

# **The annulation reactions of donor-acceptor cyclopropanes with (1-azidovinyl)benzene and 3-phenyl-2*H*-azirine**

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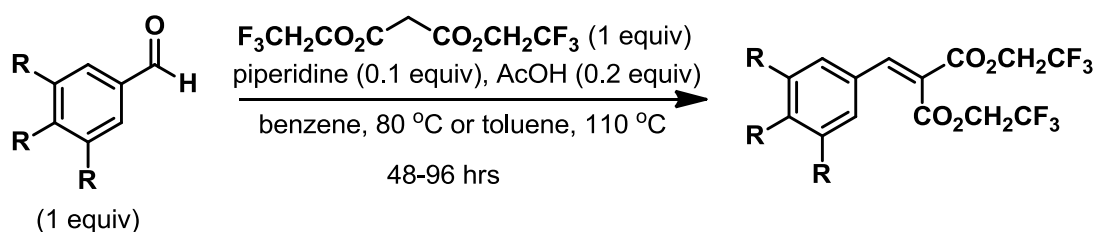
London, Ontario, Canada N6A 5B7

## General information

All reactions were carried under an Argon atmosphere unless indicated. Toluene, benzene, and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were dried and deoxygenated by passing the nitrogen purged solvents through activated alumina columns. All other reagents and solvents were used as purchased from Sigma Aldrich, Caledon or VWR. Reaction progress was followed by thin layer chromatography (TLC) (EM Science, silica gel 60  $\text{F}_{254}$ ) visualizing with UV light, and the plates were developed using acidic anisaldehyde or  $\text{KMnO}_4$  stain. Flash chromatography was performed using silica gel purchased from Silicycle Chemical Division Inc. (230-400 mesh).

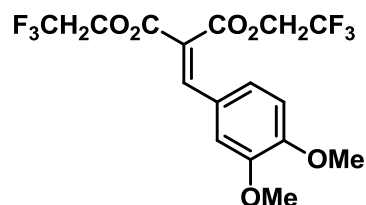
NMR experiments were performed on the Varian Mercury 400, Inova 400 and Inova 600 instruments; samples were obtained in  $\text{CDCl}_3$  (referenced to 7.26 ppm for  $^1\text{H}$  and 77.0 ppm for  $^{13}\text{C}$ ). Coupling constants ( $J$ ) are in Hz. The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dq = doublet of quartets, m = multiplet, b = broad. Infrared spectra were obtained as thin films on NaCl plates using the Bruker Vector 33 FT-IR instrument. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 8200 spectrometer at 70 eV. Melting points were determined using a Gallenkamp melting point apparatus and were uncorrected.

## Experimental Procedure A: Synthesis of bis(2,2,2-trifluoroethyl) 2-benzylidenemalonates (2dd and 2ee).



To 50-100 mL round-bottomed flask, the desired aldehyde (1.0 equiv), bis(2,2,2-trifluoroethyl) malonate<sup>1</sup> (1.0 equiv), piperidine (0.1 equiv), and acetic acid (0.2 equiv) were dissolved in benzene or toluene (30-40 mL). The reaction flask was fitted with a Dean-Stark apparatus and heated to 80 °C or 110 °C for 48-96 hours until completion (monitored by TLC). The crude mixture was washed with 5% HCl, saturated  $\text{NaHCO}_3$ ,

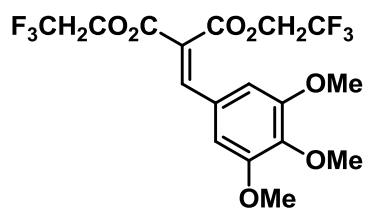
and brine. The organic portion was dried with  $\text{MgSO}_4$ , and filtered. The filtrate was concentrated and purified by column chromatography (EtOAc in Hexanes).



**Bis(2,2,2-trifluoroethyl) 2-(3,4-dimethoxybenzylidene)malonate (2dd).**

Following experimental procedure A, compound **2dd** was obtained by dissolving commercially available 3,4-dimethoxybenzaldehyde (1.17 g, 7.03 mmol), bis(2,2,2-trifluoroethyl) malonate<sup>1</sup> (1.88 g, 7.03 mmol), piperidine (0.07 mL, 0.703 mmol), and acetic acid (0.08 mL, 1.41 mmol) in toluene (30 mL). The reaction was heated at 110 °C for 48 hours. Compound **2dd** (1.02 g, 35%) was obtained as a white solid. MP = 82-85 °C. Rf = 0.70 (40% EtOAc in hexanes).

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.85 (s, 1H), 7.12 (d,  $J$  = 8.9 Hz, 1H), 7.02 (d,  $J$  = 1.6 Hz, 1H), 6.88 (d,  $J$  = 8.6 Hz, 1H), 4.64 (dq,  $J$  = 14.1, 8.2 Hz, 4H), 3.93 (s, 3H), 3.85 (s, 3H). **<sup>19</sup>F NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -73.4 (t,  $J$  = 8.5 Hz, 3F), -73.8 (t,  $J$  = 8.5 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 164.8, 162.4, 152.4, 149.2, 146.8, 125.1, 121.4 (q,  $J_{\text{C-F}}$  = 277 Hz, 1C), 121.2 (q,  $J_{\text{C-F}}$  = 277 Hz, 1C), 112.1, 111.1, 61.0 (q,  $J_{\text{C-F}}$  = 37.5 Hz, 1C), 60.9 (q,  $J_{\text{C-F}}$  = 37.5 Hz, 1C), 56.0, 55.8. **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 3022, 2947, 2840, 1841, 1616, 1514, 1470, 1271, 1144, 1084. **HRMS** calc'd for  $\text{C}_{16}\text{H}_{14}\text{F}_6\text{O}_6$  [ $\text{M}^+$ ]: 416.0695; found: 416.0681.

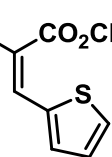


**Bis(2,2,2-trifluoroethyl) 2-(3,4,5-trimethoxybenzylidene)malonate (2ee).**

Following experimental procedure A, compound **2ee** was obtained by dissolving commercially available 3,4,5-trimethoxybenzaldehyde (1.46 g, 7.46 mmol), bis(2,2,2-trifluoroethyl) malonate<sup>1</sup> (2.00 g, 7.46 mmol), piperidine (0.07 mL, 0.75 mmol), and acetic acid (0.09 mL, 1.49 mmol) in benzene (30 mL). The reaction was heated at 80 °C for 44 hours. Compound **2ee** (2.22 g, 67%) was obtained as a white solid. MP = 66-70 °C. Rf = 0.61 (40% EtOAc in hexanes).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 7.84 (s, 1H), 6.74 (s, 2H), 4.63 (qd, *J* = 8.2, 3.5 Hz, 4H), 3.90 (s, 4H), 3.85 (s, 6H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -73.5 (t, 8.6 Hz, 3F), -73.9 (t, 8.6 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ = 164.5, 162.1, 153.4, 146.8, 146.8, 127.0, 121.3 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 121.1 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 107.4, 61.0 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 60.9 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 56.1. **FT-IR** (thin film, cm<sup>-1</sup>): 3017, 2952, 2849, 1751, 1733, 1507, 1446, 1280, 1146, 1122. **HRMS** calc'd for C<sub>17</sub>H<sub>16</sub>F<sub>6</sub>O<sub>7</sub> [M<sup>+</sup>]: 446.0800; found: 446.0808.

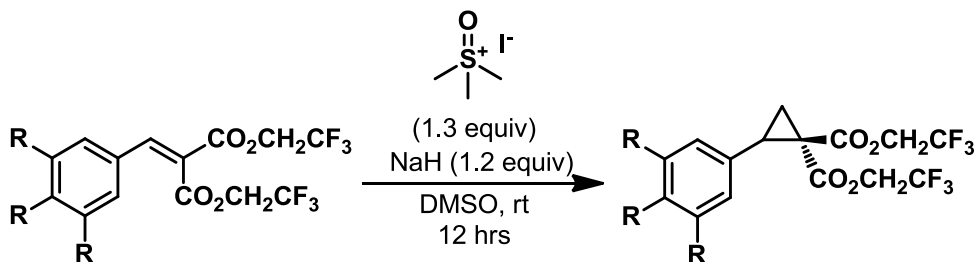
**Bis(2,2,2-trifluoroethyl) 2-(thiophen-2-ylmethylene)malonate (2ff).**



Following experimental procedure A, compound **2ff** was obtained by dissolving 2-thiophenecarboxaldehyde (1.01 g, 9.03 mmol), bis(2,2,2-trifluoroethyl) malonate<sup>1</sup> (2.42 g, 9.03 mmol), piperidine (0.09 mL, 0.90 mmol), and acetic acid (0.1 mL, 1.81 mmol) in toluene (30 mL). The reaction was heated at 110 °C for 48 hours. Compound **2ff** (2.57 g, 78%) was obtained as a yellow oil. *R*<sub>f</sub> = 0.31 (10% EtOAc in hexanes). Product was used crude in the cyclopropanation step.

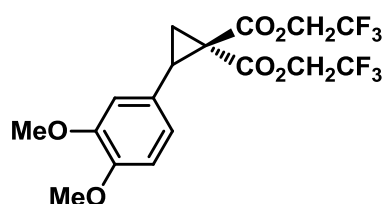
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 8.06 (s, 1H), 7.67 (d, *J* = 5.1 Hz, 1H), 7.53-7.49 (m, 1H), 7.37 (s, 1H), 7.16 (dd, *J* = 5.1, 3.9 Hz, 1H), 4.71 (q, *J* = 8.3 Hz, 2H), 4.63 (q, *J* = 8.3, 2H).

**Experimental Procedure B1: Synthesis of bis(2,2,2-trifluoroethyl)cyclopropane-1,1-dicarboxylates (2d-2f).**



To a solution of SO(CH<sub>3</sub>)<sub>3</sub>I (1.3 equiv) in DMSO (10-15mL), NaH (1.2 equiv) was added portion wise, and stirred at room temperature for 45 minutes. The desired bis(2,2,2-trifluoroethyl)2-benzylidenemalonate (1.0 equiv) was diluted in DMSO (10-15mL) and added dropwise to the reaction mixture. The reaction was stirred for 12 hours at room

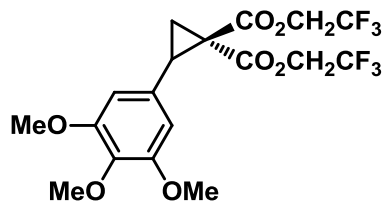
temperature. Upon completion, the mixture was diluted with H<sub>2</sub>O (60 mL) and extracted with Et<sub>2</sub>O. The organic portion was washed with water, brine, dried with MgSO<sub>4</sub>, and filtered. The filtrate was concentrated and purified by column chromatography (EtOAc in Hexanes).



**Bis(2,2,2-trifluoroethyl) 2-(3,4-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate (2d).**

Following experimental procedure B1, compound **2d** was prepared by dissolving SO(CH<sub>3</sub>)<sub>3</sub>I (650 mg, 2.93 mmol) and 60% NaH (120 mg, 2.93 mmol) in 10 mL of DMSO. After stirring at room temperature for 45 mins, bis(2,2,2-trifluoroethyl) 2-(3,4-dimethoxybenzylidene)malonate **2dd** (1.02 g, 2.44 mmol) in 10 mL DMSO was added dropwise. The reaction was stirred for 12 hours at room temperature. Compound **2d** (380 mg, 36%) was obtained as white solid. MP = 98 -101 °C. R<sub>f</sub> = 0.61 (40 % EtOAc in hexanes).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 6.75 (m, 3H), 4.62 (q, *J* = 8.2 Hz, 1H), 4.54 (q, *J* = 8.2 Hz, 1H), 4.19 (q, *J* = 8.2 Hz, 1H), 4.11 (q, *J* = 7.8 Hz, 1H), 3.85 (s, 6H), 3.36 (t, *J* = 9.0 Hz, 1H), 2.33 (dd, *J* = 5.5 Hz, 3.12 Hz, 1H), 1.86 (dd, *J* = 5.5 Hz, 3.9 Hz, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -73.9 (t, *J* = 8.6 Hz, 3F), -74.0 (t, *J* = 8.6 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ = 168.0, 164.8, 149.1, 125.5, 121.5 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 121.3 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 121.0, 112.3, 111.1, 61.6 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 61.4 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 56.1, 36.6, 34.5, 20.4. **FT-IR** (thin film, cm<sup>-1</sup>): 3010, 2968, 2838, 1727, 1519, 1253, 1157, 1137, 1023, 968. **HRMS** calc'd for C<sub>17</sub>H<sub>16</sub>F<sub>6</sub>O<sub>6</sub> [M<sup>+</sup>]: calc'd 430.0851; found: 430.0864.

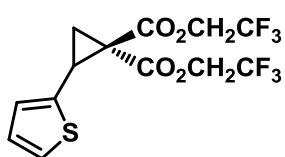


**Bis(2,2,2-trifluoroethyl) 2-(3,4,5-trimethoxyphenyl)cyclopropane-1,1-dicarboxylate (2e).**

Following experimental procedure B1, compound **2e** was prepared by dissolving SO(CH<sub>3</sub>)<sub>3</sub>I (1.29 g, 5.87 mmol), and 60% NaH (230 mg, 5.87 mmol) in 15 mL of DMSO. After stirring at room temperature for 45

mins, bis(2,2,2-trifluoroethyl) 2-(3,4,5-trimethoxybenzylidene)malonate **2ee** (2.18 g, 4.89 mmol) in 15 mL DMSO was added dropwise. The reaction was stirred for 12 hours at room temperature. Compound **2e** (760 mg, 34%) was obtained as white solid. MP = 40 - 44 °C. Rf= 0.68 (40 % EtOAc in Hexanes).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ = 6.41 (s, 2H), 4.70-4.58 (m, 2H), 4.51-4.48 (m, 1H), 4.15-4.21 (m, 1H), 3.82 (s, 6H), 3.79 (s, 3H), 3.35 (t, *J* = 8.8 Hz, 1H), 2.31 (dd, *J* = 8.2, 5.5 Hz, 1H), 1.85 (dd *J* = 9.4, 5.5 Hz, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -73.9 (t, *J* = 8.5 Hz, 3F), -74.0 (t, *J* = 8.5 Hz, 3F). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ = 167.6, 164.4, 153.4, 153.1, 147.1, 128.4, 123.9 (q, *J*<sub>C-F</sub> = 278 Hz, 1C), 123.7 (q, *J*<sub>C-F</sub> = 278 Hz, 1C), 107.4, 105.7, 61.3 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 61.1 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 56.0, 36.3, 34.4, 20.1. **FT-IR** (thin film, cm<sup>-1</sup>): 2967, 2848, 1733, 1508, 1416, 1256, 1165, 1122, 974, 658. **HRMS** calc'd for C<sub>18</sub>H<sub>18</sub>F<sub>6</sub>O<sub>7</sub> [M<sup>+</sup>]: calc'd 460.0957; found: 460.0959.



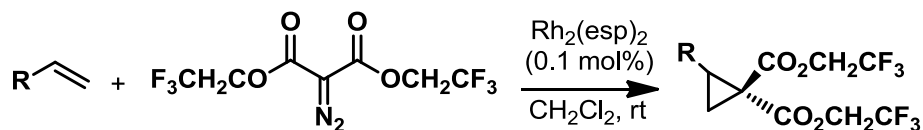
**Bis(2,2,2-trifluoroethyl) 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (2f).**

Following experimental procedure B1, compound **2f** was prepared by dissolving SO(CH<sub>3</sub>)<sub>3</sub>I (1.87 g, 8.51 mmol), and 60% NaH (355 mg, 8.51 mmol) in 15 mL of DMSO. After stirring at room temperature for 45 mins, bis(2,2,2-trifluoroethyl) 2-(thiophen-2-ylmethylene)malonate **2ff** (2.57 g, 7.09 mmol) in 15 mL DMSO was added dropwise. The reaction was stirred for 12 hours at room temperature. Compound **2f** (740 mg, 28%) was obtained as yellow oil. Rf= 0.38 (10 % EtOAc in Hexanes).

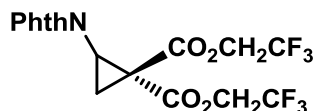
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ = 7.20 (d, *J* = 5.1 Hz, 1H), 6.91 (t, *J* = 4.7 Hz, 1H), 6.87 (d, *J* = 3.5 Hz, 1H), 4.59 (q, *J* = 8.5 Hz, 1H), 4.53 (q, *J* = 8.5 Hz, 1H), 4.31 (q, *J* = 8.5 Hz, 1H), 4.16 (q, *J* = 8.5 Hz, 1H), 3.44 (t, *J* = 7.8 Hz, 1H), 2.31 (dd, *J* = 5.15 Hz, 2.3 Hz, 1H), 1.96 (dd, *J* = 5.4 Hz, 3.1 Hz, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -73.9 (t, *J* = 8.6 Hz, 3F), -74.0 (t, *J* = 8.6 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ = 167.2, 164.1, 136.2, 126.9, 125.9, 121.1 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 121.0 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 61.2 (q, *J*<sub>C-F</sub> = 38 Hz, 1C), 61.1 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 37.1, 28.8, 21.7. **FT-IR** (thin film, cm<sup>-1</sup>): 3113,

2976, 1743, 1412, 1276, 1259, 1158, 1117, 975, 703. **HRMS** calc'd for C<sub>13</sub>H<sub>10</sub>F<sub>6</sub>O<sub>4</sub>S [M<sup>+</sup>]: 376.0204; found: 376.0202.

**Experimental Procedure B2: Synthesis of bis(2,2,2-trifluoroethyl)cyclopropane-1,1-dicarboxylates (2g-h and 2j-k).**



To a solution of the desired styrene (1.0 equiv), in CH<sub>2</sub>Cl<sub>2</sub> (4 mL - 8 mL), Rh<sub>2</sub>(esp)<sub>2</sub> catalyst (0.1 mol%) was added. The bis(2,2,2-trifluoroethyl)2-diazomalonate<sup>2</sup> (1.3 equivs) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and added dropwise over a period of 20 mins at room temperature. The reaction was stirred at room temperature until completion (monitored by TLC). The reaction mixture was quenched with saturated NaHCO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic portion was dried with MgSO<sub>4</sub> and filtered. The filtrate was concentrated and purified by column chromatography (EtOAc in Hexanes).

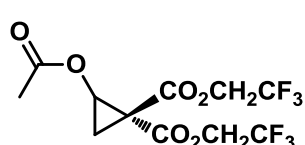


**Bis(2,2,2-trifluoroethyl) 2-(1,3-dioxoisindolin-2-yl)cyclopropane-1,1-dicarboxylate (2g).**

Following experimental procedure B2, cyclopropane **2g** was prepared by dissolving commercially available *N*-vinylphthalimide (1.00 g, 5.77 mmol) and Rh<sub>2</sub>(esp)<sub>2</sub> (4.40 mg, 0.005 mmol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> followed by the addition of bis(2,2,2-trifluoroethyl)2-diazomalonate<sup>2</sup> (2.21 g, 7.50 mmol) dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. Cyclopropane **2g** (1.87 g, 74 % yield) was obtained as a colourless oil. R<sub>f</sub> = 0.57 (20% EtOAc in hexanes).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ = 7.82 (t, *J* = 3.5 Hz, 2H), 7.73 (t, *J* = 2.9 Hz, 2H), 4.60 (q, *J* = 8.2 Hz, 2H), 4.42 (q, *J* = 8.2 Hz, 1H), 4.35 (q, *J* = 8.2 Hz, 1H), 3.81 (dd, *J* = 7.6 Hz, 1H), 2.88 (t, *J* = 6.5 Hz, 1H), 2.17 (dd, *J* = 7.0 Hz, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -73.9 (t, *J* = 8.6 Hz, 3F), -74.0 (t, *J* = 8.6 Hz, 3F). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ = 167.5, 166.2, 164.4, 134.5, 131.2, 123.6, 121.1 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 120.95 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 61.7 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 61.5 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 36.2, 32.5, 20.8. **FT-IR**

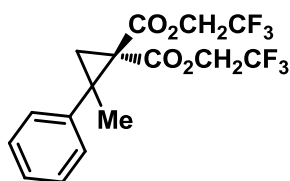
(thin film,  $\text{cm}^{-1}$ ): 3117, 3031, 2985, 1763, 1717, 1406, 1259, 1163, 1132, 965. **HRMS** calc'd for  $\text{C}_{17}\text{H}_{11}\text{F}_6\text{O}_6$  [ $\text{M}^+$ ]: 439.0491; found: 439.0474.



**Bis(2,2,2-trifluoroethyl) 2-acetoxycyclopropane-1,1-dicarboxylate (2h).**

Following experimental procedure B2, cyclopropane **2h** was prepared by dissolving commercially available vinyl acetate (200 mg, 2.32 mmol) and  $\text{Rh}_2(\text{esp})_2$  (1.76 mg, 0.002 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  followed by the addition of bis(2,2,2-trifluoroethyl)2-diazomalonate<sup>2</sup> (887 mg, 3.02 mmol) dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$ . Cyclopropane **2h** (711 g, 87 % yield) was obtained as a colourless oil.  $R_f$  = 0.49 (30% EtOAc in hexanes).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 4.89 (dd,  $J$  = 7.0, 5.5 Hz, 1H) 4.42 - 4.71 (m, 4H) 2.14 (dd,  $J$  = 6.6, 5.5 Hz, 1H) 2.04 (s, 3H) 1.87 (dd,  $J$  = 7.0, 5.5 Hz, 1H).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -73.8 (t,  $J$  = 7.9 Hz, 3F), -73.9 (t,  $J$  = 7.9 Hz, 3F).  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 169.9, 165.9, 163.3, 122.4 (d,  $J_{\text{C-F}}$  = 277 Hz, 1C), 122.3 (d,  $J_{\text{C-F}}$  = 277 Hz, 1C), 61.4 (q,  $J_{\text{C-F}}$  = 37 Hz, 1C), 61.2 (d,  $J_{\text{C-F}}$  = 37 Hz, 1C), 57.5, 33.4, 20.5, 20.2. **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 3114, 3030, 2982, 1765, 1415, 1366, 1279, 1227, 1170, 1117, 976. **HRMS** calc'd for  $\text{C}_{11}\text{H}_{10}\text{F}_6\text{O}_6$  [ $\text{M}^+$ ]: 352.0382; found: 352.0460.



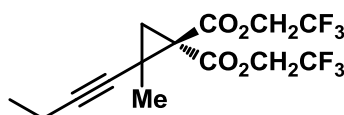
**Bis(2,2,2-trifluoroethyl) 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate (2j).**

Following experimental procedure B2, cyclopropane **2j** was prepared by dissolving commercially available  $\alpha$ -methylstyrene (200 mg, 1.70 mmol) and  $\text{Rh}_2(\text{esp})_2$  (1.50 mg, 0.002 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  followed by the addition of bis(2,2,2-trifluoroethyl)2-diazomalonate<sup>2</sup> (647 mg, 2.20 mmol) dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$ . Cyclopropane **2j** (648 mg, quantitative yield) was obtained as a clear oil.  $R_f$  = 0.60 (30% EtOAc in hexanes).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.32 - 7.23 (m, 5H), 4.73 - 4.52 (m, 2H), 4.16 (dq,  $J$  = 12.7, 8.3 Hz, 1H), 3.99 (dq,  $J$  = 12.7, 8.3 Hz, 1H), 2.35 (d,  $J$  = 5.9 Hz, 1H), 1.86 (d,  $J$  = 5.5 Hz, 1H), 1.58 (s, 3H).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -73.6 (t,  $J$  = 7.9 Hz, 3F), -73.8



(t,  $J = 7.9$  Hz, 3F).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta = 166.2, 165.5, 139.8, 128.5, 128.1, 127.6, 122.5$  (d,  $J_{\text{C-F}} = 277$  Hz, 1C),  $122.0$  (d,  $J_{\text{C-F}} = 277$  Hz, 1C),  $61.2$  (q,  $J_{\text{C-F}} = 37$  Hz, 1C),  $60.9$  (q,  $J_{\text{C-F}} = 37$  Hz, 1C),  $40.1, 39.6, 25.7, 24.1$ . **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 3063, 2975, 2935, 1751, 1498, 1448, 1412, 1286, 1168, 1103, 977. **HRMS** calc'd for  $\text{C}_{16}\text{H}_{14}\text{F}_6\text{O}_4$  [ $\text{M}^+$ ]: 384.0796; found: 384.0787.



**Bis(2,2,2-trifluoroethyl) 2-(but-1-ynyl)-2-methylcyclopropane-1,1-dicarboxylate (2k).**

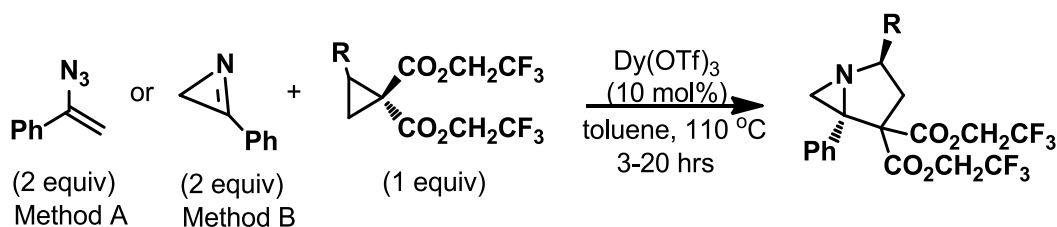
Following experimental procedure B2, cyclopropane **2k** was prepared by dissolving commercially available 2-methylhex-1-en-3-yne (500 mg, 5.30 mmol) and  $\text{Rh}_2(\text{esp})_2$  (4.02 mg, 0.005 mmol) in 7 mL of  $\text{CH}_2\text{Cl}_2$  followed by the addition of bis(2,2,2-trifluoroethyl)2-diazomalonate<sup>2</sup> (2.03 g, 6.90 mmol) dissolved in 3 mL of  $\text{CH}_2\text{Cl}_2$ . Cyclopropane **2k** (1.90 g, quantitative yield) was obtained as a colourless oil.  $R_f = 0.40$  (10% EtOAc in hexanes).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta = 4.54$  (m, 4H),  $2.13$  (q,  $J = 7.42$ , 2H),  $2.01$  (d,  $J = 5.1$  Hz, 1H),  $1.69$  (d,  $J = 5.4$  Hz, 1H),  $1.49$  (s, 3H),  $1.06$  (t,  $J = 7.4$  Hz, 3H).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta = -73.8$  (t,  $J = 8.6$  Hz, 3F),  $-73.8$  (t,  $J = 8.6$  Hz, 3F).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta = 165.8, 165.5, 121.6$  (q,  $J_{\text{C-F}} = 277$  Hz, 1C),  $121.5$  (q,  $J = 277$  Hz, 1C),  $83.8, 78.4, 61.5$  (q,  $J_{\text{C-F}} = 37$  Hz, 1C),  $61.3$  (q,  $J_{\text{C-F}} = 37$  Hz, 1C),  $40.0, 28.6, 26.6, 20.8, 14.0, 12.5$ . **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 2981, 2944, 2884, 2247, 2131, 1748, 1410, 1280, 1160, 1105. **HRMS** calc'd for  $\text{C}_{14}\text{H}_{14}\text{F}_6\text{O}_4$  [ $\text{M}^+$ ]: 360.0796; found: 360.0789.

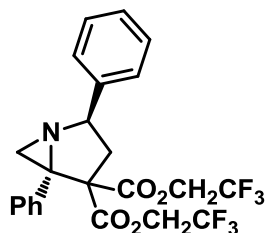
### Experimental procedure C: Synthesis of azabicyclo[3.1.0]hexane-4,4-dicarboxylates (8b-k).

**Caution!** Although we have never had any incidents, organic azides are potentially explosive substances that can decompose upon the exposure to heat, light, and pressure. Any azide synthesized should be stored in the freezer and in the dark. In addition, molecules containing the azido moiety can decompose violently which may result in injury if proper safety precautions are not taken. Reactions were performed with a blast shield.

NOTE: In addition to  $\text{Dy}(\text{OTf})_3$ , which was deemed the best, Lewis acids screened included  $\text{Yb}(\text{OTf})_3$ ,  $\text{Sc}(\text{OTf})_3$ ,  $\text{MgI}_2$ ,  $\text{CuOTf}_2$ ,  $\text{TMSOTf}$ ,  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $\text{Ni}(\text{ClO}_4)_2$ ,  $\text{TiCl}_4$ ,  $\text{FeCl}_3$ ,  $\text{GaCl}_3$ .



In a 10 mL round-bottomed flask, the appropriate bis(2,2,2-trifluoroethyl) cyclopropane-1,1-dicarboxylate (1.0 equiv) and  $\text{Dy(OTf)}_3$  (10 mol%) catalyst were dissolved in 6 mL of toluene. The reaction flask was fitted with a condenser and heated to 110 °C. To this mixture, (1-azidovinyl)benzene<sup>4</sup> **5** (2.0 equiv) (**Method A**) or 3-phenyl-2H-azirine<sup>4</sup> **6** (2.0 equiv) (**Method B**), diluted in 1 mL of toluene, was added dropwise over a period of 10-15 mins. The reaction was allowed to stir at 110 °C for 3-20 hours (monitored by TLC). The reaction flask was cooled to room temperature and the toluene was removed *in vacuo*. The crude reaction mixture was then pre-absorbed onto silica gel and purified by column chromatography (EtOAc in Hexanes).



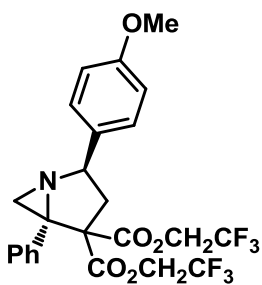
**Bis(2,2,2-trifluoroethyl) 2,5-diphenyl-1-azabicyclo[3.1.0]hexane-4,4-dicarboxylate (8b).**

Following experimental procedure C **Method A** compound **8b** was prepared by dissolving bis(2,2,2-trifluoroethyl) 2-phenylcyclopropane-1,1-dicarboxylate<sup>3</sup> (100 mg, 0.270 mmol) and  $\text{Dy(OTf)}_3$  (16.8 mg, 0.027 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (78.3 mg, 0.540 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 3.5 hours. Compound **8b** (72 mg, 55 %) was obtained as a clear oil.  $R_f$  = 0.62 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8b** was prepared by dissolving bis(2,2,2-trifluoroethyl)2-phenylcyclopropane-1,1-dicarboxylate<sup>3</sup> (150 mg, 0.405 mmol) and  $\text{Dy(OTf)}_3$  (25.0 mg, 0.041 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (95.0 mg, 0.810 mmol), in 1 mL of toluene, was added dropwise. The reaction

was heated at 110 °C for 10 hours. Compound **8b** (124 mg, 63 %) was obtained as a clear oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.61 (d,  $J$  = 1.0 Hz, 2H), 7.47 (d,  $J$  = 1.0 Hz, 2H), 7.40 (t,  $J$  = 7.4 Hz, 2H), 7.36 - 7.28 (m, 4H), 5.35 (dd,  $J$  = 10.9, 7.0 Hz, 1H), 4.64 (dq,  $J$  = 14.1, 7.0 Hz, 1H), 4.52 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 4.39 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 3.77 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 3.05 (dd,  $J$  = 14.1, 7.0 Hz, 1H), 2.23 (dd,  $J$  = 13.9, 11.1 Hz, 1H), 2.16 (s, 1H), 2.15 (s, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -73.7 (t,  $J$  = 8.6 Hz, 3F), -73.9 (t,  $J$  = 8.6 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.1, 167.9, 139.7, 136.8, 128.7, 128.5, 128.1, 128.1, 127.3, 126.6, 126.3, 123.7 (d,  $J_{C-F}$  = 277 Hz, 1C), 120.9 (d,  $J_{C-F}$  = 277 Hz, 1C), 66.2, 65.1, 61.3 (q,  $J_{C-F}$  = 37 Hz, 1C), 61.2 (q,  $J_{C-F}$  = 37 Hz, 1C), 54.9, 37.7, 32.8. **FT-IR** (thin film, cm<sup>-1</sup>): 3062, 3031, 1754, 1604, 1496, 1448, 1413, 1286, 1169, 1104, 980, 700. **HRMS** calc'd for C<sub>23</sub>H<sub>19</sub>F<sub>6</sub>NO<sub>4</sub> [M<sup>+</sup>]: 487.1218; found: 487.1144.

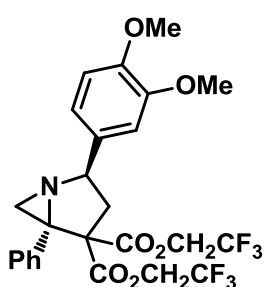


**Bis(2,2,2-trifluoroethyl) 2-(4-methoxyphenyl)-5-phenyl-1-azabicyclo[3.1.0]hexane-4,4-dicarboxylate (**8c**).**

Following experimental procedure C **Method A** compound **8c** was prepared by dissolving bis(2,2,2-trifluoroethyl) 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate<sup>3</sup> (150 mg, 0.375 mmol) and Dy(OTf)<sub>3</sub> (23.0 mg, 0.037 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (108 mg, 0.750 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 3 hours. Compound **8c** (140 mg, 72 %) was obtained as a white solid. MP = 98-100 °C. R<sub>f</sub> = 0.56 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8c** was prepared by dissolving bis(2,2,2-trifluoroethyl) 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate<sup>3</sup> (150 mg, 0.375 mmol) and Dy(OTf)<sub>3</sub> (23.0 mg, 0.037 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (87.8 mg, 0.750 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 14 hours. Compound **8c** (179 mg, 92 %) was obtained as a white solid.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.60 (dd,  $J$  = 6.6, 1.9 Hz, 2H), 7.36 (d,  $J$  = 8.2 Hz, 2H), 7.24 - 7.34 (m, 3H), 6.93 (d,  $J$  = 8.9 Hz, 2H), 5.27 (dd,  $J$  = 11.1, 7.2 Hz, 1H), 4.63 (dq,  $J$  = 12.8, 8.2 Hz, 1H), 4.52 (dq,  $J$  = 12.8, 8.2 Hz, 1H), 4.37 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 3.82 (s, 3H), 3.76 (dq,  $J$  = 12.8, 8.2 Hz, 1H), 2.98 (dd,  $J$  = 14.1, 7.0 Hz, 1H), 2.20 (dd,  $J$  = 13.9, 11.1 Hz, 1H), 2.14 (s, 1H), 2.09 (s, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -73.74 (t,  $J$  = 8.6 Hz, 3F), -73.94 (t,  $J$  = 8.6 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.2, 167.9, 158.8, 136.8, 131.5, 128.7, 128.0, 127.8, 123.7 (d,  $J_{C-F}$  = 277 Hz, 1C), 120.9 (d,  $J_{C-F}$  = 277 Hz, 1C), 113.8, 66.2, 64.6, 61.3 (q,  $J_{C-F}$  = 37 Hz, 1C), 61.2 (q,  $J_{C-F}$  = 37 Hz, 1C), 55.3, 54.8, 37.7, 32.6, 30.8. **FT-IR** (thin film, cm<sup>-1</sup>): 2969, 2838, 1753, 1612, 1514, 1413, 1287, 1249, 1170, 1103, 981, 701. **HRMS** calc'd for C<sub>24</sub>H<sub>21</sub>F<sub>6</sub>NO<sub>5</sub> [M<sup>+</sup>]: 517.1324; found: 517.1230.



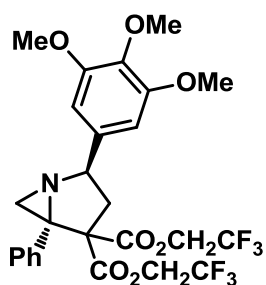
**Bis(2,2,2-trifluoroethyl) 2-(3,4-dimethoxyphenyl)-5-phenyl-1-azabicyclo[3.1.0]hexane-4,4-dicarboxylate (8d).**

Following experimental procedure C **Method A** compound **8d** was prepared by dissolving cyclopropane **2d** (155 mg, 0.360 mmol) and Dy(OTf)<sub>3</sub> (22 mg, 0.036 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (104 mg, 0.720 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 8 hours. Compound **8d** (78 mg, 40%) was obtained as a yellow oil. R<sub>f</sub> = 0.20 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8d** was prepared by dissolving cyclopropane **2d** (150 mg, 0.348 mmol) and Dy(OTf)<sub>3</sub> (21 mg, 0.035 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (81.7 mg, 0.697 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 16 hours. Compound **8d** (148 mg, 78 %) was obtained as a yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.56 (dd,  $J$  = 8.2, 1.9 Hz, 2H), 7.31 - 7.21 (m, 3H), 6.99 (d,  $J$  = 2.0 Hz, 1H), 6.89 (dd,  $J$  = 8.2, 1.9 Hz, 1H), 6.84 (s, 1H), 5.24 (dd,  $J$  = 10.9, 7.4 Hz, 1H), 4.60 (dq,  $J$  = 16.4, 8.2 Hz, 1H), 4.49 (dq,  $J$  = 16.4, 8.2 Hz, 1H), 4.35 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.72 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 2.96 (dd,  $J$  = 14.1, 7.0 Hz, 1H), 2.18 (dd,  $J$  = 13.9, 11.1 Hz, 1H), 2.11 (s, 1H), 2.07 (s, 1H). **<sup>19</sup>F NMR**

(376 MHz, CDCl<sub>3</sub>)  $\delta$  = -73.7 (t,  $J$  = 8.6 Hz, 3F), -73.9 (t,  $J$  = 8.6 Hz, 3F). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)  $\delta$  = 168.2, 167.8, 148.9, 148.3, 136.8, 132.2, 128.7, 128.1, 122.5 (q,  $J_{C-F}$  = 277 Hz, 1C), 122.1 (q,  $J_{C-F}$  = 277 Hz, 1C), 118.3, 111.0, 110.5, 66.2, 64.8, 61.3 (q,  $J_{C-F}$  = 37 Hz, 1C), 63.2 (q,  $J_{C-F}$  = 37 Hz, 1C), 56.0, 55.9, 54.8, 37.6, 32.6. **FT-IR** (thin film, cm<sup>-1</sup>): 3062, 3004, 2965, 2838, 1753, 1518, 1414, 1285, 1242, 1168, 1103, 1028, 975. **HRMS** calc'd for C<sub>25</sub>H<sub>23</sub>F<sub>6</sub>NO<sub>6</sub> [M<sup>+</sup>]: 547.1430 found; 547.1451.



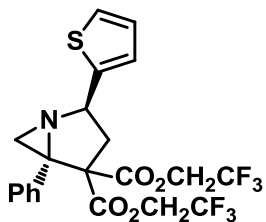
**Bis(2,2,2-trifluoroethyl) 5-phenyl-2-(3,4,5-trimethoxyphenyl)-1-azabicyclo[3.1.0] hexane-4,4-dicarboxylate (8e).**

Following experimental procedure C **Method A**, compound **8e** was prepared by dissolving cyclopropane **2e** (150 mg, 0.326 mmol) and Dy(OTf)<sub>3</sub> (20 mg, 0.033 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (94.5 mg, 0.652 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 8 hours. Compound **8e** (96 mg, 51%) was obtained as a white solid. MP = 111-113 °C. R<sub>f</sub> = 0.24 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8e** was prepared by dissolving cyclopropane **2e** (150 mg, 0.326 mmol) and Dy(OTf)<sub>3</sub> (20 mg, 0.033 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (76.3 mg, 0.652 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 18 hours. Compound **8e** (158 mg, 84 %) was obtained as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.56 - 7.60 (m, 2H), 7.34 - 7.24 (m, 3H), 6.64 (d,  $J$  = 0.8 Hz, 2H), 5.26 (dd,  $J$  = 10.9, 7.4 Hz, 1H), 4.62 (qd,  $J$  = 16.4, 8.2 Hz, 1H), 4.52 (dq,  $J$  = 16.4, 8.2 Hz, 1H), 4.38 (dq,  $J$  = 12.6, 8.3 Hz, 1H), 3.87 (s, 6H), 3.84 (s, 3 H), 3.75 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 3.00 (dd,  $J$  = 13.9, 7.2 Hz, 1H), 2.19 (dd,  $J$  = 14.0, 10.9 Hz, 1H), 2.15 (s, 3H), 2.14 (d,  $J$  = 3.1 Hz, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -73.7 (t,  $J$  = 8.6 Hz, 3F), -73.9 (t,  $J$  = 8.6 Hz, 3F). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)  $\delta$  = 168.0, 167.7, 153.2, 137.2, 136.6, 135.4, 128.7, 128.1, 122.4 (q,  $J_{C-F}$  = 277 Hz, 1C), 122.0 (q,  $J_{C-F}$  = 277 Hz, 1C), 103.8, 66.7, 65.1, 61.3 (q,  $J_{C-F}$  = 37 Hz, 1C), 61.2 (q,  $J_{C-F}$  = 37 Hz, 1C), 60.7, 56.2,

54.8, 37.7, 32.8. **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 3061, 2969, 2942, 1753, 1589, 1509, 1416, 1286, 1241, 1168, 1128, 977, 701. **HRMS** calc'd for  $\text{C}_{26}\text{H}_{25}\text{F}_6\text{NO}_7$  [ $\text{M}^+$ ]: 577.1535; found: 577.1560.

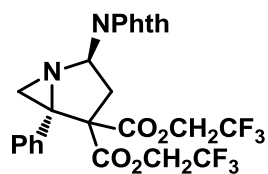


**Bis(2,2,2-trifluoroethyl) 5-phenyl-2-(thiophen-2-yl)-1-azabicyclo[3.1.0]hexane-4,4-dicarboxylate (8f).**

Following experimental procedure C **Method A**, compound **8f** was prepared by dissolving bis(2,2,2-trifluoroethyl)2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate **2f** (150 mg, 0.399 mmol) and  $\text{Dy}(\text{OTf})_3$  (24 mg, 0.039 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (115 mg, 0.798 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 12 hours. Compound **8f** (155 mg, 80%) was obtained as a yellow oil.  $R_f$  = 0.48 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8f** was prepared by dissolving bis(2,2,2-trifluoroethyl) 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate **2f** (150 mg, 0.399 mmol) and  $\text{Dy}(\text{OTf})_3$  (24 mg, 0.039 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (93.4 mg, 0.798 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 18 hours. Compound **8f** (157 mg, 80 %) was obtained as a yellow oil.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.59 - 7.55 (m, 2H), 7.32 - 7.23 (m, 4H), 7.05-6.98 (m, 2H), 5.43 (dd,  $J$  = 10.7, 6.8 Hz, 1H), 4.64 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 4.52 (dq,  $J$  = 16.4, 8.2 Hz, 1H), 4.35 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 3.75 (dq,  $J$  = 16.4, 8.2 Hz, 1H), 2.98 (dd,  $J$  = 14.1, 7.0 Hz, 1H), 2.28 (dd,  $J$  = 14.1, 7.0 Hz, 1H), 2.26 (d,  $J$  = 1.2 Hz, 1H), 2.06 (d,  $J$  = 1.2 Hz, 1H).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -73.74 (t,  $J$  = 8.6 Hz, 3F), -73.94 (t,  $J$  = 8.6 Hz, 3F).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.0, 167.6, 142.1, 136.5, 128.6, 128.2, 128.1, 126.7, 124.9, 124.8, 122.5 (q,  $J_{\text{C-F}}$  = 277 Hz, 1C), 122.1 (q,  $J_{\text{C-F}}$  = 277 Hz, 1C), 66.2, 62.0, 61.3 (q,  $J_{\text{C-F}}$  = 37 Hz, 1C), 63.2 (q,  $J_{\text{C-F}}$  = 37 Hz, 1C), 55.4, 38.6, 32.8. **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 3064, 2973, 1754, 1448, 1413, 1286, 1247, 1170, 1103, 978, 701. **HRMS** calc'd for  $\text{C}_{21}\text{H}_{17}\text{F}_6\text{NO}_4\text{S}$  [ $\text{M}^+$ ]: 493.0782; found: 493.0721.

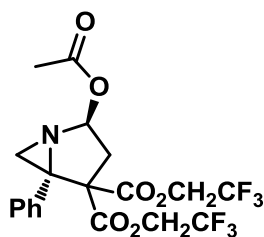


**Bis(2,2,2-trifluoroethyl) 2-(1,3-dioxoisindolin-2-yl)-5-phenyl-1-azabicyclo[3.1.0] hexane-4,4-dicarboxylate (8g).**

Following experimental procedure C **Method A**, compound **8g** was prepared by dissolving cyclopropane **2g** (150 mg, 0.342 mmol) and  $\text{Dy}(\text{OTf})_3$  (21 mg, 0.034 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (99 mg, 0.684 mmol), in 1 mL of toluene, was then added dropwise. The reaction was heated at 110 °C for 16 hours. Compound **8g** (70mg, 37%) was obtained as a yellow solid. MP = 151-153 °C. Rf = 0.41 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8g** was prepared by dissolving cyclopropane **2g** (150 mg, 0.342 mmol) and  $\text{Dy}(\text{OTf})_3$  (21 mg, 0.034 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (80 mg, 0.684 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 20 hours. Compound **8g** (140 mg, 74%) was obtained as a yellow solid.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.92 (d,  $J$  = 2.7 Hz, 1H), 7.90 (d,  $J$  = 3.1 Hz, 1H), 7.79 (d,  $J$  = 3.1 Hz, 1H), 7.77 (d,  $J$  = 3.1 Hz, 1H), 7.61 - 7.57 (m, 2H), 7.34 - 7.25 (m, 5 H), 6.36 (dd,  $J$  = 10.9, 7.0 Hz, 1H), 4.71 - 4.55 (m, 2H), 4.35 (dq,  $J$  = 12.5, 8.3 Hz, 1H), 3.73 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 3.48 (dd,  $J$  = 14.1, 10.9 Hz, 1H), 3.20 (d,  $J$  = 1.2 Hz, 1H) 2.68 (dd,  $J$  = 14.1, 7.0 Hz, 1H) 2.15 (d,  $J$  = 1.6 Hz, 1H). **<sup>19</sup>F NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -73.74 (t,  $J$  = 8.6 Hz, 3F), -73.94 (t,  $J$  = 8.6 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.2, 167.8, 167.3, 135.8, 134.5, 131.5, 128.6, 128.3, 128.1, 123.8, 123.6, 68.8, 64.9, 61.4 (q,  $J_{\text{C-F}}$  = 37 Hz, 1C), 61.3 (q,  $J_{\text{C-F}}$  = 37 Hz, 1C), 52.9, 35.1, 30.7. **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 3030, 2979, 2880, 1777, 1719, 1604, 1448, 1373, 1284, 1169, 996, 717. **HRMS** calc'd for  $\text{C}_{25}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_6$  [ $\text{M}^+$ ]: 556.1069; found: 556.1005.

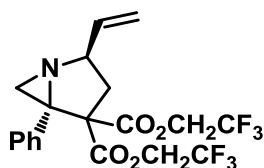


**Bis(2,2,2-trifluoroethyl) 2-acetoxy-5-phenyl-1-azabicyclo[3.1.0] hexane-4,4-dicarboxylate (8h).**

Following experimental procedure C **Method B**, compound **8h** was prepared by dissolving cyclopropane **2h** (150 mg, 0.426 mmol) and

Dy(OTf)<sub>3</sub> (26 mg, 0.043 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **5** (100 mg, 0.852 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 16 hours. Compound **8h** (67 mg, 34%) was obtained as a yellow oil. R<sub>f</sub> = 0.3 (30% EtOAc in hexanes).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 7.54 - 7.50 (m, 2H), 7.30 - 7.23 (m, 3H), 6.47 (dd, *J* = 7.9, 6.7 Hz, 1H), 4.65 (dq, *J* = 12.5, 8.3 Hz, 1H), 4.49 (dq, *J* = 12.5, 8.3 Hz, 1H), 4.29 (dq, *J* = 12.5, 8.2 Hz, 1H), 3.71 (dq, *J* = 12.5, 8.2 Hz, 1H), 2.97 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.13 (d, *J* = 1.8 Hz, 1H), 2.12 (s, 3H), 2.04 (dd, *J* = 14.4, 8.5 Hz, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -73.74 (t, *J* = 8.6 Hz, 3F), -73.94 (t, *J* = 8.6 Hz, 3F). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ = 169.4, 167.5, 167.2, 135.7, 128.5, 128.1, 122.4 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 121.9 (q, *J*<sub>C-F</sub> = 277 Hz, 1C), 87.6, 64.5, 61.4 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 61.3 (q, *J*<sub>C-F</sub> = 37 Hz, 1C), 54.2, 36.3, 33.0, 20.8. **FT-IR** (thin film, cm<sup>-1</sup>): 3064, 3031, 2975, 1755, 1496, 1448, 1413, 1285, 1111, 1031, 979. **HRMS** calc'd for C<sub>19</sub>H<sub>17</sub>F<sub>6</sub>NO<sub>6</sub> [M<sup>+</sup>]: 469.0960; found: 469.0899.



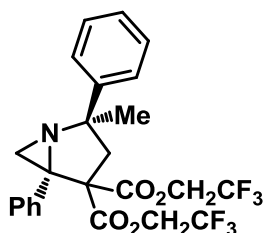
**Bis(2,2,2-trifluoroethyl) 5-phenyl-2-vinyl-1-azabicyclo[3.1.0]hexane-4,4-dicarboxylate (**8i**).**

Following experimental procedure C **Method A**, compound **8i** was prepared by dissolving bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate<sup>3</sup> (123mg, 0.384 mmol) and Dy(OTf)<sub>3</sub> (23 mg, 0.040 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (112 mg, 0.768 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 12 hours. Compound **8i** (45 mg, 27%) was obtained as a clear oil. R<sub>f</sub> = 0.52 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8i** was prepared by dissolving bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane-1,1-dicarboxylate<sup>3</sup> (128 mg, 0.400 mmol) and Dy(OTf)<sub>3</sub> (24 mg, 0.040 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (93.6 mg, 0.833 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 15 hours. Compound **8i** (44 mg, 25%) was obtained as a clear oil.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.56 - 7.52 (m, 2H), 7.32 - 7.25 (m, 3H), 6.00 - 5.91 (m, 1H), 5.36 (dt,  $J$  = 17.2, 1.4 Hz, 1H), 5.26 (dt,  $J$  = 10.6, 1.4 Hz, 1H), 4.65 (dq,  $J$  = 12.5, 8.3 Hz, 2H), 4.50 (dq,  $J$  = 12.5, 8.2 Hz, 1H), 4.33 (dq,  $J$  = 2.5, 8.3 Hz, 1H), 3.74 (dq,  $J$  = 12.7, 8.3 Hz, 1H), 2.67 (dd,  $J$  = 14.5, 7.0 Hz, 1H), 2.13 (s, 1H), 2.01 (s, 1H), 1.96 (dd,  $J$  = 14.1, 10.9 Hz, 1H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -73.77 (t,  $J$  = 8.6 Hz, 3F), -73.99 (t,  $J$  = 8.6 Hz, 3F). **<sup>3</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.0, 167.9, 136.7, 135.3, 128.6, 128.0, 122.5 (q,  $J_{C-F}$  = 277 Hz, 1C), 122.1 (q,  $J_{C-F}$  = 277 Hz, 1C), 117.3, 65.9, 64.6, 61.2 (q,  $J_{C-F}$  = 36 Hz, 1C), 61.1 (q,  $J_{C-F}$  = 37 Hz, 1C), 54.5, 36.9, 32.2. **FT-IR** (thin film, cm<sup>-1</sup>): 3063, 2976, 1754, 1496, 1448, 1413, 1286, 1233, 1170, 1103, 977, 701. **HRMS** calc'd for C<sub>19</sub>H<sub>17</sub>F<sub>6</sub>NO<sub>4</sub> [M<sup>+</sup>]: 437.1062; found: 437.0990.



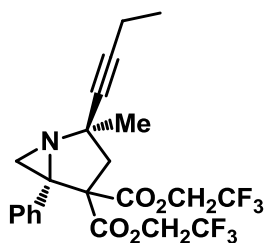
**Bis(2,2,2-trifluoroethyl) 2-methyl-2,5-diphenyl-1-azabicyclo[3.1.0]hexane-4,4-dicarboxylate (8j).**

Following experimental procedure C **Method A**, compound **8j** was prepared by dissolving cyclopropane **2j** (150 mg, 0.390 mmol) and Dy(OTf)<sub>3</sub> (24 mg, 0.039 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (113 mg, 0.781 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 12 hours. Compound **8j** (160 mg, 82%) was obtained as a yellow semi-solid in a 1:1 mixture of diastereomers. R<sub>f</sub> = 0.80 (30% EtOAc in hexanes).

Following experimental procedure C **Method B**, compound **8j** was prepared by dissolving cyclopropane **2j** (150 mg, 0.390 mmol) and Dy(OTf)<sub>3</sub> (24 mg, 0.039 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine<sup>4</sup> **6** (91 mg, 0.781 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 18 hours. Compound **8j** (169 mg, 87%) was obtained as a yellow semi-solid in a 1:1 mixture of diastereomers.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) (mixture of diastereomers)  $\delta$  = 7.83 (d,  $J$  = 8.6 Hz, 2H), 7.62 (d,  $J$  = 8.6 Hz, 2H), 7.53 (d,  $J$  = 8.2 Hz, 2H), 7.46 (t,  $J$  = 8.6 Hz, 2H), 7.43 - 7.36 (m, 5 H), 7.35- 7.23 (m, 7H), 4.76 - 4.63 (m, 1H), 4.62 - 4.41 (m, 4H), 3.94 (dq,  $J$  = 16.4, 8.2 Hz, 1H), 3.68 (dq,  $J$  = 12.6, 8.3 Hz, 1H), 3.46 (dq,  $J$  = 12.5, 8.4 Hz, 1H), 3.31 (d,  $J$  = 14.8 Hz, 1H), 3.25 (d,  $J$  = 14.5 Hz, 1H), 2.64 (d,  $J$  = 14.5 Hz, 1H), 2.59 (d,  $J$  = 14.5 Hz, 1

H), 2.41 (s, 1H), 2.26 (s, 1H), 2.13 (s, 1H), 1.90 (s, 3H), 1.87 (s, 1H), 1.57 (s, 3H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) (mixture of diastereomers)  $\delta$  = -73.64 (t,  $J$ =8.6 Hz, 3F), -73.71 (t,  $J$ =8.6 Hz, 3F), -73.99 - -73.89 (m, 6F). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) (mixture of diastereomers)  $\delta$  = 168.6, 168.3, 168.1, 166.9, 147.8, 147.0, 138.1, 137.3, 128.9, 128.4, 128.2, 128.1, 128.0, 127.9, 127.4, 126.6, 125.8, 125.6, 122.5 (d,  $J_{C-F}$  = 277 Hz, 2C), 122.1 (q,  $J_{C-F}$  = 277 Hz, 1C), 122.0 (q,  $J_{C-F}$  = 277 Hz, 1C), 70.9, 69.5, 66.8, 65.3, 61.3 (q,  $J_{C-F}$  = 37 Hz, 2C), 61.2 (q,  $J_{C-F}$  = 37 Hz, 2C), 57.2, 55.5, 45.2, 44.4, 36.1, 34.5, 33.4, 29.8. **FT-IR** (thin film, cm<sup>-1</sup>): 3061, 3028, 2974, 1757, 1603, 1495, 1447, 1285, 1231, 1170, 1102, 975, 701. **HRMS** calc'd for C<sub>24</sub>H<sub>21</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub> [M<sup>+</sup>]: 501.1375; found: 501.1306.



**Bis(2,2,2-trifluoroethyl)2-(but-1-ynyl)-2-methyl-5-phenyl-1-azabicyclo[3.1.0] hexane-4,4-dicarboxylate (8k).**

Following experimental procedure C **Method A**, compound **8k** was prepared by dissolving cyclopropane **2k** (150 mg, 0.417 mmol) and Dy(OTf)<sub>3</sub> (25 mg, 0.042 mmol) in 6 mL of toluene. (1-azidovinyl)benzene<sup>4</sup> **5** (121 mg, 0.833 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 18 hours. Compound **8k** (103 mg, 52%) was obtained as a clear oil. R<sub>f</sub> = 0.44 (30% EtOAc in hexanes).

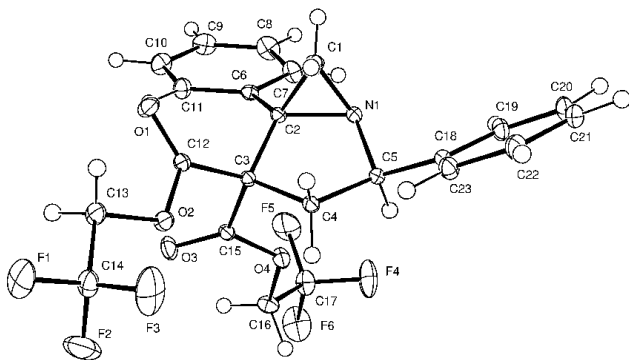
Following experimental procedure C **Method B**, compound **8k** was prepared by dissolving cyclopropane **2k** (150 mg, 0.417 mmol) and Dy(OTf)<sub>3</sub> (25 mg, 0.042 mmol) in 6 mL of toluene. 3-phenyl-2H-azirine **6** (97 mg, 0.833 mmol), in 1 mL of toluene, was added dropwise. The reaction was heated at 110 °C for 20 hours. Compound **8k** (105 mg, 53%) was obtained as a clear oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.54 - 7.50 (m, 2H), 7.31 - 7.22 (m, 3H), 4.62 (dq,  $J$  = 16.4, 8.2 Hz, 1H), 4.50 (qd,  $J$  = 16.4, 8.2 Hz, 1H), 4.38 (qd,  $J$  = 12.5, 8.6 Hz, 1H), 3.85 (qd,  $J$  = 12.5, 8.4 Hz, 1H), 2.98 (d,  $J$  = 14.4 Hz, 1H), 2.31 (d,  $J$  = 14.4 Hz, 1H), 2.25 (q,  $J$  = 7.7 Hz, 2H), 2.05 (d,  $J$  = 1.6 Hz, 1H), 1.92 (d,  $J$  = 1.2 Hz, 1H), 1.55 (s, 3H) 1.18 (t,  $J$  = 7.4 Hz, 3H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -73.74 (t,  $J$  = 8.6 Hz, 3F), -73.94 (t,  $J$  =

8.6 Hz, 3F).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.1, 166.4, 137.4, 128.9, 127.6, 122.4 (q,  $J_{\text{C-F}}$  = 277 Hz, 1C), 122.2 (q,  $J_{\text{C-F}}$  = 277 Hz, 1C), 85.2, 82.6, 65.8, 61.3 (q,  $J_{\text{C-F}}$  = 37 Hz, 1C), 61.2, 61.0 (q,  $J_{\text{C-F}}$  = 37 Hz, 1C), 55.7, 45.3, 32.9, 25.8, 13.6, 12.3. **FT-IR** (thin film,  $\text{cm}^{-1}$ ): 3062, 3030, 2978, 2939, 2881, 2248, 1759, 1497, 1448, 1411, 1285, 1229, 1170, 1129, 974, 701. **HRMS** calc'd for  $\text{C}_{22}\text{H}_{21}\text{F}_6\text{NO}_4$  [ $\text{M}^+$ ]: 477.1375; found: 477.1303.

### X-Ray Crystallography Data of 8b (CDCD 1486123)

X-ray quality crystals were prepared by vapor diffusion of cyclohexane into a solution of **8b** in minimal dichloromethane. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K.



**Table S1. Summary of Crystal Data for 8b**

Formula	$\text{C}_{23}\text{H}_{19}\text{F}_6\text{NO}_4$
Formula Weight (g/mol)	487.39
Crystal Dimensions (mm)	$0.429 \times 0.326 \times 0.270$
Crystal Color and Habit	colourless prism
Crystal System	triclinic
Space Group	P -1
Temperature, K	110

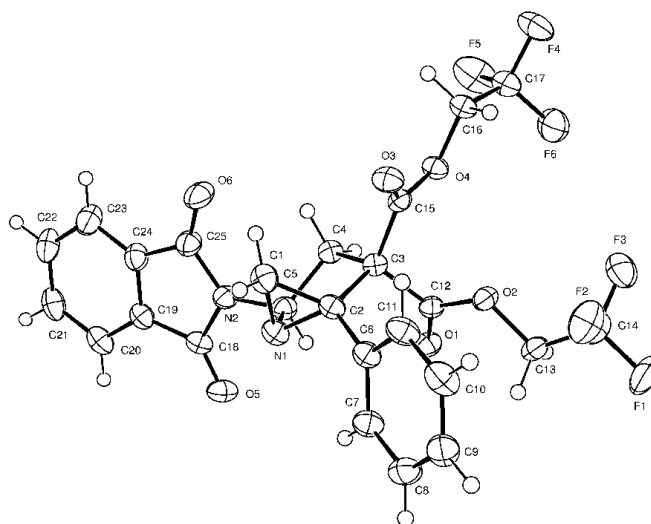
$a, \text{\AA}$	8.5114(17)
$b, \text{\AA}$	9.495(2)
$c, \text{\AA}$	13.368(4)
$\alpha, ^\circ$	98.002(14)
$\beta, ^\circ$	95.439(9)
$\gamma, ^\circ$	96.685(9)
$V, \text{\AA}^3$	1055.7(5)
Number of reflections to determine final unit cell	9127
Min and Max $2\theta$ for cell determination, $^\circ$	4.84, 88.34
Z	2
F(000)	500
$\rho$ (g/cm)	1.533
$\lambda, \text{\AA}$ , (MoK $\alpha$ )	0.71073
$\mu, (\text{cm}^{-1})$	0.139
Diffractometer Type	Bruker Kappa Axis Apex2
Scan Type(s)	phi and omega scans
Max $2\theta$ for data collection, $^\circ$	89.118
Measured fraction of data	0.998
Number of reflections measured	85998
Unique reflections measured	15039
$R_{\text{merge}}$	0.0268
Number of reflections included in refinement	15039
Cut off Threshold Expression	$I > 2\sigma(I)$
Structure refined using	full matrix least-squares using $F^2$
Weighting Scheme	$w=1/[\sigma^2(F_o^2)+(0.0645P)^2+0.1378P]$ where $P=(F_o^2+2F_c^2)/3$
Number of parameters in least-squares	383
$R_1$	0.0398
$wR_2$	0.1118
$R_1$ (all data)	0.0531
$wR_2$ (all data)	0.1202
GOF	1.035
Maximum shift/error	0.001

Min & Max peak heights on final  $\Delta F$  Map ( $e^{-}/\text{\AA}$ )

-0.468, 0.629

### X-Ray Crystallography Data of **8g** (CSDCD 1486124)

X-ray quality crystals were prepared by vapor diffusion of cyclohexane into a solution of **8g** in minimal dichloromethane. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K.



**Table 1.** Summary of Crystal Data for *n16035*

Formula	$\text{C}_{25}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_6$
Formula Weight (g/mol)	556.41
Crystal Dimensions (mm)	$0.218 \times 0.140 \times 0.102$
Crystal Color and Habit	colourless prism
Crystal System	triclinic
Space Group	P -1

Temperature, K	110
$a$ , Å	9.2060(18)
$b$ , Å	11.1007(16)
$c$ , Å	13.748(2)
$\alpha$ , °	70.276(7)
$\beta$ , °	77.582(7)
$\gamma$ , °	67.549(8)
$V$ , Å <sup>3</sup>	1216.3(4)
Number of reflections to determine final unit cell	6519
Min and Max $2\theta$ for cell determination, °	8.98, 133.14
$Z$	2
$F(000)$	568
$\rho$ (g/cm <sup>3</sup> )	1.519
$\lambda$ , Å, (CuK $\alpha$ )	1.54178
$\mu$ , (cm <sup>-1</sup> )	1.220
Diffractionmeter Type	Bruker-Nonius KappCCD Apex2
Scan Type(s)	phi and omega scans
Max $2\theta$ for data collection, °	133.132
Measured fraction of data	0.962
Number of reflections measured	15243
Unique reflections measured	4132
$R_{\text{merge}}$	0.0310
Number of reflections included in refinement	4132
Cut off Threshold Expression	$I > 2\sigma(I)$
Structure refined using	full matrix least-squares using $F^2$
Weighting Scheme	$w=1/[\sigma^2(F_o^2)+(0.0576P)^2+0.4707P]$ where $P=(F_o^2+2F_c^2)/3$
Number of parameters in least-squares	424
$R_1$	0.0384
$wR_2$	0.1009
$R_1$ (all data)	0.0445
$wR_2$ (all data)	0.1062
GOF	1.050

Maximum shift/error	0.000
Min & Max peak heights on final $\Delta F$ Map ( $e^-/\text{\AA}$ )	-0.432, 0.572

Where:

$$R_1 = \sum (|F_o| - |F_c|) / \sum F_o$$

$$wR_2 = [ \sum w (F_o^2 - F_c^2)^2 / \sum w F_o^4 ]^{1/2}$$

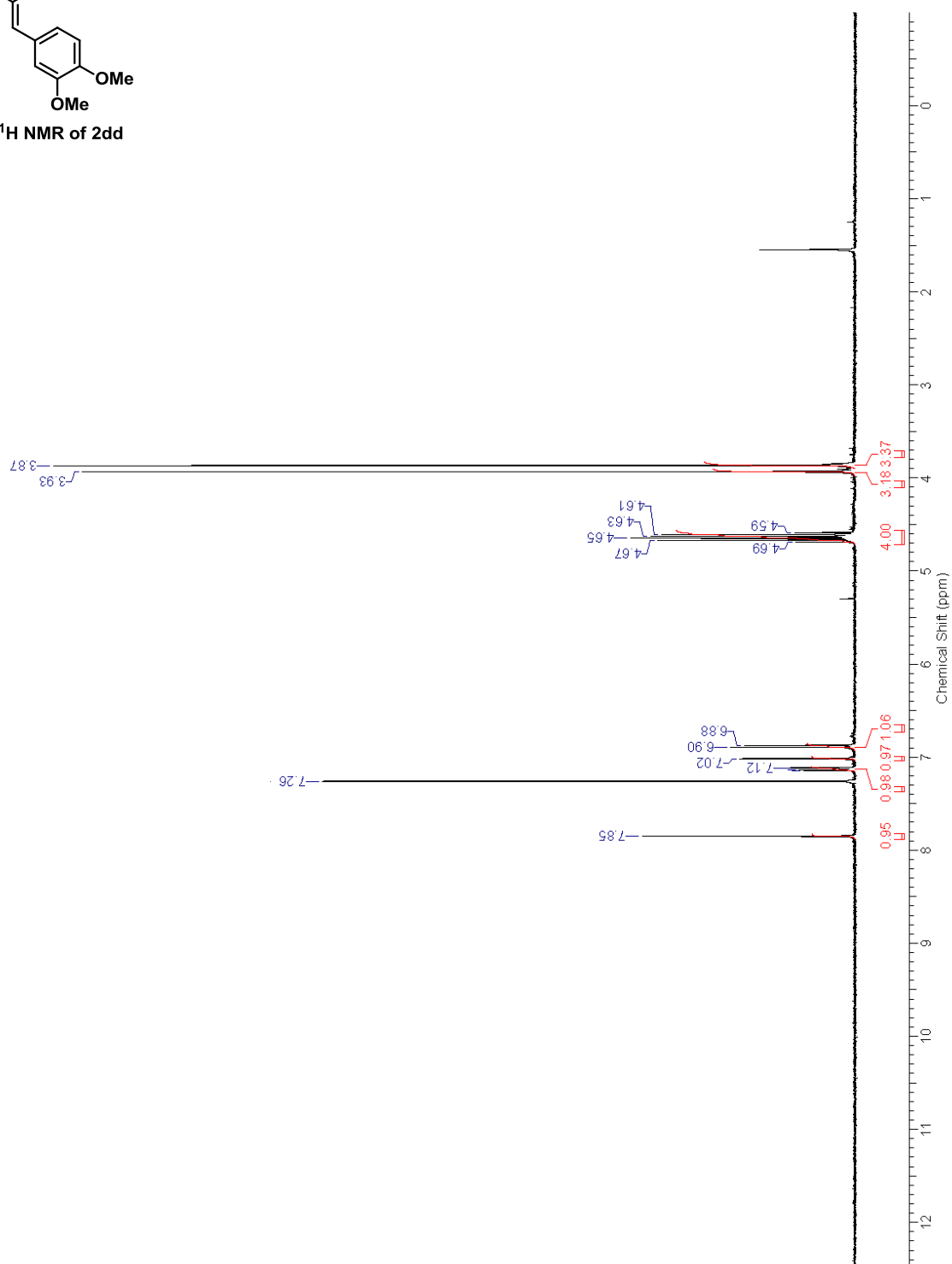
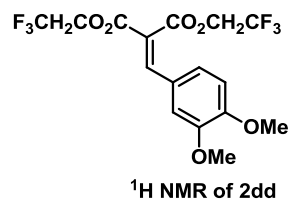
$$\text{GOF} = [ \sum w (F_o^2 - F_c^2)^2 / (\text{No. of reflns.} - \text{No. of params.}) ]^{1/2}$$

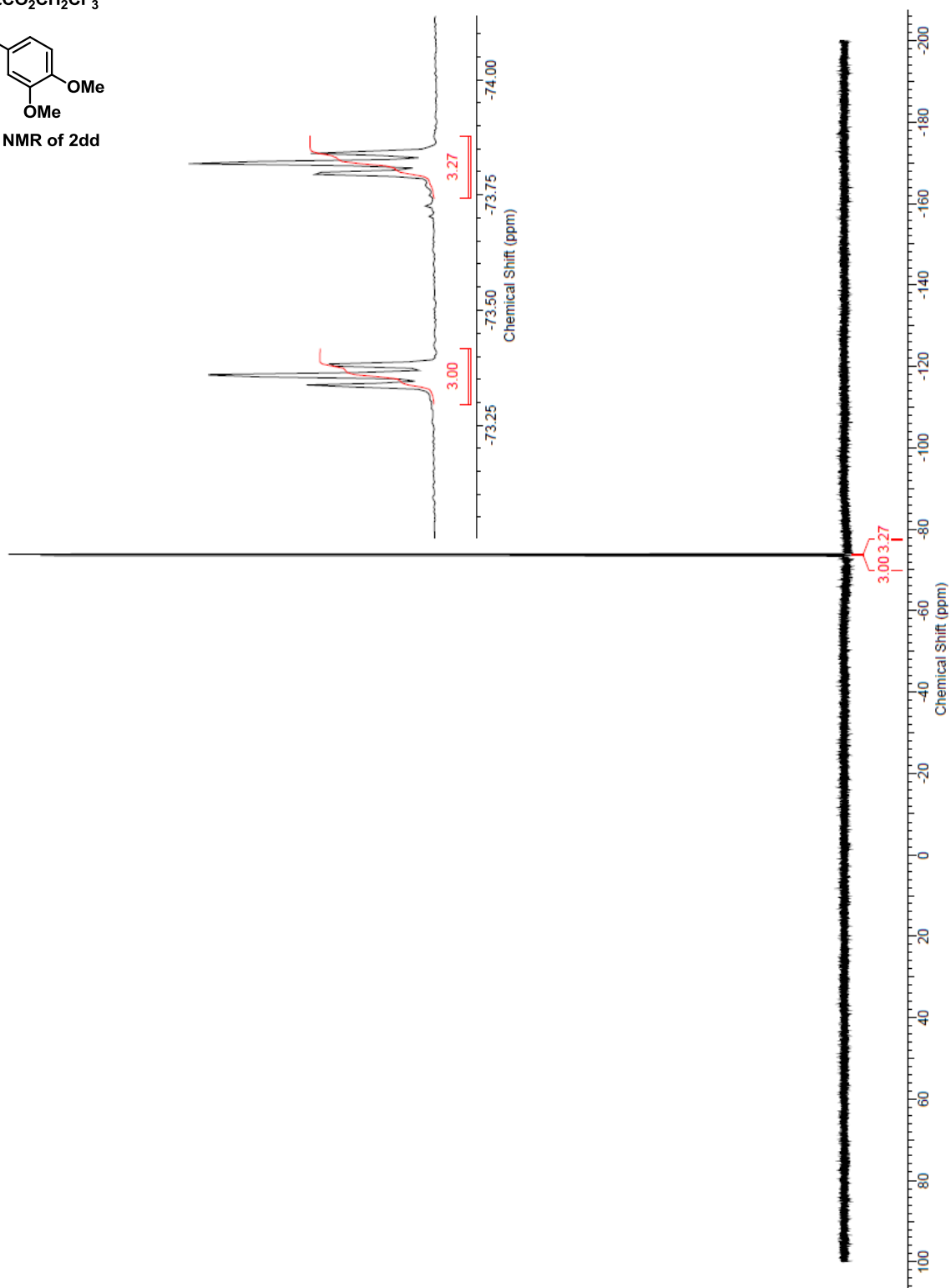
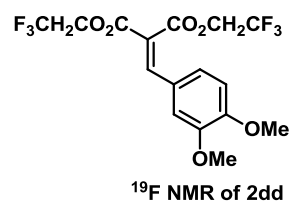
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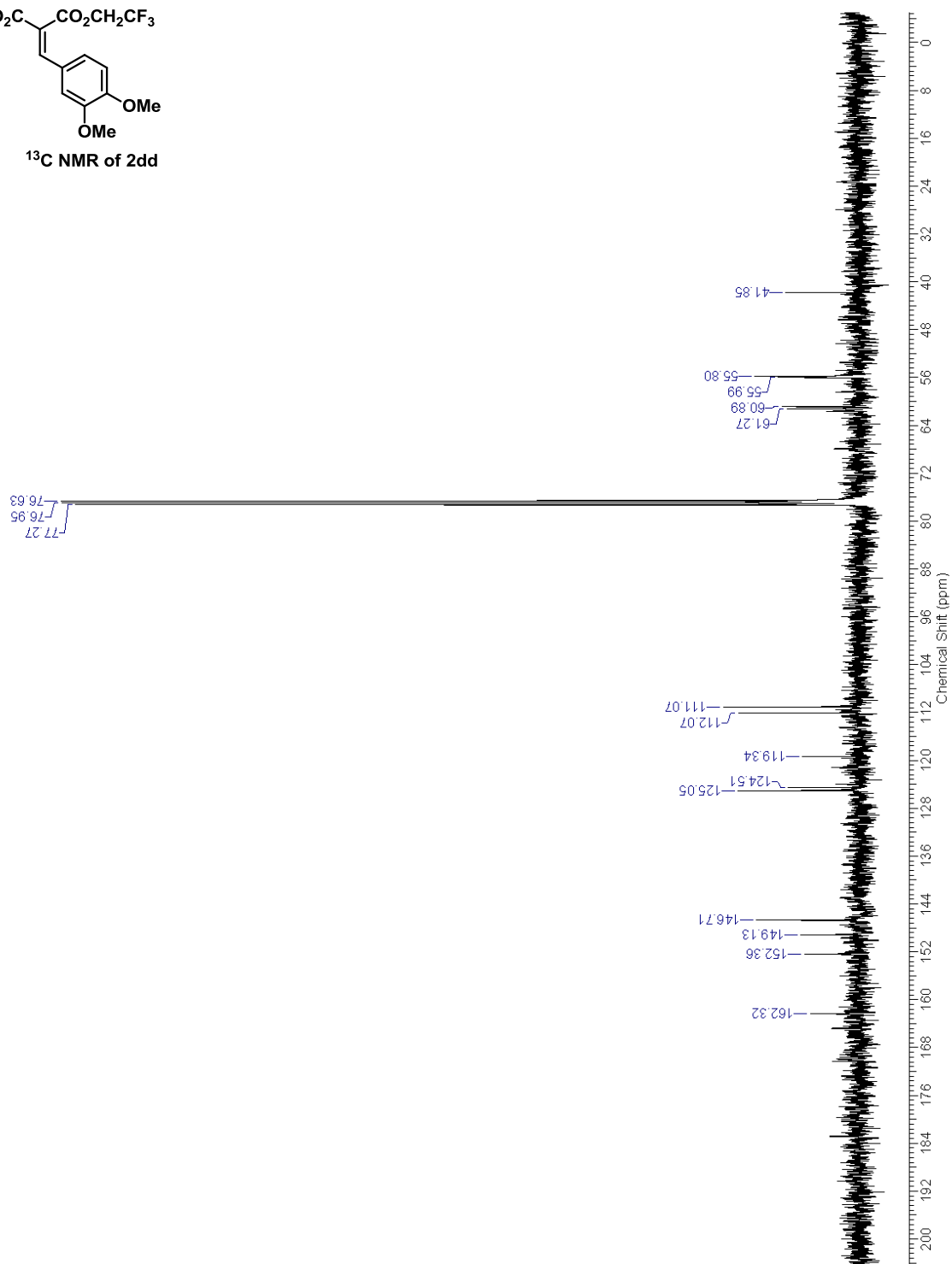
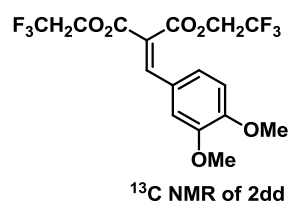
1. Takacs, J.M.; Xu, Z.; Jiang, X-T.; Leonov, A.P.; Theriot, G.C. *Org. Lett.* **2002**, *4*, 3843-3845.
2. de Nanteuil, F.; Loup, J.; Waser, J. *Org. Lett.* **2013**, *15*, 3738-3741.
3. Armstrong, E. L.; Kerr, M.A. *Org. Chem. Front.* **2015**, *2*, 1045-1047.
4. Loy, N.S.Y.; Kim, S.; Park, C-M. *Org. Lett.* **2015**, *17*, 395-397.

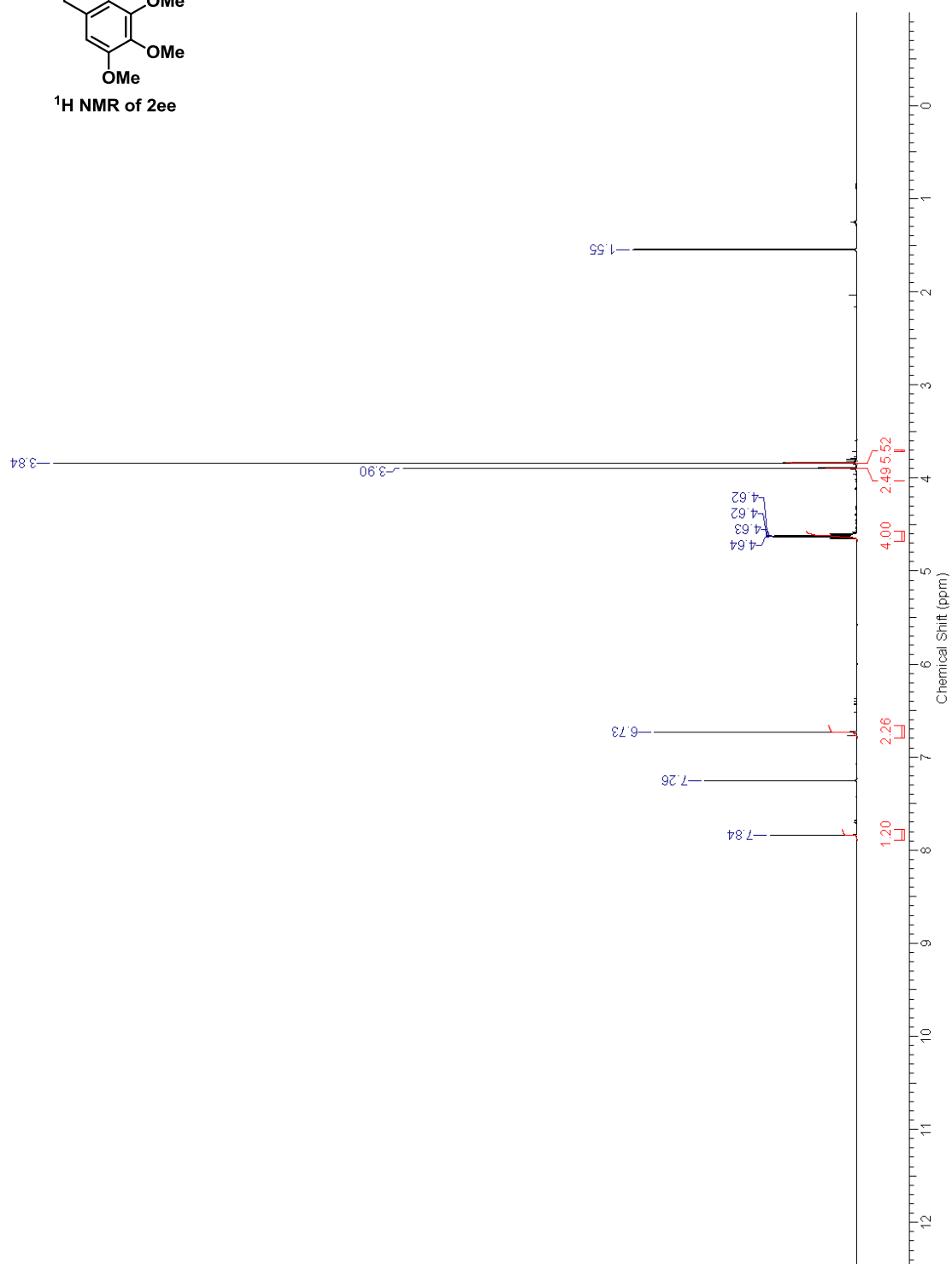
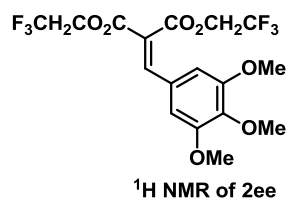
# **$^1\text{H}$ NMR, $^{19}\text{F}$ NMR and $^{13}\text{C}$ NMR Spectra**

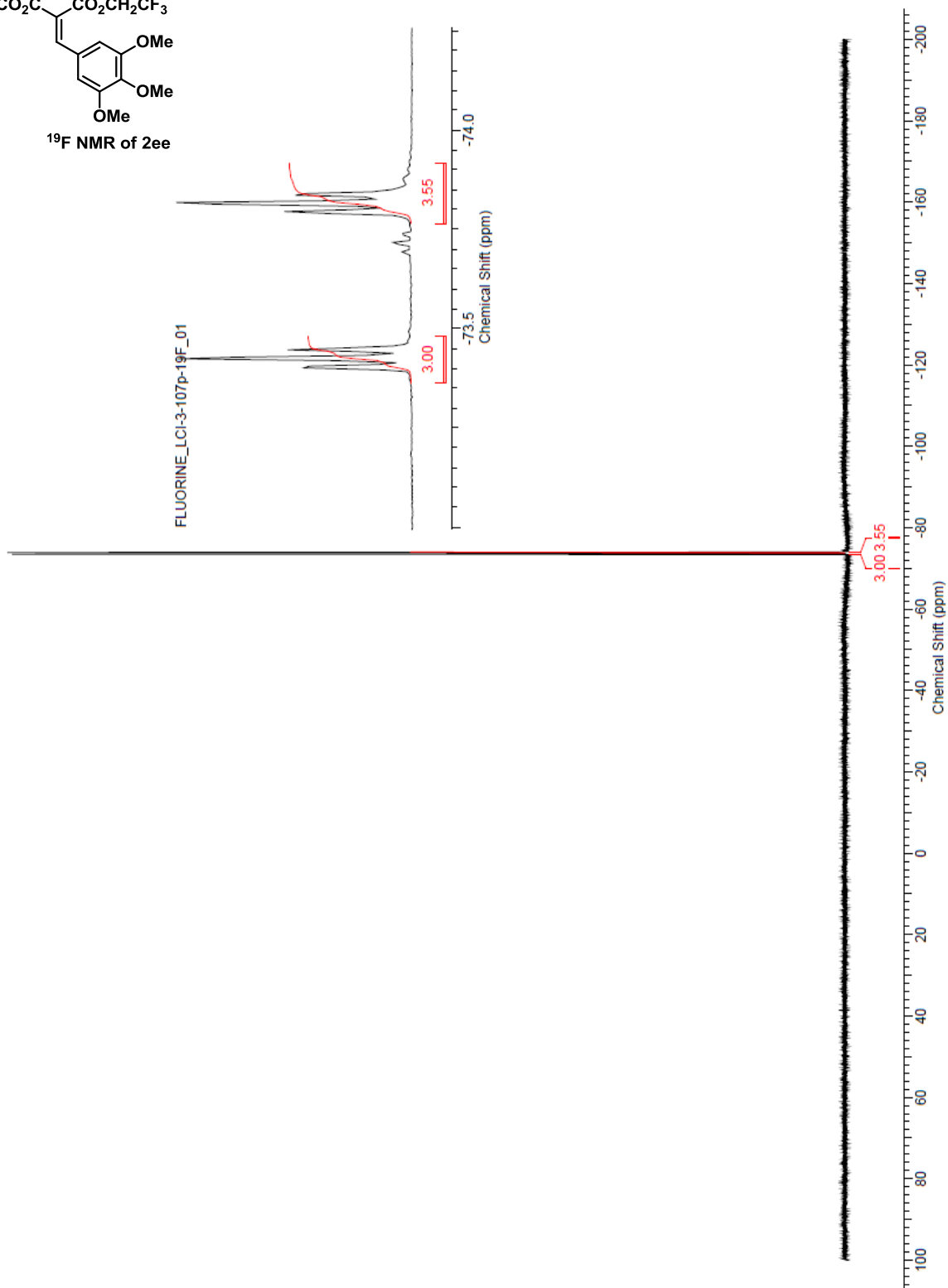
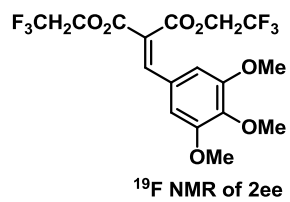


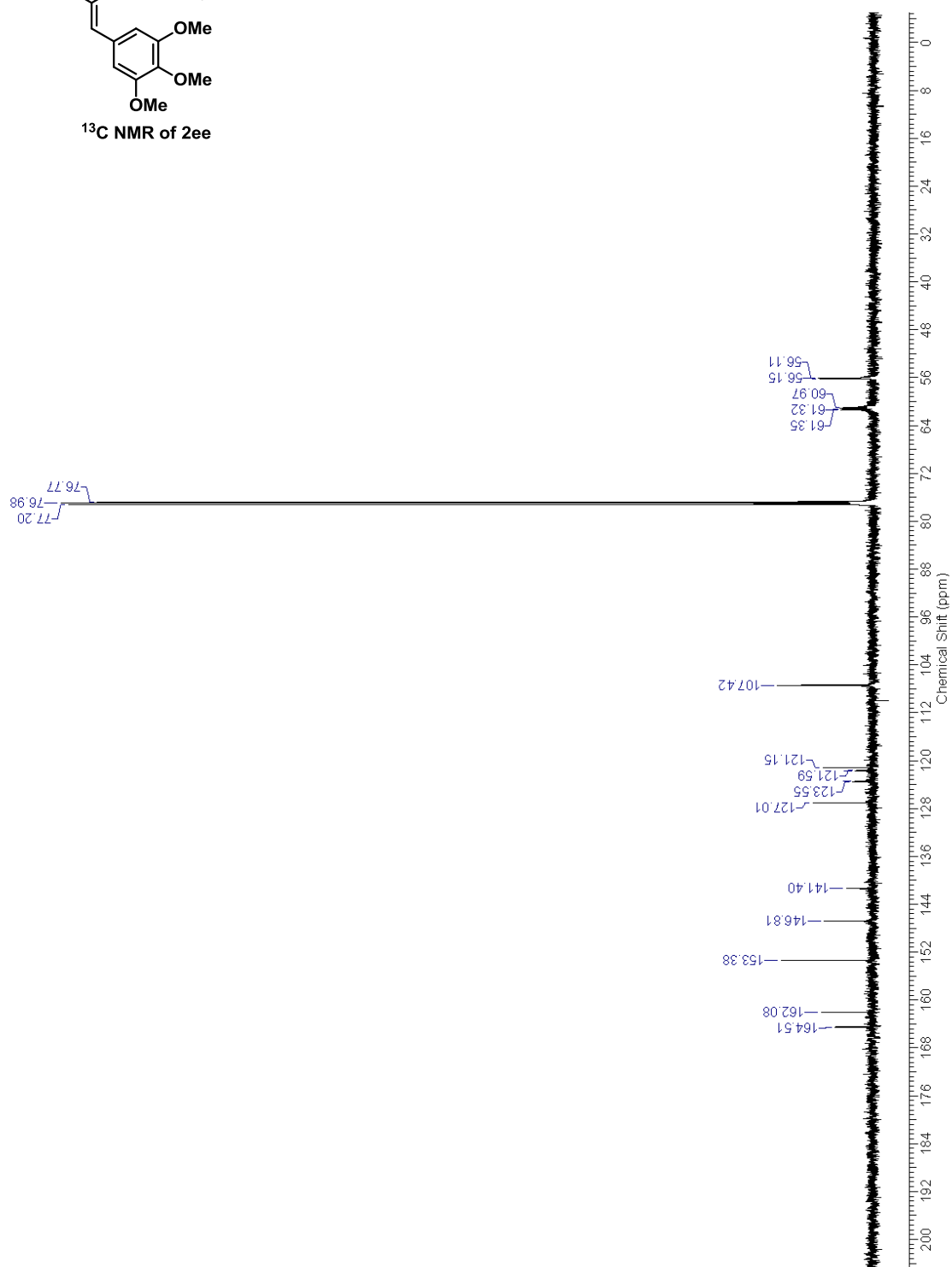
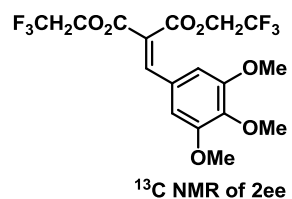


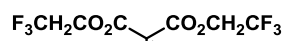




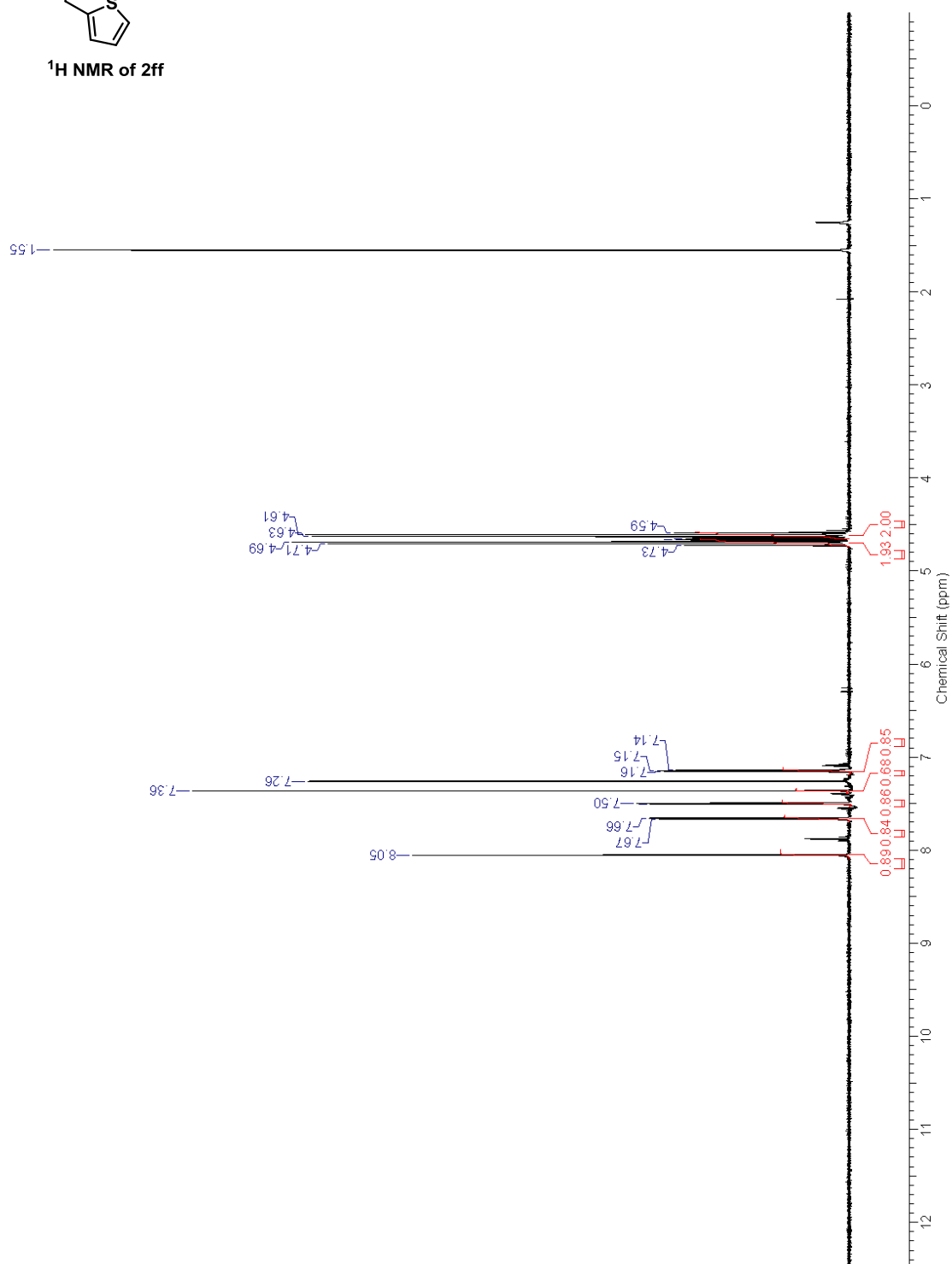


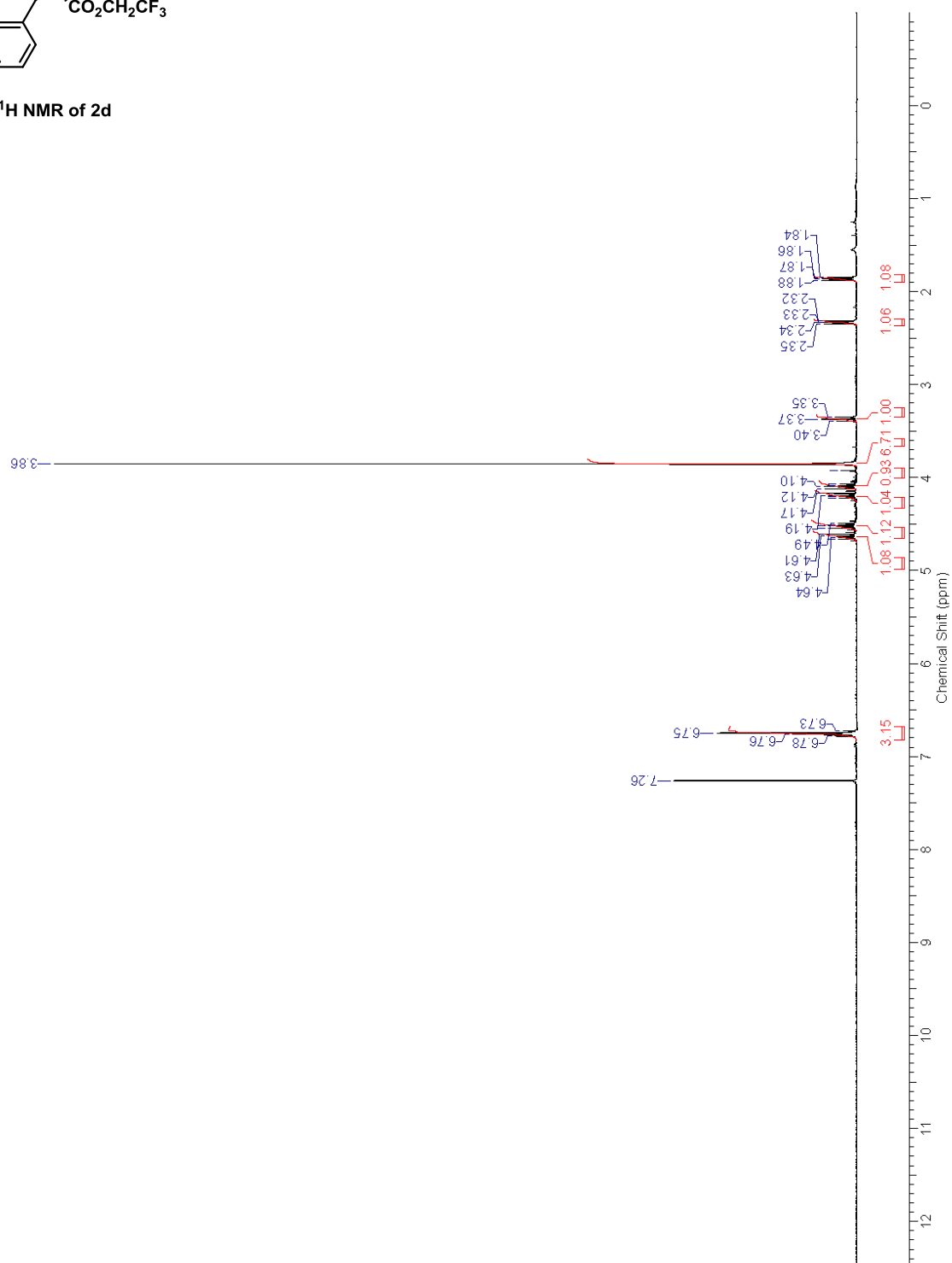
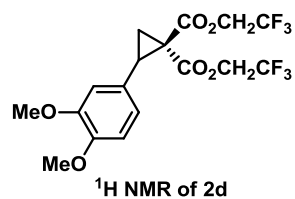




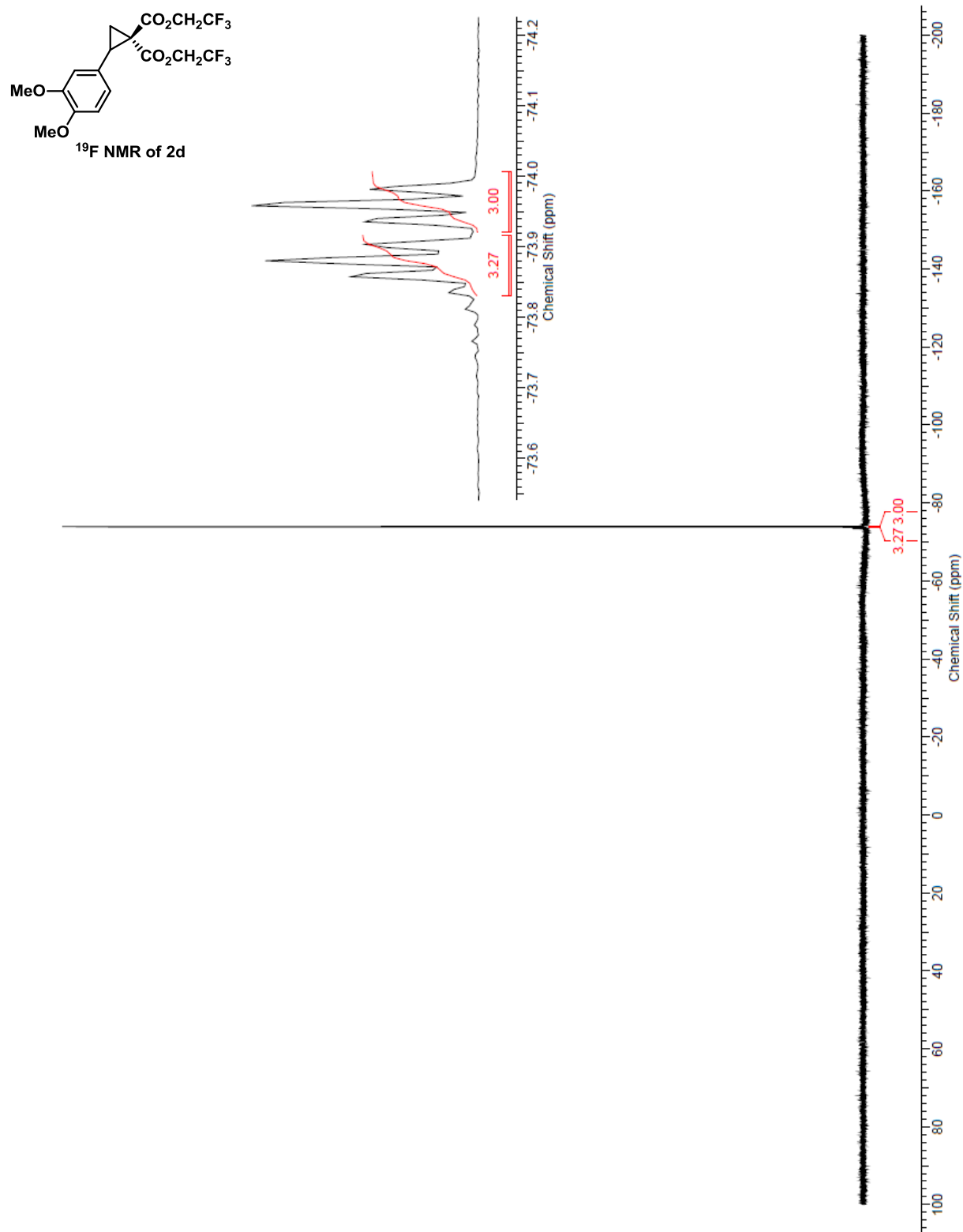


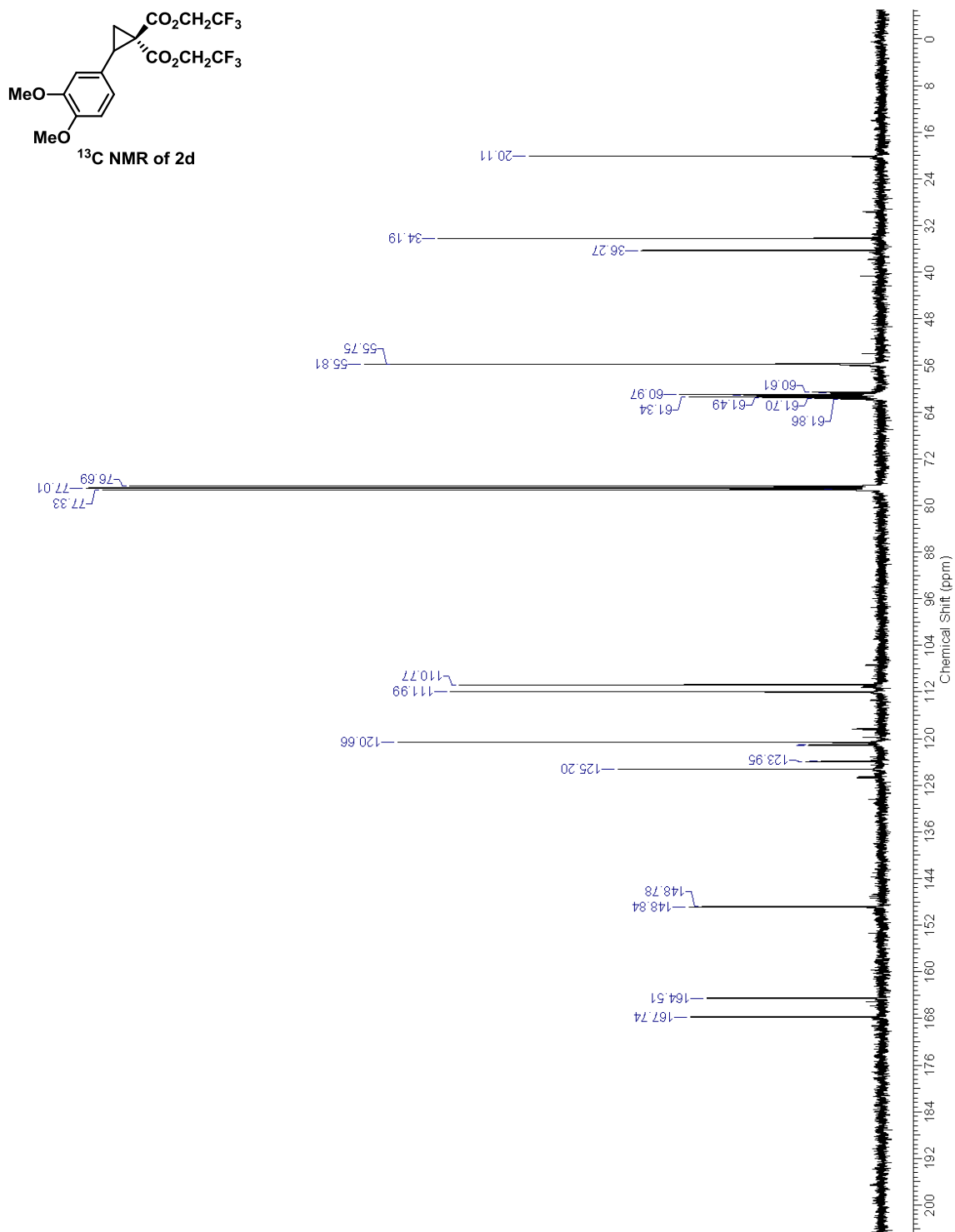
<sup>1</sup>H NMR of 2ff

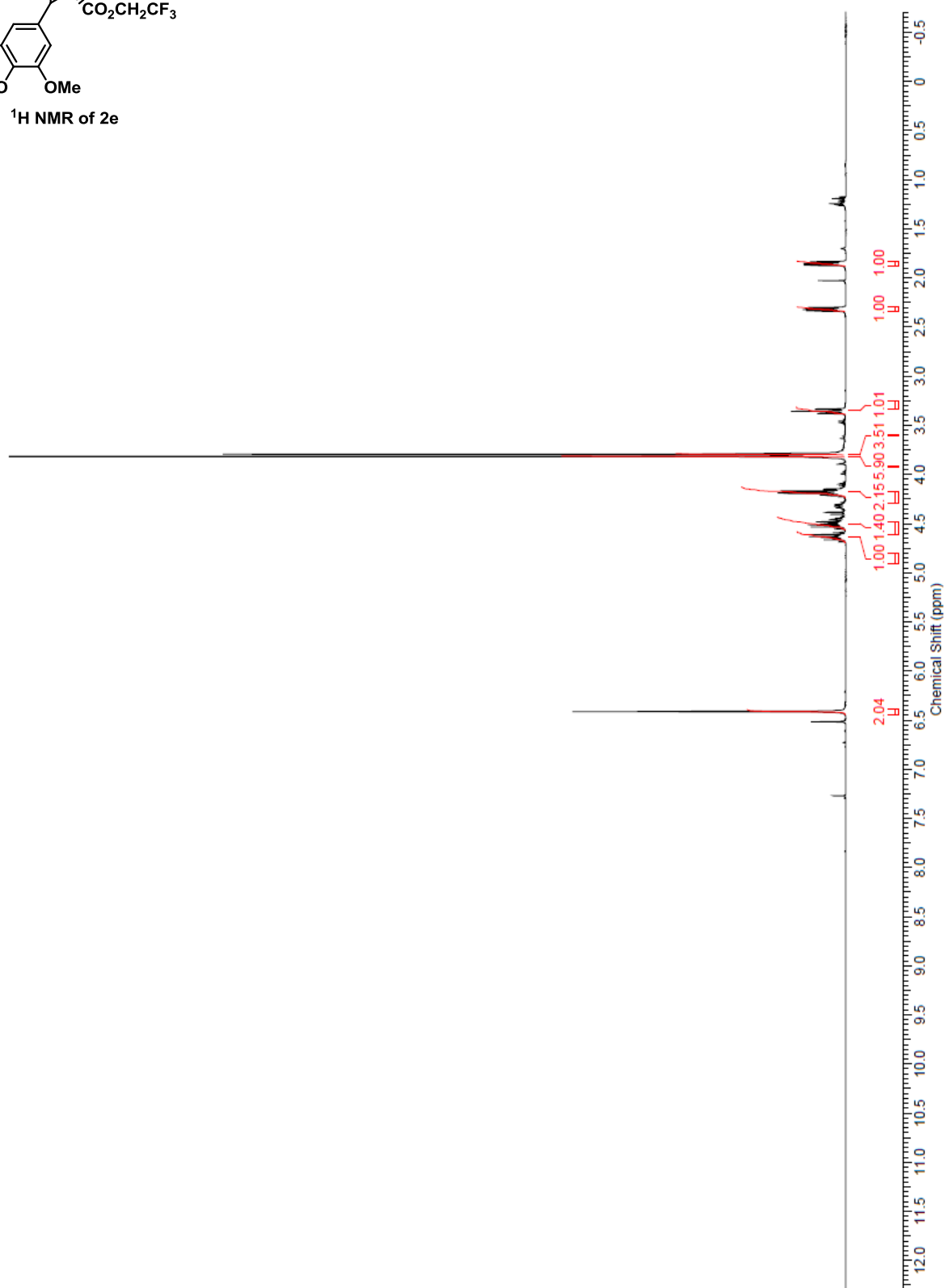
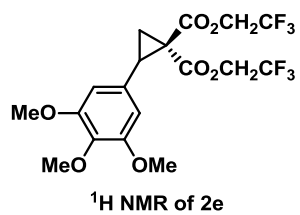


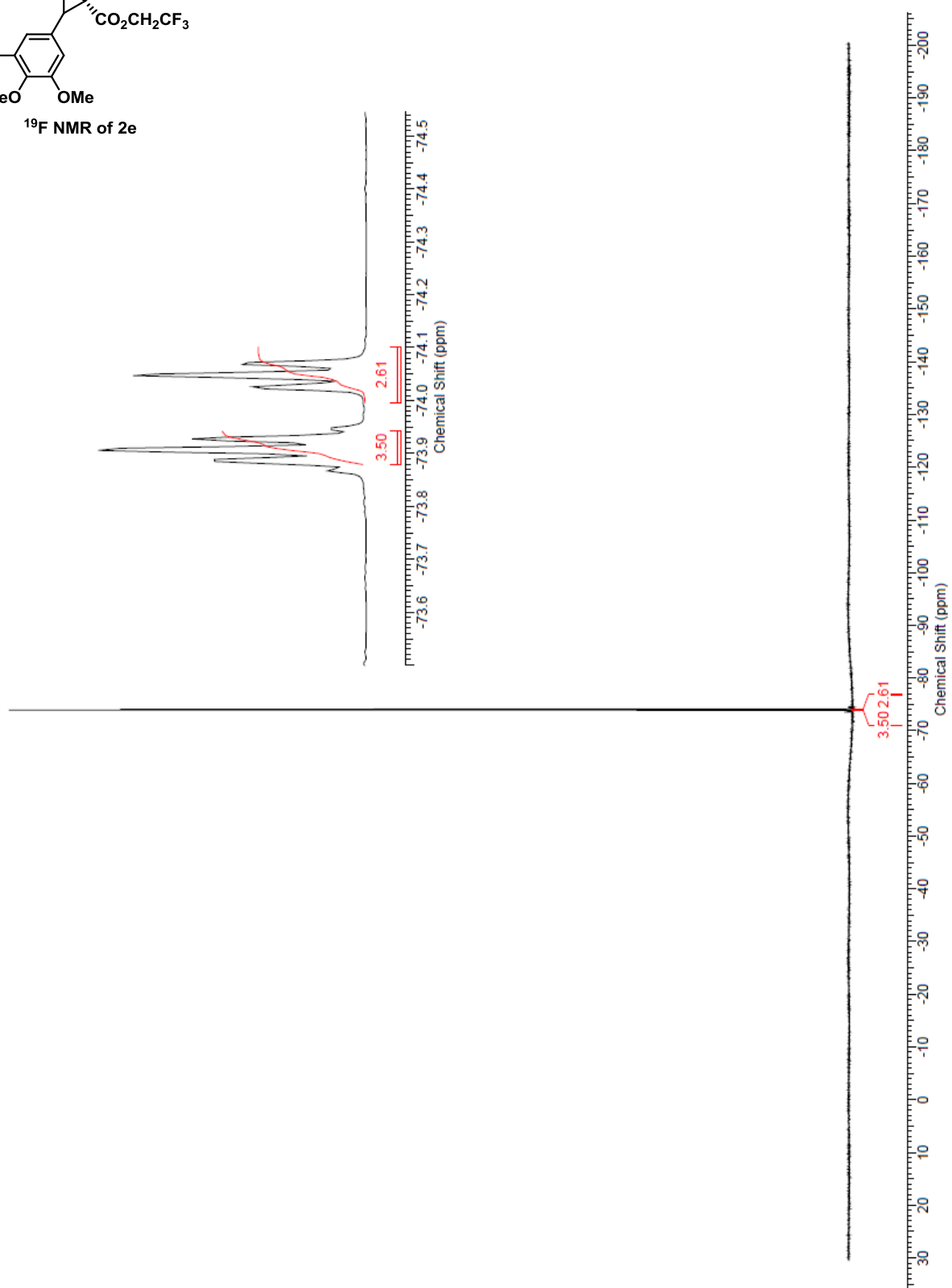
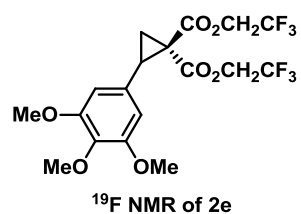


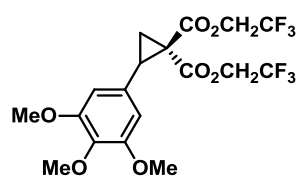




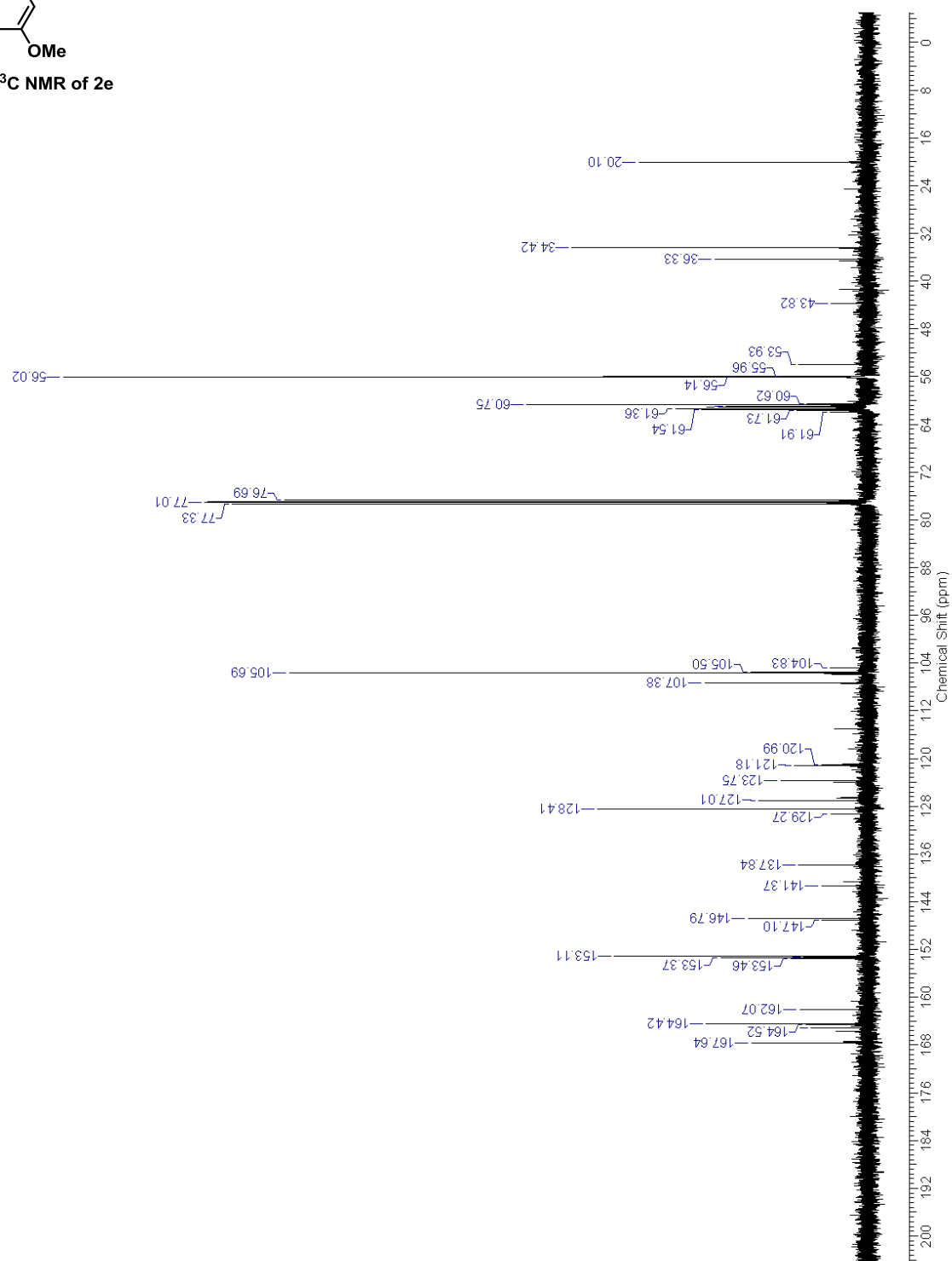


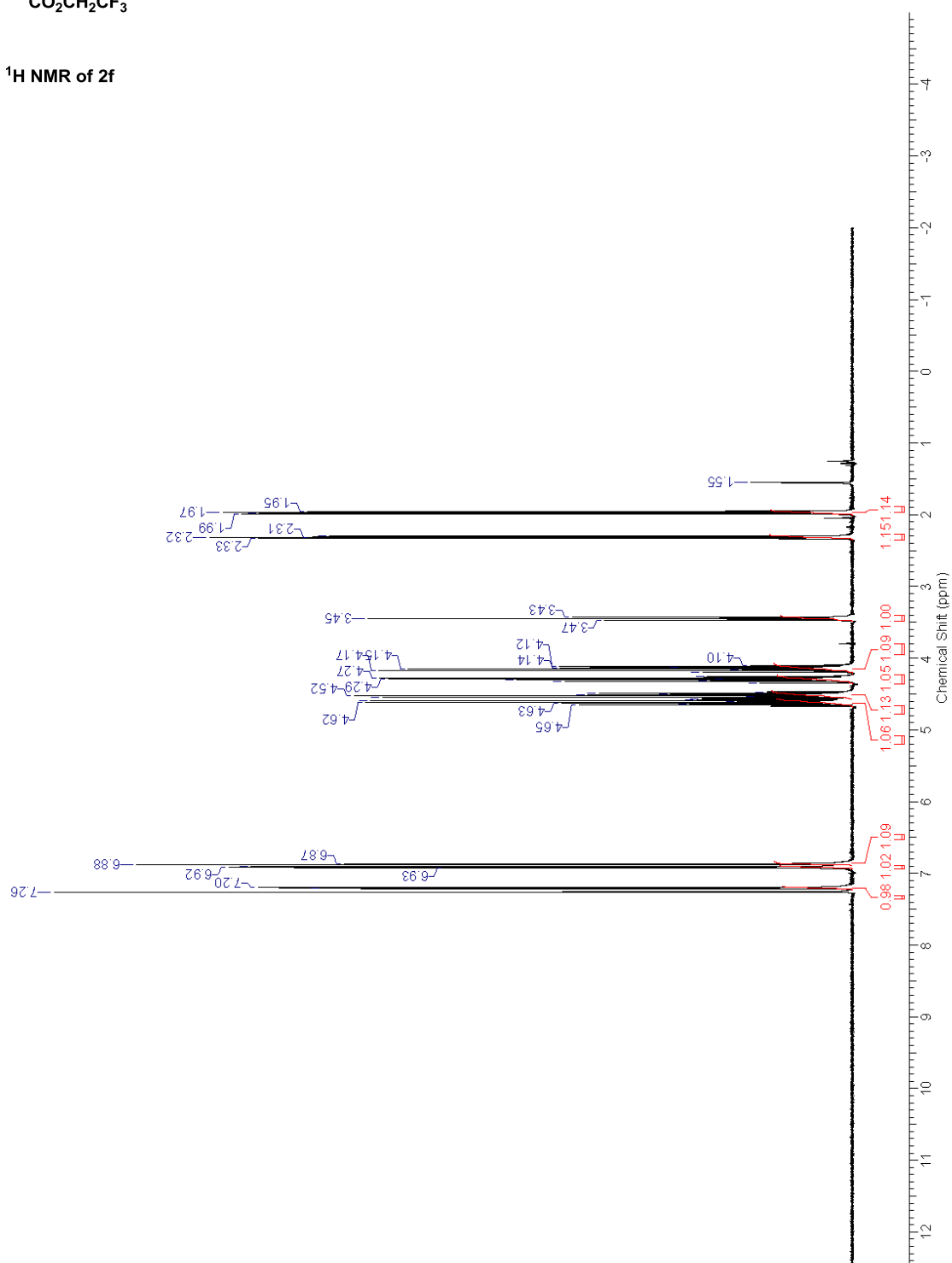
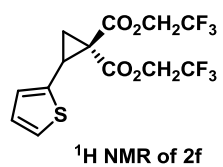


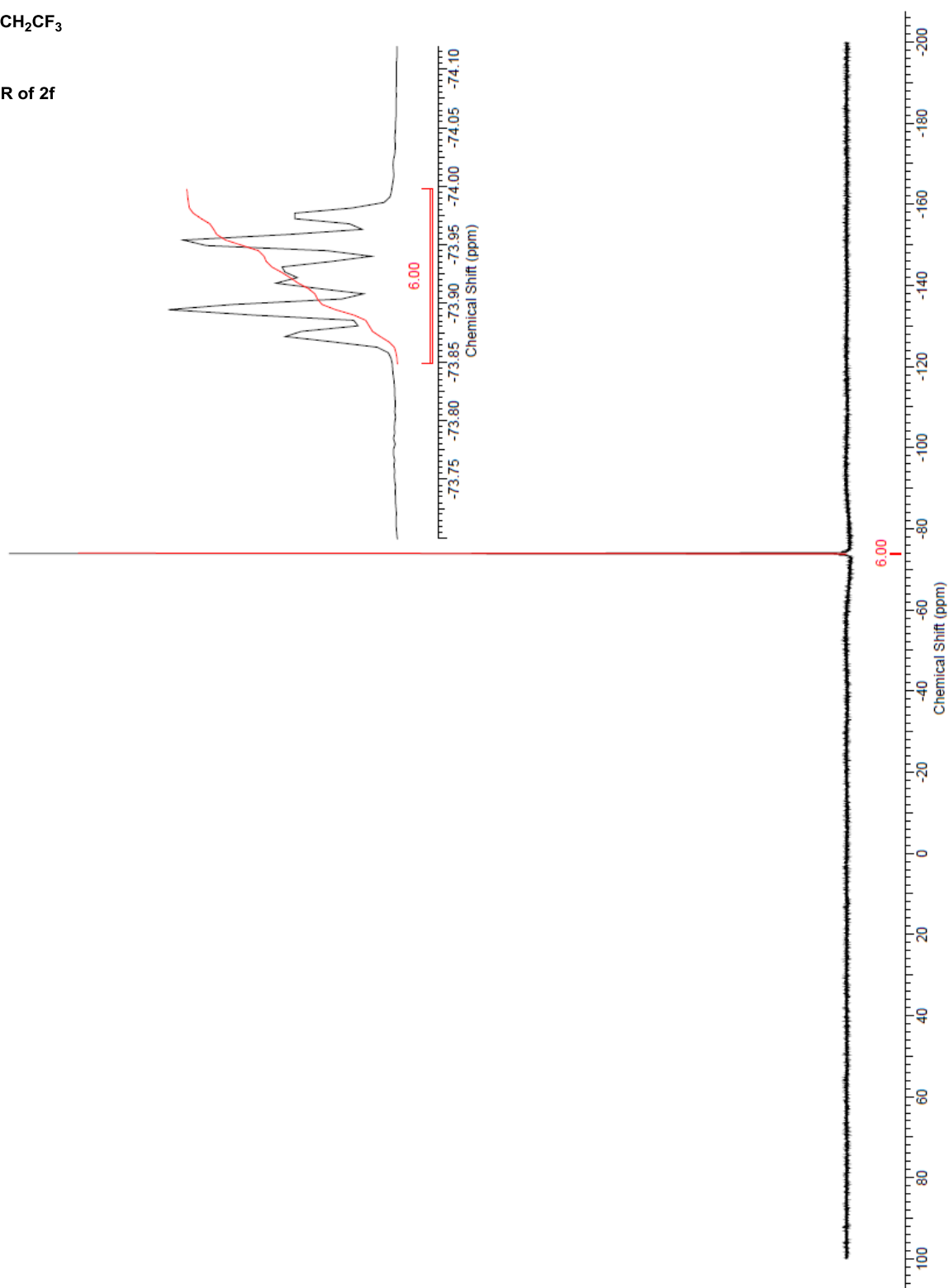
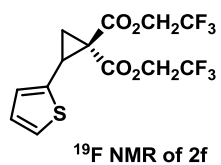


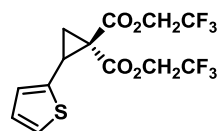


$^{13}\text{C}$  NMR of 2e

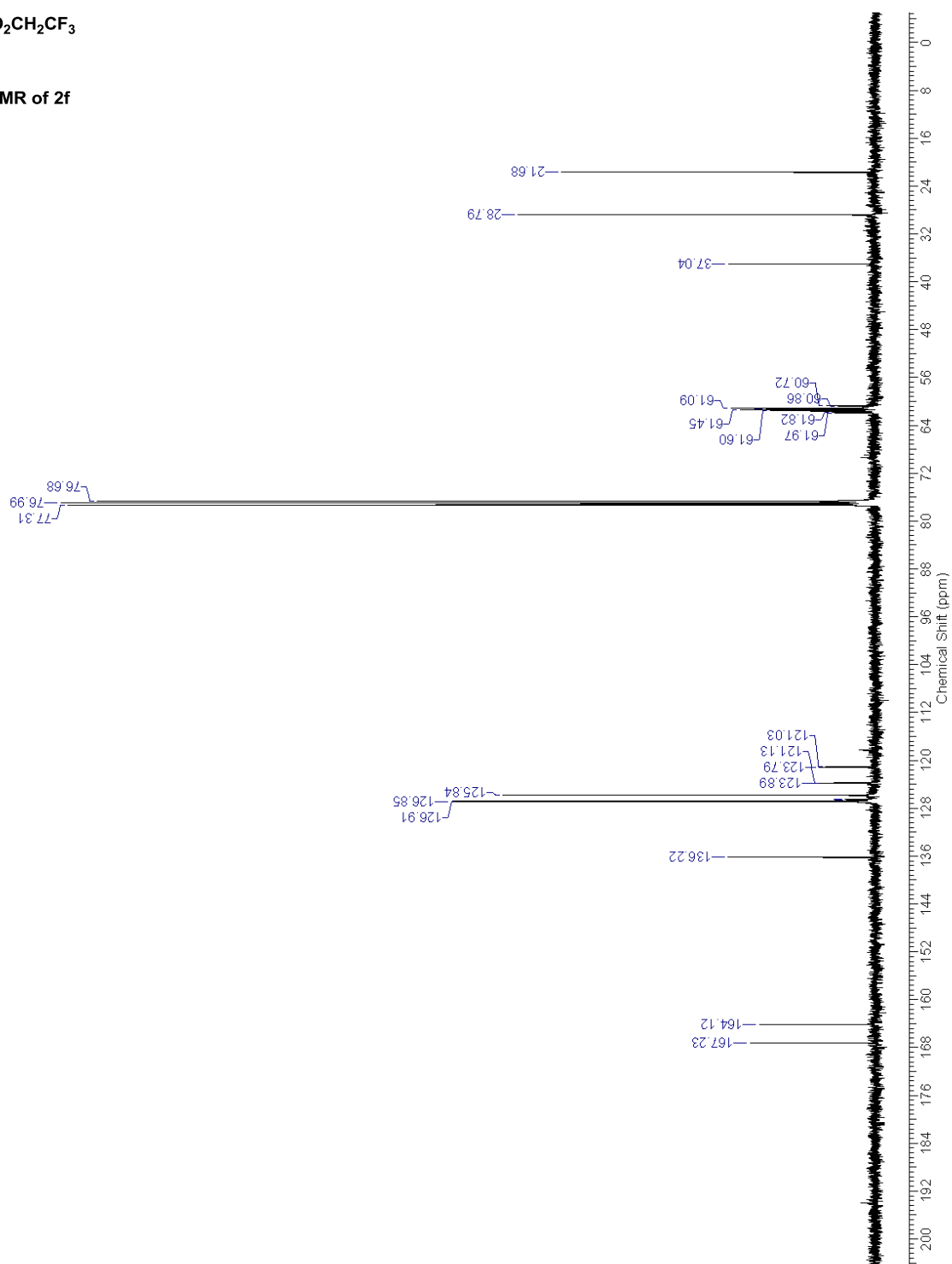




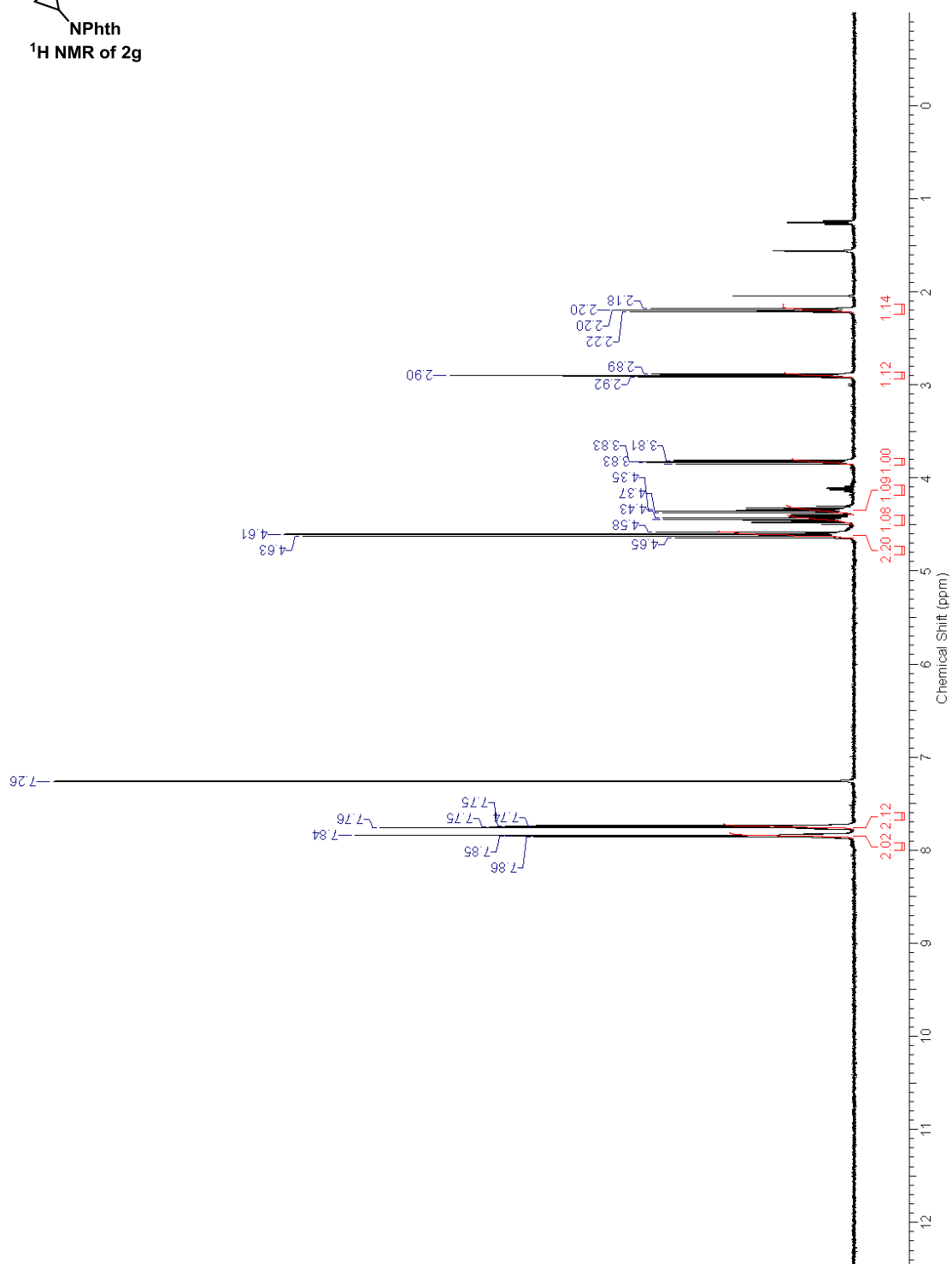
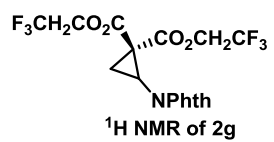


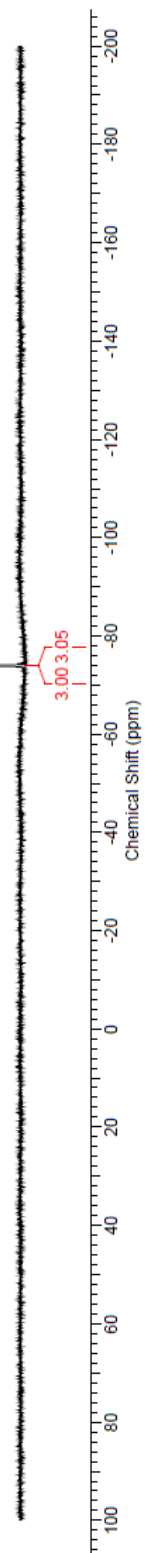
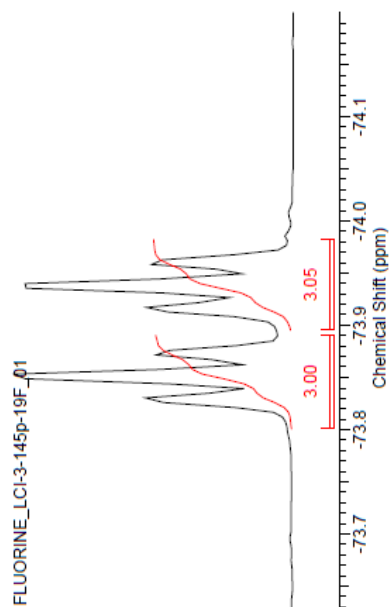
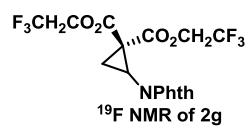


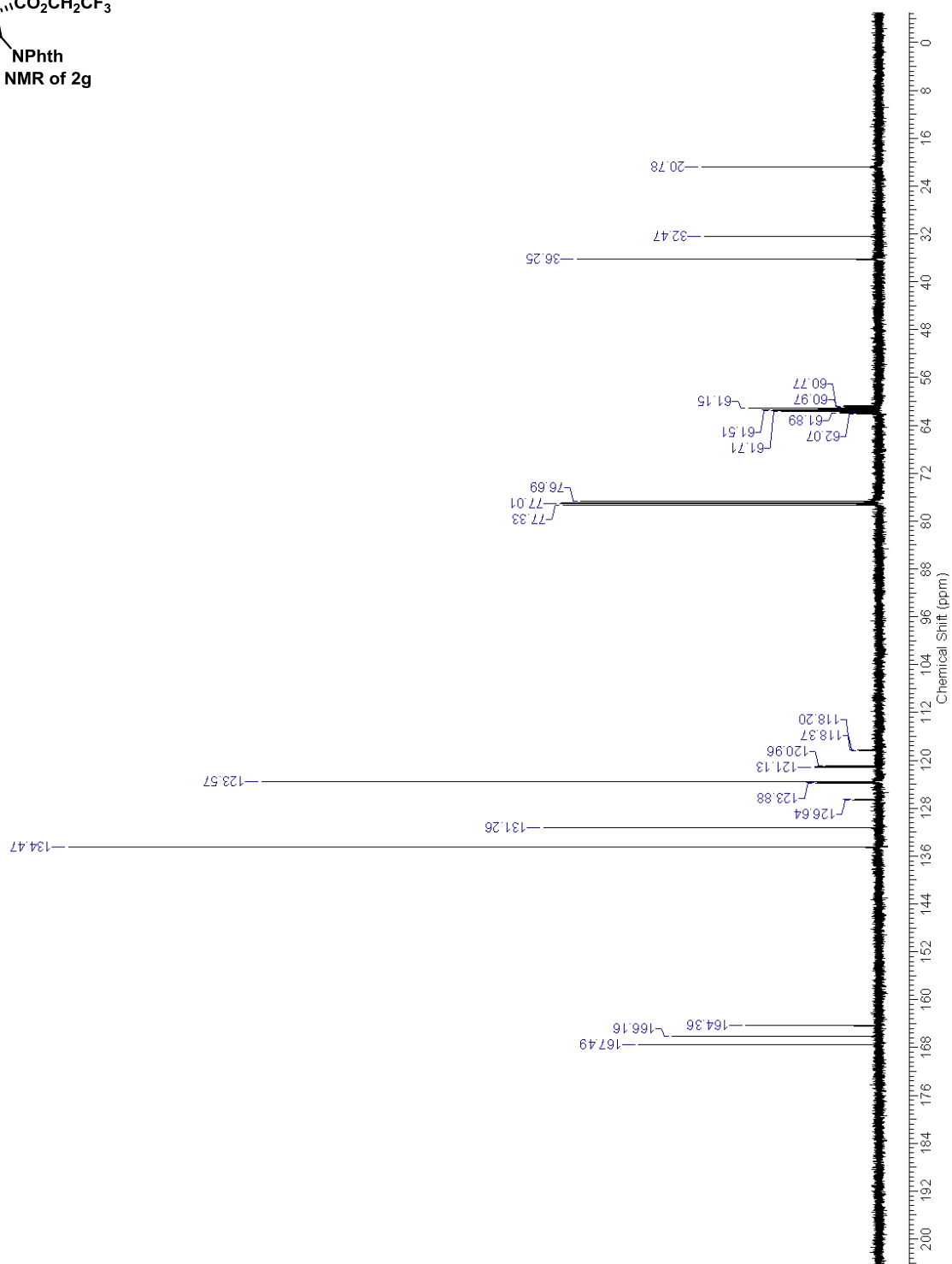
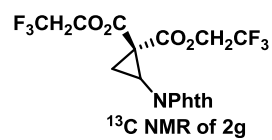
$^{13}\text{C}$  NMR of 2f

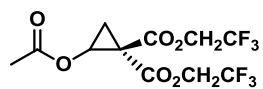




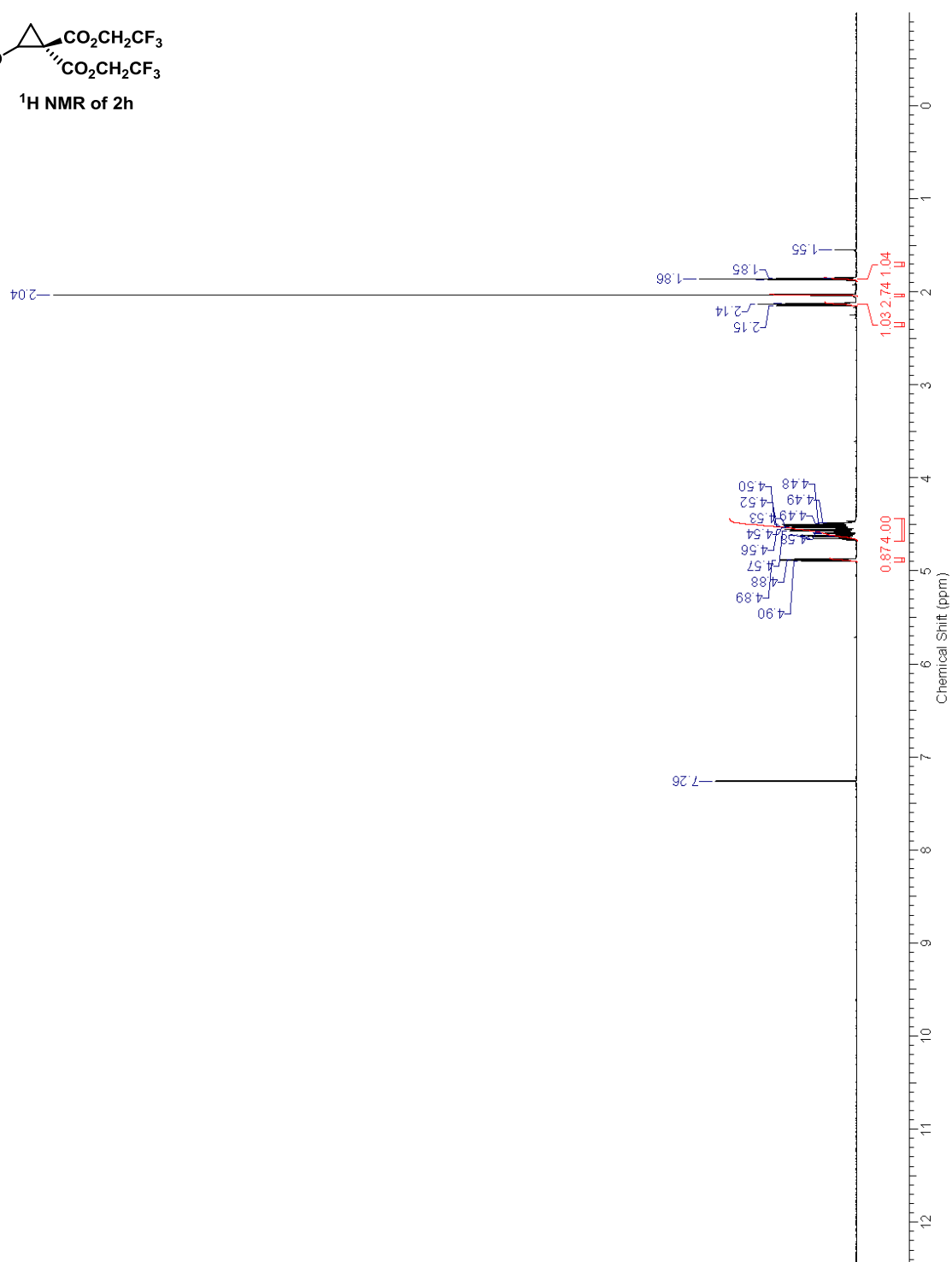


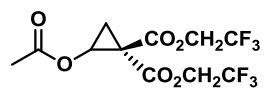




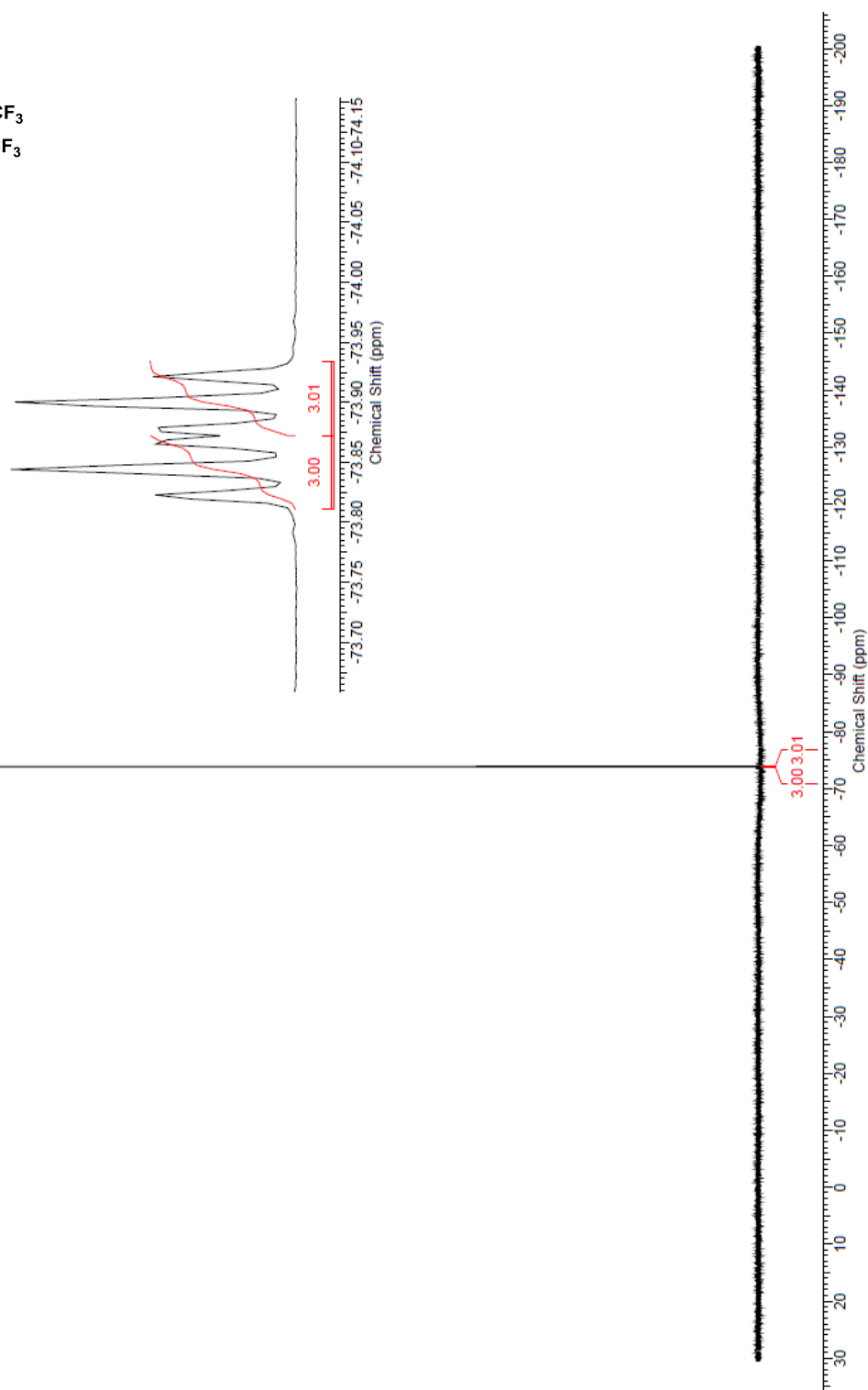


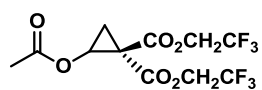
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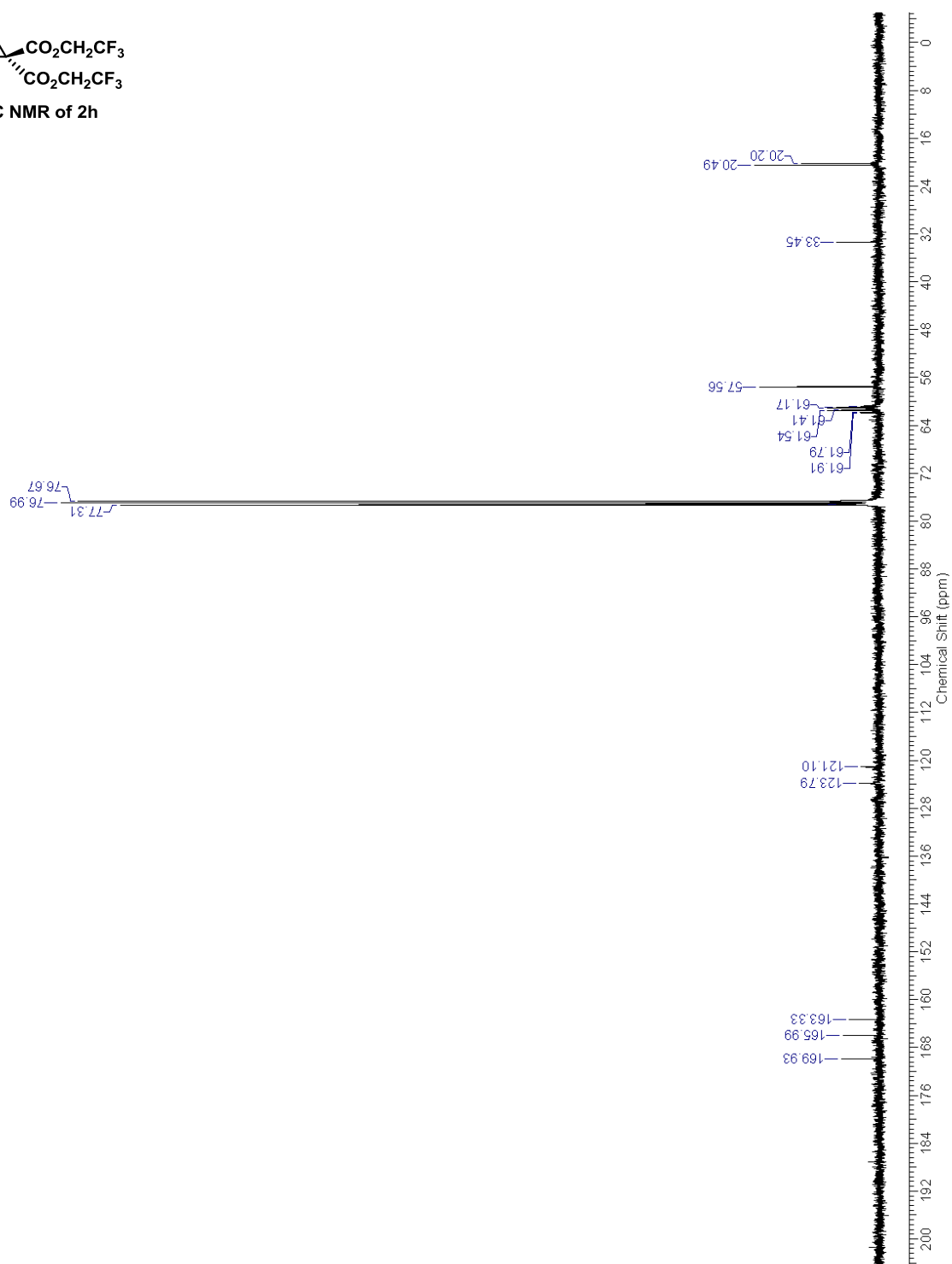


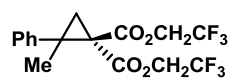
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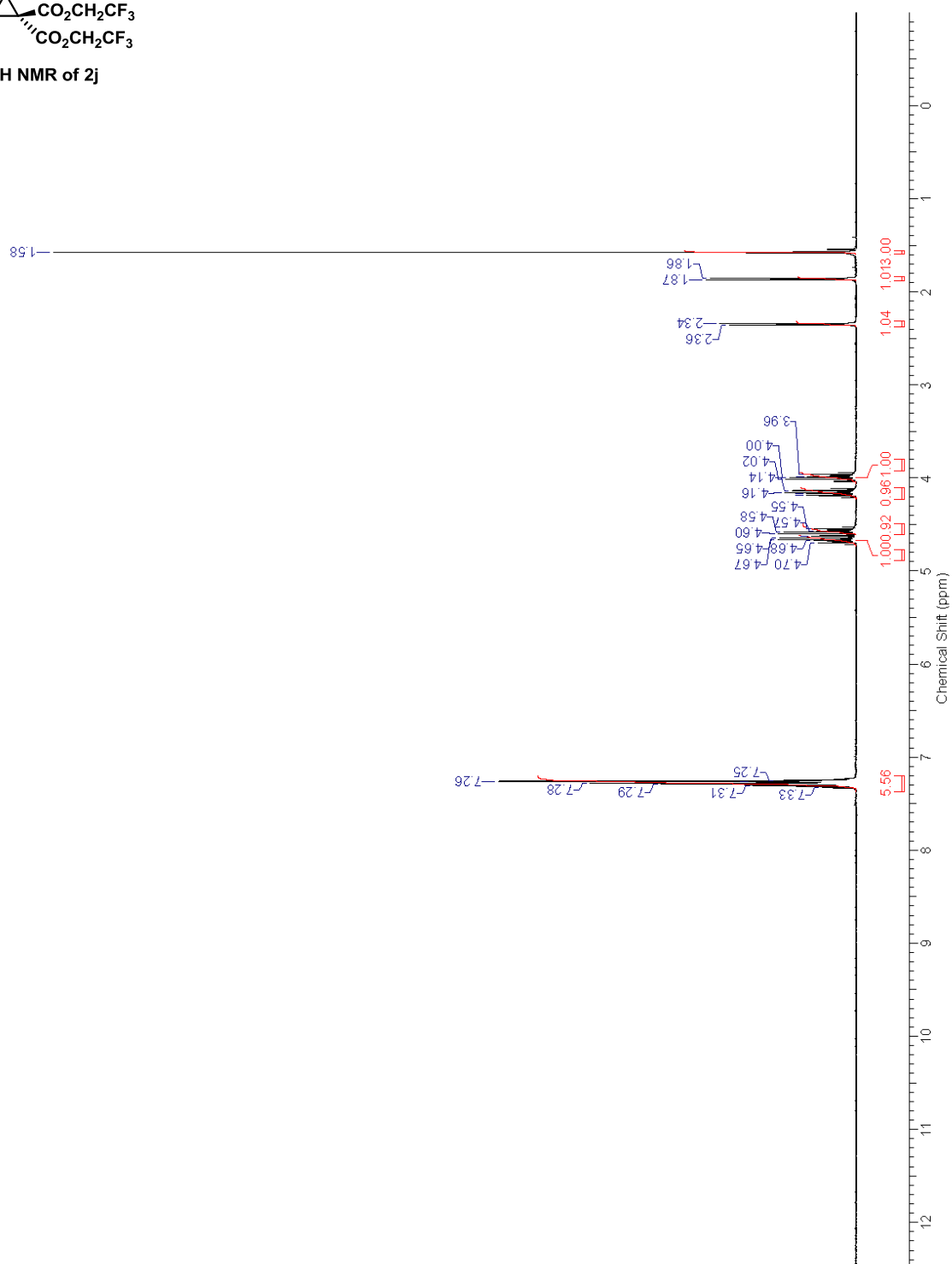


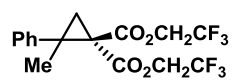
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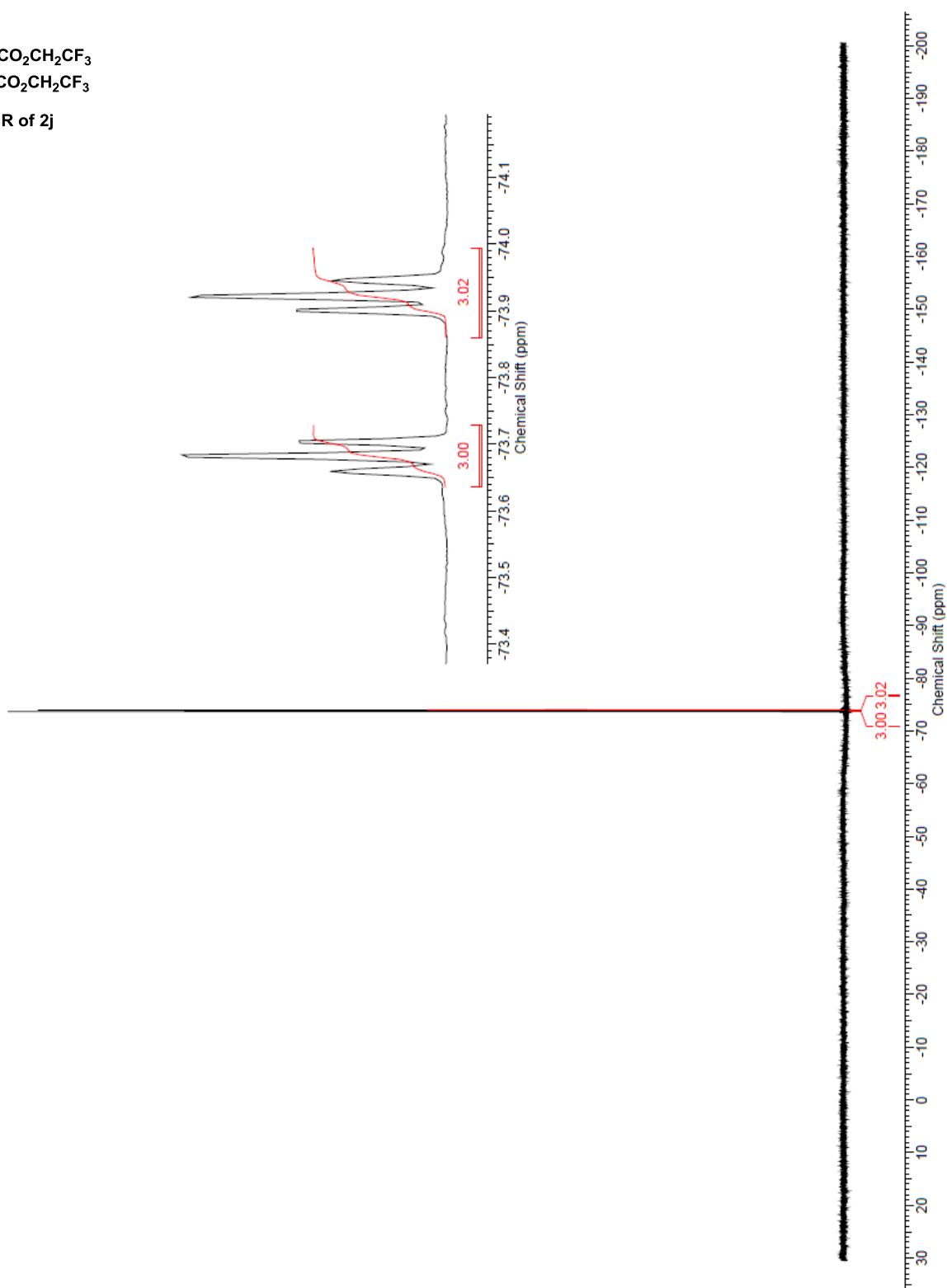


<sup>1</sup>H NMR of 2j

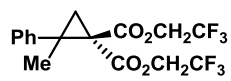




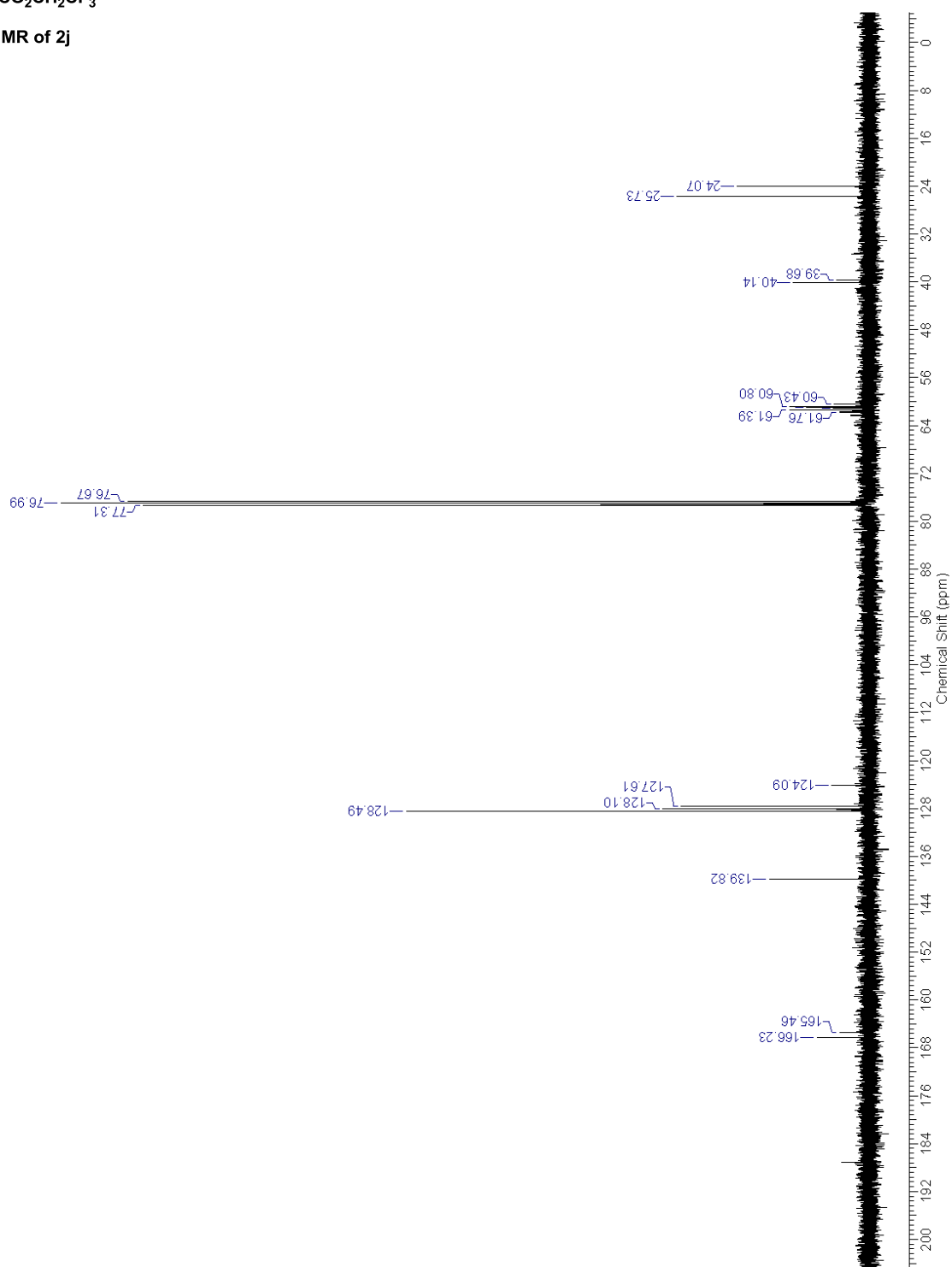
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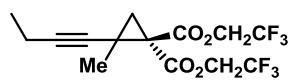




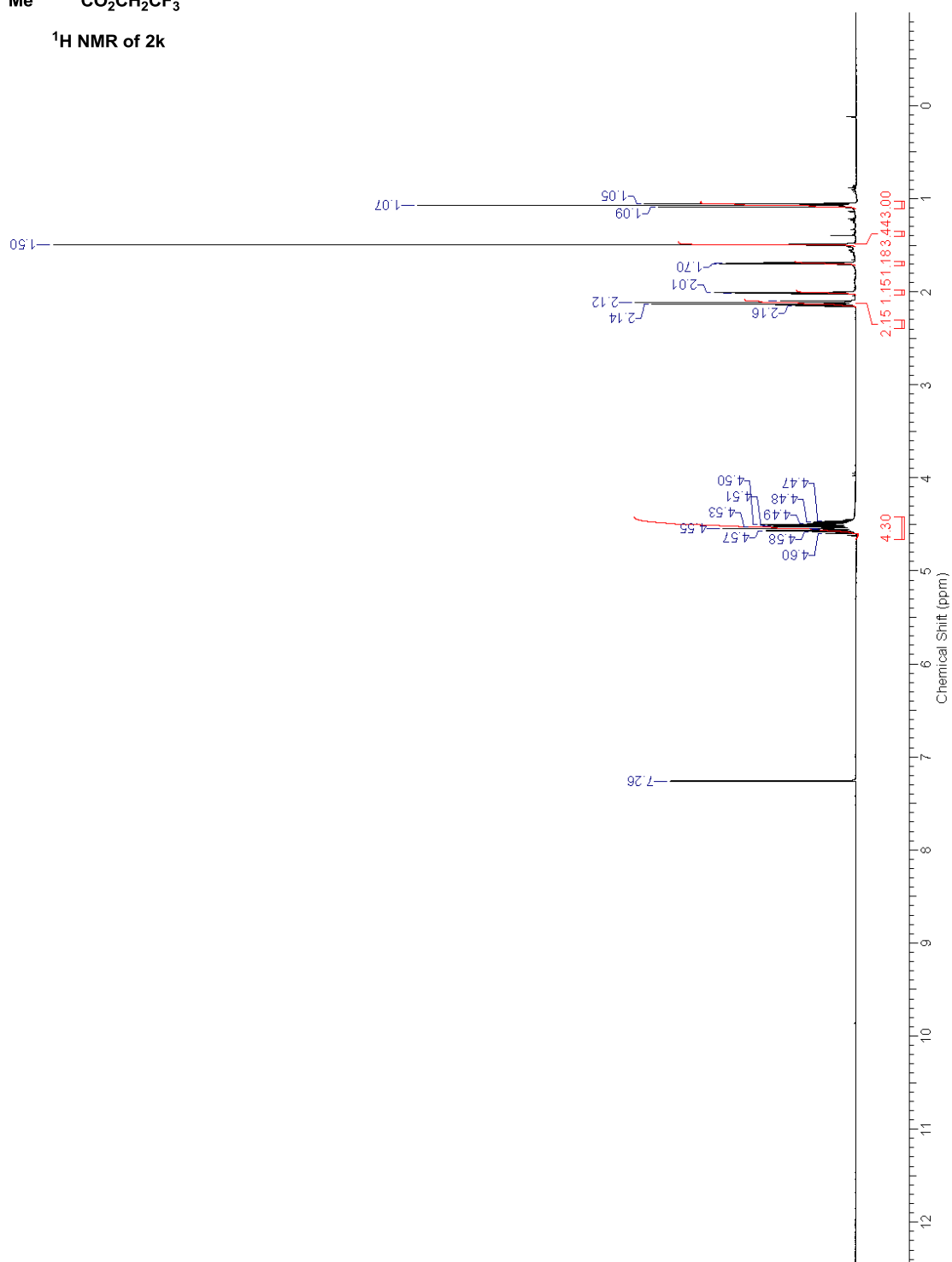


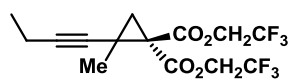
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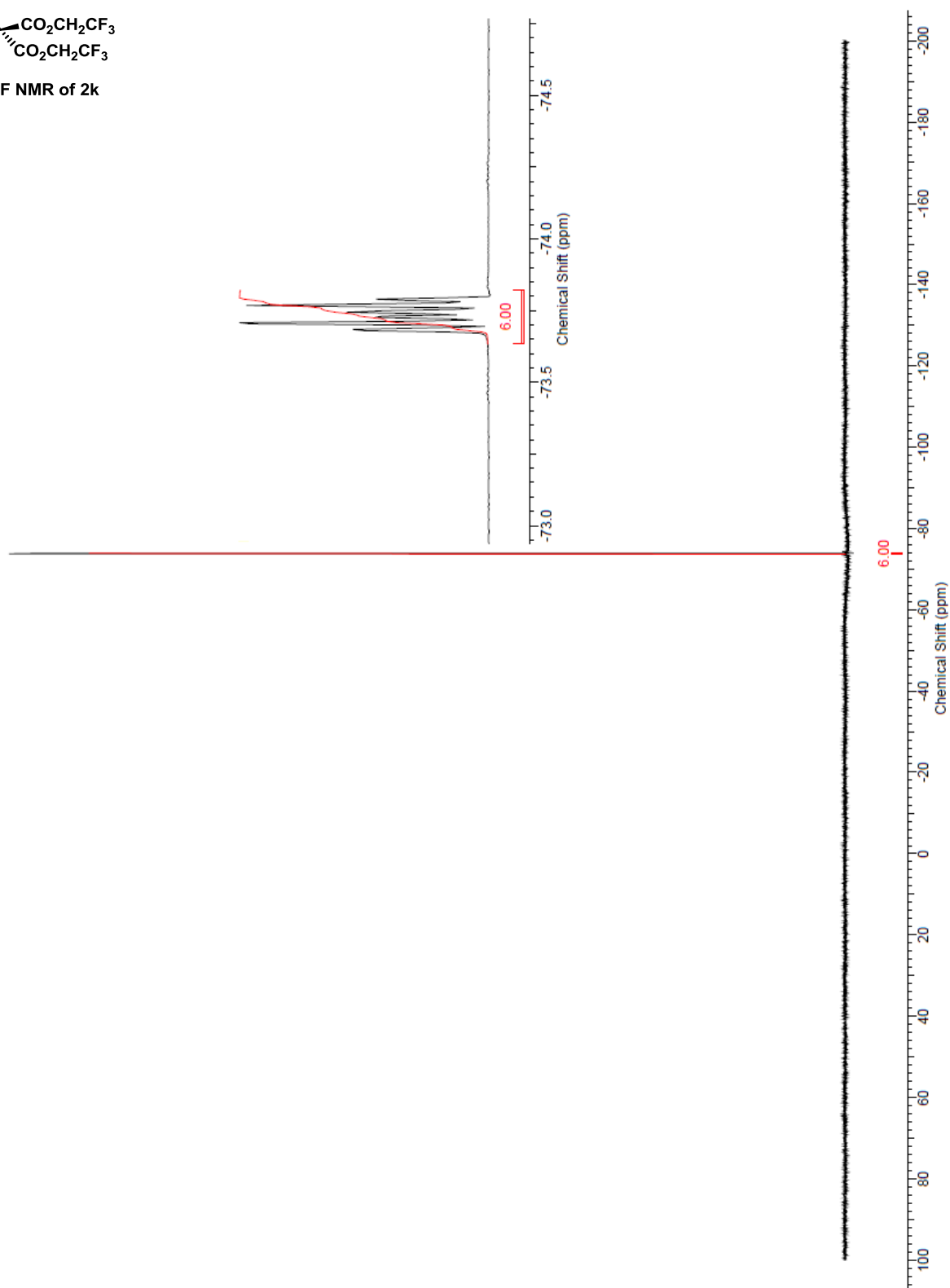


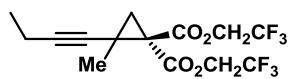
$^1\text{H}$  NMR of 2k



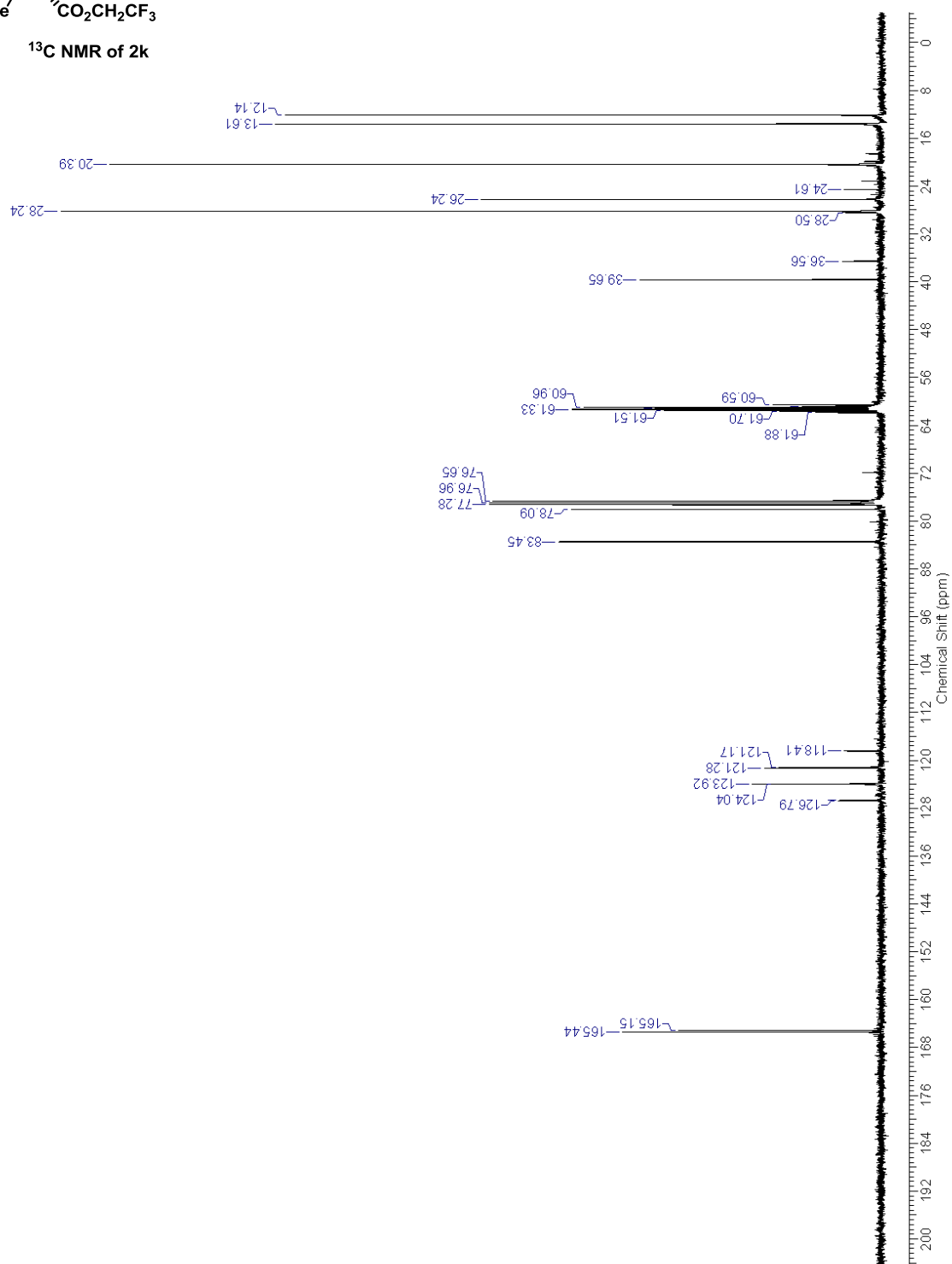


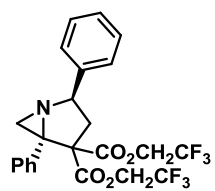
$^{19}\text{F}$  NMR of 2k



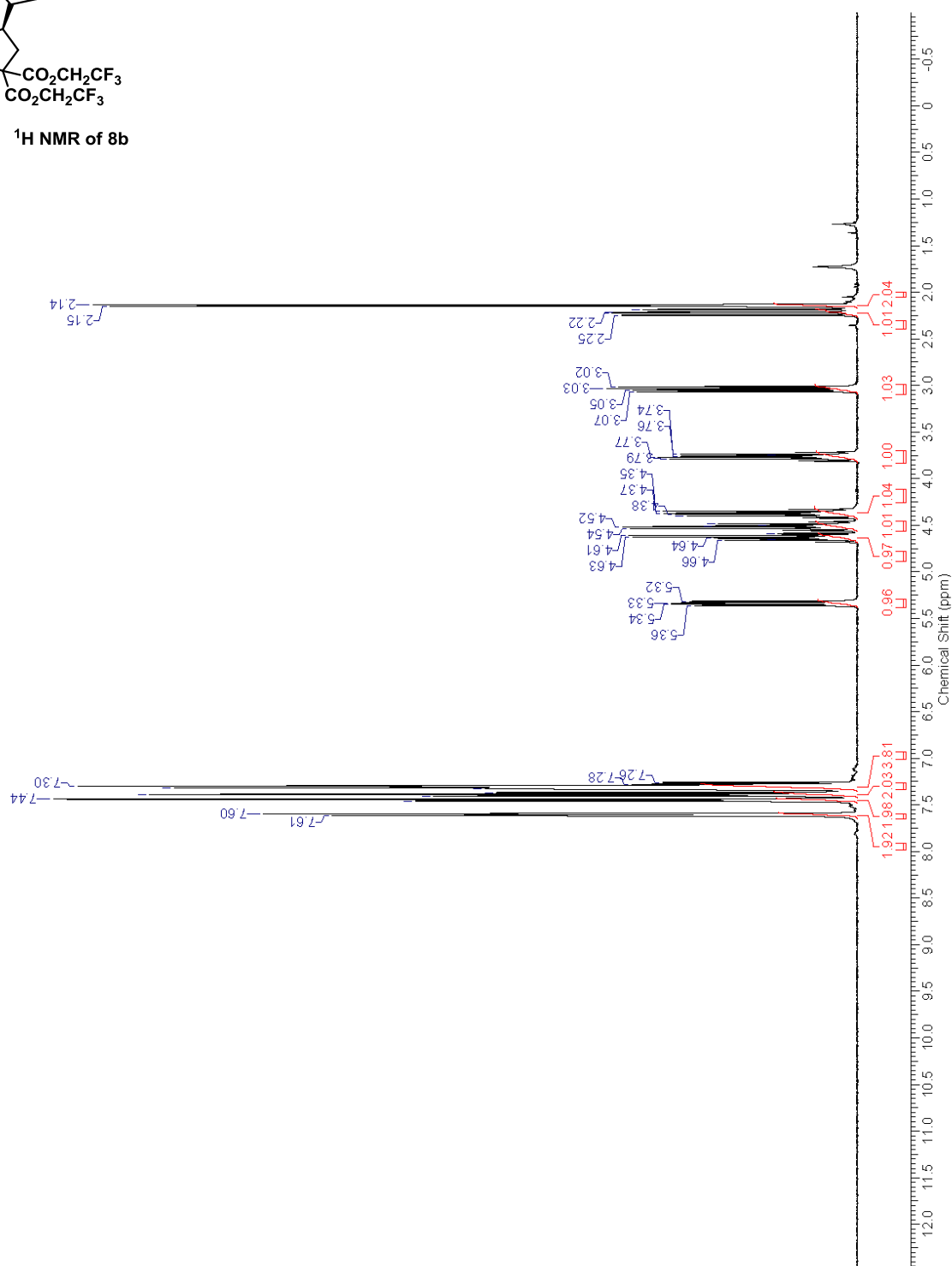


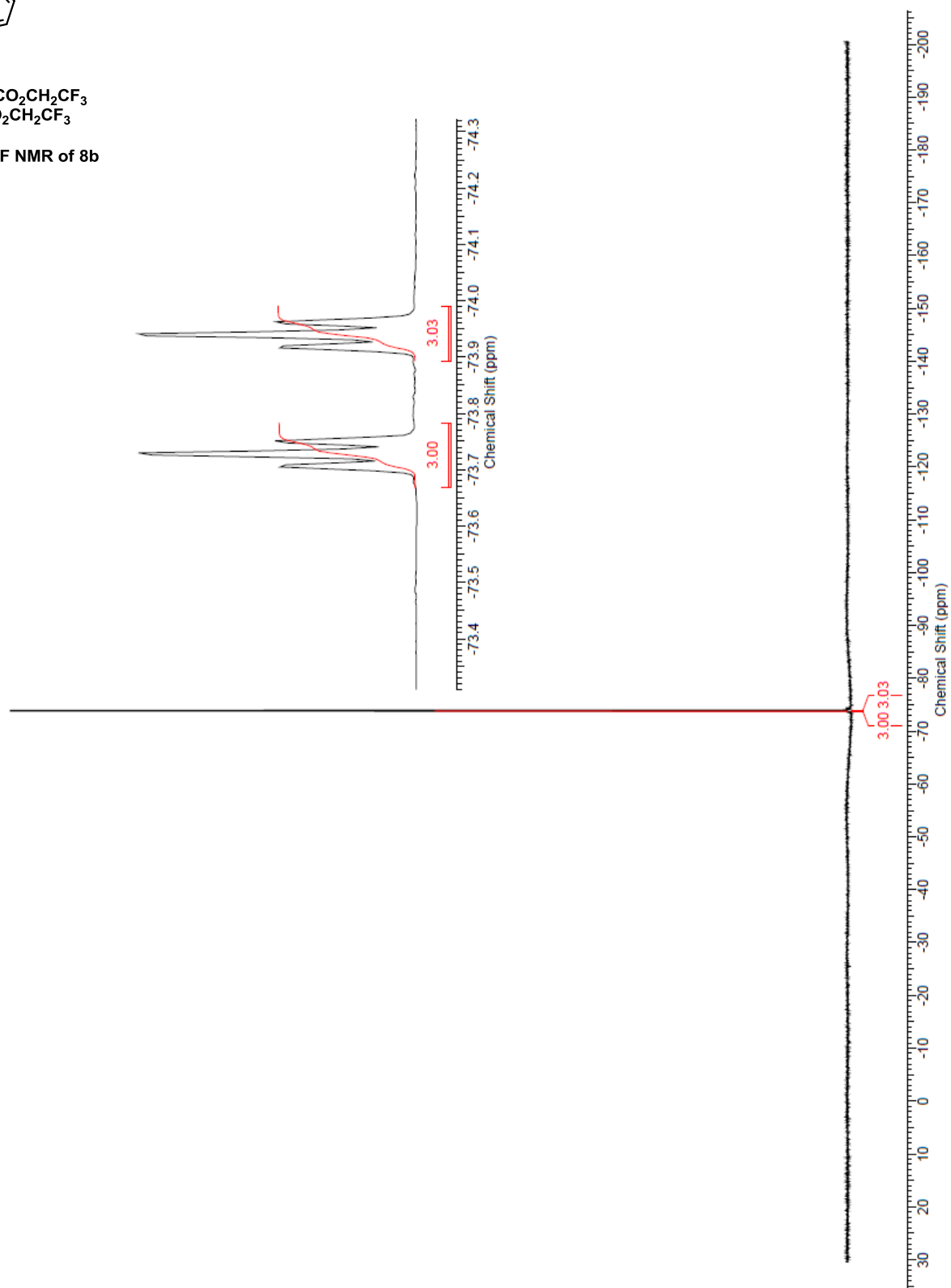
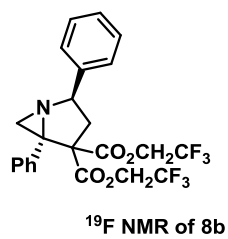
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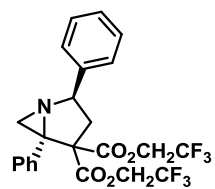




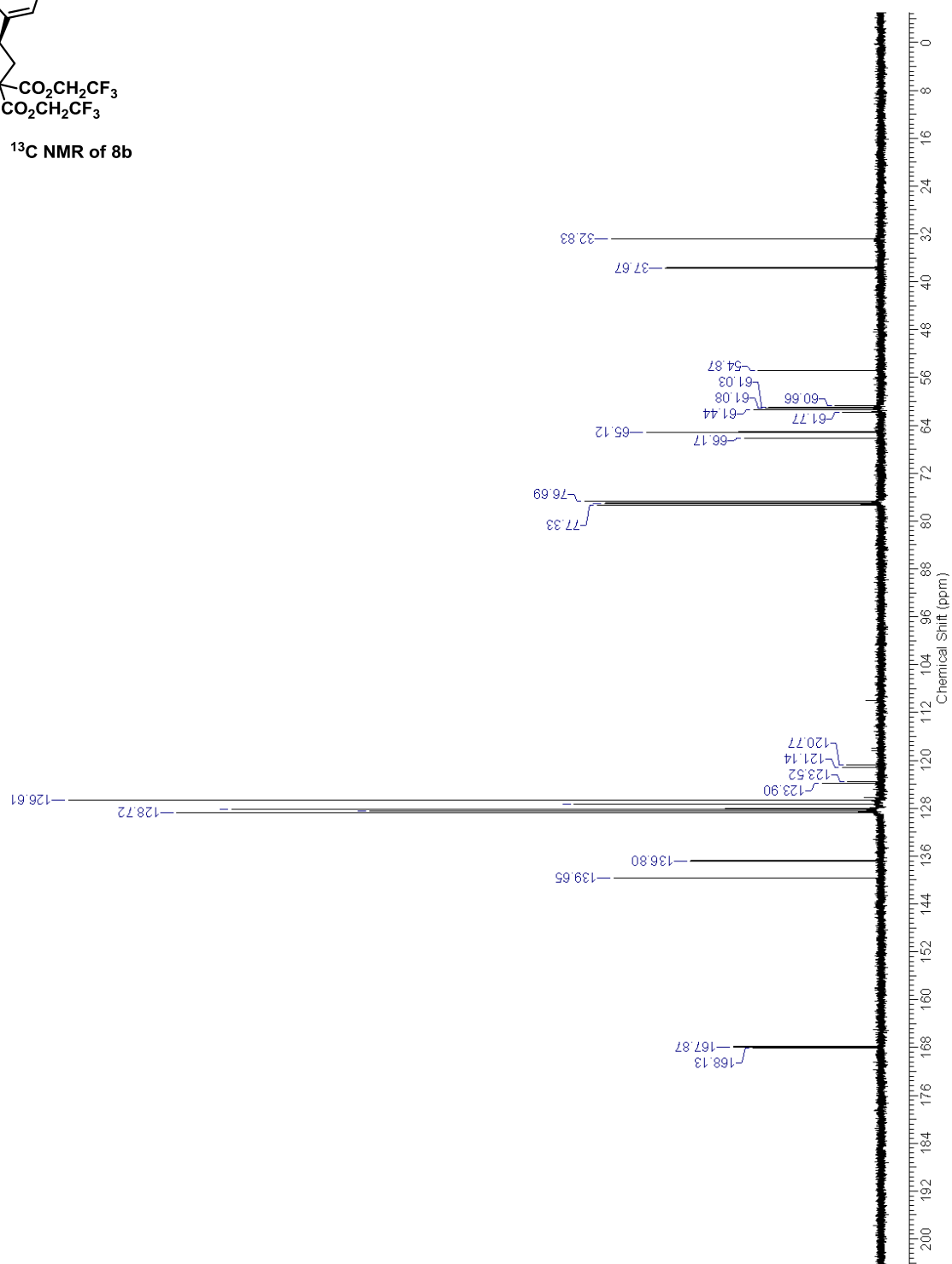
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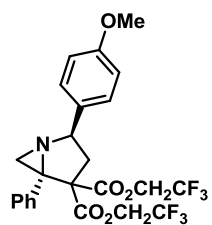




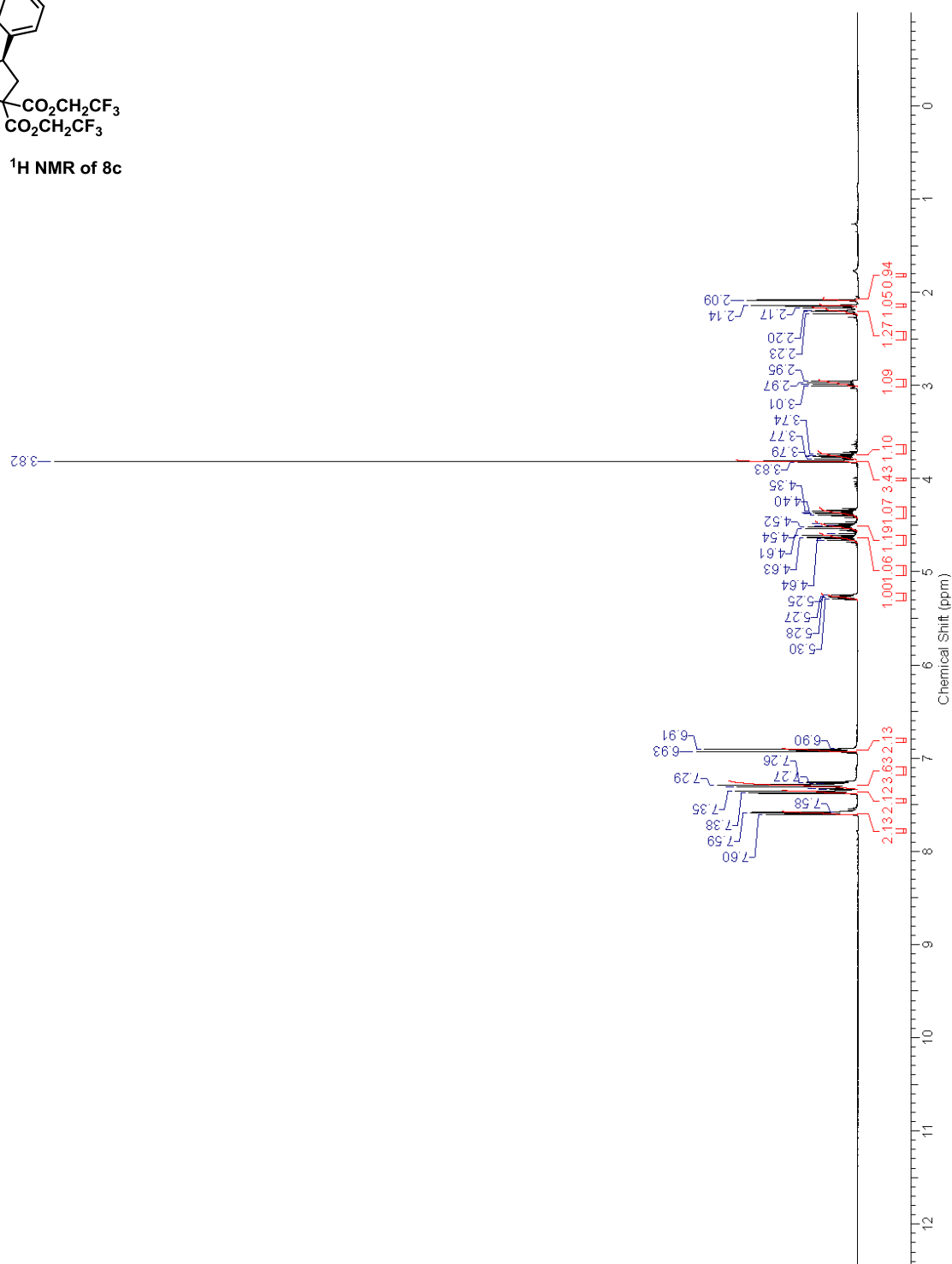


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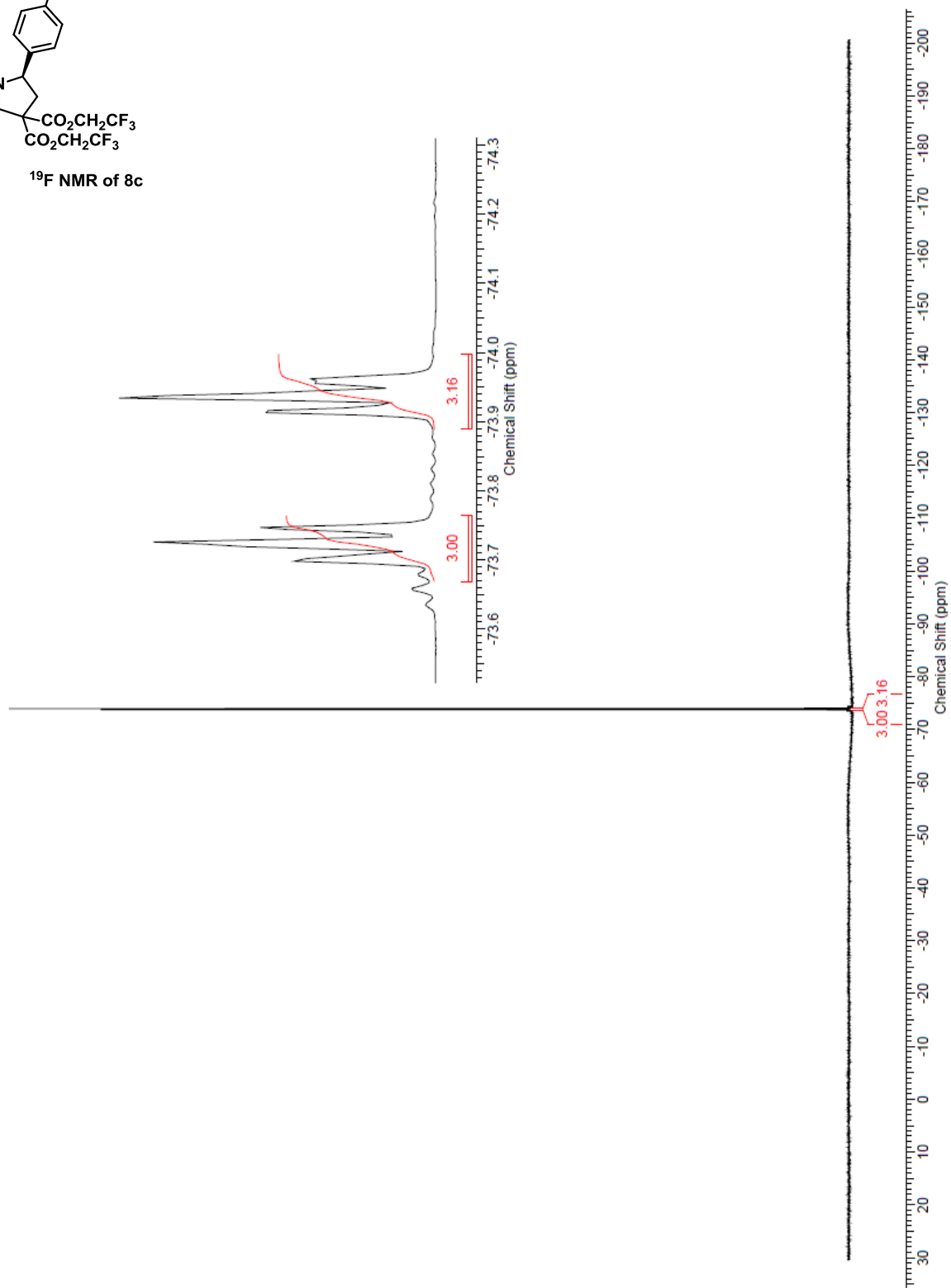
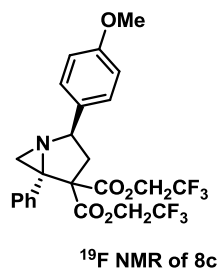


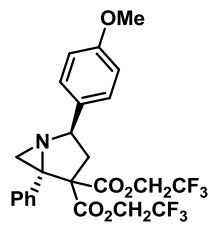


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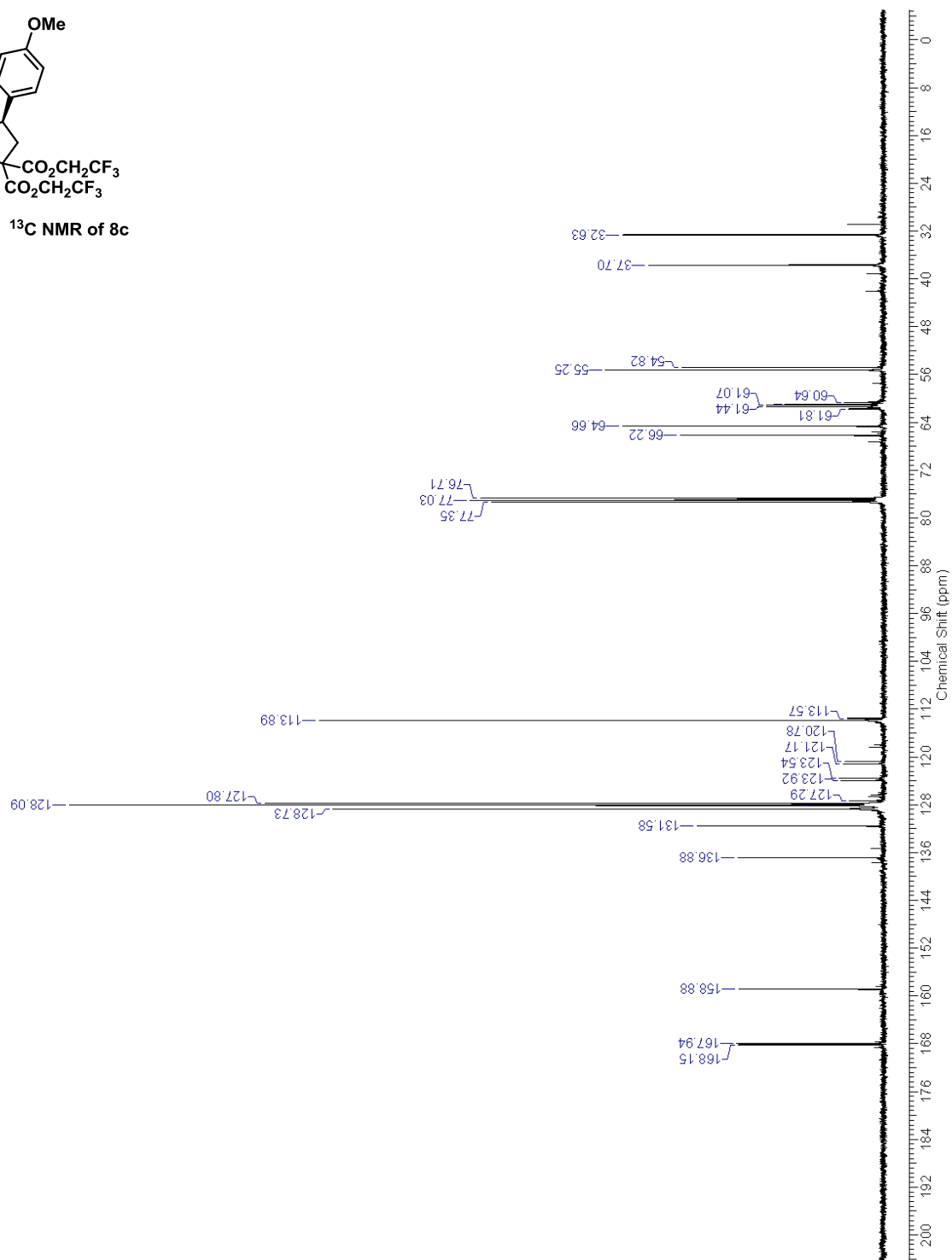


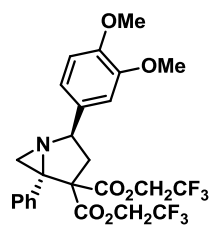




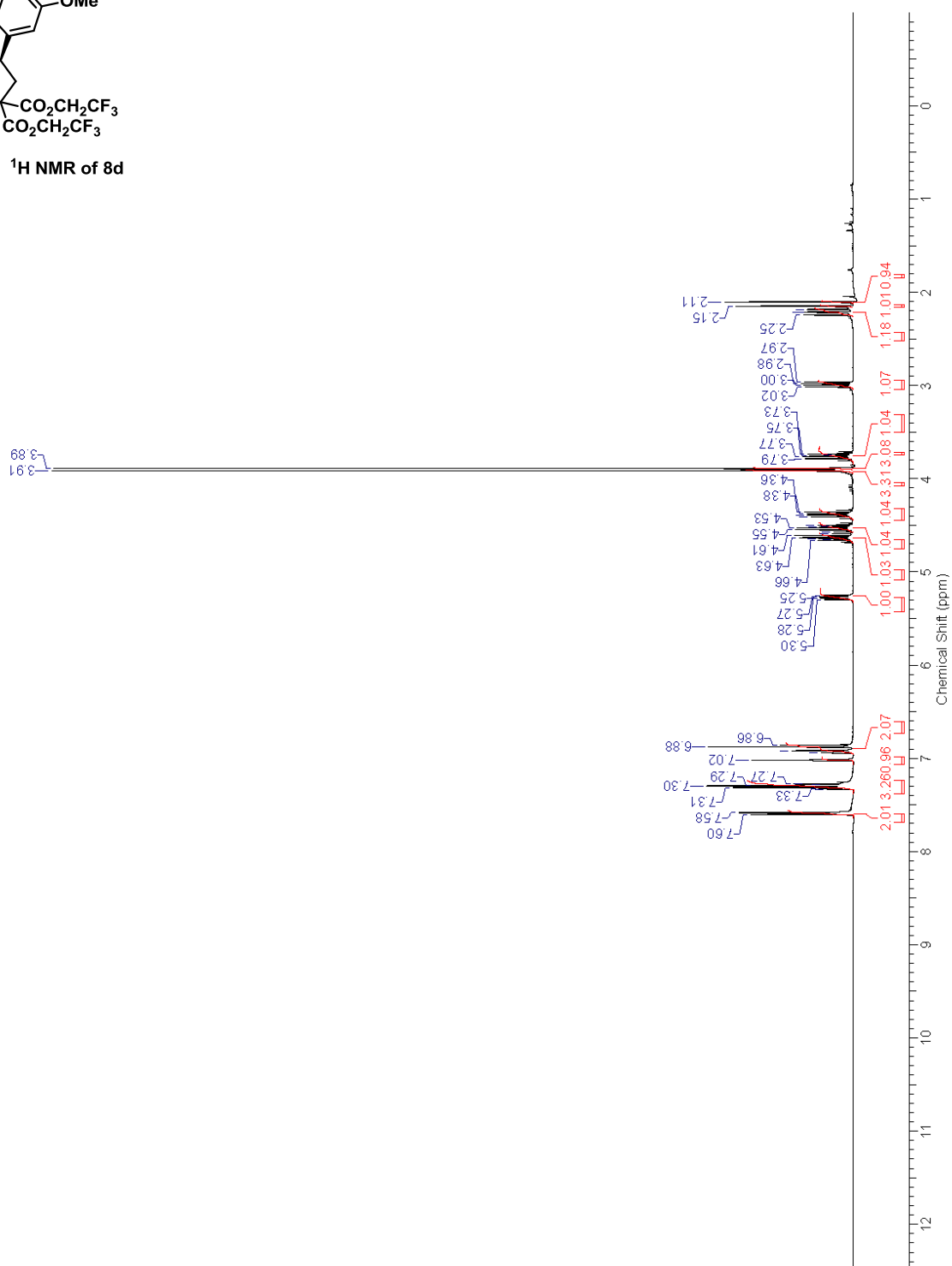


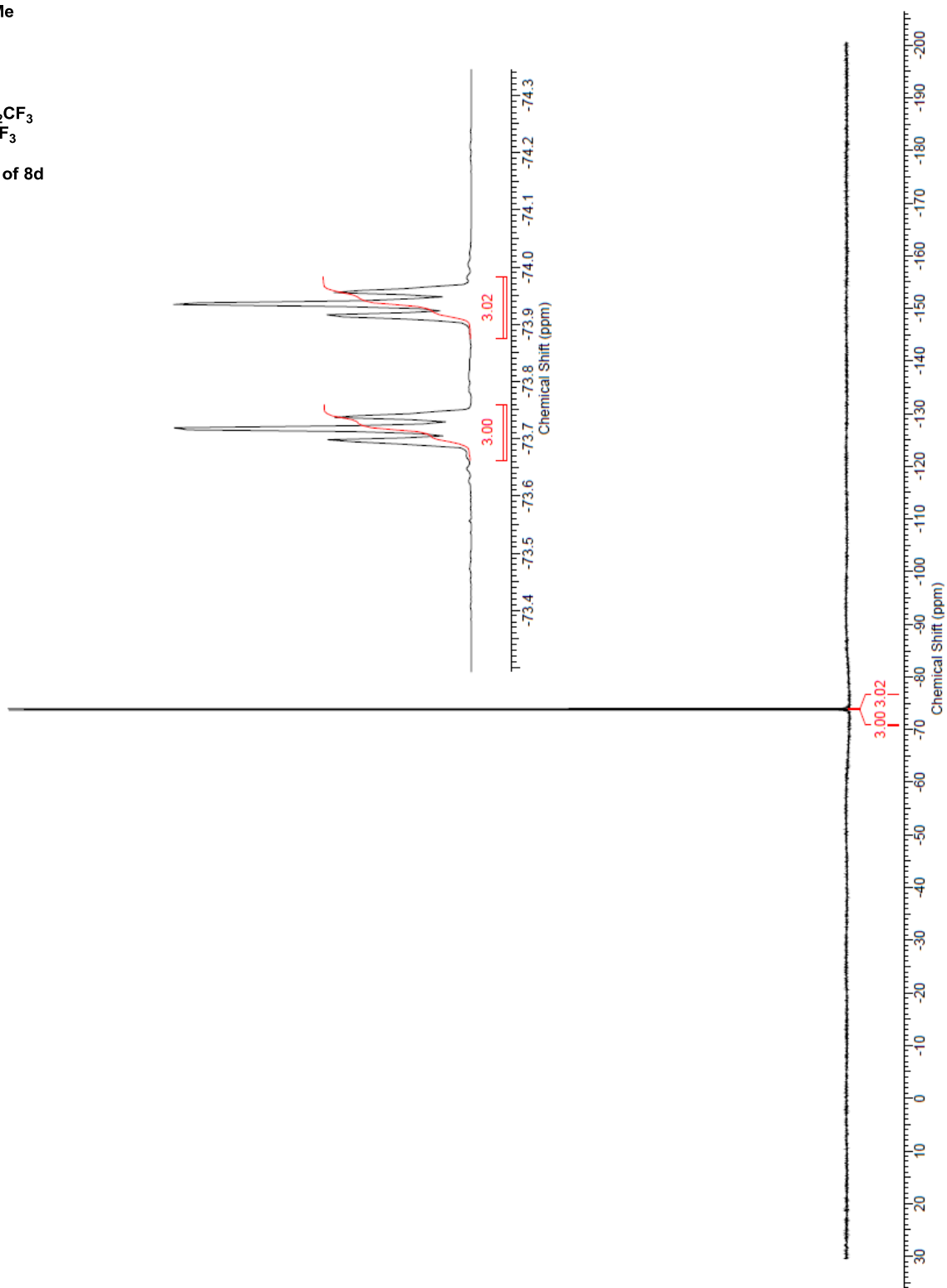
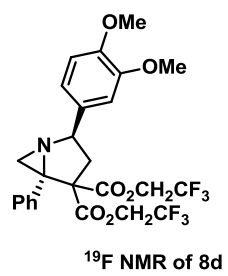
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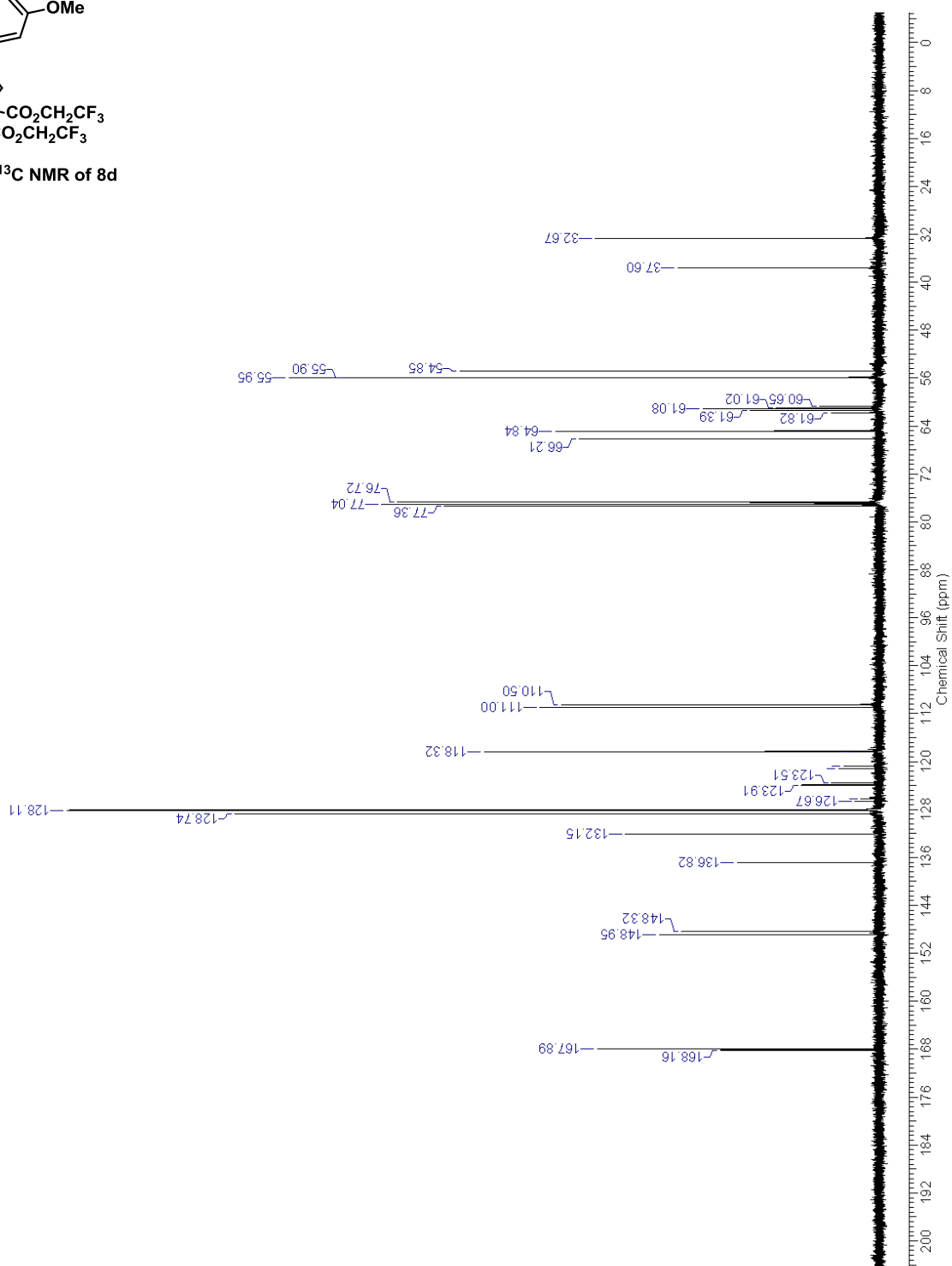
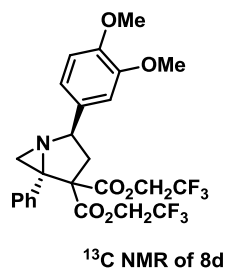


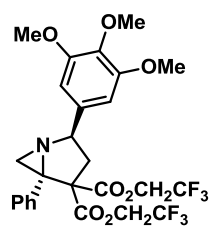


$^1\text{H}$  NMR of 8d

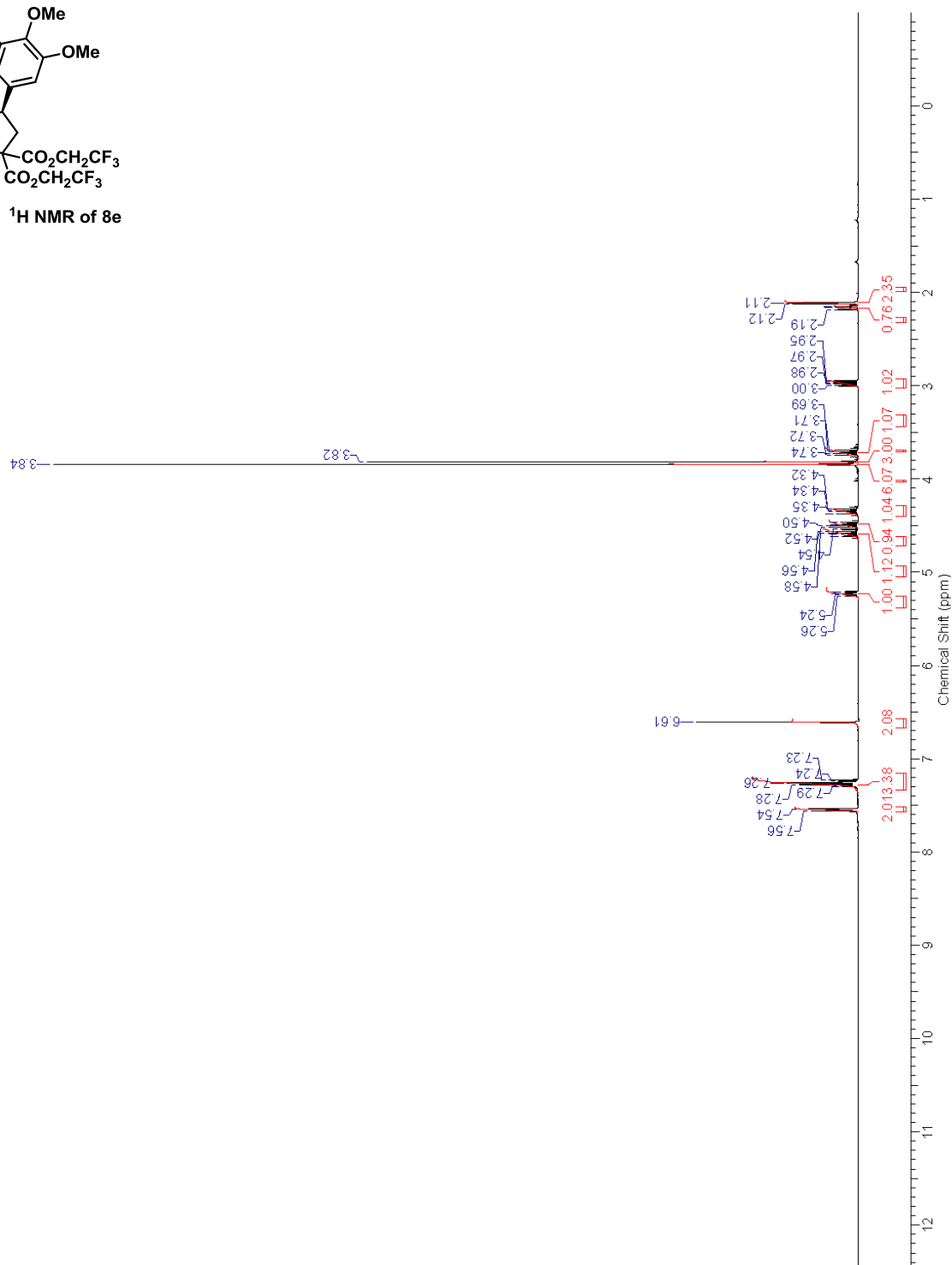


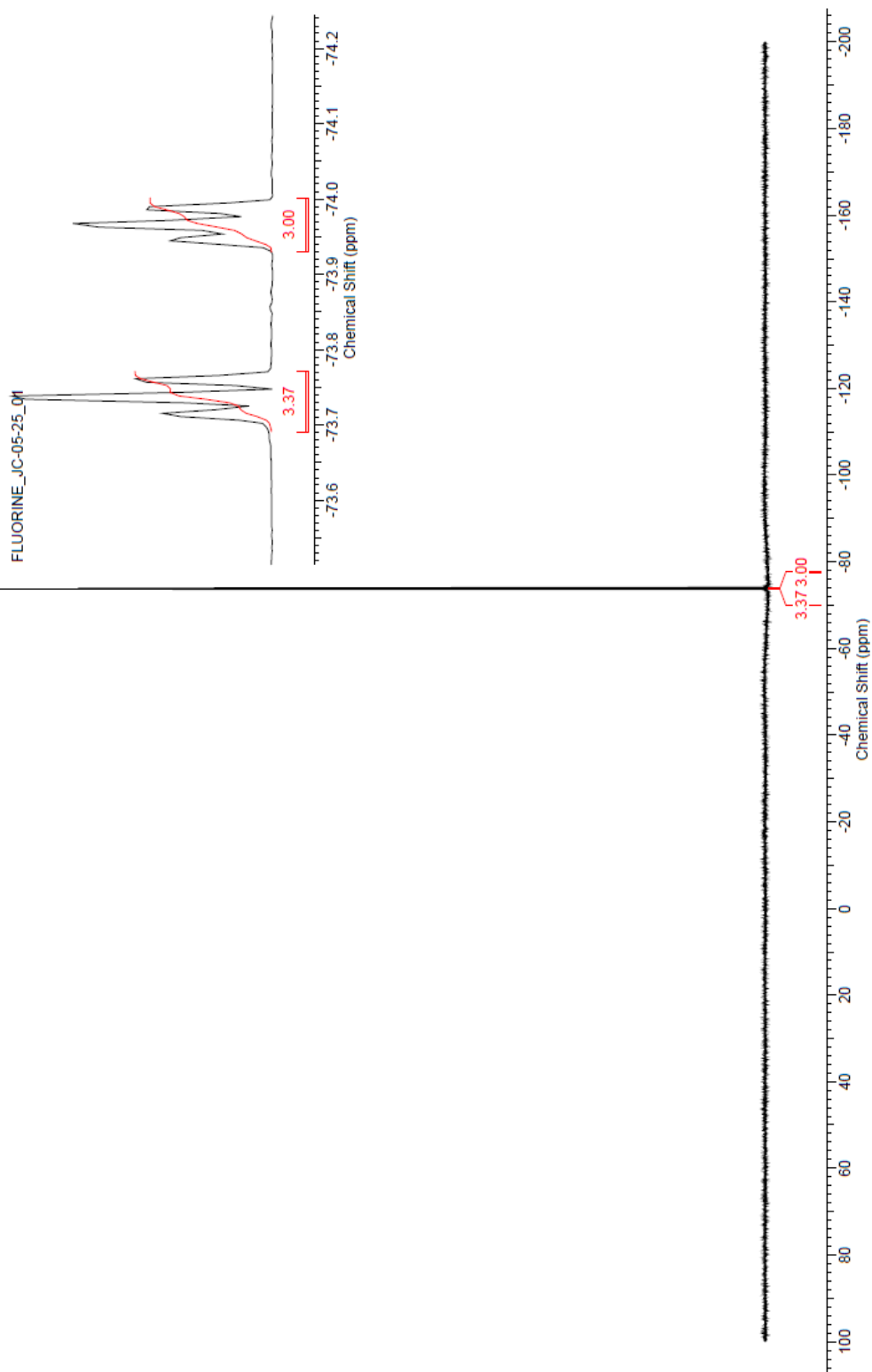
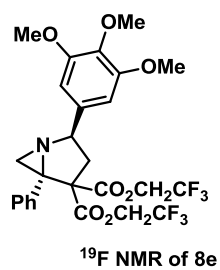


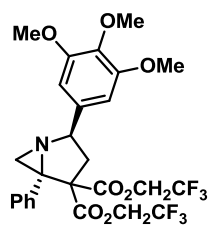




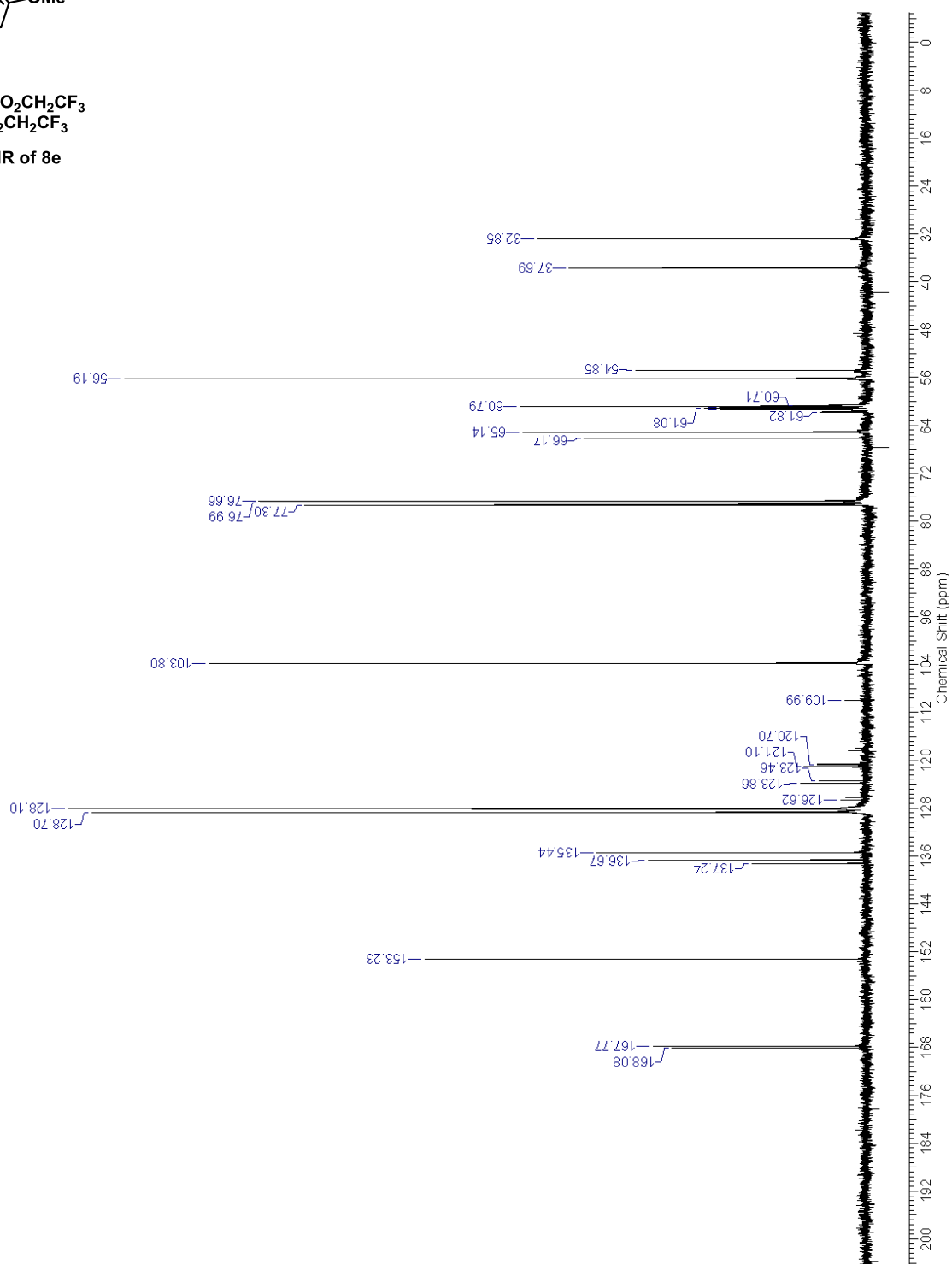
$^1\text{H}$  NMR of 8e



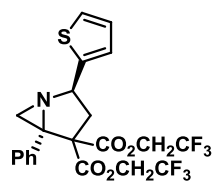




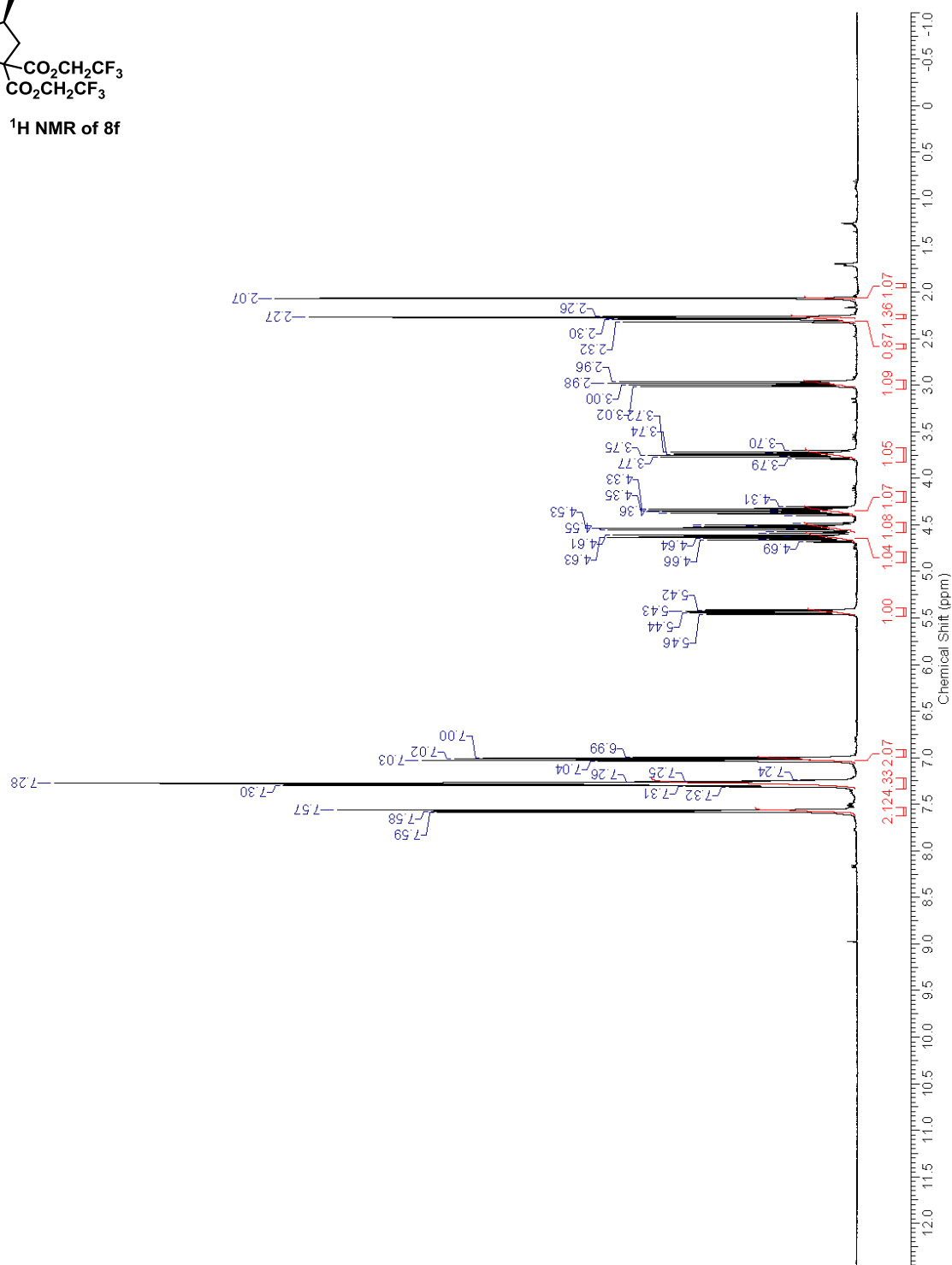
<sup>13</sup>C NMR of 8e

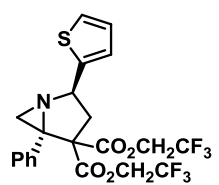




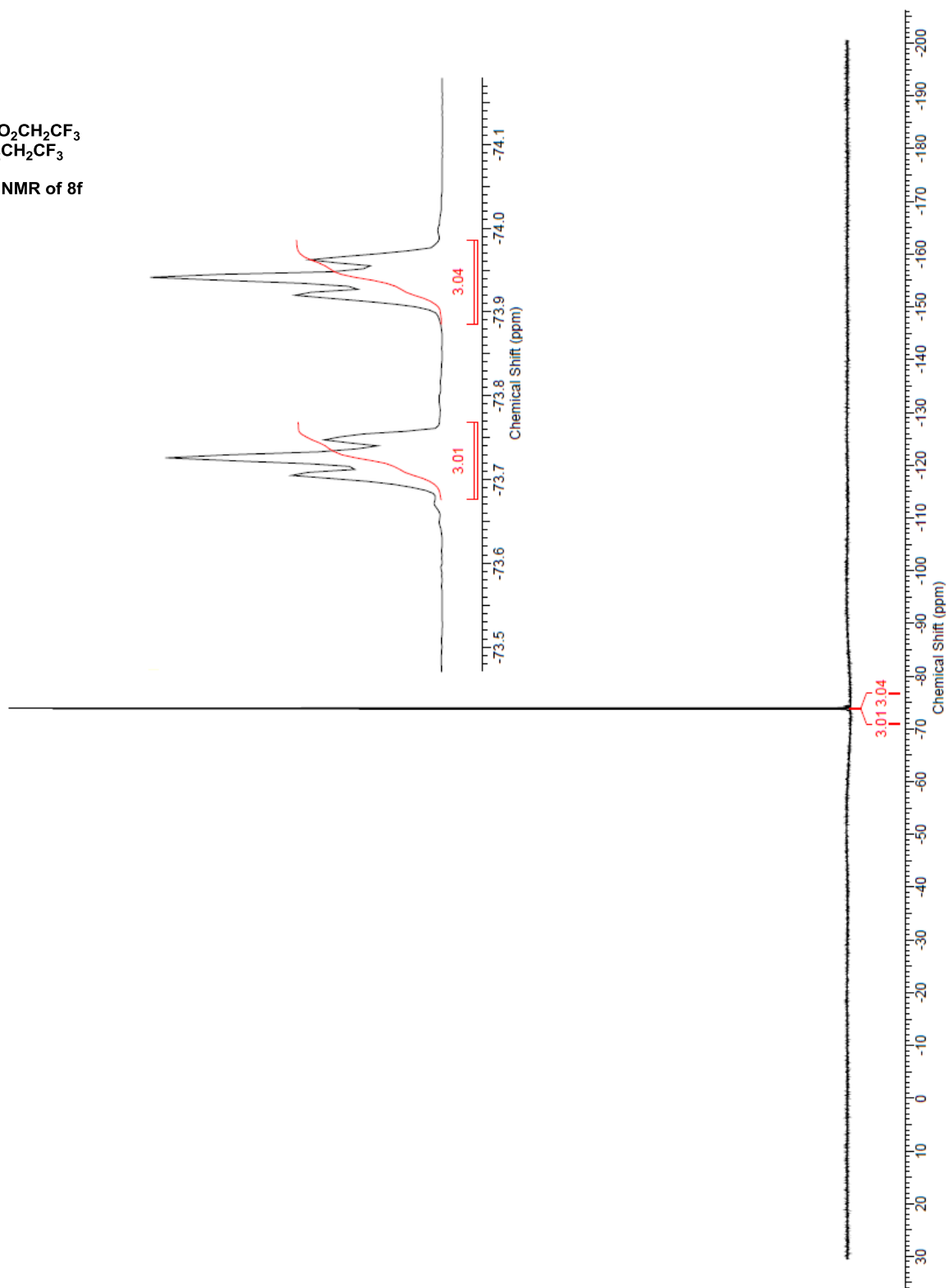


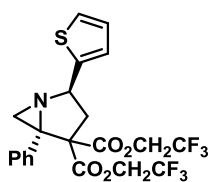
<sup>1</sup>H NMR of 8f



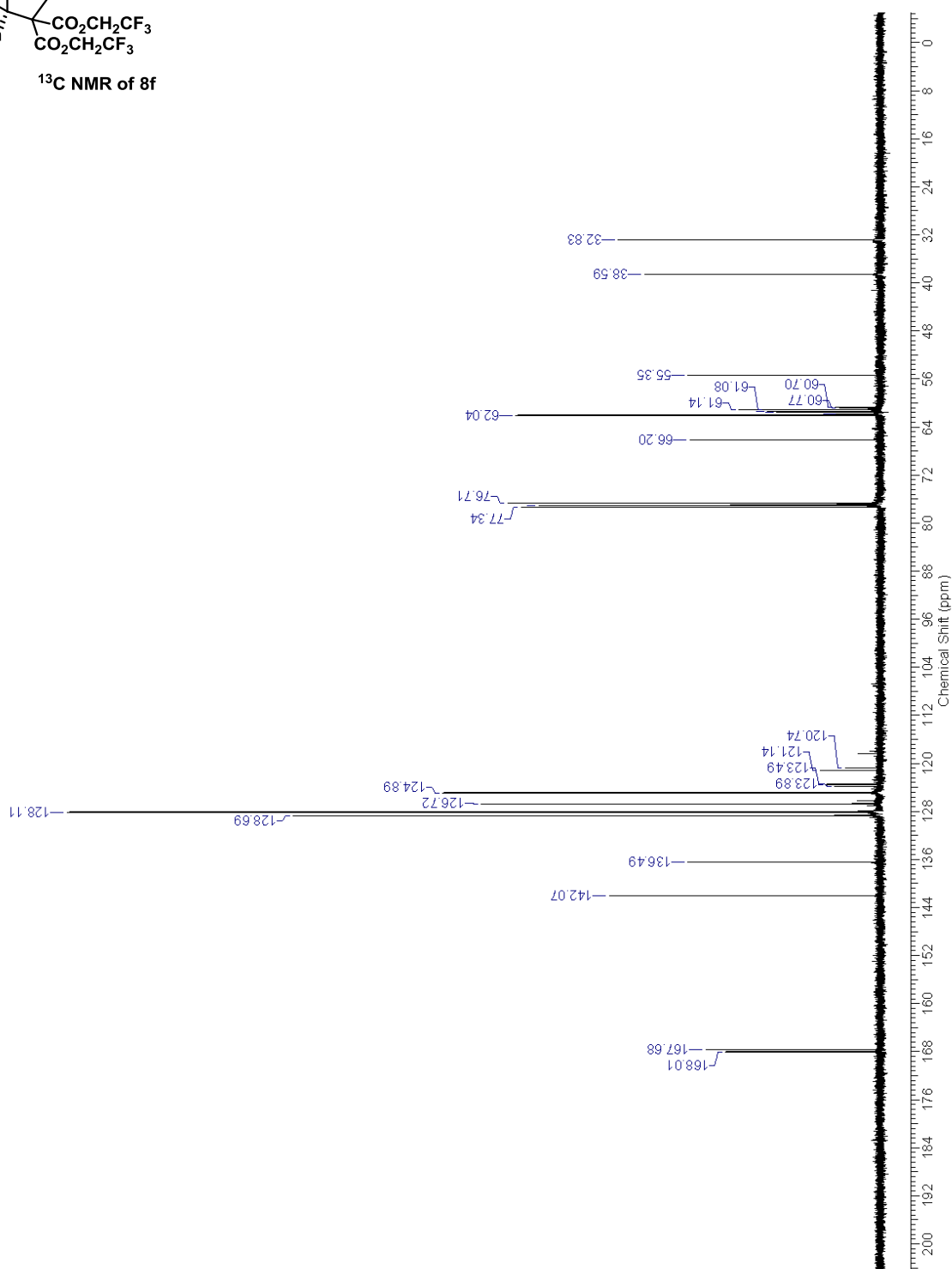


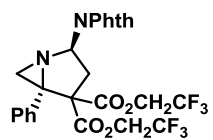
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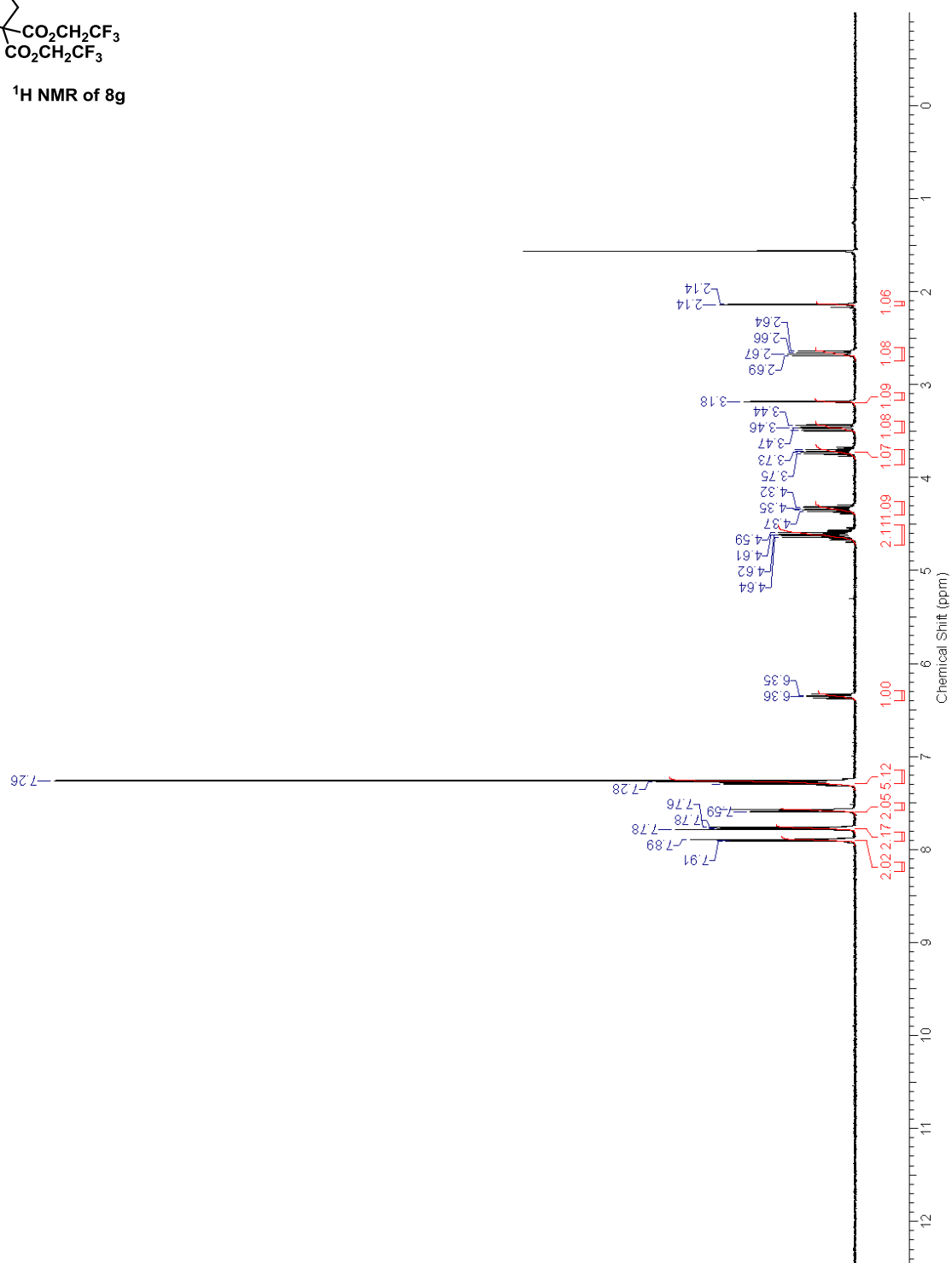


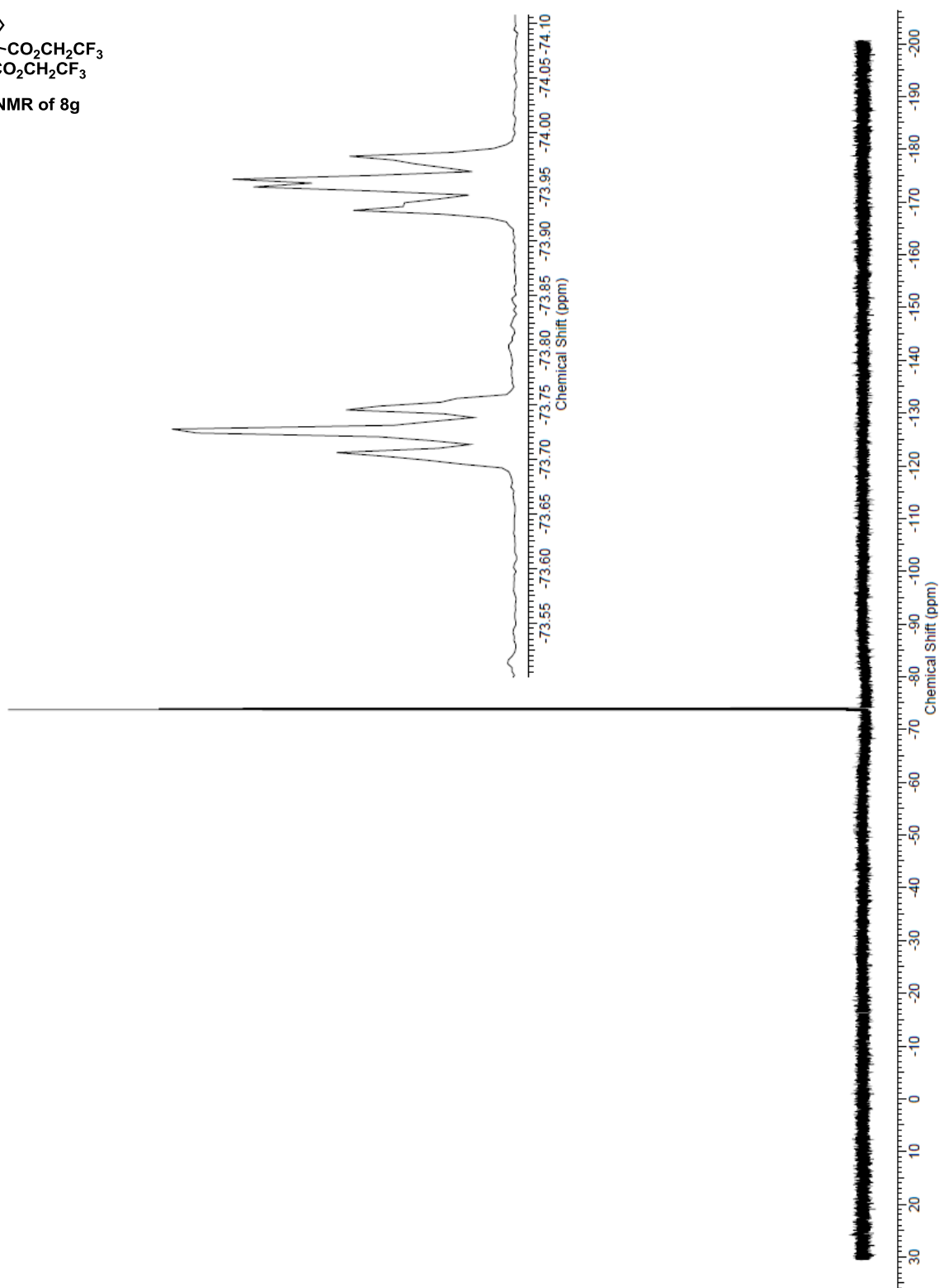
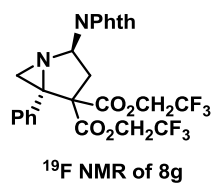
<sup>13</sup>C NMR of 8f

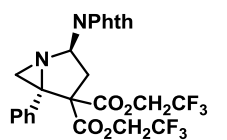




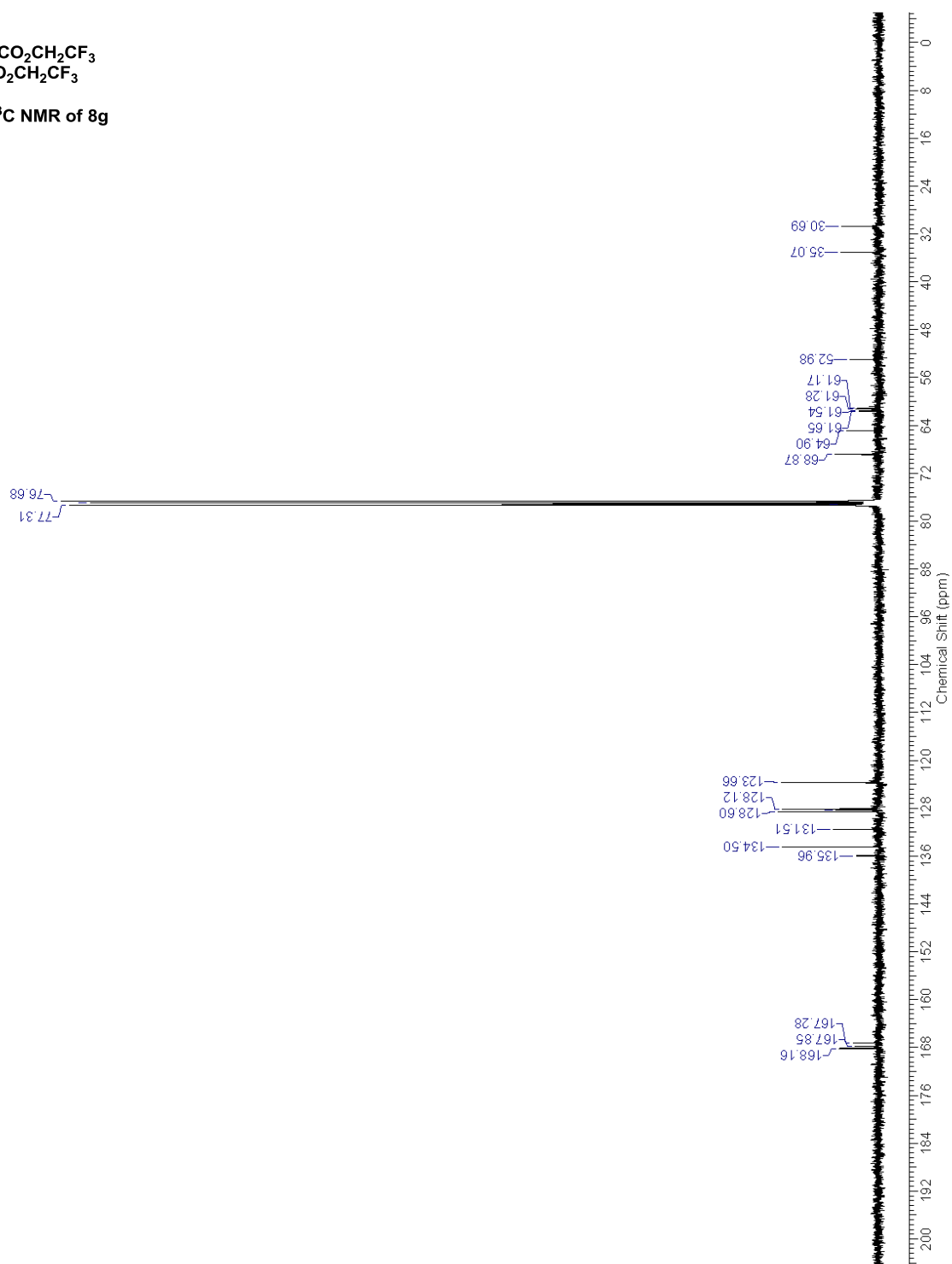
<sup>1</sup>H NMR of 8g

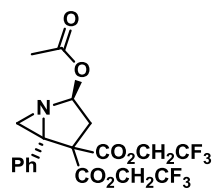




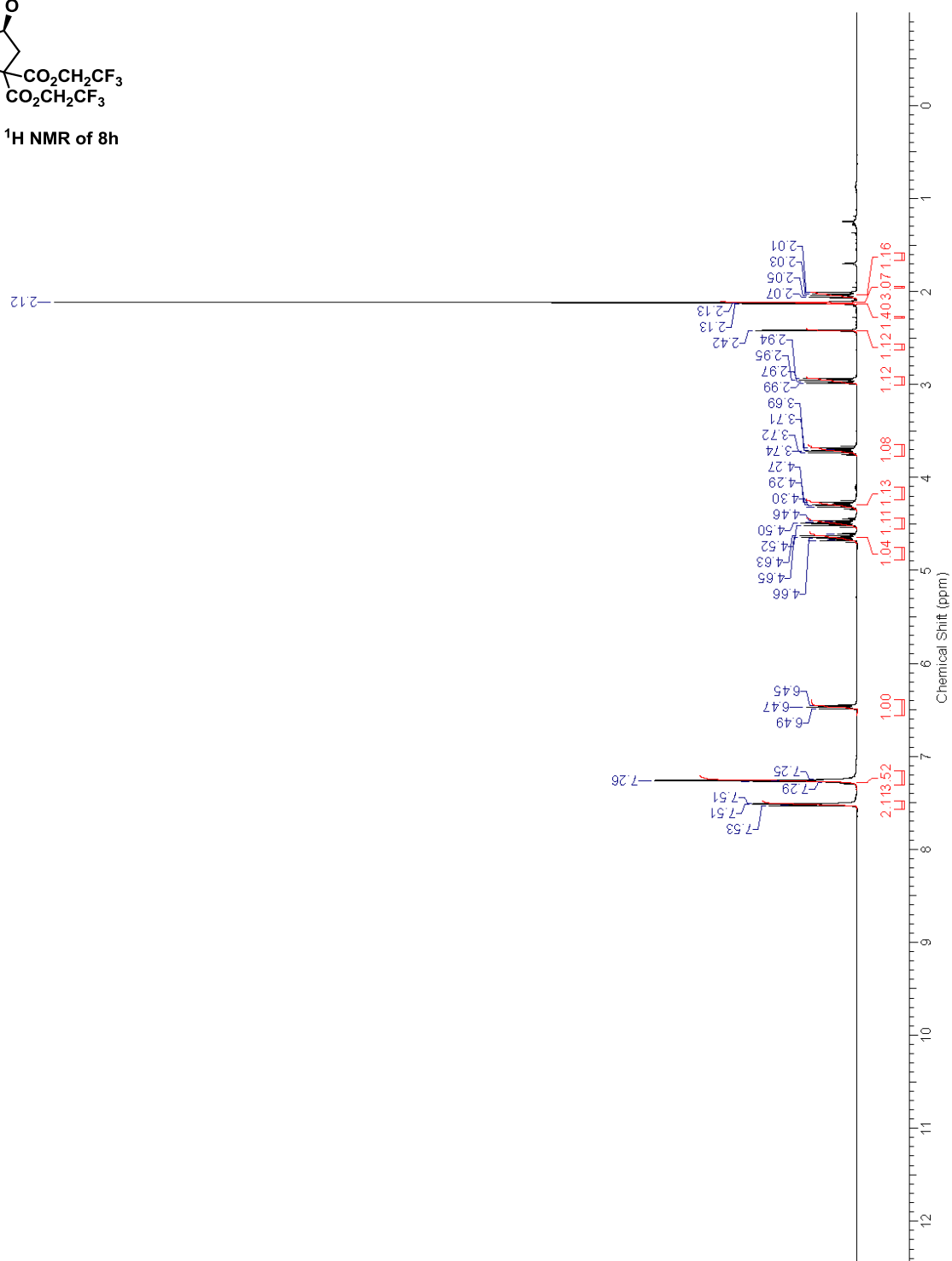


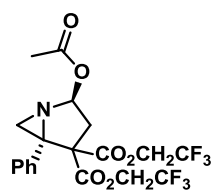
<sup>13</sup>C NMR of 8g



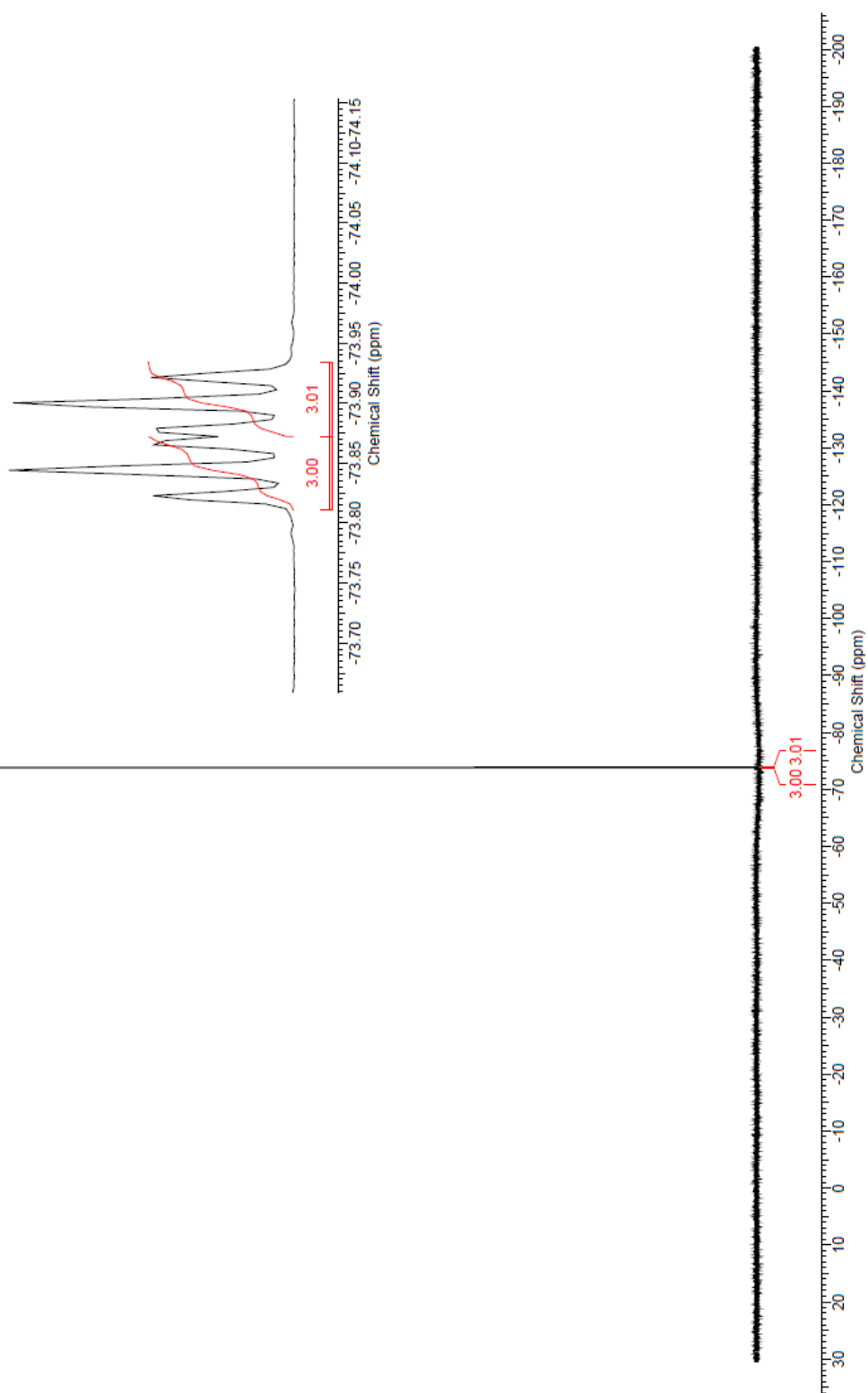


<sup>1</sup>H NMR of 8h

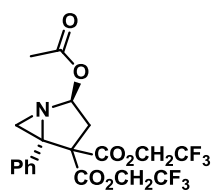




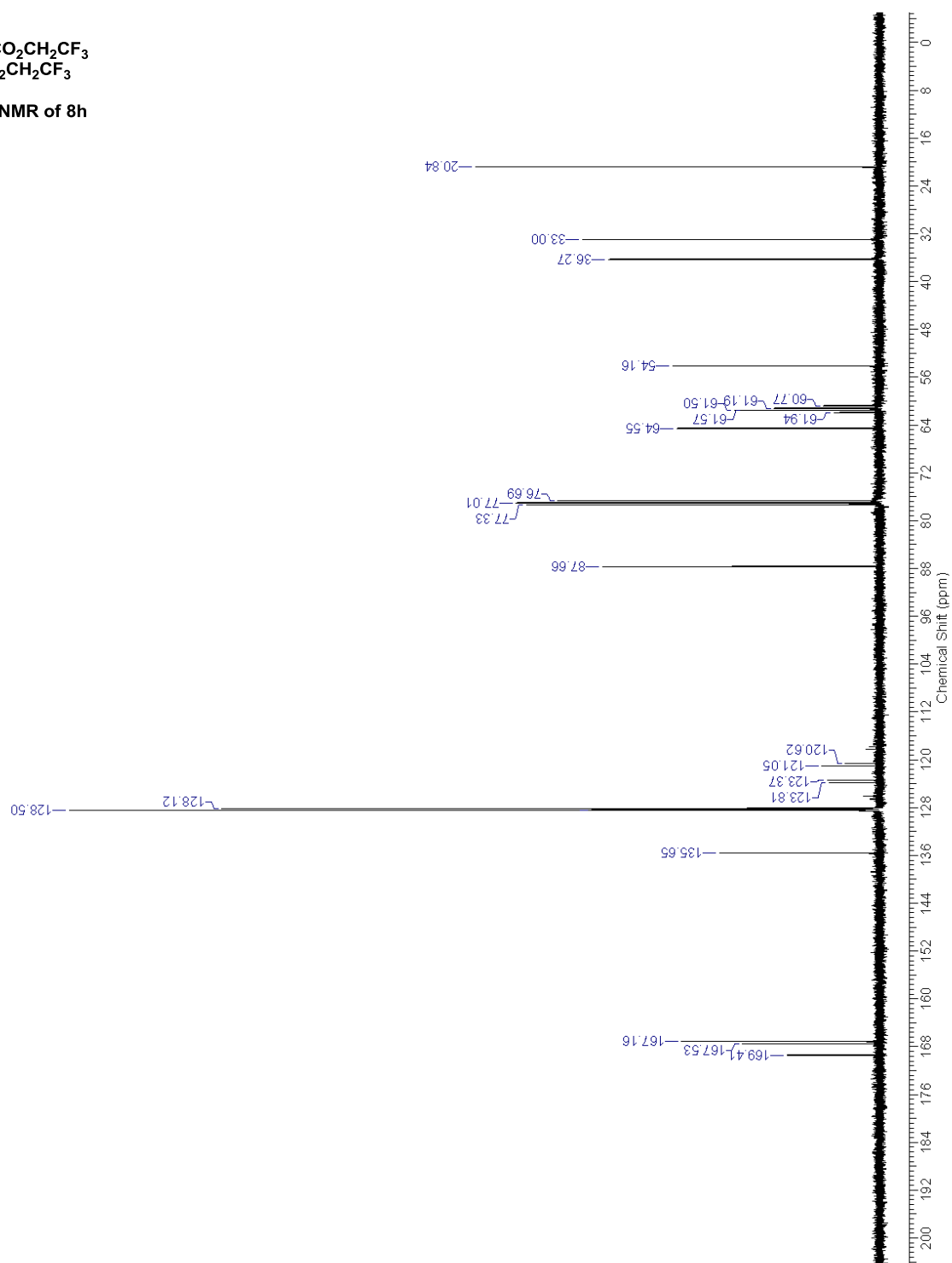
$^{19}\text{F}$  NMR of 8h

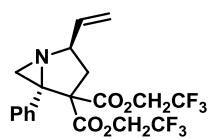




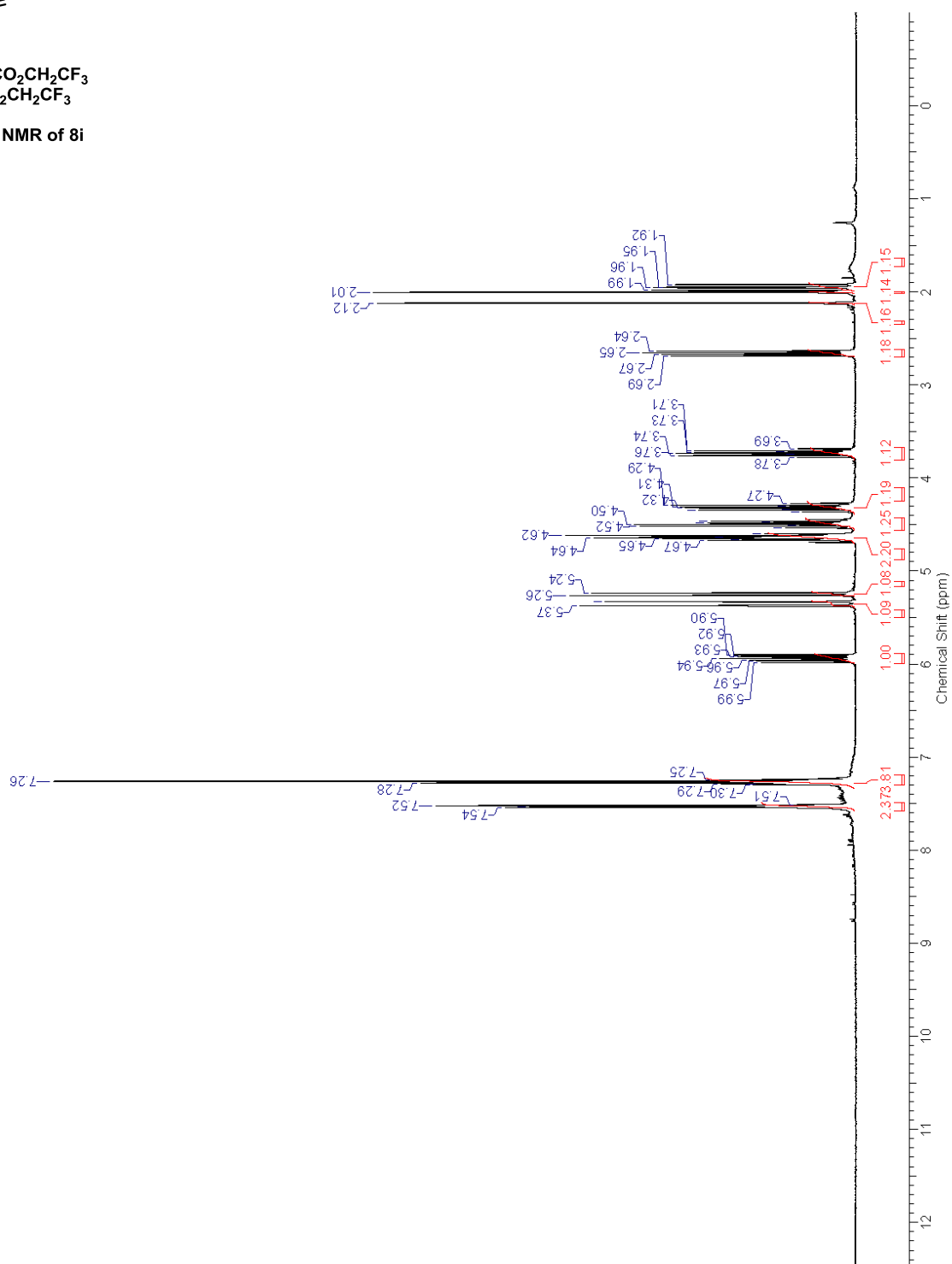


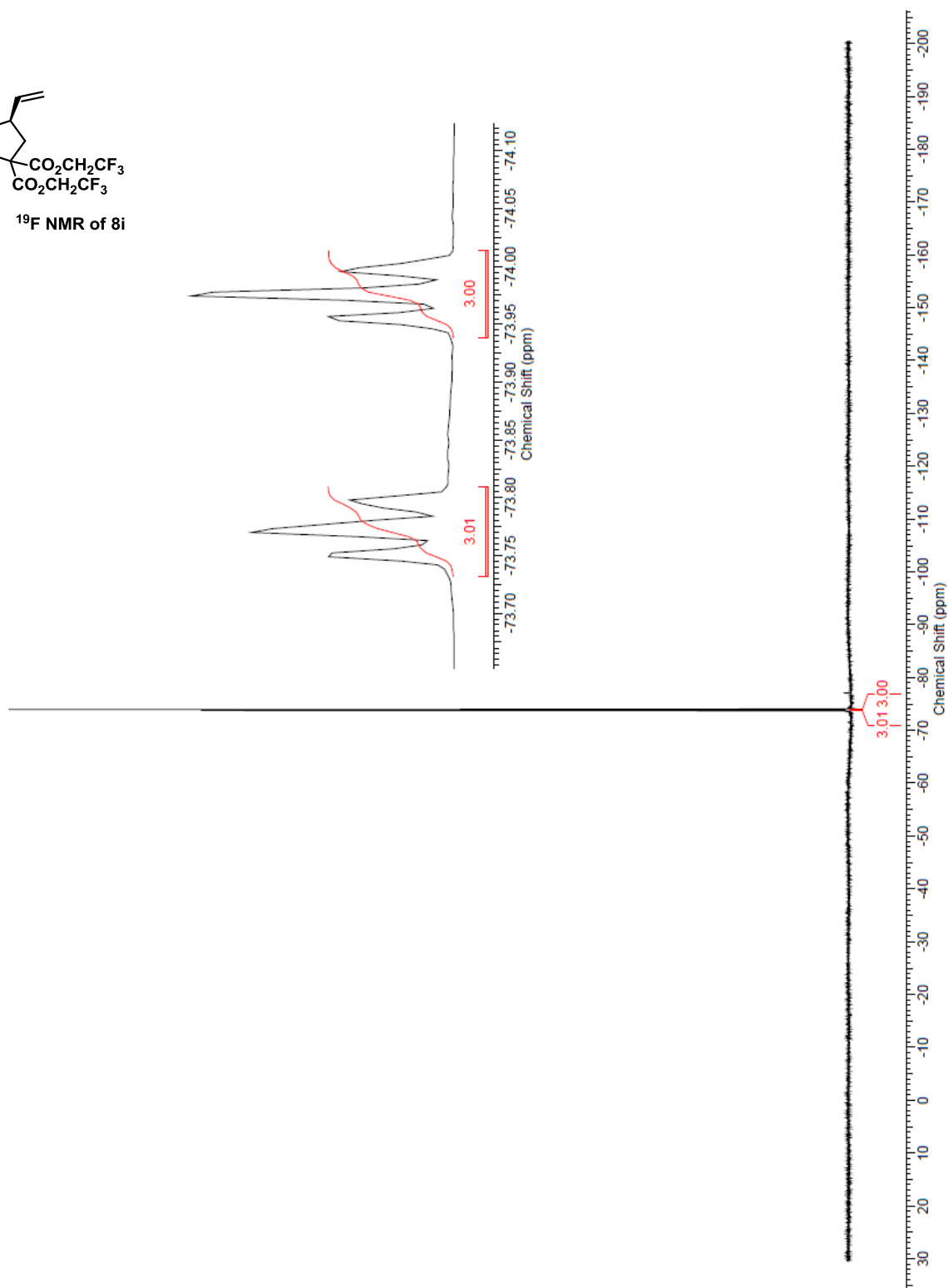
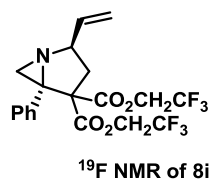
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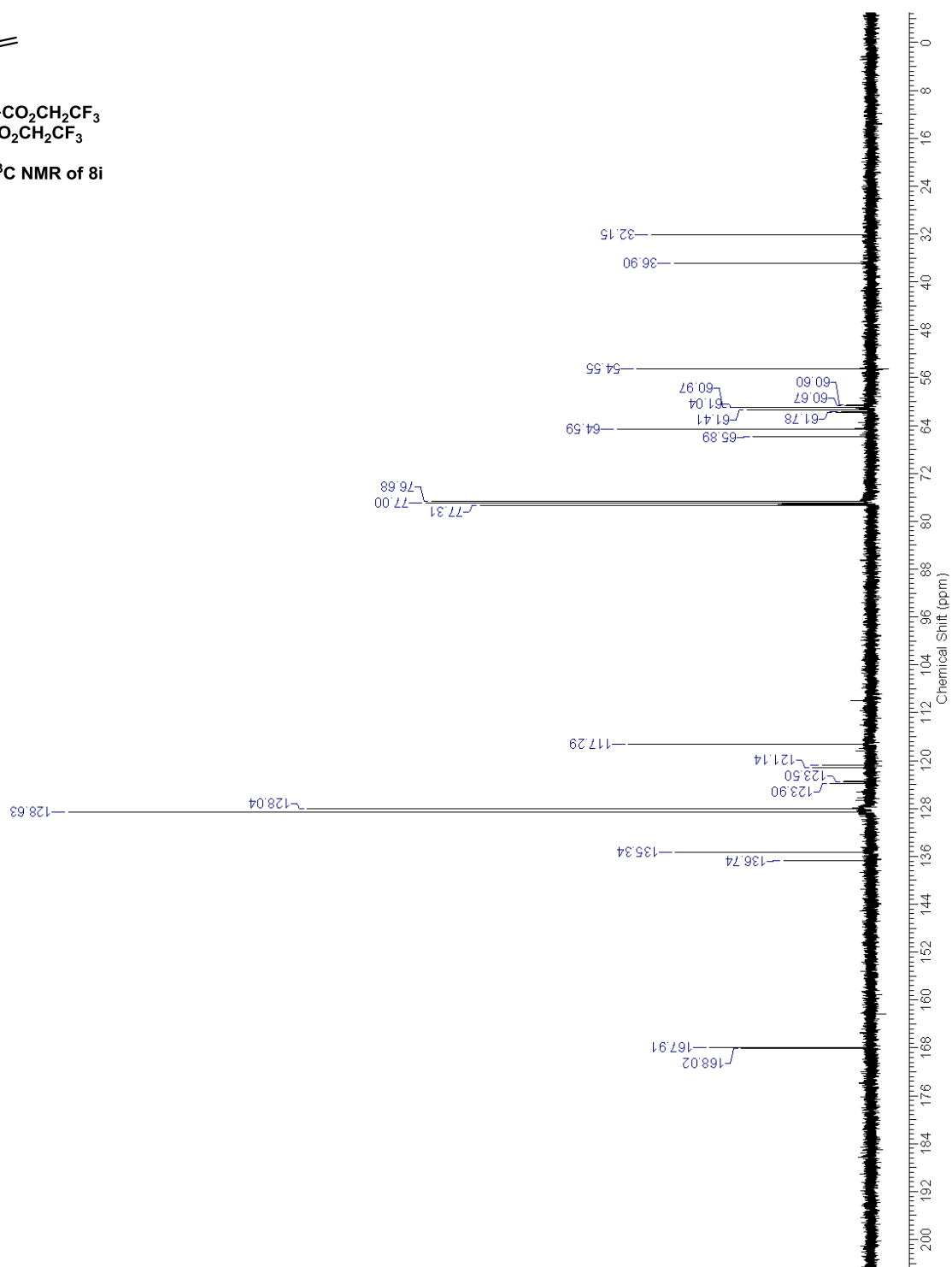
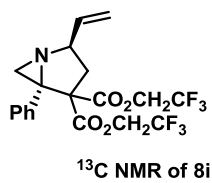


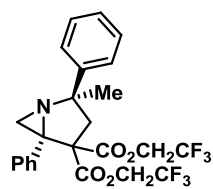


$^1\text{H}$  NMR of 8i

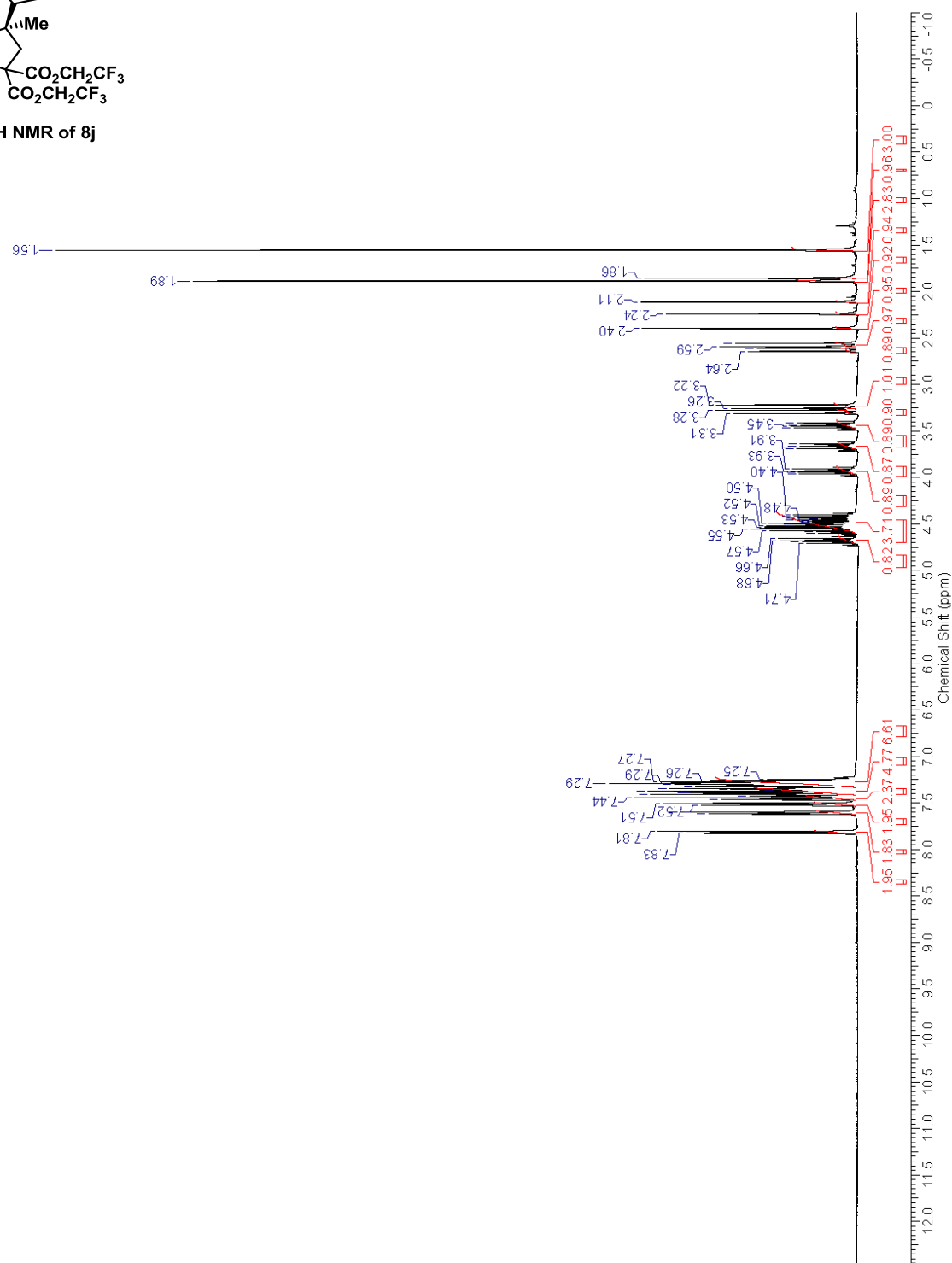


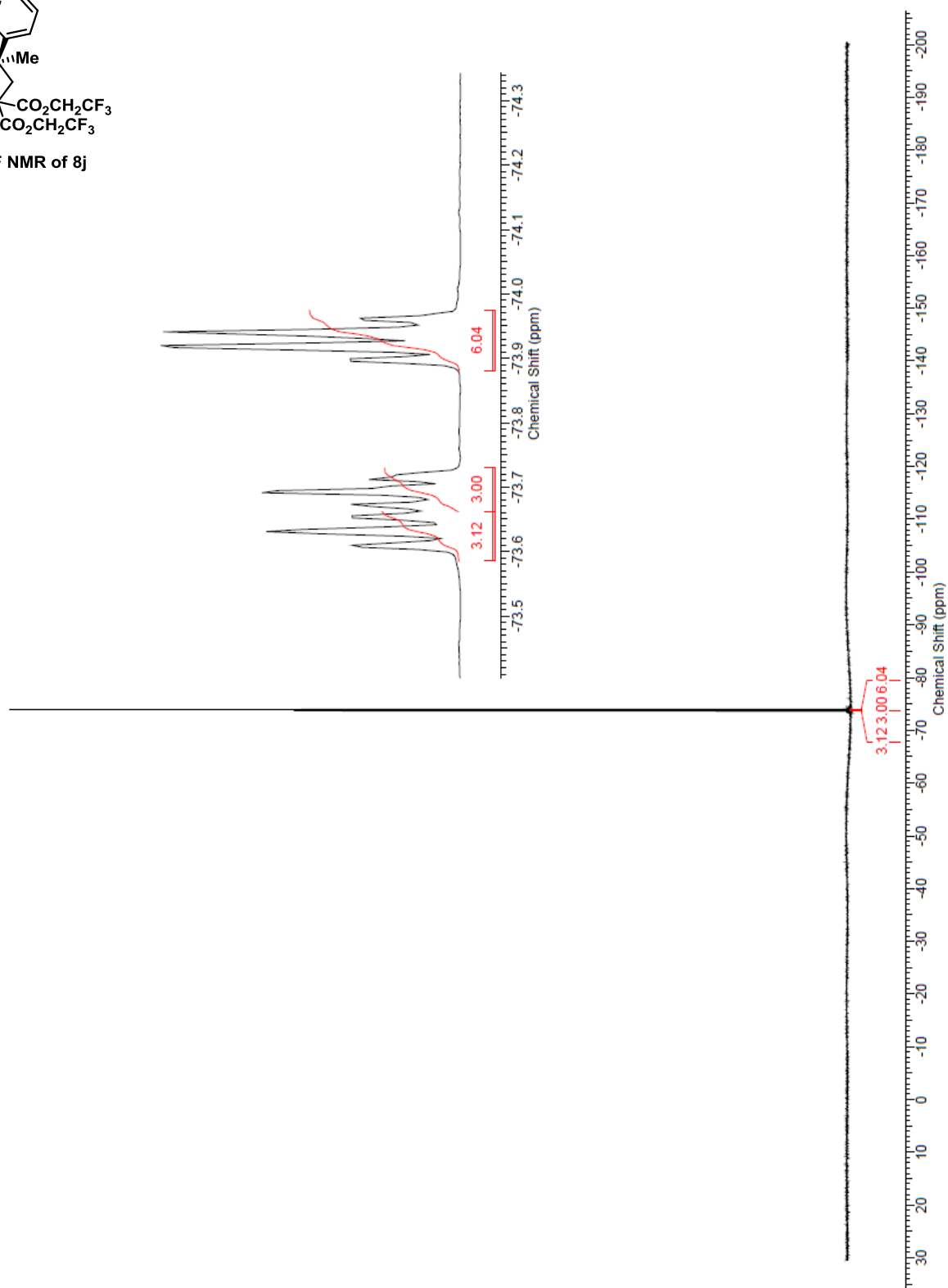
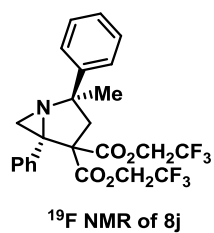


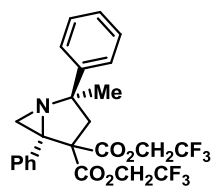




<sup>1</sup>H NMR of 8j







$^{13}\text{C}$  NMR of 8j

