Tropylium Tetrafluoroborate Promoted Hydroboration of Nitriles, Imines and Amides

Son Hoai Doan,[a] Thanh Vinh Nguyen*[a]

[a]School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

Correspondence: TVN (t.v.nguyen@unsw.edu.au)

Supporting Information

Table of Contents

General methods

Compounds purchased commercially were used without further purification, unless otherwise stated. Solvents for analysis were used after SPS purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed using aluminium plates pre-coated with silica gel 60 F_{254} (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvent systems used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using an Avance III HD 400 (400.1 MHz, ^{1}H; 100.6 MHz, ^{13}C; 376.5 MHz ^{19}F) or an Avance III 300 (300.13 MHz, ^{1}H; 75.5 MHz, ^{13}C; 282.4 MHz, ^{19}F) at the Mark Wainwright Analytical Centre at the University of New South Wales Sydney. ^{1}H NMR data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.28 ppm for deuterated chloroform, δ 2.51 for deuterated dimethyl sulfoxide) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, sep = septet, br = broad, m = multiplet), coupling constant (J in Hz) and integration (number of protons). ^{13}C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.07 ppm for the central peak of deuterated chloroform and δ 39.97 ppm for the central peak of deuterated dimethyl sulfoxide).

Images of compounds were obtained with an Apple iPhone 6 Plus. Infrared spectra were obtained on a ThermoNicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the university of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.

Optimization studies of the hydroboration of nitrile 1a

Table S1. Screening of reaction conditions.[a]

Entry	Temperature (°C)	Catalyst amount (mol%)	Nitrile/ HBpin	Solvent	Yield[b] (%)
1	RT	10	1:2	Neat	nr
2	50	10	1:2	Neat	63
3	70	10	1:2	Neat	93
4	70	10	1:2	THF	21
5	70	10	1:2	Toluene	41
6	70	10	1:2	Hexane	46
7	70	10	1:2	DCE	37
8	70	10	1:2	C_6D_6	18
9	70	0	1:2	Neat	nr
10	70	5	1:2	Neat	78
11	70	15	1:2	Neat	96
12	70	10	1:1	Neat	45
13	70	10	1:1.5	Neat	72
14	70	10	1:2.1	Neat	95
15	**70**	**10**	**1:2.2**	**Neat**	**97**
16	70	10	1:3	Neat	98

[a] Reaction conditions: benzonitrile **1a** (1.0 mmol), HBpin and tropylium tetrafluoroborate; 18h.

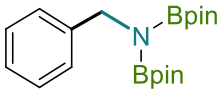
[b] Yield determined by integration of ^{1}H NMR spectrum of reaction crude mixture with mesitylene as internal standard.

General procedure 1 for hydroboration of nitriles

Tropylium tetrafluoroborate (0.1 mmol, 10 mol%), nitrile **1** (1.0 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane HBpin (2.2 mmol, 2.2 equiv) were sealed in a 4 mL vial equipped with a magnetic stir bar. The reaction mixture was stirred at 70 °C for 18 – 24 hours depending on the nature of the starting materials. After the reaction was completed, the excess of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and by-products were evaporated under reduced pressure to obtain the corresponding *N*,*N*-diborylamines, which were further purified by crystallization in pentane at –35 °C under argon atmosphere.

Characterisation data of *N*,*N*-diboryl amines 2

***N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2a**): Prepared by the general procedure **1** from benzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2a** as a white solid (348 mg, 97% yield of crude product; 305 mg, 85% yield of recrystallized product).



2a

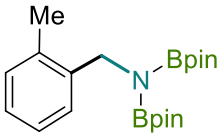
^{1}H NMR (400 MHz, C_6D_6) δ 7.53 (d, J = 7.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.12 – 7.08 (m, 1H), 4.56 (s, 2H), 1.01 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 143.3, 127.9, 127.6 126.2, 82.2, 47.5, 24.3 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.8 ppm;

The NMR data closely match those reported in literature[1].

4,4,5,5-tetramethyl-*N*-(2-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (compound **2b**): Prepared by the general procedure **1** from 2-methylbenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2b** as a white solid (369 mg, 99% yield of crude product; 321 mg, 86% yield of recrystallized product).



2b

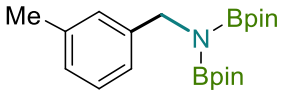
^{1}H NMR (400 MHz, C_6D_6) δ 7.56 (d, J = 7.6 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.06 – 7.02 (m, 1H), 6.97 – 6.95 (m, 1H), 4.52 (s, 2H), 2.10 (s, 3H), 1.00 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 140.7, 134.8, 129.7, 125.8, 125.6, 125.3, 82.1, 44.9, 24.2, 18.6 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.8 ppm;

The NMR data closely match those reported in literature[2].

4,4,5,5-tetramethyl-*N*-(3-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (compound **2c**): Prepared by the general procedure **1** from 3-methylbenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2c** as a white solid (369 mg, 99% yield of crude product; 313 mg, 84% yield of recrystallized product).



2c

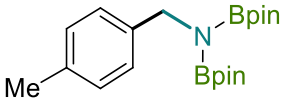
^{1}H NMR (400 MHz, C_6D_6) δ 7.29 – 7.22 (m, 2H), 7.15 – 7.07 (m, 1H), 6.93 – 6.87 (m, 1H), 4.36 (s, 2H), 2.14 (s, 3H), 0.99 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 143.1, 136.9, 132.1, 128.4, 126.9, 124.6, 82.0, 47.2, 24.3, 21.1 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.0 ppm;

The NMR data closely match those reported in literature[2].

4,4,5,5-tetramethyl-*N*-(4-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (compound **2d**): Prepared by the general procedure **1** from 4-methylbenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2d** as a white solid (370 mg, 99% yield of crude product; 336 mg, 90% yield of recrystallized product).



2d

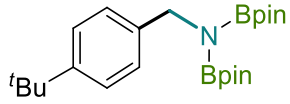
^{1}H NMR (400 MHz, C_6D_6) δ 7.45 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 4.52 (s, 2H), 2.14 (s, 3H), 1.02 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 140.4, 135.3, 128.6, 127.6, 82.1, 47.1, 24.3, 20.7 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.9 ppm;

The NMR data closely match those reported in literature[1].

***N*-(4-*tert*-butylbenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2e**): Prepared by the general procedure **1** from 4-*tert*-butylbenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2e** as a white solid (411 mg, 99% yield of crude product; 345 mg, 83% yield of recrystallized product).



2e

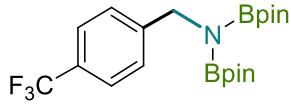
^{1}H NMR (400 MHz, C_6D_6) δ 7.43 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.47 (s, 2H), 1.20 (s, 9H), 1.00 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 148.5, 140.3, 131.6, 127.4, 124.7, 82.0, 47.0, 34.0, 31.2, 24.3 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 27.0 ppm;

The NMR data closely match those reported in literature[1].

4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolan-2-amine (compound **2f**): Prepared by the general procedure **1** from 4-(trifluoromethyl)benzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2f** as a white solid (423 mg, 99% yield of crude product; 350 mg, 82% yield of recrystallized product).



2f

^{1}H NMR (400 MHz, C_6D_6) δ 7.39 (s, 4H), 4.40 (s, 2H), 0.99 (s, 24H) ppm;

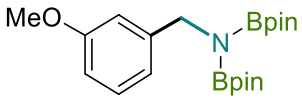
^{13}C NMR (101 MHz, C_6D_6) δ 147.3, 132.1, 127.8, 124.7 (q, J = 3.9 Hz), 82.3, 47.0, 24.2 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.4 ppm;

^{19}F NMR (376 MHz, C_6D_6) δ -62.0 ppm;

The NMR data closely match those reported in literature[3].

***N*-(3-methoxybenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2g**): Prepared by the general procedure **1** from 3-methoxybenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2g** as a white solid (268 mg, 69% yield of crude product; 225 mg, 58% yield of recrystallized product).



2g

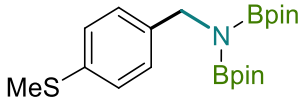
^{1}H NMR (400 MHz, C_6D_6) δ 7.16 – 7.07 (m, 3H), 6.71 – 6.67 (m, 1H), 4.46 (s, 2H), 3.43 (s, 3H), 1.00 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 159.8, 144.8, 128.8, 119.9, 113.1, 112.0, 82.1, 54.3, 47.4, 24.3 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.4 ppm;

The NMR data closely match those reported in literature[2].

4,4,5,5-tetramethyl-*N*-(4-(methylthio)benzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (compound **2h**): Prepared by the general procedure **1** from 4-(methylthio)benzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2h** as a white solid (397 mg, 98% yield of crude product; 340 mg, 84% yield of recrystallized product).



2h

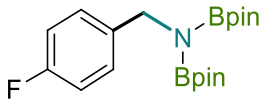
^{1}H NMR (400 MHz, C_6D_6) δ 7.37 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 4.41 (s, 2H), 2.06 (s, 3H), 1.00 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 140.3, 136.3, 128.3, 126.5, 82.2, 46.9, 24.3, 15.4 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.8 ppm;

The NMR data closely match those reported in literature[1].

***N*-(4-fluorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2i**): Prepared by the general procedure **1** from 4-fluorobenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2i** as a white solid (375 mg, 99% yield of crude product; 333 mg, 88% yield of recrystallized product).



2i

^{1}H NMR (400 MHz, C_6D_6) δ 7.33 – 7.29 (m, 1H), 6.81 (t, J = 8.8 Hz, 2H), 4.29 (s, 2H), 0.98 (s, 24H) ppm;

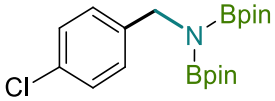
^{13}C NMR (101 MHz, C_6D_6) δ 160.4 (d, J = 244.2 Hz), 139.0, 129.2 (d, J = 8.0 Hz), 114.6 (d, J = 21.2 Hz), 82.1, 46.5, 24.2 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 25.9 ppm;

^{19}F NMR (376 MHz, C_6D_6) δ -117.0 ppm;

The NMR data closely match those reported in literature[1].

***N*-(4-fluorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2j**): Prepared by the general procedure **1** from 4-chlorobenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2j** as a white solid (390 mg, 99% yield of crude product; 315 mg, 80% yield of recrystallized product).



2j

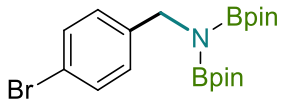
^{1}H NMR (400 MHz, C_6D_6) δ 7.27 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 4.33 (s, 2H), 0.99 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 141.8, 131.9, 129.1, 128.0, 82.2, 46.7, 24.2 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.3 ppm;

The NMR data closely match those reported in literature[2].

***N*-(4-bromobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2k**): Prepared by the general procedure **1** from 4-bromobenzonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2k** as a white solid (428 mg, 98% yield of crude product; 376 mg, 86% yield of recrystallized product).



2k

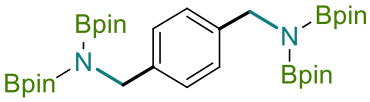
^{1}H NMR (400 MHz, C_6D_6) δ 7.27 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 4.31 (s, 2H), 0.99 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 142.3, 131.0, 129.5, 120.1, 82.2, 46.7, 24.3 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.4 ppm;

The NMR data closely match those reported in literature[1].

***N*,*N*′-(1,4-phenylenebis(methylene))bis(4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine)** (compound **2l**): Prepared by the general procedure **1** from terephthalonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2l** as a white solid (608 mg, 95% yield of crude product; 486 mg, 76% yield of recrystallized product).



2l

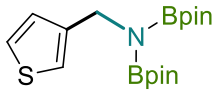
^{1}H NMR (400 MHz, C_6D_6) δ 7.58 (s, 4H), 4.57 (s, 4H), 1.01 (s, 48H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 141.3, 127.5, 82.1, 47.3, 24.3 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 27.0 ppm;

The NMR data closely match those reported in literature[1].

4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(thiophen-3-ylmethyl)-1,3,2-dioxaborolan-2-amine (compound **2m**): Prepared by the general procedure **1** from thiophene-3-carbonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2m** as a white solid (362 mg, 99% yield of crude product; 296 mg, 81% yield of recrystallized product).



2m

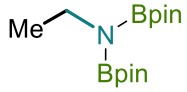
^{1}H NMR (400 MHz, C_6D_6) δ 7.24 – 7.21 (m, 2H), 7.07 – 7.04 (m, 1H), 4.47 (s, 2H), 1.07 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 144.3, 127.9, 124.7, 121.1, 82.1, 42.5, 24.3 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.4 ppm;

The NMR data closely match those reported in literature[1].

***N*-ethyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2n**): Prepared by the general procedure **1** from acetonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2n** as a white solid (291 mg, 98% yield of crude product; 205 mg, 69% yield of recrystallized product).



2n

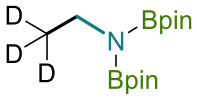
^{1}H NMR (400 MHz, C_6D_6) δ 3.33 – 3.22 (m, 2H), 1.22 – 1.12 (m, 3H), 1.01 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 81.6, 38.5, 24.3, 18.6 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.1 ppm;

The NMR data closely match those reported in literature[3].

***N*-(ethyl-2,2,2-d$_3$)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2o**): Prepared by the general procedure **1** from acetonitrile-d$_3$ and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2o** as a white solid (285 mg, 95% yield of crude product; 222 mg, 74% yield of recrystallized product).



2o

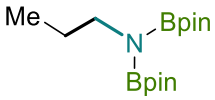
^{1}H NMR (400 MHz, C$_6$D$_6$) δ 3.34 (s, 2H), 1.03 (s, 24H) ppm;

^{13}C NMR (101 MHz, C$_6$D$_6$) δ 81.7, 38.4, 24.3, 18.1 – 17.1 (m, 1C) ppm;

^{11}B NMR (128 MHz, C$_6$D$_6$) δ 27.1 ppm;

The NMR data closely match those reported in literature[4].

4,4,5,5-tetramethyl-*N*-propyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (compound **2p**): Prepared by the general procedure **1** from propiononitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2p** as a white solid (298 mg, 96% yield of crude product; 230 mg, 74% yield of recrystallized product).



2p

^{1}H NMR (400 MHz, C$_6$D$_6$) δ 3.28 (t, J = 8.0 Hz, 2H), 1.60 (sext, J = 8.0 Hz, 2H), 1.03 (s, 24H), 0.86 (t, J = 8.0 Hz, 3H) ppm;

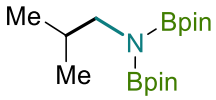
^{13}C NMR (101 MHz, C$_6$D$_6$) δ 81.7, 45.6, 26.3, 24.3, 11.1 ppm;

^{11}B NMR (128 MHz, C$_6$D$_6$) δ 26.0 ppm;

The NMR data closely match those reported in literature[1].

***N*-isobutyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2q**): Prepared by the general procedure **1** from

isobutyronitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2q** as a white solid (315 mg, 97% yield of crude product; 221 mg, 68% yield of recrystallized product).



2q

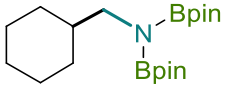
^{1}H NMR (400 MHz, C_6D_6) δ 3.12 (t, J = 8.0 Hz, 2H), 1.85 (sept, J = 8.0 Hz, 1H), 1.03 (s, 24H), 0.90 (t, J = 8.0 Hz, 6H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 81.7, 51.2, 30.7, 24.3, 19.9 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.2 ppm;

The NMR data closely match those reported in literature[1].

***N*-(cyclohexylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine** (compound **2r**): Prepared by the general procedure **1** from cyclohexanecarbonitrile and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **2r** as a white solid (339 mg, 93% yield of crude product; 284 mg, 78% yield of recrystallized product).



2r

^{1}H NMR (400 MHz, C_6D_6) δ 3.23 (d, J = 8.0 Hz, 2H), 1.82 (d, J = 8.0 Hz, 2H), 1.71 – 1.56 (m, 5H), 1.23 – 1.13 (m, 4H), 1.06 (s, 24H) ppm;

^{13}C NMR (101 MHz, C_6D_6) δ 81.8, 50.0, 40.5, 30.7, 26.8, 26.2, 24.3 ppm;

^{11}B NMR (128 MHz, C_6D_6) δ 26.5 ppm;

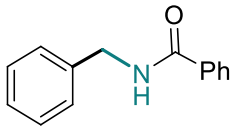
The NMR data closely match those reported in literature[1].

General procedure 2 for the one-pot formation of amides 3

After the completion of the nitrile hydroboration using our optimized protocol (general procedure 1, 1.0 mmol nitrile **1**), toluene (1.0 mL) was added to the obtained reaction mixture containing *N*,*N*-diborylamines and benzoic acid (1.0 mmol) or 2,2,2-trifluoroacetic acid (1.0 mmol) was added to this solution. The resulting reaction mixture was heated at 120 °C for 24 hours, then concentrated under reduced pressure and purified by column chromatography (silica-gel, ethyl acetate/hexanes) to give amide **3**.

Characterisation data of amides 3

***N*-benzylbenzamide** (compound **3a**): Prepared by the general procedure **2** from benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3a** as a white solid (181 mg, 86% yield).



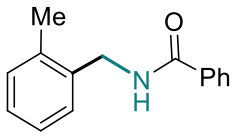
3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 5.6 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.35 – 7.28 (m, 5H), 6.88 (s, 1H), 4.61 (d, J = 5.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 138.3, 134.4, 131.5, 128.7, 128.5, 127.8, 127.5, 127.0, 44.0 ppm;

The NMR data closely match those reported in literature[5].

***N*-(2-methylbenzyl)benzamide** (compound **3b**): Prepared by the general procedure **2** from 2-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3b** as a white solid (202 mg, 90% yield).



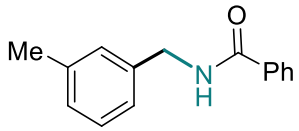
3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.41 (m, 2H), 7.33 – 7.28 (m, 1H), 7.27 – 7.19 (m, 3H), 6.46 (s, 1H), 4.63 (d, J = 5.6 Hz, 2H), 2.38 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 136.5, 135.8, 134.3, 131.5, 130.6, 128.6, 128.5, 127.8, 127.0, 126.2, 42.3, 19.0 ppm;

The NMR data closely match those reported in literature[6].

***N*-(3-methylbenzyl)benzamide** (compound **3c**): Prepared by the general procedure **2** from 3-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3c** as a white solid (211 mg, 94% yield).



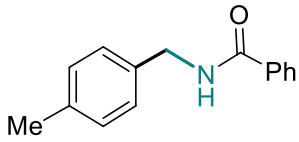
3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.40 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.11 (m, 3H), 6.70 (s, 1H), 4.60 (d, J = 5.6 Hz, 2H), 2.36 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 138.4, 138.2, 134.4, 131.5, 128.6, 128.5, 128.3, 127.0, 124.9, 44.1, 21.4 ppm;

The NMR data closely match those reported in literature[6].

***N*-(4-methylbenzyl)benzamide** (compound **3d**): Prepared by the general procedure **2** from 4-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3d** as a white solid (214 mg, 95% yield).



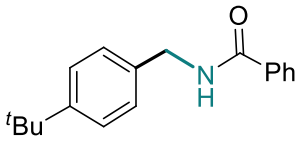
3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.54 – 7.41 (m, 3H), 7.25 (d, J = 10.0 Hz, 2H), 7.17 (d, J = 10.8 Hz, 2H), 6.44 (s, 1H), 4.61 (d, J = 7.6 Hz, 2H), 2.37 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 137.3, 135.1, 134.4, 131.5, 129.4, 128.5, 127.9, 126.9, 43.9, 21.1 ppm;

The NMR data closely match those reported in literature[5].

***N*-(4-*tert*-butylbenzyl)benzamide** (compound **3e**): Prepared by the general procedure **2** from 4-*tert*-butylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3e** as a white solid (248 mg, 93% yield).



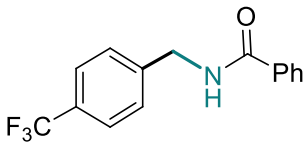
3e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.38 (m, 4H), 7.30 (d, J = 8.4 Hz, 2H), 6.74 (s, 1H), 4.61 (d, J = 5.6 Hz, 2H), 1.35 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 150.5, 135.2, 134.4, 131.4, 128.5, 127.7, 127.0, 125.6, 43.8, 34.5, 31.3 ppm;

The NMR data closely match those reported in literature[5].

***N*-(4-(trifluoromethyl)benzyl)benzamide** (compound **3f**): Prepared by the general procedure **2** from 4-(trifluoromethyl)benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3f** as a white solid (226 mg, 81% yield).



3f

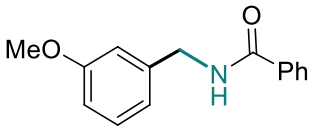
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.48 – 7.40 (m, 4H), 6.87 (s, 1H), 4.67 (d, J = 7.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 142.4, 133.9, 131.8, 129.5 (q, J = 52.8 Hz), 128.6, 127.9, 127.0, 125.5 (q, J = 5.0 Hz), 122.2 (q, J = 363.3 Hz), 43.5 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5 ppm;

The NMR data closely match those reported in literature[5].

***N*-(3-methoxybenzyl)benzamide** (compound **3g**): Prepared by the general procedure **2** from 3-methoxybenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3g** as a light grey solid (159 mg, 66% yield).



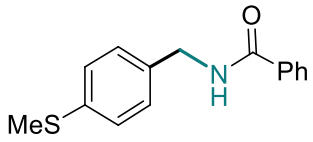
3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 7.30 – 7.26 (m, 1H), 6.96 – 6.93 (m, 1H), 6.92 – 6.90 (m, 1H), 6.84 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 6.61 (s, 1H), 4.62 (d, J = 5.6 Hz, 2H), 3.81 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 159.9, 139.8, 134.3, 131.5, 129.8, 128.5, 127.0, 120.1, 113.5, 113.0, 55.2, 44.0 ppm;

The NMR data closely match those reported in literature[6].

***N*-(4-(methylthio)benzyl)benzamide** (compound **3h**): Prepared by the general procedure **2** from 4-(methylthio)benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3h** as a white solid (229 mg, 89% yield).



3h

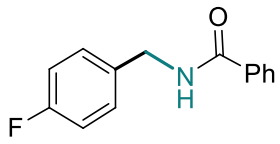
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.41 (m, 2H), 7.29 – 7.23 (m, 4H), 6.62 (s, 1H), 4.58 (d, J = 5.6 Hz, 2H), 2.48 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 137.8, 135.1, 134.3, 131.5, 128.6, 128.4, 126.9, 43.6, 15.9 ppm;

ESI-HRMS: calcd for $C_{15}H_{15}NOSNa^+$: m/z = 280.0767, found: m/z = 280.0759;

FTIR (neat): 3301, 2922, 1637, 1578, 1528, 1490, 1426, 1357, 1291, 1184, 1154 cm^{-1}.

***N*-(4-fluorobenzyl)benzamide** (compound **3i**): Prepared by the general procedure **2** from 4-fluorobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3i** as a white solid (195 mg, 85% yield).



3i

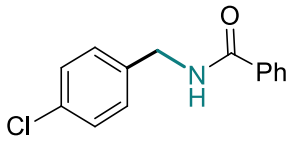
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.36 (m, 2H), 7.29 – 7.25 (m, 2H), 7.03 – 6.96 (m, 2H), 4.54 (d, J = 8.0 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 160.5 (d, J = 328.4 Hz), 134.2, 134.1 (d, J = 4.4 Hz), 131.6, 129.4 (d, J = 10.8 Hz), 128.5, 127.0, 115.3 (d, J = 28.7 Hz), 43.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0 ppm;

The NMR data closely match those reported in literature[7].

***N*-(4-chlorobenzyl)benzamide** (compound **3j**): Prepared by the general procedure **2** from 4-chlorobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3j** as a white solid (206 mg, 84% yield).



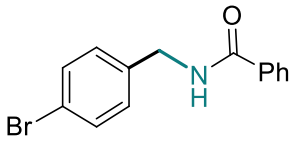
3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.30 – 7.24 (m, 4H), 6.88 (s, 1H), 4.56 (d, J = 6.0 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 136.9, 134.1, 133.2, 131.6, 129.1, 128.8, 128.6, 127.0, 43.3 ppm;

The NMR data closely match those reported in literature[5].

***N*-(4-bromobenzyl)benzamide** (compound **3k**): Prepared by the general procedure **2** from 4-bromobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3k** as a white solid (231 mg, 80% yield).



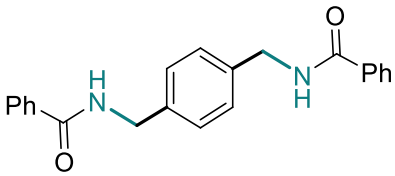
3k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.41 (m, 4H), 7.20 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 4.57 (d, J = 5.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 137.3, 134.1, 131.8, 131.7, 129.5, 128.6, 127.0, 121.4, 43.3 ppm;

The NMR data closely match those reported in literature[6].

***N,N'*-(1,4-phenylenebis(methylene))dibenzamide** (compound **3l**): Prepared by the general procedure **2** from terephthalonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3l** as a white solid (193 mg, 56% yield).



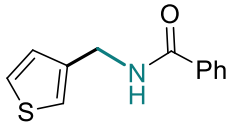
3l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.6 Hz, 4H), 7.51 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 8.0 Hz, 4H), 7.36 (s, 4H), 6.48 (s, 2H), 4.65 (d, J = 6.4 Hz, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 137.6, 134.3, 131.6, 130.1, 128.6, 128.3, 126.9, 43.8 ppm;

The NMR data closely match those reported in literature[7].

***N*-(thiophen-3-ylmethyl)benzamide** (compound **3m**): Prepared by the general procedure **2** from thiophene-3-carbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3m** as a light grey solid (206 mg, 95% yield).



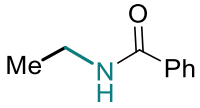
3m

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.41 (m, 2H), 7.31 (dd, J_1 = 5.2 Hz, J_2 = 3.2 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.09 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 6.63 (s, 1H), 4.64 (d, J = 5.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 139.0, 134.3, 131.5, 128.5, 127.4, 127.0, 126.4, 122.5, 39.2 ppm;

The NMR data closely match those reported in literature[6].

***N*-ethylbenzamide** (compound **3n**): Prepared by the general procedure **2** from acetonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3n** as a white solid (80 mg, 54% yield).



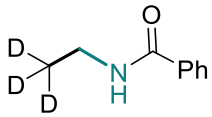
3n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.2 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.46 – 7.41 (m, 2H), 6.29 (s, 1H), 3.48 (p, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 134.8, 131.3, 128.5, 126.8, 34.9, 14.9 ppm;

The NMR data closely match those reported in literature[8].

***N*-(ethyl-2,2,2-d$_3$)benzamide** (compound **3o**): Prepared by the general procedure **2** from acetonitrile-d$_3$, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3o** as a white solid (88 mg, 58% yield).



3o

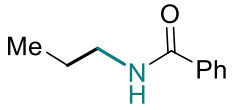
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.53 – 7.47 (m, 1H), 7.46 – 7.42 (m, 2H), 6.21 (s, 1H), 3.50 (d, J = 6.0 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 134.8, 131.3, 128.5, 126.8, 34.7, 14.4 – 13.6 (m, 1C) ppm;

ESI-HRMS: calcd for $C_9H_8D_3NONa^+$: m/z = 175.0921, found: m/z = 175.0918;

FTIR (neat): 3070.8, 2936.6, 2241.4, 1638.8, 1578.1, 1536.0, 1490.2, 1307.2, 1091.3, 906.8, 729.3 cm^{-1}.

***N*-propylbenzamide** (compound **3p**): Prepared by the general procedure **2** from propiononitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3p** as a white solid (127 mg, 78% yield).



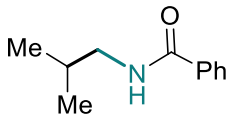
3p

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.50 – 7.45 (m, 1H), 7.43 – 7.38 (m, 2H), 6.51 (s, 1H), 3.38 (q, J = 6.8 Hz, 2H), 1.59 (sext, J = 7.4 Hz, 2H), 0.95 (t, J = 7.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 134.8, 131.2, 128.4, 126.9, 41.7, 22.9, 11.4 ppm;

The NMR data closely match those reported in literature[9].

***N*-isobutylbenzamide** (compound **3q**): Prepared by the general procedure **2** from isobutyronitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3q** as a white solid (112 mg, 64% yield).



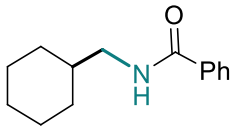
3q

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.52 – 7.47 (m, 1H), 7.45 – 7.41 (m, 2H), 6.38 (s, 1H), 3.27 (t, J = 6.4 Hz, 2H), 1.86 (sept, J = 6.8 Hz, 1H), 0.98 (d, J = 6.8 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 134.9, 131.3, 128.5, 126.8, 47.3, 28.6, 20.1 ppm;

The NMR data closely match those reported in literature[9].

***N*-(cyclohexylmethyl)benzamide** (compound **3r**): Prepared by the general procedure **2** from cyclohexanecarbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **3r** as a light grey solid (137 mg, 63% yield).



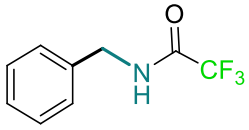
3r

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 2H), 6.45 (s, 1H), 3.28 (t, J = 6.4 Hz, 2H), 1.80 – 1.72 (m, 4H), 1.69 – 1.65 (m, 1H), 1.63 – 1.54 (m, 1H), 1.29 – 1.16 (m, 3H), 1.04 – 0.94 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 134.9, 131.2, 128.5, 126.9, 46.2, 38.0, 30.9, 26.4, 25.8 ppm;

The NMR data closely match those reported in literature[10].

***N*-benzyl-2,2,2-trifluoroacetamide** (compound **3s**): Prepared by the general procedure **2** from benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **3s** as a white solid (169 mg, 83% yield).



3s

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 3H), 7.33 – 7.28 (m, 2H), 7.15 (br, 1H), 4.50 (d, J = 5.6 Hz, 2H) ppm;

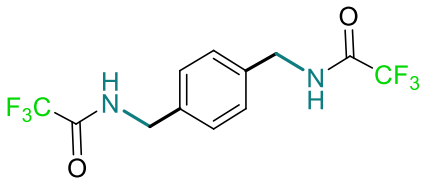
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 (q, J = 37.8 Hz), 135.9, 128.9, 128.2, 127.9, 111.6 (q, J = 288.6 Hz), 43.8 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.8 ppm;

The NMR data closely match those reported in literature[11].

***N,N'*-(1,4-phenylenebis(methylene))bis(2,2,2-trifluoroacetamide)** (compound **3w**): Prepared by the general procedure **2** from terephthalonitrile, 4,4,5,5-tetramethyl-1,3,2-

dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **3w** as a white solid (246 mg, 75% yield).



3w

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.99 (br, 2H), 7.27 (s, 4H), 4.38 (s, 4H) ppm;

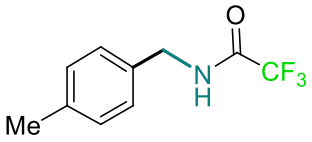
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 156.2 (q, J = 36.3 Hz), 137.0, 128.0, 112.1 (q, J = 289.2 Hz), 42.7 ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -74.3 ppm;

ESI-HRMS: calcd for $C_{12}H_{10}F_6N_2O_2Na^+$: m/z = 351.0539, found: m/z = 351.0531;

FTIR (neat): 3287, 3094, 1700, 1555, 1459, 1427, 1372, 1333, 1152 cm^{-1}.

2,2,2-trifluoro-*N*-(4-methylbenzyl)acetamide (compound **3t**): Prepared by the general procedure **2** from 4-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **3t** as a white solid (187 mg, 86% yield).



3t

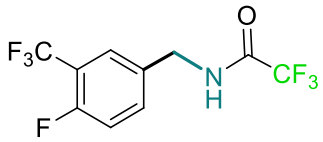
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 (s, 4H), 7.05 (br, 1H), 4.46 (d, J = 5.6 Hz, 2H), 2.38 (s, 3H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$) δ 156.7 (q, J = 37.2 Hz), 138.0, 132.9, 129.6, 127.9, 111.6 (q, J = 288.8 Hz), 43.6, 21.0 ppm;

^{19}F NMR (376 MHz, CDCl$_3$) δ -75.8 ppm;

The NMR data closely match those reported in literature[11].

2,2,2-trifluoro-*N*-(4-fluoro-3-(trifluoromethyl)benzyl)acetamide (compound **3x**): Prepared by the general procedure **2** from 4-fluoro-3-(trifluoromethyl)benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **3x** as a white solid (243 mg, 84% yield).



3x

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.20 (t, J = 9.4 Hz, 1H), 7.05 (br, 1H), 4.54 (d, J = 6.0 Hz, 2H) ppm;

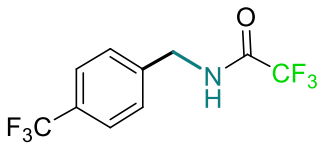
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (d, J = 258.4 Hz), 157.0 (q, J = 38.4 Hz), 133.5 (d, J = 8.8 Hz), 132.3 (d, J = 4.0 Hz), 126.8 – 126.7 (m), 119.3 – 118.2 (m), 118.1 (q, J = 273.4 Hz), 117.4 (d, J = 20.9 Hz), 111.4 (q, J = 288.5 Hz), 42.7 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7 (d, J = 12.4 Hz), -75.9, -114.9 – -115.0 (m) ppm;

ESI-HRMS: calcd for $C_{10}H_6F_7NONa^+$: m/z = 312.0229, found: m/z = 312.0230;

FTIR (neat): 3286, 3096, 1703, 1627, 1559, 1507, 1439, 1383, 1320, 1276, 1244, 1201, 1134 cm^{-1}.

2,2,2-trifluoro-*N*-(4-(trifluoromethyl)benzyl)acetamide (compound **3u**): Prepared by the general procedure **2** from 4-(trifluoromethyl)benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **3u** as a white solid (225 mg, 83% yield).



3u

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.34 (br, 1H), 4.54 (d, J = 6.4 Hz, 2H) ppm;

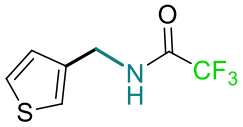
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (q, J = 37.6 Hz), 139.9, 129.9 (q, J = 32.6 Hz), 128.0, 125.7 (q, J = 3.8 Hz), 120.0 (q, J = 273.1 Hz), 111.5 (q, J = 288.5 Hz), 43.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8, -75.9 ppm;

ESI-HRMS: calcd for $C_{10}H_7F_6NONa^+$: m/z = 294.0324, found: m/z = 294.0322;

FTIR (neat): 3309, 1705, 1563, 1419, 1337, 1177, 1125, 1070 cm^{-1}.

2,2,2-trifluoro-*N*-(thiophen-3-ylmethyl)acetamide (compound **3y**): Prepared by the general procedure **2** from thiophene-3-carbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **3y** as a white solid (174 mg, 83% yield).



3y

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 1H), 7.22 – 7.21 (m, 1H), 7.07 (br, 1H), 7.03 (dd, J_1 = 5.2 Hz, J_2 = 1.0 Hz, 1H), 4.52 (d, J = 6.0 Hz, 2H) ppm;

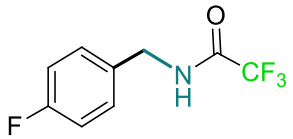
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (q, J = 37.4 Hz), 136.4, 127.1, 126.9, 123.4, 111.5 (q, J = 288.7 Hz), 38.9 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.8 ppm;

ESI-HRMS: calcd for $C_7H_6F_3NOSNa^+$: m/z = 232.0014, found: m/z = 232.0012;

FTIR (neat): 3297, 3108, 1704, 1560, 1354, 1271, 1174 cm^{-1}.

2,2,2-trifluoro-*N*-(4-fluorobenzyl)acetamide (compound **3v**): Prepared by the general procedure **2** from 4-fluorobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **3v** as a white solid (175 mg, 79% yield).



3v

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.16 (br, 1H), 7.07 – 7.01 (m, 2H), 4.46 (d, J = 6.4 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, J = 247.8 Hz), 156.8 (q, J = 37.2 Hz), 131.8 (d, J = 3.2 Hz), 129.6 (d, J = 8.2 Hz), 115.7 (d, J = 21.7 Hz), 111.5 (q, J = 288.6 Hz), 43.1 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.9, -113.8 ppm;

ESI-HRMS: calcd for $C_9H_7F_4NOH^+$: m/z = 222.0537, found: m/z = 222.0530;

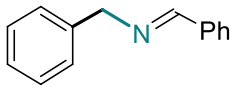
FTIR (neat): 3316, 1697, 1554, 1513, 1437, 1348, 1227, 1170 cm^{-1}.

General procedure 3 for the one-pot formation of secondary imines 4

After the completion of the nitrile hydroboration using our optimized protocol (general procedure 1, 1.0 mmol nitrile **1**), MeCN (0.5 mL) was added to the obtained reaction mixture containing *N*,*N*-diborylamines and benzaldehyde (1.0 mmol) was added to this solution. The resulting reaction mixture was heated at 50 °C for 3 hours, then concentrated under reduced pressure and purified by column chromatography (using a base-washed silica gel column by adding 2% Et_3N into the mixture of hexane and ethyl acetate) to afford the corresponding imine **4**.

Characterisation data of imines 4

***N*-benzylidene-1-phenylmethanamine** (compound **4a**): Prepared by the general procedure **3** from benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzaldehyde to give compound **4a** as a yellow oil (187 mg, 96% yield).



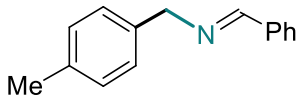
4a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.87 – 7.85 (m, 2H), 7.50 – 7.46 (m, 3H), 7.41 (d, J = 4.4 Hz, 4H), 7.36 – 7.30 (m, 1H), 4.89 (s, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 139.3, 136.2, 130.8, 128.6, 128.5, 128.3, 128.0, 127.0, 65.1 ppm;

The NMR data closely match those reported in literature[12].

***N*-benzylidene-1-*p*-tolylmethanamine** (compound **4b**): Prepared by the general procedure **3** from 4-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzaldehyde to give compound **4b** as a yellow oil (176 mg, 84% yield).



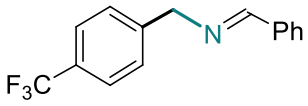
4b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.86 – 7.83 (m, 2H), 7.49 – 7.46 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 4.86 (s, 2H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 136.6, 136.3, 136.3, 130.7, 129.2, 128.6, 128.3, 128.0, 64.8, 21.1 ppm;

The NMR data closely match those reported in literature[13].

***N*-benzylidene-1-(4-(trifluoromethyl)phenyl)methanamine** (compound **4c**): Prepared by the general procedure **3** from 4-(trifluoromethyl)benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzaldehyde to give compound **4c** as a brown oil (239 mg, 91% yield).



4c

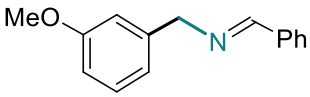
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.85 – 7.83 (m, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.49 – 7.44 (m, 3H), 4.90 (s, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 143.5, 135.9, 131.0, 129.0 (q, J = 32.3 Hz), 128.7, 128.3, 128.1, 125.3 (q, J = 3.8 Hz), 120.2 (q, J = 271.9 Hz), 64.4 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3 ppm;

The NMR data closely match those reported in literature[12].

***N*-benzylidene-1-(3-methoxyphenyl)methanamine** (compound **4d**): Prepared by the general procedure **3** from 3-methoxybenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzaldehyde to give compound **4d** as a brown oil (144 mg, 64% yield).



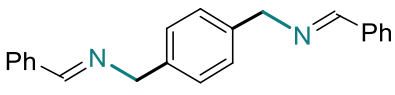
4d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.85 – 7.82 (m, 2H), 7.48 – 7.44 (m, 3H), 7.33 – 7.29 (m, 1H), 6.99 – 6.95 (m, 2H), 6.87 – 6.84 (m, 1H), 4.85 (s, 2H), 3.85 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 159.8, 140.9, 136.2, 130.8, 129.5, 128.6, 128.3, 120.3, 113.6, 112.4, 64.9, 55.2 ppm;

The NMR data closely match those reported in literature[12].

(*N*,*N'*)-1,1'-(1,4-phenylene)bis(*N*-benzylidenemethanamine) (compound **4e**): Prepared by the general procedure **3** from terephthalonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzaldehyde to give compound **4e** as a white solid (203 mg, 65% yield).



4e

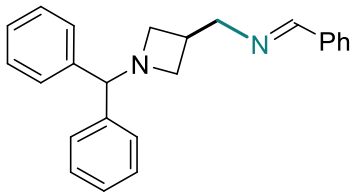
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 2H), 7.81 – 7.79 (m, 4H), 7.45 – 7.42 (m, 6H), 7.35 (s, 4H), 4.85 (s, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 138.0, 136.2, 132.7, 130.7, 128.5, 128.2, 128.2, 64.7 ppm;

ESI-HRMS: calcd for $C_{22}H_{20}N_2H^+$ m/z = 313.1699, found: m/z = 313.1694;

FTIR (neat): 1646.3, 1418.1, 1322.3, 1160.7, 1118.8, 1066.1, 1019.1, 818.1, 760.6, 693.2 cm^{-1}.

1-(1-benzhydrylazetidin-3-yl)-*N*-benzylidenemethanamine (compound **4f**): Prepared by the general procedure **3** from 1-benzhydrylazetidine-3-carbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzaldehyde to give compound **4f** as a yellow oil (163 mg, 48% yield).



4f

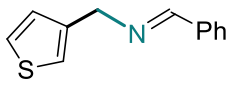
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.77 – 7.73 (m, 2H), 7.48 – 7.42 (m, 7H), 7.33 – 7.28 (m, 4H), 7.24 – 7.19 (m, 2H), 4.42 (s, 1H), 3.85 (dd, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 2H), 3.37 (t, J = 7.6 Hz, 2H), 2.97 (t, J = 6.8 Hz, 2H), 2.85 (sep, J = 6.8 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 142.4, 136.2, 130.6, 128.6, 128.4, 128.1, 127.5, 127.0, 78.2, 65.2, 57.4, 30.6 ppm;

ESI-HRMS: calcd for $C_{24}H_{24}N_2H^+$: m/z = 341.2012, found: m/z = 341.2004;

FTIR (neat): 3027.3, 2949.2, 2829.3, 1645.2, 1491.5, 1451.4, 1205.0, 1073.8, 1028.5, 907.6, 729.6, 690.5 cm^{-1}.

***N*-benzylidene-1-(thiophen-3-yl)methanamine** (compound **4g**): Prepared by the general procedure **3** from thiophene-3-carbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzaldehyde to give compound **4g** as a yellow oil (143 mg, 71% yield).



4g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.85 – 7.81 (m, 2H), 7.49 – 7.45 (m, 3H), 7.34 (dd, J_1 = 5.2 Hz, J_2 = 3.0 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.11 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1H), 4.88 (s, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 140.1, 136.1, 130.8, 128.6, 128.3, 127.4, 125.8, 121.6, 60.2 ppm;

ESI-HRMS: calcd for $C_{12}H_{11}NSH^+$: m/z = 202.0685, found: m/z = 202.0684;

FTIR (neat): 3097.2, 2169.3, 1698.9, 1644.5, 1451.6, 1320.3, 1155.4, 1077.0, 1026.6, 909.0, 855.2, 830.1, 779.5, 730.8, 693.4 cm^{-1}.

General procedure 4 for the four-step one-pot formation of secondary amines 5

General procedure 4.1 for the four-step one-pot formation of secondary amines via amidation pathway

After the completion of the nitrile hydroboration and amidation using our optimized protocol (general procedures 1 and 2, 1.0 mmol nitrile **1**), the obtained reaction mixture containing amides was put under vacuum to remove all the volatiles. Tropylium tetrafluoroborate (0.1 mmol, 10 mol%) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 mmol) were then added to this crude mixture. The resulting reaction mixture was then heated at 80 °C for 24-32 hours. After that, the reaction mixture was stirred with 4.0 mL of NaOH (2.0 M) and 4.0 mL of diethyl ether for 3 hours. The reaction mixture was subsequently partitioned between water and diethyl ether (2 x 10 mL). The combined ether phases containing corresponding reduced amines was treated with 4.0 mL of HCl (1.0 M), which led to the formation of a white precipitate. The white precipitate was filtered, washed with diethyl ether and then dried under reduced pressure to afford the corresponding amine hydrochloride salt **5**.

General procedure 4.2 for the four-step one-pot formation of secondary amines via imination pathway

After the completion of the nitrile hydroboration and imination using our optimized protocol (general procedures 1 and 3, 1.0 mmol nitrile **1** and 1.0 mmol benzaldehyde), the obtained reaction mixture containing amides was put under vacuum to remove all the volatiles. Tropylium tetrafluoroborate (0.1 mmol, 10 mol%) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 mmol) were then added to this crude mixture. The resulting reaction mixture was then heated at 80 °C for 24-32 hours. After that, the reaction mixture was stirred with 4.0 mL of NaOH (2.0 M) and 4.0 mL of diethyl ether for 3 hours. The reaction mixture was subsequently partitioned between water and diethyl ether (2 x 10 mL). The combined ether phases containing corresponding reduced amines was treated with 4.0 mL of HCl (1.0 M), which led to the formation of a white precipitate. The white precipitate was filtered, washed with diethyl ether and then dried under reduced pressure to afford the corresponding amine hydrochloride salt **5**.

NMR evidence of the formation of imine intermediate in the hydroboration of amide

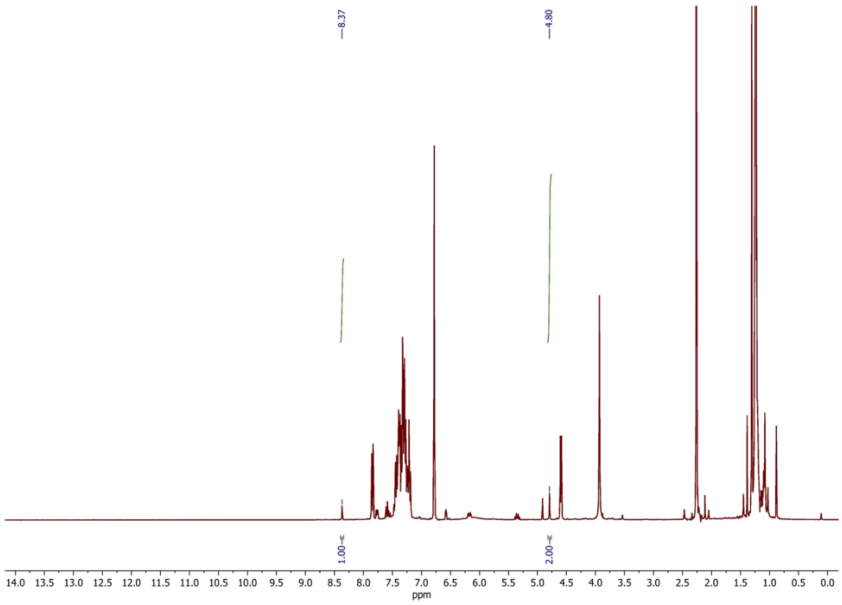


Figure S1. ^{1}H NMR spectrum of *in situ* generated *N*-benzylidene-1-phenylmethanamine recorded in $CDCl_3$. The signal at 8.4 ppm indicates that an imine intermediate was formed during the reaction.

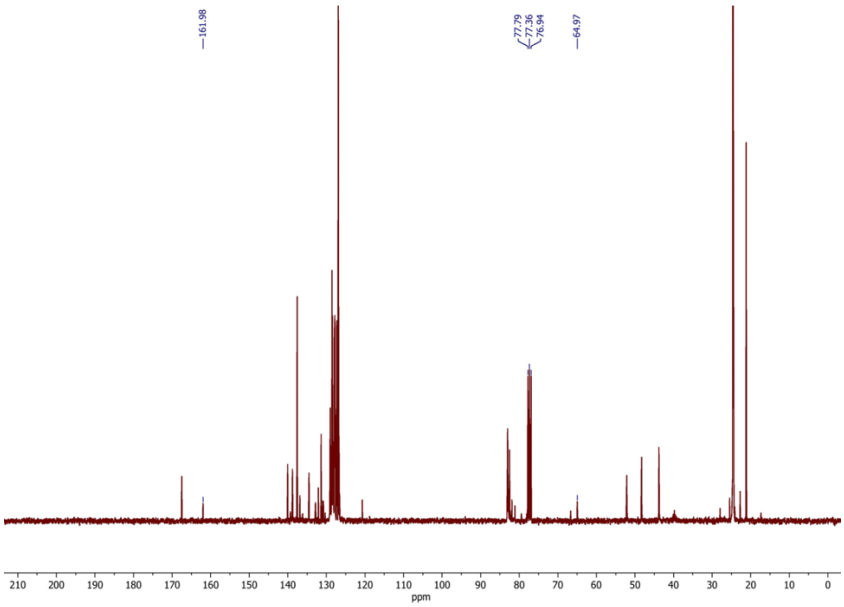
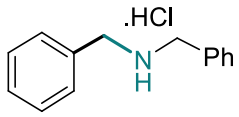


Figure S2. ^{13}C NMR spectrum of *in situ* generated *N*-benzylidene-1-phenylmethanamine recorded in $CDCl_3$. The signal at 162 ppm indicates that an imine intermediate was formed during the reaction.

Characterisation data of secondary amines 5

dibenzylamine hydrochloride (compound **5a**): Prepared by the general procedure **4.1** from benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5a** as a white solid (165 mg, 71% yield).



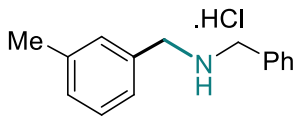
5a

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.78 (s, 2H), 7.59 – 7.56 (m, 4H), 7.46 – 7.38 (m, 6H), 4.13 (s, 4H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.4, 130.6, 129.3, 129.0, 50.2 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-*m*-tolylmethanamine hydrochloride** (compound **5b**): Prepared by the general procedure **4.1** from 3-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5b** as a white solid (195 mg, 79% yield).



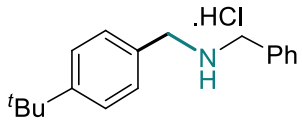
5b

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.86 (s, 2H), 7.60 – 7.57 (m, 2H), 7.45 – 7.37 (m, 5H), 7.29 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 4.11 (s, 2H), 4.07 (s, 2H), 2.32 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 138.2, 132.4, 132.3, 131.1, 130.6, 129.8, 129.3, 129.0, 128.9, 127.6, 50.1, 50.1, 21.4 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(4-*tert*-butylphenyl)methanamine hydrochloride** (compound **5c**): Prepared by the general procedure **4.1** from 4-tert-butylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5c** as a white solid (191 mg, 66% yield).



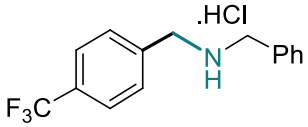
5c

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.89 (s, 2H), 7.61 – 7.58 (m, 2H), 7.53 – 7.50 (m, 2H), 7.44 – 7.39 (m, 5H), 4.11 (s, 2H), 4.06 (s, 2H), 1.28 (s, 9H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 151.7, 132.5, 130.6, 130.4, 129.5, 129.2, 129.0, 125.7, 50.1, 49.7, 34.8, 31.5 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(4-(trifluoromethyl)phenyl)methanamine hydrochloride** (compound **5e**): Prepared by the general procedure **4.1** from 4-(trifluoromethyl)benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5e** as a white solid (123 mg, 41% yield).



5e

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.93 (s, 2H), 7.84 – 7.78 (m, 4H), 7.61 – 7.58 (m, 2H), 7.45 – 7.38 (m, 3H), 4.23 (s, 2H), 4.15 (s, 2H) ppm;

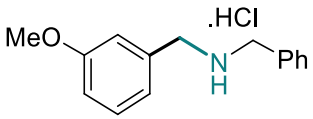
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 137.4, 132.6, 131.4, 130.6, 129.2, 129.1 (q, J = 32.0 Hz), 129.0, 125.7 (q, J = 3.8 Hz), 123.2 (q, J = 273.2 Hz), 50.4, 49.6 ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.1 ppm;

ESI-HRMS: calcd for $C_{15}H_{14}F_3NH^+$: m/z = 266.1151, found: m/z = 266.1144;

FTIR (neat): 2786.6, 1571.1, 1465.2, 1425.8, 1328.5, 1166.7, 1125.8, 1069.9, 1024.5, 978.6, 836.8, 748.7, 681.8 cm^{-1}.

***N*-benzyl-1-(3-methoxyphenyl)methanamine hydrochloride** (compound **5f**): Prepared by the general procedure **4.1** from 3-methoxybenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5f** as a white solid (124 mg, 47% yield).



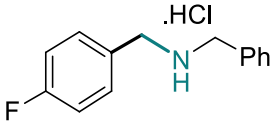
5f

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.92 (s, 2H), 7.60 – 7.57 (m, 2H), 7.44 – 7.40 (m, 3H), 7.31 (t, J = 8.0 Hz, 1H), 7.28 – 7.27 (m, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.95 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 4.11 (s, 2H), 4.09 (s, 2H), 3.78 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 159.7, 133.7, 132.3, 130.6, 130.1, 129.3, 129.0, 122.6, 115.9, 115.0, 55.6, 50.0 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(4-fluorophenyl)methanamine hydrochloride** (compound **5g**): Prepared by the general procedure **4.1** from 4-fluorobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5g** as a white solid (110 mg, 44% yield).



5g

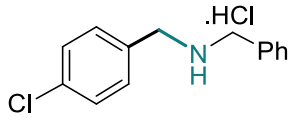
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.98 (s, 2H), 7.69 – 7.64 (m, 2H), 7.61 – 7.58 (m, 2H), 7.44 – 7.38 (m, 3H), 7.29 – 7.23 (m, 2H), 4.12 (s, 2H), 4.11 (s, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 161.5 (d, J = 246.2 Hz), 133.0 (d, J = 8.5 Hz), 132.4, 130.6, 129.2, 129.0, 128.7 (d, J = 3.1 Hz), 115.7 (d, J = 21.6 Hz), 50.0, 49.3 ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -113.0 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(4-chlorophenyl)methanamine hydrochloride** (compound **5h**): Prepared by the general procedure **4.1** from 4-chlorobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5h** as a white solid (115 mg, 43% yield).



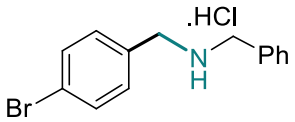
5h

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.85 (s, 2H), 7.64 – 7.57 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 – 7.39 (m, 3H), 4.13 (s, 2H), 4.11 (s, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 134.0, 132.6, 131.6, 130.5, 130.5, 129.2, 129.0, 128.9, 50.2, 49.4 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(4-bromophenyl)methanamine hydrochloride** (compound **5i**): Prepared by the general procedure **4.1** from 4-bromobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5i** as a white solid (171 mg, 55% yield).



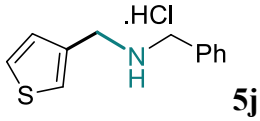
5i

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.94 (s, 2H), 7.65 – 7.53 (m, 6H), 7.45 – 7.38 (m, 3H), 4.11 (s, 4H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.9, 132.4, 131.9, 131.9, 130.6, 129.2, 129.0, 122.7, 50.1, 49.4 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(thiophen-3-yl)methanamine hydrochloride** (compound **5j**): Prepared by the general procedure **4.1** from thiophene-3-carbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5j** as a white solid (148 mg, 62% yield).



5j

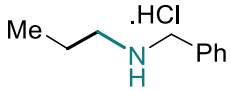
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.92 (s, 2H), 7.75 (dd, J_1 = 3.0 Hz, J_2 = 1.2 Hz, 1H), 7.60 (dd, J_1 = 5.0 Hz, J_2 = 3.0 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.45 – 7.40 (m, 3H), 7.37 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 4.13 (s, 2H), 4.09 (s, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.9, 132.3, 130.6, 129.3, 129.3, 129.0, 127.4, 127.3, 49.9, 44.8 ppm;

ESI-HRMS: calcd for $C_{12}H_{13}NSH^+$: m/z = 204.0841, found: m/z = 204.0837;

FTIR (neat): 2918.8, 2781.9, 2718.6, 2598.0, 2397.4, 1573.3, 1498.7, 1460.3, 1422.0, 1241.8, 1215.0, 1159.1, 1030.5, 983.3, 944.9, 834.6, 784.4, 748.7, 691.0 cm^{-1}.

***N*-benzylpropan-1-amine hydrochloride** (compound **5k**): Prepared by the general procedure **4.1** from propiononitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5k** as a white solid (94 mg, 51% yield).



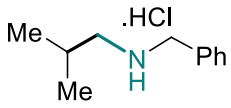
5k

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.52 (s, 2H), 7.62 – 7.58 (m, 2H), 7.45 – 7.39 (m, 3H), 4.10 (s, 2H), 2.77 (t, J = 7.6 Hz, 2H), 1.65 (sext, J = 7.6 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.5, 130.5, 129.2, 129.0, 50.1, 48.3, 19.2, 11.5 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-2-methylpropan-1-amine hydrochloride** (compound **5l**): Prepared by the general procedure **4.1** from isobutyronitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5l** as a white solid (54 mg, 27% yield).



5l

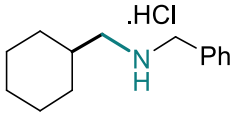
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.42 (s, 2H), 7.64 – 7.61 (m, 2H), 7.45 – 7.40 (m, 3H), 4.11 (s, 2H), 2.65 (d, J = 7.2 Hz, 2H), 2.01 (sep, J = 6.8 Hz, 1H), 0.92 (d, J = 6.8 Hz, 6H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.3, 130.7, 129.2, 129.0, 53.7, 50.6, 25.6, 20.7 ppm;

ESI-HRMS: calcd for $C_{11}H_{17}NH^+$: m/z = 164.1434, found: m/z = 164.1429;

FTIR (neat): 2932.6, 2769.9, 2731.1, 2586.1, 2414.7, 1585.6, 1466.2, 1436.0, 1215.6, 1014.7, 990.7, 833.1, 747.1, 700.9 cm^{-1}.

***N*-benzyl-1-cyclohexylmethanamine hydrochloride** (compound **5m**): Prepared by the general procedure **4.1** from cyclohexanecarbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and benzoic acid to give compound **5m** as a white solid (76 mg, 32% yield).



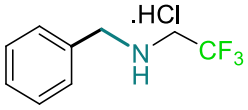
5m

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.43 (s, 2H), 7.63 – 7.61 (m, 2H), 7.44 – 7.38 (m, 3H), 4.10 (s, 2H), 2.66 (d, *J* = 6.4 Hz, 2H), 1.80 – 1.70 (m, 3H), 1.69 – 1.56 (m, 3H), 1.24 – 1.06 (m, 3H), 0.95 – 0.85 (m, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.4, 130.7, 129.2, 129.0, 52.4, 50.6, 34.6, 30.6, 26.0, 25.5 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-2,2,2-trifluoroethanamine hydrochloride** (compound **5n**): Prepared by the general procedure **4.1** from benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **5n** as a white solid (121 mg, 54% yield).



5n

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.65 (br, 1H), 7.67 – 7.63 (m, 2H), 7.46 – 7.40 (m, 3H), 4.24 (s, 2H), 3.91 (q, *J* = 9.6 Hz, 2H) ppm;

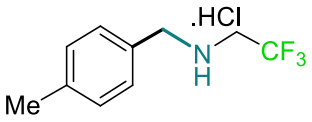
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 131.6, 131.0, 129.5, 129.0, 119.5 (q, J = 279.5 Hz), 51.0, 45.6 (q, J = 34.0 Hz) ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -65.5 ppm;

ESI-HRMS: calcd for $C_9H_{10}F_3NH^+$: m/z = 190.0838, found: m/z = 190.0833;

FTIR (neat): 3265.6, 2707.6, 1638.0, 1411.7, 1339.1, 1266.9, 1151.5, 1024.4, 917.7, 823.6, 753.9, 694.5 cm^{-1}.

2,2,2-trifluoro-*N*-(4-methylbenzyl)ethanamine hydrochloride (compound **5o**): Prepared by the general procedure **4.1** from 4-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **5o** as a white solid (165 mg, 69% yield).



5o

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.63 (br, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 4.20 (s, 2H), 3.88 (q, J = 9.6 Hz, 2H), 2.32 (s, 3H) ppm;

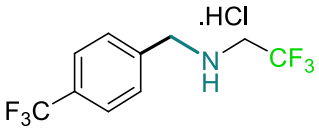
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 139.0, 131.0, 129.5, 128.4, 119.5 (q, J = 276.7 Hz), 50.7, 45.4 (q, J = 33.8 Hz), 21.2 ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -65.5 ppm;

ESI-HRMS: calcd for $C_{10}H_{12}F_3NH^+$: m/z = 204.0995, found: m/z = 204.0995;

FTIR (neat): 2931.0, 2705.2, 2584.7, 2415.6, 1517.2, 1464.1, 1408.3, 1337.3, 1245.9, 1146.5, 1025.6, 1004.5, 967.7, 911.7, 805.7, 754.7 cm^{-1}.

2,2,2-trifluoro-*N*-(4-(trifluoromethyl)benzyl)ethanamine hydrochloride (compound **5p**): Prepared by the general procedure **4.1** from 4-(trifluoromethyl)benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **5p** as a white solid (234 mg, 80% yield).



5p

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.50 (br, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 4.35 (s, 2H), 3.96 (q, J = 9.6 Hz, 2H) ppm;

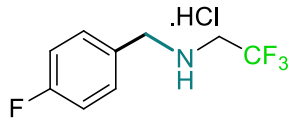
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 136.6, 131.8, 129.4 (q, J = 31.9 Hz), 125.7 (q, J = 3.8 Hz), 120.4 (q, J = 273.2 Hz), 119.5 (q, J = 279.5 Hz), 50.4, 45.9 (q, J = 34.0 Hz) ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.2, -65.8 ppm;

ESI-HRMS: calcd for $C_{10}H_9F_6NH^+$: m/z = 258.0712, found: m/z = 258.0711;

FTIR (neat): 2715.7, 1576.8, 1416.1, 1324.6, 1246.4, 1161.5, 1127.2, 1030.0, 974.7, 913.1, 837.2, 761.0, 737.3, 663.0 cm^{-1}.

2,2,2-trifluoro-*N*-(4-fluorobenzyl)ethanamine hydrochloride (compound **5q**): Prepared by the general procedure **4.1** from 4-fluorobenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **5q** as a white solid (165 mg, 68% yield).



5q

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.57 (br, 2H), 7.73 – 7.67 (m, 2H), 7.29 – 7.23 (m, 2H), 4.24 (s, 2H), 3.92 (q, J = 9.6 Hz, 2H) ppm;

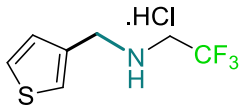
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 161.7 (d, J = 246.6 Hz), 133.4 (d, J = 8.7 Hz), 127.9 (d, J = 3.1 Hz), 119.5 (d, J = 279.4 Hz), 115.7 (d, J = 21.7 Hz), 50.2, 45.5 (q, J = 34.0 Hz) ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -65.6, -112.6 ppm;

ESI-HRMS: calcd for $C_9H_9F_4NH^+$: m/z = 208.0744, found: m/z = 208.0739;

FTIR (neat): 2728.3, 2702.1, 2589.4, 1603.0, 1577.9, 1513.1, 1413.5, 1349.9, 1233.7, 1182.8, 1153.5, 1034.2, 975.0, 912.1, 840.0, 766.8 cm^{-1}.

2,2,2-trifluoro-*N*-(thiophen-3-ylmethyl)ethanamine hydrochloride (compound **5s**): Prepared by the general procedure **4.1** from thiophene-3-carbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2,2-trifluoroacetic acid to give compound **5s** as a white solid (132 mg, 57% yield).



5s

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.58 (br, 2H), 7.79 (dd, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H), 7.60 (dd, J_1 = 5.0 Hz, J_2 = 3.0 Hz, 1H), 7.39 (dd, J_1 = 5.0 Hz, J_2 = 1.4 Hz, 1H), 4.25 (s, 2H), 3.89 (q, J = 9.6 Hz, 2H) ppm;

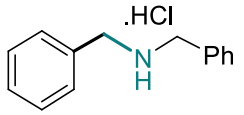
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.1, 129.5, 128.3, 127.4, 119.5 (q, J = 279.4 Hz), 45.7, 45.4 (q, J = 34.1 Hz) ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -65.7 ppm;

ESI-HRMS: calcd for $C_7H_8F_3NSH^+$: m/z = 196.0402, found: m/z = 196.0401;

FTIR (neat): 2701.7, 2582.0, 2410.6, 1578.4, 1461.7, 1416.7, 1334.4, 1259.5, 1231.4, 1161.8, 1142.7, 1038.5, 967.5, 844.3, 780.2, 688.2 cm^{-1}.

dibenzylamine hydrochloride (compound **5a**): Prepared by the general procedure **4.2** from benzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and benzaldehyde to give compound **5a** as a white solid (168 mg, 72% yield).



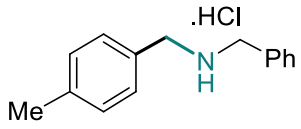
5a

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.03 (s, 2H), 7.62 – 7.58 (m, 4H), 7.45 – 7.38 (m, 6H), 4.11 (s, 4H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.4, 130.6, 129.2, 129.0, 50.0 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-*p*-tolylmethanamine hydrochloride** (compound **5t**): Prepared by the general procedure **4.2** from 4-methylbenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and benzaldehyde to give compound **5t** as a white solid (183 mg, 74% yield).



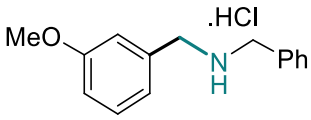
5t

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.97 (s, 2H), 7.61 – 7.58 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 4.08 (s, 2H), 4.06 (s, 2H), 2.32 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 138.7, 132.4, 130.6, 130.6, 129.5, 129.3, 129.2, 129.0, 49.8, 49.7, 21.2 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(3-methoxyphenyl)methanamine hydrochloride** (compound **5f**): Prepared by the general procedure **4.2** from 4-methoxybenzonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and benzaldehyde to give compound **5f** as a white solid (150 mg, 57% yield).



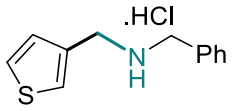
5f

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.03 (s, 2H), 7.61 – 7.59 (m, 2H), 7.43 – 7.39 (m, 3H), 7.30 (t, J = 8.0 Hz, 1H), 7.30 – 7.29 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.95 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 4.10 (s, 2H), 4.09 (s, 2H), 3.78 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 159.7, 133.7, 132.3, 130.6, 130.1, 129.2, 129.0, 122.6, 115.9, 115.0, 55.6, 50.0 ppm;

The NMR data closely match those reported in literature[14].

***N*-benzyl-1-(thiophen-3-yl)methanamine hydrochloride** (compound **5j**): Prepared by the general procedure **4.2** from thiophene-3-carbonitrile, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and benzaldehyde to give compound **5j** as a white solid (162 mg, 68% yield).



5j

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.02 (s, 2H), 7.76 (dd, J_1 = 3.2 Hz, J_2 = 1.2 Hz, 1H), 7.62 – 7.58 (m, 3H), 7.45 – 7.39 (m, 4H), 4.13 (s, 2H), 4.09 (s, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 132.9, 132.3, 130.6, 129.4, 129.2, 129.0, 127.4, 127.3, 49.8, 44.7 ppm;

ESI-HRMS: calcd for $C_{12}H_{13}NSH^{+}$: m/z = 204.0841, found: m/z = 204.0840;

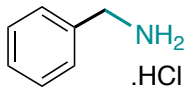
FTIR (neat): 2924.9, 2783.0, 2721.8, 2597.8, 2345.6, 1573.3, 1498.6, 1460.5, 1420.8, 1241.9, 1214.9, 1159.7, 1031.7, 982.0, 944.7, 834.7, 784.4, 748.4, 690.3 cm^{-1}.

General procedure 5 for the one-pot formation of primary amines 7

Tropylium tetrafluoroborate (0.1 mmol), primary amide **6** (1.0 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 mmol) were added to a 4 mL vial equipped with a magnetic stirrer bar. The resulting reaction mixture was then heated at 80 °C for 24 hours. After that, the reaction mixture was stirred with 4.0 mL of NaOH (2.0 M) and 4.0 mL of diethyl ether for 3 hours. The reaction mixture was subsequently partitioned between water and diethyl ether (2 x 10 mL). The combined ether phases containing corresponding reduced amines was treated with 4.0 mL of HCl (1.0 M), which led to the formation of a white precipitate. The white precipitate was filtered, washed with diethyl ether and then dried under reduced pressure to afford the corresponding amine hydrochloride salt **7**.

Characterisation data of primary amines 7

phenylmethanamine hydrochloride (compound **7a**): Prepared by the general procedure **5** from benzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7a** as a white solid (136 mg, 95% yield).



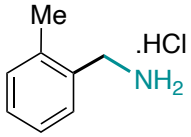
7a

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.59 (s, 3H), 7.53 – 7.49 (m, 2H), 7.44 – 7.34 (m, 3H), 4.00 (s, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 134.5, 129.4, 129.0, 128.8, 42.5 ppm;

The NMR data closely match those reported in literature[15].

***o*-tolylmethanamine hydrochloride** (compound **7b**): Prepared by the general procedure **5** from 2-methylbenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7b** as a white solid (136 mg, 86% yield).



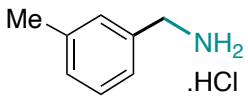
7b

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.63 (s, 3H), 7.46 – 7.44 (m, 1H), 7.29 – 7.21 (m, 3H), 3.96 (q, J = 6.0 Hz, 2H), 2.36 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 137.1, 132.8, 130.7, 129.7, 128.8, 126.4, 39.8, 19.3 ppm;

The NMR data closely match those reported in literature[16].

***m*-tolylmethanamine hydrochloride** (compound **7c**): Prepared by the general procedure **5** from 3-methylbenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7c** as a white solid (114 mg, 73% yield).



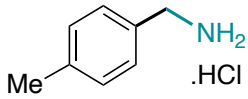
7c

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.59 (s, 3H), 7.33 – 7.27 (m, 3H), 7.17 (d, J = 6.4 Hz, 1H), 3.95 (s, 2H), 2.31 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 138.1, 134.5, 129.9, 129.3, 128.9, 126.4, 42.5, 21.4 ppm;

The NMR data closely match those reported in literature[16].

***p*-tolylmethanamine hydrochloride** (compound **7d**): Prepared by the general procedure **5** from 4-methylbenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7d** as a white solid (118 mg, 75% yield).



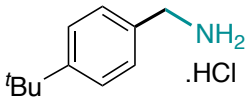
7d

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.54 (s, 3H), 7.38 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 3.94 (s, 2H), 2.31 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 138.1, 131.5, 129.5, 129.4, 42.3, 21.2 ppm;

The NMR data closely match those reported in literature[15].

(4-*tert*-butylphenyl)methanamine hydrochloride (compound **7e**): Prepared by the general procedure **5** from 4-*tert*-butylbenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7e** as a white solid (167 mg, 84% yield).



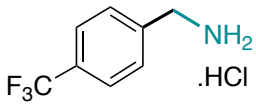
7e

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.65 (s, 3H), 7.47 – 7.40 (m, 4H), 3.94 (s, 2H), 1.27 (s, 9H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 151.3, 131.6, 129.2, 125.7, 42.2, 34.7, 31.5 ppm;

The NMR data closely match those reported in literature[16].

(4-(trifluoromethyl)phenyl)methanamine hydrochloride (compound **7f**): Prepared by the general procedure **5** from 4-(trifluoromethyl)benzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7f** as a white solid (114 mg, 54% yield).



7f

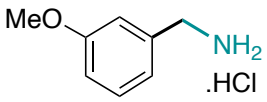
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.80 (s, 3H), 7.77 (s, 4H), 4.10 (q, J = 5.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 139.3, 130.2, 128.8 (q, J = 31.9 Hz), 125.7 (q, J = 3.8 Hz), 120.5 (q, J = 273.2 Hz), 42.0 ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.1 ppm;

The NMR data closely match those reported in literature[15].

(3-methoxyphenyl)methanamine hydrochloride (compound **7g**): Prepared by the general procedure **5** from 3-methoxybenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7g** as a white solid (137 mg, 79% yield).



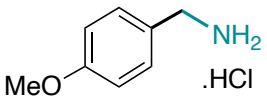
7g

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.65 (s, 3H), 7.29 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 2.4 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.94 – 6.91 (m, 1H), 3.97 (s, 2H), 3.77 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 159.7, 136.0, 130.0, 121.4, 114.9, 114.3, 55.6, 42.5 ppm;

The NMR data closely match those reported in literature[16].

(4-methoxyphenyl)methanamine hydrochloride (compound **7h**): Prepared by the general procedure **5** from 4-methoxybenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7h** as a white solid (124 mg, 72% yield).



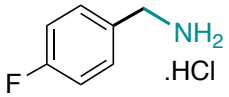
7h

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.41 (s, 3H), 7.45 – 7.41(m, 3H), 6.98 – 6.95 (m, 3H), 3.93 (s, 2H), 3.76 (s, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 159.8, 131.0, 126.4, 114.3, 55.6, 42.1 ppm;

The NMR data closely match those reported in literature[16].

(4-fluorophenyl)methanamine hydrochloride (compound **7i**): Prepared by the general procedure **5** from 4-fluorobenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7i** as a white solid (126 mg, 78% yield).



7i

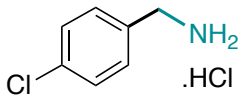
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.66 (s, 3H), 7.58 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 2H), 7.22 (t, J = 9.0 Hz, 2H), 3.97 (q, J = 5.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 161.3 (d, J = 245.2 Hz), 131.8 (d, J = 8.3 Hz), 130.8 (d, J = 3.2 Hz), 115.6 (d, J = 21.6 Hz), 41.7 ppm;

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -113.7 ppm;

The NMR data closely match those reported in literature[15].

(4-chlorophenyl)methanamine hydrochloride (compound **7j**): Prepared by the general procedure **5** from 4-chlorobenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7j** as a white solid (160 mg, 90% yield).



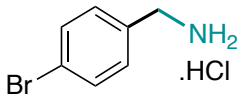
7j

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.70 (s, 3H), 7.56 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 3.98 (q, J = 5.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 133.6, 133.5, 131.5, 128.9, 41.8 ppm;

The NMR data closely match those reported in literature[15].

(4-bromophenyl)methanamine hydrochloride (compound **7k**): Prepared by the general procedure **5** from 4-bromobenzamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7k** as a white solid (186 mg, 84% yield).



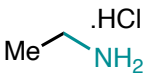
7k

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.72 (s, 3H), 7.59 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 3.96 (q, J = 5.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 134.0, 131.8, 131.8, 122.1, 41.8 ppm;

The NMR data closely match those reported in literature[15].

ethanamine hydrochloride (compound **7l**): Prepared by the general procedure **5** from acetamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7l** as a white solid (72 mg, 90% yield).



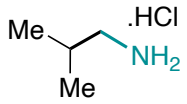
7l

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.18 (s, 3H), 2.74 (q, J = 7.2 Hz, 2H), 1.12 (t, J = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 34.4, 12.8 ppm;

The NMR data closely match those reported in literature[15].

2-methylpropan-1-amine hydrochloride (compound **7m**): Prepared by the general procedure **5** from isobutyramide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7m** as a white solid (80 mg, 73% yield).



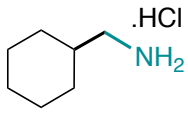
7m

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.25 (s, 3H), 2.56 (d, J = 6.8 Hz, 2H), 1.85 (sept, J = 6.8 Hz, 1H), 0.89 (d, J = 7.2 Hz, 6H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 46.0, 26.7, 20.3 ppm;

The NMR data closely match those reported in literature[15].

cyclohexylmethanamine hydrochloride (compound **7n**): Prepared by the general procedure **5** from cyclohexanecarboxamide and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7n** as a white solid (122 mg, 82% yield).



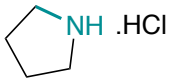
7n

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.22 (s, 3H), 2.55 (p, J = 6.0 Hz, 2H), 1.77 – 1.72 (m, 2H), 1.69 – 1.54 (m, 4H), 1.22 – 1.06 (m, 3H), 0.94 – 0.85 (m, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 44.8, 35.7, 30.3, 26.1, 25.5 ppm;

The NMR data closely match those reported in literature[15].

pyrrolidine hydrochloride (compound **7o**): Prepared by the general procedure **5** from pyrrolidin-2-one and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7o** as a white solid (68 mg, 63% yield).



7o

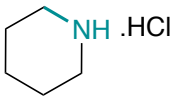
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.45 (s, 2H), 3.07 – 3.04 (m, 4H), 1.83 – 1.80 (m, 4H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 44.7, 24.2 ppm;

ESI-HRMS: calcd for $C_4H_9NH^+$: m/z = 72.0808, found: m/z = 72.0806;

FTIR (neat): 2739.2, 2641.0, 2566.8, 2445.2, 2004.0, 1598.2, 1459.5, 1401.0, 1297.8, 1027.9, 911.3, 879.0, 695.6 cm^{-1}.

piperidine hydrochloride (compound **7p**): Prepared by the general procedure **5** from piperidin-2-one and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7p** as a white solid (79 mg, 65% yield).



7p

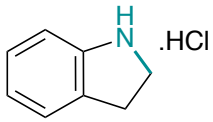
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.18 (s, 2H), 2.94 (t, J = 5.6 Hz, 4H), 1.71 – 1.65 (m, 4H), 1.57 – 1.51 (m, 2H) ppm;

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 43.8, 22.4, 22.1 ppm;

ESI-HRMS: calcd for $C_5H_{11}NH^+$: m/z = 86.0964, found: m/z = 86.0961;

FTIR (neat): 2948.9, 2796.5, 2733.4, 2636.7, 2526.4, 2428.7, 2040.9, 1882.7, 1592.9, 1459.6, 1388.3, 1276.8, 1163.9, 1078.2, 1032.1, 942.8, 862.3, 659.1 cm^{-1}.

indoline hydrochloride (compound **7q**): Prepared by the general procedure **5** from indolin-2-one and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **7q** as a white solid (107 mg, 69% yield).



7q

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.71 (s, 2H), 7.48 – 7.34 (m, 4H), 3.67 (t, J = 8.0 Hz, 2H), 3.17 (t, J = 8.0 Hz, 2H) ppm;

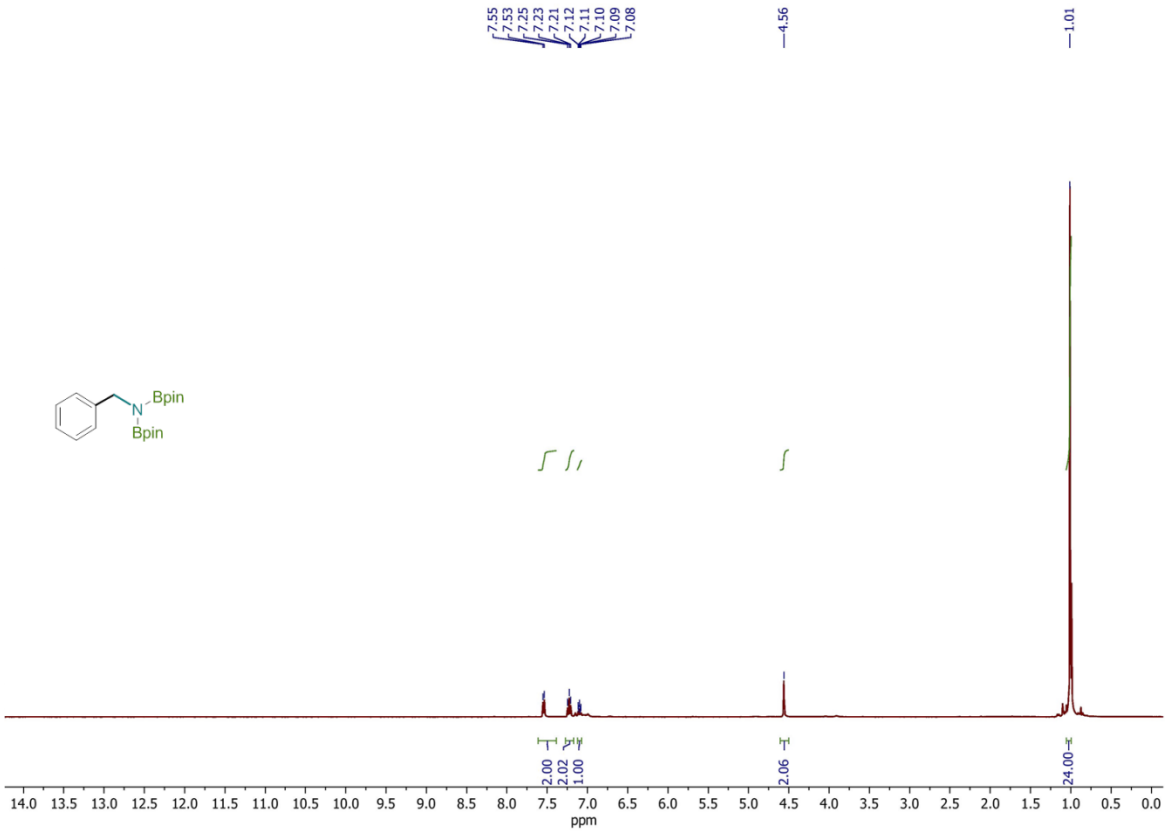
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 137.1, 135.9, 129.4, 128.3, 126.3, 119.8, 45.0, 29.3 ppm;

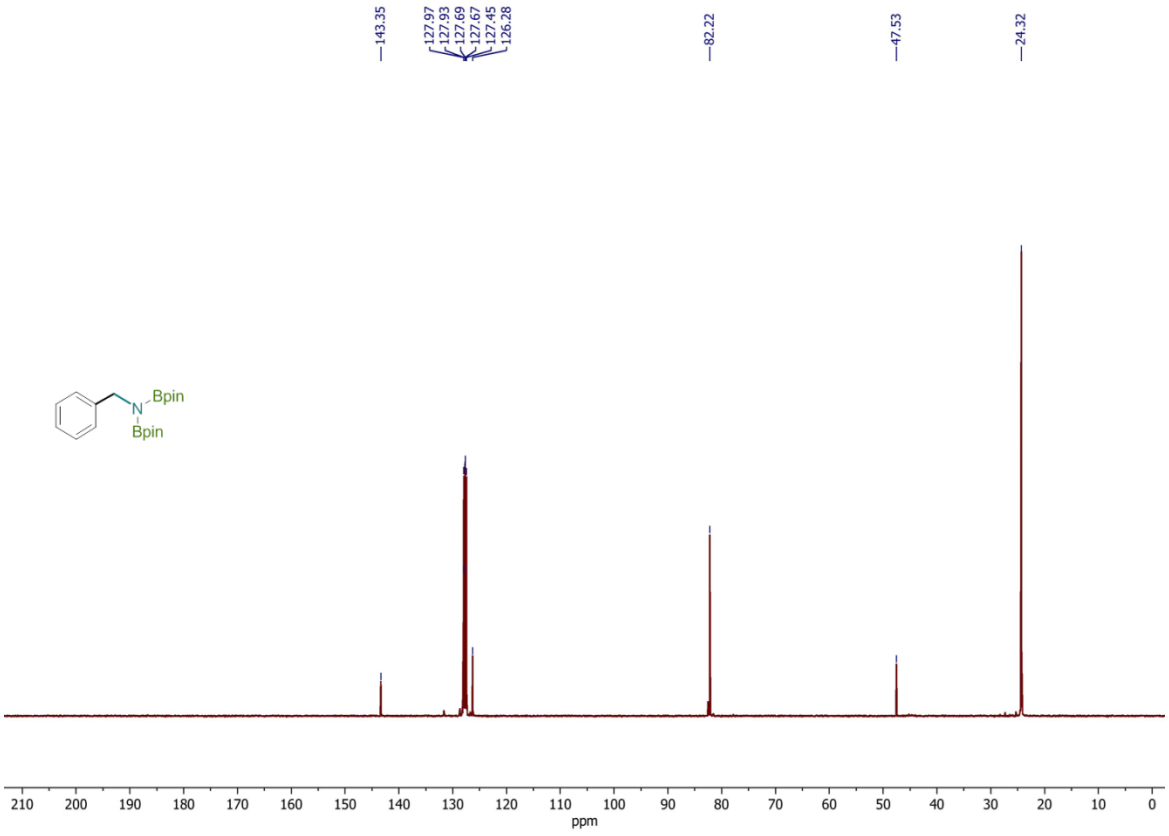
ESI-HRMS: calcd for $C_8H_9NH^+$: m/z = 120.0808, found: m/z = 120.0805;

FTIR (neat): 2826.5, 2792.1, 2469.8, 2217.7, 1617.6, 1567.7, 1485.1, 1460.7, 1404.6, 1290.1, 1148.4, 1090.9, 999.8, 919.8 cm^{-1}.

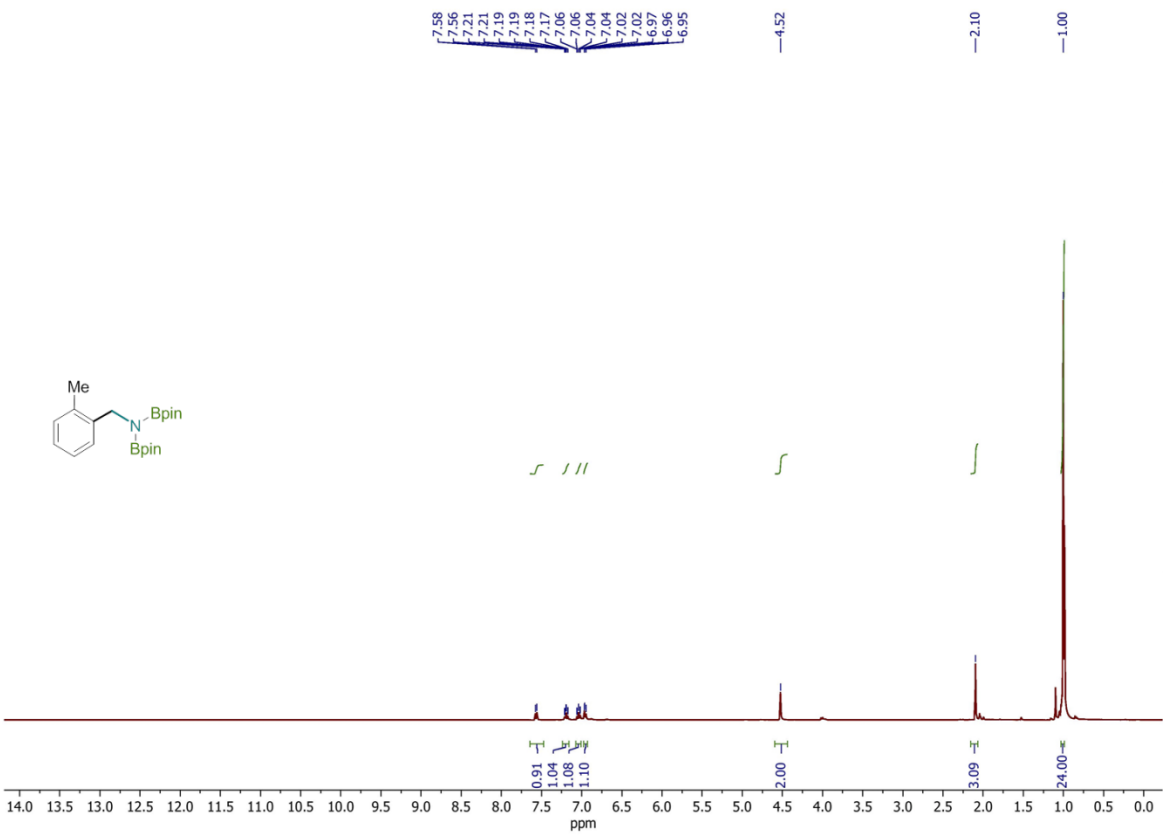
NMR spectra

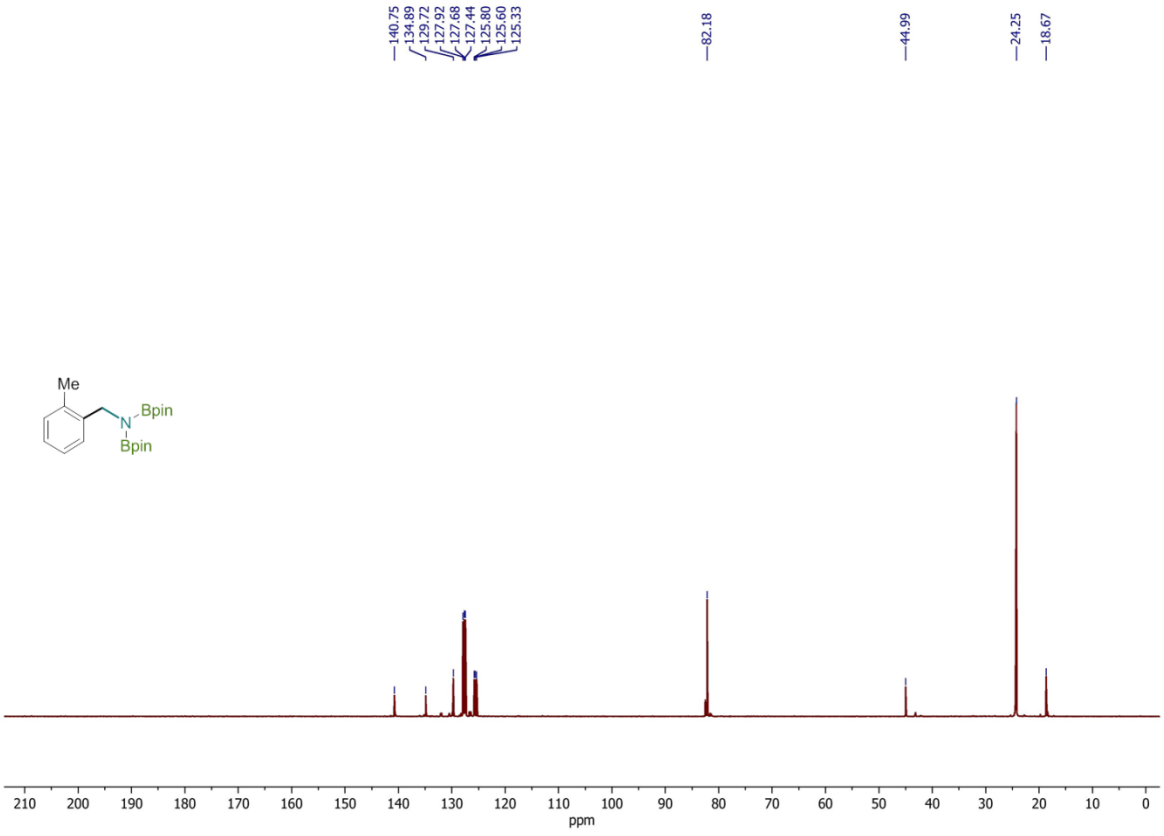
N-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2a**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



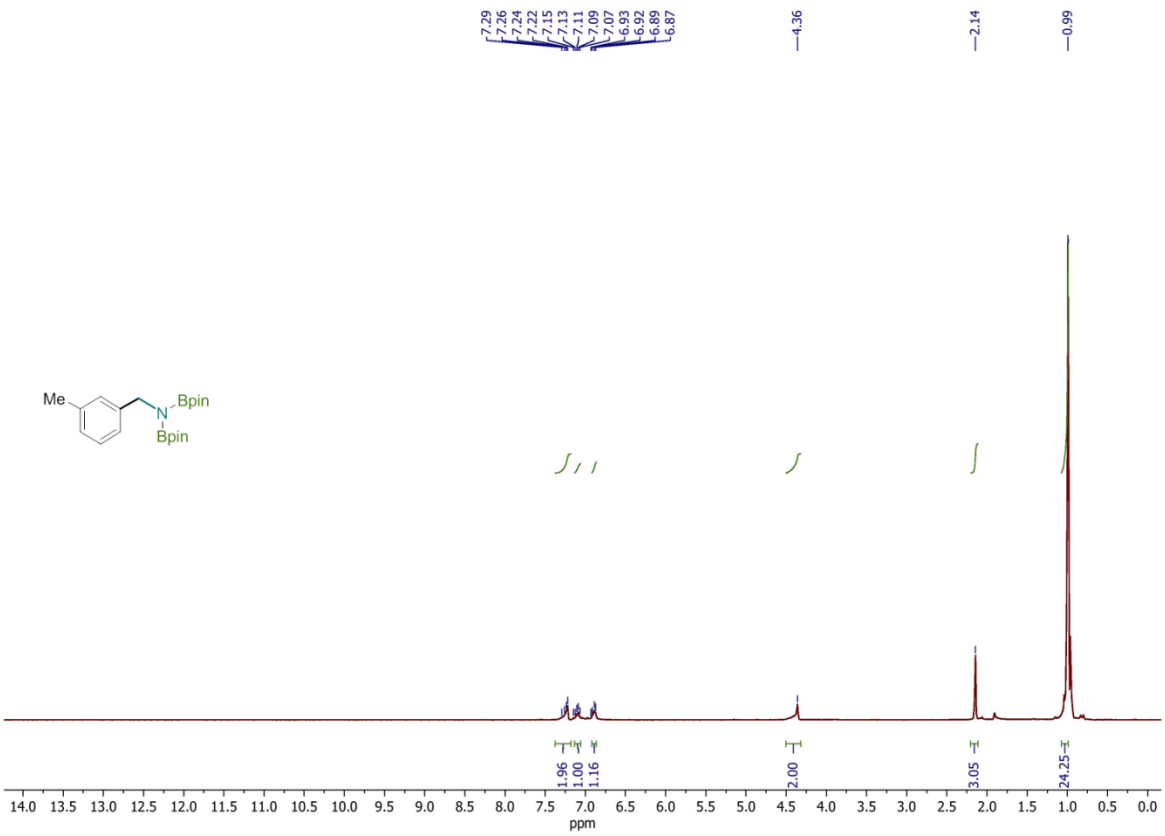


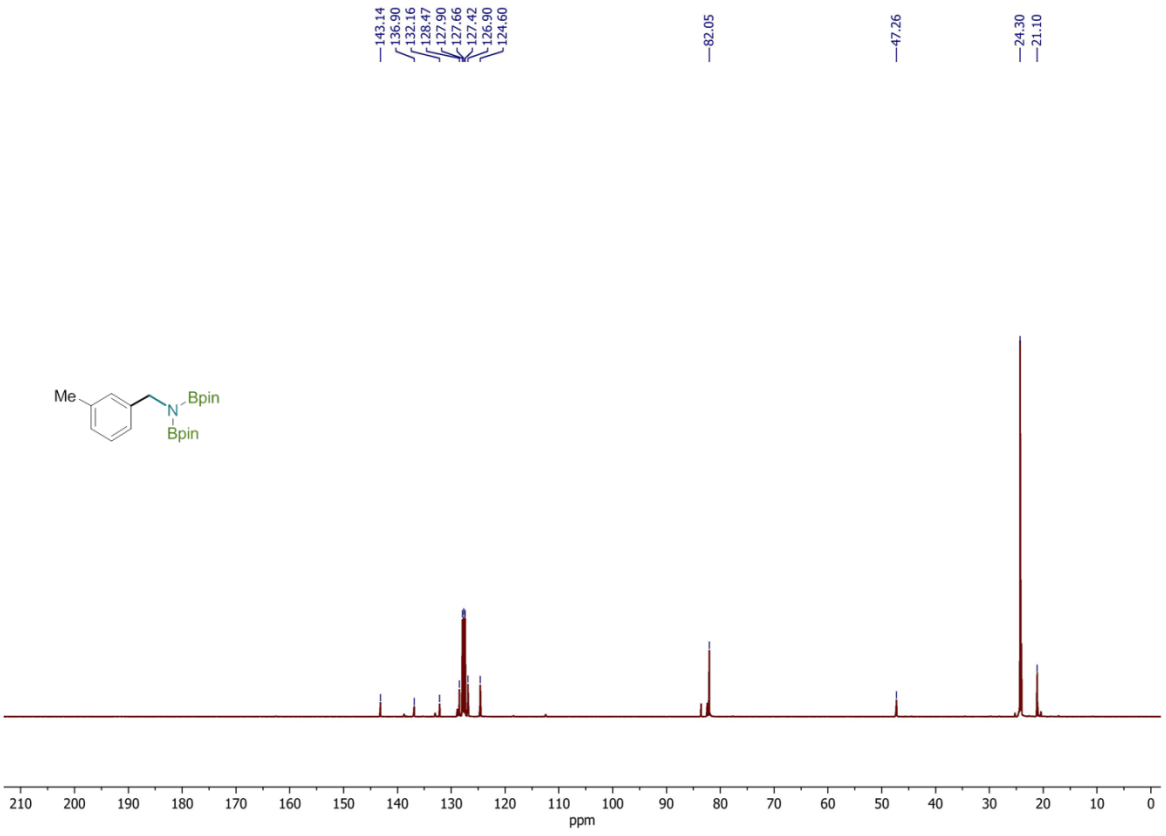
4,4,5,5-tetramethyl-*N*-(2-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2b**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



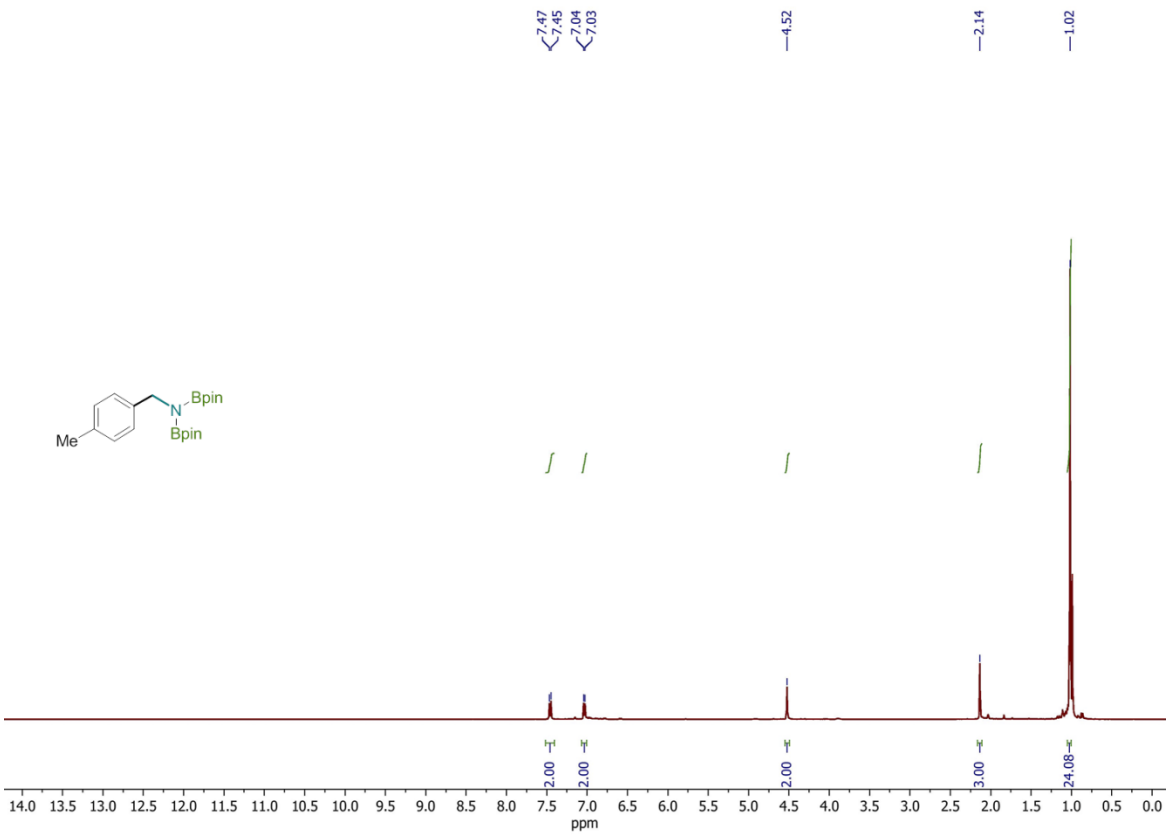


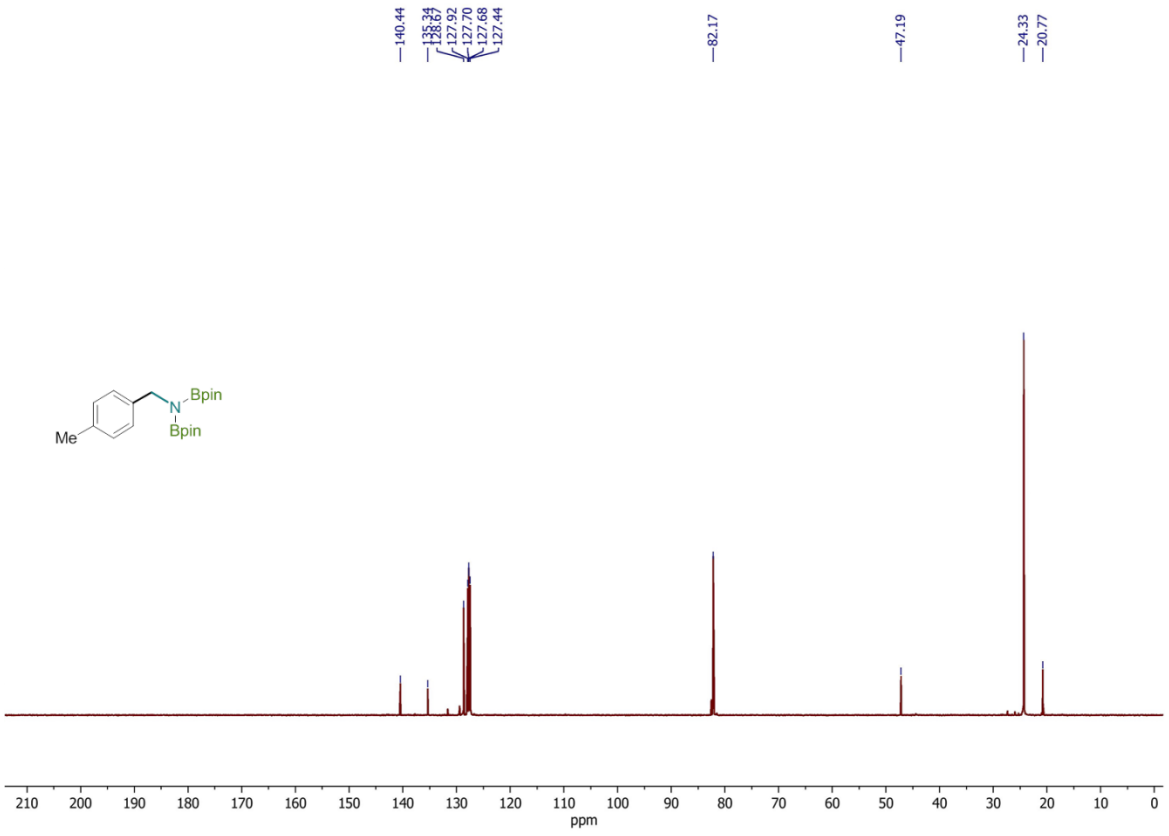
4,4,5,5-tetramethyl-*N*-(3-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2c**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



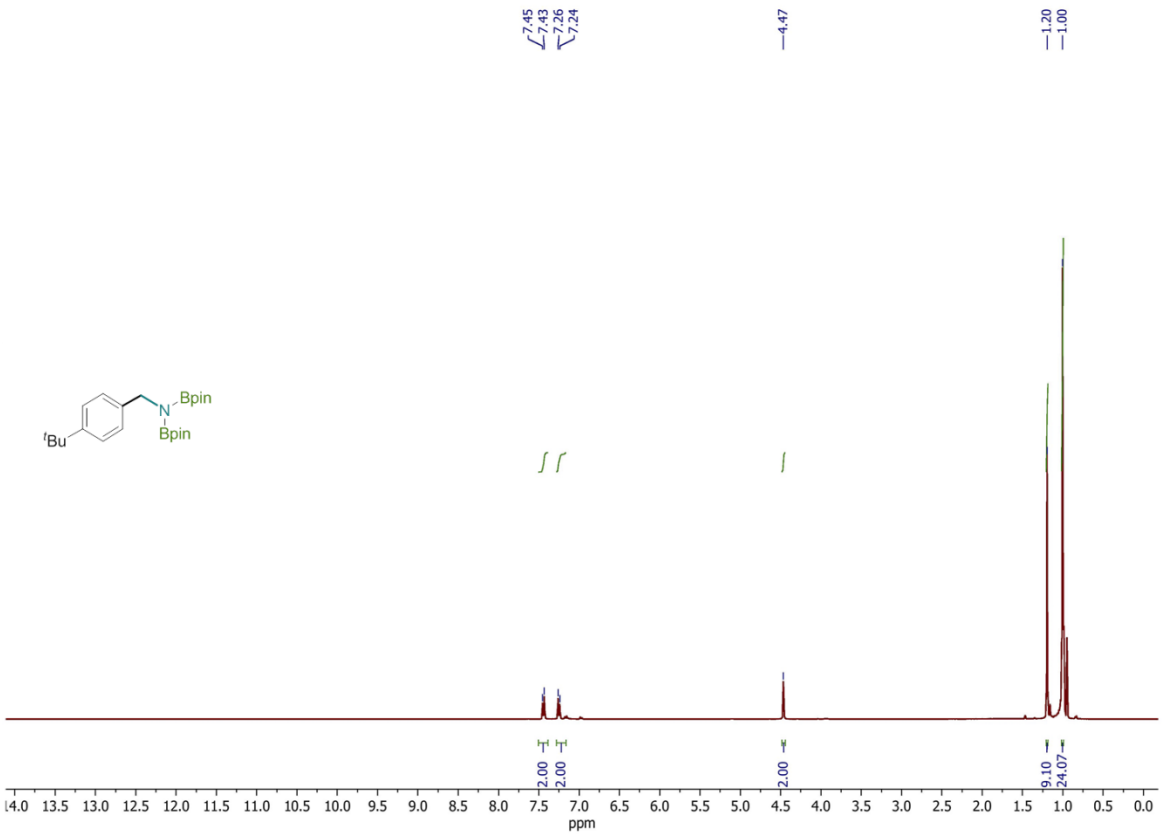


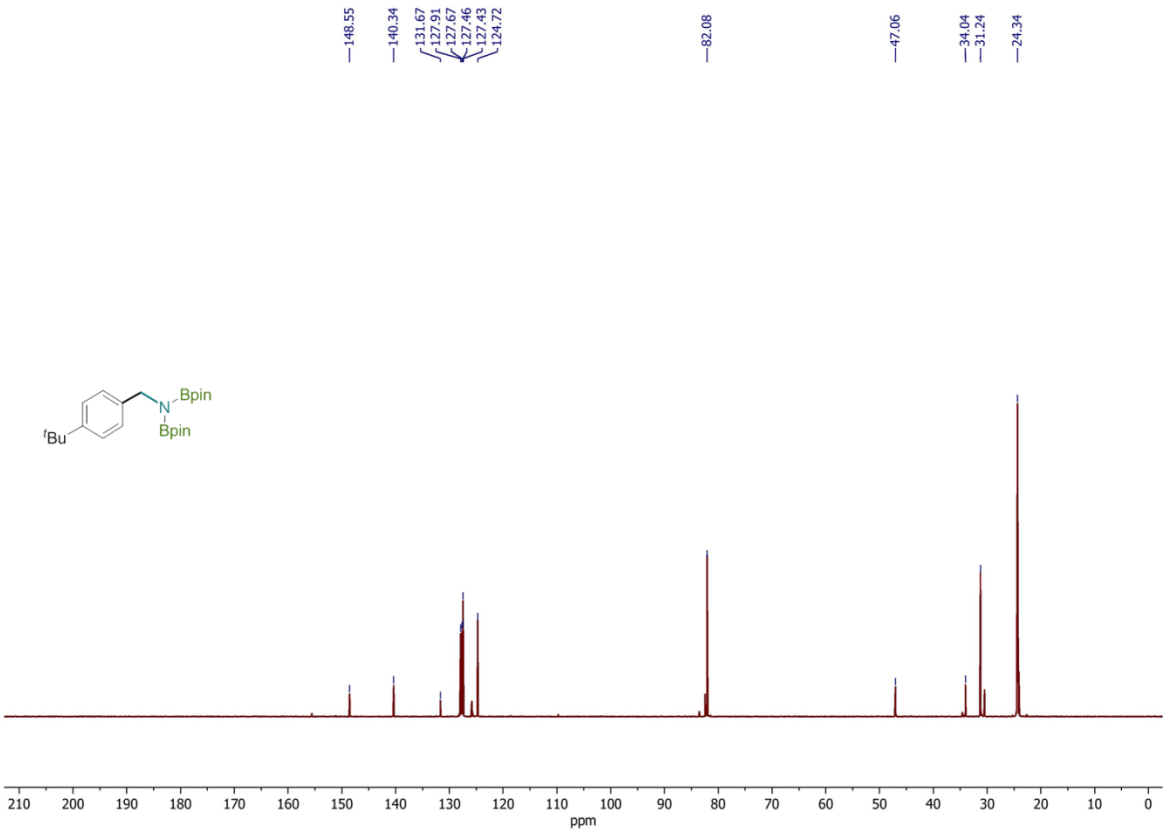
4,4,5,5-tetramethyl-*N*-(4-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2d**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



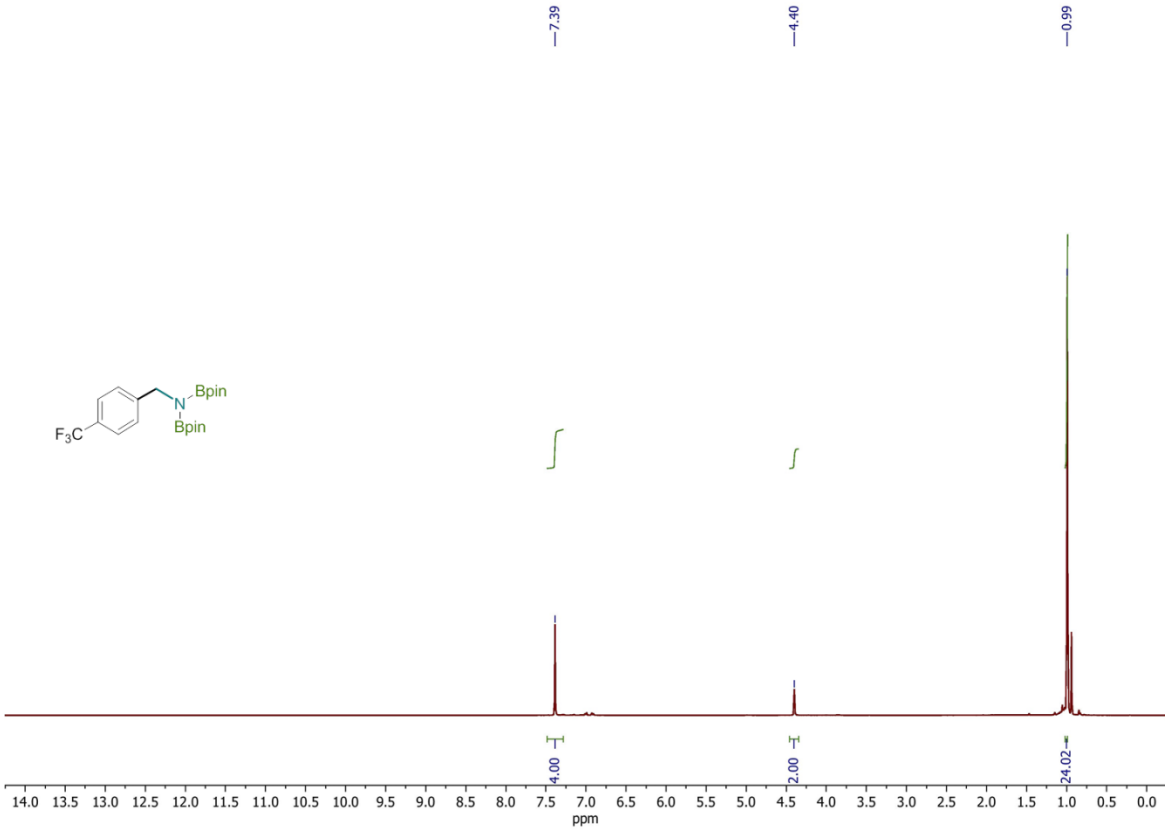


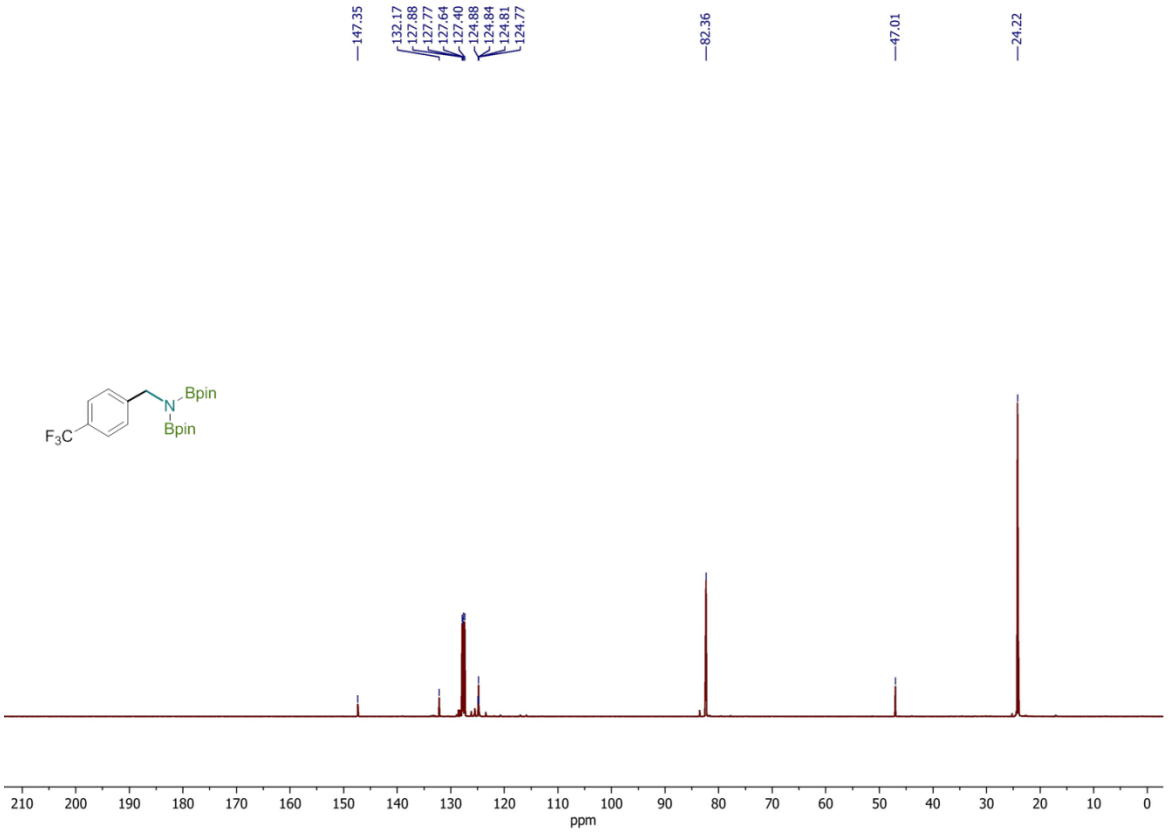
N-(4-*tert*-butylbenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2e**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**

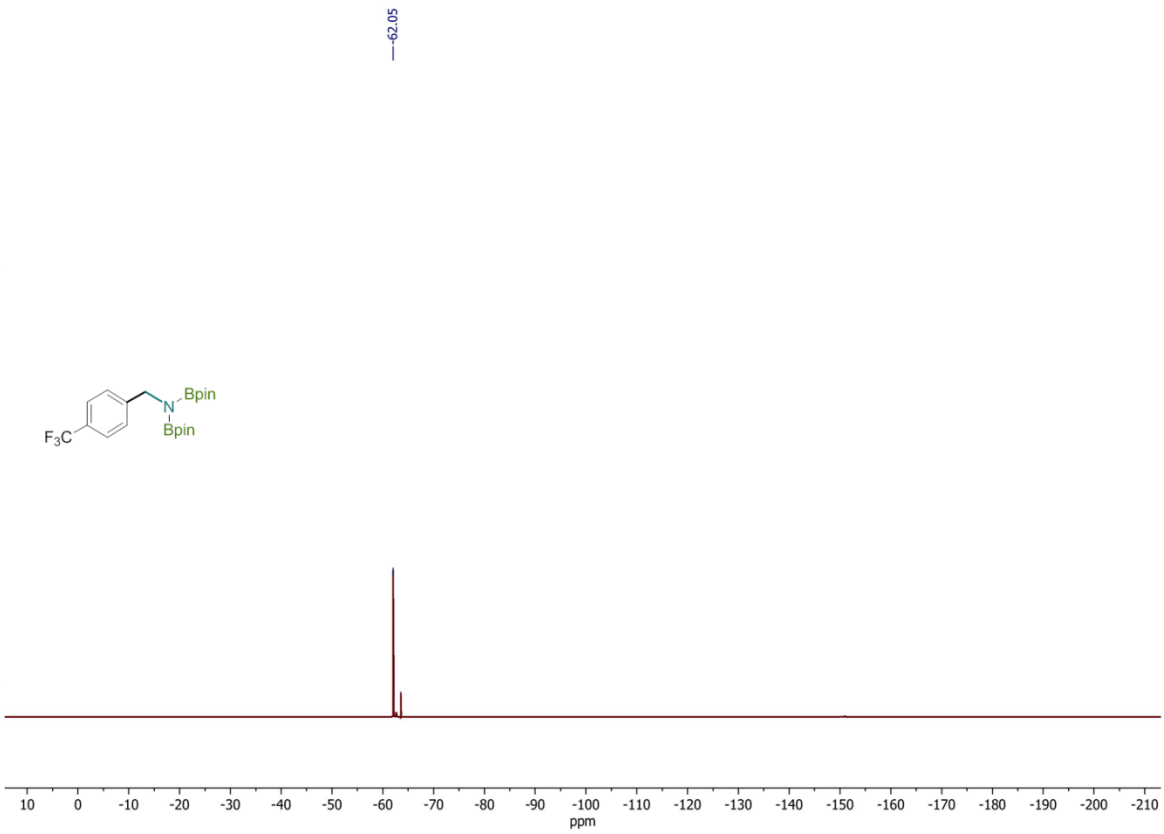




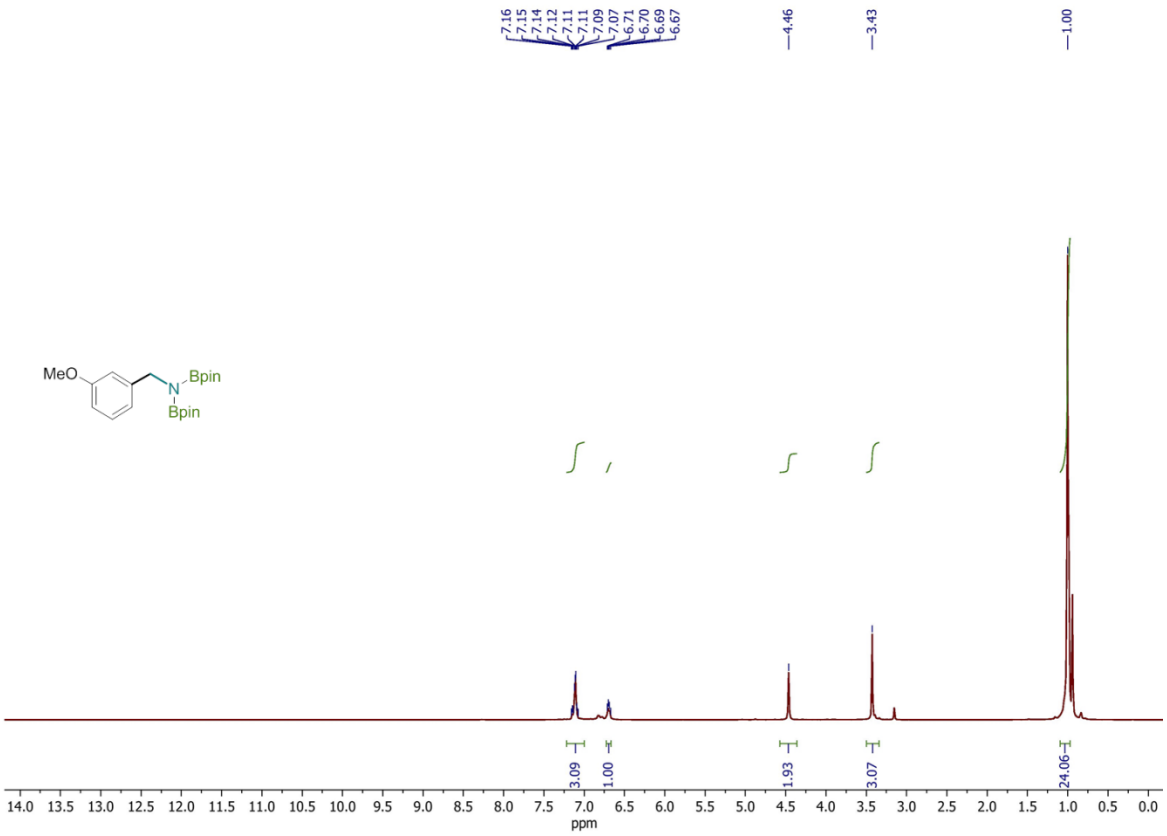
4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolan-2-amine (**2f**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6), ^{19}F NMR (376 MHz, C_6D_6).**

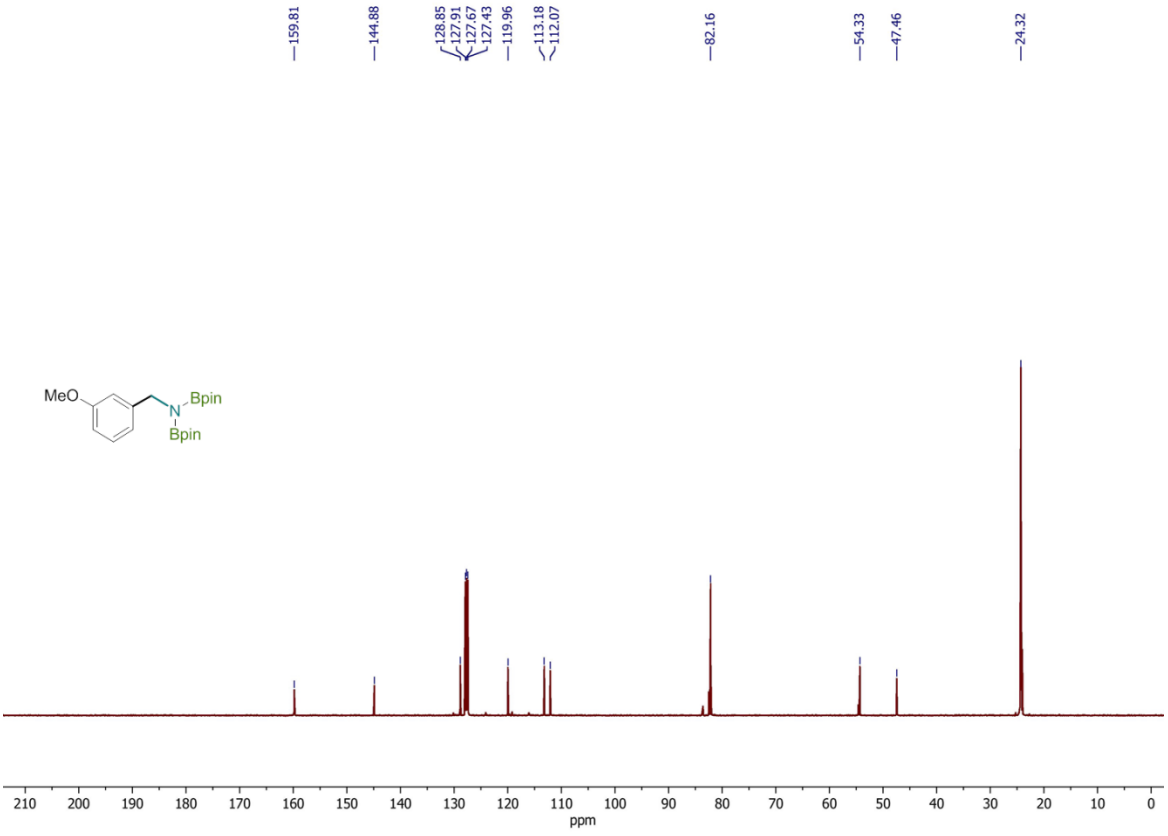




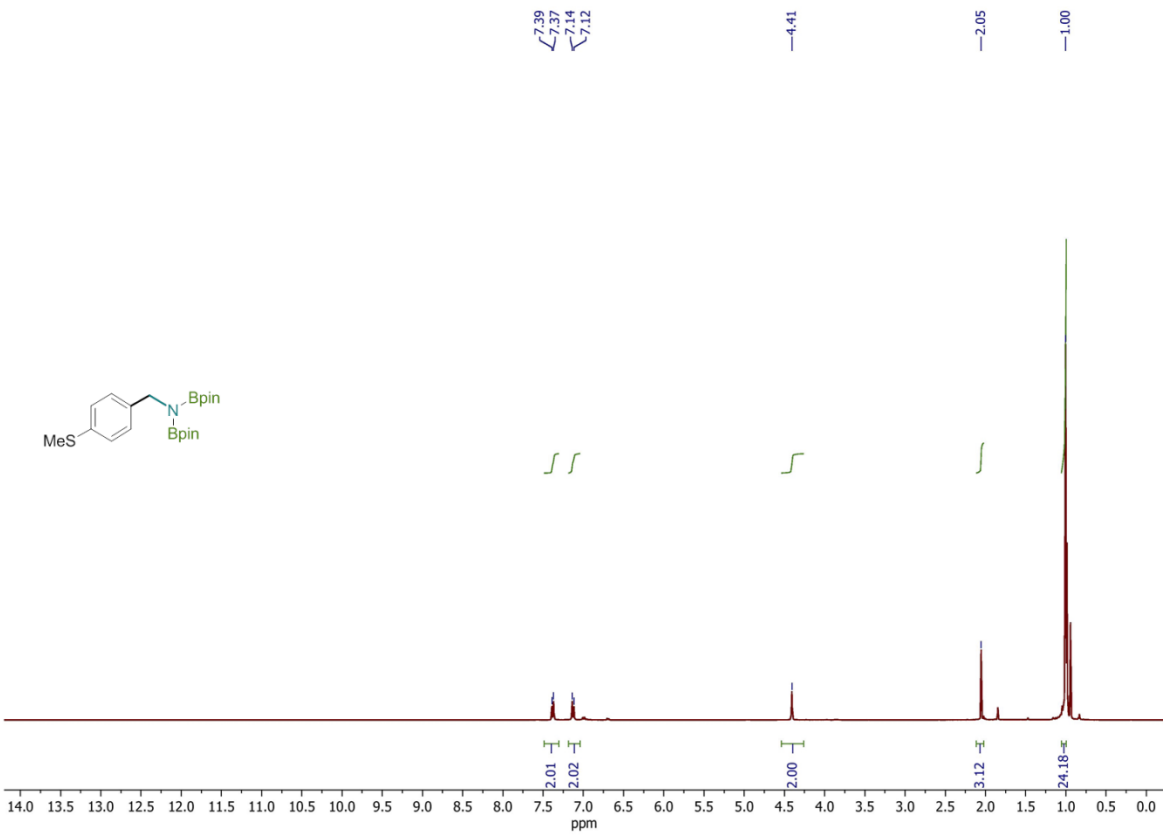

-62.05
Bpin
N
Bpin
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

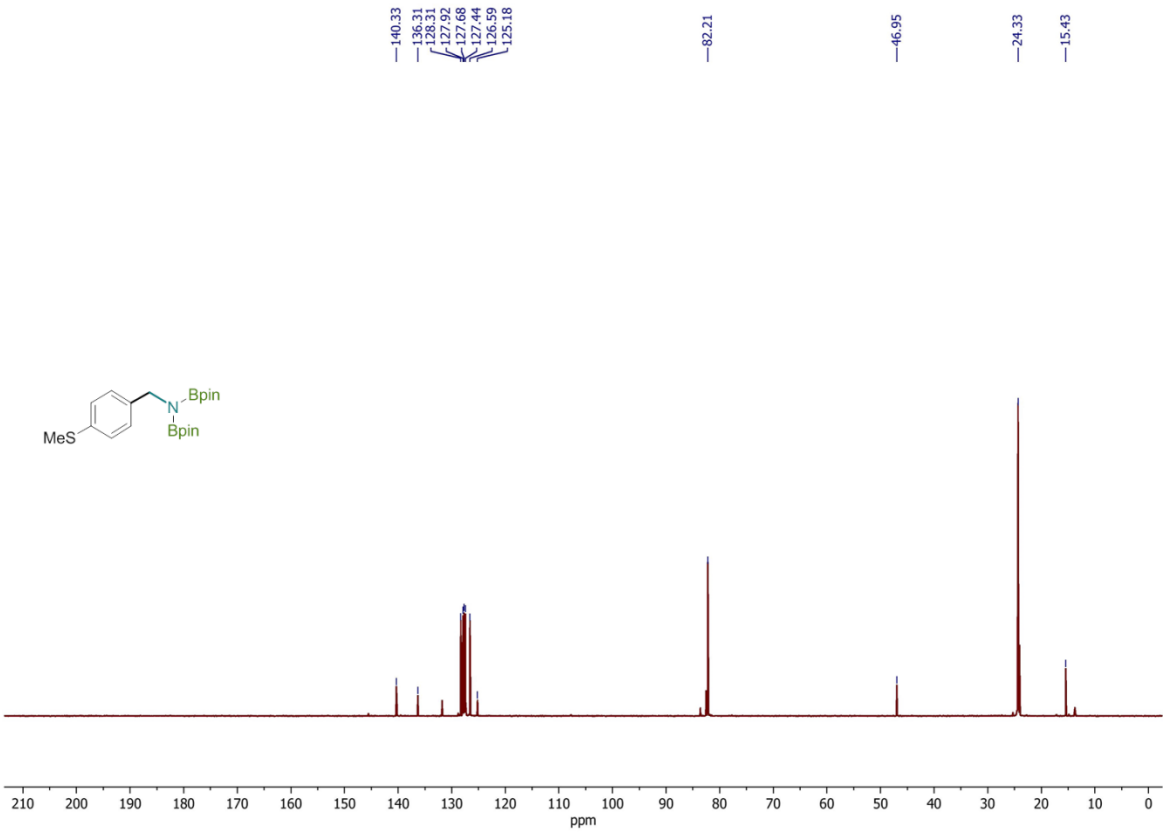
N-(3-methoxybenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2g**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



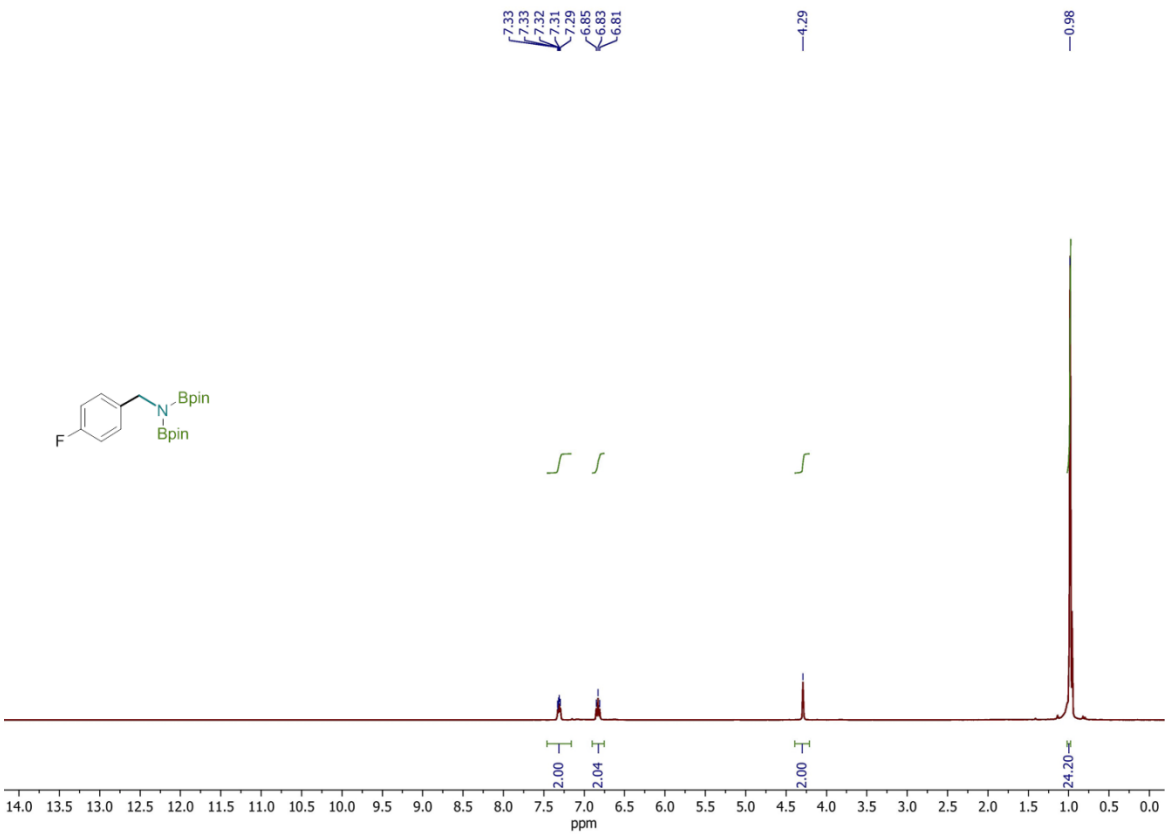


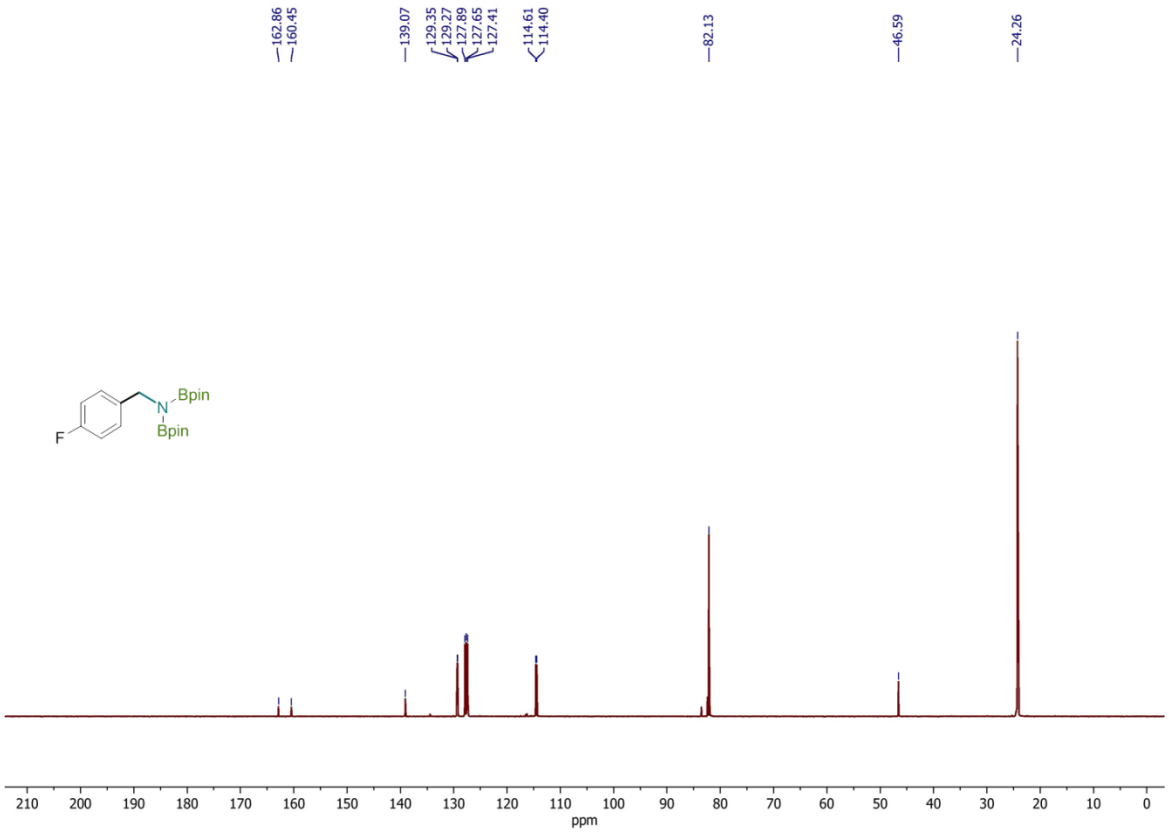
4,4,5,5-tetramethyl-*N*-(4-(methylthio)benzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2h**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**

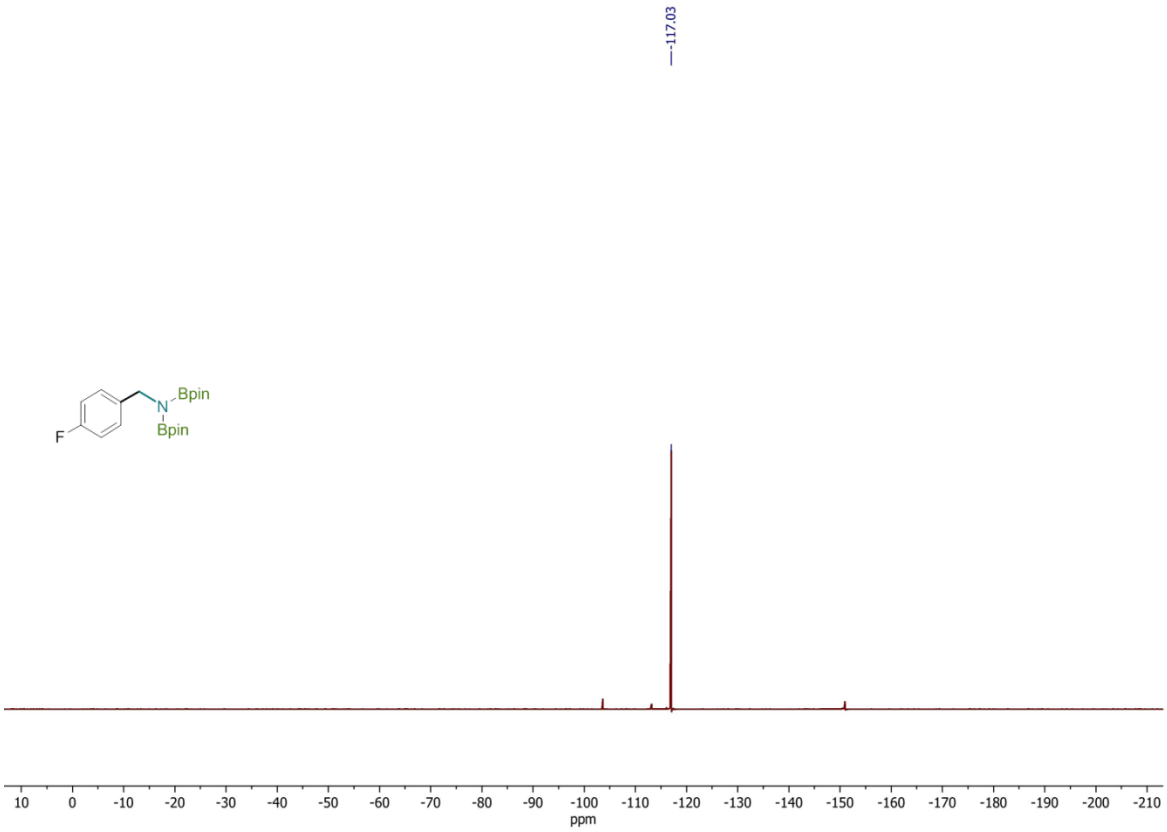




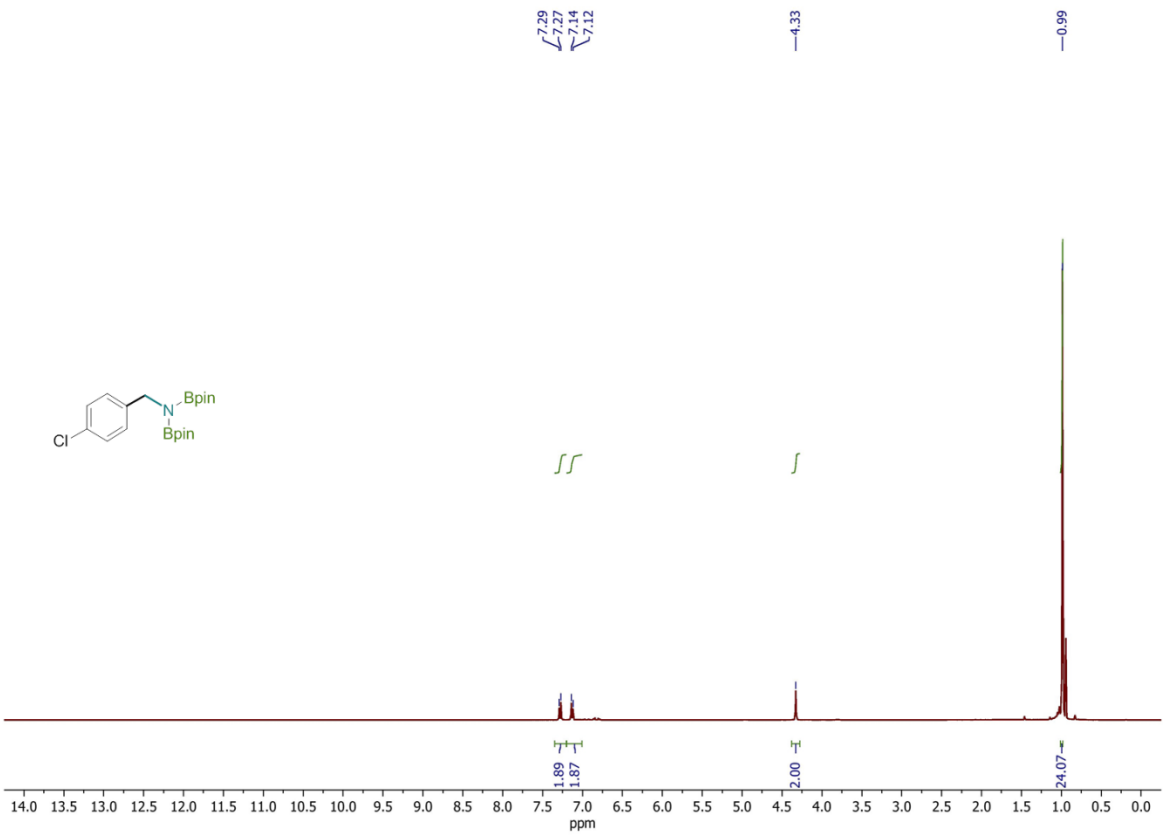
N-(4-fluorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2i**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6), ^{19}F NMR (376 MHz, C_6D_6).**

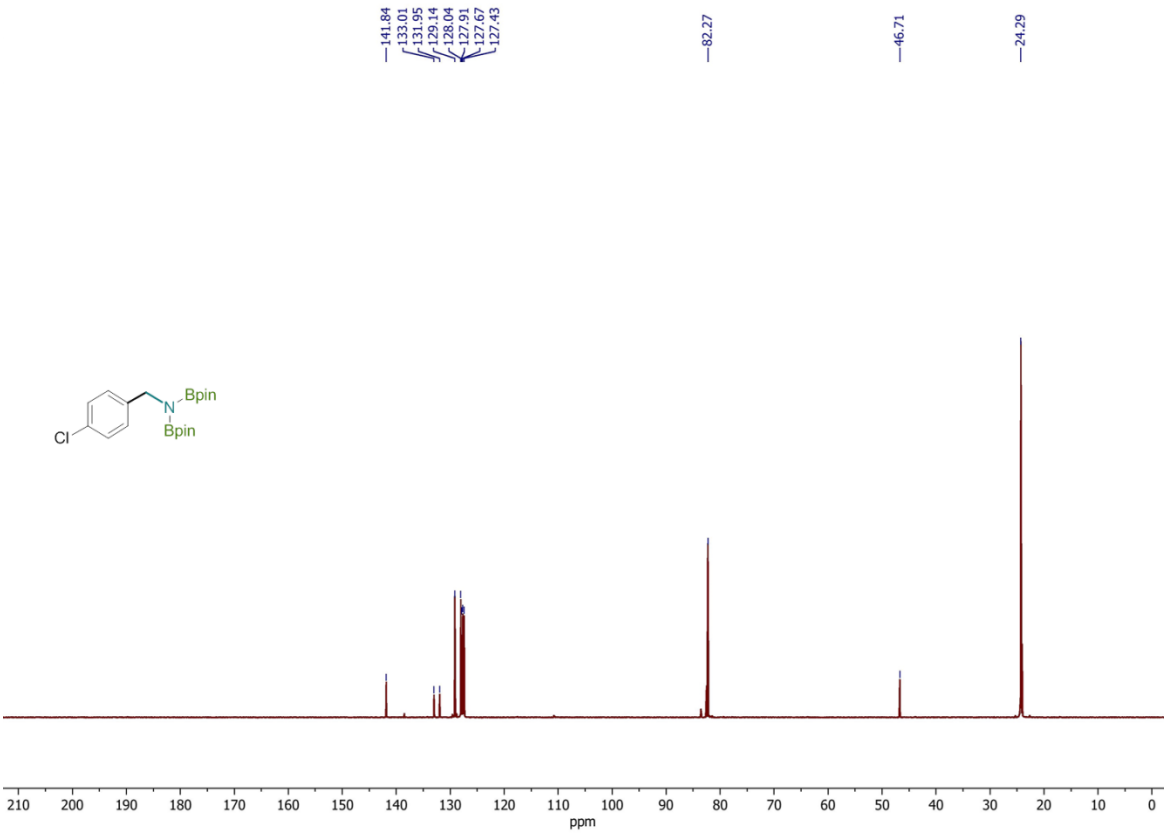




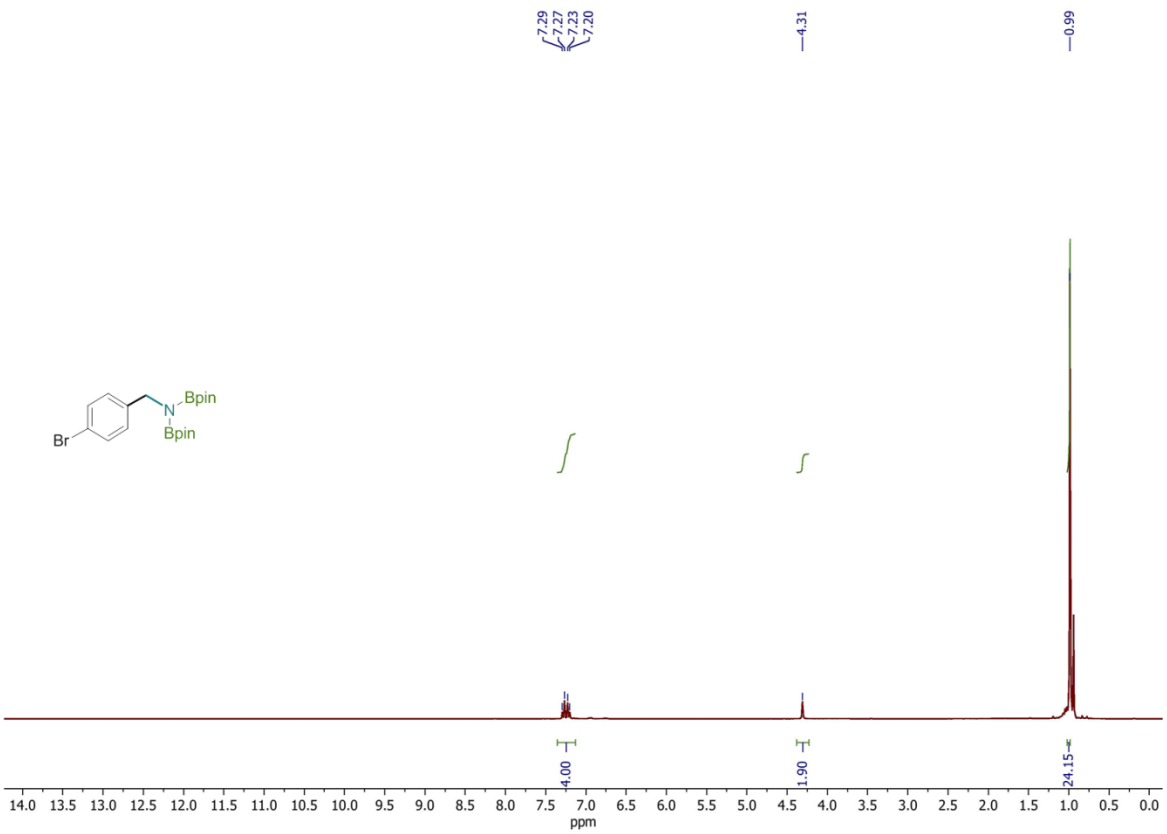

-117.03
Bpin
N
Bpin
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

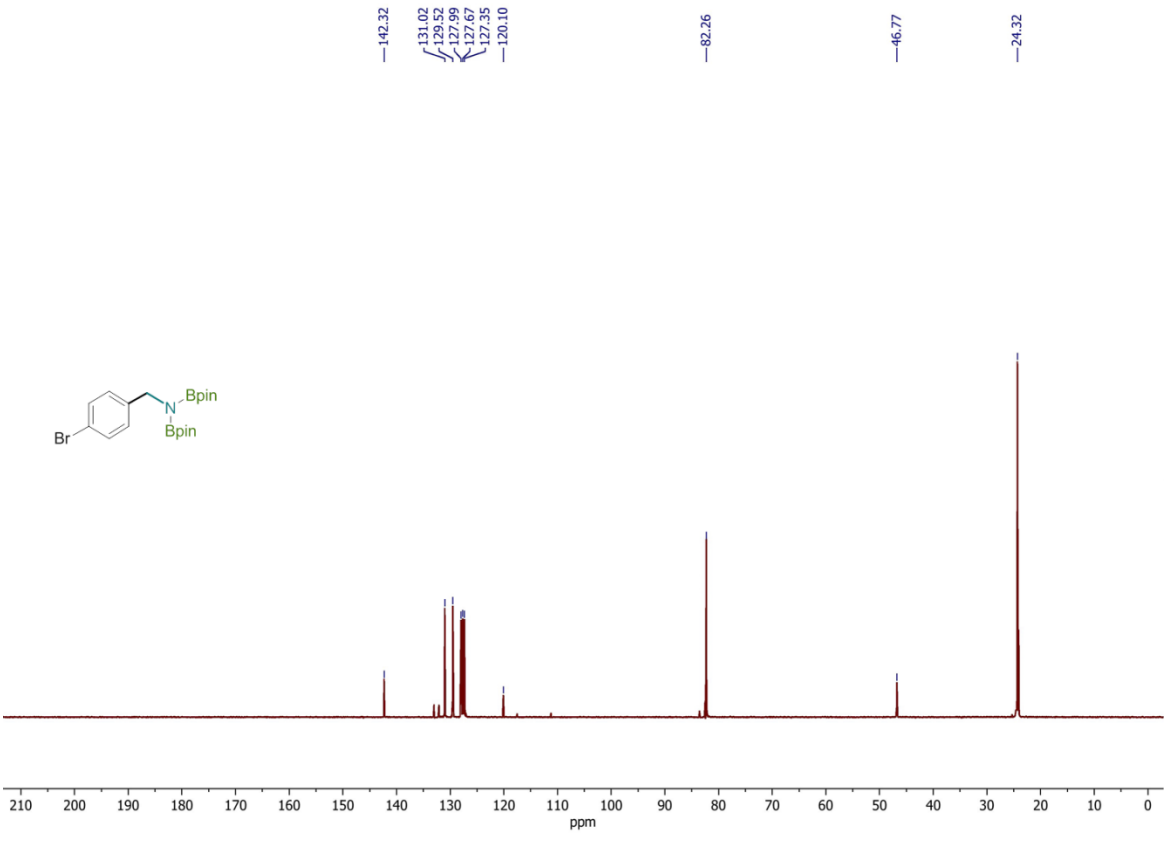
N-(4-chlorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2j**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



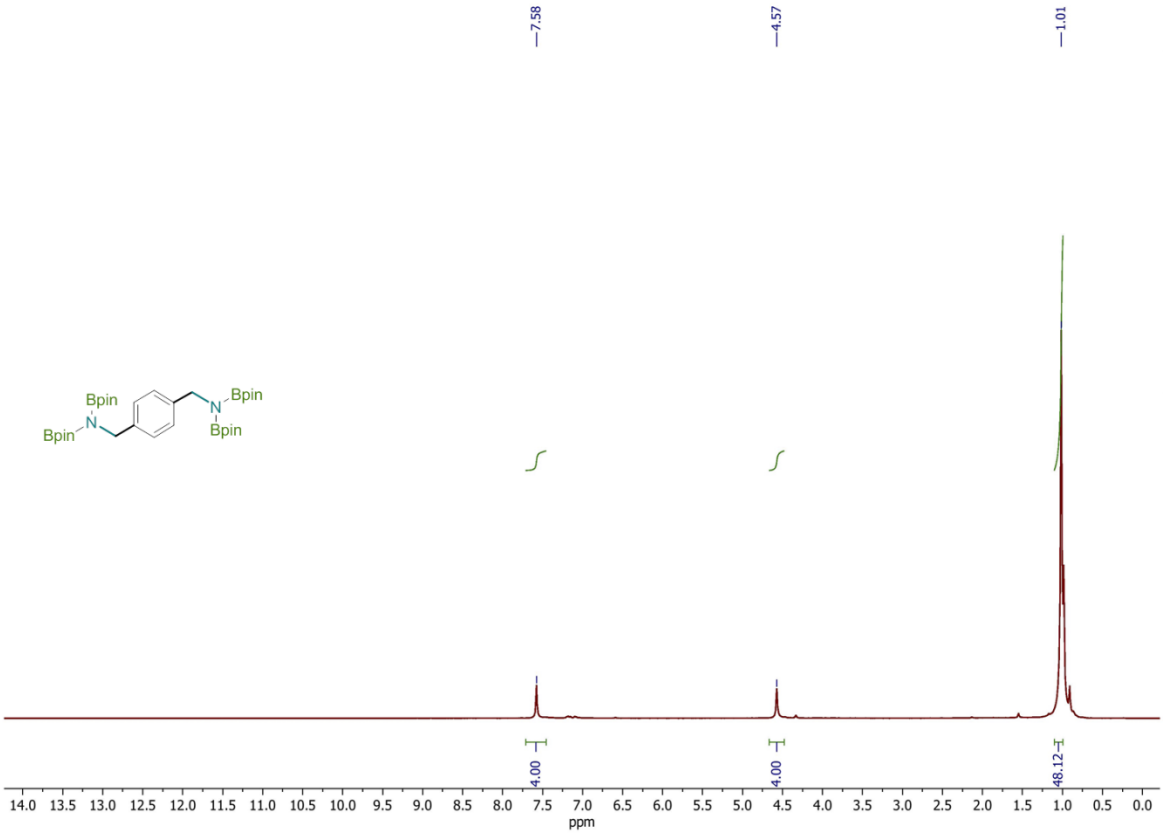


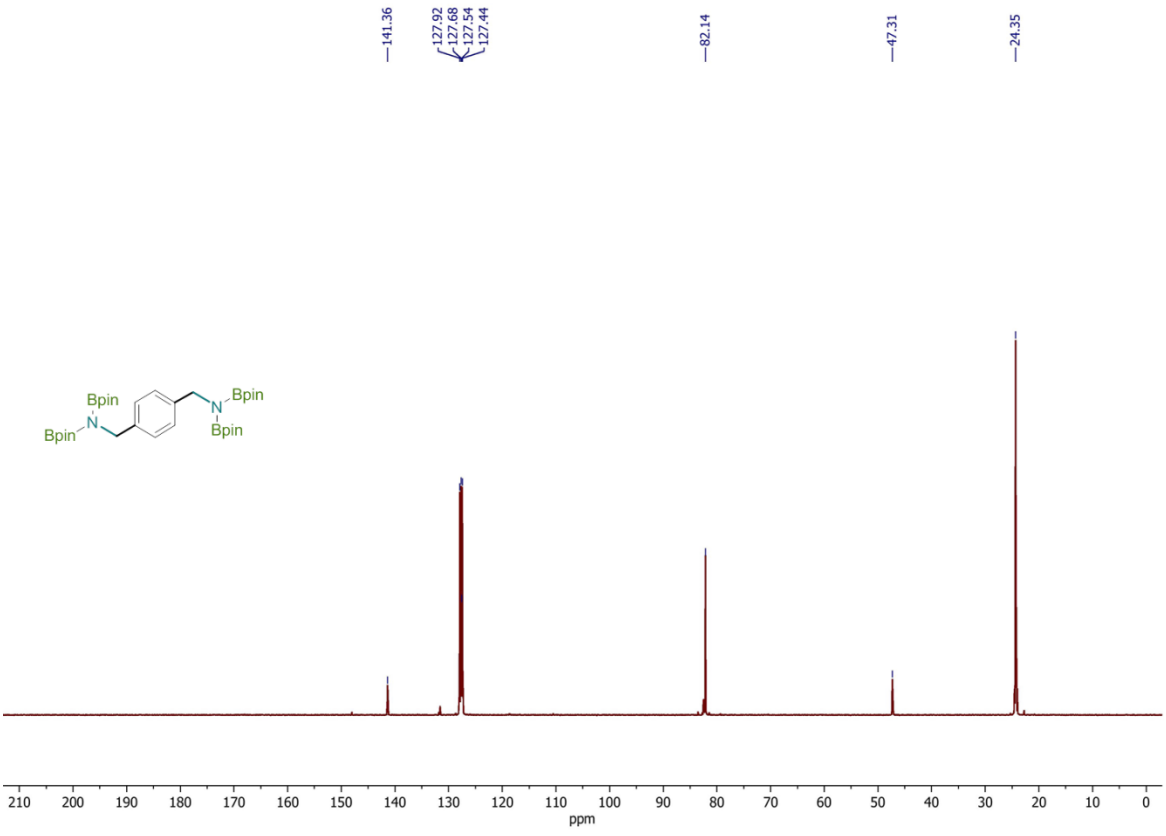
N-(4-bromobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2k**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



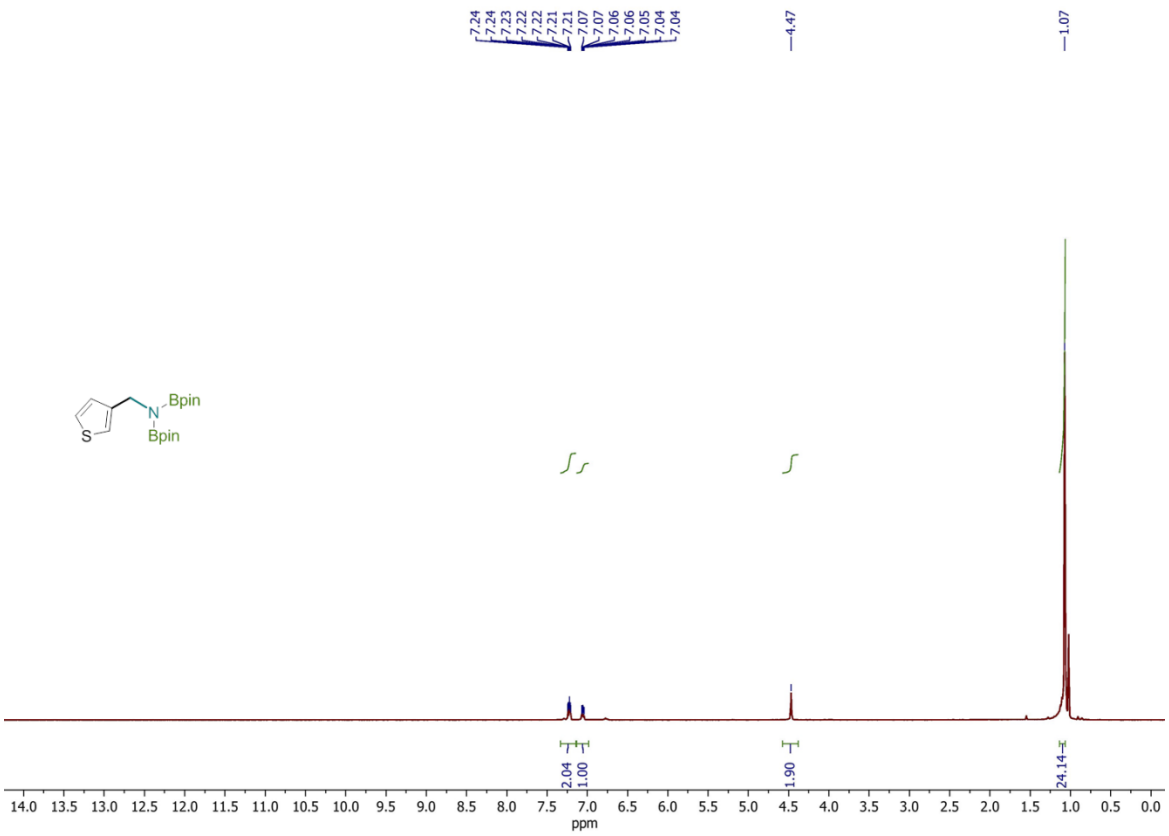


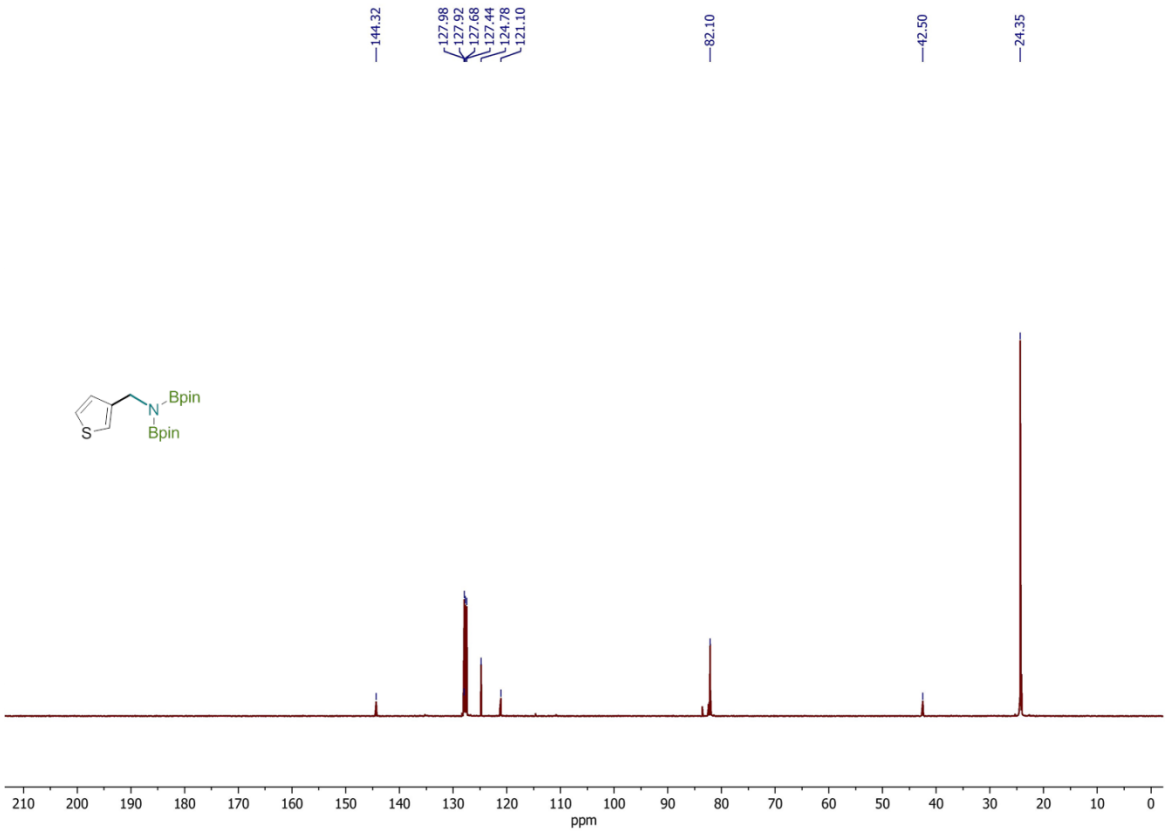
N,N′-(1,4-phenylenebis(methylene))bis(4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine) (**2l**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



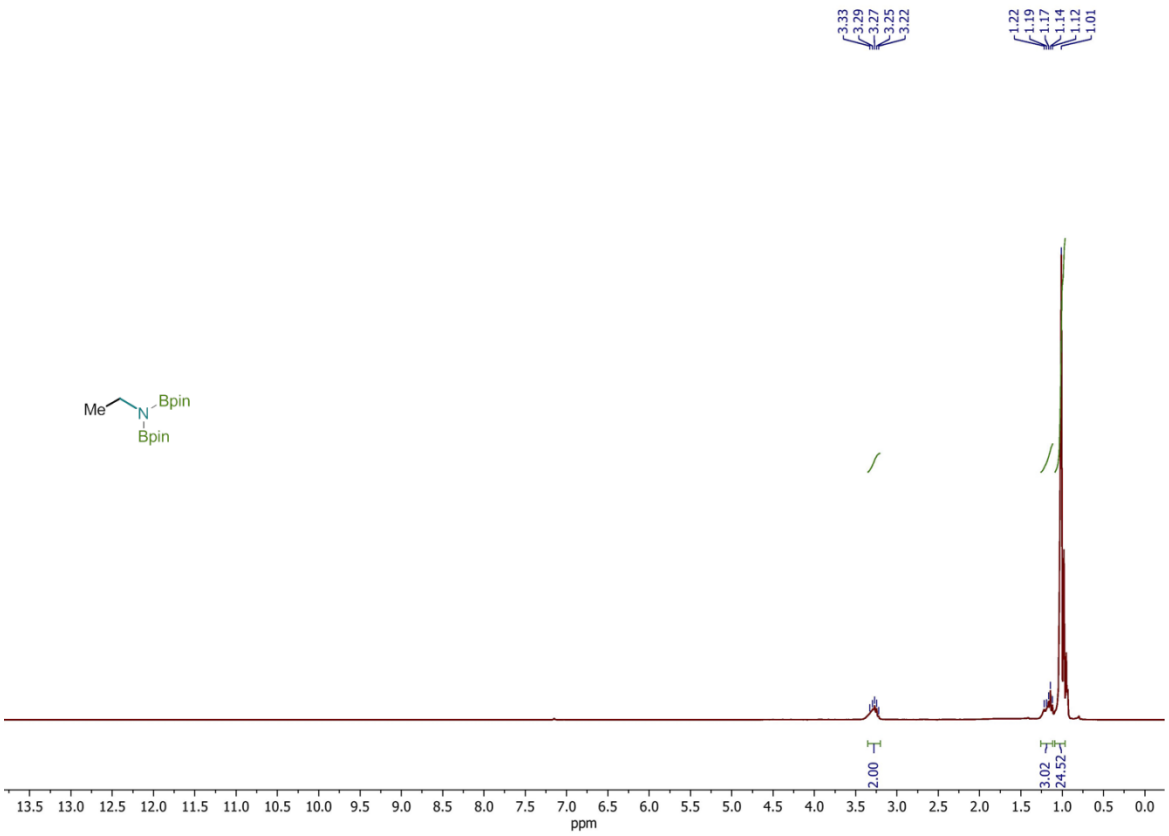


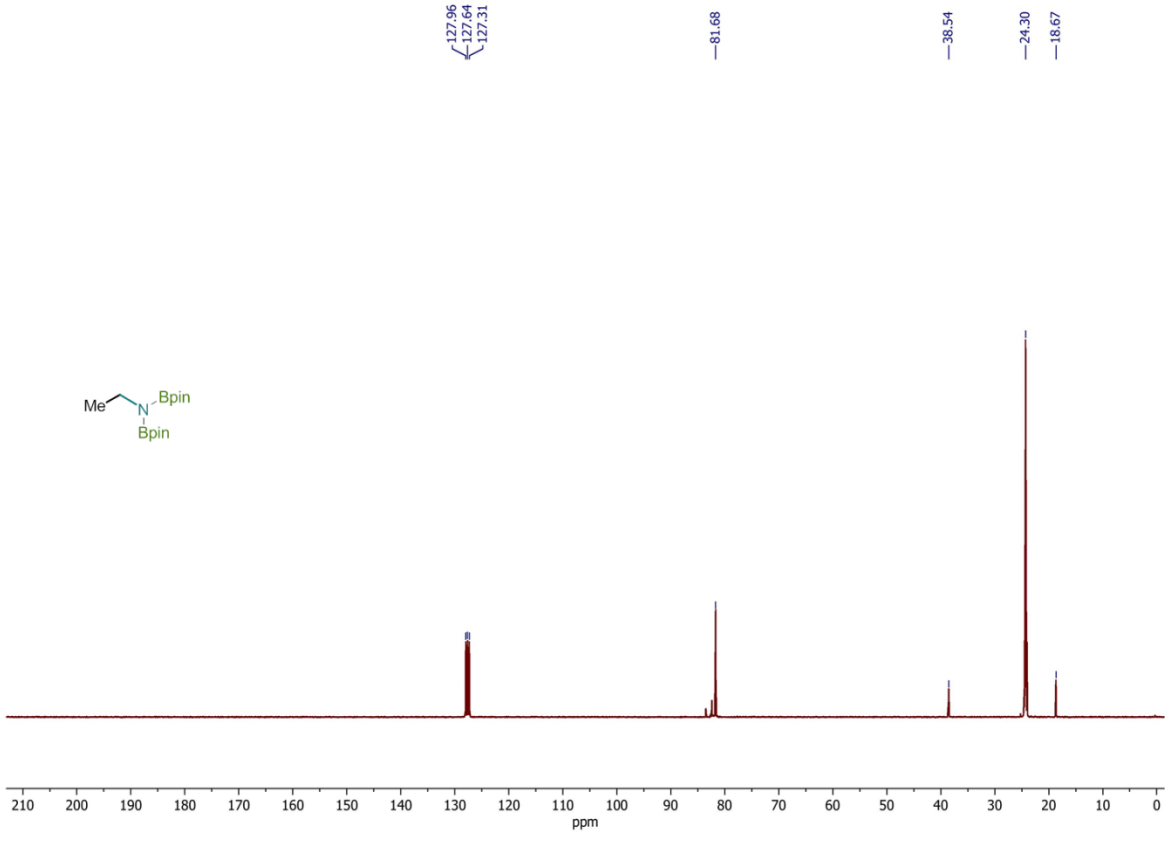
4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(thiophen-3-ylmethyl)-1,3,2-dioxaborolan-2-amine (**2m**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



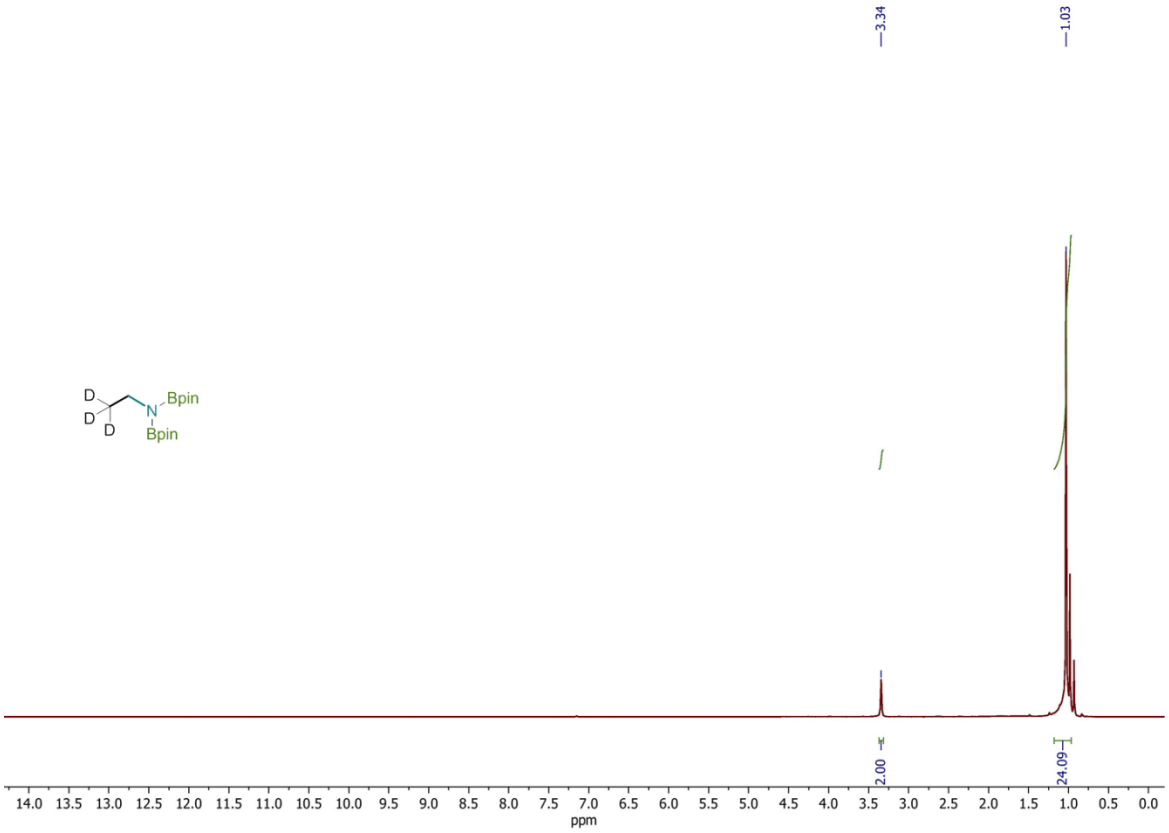


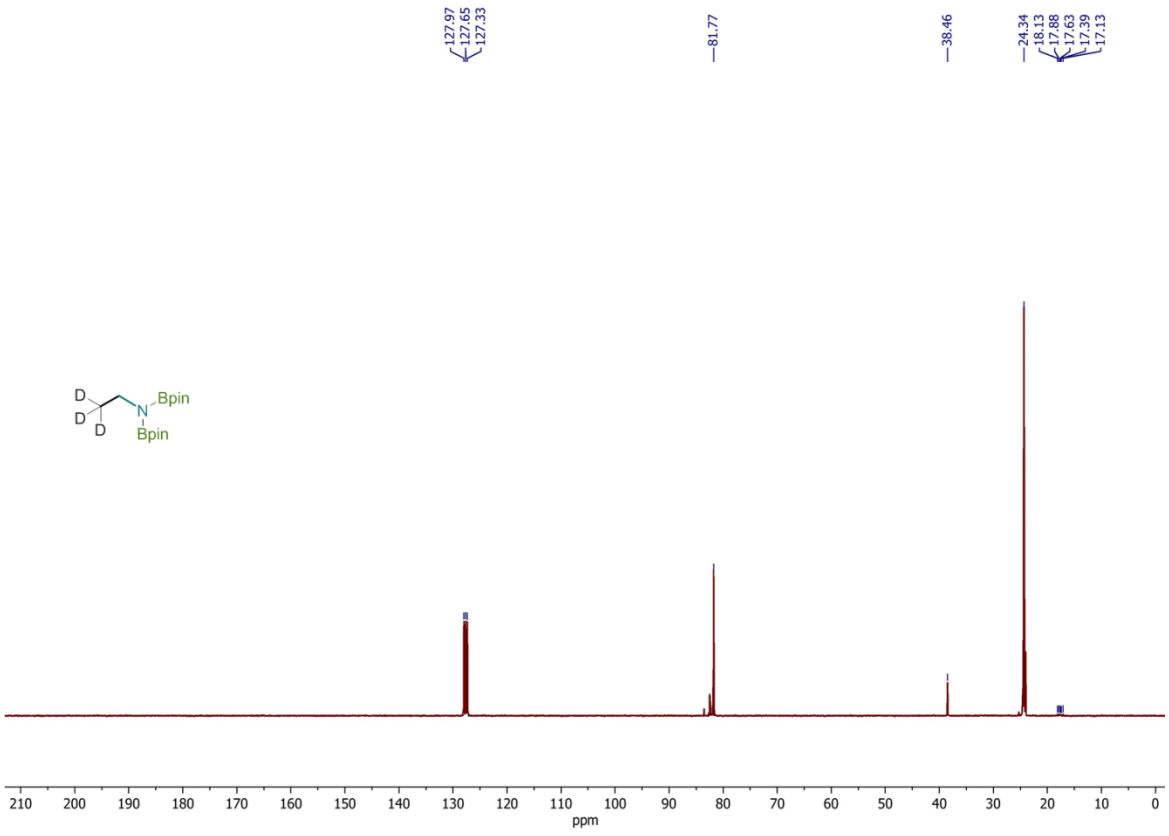
N-ethyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2n**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



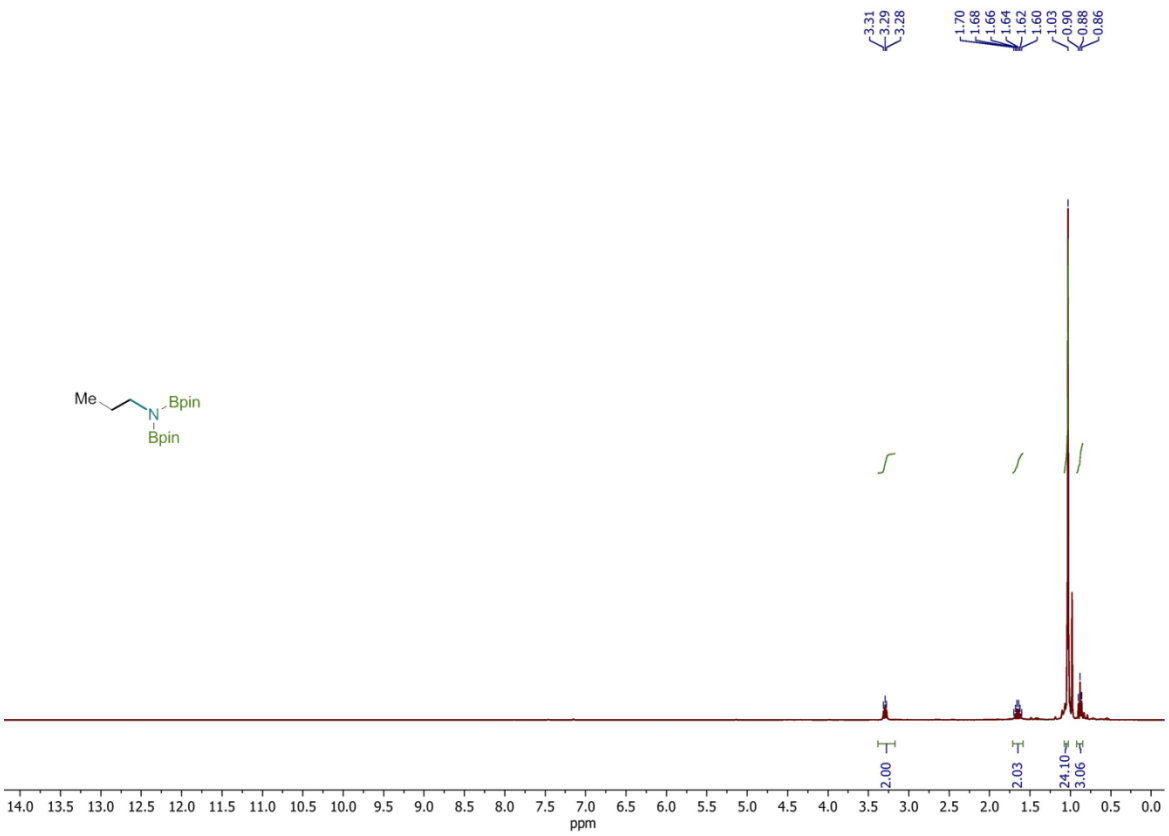


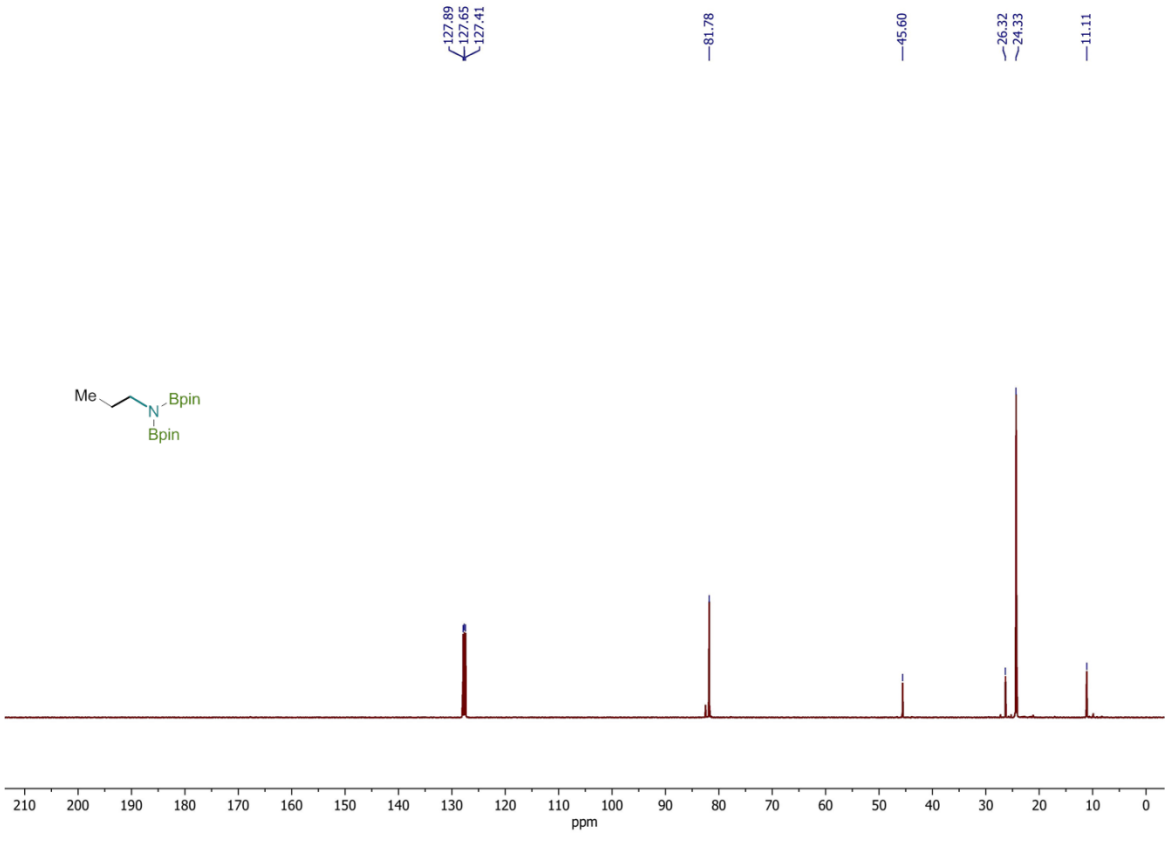
N-(ethyl-2,2,2-d$_3$)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2o**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



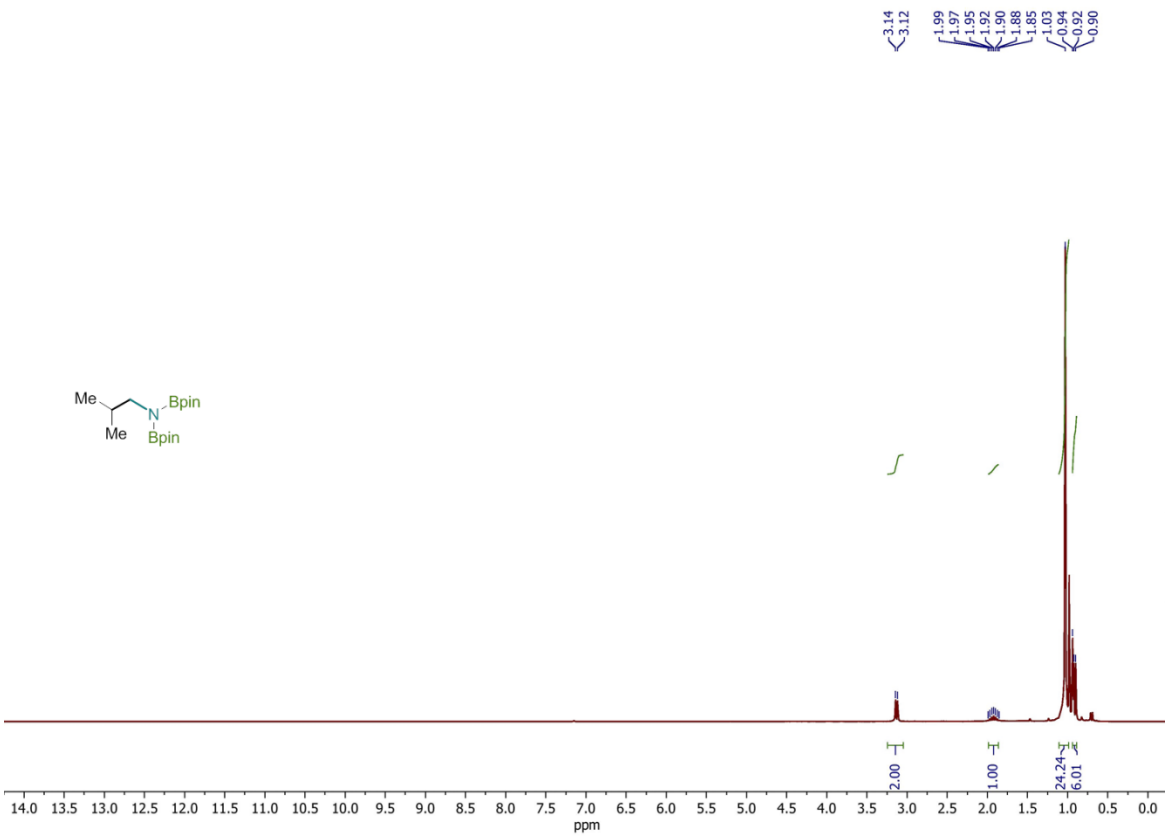


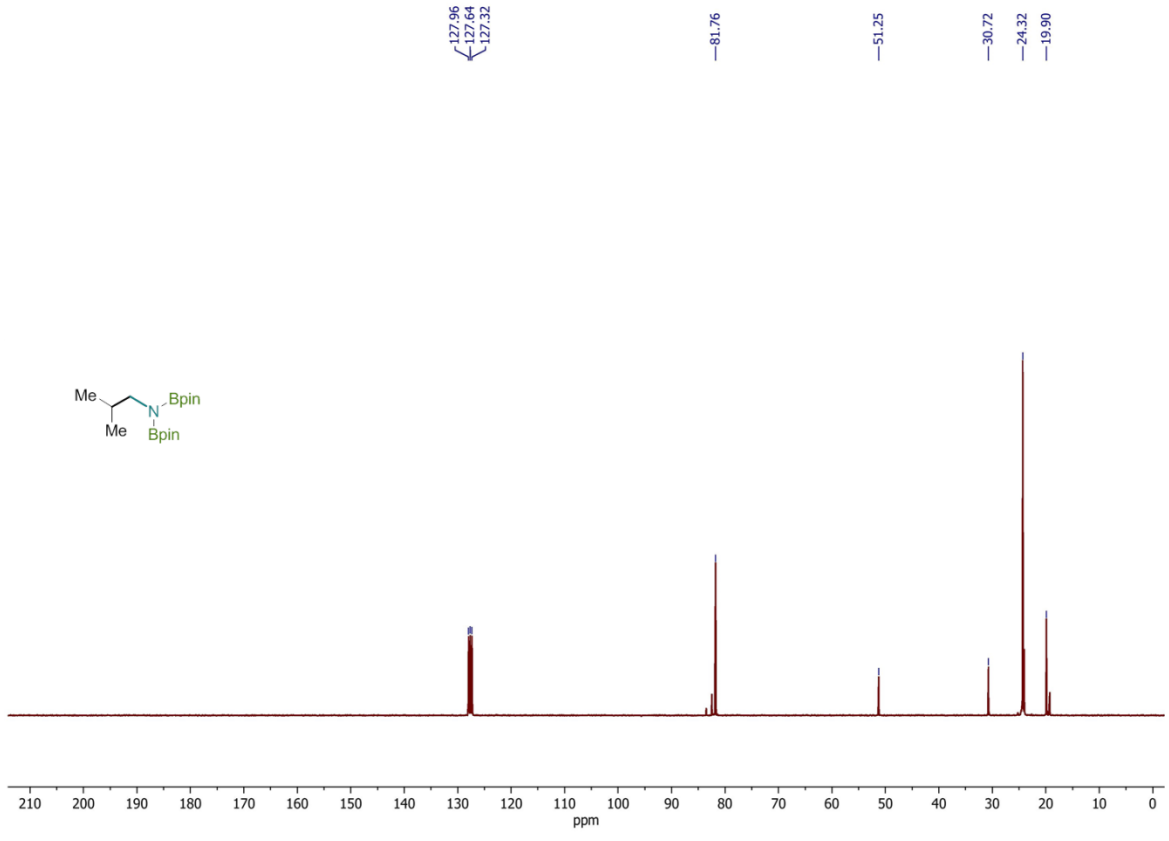
4,4,5,5-tetramethyl-*N*-propyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2p**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



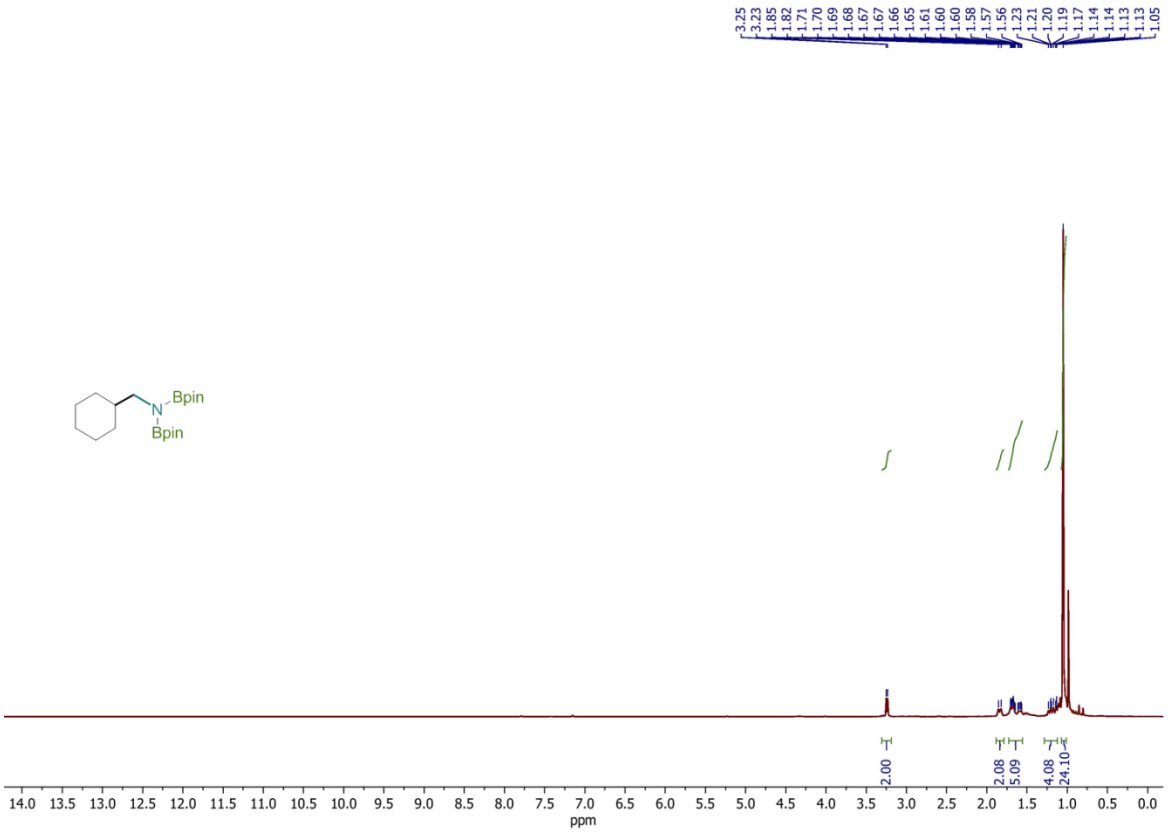


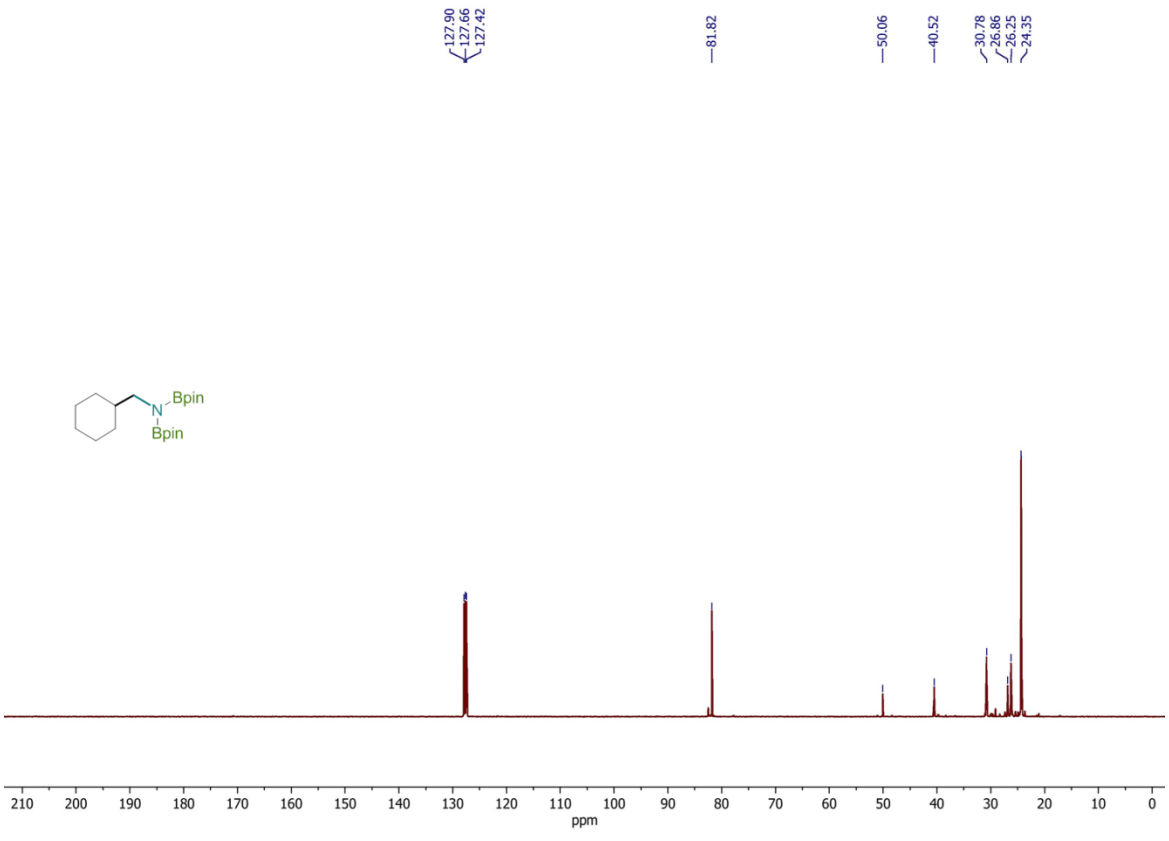
N-isobutyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2q**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



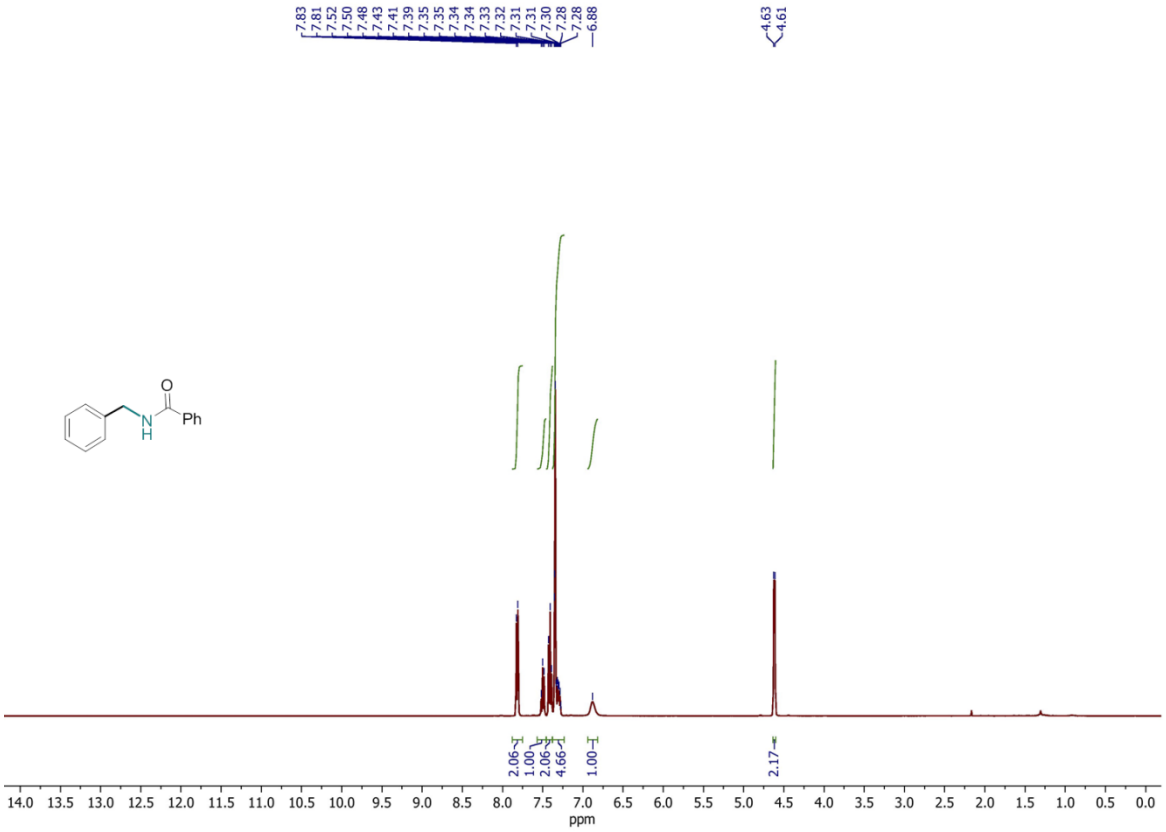


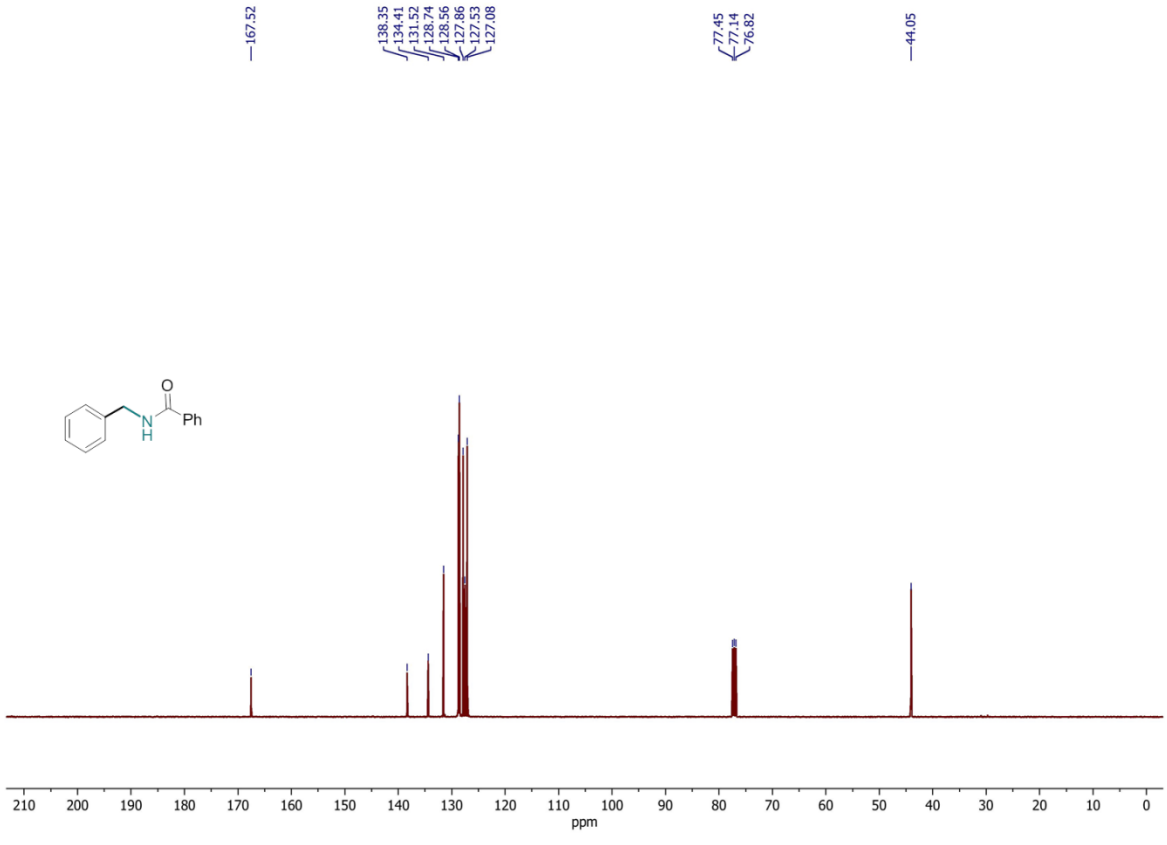
N-(cyclohexylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**2r**); **^{1}H NMR (400 MHz, C_6D_6), ^{13}C NMR (101 MHz, C_6D_6), ^{11}B NMR (128 MHz, C_6D_6).**



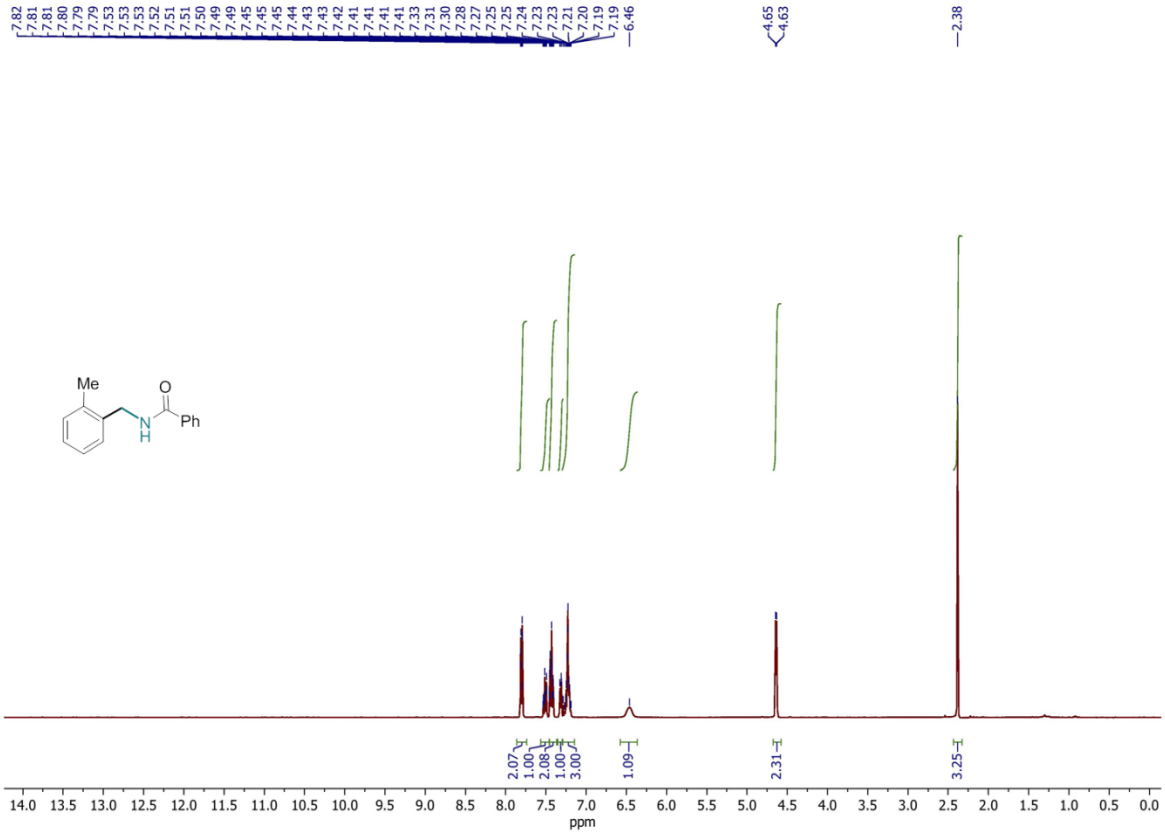


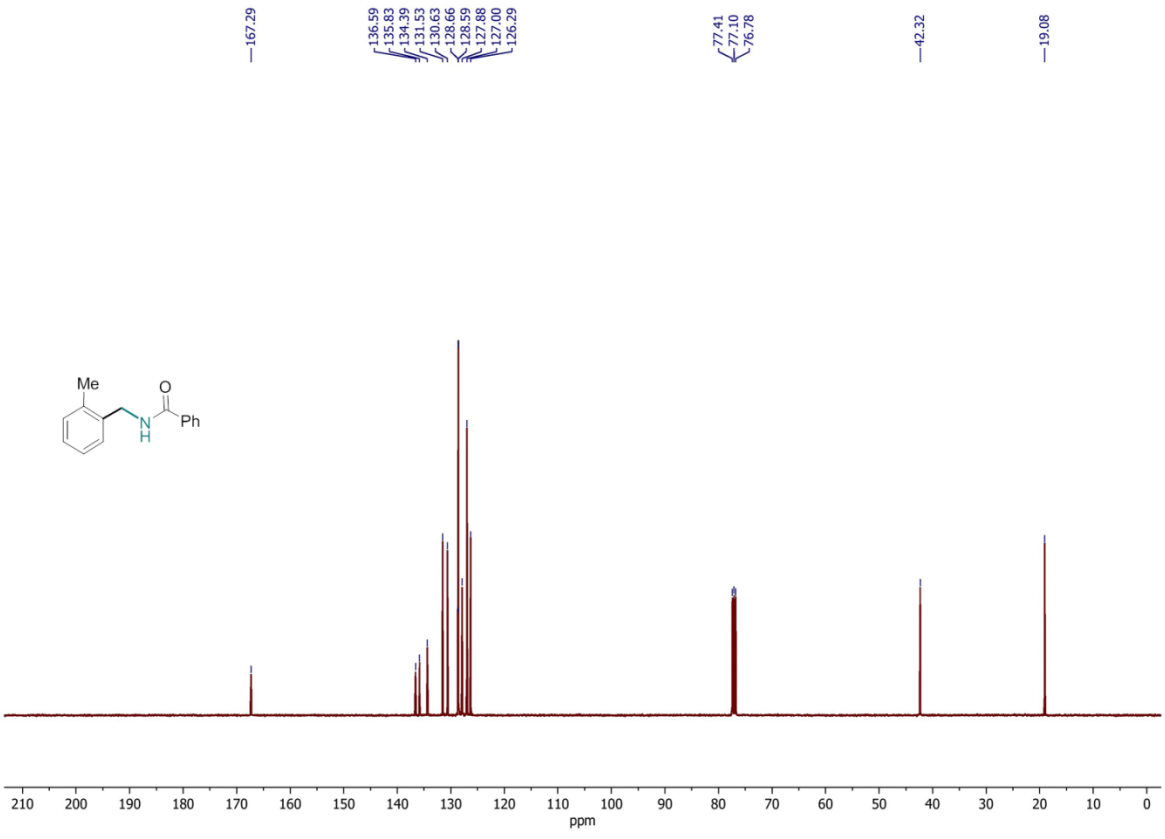
N-benzylbenzamide (**3a**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



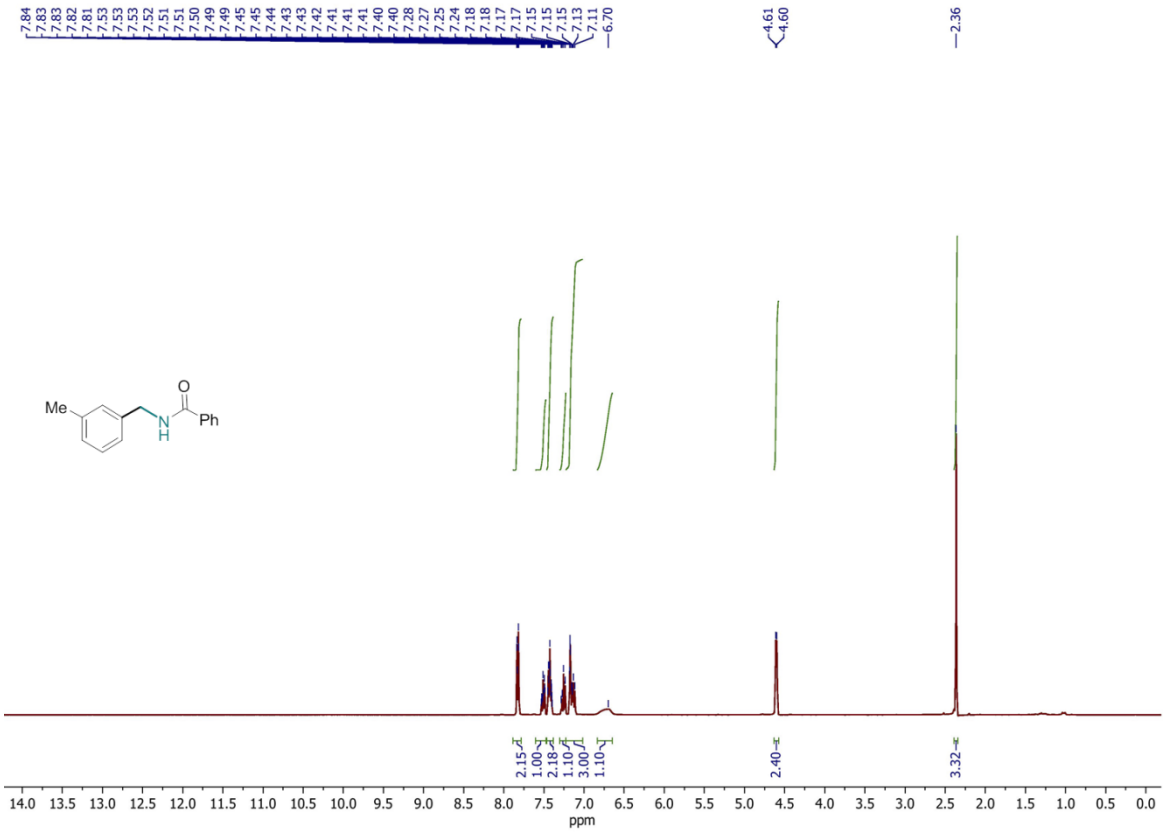


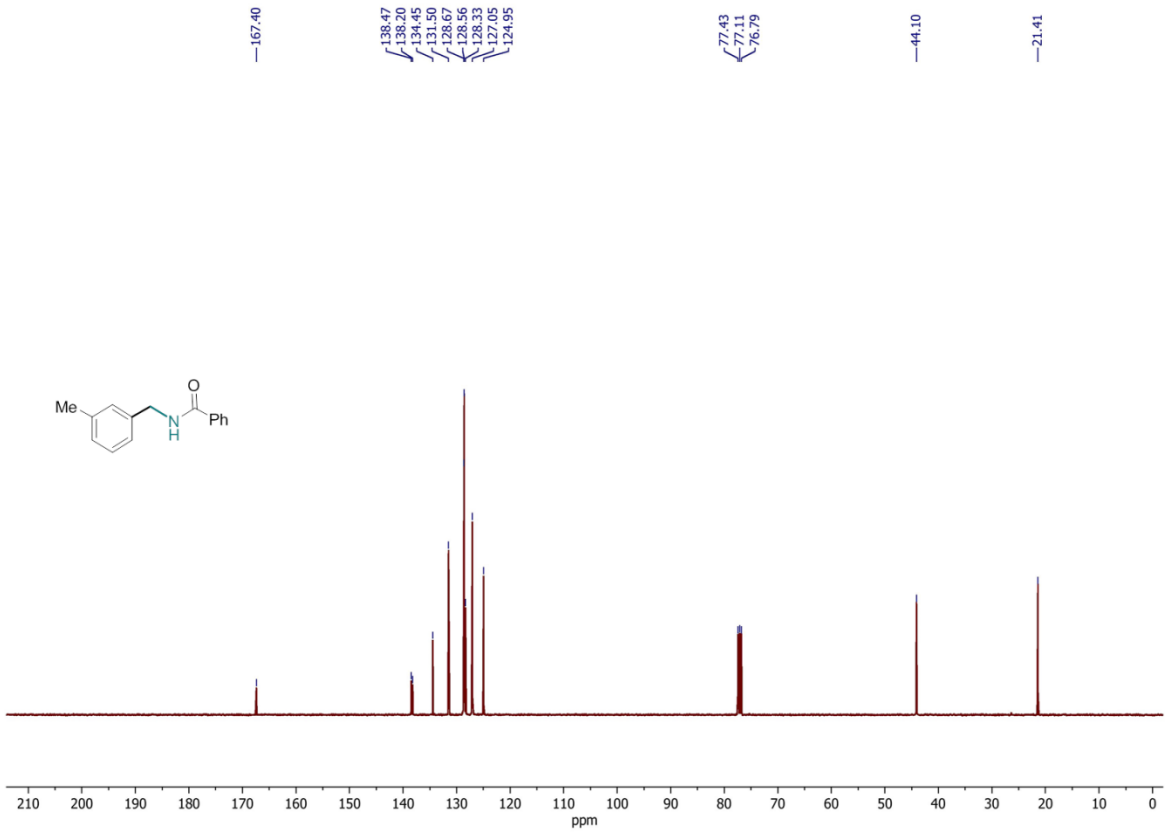
N-(2-methylbenzyl)benzamide (**3b**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



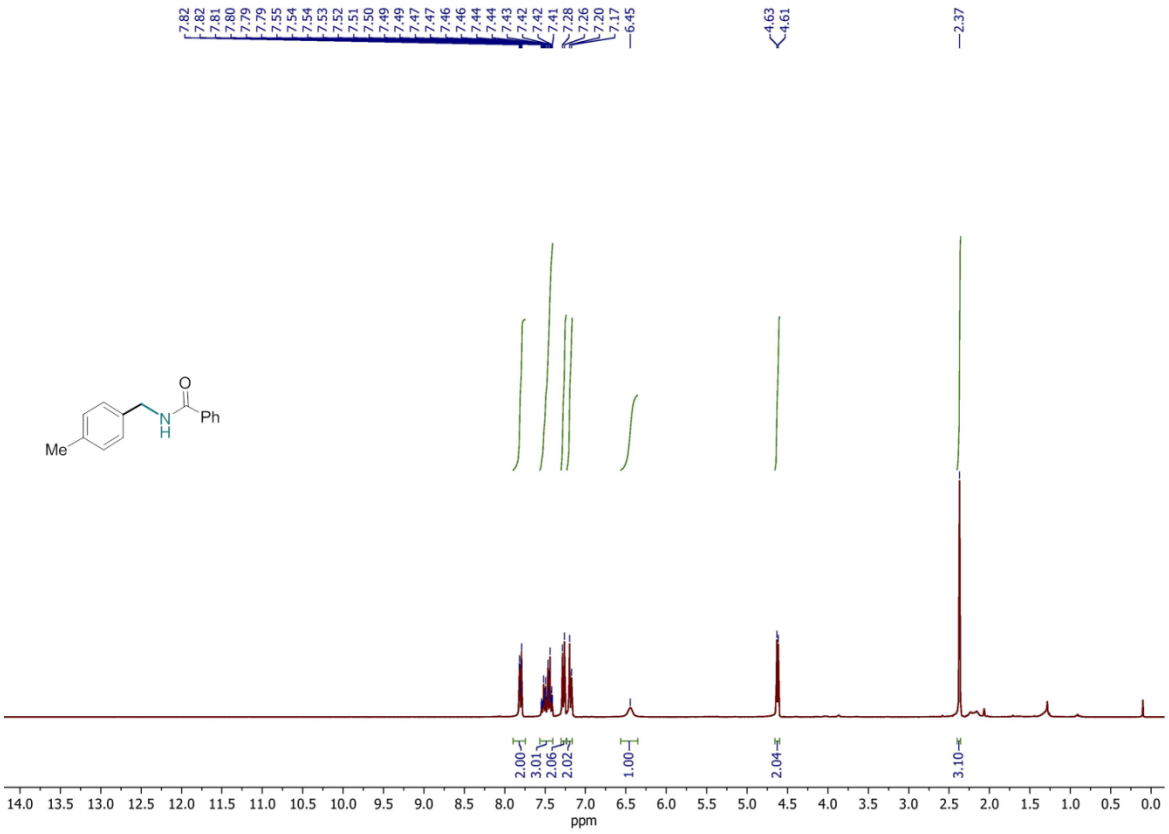


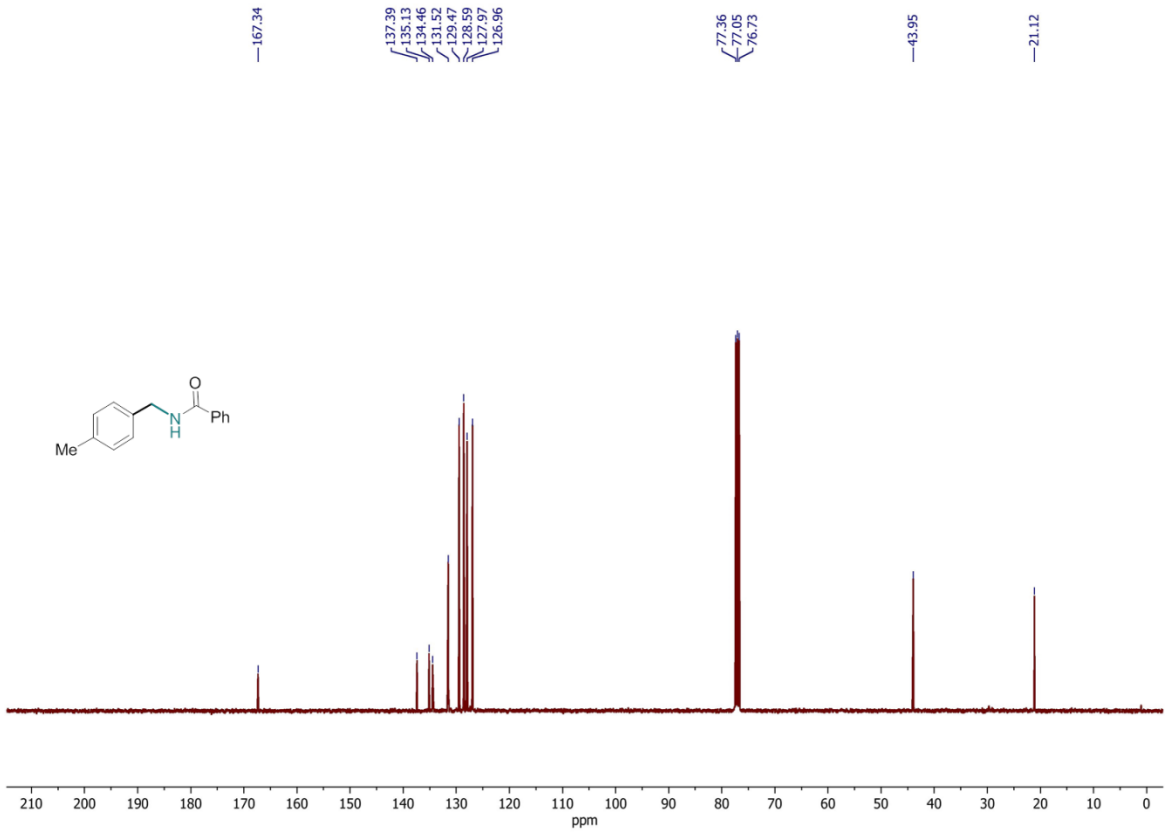
N-(3-methylbenzyl)benzamide (**3c**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



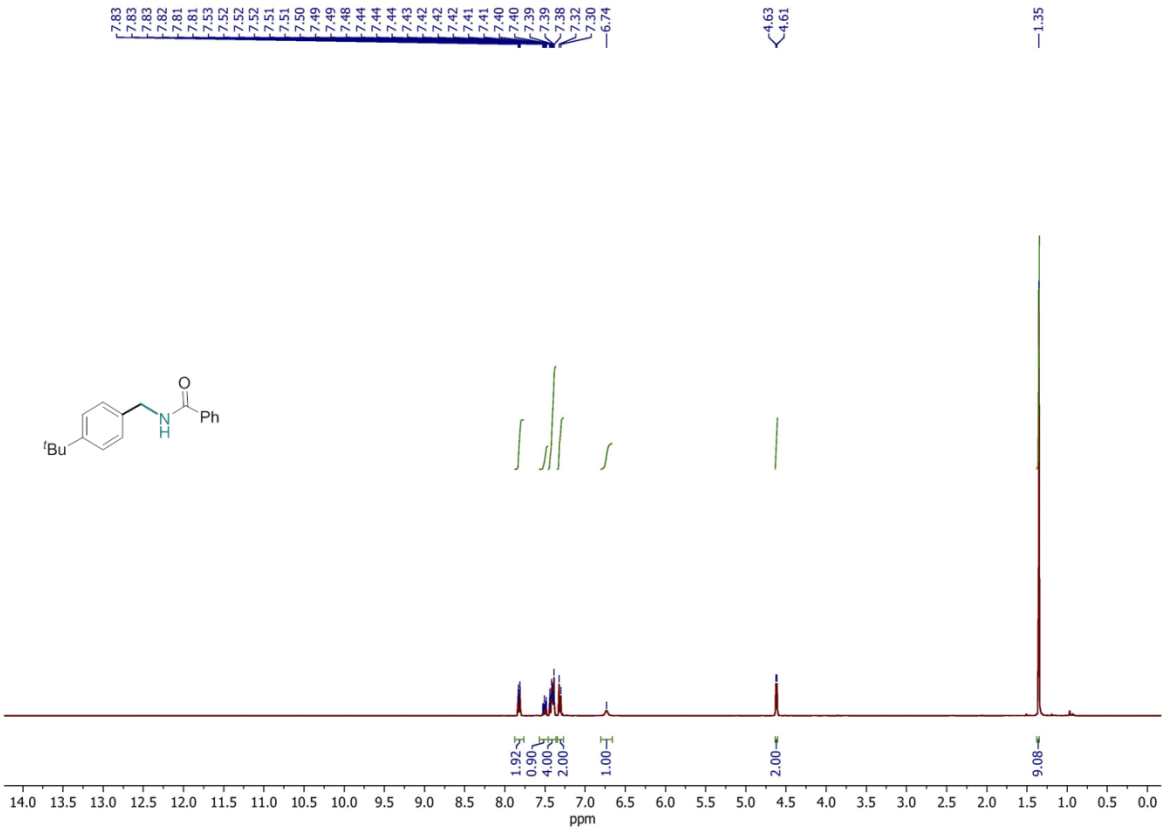


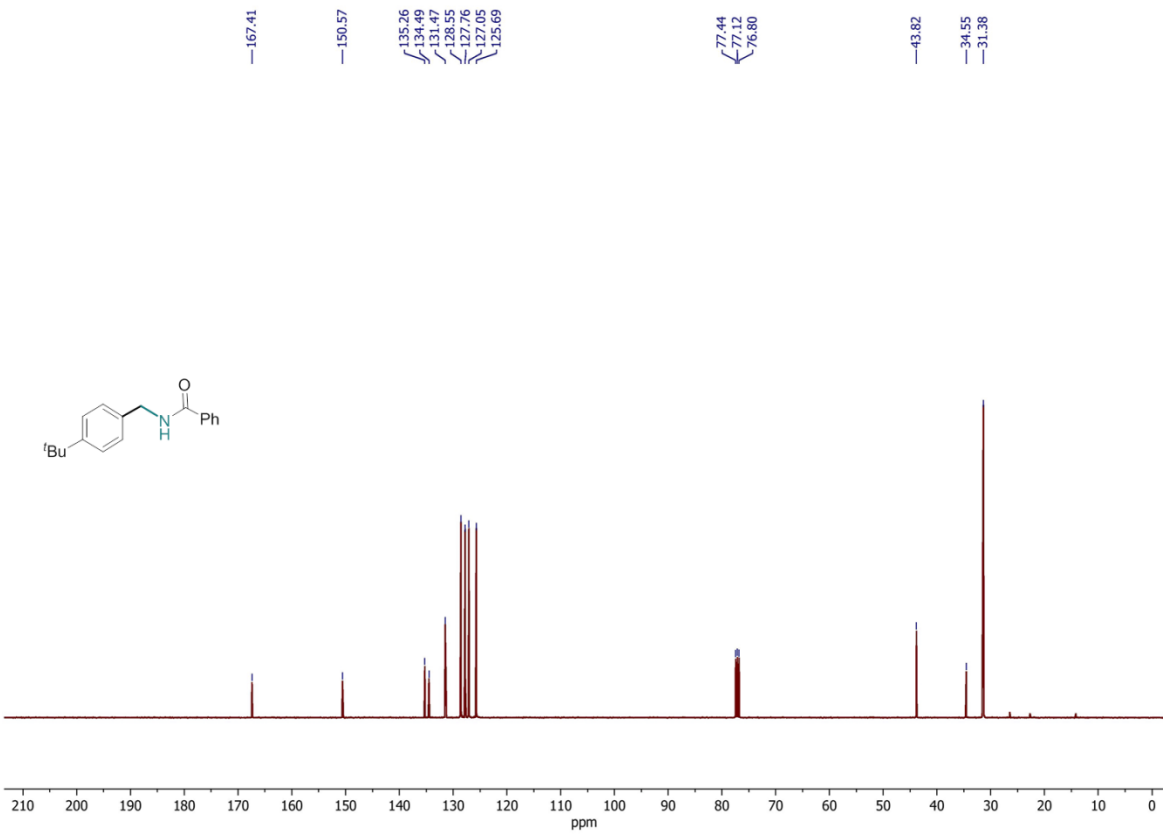
N-(4-methylbenzyl)benzamide (**3d**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



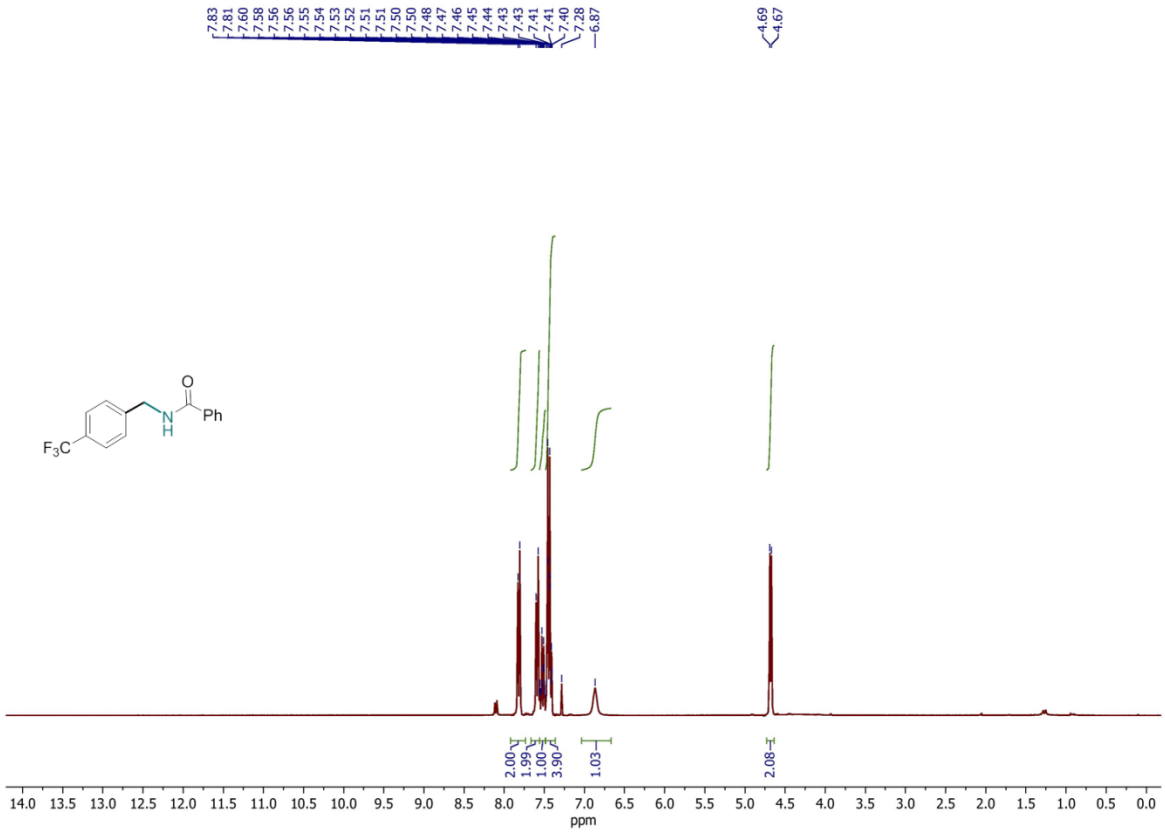


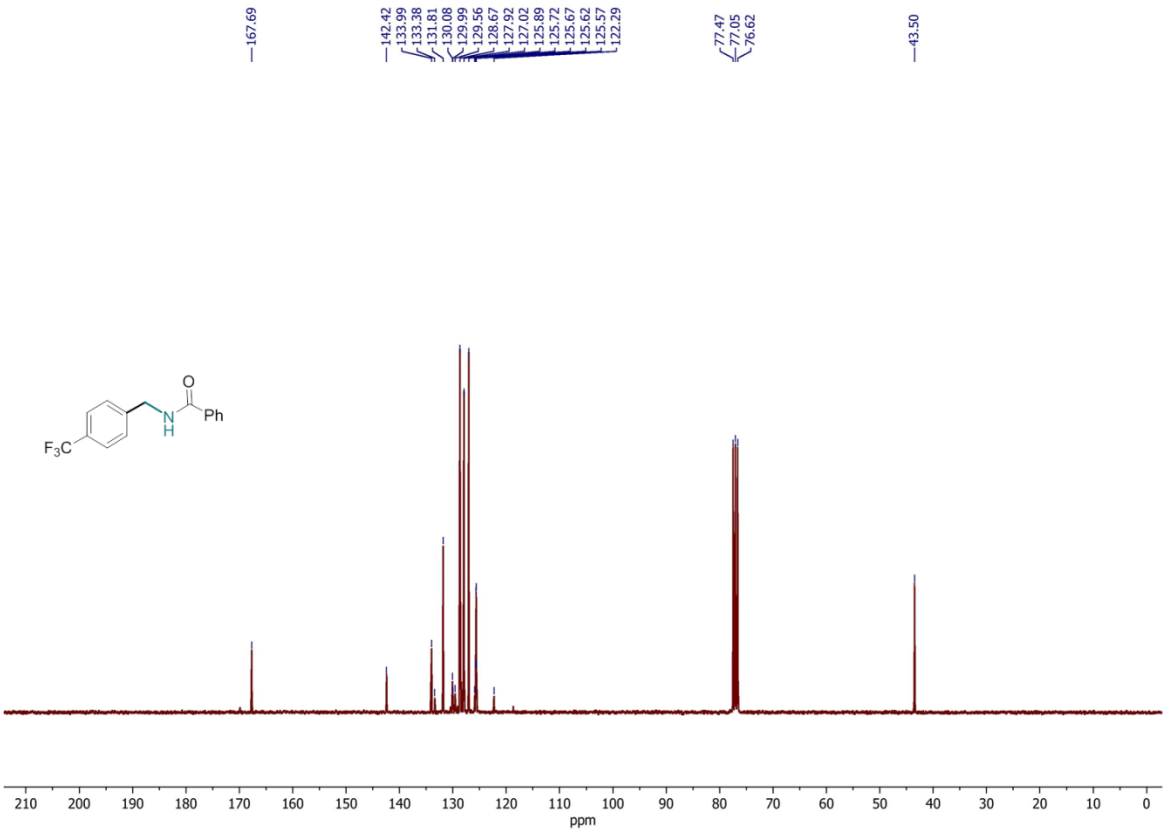
N-(4-*tert*-butylbenzyl)benzamide (**3e**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**

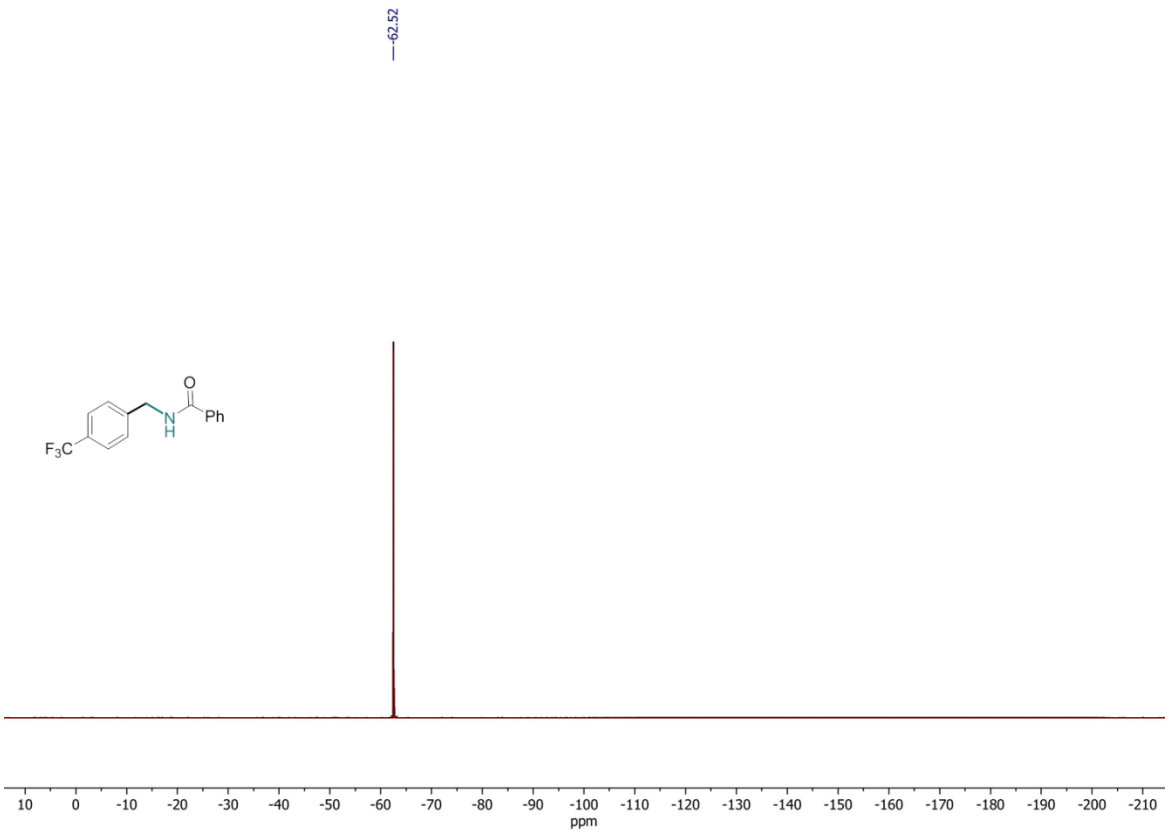




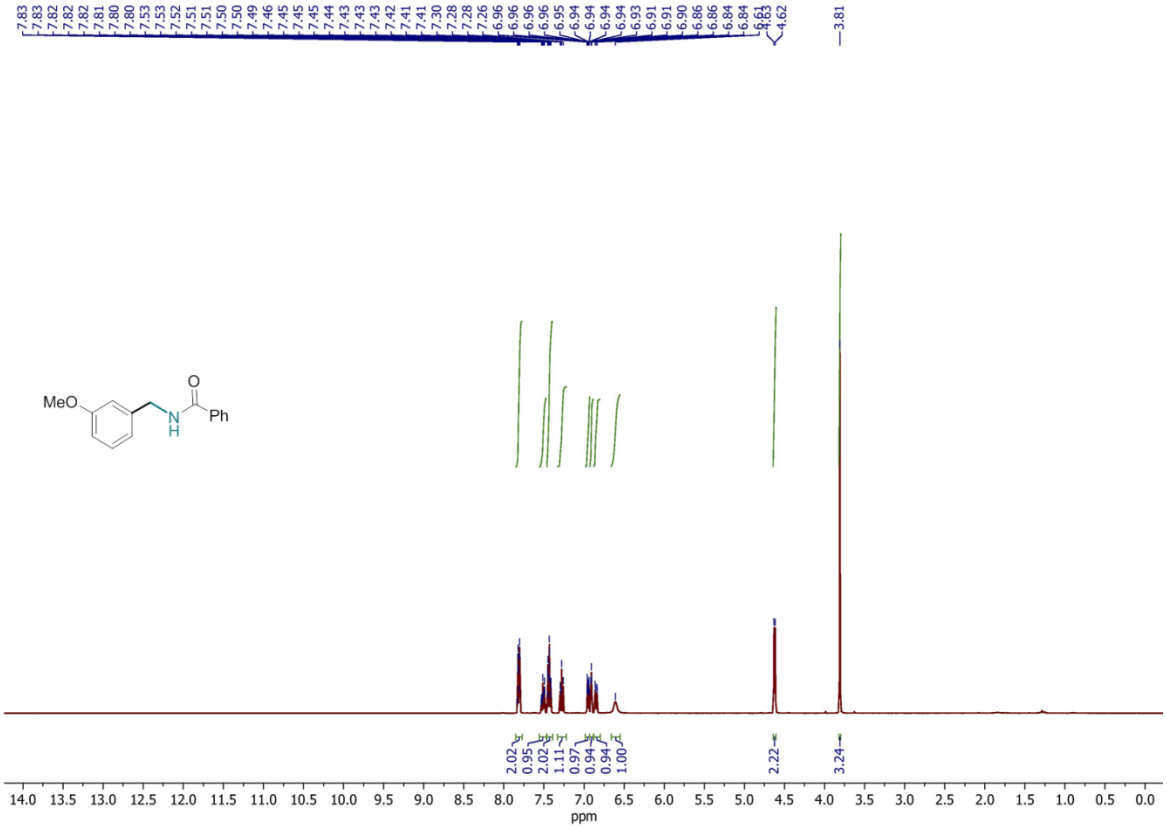
N-(4-(trifluoromethyl)benzyl)benzamide (**3f**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

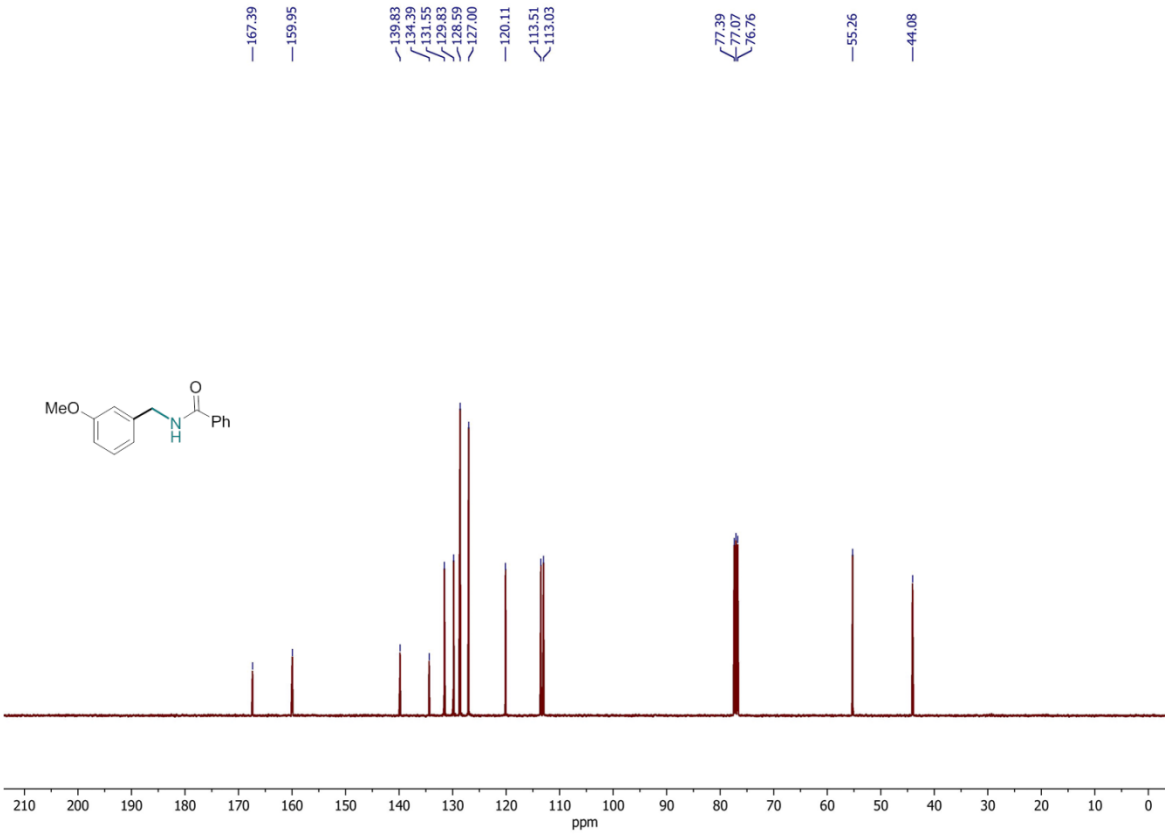




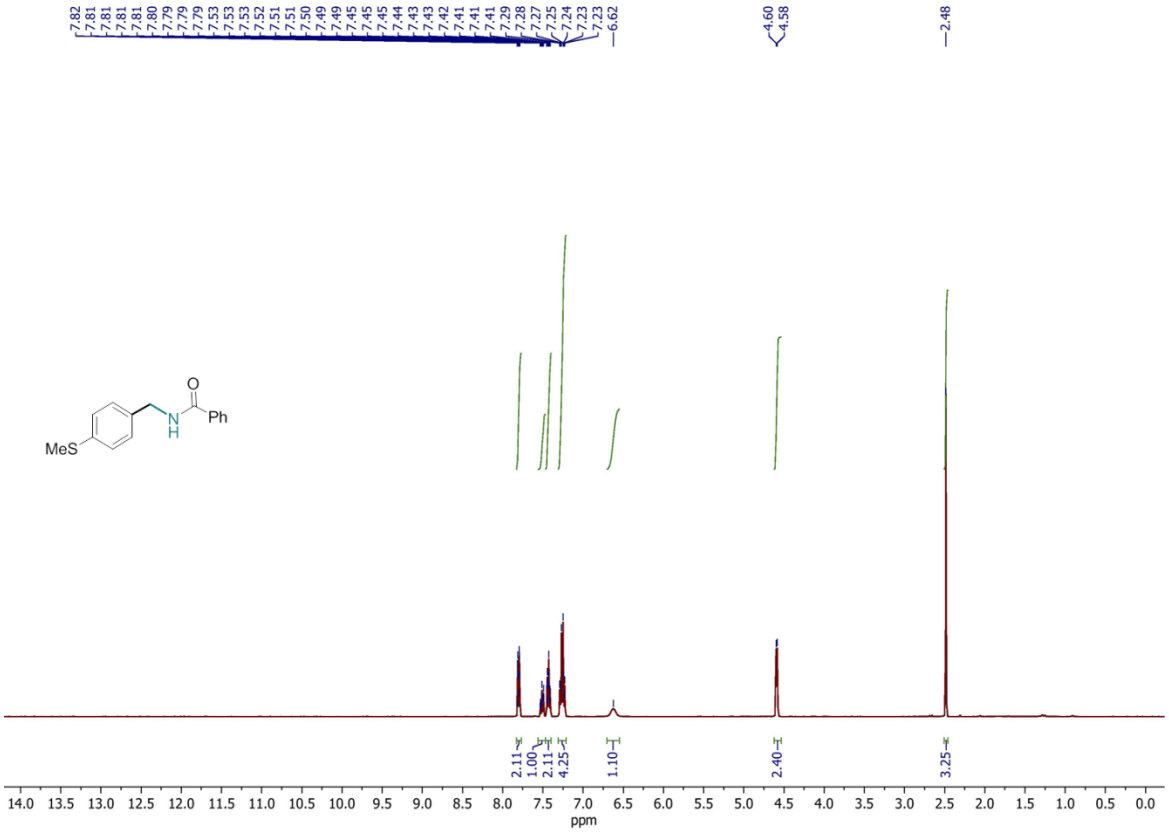

-62.52
O
N
H
Ph
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

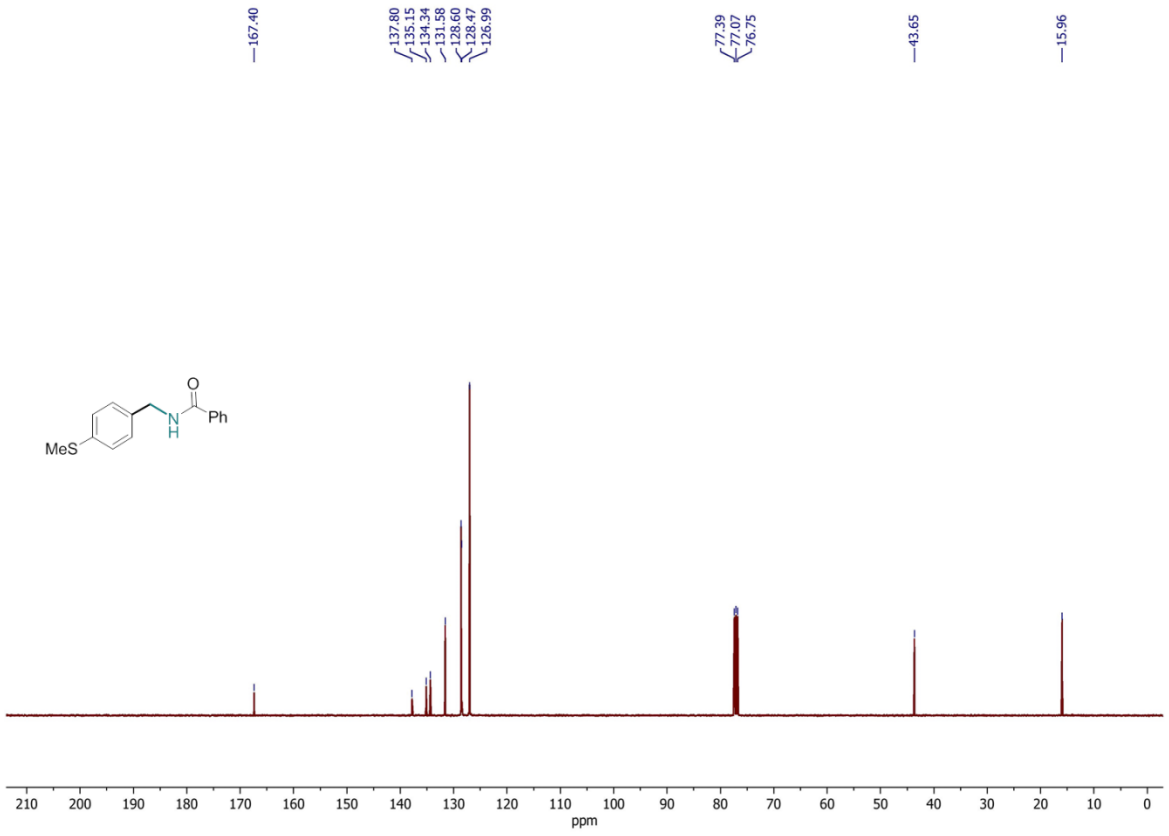
N-(3-methoxybenzyl)benzamide (**3g**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



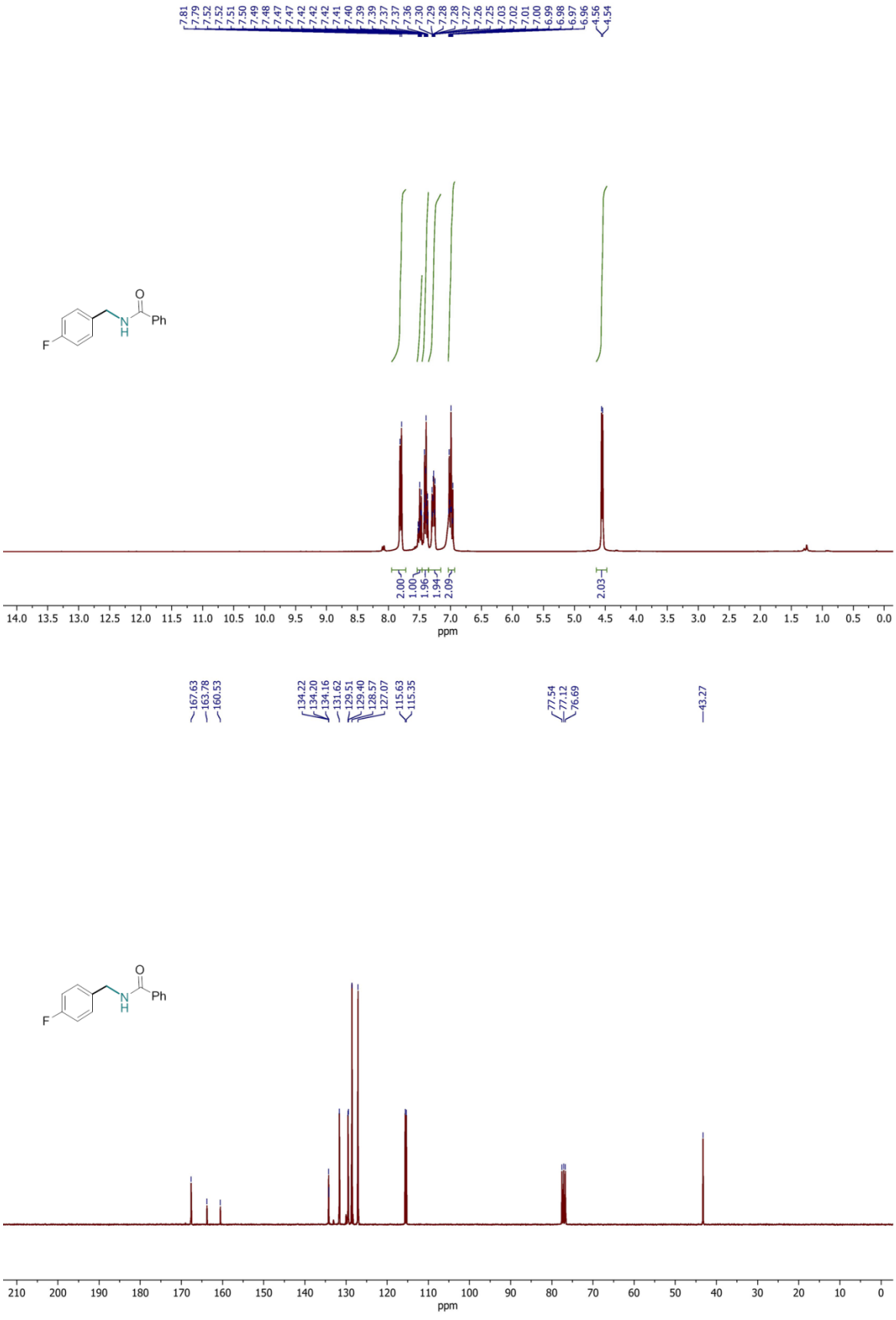


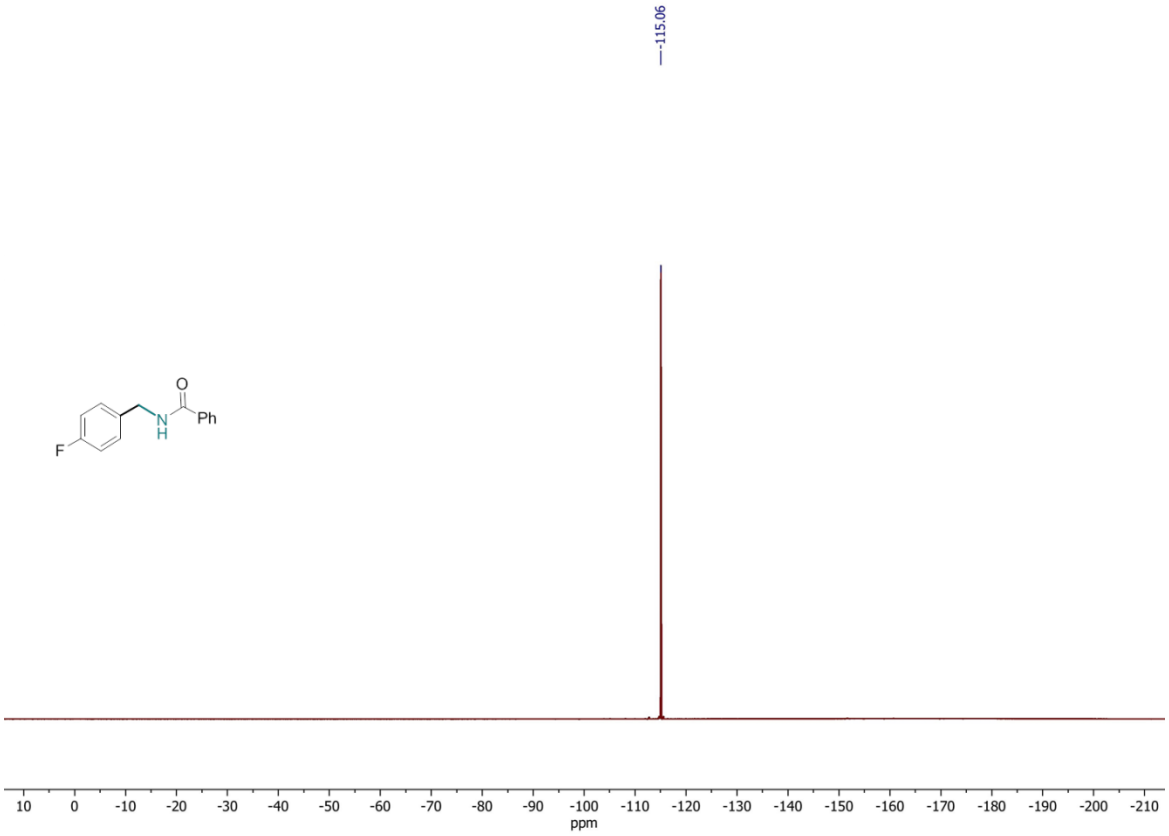
N-(4-(methylthio)benzyl)benzamide (**3h**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



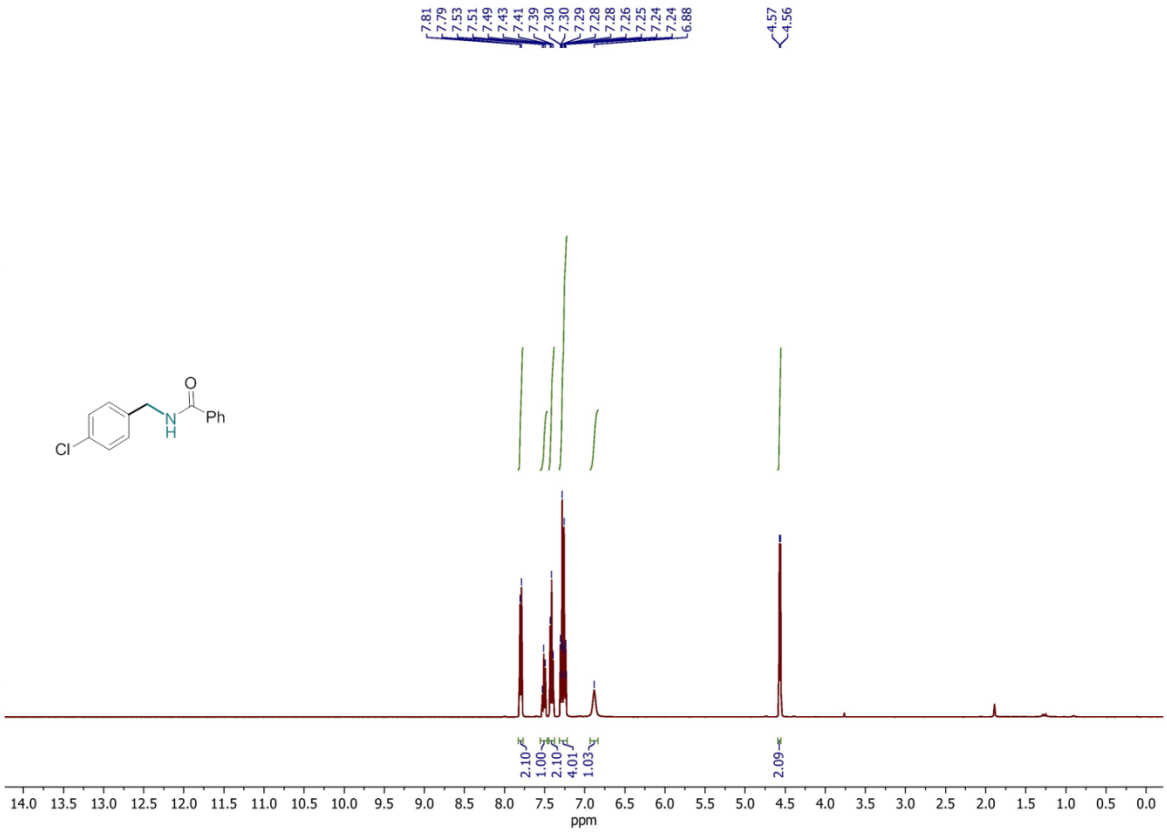


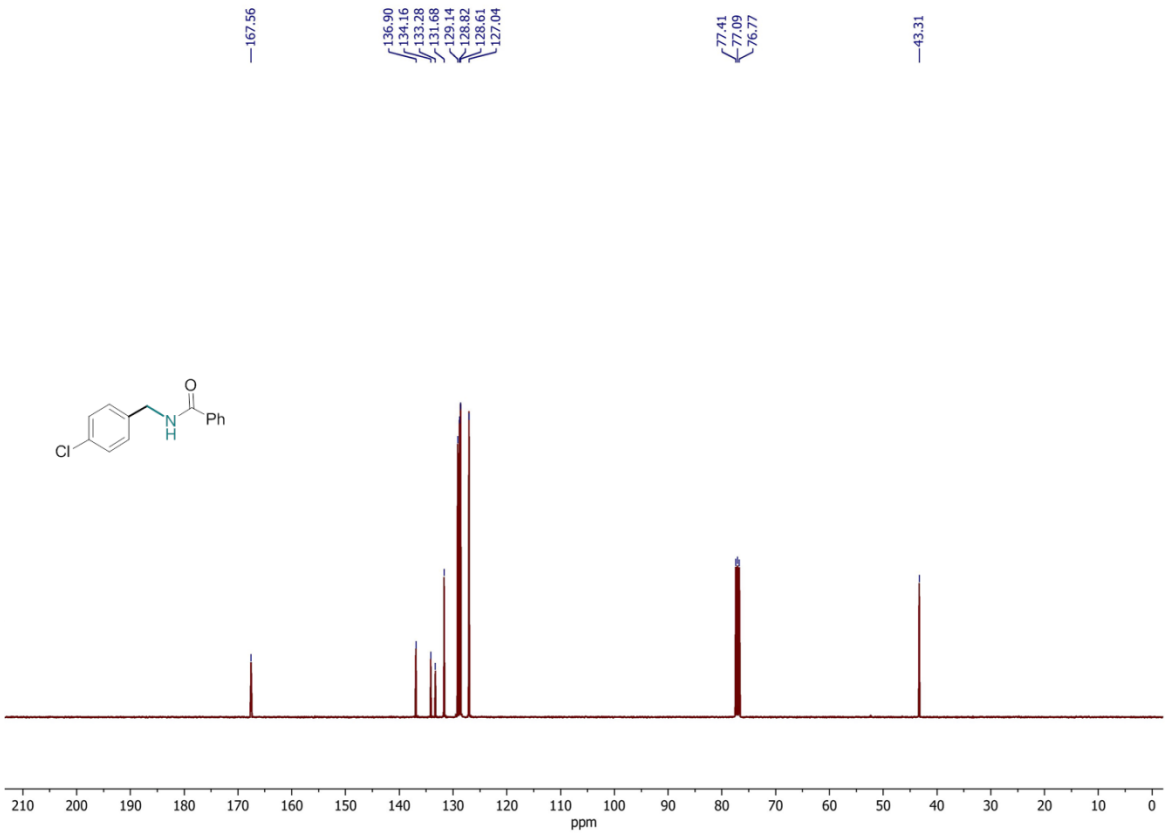
N-(4-fluorobenzyl)benzamide (**3i**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**



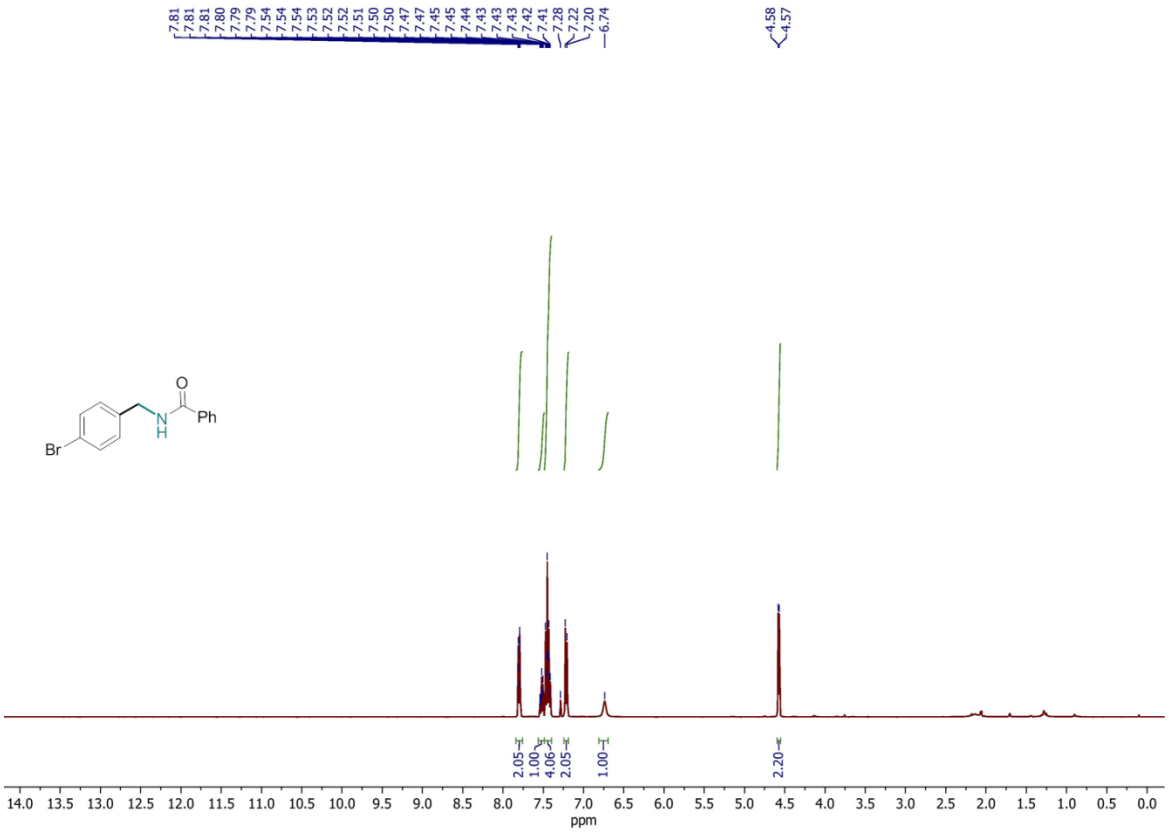

-115.06
O
Ph
N
H
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

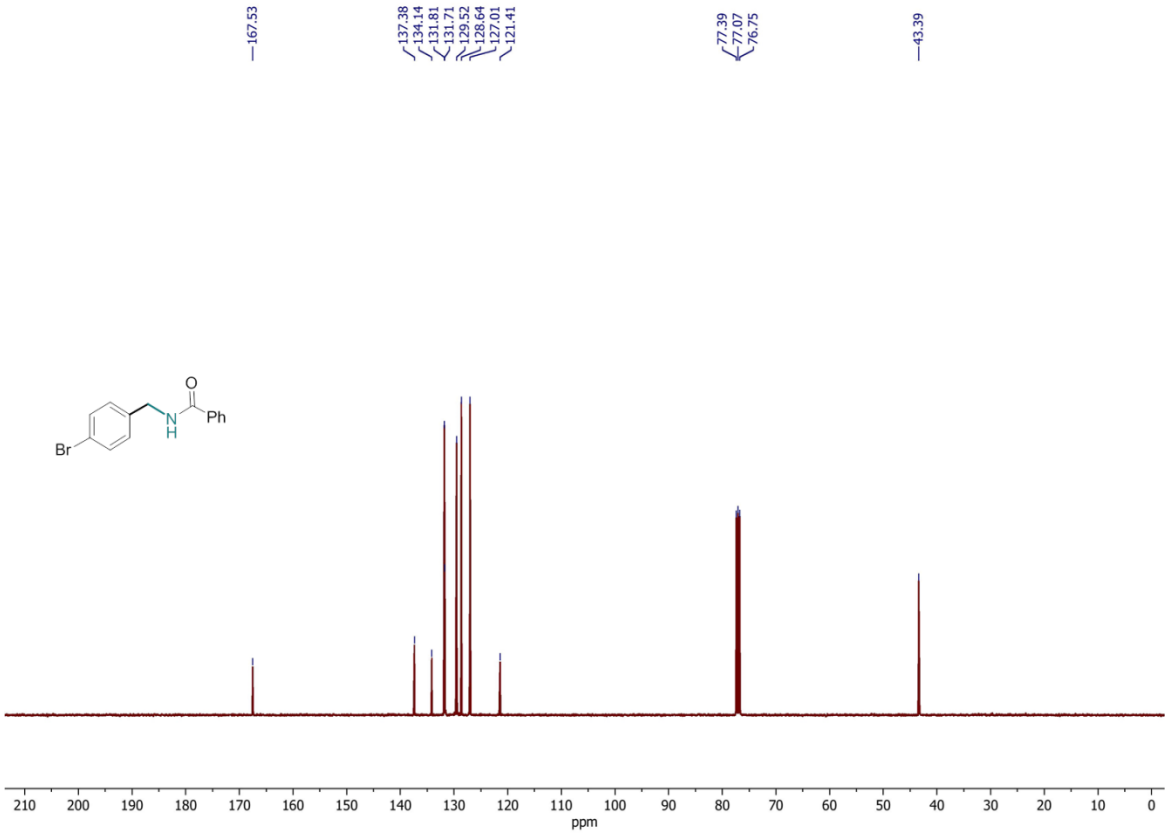
N-(4-chlorobenzyl)benzamide (**3j**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



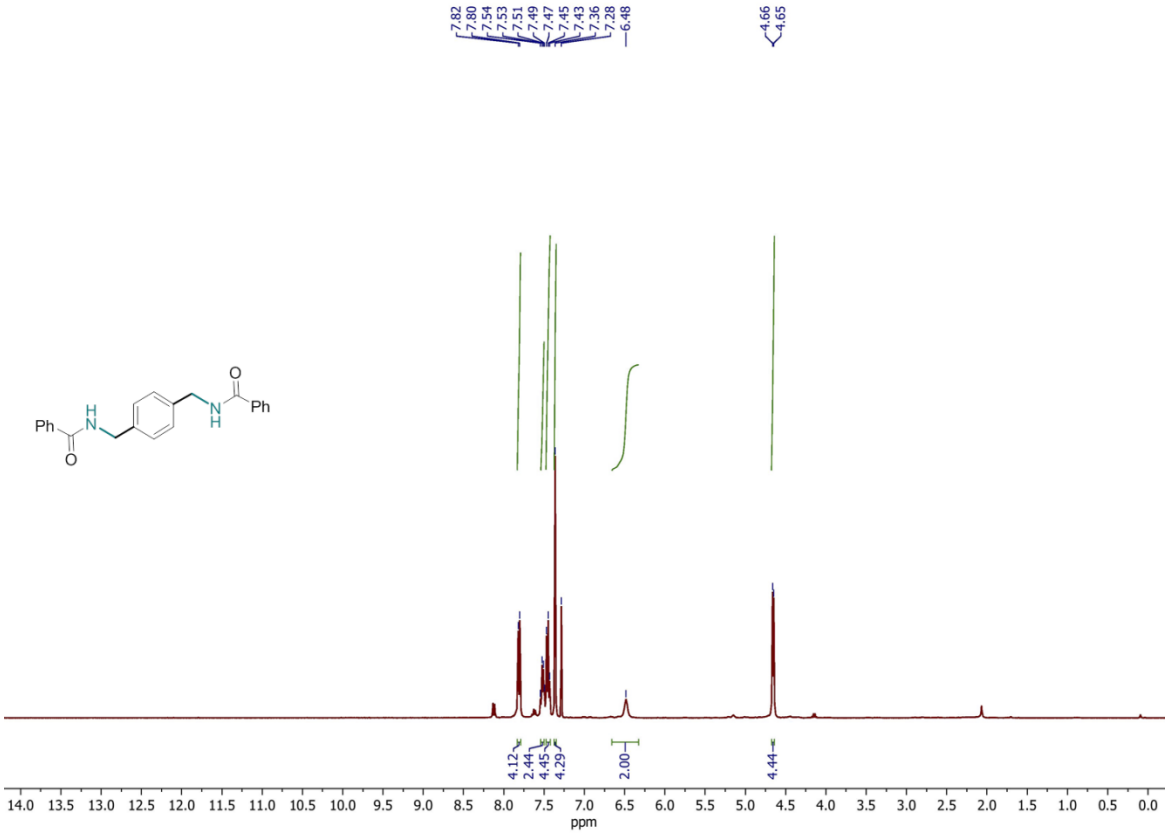


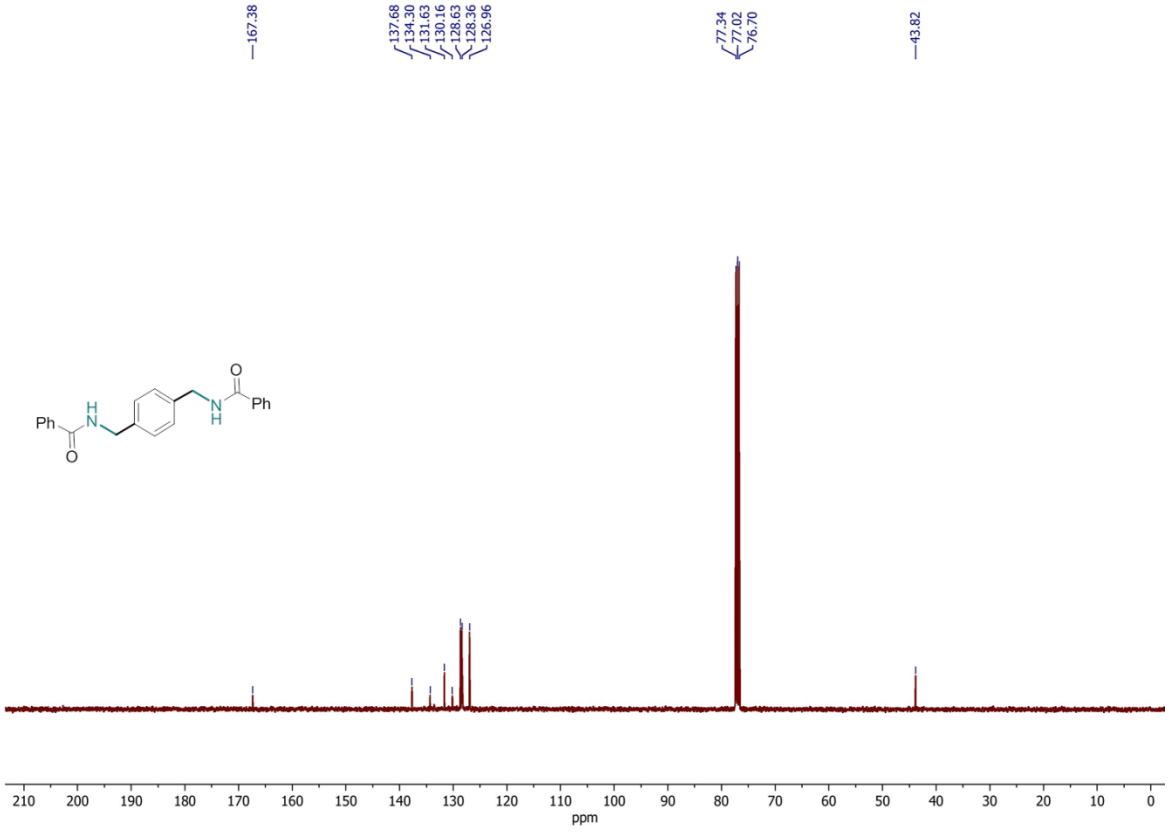
N-(4-bromobenzyl)benzamide (**3k**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



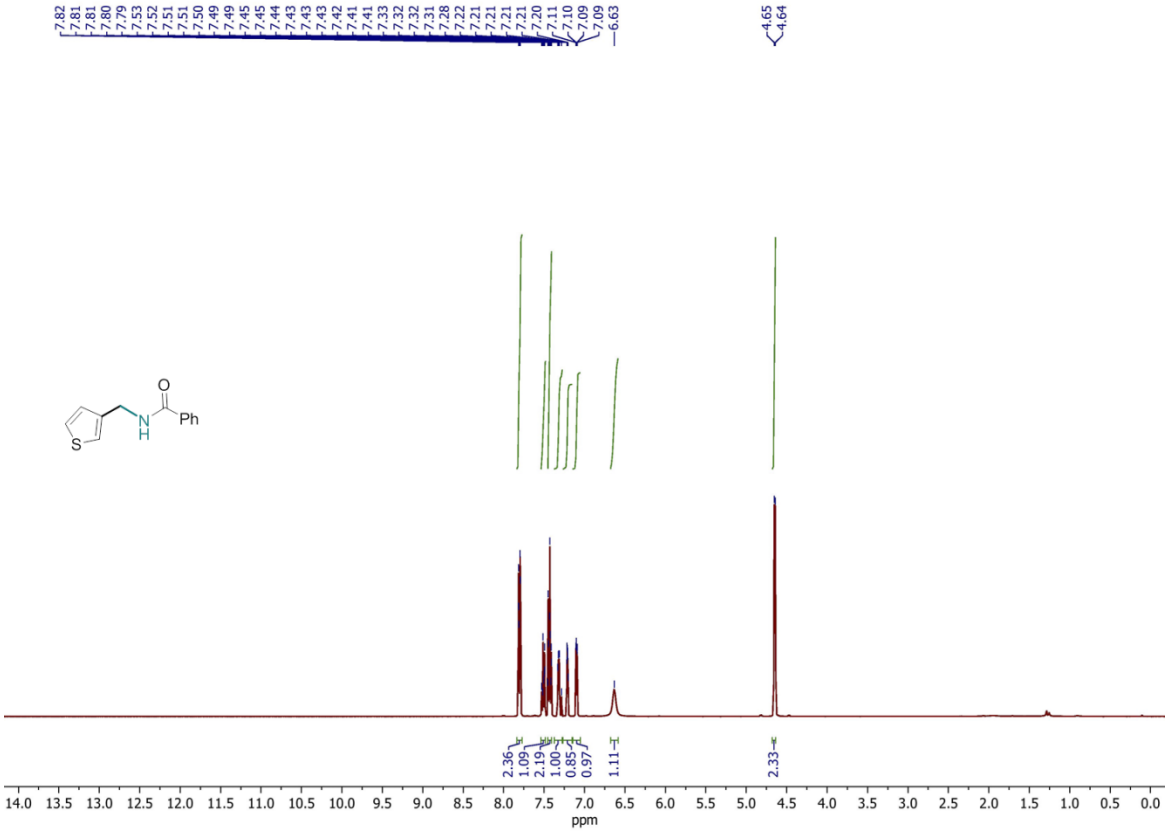


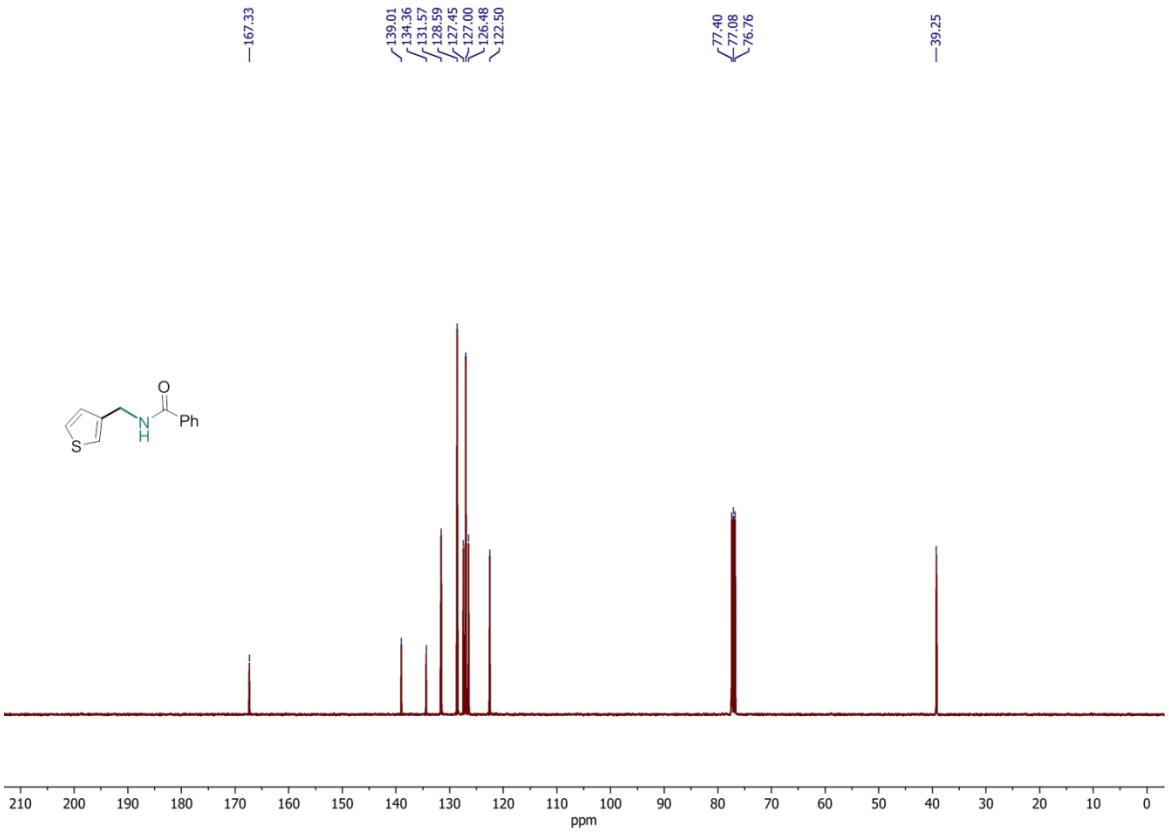
N,N′-(1,4-phenylenebis(methylene))dibenzamide (**3l**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



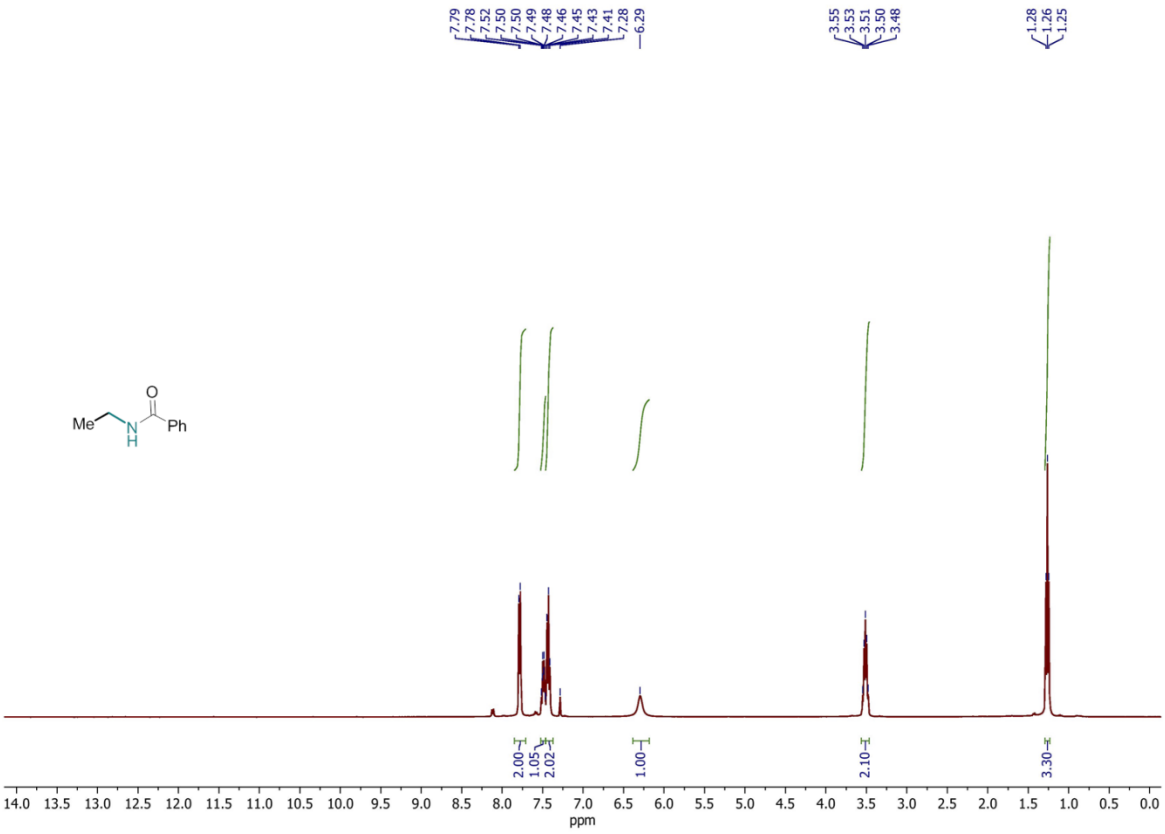


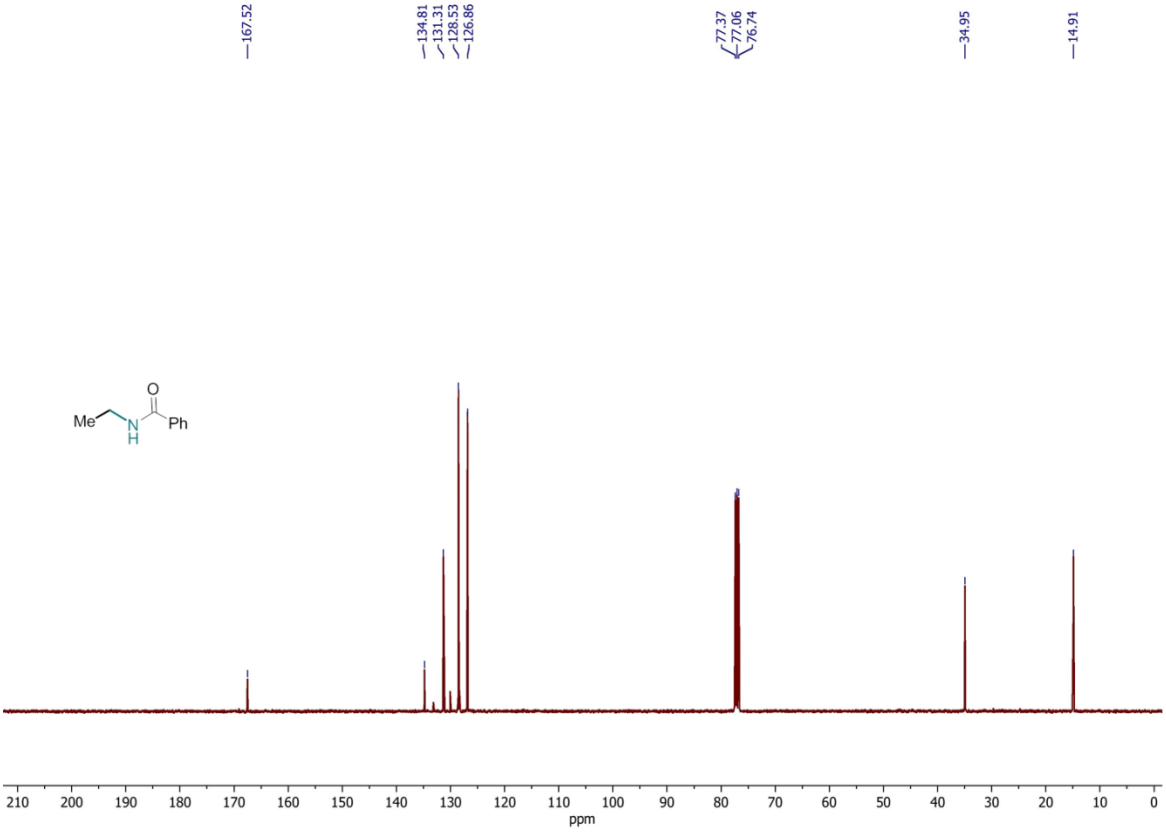
N-(thiophen-3-ylmethyl)benzamide (**3m**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



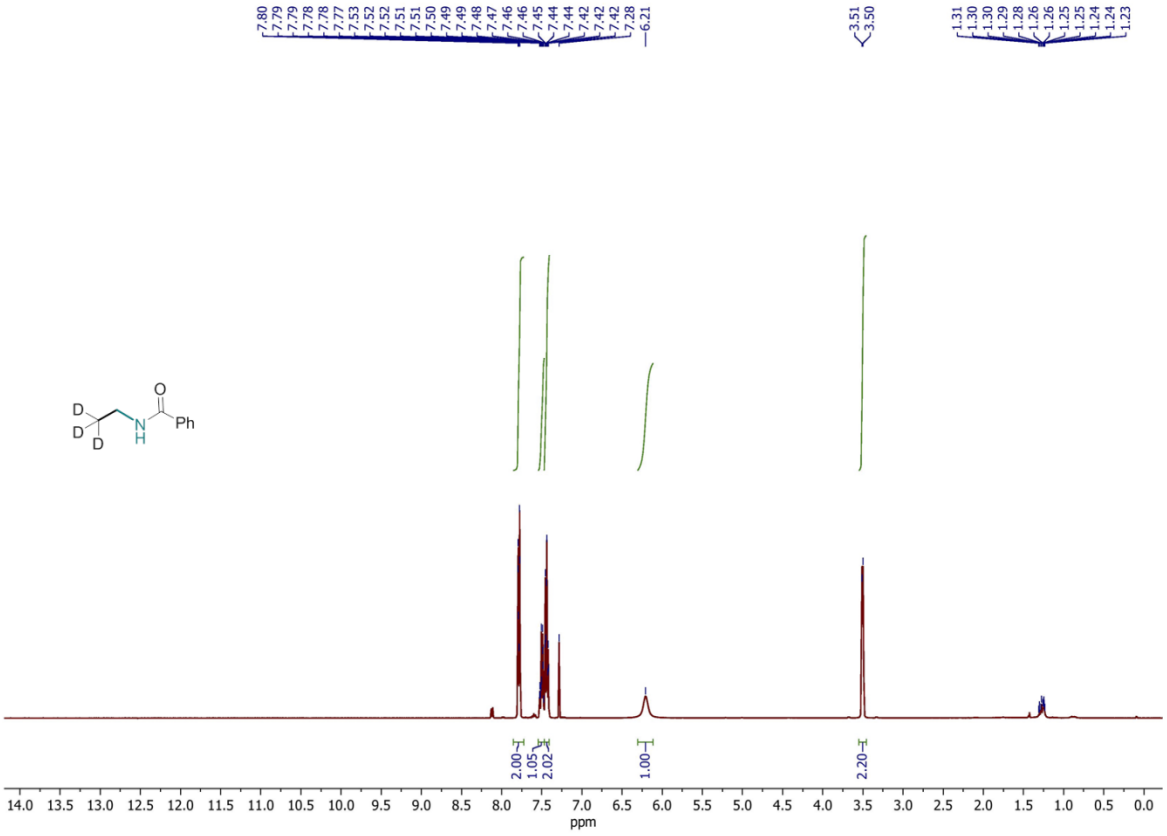


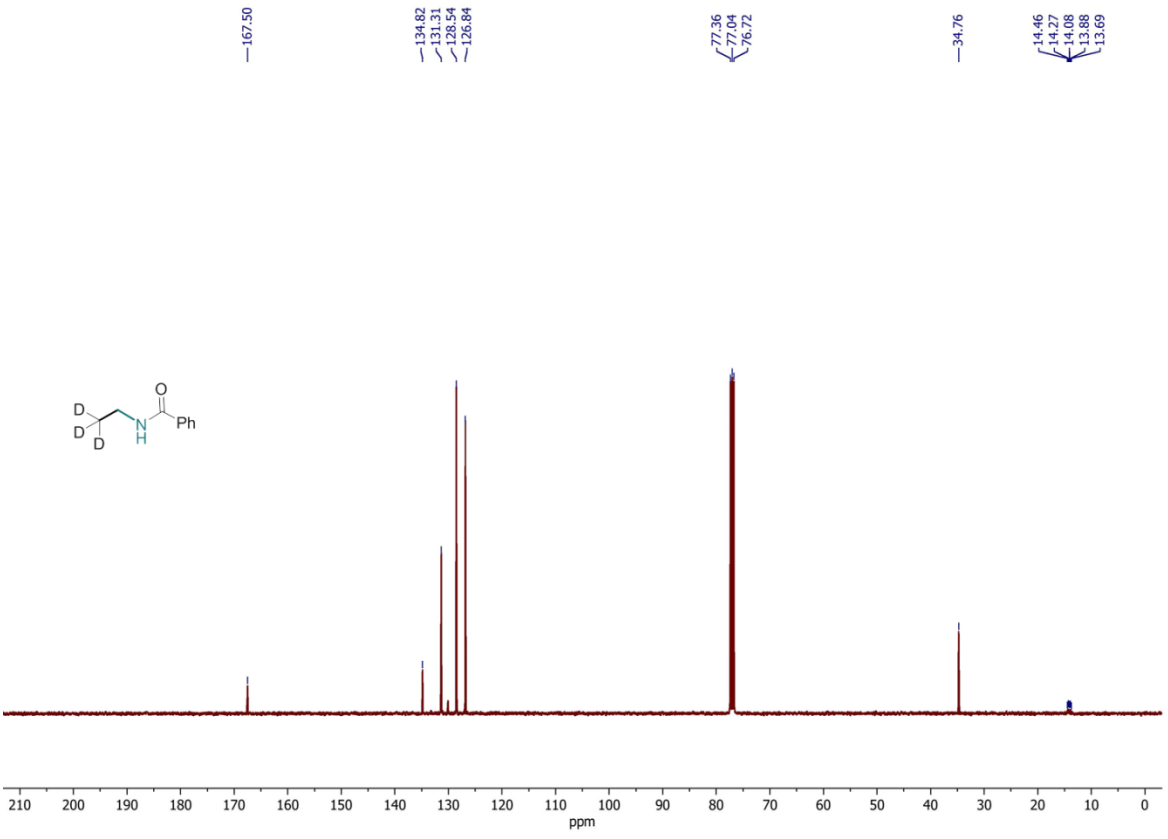
N-ethylbenzamide (**3n**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



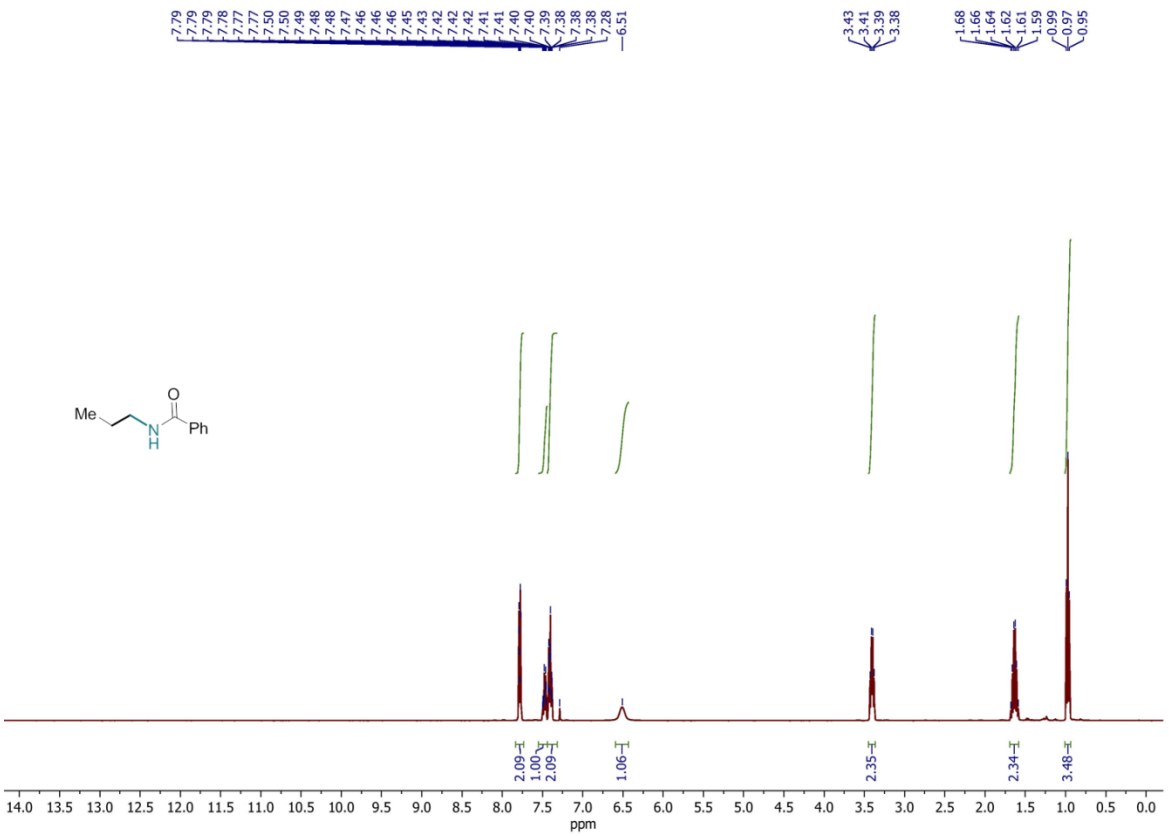


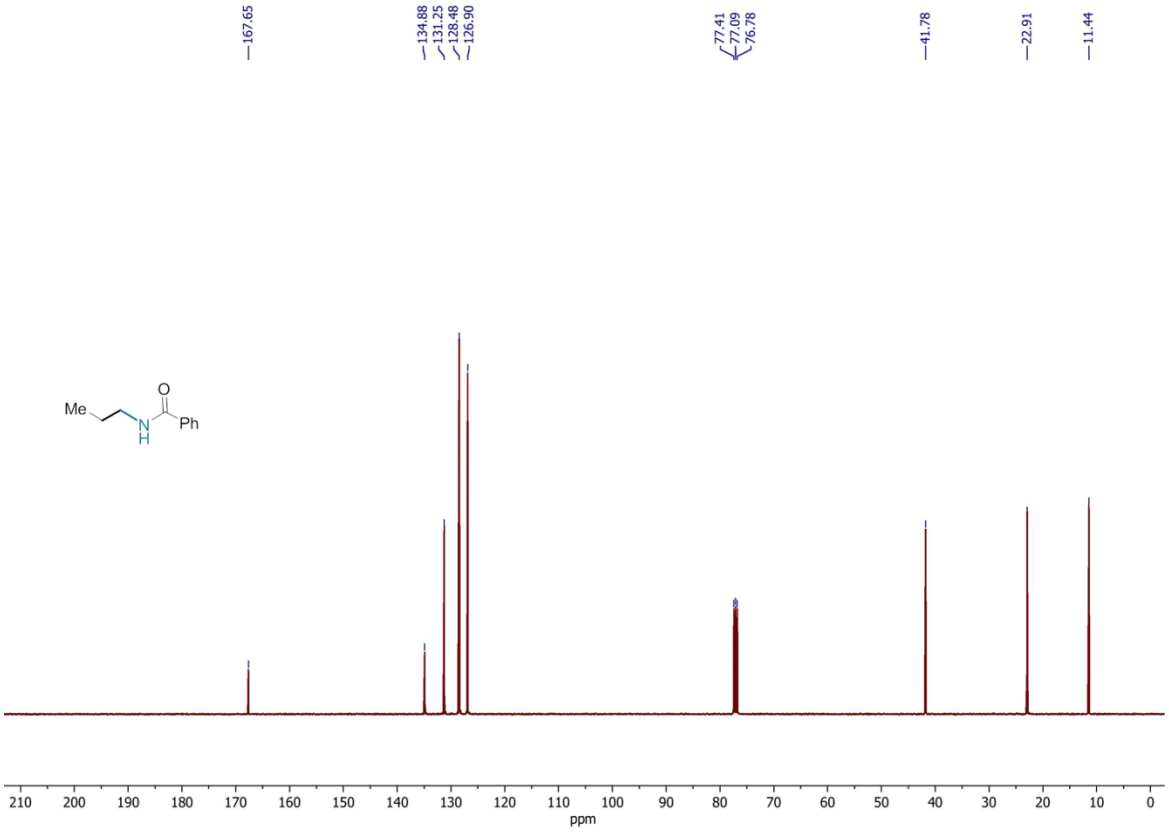
N-(ethyl-2,2,2-d_3)benzamide (**3o**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



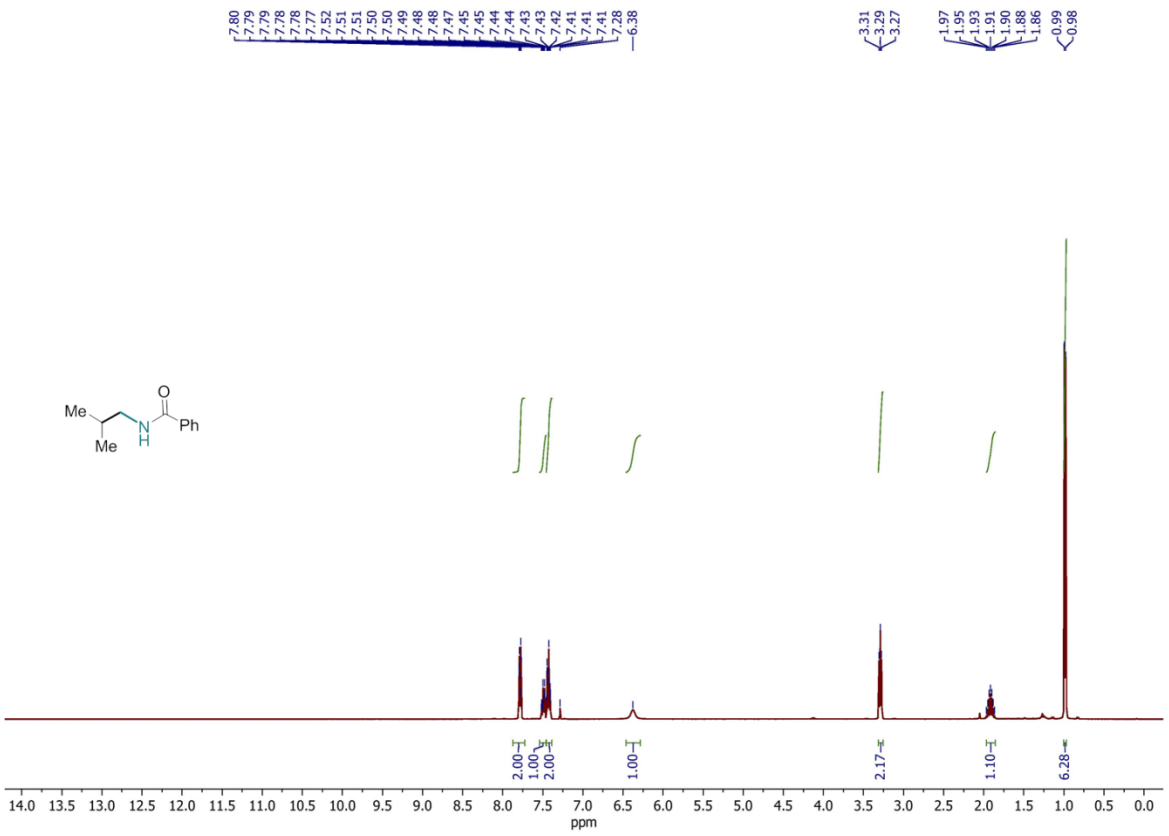


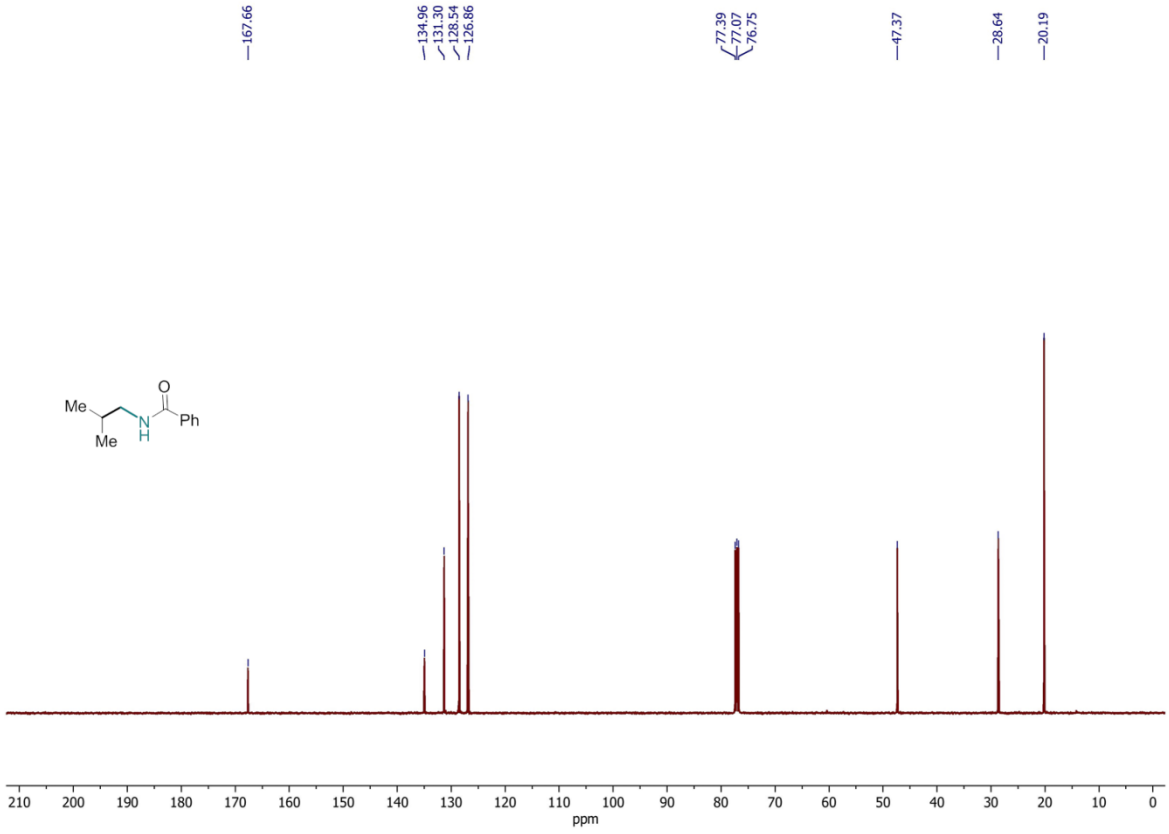
N-propylbenzamide (**3p**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



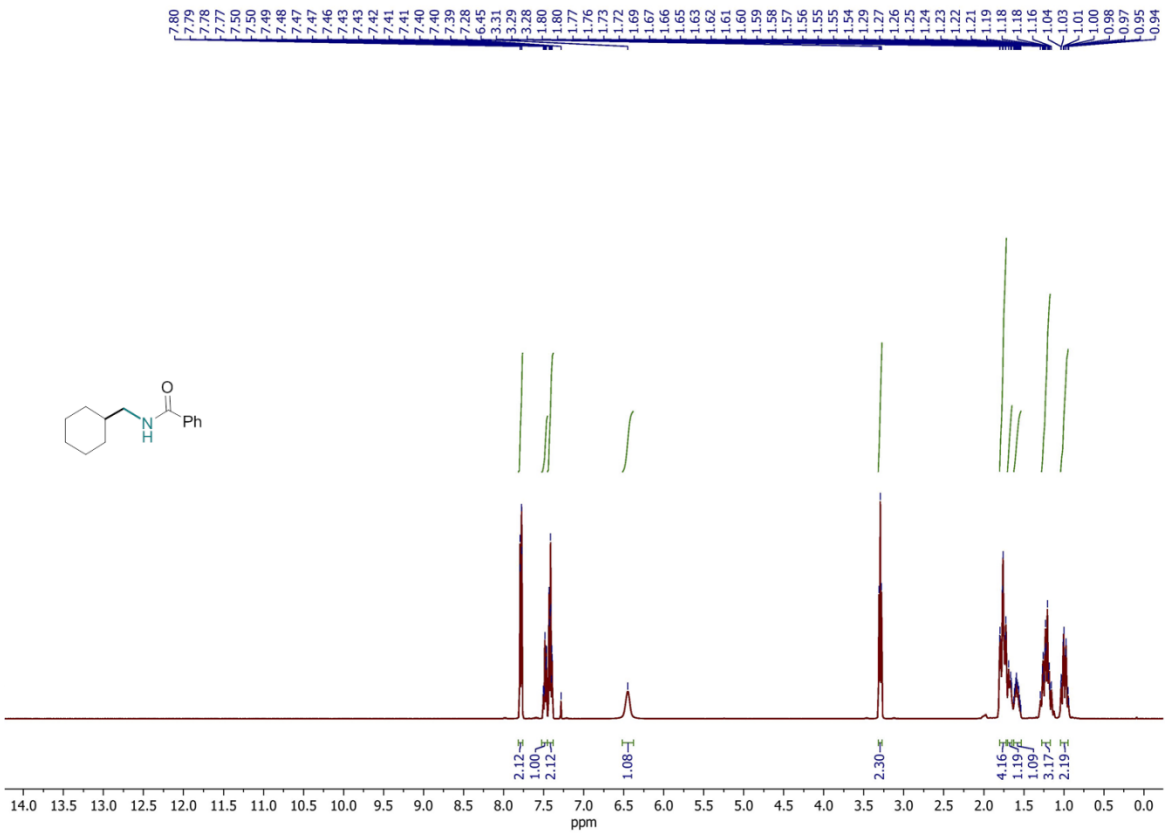


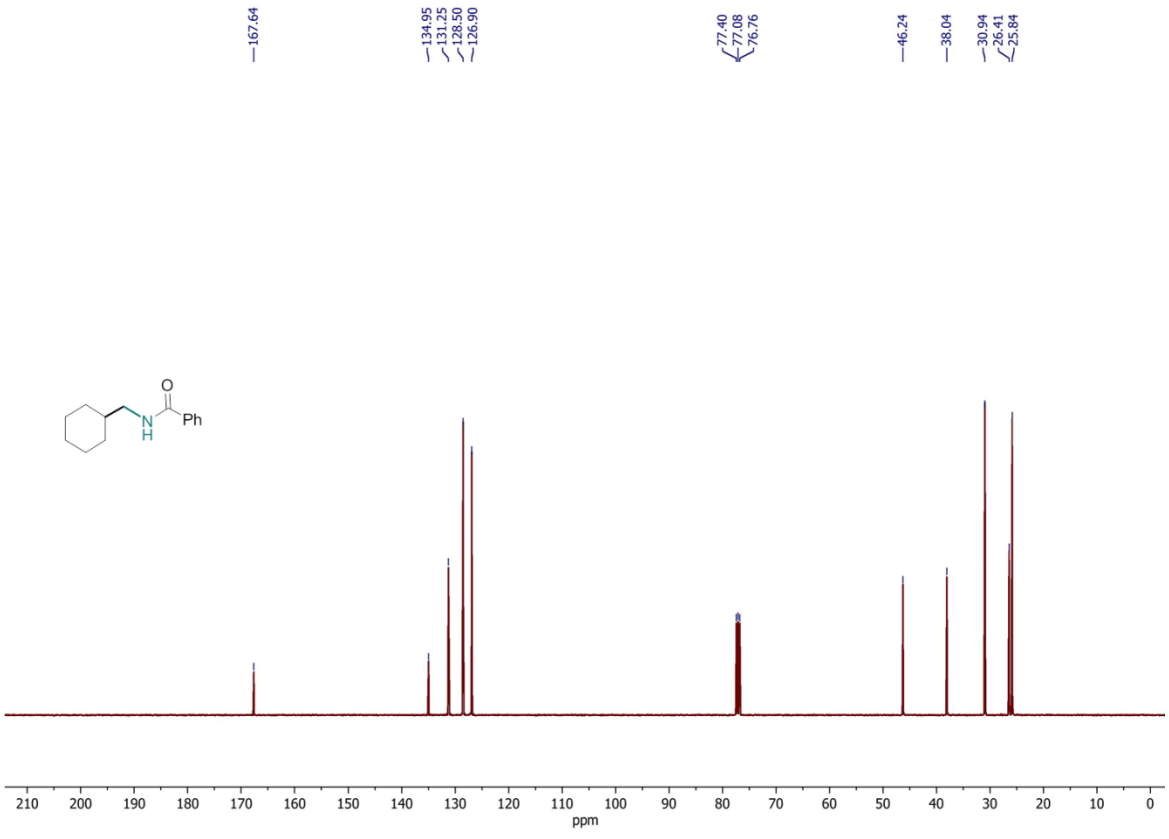
N-isobutylbenzamide (**3q**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



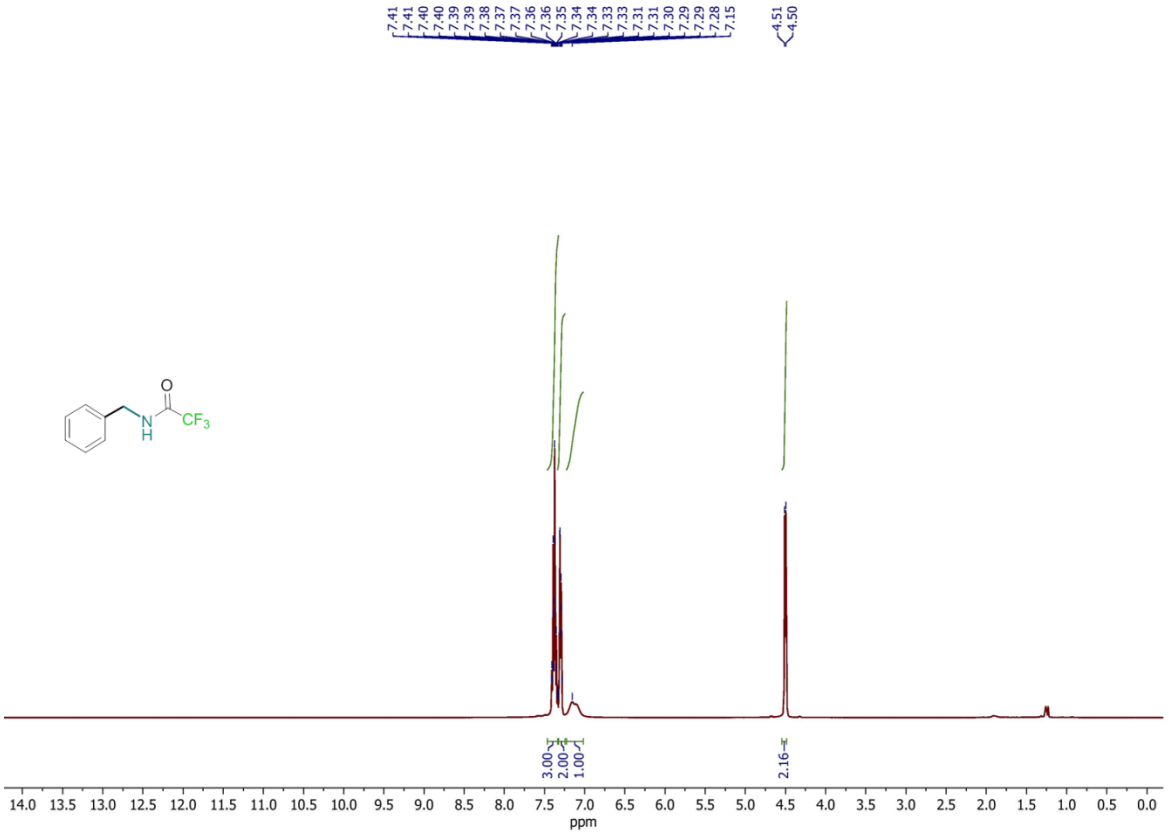


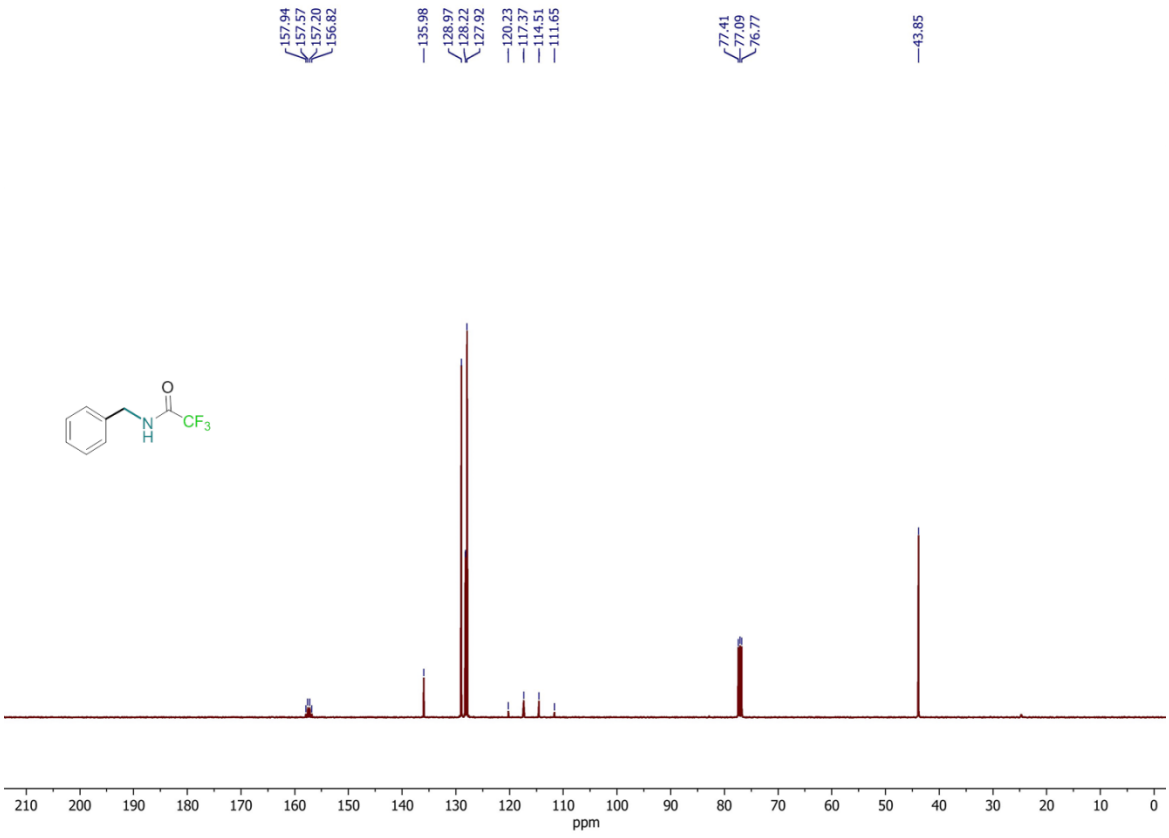
N-(cyclohexylmethyl)benzamide (**3r**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**

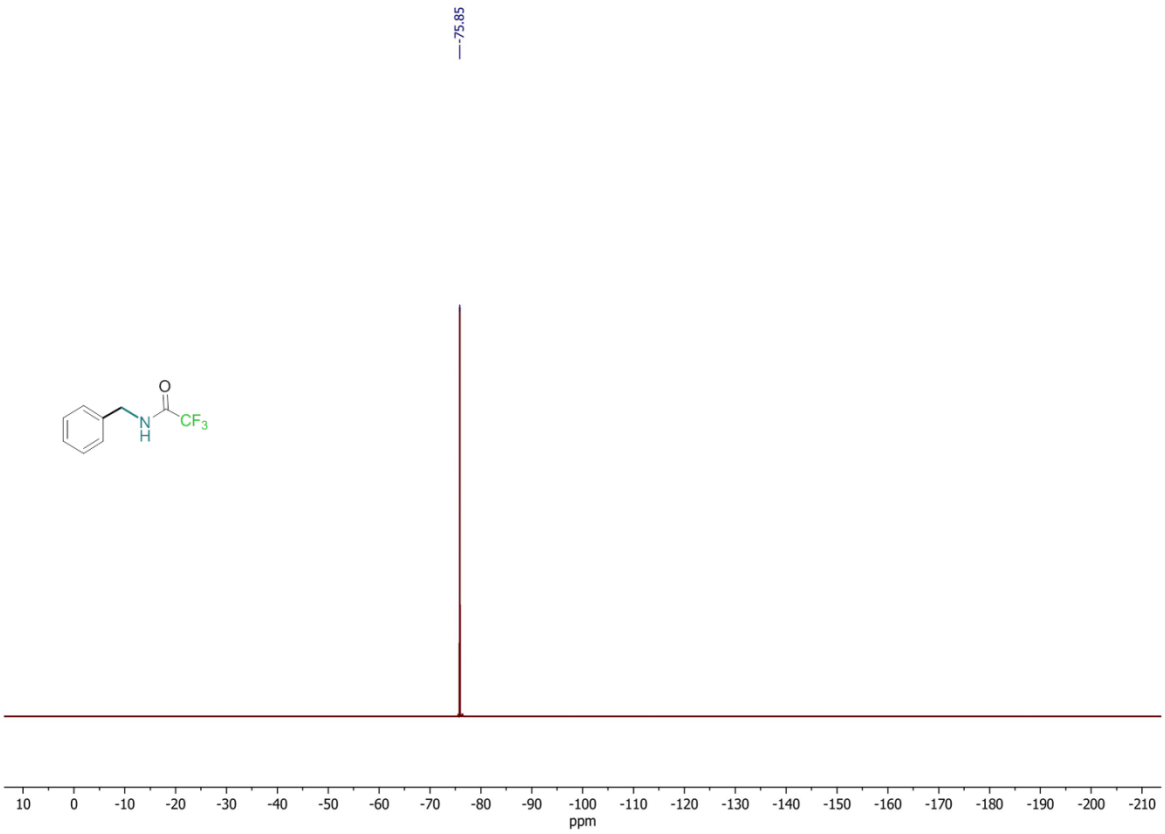




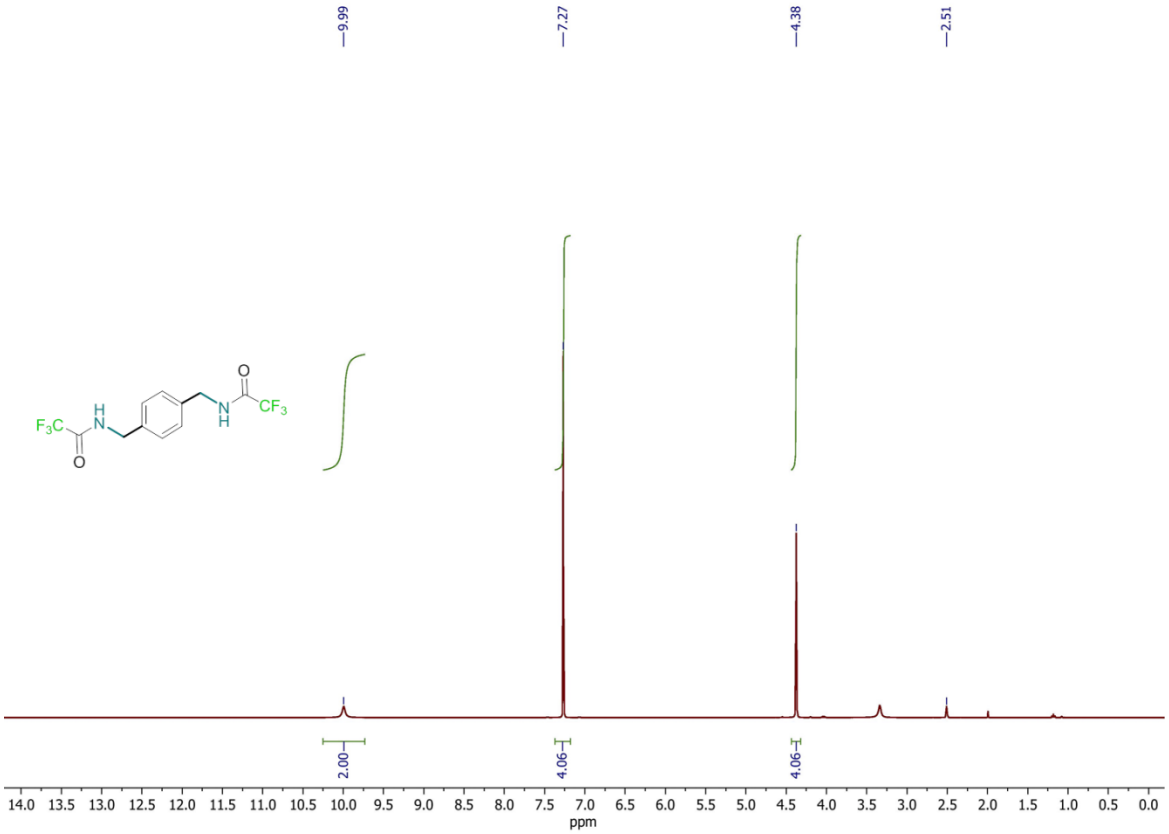
N-benzyl-2,2,2-trifluoroacetamide (**3s**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

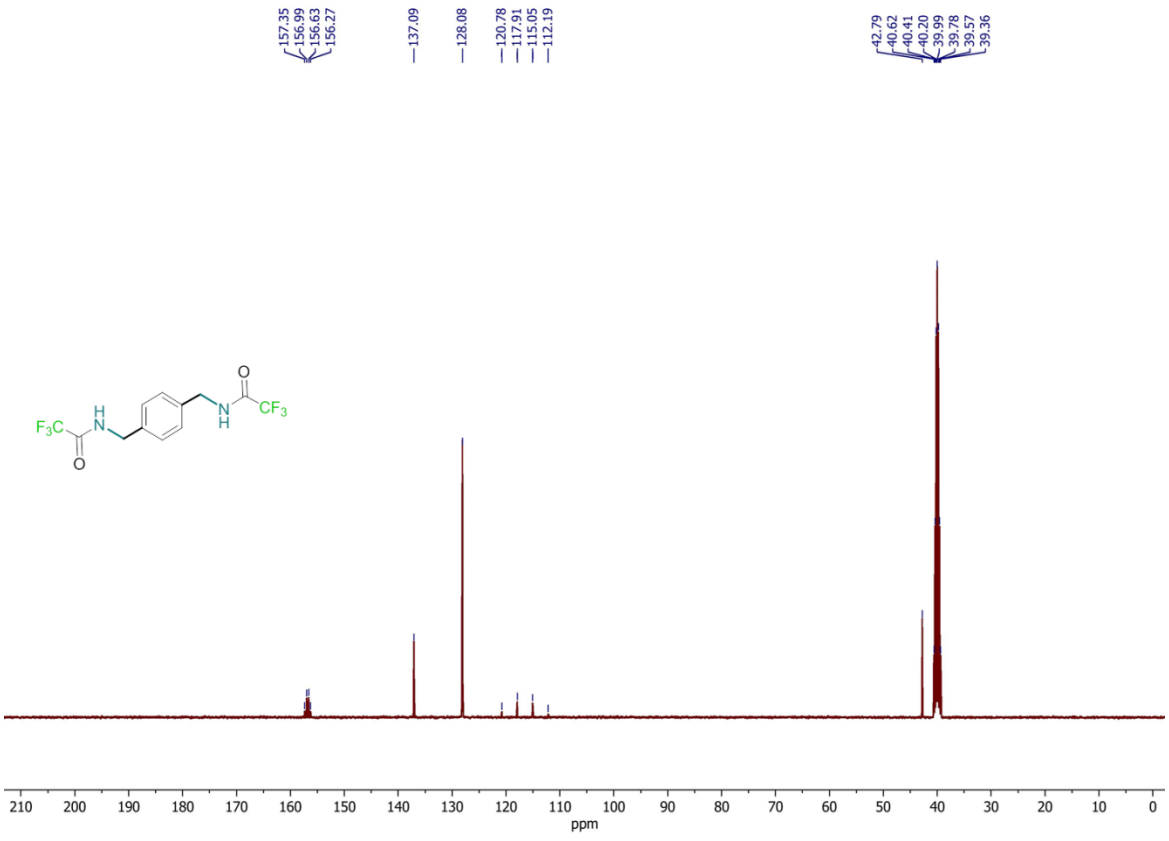


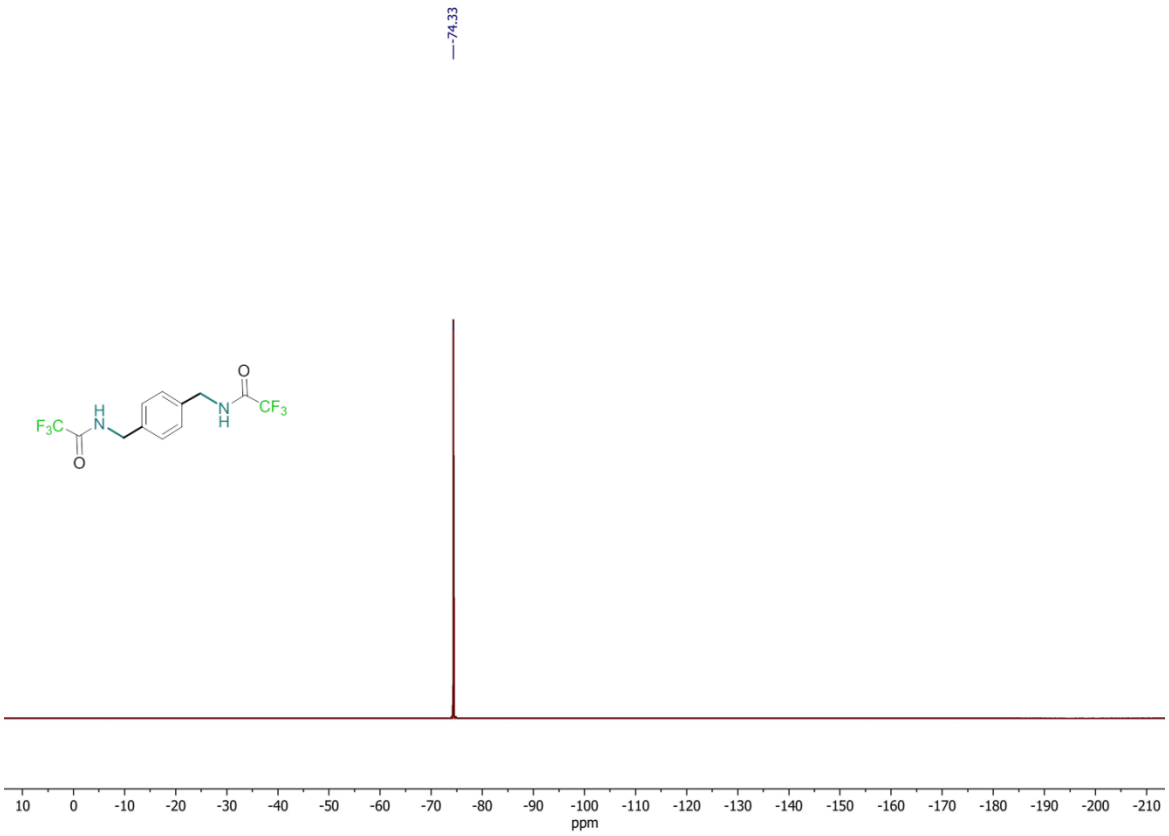



-75.85
O
N
H
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

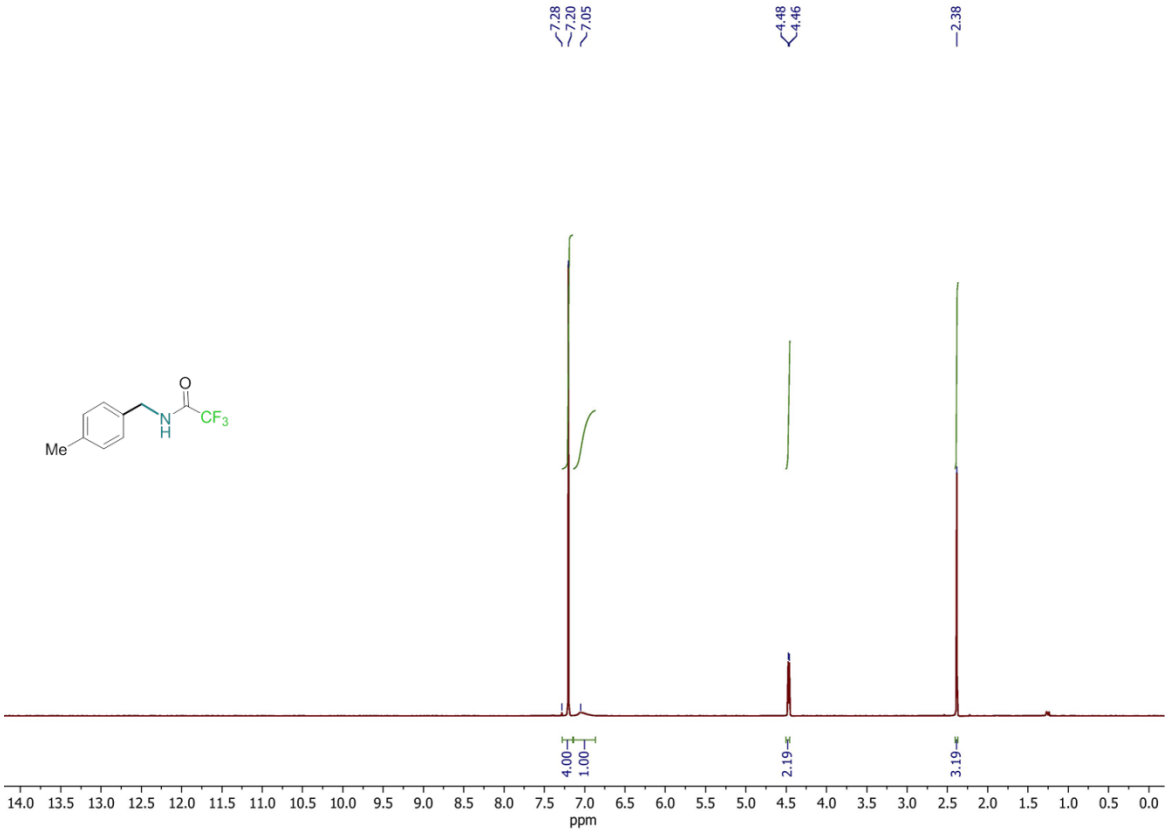
N,N′-(1,4-phenylenebis(methylene))bis(2,2,2-trifluoroacetamide) (**3w**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

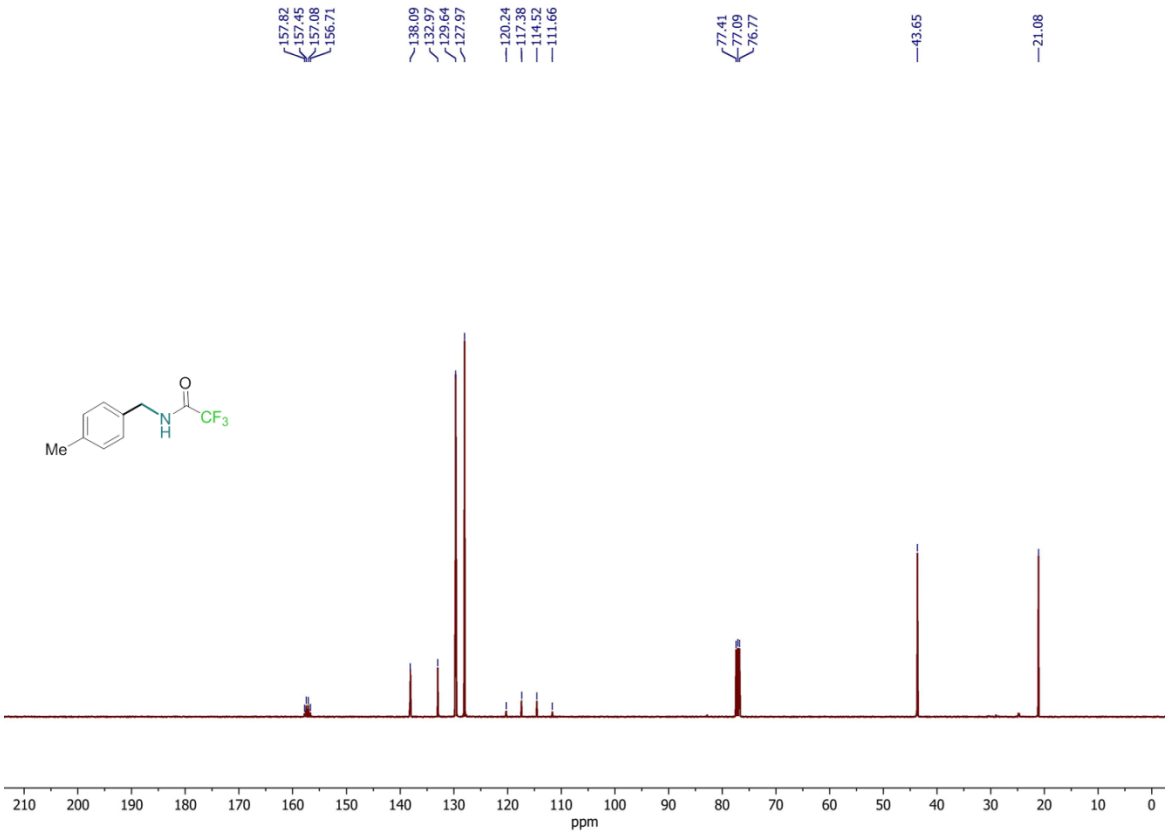


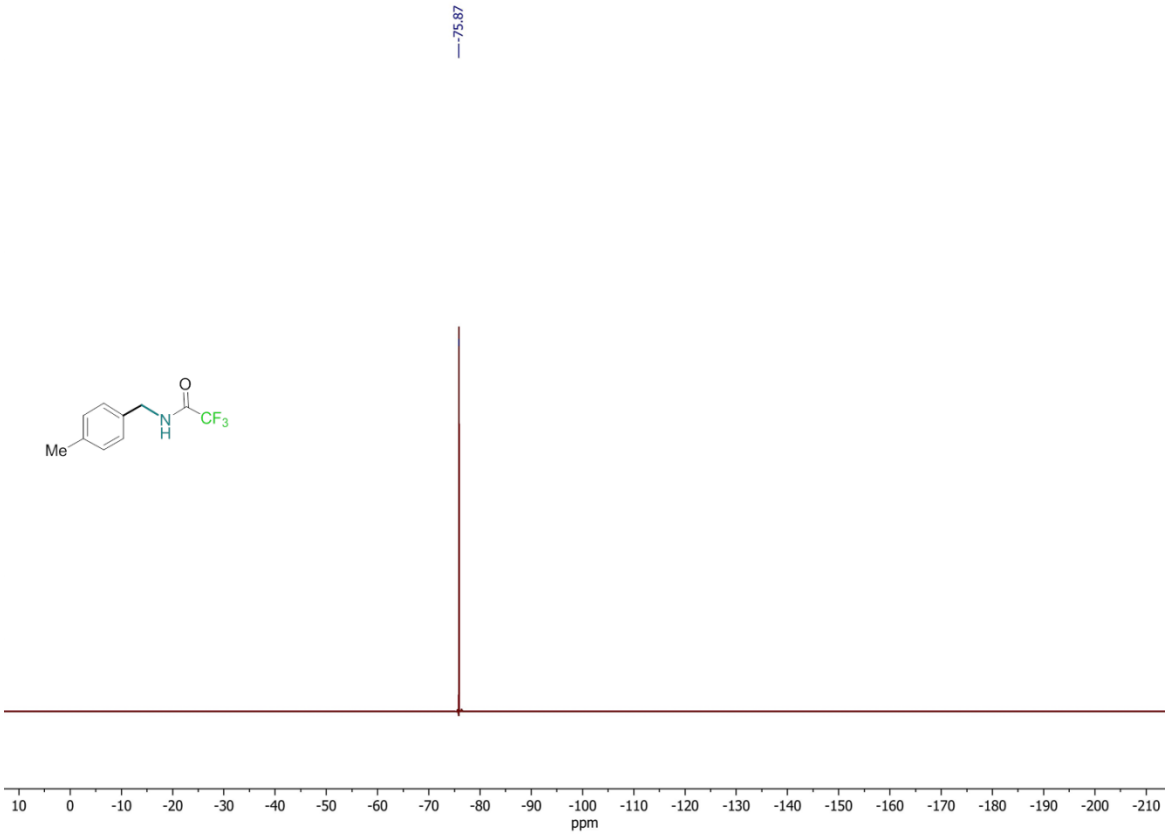



-74.33
F3C
H
N
O
N
H
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

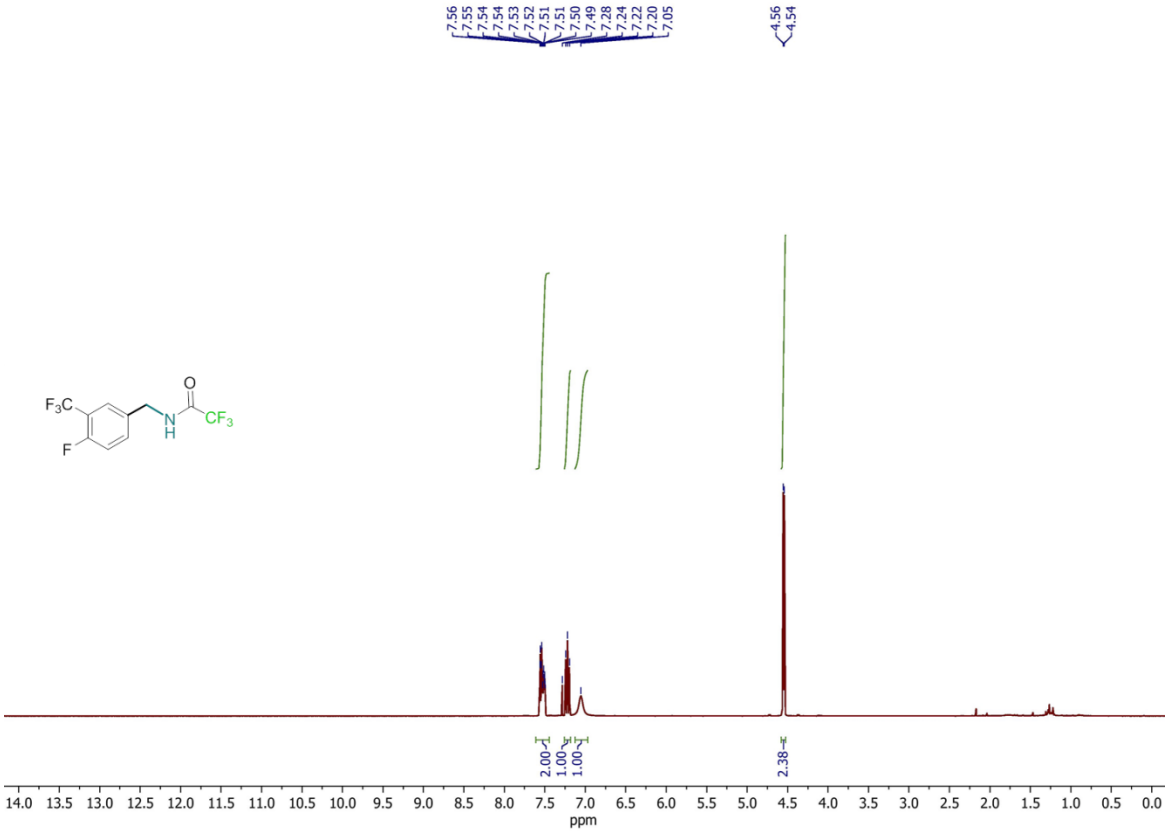
2,2,2-trifluoro-*N*-(4-methylbenzyl)acetamide (**3t**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

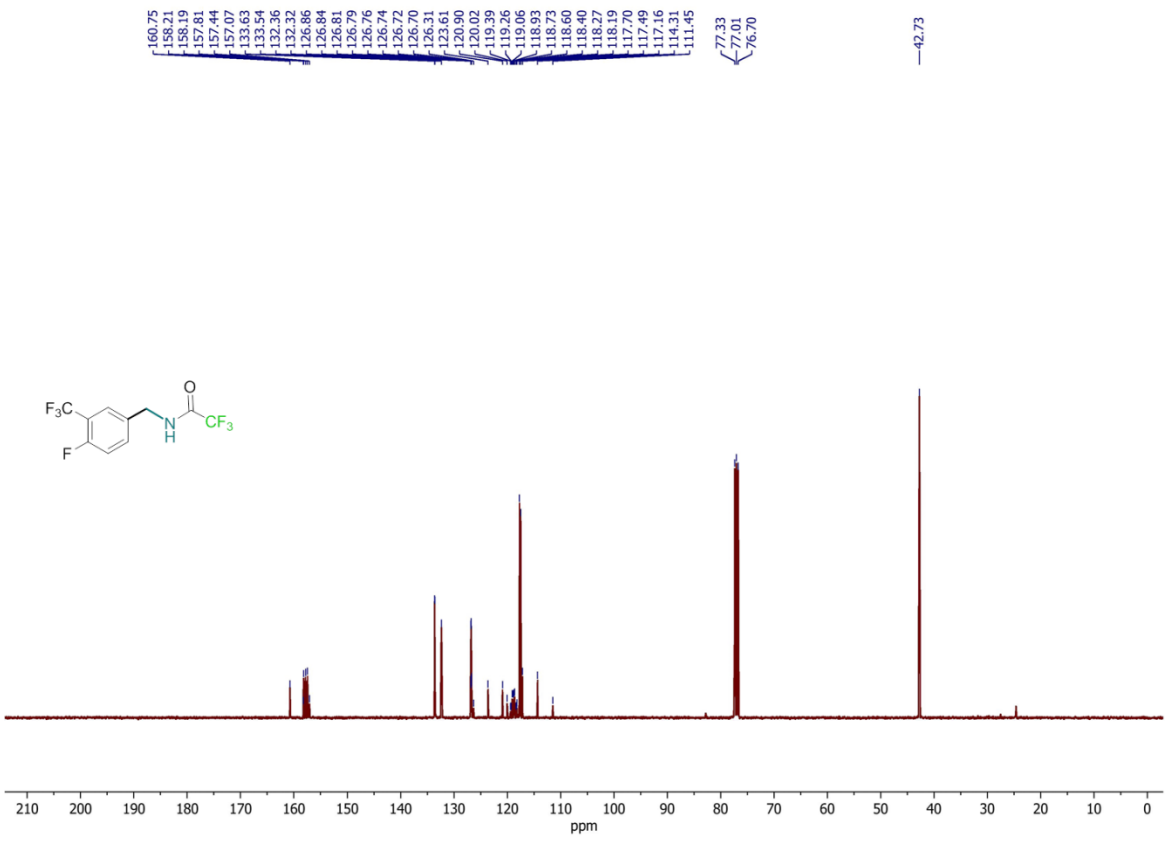


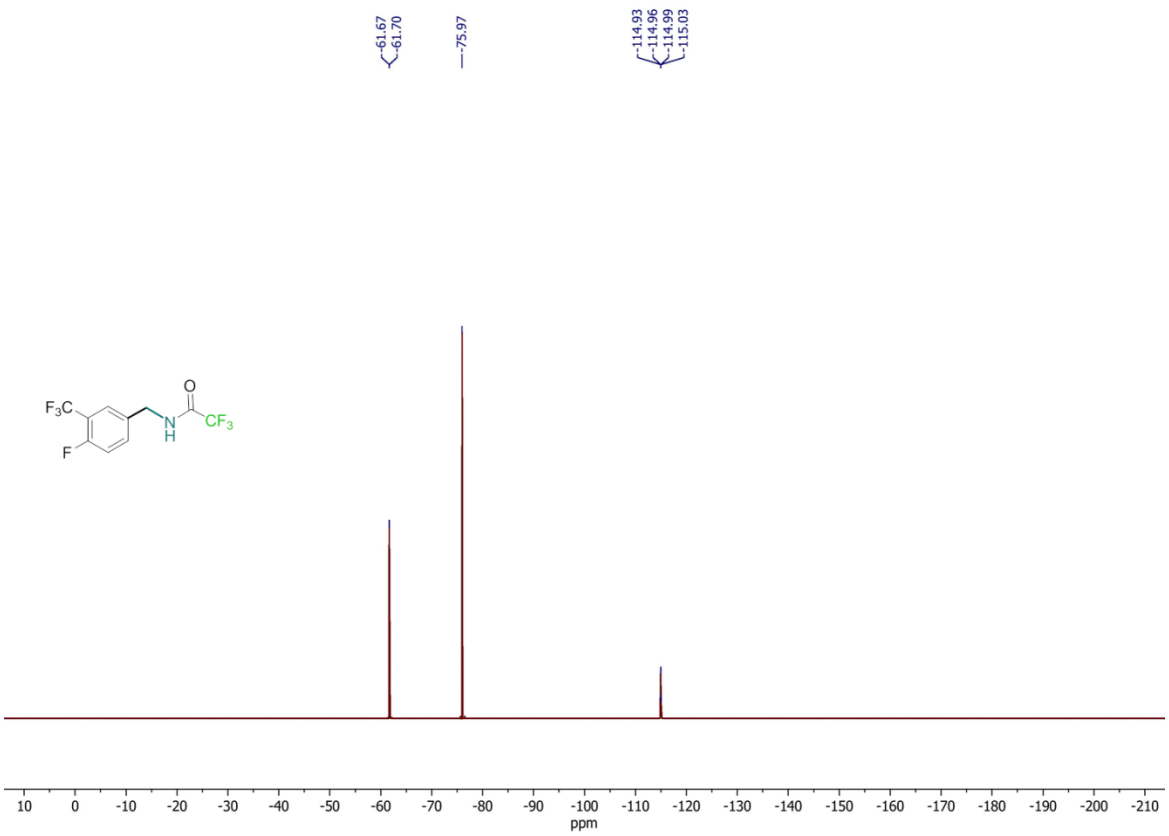



-75.87
O
N
H
CF3
Me
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

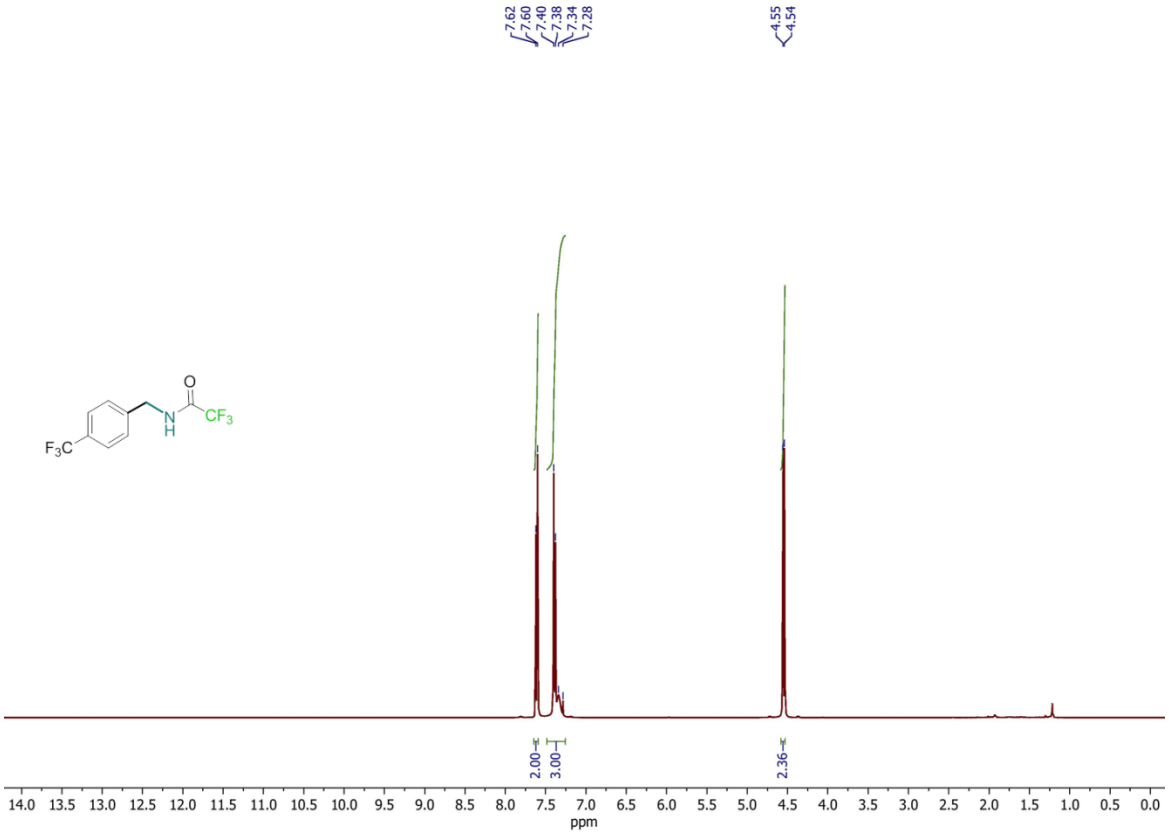
2,2,2-trifluoro-*N*-(4-fluoro-3-(trifluoromethyl)benzyl)acetamide (**3x**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

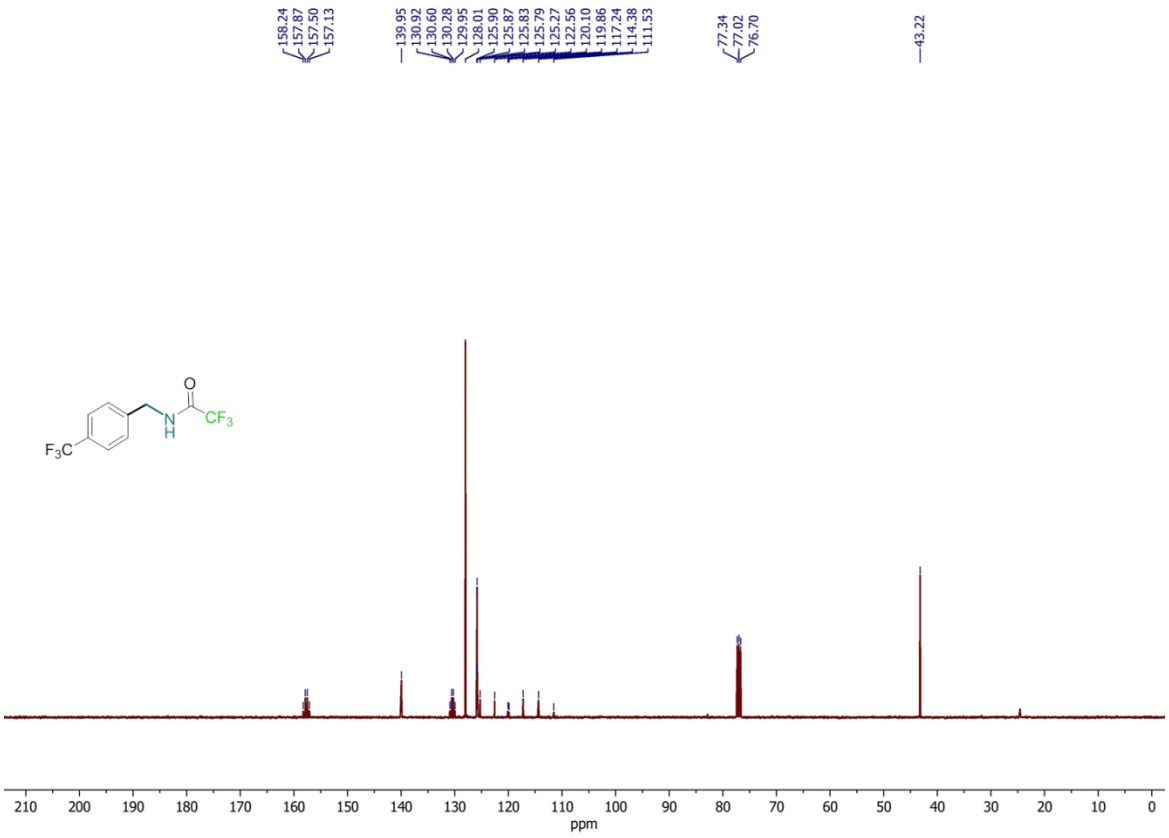


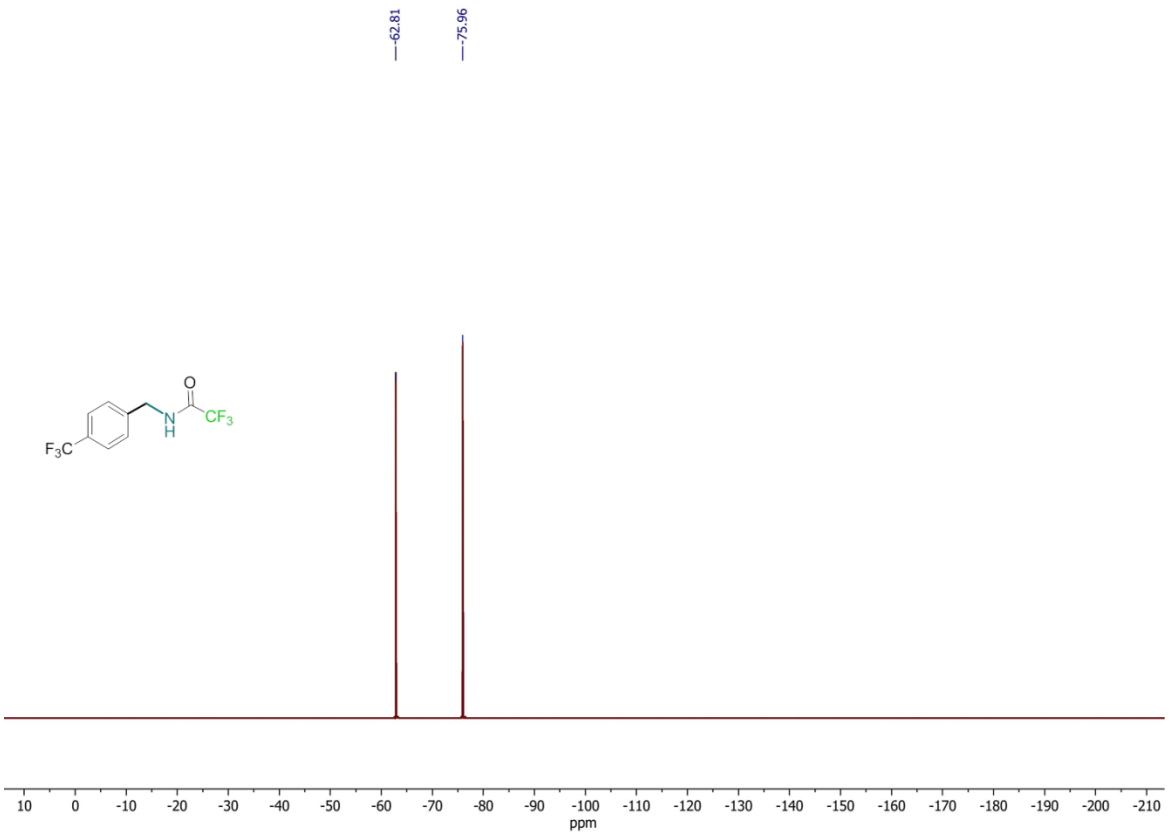



-61.67
-61.70
-75.97
-114.93
-114.96
-114.99
-115.03
F3C
F
O
N
H
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

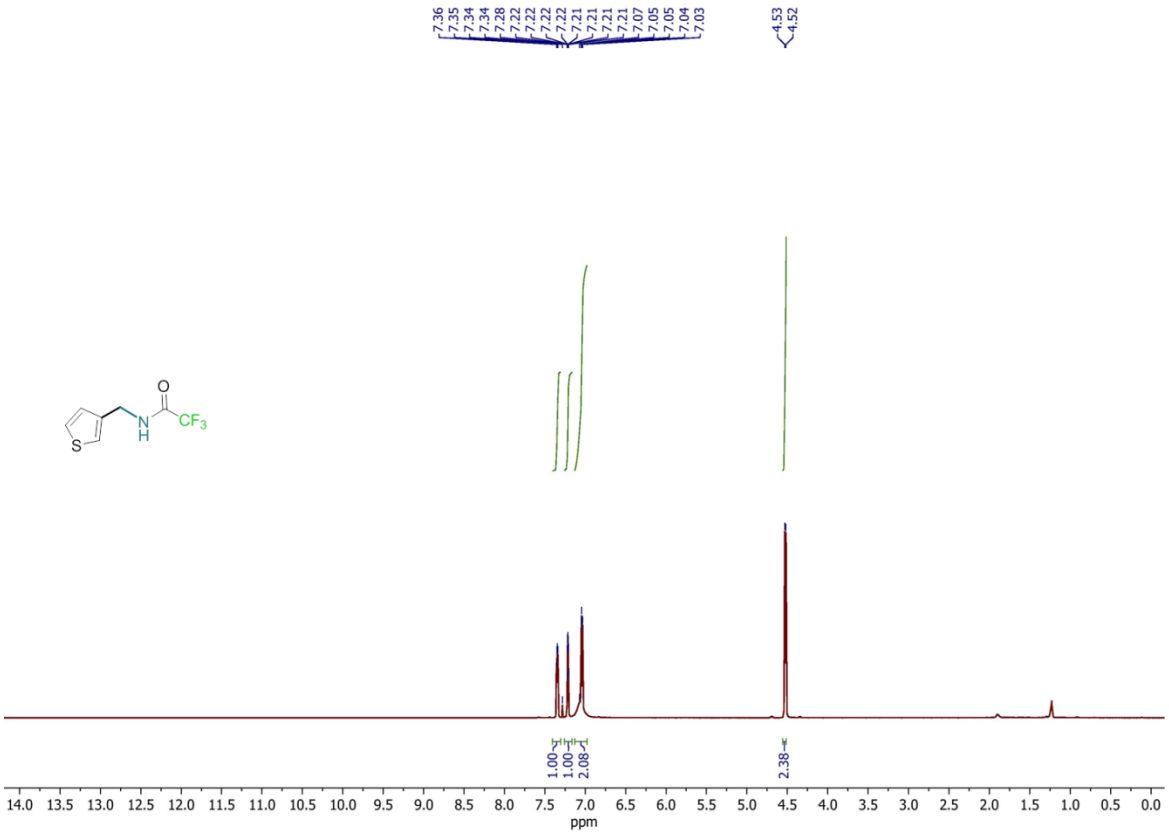
2,2,2-trifluoro-*N*-(4-(trifluoromethyl)benzyl)acetamide (**3u**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

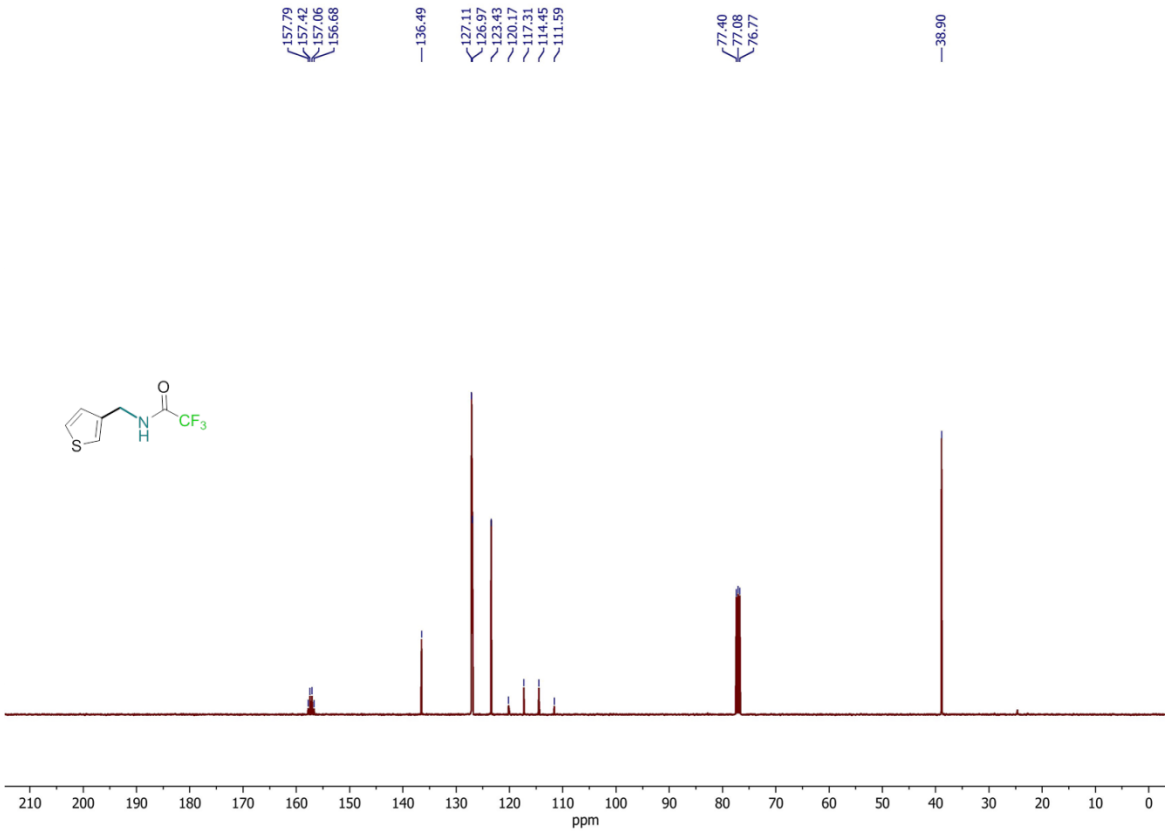


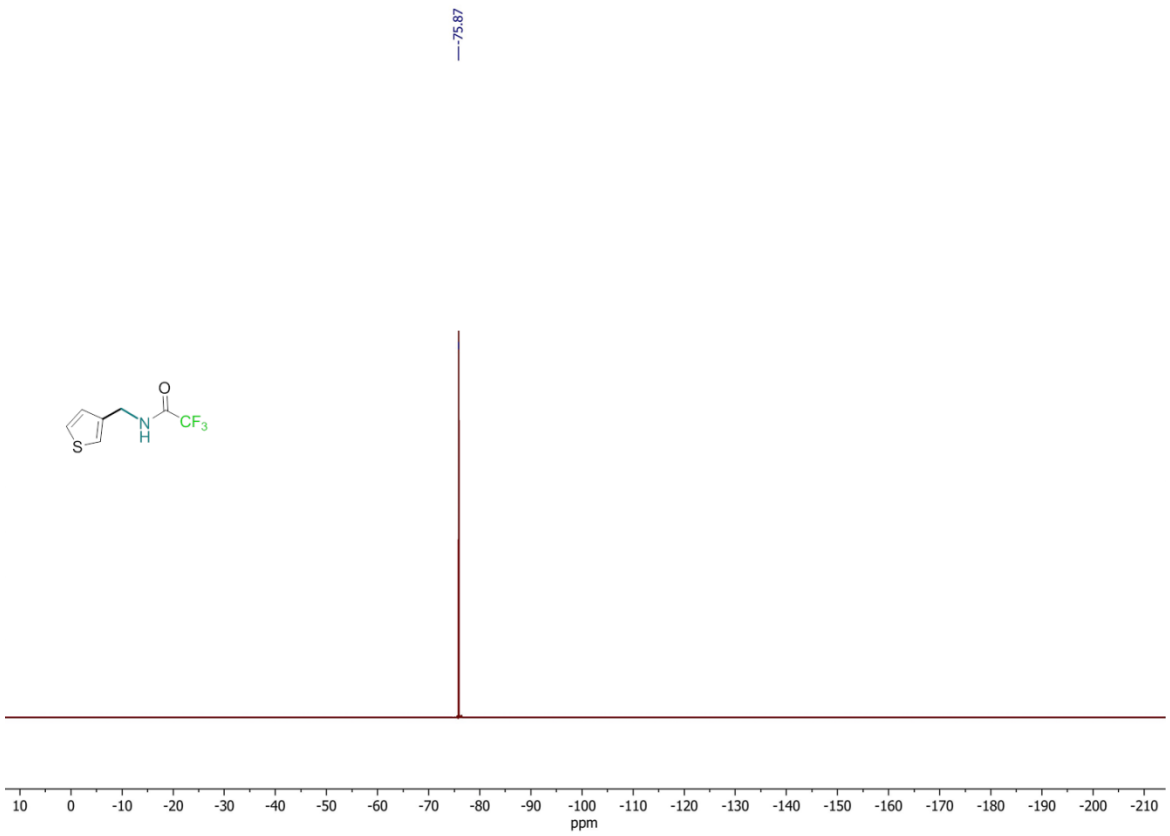



-62.81
-75.96
O
N
H
CF3
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

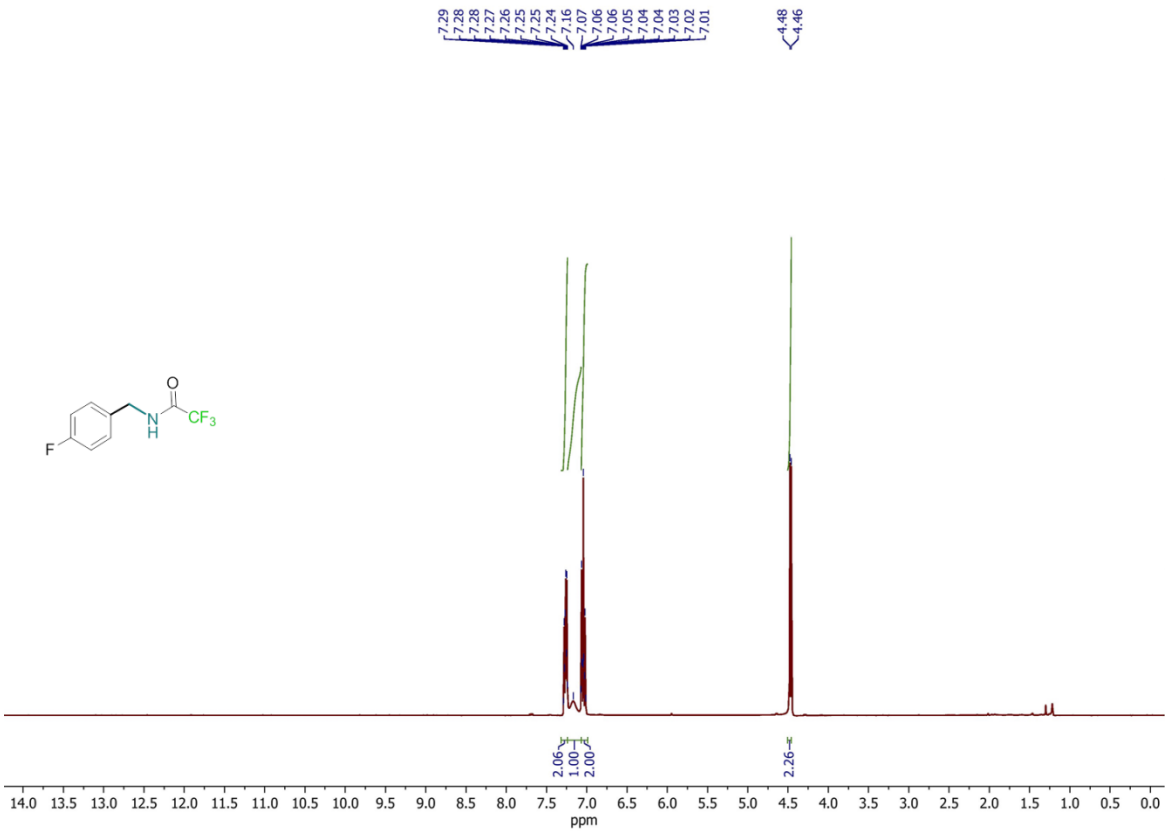
2,2,2-trifluoro-*N*-(thiophen-3-ylmethyl)acetamide (**3y**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

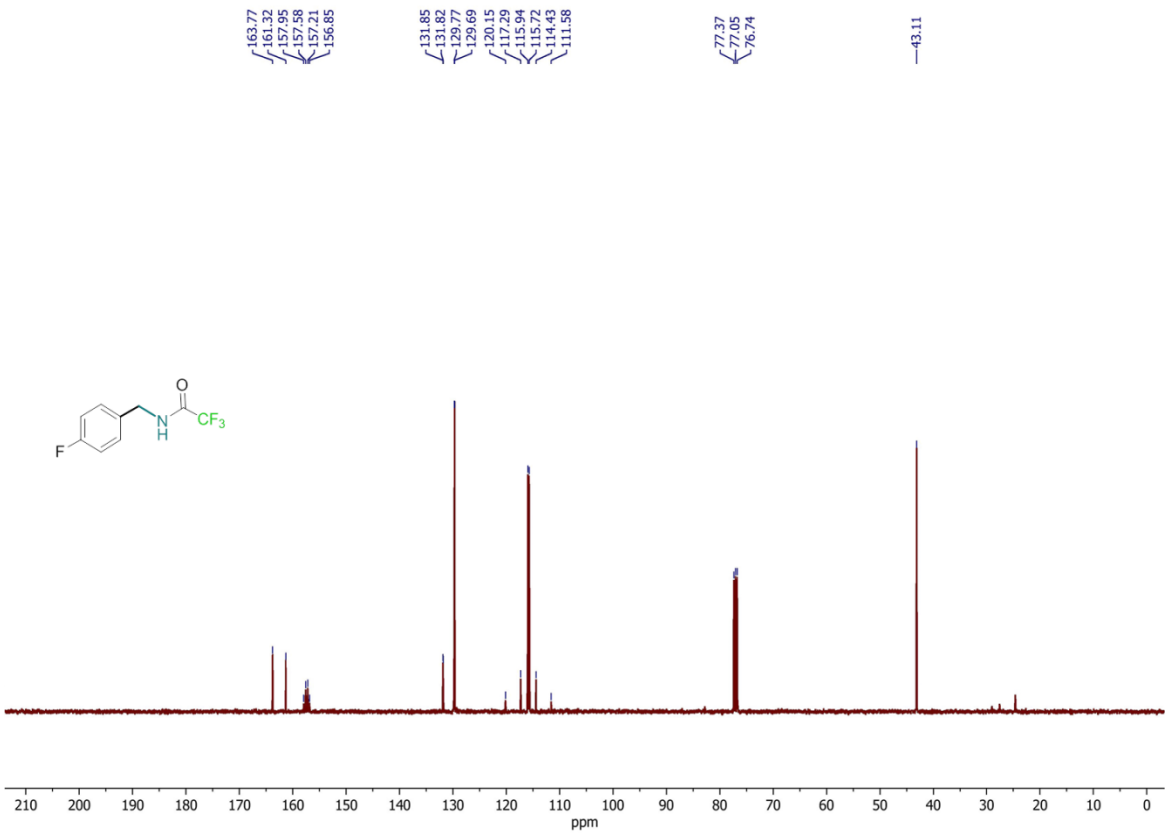


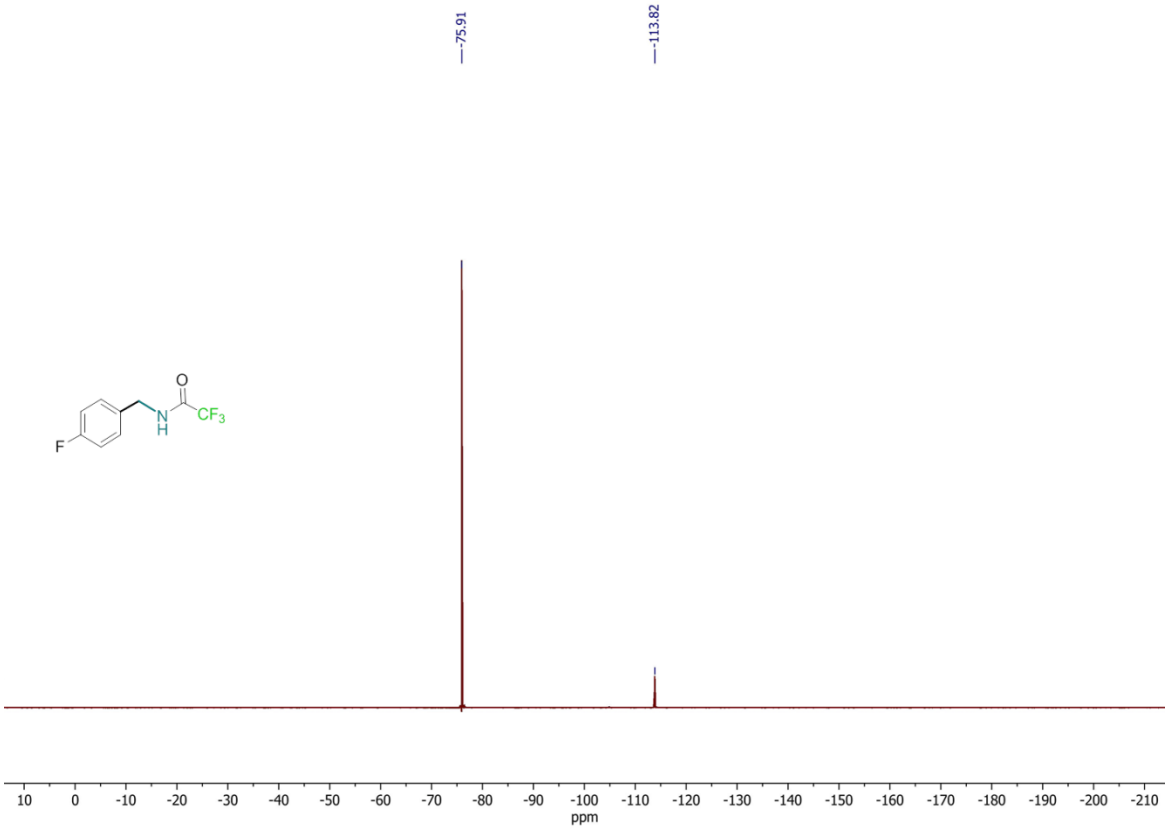



-75.87
O
N
H
CF3
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

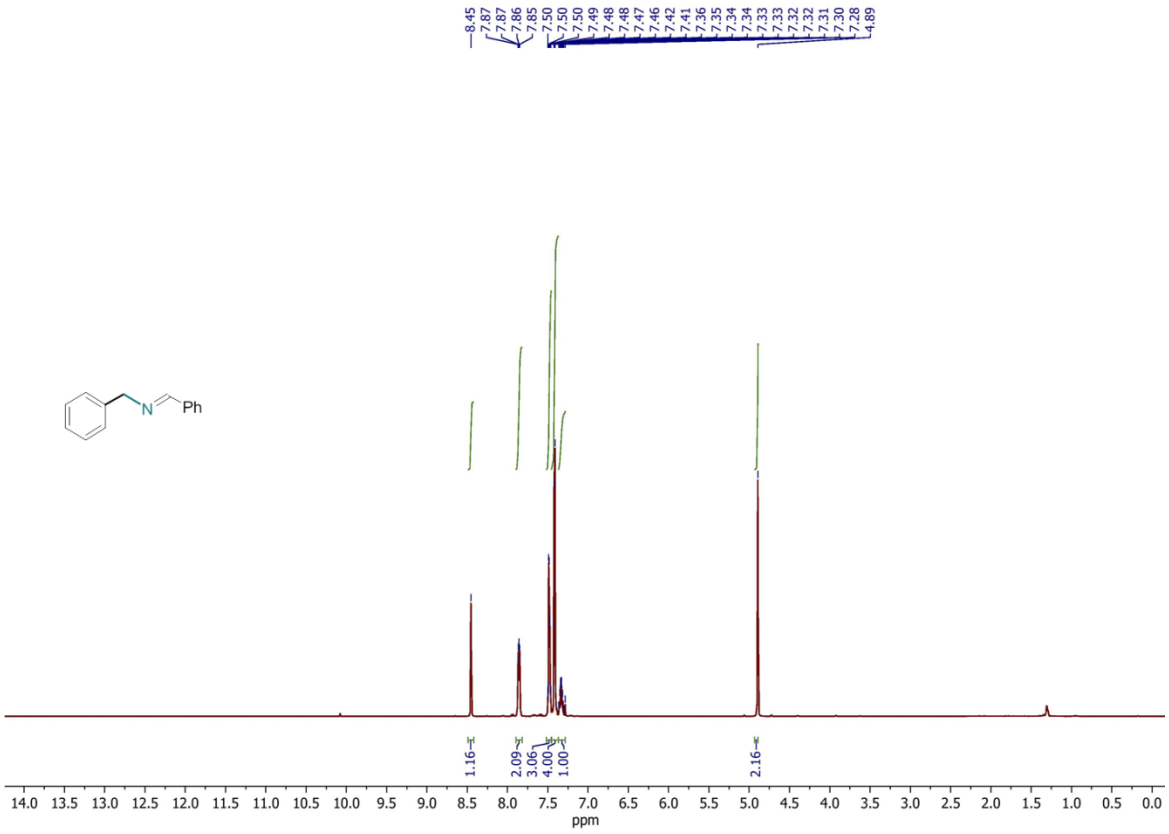
2,2,2-trifluoro-*N*-(4-fluorobenzyl)acetamide (**3v**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

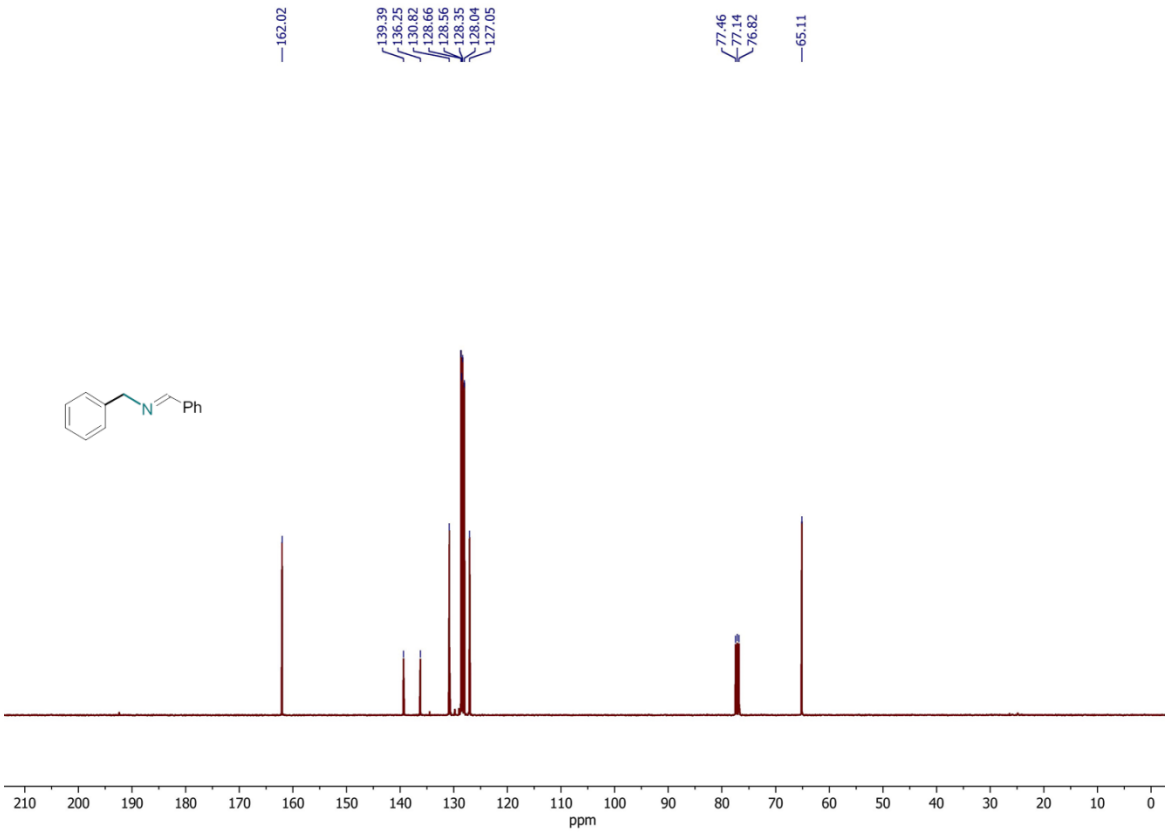




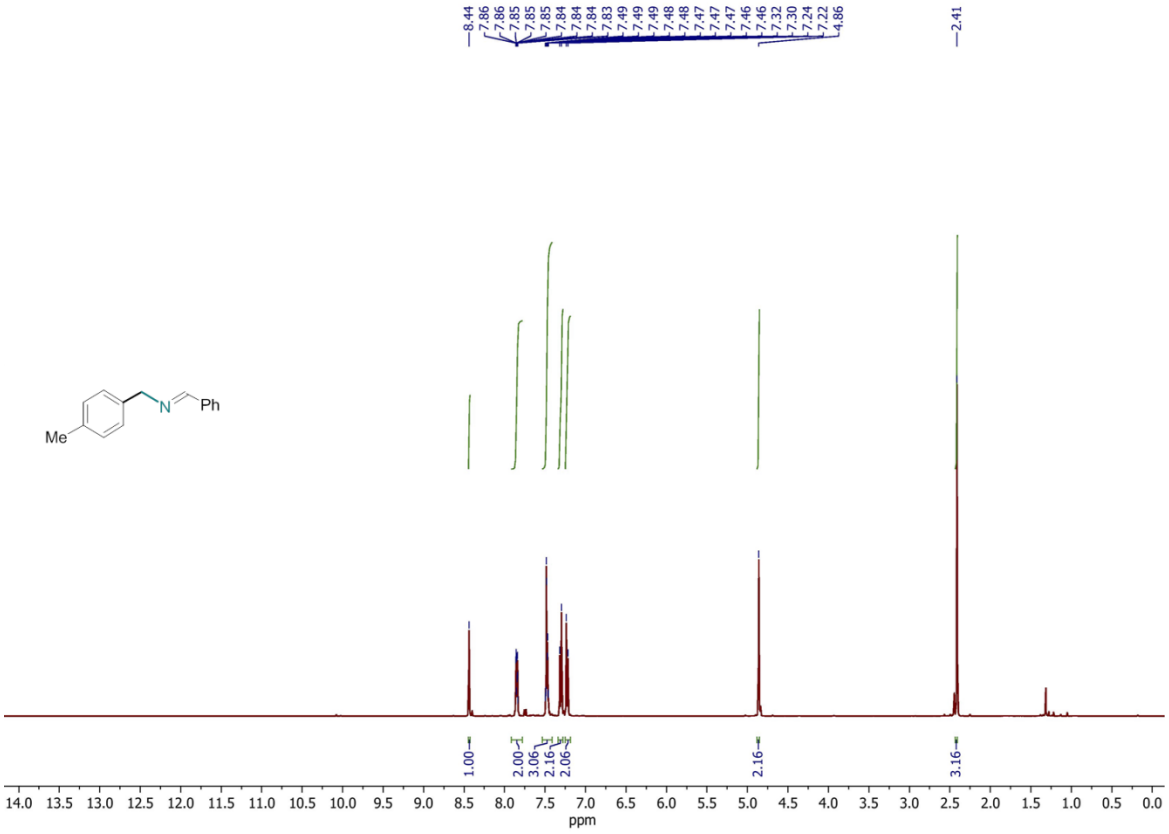

-75.91
-113.82
O
N
H
CF3
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

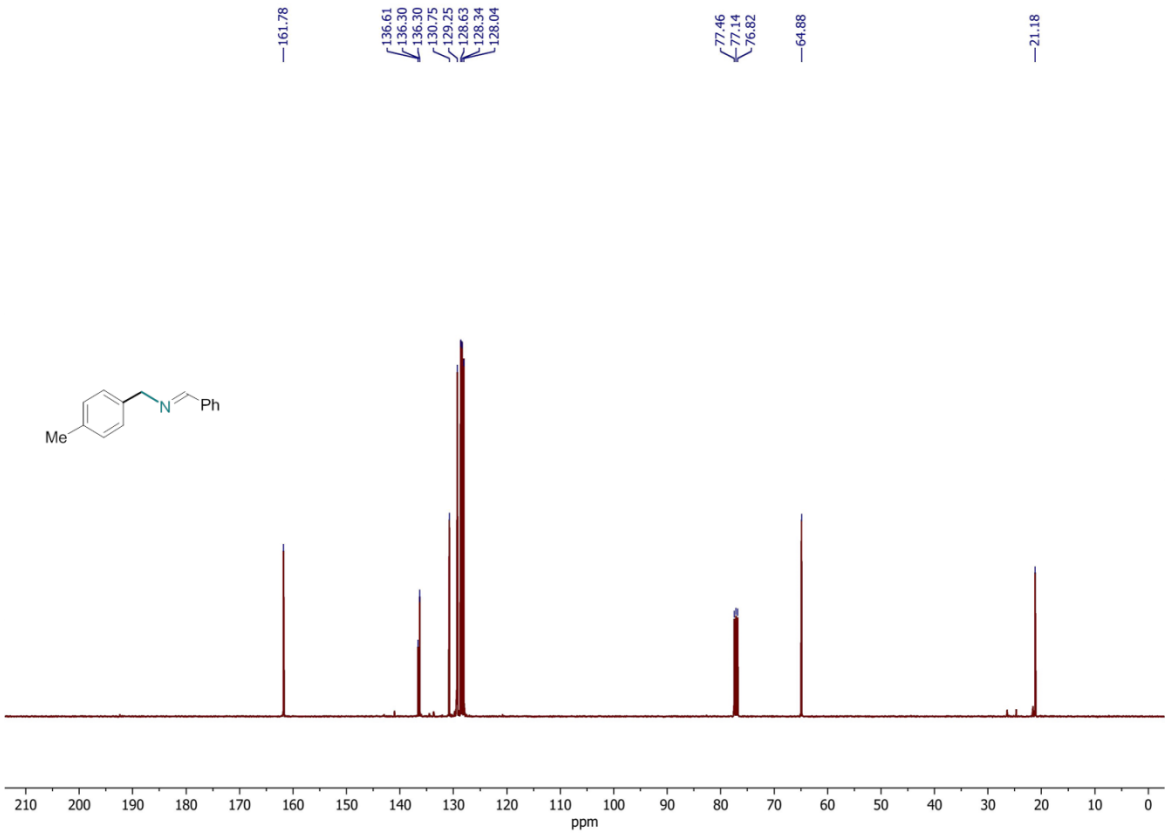
(E)-*N*-benzylidene-1-phenylmethanamine (**4a**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



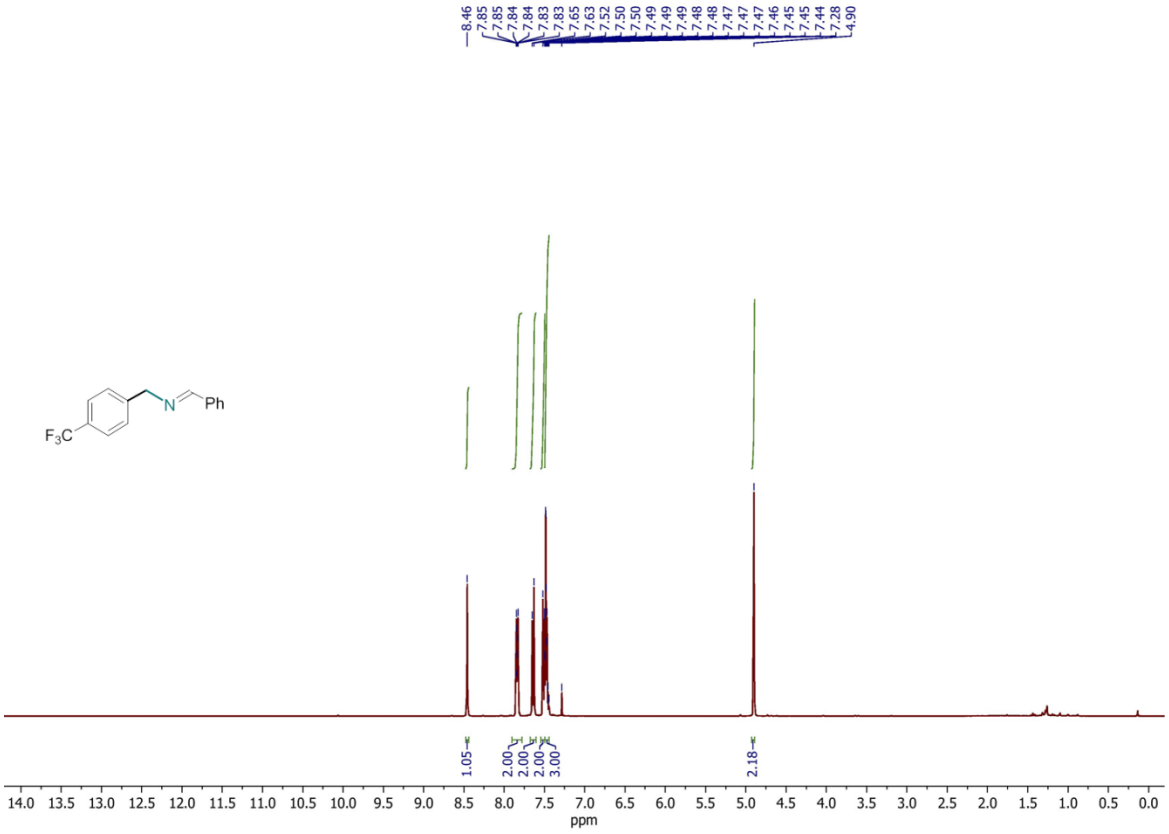


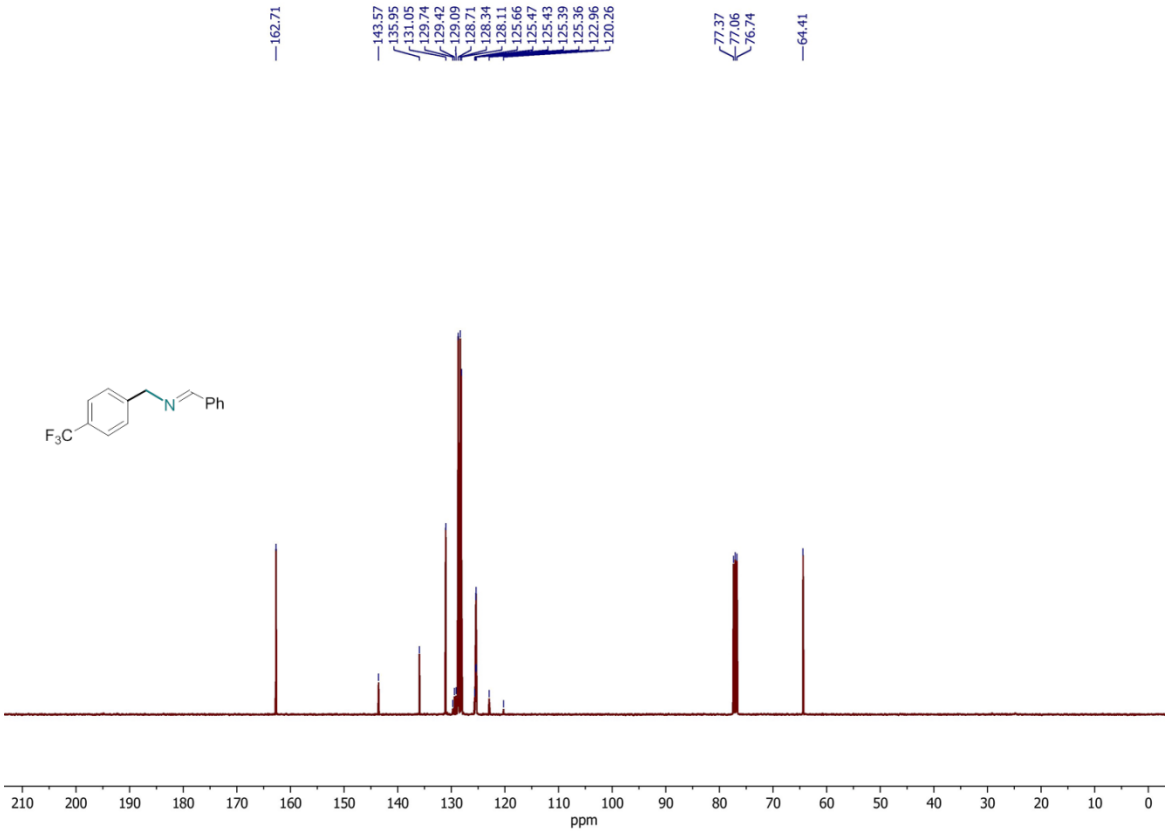
N-benzylidene-1-*p*-tolylmethanamine (**4b**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**

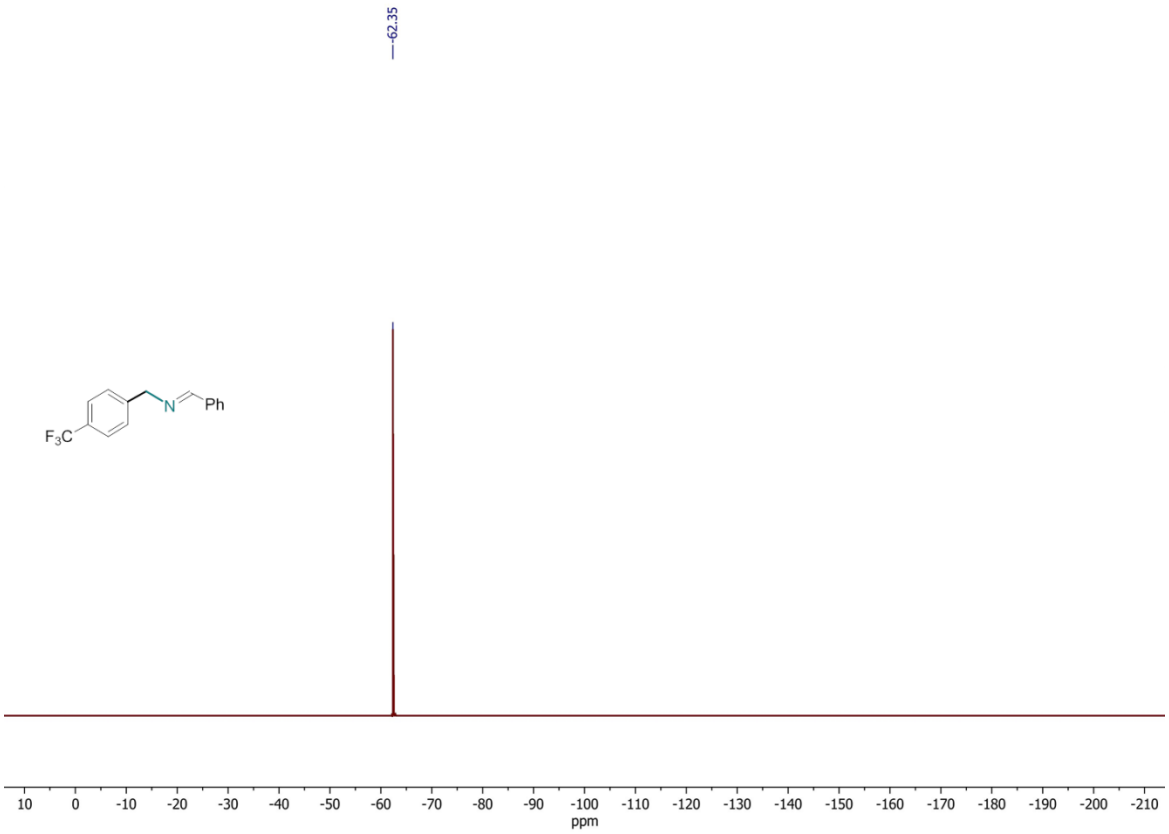




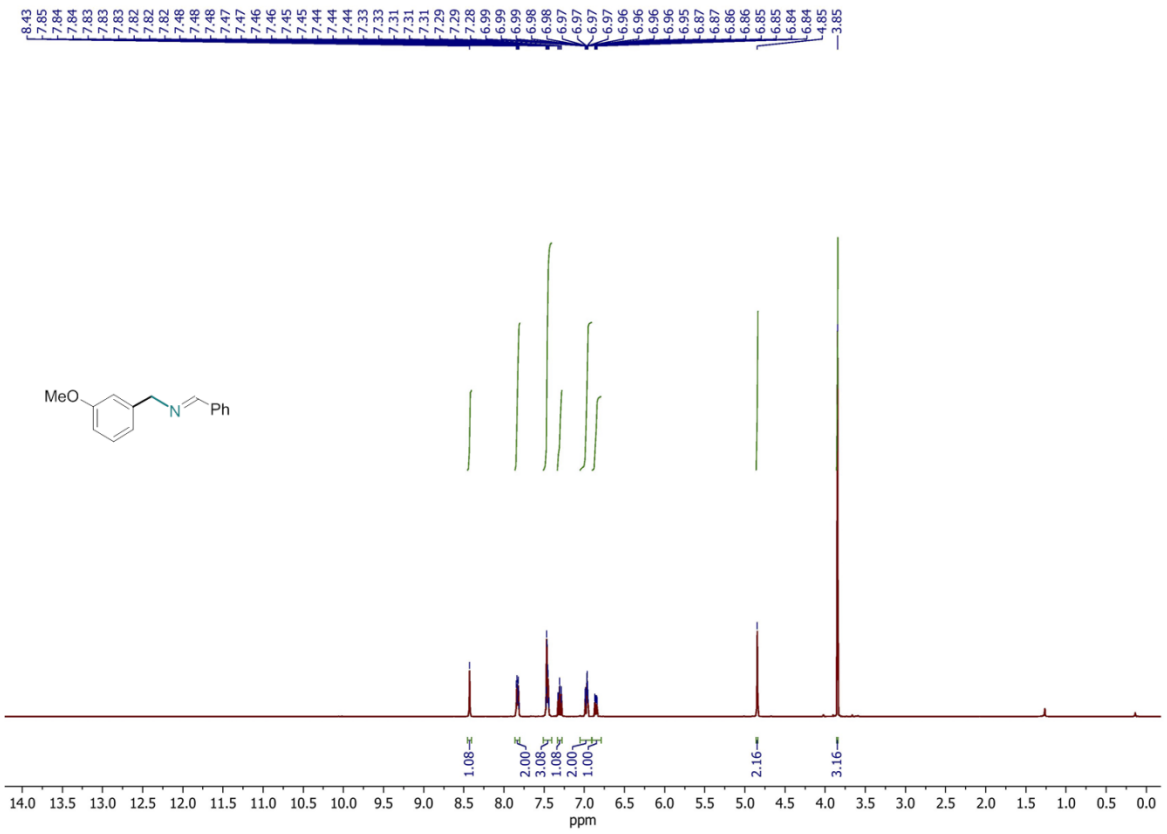
N-benzylidene-1-(4-(trifluoromethyl)phenyl)methanamine (**4c**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$).**

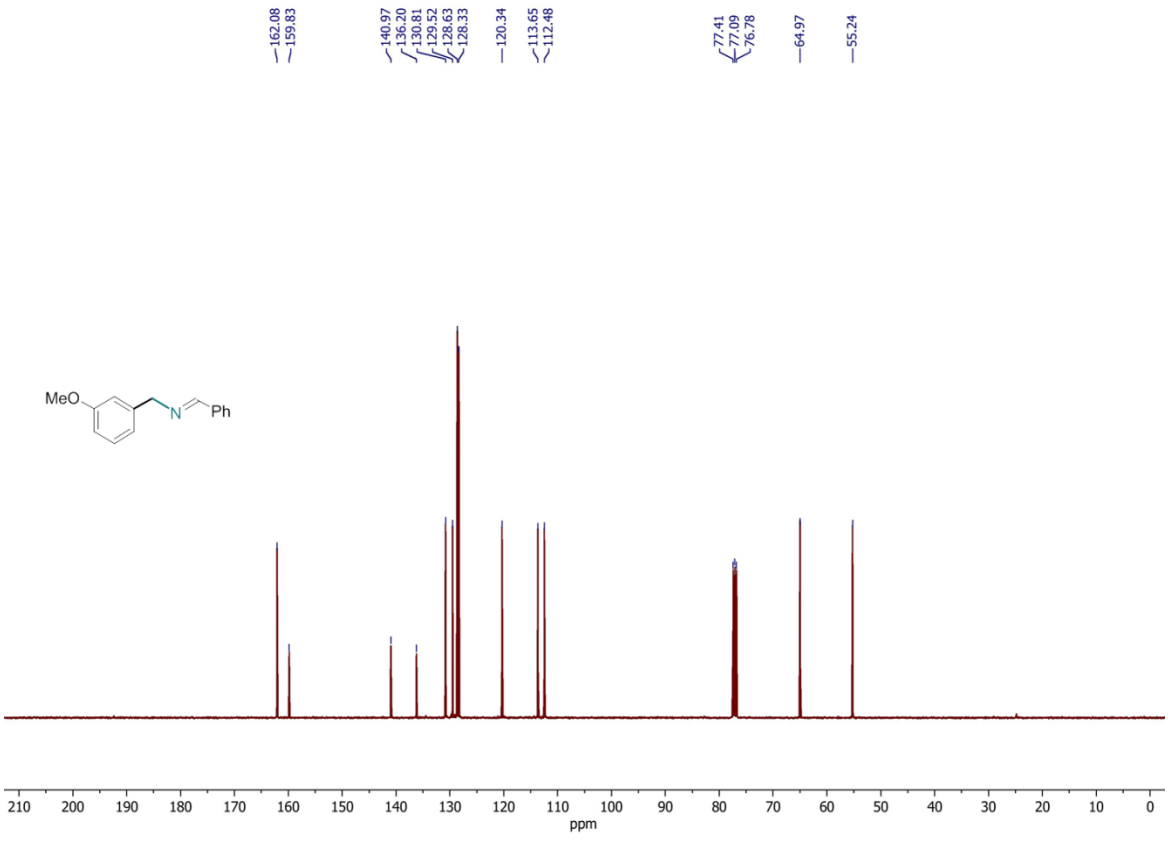




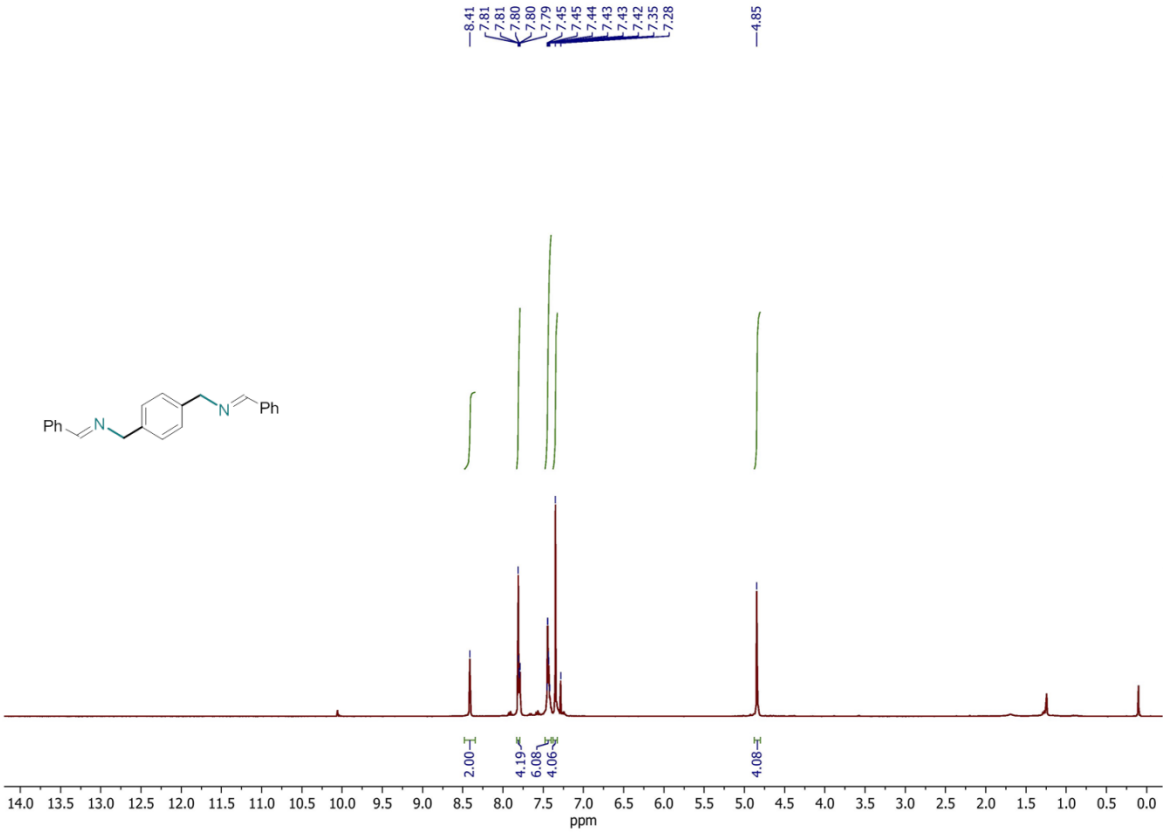

-62.35
N
Ph
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

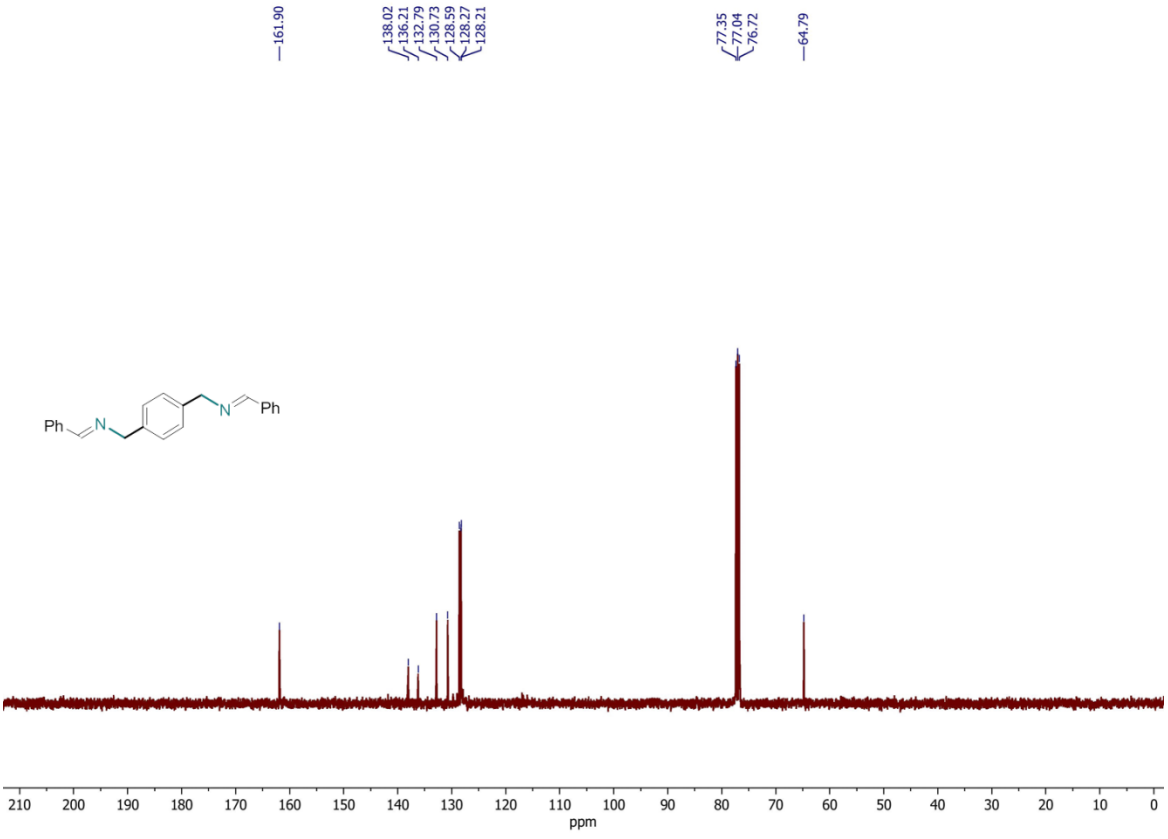
N-benzylidene-1-(3-methoxyphenyl)methanamine (**4d**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



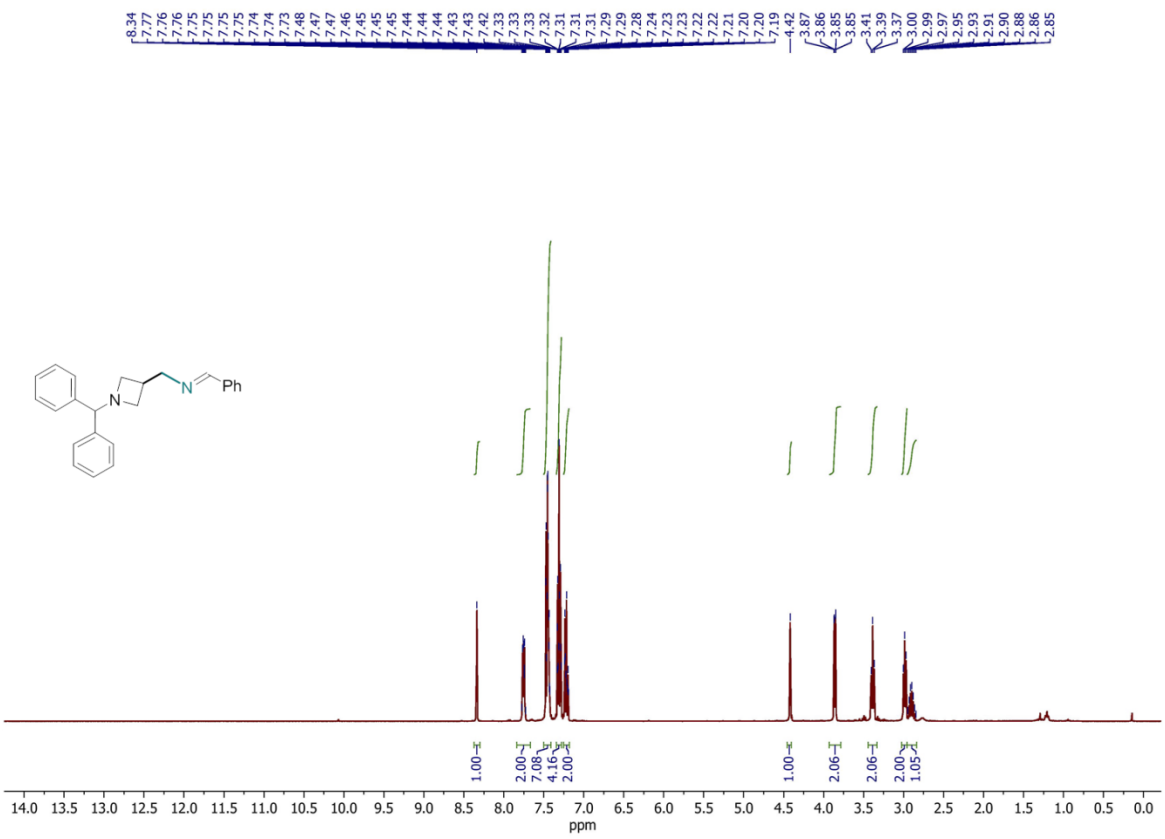


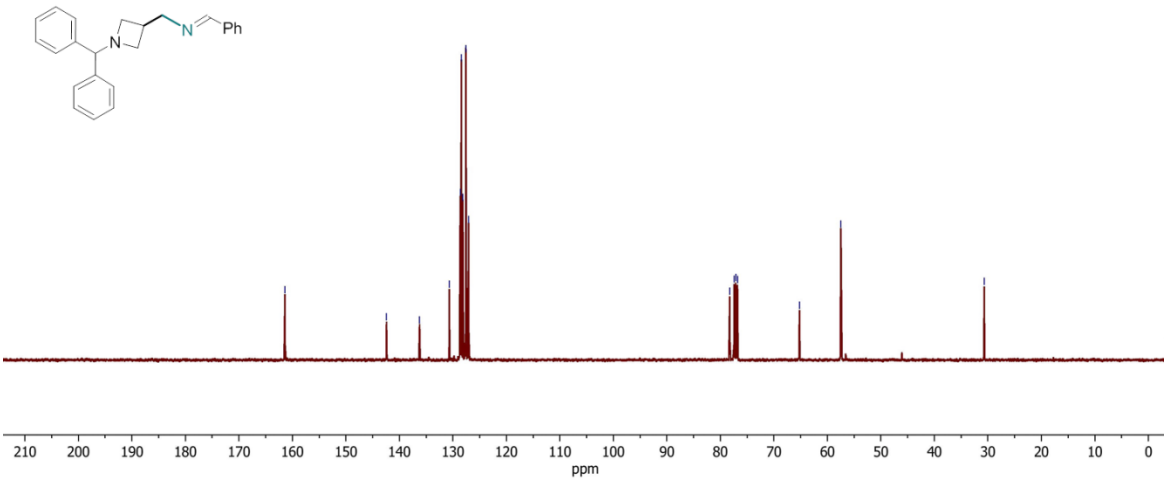
(*N*,*N*′)-1,1'-(1,4-phenylene)bis(*N*-benzylidenemethanamine) (**4e**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



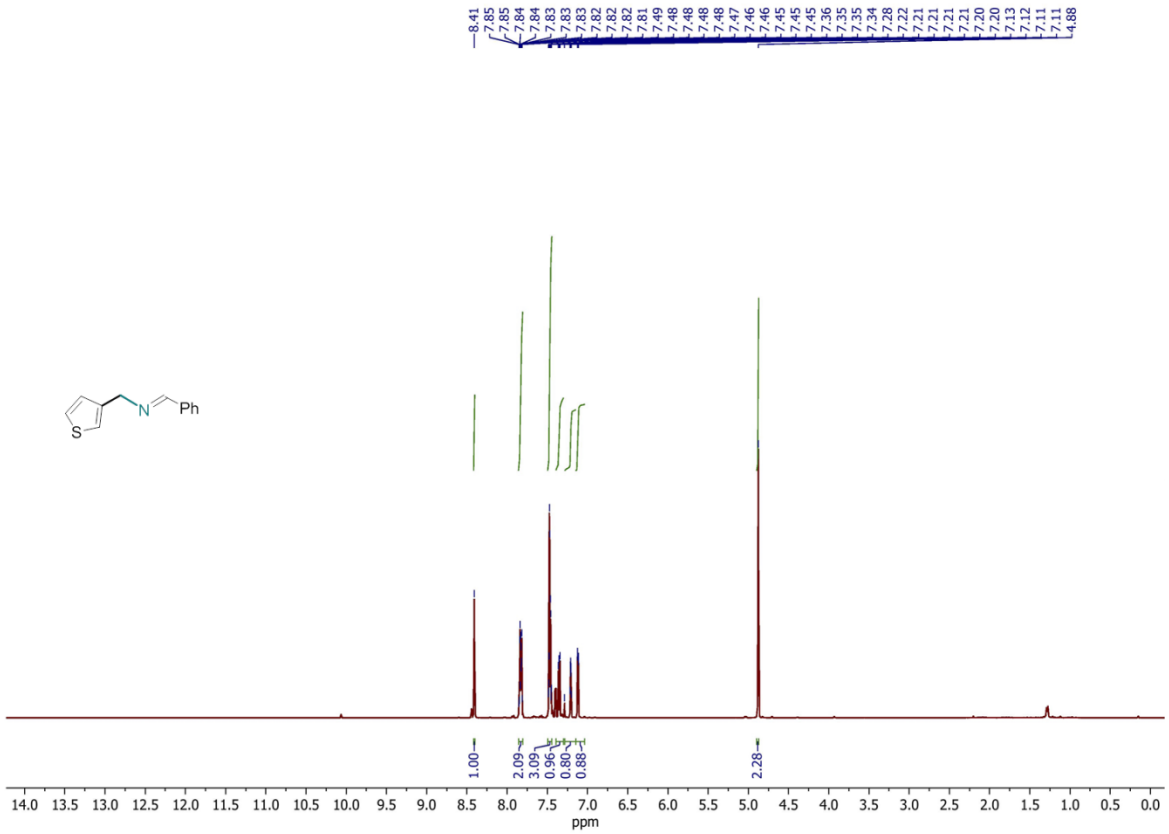


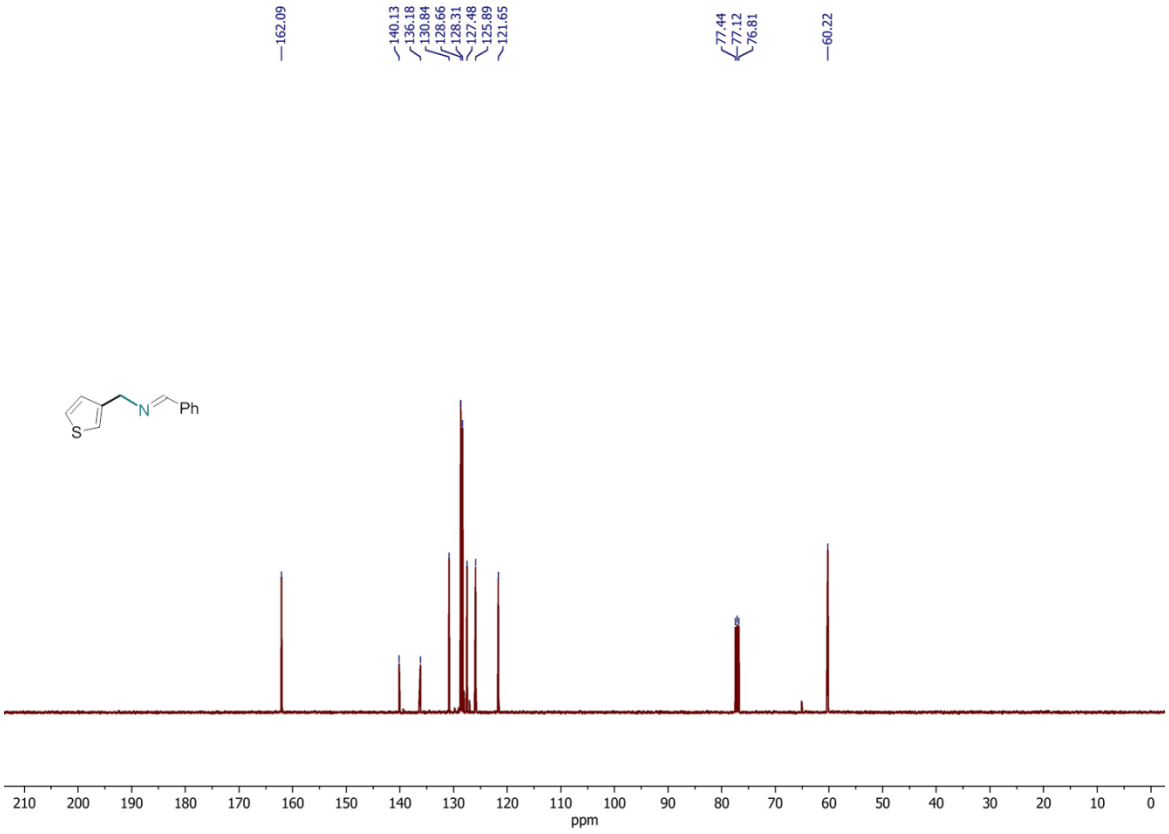
1-(1-benzhydrylazetidin-3-yl)-*N*-benzylidenemethanamine (**4f**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



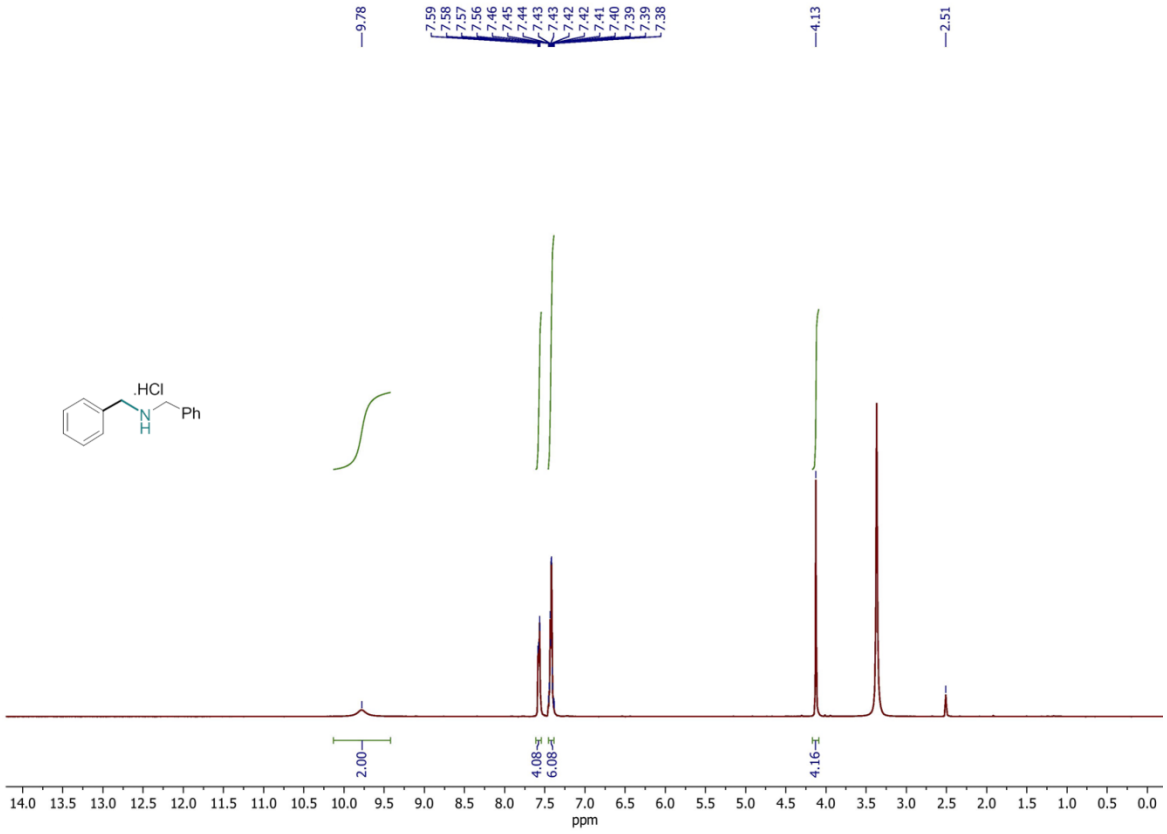


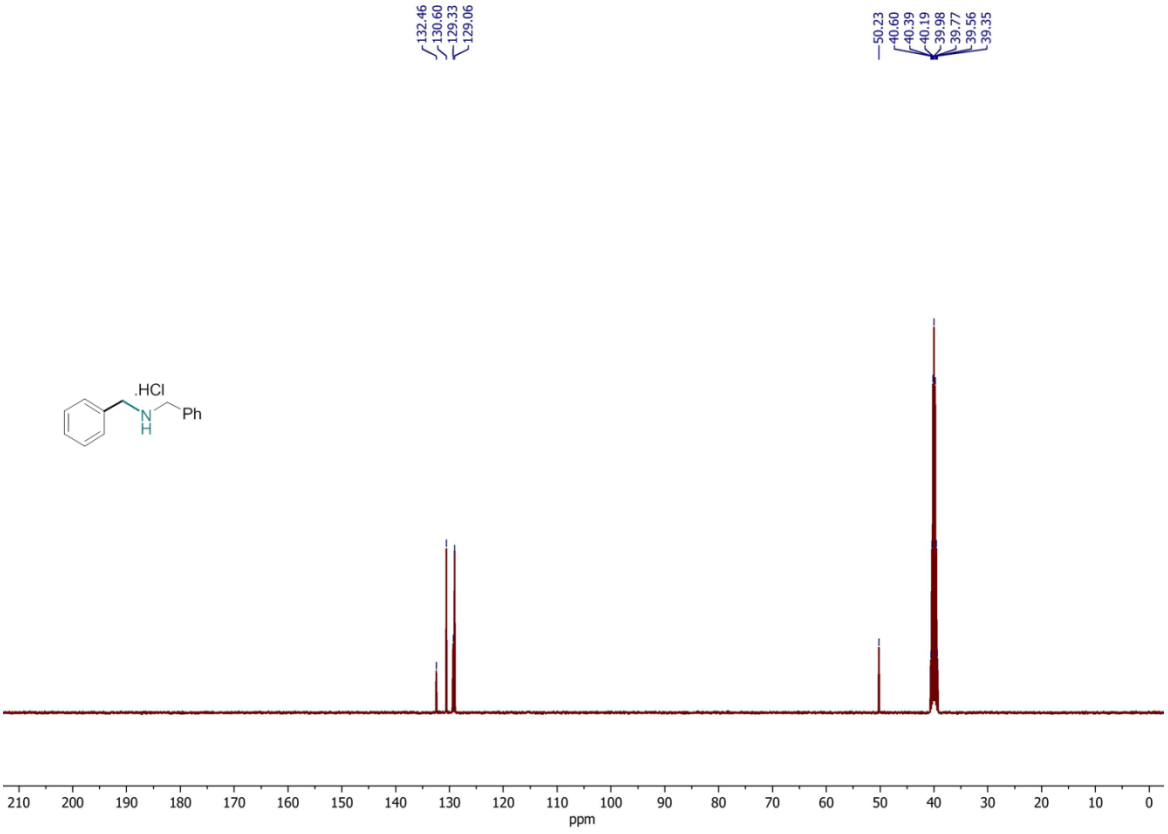
N-benzylidene-1-(thiophen-3-yl)methanamine (**4g**); **^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$).**



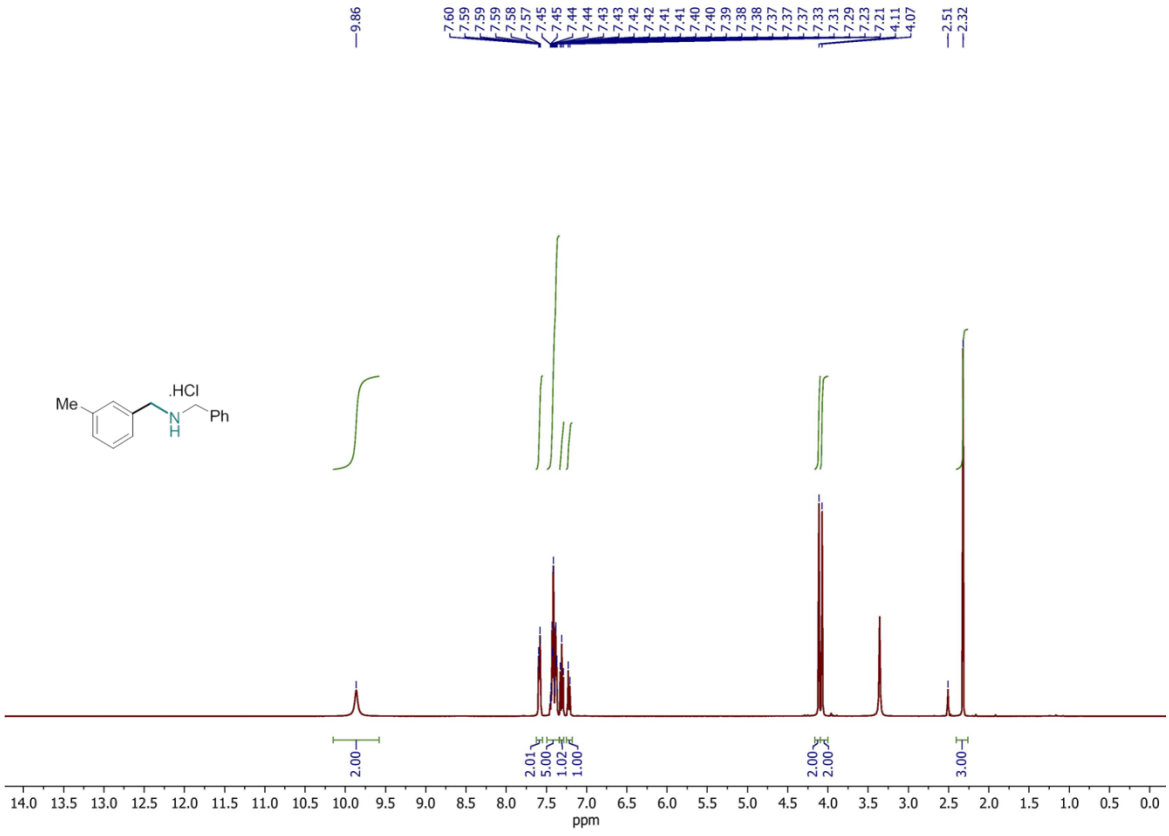


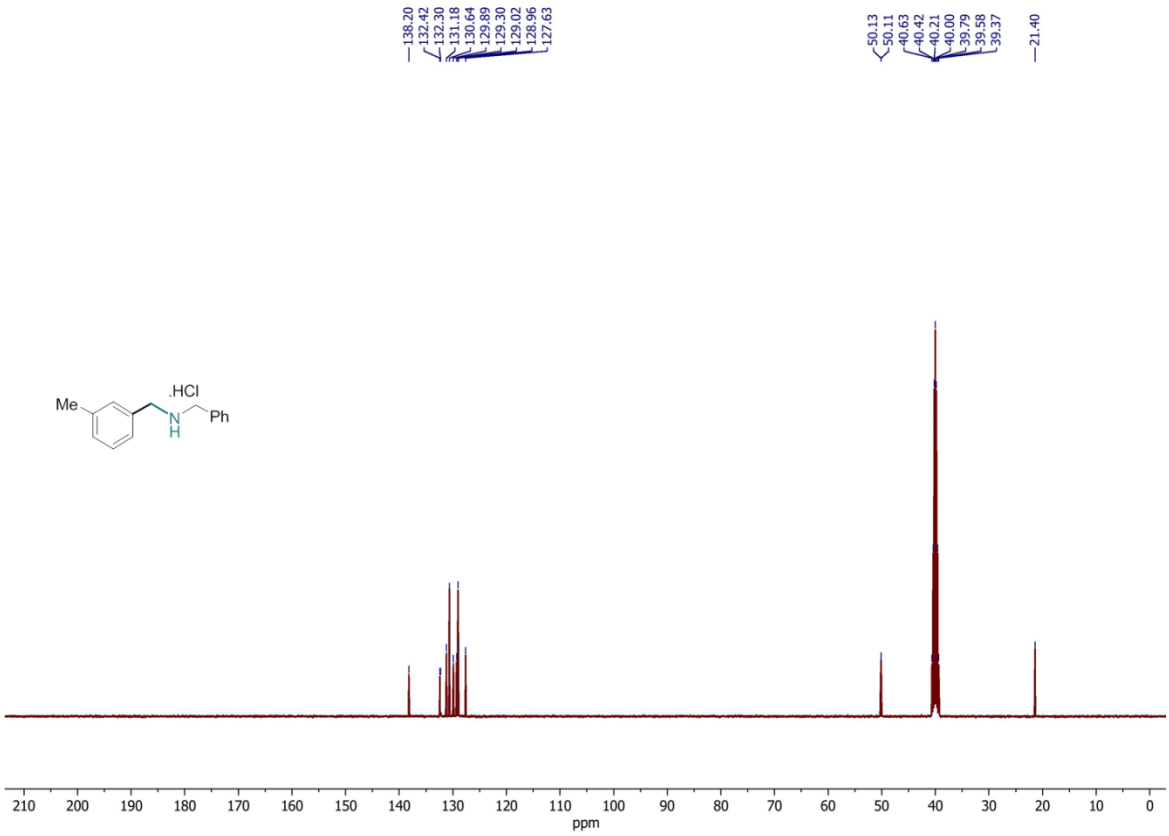
dibenzylamine hydrochloride (**5a**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



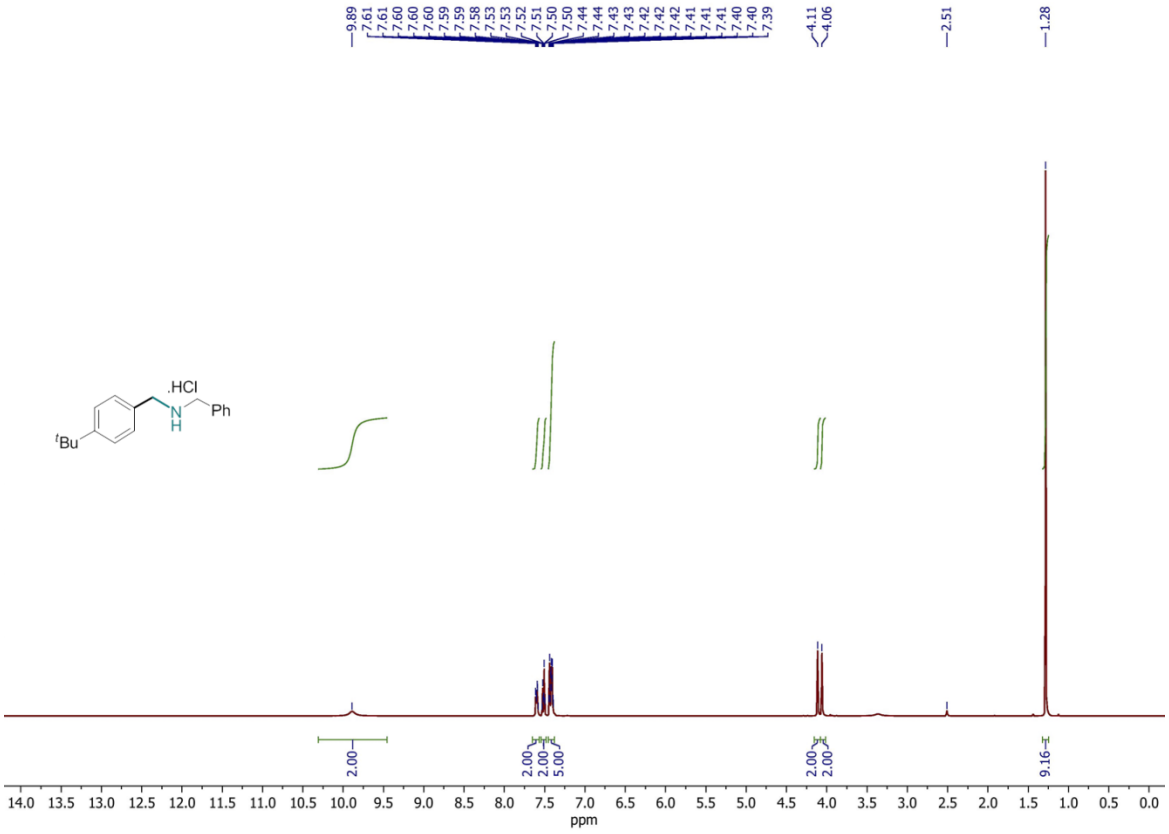


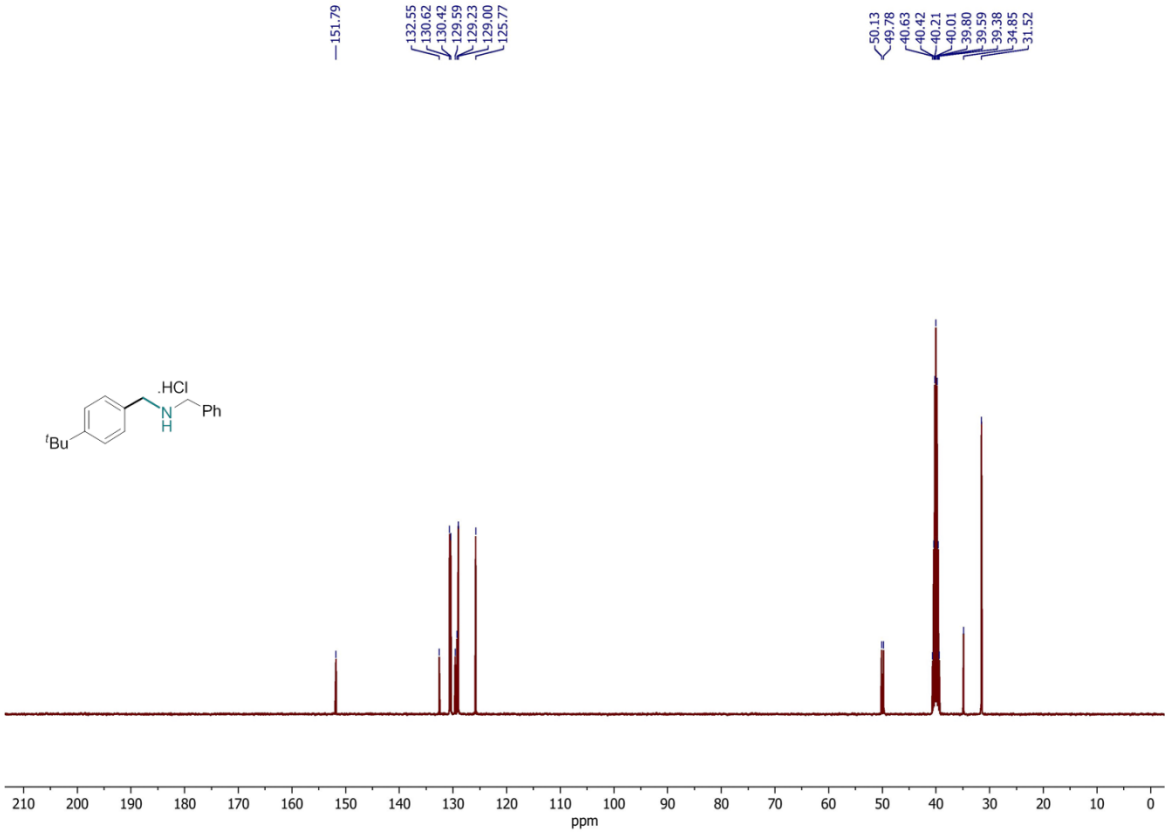
N-benzyl-1-*m*-tolylmethanamine hydrochloride (**5b**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6).**



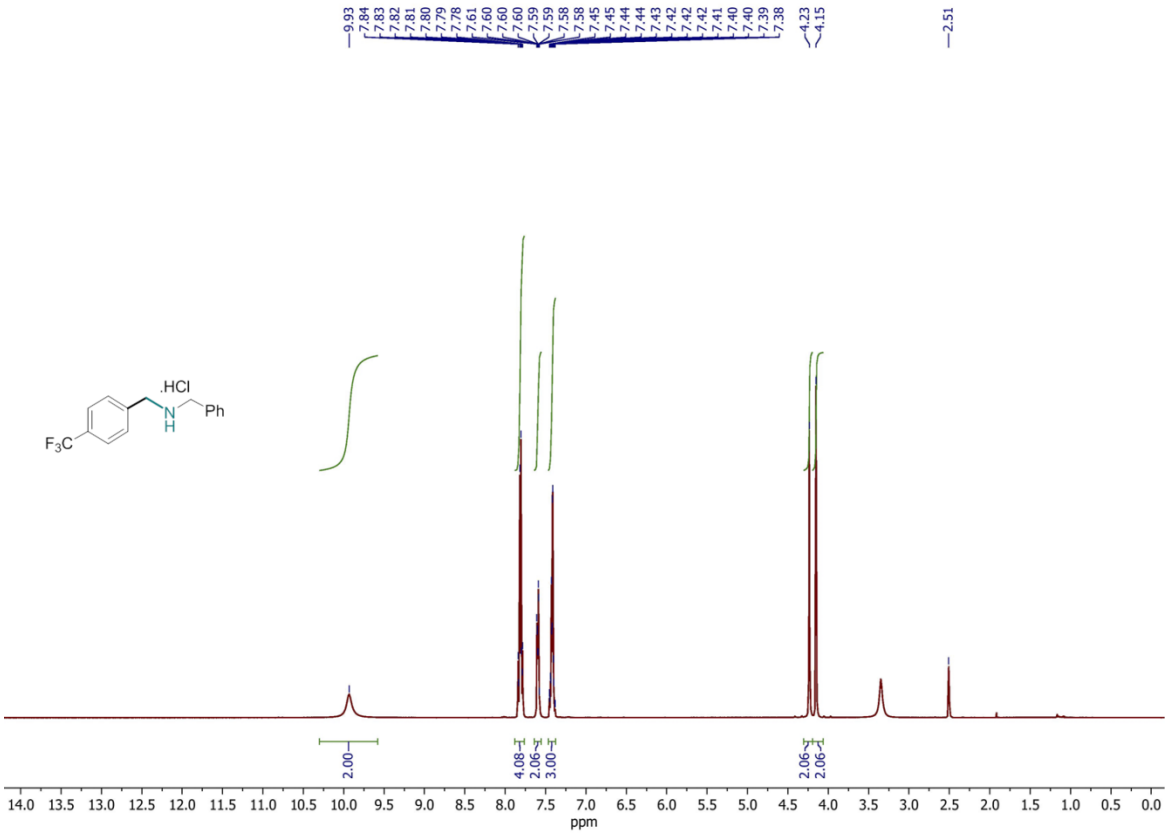


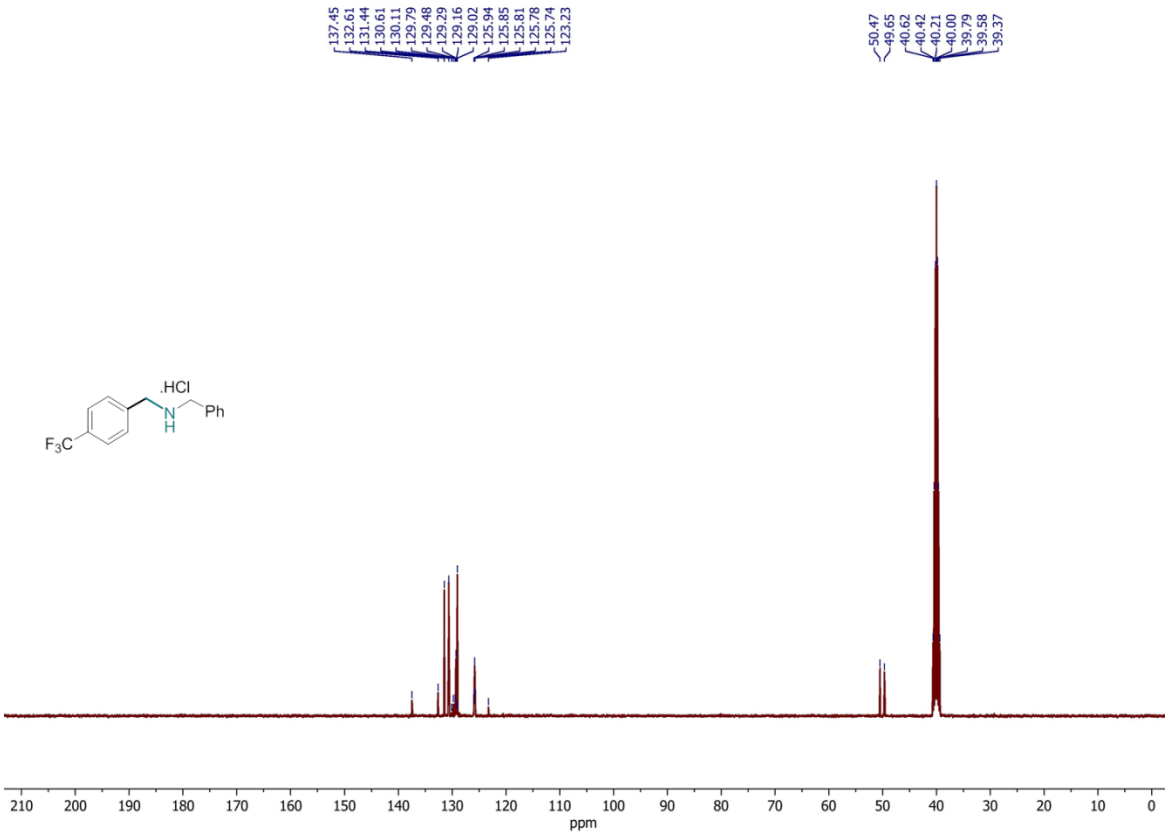
N-benzyl-1-(4-*tert*-butylphenyl)methanamine hydrochloride (**5c**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6).**

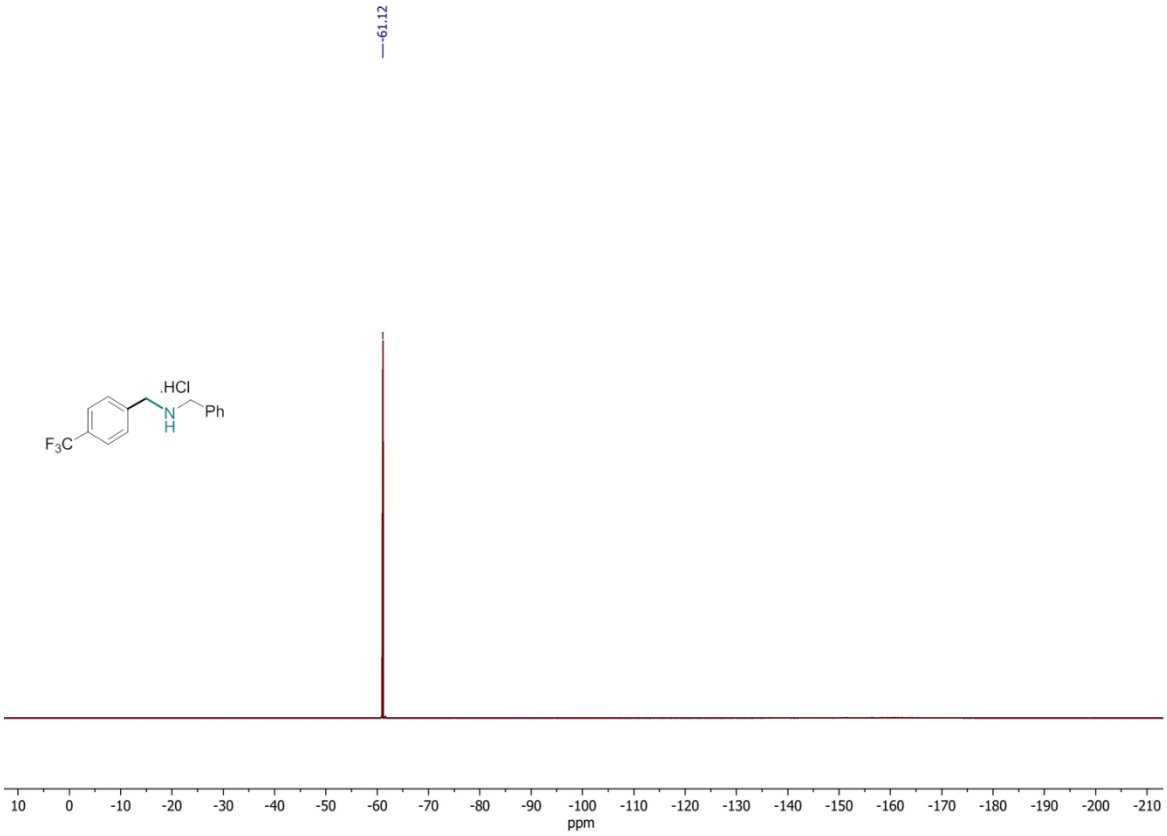




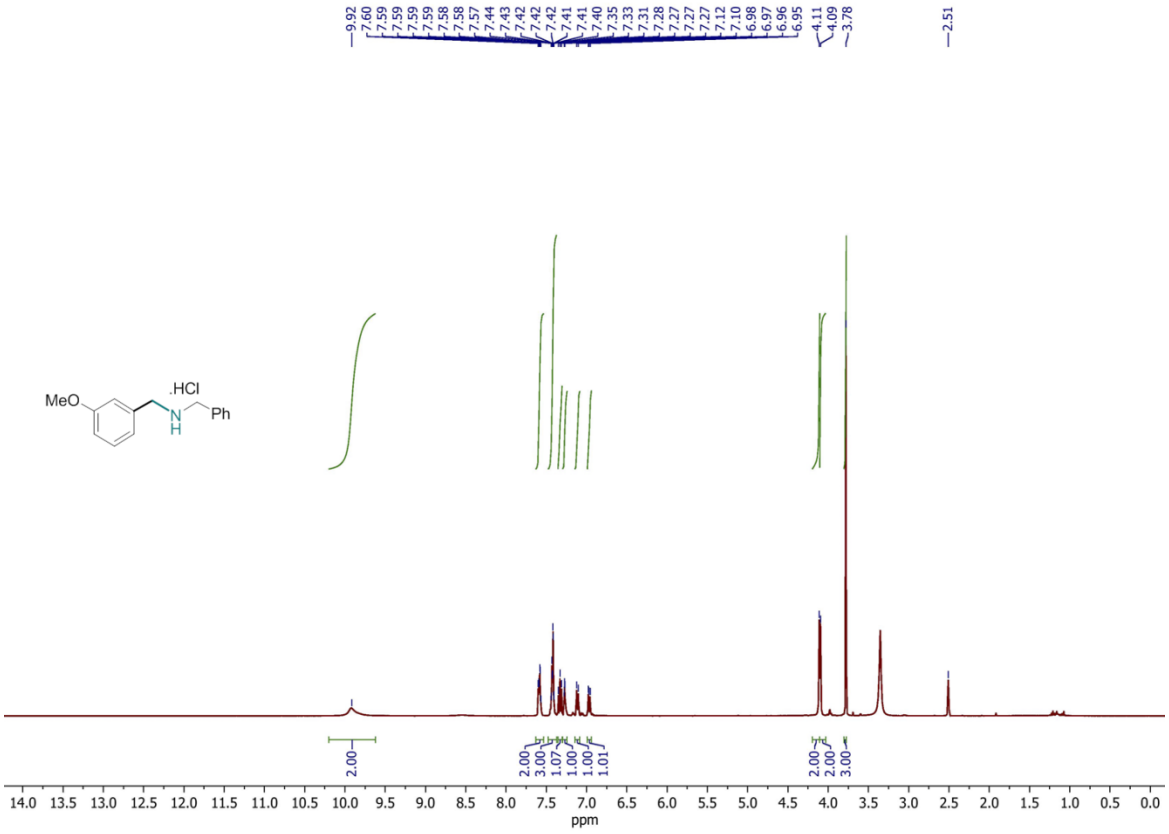
N-benzyl-1-(4-(trifluoromethyl)phenyl)methanamine hydrochloride (**5e**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

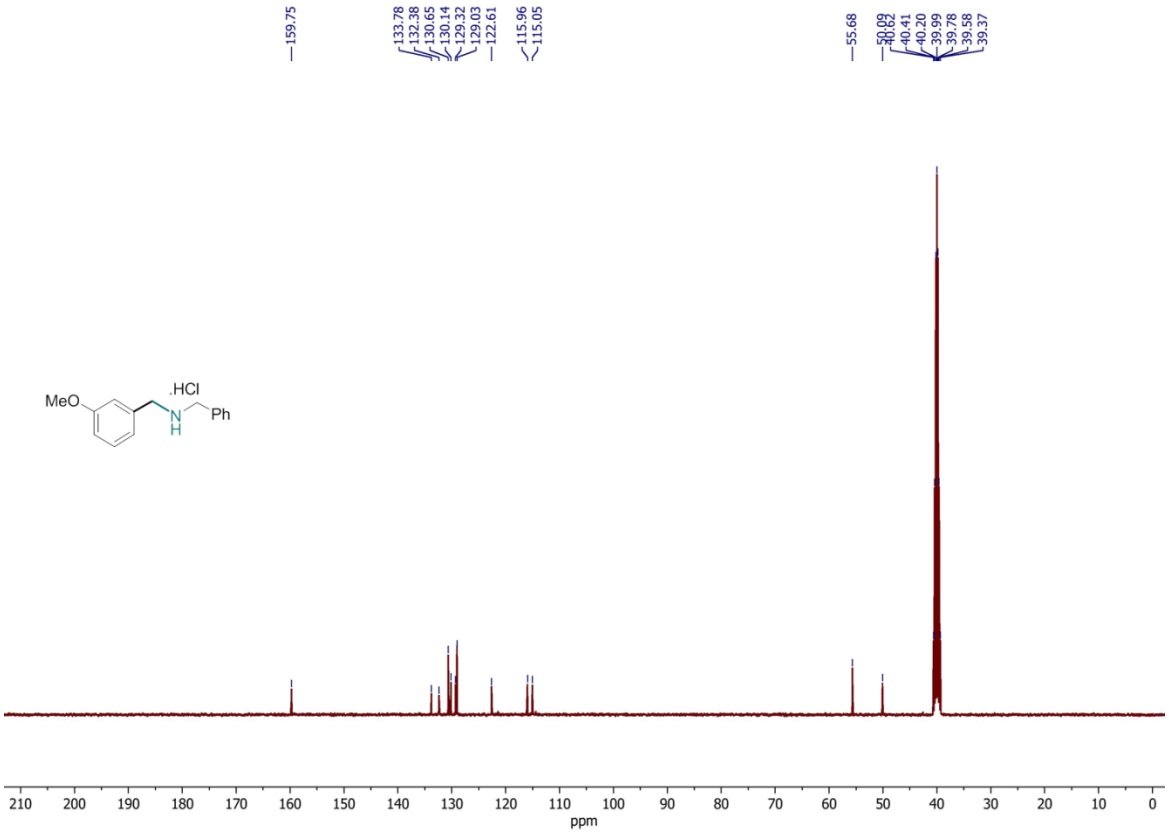




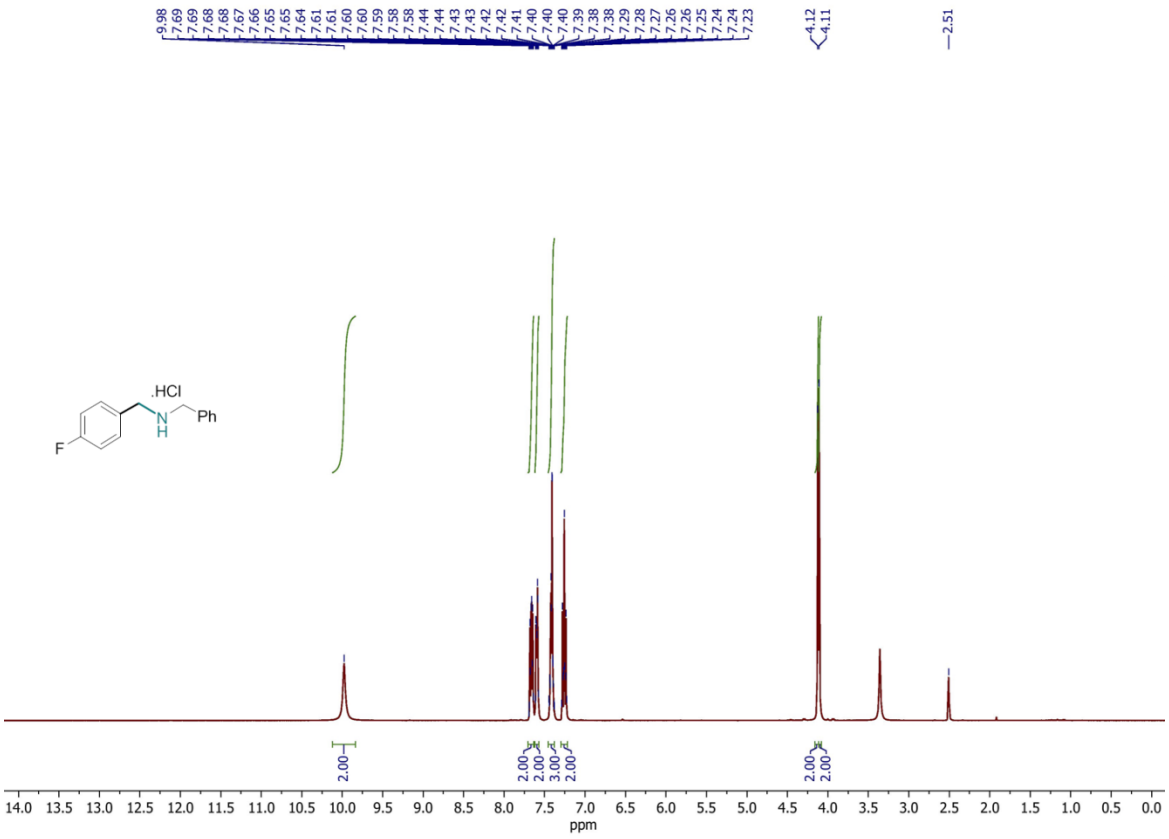

-61.12
.HCl
N
H
Ph
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

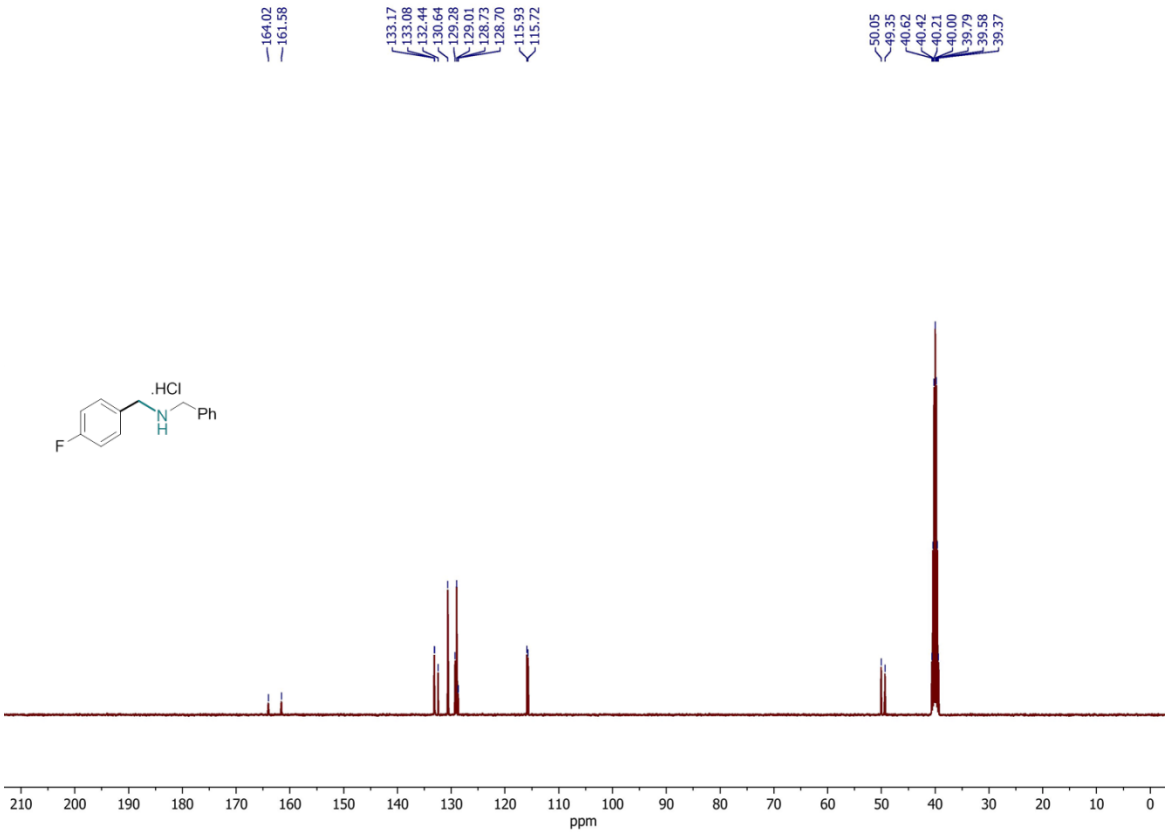
N-benzyl-1-(3-methoxyphenyl)methanamine hydrochloride (**5f**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6).**

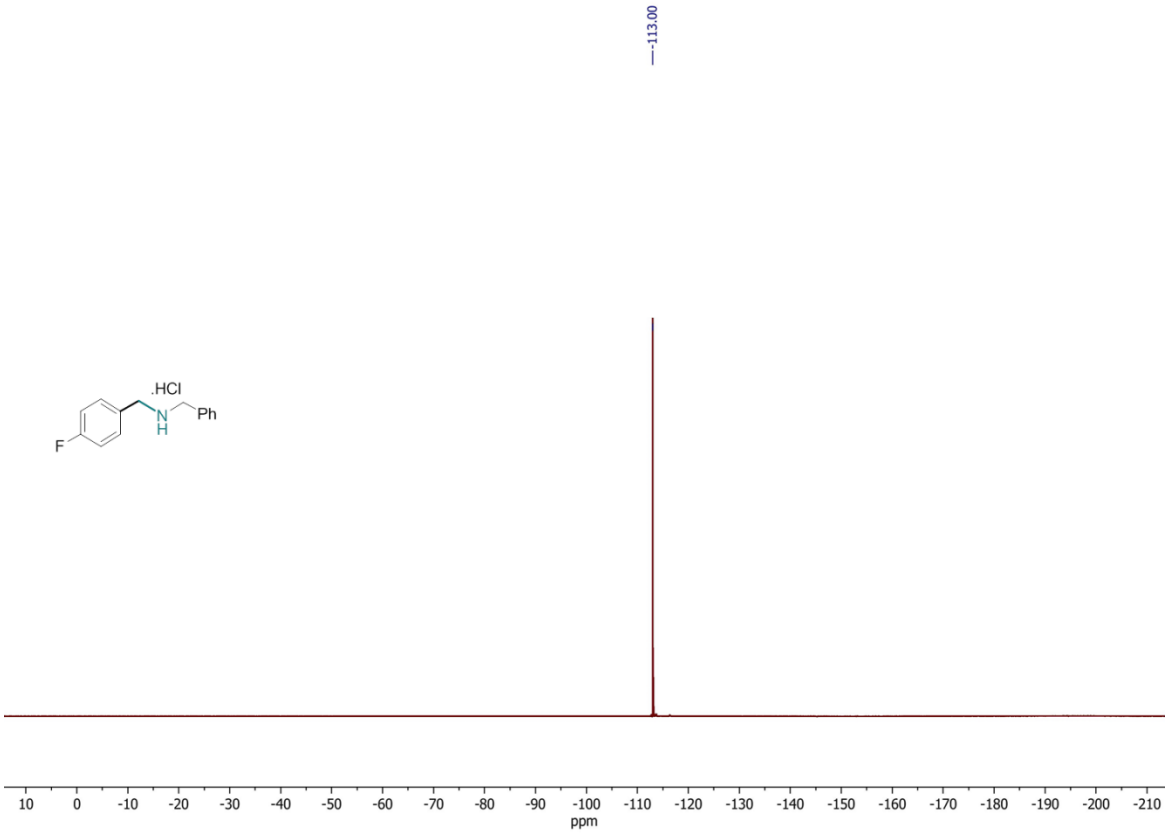




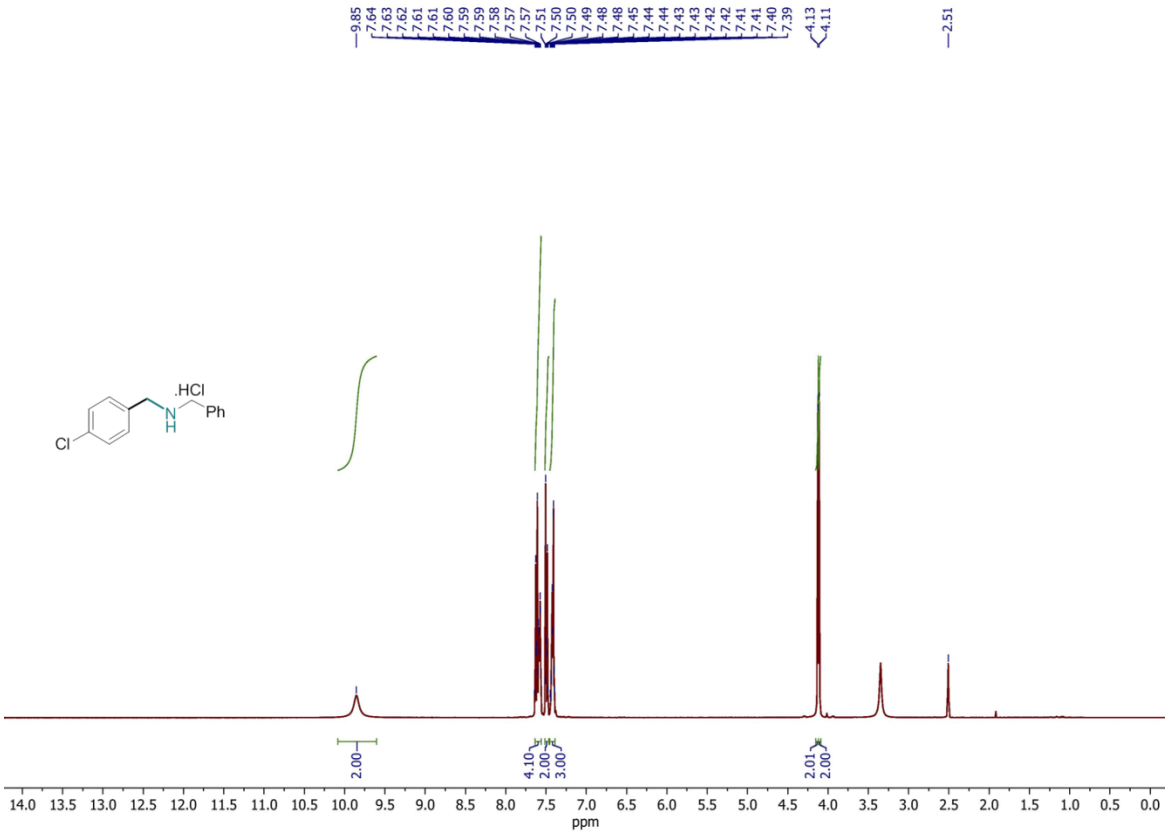
N-benzyl-1-(4-fluorophenyl)methanamine hydrochloride (**5g**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

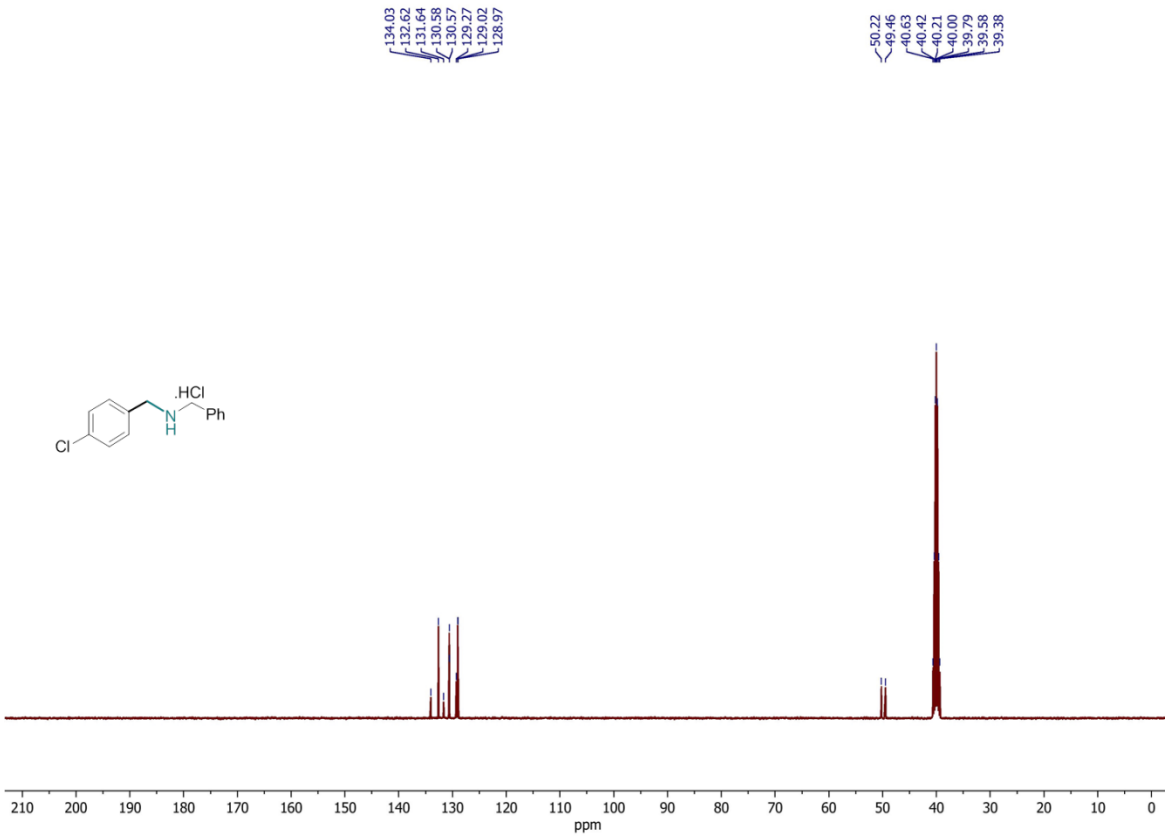




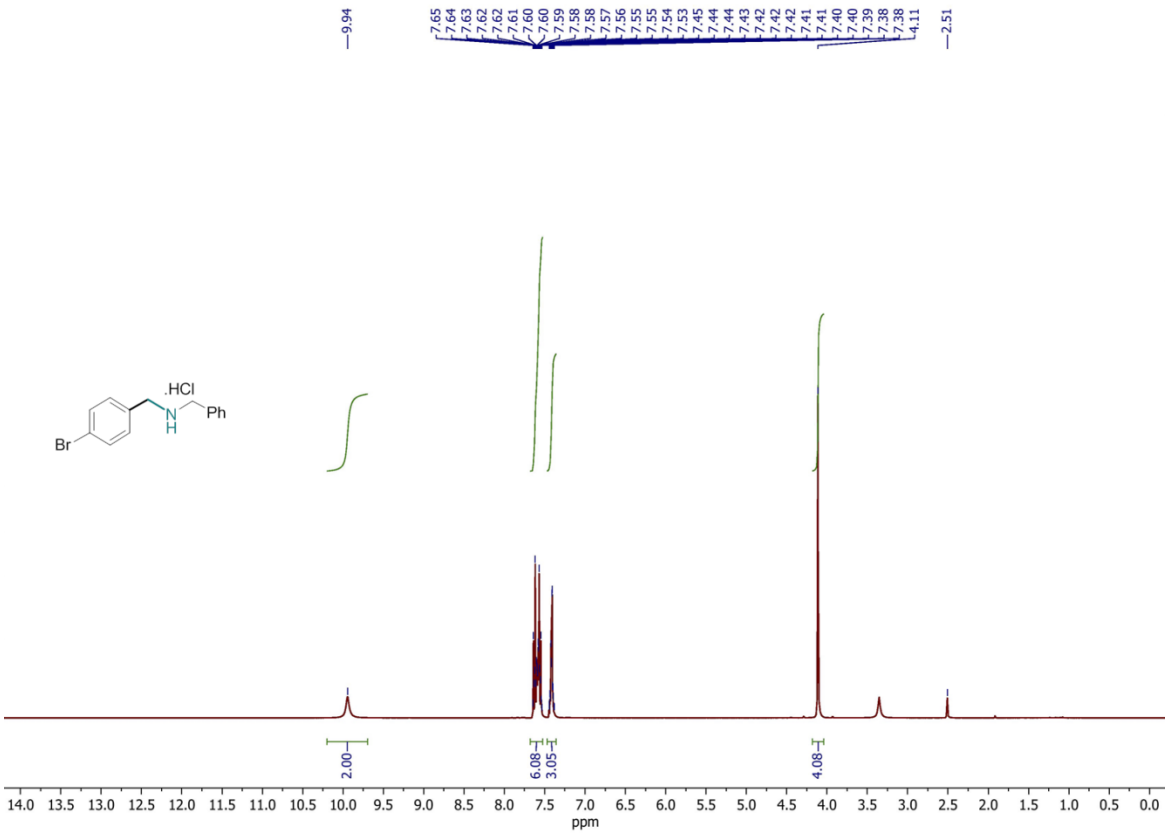

-113.00
.HCl
N
H
Ph
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

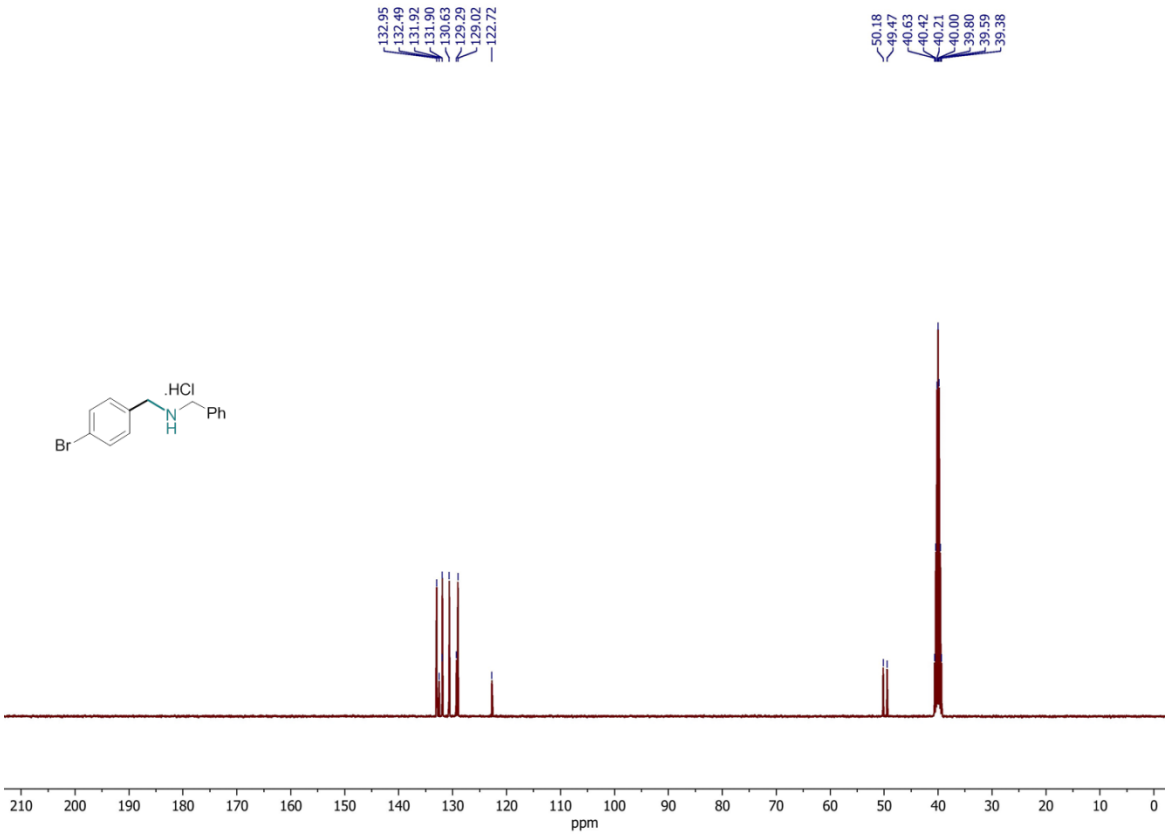
N-benzyl-1-(4-chlorophenyl)methanamine hydrochloride (**5h**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



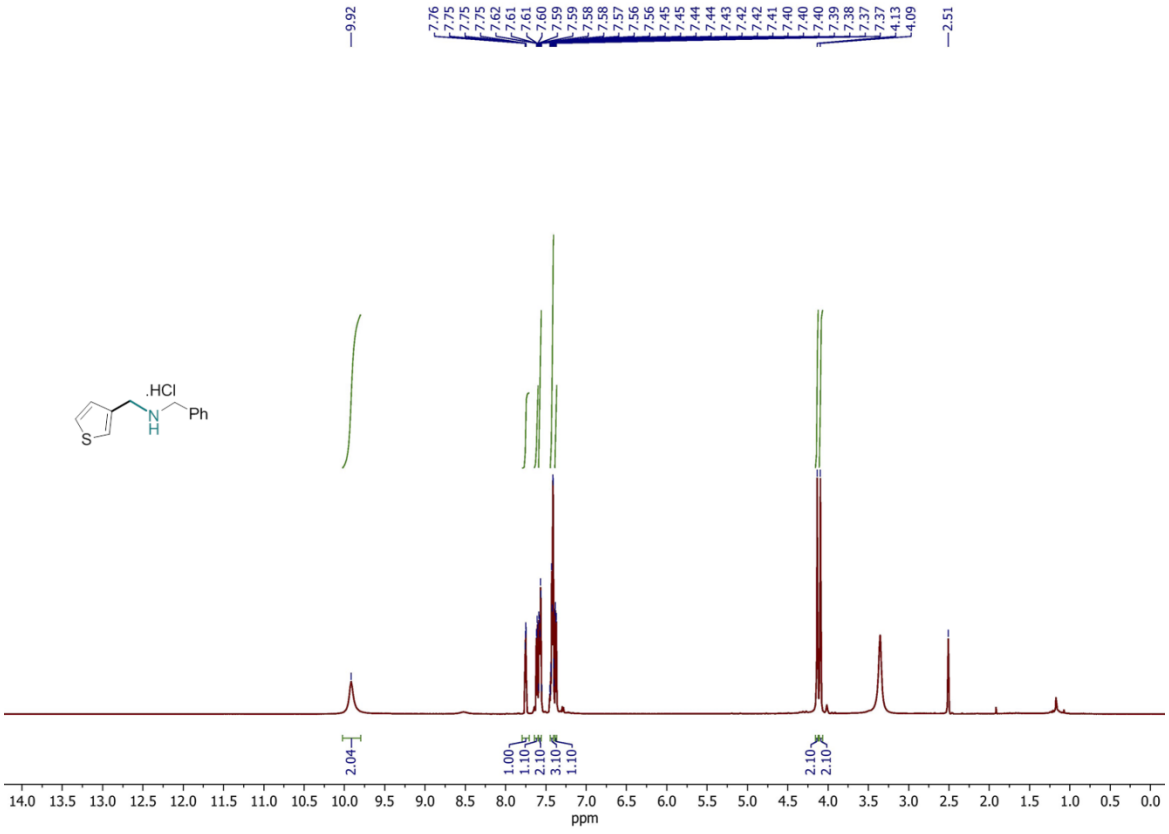


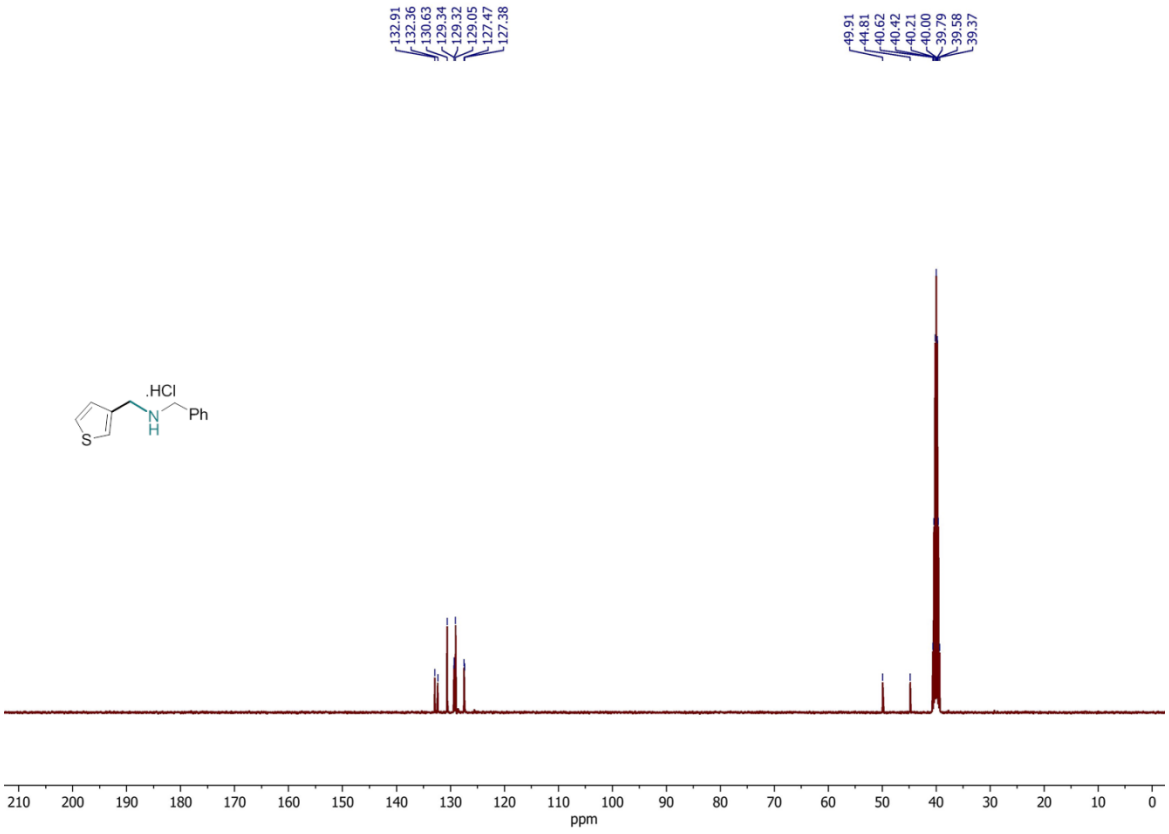
N-benzyl-1-(4-bromophenyl)methanamine hydrochloride (**5i**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



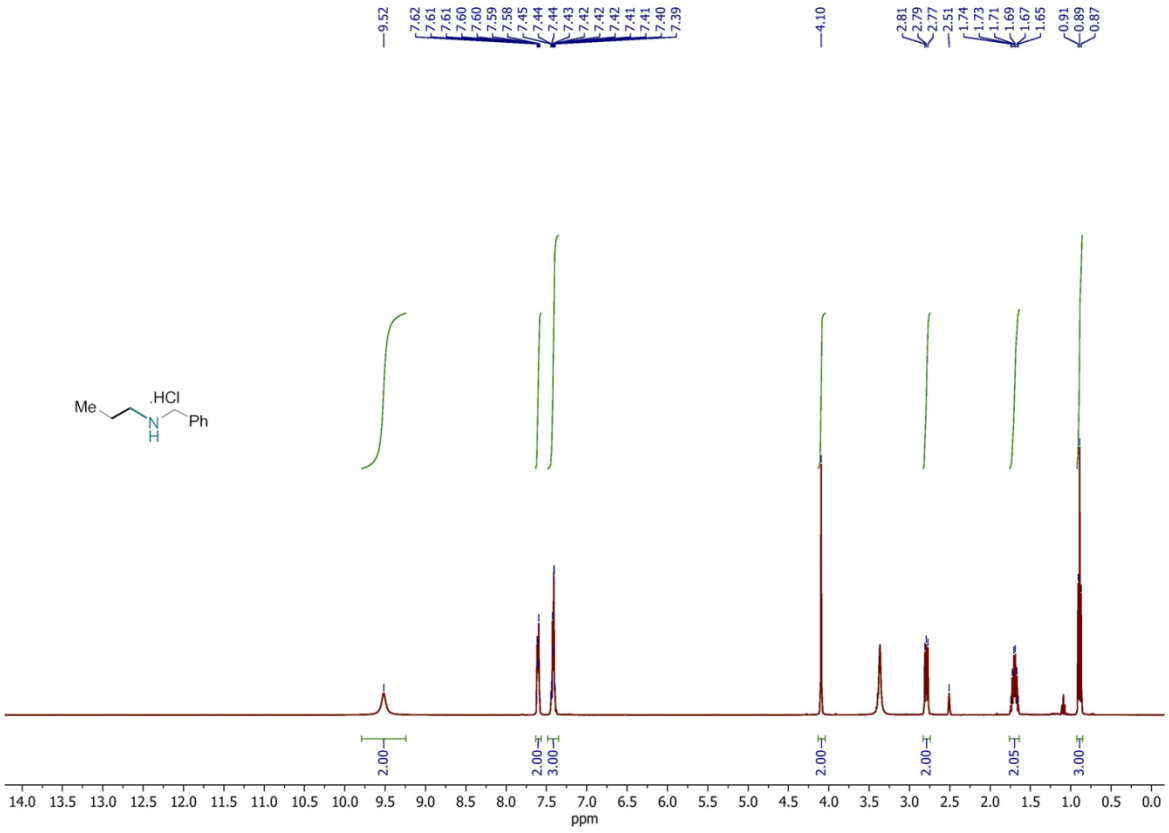


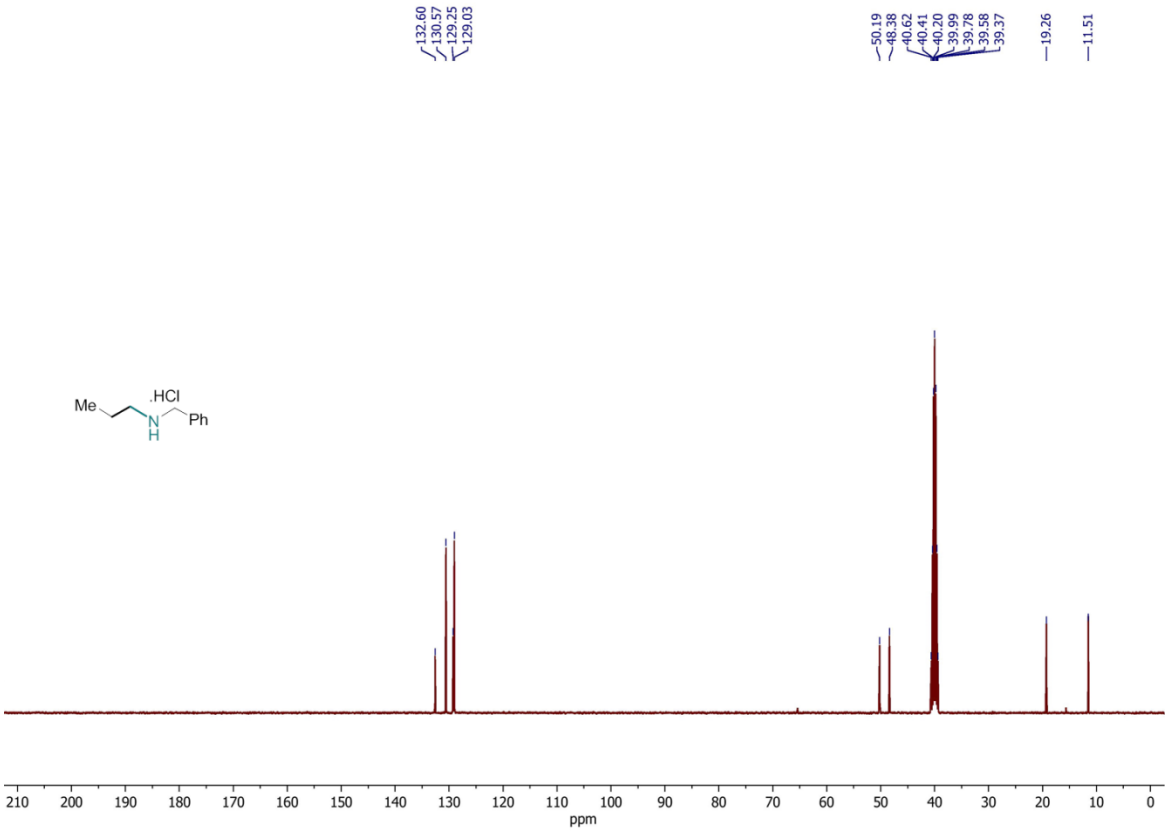
N-benzyl-1-(thiophen-3-yl)methanamine hydrochloride (**5j**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



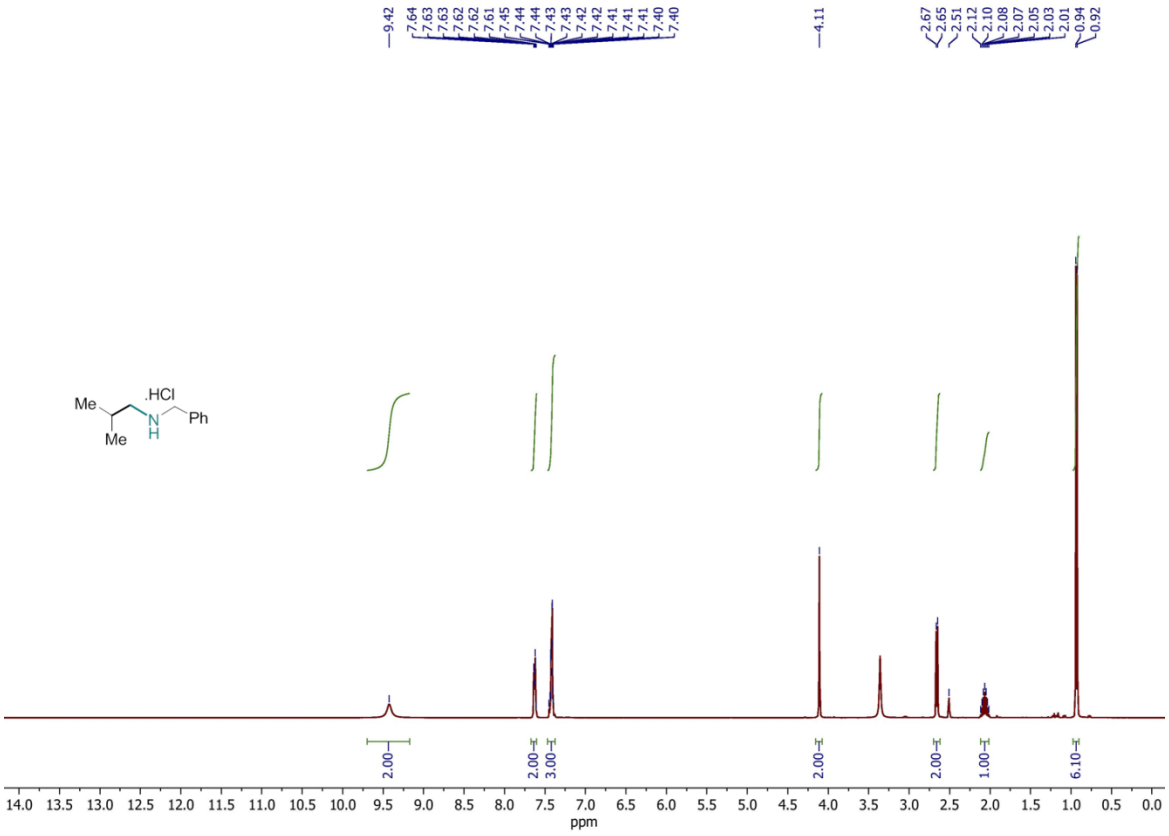


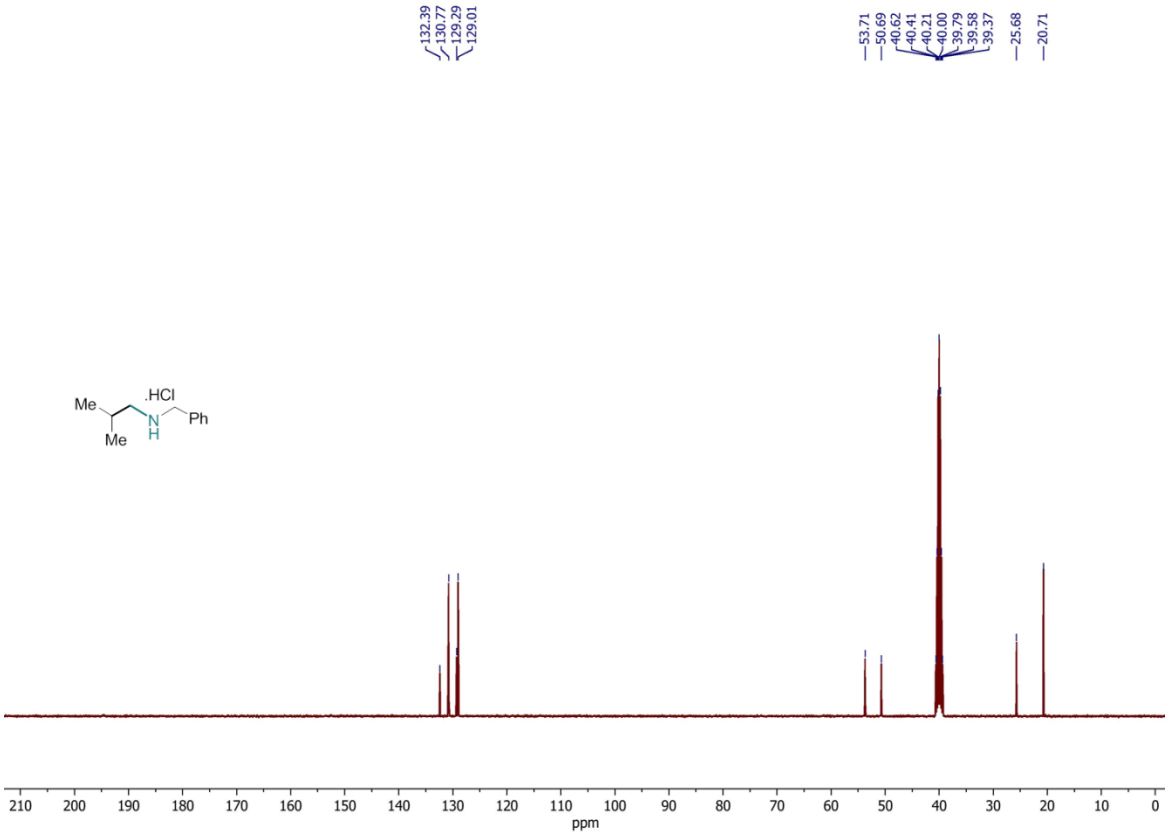
N-benzylpropan-1-amine hydrochloride (**5k**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



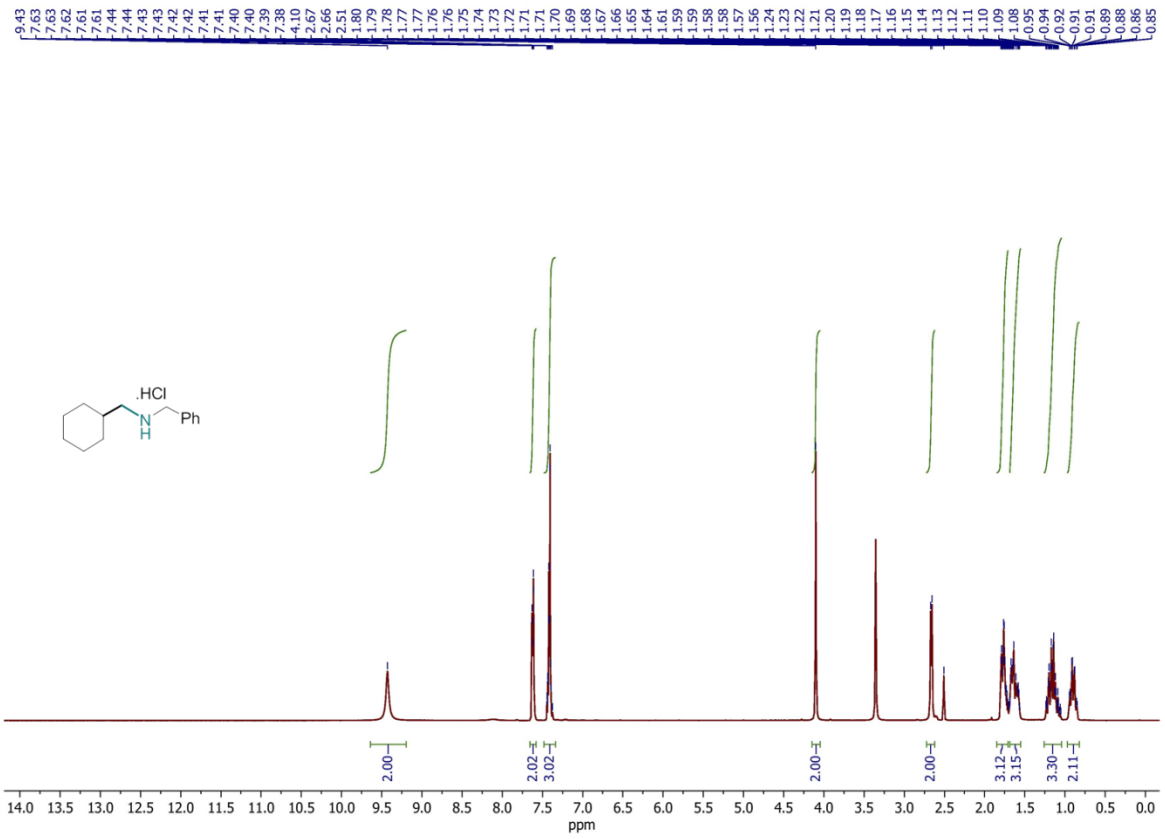


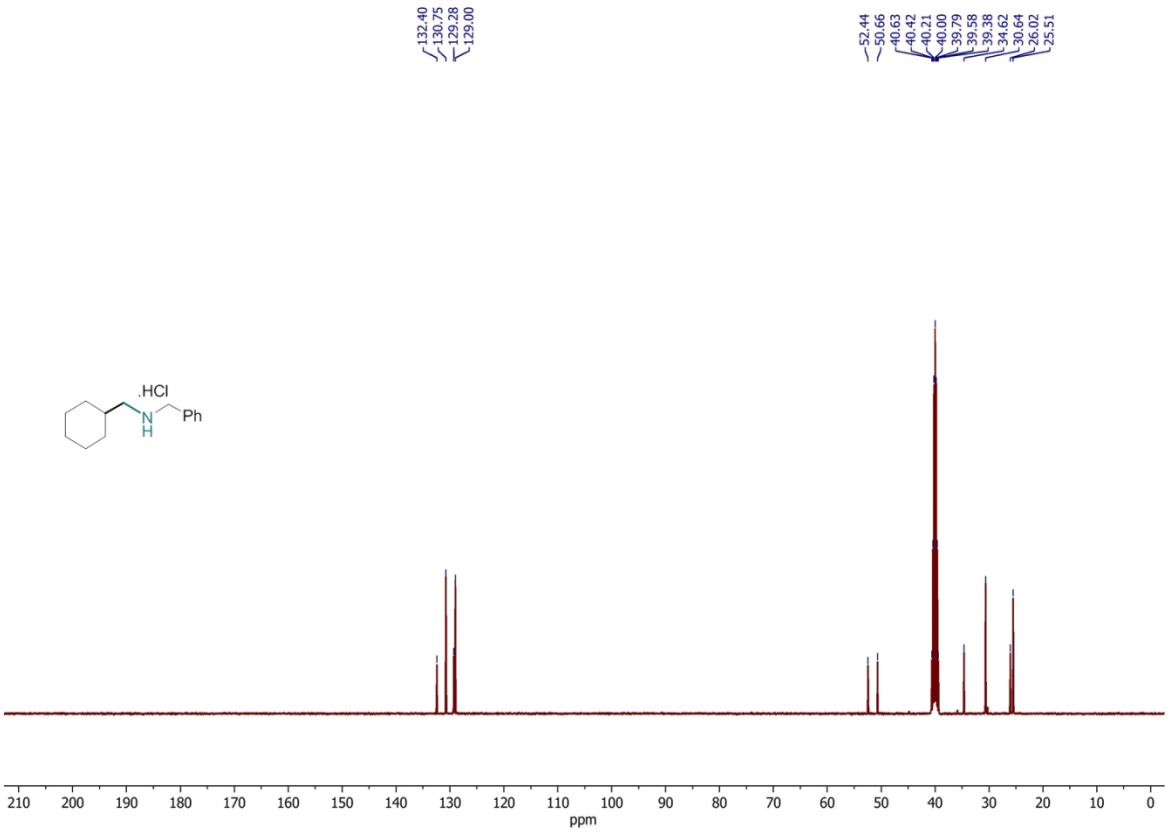
N-benzyl-2-methylpropan-1-amine hydrochloride (**5l**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



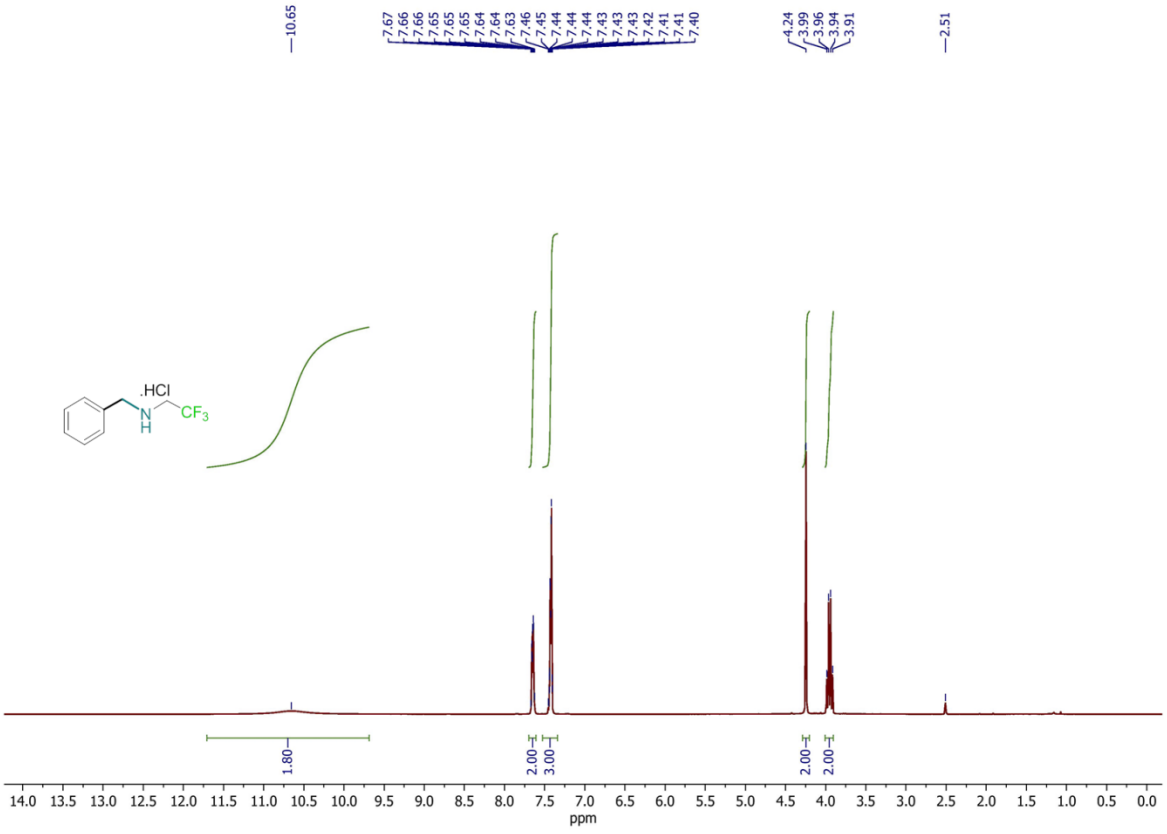


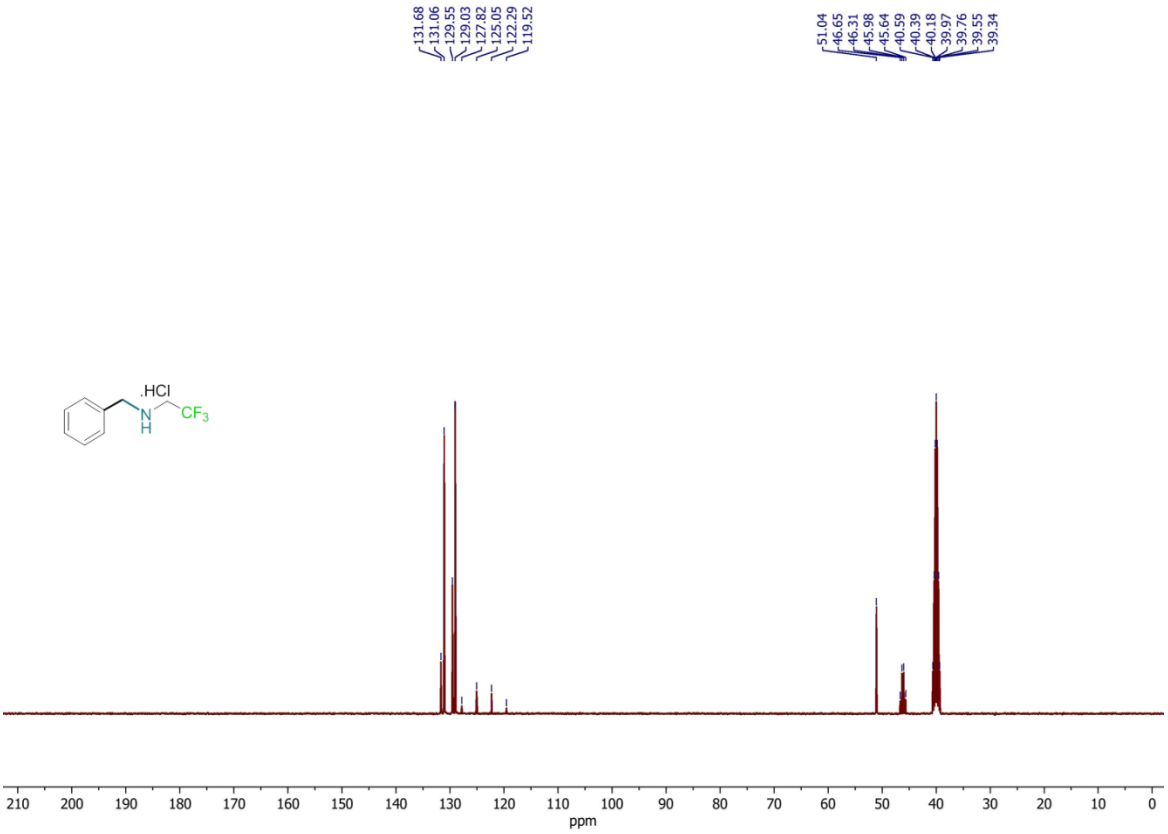
N-benzyl-1-cyclohexylmethanamine hydrochloride (**5m**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6).**

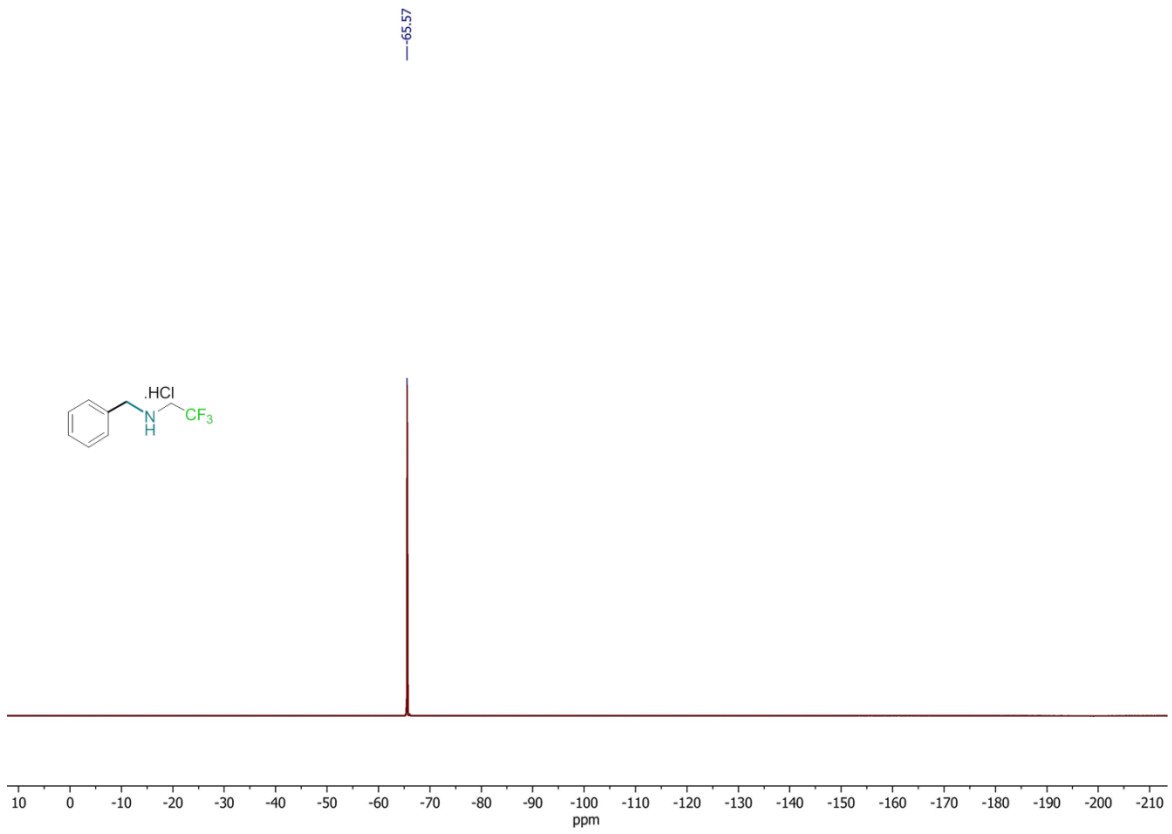




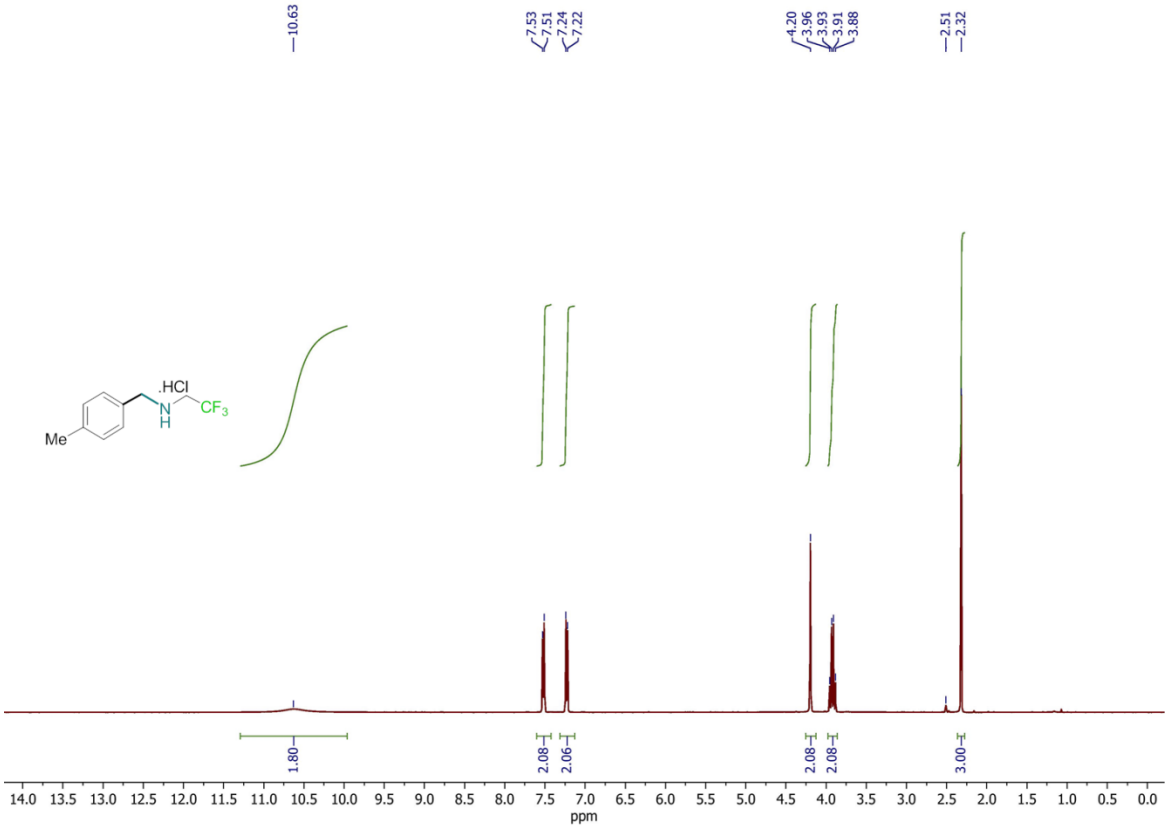
N-benzyl-2,2,2-trifluoroethanamine hydrochloride (**5n**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

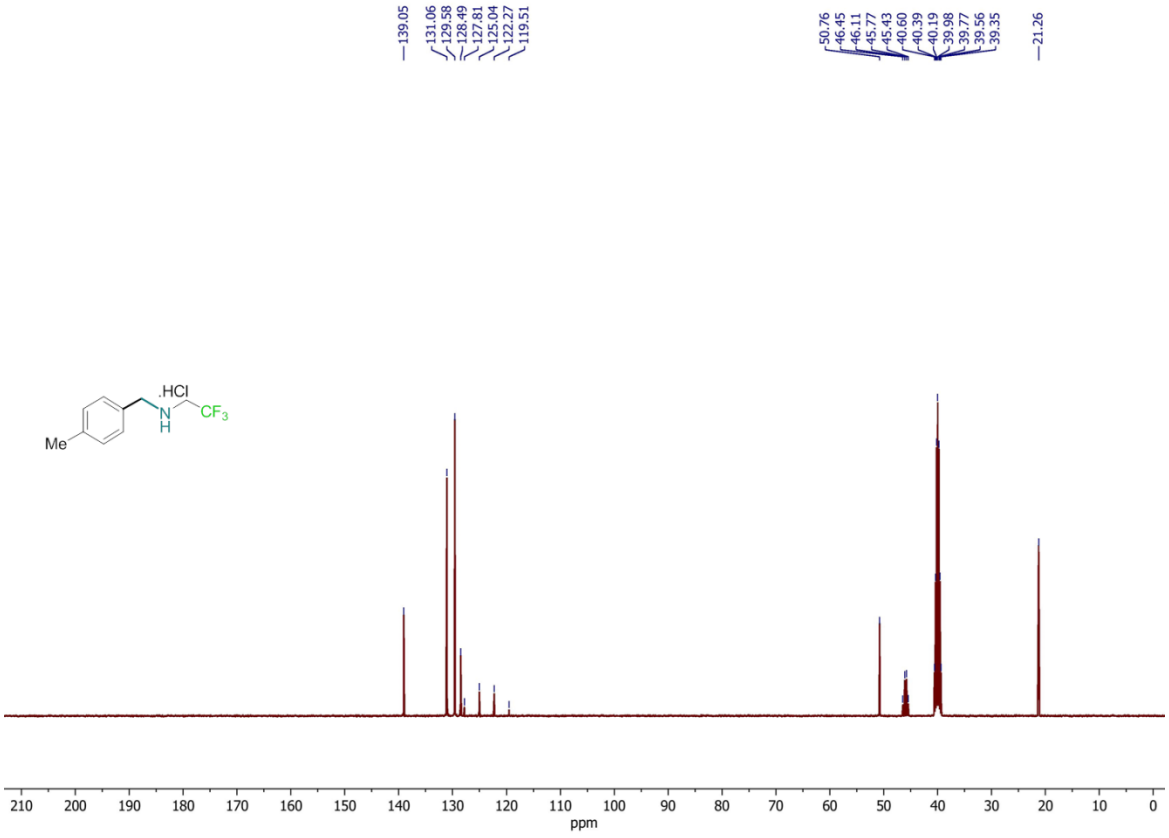


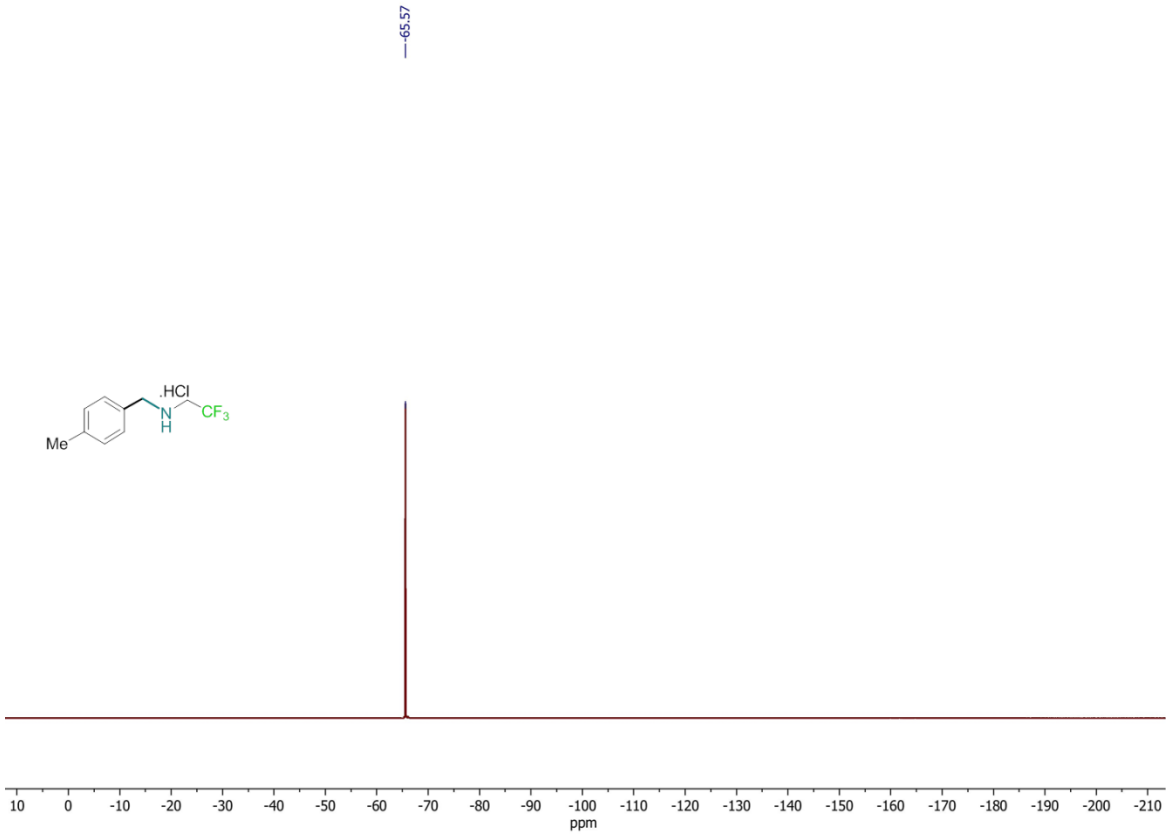



-65.57
.HCl
N
H
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

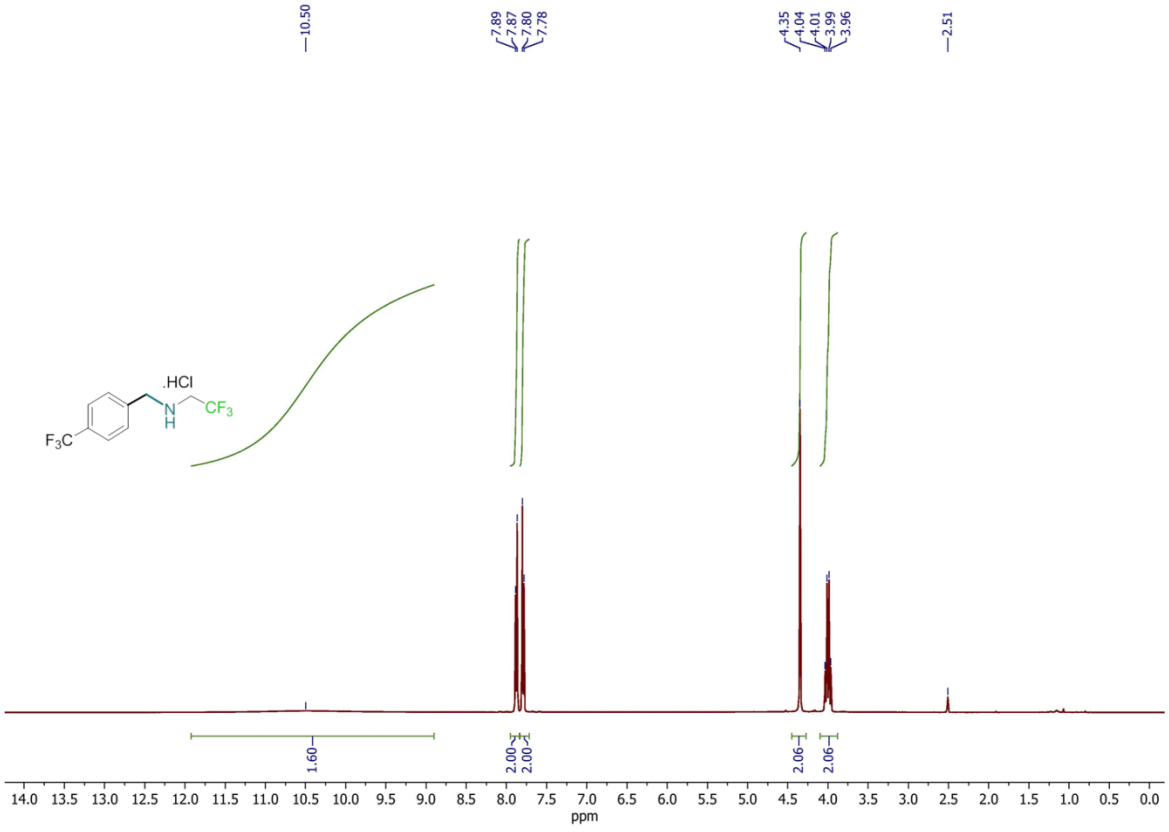
2,2,2-trifluoro-*N*-(4-methylbenzyl)ethanamine hydrochloride (**5o**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

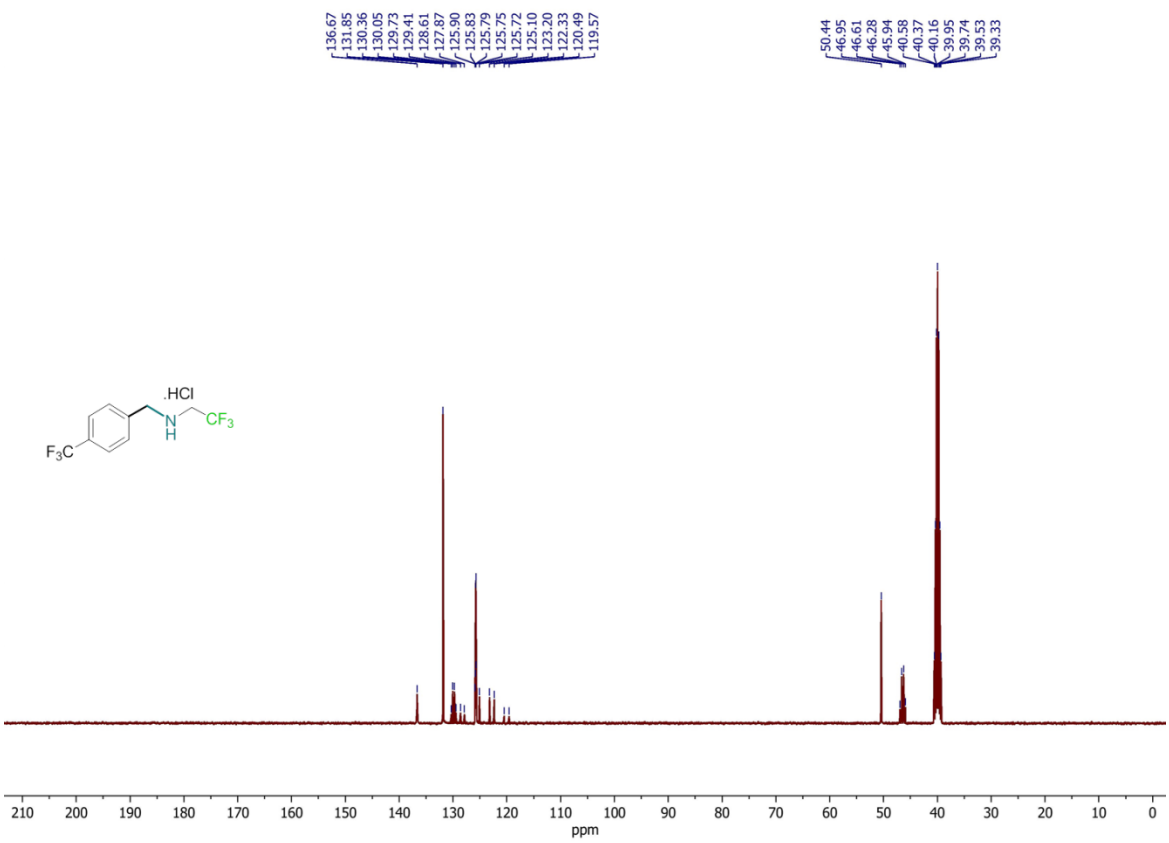


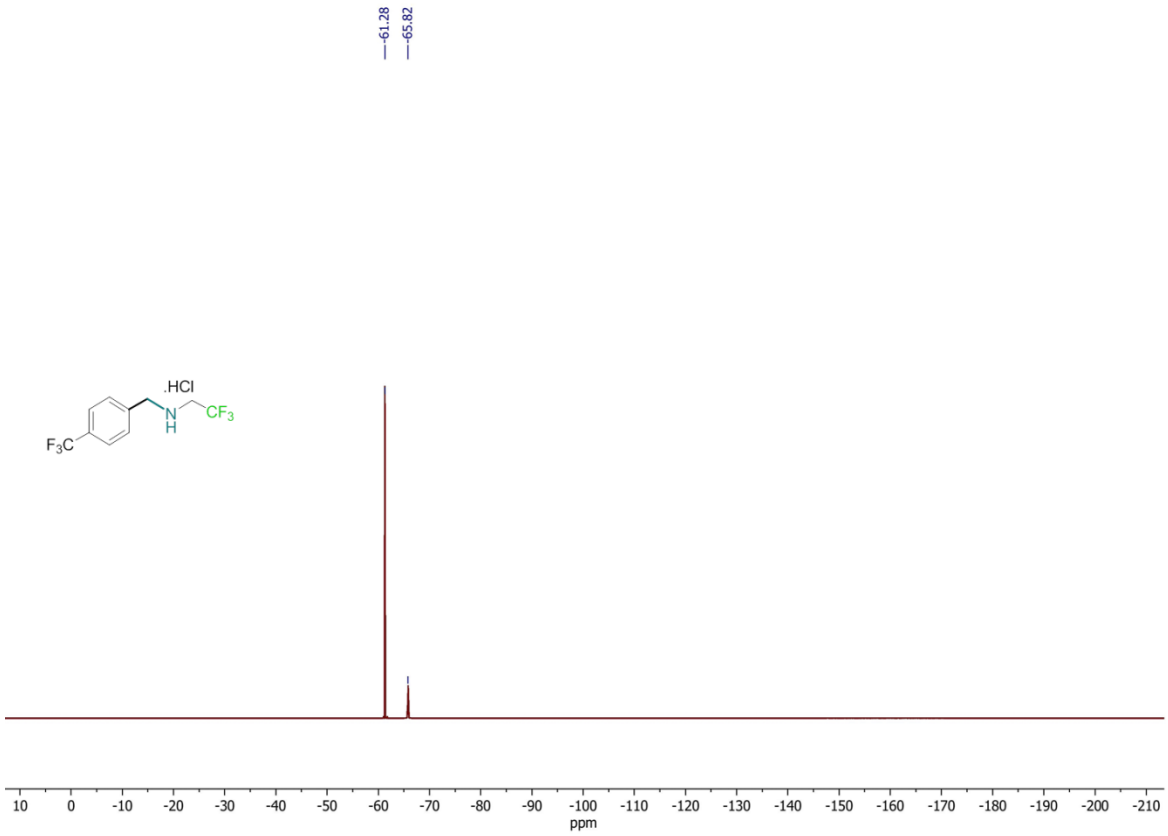



-65.57
.HCl
N
H
CF3
Me
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

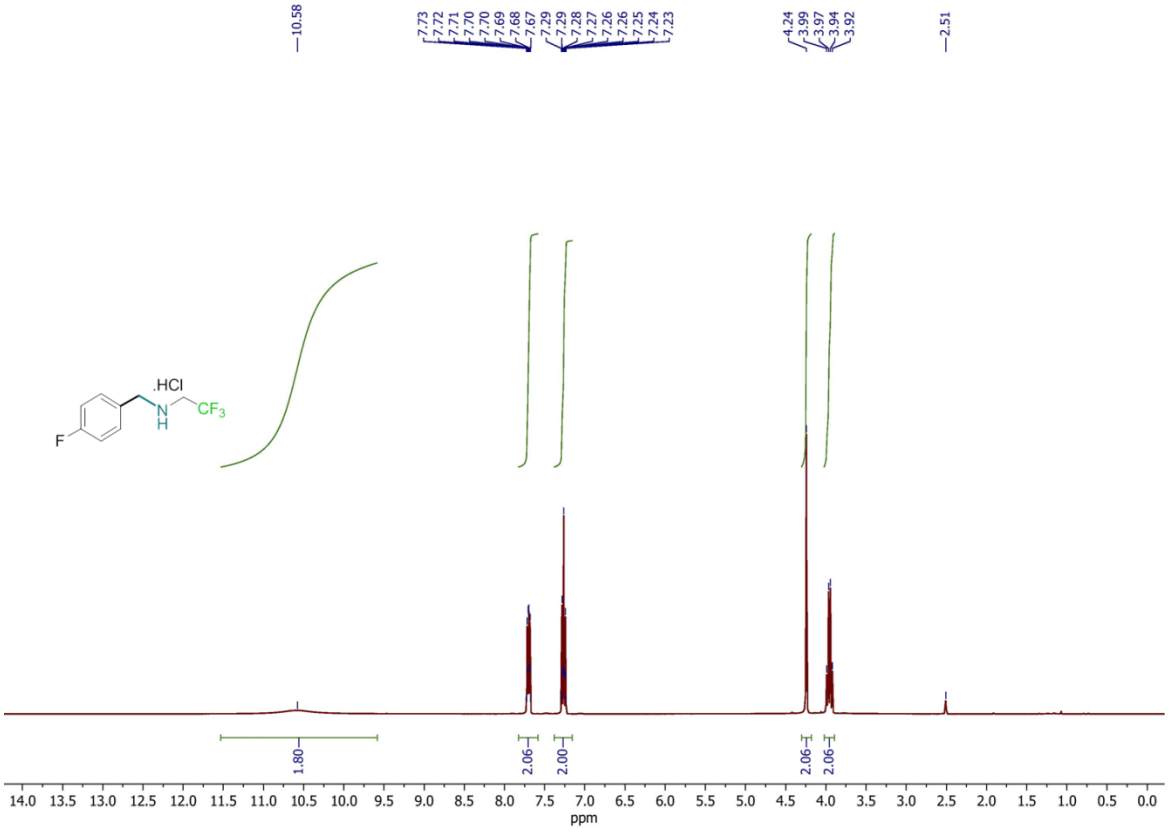
2,2,2-trifluoro-*N*-(4-(trifluoromethyl)benzyl)ethanamine hydrochloride (**5p**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6), ^{19}F NMR (376 MHz, DMSO-d_6).**

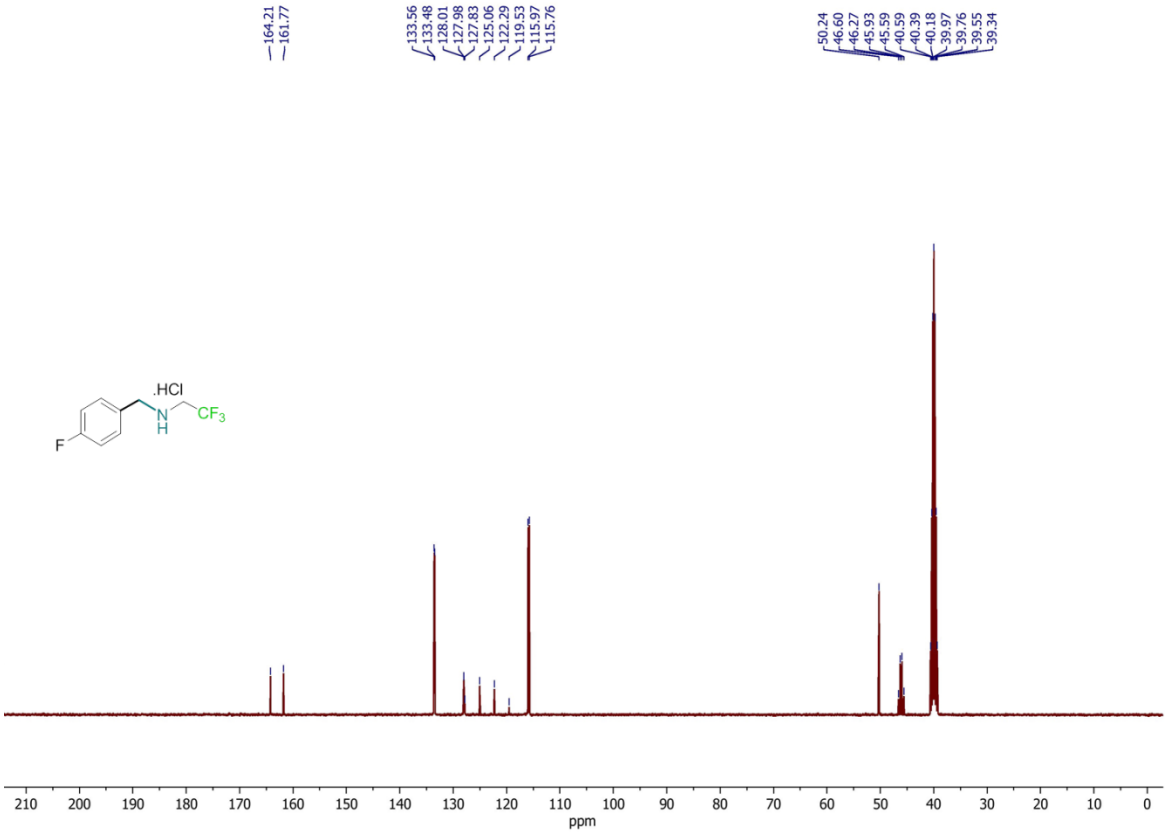


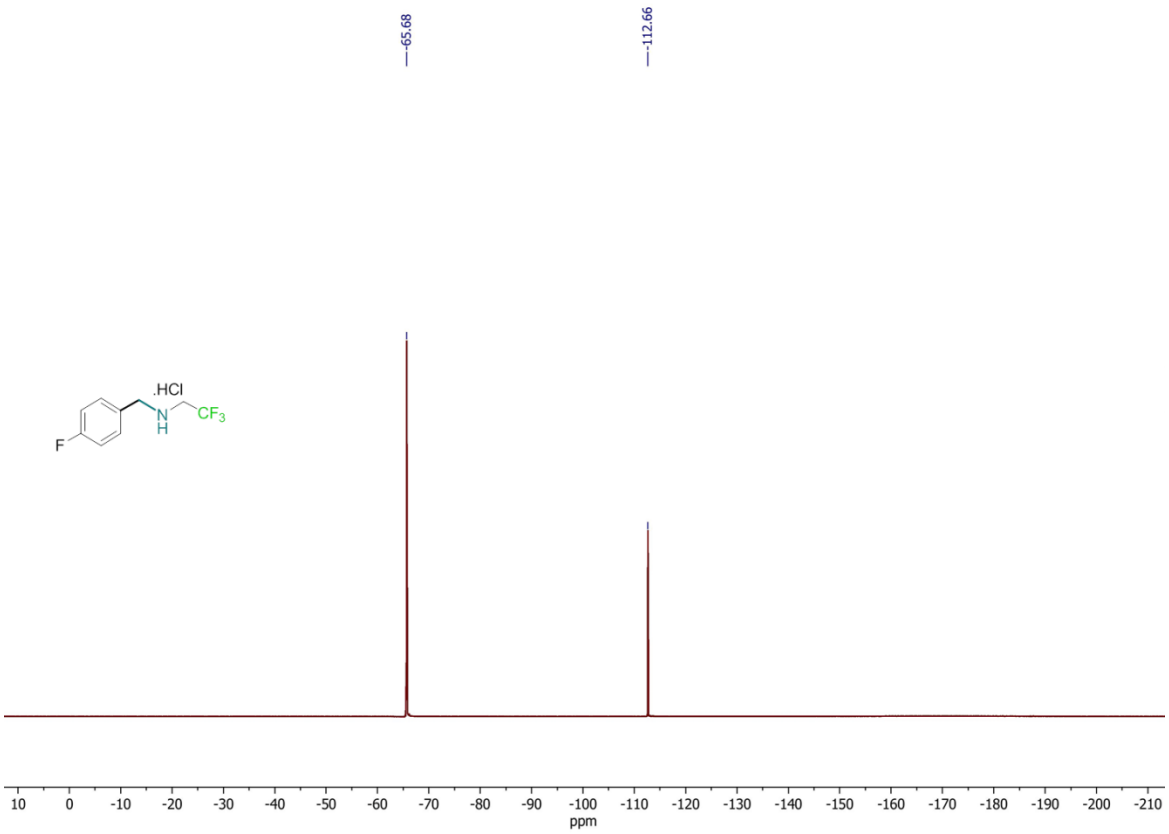



-61.28
-65.82
.HCl
N
H
CF3
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

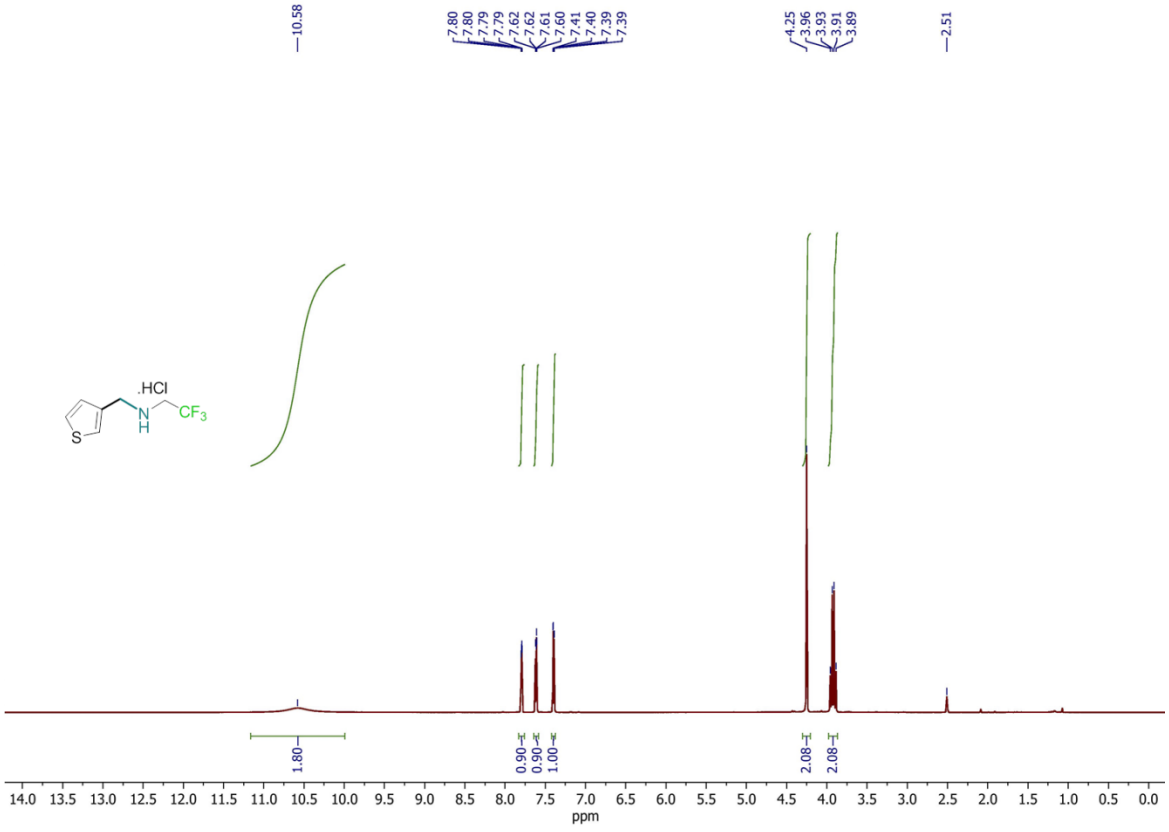
2,2,2-trifluoro-*N*-(4-fluorobenzyl)ethanamine hydrochloride (**5q**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

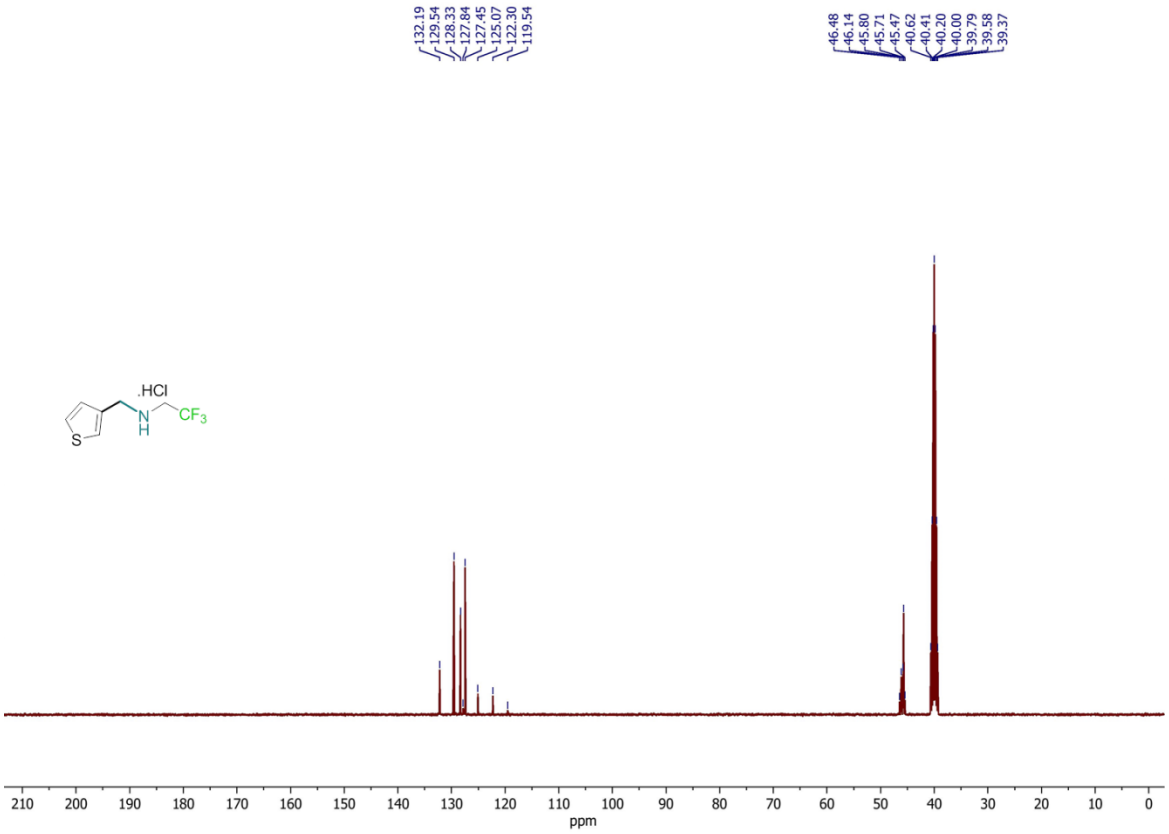


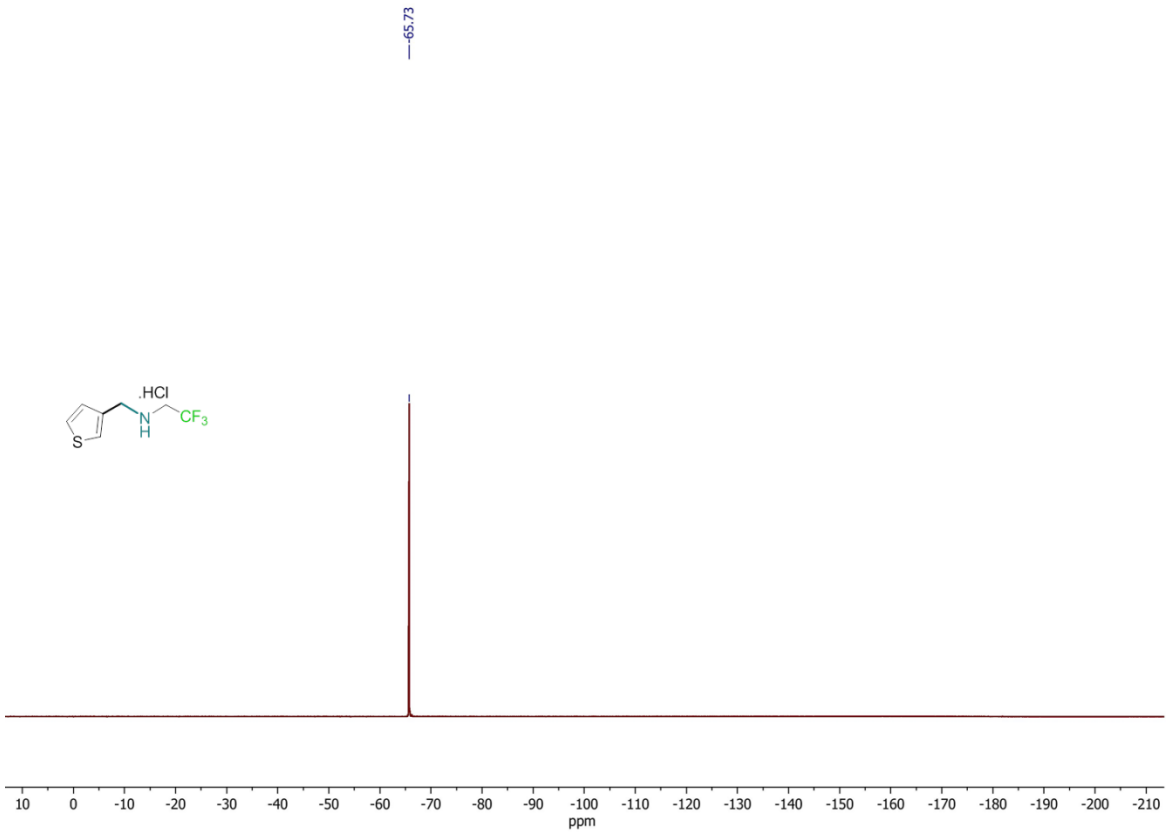



-65.68
-112.66
.HCl
N
H
CF3
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

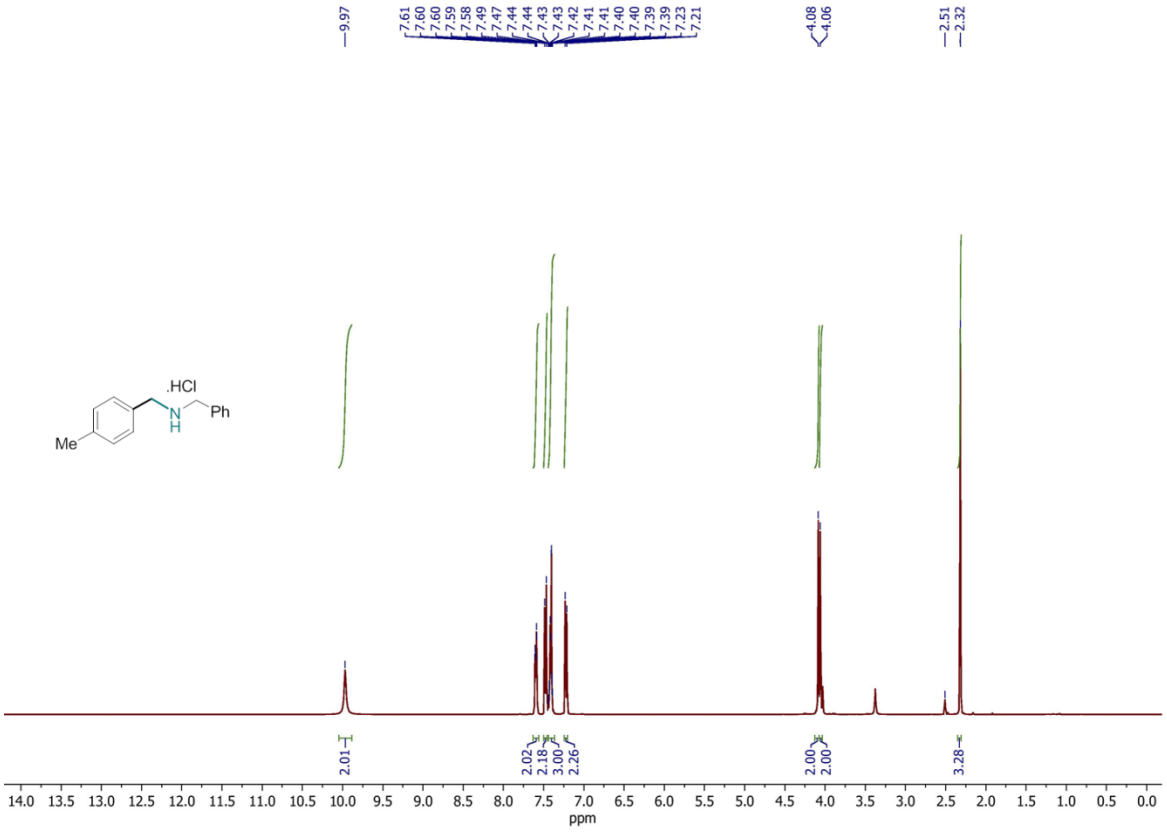
2,2,2-trifluoro-*N*-(thiophen-3-ylmethyl)ethanamine hydrochloride (**5s**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

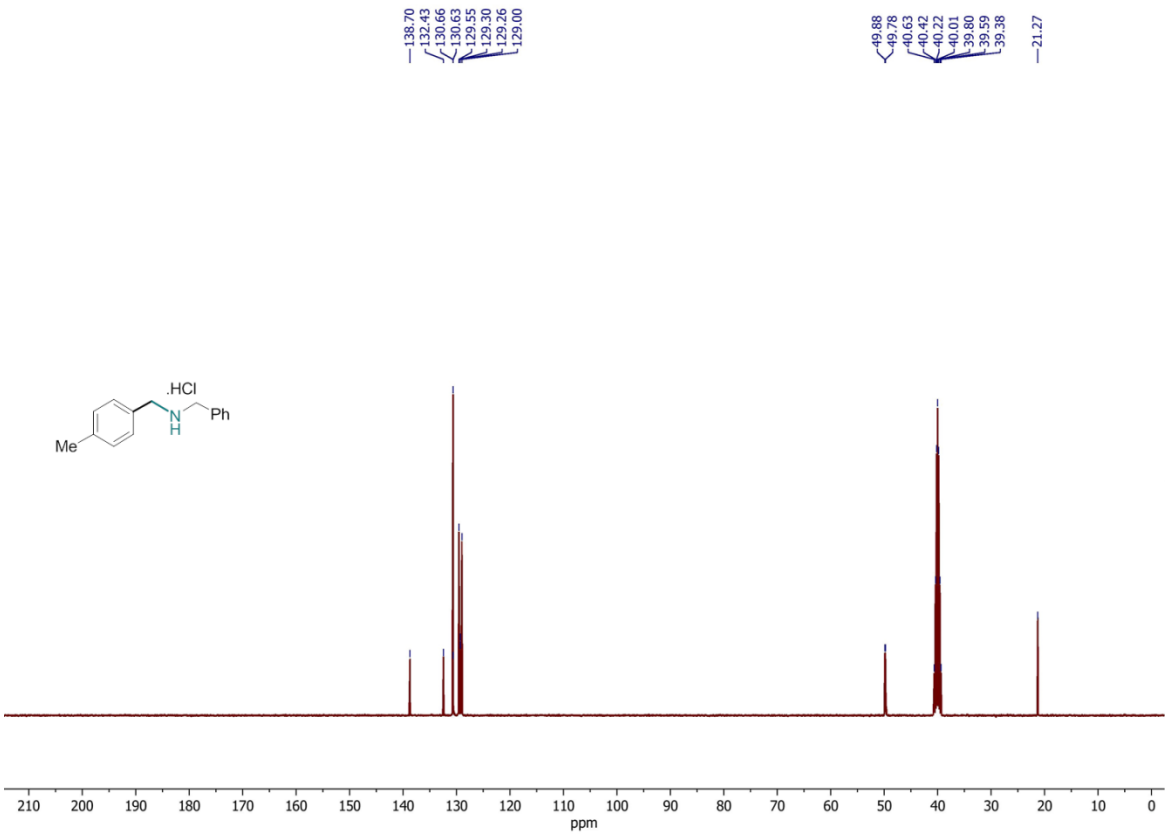




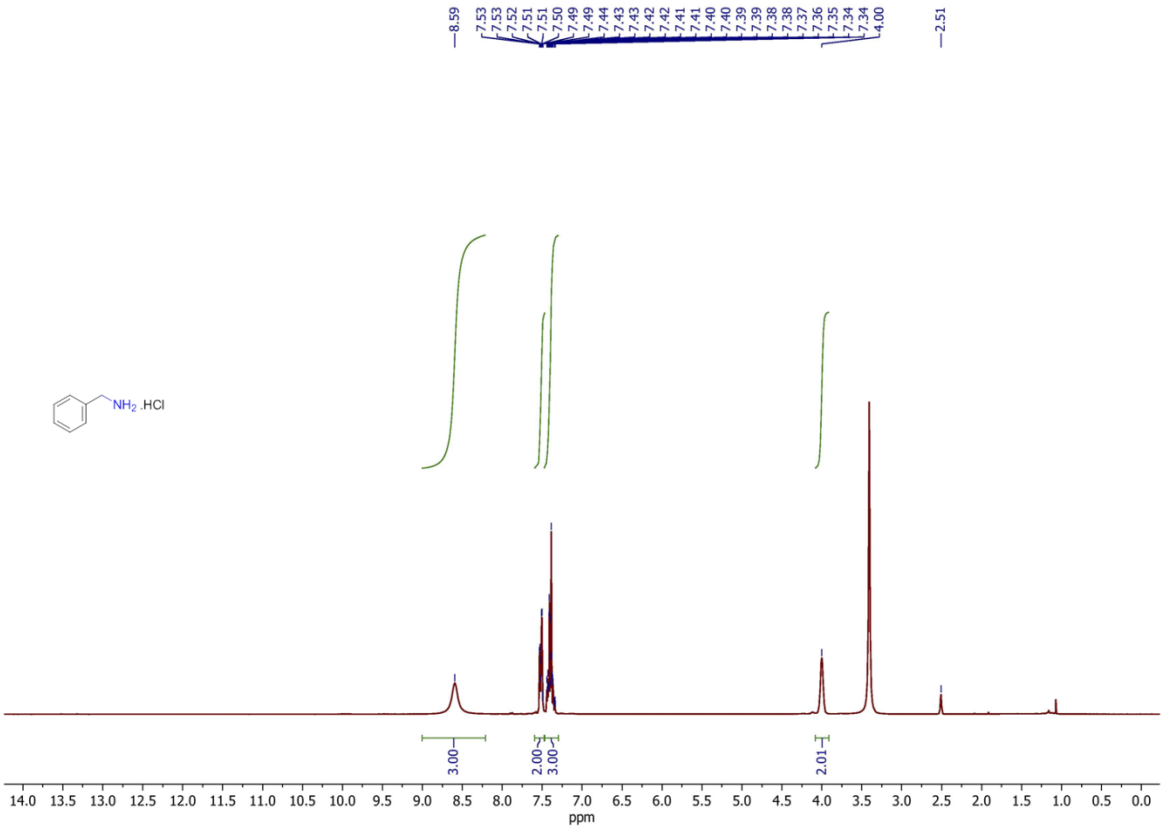

-65.73
.HCl
N
H
CF3
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

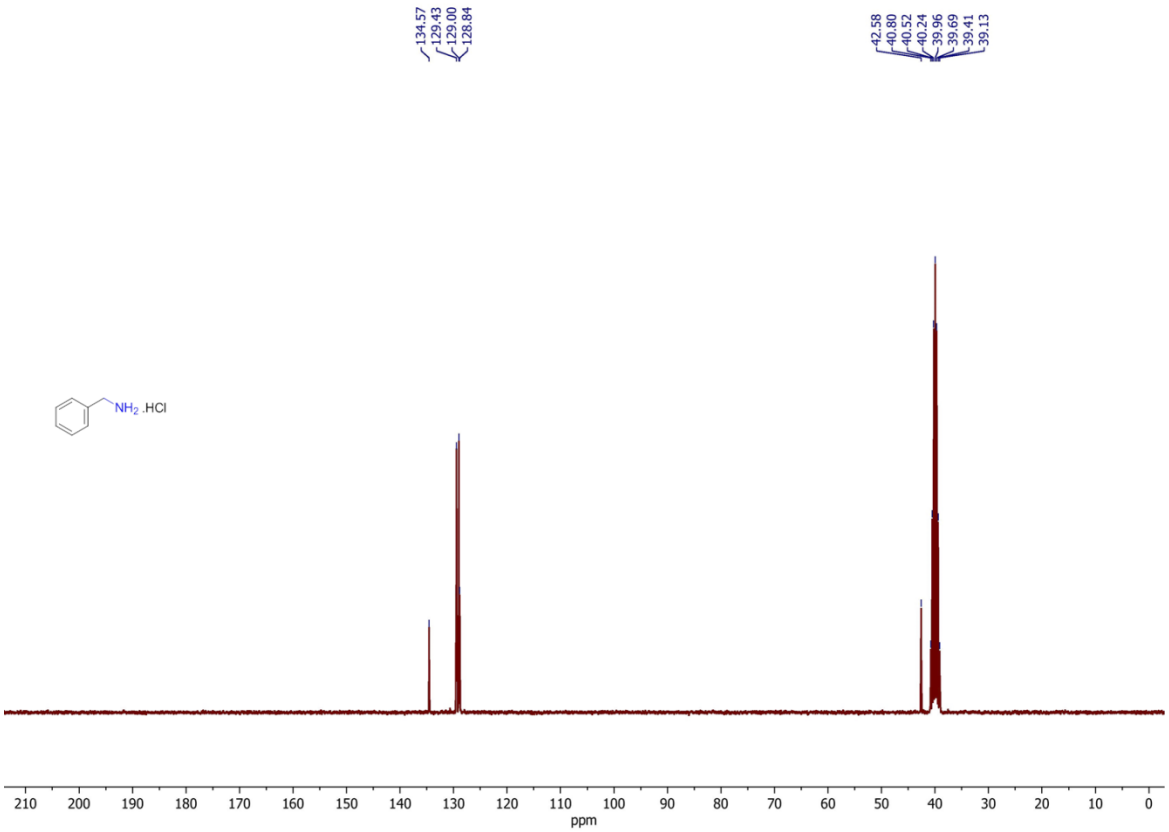
N-benzyl-1-*p*-tolylmethanamine hydrochloride (**5t**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



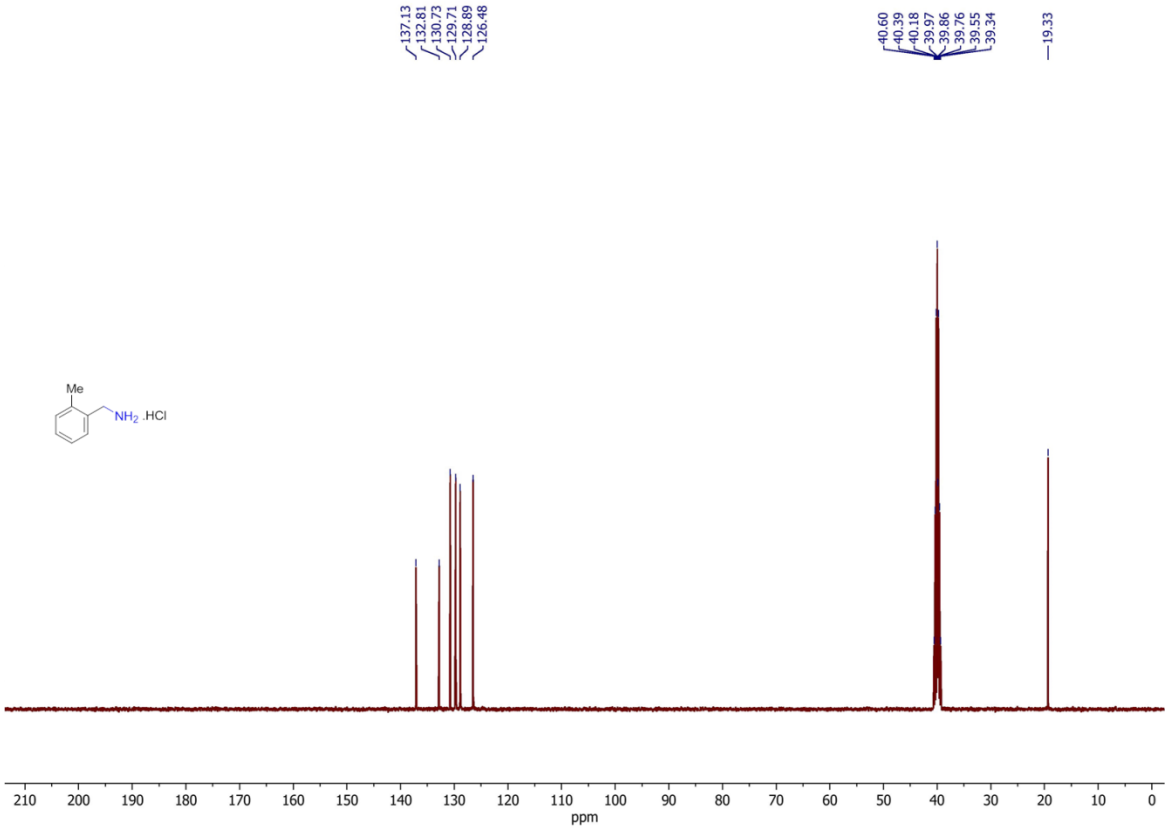


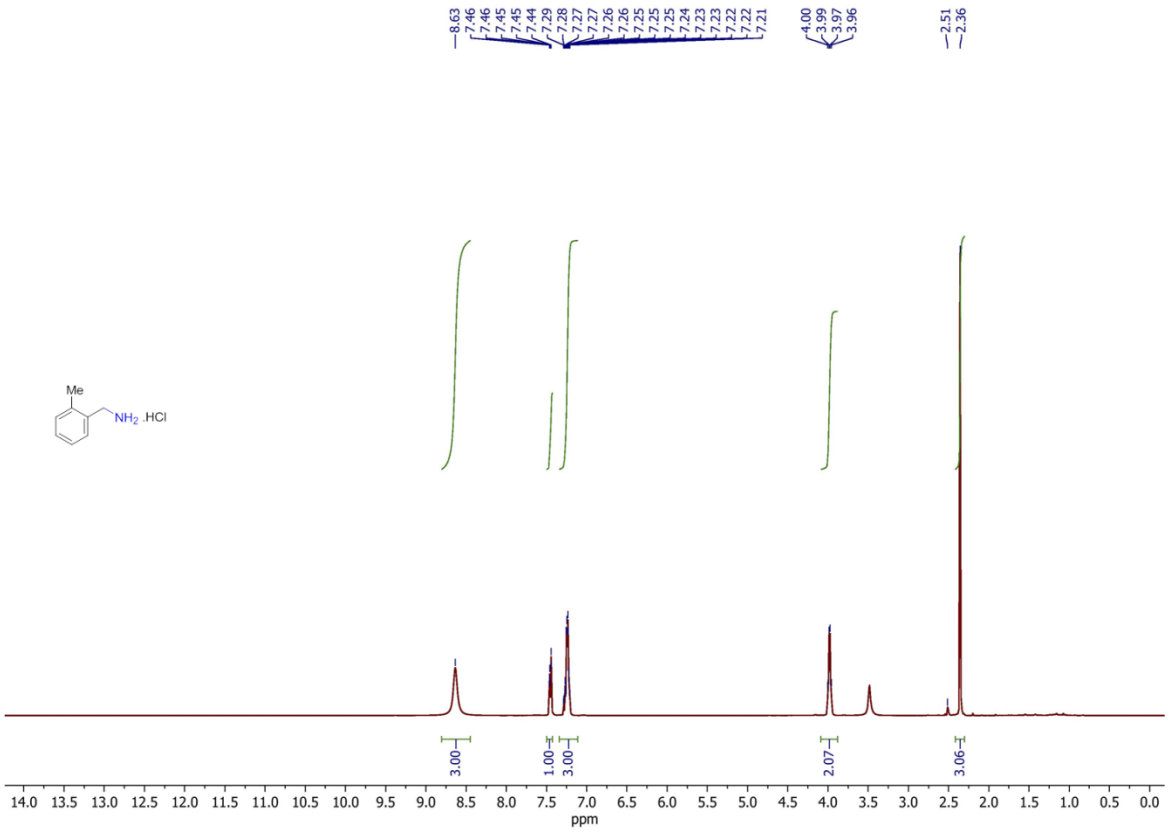
phenylmethanamine hydrochloride (**7a**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



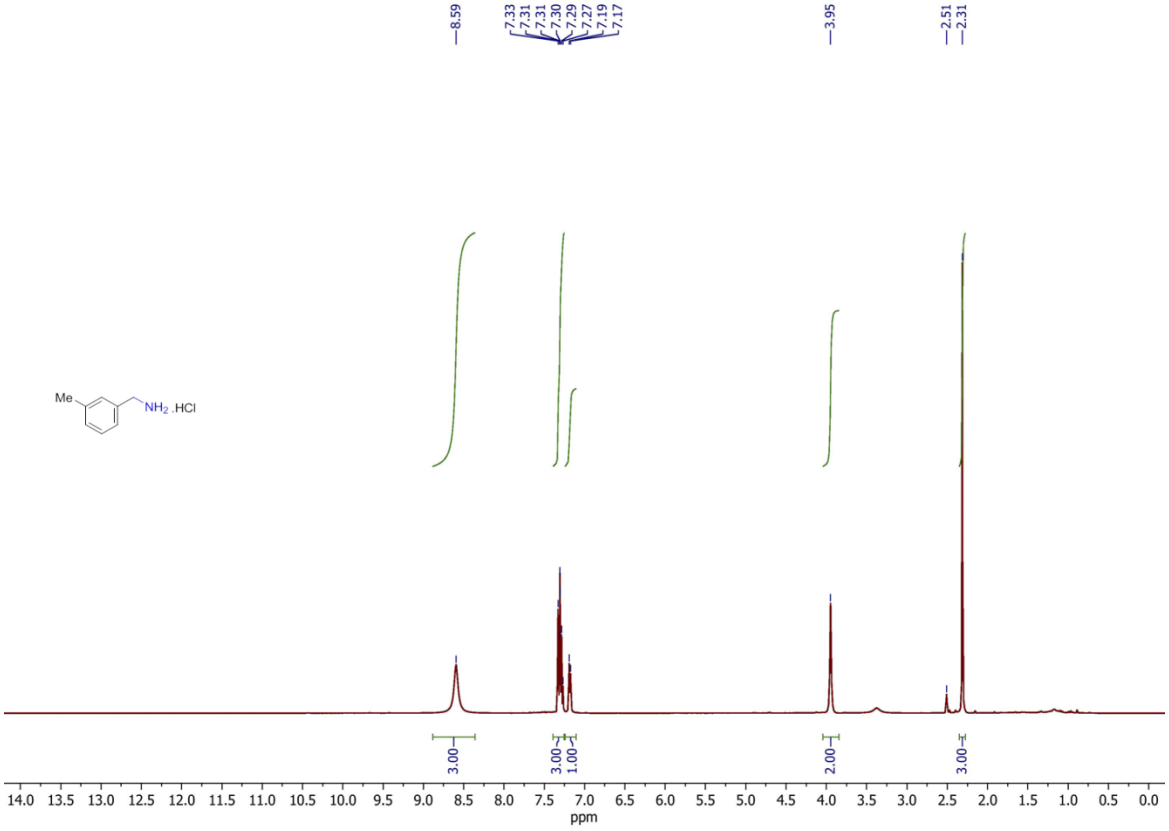


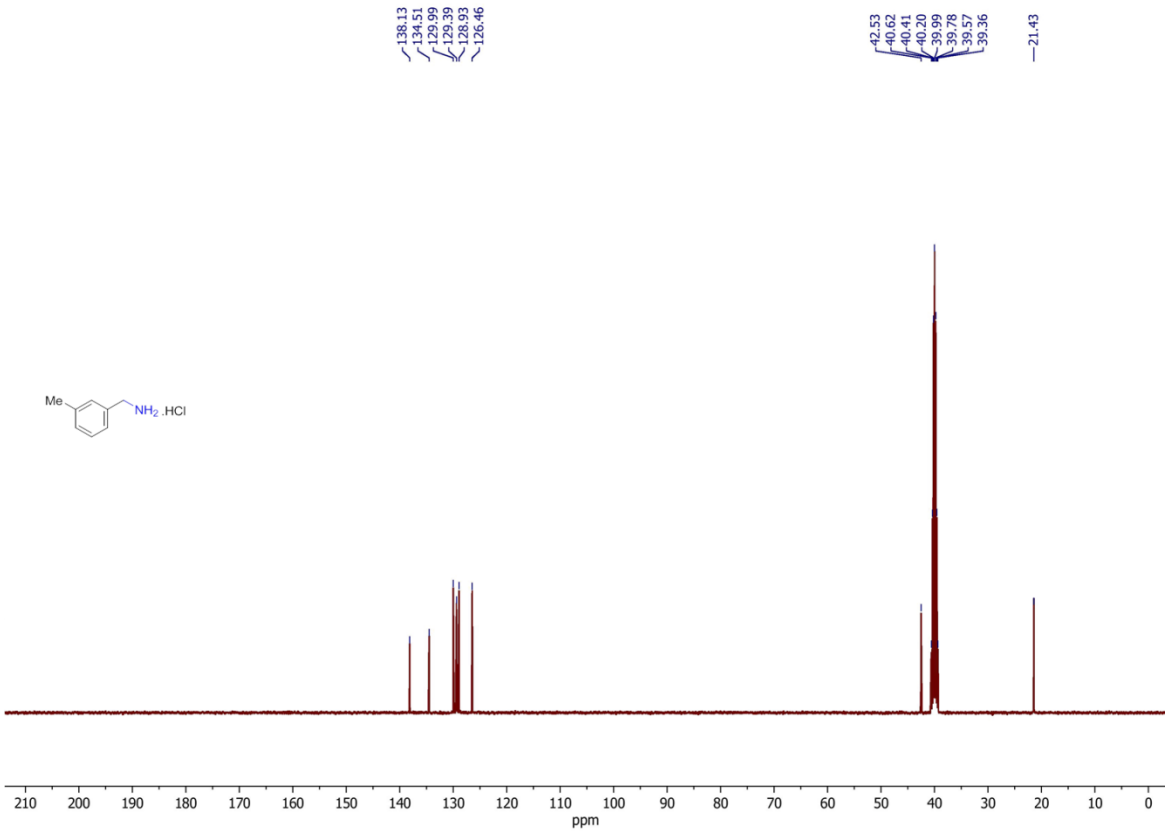
o-tolylmethanamine hydrochloride (**7b**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6).**



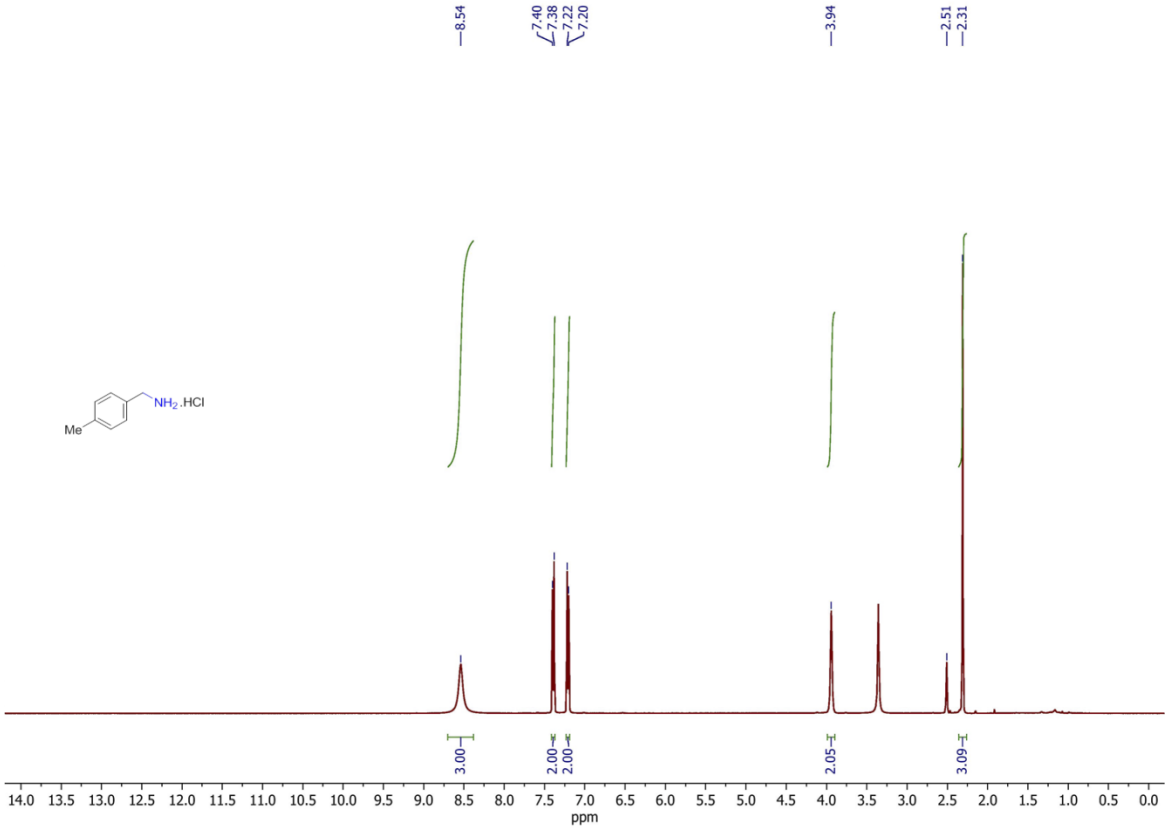


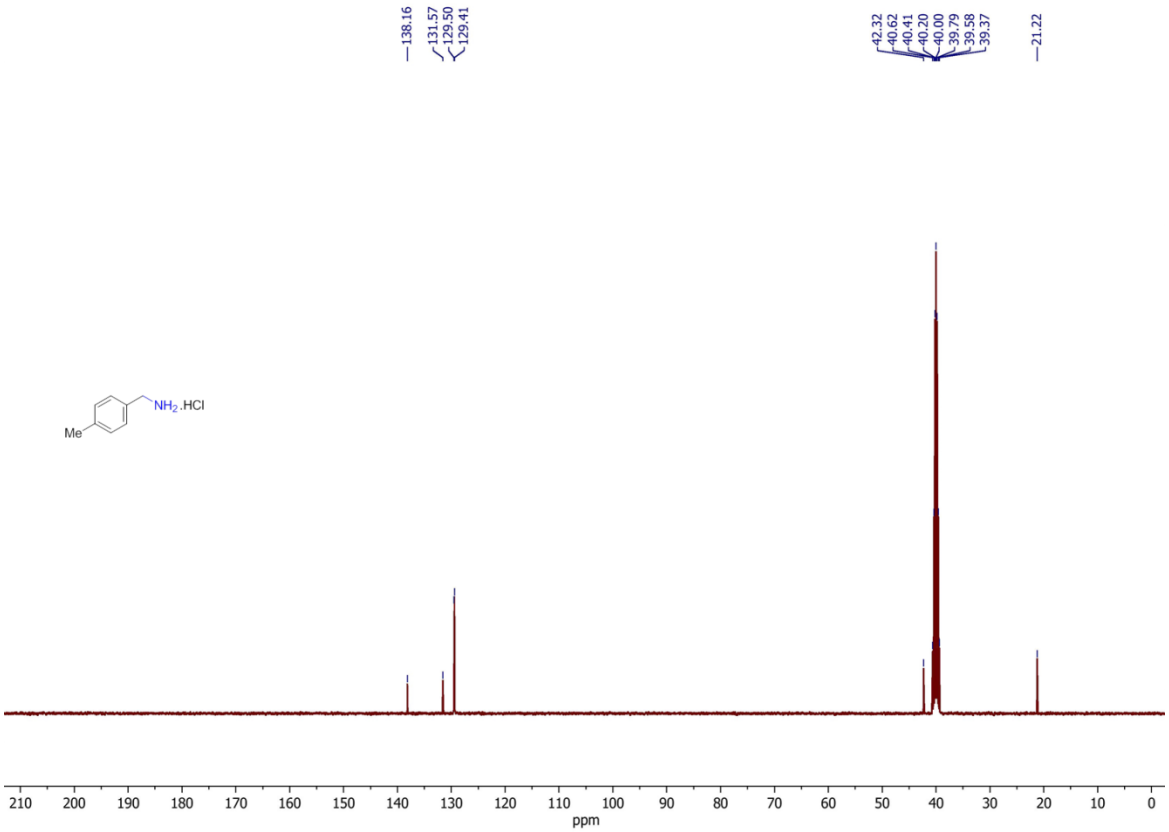
m-tolylmethanamine hydrochloride (**7c**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6).**



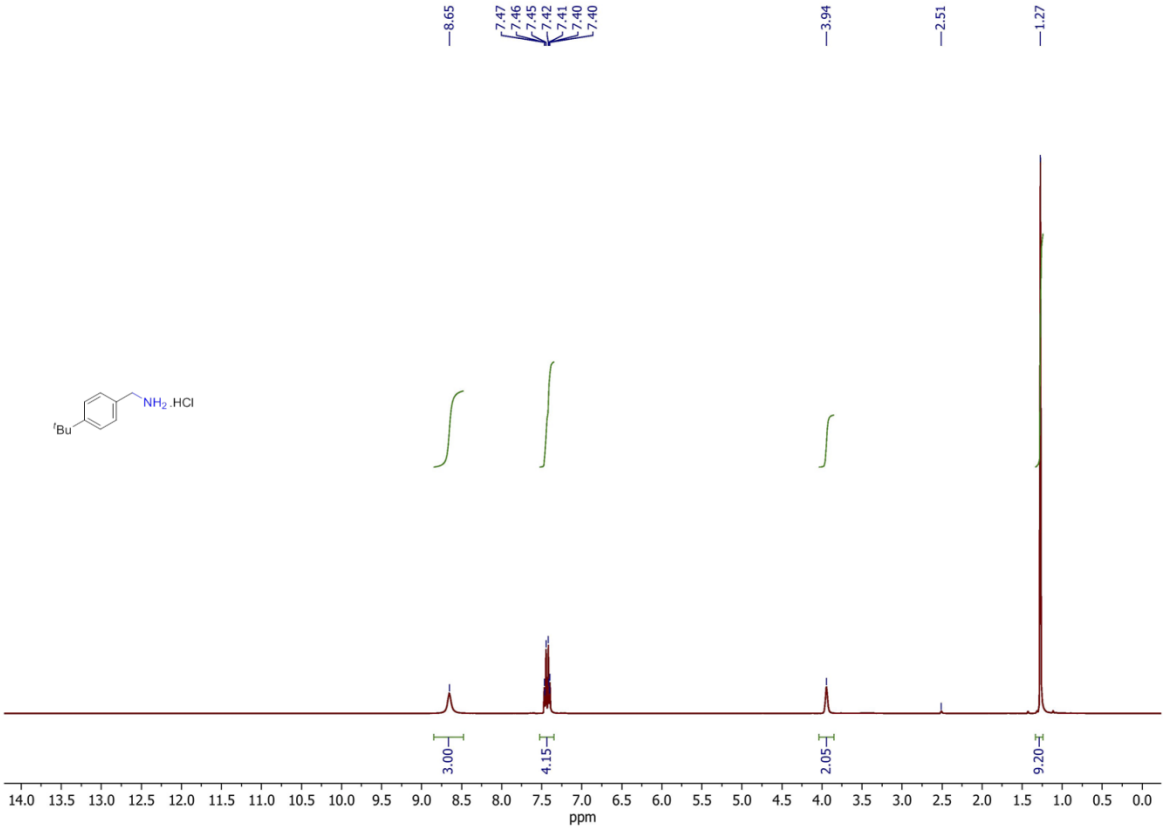


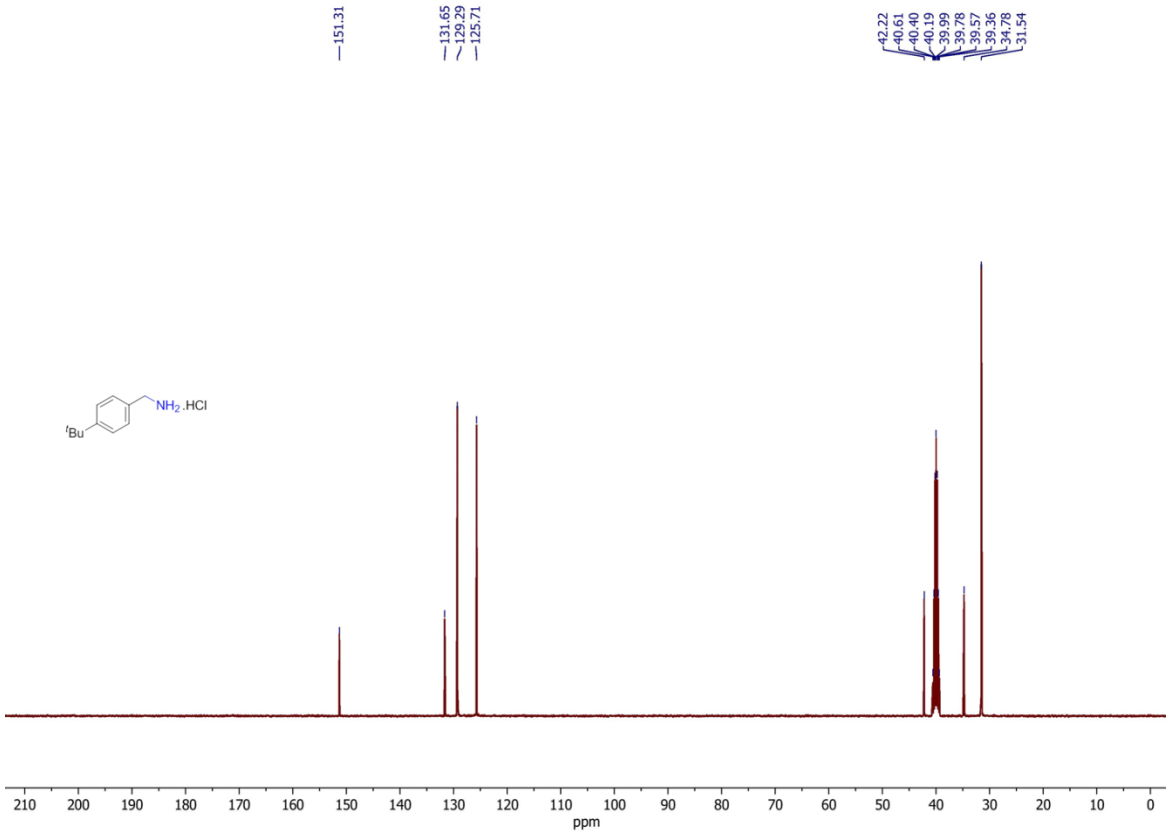
p-tolylmethanamine hydrochloride (**7d**); **^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6).**



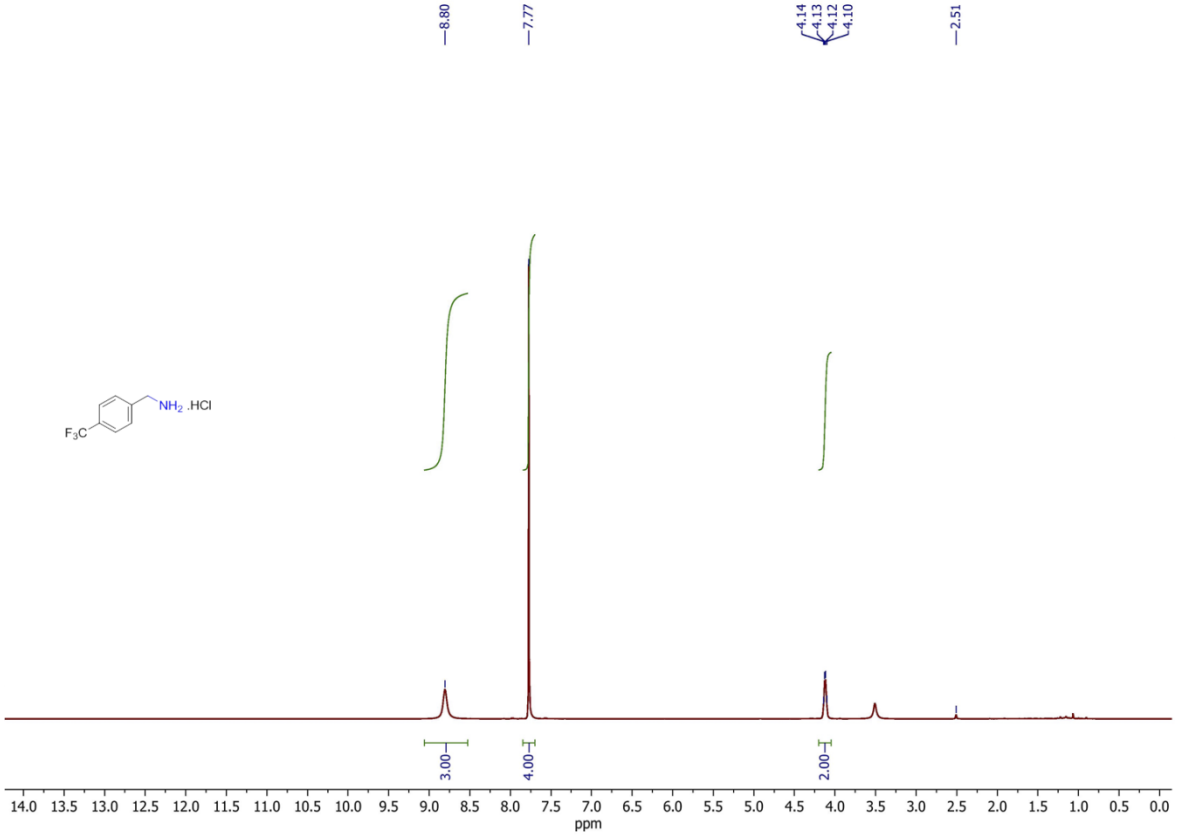


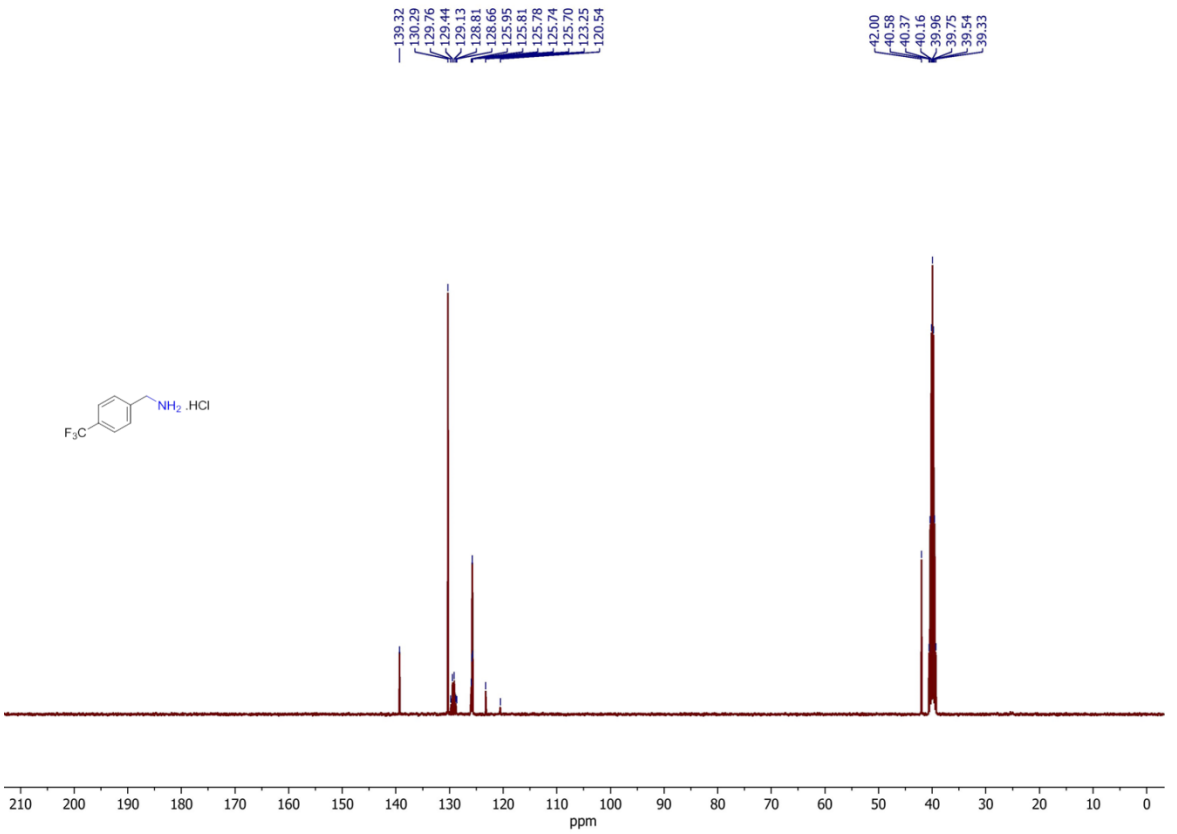
(4-*tert*-butylphenyl)methanamine hydrochloride (**7e**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**

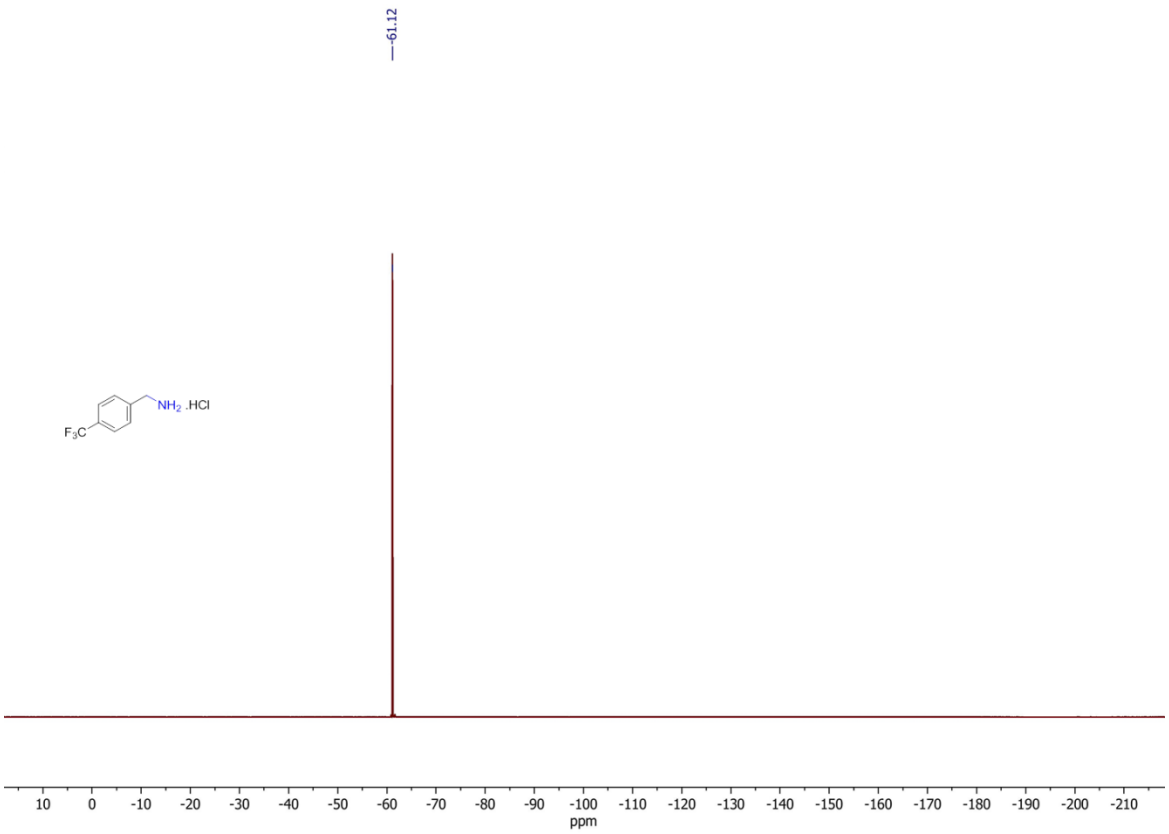




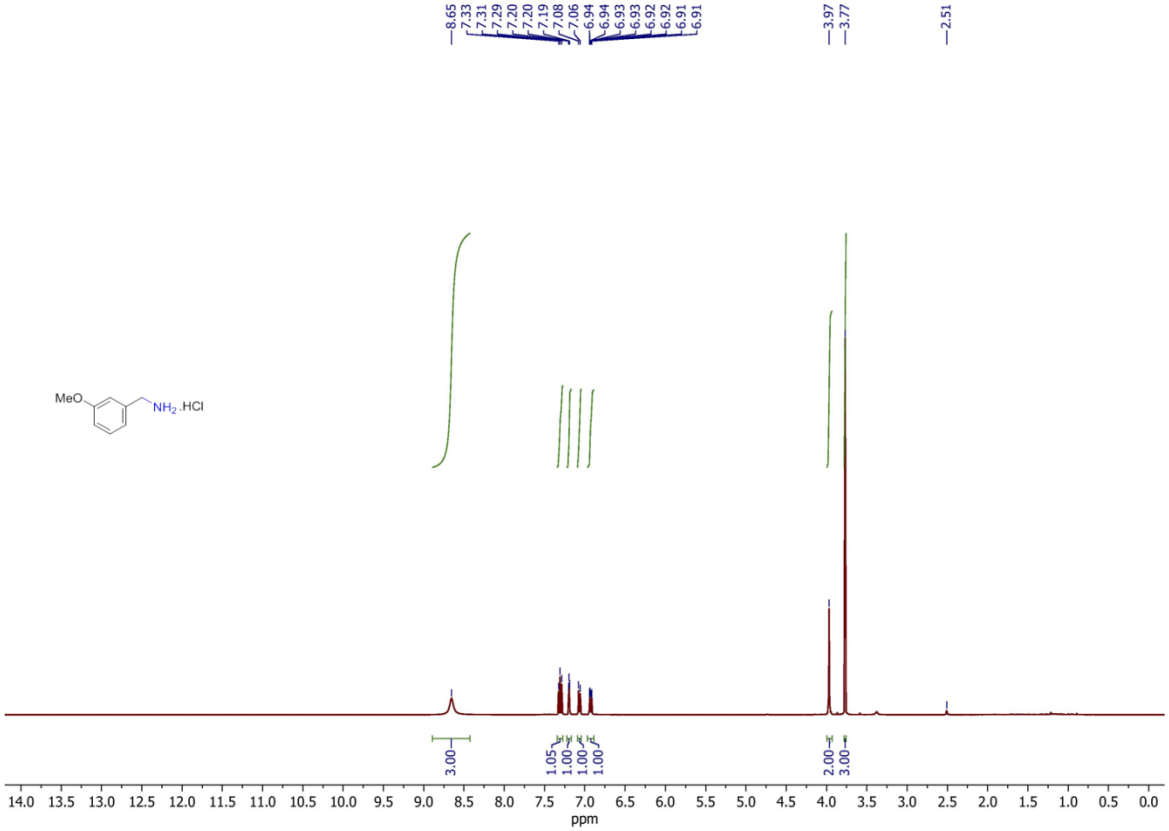
(4-(trifluoromethyl)phenyl)methanamine hydrochloride (**7f**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

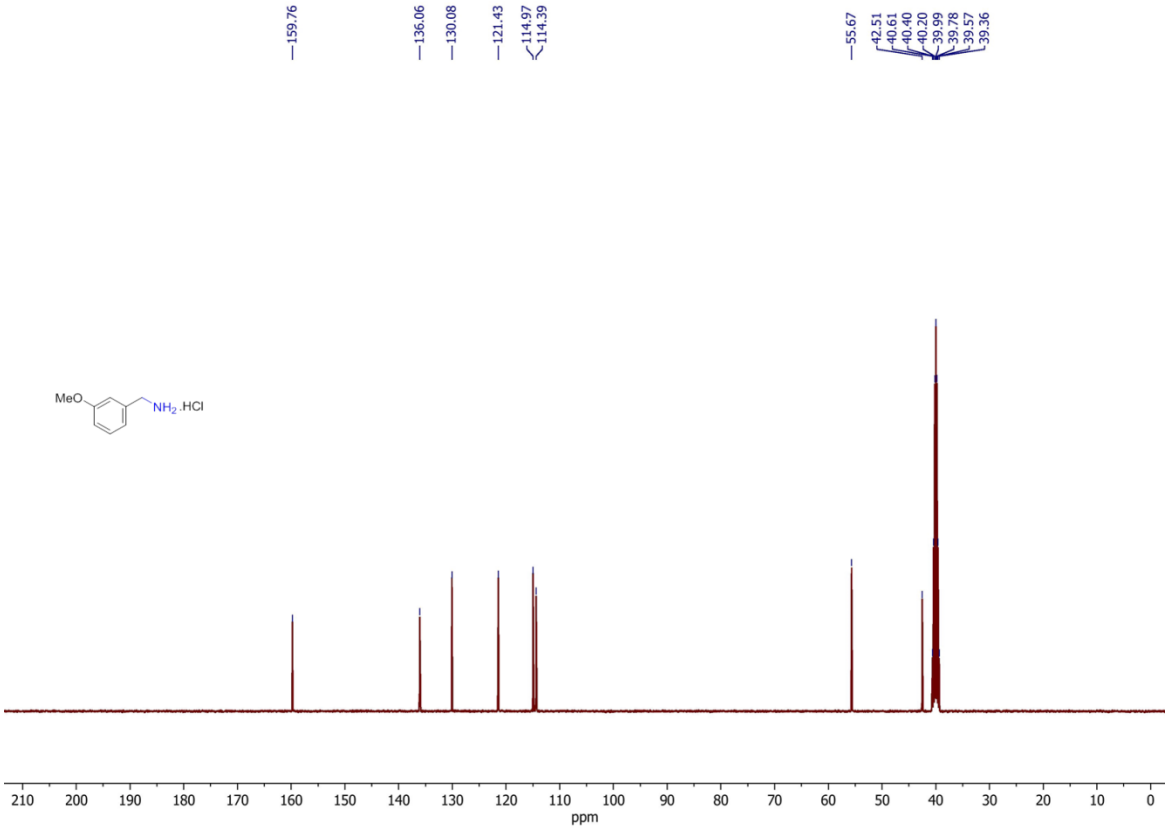




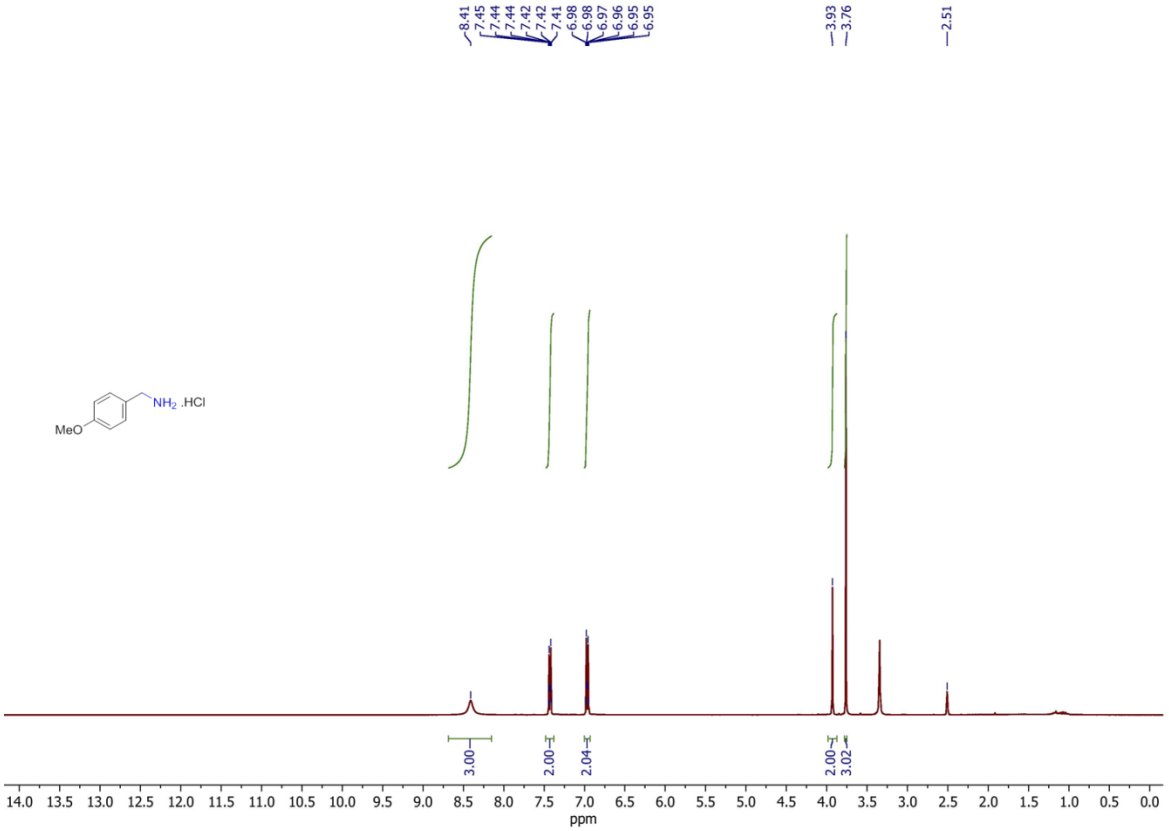

-61.12
NH2 .HCl
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

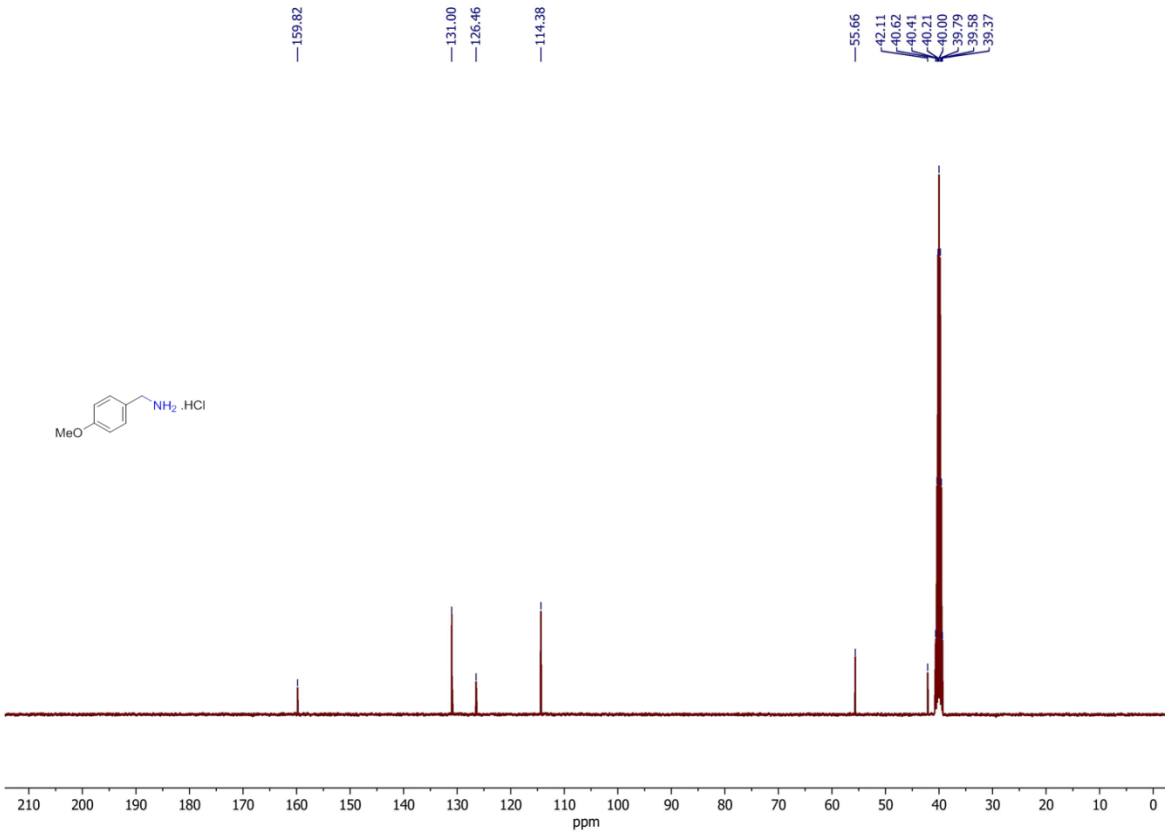
(3-methoxyphenyl)methanamine hydrochloride (**7g**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



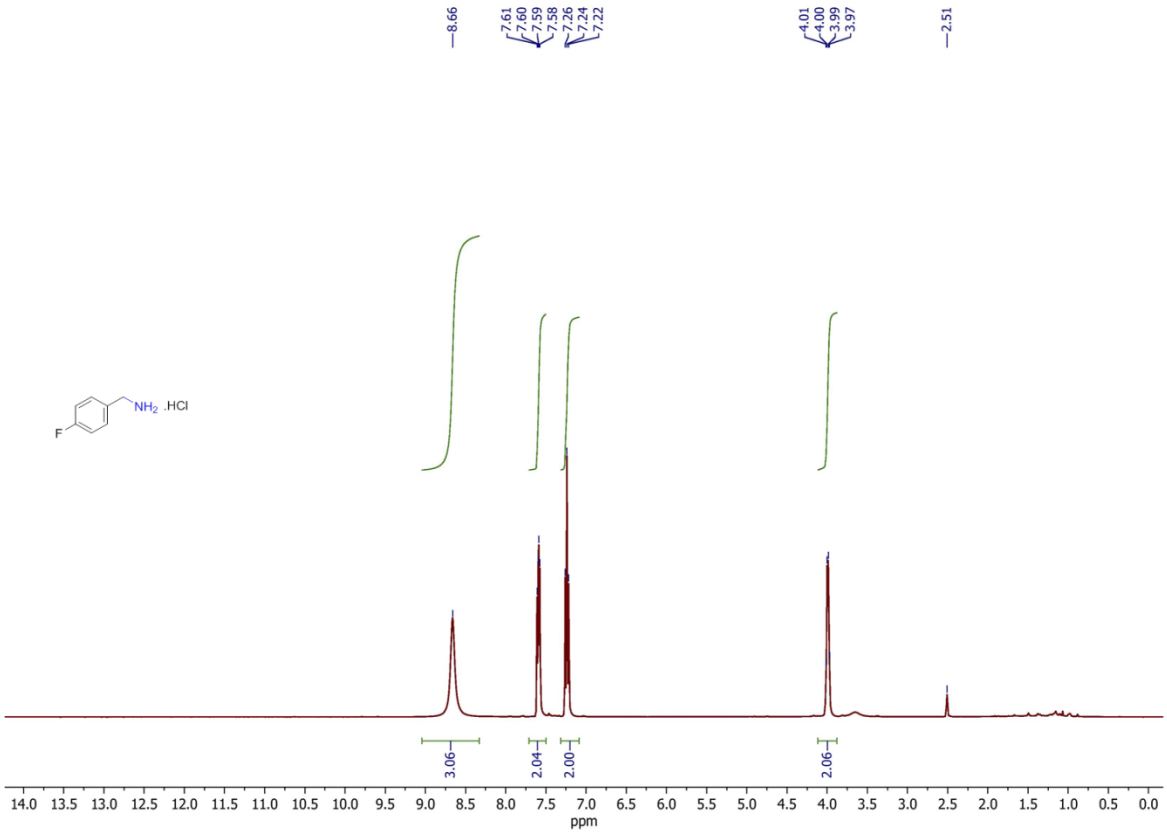


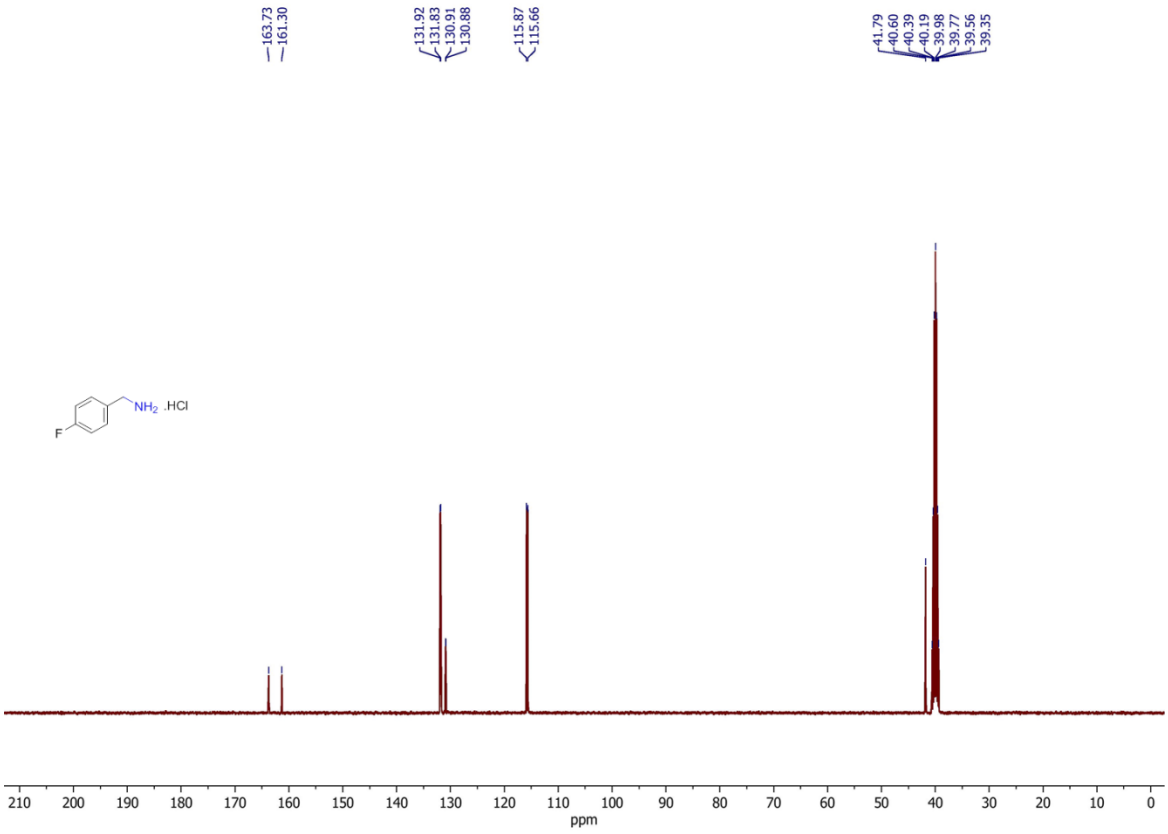
(4-methoxyphenyl)methanamine hydrochloride (**7h**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**

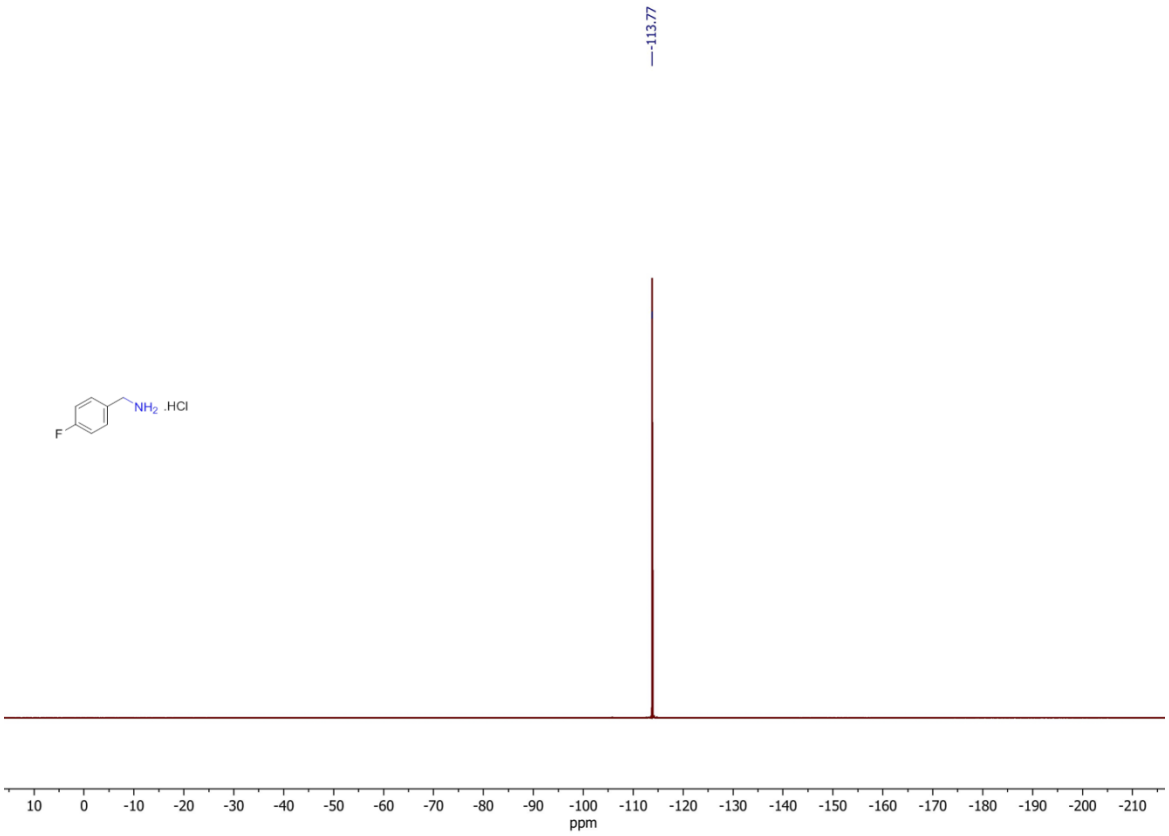




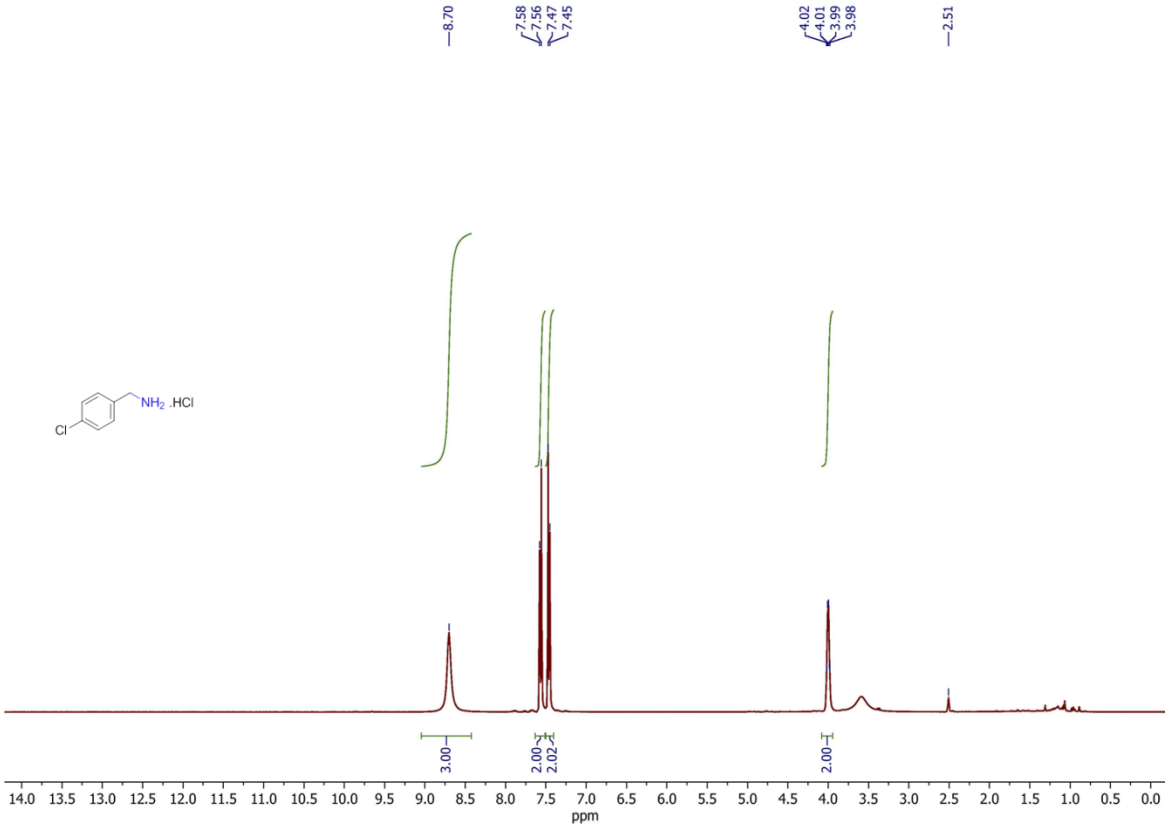
(4-fluorophenyl)methanamine hydrochloride (**7i**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$), ^{19}F NMR (376 MHz, DMSO-*d*$_6$).**

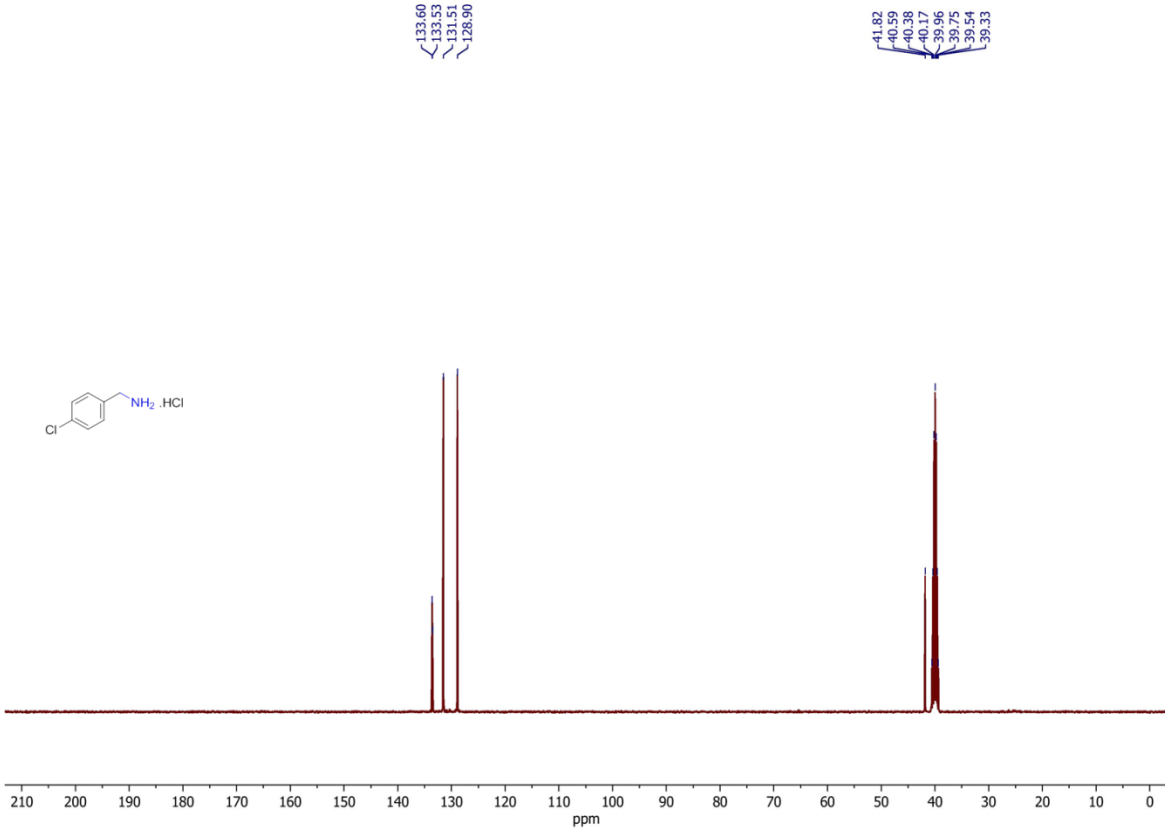




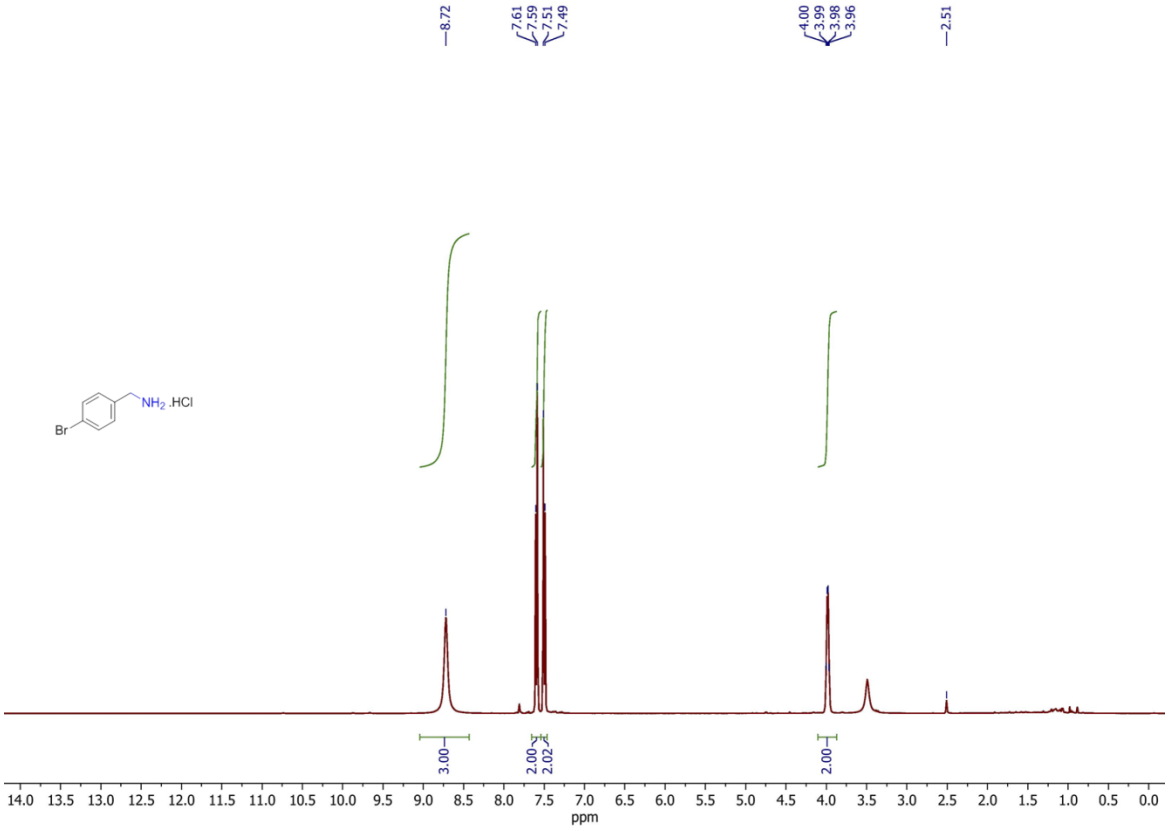

-113.77
NH2 .HCl
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

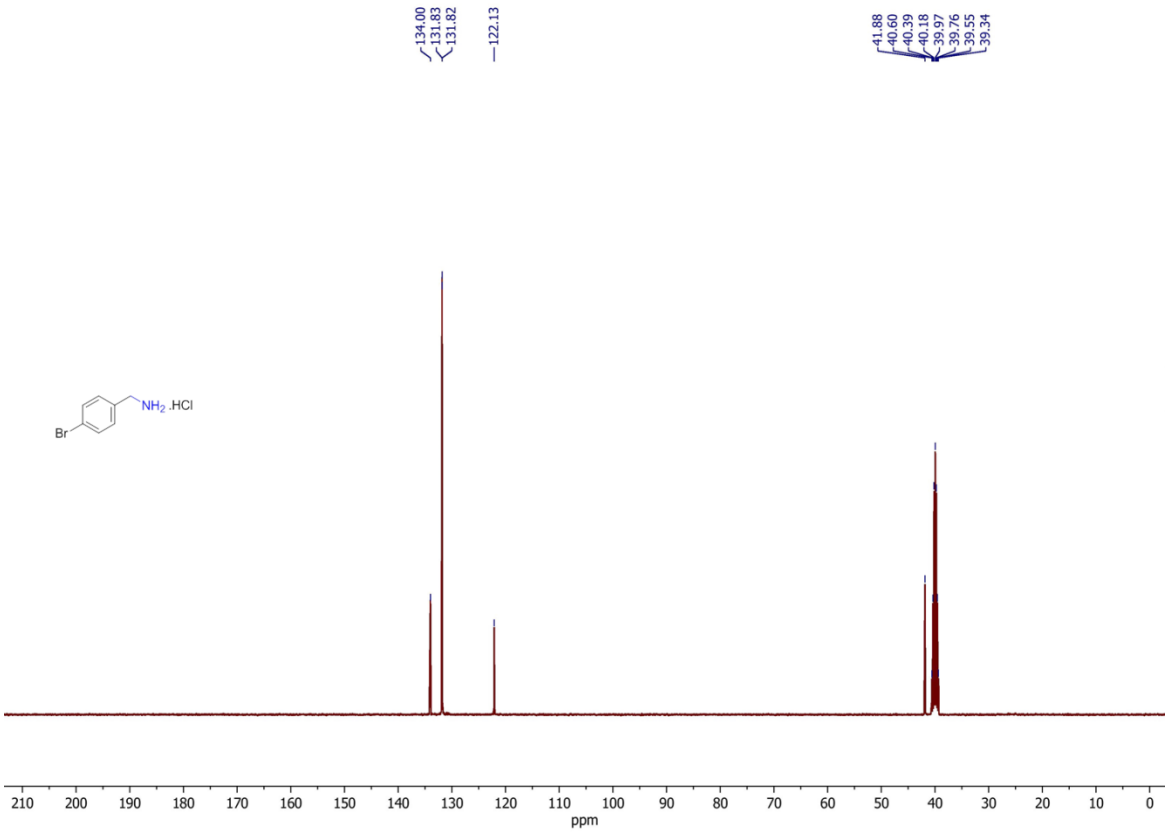
(4-chlorophenyl)methanamine hydrochloride (**7j**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



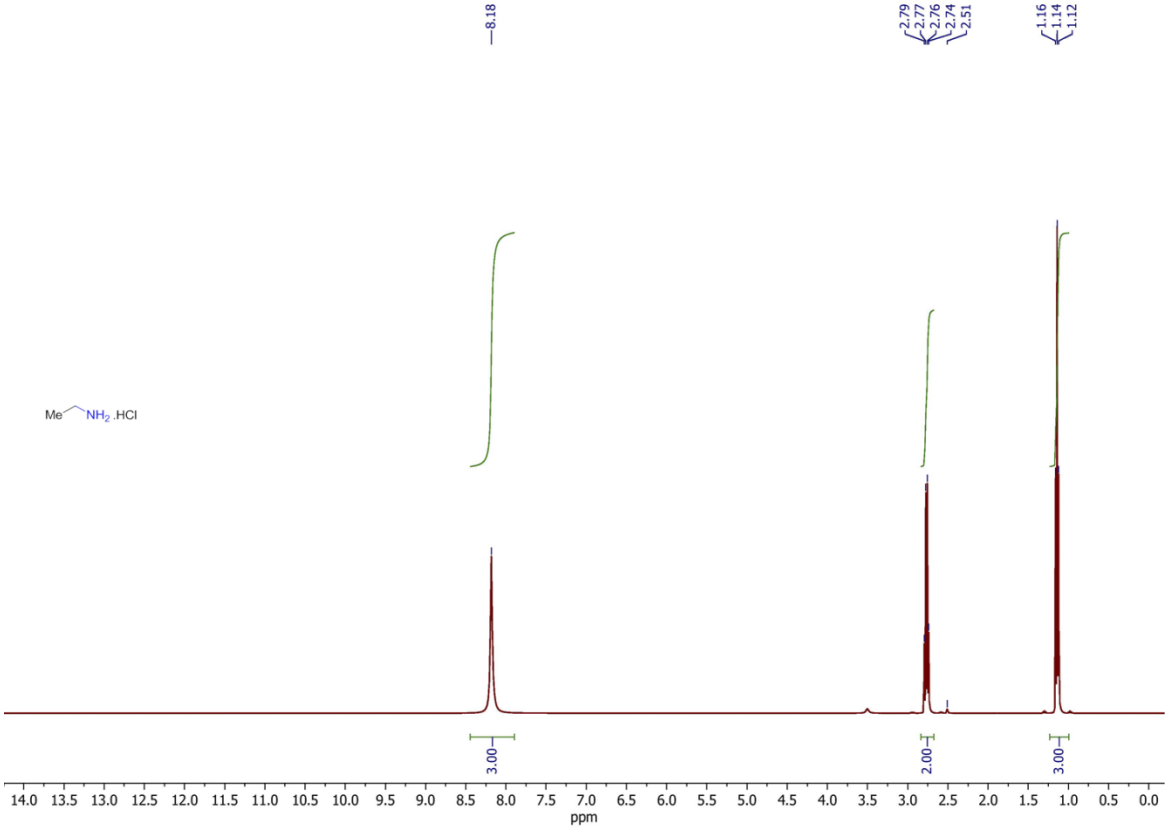


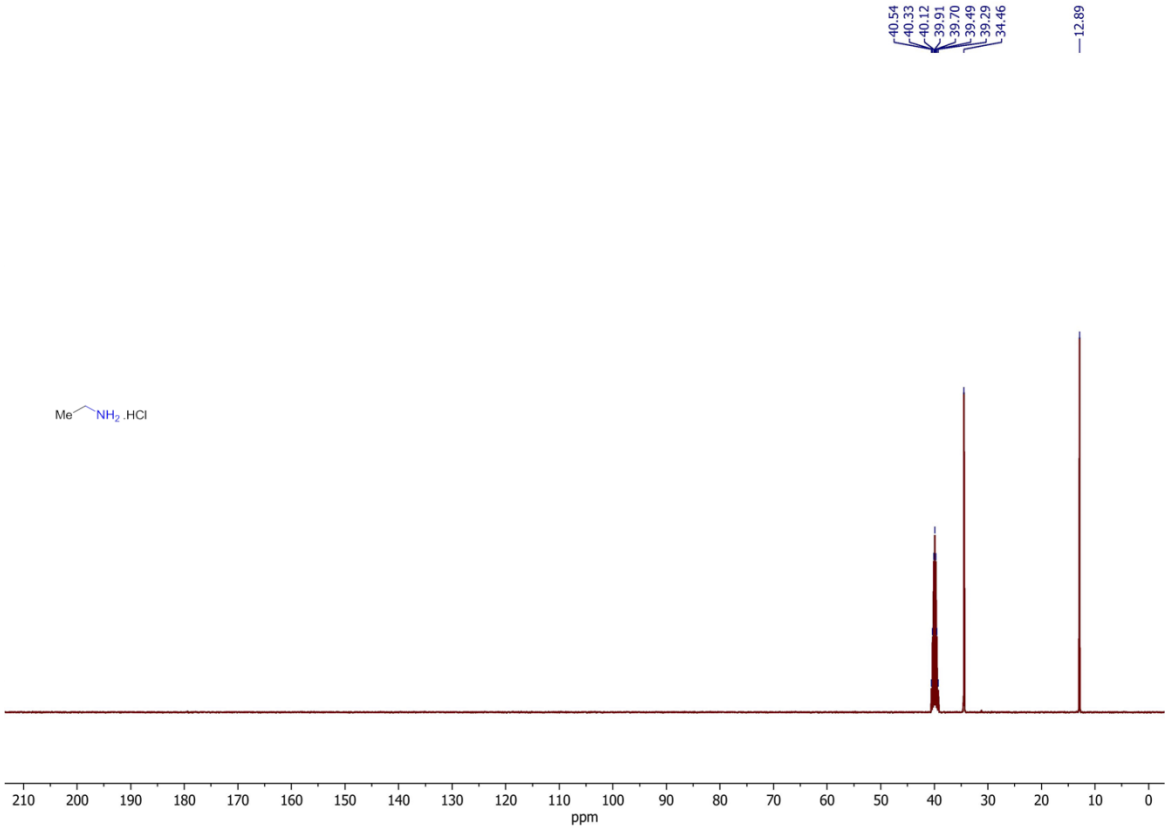
(4-bromophenyl)methanamine hydrochloride (**7k**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



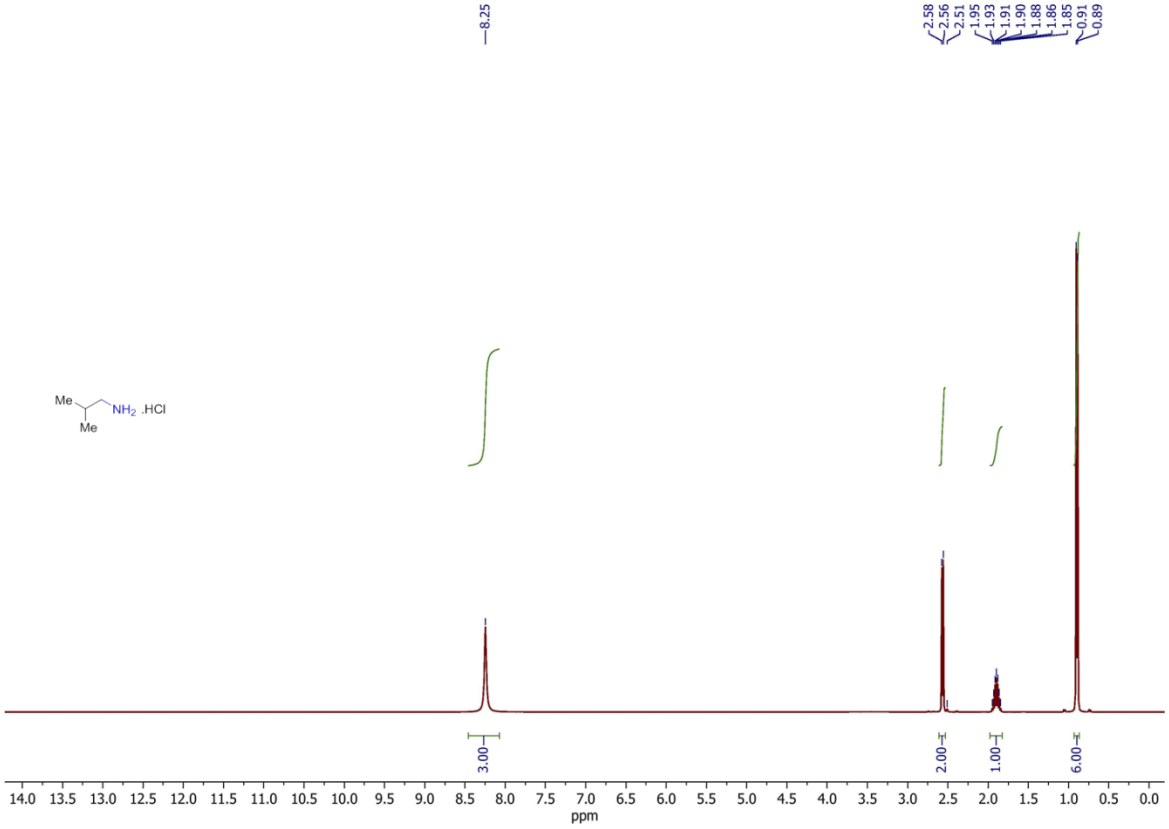


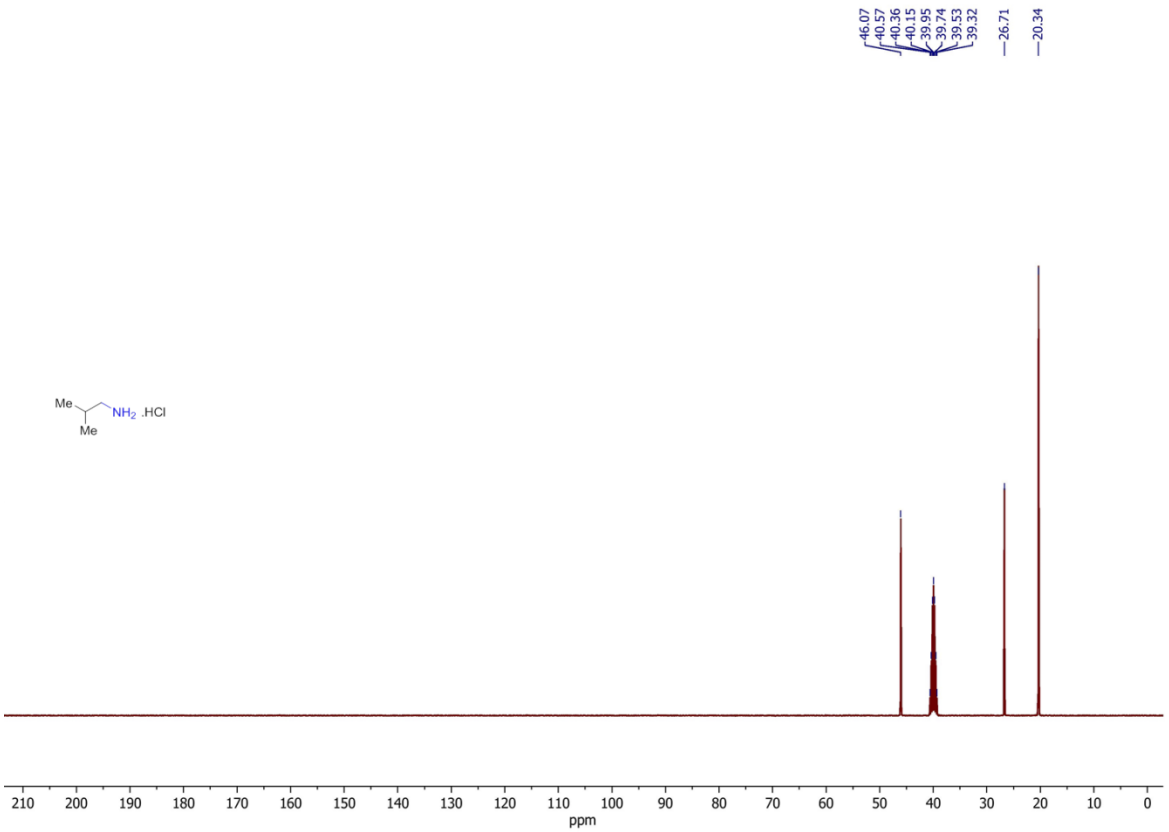
ethanamine hydrochloride (**7l**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



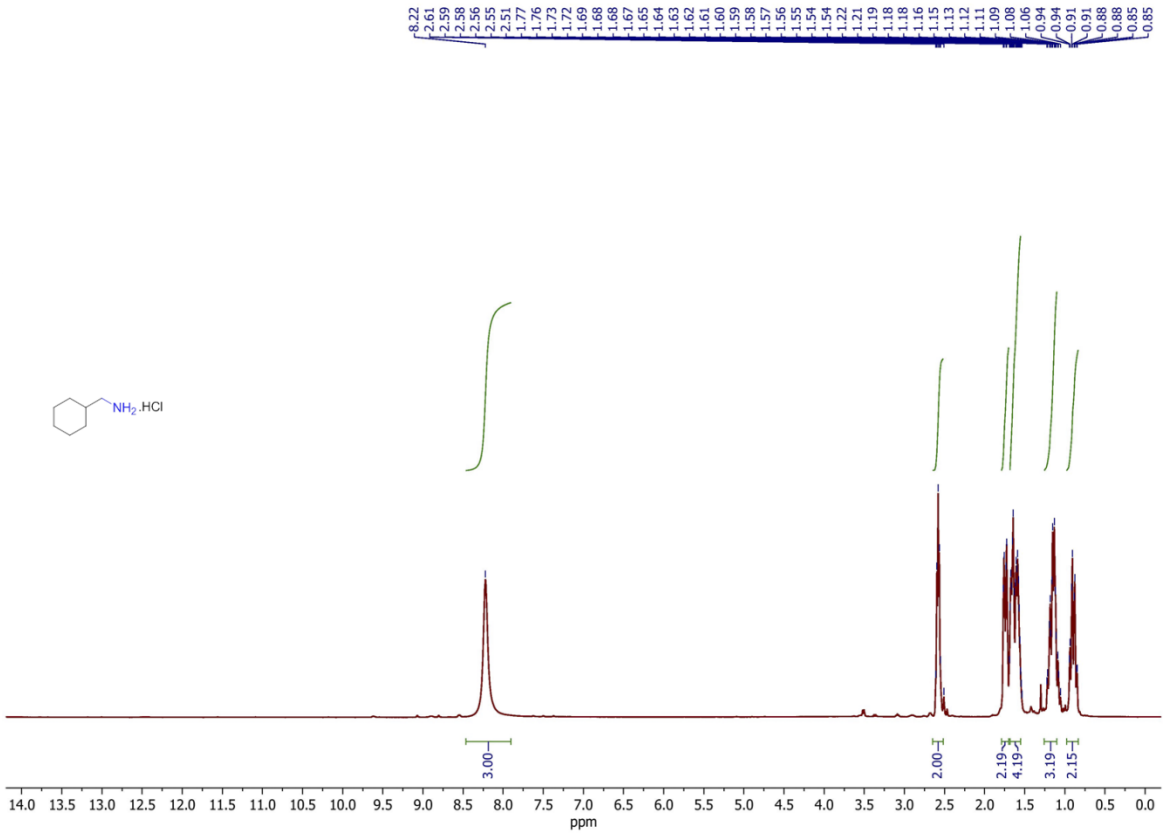


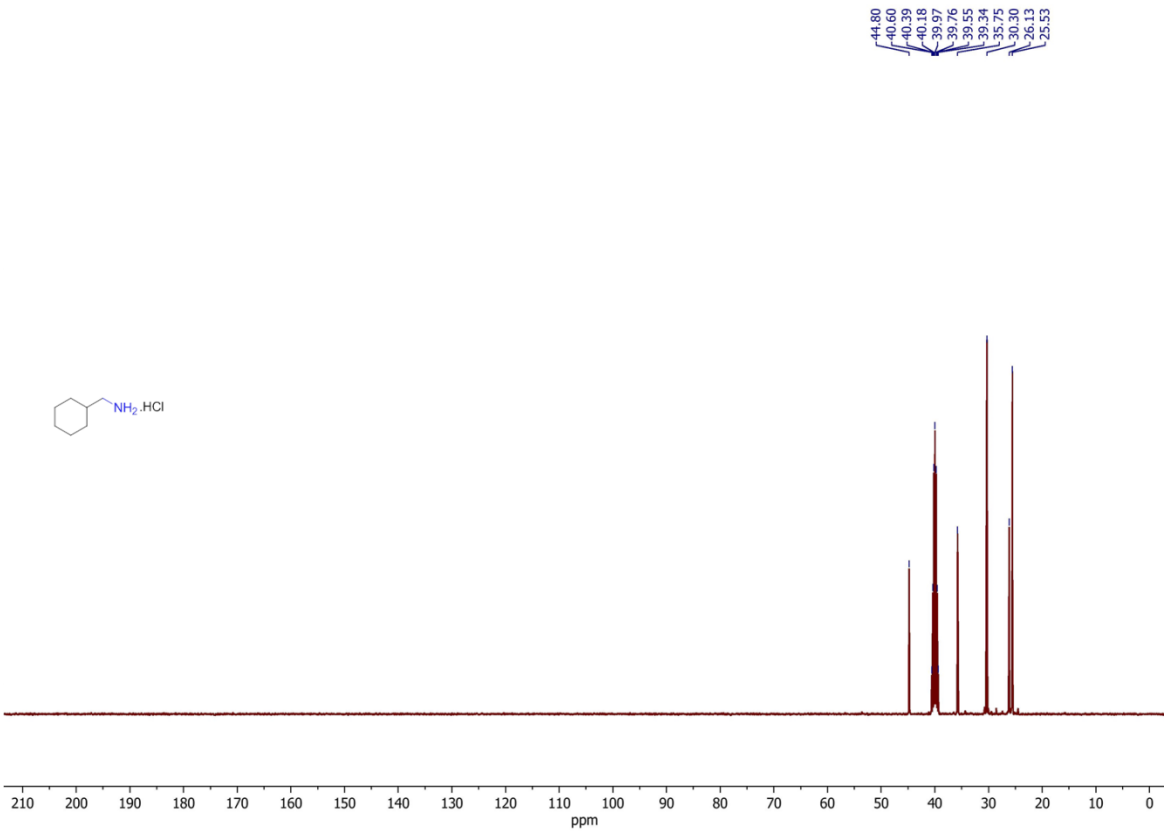
2-methylpropan-1-amine hydrochloride (**7m**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



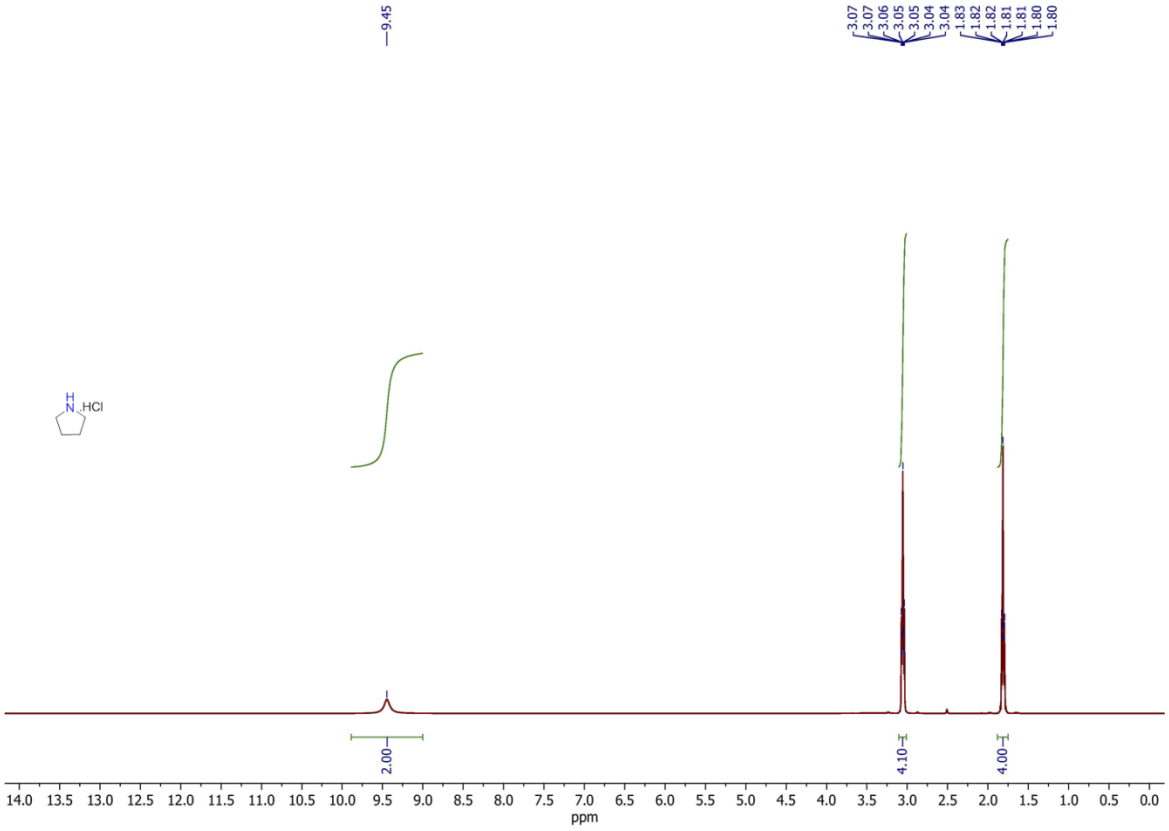


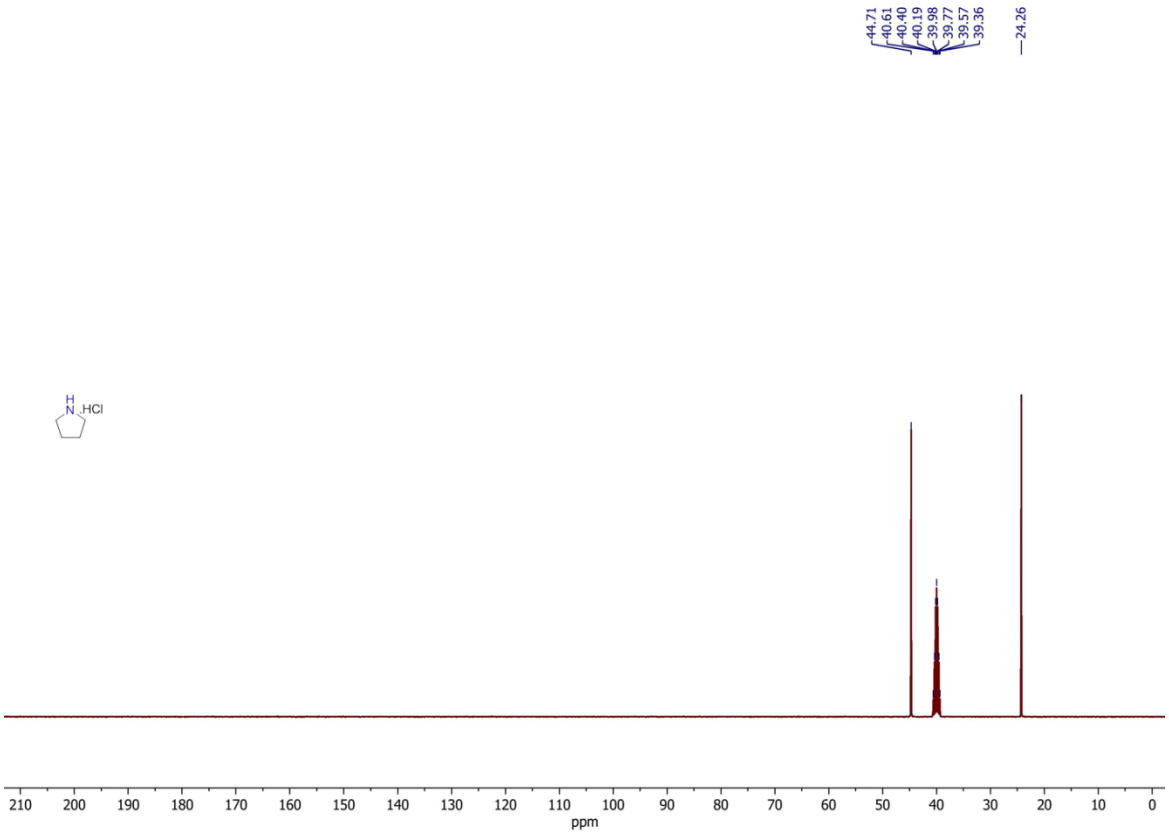
cyclohexylmethanamine hydrochloride (**7n**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



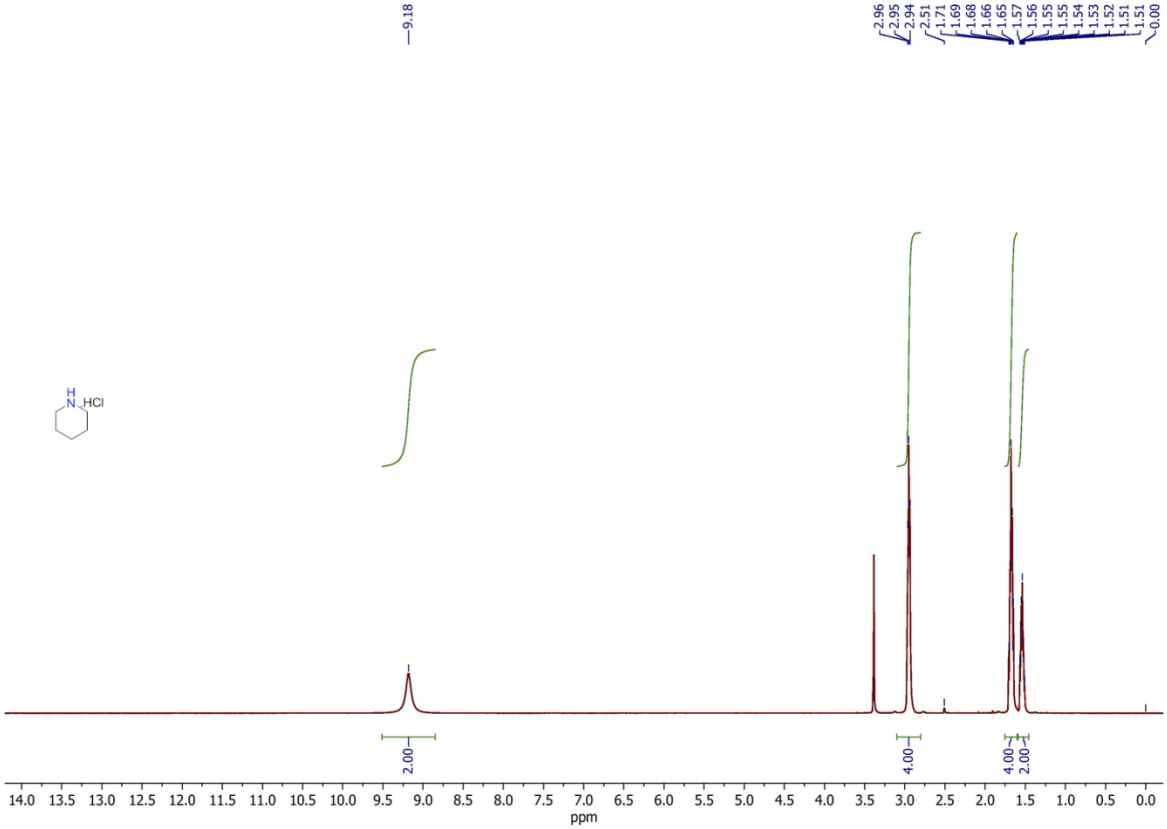


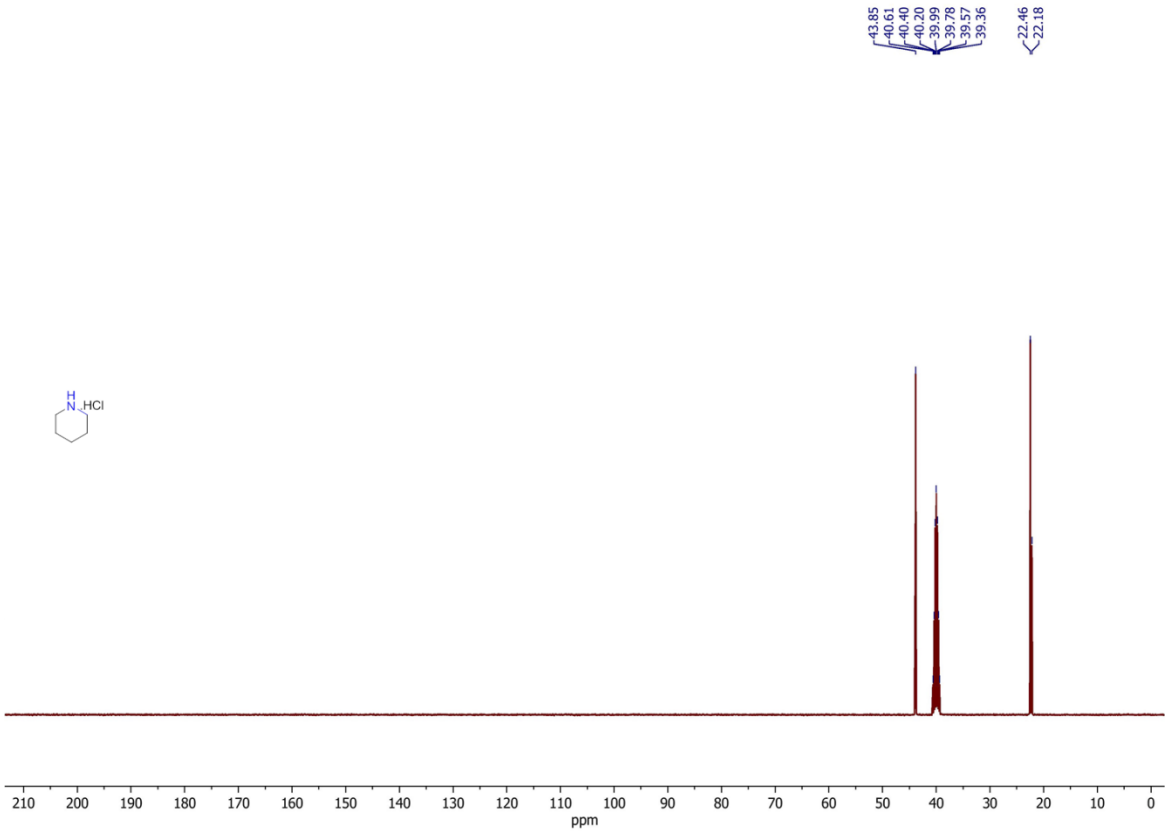
pyrrolidine hydrochloride (**7o**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**



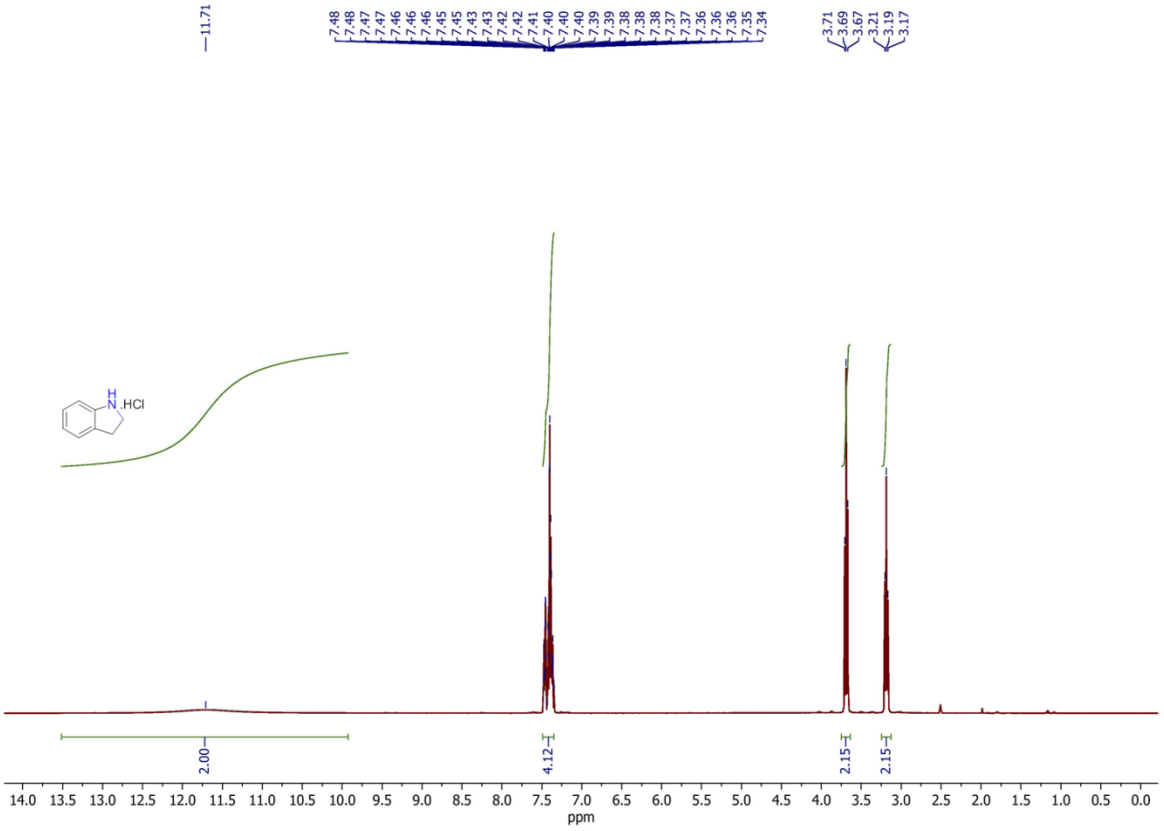


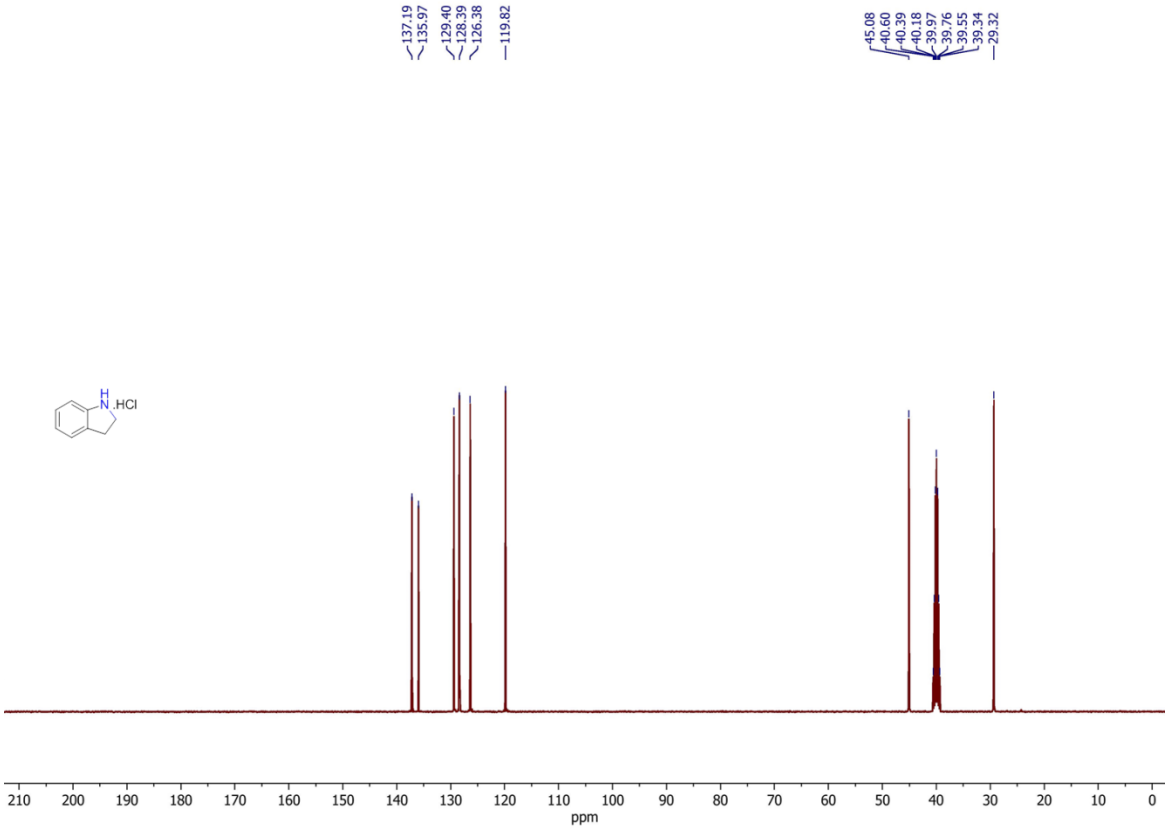
piperidine hydrochloride (**7p**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**





indoline hydrochloride (**7q**); **^{1}H NMR (400 MHz, DMSO-*d*$_6$), ^{13}C NMR (101 MHz, DMSO-*d*$_6$).**





References

1. Saha, S.; Eisen, M. S., Catalytic Recycling of a Th–H Bond via Single or Double Hydroboration of Inactivated Imines or Nitriles. *ACS Catal.* **2019,** *9* (7), 5947-5956.
2. Weetman, C.; Anker, M. D.; Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F., Magnesium-catalysed nitrile hydroboration. *Chemical Science* **2016,** *7* (1), 628-641.
3. Nguyen, T. T.; Kim, J.-H.; Kim, S.; Oh, C.; Flores, M.; Groy, T. L.; Baik, M.-H.; Trovitch, R. J., Scope and mechanism of nitrile dihydroboration mediated by a β-diketiminate manganese hydride catalyst. *Chemical Communications* **2020,** *56* (28), 3959-3962.
4. Sarkar, N.; Bera, S.; Nembenna, S., Aluminum-Catalyzed Selective Hydroboration of Nitriles and Alkynes: A Multifunctional Catalyst. *The Journal of organic chemistry* **2020,** *85* (7), 4999-5009.
5. Cheng, G.; Lv, W.; Kuai, C.; Wen, S.; Xiao, S., Base-promoted amide synthesis from aliphatic amines and ynones as acylation agents through C–C bond cleavage. *Chemical Communications* **2018,** *54* (14), 1726-1729.
6. Kerdphon, S.; Quan, X.; Parihar, V. S.; Andersson, P. G., C–N Coupling of Amides with Alcohols Catalyzed by N-Heterocyclic Carbene–Phosphine Iridium Complexes. *The Journal of organic chemistry* **2015,** *80* (22), 11529-11537.
7. Das, J.; Banerjee, D., Nickel-Catalyzed Phosphine Free Direct N-Alkylation of Amides with Alcohols. *The Journal of organic chemistry* **2018,** *83* (6), 3378-3384.
8. Ghosh, S. C.; Ngiam, J. S. Y.; Chai, C. L. L.; Seayad, A. M.; Dang, T. T.; Chen, A., Iron-Catalyzed Efficient Synthesis of Amides from Aldehydes and Amine Hydrochloride Salts. *Advanced Synthesis & Catalysis* **2012,** *354* (8), 1407-1412.
9. Nikitas, N. F.; Apostolopoulou, M. K.; Skolia, E.; Tsoukaki, A.; Kokotos, C. G., Photochemical Activation of Aromatic Aldehydes: Synthesis of Amides, Hydroxamic Acids and Esters. *Chemistry – A European Journal* **2021,** *27* (29), 7915-7922.
10. Wang, N.; Zou, X.; Ma, J.; Li, F., The direct synthesis of N-alkylated amides via a tandem hydration/N-alkylation reaction from nitriles, aldoximes and alcohols. *Chemical Communications* **2014,** *50* (61), 8303-8305.
11. Augurusa, A.; Mehta, M.; Perez, M.; Zhu, J.; Stephan, D. W., Catalytic reduction of amides to amines by electrophilic phosphonium cations via FLP hydrosilylation. *Chemical Communications* **2016,** *52* (82), 12195-12198.
12. Gudun, K. A.; Slamova, A.; Hayrapetyan, D.; Khalimon, A. Y., Efficient Co-Catalyzed Double Hydroboration of Nitriles: Application to One-Pot Conversion of Nitriles to Aldimines. *Chemistry – A European Journal* **2020,** *26* (22), 4963-4968.
13. Li, H.; Lupp, D.; Das, P. K.; Yang, L.; Gonçalves, T. P.; Huang, M.-H.; El Hajoui, M.; Liang, L.-C.; Huang, K.-W., Redox-Neutral Imination of Alcohol with Azide: A Sustainable Alternative to the Staudinger/Aza-Wittig Reaction. *ACS Catalysis* **2021,** *11* (7), 4071-4076.
14. Schönauer, T.; Thomä, S. L. J.; Kaiser, L.; Zobel, M.; Kempe, R., General Synthesis of Secondary Alkylamines by Reductive Alkylation of Nitriles by Aldehydes and Ketones. *Chemistry – A European Journal* **2021,** *27* (5), 1609-1614.
15. Yao, W.; Wang, J.; Zhong, A.; Wang, S.; Shao, Y., Transition-metal-free catalytic hydroboration reduction of amides to amines. *Org. Chem. Front.* **2020,** *7* (21), 3515-3520.
16. Bhunia, M.; Sahoo, S. R.; Das, A.; Ahmed, J.; P, S.; Mandal, S. K., Transition metal-free catalytic reduction of primary amides using an abnormal NHC based potassium complex: integrating nucleophilicity with Lewis acidic activation. *Chemical Science* **2020,** *11* (7), 1848-1854.