

## Supporting Information for:

### **Photoinduced tandem radical cyclization/heteroarylation of *N*-allylbromodifluoroacetamides with quinoxalin-2(1*H*)-ones or coumarins under metal- and photocatalyst-free conditions**

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## 1. General Information

Flash column chromatography was performed using silica gel from Qingdao Haiyang. Anhydrous solvents [tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), benzotrifluoride ( $\text{PhCF}_3$ ), ethyl acetate ( $\text{EtOAc}$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ), methanol ( $\text{CH}_3\text{OH}$ ), dichloromethane (DCM), methylsulfoxide (DMSO), *N*-Methyl-2-pyrrolidone (NMP), and 1,4-dioxane] were purchased from Adamas, Energy Chemicals, or Innochem, and used as received. All commercial reagents were purchased from Bidepharm, Energy Chemical, Aladdin, and Adamas of the highest purity grade.

## General Analytical Information

All new compounds were characterized by NMR spectroscopy, high-resolution mass spectroscopy, and melting point (if solids). NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer and were calibrated using TMS or residual deuterated solvent as an internal reference (Chloroform-*d*: 7.26 ppm for  $^1\text{H}$  NMR and 77.16 ppm for  $^{13}\text{C}$  NMR, DMSO-*d*<sub>6</sub>: 2.50 ppm for  $^1\text{H}$  NMR and 39.52 ppm for  $^{13}\text{C}$  NMR). Data were reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants (hertz), and integration. HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD MSMS. Melting points (Mp) were recorded on a MP450 melting point apparatus.

## Experimental Set-up

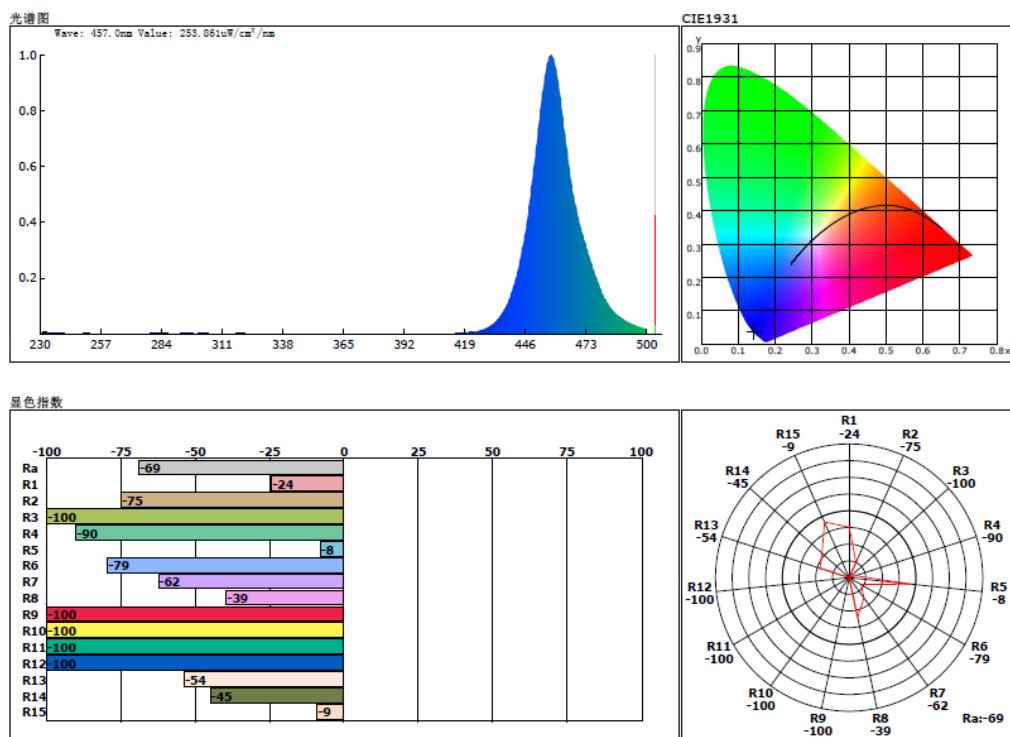


Figure S1 The emission spectra and spectral distribution of the blue LEDs

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### The Material of the Irradiation Vessel

Manufacturer: GeAo Chemical

Model: 24 W, blue LEDs

Broadband source:  $\lambda = 450\text{-}460 \text{ nm}$  ( $\lambda_{\max} = 457 \text{ nm}$ )

Material of the irradiation vessel: borosilicate reaction tube

Distance from the light source to the irradiation vessel: 3.0 cm

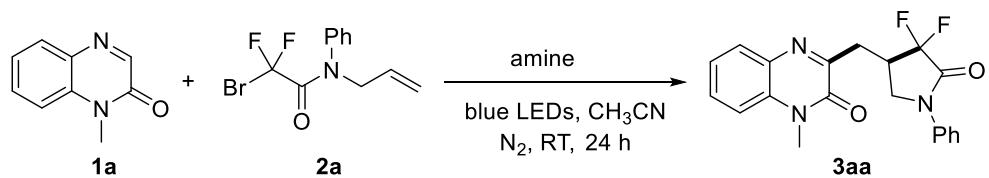
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**Figure S2** The set-up for the reaction

## 2. Reaction Optimization

**Table S1.** Effect of organoamines on this reaction<sup>[a]</sup>



Entry	Organooamine	Yield of <b>3aa</b> (%) <sup>[b]</sup>
1	DIPEA	33
2	TMEDA	28
3	HE	0
4	Et <sub>3</sub> N	33
5	Bn <sub>3</sub> N	31
6	DABCO	31
7	PMDETA	40

[a] Optimizations were performed on 0.1 mmol scale using **1a** (0.1 mmol, 1 equiv.), **2a** (1.5 equiv.), amine (2 equiv.), CH<sub>3</sub>CN (1 mL), and 24 W blue LEDs (460 nm) over a period of 24 h. [b] The yield was determined by crude <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S2.** Effect of the dosage of substrates and light source on this reaction<sup>[a]</sup>

Entry	Light source	1a (mmol)	2a (mmol)	Yield of 3aa (%) <sup>[b]</sup>
1	460 nm	0.1	0.1	20
2	460 nm	0.1	0.15	40
3	460 nm	0.15	0.1	34
4	460 nm	0.1	0.2	65
5	365 nm	0.1	0.2	0
6	400 nm	0.1	0.2	0
7	white LEDs	0.1	0.2	0

[a] Optimizations were performed in 1.0 mL CH<sub>3</sub>CN irradiated with light from 24 W LEDs at room temperature for 24 h. [b] The yield was determined by crude <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S3.** Effect of bases on this reaction<sup>[a]</sup>

Entry	Base	Yield of 3aa (%) <sup>[b]</sup>
1	CsF	55
2	K <sub>2</sub> CO <sub>3</sub>	61
3	Li <sub>2</sub> CO <sub>3</sub>	42
4	LiOtBu	55
5	Cs <sub>2</sub> CO <sub>3</sub>	88
6	K <sub>3</sub> PO <sub>4</sub>	66
7	LiOH	90
8	NaOH	49
9 <sup>[c]</sup>	LiOH	98

[a] Optimizations were performed on 0.1 mmol scale using 1a (0.1 mmol, 1 equiv.), 2a (2 equiv.), PMDETA (2 equiv.), base (1 equiv.), CH<sub>3</sub>CN (1 mL), and 24 W blue LEDs (460 nm) over a period of 24 h. [b] The yield was determined by crude <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as the internal standard. [c] 36 h.

**Table S4.** Effect of solvents on this reaction<sup>[a]</sup>

Entry	Solvent	Yield of 3aa (%) <sup>[b]</sup>
1	CH <sub>3</sub> CN	65
2	CH <sub>2</sub> Cl <sub>2</sub>	55
3	CH <sub>3</sub> Cl	40
4	CH <sub>3</sub> OH	40
5	CH <sub>3</sub> COCH <sub>3</sub>	40
6	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	40
7	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	40
8	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	40
9 <sup>[c]</sup>	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	40

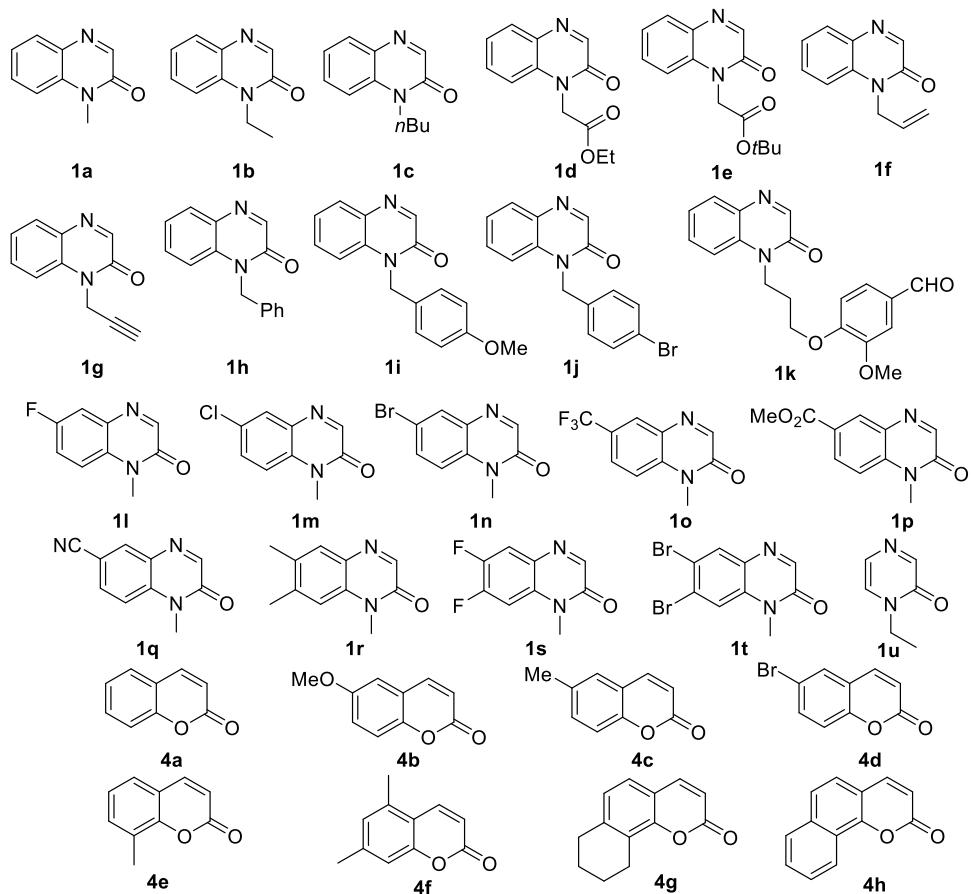
Entry	Solvent	Yield of <b>3aa</b> (%) <sup>[b]</sup>
1	THF	20
2	EtOAc	22
3	DCM	24
4	DMF	69
5	DMSO	90
6	PhCF <sub>3</sub>	61
7	PhCH <sub>3</sub>	37
8	CH <sub>3</sub> CN	90
9	NMP	trace
10	1,4-dioxane	35

[a] Optimizations were performed on 0.1 mmol scale using **1a** (0.1 mmol, 1 equiv.), **2a** (2 equiv.), PMDETA (2 equiv.), LiOH (1 equiv.), solvent (1 mL), and 24 W blue LEDs (460 nm) over a period of 24 h. [b] The yield was determined by crude <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

### 3. Product Synthesis and Characterization

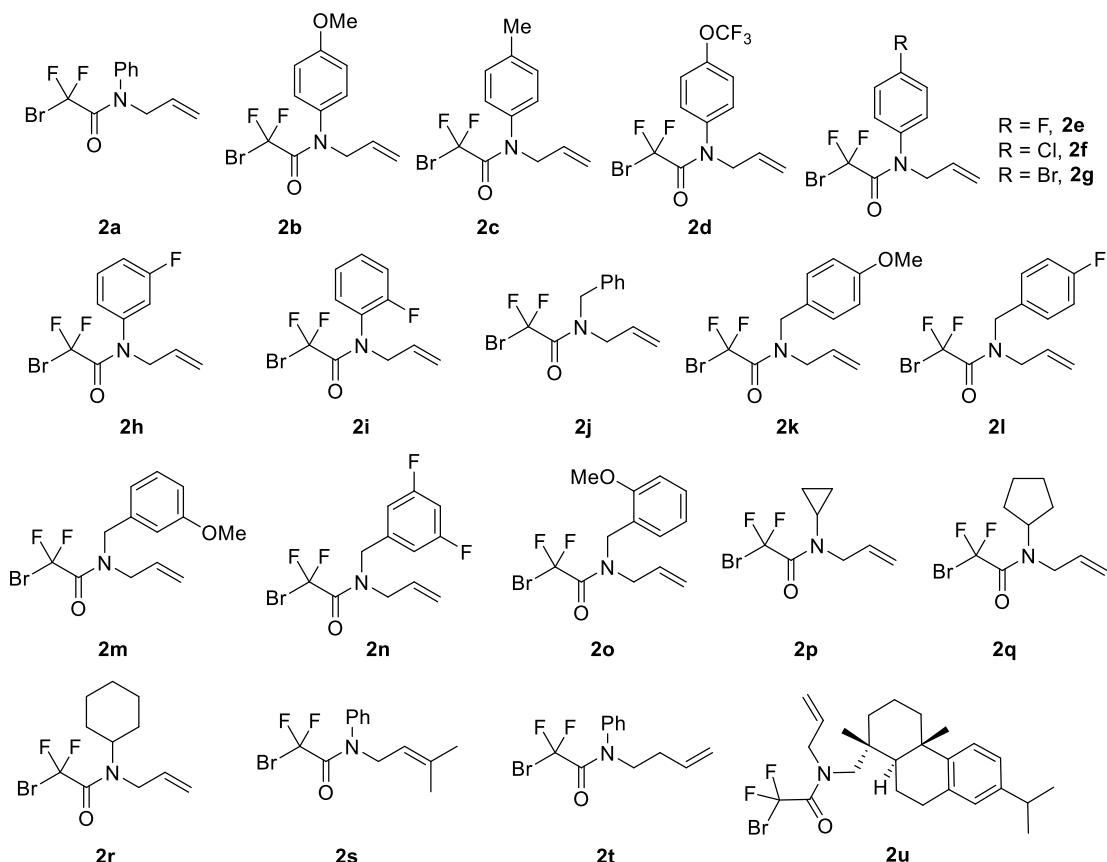
#### 3.1 List of Substrates

##### *List of quinoxalin-2(1*H*)-ones and coumarins*



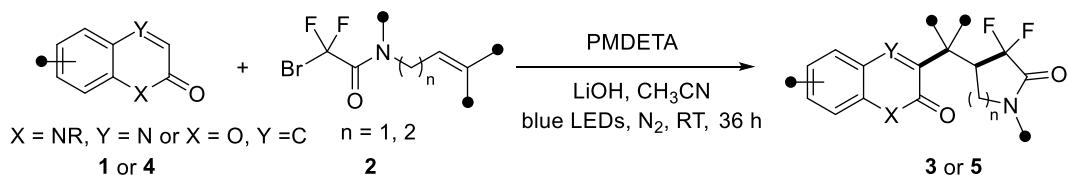
All the quinoxalin-2(1*H*)-ones and coumarins were synthesized according to the reported procedure.<sup>1,2</sup>

*List of N-allylbromodifluoroacetamides*



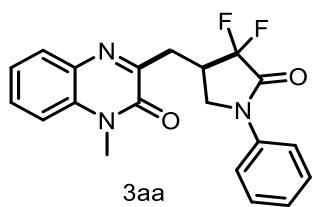
All the *N*-allylbromodifluoroacetamides were synthesized according to the reported procedure.<sup>3</sup>

### 3.2 General procedure for the visible-light-promoted tandem radical cyclization/heteroarylation of bromodifluoroacetamides

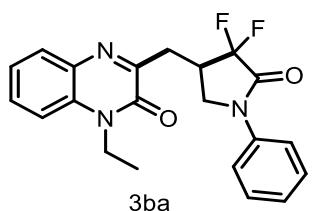


#### General Procedure:

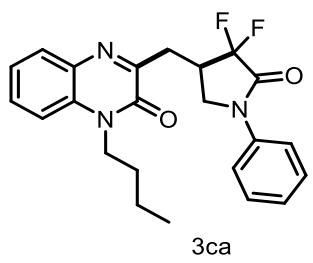
To an oven-dried quartz vial, quinoxalin-2(1*H*)-one **1** (0.1 mmol, 1.0 equiv.) or coumarin **4** (0.1 mmol, 1.0 equiv.) and LiOH (0.1 mmol, 1.0 equiv.) were added sequentially. The vial was charged with a stir bar and transferred to a glovebox, where the solids were backfilled with an inert atmosphere. In the glovebox, *N*-allylbromodifluoroacetamide **2** (0.2 mmol, 2.0 equiv.) and PMDETA (0.2 mmol, 2.0 equiv.) were added into the vial, followed by CH<sub>3</sub>CN (1.0 mL). The vial was sealed with a rubber plug, removed from the glove box, and irradiated and stir by 24 W 460 nm LEDs at room temperature for 36 h. After removal of solvents, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the pure products **3aa-3ua**, **3ab-3au**, **5aa-5ha**.



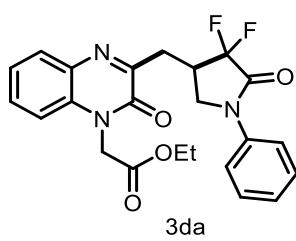
**3-((4,4-Difluoro-1-(4-fluorophenyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3aa).**<sup>3</sup> General Procedure was used to prepare the desired product **3aa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **3aa** as a pale yellow solid (37.2 mg, 0.096 mmol, 96%); **Mp:** 196–198 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.75 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.51 (dd, *J* = 8.6, 7.4 Hz, 1H), 7.34 – 7.26 (m, 4H), 7.18 – 7.12 (m, 1H), 4.17 (dd, *J* = 9.5, 7.8 Hz, 1H), 3.65 (s, 3H), 3.62 – 3.53 (m, 1H), 3.50 – 3.37 (m, 2H), 3.24 – 3.14 (m, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.9 – 161.6 (m), 156.4, 154.6, 138.1, 133.2, 132.3, 130.4, 129.9, 129.1, 126.1, 123.9, 120.0, 117.7 (dd, *J* = 253.7, 250.3 Hz), 113.8, 48.9 (d, *J* = 6.1 Hz), 36.8 (dd, *J* = 22.0, 19.9 Hz), 30.1 (d, *J* = 7.4 Hz), 29.2. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.31 (dd, *J* = 268.6, 14.3 Hz), -116.45 (dd, *J* = 267.4, 17.8 Hz). **HRMS (DART-TOF)** calculated for C<sub>20</sub>H<sub>17</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 388.1267, found 388.1267.



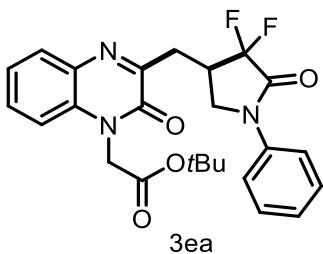
**3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-ethylquinoxalin-2(1H)-one (3ba).** General Procedure was used to prepare the desired product **3ba**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **3ba** as a pale yellow solid (30.0 mg, 0.078 mmol, 78%); **Mp:** 184–185 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.74 – 7.51 (m, 3H), 7.45 – 7.30 (m, 4H), 7.30 – 7.18 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.26 (dd, *J* = 9.9, 7.7 Hz, 1H), 3.67 (dd, *J* = 9.5, 7.2 Hz, 1H), 3.62 – 3.39 (m, 2H), 3.33 – 3.17 (m, 1H), 1.40 (t, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.7 – 162.1 (m), 156.5, 154.1, 138.1, 132.7, 132.1, 130.4, 130.2, 129.1, 126.1, 123.7, 120.0, 117.8 (dd, *J* = 253.8, 250.3 Hz), 113.6, 49.0 (d, *J* = 6.1 Hz), 37.4, 36.9 (dd, *J* = 22.1, 19.9 Hz), 30.0 (d, *J* = 7.4 Hz), 12.4. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -102.74 – -111.69 (m), -116.46 (dd, *J* = 267.3, 17.8 Hz). **HRMS (DART-TOF)** calculated for C<sub>21</sub>H<sub>20</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 384.1518, found 384.1523.



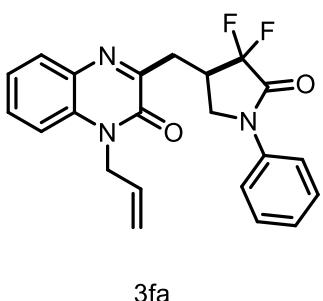
**1-Butyl-3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)quinoxalin-2(1H)-one (3ca).** General Procedure was used to prepare the desired product **3ca**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ca** as a pale yellow solid (33.0 mg, 0.08 mmol, 80%); **Mp:** 197–198 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.83 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.62 – 7.50 (m, 1H), 7.48 – 7.31 (m, 4H), 7.24 (dd, *J* = 12.7, 5.5 Hz, 1H), 4.26 (q, *J* = 9.3, 8.4 Hz, 3H), 3.67 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.62 – 3.43 (m, 2H), 3.36 – 3.13 (m, 1H), 1.83 – 1.68 (m, 2H), 1.51 (p, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 163.3 – 161.0 (m), 156.5, 154.4, 138.1, 132.6, 132.4, 130.3, 130.2, 129.1, 126.1, 123.6, 120.0, 120.6 – 114.5 (m), 113.8, 49.0 (d, *J* = 6.1 Hz), 42.2, 36.9 (dd, *J* = 22.1, 19.9 Hz), 30.1 (d, *J* = 7.4 Hz), 29.3, 20.3, 13.8. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.40 (dd, *J* = 267.8, 14.2 Hz), -116.53 (dd, *J* = 267.4, 17.8 Hz). **HRMS (DART-TOF)** calculated for C<sub>23</sub>H<sub>23</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> m/z 434.1651, found 434.1653.



**Ethyl 2-(3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-2-oxoquinoxalin-1(2H)-yl)acetate (3da).**<sup>3</sup> General Procedure was used to prepare the desired product **3da**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3da** as an orange oil (34.0 mg, 0.077 mmol, 77%). **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.39 (dt, *J* = 15.5, 7.7 Hz, 3H), 7.26 – 7.19 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 5.15 – 4.92 (m, 2H), 4.27 (q, *J* = 7.3 Hz, 3H), 3.75 – 3.63 (m, 1H), 3.53 (td, *J* = 17.9, 15.5, 6.1 Hz, 2H), 3.28 (dd, *J* = 17.9, 10.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 166.9, 162.3 (t, *J* = 31.4 Hz), 156.3, 154.2, 138.1, 132.4, 132.3, 130.6, 130.3, 129.2, 126.1, 124.2, 120.0, 117.7 (dd, *J* = 254.2, 250.2 Hz), 113.2, 62.3, 48.9 (d, *J* = 6.1 Hz), 43.6, 37.9 – 35.7 (m), 30.0 (d, *J* = 7.4 Hz), 14.1. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.43 (dd, *J* = 268.0, 14.2 Hz), -116.44 (dd, *J* = 267.5, 18.0 Hz). **HRMS (DART-TOF)** calculated for C<sub>23</sub>H<sub>22</sub>F<sub>2</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 442.1573, found 442.1578.

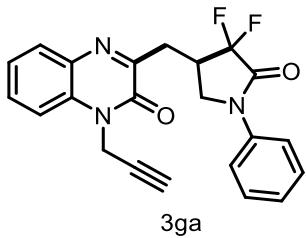


**Tert-butyl 2-(3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-2-oxoquinoxalin-1(2H)-yl)acetate (3ea).** General Procedure was used to prepare the desired product **3ea**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ea** as a pale yellow solid (37.0 mg, 0.079 mmol, 79%); **Mp:** 161–162 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.55 (dd, *J* = 8.5, 7.3, 1H), 7.45 – 7.33 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 4.96 (q, *J* = 17.2 Hz, 2H), 4.29 – 4.21 (m, 1H), 3.72 – 3.62 (m, 1H), 3.60 – 3.43 (m, 2H), 3.28 (dd, *J* = 17.7, 10.2 Hz, 1H), 1.48 (s, 9H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 165.9, 162.3 (t, *J* = 31.4 Hz), 156.3, 154.2, 138.1, 132.4, 130.5, 130.2, 129.1 (2C), 126.1, 124.1, 120.0, 117.7 (dd, *J* = 253.8, 250.0 Hz), 113.3, 83.5, 48.9 (d, *J* = 6.0 Hz), 44.2, 38.2 – 35.6 (m), 30.0 (d, *J* = 7.5 Hz), 28.0. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.46 (dd, *J* = 267.9, 14.1 Hz), -116.46 (dd, *J* = 267.4, 17.9 Hz). **HRMS (DART-TOF)** calculated for C<sub>25</sub>H<sub>25</sub>F<sub>2</sub>N<sub>3</sub>O<sub>4</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> m/z 492.1705, found 492.1708.

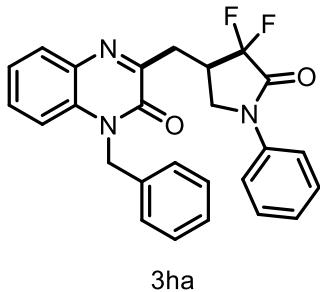


**1-Allyl-3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)quinoxalin-2(1H)-one (3fa).**<sup>3</sup> General Procedure was used to prepare the desired product **3fa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3fa** as a pale yellow solid (25.0 mg, 0.063 mmol, 63%); **Mp:** 185–187 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.44 – 7.31 (m, 4H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.00 – 5.88 (m, 1H), 5.35 – 5.13 (m, 2H), 4.93 (d, *J* = 5.0 Hz, 2H), 4.26 (t, *J* = 8.9 Hz, 1H), 3.68 (dd, *J* = 9.8, 7.1 Hz, 1H), 3.62 – 3.44 (m, 2H), 3.35 – 3.22 (m, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.4 (t, *J* = 31.3 Hz), 156.5, 154.2, 138.1, 132.5, 132.4, 130.4, 130.3, 130.0, 129.1, 126.1, 123.9, 120.0, 118.4, 117.7 (dd, *J* = 253.6, 250.3 Hz), 114.3, 49.0 (d, *J* =

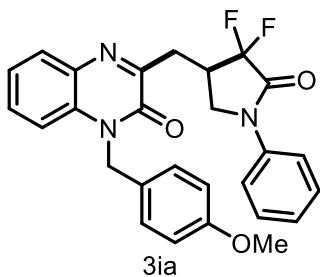
6.1 Hz), 44.6, 38.8 – 35.5 (m), 30.1 (d,  $J$  = 7.5 Hz).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  - 109.38 (dd,  $J$  = 268.3, 14.1 Hz), -116.48 (dd,  $J$  = 267.5, 17.8 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{20}\text{F}_2\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 396.1518, found 396.1525.



**3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3ga).** General Procedure was used to prepare the desired product **3ga**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ga** as an orange oil (30.0 mg, 0.076 mmol, 76%).  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.85 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.71 – 7.59 (m, 3H), 7.50 (d,  $J$  = 8.3 Hz, 1H), 7.40 (td,  $J$  = 7.6, 4.1 Hz, 3H), 7.27 – 7.20 (m, 1H), 5.17 – 4.96 (m, 2H), 4.26 (t,  $J$  = 8.9 Hz, 1H), 3.67 (dd,  $J$  = 9.9, 7.1 Hz, 1H), 3.62 – 3.41 (m, 2H), 3.27 (dd,  $J$  = 17.9, 10.1 Hz, 1H), 2.31 (d,  $J$  = 2.4 Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.3 (t,  $J$  = 31.3 Hz), 156.4, 153.6, 138.1, 132.5, 131.6, 130.5, 130.1, 129.2, 126.1, 124.3, 120.0, 117.7 (dd,  $J$  = 254.0, 250.3 Hz), 114.3, 76.5, 73.5, 48.9 (d,  $J$  = 6.0 Hz), 36.8 (dd,  $J$  = 22.0, 19.9 Hz), 31.6, 30.1 (d,  $J$  = 7.5 Hz).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.33 (dd,  $J$  = 267.9, 14.2 Hz), -116.41 (dd,  $J$  = 267.4, 17.9 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{18}\text{F}_2\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 394.1362, found 394.1366.

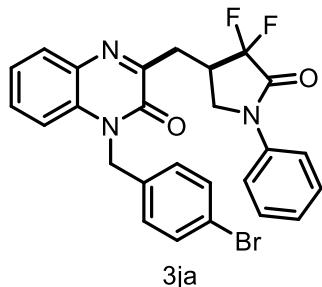


**1-Benzyl-3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)quinoxalin-2(1*H*)-one (3ha).**<sup>3</sup> General Procedure was used to prepare the desired product **3ha**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ha** as a pale yellow solid (36.0 mg, 0.081 mmol, 81%); **Mp:** 173–175 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.83 (dd,  $J$  = 7.9, 1.4 Hz, 1H), 7.67 (d,  $J$  = 8.2 Hz, 2H), 7.43 (dt,  $J$  = 18.2, 8.1 Hz, 4H), 7.33 – 7.22 (m, 7H), 5.52 (s, 2H), 4.29 (t,  $J$  = 8.8 Hz, 1H), 3.79 – 3.47 (m, 3H), 3.33 (dd,  $J$  = 17.6, 9.8 Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.7 – 162.1 (m), 156.6, 154.7, 138.1, 135.0, 132.6 (2C), 130.4, 130.1, 129.2, 129.0, 127.9, 126.9, 126.1, 123.9, 120.0, 117.7 (dd,  $J$  = 253.7, 250.3 Hz), 114.6, 49.0 (d,  $J$  = 6.1 Hz), 46.0, 37.1 – 36.7 (m), 30.2 (d,  $J$  = 7.4 Hz).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.34 (dd,  $J$  = 267.3, 14.2 Hz), -116.42 (dd,  $J$  = 267.6, 17.8 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{26}\text{H}_{22}\text{F}_2\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 446.1675, found 446.1681.



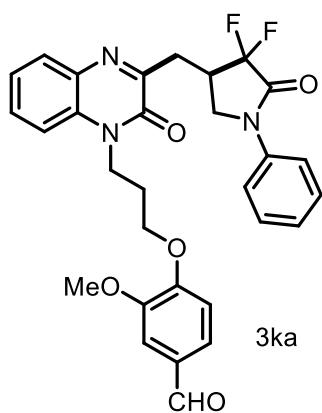
**3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-(4-methoxybenzyl)quinoxalin-2(1*H*)-one (3ia).** General Procedure was used to prepare the desired product **3ia**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3ia** as a pale yellow solid (36.0 mg, 0.076 mmol, 76%); **Mp:** 187–189 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.82 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.49 – 7.30 (m, 5H), 7.23 (dd,  $J$  = 13.5, 8.1 Hz, 3H), 6.89 – 6.79 (m, 2H), 5.44 (s, 2H), 4.37 – 4.16 (m, 1H), 3.76 (d,  $J$  = 1.2 Hz, 3H), 3.73 – 3.66 (m, 1H), 3.64 – 3.48 (m, 2H),

3.32 (dd,  $J = 17.7, 9.8$  Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.7 – 162.1 (m), 159.2, 156.6, 154.7, 138.1, 132.6, 132.5, 130.4, 130.1, 129.1, 128.5, 127.1, 126.1, 123.8, 120.0, 117.8 (dd,  $J = 253.3, 250.4$  Hz), 114.6, 114.4, 55.3, 49.0 (d,  $J = 6.1$  Hz), 45.5, 37.1 – 36.7 (m), 30.2 (d,  $J = 7.5$  Hz).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.33 (dd,  $J = 267.4, 14.2$  Hz), -116.42 (dd,  $J = 267.5, 17.8$  Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{27}\text{H}_{24}\text{F}_2\text{N}_3\text{O}_3^+ [\text{M}+\text{H}]^+$  m/z 476.1780, found 476.1787.



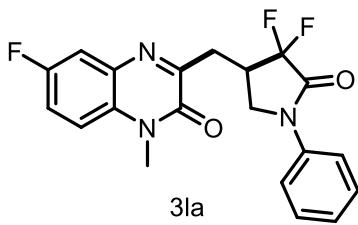
**1-(4-Bromobenzyl)-3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)quinoxalin-2(1*H*)-one (3ja).**

**General Procedure** was used to prepare the desired product **3ja**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3ja** as a pale yellow solid (43.0 mg, 0.082 mmol, 82%); **Mp:** 183–185 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.84 (d,  $J = 8.0$  Hz, 1H), 7.67 (d,  $J = 8.1$  Hz, 2H), 7.45 (dt,  $J = 16.5, 8.1$  Hz, 5H), 7.34 (t,  $J = 7.6$  Hz, 1H), 7.27 – 7.22 (m, 2H), 7.13 (d,  $J = 8.1$  Hz, 2H), 5.45 (s, 2H), 4.29 (t,  $J = 8.8$  Hz, 1H), 3.70 (t,  $J = 8.5$  Hz, 1H), 3.66 – 3.47 (m, 2H), 3.32 (dd,  $J = 17.8, 9.8$  Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.7 – 161.9 (m), 156.6, 154.6, 138.1, 134.0, 132.6, 132.3, 132.2, 130.5, 130.2, 129.2, 128.7, 126.1, 124.1, 121.9, 120.0, 121.2 – 115.9 (m), 114.3, 49.0 (d,  $J = 6.1$  Hz), 45.5, 37.1 – 36.6 (m), 30.2 (d,  $J = 7.4$  Hz).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.27 (dd,  $J = 267.6, 14.3$  Hz), -116.39 (dd,  $J = 267.5, 17.8$  Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{26}\text{H}_{21}\text{BrF}_2\text{N}_3\text{O}_2^+ [\text{M}+\text{H}]^+$  m/z 524.0780, found 524.0799.

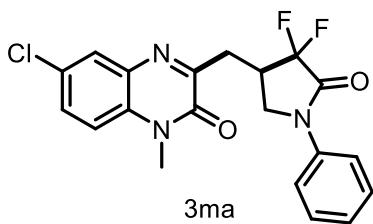


**2-(3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-2-oxoquinoxalin-1(2*H*)-yl)propoxy)-5-methoxybenzaldehyde (3ka).**

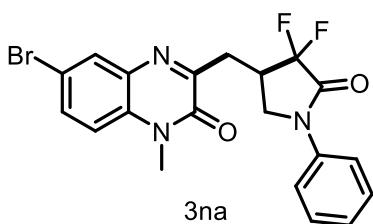
**General Procedure** was used to prepare the desired product **3ka**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3ka** as a pale yellow solid (10.0 mg, 0.018 mmol, 18%); **Mp:** 165–166 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  9.75 (s, 1H), 7.86 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.74 (dd,  $J = 8.3, 1.4$  Hz, 1H), 7.61 – 7.53 (m, 3H), 7.48 (dd,  $J = 8.4, 7.0$  Hz, 1H), 7.38 – 7.28 (m, 4H), 7.18 – 7.13 (m, 1H), 6.94 (d,  $J = 8.2$  Hz, 1H), 4.78 – 4.63 (m, 2H), 4.28 (t,  $J = 6.1$  Hz, 2H), 4.23 – 4.15 (m, 1H), 3.81 (s, 3H), 3.59 (dd,  $J = 9.6, 7.0$  Hz, 1H), 3.55 – 3.41 (m, 2H), 3.17 – 3.07 (m, 1H), 2.41 (p,  $J = 6.2$  Hz, 2H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  190.8, 162.2 (t,  $J = 29.5$  Hz), 155.5, 153.8, 150.0, 146.1, 139.9, 138.3, 138.1, 130.4, 129.7, 129.2, 128.4, 126.9, 126.8, 126.7, 126.1, 120.0, 122.3 – 112.2 (m), 111.8, 109.5, 65.9, 63.5, 56.0, 49.0 (d,  $J = 5.7$  Hz), 37.0 (d,  $J = 20.8$  Hz), 29.0 (d,  $J = 7.5$  Hz), 28.6.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.09 (dd,  $J = 14.2, 2.4$  Hz), -116.50 (dd,  $J = 267.2, 17.7$  Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{30}\text{H}_{28}\text{F}_2\text{N}_3\text{O}_5^+ [\text{M}+\text{H}]^+$  m/z 548.1992, found 548.1996.



**3-(4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-7-fluoro-1-methylquinoxalin-2(1H)-one (3la).**<sup>3</sup> General Procedure was used to prepare the desired product 3la. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded 3la as a pale yellow solid (32.0 mg, 0.083 mmol, 83%); **Mp:** 190–191 °C. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.53 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.32 (td, *J* = 6.4, 5.8, 3.2 Hz, 2H), 7.27 – 7.20 (m, 1H), 4.24 (t, *J* = 8.8 Hz, 1H), 3.73 (s, 3H), 3.66 (t, *J* = 8.1 Hz, 1H), 3.61 – 3.42 (m, 2H), 3.27 (dd, *J* = 17.8, 9.8 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 163.1 – 161.1 (m), 158.8 (d, *J* = 244.5 Hz), 158.2, 154.3, 138.0, 132.9 (d, *J* = 11.3 Hz), 129.8 (d, *J* = 2.2 Hz), 129.2, 126.2, 120.0, 118.2 (d, *J* = 24.0 Hz), 117.6 (dd, *J* = 254.0, 250.5 Hz), 115.4 (d, *J* = 22.6 Hz), 114.9 (d, *J* = 8.8 Hz), 48.9 (d, *J* = 5.9 Hz), 36.8 (dd, *J* = 22.1, 20.0 Hz), 30.3 (d, *J* = 7.4 Hz), 29.5. **<sup>19</sup>F NMR** (376 MHz, Chloroform-*d*) δ -109.29 (dd, *J* = 267.5, 14.3 Hz), -116.42 (dd, *J* = 267.6, 17.7 Hz), -118.43 (td, *J* = 8.0, 5.1 Hz). **HRMS (DART-TOF)** calculated for C<sub>20</sub>H<sub>17</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 388.1267, found 388.1286.

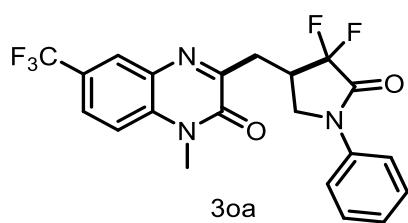


**7-Chloro-3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ma).**<sup>3</sup> General Procedure was used to prepare the desired product 3ma. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded 3ma as a pale yellow solid (34.0 mg, 0.084 mmol, 84%); **Mp:** 182–184 °C. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 2.4 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.46 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.20 – 7.11 (m, 2H), 4.17 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.63 (s, 3H), 3.58 (dd, *J* = 9.7, 7.2 Hz, 1H), 3.51 – 3.30 (m, 2H), 3.18 (dd, *J* = 17.8, 9.8 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 162.2 (t, *J* = 31.3 Hz), 158.0, 154.3, 138.0, 132.8, 131.9, 130.4, 129.2 (3C), 126.1, 120.0, 117.6 (dd, *J* = 253.8, 250.3 Hz), 115.0, 48.9 (d, *J* = 6.2 Hz), 36.8 (t, *J* = 21.1 Hz), 30.2 (d, *J* = 7.6 Hz), 29.4. **<sup>19</sup>F NMR** (376 MHz, Chloroform-*d*) δ -109.27 (dd, *J* = 267.3, 14.3 Hz), -116.34 (dd, *J* = 267.4, 17.6 Hz). **HRMS (DART-TOF)** calculated for C<sub>20</sub>H<sub>17</sub>ClF<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 404.0972, found 404.0989.



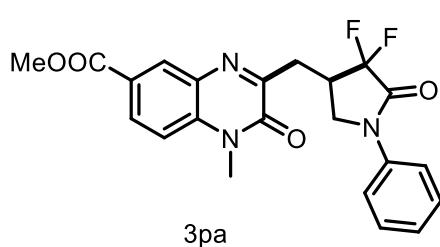
**7-bromo-3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3na).**<sup>3</sup> General Procedure was used to prepare the desired product 3na. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded 3na as a pale yellow solid (34.0 mg, 0.076 mmol, 76%); **Mp:** 170–172 °C. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.3 Hz, 1H), 7.58 (dd, *J* = 8.8, 4.8 Hz, 3H), 7.39 – 7.27 (m, 2H), 7.24 – 7.08 (m, 2H), 4.17 (dd, *J* = 9.7, 7.8 Hz, 1H), 3.62 (s, 3H), 3.57 (dd, *J* = 9.7, 7.1 Hz, 1H), 3.51 – 3.30 (m, 2H), 3.17 (dd, *J* = 17.8, 9.8 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 162.1 (m), 158.0, 154.3, 138.0, 133.2, 133.1, 132.3 (2C), 129.2, 126.1, 120.0, 116.4, 117.6 (dd, *J* = 253.8, 250.3 Hz), 115.3, 48.9 (d, *J* = 5.9 Hz), 36.8 (dd, *J* = 22.1, 19.9 Hz), 30.2 (d, *J* = 7.6 Hz), 29.3. **<sup>19</sup>F NMR** (376 MHz, Chloroform-*d*) δ -109.26 (dd,

*J* = 267.4, 14.2 Hz), -116.34 (dd, *J* = 267.4, 17.5 Hz). **HRMS (DART-TOF)** calculated for C<sub>20</sub>H<sub>17</sub>BrF<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 448.0467, found 448.0477.



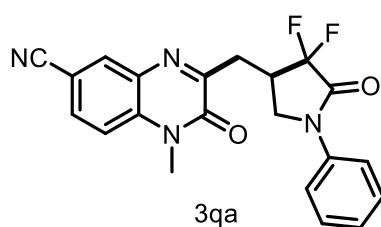
**3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-methyl-7-(trifluoromethyl)quinoxalin-2(1H)-one (3oa).**<sup>3</sup> **General Procedure** was used to prepare the desired product **3oa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3oa** as a pale yellow solid

(29.7 mg, 0.068 mmol, 68%); **Mp:** 192–193 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 8.15 – 8.09 (m, 1H), 7.81 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.49 – 7.38 (m, 3H), 7.26 – 7.22 (m, 1H), 4.27 (dd, *J* = 9.8, 7.9 Hz, 1H), 3.76 (s, 3H), 3.67 (dd, *J* = 9.6, 7.3 Hz, 1H), 3.62 – 3.43 (m, 2H), 3.28 (dd, *J* = 18.0, 9.7 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.2 (t, *J* = 32.7 Hz), 158.4, 154.4, 138.0, 135.5, 131.7, 129.2, 127.4 (q, *J* = 4.0 Hz), 126.7 (q, *J* = 3.7 Hz), 126.3 (q, *J* = 33.8 Hz), 126.2, 123.6 (q, *J* = 271.6 Hz), 120.1, 120.8 – 114.7 (m), 114.5, 48.9 (d, *J* = 5.9 Hz), 39.2 – 35.5 (m), 30.2 (d, *J* = 7.6 Hz), 29.5. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -62.00, -109.62, -116.77. **HRMS (DART-TOF)** calculated for C<sub>21</sub>H<sub>17</sub>F<sub>5</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 438.1235, found 438.1245.



**Methyl 2-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-4-methyl-3-oxo-3,4-dihydroquinoxaline-6-carboxylate (3pa).**<sup>3</sup> **General Procedure** was used to prepare the desired product **3pa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3pa** as a pale yellow solid (27.0 mg, 0.063 mmol, 63%);

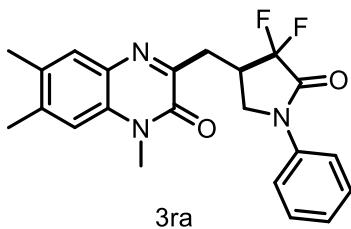
**Mp:** 215–216 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 8.50 (d, *J* = 1.9 Hz, 1H), 8.23 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.41 (q, *J* = 9.2, 8.5 Hz, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 4.30 (t, *J* = 8.9 Hz, 1H), 3.97 (s, 3H), 3.75 (s, 3H), 3.71 – 3.63 (m, 1H), 3.63 – 3.42 (m, 2H), 3.26 (dd, *J* = 18.0, 10.0 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 165.9, 162.2 (t, *J* = 31.4 Hz), 157.6, 154.5, 138.0, 136.4, 131.7 (2C), 131.1, 129.2, 126.2, 125.8, 120.1, 117.6 (dd, *J* = 254.0, 250.4 Hz), 113.9, 52.4, 49.0 (d, *J* = 6.0 Hz), 37.0 – 36.6 (m), 30.1 (d, *J* = 7.4 Hz), 29.5. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.40 (dd, *J* = 267.7, 14.1 Hz), -116.36 (dd, *J* = 267.5, 17.6 Hz). **HRMS (DART-TOF)** calculated for C<sub>22</sub>H<sub>20</sub>F<sub>2</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 428.1416, found 428.1442.



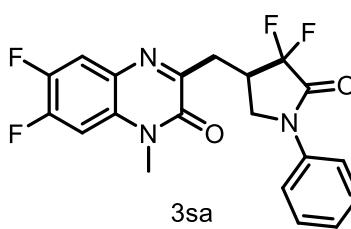
**2-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-4-methyl-3-oxo-3,4-dihydroquinoxaline-6-carbonitrile (3qa).**<sup>3</sup> **General Procedure** was used to prepare the desired product **3qa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3qa** as a pale yellow solid (19.0 mg, 0.045 mmol, 45%); **Mp:**

188–189 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.51 (m, 4H), 7.37 – 7.31 (m, 2H), 7.17 (d, *J* = 7.3 Hz, 1H), 4.17 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.66 (s, 3H),

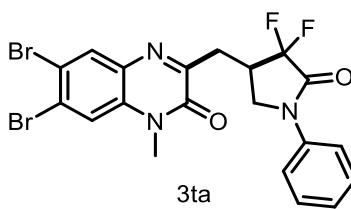
3.60 (dd,  $J = 9.4, 7.0$  Hz, 1H), 3.56 – 3.36 (m, 2H), 3.23 (dd,  $J = 17.9, 9.3$  Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.1 (t,  $J = 31.1$  Hz), 160.3, 154.0, 138.0, 134.3, 133.6, 130.9, 129.2, 126.7, 126.2, 120.0, 117.9, 117.8, 120.1 – 114.3 (m), 113.7, 48.8 (d,  $J = 5.9$  Hz), 36.9 – 36.5 (m), 30.5 (d,  $J = 7.6$  Hz), 29.4.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.02 (dd,  $J = 267.1, 14.1$  Hz), -116.36 (dd,  $J = 267.7, 16.8$  Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{21}\text{H}_{16}\text{F}_2\text{N}_4\text{O}_2\text{Na}^+$  [M+Na]<sup>+</sup> m/z 417.1134, found 417.1140.



**3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1,6,7-trimethylquinoxalin-2(1H)-one (3ra).**<sup>3</sup> **General Procedure** was used to prepare the desired product **3ra**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ra** as a pale yellow solid (31.0 mg, 0.078 mmol, 78%); **Mp:** 189–190 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.69 – 7.62 (m, 1H), 7.58 (s, 1H), 7.45 – 7.36 (m, 1H), 7.26 – 7.18 (m, 1H), 7.10 (s, 1H), 4.23 (dd,  $J = 9.5, 7.9$  Hz, 1H), 3.70 (s, 1H), 3.68 – 3.62 (m, 0H), 3.56 – 3.40 (m, 1H), 3.29 – 3.18 (m, 1H), 2.43 (s, 2H), 2.35 (s, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.7 – 162.1 (m), 155.0, 154.7, 140.3, 138.1, 132.8, 131.2, 130.8, 130.0, 129.1, 126.0, 120.0, 117.8 (dd,  $J = 253.7, 250.3$  Hz), 114.3, 49.0 (d,  $J = 6.1$  Hz), 37.0 (dd,  $J = 22.0, 19.9$  Hz), 30.0 (d,  $J = 7.4$  Hz), 29.1, 20.6, 19.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -106.08 – -114.03 (m), -116.55 (dd,  $J = 267.5, 17.6$  Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{22}\text{F}_2\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 398.1675, found 398.1688.

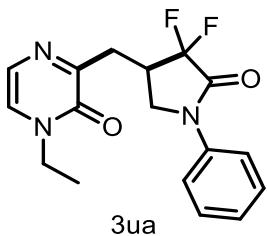


**3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-6,7-difluoro-1-methylquinoxalin-2(1H)-one (3sa).**<sup>3</sup> **General Procedure** was used to prepare the desired product **3sa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3sa** as a pale yellow solid (30.0 mg, 0.074 mmol, 74%); **Mp:** 192–194 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.71 – 7.58 (m, 3H), 7.44 – 7.36 (m, 2H), 7.28 – 7.20 (m, 1H), 7.15 (dd,  $J = 11.2, 7.0$  Hz, 1H), 4.21 (dd,  $J = 9.6, 7.8$  Hz, 1H), 3.68 (s, 3H), 3.66 – 3.60 (m, 1H), 3.57 – 3.35 (m, 2H), 3.23 (dd,  $J = 17.7, 9.5$  Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.2 (t,  $J = 31.2$  Hz), 157.1 (d,  $J = 3.5$  Hz), 154.2, 151.5 (dd,  $J = 254.1, 14.4$  Hz), 146.8 (dd,  $J = 247.8, 14.1$  Hz), 138.0, 130.6 – 130.0 (m), 129.2, 128.9 – 128.0 (m), 126.2, 120.6 – 114.4 (m), 120.0, 117.6 (dd,  $J = 18.0, 2.4$  Hz), 102.5 (d,  $J = 23.1$  Hz), 48.8 (d,  $J = 6.1$  Hz), 36.7 (dd,  $J = 22.0, 19.9$  Hz), 30.1 (d,  $J = 7.6$  Hz), 29.7.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.13 (dd,  $J = 267.7, 14.3$  Hz), -116.43 (dd,  $J = 267.5, 17.5$  Hz), -130.09 (ddd,  $J = 22.4, 11.2, 8.0$  Hz), -141.51 (dd,  $J = 22.3, 10.1, 6.9$  Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{20}\text{H}_{16}\text{F}_4\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 406.1173, found 406.1187.

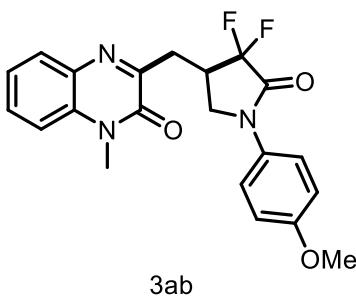


**6,7-Dibromo-3-((4,4-difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ta).** **General Procedure** was used to prepare the desired product **3ta**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ta** as a pale yellow

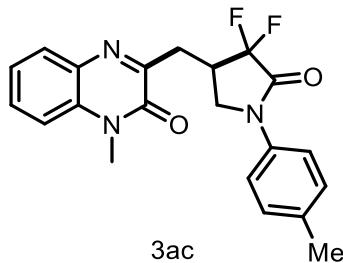
solid (23.0 mg, 0.044 mmol, 44%); **Mp:** 193–194 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 8.07 (d, *J* = 1.3 Hz, 1H), 7.69 – 7.58 (m, 4H), 7.47 – 7.36 (m, 3H), 7.31 – 7.18 (m, 2H), 4.27 – 4.18 (m, 1H), 3.73 – 3.57 (m, 5H), 3.57 – 3.36 (m, 2H), 3.23 (dd, *J* = 18.0, 9.7 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.4 – 161.6 (m), 158.3, 154.0, 138.0, 133.8, 133.1, 132.0, 129.2, 126.8, 126.2, 120.0, 119.1, 121.0 – 116.4 (m), 118.5, 48.9 (d, *J* = 6.0 Hz), 36.9 – 36.5 (m), 30.3 (d, *J* = 7.5 Hz), 29.4. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.23 (dd, *J* = 267.5, 14.0 Hz), -116.37 (dd, *J* = 267.6, 17.4 Hz). **HRMS (DART-TOF)** calculated for C<sub>20</sub>H<sub>16</sub>Br<sub>2</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 527.9551, found 527.9565.



**3-((4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)methyl)-1-ethylpyrazin-2(1H)-one (3ua).** General Procedure was used to prepare the desired product **3ua**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ua** as a brown oil (23.0 mg, 0.068 mmol, 68%). **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.62 – 7.52 (m, 2H), 7.37 – 7.29 (m, 2H), 7.23 – 7.11 (m, 2H), 7.03 (d, *J* = 4.4 Hz, 1H), 4.09 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 3.54 (dd, *J* = 9.8, 7.1 Hz, 1H), 3.42 – 3.17 (m, 2H), 3.05 (dd, *J* = 17.4, 10.1 Hz, 1H), 1.32 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 163.3 – 161.2 (m), 156.4, 155.5, 138.1, 129.1, 127.3, 126.1, 122.6, 120.0, 117.7 (dd, *J* = 253.7, 250.3 Hz), 48.9 (d, *J* = 6.0 Hz), 44.8, 37.0 (dd, *J* = 21.9, 20.0 Hz), 29.5 (d, *J* = 7.3 Hz), 14.0. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.70 (dd, *J* = 267.8, 14.2 Hz), -116.80 (dd, *J* = 267.3, 17.9 Hz). **HRMS (DART-TOF)** calculated for C<sub>17</sub>H<sub>18</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 334.1362, found 334.1374.

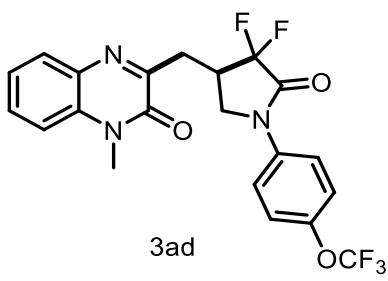


**3-((4,4-Difluoro-1-(4-methoxyphenyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ab).** General Procedure was used to prepare the desired product **3ab**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3ab** as a pale yellow solid (8.0 mg, 0.02 mmol, 20%); **Mp:** 183–184 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.83 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.42 – 7.31 (m, 2H), 6.96 – 6.87 (m, 2H), 4.19 (t, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.70 – 3.59 (m, 1H), 3.59 – 3.44 (m, 2H), 3.33 – 3.19 (m, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.2 (t, *J* = 31.2 Hz), 157.6, 156.6, 154.7, 133.2, 132.4, 131.2, 130.4, 130.0, 123.9, 121.8, 116.6 (dd, *J* = 253.4, 2.4 Hz), 114.3, 113.8, 55.5, 49.3 (d, *J* = 6.1 Hz), 37.5 – 35.8 (m), 30.2 (d, *J* = 7.6 Hz), 29.2. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.11 (dd, *J* = 268.0, 14.4 Hz), -116.28 (dd, *J* = 267.4, 17.5 Hz). **HRMS (DART-TOF)** calculated for C<sub>21</sub>H<sub>20</sub>F<sub>2</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 400.1467, found 400.1478.



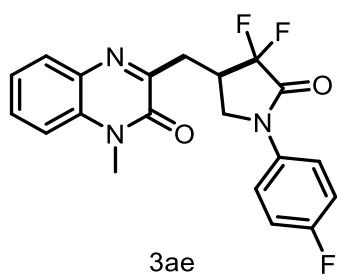
**3-((4,4-Difluoro-5-oxo-1-(p-tolyl)pyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ac).** General Procedure was used to prepare the desired product **3ac**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3ac** as a brown oil (3.8 mg, 0.01 mmol, 10%). **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.83 (dd, *J* = 8.0,

1.5 Hz, 1H), 7.59 (dd,  $J$  = 8.6, 7.3 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.40 – 7.32 (m, 2H), 7.20 (d,  $J$  = 8.2 Hz, 2H), 4.22 (dd,  $J$  = 9.6, 7.8 Hz, 1H), 3.73 (s, 3H), 3.64 (dd,  $J$  = 10.0, 7.1 Hz, 1H), 3.59 – 3.43 (m, 2H), 3.33 – 3.21 (m, 1H), 2.34 (s, 3H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.4 – 160.8 (m), 156.5, 154.6, 136.0, 135.6, 133.2, 132.4, 130.4, 129.9, 129.7, 123.9, 120.0, 117.8 (dd,  $J$  = 253.5, 250.3 Hz), 113.8, 49.0 (d,  $J$  = 6.0 Hz), 37.5 – 36.2 (m), 30.2 (d,  $J$  = 7.4 Hz), 29.2, 21.0.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.26 (dd,  $J$  = 267.7, 14.2 Hz), -116.34 (dd,  $J$  = 267.3, 17.8 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{21}\text{H}_{20}\text{F}_2\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 384.1518, found 384.1520.

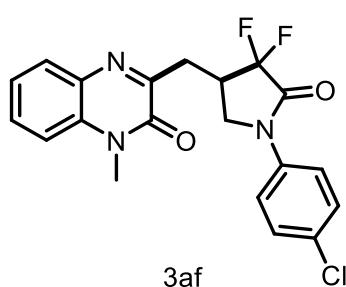


**3-((4,4-Difluoro-5-oxo-1-(4-(trifluoromethoxy)phenyl)pyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1*H*)-one (3ad).** General Procedure was used to prepare the desired product **3ad**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3ad** as a pale yellow solid (32.2 mg, 0.071 mmol, 71%); **Mp:** 189–190 °C.

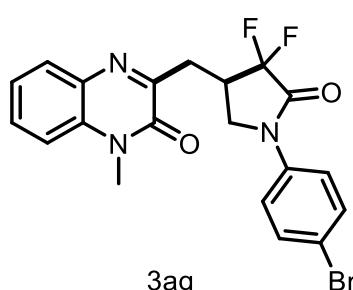
**$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.83 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.60 (dd,  $J$  = 8.6, 7.4 Hz, 1H), 7.43 – 7.32 (m, 2H), 7.30 – 7.20 (m, 2H), 4.32 – 4.18 (m, 1H), 3.73 (s, 3H), 3.67 (dd,  $J$  = 9.3, 7.2 Hz, 1H), 3.59 – 3.42 (m, 2H), 3.36 – 3.16 (m, 1H).  **$^{13}\text{C}\{\text{H}\}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.9 – 160.7 (m), 156.3, 154.6, 146.5 (q,  $J$  = 1.9 Hz), 136.6, 133.2, 132.3, 130.5, 129.9, 123.9, 121.8, 121.2, 120.4 (q,  $J$  = 257.5 Hz), 117.5 (dd,  $J$  = 254.0, 250.4 Hz), 113.8, 48.9 (d,  $J$  = 6.1 Hz), 36.8 (dd,  $J$  = 22.1, 20.0 Hz), 30.1 (d,  $J$  = 7.3 Hz), 29.2.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -58.06, -109.47 (dd,  $J$  = 268.5, 14.1 Hz), -116.36 (dd,  $J$  = 268.1, 17.6 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{21}\text{H}_{17}\text{F}_5\text{N}_3\text{O}_3^+$  [M+H]<sup>+</sup> m/z 454.1185, found 454.1190.



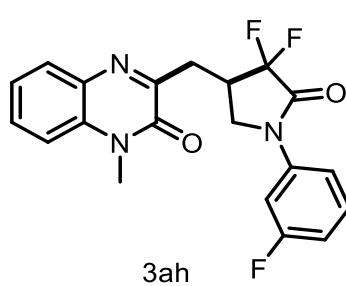
**3-((4,4-Difluoro-1-(4-fluorophenyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1*H*)-one (3ae).** General Procedure was used to prepare the desired product **3ae**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ae** as a pale yellow solid (26.0 mg, 0.067 mmol, 67%); **Mp:** 190–192 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.83 (dd,  $J$  = 8.0, 1.4 Hz, 1H), 7.68 – 7.55 (m, 3H), 7.37 (td,  $J$  = 8.3, 3.8 Hz, 2H), 7.10 (t,  $J$  = 8.5 Hz, 2H), 4.22 (t,  $J$  = 8.8 Hz, 1H), 3.74 (s, 3H), 3.65 (dd,  $J$  = 9.5, 7.1 Hz, 1H), 3.53 (dt,  $J$  = 15.8, 3.8 Hz, 2H), 3.27 (dd,  $J$  = 17.9, 10.3 Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.3 (t,  $J$  = 31.5 Hz), 160.3 (d,  $J$  = 246.4 Hz), 156.4, 154.6, 134.2 (d,  $J$  = 3.1 Hz), 133.2, 132.3, 130.5, 129.9, 123.9, 121.9 (d,  $J$  = 8.1 Hz), 117.6 (dd,  $J$  = 253.8, 250.3 Hz), 116.0 (d,  $J$  = 22.5 Hz), 113.8, 49.2 (d,  $J$  = 6.1 Hz), 36.9 (dd,  $J$  = 22.1, 20.0 Hz), 30.1 (d,  $J$  = 7.5 Hz), 29.2.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.3 (dd,  $J$  = 268.4, 14.3 Hz), -115.2 – -115.4 (m), -116.4 (dd,  $J$  = 268.0, 17.6 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{20}\text{H}_{17}\text{F}_3\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 388.1267, found 388.1267.



**3-((1-(4-Chlorophenyl)-4,4-difluoro-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3af).** General Procedure was used to prepare the desired product **3af**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (7/1) as eluent afforded **3af** as a pale yellow solid (32.0 mg, 0.08 mmol, 80%); **Mp:** 200–201 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.83 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.67 – 7.52 (m, 3H), 7.42 – 7.28 (m, 4H), 4.23 (t, *J* = 8.5 Hz, 1H), 3.76 – 3.69 (m, 3H), 3.69 – 3.60 (m, 1H), 3.60 – 3.46 (m, 3H), 3.31 – 3.21 (m, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.7 – 162.1 (m), 156.3, 154.6, 136.6, 133.2, 132.3, 131.3, 130.5, 129.9, 129.2, 123.9, 121.1, 117.6 (dd, *J* = 253.8, 250.4 Hz), 113.8, 48.9 (d, *J* = 6.1 Hz), 36.8 (dd, *J* = 22.2, 20.0 Hz), 30.1 (d, *J* = 7.4 Hz), 29.2. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.30 (dd, *J* = 268.6, 14.0 Hz), -116.30 (dd, *J* = 268.0, 17.7 Hz). **HRMS (DART-TOF)** calculated for C<sub>20</sub>H<sub>17</sub>ClF<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 404.0972, found 404.1001.

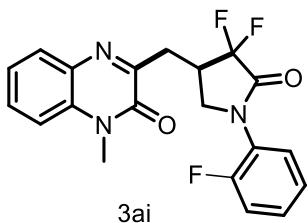


**3-((1-(4-Bromophenyl)-4,4-difluoro-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ag).** General Procedure was used to prepare the desired product **3ag**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (8/1) as eluent afforded **3ag** as a pale yellow solid (33.0 mg, 0.074 mmol, 74%); **Mp:** 193–195 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.64 – 7.49 (m, 5H), 7.42 – 7.30 (m, 2H), 4.22 (dd, *J* = 9.7, 7.8 Hz, 1H), 3.73 (s, 3H), 3.63 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.59 – 3.40 (m, 2H), 3.26 (dd, *J* = 18.0, 10.3 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.7 – 162.1 (m), 156.3, 154.6, 137.1, 133.2, 132.3, 132.2, 130.5, 129.9, 123.9, 121.4, 119.1, 117.5 (dd, *J* = 253.9, 250.3 Hz), 113.8, 48.8 (d, *J* = 6.0 Hz), 36.7 (dd, *J* = 22.0, 19.9 Hz), 30.1 (d, *J* = 7.5 Hz), 29.2. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -102.74 – -112.04 (m), -112.04 – -125.61 (m). **HRMS (DART-TOF)** calculated for C<sub>20</sub>H<sub>17</sub>BrF<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 448.0467, found 448.0448.

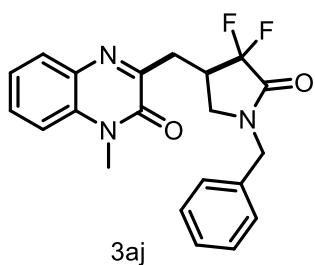


**3-((4,4-Difluoro-1-(3-fluorophenyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ah).** General Procedure was used to prepare the desired product **3ah**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (9/1) as eluent afforded **3ah** as a pale yellow solid (34.9 mg, 0.090 mmol, 90 %); **Mp:** 210–211 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.65 – 7.48 (m, 2H), 7.47 – 7.31 (m, 4H), 6.99 – 6.88 (m, 1H), 4.25 (t, *J* = 8.7 Hz, 1H), 3.74 (s, 3H), 3.64 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.60 – 3.41 (m, 2H), 3.27 (dd, *J* = 17.9, 10.2 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.9 (d, *J* = 246.2 Hz), 162.5 (t, *J* = 31.6 Hz), 156.3, 154.6, 139.5 (d, *J* = 10.3 Hz), 133.2, 132.3, 130.5, 130.3 (d, *J* = 9.1 Hz), 129.9, 123.9, 120.5 – 114.3 (m), 115.0 (d, *J* = 3.0 Hz), 113.8, 112.8 (d, *J* = 21.3 Hz), 107.5 (d, *J* = 26.4 Hz), 48.8 (d, *J* = 6.1 Hz), 36.7 (dd, *J* = 21.9, 20.0 Hz), 30.1 (d, *J* = 7.4 Hz), 29.2. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -108.59 – -111.40 (m), -116.03 (d, *J* = 17.9 Hz),

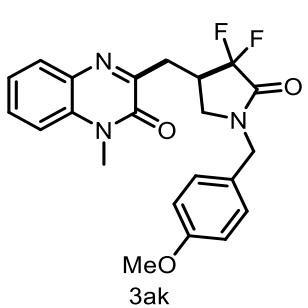
-116.74 (d,  $J = 17.5$  Hz). **HRMS (DART-TOF)** calculated for  $C_{20}H_{17}F_3N_3O_2^+ [M+H]^+$  m/z 388.1267, found 388.1280.



**3-((4,4-Difluoro-1-(2-fluorophenyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ai).** General Procedure was used to prepare the desired product **3ai**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (9/1) as eluent afforded **3ai** as a pale yellow solid (20.0 mg, 0.052 mmol, 52%); **Mp:** 162-164 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.82 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.62 – 7.53 (m, 1H), 7.49 (td,  $J = 7.7, 1.7$  Hz, 1H), 7.39 – 7.28 (m, 3H), 7.24 – 7.14 (m, 2H), 4.24 – 4.12 (m, 1H), 3.73 (s, 3H), 3.69 (d,  $J = 6.5$  Hz, 1H), 3.61 – 3.47 (m, 2H), 3.27 (dd,  $J = 18.1, 10.6$  Hz, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 163.6 – 162.0 (m), 156.8 (d,  $J = 251.5$  Hz), 156.4, 154.6, 133.2, 132.3, 130.4, 129.9, 129.5 (d,  $J = 8.0$  Hz), 127.4, 124.9, 124.7 (d,  $J = 3.7$  Hz), 123.8, 117.3 (dd,  $J = 254.2, 251.2$  Hz), 116.9 (d,  $J = 19.7$  Hz), 113.8, 50.6 (t,  $J = 5.3$  Hz), 37.8 (dd,  $J = 22.0, 19.8$  Hz), 30.1 (d,  $J = 7.6$  Hz), 29.2. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -110.73 (dd,  $J = 268.4, 14.4$  Hz), -116.96 (dd,  $J = 268.7, 17.7$  Hz), -119.89 (dd,  $J = 11.8, 7.4$  Hz). **HRMS (DART-TOF)** calculated for  $C_{20}H_{17}F_3N_3O_2^+ [M+H]^+$  m/z 388.1267, found 388.1260.

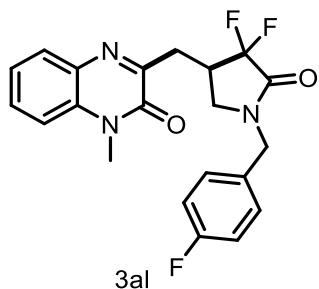


**3-((1-Benzyl-4,4-difluoro-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3aj).** General Procedure was used to prepare the desired product **3aj**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3aj** as a pale yellow solid (23.0 mg, 0.06 mmol, 60%); **Mp:** 175-176 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.78 – 7.72 (m, 1H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.32 (dd,  $J = 11.0, 7.5$  Hz, 6H), 7.25 (d,  $J = 6.2$  Hz, 1H), 4.55 (s, 2H), 3.69 (s, 3H), 3.62 (t,  $J = 9.2$  Hz, 1H), 3.41 (dd,  $J = 28.0, 17.4$  Hz, 2H), 3.15 – 3.02 (m, 2H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 163.6 (t,  $J = 30.8$  Hz), 156.5, 154.6, 134.7, 133.1, 132.3, 130.3, 129.9, 129.0, 128.2 (2C), 123.8, 118.1 (dd,  $J = 254.1, 251.6$  Hz), 113.7, 47.4, 47.3 (d,  $J = 6.2$  Hz), 37.4 – 36.9 (m), 30.4 (d,  $J = 8.0$  Hz), 29.1. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -109.81 (dd,  $J = 267.8, 15.4$  Hz), -116.34 (dd,  $J = 267.8, 16.8$  Hz). **HRMS (DART-TOF)** calculated for  $C_{21}H_{20}F_2N_3O_2^+ [M+H]^+$  m/z 384.1518, found 384.1524.

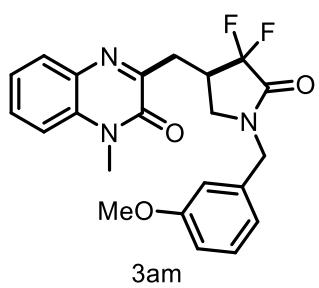


**3-((4,4-Difluoro-1-(4-methoxybenzyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ak).** General Procedure was used to prepare the desired product **3ak**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ak** as a pale yellow solid (32.0 mg, 0.078 mmol, 78%); **Mp:** 180-181 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.68 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.56 – 7.42 (m, 1H), 7.34 – 7.21 (m, 2H), 7.15 – 7.03 (m, 2H), 6.83 – 6.73 (m, 2H), 4.49 – 4.30 (m, 2H), 3.72 (s, 3H), 3.61 (s, 3H), 3.53 (dd,  $J = 10.1, 7.9, 1$  H), 3.40 – 3.16 (m, 2H), 3.09 – 2.90 (m, 2H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 163.7 – 163.1 (m), 159.5, 156.5, 154.6, 133.1, 132.3, 130.3, 129.9, 129.6, 126.7, 123.8, 118.2 (dd,  $J = 254.0, 251.1$  Hz).

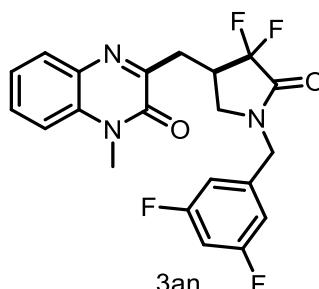
Hz), 114.3, 113.7, 55.3, 47.2 (d,  $J$  = 6.2 Hz), 46.8, 37.1 (dd,  $J$  = 22.5, 20.0 Hz), 30.4 (d,  $J$  = 8.0 Hz), 29.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.64 (dd,  $J$  = 267.7, 15.5 Hz), -116.33 (dd,  $J$  = 267.3, 16.6 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{22}\text{F}_2\text{N}_3\text{O}_3^+$  [M+H]<sup>+</sup> m/z 414.1624, found 414.1602.



**3-((4,4-Difluoro-1-(4-fluorobenzyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3al).** **General Procedure** was used to prepare the desired product **3al**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3al** as a pale yellow solid (27.0 mg, 0.067 mmol, 67%); **Mp:** 177-179 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.76 (d,  $J$  = 7.9 Hz, 1H), 7.57 (t,  $J$  = 7.6 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.22 (dd,  $J$  = 8.5, 5.4 Hz, 2H), 7.03 (t,  $J$  = 8.5 Hz, 2H), 4.58 – 4.45 (m, 2H), 3.70 (s, 3H), 3.62 (ddd,  $J$  = 10.1, 7.9, 1.9 Hz, 1H), 3.47 – 3.28 (m, 2H), 3.19 – 3.00 (m, 2H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.9 – 163.0 (m), 162.6 (d,  $J$  = 246.9 Hz), 156.5, 154.6, 133.1, 132.3, 130.6 – 130.4 (m), 130.4, 130.0 (d,  $J$  = 8.4 Hz), 129.9, 123.8, 121.2 – 114.8 (m), 116.0, 115.8, 47.3 (d,  $J$  = 6.2 Hz), 46.7, 37.1 (t,  $J$  = 20.9 Hz), 30.3 (d,  $J$  = 8.0 Hz), 29.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.82 (dd,  $J$  = 268.1, 15.0 Hz), -112.90 – -115.23 (m), -115.77 – -118.52 (m). **HRMS (DART-TOF)** calculated for  $\text{C}_{21}\text{H}_{19}\text{F}_3\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 402.1424, found 402.1429.

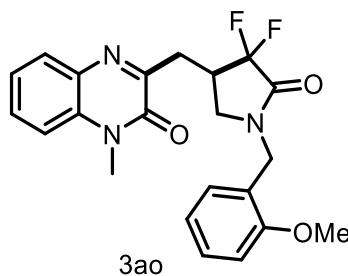


**3-((4,4-Difluoro-1-(3-methoxybenzyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3am).** **General Procedure** was used to prepare the desired product **3am**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3am** as a pale yellow solid (21.0 mg, 0.051 mmol, 51%); **Mp:** 167-168 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.76 (dd,  $J$  = 8.0, 1.4 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.39 – 7.29 (m, 2H), 7.24 (d,  $J$  = 7.9 Hz, 1H), 6.88 – 6.73 (m, 3H), 4.60 – 4.42 (m, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 3.63 (dd,  $J$  = 10.1, 7.8 Hz, 1H), 3.40 (dd,  $J$  = 24.3, 17.2 Hz, 2H), 3.16 – 3.01 (m, 2H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.9 – 163.3 (m), 160.1, 156.5, 154.6, 136.2, 133.1, 132.3, 130.3, 130.0, 129.9, 123.8, 120.4, 118.1 (dd,  $J$  = 254.1, 251.3 Hz), 113.7 (2C), 113.6, 55.3, 47.3, 47.3 (d,  $J$  = 5.0 Hz), 37.1 (dd,  $J$  = 22.4, 20.0 Hz), 30.3 (d,  $J$  = 8.0 Hz), 29.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.52 (dd,  $J$  = 267.2, 15.3 Hz), -116.67 (dd,  $J$  = 267.2, 16.8 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{22}\text{F}_2\text{N}_3\text{O}_3^+$  [M+H]<sup>+</sup> m/z 414.1624, found 414.1624.

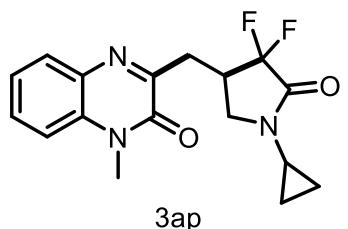


**3-((1-(3,5-Difluorobenzyl)-4,4-difluoro-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3an).** **General Procedure** was used to prepare the desired product **3an**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3an** as a pale yellow solid (23.0 mg, 0.055 mmol, 55%); **Mp:** 181-183 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.77 (d,  $J$  = 8.0 Hz, 1H), 7.57 (t,  $J$

= 7.9 Hz, 1H), 7.42 – 7.29 (m, 2H), 6.78 (d,  $J$  = 7.4 Hz, 3H), 4.51 (s, 2H), 3.70 (s, 3H), 3.69 – 3.62 (m, 1H), 3.51 – 3.31 (m, 2H), 3.20 – 3.06 (m, 2H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  164.6 (d,  $J$  = 12.8 Hz), 163.6 (t,  $J$  = 30.8 Hz), 162.1 (d,  $J$  = 12.6 Hz), 156.4, 154.6, 138.6 (t,  $J$  = 8.8 Hz), 133.2, 132.3, 130.4, 129.9, 123.8, 121.1 – 114.4 (m), 113.7, 111.0 (d,  $J$  = 25.7 Hz), 111.0 (d,  $J$  = 11.3 Hz), 103.8 (t,  $J$  = 25.2 Hz), 47.5 (d,  $J$  = 6.2 Hz), 46.7, 38.6 – 35.9 (m), 30.2 (d,  $J$  = 7.8 Hz), 29.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -108.33 (t,  $J$  = 7.8 Hz), -110.10 (dd,  $J$  = 268.8, 15.3 Hz), -116.39 (dd,  $J$  = 268.6, 16.9 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{21}\text{H}_{18}\text{F}_4\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 420.1330, found 420.1335.

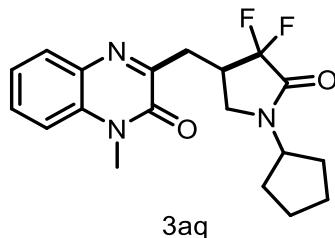


**3-((4,4-Difluoro-1-(2-methoxybenzyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ao).** General Procedure was used to prepare the desired product **3ao**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3ao** as a pale yellow solid (30.0 mg, 0.073 mmol, 73%); **Mp:** 166–168 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.68 (dd,  $J$  = 8.0, 1.4 Hz, 1H), 7.48 (dd,  $J$  = 8.5, 7.3, 1H), 7.31 – 7.17 (m, 3H), 7.11 (dd,  $J$  = 7.5, 1.7 Hz, 1H), 6.90 – 6.70 (m, 2H), 4.60 – 4.40 (m, 2H), 3.73 (s, 3H), 3.61 (s, 3H), 3.50 – 3.39 (m, 1H), 3.34 – 3.14 (m, 2H), 3.07 – 2.91 (m, 2H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.5 (t,  $J$  = 30.6 Hz), 157.6, 156.6, 154.6, 133.1, 132.3, 130.3, 130.1, 129.8, 129.5, 123.8, 122.7, 120.8, 120.9 – 115.3 (m), 113.7, 110.5, 55.3, 47.6 (d,  $J$  = 6.2 Hz), 42.4, 38.4 – 35.2 (m), 30.3 (d,  $J$  = 8.1 Hz), 29.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.75 (dd,  $J$  = 266.9, 15.4 Hz), -116.53 (dd,  $J$  = 266.9, 16.8 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{22}\text{F}_2\text{N}_3\text{O}_3^+$  [M+H]<sup>+</sup> m/z 414.1624, found 414.1621.

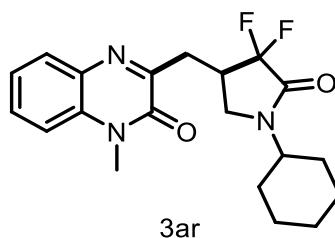


**3-((1-Cyclopropyl-4,4-difluoro-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ap).** General Procedure was used to prepare the desired product **3ap**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **3ap** as a pale yellow solid (23.0 mg, 0.069 mmol, 69%); **Mp:** 210–212 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.76 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.51 (dd,  $J$  = 8.7, 7.4 Hz, 1H), 7.34 – 7.24 (m, 2H), 3.65 (s, 3H), 3.60 (dd,  $J$  = 9.9, 7.9, Hz, 1H), 3.36 (dd,  $J$  = 17.3, 4.1 Hz, 1H), 3.30 – 3.15 (m, 1H), 3.10 – 2.99 (m, 2H), 2.68 (dd,  $J$  = 8.0, 3.6 Hz, 1H), 0.78 – 0.73 (m, 4H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  164.7 – 164.1 (m), 156.6, 154.6, 133.1, 132.4, 130.4, 129.9, 123.8, 118.3 (dd,  $J$  = 253.7, 251.1 Hz), 113.8, 48.2 (d,  $J$  = 5.9 Hz), 37.2 (dd,  $J$  = 22.3, 19.9 Hz), 30.3 (d,  $J$  = 8.1 Hz), 29.2, 26.2, 5.0, 4.9.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.52 (dd,  $J$  = 267.2, 15.3 Hz), -116.67 (dd,  $J$  = 267.2, 16.8 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{17}\text{H}_{18}\text{F}_2\text{N}_3\text{O}_2^+$  [M+H]<sup>+</sup> m/z 334.1362, found 334.1366.

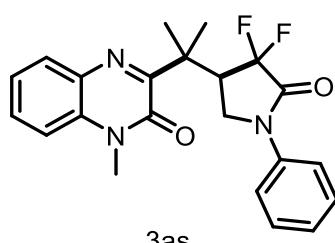
**3-((1-Cyclopentyl-4,4-difluoro-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3aq).** General Procedure was used to prepare the desired product **3aq**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **3aq** as a brown oil (20.0 mg, 0.056 mmol, 56%).  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.84 (dd,  $J$  =



8.0, 1.5 Hz, 1H), 7.59 (dd,  $J$  = 8.6, 7.4 Hz, 1H), 7.46 – 7.31 (m, 2H), 4.52 (t,  $J$  = 8.0 Hz, 1H), 3.73 (s, 4H), 3.46 (dd,  $J$  = 17.2, 4.1 Hz, 2H), 3.22 – 3.04 (m, 2H), 1.98 – 1.85 (m, 2H), 1.75 – 1.69 (m, 2H), 1.66 – 1.50 (m, 4H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.7 – 163.1 (m), 156.7, 154.7, 133.2, 132.4, 130.4, 129.9, 123.8, 118.3 (dd,  $J$  = 253.2, 251.0 Hz), 113.8, 43.9 (d,  $J$  = 6.2 Hz), 37.3 (dd,  $J$  = 22.4, 20.0 Hz), 30.4 (d,  $J$  = 8.0 Hz), 29.2, 28.7, 28.6, 24.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.78 (dd,  $J$  = 266.7, 15.4 Hz), -116.83 (dd,  $J$  = 266.8, 16.7 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{19}\text{H}_{22}\text{F}_2\text{N}_3\text{O}_2^+ [\text{M}+\text{H}]^+$  m/z 362.1675, found 362.1679.

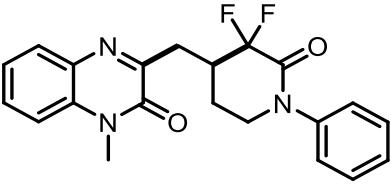


**3-((1-Cyclohexyl-4,4-difluoro-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ar).** General Procedure was used to prepare the desired product **3ar**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **3ar** as a pale yellow solid (15.0 mg, 0.040 mmol, 40%); **Mp:** 171–173 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.84 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.62 – 7.50 (m, 1H), 7.41 – 7.29 (m, 2H), 4.01 (q,  $J$  = 9.6 Hz, 1H), 3.73 (s, 3H), 3.69 (d,  $J$  = 1.8 Hz, 1H), 3.49 – 3.27 (m, 2H), 3.19 – 3.04 (m, 2H), 1.87 – 1.64 (m, 6H), 1.44 – 1.32 (m, 4H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.0 (t,  $J$  = 30.1 Hz), 156.8, 154.7, 133.2, 132.4, 130.4, 130.0, 123.8, 117.2 (dd,  $J$  = 251.3, 252.6 Hz), 113.8, 51.5, 43.8 (d,  $J$  = 6.2 Hz), 37.3 (dd,  $J$  = 22.5, 20.0 Hz), 30.4 (d,  $J$  = 8.0 Hz), 29.8, 29.6, 29.2, 25.2 (3C).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.96 (dd,  $J$  = 266.5, 15.3 Hz), -116.82 (dd,  $J$  = 266.5, 16.7 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{20}\text{H}_{24}\text{F}_2\text{N}_3\text{O}_2^+ [\text{M}+\text{H}]^+$  m/z 376.1831, found 376.1846.

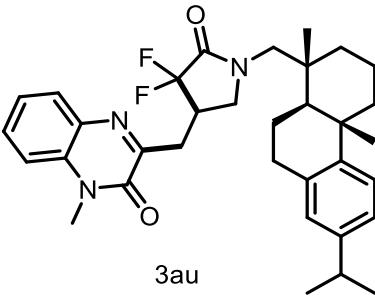


**3-(2-(4,4-Difluoro-5-oxo-1-phenylpyrrolidin-3-yl)propan-2-yl)-1-methylquinoxalin-2(1H)-one (3as).** General Procedure was used to prepare the desired product **3as**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3as** as a pale yellow solid (9.0 mg, 0.023 mmol, 23%); **Mp:** 195–197 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.75 (dd,  $J$  = 8.4, 1.5 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.54 (dd,  $J$  = 8.7, 7.3 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.31 (dd,  $J$  = 8.4, 6.7 Hz, 2H), 7.25 – 7.20 (m, 1H), 4.01 – 3.92 (m, 1H), 3.90 – 3.77 (m, 2H), 3.70 (s, 3H), 1.78 – 1.68 (m, 6H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.8 (t,  $J$  = 31.5 Hz), 160.7, 153.6, 138.2, 133.3, 131.6, 130.4, 130.3, 129.1, 125.9, 123.7, 120.1, 118.8 (dd,  $J$  = 256.7, 247.5 Hz), 113.4, 45.9 (d,  $J$  = 4.9 Hz), 45.4 (dd,  $J$  = 21.9, 17.4 Hz), 44.2, 29.0, 23.3 (2C).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -94.91 (d,  $J$  = 269.9 Hz), -114.06 (dd,  $J$  = 268.9, 14.0 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{22}\text{F}_2\text{N}_3\text{O}_2^+ [\text{M}+\text{H}]^+$  m/z 398.1675, found 398.1681.

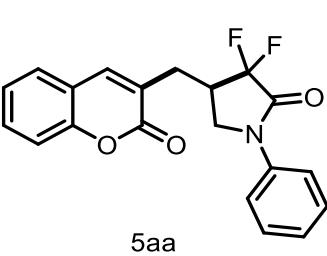
**3-((3,3-Difluoro-2-oxo-1-phenylpiperidin-4-yl)methyl)-1-methylquinoxalin-2(1H)-one (3at).** General Procedure was used to prepare the desired product **3at**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **3at** as a

  
**3at**

pale yellow solid (18.0 mg, 0.047 mmol, 47%); **Mp:** 196–197 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.47–7.27 (m, 7H), 3.92–3.80 (m, 1H), 3.73 (s, 4H), 3.48 (dd, *J* = 16.2, 3.7 Hz, 1H), 3.30 (td, *J* = 13.8, 13.2, 6.2 Hz, 1H), 3.17 (dd, *J* = 16.1, 9.5 Hz, 1H), 2.28–2.04 (m, 2H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 161.5 (t, *J* = 30.1 Hz), 157.2, 154.9, 141.3, 133.2, 132.5, 130.2, 129.9, 129.4, 127.6, 125.7, 123.8, 113.8 (d, *J* = 495.4 Hz), 113.7, 49.9, 38.7 (t, *J* = 20.9 Hz), 31.1 (dd, *J* = 5.2, 1.9 Hz), 29.2, 24.7 (d, *J* = 7.2 Hz). **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -108.12 (dd, *J* = 279.3, 8.0 Hz), -110.17 (dd, *J* = 279.5, 22.0 Hz). **HRMS (DART-TOF)** calculated for C<sub>21</sub>H<sub>20</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 384.1518, found 384.1522.

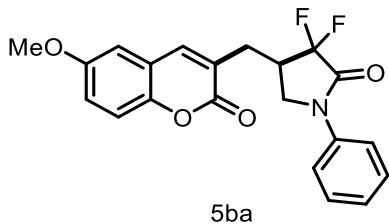
  
**3au**

**3-((4,4-Difluoro-1-(((1*R*,4*aS*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl)-5-oxopyrrolidin-3-yl)methyl)-1-methylquinoxalin-2(1*H*)-one (**3au**). General Procedure** was used to prepare the desired product **3au**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (3/1) as eluent afforded **3au** as a pale yellow solid (51.0 mg, 0.09 mmol, 90%); **Mp:** 164–165 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.57 (td, *J* = 7.9, 3.8 Hz, 1H), 7.35 (dd, *J* = 18.1, 8.1 Hz, 2H), 7.15 (dd, *J* = 8.8, 5.9 Hz, 1H), 7.01–6.93 (m, 1H), 6.88 (d, *J* = 4.3 Hz, 1H), 3.93–3.76 (m, 1H), 3.69 (d, *J* = 4.4 Hz, 3H), 3.44–3.23 (m, 5H), 3.12 (dt, *J* = 11.9, 3.8 Hz, 2H), 2.83 (dd, *J* = 13.1, 6.4 Hz, 3H), 2.28 (d, *J* = 12.9 Hz, 1H), 1.95 (d, *J* = 7.0 Hz, 1H), 1.74 (d, *J* = 13.7 Hz, 2H), 1.43–1.35 (m, 4H), 1.26 (s, 3H), 1.17 (d, *J* = 7.1 Hz, 6H), 0.99 (d, *J* = 4.3 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 165.1 (td, *J* = 30.7, 8.2 Hz), 156.7, 154.6, 147.0, 145.7, 145.6, 134.5, 134.4, 133.2, 132.4, 130.3, 129.9, 126.9, 126.9, 124.2, 124.0, 123.9, 123.9, 123.8, 123.8, 120.5–114.7 (m), 113.8, 113.7, 56.5, 56.2, 51.9 (d, *J* = 6.3 Hz), 46.4, 46.1, 39.6, 39.6, 38.2, 37.8, 37.7, 37.7, 37.6–37.1 (m), 37.3, 33.5, 33.4, 30.6–29.2 (m), 30.2, 30.1, 30.1, 29.2, 29.1, 25.7, 25.6, 24.0, 24.0, 24.0, 23.9. **<sup>19</sup>F NMR (376 MHz, Chloroform-d)** δ -105.44–115.31 (m), -116.84 (dd, *J* = 266.0, 17.3 Hz). **HRMS (DART-TOF)** calculated for C<sub>34</sub>H<sub>42</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 562.3240, found 562.3240.

  
**5aa**

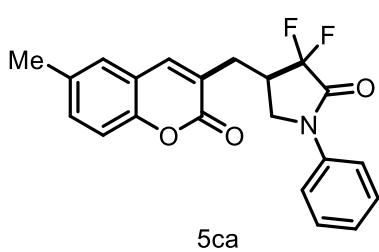
**3,3-Difluoro-4-((2-oxo-2*H*-chromen-3-yl)methyl)-1-phenylpyrrolidin-2-one (**5aa**).<sup>3</sup>** General Procedure was used to prepare the desired product **5aa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5aa** as a pale yellow solid (10.0 mg, 0.028 mmol, 28%); **Mp:** 160–162 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.65 (s, 1H), 7.59–7.52 (m, 2H), 7.51–7.40 (m, 2H), 7.37–7.20 (m, 4H), 7.18–7.12 (m, 1H), 3.90 (dd, *J* = 9.6, 8.1 Hz, 1H), 3.62 (dd, *J* = 9.8, 7.8 Hz, 1H), 3.16 (dt, *J* = 18.3, 7.5 Hz, 1H), 2.97 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.87 (dd, *J* = 14.1, 7.1 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 162.0 (t, *J* = 31.2 Hz), 161.5, 153.5, 141.8, 137.8, 131.6, 129.2, 127.7, 126.3, 124.8, 124.7, 120.0, 119.0, 120.6–114.6 (m), 116.6,

48.3 (d,  $J = 6.4$  Hz), 38.4 (t,  $J = 20.6$  Hz), 27.8 (d,  $J = 7.6$  Hz).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -108.68 (dd,  $J = 267.7, 13.8$  Hz), -117.61 (dd,  $J = 267.4, 18.3$  Hz). HRMS (DART-TOF) calculated for  $\text{C}_{20}\text{H}_{16}\text{F}_2\text{NO}_3^+ [\text{M}+\text{H}]^+$  m/z 356.1093, found 356.1098.



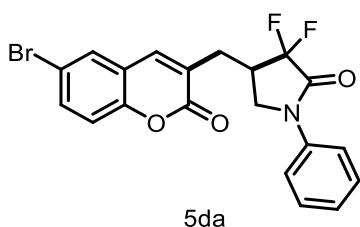
**3,3-Difluoro-4-((7-methoxy-2-oxo-2*H*-chromen-3-yl)methyl)-1-phenylpyrrolidin-2-one (5ba).** General Procedure was used to prepare the desired product **5ba**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5ba** as a pale yellow solid (16.0 mg, 0.042 mmol, 42%); **Mp:** 208-210 °C.

**$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.71 – 7.61 (m, 3H), 7.46 – 7.38 (m, 3H), 7.28 – 7.19 (m, 1H), 6.94 – 6.83 (m, 2H), 3.98 (dd,  $J = 9.7, 8.1$  Hz, 1H), 3.91 (s, 3H), 3.71 (dd,  $J = 9.8, 7.8$  Hz, 1H), 3.23 (dt,  $J = 18.3, 7.5$  Hz, 1H), 3.07 – 2.87 (m, 2H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.7, 162.1 (t,  $J = 32.3$  Hz), 161.9, 155.3, 141.8, 137.9, 129.2, 128.6, 126.2, 121.0, 120.0, 117.5 (dd,  $J = 250.1, 250.3$  Hz), 112.9, 112.7, 100.7, 55.8, 48.3 (d,  $J = 6.4$  Hz), 38.6 (t,  $J = 20.5$  Hz), 27.6 (d,  $J = 7.6$  Hz).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -108.75 (dd,  $J = 267.5, 13.6$  Hz), -117.71 (dd,  $J = 267.5, 18.3$  Hz). HRMS (DART-TOF) calculated for  $\text{C}_{21}\text{H}_{18}\text{F}_2\text{NO}_4^+ [\text{M}+\text{H}]^+$  m/z 386.1198, found 386.1200.



**3,3-Difluoro-4-((7-methyl-2-oxo-2*H*-chromen-3-yl)methyl)-1-phenylpyrrolidin-2-one (5ca).** General Procedure was used to prepare the desired product **5ca**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5ca** as a pale yellow solid (18.0 mg, 0.049 mmol, 49%); **Mp:** 168-170 °C.

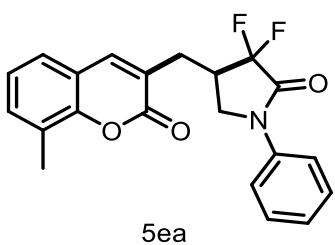
**$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.61 (s, 1H), 7.58 – 7.52 (m, 2H), 7.36 – 7.28 (m, 3H), 7.18 – 7.10 (m, 1H), 7.10 – 7.02 (m, 2H), 3.89 (dd,  $J = 9.7, 8.1$  Hz, 1H), 3.61 (dd,  $J = 9.8, 7.8$  Hz, 1H), 3.14 (dt,  $J = 18.3, 7.6$  Hz, 1H), 2.99 – 2.79 (m, 2H), 2.39 (s, 3H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.1 (t,  $J = 32.1$  Hz), 161.8, 153.6, 142.9, 141.8, 137.8, 129.2, 127.3, 126.2, 125.9, 123.4, 120.0, 117.5 (dd,  $J = 249.9, 250.2$  Hz), 116.8, 116.7, 48.3 (d,  $J = 6.4$  Hz), 38.5 (t,  $J = 20.6$  Hz), 27.7 (d,  $J = 7.7$  Hz), 21.8.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -108.75 (dd,  $J = 267.5, 13.5$  Hz), -117.68 (dd,  $J = 267.5, 18.3$  Hz). HRMS (DART-TOF) calculated for  $\text{C}_{21}\text{H}_{18}\text{F}_2\text{NO}_3^+ [\text{M}+\text{H}]^+$  m/z 370.1249, found 370.1259.



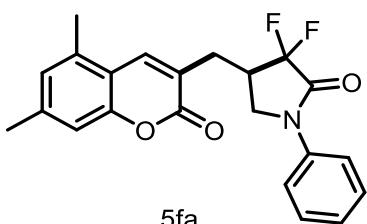
**4-((7-Bromo-2-oxo-2*H*-chromen-3-yl)methyl)-3,3-difluoro-1-phenylpyrrolidin-2-one (5da).** General Procedure was used to prepare the desired product **5da**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5da** as a pale yellow solid (13.6 mg, 0.03 mmol, 30%); **Mp:** 188-189 °C.

**$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.62 – 7.52 (m, 3H), 7.46 (d,  $J = 1.8$  Hz, 1H), 7.39 – 7.27 (m, 4H), 7.18 – 7.13 (m, 1H), 3.91 (dd,  $J = 9.6, 8.1$  Hz, 1H), 3.61 (dd,  $J = 9.8, 7.8$  Hz, 1H), 3.14 (dt,  $J = 18.4, 7.5$  Hz, 1H), 2.93 (dd,  $J = 14.1, 7.7$  Hz, 1H), 2.86 (dd,  $J = 14.1, 6.9$  Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  161.9 (t,  $J = 31.7$

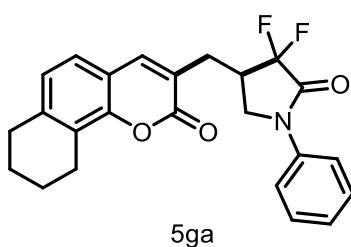
Hz), 160.8, 153.7, 141.1, 137.7, 129.2, 128.6, 128.2, 126.3, 125.5, 125.1, 120.0, 119.9, 117.9, 117.5 (dd,  $J$  = 249.8, 250.1 Hz), 48.2 (d,  $J$  = 6.3 Hz), 38.3 (t,  $J$  = 20.5 Hz), 27.9 (d,  $J$  = 7.6 Hz).  **$^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)**  $\delta$  -108.49 (dd,  $J$  = 267.7, 13.2 Hz), -117.53 (dd,  $J$  = 267.5, 18.3 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{20}\text{H}_{14}\text{BrF}_2\text{NO}_3\text{Na}^+$  [M+H]<sup>+</sup> m/z 456.0017, found 456.0019.



**3,3-Difluoro-4-((8-methyl-2-oxo-2*H*-chromen-3-yl)methyl)-1-phenylpyrrolidin-2-one (5ea).** General Procedure was used to prepare the desired product **5ea**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5ea** as a pale yellow solid (12.0 mg, 0.033 mmol, 33%); **Mp:** 169–170 °C.  **$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)**  $\delta$  7.67 – 7.50 (m, 3H), 7.36 – 7.22 (m, 4H), 7.18 – 7.08 (m, 2H), 3.90 (dd,  $J$  = 9.6, 8.0, 1H), 3.63 (dd,  $J$  = 9.7, 7.7 Hz, 1H), 3.16 (dt,  $J$  = 18.3, 7.6 Hz, 1H), 2.97 (dd,  $J$  = 14.0, 7.3 Hz, 1H), 2.87 (dd,  $J$  = 14.0, 7.3 Hz, 1H), 2.40 (s, 3H).  **$^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)**  $\delta$  162.1 (t,  $J$  = 31.3 Hz), 161.7, 151.9, 142.2, 137.8, 132.9, 129.2, 126.2, 126.1, 125.4, 124.3, 124.3, 120.0, 118.8, 117.5 (dd,  $J$  = 249.7, 249.8 Hz), 48.3 (d,  $J$  = 6.4 Hz), 38.5 (t,  $J$  = 20.5 Hz), 27.7 (d,  $J$  = 7.6 Hz), 15.4.  **$^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)**  $\delta$  -108.73 (dd,  $J$  = 267.6, 13.8 Hz), -117.63 (dd,  $J$  = 267.5, 18.3 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{21}\text{H}_{18}\text{F}_2\text{NO}_3^+$  [M+H]<sup>+</sup> m/z 370.1249, found 370.1274.

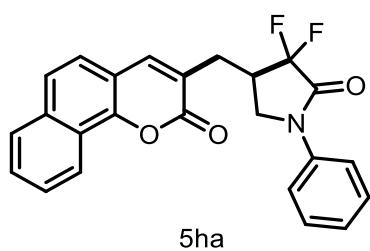


**4-((5,7-Dimethyl-2-oxo-2*H*-chromen-3-yl)methyl)-3,3-difluoro-1-phenylpyrrolidin-2-one (5fa).** General Procedure was used to prepare the desired product **5fa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5fa** as a pale yellow solid (13.0 mg, 0.034 mmol, 34%); **Mp:** 190–192 °C.  **$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)**  $\delta$  7.79 (s, 1H), 7.61 – 7.51 (m, 2H), 7.40 – 7.28 (m, 2H), 7.16 (d,  $J$  = 7.5 Hz, 1H), 6.90 (d,  $J$  = 18.1 Hz, 2H), 3.89 (dd,  $J$  = 9.6, 8.1 Hz, 1H), 3.63 (dd,  $J$  = 9.8, 7.8 Hz, 1H), 3.15 (dt,  $J$  = 18.3, 7.5 Hz, 1H), 2.96 (dd,  $J$  = 14.1, 7.3 Hz, 1H), 2.88 (dd,  $J$  = 14.1, 7.2 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H).  **$^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)**  $\delta$  162.1 (t,  $J$  = 32.0 Hz), 161.8, 154.2, 142.6, 138.9, 137.8, 135.5, 129.2, 127.3, 126.2, 122.6, 120.0, 115.5, 117.6 (dd,  $J$  = 249.8, 249.8 Hz), 114.8, 48.3 (d,  $J$  = 6.3 Hz), 38.6 (t,  $J$  = 20.5 Hz), 27.9 (d,  $J$  = 7.5 Hz), 21.7, 18.3.  **$^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)**  $\delta$  -108.60 (dd,  $J$  = 267.4, 13.6 Hz), -117.58 (dd,  $J$  = 267.4, 18.3 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{22}\text{H}_{20}\text{F}_2\text{NO}_3^+$  [M+H]<sup>+</sup> m/z 384.1406, found 384.1400.



**3,3-Difluoro-4-((2-oxo-7,8,9,10-tetrahydro-2*H*-benzo[*h*]chromen-3-yl)methyl)-1-phenylpyrrolidin-2-one (5ga).** General Procedure was used to prepare the desired product **5ga**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5ga** as a pale yellow solid (12.0 mg, 0.029 mmol, 29%); **Mp:** 177–178 °C.  **$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)**  $\delta$  7.63 – 7.50 (m,

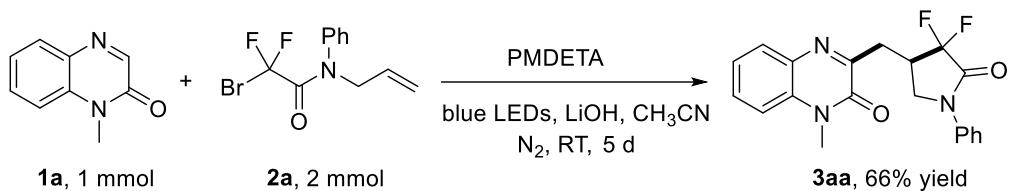
3H), 7.37 – 7.28 (m, 2H), 7.18 – 7.09 (m, 2H), 6.95 (d,  $J$  = 7.9 Hz, 1H), 3.88 (dd,  $J$  = 9.7, 8.1 Hz, 1H), 3.61 (dd,  $J$  = 9.8, 7.7 Hz, 1H), 3.15 (dt,  $J$  = 18.3, 7.6 Hz, 1H), 2.94 (dd,  $J$  = 14.0, 7.2 Hz, 1H), 2.90 – 2.69 (m, 5H), 1.86 – 1.68 (m, 4H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.2 (t,  $J$  = 30.9 Hz), 162.0, 151.7, 142.3 (2C), 137.9, 129.2, 126.2, 125.5, 125.3, 124.2, 122.8, 120.0, 117.5 (dd,  $J$  = 249.0, 249.3 Hz), 116.3, 48.3 (d,  $J$  = 6.3 Hz), 38.5 (t,  $J$  = 20.5 Hz), 29.9, 27.7 (d,  $J$  = 7.7 Hz), 22.6, 22.5, 22.1.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -108.78 (dd,  $J$  = 267.6, 13.7 Hz), -117.67 (dd,  $J$  = 267.5, 18.3 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{24}\text{H}_{22}\text{F}_2\text{NO}_3^+ [\text{M}+\text{H}]^+$  m/z 410.1562, found 410.1565.



**3,3-difluoro-4-((2-oxo-2*H*-benzo[*h*]chromen-3-yl)methyl)-1-phenylpyrrolidin-2-one (5ha).** General Procedure was used to prepare the desired product **5ha**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (5/1) as eluent afforded **5ha** as a pale yellow solid (14.0 mg, 0.035 mmol, 35%); **Mp:** 160–161 °C.  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.53 – 8.42 (m, 1H), 7.86 – 7.74 (m, 2H), 7.68 – 7.52 (m, 5H), 7.42 – 7.29 (m, 3H), 7.18 – 7.12 (m, 1H), 3.93 (dd,  $J$  = 9.6, 8.1 Hz, 1H), 3.66 (dd,  $J$  = 9.8, 7.8 Hz, 1H), 3.21 (dt,  $J$  = 18.2, 7.6 Hz, 1H), 3.03 (dd,  $J$  = 14.1, 7.3 Hz, 1H), 2.93 (dd,  $J$  = 14.1, 7.3 Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.1 (t,  $J$  = 30.7 Hz), 161.7, 150.7, 142.6, 137.8, 134.7, 129.2, 128.7, 127.9, 127.3, 126.3, 124.8, 124.2, 123.4, 122.9, 122.2, 120.0, 117.5 (dd,  $J$  = 249.6, 249.8 Hz), 114.5, 48.3 (d,  $J$  = 6.3 Hz), 38.5 (t,  $J$  = 20.6 Hz), 27.8 (d,  $J$  = 7.7 Hz).  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -108.64 (dd,  $J$  = 267.5, 13.5 Hz), -117.55 (dd,  $J$  = 267.4, 18.3 Hz). **HRMS (DART-TOF)** calculated for  $\text{C}_{24}\text{H}_{18}\text{F}_2\text{NO}_3^+ [\text{M}+\text{H}]^+$  m/z 406.1249, found 406.1258.

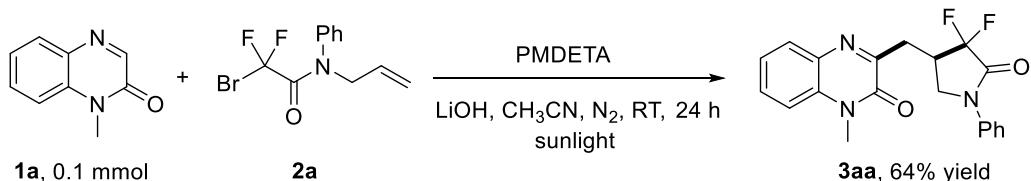
## 4. Scale-Up and Sunlight Experiment

### 4.1 Gram-scale synthesis



A mixture of quinoxalin-2(1*H*)-one **1a** (1.0 mmol), *N*-allylbromodifluoroacetamide **2a** (2.0 mmol, 2.0 equiv.), LiOH (1.0 mmol, 1.0 equiv.), PMDETA (2.0 mmol, 2.0 equiv.), and CH<sub>3</sub>CN (4 mL) was degassed by three cycles of freeze-pump-thaw. The mixture was irradiated by 24 W 460 nm blue LEDs at room temperature for 5 days. After removal of solvents, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the pure product **3aa** (0.25 g, 0.66 mmol, 66%).

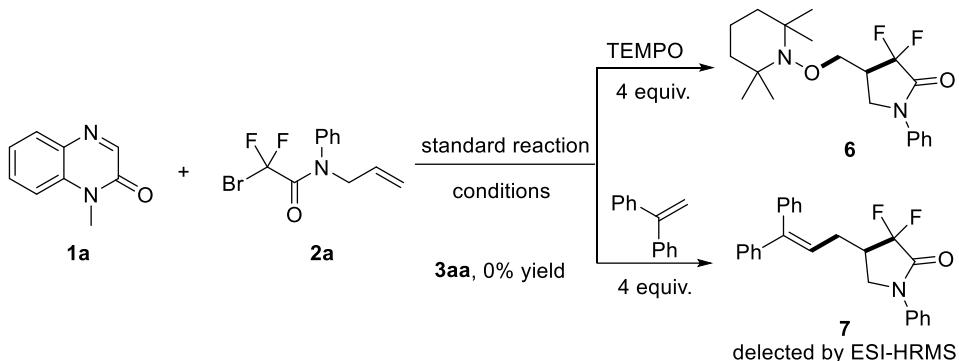
### 4.2 Sunlight driven experiment



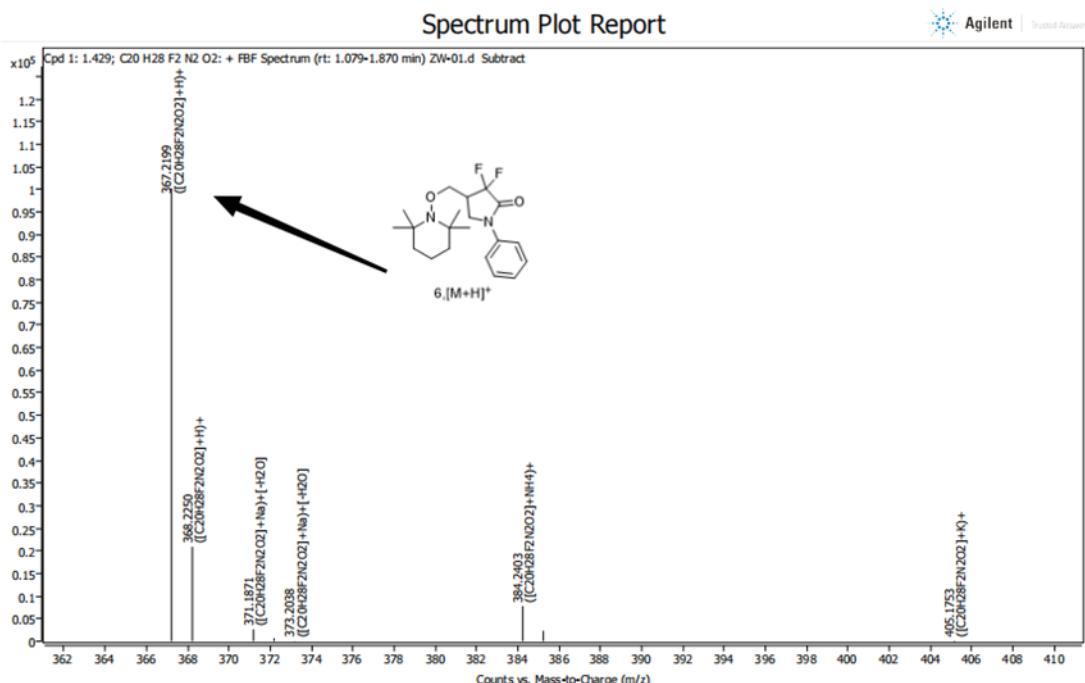
A mixture of quinoxalin-2(1*H*)-one **1a** (0.1 mmol), *N*-allylbromodifluoroacetamide **2a** (0.2 mmol, 2.0 equiv.), LiOH (0.1 mmol, 1.0 equiv.), PMDETA (0.2 mmol, 2.0 equiv.), and CH<sub>3</sub>CN (1 mL) was degassed by three cycles of freeze-pump-thaw. The resulting mixture was stirred upon sunlight irradiation under nitrogen atmosphere for 24 h (as an on/off visible light irradiation experiment, the reaction solution was kept in dark place at night). After completion of the reaction, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the pure product **3aa** (0.023 g, 0.064 mmol, 64%).

## 5. Mechanistic Experiments

### 5.1 Radical Inhibition Experiments

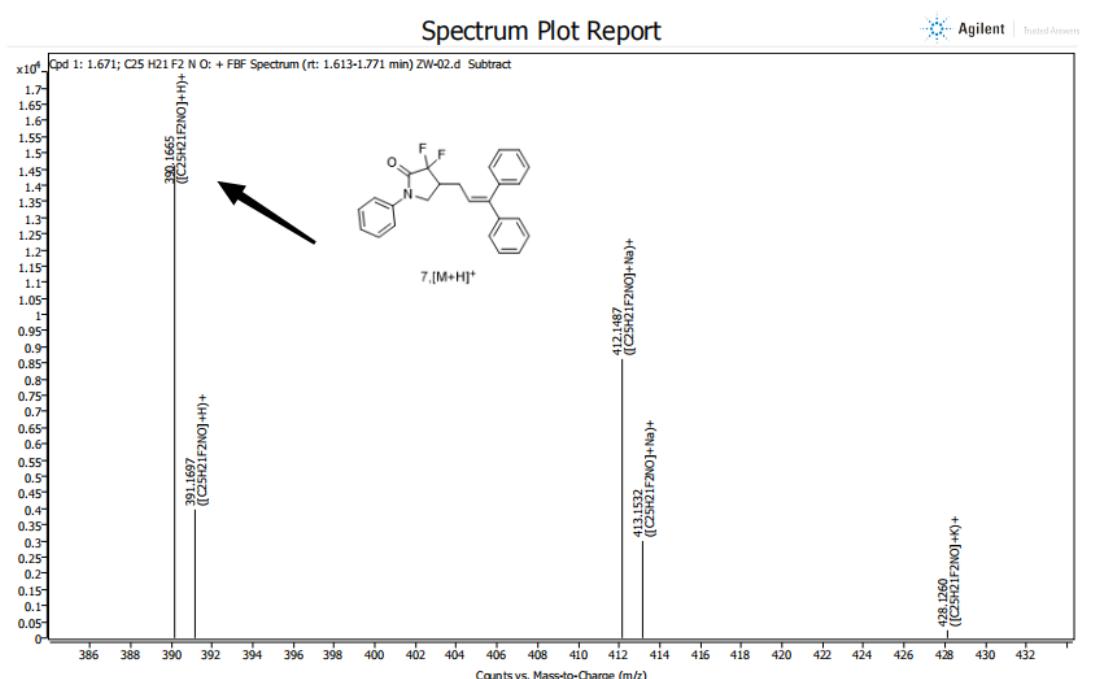


To an oven-dried quartz vial, quinoxalin-2(1*H*)-one **1a** (0.1 mmol, 1.0 equiv.), TEMPO (4.0 equiv.), PMDETA (0.2 mmol, 2.0 equiv), and LiOH (0.1 mmol, 1.0 equiv.) were added sequentially. The vial was charged with a stir bar and transferred to a glovebox, where the solids were backfilled with an inert atmosphere. In the glovebox, *N*-allylbromodifluoroacetamide **2a** (0.2 mmol, 2.0 equiv.) was added into the vial, followed by CH<sub>3</sub>CN (1.0 mL). The vial was sealed with a rubber plug, removed from the glove box, and irradiated and stir by 24 W 460 nm LEDs at room temperature for 36 h. **HRMS (DART-TOF)**: compound **6** calculated for C<sub>21</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 347.2699, found 347.2705



**Figure S3** Quinoxalin-2(1*H*)-one **1a** and *N*-allylbromodifluoroacetamide **2a** under standard conditions with TEMPO (4.0 equiv.).

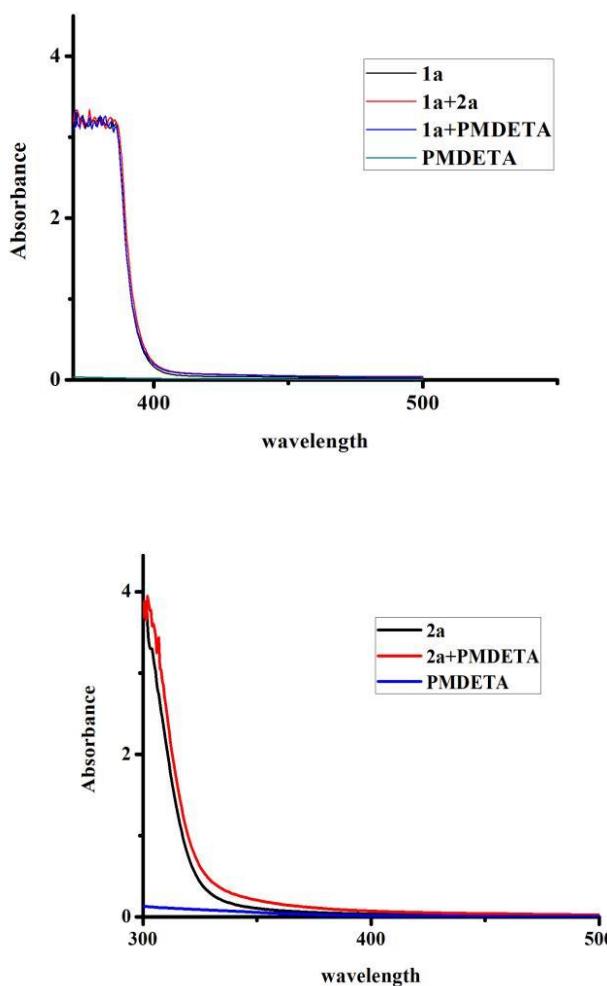
To an oven-dried quartz vial, quinoxalin-2(1*H*)-one **1a** (0.1 mmol, 1.0 equiv.), ethene-1,1-diylidibenzene (4 equiv.), PMDETA (0.2 mmol, 2.0 equiv.), and LiOH (0.1 mmol, 1.0 equiv.) were added sequentially. The vial was charged with a stir bar and transferred to a glovebox, where the solids were backfilled with an inert atmosphere. In the glovebox, *N*-allylbromodifluoroacetamide **2a** (0.2 mmol, 2.0 equiv.) was added into the vial, followed by CH<sub>3</sub>CN (1.0 mL). The vial was sealed with a rubber plug, removed from the glove box, and irradiated and stir by 24 W 460 nm LEDs at room temperature for 36 h. **HRMS (DART-TOF)**: compound **7** calculated for C<sub>25</sub>H<sub>22</sub>F<sub>2</sub>NO<sup>+</sup> [M+H]<sup>+</sup> m/z 390.1664, found 390.1665.



**Figure S4** Quinoxalin-2(1*H*)-one **1a** and *N*-allylbromodifluoroacetamide **2a** under standard conditions with ethene-1,1-diylidibenzene (4.0 equiv.)

### 5.3 UV-vis absorption spectrometry

UV-vis absorption spectra of **1a** (0.05 M), **2a** (0.05 M), PMDETA, **1a+2a**, **1a+PMDETA**, **2a+PMDETA** in 3 mL CH<sub>3</sub>CN were recorded in 1 cm path quartz cuvettes using a Shimadzu UV-1900i UV-vis spectrometer

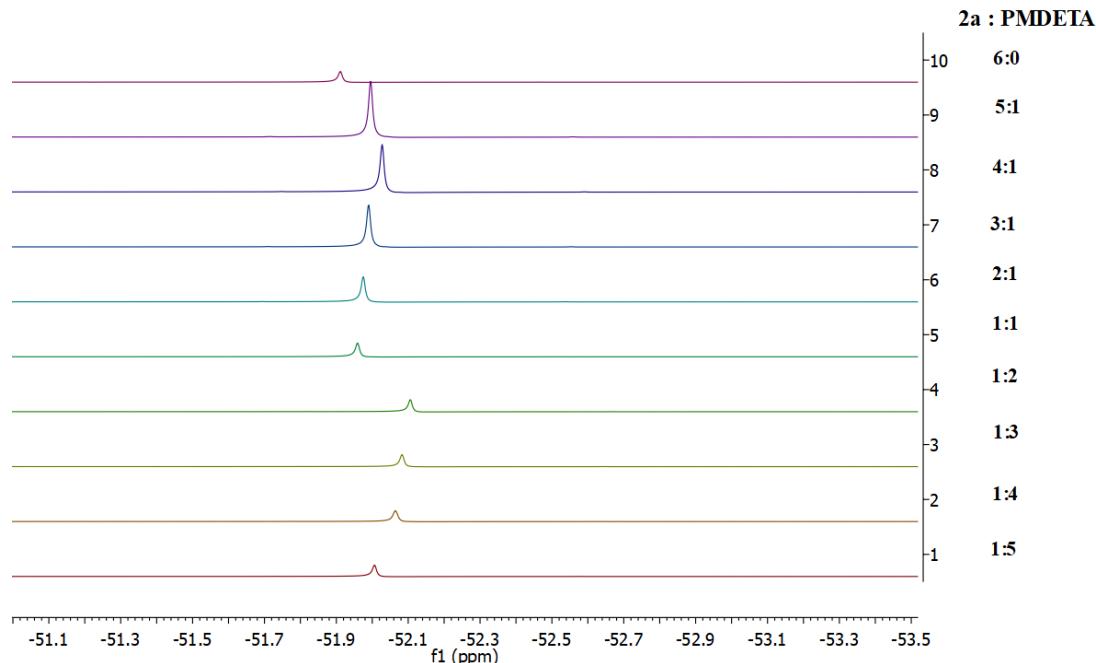


**Figure S5** UV-vis absorption spectra

#### 5.4 $^{19}\text{F}$ NMR Titration Experiments

Solutions containing equal molar concentrations of the *N*-allylbromodifluoroacetamide **2a** (0.05 M in  $\text{CH}_3\text{CN}$ ) and PMDETA (0.05 M in  $\text{CH}_3\text{CN}$ ) were prepared and mixed to cover the ratio of **2a** from 100% to 20%. In NMR titration experiments, we observed  $^{19}\text{F}$  NMR (376 MHz) signal of **2a** shifted with the addition of PMDETA, while  $^{19}\text{F}$  NMR signal didn't shift only with concentration change of **2a** without the addition of PMDETA.

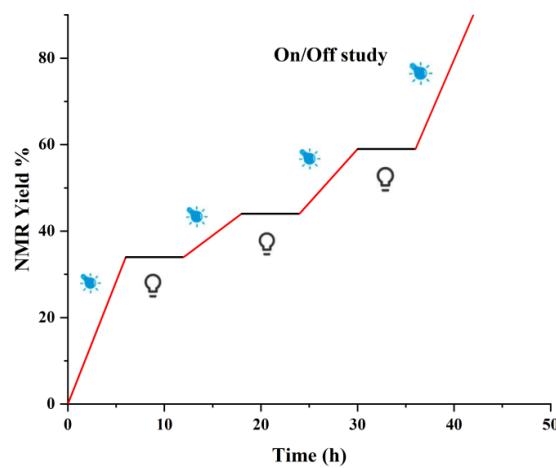
**19F (CDCl<sub>3</sub>, 376 MHz)**



**Figure S6** <sup>19</sup>F NMR titration between **2a** and PMDETA

## 5.5 Time profile of the transformation with the light ON/OFF over time

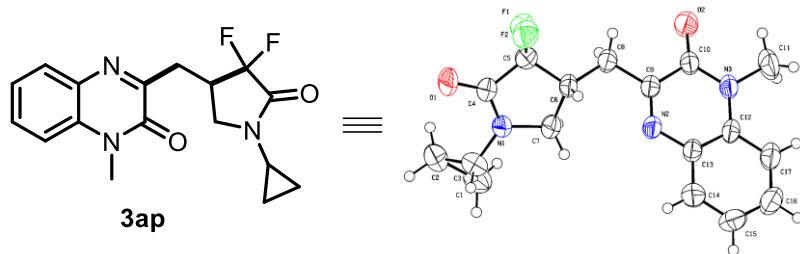
The standard reaction was set up on a 0.20 mmol scale according to the general procedure. After being irradiated for 6 h, an aliquot (100  $\mu$ L) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.55 mL of CDCl<sub>3</sub>-d<sub>1</sub>. The yield of product was determined by <sup>1</sup>H NMR. Then the reaction mixture was stirred for 6 h with light-off. All of the following yields were analyzed in the identical way after a 6 h light on or off.



**Figure S7** Time profile of the transformation with the light ON/OFF over time

## 6. X-Ray Structure of Product 3ap

X-ray crystallography of **3ap**



**Figure S8** ORTEP diagram (50% probability) of **3ap**

A single crystal of **3ap** was obtained *via* evaporation of its hexanes/dichloromethane solvent mixture. A suitable crystal of **3ap** was selected and analyzed by an Agilent Gemini X-ray Single Crystal Diffractometer. Using Olex2<sup>5</sup>, the structure was solved with the ShelXT<sup>4</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>6</sup> refinement package using Least Squares minimization. Details of the crystal, data collection, and structure refinement parameters for crystallographic analysis of **3ap** are summarized in **Table S5**. Crystallographic data (CCDC 2219240) for **3ap** can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S5.** Parameters for crystallographic analysis of **3ap**

Identification code	1_a
Empirical formula	C <sub>17</sub> H <sub>17</sub> F <sub>2</sub> N <sub>3</sub> O <sub>2</sub>
Formula weight	333.33
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.850(2) Å α= 108.912(7)° b = 10.152(3) Å β= 101.164(6)° c = 10.835(3) Å γ = 96.073(6)°
Volume	788.1(4) Å <sup>3</sup>
Z	2
Density (calculated)	1.405 Mg/m <sup>3</sup>
Absorption coefficient	0.110 mm <sup>-1</sup>
F(000)	348
Crystal size	0.200 x 0.200 x 0.200 mm <sup>3</sup>
Theta range for data collection	2.393 to 24.996°.
Index ranges	-9<=h<=9, -12<=k<=11, -12<=l<=12
Reflections collected	20998

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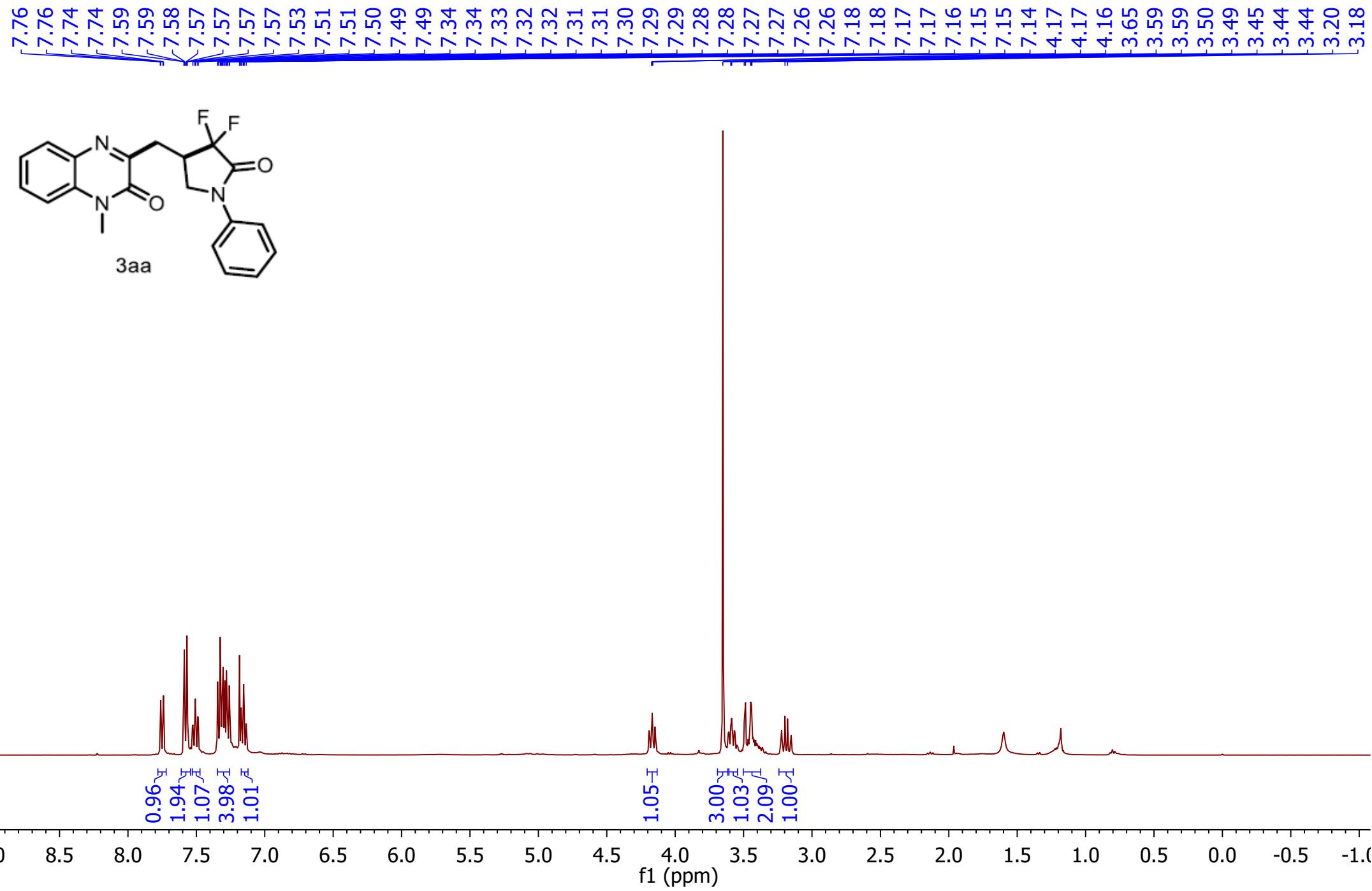
Independent reflections	2755 [R(int) = 0.0880]
Completeness to theta = 24.996°	99.3 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2755 / 0 / 206
Goodness-of-fit on F <sup>2</sup>	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0690, wR2 = 0.1770
R indices (all data)	R1 = 0.1407, wR2 = 0.2173
Extinction coefficient	n/a
Largest diff. peak and hole	0.237 and -0.246 e.Å <sup>-3</sup>

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## 7. References

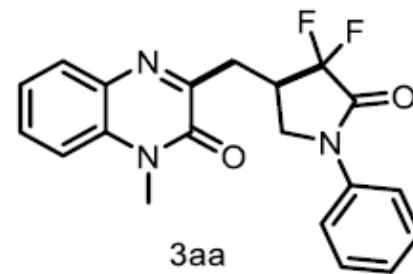
1. Ghosh, P.; Kwon, N. Y.; Kim, S.; Han, S.; Lee, S. H.; An, W.; Mishra, N. K.; Han, S. B.; Kim, I. S. *Angew. Chem., Int. Ed.* **2021**, *60*, 191.
2. Chen, X.-Y; Li, L.-L.; Pei, C.-C.; Jingya Li, J.-Y.; Zou, D.-P.; Wu, Y.-J.; Wu, Y.-S. *J. Org. Chem.* **2021**, *86*, 2772.
3. (a) Ye, Z.-P.; Liu, F.; Duan, X.-Y.; Gao, J.; Guan, J.-P.; Xiao, J.-A.; Xiang, H.-Y.; Chen, K.; Yang, H. *J. Org. Chem.* **2021**, *86*, 17173. (b) Zhang, Y.-C.; Chen, Y.; Sun, J.; Wang, J.-Y.; Zhou, M.-D. *Chin. J. Chem.* **2022**, *40*, 713.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
5. Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2015**, *71*, 3.
6. Sheldrick, G. M. *Acta Crystallogr. Sect. C* **2015**, *71*, 3.

## **1H (CDCl<sub>3</sub>, 400 MHz)**

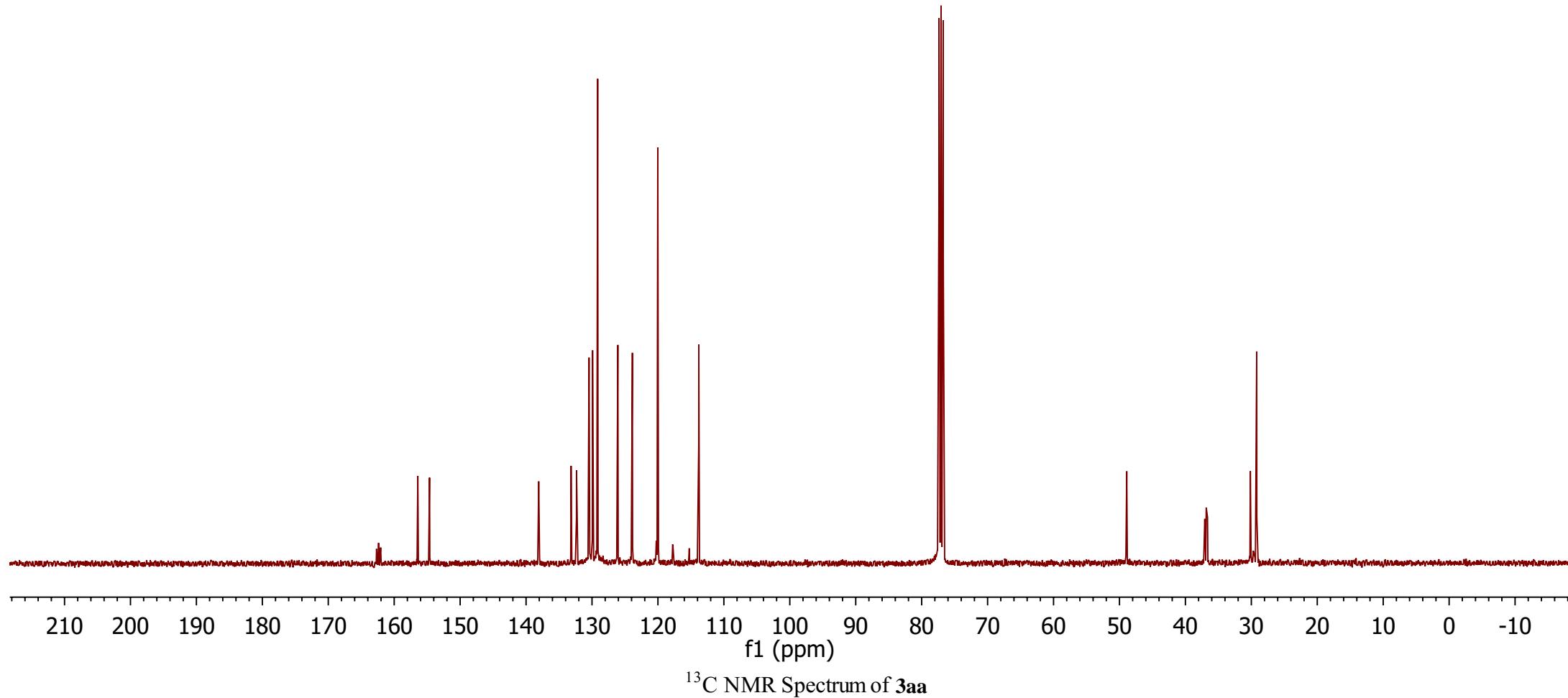


<sup>1</sup>H NMR Spectrum of 3aa

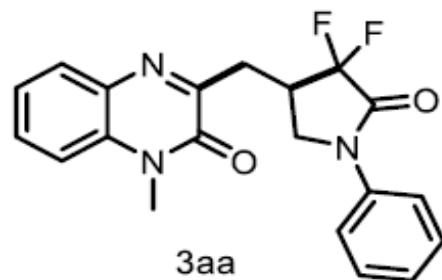
<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



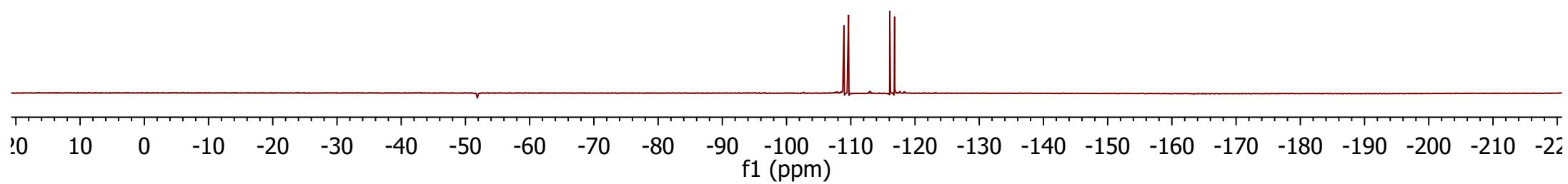
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162.4  
162.1  
156.4  
154.6  
138.1  
133.2  
132.3  
130.4  
130.0  
129.9  
129.1  
126.1  
123.9  
120.3  
120.0  
117.8  
117.7  
115.2  
113.8  
77.4  
77.3  
77.1  
76.8  
76.7  
49.0  
48.9  
37.1  
36.9  
36.8  
36.6  
30.2  
30.1  
29.7  
29.2



**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

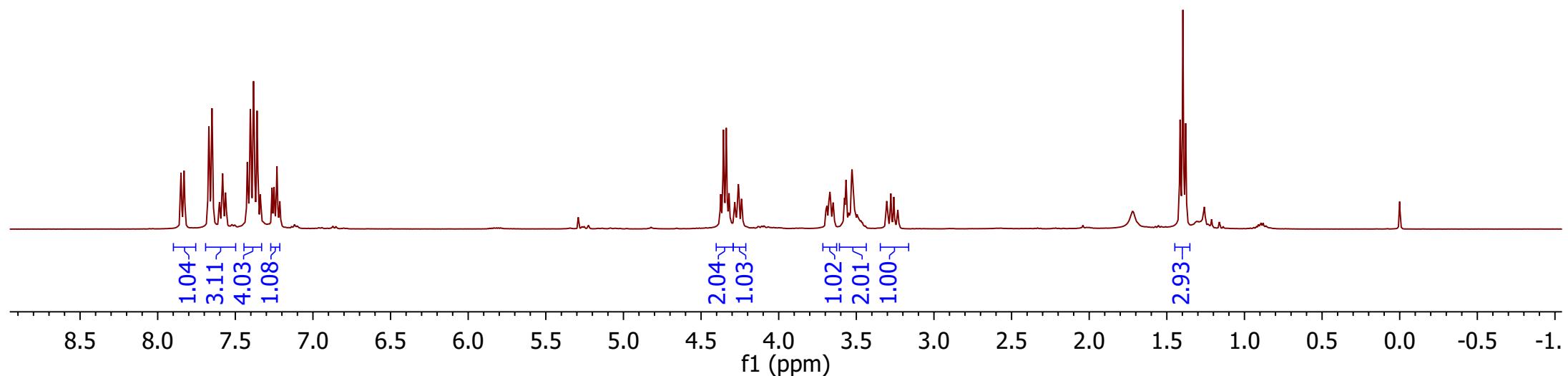
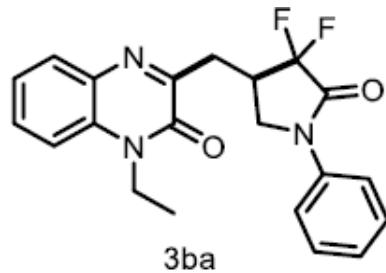
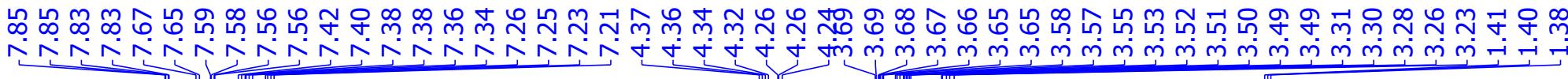


-108.94  
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-109.69  
-116.07  
-116.12  
-116.78  
-116.83



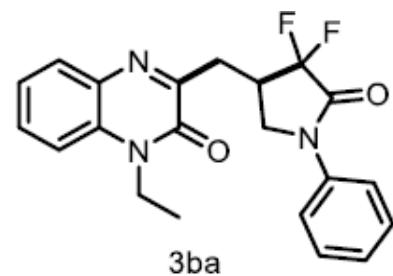
<sup>19</sup>F NMR Spectrum of 3aa

**1H (CDCl<sub>3</sub>, 400 MHz)**



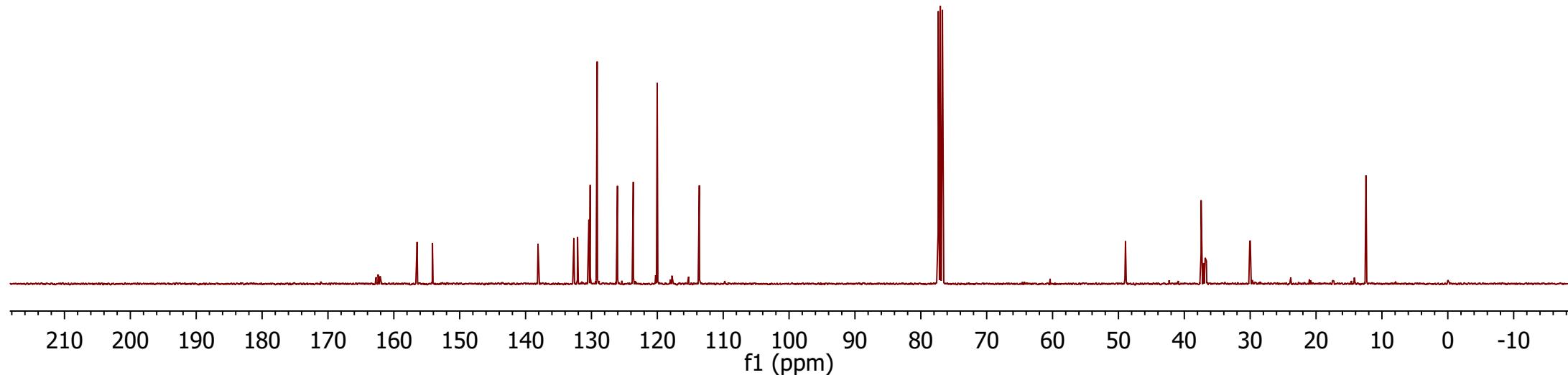
<sup>1</sup>H NMR Spectrum of 3ba

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



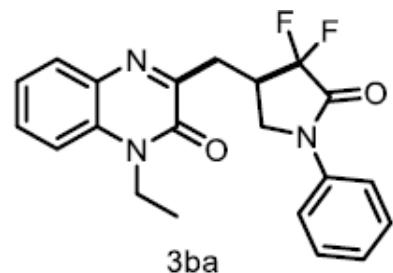
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162.1  
156.5  
154.1  
138.1  
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132.1  
130.4  
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126.1  
123.7  
120.3  
120.0  
117.8  
117.7  
115.3  
113.6

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36.6  
30.1  
30.0  
12.4

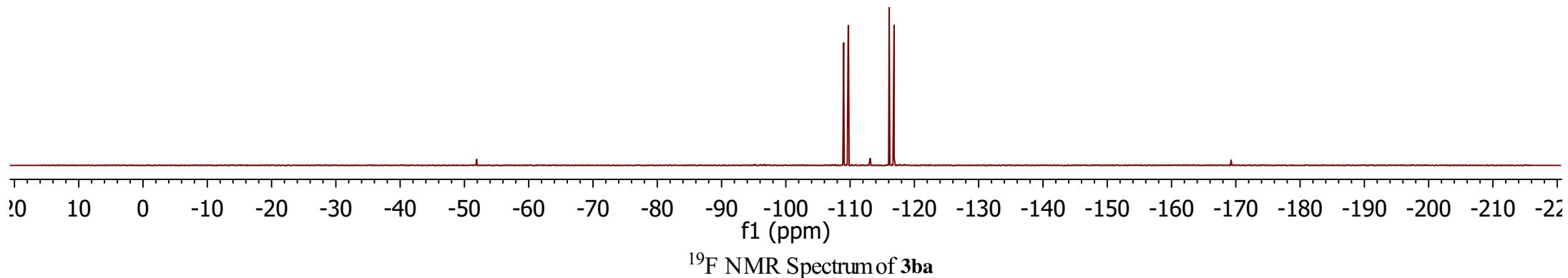


<sup>13</sup>C NMR Spectrum of 3ba

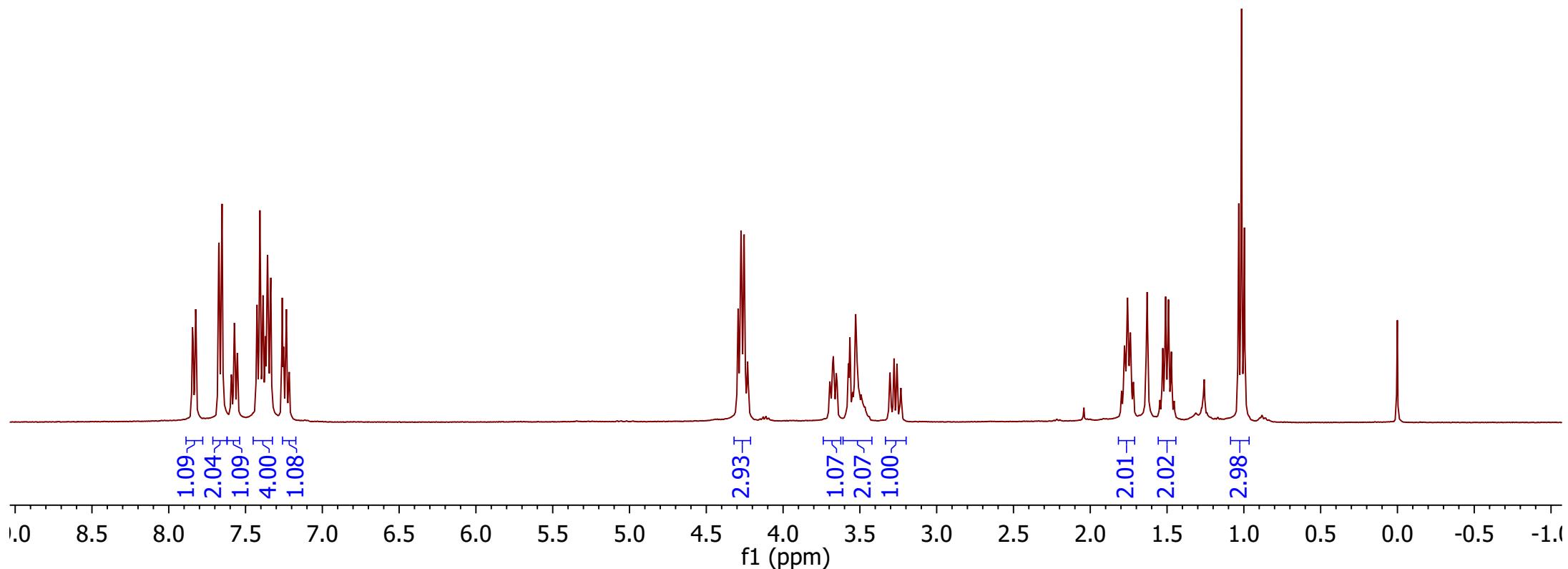
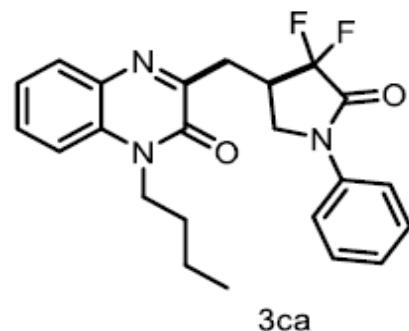
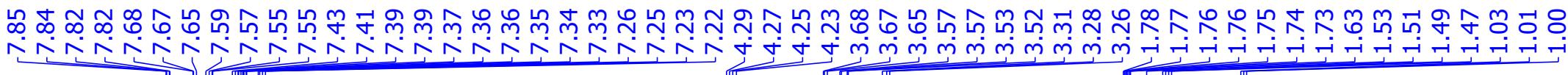
**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



-108.99  
-109.03  
-109.70  
-109.74  
-116.08  
-116.13  
-116.79  
-116.84

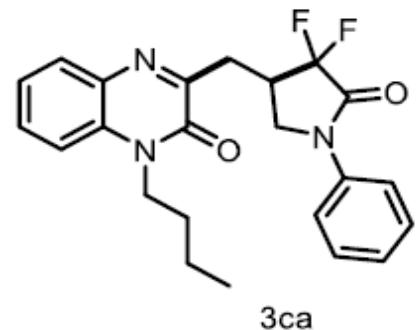


**1H (CDCl<sub>3</sub>, 400 MHz)**



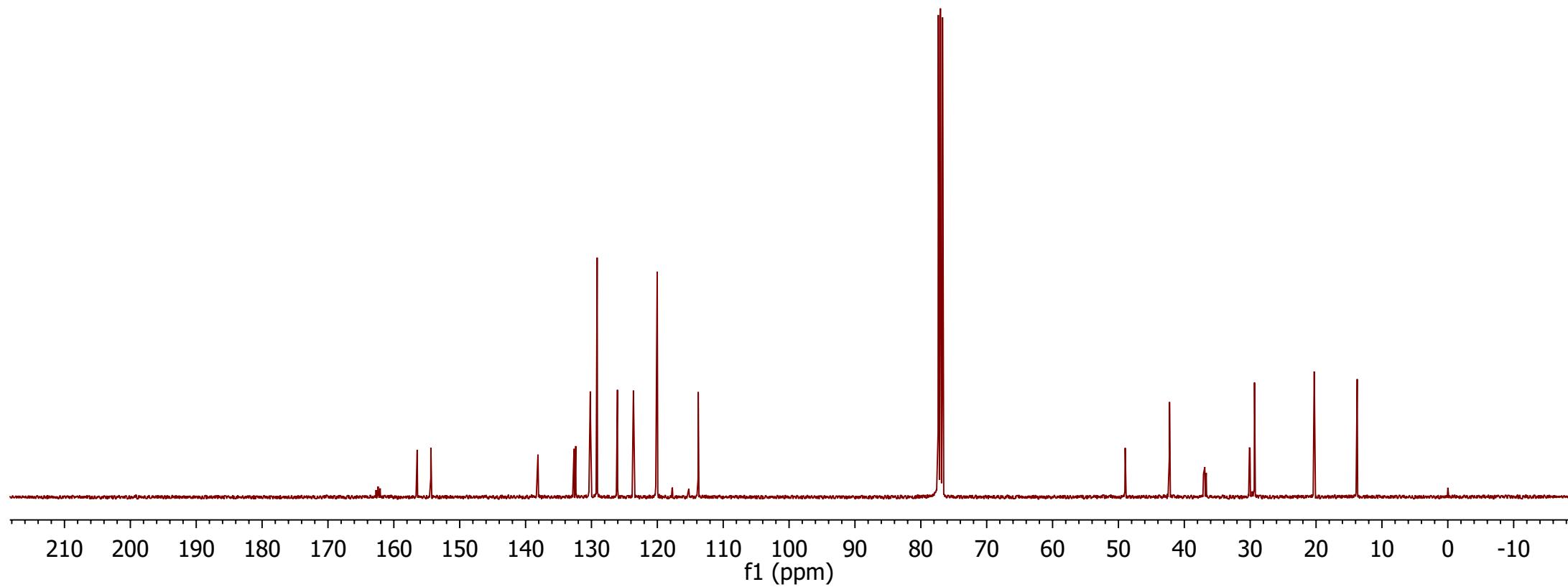
<sup>1</sup>H NMR Spectrum of 3ca

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



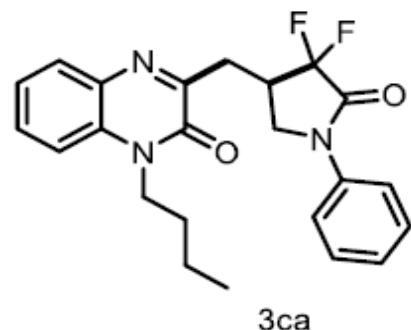
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117.7  
115.2  
113.8

49.0  
48.9  
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36.9  
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30.0  
29.3  
20.3  
-13.8

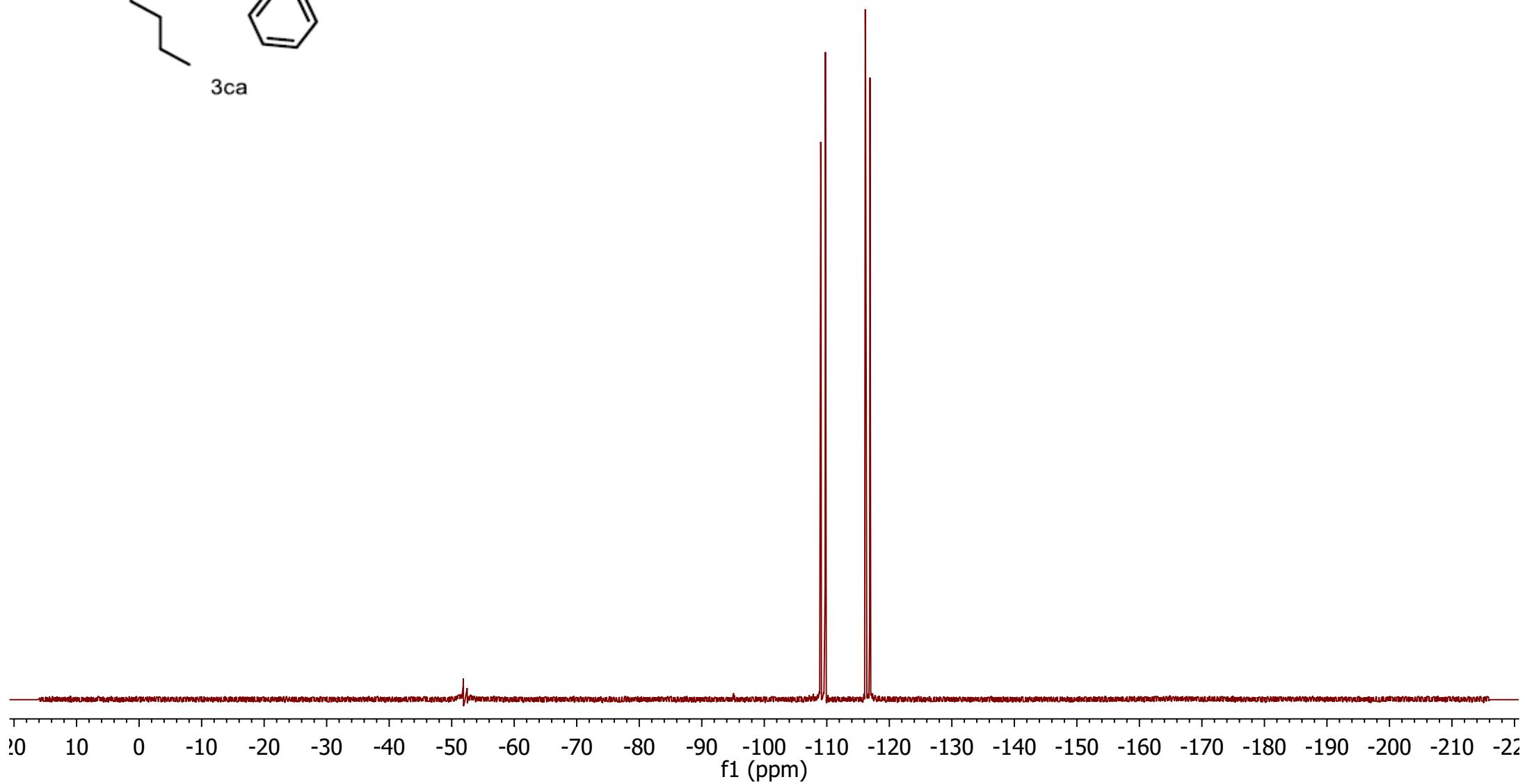


<sup>13</sup>C NMR Spectrum of 3ca

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



-109.03  
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-109.74  
-109.78  
-116.15  
-116.20  
-116.86  
-116.91

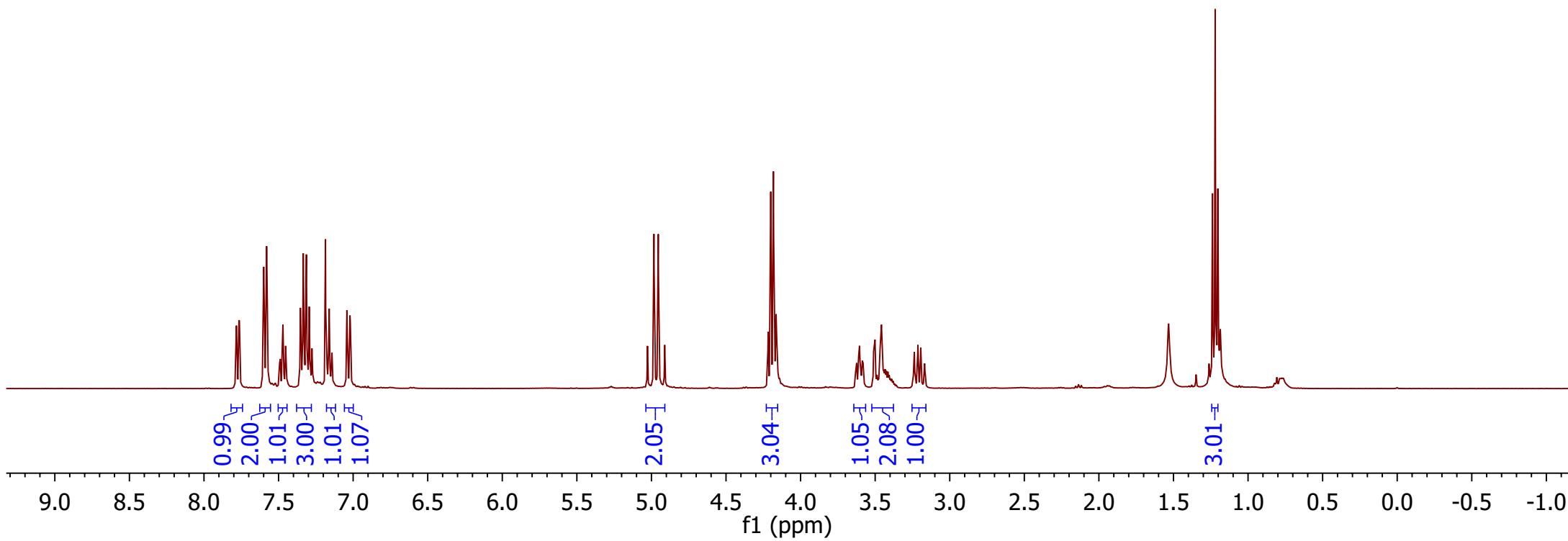


<sup>19</sup>F NMR Spectrum of 3ca

**1H (CDCl<sub>3</sub>, 400 MHz)**

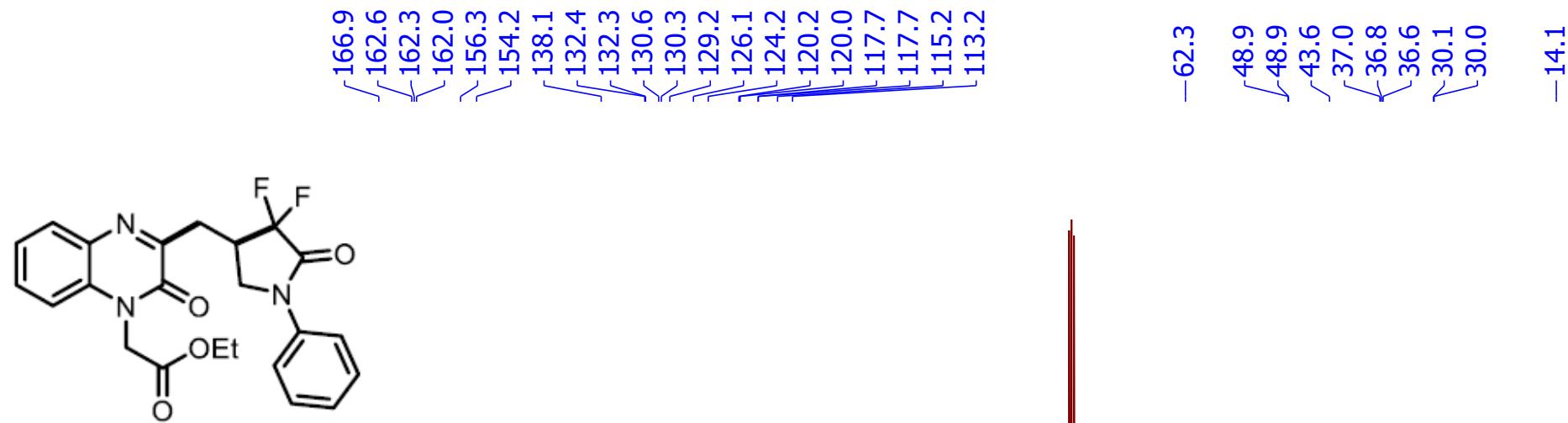


3da

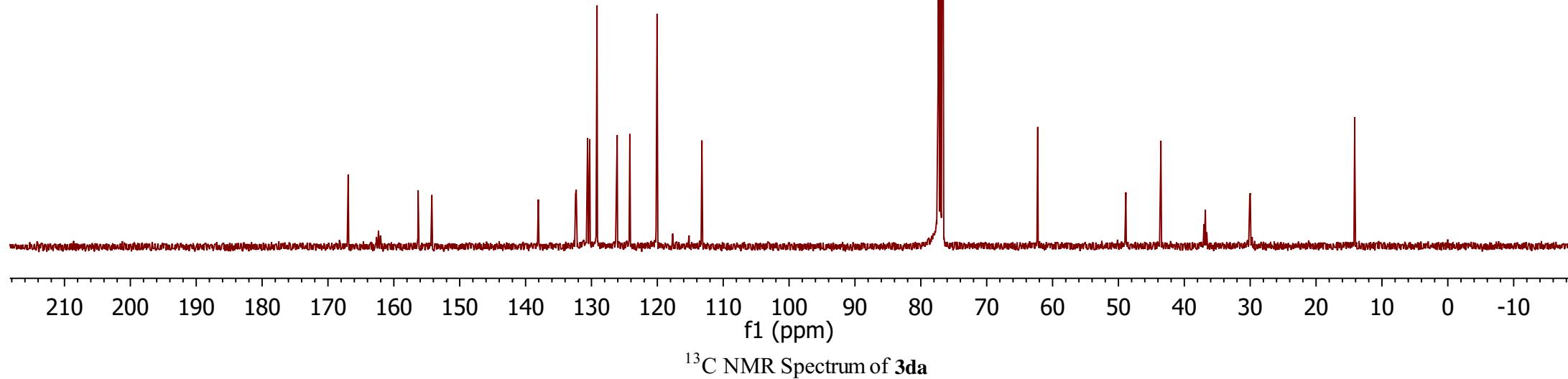


<sup>1</sup>H NMR Spectrum of 3da

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)

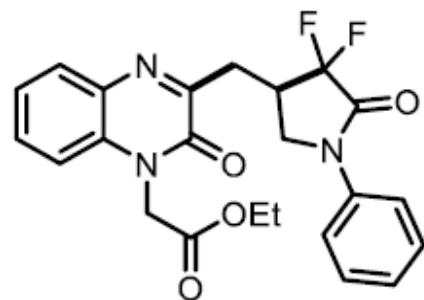


3da



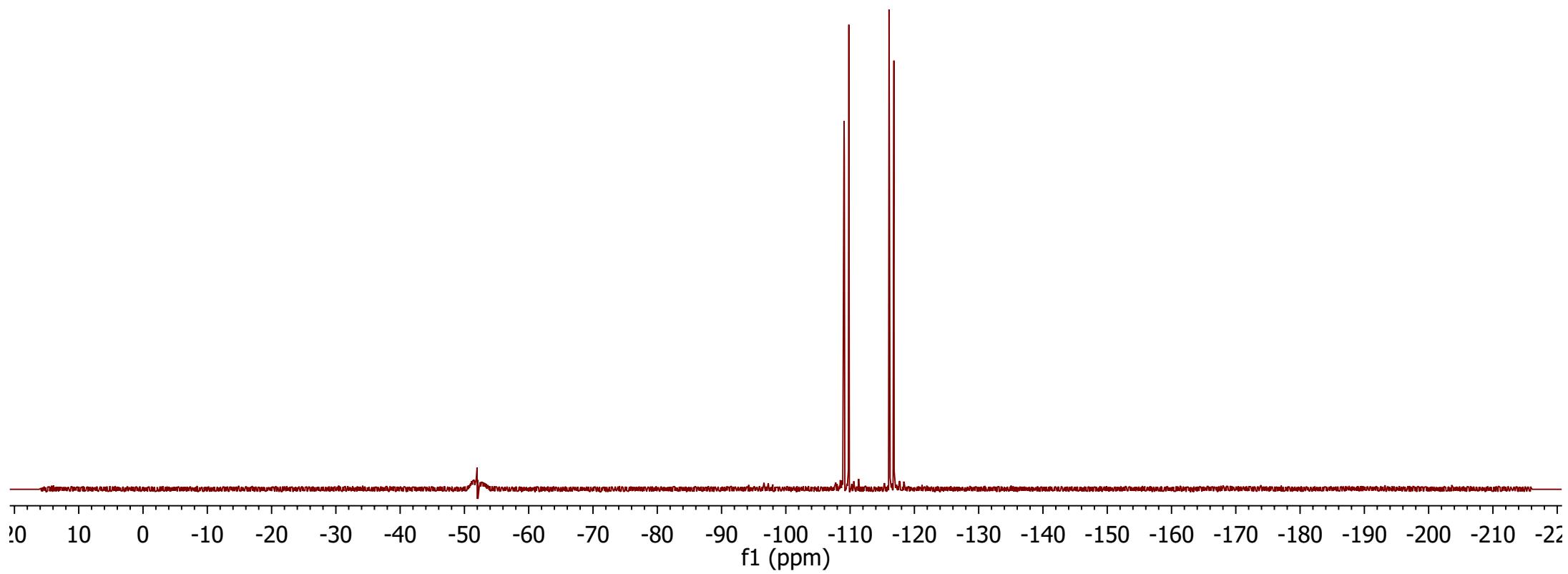
<sup>13</sup>C NMR Spectrum of 3da

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



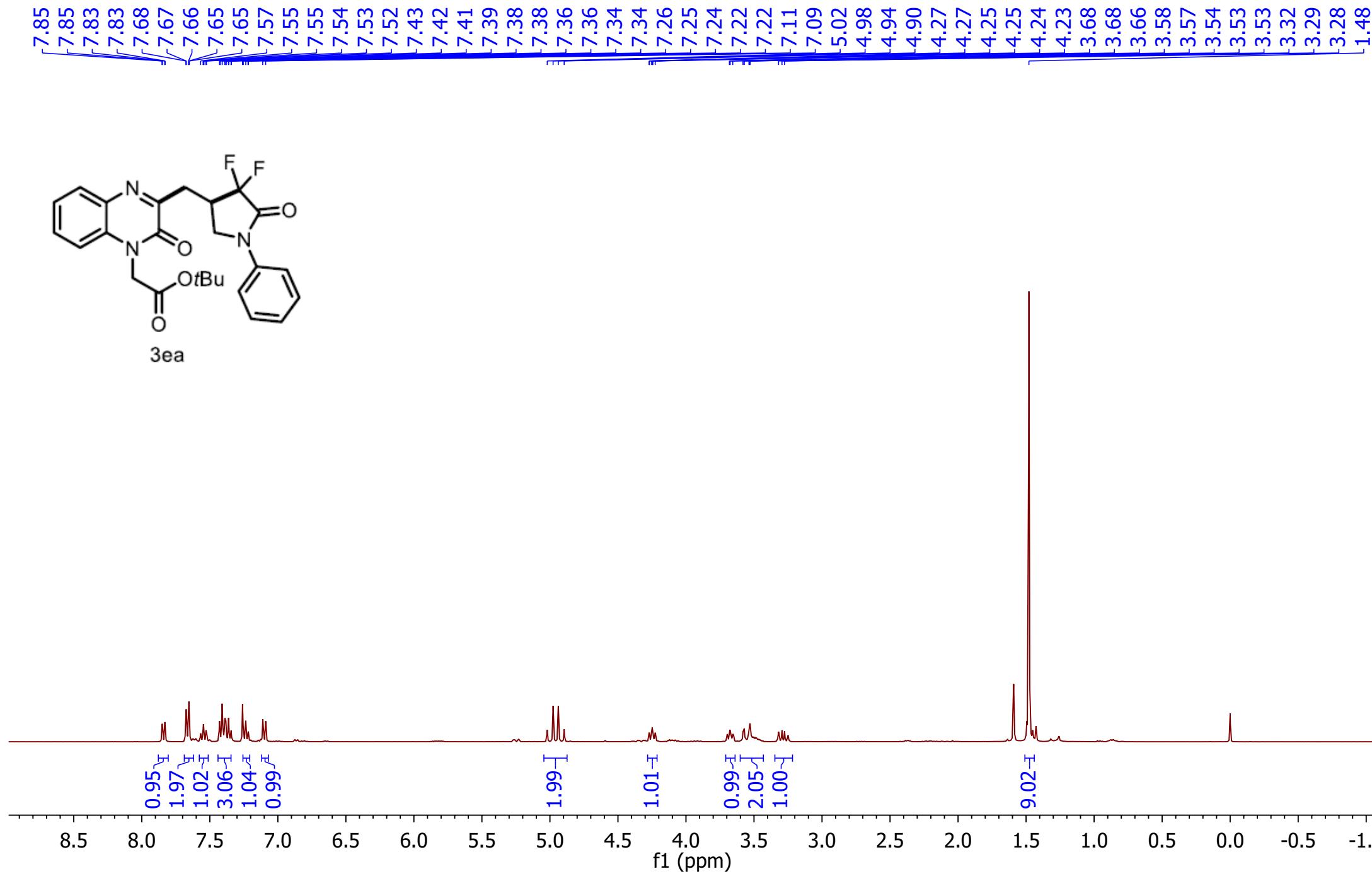
3da

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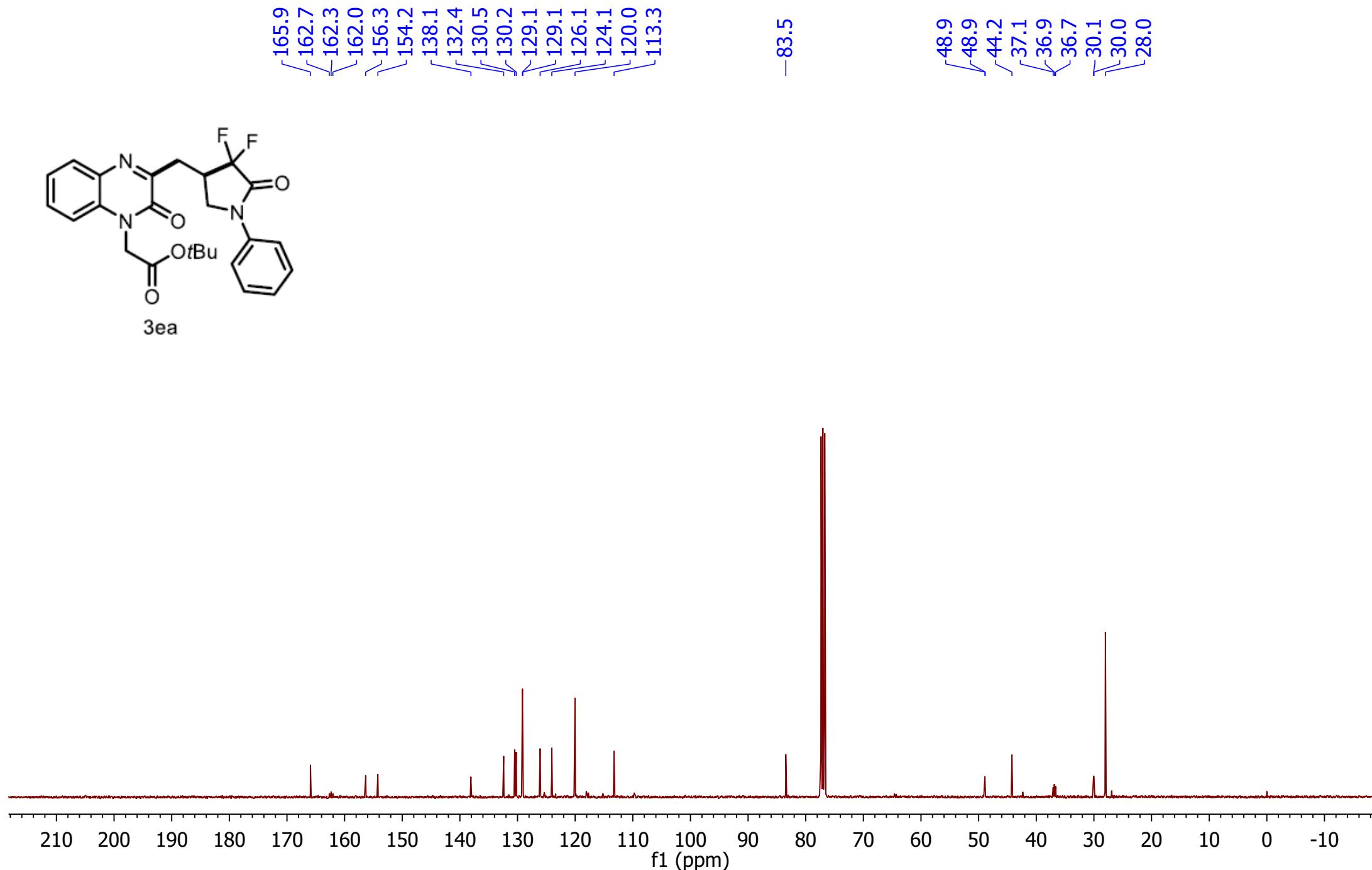
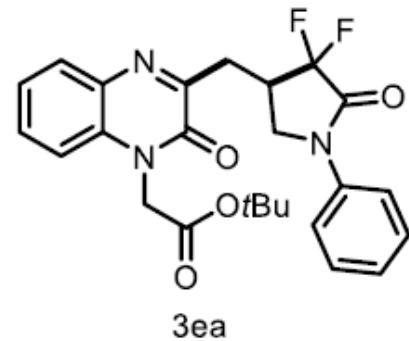
<sup>19</sup>F NMR Spectrum of 3da

**<sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz)**



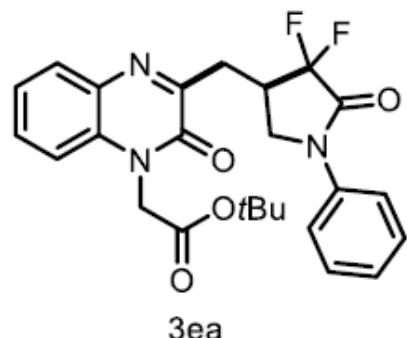
<sup>1</sup>H NMR Spectrum of 3ea

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

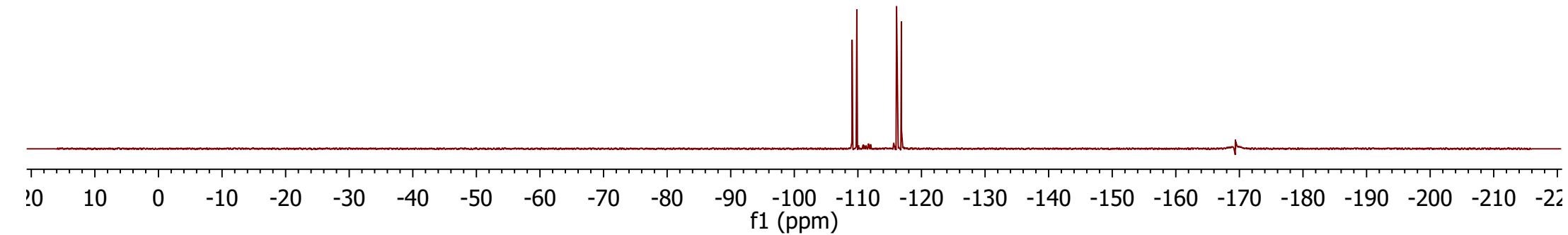


<sup>13</sup>C NMR Spectrum of 3ea

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

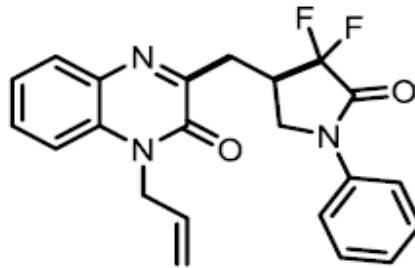


-109.09  
-109.12  
-109.80  
-109.83  
-116.08  
-116.13  
-116.79  
-116.84

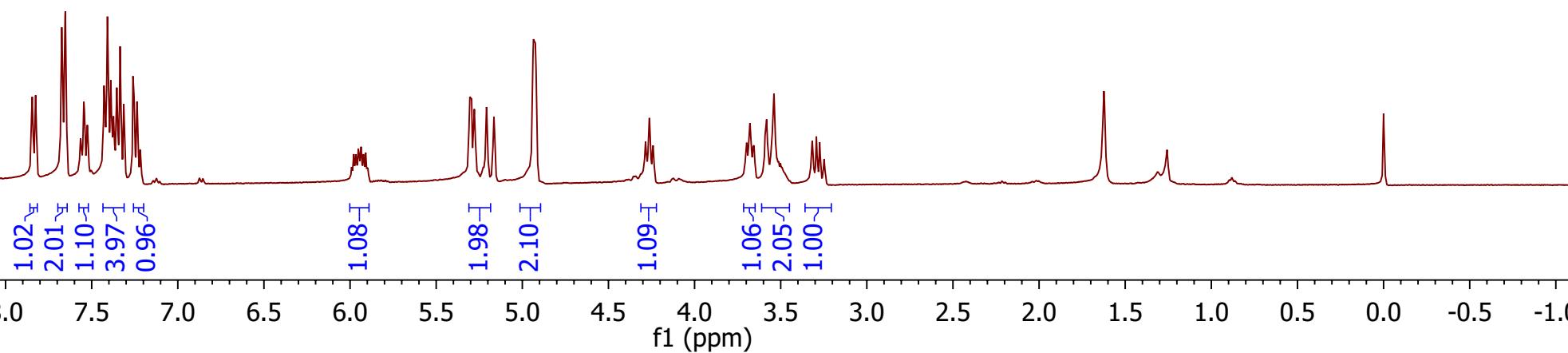


<sup>19</sup>F NMR Spectrum of 3ea

**1H (CDCl<sub>3</sub>, 400 MHz)**

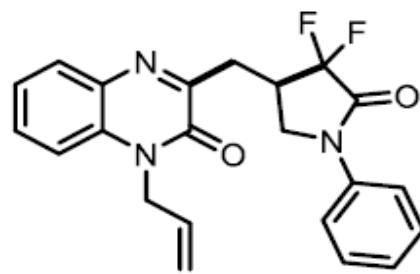


3fa



<sup>1</sup>H NMR Spectrum of 3fa

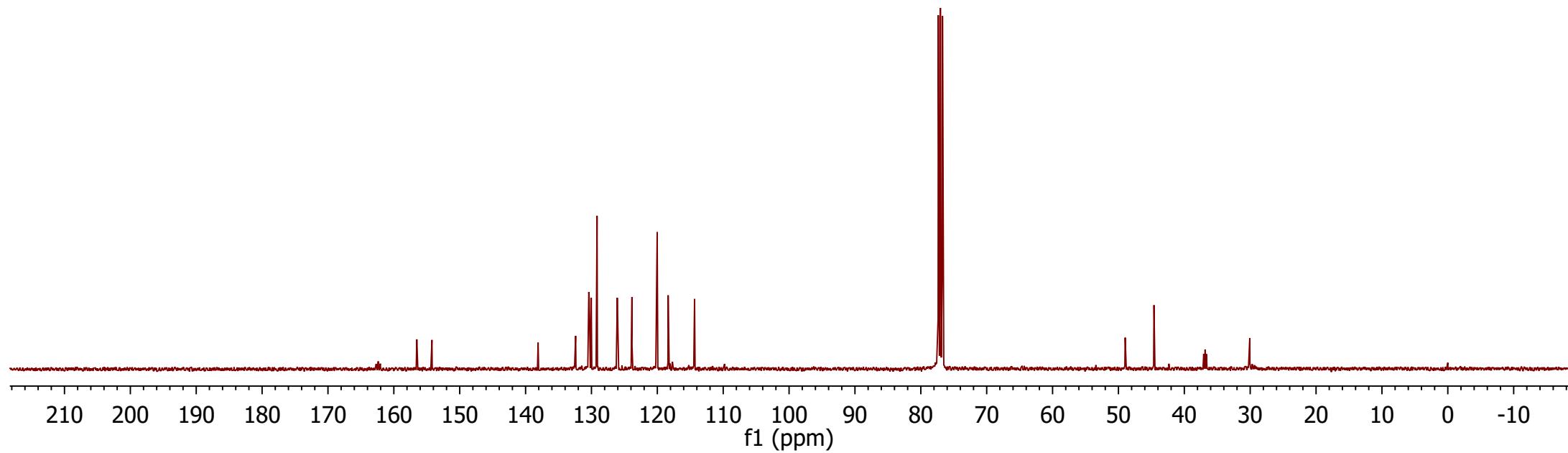
**13C (CDCl<sub>3</sub>, 101 MHz)**



3fa

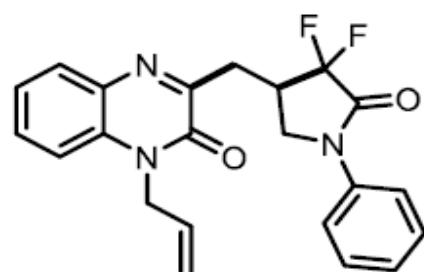
162.7  
162.4  
162.1  
156.5  
154.2  
138.1  
132.5  
132.4  
130.4  
130.3  
130.0  
129.1  
126.1  
123.9  
120.2  
120.0  
118.4  
117.7  
114.3  
109.8

49.0  
48.9  
44.6  
37.1  
36.9  
36.8  
36.6  
30.1  
29.7



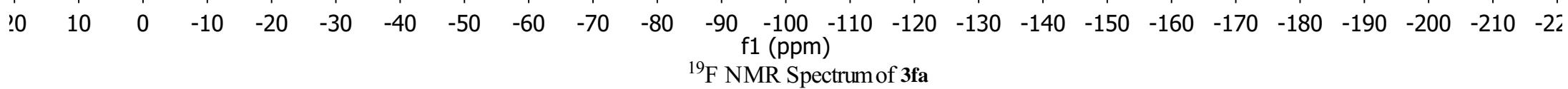
<sup>13</sup>C NMR Spectrum of 3fa

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



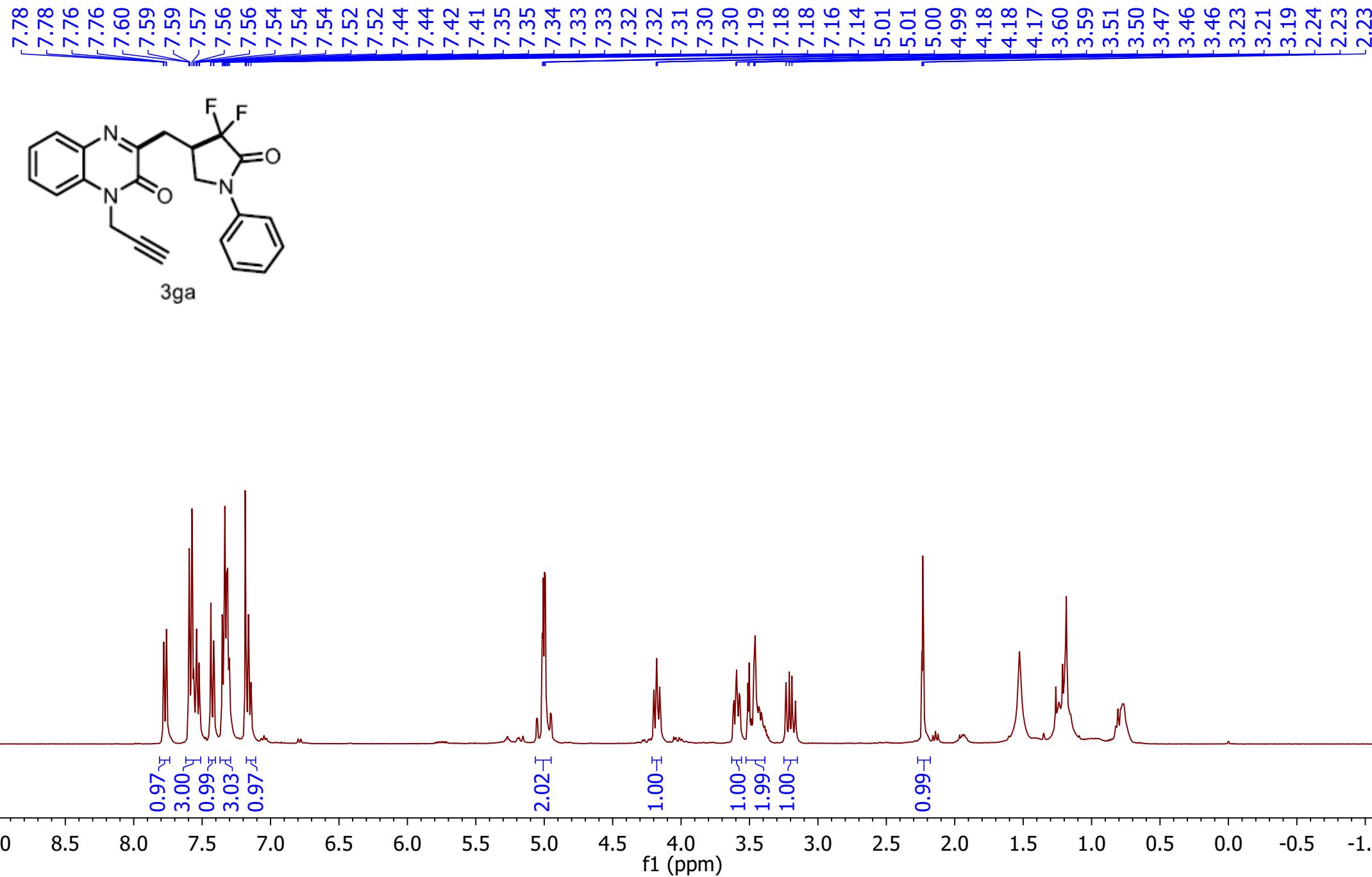
3fa

-109.00  
-109.04  
-109.71  
-109.75  
-116.10  
-116.15  
-116.81  
-116.86



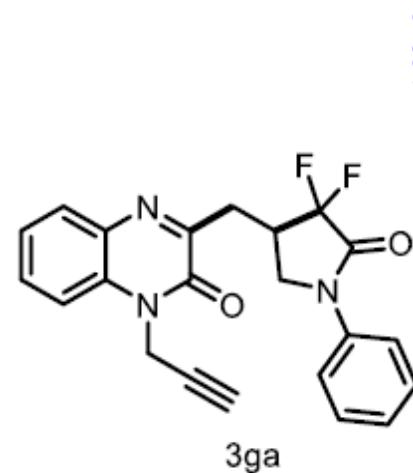
<sup>19</sup>F NMR Spectrum of 3fa

## **1H (CDCl<sub>3</sub>, 400 MHz)**



### <sup>1</sup>H NMR Spectrum of 3ga

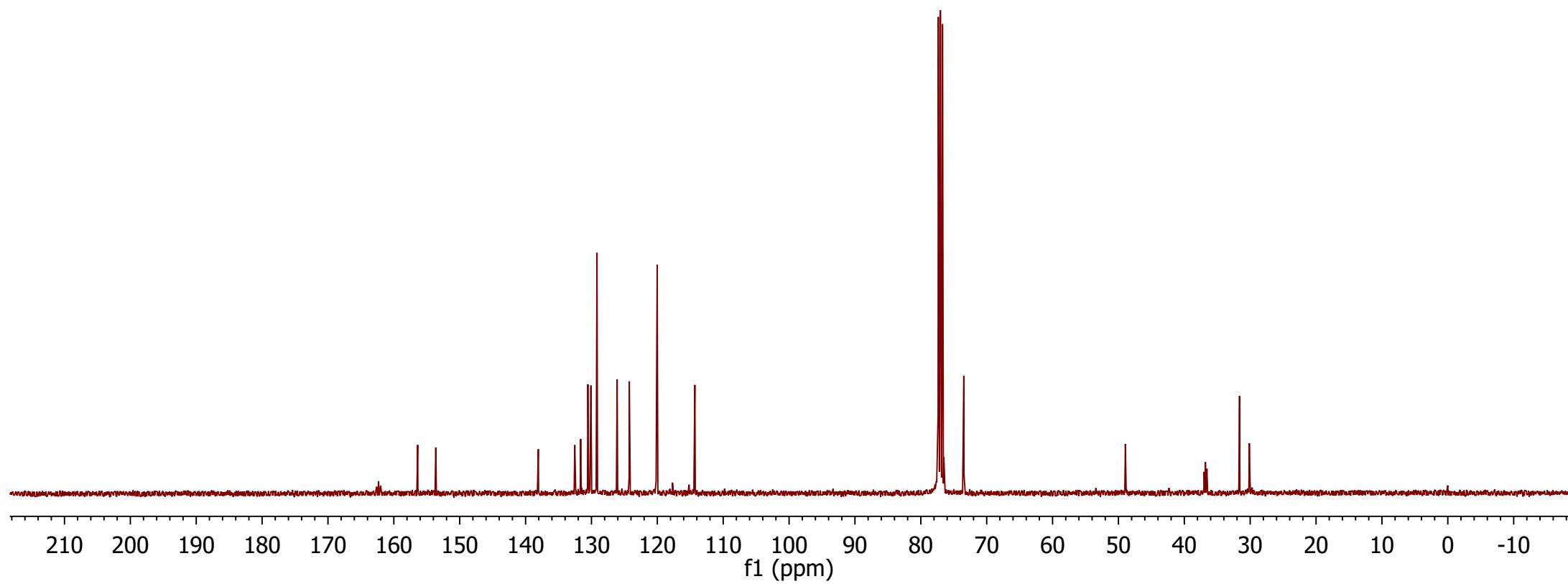
**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



162.6  
162.3  
162.0  
156.4  
153.6  
138.1  
132.5  
131.6  
130.5  
130.1  
129.2  
126.1  
124.3  
120.2  
120.0  
117.7  
115.2  
114.3

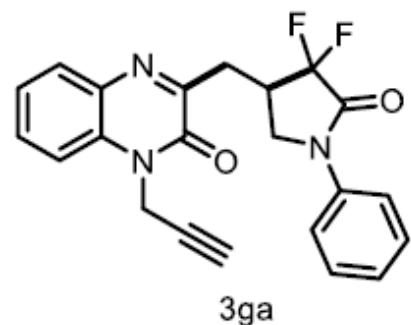
~76.5  
~73.5

48.9  
48.9  
37.0  
36.8  
36.8  
36.6  
36.6  
31.6  
30.1  
30.1

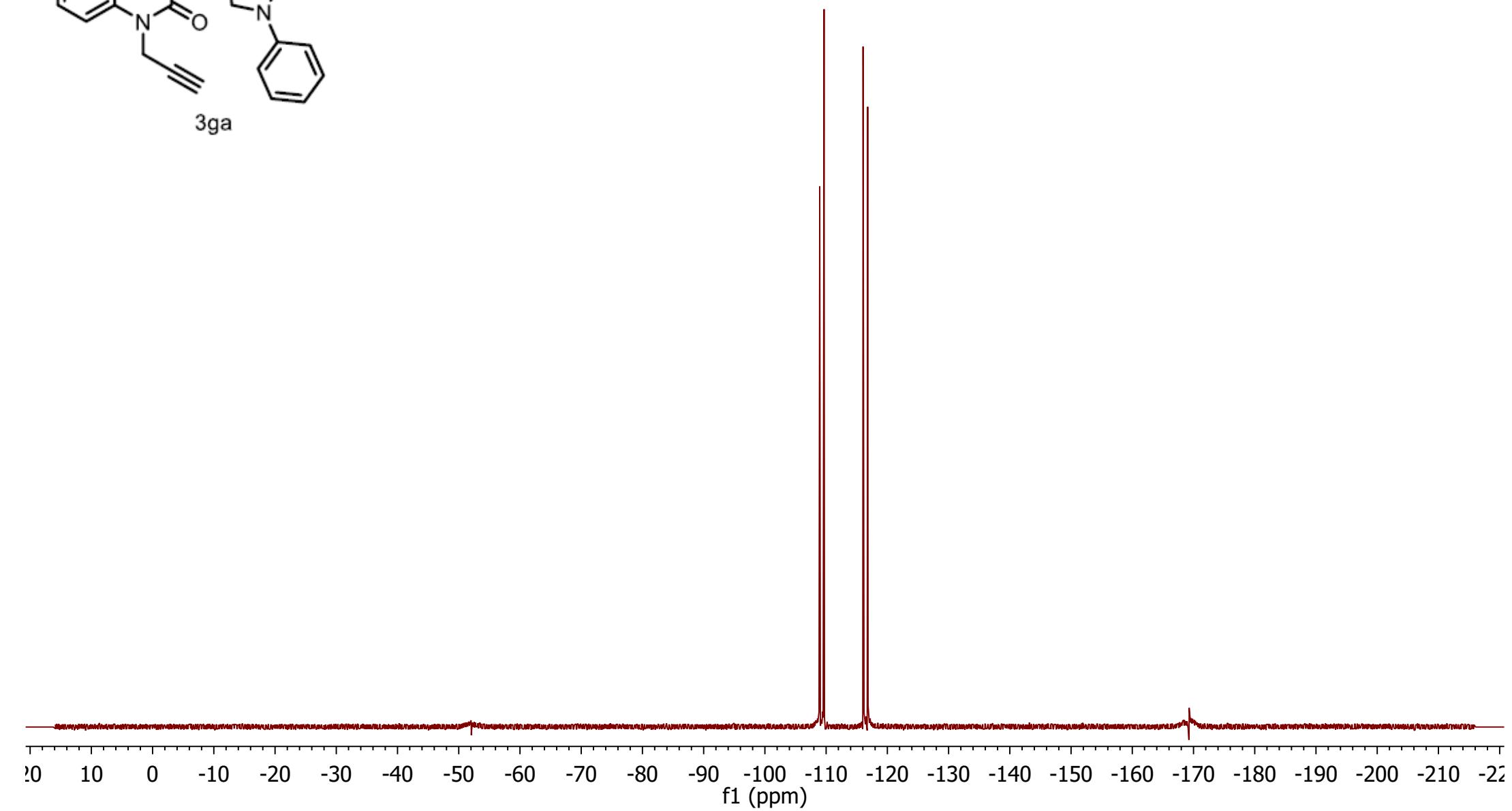


<sup>13</sup>C NMR Spectrum of 3ga

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

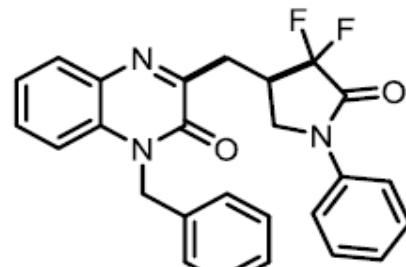
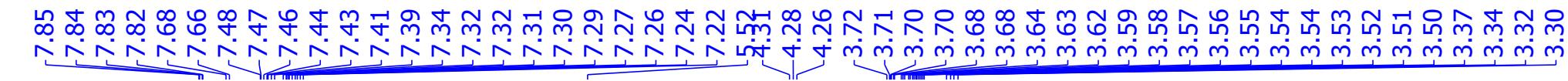


-108.95  
-108.99  
-109.67  
-109.70  
-116.03  
-116.08  
-116.74  
-116.79

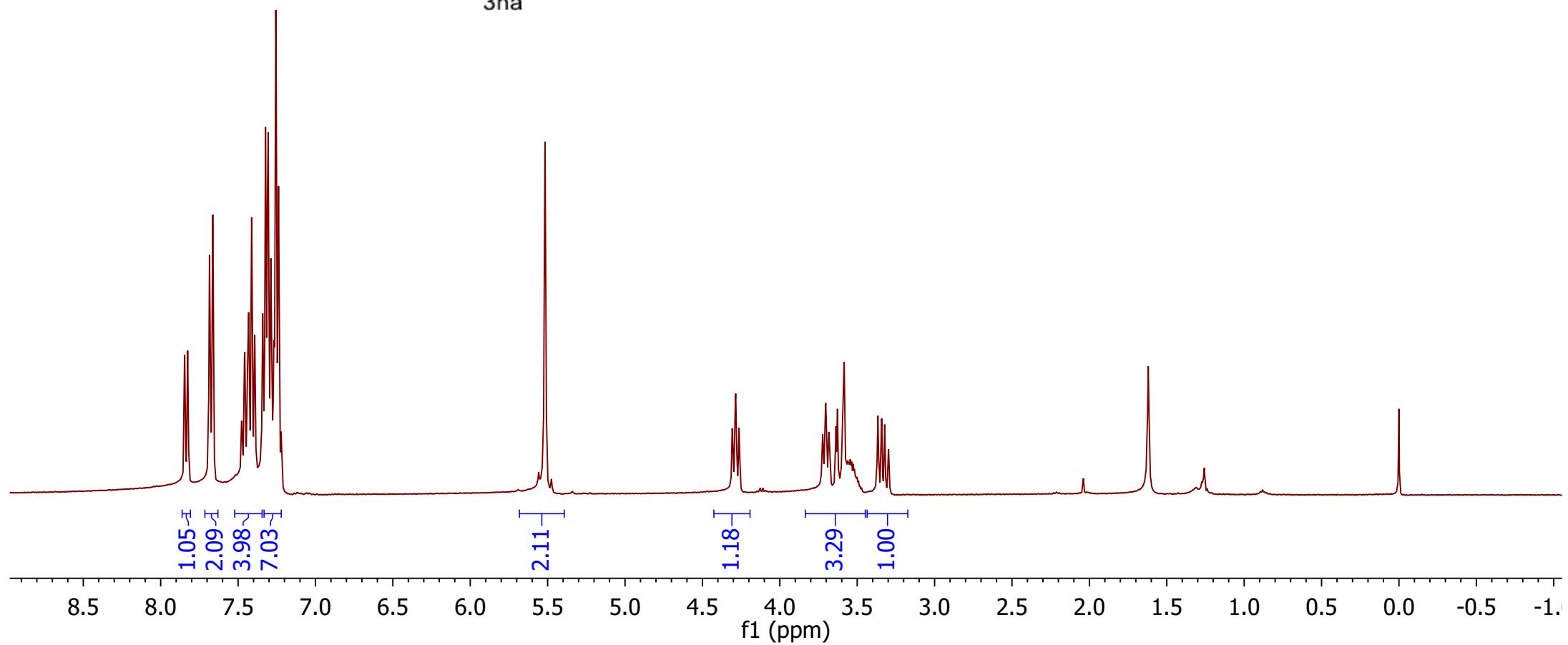


<sup>19</sup>F NMR Spectrum of 3ga

**1H (CDCl<sub>3</sub>, 400 MHz)**

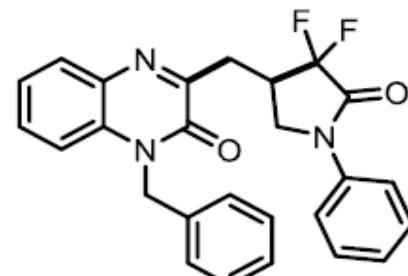


3ha

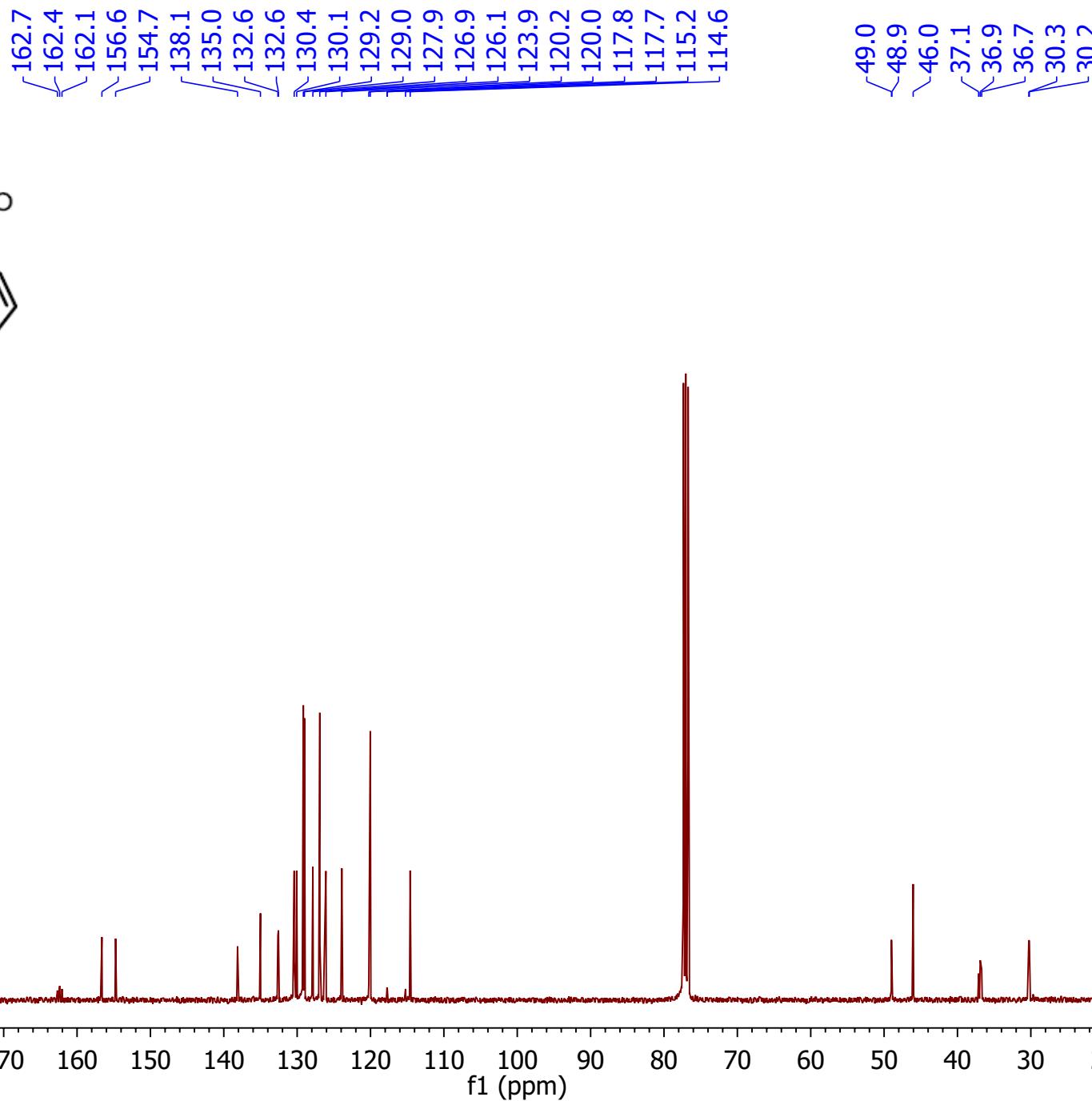


$^1\text{H}$  NMR Spectrum of 3ha

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)

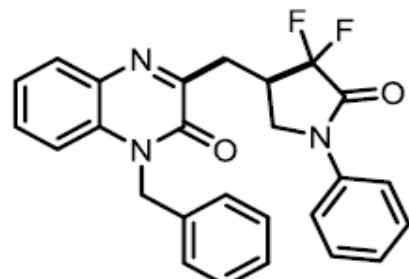


3ha



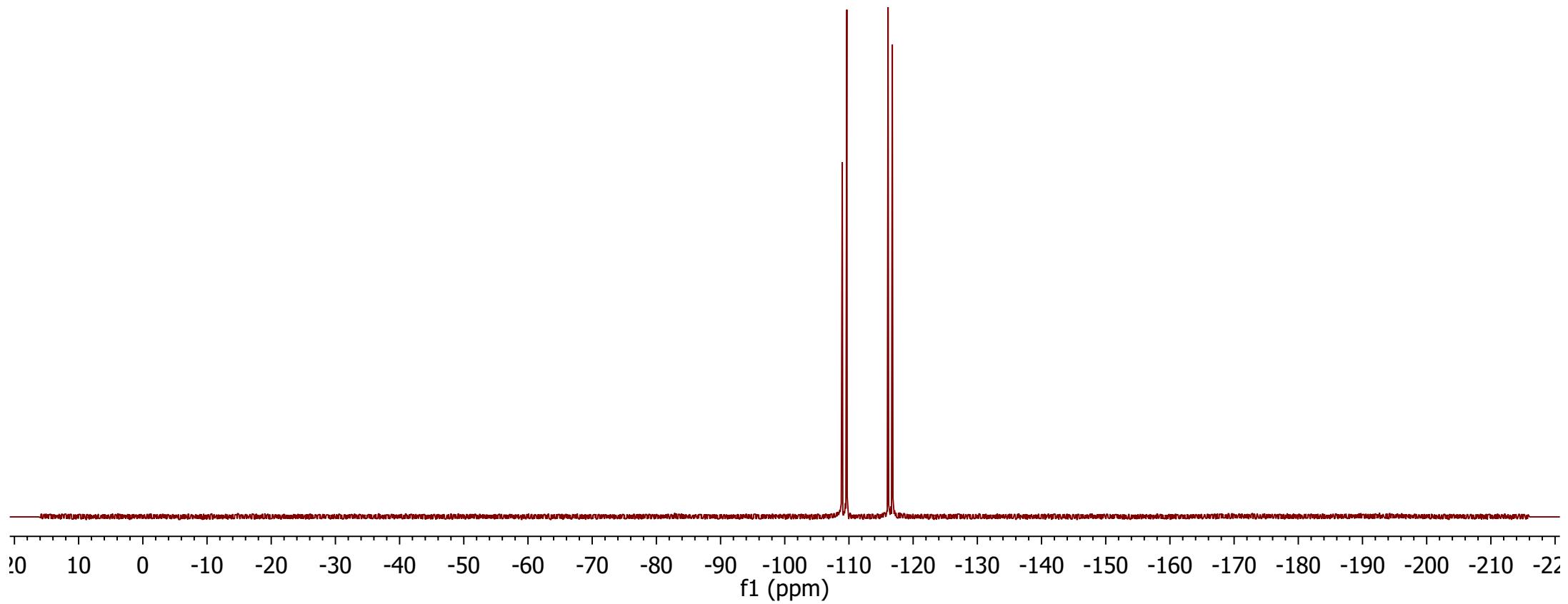
<sup>13</sup>C NMR Spectrum of 3ha

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



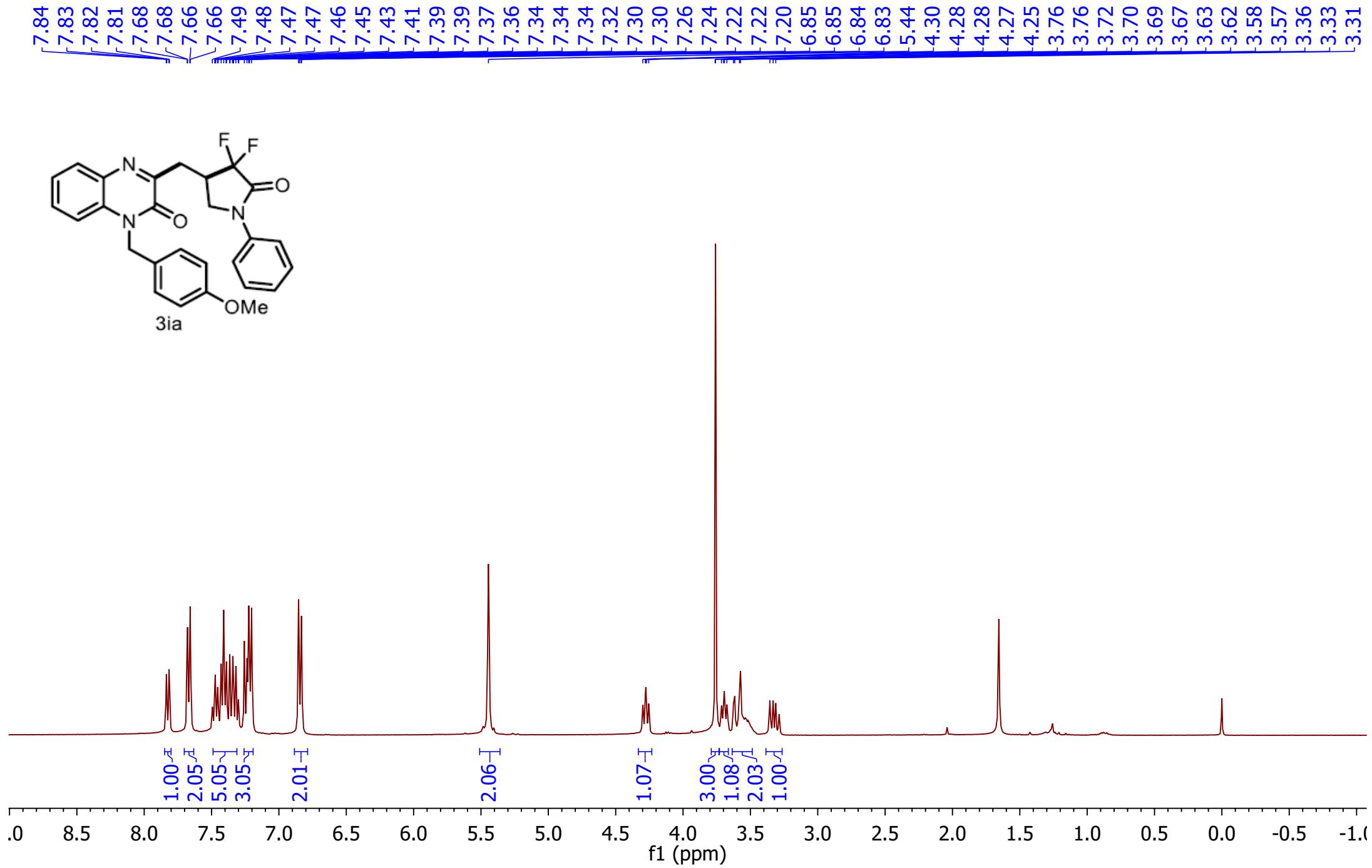
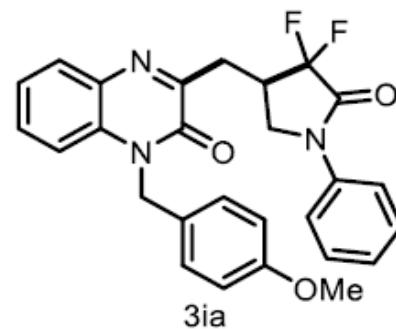
3ha

-108.96  
-109.00  
-109.67  
-109.71  
-116.04  
-116.09  
-116.76  
-116.80



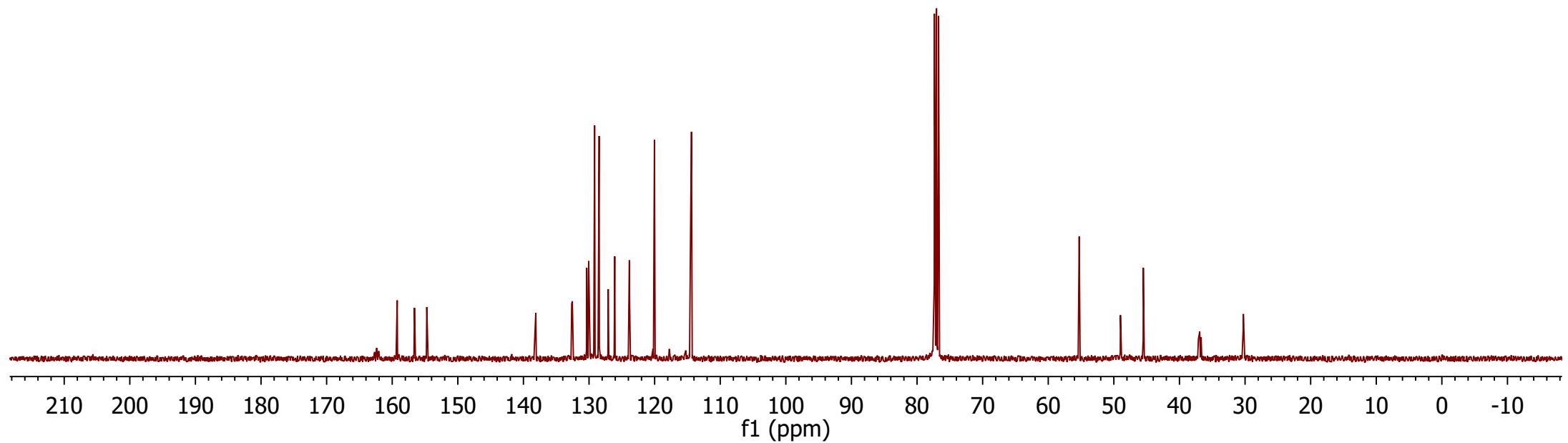
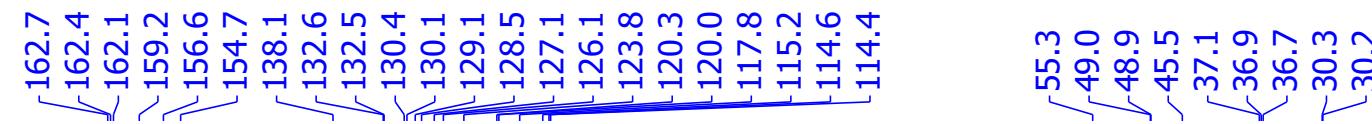
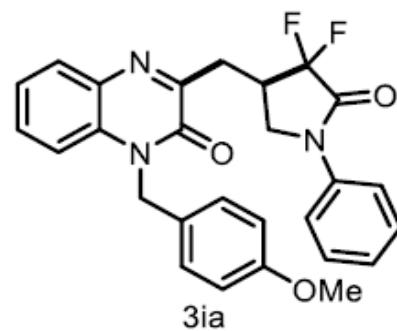
<sup>19</sup>F NMR Spectrum of 3ha

## **1H (CDCl<sub>3</sub>, 400 MHz)**



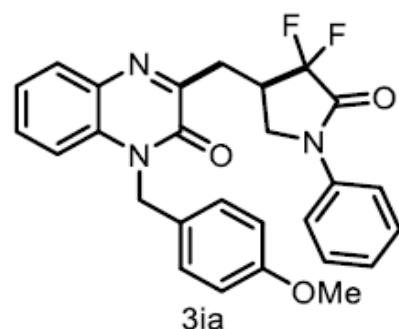
### <sup>1</sup>H NMR Spectrum of 3ia

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

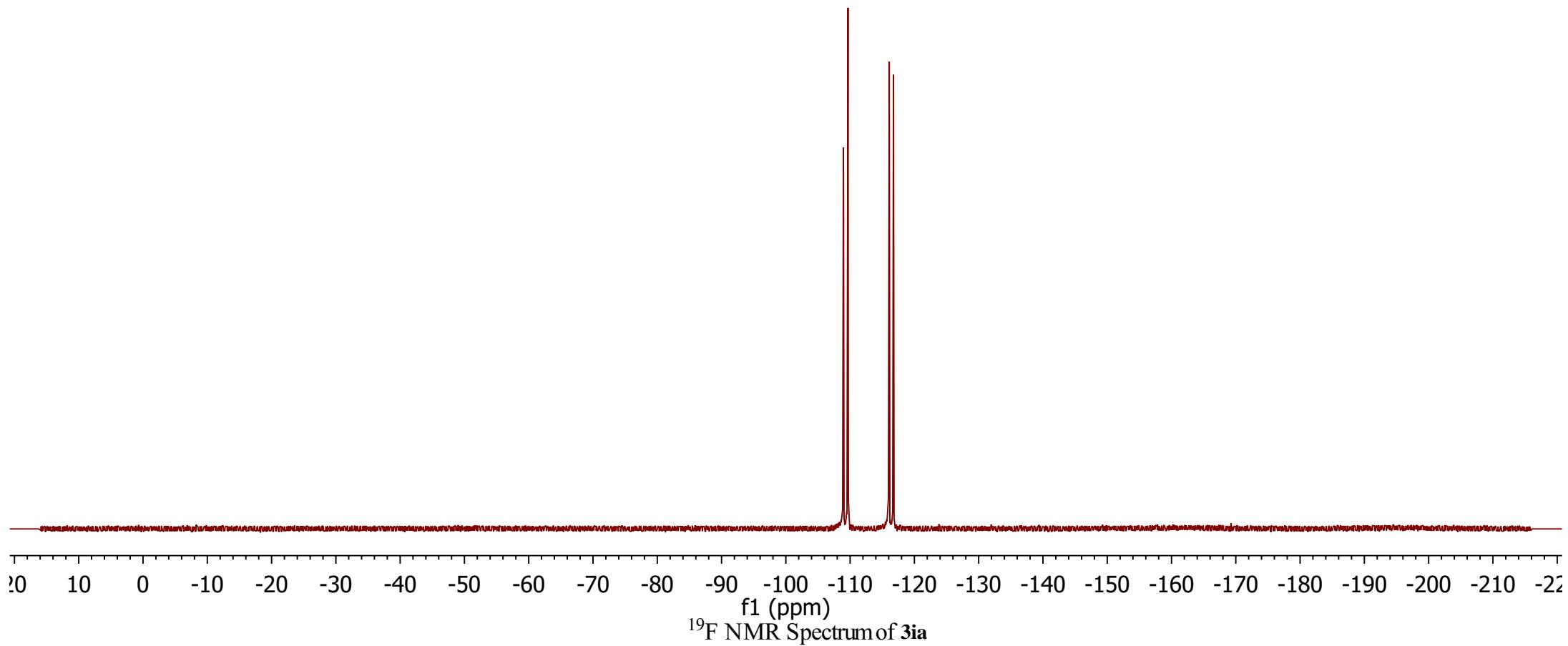


<sup>13</sup>C NMR Spectrum of 3ia

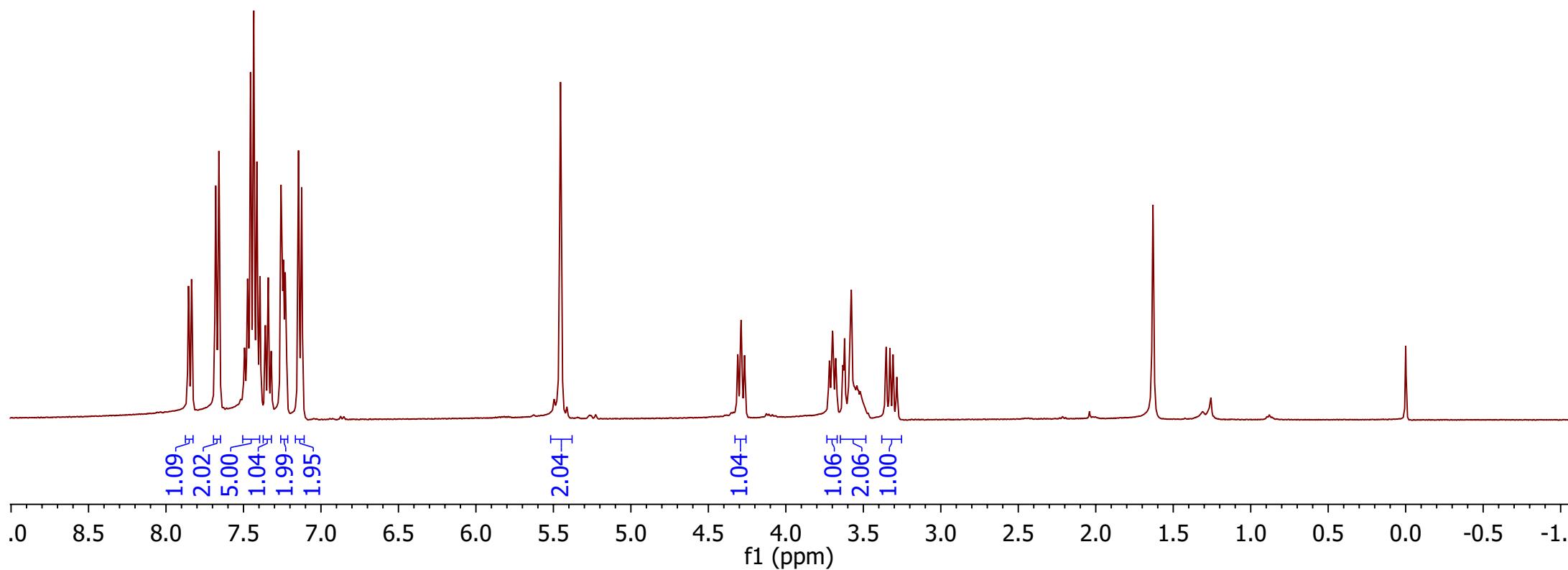
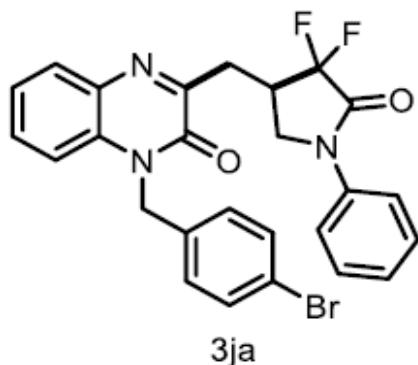
<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



-108.96  
-109.00  
-109.67  
-109.71  
-116.04  
-116.09  
-116.75  
-116.80

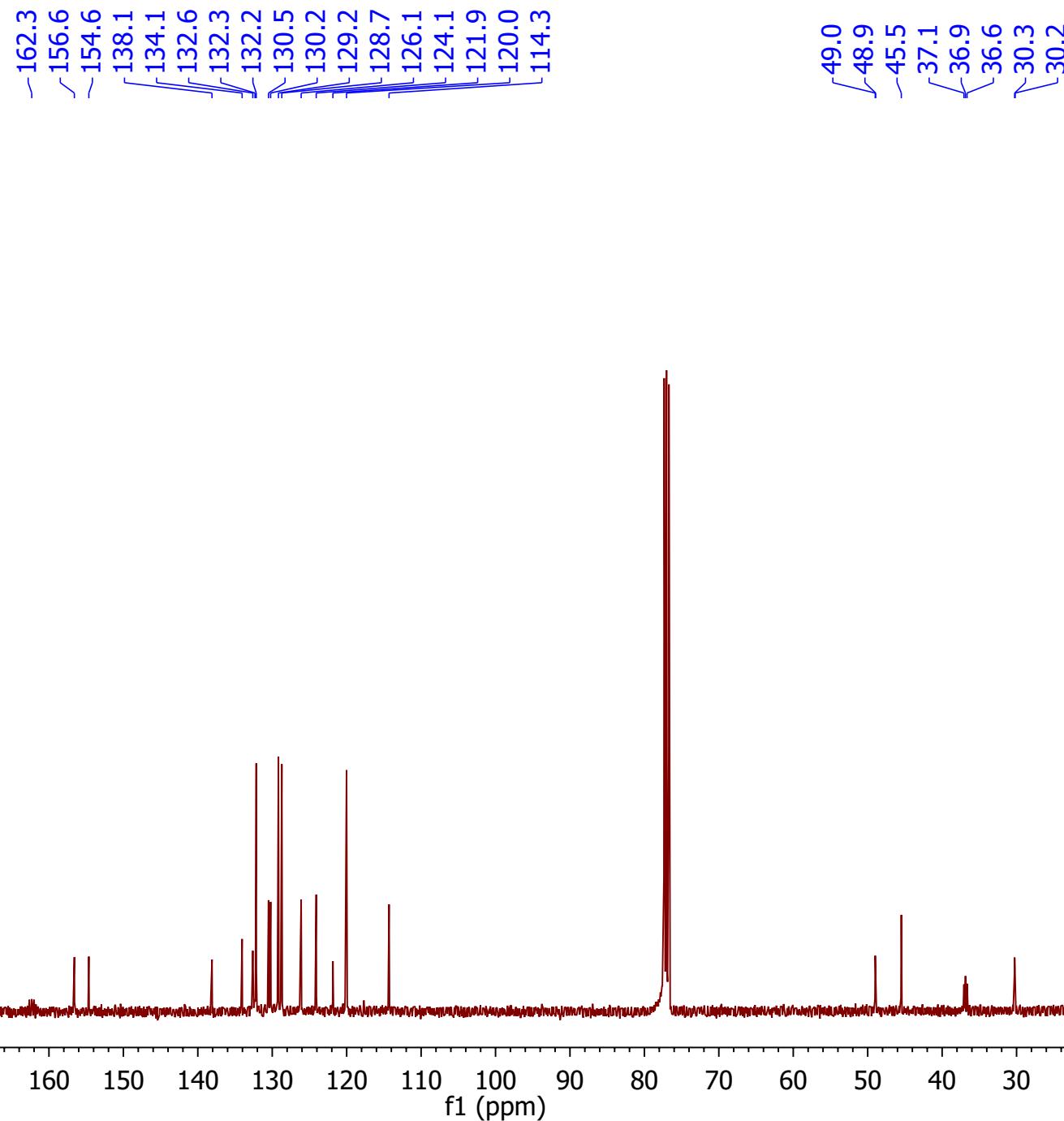
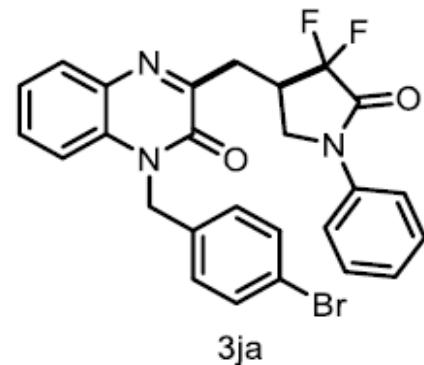


**1H (CDCl<sub>3</sub>, 400 MHz)**



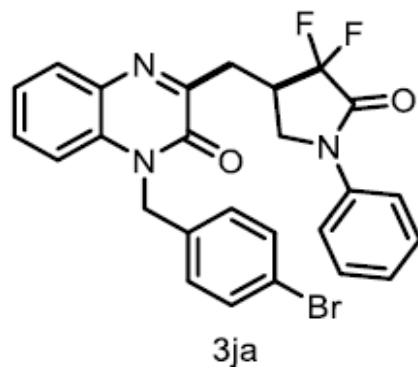
<sup>1</sup>H NMR Spectrum of **3ja**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

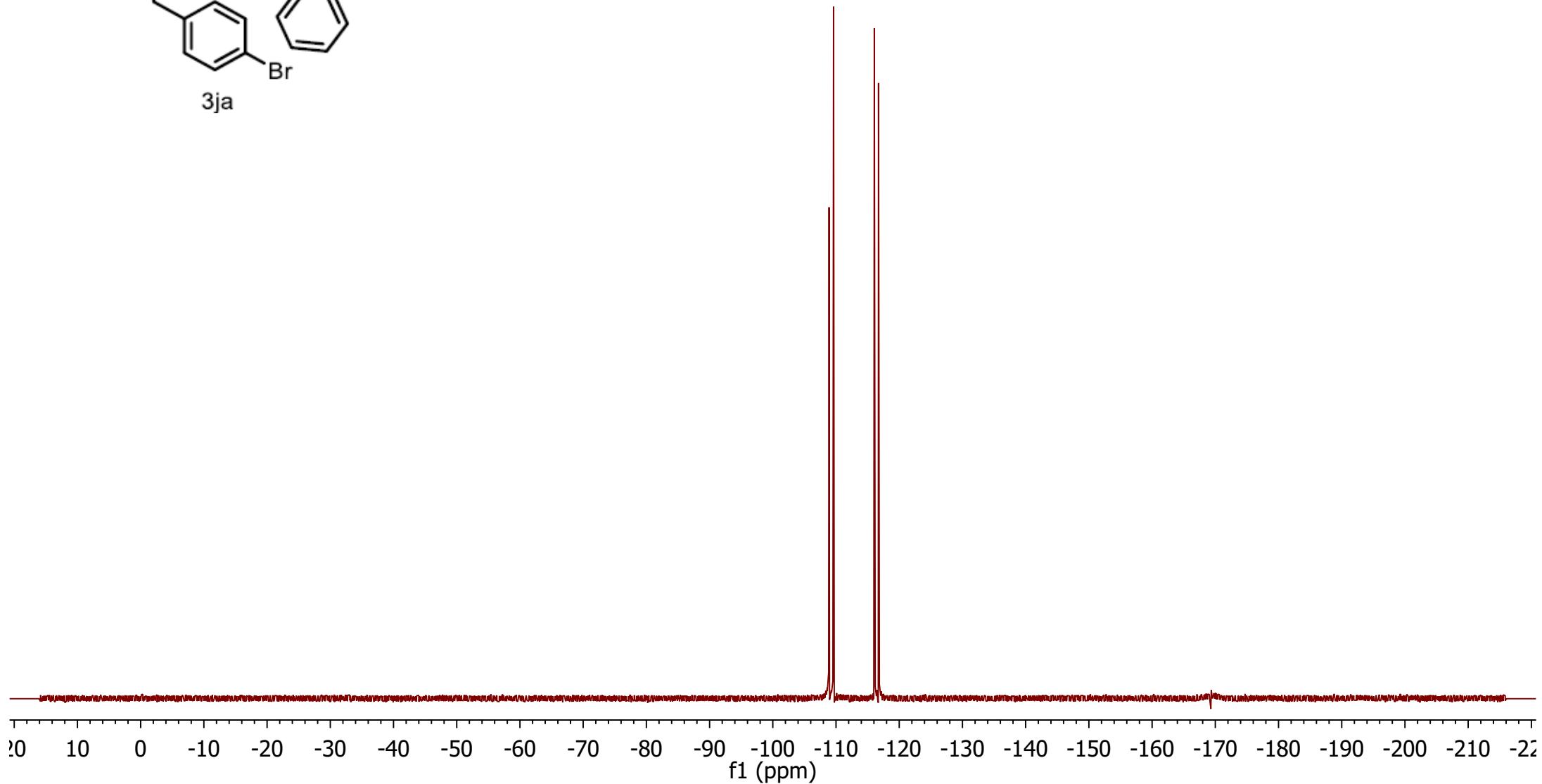


<sup>13</sup>C NMR Spectrum of 3ja

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

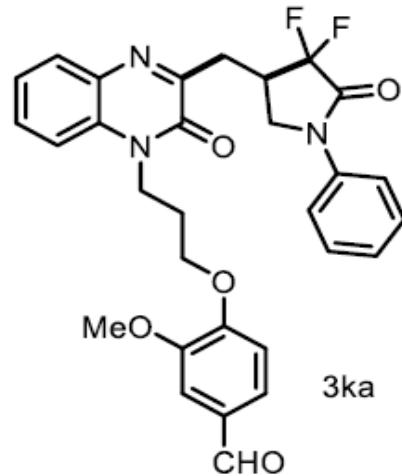


-108.90  
-108.94  
-109.61  
-109.65  
-116.01  
-116.06  
-116.72  
-116.77



<sup>19</sup>F NMR Spectrum of 3ja

**1H (CDCl<sub>3</sub>, 400 MHz)**



3ka

CHO

0.97<sup>—</sup>

0.95<sup>—</sup>  
0.97<sup>—</sup>  
3.13<sup>—</sup>  
1.07<sup>—</sup>  
4.02<sup>—</sup>  
1.05<sup>—</sup>  
0.99<sup>—</sup>

2.10<sup>—</sup>  
2.18<sup>—</sup>  
1.04<sup>—</sup>  
3.00<sup>—</sup>  
1.05<sup>—</sup>  
1.96<sup>—</sup>  
1.05<sup>—</sup>

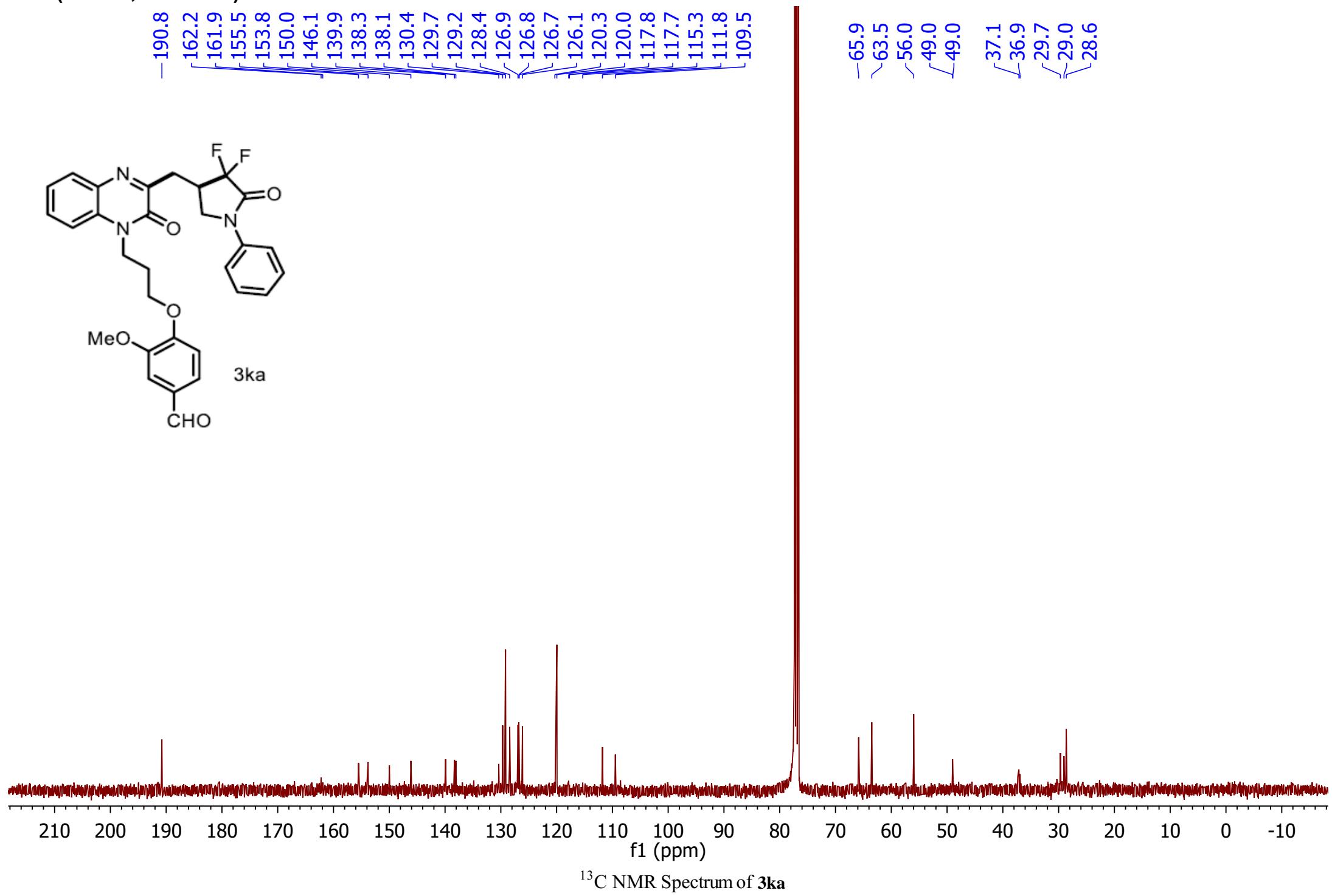
2.02<sup>—</sup>

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

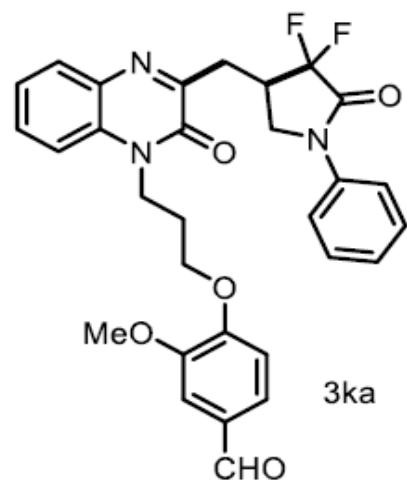
f1 (ppm)

<sup>1</sup>H NMR Spectrum of 3ka

**13C (CDCl<sub>3</sub>, 101 MHz)**

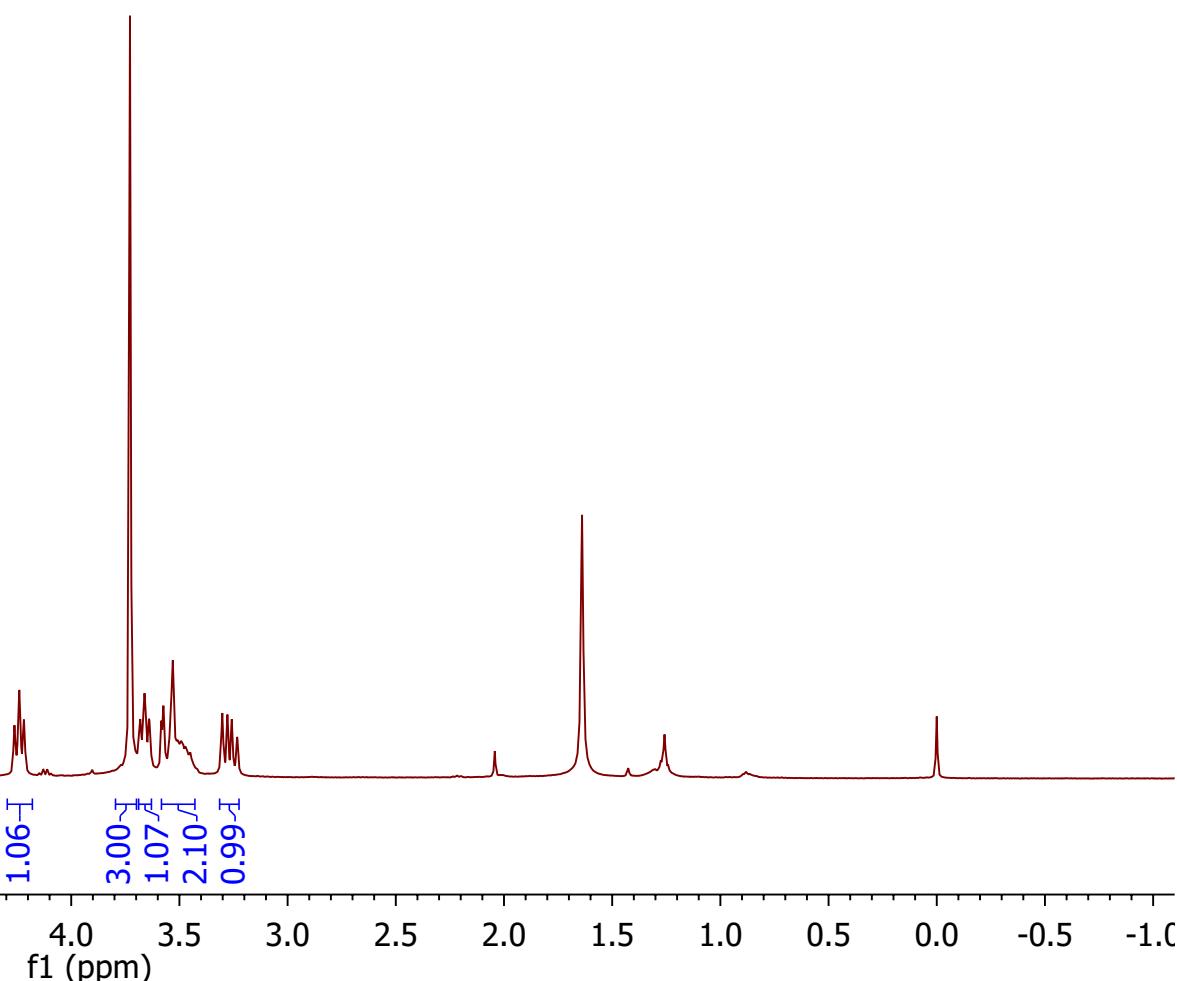
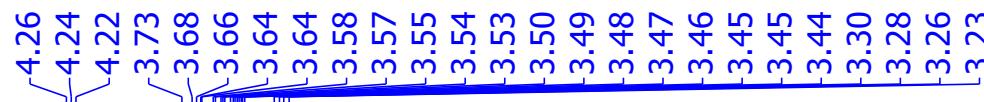
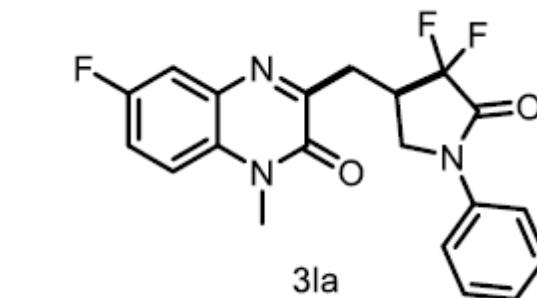


<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



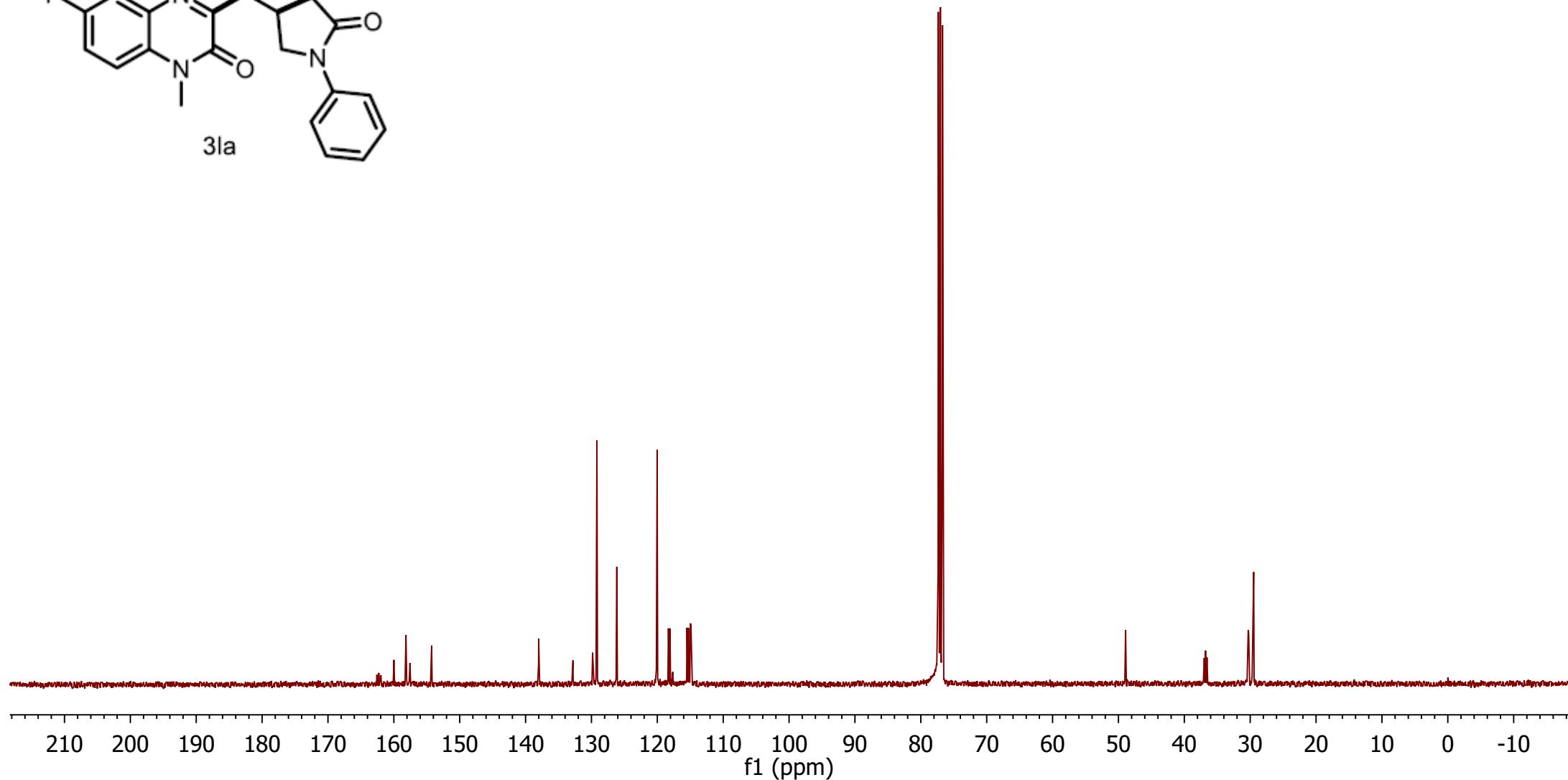
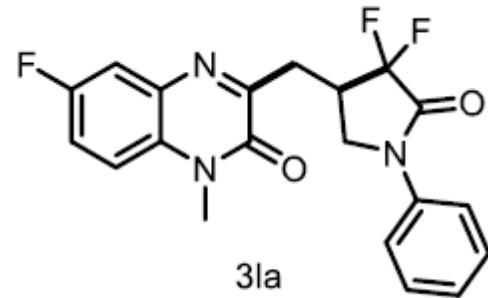
<sup>19</sup>F NMR Spectrum of 3ka

**1H (CDCl<sub>3</sub>, 400 MHz)**



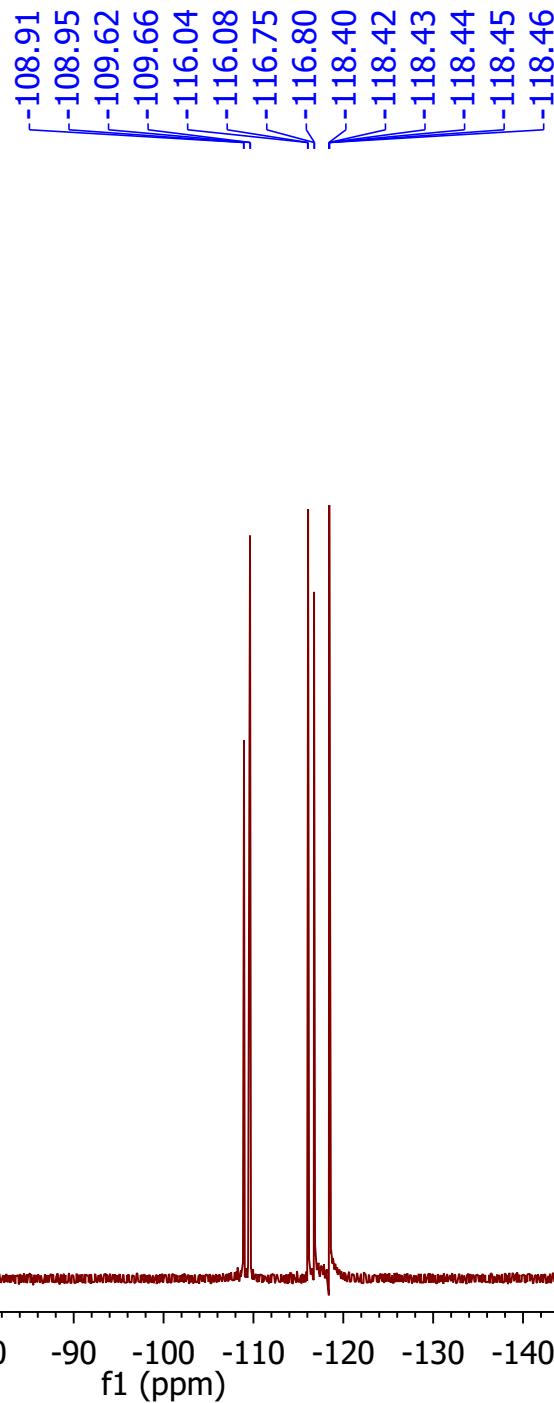
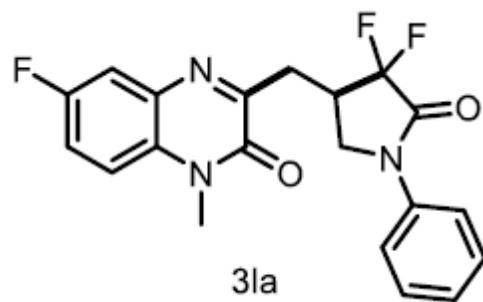
<sup>1</sup>H NMR Spectrum of **3la**

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



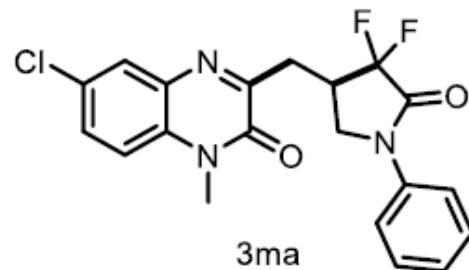
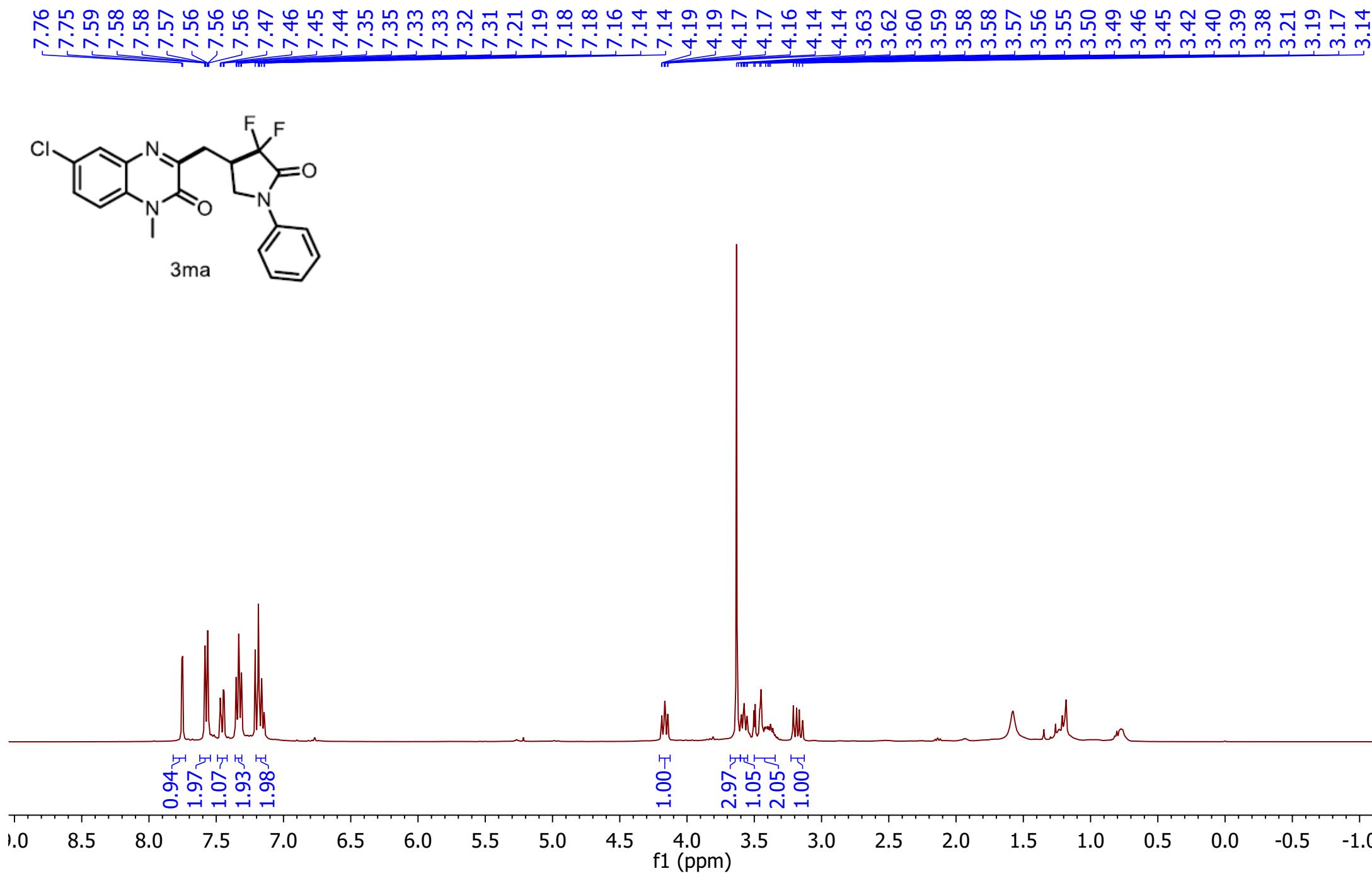
<sup>13</sup>C NMR Spectrum of 3la

**$^{19}\text{F}$  (CDCl<sub>3</sub>, 376 MHz)**



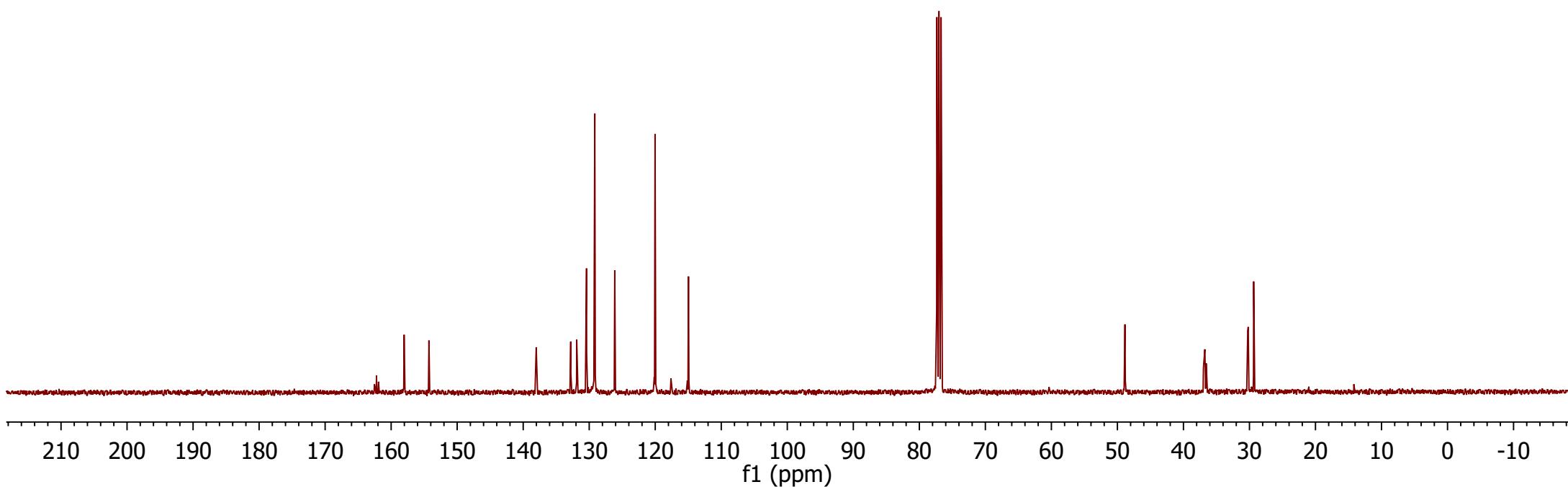
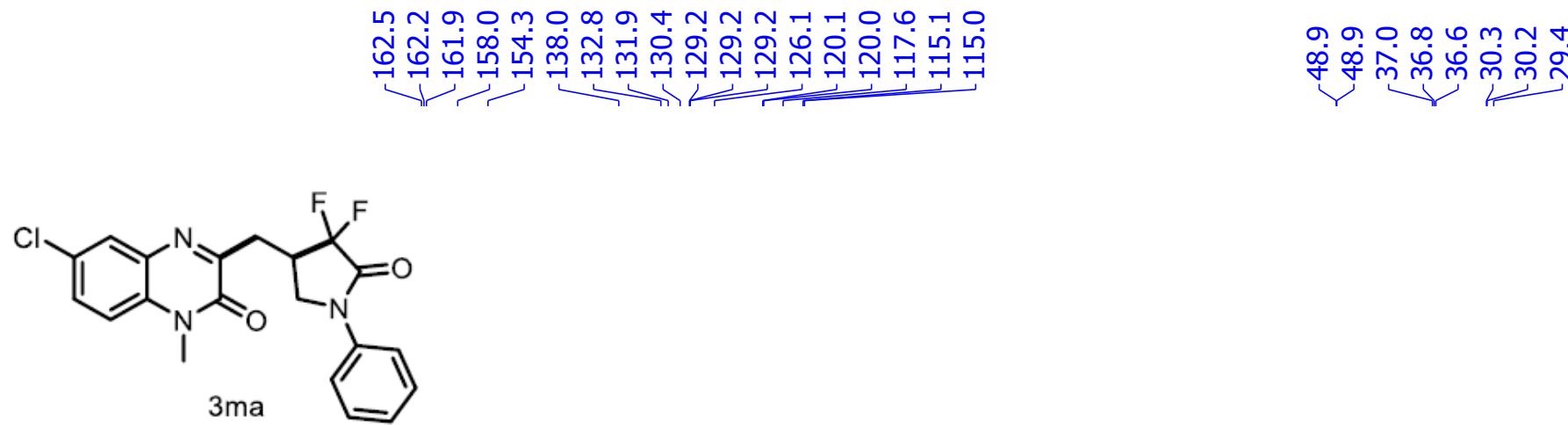
$^{19}\text{F}$  NMR Spectrum of 3la

**<sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz)**



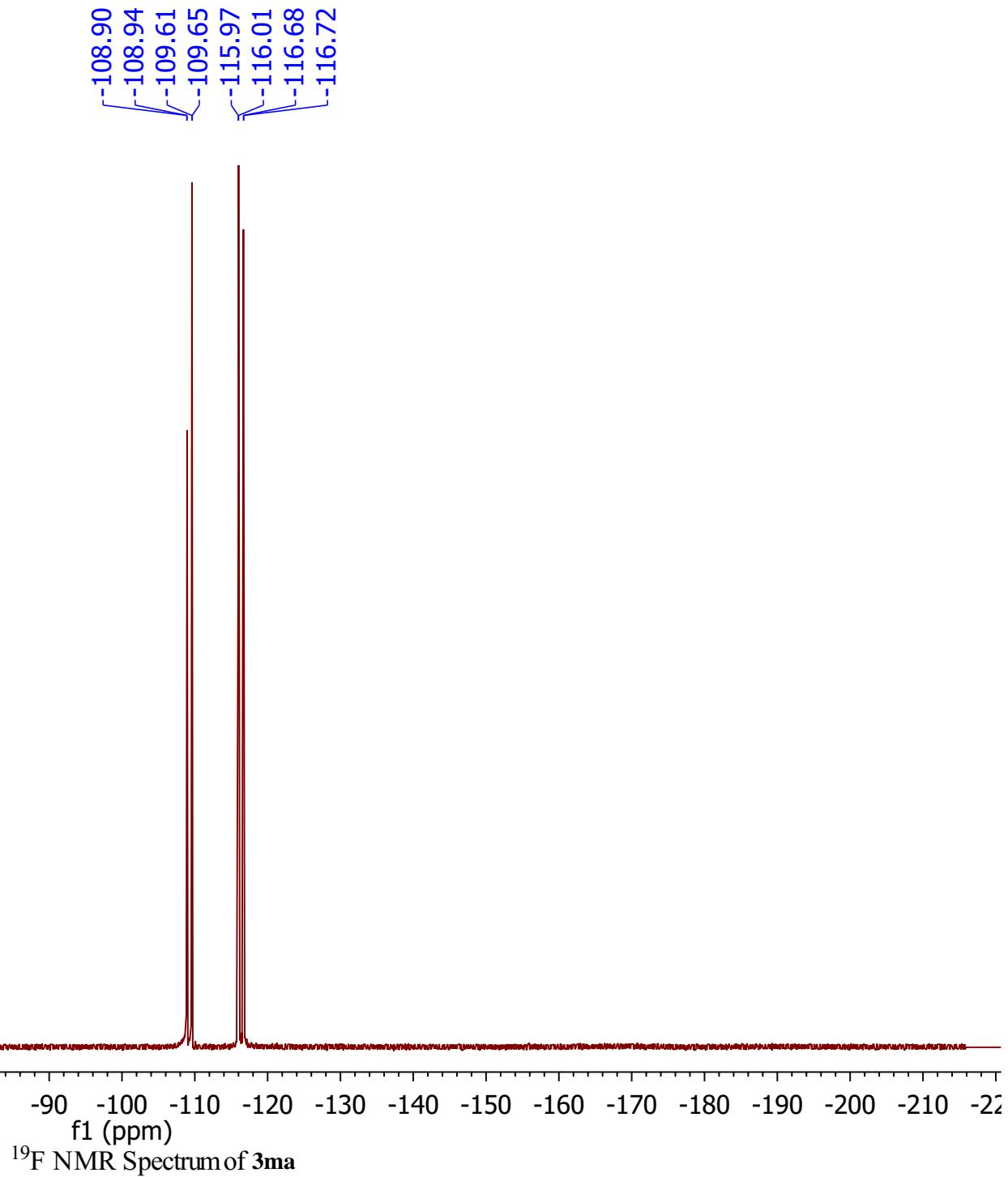
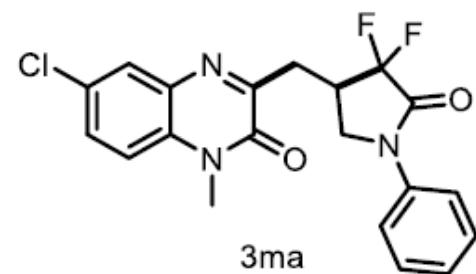
<sup>1</sup>H NMR Spectrum of **3ma**

**13C (CDCl<sub>3</sub>, 101 MHz)**

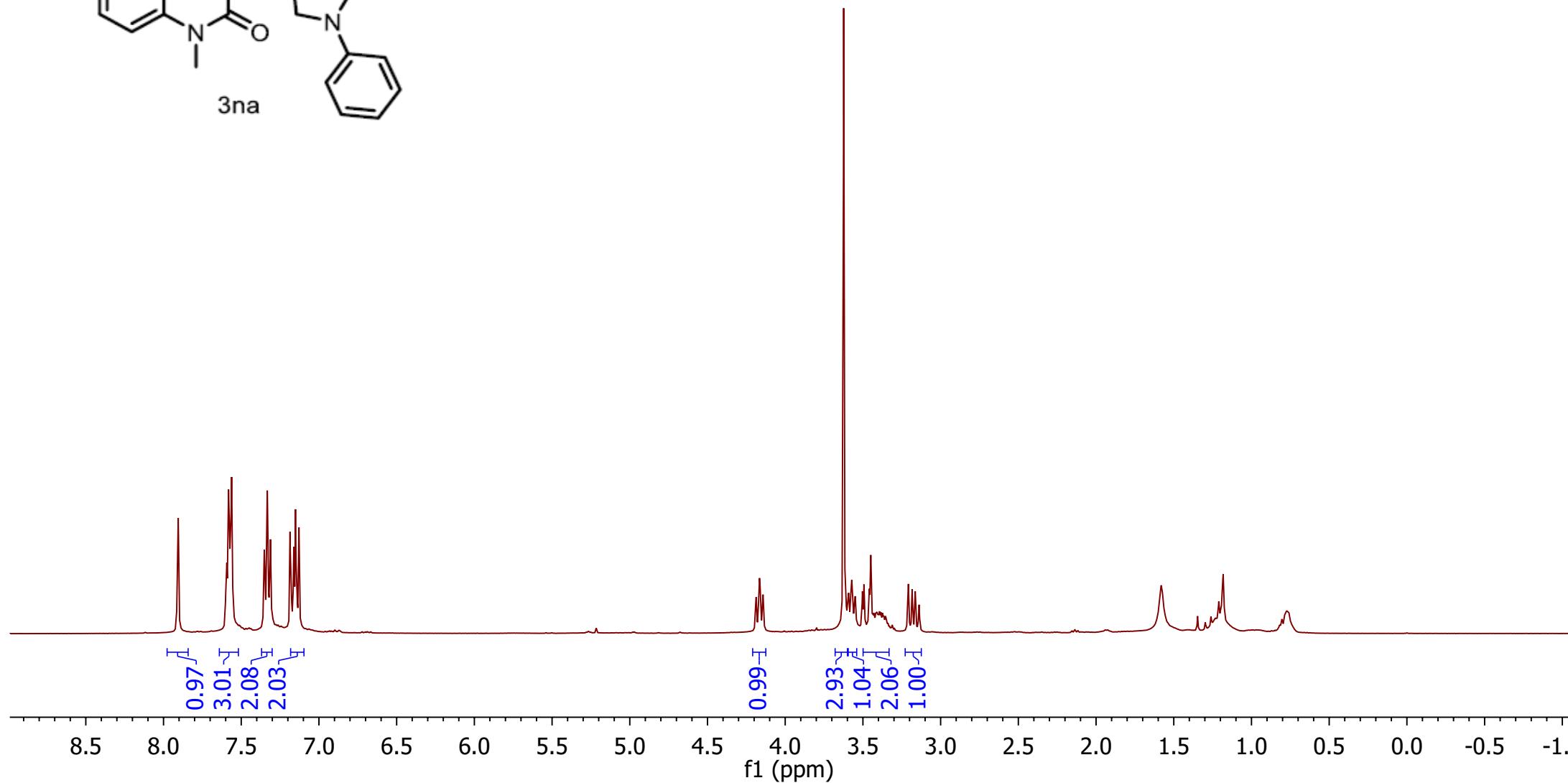
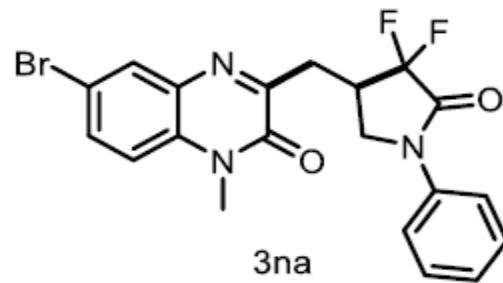


<sup>13</sup>C NMR Spectrum of **3ma**

## 19F (CDCl<sub>3</sub>, 376 MHz)

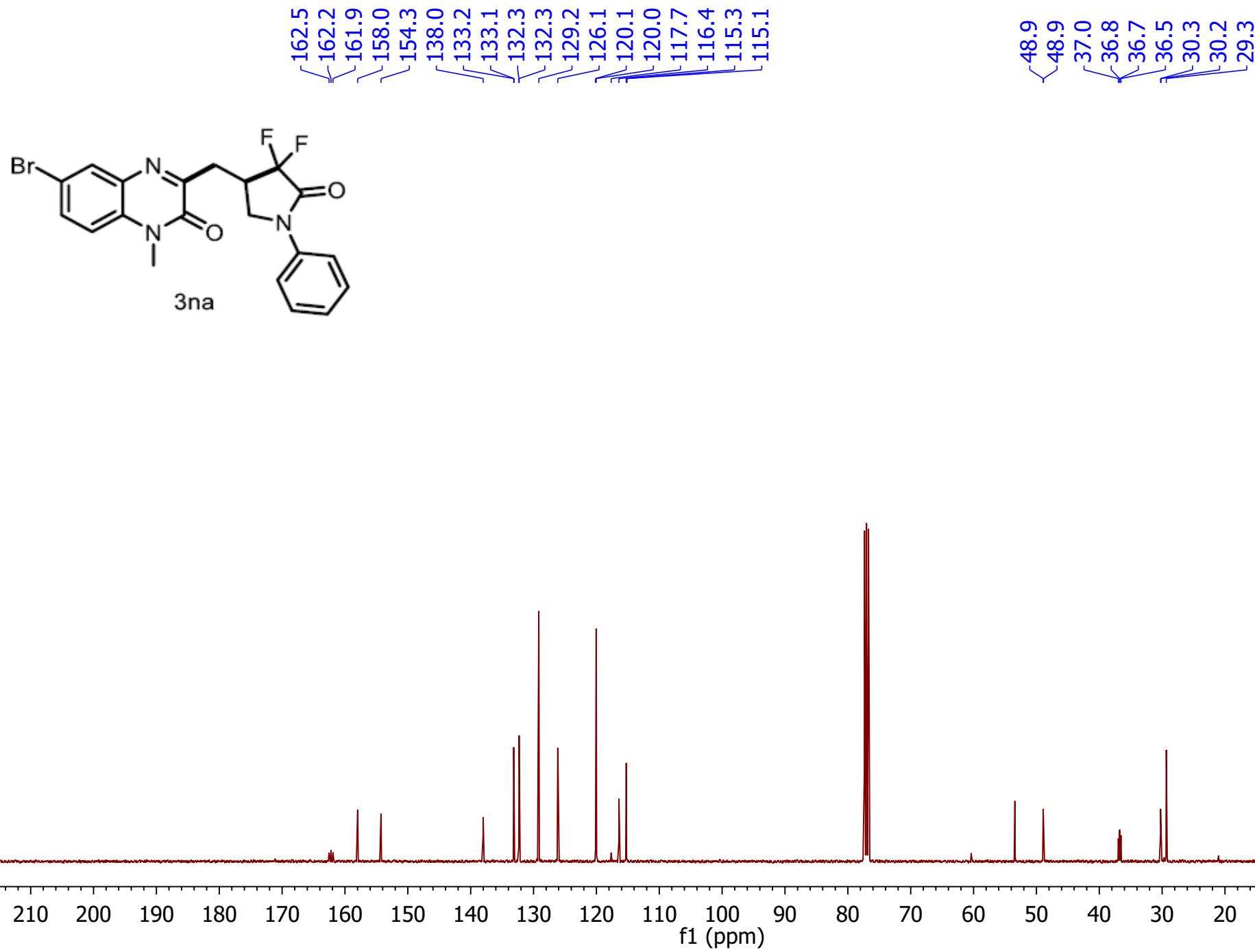


**1H (CDCl<sub>3</sub>, 400 MHz)**



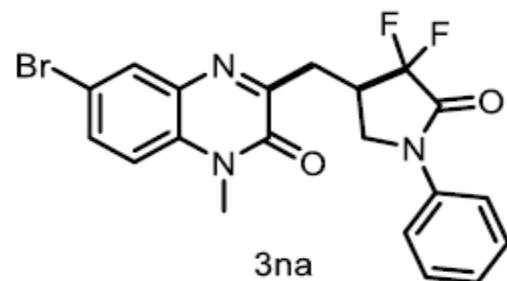
<sup>1</sup>H NMR Spectrum of 3na

**13C (CDCl<sub>3</sub>, 101 MHz)**

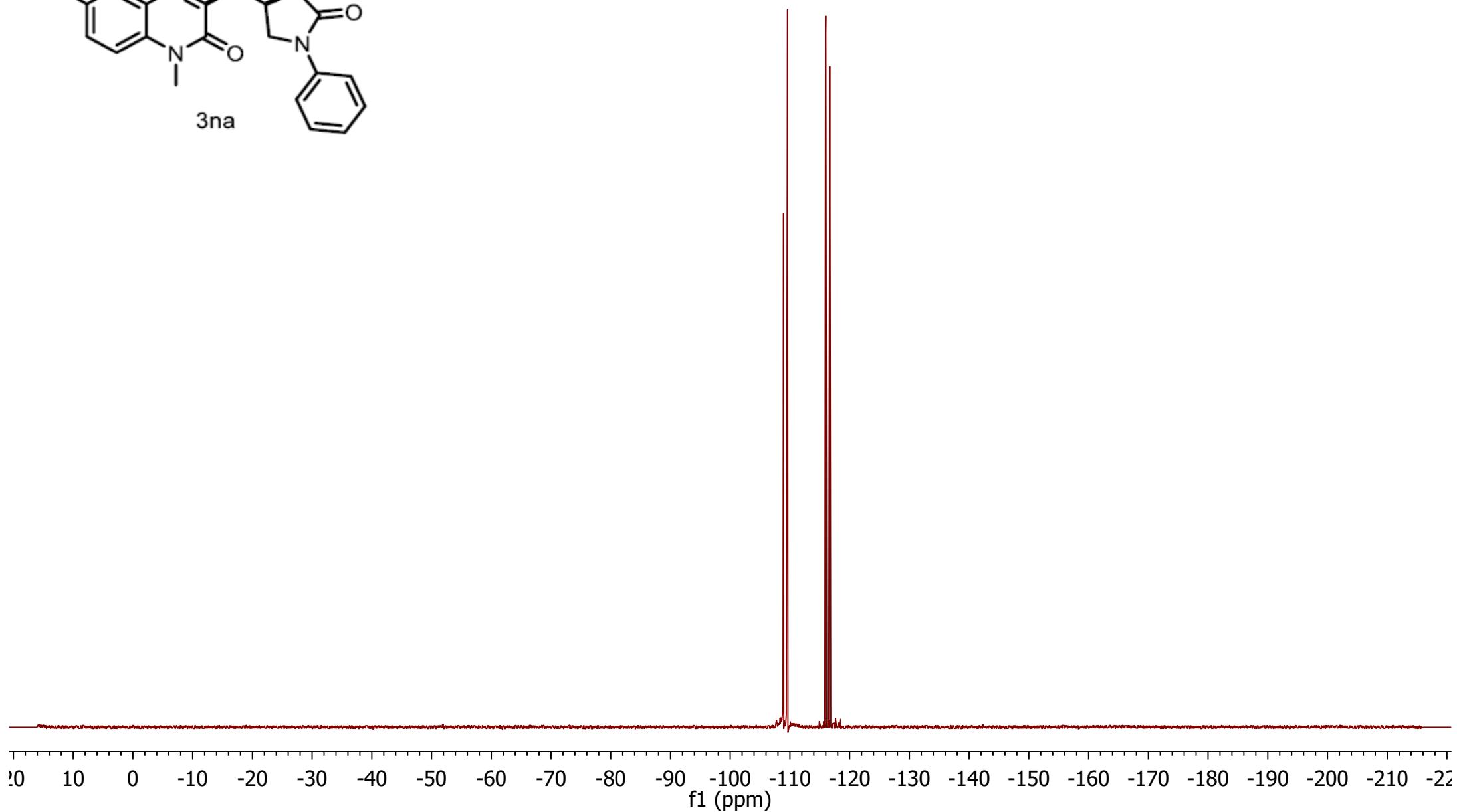


<sup>13</sup>C NMR Spectrum of **3na**

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

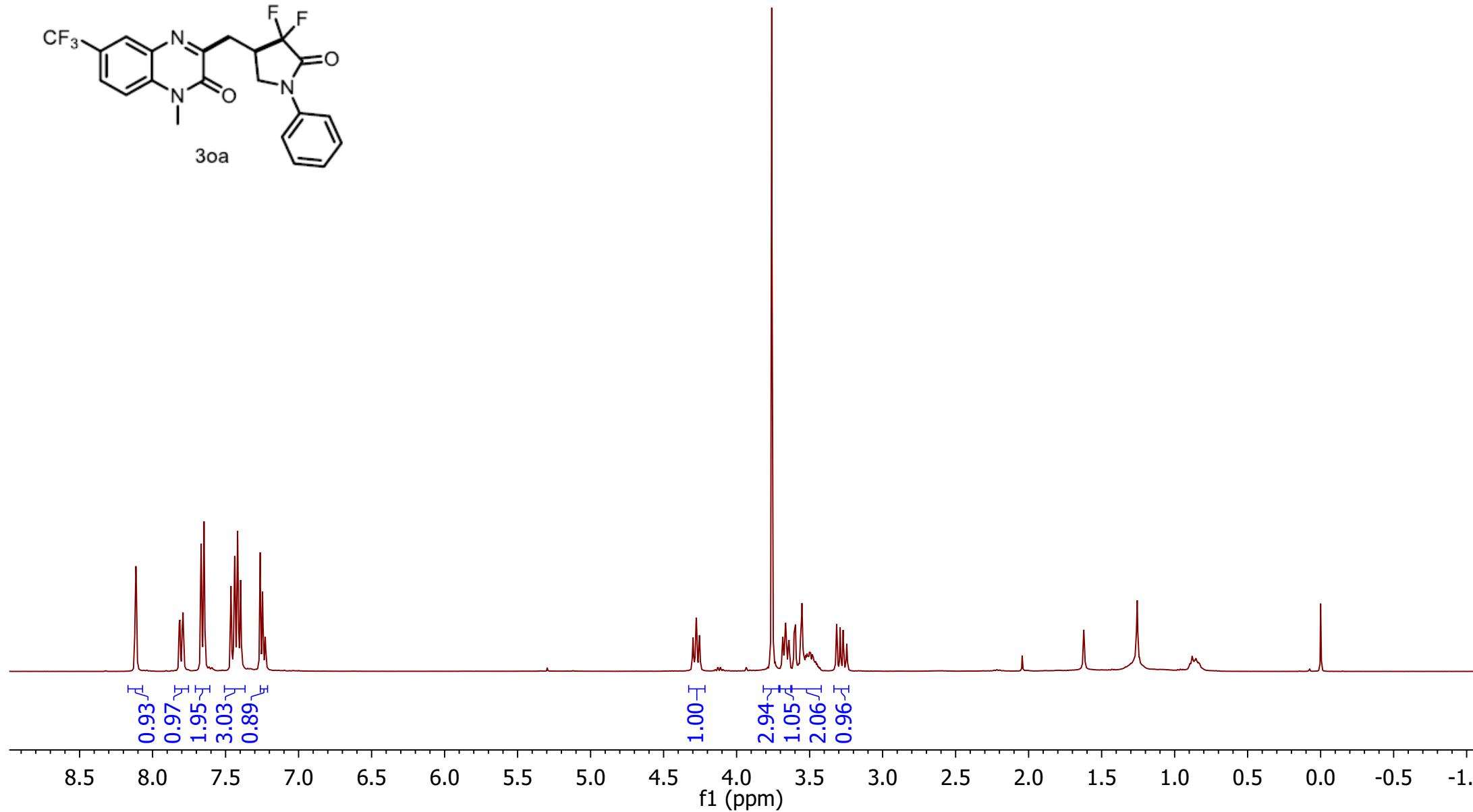
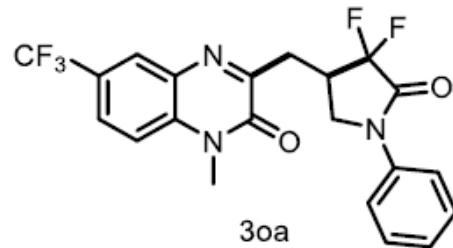


-108.89  
-108.93  
-109.60  
-109.64  
-115.96  
-116.01  
-116.67  
-116.72



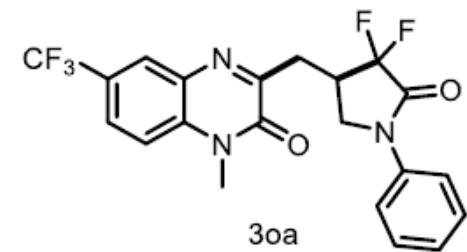
<sup>19</sup>F NMR Spectrum of 3na

**1H (CDCl<sub>3</sub>, 400 MHz)**



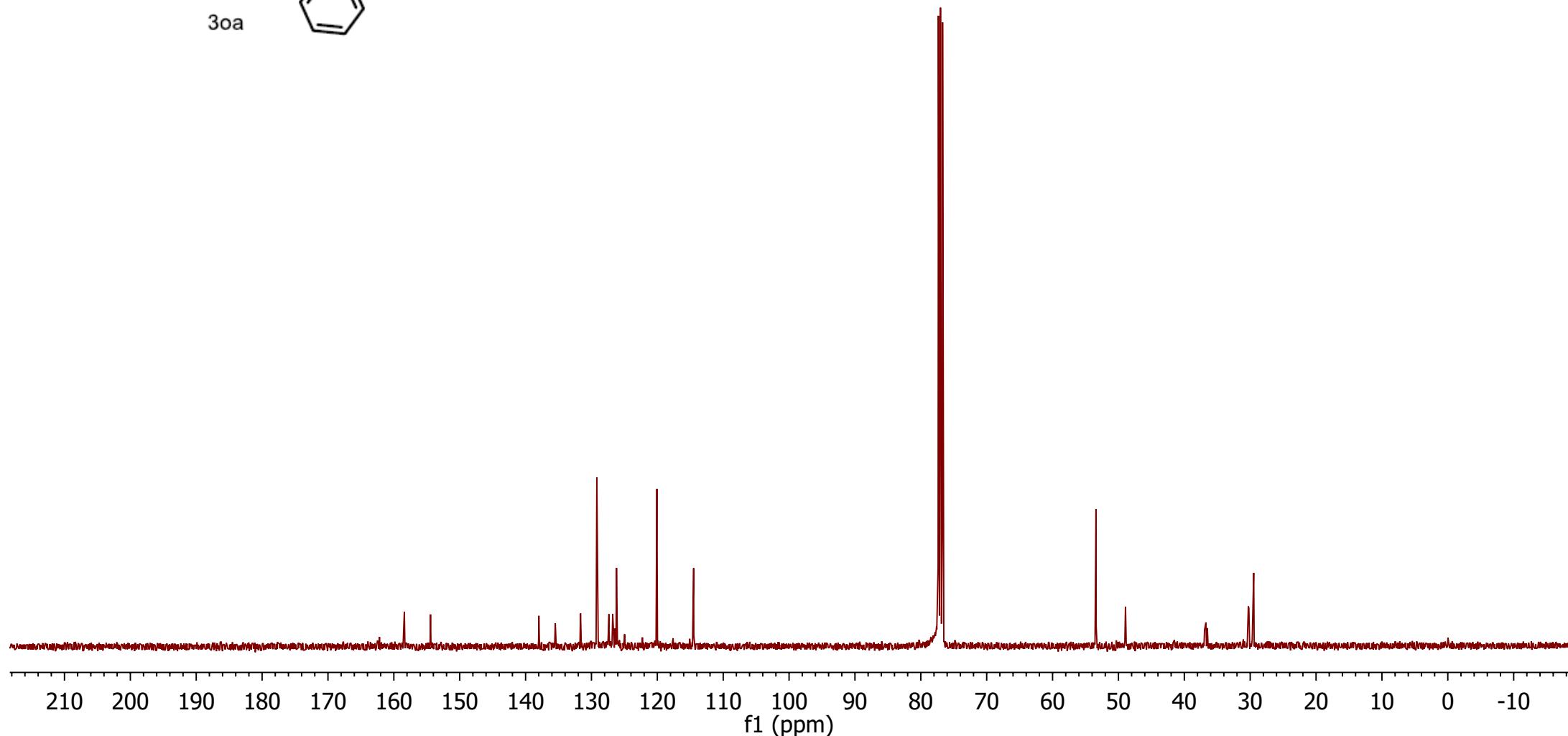
<sup>1</sup>H NMR Spectrum of **3oa**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



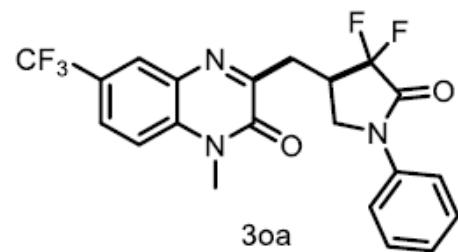
-158.4  
-154.4  
-138.0  
135.5  
131.7  
129.2  
127.4  
127.3  
126.8  
126.7  
126.4  
126.2  
126.1  
125.0  
120.1  
114.5

48.9  
48.9  
36.9  
36.7  
36.5  
30.3  
30.2  
29.5



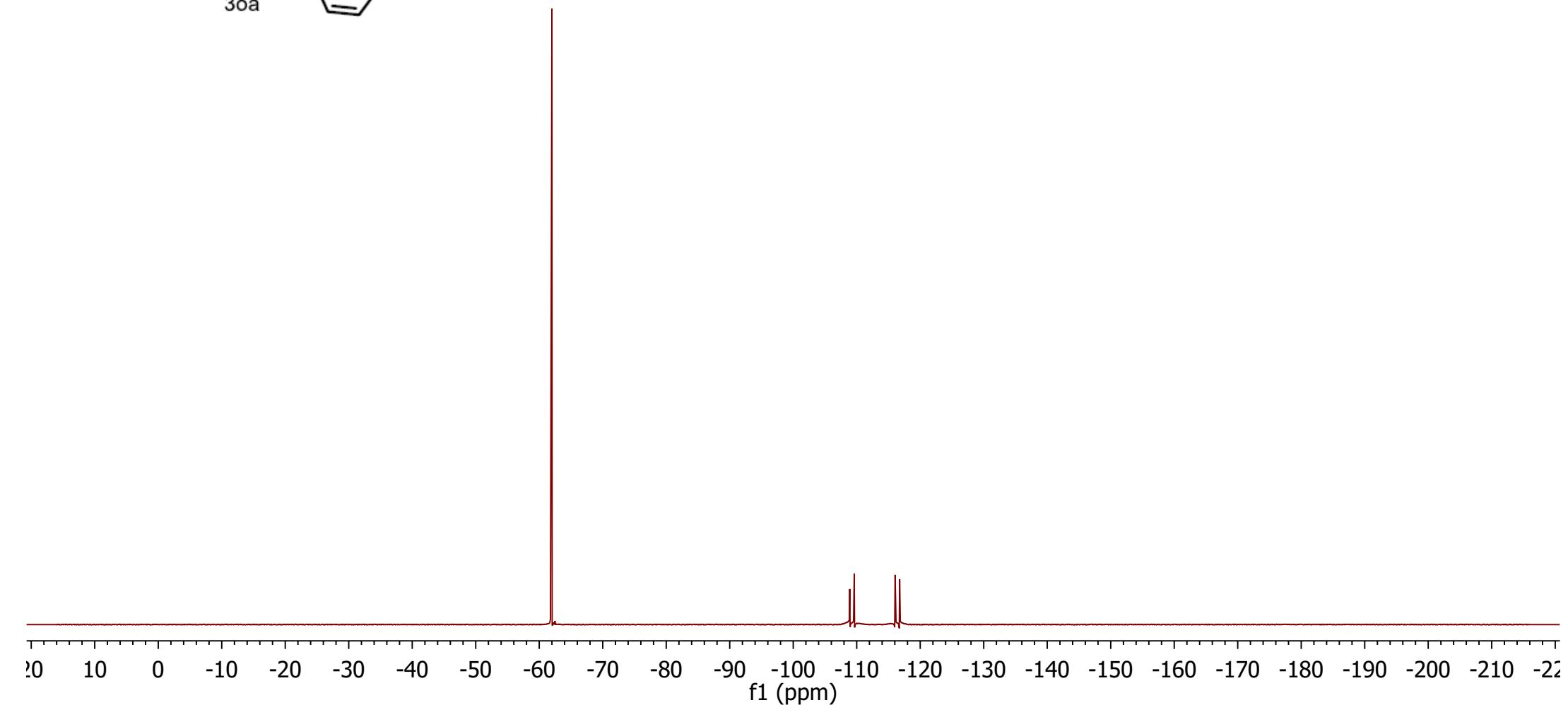
<sup>13</sup>C NMR Spectrum of 3oa

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



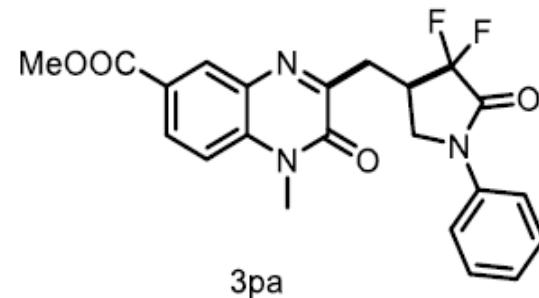
—62.00

-108.95  
-109.62  
-109.66  
-116.06  
-116.77

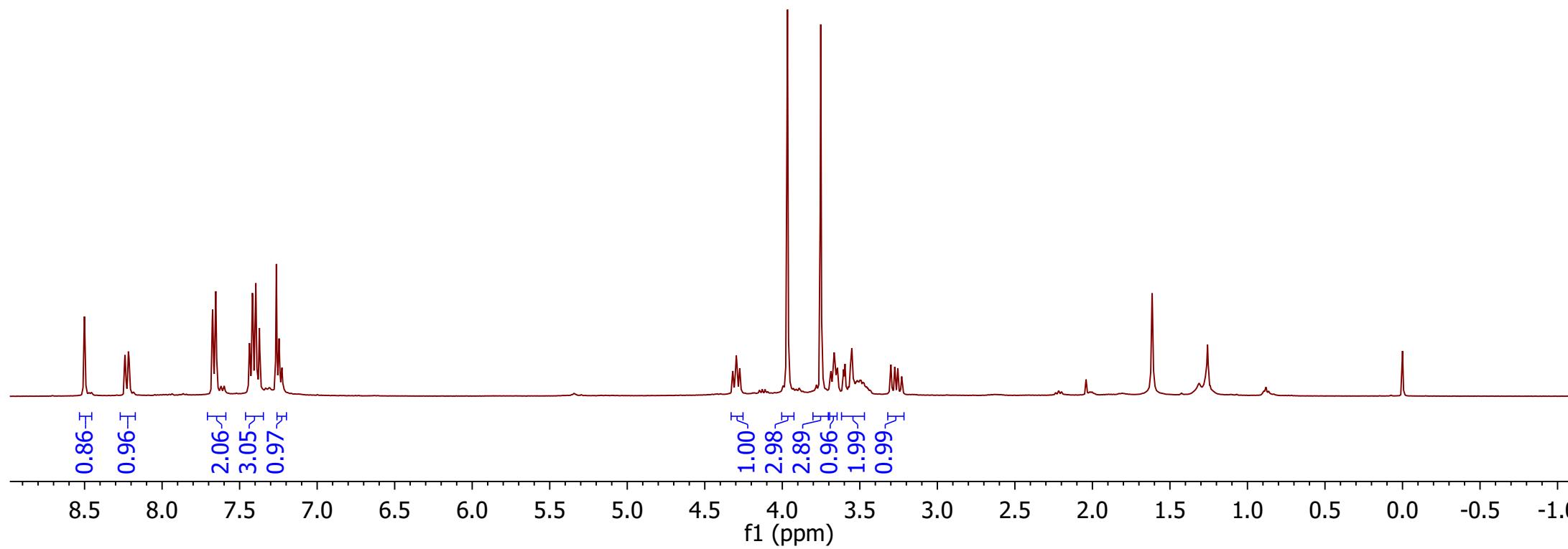


<sup>19</sup>F NMR Spectrum of 3oa

**1H (CDCl<sub>3</sub>, 400 MHz)**

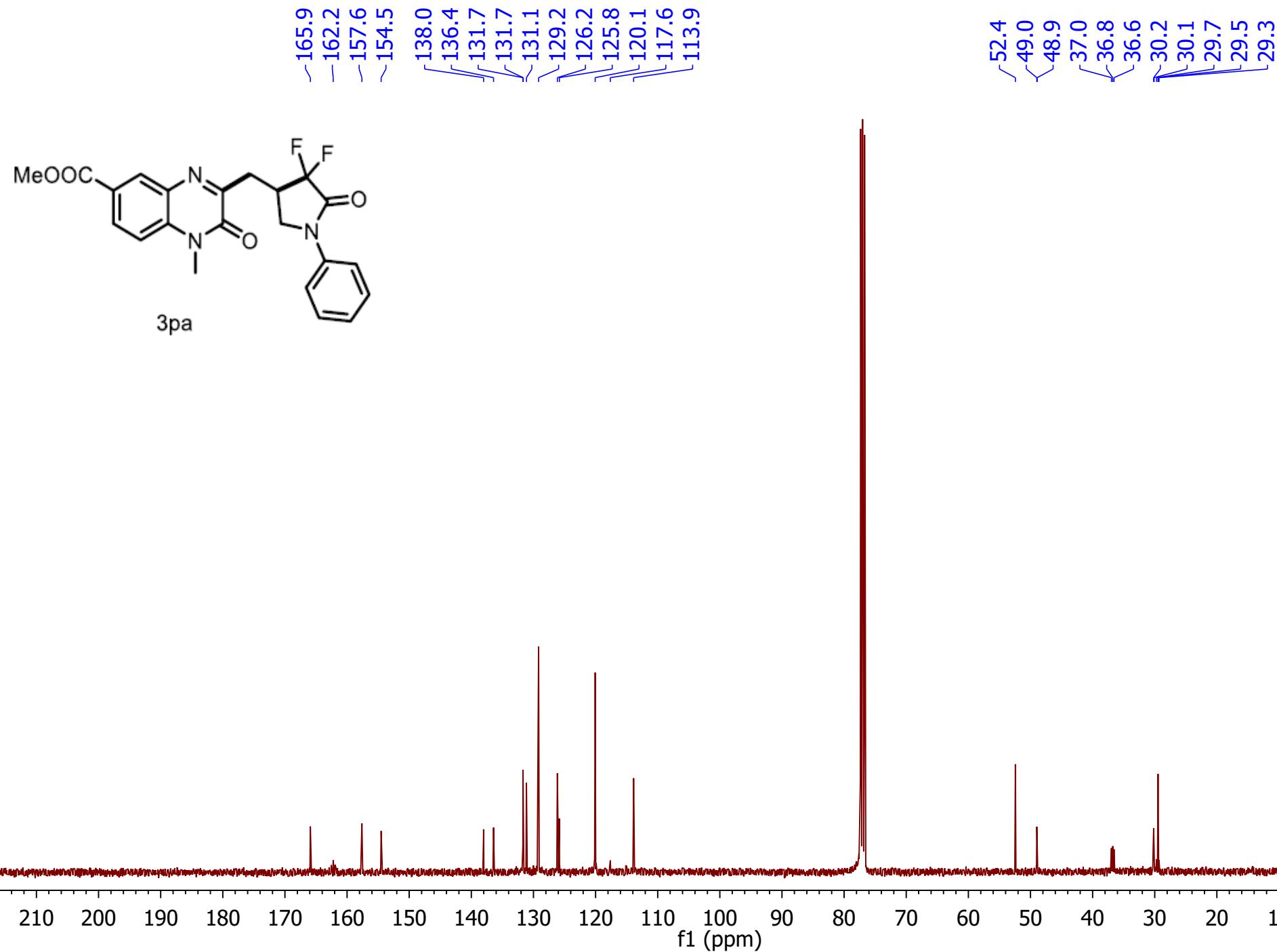


3pa



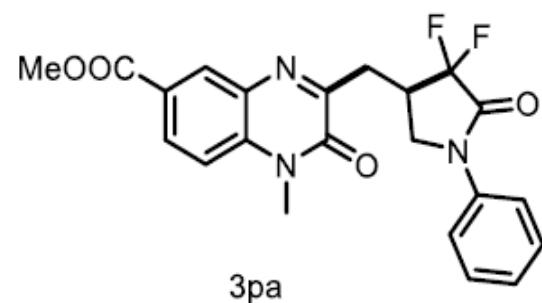
<sup>1</sup>H NMR Spectrum of 3pa

**13C (CDCl<sub>3</sub>, 101 MHz)**

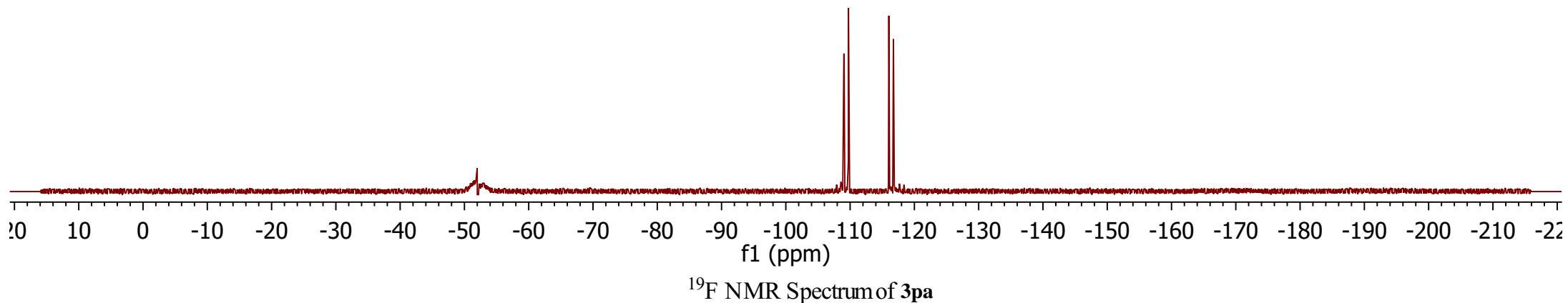


<sup>13</sup>C NMR Spectrum of 3pa

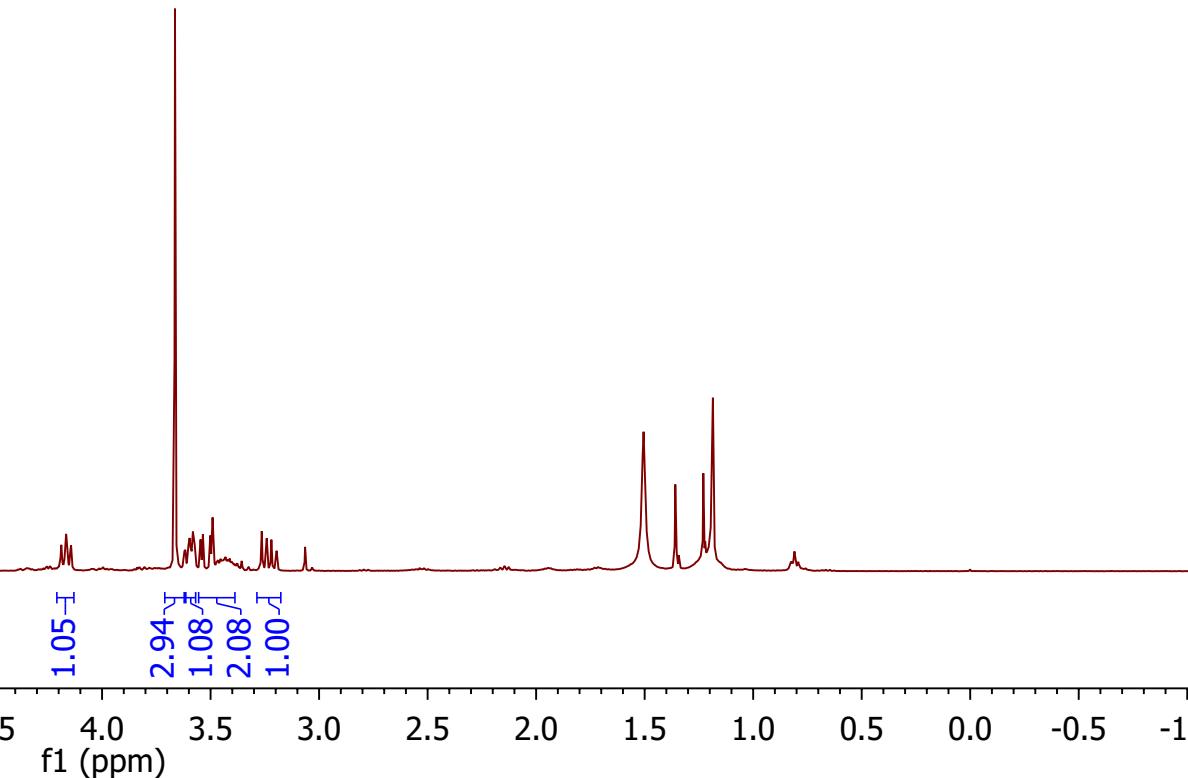
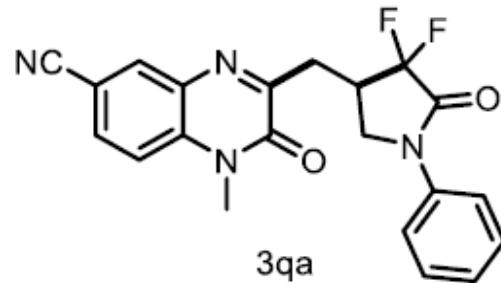
<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



-109.03  
-109.07  
-109.74  
-109.78  
-115.98  
-116.03  
-116.69  
-116.74

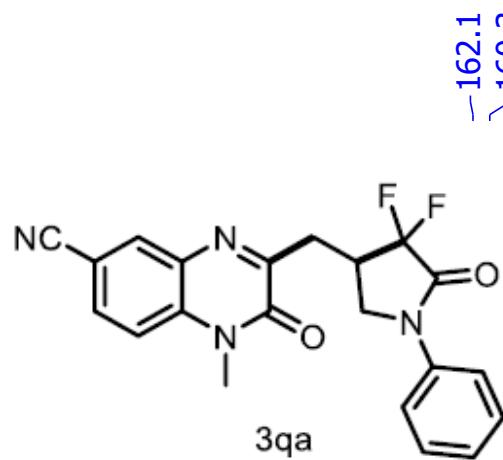


**1H (CDCl<sub>3</sub>, 400 MHz)**



<sup>1</sup>H NMR Spectrum of **3qa**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

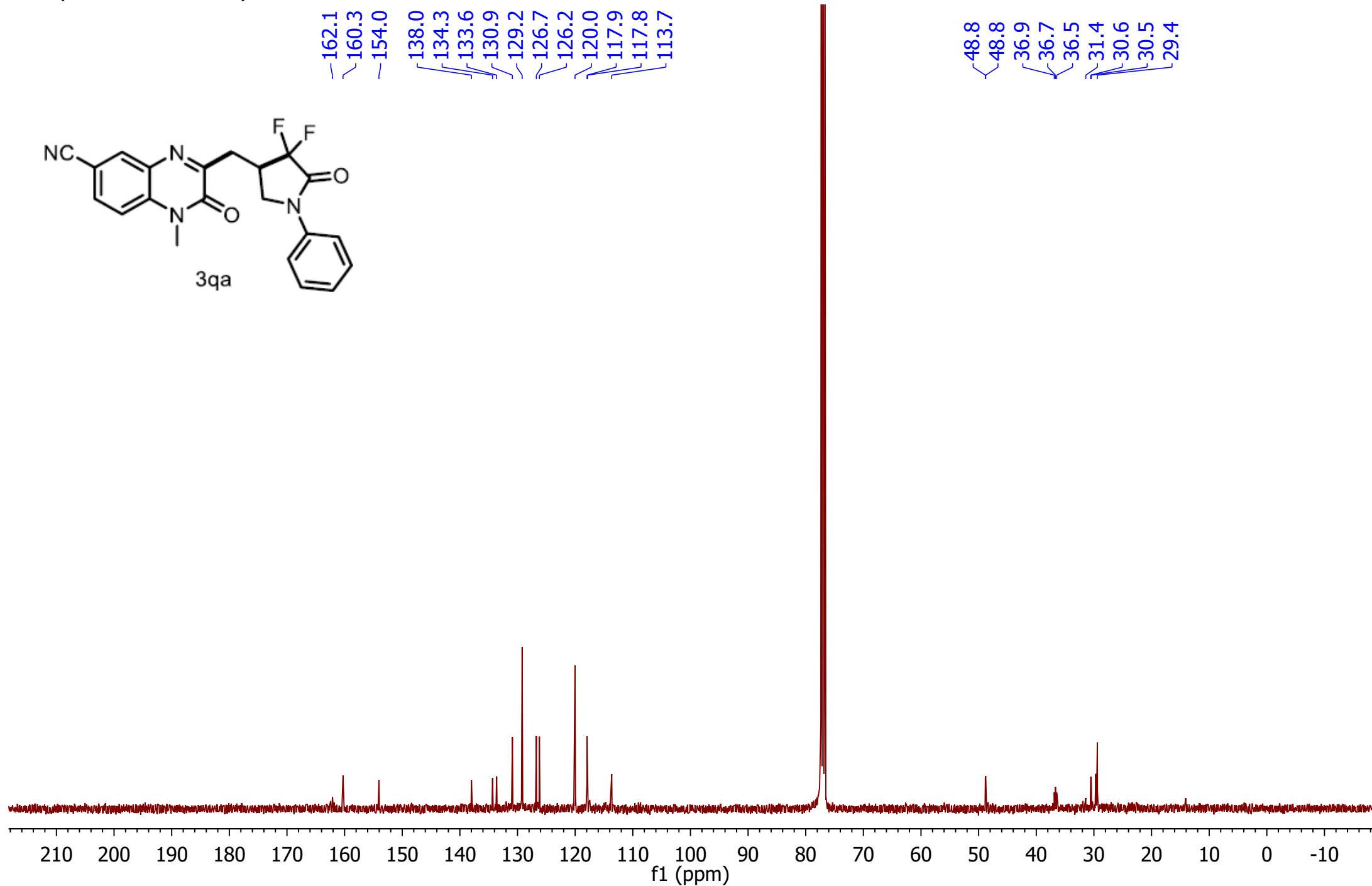


Peak assignments for the <sup>13</sup>C NMR spectrum:

- 162.1
- 160.3
- 154.0
- 138.0
- 134.3
- 133.6
- 130.9
- 129.2
- 126.7
- 126.2
- 120.0
- 117.9
- 117.8
- 113.7

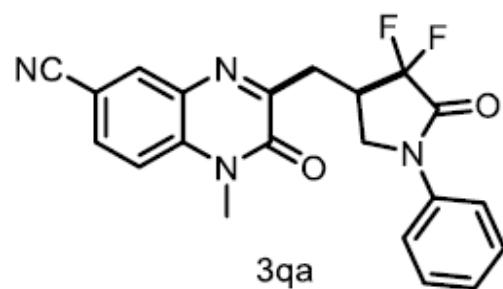
Peak assignments for the <sup>13</sup>C NMR spectrum:

- 48.8
- 48.8
- 36.9
- 36.7
- 36.5
- 31.4
- 30.6
- 30.5
- 29.4

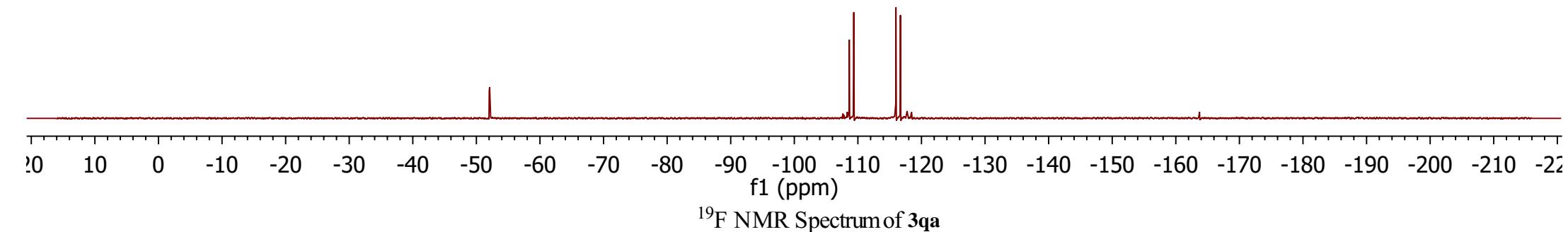


<sup>13</sup>C NMR Spectrum of 3qa

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

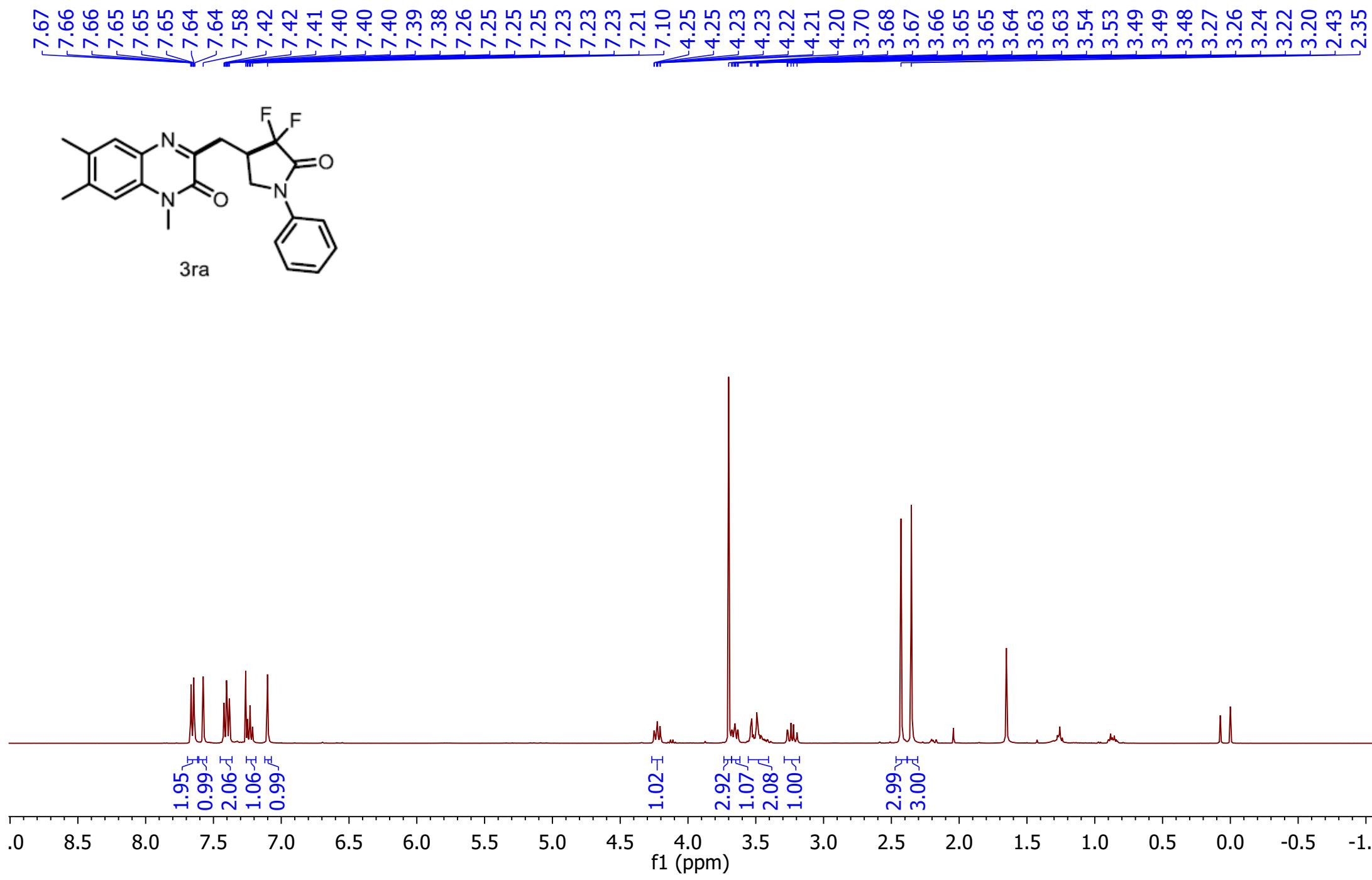
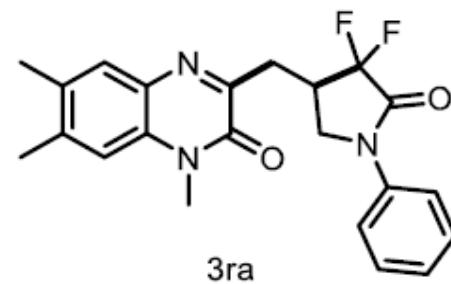


-108.64  
-108.68  
-109.35  
-109.39  
-115.98  
-116.02  
-116.69  
-116.74



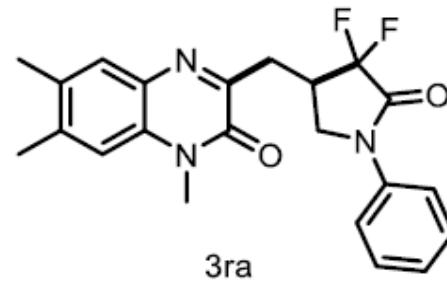
<sup>19</sup>F NMR Spectrum of 3qa

## **1H (CDCl<sub>3</sub>, 400 MHz)**

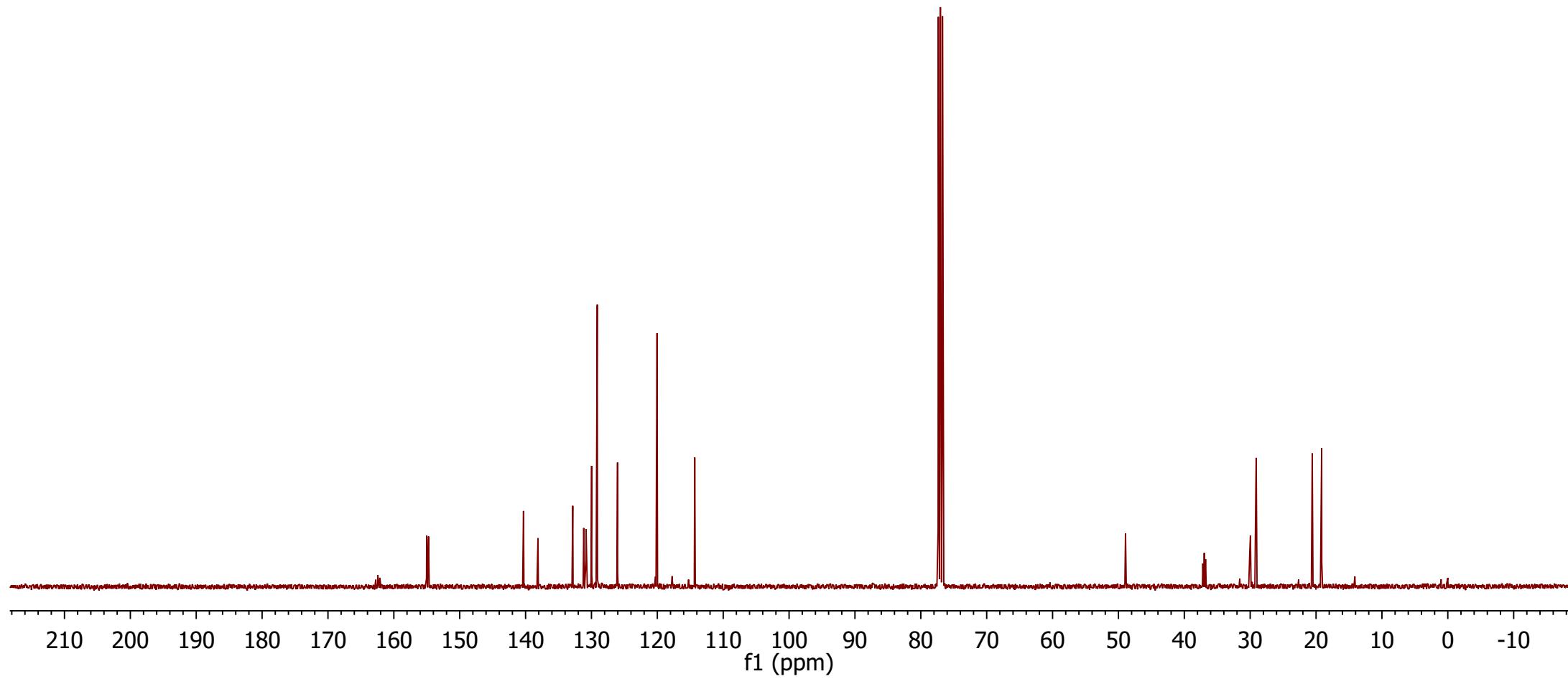


### <sup>1</sup>H NMR Spectrum of 3ra

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

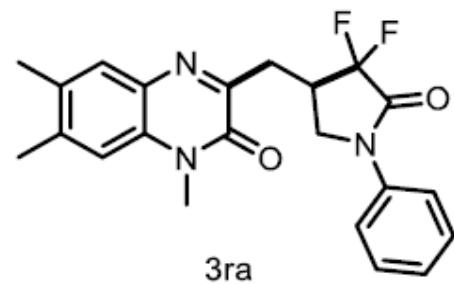


162.7  
162.4  
162.1  
155.0  
154.7  
140.3  
138.1  
132.8  
131.2  
130.8  
130.0  
129.1  
126.0  
120.3  
120.0  
117.8  
117.7  
115.3  
114.3  
49.0  
48.9  
37.2  
37.0  
37.0  
36.8  
30.0  
30.0  
29.1  
20.6  
19.1

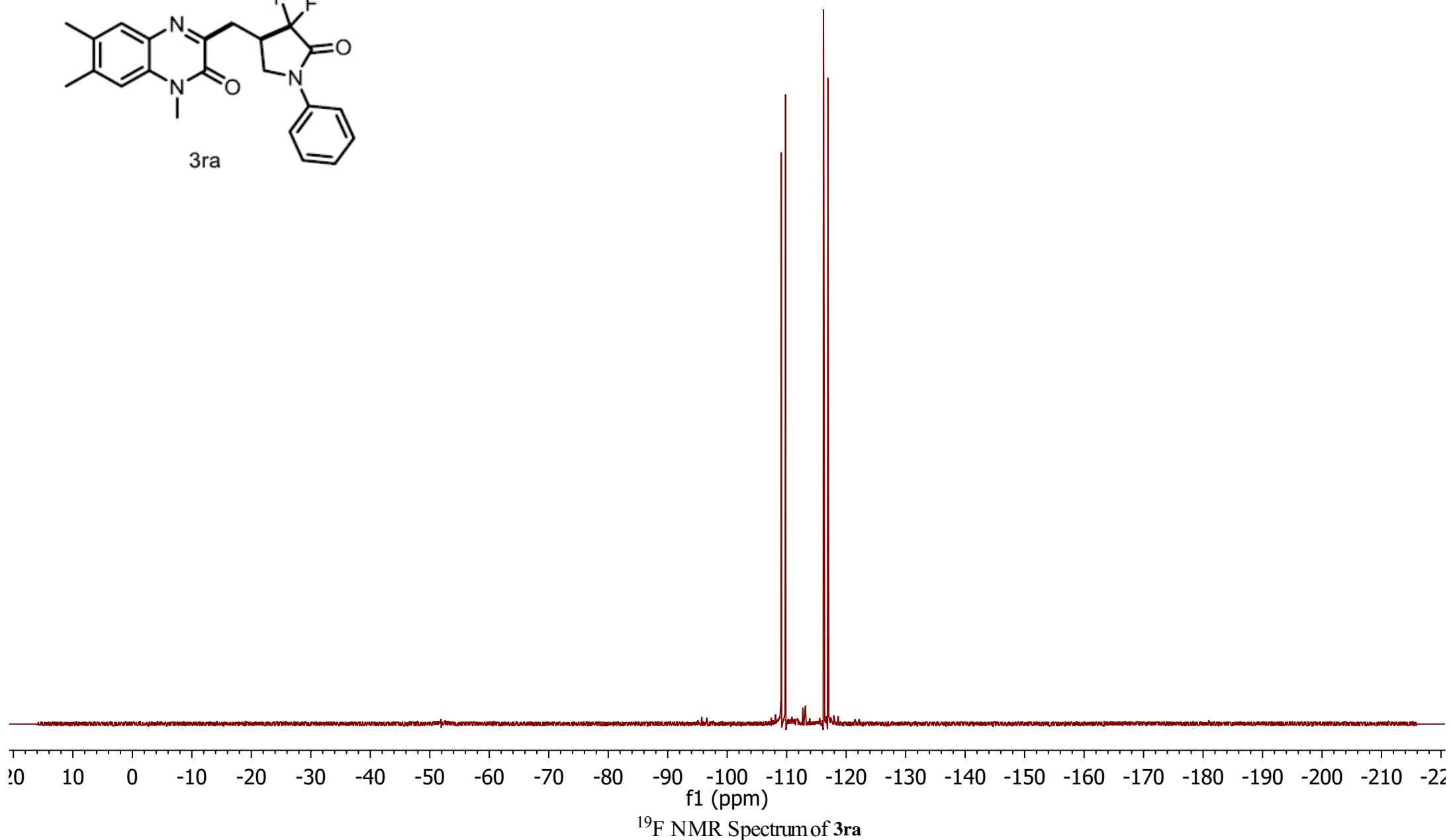


<sup>13</sup>C NMR Spectrum of 3ra

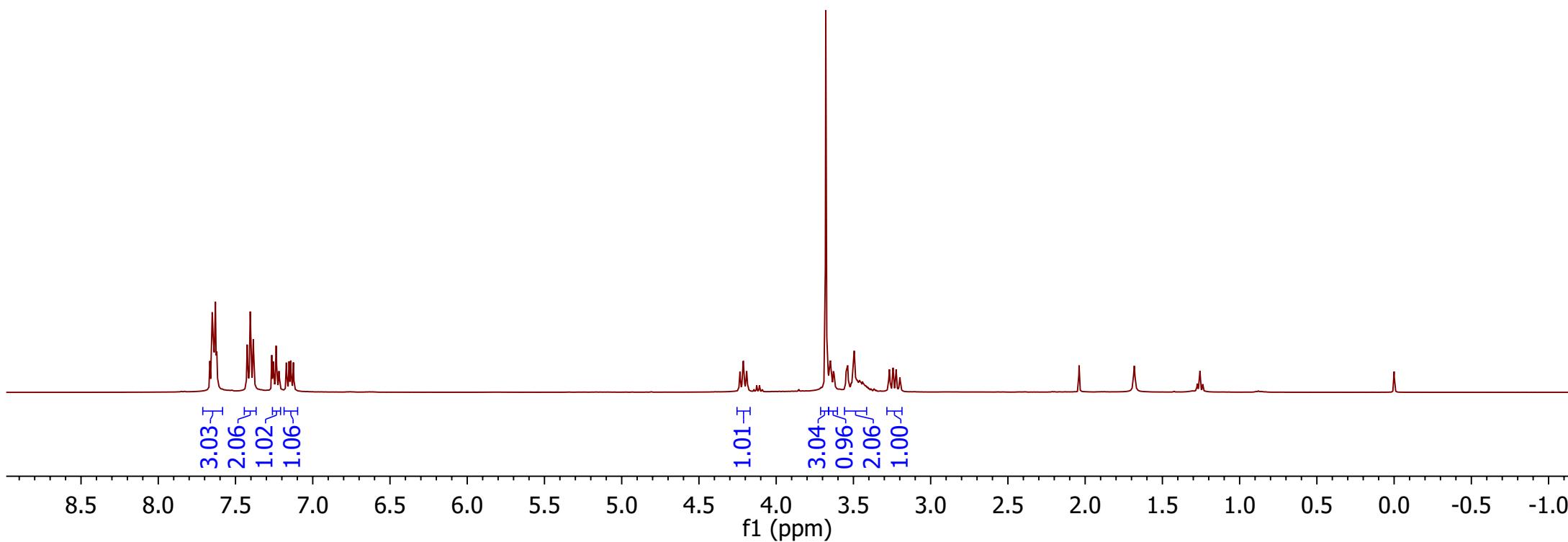
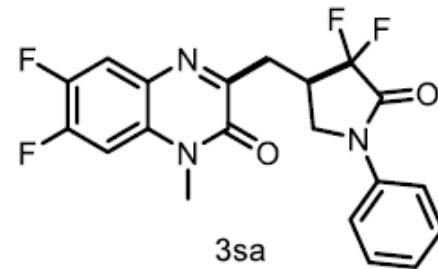
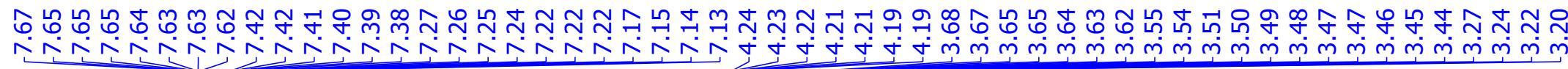
<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



-109.09  
-109.13  
-109.80  
-109.81  
-109.84  
-116.18  
-116.22  
-116.89  
-116.93



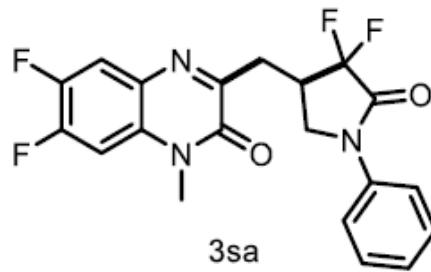
**<sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz)**



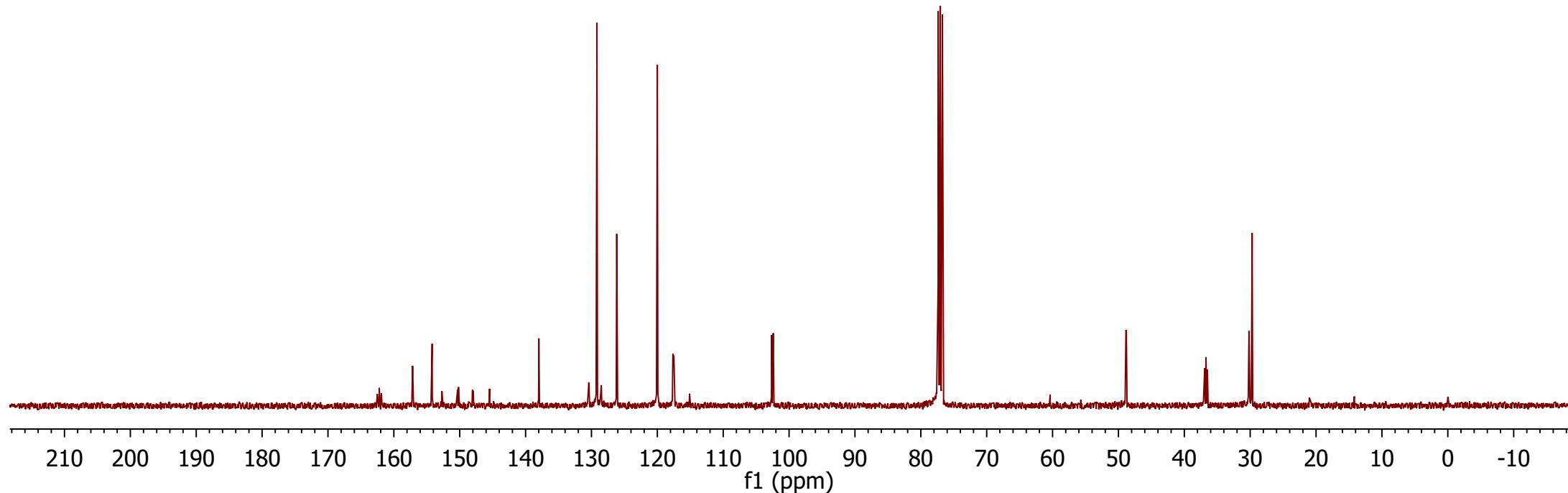
<sup>1</sup>H NMR Spectrum of 3sa

**13C (CDCl<sub>3</sub>, 101 MHz)**

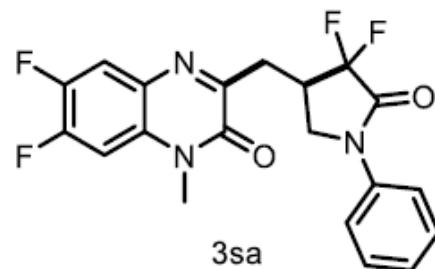
162.2	157.2	157.1	154.2	150.3	150.2	148.1	145.6	145.5	138.0	130.5	130.5	130.4	129.2	128.6	128.5	128.5	126.2	120.1	120.0	117.7	117.6	117.6	117.5	102.6	102.4



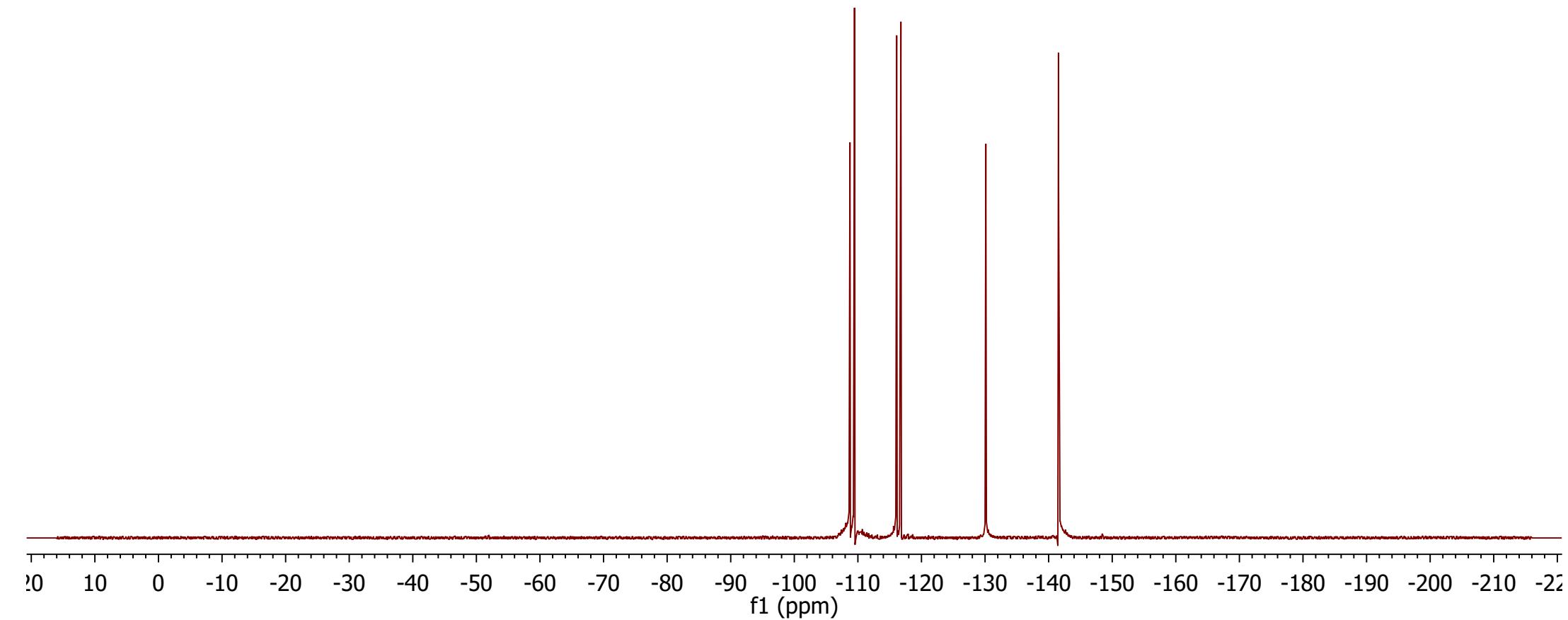
<sup>13</sup>C NMR Spectrum of 3sa



<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

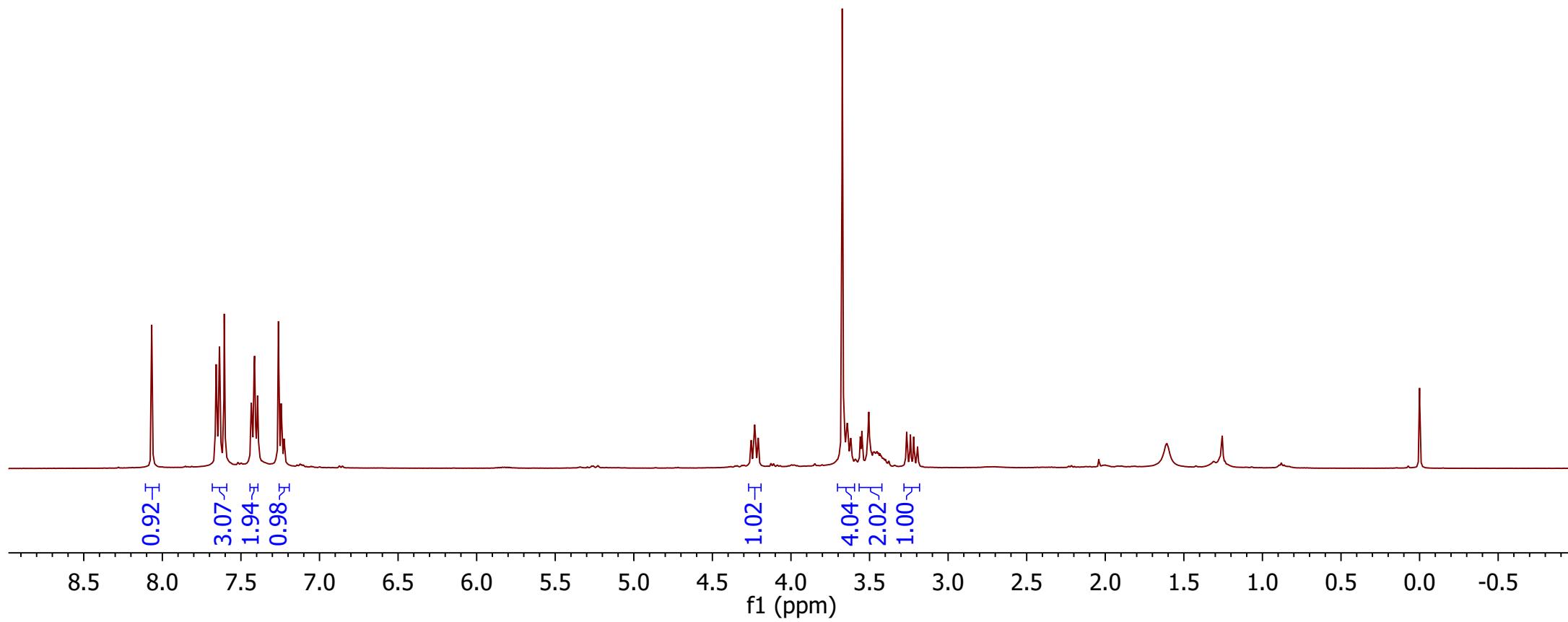
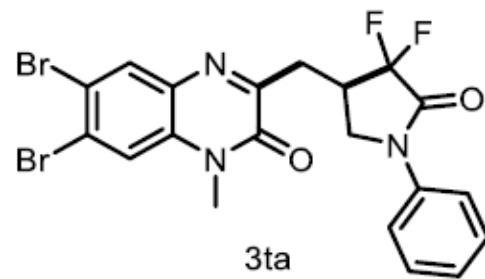


-108.75  
-108.79  
-109.47  
-109.50  
-116.05  
-116.10  
-116.16  
-116.81  
-130.03  
-130.05  
-130.06  
-130.08  
-130.09  
-130.11  
-130.12  
-141.46  
-141.48  
-141.49  
-141.50  
-141.52  
-141.54  
-141.55  
-141.55  
-141.56



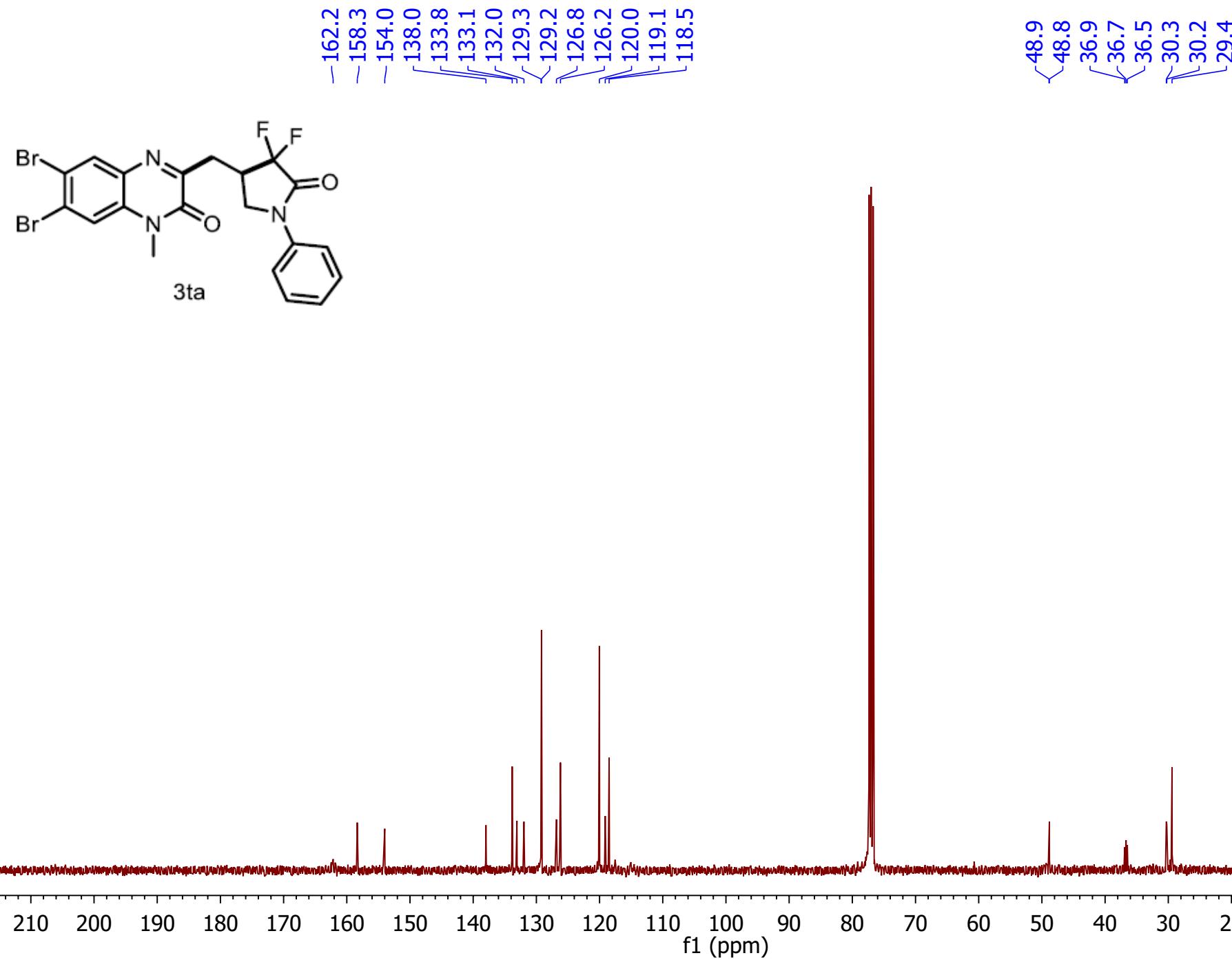
<sup>19</sup>F NMR Spectrum of 3sa

## **1H (CDCl<sub>3</sub>, 400 MHz)**



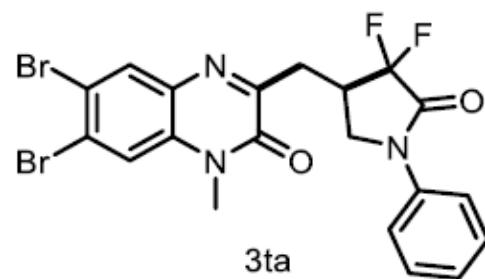
### <sup>1</sup>H NMR Spectrum of 3ta

**13C (CDCl<sub>3</sub>, 101 MHz)**

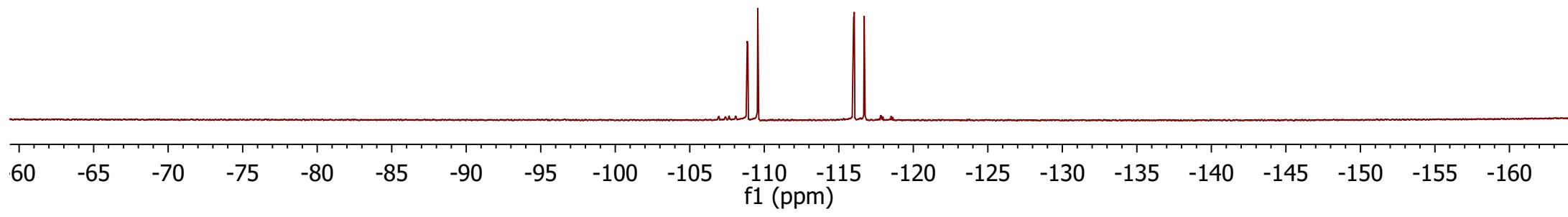


<sup>13</sup>C NMR Spectrum of 3ta

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

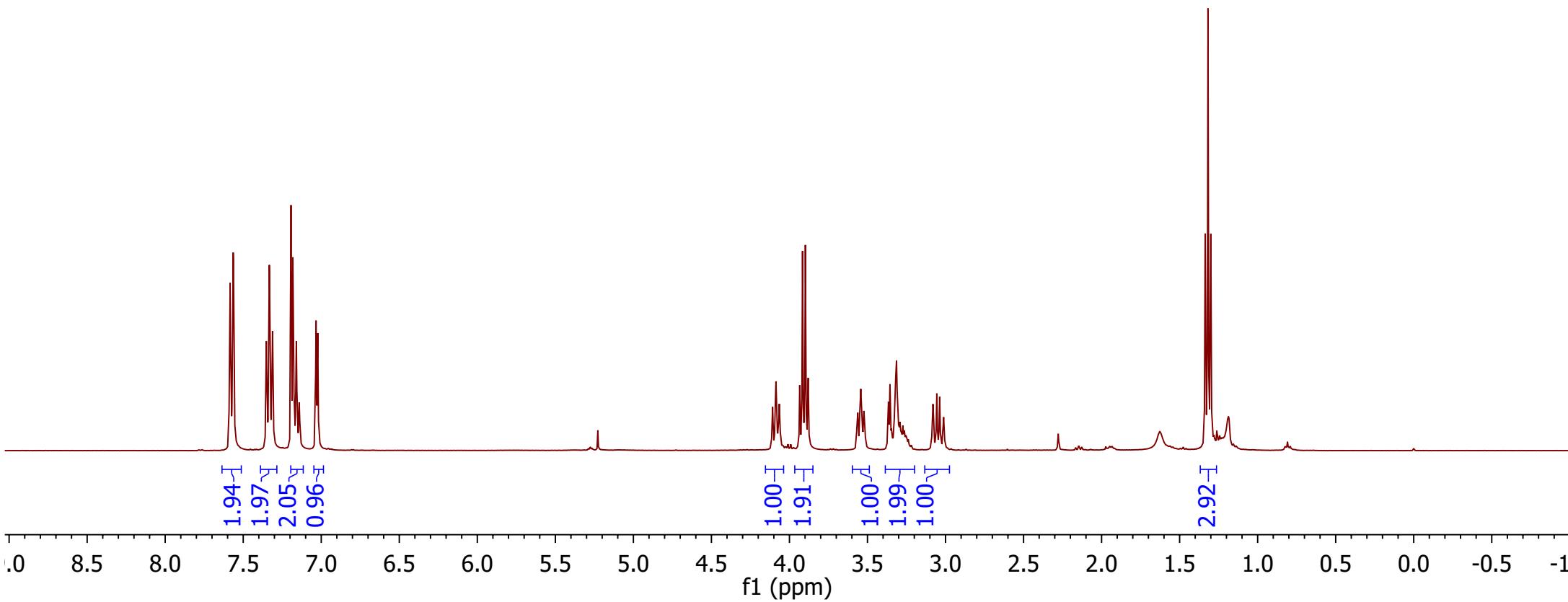
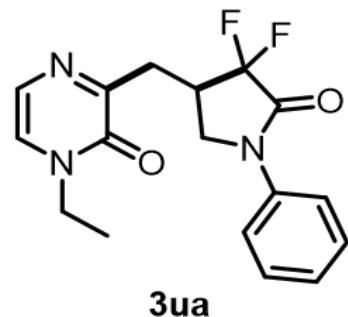


-108.85  
-108.89  
-109.56  
-109.60  
-115.99  
-116.04  
-116.70  
-116.75



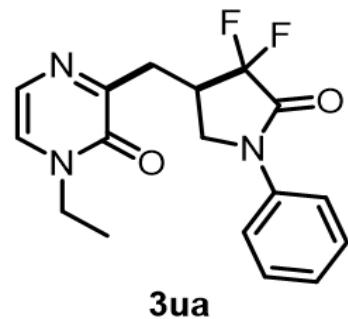
<sup>19</sup>F NMR Spectrum of 3ta

**1H (CDCl<sub>3</sub>, 400 MHz)**



<sup>1</sup>H NMR Spectrum of **3ua**

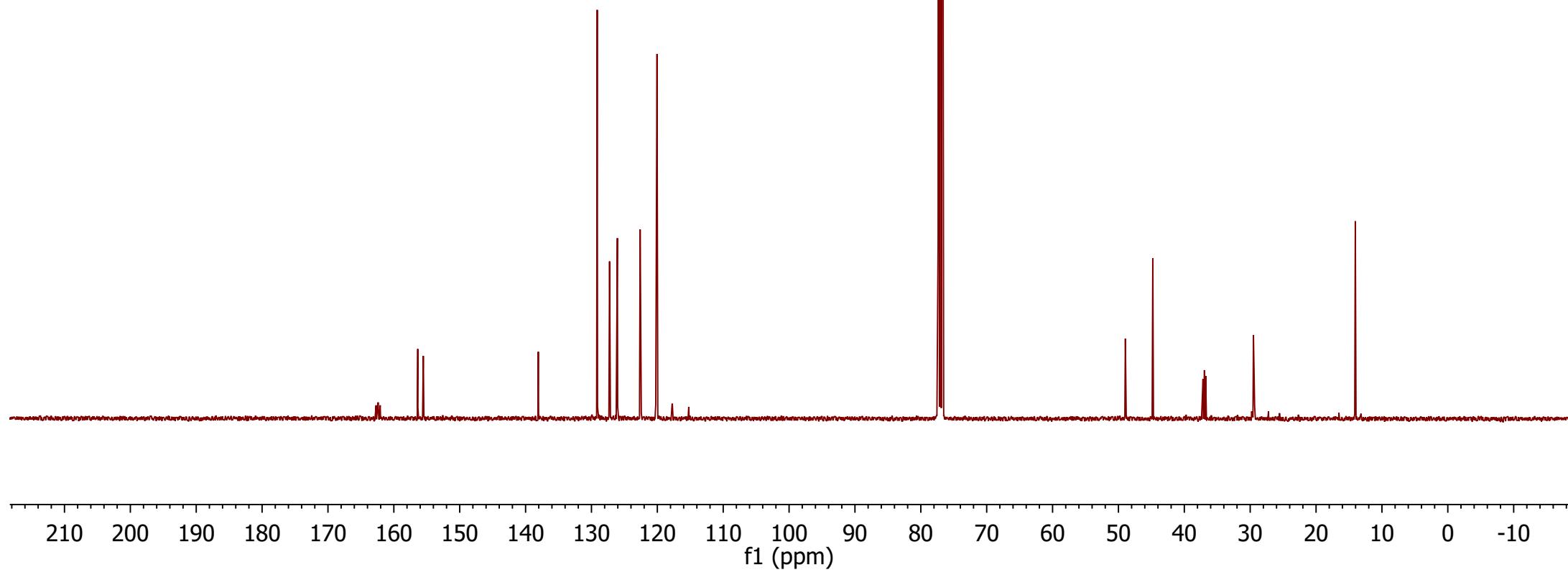
**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



162.7  
162.4  
162.1  
156.4  
155.5

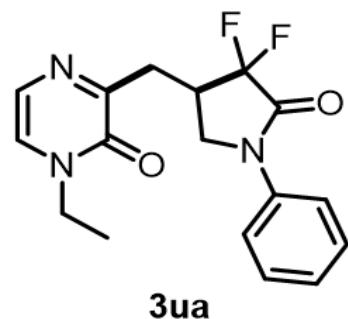
138.1  
129.1  
127.3  
126.1  
122.6  
120.2  
120.0  
117.8  
117.7  
115.2

49.0  
48.9  
44.8  
37.2  
37.0  
36.9  
36.8  
29.5  
29.4  
14.0

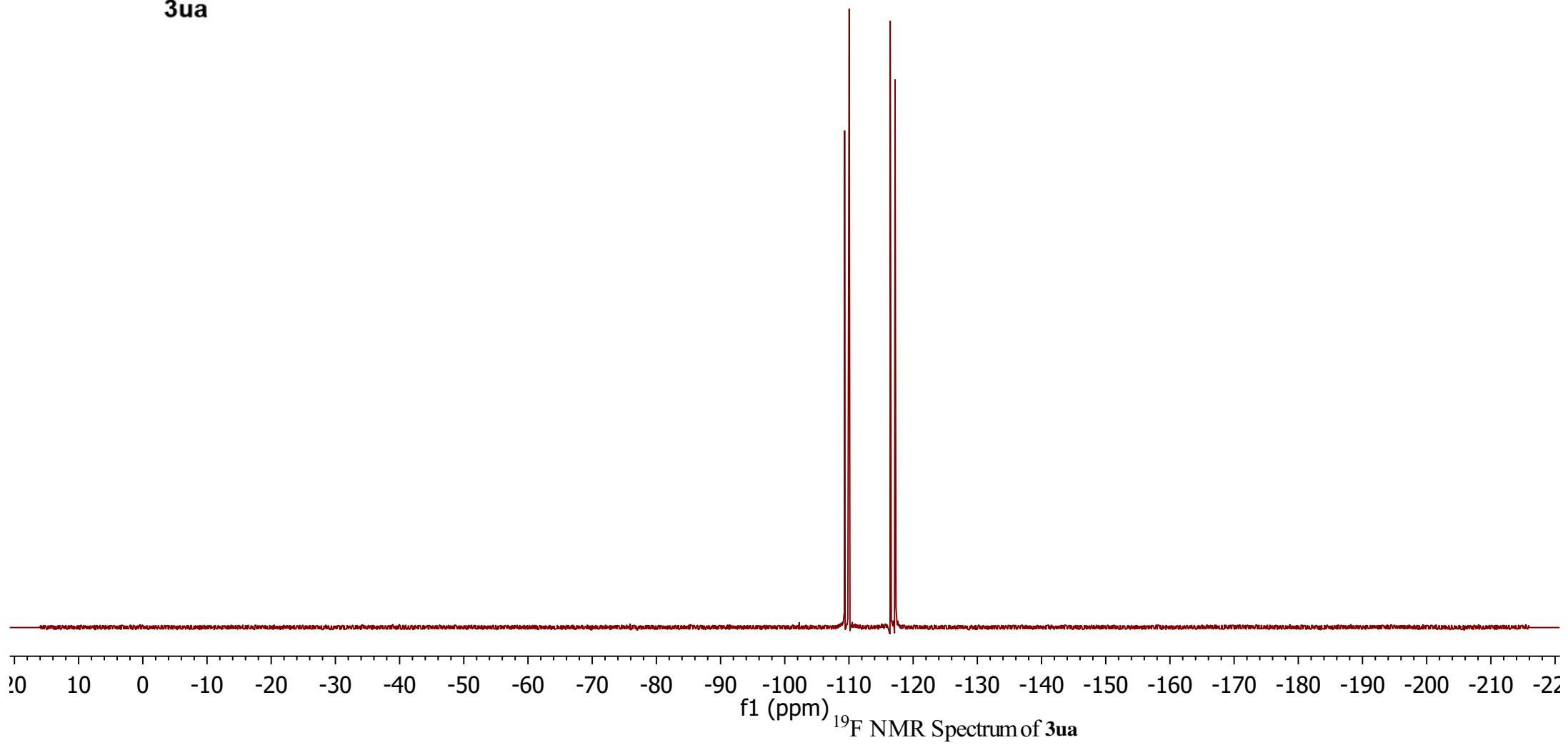


<sup>13</sup>C NMR Spectrum of **3ua**

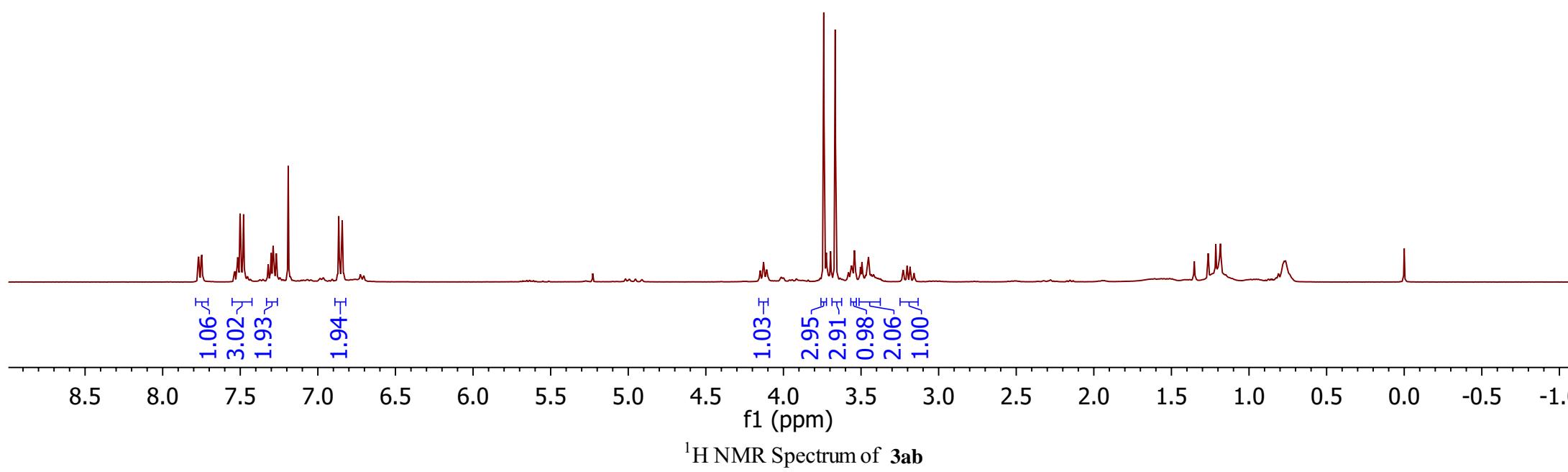
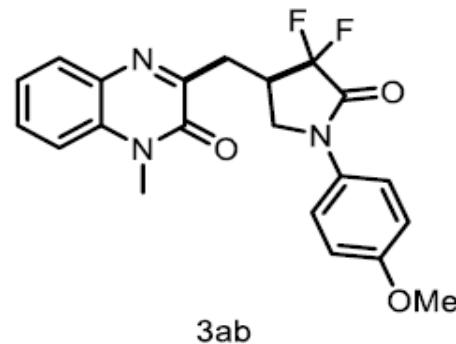
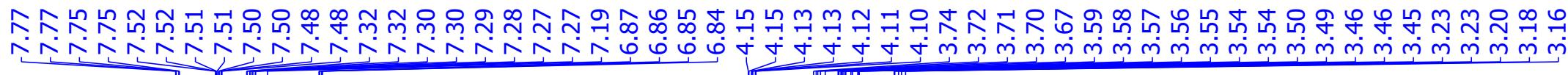
**19F (CDCl<sub>3</sub>, 376 MHz)**



-109.33  
-109.36  
-110.04  
-110.07  
-116.43  
-116.47  
-117.14  
-117.18

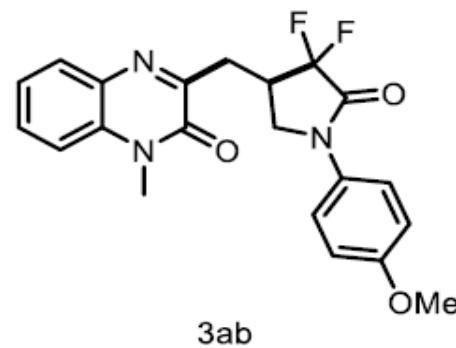


**1H (CDCl<sub>3</sub>, 400 MHz)**



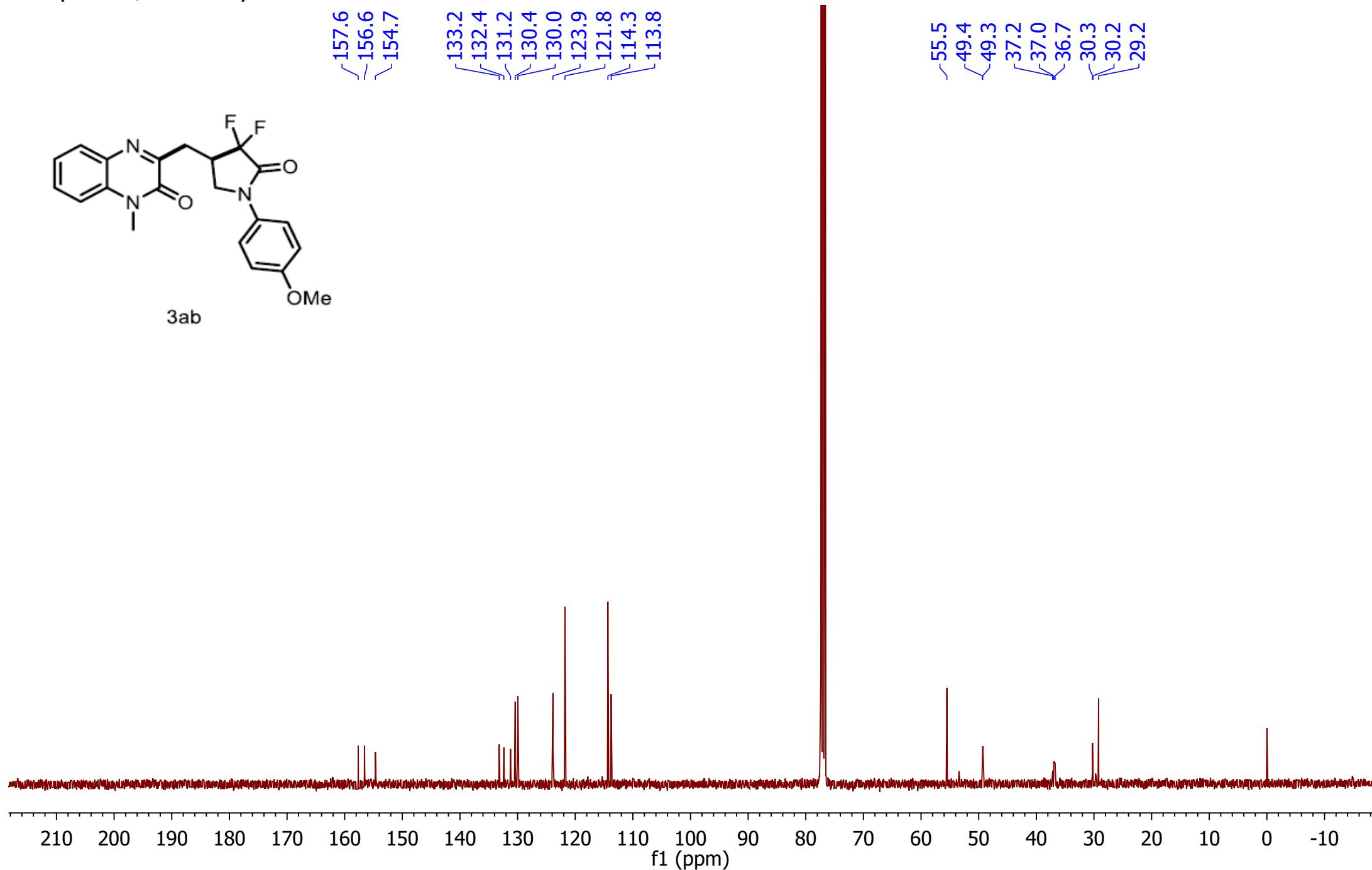
<sup>1</sup>H NMR Spectrum of 3ab

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



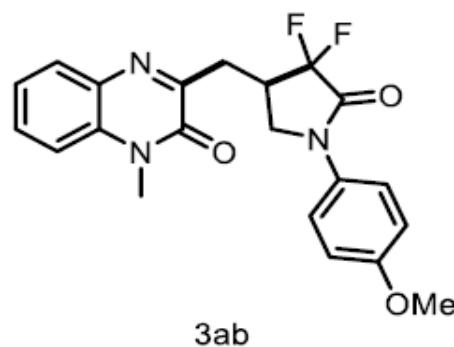
157.6  
156.6  
154.7

133.2  
132.4  
131.2  
130.4  
130.0  
123.9  
121.8  
114.3  
113.8

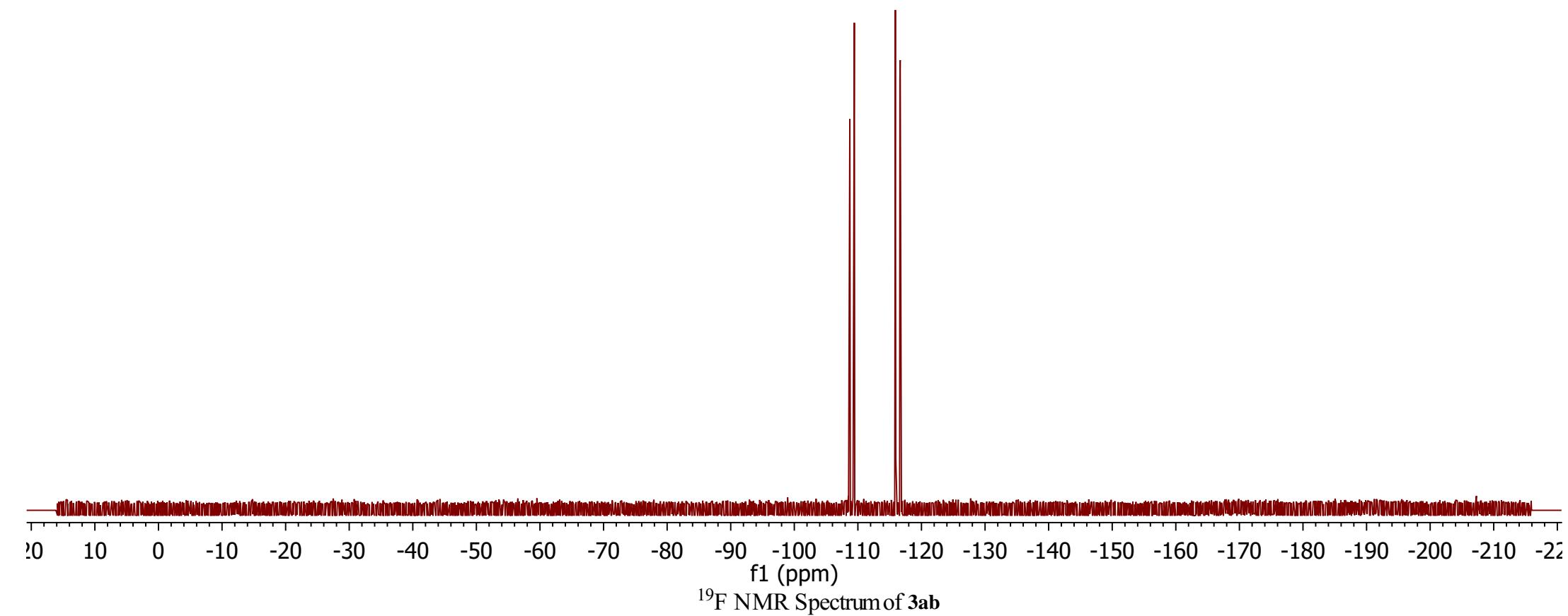


<sup>13</sup>C NMR Spectrum of 3ab

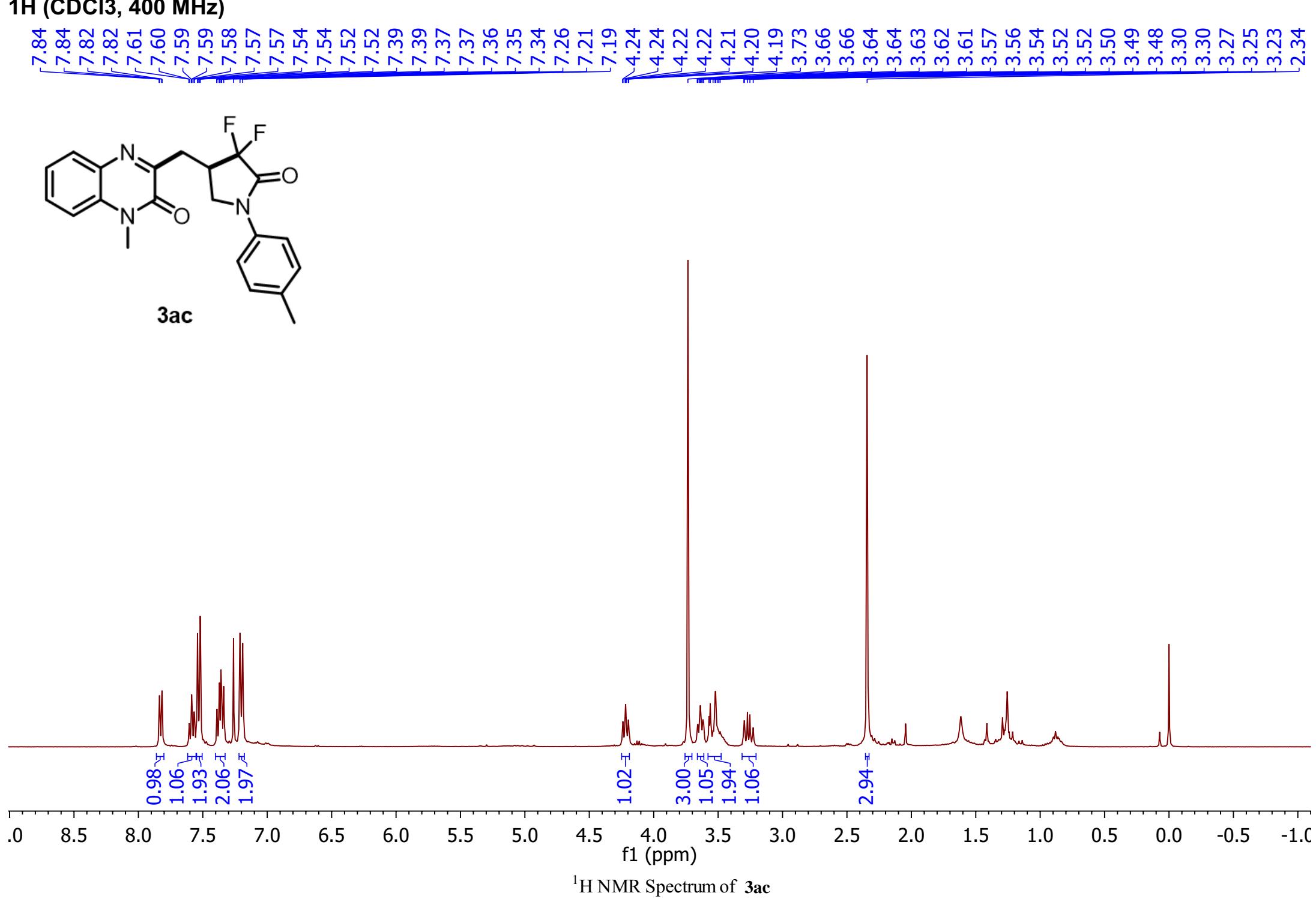
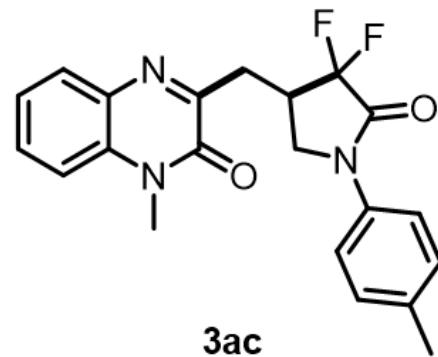
**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



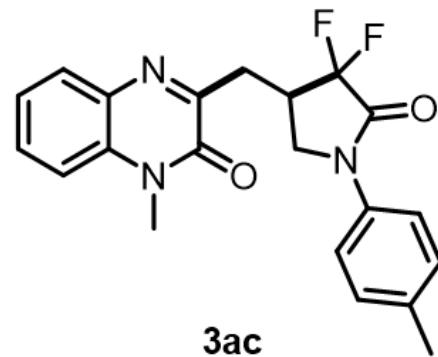
-108.73  
-108.77  
-109.44  
-109.48  
-115.90  
-115.95  
-116.61  
-116.66



**1H (CDCl3, 400 MHz)**

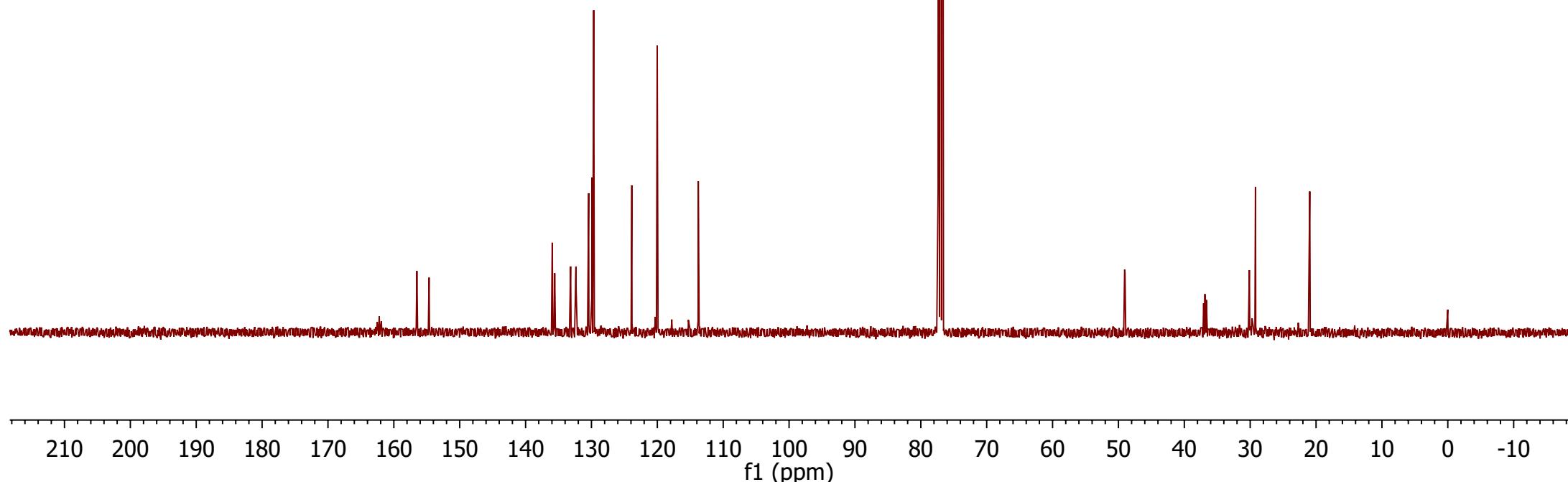


**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



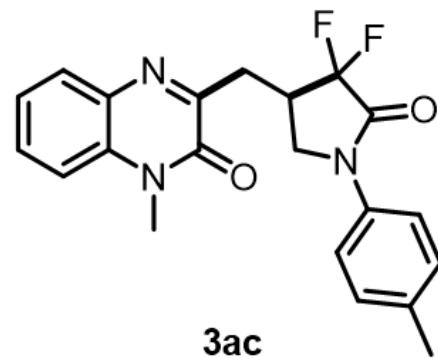
162.2  
161.9  
156.5  
154.6  
136.0  
135.6  
133.2  
132.4  
130.4  
129.9  
129.7  
123.9  
120.3  
120.0  
117.8  
115.3  
113.8

49.1  
49.0  
37.1  
36.9  
36.7  
30.2  
30.1  
29.7  
29.2  
21.0

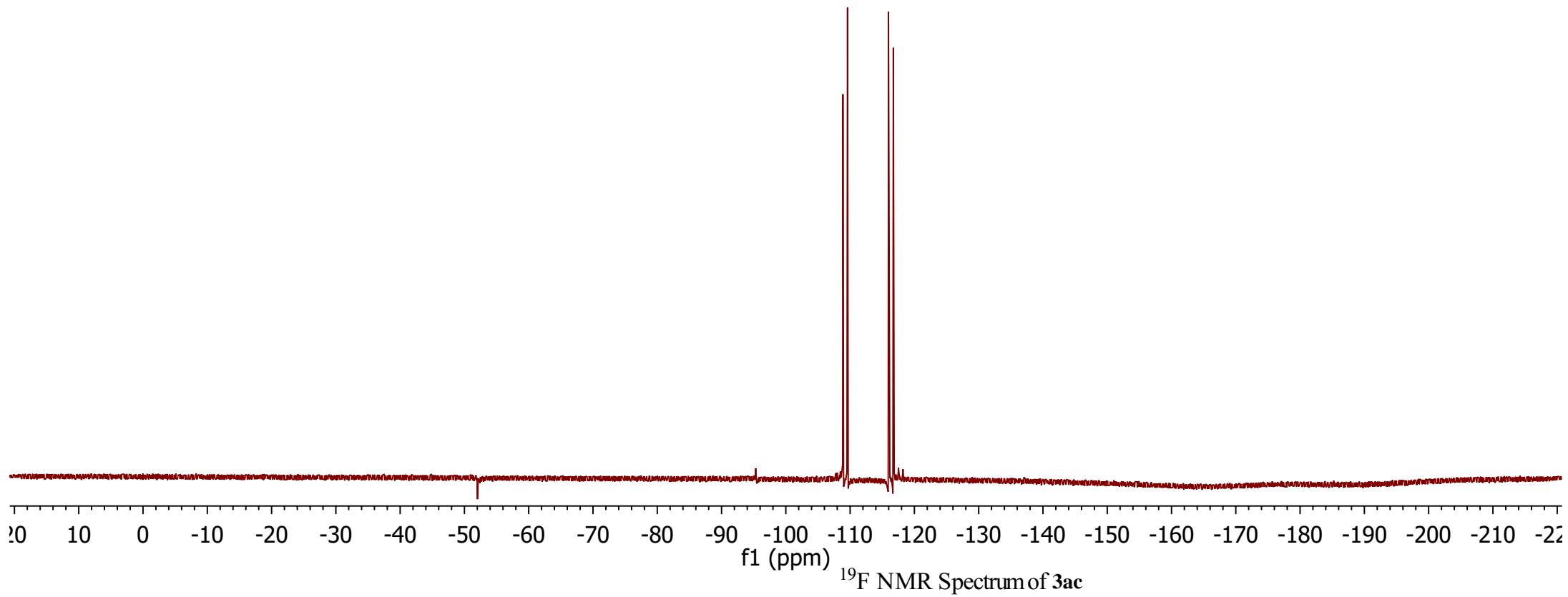


<sup>13</sup>C NMR Spectrum of 3ac

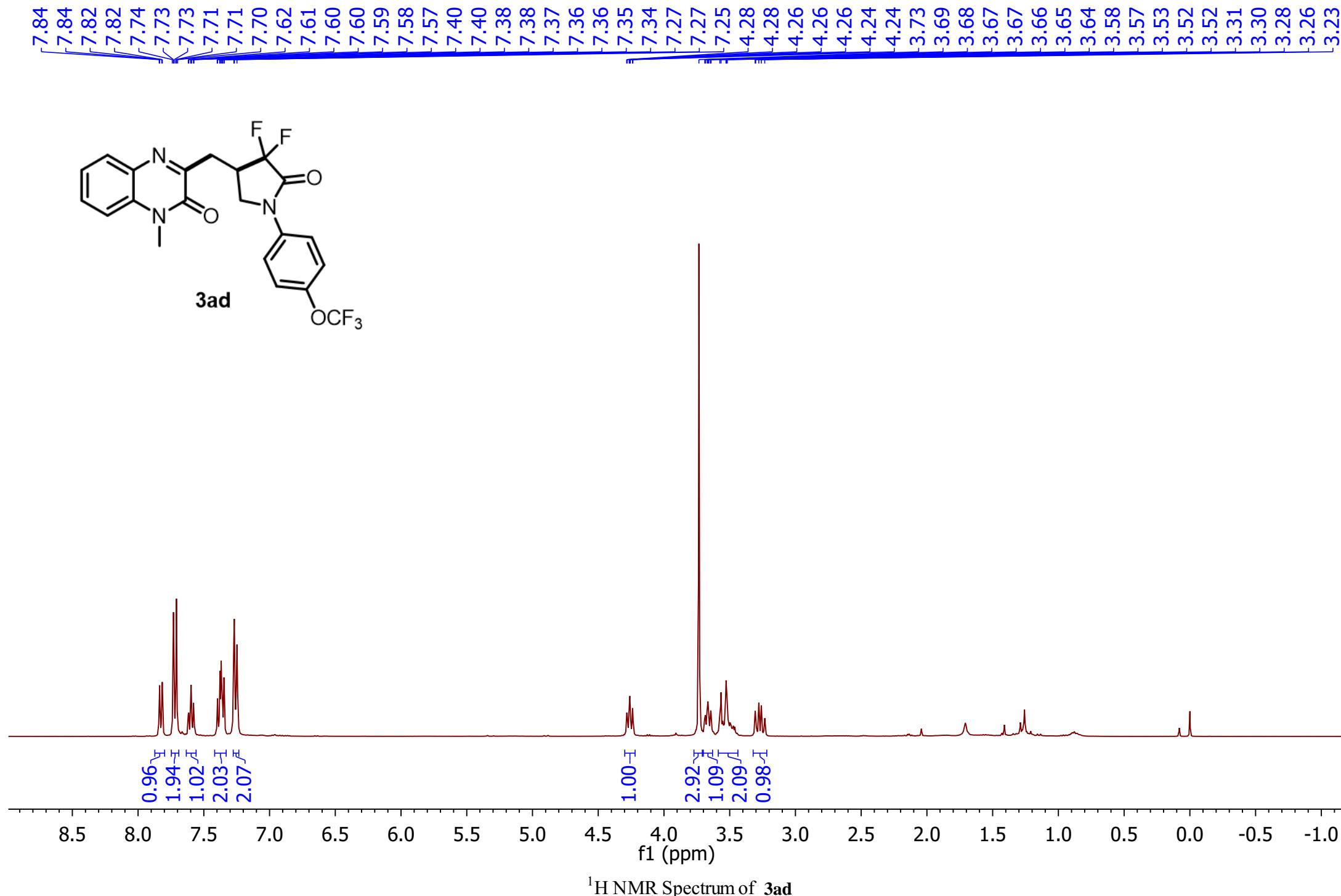
<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



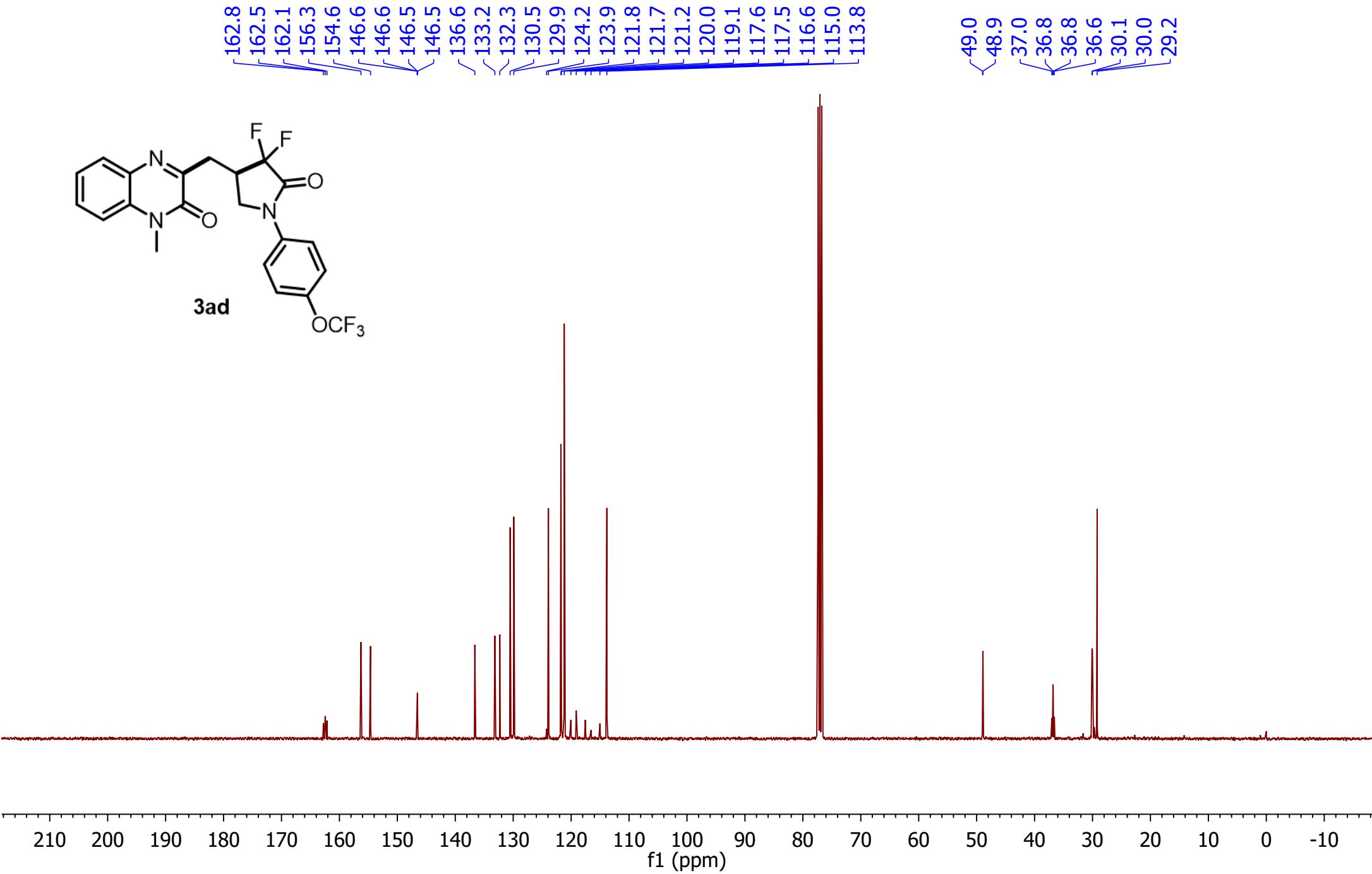
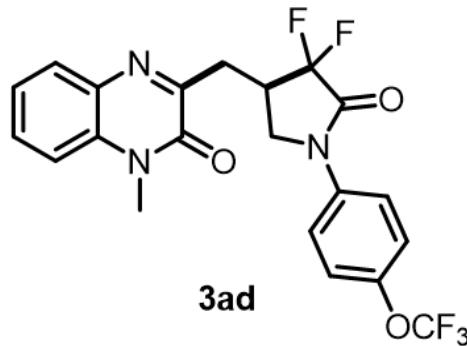
-108.88  
-108.92  
-109.59  
-109.63  
-115.97  
-116.01  
-116.68  
-116.72



**1H (CDCl<sub>3</sub>, 400 MHz)**

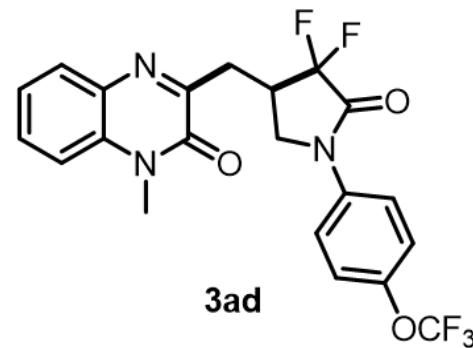


**13C (CDCl3, 101 MHz)**



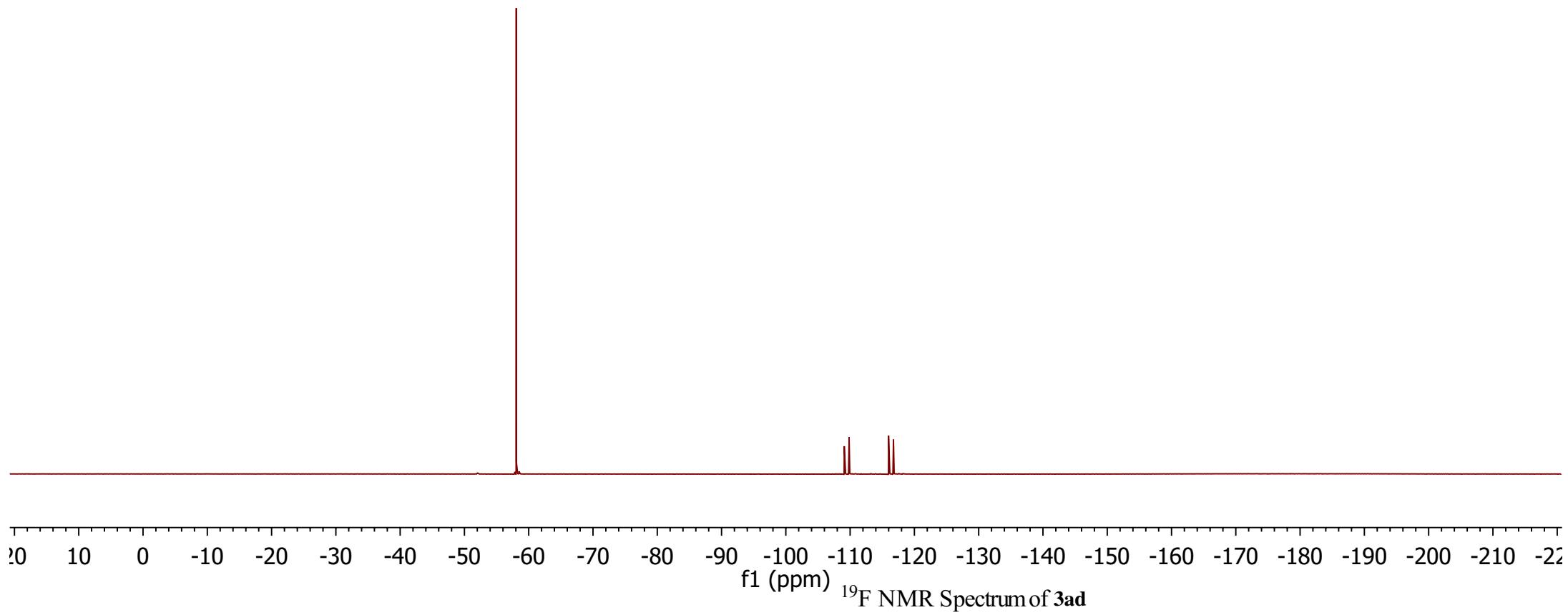
### <sup>13</sup>C NMR Spectrum of 3ad

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

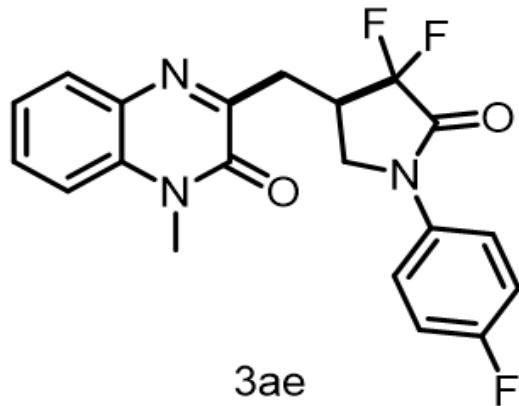


—58.06

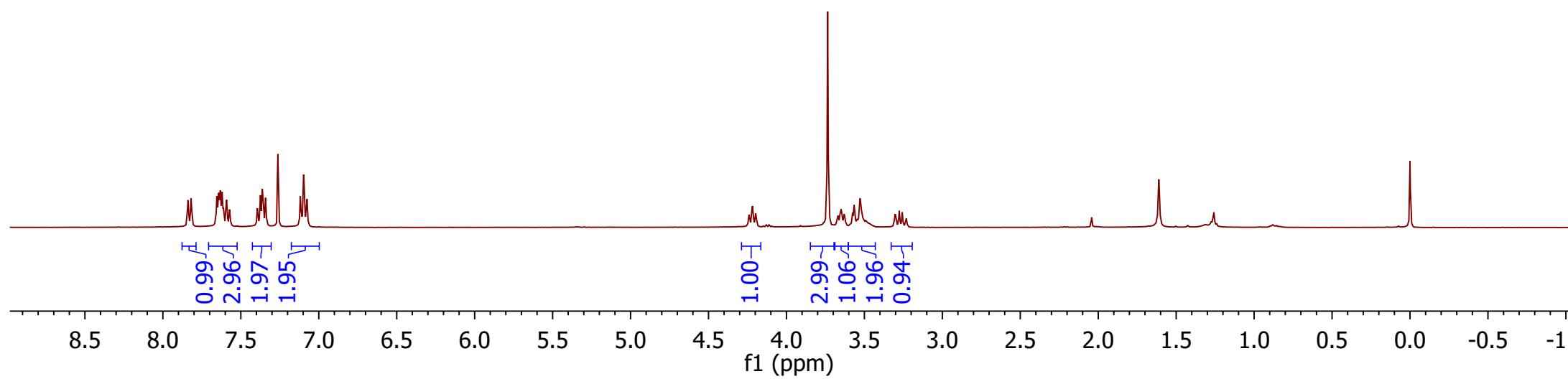
-109.09  
-109.13  
-109.81  
-109.84  
-115.98  
-116.03  
-116.70  
-116.74



**1H (CDCl<sub>3</sub>, 400 MHz)**

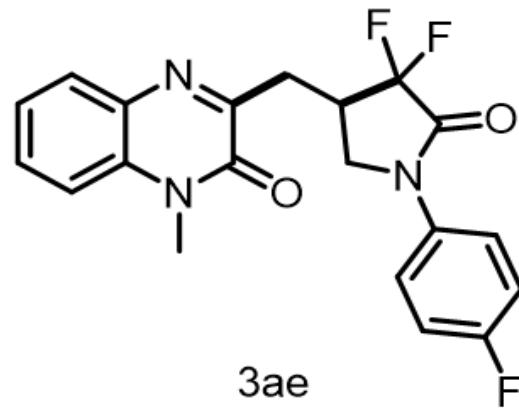


3ae



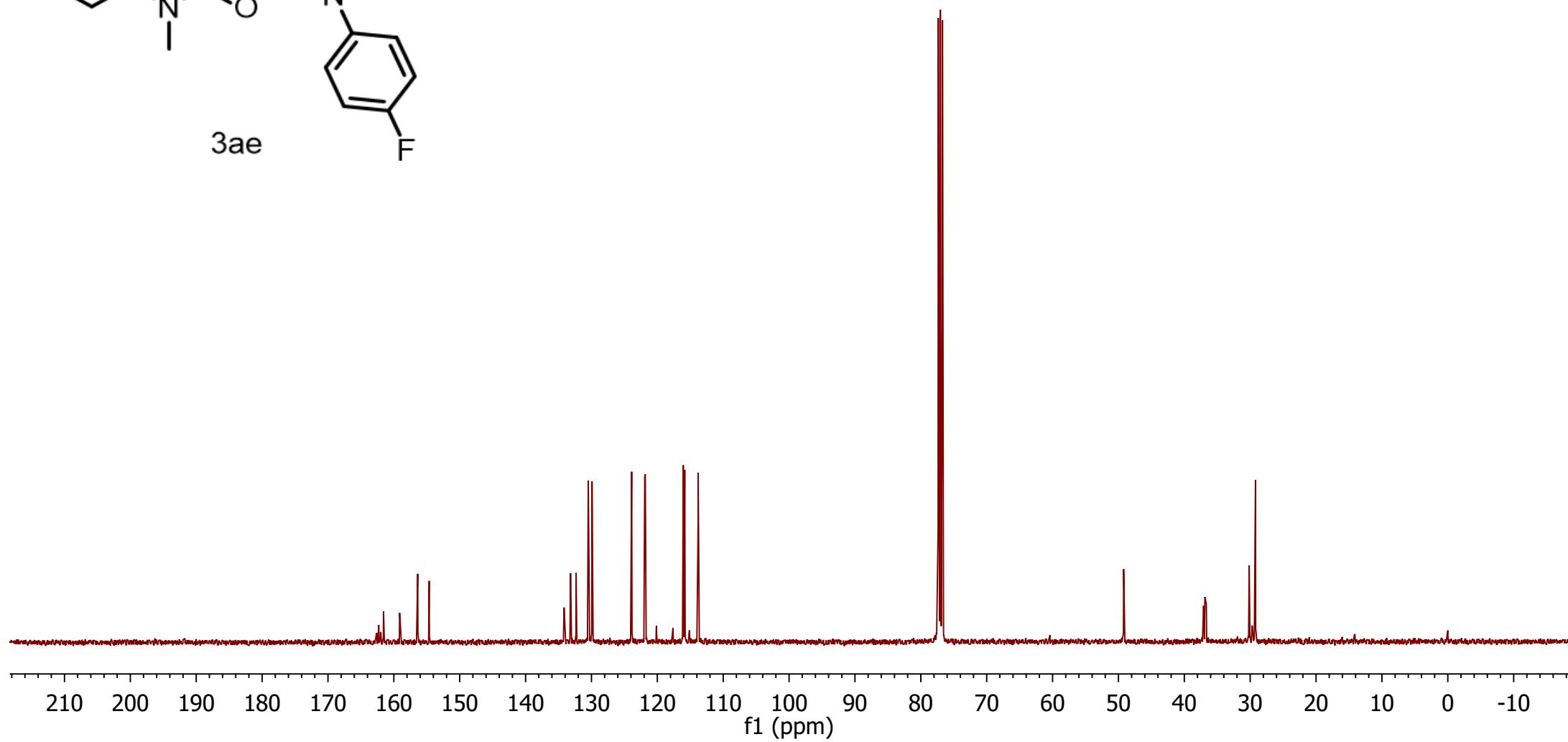
<sup>1</sup>H NMR Spectrum of 3ae

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



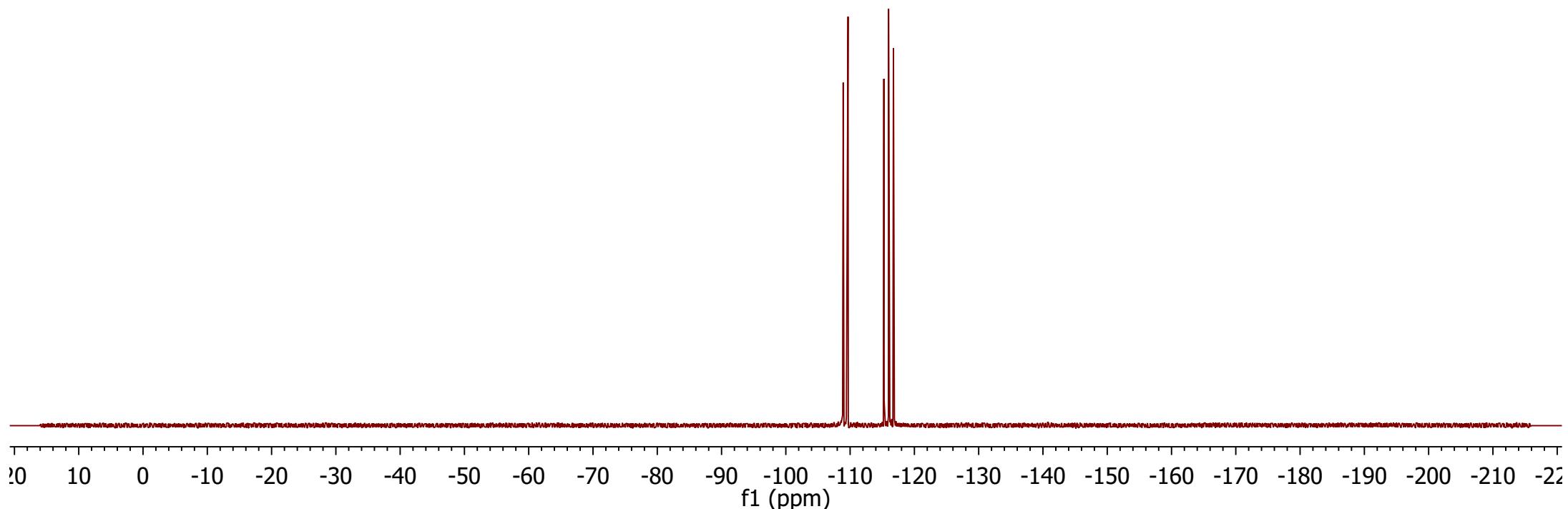
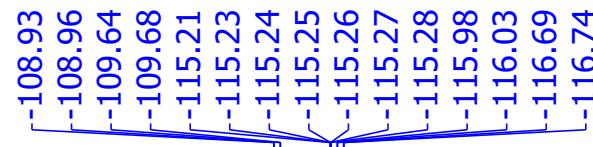
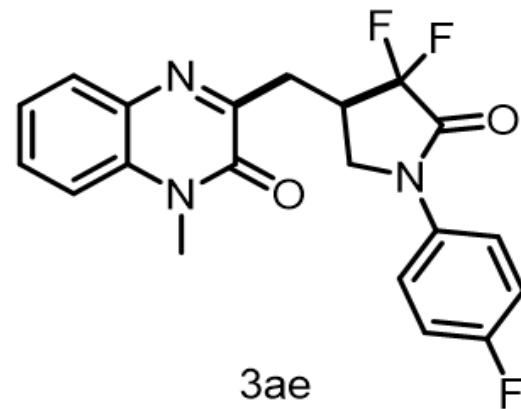
162.6  
162.3  
162.0  
161.6  
159.1  
156.4  
154.6  
134.2  
134.2  
133.2  
132.3  
130.5  
129.9  
123.9  
121.9  
121.8  
120.1  
117.6  
116.1  
115.8  
115.1  
113.8

49.2  
49.1  
37.1  
36.9  
36.9  
36.7  
30.2  
30.1  
29.2



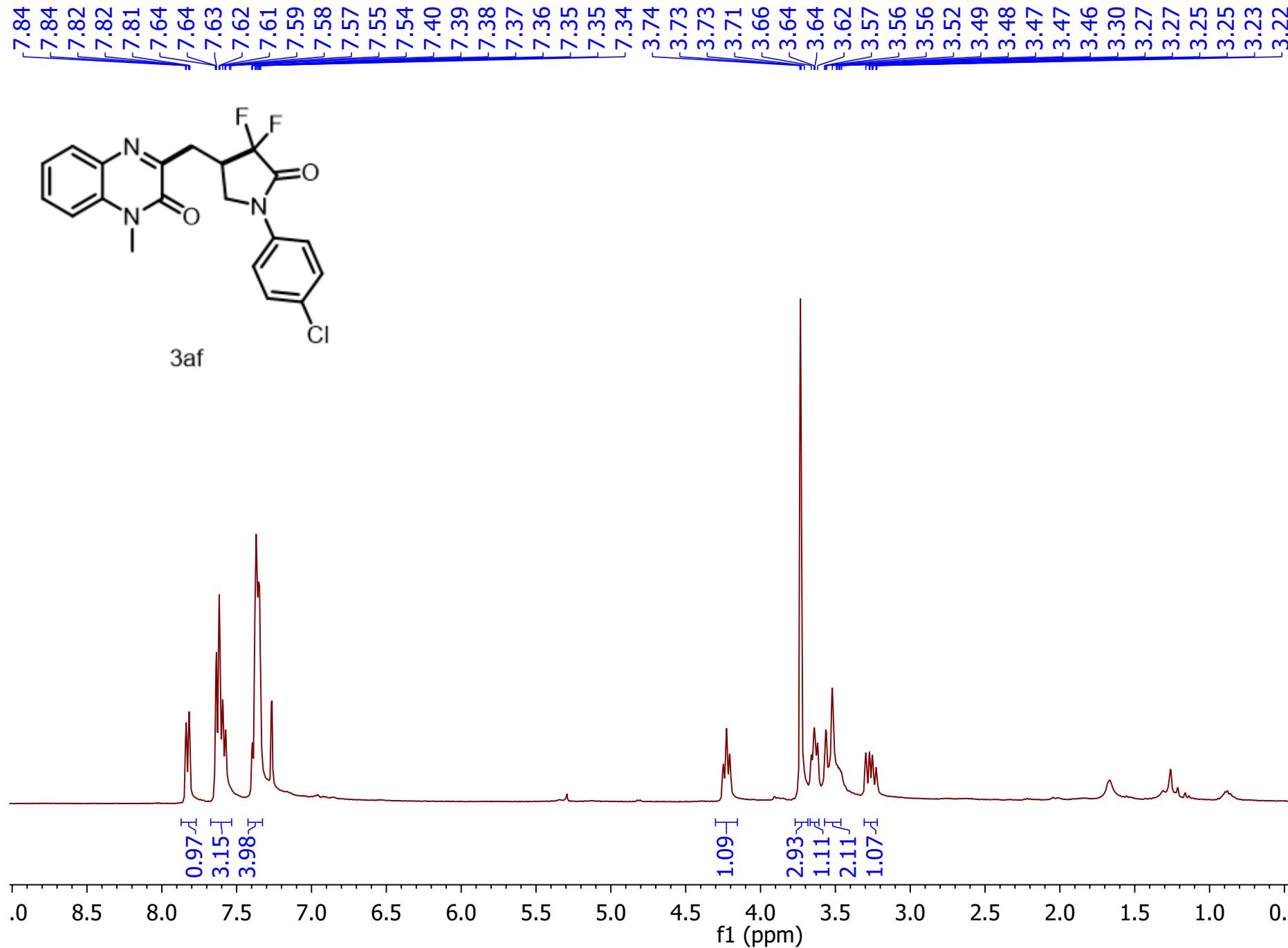
<sup>13</sup>C NMR Spectrum of 3ae

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



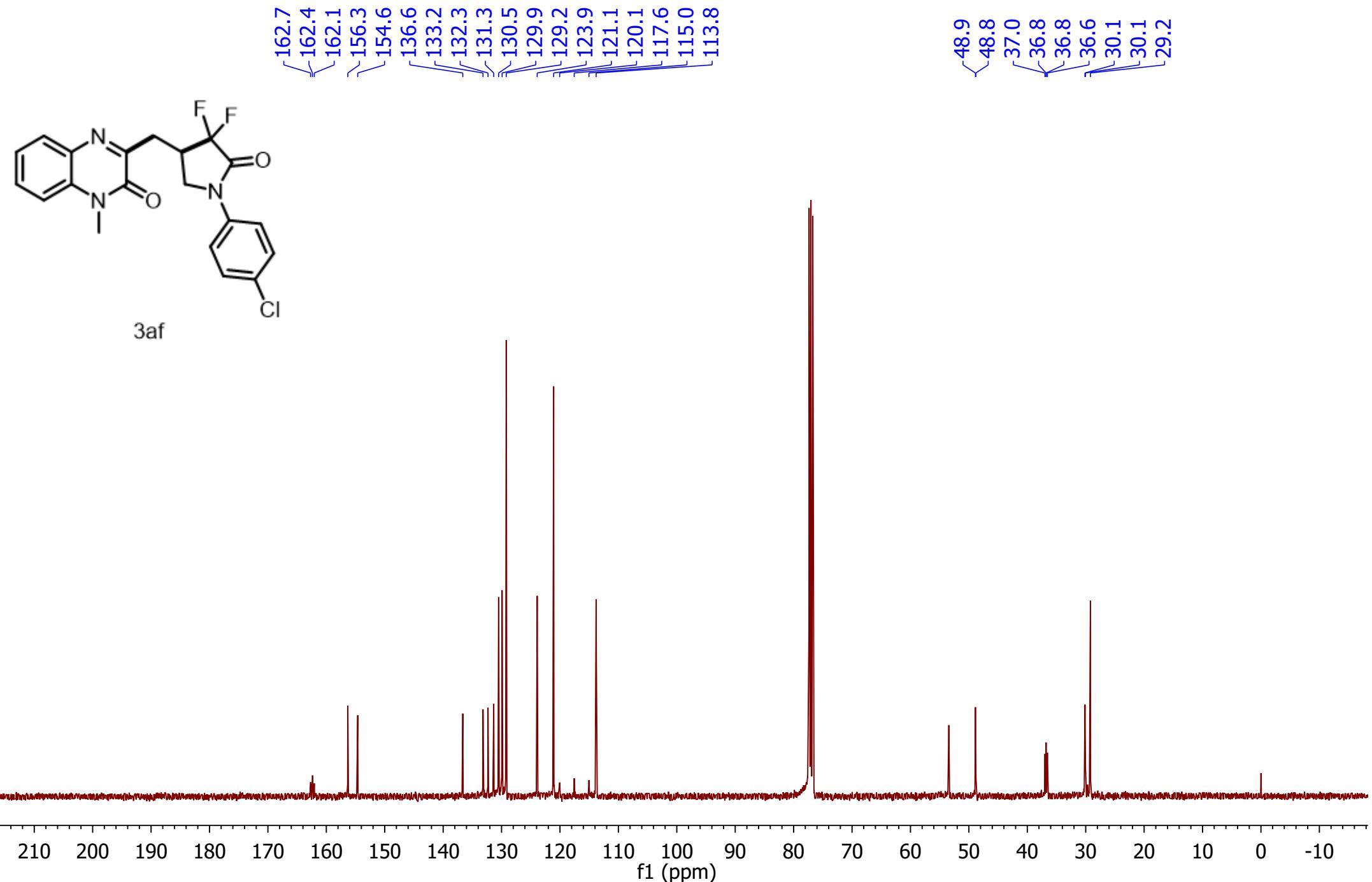
<sup>19</sup>F NMR Spectrum of 3ae

**1H (CDCl<sub>3</sub>, 400 MHz)**



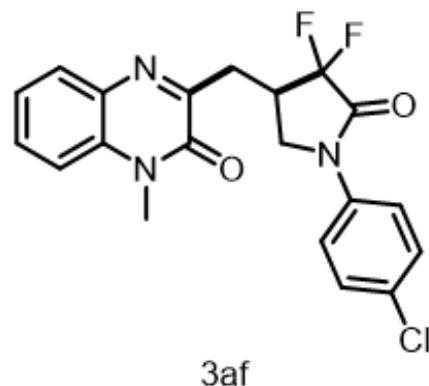
<sup>1</sup>H NMR Spectrum of **3af**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

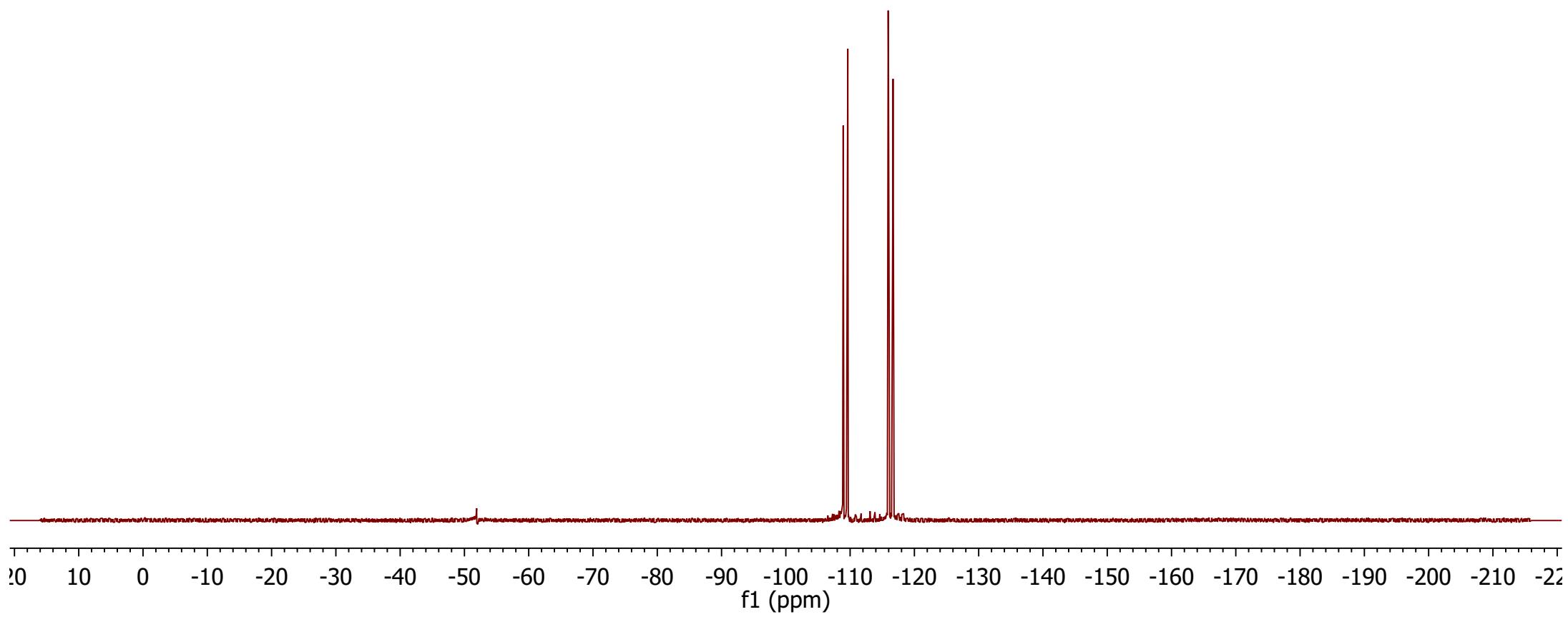


<sup>13</sup>C NMR Spectrum of 3af

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



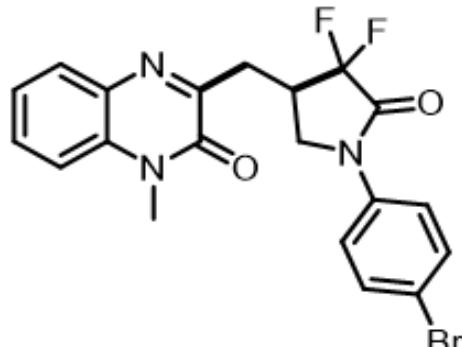
-108.93  
-108.96  
-109.64  
-109.68  
-115.92  
-115.97  
-116.63  
-116.68



<sup>19</sup>F NMR Spectrum of 3af

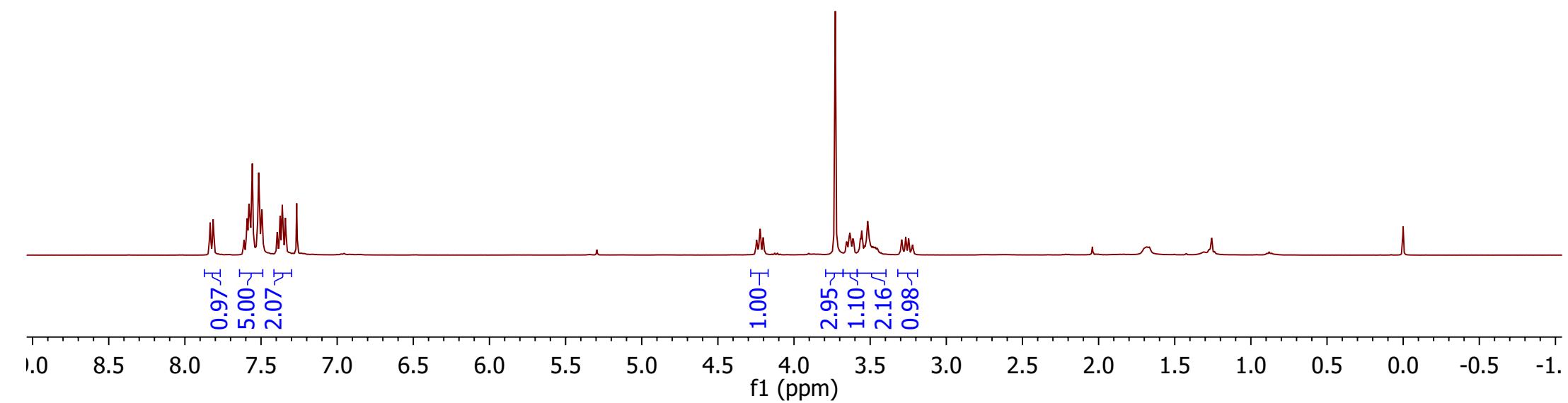
**1H (CDCl<sub>3</sub>, 400 MHz)**

7.84  
7.83  
7.81  
7.61  
7.61  
7.59  
7.58  
7.57  
7.57  
7.56  
7.52  
7.49  
7.39  
7.37  
7.36  
7.34



3ag

4.25  
4.23  
4.22  
4.20  
3.73  
3.71  
3.66  
3.65  
3.64  
3.63  
3.61  
3.61  
3.56  
3.56  
3.54  
3.52  
3.49  
3.48  
3.47  
3.47  
3.45  
3.29  
3.27  
3.25  
3.22

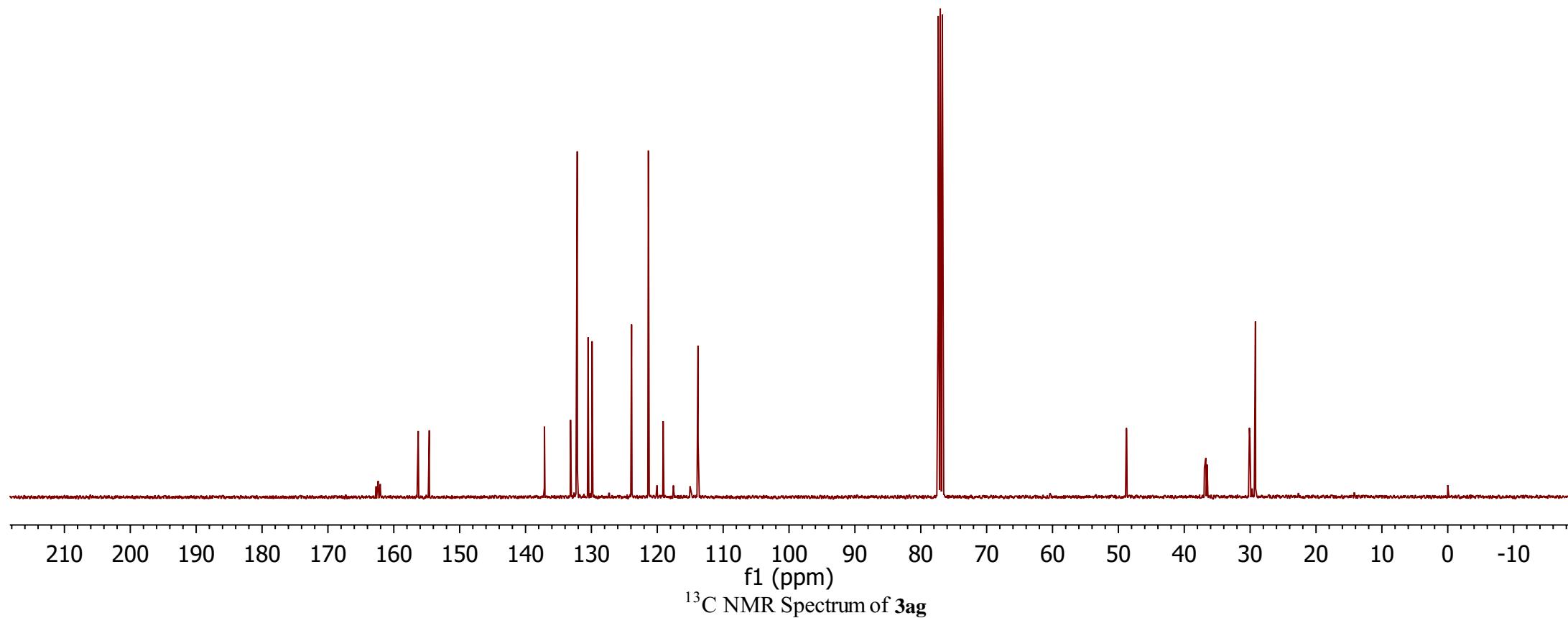


<sup>1</sup>H NMR Spectrum of 3ag

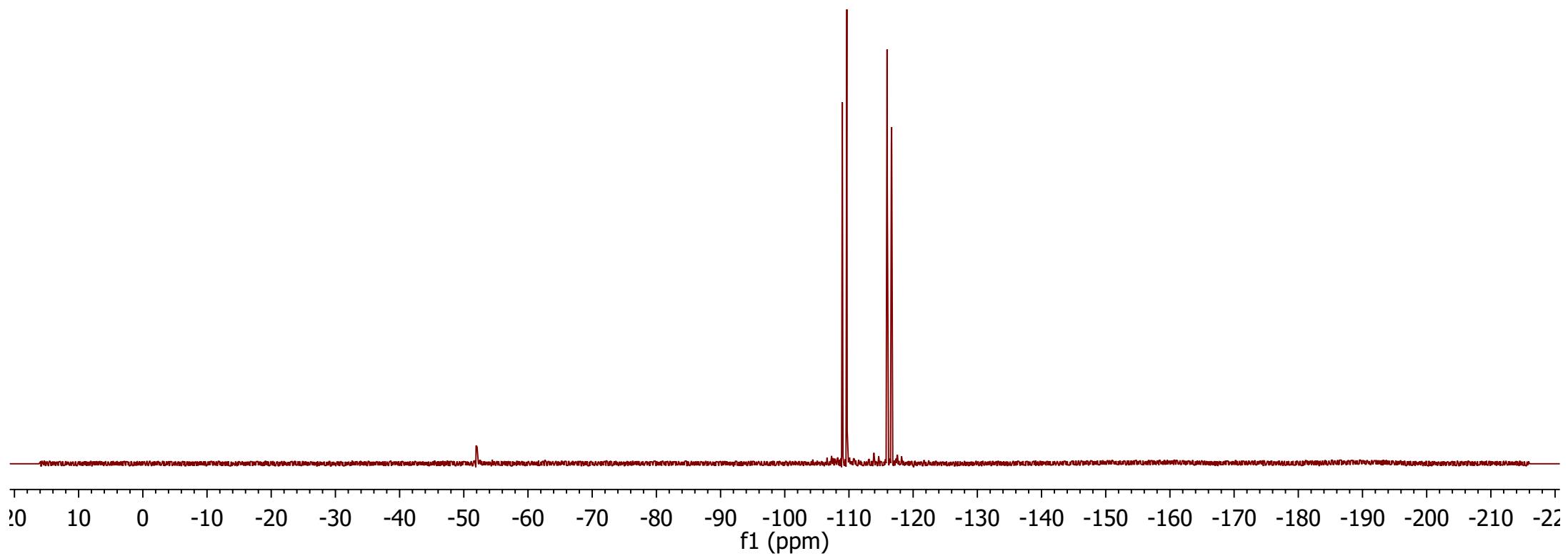
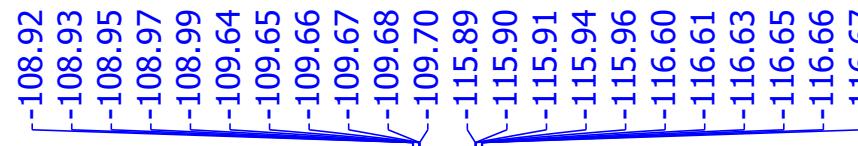
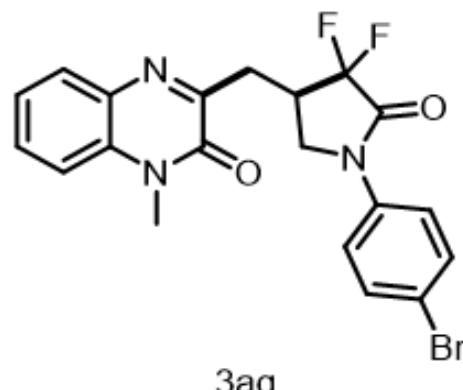
<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



3ag

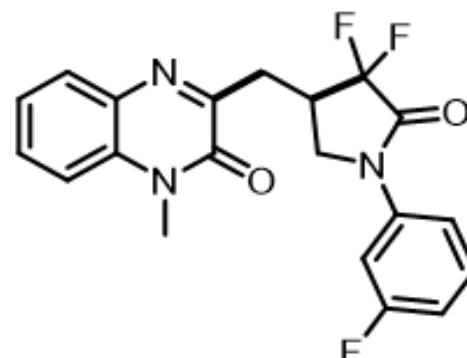


<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

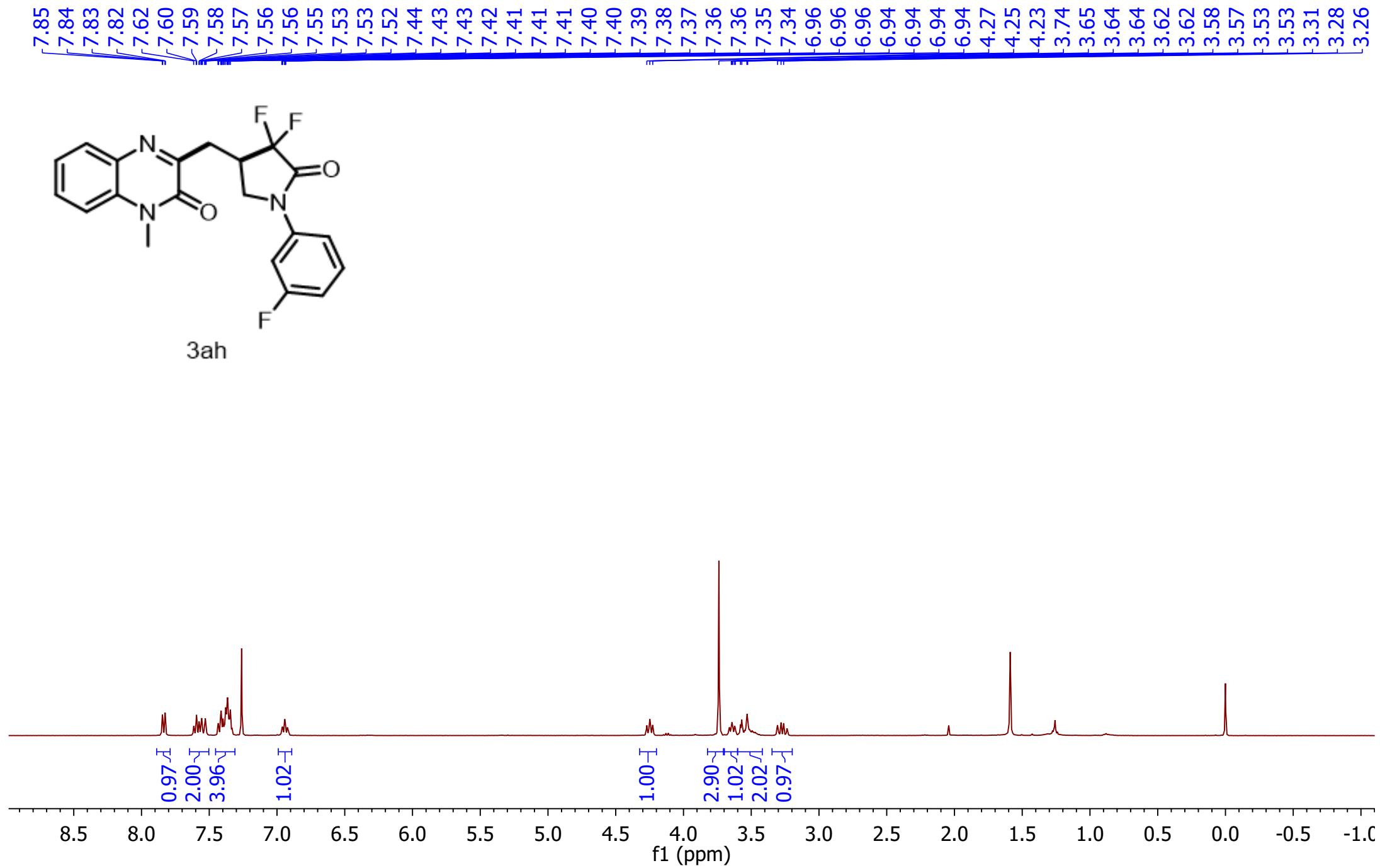


<sup>19</sup>F NMR Spectrum of 3ag

## **1H (CDCl<sub>3</sub>, 400 MHz)**



3ah

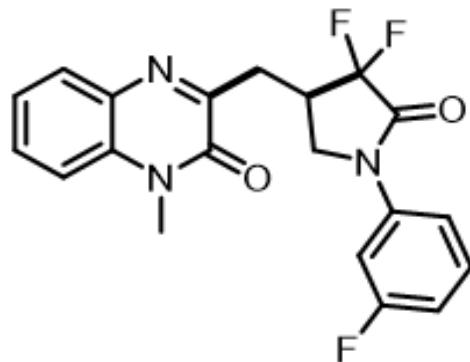


### <sup>1</sup>H NMR Spectrum of 3ah

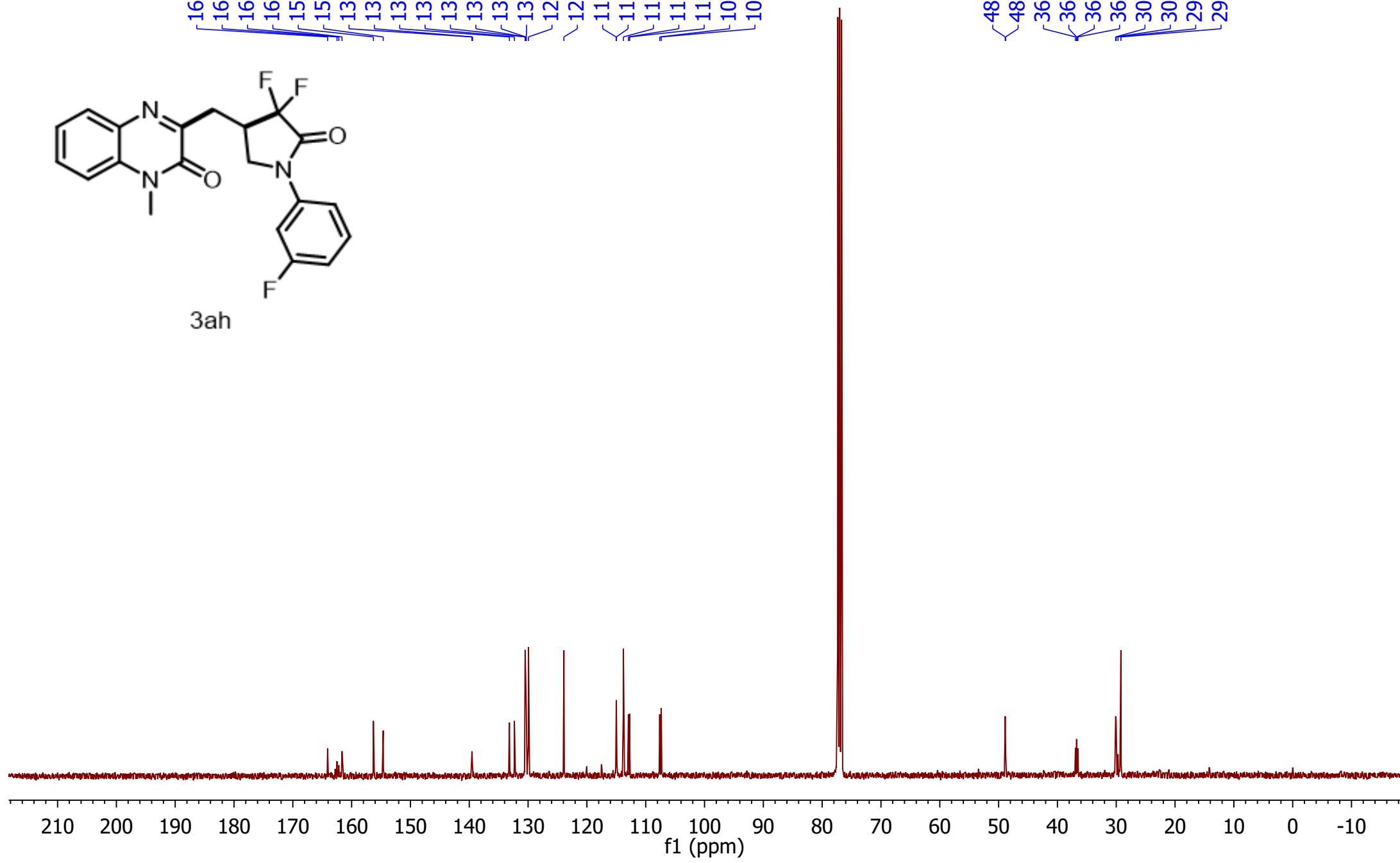
<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)

164.1  
162.5  
162.2  
161.6  
156.3  
154.6  
139.5  
139.4  
133.2  
132.3  
130.5  
130.4  
130.3  
129.9  
123.9  
115.0  
115.0  
113.8  
112.9  
112.7  
107.6  
107.4

48.9  
48.8  
36.9  
36.7  
36.7  
36.5  
30.1  
30.0  
29.7  
29.2

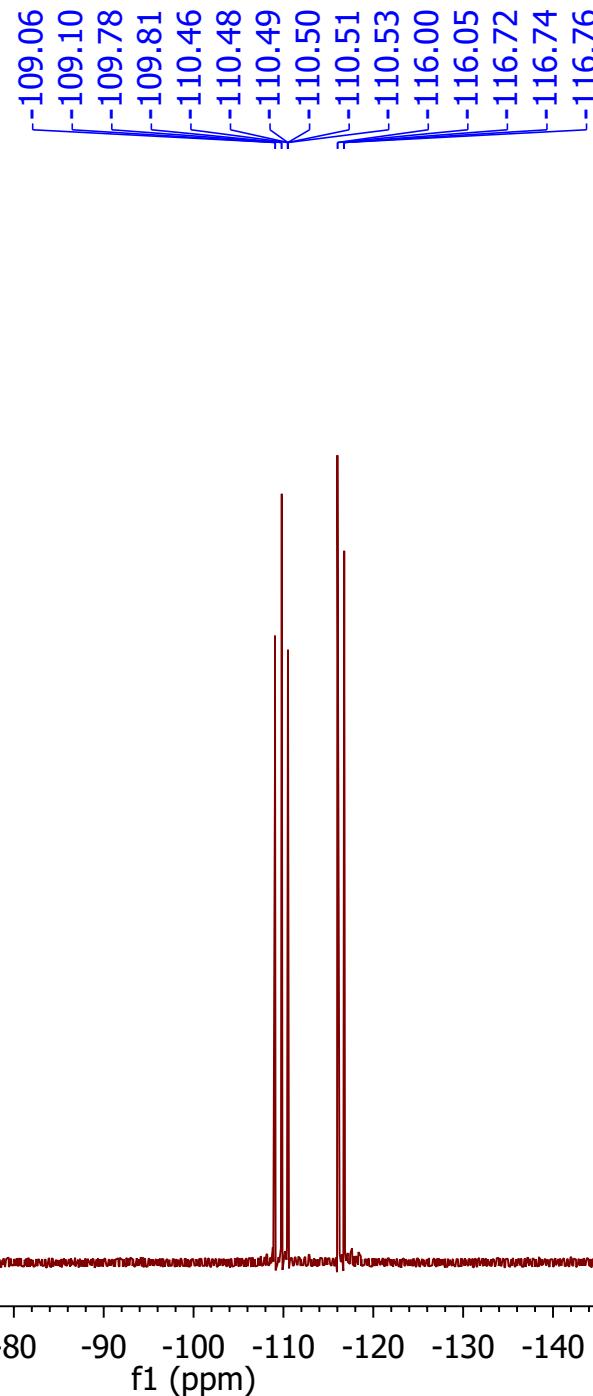
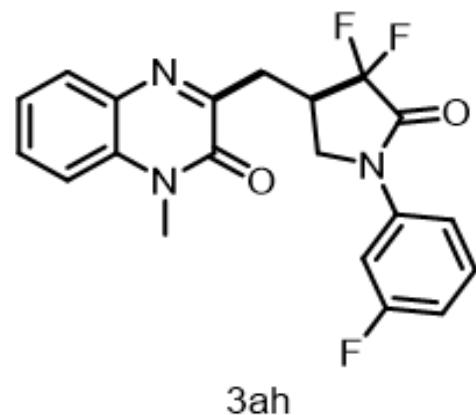


3ah



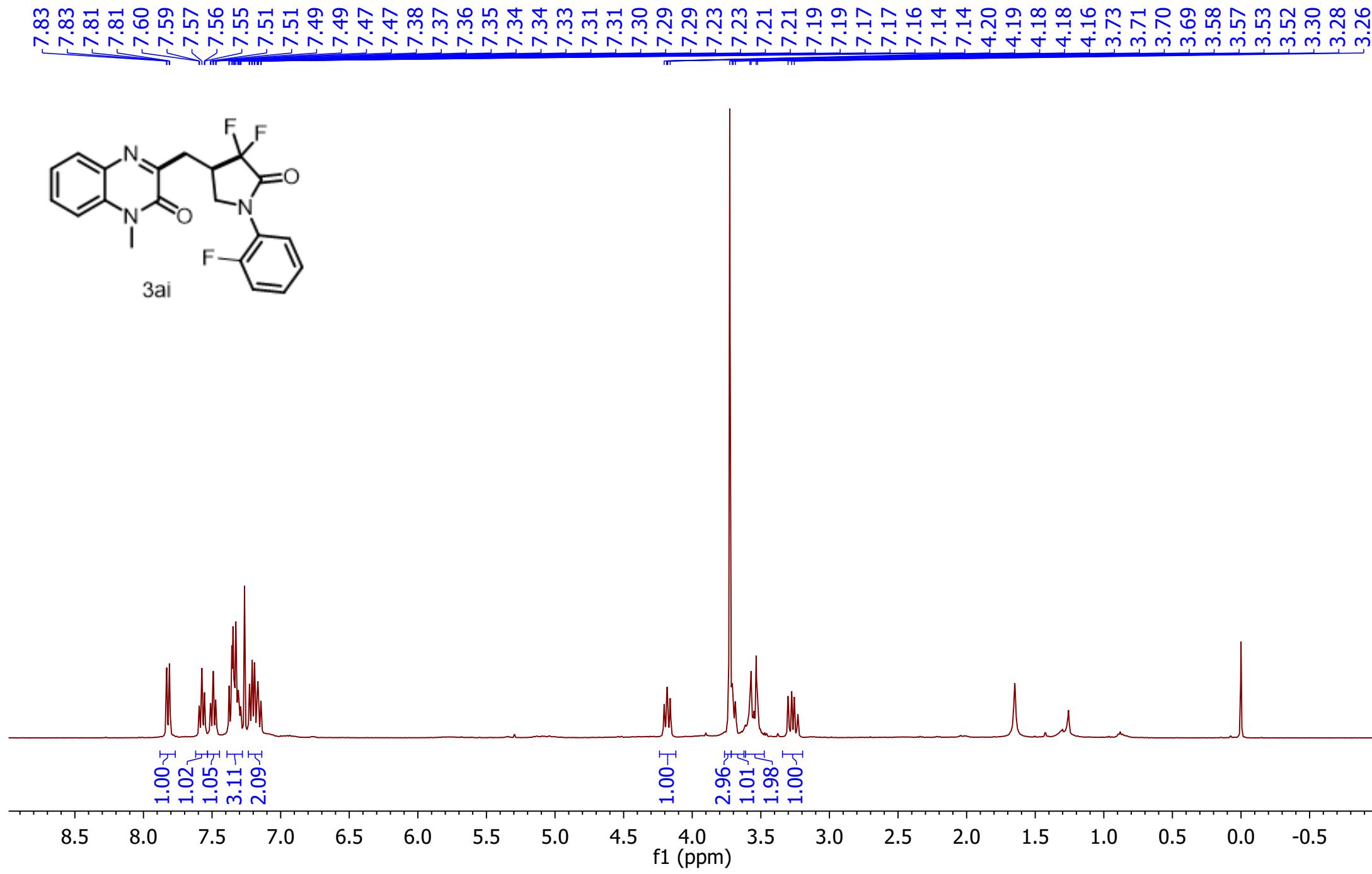
<sup>13</sup>C NMR Spectrum of 3ah

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

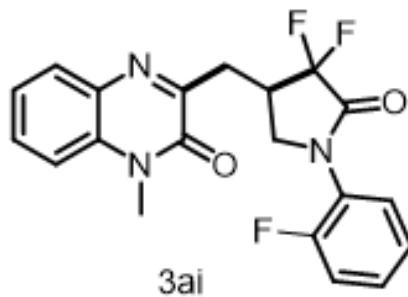


<sup>19</sup>F NMR Spectrum of 3ah

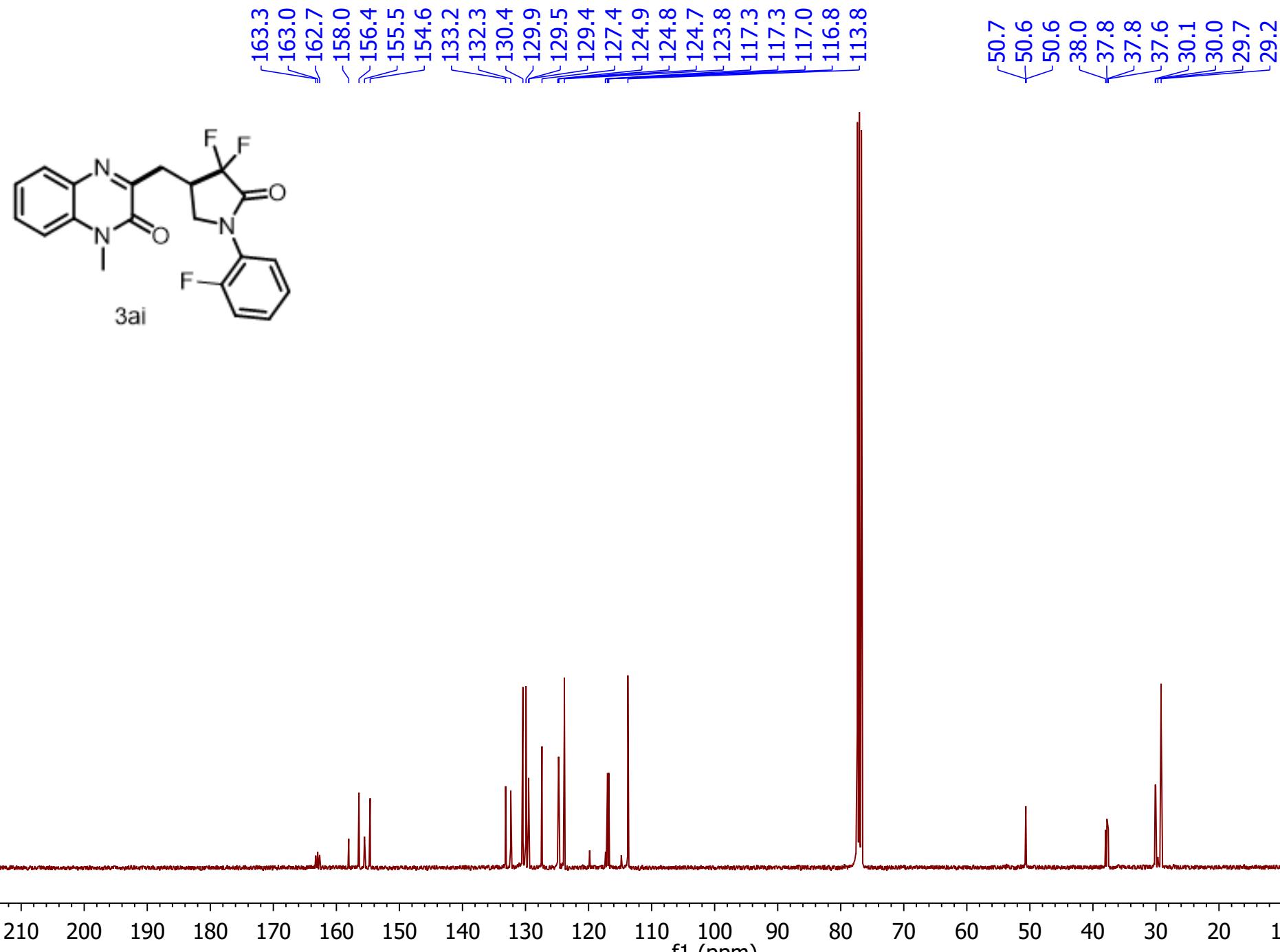
**1H (CDCl<sub>3</sub>, 400 MHz)**



<sup>1</sup>H NMR Spectrum of **3ai**

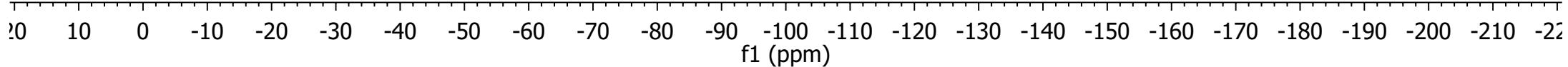
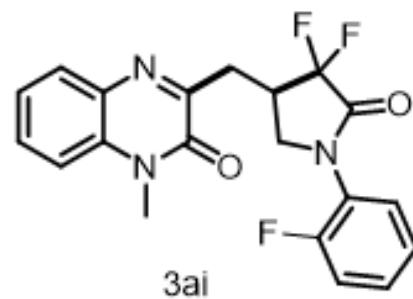


<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



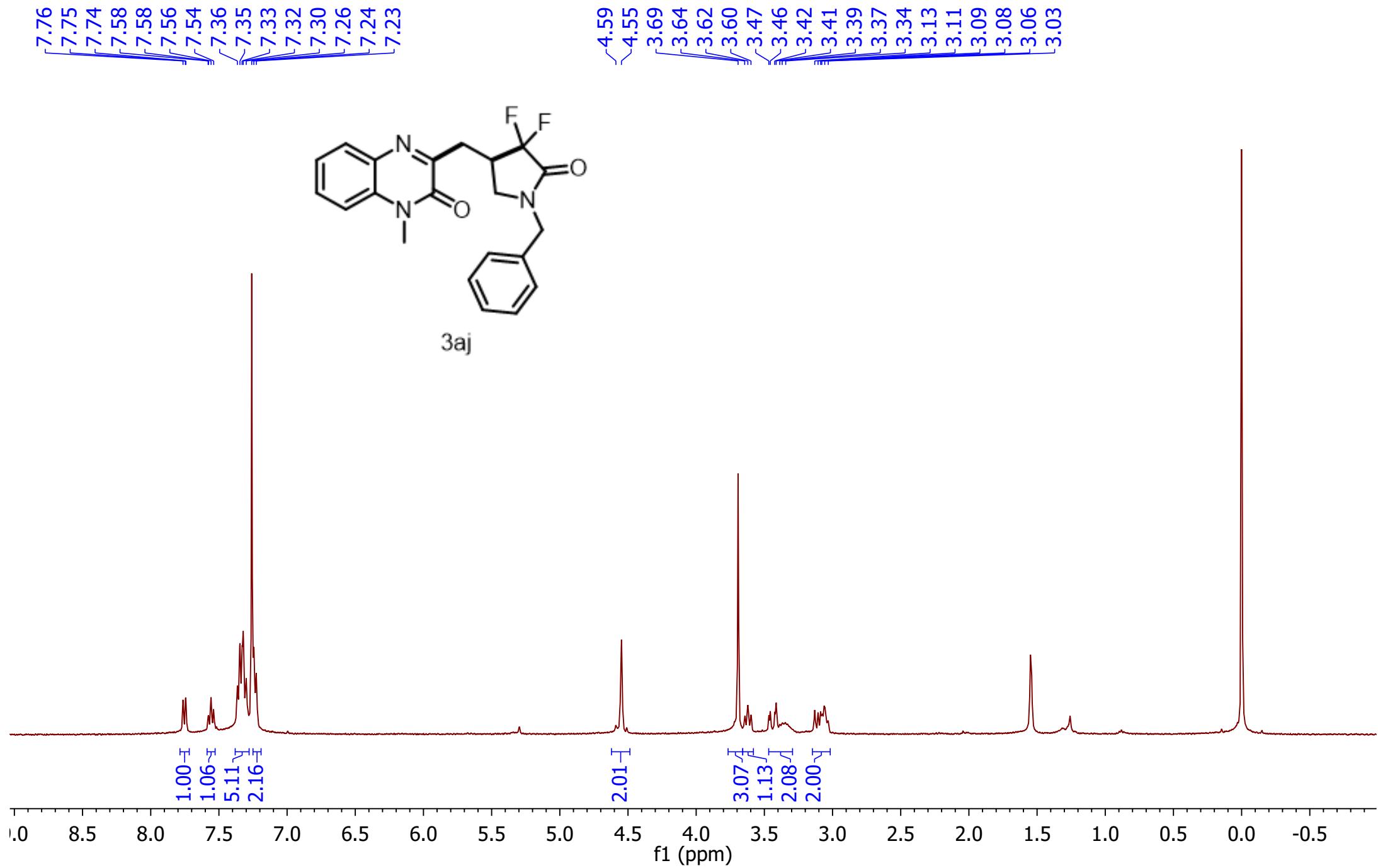
<sup>13</sup>C NMR Spectrum of 3ai

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



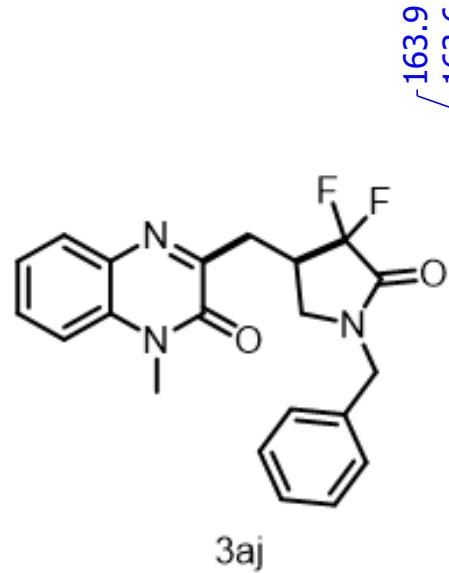
<sup>19</sup>F NMR Spectrum of 3ai

## **1H (CDCl<sub>3</sub>, 400 MHz)**



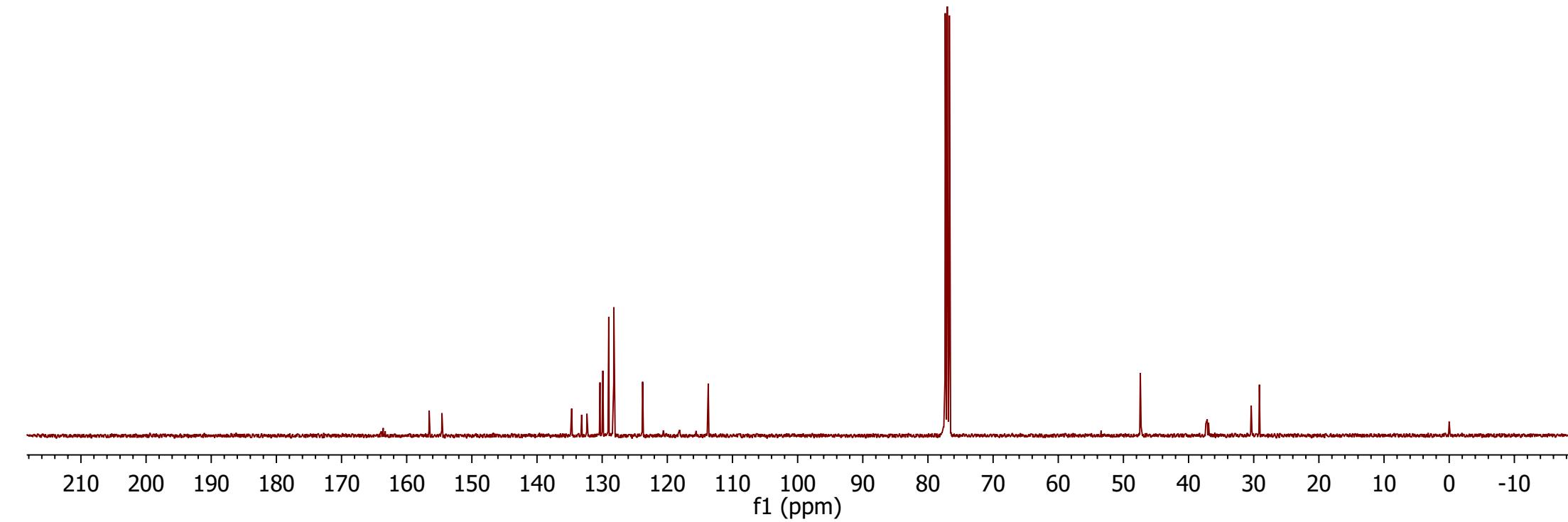
### <sup>1</sup>H NMR Spectrum of 3aj

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



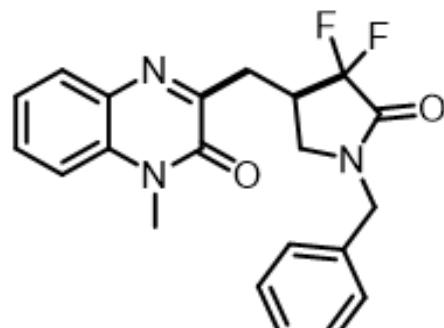
163.9  
163.6  
163.3  
156.5  
154.6  
154.6  
134.7  
133.1  
132.3  
130.3  
129.9  
129.0  
128.2  
128.2  
123.8  
120.6  
118.1  
113.7

47.4  
47.3  
37.4  
37.1  
36.9  
30.4  
30.3  
29.1



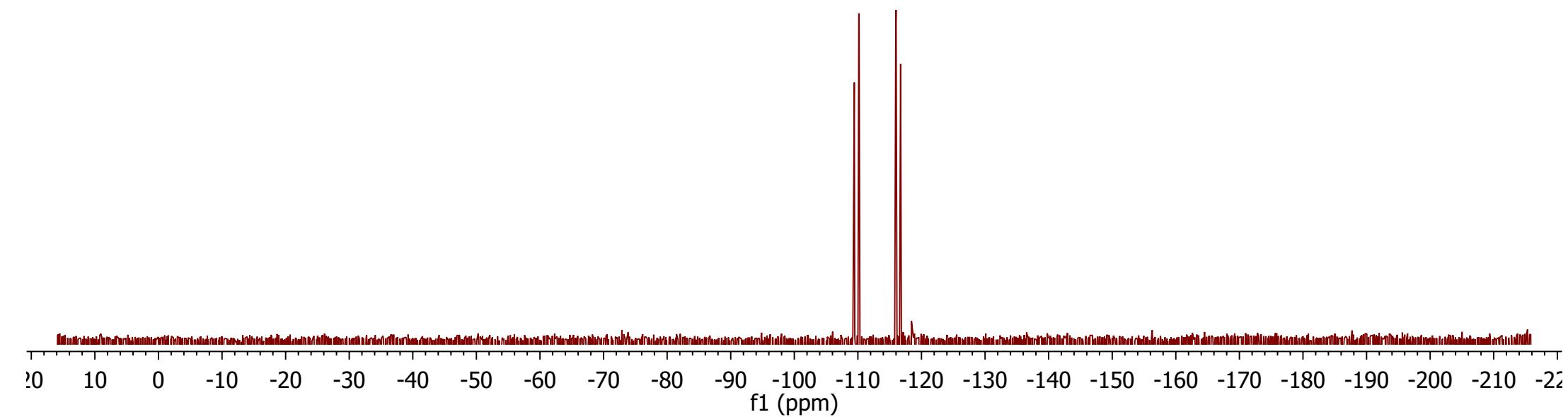
<sup>13</sup>C NMR Spectrum of 3aj

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



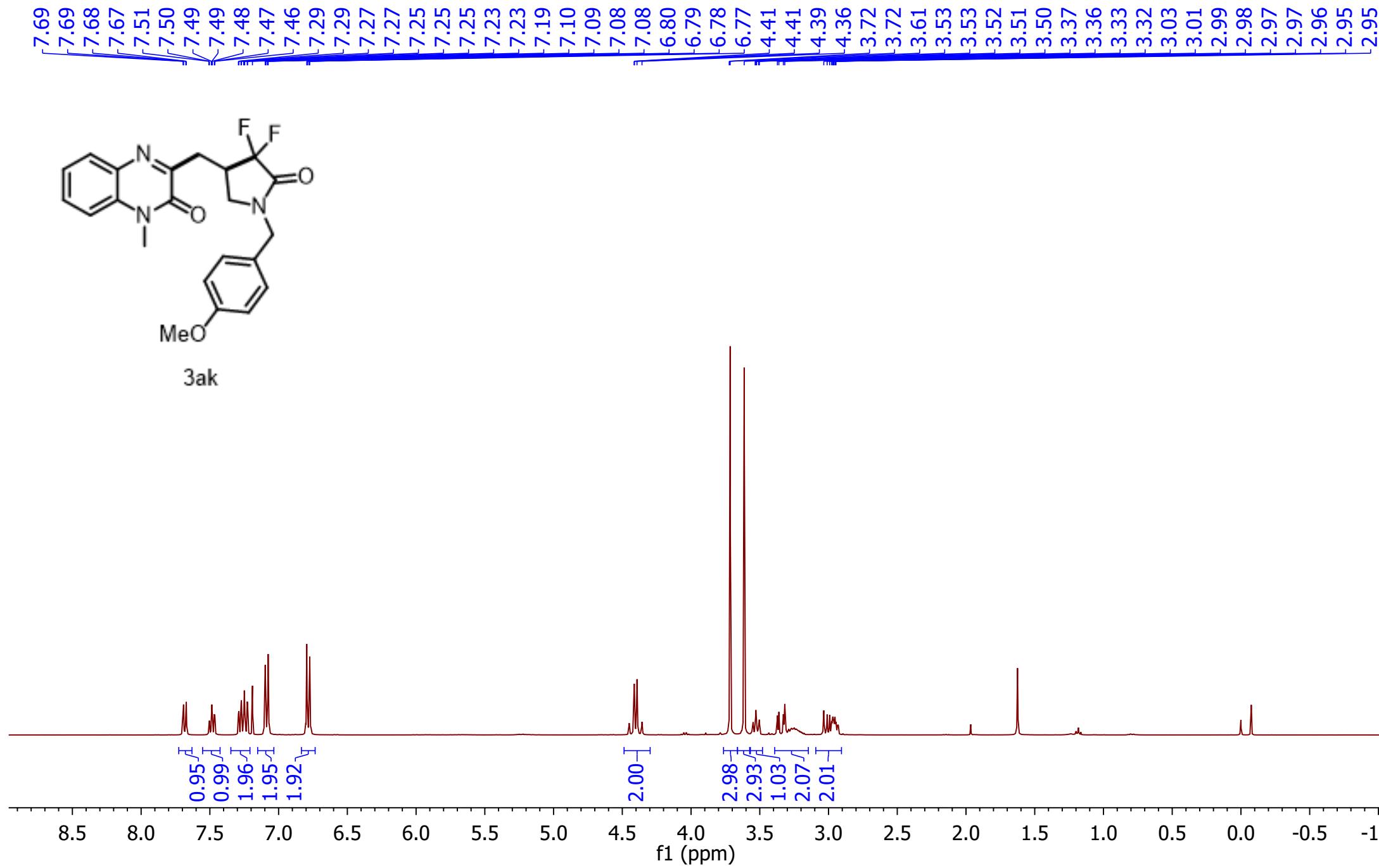
3aj

-109.43  
-109.48  
-110.15  
-110.19  
-115.96  
-116.01  
-116.67  
-116.72



<sup>19</sup>F NMR Spectrum of 3aj

**1H (CDCl<sub>3</sub>, 400 MHz)**

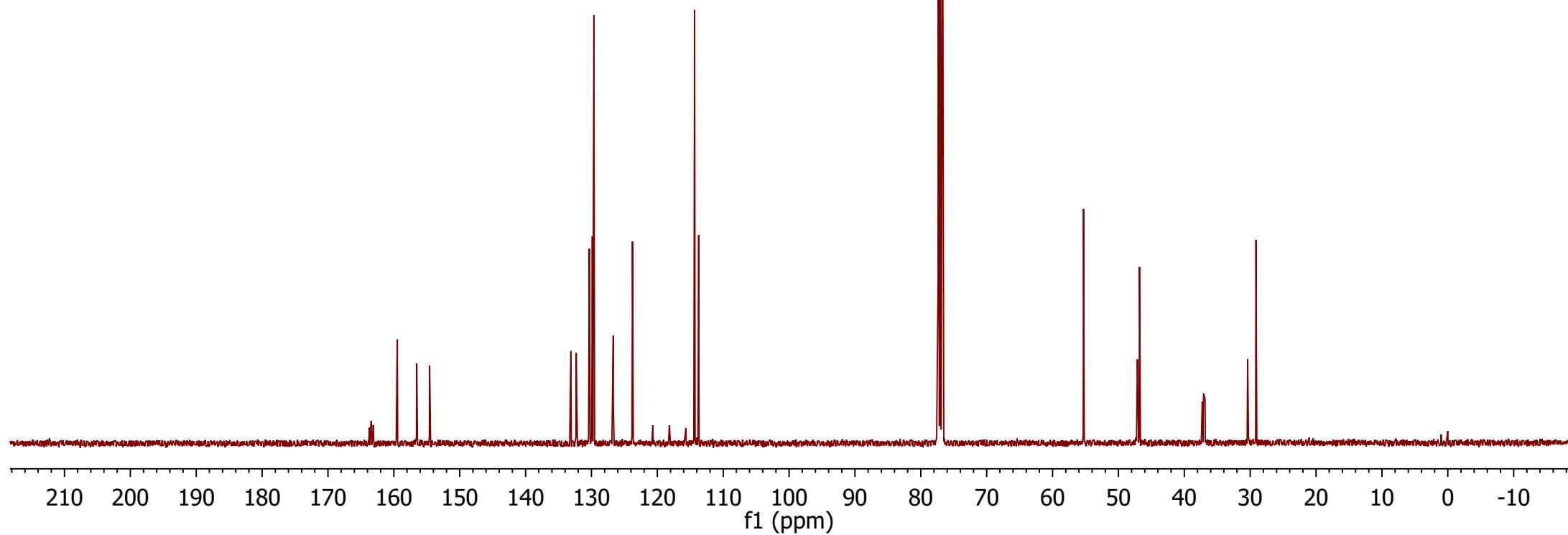


<sup>1</sup>H NMR Spectrum of **3ak**

**13C (CDCl<sub>3</sub>, 101 MHz)**

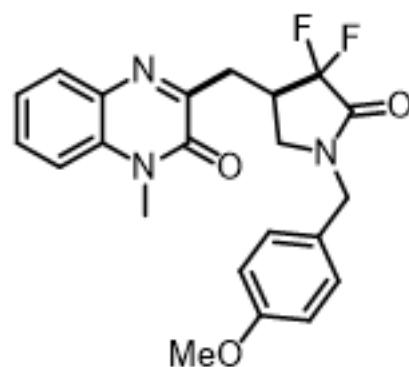


3ak

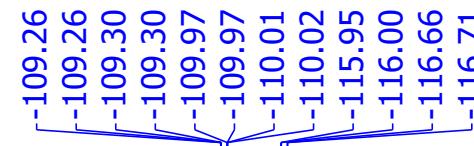


<sup>13</sup>C NMR Spectrum of 3ak

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

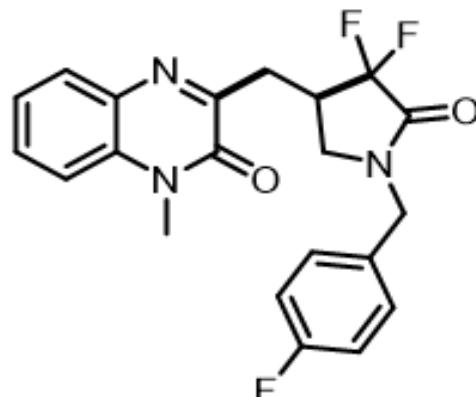


3ak

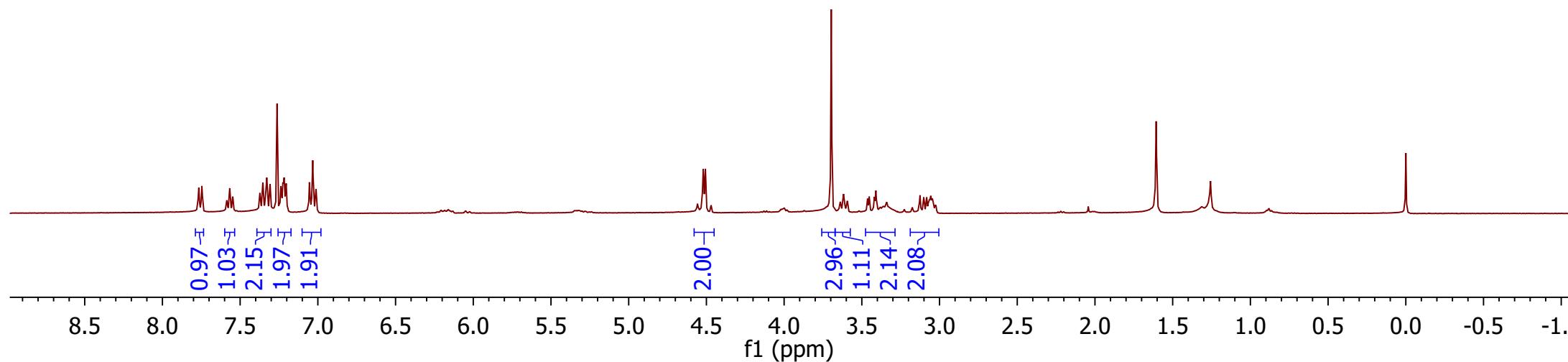


<sup>19</sup>F NMR Spectrum of 3ak

**1H (CDCl<sub>3</sub>, 400 MHz)**

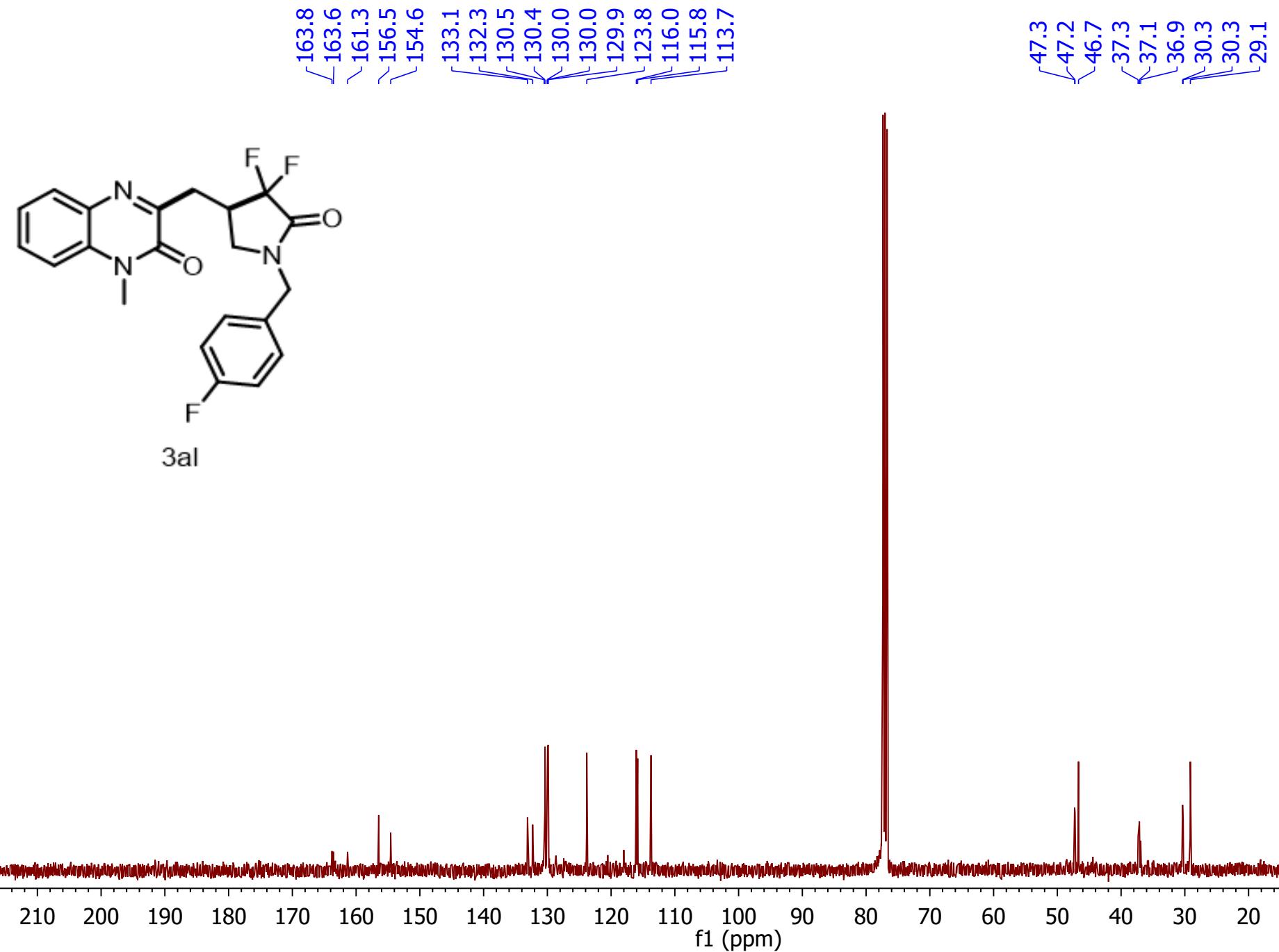


3al



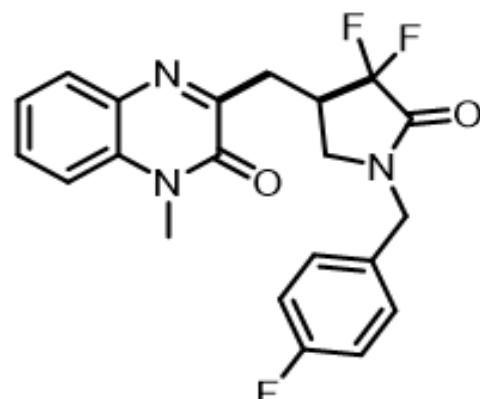
<sup>1</sup>H NMR Spectrum of 3al

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)

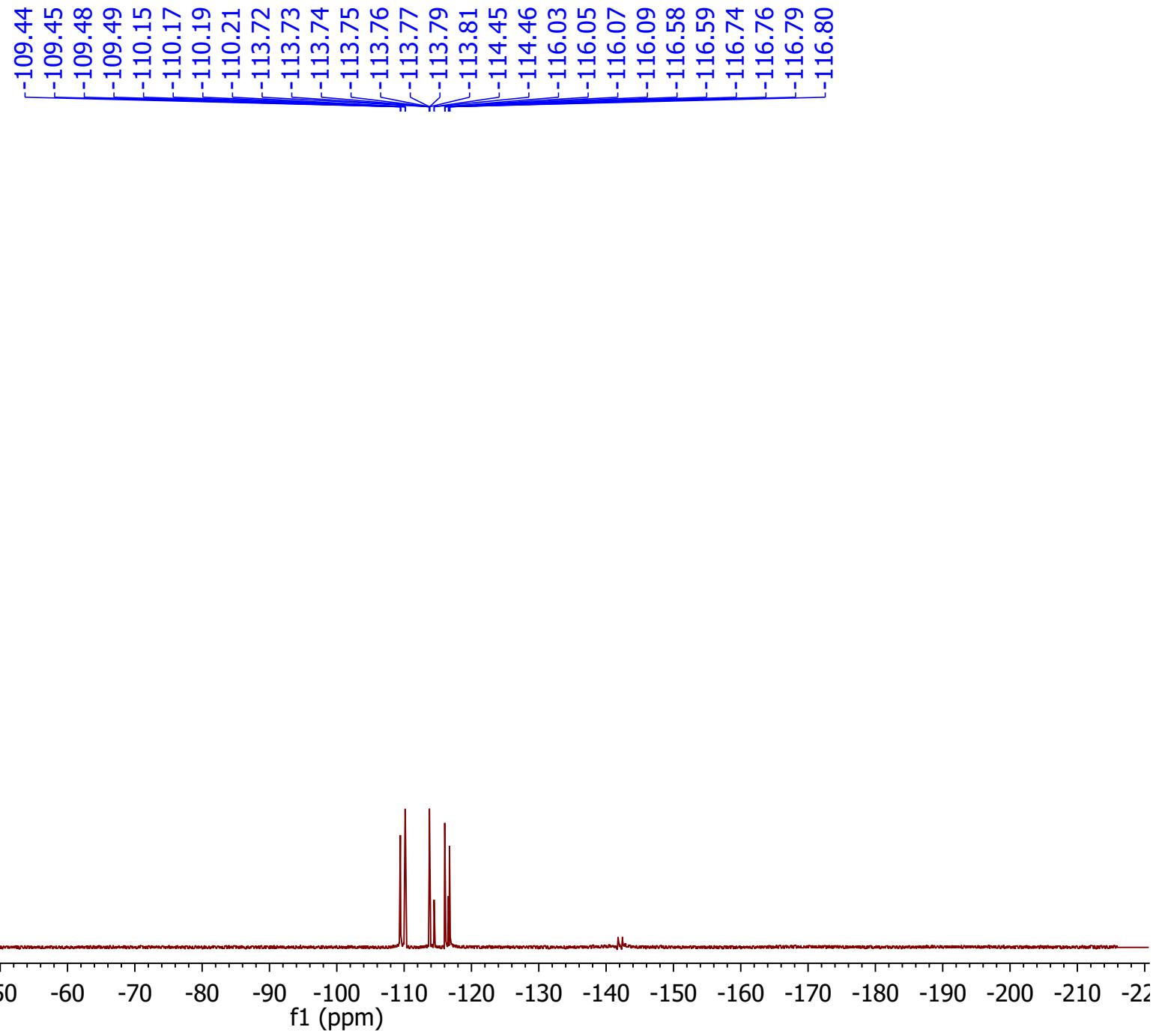


<sup>13</sup>C NMR Spectrum of 3al

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

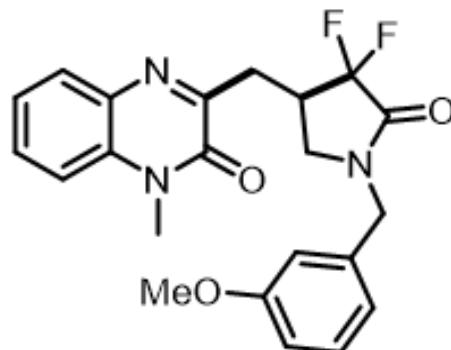


3al

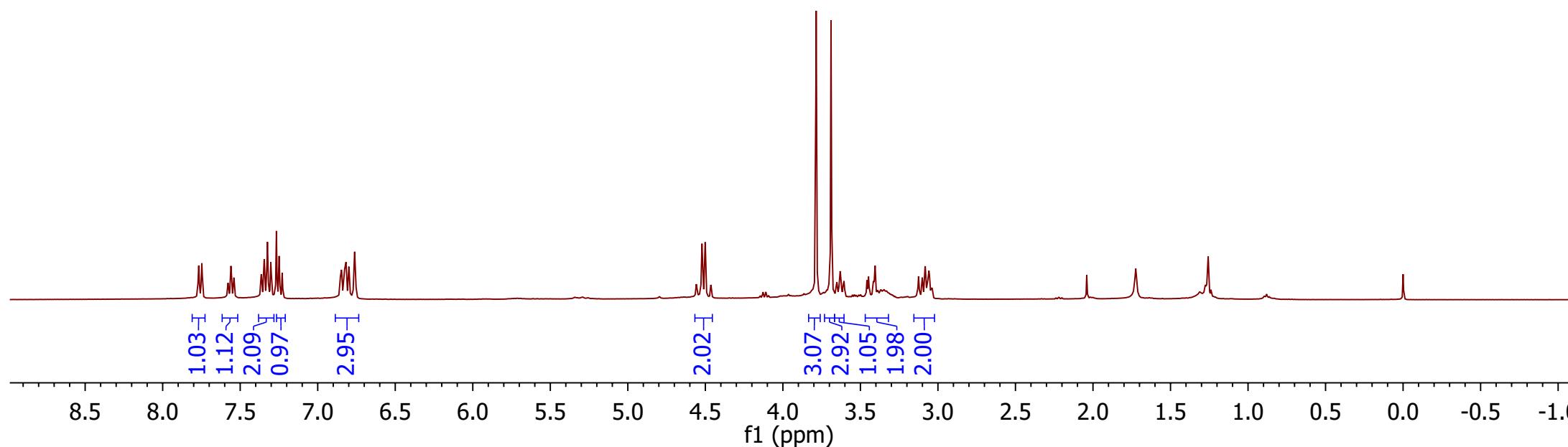


<sup>19</sup>F NMR Spectrum of 3al

**1H (CDCl<sub>3</sub>, 400 MHz)**

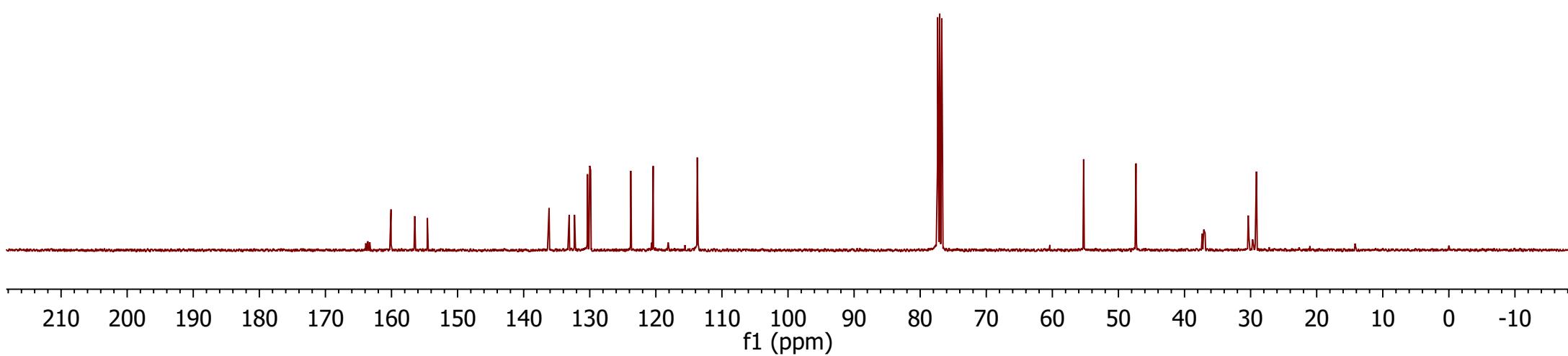
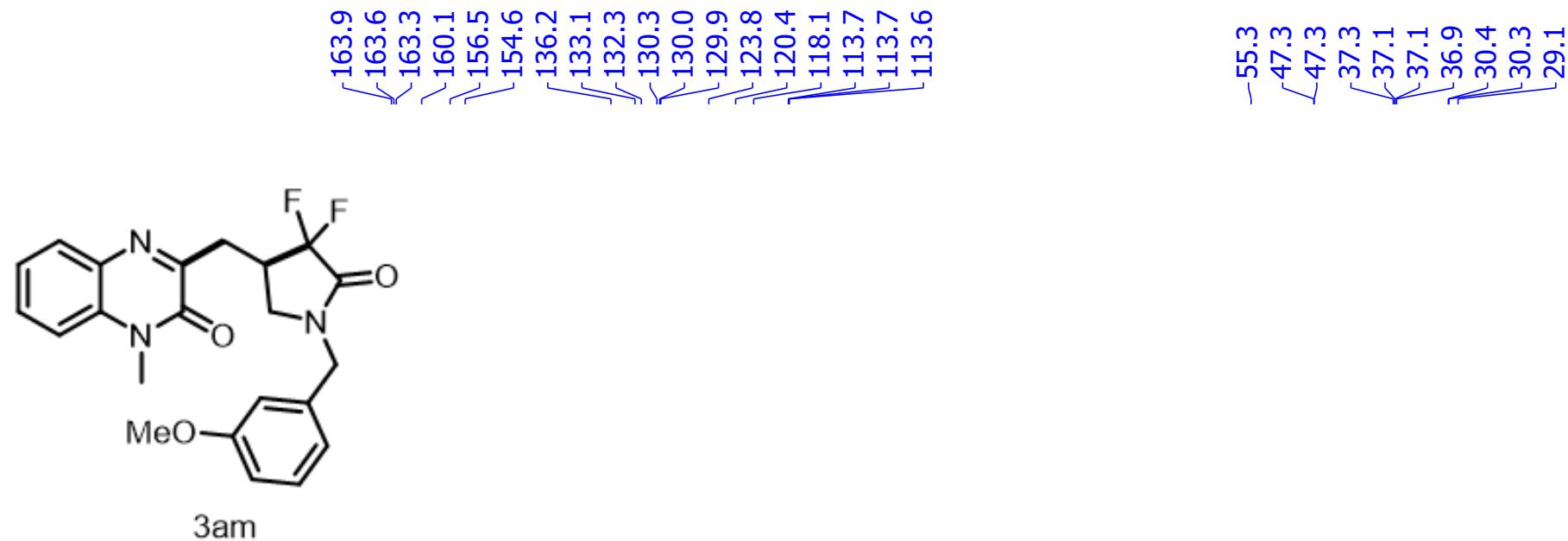


3am



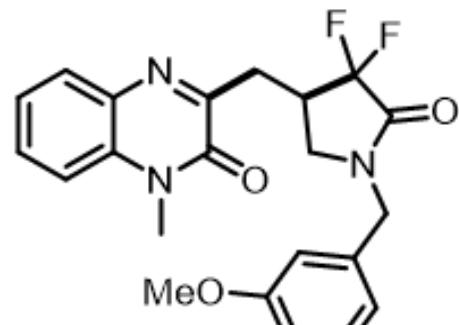
<sup>1</sup>H NMR Spectrum of 3am

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



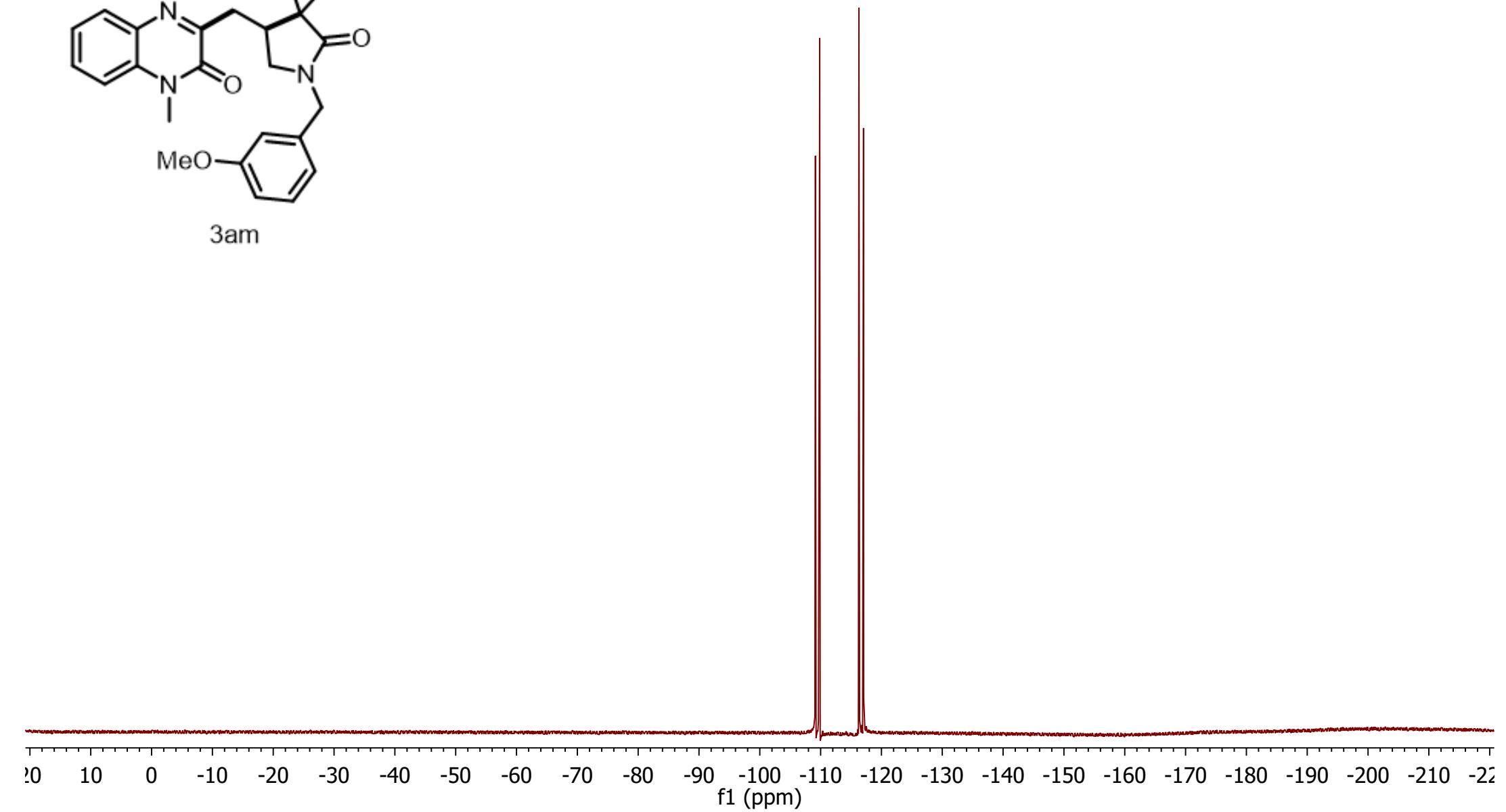
<sup>13</sup>C NMR Spectrum of **3am**

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



3am

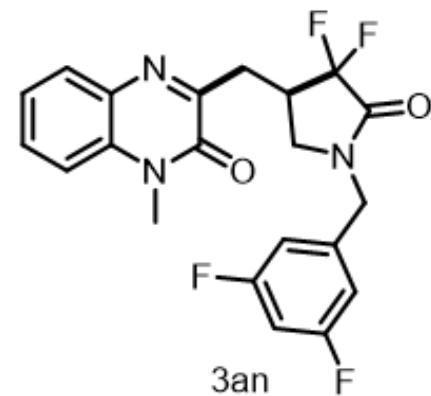
-109.14  
-109.15  
-109.18  
-109.19  
-109.85  
-109.86  
-109.89  
-109.90  
-116.30  
-116.34  
-117.01  
-117.05



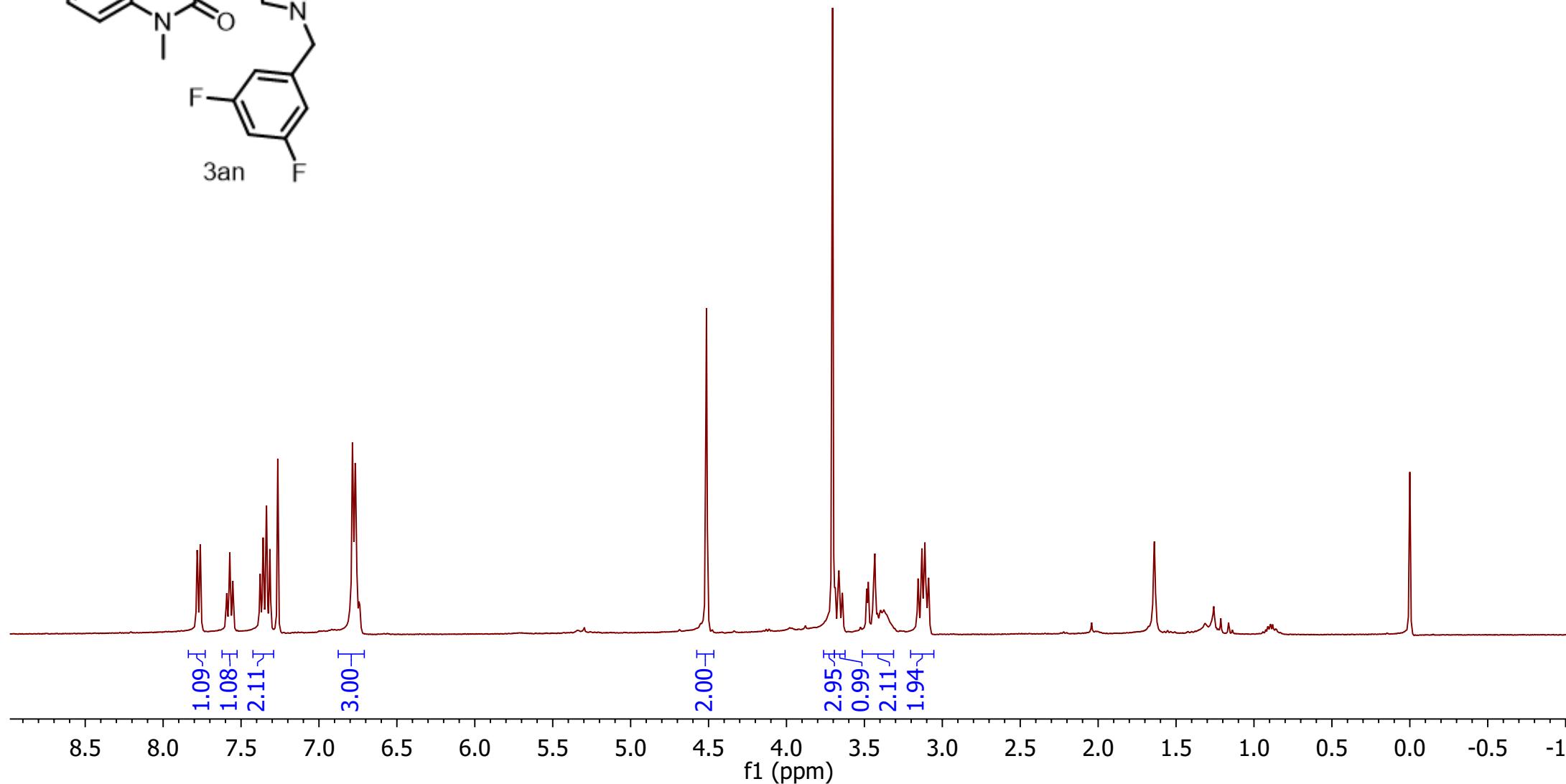
<sup>19</sup>F NMR Spectrum of 3am

**1H (CDCl<sub>3</sub>, 400 MHz)**

7.78  
7.76  
7.59  
7.57  
7.55  
7.38  
7.36  
7.34  
7.31  
7.26  
6.79  
6.77  
6.74  
6.74

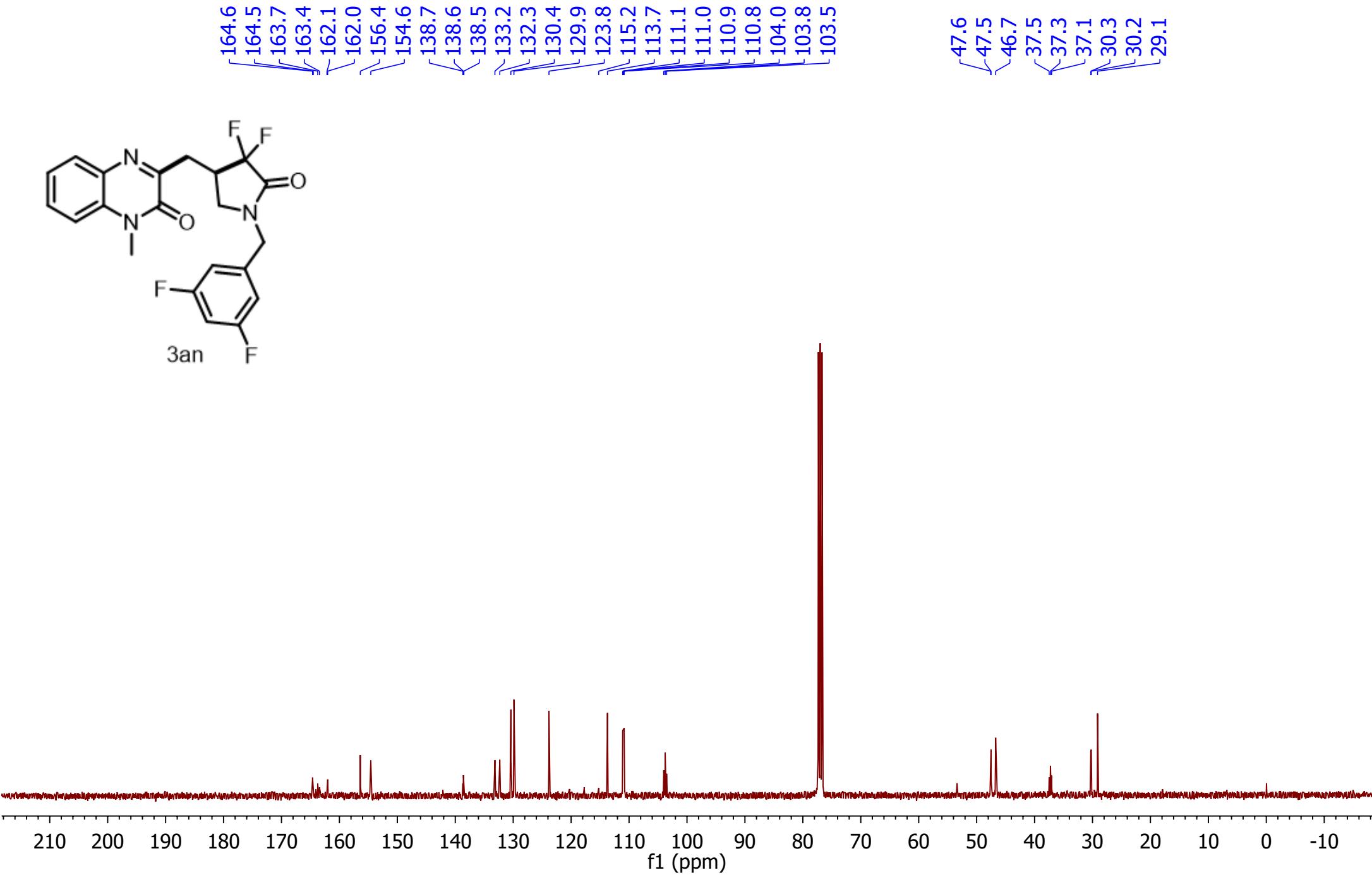
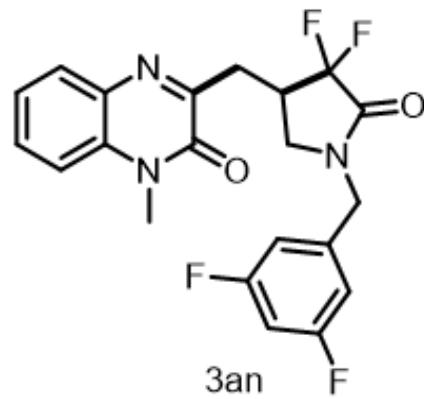


4.51  
3.73  
3.70  
3.69  
3.68  
3.66  
3.64  
3.49  
3.47  
3.44  
3.43  
3.42  
3.41  
3.40  
3.38  
3.16  
3.13  
3.11  
3.10  
3.09



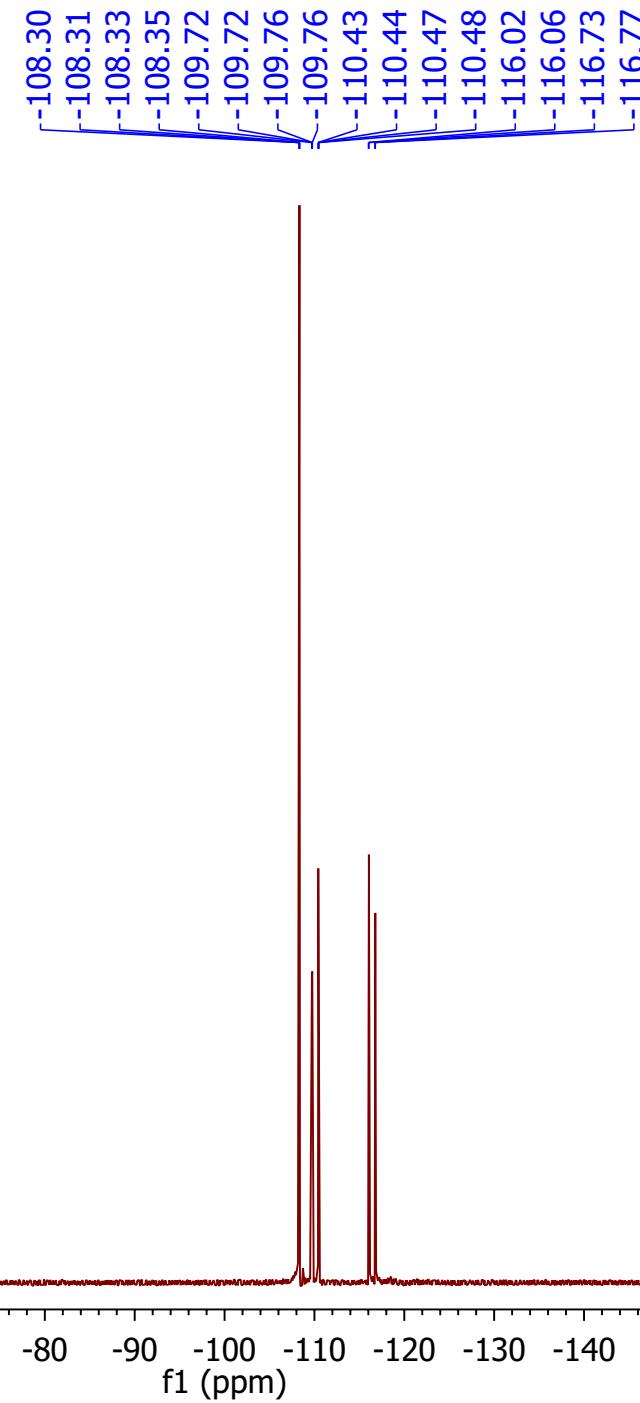
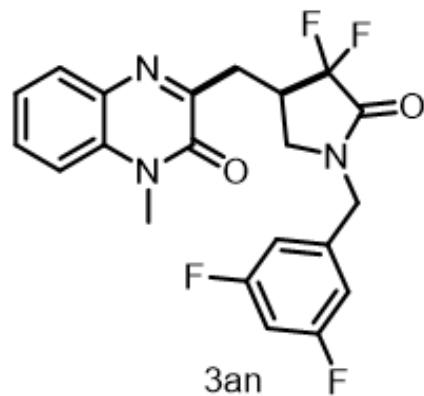
<sup>1</sup>H NMR Spectrum of 3an

## **13C (CDCl3, 101 MHz)**



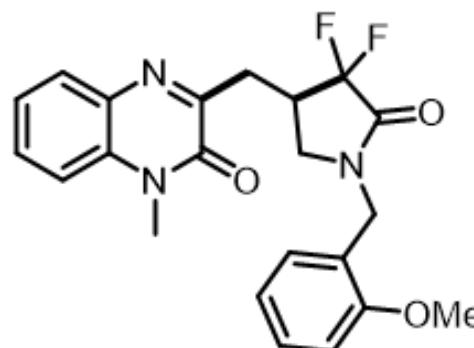
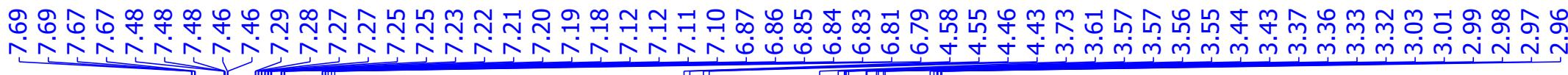
### <sup>13</sup>C NMR Spectrum of **3an**

## 19F (CDCl<sub>3</sub>, 376 MHz)

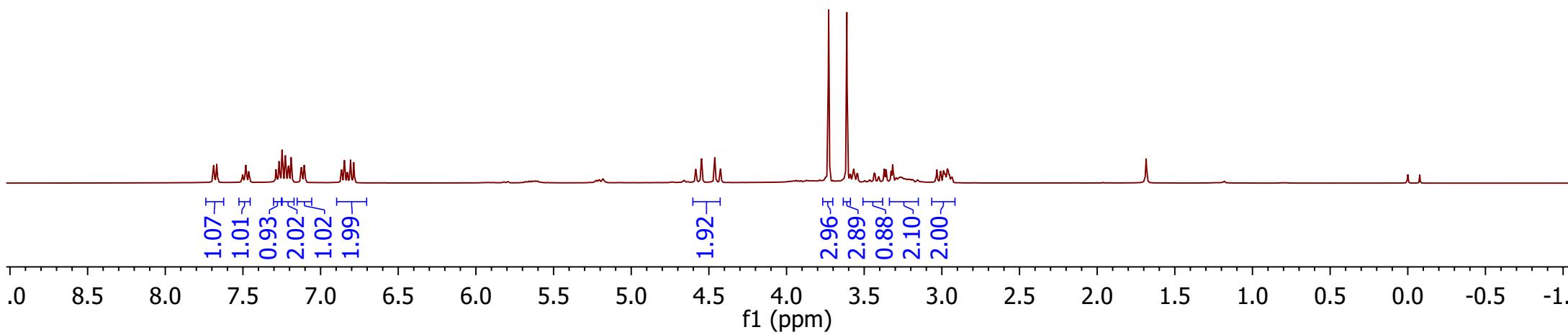


### <sup>19</sup>F NMR Spectrum of 3an

**1H (CDCl<sub>3</sub>, 400 MHz)**

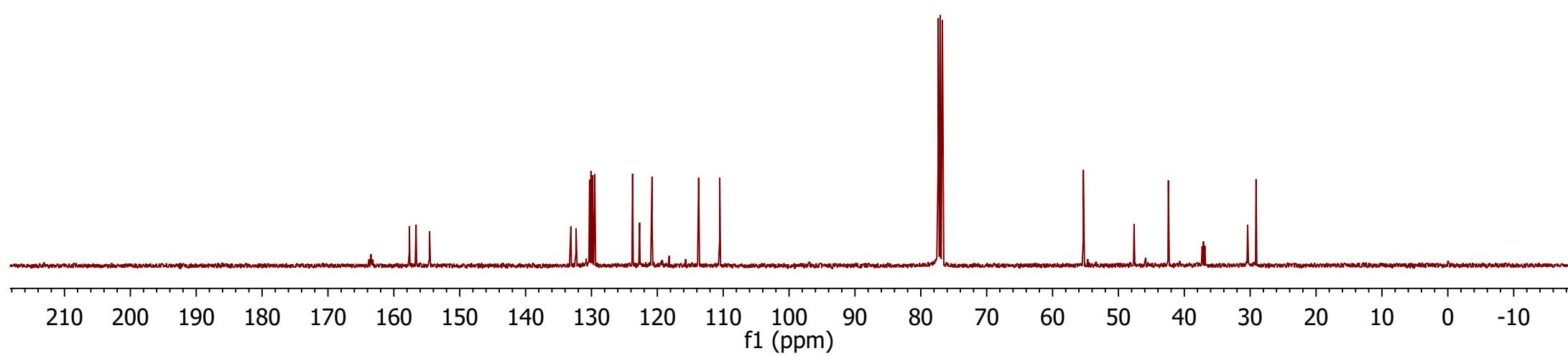
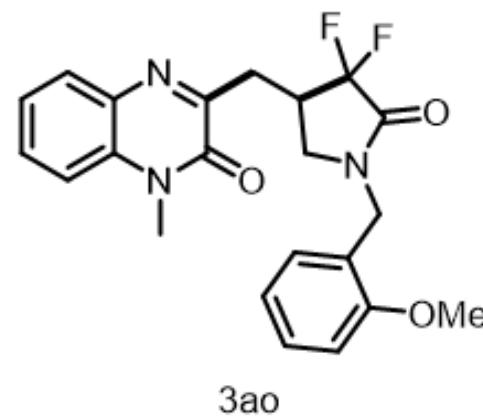


3ao



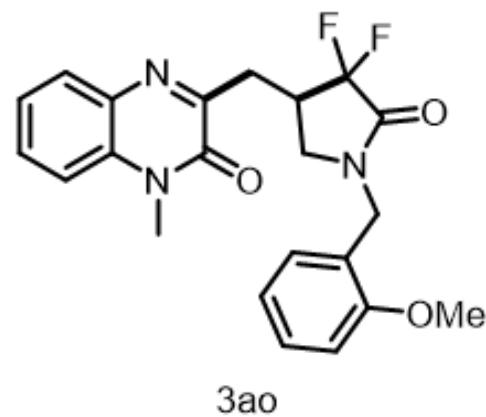
<sup>1</sup>H NMR Spectrum of 3ao

**13C (CDCl<sub>3</sub>, 101 MHz)**

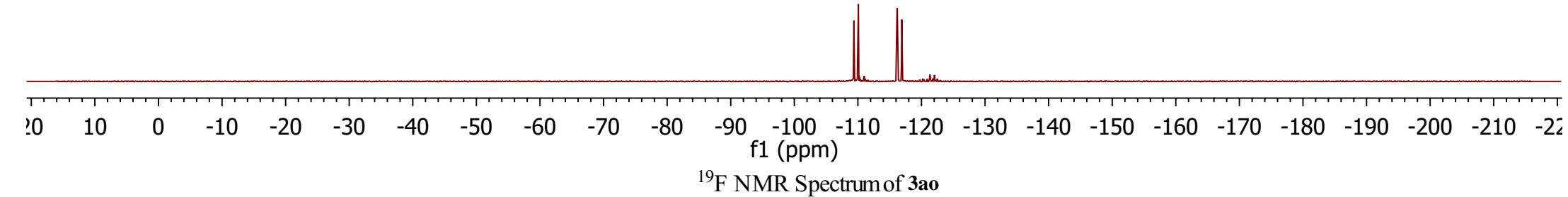


<sup>13</sup>C NMR Spectrum of 3ao

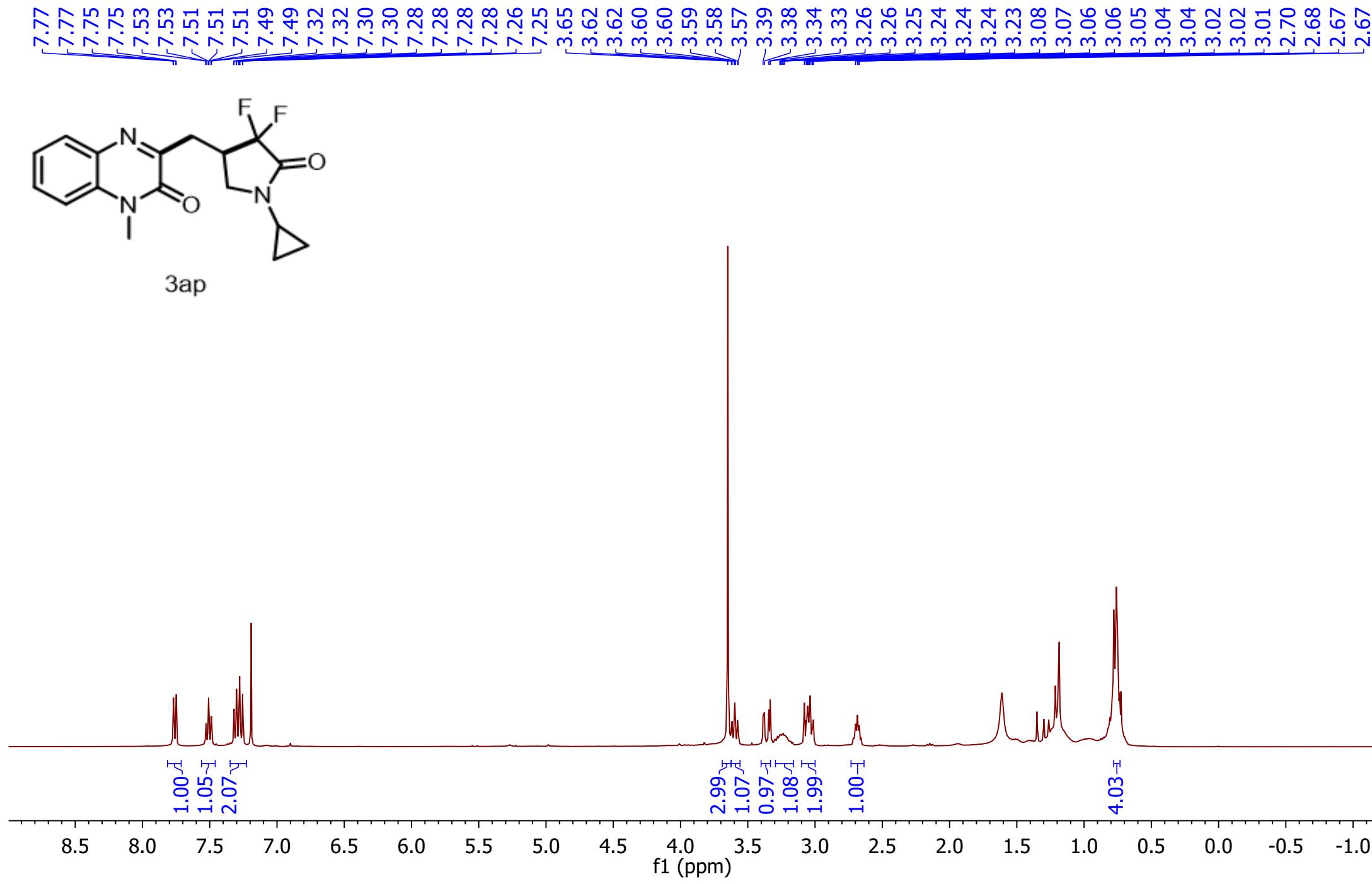
<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



-109.37  
-109.41  
-110.08  
-110.12  
-116.15  
-116.20  
-116.86  
-116.91

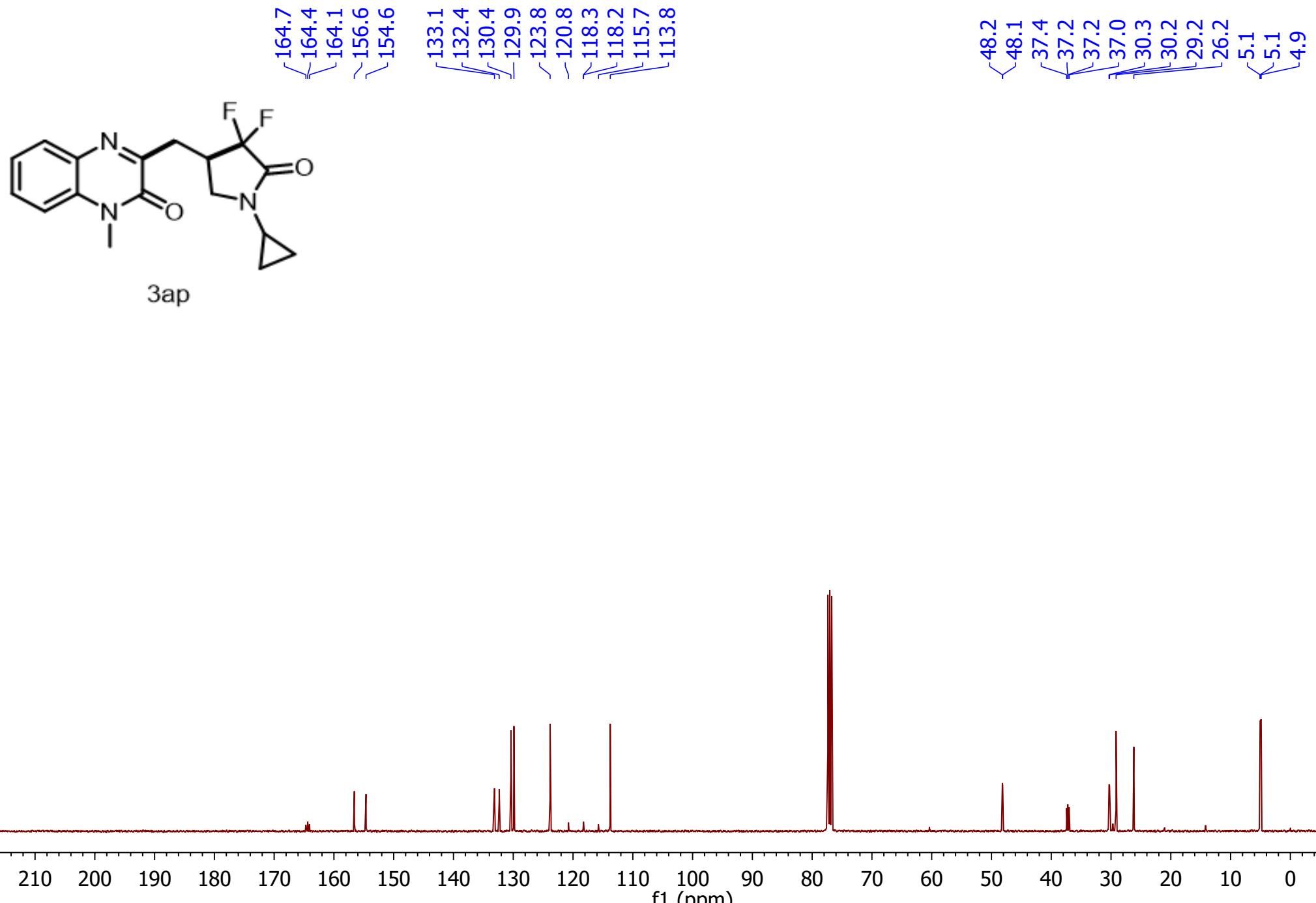


**1H (CDCl<sub>3</sub>, 400 MHz)**



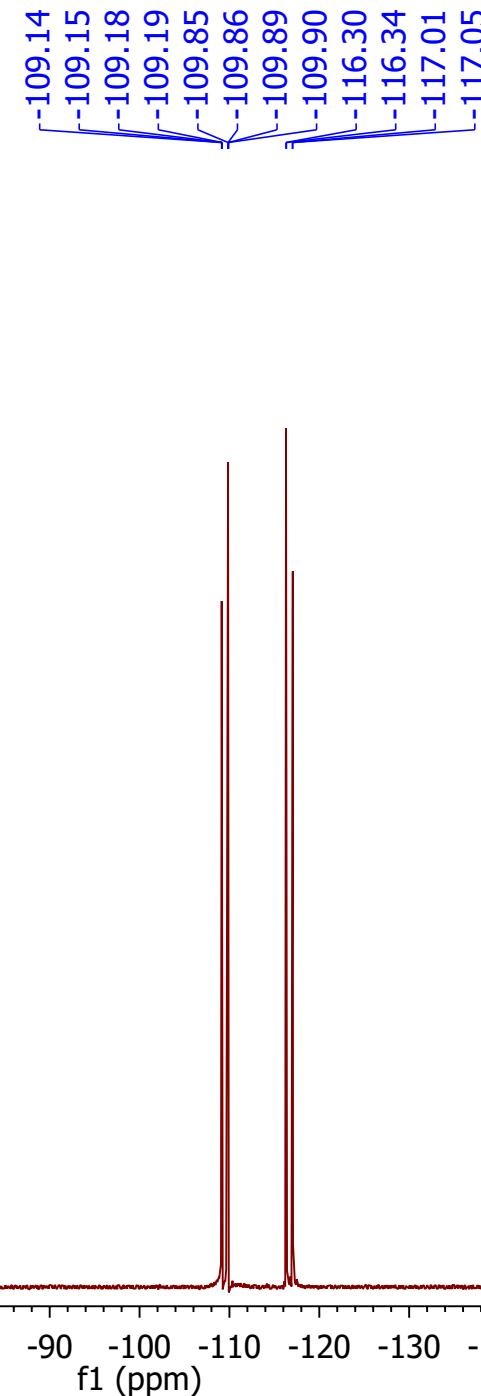
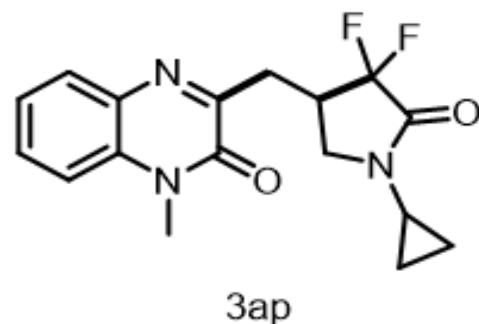
<sup>1</sup>H NMR Spectrum of **3ap**

**13C (CDCl<sub>3</sub>, 101 MHz)**



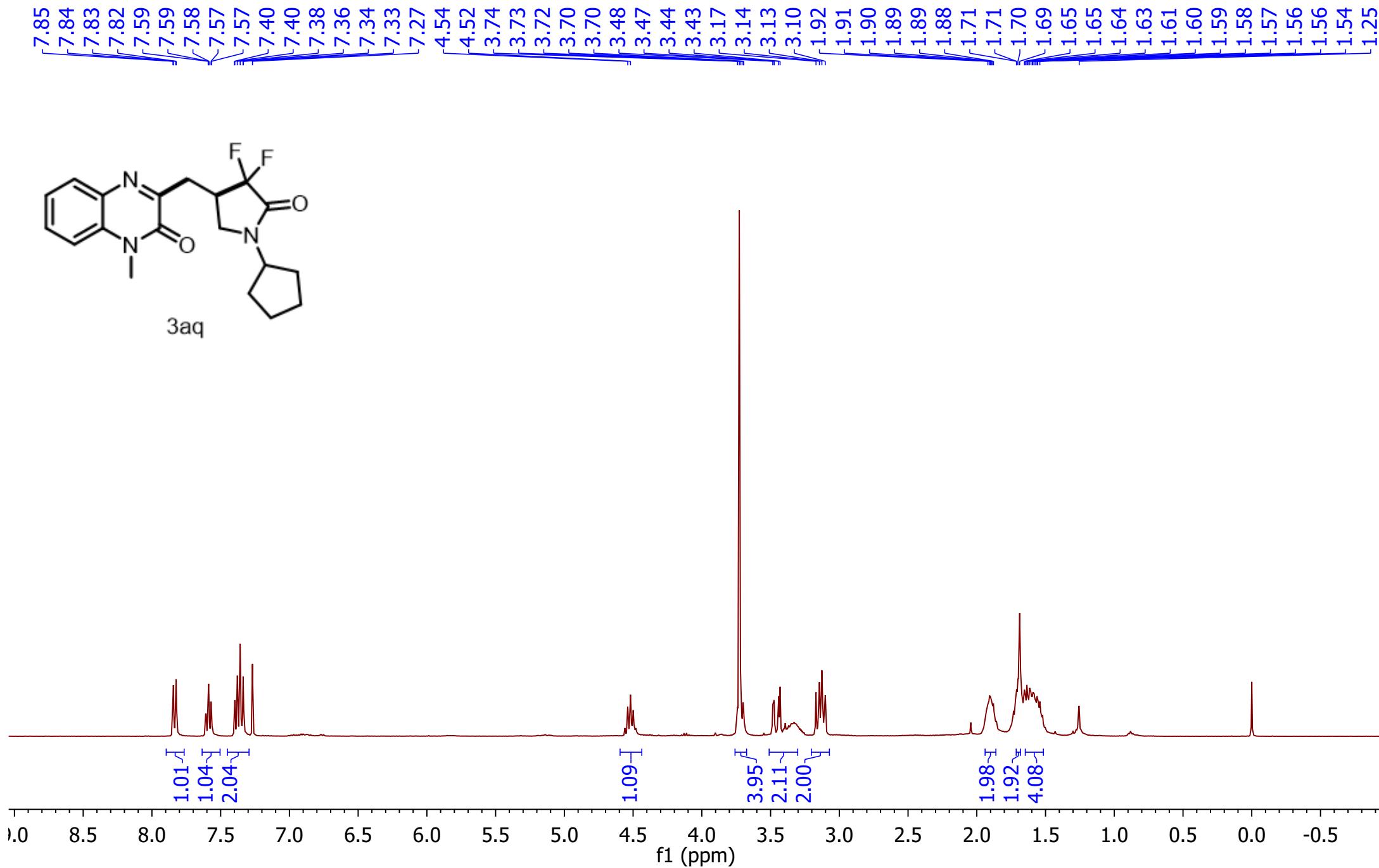
<sup>13</sup>C NMR Spectrum of 3ap

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



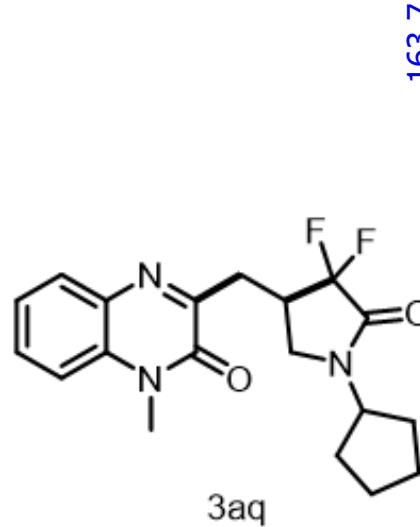
<sup>19</sup>F NMR Spectrum of 3ap

**$^1\text{H}$  (CDCl<sub>3</sub>, 400 MHz)**



$^1\text{H}$  NMR Spectrum of **3aq**

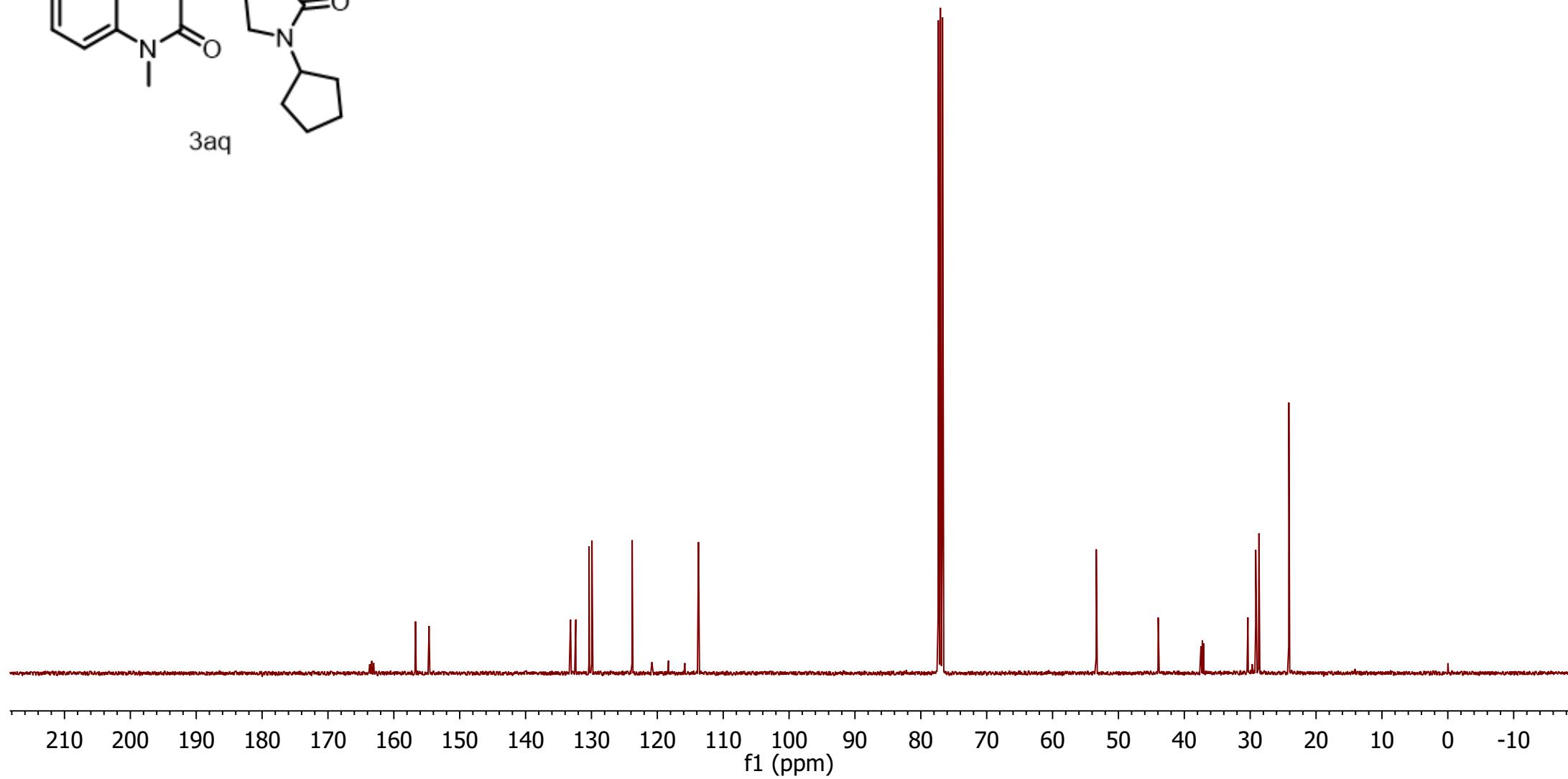
**$^{13}\text{C}$  (CDCl<sub>3</sub>, 101 MHz)**



163.7  
163.4  
163.1  
156.7  
154.7

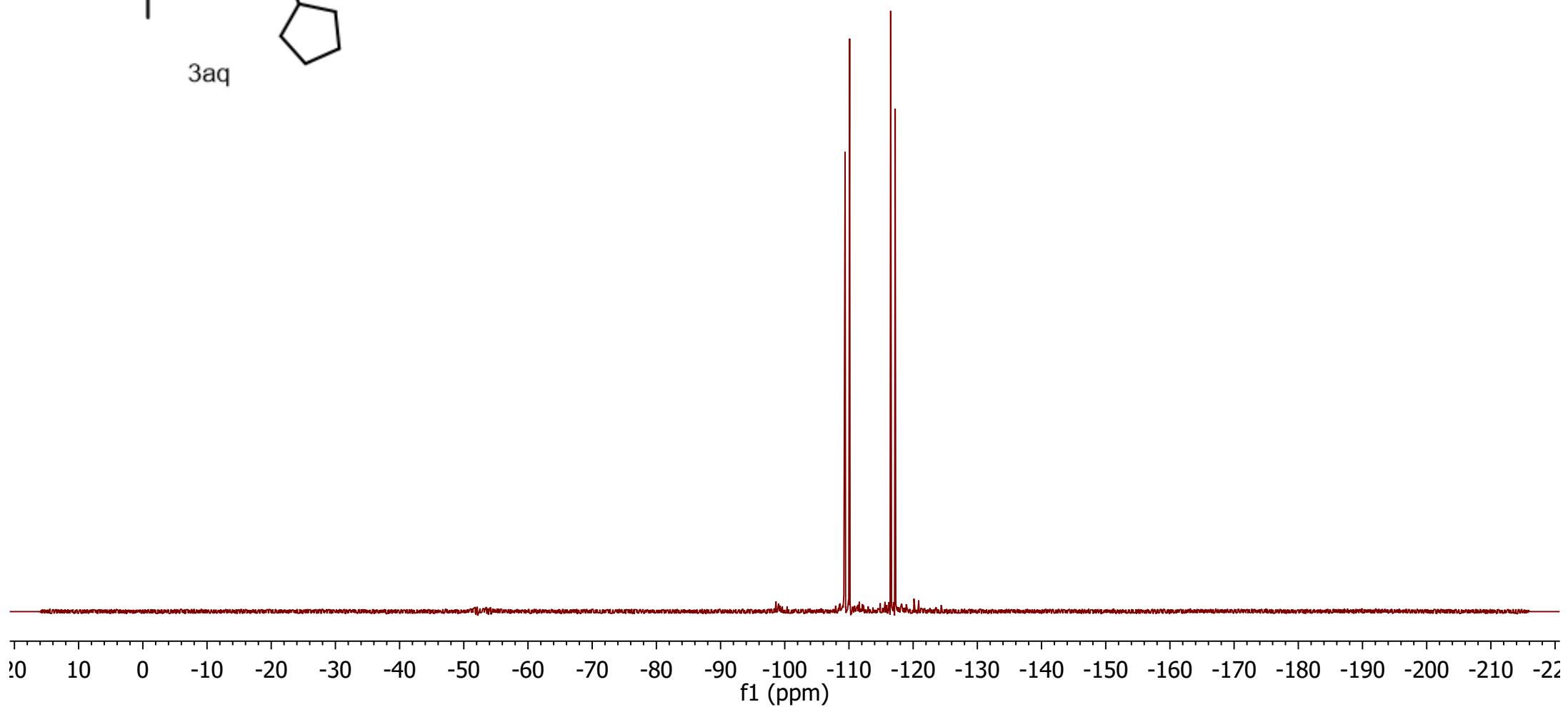
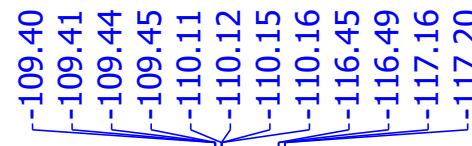
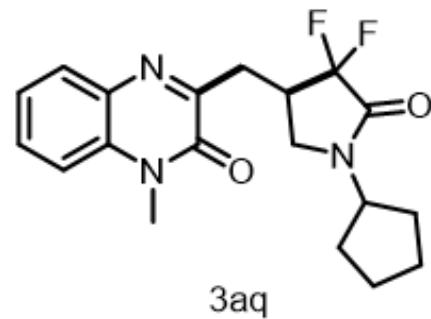
133.2  
132.4  
130.4  
129.9  
123.8  
120.8  
118.3  
115.8  
113.8

44.0  
43.9  
37.5  
37.3  
37.3  
37.1  
30.4  
30.3  
29.2  
28.7  
28.6  
24.1



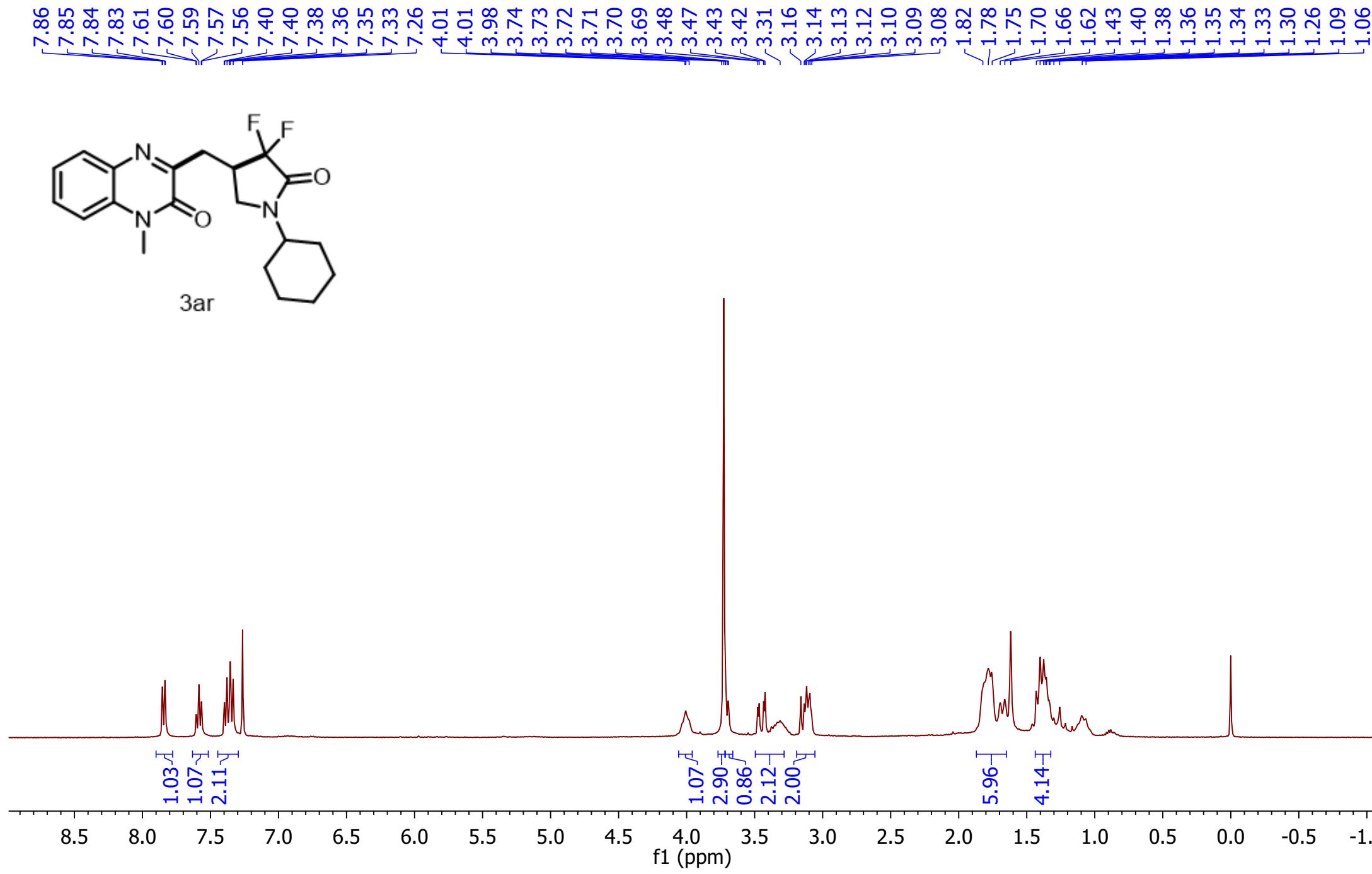
$^{13}\text{C}$  NMR Spectrum of **3aq**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



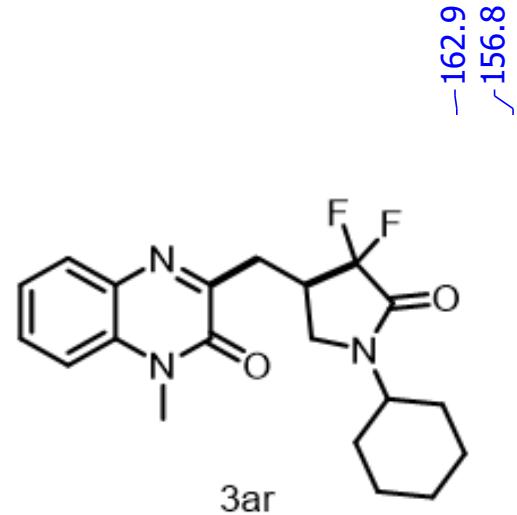
<sup>19</sup>F NMR Spectrum of **3aq**

**1H (CDCl<sub>3</sub>, 400 MHz)**



<sup>1</sup>H NMR Spectrum of **3ar**

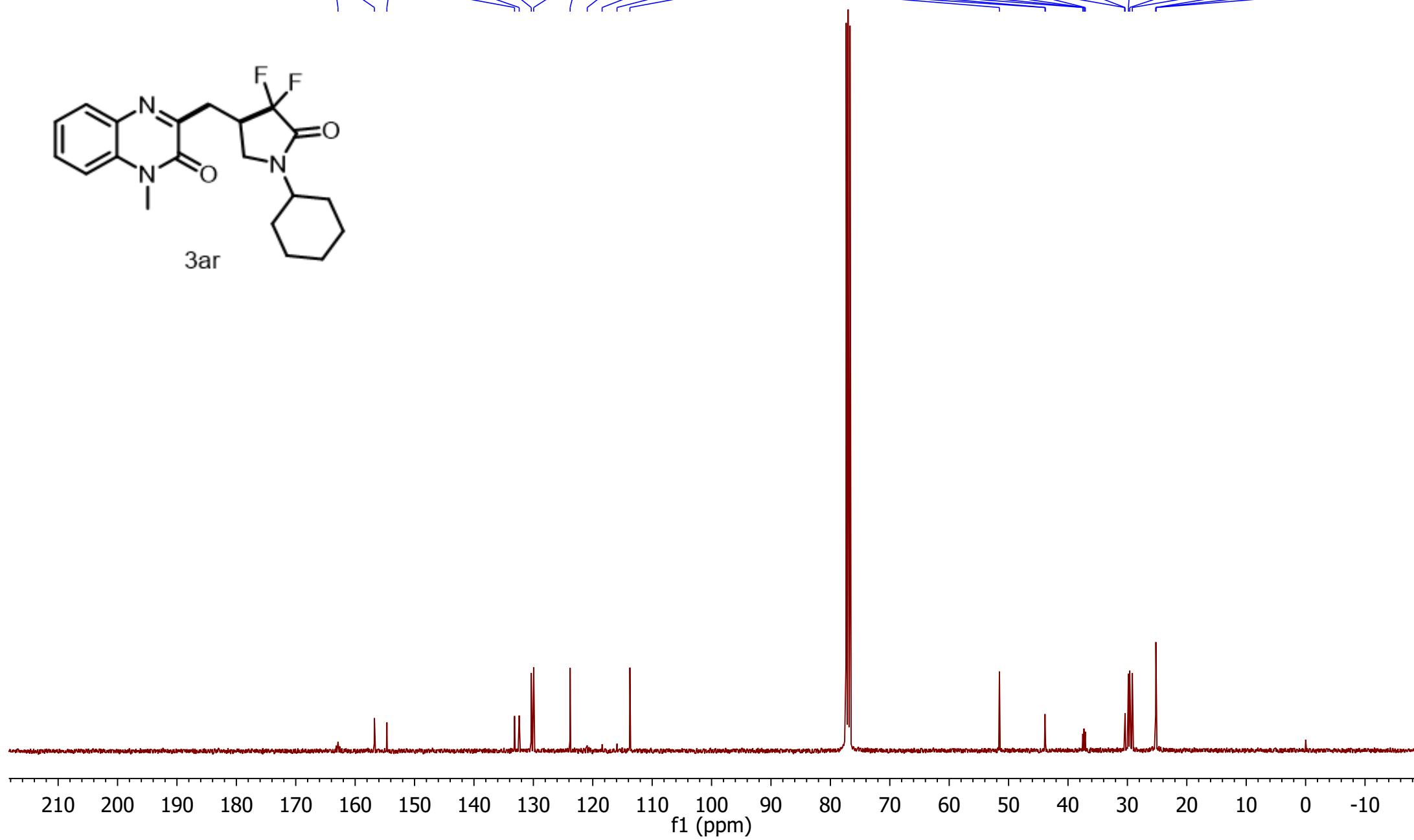
**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



-162.9  
-156.8  
-154.7

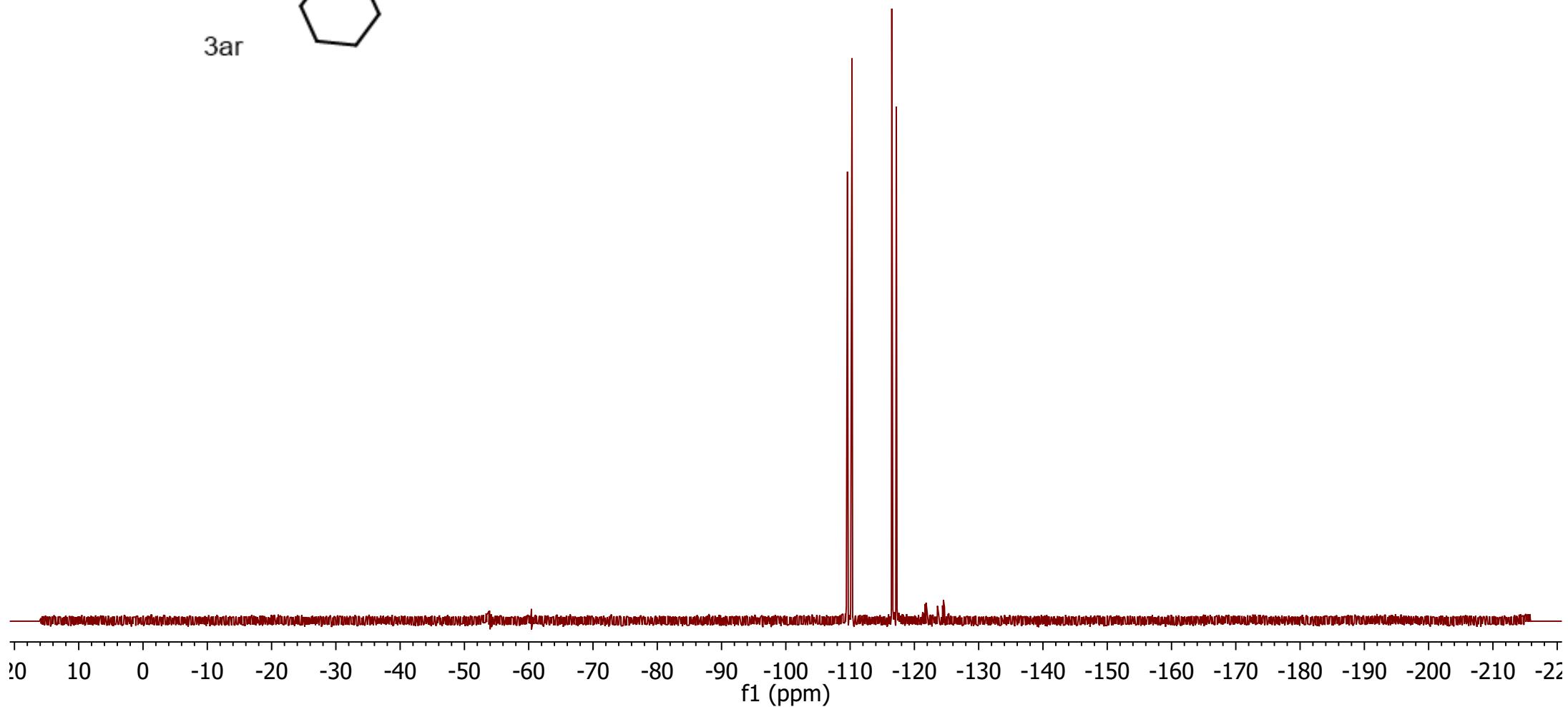
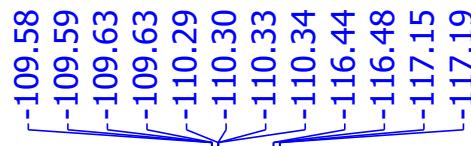
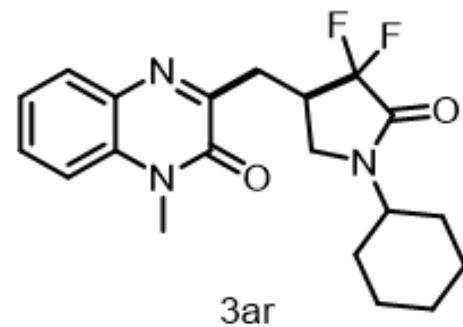
133.2  
132.4  
130.4  
130.0  
-123.8  
-120.9  
-118.4  
-115.9  
-113.8

51.5  
43.9  
43.8  
37.5  
37.3  
37.3  
37.1  
30.5  
30.4  
29.8  
29.6  
29.2  
25.2  
25.2



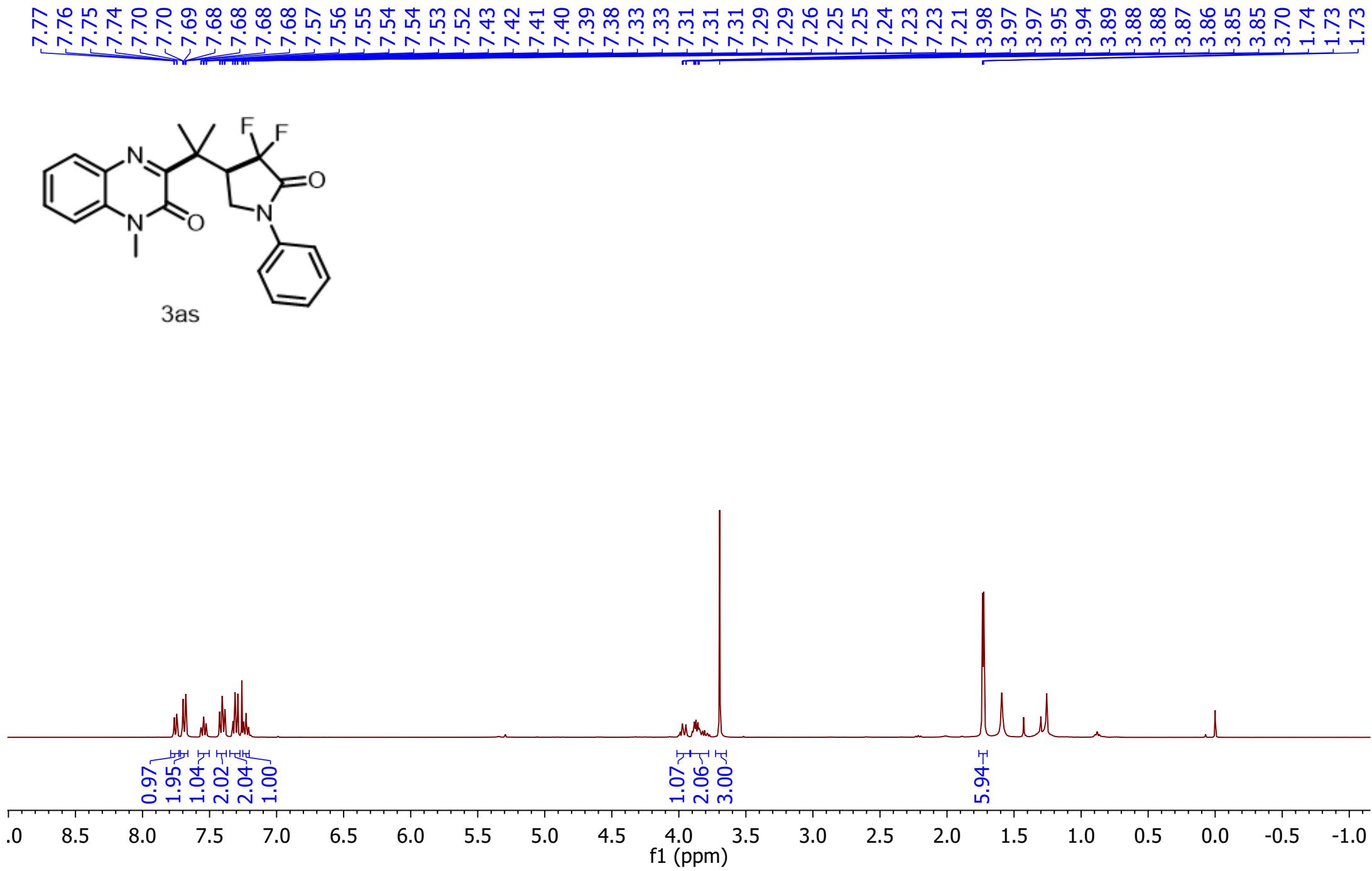
<sup>13</sup>C NMR Spectrum of 3ar

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



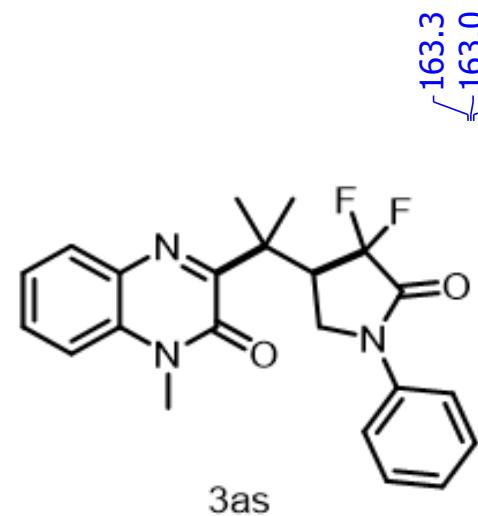
<sup>19</sup>F NMR Spectrum of 3ar

**1H (CDCl<sub>3</sub>, 400 MHz)**



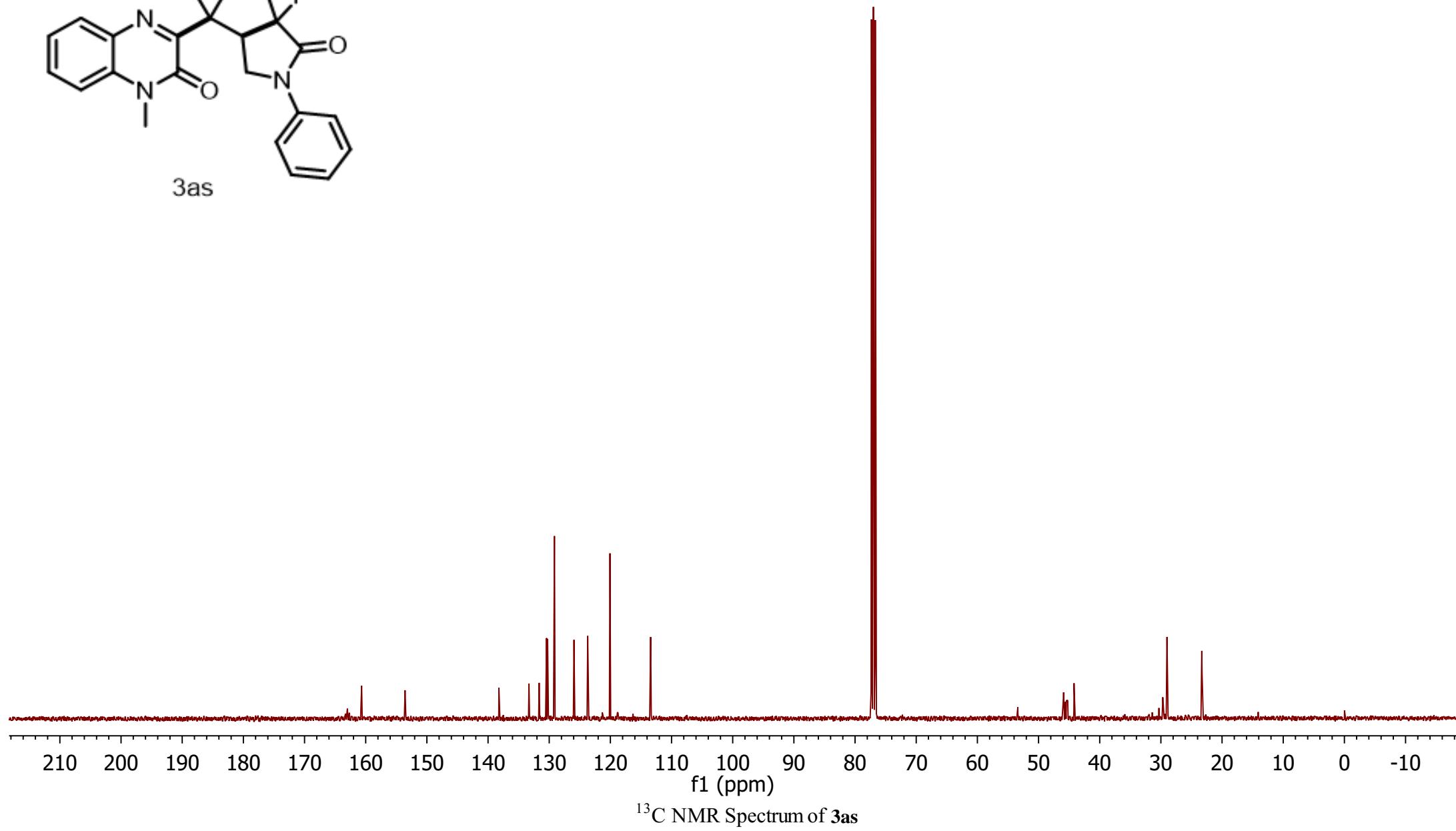
### <sup>1</sup>H NMR Spectrum of 3as

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)

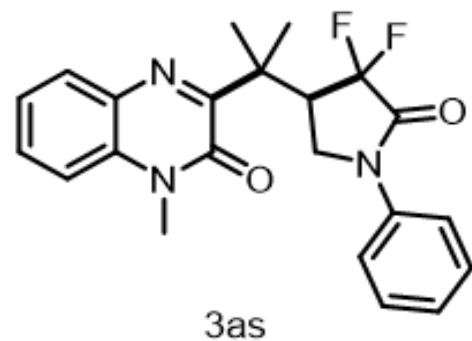


163.3  
163.0  
162.7  
160.7  
153.6  
138.2  
133.3  
131.6  
130.4  
130.3  
129.1  
125.9  
123.7  
120.1  
113.4

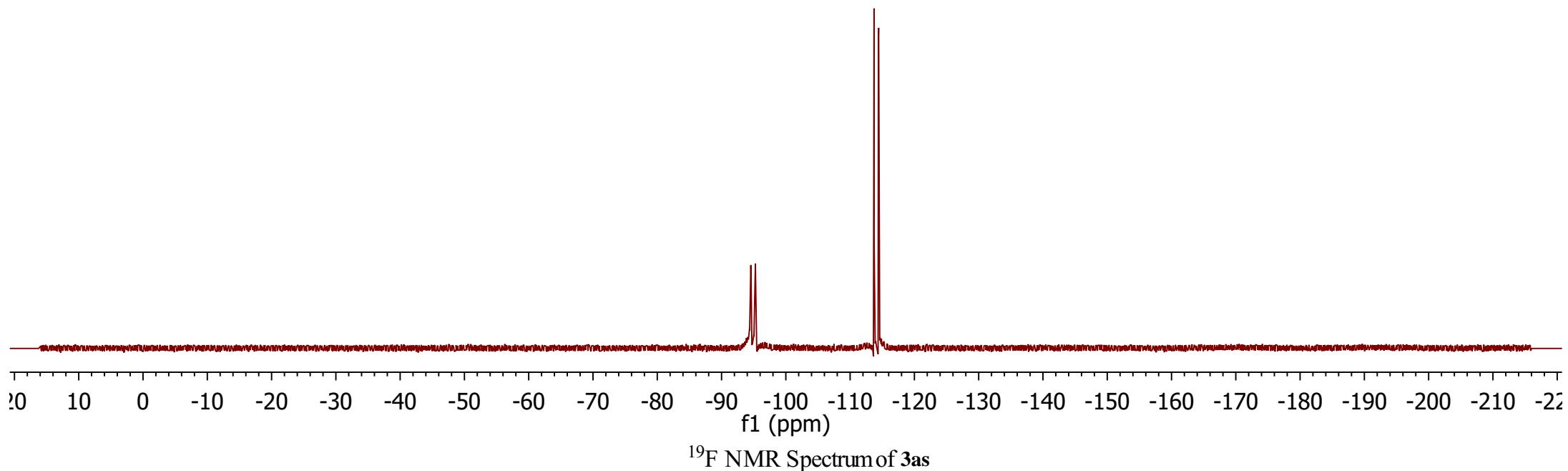
46.0  
45.9  
45.6  
45.4  
45.4  
45.2  
44.2  
29.0  
23.3  
23.3  
23.3



**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

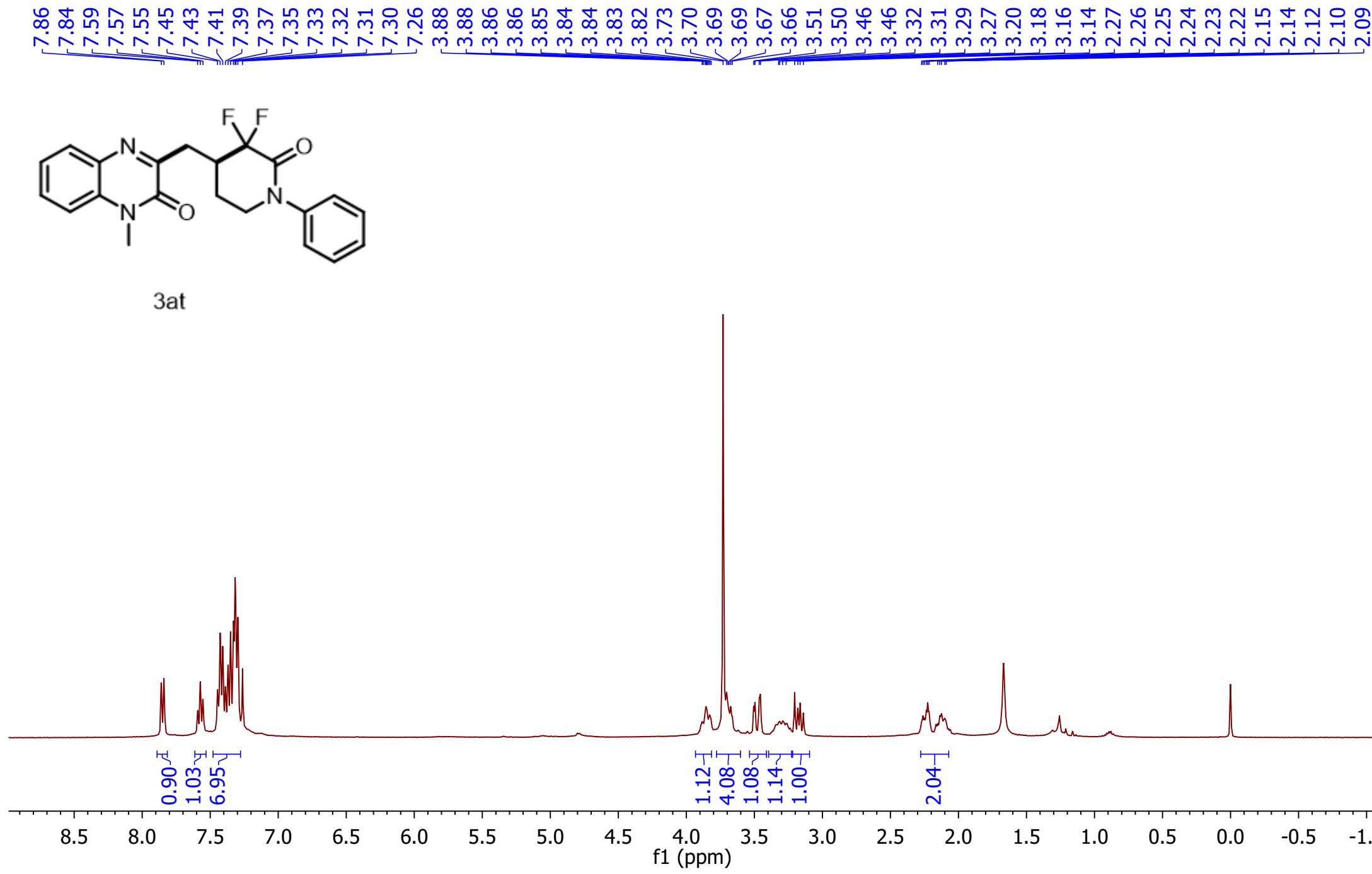


-94.55  
-95.27  
-113.68  
-113.69  
-113.73  
-114.40  
-114.44



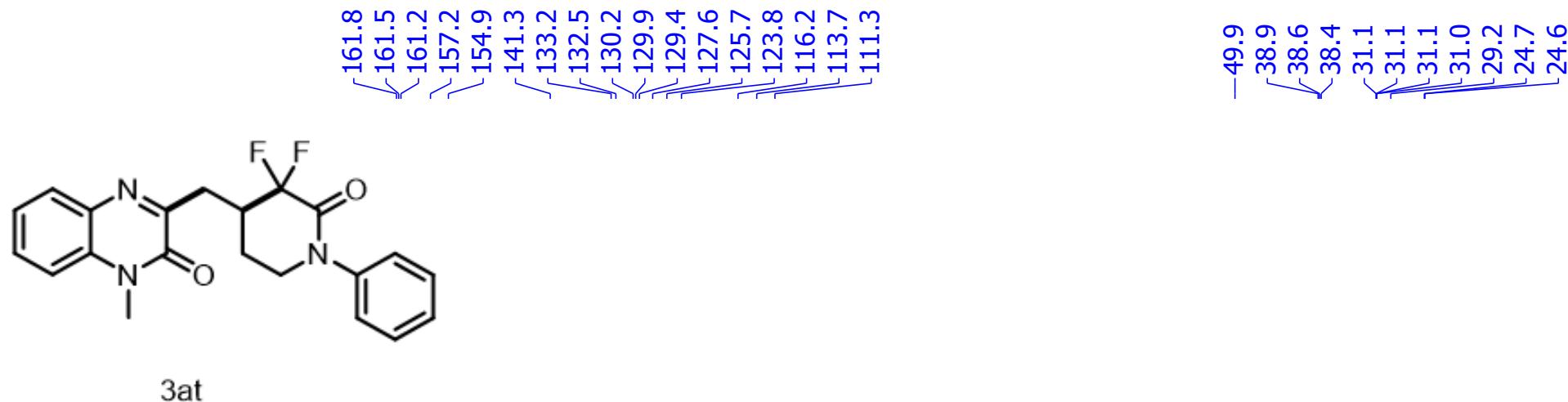
<sup>19</sup>F NMR Spectrum of 3as

**1H (CDCl<sub>3</sub>, 400 MHz)**



<sup>1</sup>H NMR Spectrum of 3at

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

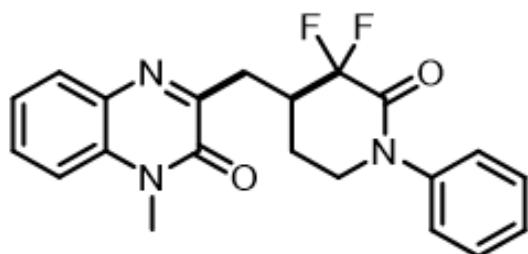


3at

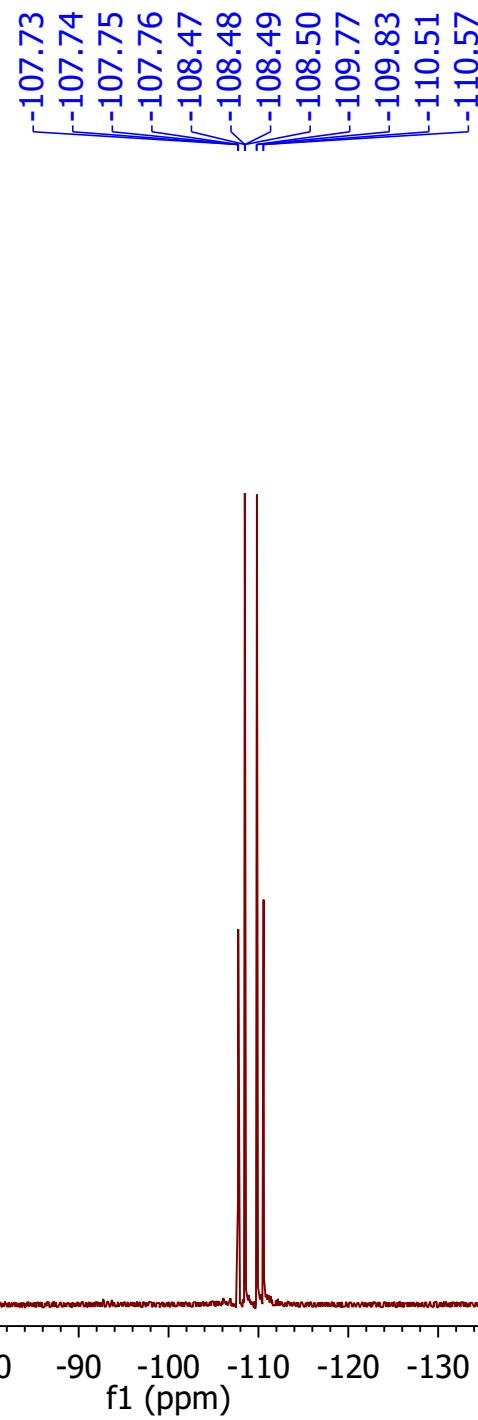
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

<sup>13</sup>C NMR Spectrum of 3at

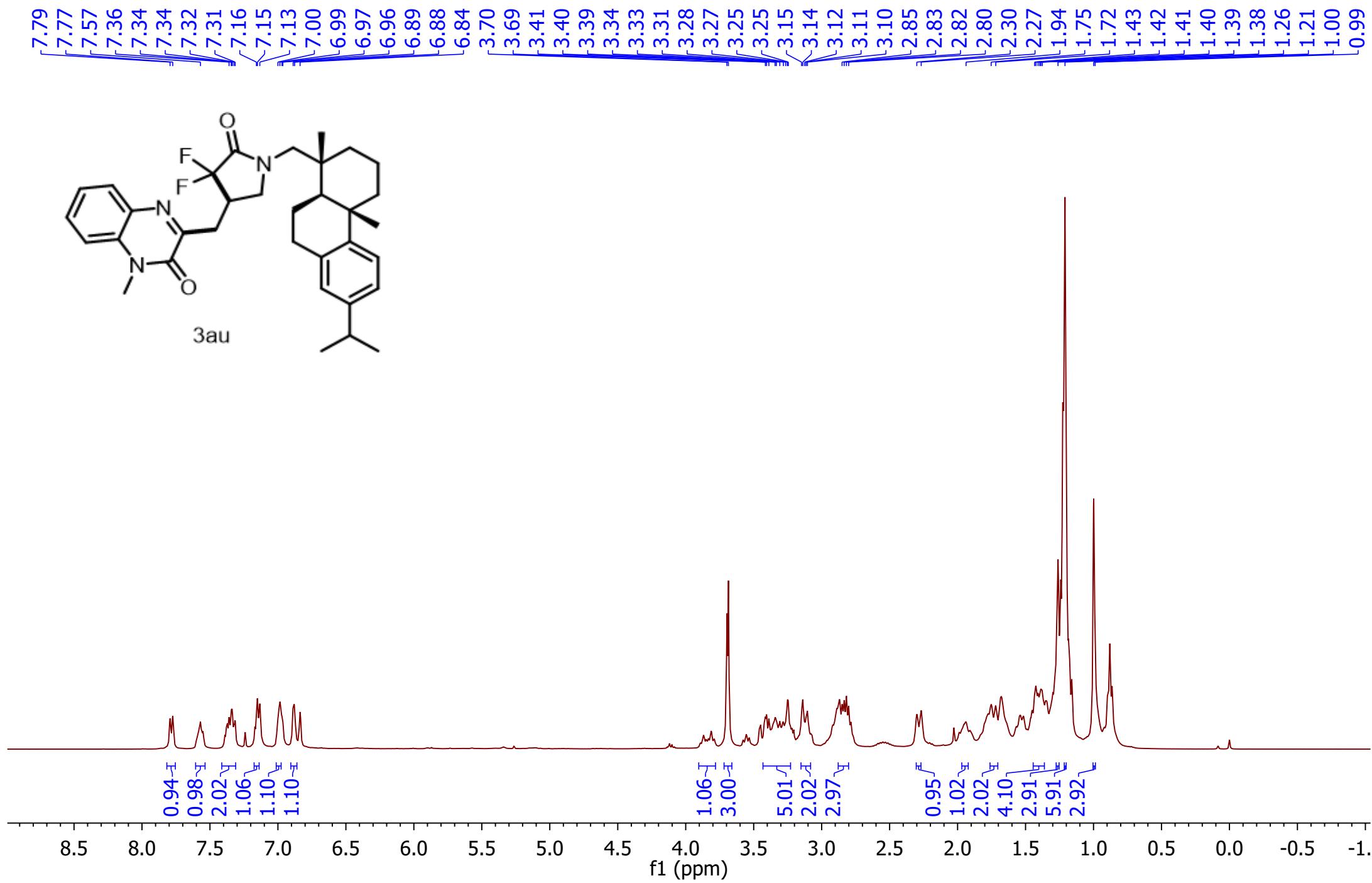
## **19F (CDCl<sub>3</sub>, 376 MHz)**



3at

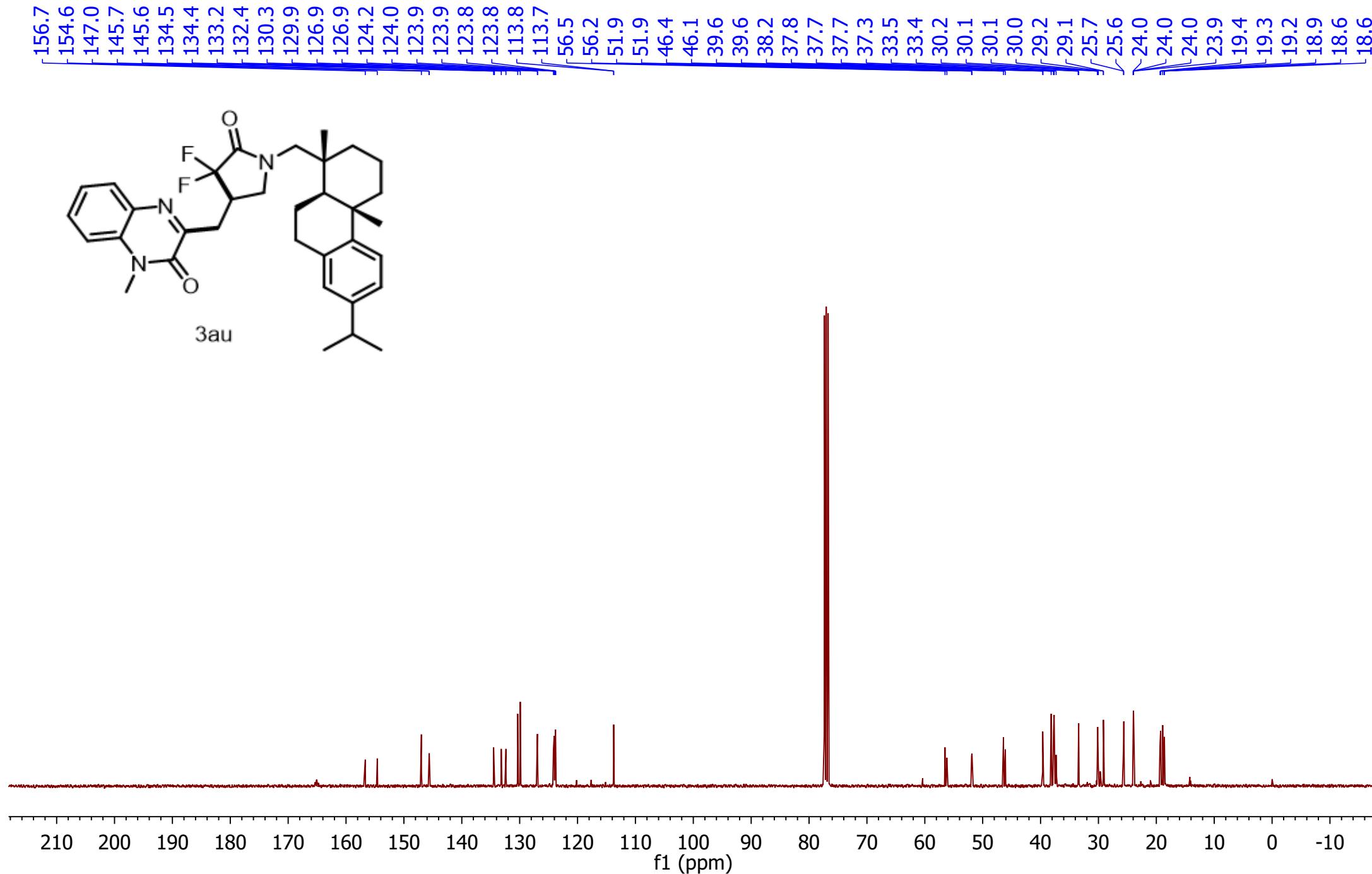


**1H (CDCl<sub>3</sub>, 400 MHz)**



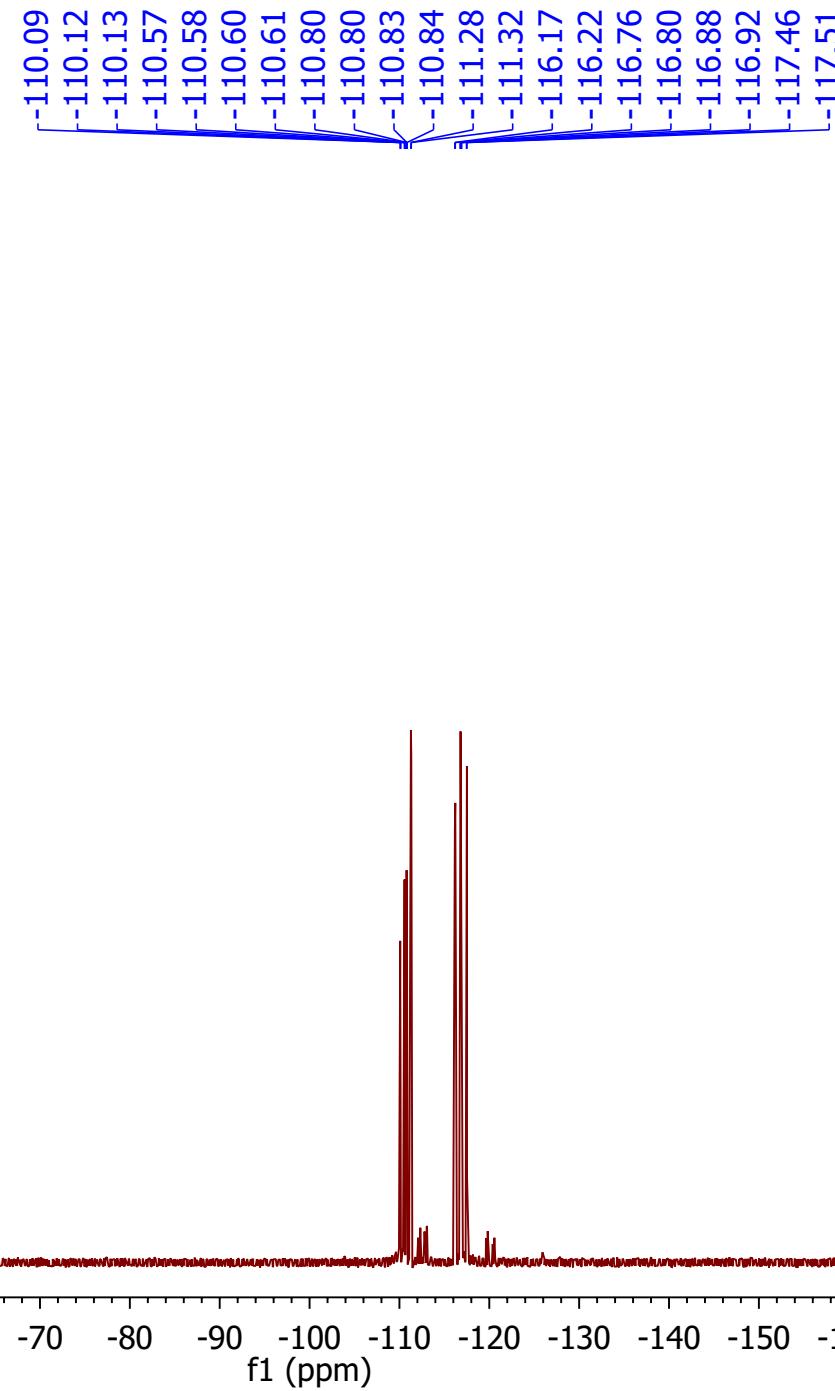
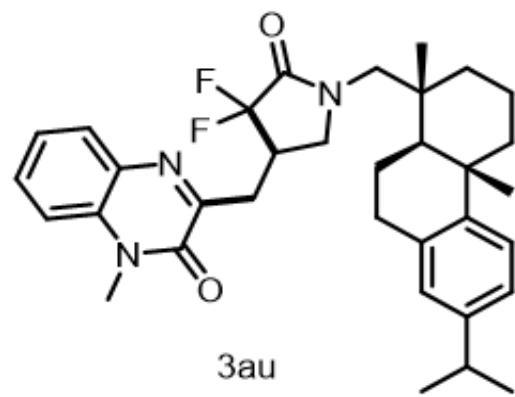
### <sup>1</sup>H NMR Spectrum of **3au**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



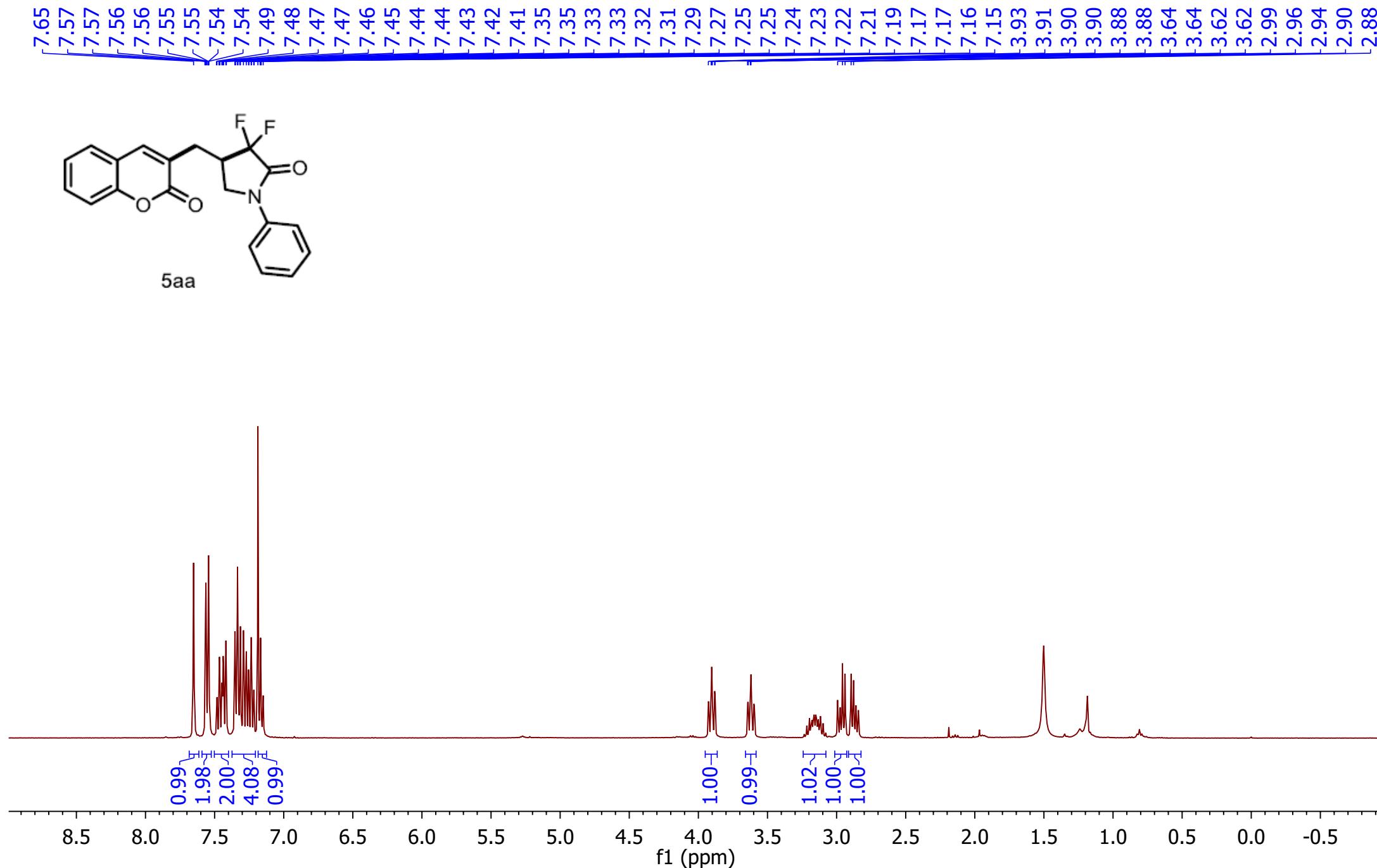
<sup>13</sup>C NMR Spectrum of 3au

<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)



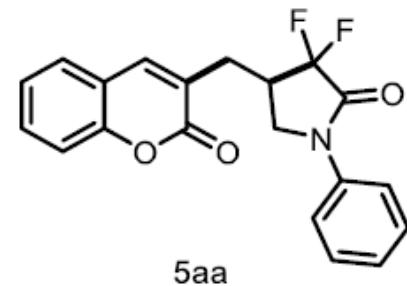
<sup>19</sup>F NMR Spectrum of 3au

**1H (CDCl<sub>3</sub>, 400 MHz)**



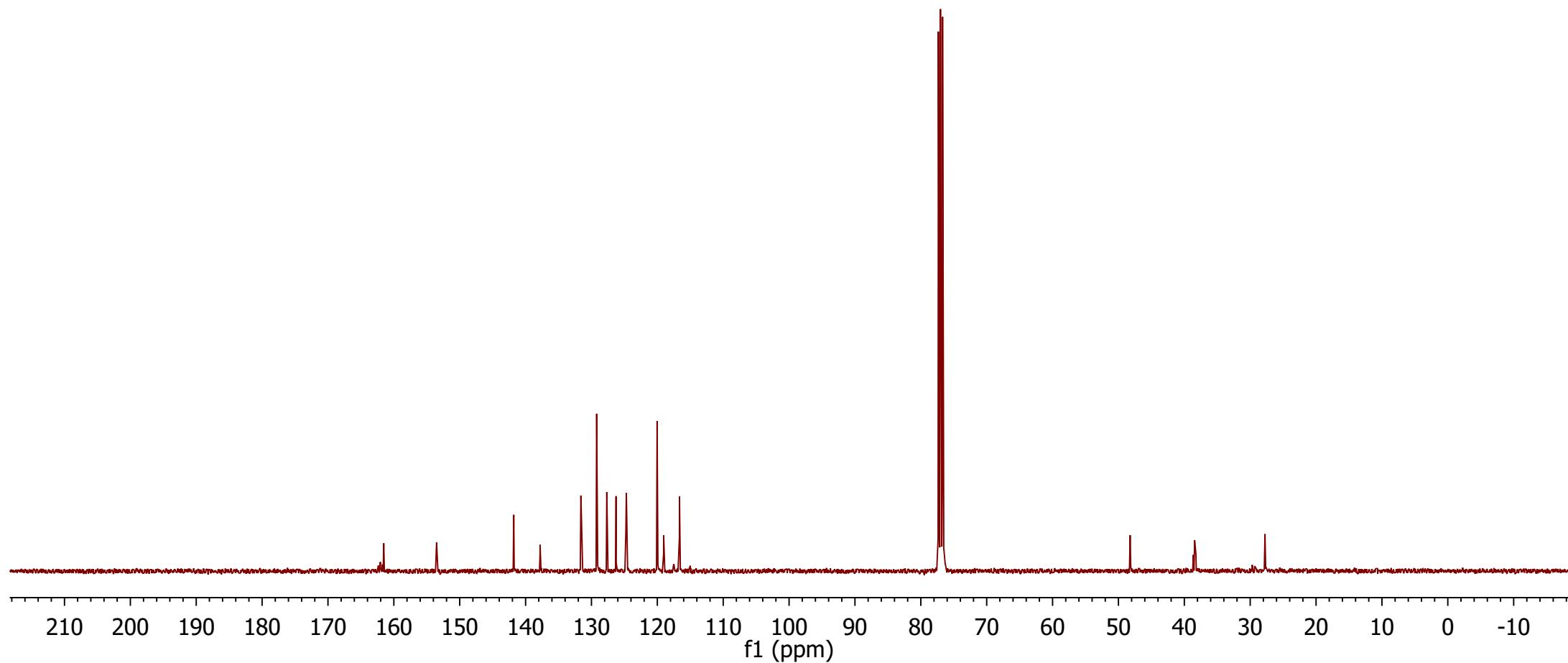
<sup>1</sup>H NMR Spectrum of **5aa**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



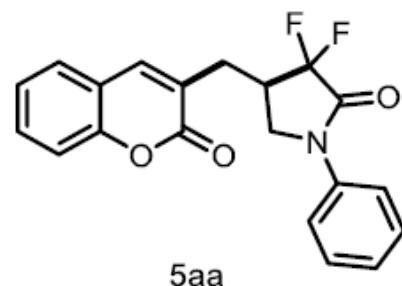
162.0  
161.5  
153.5  
141.8  
137.8  
131.6  
129.2  
127.7  
126.3  
124.8  
124.7  
120.0  
119.0  
117.5  
117.5  
116.6

48.3  
48.2  
38.6  
38.4  
38.2  
29.7  
27.8  
27.8

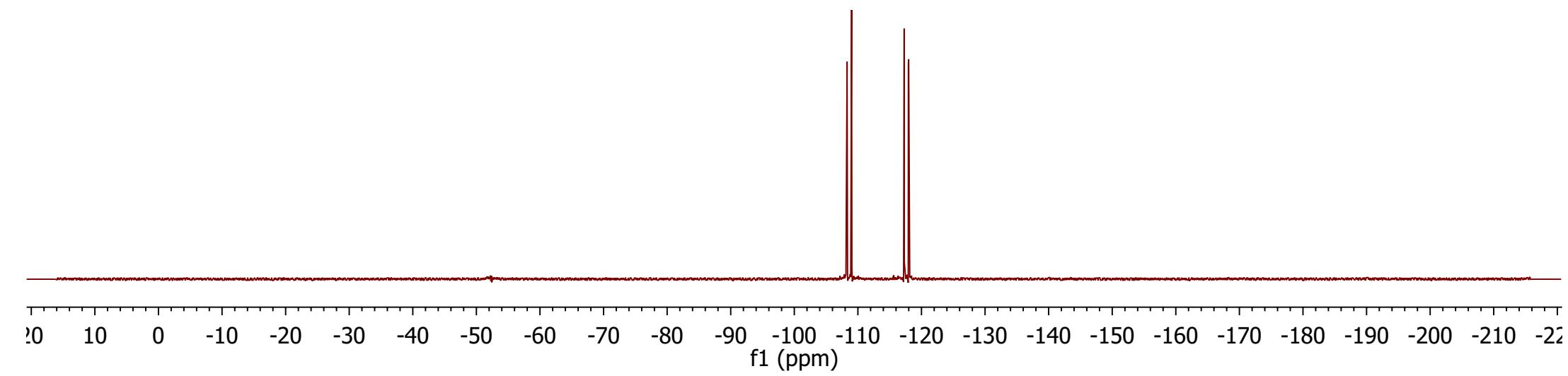


<sup>13</sup>C NMR Spectrum of 5aa

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

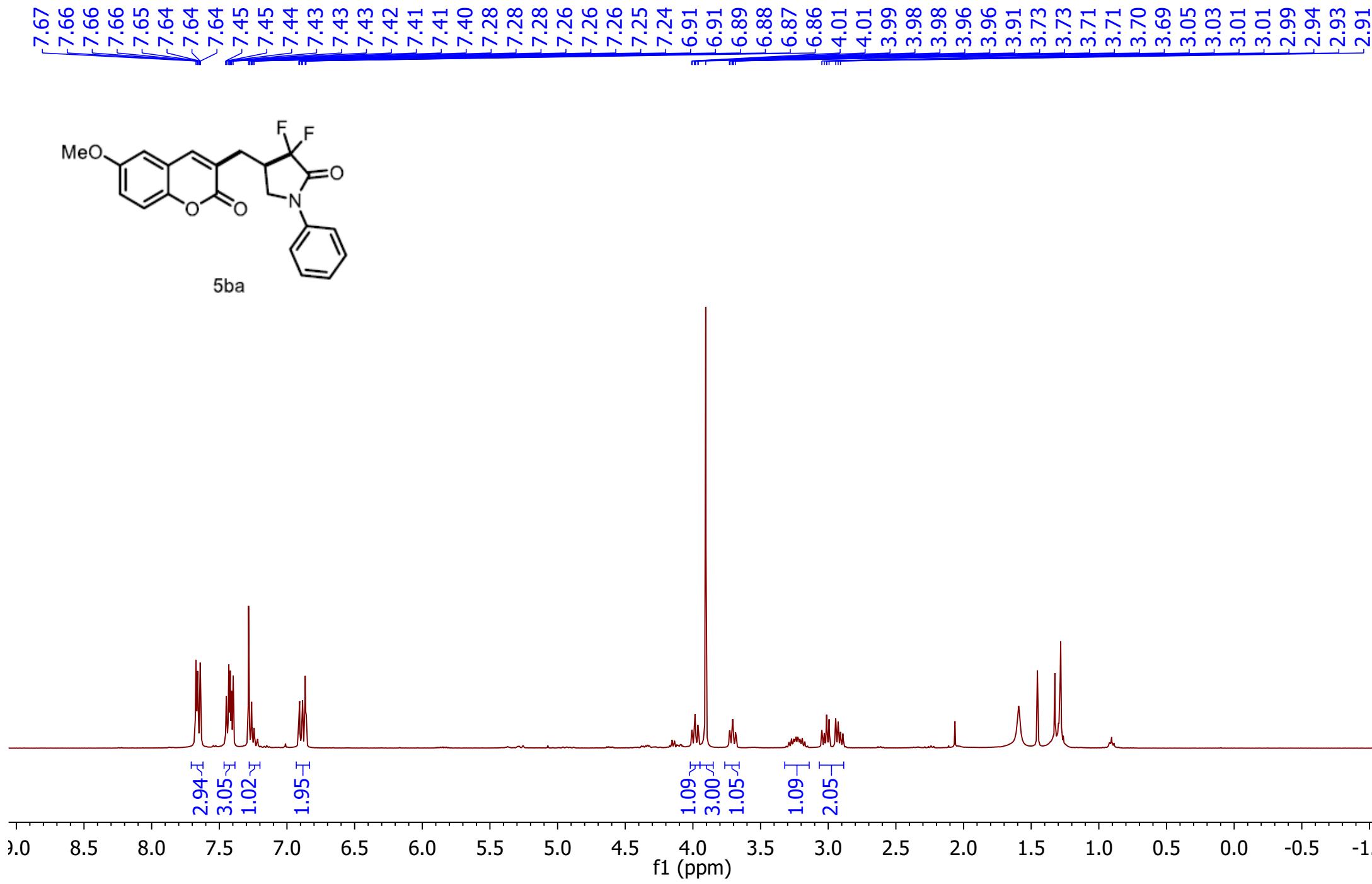


-108.30  
-108.34  
-109.01  
-109.05  
-117.23  
-117.28  
-117.94  
-117.99

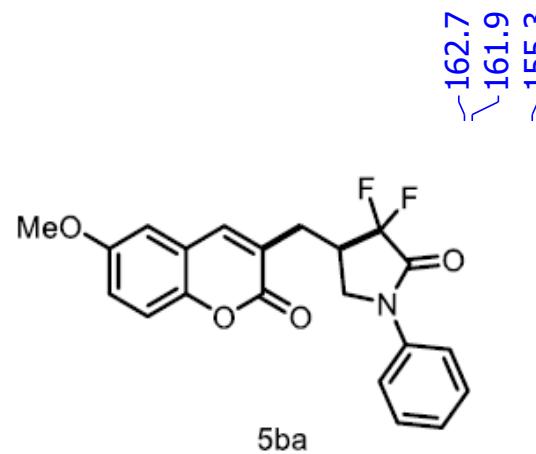


<sup>19</sup>F NMR Spectrum of **5aa**

**1H (CDCl<sub>3</sub>, 400 MHz)**

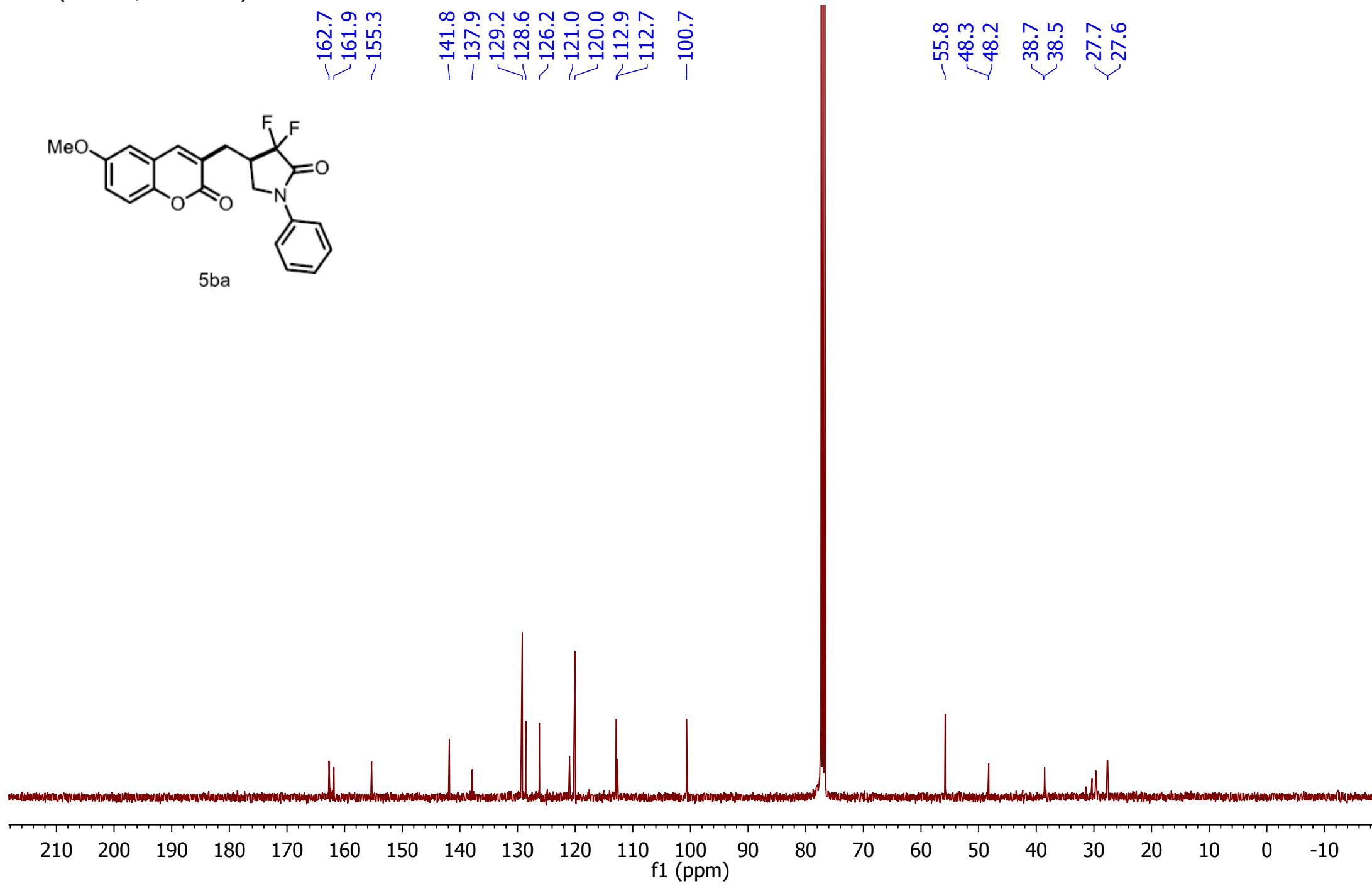


**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



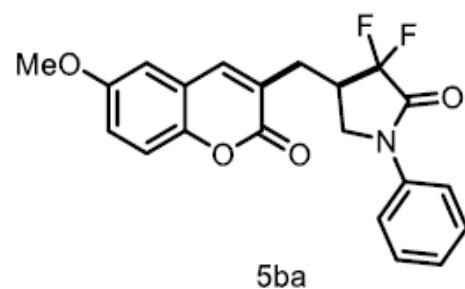
Peak labels (ppm):

- ~162.7
- ~161.9
- ~155.3
- 141.8
- 137.9
- ~129.2
- ~128.6
- ~126.2
- ~121.0
- ~120.0
- ~112.9
- ~112.7
- 100.7

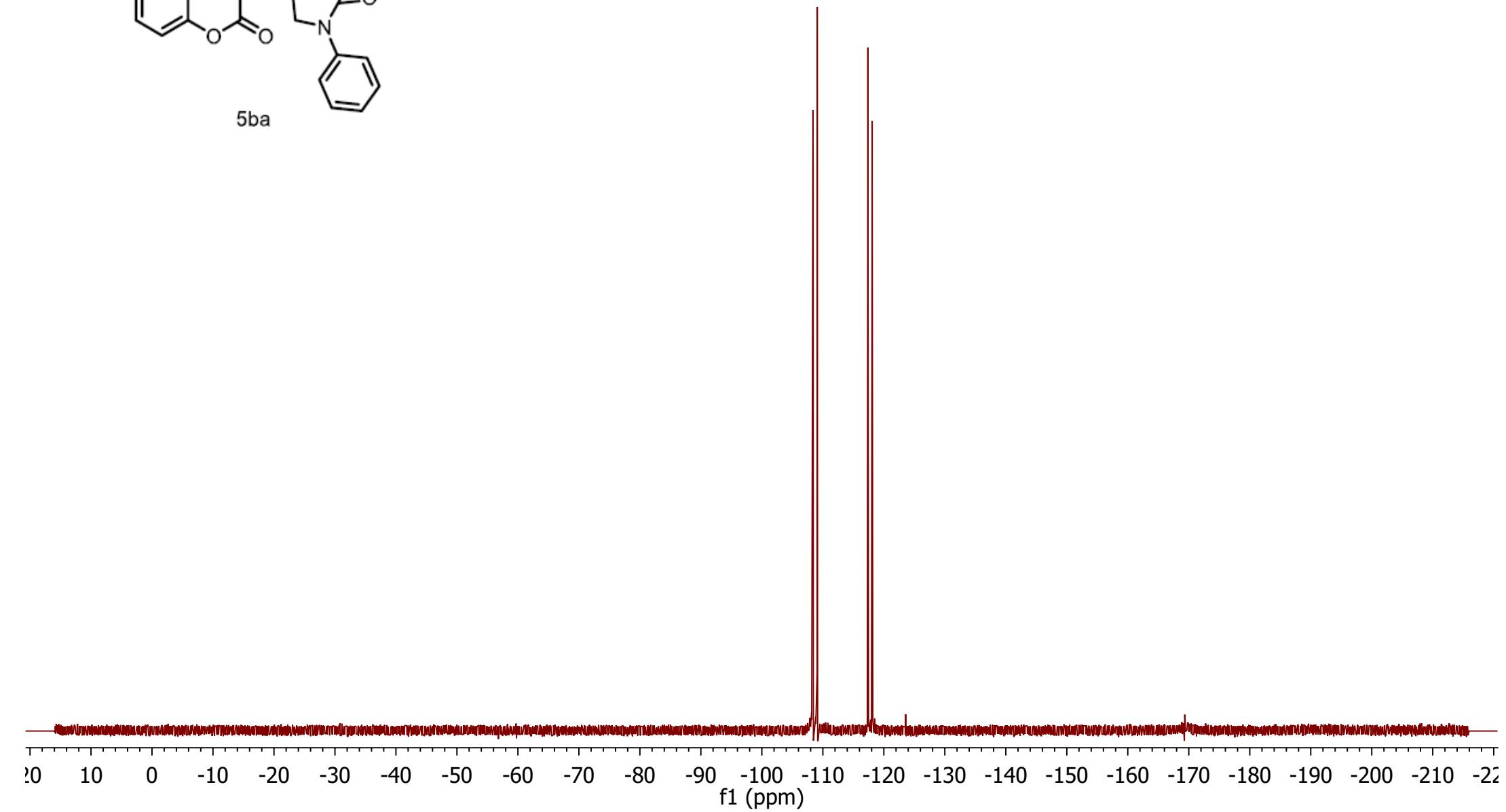


<sup>13</sup>C NMR Spectrum of **5ba**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

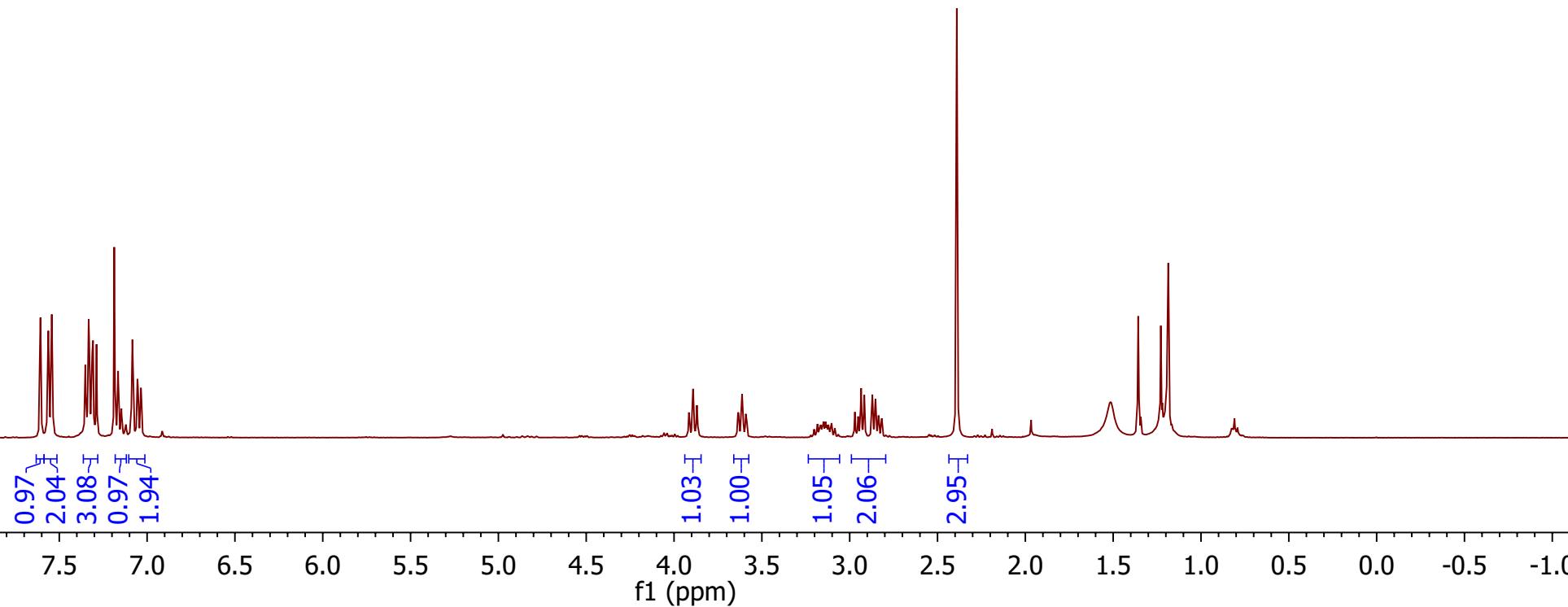
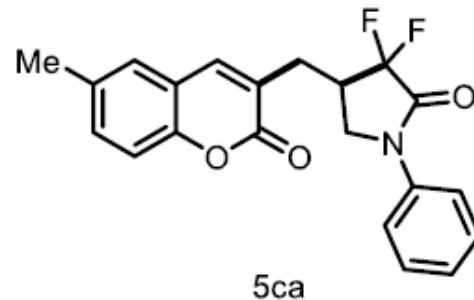
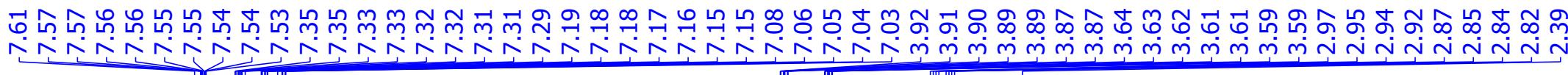


-108.38  
-108.41  
-109.09  
-109.12  
-117.33  
-117.38  
-118.04  
-118.09



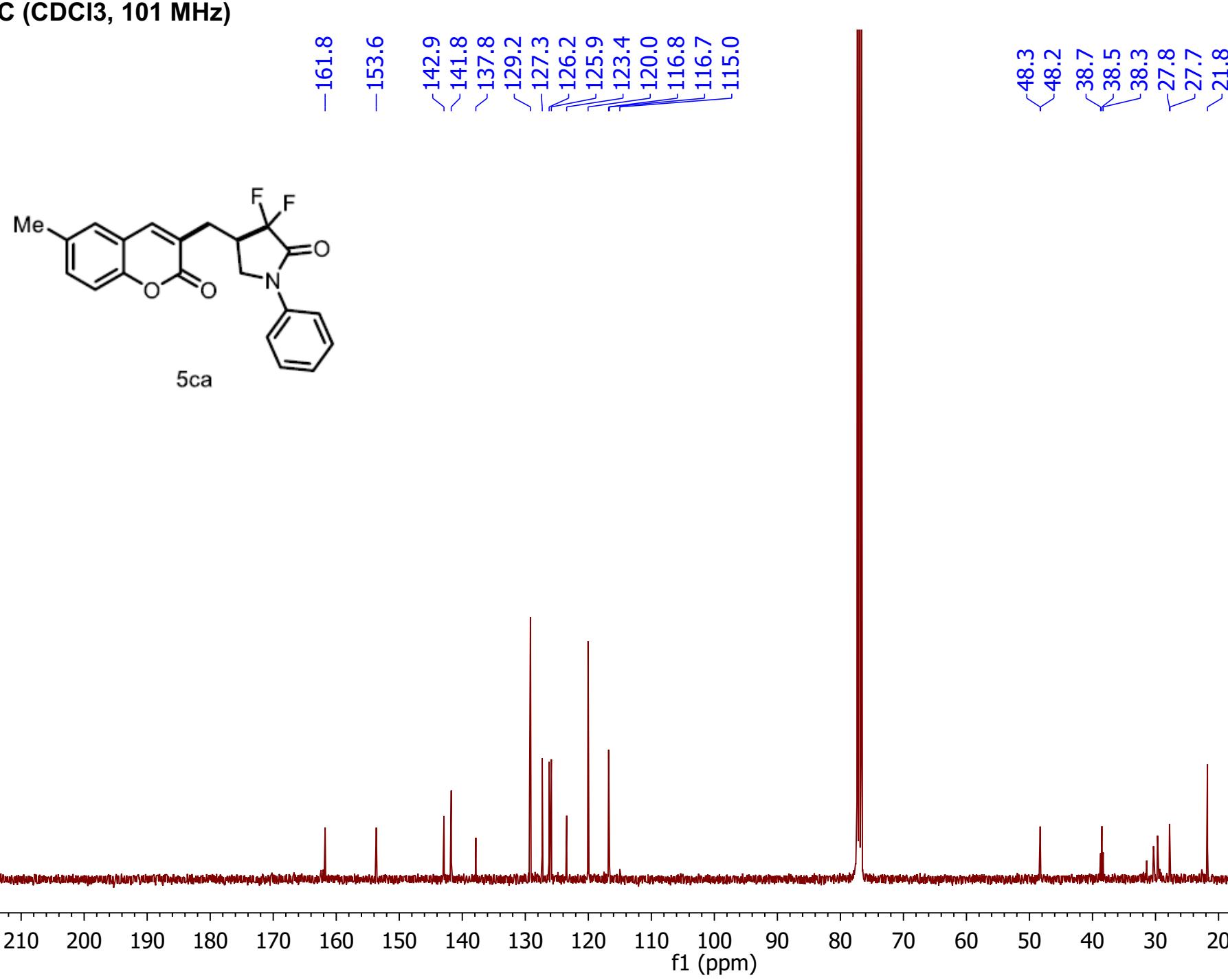
<sup>19</sup>F NMR Spectrum of **5ba**

**1H (CDCl<sub>3</sub>, 400 MHz)**



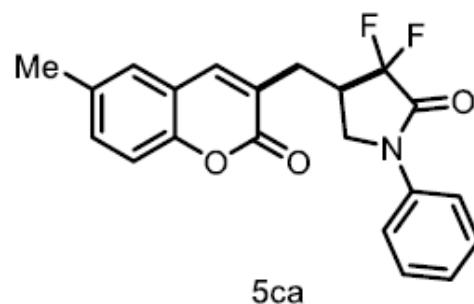
<sup>1</sup>H NMR Spectrum of **5ca**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

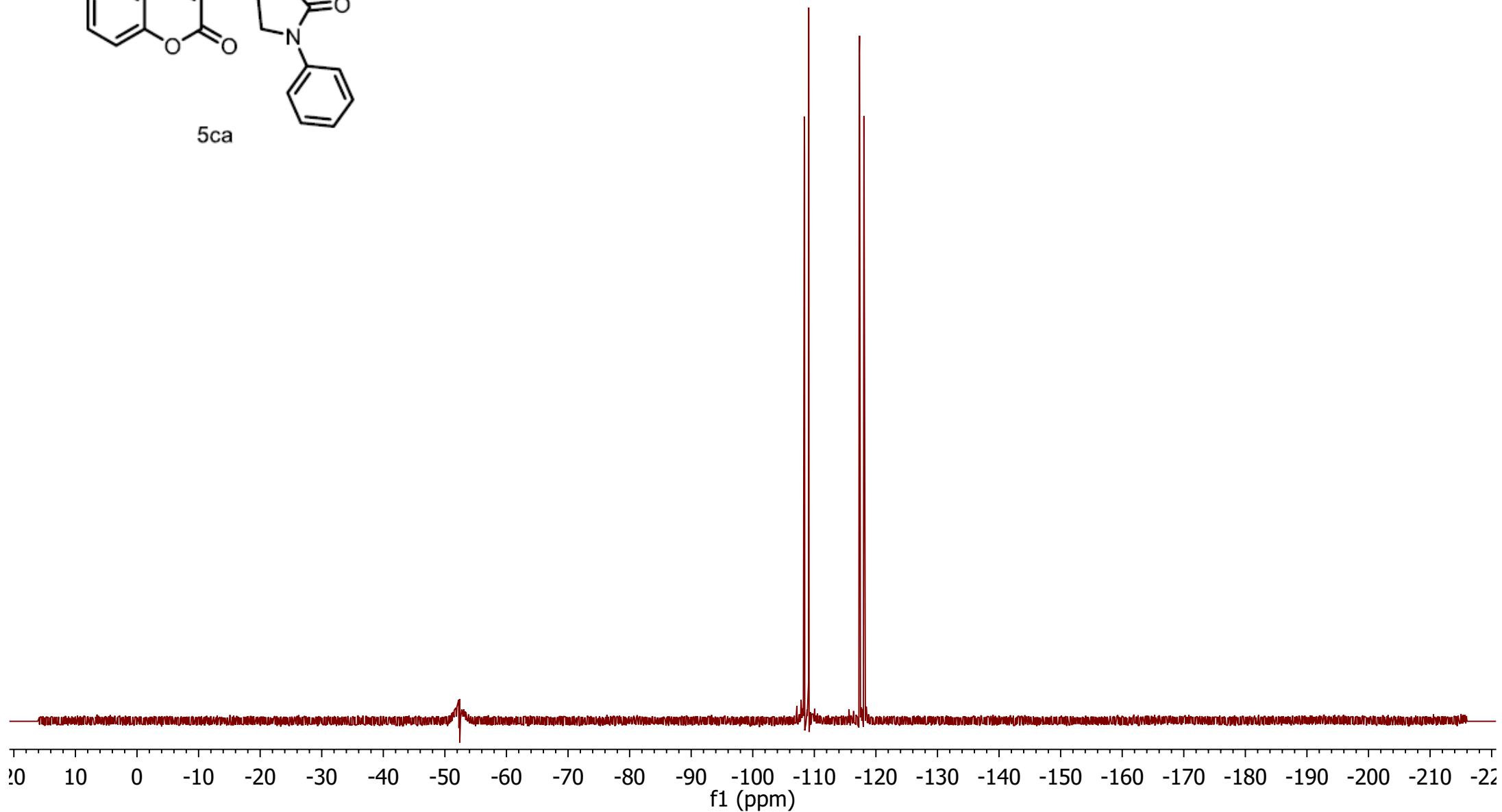


<sup>13</sup>C NMR Spectrum of **5ca**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

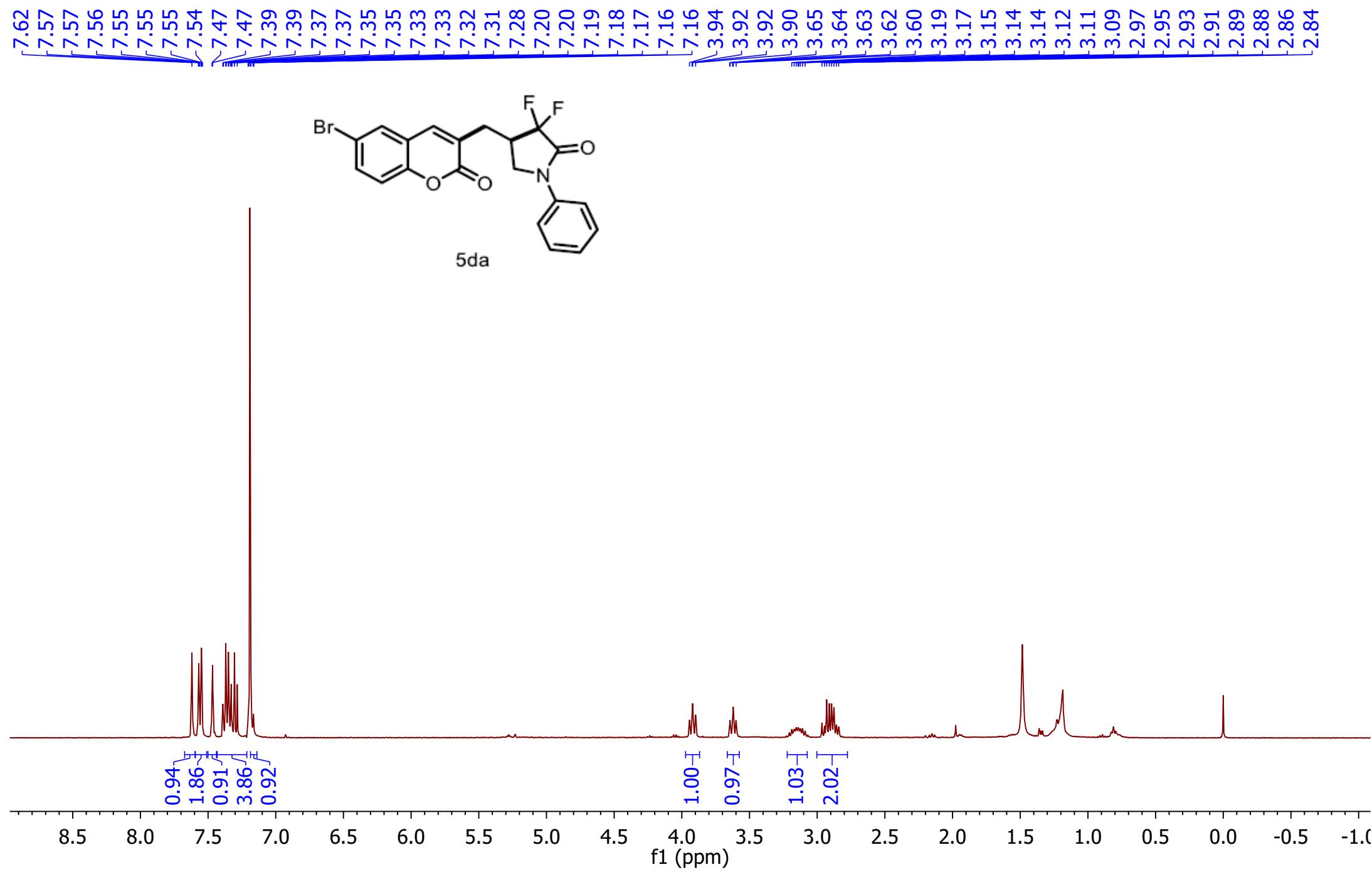


-108.38  
-108.41  
-109.09  
-109.12  
-117.30  
-117.35  
-118.01  
-118.06



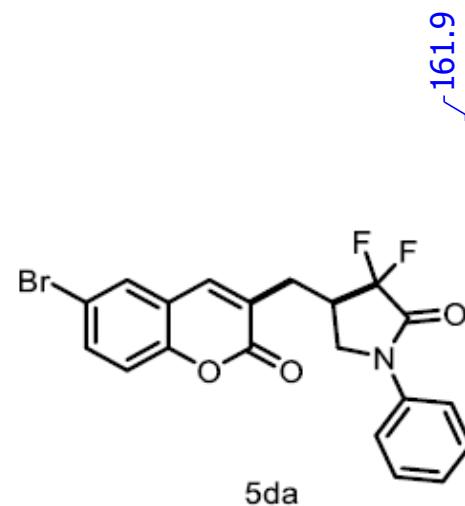
<sup>19</sup>F NMR Spectrum of **5ca**

## **1H (CDCl<sub>3</sub>, 400 MHz)**



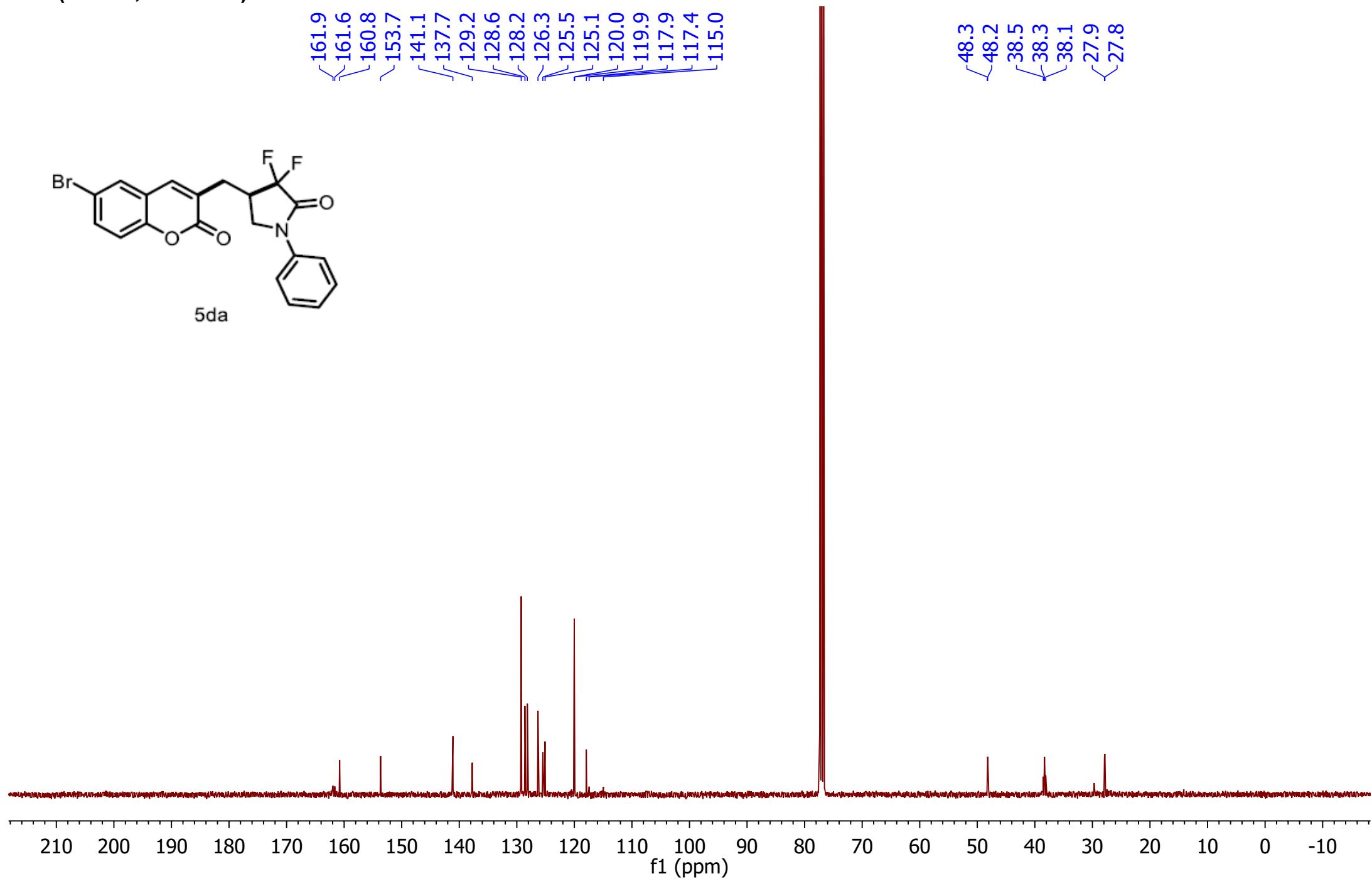
### <sup>1</sup>H NMR Spectrum of **5da**

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



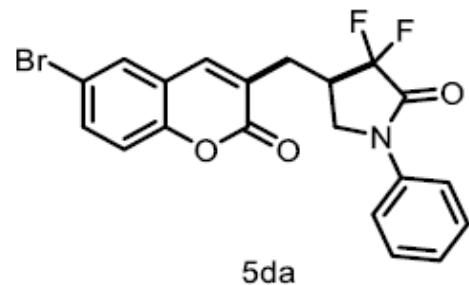
161.9  
161.6  
160.8  
153.7  
141.1  
137.7  
129.2  
128.6  
128.2  
126.3  
125.5  
125.1  
120.0  
119.9  
117.9  
117.4  
115.0

48.3  
48.2  
38.5  
38.3  
38.1  
27.9  
27.8

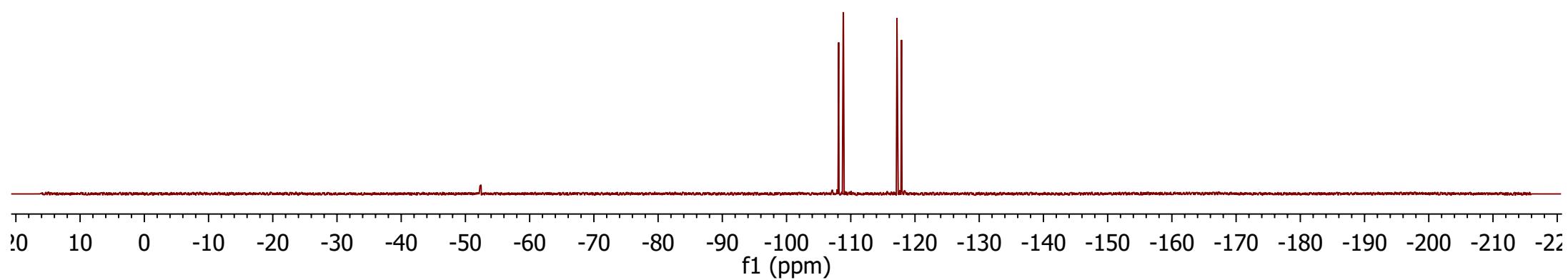


<sup>13</sup>C NMR Spectrum of **5da**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

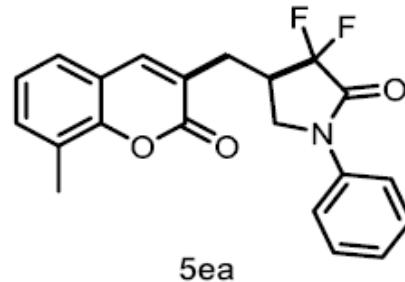


-108.11  
-108.15  
-108.82  
-108.86  
-117.15  
-117.20  
-117.86  
-117.91



<sup>19</sup>F NMR Spectrum of **5da**

**1H (CDCl<sub>3</sub>, 400 MHz)**



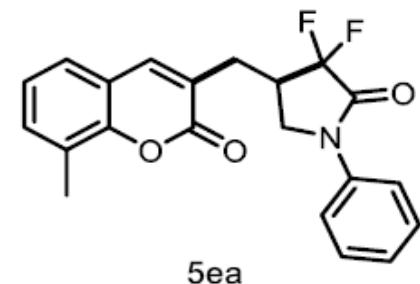
5ea

3.09  
3.98  
1.97

1.00  
1.00  
1.00  
0.98  
1.00  
1.00  
3.07

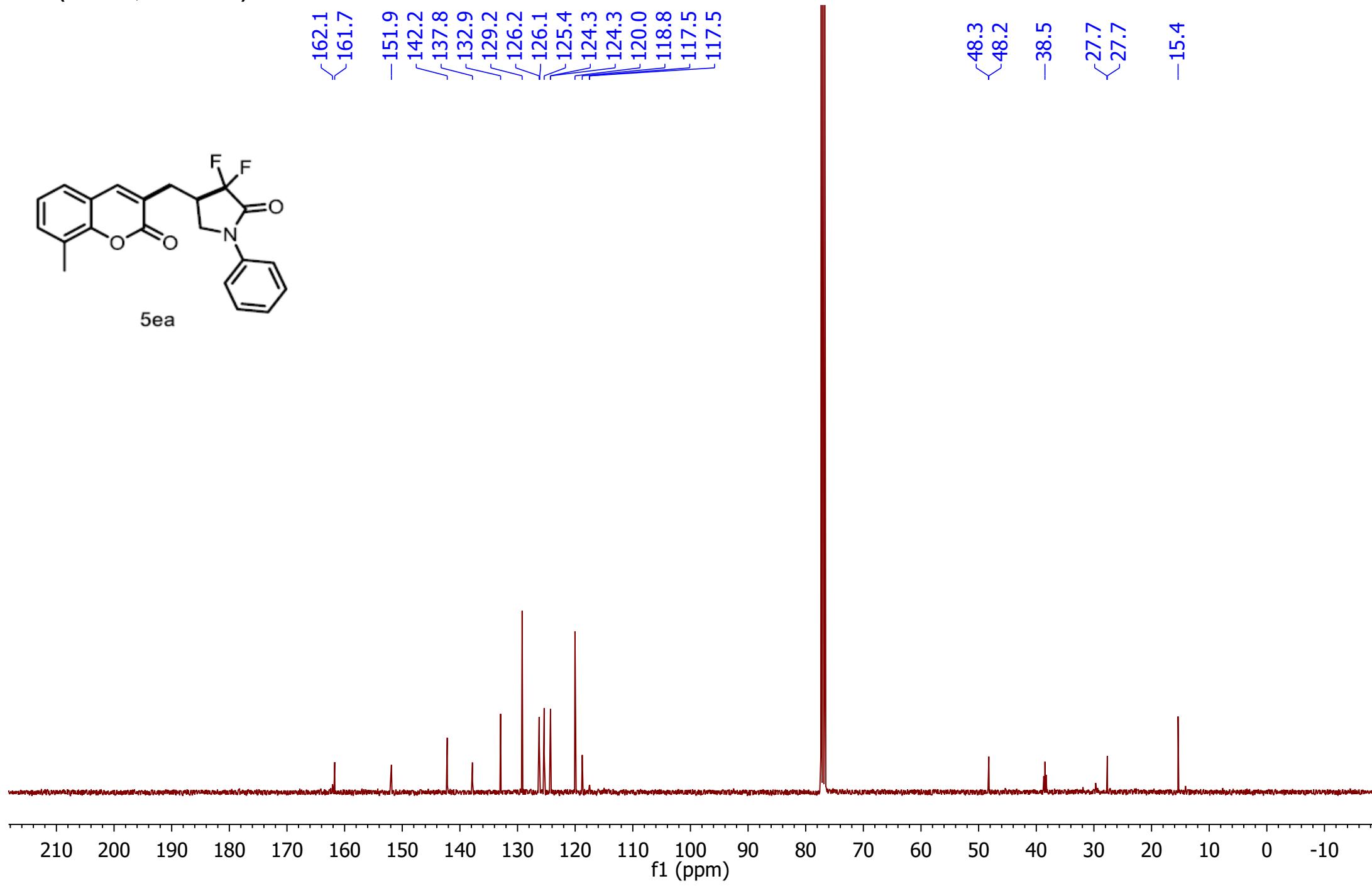
<sup>1</sup>H NMR Spectrum of **5ea**

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



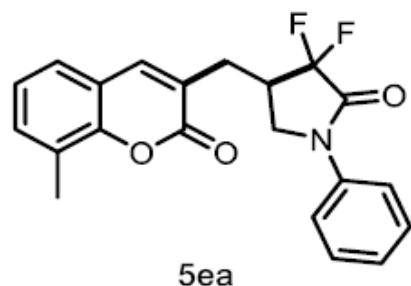
162.1  
161.7  
151.9  
142.2  
137.8  
132.9  
129.2  
126.2  
126.1  
125.4  
124.3  
124.3  
120.0  
118.8  
117.5  
117.5

48.3  
48.2  
38.5  
27.7  
27.7  
-15.4

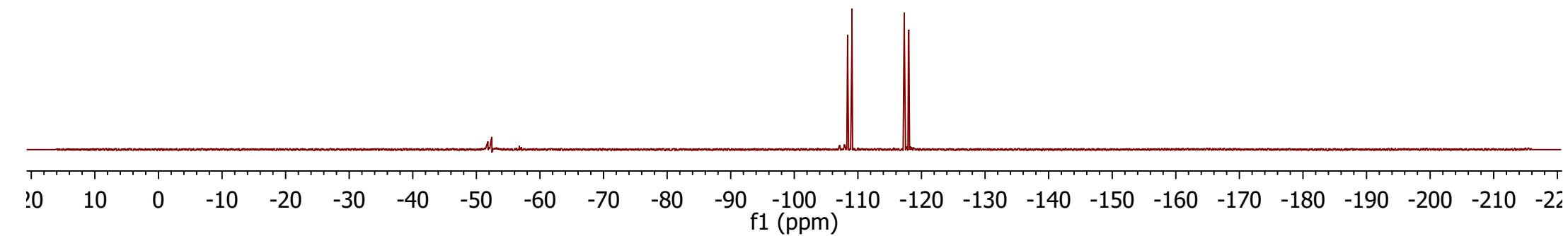


<sup>13</sup>C NMR Spectrum of **5ea**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

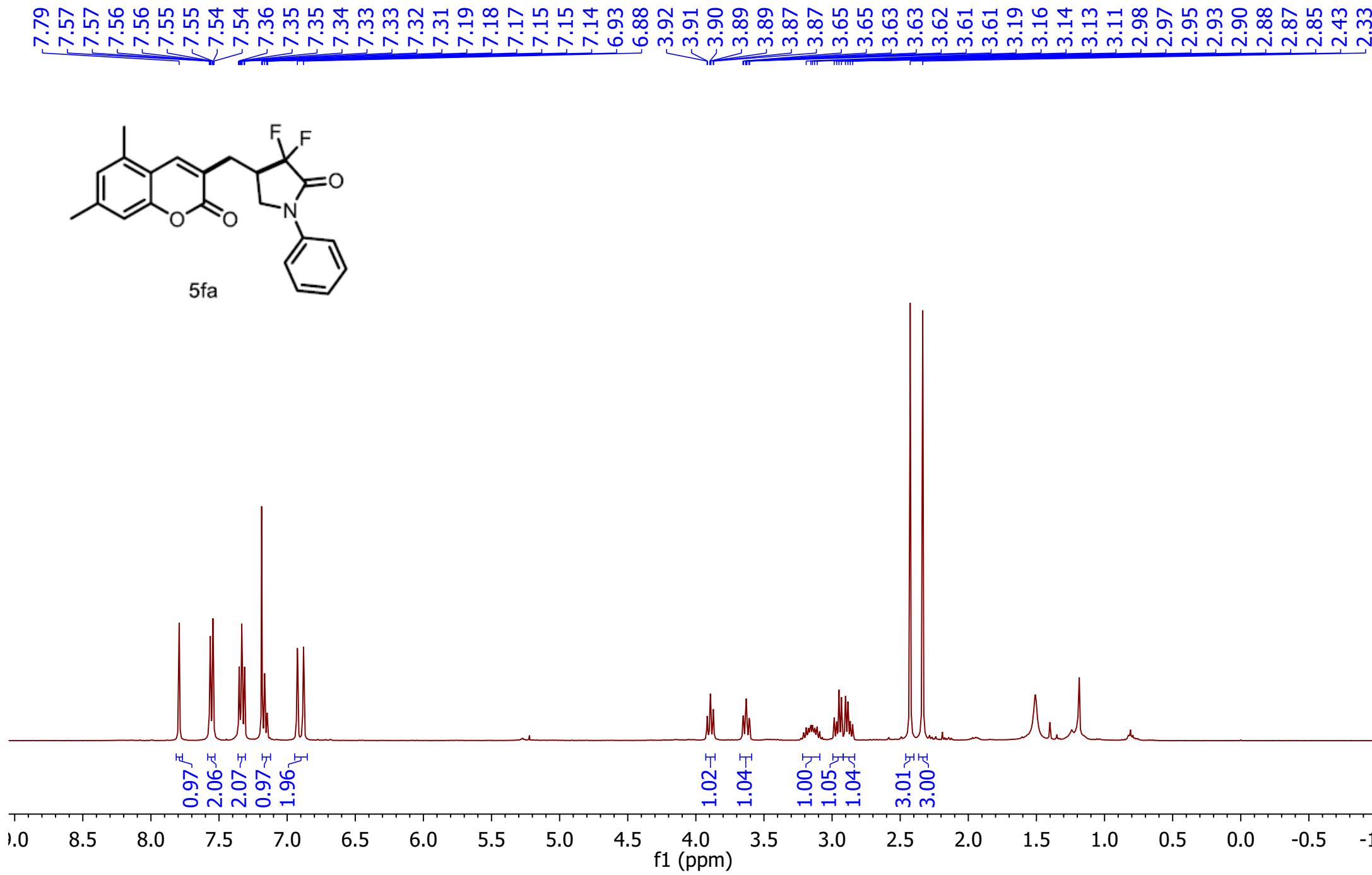


-108.35  
-108.39  
-109.06  
-109.10  
-117.25  
-117.30  
-117.96  
-118.01



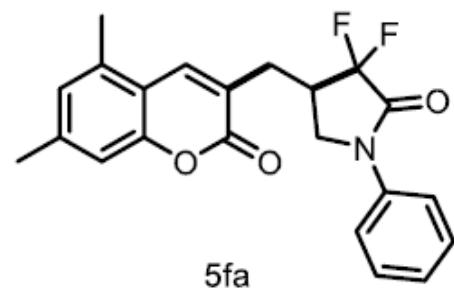
<sup>19</sup>F NMR Spectrum of **5ea**

**1H (CDCl<sub>3</sub>, 400 MHz)**



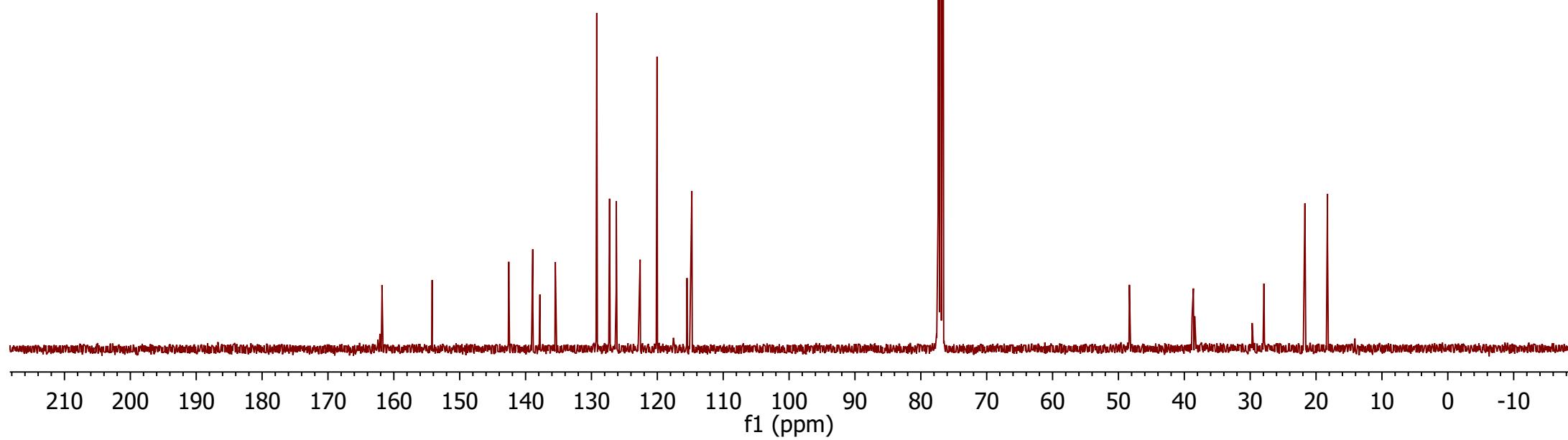
<sup>1</sup>H NMR Spectrum of **5fa**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



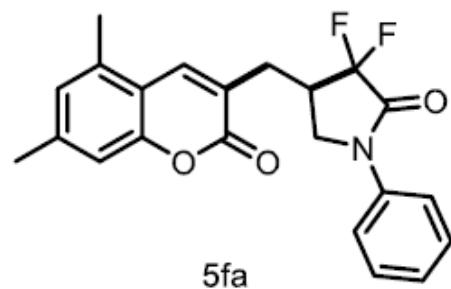
162.1  
161.8  
154.2  
142.6  
138.9  
137.8  
135.5  
129.2  
127.2  
126.2  
122.6  
120.1  
115.5  
114.8

48.3  
48.3  
38.8  
38.6  
38.4  
28.0  
27.9  
21.7  
18.3

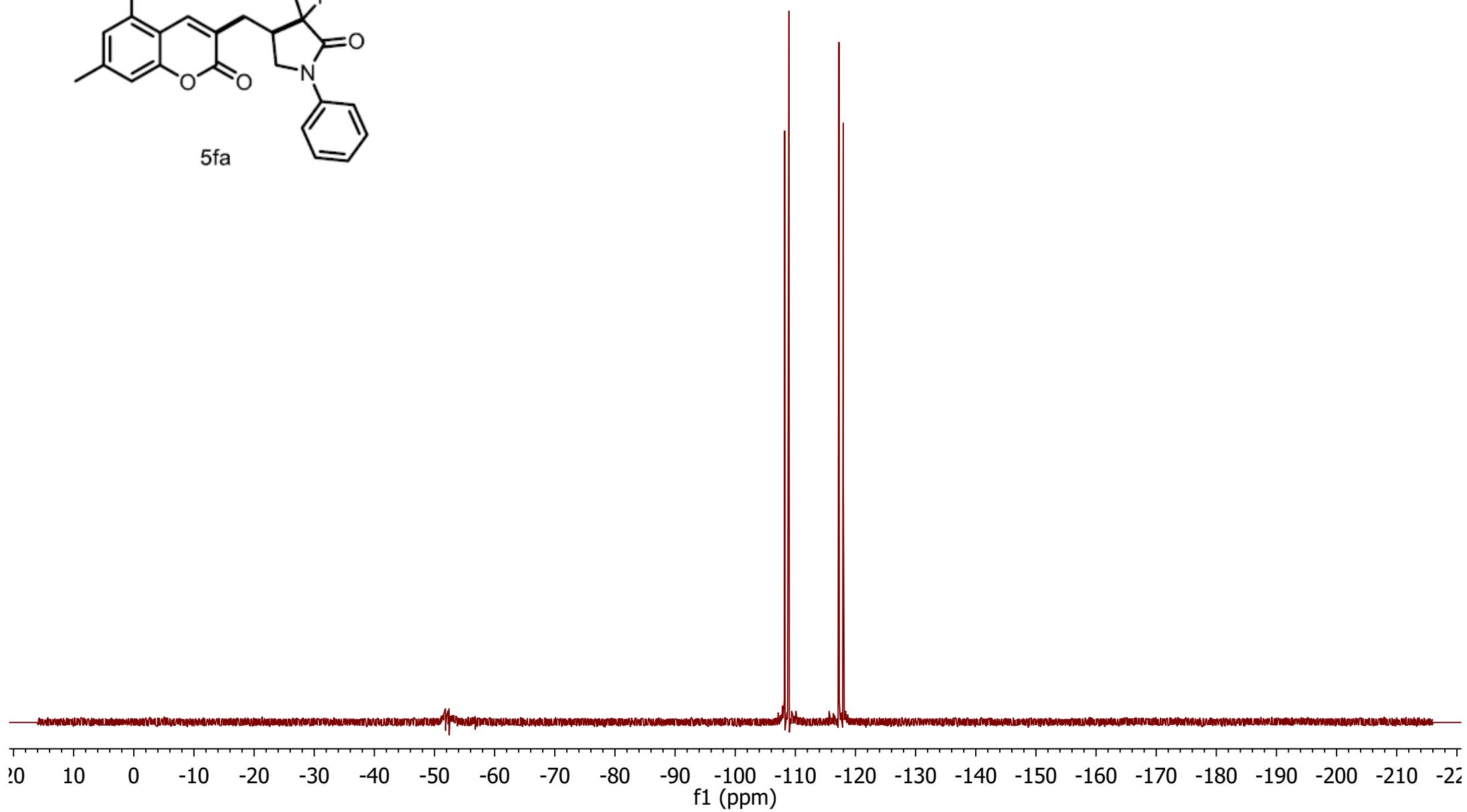


<sup>13</sup>C NMR Spectrum of **5fa**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

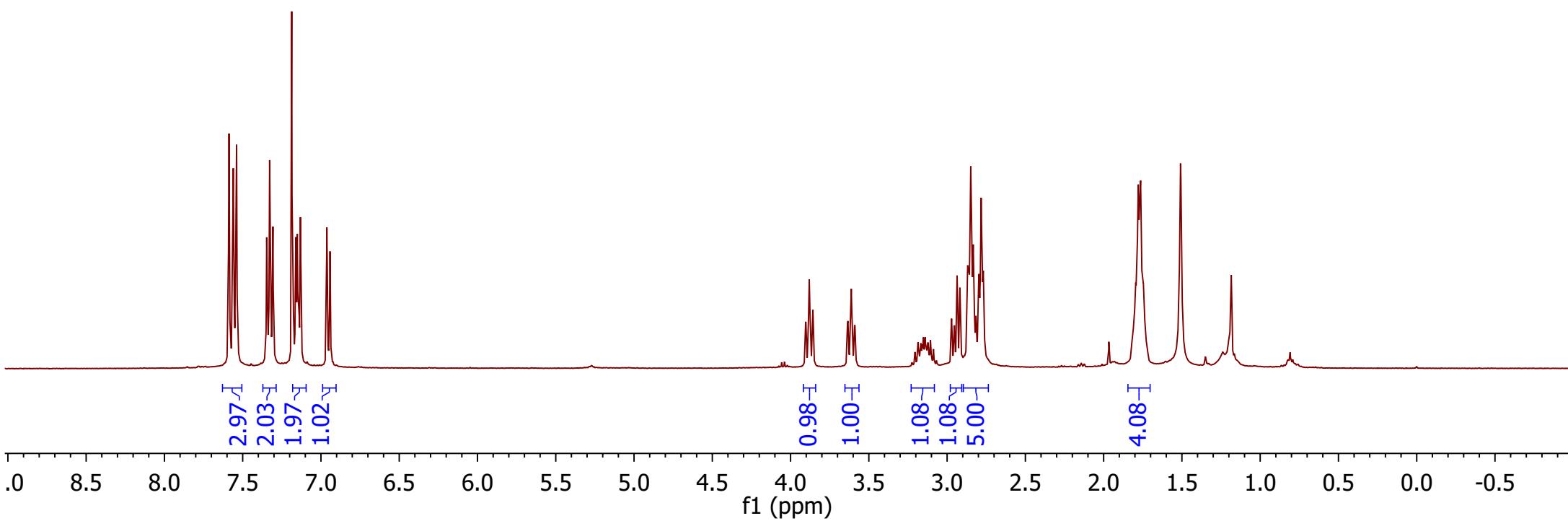
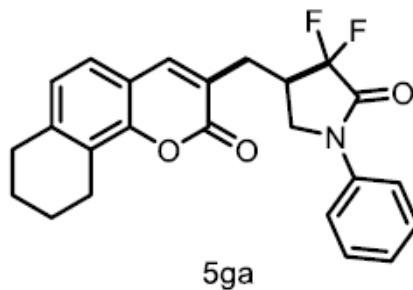
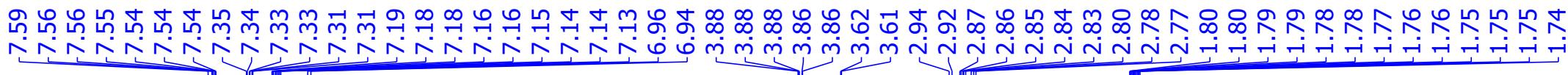


-108.22  
-108.26  
-108.93  
-108.97  
-117.20  
-117.25  
-117.91  
-117.96



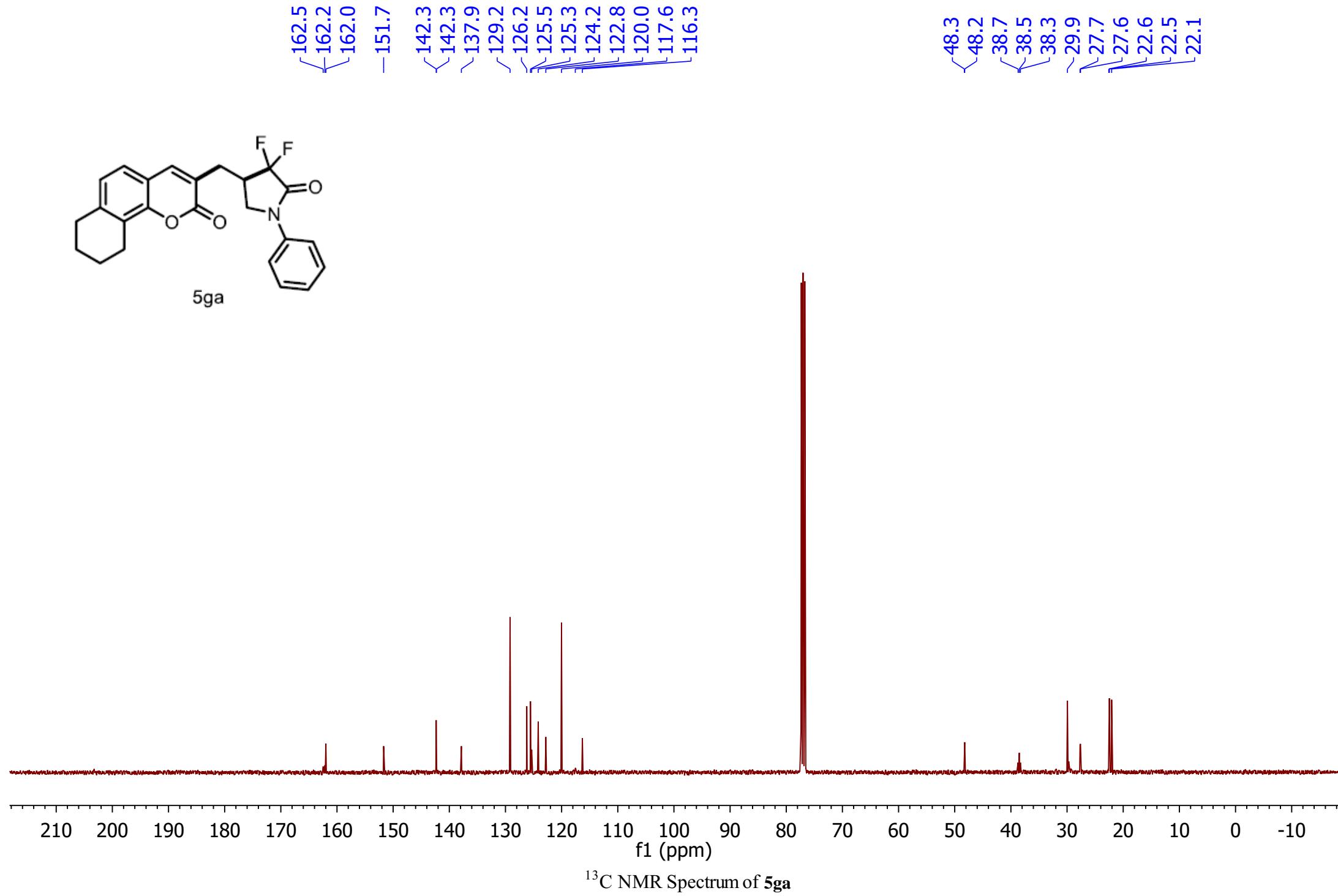
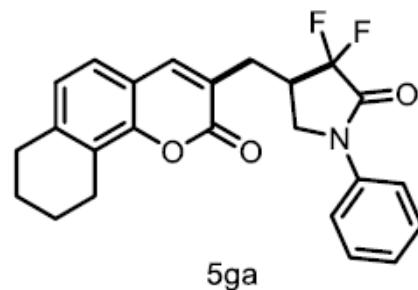
<sup>19</sup>F NMR Spectrum of **5fa**

**<sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz)**

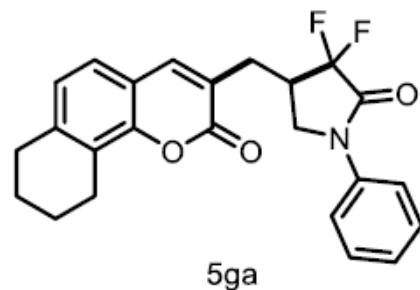


<sup>1</sup>H NMR Spectrum of **5ga**

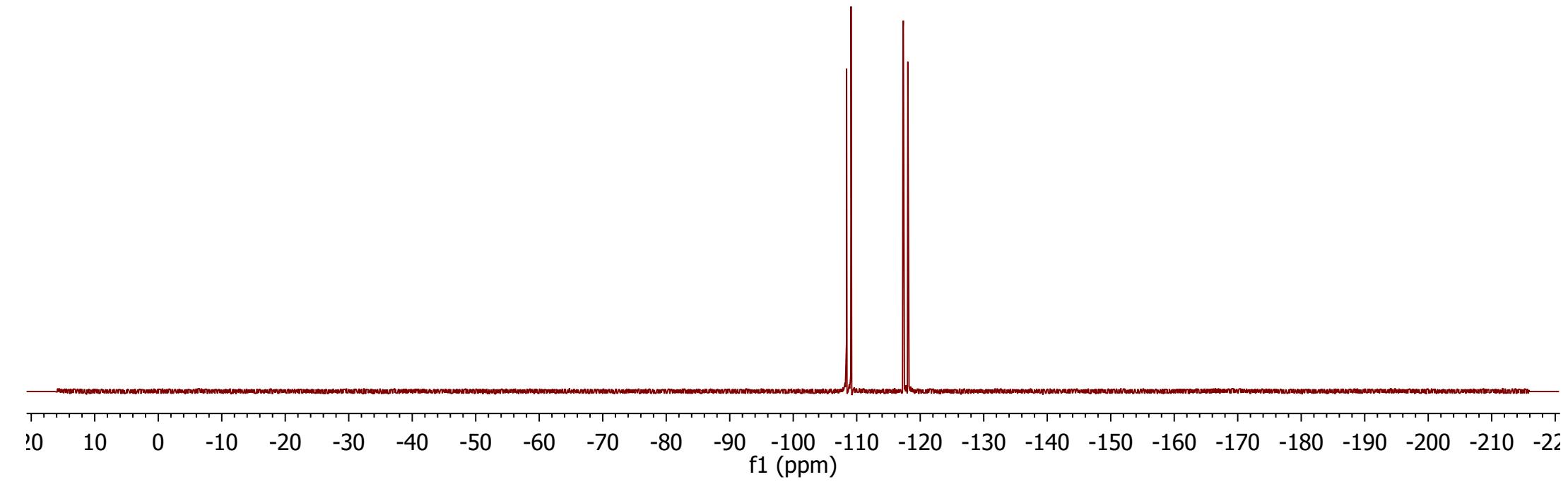
### **13C (CDCl3, 101 MHz)**



<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)

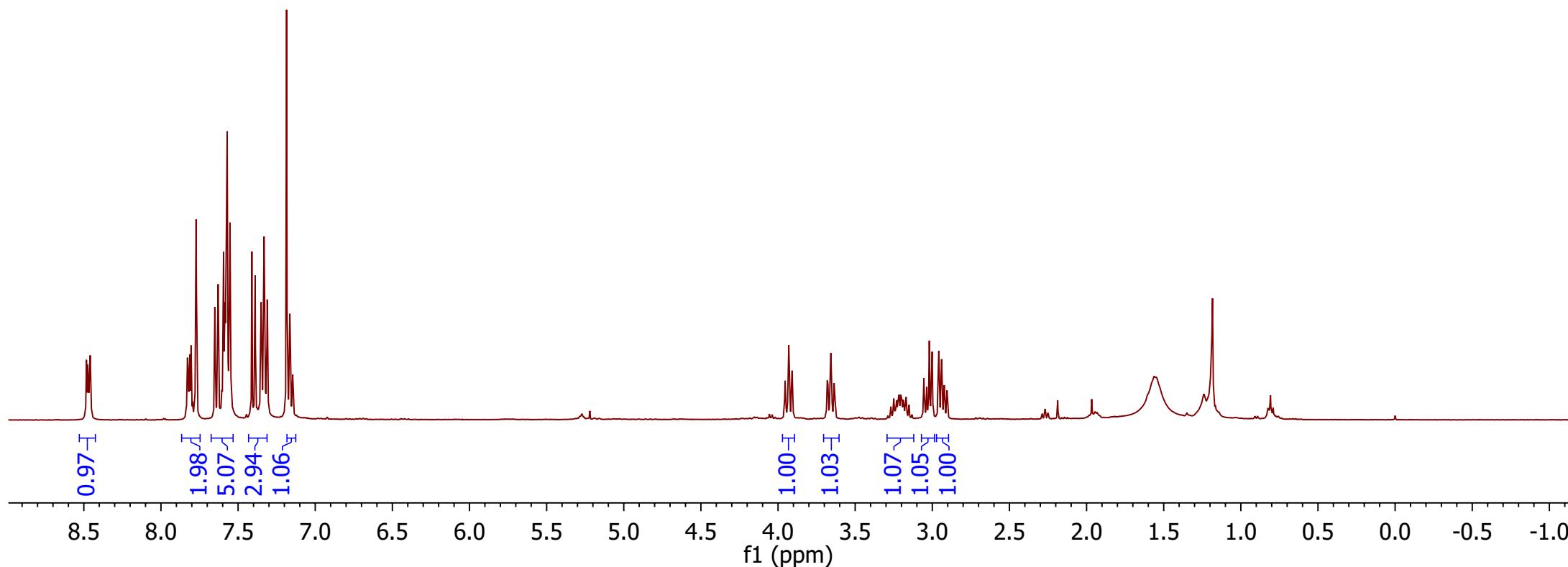
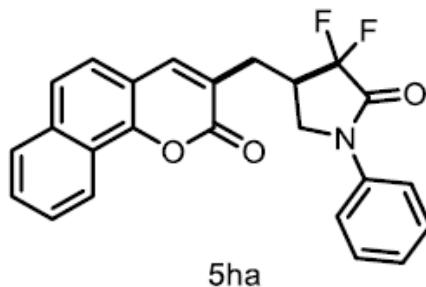


-108.40  
-108.44  
-109.11  
-109.15  
-117.29  
-117.34  
-118.00  
-118.05



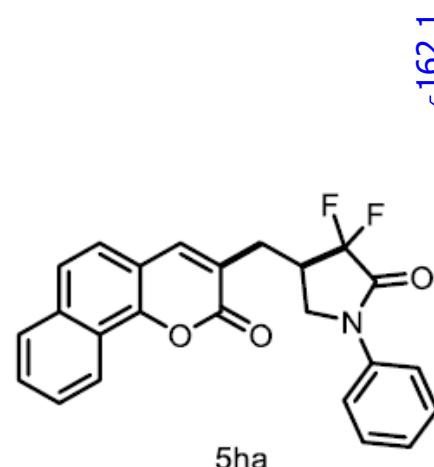
<sup>19</sup>F NMR Spectrum of 5ga

**1H (CDCl<sub>3</sub>, 400 MHz)**

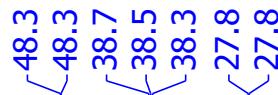


### <sup>1</sup>H NMR Spectrum of **5ha**

<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)



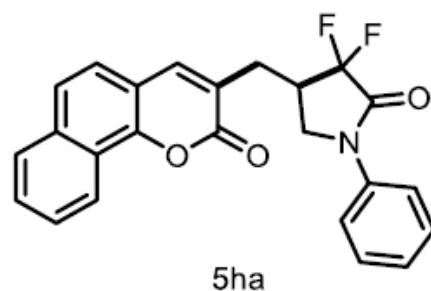
**5ha**



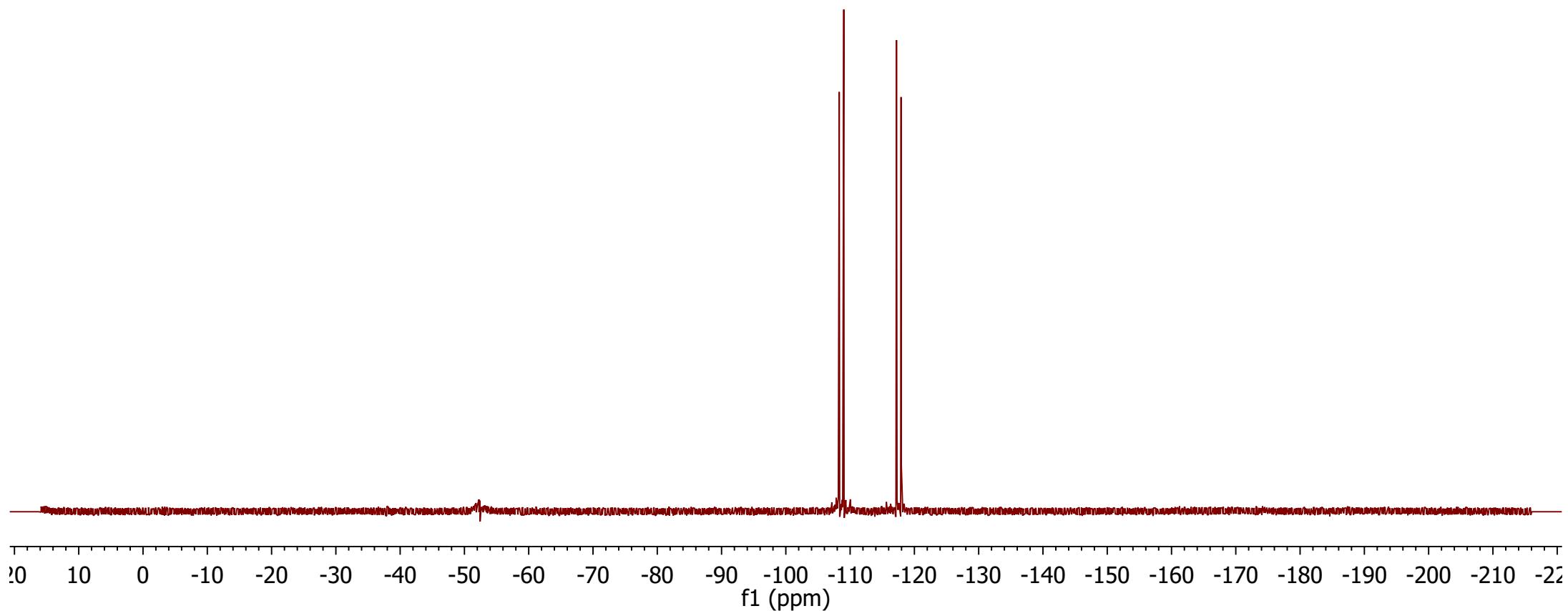
<sup>13</sup>C NMR Spectrum of **5ha**

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



-108.27  
-108.31  
-108.98  
-109.02  
-117.17  
-117.22  
-117.88  
-117.93



<sup>19</sup>F NMR Spectrum of **5ha**