

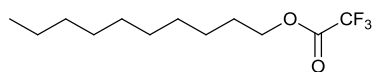
## Supporting information

### General methods

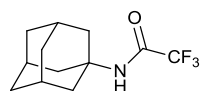
All reactions were performed under nitrogen atmosphere (using standard Schlenk technique or glove box). All reagents were used as received unless otherwise stated. Tetrahydrofuran was distilled from benzophenone/sodium under nitrogen and stored over sodium in a glove box. Dissolving the substrate to be defluorinated in THF is not necessary. Same results are obtained when used neat. The dilute reaction mixtures described for the defluorination reactions originate from the use of stock solution used to facilitate the addition of the accurate amount of substrate. Column chromatography was performed using Silica Gel 60, 0.04–0.06 mm.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded at a 400 MHz JEOL Eclipse 400 instrument, operating at 400 MHz for  $^1\text{H}$  nuclei. An 800 MHz Varian instrument was used as complement for menthyl-2,3,3,3-tetrafluoropropanoate. Samples were dissolved in  $\text{CDCl}_3$  and chemical shifts are given in ppm (parts per million) relative to residual  $\text{CHCl}_3$  (7.26 ppm),  $\alpha,\alpha,\alpha$ -trifluorotoluene (-63.6 ppm) was used as internal standard for  $^{19}\text{F}$  NMR. Gas chromatography/mass spectrometry analyses were performed on a DB-5 equivalent capillary column (length 30m, i.d. 25  $\mu\text{m}$ ) using helium as carrier gas. Injector temperature 300 °C. Temperature program: 40 to 330 °C (12 °C/min) with 4 minutes hold time. The MS detector consisted of an ion trap with 70 eV ionization.

### Preparation of $\text{SmI}_2$ in THF

Diiodoethane (23 mmol, 6.58 g) was added to dry THF (194 ml). Samarium metal (19 mmol, 4.21 g, powder) was added. The mixture was allowed to stir at room temperature in the glove box. This yields a deep-blue 0.12 M solution of  $\text{SmI}_2$ .



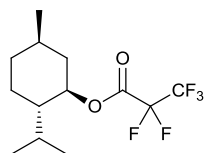
**Decyl-2,2,2-trifluoroacetate.** Decanol (0.48 ml, 2.5 mmol) was solvated in DCM (15 ml) and cooled to 0 °C. Triethylamine (0.45 ml, 3.3 mmol) was added, followed by trifluoro acetic anhydride (0.45 ml, 3.25 mmol). Cooling bath was removed and the reaction was stirred over night. The reaction mixture was washed with 1) 50 ml  $\text{H}_2\text{O}$ , 2) 50 ml  $\text{NH}_4\text{Cl}$  (aq), 3) brine. Organic layer was dried using  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure yielding a pale yellow liquid. The crude mixture was purified by column chromatography (4:1, pentane-diethyl ether) and afforded the product as a colorless liquid, 80% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CHLOROFORM-D}$ )  $\delta$  4.34 ( $\text{CH}_2\text{O}$ , t,  $^3J = 6.7$  Hz, 2H), 1.81 – 1.67 ( $\text{CH}_2\text{CH}_2\text{O}$ , m, 2H), 1.46 – 1.18 ( $7^*\text{CH}_2$ , br m, 14H), 0.88 ( $\text{CH}_3$ , t,  $^3J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CHLOROFORM-D}$ )  $\delta$  157.8 (CO, q,  $^2J = 42.1$  Hz), 114.7 ( $\text{CF}_3$ , q,  $^1J = 285.7$  Hz), 68.5 ( $\text{CH}_2\text{O}$ ), 32.0 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.57 ( $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 28.3 ( $\text{CH}_2$ ), 25.7 ( $\text{CH}_2$ ), 22.8 ( $\text{CH}_2$ ), 14.2 ( $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (376 MHz) -75.0. HRMS (CI,  $\text{NH}_3$ ) Calculated for  $\text{C}_{12}\text{H}_{25}\text{NO}_2\text{F}_3$  [ $\text{M} + \text{NH}_4$ ] $^+$ : 272.1837, found: 272.1825.



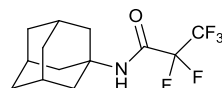
**1-Adamantyl-2,2,2-trifluoroacetamide.** 1-adamantylamine (342 mg, 2.3 mmol) was dissolved in DCM (50 ml) and cooled to 0 °C. Triethylamine (0.35 ml, 2.5 mmol) was added, followed by trifluoroacetic anhydride (0.38 ml, 2.7 mmol). Cooling bath was removed and the reaction was stirred over night. The reaction mixture was washed with 1) 50 ml  $\text{H}_2\text{O}$  2) 50 ml  $\text{NH}_4\text{Cl}$  (aq) 3) brine. Organic layer was dried using  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure yielding a yellow solid. The crude mixture was purified

by column chromatography (5:1, heptane-diethyl ether) and afforded the desired product as a white solid in 84 % yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  5.86 (br s, 1H), 2.13 (m, 3H), 2.03 (m, 6H), 1.70 (m, 6H).

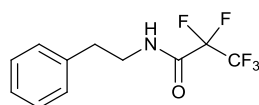
$^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  155.8 (CO, d,  $^2J = 35.7$  Hz), 115.7 (CF<sub>3</sub>, d,  $^1J = 289.7$  Hz), 53.5 (CNH), 41.1 (3\*CH<sub>2</sub>), 36.1 (3\*CH<sub>2</sub>), 29.4 (3\*CH).  $^{19}\text{F}$  NMR (376 MHz) -76.1 (CF<sub>3</sub>). HRMS (ESI) Calculated for C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub>F<sub>3</sub> [M - H]<sup>-</sup>: 246.1106, found: 246.1103.



**Menthyl-2,2,3,3,3-pentafluoropropanoate.** (-)-Menthol (588 mg, 3.8 mmol) was dissolved in DCM (25 ml) and cooled to 0 °C. Triethylamine (0.63 ml, 4.5 mmol) was added, followed by 2,2,3,3,3-pentafluoropropionic anhydride (0.88 ml, 4.5 mmol). Cooling bath was removed and the reaction was stirred over night. The reaction mixture was washed with 1) 50 ml H<sub>2</sub>O 2) 50 ml NH<sub>4</sub>Cl (aq) 3) brine. Organic layer was dried using Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure yielding a yellow solid. The crude mixture was purified by column chromatography (4:1, pentane-diethyl ether) and afforded the desired product as a white solid in 75 % yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  4.91 (CHO, ddd (appear as an dt),  $J = 11.0, 5.5, 5.5$  Hz, 1H), 2.06 – 2.03 (m, 1H), 1.88 – 1.80 (m, 1H), 1.75-1.71 (m, 2H), 1.57 – 1.48 (m, 2H), 1.18 – 1.01 (m, 2H), 0.94 (CH<sub>3</sub>CH, d,  $J = 6.6$  Hz, 3H), 0.91 (CH<sub>3</sub>, d,  $J = 7.0$  Hz, 3H), 0.77 (CH<sub>3</sub>, d,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  158.2 (CO, t,  $^2J = 29.0$  Hz), 117.9 (CF<sub>3</sub>, dt,  $^1J = 286.3, ^2J = 34.2$  Hz), 106.1 (CF<sub>2</sub>, td,  $^1J = 264.6, ^2J = 39.7$  Hz), 79.9 (C-O), 46.8 (CHCH-O), 40.1 (CH<sub>2</sub>CH-O), 34.0 (CH<sub>2</sub>), 31.6 (CHCH<sub>3</sub>), 26.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.3 (CH<sub>2</sub>CH), 22.0 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 16.0 (CH<sub>3</sub>).  $^{19}\text{F}$  NMR (376 MHz) -83.7 (CF<sub>3</sub>), -122.6 (CF<sub>2</sub>). HRMS (CI, NH<sub>3</sub>) Calculated for C<sub>13</sub>H<sub>23</sub>NO<sub>2</sub>F<sub>5</sub> [M + NH<sub>4</sub>]<sup>+</sup>: 320.1649, found: 320.1634.

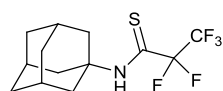


**1-Adamantyl-2,2,3,3,3-pentafluoropropanamide.** 1-adamantylamine (400 mg, 2.6 mmol) was dissolved in DCM (50 ml) and cooled to 0 °C. Triethylamine (0.44 ml, 3.2 mmol) was added, followed by pentafluoropropionic anhydride (0.56 ml, 2.9 mmol). Cooling bath was removed and the reaction was stirred over night. The reaction mixture was washed with 1) 50 ml H<sub>2</sub>O, 2) 50 ml NH<sub>4</sub>Cl (aq), 3) brine. Organic layer was dried using Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure yielding a yellow solid. The crude mixture was purified by column chromatography (5:1, heptane-diethyl ether) and afforded the desired product as a white solid in 88 % yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  5.96 (NH, s, 1H), 2.14-2.09 (3\*CH, m, 3H), 2.05-2.02 (3\*CH<sub>2</sub>, m, 6H), 1.70 (3\*CH<sub>2</sub>, t,  $J = 2.8$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  156.3 (CO, t,  $J = 24.5$  Hz), 118.0 (CF<sub>3</sub>, q of t,  $^1J = 236.1$  Hz,  $^2J = 34.9$  Hz), 106.5 (CF<sub>2</sub>, t of q,  $^1J = 268.7$  Hz,  $^2J = 34.9$  Hz), 53.7 (CNH), 40.9 (3\*CH<sub>2</sub>), 36.1 (3\*CH<sub>2</sub>), 29.4 (3\*CH).  $^{19}\text{F}$  NMR (376 MHz) -83.7 (CF<sub>3</sub>), -123.5 (CF<sub>2</sub>). HRMS (ESI) Calculated for C<sub>13</sub>H<sub>15</sub>NOF<sub>5</sub> [M - H]<sup>-</sup>: 296.1074, found: 296.1075.



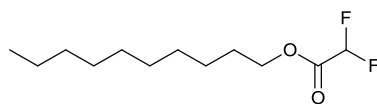
**2,2,2,3,3-Pentafluorophenylethylpropanamide.** Phenylethylamine (0.52 mL, 4.1 mmol) was dissolved in DCM (25 ml) and cooled to 0 °C. Triethylamine (0.7 ml, 5.0 mmol) was added, followed by pentafluoropropionic anhydride (0.97 ml, 5.0 mmol). Cooling bath was removed and the reaction was stirred for two hours. The reaction mixture

was washed with 1) 50 ml H<sub>2</sub>O, 2) 50 ml NH<sub>4</sub>Cl (aq), 3) brine. Organic layer was dried using Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure yielding a yellow solid. The crude mixture was purified by column chromatography (2:1, pentane-diethyl ether) and afforded the desired product as a white solid in 90 % yield. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 7.36-7.32 (m, 2\*Ar-H) 7.29-7.27 (m, Ar-H) 7.20-7.17 (m, 2\*Ar-H), 6.36 (br s, NH), 3.65 (CH<sub>2</sub>, td, *J* = 6.9, 6.2 Hz, 2H), 2.89 (CH<sub>2</sub>, t, *J* = 6.9 Hz). <sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 157.8 (CO), 137.6 (C), 129.0 (2\*CH), 128.8 (2\*CH), 127.1 (CH), 41.3 (CH<sub>2</sub>NH), 35.1 (CH<sub>2</sub>Ar). <sup>19</sup>F NMR (376 MHz) -83.7 (CF<sub>3</sub>), -124.0 (CF<sub>2</sub>). HRMS (ESI) Calculated for C<sub>11</sub>H<sub>9</sub>NOF<sub>5</sub> [M - H]<sup>-</sup>: 266.0604, found: 266.0593.



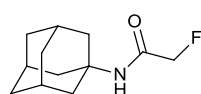
**1-Adamantyl-2,2,3,3,3-pentafluoropropanthioamide**

1-adamantyl-2,2,3,3,3-pentafluoropropanamide (354.7 mg, 1.19 mmol) and Lawesson reagent (287.9 mg, 0.71 mmol) were mixed in the reaction vessel and toluene (10 mL) was added. The mixture was heated using microwave irradiation at 180 °C for 75 min. Chromatography (20:1, heptane-diethyl ether) afforded a bright orange solid in 84% yield. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 7.44 (NH, br s, 1H), 2.31 – 2.25 (3\*CH<sub>2</sub>, m, 6H), 2.21 – 2.12 (3\*CH, m, 3H), 1.76 – 1.69 (3\*CH<sub>2</sub>, m, 6H). <sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 180.2 (CO, t, <sup>2</sup>*J* = 23.6 Hz), 118.0 (CF<sub>3</sub>, appear as a dt, <sup>1</sup>*J* = 287.5, <sup>2</sup>*J* = 37.4 Hz), 108.0 (CF<sub>2</sub>), 57.9 (CNH), 39.5 (3\*CH<sub>2</sub>), 36.2 (3\*CH<sub>2</sub>), 29.5 (3\*CH). <sup>19</sup>F NMR (376 MHz) -82.3 (CF<sub>3</sub>), -114.9 (CF<sub>2</sub>). HRMS (ESI) Calculated for C<sub>13</sub>H<sub>15</sub>NF<sub>5</sub>S [M - H]<sup>-</sup>: 312.0833, found: 312.0847.



**Decyl-2,2,2-difluoroacetate**, (Table 1, entry1).

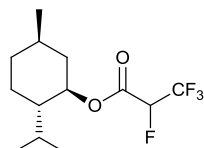
The decyl-trifluoroacetate (91.5 mg, 0.3 mmol) was solvated in dry THF (21.5 mL). The solution was cooled to -78 °C. A mixture of SmI<sub>2</sub> (20 ml, 2.4 mmol) and H<sub>2</sub>O (130 μL, 7.2 mmol) was also cooled to -78 °C and then added dropwise to the ester solution. The reaction mixture was stirred for 45 minutes before it was quenched with air until colorless, followed by 1 mL Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq). The crude mixture was concentrated under reduced pressure. Column chromatography, pentane: diethyl ether (1:1) as eluent to yield the decyl fluoroacetate as a colorless liquid (21 mg, 30% yield). <sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 5.90 (CHF<sub>2</sub>, t, <sup>2</sup>*J* = 53.4 Hz, 1H), 4.28 (CH<sub>2</sub>O, t, <sup>3</sup>*J* = 6.7 Hz, 2H), 1.70 (CH<sub>2</sub>CH<sub>2</sub>O, quintet, 2H), 1.27 (m, 1.44-1.20, 15 H), 0.88 (CH<sub>3</sub>CH<sub>2</sub>, t, <sup>3</sup>*J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 162.8 (CO), 106.9 (CHF<sub>2</sub>, t, <sup>1</sup>*J* = 249.3 Hz), 67.2 (CH<sub>2</sub>O), 32.0, 29.6, 29.6, 29.4, 29.3, 28.4, 25.8, 22.8, 14.3. <sup>19</sup>F NMR (376 MHz) -127.5 (CF<sub>2</sub>H, d, <sup>2</sup>*J* = 53.4 Hz). HRMS (CI, NH<sub>3</sub>) Calculated for C<sub>12</sub>H<sub>26</sub>NO<sub>2</sub>F<sub>2</sub> [M + NH<sub>4</sub>]<sup>+</sup>: 254.1932, found: 254.1923.



**1-Adamantyl-fluororacetamide** (table 1, entry 2).

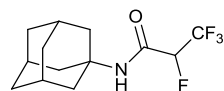
1-adamantyl-trifluoroacetamide (75.6 mg, 0.3 mmol) was solvated in dry THF (21.5 mL) and triethylamine (670 μL, 4.8 mmol) was added. The solution was cooled to -78 °C. A mixture

of  $\text{SmI}_2$  (20.5 ml, 2.46 mmol) and  $\text{H}_2\text{O}$  (133  $\mu\text{L}$ , 7.4 mmol) was also cooled to  $-78\text{ }^\circ\text{C}$  and then added dropwise to the amide solution. The reaction was stirred for 30 min and quenched by removing the lid and let air into the vessel, followed by adding 1 mL  $\text{Na}_2\text{S}_2\text{O}_3$  (aq). The crude mixture was purified by column chromatography (1:2, heptane-diethyl ether) and afforded the desired product as a white solid in 28 % yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  5.92 (NH, br s, 1H), 4.65 ( $\text{CH}_2\text{F}$ , d,  $^2J = 47.7$  Hz, 2H), 2.14-2.06 ( $3^*\text{CH}$ , m, 3H), 2.06-2.01 ( $3^*\text{CH}_2$ , m, 6H), 1.72-1.67 ( $3^*\text{CH}_2$ , m, 6H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  166.4 (CO), 80.3 ( $\text{CH}_2\text{F}$ , d,  $^1J=187.7$  Hz), 52.3 (CNH), 41.7 ( $3^*\text{CH}_2$ ), 36.4 ( $3^*\text{CH}_2$ ), 29.5 ( $3^*\text{CH}$ ).  $^{19}\text{F}$  NMR (376 MHz) -220.9 ( $\text{CFH}_2$ , t,  $^2J = 47.7$  Hz). HRMS (ESI) Calculated for  $\text{C}_{12}\text{H}_{19}\text{NO}_2\text{F}$   $[\text{M} + \text{H}]^+$ : 212.1451, found: 212.1447.



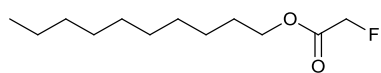
**Menthyl-2,3,3,3-tetrafluoropropanoate**, table 1 entry 3. Menthyl-2,2,3,3,3-pentafluoropropanoate (92.2 mg, 0.31 mmol) was dissolved in dry THF (21.5 mL) and cooled to  $-78\text{ }^\circ\text{C}$ . A mixture of  $\text{SmI}_2$  (20.5 ml, 2.46 mmol) and  $\text{H}_2\text{O}$  (130  $\mu\text{L}$ , 7.4 mmol) was also cooled to  $-78\text{ }^\circ\text{C}$  and then added dropwise to the amide solution. The reaction was stirred for 45 min and quenched by removing the lid and let air into the vessel, followed by adding 1 mL  $\text{Na}_2\text{S}_2\text{O}_3$ . The crude mixture was purified by column chromatography (pure diethyl ether) and afforded the desired product as a pale yellow solid in 82 % yield, diastereomeric mixture 2:1. The mixture could not be separated using column chromatography.

$^1\text{H}$  NMR (800 MHz,  $\text{CDCl}_3$ )  $\delta$  5.09 (dq,  $J = 13.1, 6.5$  Hz, 1H), 5.04 (dq,  $J = 13.1, 6.5$  Hz, 1H), 4.93 – 4.85 (m, 2H), 2.09 – 2.04 (m, 2H), 2.04 – 1.98 (m, 1H), 1.90 – 1.81 (m, 2H), 1.76 – 1.68 (m, 5H), 1.55 – 1.45 (m, 5H), 1.12 – 1.02 (m, 5H), 0.97-0.86 (m, 15H), 0.77 (d,  $J = 6.9$  Hz, 2H), 0.75 (d,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  161.7 ( $\text{COCFH}$ , dq,  $^2J = 23.3$  Hz, 2.0 Hz), 120.6 (qd,  $\text{CF}_3$ ,  $^1J = 283.8$  Hz,  $^2J = 26.0$  Hz), 84.21 (dq,  $\text{CFH}$ ,  $^1J = 200.4$  Hz,  $^2J = 35.4$  Hz), 84.11 (dq,  $\text{CFH}$ ,  $^1J = 200.4$  Hz,  $^2J = 35.4$  Hz), 78.3 (C-O), 78.1 (C-O), 46.8 (CH), 40.5 ( $\text{CH}_2$ ), 40.3 ( $\text{CH}_2$ ), 34.1 ( $\text{CH}_2$ ), 34.1 ( $\text{CH}_2$ ), 31.6 (CH), 31.5 (CH), 26.3 ( $\text{CH}(\text{CH}_3)_2$ ), 25.9 ( $\text{CH}(\text{CH}_3)_2$ ), 23.4 ( $\text{CH}_2$ ), 23.1 ( $\text{CH}_2$ ), 22.0 ( $\text{CH}(\text{CH}_3)_2$ ), 22.0 ( $\text{CH}(\text{CH}_3)_2$ ), 20.8 ( $\text{CH}(\text{CH}_3)_2$ ), 20.8 ( $\text{CH}(\text{CH}_3)_2$ ), 16.2 ( $\text{CH}_3\text{CH}$ ), 15.8 ( $\text{CH}_3\text{CH}$ ).  $^{19}\text{F}$  NMR (376 MHz) -76.6 ( $\text{CF}_3$ ), -204.5- (-205.0) (m,  $\text{CFH}$ ). HRMS (CI,  $\text{NH}_3$ ) Calculated for  $\text{C}_{13}\text{H}_{24}\text{NO}_2\text{F}_4$   $[\text{M} + \text{NH}_4]^+$ : 302.1743, found: 302.1719.

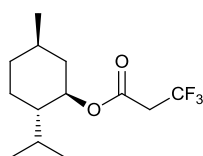


**1-Adamantyl-2,3,3,3-tetrafluoropropionamide**, table 1, entry 4. 1-adamantyl-2,2,3,3,3-pentafluoropropionamide (108.3 mg, 0.36 mmol) ) was solvated in dry THF (23 mL) and dry triethylamine (600  $\mu\text{L}$ , 4.3 mmol) was added. The solution was cooled to  $-78\text{ }^\circ\text{C}$ . A mixture of  $\text{SmI}_2$  (18 ml, 2.16 mmol) and  $\text{H}_2\text{O}$  (115  $\mu\text{L}$ , 6.4 mmol) was also cooled to  $-78\text{ }^\circ\text{C}$  and then added dropwise to the amide solution. The reaction was stirred for 30 min and quenched by removing the lid and let air into the vessel followed by adding 1 mL sat.  $\text{Na}_2\text{S}_2\text{O}_3$  (aq). The crude mixture was purified by column chromatography (95:5, pentane-diethyl ether) and afforded the desired product as a white solid in 75 % yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  5.96 (NH, s, 1H),  $\delta$  4.93 (CHF, dq,  $J = 46.8, 6.5$  Hz, 1H) 2.15-2.08 ( $3^*\text{CH}$ , m, 3H), 2.05-2.01 ( $3^*\text{CH}_2$ , m, 6H), 1.70 ( $3^*\text{CH}_2$ , t,  $J = 3.2$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  159.9 (CO, d,  $^2J = 18.6$  Hz), 120.8 (CHF, qd,  $^1J = 282.2$ ,  $^2J = 25.5$  Hz), 85.5 ( $\text{CF}_3$ , dq,  $^1J = 204.8$ ,  $^2J = 33.0$  Hz), 53.2 (CNH), 41.3 ( $3^*\text{CH}_2$ ), 36.2

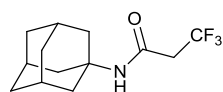
(3\*CH<sub>2</sub>), 29.5 (3\*CH). <sup>19</sup>F NMR (376 MHz) -76.9 (CF<sub>3</sub>), -199.3 (CFH, d, <sup>2</sup>J = 46.8 Hz). HRMS (ESI) Calculated for C<sub>13</sub>H<sub>16</sub>NOF<sub>4</sub> [M - H]<sup>-</sup>: 278.1168, found: 278.1164.



**Decyl-2-fluoroacetate**, Table 2 entry 1. The decyl-trifluoroacetate (91.5 mg, 0.3 mmol) was solvated in dry THF (21.5 mL). The solution was cooled to -78 °C. A mixture of SmI<sub>2</sub> (20 ml, 2.4 mmol) and H<sub>2</sub>O (130 μL, 7.2 mmol) was also cooled to -78 °C and then added dropwise to the ester solution. The reaction mixture was stirred for 45 minutes before it was quenched using air until colorless, followed by 1 mL Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq). The crude mixture was concentrated under reduced pressure. The crude mixture was purified by column chromatography (pentane: diethyl ether, 1:1) as eluent, to yield the decyl fluoroacetate as a colorless liquid in 30% yield. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 4.84 (CFH<sub>2</sub>, d, J = 47.1 Hz, 2H), 4.21 (CH<sub>2</sub>O, t, J = 6.8 Hz, 2H), 1.67 (CH<sub>2</sub>-CH<sub>2</sub>O, quintet, J = 6.8 Hz, 2H), 1.40-1.20 (m, 16 H), 0.88 (t, <sup>3</sup>J = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 168.1 (CO, d, <sup>2</sup>J = 21.7 Hz), 78.6 (CH<sub>2</sub>F), 65.8 (CH<sub>2</sub>O), 32.0, 29.6, 29.4, 29.3, 28.6, 25.9, 22.8, 14.3. <sup>19</sup>F NMR (376 MHz) -230.6 (CFH<sub>2</sub>, d, <sup>2</sup>J = 47.1 Hz). HRMS (CI, NH<sub>3</sub>) Calculated for C<sub>12</sub>H<sub>27</sub>NO<sub>2</sub>F [M + NH<sub>4</sub>]<sup>+</sup>: 236.2026, found: 236.2023.

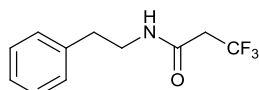


**(-)-Menthyl-3,3,3-trifluoropropanoate**, Table 2 entry 2. The menthyl 2,2,3,3,3-pentafluoropropanoate (91.5 mg, 0.3 mmol) was solvated in dry THF (21.5 mL) and triethylamine (670 μL, 4.8 mmol) was added. The solution was cooled to -78 °C. A mixture of SmI<sub>2</sub> (20 ml, 2.4 mmol) and H<sub>2</sub>O (130 μL, 7.2 mmol) was also cooled to -78 °C and then added dropwise to the ester solution. The reaction mixture was stirred for 45 minutes before it was quenched using air until colorless, followed by 1 mL Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The crude mixture was concentrated under reduced pressure. The mixture was purified using column chromatography, Et<sub>2</sub>O as eluent, to yield the product as a pale yellow oil (66 mg, 83% yield). <sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 4.76 (CH-O, td, J = 10.9, 4.4 Hz, 1H), 3.47 (q, J = 7.0 Hz, 1H), 3.14 (CH<sub>2</sub>CF<sub>3</sub>, q, J = 10.2 Hz, 2H), 2.05 – 1.97 (CHCHO, m, 1H), 1.91-1.79 (CH, m, 1H), 1.74 – 1.63 (CH<sub>2</sub>CHO, m, 2H), 1.55 – 1.35 (m, 3H), 0.91 (CH<sub>3</sub>CH, d, J = 6.1 Hz, 3H), 0.89 (CH(CH<sub>3</sub>)<sub>2</sub>, d, J = 6.8 Hz, 3H), 0.75 ((CH(CH<sub>3</sub>)<sub>2</sub>), d, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 163.8 (CO, q, J = 4.2 Hz), 123.6 (q, J = 276.3 Hz) 76.3 (CH-O), 46.9 (CH), 40.2 (CH<sub>2</sub>CF<sub>3</sub>, q, J = 30.8 Hz), 34.2, 31.5, 26.2, 23.4, 22.1, 20.8, 16.2. <sup>19</sup>F NMR (376 MHz) -64.3 (CF<sub>3</sub>). HRMS (ESI) Calculated for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>F<sub>3</sub> [M - H]<sup>-</sup>: 265.1415, found: 265.1469.



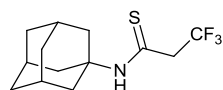
**1-Adamantyl-3,3,3-trifluoropropanamide**, table 2 entry 3. 1-adamantyl-2,2,3,3,3-pentafluoropropionamide (89.2 mg, 0.30 mmol) ) was solvated in dry THF (21.5 mL) and dry triethylamine (670 μL, 4.8 mmol) was added. A mixture of SmI<sub>2</sub> (18 ml, 2.16 mmol) and H<sub>2</sub>O (115 μL, 6.4 mmol) was added dropwise to the amide solution at room temperature. The reaction was stirred for 15 min and quenched by removing the lid and let air

into the vessel, followed by adding 1 mL sat.  $\text{Na}_2\text{S}_2\text{O}_3$  (aq.). The crude mixture was purified by column chromatography (1:1, pentane-diethyl ether) and afforded the desired product as a white solid in 69 % yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  5.42 (NH, s, 1H), 2.96 ( $\text{CH}_2\text{CF}_3$ , q,  $^3J = 10.7$  Hz, 2H), 2.08 ( $3*\text{CH}_2$ , br s, 3H), 2.03-1.96 ( $3*\text{CH}_2$ , m, 6H), 1.72-1.63 ( $3*\text{CH}_2$ , m, 6H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  161.6 (CO, d,  $^3J = 3.5$  Hz), 124.3 ( $\text{CF}_3$ , q,  $^1J = 277.8$  Hz), 52.9 (C-NH), 42.9 ( $\text{CH}_2\text{CF}_3$ , q,  $^2J = 28.9$  Hz), 41.5 ( $\text{CH}_2\text{CHNH}$ ), 36.3 ( $3*\text{CH}_2$ ), 29.5 ( $3*\text{CH}$ ).  $^{19}\text{F}$  NMR (376 MHz) -64.1 ( $\text{CF}_3$ ). HRMS (ESI) Calculated for  $\text{C}_{13}\text{H}_{19}\text{NOF}_3$   $[\text{M} + \text{H}]^+$ : 262.1419, found: 262.1409.



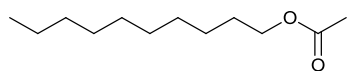
**3,3,3-Trifluorophenylethylpropanamide**, table 3 entry 4. The

2,2,3,3,3-pentafluorophenylethylpropanamide (81.2 mg, 0.3 mmol) was solvated in dry THF (21.5 mL) and triethylamine (670  $\mu\text{L}$ , 4.8 mmol) was added. The solution was cooled to  $-78$   $^\circ\text{C}$ . A mixture of  $\text{SmI}_2$  (20 ml, 2.4 mmol) and  $\text{H}_2\text{O}$  (130  $\mu\text{L}$ , 7.2 mmol) was also cooled to  $-78$   $^\circ\text{C}$  and then added dropwise to the amide solution. The reaction mixture was stirred for 30 minutes before it was quenched using air, followed by 1 mL  $\text{Na}_2\text{S}_2\text{O}_3$  (aq.). The crude mixture was concentrated under reduced pressure. Column chromatography (2:1, pentane:ethyl acetate) to yield 3,3,3- trifluorophenylethylpropanamide as a colorless liquid (35 mg, 50% yield).  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  7.24 (Ar-H, m, 5H), 6.06 (NH, br s, 1 H), 3.53 ( $\text{CH}_2\text{NH}$ , dd,  $J = 13.0, 6.9$  Hz, 2H), 2.99 ( $\text{CH}_2\text{CF}_3$ , q,  $J = 10.6$  Hz, 1H), 2.82 (Ar $\text{CH}_2$ , t,  $J = 6.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  162.8 (CO), 138.5 (C), 128.8 ( $2*\text{CH}$ ), 128.8 ( $2*\text{CH}$ ), 126.8 (CH), 124.2 ( $\text{CF}_3$ , d,  $^1J = 276.7$  Hz) 41.7 ( $\text{CH}_2\text{CF}_3$ , q,  $^2J = 29.4$  Hz), 35.43 ( $\text{CH}_2$ ), 21.14 ( $\text{CH}_2$ ).  $^{19}\text{F}$  NMR (376 MHz) -63.9 ( $\text{CF}_3$ ). HRMS (ESI) Calculated for  $\text{C}_{11}\text{H}_{13}\text{NOF}_3$   $[\text{M} + \text{H}]^+$ : 232.0949, found: 232.0935.

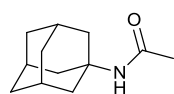


**1-Adamantyl-3,3,3-trifluoropropanthioamide**, table 2 entry 4. 1-

adamantyl-2,2,3,3,3-pentafluoropropanthioamide (93.7 mg, 0.30 mmol) ) was solvated in dry THF (21.5 mL) and dry triethylamine (500  $\mu\text{L}$ , 3.6 mmol) was added. A mixture of  $\text{SmI}_2$  (15 ml, 1.8 mmol) and  $\text{H}_2\text{O}$  (100  $\mu\text{L}$ , 5.5 mmol) was added dropwise to the thioamide solution. The reaction instantly turned green/brown and 1 mL sat.  $\text{Na}_2\text{S}_2\text{O}_3$  (aq) was added. The crude mixture was solvated in DCM and  $\text{NH}_4\text{Cl}$ . The organic phase was dried and concentrated under reduced pressure yielding the desired product in 30% yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  6.97 (NH), 3.51-3.43 (m,  $\text{CH}_2\text{CF}_3$ ), 2.35-2.25(m,  $3*\text{CH}_2$ ), 2.19-2.09 (m,  $3*\text{CH}$ ), 1.76-1.69 (m,  $3*\text{CH}_2$ ).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  188.8 (CO), 123.9 (d,  $\text{CF}_3$ ), 57.5(CNH), 53.8 (q,  $\text{CH}_2\text{CF}_3$ ,  $J = 28.0$  Hz), 39.8 ( $\text{CH}_2$ ), 36.3 ( $\text{CH}_2$ ), 29.5 ( $3*\text{CH}$ ).  $^{19}\text{F}$  NMR (376 MHz) -65.3 ( $\text{CF}_3$ ). HRMS (ESI) Calculated for  $\text{C}_{13}\text{H}_{17}\text{NF}_3\text{S}$   $[\text{M} - \text{H}]^-$ : 276.1034, found: 276.1032.



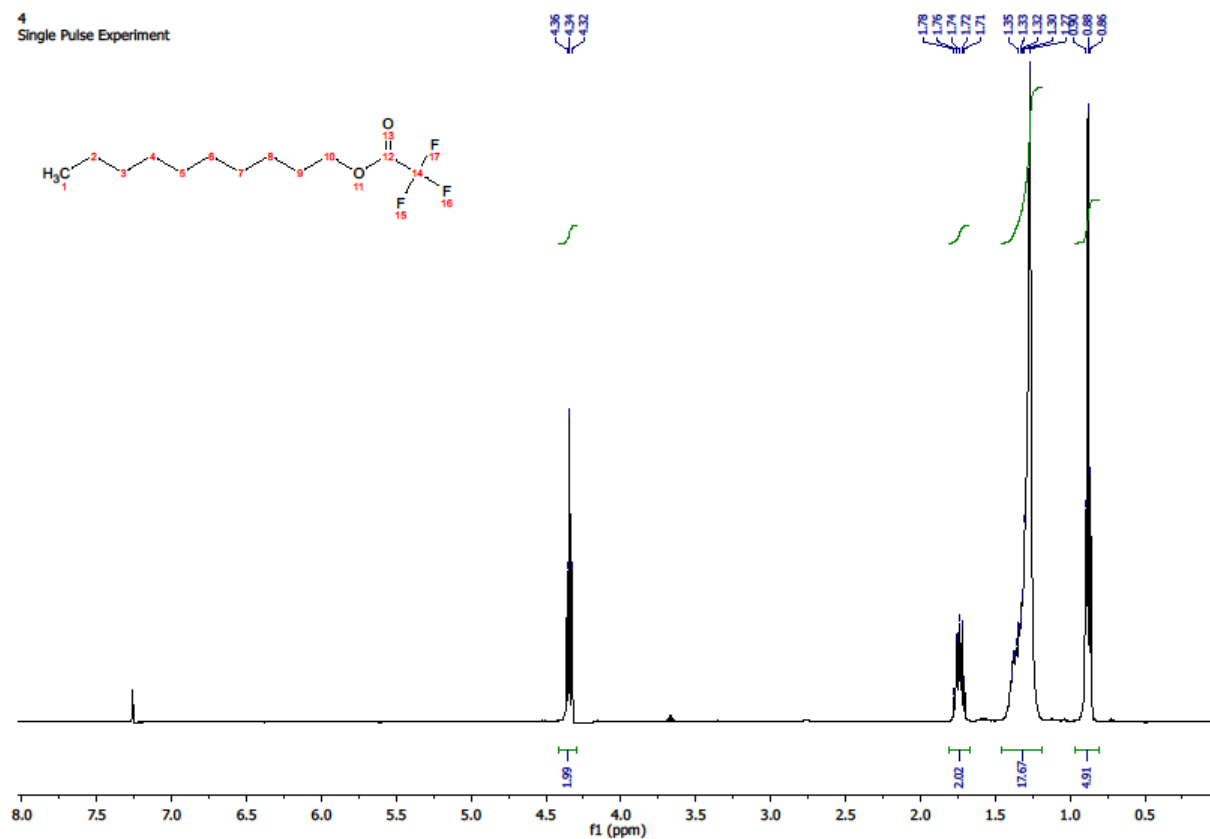
**Decyl acetate**, table 2, entry 5. The 2,2,2-trifluoroacetate (91.5 mg, 0.3 mmol) was solvated in dry THF (21.5 mL) and triethylamine (670  $\mu$ L, 4.8 mmol) was added. The solution was cooled to  $-78$   $^{\circ}$ C. A mixture of  $\text{SmI}_2$  (20 mL, 2.4 mmol) and  $\text{H}_2\text{O}$  (130  $\mu$ L, 7.2 mmol) was also cooled to  $-78$   $^{\circ}$ C and then added dropwise to the ester solution. The reaction mixture was stirred for 45 minutes before it was quenched using air until colorless, followed by 1 mL  $\text{Na}_2\text{S}_2\text{O}_3$ . The crude mixture was concentrated under reduced pressure. Column chromatography, 1:1 pentane:diethyl ether as eluent to yield the product as a colorless oil in 73% yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  4.34 (t,  $J = 6.7$  Hz, 2H), 1.74 (dq,  $J = 13.5, 6.7$  Hz, 2H), 1.43-1.19 (s, 9H), 0.88 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  171.3, 64.7, 32.0, 29.6, 29.6, 29.4, 29.4, 28.7, 26.0, 22.8, 21.1, 14.2.



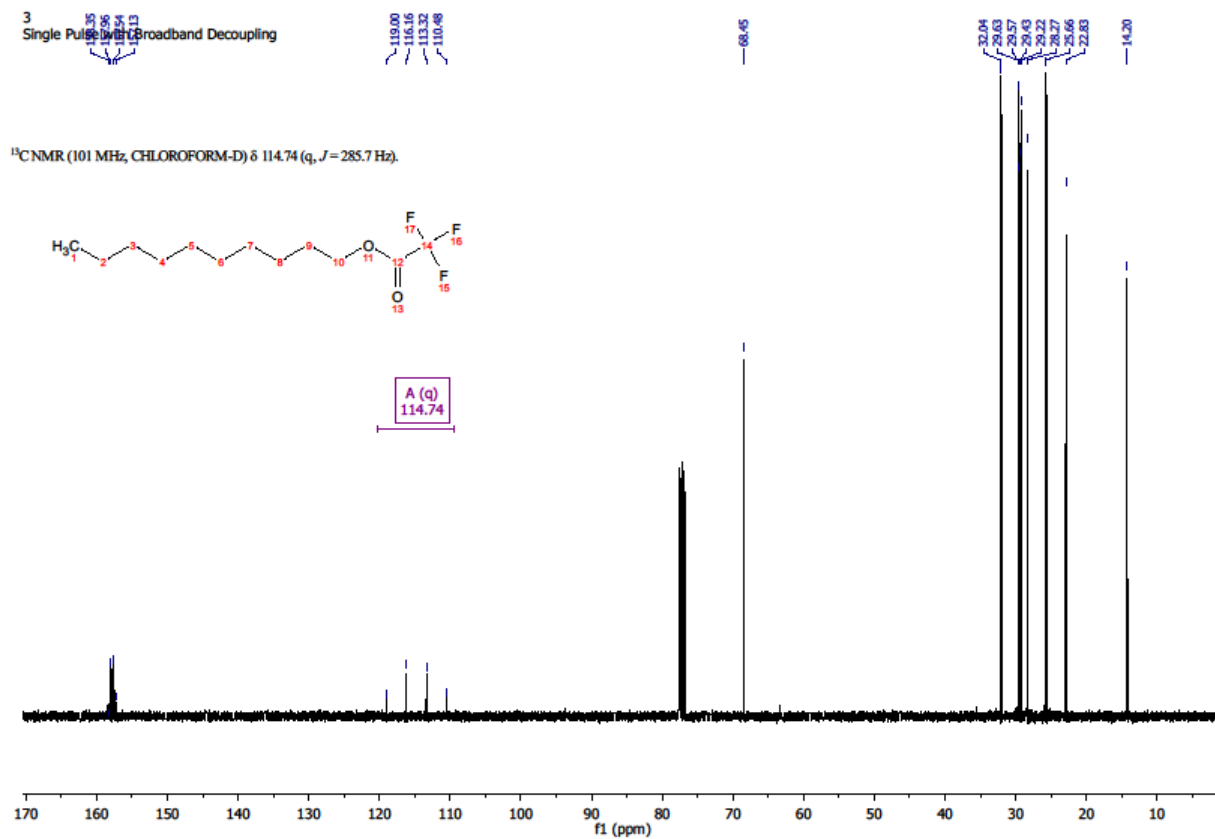
**1-Adamantyl acetamide**, table 2 entry 6. 1-adamantyl-2,2,2-trifluoroacetamide (76.8 mg, 0.31 mmol) was solvated in dry THF (21.5 mL) and dry triethylamine (670  $\mu$ L, 4.8 mmol) was added. A mixture of  $\text{SmI}_2$  (20 mL, 2.4 mmol) and  $\text{H}_2\text{O}$  (130  $\mu$ L, 7.2 mmol) was added dropwise to the amide solution at room temperature. The reaction was stirred for 15 min and quenched by removing the lid and let air into the vessel, followed by adding 1 mL sat.  $\text{Na}_2\text{S}_2\text{O}_3$  (aq.). The crude mixture was purified by column chromatography (1:2, pentane:diethyl ether) and afforded the desired product as a white solid in 89 % yield.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM-D)  $\delta$  5.23 (br s, NH), 2.04 (br s,  $3^*\text{CH}_2$ , 3H), 1.99-1.96 (m,  $3^*\text{CH}_2$ , 6H), 1.89 (s,  $\text{CH}_3$ , 3H), 1.68-1.63 (m,  $3^*\text{CH}$ , 6H).  $^{13}\text{C}$  NMR (101 MHz, CHLOROFORM-D)  $\delta$  169.4 (CO), 51.9 ( $\text{CNH}$ ), 41.7 ( $3^*\text{CH}_2$ ), 36.5 ( $3^*\text{CH}_2$ ), 29.5 ( $3^*\text{CH}$ ), 24.8 ( $\text{CH}_3$ ).

- <sup>1)</sup> Analysis performed in 800 MHz showed two partially overlapping quartets and not a doublet of quartets.

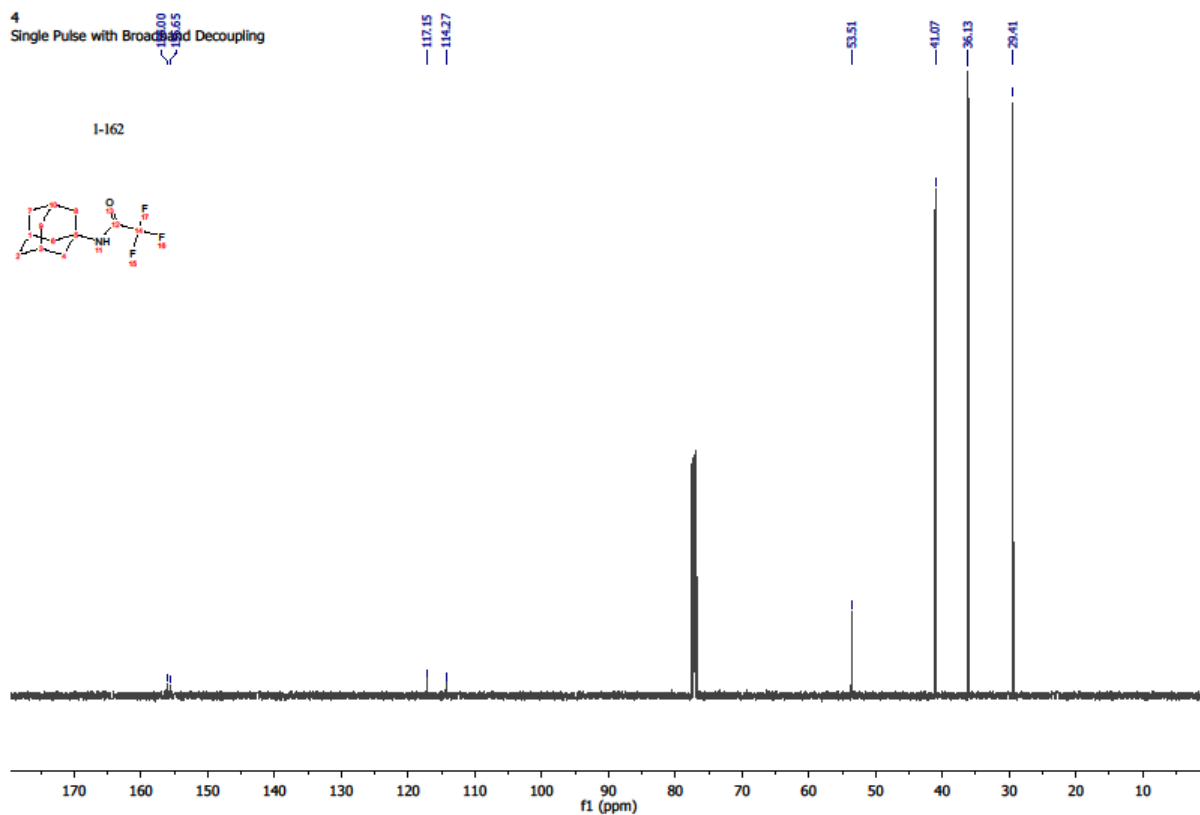
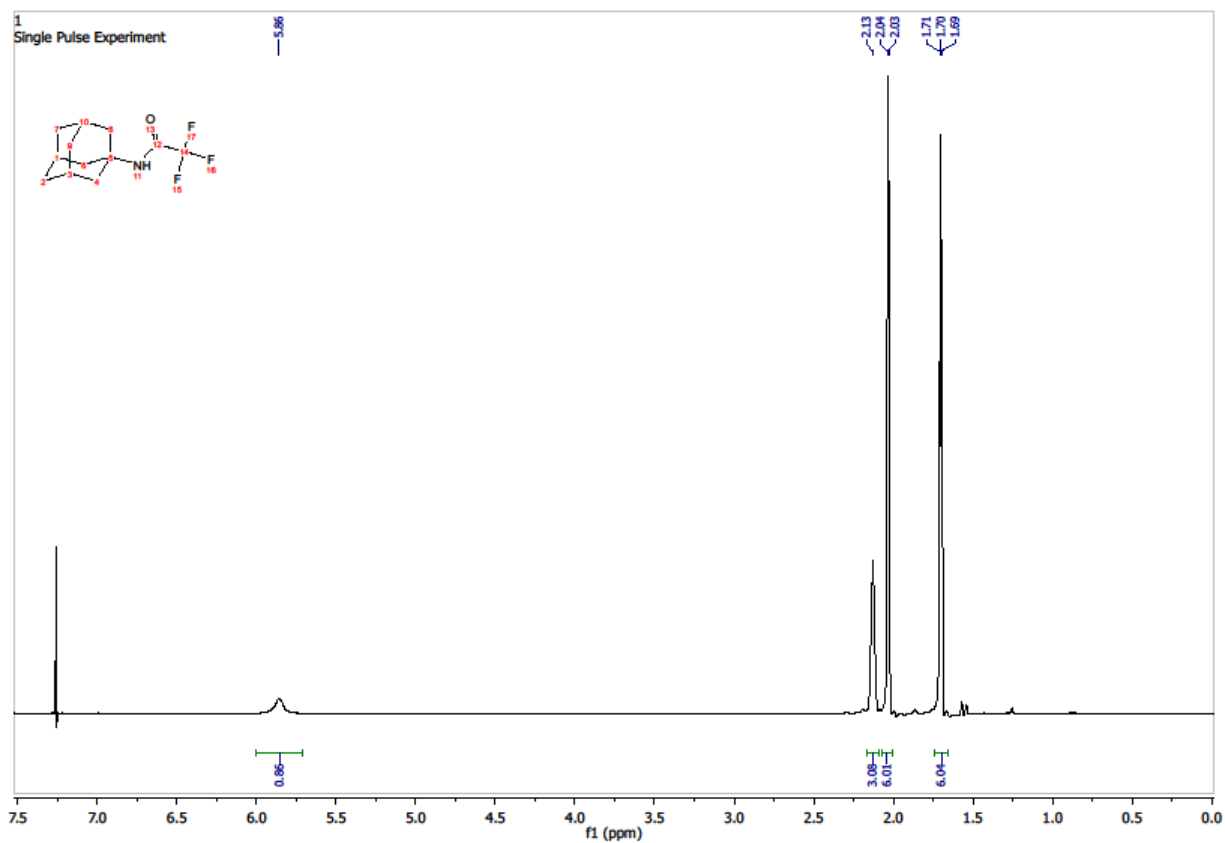
4  
Single Pulse Experiment



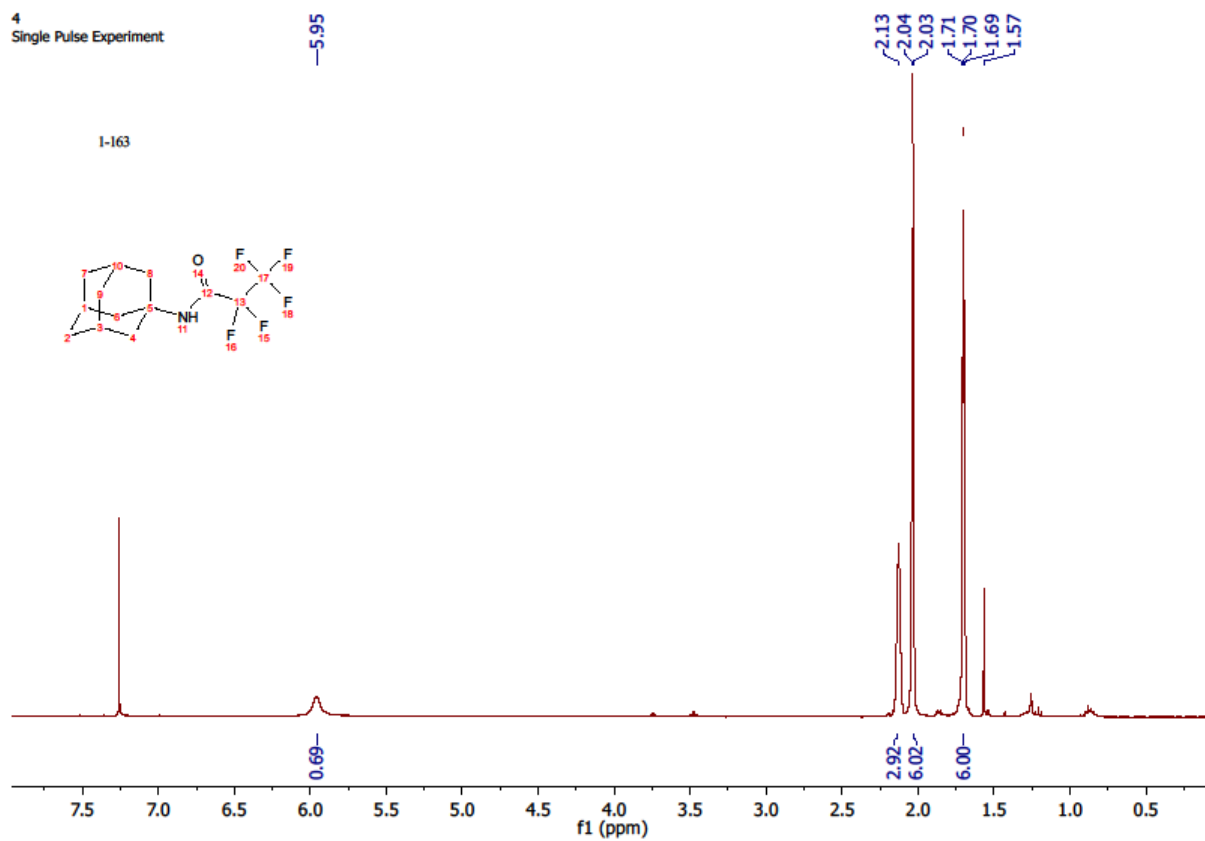
3  
Single Pulse with Broadband Decoupling



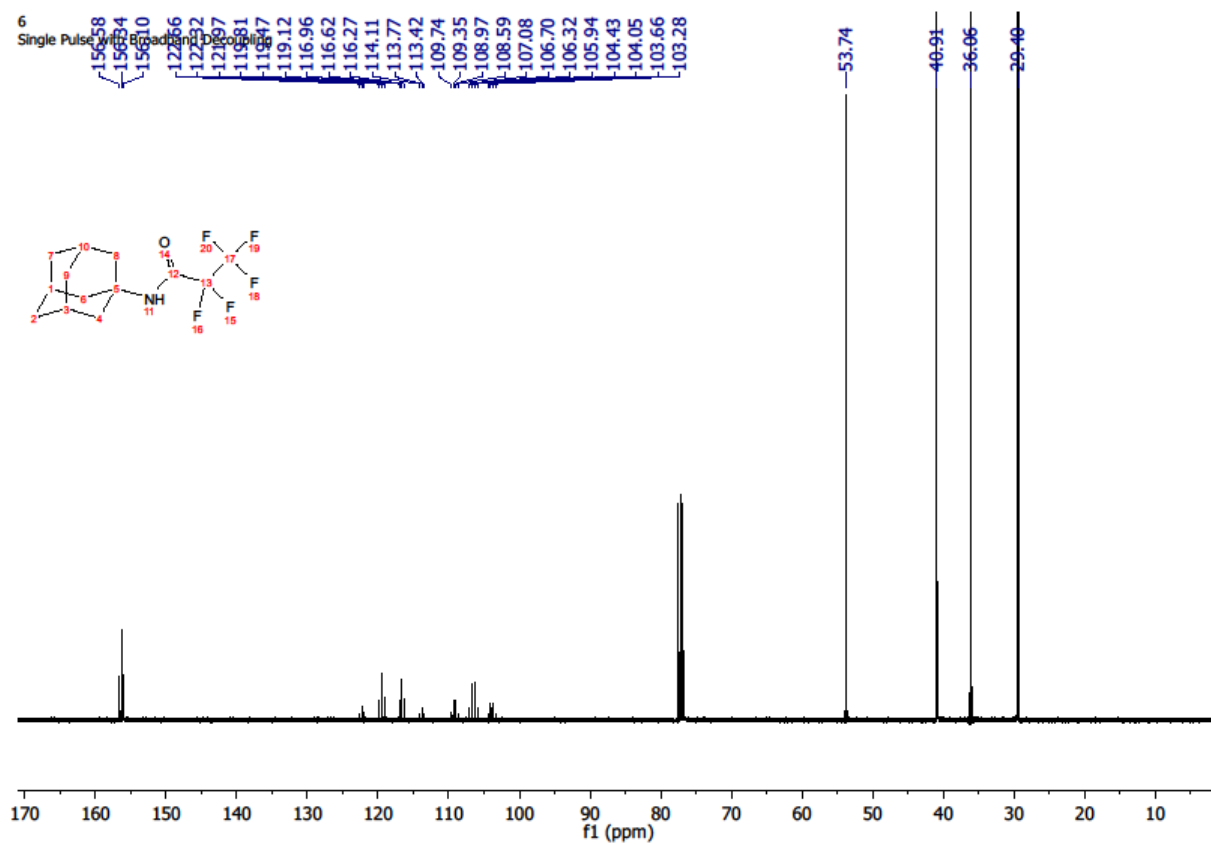


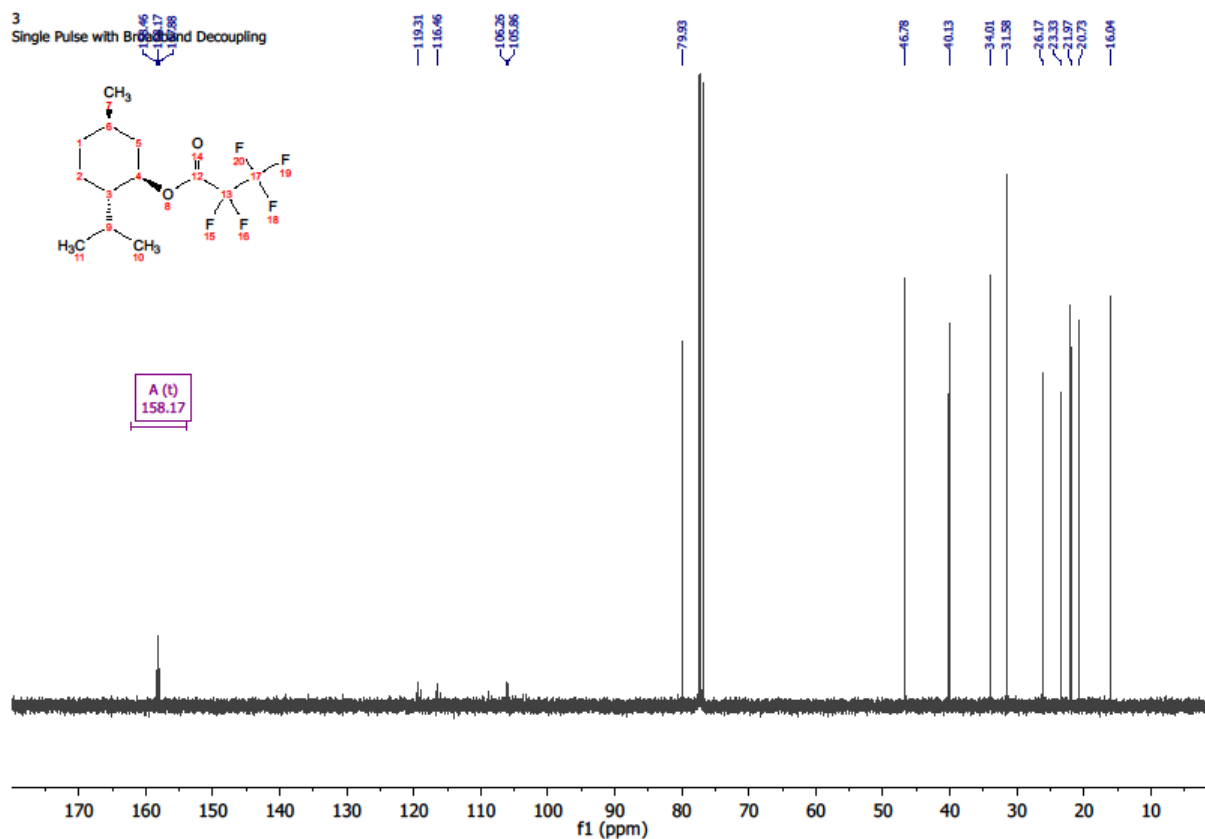
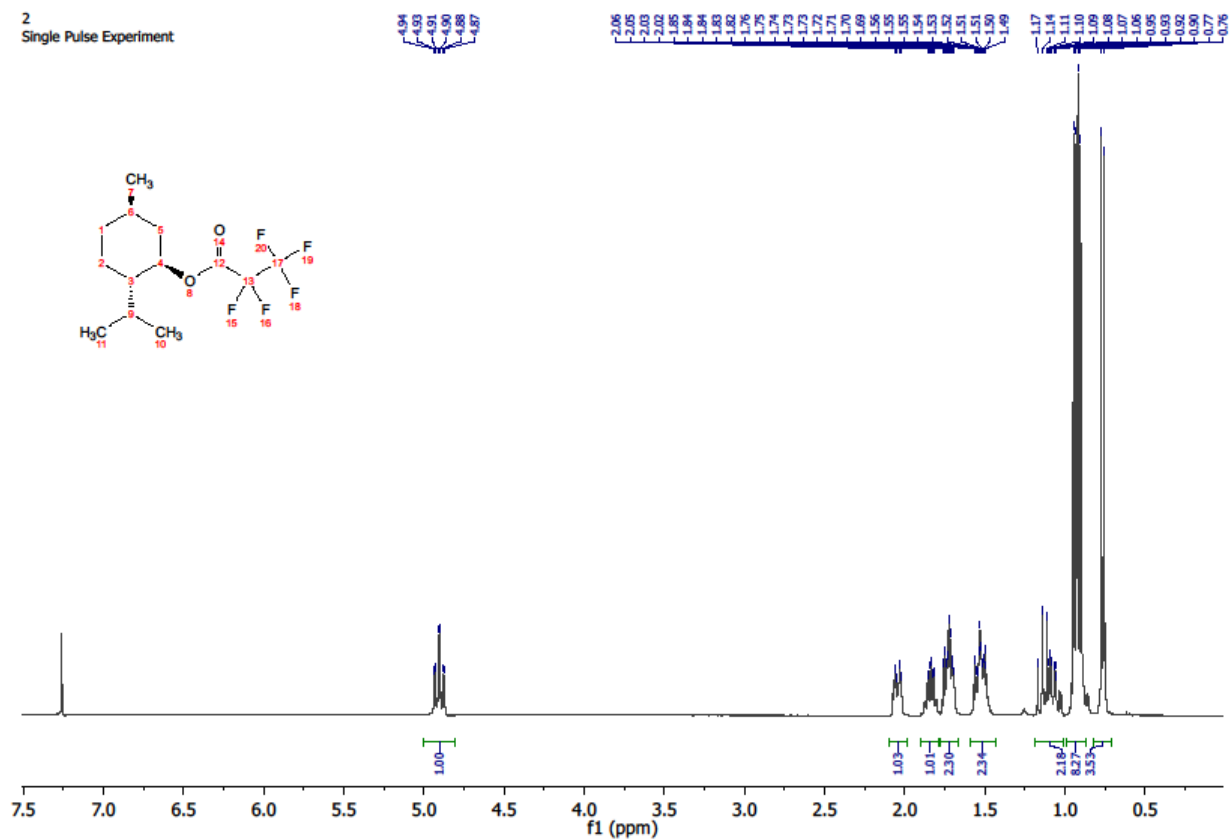


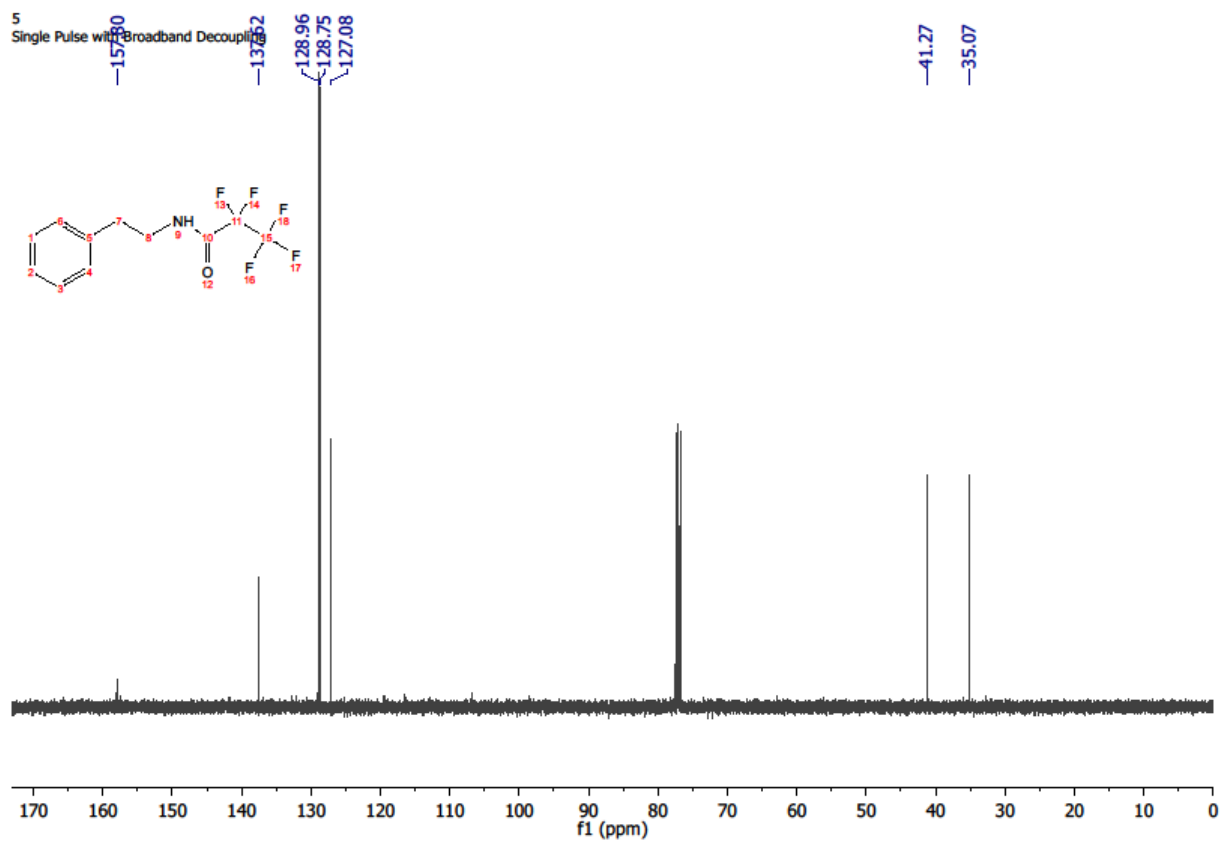
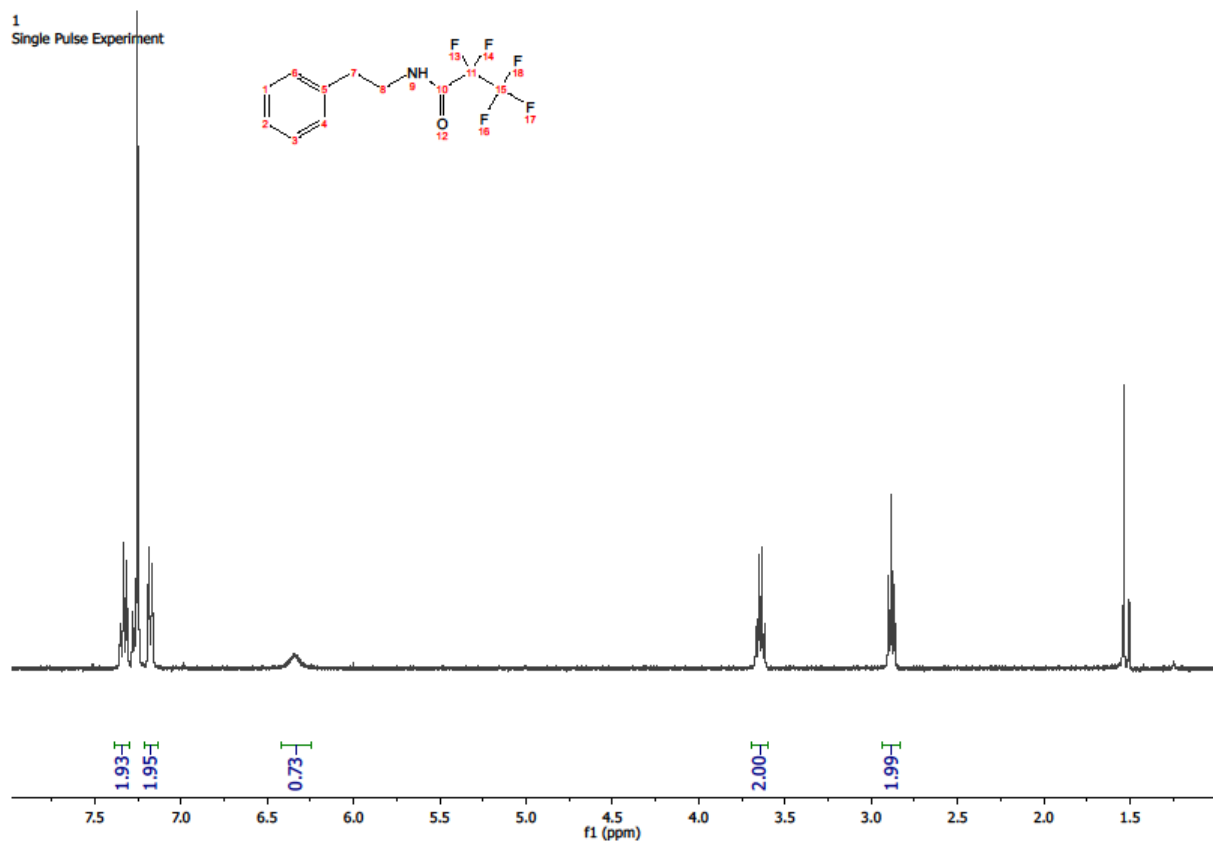
4  
Single Pulse Experiment

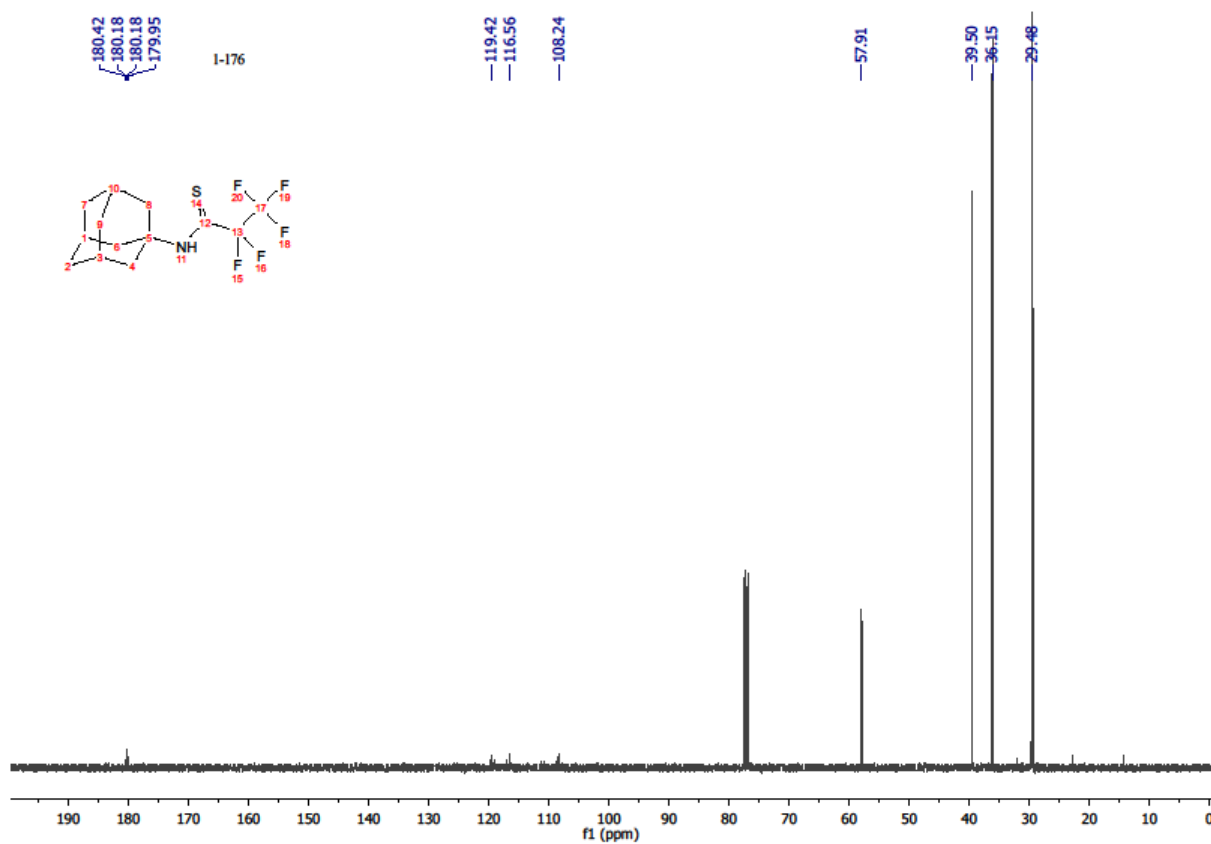
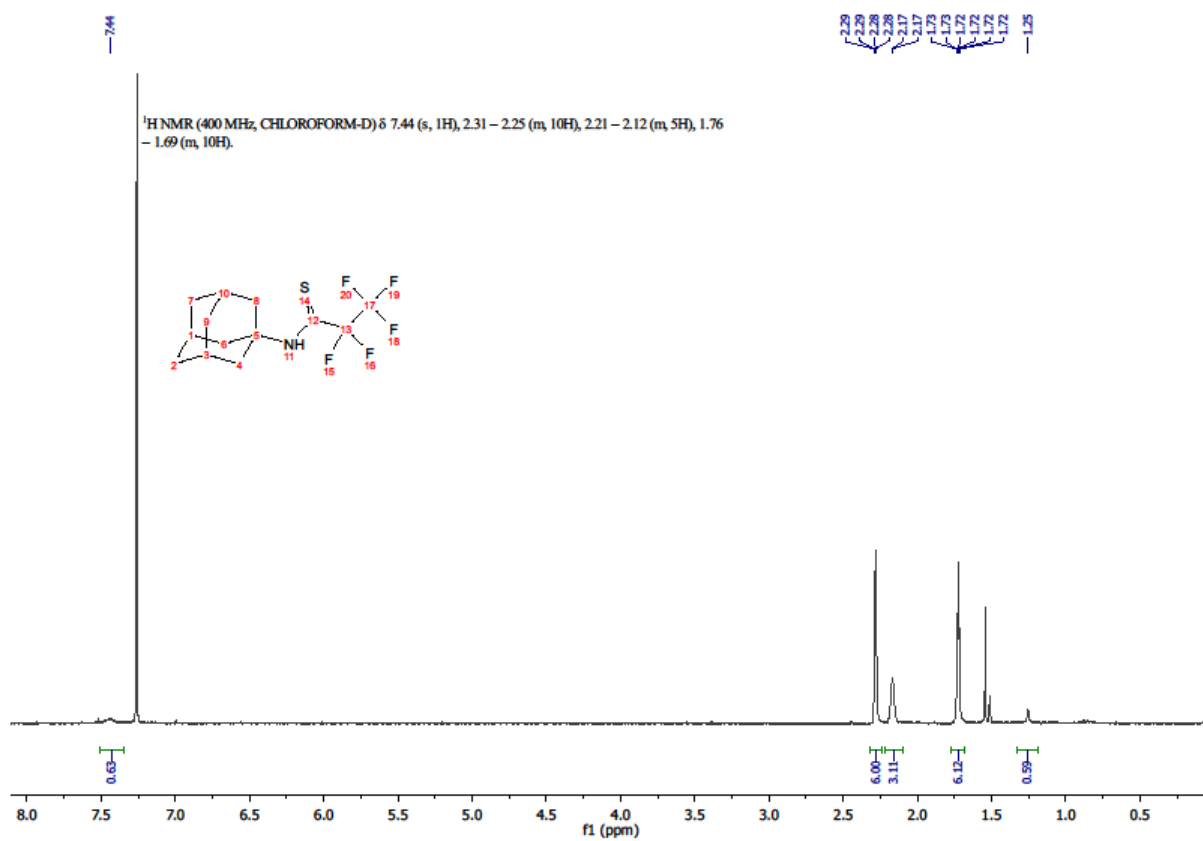


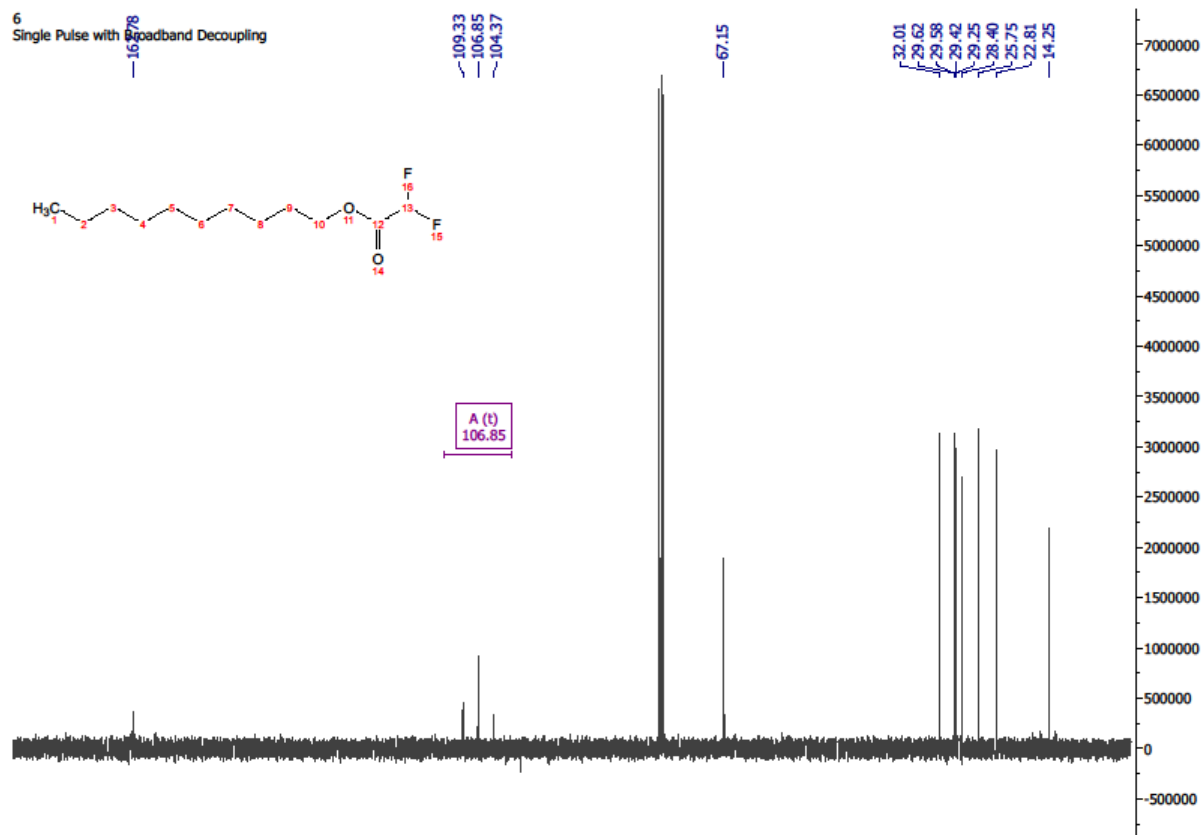
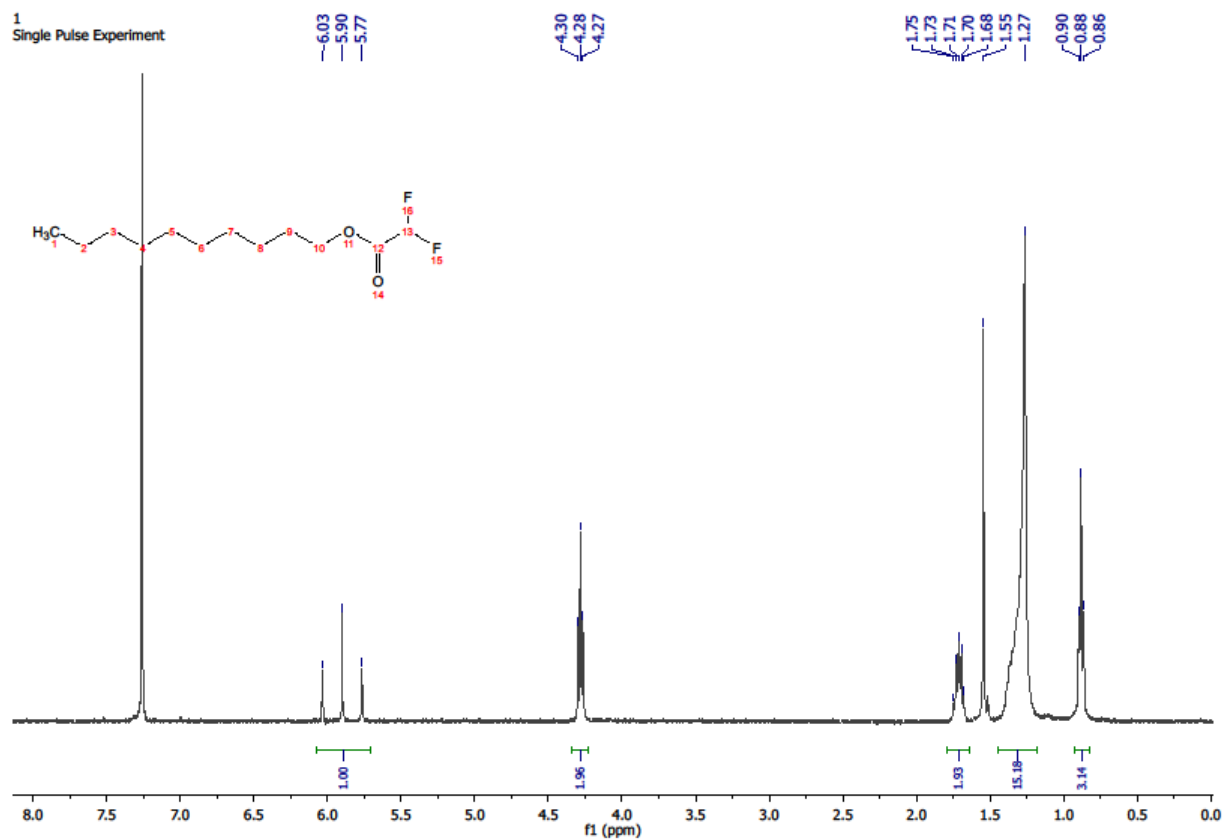
6  
Single Pulse with Broadband Decoupling

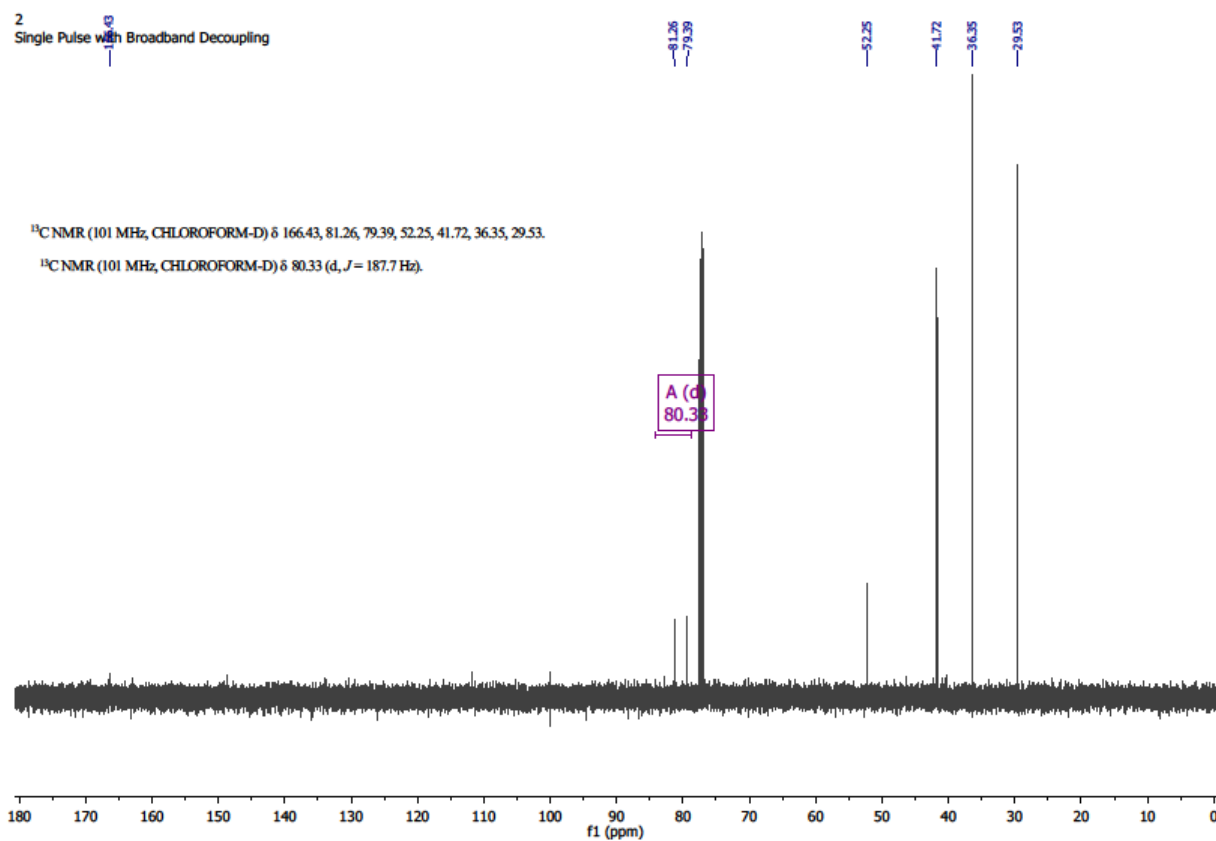
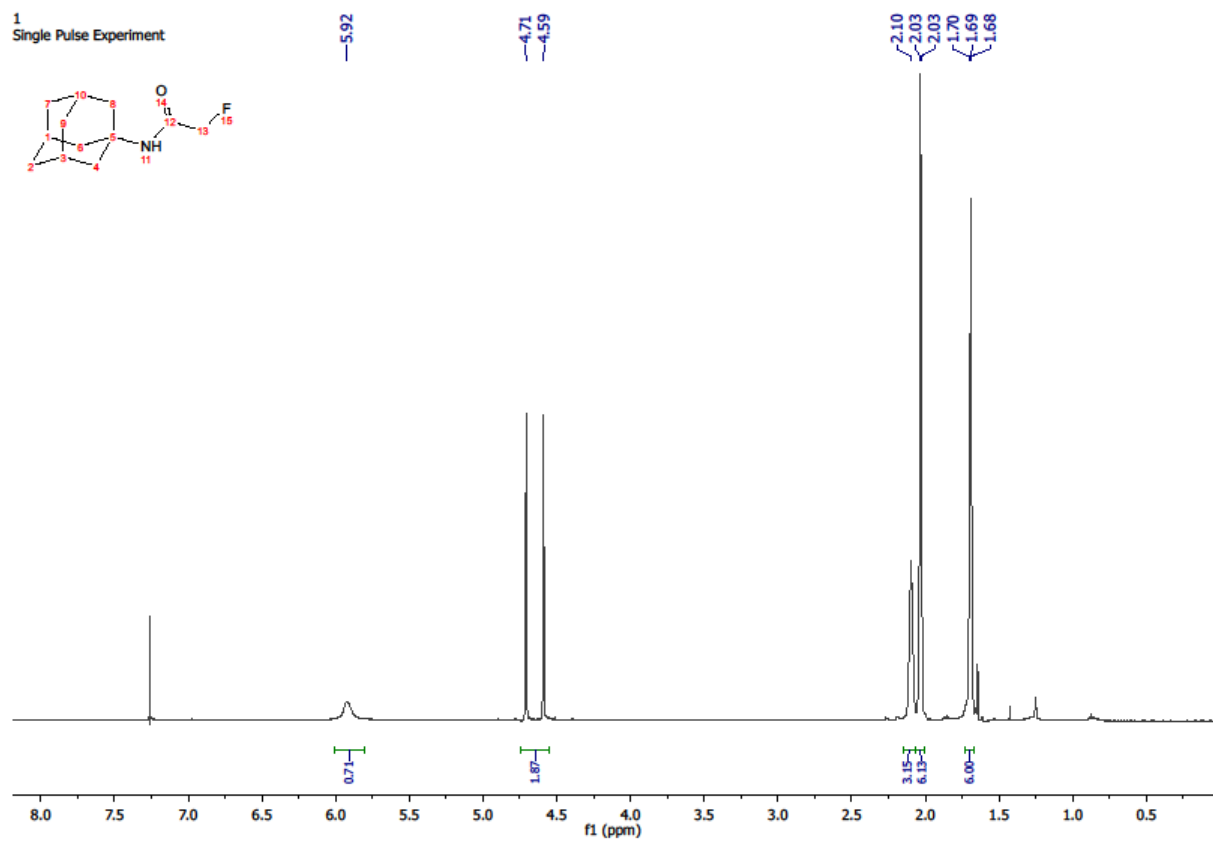






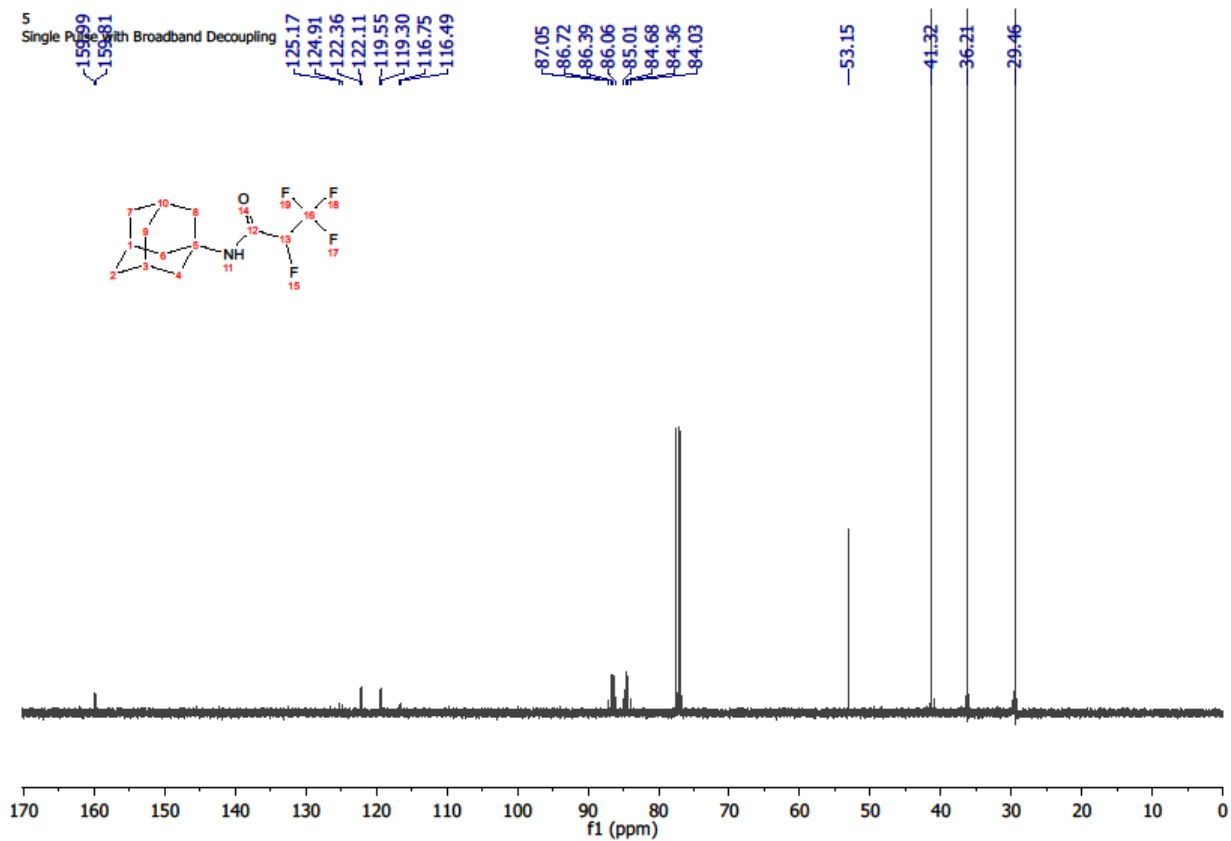
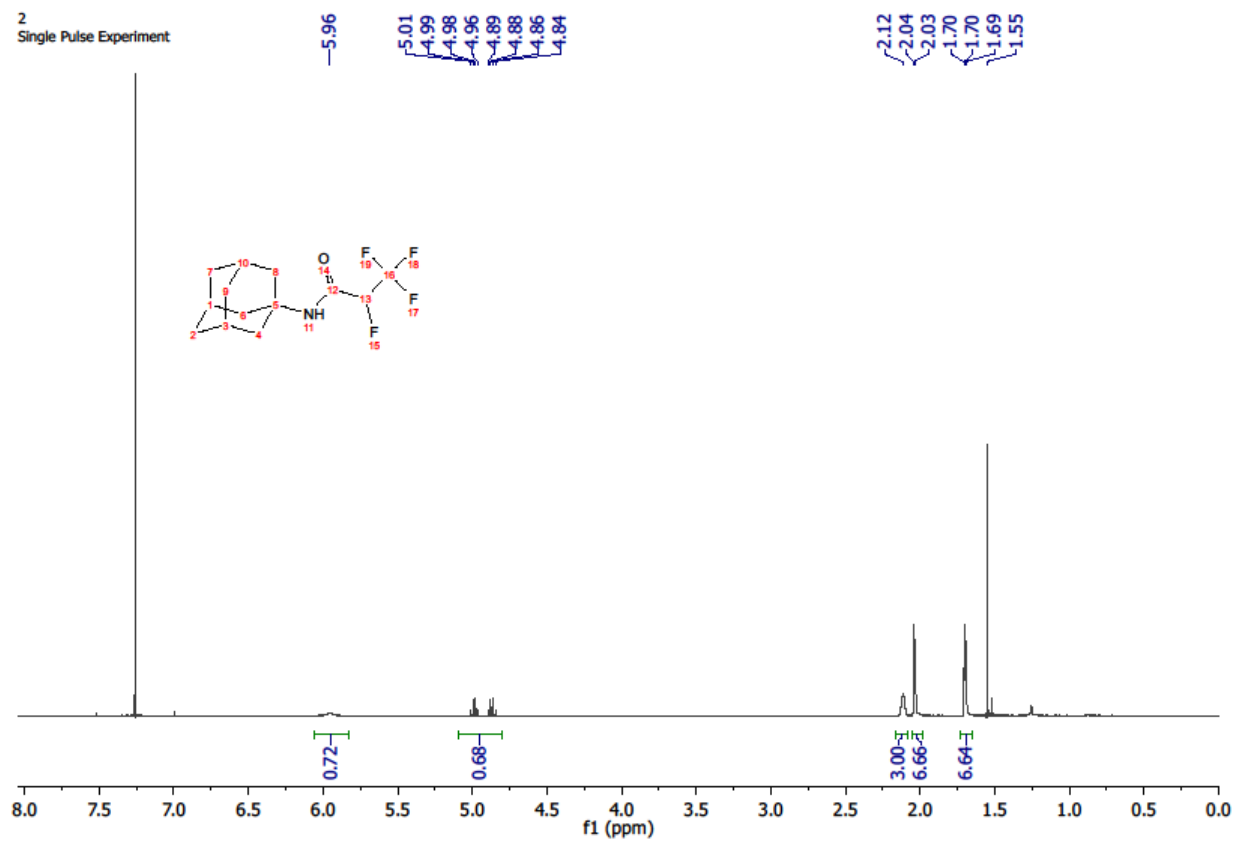


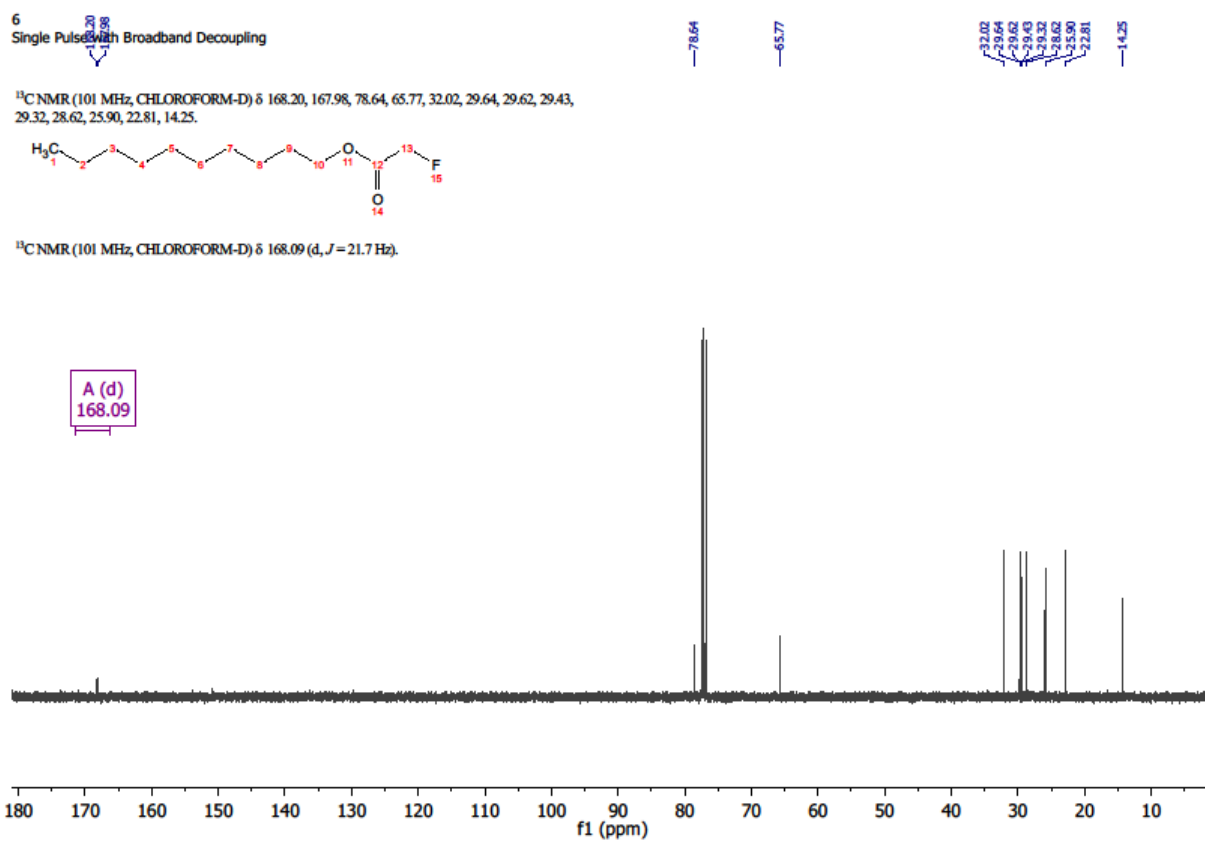
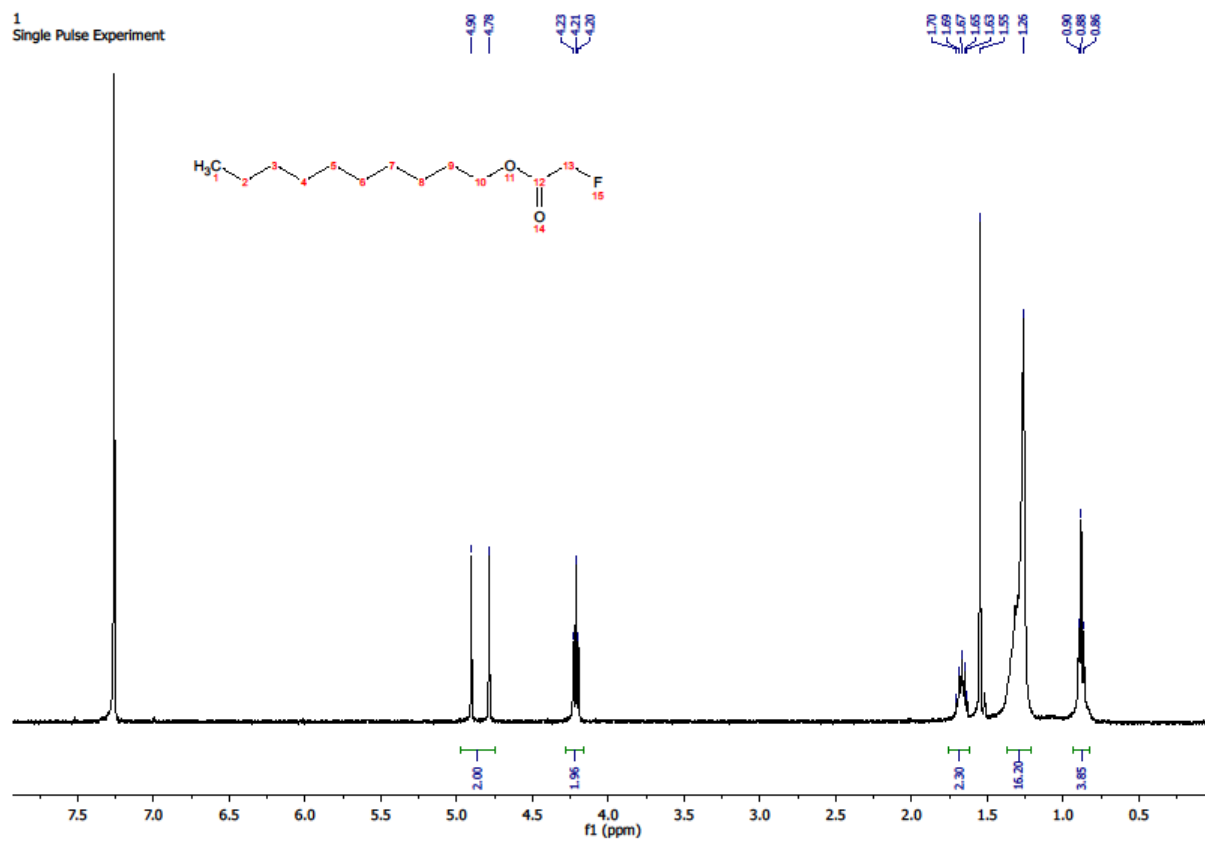


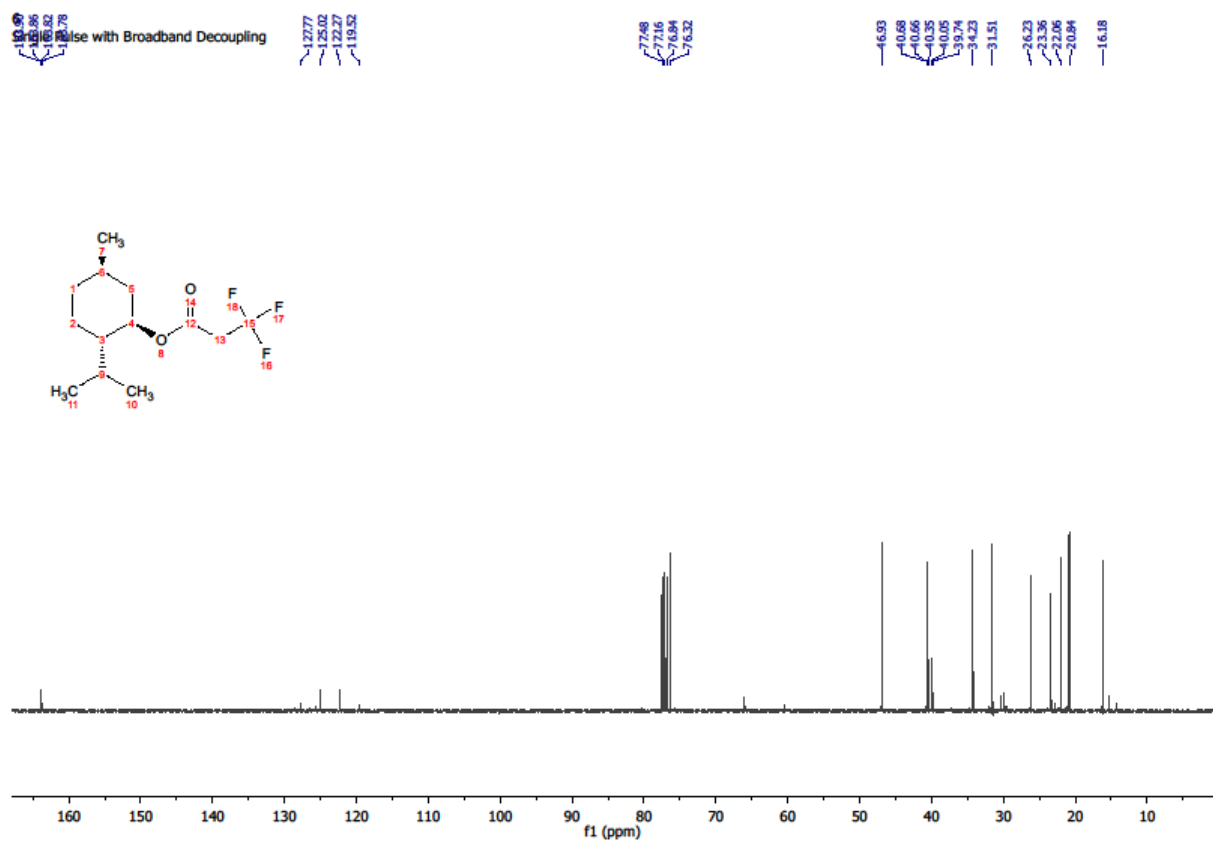
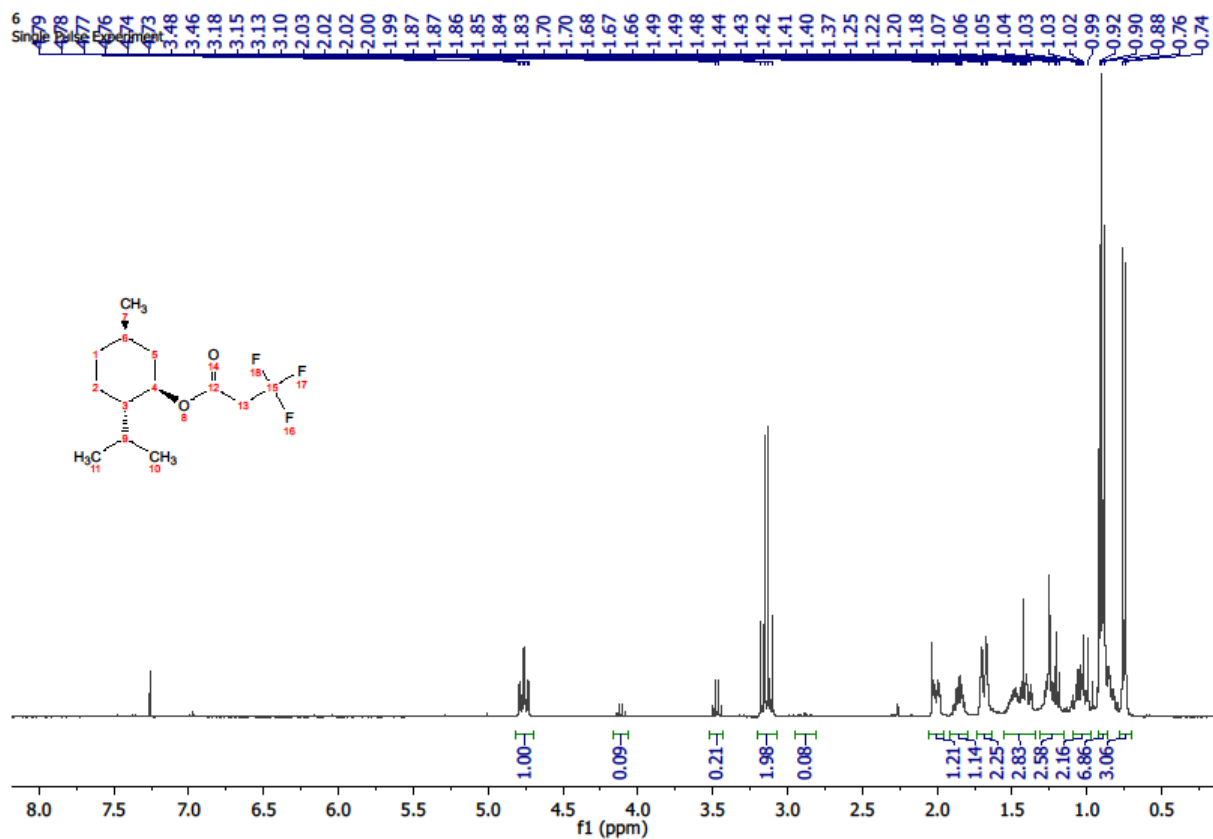






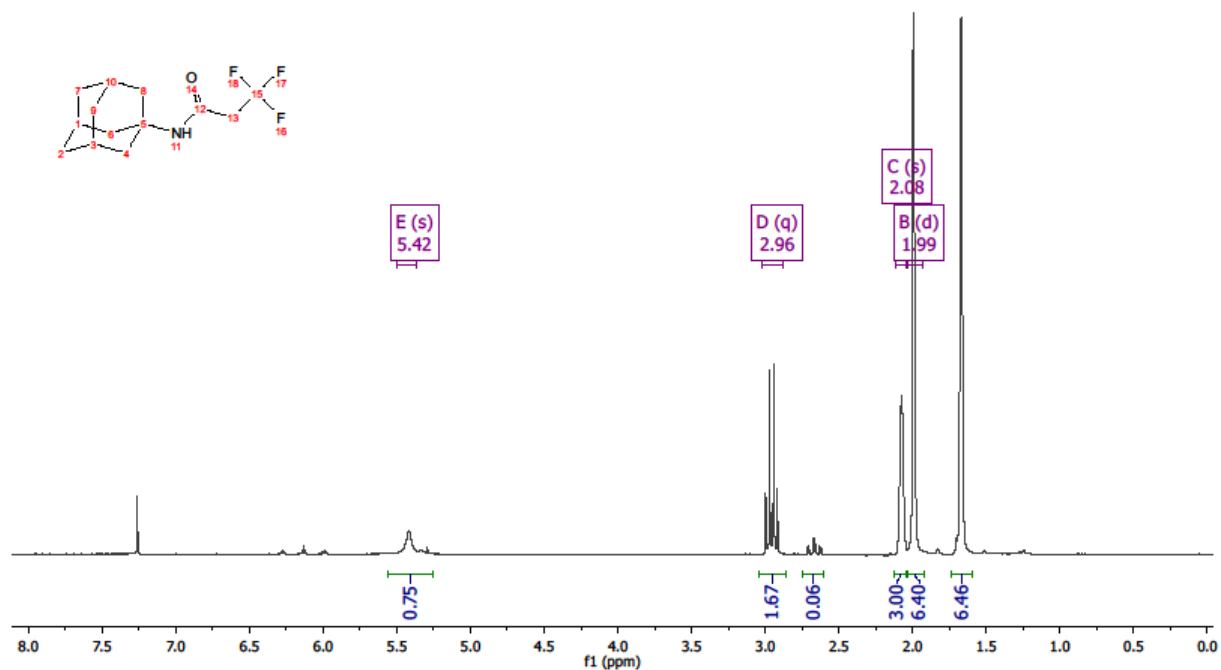






5  
Single Pulse Experiment

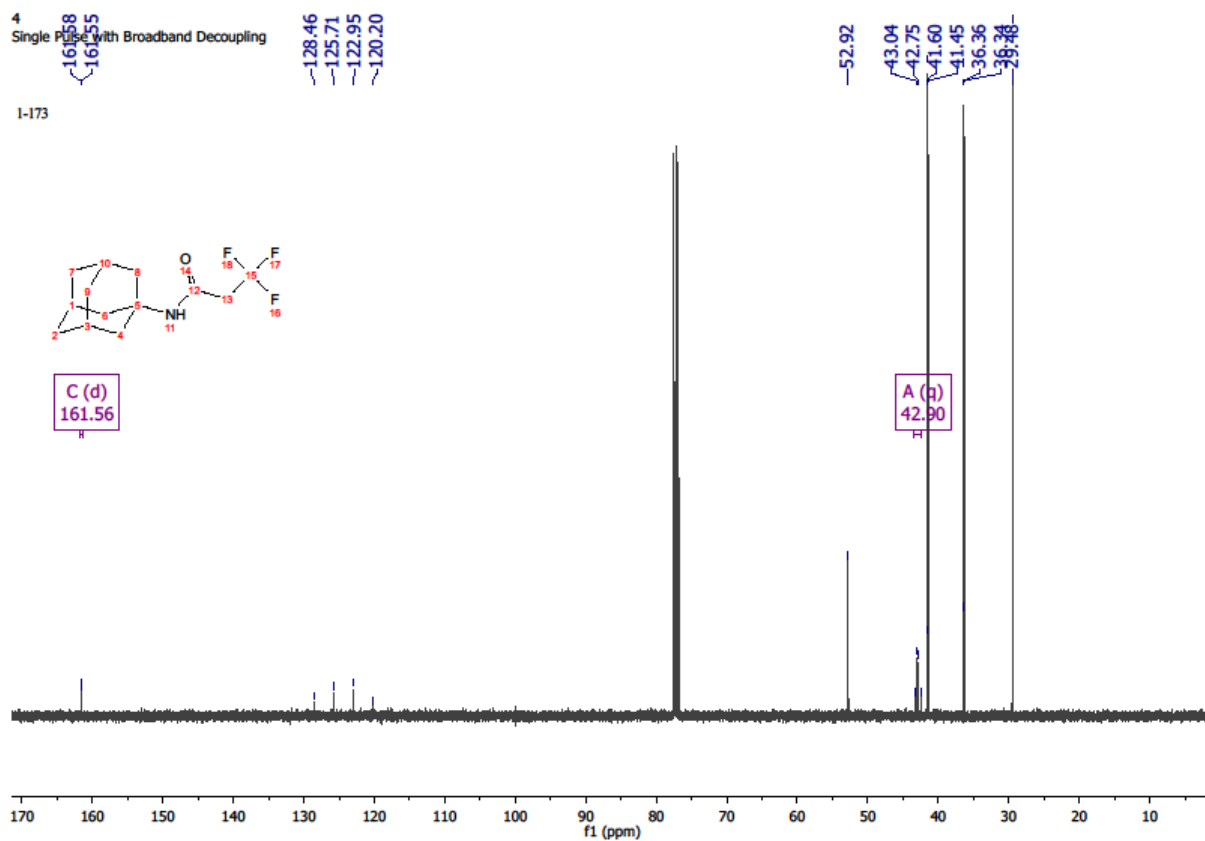
6.13  
5.42



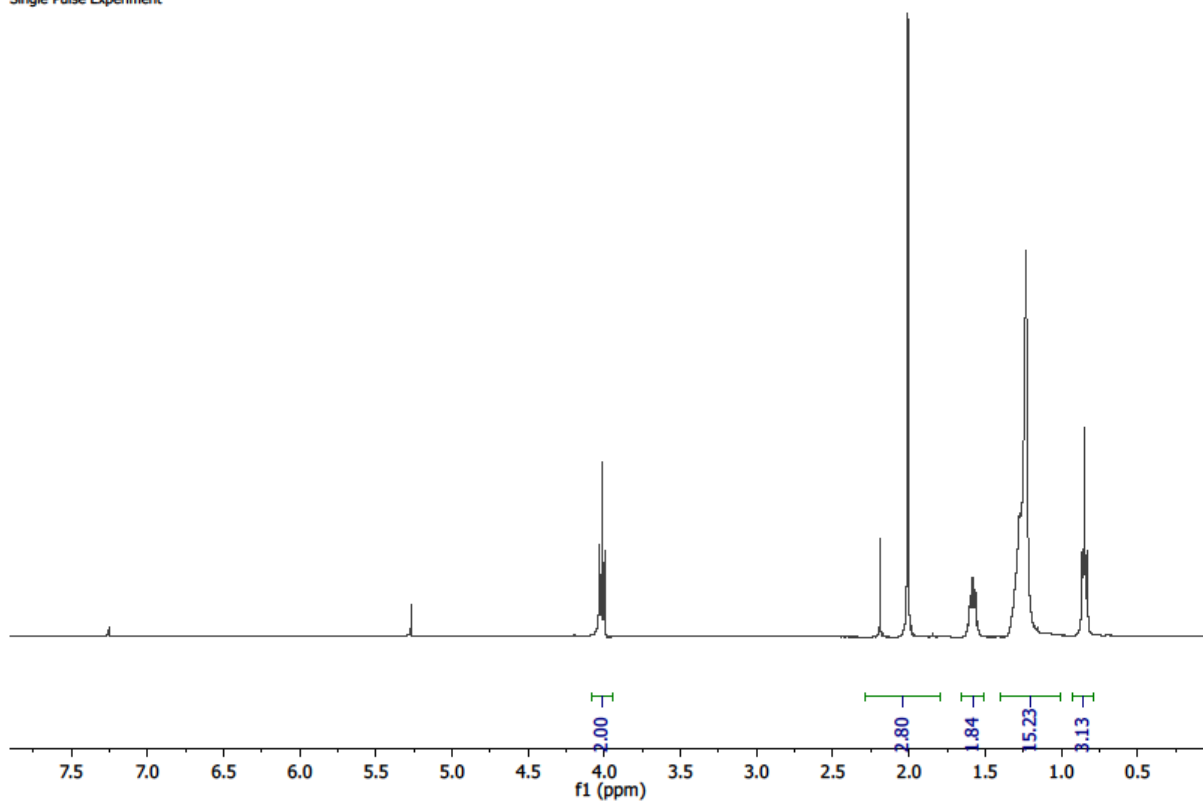
4  
Single Pulse with Broadband Decoupling

161.56  
161.55  
128.46  
125.71  
122.95  
120.20

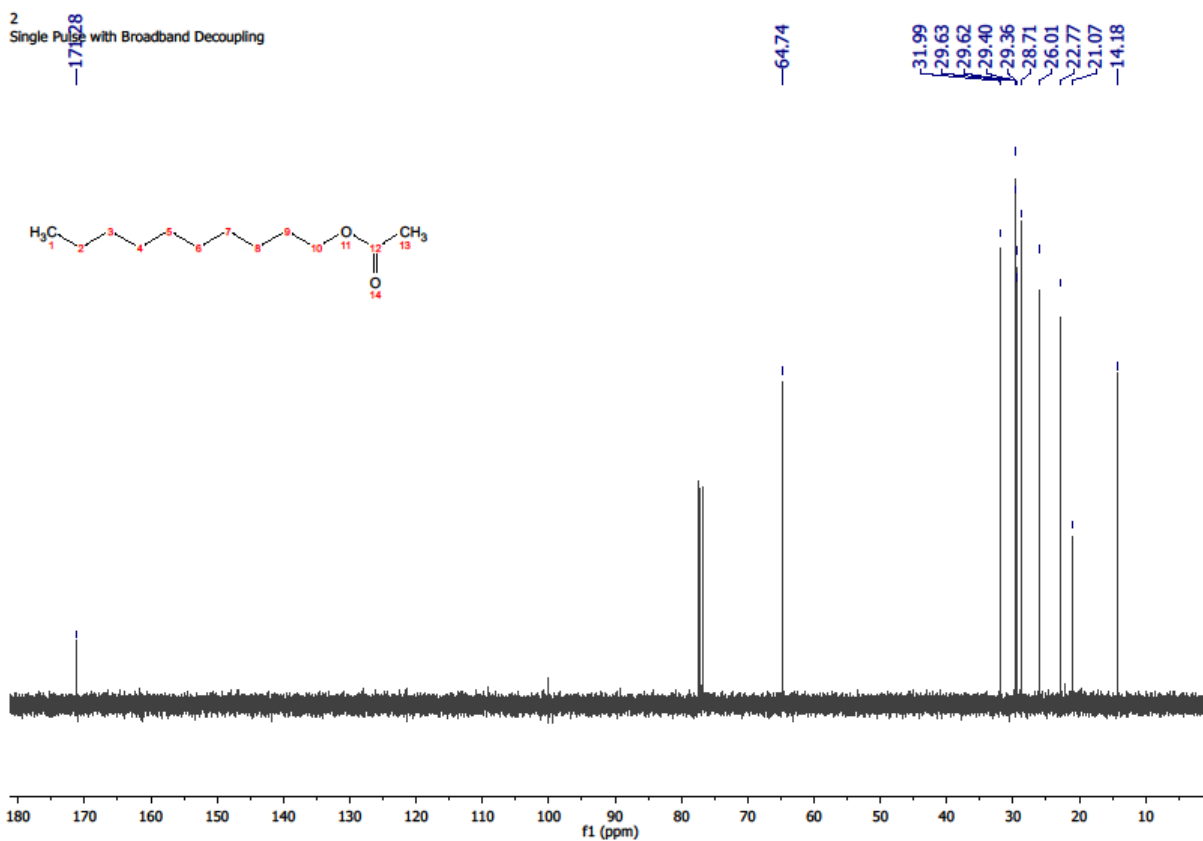
1-173



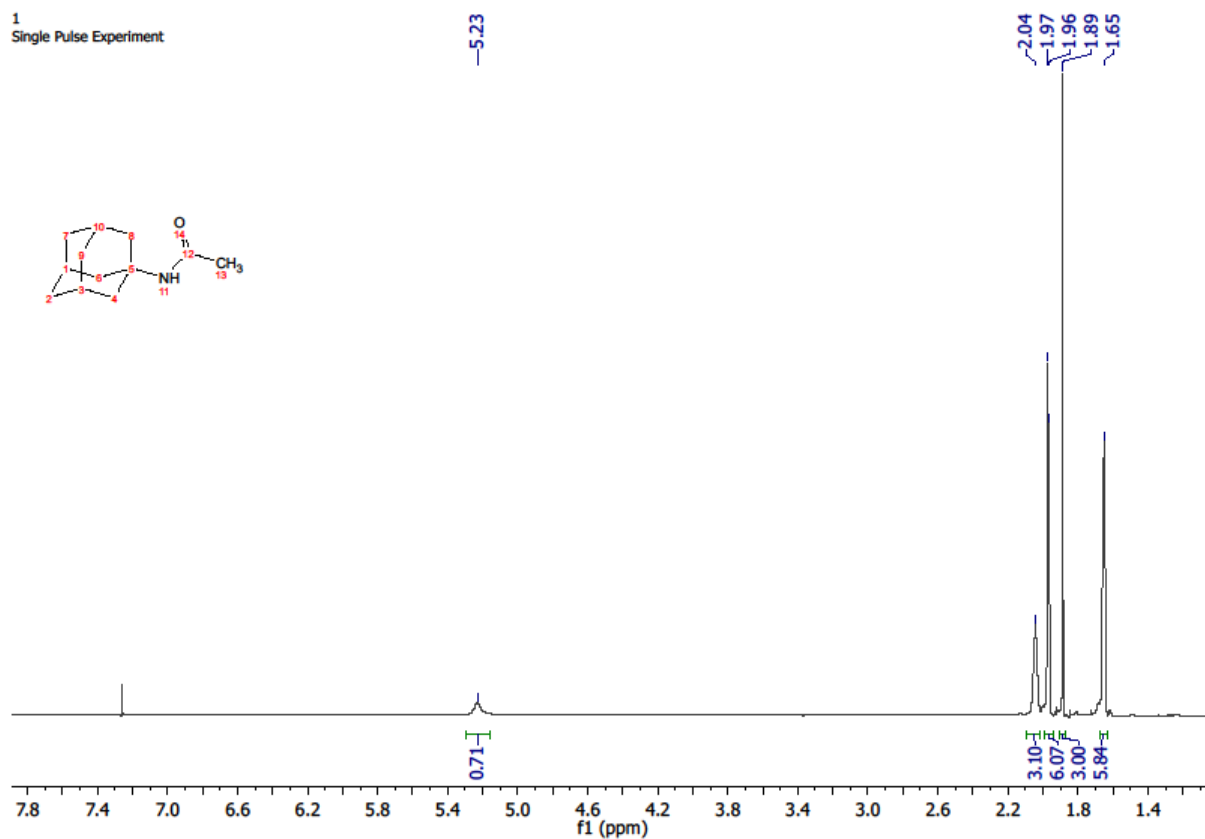
1  
Single Pulse Experiment



2  
Single Pulse with Broadband Decoupling



1  
Single Pulse Experiment



2  
Single Pulse with Broadband Decoupling

