



## Supporting Information

for

### **Synthesis of *N*-perfluoroalkyl-3,4-disubstituted pyrroles by rhodium-catalyzed transannulation of *N*-fluoroalkyl-1,2,3-triazoles with terminal alkynes**

Olga Bakhanovich, Viktor Khutorianskyi, Vladimir Motornov and Petr Beier

*Beilstein J. Org. Chem.* **2021**, *17*, 504–510. [doi:10.3762/bjoc.17.44](https://doi.org/10.3762/bjoc.17.44)

## Experimental part

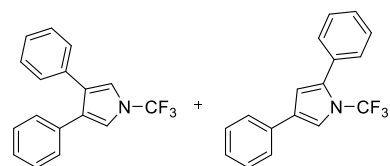
## General

Chloroform stabilized with ethanol ( $\approx 1\%$ ) was distilled over sulfuric acid and stored under argon. All commercially available chemicals were used as received unless stated otherwise. The starting triazoles **1a–i** were prepared according to procedures published in the literature [1]. Flash column chromatography was performed using silica gel 60 (0.040–0.063 mm) and pure pentane as the mobile phase or C18 silica gel using a MeCN/H<sub>2</sub>O mixture as the mobile phase. Automated flash column chromatography was performed on Teledyne ISCO CombiFlash Rf+ Lumen Automated Flash Chromatography System with UV–vis detection. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were measured at ambient temperature using 5 mm diameter NMR tubes. <sup>13</sup>C NMR spectra were proton decoupled. The chemical shift values ( $\delta$ ) are reported in ppm relative to internal Me<sub>4</sub>Si (0 ppm for <sup>1</sup>H and <sup>13</sup>C NMR) or residual solvents and internal CFC1<sub>3</sub> (0 ppm for <sup>19</sup>F NMR). Coupling constants ( $J$ ) are reported in hertz. The structural elucidation was aided by the additional acquisition of <sup>13</sup>C APT and/or various 2D spectra (<sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C HSQC, <sup>1</sup>H-<sup>13</sup>C HMBC, <sup>13</sup>C-<sup>19</sup>F HMBC). High resolution MS spectra (HRMS) were recorded on a Waters Micromass AutoSpec Ultima or an Agilent 7890A GC coupled with a Waters GCT Premier orthogonal acceleration time-of-flight detector using electron impact (EI) ionization or chemical ionization (CI), Q-Tof micro (Waters) is a quadrupole orthogonal acceleration time-of-flight tandem mass spectrometer using atmospheric-pressure chemical ionization (APCI). A CEM Discover System (150 W power) was used for reactions carried out in a microwave reactor.

## General procedure for reactions of triazoles and alkynes

The *N*-(per)fluoroalkyl-triazole **1a–i** (0.20 mmol) was dissolved in dry CHCl<sub>3</sub> (2 mL) in a 10 mL microwave tube. The alkyne (3 equiv, 0.60 mmol) and bis[rhodium( $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-benzenedipropionic acid)] (0.002 mmol; 1.52 mg) were added, the vial capped and heated at 100 °C for 20 min in a microwave reactor. The solvent and unreacted alkyne were removed under reduced pressure and the product was purified by CombiFlash automatic column chromatography (silica gel using pentane as the mobile phase – general procedure A or reversed phase chromatography using water/MeCN as the mobile phase – general procedure B).

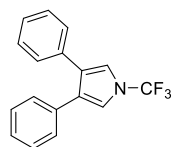
*3,4-Diphenyl-1-(trifluoromethyl)-1H-pyrrole* and *2,4-diphenyl-1-(trifluoromethyl)-1H-pyrrole* (**2a** + **2a'**): Prepared according to the **general**



**procedure A** with phenylacetylene as the starting alkyne.

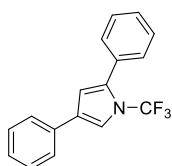
Yield: 56%; colourless oil; crude <sup>19</sup>F NMR ratio: 75:25; <sup>1</sup>H NMR (401 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.53 (m, 2H, **2a'**), 7.53 – 7.48 (m, 2H, **2a'**), 7.47 – 7.43 (m, 4H, **2a'**), 7.43 – 7.41 (m, 1H, **2a'**), 7.41 – 7.39 (m, 1H, **2a'**), 7.36 (dq, *J* = 1.7, 0.9 Hz, 1H, **2a'**), 7.35 – 7.23 (m, 10H, **2a**), 7.11 (s, 2H, **2a'**), 6.61 (dq, *J* = 1.7, 0.8 Hz, 1H, **2a'**); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  134.7, 133.9, 133.8, 132.6, 131.7, 129.7, 129.0, 128.7, 128.6, 128.5, 128.3, 127.3, 127.0, 127.0, 125.7, 119.1 (q, <sup>1</sup>*J*<sub>C-F</sub> = 260.5 Hz), 116.4, 115.4, 112.4; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -52.18 (s, **2a'**), -57.67 (s, **2a**); HRMS (EI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>12</sub>F<sub>3</sub>N [M]<sup>+</sup>: 287.0922, found 287.0920.

**3,4-Diphenyl-1-(trifluoromethyl)-1H-pyrrole (2a)**: white crystalline solid;  $^1\text{H}$  NMR (401



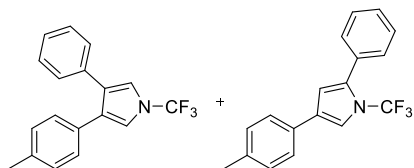
MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 7.11 (m, 10H), 7.01 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9, 128.7, 128.5, 127.3, 127.0, 119.1 (q,  $^1J_{\text{C-F}} = 260.7$  Hz), 116.4;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.68 (s).

**2,4-Diphenyl-1-(trifluoromethyl)-1H-pyrrole (2a')**: colourless oil;  $^1\text{H}$  NMR (401 MHz,



$\text{CDCl}_3$ )  $\delta$  7.57 – 7.52 (m, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.36 (m, 4H), 7.34 (dd,  $J = 2.0, 0.9$  Hz, 1H), 7.30 – 7.27 (m, 1H), 6.59 (dd,  $J = 2.0, 1.0$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.7, 133.8, 131.7, 129.7, 129.7, 129.0, 128.6, 128.3, 127.0, 126.8, 126.8, 125.7, 119.6 (q,  $^1J_{\text{C-F}} = 262.6$  Hz), 115.41, 115.39, 115.37, 115.35, 112.39, 112.38;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -52.18 (s).

**3-Phenyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-pyrrole** in mixture with **2-phenyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-pyrrole (2b + 2b')**: Prepared

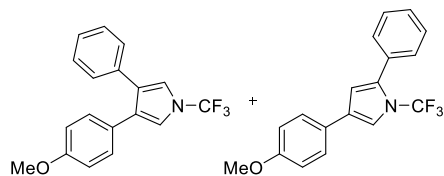


according to the **general procedure A** with

phenylacetylene as the starting alkyne. Yield: 66%; colourless oil; crude  $^{19}\text{F}$  NMR ratio:

73:27;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.05 (m, 11H + 10H', **2b + 2b'**), 6.58 (dd,  $J = 1.9, 0.9$  Hz, 1H, **2b'**), 2.39 (s, 3H, **2b'**), 2.36 (s, 3H, **2b**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.7, 136.7, 134.6, 134.0, 131.8, 130.9, 129.6, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 127.2, 126.9, 126.8, 125.6, 119.4 (q,  $^1J_{\text{C-F}} = 262.3$  Hz), 119.1 (q,  $^1J_{\text{C-F}} = 260.4$  Hz), 116.4, 116.2, 115.1, 115.0, 112.4, 112.4, 21.3;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -51.61 (s, **2b'**), -57.14 (s, **2b**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_3\text{N}$   $[\text{M}]^+$ : 301.1078, found 301.1076.

3-(4-Methoxyphenyl)-4-phenyl-1-(trifluoromethyl)-1H-pyrrole and 4-(4-methoxyphenyl)-2-

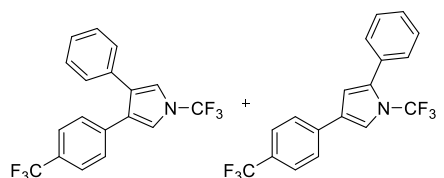


phenyl-1-(trifluoromethyl)-1H-pyrrole (**2c** + **2c'**):

Prepared according to the **general procedure A** with phenylacetylene as the starting alkyne. Yield: 54%; colourless oil; crude  $^{19}\text{F}$  NMR ratio:

72:28;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.24 (m, 5H + 9H', **2c** + **2c'**), 7.23 – 7.14 (m, 2H, **2c**), 7.09 (dd,  $J$  = 15.5, 2.5 Hz, 2H, **2c**), 7.01 – 6.92 (m, 2H, **2c'**), 6.91 – 6.80 (m, 2H, **2c**), 6.56 (dq,  $J$  = 1.7, 0.8 Hz, 1H, **2c'**), 3.87 (s, 3H, **2c'**), 3.84 (s, 3H, **2c**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 134.0, 129.9, 129.6, 128.7, 128.5, 128.5, 128.3, 127.2, 126.9, 126.8, 126.3, 119.4 (q,  $^1J_{\text{C-F}}$  = 262.1 Hz), 119.1 (q,  $^1J_{\text{C-F}}$  = 260.6 Hz), 117.8, 116.3, 119.0, 114.4, 113.9, 112.4, 55.4, 55.4;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -52.11 (s, **2c'**), -57.65 (s, **2c**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}$  [ $\text{M}$ ] $^+$ : 317.1027, found 317.1026.

3-Phenyl-1-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1H-pyrrole with 2-phenyl-1-



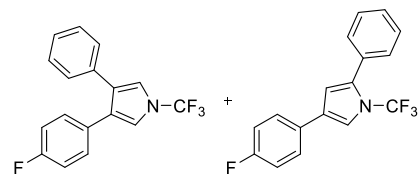
(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1H-pyrrole

(**2d** + **2d'**): Prepared according to the **general procedure A** with phenylacetylene as the starting

alkyne. Yield: 55%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 59:41;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (s, 4H, **2d'**), 7.55 – 7.51 (m, 2H, **2d**), 7.50 – 7.46 (m, 2H, **2d'**), 7.46 – 7.42 (m, 1H, **2d**), 7.42 – 7.39 (m, 1H, **2d'**), 7.36 – 7.28 (m, 4H + 3H', **2d** + **2d'**), 7.24 – 7.20 (m, 2H, **2d**), 7.13 (dd,  $J$  = 16.3, 2.5 Hz, 2H, **2d**), 6.60 (dd,  $J$  = 2.0, 0.9 Hz, 1H, **2d'**);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  136.4, 136.2, 134.0, 132.2, 130.1, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8,

127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.5, 127.4, 127.3, 127.2, 126.9, 126.9, 126.9, 126.9, 126.8, 126.5, 126.1, 126.1, 124.9, 124.8, 124.8, 124.8, 124.7, 124.7, 124.6, 124.6, 124.5, 124.4, 124.3, 124.3, 124.3, 124.2, 124.2, 124.1, 124.0, 123.7, 123.5, 123.2 (q,  $J = 271.7$  Hz, **2d'**), 123.2 (q,  $J = 272.1$  Hz, **2d**), 123.0, 118.1, 118.1, 118.0 (q,  $J = 263.0$  Hz, **2d'**), 117.8 (q,  $J = 261.0$  Hz, **2d**), 115.8, 115.7, 115.0, 115.0, 115.0, 115.0, 114.9, 114.4, 110.9;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -52.33 (s,  $N\text{-CF}_3$ , **2d'**), -57.76 (s,  $N\text{-CF}_3$ , **2d**), -62.93 (s, **2d'**), -62.94 (s, **2d**); HRMS (APCI $^+$ )  $m/z$  calcd for  $\text{C}_{18}\text{H}_{11}\text{F}_6\text{N}$   $[\text{M} + \text{H}]^+$ : 356.08685, found 356.08675.

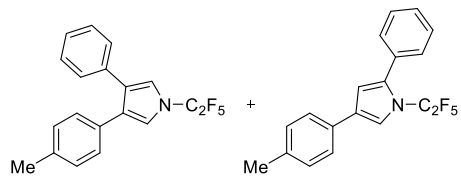
*3-(4-Fluorophenyl)-4-phenyl-1-(trifluoromethyl)-1H-pyrrole* and *4-(4-fluorophenyl)-2-phenyl-1-(trifluoromethyl)-1H-pyrrole* (**2e** + **2e'**): Prepared



according to the **general procedure A** with

phenylacetylene as the starting alkyne. Yield: 58%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 79:21;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.39 (m, 7H, **2e'**), 7.38 – 7.27 (m, 3H + 1H', **2e** + **2e'**), 7.25 – 7.16 (m, 4H, **2e**), 7.14 – 7.06 (m, 2H + 2H', **2e** + **2e'**), 7.04 – 6.95 (m, 2H, **2e**), 6.55 (dq,  $J = 1.6, 0.8$  Hz, 1H, **2e'**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1 (d,  $J = 245.8$  Hz), 162.1 (d,  $J = 245.6$  Hz), 134.7, 133.6, 131.5, 131.1, 130.3, 130.2, 130.0, 129.9, 129.9, 129.9, 129.8, 129.8, 129.6, 129.6, 129.5, 129.5, 129.2, 129.1, 128.9, 128.6, 128.5, 128.5, 128.5, 128.2, 128.0, 127.9, 127.5, 127.2, 127.1, 127.0, 127.0, 126.6, 126.6, 126.2, 125.8, 125.4, 122.8, 119.4 (q,  $J = 262.7$  Hz), 119.1 (q,  $J = 260.8$  Hz), 116.3, 116.2, 115.8, 115.8, 115.6, 115.4, 115.2, 115.0, 112.2, 112.2.;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -51.69 (s,  $N\text{-CF}_3$ , **2e'**), -57.18 (s,  $N\text{-CF}_3$ , **2e**), -115.61 to -115.73 (m, **2e**, **2e'**); HRMS (APCI $^+$ )  $m/z$  calcd for  $\text{C}_{17}\text{H}_{11}\text{F}_4\text{N}$   $[\text{M} + \text{H}]^+$ : 306.09004, found 306.08998.

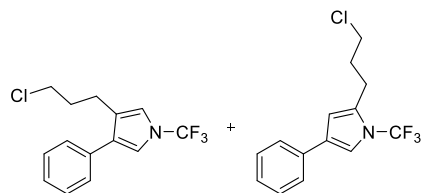
*1-(Perfluoroethyl)-3-phenyl-4-(p-tolyl)-1H-pyrrole* with *1-(perfluoroethyl)-2-phenyl-4-(p-tolyl)-1H-pyrrole (2f + 2f')*: Prepared according to the



**general procedure A** with phenylacetylene as the

starting alkyne. Yield: 52%; colourless oil; crude <sup>19</sup>F NMR ratio: 69:31; <sup>1</sup>H NMR (401 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.22 (m, 5H + 8H', **2f'** + **2f**), 7.21 – 7.12 (m, 4H + 1H', **2f'** + **2f**), 7.10 – 7.02 (m, 2H + 1H', **2f'** + **2f**), 6.60 (dt, *J* = 2.0, 1.0 Hz, 1H, **2f'**), 2.42 (s, 3H, **2f'**), 2.39 (s, 3H, **2f**); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.11, 139.56, 139.35, 139.16, 136.83, 136.70, 135.91, 135.11, 135.05, 133.98, 132.48, 132.30, 132.09, 131.22, 130.88, 130.78, 130.39, 130.31, 129.79, 129.65, 129.36, 129.22, 128.88, 128.84, 128.74, 128.61, 128.49, 128.46, 128.27, 128.19, 128.15, 128.09, 128.03, 127.92, 127.88, 127.81, 127.75, 127.69, 127.51, 127.49, 127.48, 127.24, 126.96, 125.58, 124.14, 124.02, 123.98, 123.19, 123.01, 122.41, 122.32, 122.13, 121.83, 120.71, 119.74, 119.28, 118.81, 116.89, 116.75, 115.80, 113.58, 113.29, 112.02, 111.60, 111.08, 110.67, 109.01, 108.68, 108.46, 108.29, 107.96, 21.30; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -84.75 (s, -CF<sub>3</sub>, **2f'**), -85.70 (s, -CF<sub>3</sub>, **2f**), -93.82 (s, *N*-CF<sub>2</sub>, **2f'**), -99.11 (s, *N*-CF<sub>2</sub>, **2f**); HRMS (EI<sup>+</sup>) *m/z* calcd for C<sub>19</sub>H<sub>14</sub>F<sub>5</sub>N [M]<sup>+</sup>: 351.1046, found 351.1045.

*3-Chloropropyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole* and *2-chloropropyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole (3a + 3a')*: Prepared

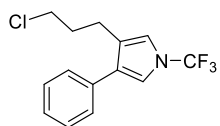


according to the **general procedure A** with 1-chloro-

pent-4-yne the as starting alkyne. Yield: 84%; colourless oil; crude <sup>19</sup>F NMR ratio: 95:5; <sup>1</sup>H NMR (401 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.47 (m, 2H, **3a'**),

7.44 – 7.36 (m, 4H + 2H', **3a** + **3a'**), 7.35 – 7.29 (m, 1H, **3a**), 7.27 – 7.22 (m, 1H, **3a'**), 7.21 – 7.18 (m, 1H, **3a'**), 7.00 (d,  $J = 2.5$  Hz, 1H, **3a**), 6.86 (dd,  $J = 2.3, 1.1$  Hz, 1H, **3a**), 6.41 (dq,  $J = 1.9, 0.9$  Hz, 1H, **3a'**), 3.65 (t,  $J = 6.4$  Hz, 2H, **3a'**), 3.51 (ddt,  $J = 6.4$  Hz, 2H, **3a**), 2.91 (td,  $J = 7.6, 2.1$  Hz, 2H, **3a'**), 2.75 (td,  $J = 7.5, 1.0$  Hz, 2H, **3a**), 2.24 – 2.12 (m, 2H, **3a'**), 1.95 (ddt,  $J = 8.7, 7.5, 6.4$  Hz, 2H, **3a**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.4, 133.9, 132.6, 132.6, 128.9, 128.7, 128.7, 128.6, 128.3, 127.1, 126.9, 126.4, 125.5, 124.5, 119.1 (q,  $^1J_{\text{C-F}} = 260.0$  Hz), 115.9, 114.3, 110.0, 44.5, 44.1, 32.4, 31.4, 22.9;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.00 (s, **4a'**), -57.55 (s, **4a**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{14}\text{H}_{13}\text{ClF}_3\text{N}$   $[\text{M}]^+$ : 287.0689, found 287.0687.

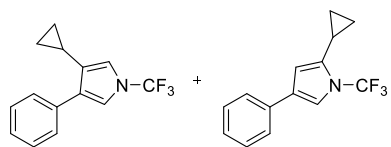
**3-(3-Chloropropyl)-4-phenyl-1-(trifluoromethyl)-1H-pyrrole (3a)**: Prepared according to



the **general procedure A** with 1-chloro-pent-4-yne the as starting alkyne. Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.33 (m,

4H), 7.36 – 7.27 (m, 1H), 6.99 (d,  $J = 2.5$  Hz, 1H), 6.85 (dd,  $J = 2.4, 1.2$  Hz, 1H), 3.50 (t,  $J = 6.4$  Hz, 2H), 2.78 – 2.70 (m, 2H), 2.00 – 1.89 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.4, 128.8, 128.3, 127.1, 124.6, 119.1 (q,  $^1J_{\text{C-F}} = 260.1$  Hz), 115.9, 44.5, 32.5, 22.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.56 (s).

**3-Cyclopropyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole and 2-cyclopropyl-4-phenyl-1-**



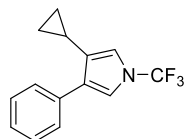
**(trifluoromethyl)-1H-pyrrole (3b + 3b')**: Prepared according to the **general procedure A** with cyclopropylacetylene as

the starting alkyne. Yield: 56%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 94:6;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.58 (m, 2H, **3b**), 7.57 – 7.50 (m, 1H, **3b'**), 7.45 – 7.28 (m, 3H +



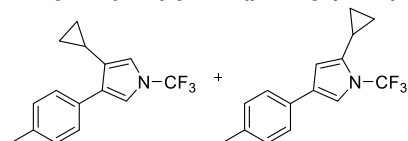
3H', **3b** + **3b'**), 7.26 – 7.21 (m, 1H, **3b'**), 7.17 (dt,  $J = 2.1, 0.8$  Hz, 1H, **3b'**), 7.03 (d,  $J = 2.5$  Hz, 1H, **3b**), 6.67 (dd,  $J = 2.5, 1.0$  Hz, 1H, **3b**), 6.24 (dt,  $J = 1.9, 1.0$  Hz, 1H, **3b'**), 1.90 (ttt,  $J = 8.6, 6.8, 4.5$  Hz, 1H, **3b'**), 1.75 (ttt,  $J = 8.3, 5.2, 1.0$  Hz, 1H, **3b**), 0.97 – 0.82 (m, 2H + 2H', **3b** + **3b'**), 0.78 – 0.71 (m, 2H, **3b'**), 0.64 – 0.56 (m, 2H, **3b**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.6, 134.5, 134.1, 132.7, 129.4, 128.9, 128.9, 128.7, 128.6, 128.6, 128.4, 128.3, 128.1, 126.8, 126.7, 125.9, 125.5, 125.1, 119.1 (q,  $J = 259.9$  Hz), 115.4, 114.4, 114.2, 114.2, 108.2, 8.0, 7.5, 6.7;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.31 (s, **3b'**), -57.59 (s, **3b**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{F}_3\text{N}$  [ $\text{M}]^+$ : 251.0922, found 251.0923.

**3-Cyclopropyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole (3b)**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$



7.63 – 7.57 (m, 2H), 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 1H), 7.02 (d,  $J = 2.5$  Hz, 1H), 6.66 (dd,  $J = 2.5, 1.0$  Hz, 1H), 1.74 (ttt,  $J = 8.3, 5.2, 1.0$  Hz, 1H), 0.93 – 0.82 (m, 2H), 0.64 – 0.52 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.5, 128.9, 128.7, 128.6, 128.2, 128.1, 126.8, 125.5, 119.1 (q,  $J = 259.8$  Hz); 115.4, 114.4, 8.0, 7.5, 6.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.61 (s).

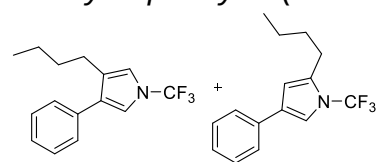
**3-Cyclopropyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-pyrrole and 2-cyclopropyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-pyrrole (3c + 3c')**: Prepared according



to the **general procedure A** with cyclopropylacetylene as the starting alkyne. Yield: 56%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 91:9;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.45 (m, 2H, **3c**), 7.38 – 7.32 (m, 2H, **3c'**), 7.24 – 7.18 (m, 2H, **3c'**), 7.18 – 7.14 (m, 3H, **3c'**), 7.12 (q,  $J = 0.9$  Hz, 1H, **3c'**), 6.98 (d,  $J = 2.5$  Hz, 1H, **3c**), 6.64 (dd,  $J = 2.5, 1.0$  Hz, 1H, **3c**), 6.20 (dt,  $J = 2.0, 1.0$  Hz, 1H, **3c'**), 2.39 (s, 3H, **3c'**), 2.35 (s,

3H, **3c'**), 1.73 (ttd,  $J = 8.4, 5.2, 1.0$  Hz, 1H, **3c**), 0.95 – 0.81 (m, 2H, **3c**), 0.63 – 0.53 (m, 2H, **3c**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.5, 131.5, 129.5, 129.3, 128.8, 128.7, 128.0, 125.4, 119.1 (q,  $^1J_{\text{C-F}} = 259.8$  Hz), 115.1, 115.1, 114.3, 21.3, 21.3, 8.0, 7.5;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -54.76 (s, **3c'**), -57.05 (s, **3c**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{F}_3\text{N}$   $[\text{M}]^+$ : 265.1078, found 265.1073.

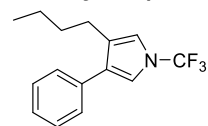
*3-Butyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole* and *2-butyl-4-phenyl-1-(trifluoromethyl)-*



*1H-pyrrole (3d + 3d')*: Yield: 48%; colourless oil; Prepared according to the **general procedure A** with 1-hexyne as the

starting alkyne; crude  $^{19}\text{F}$  NMR ratio: 97:3;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.48 (m, 2H, **3d'**), 7.44 – 7.34 (m, 4H + 3H', **3d + 3d'**), 7.33 – 7.28 (m, 1H, **3d**), 7.18 – 7.16 (m, 1H, **3d'**), 6.98 (d,  $J = 2.5$  Hz, 1H, **3d**), 6.82 (dt,  $J = 2.3, 1.1$  Hz, 1H, **3d**), 6.37 (dq,  $J = 1.9, 1.0$  Hz, 2H, **3d'**), 2.75 – 2.66 (m, 2H, **3d'**) 2.60 – 2.52 (m, 2H, **3d**), 1.76 – 1.64 (m, 3H, **3d'**), 1.58 – 1.49 (m, 3H, **3d**), 1.50 – 1.43 (m, 2H, **3d'**), 1.42 – 1.30 (m, 2H, **3d**), 0.99 (t,  $J = 7.4$  Hz, 3H, **3d'**), 0.90 (t,  $J = 7.3$  Hz, 3H, **3d**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.7, 134.2, 128.8, 128.6, 128.4, 128.4, 126.9, 126.7, 126.7, 125.5, 119.2 (q,  $^1J_{\text{C-F}} = 259.8$  Hz), 115.5, 115.5, 113.8, 113.7, 109.1, 32.0, 30.6, 26.3, 25.5, 22.7, 22.6, 14.0, 14.0;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.07 (s, **3d'**), -57.51 (s, **3d**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}$   $[\text{M}]^+$ : 267.1235, found 267.1239.

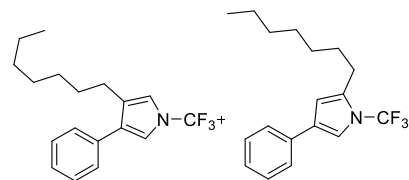
*3-Butyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole (3d)*:  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39



(d,  $J = 1.0$  Hz, 1H), 7.38 (s, 1H), 7.33 – 7.28 (m, 1H), 6.98 (d,  $J = 2.6$  Hz, 1H), 6.81 (dt,  $J = 2.3, 1.1$  Hz, 1H), 2.59 – 2.51 (m, 2H), 1.58 – 1.46 (m,

1H), 1.34 (dq,  $J = 14.4, 7.2$  Hz, 1H), 0.89 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.74, 128.59, 128.39, 128.35, 126.87, 126.66, 119.2 (q,  $^1J_{\text{C-F}} = 259.8$  Hz), 115.5, 115.5, 32.0, 25.5, 22.7, 14.0;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.51 (s).

*3-Heptyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole* and *2-heptyl-4-phenyl-1-*

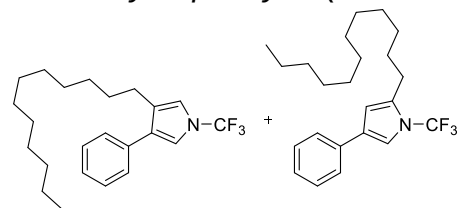


(trifluoromethyl)-1H-pyrrole (**3e** + **3e'**): Prepared

according to the **general procedure B** with 1-nonyne as the starting alkyne. Yield: 36%; colourless oil; crude  $^{19}\text{F}$

NMR ratio: 98:2;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.48 (m, 2H, **3e'**), 7.39 (d,  $J = 4.9$  Hz, 4H + 3H', **3e** + **3e'**), 7.33 – 7.26 (m, 1H, **3e**), 7.17 (d,  $J = 2.0$  Hz, 1H, **3e'**), 6.98 (d,  $J = 2.5$  Hz, 1H, **3e**), 6.81 (dd,  $J = 2.5, 1.3$  Hz, 1H, **3e**), 6.38 – 6.33 (m, 1H, **3e'**), 2.69 (t,  $J = 7.8$  Hz, 2H, **3e'**), 2.59 – 2.50 (m, 2H, **3e**), 1.71 (q,  $J = 7.4$  Hz, 2H, **3e'**), 1.59 – 1.47 (m, 2H, **3e**), 1.38 – 1.18 (m, 8H + 8H', **3e** + **3e'**), 0.88 (t,  $J = 6.8$  Hz, 3H + 3H', **3e** + **3e'**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.8, 128.9, 128.6, 128.4, 128.4, 126.9, 126.8, 126.7, 125.6, 119.2 (q,  $^1J_{\text{C-F}} = 259.8$  Hz), 115.5, 115.5, 31.9, 29.9, 29.6, 29.2, 25.8, 22.8, 14.2;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -54.54 (s, **3e'**), -56.97 (s, **3e**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{18}\text{H}_{22}\text{F}_3\text{N}$   $[\text{M}]^+$ : 309.1704, found 309.1709.

*3-Dodecyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole* and *2-dodecyl-4-phenyl-1-*



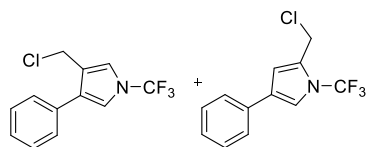
(trifluoromethyl)-1H-pyrrole (**3f** + **3f'**): Prepared

according to the **general procedure B** with 1-tetradecyne as the starting alkyne. Yield: 43%;

colourless oil; crude  $^{19}\text{F}$  NMR ratio: 94:6;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.48 (m,

2H, **3f'**), 7.43 – 7.37 (m, 4H + 3H', **3f** + **3f'**), 7.35 – 7.20 (m, 1H, **3f**), 7.19 – 7.16 (m, 1H, **3f'**), 6.99 (d,  $J$  = 2.5 Hz, 1H, **3f**), 6.82 (dd,  $J$  = 2.4, 1.2 Hz, 1H, **3f**), 6.37 (dq,  $J$  = 1.9, 0.9 Hz, 1H, **3f'**), 2.70 (t,  $J$  = 7.8 Hz, 2H, **3f'**), 2.55 (t,  $J$  = 8.3 Hz, 2H, **3f**), 1.82 – 1.65 (m, 2H, **3f'**), 1.60 – 1.48 (m, 2H, **3f**), 1.41 – 1.13 (m, 18H + 18H', **3f** + **3f'**), 0.89 (t, 3H + 3H', **3f** + **3f'**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.96, 134.76, 134.22, 128.84, 128.59, 128.41, 128.36, 126.87, 126.74, 126.70, 125.54, 115.50, 115.46, 119.2 (q,  $^1J_{\text{C-F}}$  = 259.7 Hz), 113.75, 109.07, 32.09, 29.85, 29.84, 29.81, 29.79, 29.71, 29.63, 29.55, 29.52, 25.80, 22.86, 14.27;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.07 (s, **3f'**), -57.51 (s, **3f**); HRMS (EI $^+$ )  $m/z$  calcd for  $\text{C}_{23}\text{H}_{32}\text{F}_3\text{N}$  [ $\text{M}$ ] $^+$ : 379.2487, found 379.2490.

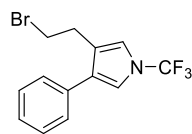
*3-(Chloromethyl)-4-phenyl-1-(trifluoromethyl)-1H-pyrrole and 2-(chloromethyl)-4-phenyl-*



*1-(trifluoromethyl)-1H-pyrrole (**3g** + **3g'**):* Prepared according

to the **general procedure A** with propargyl chloride as the starting alkyne. Yield: 43%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 87:13;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.52 (m, 1H, **3g'**), 7.51 – 7.40 (m, 4H + 1H', **3g** + **3g'**), 7.40 – 7.32 (m, 1H + 2H', **3g** + **3g'**), 7.30 – 7.27 (m, 2H, **3g'**), 7.17 (d,  $J$  = 2.5 Hz, 1H, **3g**), 7.04 (d,  $J$  = 2.5 Hz, 1H, **3g**), 6.75 – 6.69 (m, 1H, **3g'**), 4.72 (s, 2H, **3g'**), 4.58 (s, 2H, **3g**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.5, 133.2, 133.1, 132.6, 130.6, 129.3, 129.0, 129.0, 128.9, 128.4, 128.1, 127.5, 127.3, 127.0, 125.6, 122.4, 120.4, 118.8 (q,  $^1J_{\text{C-F}}$  = 259.9 Hz), 118.7, 116.9, 116.6 (q,  $J$  = 1.8 Hz), 115.8, 114.3, 114.3, 37.9, 36.9, 36.9;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.17 (s, **3g'**), -57.74 (s, **3g**); HRMS (EI $^+$ )  $m/z$  calcd for  $\text{C}_{12}\text{H}_9\text{ClF}_3\text{N}$  [ $\text{M}$ ] $^+$ : 259.0376, found 259.0377.

**3-(2-Bromoethyl)-4-phenyl-1-(trifluoromethyl)-1H-pyrrole (3h):** Prepared according to the



**general procedure A** with 1-bromo-4-butyne as the starting alkyne. Yield:

48%; pale-yellow oil; crude  $^{19}\text{F}$  NMR ratio to **3h'**: 93:7;  $^1\text{H}$  NMR (401 MHz,

$\text{CDCl}_3$ )  $\delta$  7.45 – 7.37 (m, 2H), 7.36 – 7.30 (m, 4H), 6.99 (d,  $J$  = 2.6 Hz, 1H), 6.94 (dd,  $J$  =

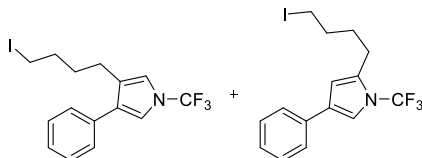
2.3, 1.2 Hz, 1H), 3.41 (t,  $J$  = 7.8 Hz, 2H), 3.14 (t,  $J$  = 7.3 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,

$\text{CDCl}_3$ )  $\delta$  134.0, 128.9, 128.4, 128.3, 128.2, 127.3, 123.0, 119.0 (q,  $^1J_{\text{C-F}}$  = 260.4 Hz),

116.4, 115.9, 31.8, 29.5;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.58 (s); HRMS ( $\text{EI}^+$ )  $m/z$  calcd

for  $\text{C}_{13}\text{H}_{11}\text{BrF}_3\text{N}$  [ $\text{M}$ ] $^+$ : 317.0027, found 317.0026.

**3-(4-Iodobutyl)-4-phenyl-1-(trifluoromethyl)-1H-pyrrole and 2-(4-iodobutyl)-4-phenyl-1-**



**(trifluoromethyl)-1H-pyrrole (3i + 3i')**: Prepared according

to the **general procedure A** with 6-iodo-1-hexyne as the

starting alkyne. Yield: 36%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 98:2;  $^1\text{H}$  NMR (401 MHz,

$\text{CDCl}_3$ )  $\delta$  7.57 – 7.48 (m, 2H, **3i'**), 7.43 – 7.36 (m, 4H + 3H', **3i + 3i'**), 7.35 – 7.29 (m, 1H,

**3i**), 7.20 – 7.16 (m, 1H, **3i'**), 6.99 (d,  $J$  = 2.5 Hz, 1H, **3i**), 6.84 (dt,  $J$  = 2.3, 1.0 Hz, 1H, **3i**),

6.40 (dq,  $J$  = 1.9, 1.0 Hz, 1H, **3i'**), 3.25 (t,  $J$  = 6.7 Hz, 2H, **3i'**), 3.15 (t,  $J$  = 6.9 Hz, 2H, **3i**),

2.78 – 2.70 (m, 2H, **3i'**), 2.59 (td,  $J$  = 7.7, 1.0 Hz, 2H, **3i**), 2.02 – 1.91 (m, 2H, **3i'**), 1.91 –

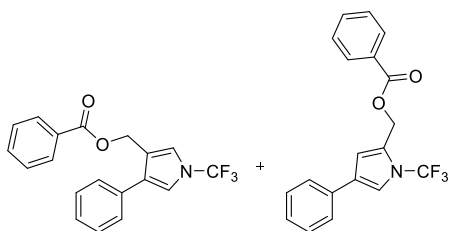
1.79 (m, 2H + 2H', **3i + 3i'**), 1.69 – 1.59 (m, 2H, **3i**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.5,

128.9, 128.7, 128.6, 128.4, 128.4, 127.0, 126.8, 125.7, 125.5, 119.1 (q,  $J$  = 260.0 Hz),

115.7, 115.6, 114.0, 33.3, 30.6, 24.8, 6.7;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -54.98 (s, **3i'**), -

57.49 (s, **3i**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{F}_3\text{IN}$  [ $\text{M}$ ] $^+$ : 393.0201, found 393.0205.

(4-Phenyl-1-(trifluoromethyl)-1H-pyrrol-3-yl)methyl benzoate and (4-phenyl-1-



(trifluoromethyl)-1H-pyrrol-2-yl)methyl benzoate (**3j** +

**3j'**): Prepared according to the **general procedure B**

with propargyl benzoate as the starting alkyne. Yield:

50%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 89:11;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 7.90

(m, 2H + 2H', **3j** + **3j'**), 7.65 – 7.28 (m, 10H + 10H', **3j** + **3j'**), 7.24 (d,  $J$  = 2.5 Hz, 1H, **3j**),

7.09 (d,  $J$  = 2.5 Hz, 1H, **3j**), 6.82 – 6.77 (m, 1H, **3j'**), 5.43 (s, 2H, **3j'**), 5.31 (s, 2H, **3j**);  $^{13}\text{C}$

NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 166.2, 133.4, 133.3, 133.2, 130.2, 129.8, 129.4, 129.0,

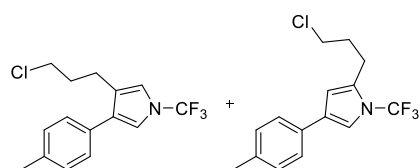
128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.3, 127.4, 127.2, 125.7, 120.4, 119.4,

119.1, 119.0 (q,  $^1J_{\text{C-F}}$  = 261.2 Hz), 118.9 (q,  $^1J_{\text{C-F}}$  = 261.9 Hz), 116.5, 116.5, 115.6, 58.8,

58.2;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.35 (s, **3j'**), -57.59 (s, **3j**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd

for  $\text{C}_{19}\text{H}_{14}\text{F}_3\text{NO}_2$   $[\text{M}]^+$ : 345.0977, found 345.0974.

3-(3-Chloropropyl)-4-(p-tolyl)-1-(trifluoromethyl)-1H-pyrrole and 2-(3-chloropropyl)-4-(p-



tolyl)-1-(trifluoromethyl)-1H-pyrrole (**3k** + **3k'**): Prepared

according to the **general procedure A** with 1-chloro—4-

pentyne as the starting alkyne. Yield: 60%; colourless oil;

crude  $^{19}\text{F}$  NMR ratio: 92:8;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.35 (m, 2H, **3k'**), 7.33 –

7.26 (m, 2H), 7.24 – 7.18 (m, 2H + 2H', **3k** + **3k'**), 7.18 – 7.14 (m, 2H, **3k'**), 6.98 (d,  $J$  =

2.4 Hz, 1H, **3k**), 6.85 (dt,  $J$  = 2.3, 1.0 Hz, 1H, **3k**), 6.39 (dq,  $J$  = 1.9, 1.0 Hz, 1H, **3k'**), 3.65

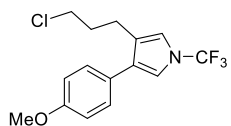
(t,  $J$  = 6.4 Hz, 2H, **3k'**), 3.52 (t,  $J$  = 6.4 Hz, 2H, **3k**), 2.94 – 2.84 (m, 2H, **3k'**), 2.74 (td,  $J$  =

7.5, 1.0 Hz, 2H, **3k**), 2.40 (s, 3H, **3k**), 2.37 (s, 3H, **3k'**), 2.23 – 2.13 (m, 2H, **3k'**), 1.96 (ddt,

$J$  = 8.6, 7.4, 6.5 Hz, 2H, **3k**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 136.6, 132.4, 131.4,

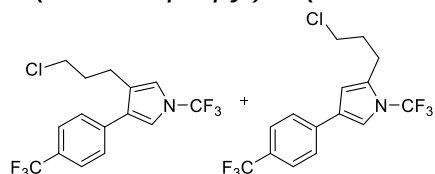
131.0, 129.6, 129.4, 128.2, 128.2, 128.2, 126.4, 125.4, 124.6, 119.1 (q,  $J = 260.0$  Hz), 115.8, 115.7, 113.9, 113.9, 110.0, 110.0, 44.5, 32.4, 22.9, 21.3;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -54.96 (s, **3k'**), -57.53 (s, **3k**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{ClF}_3\text{N}$   $[\text{M}]^+$ : 301.0845, found 301.0844.

*3-(3-Chloropropyl)-4-(4-methoxyphenyl)-1-(trifluoromethyl)-1H-pyrrole* and *2-(3-chloropropyl)-4-(4-methoxyphenyl)-1-(trifluoromethyl)-1H-pyrrole* (**3l**):



Prepared according to the **general procedure A** with 1-chloro-4-pentyne as the starting alkyne. Yield: 49%; colourless oil; crude  $^{19}\text{F}$  NMR ratio to **3l'**: 90:10;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.27 (m, 2H), 6.96 – 6.91 (m, 3H), 6.83 (dt,  $J = 2.3, 1.0$  Hz, 1H), 3.84 (s, 3H), 3.50 (t,  $J = 6.4$  Hz, 2H), 2.81 – 2.58 (m, 2H), 2.03 – 1.85 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 129.4, 128.6, 128.4, 128.0, 126.9, 126.8, 124.6, 119.1 (q,  $J = 259.9$  Hz), 115.7, 115.5, 114.2, 55.4, 44.6, 32.4, 22.9;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.52 (s); HRMS ( $\text{CI}^+$ )  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{ClF}_3\text{NO}$   $[\text{M}+\text{H}]^+$ : 318.0873, found 318.0877.

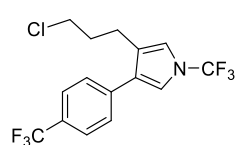
*3-(3-Chloropropyl)-1-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1H-pyrrole* and *2-heptyl-4-phenyl-1-(trifluoromethyl)-1H-pyrrole* (**3m** + **3m'**): Prepared according to the **general procedure A**



with 1-chloro-4-pentyne as the starting alkyne. Yield: 59%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 95:5;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.62 (m, 2H, **3m**), 7.65 – 7.54 (m, 4H, **3m'**), 7.49 (dtd,  $J = 8.5, 1.9, 1.0$  Hz, 2H), 7.05 (d,  $J = 2.5$  Hz, 1H, **3m**), 6.89 (dt,  $J = 2.2, 1.0$  Hz, 1H, **3m**), 6.43 (dq,  $J = 1.9, 0.9$  Hz, 1H, **3m'**), 3.65 (t,  $J = 6.3$  Hz, 2H, **3m**), 3.52 (t,

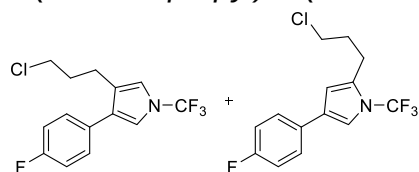
$J = 6.4$  Hz, 2H, **3m**), 2.96 – 2.87 (m, 2H, **3m'**), 2.80 – 2.71 (m, 2H, **3m**), 2.18 (ddt,  $J = 8.5, 7.4, 6.4$  Hz, 2H, **3m'**), 1.96 (ddt,  $J = 8.8, 7.5, 6.3$  Hz, 2H, **3m**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 138.1, 129.2 (q,  $J = 32.5$  Hz), 128.4, 127.0, 125.9, 125.9, 125.7 (q,  $J = 3.8$  Hz), 125.6, 124.4, 123.0, 120.3, 120.2, 118.9 (q,  $J = 260.6$  Hz), 116.4, 116.3, 109.8, 44.4, 32.4, 22.8;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.14 (s,  $N\text{-CF}_3$ , **3m'**), -57.64 (s,  $N\text{-CF}_3$ , **3m**), -62.92 (s, **3m'**), -62.96 (s, **3m**); HRMS ( $\text{Cl}^+$ )  $m/z$  calcd for  $\text{C}_{15}\text{H}_{12}\text{ClF}_6\text{N}$   $[\text{M}+\text{H}]^+$ : 356.0641, found 356.0647.

**3-(3-Chloropropyl)-1-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1H-pyrrole (3m):**



colourless oil;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (dd,  $J = 65.5, 7.9$  Hz, 2H), 7.05 (d,  $J = 2.4$  Hz, 1H), 6.88 (dd,  $J = 2.4, 1.1$  Hz, 1H), 3.52 (t,  $J = 6.3$  Hz, 2H), 2.75 (td,  $J = 7.5, 1.0$  Hz, 2H), 1.95 (ddt,  $J = 8.8, 7.5, 6.3$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 129.2 (q,  $J = 32.5$  Hz), 128.4, 127.0, 125.7 (q,  $J = 3.8$  Hz), 124.4, 123.0, 120.3, 118.9 (q,  $J = 260.7$  Hz), 116.4, 116.3, 44.4, 32.4, 22.8;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.64 (s,  $N\text{-CF}_3$ ), -62.97 (s).

**3-(3-Chloropropyl)-4-(4-fluorophenyl)-1-(trifluoromethyl)-1H-pyrrole and 2-(3-chloropropyl)-4-(4-fluorophenyl)-1-(trifluoromethyl)-1H-pyrrole (3n + 3n')**: Prepared according to the **general**

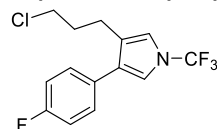


**procedure A** with 1-chloro-4-pentyne as the starting alkyne. Yield: 70%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 92:8;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J = 8.7, 0.8$  Hz, 1H, **3n'**), 7.50 – 7.39 (m, 3H, **3n'**), 7.38 – 7.32 (m, 1H, **3n**), 7.21 – 7.04 (m, 2H + 1H', **3n** + **3n'**), 6.99 (d,  $J = 2.5$  Hz, 1H, **3n**), 6.87 (dt,  $J = 2.3, 1.0$  Hz, 1H, **3n**), 6.37 (dq,  $J = 1.8, 0.9$



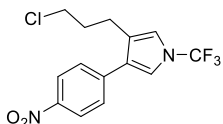
Hz, 1H, **3n'**), 3.66 (t,  $J = 6.4$  Hz, 2H, **3n'**), 3.53 (t,  $J = 6.4$  Hz, 2H, **3n**), 2.93 (t,  $J = 7.6$  Hz, 2H, **3n'**), 2.82 – 2.63 (m, 2H, **3n**), 2.19 (dq,  $J = 8.0, 6.5$  Hz, 2H, **3n'**), 1.96 (ddt,  $J = 8.7, 7.4, 6.4$  Hz, 2H, **3n**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.07 (d,  $J = 246.1$  Hz),  $\delta$  161.9 (d,  $J = 245.5$  Hz), 147.1, 133.4, 132.6, 130.2, 130.2, 129.9, 129.8, 127.3, 127.0, 126.9, 124.8, 124.5, 124.4, 124.0, 122.8, 120.2, 118.9 (q,  $J = 260.2$  Hz), 119.1, 117.6, 115.8, 115.7, 115.6, 115.5, 115.4, 115.2, 115.0, 113.9, 109.8, 44.30, 32.3, 22.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -54.52 (s, **3n'**), -57.08 (s, **3n**), -115.42 to -115.59 (m, 1F, **3n**), -115.80 to -116.00 (m, 1F, **3n'**); HRMS ( $\text{Cl}^+$ )  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{ClF}_4\text{N}$  [ $\text{M} + \text{H}$ ] $^+$ : 306.0673, found 306.0674.

**3-(3-Chloropropyl)-4-(4-fluorophenyl)-1-(trifluoromethyl)-1H-pyrrole (3n)**: colourless oil;



$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.28 (m, 2H), 7.14 – 7.04 (m, 2H), 6.96 (d,  $J = 2.5$  Hz, 1H), 6.84 (dt,  $J = 2.3, 1.0$  Hz, 1H), 3.50 (t,  $J = 6.4$  Hz, 2H), 2.84 – 2.44 (m, 2H), 2.12 – 1.76 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2 (d,  $J = 246.1$  Hz), 130.4, 130.3, 130.0, 129.9, 127.4, 124.5, 118.9 (q,  $J = 260.2$  Hz), 115.9, 115.8, 115.8, 115.6, 44.5, 32.4, 22.8;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.58 (s,  $\text{N-CF}_3$ ), -116.04 (m, 1F).

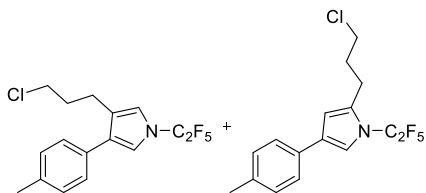
**3-(3-Chloropropyl)-4-(4-nitrophenyl)-1-(trifluoromethyl)-1H-pyrrole (3o)**: Prepared



according to the **general procedure A** with 1-chloro-4-pentyne as the starting alkyne. Yield: 27%; colourless oil; crude  $^{19}\text{F}$  NMR ratio to **3o'**: 96:4;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 – 8.24 (m, 2H), 7.61 – 7.51 (m, 2H), 7.12 (d,  $J = 2.5$  Hz, 1H), 6.91 (dt,  $J = 2.3, 1.0$  Hz, 1H), 3.53 (t,  $J = 6.3$  Hz, 2H), 2.82 – 2.73 (m, 2H), 1.96 (ddt,  $J = 8.9, 7.5, 6.3$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 141.3, 128.6,

126.2, 126.1, 124.4, 124.2, 118.8 (q,  $J = 261.1$  Hz), 116.9, 116.7, 44.3, 32.4, 22.9;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.73 (s); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{ClF}_3\text{N}_2\text{O}_2$   $[\text{M}]^+$ : 332.0539, found 332.0538.

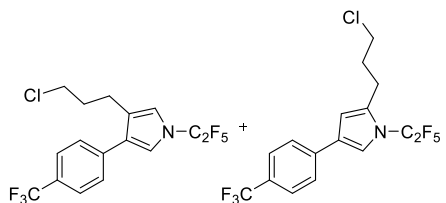
3-(3-Chloropropyl)-1-(perfluoroethyl)-4-(*p*-tolyl)-1*H*-pyrrole and 2-(3-chloropropyl)-1-(perfluoroethyl)-4-(*p*-tolyl)-1*H*-pyrrole (**3p** + **3p'**):



Prepared according to the **general procedure A** with 1-chloro-4-pentyne as the starting alkyne. Yield: 51%;

colourless oil; crude  $^{19}\text{F}$  NMR ratio: 97:3;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.1$  Hz, 2H, **3p'**), 7.28 (d,  $J = 8.2$  Hz, 2H, **3p**), 7.24 – 7.16 (m, 2H + 2H', **3p** + **3p'**), 7.06 (q,  $J = 1.0$  Hz, 1H, **3p'**), 6.93 (d,  $J = 2.5$  Hz, 1H, **3p**), 6.84 – 6.73 (m, 1H, **3p**), 6.42 (dt,  $J = 1.9$ , 0.9 Hz, 1H, **3p'**), 3.64 (t,  $J = 6.4$  Hz, 2H, **3p'**), 3.51 (t,  $J = 6.4$  Hz, 2H, **3p**), 2.91 – 2.83 (m, 2H, **3p'**), 2.85 – 2.62 (m, 2H, **3p**), 2.39 (s, 3H, **3p**), 2.37 (s, 3H, **3p'**), 2.22 – 2.12 (m, 2H, **3p'**), 1.96 (ddt,  $J = 8.7$ , 7.5, 6.4 Hz, 2H, **3p**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 131.3, 129.6, 129.4, 128.5, 128.2, 125.4, 124.8, 122.1 (t,  $J = 47.5$  Hz), 119.3 (t,  $J = 47.4$  Hz), 116.4 (q,  $^1J_{\text{C-F}} = 47.5$  Hz), 116.3, 116.2, 113.6 (q,  $^1J_{\text{C-F}} = 47.4$  Hz), 113.4 (q,  $J = 41.7$  Hz), 110.8 (q,  $J = 41.7$  Hz), 108.2 (q,  $J = 41.5$  Hz); 44.5, 32.4, 23.0, 21.3;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.98 (s,  $-\text{CF}_3$ , **3p'**), -85.78 (s,  $-\text{CF}_3$ , **3p**), -96.06 (s,  $\text{N}-\text{CF}_2$ -, **3p'**), -98.97 (s,  $\text{N}-\text{CF}_2$ -, **3p**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{ClF}_5\text{N}$   $[\text{M}]^+$ : 351.0813, found 351.0813.

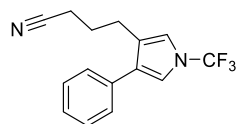
*3-(3-Chloropropyl)-1-(perfluoroethyl)-4-(4-(trifluoromethyl)phenyl)-1H-pyrrole and 2-(3-chloropropyl)-1-(perfluoroethyl)-4-(4-(trifluoromethyl)phenyl)-1H-pyrrole (3q + 3q')*: Prepared



according to the **general procedure A** with 1-chloro-4-pentyne as the starting alkyne. Yield: 42%; colourless oil; crude  $^{19}\text{F}$  NMR ratio: 98:2;  $^1\text{H}$

NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.56 (m, 4H + 4H', **3q** + **3q'**), 7.58 (dd,  $J = 62.7$ , 8.1 Hz, 4H, **3q**), 7.17 – 7.13 (m, 1H, **3q'**), 7.00 (d,  $J = 2.4$  Hz, 1H, **3q**), 6.84 (d,  $J = 2.4$  Hz, 1H, **3q**), 6.46 (dt,  $J = 2.1$ , 1.0 Hz, 1H, **3q'**), 3.64 (t,  $J = 6.3$  Hz, 2H, **3q'**), 3.52 (t,  $J = 6.3$  Hz, 2H, **3q**), 2.89 (t,  $J = 7.4$  Hz, 2H, **3q'**), 2.92 – 2.61 (m, 2H, **3q**), 2.23 – 2.13 (m, 2H, **3q'**), 1.96 (ddt,  $J = 8.8$ , 7.5, 6.3 Hz, 2H, **3q**);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 138.0, 138.0, 129.2 (q,  $J = 32.6$  Hz), 128.4, 127.2, 125.7 (q,  $J = 3.8$  Hz), 124.6, 123.0, 122.0 (t,  $J = 47.1$  Hz), 120.3, 119.2 (t,  $J = 47.0$  Hz), 116.9, 116.9, 116.1 (t,  $J = 47.1$  Hz), 113.5 (t,  $^1J_{\text{C-F}} = 47.1$  Hz), 113.4 (q,  $J = 41.7$  Hz), 110.7 (q,  $J = 41.8$  Hz), 108.1 (q,  $J = 41.9$  Hz), 44.4, 32.4, 22.9;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.95 ( $\text{CF}_3$ , **3q'**), -62.98 ( $\text{CF}_3$ , **3q**), -85.05 ( $-\text{CF}_3$ , **3q'**), -85.84 ( $-\text{CF}_3$ , **3q**), -96.33 ( $\text{N}-\text{CF}_2$ , **3q'**), -99.26 ( $\text{N}-\text{CF}_2$ , **3q**); HRMS ( $\text{EI}^+$ )  $m/z$  calcd for  $\text{C}_{16}\text{H}_{12}\text{ClF}_8\text{N}$   $[\text{M}]^+$ : 405.0531, found 405.0539.

*4-(4-Phenyl-1-(trifluoromethyl)-1H-pyrrol-3-yl)butanenitrile (4)*: Yield: 32%; colourless oil;

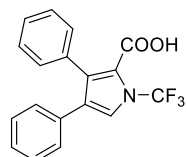


crude  $^{19}\text{F}$  NMR ratio to **4'** and **5**: 63:6:31;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$

7.47 – 7.29 (m, 5H), 7.00 (d,  $J = 2.5$  Hz, 1H), 6.86 (dt,  $J = 2.3$ , 1.0 Hz, 1H), 2.84 – 2.56 (m, 2H), 2.28 (t,  $J = 7.1$  Hz, 2H), 1.89 – 1.72 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.14, 128.95, 128.86, 128.26, 128.18, 127.29, 123.73, 119.48, 119.0

(q,  $J = 260.7$  Hz), 116.15, 116.03, 25.39, 24.62, 16.72;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.58 (s); HRMS ( $\text{Cl}^+$ )  $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{F}_3\text{N}_2$   $[\text{M} + \text{H}]^+$ : 279.1109, found 279.1107.

**3,4-Diphenyl-1-(trifluoromethyl)-1H-pyrrole-2-carboxylic acid (6)**: The crude mixture of **2a**



+ **2a'** (0.2 mmol) prepared according to the **general procedure A** was

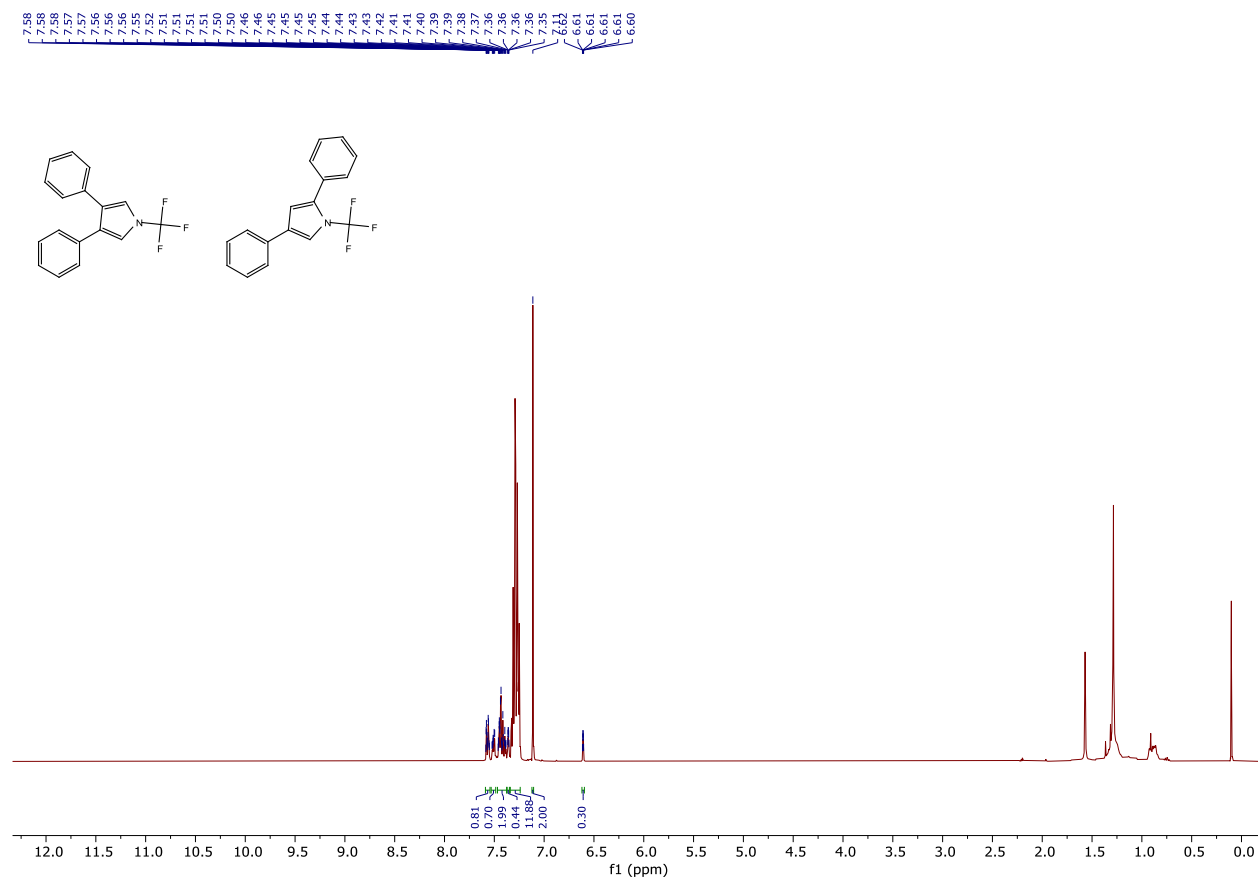
dried under reduced pressure, then THF (8 mL) was added. The solution

was cooled down to  $-78$  °C and  $n\text{-BuLi}$  (2.5M in hexane, 160  $\mu\text{L}$ , 0.4 mmol, 2 eq.) was added. The reaction was stirred for 30 minutes under nitrogen atmosphere. Then, excess of  $\text{CO}_2$  (in form of dry ice,  $\sim 2\text{g}$ ) was added to the reaction mixture. After 15 minutes of stirring the reaction was quenched with acetic acid (1 mL). The reaction mixture was extracted with ether; the organic layer was washed with brine ( $3 \times 20$  mL), brine/water (1:1,  $3 \times 20$  mL) and water ( $3 \times 20$  mL). Solvent evaporation afforded pure product. Yield: 75%, white crystalline solid;  $^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (s, 1H), 7.34 – 7.28 (m, 3H), 7.23 – 7.16 (m, 5H), 7.04 – 6.97 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8, 136.4, 132.8, 132.3, 130.28, 128.45, 128.31, 127.95, 127.83, 127.15, 122.08, 118.57 (q,  $J = 264.3$  Hz);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -53.50 (s); HRMS ( $\text{Cl}^+$ )  $m/z$  calcd for  $\text{C}_{18}\text{H}_{12}\text{F}_3\text{NO}_2$   $[\text{M} + \text{H}]^+$ : 331.0820, found 331.07778

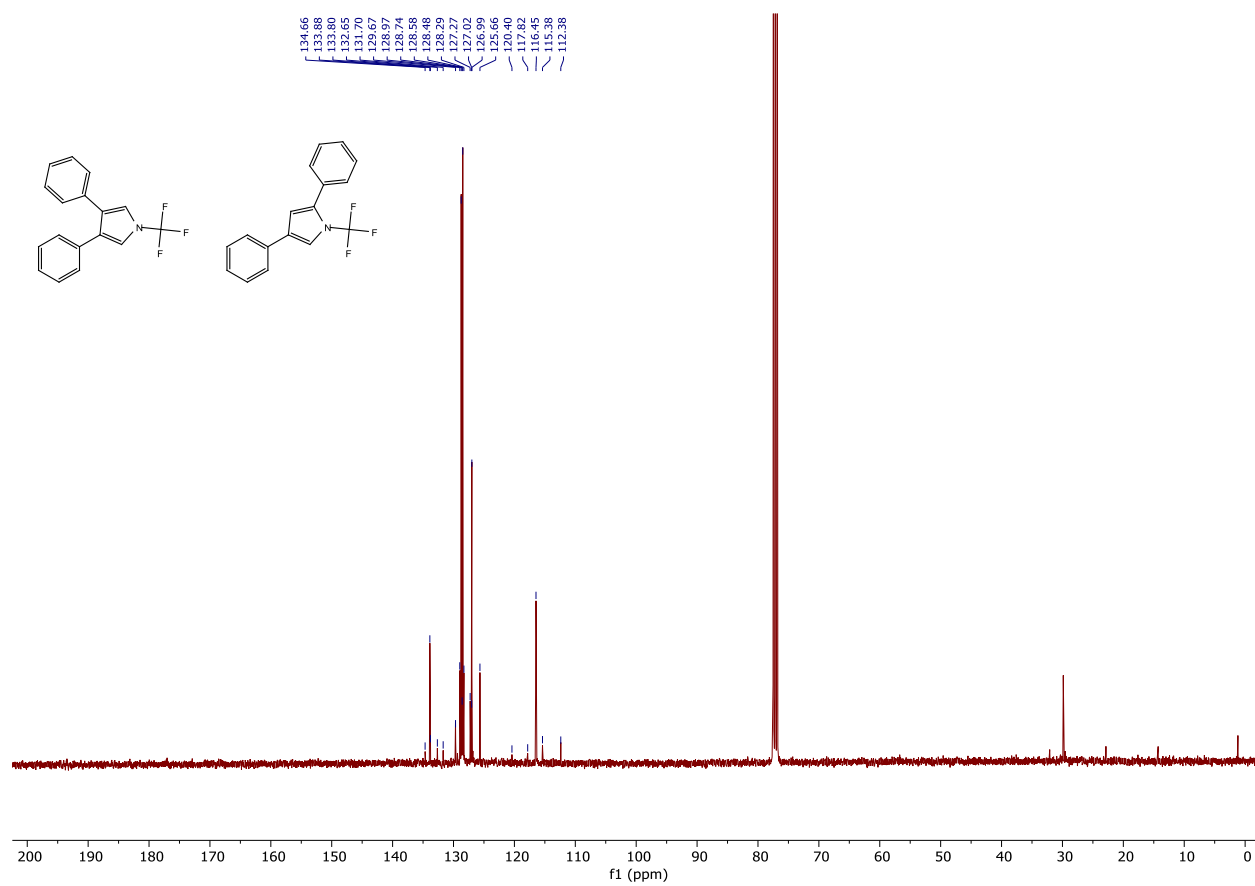
## References

- [1] Z. E. Blastik, S. Voltrová, V. Matoušek, B. Jurásek, D. W. Manley, B. Klepetářová, P. Beier, *Angew. Chem. - Int. Ed.* **2017**, 56, 346–349.

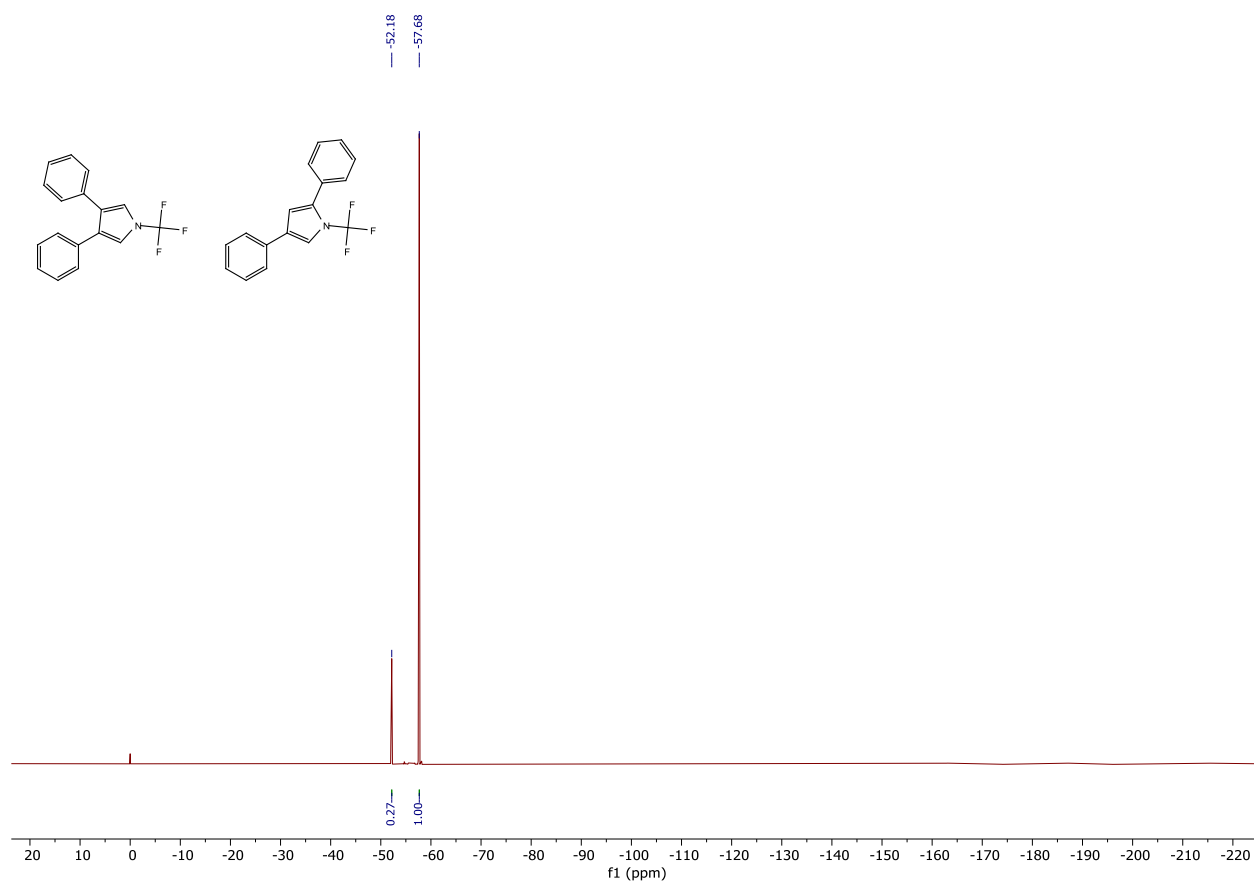
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **2a** + **2a'**



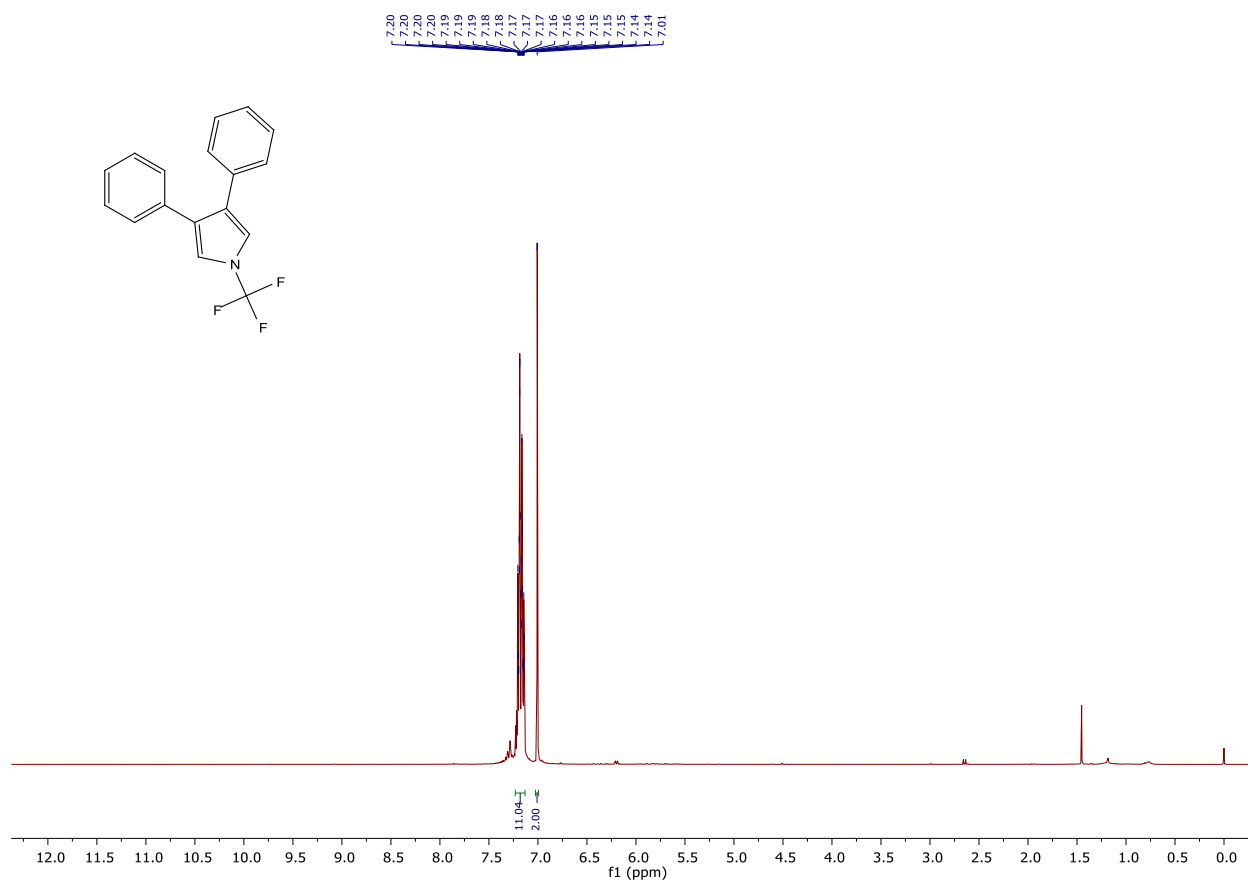
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2a** + **2a'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2a** + **2a'**

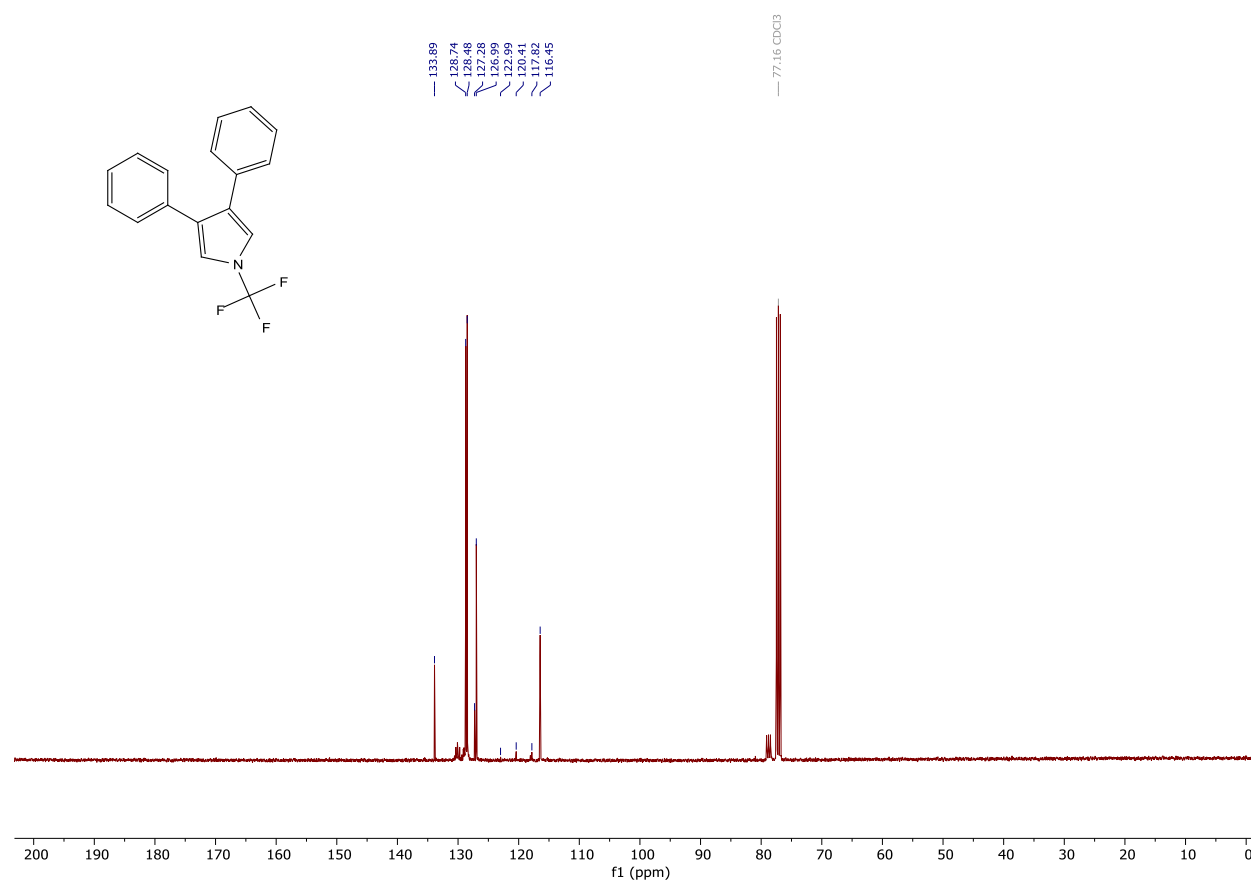


$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **2a**

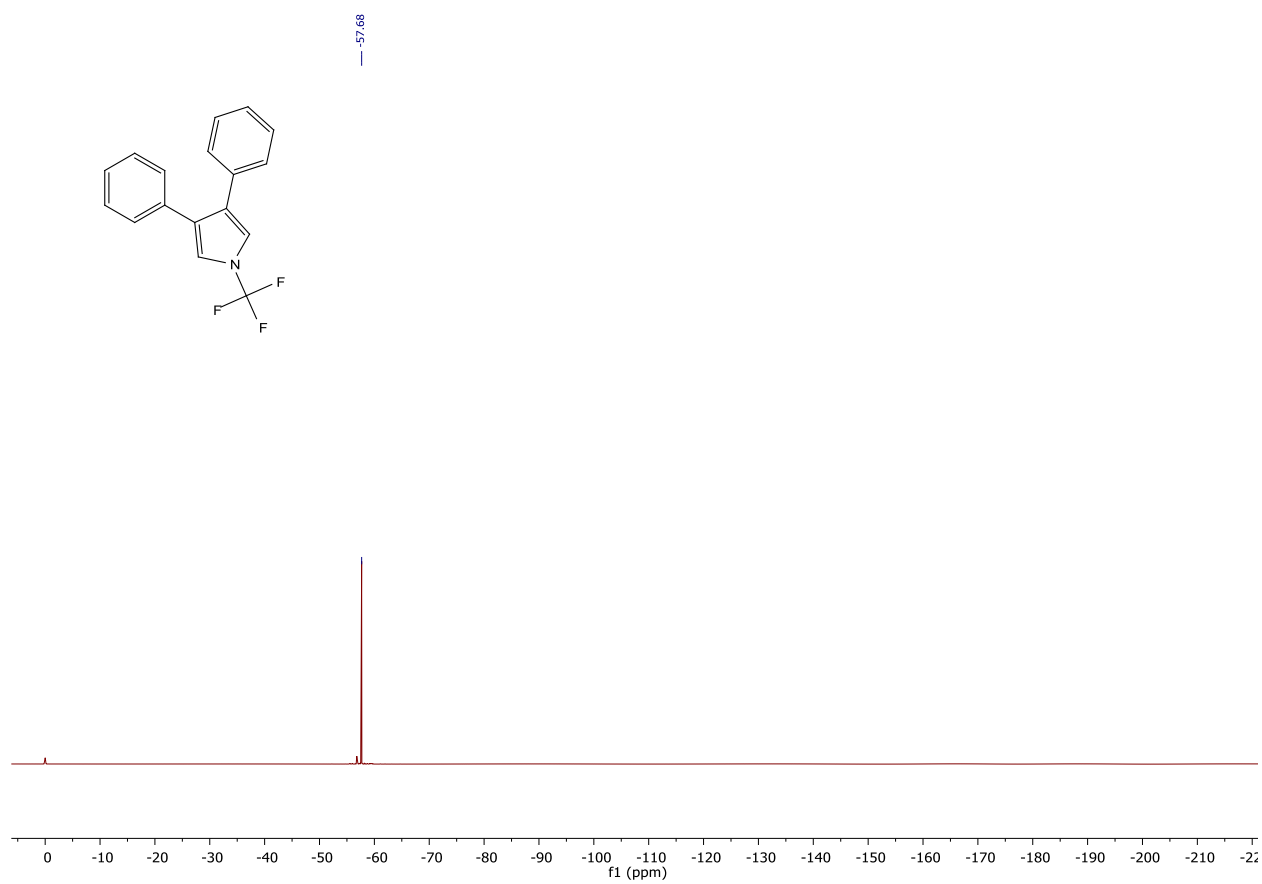




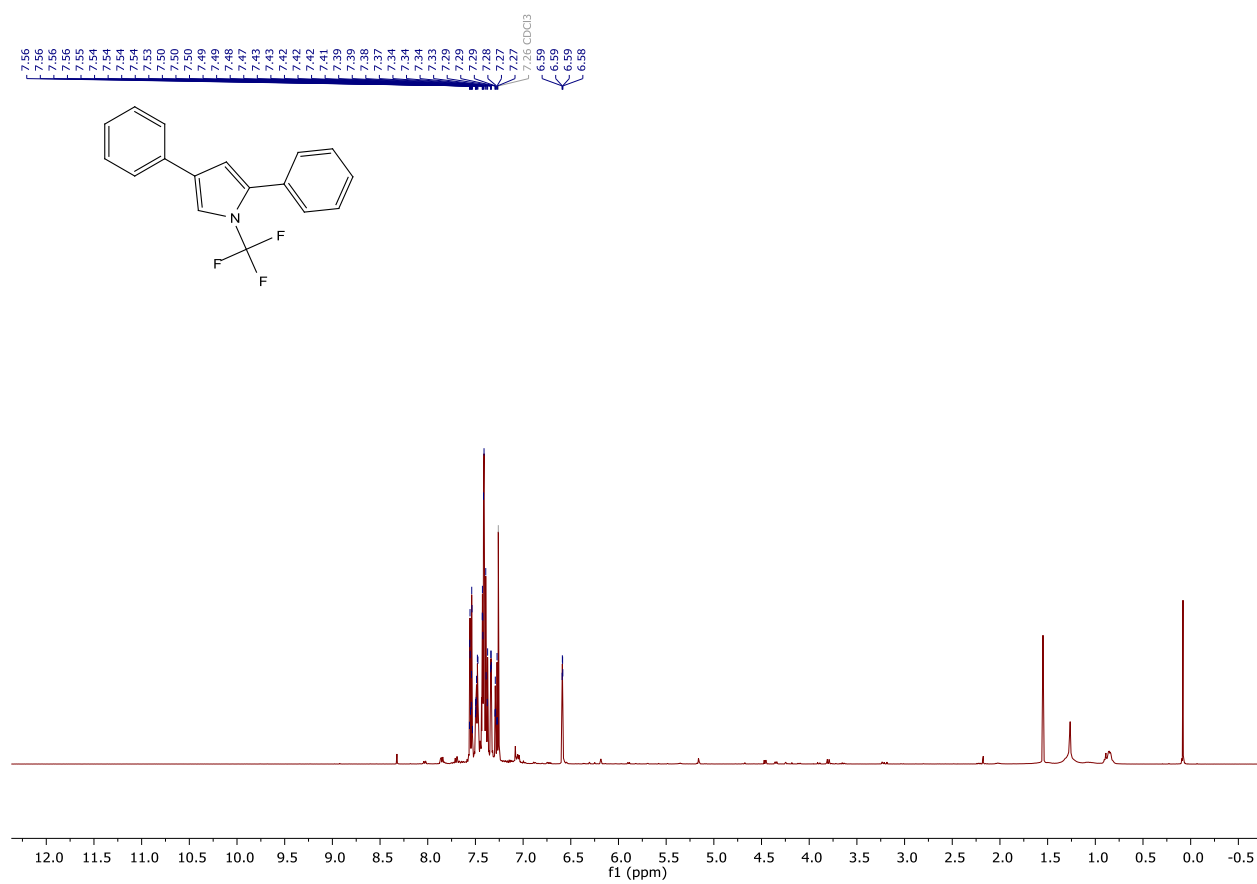
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2a**



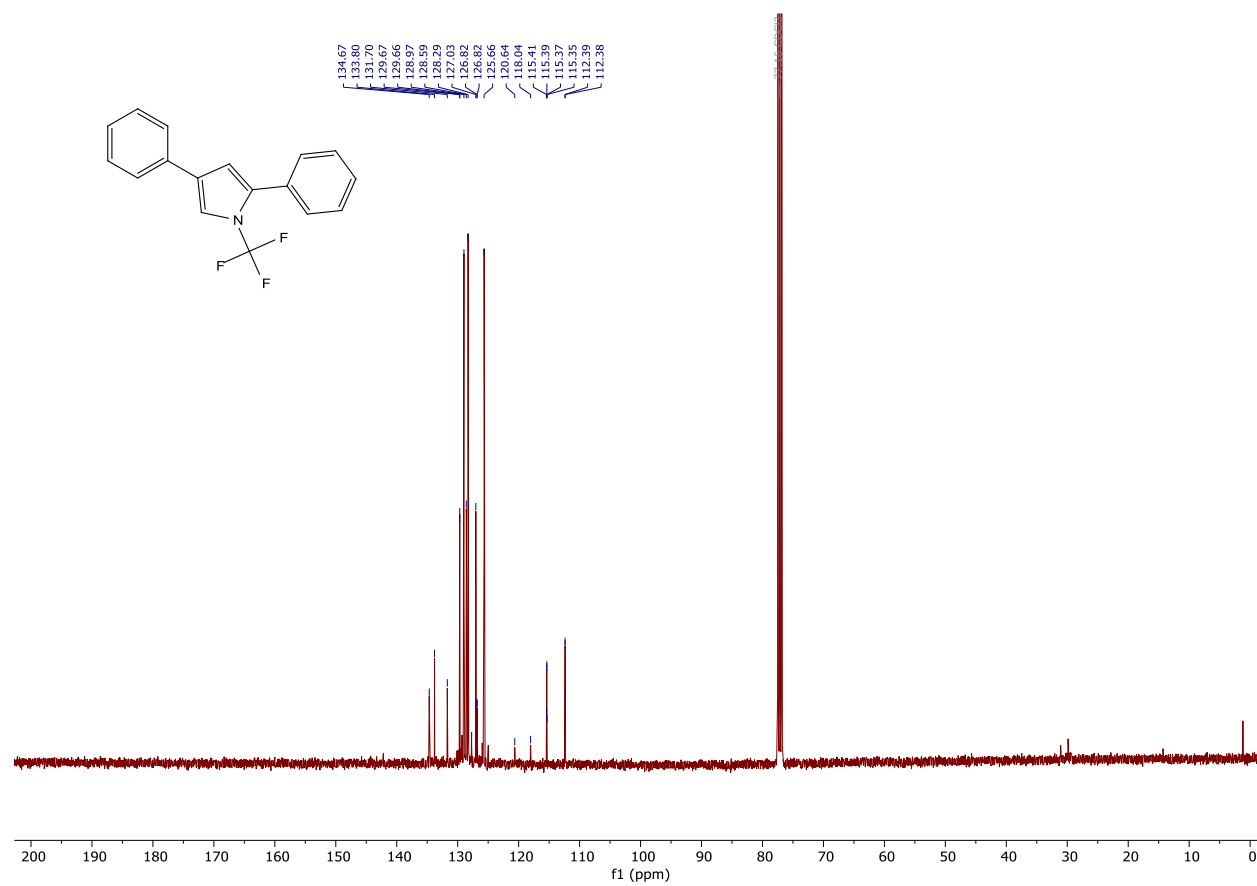
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2a**



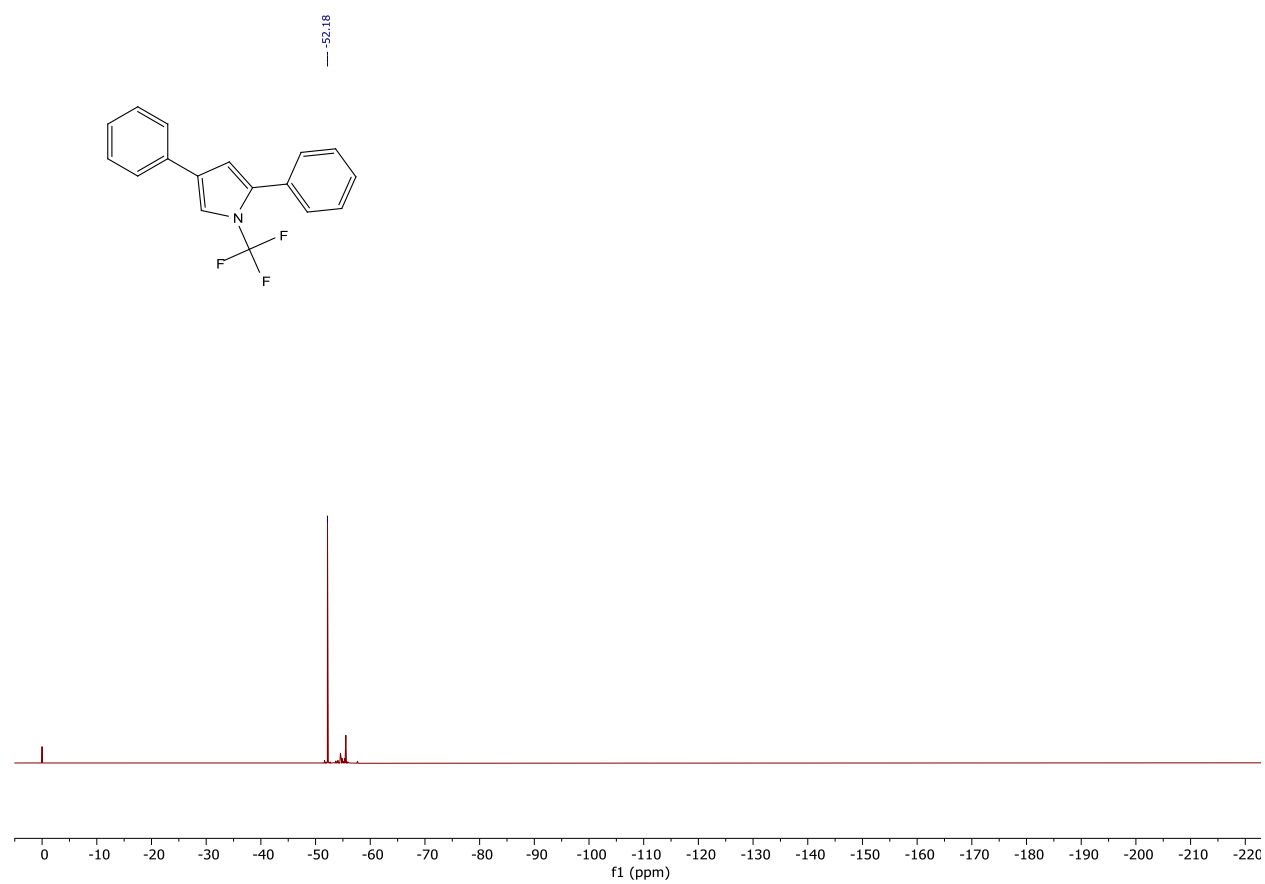
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **2a'**



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2a'**



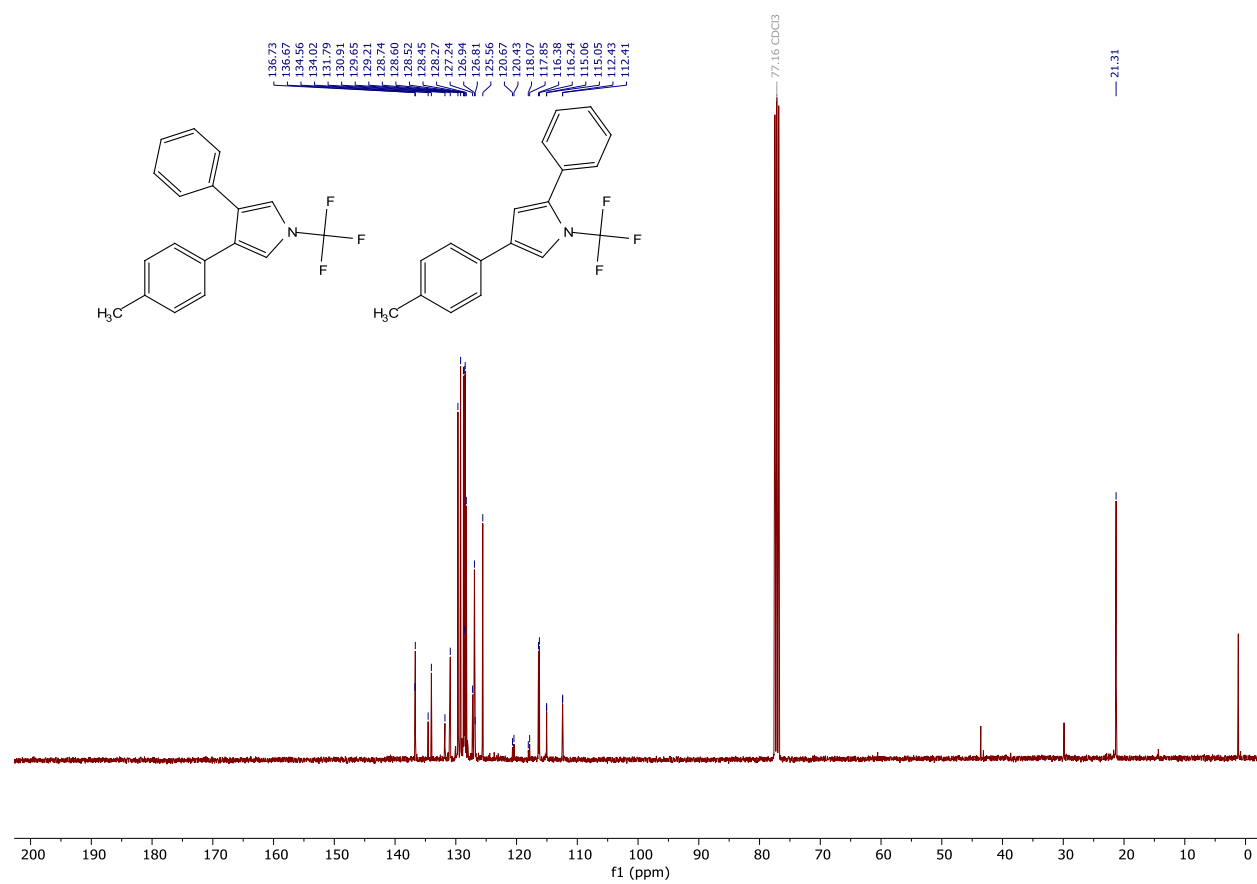
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2a'**



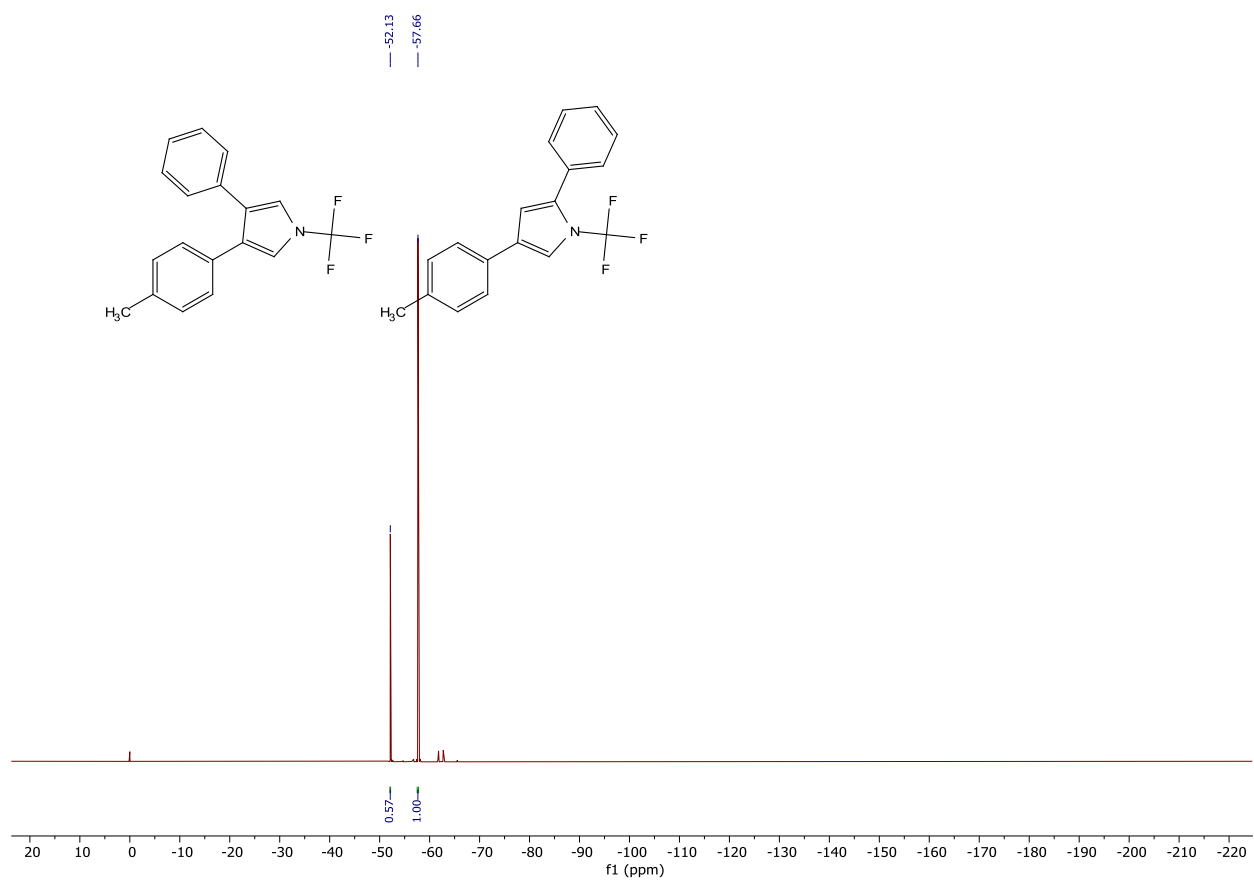
Chemical structures shown: Cc1ccc(cc1)-c2cc(C3=CC=CC=C3)n(C(F)(F)F)c2 (Target compound) and Cc1ccc(cc1)-c2cc(C3=CC=CC=C3)n(C(F)(F)F)c2-c4cc(C5=CC=CC=C5)n(C(F)(F)F)c4 (Dimeric impurity).

<sup>1</sup>H NMR spectrum (ppm): 7.48, 7.49, 7.49, 7.45, 7.44, 7.44, 7.43, 7.43, 7.42, 7.42, 7.32, 7.32, 7.31, 7.31, 7.30, 7.30, 7.30, 7.29, 7.29, 7.29, 7.29, 7.28, 7.28, 7.27, 7.27, 7.27, 7.26, 7.26, 7.25, 7.25, 7.25, 7.25, 7.23, 7.23, 7.22, 7.21, 7.21, 7.21, 7.16, 7.15, 7.14, 7.14, 7.13, 7.13, 7.11, 7.11, 7.10, 7.09, 7.08, 6.58, 6.58, 6.58, 2.39, 2.36.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2b** + **2b'**

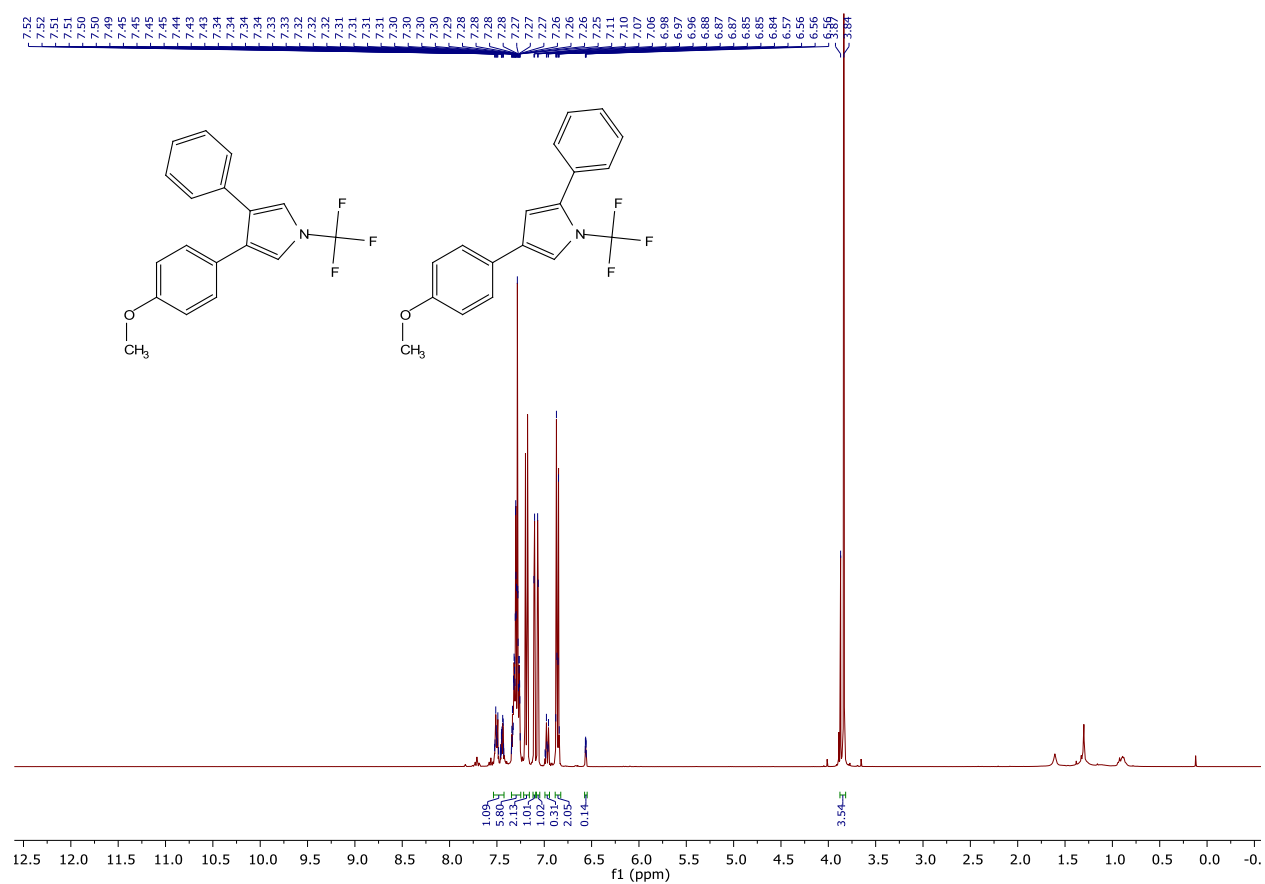


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2b** + **2b'**

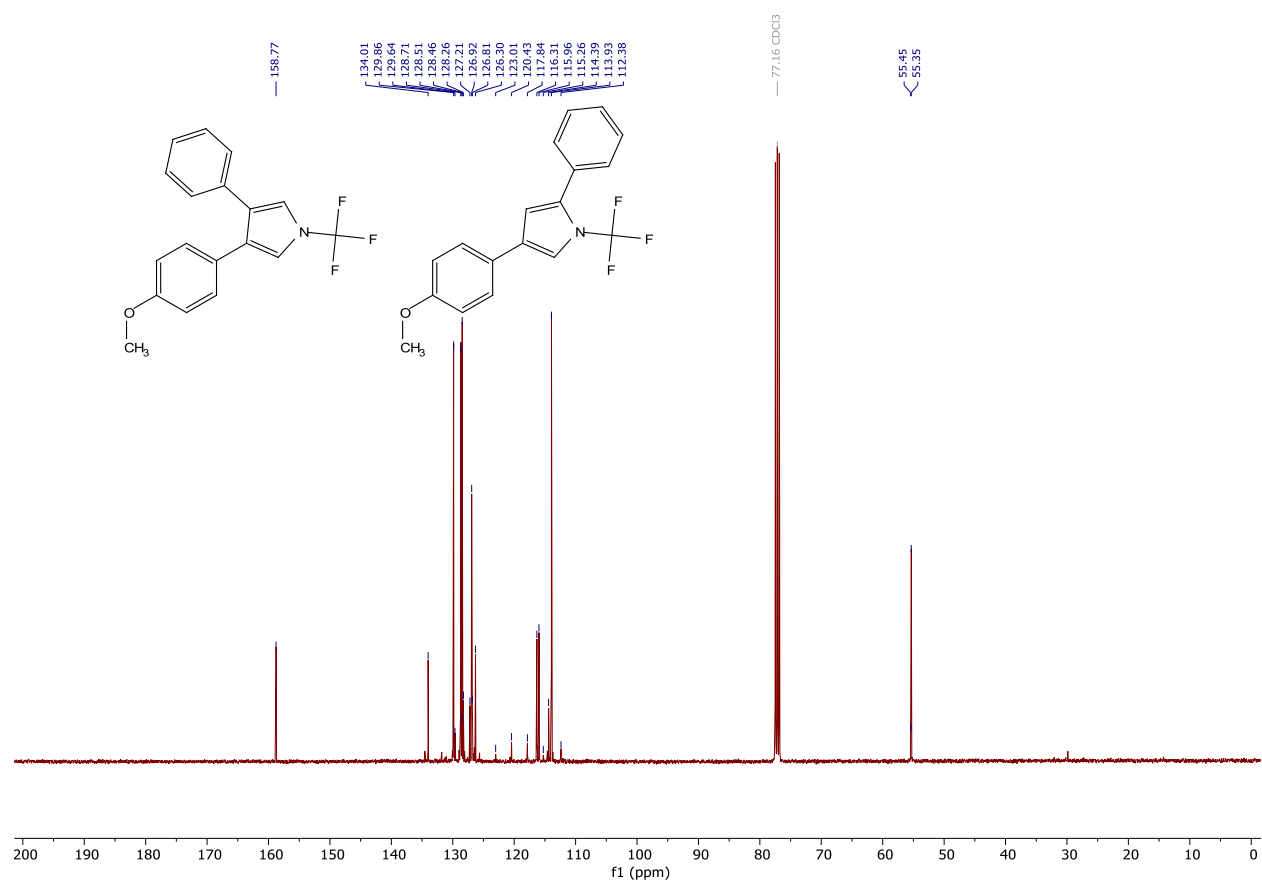




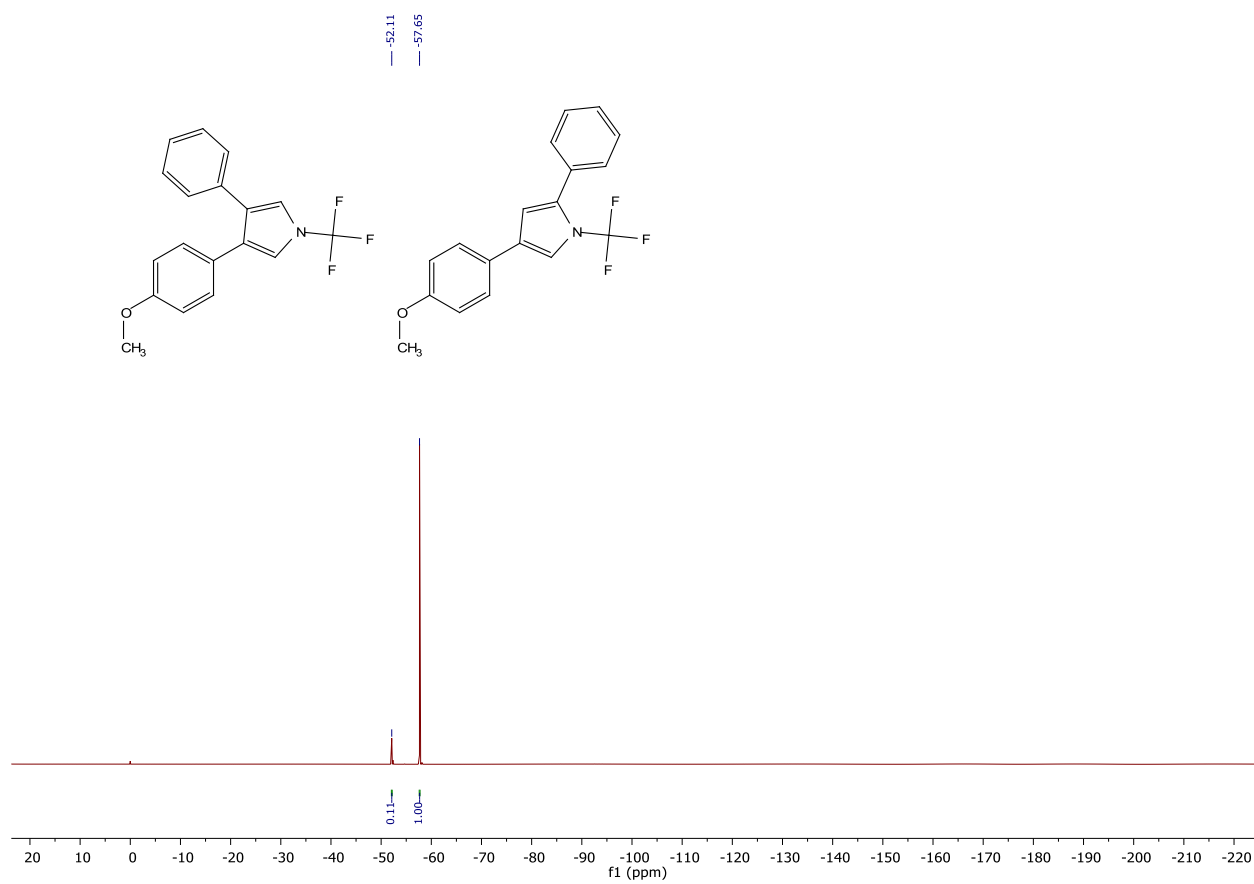
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **2c** + **2c'**



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2c** + **2c'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2c** + **2c'**

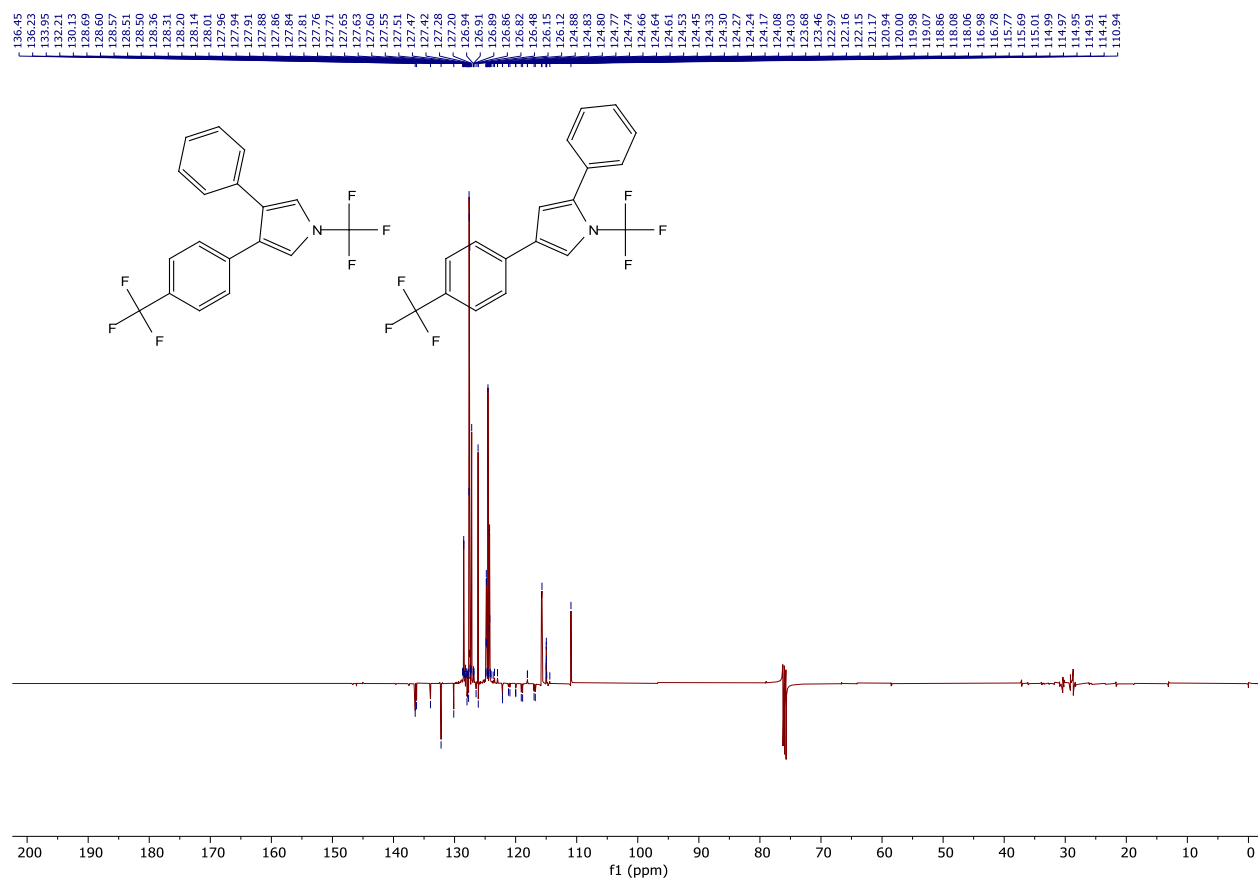


Chemical structure: C1=CC=C(C=C1)-c2cc(C(F)(F)F)nc(C3=CC=CC=C3)c2-c4ccc(C(F)(F)F)cc4

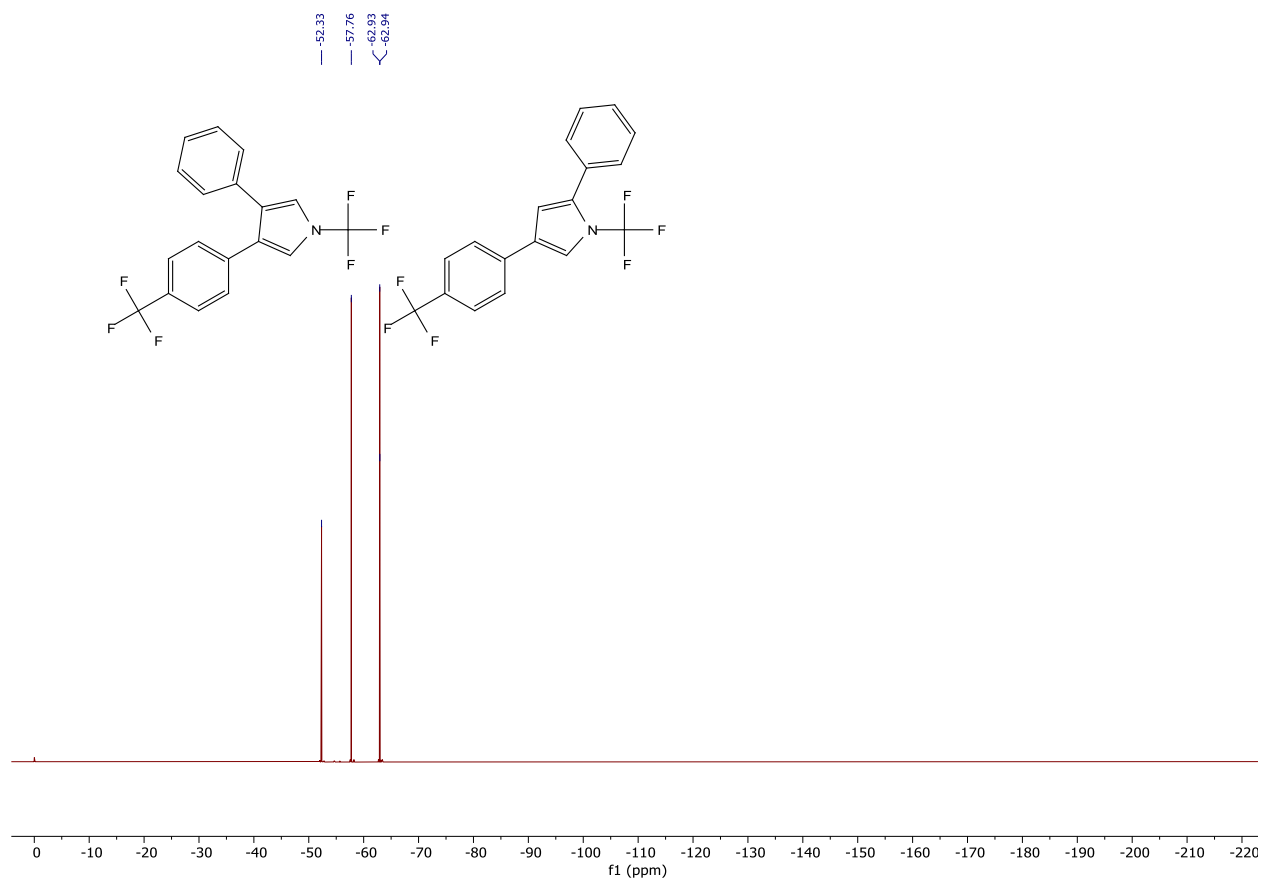
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing chemical shifts (ppm) and integration values.

| Chemical Shift (ppm)                                                                                                                                                                                             | Integration                                    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|
| 7.64, 7.54, 7.52, 7.52, 7.44, 7.43, 7.46, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.31, 7.30, 7.30, 7.29, 7.29, 7.22, 7.22, 7.22, 7.21, 7.21, 7.16, 7.16, 7.15, 7.12, 6.61, 6.61, 6.60, 6.60 | 1.14, 0.93, 0.01, 1.18, 1.12, 4.96, 1.97, 0.29 |
| 2.9                                                                                                                                                                                                              | 1.00                                           |

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2d** + **2d'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2d** + **2d'**

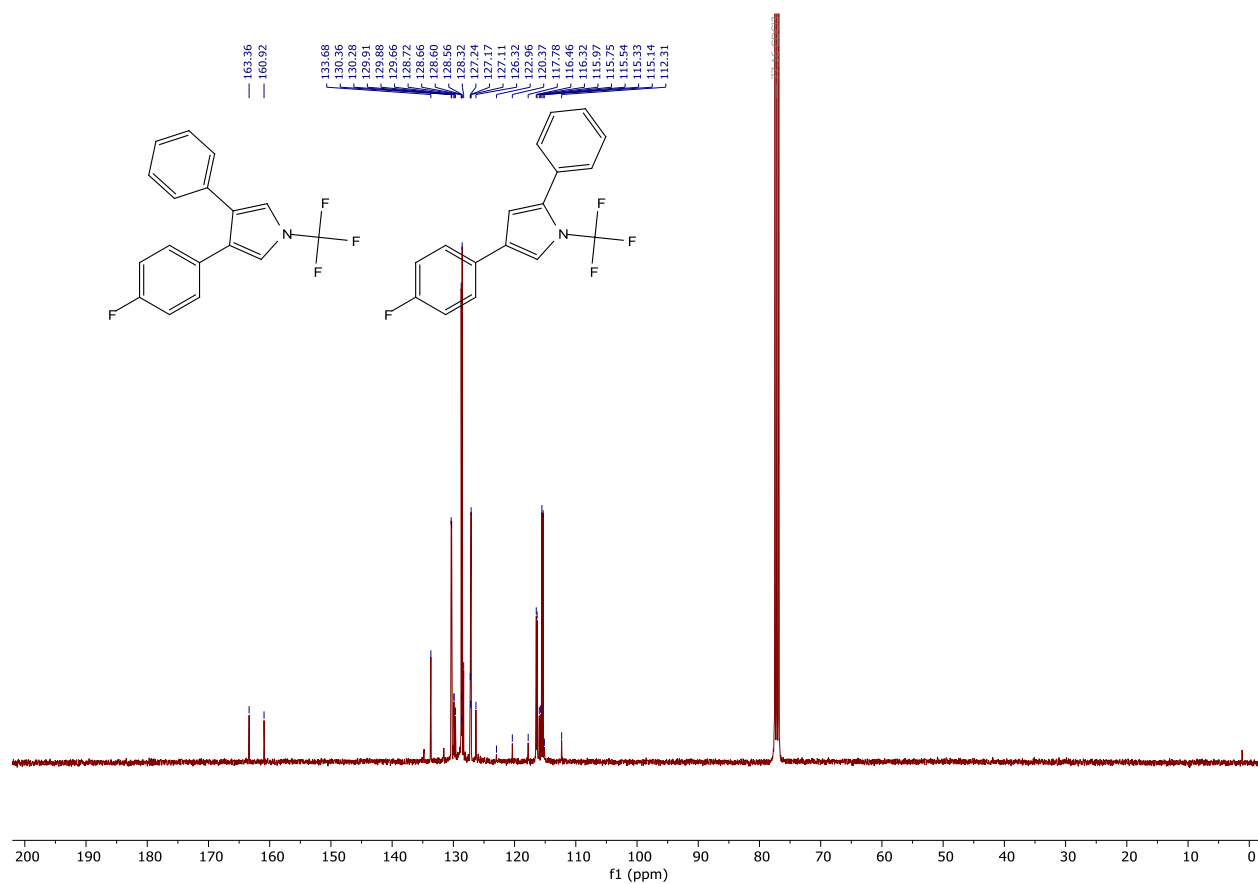


Cc1cc(Cc2ccc(F)cc2)c(Cc3ccc(C(F)(F)F)cc3)n1

Chemical structure of 2-(4-fluorophenyl)-3-(4-(trifluoromethyl)phenyl)pyrrole is shown. The  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) displays the following peaks and integrations:

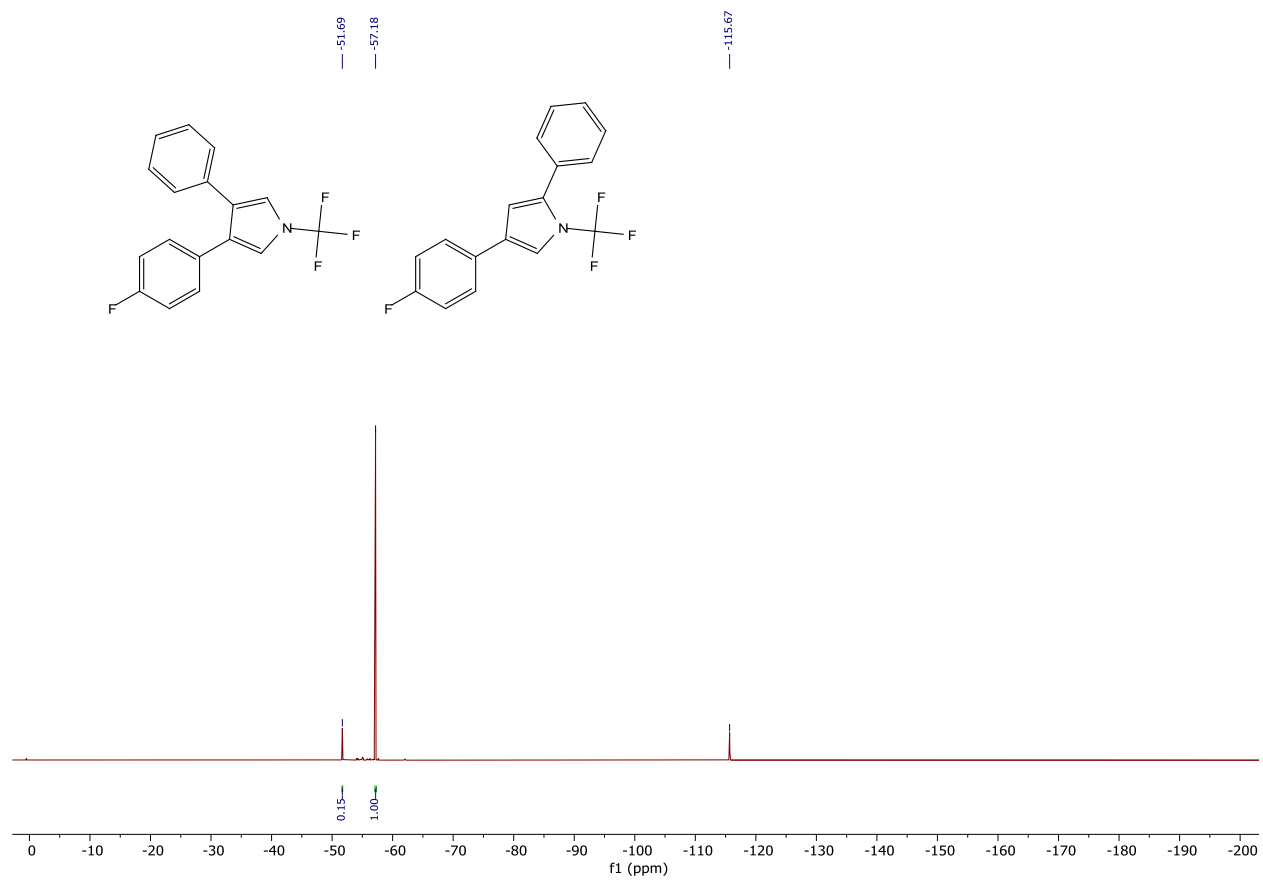
| Chemical Shift (ppm)                                                                                                                                                                                                         | Integration                  |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| 7.51, 7.44, 7.33, 7.32, 7.32, 7.31, 7.30, 7.30, 7.29, 7.28, 7.25, 7.24, 7.23, 7.23, 7.22, 7.22, 7.21, 7.21, 7.20, 7.20, 7.12, 7.11, 7.11, 7.09, 7.08, 7.07, 7.02, 7.01, 7.00, 6.99, 6.98, 6.98, 6.88, 6.85, 6.85, 6.55, 6.55 | 1.80, 3.69, 2.05, 1.89, 0.15 |
| 2.0                                                                                                                                                                                                                          |                              |
| 1.5                                                                                                                                                                                                                          |                              |
| 1.2                                                                                                                                                                                                                          |                              |
| 0.8                                                                                                                                                                                                                          |                              |
| 0.0                                                                                                                                                                                                                          |                              |

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2e** + **2e'**

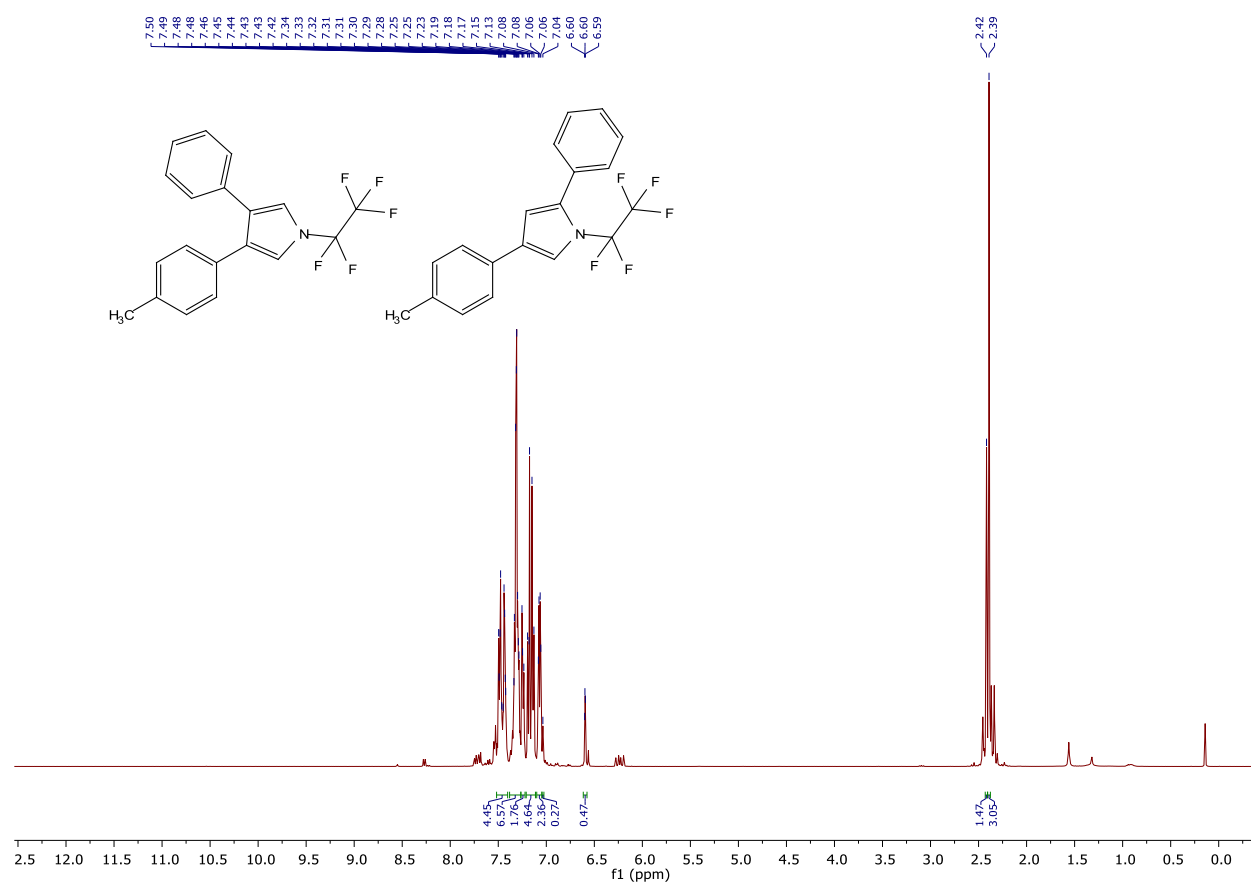




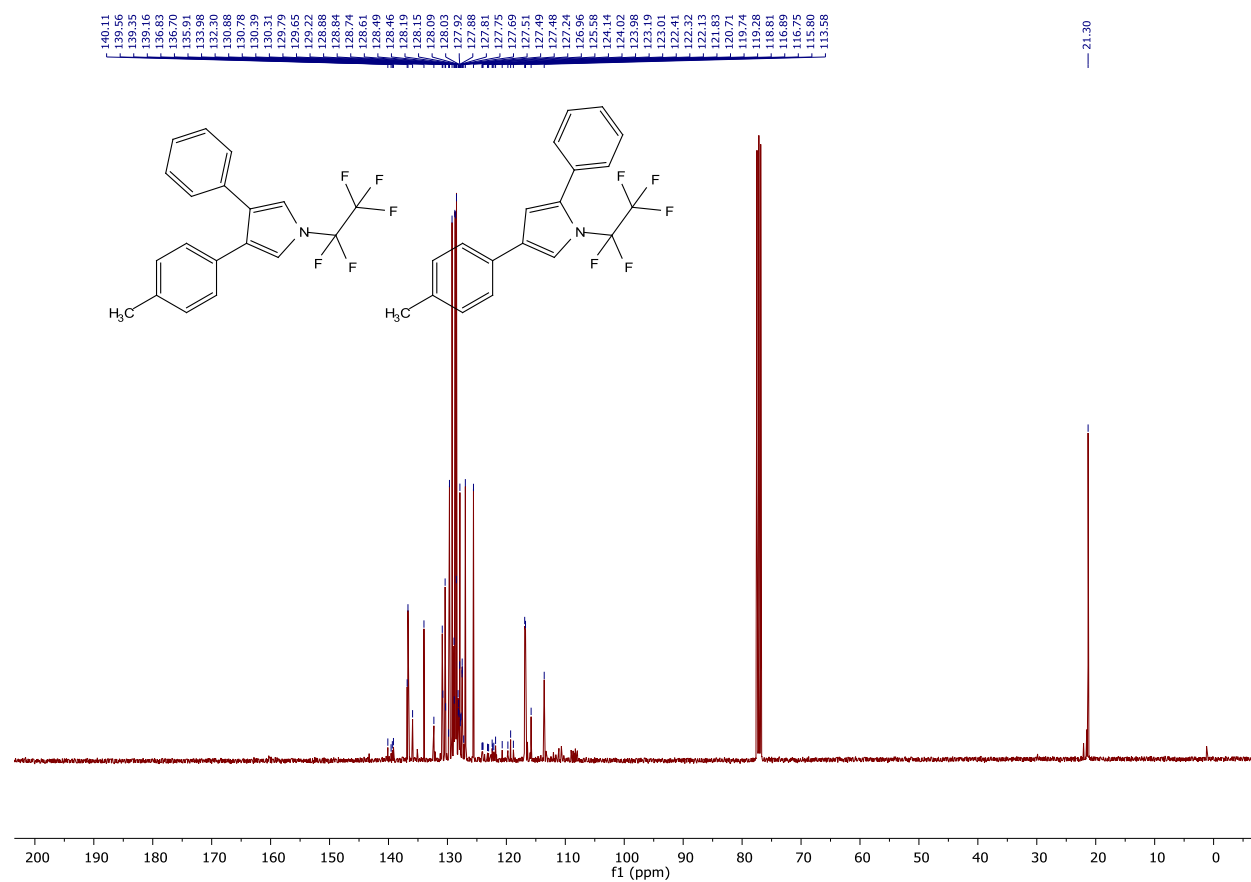
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2e** + **2e'**



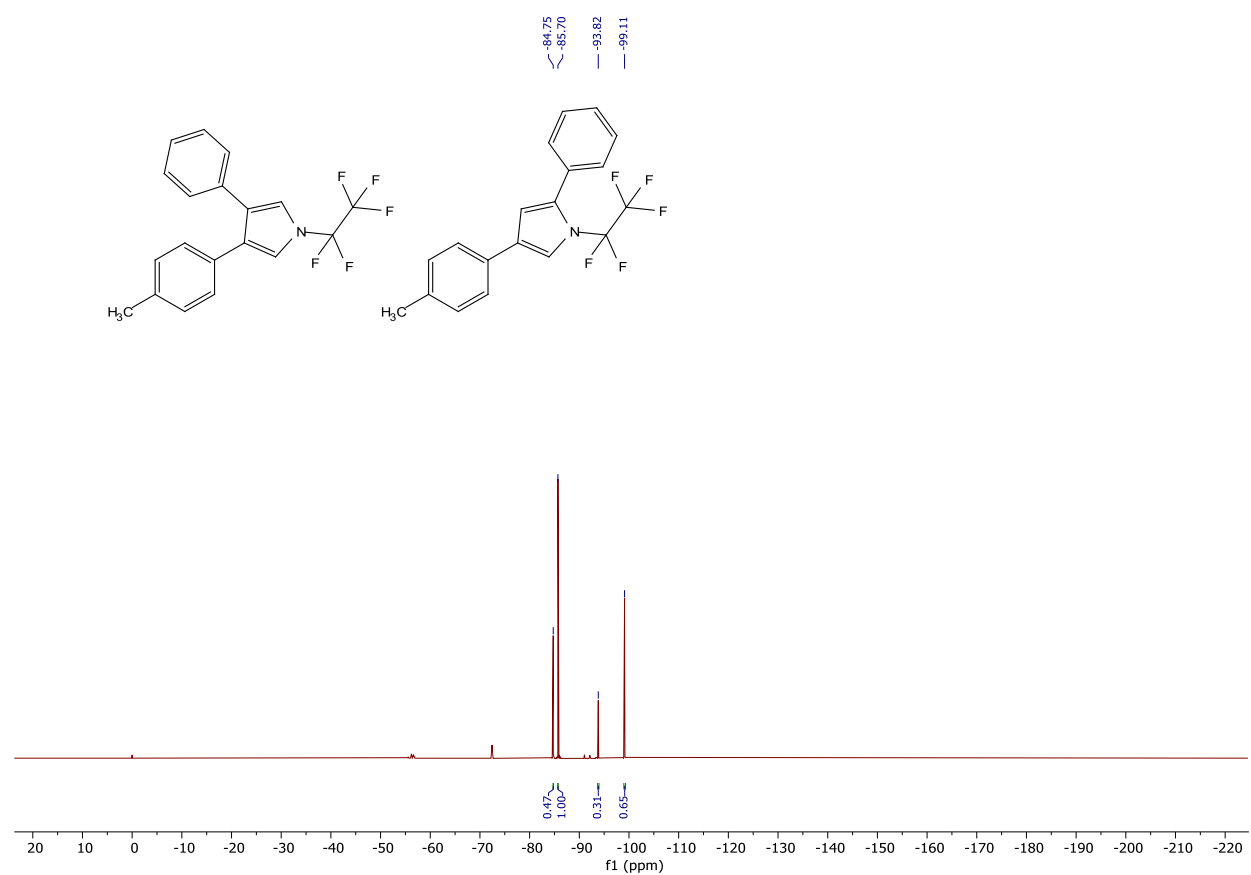
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **2f** + **2f'**



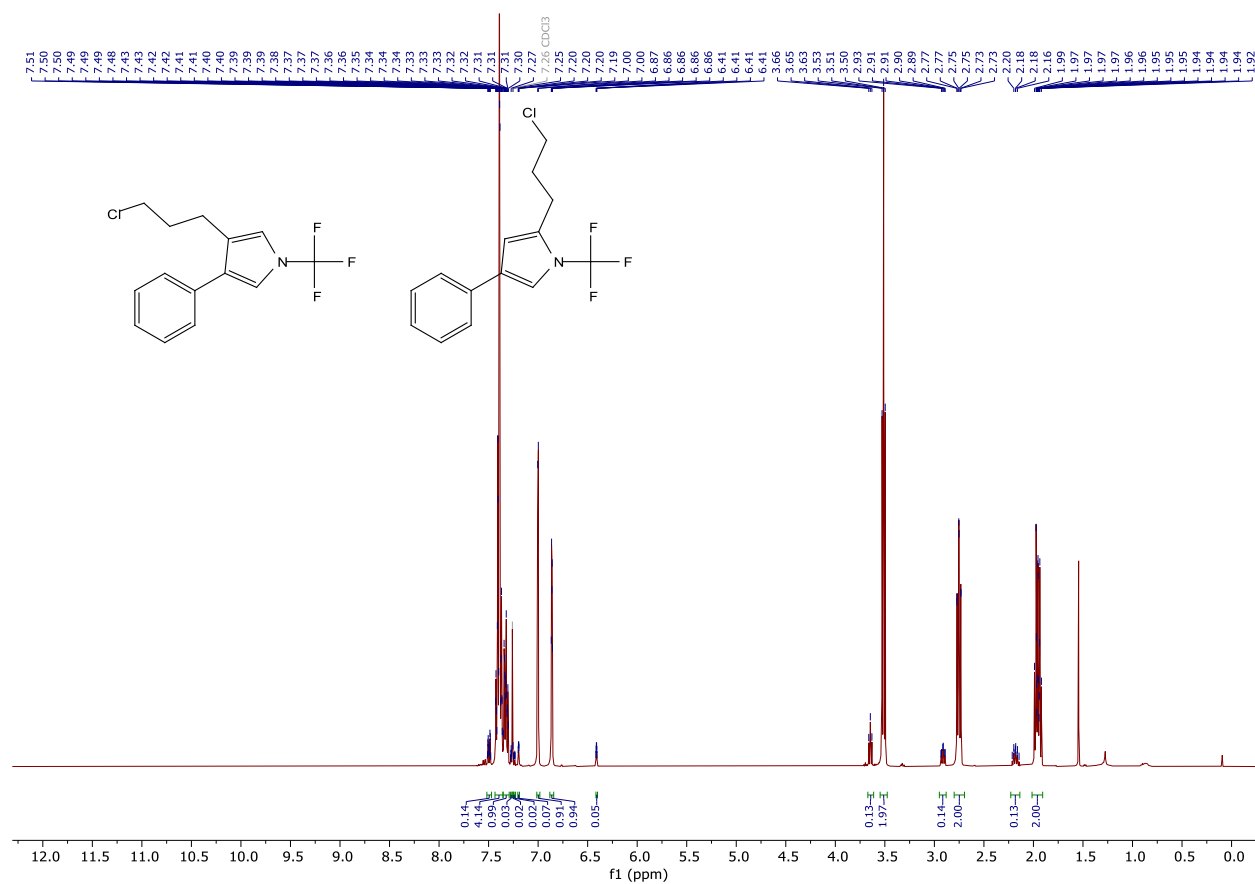
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **2f** + **2f'**



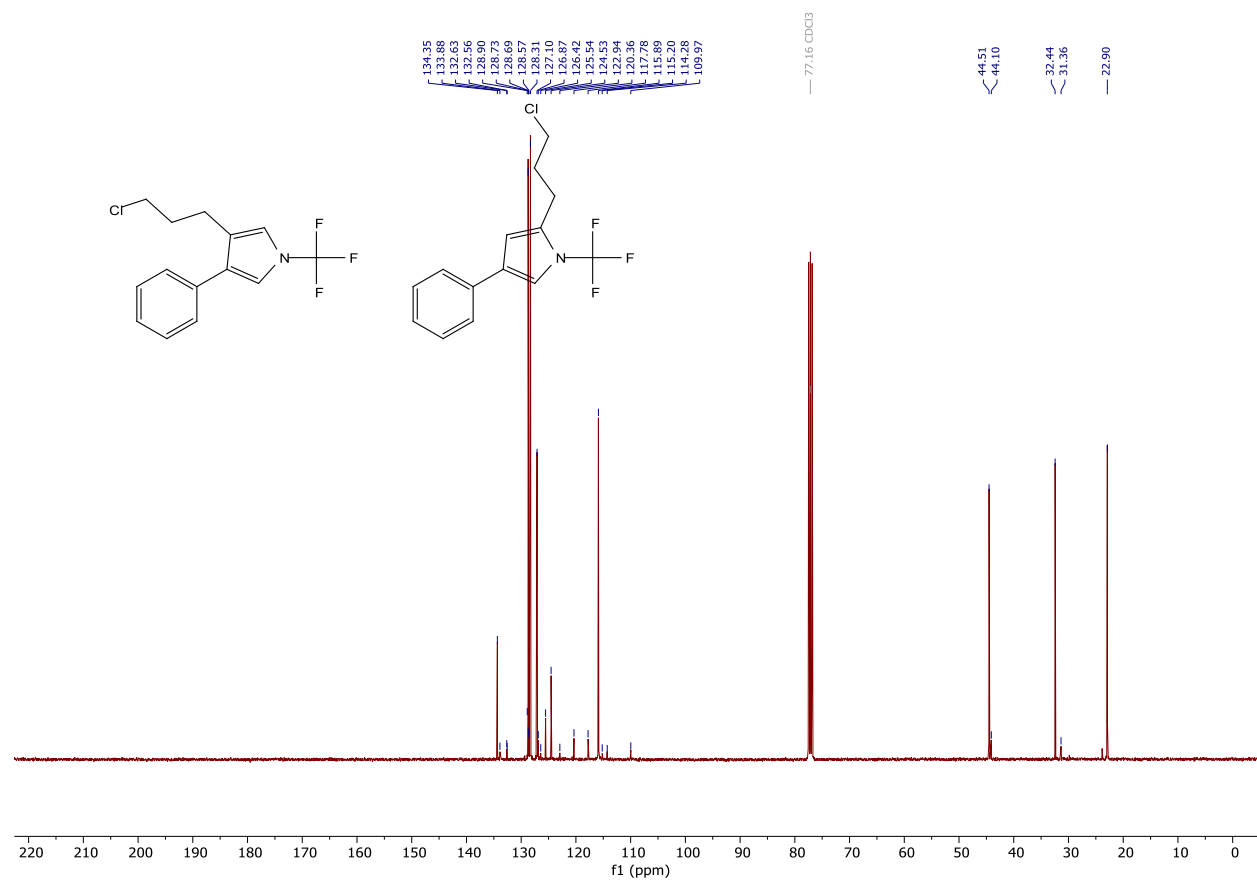
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **2f** + **2f'**



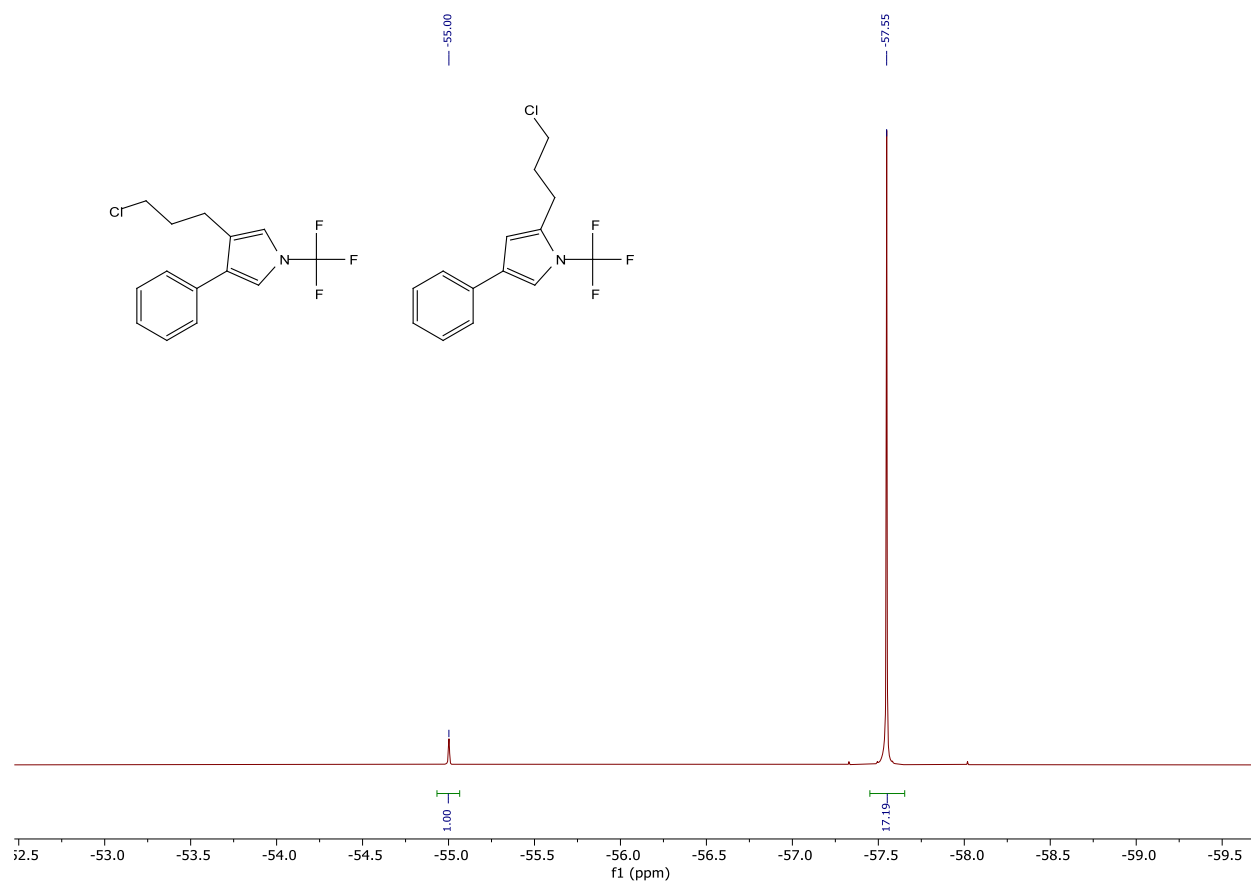
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3a** + **3a'**



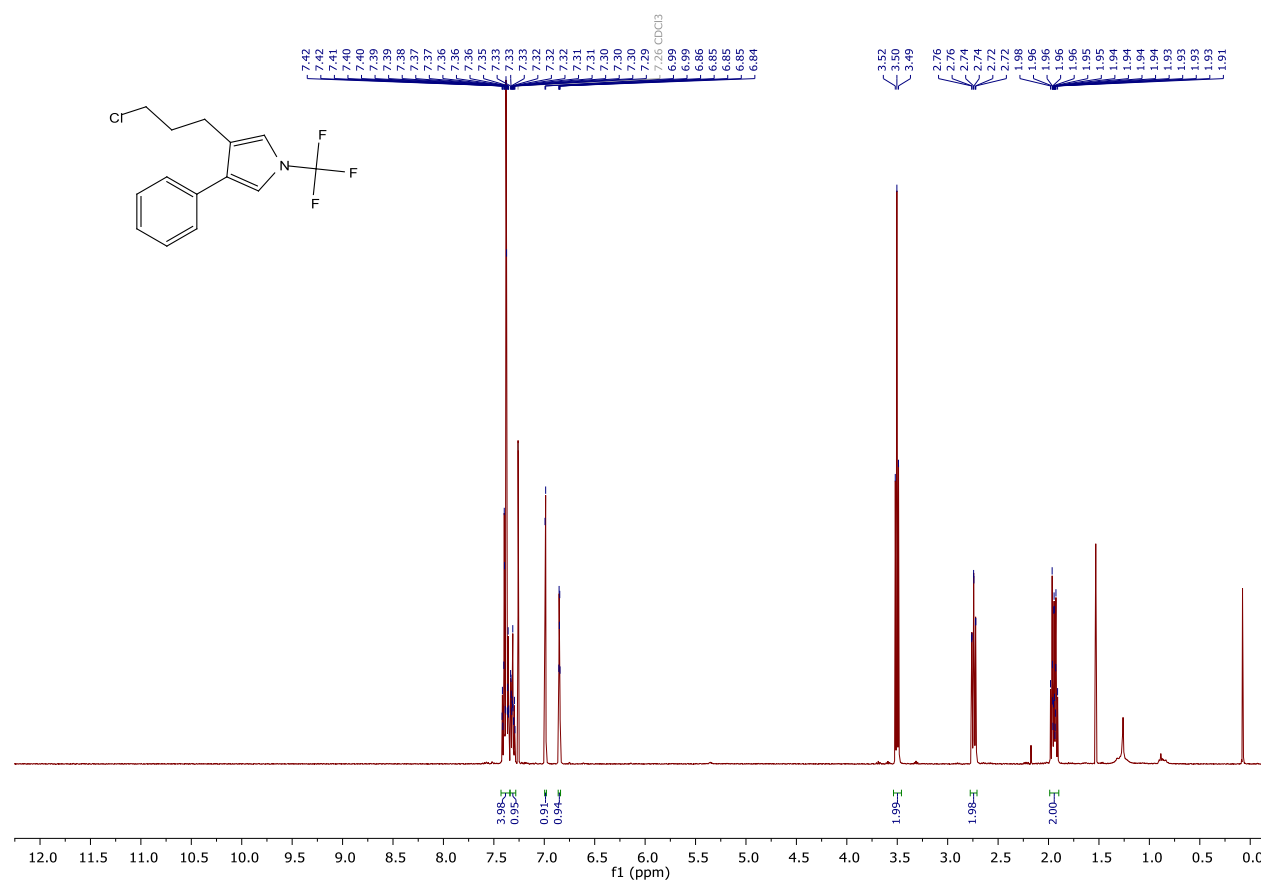
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3a** + **3a'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3a** + **3a'**

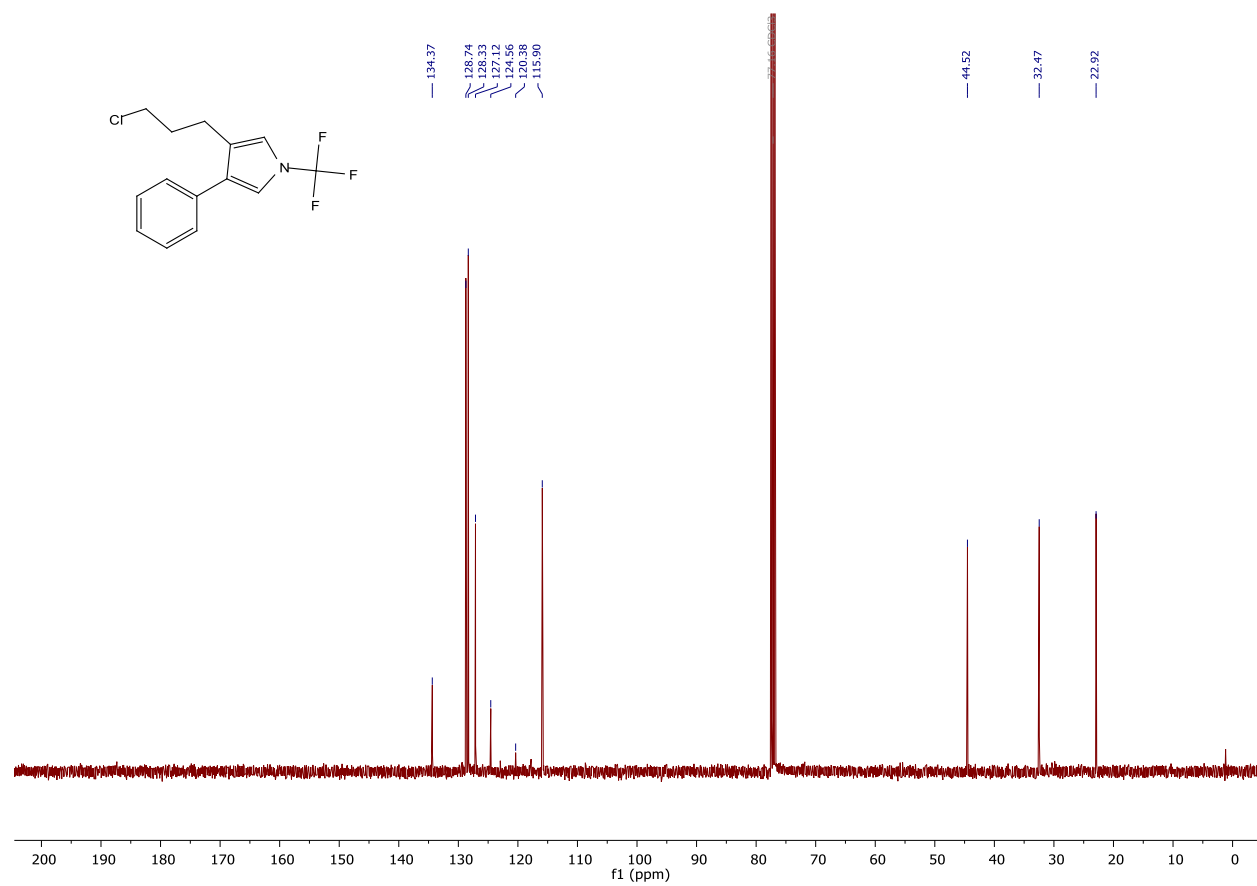


$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3a**

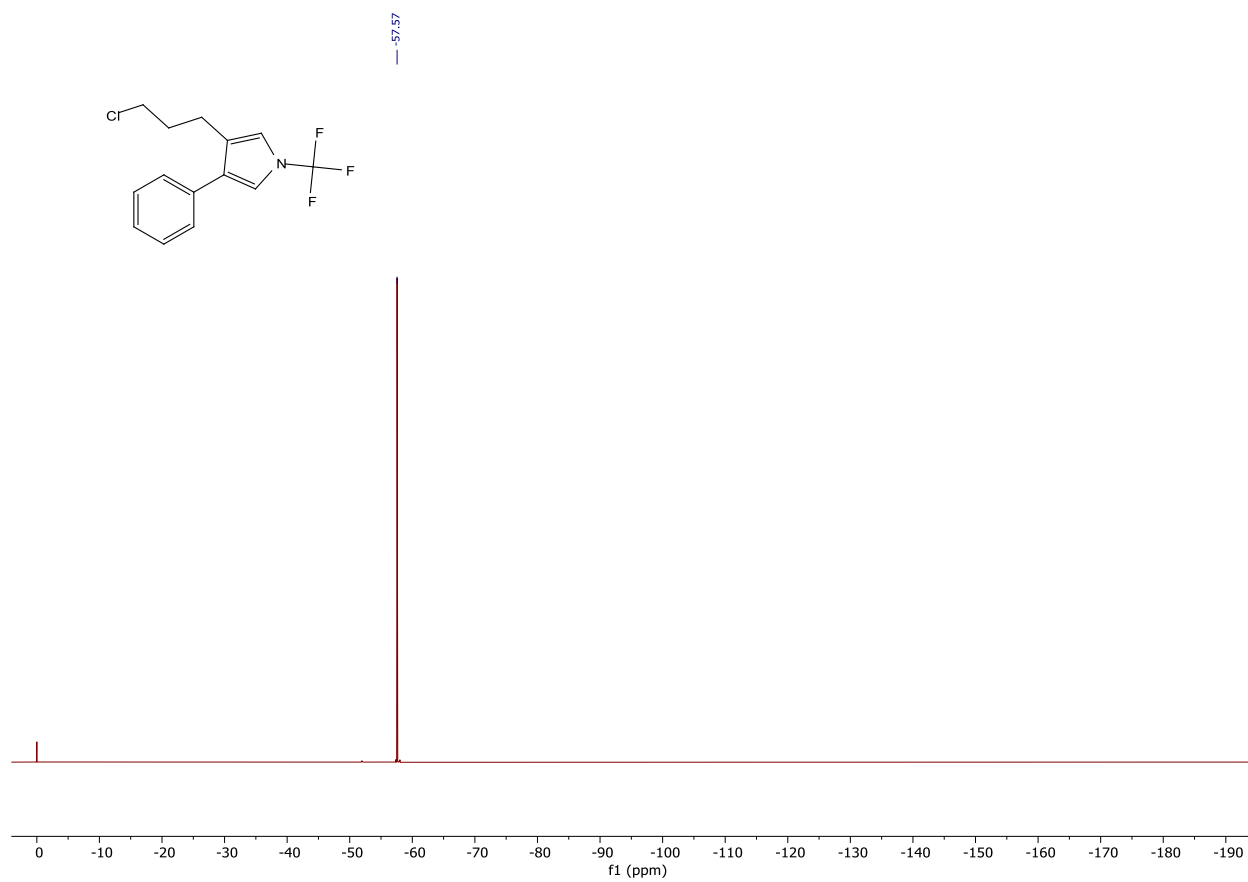




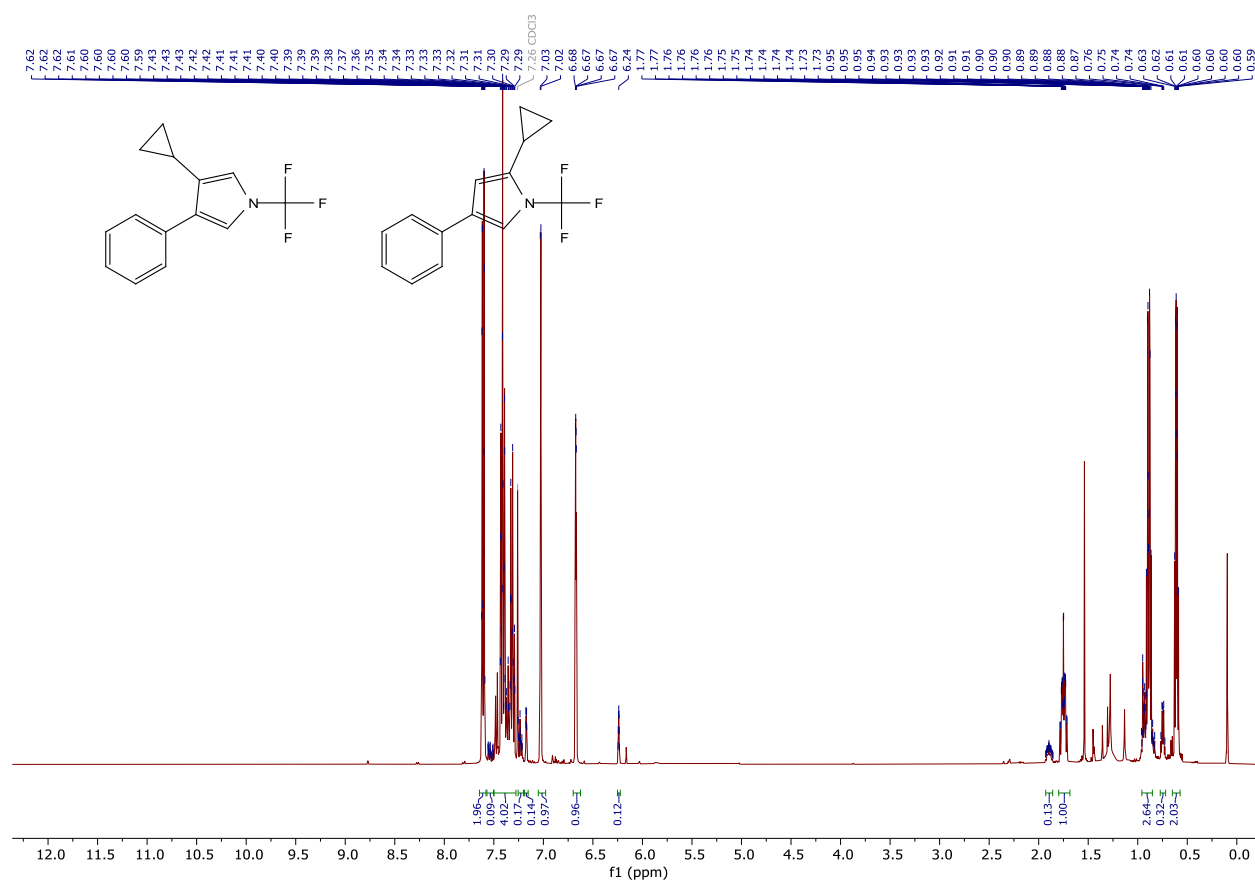
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3a**



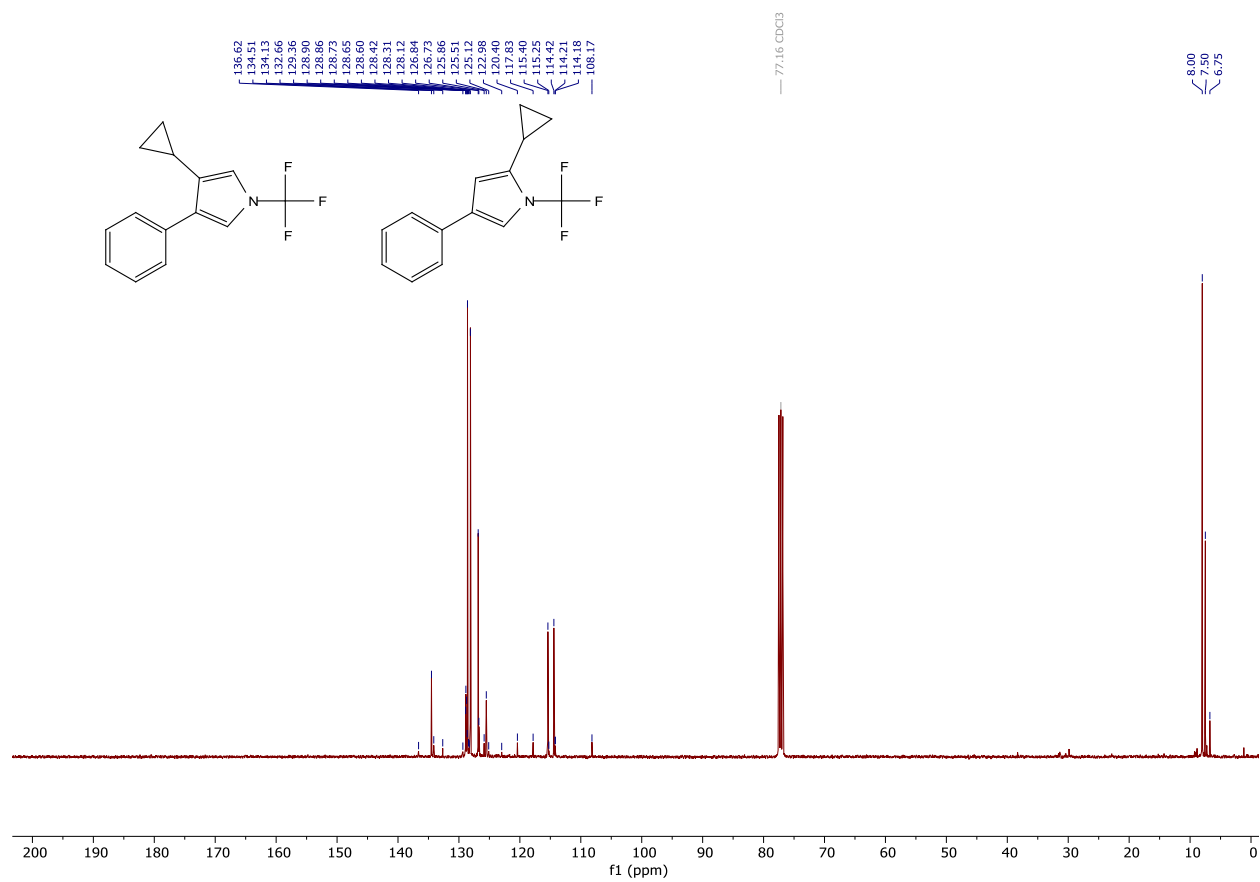
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3a**

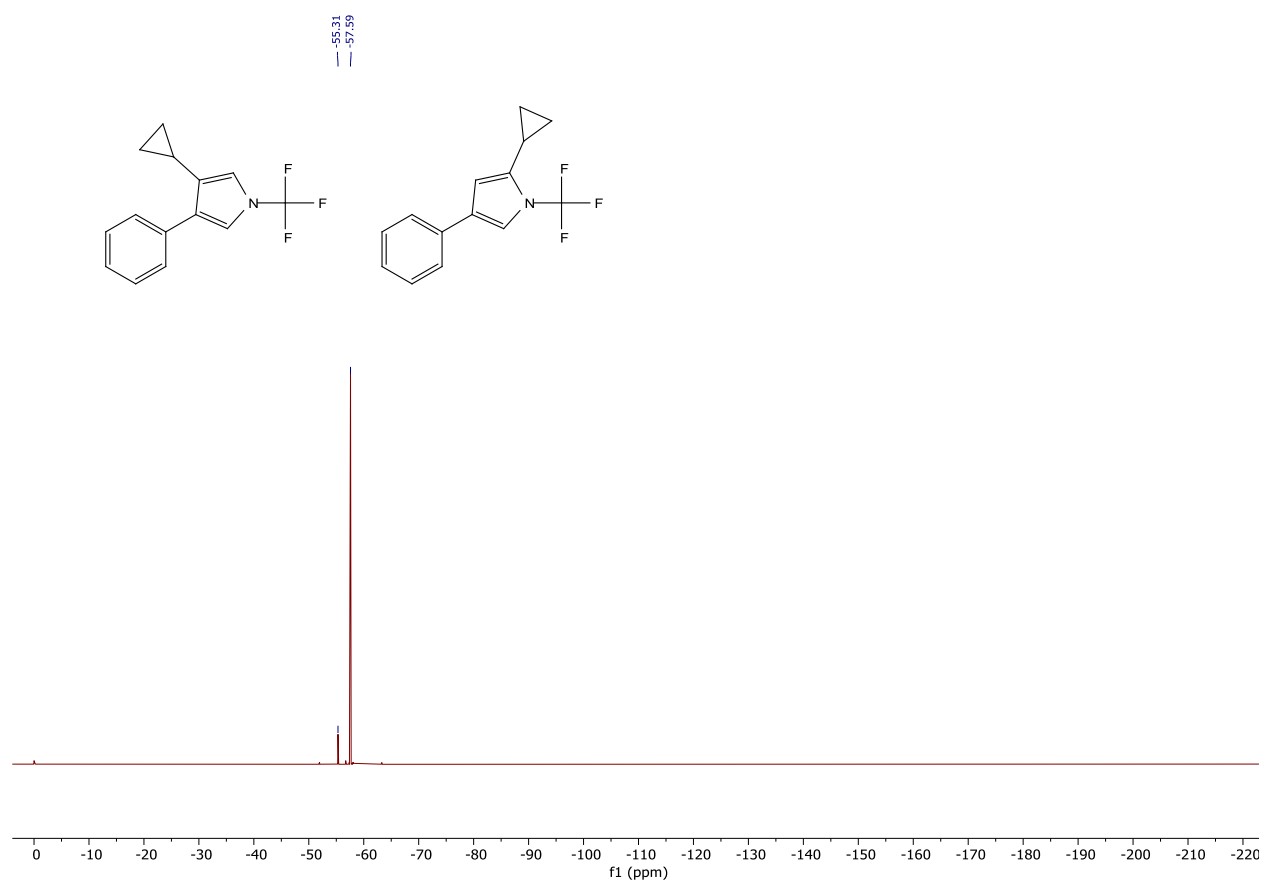


$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3b** + **3b'**

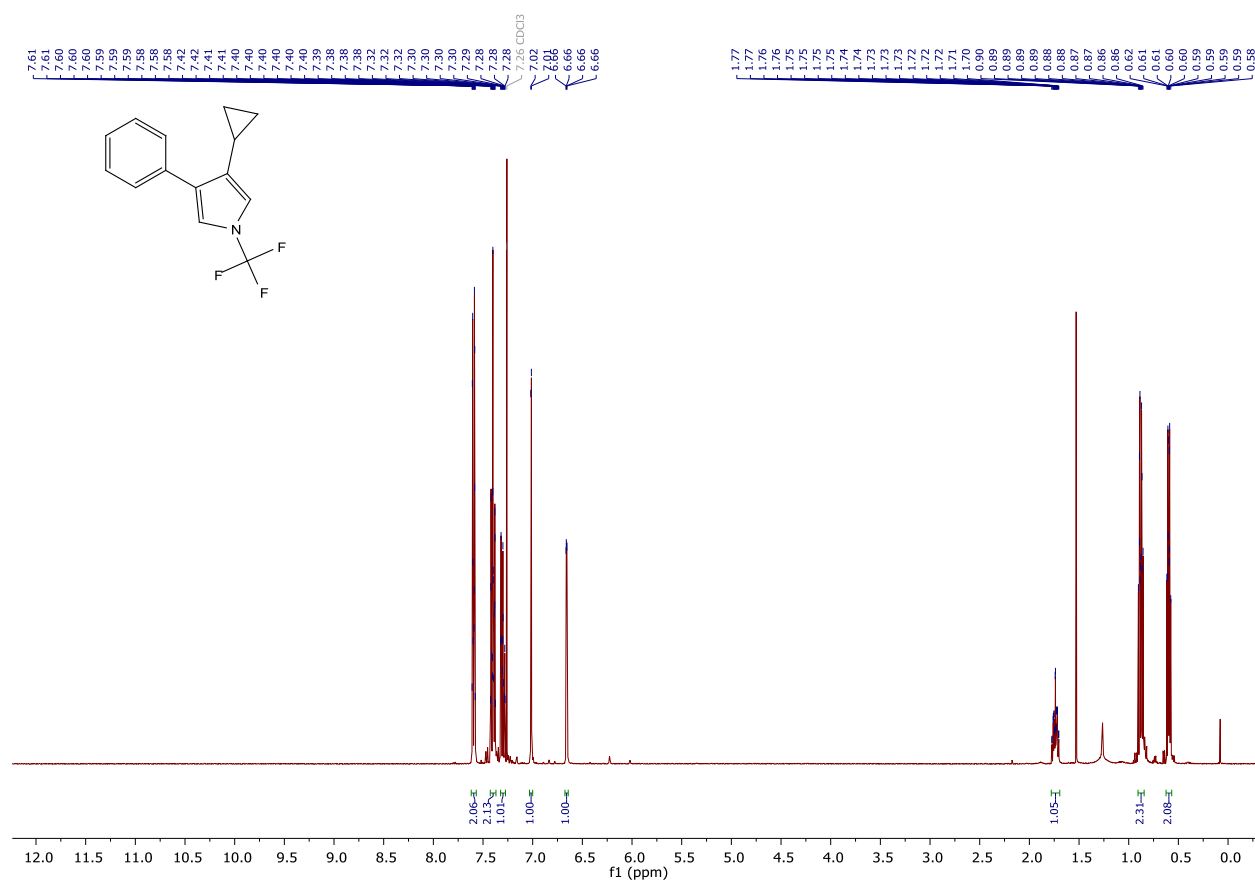


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3b** + **3b'**

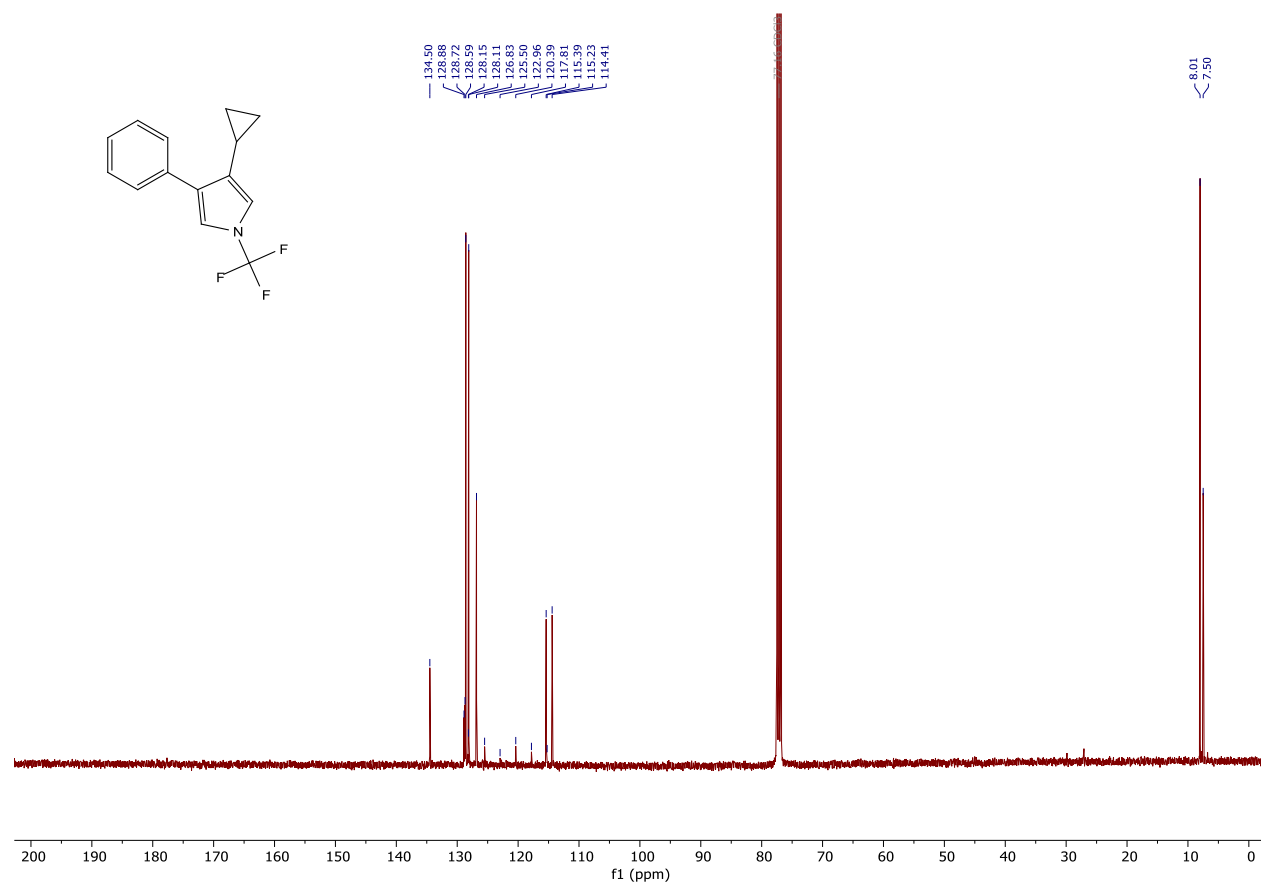


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3b** + **3b'**

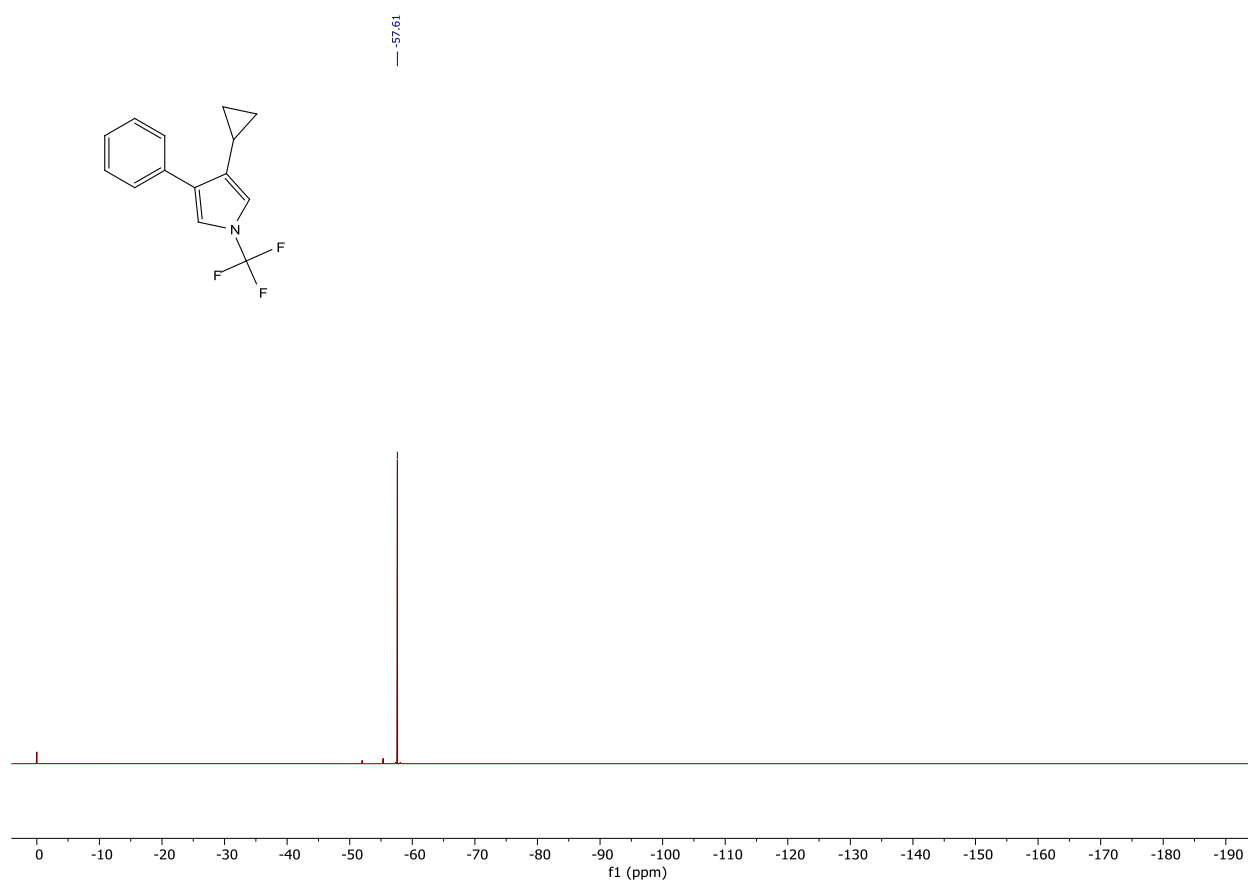
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3b**



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3b**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3b**



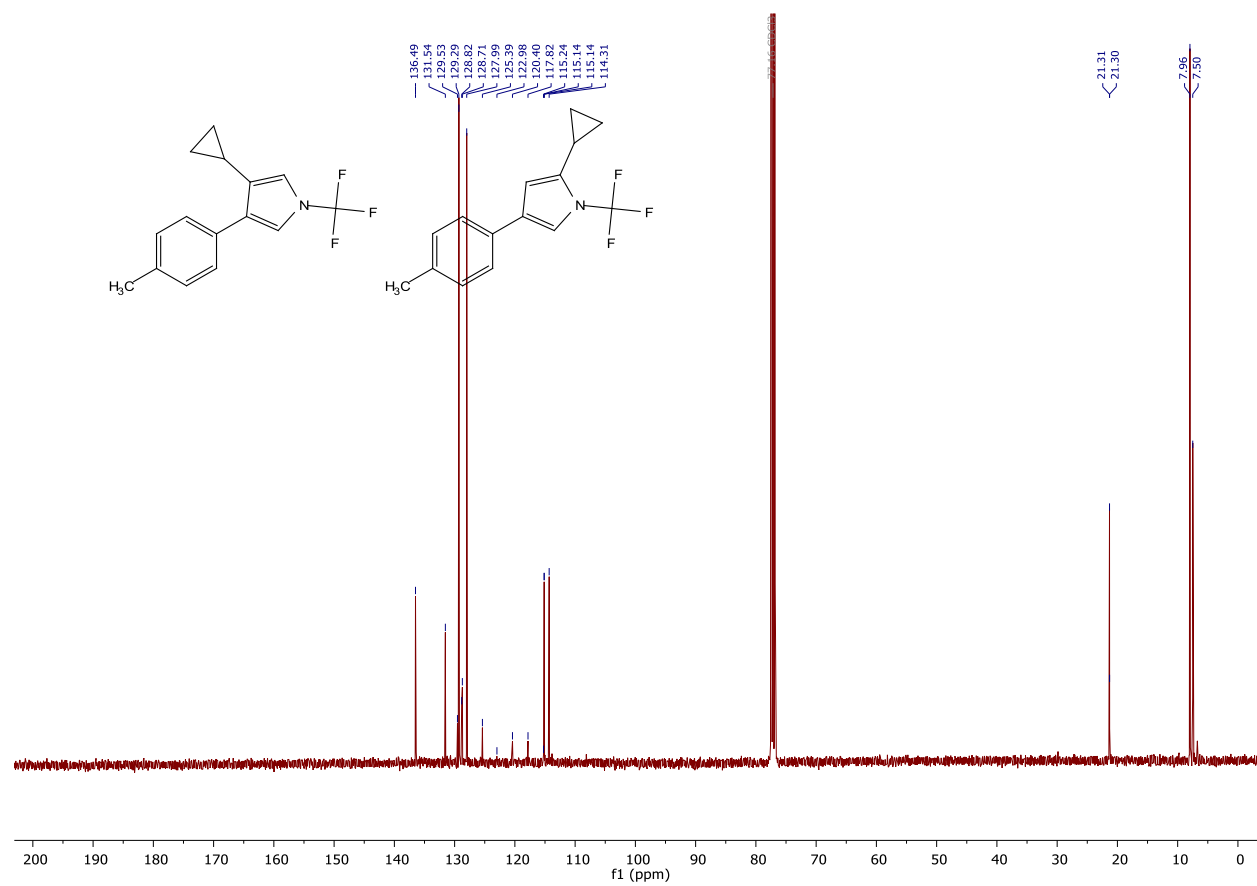


Chemical structure: Cc1ccc(cc1)-c2cc(C3CC3)n(C(F)F)c2

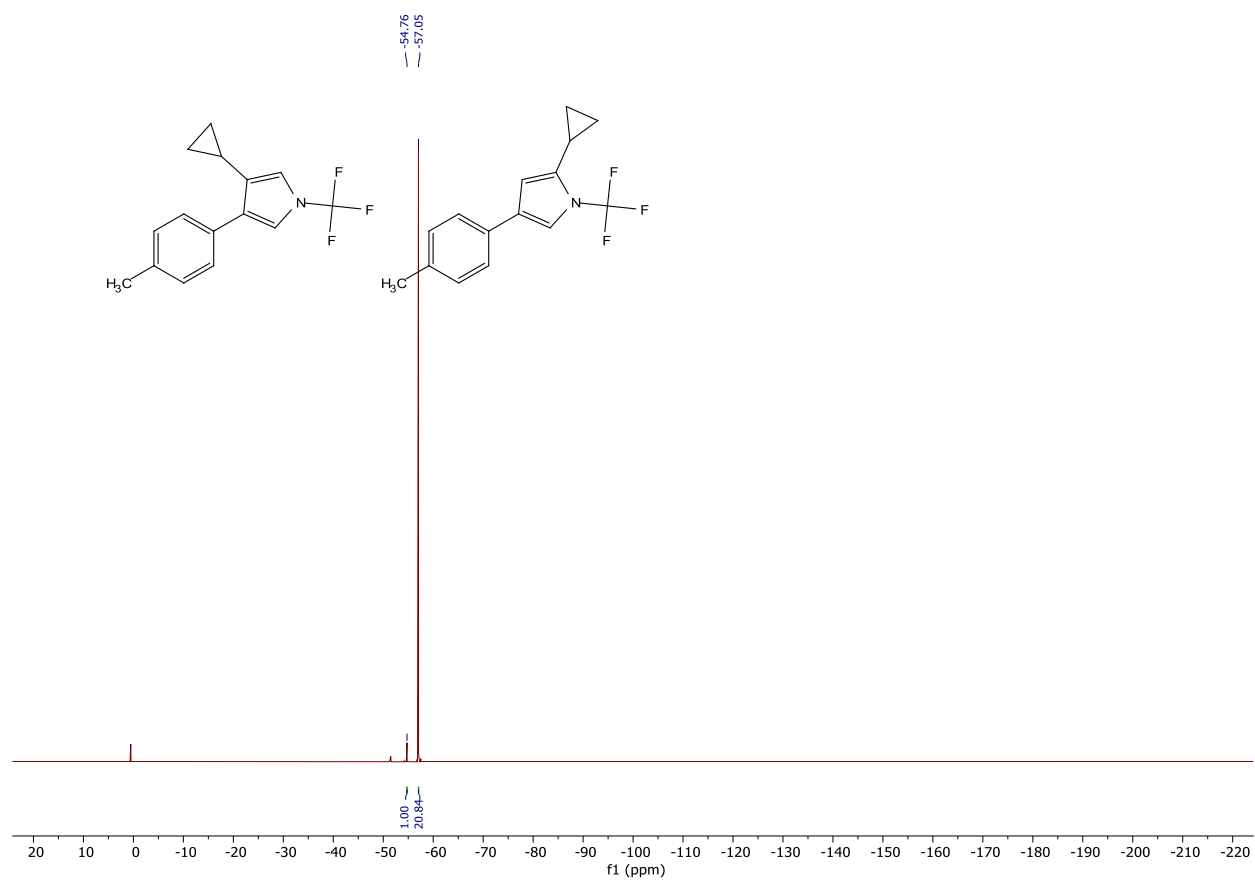
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing peaks from 0 to 8 ppm. Integration values are provided below the baseline.

| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 7.45                 | 2.04        |
| 7.35                 | 0.12        |
| 7.25                 | 2.05        |
| 7.15                 | 0.16        |
| 7.05                 | 0.06        |
| 6.95                 | 1.01        |
| 6.55                 | 1.00        |
| 6.15                 | 0.05        |
| 2.35                 | 3.09        |
| 2.30                 | 0.18        |
| 1.05                 | 1.04        |
| 0.95                 | 2.36        |
| 0.85                 | 2.12        |

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3c** + **3c'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3c** + **3c'**



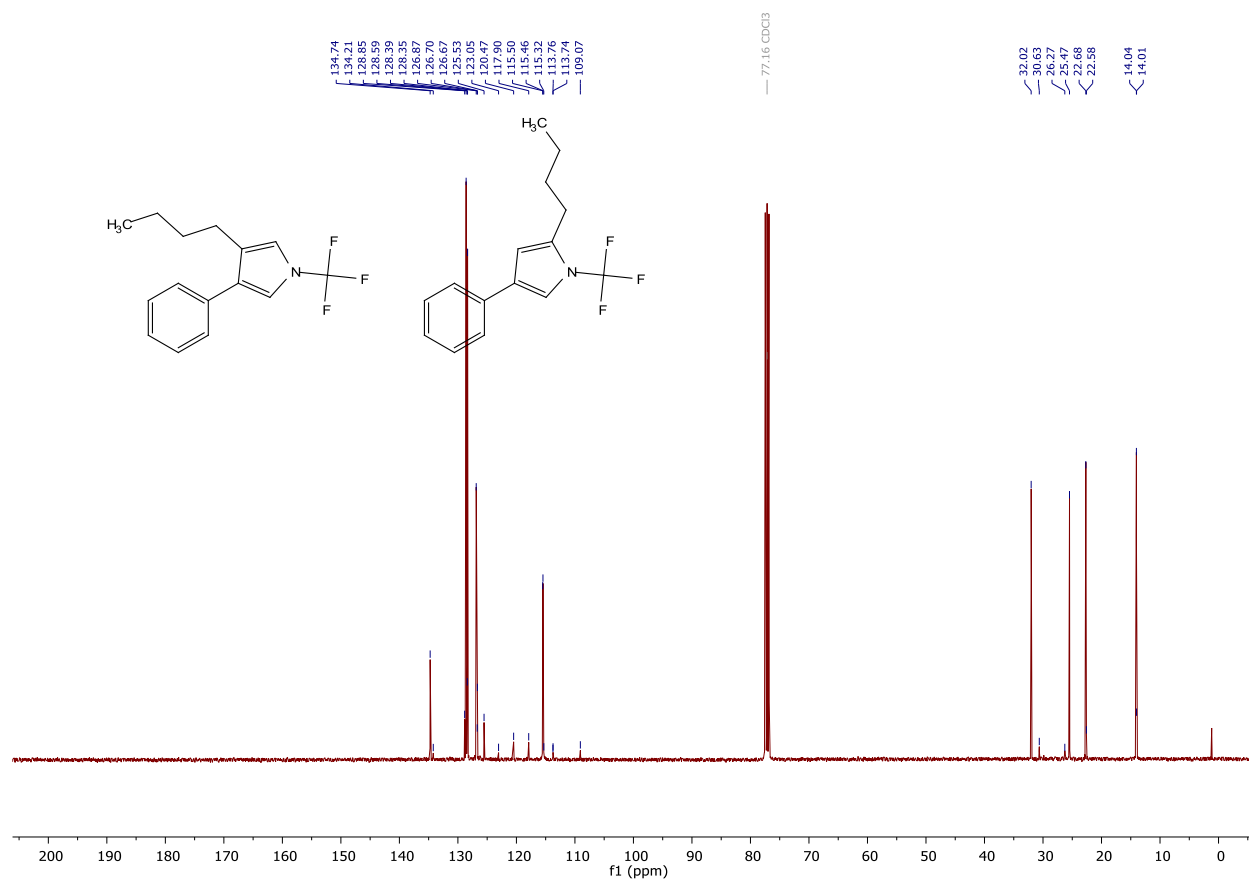
**<sup>1</sup>H NMR Spectrum (CDCl<sub>3</sub>)**

**Chemical Structure:** 1-(4-(2,2,2-trifluoroethyl)phenyl)-2,2,2-trifluoroethylbenzene

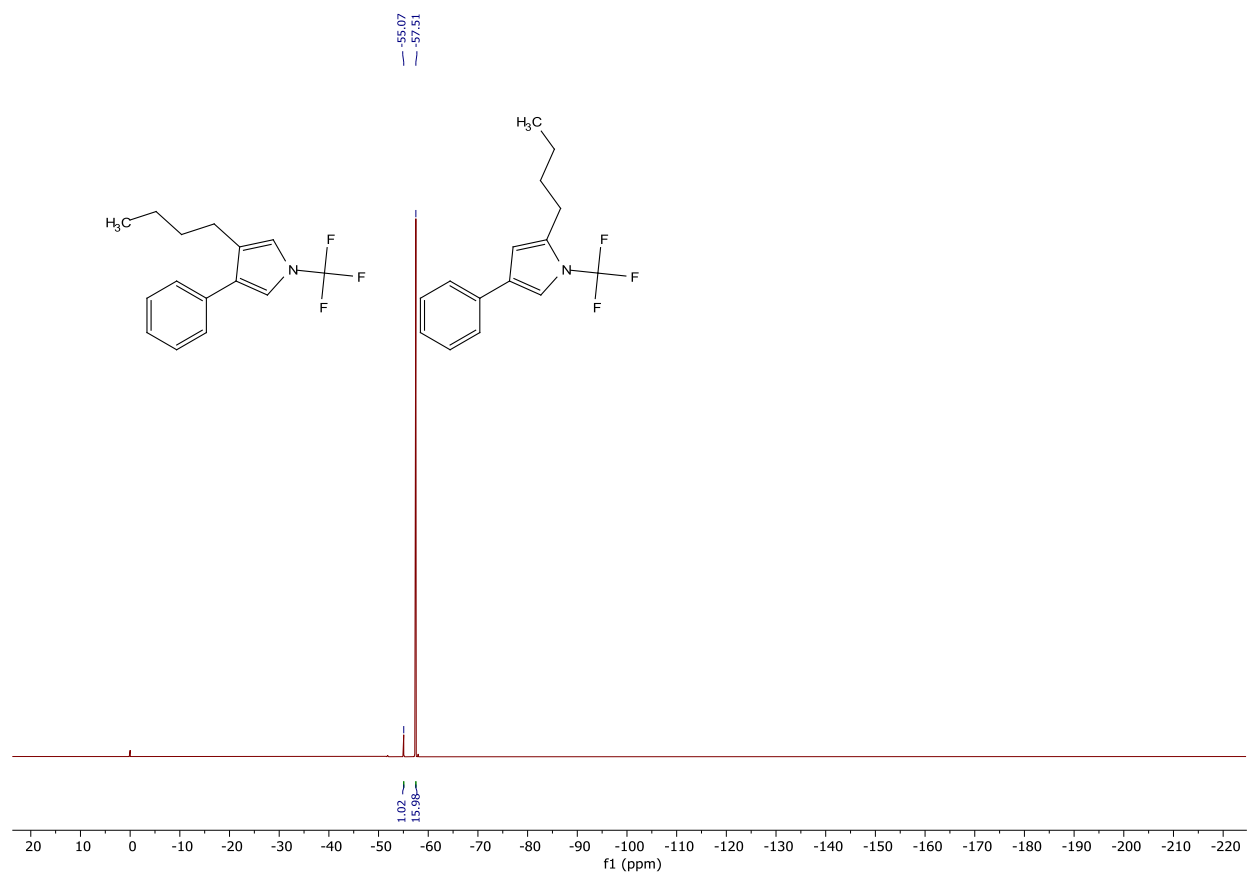
**Peak Data:**

| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 7.49                 | 0.17        |
| 7.42                 | 1.14        |
| 7.31                 | 0.07        |
| 7.26                 | 1.00        |
| 7.17                 | 0.07        |
| 3.00                 | 0.16        |
| 2.53                 | 2.19        |
| 1.44                 | 0.16        |
| 1.38                 | 2.22        |
| 1.36                 | 2.32        |
| 1.34                 | 0.29        |
| 1.31                 | 3.37        |
| 0.90                 | -           |

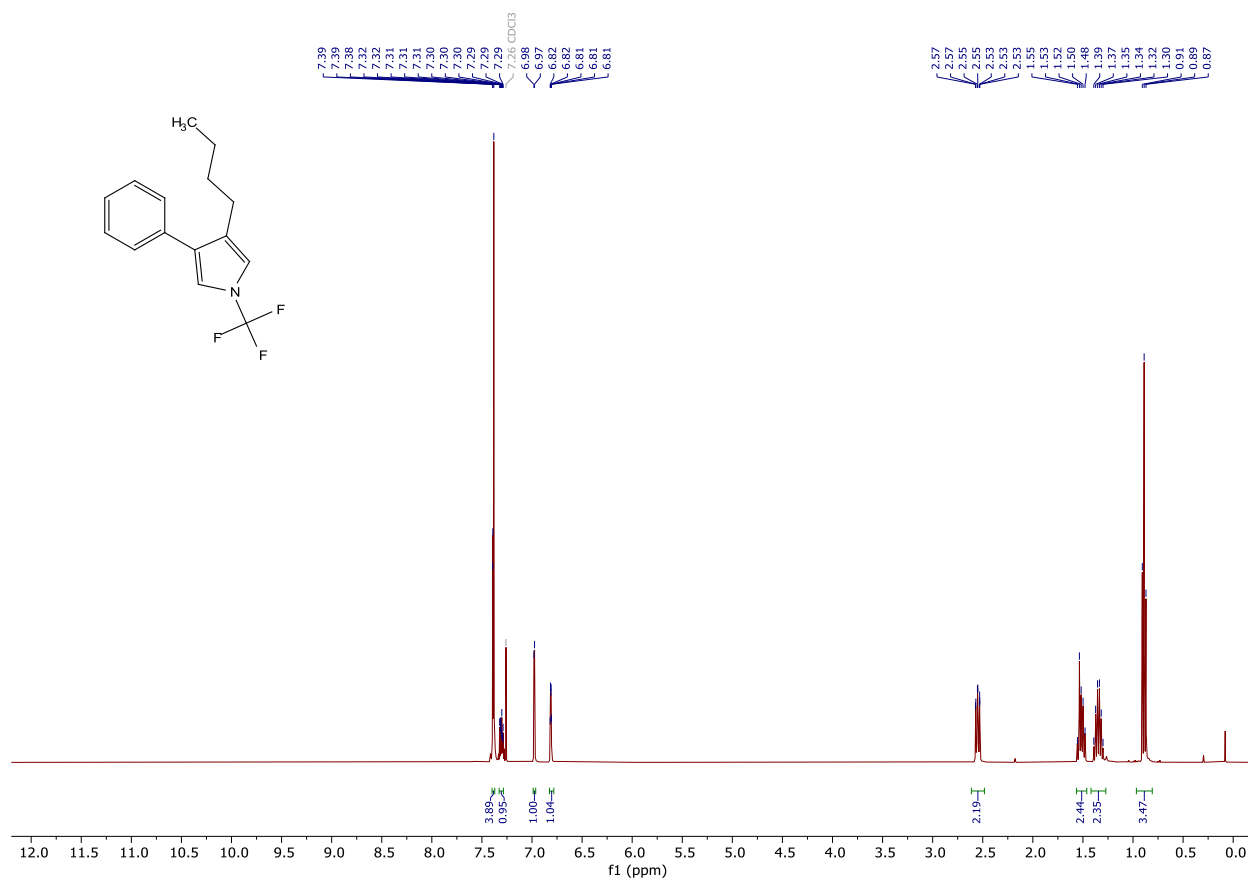
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3d** + **3d'**



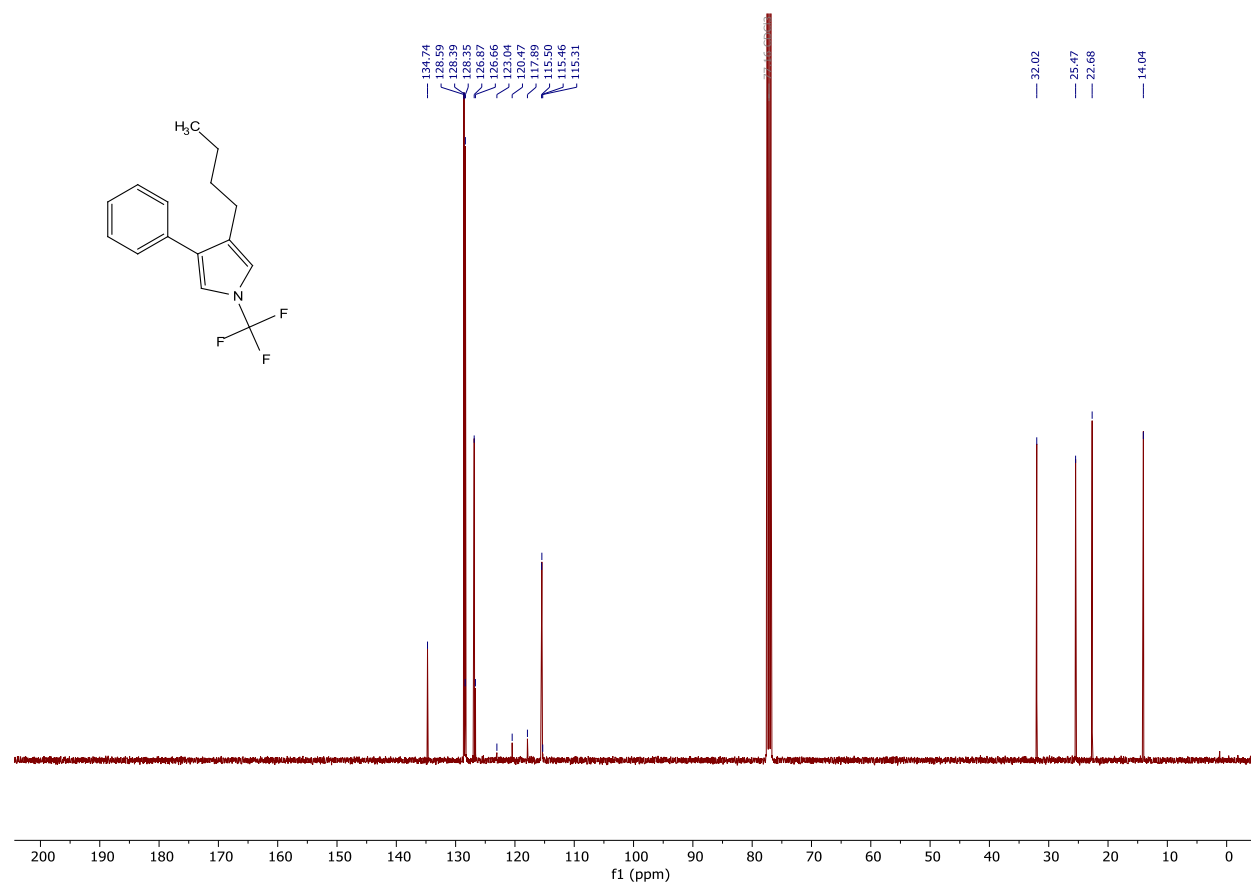
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3d** + **3d'**



$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3d**

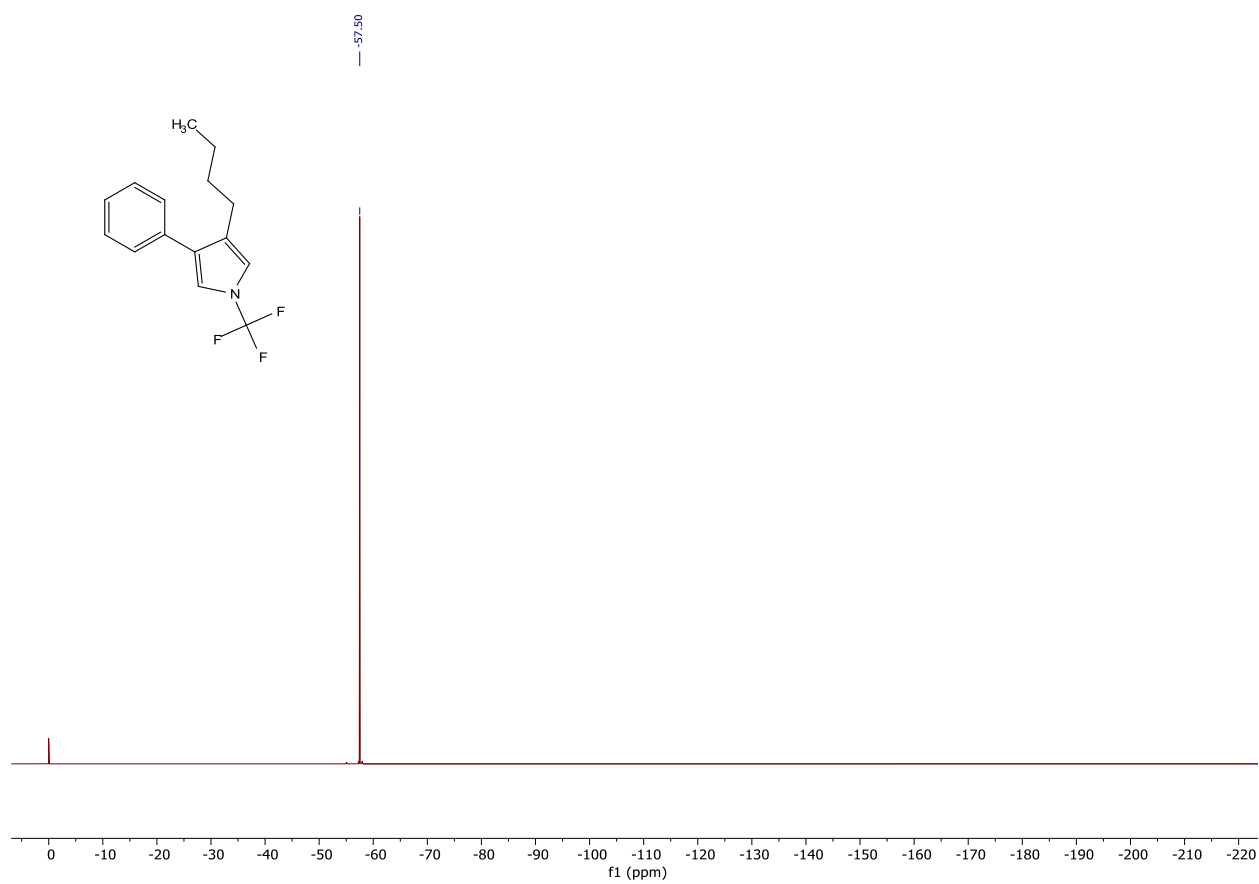


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3d**

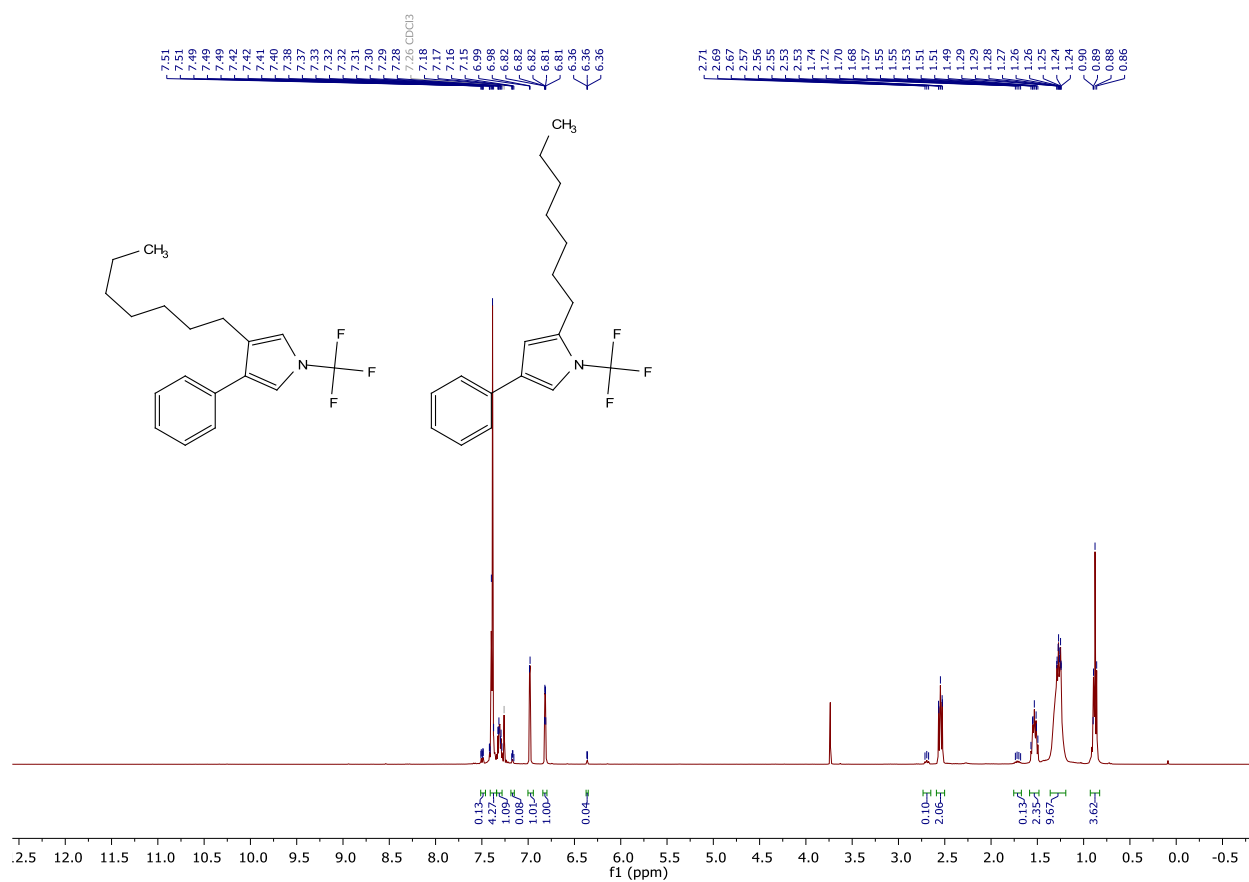




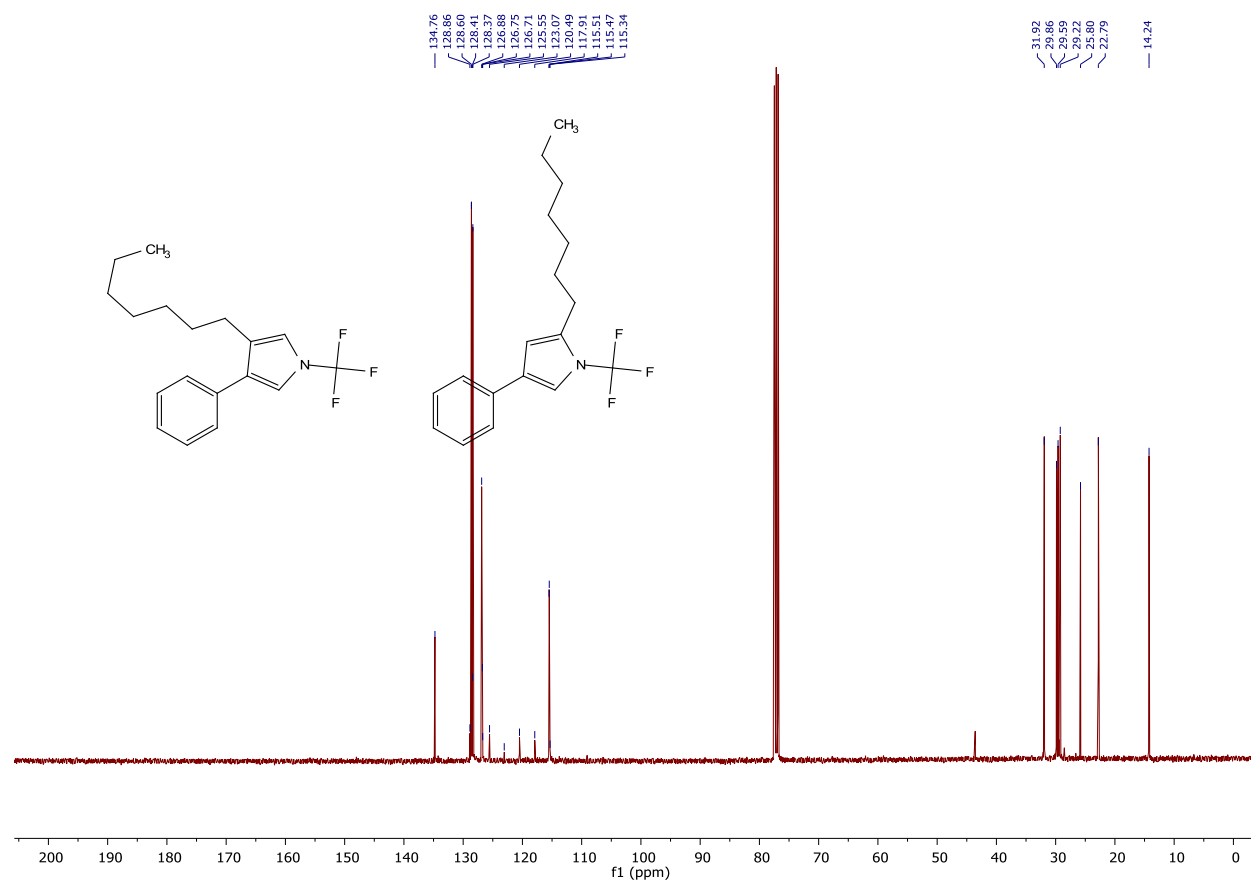
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3d**



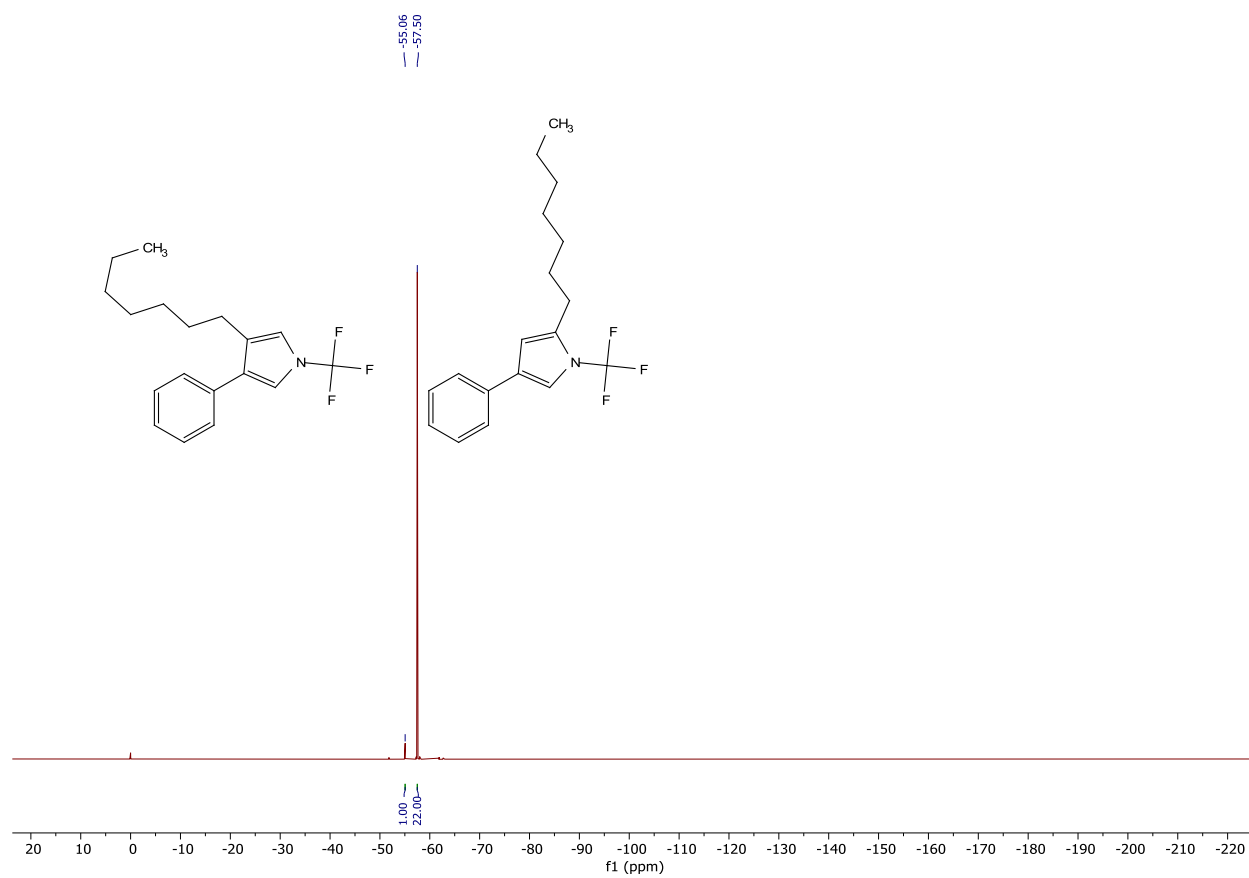
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3e** + **3e'**



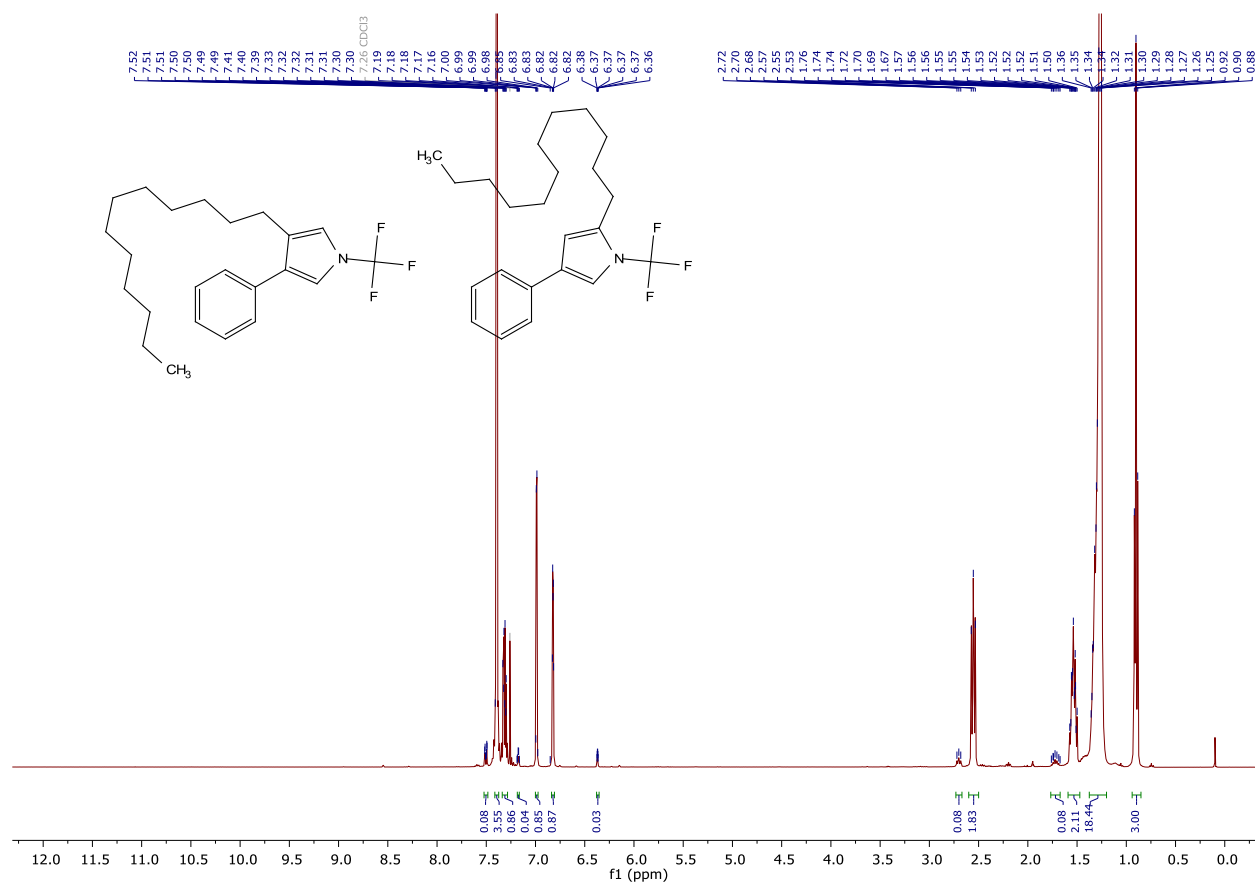
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3e** + **3e'**



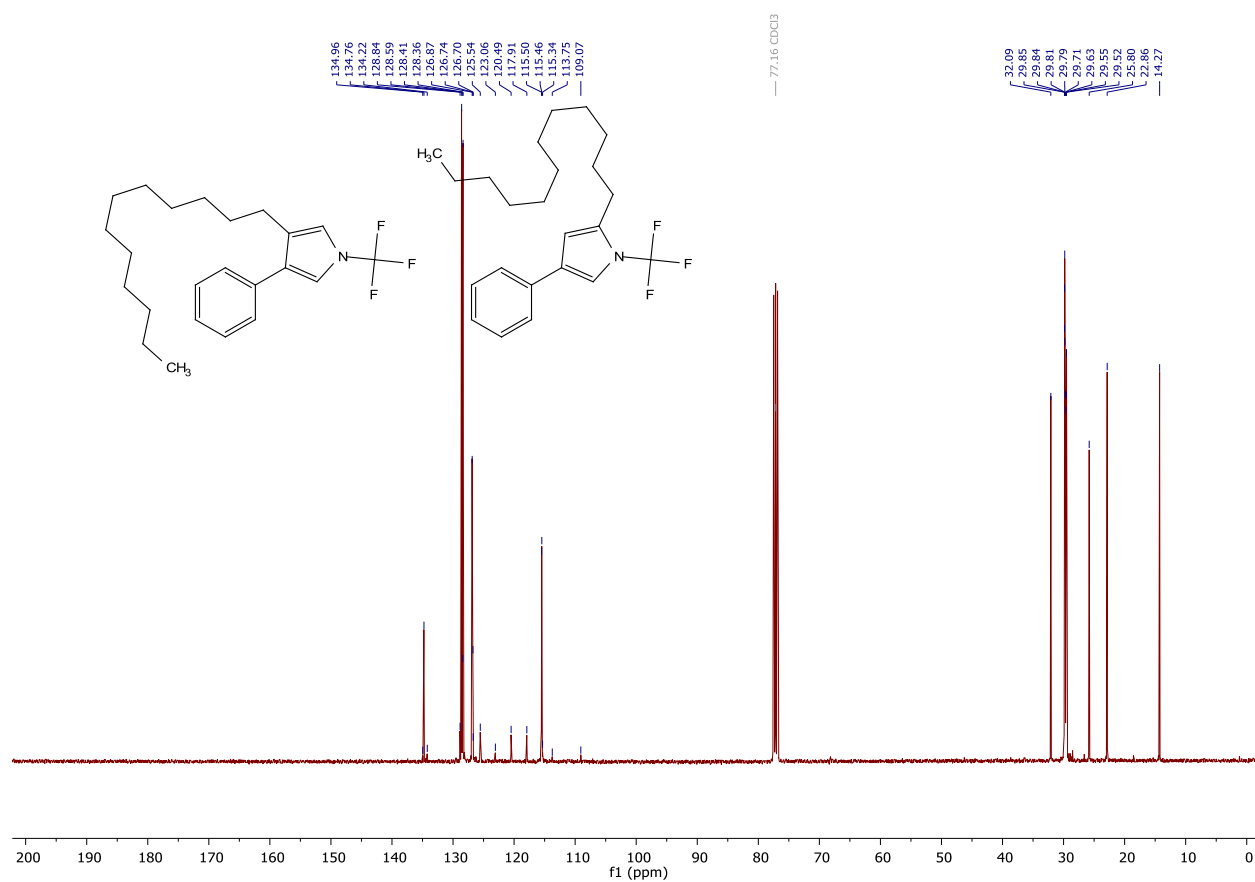
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3e** + **3e'**



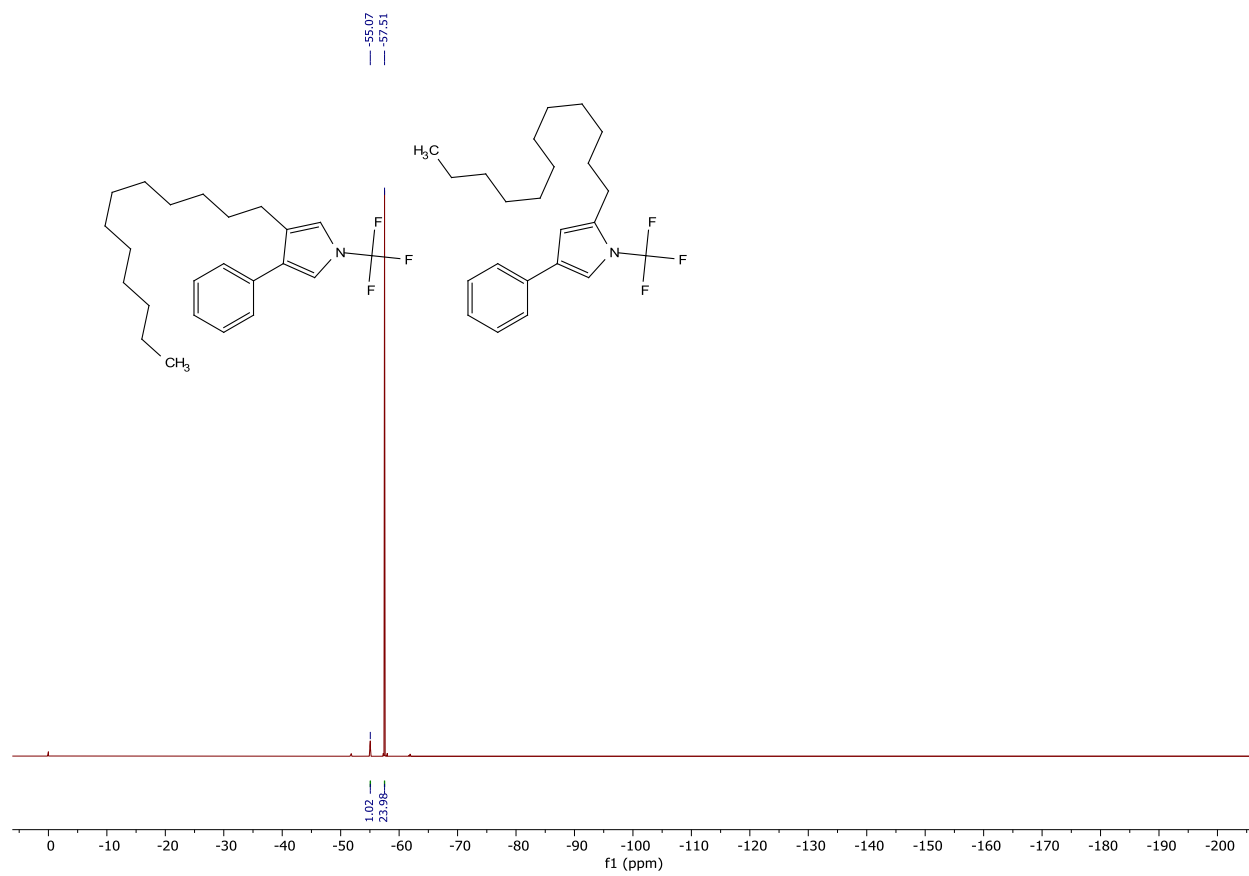
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3f** + **3f'**



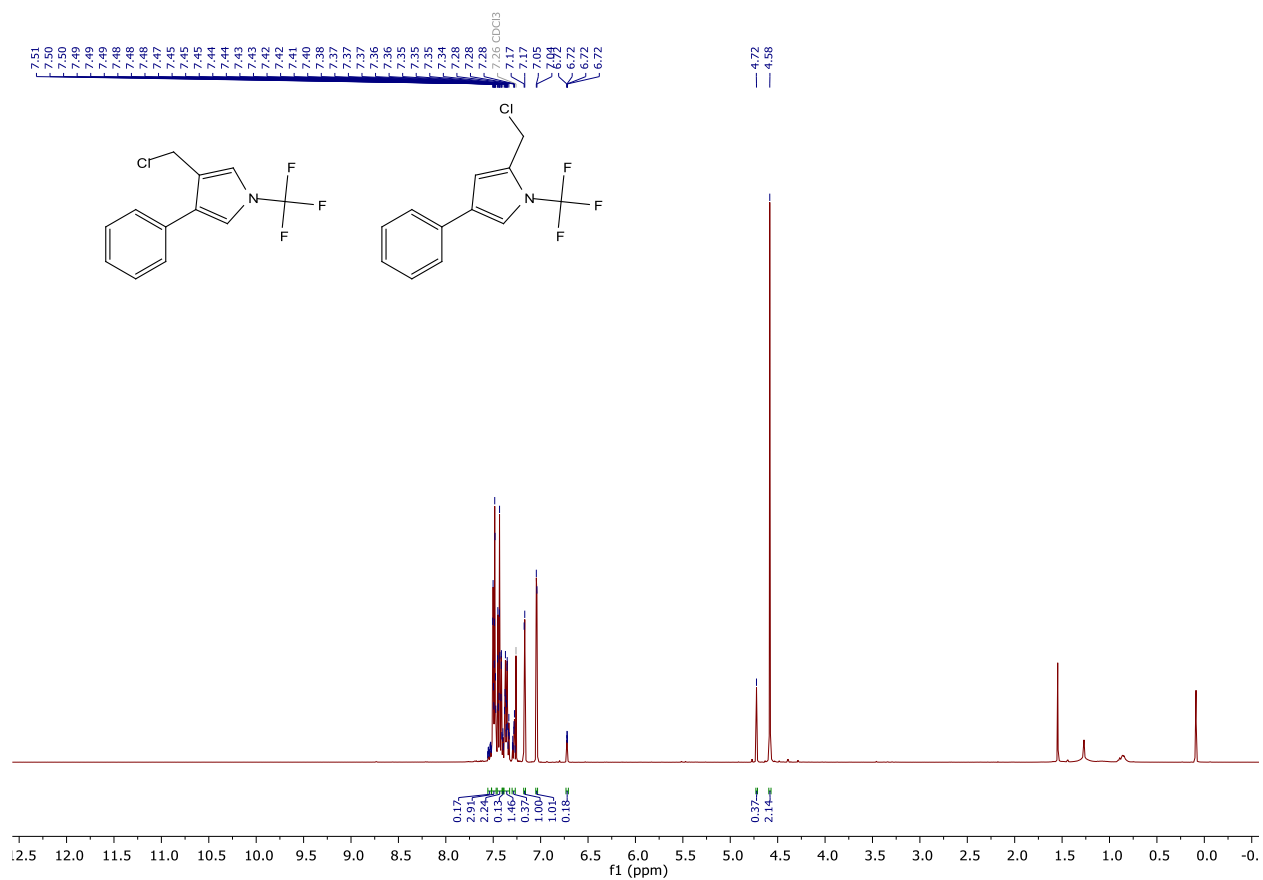
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3f** + **3f'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3f** + **3f'**

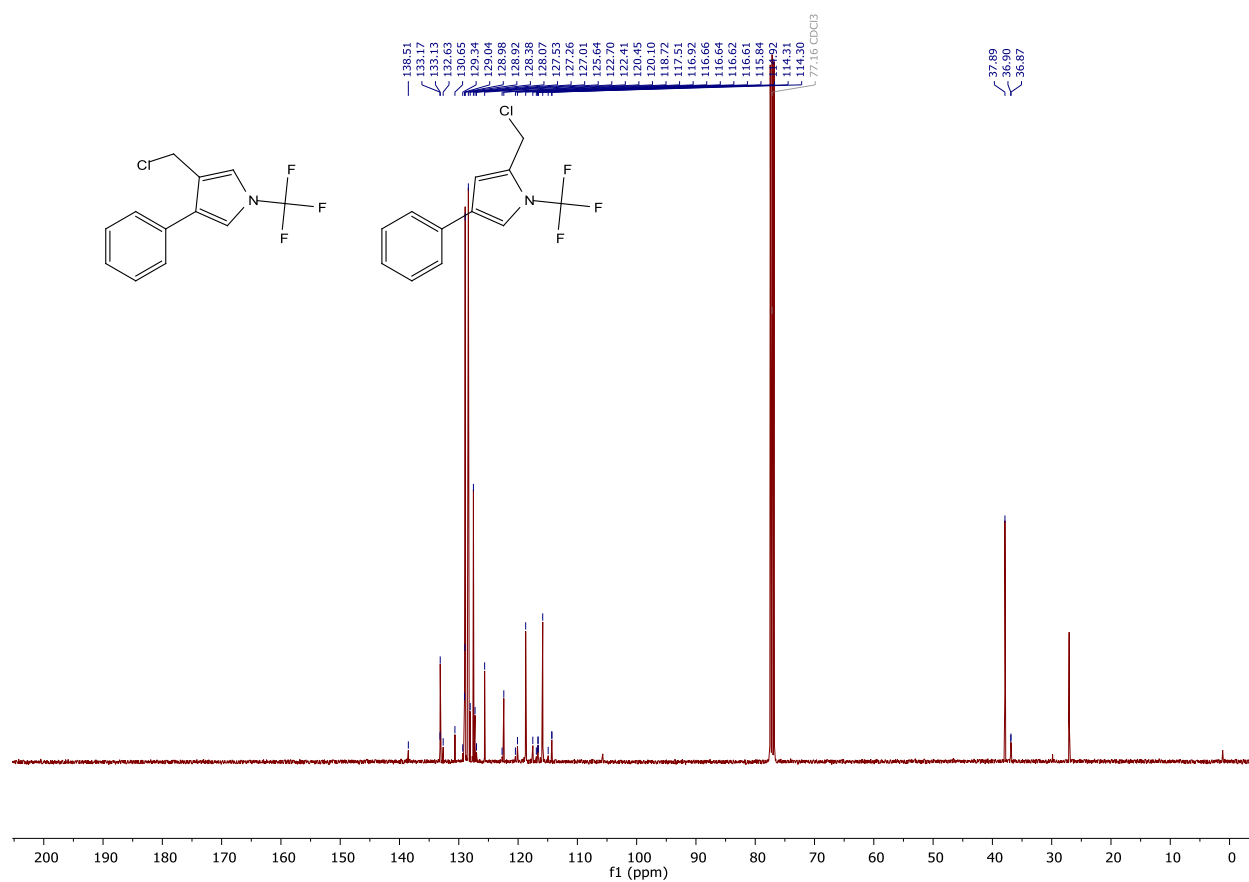


$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3g** + **3g'**

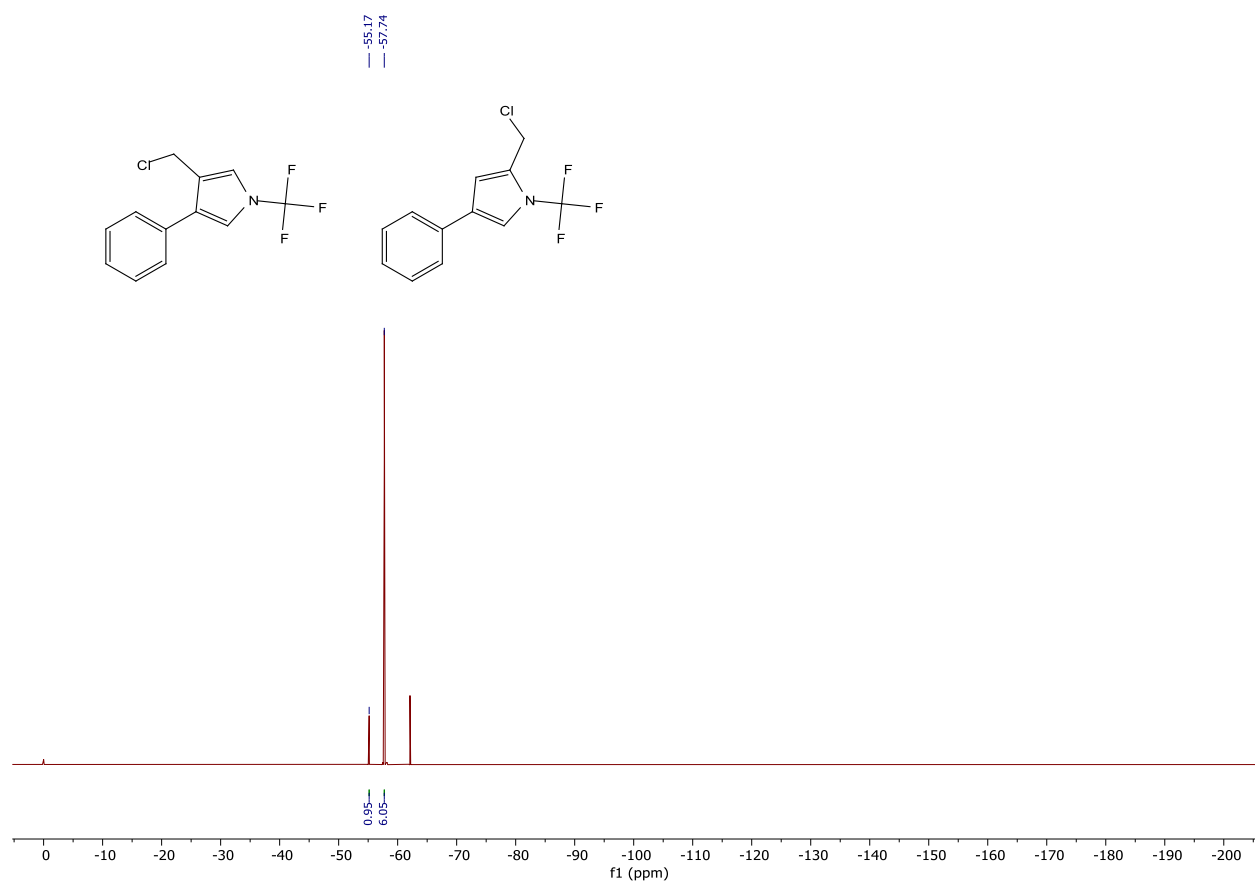




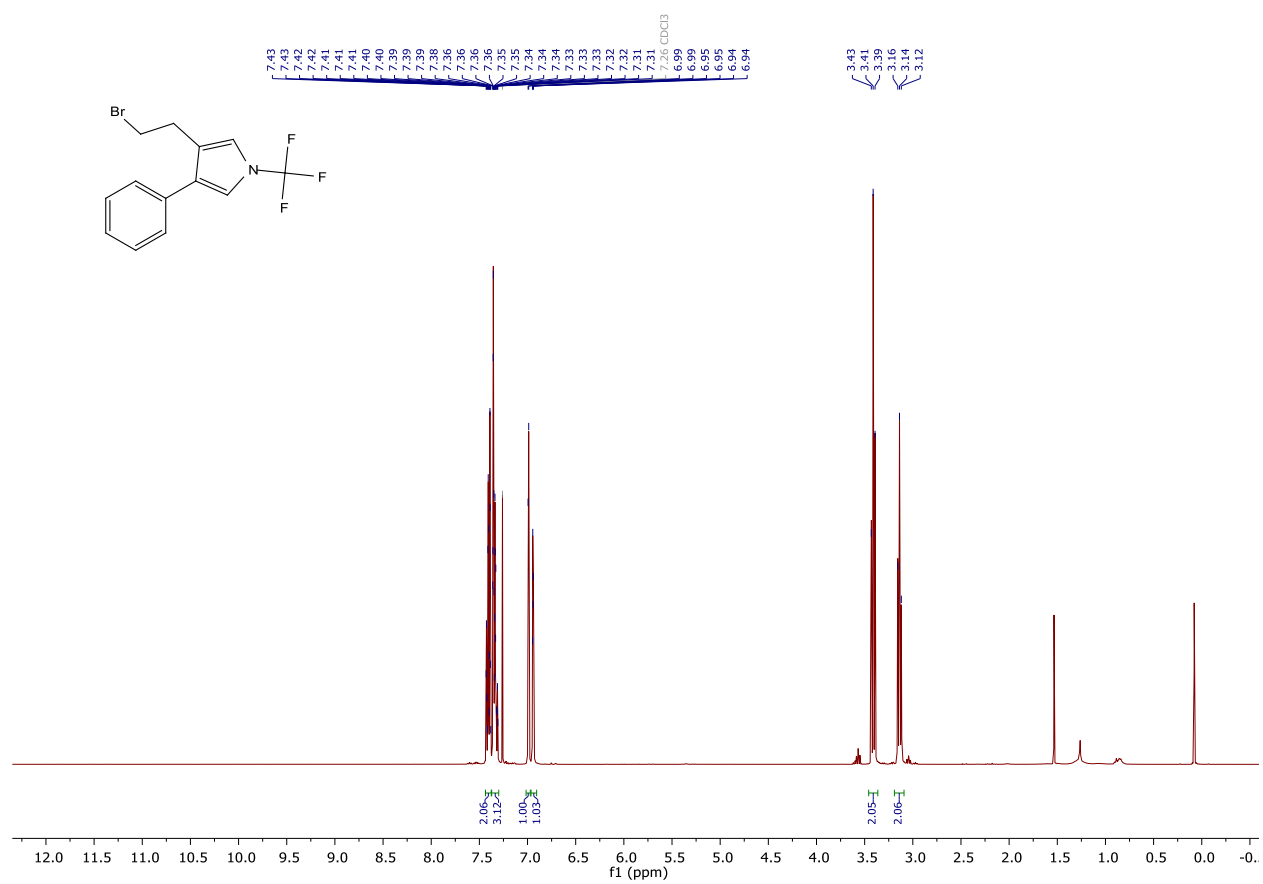
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3g** + **3g'**



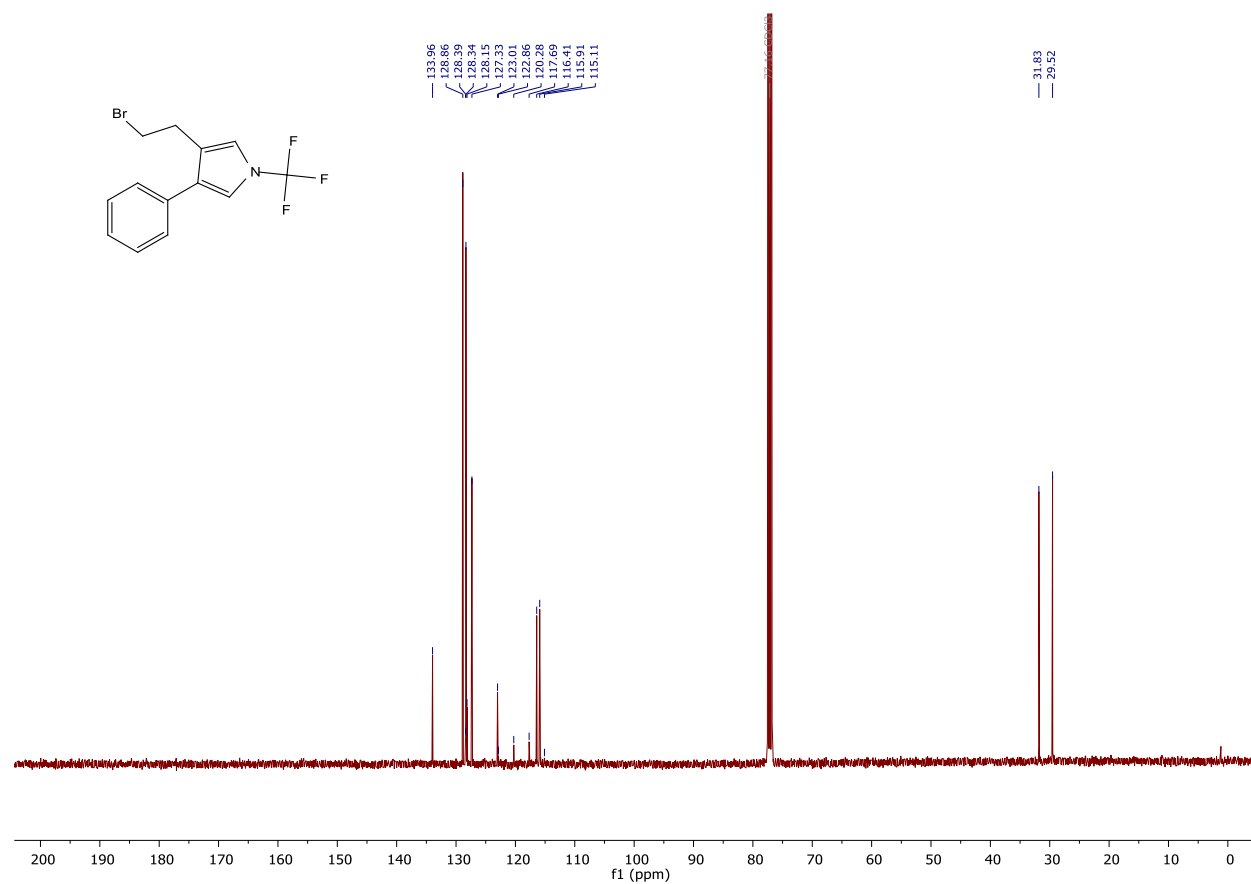
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3g** + **3g'**



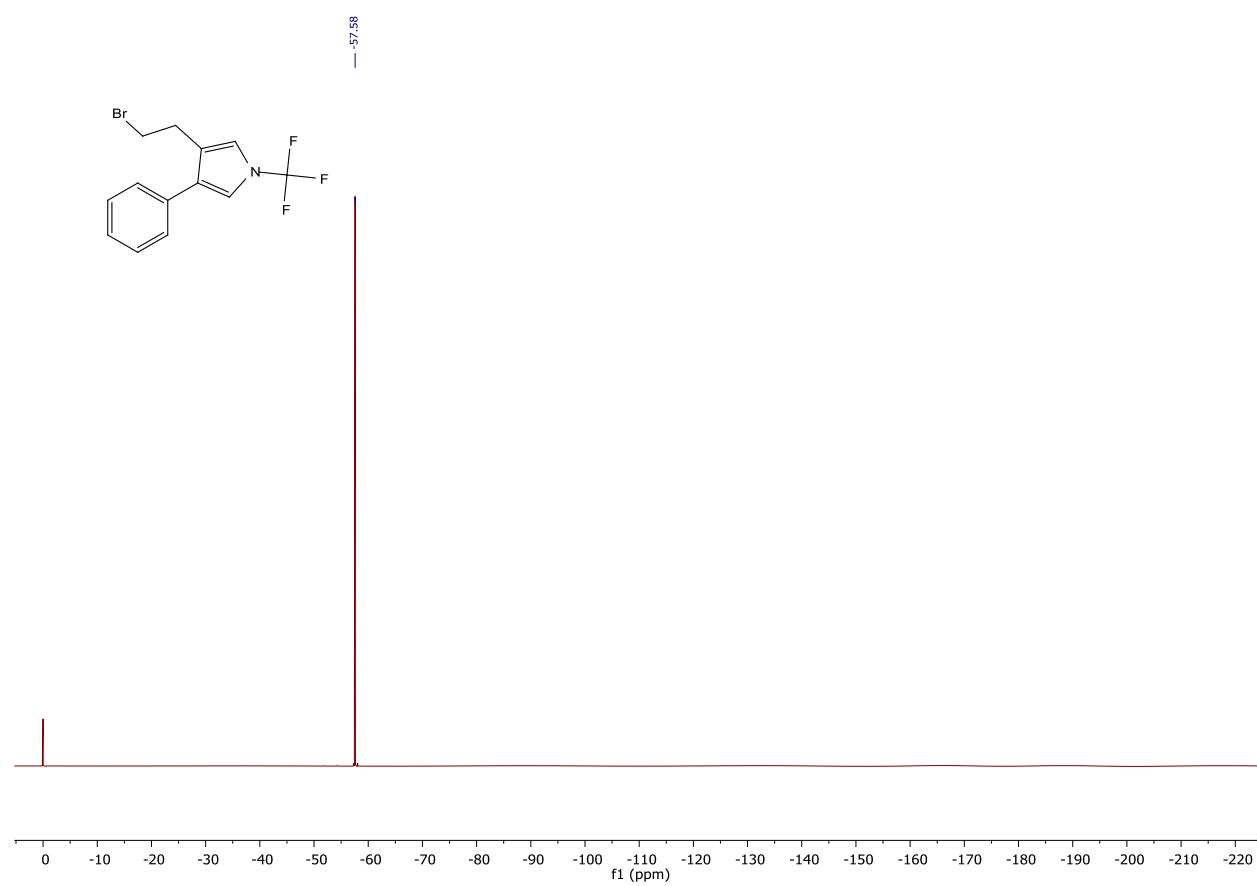
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3h**



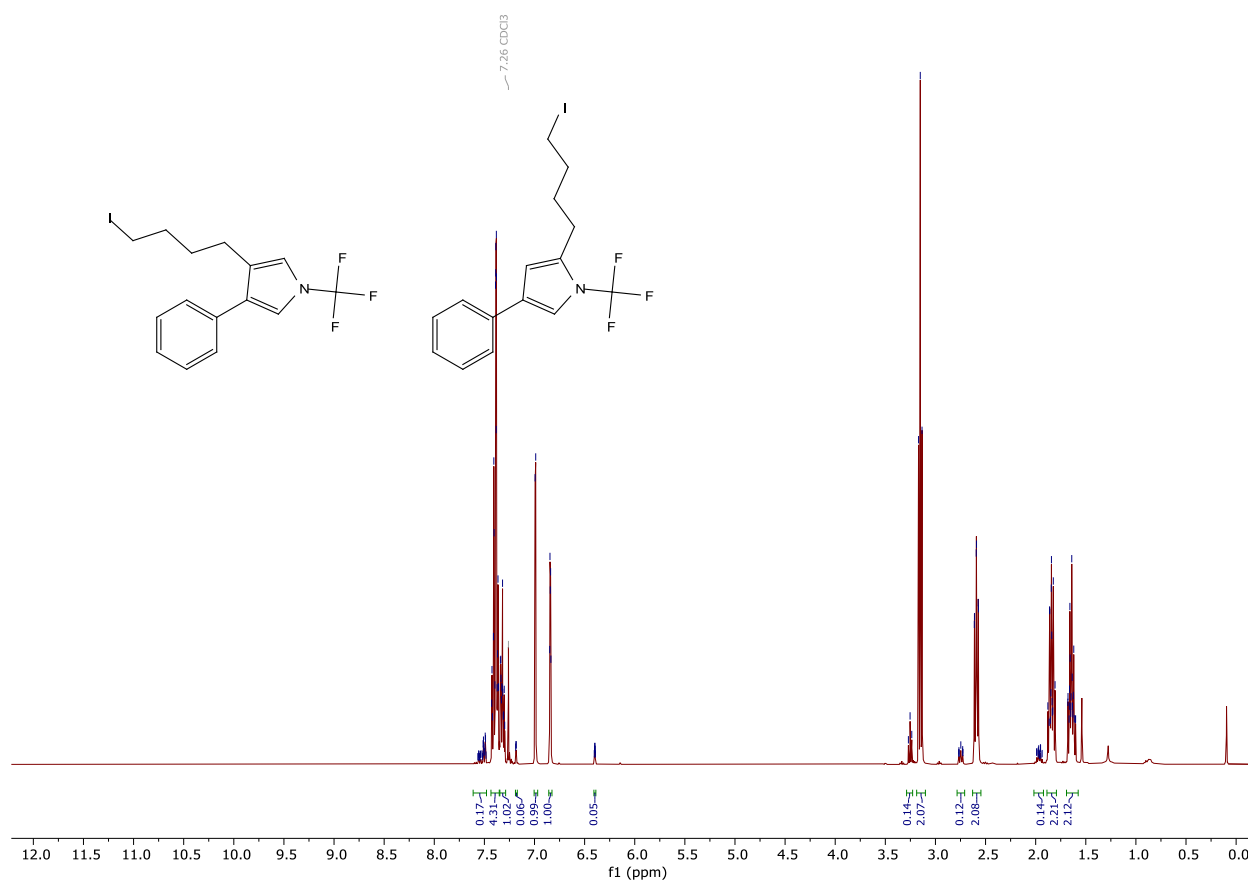
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3h**



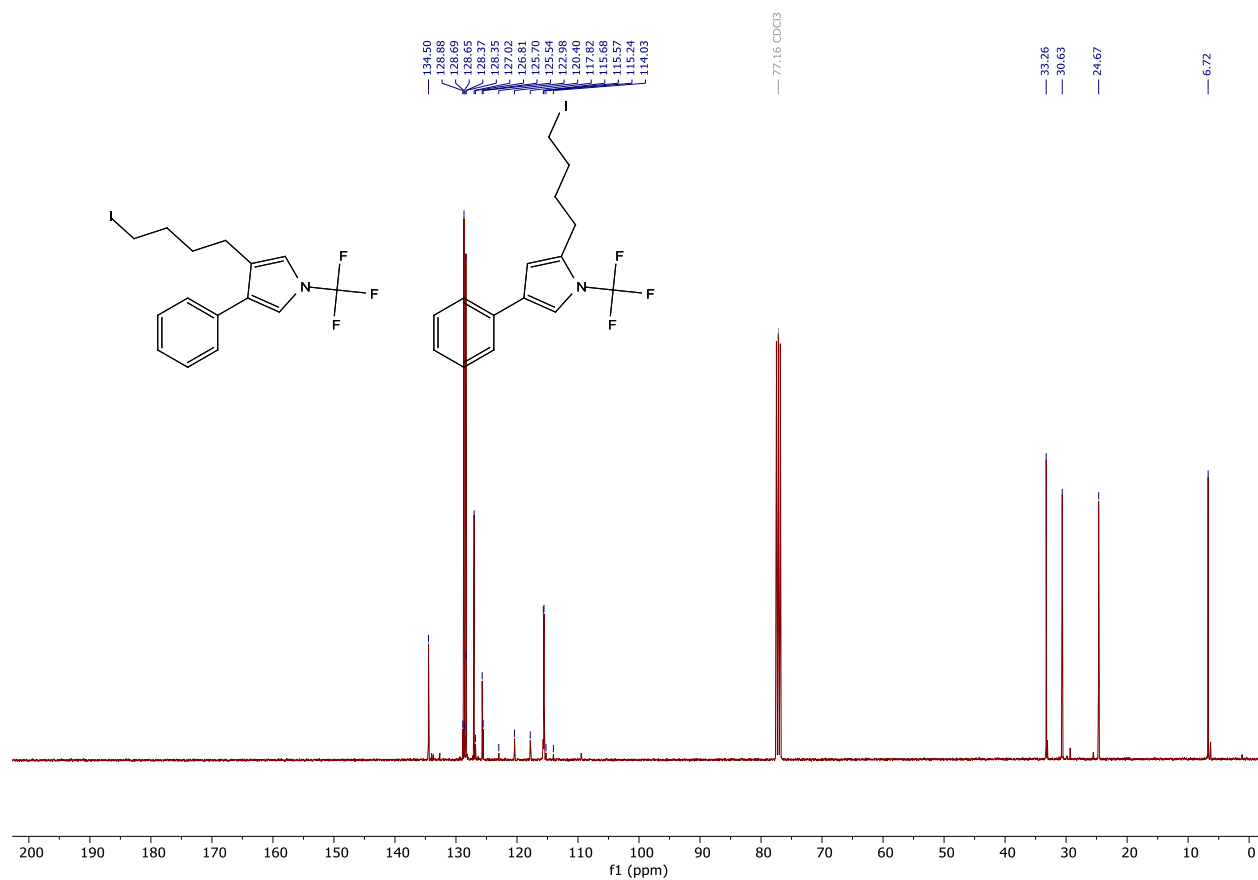
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3h**



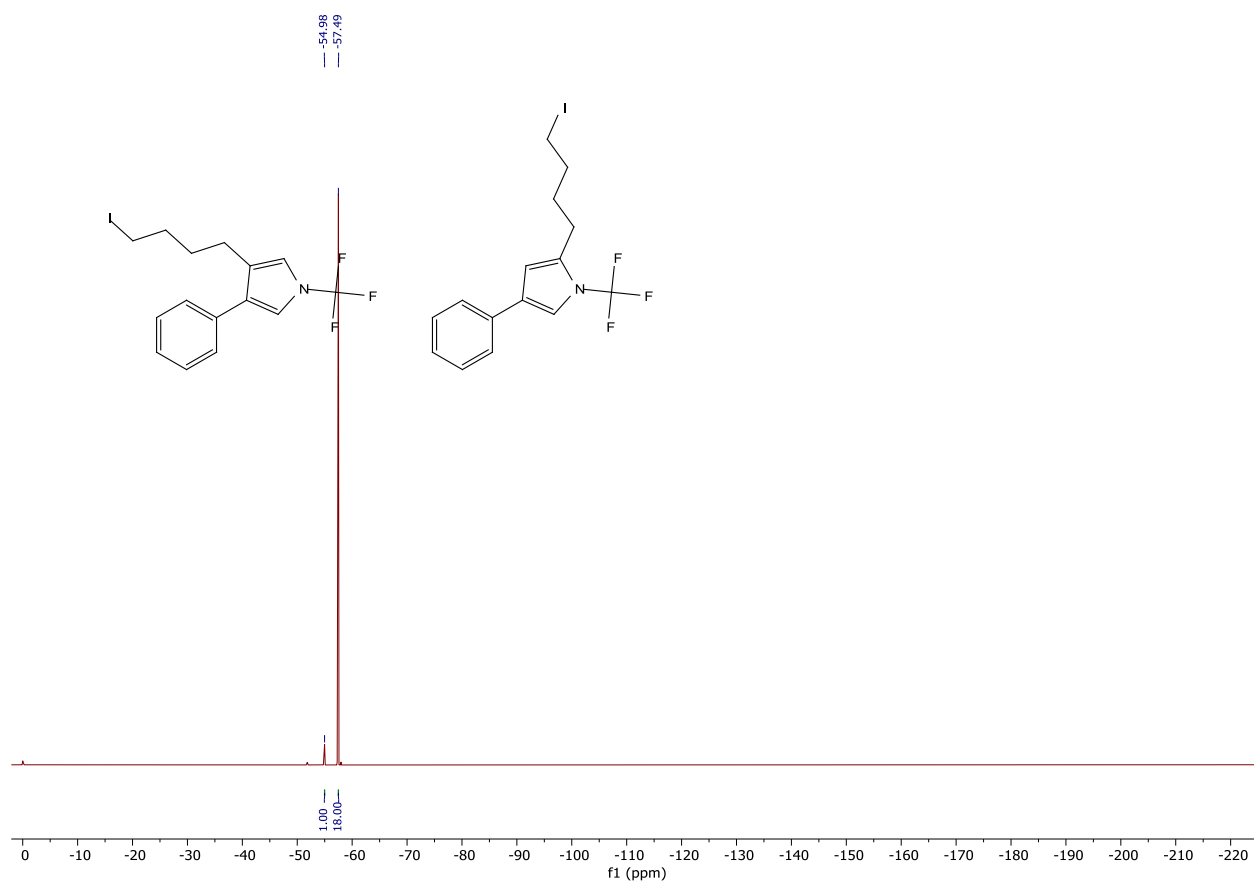
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3i** + **3i'**



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3i** + **3i'**

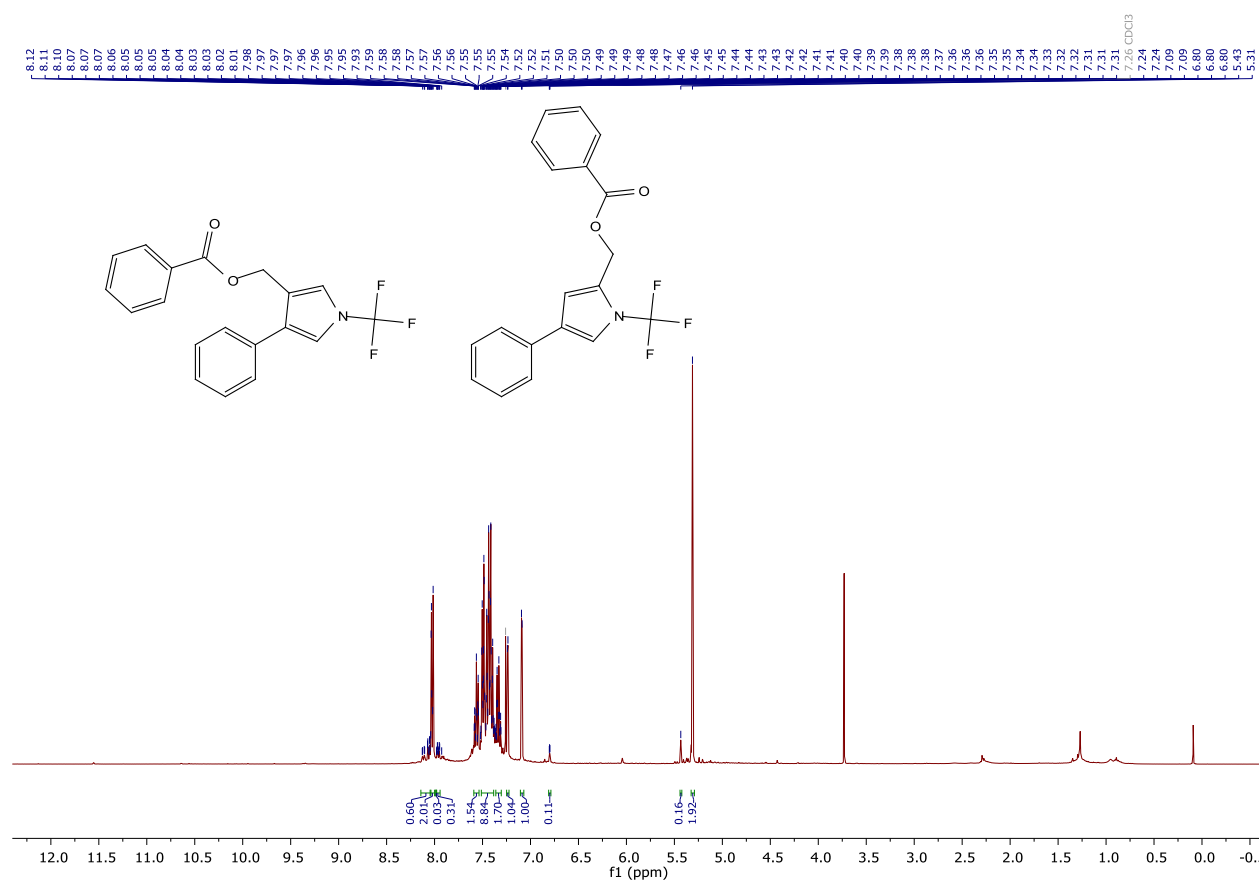


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3i** + **3i'**

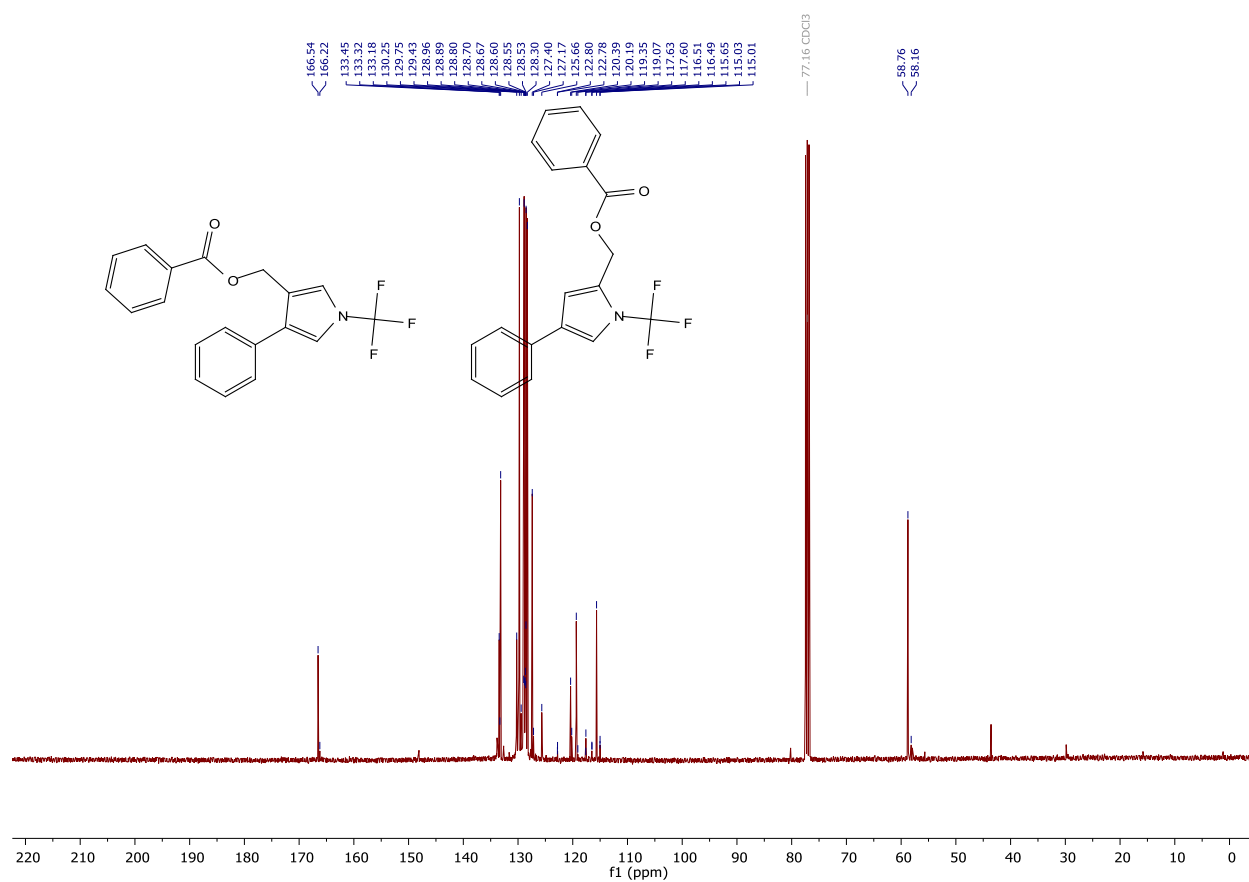




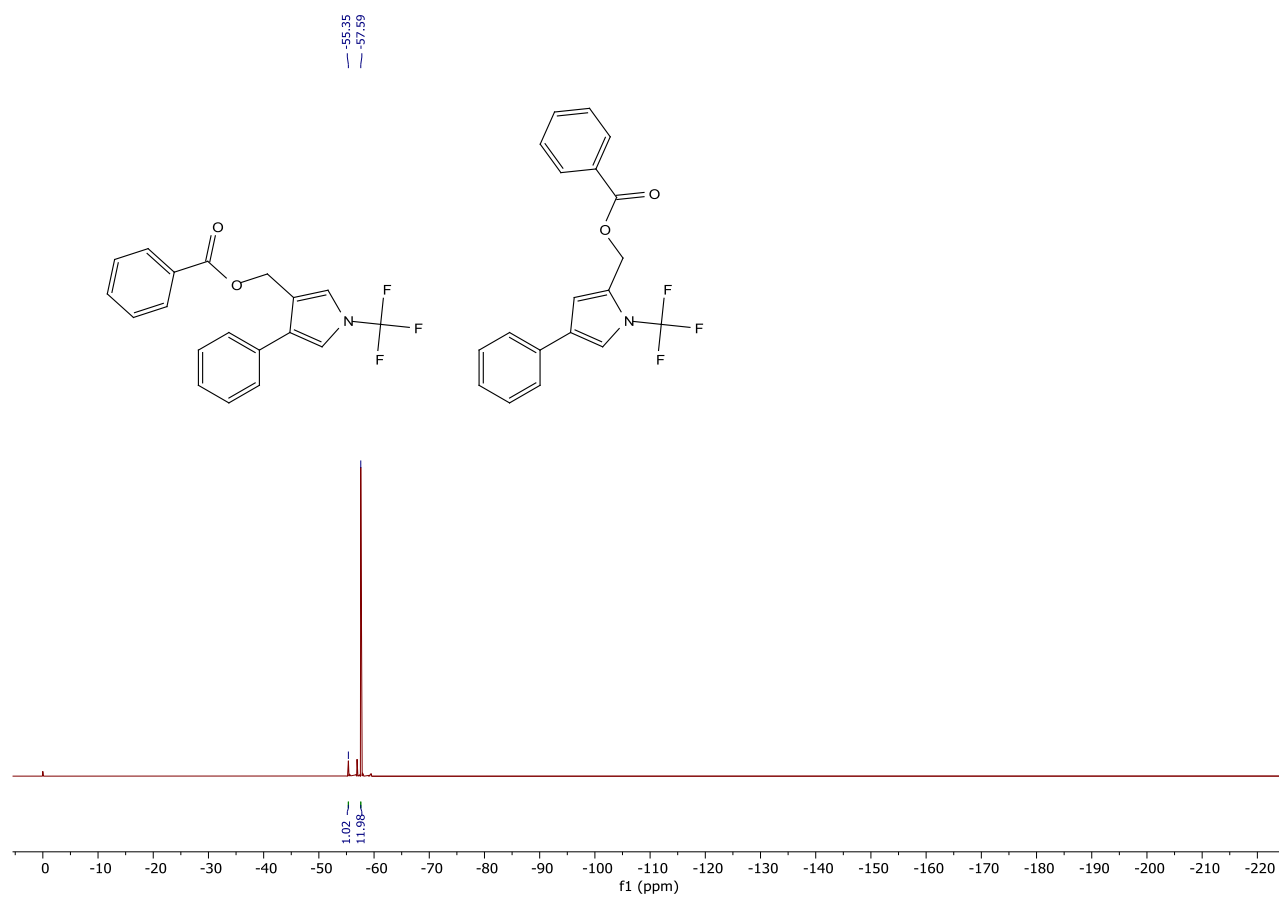
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3j** + **3j'**



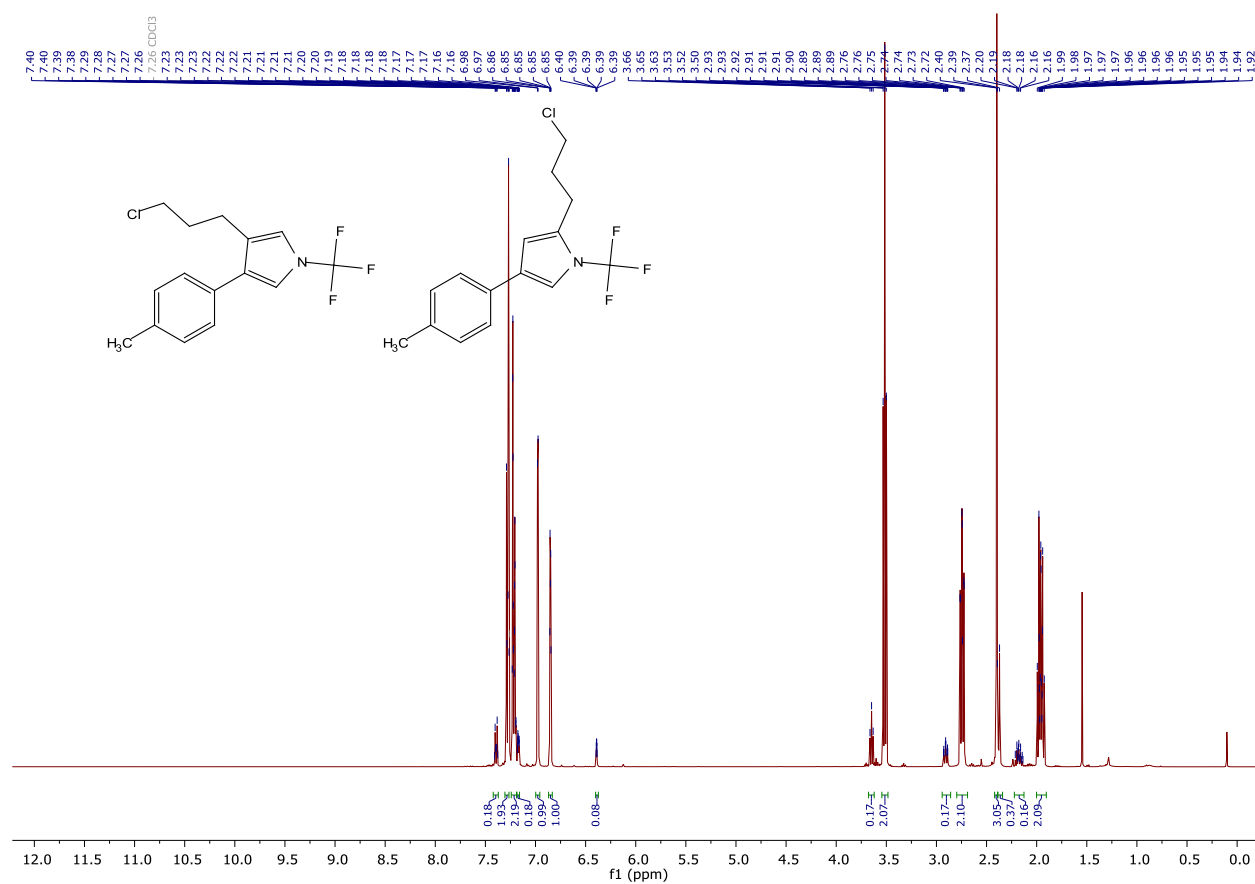
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3j** + **3j'**



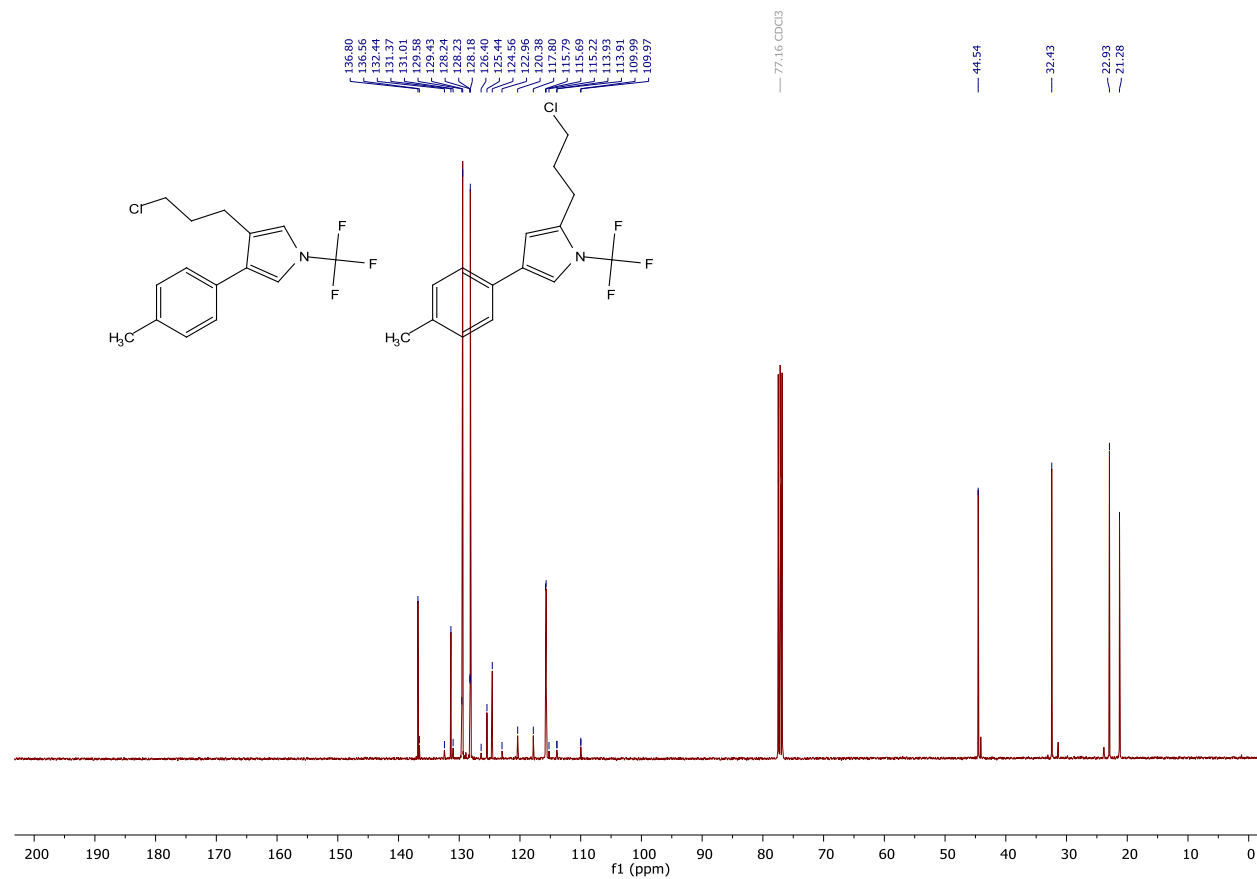
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3j** + **3j'**



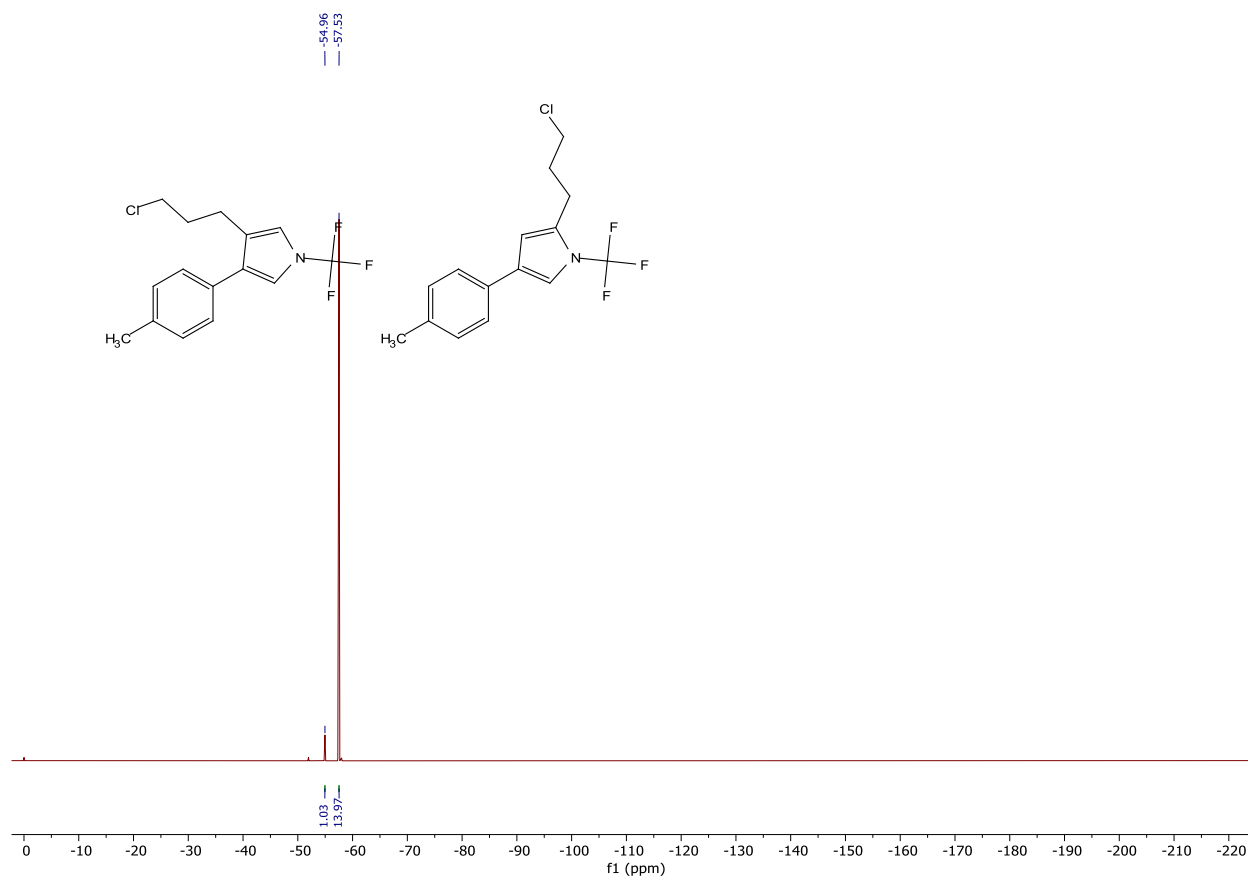
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3k** + **3k'**



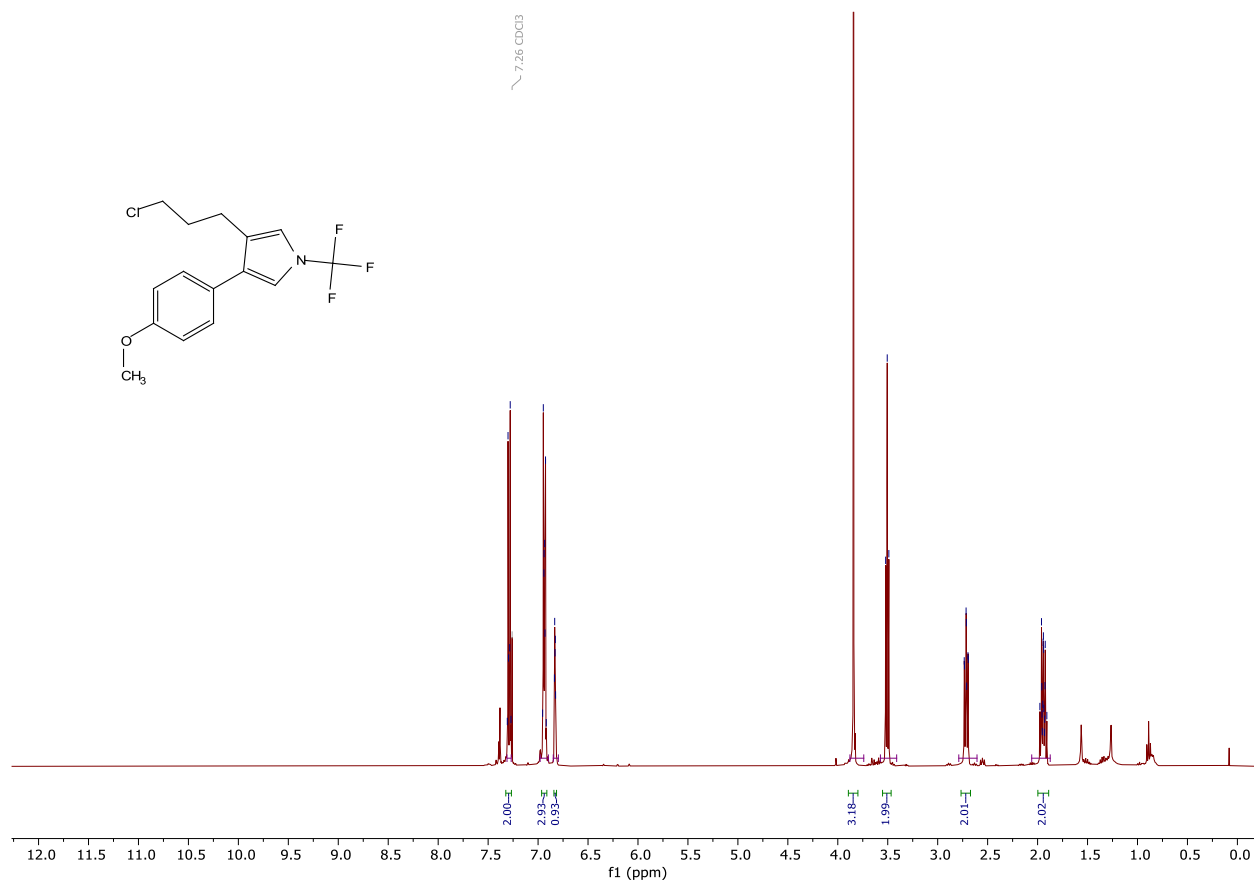
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3k** + **3k'**



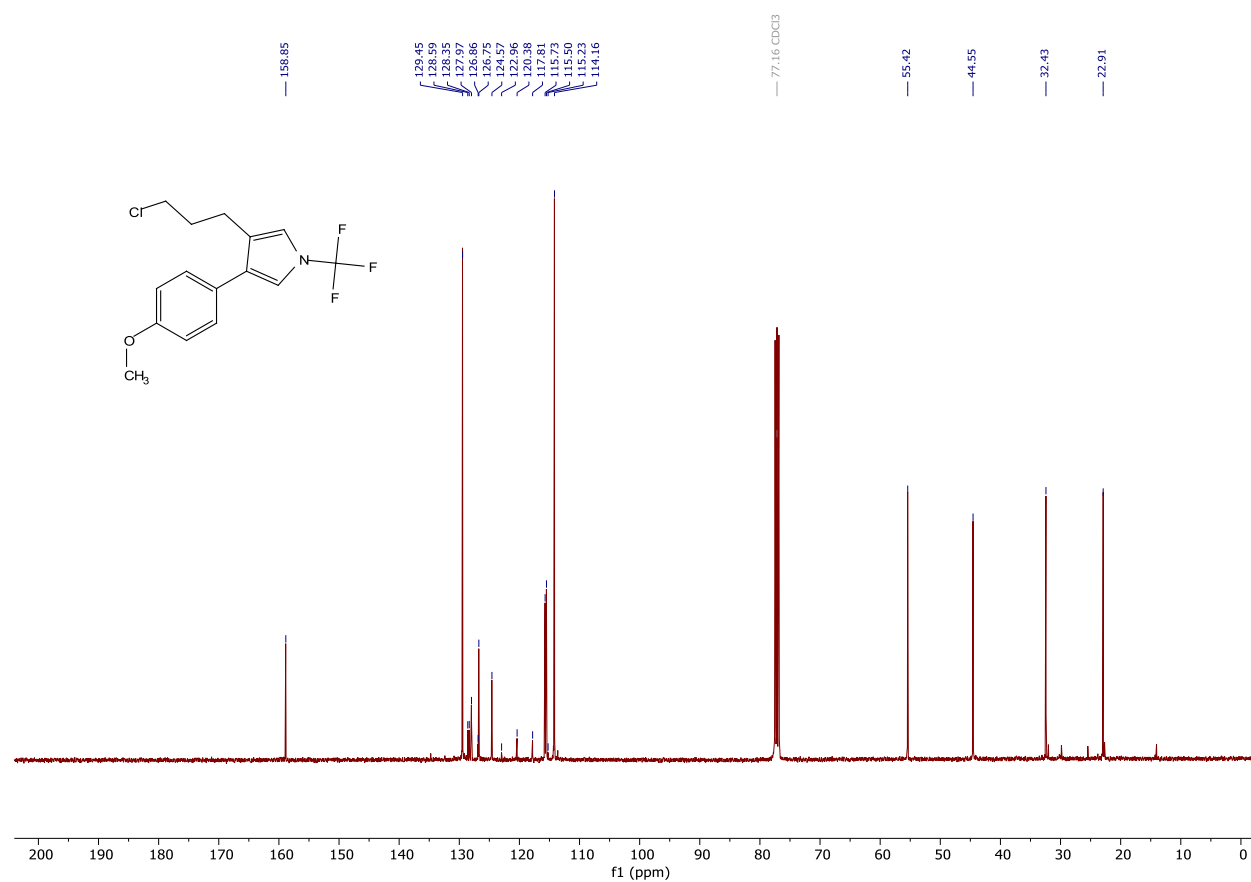
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3k** + **3k'**



$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3I**

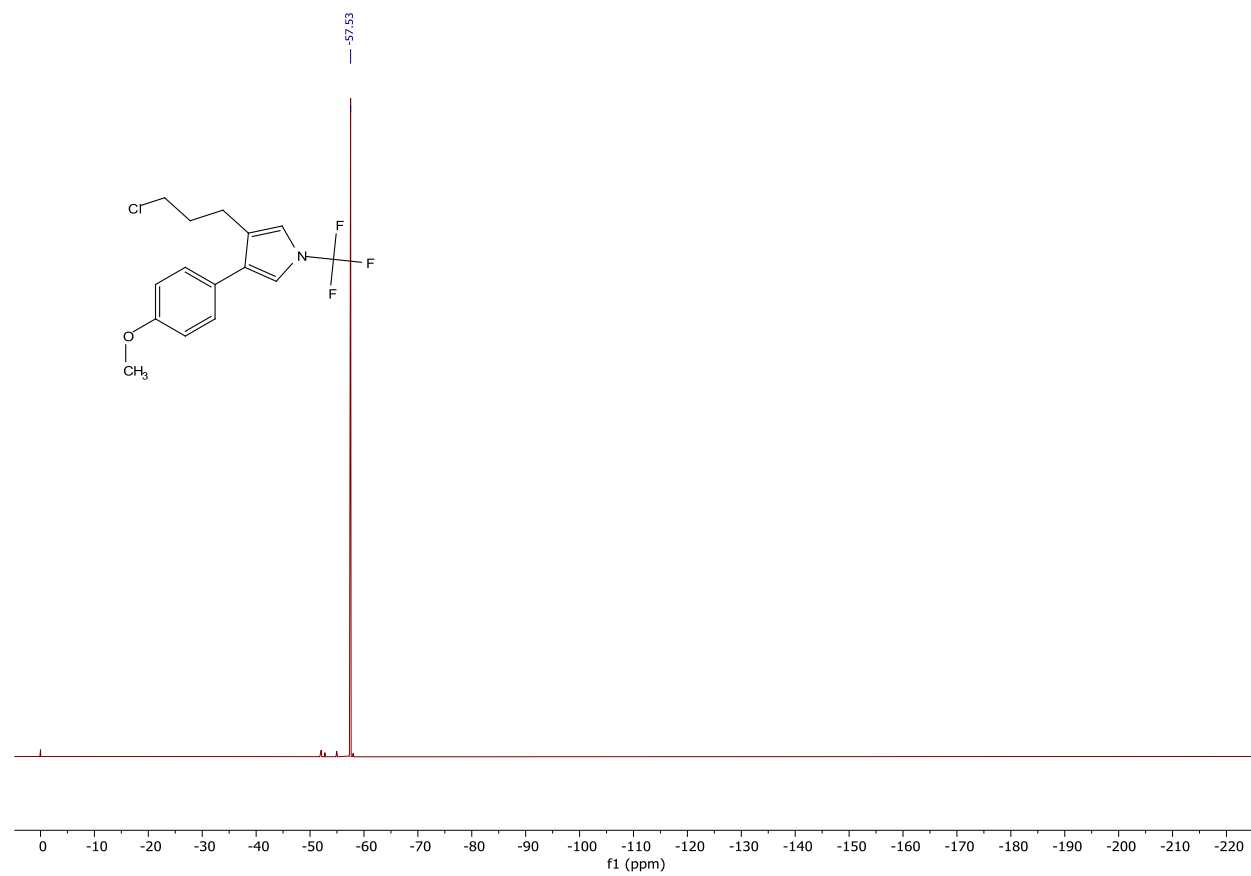


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3l**

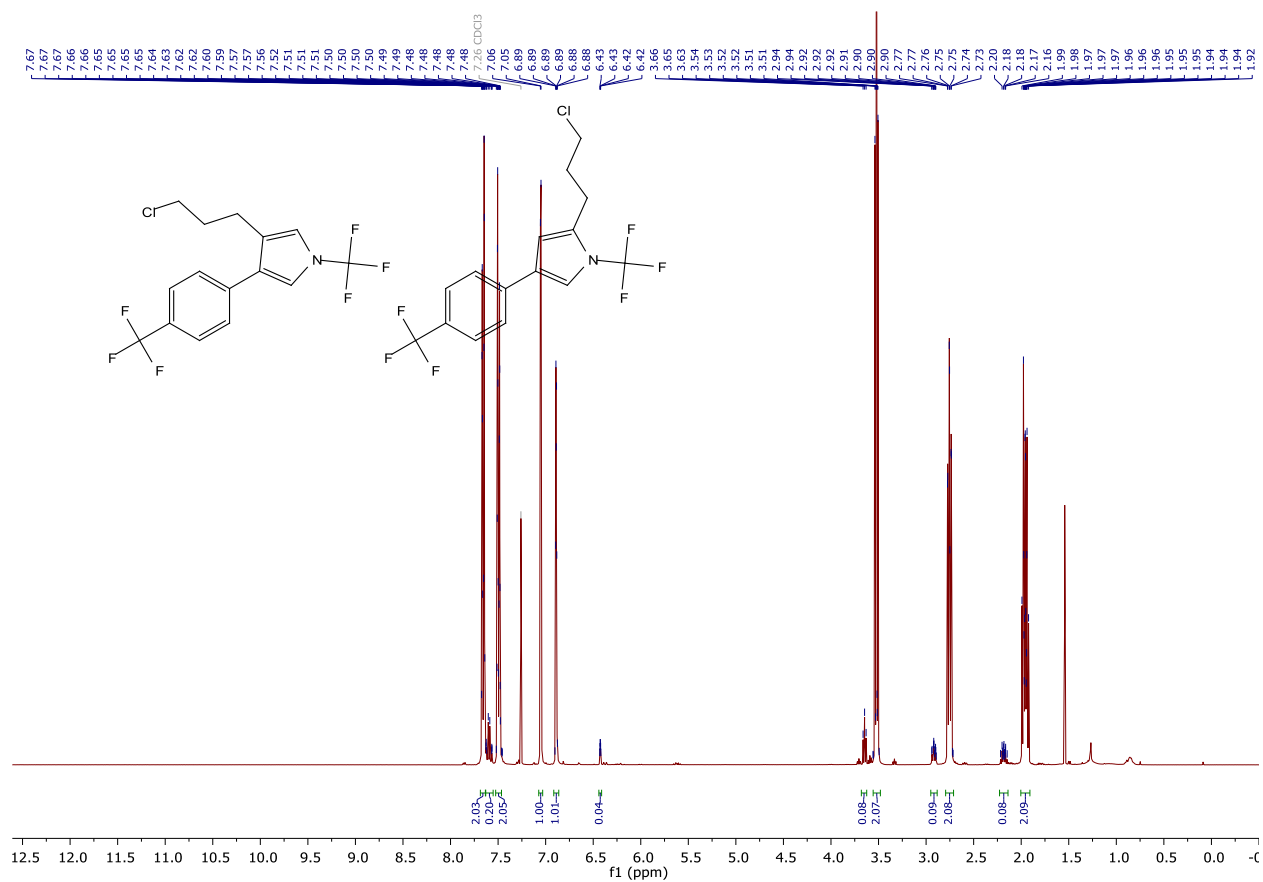




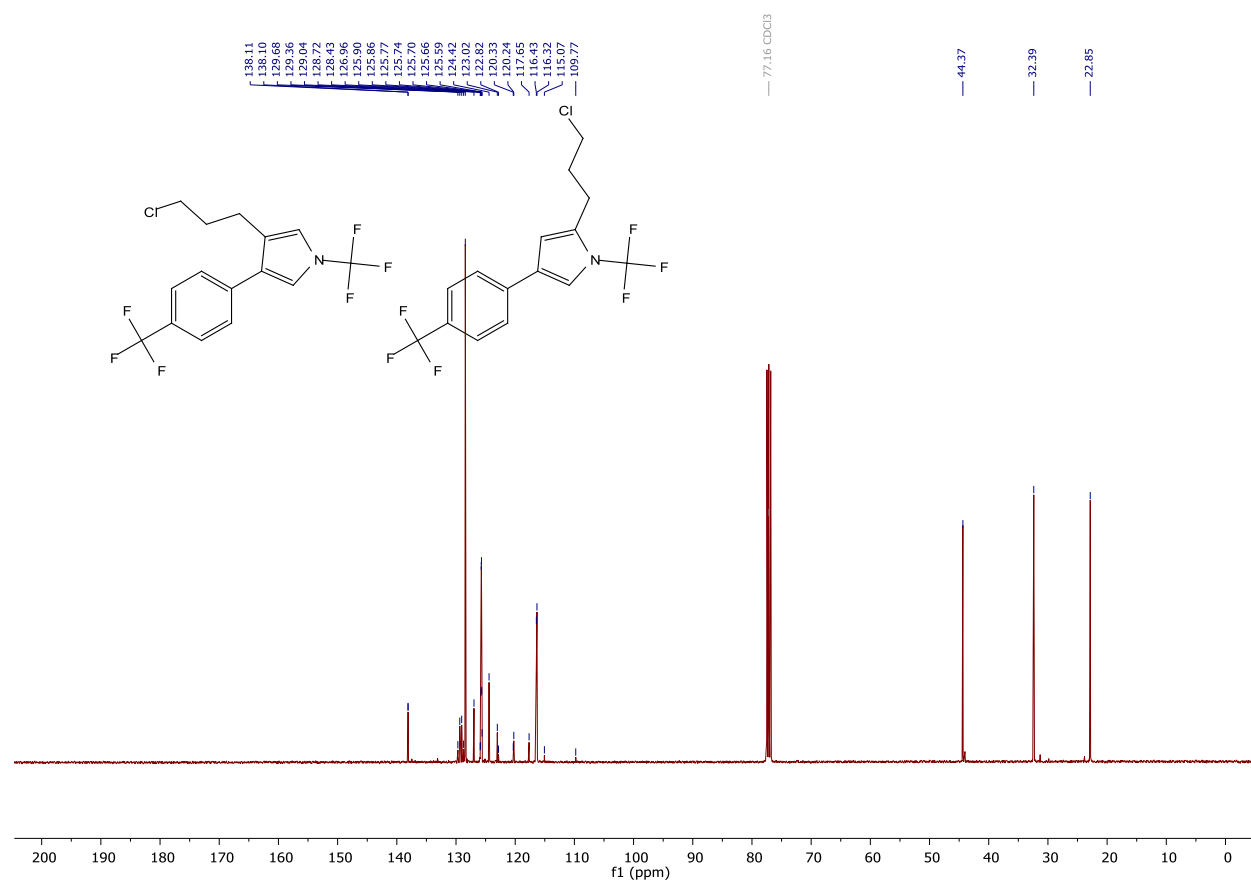
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3I**



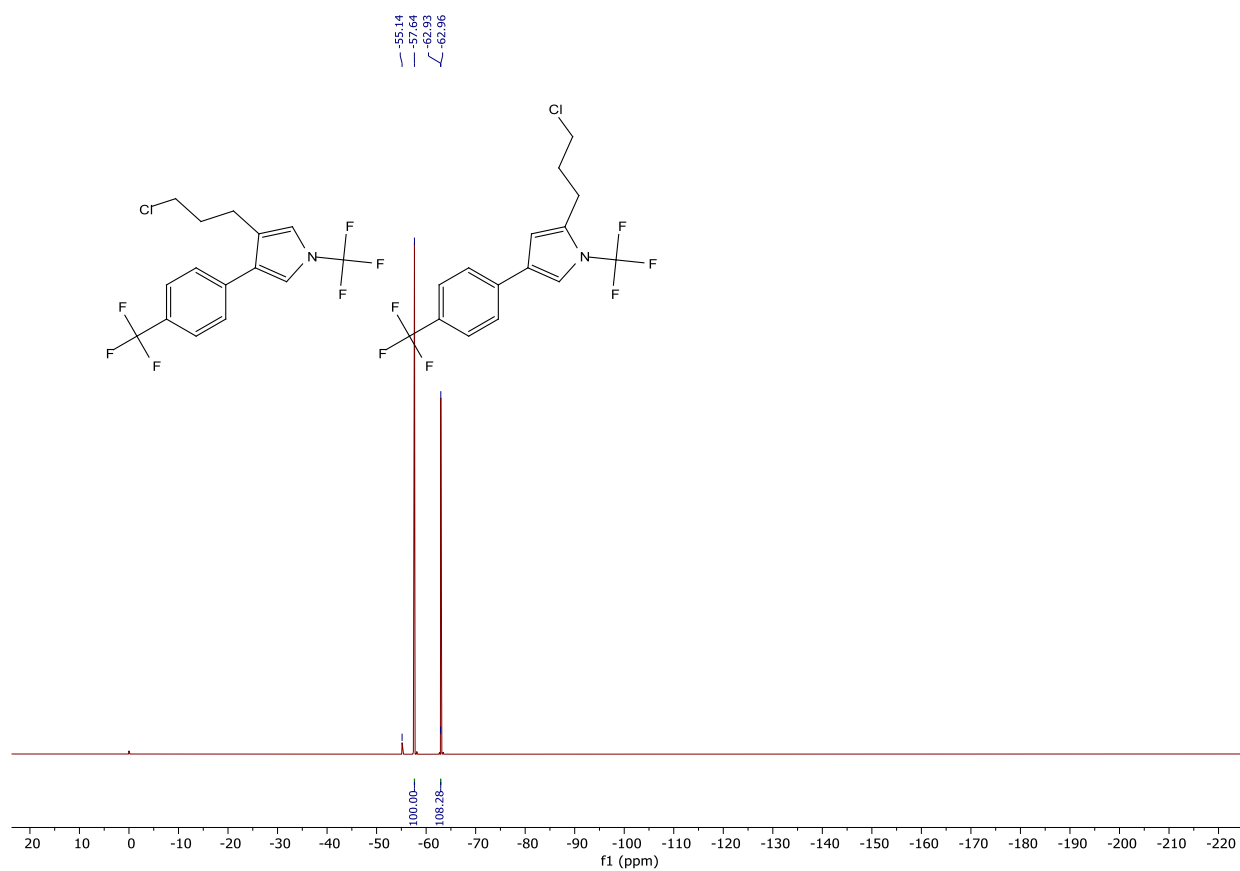
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3m** + **3m'**



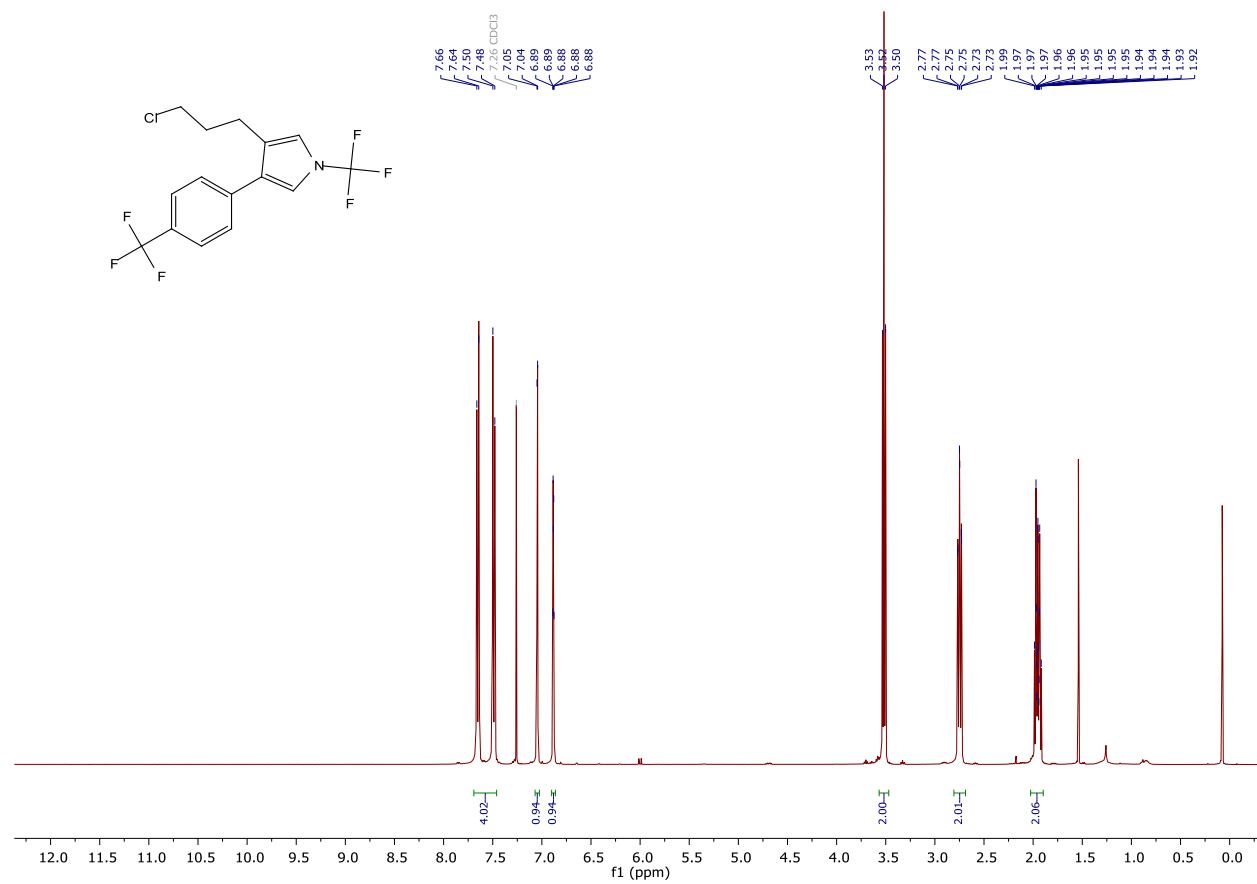
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3m** + **3m'**



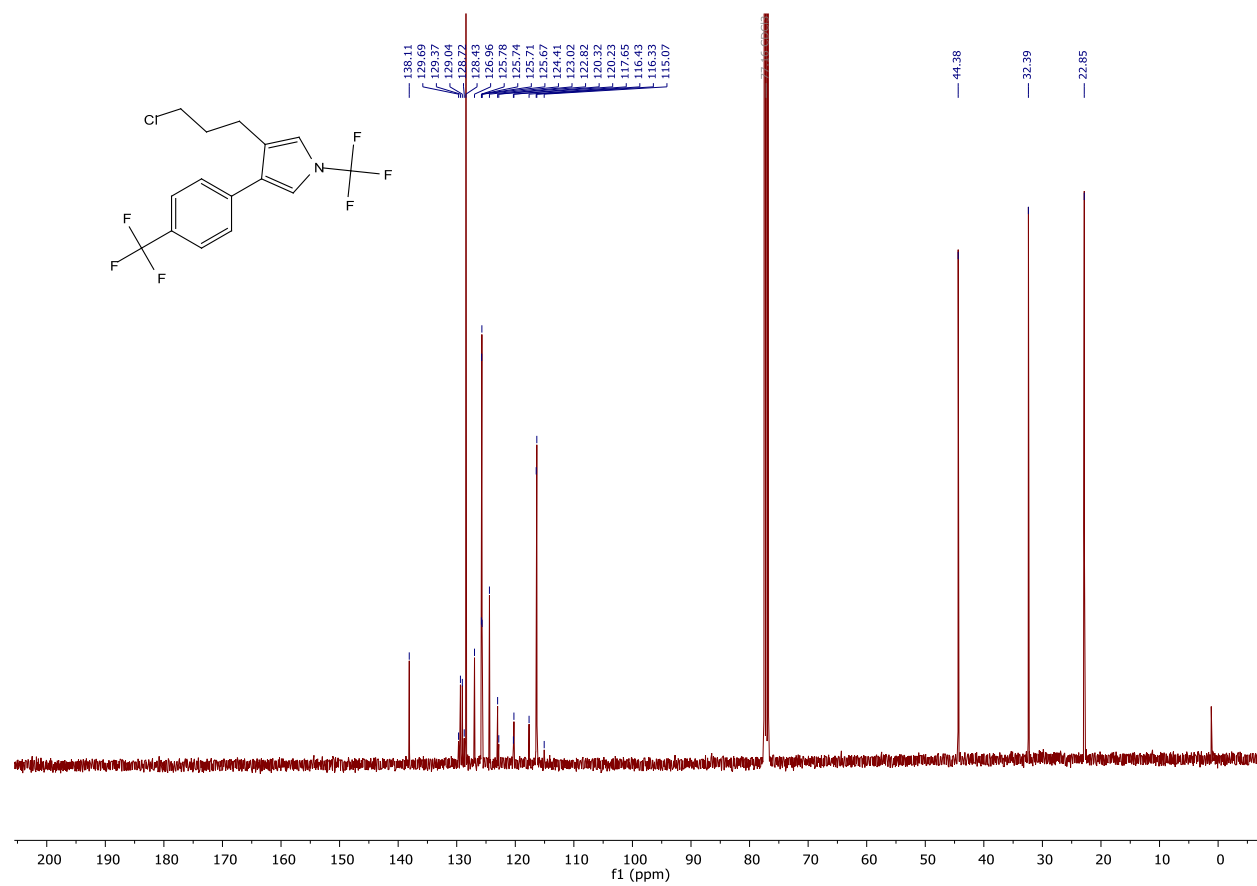
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3m** + **3m'**



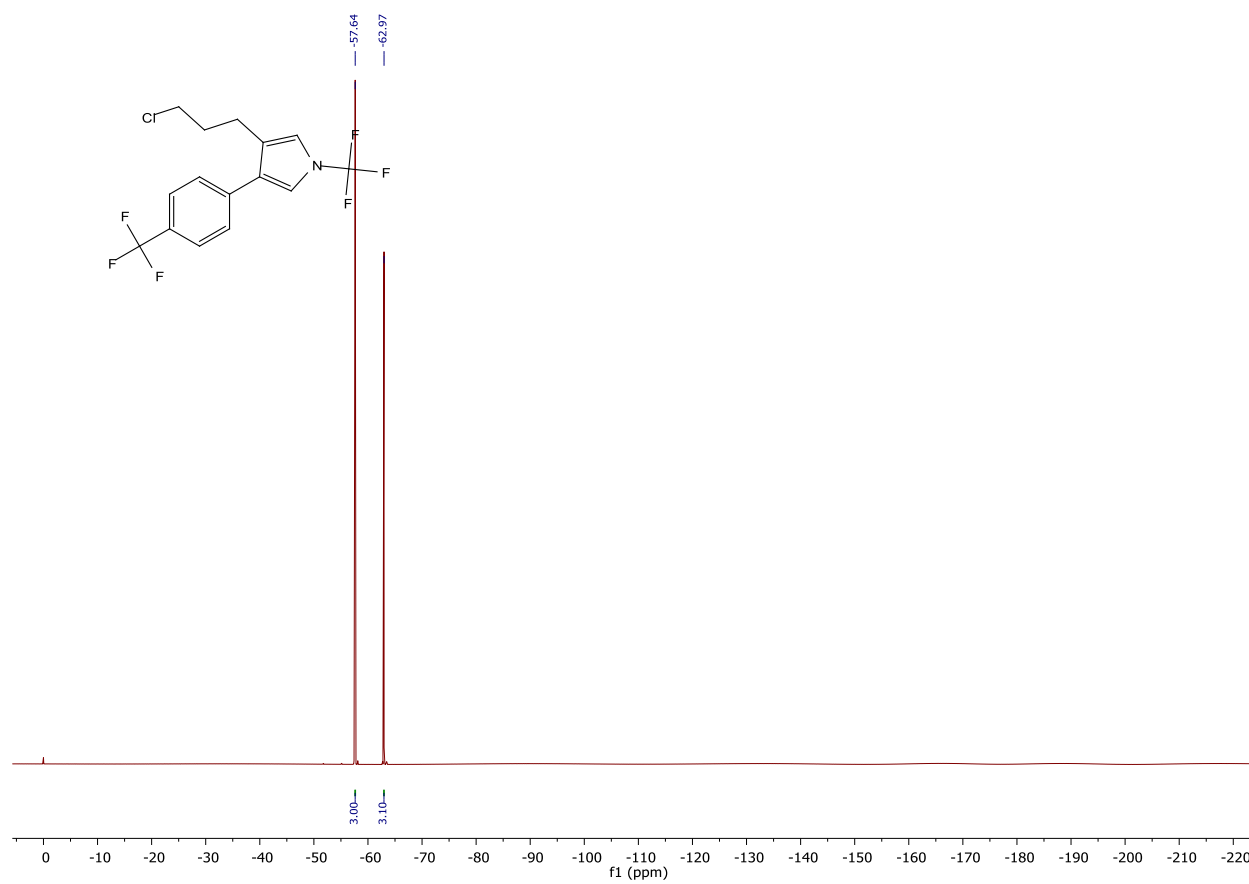
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3m**



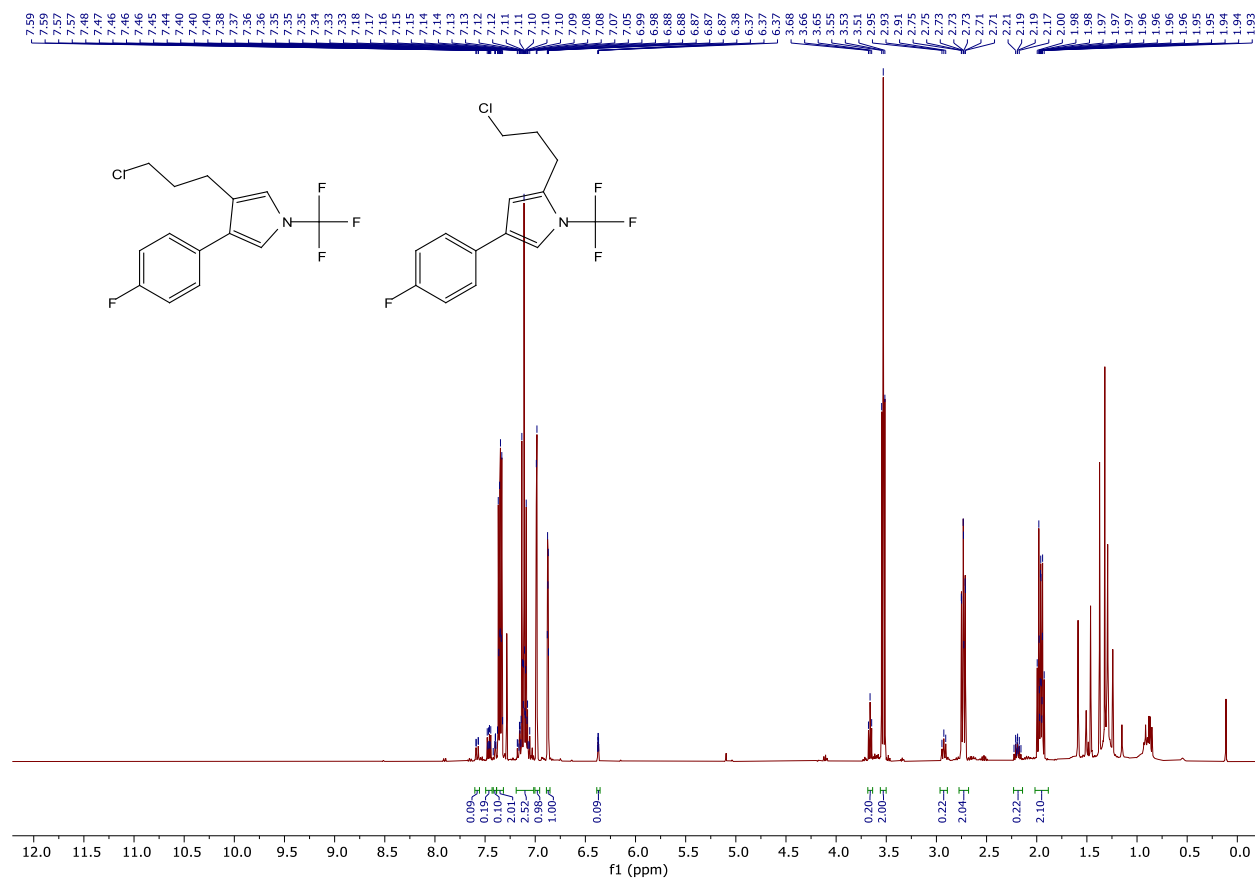
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3m**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3m**

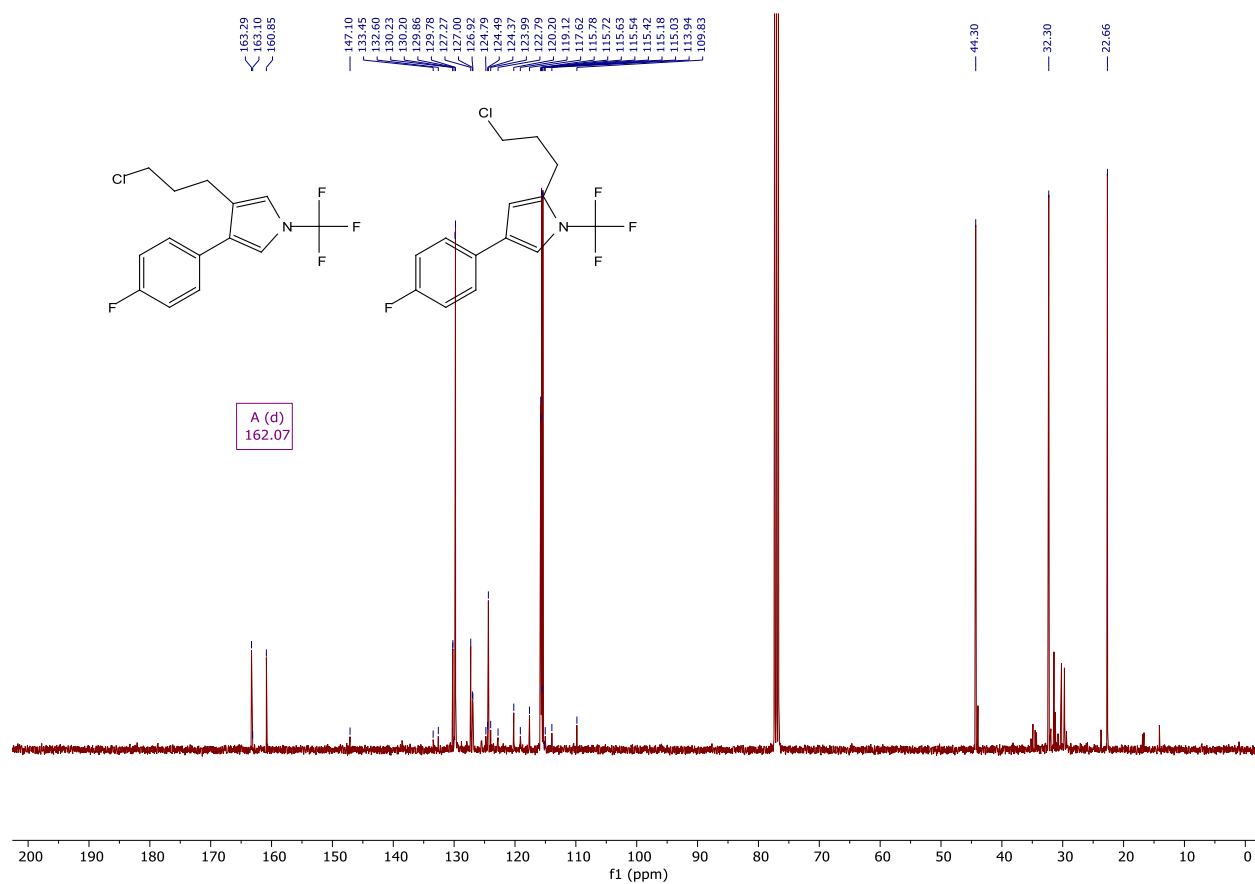


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3n** + **3n'**

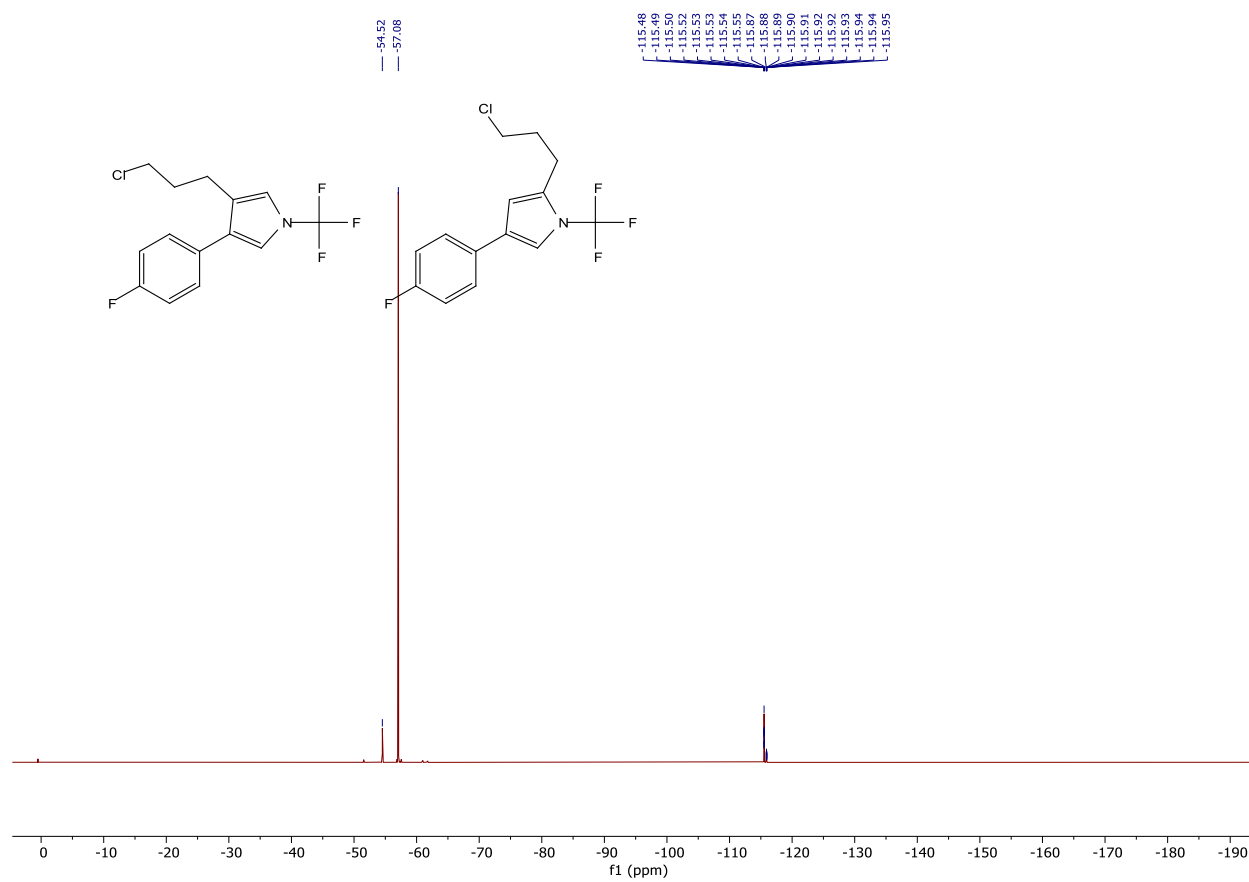




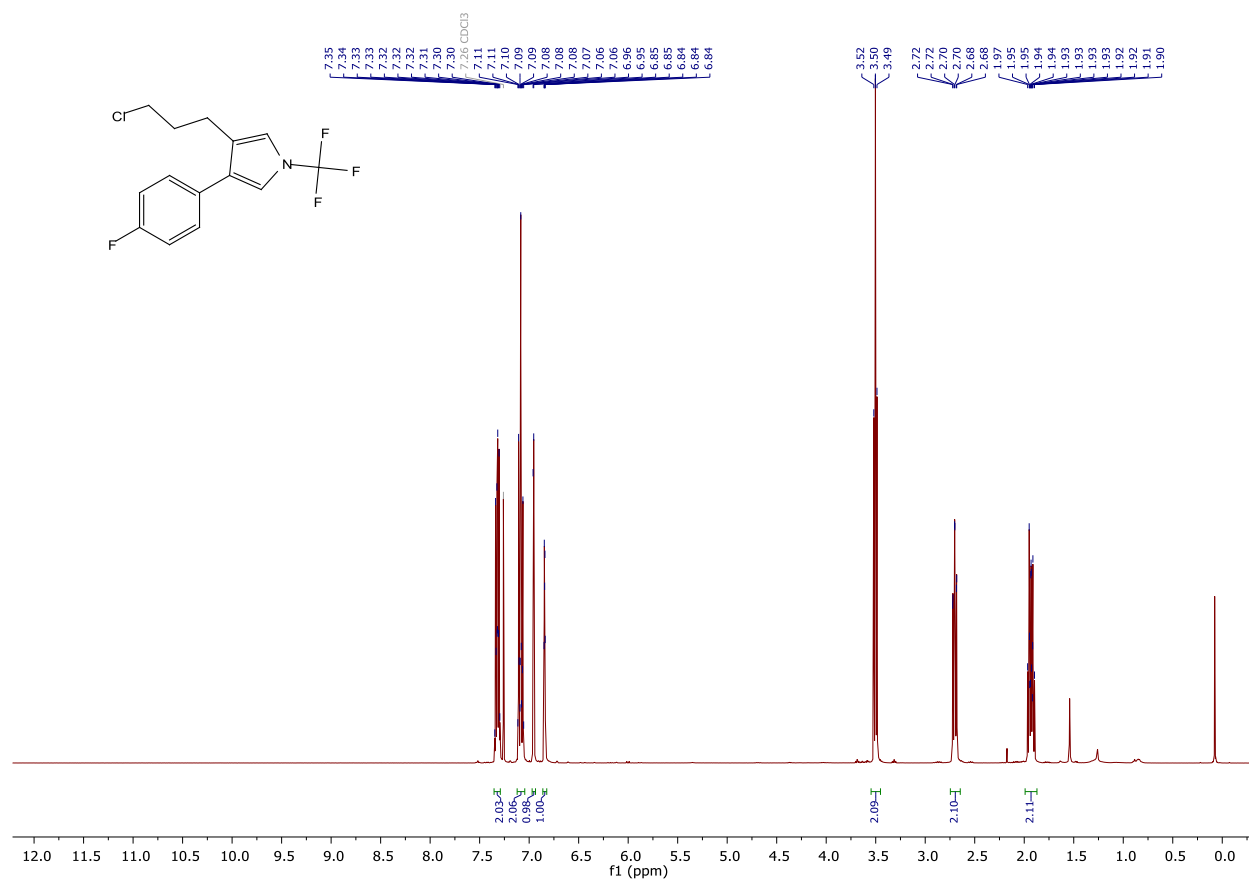
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3n** + **3n'**



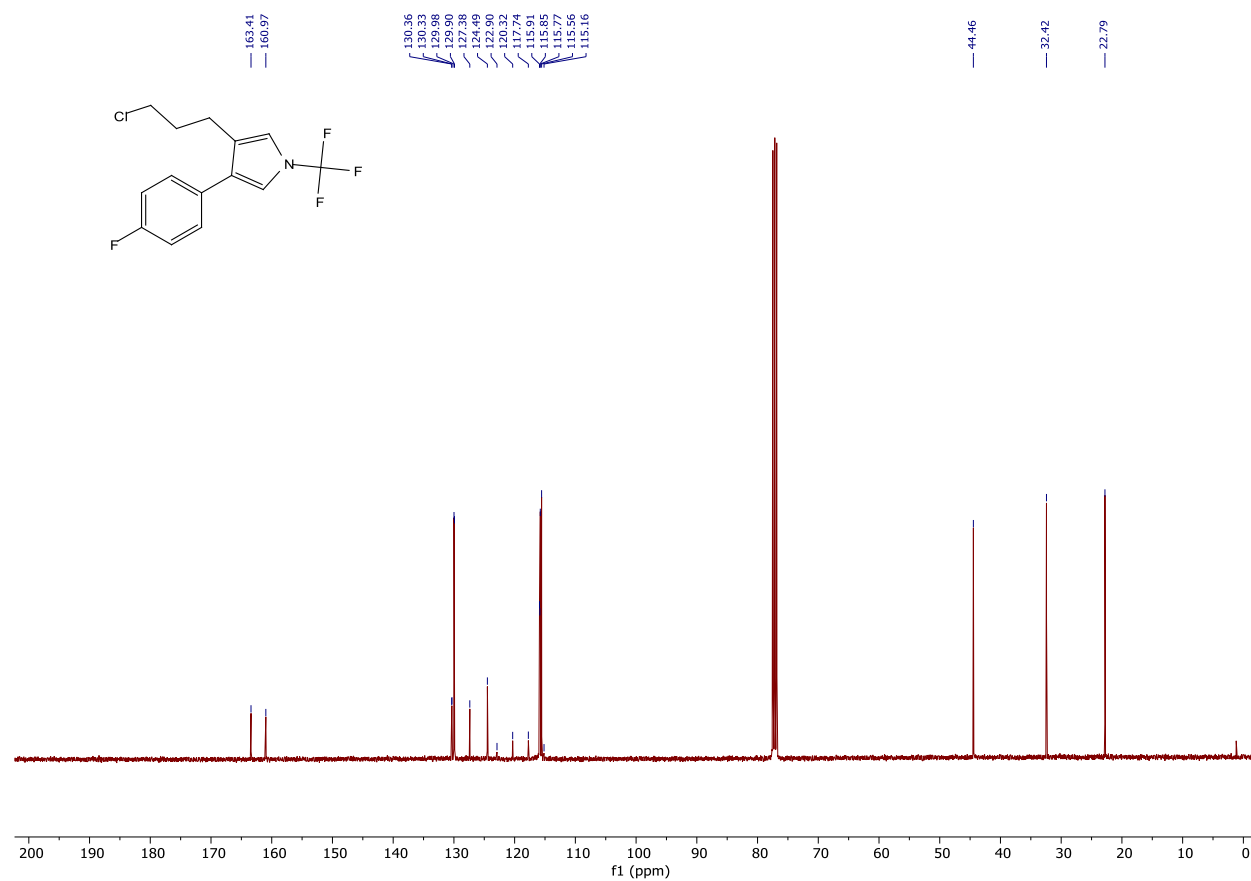
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3n** + **3n'**



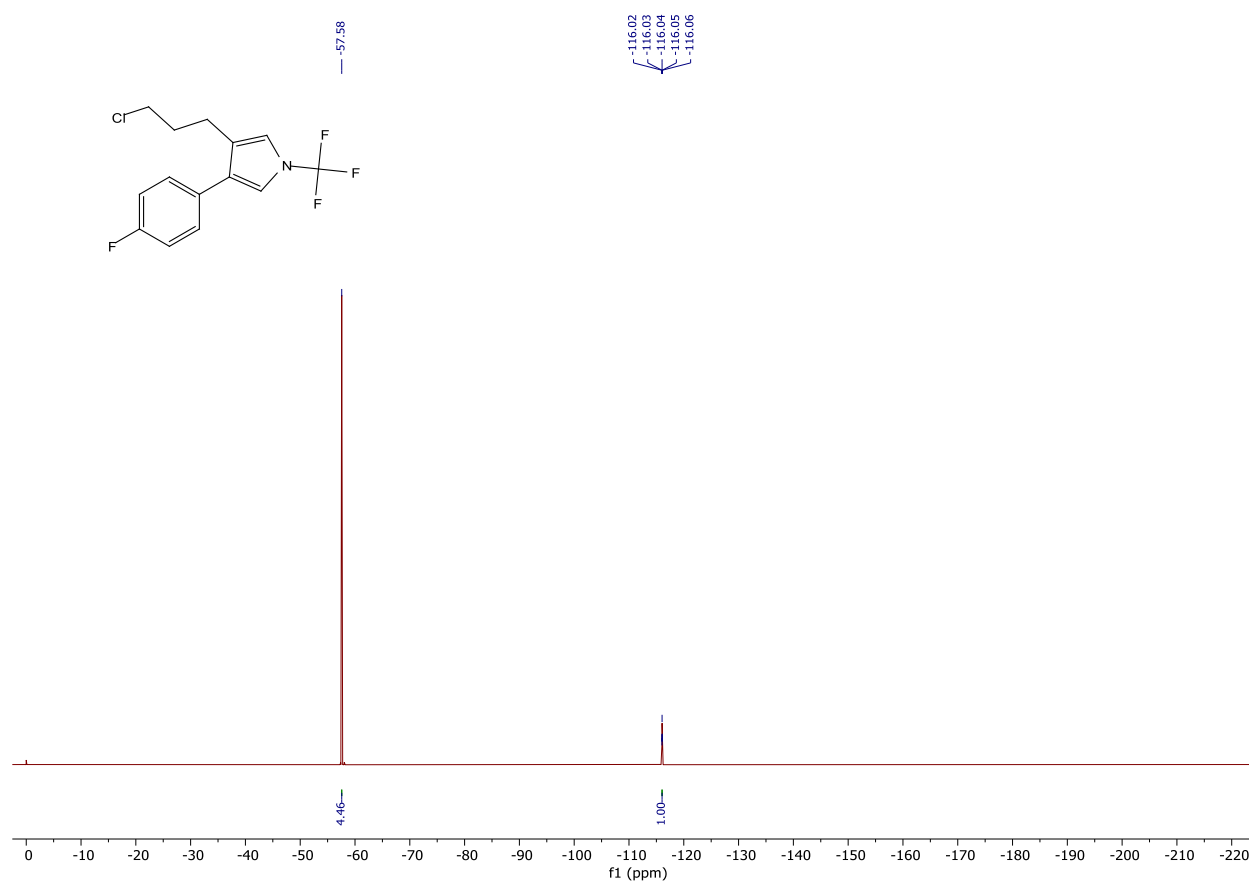
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3n**



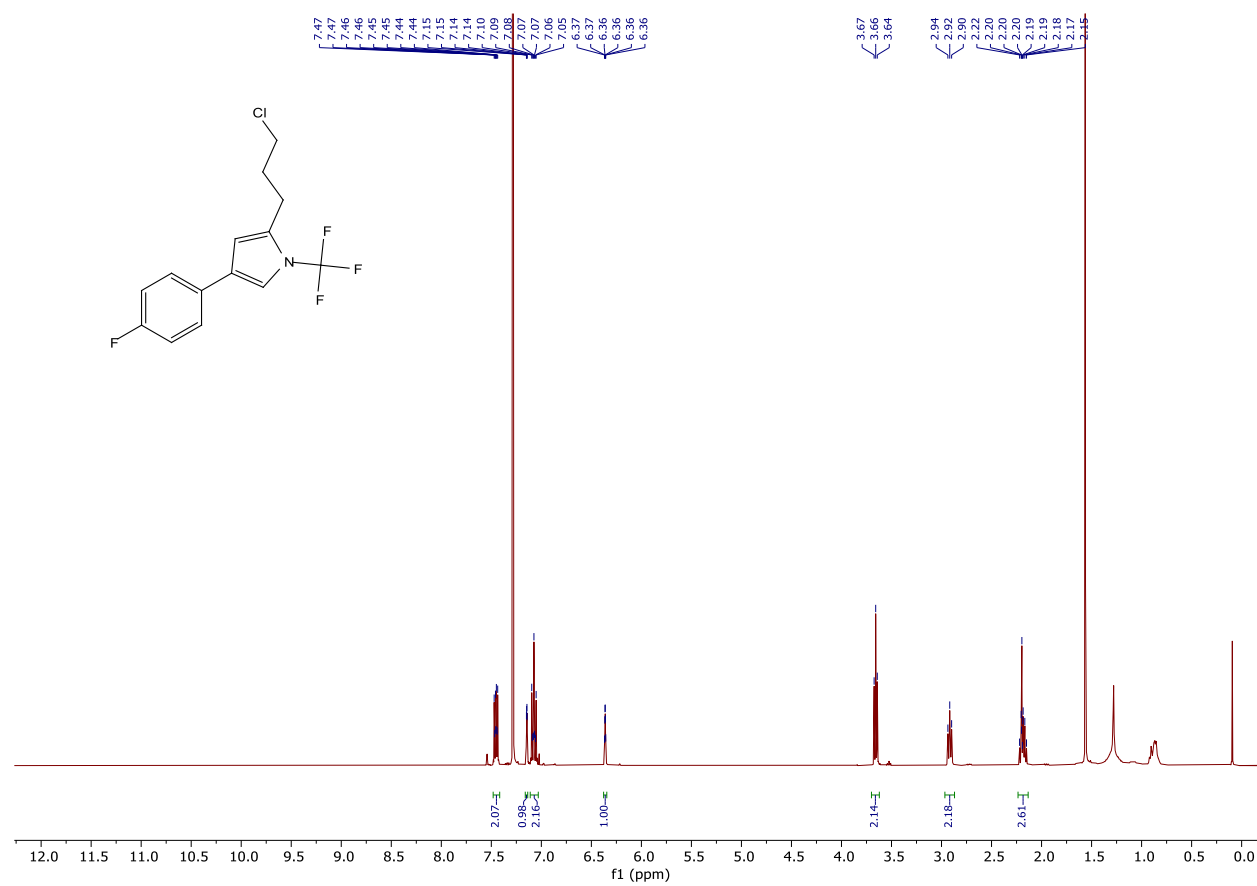
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3n**



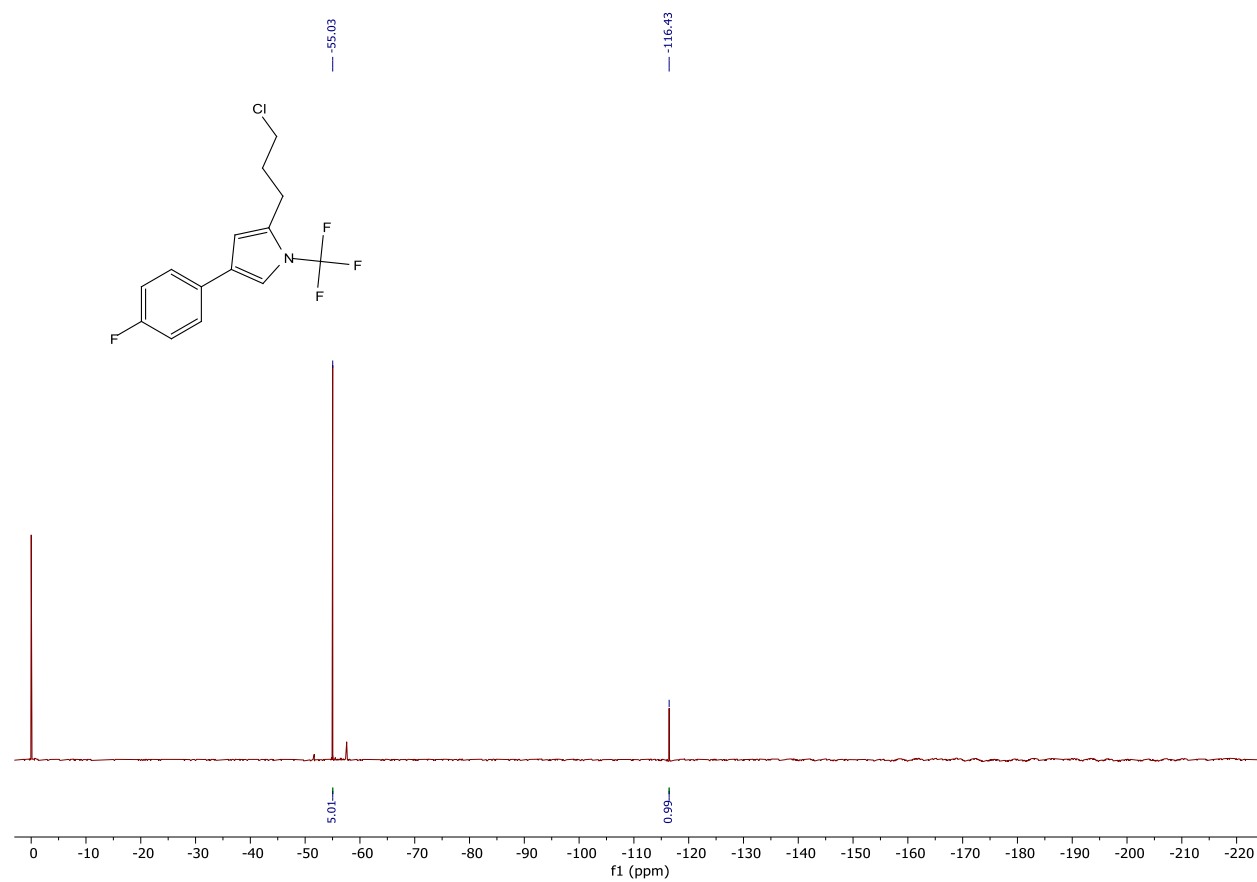
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3n**



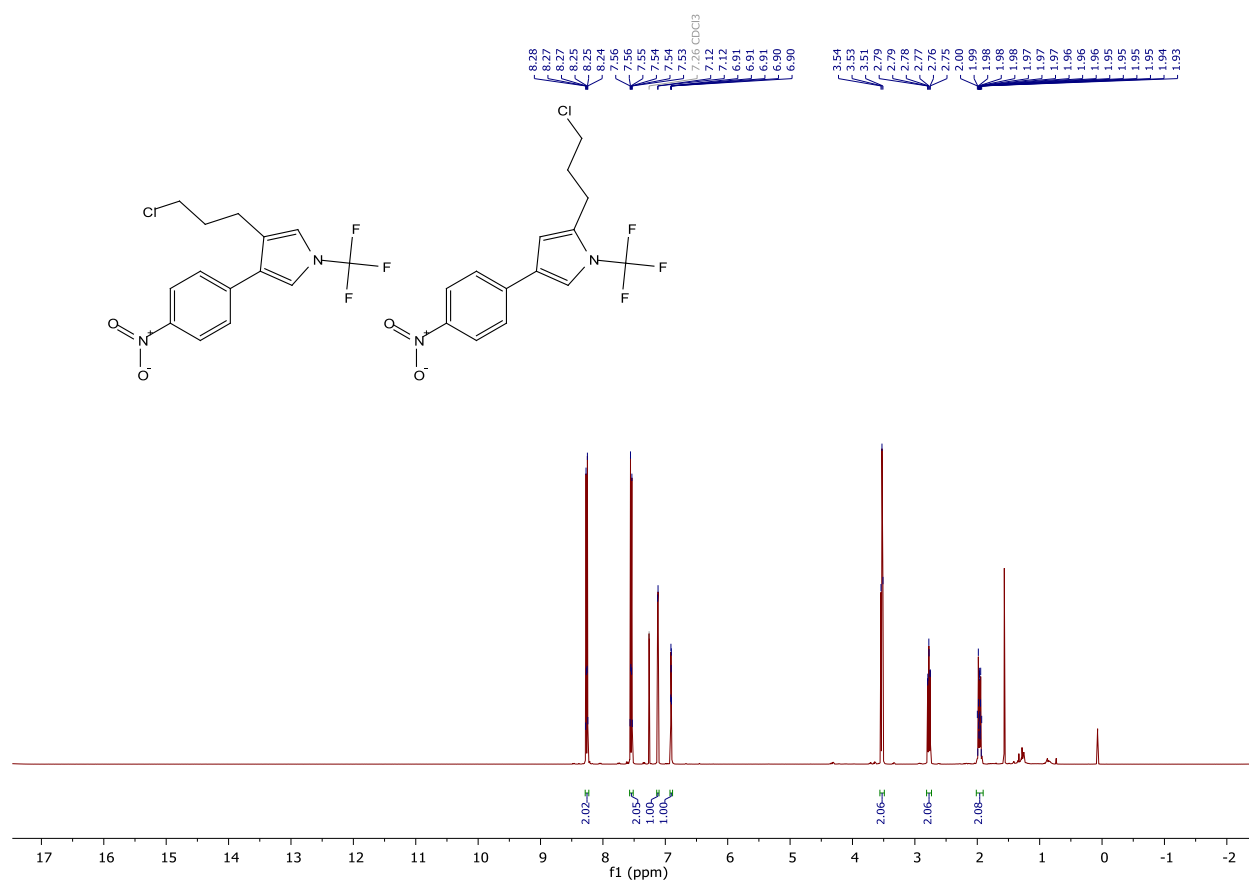
$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3n'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3n'**

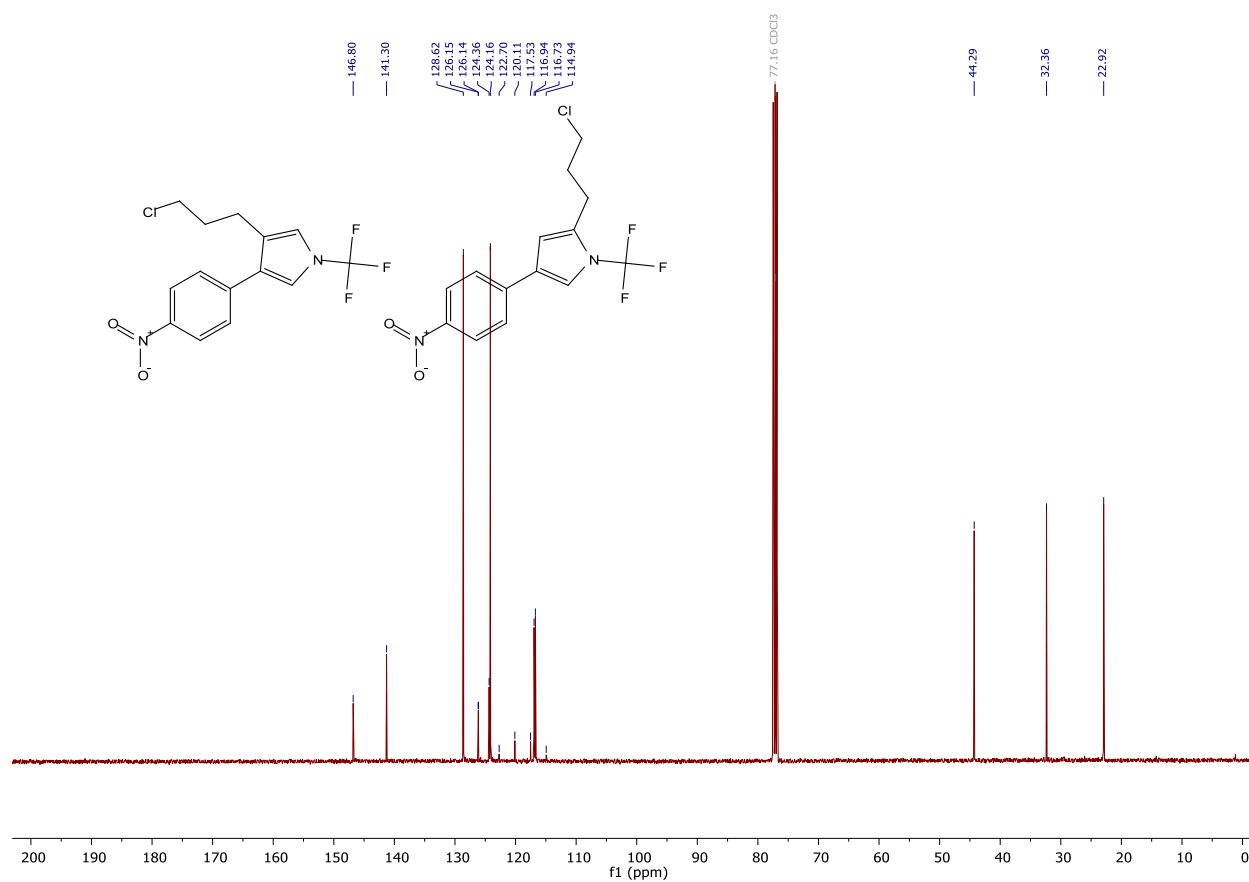


$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3o** + **3o'**

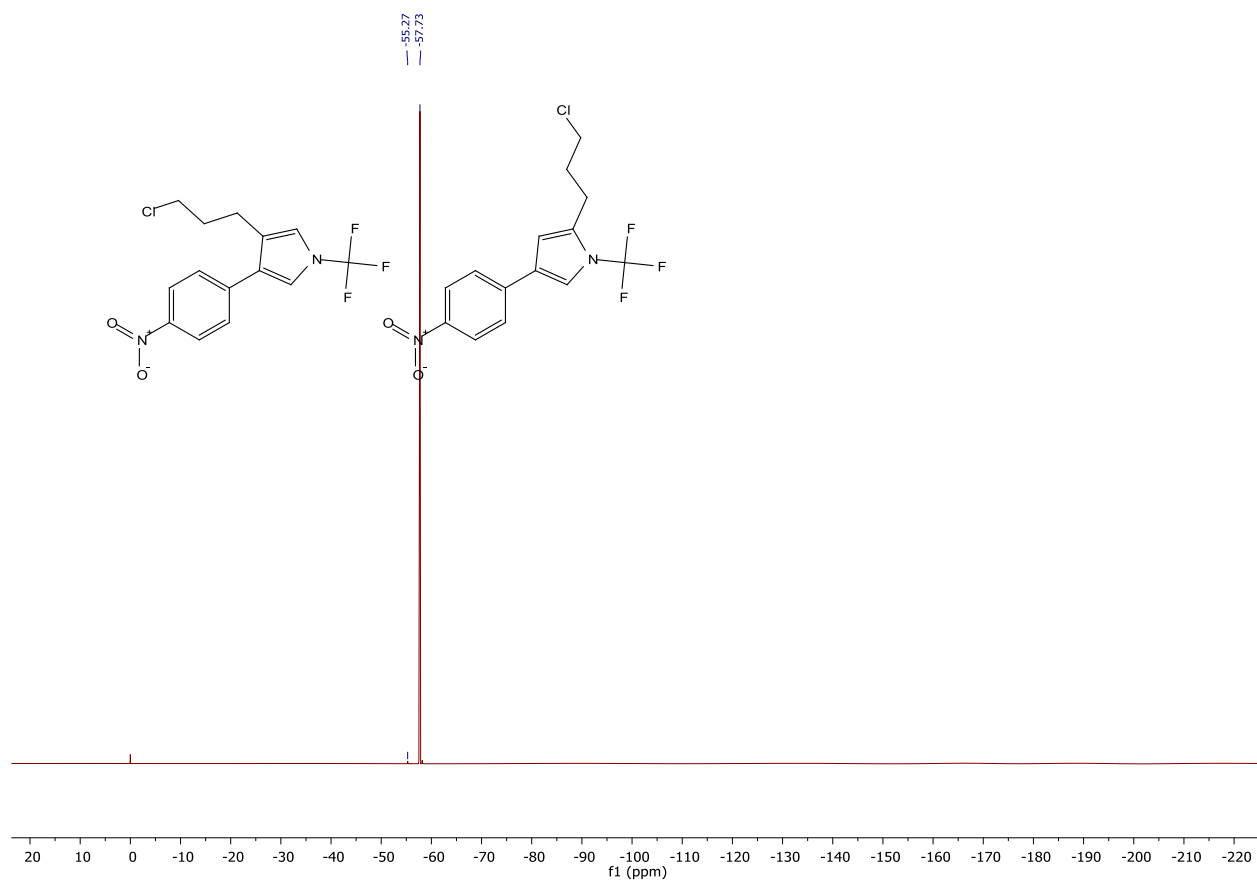




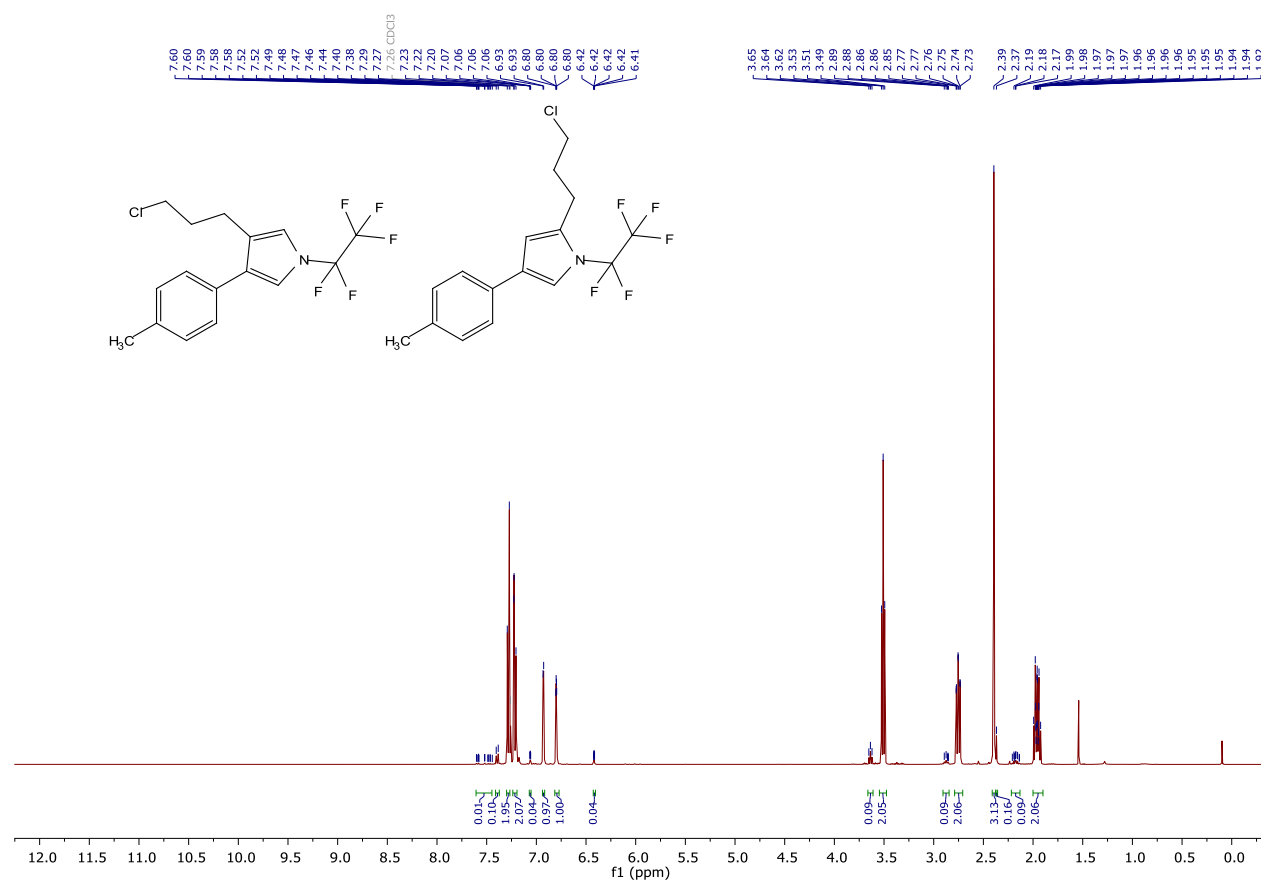
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3o** + **3o'**



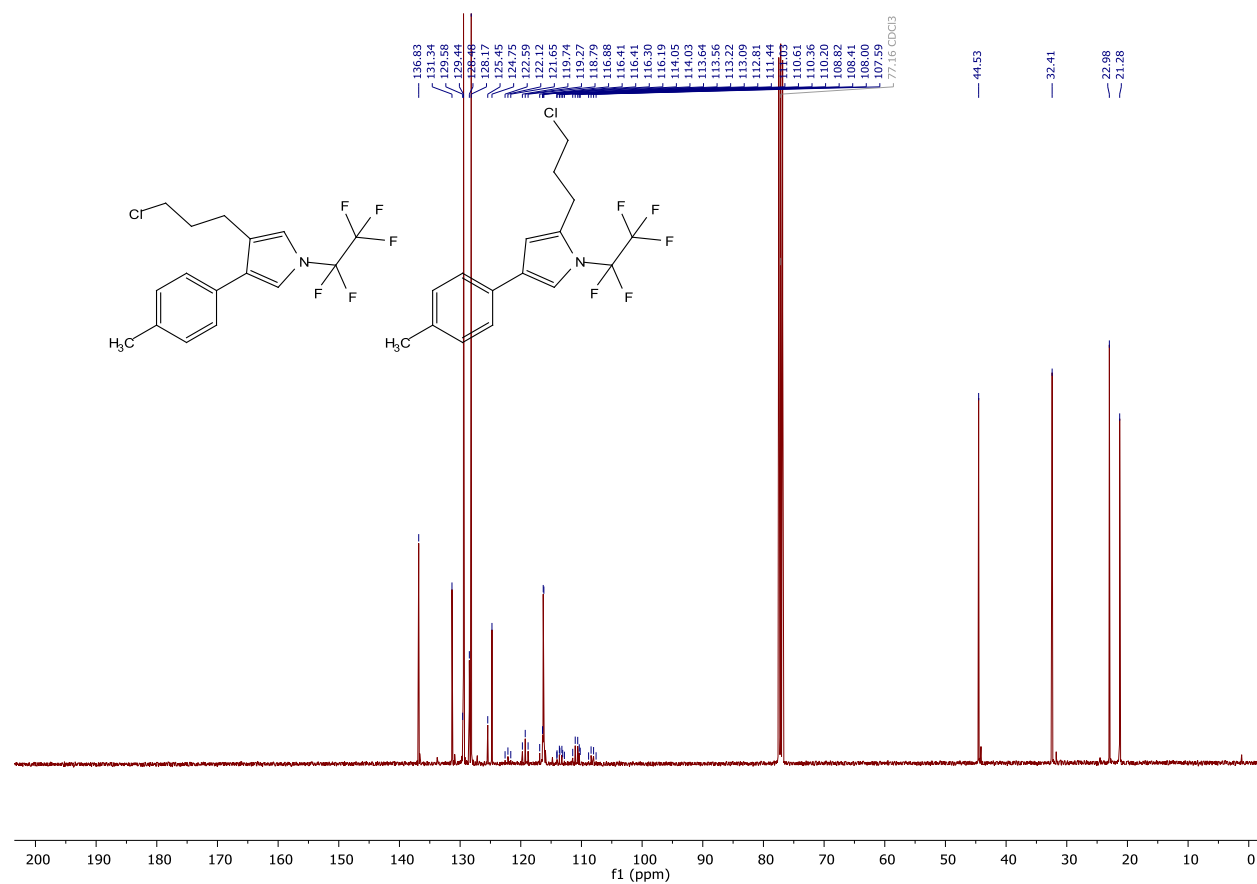
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3o** + **3o'**



$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3p** + **3p'**



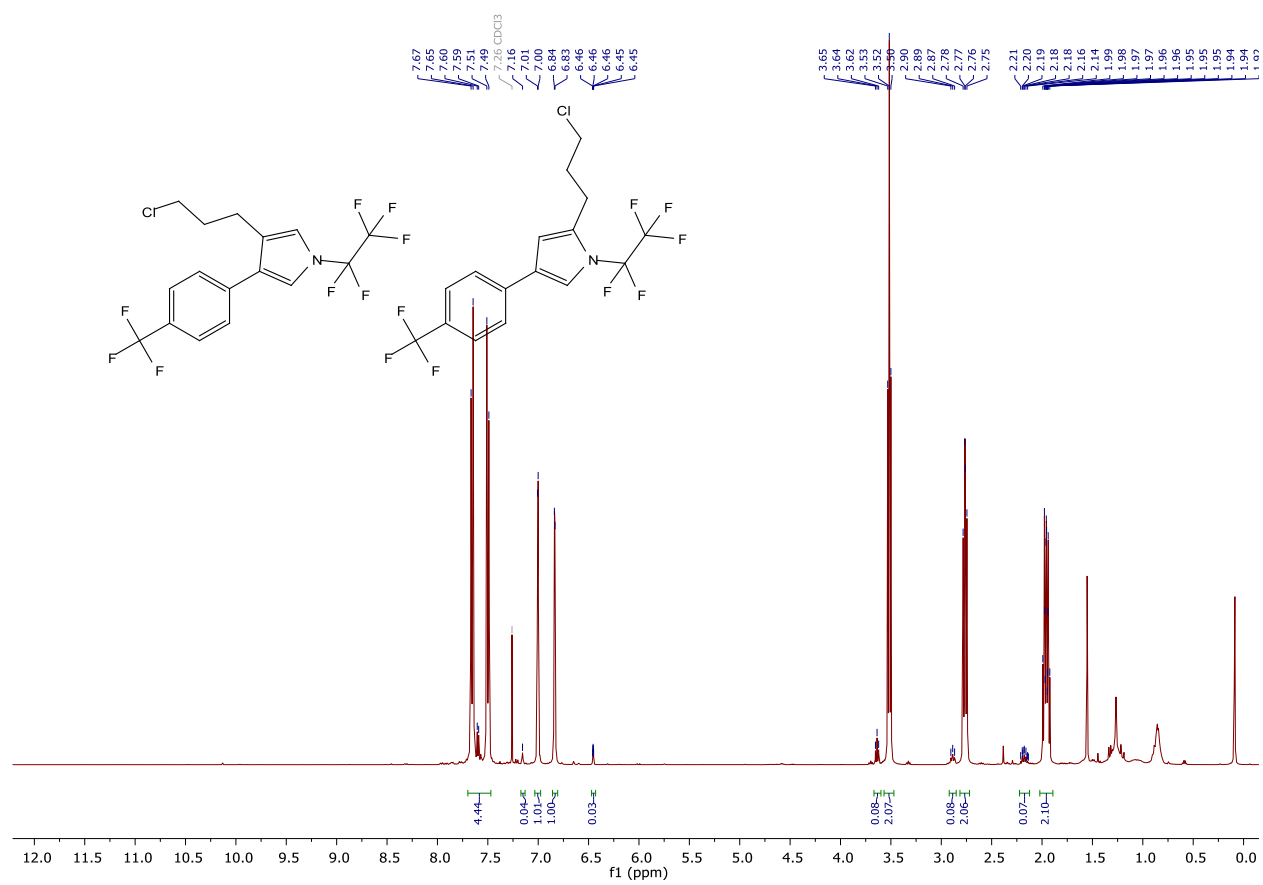
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3p** + **3p'**



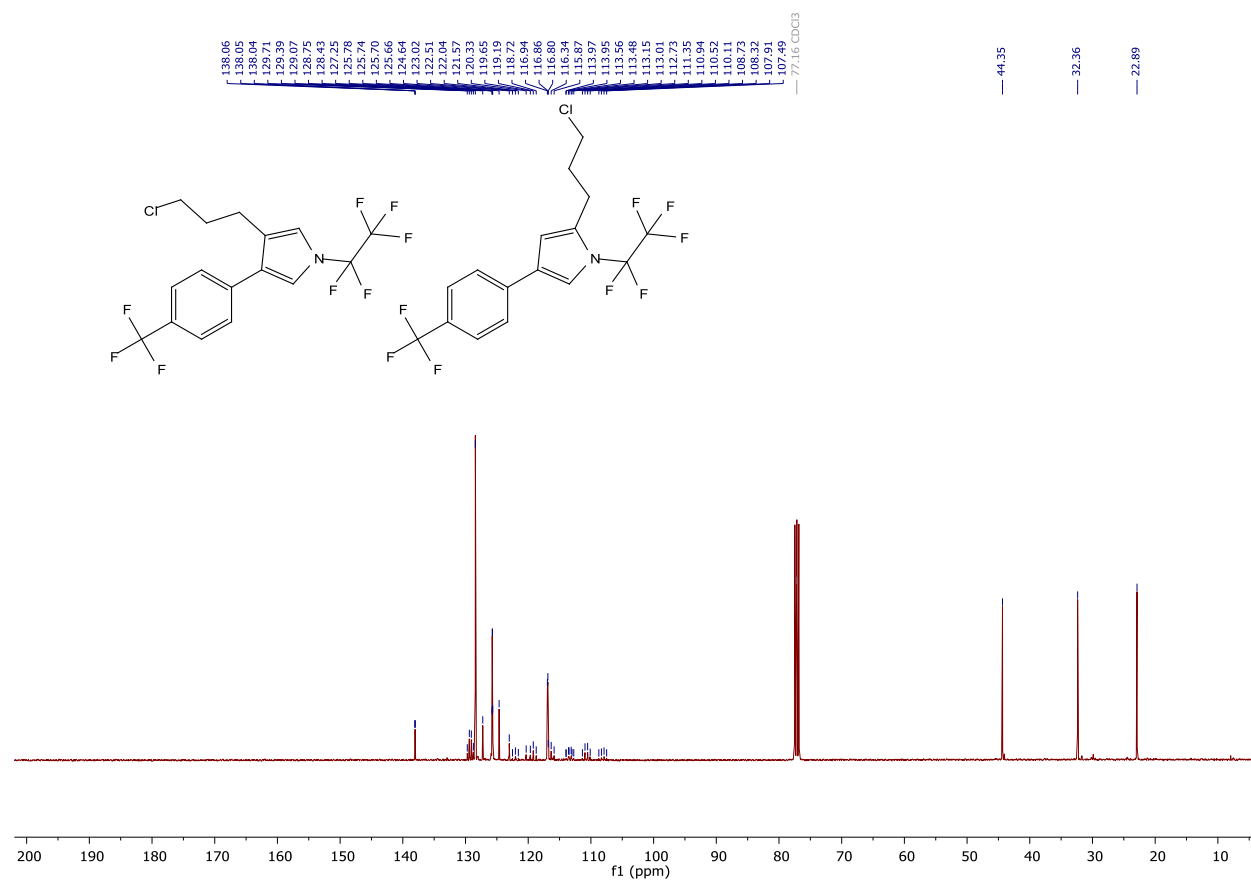
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3p** + **3p'**



$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **3q** + **3q'**



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3q** + **3q'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3q** + **3q'**



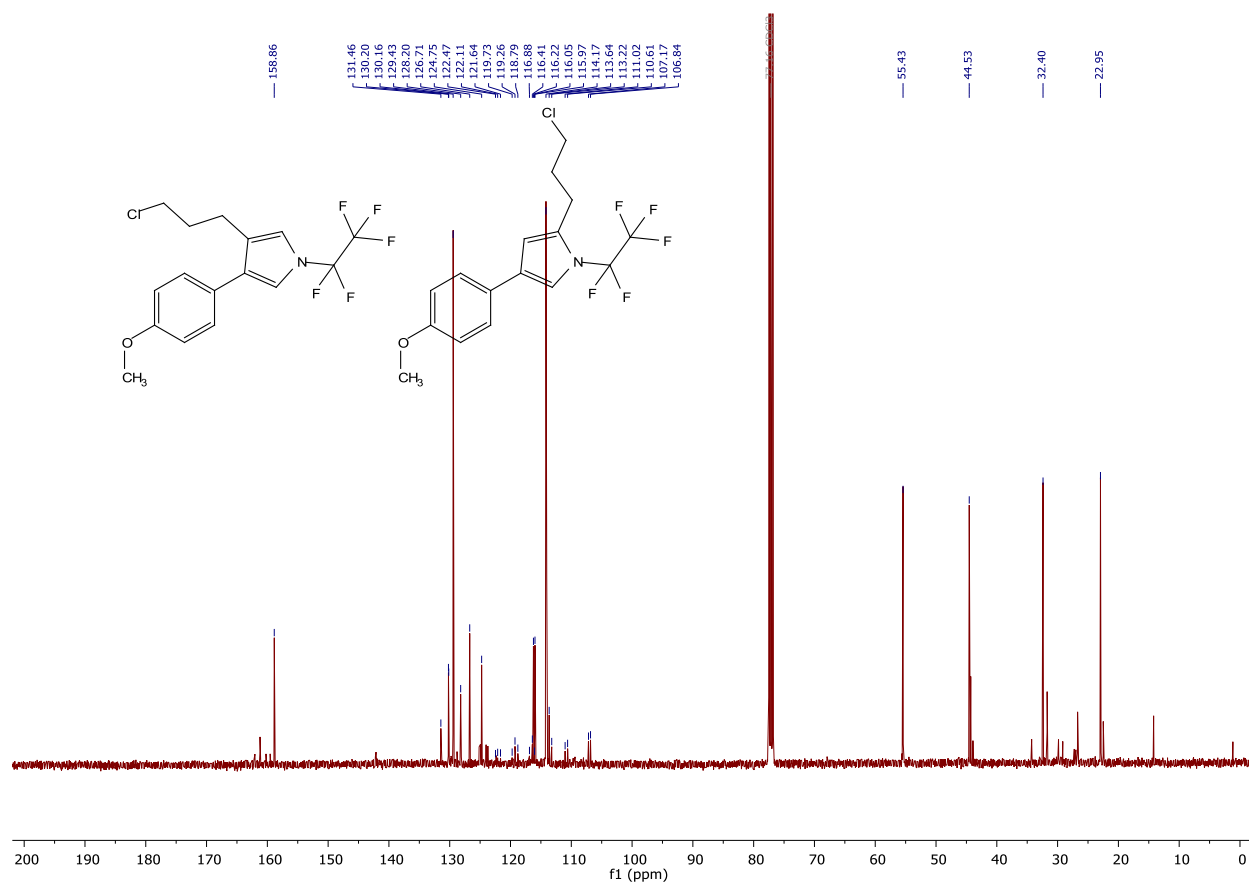


Chemical structure of compound 10: COc1ccc(cc1)-c2ccn(c2)C(F)(F)F

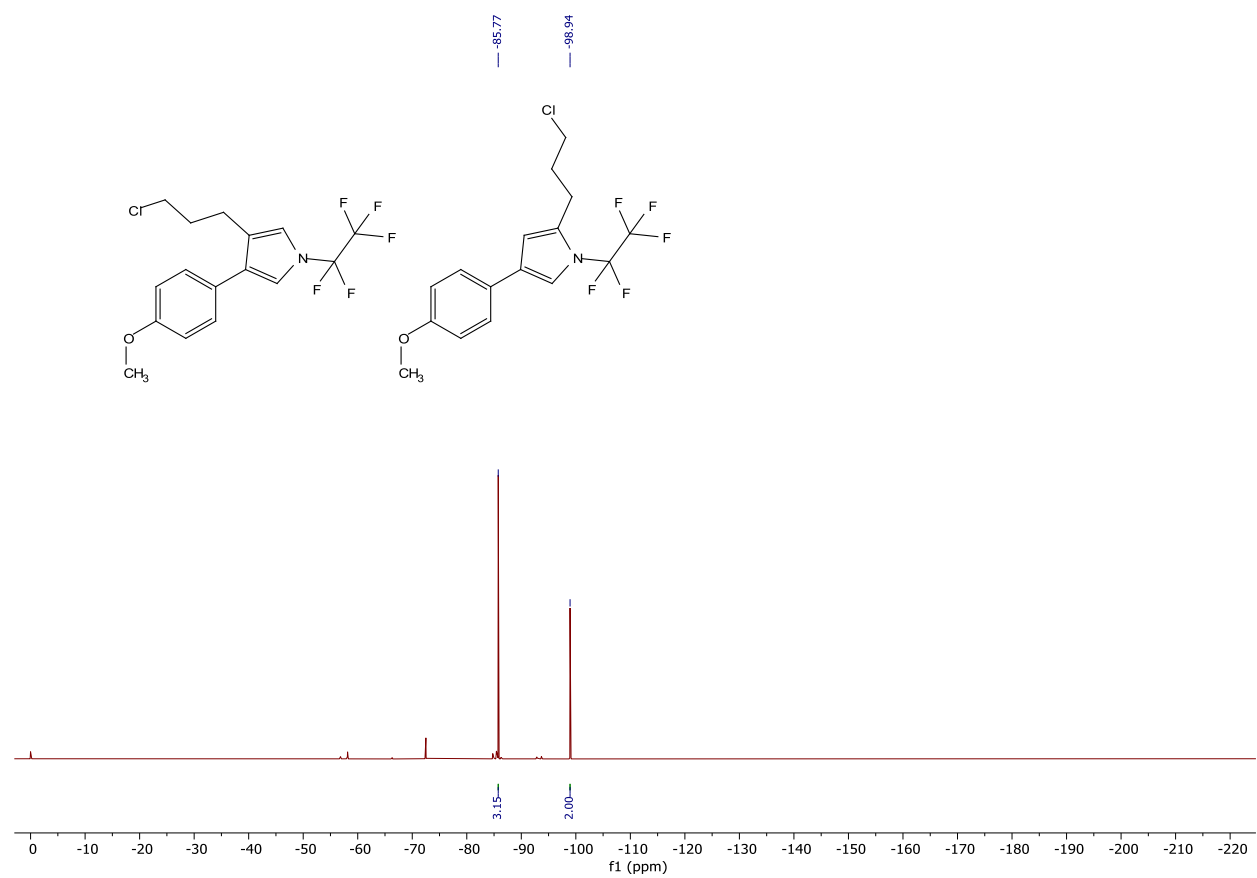
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10. The spectrum shows peaks from 0 to 8 ppm. The chemical structure of compound 10 is shown above the spectrum.

Peak positions (ppm): 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25, 1.24, 1.23,

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3r** + **3r'**



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **3r** + **3r'**

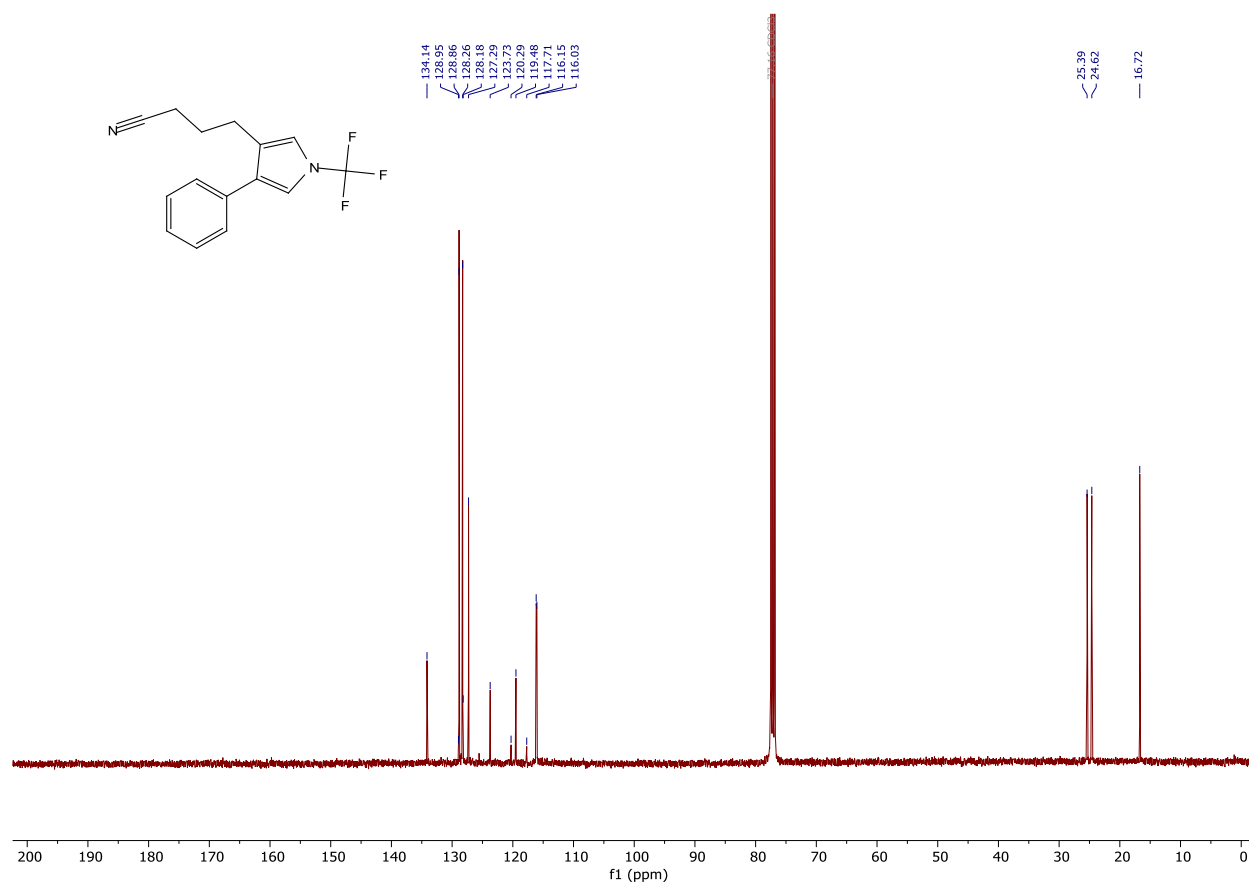


Chemical structure: N#CCCC1=C(C2=CC=CC=C2)N(C1)C(F)(F)F

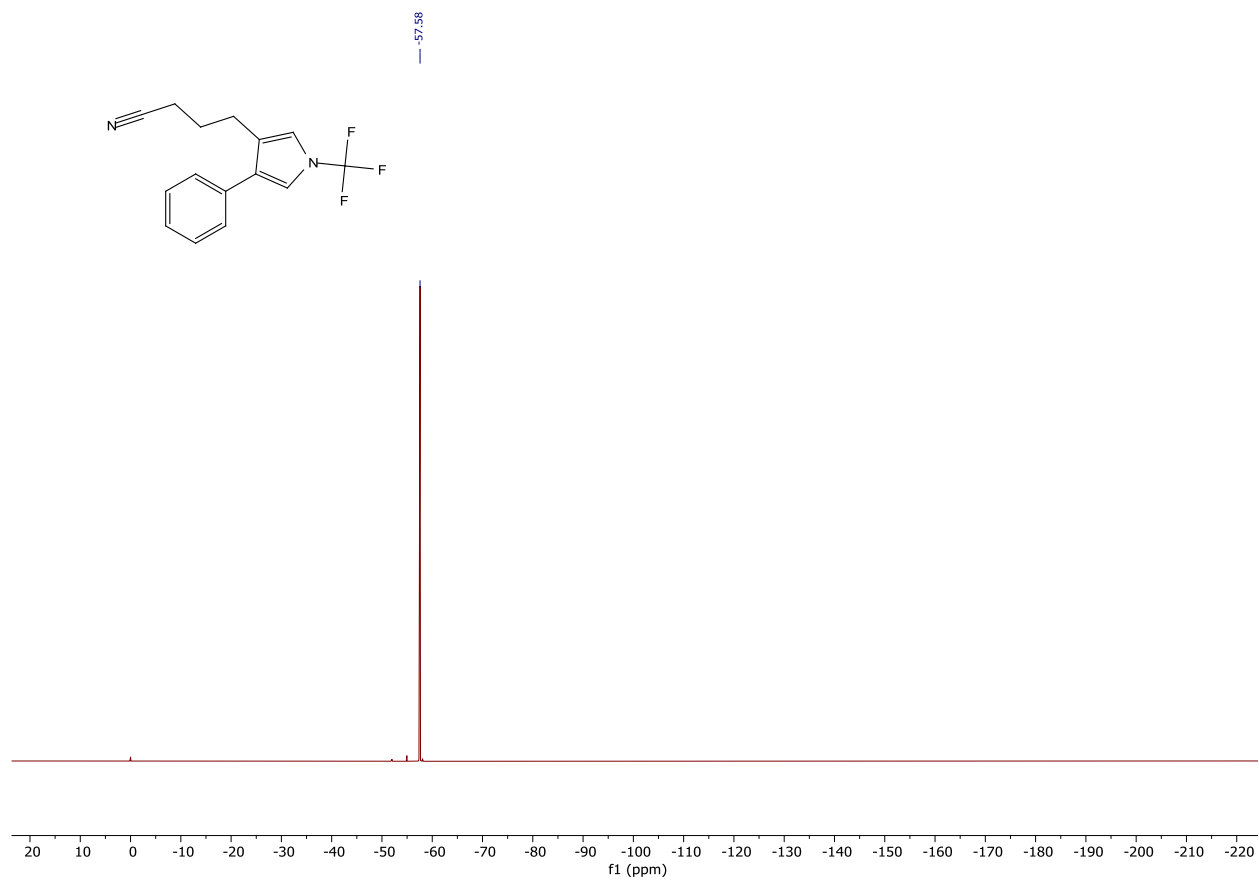
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing peaks from 0.0 to 12.0 ppm. The spectrum includes aromatic and nitrile protons (6.8-7.5 ppm), the CDCl<sub>3</sub> solvent triplet (7.26 ppm), and aliphatic protons from the 2,2,2-trifluoroethyl and 2-cyanoethyl groups (1.7-2.8 ppm). Integration values are provided below the baseline.

| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 7.42                 | 5.47        |
| 7.34                 | 1.01        |
| 7.32                 | 1.00        |
| 7.26                 |             |
| 2.77                 | 2.17        |
| 2.30                 | 2.19        |
| 2.26                 | 2.18        |
| 1.77                 |             |

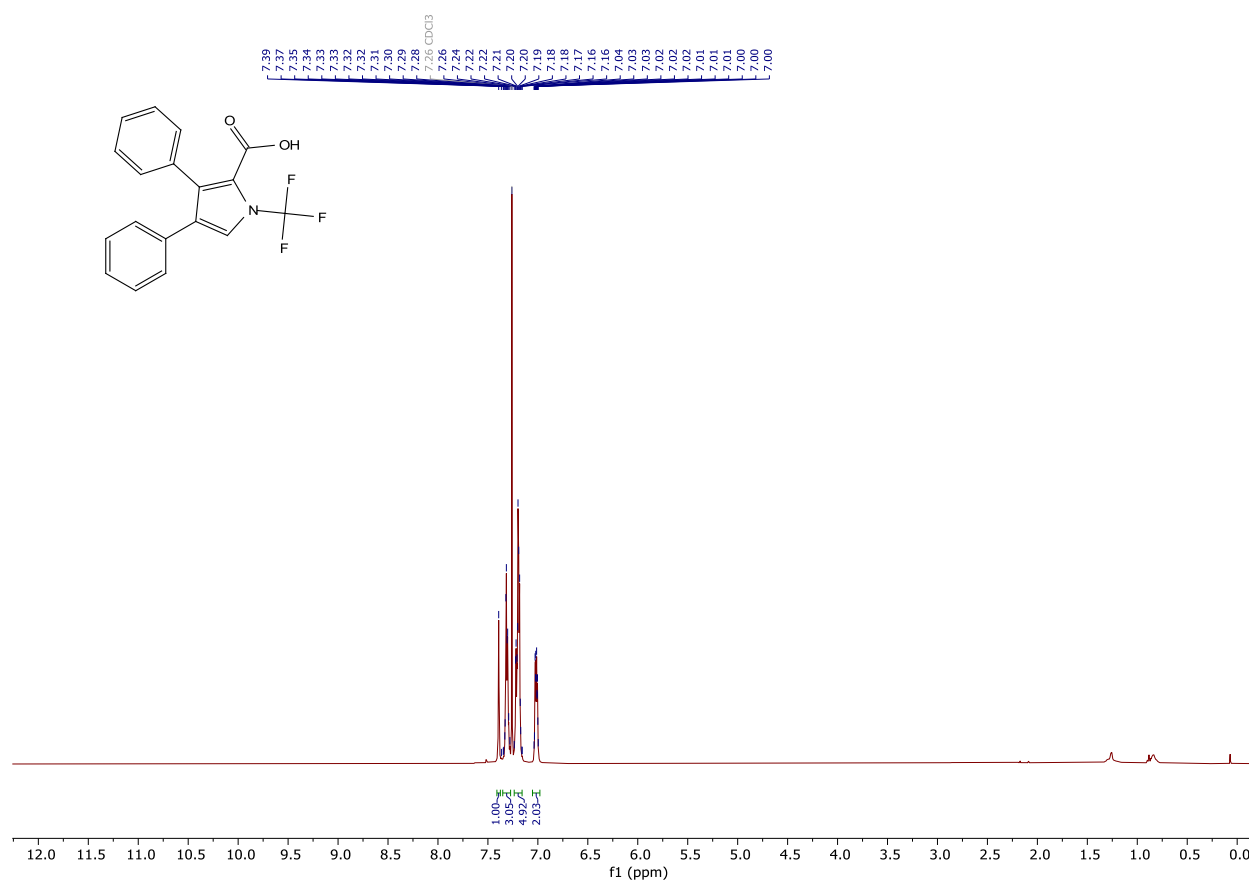
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **4**



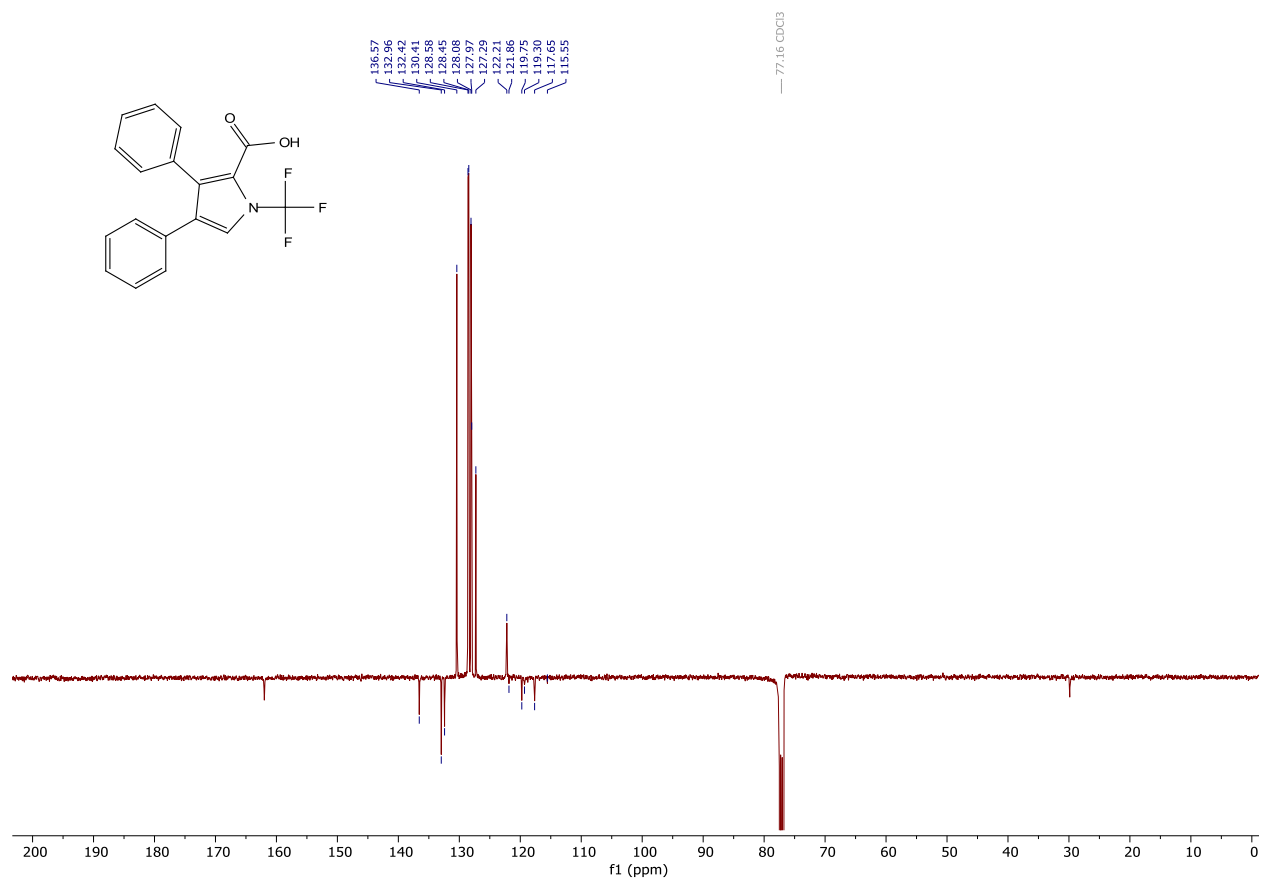
$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **4**



$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ) of **6**



$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of **6**





$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) of **6**

