

# **Intermolecular Trifluoromethyl-Hydrazination of Alkenes Enabled by Organic Photo-Redox Catalysis**

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## I. General Information

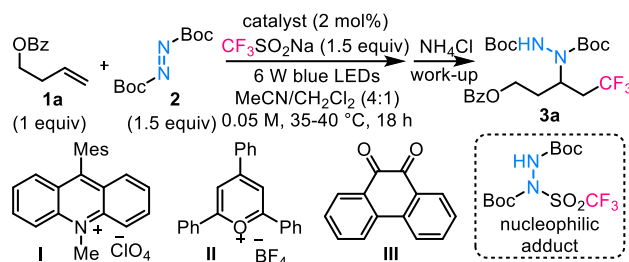
**General procedures.**  $\text{CF}_3\text{SO}_2\text{Na}$ , di-*tert*-butyl azodicarboxylate and  $\text{MesAcrMe}^+\text{ClO}_4^-$  were stored and weighed in a glovebox. Solvents were dried and freshly distilled before use. Reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F-254 plates. TLC plates were normally visualized by UV irradiation (254 nm or 365 nm), stained with basic  $\text{KMnO}_4$  or phosphomolybdic acid. Flash chromatography was performed using silica gel 60 (200-300 mesh).

**Instrumentation.** Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra and proton-decoupled carbon nuclear magnetic resonance ( $^{13}\text{C}\{^1\text{H}\}$  NMR) spectra were recorded on Bruker Ascend 400 MHz or 600 MHz. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak ( $\text{D}_2\text{O}$ :  $\delta$  4.79,  $\text{CD}_3\text{OD}$ :  $\delta$  3.31). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ( $\text{CD}_3\text{OD}$ :  $\delta$  49.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants in Hertz (Hz), and integration. IR spectra were recorded on a Bruker FT-IR spectrometer. HRMS was measured on a TOF-Q mass spectrometer equipped with an ESI source. High-performance liquid chromatography (HPLC) analysis was recorded on Shimadzu CBM-10A with a commercial Inertsil  $4.6 \times 250$  mm column.

### Abbreviations:

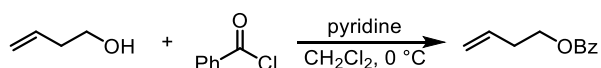
LED—light-emitting diode; TLC—thin layer chromatography; PE—Petroleum Ethers; THF—tetrahydrofuran; DMSO—dimethyl sulfoxide; AIBN—Azobisisobutyronitrile; PTFE—Polytetrafluoroethylene

## II. Catalyst Discovery and Condition Optimization



entry	catalyst	variation from standard conditions	conv. (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1	<b>I</b>	none	>95	85
2	<b>I</b>	AcOH (1 equiv.) added	89	69 <sup>d</sup>
3	<b>II</b>	none	82	35
4	<b>III</b>	none	95	79
5	$\text{Na}_2$ -Eosin Y	none	90	60
6	none	none	<5	<5
7	<b>I</b>	performed in darkness	<5	<5
8	<b>I</b>	in pure $\text{CH}_2\text{Cl}_2$	>95	64
9	<b>I</b>	in pure MeCN	>95	80
10	<b>I</b>	<b>2</b> & $\text{CF}_3\text{SO}_2\text{Na}$ (2 equiv)	>95	91 (88) <sup>e</sup>

<sup>a</sup>Unless otherwise stated, the reaction was performed under  $\text{N}_2$  with **1a** (35  $\mu\text{L}$ , 0.2 mmol),  $\text{CF}_3\text{SO}_2\text{Na}$  (47 mg, 0.3 mmol), **2** (69 mg, 0.3 mmol) and a corresponding catalyst (0.004 mmol) in  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  (4:1, 4 mL) at 35 to 40 °C under the irradiation of 6 W blue LEDs. <sup>b</sup>The conversion of **1a** was determined by HPLC with an internal standard. <sup>c</sup>The yield of **3a** was also measured by HPLC. <sup>d</sup>A nucleophilic adduct was observed. <sup>e</sup>Isolated yield

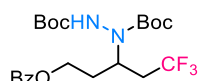


Compound **1a** is a known compound and it was prepared according to a literature procedure.<sup>[1]</sup>

Di-*tert*-butyl azodicarboxylate **2** is commercially available and it was used as received.

**General Procedures for catalyst discovery:** To a sealable 2-dram vial equipped with a stir bar were added di-*tert*-butyl azodicarboxylate **2** (69 mg, 0.3 mmol),  $\text{CF}_3\text{SO}_2\text{Na}$  (47 mg, 0.3 mmol) and a corresponding photo-sensitizer (0.004 mmol) in a glovebox. After the vial was taken out of the glovebox, anhydrous  $\text{CH}_2\text{Cl}_2$  (0.8 mL),  $\text{CH}_3\text{CN}$  (3.2 mL) and alkene **1a** were added successively through syringes under  $\text{N}_2$ . The reaction was then stirred under the irradiation of blue light (6 W LEDs. Note: the heat was generated by the LED bulbs, and the photoreactor was maintained at between 35 to 40 °C by circulating water cooling). The reaction

process was monitored with TLC. Upon the completion of reaction, the resulted mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  (aq., 2 mL), extracted with EtOAc (2 mL  $\times$  3), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The residue was redissolved in hexanes/*i*PrOH (5:1, 20 mL) together with dimethyl phthalate as an internal standard. After the insolubles were removed by a Nylon 66 syringe filter, the filtrate was subjected for HPLC analysis to determine the conversion (**1a**) and the yield (**3a**).



**Di-tert-butyl 1-(5-(benzoyloxy)-1,1,1-trifluoropentan-3-yl)hydrazine-1,2-dicarboxylate**

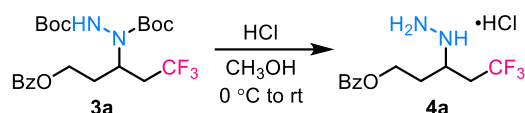
**(3a)**: Pure **3a** was isolated through a silica gel flash column (hexanes:EtOAc from 20:1 to 10:1) as colorless oil (84 mg, 88% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ , 343K)  $\delta$  8.93 – 8.19 (brs, 1H), 8.20 – 7.87 (m, 2H), 7.64 (t,  $J = 7.5$  Hz, 1H), 7.52 (t,  $J = 7.7$  Hz, 2H), 4.81 – 4.57 (brs, 1H), 4.57 – 4.37 (brs, 1H), 4.37 – 4.20 (brs, 1H), 2.75 – 2.56 (m, 1H), 2.46 – 2.30 (m, 1H), 2.11 – 1.96 (m, 1H), 1.96 – 1.79 (m, 1H), 1.45 (s, 9H), 1.41 – 1.28 (m, 9H);  $^{19}\text{F}$  NMR (565 MHz,  $\text{DMSO-}d_6$ , 343K)  $\delta$  -58.00 – -71.18 (m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{DMSO-}d_6$ , 343K)  $\delta$  166.1, 156.3, 154.0, 133.5, 130.6, 129.4, 129.0, 127.0 (q,  $J = 277.0$  Hz), 80.8, 80.2, 62.0, 50.1, 48.6, 36.2 (q,  $J = 24.1$  Hz), 31.6, 28.4, 28.1; IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3313, 2979, 1713, 1453, 1376, 1271, 1149, 712; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{22}\text{H}_{31}\text{F}_3\text{N}_2\text{NaO}_6^+$  [ $\text{M} + \text{Na}$ ] $^+$  499.2026, found 499.2022.



**Di-tert-butyl 1-((trifluoromethyl)sulfonyl)hydrazine-1,2-dicarboxylate (9)**: compound **9**

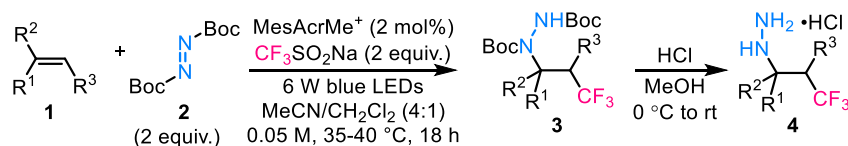
was isolated from the reaction described in entry 2 as a side product (white solid, m.p. 95.5 – 95.6  $^\circ\text{C}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (s, 1H), 1.48 (s, 9H), 1.42 (s, 9H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.21, -72.49 (atropisomer);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 148.3, 119.3 (q,  $J = 324.4$  Hz), 88.2, 83.5, 27.9, 27.6; IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 3329, 2986, 1777, 1729, 1418, 1216, 1129, 1048, 1151, 604, 579; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_6\text{S}^+$  [ $\text{M} + \text{Na}$ ] $^+$  387.0808, found 387.0810.

Due to the presence of the two carbamate groups, **3a** is probably conformationally constrained and shows broad absorption peaks on NMR spectra even at an elevated temperature. Because this phenomenon will cause difficulties in structure determination during substrates exploration, we decided to remove the protecting groups and characterize the hydrazinium hydrochloride salt instead.



**5,5,5-Trifluoro-3-hydrazinylpentyl benzoate hydrochloride (4a):** To a 25 mL round bottom flask charged with a stir bar, **3a** and CH<sub>3</sub>OH (2 mL) was slowly added HCl (4 M in CH<sub>3</sub>OH, 0.5 mL) at 0 °C. The reaction was then sealed with a PTFE septum and stirred at room temperature until the consumption of **3a**. After the solvent was removed under reduced pressure, the residue was washed with anhydrous ether (1 mL × 3) and then dried *in vacuo* to afford the corresponding hydrazine hydrochloride **4a** as colorless oil, (51 mg, 82% yield). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O) δ 8.03 – 7.92 (m, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 4.50 – 4.39 (m, 2H), 3.63 (t, *J* = 6.1 Hz, 1H), 2.70 – 2.60 (m, 2H), 2.22 – 2.11 (m, 2H). <sup>19</sup>F NMR (376 MHz, D<sub>2</sub>O) δ -64.58 (t, *J* = 11.0 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD) δ 166.5, 133.0, 129.8, 129.1, 128.3, 126.1 (q, *J* = 273.6 Hz), 60.9, 51.4, 35.4 (d, *J* = 28.0 Hz), 30.9; IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 2904, 1713, 1602, 1451, 1397, 1272, 1254, 1115, 1070, 710, 686; HRMS (ESI, *m/z*): calcd for C<sub>12</sub>H<sub>17</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [*M* + *H*]<sup>+</sup> 313.0931, found 313.0935.

### III. Trifluoromethyl-Hydrazination of Different Alkenes

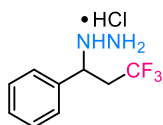


#### i. General procedure for preparation of trifluoromethylated hydrazinium salts **4** from corresponding alkenes:

To a sealable 2-dram vial equipped with a stir bar were added di-*tert*-butyl azodicarboxylate **2** (93 mg, 0.4 mmol) and CF<sub>3</sub>SO<sub>2</sub>Na (63 mg, 0.4 mmol) and MesAcrMe<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (1.6 mg, 0.004 mmol) in a glovebox. After the vial was taken out of the glovebox, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.8 mL),

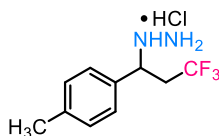
CH<sub>3</sub>CN (3.2 mL) and alkene **1** (0.2 mmol) were added successively through syringes under N<sub>2</sub>. The reaction was then stirred under the irradiation of blue light (6 W LEDs, the photoreactor was maintained at between 35 to 40 °C by circulating water cooling). The reaction process was monitored with TLC. Upon the completion of reaction, the resulted mixture was quenched with saturated NH<sub>4</sub>Cl (aq., 2 mL), extracted with EtOAc (2 mL × 3), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo* to afford the crude product, which was then purified through a silica gel flash column to afford a pure product **3**. Compound **3** was then dissolved in CH<sub>3</sub>OH (2 mL) in a round bottom flask, to which HCl (4 M in CH<sub>3</sub>OH, 0.5 mL) was slowly added at 0 °C. The reaction was then sealed with a PTFE septum and stirred at room temperature until the consumption of compound **3**. After the solvent was removed under reduced pressure, the residue was washed with anhydrous ether (1 mL × 2) and then dried *in vacuo* to afford the corresponding hydrazine hydrochloride **4**.

## ii. The characterization data of trifluoro-hydrazination products



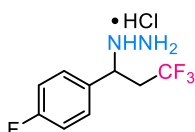
Styrene **1b** is commercially available and it was distilled before use.

**(3,3,3-Trifluoro-1-phenylpropyl)hydrazine hydrochloride (4b)**: compound **4b** was prepared from styrene by following the general procedure (foam, 35 mg, 73% yield). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 7.52 – 7.34 (m, 5H), 4.40 (t, *J* = 6.9 Hz, 1H), 2.88 – 2.67 (m, 2H); <sup>19</sup>F NMR (376 MHz, D<sub>2</sub>O) δ -63.28 (t, *J* = 10.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD) δ 136.7, 129.1, 129.0, 127.6, 125.6 (q, *J* = 276.1 Hz), 58.2, 38.2 (q, *J* = 27.6 Hz); IR *v*<sub>max</sub> (neat)/cm<sup>-1</sup>: 2980, 1715, 1393, 1368, 1264, 1153, 735, 713; HRMS (ESI, *m/z*): calcd for C<sub>9</sub>H<sub>13</sub>ClF<sub>3</sub>N<sub>2</sub><sup>+</sup> [*M* + H]<sup>+</sup> 241.0514, found 241.0510.



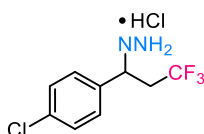
4-Methylstyrene **1c** is commercially available and it was distilled before use.

**(3,3,3-Trifluoro-1-(p-tolyl)propyl)hydrazine hydrochloride (4c):** compound **4c** was prepared from 4-methylstyrene **1c** by following the general procedure (foam, 33 mg, 65% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.33 – 7.18(m, 4H), 4.33 (t,  $J$  = 6.9 Hz, 1H), 2.84 – 2.61 (m, 2H), 2.25 (s, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.36 (t,  $J$  = 10.7 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  139.2, 133.5, 129.6, 127.6, 125.6 (q,  $J$  = 276.1 Hz), 58.0, 38.1 (q,  $J$  = 28.2 Hz), 19.9; IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2930, 1698, 1612, 1515, 1373, 1262, 1137, 737, 702; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{10}\text{H}_{15}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  255.0871, found 255.0865.



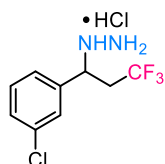
4-Fluorostyrene **1d** is commercially available and it was distilled before use.

**(3,3,3-Trifluoro-1-(4-fluorophenyl)propyl)hydrazine hydrochloride (4d):** compound **4d** was prepared from 1-fluoro-4-vinylbenzene **1d** by following the general procedure (foam, 42 mg, 82% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.47 – 7.32 (m, 2H), 7.10 (t,  $J$  = 8.6 Hz, 2H), 4.36 (t,  $J$  = 6.9 Hz, 1H), 2.82 – 2.56 (m, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.34 (t,  $J$  = 10.7 Hz), -112.61 (t,  $J$  = 5.2 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{D}_2\text{O}$ )  $\delta$  163.1 (d,  $J$  = 245.9 Hz), 131.7 (d,  $J$  = 3.1 Hz), 130.0 (d,  $J$  = 8.7 Hz), 125.4 (q,  $J$  = 276.3 Hz), 116.3 (d,  $J$  = 21.8 Hz), 57.2, 37.6 (q,  $J$  = 28.3 Hz); IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2950, 1697, 1598, 1508, 1370, 1225, 1094, 998, 836, 593; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_9\text{H}_{12}\text{ClF}_4\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  259.0620, found 259.0624.



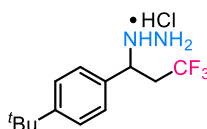
4-Chlorostyrene **1e** is commercially available and it was distilled before use.

**(1-(4-Chlorophenyl)-3,3,3-trifluoropropyl)hydrazine hydrochloride (4e):** compound **4e** was prepared from 4-chlorostyrene **1e** by following the general procedure (white solid, 38 mg, 70% yield, b.p. 165.1 – 165.2  $^{\circ}\text{C}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.57 – 7.27 (m, 4H), 4.35 (t,  $J$  = 6.9 Hz, 1H), 2.84 – 2.56 (m, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.34 (t,  $J$  = 10.8 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  134.9, 134.6, 129.5, 129.4, 125.4 (q,  $J$  = 276.6 Hz), 57.2 (q,  $J$  = 3.0 Hz), 37.6 (q,  $J$  = 28.4 Hz); IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2885, 1681, 1516, 1393, 1262, 1138, 1118, 1097, 824, 735, 701; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_9\text{H}_{11}\text{Cl}_2\text{F}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  274.0246, found 274.0240.



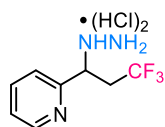
3-Chlorostyrene **1f** is commercially available and it was distilled before use.

**(1-(3-Chlorophenyl)-3,3,3-trifluoropropyl)hydrazine hydrochloride (4f)**: compound **4f** was prepared from 3-chlorostyrene **1f** by following the general procedure (foam, 33 mg, 60% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.42 (s, 1H), 7.38 – 7.21 (m, 3H), 4.34 (t,  $J = 6.9$  Hz, 1H), 2.83 – 2.55 (m, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.22 (t,  $J = 10.2$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  138.2, 134.5, 131.0, 129.7, 127.9, 128.1, 125.4 (q,  $J = 277.1$  Hz), 57.4, 37.6 (q,  $J = 28.6$  Hz); IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2891, 1685, 1510, 1393, 1260, 1141, 1118, 1091, 820, 731, 707; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_9\text{H}_{11}\text{Cl}_2\text{F}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  274.0246, found 274.0241.



4-*tert*-Butylstyrene **1g** is commercially available and it was distilled before use.

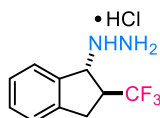
**(1-(4-(*tert*-Butyl)phenyl)-3,3,3-trifluoropropyl)hydrazine hydrochloride (4g)**: compound **4g** was prepared from 4-*tert*-butylstyrene **1g** by following the general procedure (foam, 45 mg, 76% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.47 (d,  $J = 8.2$  Hz, 2H), 7.32 (d,  $J = 8.3$  Hz, 2H), 4.34 (t,  $J = 6.9$  Hz, 1H), 2.90 – 2.59 (m, 2H), 1.19 (s, 9H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.37 (t,  $J = 10.7$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  152.3, 133.7, 127.3, 126.0, 125.8 (q,  $J = 277.1$  Hz), 57.9, 38.2 (q,  $J = 28.2$  Hz), 34.1, 30.3; IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2965, 1693, 1605, 1515, 1416, 1367, 1266, 1134, 1104, 997, 739, 641; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{21}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  297.1340, found 297.1346.



2-Vinylpyridine **1h** is commercially available and it was distilled before use.

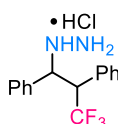
**2-(3,3,3-trifluoro-1-hydrazinylpropyl)pyridine hydrochloride (4h)**: compound **4h** was prepared from 2-vinylpyridine **1h** by following the general procedure (foam, 41 mg, 73% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.69 (d,  $J = 5.8$  Hz, 1H), 8.56 – 8.44 (m, 1H), 8.10 (d,  $J = 8.0$  Hz, 1H), 8.00 – 7.90 (m, 1H), 4.86 (t,  $J = 6.6$  Hz, 1H), 3.02 – 2.62 (m, 2H),  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.14 (d,  $J = 8.8$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  150.9, 148.1, 142.7, 127.9, 127.3, 124.7 (q,  $J = 276.7$  Hz), 55.1, 37.0 (q,  $J = 29.5$  Hz); IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2924, 1714, 1704, 1633, 1455, 1393, 1368, 1256, 1153, 740, 681; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_8\text{H}_{12}\text{ClF}_3\text{N}_3^+$  [ $\text{M} + \text{H}$ ] $^+$  242.0667, found 242.0670.



Indene **1i** is commercially available and it was distilled before use.

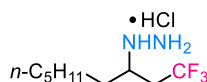
**(2-(Trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)hydrazine hydrochloride (4i)**: compound **4i** was prepared from indene **1i** by following the general procedure (white solid, 35 mg, 69% yield, m.p. 140.1 – 140.2 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.45 (d,  $J = 7.6$  Hz, 1H), 7.42 – 7.27 (m, 3H), 5.03 – 4.96 (m, 1H), 3.49 – 3.29 (m, 2H), 3.16 (d,  $J = 13.8$  Hz, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -71.55 (d,  $J = 8.8$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  142.4, 135.2, 130.5, 127.8, 127.2 (q,  $J = 277.4$  Hz), 125.36, 125.34, 64.6, 45.2 (q,  $J = 27.1$  Hz), 30.9; IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2932, 1714, 1394, 1373, 1263, 1161, 1111, 732, 702; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{10}\text{H}_{13}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  253.0719, found 253.0723.



*trans*-Stilbene **1j** is commercially available and it was recrystallized from ethanol before use.

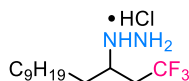
**(3,3,3-Trifluoro-1,2-diphenylpropyl)hydrazine hydrochloride (4j)**: compound **4j** was prepared from *trans*-stilbene **1j** by following the general procedure (foam, 46 mg, 73% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.48 – 7.36 (m, 2H), 7.16 (s, 4H), 7.11 (s, 4H), 4.65 (d,  $J = 10.6$  Hz, 1H), 4.12 – 3.90 (m, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.87 (d,  $J = 8.9$  Hz) (major), -64.11 (d,  $J = 8.8$  Hz) (minor);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  135.9 (minor), 135.3 (major), 132.4 (major), 131.9 (minor), 129.3 (major), 129.1 (minor), 128.9 (major+minor), 128.72 (major), 128.66 (minor), 128.6 (minor), 128.53 (major), 128.46 (major), 128.3 (minor),

128.0 (major), 127.8 (minor), 126.3 (q,  $J = 278.4$  Hz) (major), 125.6 (q,  $J = 278.4$  Hz) (minor), 63.6 (major), 62.6 (minor), 54.8 (d,  $J = 25.7$  Hz) (minor), 53.8 (q,  $J = 26.2$  Hz) (major); IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 3033, 1691, 1597, 1496, 1455, 1362, 1253, 1149, 1113, 892, 837, 756, 699, 650, 615, 594; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{17}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  317.1032, found 317.1035.



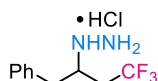
1-Octene **1k** is commercially available and it was distilled before use.

**(1,1,1-Trifluorononan-3-yl)hydrazine hydrochloride (4k)**: compound **4k** was prepared from 1-octene **1k** by following the general procedure (colorless oil, 40 mg, 80% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$  3.46 – 3.34 (m, 1H), 2.63 – 2.45 (m, 2H), 1.69 – 1.52 (m, 2H), 1.30 – 1.19 (m, 4H), 1.18 – 1.12 (m, 4H), 0.76 – 0.69 (m, 3H);  $^{19}\text{F}$  NMR (565 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.48 (t,  $J = 11.2$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  125.9 (q,  $J = 276.2$  Hz), 54.9 (q,  $J = 2.6$  Hz), 33.7 (q,  $J = 28.6$  Hz), 30.7, 30.0, 28.0, 23.9, 21.8, 13.3; IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 2929, 1704, 1456, 1392, 1367, 1262, 1152, 1047, 1019, 940, 855, 736, 703; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_9\text{H}_{21}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  249.1345, found 249.1350.



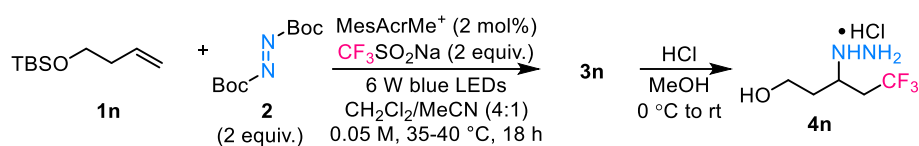
1-Dodecene **1l** is commercially available and it was distilled before use.

**(1,1,1-trifluorotridecan-3-yl)hydrazine hydrochloride (4l)**: compound **4l** was prepared from 1-dodecene **1l** by following the general procedure (colorless oil, 45 mg, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  3.32 – 3.05 (m, 1H), 2.77 – 2.44 (m, 1H), 2.45 – 2.27 (m, 1H), 1.78 – 1.45 (m, 2H), 1.40 – 1.08 (m, 16H), 0.80 (t,  $J = 6.6$  Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  -64.72 (t,  $J = 11.1$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  126.2 (q,  $J = 276.2$  Hz), 54.3, 34.7 (q,  $J = 28.2$  Hz), 31.7, 31.1, 29.29, 29.27, 29.11, 29.09, 29.0, 24.5, 22.3, 13.1; IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 2924, 2854, 1731, 1601, 1509, 1466, 1254, 1145, 740; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{29}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  305.1971, found 305.1976.



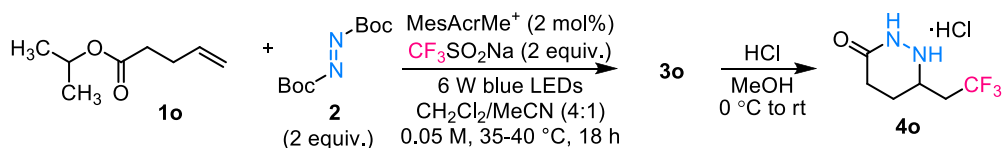
Allylbenzene **1m** is commercially available and it was distilled before use.

**(4,4,4-Trifluoro-1-phenylbutan-2-yl)hydrazine hydrochloride (4m):** compound **4m** was prepared from allylbenzene **1m** by following the general procedure (foam, 31 mg, 72% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.35 – 7.23 (m, 2H), 7.23 – 7.08 (m, 3H), 3.80 – 3.46 (m, 1H), 2.95 (dd,  $J = 14.1, 6.7$  Hz, 1H), 2.81 (dd,  $J = 14.1, 7.9$  Hz, 1H), 2.57 – 2.25 (m, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -63.22 (t,  $J = 11.1$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  135.5, 129.5, 129.1, 127.5, 125.9 (q,  $J = 272.6$  Hz), 55.5 (q,  $J = 2.5$  Hz), 36.9, 33.9 (q,  $J = 28.7$  Hz); IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2924, 1585, 1496, 1455, 1393, 1253, 1135, 919, 793, 738, 699, 663; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{10}\text{H}_{15}\text{ClF}_3\text{N}_2^+ [\text{M} + \text{H}]^+$  255.0876, found 255.0872.



(But-3-en-1-yloxy)(tert-butyl)dimethylsilane **1n** is a known compound and it was prepared according to a literature procedure.<sup>[2]</sup>

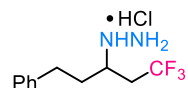
**5,5,5-Trifluoro-3-hydrazinylpentan-1-ol hydrochloride (4n):** compound **4n** was prepared from (but-3-en-1-yloxy)(tert-butyl)dimethylsilane **1n** by following the general procedure (colorless oil, 38 mg, 92% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  3.87 – 3.76 (m, 1H), 3.76 – 3.64 (m, 1H), 3.57 – 3.44 (m, 1H), 2.77 – 2.42 (m, 2H), 2.01 – 1.79 (m, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  -64.61 (t,  $J = 10.9$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  126.1 (q,  $J = 276.2$  Hz), 58.1, 53.5, 35.5 (q,  $J = 30.4$  Hz), 33.7; IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2978, 2929, 1703, 1454, 1365, 1256, 1129, 1083, 738; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_5\text{H}_{13}\text{ClF}_3\text{N}_2\text{O}^+ [\text{M} + \text{H}]^+$  209.0669, found 209.0665.



Isopropyl pent-4-enoate **1o** is a known compound and it was prepared according to a literature procedure.<sup>[3]</sup>

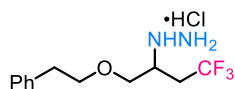
**6-(2,2,2-Trifluoroethyl)tetrahydropyridazin-3(2H)-one hydrochloride (4o):** compound **4o** was prepared from isopropyl pent-4-enoate **1o** by following the general procedure (foam, 36 mg, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  4.11 – 3.98 (m, 1H), 2.86 – 2.63 (m, 1H), 2.56 – 2.26 (m, 4H), 2.03 – 1.87 (m, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  -63.34 (t,  $J = 11.3$  Hz);  $^{13}\text{C}\{^1\text{H}\}$

NMR (101 MHz, CD<sub>3</sub>OD)  $\delta$  173.7, 125.8 (q,  $J = 276.7$  Hz), 53.4, 36.2 (q,  $J = 27.6$  Hz), 26.3, 23.3; IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 2925, 1729, 1682, 1516, 1395, 1354, 1253, 1145, 1106, 1026, 735, 646; HRMS (ESI, m/z): calcd for C<sub>6</sub>H<sub>11</sub>ClF<sub>3</sub>N<sub>2</sub>O<sup>+</sup> [M + H]<sup>+</sup> 219.0512, found 219.0515.



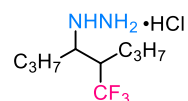
4-Phenyl-1-butene **1p** is commercially available and it was distilled before use.

**(1,1,1-Trifluoro-5-phenylpentan-3-yl)hydrazine hydrochloride (4p)**: compound **4p** was prepared from 4-phenyl-1-butene **1p** by following the general procedure (colorless oil, 42 mg, 78% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  6.96 – 6.85 (m, 4H), 6.86 – 6.77 (m, 1H), 3.11 – 2.71 (m, 1H), 2.39 (t,  $J = 8.1$  Hz, 2H), 2.34 – 2.11 (m, 2H), 1.70 – 1.47 (m, 2H); <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>OD)  $\delta$  -64.53 (t,  $J = 11.3$  Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD)  $\delta$  141.8, 129.3, 129.2, 127.4 (q,  $J = 276.8$  Hz), 127.0, 54.9, 36.0 (q,  $J = 28.0$  Hz), 34.4, 31.9; IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 2925, 1729, 1682, 1516, 1395, 1354, 1253, 1145, 1026, 735, 646; HRMS (ESI, m/z): calcd for C<sub>11</sub>H<sub>17</sub>ClF<sub>3</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 269.1032, found 269.1030.



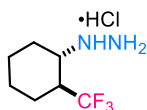
(2-(Allyloxy)ethyl)benzene **1q** is a known compound and it was prepared according to a literature procedure.<sup>[4]</sup>

**(4,4,4-Trifluoro-1-phenethoxybutan-2-yl)hydrazine hydrochloride (4q)**: compound **4q** was prepared (2-(allyloxy)ethyl)benzene **1q** by following the general procedure (foam, 42 mg, 71% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  7.42 – 7.34 (m, 2H), 7.34 – 7.23 (m, 3H), 3.88 – 3.71 (m, 3H), 3.69 – 3.61 (m, 1H), 3.61 – 3.54 (m, 1H), 2.94 (t,  $J = 6.6$  Hz, 2H), 2.60 – 2.37 (m, 2H); <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>OD)  $\delta$  -64.10 (t,  $J = 11.1$  Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, D<sub>2</sub>O)  $\delta$  140.4, 130.2, 129.9, 127.8, 127.3 (q,  $J = 275.9$  Hz), 73.4, 72.2, 54.5 (q,  $J = 2.6$  Hz), 36.6, 34.0 (q,  $J = 29.1$  Hz); IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 2960, 1455, 1208, 1117, 1085, 967, 823; HRMS (ESI, m/z): calcd for C<sub>12</sub>H<sub>19</sub>ClF<sub>3</sub>N<sub>2</sub>O<sup>+</sup> [M + H]<sup>+</sup> 299.1138, found 299.1135.



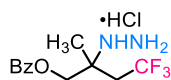
*trans*-4-Octene **1r** is commercially available and it was distilled before use.

**(5-(Trifluoromethyl)octan-4-yl)hydrazine hydrochloride (4r)**: compound **4r** was prepared from *trans*-4-octene **1r** by following the general procedure (colorless oil, 32 mg, 65% yield, *dr* = 1.2). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 3.33 – 3.15 (m, 1H), 2.74 – 2.51 (m, 1H), 1.71 – 1.40 (m, 4H), 1.40 – 1.22 (m, 4H), 0.90 – 0.73 (m, 6H), <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>OD) δ -65.60 (d, *J* = 9.8 Hz, isomer 1), -65.93 (d, *J* = 9.9 Hz, isomer 2), <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, D<sub>2</sub>O) δ 127.6 (q, *J* = 281.4 Hz), 127.5 (q, *J* = 281.4 Hz), 59.6, 59.1, 42.5 (q, *J* = 24.1 Hz), 42.1 (q, *J* = 24.6 Hz), 29.7, 26.04, 25.95, 20.3, 20.2, 19.3, 18.9, 13.2), 13.1, 12.98, 12.95; IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 2964, 1603, 1533, 1470, 1263, 1244, 1154, 737, 701; HRMS (ESI, *m/z*): calcd for C<sub>9</sub>H<sub>21</sub>ClF<sub>3</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 249.1345, found 249.1350.



Cyclohexene **1s** is commercially available and it was distilled before use.

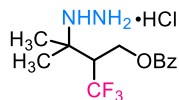
**(2-(Trifluoromethyl)cyclohexyl)hydrazine hydrochloride (4s)**: compound **4s** was prepared from cyclohexene **1s** by following the general procedure (white solid, 31 mg, 71% yield, m.p. 166.2 – 166.3 °C). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O) δ 3.35 – 3.24 (m, 1H), 2.56 – 2.35 (m, 1H), 2.12 – 2.04 (m, 1H), 2.06 – 1.98 (m, 1H), 1.84 – 1.76 (m, 1H), 1.72 (d, *J* = 12.7 Hz, 1H), 1.44 – 1.30 (m, 2H), 1.30 – 1.15 (m, 2H); <sup>19</sup>F NMR (376 MHz, D<sub>2</sub>O) δ -68.32 (d, *J* = 8.6 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD) δ 127.0 (q, *J* = 279.7 Hz), 56.2, 43.3 (q, *J* = 25.2 Hz); 28.2, 24.0 (q, *J* = 3.2 Hz) 23.3, 23.0; IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup>: 2939, 1714, 1594, 1454, 1334, 1260, 1140, 1090, 735, 690; HRMS (ESI, *m/z*): calcd for C<sub>7</sub>H<sub>15</sub>ClF<sub>3</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 219.0876, found 219.0880.



2-Methylallyl benzoate **1t** is a known compound and it was prepared according to a literature procedure.<sup>[5]</sup>

**4,4-Trifluoro-2-hydrazinyl-2-methylbutyl benzoate hydrochloride (4t)**: compound **4t** was prepared from 2-methylallyl benzoate **1t** by following the general procedure (foam, 53 mg, 83% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 8.22 – 8.06 (m, 2H), 7.70 – 7.61 (m, 1H), 7.58 – 7.47 (m, 2H), 4.51 (d, *J* = 12.4 Hz, 1H), 4.42 (d, *J* = 12.4 Hz, 1H), 3.00 – 2.52 (m, 2H), 1.49 (s, 3H); <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>OD) δ -61.04 (t, *J* = 11.4 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz,

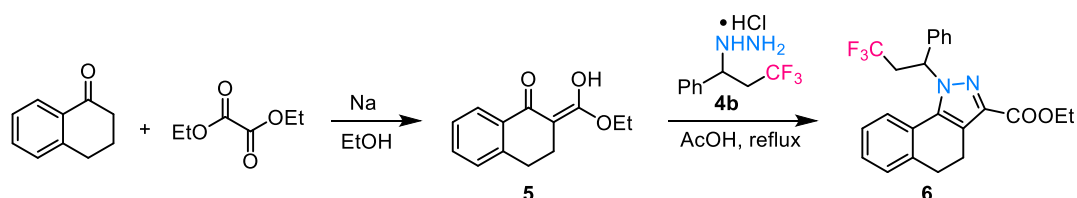
CD<sub>3</sub>OD)  $\delta$  166.1, 133.4, 129.5, 129.1, 128.4, 125.7 (q,  $J = 270.4$  Hz), 65.8, 57.0, 37.0 (q,  $J = 28.8$  Hz), 18.2; IR  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup>: 2944, 1722, 1601, 1451, 1381, 1256, 1176, 1105, 1070, 1027, 709; HRMS (ESI, m/z): calcd for C<sub>12</sub>H<sub>17</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 313.0931, found 313.0935.



3-Methylbut-2-en-1-yl benzoate **1u** is a known compound and it was prepared according to a literature procedure.<sup>[6]</sup>

**3-Hydrazinyl-3-methyl-2-(trifluoromethyl)butyl benzoate hydrochloride (4u)**: compound **4u** was prepared from 3-methylbut-2-en-1-yl benzoate **1u** by following the general procedure (foam, 51 mg, 78% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.13 – 7.98 (m, 2H), 7.70 – 7.58 (m, 1H), 7.55 – 7.44 (m, 2H), 4.82 (dd,  $J = 12.6, 3.3$  Hz, 1H), 4.62 (dd,  $J = 12.6, 5.5$  Hz, 1H), 3.38 – 2.98 (m, 1H), 1.51 (s, 3H), 1.44 (s, 3H); <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>OD)  $\delta$  -63.55; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD)  $\delta$  165.6, 134.1, 129.7, 129.6, 129.3, 127.3 (q,  $J = 286.8$  Hz), 60.2, 56.7, 47.0, 24.2, 22.8; IR  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup>: 2972, 1725, 1646, 1379, 1086, 1044, 879; HRMS (ESI, m/z): calcd for C<sub>13</sub>H<sub>19</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 327.1087, found 327.1082.

## IV. Synthetic Applications



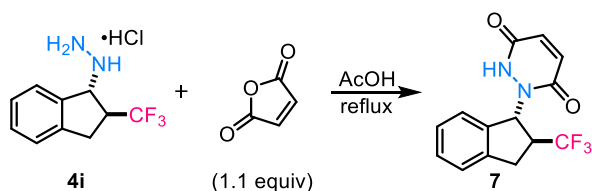
Compound **5** was synthesized according to a literature procedure.<sup>[7]</sup> Sodium lumps (276 mg, 12 mmol) were added in small portions to dry ethanol (5 ml) and stirred until the sodium was completely dissolved. Ethyl oxalate (813  $\mu$ L, 6 mmol) was added, followed by the dropwise addition of a solution of  $\alpha$ -tetralone (798  $\mu$ L, 6 mmol in 30 mL EtOH). The solution was stirred at room temperature for 2h. The mixture was slowly poured into hydrochloride acid (2 N) and the resulting precipitate was collected by filtration and washed with a small volume of ice-cooled ethanol and water to afford product **5** (yellow solid, 1.1 g, 84% yield, m.p. 44 – 45 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  15.75 (s, 1H), 8.00 (d,  $J = 7.7$ , 1H), 7.53 – 7.44 (m, 1H), 7.40 –

7.32 (m, 1H), 7.25 (d,  $J = 7.7$  Hz, 1H), 4.41 (q,  $J = 7.2$  Hz, 2H), 2.98 – 2.88 (m, 4H), 1.43 (t,  $J = 7.1$  Hz, 3H).

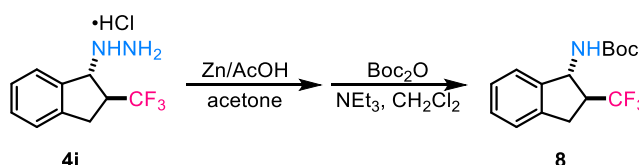
**4b** was prepared on a larger scale through a slightly modified procedure: To a sealable test tube (inner diameter = 15 mm, length = 100 mm) equipped with a stir bar were added di-*tert*-butyl azodicarboxylate **2** (372 mg, 1.6 mmol) and CF<sub>3</sub>SO<sub>2</sub>Na (252 mg, 1.6 mmol) and MesAcrMe<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (6.4 mg, 0.016 mmol) in a glovebox. After the vial was taken out of the glovebox, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.6 mL), CH<sub>3</sub>CN (6.4 mL) and styrene (92 μL, 0.8 mmol) were added successively through syringes under N<sub>2</sub>. The reaction was then stirred vigorously under the irradiation of blue light (6 W LEDs, the photoreactor was maintained at between 35 to 40 °C by circulating water cooling). The reaction process was monitored with TLC. Upon the completion of reaction, *two of the above parallel reactions* were combined and quenched with saturated NH<sub>4</sub>Cl (aq., 10 mL), extracted with EtOAc (10 mL × 3), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo* to afford the crude product, which was then purified through a silica gel flash column to afford a pure product **3**. Compound **3** was then dissolved in CH<sub>3</sub>OH (12 mL) in a round bottom flask, to which HCl (4 M in CH<sub>3</sub>OH, 4 mL) was slowly added at 0 °C. The reaction was then sealed with a PTFE septum and stirred at room temperature until the consumption of compound **3**. After the solvent was removed under reduced pressure, the residue was washed with anhydrous ether (5 mL × 2) and then dried *in vacuo* to afford compound **4b** (269 mg, 70% yield).

A stirred mixture of the **5** (87.3 mg, 0.4 mmol) and the hydrazinium chloride **4b** (110.5 mg, 0.46 mmol) in AcOH (3 ml) was heated under reflux in an oil bath for 2 h. The reaction was allowed to cool to room temperature and carefully quenched with saturated NaHCO<sub>3</sub> (aq., 10 mL) and extracted with EtOAc (5 mL × 3). The organic layers were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After being concentrated *in vacuo*, the crude product was purified through a silica gel flash column to afford pyrazole **6** (yellowish oil, 144 mg, 87% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.34 (m, 5H), 7.34 – 7.27 (m, 2H), 7.27 – 7.18 (m, 2H), 6.15 (dd,  $J = 9.0, 4.1$  Hz, 1H), 4.44 (q,  $J = 7.2$ , 2H), 3.99 – 3.82 (m, 1H), 3.15 (dt,  $J = 15.3, 5.4$ , 1H), 3.06 – 2.73 (m, 4H), 1.43 (t,  $J = 7.2$ , 3H), <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -64.93 (t,  $J = 10.4$  Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 162.9, 140.3, 139.2, 138.8, 138.2, 129.14,

129.09, 128.5, 128.1, 127.0, 126.6, 126.2, 125.6 (q,  $J = 275.7$  Hz), 122.5, 122.4, 60.8, 58.7, 40.5 (q,  $J = 28.4$  Hz), 30.5, 20.2, 14.4; IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 2980, 1715, 1436, 1376, 1176, 1213, 1156, 1098, 1006, 908, 762, 733, 700; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{23}\text{H}_{21}\text{F}_3\text{N}_2\text{NaO}_2^+$  [ $\text{M} + \text{Na}$ ] $^+$  437.1447, found 437.1450.



**1-(*trans*-2-Trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)-1,2-dihydropyridazine-3,6-dione (7):** compound 7 was synthesized by following a literature procedure.<sup>[8]</sup> To a solution of **4i** (0.2 mmol) in AcOH (2 mL) was added maleic anhydride (22 mg, 0.22 mmol). The mixture was heated under reflux in an oil bath for 4 h until **4i** was consumed (monitored by TLC). The reaction was then cooled down, carefully quenched with saturated  $\text{NaHCO}_3$  (aq., 10 mL) and extracted with EtOAc (5 mL  $\times$  3). The organic layers were combined and washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After being concentrated *in vacuo*, the crude product was purified through a silica gel flash column (PE:EtOAc = 2:1) to give compound 7 as colorless oil (48 mg, 75% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  11.28 (brs, 1H), 7.35 (d,  $J = 7.5$  Hz, 1H), 7.33 – 7.28 (m, 1H), 7.27 – 7.20 (m, 1H), 7.10 (d,  $J = 9.8$  Hz, 1H), 7.03 (d,  $J = 9.8$  Hz, 1H), 6.98 (d,  $J = 7.5$  Hz, 1H), 6.69 (d,  $J = 7.7$  Hz, 1H), 3.74 (hept,  $J = 9.2$  Hz, 1H), 3.45 (dd,  $J = 16.2, 9.4$  Hz, 1H), 3.13 (dd,  $J = 16.2, 8.4$  Hz, 1H);  $^{19}\text{F}$  NMR (565 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -69.27 (d,  $J = 9.4$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{DMSO-}d_6$ )  $\delta$  158.7, 153.5, 140.4, 140.3, 133.1, 129.0, 128.03 (q,  $J = 277.5$  Hz), 128.95, 127.9, 125.4, 124.0, 60.6, 60.2, 46.9 (d,  $J = 26.8$  Hz), 31.0, 21.2, 14.5; IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 2924, 1667, 1583, 1543, 1462, 1374, 1264, 1159, 1111, 739, 702; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{11}\text{F}_3\text{N}_2\text{NaO}_2^+$  [ $\text{M} + \text{Na}$ ] $^+$  319.0665, found 319.0661.

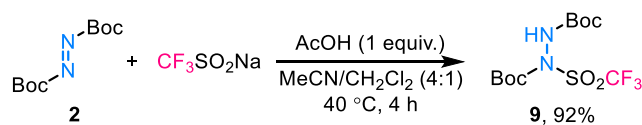


***tert*-Butyl (2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)carbamate (8):** compound 8 was prepared according to a literature procedure.<sup>[9]</sup> To a solution of **4i** (0.2 mmol, dissolved in 2 mL of acetone) acetic acid (3 mL) and freshly activated Zn dust (130 mg, 2 mmol) were

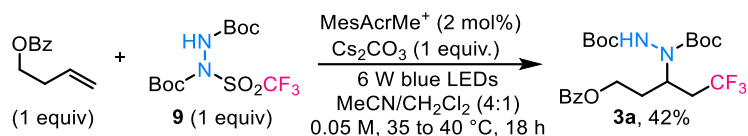
added. After 2 h, the reaction was filtered through Celite and washed with MeOH (4 mL). The mixture was acidified with 37% HCl (pH = 1), and the solvents were removed under reduced pressure. The residue was then dissolved in HCl (1 M, 20 mL) and washed with Et<sub>2</sub>O (3 × 15 mL). The pH of the aqueous phase was adjusted to 12 with NaOH pellets and the resulting solution was saturated with NaCl and extracted with Et<sub>2</sub>O (3 × 20 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo* to afford the crude amine. The crude product was then dissolved in CH<sub>2</sub>Cl<sub>2</sub>, NEt<sub>3</sub> (55 μL, 0.4 mmol) and (Boc)<sub>2</sub>O (87.3 mg, 0.4 mmol) was added to the solution and stirred at room temperature for 5 h. Compound **8** was then isolated through a silica gel flash column (PE:EtOAc = 20:1) as colorless oil (44 mg, 68% yield, over 2 steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.06 (m, 4H), 5.57 – 5.19 (m, 1H), 5.00 – 4.59 (m, 1H), 3.21 (dd, *J* = 16.0, 8.9 Hz, 1H), 3.04 (dd, *J* = 16.0, 8.7 Hz, 1H), 2.93 (hept, *J* = 8.8 Hz, 1H), 1.46 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -70.25 (d, *J* = 8.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 155.1, 141.3, 139.0, 128.6, 127.5, 127.1 (q, *J* = 277.1 Hz), 124.7, 124.0, 80.0, 56.1, 51.0 (q, *J* = 26.6 Hz), 30.7, 28.3; IR *v*<sub>max</sub> (neat)/cm<sup>-1</sup>: 3333, 2979, 1688, 1525, 1393, 1367, 1265, 1158, 1151, 1010, 907, 733; HRMS (ESI, *m/z*): calcd for C<sub>15</sub>H<sub>18</sub>F<sub>3</sub>NNaO<sub>2</sub><sup>+</sup> [*M* + Na]<sup>+</sup> 324.1182, found 324.1185.

## V. Mechanistic Studies

### i. The reaction with nucleophilic addition product.

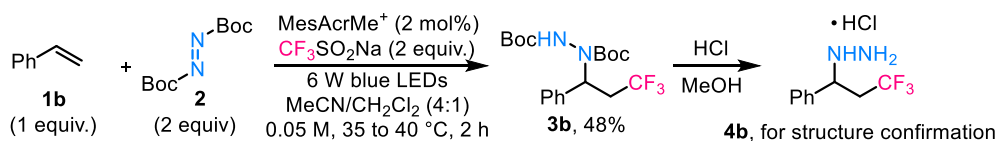


**Di-tert-butyl 1-((trifluoromethyl)sulfonyl)hydrazine-1,2-dicarboxylate (9)**: To a oven-dried 2-dram vial charged with a stir bar, di-tert-butyl azodicarboxylate **2** (93 mg, 0.4 mmol) and CF<sub>3</sub>SO<sub>2</sub>Na (63 mg, 0.4 mmol) were added CH<sub>3</sub>CN (3.2 mL), CH<sub>2</sub>Cl<sub>2</sub> (0.8 mL) and AcOH (24 μL, 0.4 mmol) successively. The mixture was stirred at 40 °C in an oil bath for 4 h and concentrated *in vacuo*. The nucleophilic adduct **9** was isolated through a silica gel flash column (Hexanes/EtOAc from 20:1 to 10:1) as a white solid (134 mg, 92% yield).



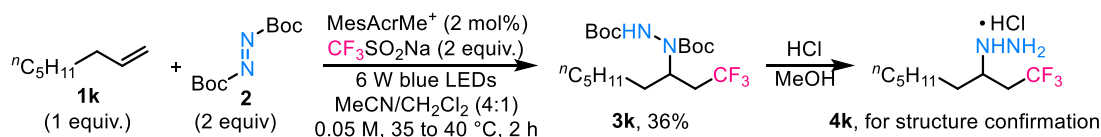
To a sealable 2-dram vial equipped with a stir bar were added  $\text{Cs}_2\text{CO}_3$  (65 mg, 0.2 mmol), **9** (73 mg, 0.2 mmol) and  $\text{MesAcrMe}^+\text{ClO}_4^-$  (1.6 mg, 0.004 mmol) in glovebox. After the vial was taken out of the glovebox, anhydrous  $\text{CH}_2\text{Cl}_2$  (0.8 mL),  $\text{CH}_3\text{CN}$  (3.2 mL) and alkene **1a** (35  $\mu\text{L}$ , 0.2 mmol) were added to the vial successively through syringes. The reaction was then stirred under the irradiation of blue light (6 W LEDs) (the photoreactor was maintained at between 35 to 40  $^\circ\text{C}$  by circulating water cooling) for 18 h. The resulted mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  (aq., 2 mL), extracted with  $\text{EtOAc}$  (2 mL  $\times$  3), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The residue was then purified through a silica gel flash column to afford product **3a** (40 mg, 42% yield).

## ii. Competing reactions between a conjugated and an isolated alkene.

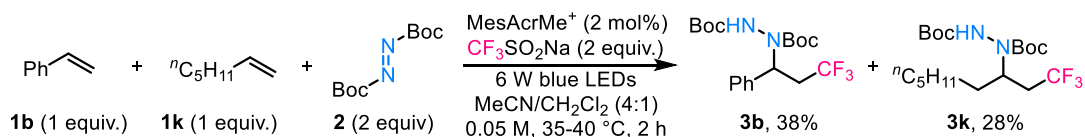


The reaction of styrene (23  $\mu\text{L}$ , 0.2 mmol) was performed by following the general procedure but quenched after 2 h. **3b** was isolated through a silica gel flash column (39 mg, 48% yield).

The purity of product **3b** was confirmed by NMR after deprotection.



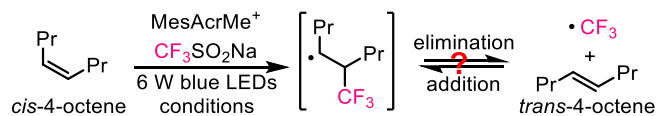
The reaction of 1-octene (32  $\mu\text{L}$ , 0.2 mmol) was also performed by following the general procedure but quenched after 3 h. **3k** was then isolated through a silica gel flash column (25 mg, 36% yield). The purity of product **3k** was confirmed by NMR after deprotection.



Styrene (23  $\mu\text{L}$ , 0.2 mmol) and 1-octene (32  $\mu\text{L}$ , 0.2 mmol) were subjected to the same reaction

by following otherwise the same procedure. When the reaction was quenched after 2 h, **3b** and **3k** were isolated through a silica gel flash column (31 mg, 38% for **3b** and 19 mg, 28% for **3k**), respectively.

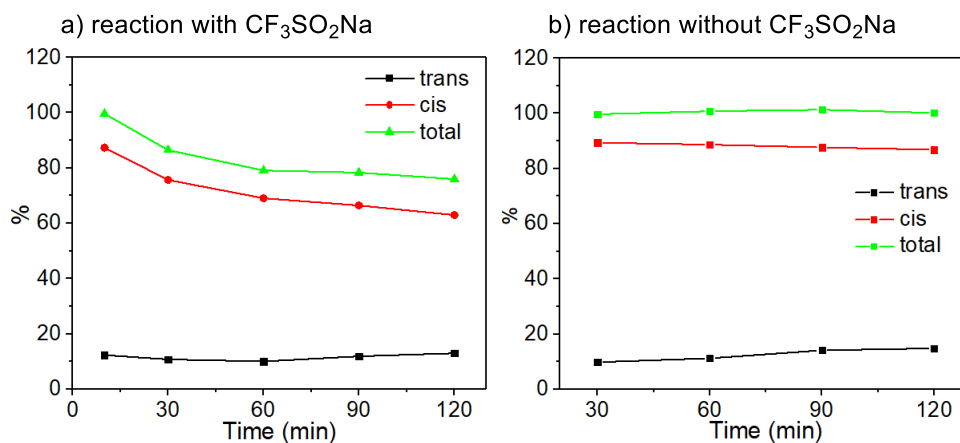
### iii. Evaluating the reversibility of trifluoromethyl radical addition.



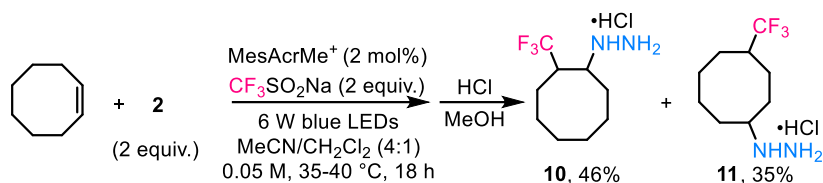
*cis*-4-Octene is commercially available and it was distilled before use.

To a sealable 2-dram vial equipped with a stir bar were added  $\text{CF}_3\text{SO}_2\text{Na}$  (62 mg, 0.4 mmol) and  $\text{MesAcrMe}^+$  (1.6 mg, 0.004 mmol) in a glovebox. After the vial was taken out of the glovebox, anhydrous  $\text{CH}_2\text{Cl}_2$  (0.8 mL) and  $\text{CH}_3\text{CN}$  (3.2 mL) were added. Then, *cis*-4-octene (32  $\mu\text{L}$ , 0.2 mmol) and dodecane (10  $\mu\text{L}$ , 0.044 mmol, as an internal standard) were added to the solution successively through syringes. The reaction was then stirred under the irradiation of blue light (6 W LEDs, the photoreactor was maintained at between 35 to 40 °C by circulating water cooling). Aliquots (20  $\mu\text{L}$ ) were taken at 30, 60, 90 and 120 min. The samples were diluted with  $\text{CH}_2\text{Cl}_2$  (0.5 mL), filtered through a Nylon 66 syringe filter and submitted for gas chromatography analysis. The recovery yields of *cis*- (red dots) and *trans*-4-octene (black dots) were summarized below. The other set of control experiments was performed accordingly but in the absence of  $\text{CF}_3\text{SO}_2\text{Na}$ .

Based on the data obtained, the generation of small amount of *trans*-4-octene could be ascribed to the photosensitizer and light irradiation. The presence of trifluoromethyl radical gradually consumed alkenes, but did not expedite the *cis*-alkene isomerization process.

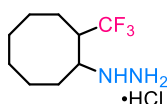


#### iv. Probing for the rate-determining step.



Cyclooctene is commercially available and it was distilled before use.

To a sealable 2-dram vial equipped with a stir bar were added di-*tert*-butyl azodicarboxylate **2** (93 mg, 0.4 mmol) and CF<sub>3</sub>SO<sub>2</sub>Na (62 mg, 0.4 mmol) and MesAcrMe<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (1.6 mg, 0.004 mmol) in glovebox. After the vial was taken out of the glovebox, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.8 mL), CH<sub>3</sub>CN (3.2 mL) and cyclooctene (26 μL, 0.2 mmol) were added successively through syringes under N<sub>2</sub>. The reaction was then stirred under the irradiation of blue light (6 W LEDs, the photoreactor was maintained at between 35 to 40 °C by circulating water cooling). The reaction process was monitored with TLC. Upon the completion of reaction, the resulted mixture was quenched with saturated NH<sub>4</sub>Cl (aq., 2 mL), extracted with EtOAc (2 mL × 3), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was then purified through a silica gel flash column to afford 2 major products, which were then subjected for deprotection with HCl in MeOH (same as the general procedure). After the removal of the solvent, hydrazinium chlorides **10** (foam, 23 mg, 46% yield) and **11** (foam, 18 mg, 35% yield) were obtained, respectively.

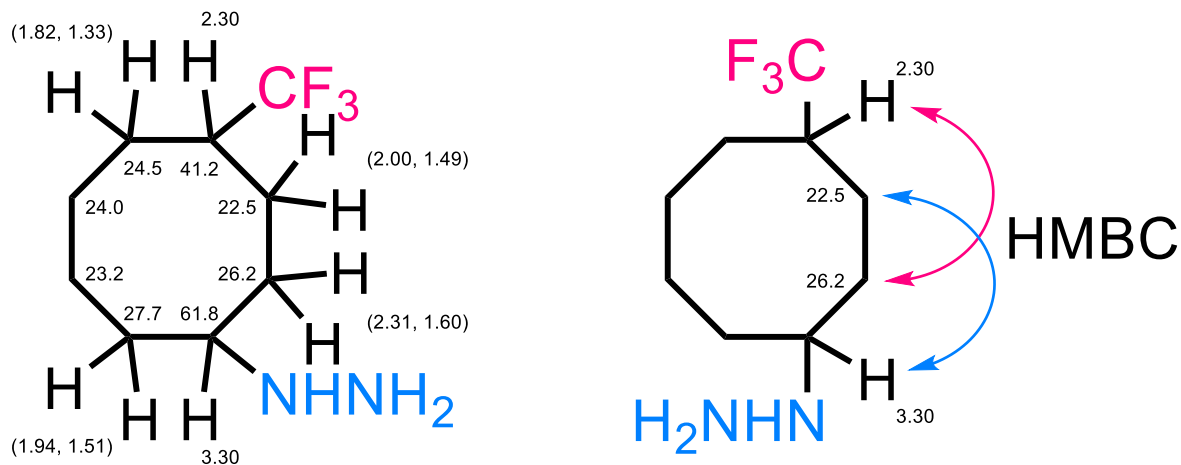


**(2-(Trifluoromethyl)cyclooctyl)hydrazine hydrochloride (10)**: Compound **10** was derived from the less polar isomer and confirmed as a single diastereomer of 1,2-difunctionalization product by <sup>1</sup>H-<sup>1</sup>H COSY analysis. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 3.59 – 3.39 (m, 1H), 2.58 – 2.33 (m, 1H), 1.98 – 1.76 (m, 4.3 Hz, 3H), 1.75 – 1.49 (m, 5H), 1.46 – 1.29 (m, 2H), 1.25 (d, *J* = 9.7 Hz, 2H); <sup>19</sup>F NMR (376 MHz, D<sub>2</sub>O) δ -68.31; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD) δ 128.2 (q, *J* = 280.3 Hz), 57.0, 44.8 (q, *J* = 23.4 Hz), 27.1, 25.7, 25.3, 25.2, 23.8, 22.6 (q, *J* = 2.8 Hz); IR  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup>: 2925, 2855, 1731, 1601, 1507, 1373, 1255, 1145, 742; HRMS (ESI, *m/z*): calcd for C<sub>9</sub>H<sub>19</sub>ClF<sub>3</sub>N<sub>2</sub><sup>+</sup> [*M* + *H*]<sup>+</sup> 247.1189, found 247.1185.

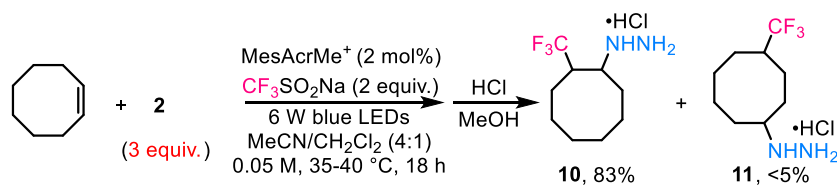
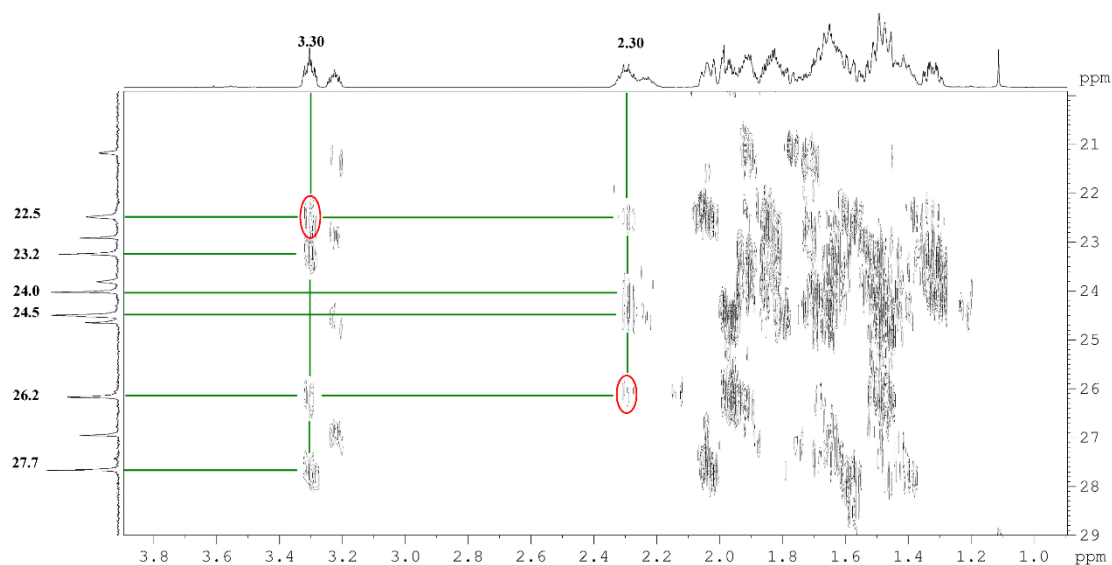


**(4-(Trifluoromethyl)cyclooctyl)hydrazine hydrochloride (11):** Compound **11** was derived from the more polar isomer as a pair of diastereomers (2:1).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  3.28 – 3.19 (m, 1H, major), 3.19 – 3.10 (m, 1H, minor), 2.35 – 2.06 (m, 1H), 2.02 – 1.68 (m, 4H), 1.68 – 1.18 (m, 8H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -72.92 (d,  $J = 10.1$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  128.67 (q,  $J = 279.2$  Hz) (minor), 128.64 (q,  $J = 279.2$  Hz) (major), 61.8 (major), 61.6 (minor), 41.2 (q,  $J = 24.5$  Hz) (major), 40.6 (q,  $J = 24.4$  Hz) (minor), 27.7 (major), 27.0 (minor), 26.2 (major), 24.7 (minor), 24.5 (major + minor), 24.0 (major), 23.8 (minor), 23.3 (major), 23.0 (minor), 22.5 (q,  $J = 2.3$  Hz) (major), 21.2 (q,  $J = 2.3$  Hz) (minor); IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$ : 2930, 2858, 1601, 1471, 1396, 1340, 1266, 1164, 1137, 1115, 740; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_9\text{H}_{19}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  247.1189, found 247.1186.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift of the major isomer was assigned by using  $^1\text{H}$ - $^1\text{H}$  COSY and HSQC, and the values are depicted as follows

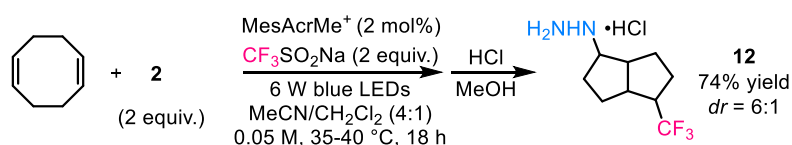


The major isomer was then identified as a 1,4-trifluoromethyl-hydrazination product by HMBC analysis. In addition, the minor isomer follows the same pattern on HMBC, so, the two isomers are highly likely a pair of diastereomers.



As a consequence, when the amount of BocN=NBoc was increased to 3 equiv. (0.6 mmol), the selectivity towards 1,2-trifluoro-hydrazination was significantly improved, affording **10** in 83% yield (41 mg) after deprotection.

#### v. The reaction of 1,5-cyclooctadiene.



1,5-cyclooctadiene is commercially available and it was distilled before use.

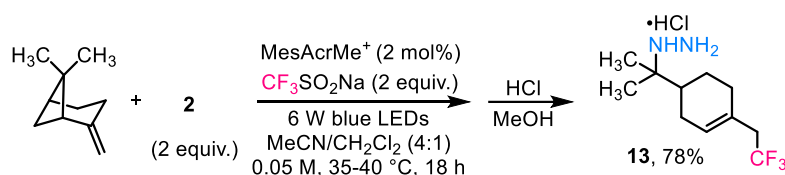
**(4-(Trifluoromethyl)octahydropentalen-1-yl)hydrazine (12):** The reaction of 1,5-cyclooctadiene (25  $\mu$ L, 0.2 mmol) was performed by following the general procedure. After deprotection, two diastereomers of a bicyclic hydrazinium salt **12** were afforded in 63% (31 mg) and 11% (5 mg) yields, respectively.

**Major isomer:** (foam, 31 mg, 63% yield),  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  3.32 – 3.08 (m, 1H), 2.71 – 2.53 (m, 1H), 2.53 – 2.44 (m, 1H), 2.40 – 2.21 (m, 1H), 2.04 – 1.90 (m, 2H), 1.90 – 1.74 (m, 2H), 1.76 – 1.60 (m, 1H), 1.62 – 1.50 (m, 1H), 1.50 – 1.36 (m, 1H), 1.36 – 1.22 (m, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -70.53 (d,  $J = 9.5$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  128.3

(q,  $J = 277.2$  Hz), 68.4, 49.1 (q,  $J = 26.1$  Hz), 46.2, 43.2, 30.7, 29.5, 28.5, 27.2; IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 2973, 1682, 1517, 1395, 1316, 1267, 1158, 1103, 1088, 1047, 734, 701; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_9\text{H}_{17}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  245.1032, found 245.1037.

**Minor isomer:** (foam, 5 mg, 11% yield),  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  3.58 – 3.45 (m, 1H), 2.89 – 2.73 (m, 1H), 2.62 – 2.53 (m, 1H), 2.45 – 2.28 (m, 1H), 2.16 – 2.06 (m, 1H), 2.04 – 1.76 (m, 4H), 1.72 – 1.57 (m, 1H), 1.41 – 1.34 (m, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -70.58 (d,  $J = 10.0$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  128.2 (q,  $J = 277.2$  Hz), 68.4, 49.1 (q,  $J = 26.1$  Hz), 46.3, 43.2, 30.7, 29.5, 28.5, 27.2; IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 2966, 1682, 1516, 1395, 1317, 1264, 1154, 1104, 735, 701; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_9\text{H}_{17}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  245.1032, found 245.1030.

## vi. The reaction of $\beta$ -pinene.

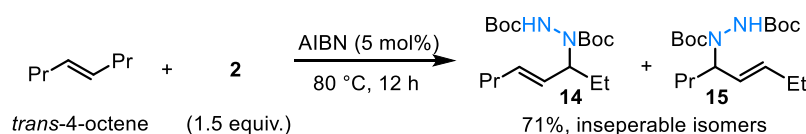


$\beta$ -pinene is commercially available and it was distilled before use.

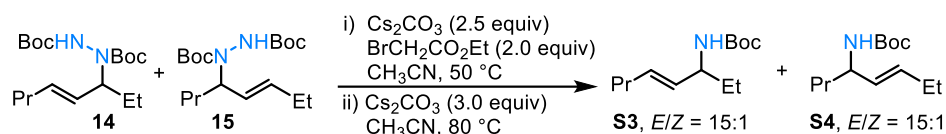
### (2-(4-(2,2,2-Trifluoroethyl)cyclohex-3-en-1-yl)propan-2-yl)hydrazine hydrochloride (**13**):

The reaction of  $\beta$ -pinene (31  $\mu\text{L}$ , 0.2 mmol) was performed by following the general procedure. A ring-opening compound **13** was obtained after deprotection (foam, 43 mg, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  5.79 – 5.71 (m, 1H), 2.85 (q,  $J = 11.4$  Hz, 2H), 2.33 – 2.09 (m, 3H), 2.06 – 1.86 (m, 3H), 1.38 – 1.34 (m, 1H), 1.33 (s, 3H), 1.31 (s, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  -67.82 (t,  $J = 11.3$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  127.8, 127.2, 126.4 (q,  $J = 278.2$  Hz), 63.6, 40.7 (q,  $J = 28.8$  Hz), 38.1, 28.8, 25.9, 23.1, 18.8, 18.7; IR  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$ : 2978, 1703, 1454, 1365, 1256, 1160, 1129, 1083, 737; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{21}\text{ClF}_3\text{N}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  273.1345, found 273.1350.

## vi. Allylic hydrazination via a radical chain process.

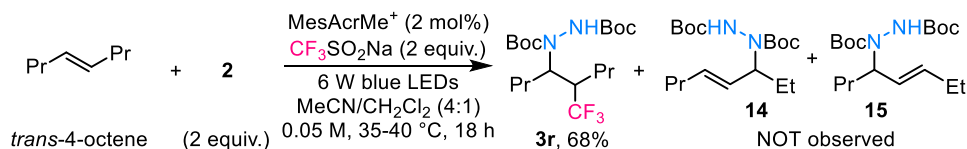


To a sealable tube equipped with a stir bar were added di-*tert*-butyl azodicarboxylate **2** (70 mg, 0.3 mmol) and AIBN (1.7 mg, 0.01 mmol). After the vial was evacuated and backfilled with N<sub>2</sub> three times, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.6 mL) and CH<sub>3</sub>CN (0.4 mL) and *trans*-4-octene (31 μL, 0.2 mmol) were added successively through syringes. The reaction was then stirred at 80 °C in an oil bath for 12 h. After the completion of the reaction, the resulted mixture was concentrated *in vacuo* to afford the crude product, which was then purified through a silica gel flash column to afford products **14** and **15** as a pair of inseparable isomers.

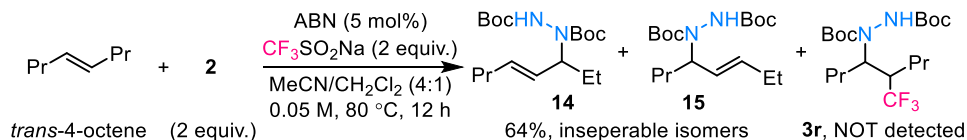


Compounds **14** and **15** were identified after N–N cleavage according to a literature procedure,<sup>[10]</sup> and the characterization data of **S3** and **S4** are in accordance with the literature. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.70 – 5.53 (m, 1H), 5.32 (dd, *J* = 15.4, 6.4 Hz, 1H), 4.43 (brs, 1H), 4.15 – 3.70 (m, 1H), 2.10 – 1.92 (m, 2H), 1.58 – 1.48 (m, 2H), 1.46 (s, 9H), 1.43 – 1.31 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 1.5H), 0.96 – 0.87 (m, 4.5H).

### vii. Side product analysis in catalytic reaction and chain reaction.



Compound **3r** was obtained from the reaction of *trans*-4-octene (31 μL, 0.2 mmol) under the standard conditions (56 mg, 68% yield), while **14** and **15** were not observed.



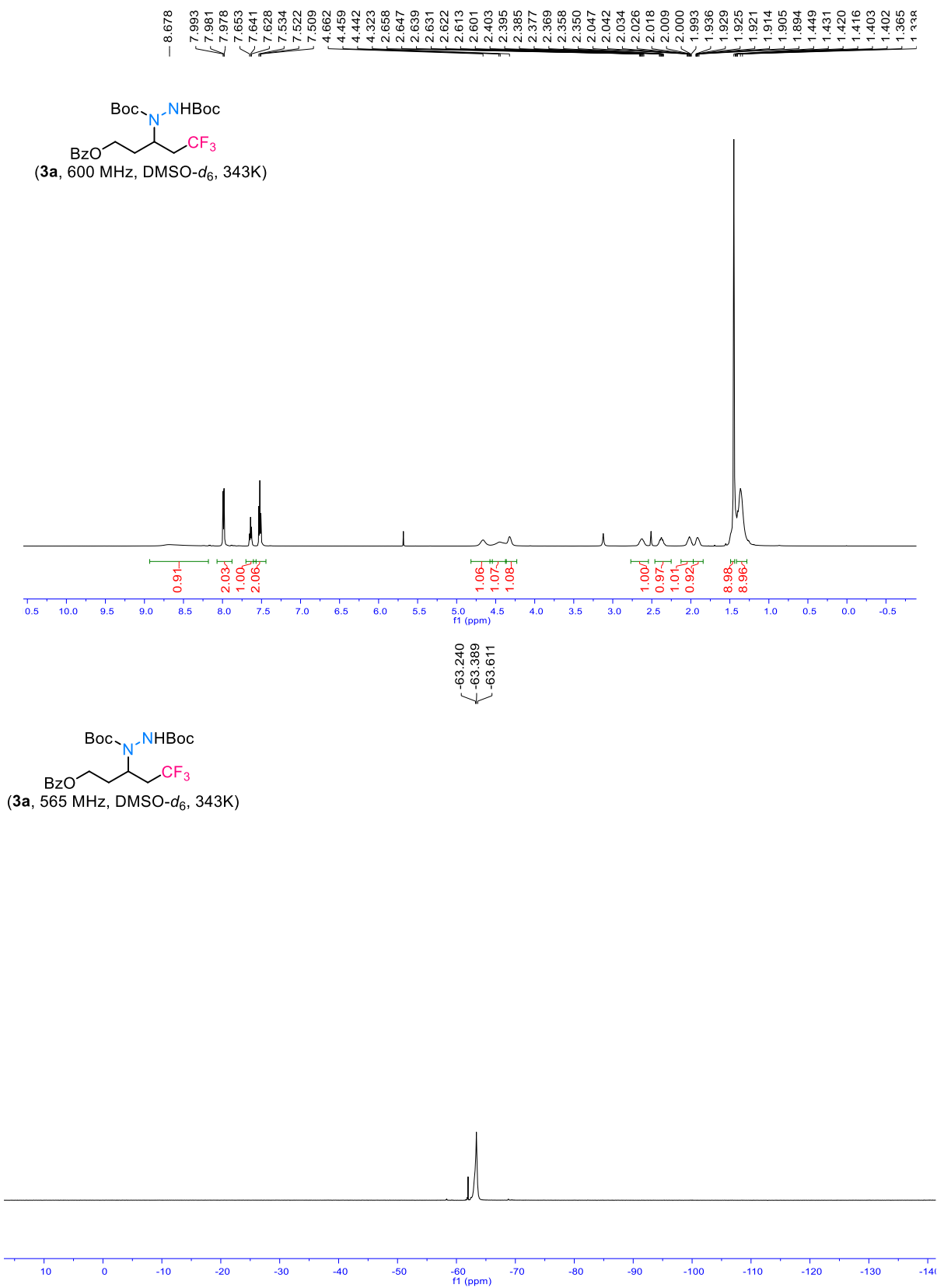
To a sealable 2-dram vial equipped with a stir bar were added di-*tert*-butyl azodicarboxylate **2** (93 mg, 0.4 mmol), CF<sub>3</sub>SO<sub>2</sub>Na (64 mg, 0.4 mmol) and AIBN (1.7 mg, 0.01 mmol). After the vial was evacuated and backfilled with N<sub>2</sub> three times, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.6 mL) and CH<sub>3</sub>CN (0.4 mL) and *trans*-4-octene (31 μL, 0.2 mmol) were added successively through syringes. The reaction was then stirred at 80 °C in an oil bath for 12 h. After the completion of the reaction,

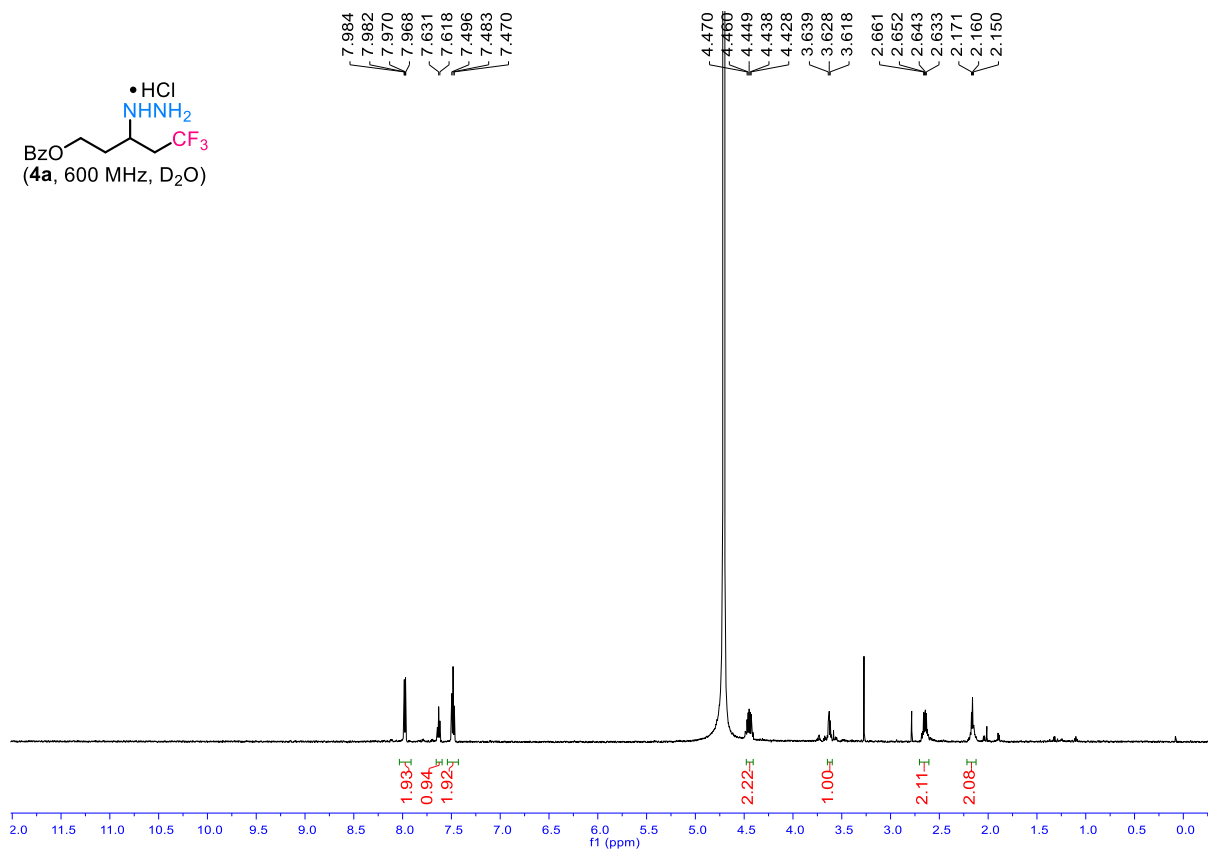
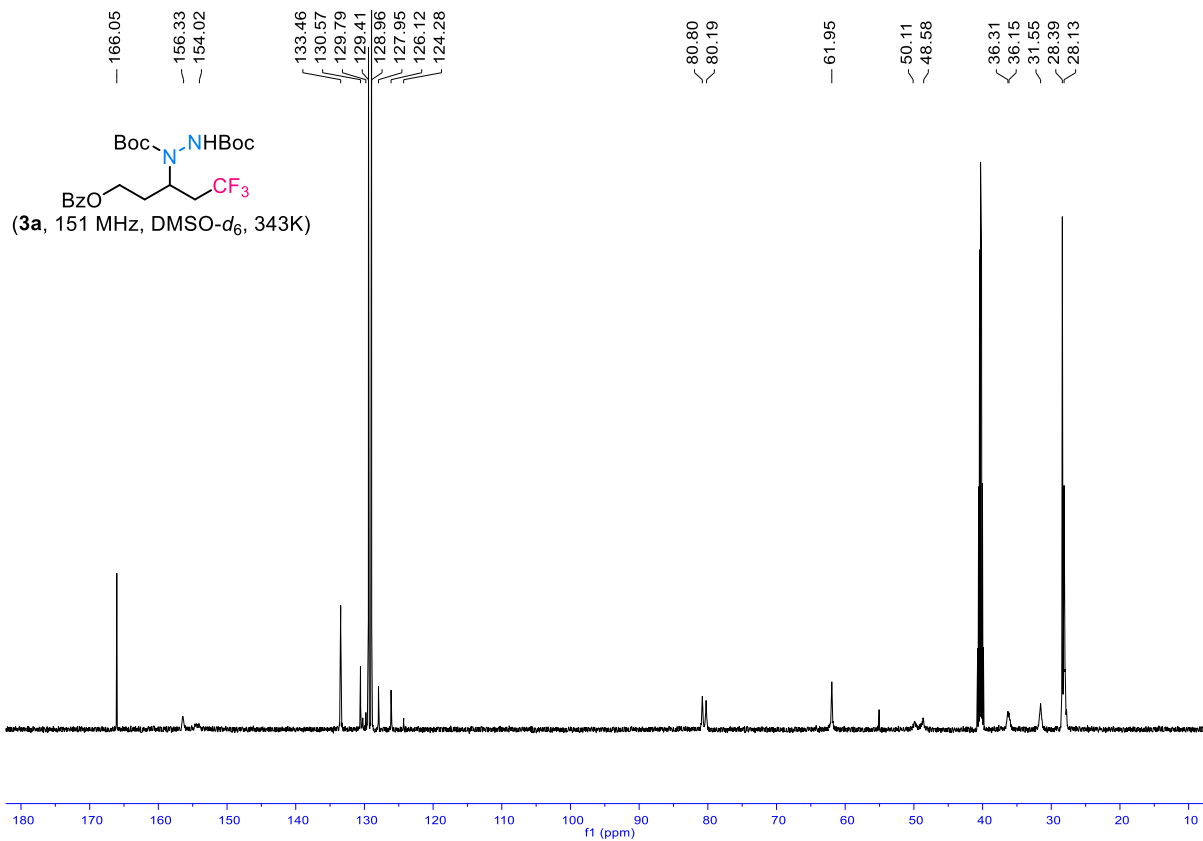
allylic hydrazination products **14** and **15** were generated as the major product without the detection of **3r**.

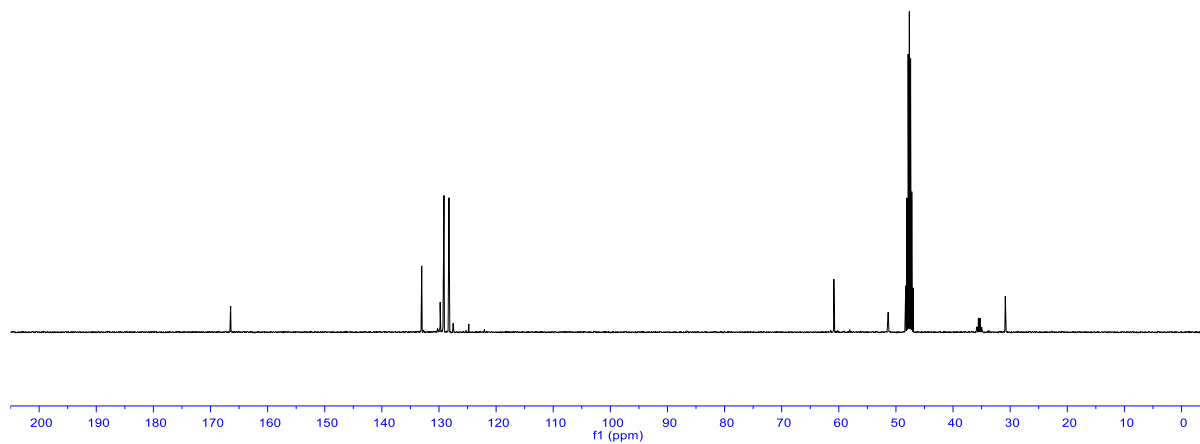
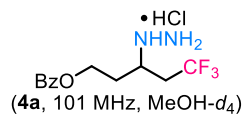
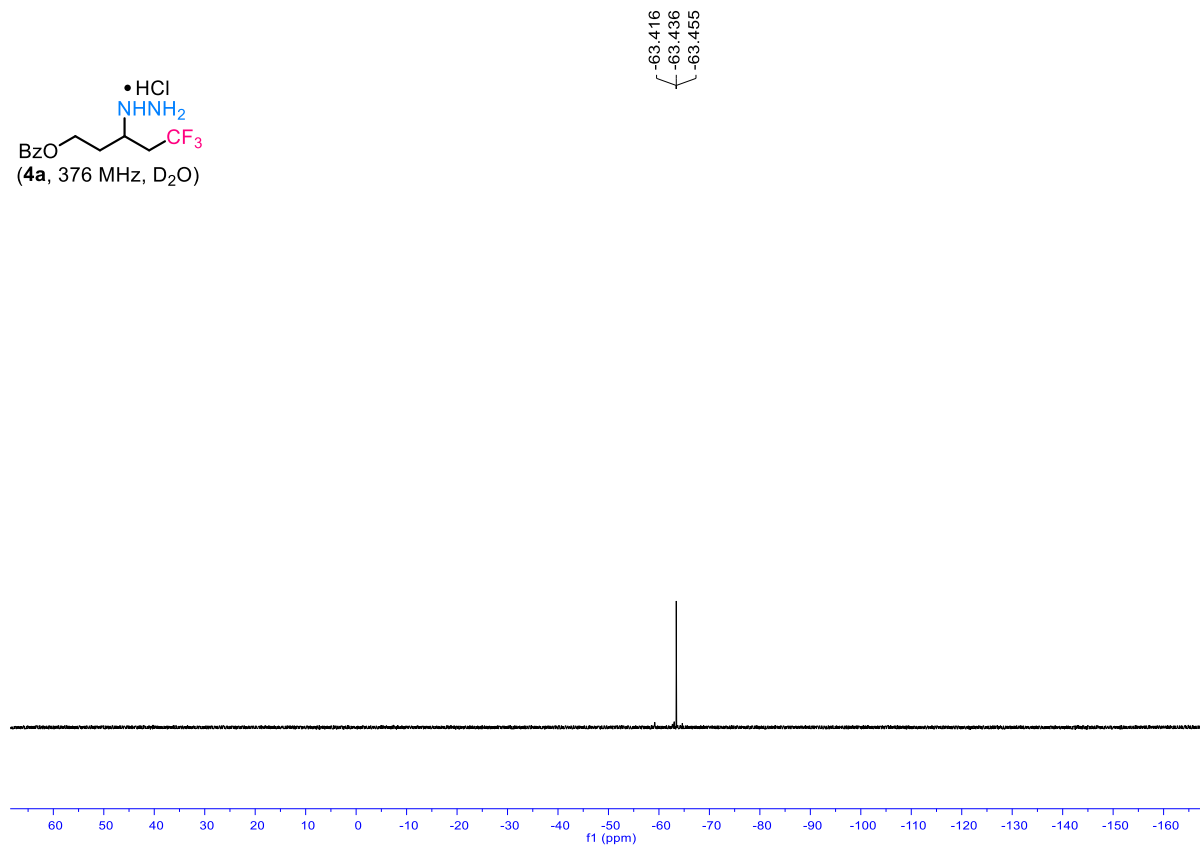
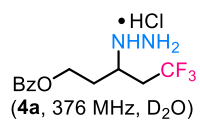
## VI. References

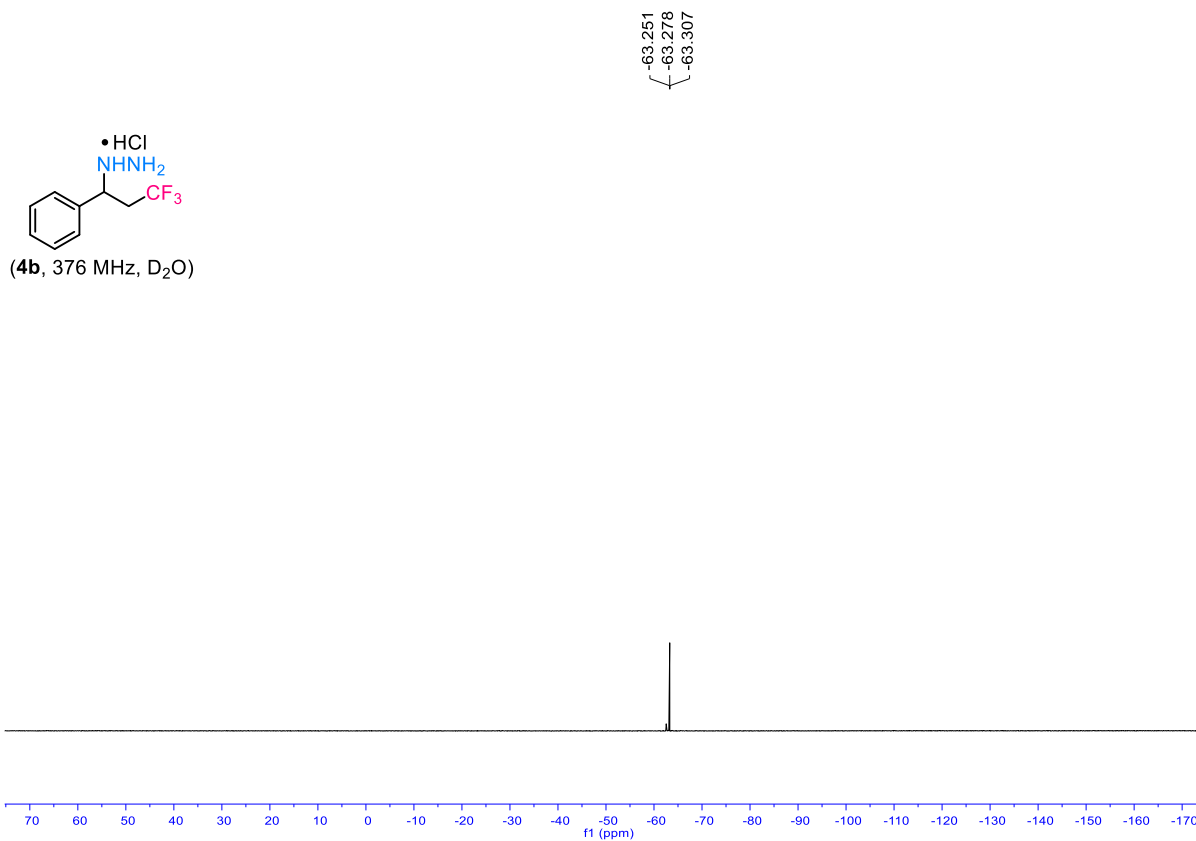
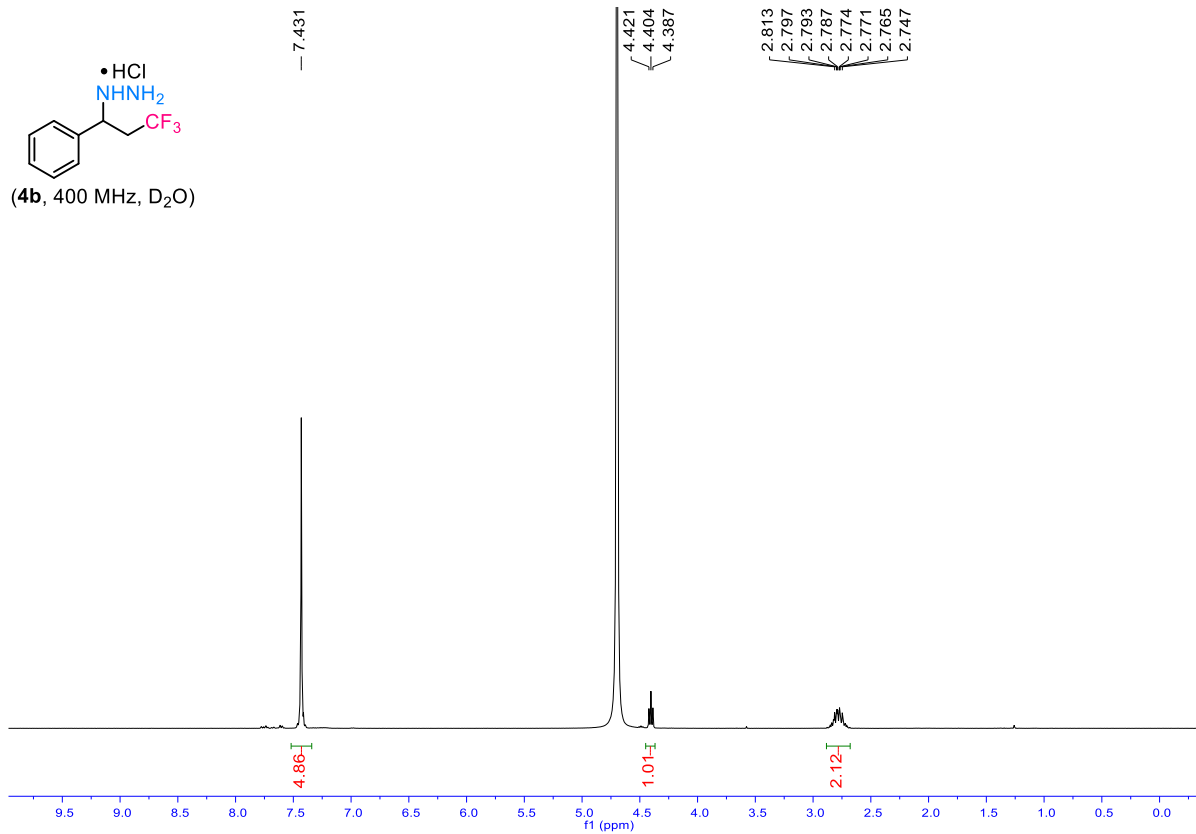
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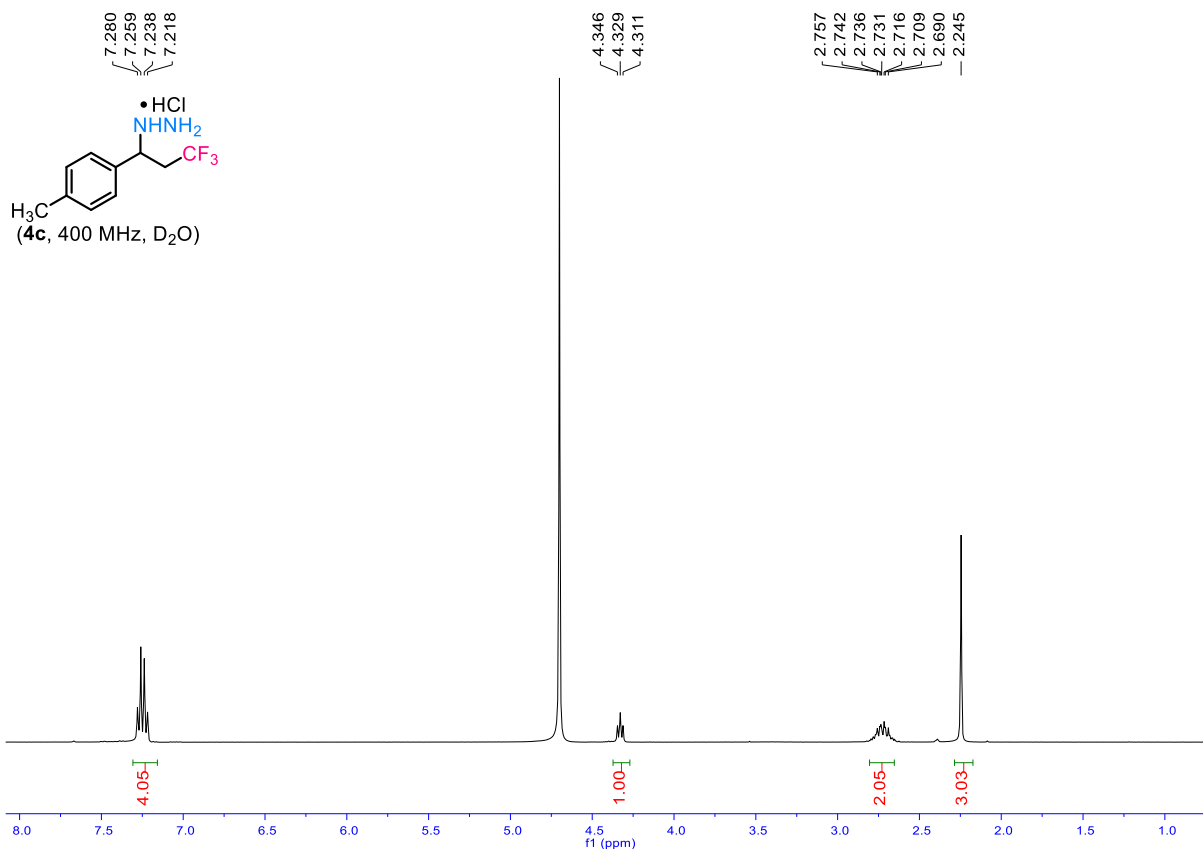
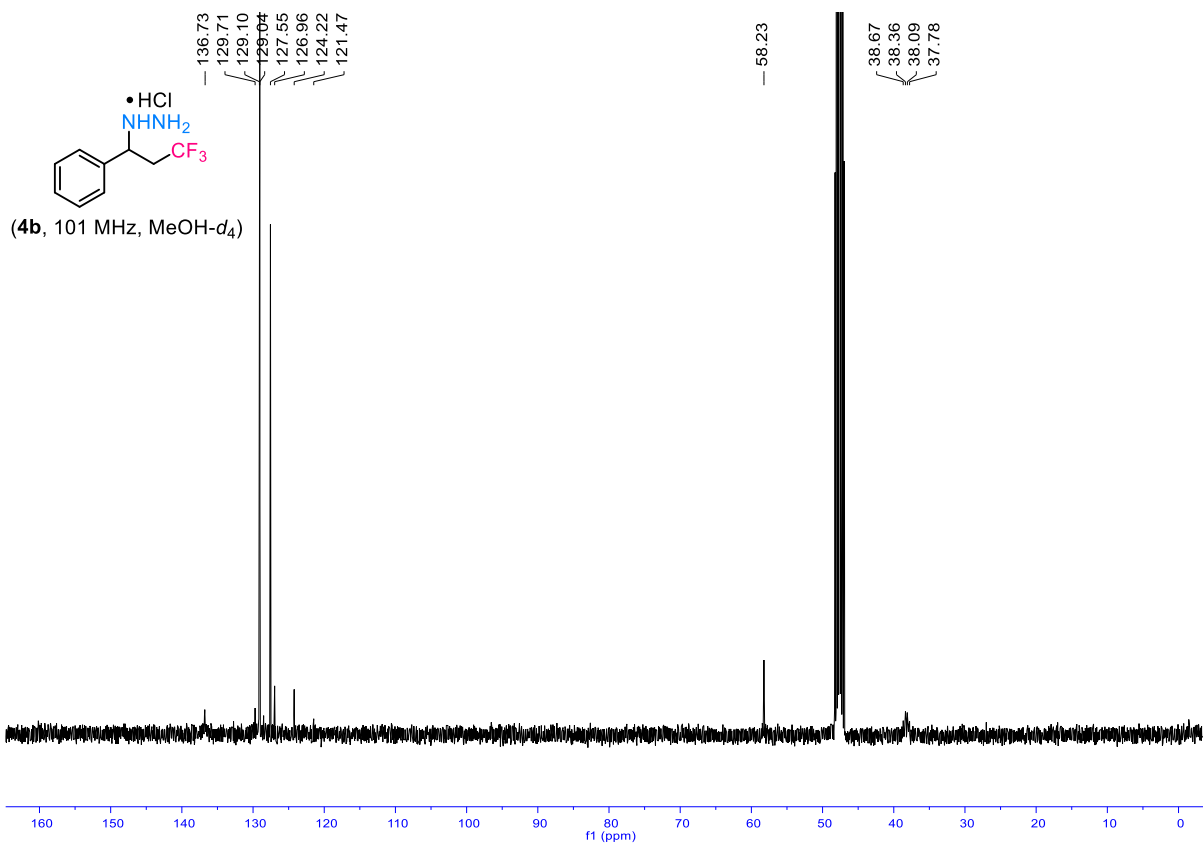
# VII. $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra of New Compounds

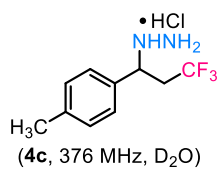




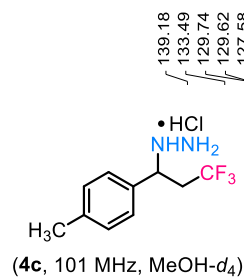
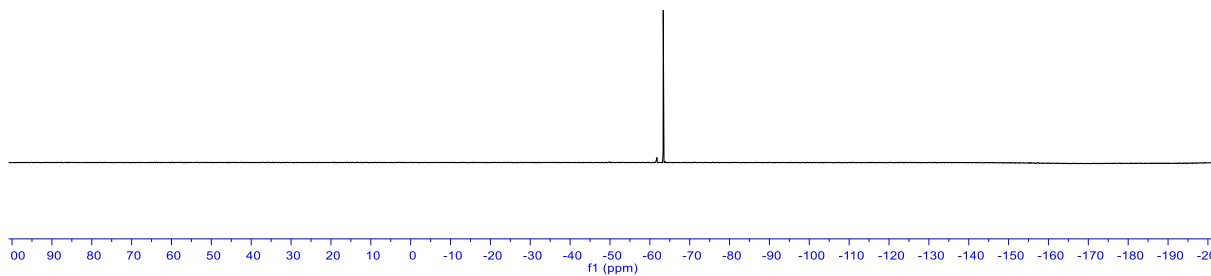








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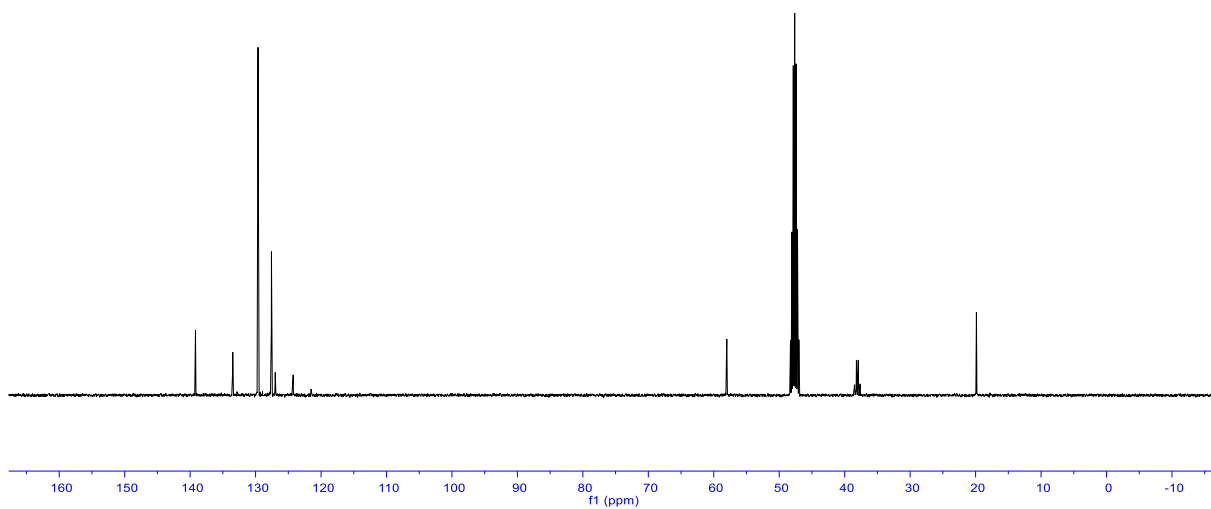


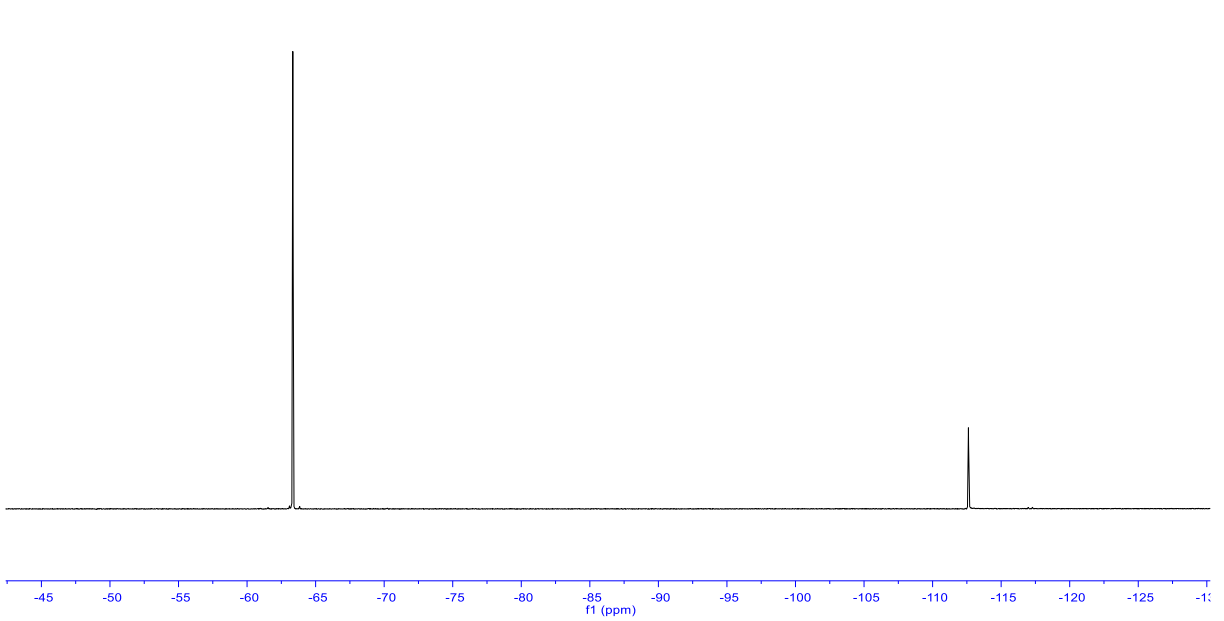
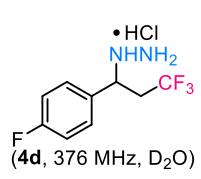
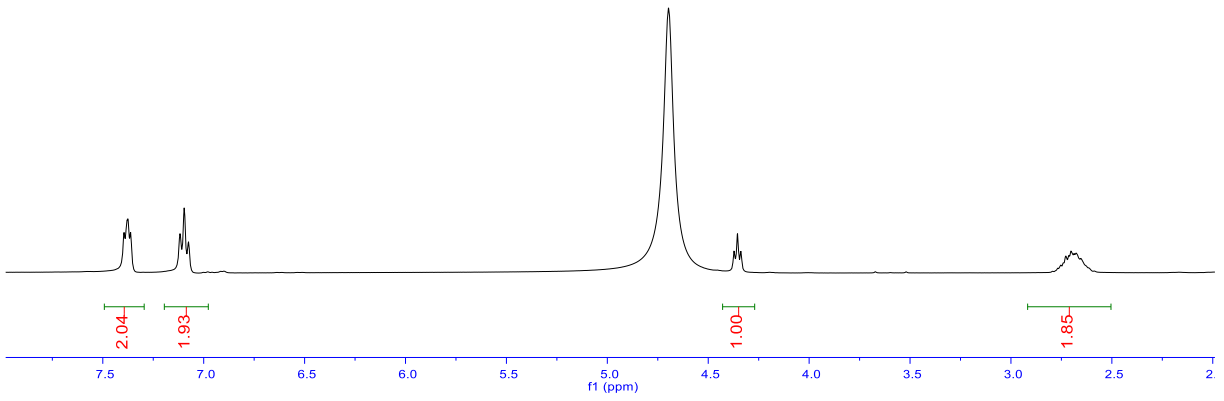
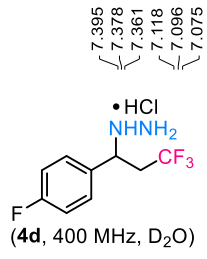
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58.01

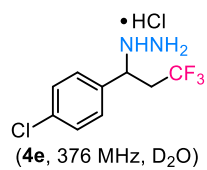
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19.88

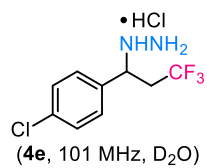
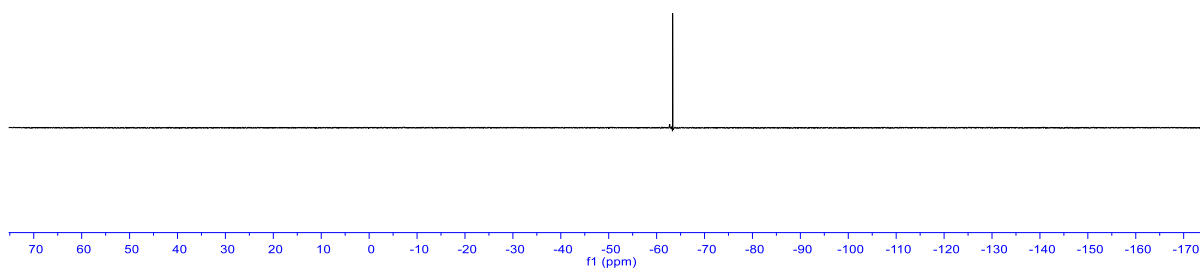








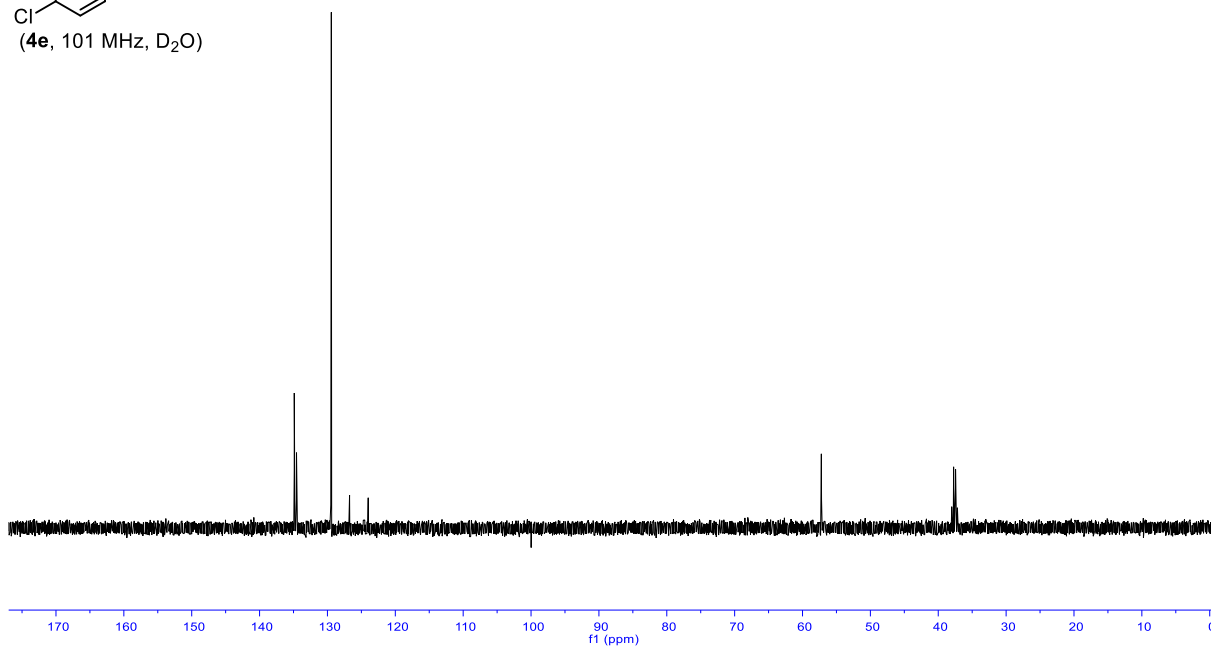
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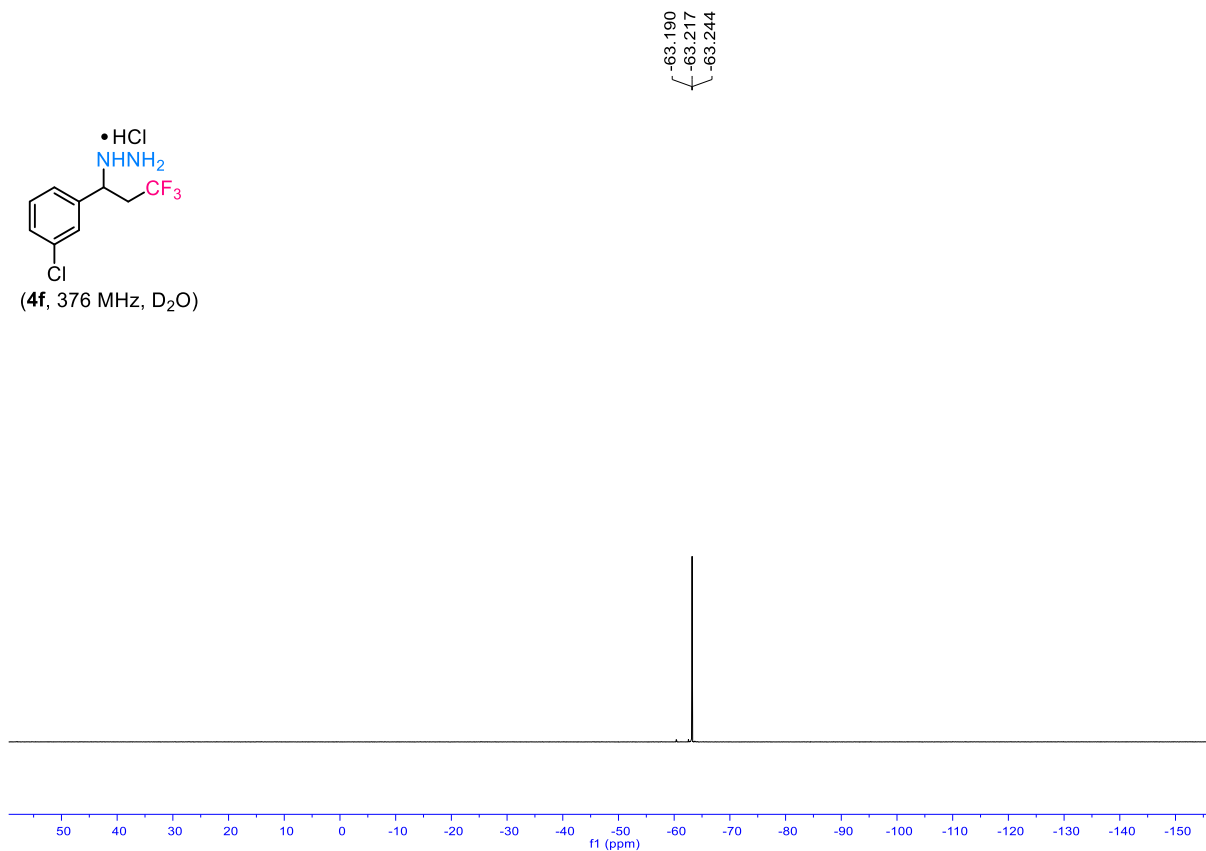
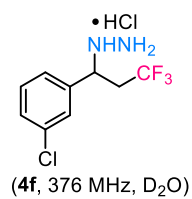
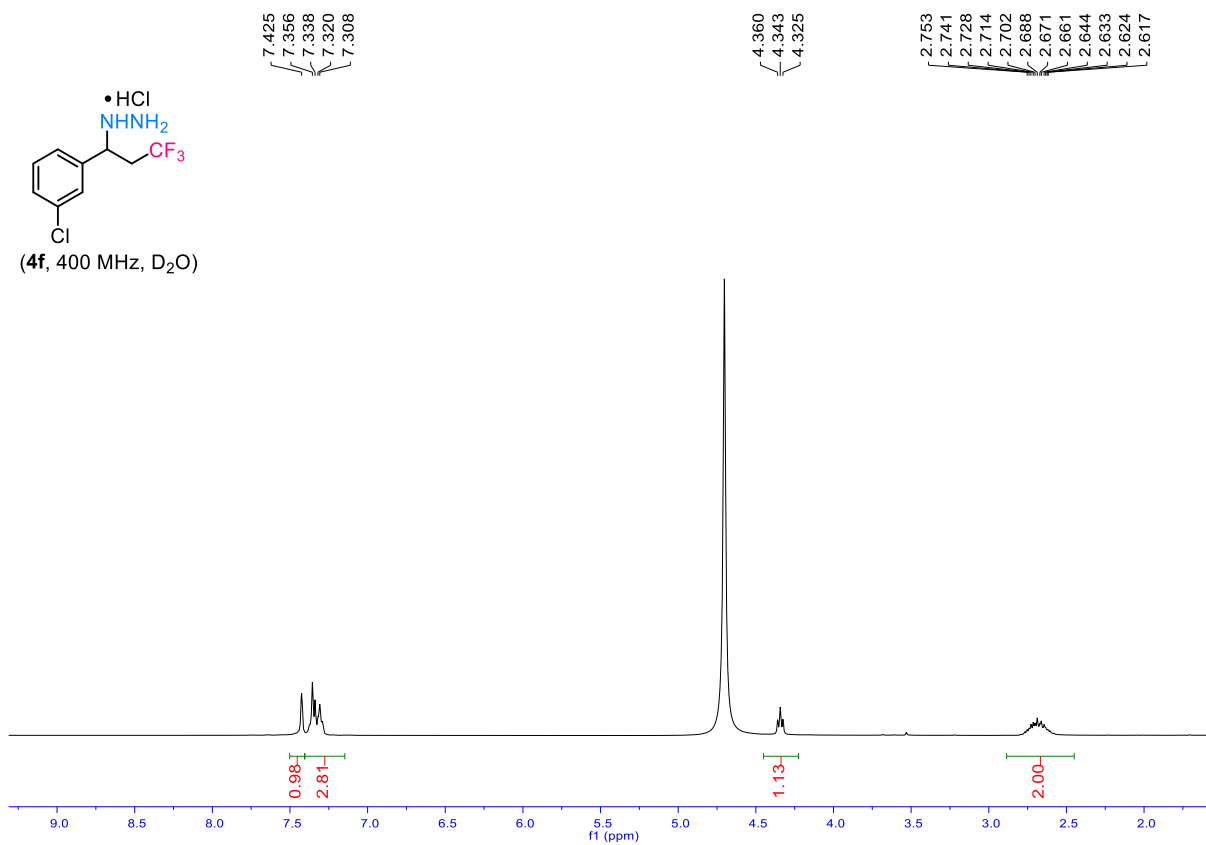
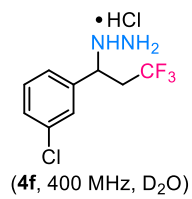


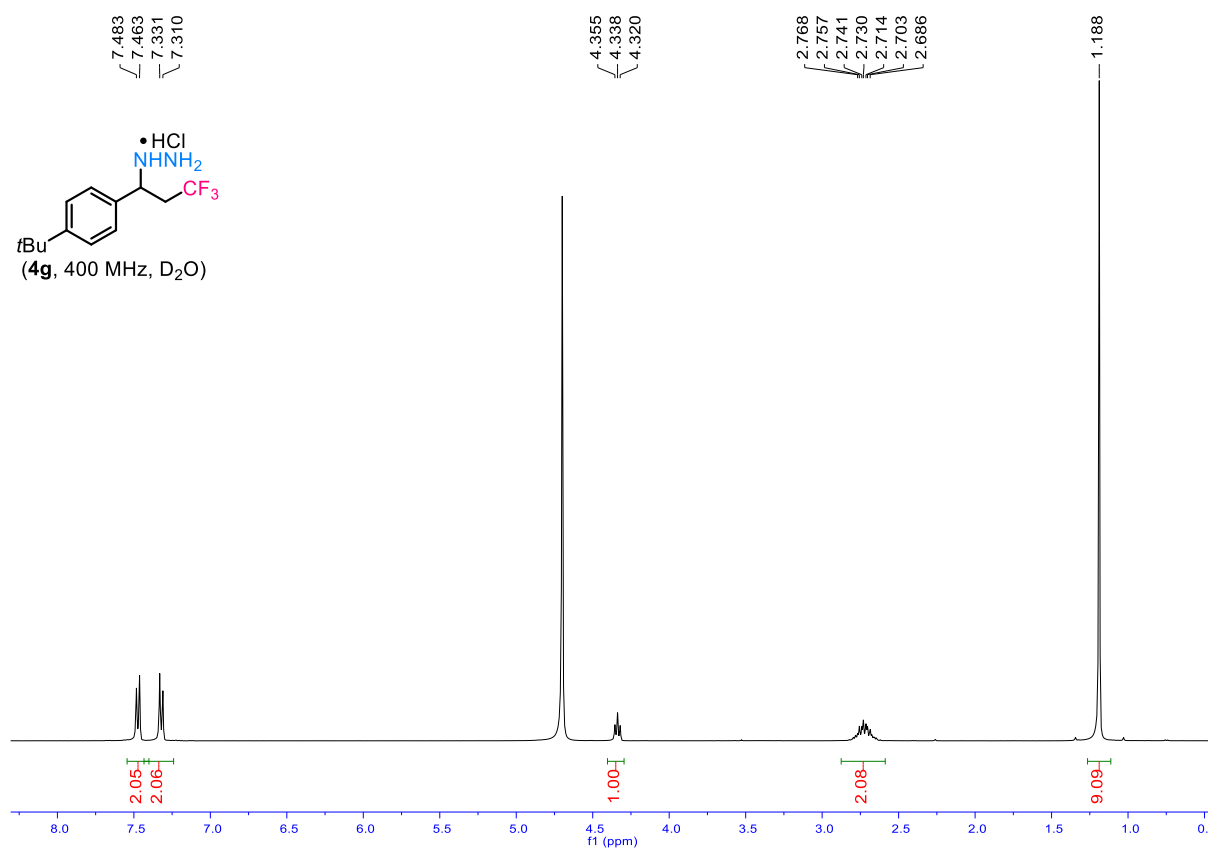
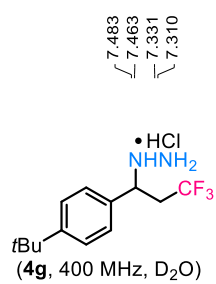
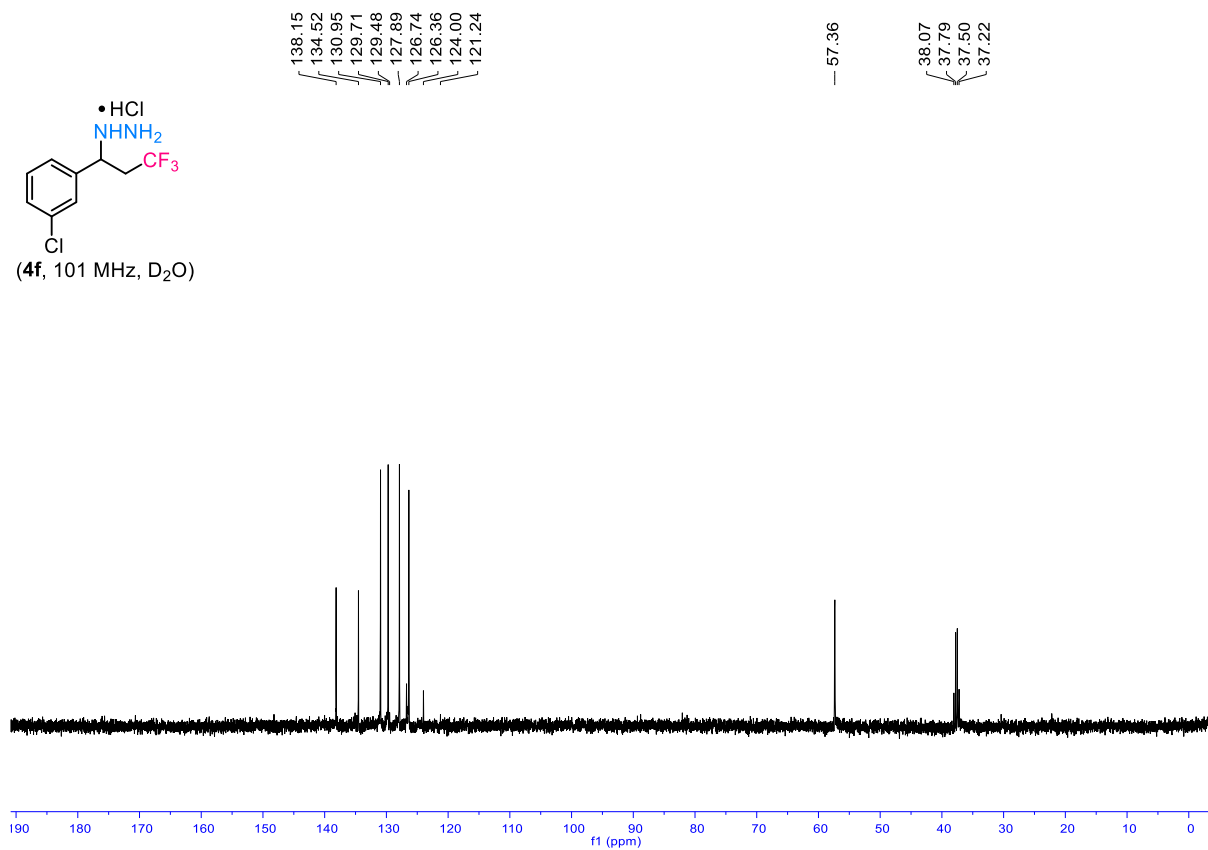
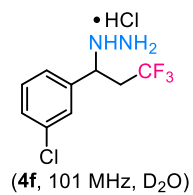
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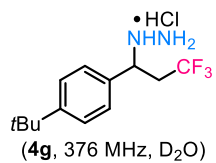
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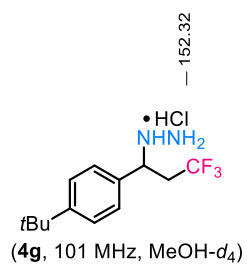
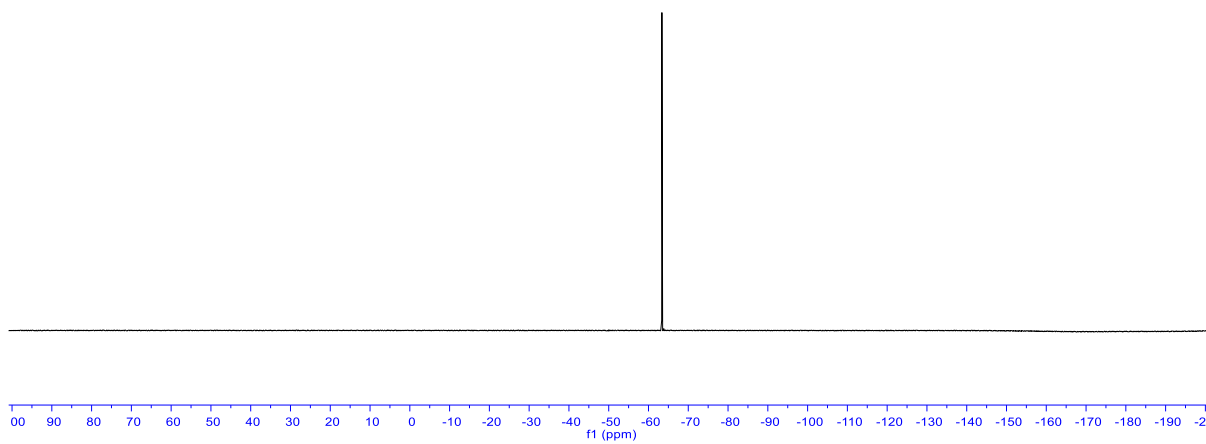








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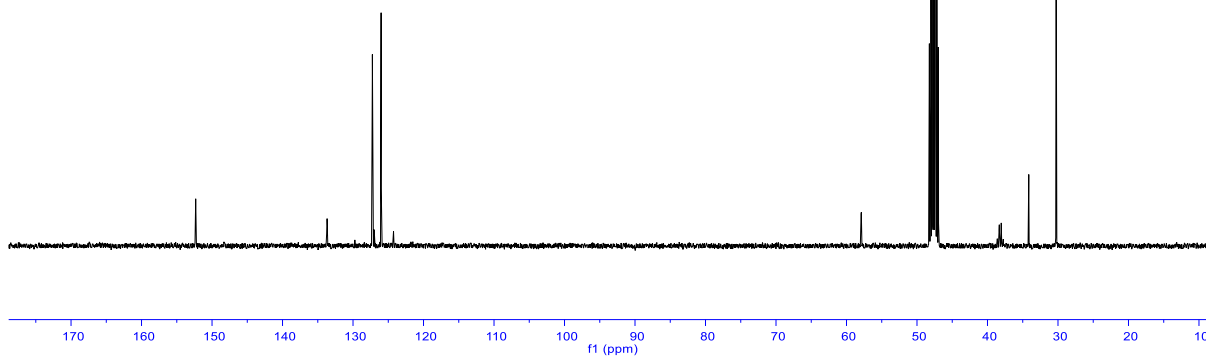


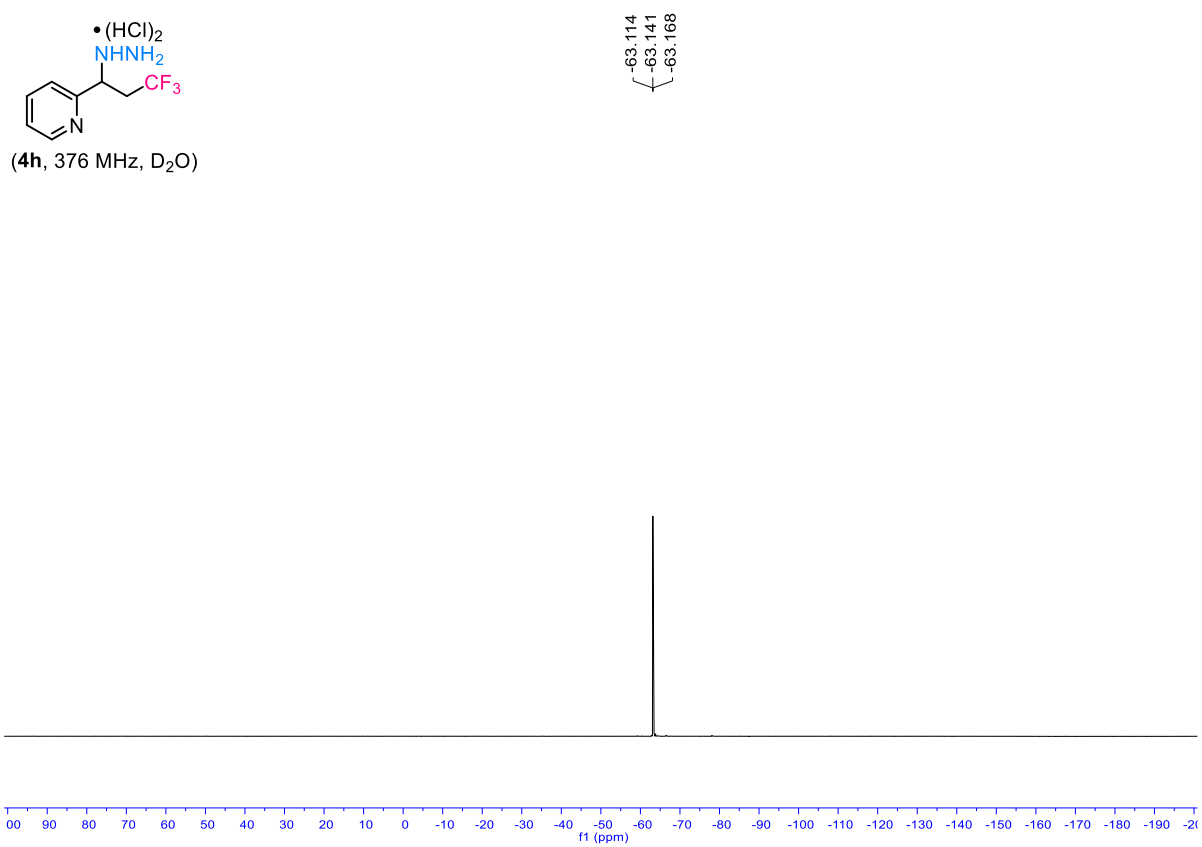
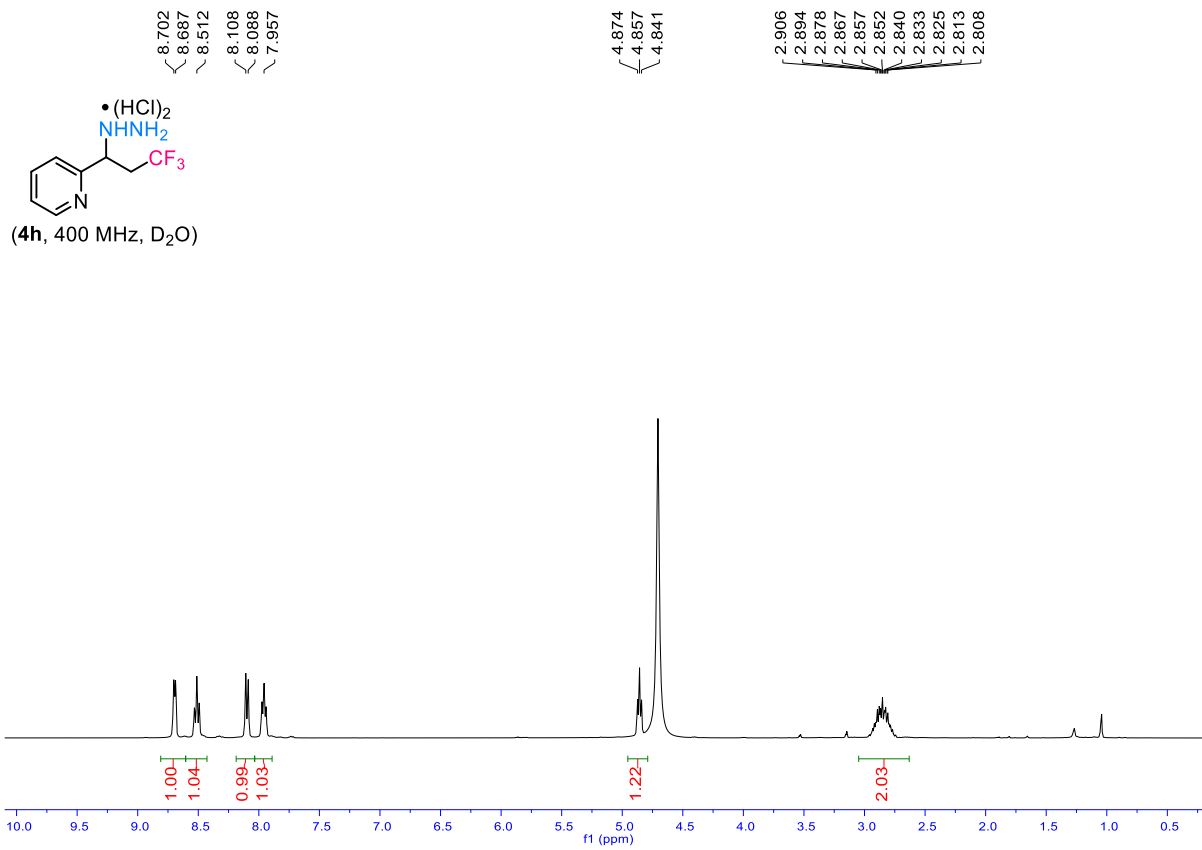
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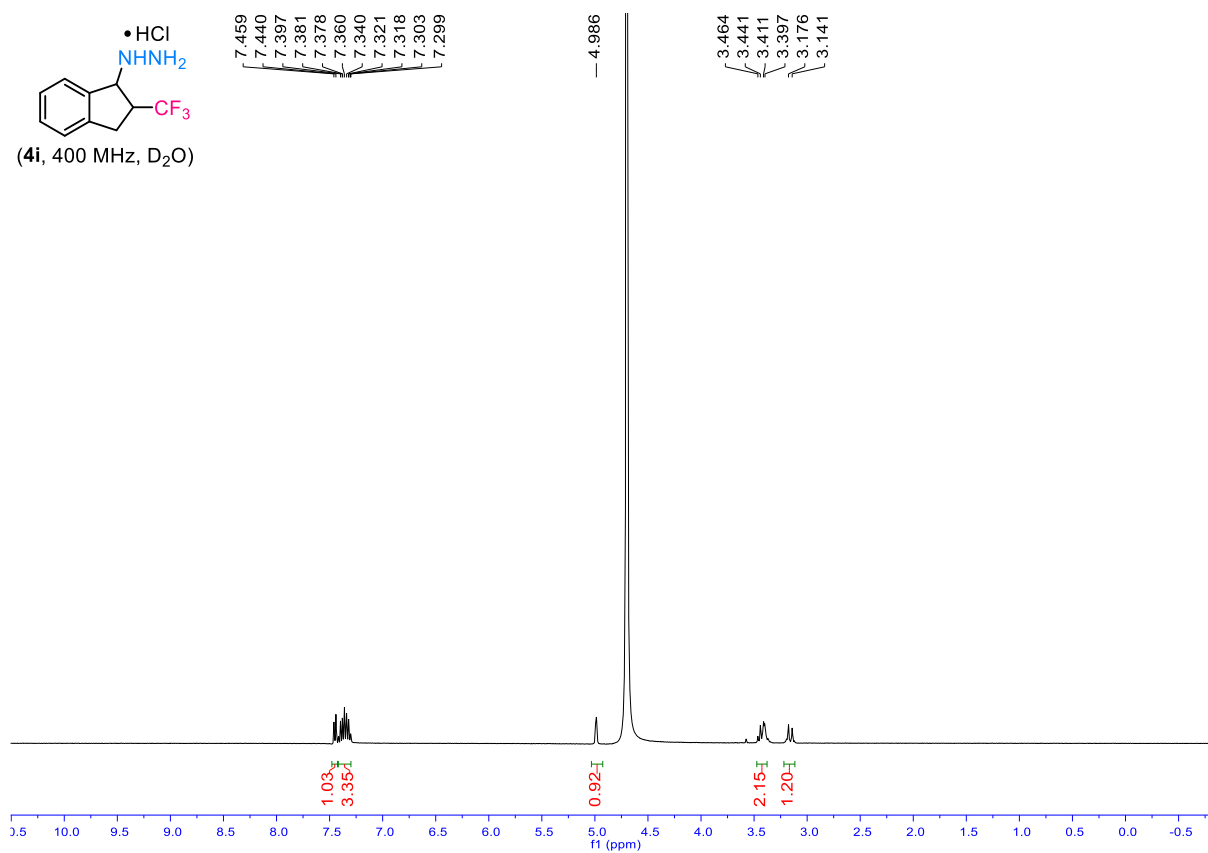
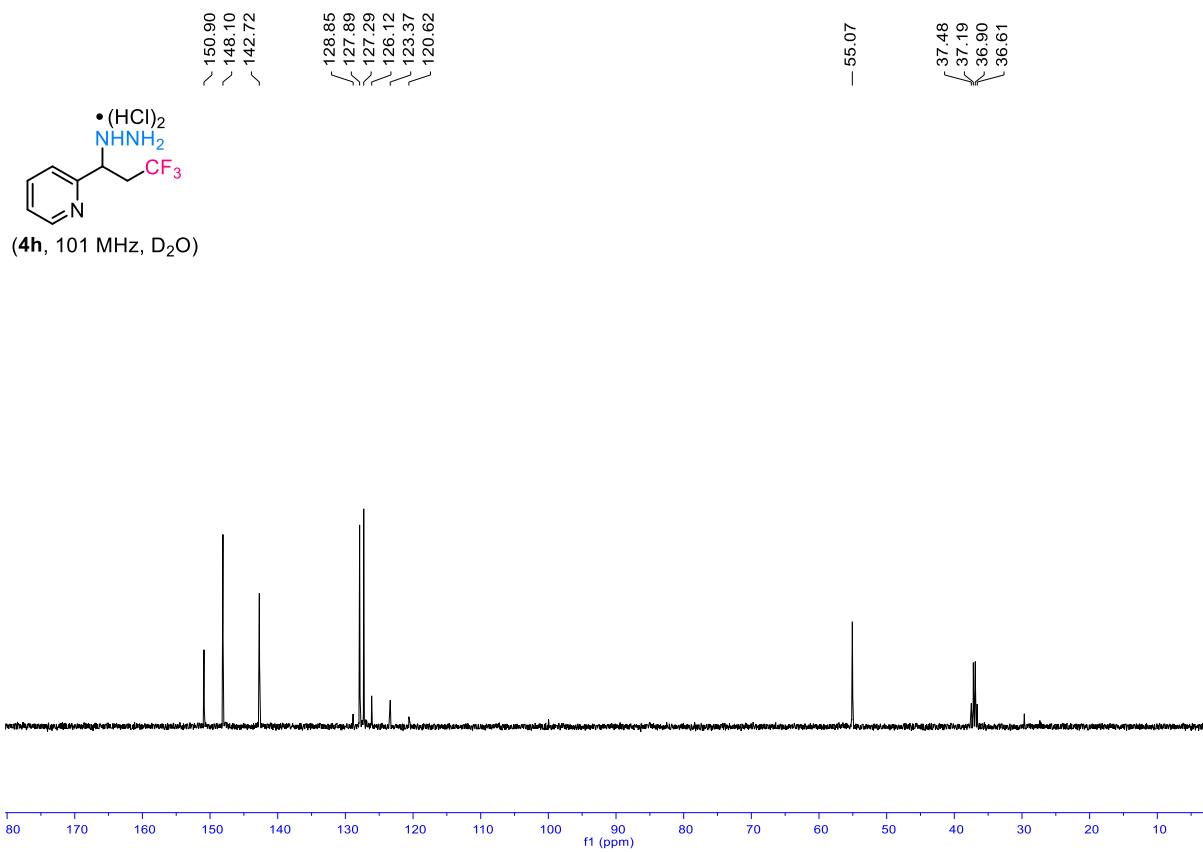
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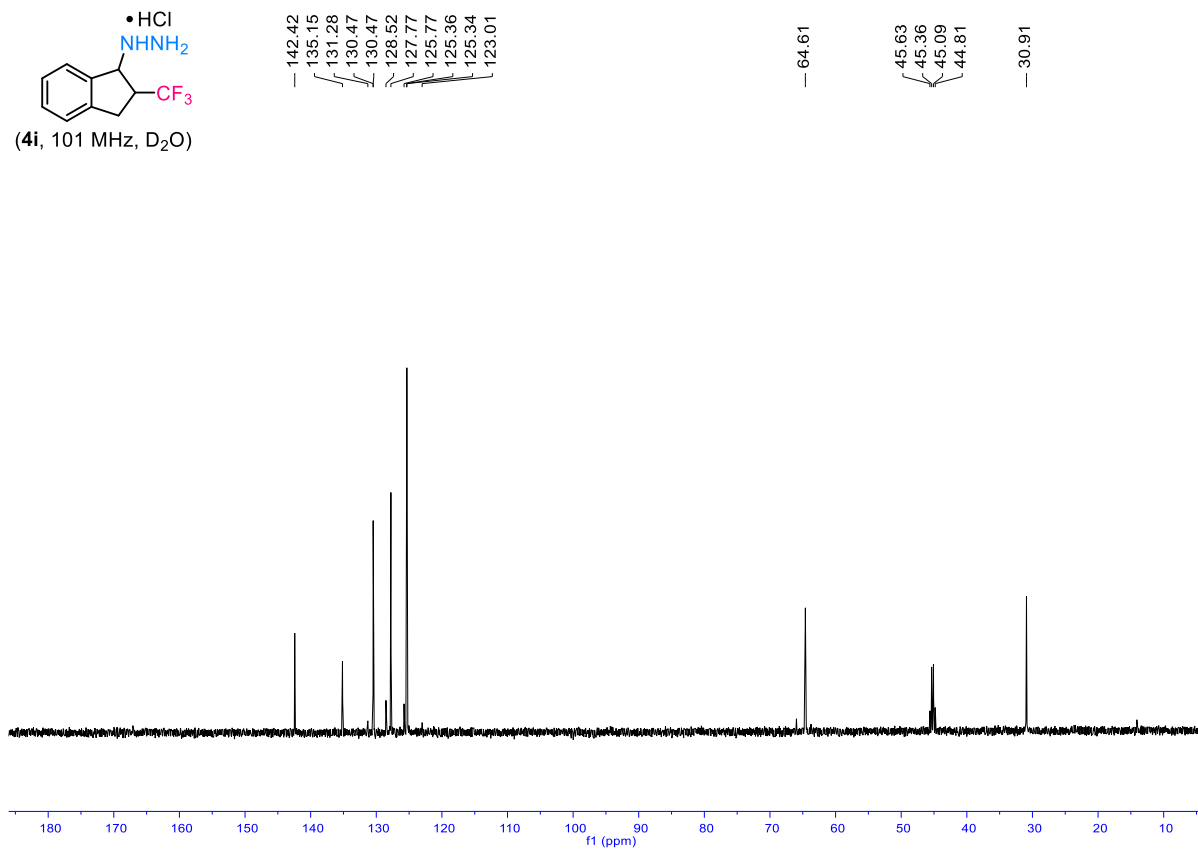
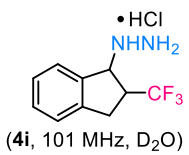
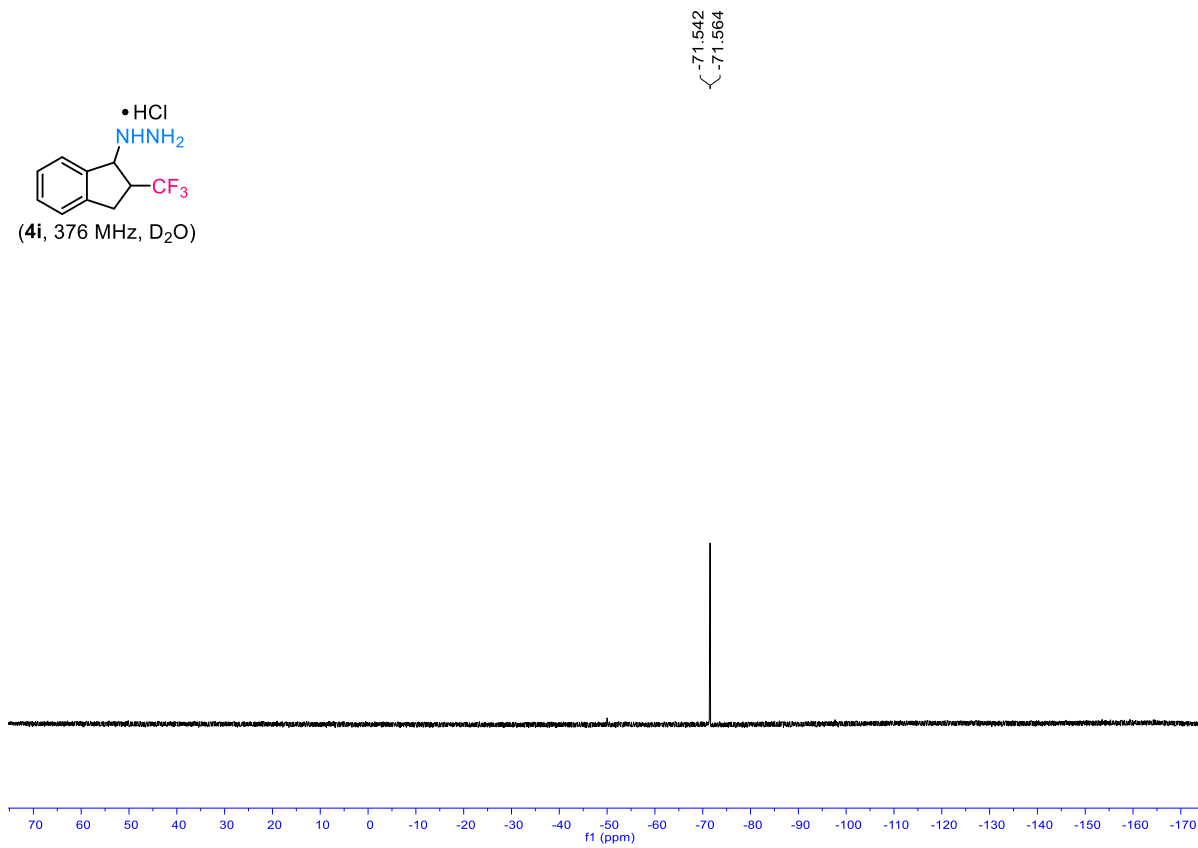
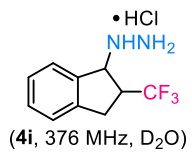
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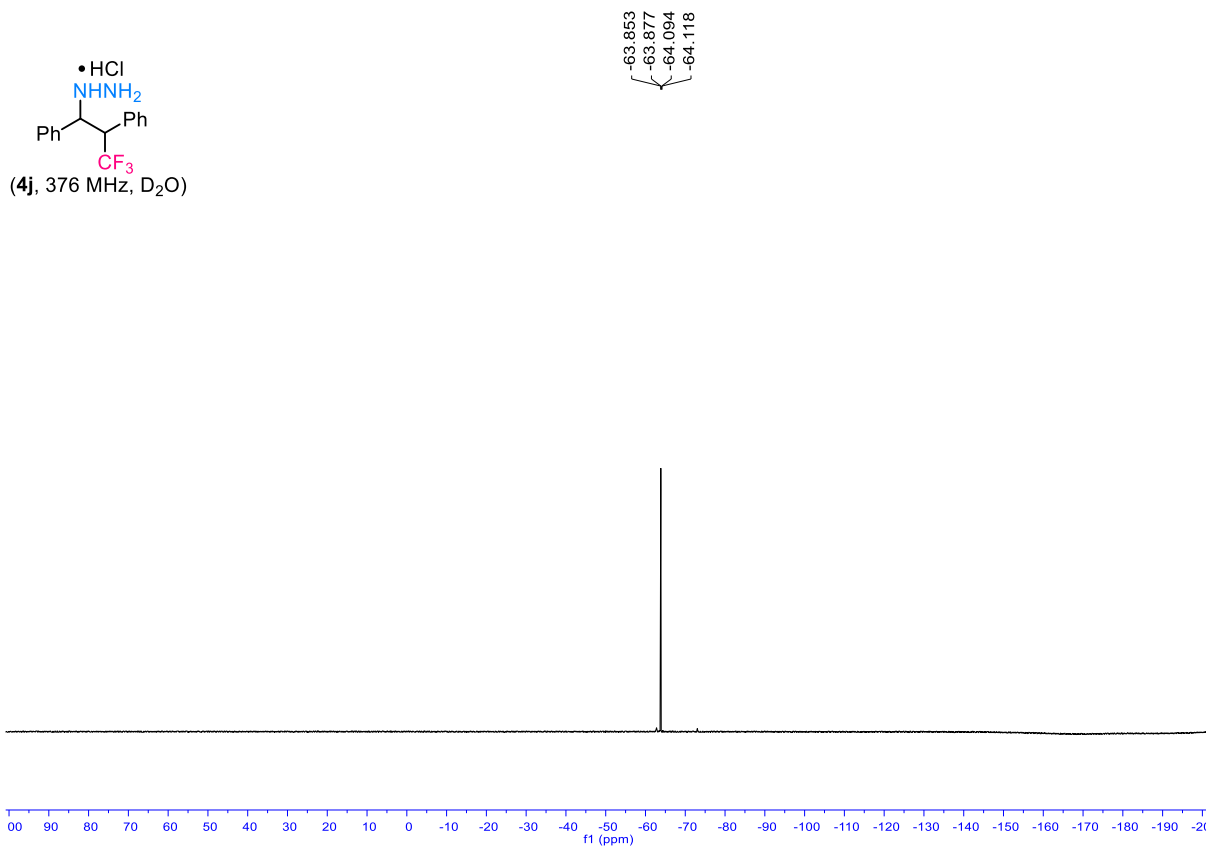
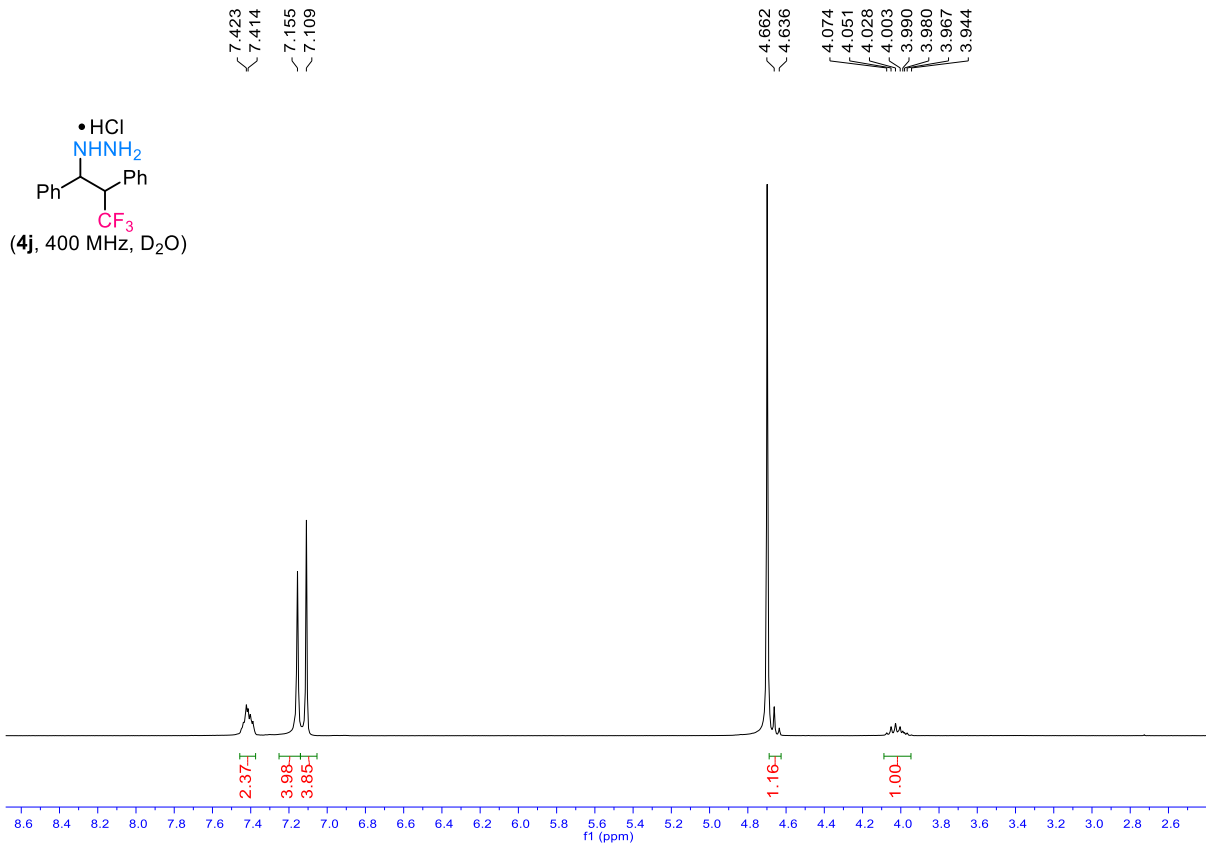
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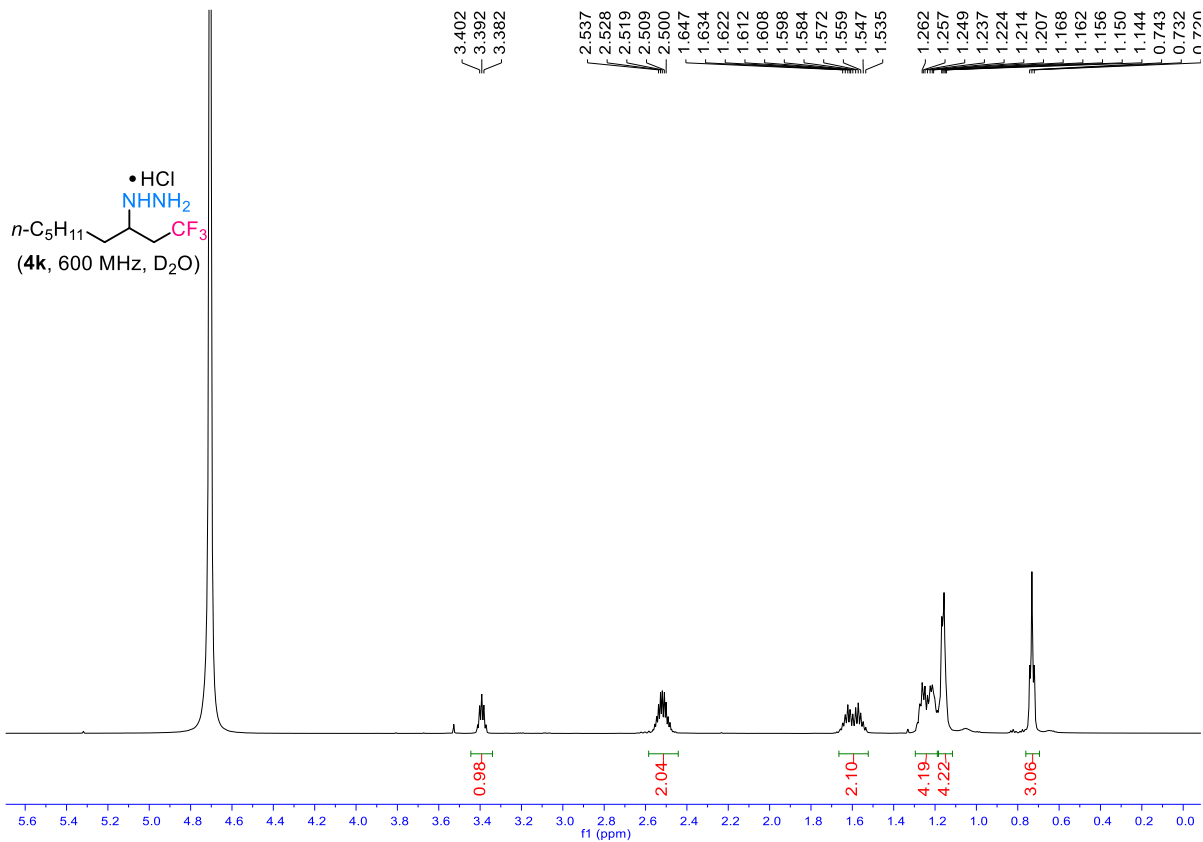
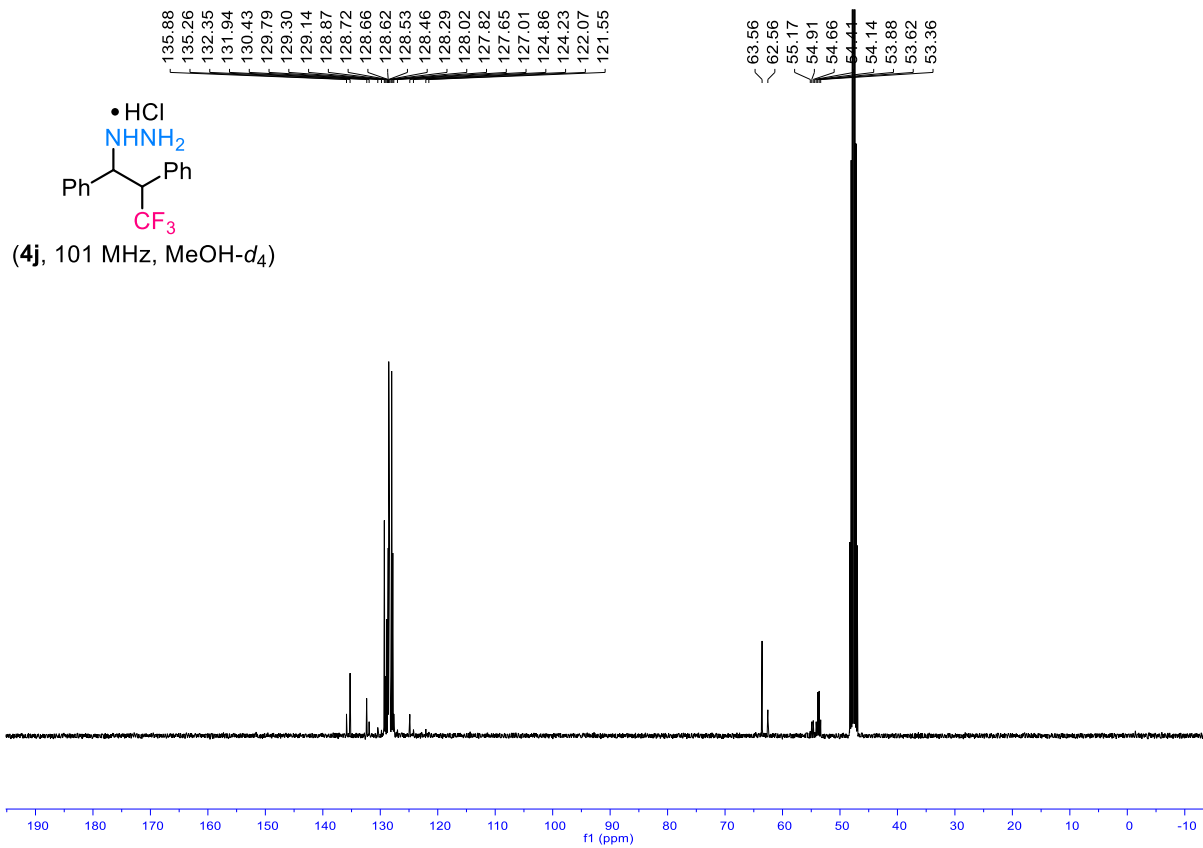


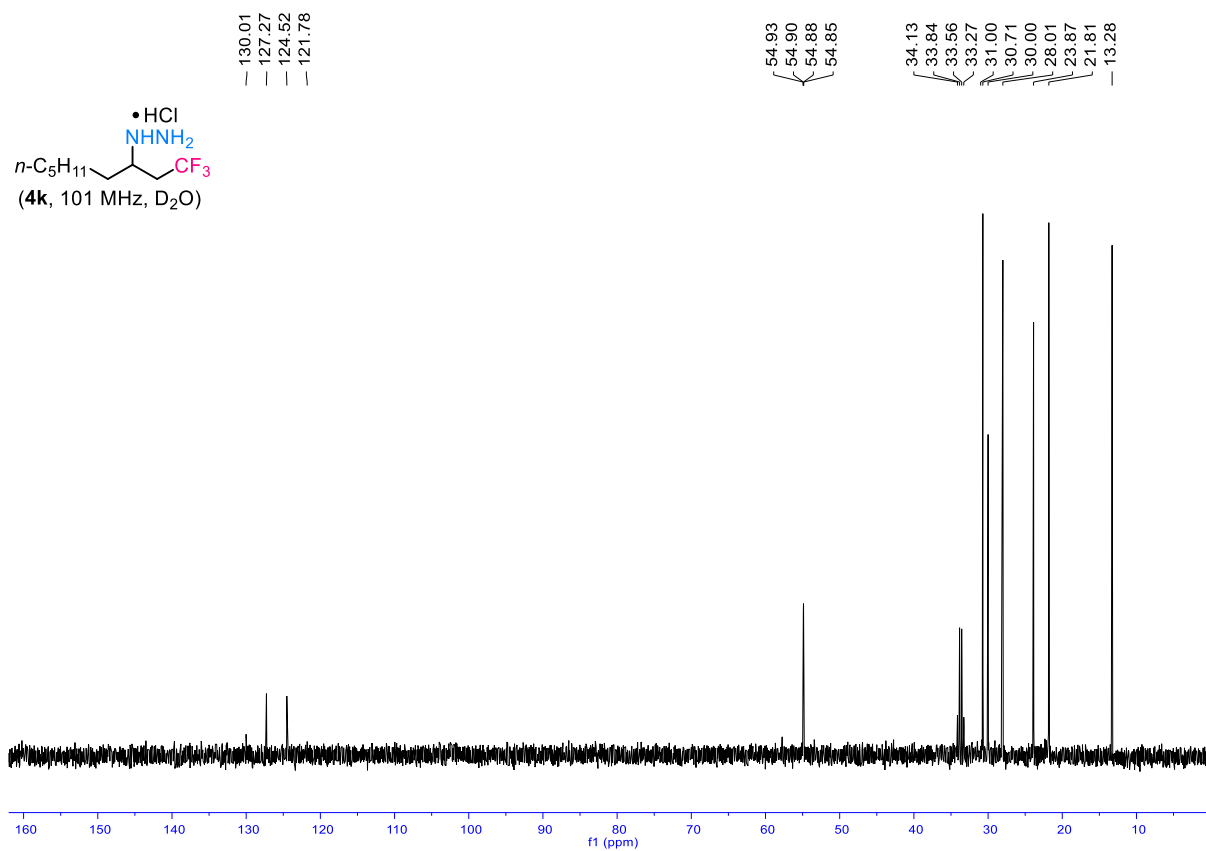
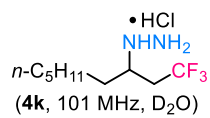
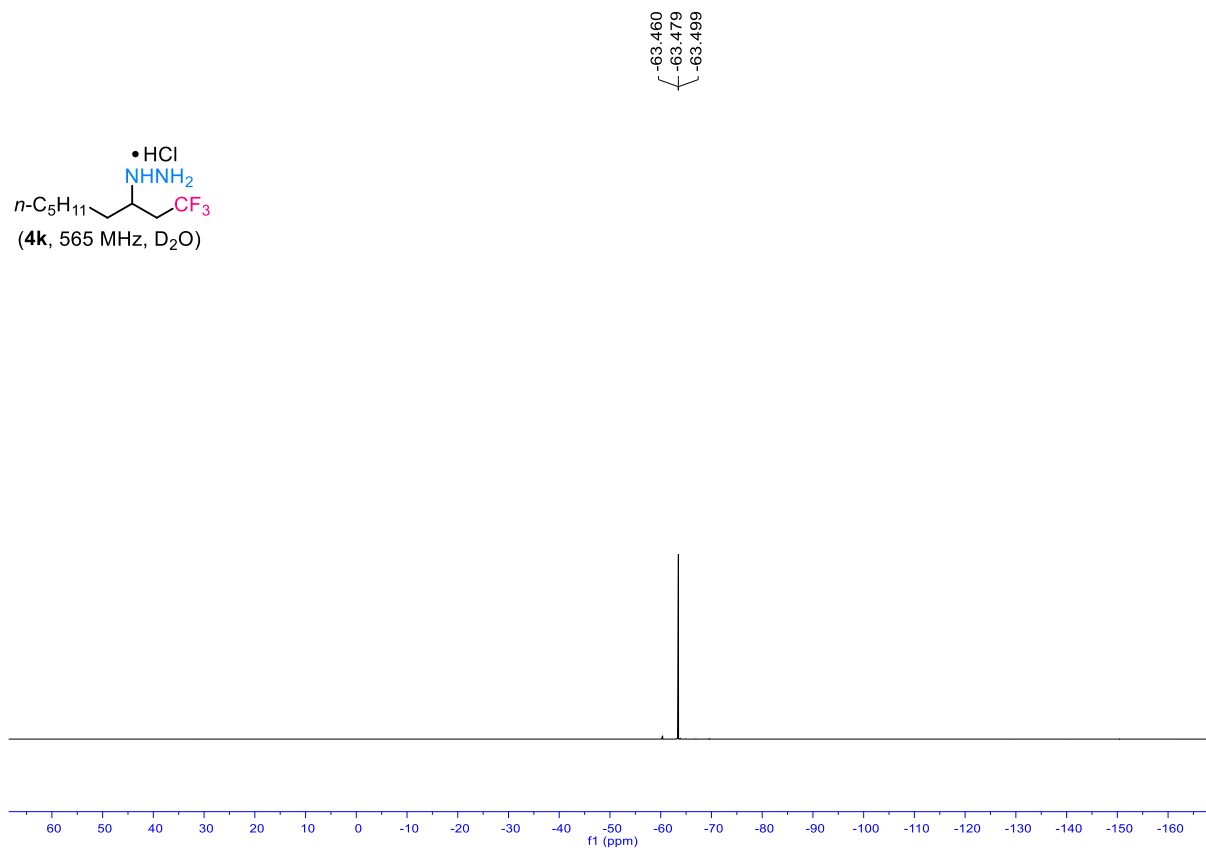
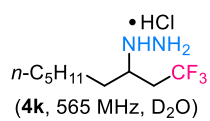


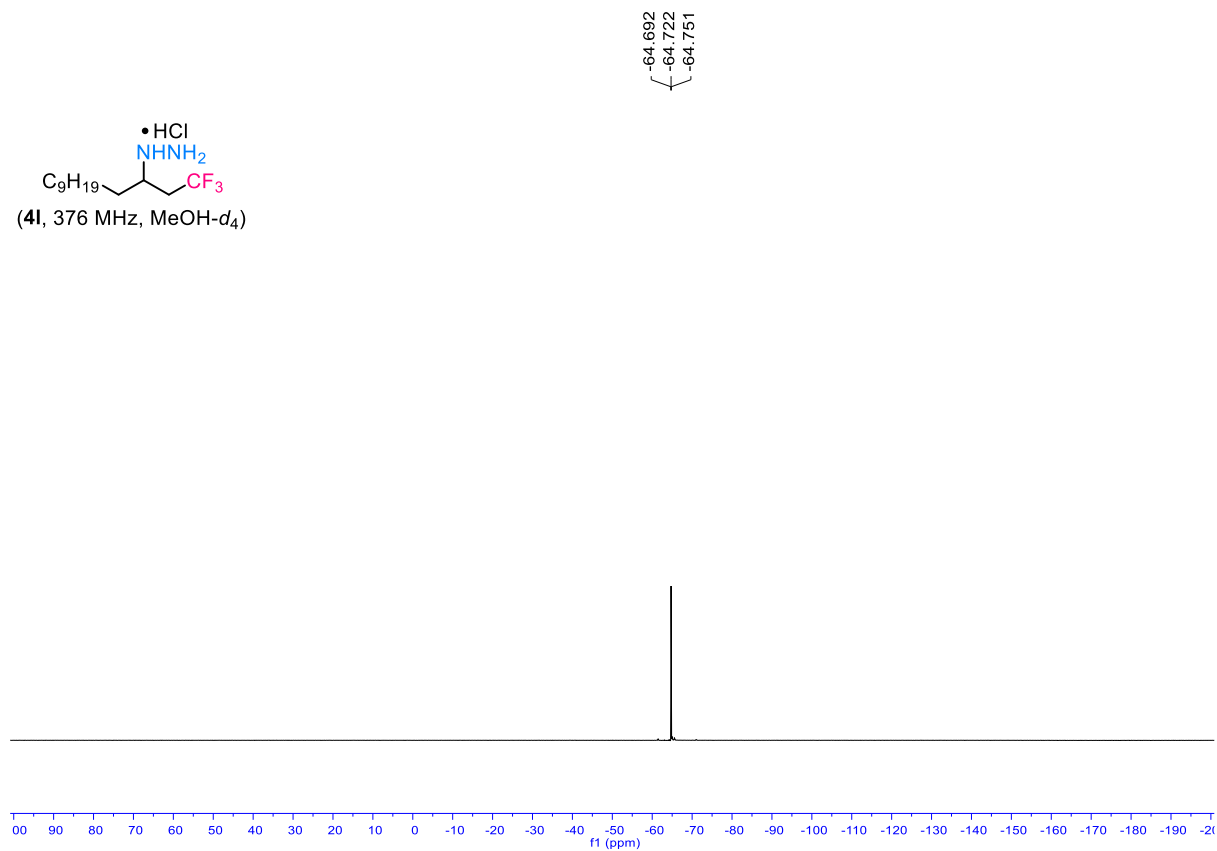
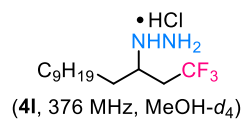
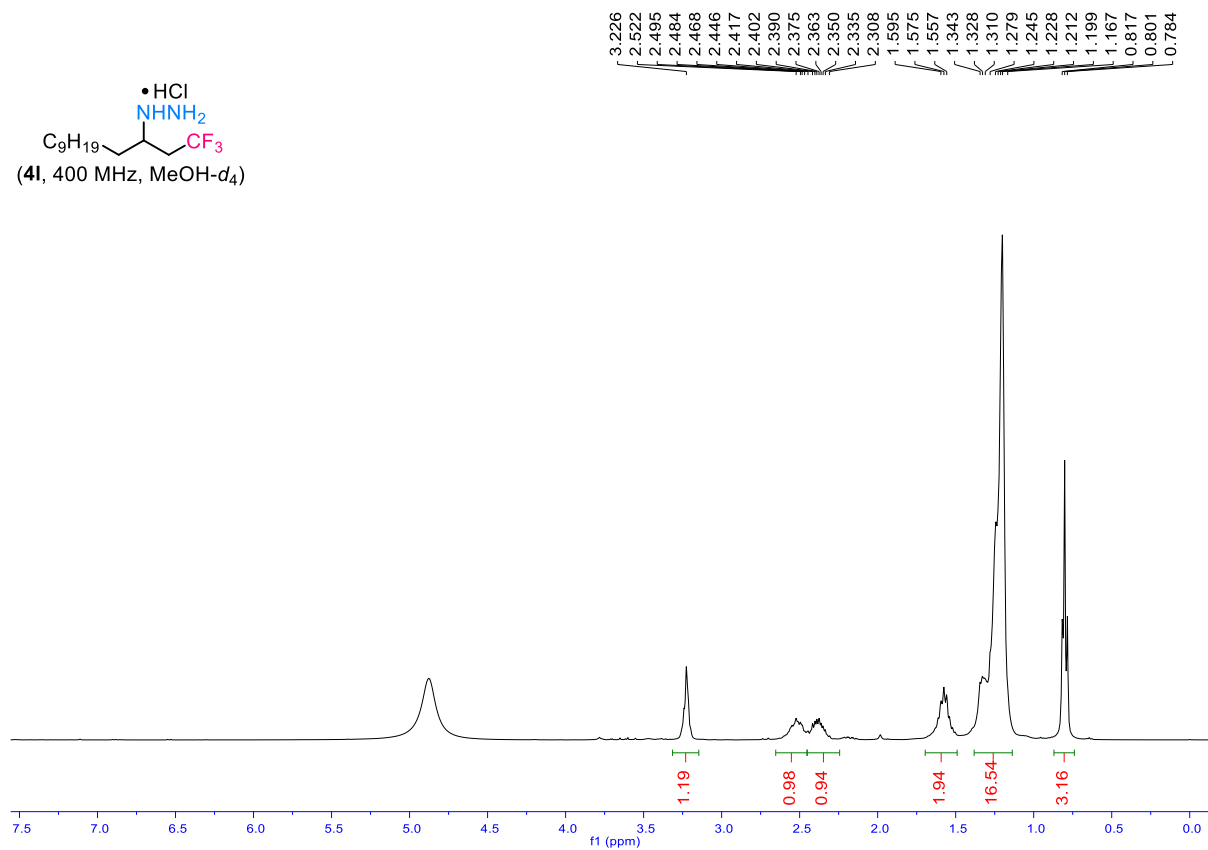
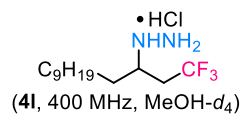


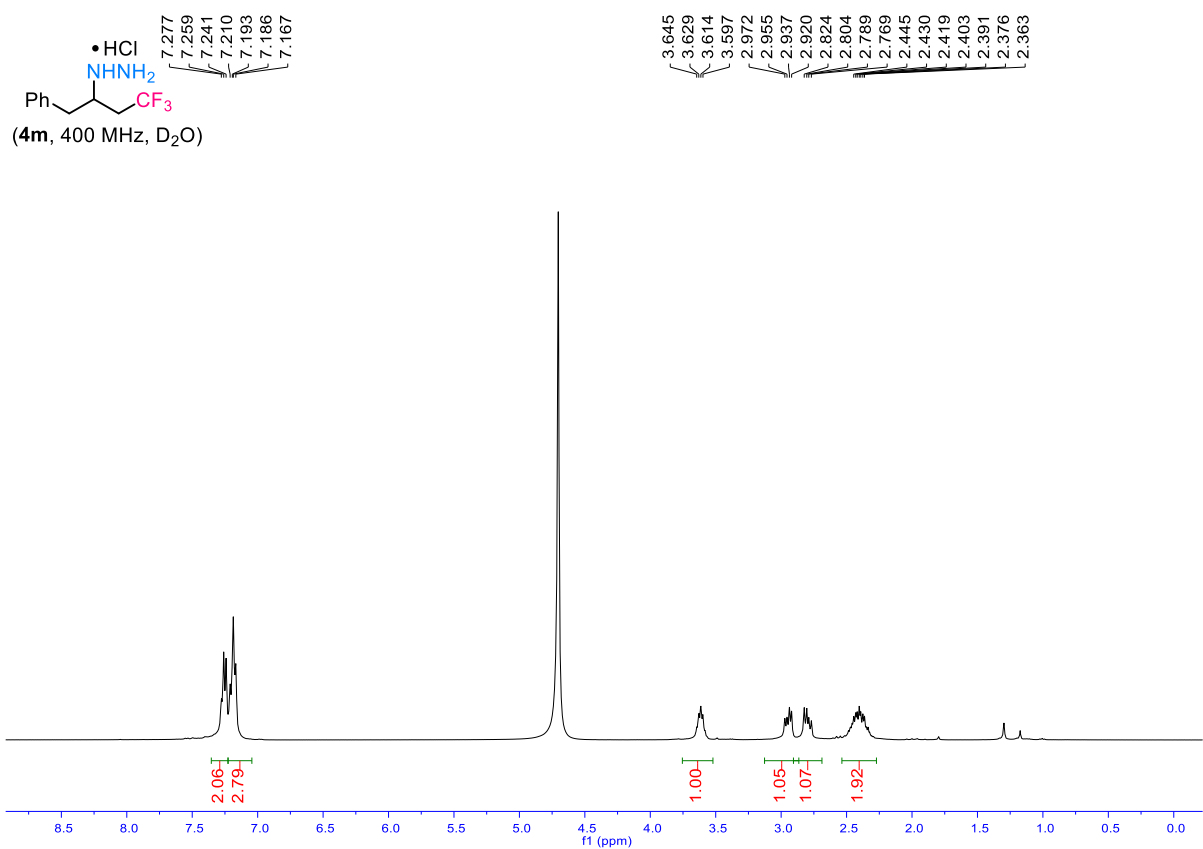
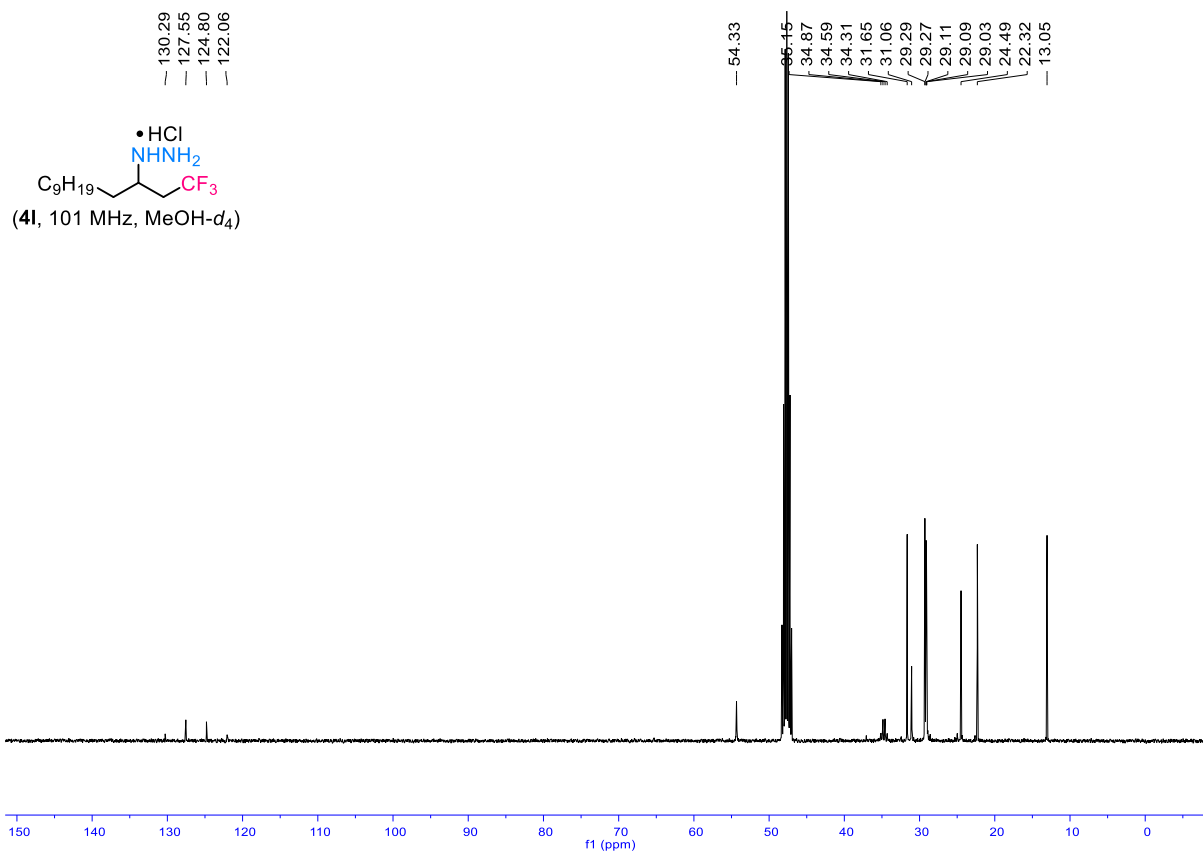


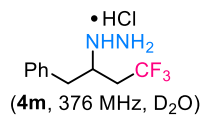




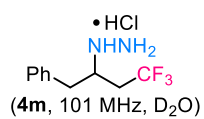
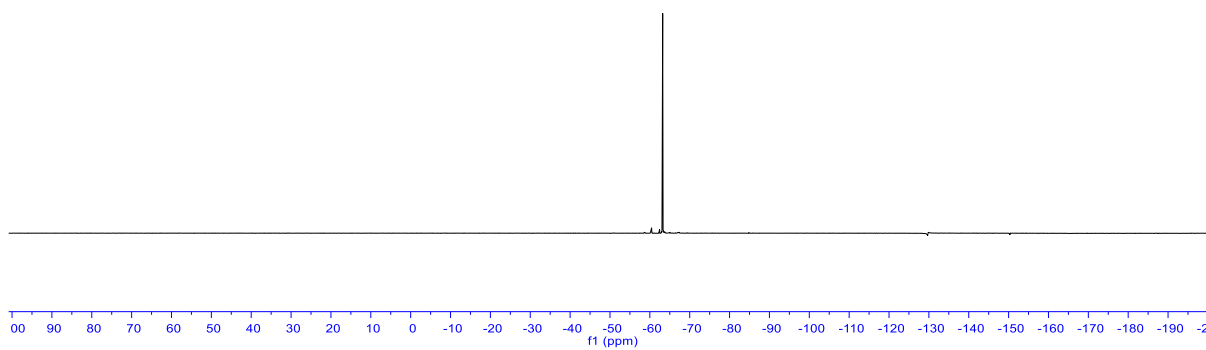








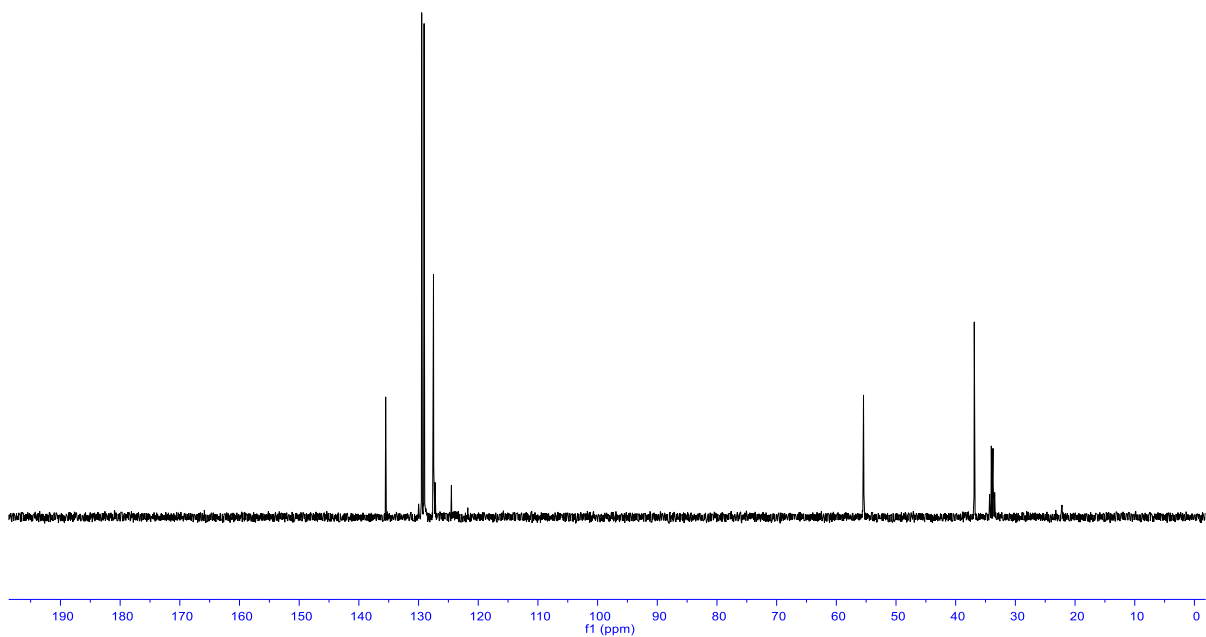
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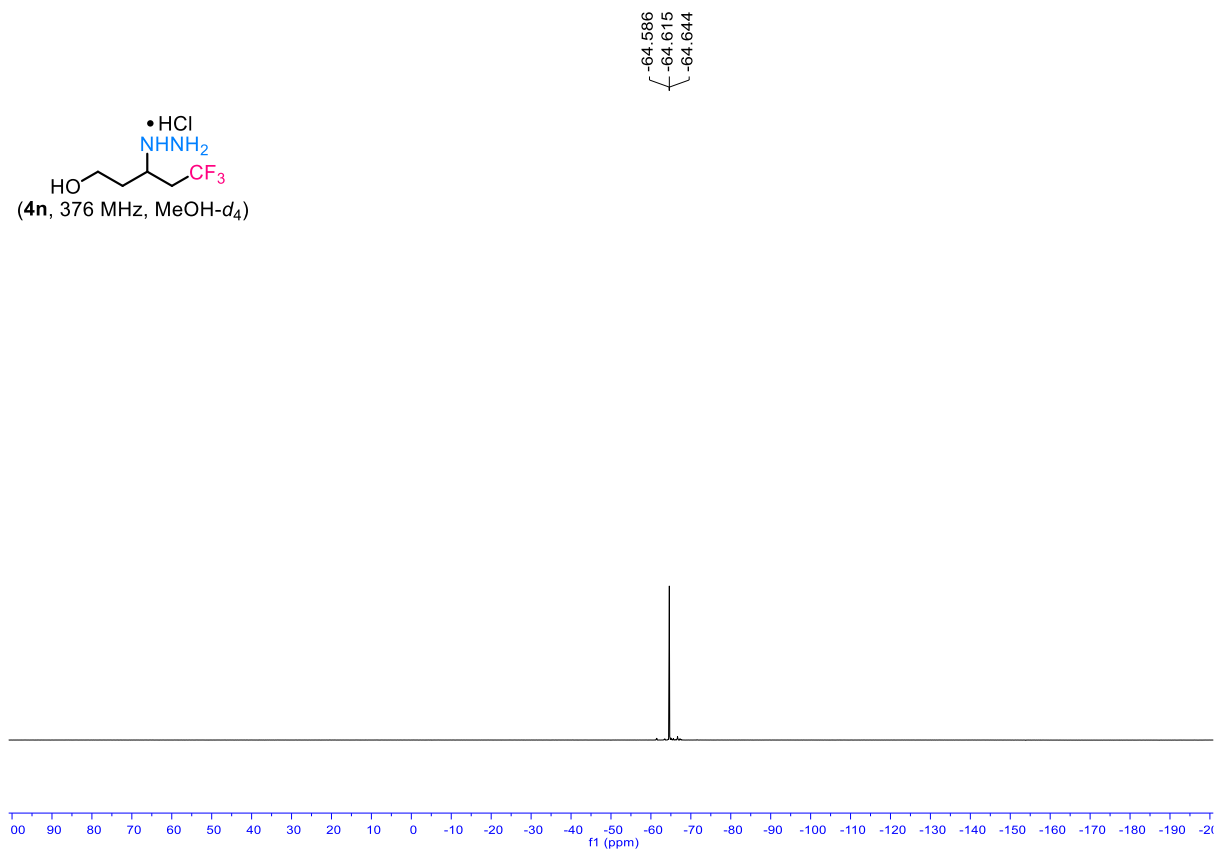
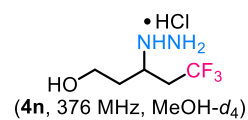
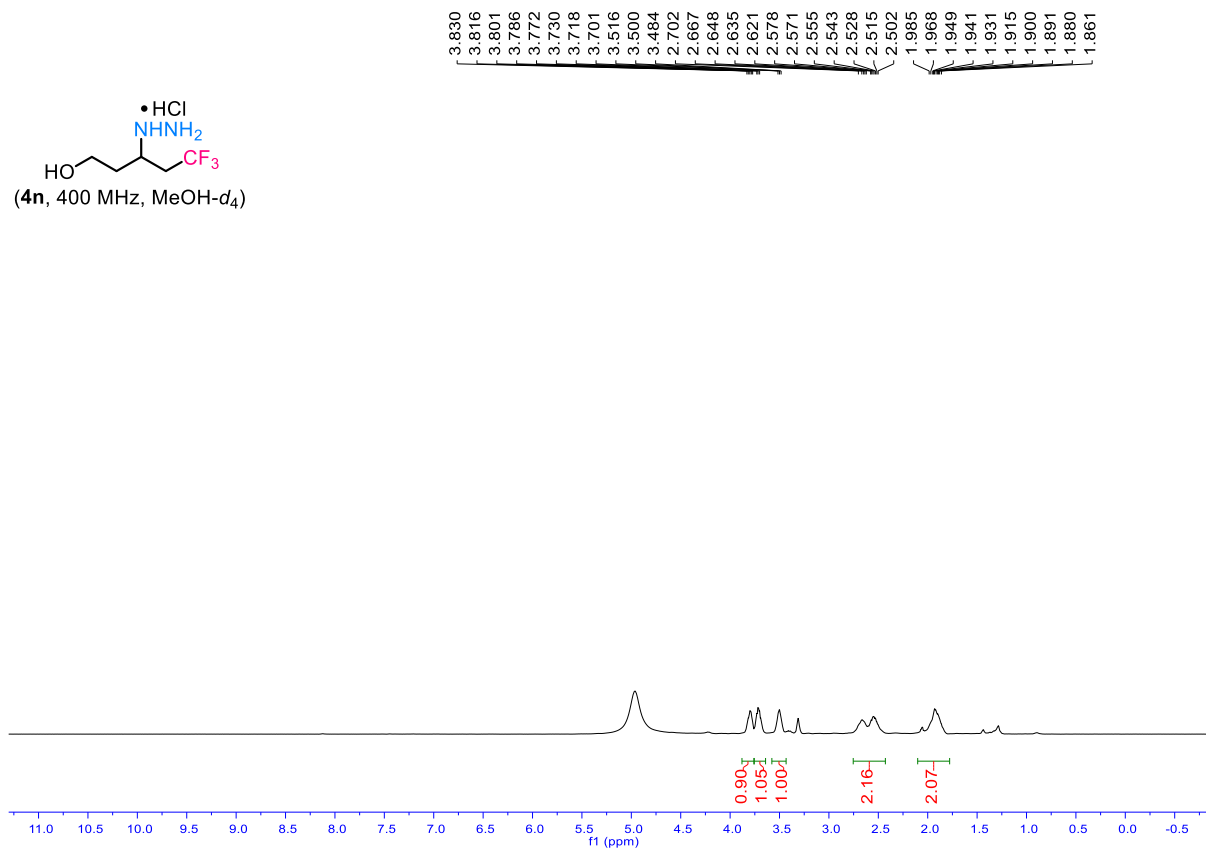
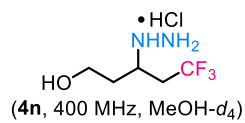


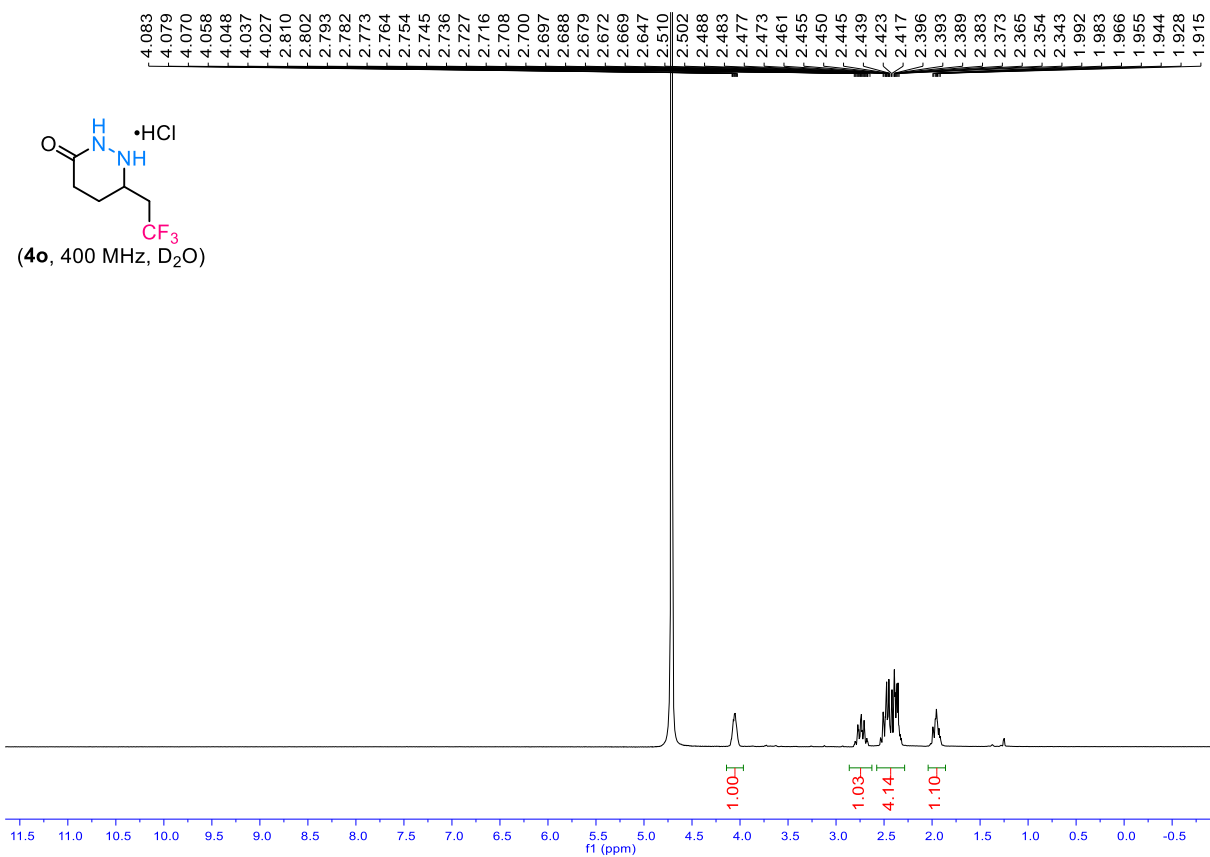
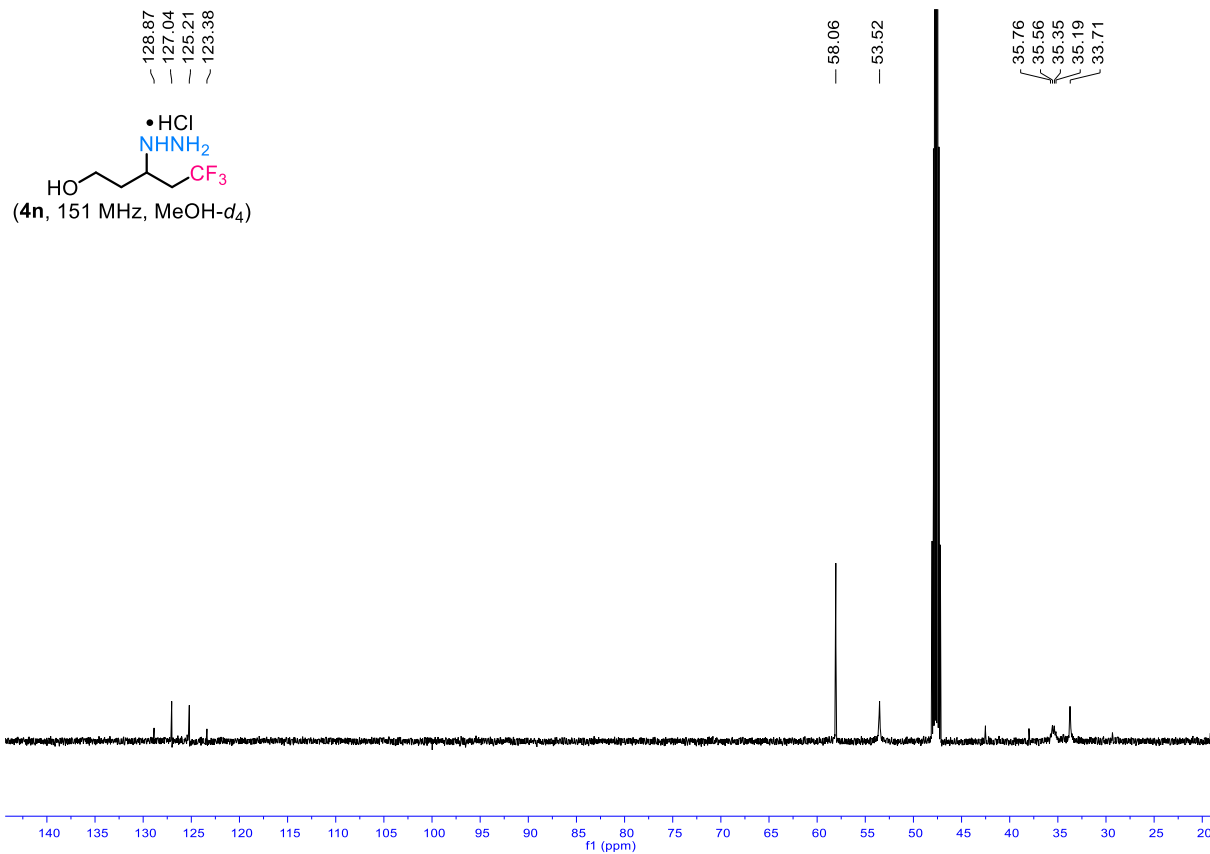
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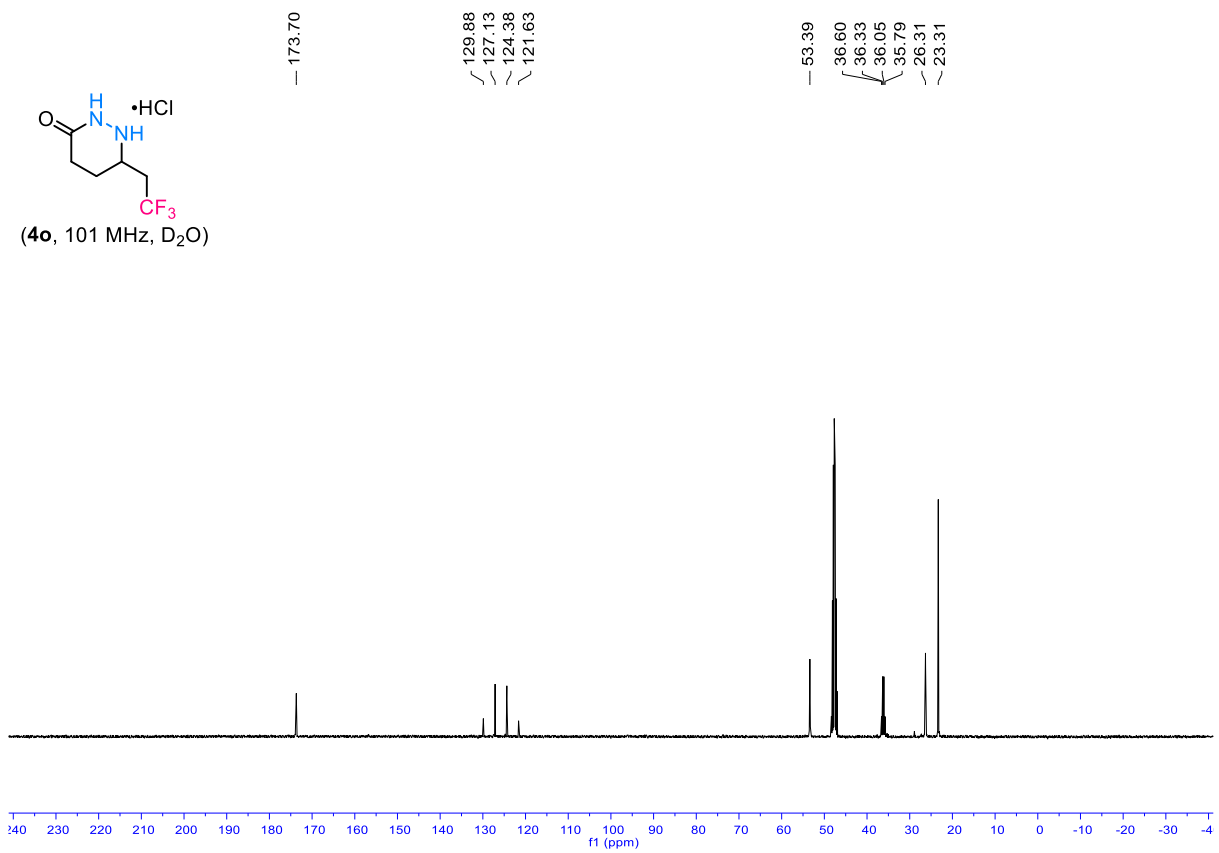
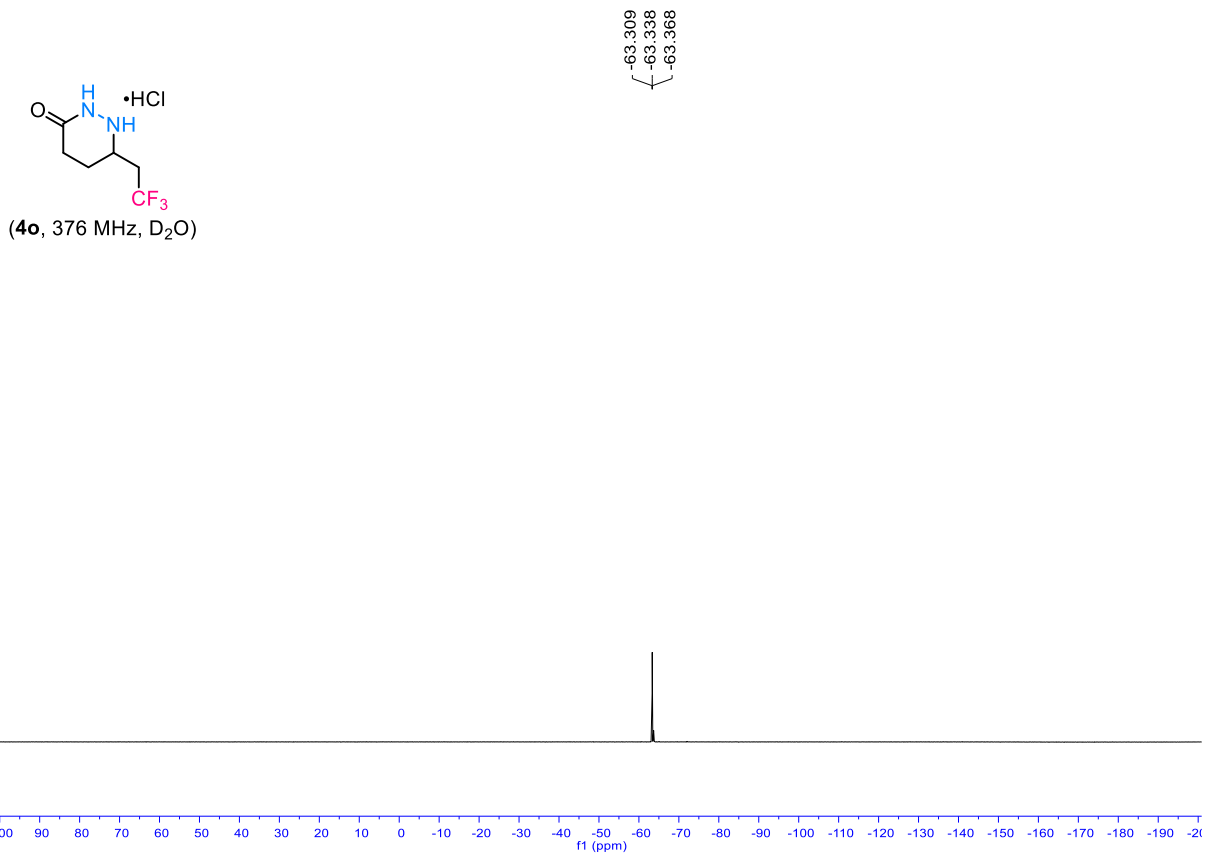
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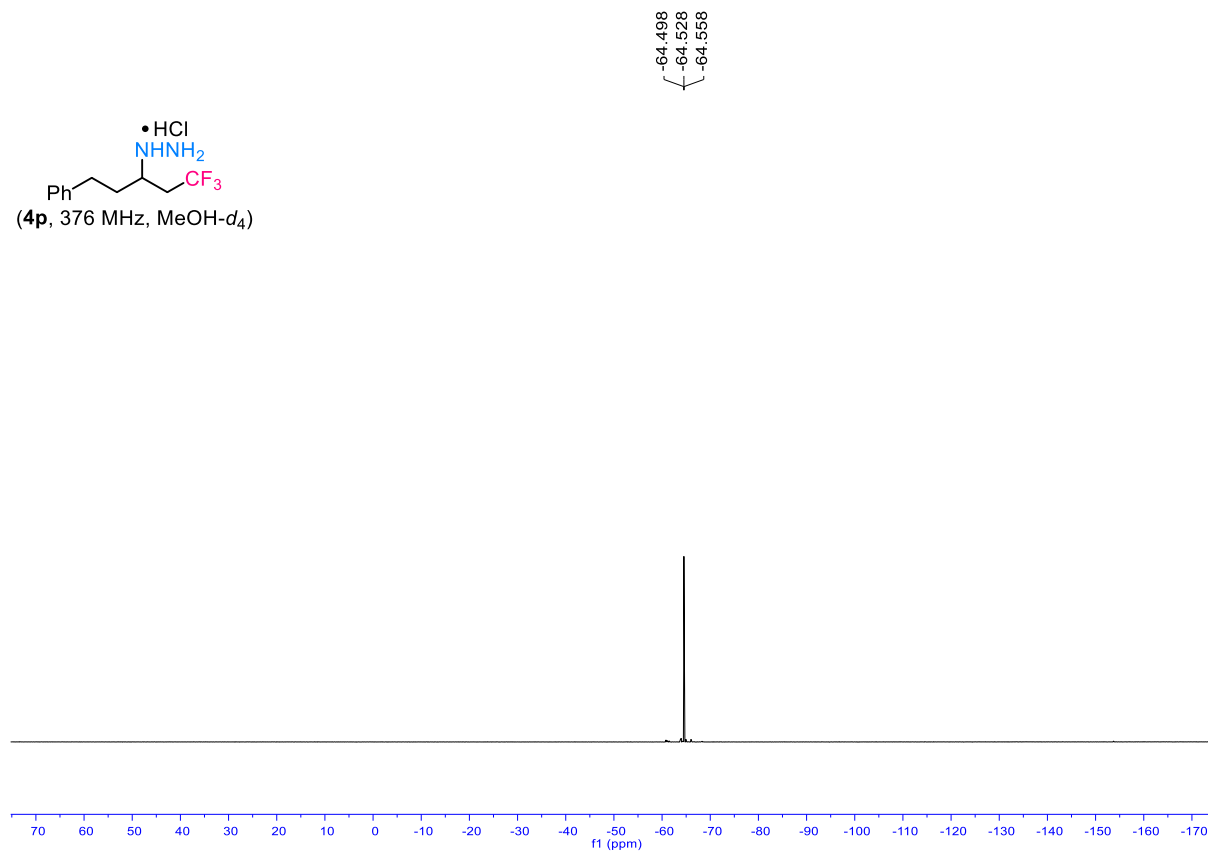
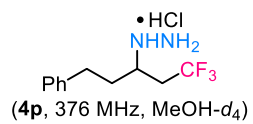
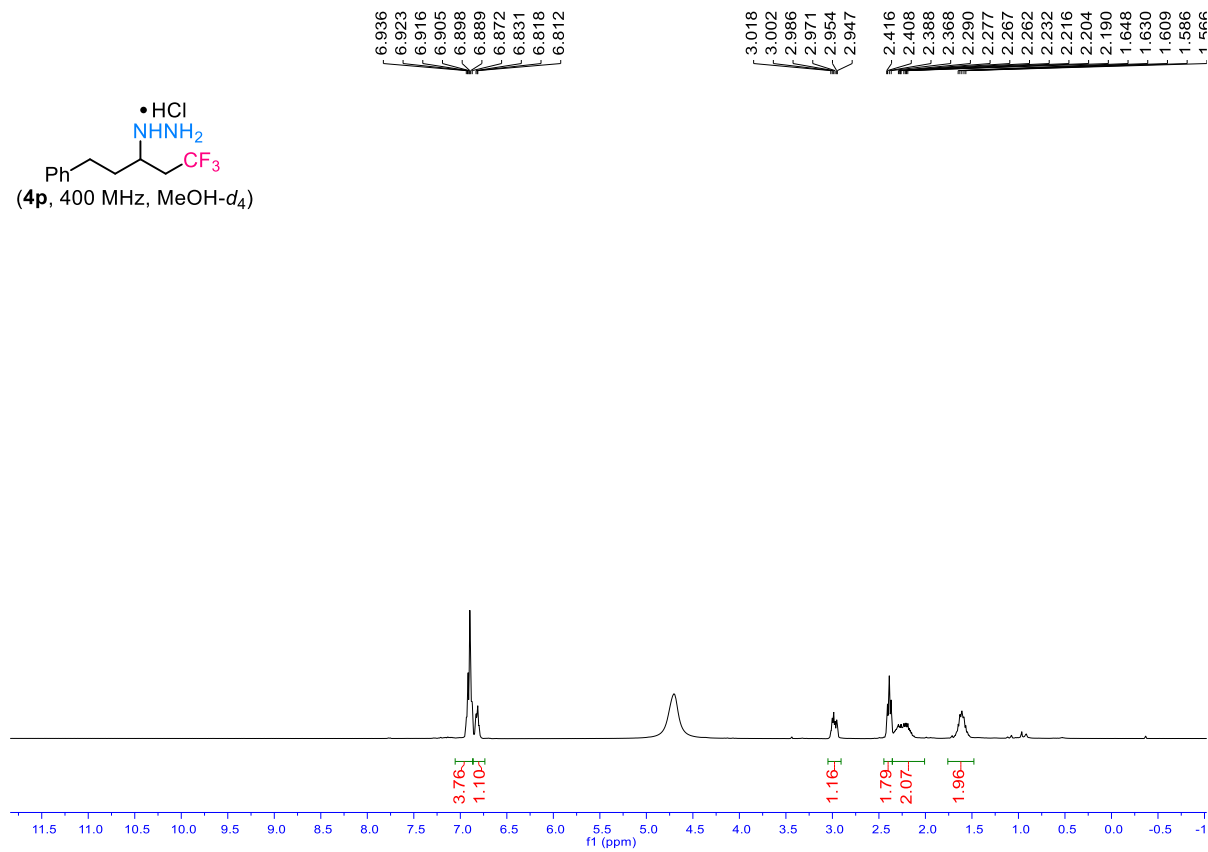
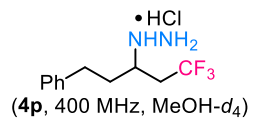
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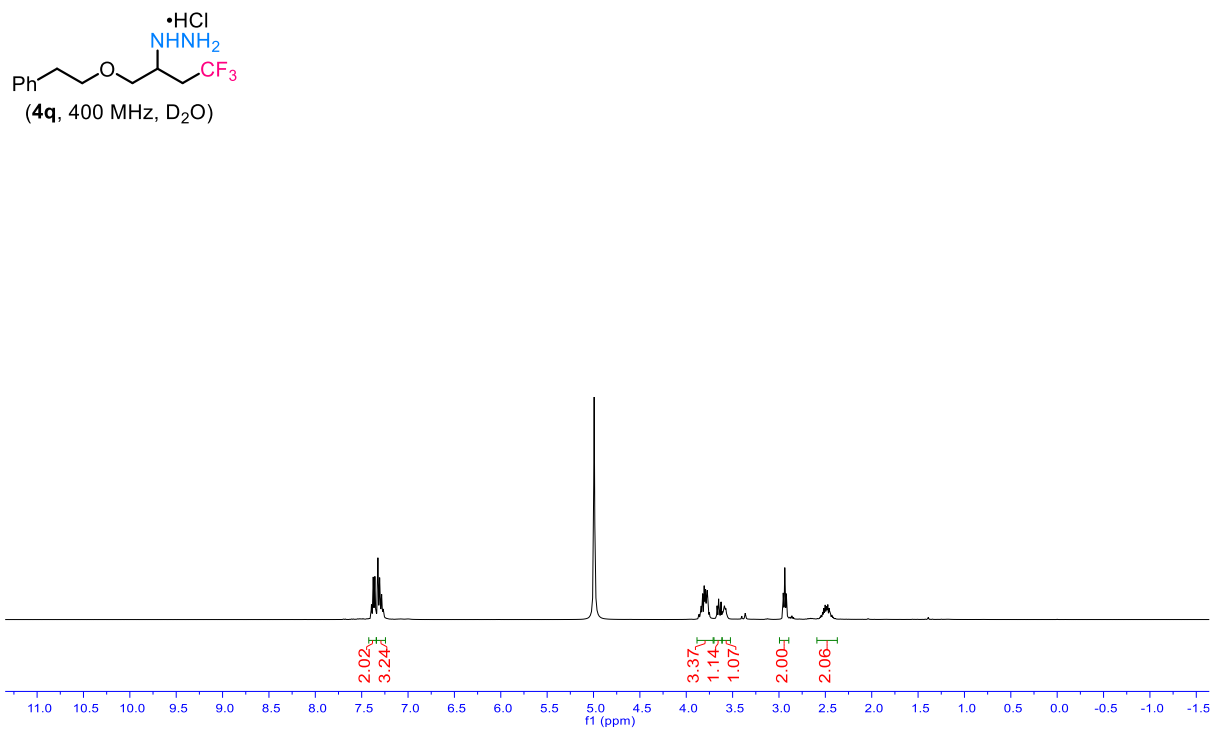
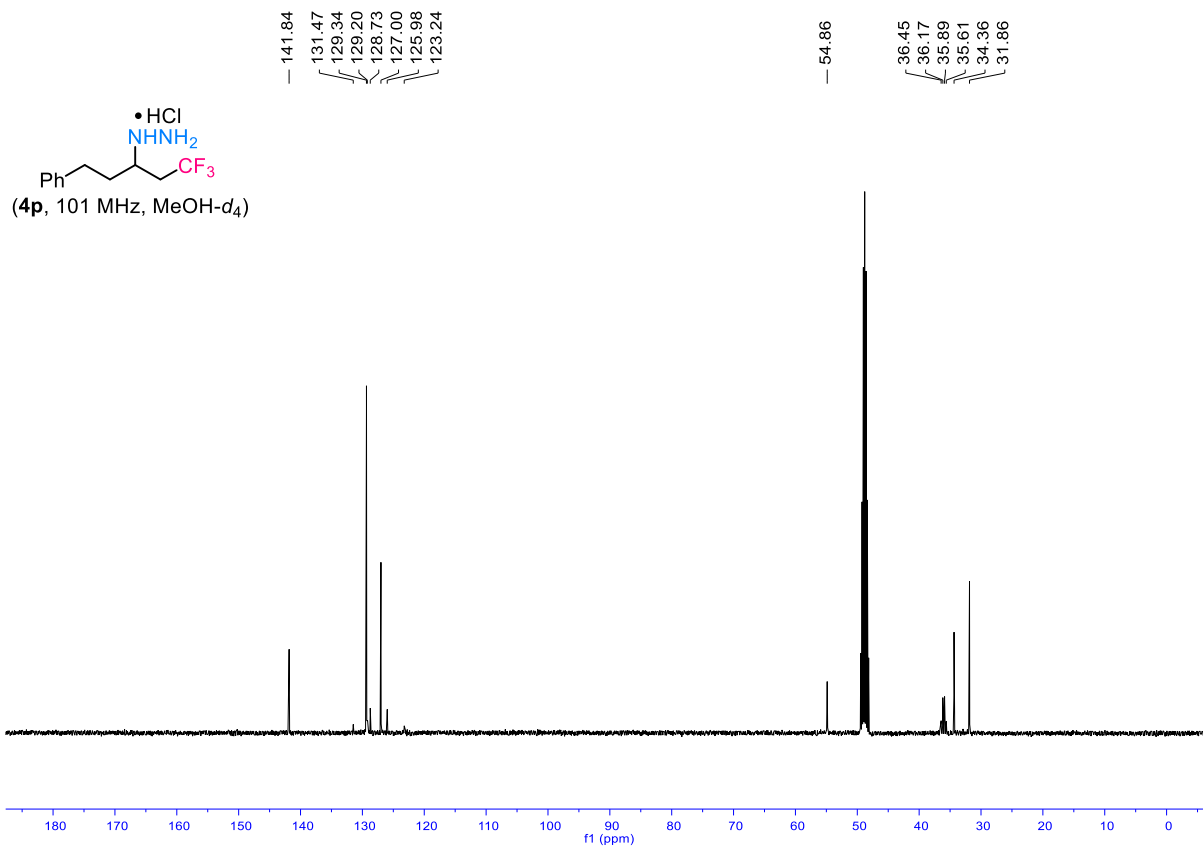


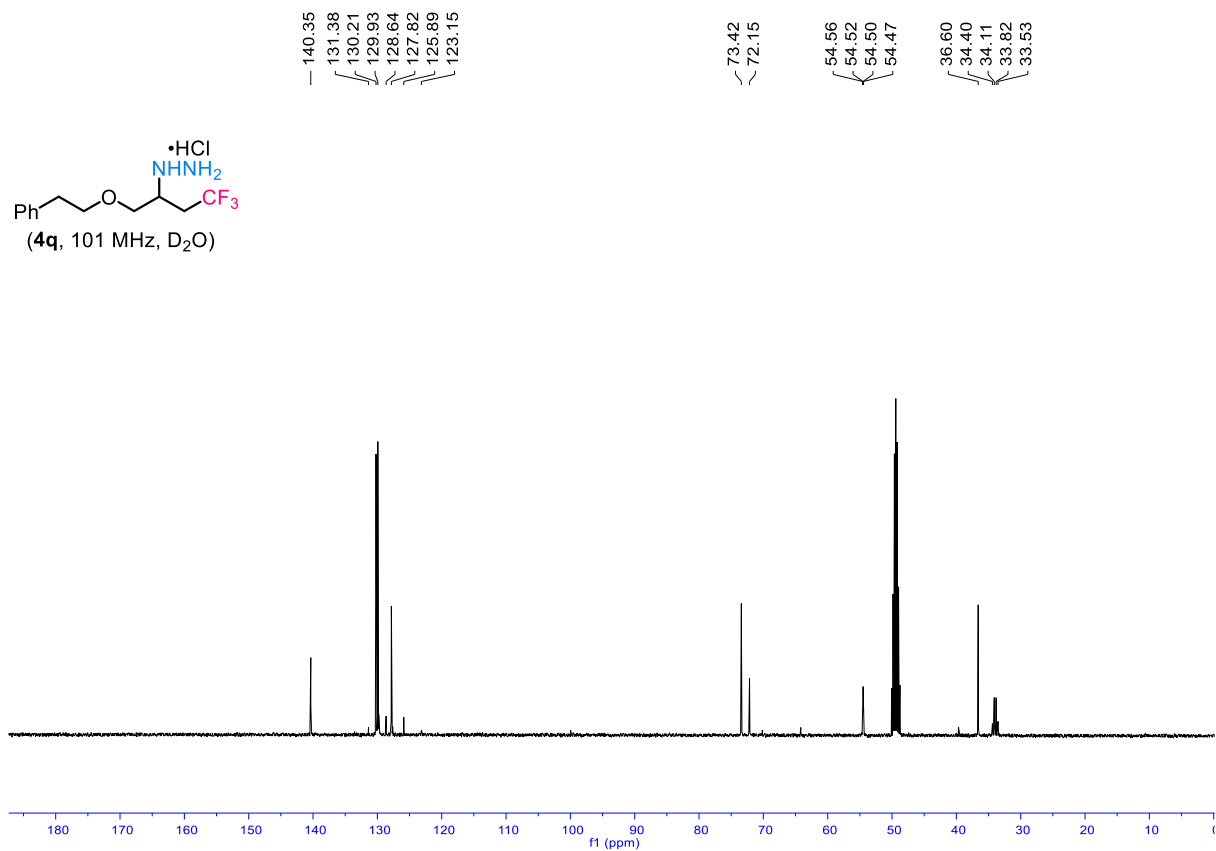
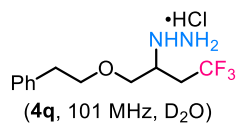
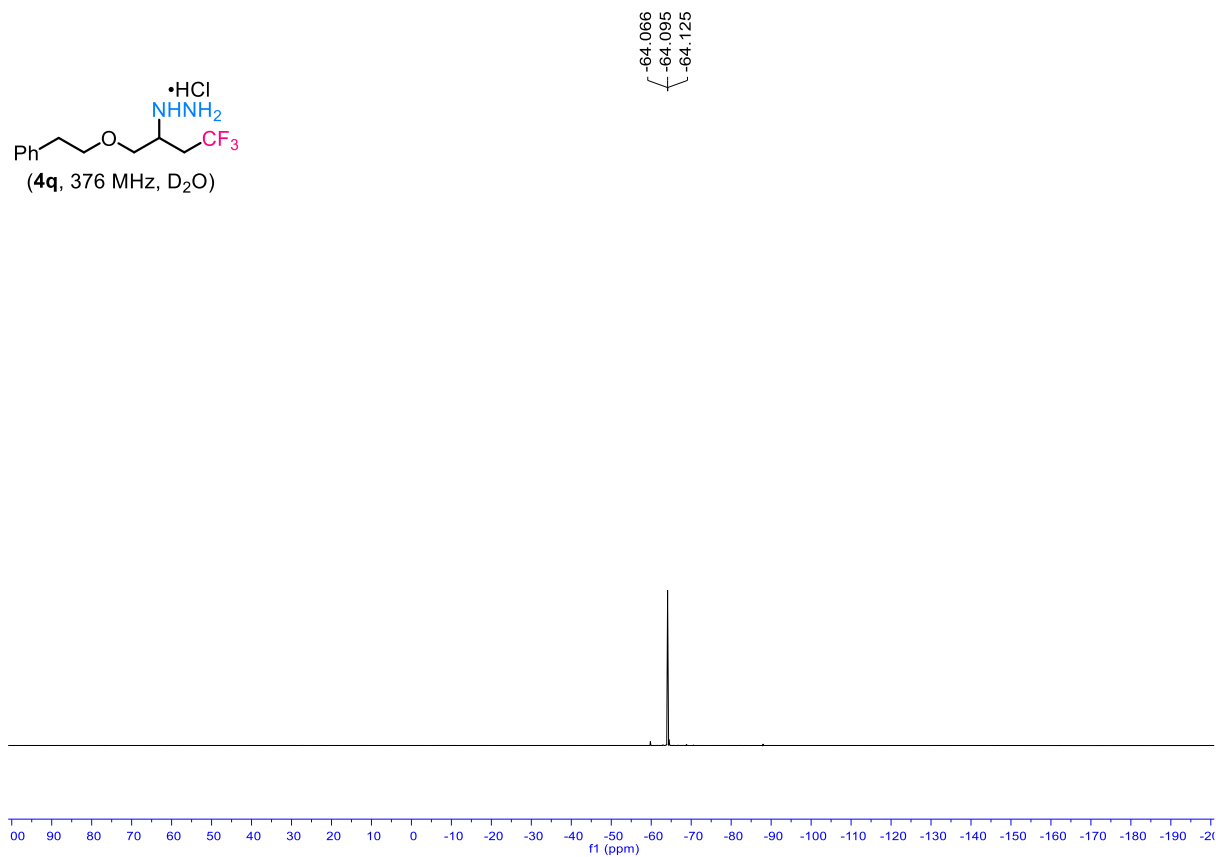
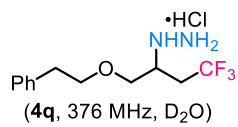


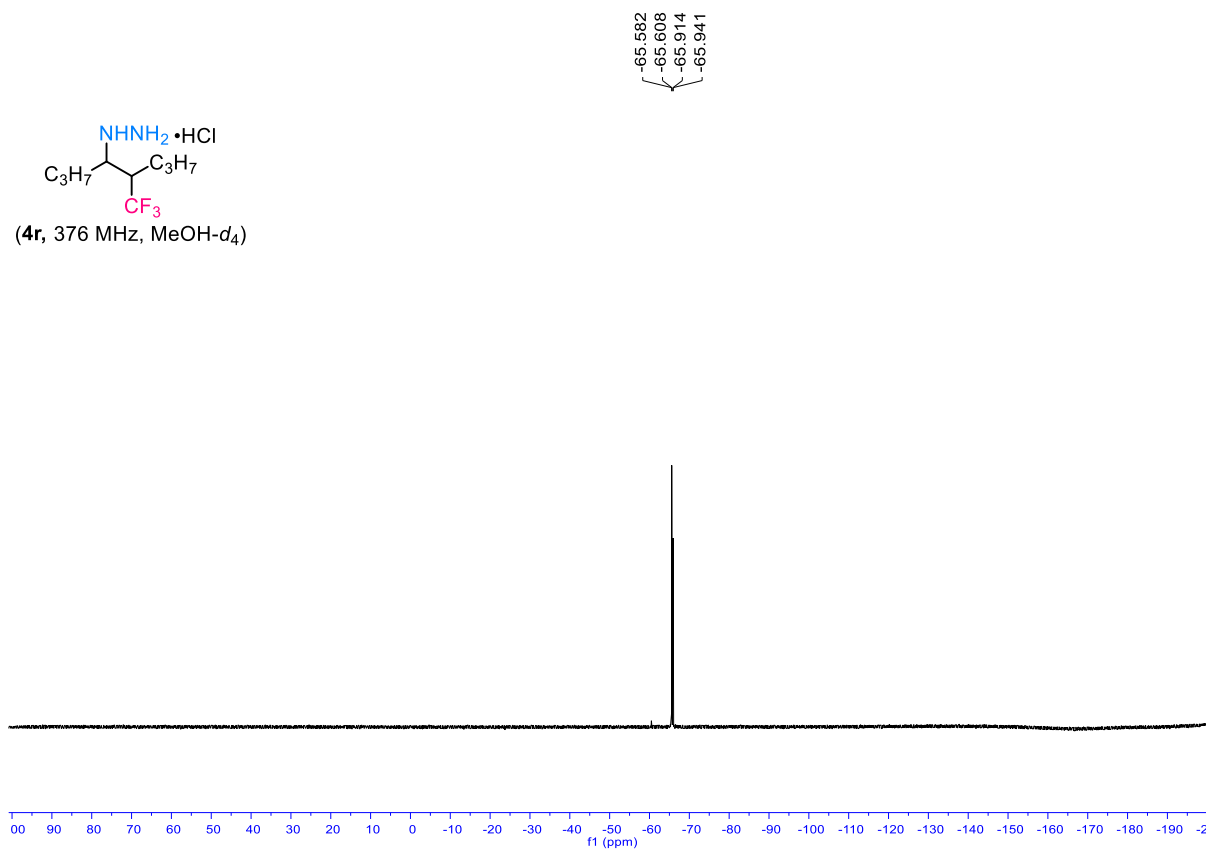
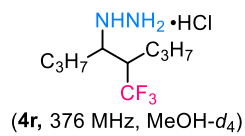
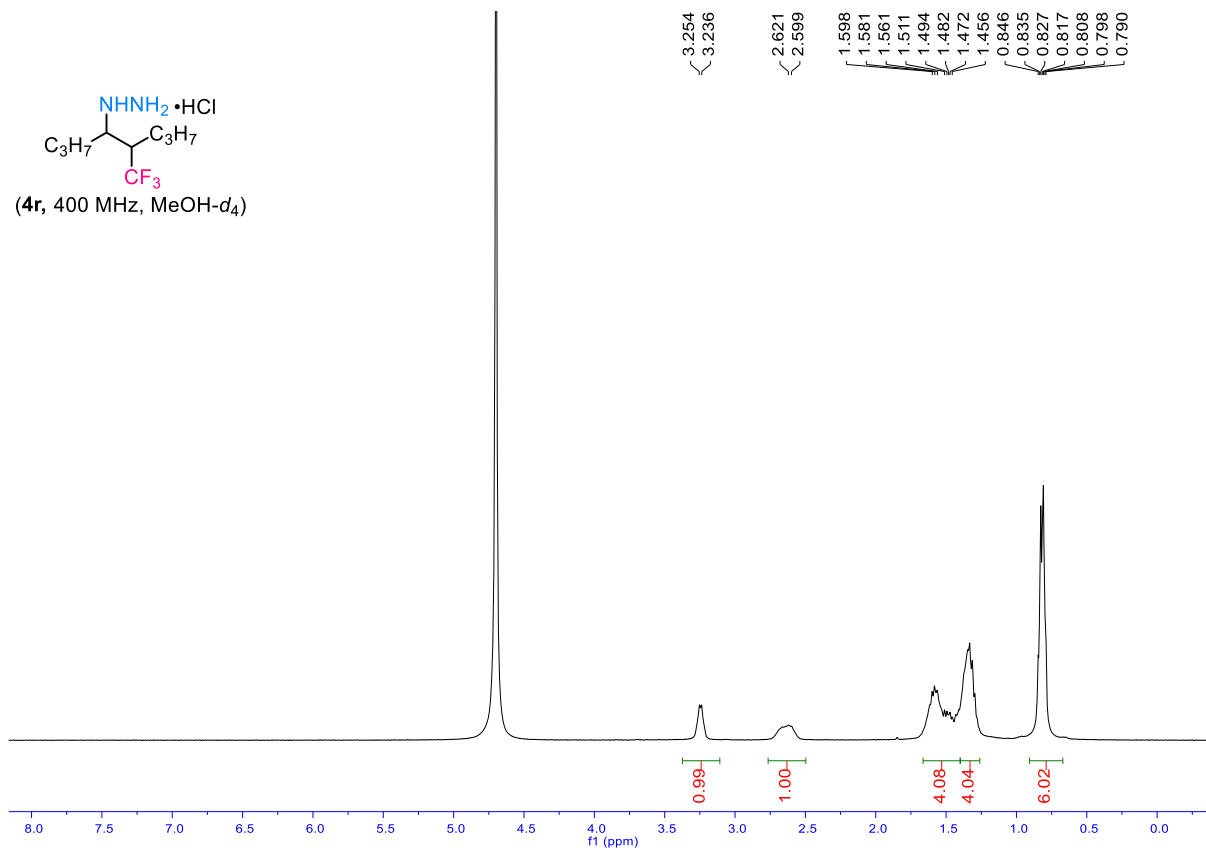
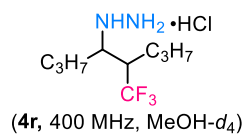


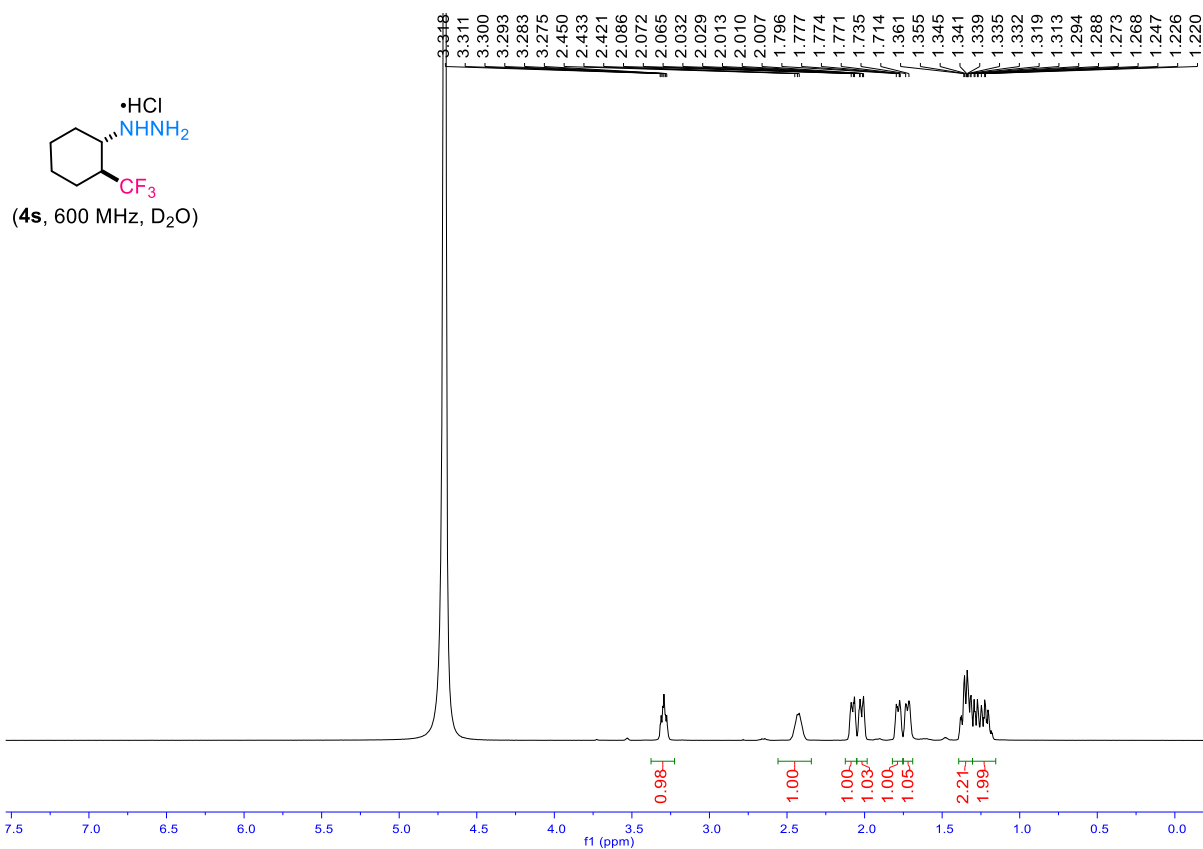
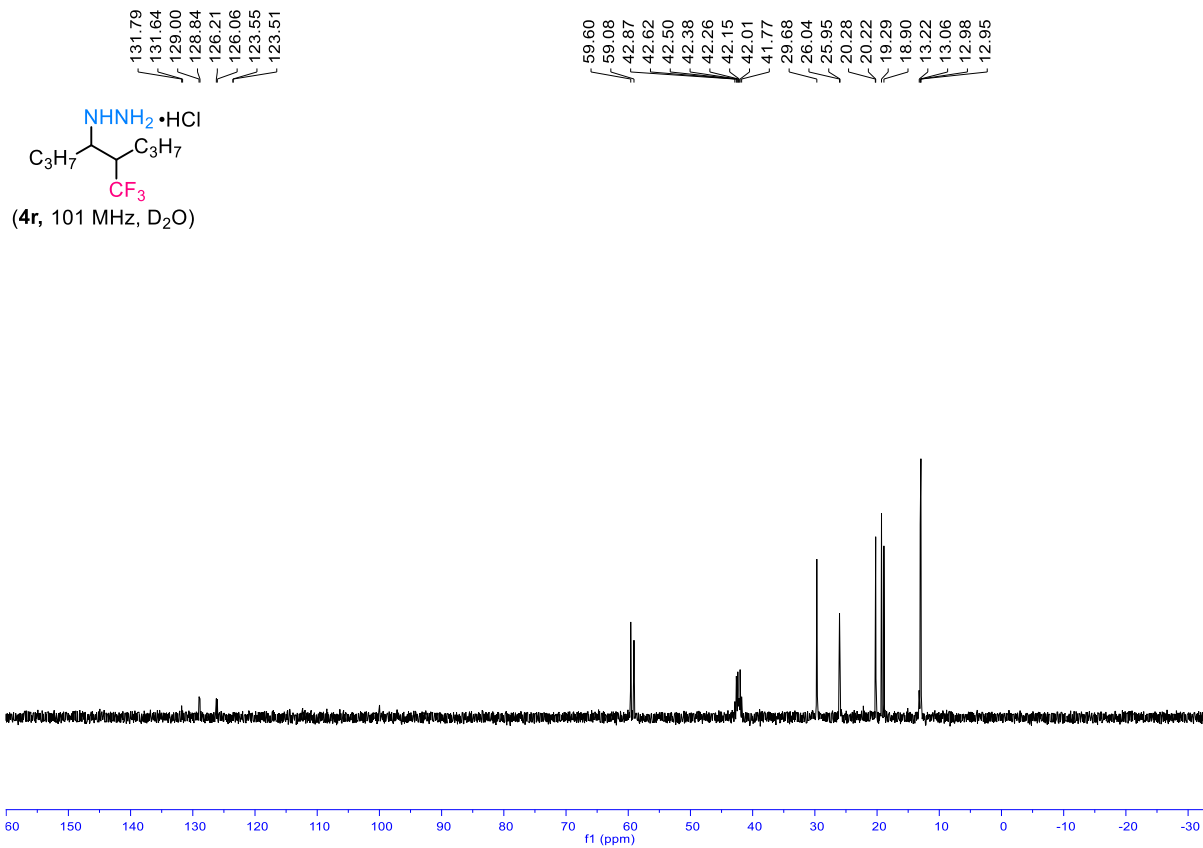


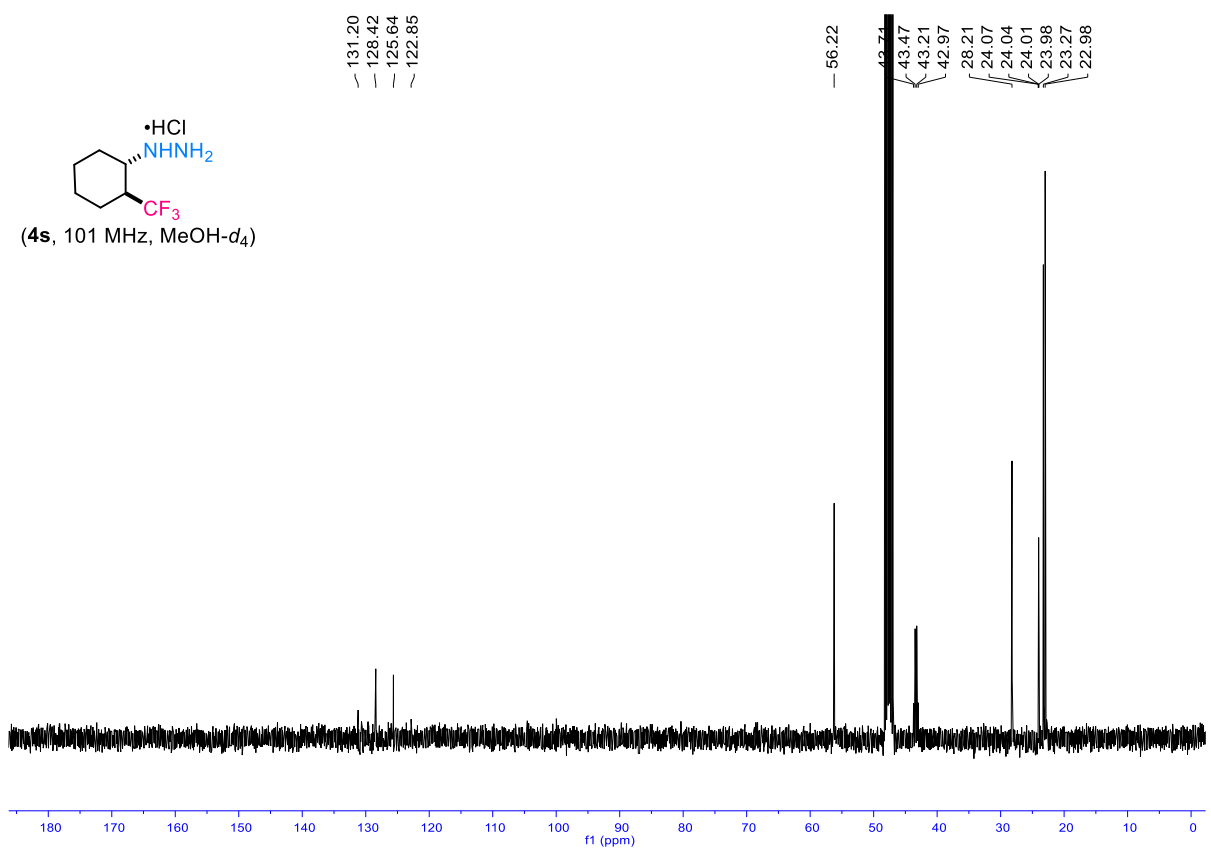
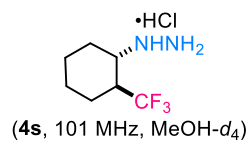
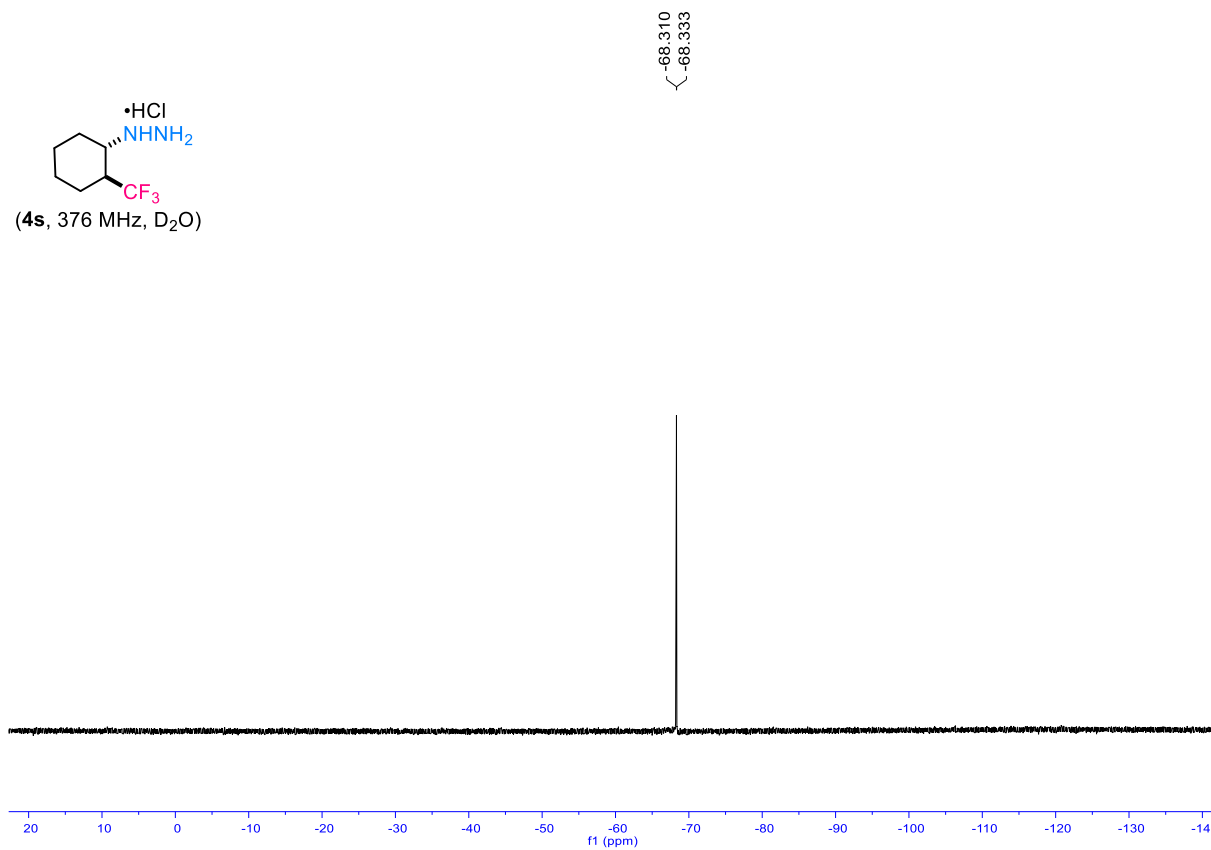
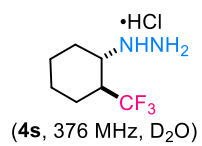


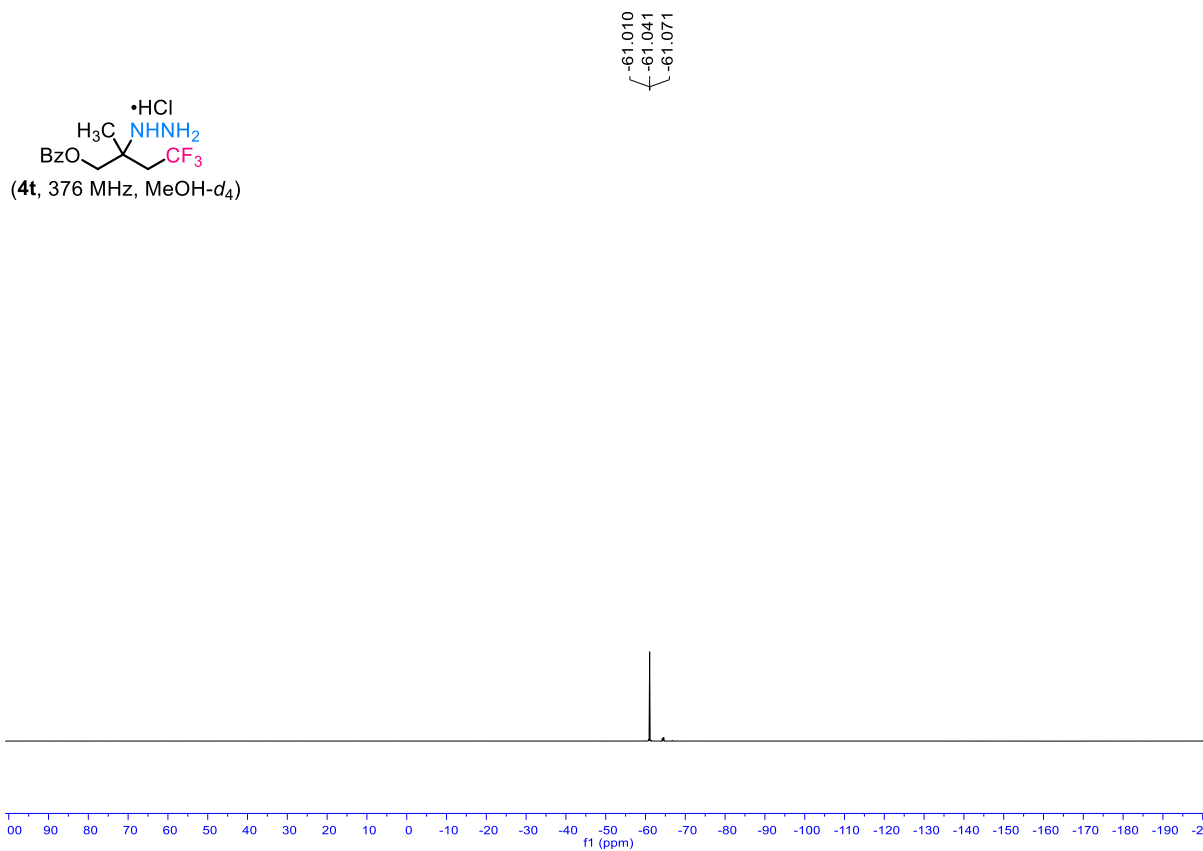
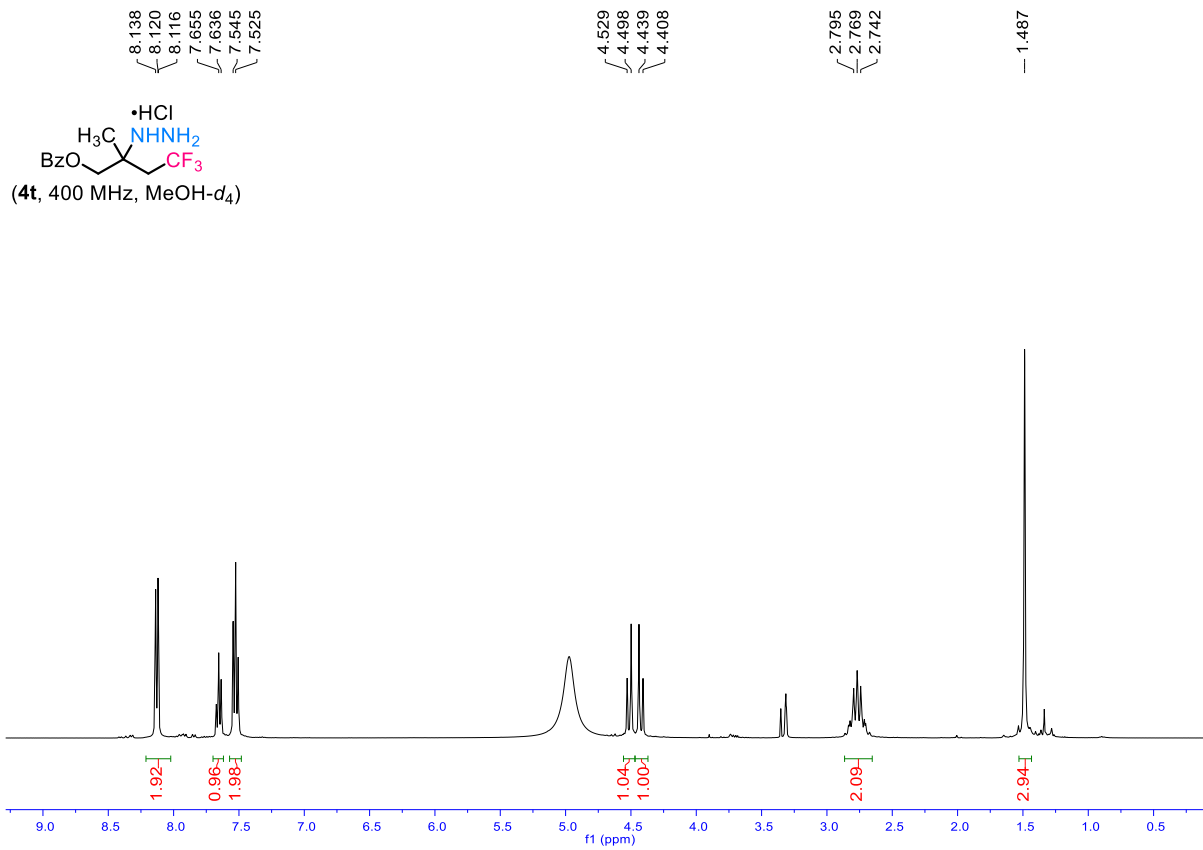


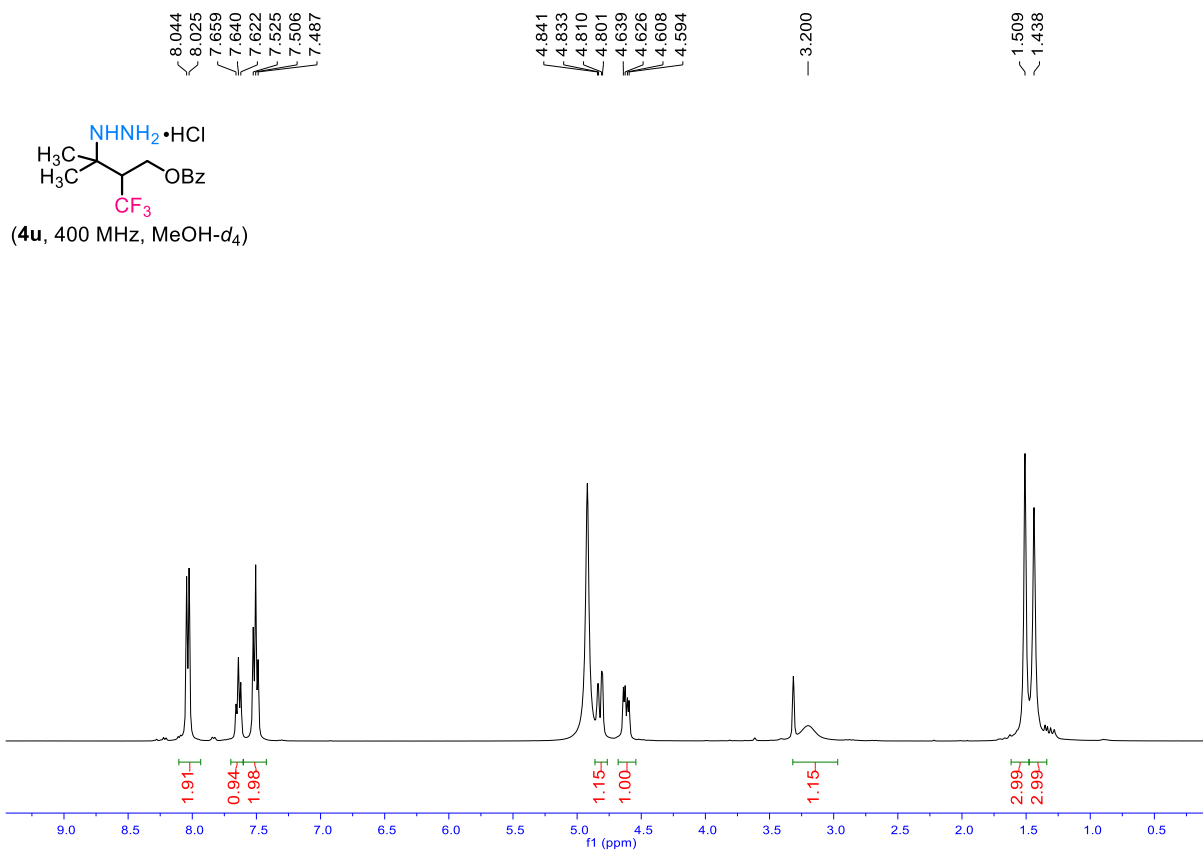
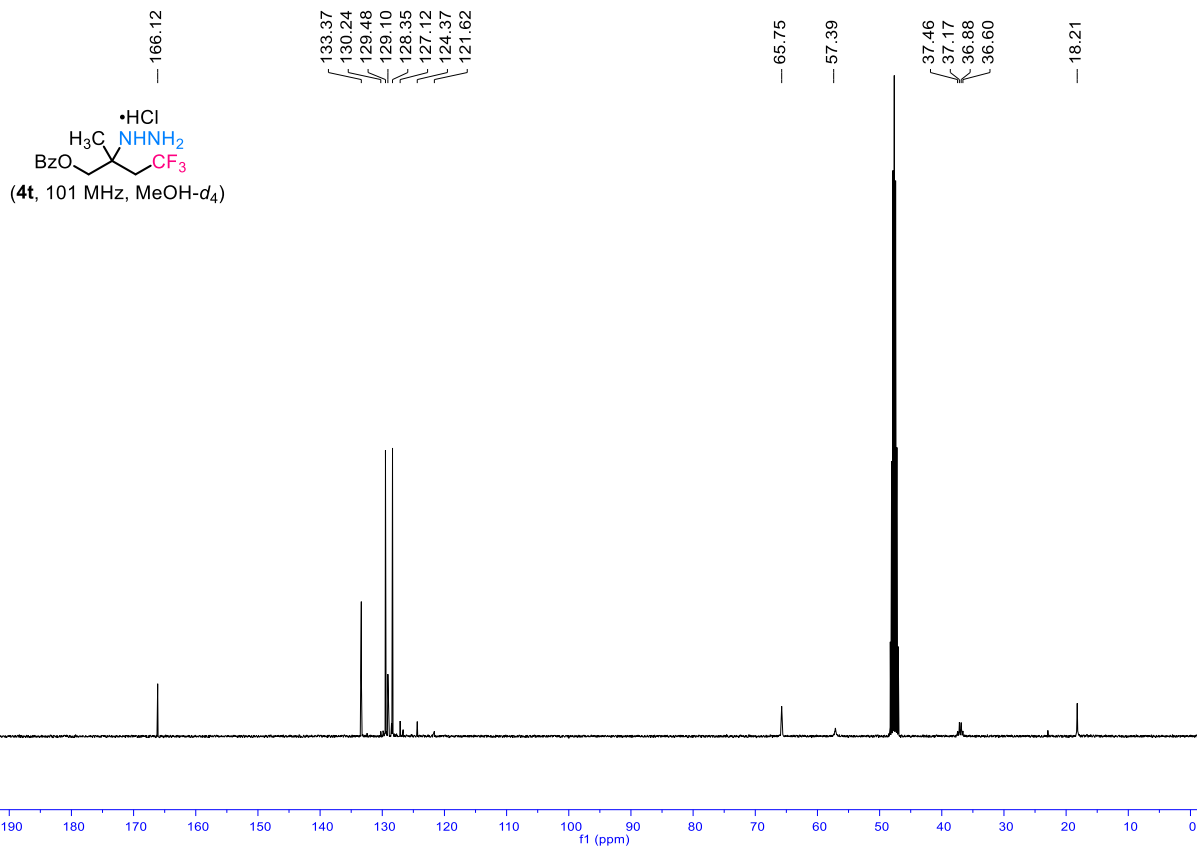


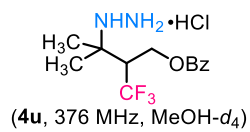




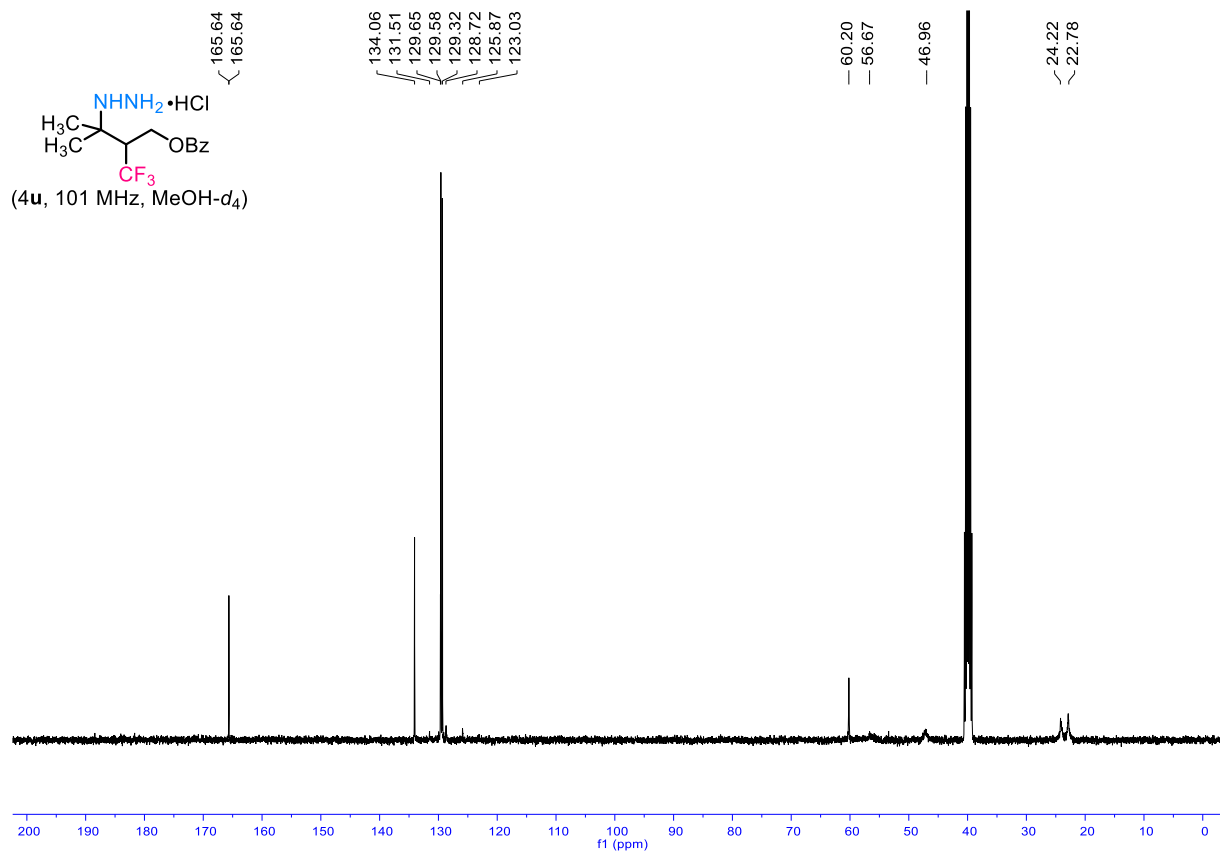
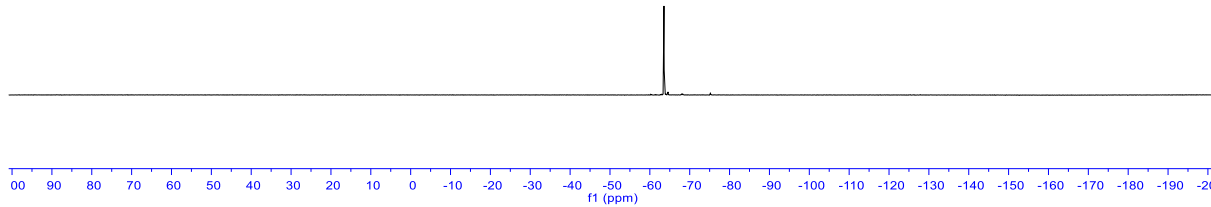


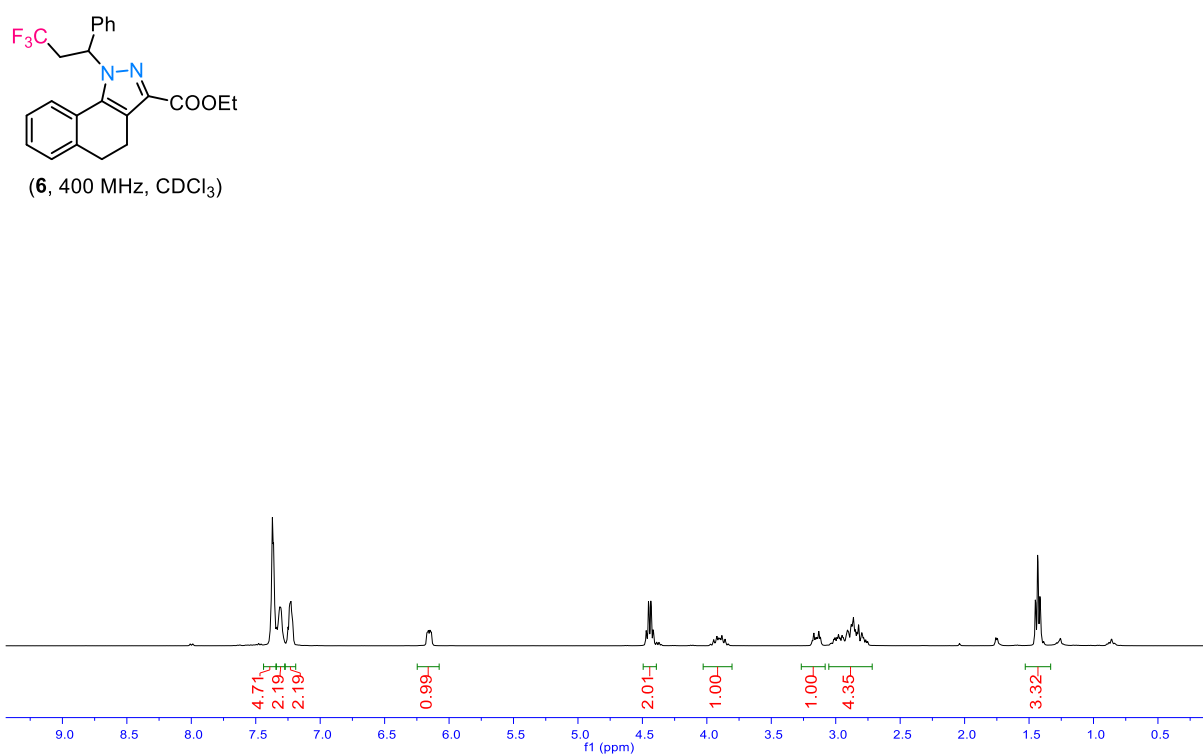
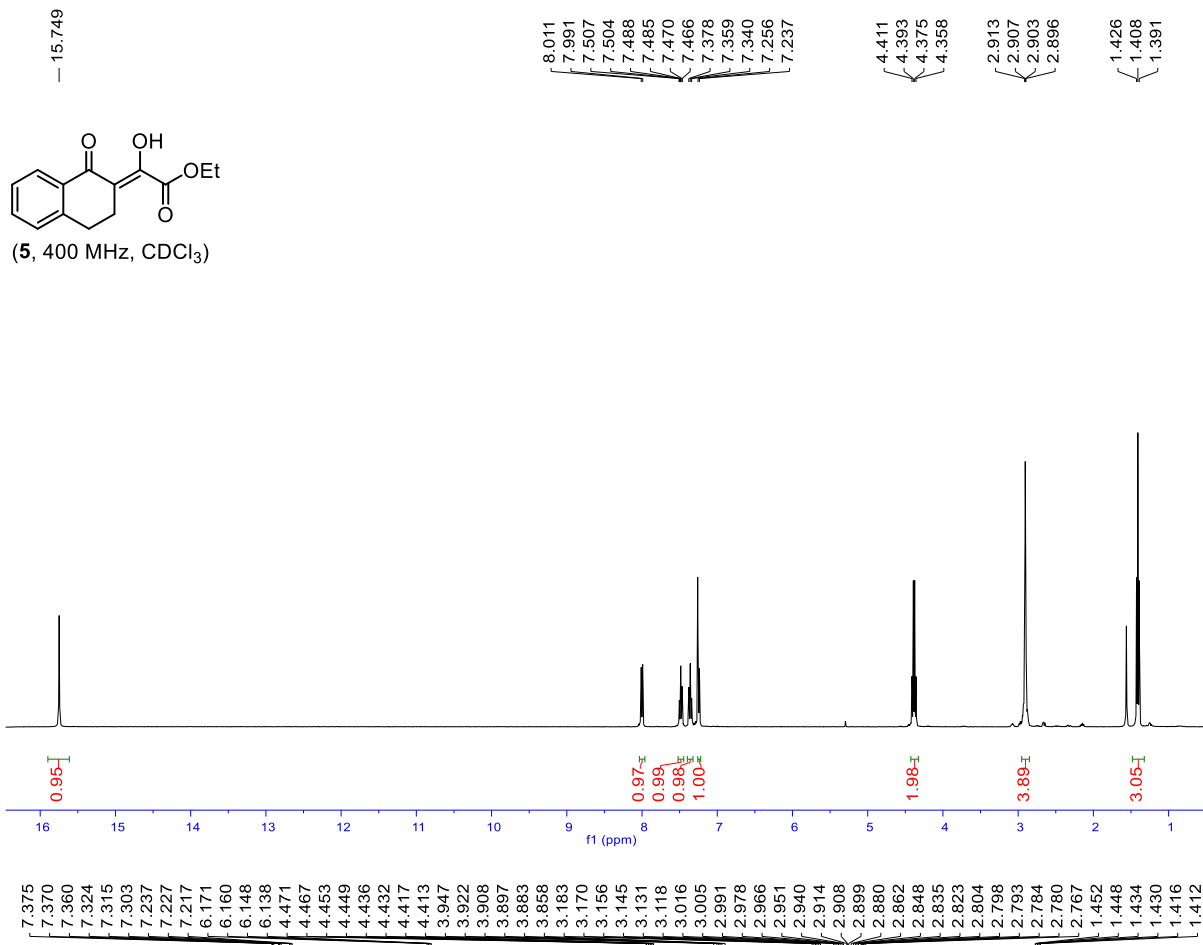


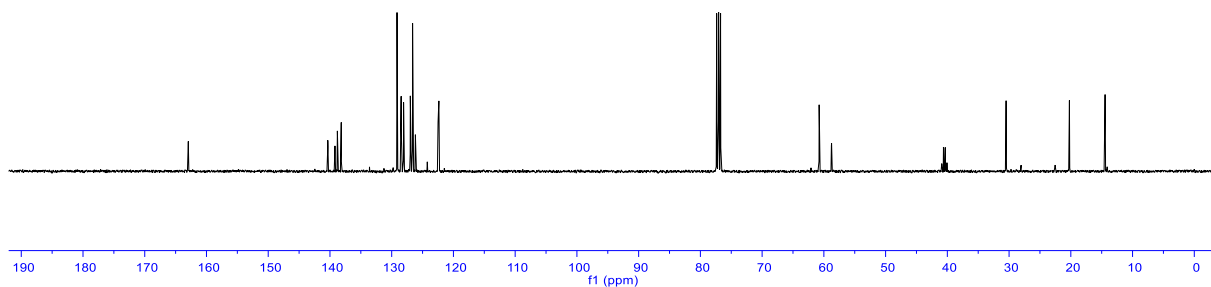
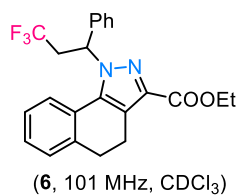
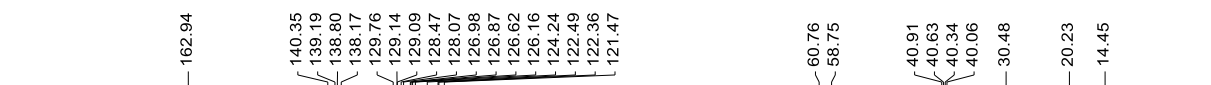
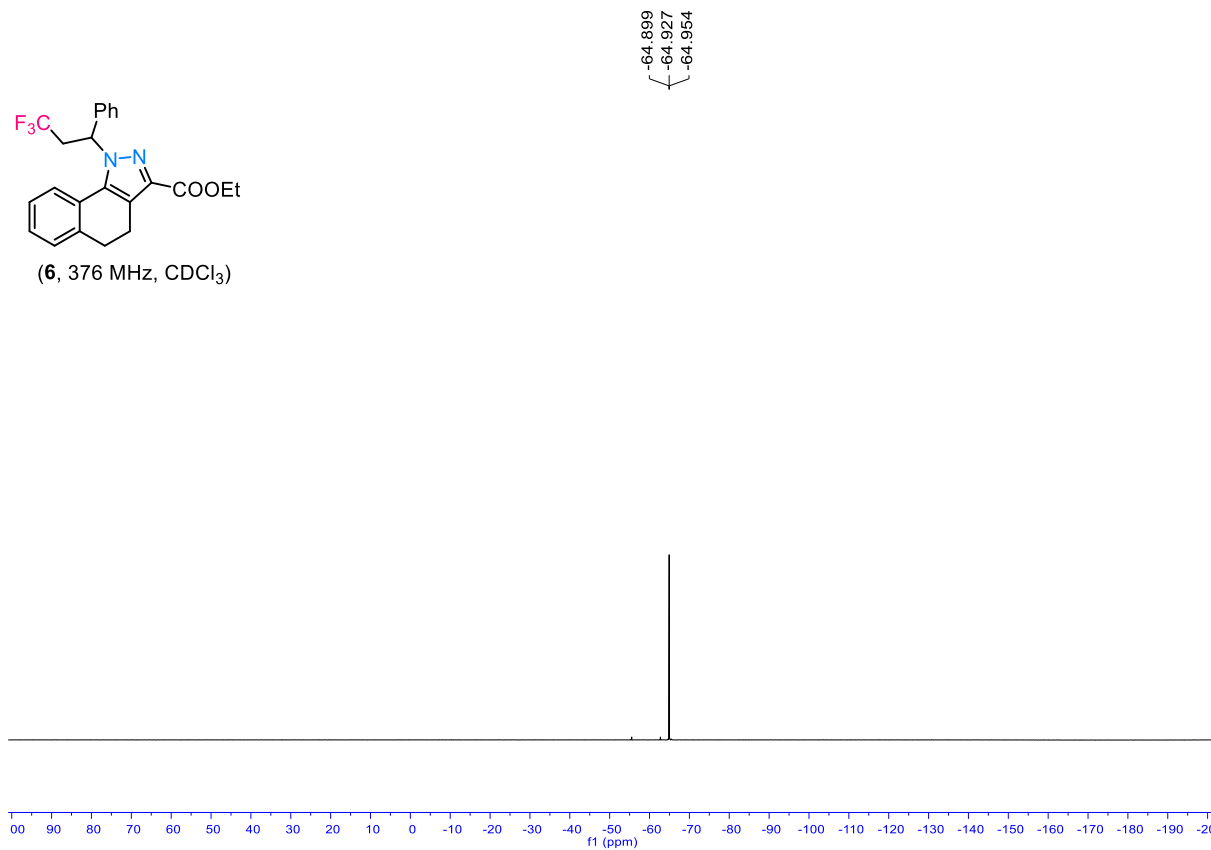
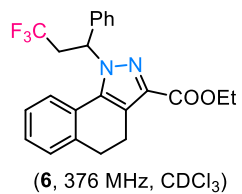


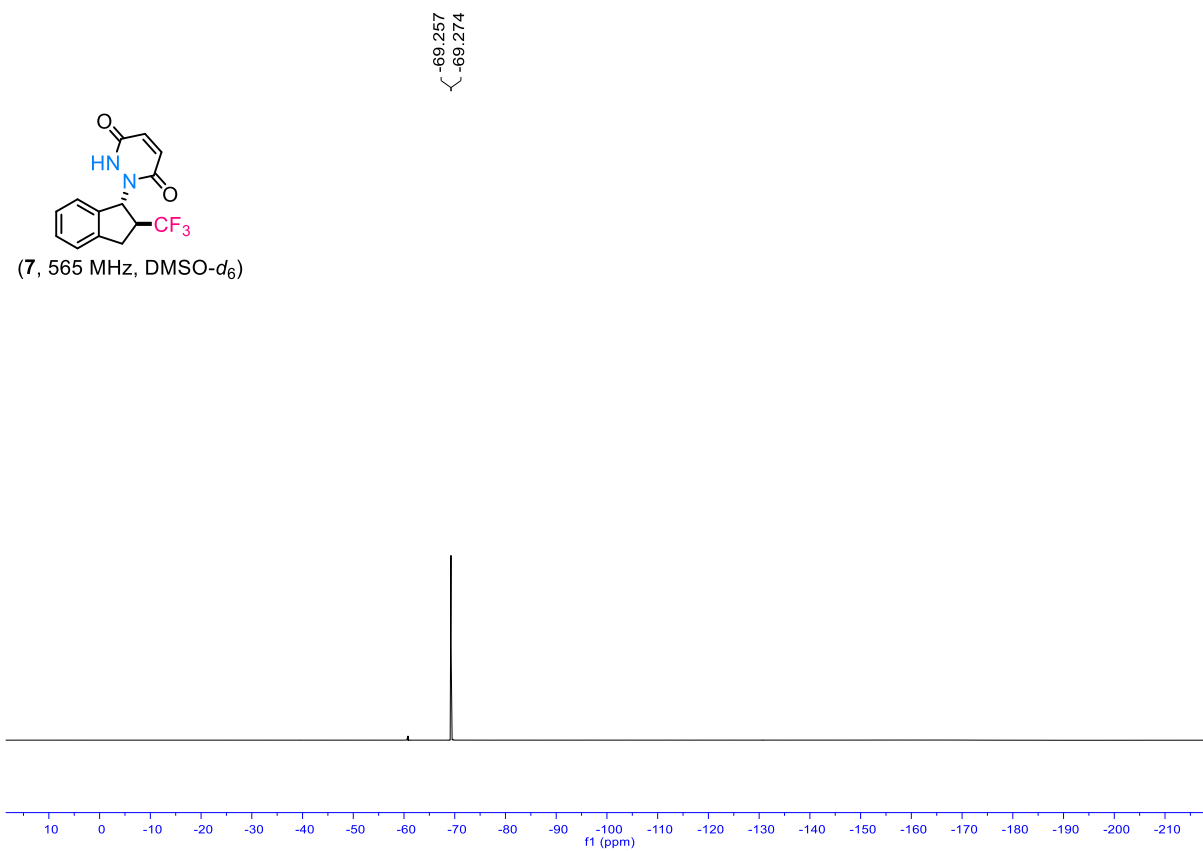
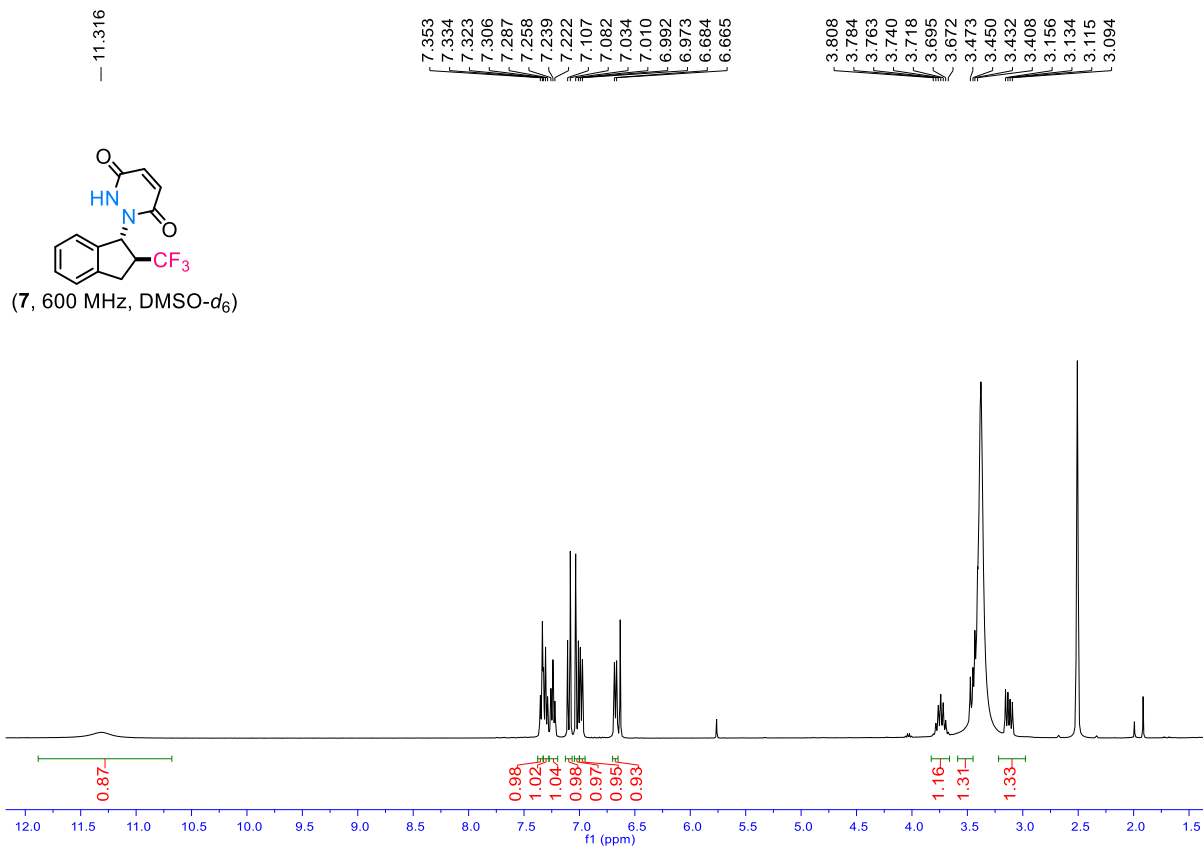


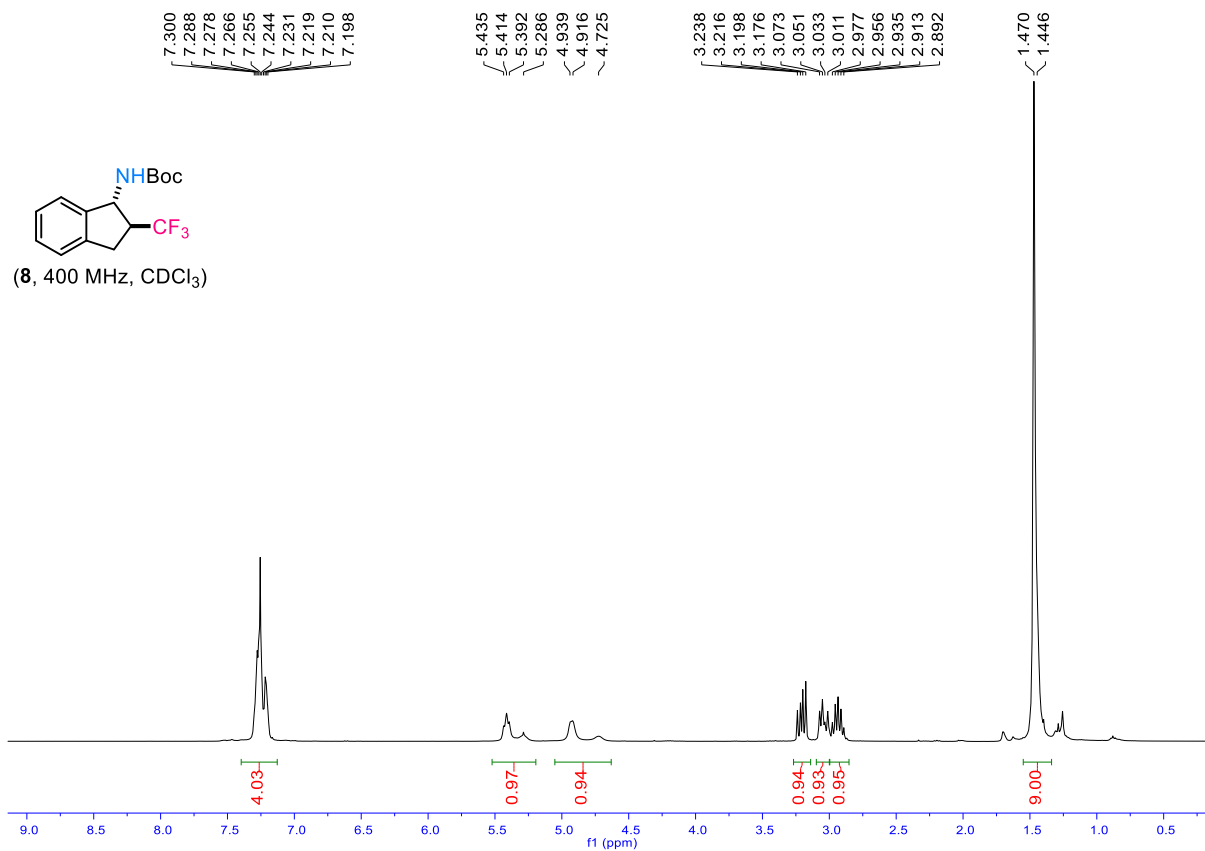
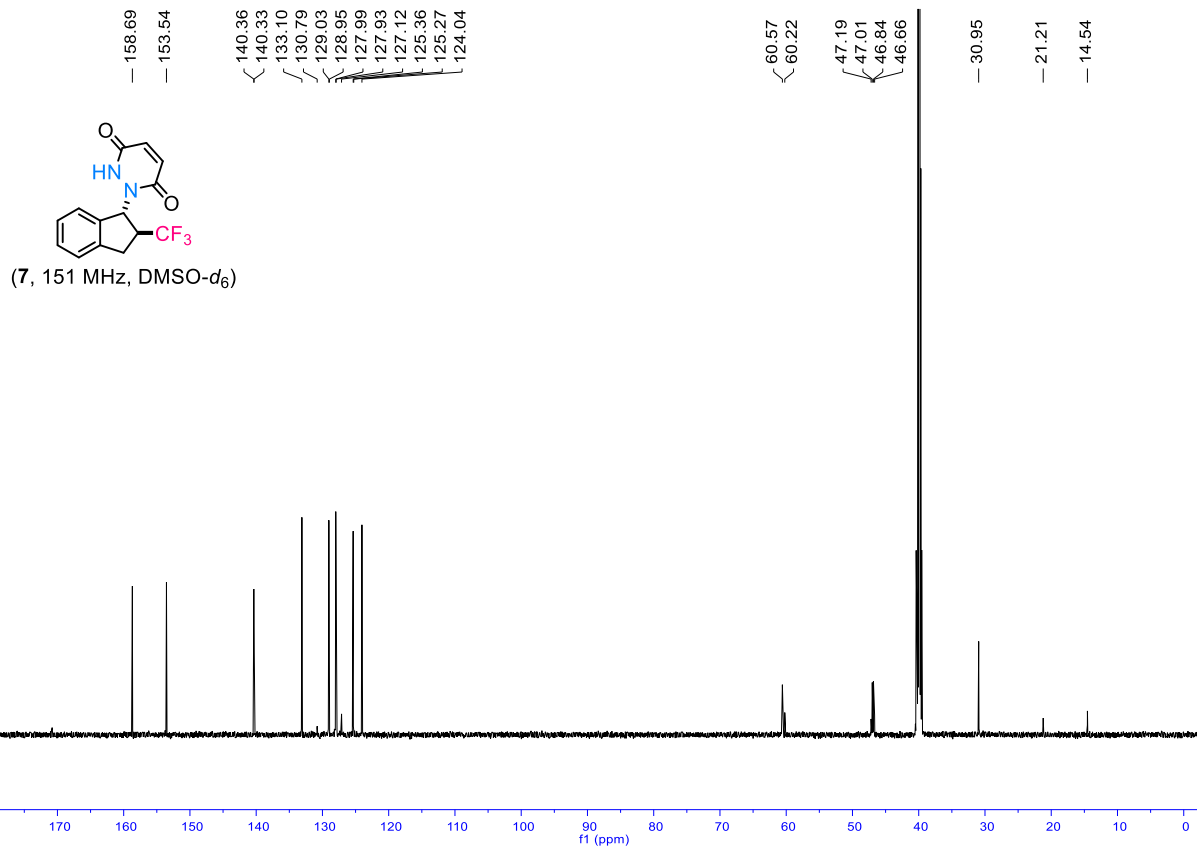
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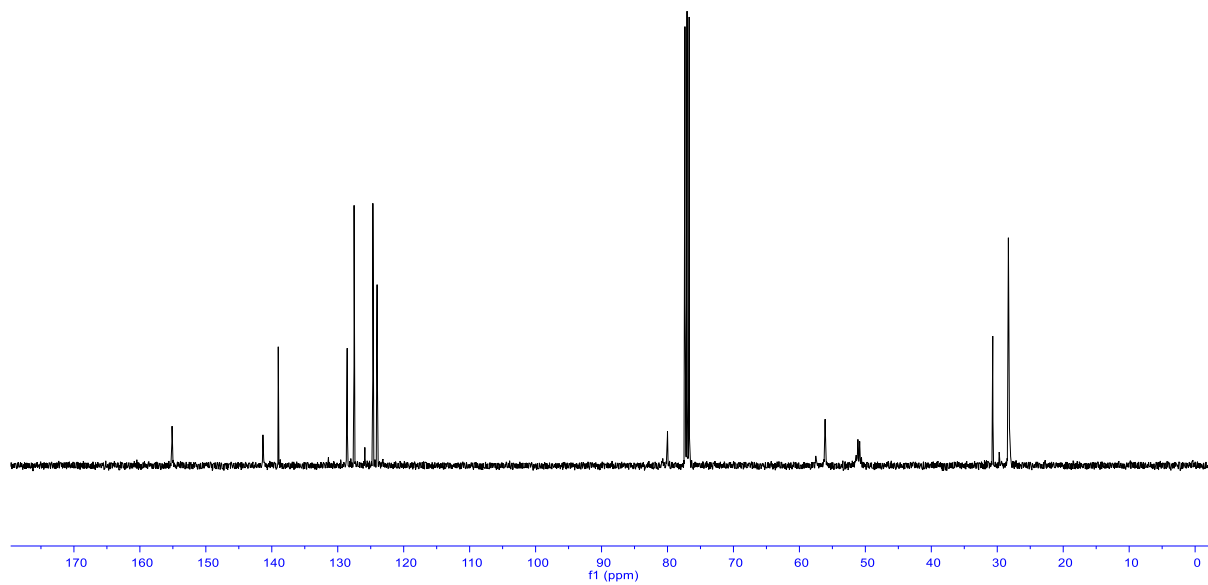
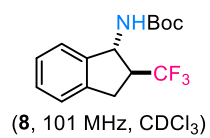
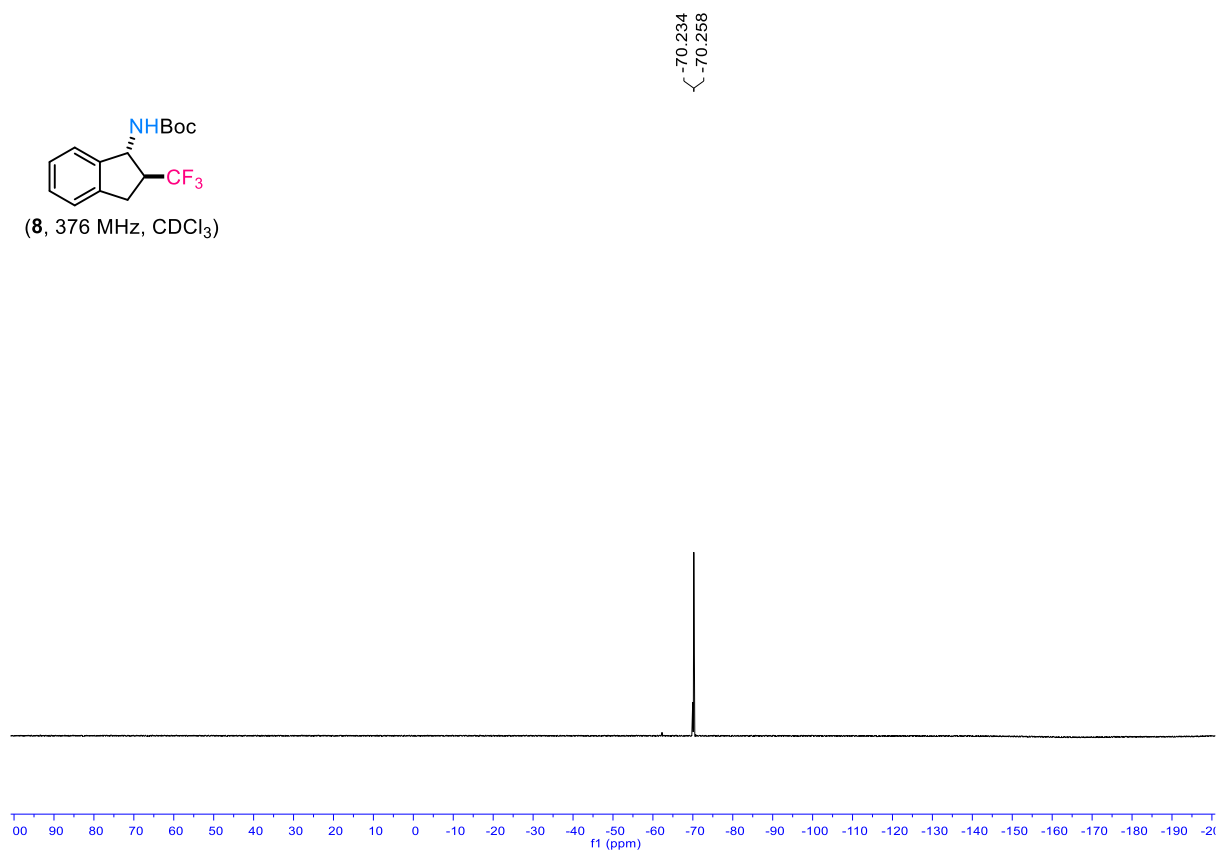
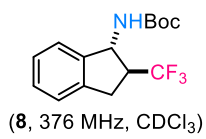


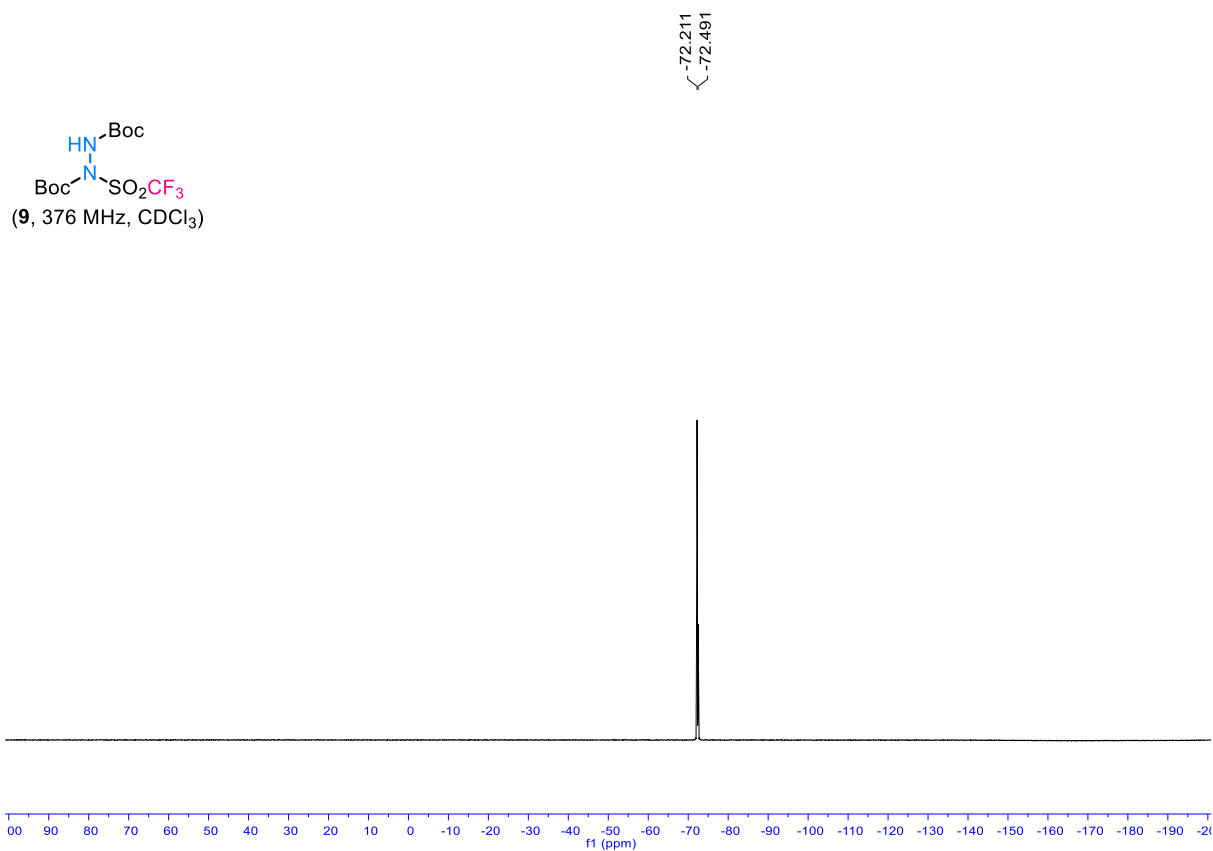
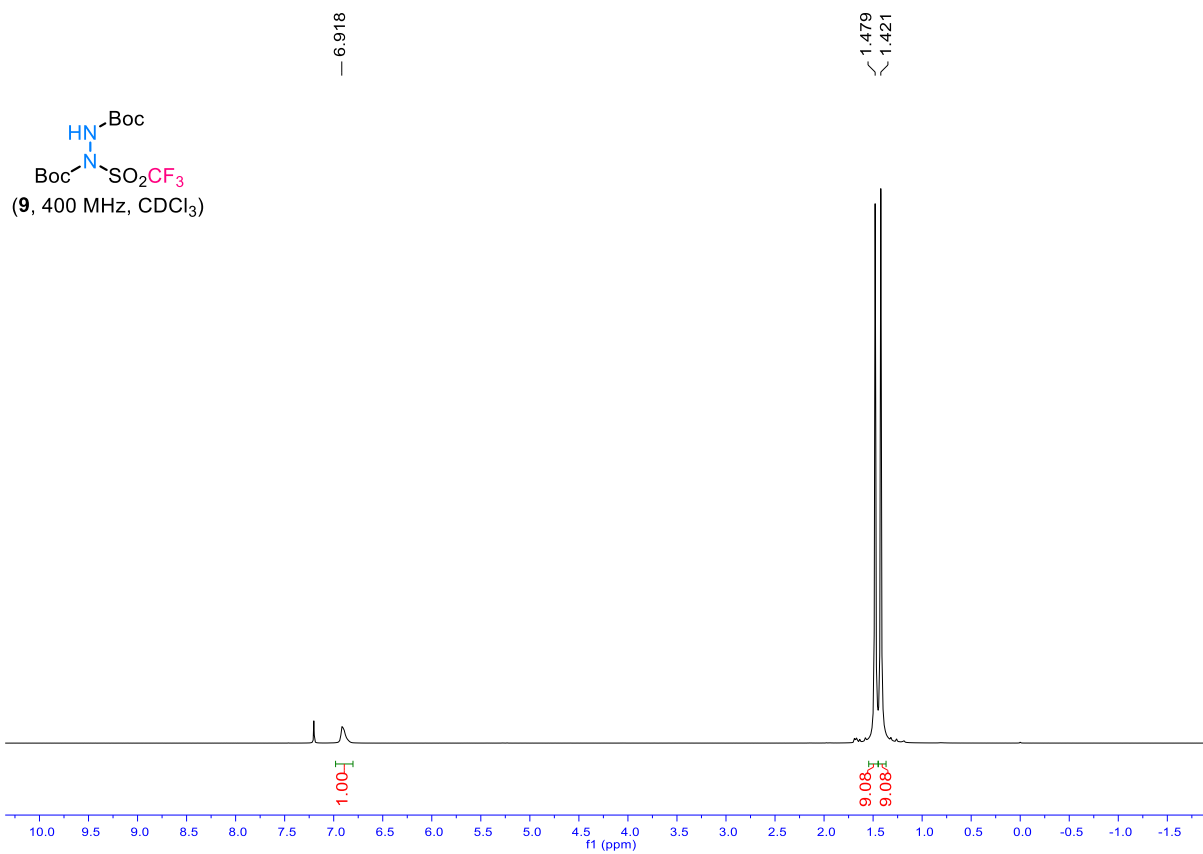


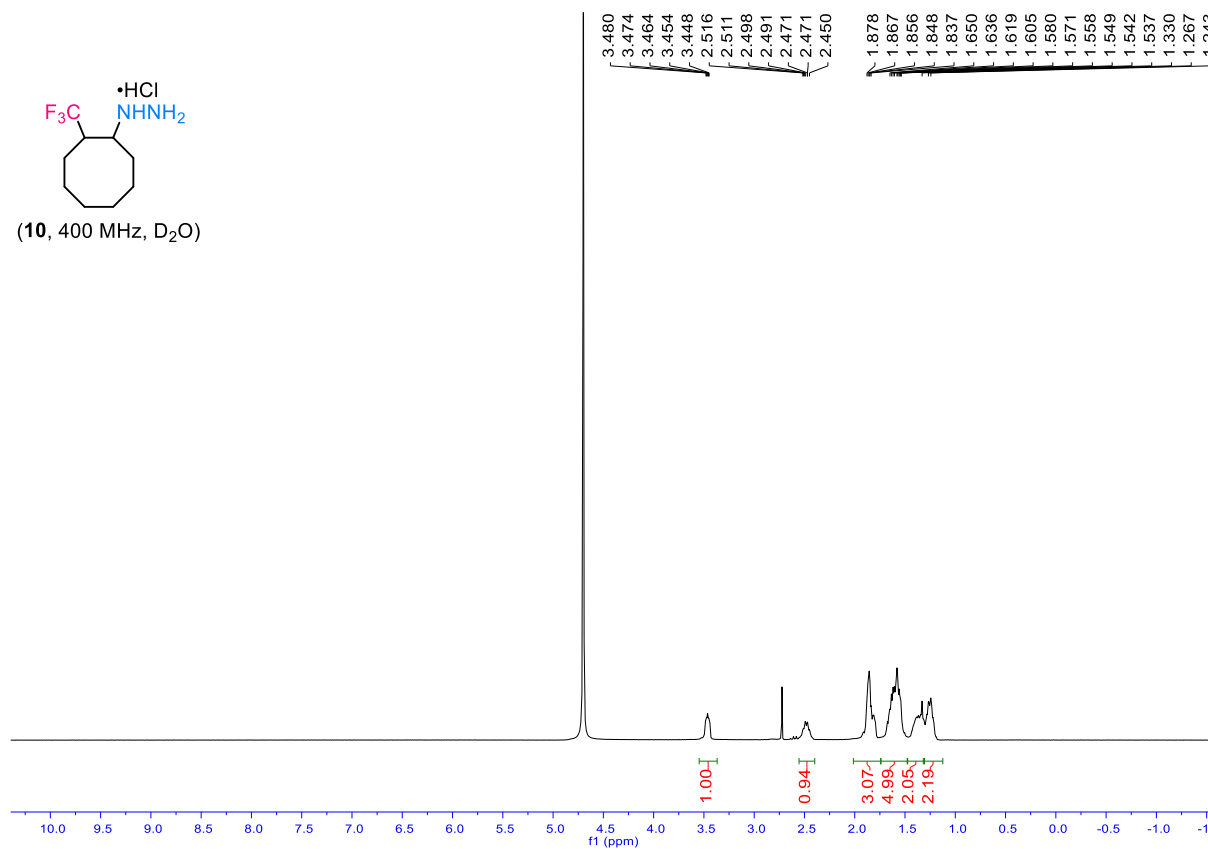
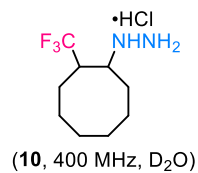
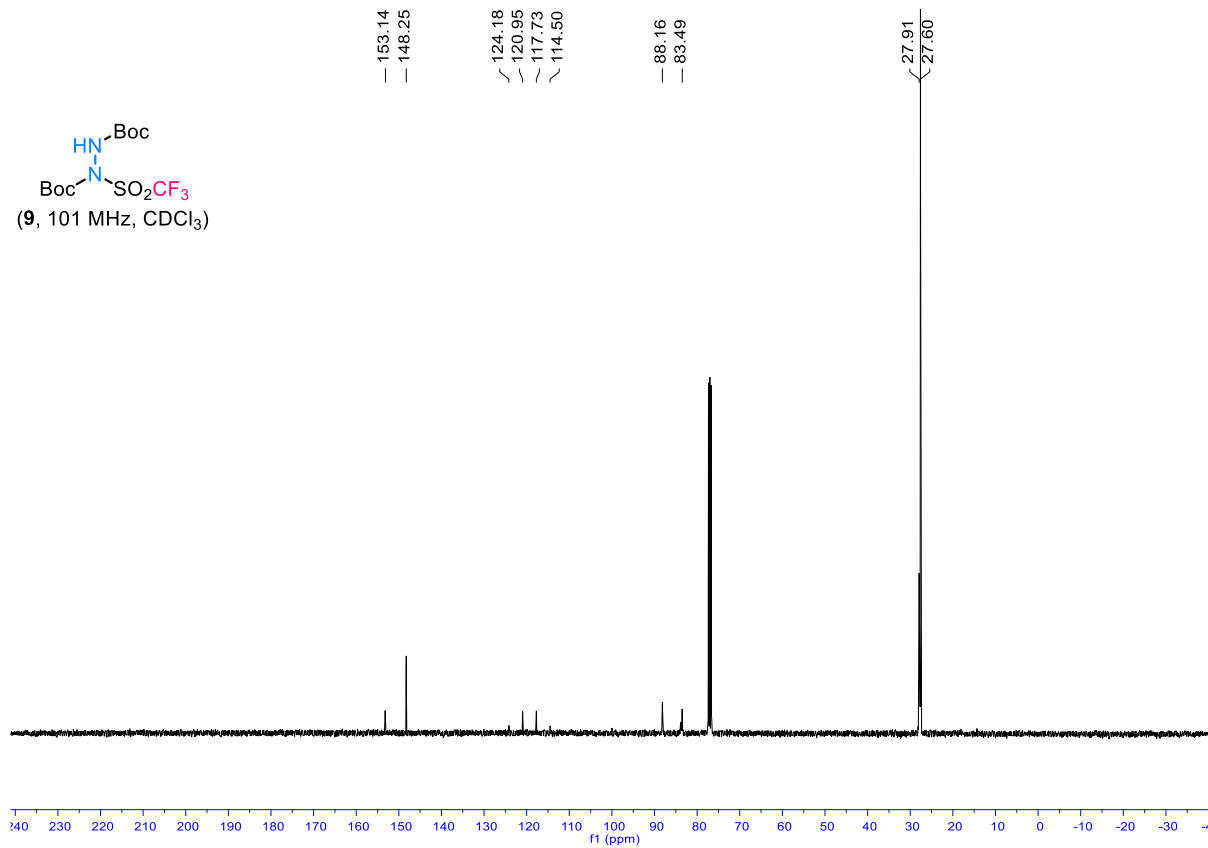
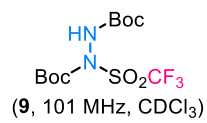


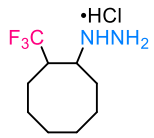




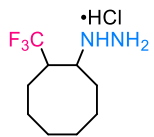
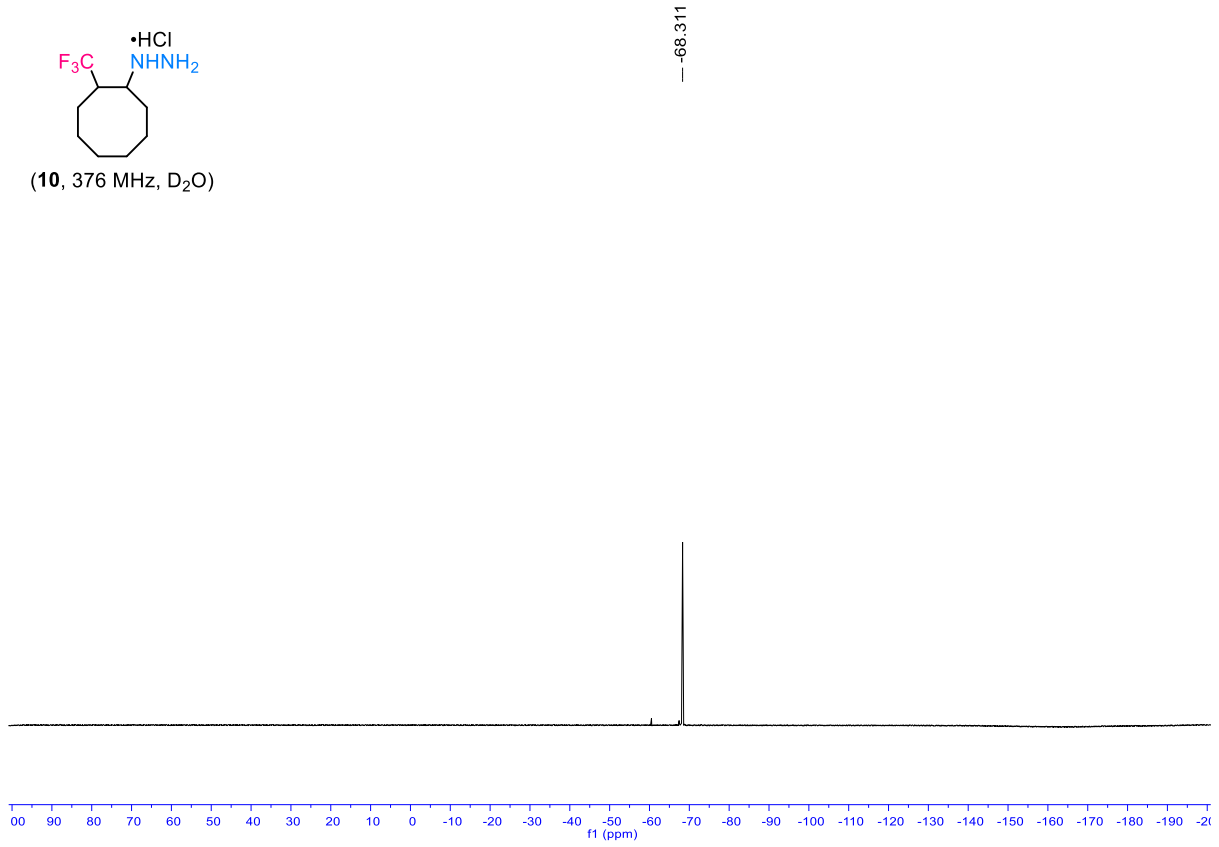








(10, 376 MHz, D<sub>2</sub>O)



(10, 101 MHz, D<sub>2</sub>O)

