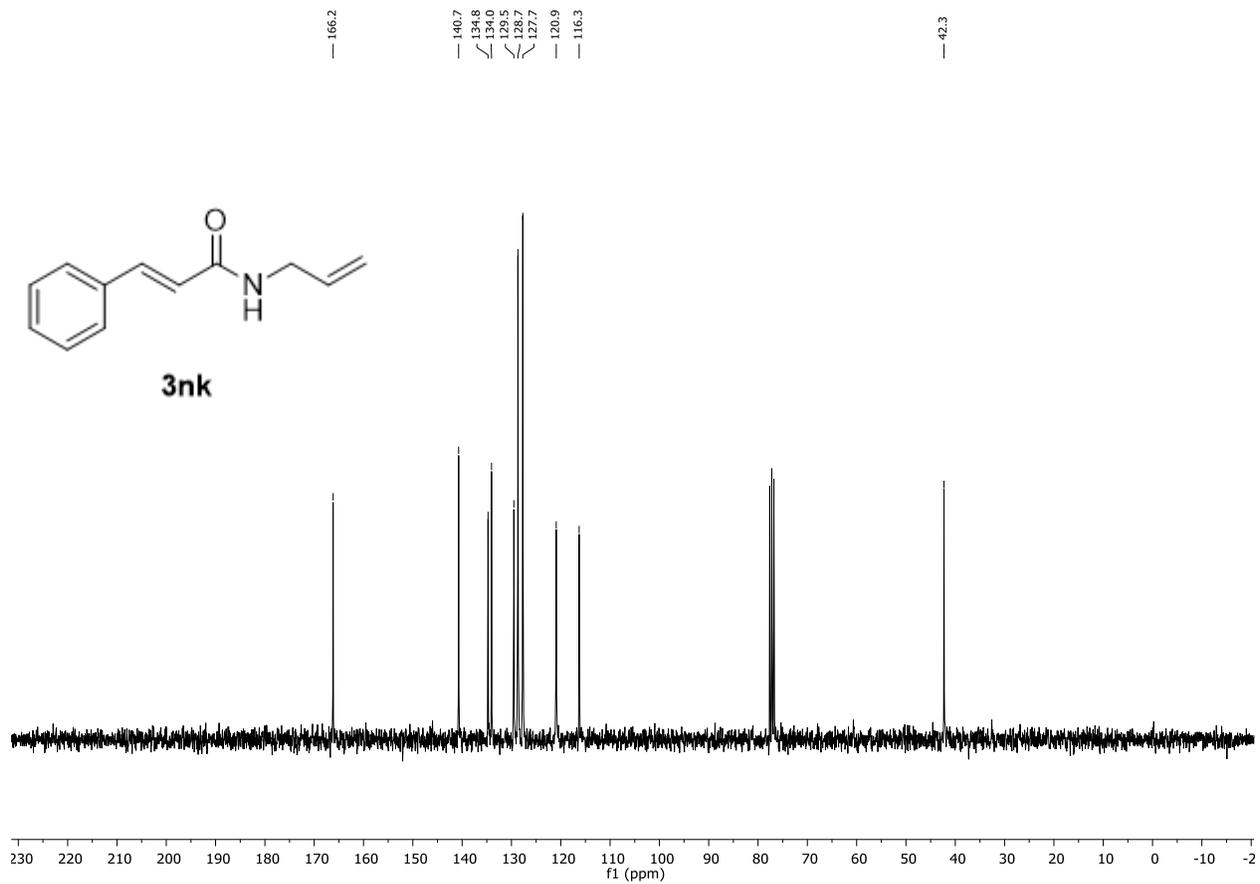


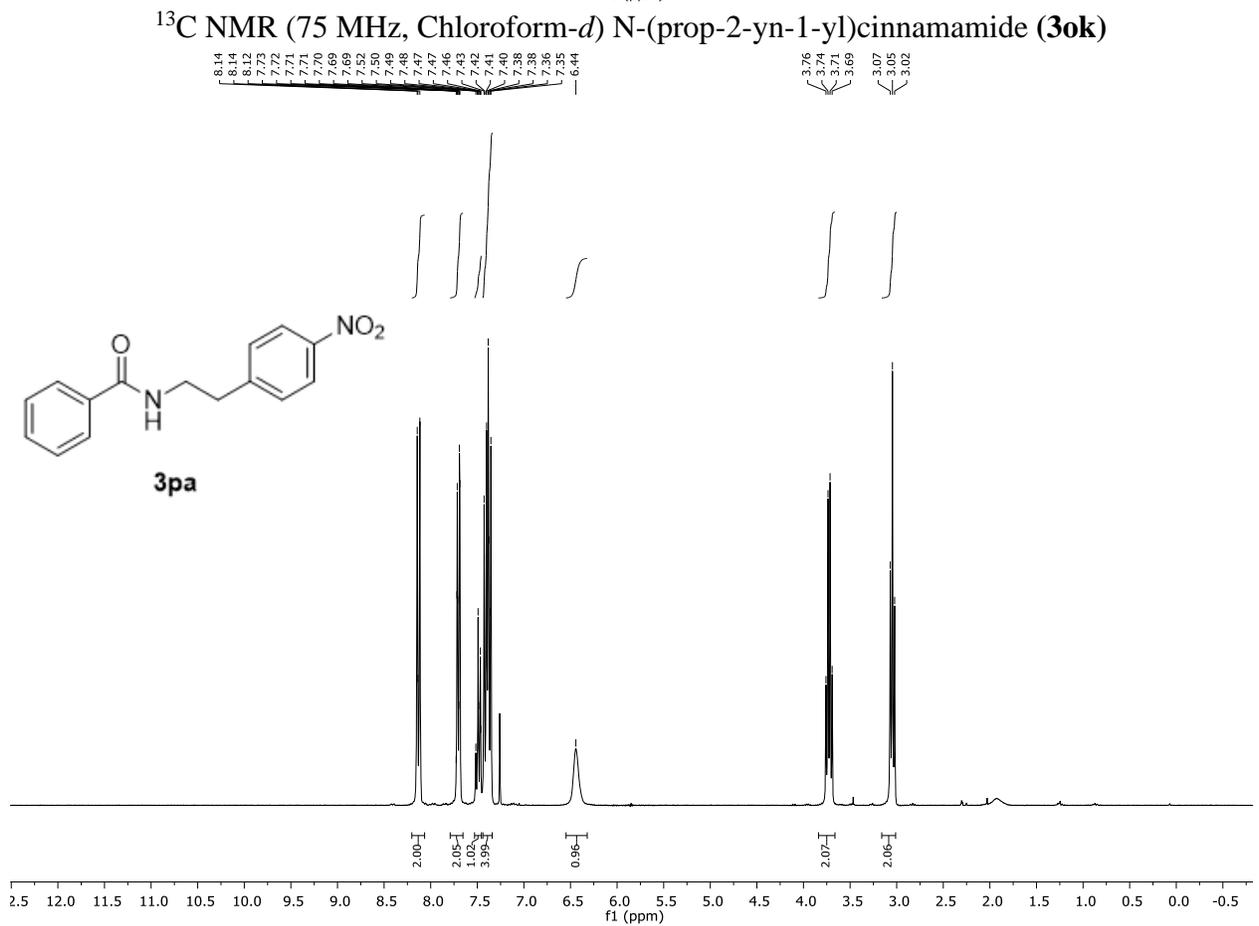
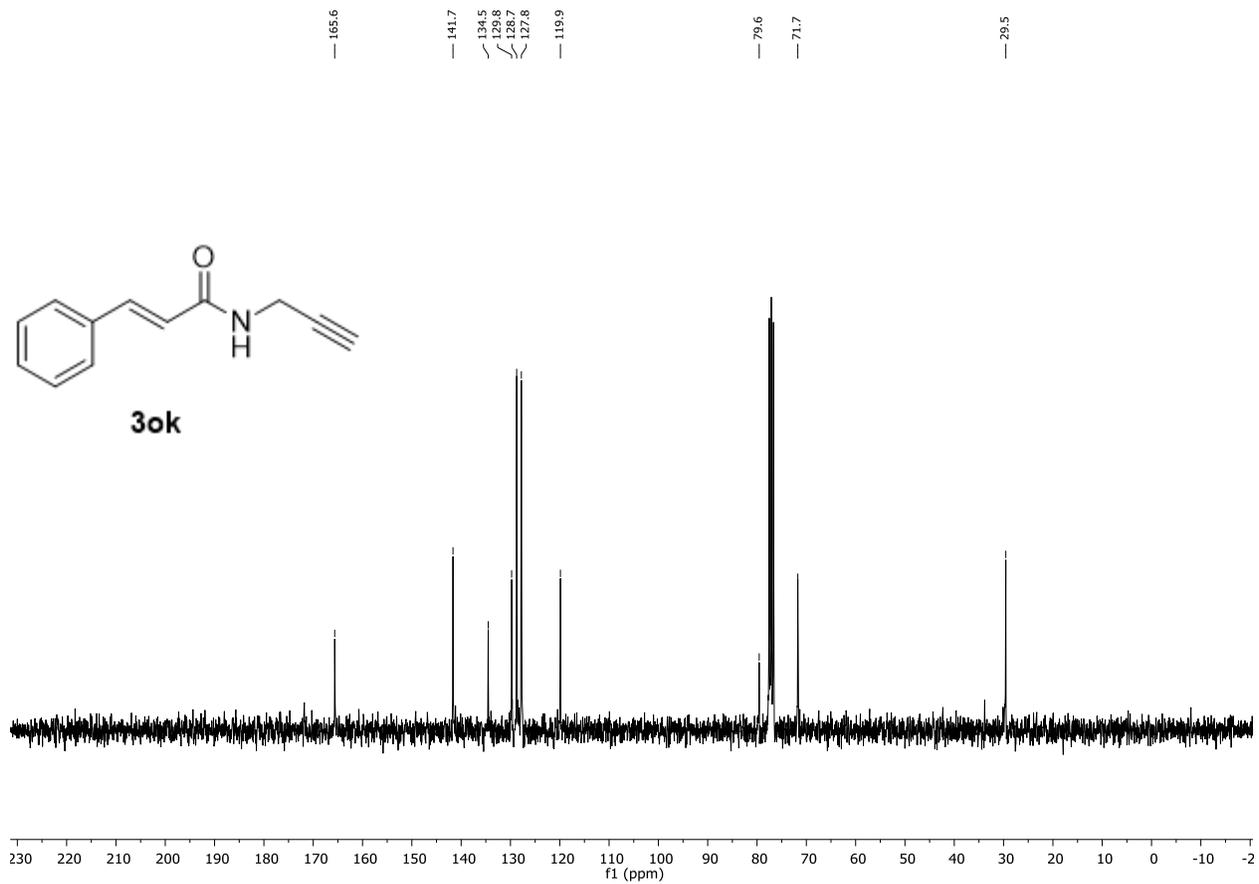
¹⁹F NMR (282 MHz, Chloroform-*d*) N-(2,2,2-trifluoroethyl)benzamide (**3la**)

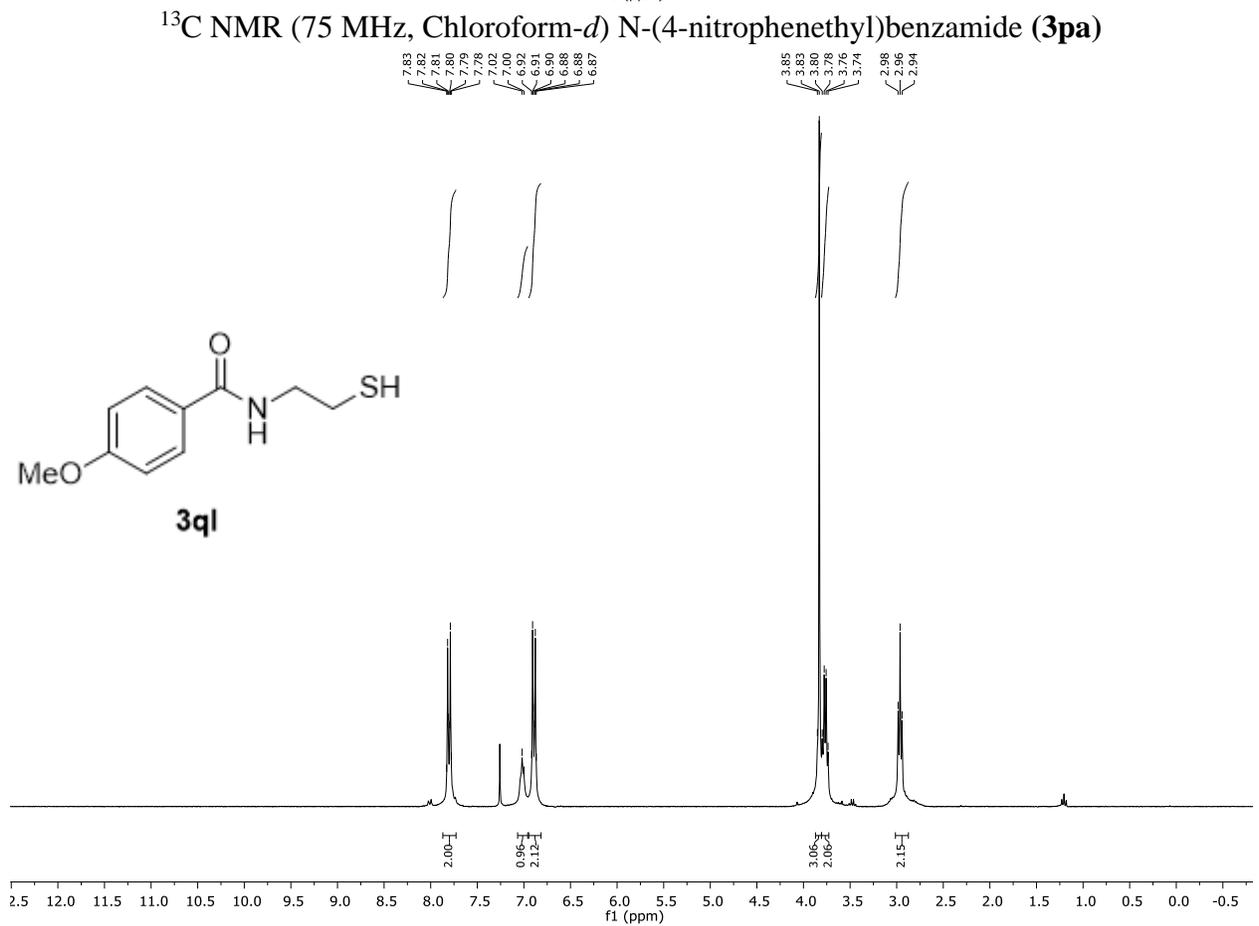
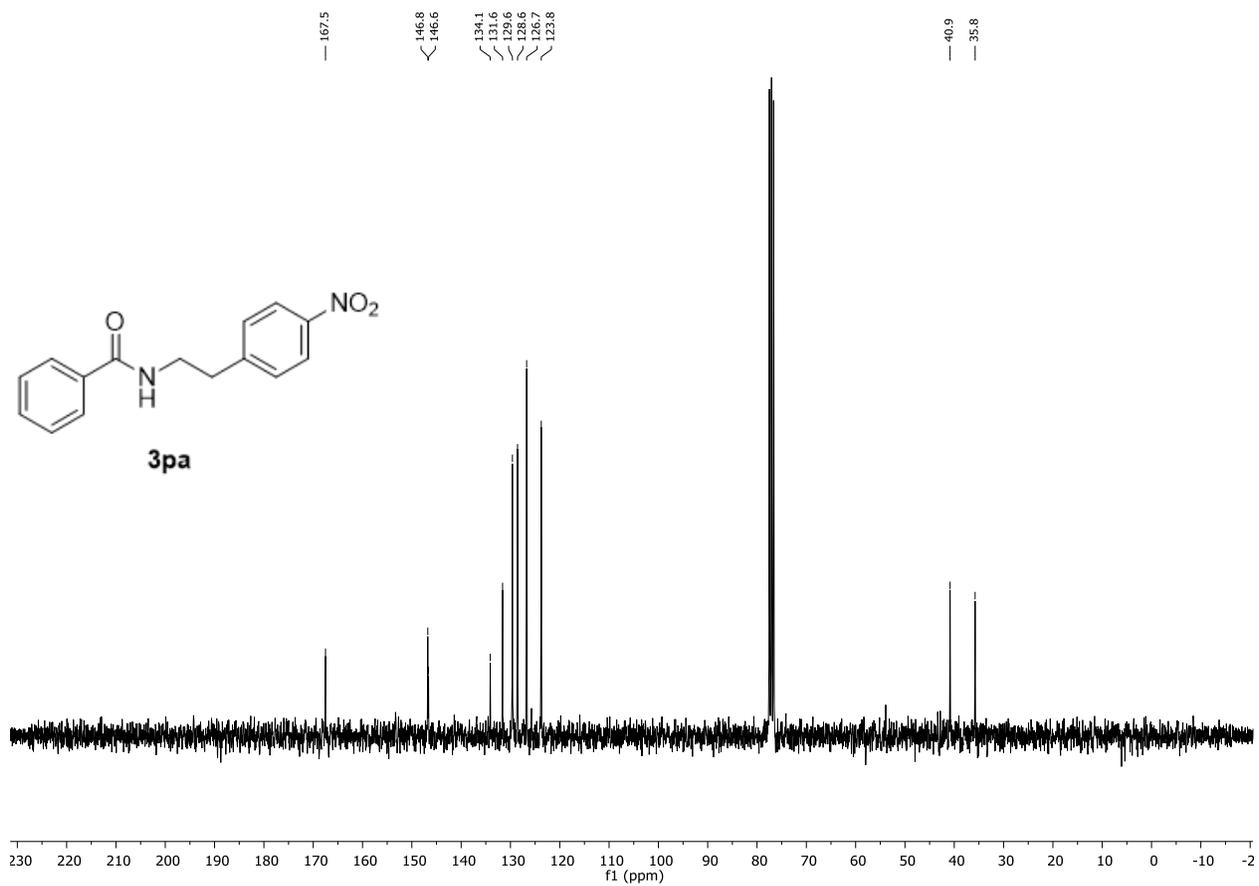


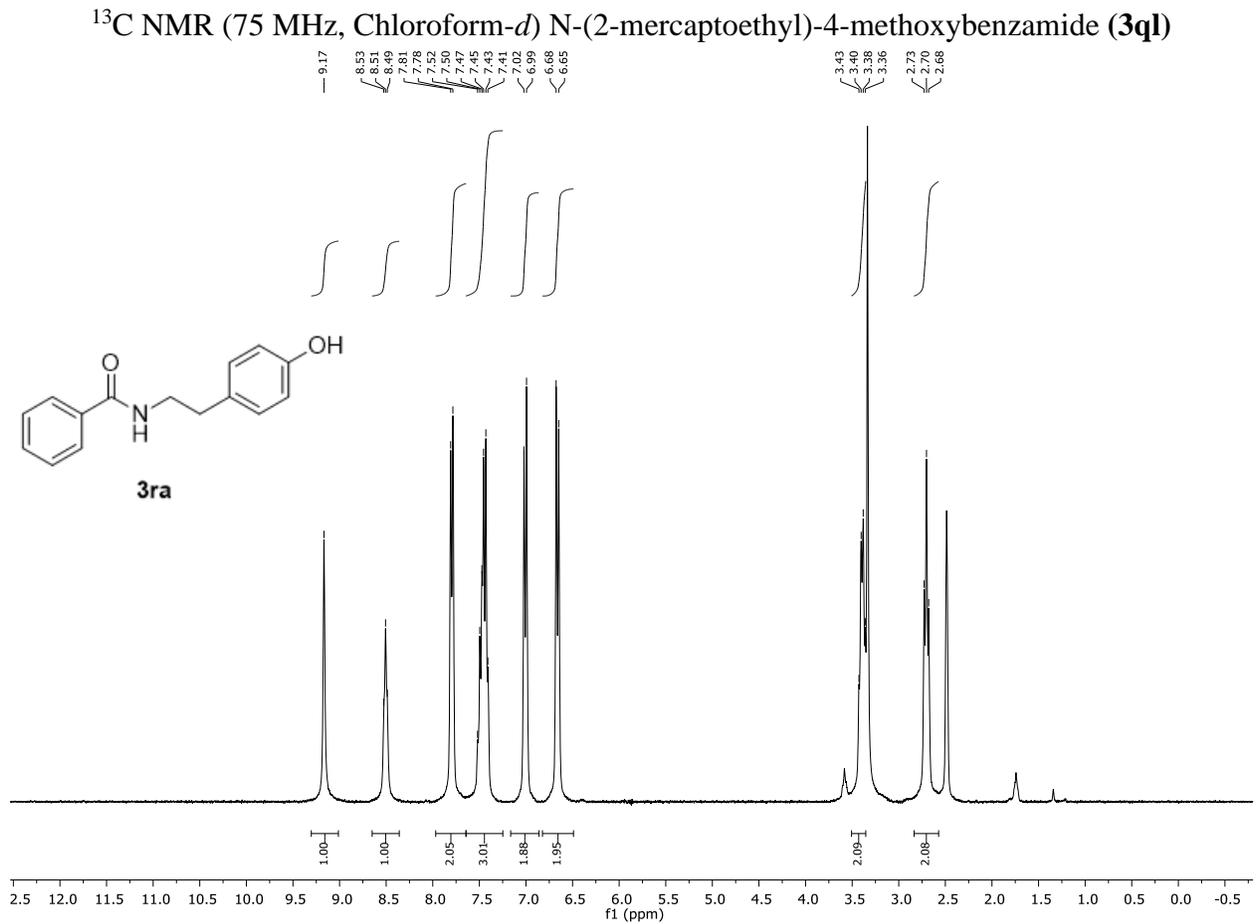
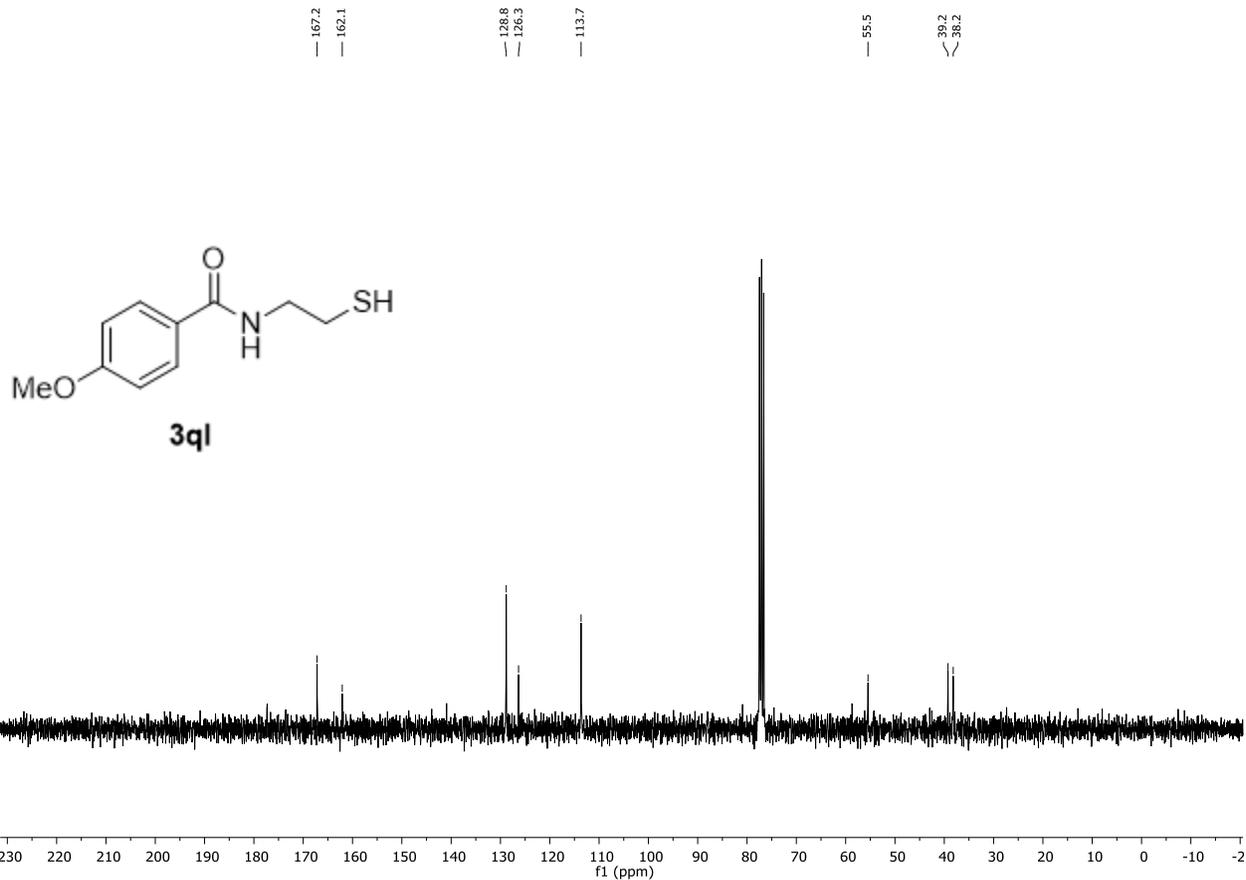
¹H NMR (300 MHz, Chloroform-*d*) morpholino(phenyl)methanone (**3ma**)

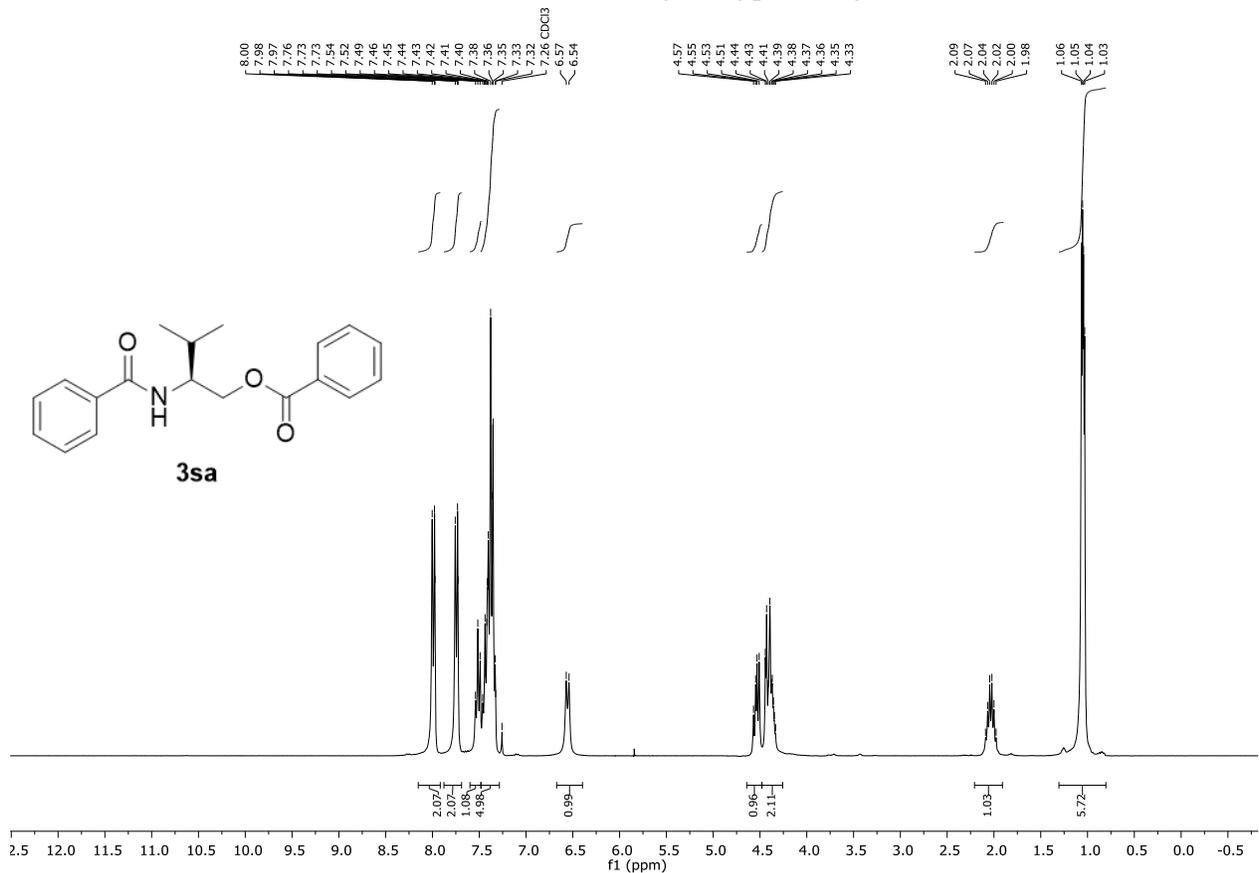
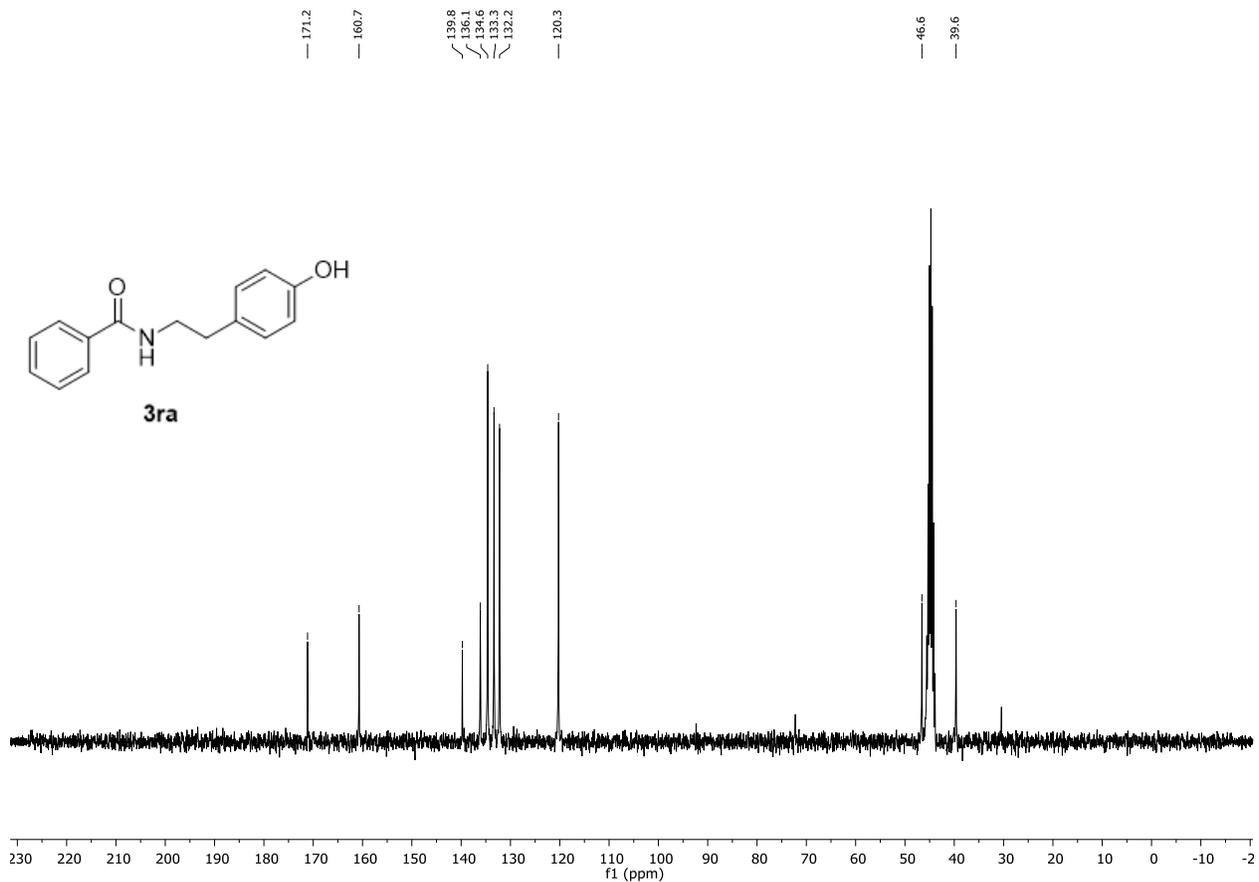


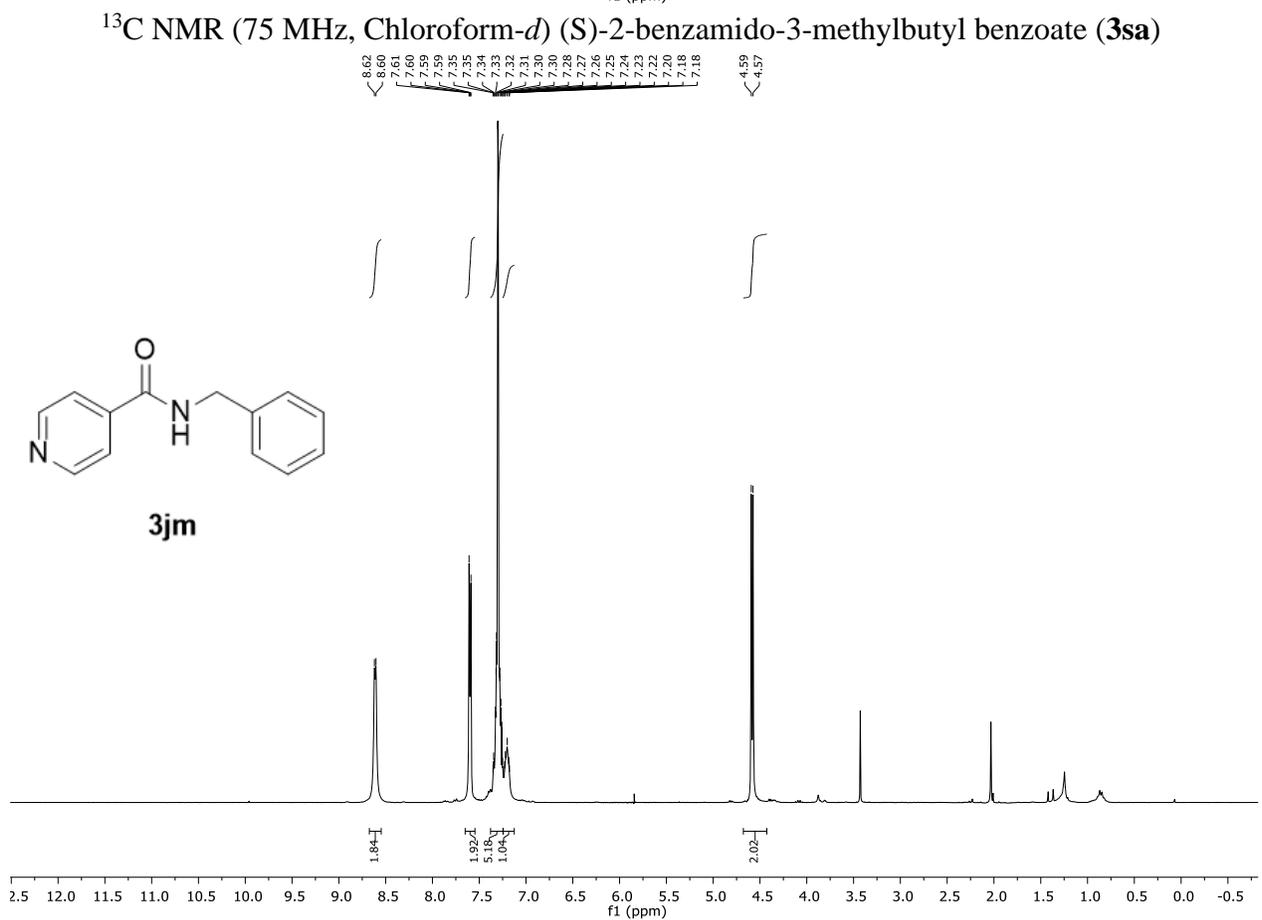
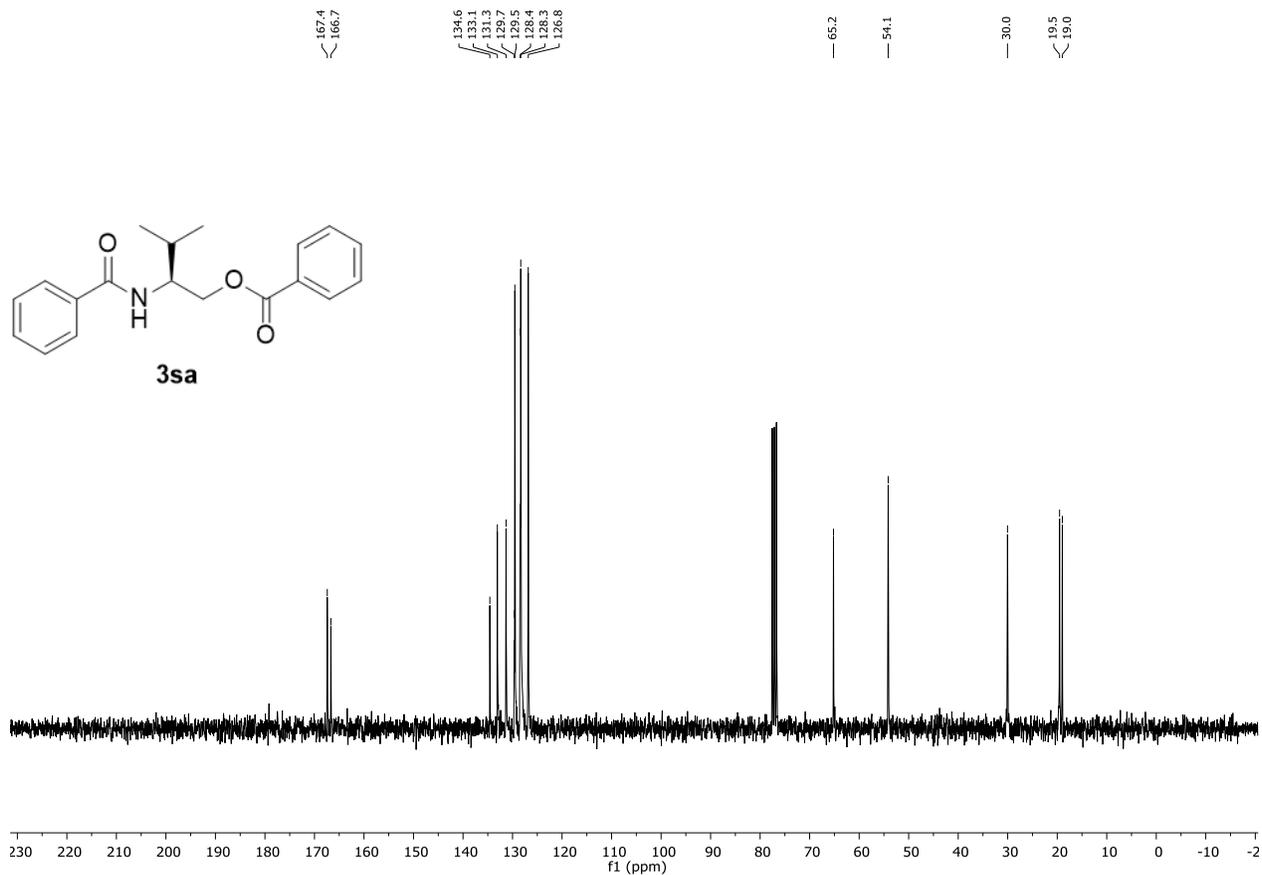




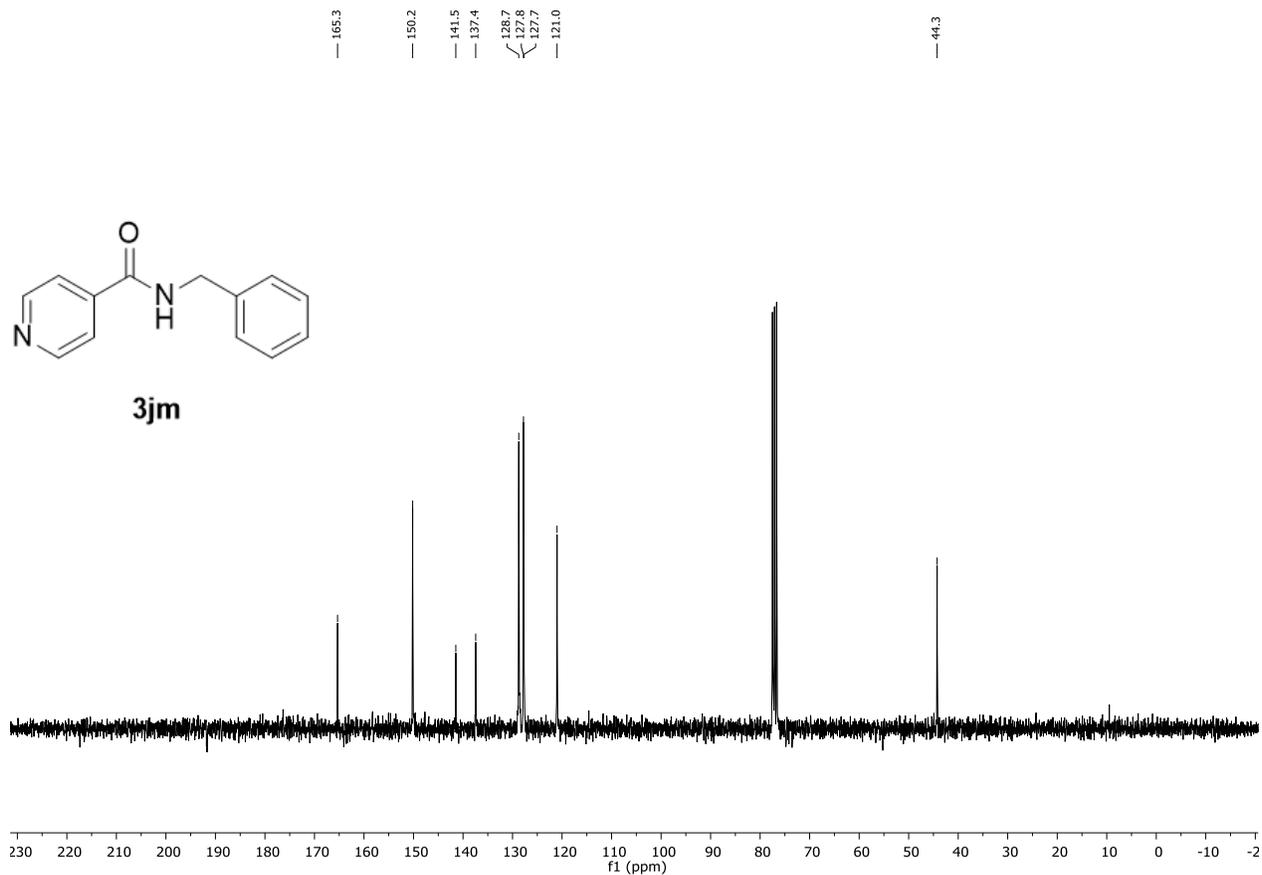




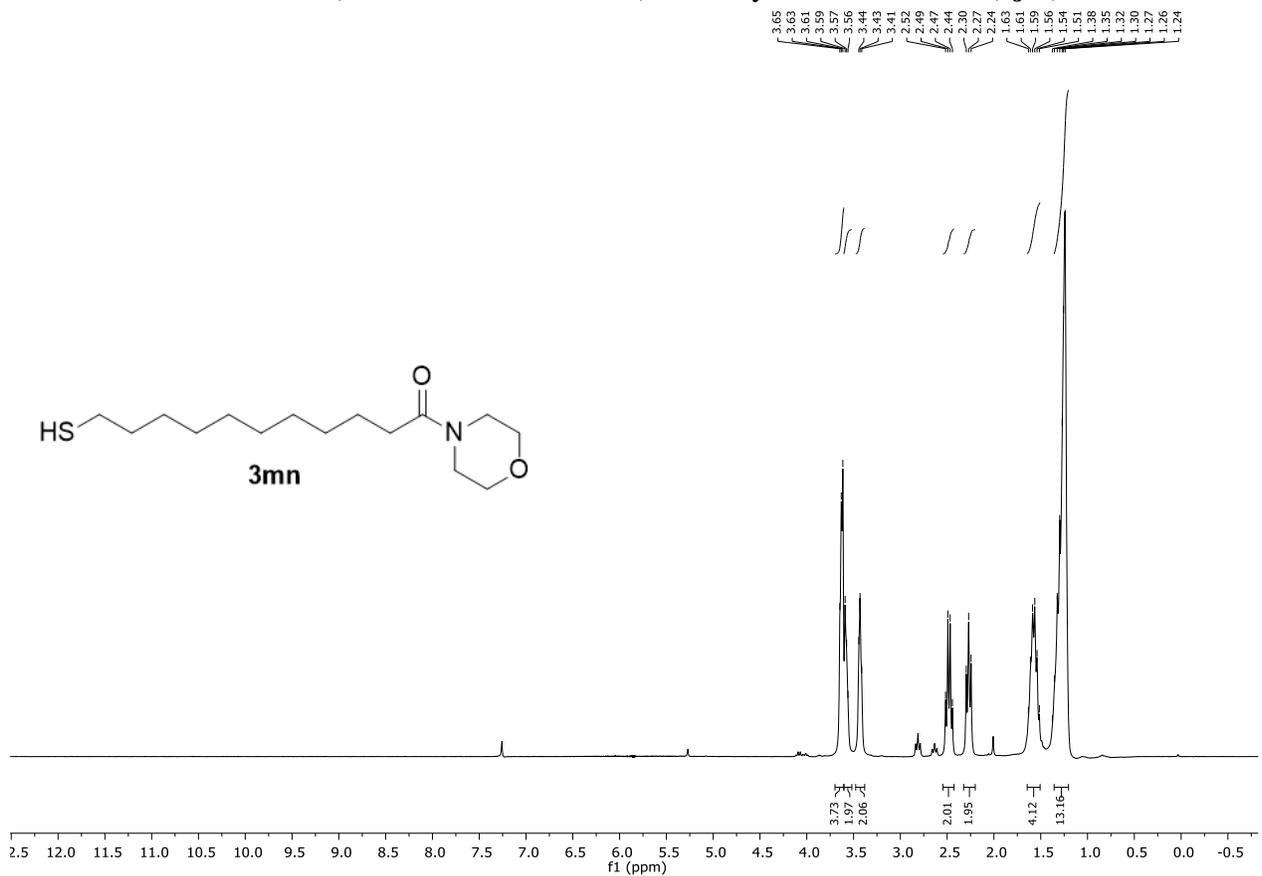




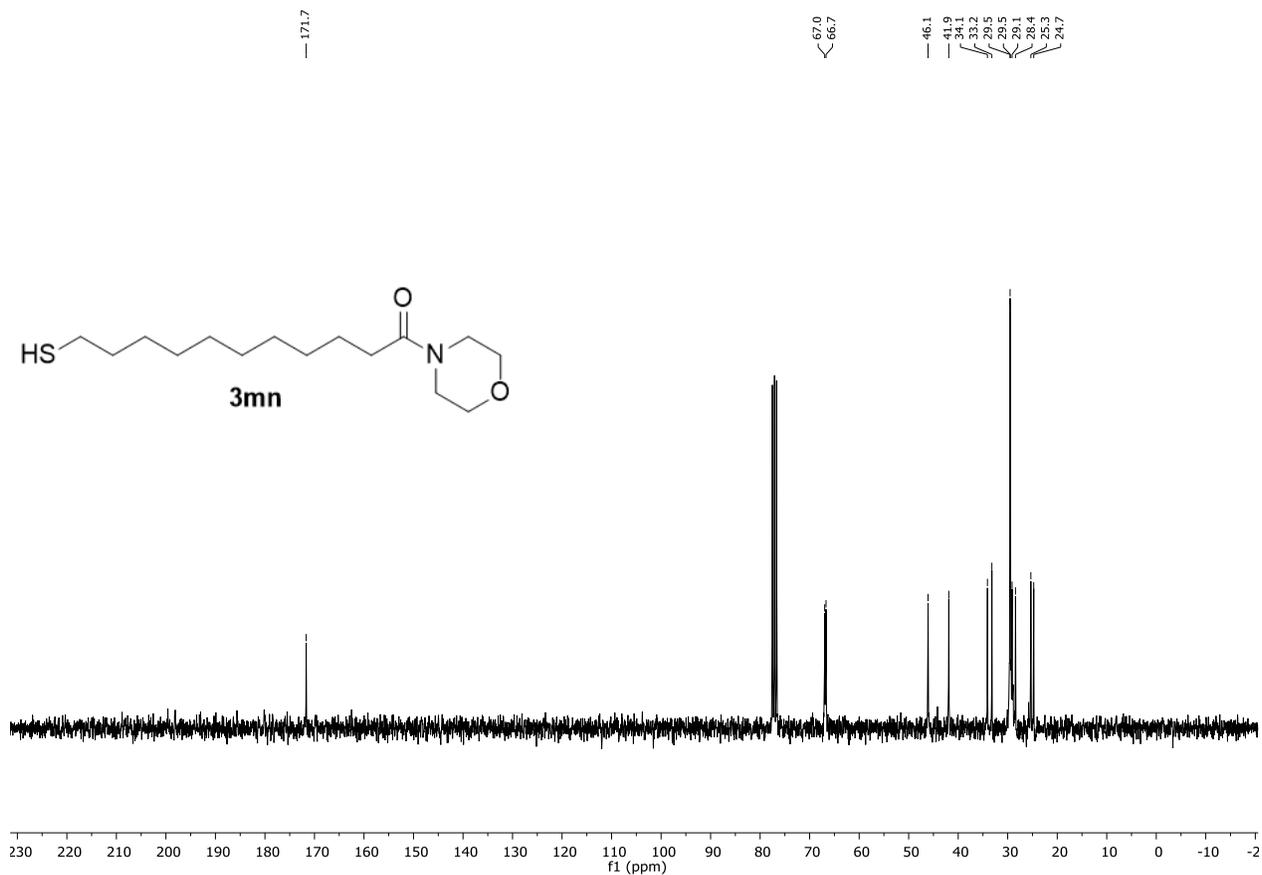
¹H NMR (300 MHz, Chloroform-*d*) N-benzylisonicotinamide (**3jm**)



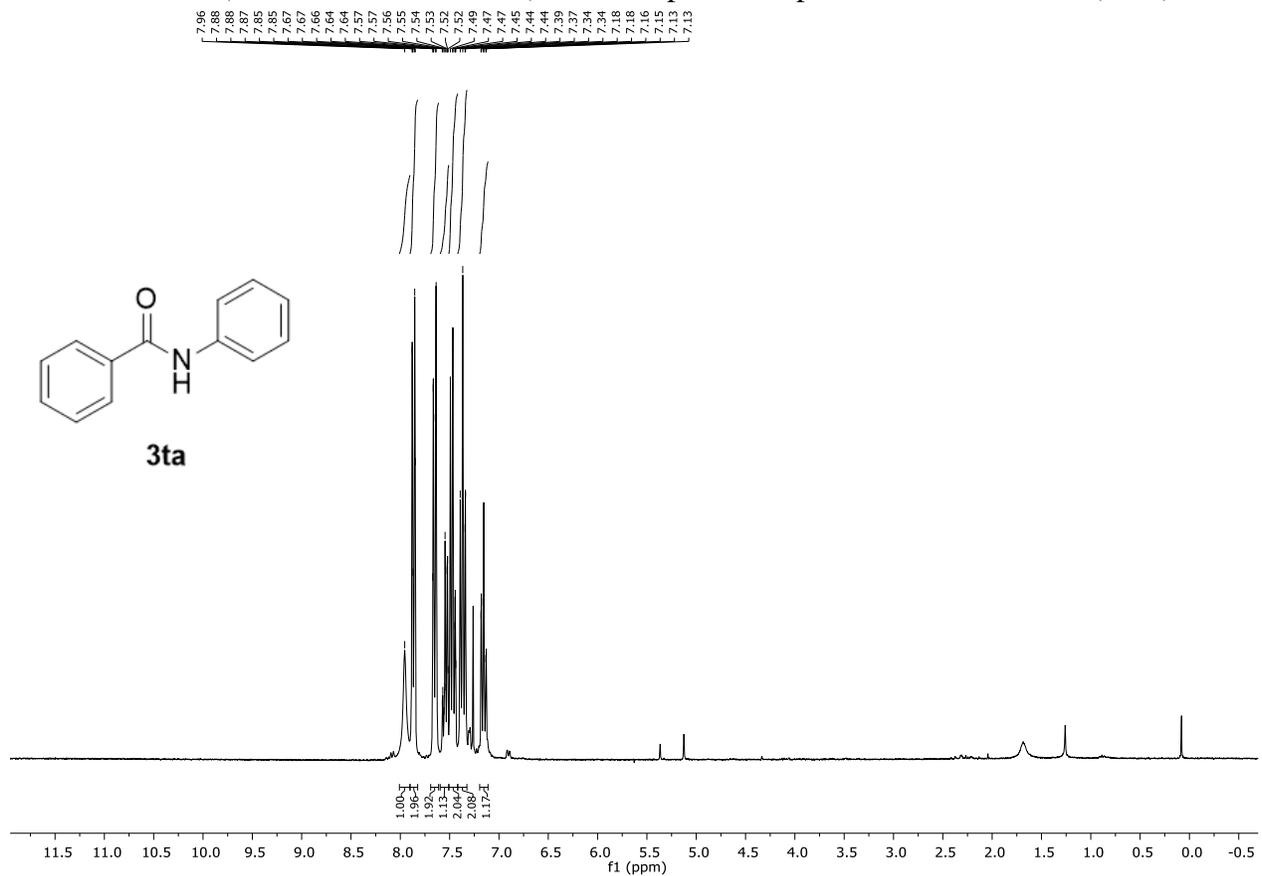
¹³C NMR (75 MHz, Chloroform-*d*) N-benzylisonicotinamide (**3jm**)



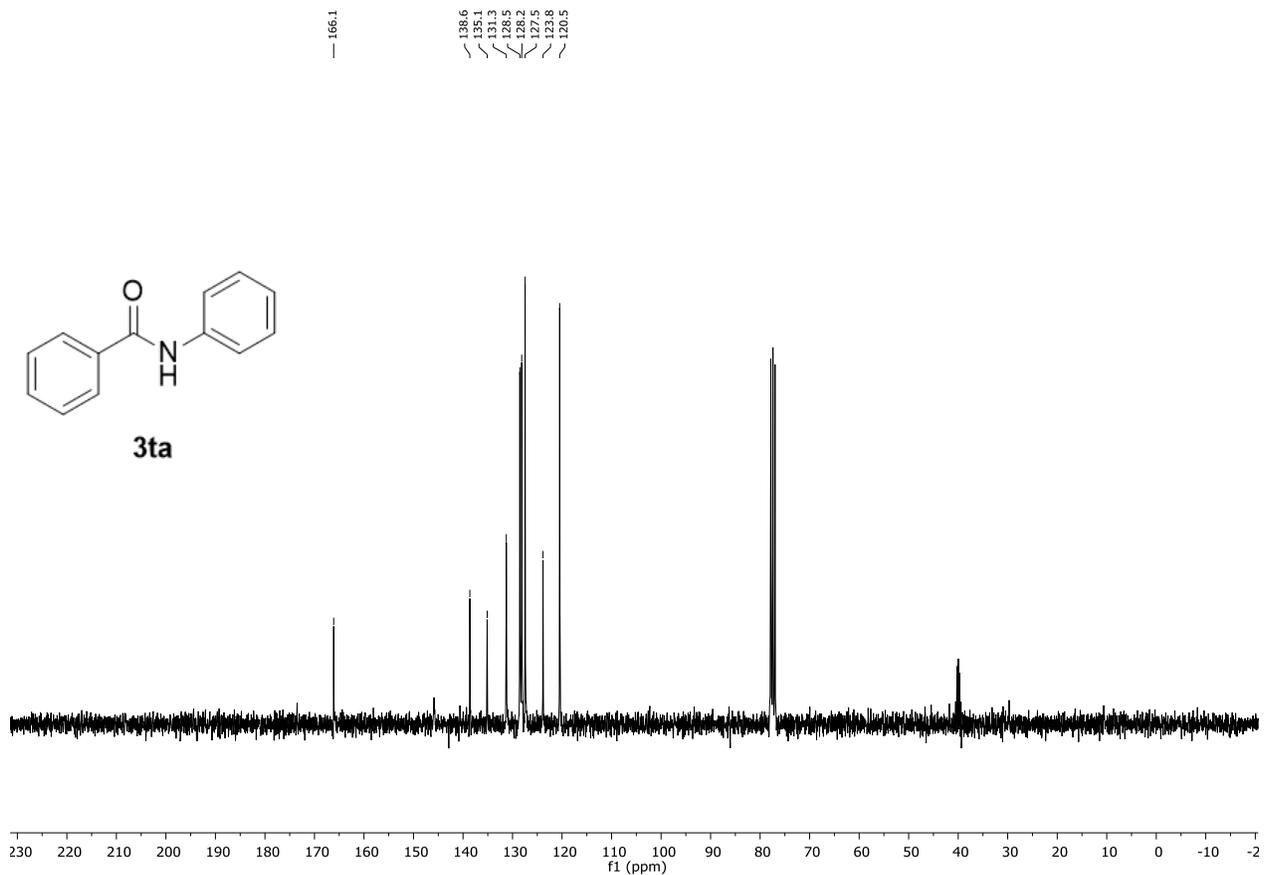
¹H NMR (300 MHz, Chloroform-*d*) 11-mercapto-1-morpholinoundecan-1-one (**3mn**)



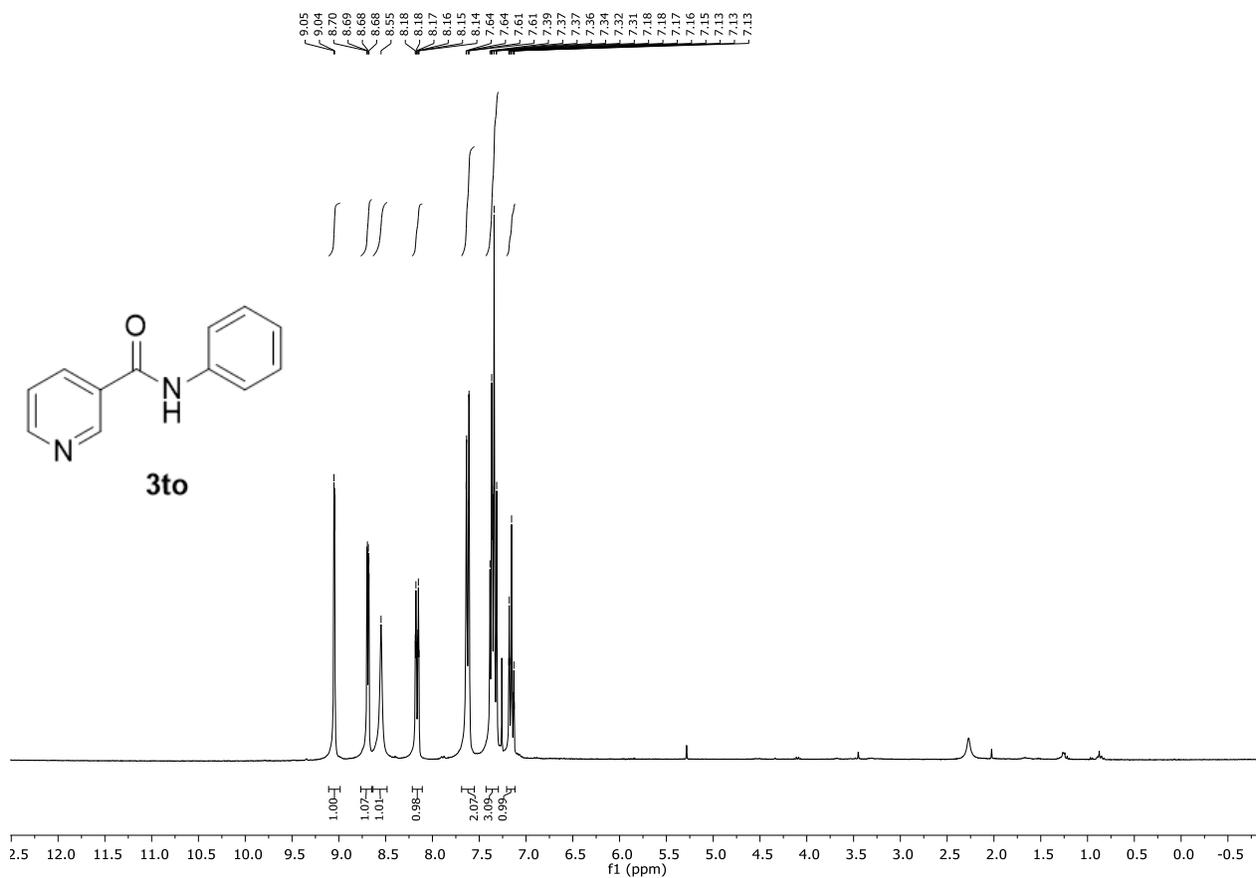
¹³C NMR (75 MHz, Chloroform-*d*) 11-mercapto-1-morpholinoundecan-1-one (**3mn**)



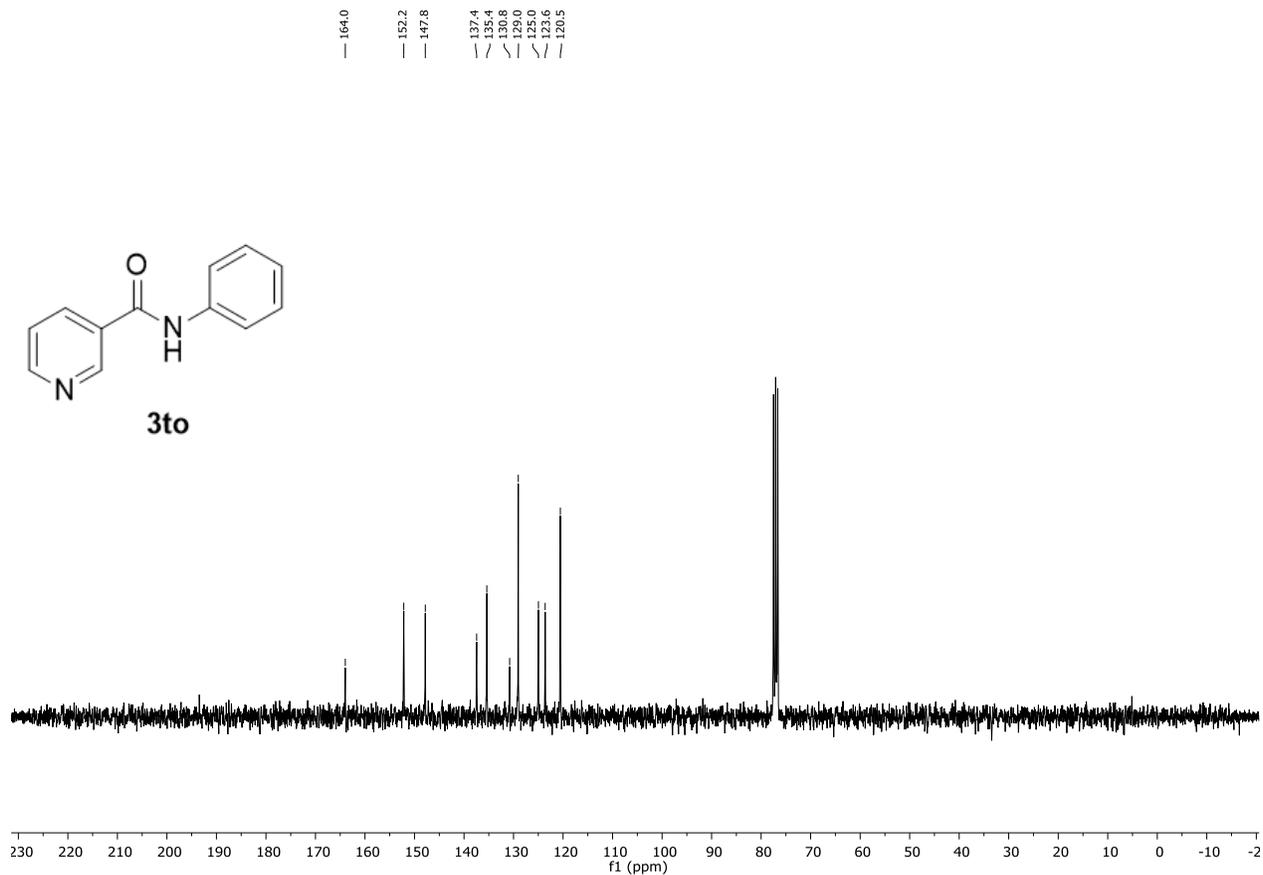
¹H NMR (300 MHz, Chloroform-*d*) N-phenylbenzamide (**3ta**)



^{13}C NMR (75 MHz, Chloroform-*d*) N-phenylbenzamide (3ta)

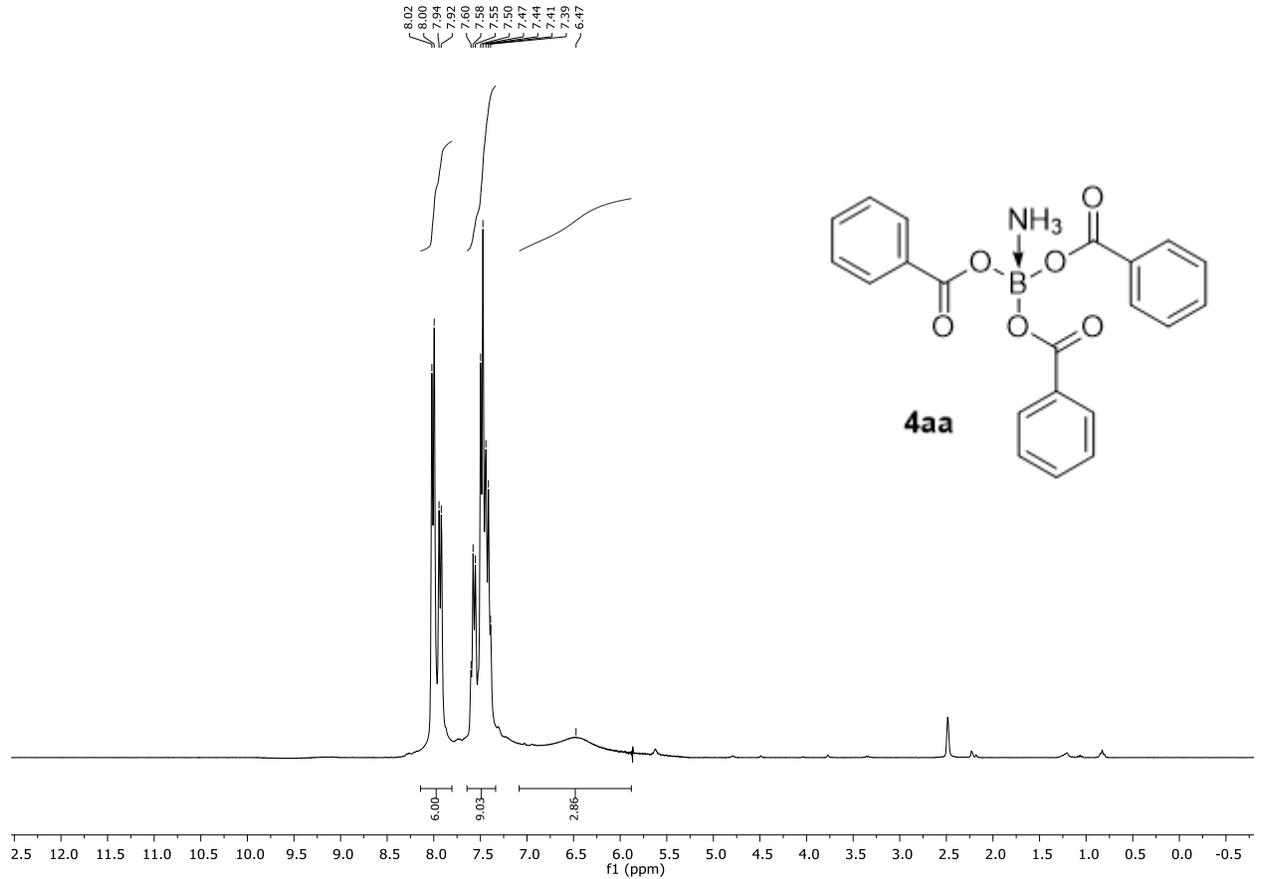


^1H NMR (300 MHz, Chloroform-*d*) N-phenylnicotinamide (3to)



¹³C NMR (75 MHz, Chloroform-*d*) N-phenylnicotinamide (**3to**)

Spectra from mechanistic studies:



¹H NMR (300 MHz, DMSO-*d*₆) Ammonia-tribenzyloxyborane (**4aa**)

