

## ELECTRONIC SUPPLEMENTARY INFORMATION

### **Simultaneous Introduction of Trifluoromethyl and $\lambda^6$ -Pentafluorosulfanyl Substituents using $\text{SF}_5\text{-C}\equiv\text{C-CF}_3$ as Dienophile**

Blazej Duda\* and Dieter Lentz\*

*Freie Universität Berlin, Institut für Chemie und Biochemie,  
Fabeckstraße 34-36, 14195 Berlin, Germany*

Email:

blazejduda@gmail.com

dieter.lentz@fu-berlin.de

**General remarks**

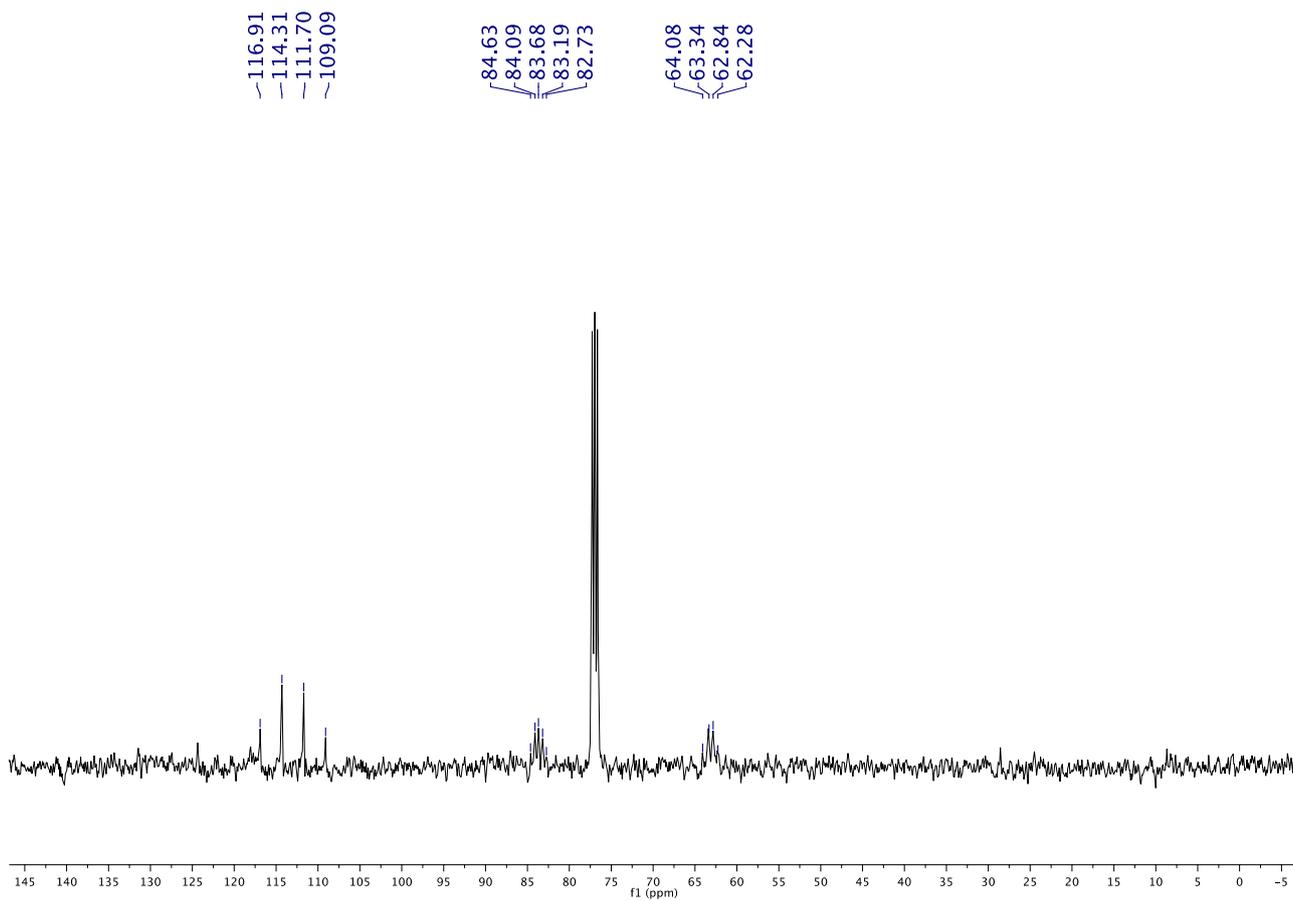
All reagents from commercial suppliers were used without further purification. All solvents were freshly distilled from appropriate drying agents before use. Volatile reagents were transferred using a glass vacuum line system. Reactions were carried out under atmosphere of dry argon. TLC/PTLCs were performed with silica gel 60 F<sub>254</sub> plates. Column chromatography was carried out using silica gel 60. The NMR spectra were recorded on JEOL ECS 400 in CDCl<sub>3</sub>; <sup>1</sup>H-NMR (Me<sub>4</sub>Si) at 400 MHz, <sup>13</sup>C-NMR (Me<sub>4</sub>Si) at 100 MHz and <sup>19</sup>F-NMR (CFCl<sub>3</sub>) at 376 MHz. EI mass spectra were recorded on a MAT 711 (Varian MAT Bremen). ESI mass spectra were recorded on an Agilent 6210 ESI-TOF, Agilent Technologies.

### Procedure for the preparation of SF<sub>5</sub>-C≡C-CF<sub>3</sub>

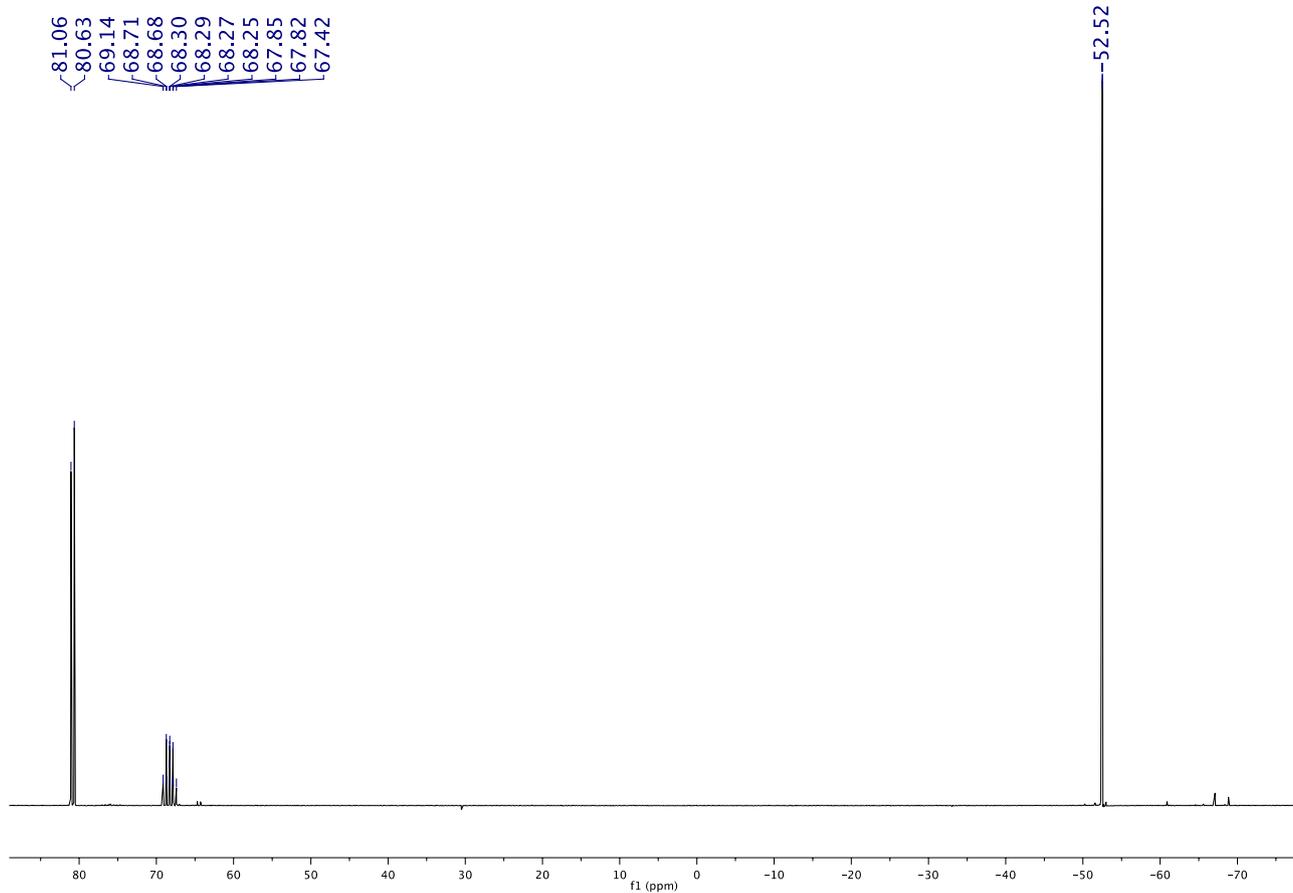
3,3,3-Trifluoropropyne (22 mmol) and SF<sub>5</sub>Br (22 mmol) were condensed into a 100 mL flask equipped with a Young-valve using a glass vacuum line. The valve was closed and the reaction mixture was kept at 80 °C for 2 days. The product was isolated and purified by fractional condensation under vacuum through traps kept at -78 and -196 °C. The product was collected in the -78 °C trap as a mixture of the *E* and *Z* alkenes **1a-b** in a ratio of 1:2. **1a-b** was slowly evaporated under vacuum and passed over KOH pellets in a U-tube kept at 90 °C. The alkyne **2** (2.65 g, 65 %) was collected in the trap kept at -196 °C.



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 63.2 (q, <sup>2</sup>J<sub>CF</sub> = 57 Hz, C-CF<sub>3</sub>), 83.5 (quintet, <sup>2</sup>J<sub>CF(eq)}</sub> = 40 Hz, F<sub>5</sub>S-C), 112.9 (q, <sup>1</sup>J<sub>CF</sub> = 262 Hz, -CF<sub>3</sub>); <sup>19</sup>F NMR (376 MHz) δ 80.8 (B<sub>4</sub>-part, d, <sup>2</sup>J<sub>F(eq)F(ax)}</sub> = 161 Hz, 4F), 68.2 (A-part, 8 lines, 1F), -52.5 (s, CF<sub>3</sub>).



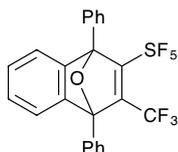
<sup>13</sup>C NMR of 2



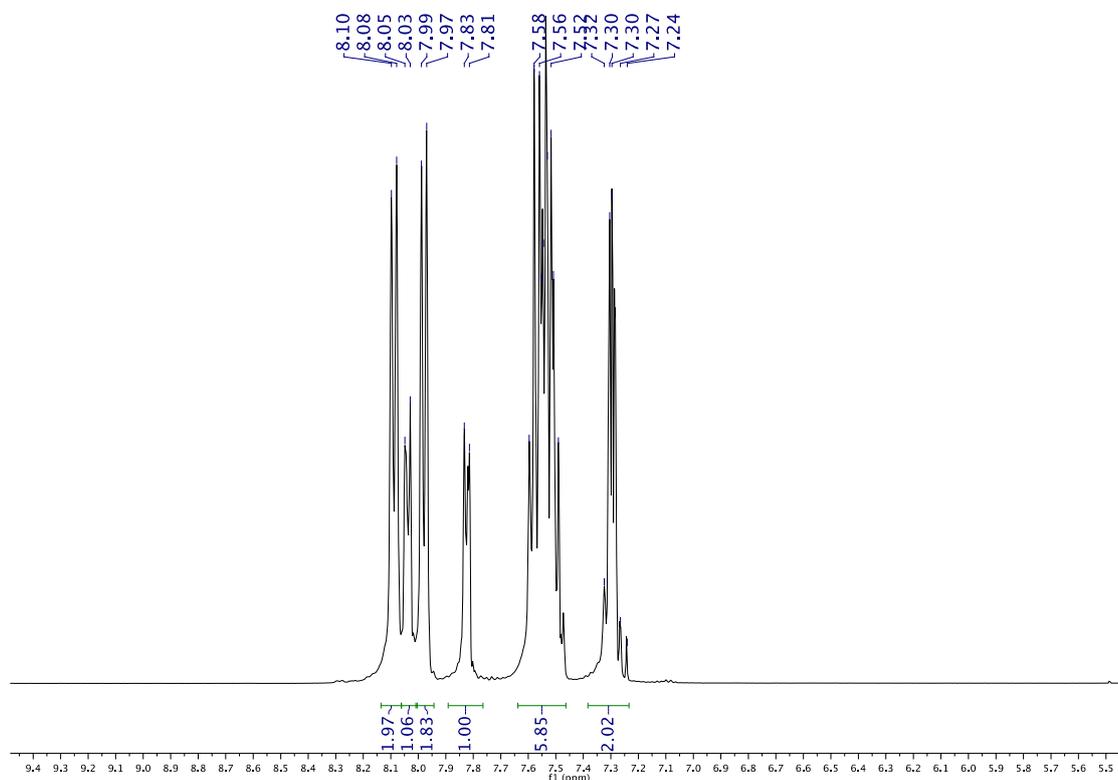
<sup>19</sup>F NMR of 2

## General procedure for the synthesis of 4a-h

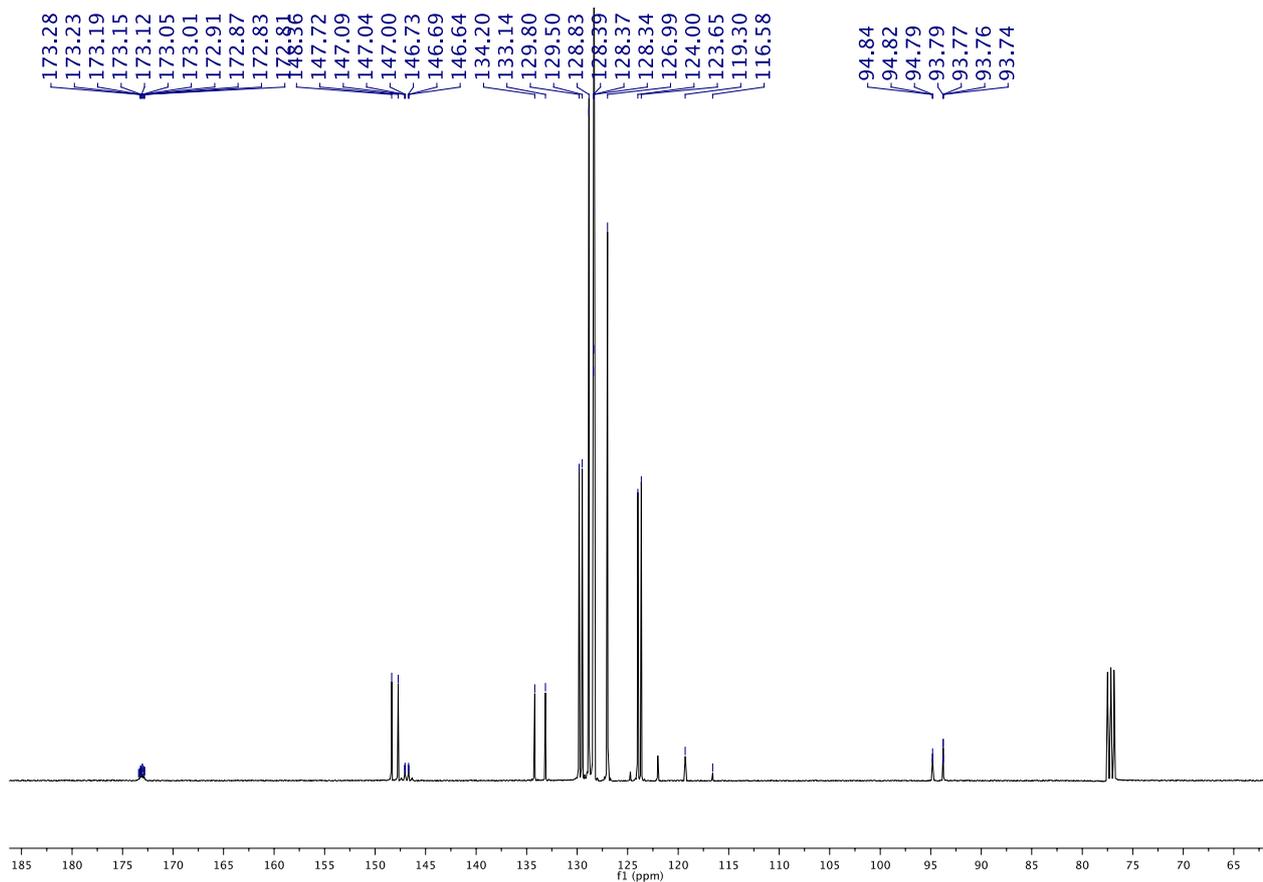
Diene **3a-h** (1 mmol) was dissolved in dry DCM (3 mL) in a round-bottomed flask equipped with a Young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne **2** (1.2 mmol) was condensed to the reaction mixture. After allowing to warm to room temperature within 15-20 min the reaction mixture was stirred at ambient temperature. All volatile materials were removed under reduced pressure. The crude product was purified by flash column chromatography using DCM/*n*-pentane (1:2 *v/v*) as eluent to obtain pure **4a-h**.



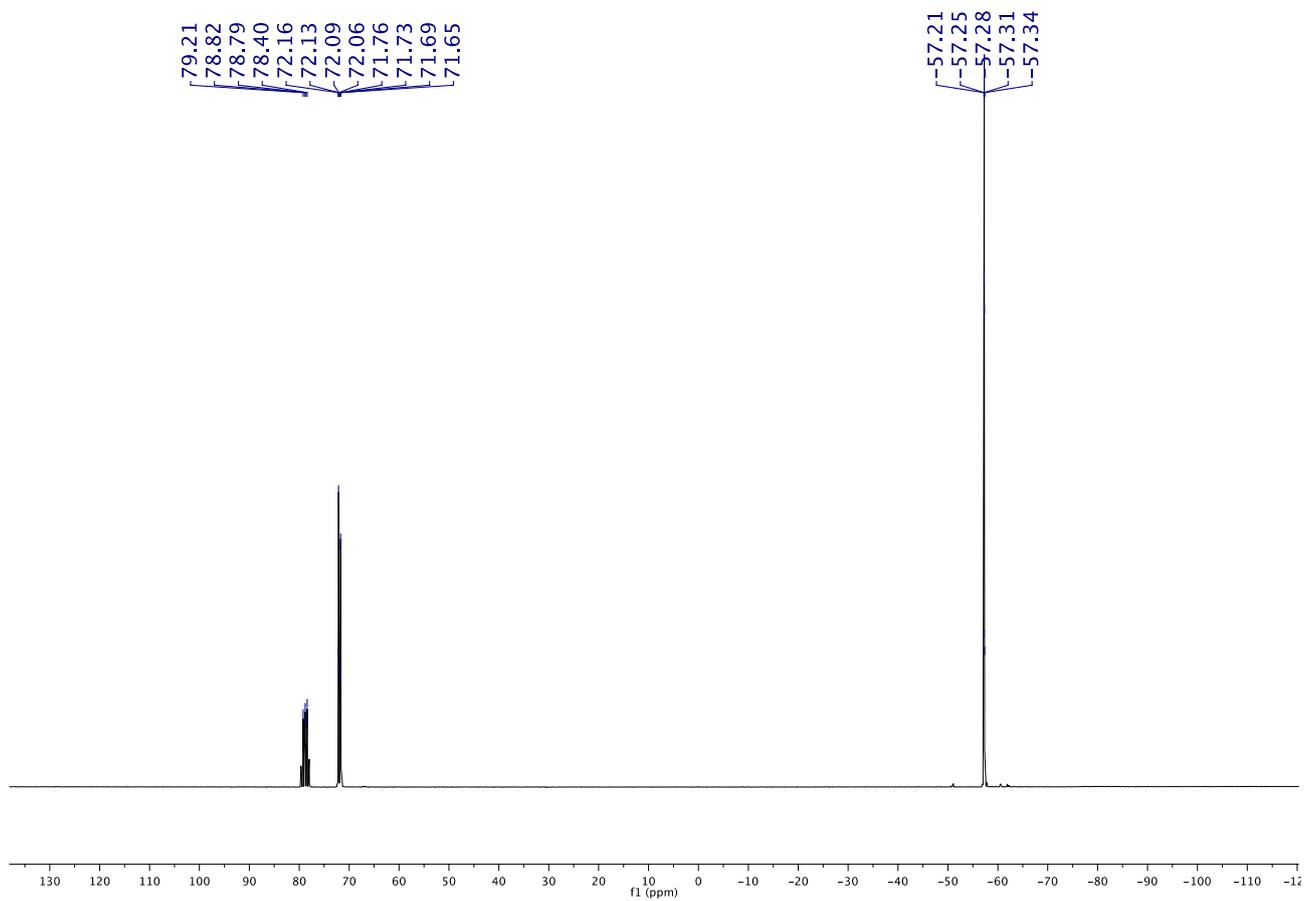
**4a**: solidified oil; Yield (100%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.30 (m, 2H), 7.55 (m, 6H), 7.83 (AB,  $J_{\text{AB}} = 8$  Hz, 1H, B-part), 7.98 (d,  $J = 8$  Hz, 2H), 8.04 (AB,  $J_{\text{AB}} = 8$  Hz, 1H, A-Part), 8.09 (d,  $J = 8$  Hz, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  93.7, 94.8, 120.6 (q,  $^1J_{\text{CF}} = 273$  Hz), 123.6, 123.9, 126.9, 128.3, 128.4, 128.8, 129.8, 133.1, 134.2, 146.9 (quintet,  $^2J_{\text{CF}} = 35$  Hz,  $^3J_{\text{CF}(\text{eq})} = 4$  Hz), 147.7, 148.4, 173.0 (quintetq,  $^2J_{\text{CF}(\text{eq})} = 18$  Hz,  $^3J_{\text{CF}} = 4$  Hz);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  78.8 (9 lines, A-part), 71.9 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 150$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 12$  Hz, B<sub>4</sub>-part), -57.2 (quintet,  $^5J_{\text{FF}(\text{eq})} = 12$  Hz); HRMS (ESI)  $[\text{M}+\text{Na}]^+$   $\text{C}_{23}\text{H}_{14}\text{F}_8\text{SONa}$  found: 513.0548, calcd: 513.0529.



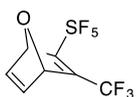
$^1\text{H NMR}$  of **4a**.



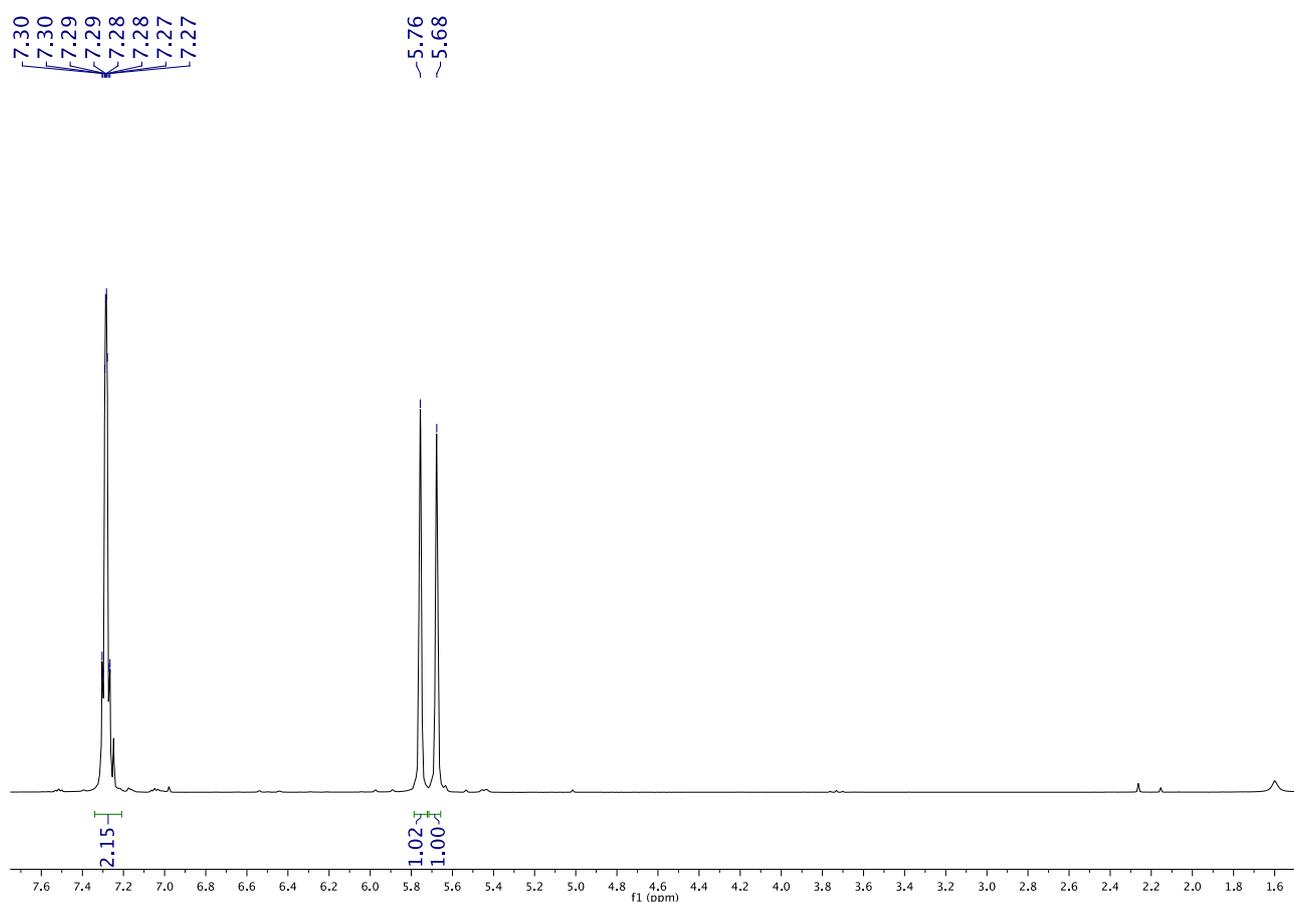
**<sup>13</sup>C NMR of 4a**



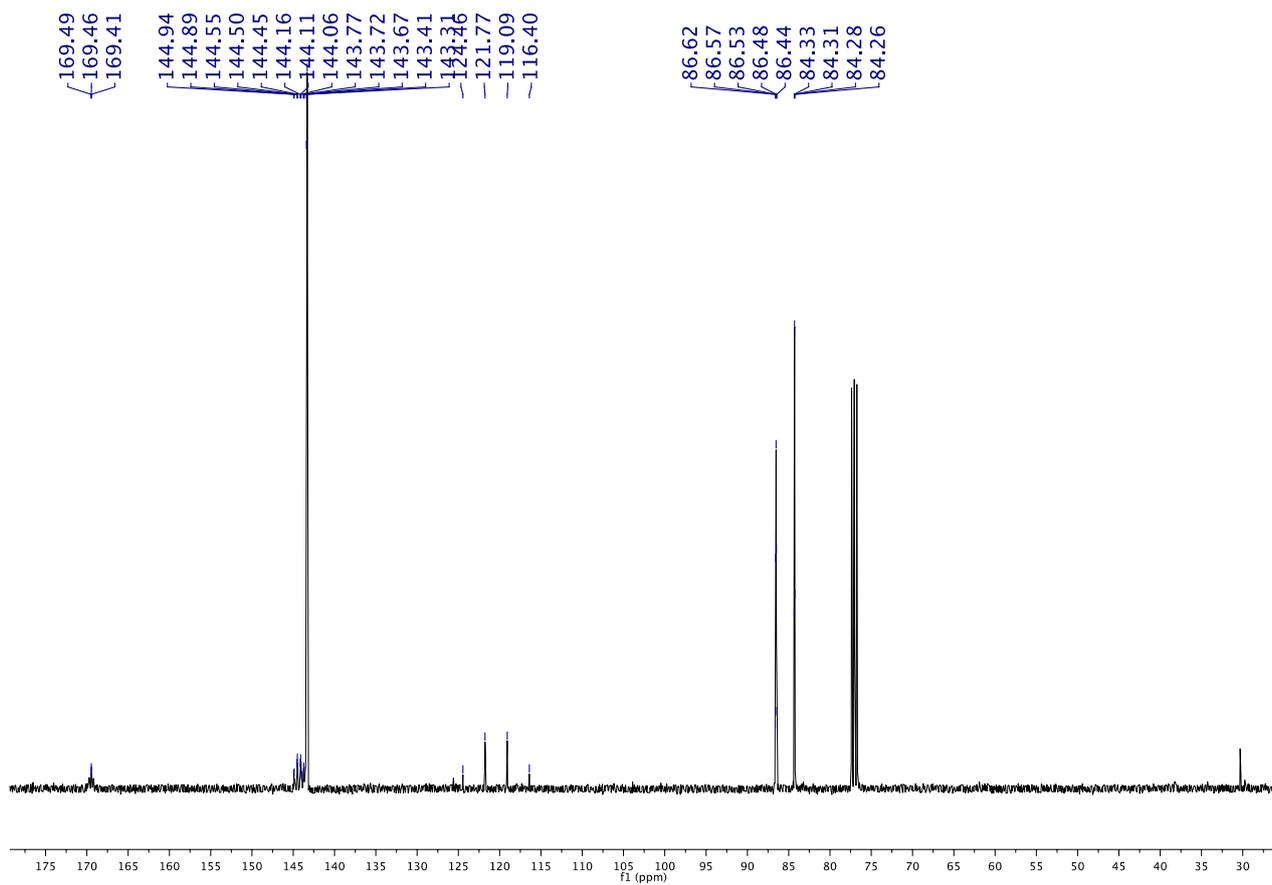
**<sup>19</sup>F NMR of 4a**



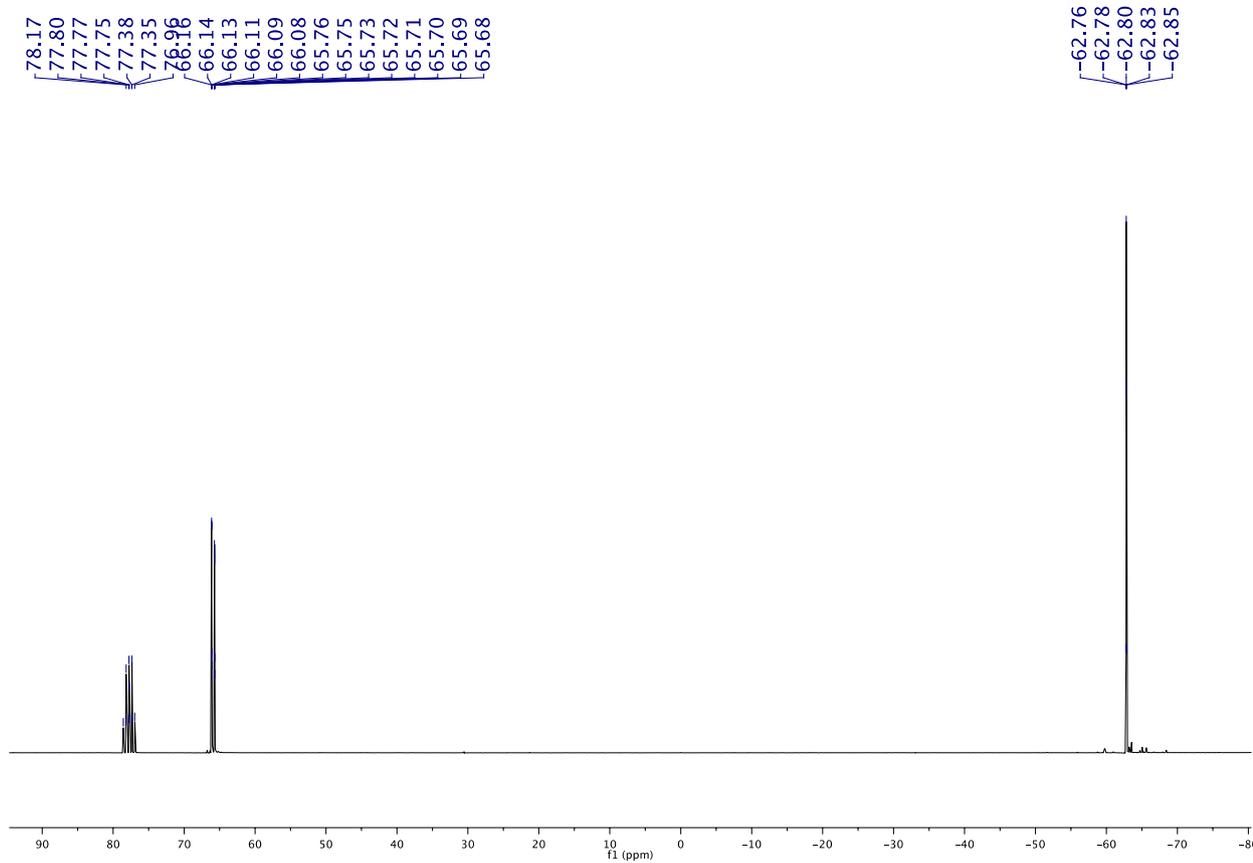
**4b**: colorless oil; Yield (98%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  5.68 (br s, 1H), 5.76 (br s, 1H), 7.27 – 7.30 (ABXY,  $J_{\text{AB}} = 5$  Hz,  $J_{\text{AX}} = J_{\text{BY}} = 2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  84.2 (q,  $^3J_{\text{CF}} = 3$  Hz), 86.5 (quintet,  $^3J_{\text{CF}(\text{eq})} = 4$  Hz), 120.4 (q,  $^1J_{\text{CF}} = 269$  Hz), 143.2, 143.3, 144.4 (qq,  $^2J_{\text{CF}} = 39$  Hz,  $^3J_{\text{CF}(\text{eq})} = 5$  Hz), 169.5 (quintetqd,  $^3J_{\text{CF}(\text{eq})} = 23$  Hz,  $^3J_{\text{CF}} = 5$  Hz,  $^2J_{\text{CF}(\text{ax})} = 2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  77.5 (9-lines, A-part), 65.6 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 152$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 10$  Hz, B<sub>4</sub>-part), -62.8 (quintet,  $^5J_{\text{FF}(\text{eq})} = 10$  Hz); HRMS (ESI)  $[\text{M}-\text{H}]^-$   $\text{C}_7\text{H}_4\text{F}_8\text{SO}$  found: 286.9835, calcd: 286.9837.



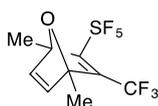
$^1\text{H}$  NMR of **4b**



**<sup>13</sup>C NMR of 4b**



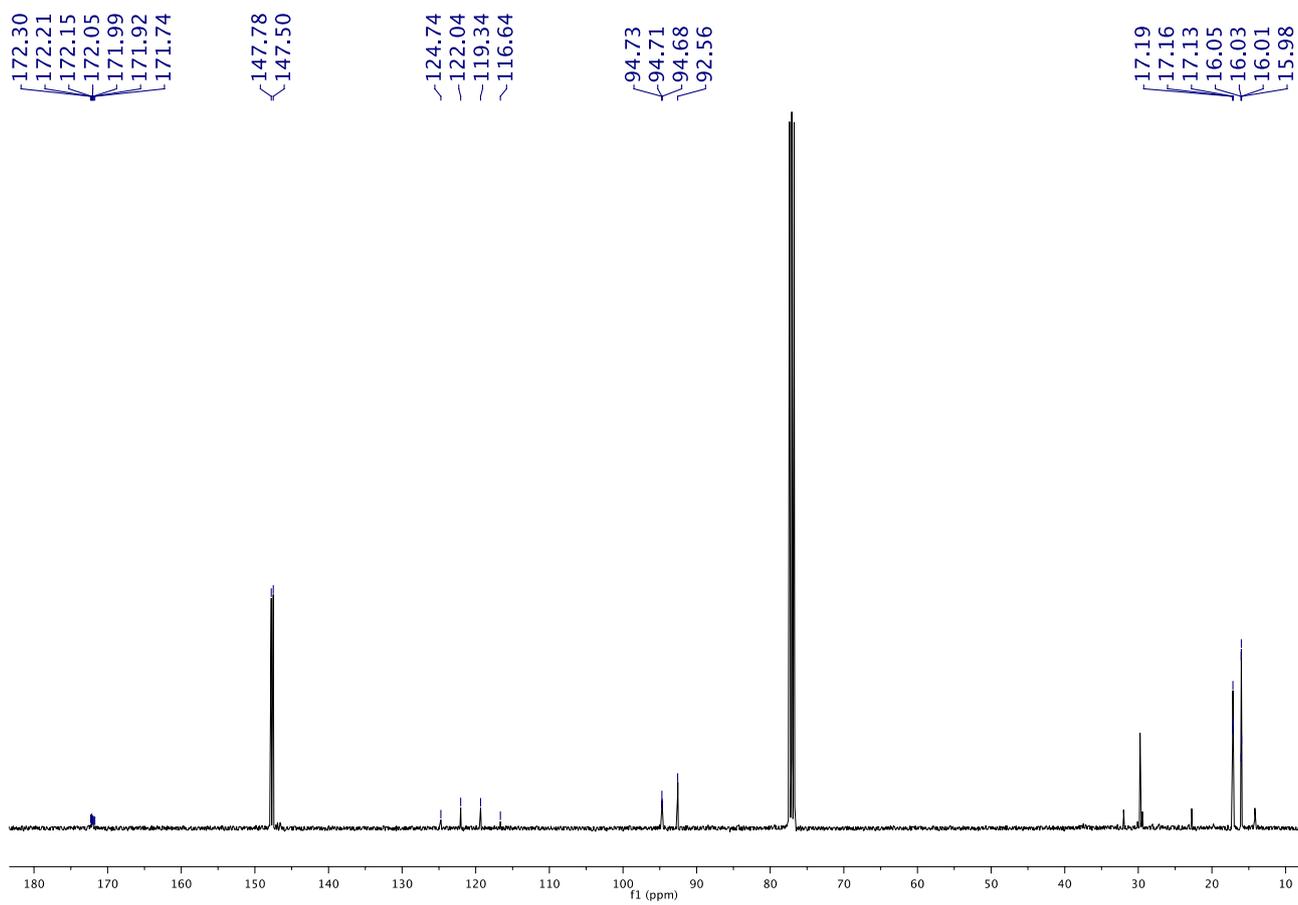
**<sup>19</sup>F NMR of 4b**



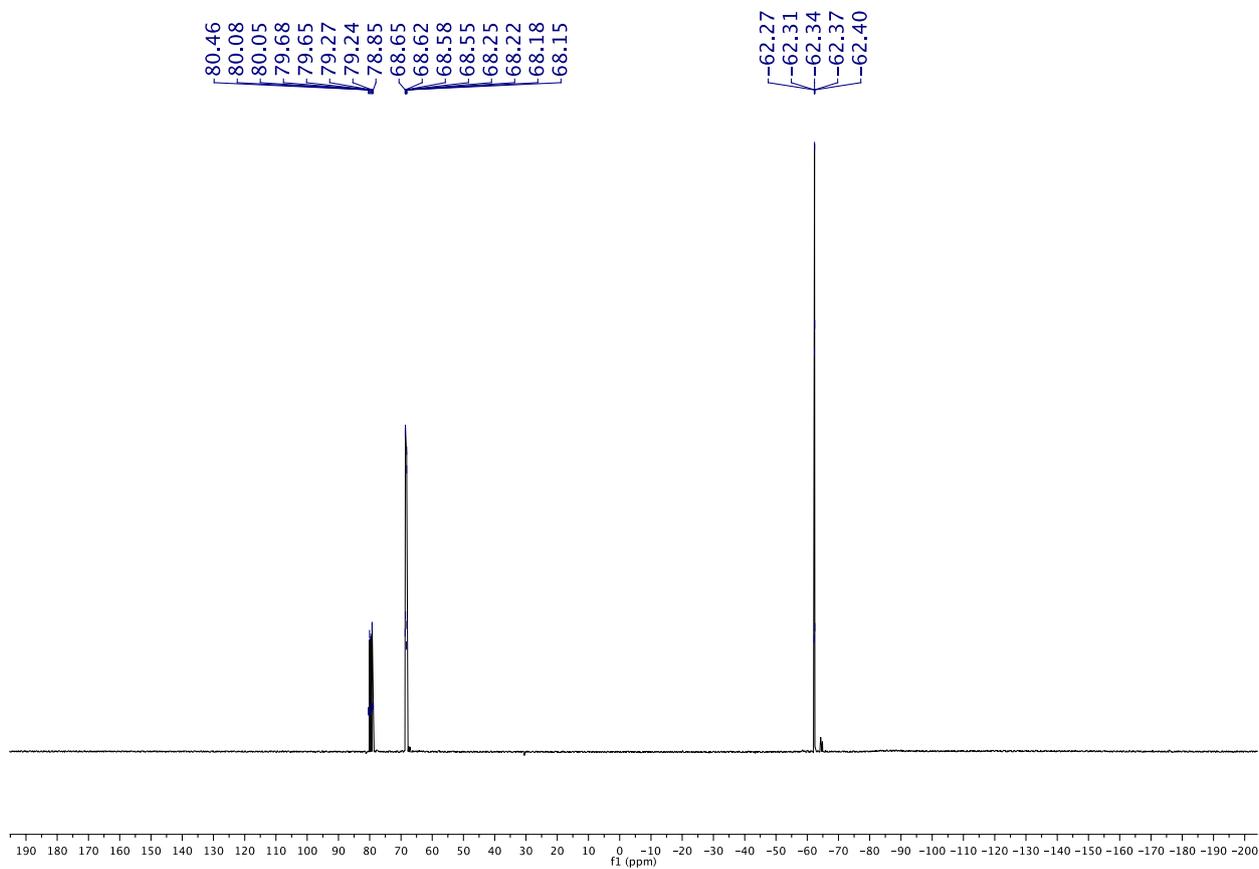
**4c**: colorless oil; Yield (78%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.80 (quintet,  $^5J_{\text{HF}(\text{eq})} = 1$  Hz, 3H), 1.85 (q,  $^5J_{\text{HF}} = 1$  Hz, 3H), 6.96 – 7.00 (AB,  $J_{\text{AB}} = 6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  16.1 (q,  $^4J_{\text{CF}} = 2$  Hz), 17.1 (quintet,  $^4J_{\text{CF}(\text{eq})} = 3$  Hz), 92.5 (q,  $^3J_{\text{CF}} = 1$  Hz), 94.7 (quintet,  $^4J_{\text{CF}(\text{eq})} = 2$  Hz), 120.7 (q,  $^1J_{\text{CF}} = 271$  Hz), 147.4, 147.9, 148.2 (qq,  $^2J_{\text{CF}} = 35$  Hz,  $^3J_{\text{CF}(\text{eq})} = 4$  Hz), 171.8 (quintet,  $^3J_{\text{CF}(\text{eq})} = 24$  Hz,  $^3J_{\text{CF}} = 6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  79.6 (9-lines, A-part), 68.5 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 150$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 10$  Hz, B<sub>4</sub>-part), -62.3 (quintet,  $^5J_{\text{FF}(\text{eq})} = 10$  Hz); HRMS (ESI)  $[\text{M}+\text{H}]^+$   $\text{C}_9\text{H}_9\text{F}_8\text{SO}$  found: 317.4226, calcd: 317.4220.



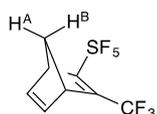
$^1\text{H}$  NMR of **4c**



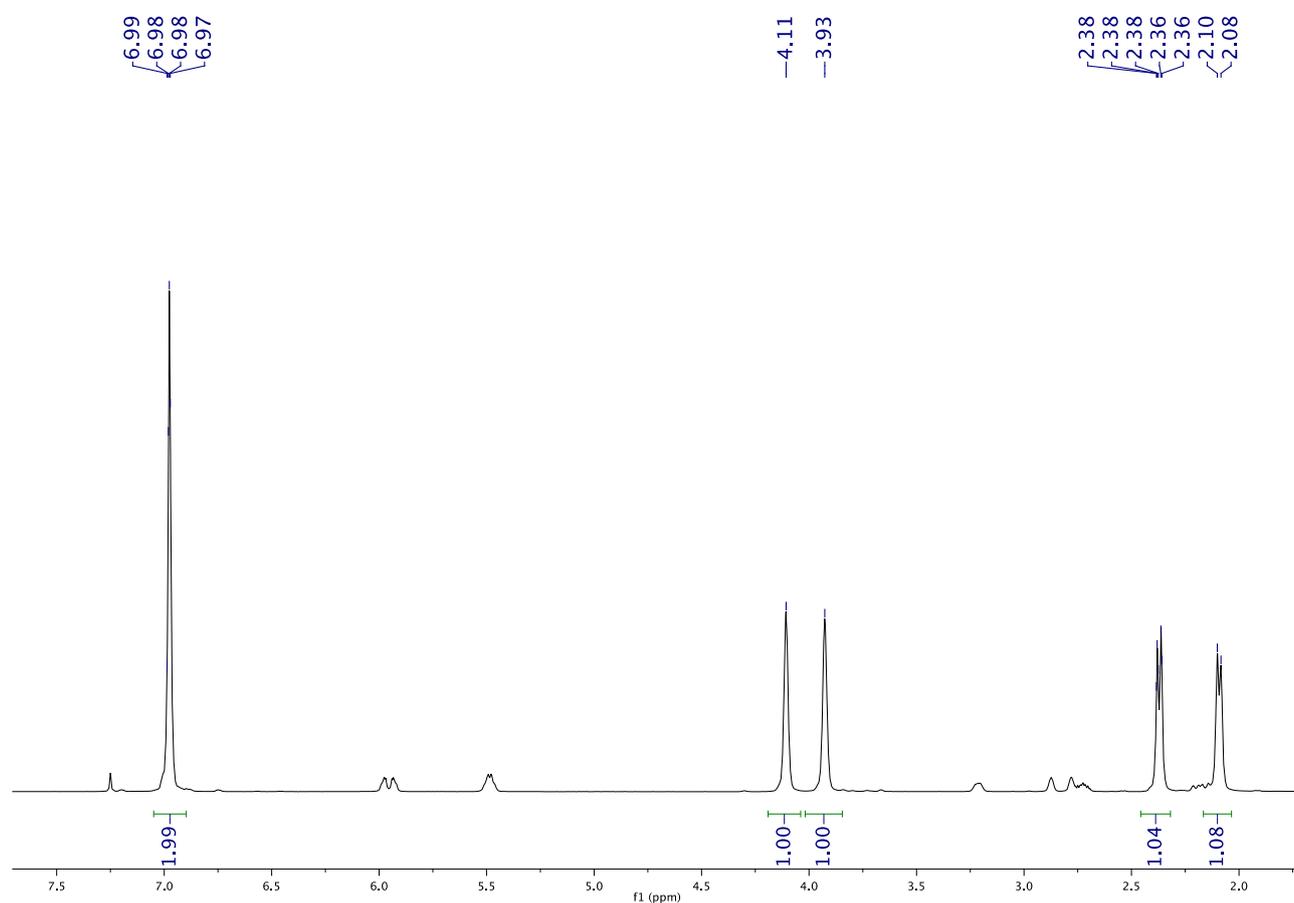
$^{13}\text{C}$  NMR of **4c**



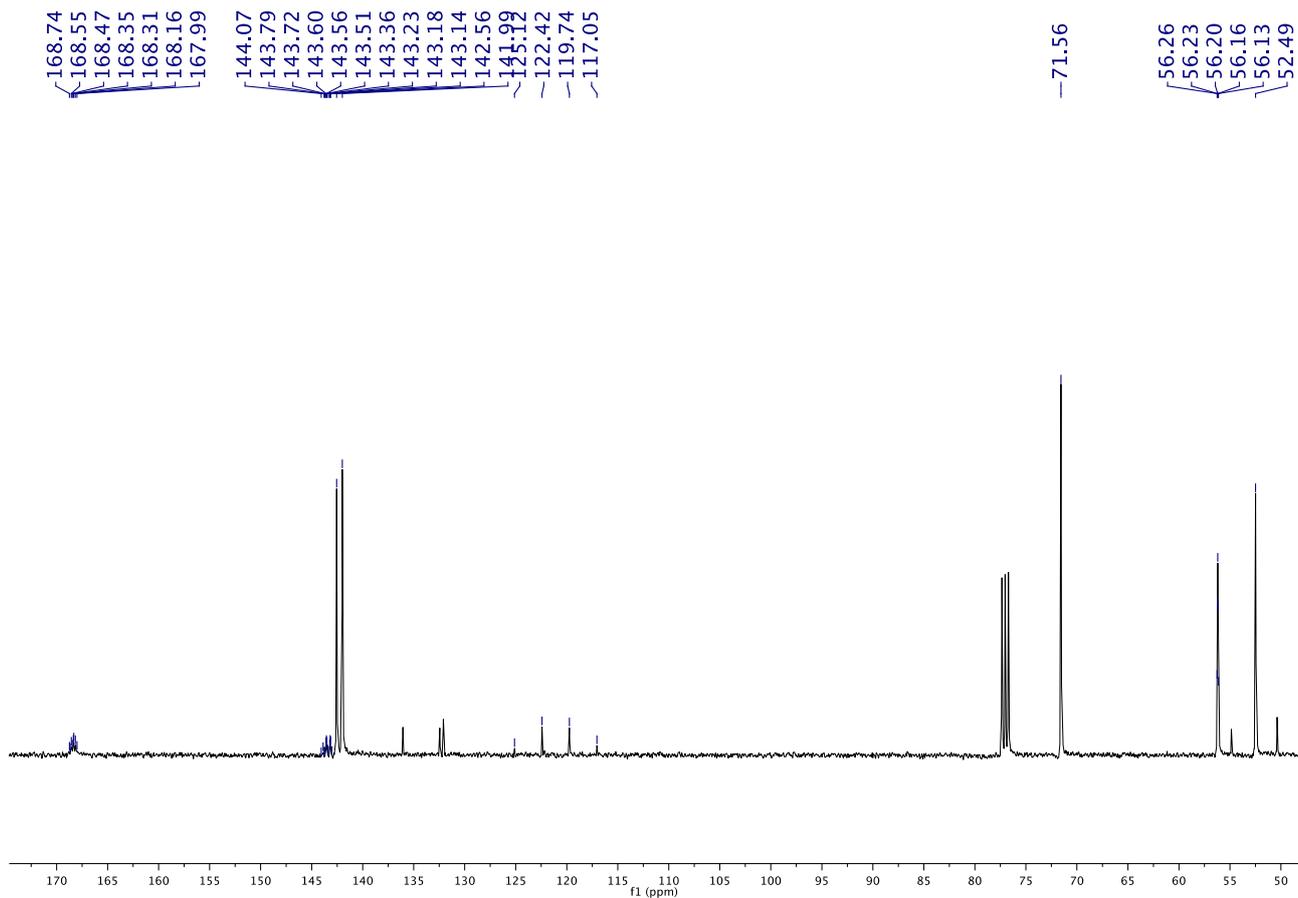
$^{19}\text{F}$  NMR of **4c**



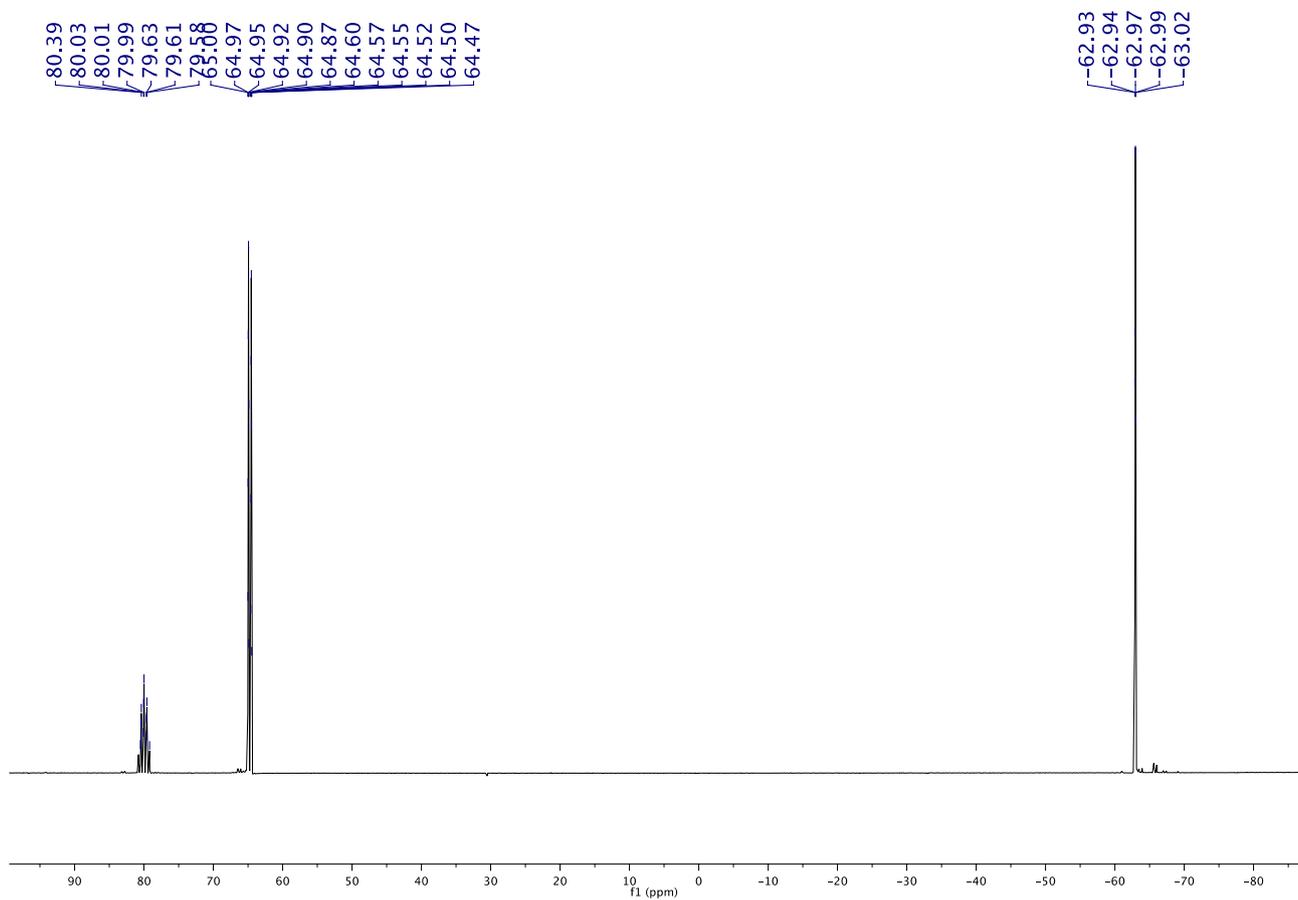
**4d**: colorless oil; Yield (98% without correction for the dicyclopentadiene impurity);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  2.09 (d,  $^2J_{\text{HH}} = 7$  Hz, C-H<sub>A</sub>, 1H); 2.37 (dq,  $^2J_{\text{HH}} = 7$  Hz,  $^5J_{\text{HF}(\text{eq})} = 1$  Hz, C-H<sub>B</sub>, 1H), 3.92 (br s, 1H), 4.11 (br s, 1H), 6.97 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  52.4, 56.2 (quintet,  $^3J_{\text{CF}(\text{eq})} = 4$  Hz), 71.5, 121.1 (q,  $^1J_{\text{CF}} = 270$  Hz), 141.9, 142.5, 143.4 (qq,  $^2J_{\text{CF}} = 38$  Hz,  $^3J_{\text{CF}(\text{eq})} = 5$  Hz), 168.3 (quintetq,  $^2J_{\text{CF}(\text{eq})} = 15$  Hz,  $^3J_{\text{CF}} = 5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  80.1 (A-Part, 9 lines), 64.7 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 151$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 10$  Hz, B<sub>4</sub>-Part), -62.9 (quintet,  $^5J_{\text{F}(\text{eq})} = 10$  Hz); HRMS (EI, 80 eV):  $[\text{M}]^+$   $\text{C}_8\text{H}_6\text{F}_8\text{S}$  calcd. 286.0063, found 286.0070.



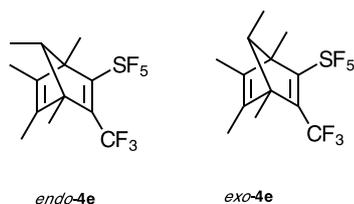
$^1\text{H}$  NMR of **4d**, impurity signals are due to the Diels-Alder dimer of cyclopentadiene (dicyclopentadiene, tricyclo[5,2,1,0<sup>2,6</sup>]deca-3,8-diene).



**<sup>13</sup>C NMR of 4d**



## $^{19}\text{F}$ NMR of **4d**

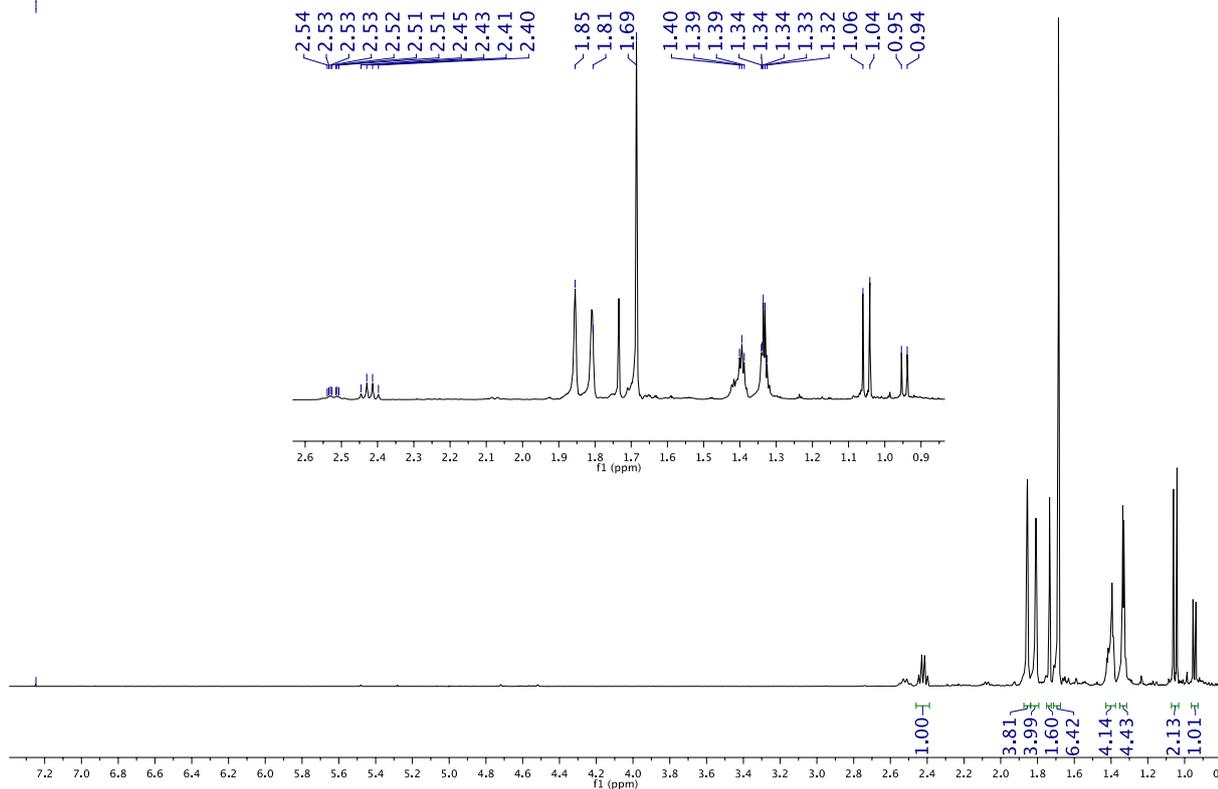


Yellowish oil; Yield (98%); HRMS (EI, 80 eV):  $[\text{M}]^{+\bullet}$   $\text{C}_{13}\text{H}_{16}\text{F}_8\text{S}$ ; calcd: 356.2126; found: 356.2122.

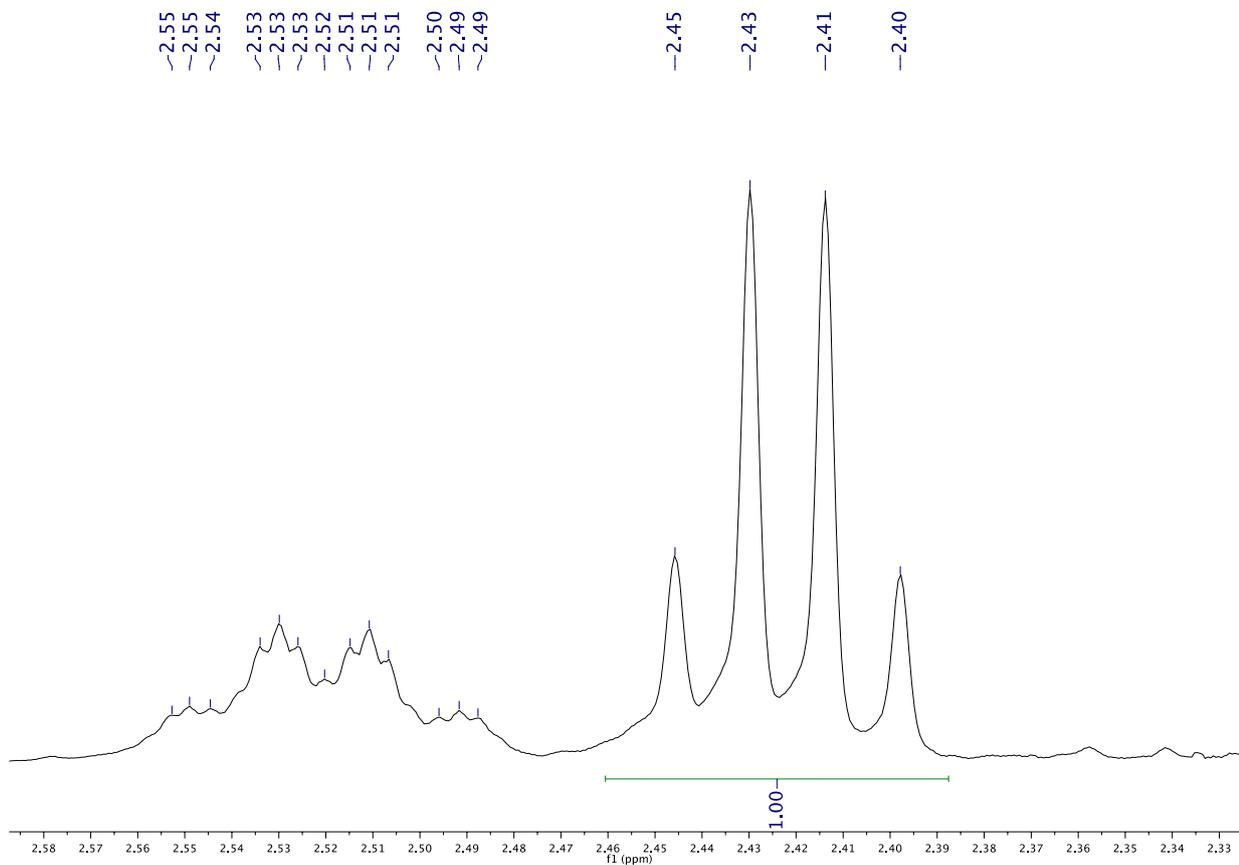
**endo-4e**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.05 (d,  $^3J_{\text{HH}} = 7$  Hz, 3H), 1.34 (q,  $^4J_{\text{HF}} = 2$  Hz, 3H), 1.42 (quintet,  $^4J_{\text{HF}(\text{eq})} = 3$  Hz, 3H), 1.80 (s, 3H,  $\text{CH}_3$ ), 1.85 (s, 3H,  $\text{CH}_3$ ), 2.52 (qq,  $^3J_{\text{HH}} = 6$  Hz,  $^5J_{\text{HF}(\text{eq})} = 1$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  9.6, 11.37, 11.38, 12.4 (q,  $^4J_{\text{CF}} = 3$  Hz), 14.1 (quintet,  $^4J_{\text{CF}(\text{eq})} = 4$  Hz), 63.7, 66.5, 80.5, 121.8 (q,  $^1J_{\text{CF}} = 271$  Hz), 141.1, 141.5, 143.0 (qq,  $^2J_{\text{CF}} = 34$  Hz,  $^3J_{\text{CF}(\text{eq})} = 5$  Hz), 168.2 (quintetqd,  $^2J_{\text{CF}(\text{eq})} = 16$  Hz,  $^3J_{\text{CF}} = 5$  Hz,  $^2J_{\text{CF}(\text{ax})} = 2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  82.4 (quintet,  $^2J_{\text{F}(\text{ax})\text{F}(\text{eq})} = 150$  Hz), 69.7 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 150$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 14$  Hz), -59.7 (quintet,  $^5J_{\text{FF}(\text{eq})} = 15$  Hz).

**exo-4e**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  0.76 (d,  $^3J_{\text{HH}} = 7$  Hz, 3H), 1.33 (q,  $^4J_{\text{HF}} = 2$  Hz, 3H), 1.40 (quintet,  $^4J_{\text{HF}(\text{eq})} = 3$  Hz, 3H), 1.66 (s, 6H), 2.44 (q,  $^3J_{\text{HH}} = 6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  10.0, 10.90, 10.92, 11.8 (q,  $^4J_{\text{CF}} = 3$  Hz), 13.6 (quintet,  $^4J_{\text{CF}(\text{eq})} = 4$  Hz), 63.8, 66.2, 78.7, 121.9 (q,  $^1J_{\text{CF}} = 271$  Hz), 134.2, 137.7, 147.7 (qq,  $^2J_{\text{CF}} = 34$  Hz,  $^3J_{\text{CF}(\text{eq})} = 5$  Hz), 172.3 (quintetqd,  $^2J_{\text{CF}(\text{eq})} = 16$  Hz,  $^3J_{\text{CF}} = 5$  Hz,  $^2J_{\text{CF}(\text{ax})} = 2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  82.3 (quintet,  $^2J_{\text{F}(\text{ax})\text{F}(\text{eq})} = 150$  Hz), 70.5 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 150$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 14$  Hz), -59.4 (quintet,  $^5J_{\text{FF}(\text{eq})} = 15$  Hz).

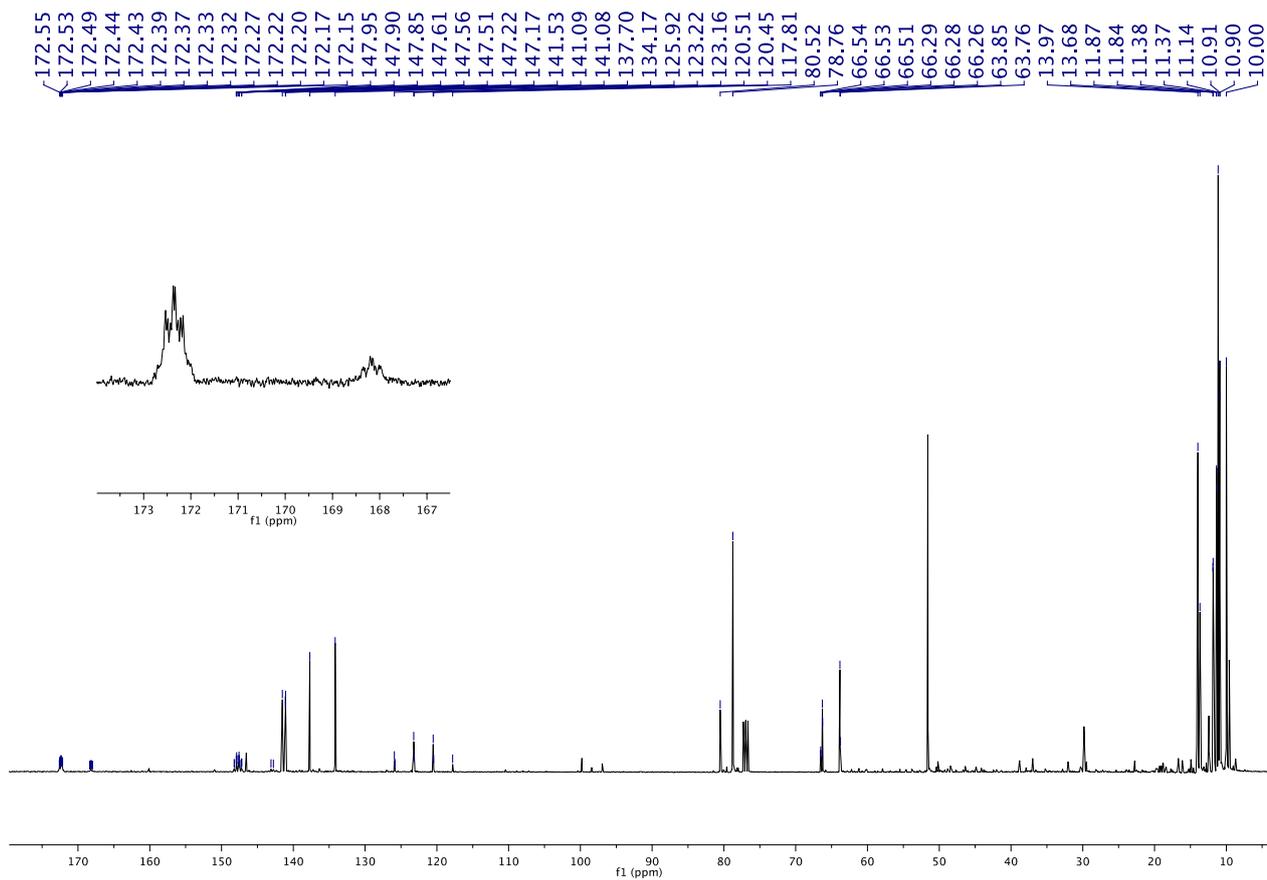
-7.25



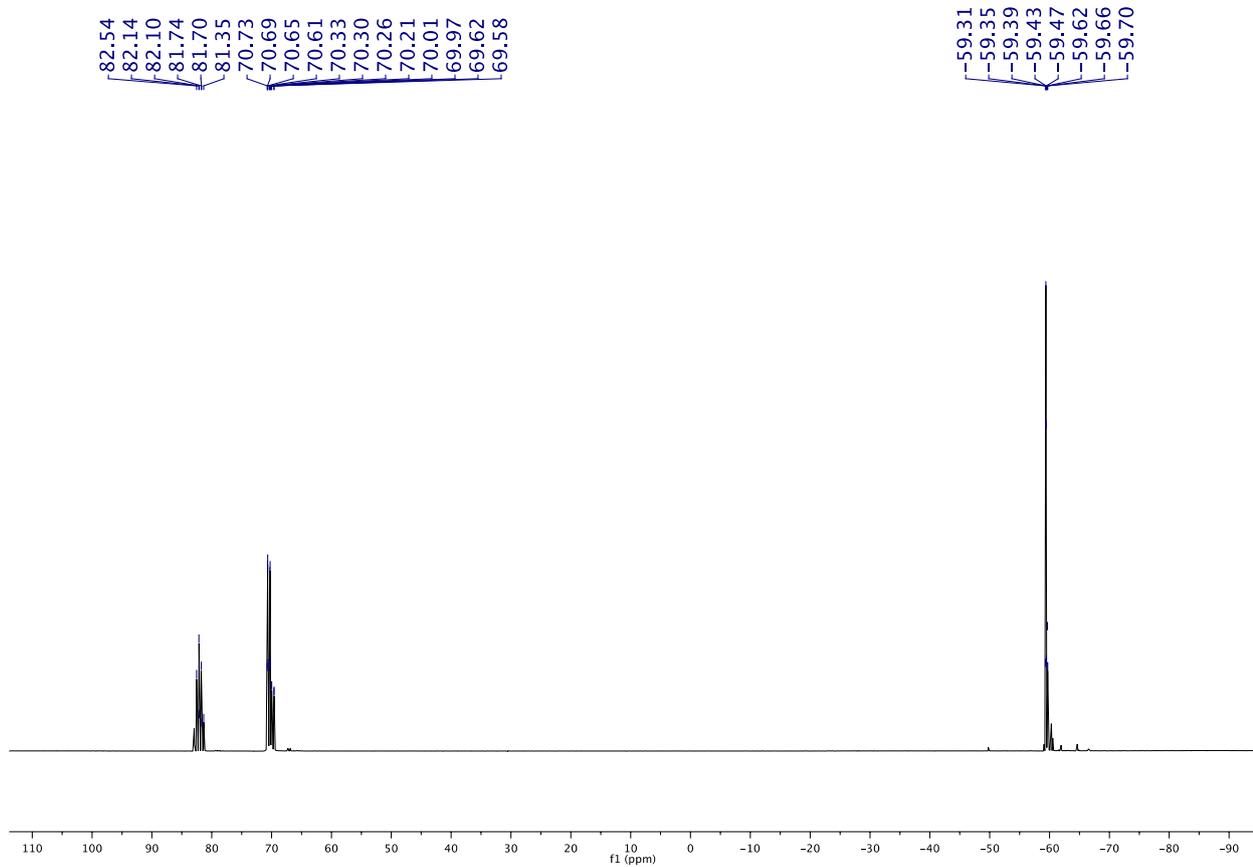
<sup>1</sup>H NMR of 4e



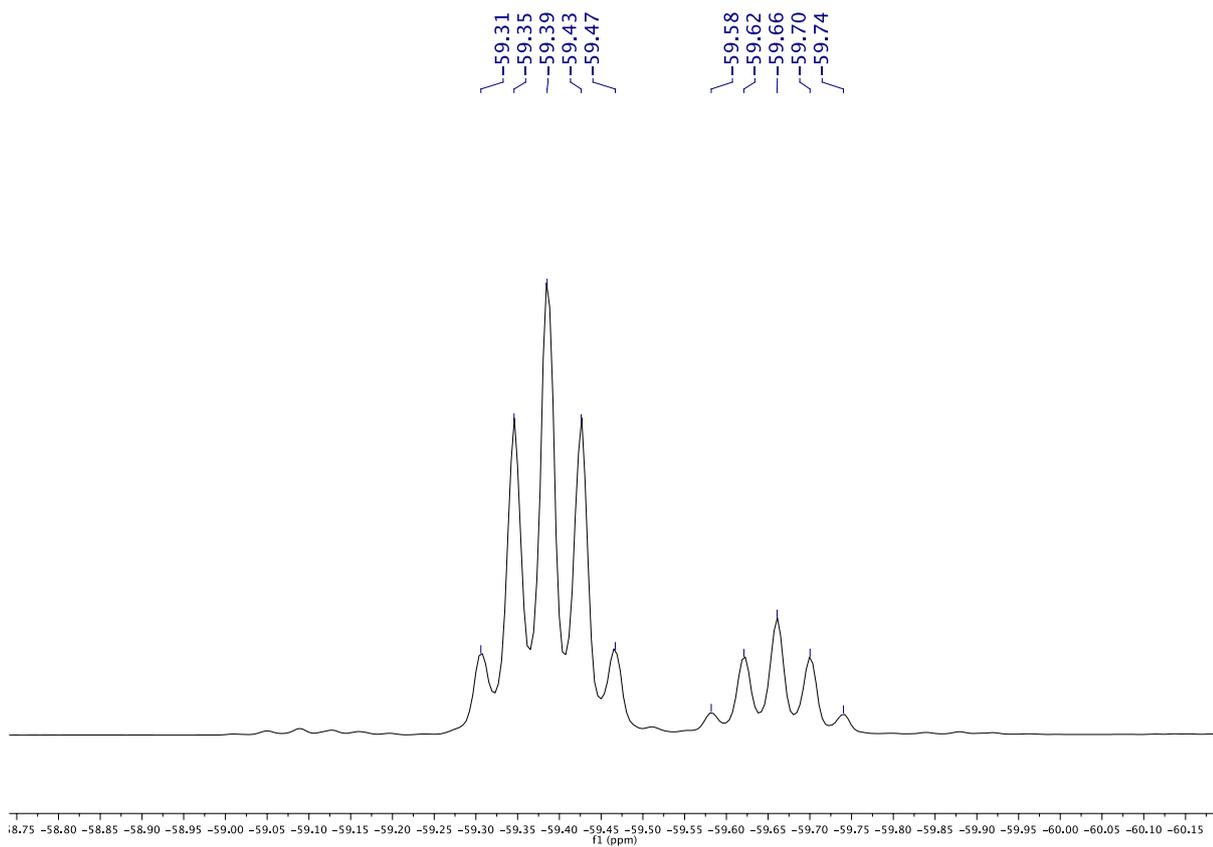
<sup>1</sup>H NMR of 4e indicating the C-H group



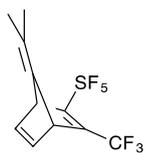
<sup>13</sup>C NMR of 4e



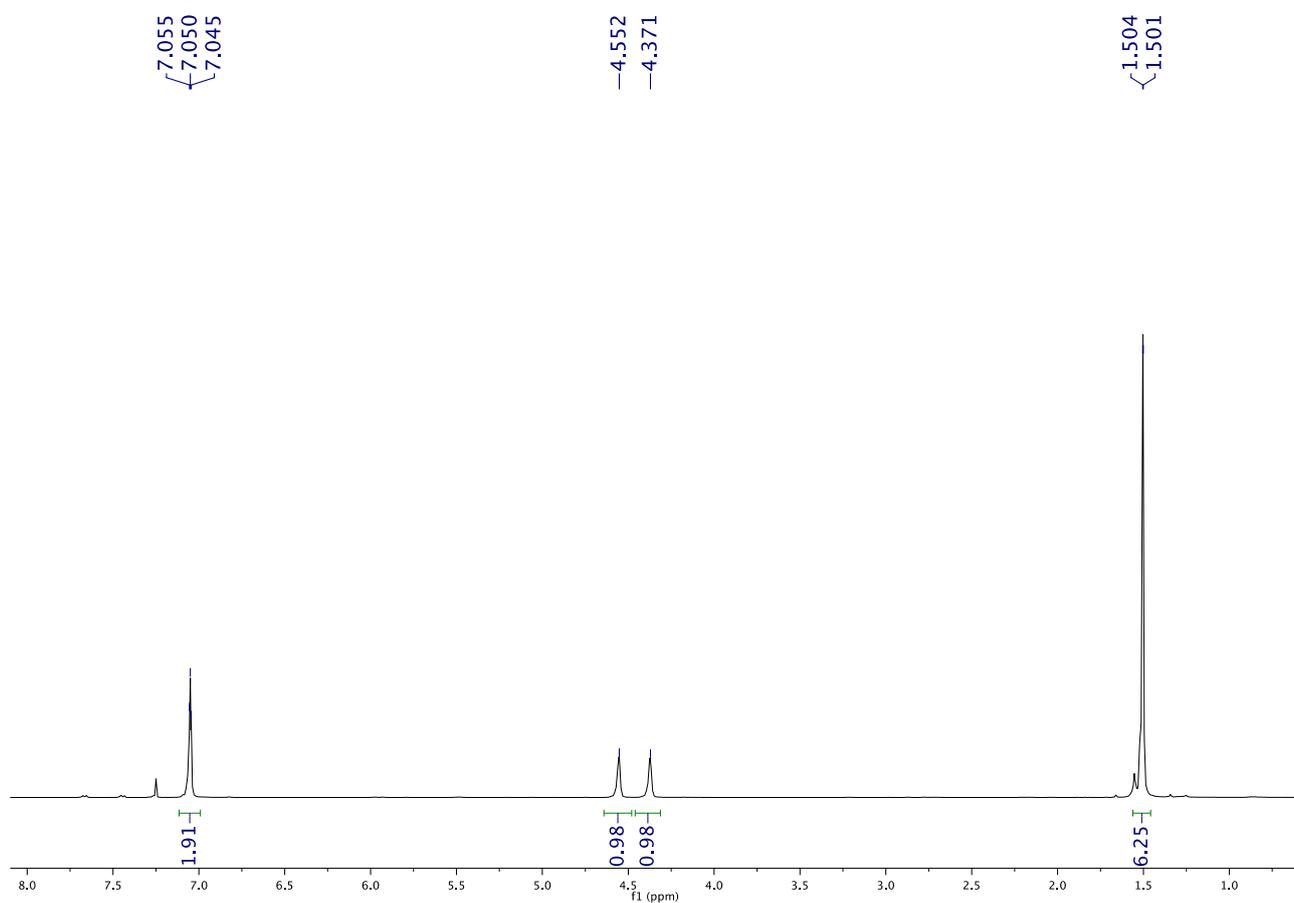
<sup>19</sup>F NMR of 4e



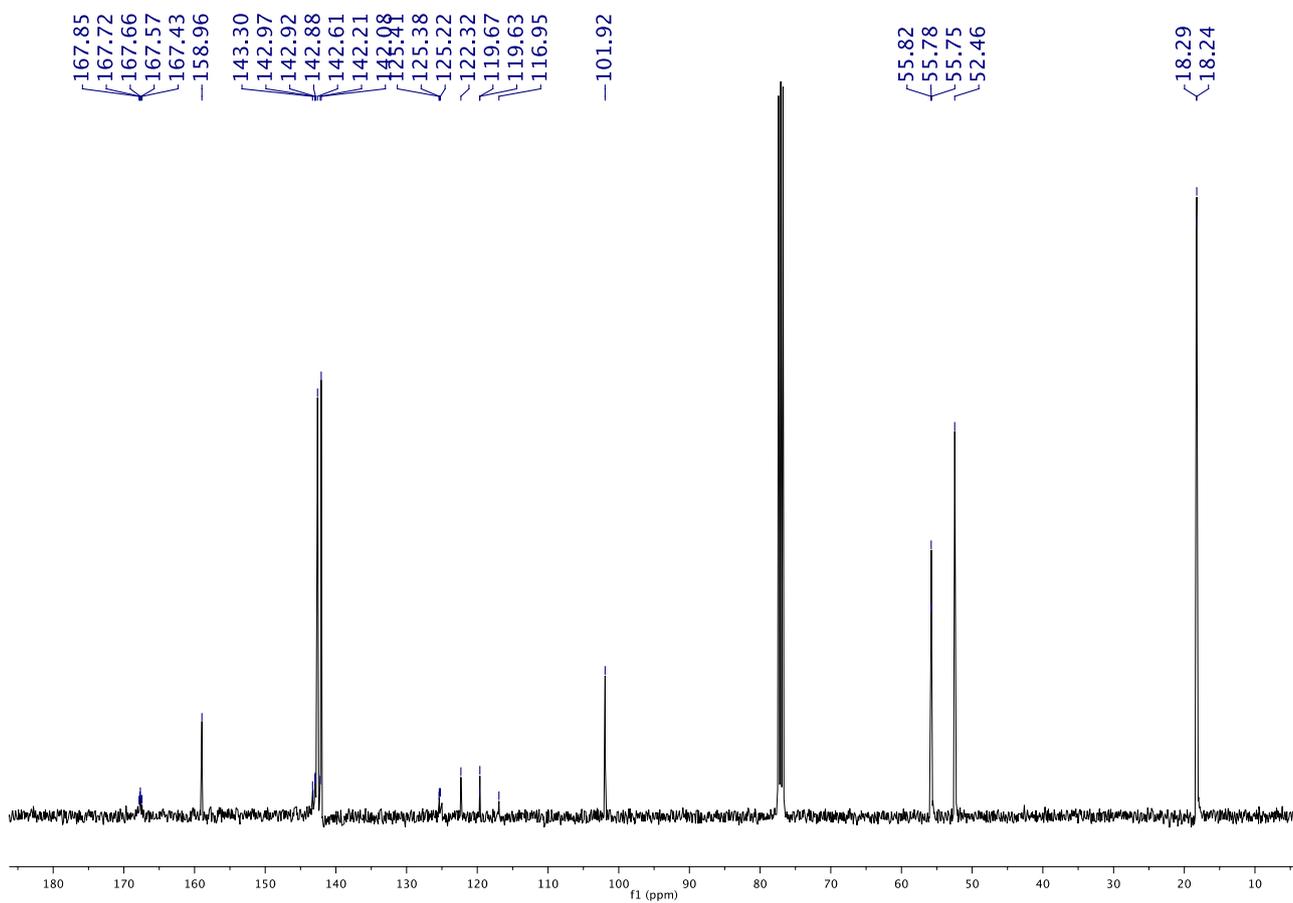
$^{19}\text{F}$  NMR of **4e** indicating the  $-\text{CF}_3$  groups of both regioisomers



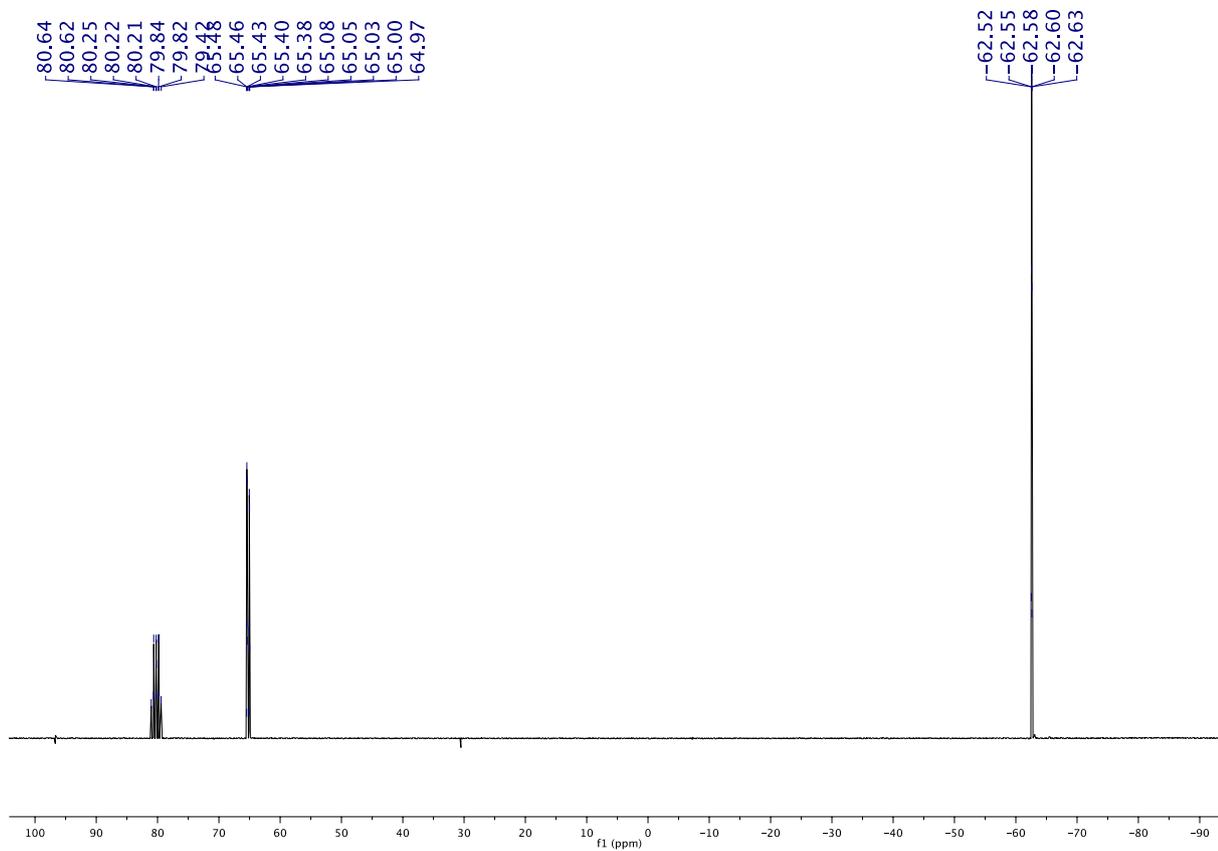
**4f**: Colorless oil; Yield (65% due to incomplete conversion);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.501 (s,  $\text{CH}_3$ , 3H), 1.504 (s,  $\text{CH}_3$ , 3H), 4.37 (br s, 1H), 4.55 (br s, 1H), 7.05 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  18.2, 18.3, 52.4, 55.7, 101.9, 120.9 (q,  $^1J_{\text{CF}} = 270$  Hz), 142.0, 142.6, 143.1 (qqintet,  $^2J_{\text{CF}} = 36$  Hz,  $^3J_{\text{CF}(\text{eq})} = 4$  Hz), 158.9, 167.6 (quintetq,  $^2J_{\text{CF}(\text{eq})} = 18$  Hz,  $^3J_{\text{CF}} = 4$  Hz);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  80.2 (9-lines, A-part), 65.2 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 150$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 11$  Hz, B<sub>4</sub>-part), -62.5 (quintet,  $^5J_{\text{FF}(\text{eq})} = 11$  Hz); HRMS (EI, 80 eV):  $[\text{M}]^{+\bullet}$   $\text{C}_{11}\text{H}_{10}\text{F}_8\text{S}$ ; calcd: 326.0375; found: 326.0367.



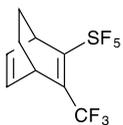
$^1\text{H NMR}$  of **4f**



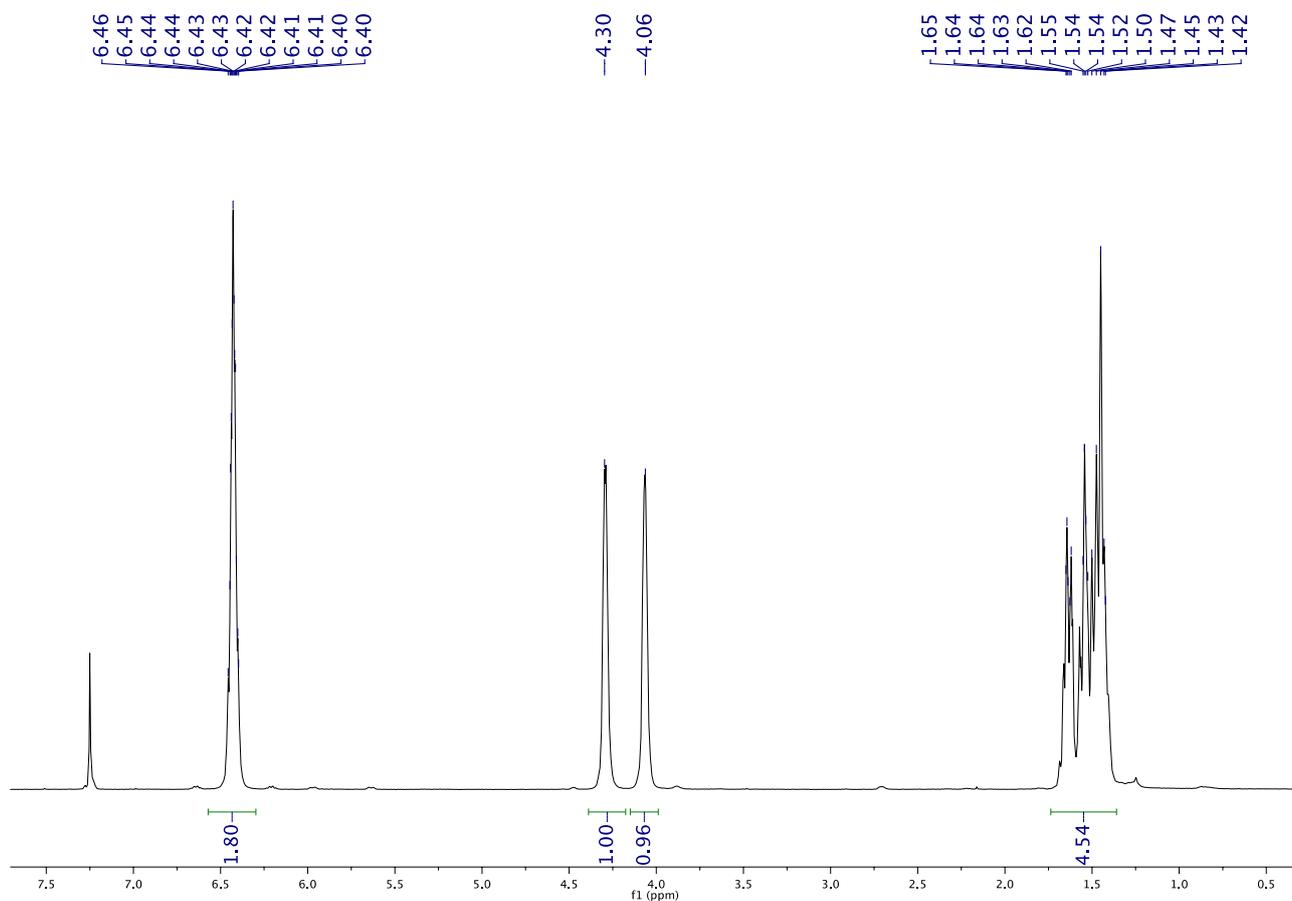
<sup>13</sup>C NMR of 4f



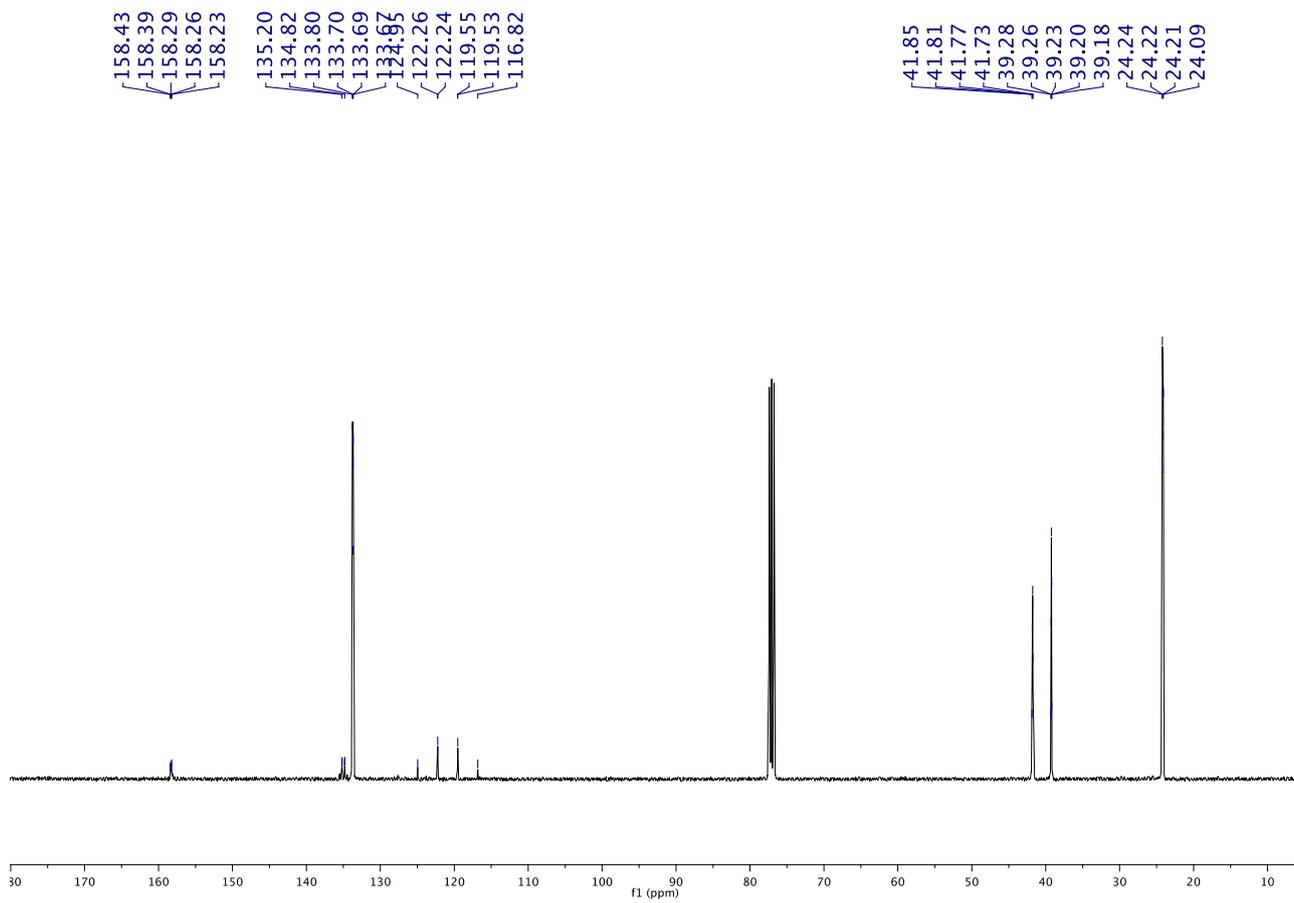
<sup>19</sup>F NMR of 4f



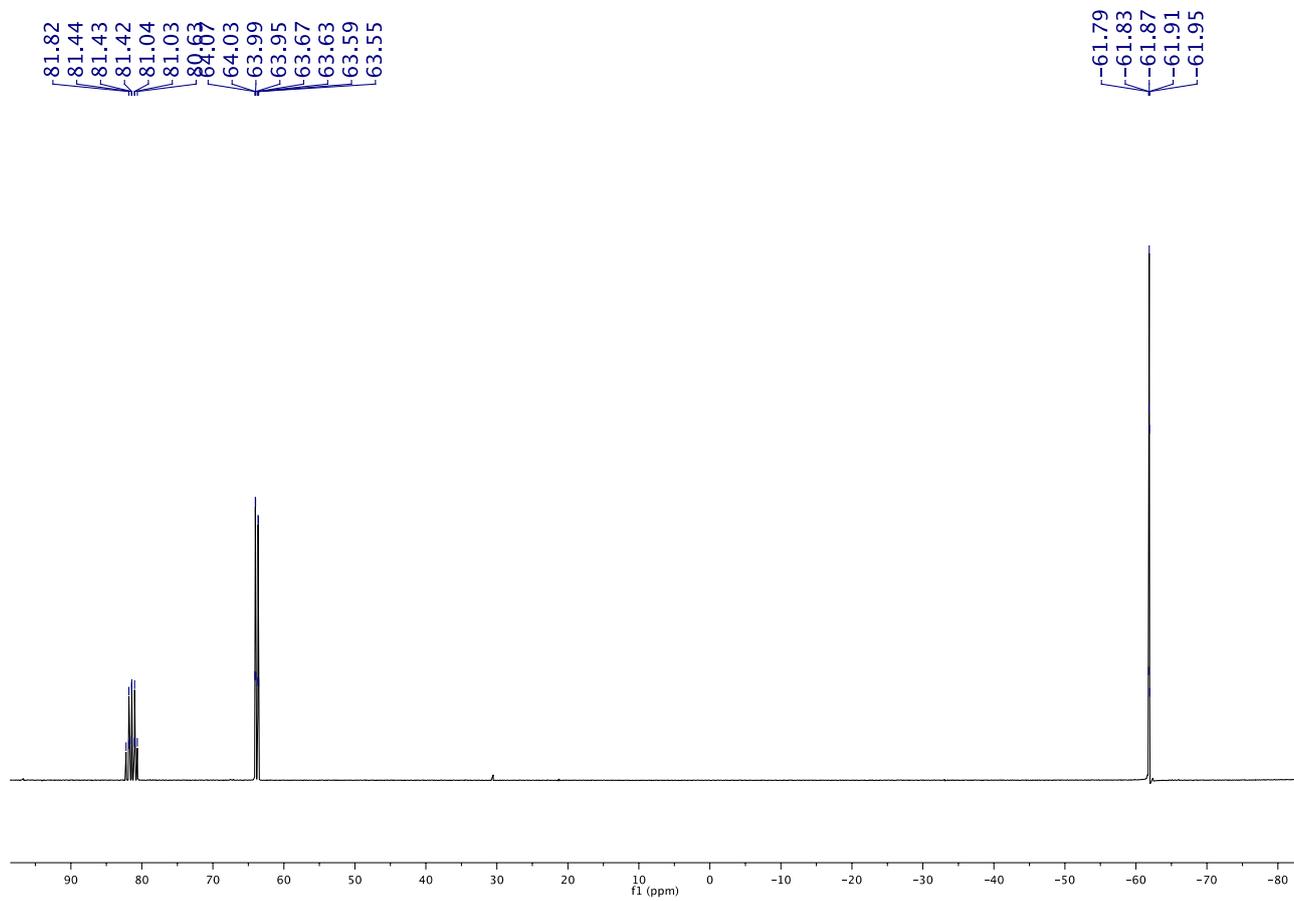
**4g**: yellowish oil; Yield (97%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  1.55 (m, 4H), 4.06 (br s, 1H), 4.29 (quintet,  $^4J_{\text{HF}(\text{eq})} = 2$  Hz, 1H), 6.42 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  24.0, 24.2, 39.2, 41.7 (quintet,  $^3J_{\text{CF}(\text{eq})} = 4$  Hz), 120.8 (q,  $^1J_{\text{CF}} = 272$  Hz), 133.6, 133.8, 134.9 (quintet,  $^2J_{\text{CF}} = 35$  Hz,  $^3J_{\text{CF}(\text{eq})} = 3$  Hz), 158.2 (quintetq,  $^3J_{\text{CF}(\text{eq})} = 17$  Hz,  $^3J_{\text{CF}} = 3$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$  81.4 (9-lines, A-part), 63.7 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 152$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 10$  Hz, B4-part), -61.8 (quintet,  $^5J_{\text{FF}(\text{eq})} = 10$  Hz); HRMS (EI, 80 eV):  $[\text{M}]^+$   $\text{C}_9\text{H}_8\text{F}_8\text{S}$ ; calcd: 300.0219; found: 300.0224.



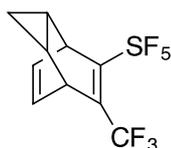
$^1\text{H}$  NMR of **4g**



<sup>13</sup>C NMR of 4g

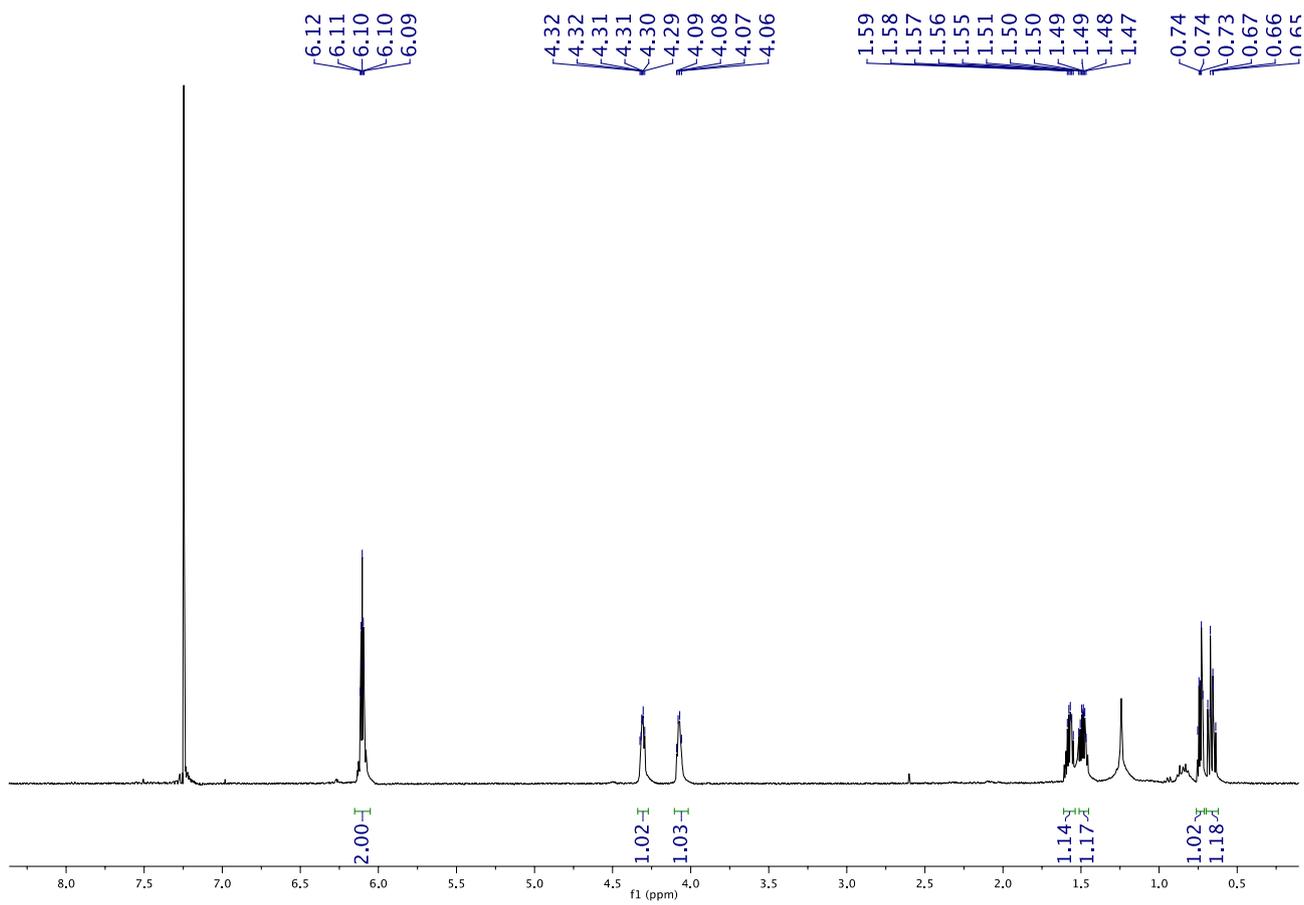


<sup>19</sup>F NMR of 4g

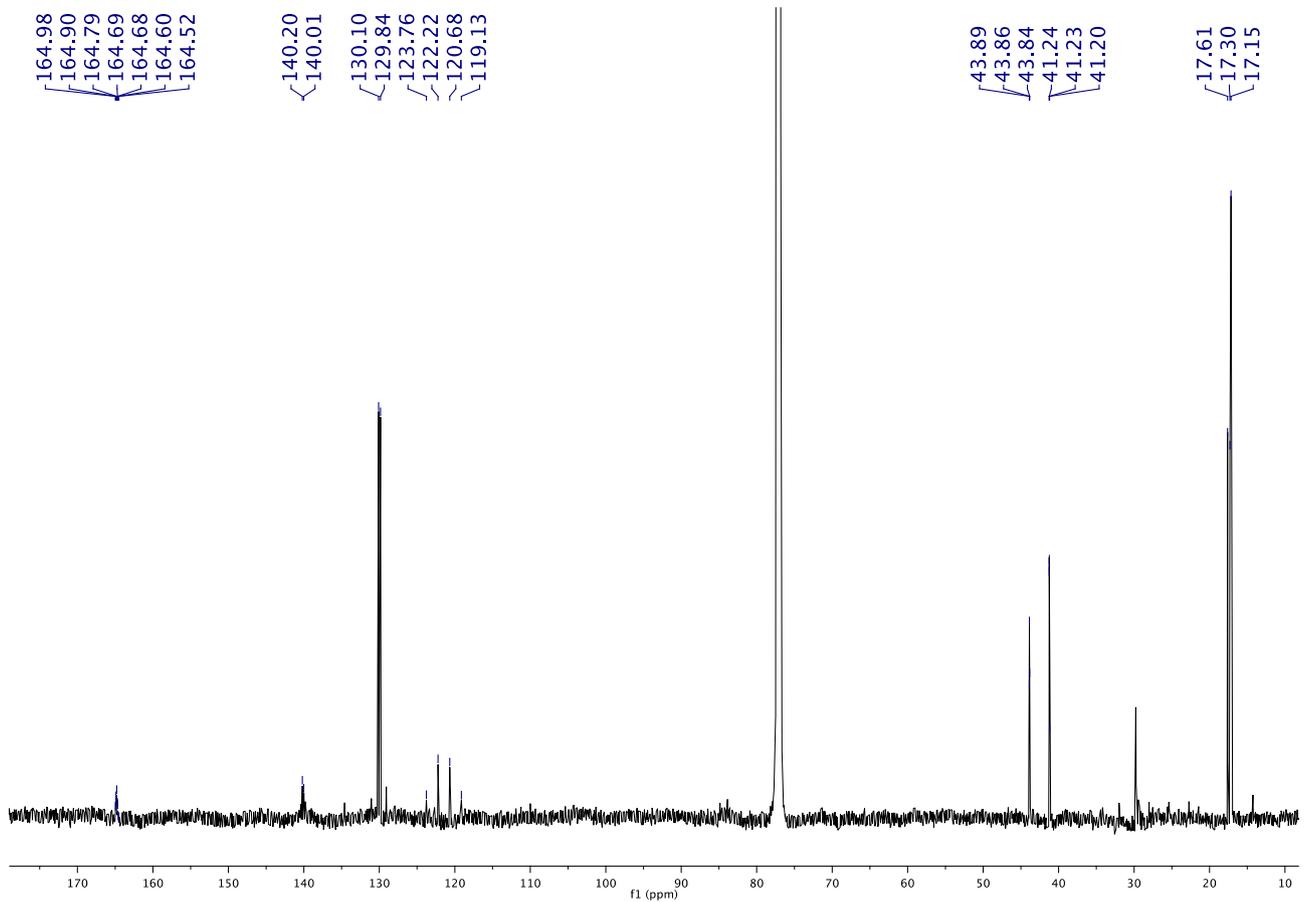


Diene **3h** (1 mmol, 100 mg) was dissolved in dry toluene (2 mL) in a round-bottomed flask with a young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne **2** (1.2 mmol, 275 mg) was condensed to the reaction mixture and slowly warmed to room temperature within 10 min. After 24 h of stirring at 110°C all volatile materials were removed under reduced pressure. The crude product was purified by fractional condensation under vacuum through traps kept at -30, -78 and -196 °C. The product **4h** (yield 37%, 0.41 mmol, 128 mg, due to low conversion) was collected in the -30 °C trap.

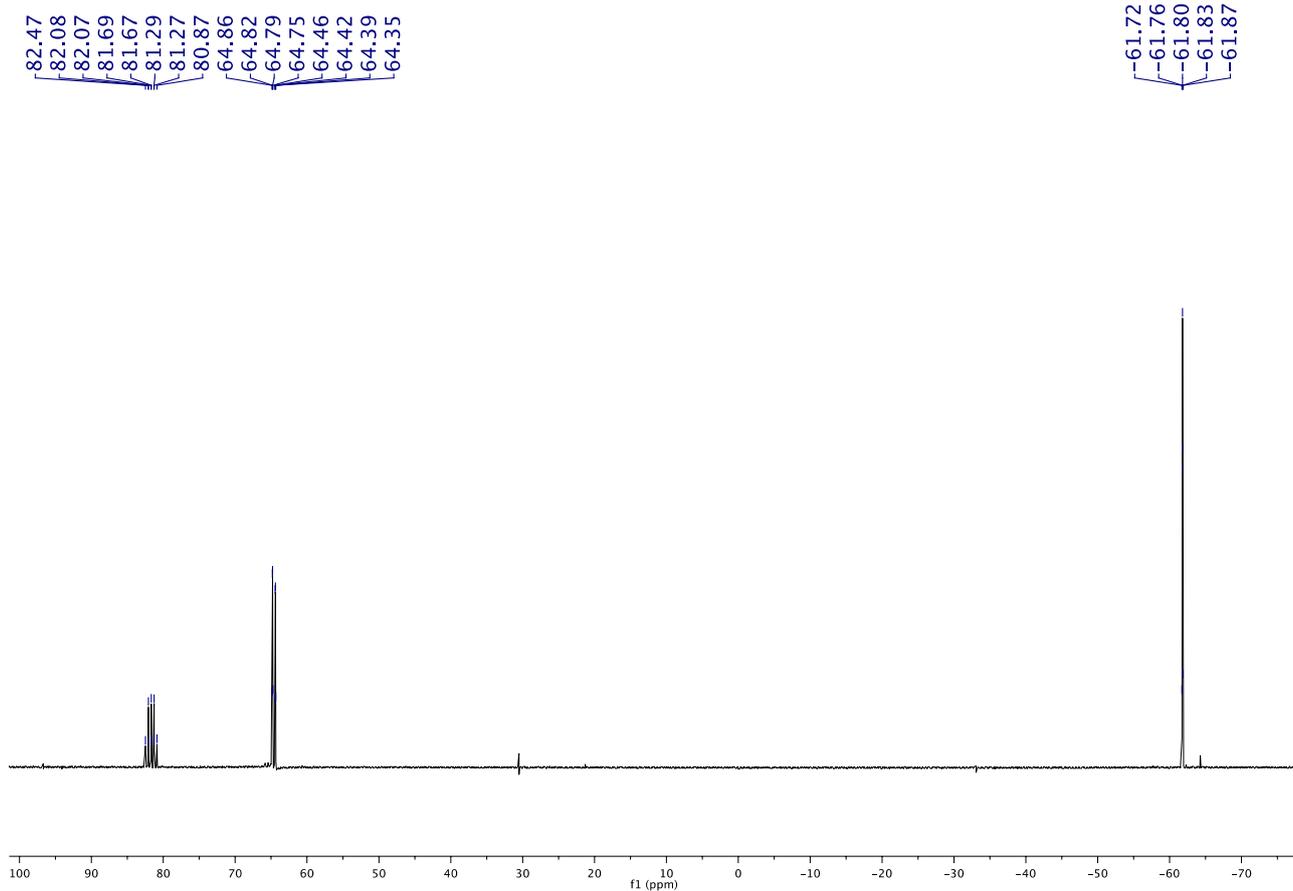
**4h**: Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta_{\text{H}}$  0.71 (dd,  $^2J_{\text{HH}} = 7$  Hz,  $^3J_{\text{HH}} = 4$  Hz, 1H), 0.74 (dd,  $^2J_{\text{HH}} = 7$  Hz,  $^3J_{\text{HH}} = 4$  Hz, 1H) 1.49 (m, 1H), 1.58 (m, 1H), 4.08 (q,  $^4J_{\text{HF}} = 2$  Hz, 1H), 4.31 (quintet,  $^4J_{\text{HF}(\text{eq})} = 2.0$  Hz, 1H), 6.11 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta_{\text{C}}$  17.1, 17.3, 17.6, 41.2 (q,  $^3J_{\text{CF}} = 3$  Hz), 43.8 (quintet,  $^3J_{\text{CF}(\text{eq})} = 3$  Hz), 121.4 (q,  $^1J_{\text{CF}} = 273$  Hz), 129.8, 130.1, 140.1 (qq,  $^2J_{\text{CF}} = 34$  Hz,  $^3J_{\text{CF}(\text{eq})} = 2$  Hz), 164.8 (quintetq,  $^2J_{\text{CF}(\text{eq})} = 18$  Hz,  $^3J_{\text{CF}(\text{eq})} = 2$  Hz);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz)  $\delta_{\text{F}}$  81.7 (9 lines, A-part, 1F), 64.6 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 165$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 14$  Hz, 4F, B<sub>4</sub>-part), -61.7 (quintet,  $^5J_{\text{FF}(\text{eq})} = 14$  Hz, 3F); HRMS (EI, 80 eV): 312 [ $\text{M}^{+}$ ]  $\text{C}_{10}\text{H}_8\text{F}_8\text{S}$ ; calcd: 312.0219; found: 312.0213.



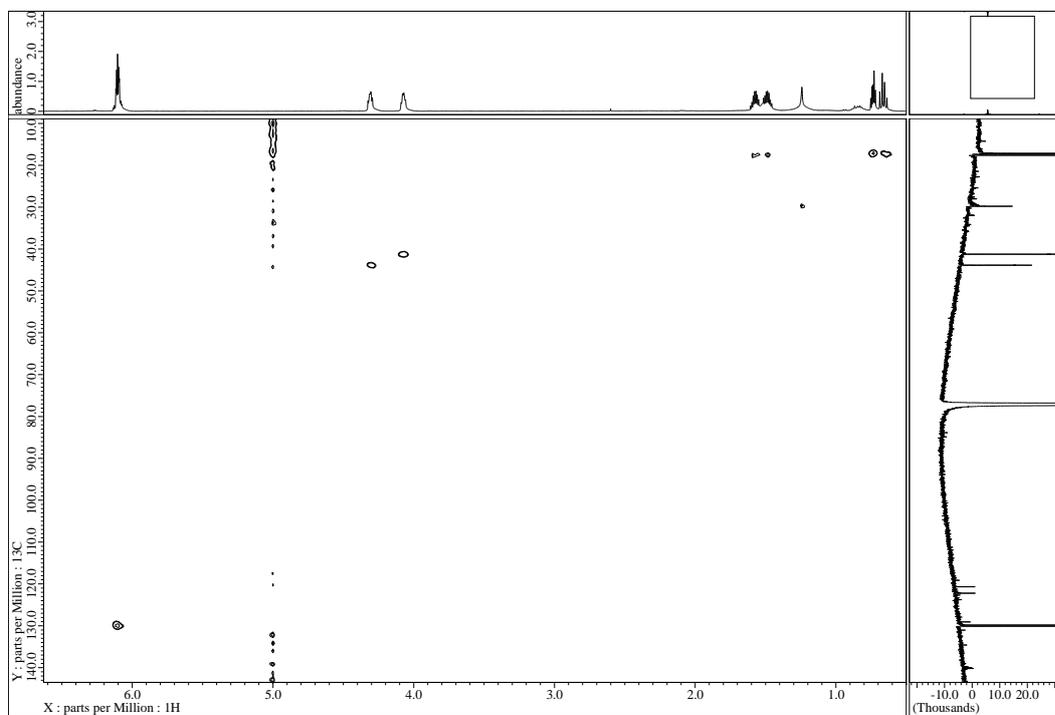
<sup>1</sup>H NMR of 4h



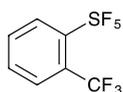
<sup>13</sup>C NMR of 4h



$^{19}\text{F}$  NMR of **4h**

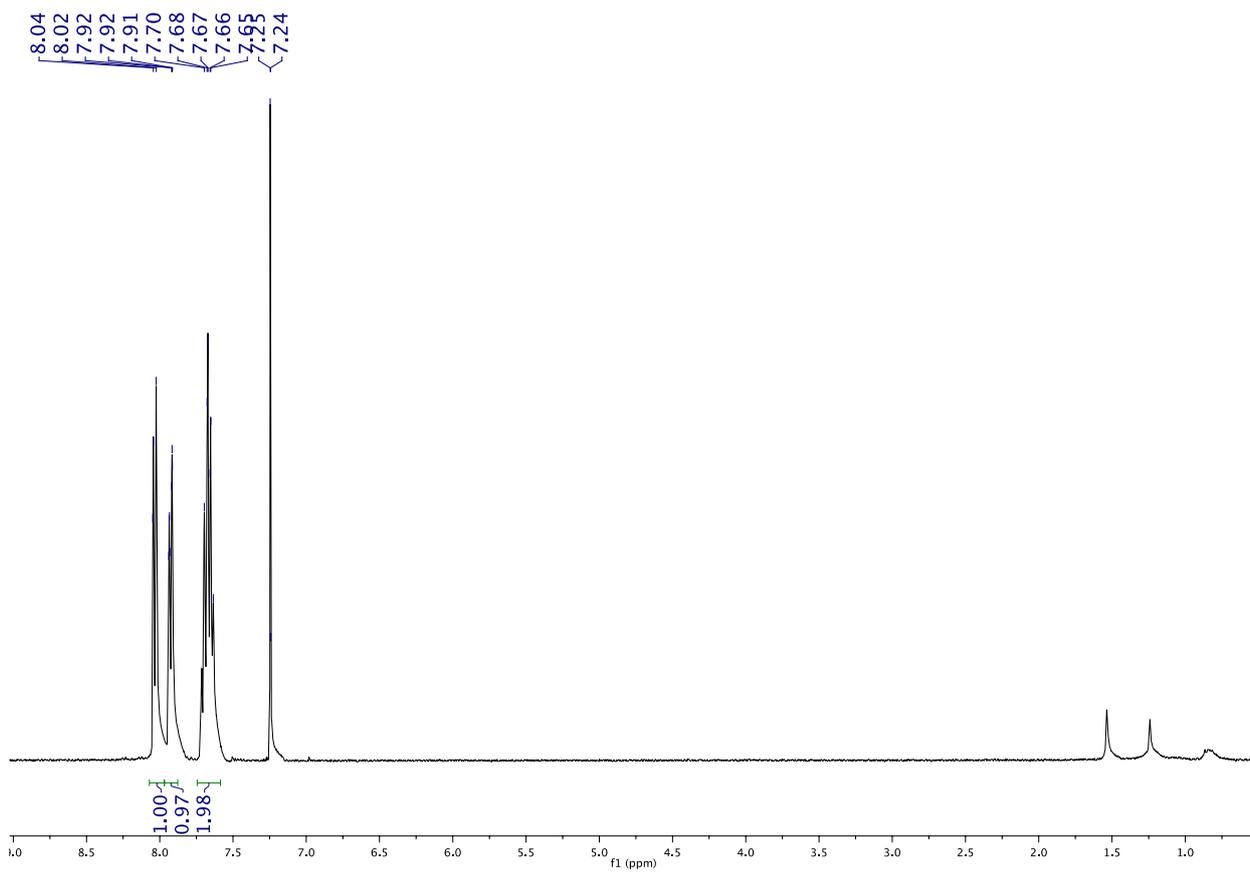


$^1\text{H}$ - $^{13}\text{C}$  HMQC of **4h**

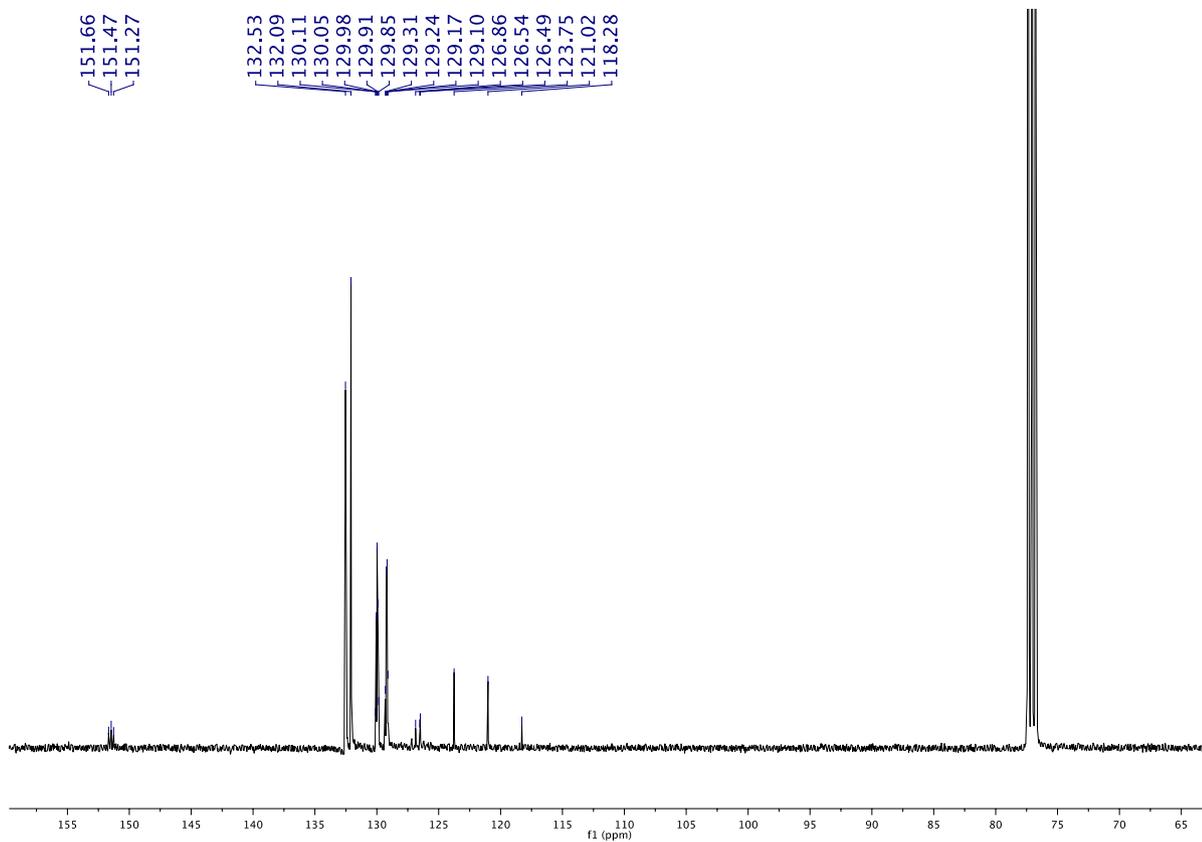


2H-pyran-2-on **3i** (1 mmol, 100 mg) was dissolved in dry toluene (2 mL) in a round-bottomed flask equipped with a young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne **2** (1.2 mmol, 275 mg) was condensed to the reaction mixture and slowly warmed up to room temperature within 10 min. After 48 h of stirring at 120°C all volatile materials were removed under reduced pressure. The crude product was purified by flash column chromatography using *n*-pentane as eluent ( $R_f = 0,5$ ) affording the pure benzene **4i** in 54% (0.56 mmol, 154 mg) yield due to low conversion.

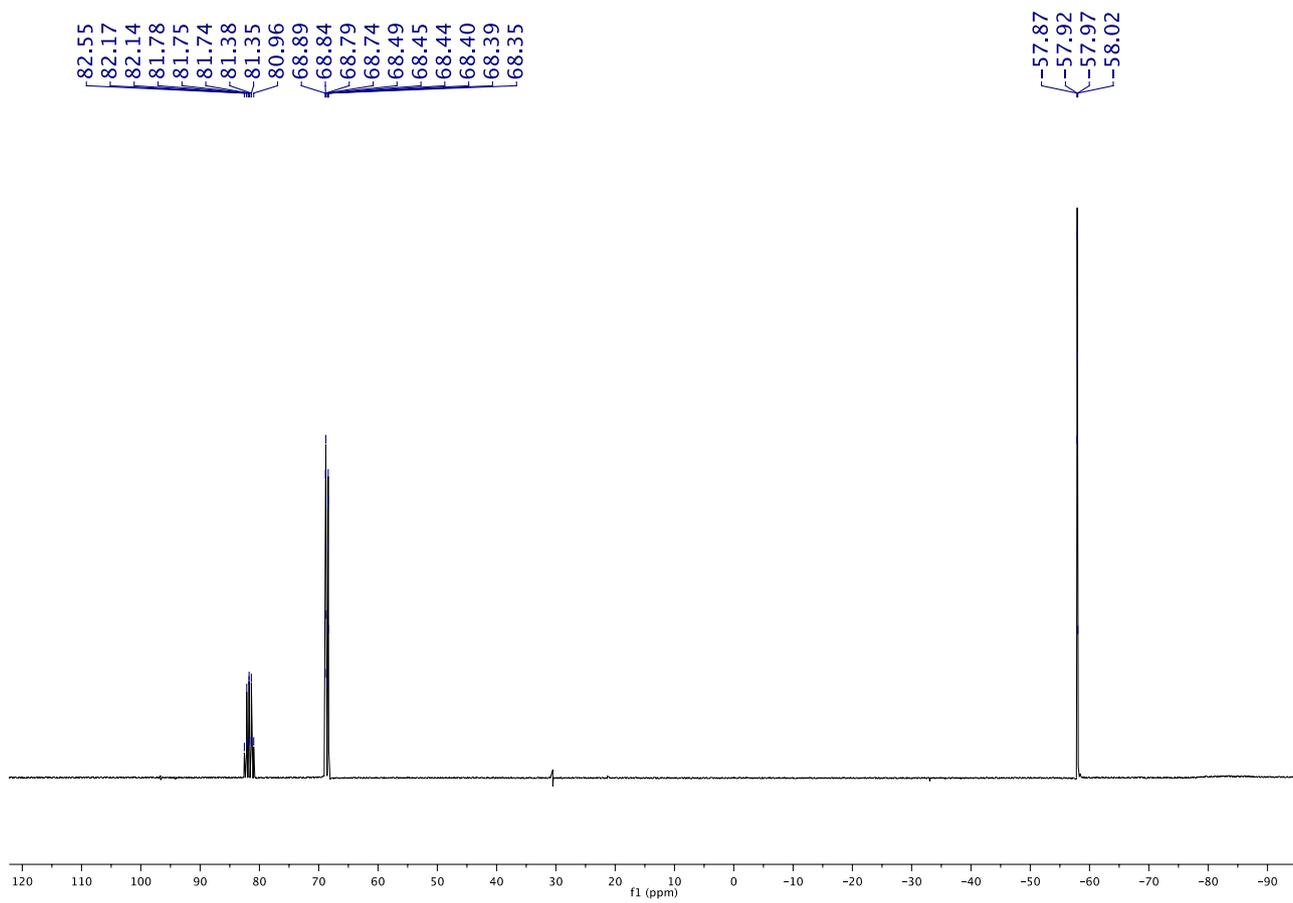
**4i**: Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta_H$  7.65 (t,  $^3J_{\text{HH}} = 7$  Hz, 1H), 7.70 (t,  $^3J_{\text{HH}} = 7$  Hz, 1H), 7.93 (d,  $^3J_{\text{HH}} = 8$  Hz, 1H), 8.02 (d,  $^3J_{\text{HH}} = 8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta_C$  122.5 (q,  $^1J_{\text{CF}} = 269$  Hz), 126.5 (q,  $^2J_{\text{CF}} = 33$  Hz), 129.2 (q,  $^3J_{\text{CF}} = 8$  Hz), 129.9 (quintet,  $^3J_{\text{CF}(\text{eq})} = 6$  Hz) 132.1, 132.5, 151.1 (quintet,  $^2J_{\text{CF}(\text{eq})} = 21$  Hz);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz)  $\delta_F$  81.7 (9 lines, A-part, 1F), 68.6 (dq,  $^2J_{\text{F}(\text{eq})\text{F}(\text{ax})} = 149$  Hz,  $^5J_{\text{F}(\text{eq})\text{F}} = 18$  Hz, 4F, B4-part), -57.9 (quintet,  $^5J_{\text{FF}(\text{eq})} = 18$  Hz, 3F); HRMS (EI, 80 eV): 271 [ $\text{M}^+$ ]  $\text{C}_7\text{H}_4\text{F}_8\text{S}$ ; calcd: 271.9906; found: 271.9910.



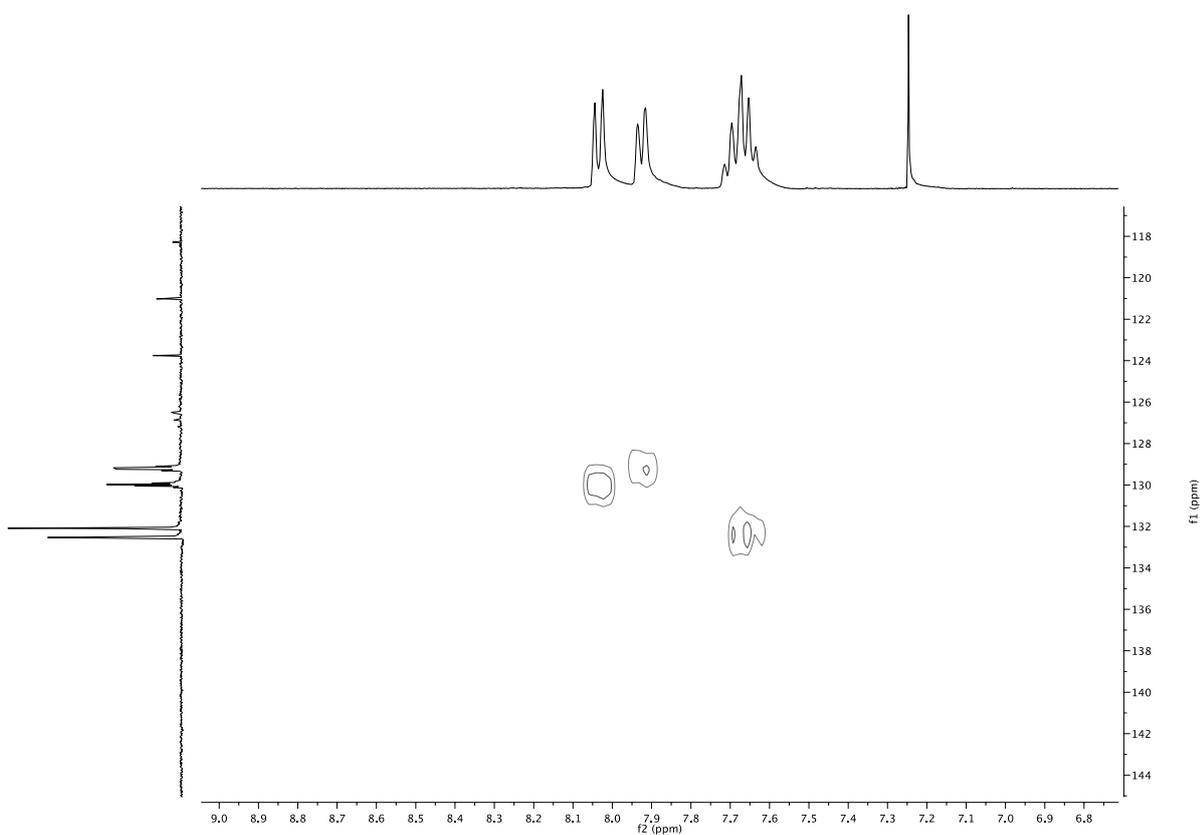
<sup>1</sup>H NMR of **4i**



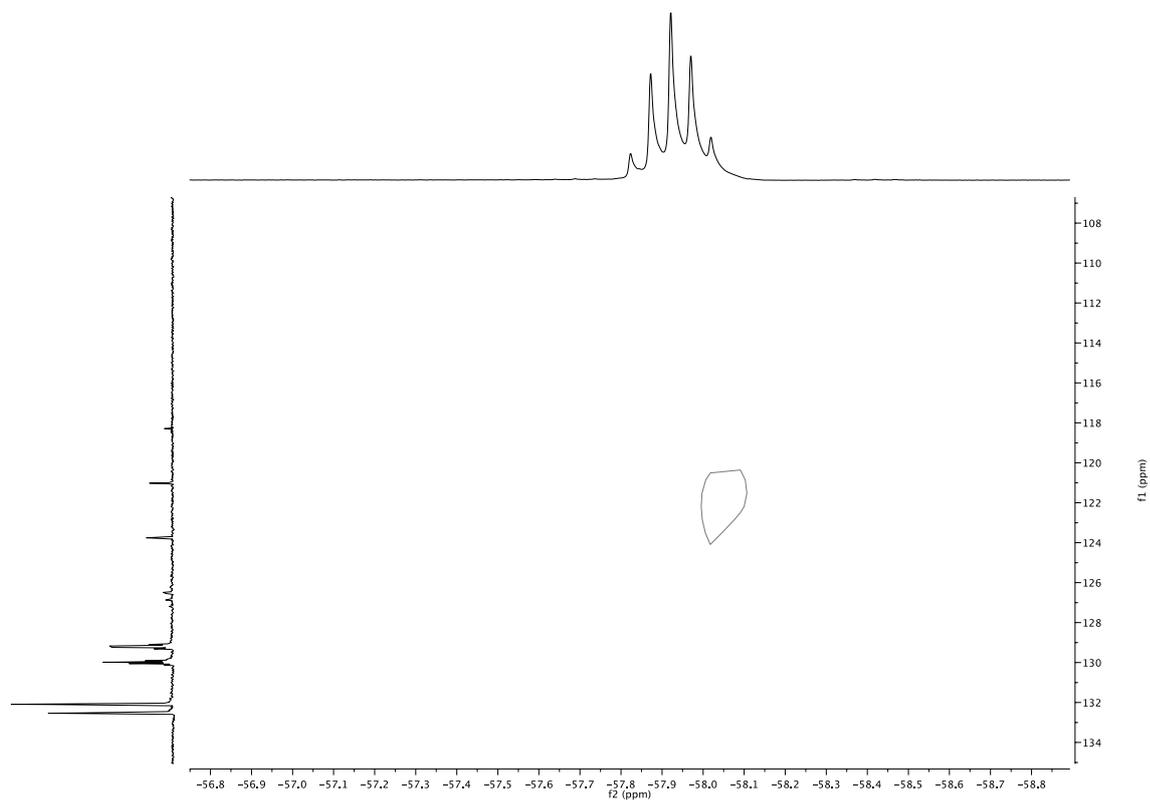
<sup>13</sup>C NMR of **4i**



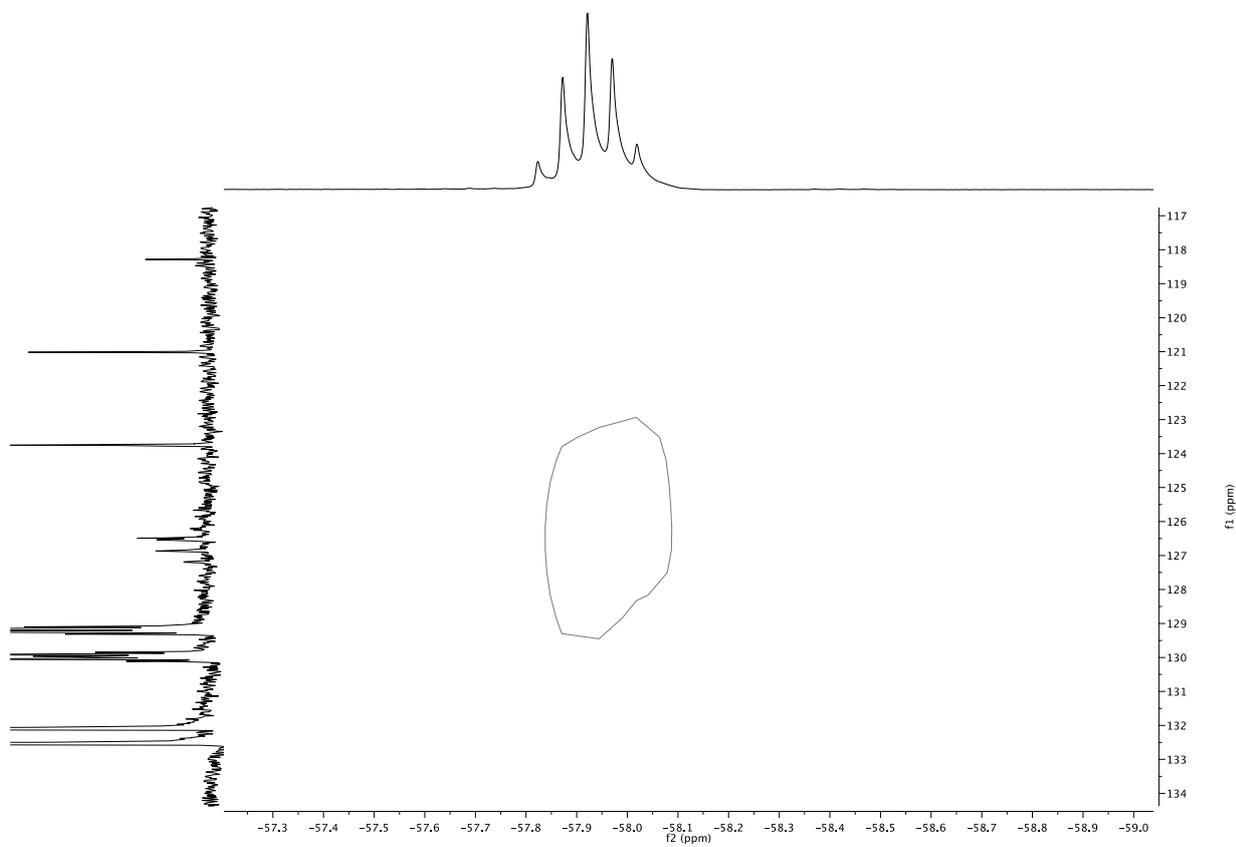
$^{19}\text{F}$  NMR of **4i**



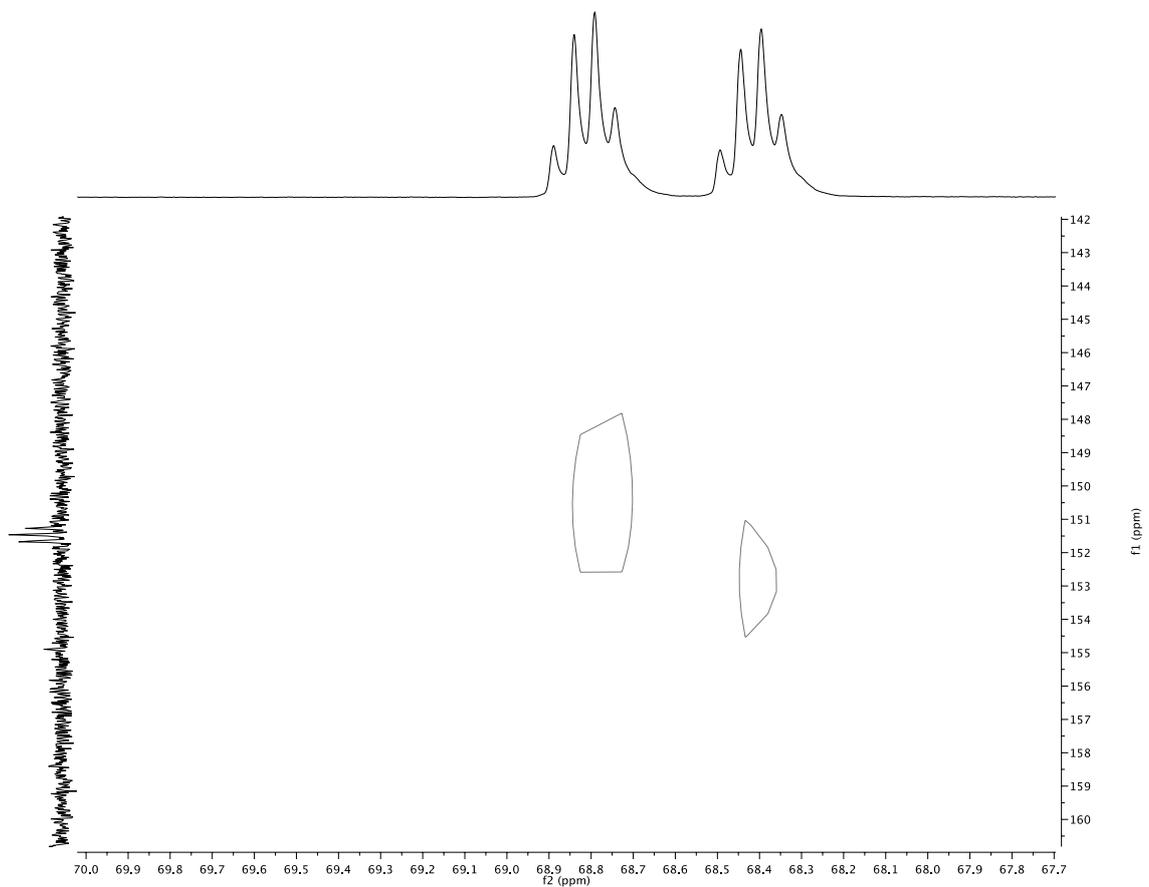
$^1\text{H}$ - $^{13}\text{C}$  HMQC of **4i**



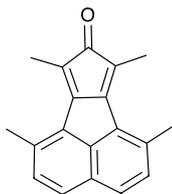
$^{19}\text{F}$ - $^{13}\text{C}$  HMQC of **4i**



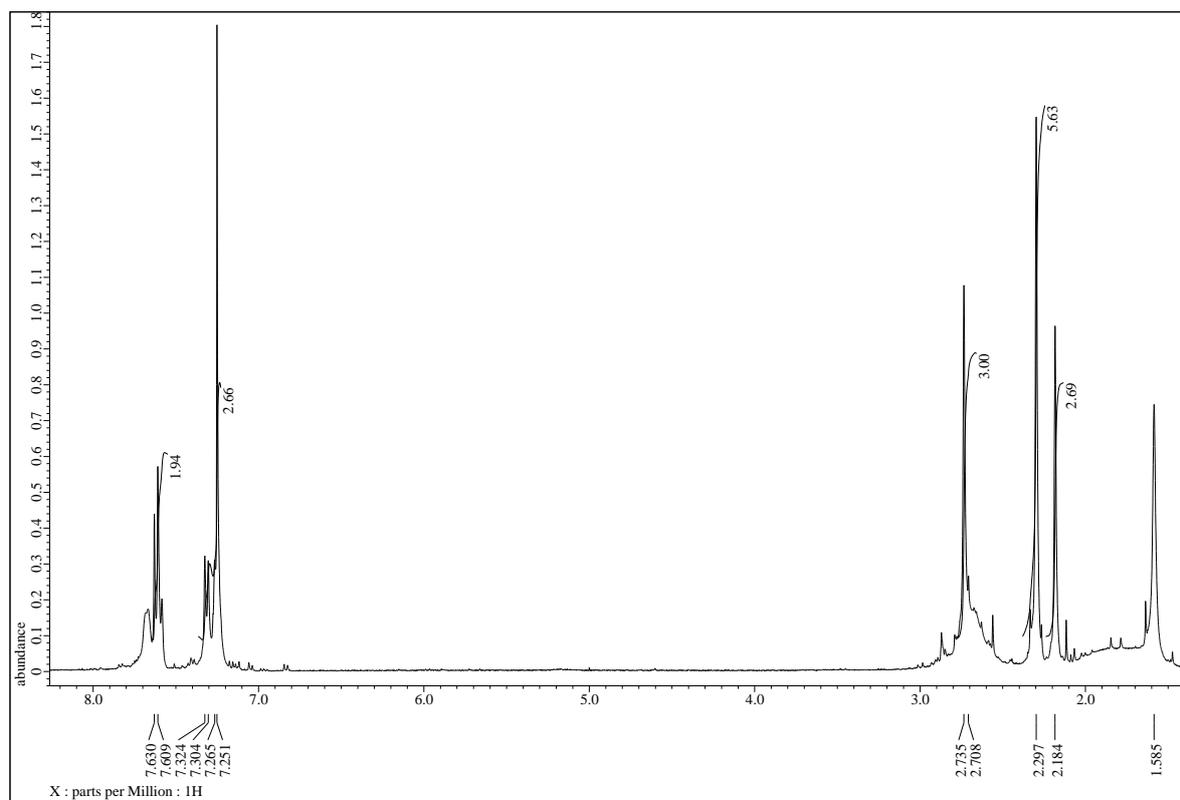
$^{19}\text{F}$ - $^{13}\text{C}$  HMBC of **4i** ( $\text{C-CF}_3$ )



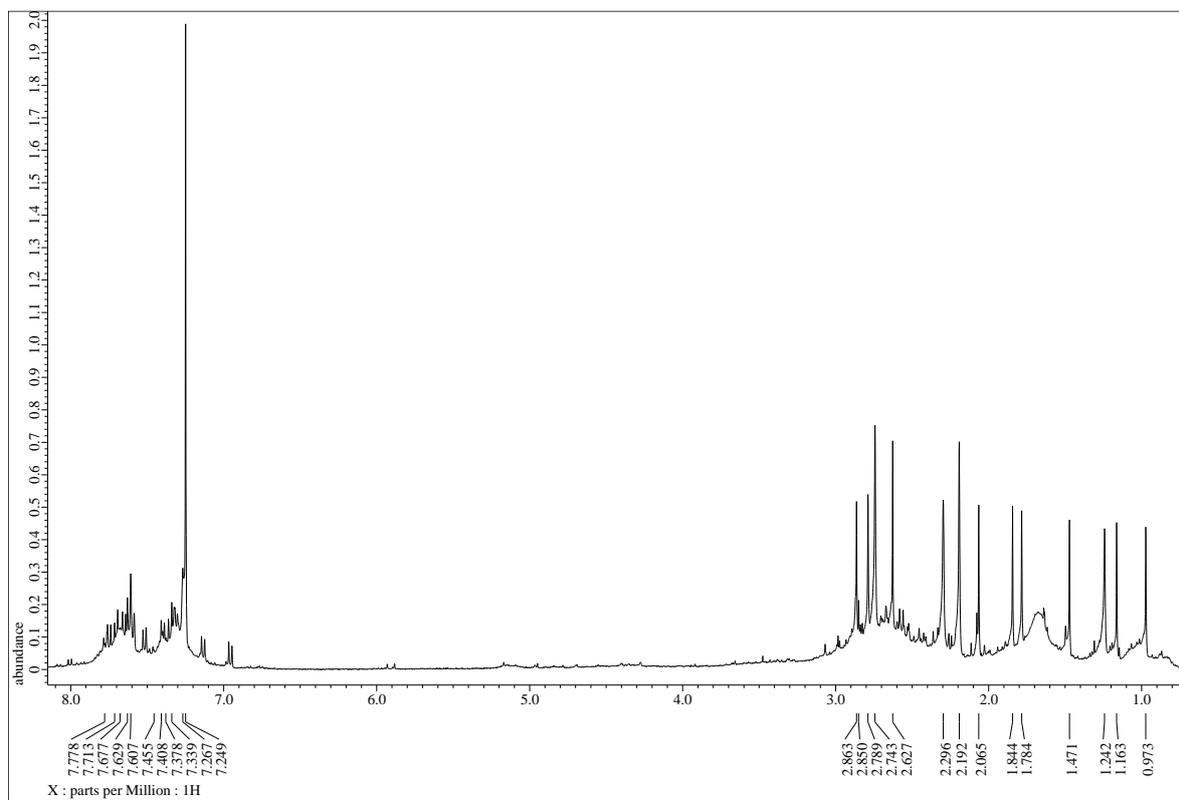
$^{19}\text{F}$ - $^{13}\text{C}$  HMBC of **4i** ( $\text{C-SF}_5$ )



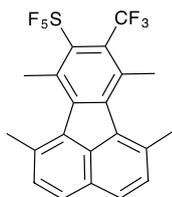
**6**, Dark-purple crystals, mp 221-225 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  2.25 (s, 6H), 2.77 (s, 6H), 7.33 (m, 2H), 7.61 (dd,  $J = 7$  Hz,  $J = 4$  Hz, 2H); HRMS (ESI)  $[\text{M}+\text{H}]^+$   $\text{C}_{19}\text{H}_{17}\text{O}$  found: 261.1269, calcd: 261.1264.



$^1\text{H}$  NMR of **6**

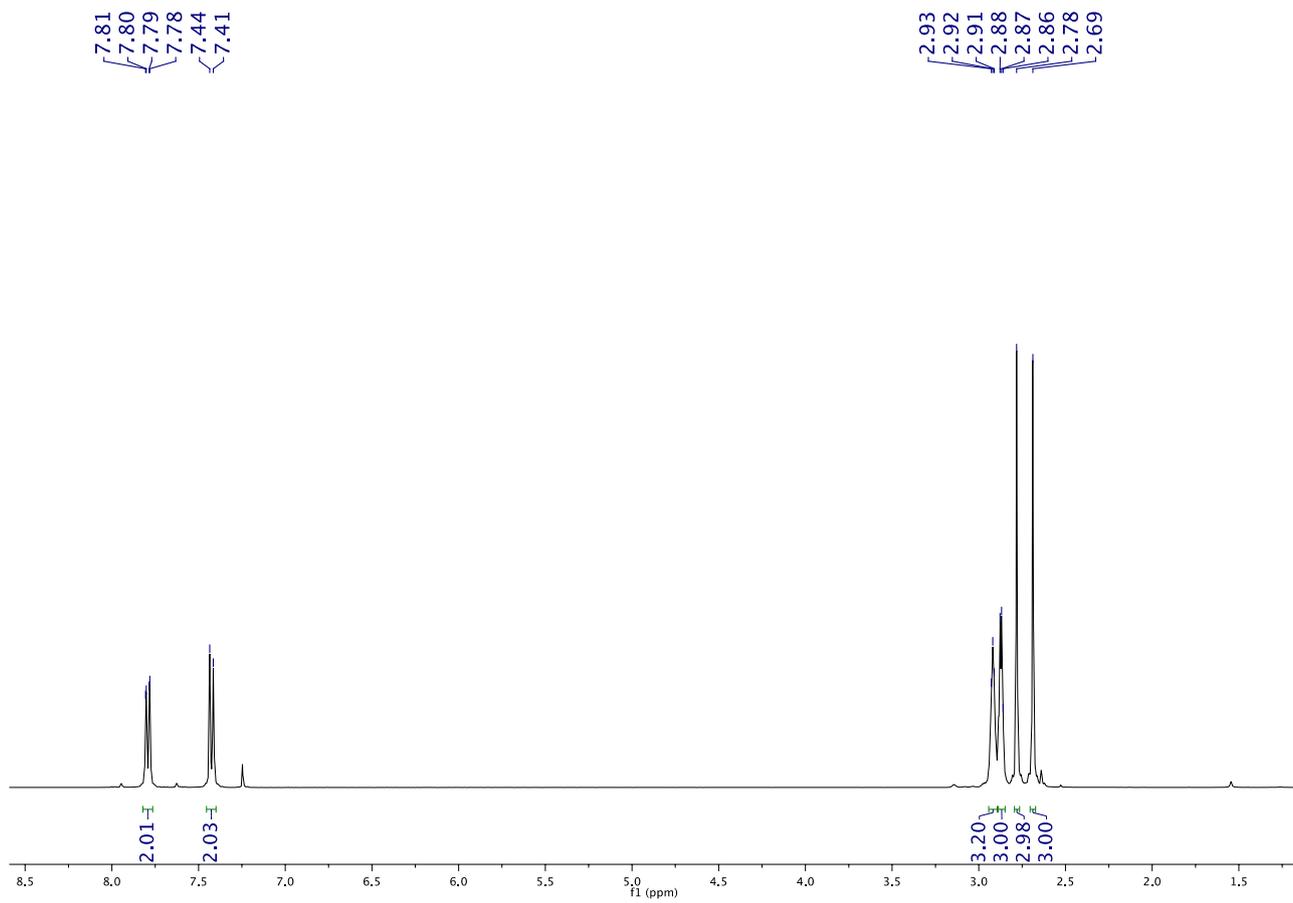


$^1\text{H}$  NMR after 4h indicating the decomposition of **6** in the solution

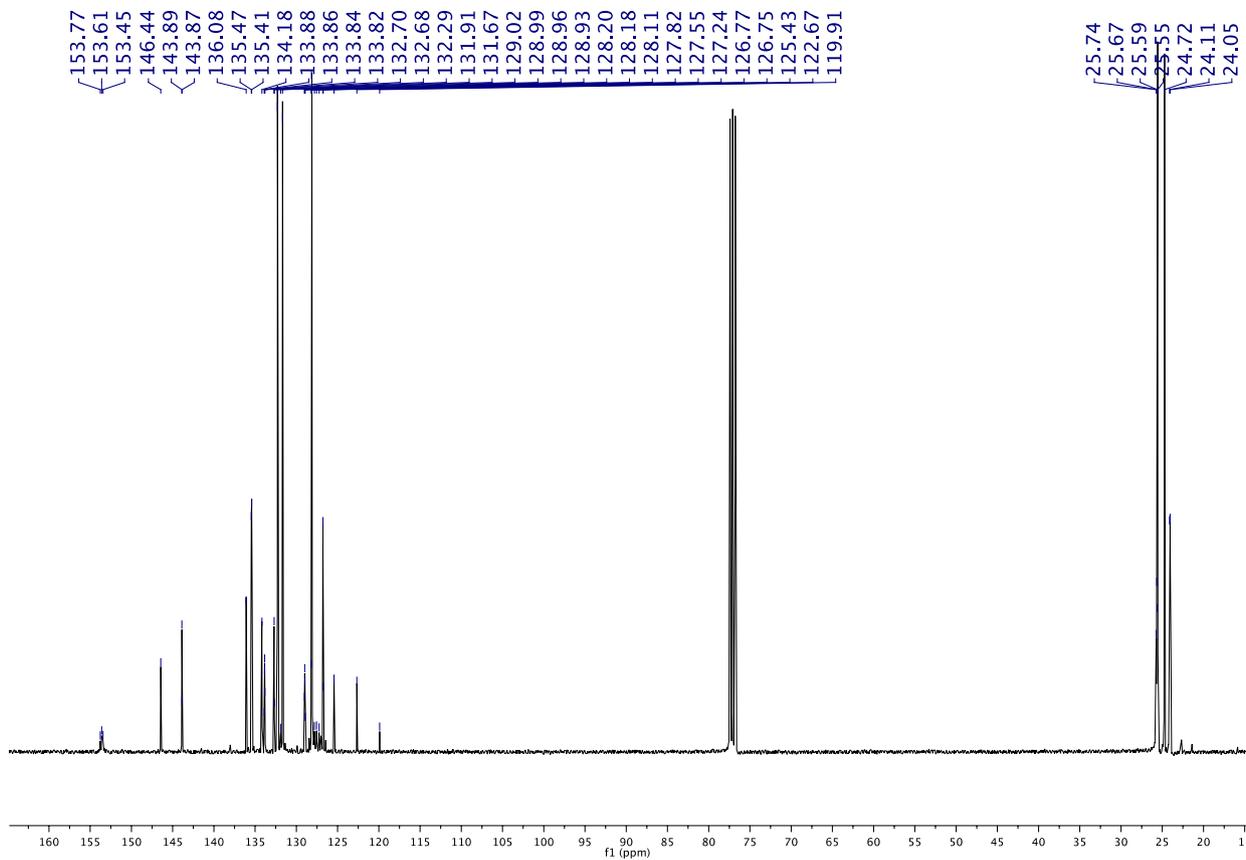


The *in situ* prepared compound **6** (2 mmol, 0.5 g) was dissolved in acetic anhydride (5 mL) in a round-bottomed flask equipped with a young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne **2** (6 mmol, 1.3 g) was condensed to the reaction mixture and slowly warmed up to room temperature. After 24 h of stirring at 80°C the crude mixture was diluted with 50 mL of dichloromethane and extracted with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> for 1h, filtered off and concentrated on the rotary evaporator. The crude product was purified by column chromatography using *n*-pentane as eluent (*R*<sub>f</sub> = 0.3) affording the pure fluoranthene **7** in 75% (1.5 mmol, 0.67 g) yield.

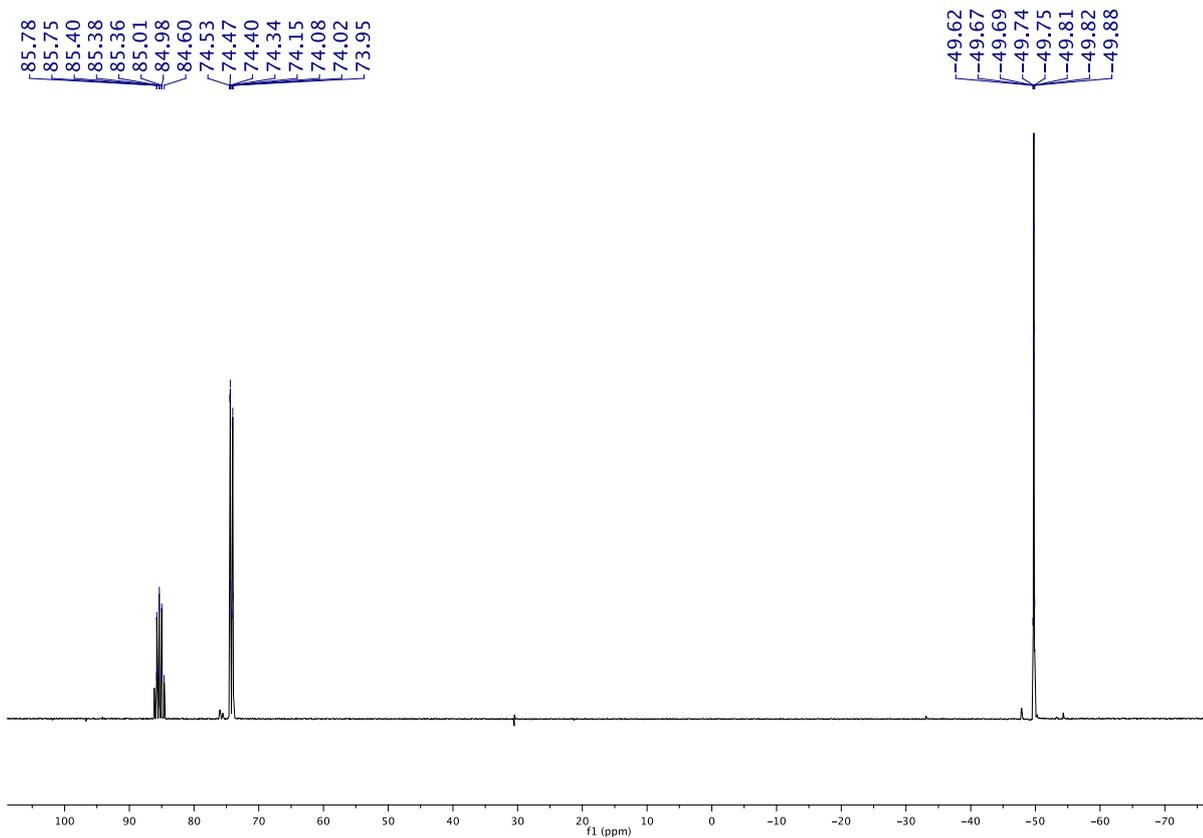
**7**, Yellowish crystals, Yield (75%), mp = 121-123 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 2.69 (s, 3H), 2.78 (s, 3H), 2.87 (q, <sup>5</sup>J<sub>H-F</sub> = 3 Hz, 3H), 2.92 (quintet, <sup>5</sup>J<sub>H-F(eq)</sub> = 1 Hz, 3H), 7.37 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H), 7.37 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.1 (q, <sup>4</sup>J<sub>C-F</sub> = 6 Hz), 24.7, 25.5, 25.7 (quintet, <sup>4</sup>J<sub>C-F(eq)</sub> = 7 Hz), 124.1 (q, <sup>1</sup>J<sub>C-F</sub> = 277 Hz), 128.1, 128.9, 131.7, 132.3, 132.7 (qq, <sup>2</sup>J<sub>C-F</sub> = 28 Hz, <sup>3</sup>J<sub>C-F(eq)</sub> = 3 Hz), 133.5, 135.4, 143.4, 153.6 (quintet, <sup>2</sup>J<sub>C-F(eq)</sub> = 14 Hz, <sup>3</sup>J<sub>C-F</sub> = 4 Hz); <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ 85.4 (A-part, 8-lines, 1F), 74.2 (dq, B<sub>4</sub>-part, J<sub>F(eq)F(ax)}</sub> = 144 Hz, <sup>5</sup>J<sub>F(eq)F}</sub> = 24 Hz, 1F), -49.7 (quintet, <sup>5</sup>J<sub>F-F(eq)}</sub> = 25 Hz, 3F); HRMS (EI, 80 eV): 452 [M<sup>+</sup>] C<sub>21</sub>H<sub>16</sub>F<sub>8</sub>S found: 452.0854, calcd: 452.0845.



<sup>1</sup>H NMR of 7



<sup>13</sup>C NMR of 7



$^{19}\text{F}$  NMR of 7