

## Supporting Information

### **A portal to highly valuable indole-functionalized vinyl sulfonyl fluorides and allylic sulfonyl fluorides**

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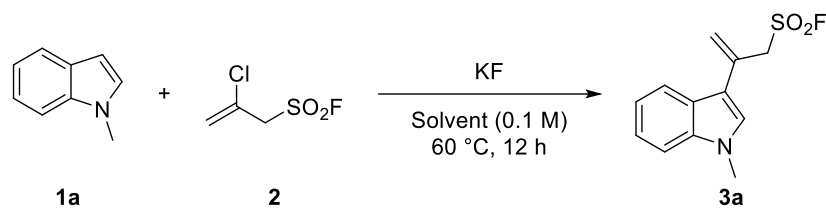
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## 1. General Information

All reactions were carried out under an air atmosphere unless otherwise specified. Reagents used in the reactions were all purchased from commercial sources and used without further purification. Unless otherwise specified, NMR spectra were recorded in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> on a 500 MHz (for <sup>1</sup>H), 471 MHz (for <sup>19</sup>F), and 126 MHz (for <sup>13</sup>C) Bruker Avance spectrometer, and were internally referenced to solvent residual signals (note: CDCl<sub>3</sub>:  $\delta$  H = 7.260 ppm,  $\delta$  C = 77.16 ppm; DMSO-*d*<sub>6</sub>:  $\delta$  H = 2.500 ppm,  $\delta$  C = 39.52 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All chemical shifts were reported in ppm relative to TMS (0 ppm) as internal standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5  $\mu$ m, 4.6  $\times$  150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. HRMS experiments were performed on a TOF-Q ESI or CI/EI instrument. The coupling constants were reported in Hertz (Hz). The product spots on the thin layer chromatography (TLC) were visualized under ultraviolet light (254 nm or 365 nm) followed by staining with potassium permanganate or phosphomolybdic acid.

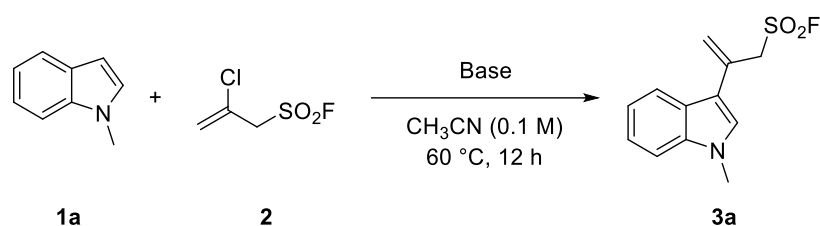
## 2. Optimization of the Reaction Conditions

Table S1 Screening the Solvent<sup>a</sup>



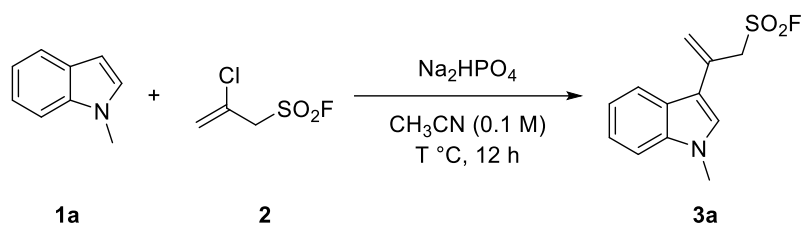
Entry	Solvent	Yield ( <b>3a</b> , %) <sup>b</sup>
1	DCE	3
2	MeOH	1
3	THF	14
4	Toluene	18
<b>5</b>	<b>CH<sub>3</sub>CN</b>	<b>41</b>
6	DMF	1
7	1,4-Dioxane	9
8	EtOAc	26
9	DMSO	1
10	NMP	6

<sup>a</sup>Reaction conditions: a mixture of 1-methylindole (**1a**, 13 mg, 0.1 mmol, 1.0 equiv.), CESF (**2**, 32 mg, 0.2 mmol, 2.0 equiv.) and KF (23 mg, 0.4 mmol, 4.0 equiv.) in solvent (1.0 mL) was stirred at 60 °C for 12 h under air. <sup>b</sup>The yield was determined by HPLC using pure **3a** as the external standard ( $t_R = 5.863$  min,  $\lambda_{max} = 226.4$  nm, CH<sub>3</sub>CN / H<sub>2</sub>O = 60:40 (v/v)).

**Table S2** Screening the Base<sup>a</sup>

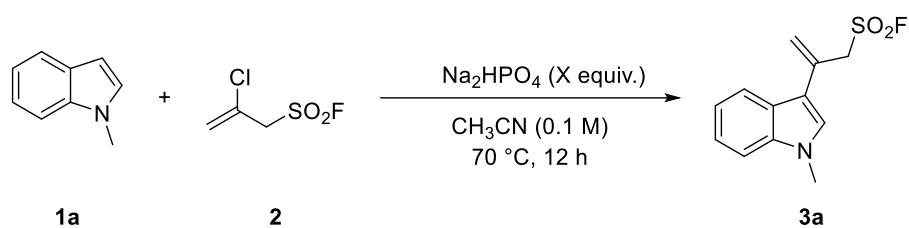
Entry	Base	Yield ( <b>3a</b> , %) <sup>b</sup>
1	DIPEA	n.d.
2	TEA	n.d.
3	DBU	n.d.
4	TMEDA	n.d.
5	DMAP	n.d.
6	NaF	11
7	KF	38
8	CsF	7
9	KOAc	n.d.
10	KHCO <sub>3</sub>	10
11	K <sub>2</sub> HPO <sub>4</sub>	49
12	K <sub>3</sub> PO <sub>4</sub>	3
13	NaOAc	5
14	HCOONa	3
15	NaHCO <sub>3</sub>	48
16	Na <sub>3</sub> PO <sub>4</sub>	51
<b>17</b>	<b>Na<sub>2</sub>HPO<sub>4</sub></b>	<b>53</b>

<sup>a</sup>Reaction conditions: a mixture of 1-methylindole (**1a**, 13 mg, 0.1 mmol, 1.0 equiv.), CESF (**2**, 32 mg, 0.2 mmol, 2.0 equiv.) and base (0.4 mmol, 4.0 equiv.) in CH<sub>3</sub>CN (1.0 mL) was stirred at 60 °C for 12 h under air. <sup>b</sup>The yield was determined by HPLC using pure **3a** as the external standard ( $t_R = 5.863$  min,  $\lambda_{max} = 226.4$  nm, CH<sub>3</sub>CN / H<sub>2</sub>O = 60:40 (v/v)). n.d. = Not detectable.

**Table S3** Screening of the Temperature<sup>a</sup>

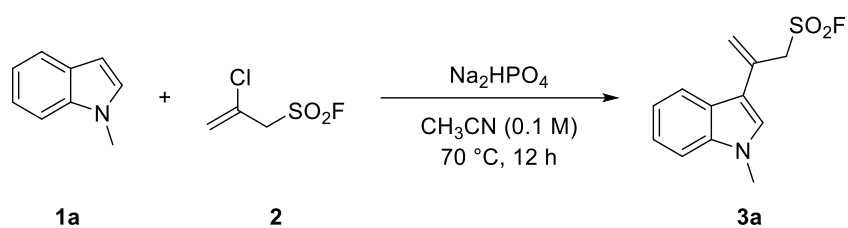
Entry	Temperature (°C)	Yield ( <b>3a</b> , %) <sup>b</sup>
1	30	3
2	40	24
3	50	41
4	60	53
<b>5</b>	<b>70</b>	<b>64</b>
6	80	64

<sup>a</sup>Reaction conditions: a mixture of 1-methylindole (**1a**, 13 mg, 0.1 mmol, 1.0 equiv.), CESF (**2**, 32 mg, 0.2 mmol, 2.0 equiv.) and  $\text{Na}_2\text{HPO}_4$  (56mg, 0.4 mmol, 4.0 equiv.) in  $\text{CH}_3\text{CN}$  (1.0 mL) was stirred at the corresponding temperature for 12 h under air. <sup>b</sup>The yield was determined by HPLC using pure **3a** as the external standard ( $t_{\text{R}} = 5.863$  min,  $\lambda_{\text{max}} = 226.4$  nm,  $\text{CH}_3\text{CN} / \text{H}_2\text{O} = 60:40$  (v/v)).

**Table S4** Screening the Loading of Na<sub>2</sub>HPO<sub>4</sub><sup>a</sup>

Entry	X equiv.	Yield ( <b>3a</b> , %) <sup>b</sup>
1	2.0	43
2	2.4	52
3	2.8	55
<b>4</b>	<b>3.2</b>	<b>63</b>
5	3.6	63
6	4.0	62

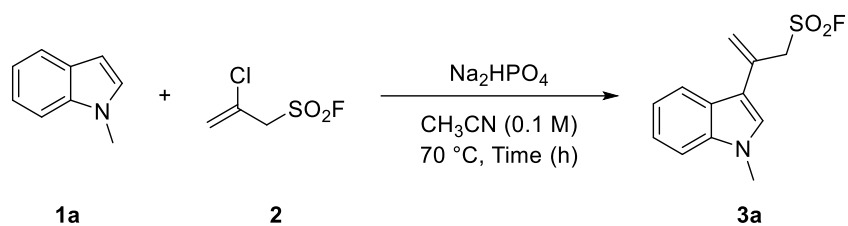
<sup>a</sup>Reaction conditions: a mixture of 1-methylindole (**1a**, 13 mg, 0.1 mmol, 1.0 equiv.), CESF (**2**, 32 mg, 0.2 mmol, 2.0 equiv.) and Na<sub>2</sub>HPO<sub>4</sub> (X equiv.) in CH<sub>3</sub>CN (1.0 mL) was stirred at 70 °C for 12 h under air. <sup>b</sup>The yield was determined by HPLC using pure **3a** as the external standard ( $t_R = 5.863$  min,  $\lambda_{max} = 226.4$  nm, CH<sub>3</sub>CN / H<sub>2</sub>O = 60:40 (v/v)).

**Table S5** Screening the Loading of CESF (**2**)<sup>a</sup>

Entry	CESF ( <b>2</b> , X equiv.)	Yield ( <b>3a</b> , %) <sup>b</sup>
1	1.0	33
2	1.5	46
<b>3</b>	<b>2.0</b>	<b>62</b>
4	2.5	61
5	3.0	61
6	3.5	62
7	4.0	61

<sup>a</sup>Reaction conditions: a mixture of 1-methylindole (**1a**, 13 mg, 0.1 mmol, 1.0 equiv.), CESF (**2**, X equiv.) and  $\text{Na}_2\text{HPO}_4$  (1.6 X equiv.) in  $\text{CH}_3\text{CN}$  (1.0 mL) was stirred at  $70\text{ }^\circ\text{C}$  for 12 h under air. <sup>b</sup>The yield was determined by HPLC using pure **3a** as the external standard ( $t_{\text{R}} = 5.863\text{ min}$ ,  $\lambda_{\text{max}} = 226.4\text{ nm}$ ,  $\text{CH}_3\text{CN} / \text{H}_2\text{O} = 60:40$  (v/v)).



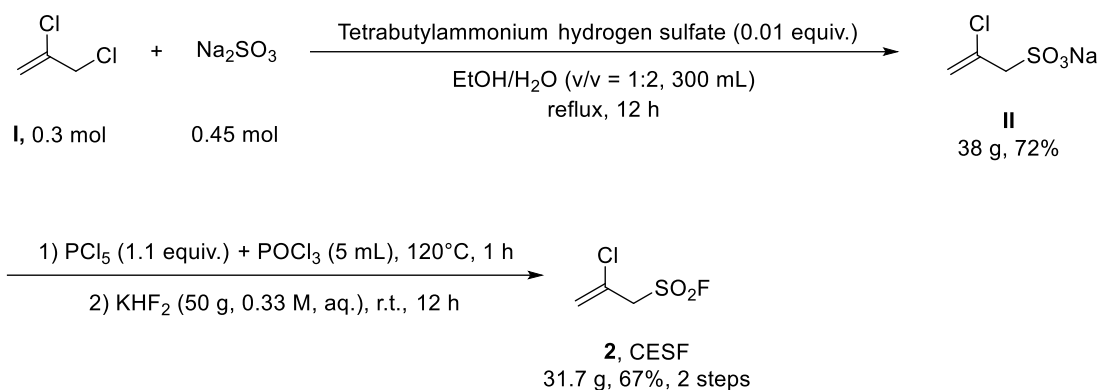
**Table S6** Screening the Time<sup>a</sup>

Entry	Time (h)	Yield ( <b>3a</b> , %) <sup>b</sup>
1	12	61
2	15	68
<b>3</b>	<b>18</b>	<b>71</b>
4	21	70
5	24	71

<sup>a</sup>Reaction conditions: a mixture of 1-methylindole (**1a**, 13 mg, 0.1 mmol, 1.0 equiv.), CESF (**2**, 32 mg, 0.2 mmol, 2.0 equiv.) and  $\text{Na}_2\text{HPO}_4$  (45 mg, 0.32 mmol, 3.2 equiv.) in  $\text{CH}_3\text{CN}$  (1.0 mL) was stirred at  $70\text{ }^\circ\text{C}$  for the corresponding time under air. <sup>b</sup>The yield was determined by HPLC using pure **3a** as the external standard ( $t_{\text{R}} = 5.863\text{ min}$ ,  $\lambda_{\text{max}} = 226.4\text{ nm}$ ,  $\text{CH}_3\text{CN} / \text{H}_2\text{O} = 60:40$  (v/v)).

### 3. Experimental Procedures

#### 3.1 Preparation of 2-chloroprop-2-ene-1-sulfonyl fluoride (CESF)<sup>1</sup>



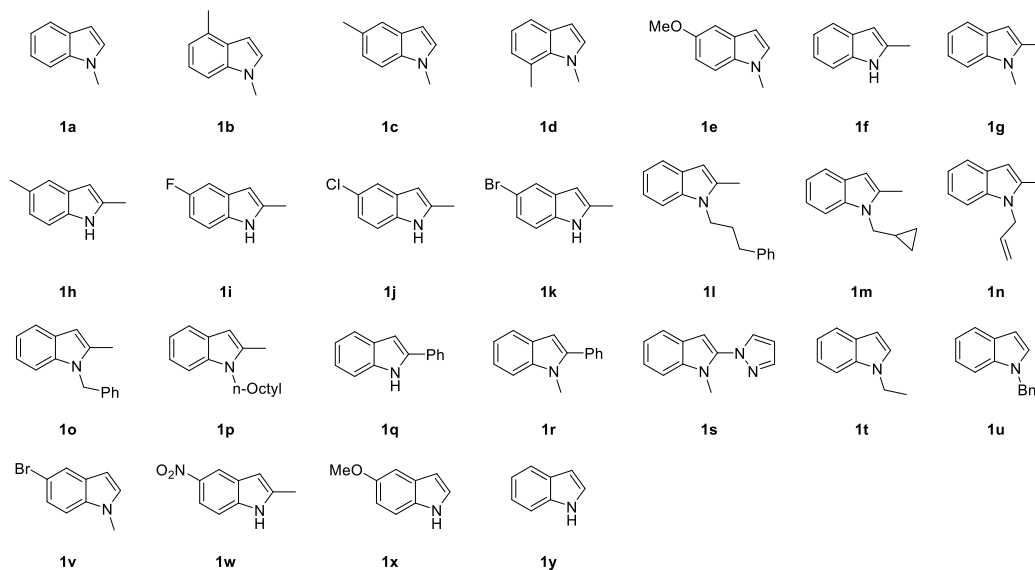
**Step 1:** 1,2-Dichloro-2-propene (33 g, 0.3 mol), Na<sub>2</sub>SO<sub>3</sub> (56 g, 0.45 mol, 1.5 equiv.) and tetrabutylammonium hydrogen sulfate (1.0 g, 0.003 mol, 0.01 equiv.) were added to a solution of EtOH and H<sub>2</sub>O (v/v = 1:2, 300 mL) with stirring and heating. The mixture was then refluxed for 12 h and the solvent evaporated in vacuo. To the residue was added EtOH (250 mL), and the mixture was refluxed with stirring for 1 h. After removing some insoluble material by filtration of the hot mixture, the filtrate was cooled. The crystalline sodium 2-chloro-2-propene-1-sulfonate was collected by filtration: 38.0 g (0.216 mol, 72%).

**Step 2:** A mixture of this sodium salt (38.0 g, 0.216 mol) and PCl<sub>5</sub> (49.5 g, 0.238 mol, 1.1 equiv.) was stirred vigorously until the mixture liquified. The solids remaining on the walls of the bottle were rinsed with phosphorus oxychloride (5 mL), then the mixture was rapidly heated to 120 °C for 1 hour, cooled, and poured onto ice with vigorous stirring. Kept the reaction mixture stirring at low temperature and extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic phase was washed with ice water, 5% NaHCO<sub>3</sub> solution (2×100 mL), then dried, and evaporated in vacuo. The evaporated 2-chloro-2-propene sulfonyl chloride was added dropwise to the solution of KHF<sub>2</sub> (50 g, 0.33 M) with stirring for 12 hours. The reaction mixture was further extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×25 mL), then dried, and evaporated in vacuo. 2-Chloroprop-2-ene-1-sulfonyl fluoride (CESF) was distilled under reduced pressure to give colorless oil 31.7 g (2, 67%, 2 steps). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.76 (d, J

= 2.5 Hz, 1H), 5.72 (d,  $J$  = 1.5 Hz, 1H), 4.32 (d,  $J$  = 3.5 Hz, 2H).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  56.4 (s, 1F). The NMR data is identical to that reported in literature.<sup>1</sup>

### 3.2 Preparation of indoles (1)

**1a**, **1f**, **1h-1k**, **1q-1r**, **1v**, and **1x-1y** are received from commercial suppliers. **1b-1e**,<sup>2</sup> **1g**,<sup>2</sup> **1l-1p**,<sup>2</sup> **1s**,<sup>3</sup> **1t**,<sup>2</sup> **1u**<sup>2</sup> and **1w**<sup>4</sup> are known compounds and were synthesized according to the literature.



### 3.3 General procedure for preparation of indole-functionalized allylic sulfonyl fluorides (3)

An oven-dried reaction tube (20 mL) equipped with a magnetic stirring bar was charged with indoles (**1**, 1.0 mmol, 1.0 equiv.), CESF (**2**, 316 mg, 2.0 mmol, 2.0 equiv.) and 5.0 mL  $\text{CH}_3\text{CN}$ . Then,  $\text{Na}_2\text{HPO}_4$  (454 mg, 3.2 mmol, 3.2 equiv.) was added to the above solution. The mixture was stirred at 70 °C for 18 h under an air atmosphere monitored by TLC. After the reaction was completed, the mixture was filtered, and the filter cake was washed with ethyl acetate. The solvent was concentrated under reduced pressure and the residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product **3**.

### 3.4 General procedure for preparation of indole-functionalized vinyl sulfonyl fluorides (4)

An oven-dried reaction tube (20 mL) equipped with a magnetic stirring bar was

charged with indoles (**1**, 1.0 mmol, 1.0 equiv.), CESF (**2**, 316 mg, 2.0 mmol, 2.0 equiv.) and 5.0 mL CH<sub>3</sub>CN. Then, Na<sub>2</sub>HPO<sub>4</sub> (454 mg, 3.2 mmol, 3.2 equiv.) was added to the above solution. The mixture was stirred at 70 °C for 18 h under an air atmosphere before MsOH (577 mg, 6.0 mmol, 6.0 equiv) was added, and then the mixture was reacted at room temperature for an additional 1 h. Once the reaction reached its completion, the mixture was filtered, and the filter cake was washed with ethyl acetate. The solution was washed with saturated sodium bicarbonate solution and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and the residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product **4**.

### 3.5 General procedure for preparation of **5**

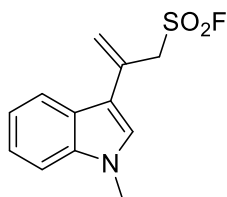
To a solution of compound **4a** (127 mg, 0.5 mmol) and TBS-protected estrone (202 mg, 0.53 mmol) dissolved in acetonitrile (4 mL) was added a catalytic amount (60 mol %, 46 mg) of DBU, and the resulting mixture was stirred at 50 °C for 6 h. The reaction mixture was diluted with water, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> before being concentrated to dryness under vacuum. The residue was purified through silica gel chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluents to obtain the desired product **5** (458 mg, 91% yield).

### 3.6 General procedure for preparation of **6**

An oven-dried reaction tube (20 mL) equipped with a magnetic stirring bar was charged with **4a** (253 mg, 1.0 mmol, 1.0 equiv.), Cu(OAc)<sub>2</sub> (363 mg, 2.0 mmol, 2.0 equiv.) and 3.0 mL Toluene. Then, Acrylonitrile (159 mg, 3.0 mmol, 3.0 equiv.) was added to the above solution. The mixture was stirred at 100 °C for 24 h under an air

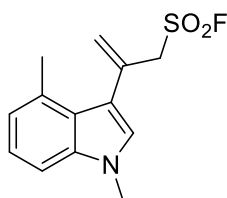
atmosphere monitored by TLC. After the reaction was completed, the mixture was filtered, and the filter cake was washed with ethyl acetate. The solvent was concentrated under reduced pressure and the residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (5:1, v/v) as eluents to give the desired product **6** (134 mg, 61% yield).

#### 4. Characterization



**3a**

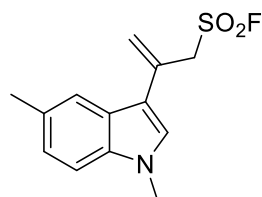
*2-(1-Methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3a)*. White solid, 165 mg, 65% yield. M.p. 69–70 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  7.87 (d,  $J$  = 8.0 Hz, 1H), 7.76 (s, 1H), 7.48(d,  $J$  = 8.0 Hz, 1H), 7.25 (t,  $J$  = 15 Hz, 1H), 7.16 (t,  $J$  = 14.5 Hz, 1H), 5.91 (s, 1H), 5.51 (s, 1H), 5.16 (d,  $J$  = 4.0 Hz, 2H), 3.79 (s, 3H)  $^{19}\text{F NMR}$  (471 MHz, DMSO- $d_6$ )  $\delta$  54.8 (s, 1F).  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  137.9, 130.5, 129.1, 125.6, 122.5, 120.7, 120.5, 117.8, 112.8, 110.8, 57.1 (d,  $J$  = 13.6 Hz), 33.2. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{12}\text{H}_{13}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 254.0646, found: 254.0648.



**3b**

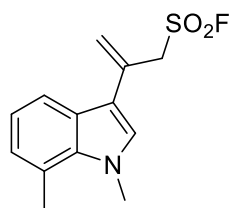
*2-(1,4-Dimethyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3b)*. White solid, 147 mg, 55% yield. M.p. 57-58 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent.  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  7.42 (s, 1H), 7.27 (d,  $J$  = 8.0 Hz, 1H), 7.09 (t,  $J$  = 8.0 Hz, 1H), 6.84 (d,  $J$  =

7.0 Hz, 1H), 5.82 – 5.74 (m, 1H), 5.42 (d,  $J = 1.5$  Hz, 1H), 5.10 (d,  $J = 4.0$  Hz, 2H), 3.75 (s, 3H), 2.49 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  55.7 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  137.23, 130.29, 130.28, 129.18, 125.17, 125.11, 122.05, 121.89, 114.32, 108.18, 59.61 (d,  $J = 11.8$  Hz), 32.99 (d,  $J = 1.8$  Hz), 20.36. HRMS-ESI (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 268.0802, found: 268.0804.



**3c**

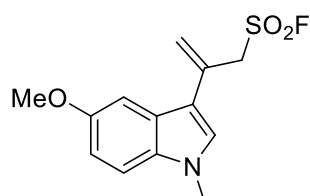
*2-(1,5-Dimethyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3c)*. White solid, 136 mg, 51% yield. M.p. 94–95 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.69 (s, 1H), 7.66 (s, 1H), 7.36 (d,  $J = 8.5$  Hz, 1H), 7.07 (d,  $J = 8.5$  Hz, 1H), 5.89 (s, 1H), 5.49 (s, 1H), 5.14 (d,  $J = 4.0$  Hz, 2H), 3.75 (s, 3H), 2.43 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  54.8 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  136.4, 130.5, 129.5, 129.2, 125.8, 124.0, 120.2, 117.5, 112.3, 110.5, 57.1 (d,  $J = 13.6$  Hz), 33.2, 21.7. HRMS-ESI (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 268.0802, found: 268.0803.



**3d**

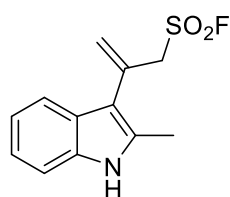
*2-(1,7-Dimethyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3d)*. White solid, 155 mg, 58% yield. M.p. 96–97 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.67 (d,  $J = 8.0$  Hz, 1H), 6.99 (t,  $J = 8.0$  Hz, 1H), 6.92 (d,  $J = 7.0$  Hz, 1H),

5.84 (s, 1H), 5.50 (s, 1H), 5.12 (d,  $J = 4.0$  Hz, 2H), 4.04 (s, 3H), 2.73 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  54.9 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  136.4, 132.0, 128.9, 126.7, 124.9, 122.2, 120.8, 118.4, 117.8, 112.3, 57.3 (d,  $J = 13.7$  Hz), 37.1, 19.6. HRMS-ESI (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 268.0803, found: 268.0804.



**3e**

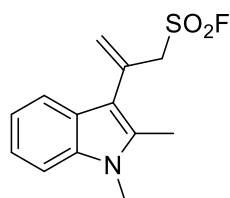
2-(5-Methoxy-1-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3e**). White solid, 142 mg, 50% yield. M.p. 78–79 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.71 (s, 1H), 7.39 (d,  $J = 9.0$  Hz, 1H), 7.29 (d,  $J = 2.5$  Hz, 1H), 6.89 (dd,  $J = 9.0, 2.5$  Hz, 1H), 5.87 (s, 1H), 5.49 (s, 1H), 5.14 (d,  $J = 4.0$  Hz, 2H), 3.81 (s, 3H), 3.75 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  54.8 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  155.0, 133.1, 131.0, 129.1, 126.0, 117.3, 112.4, 112.2, 111.6, 102.7, 57.1 (d,  $J = 13.6$  Hz) 56.0, 33.3. HRMS-ESI (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{FNO}_3\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 284.0752, found: 284.0752.



**3f**

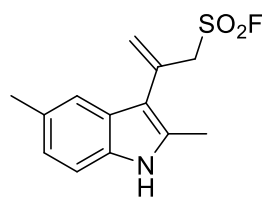
2-(2-Methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3f**). White solid, 228 mg, 90% yield. M.p. 104–105 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (s, 1H), 7.42 (d,  $J = 7.6$ , 1H), 7.29 (d,  $J = 8.0$ , 1H), 7.18 (t,  $J = 7.5$ , 1H),

7.14 (t,  $J = 7.5$  Hz, 1H), 5.82 (s, 1H), 5.55 (s, 1H), 4.53 (d,  $J = 3.0$  Hz, 2H), 2.44 (s, 2H).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  54.7 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 133.5, 128.9, 126.9, 125.1, 121.9, 120.4, 118.0, 57.5 (d,  $J = 15.5$  Hz), 12.2. HRMS-ESI (m/z) calcd. for  $[\text{C}_{12}\text{H}_{13}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 254.0646, found: 254.0647.



**3g**

2-(1,2-Dimethyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3g**). White solid, 233 mg, 87% yield. M.p. 129–130 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.51 (d,  $J = 8.0$  Hz, 1H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.16 – 7.09 (t,  $J = 15.0$  Hz, 1H), 7.06 – 6.96 (t,  $J = 15$  Hz, 1H), 5.85 (s, 1H), 5.44 (s, 1H), 5.08 (d,  $J = 4.0$  Hz, 2H), 3.68 (s, 3H), 3.33 (s, 1H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ )  $\delta$  136.6, 135.6, 130.0, 126.2, 125.1, 121.1, 119.8, 118.5, 110.9, 109.8, 57.8 (d,  $J = 11.8$  Hz), 29.9, 11.0. HRMS-ESI (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 268.0803, found: 268.0805.

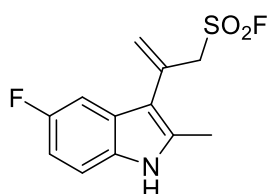


**3h**

2-(2,5-Dimethyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3h**). White solid, 233 mg, 87% yield. M.p. 110–111 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.99 (s, 1H), 7.28 (s, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 6.86 (dd,  $J = 8.0, 1.5$  Hz, 1H), 5.77 (s, 1H), 5.43 (s, 1H), 5.06 (d,  $J = 3.5$  Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H).

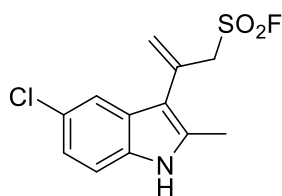


$^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  55.5 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  134.2, 133.8, 130.1, 128.1, 127.4, 124.1, 122.5, 118.2, 110.9, 110.3, 57.6 (d,  $J$  = 11.8 Hz), 21.8, 12.6. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{ClFNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 268.0803, found: 268.0805.



**3i**

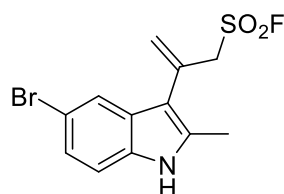
*2-(5-Fluoro-2-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3i)*. White solid, 195 mg, 72% yield. M.p. 90–91 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.25 (s, 1H), 7.28 (m, 2H), 6.87 (m, 1H), 5.80 (s, 1H), 5.45 (s, 1H), 5.09 (d,  $J$  = 4.0 Hz, 2H), 2.39 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  55.6 (s, 1F), -124.6 (dt,  $J$  = 11.6, 4.6 Hz, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  157.6 (d,  $J$  = 232.1 Hz), 136.4, 132.0, 129.6, 127.4 (d,  $J$  = 10.0 Hz), 124.6, 112.0 (d,  $J$  = 10.0 Hz), 111.0 (d,  $J$  = 4.5 Hz), 108.9, 103.5 (d,  $J$  = 23.7 Hz), 57.5 (d,  $J$  = 12.7 Hz), 12.5 (d,  $J$  = 1.9 Hz). **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{12}\text{H}_{12}\text{F}_2\text{NO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 272.0552, found: 272.0552.



**3j**

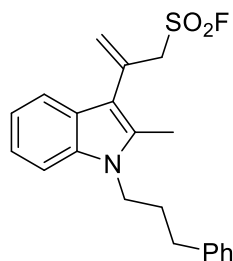
*2-(5-Chloro-2-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3j)*. Slight yellow solid, 236 mg, 82% yield. M.p. 92–93 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500

MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.35 (s, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.82 (s, 1H), 5.46 (s, 1H), 5.10 (d, *J* = 3.5 Hz, 2H), 2.39 (s, 3H). <sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.5 (s, 1F). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  136.2, 133.9, 129.5, 128.3, 125.2, 124.4, 121.0, 117.8, 112.7, 110.6, 57.6 (d, *J* = 12.9 Hz), 12.5. **HRMS-ESI** (*m/z*) calcd. for [C<sub>12</sub>H<sub>12</sub>ClFNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 288.0256, found: 288.0257.



**3k**

*2-(5-Bromo-2-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3k)*. White solid, 262 mg, 79% yield. M.p. 93–94 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.35 (s, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.82 (s, 1H), 5.46 (s, 1H), 5.09 (d, *J* = 4.0 Hz, 2H), 2.39 (s, 3H). <sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.6 (s, 1F). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  135.9, 134.1, 129.4, 128.9, 125.1, 123.5, 120.6, 113.1, 112.3, 110.5, 57.6 (d, *J* = 12.7 Hz), 12.4. **HRMS-ESI** (*m/z*) calcd. for [C<sub>12</sub>H<sub>12</sub>BrFNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 331.9751, found: 331.9752.

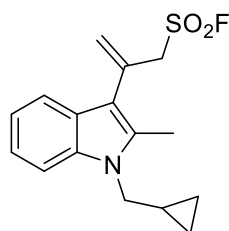


**3l**

*2-(2-Methyl-1-(3-phenylpropyl)-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3l)*. White solid, 308 mg, 83% yield. M.p. 92–93 °C. Purification by column

chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 5.86 (s, 1H), 5.45 (s, 1H), 5.07 (d, *J* = 4.0 Hz, 2H), 4.17 (t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 1.96 (m, 2H).

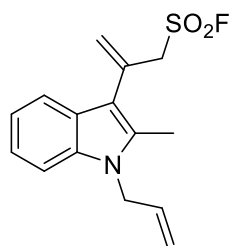
**<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>) δ 55.6 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>) δ 141.7, 135.9, 135.0, 130.0, 128.7, 128.6, 126.4, 126.3, 125.3, 121.2, 119.8, 118.6, 111.2, 109.9, 57.8 (d, *J* = 11.8 Hz), 42.7, 32.6, 31.6, 10.9. **HRMS-ESI** (m/z) calcd. for [C<sub>21</sub>H<sub>23</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 372.1429, found: 372.1429.



**3m**

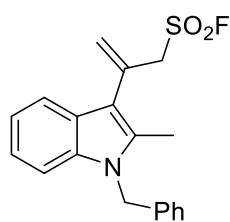
*2-(1-(Cyclopropylmethyl)-2-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3m).*

White solid, 283 mg, 92% yield. M.p. 64–65 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 5.86 (s, 1H), 5.46 (s, 1H), 5.08 (d, *J* = 4.0 Hz, 2H), 4.09 (d, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 1.15 (h, *J* = 6.5 Hz, 1H), 0.46 (d, *J* = 7.5 Hz, 2H), 0.36 (d, *J* = 5.0 Hz, 2H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>) δ 55.5 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>) δ 136.3, 134.9, 130.0, 126.3, 125.3, 121.1, 119.7, 118.5, 111.2, 110.2, 57.7 (d, *J* = 11.8 Hz), 46.7, 11.8, 11.2, 3.9. **HRMS-ESI** (m/z) calcd. for [C<sub>16</sub>H<sub>19</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 308.1116, found: 308.1118.



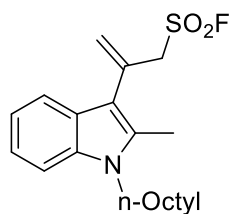
**3n**

*2-(1-Allyl-2-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3n)*. White solid, 223 mg, 76% yield. M.p. 78–79 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.53 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 5.97 (m, 1H), 5.87 (s, 1H), 5.46 (s, 1H), 5.10 (d, *J* = 4.0 Hz, 2H), 5.06 (m, 1H), 4.81 (m, 2H), 4.65 (m, 1H), 2.36 (s, 3H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>) δ 55.6 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>) δ 136.0, 135.3, 134.4, 130.0, 126.4, 125.4, 121.3, 120.0, 118.6, 115.8, 111.3, 110.0, 57.8 (d, *J* = 11.8 Hz), 45.2, 10.7. **HRMS-ESI** (m/z) calcd. for [C<sub>15</sub>H<sub>17</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 294.0959, found: 294.0959.



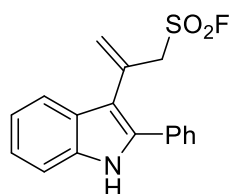
**3o**

*2-(1-Benzyl-2-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3o)*. White solid, 216 mg, 63% yield. M.p. 102–103 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.15 – 7.02 (m, 2H), 6.98 (d, *J* = 7.0 Hz, 2H), 5.89 (s, 1H), 5.49 (s, 1H), 5.45 (s, 2H), 5.11 (d, *J* = 4.0 Hz, 2H), 2.36 (s, 3H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>) δ 55.6 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>) δ 138.4, 136.4, 135.3, 129.9, 129.0, 127.4, 126.5, 126.4, 125.6, 121.4, 120.1, 118.7, 111.6, 110.2, 57.8 (d, *J* = 12.9 Hz), 46.3, 11.0. **HRMS-ESI** (m/z) calcd. for [C<sub>19</sub>H<sub>19</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 344.1116, found: 344.1117.



**3p**

*2-(2-Methyl-1-octyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3p)*. Yellow oil, 285 mg, 78% yield. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 40:1 (v/v) as eluent.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.50 (d,  $J = 8.0$  Hz, 1H), 7.40 (d,  $J = 8.0$  Hz, 1H), 7.10 (t,  $J = 14.5$  Hz, 1H), 7.01 (t,  $J = 14.0$  Hz, 1H), 5.85 (s, 1H), 5.44 (s, 1H), 5.06 (d,  $J = 4.0$  Hz, 2H), 2.40 (s, 3H), 1.63 (m, 2H), 1.44 – 1.08 (m, 10H), 0.83 (t,  $J = 7.0$  Hz, 3H).  $^{19}\text{F NMR}$  (471 MHz,  $\text{DMSO-}d_6$ )  $\delta$  55.5 (s, 1F).  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  135.9, 135.0, 130.1, 126.4, 125.2, 121.1, 119.7, 118.5, 111.1, 109.9, 57.8 (d,  $J = 12.7$  Hz), 43.1, 31.5, 30.0, 29.1, 29.0, 26.6, 22.4, 14.3, 10.9. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{20}\text{H}_{29}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 366.1898, found: 366.1899

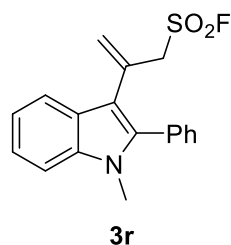


**3q**

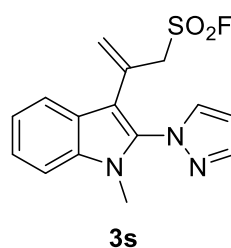
*2-(2-Phenyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3q)*. White solid, 255 mg, 81% yield. M.p. 130–131 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  11.63 (s, 1H), 7.66 (d,  $J = 7.0$  Hz, 2H), 7.61 (d,  $J = 8.0$  Hz, 1H), 7.52 (t,  $J = 7.7$  Hz, 2H), 7.46 – 7.37 (m, 2H), 7.17 (t,  $J = 6.9$  Hz, 1H), 7.09 (t,  $J = 8.0$  Hz, 1H), 5.90 (s, 1H), 5.68 (s, 1H), 4.77 (d,  $J = 4.0$  Hz, 2H).  $^{19}\text{F NMR}$  (471 MHz,  $\text{DMSO-}d_6$ )  $\delta$  55.5 (s, 1F).  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  136.4, 135.3, 132.6, 129.5, 129.4,

128.7, 128.4, 128.1, 126.0, 122.6, 120.3, 119.3, 112.0, 111.1, 57.3 (d,  $J = 12.7$  Hz).

**HRMS-ESI** (m/z) calcd. for  $[\text{C}_{17}\text{H}_{15}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 316.0803, found: 316.0803.

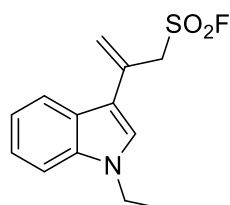


*2-(1-Methyl-2-phenyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3r)*. White solid, 267 mg, 81% yield. M.p. 135–136 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.69 (d,  $J = 8.0$  Hz, 1H), 7.63 – 7.52 (m, 4H), 7.50 – 7.39 (m, 2H), 7.26 (t,  $J = 15$  Hz, 1H), 7.16 (t,  $J = 14.5$  Hz, 1H), 5.74 (s, 1H), 5.55 (s, 1H), 4.53 (d,  $J = 4.0$  Hz, 2H), 3.59 (s, 3H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.3 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  138.3, 137.2, 131.4, 130.8, 129.4, 129.3, 128.9, 126.4, 125.4, 122.6, 120.7, 119.4, 111.9, 110.8, 56.9 (d,  $J = 12.7$  Hz), 31.1. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{18}\text{H}_{17}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 330.0959, found: 330.0959.



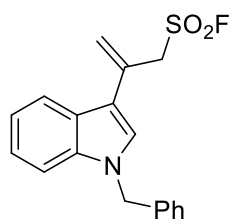
*2-(1-Methyl-2-(1H-pyrazol-1-yl)-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3s)*. White solid, 102 mg, 32% yield. M.p. 131–132 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.04 (d,  $J = 2.5$  Hz, 1H), 7.96 (d,  $J = 2.0$  Hz, 1H), 7.79 (d,  $J = 8.0$  Hz, 1H), 7.59 (d,  $J = 8.5$  Hz, 1H), 7.36 (t,  $J = 15.5$  Hz, 1H), 7.23 (t,  $J = 14.5$  Hz, 1H), 6.67 (t,  $J = 2.0$  Hz, 1H), 5.74 (s, 1H), 5.59 (s, 1H), 4.47 (d,  $J = 4.5$  Hz,

2H), 3.49 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  54.6 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  142.8, 134.7, 134.6, 132.5, 127.0, 125.5, 124.3, 123.8, 121.4, 120.3, 111.1, 108.6, 108.2, 56.1 (d,  $J = 13.6$  Hz), 29.6. HRMS-ESI (m/z) calcd. for  $[\text{C}_{15}\text{H}_{15}\text{FN}_3\text{O}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 320.0864, found: 320.0865.



**3t**

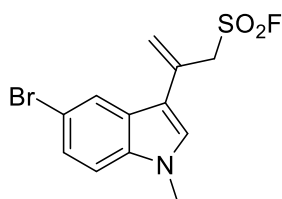
*2-(1-Ethyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3t)*. White solid, 166 mg, 62% yield. M.p. 82–83 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.87 (d,  $J = 8.0$  Hz, 1H), 7.83 (s, 1H), 7.53 (d,  $J = 8.0$  Hz, 1H), 7.23 (t,  $J = 7.5$  Hz, 1H), 7.14 (t,  $J = 7.5$  Hz, 1H), 5.90 (s, 1H), 5.51 (s, 1H), 5.17 (d,  $J = 4.0$  Hz, 2H), 4.20 (q,  $J = 7.0$  Hz, 2H), 1.38 (t,  $J = 7.0$  Hz, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  54.9 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  136.9, 129.1, 128.9, 125.7, 122.3, 120.6, 120.5, 117.6, 112.9, 110.7, 57.1 (d,  $J = 13.7$  Hz), 40.9, 15.6. HRMS-ESI (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 268.0803, found: 268.0805.



**3u**

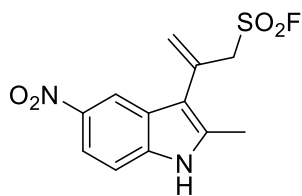
*2-(1-Benzyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (3u)*. Slight yellow solid, 142 mg, 43% yield. M.p. 112–113 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.99 (s, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.51 (d,  $J = 8.0$  Hz, 1H), 7.36

– 7.07 (m, 7H), 5.94 (s, 1H), 5.55 (s, 1H), 5.42 (s, 2H), 5.20 (d,  $J = 4.0$  Hz, 2H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  55.0 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  138.1, 137.2, 130.2, 129.1, 129.0, 127.9, 127.4, 125.9, 122.6, 120.9, 120.6, 118.2, 113.3, 111.2, 57.2 (d,  $J = 13.6$  Hz), 49.8. HRMS-ESI (m/z) calcd. for  $[\text{C}_{18}\text{H}_{17}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 330.0959, found: 330.0959.



**3v**

2-(5-Bromo-1-methyl-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3v**). Slight yellow solid, 184 mg, 57% yield. M.p. 107–108 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.97 (d,  $J = 2.0$  Hz, 1H), 7.80 (s, 1H), 7.48 (d,  $J = 8.5$  Hz, 1H), 7.36 (dd,  $J = 8.5, 2.0$  Hz, 1H), 5.86 (s, 1H), 5.54 (s, 1H), 5.16 (d,  $J = 4.0$  Hz, 2H), 3.79 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  54.8 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  136.6, 131.8, 128.5, 127.2, 125.0, 122.5, 118.9, 113.6, 113.0, 112.5, 57.0 (d,  $J = 13.6$  Hz), 33.4. HRMS-ESI (m/z) calcd. for  $[\text{C}_{12}\text{H}_{12}\text{BrFNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 331.9751, found: 331.9754.

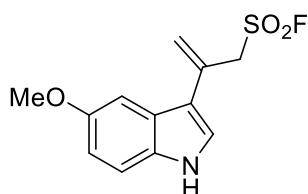


**3w**

2-(2-Methyl-5-nitro-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3w**). Yellow solid, 152 mg, 51% yield. M.p. 188–189 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.91 (s, 1H), 8.41 (s, 1H), 7.96 (d,  $J = 9.0$  Hz, 1H), 7.46 (d,  $J = 9.0$

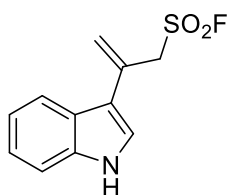


Hz, 1H), 5.93 (s, 1H), 5.57 (s, 1H), 5.17 (d,  $J = 4.0$  Hz, 2H), 2.43 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  55.3 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  141.4, 138.7, 138.2, 128.8, 126.6, 126.5, 116.7, 115.3, 113.1, 111.5, 57.6 (d,  $J = 11.8$  Hz), 12.5. HRMS-ESI (m/z) calcd. for  $[\text{C}_{12}\text{H}_{12}\text{FN}_2\text{O}_4\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 299.0497, found: 299.0498.



**3x**

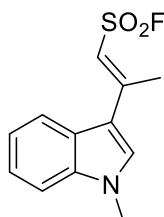
2-(5-Methoxy-1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3x**). Red solid, 175 mg, 65% yield. M.p. 102–103 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.28 (s, 1H), 7.73 (d,  $J = 3.0$  Hz, 1H), 7.34 (d,  $J = 9.0$  Hz, 1H), 7.28 (d,  $J = 2.5$  Hz, 1H), 6.83 (dd,  $J = 9.0, 2.5$  Hz, 1H), 5.87 (s, 1H), 5.49 (s, 1H), 5.17 (d,  $J = 4.0$  Hz, 2H), 3.80 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  55.0 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  154.7, 132.5, 129.5, 127.1, 125.5, 117.1, 113.3, 113.1, 112.1, 102.5, 57.3 (d,  $J = 12.7$  Hz), 55.9. HRMS-ESI (m/z) calcd. for  $[\text{C}_{12}\text{H}_{13}\text{FNO}_3\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 270.0595, found: 270.0595.



**3y**

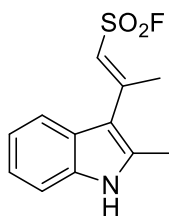
2-(1H-indol-3-yl)prop-2-ene-1-sulfonyl fluoride (**3y**). White solid, 146 mg, 61% yield. M.p. 126–127 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.42 (s, 1H), 7.85 (d,  $J = 8.0$  Hz, 1H), 7.78 (d,  $J = 3.0$  Hz, 1H), 6.57 (d,  $J = 8.0$  Hz, 1H), 7.19–7.16 (m, 1H), 7.13–7.10 (m, 1H), 5.05 (s, 1H), 4.64 (s, 1H), 4.33 (d,  $J = 4.0$

Hz, 2H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  54.9 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  137.1, 129.0, 126.2, 124.7, 121.9, 120.1, 119.9, 117.0, 113.1, 112.0, 56.7 (d, *J* = 12.7 Hz), 145.1, 140.7, 131.6, 125.7, 125.0, 121.9, 112.4, 110.8 (d, *J* = 29.2 Hz), 18.5. **HRMS-ESI** (*m/z*) calcd. for [C<sub>11</sub>H<sub>11</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 240.0490, found: 240.0490.



**4a**

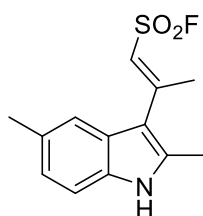
(*E*)-2-(1-methyl-1H-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4a**). White solid, 132 mg, 52% yield. M.p. 94–95 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.22 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.30 (m, 1H), 7.28 – 7.25 (m, 1H), 6.88 (s, 1H), 3.85 (s, 3H), 2.64 (s, 3H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  70.2 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  156.0, 138.5, 136.2, 124.7, 123.3, 122.5, 120.8, 113.0 (d, *J* = 1.9 Hz), 111.6, 108.6 (d, *J* = 22.8 Hz), 33.6 (d, *J* = 1.8 Hz), 18.4 (d, *J* = 1.8 Hz). **HRMS-ESI** (*m/z*) calcd. for [C<sub>12</sub>H<sub>13</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 254.0646, found: 254.0647.



**4b**

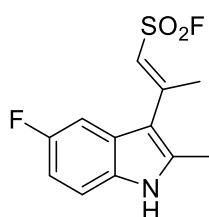
(*E*)-2-(2-methyl-1H-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4b**). White solid, 190 mg, 75% yield. M.p. 149–150 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.83 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.13 (m,

2H), 6.62 (s, 1H), 2.69 (s, 3H), 2.57 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  69.1 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  158.3, 139.4, 135.9, 126.4, 122.2, 121.2, 119.5, 112.4 (d,  $J = 21.8$  Hz), 112.0 (d,  $J = 1.9$  Hz), 111.9, 20.3, 14.4. HRMS-ESI (m/z) calcd. for  $[\text{C}_{12}\text{H}_{13}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 254.0646, found: 254.0646.



**4c**

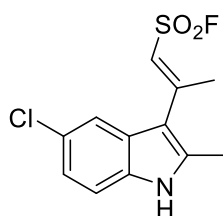
(*E*)-2-(2,5-dimethyl-1H-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4c**). Slight yellow solid, 192 mg, 72% yield. M.p. 136 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.71 (s, 1H), 7.48 (s, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H), 6.97 (dd,  $J = 8.0, 1.5$  Hz, 1H), 6.58 (s, 1H), 2.68 (s, 3H), 2.55 (s, 3H), 2.39 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  69.2 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  158.5, 139.5, 134.2, 130.0, 126.6, 123.7, 119.3, 112.0 (d,  $J = 21.9$  Hz), 111.6, 21.8, 20.3, 14.5. HRMS-ESI (m/z) calcd. for  $[\text{C}_{13}\text{H}_{15}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 268.0803, found: 268.0804.



**4d**

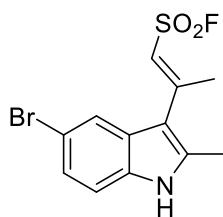
(*E*)-2-(5-fluoro-2-methyl-1H-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4d**). Slight yellow solid, 149 mg, 55% yield. M.p. 123–124 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.90 (s, 1H), 7.44 (dd,  $J = 10.5, 2.5$  Hz, 1H), 7.37 (dd,  $J = 9.0, 4.5$  Hz, 1H), 6.98 (td,  $J = 9.0, 2.5$  Hz, 1H), 6.63 (s, 1H), 2.66 (s, 3H), 2.55 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  68.9 (s, 1F), -122.2 – -122.5 (m, 1F).

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  158.3 (d,  $J = 233.0$ ), 141.0, 132.4, 126.8 (d,  $J = 10.0$  Hz), 113.0 (d,  $J = 21.8$  Hz), 112.9 (d,  $J = 10.1$  Hz), 112.2 (dd,  $J = 4.5, 2.8$  Hz), 110.1 (d,  $J = 26.5$  Hz), 104.9 (d,  $J = 25.5$  Hz), 20.2, 14.5. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{12}\text{H}_{12}\text{F}_2\text{NO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 272.0552, found: 272.0553.



**4e**

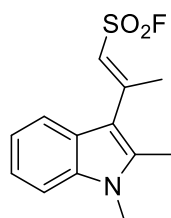
(*E*)-2-(5-chloro-2-methyl-1*H*-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4e**). Slight yellow solid, 190 mg, 66% yield. M.p. 152–153 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.97 (s, 1H), 7.68 (d,  $J = 2.0$  Hz, 1H), 7.38 (d,  $J = 8.5$  Hz, 1H), 7.14 (dd,  $J = 8.5, 2.0$  Hz, 1H), 6.67 (s, 1H), 2.66 (s, 3H), 2.55 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )  $\delta$  68.8 (s, 1F).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  157.5, 140.6, 134.3, 127.5, 125.8, 122.1, 118.8, 113.7 (d,  $J = 21.9$  Hz), 113.3, 111.8 (d,  $J = 1.8$  Hz), 20.3, 14.3. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{12}\text{H}_{12}\text{ClFNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 288.0256, found: 288.0256.



**4f**

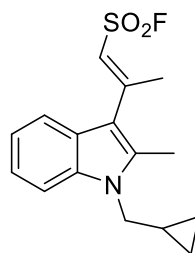
(*E*)-2-(5-bromo-2-methyl-1*H*-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4f**). White solid, 216 mg, 65% yield. M.p. 151–152 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.97 (s, 1H), 7.81 (d,  $J = 2.0$  Hz, 1H), 7.34 (d,  $J = 8.5$  Hz, 1H), 7.26 (d,  $J = 6.5$  Hz, 1H), 6.67 (s, 1H), 2.66 (s, 3H), 2.55 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz,

DMSO-*d*<sub>6</sub>)  $\delta$  68.7 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  157.4 (d, *J* = 1.9 Hz), 140.4, 134.6, 128.1, 124.8, 121.7, 113.9 (d, *J* = 23.7 Hz), 113.8, 111.8 (d, *J* = 1.9 Hz), 20.3, 14.2. **HRMS-ESI** (*m/z*) calcd. for [C<sub>12</sub>H<sub>12</sub>BrFNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 331.9751, found: 331.9752.



**4g**

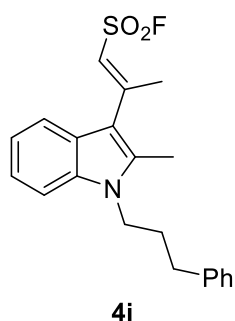
(*E*)-2-(1,2-dimethyl-1*H*-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4g**). White solid, 198 mg, 74% yield. M.p. 108–109 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.67 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.73 (s, 3H), 2.68 (s, 3H), 2.54 (s, 3H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  68.6 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  158.0, 139.4, 137.2, 125.5, 122.2, 121.3, 119.3, 114.2 (d, *J* = 21.9 Hz), 112.5 (d, *J* = 1.9 Hz), 110.6, 30.3, 20.7 (d, *J* = 1.9 Hz), 12.4. **HRMS-ESI** (*m/z*) calcd. for [C<sub>13</sub>H<sub>15</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 268.0803, found: 268.0803.



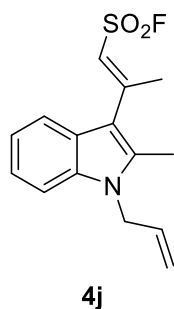
**4h**

(*E*)-2-(1-(cyclopropylmethyl)-2-methyl-1*H*-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4h**). White solid, 240 mg, 78% yield. M.p. 64–65 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.67 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz,

1H), 7.20 (t,  $J = 7.5$  Hz, 1H), 7.14 (t,  $J = 7.5$  Hz, 1H), 6.67 (s, 1H), 4.14 (d,  $J = 7.0$  Hz, 2H), 2.69 (s, 3H), 2.58 (s, 3H), 1.26 – 1.12 (m, 1H), 0.45 (dd,  $J = 30.5, 6.5$  Hz, 4H).  **$^{19}\text{F}$  NMR** (471 MHz, DMSO- $d_6$ )  $\delta$  68.5 (s, 1F).  **$^{13}\text{C}$  NMR** (126 MHz, DMSO- $d_6$ )  $\delta$  157.9, 138.6, 136.8, 125.6, 122.2, 121.3, 119.4, 114.6 (d,  $J = 21.9$  Hz), 112.8, 111.0, 47.0, 20.7, 12.5, 11.6, 4.0. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{16}\text{H}_{19}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 308.1116, found: 308.1117.

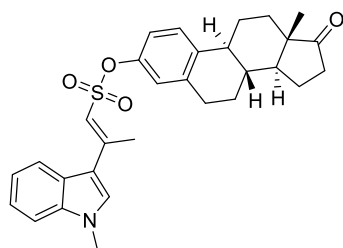


*(E)*-2-(2-methyl-1-(3-phenylpropyl)-1H-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4i**). White solid, 264 mg, 71% yield. M.p. 60–61 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent.  **$^1\text{H}$  NMR** (500 MHz, DMSO- $d_6$ )  $\delta$  7.66 (d,  $J = 7.9$  Hz, 1H), 7.44 (d,  $J = 8.1$  Hz, 1H), 7.27 (t,  $J = 7.5$  Hz, 2H), 7.23 – 7.09 (m, 5H), 6.64 (s, 1H), 4.20 (t,  $J = 7.6$  Hz, 2H), 2.67 (m, 5H), 2.50 (s, 3H), 1.97 (m, 2H).  **$^{19}\text{F}$  NMR** (471 MHz, DMSO- $d_6$ )  $\delta$  68.5 (s, 1F).  **$^{13}\text{C}$  NMR** (126 MHz, DMSO- $d_6$ )  $\delta$  157.9, 141.5, 138.7, 136.5, 128.7, 128.6, 126.3, 125.6, 122.3, 121.3, 119.5, 114.5 (d,  $J = 21.9$  Hz), 112.7 (d,  $J = 1.9$  Hz), 110.6, 42.9, 32.6, 31.2, 20.7 (d,  $J = 1.9$  Hz), 12.3. **HRMS-ESI** (m/z) calcd. for  $[\text{C}_{21}\text{H}_{23}\text{FNO}_2\text{S}]^+$  ( $[\text{M}+\text{H}]^+$ ): 372.1429, found: 372.1429.



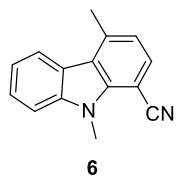
*(E)*-2-(1-allyl-2-methyl-1H-indol-3-yl)prop-1-ene-1-sulfonyl fluoride (**4j**). White solid,

191 mg, 65% yield. M.p. 74–75 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 4:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.68 (s, 1H), 5.97 (m, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 4.88 (d, *J* = 5.0 Hz, 2H), 4.83 (d, *J* = 17.0 Hz, 1H), 2.69 (s, 3H), 2.52 (s, 3H). **<sup>19</sup>F NMR** (471 MHz, DMSO-*d*<sub>6</sub>) δ 68.4 (s, 1F). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>) δ 157.8, 138.8, 136.6, 133.7, 125.6, 122.3, 121.4, 119.4, 116.7, 114.8 (d, *J* = 21.8 Hz), 112.9 (d, *J* = 1.8 Hz), 110.8, 45.5, 20.7 (d, *J* = 2.6 Hz), 12.1 (d, *J* = 2.6 Hz). **HRMS-ESI** (*m/z*) calcd. for [C<sub>15</sub>H<sub>17</sub>FNO<sub>2</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 294.0959, found: 294.0959.



5

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl (*E*)-2-(1-methyl-1*H*-indol-3-yl)prop-1-ene-1-sulfonate (**5**). White solid, 458 mg, 91% yield. M.p. 166–167 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.07 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.25 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.11 – 6.97 (m, 2H), 6.62 (s, 1H), 3.84 (s, 3H), 2.93 – 2.73 (m, 2H), 2.54 (s, 3H), 2.52 – 1.21 (m, 13H), 0.81 (s, 3H). **<sup>13</sup>C NMR** (126 MHz, DMSO-*d*<sub>6</sub>) δ 152.1, 147.7, 139.0, 138.8, 138.3, 134.5, 127.2, 124.7, 123.0, 122.4, 122.0, 120.3, 119.6, 113.5, 113.3, 111.4, 50.0, 47.6, 43.9, 37.7, 35.7, 33.4, 31.7, 29.2, 26.0, 25.6, 21.5, 18.2, 13.9. **HRMS-ESI** (*m/z*) calcd. for [C<sub>30</sub>H<sub>34</sub>NO<sub>4</sub>S]<sup>+</sup> ([M+H]<sup>+</sup>): 504.2204, found: 504.2206.



*4,9-dimethyl-9H-carbazole-1-carbonitrile (6)*. White solid, 134 mg, 61% yield. M.p. 139–140 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 4.04 (s, 3H), 2.77 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 141.4, 139.5, 139.3, 131.6, 126.8, 122.8, 122.5, 121.8, 121.2, 120.6, 119.1, 109.8, 90.0, 30.6, 21.1. HRMS-ESI (*m/z*) calcd. for [C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>]<sup>+</sup> ([M+H]<sup>+</sup>): 221.1074, found: 221.1074.



### 5. Procedure for Scale-up Reaction of **3**

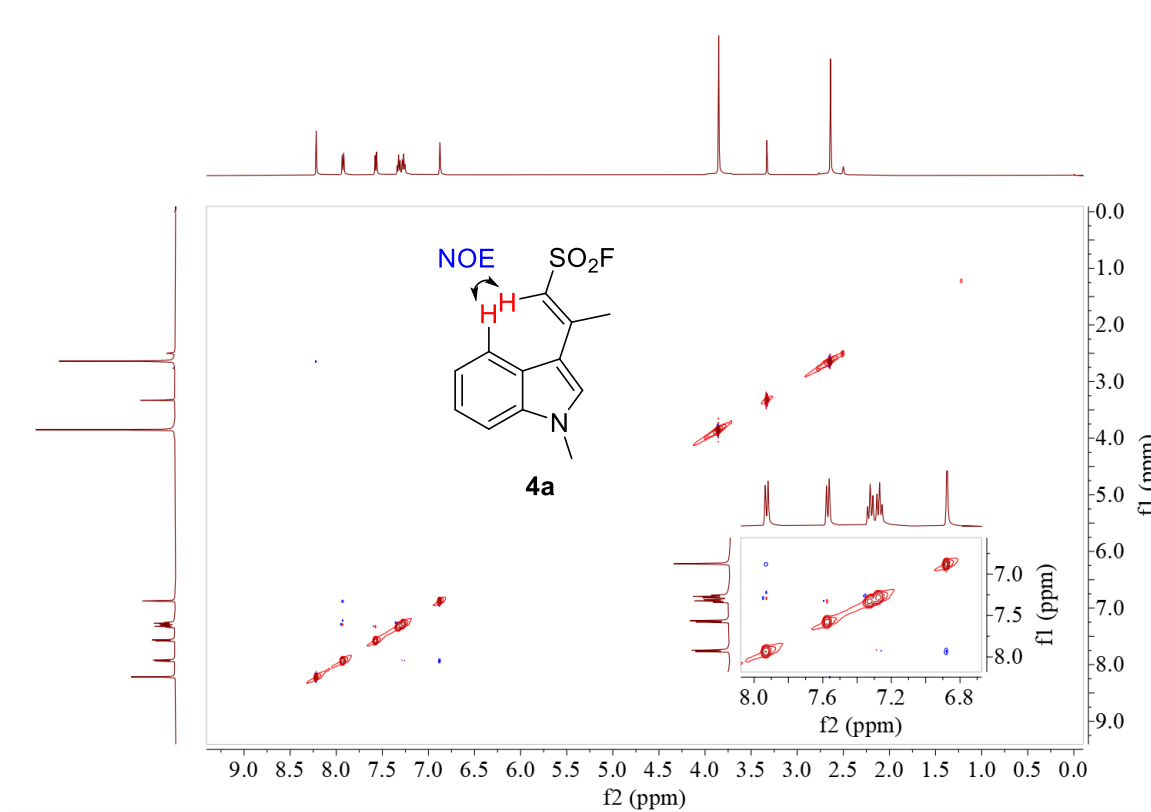
An oven-dried reaction tube (100 mL) equipped with a magnetic stirring bar was charged with indoles (**1**, 10.0 mmol, 1.0 equiv.), CESF (**2**, 3.17 g, 20.0 mmol, 2.0 equiv.) and 50.0 mL CH<sub>3</sub>CN. Then, Na<sub>2</sub>HPO<sub>4</sub> (4.54 g, 32 mmol, 3.2 equiv.) was added to the above solution. The mixture was stirred at 70 °C for 18 h under an air atmosphere monitored by TLC. After the reaction was completed, the mixture was filtered, and the filter cake was washed with ethyl acetate. The solvent was concentrated under reduced pressure and the residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product **3**.

## 6. Procedure for Scale-up Reaction of 4

An oven-dried reaction tube (100 mL) equipped with a magnetic stirring bar was charged with indoles (**1**, 10.0 mmol, 1.0 equiv.), CESF (**2**, 3.17 g, 20.0 mmol, 2.0 equiv.) and 50.0 mL CH<sub>3</sub>CN. Then, Na<sub>2</sub>HPO<sub>4</sub> (4.54 g, 32 mmol, 3.2 equiv.) was added to the above solution. The mixture was stirred at 70 °C for 18 h under an air atmosphere before MsOH (5.77 g, 60.0 mmol, 6.0 equiv.) was added, and then the mixture was reacted at room temperature for an additional 1 h. Once the reaction reached its completion, the mixture was filtered, and the filter cake was washed with ethyl acetate. The solution was washed with saturated sodium bicarbonate solution and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and the residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product **4**.

## 7. NOESY of 4a

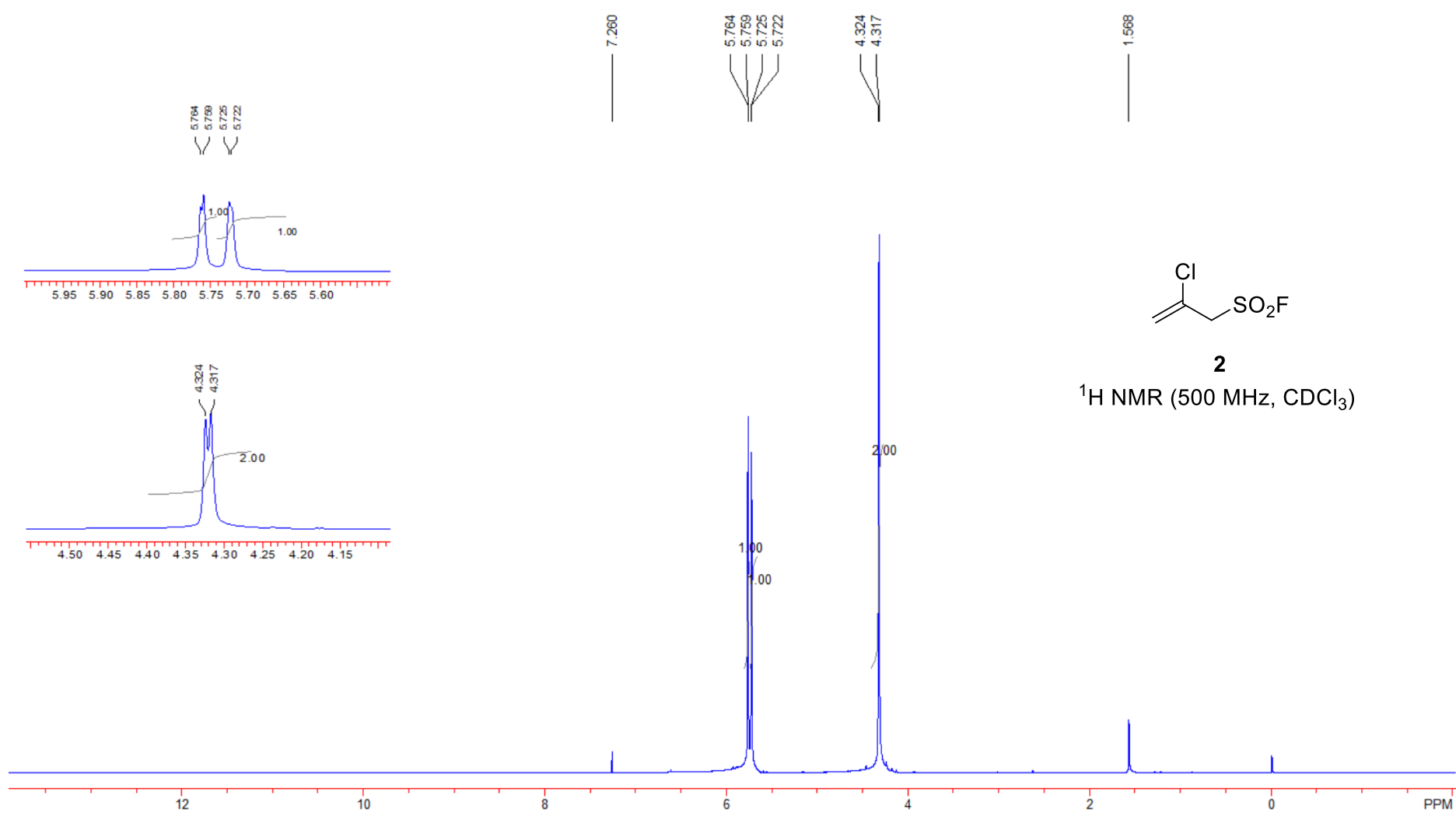
Figure S1 NOESY spectrum of compound 4a (in DMSO-*d*<sub>6</sub>)

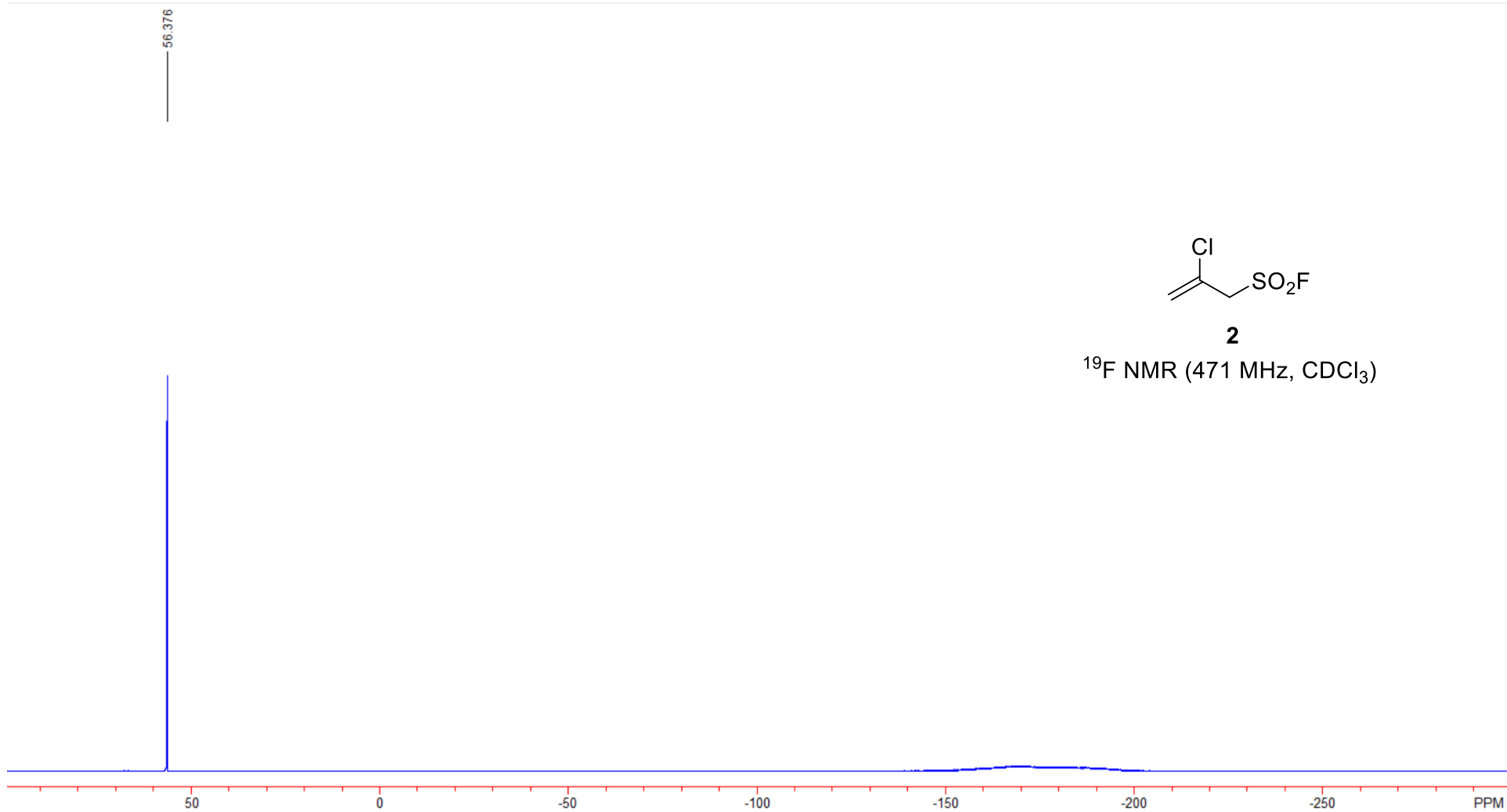


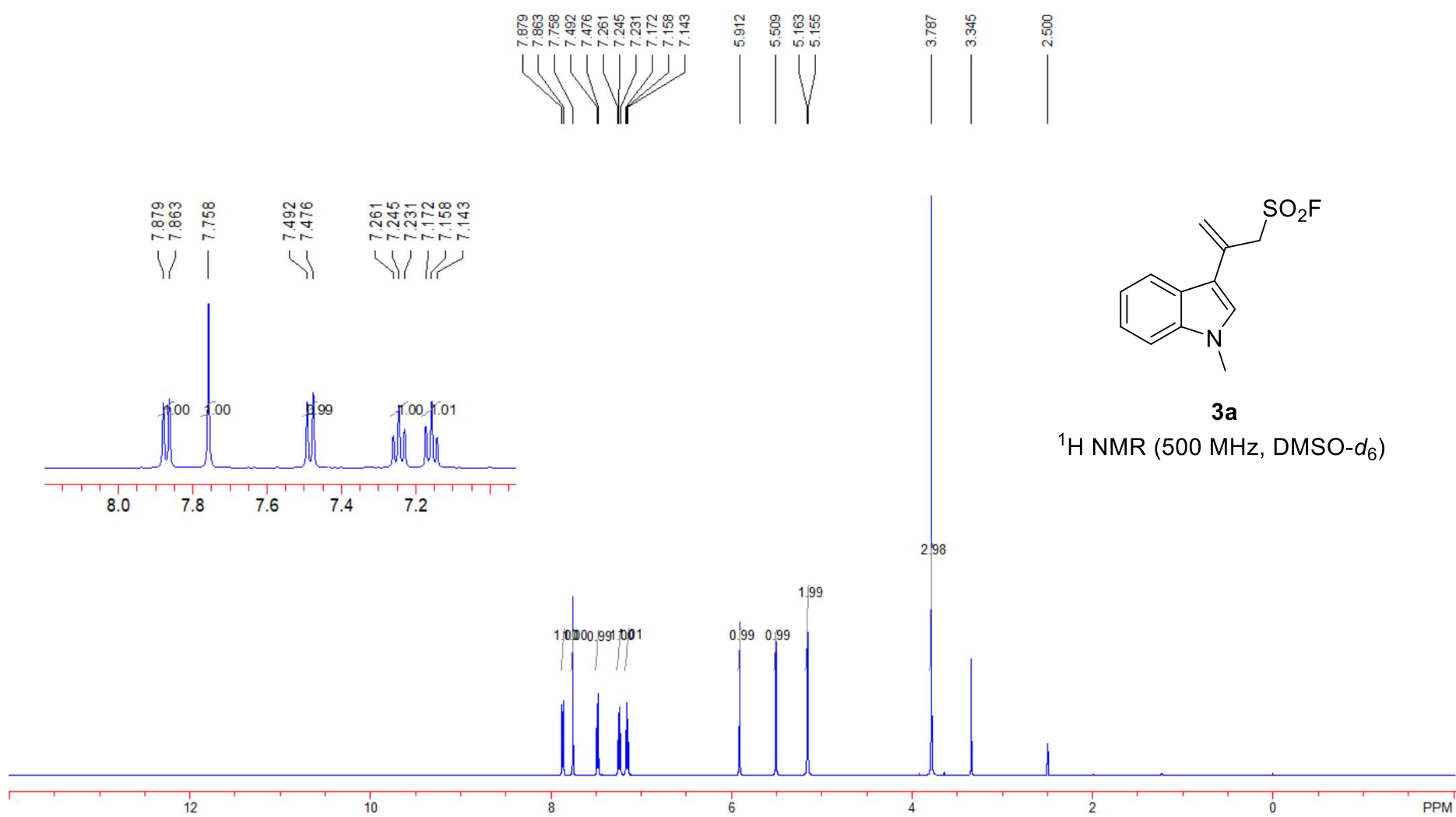
## 8. References

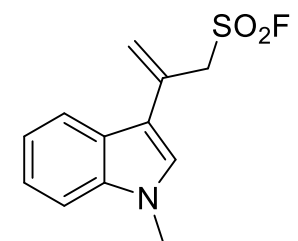
1. L.-Y. Chen, K. Rakesh and H.-L. Qin, *Org. Chem. Front.*, 2023, **10**, 951-956.
2. J. Zhang, S. Torabi Kohlbouni and B. Borhan, *Org.Lett.*, 2018, **21**, 14-17.
3. D. Beukeaw, K. Udomsasporn and S. Yotphan, *J. Org. Chem.*, 2015, **80**, 3447-3454.
4. M. W. Robinson, J. H. Overmeyer, A. M. Young, P. W. Erhardt and W. A. Maltese, *J. Med. Chem.*, 2012, **55**, 1940-1956.

## 9. NMR Spectra



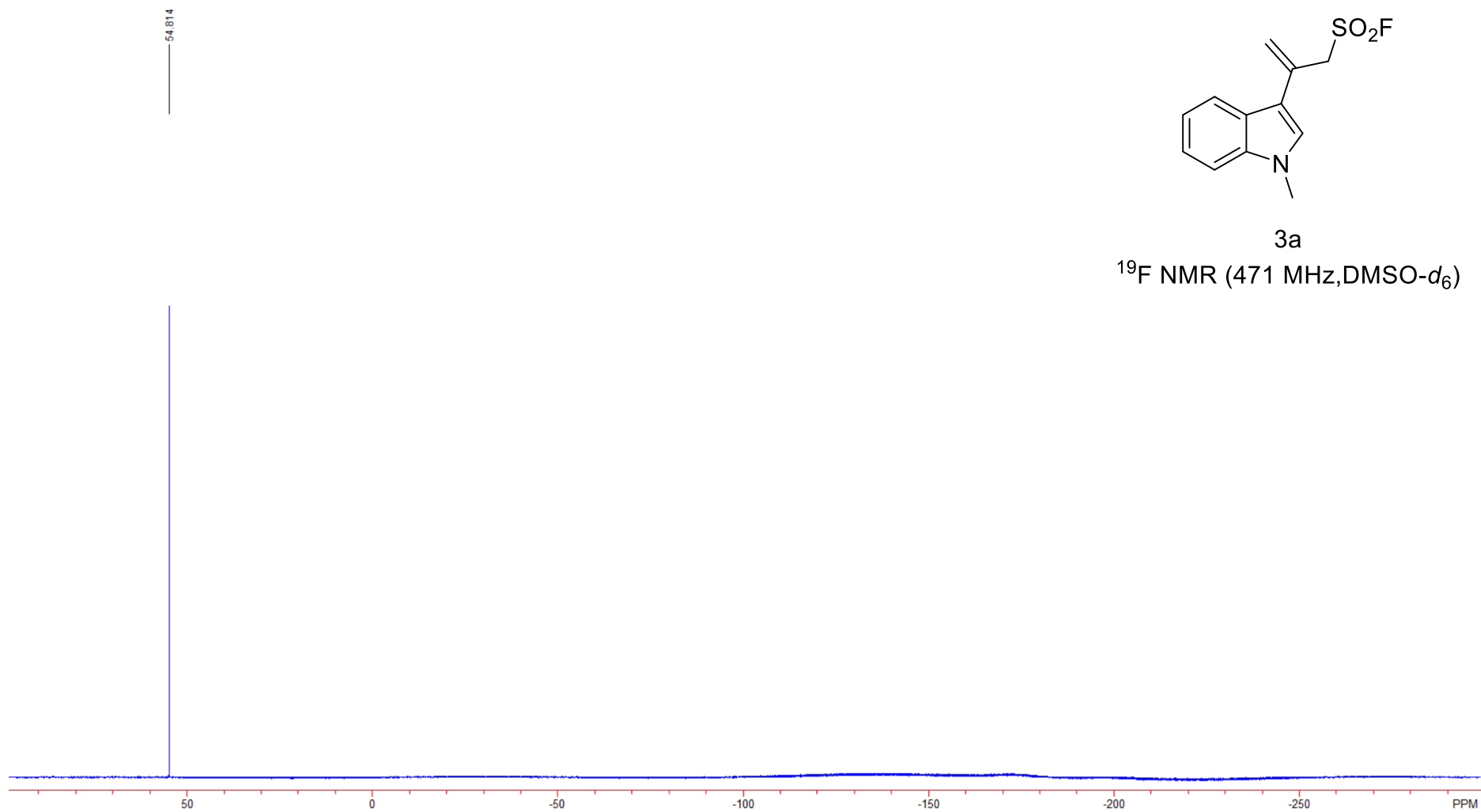




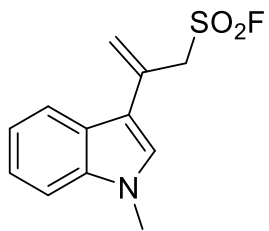


3a

$^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )







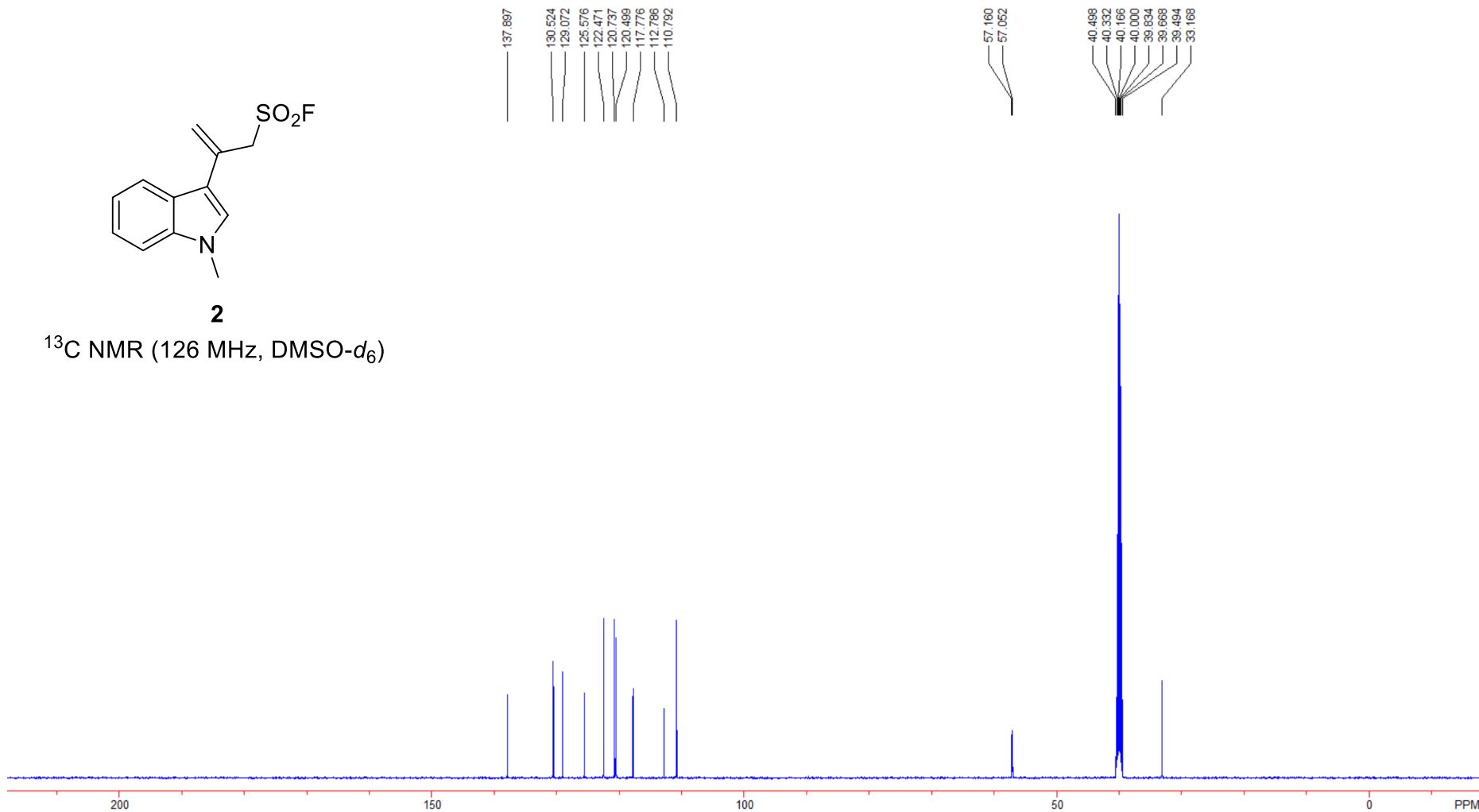
**2**

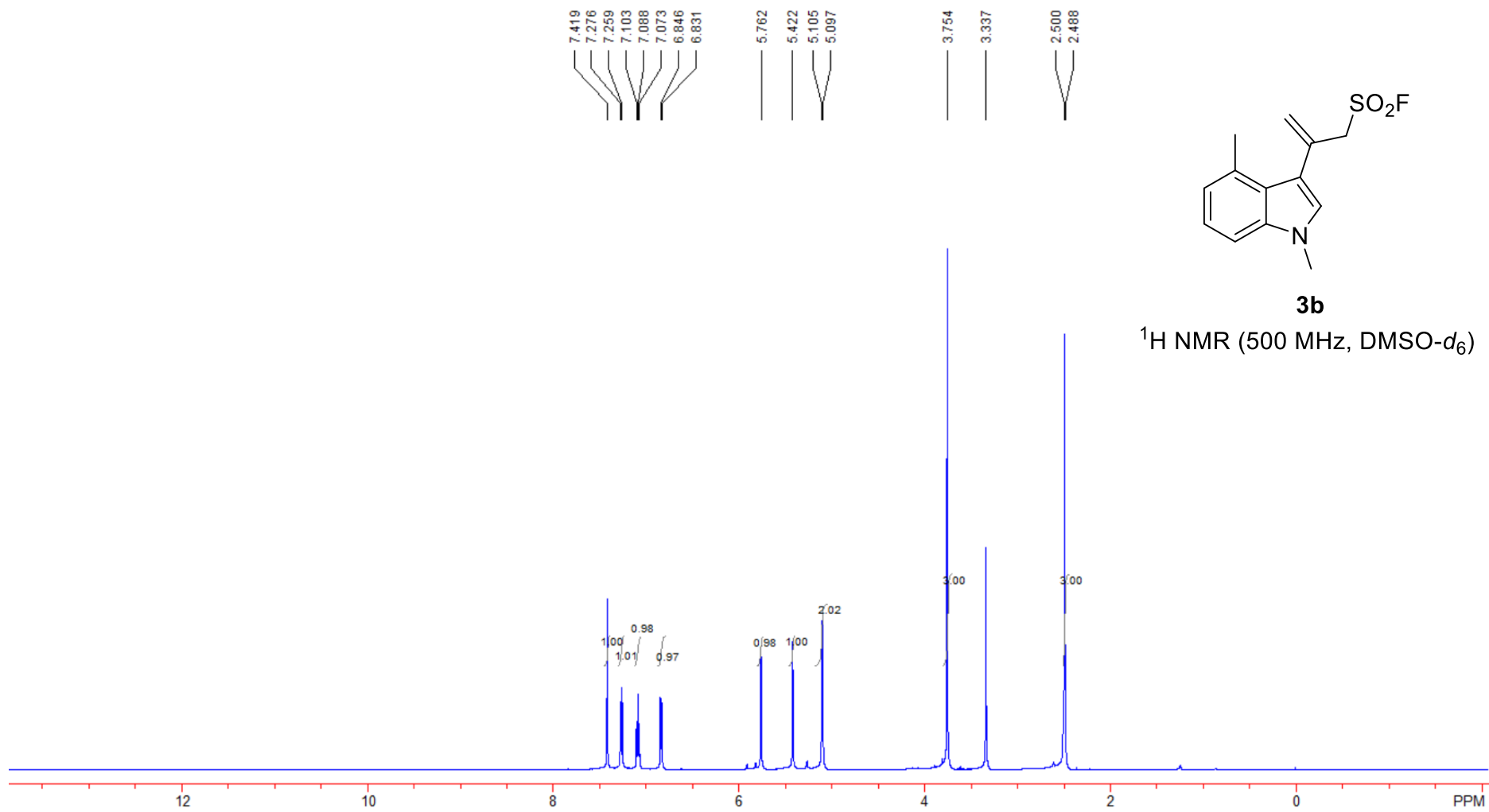
<sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>)

137.897  
130.524  
129.072  
125.576  
122.471  
120.737  
120.499  
117.776  
112.786  
110.792

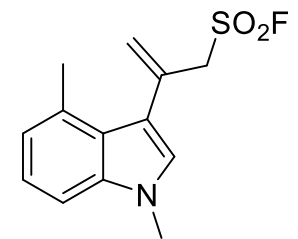
57.160  
57.062

40.486  
40.332  
40.166  
40.000  
39.834  
39.668  
39.494  
33.168



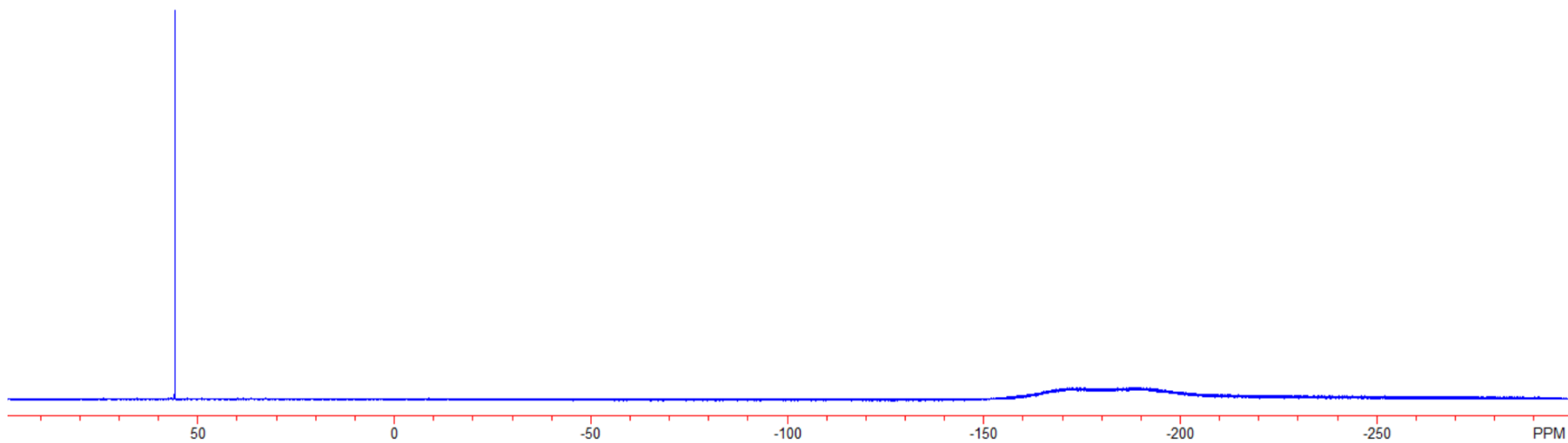


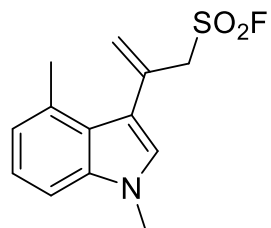
55.744



**3b**

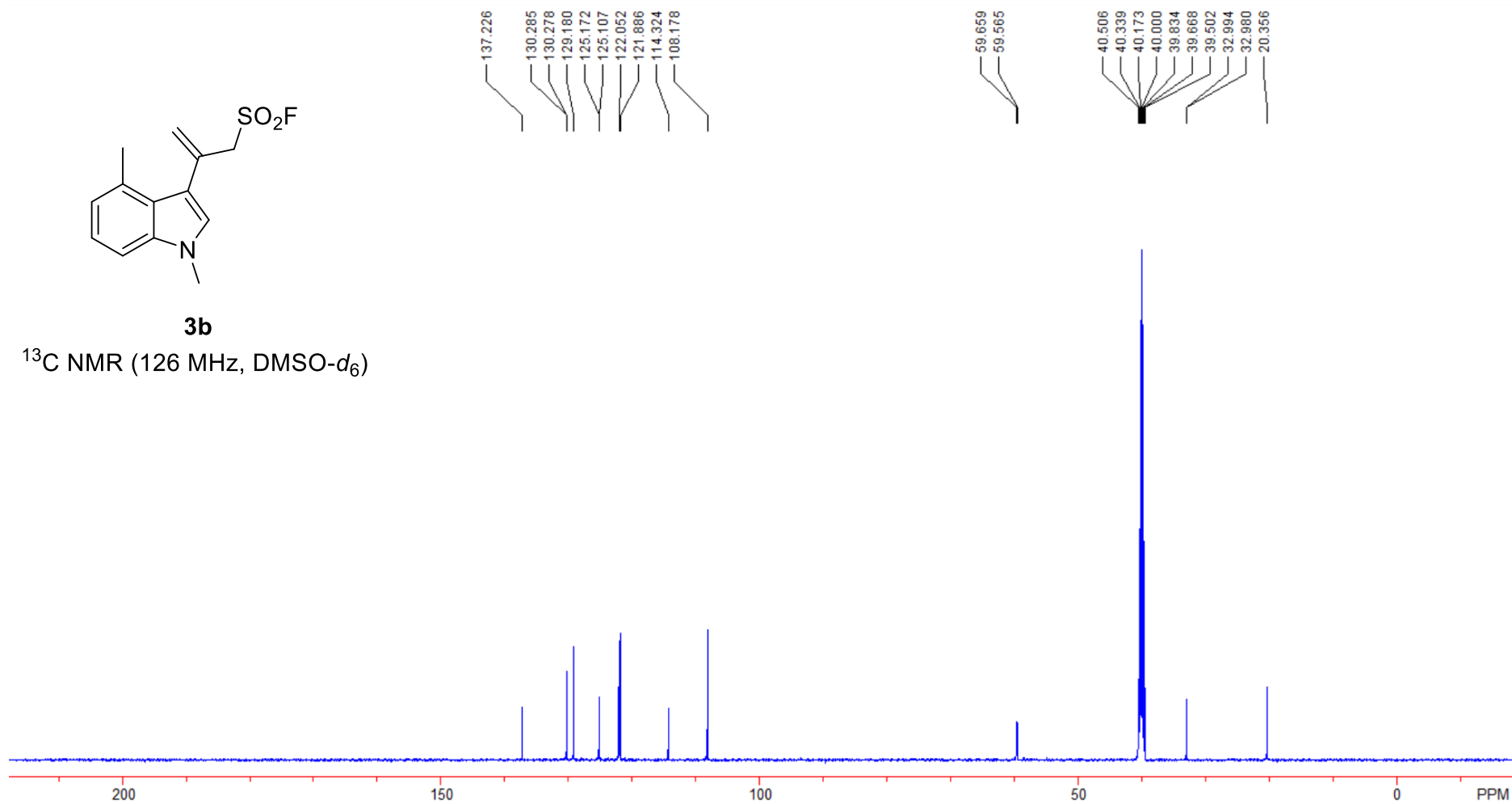
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

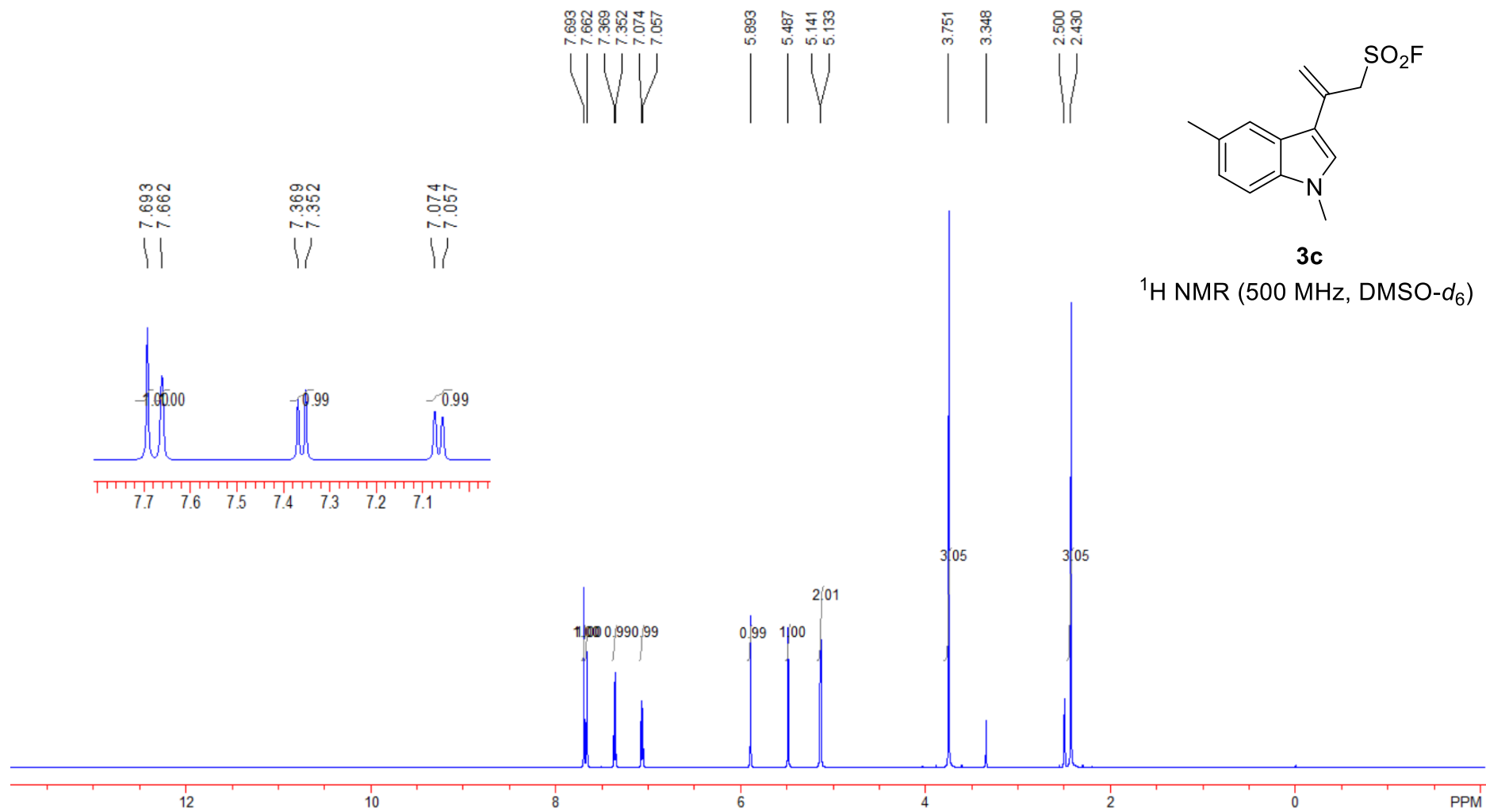




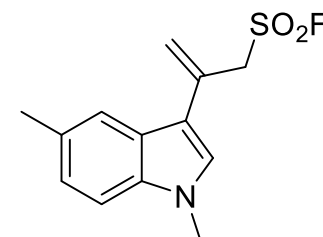
**3b**

$^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )



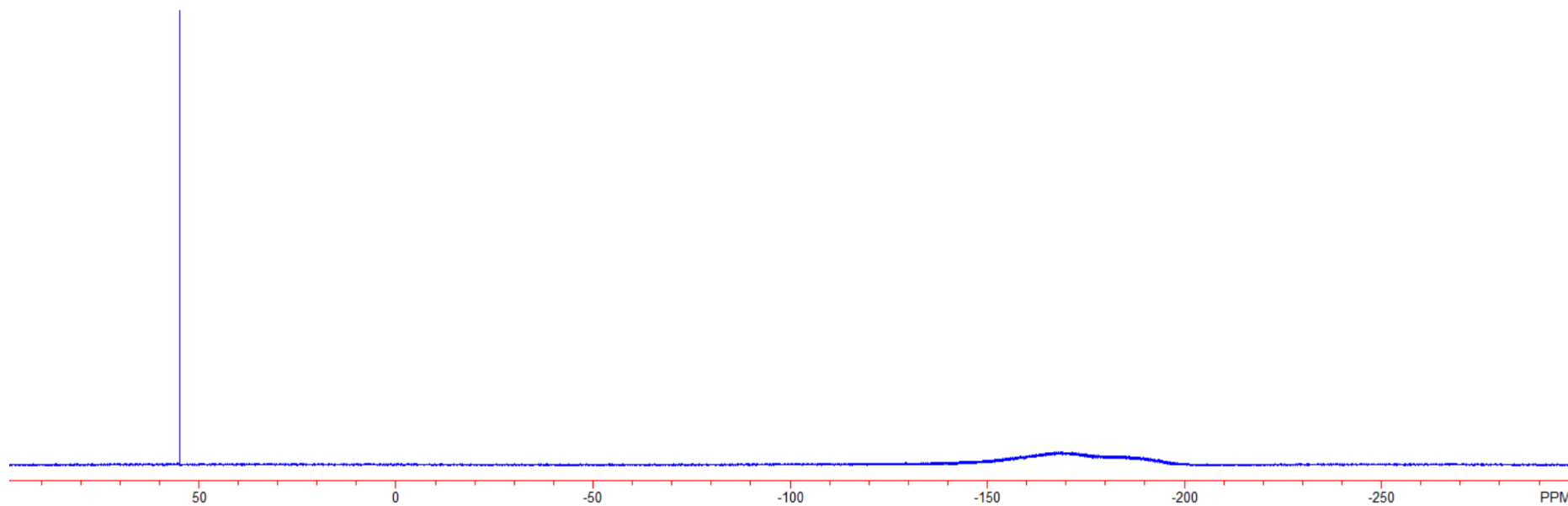


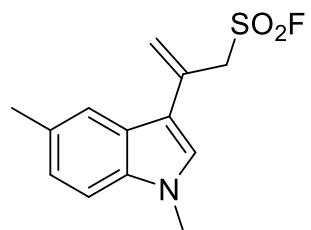
54.808



**3c**

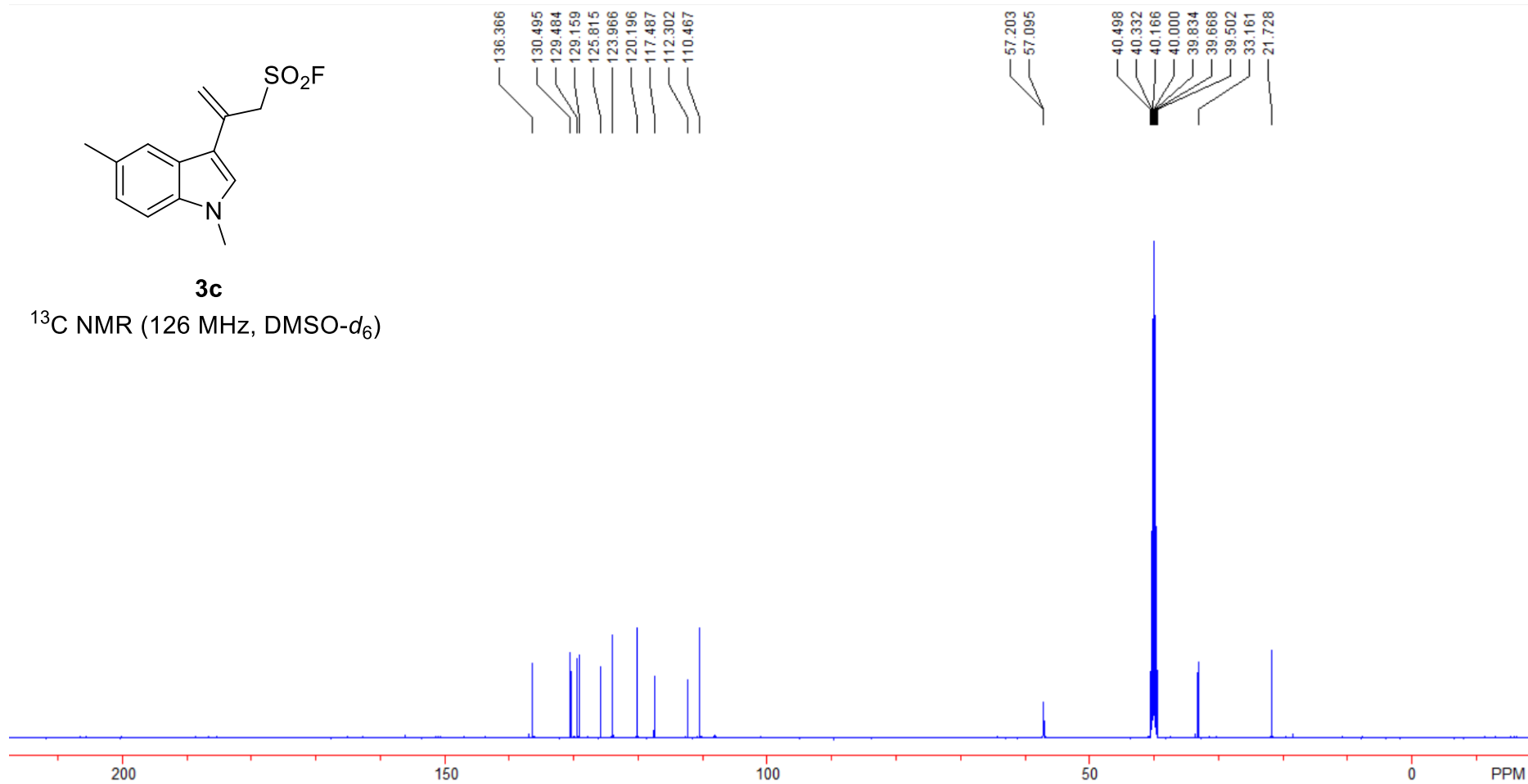
$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

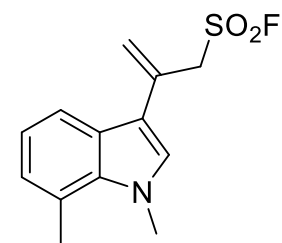
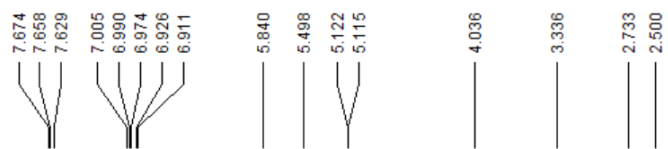




**3c**

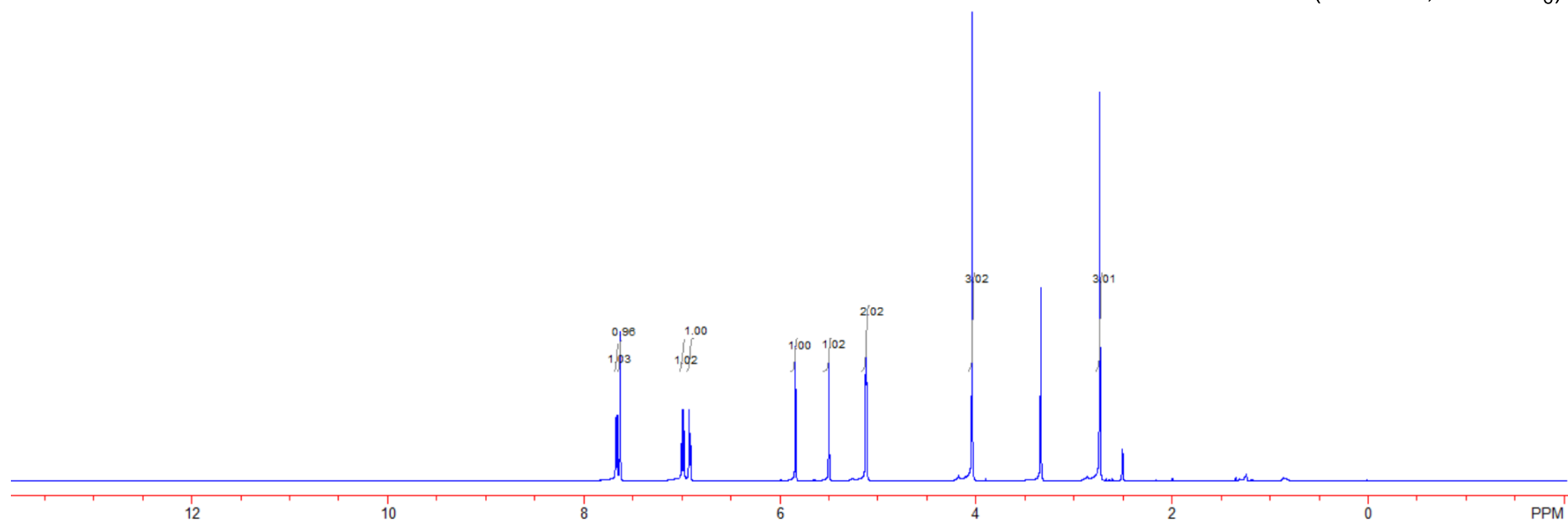
$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )





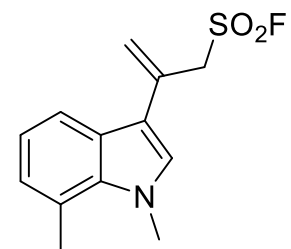
**3d**

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)



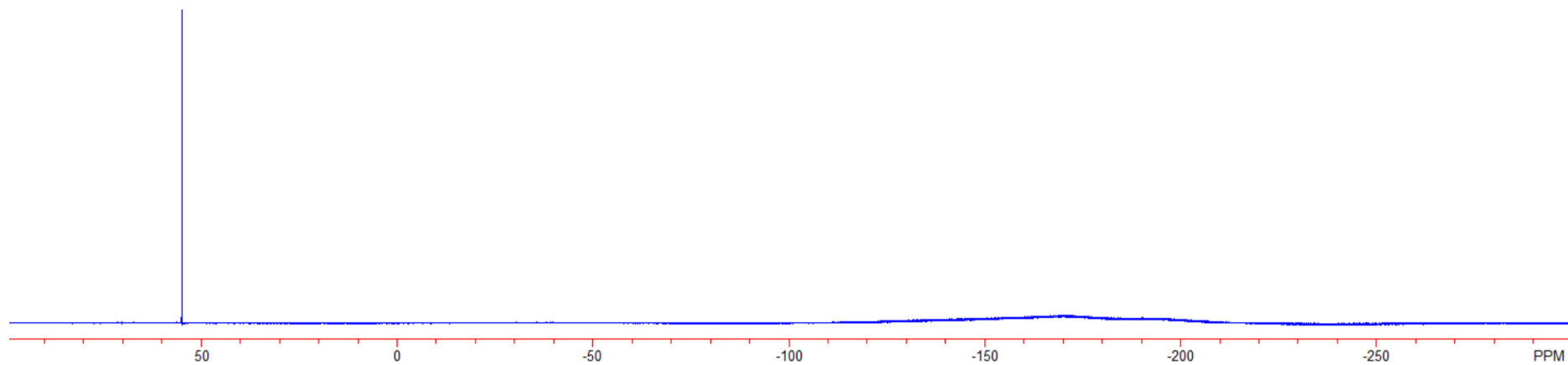


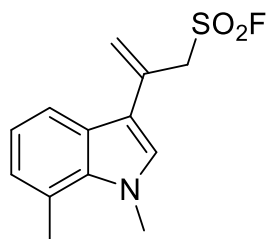
54.899



**3d**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)





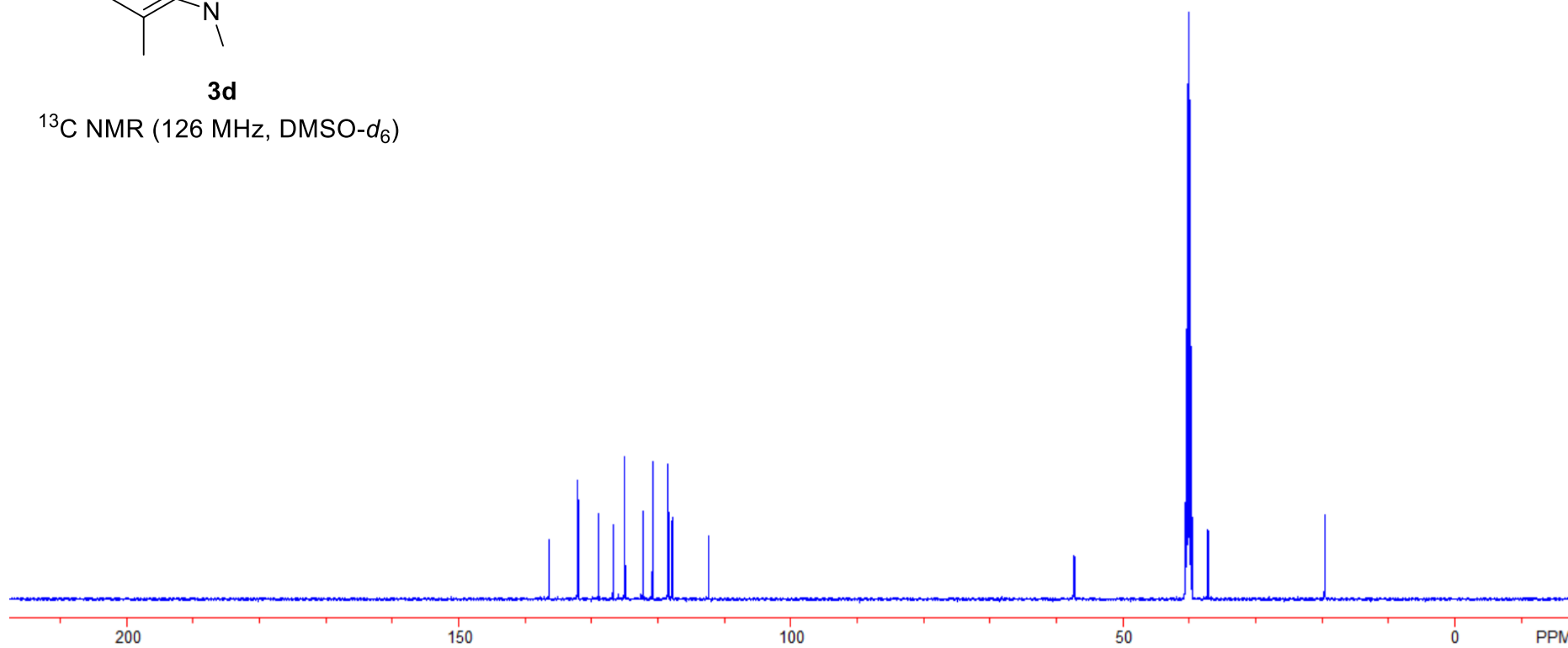
**3d**

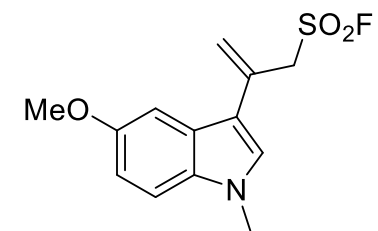
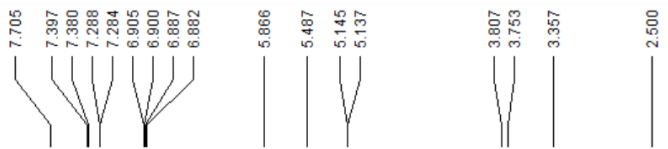
$^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )

136.410  
131.990  
128.942  
126.746  
124.926  
122.240  
120.781  
118.397  
117.820  
112.302

57.348  
57.239

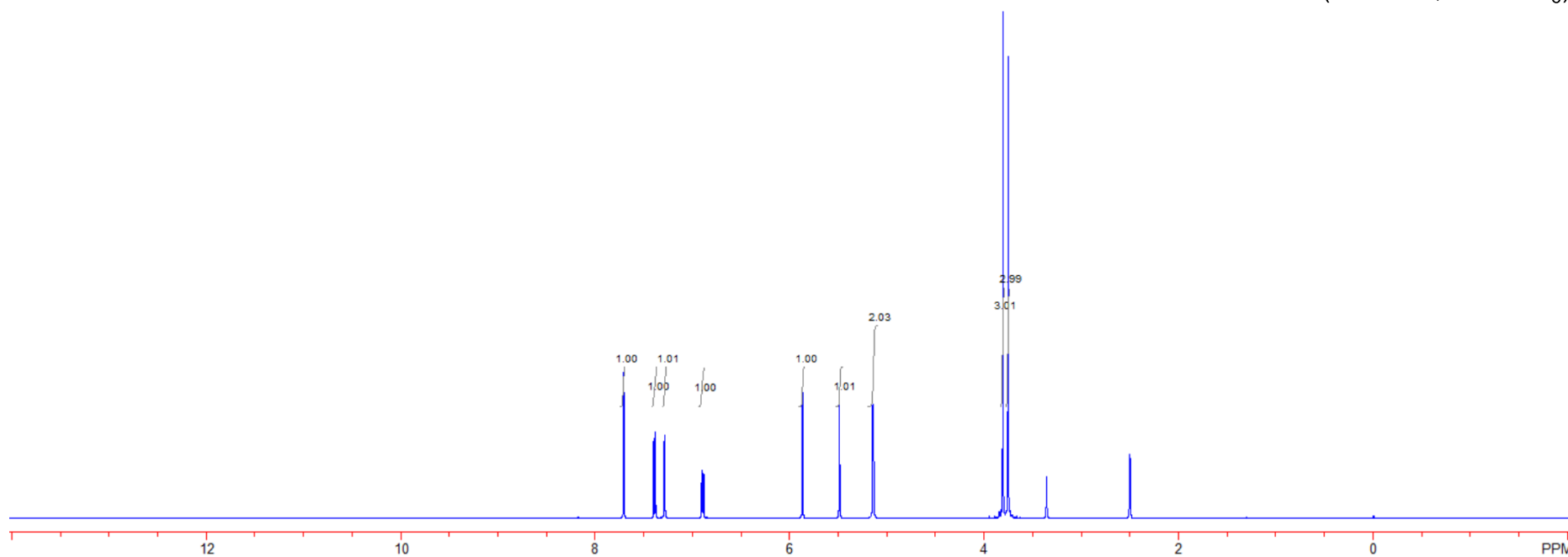
40.498  
40.332  
40.166  
40.000  
39.827  
39.661  
39.494  
37.147  
19.568

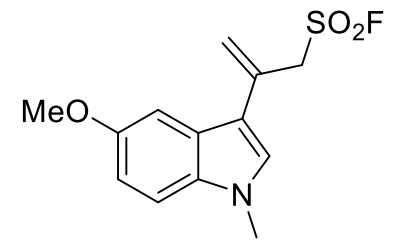




**3e**

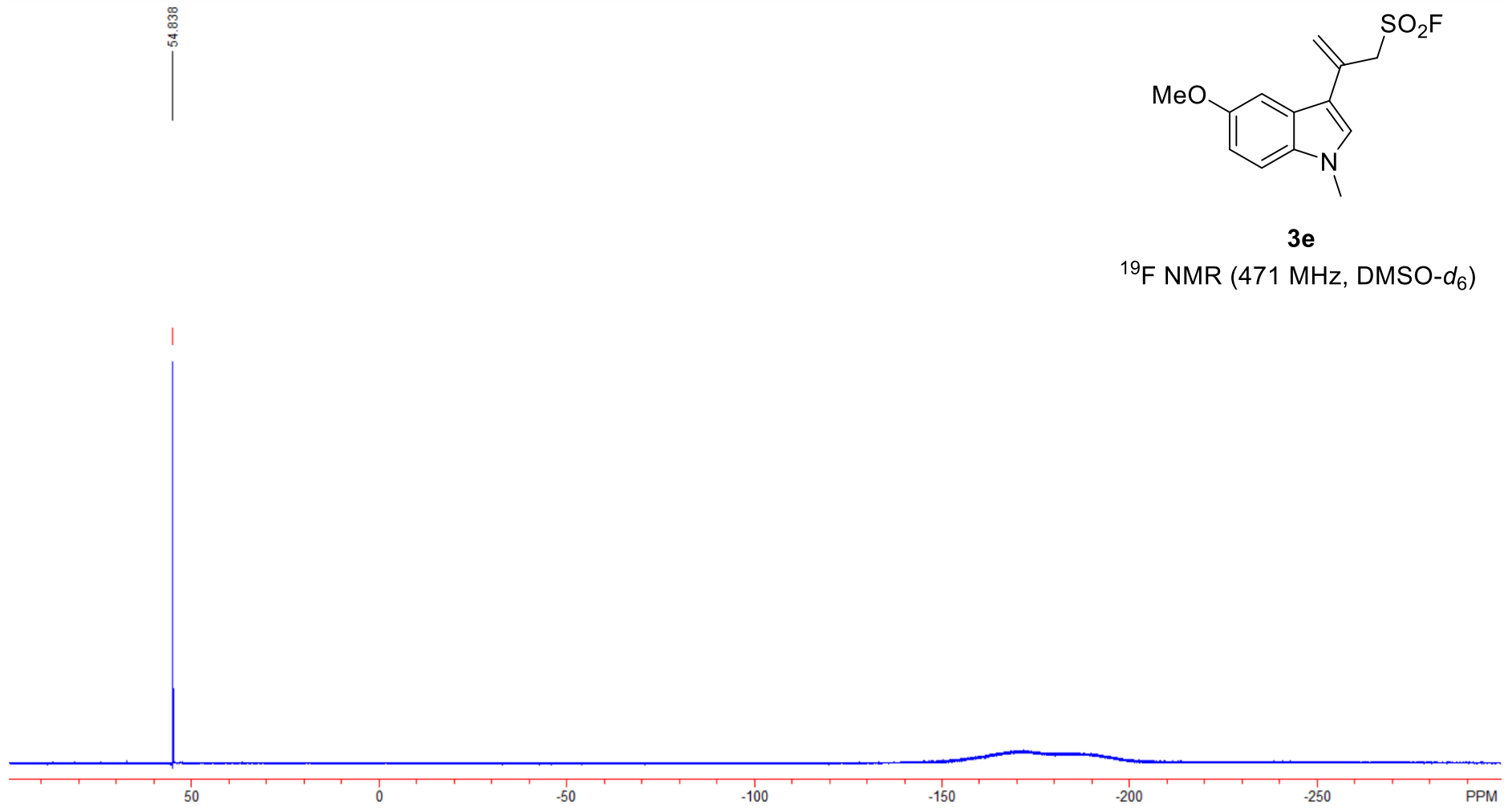
<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)

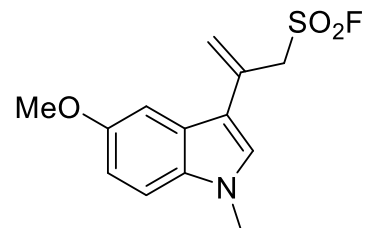




**3e**

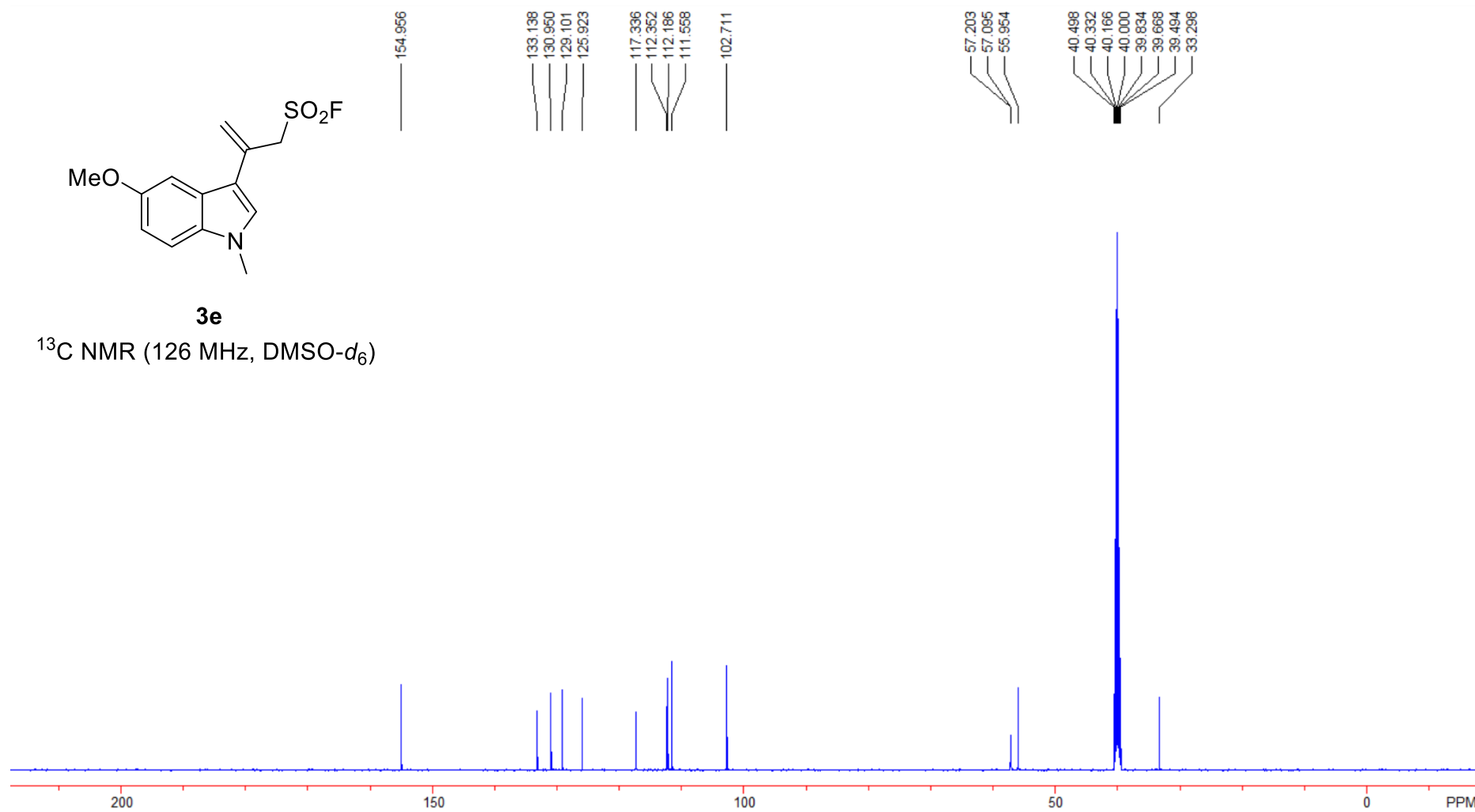
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

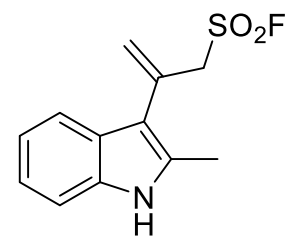




**3e**

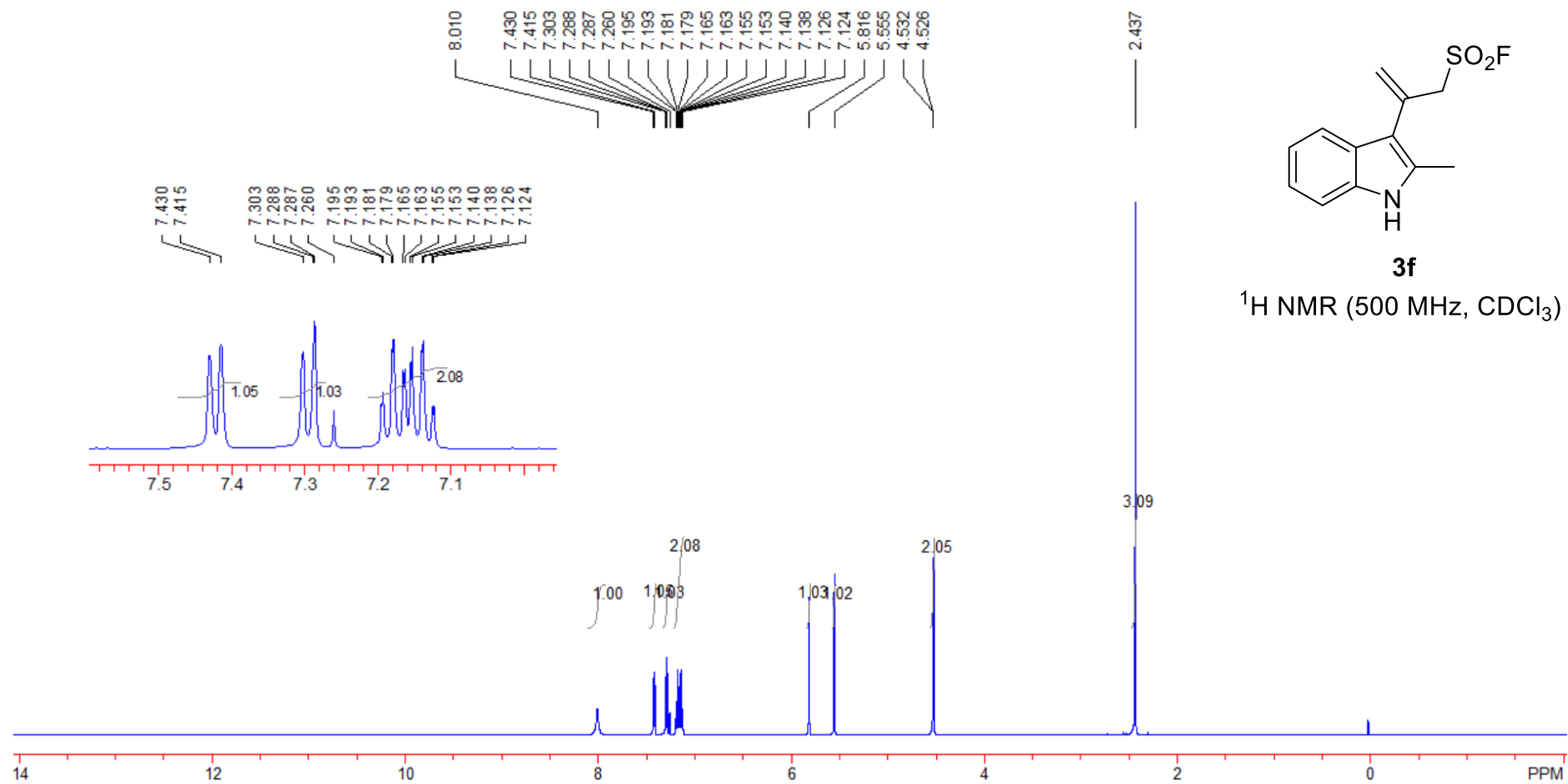
$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

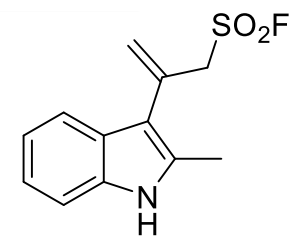




**3f**

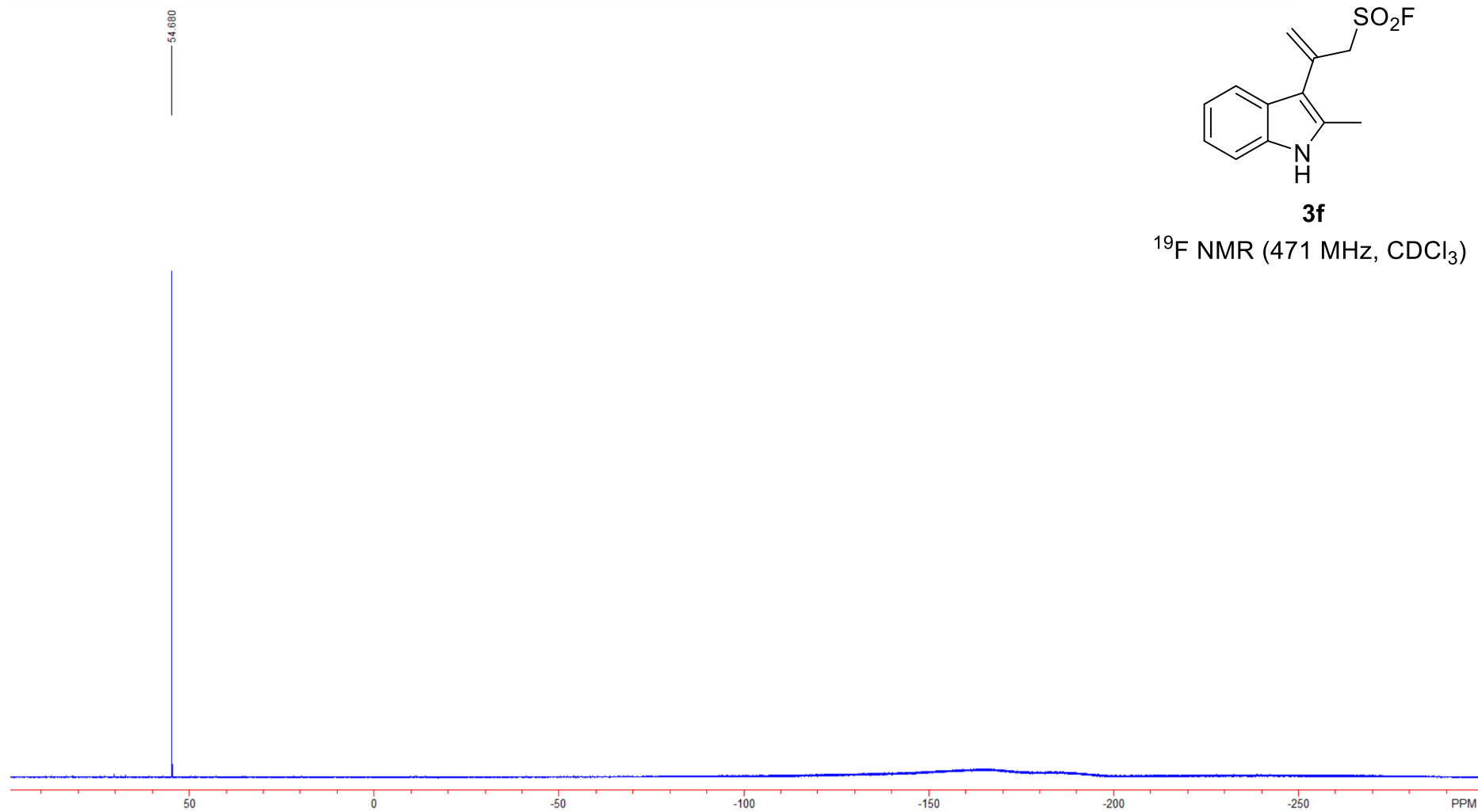
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

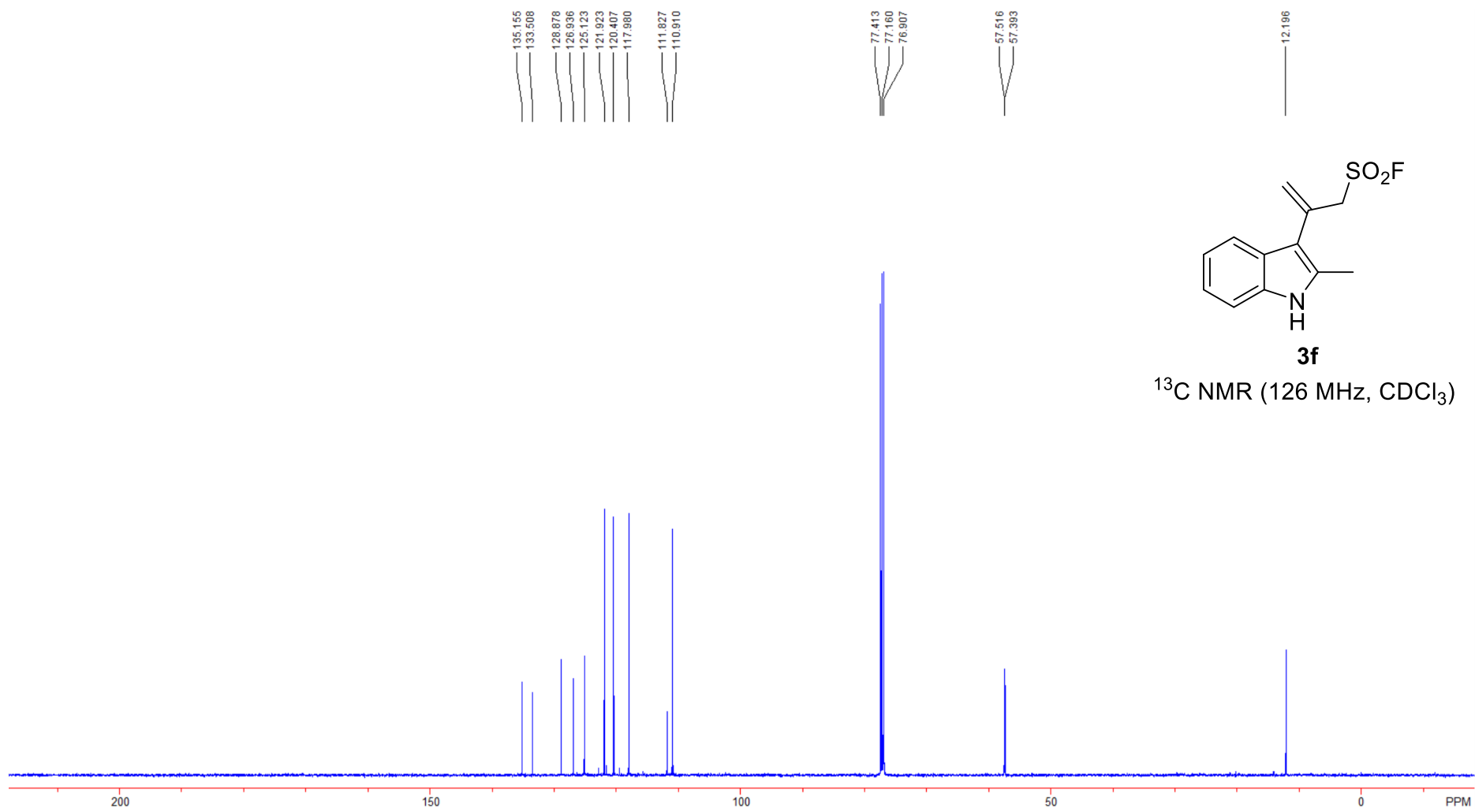




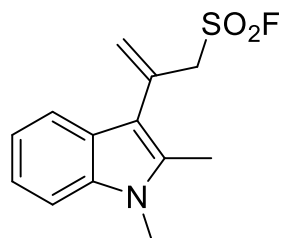
**3f**

$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )



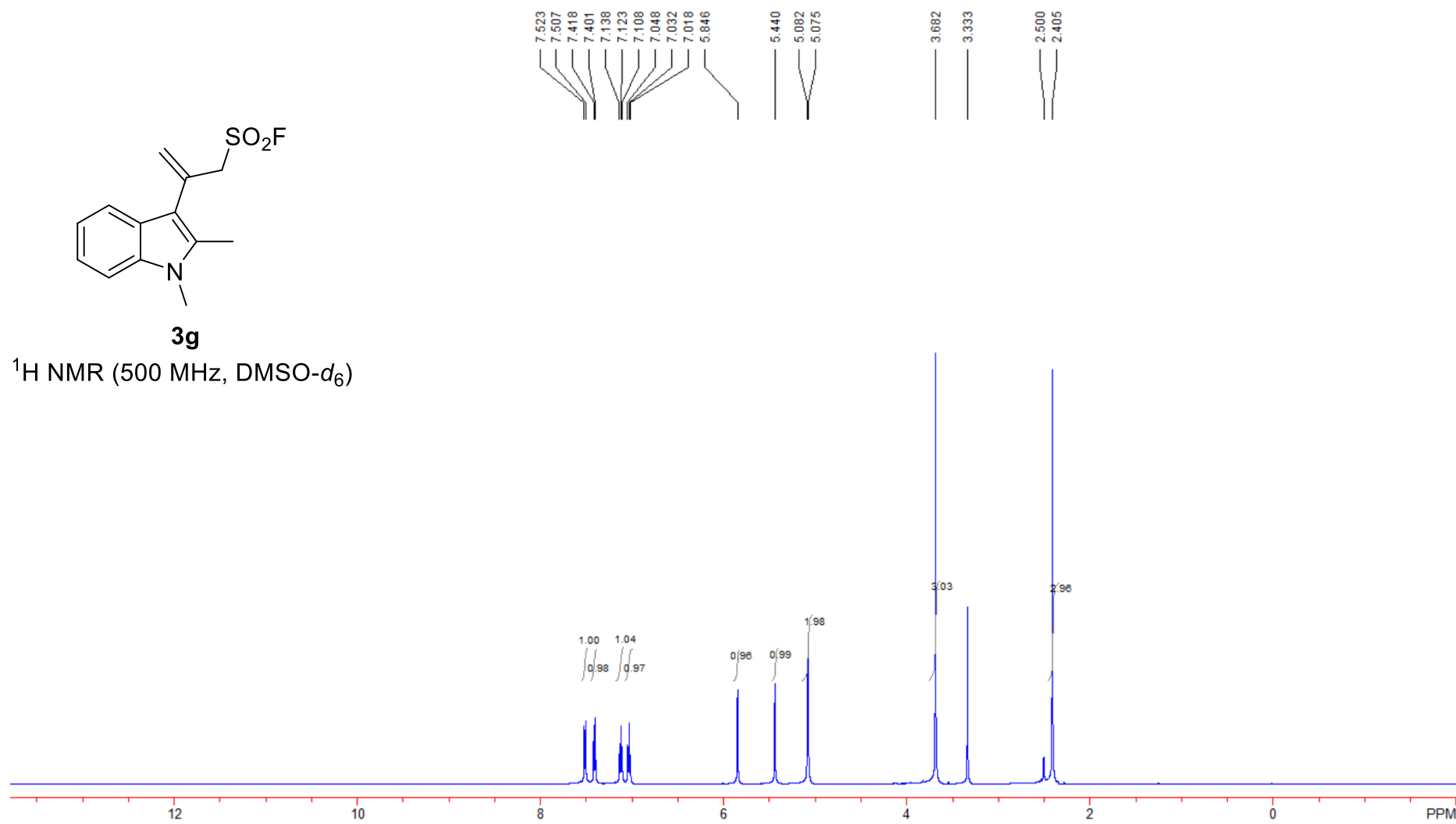


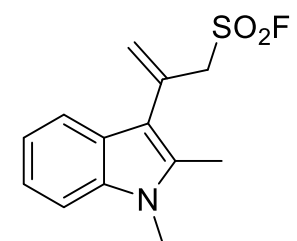




**3g**

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

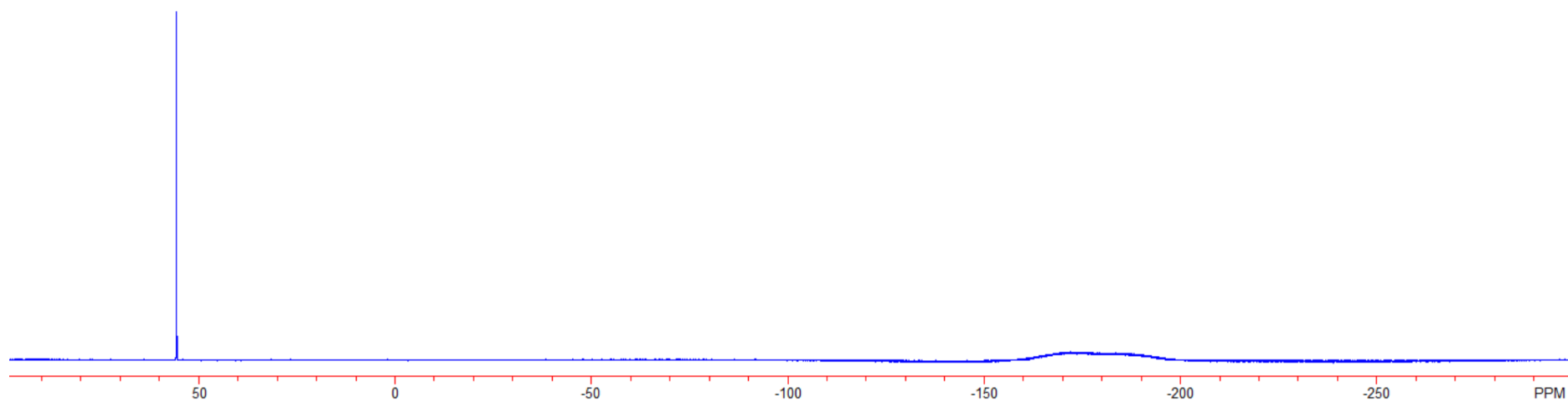


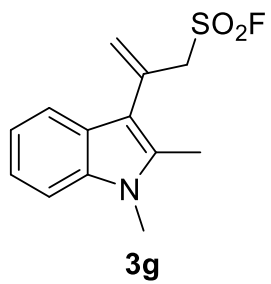


**3g**

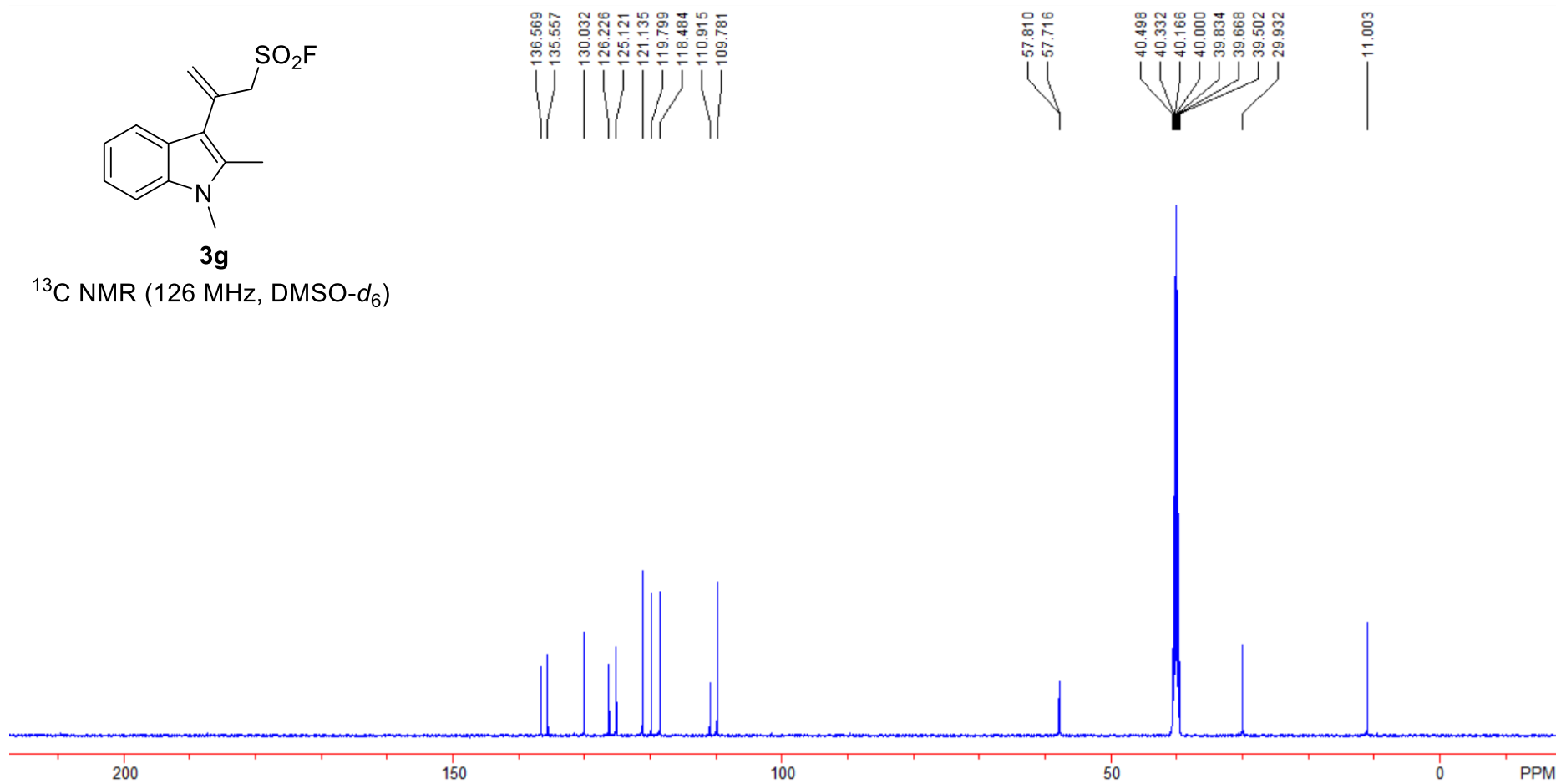
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

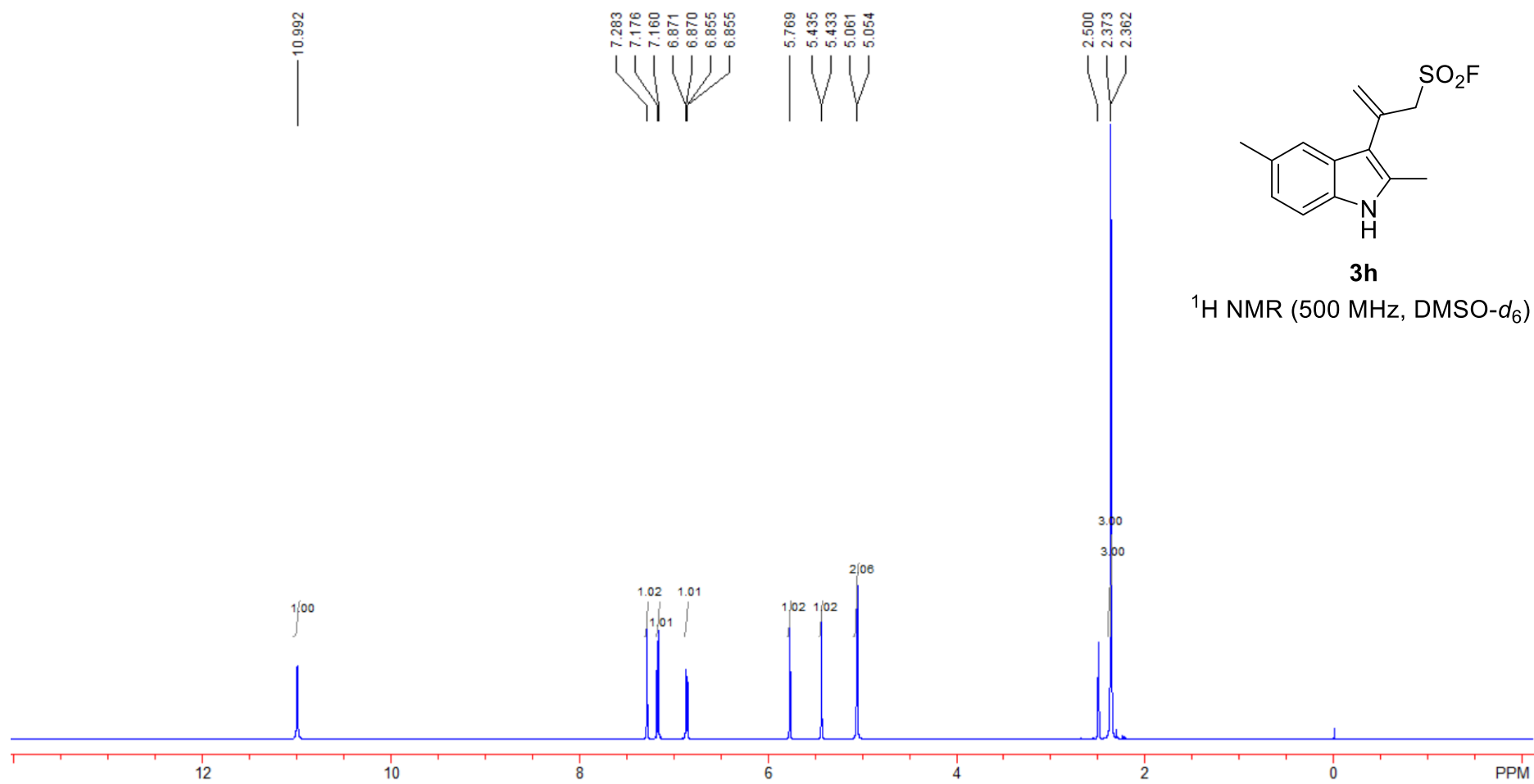
55.598



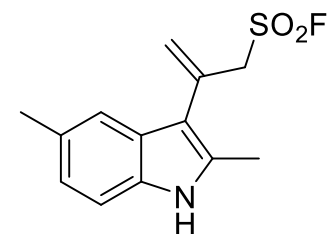


$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )



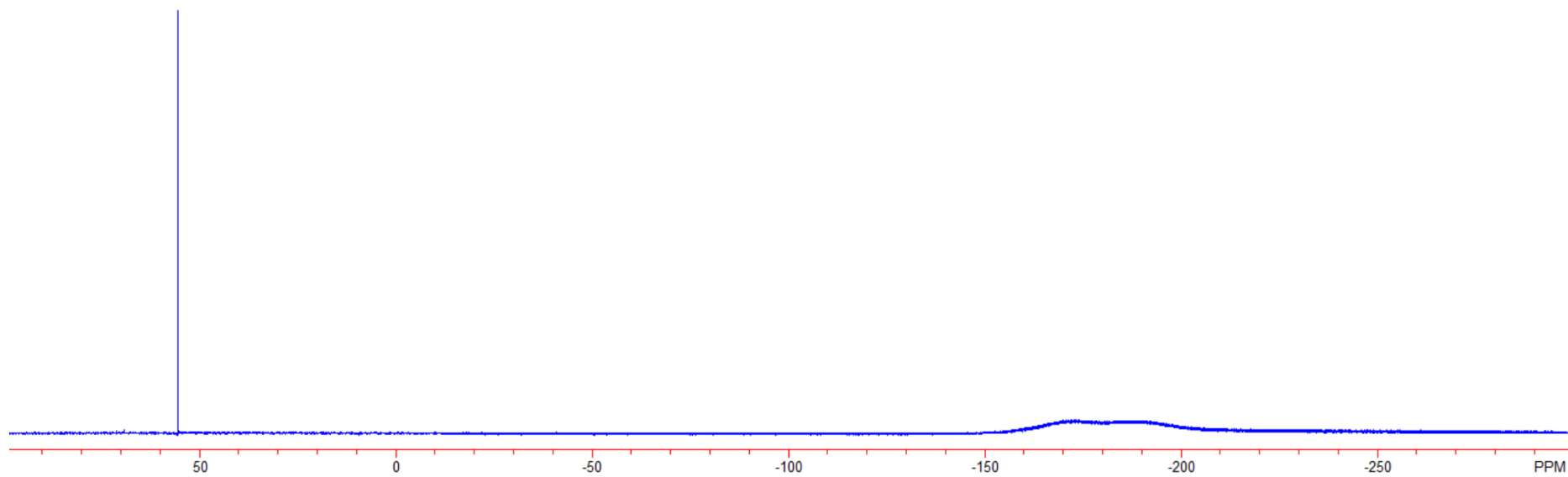


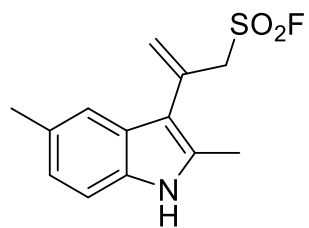
55.458



**3h**

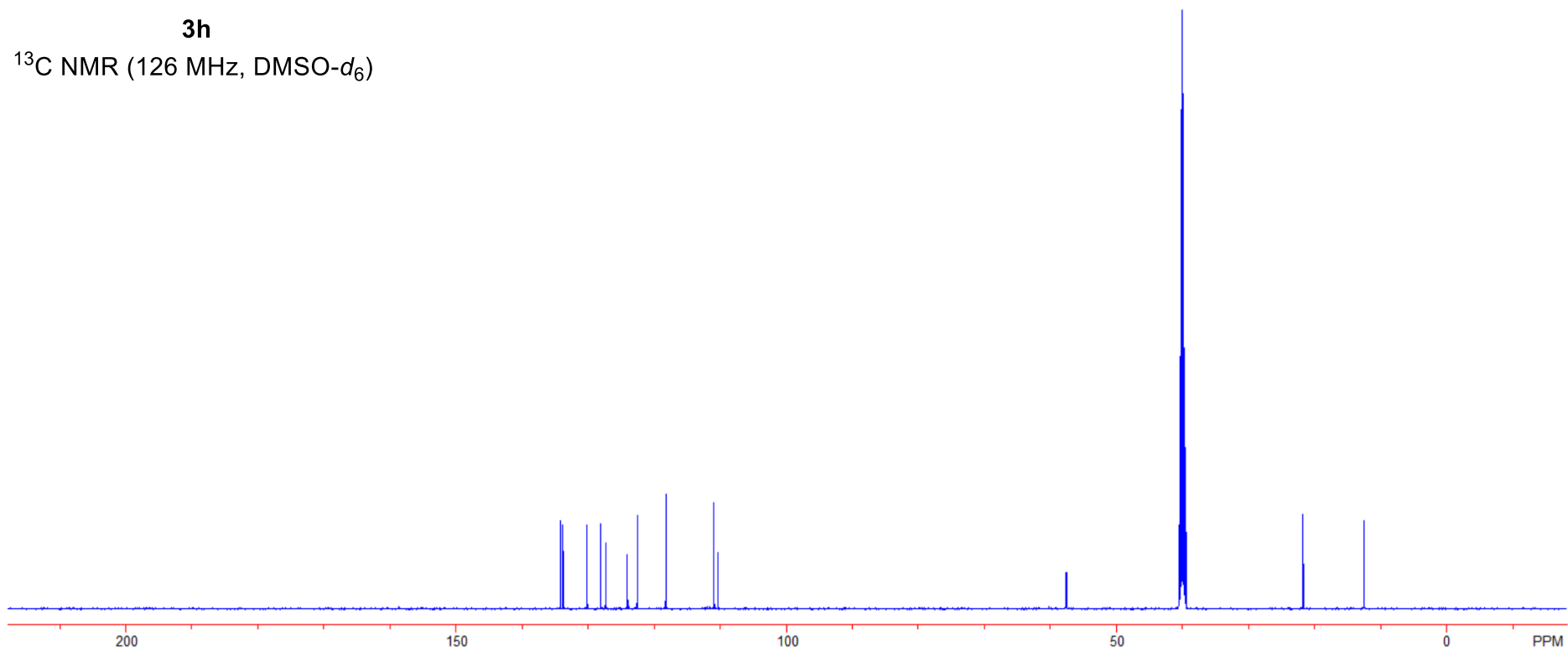
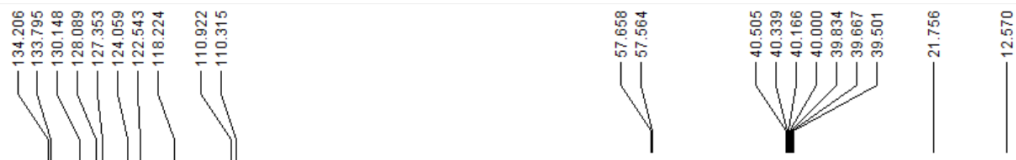
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

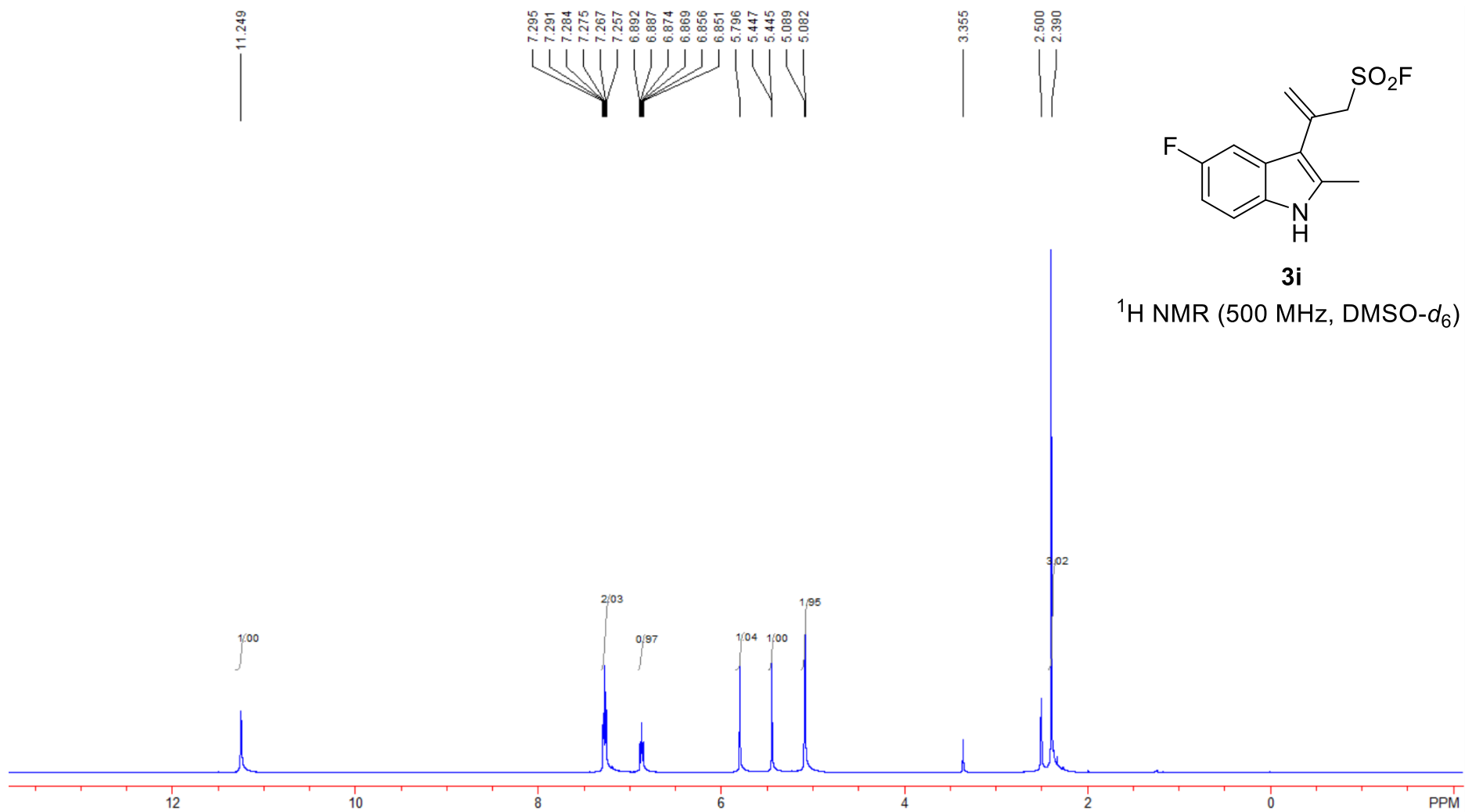




**3h**

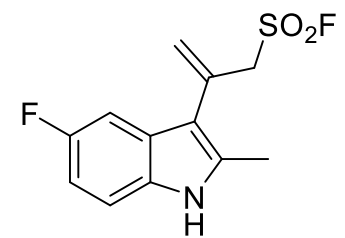
$^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )





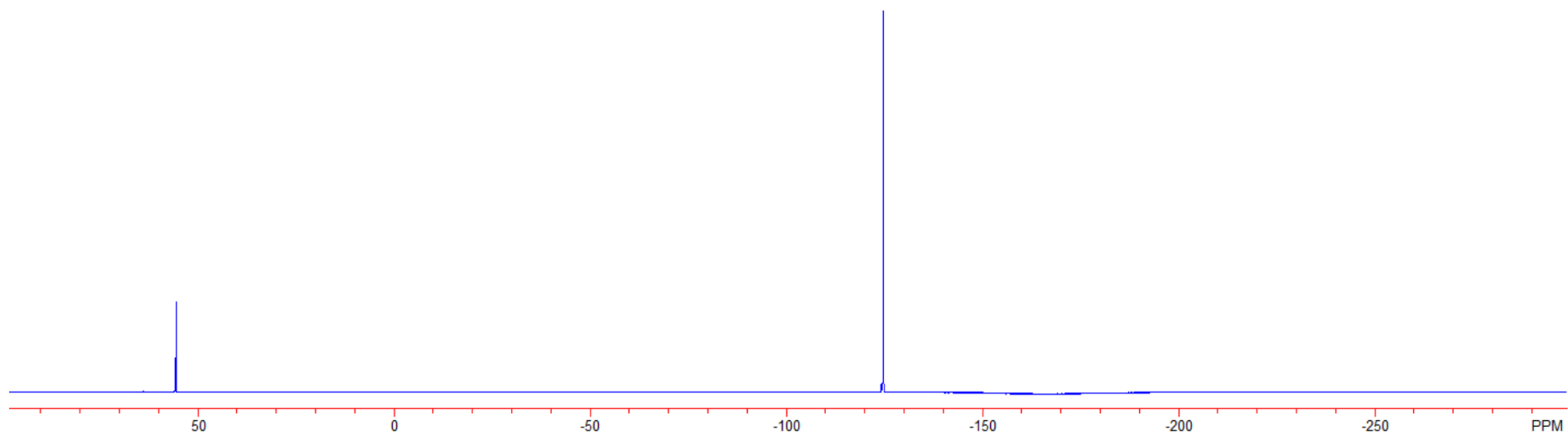
55.586

124.586  
124.598  
124.610  
124.628

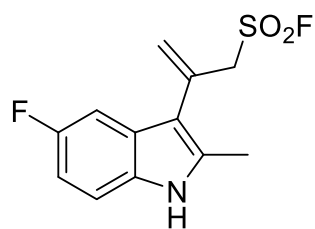


**3i**

$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

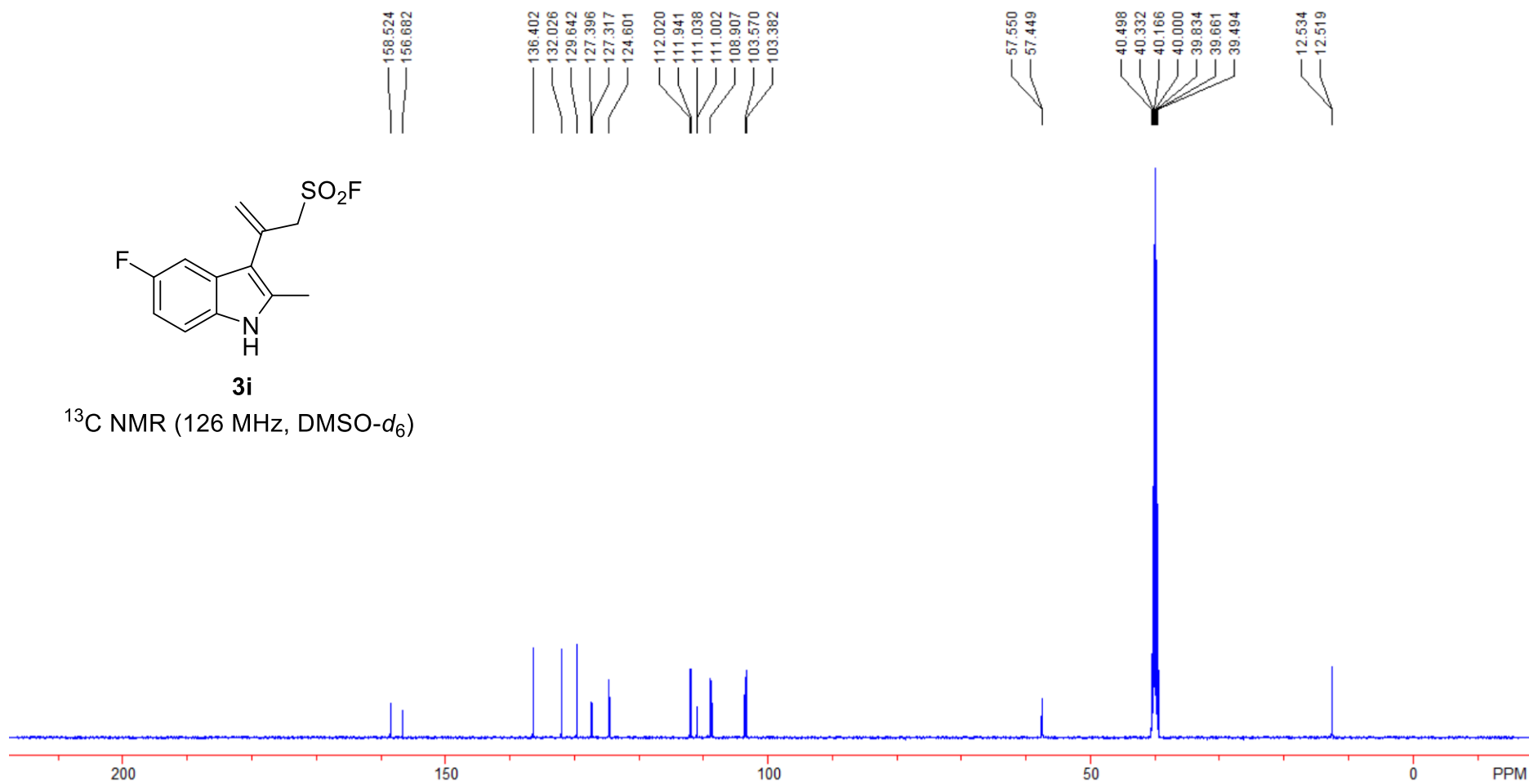


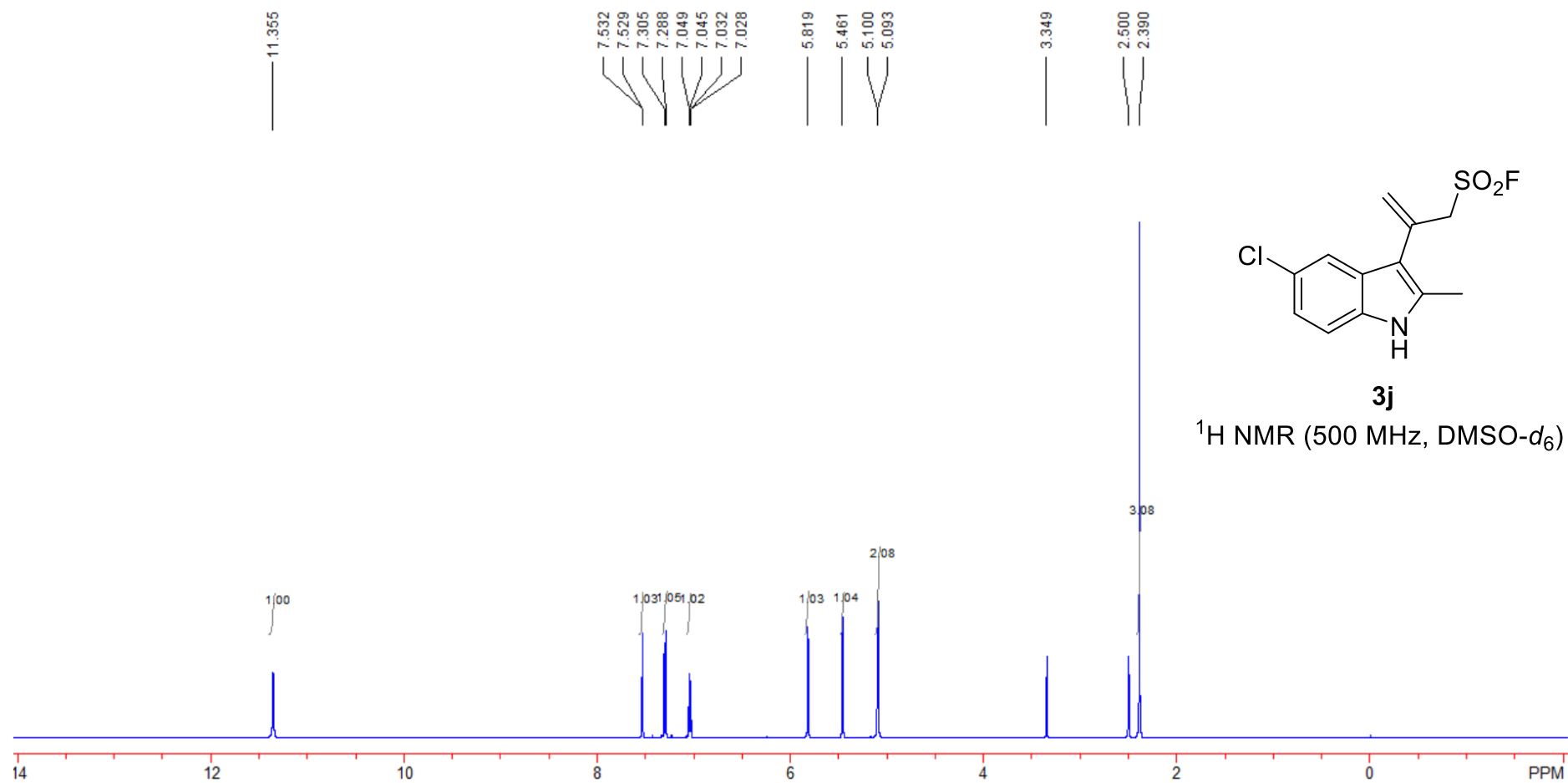


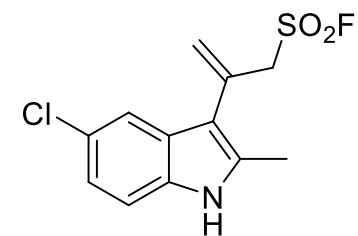


**3i**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

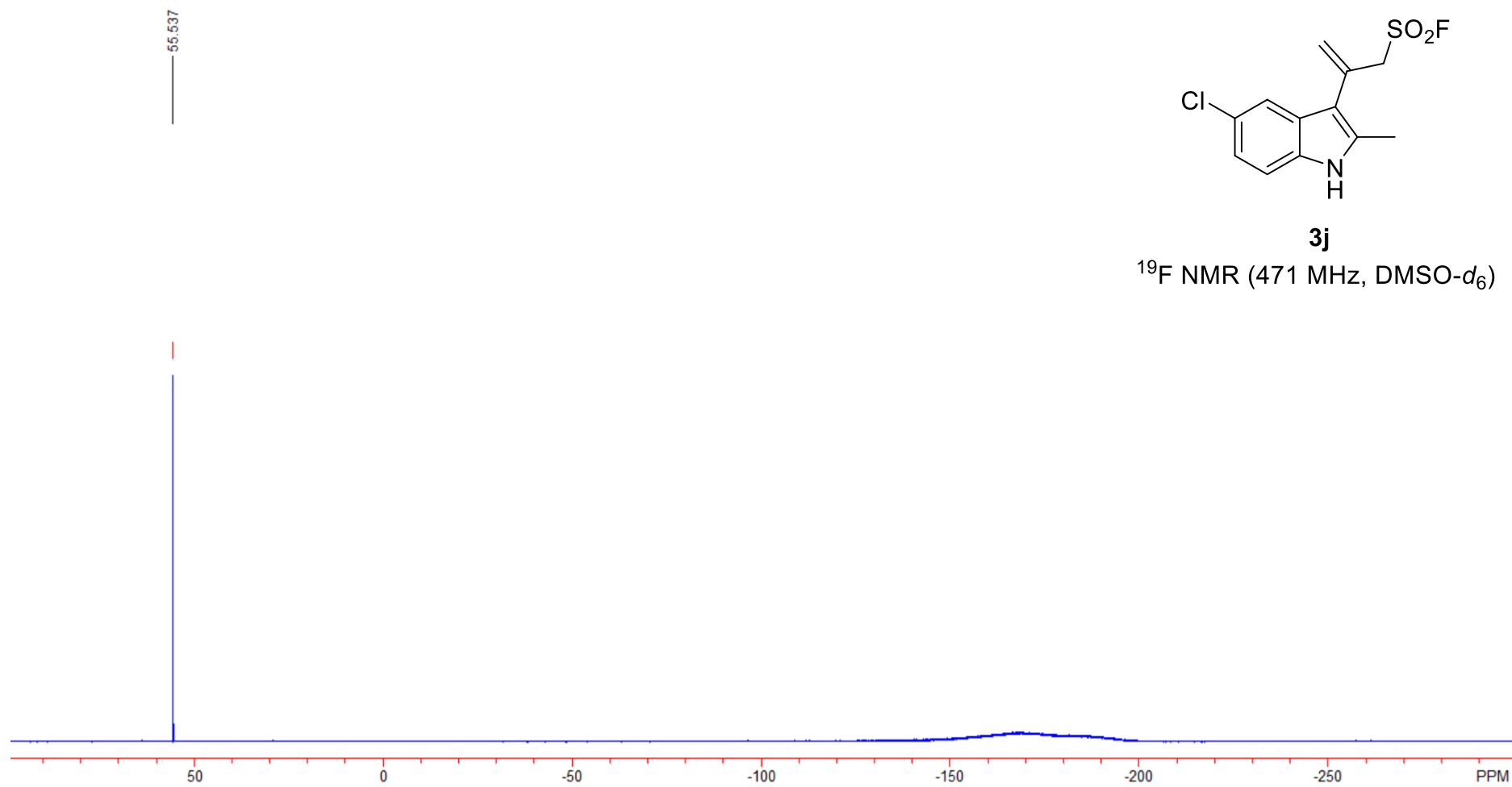


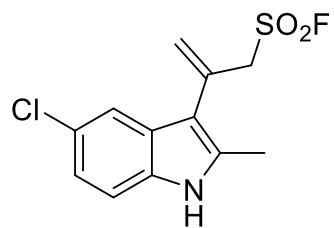




**3j**

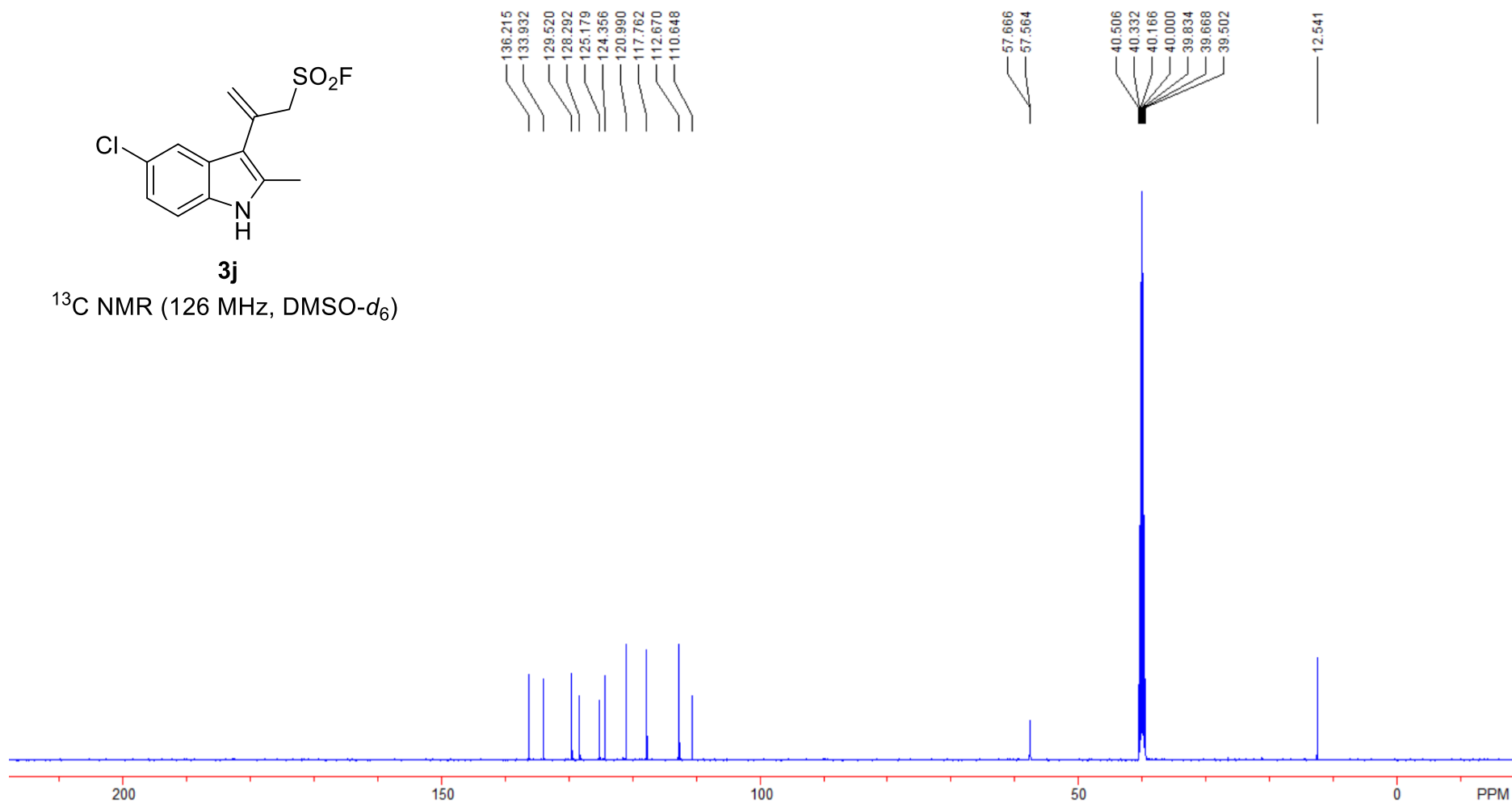
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

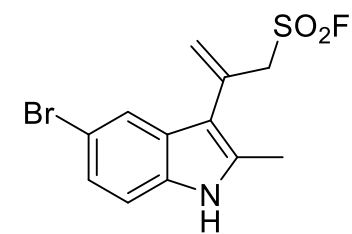




**3j**

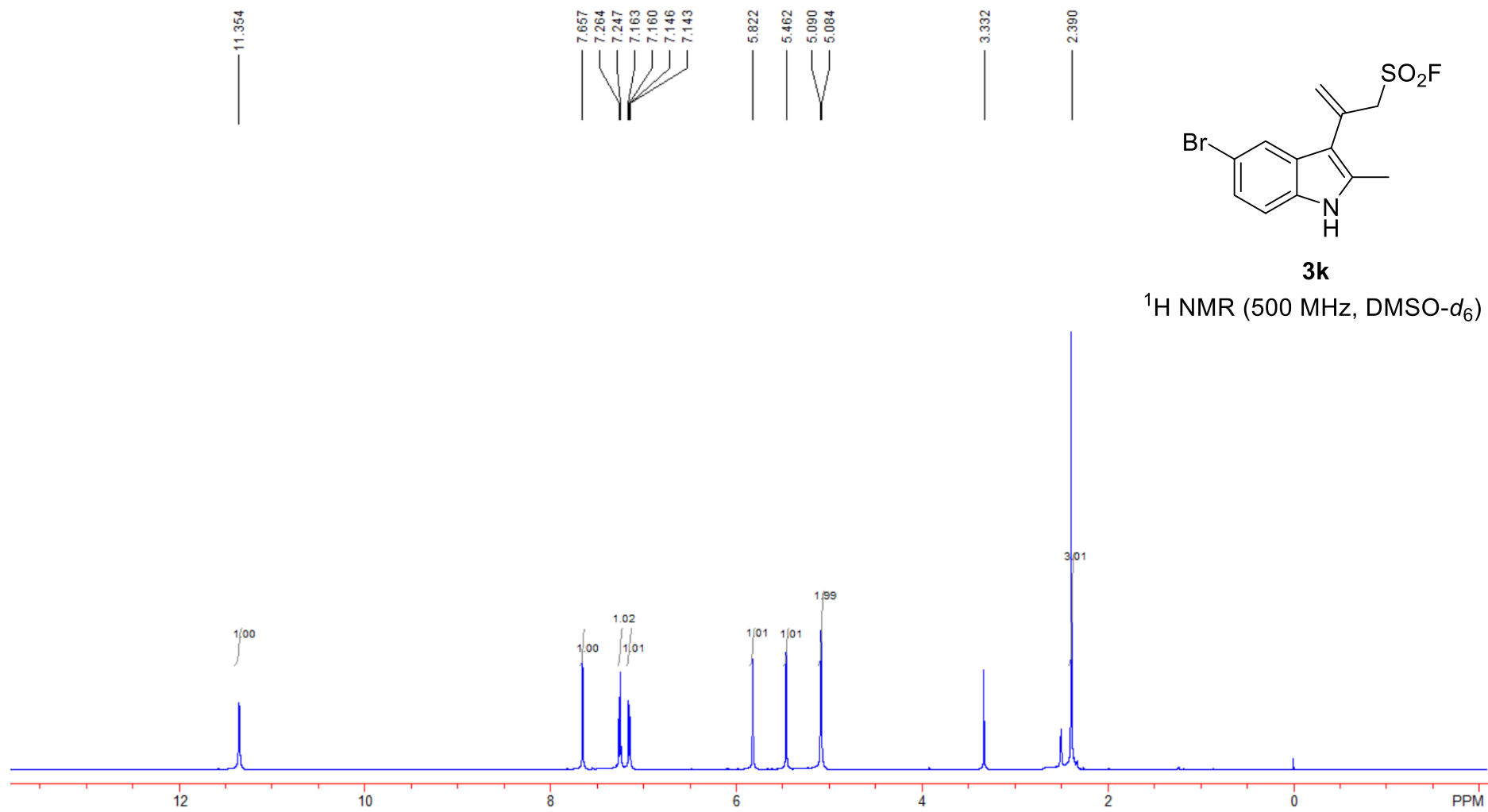
<sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>)

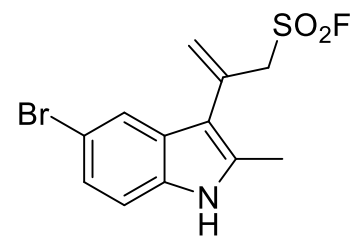




**3k**

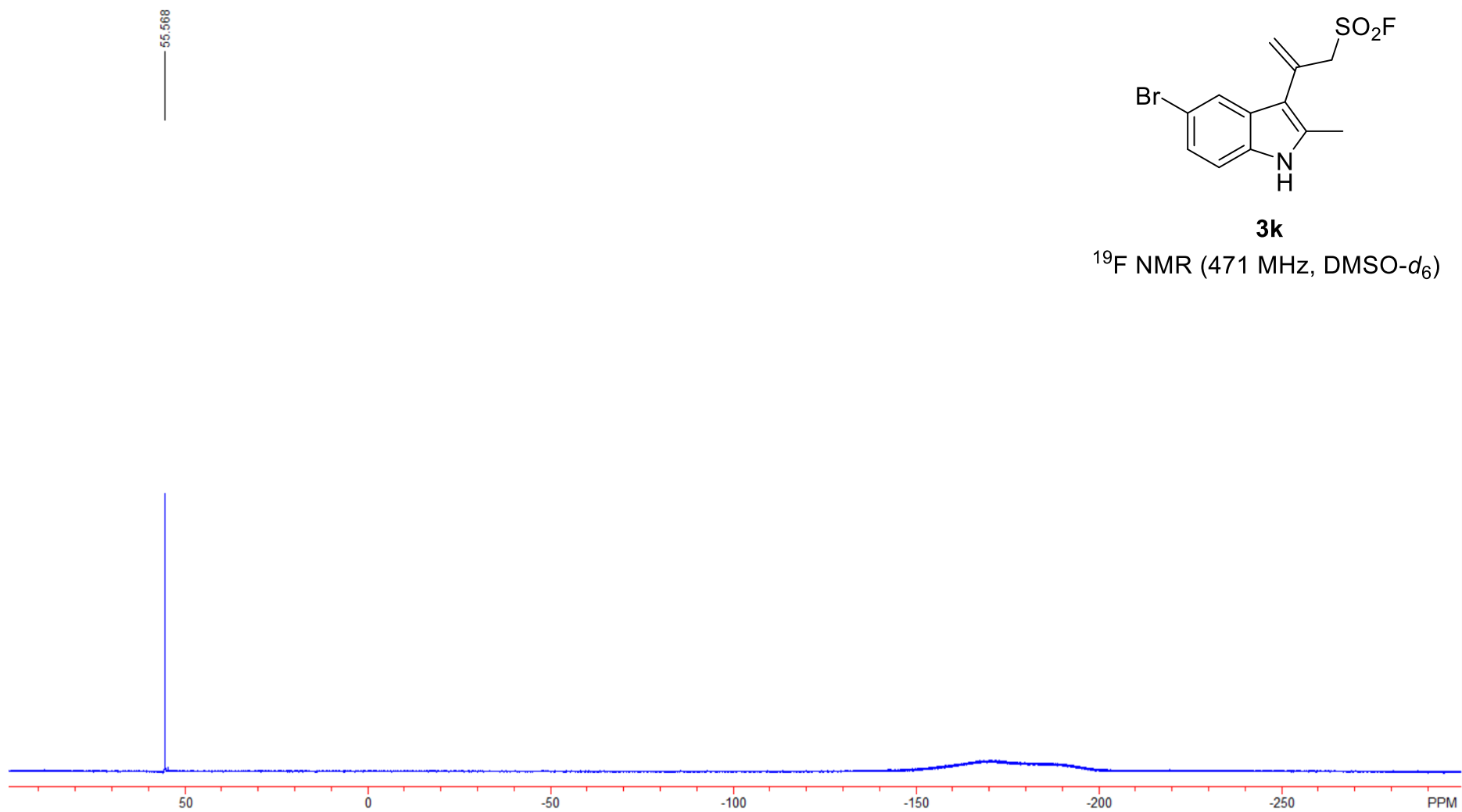
<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

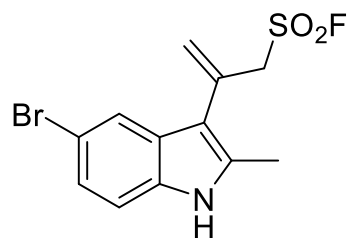




**3k**

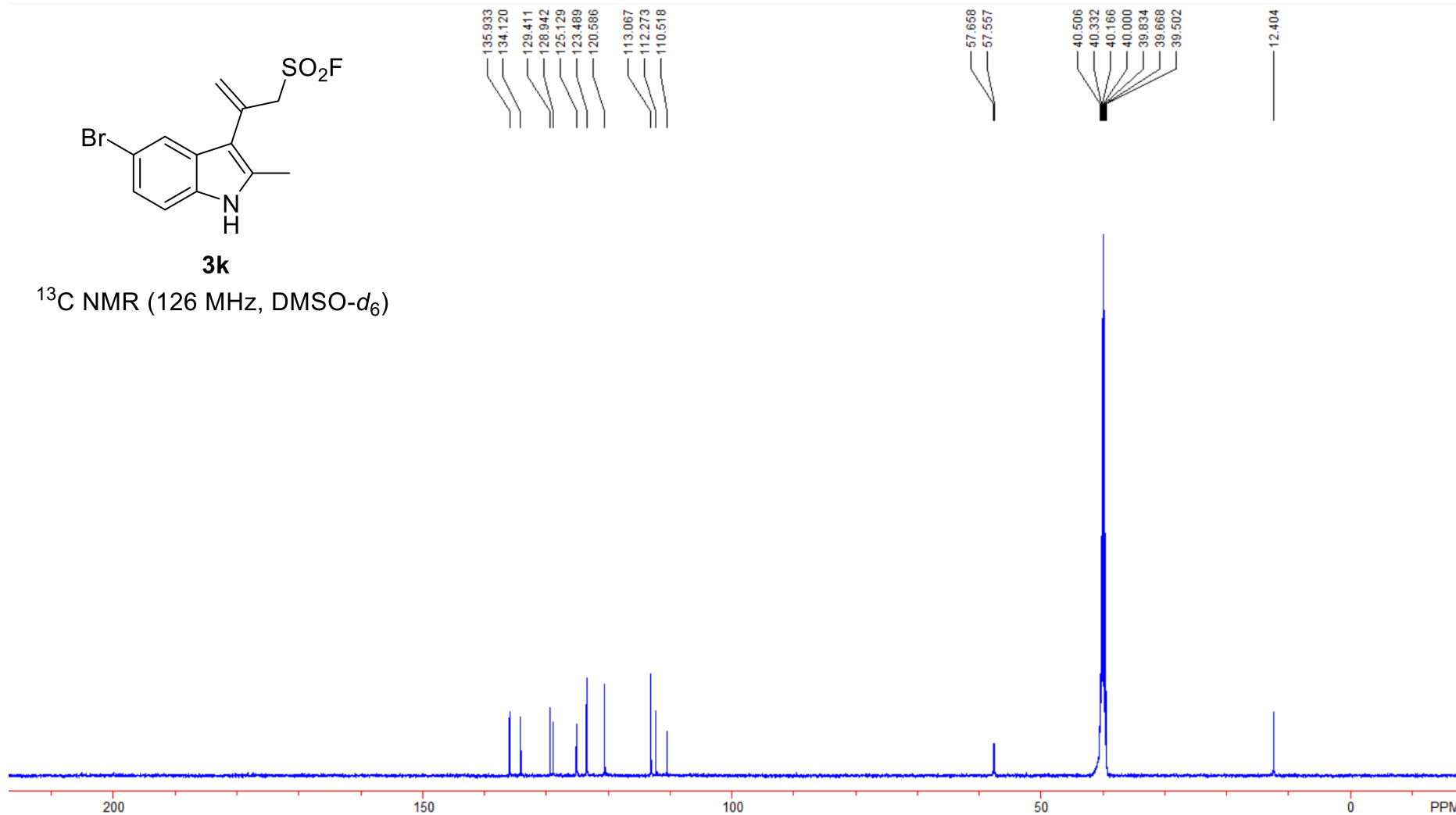
$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

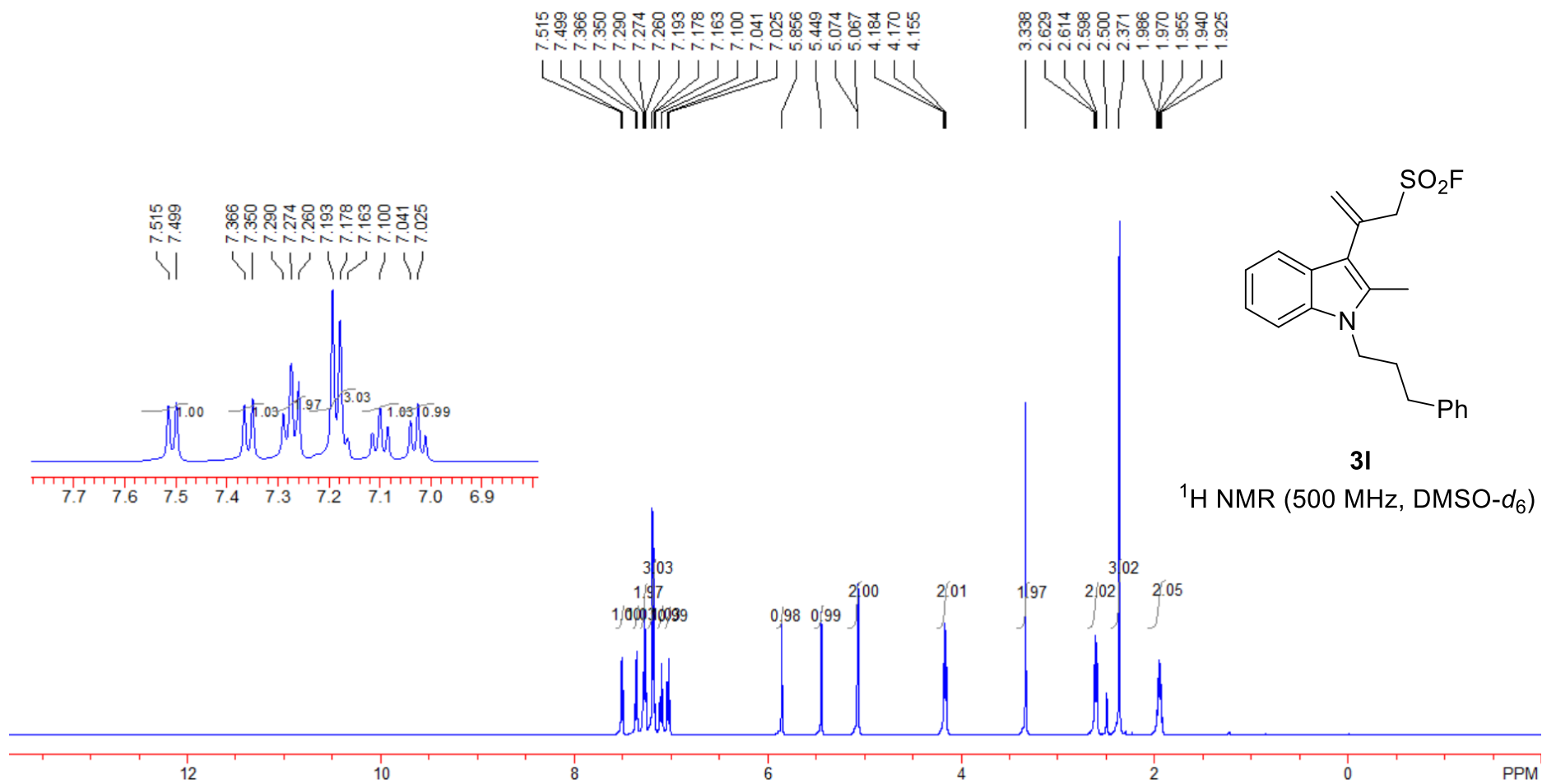




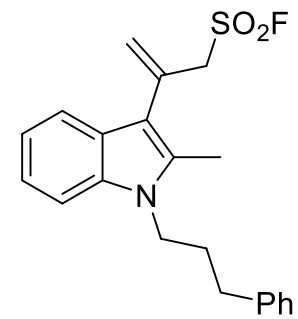
**3k**

$^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )



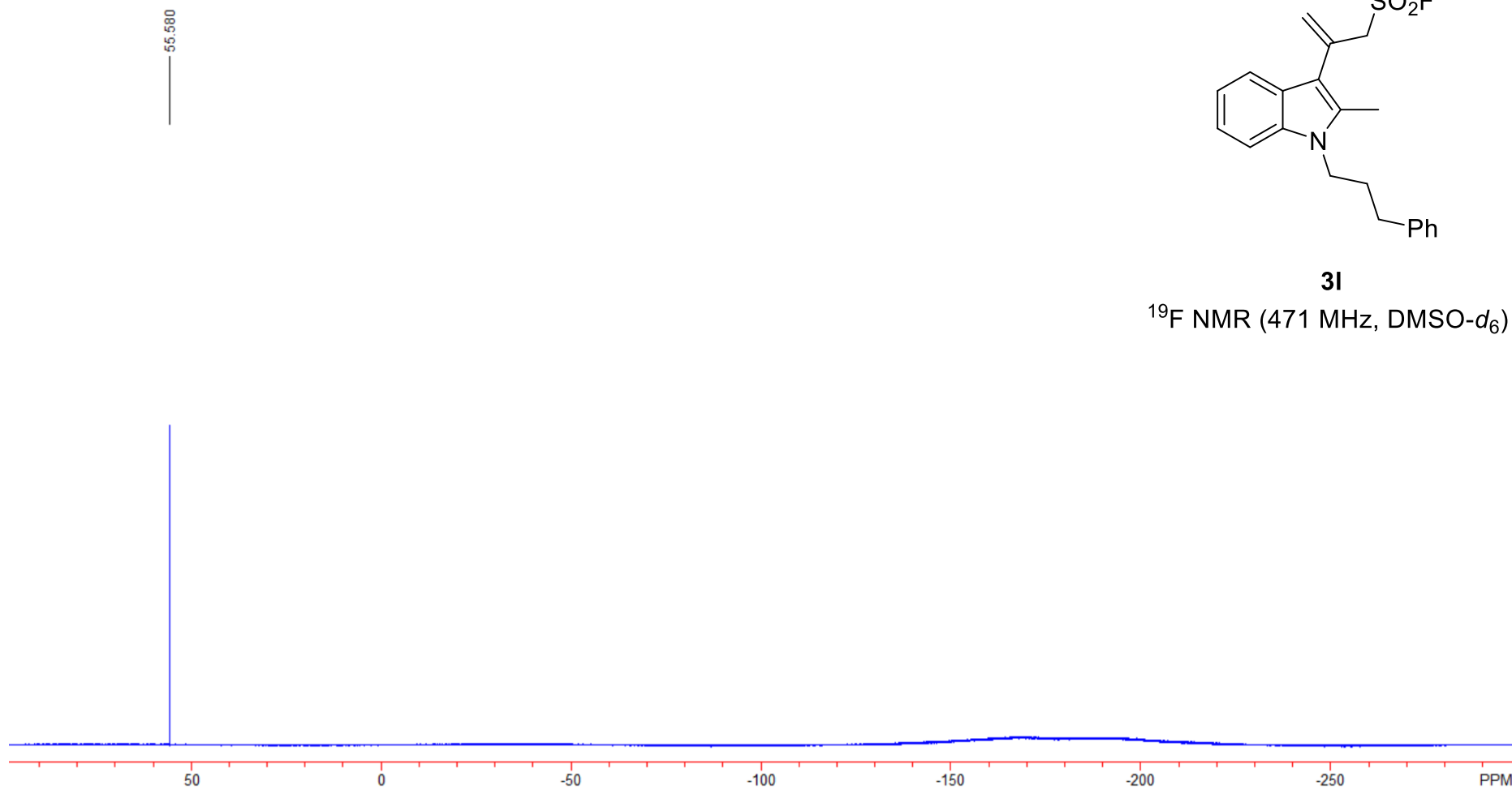


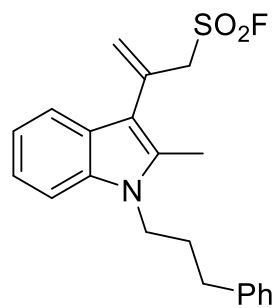




**31**

$^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )





**3I**

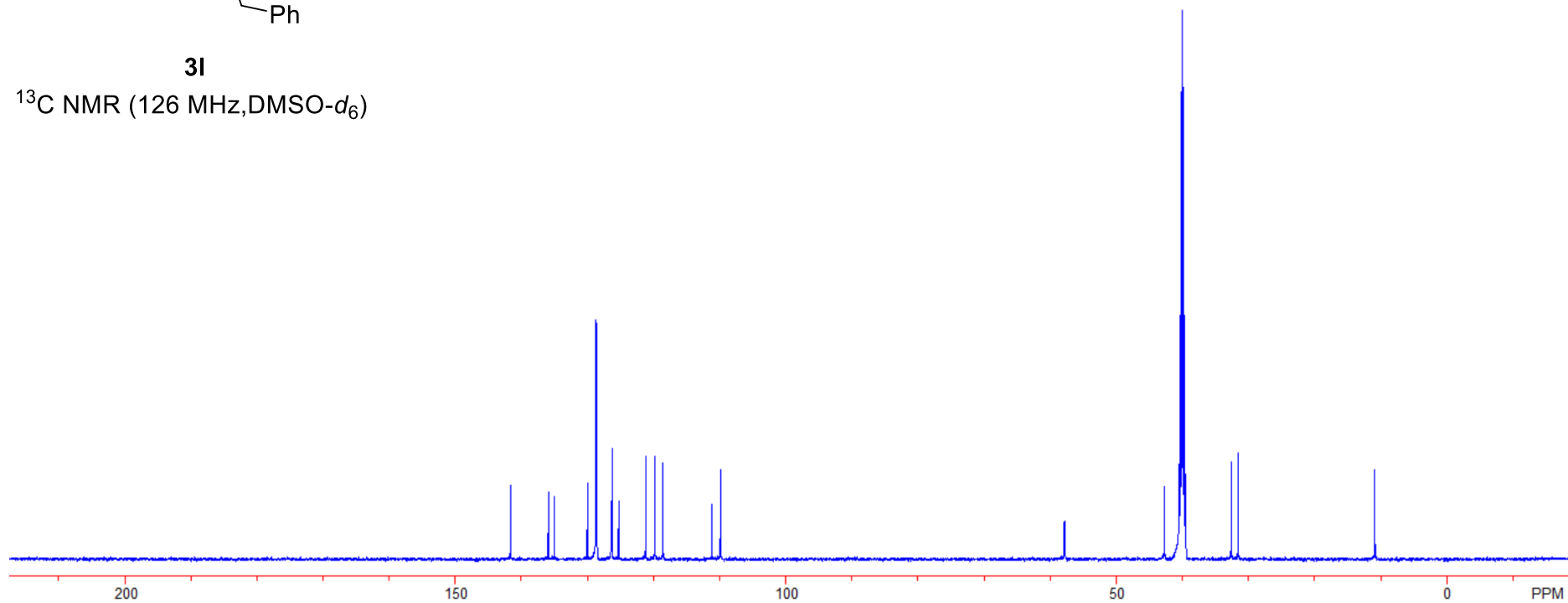
<sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>)

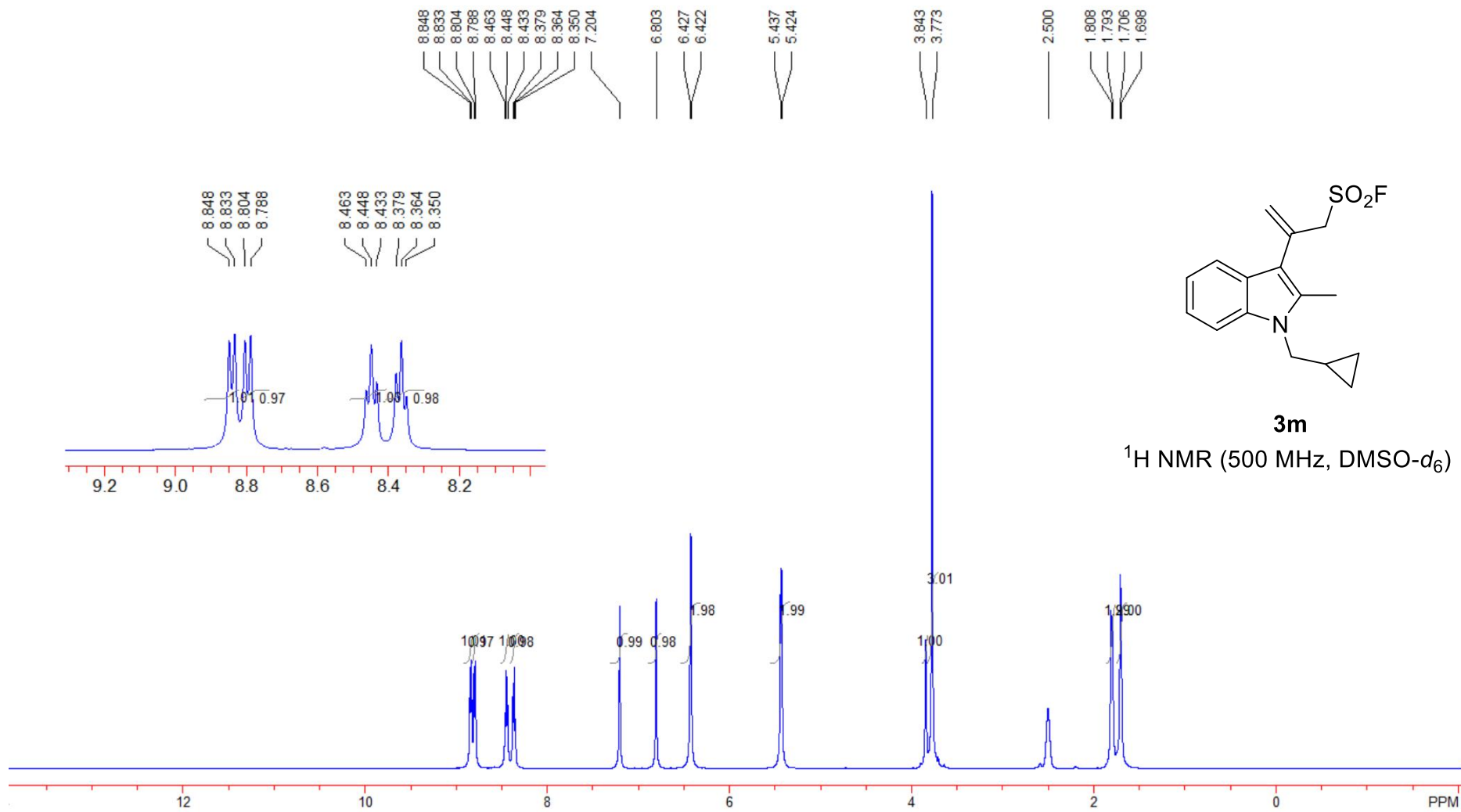
141.653  
135.926  
134.994  
130.011  
128.747  
128.552  
126.414  
126.291  
125.259  
121.185  
119.806  
118.585  
111.204  
109.875

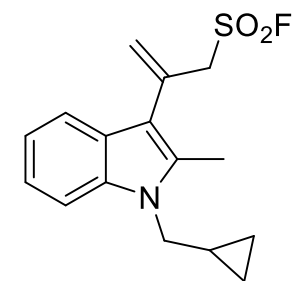
57.839  
57.745

42.687  
40.506  
40.332  
40.166  
40.000  
39.834  
39.668  
39.502  
32.604  
31.579

10.880

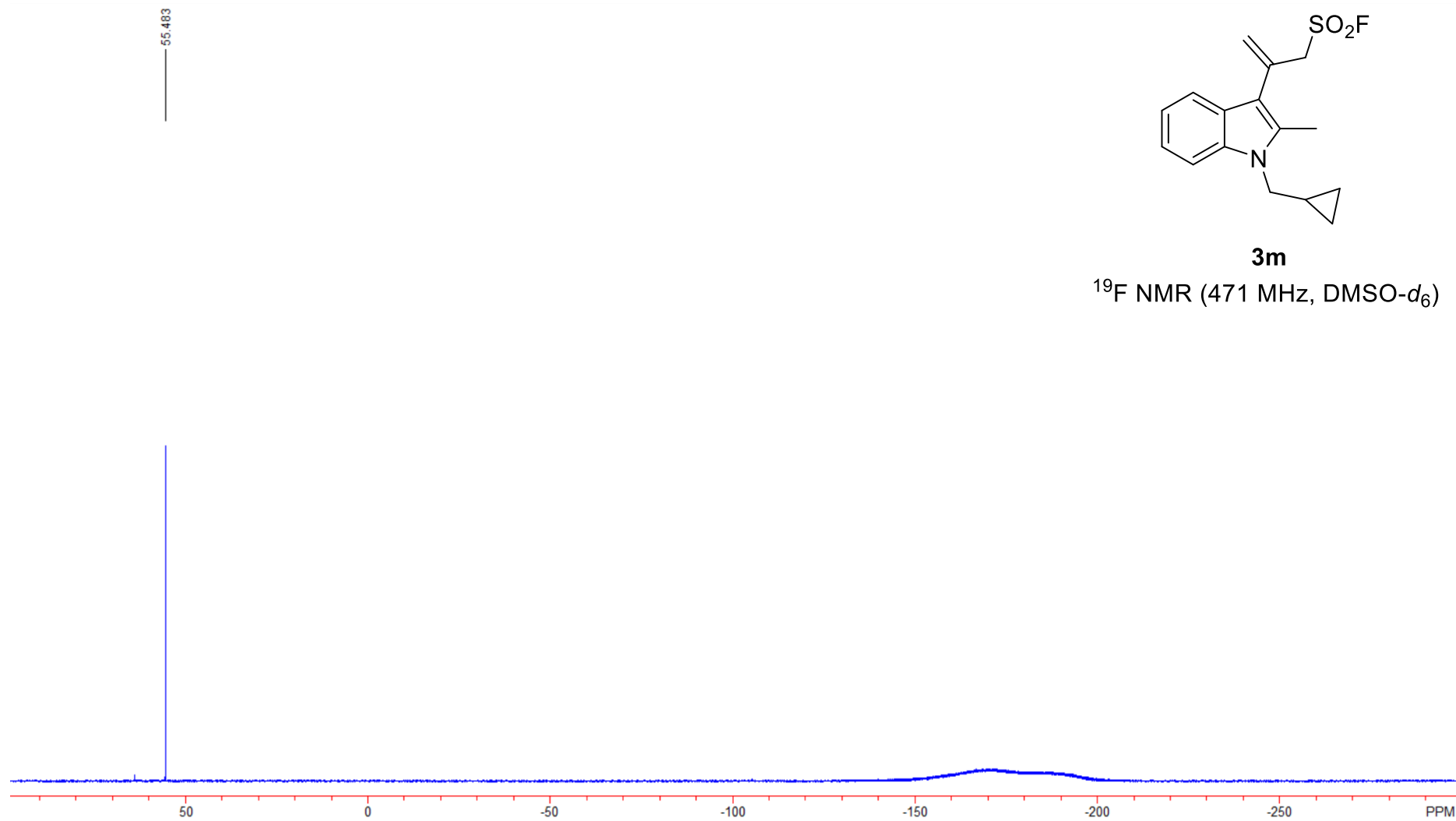


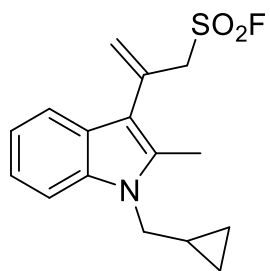




**3m**

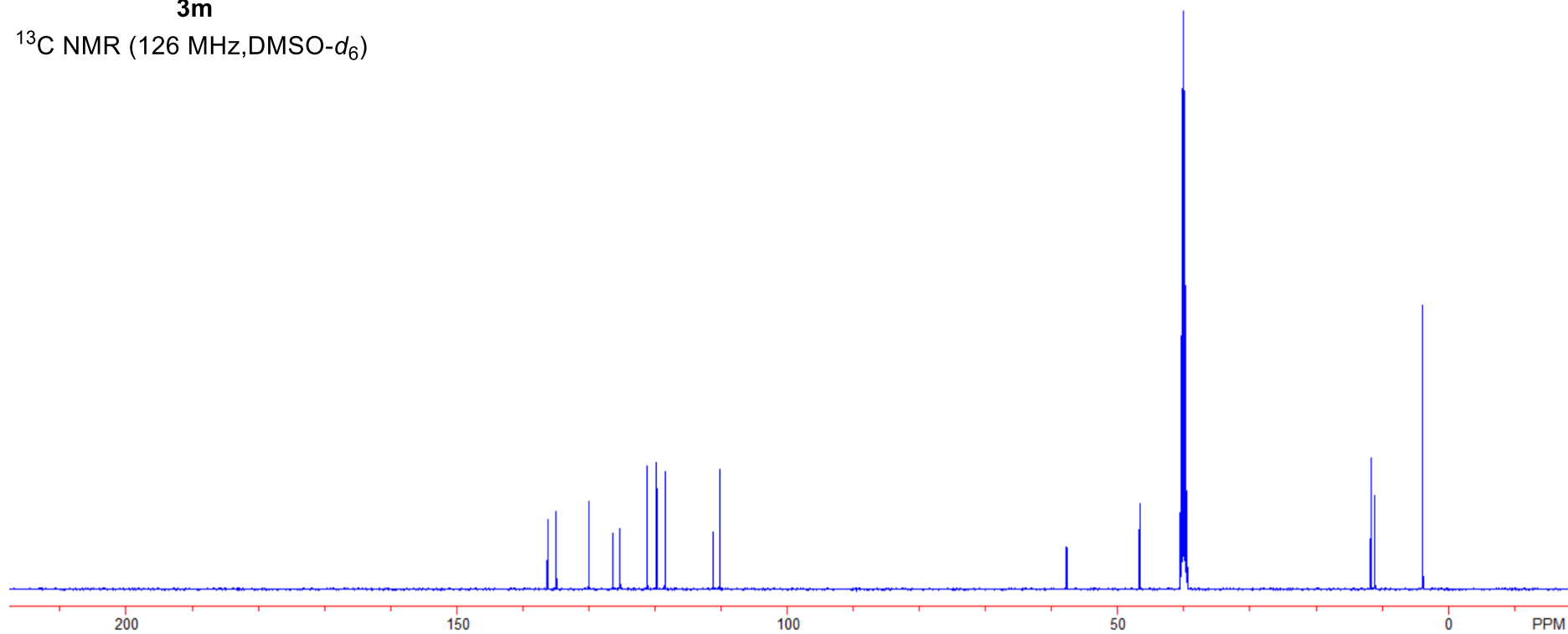
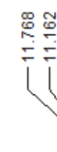
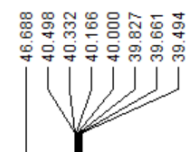
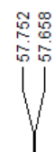
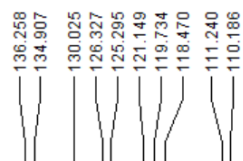
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

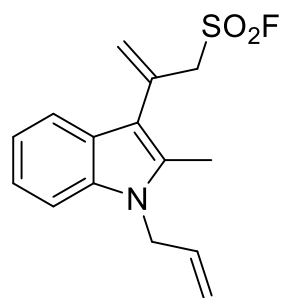




**3m**

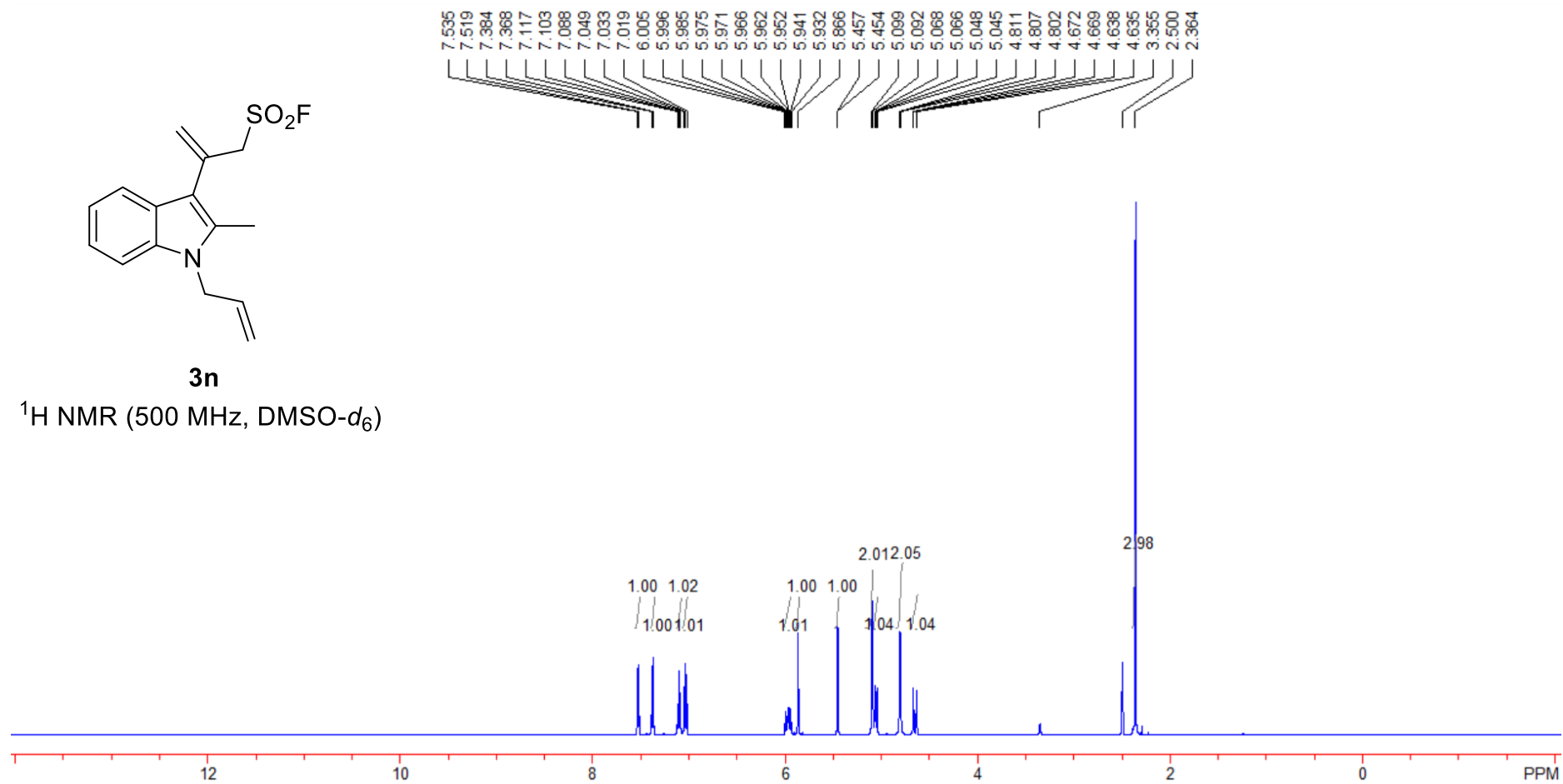
$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

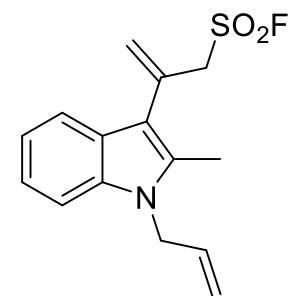




**3n**

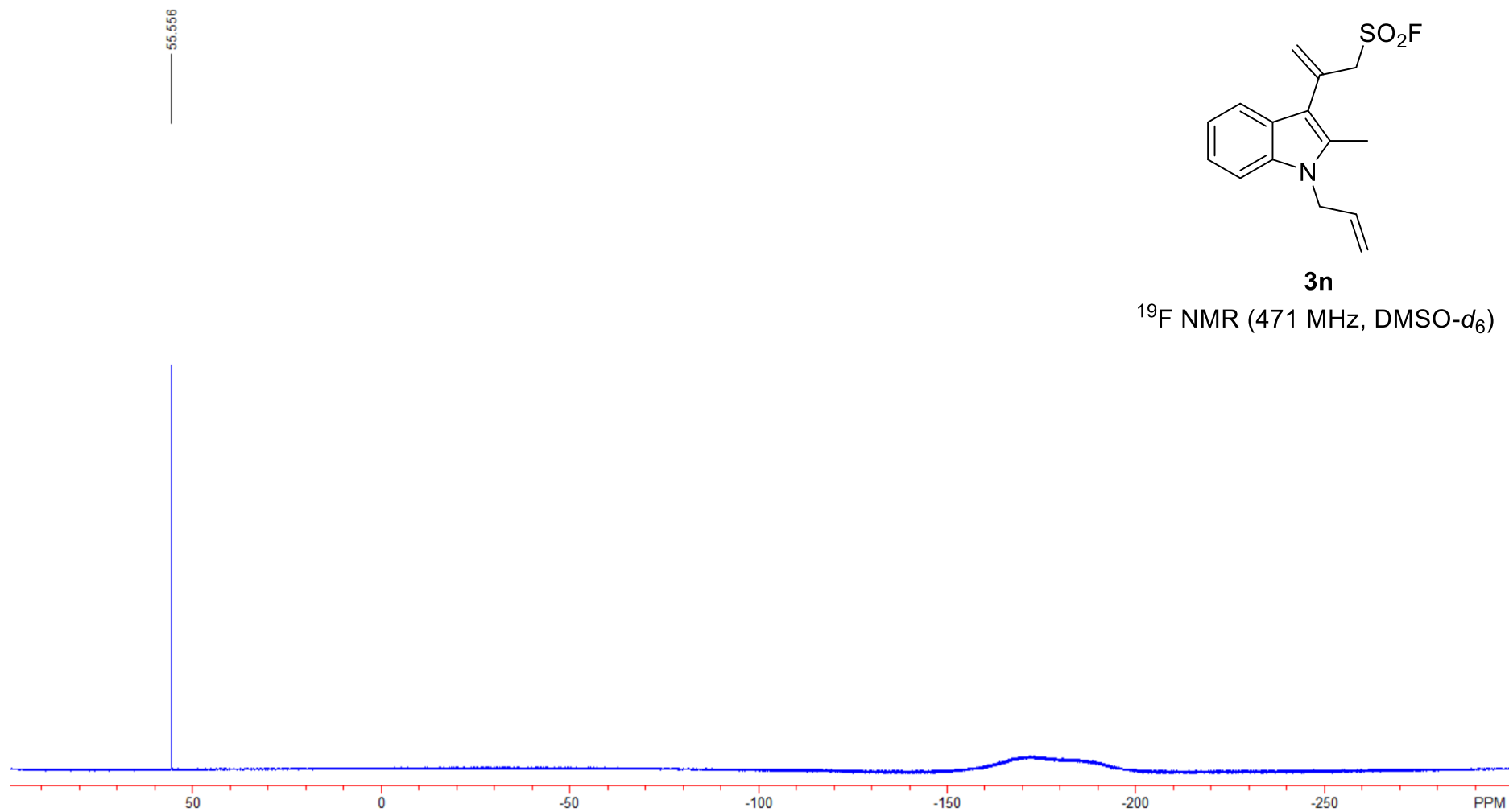
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )

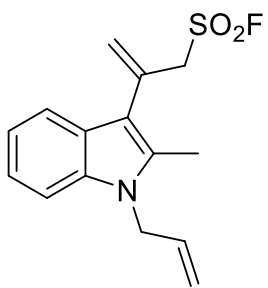




**3n**

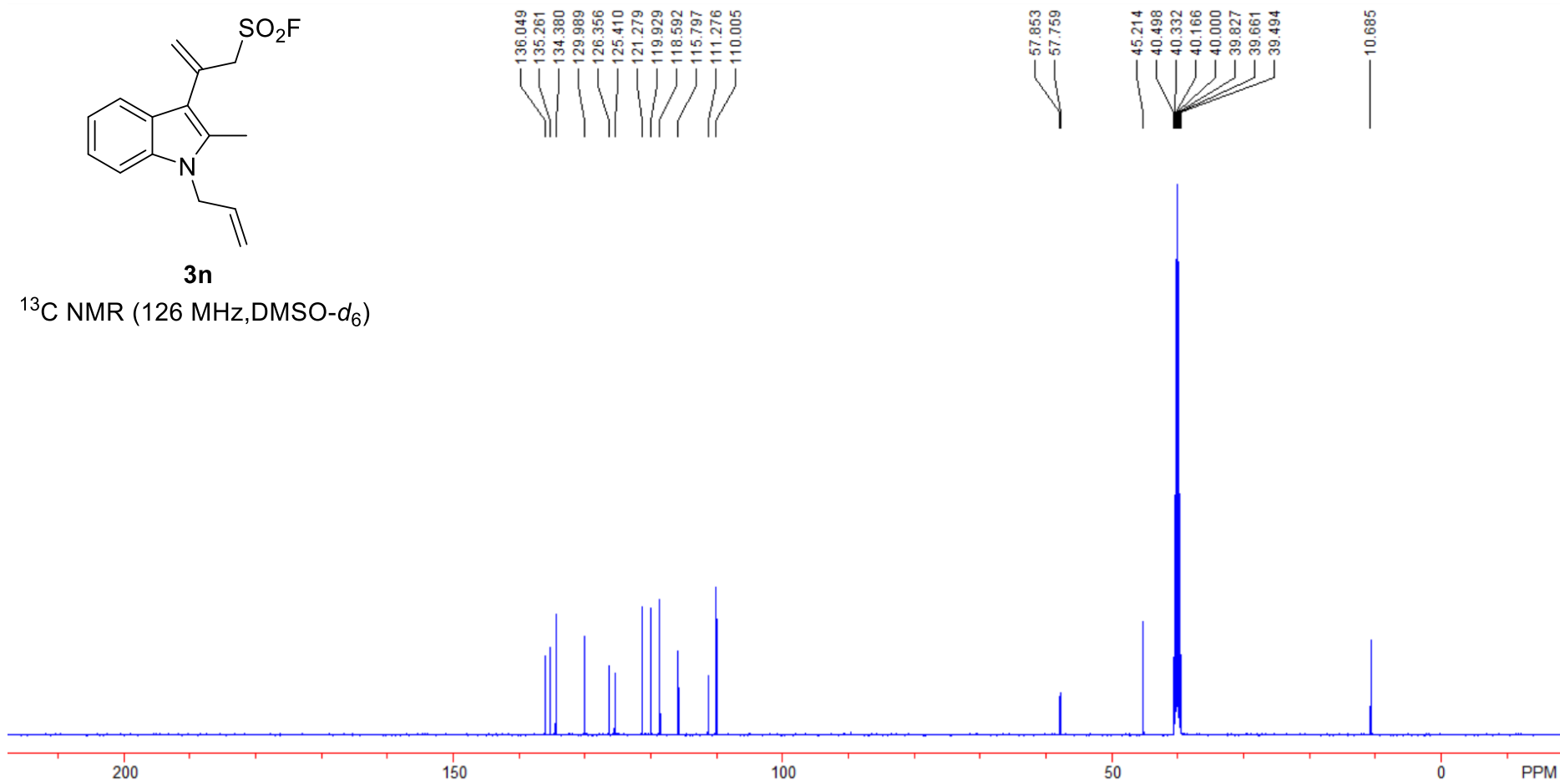
$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )



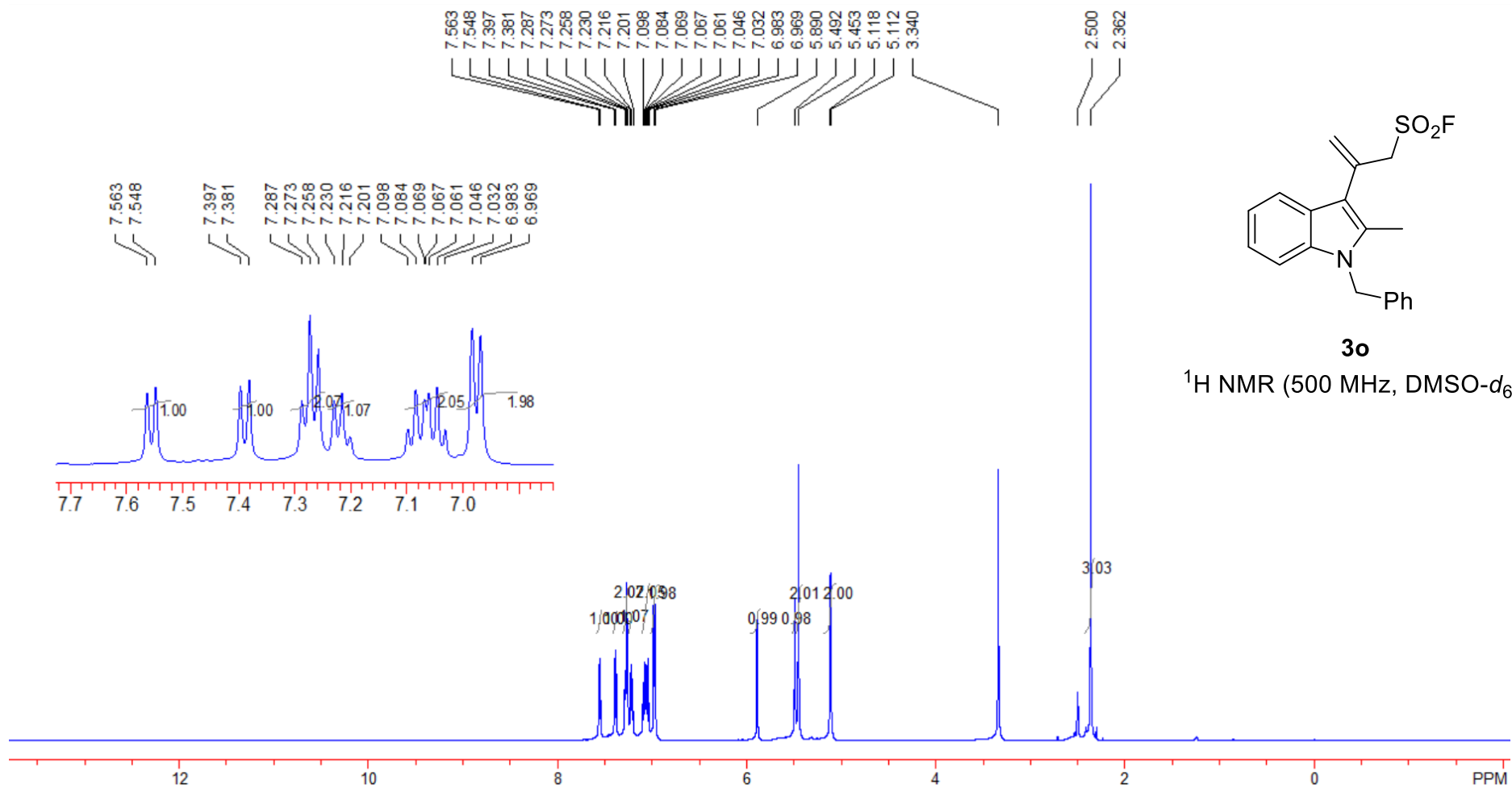


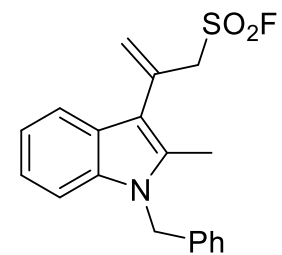
**3n**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )



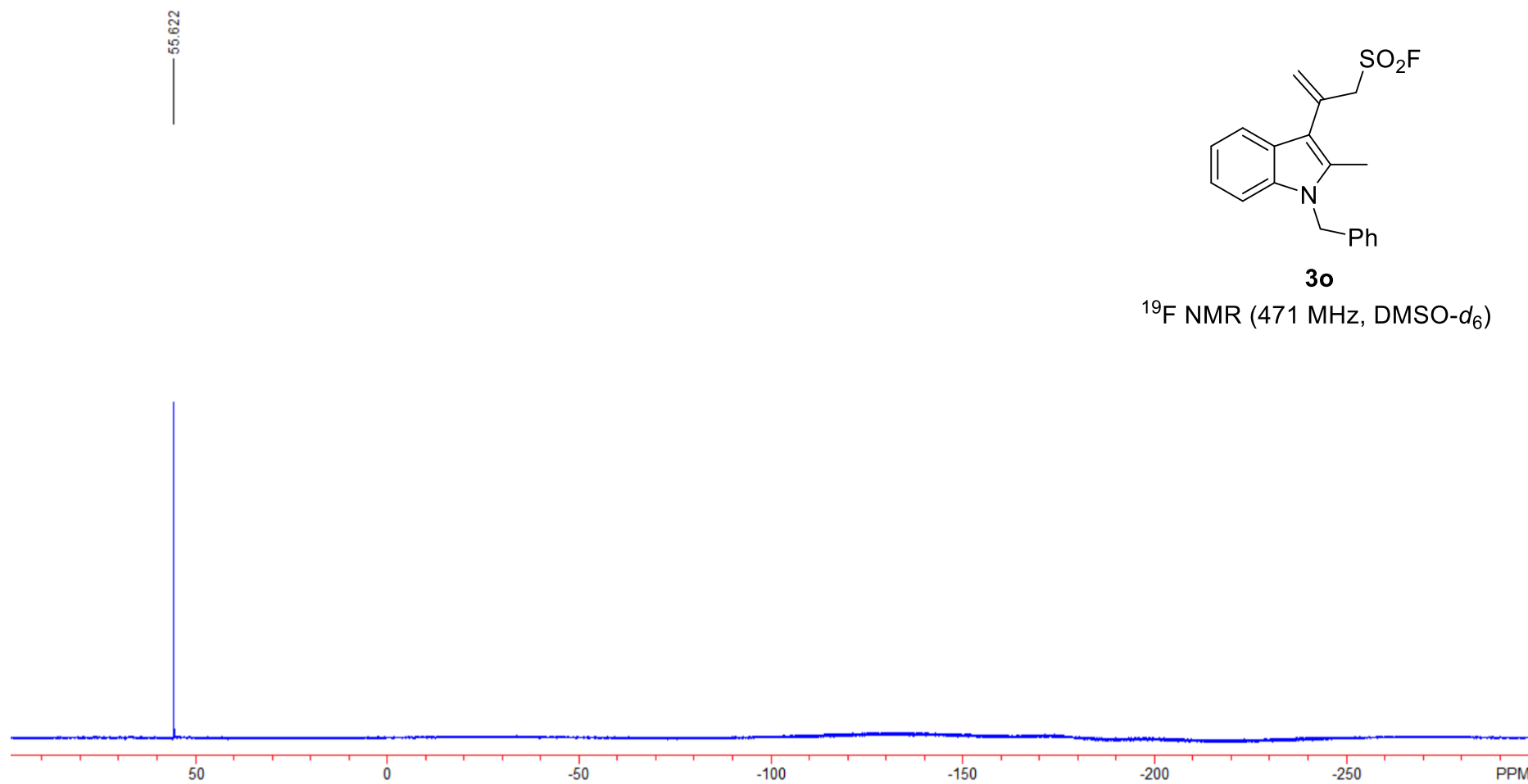


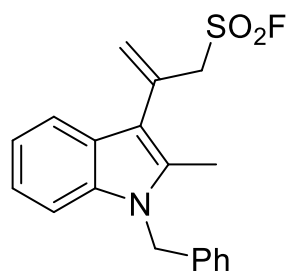




**3o**

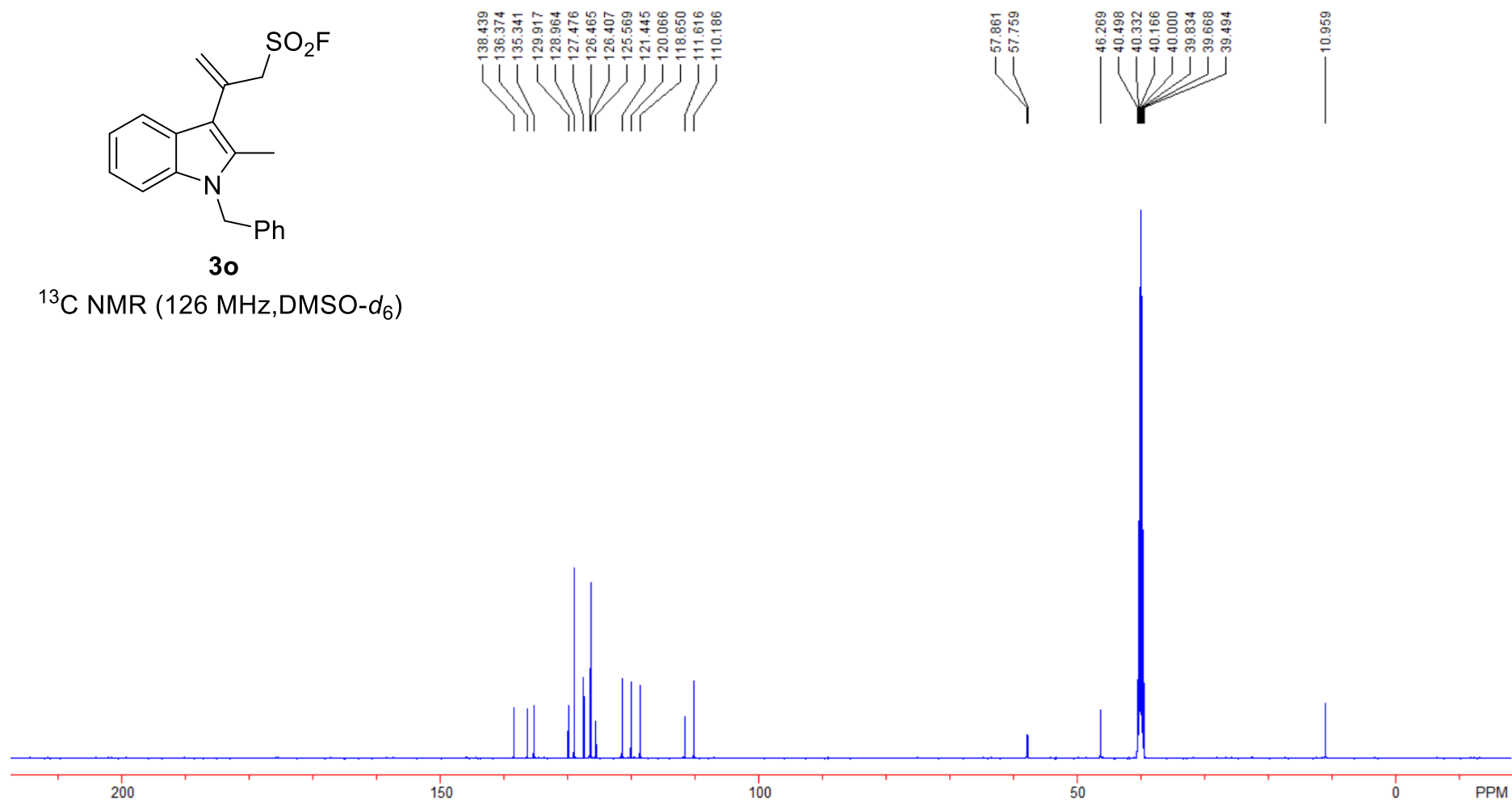
$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

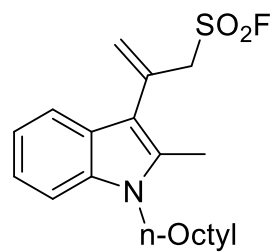




**3o**

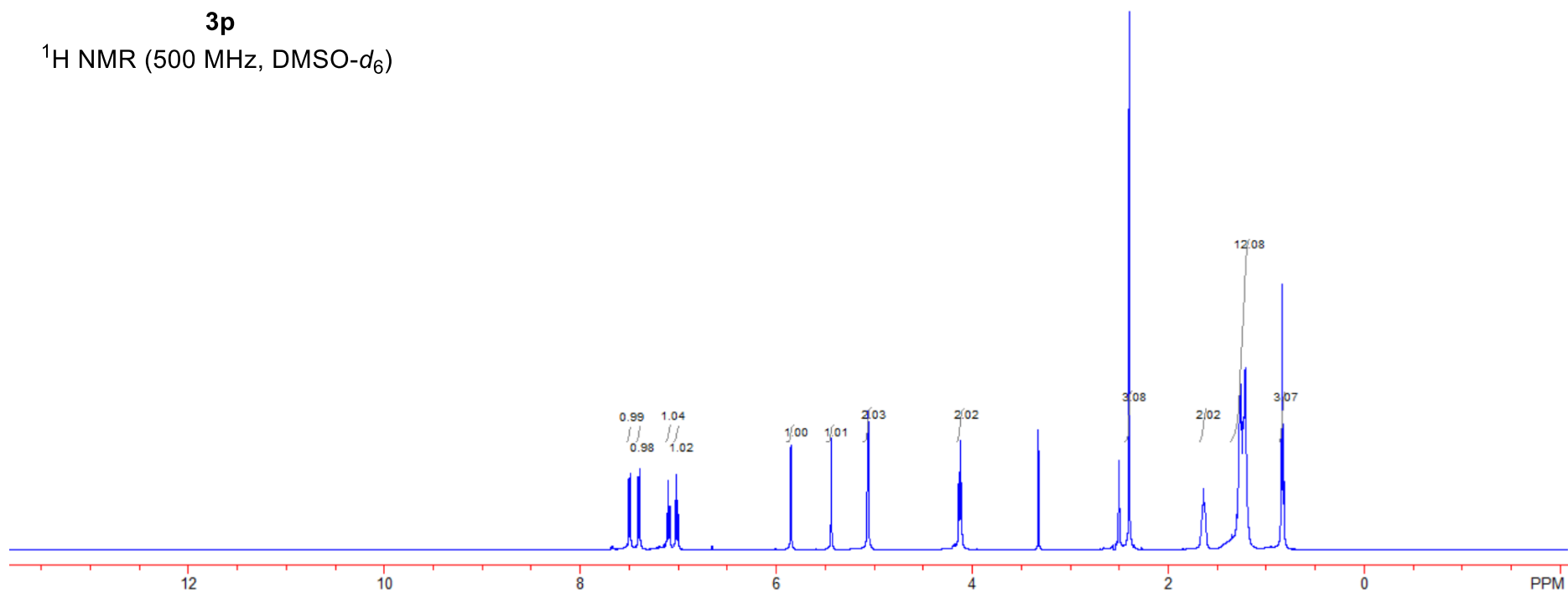
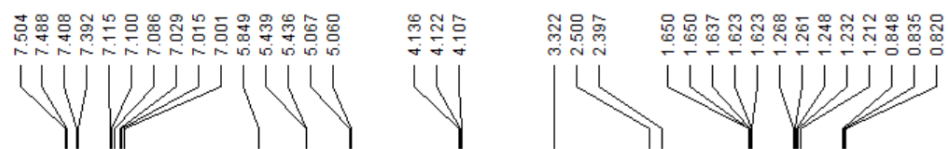
$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )



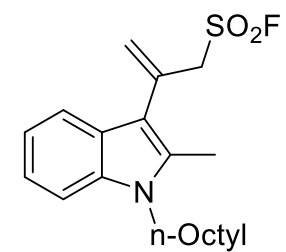


**3p**

$^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )

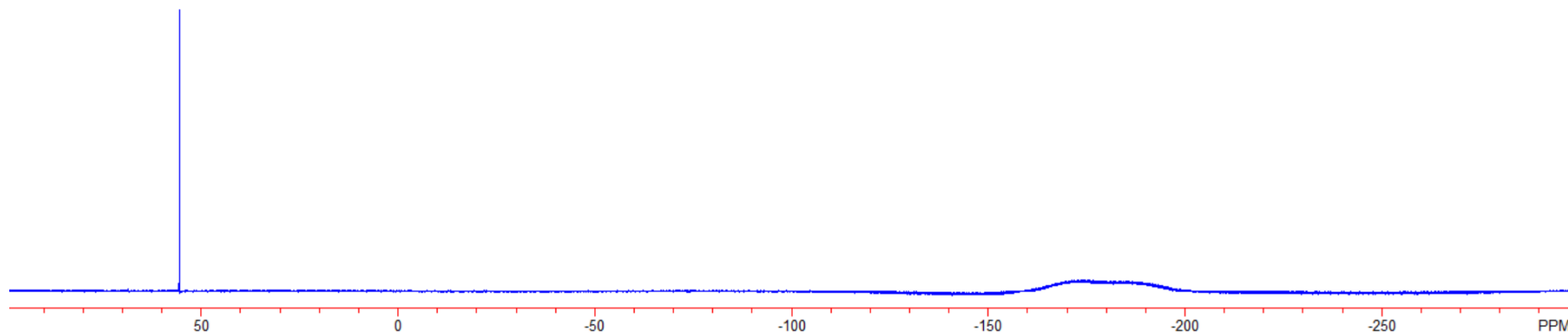


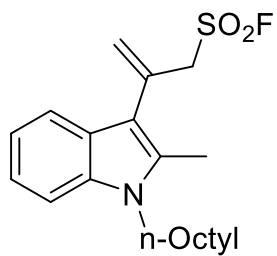
55.531



**3p**

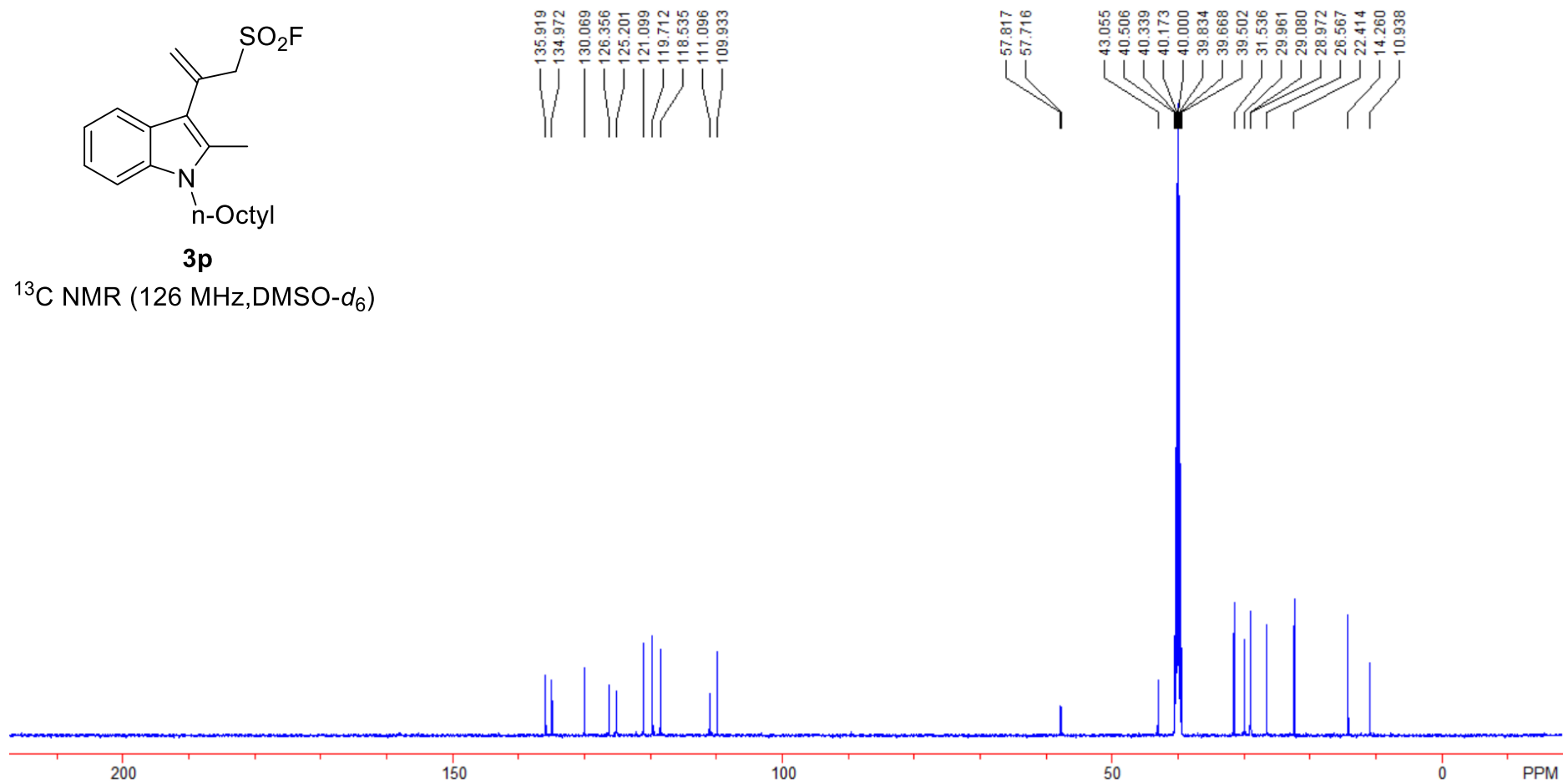
$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

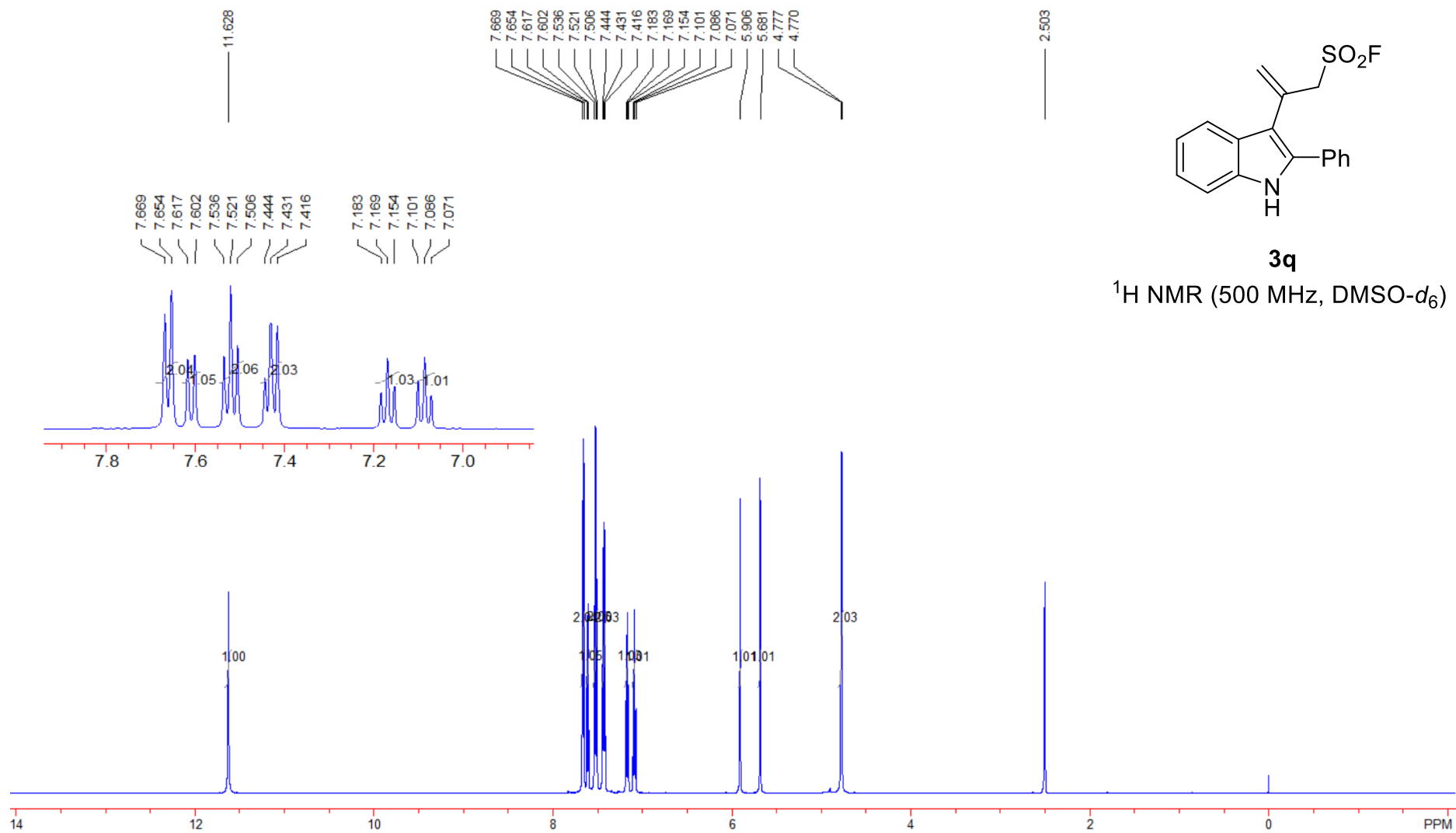


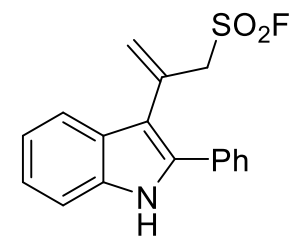


**3p**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

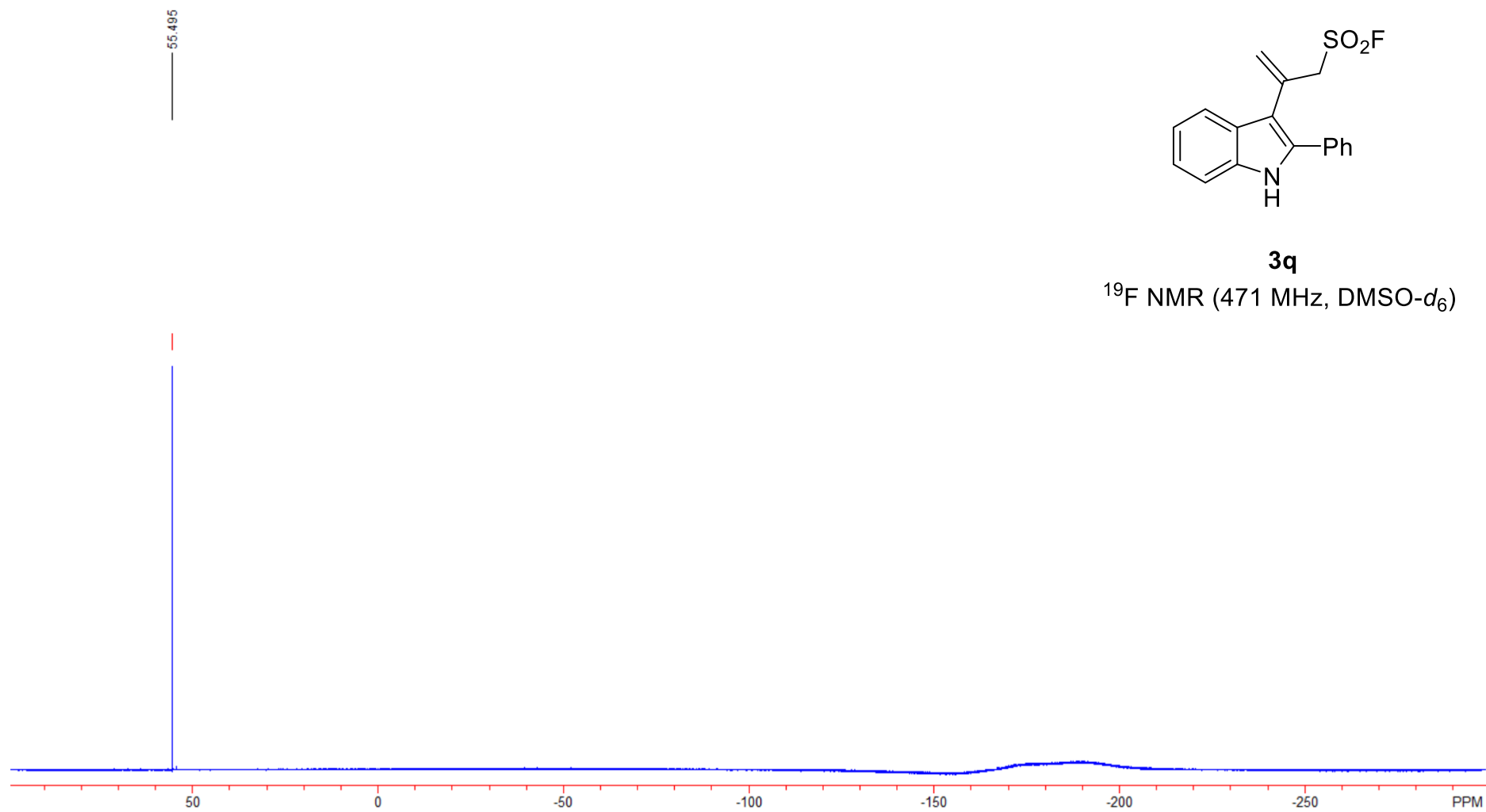




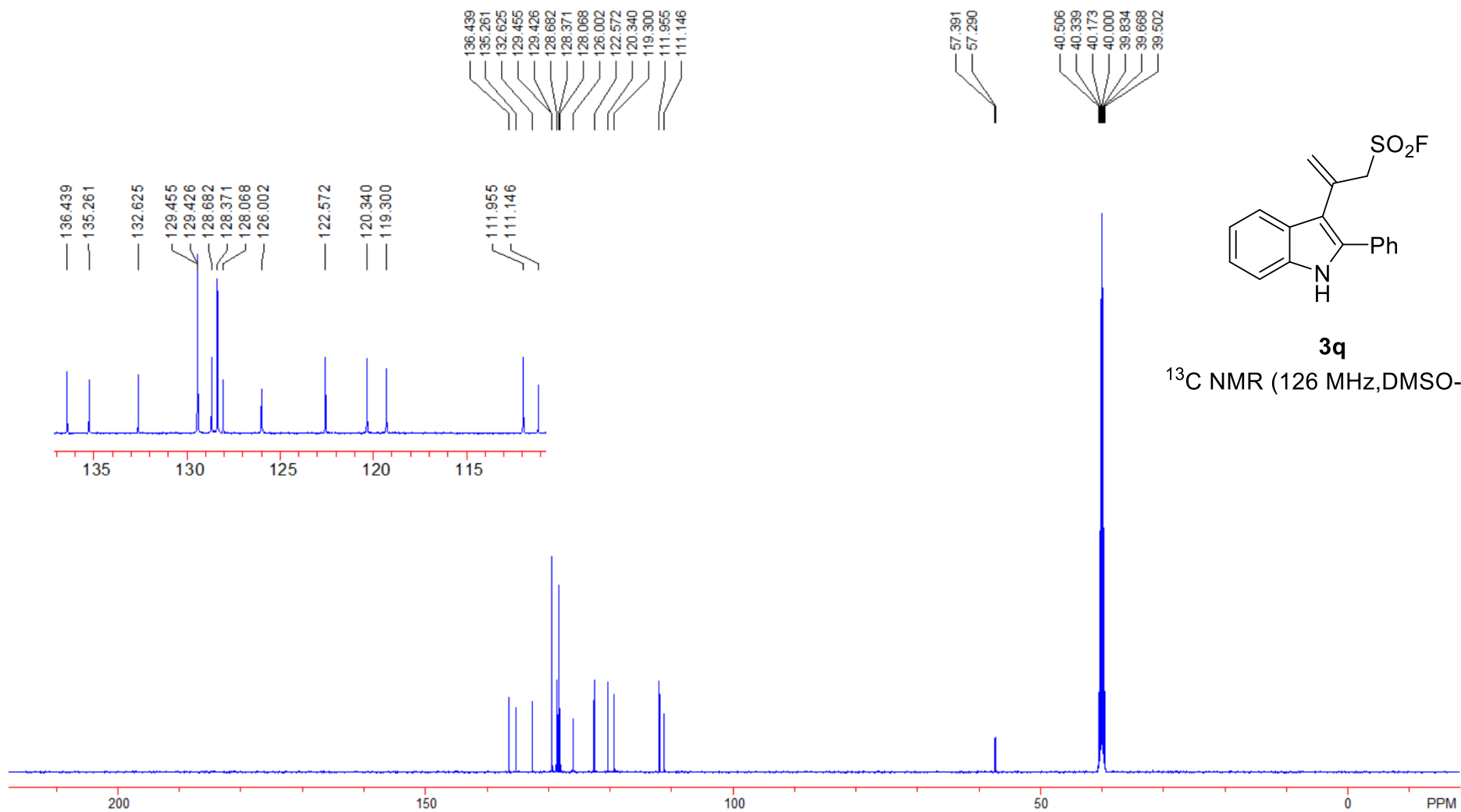


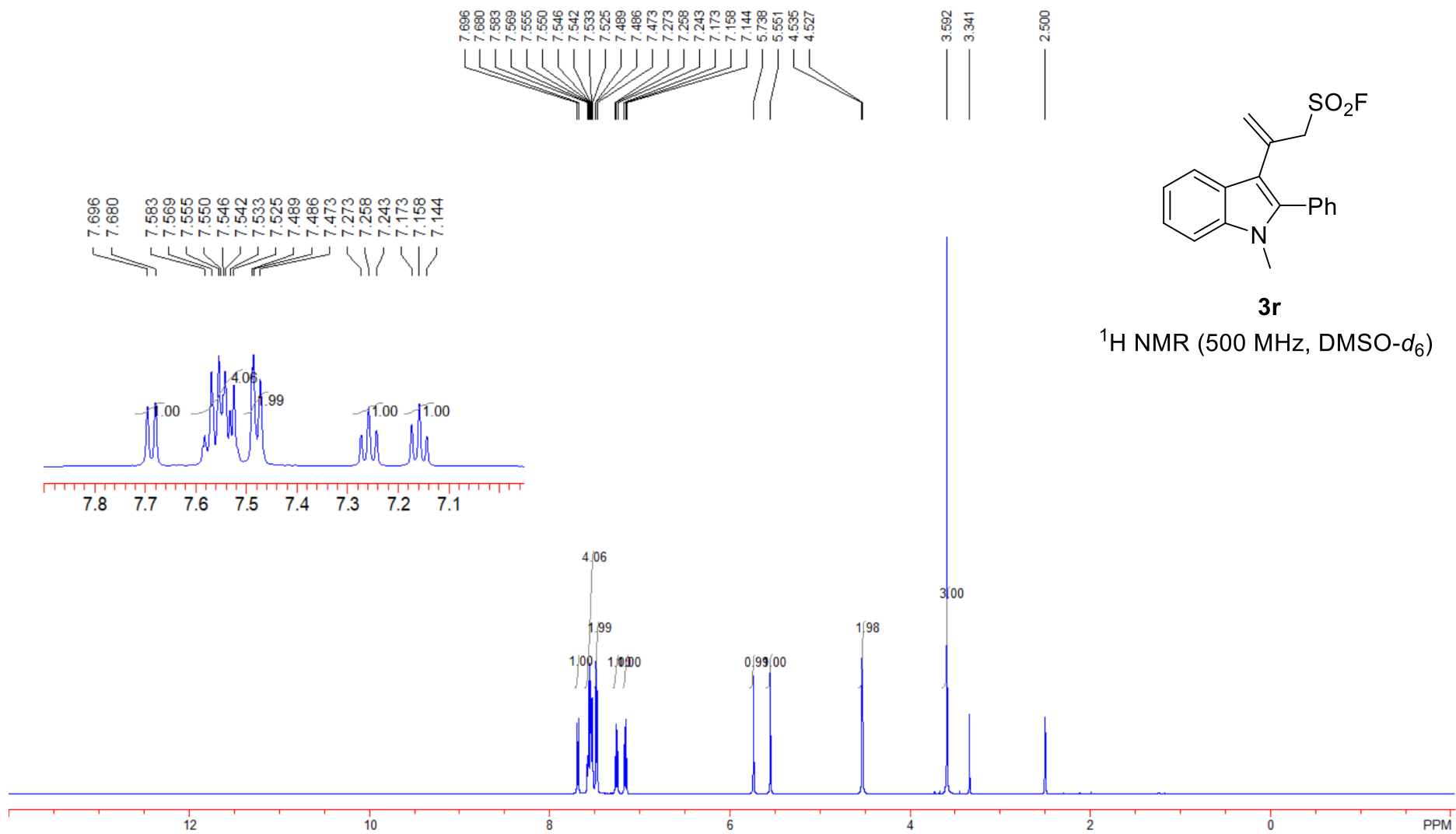
**3q**

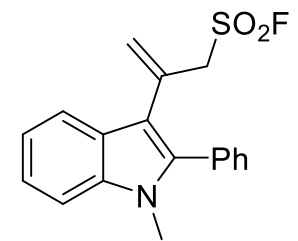
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)







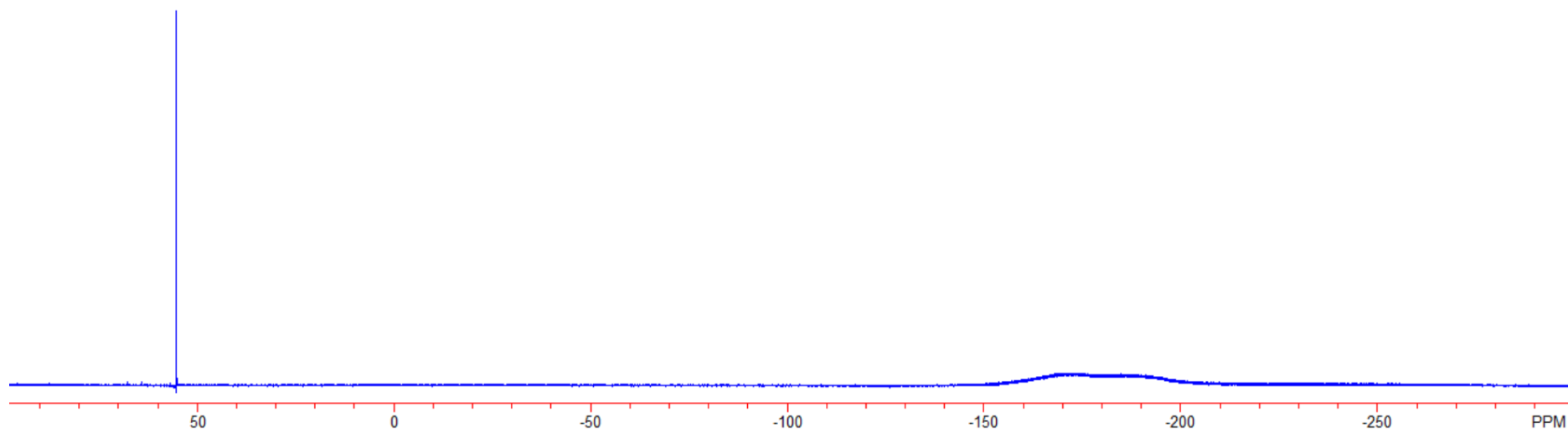


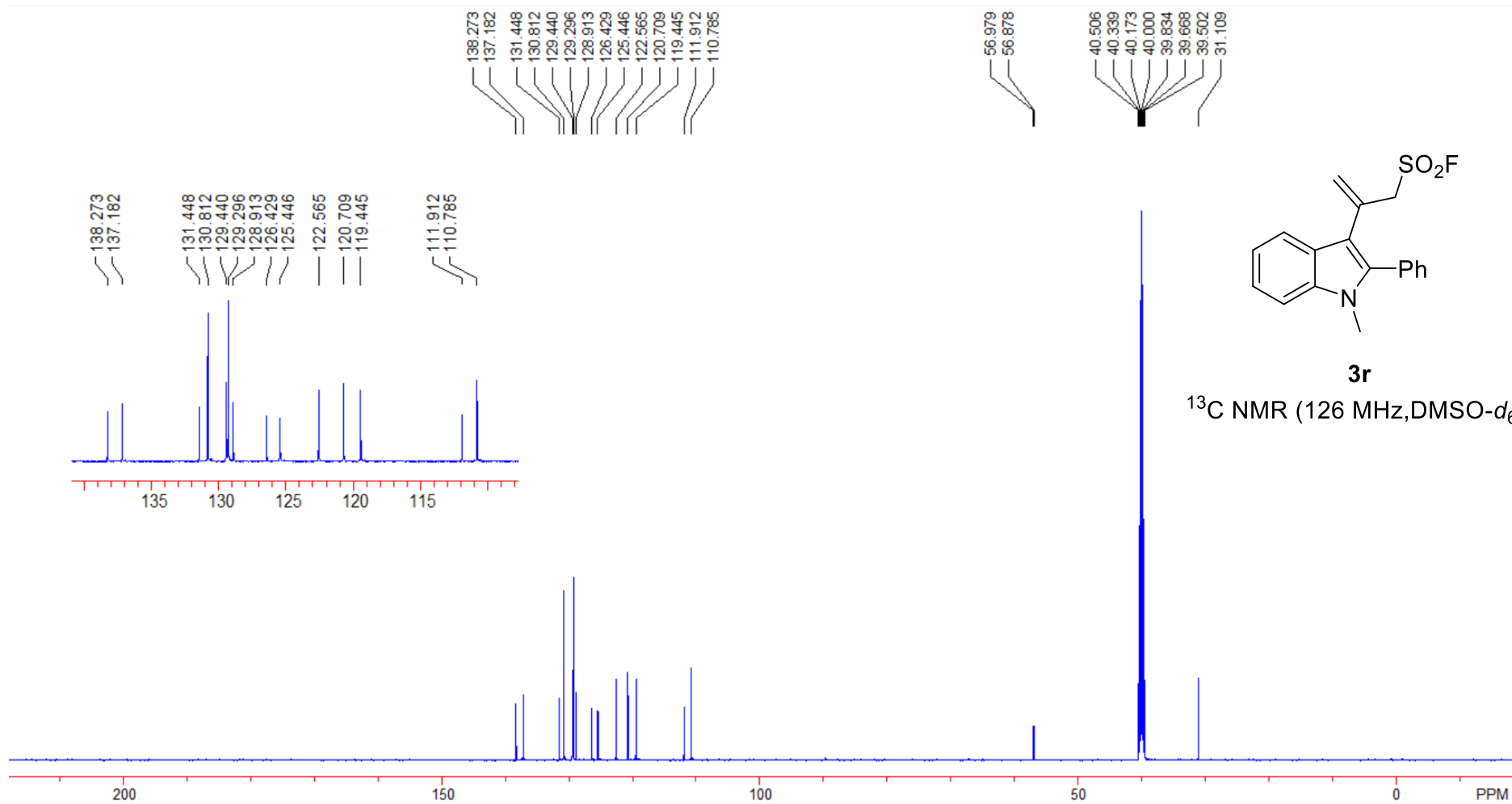


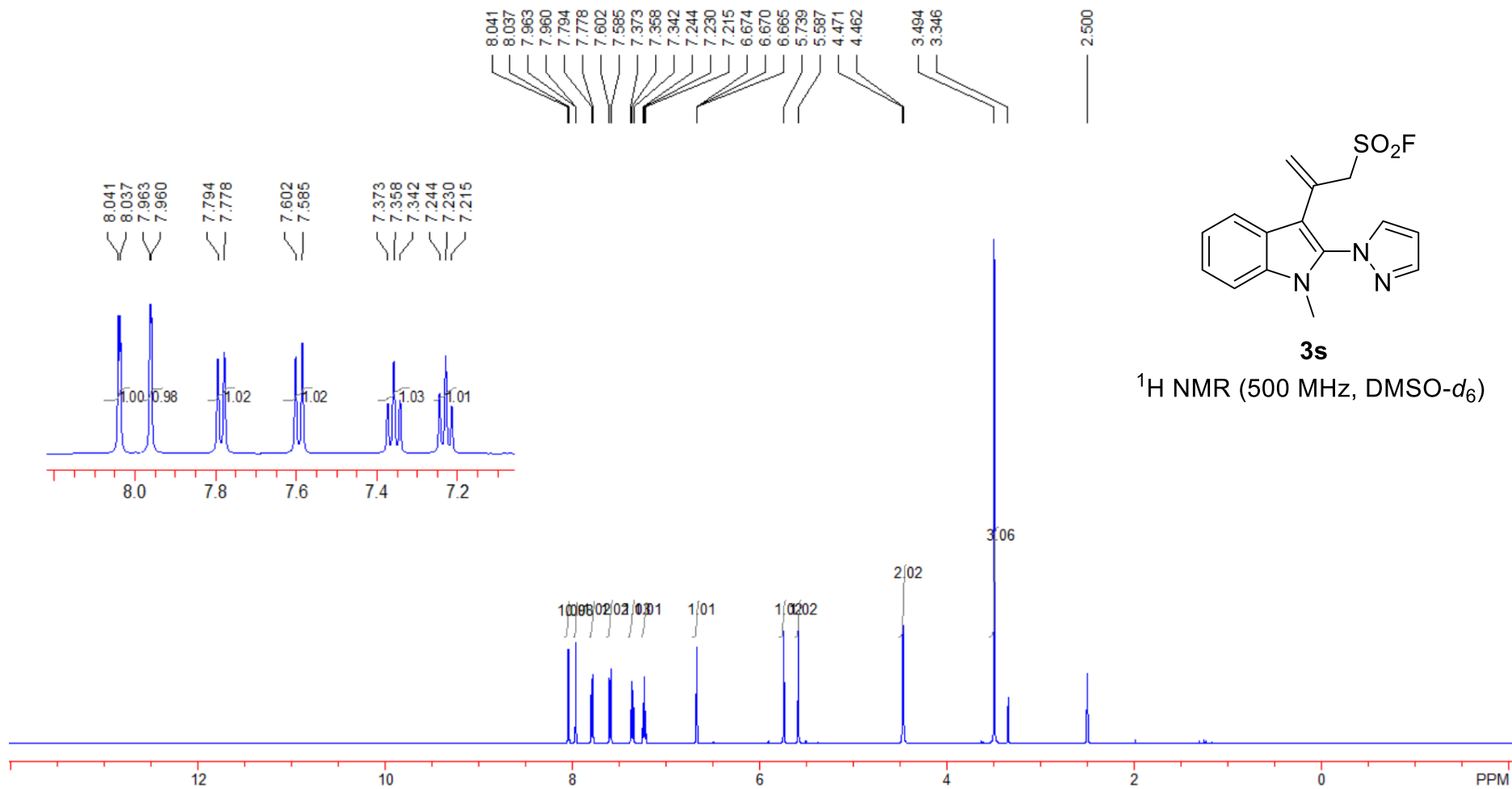
**3r**

$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

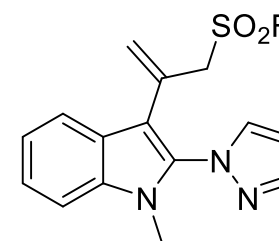
55.288





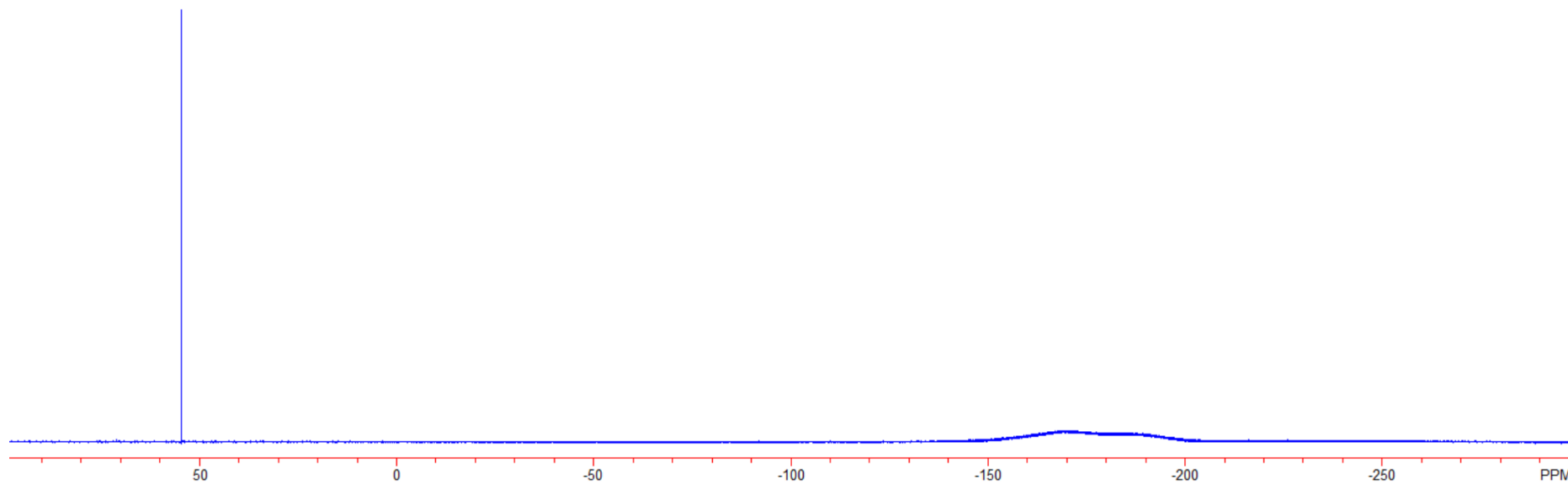


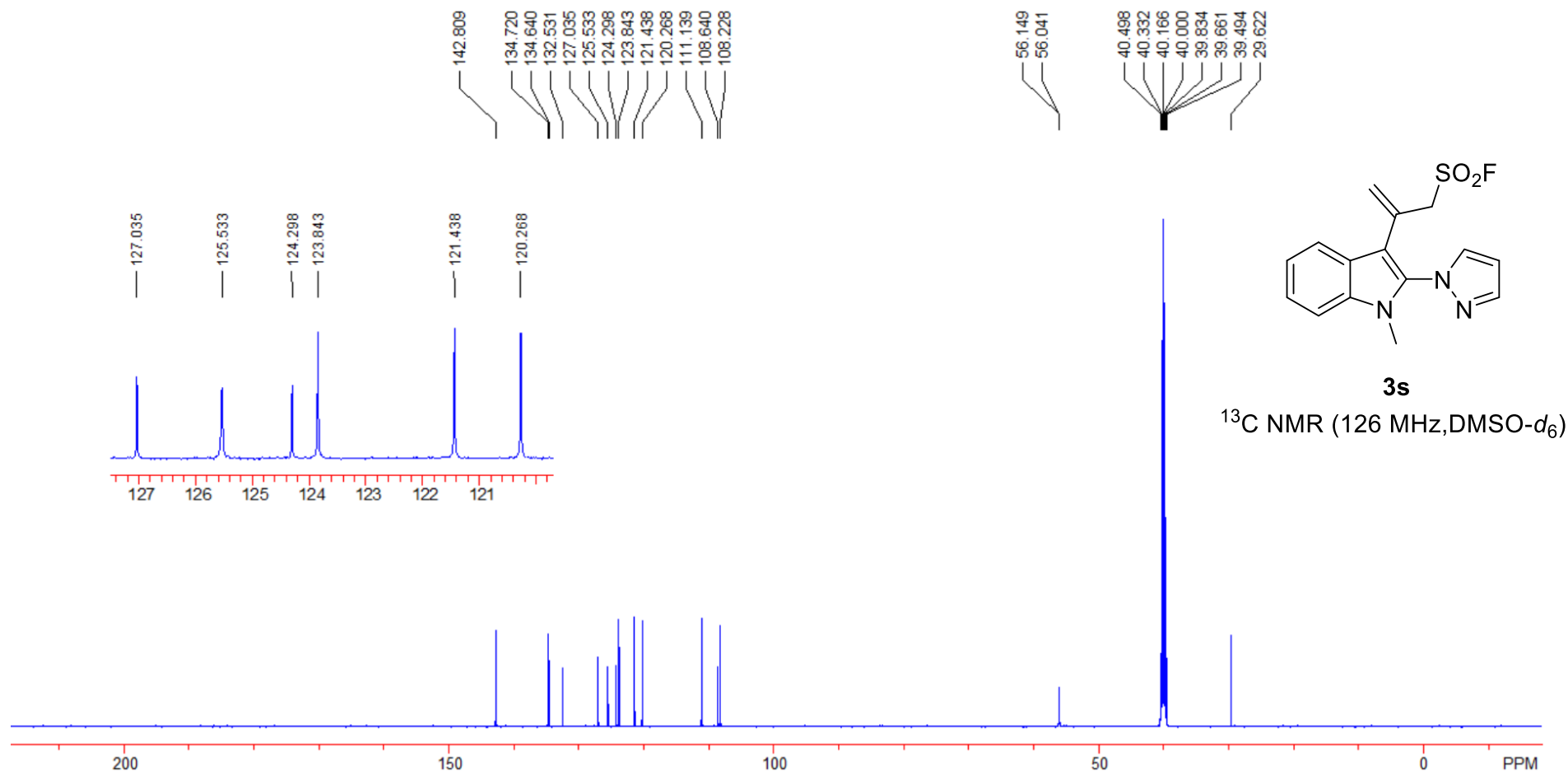
54.5883

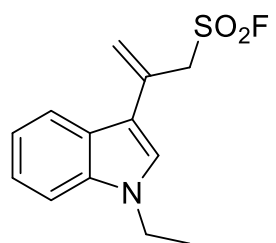


**3s**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

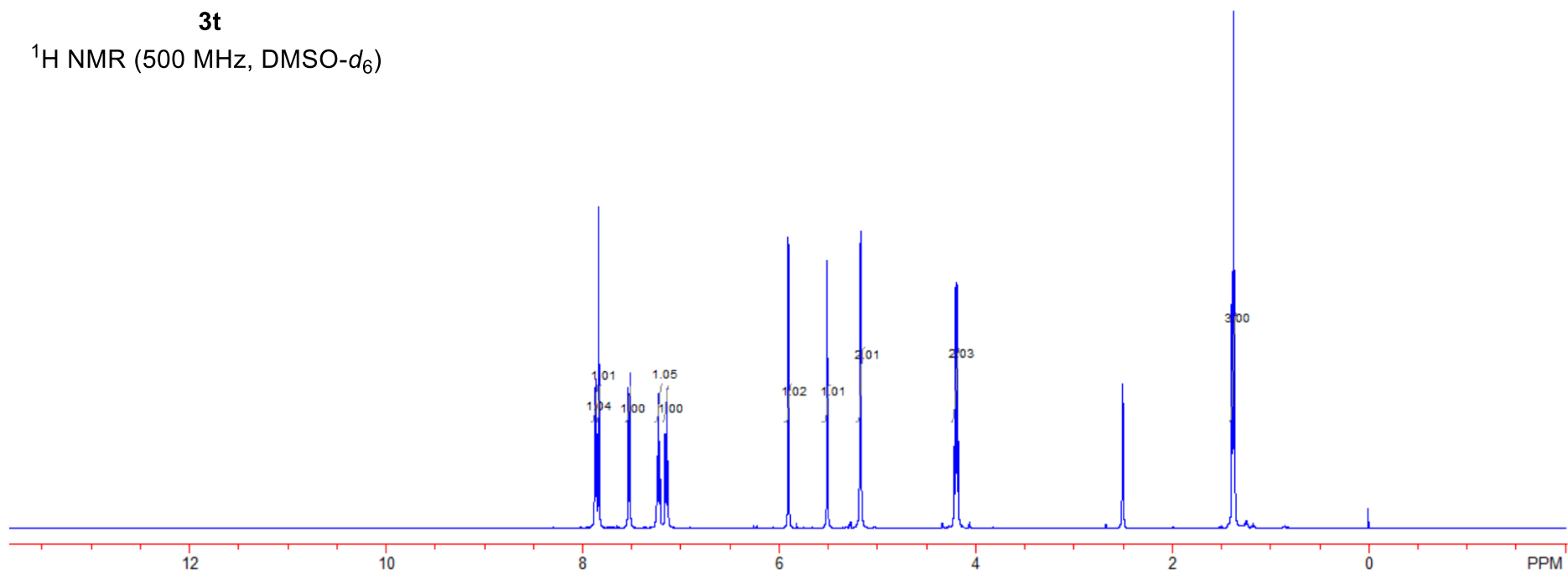
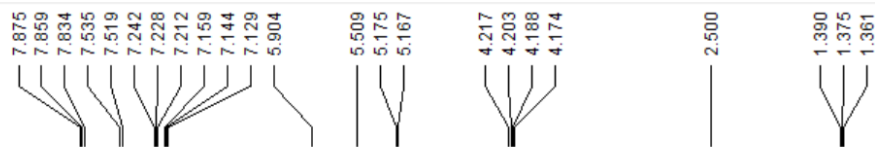




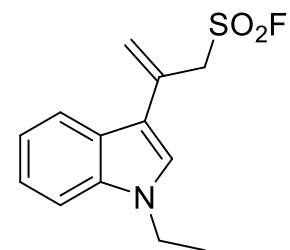


**3t**

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )

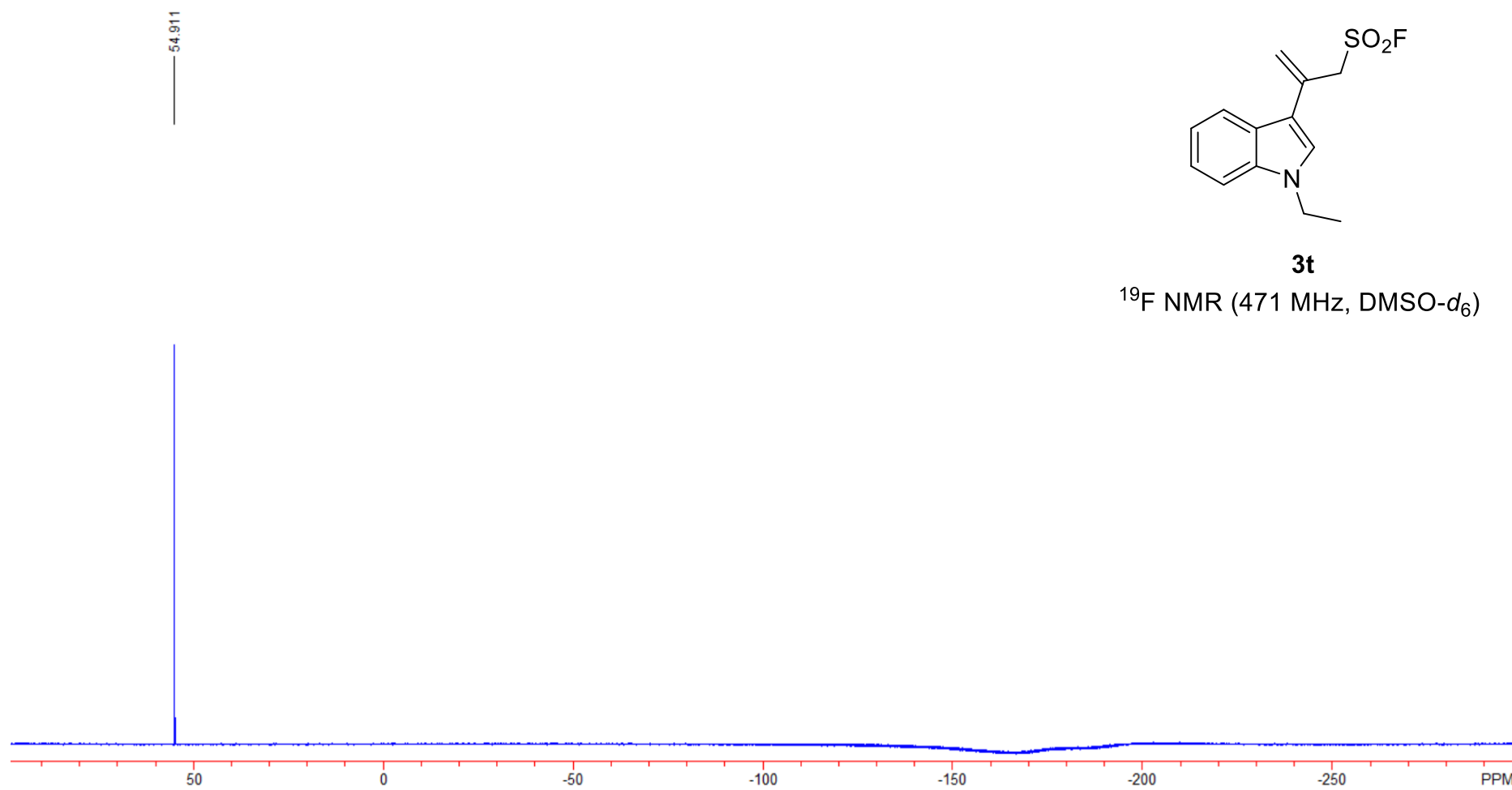


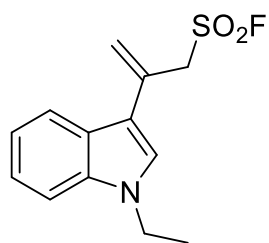




**3t**

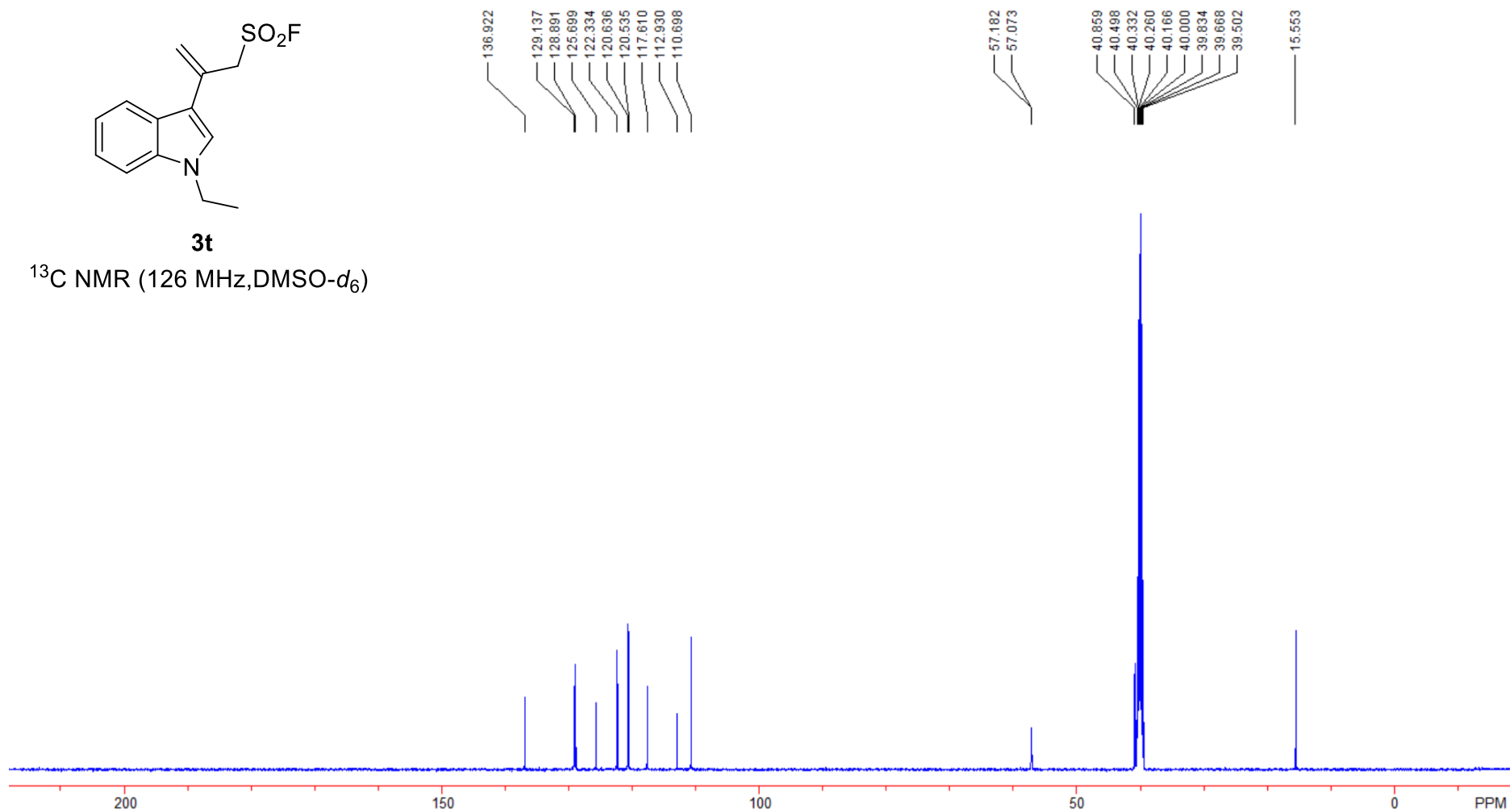
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

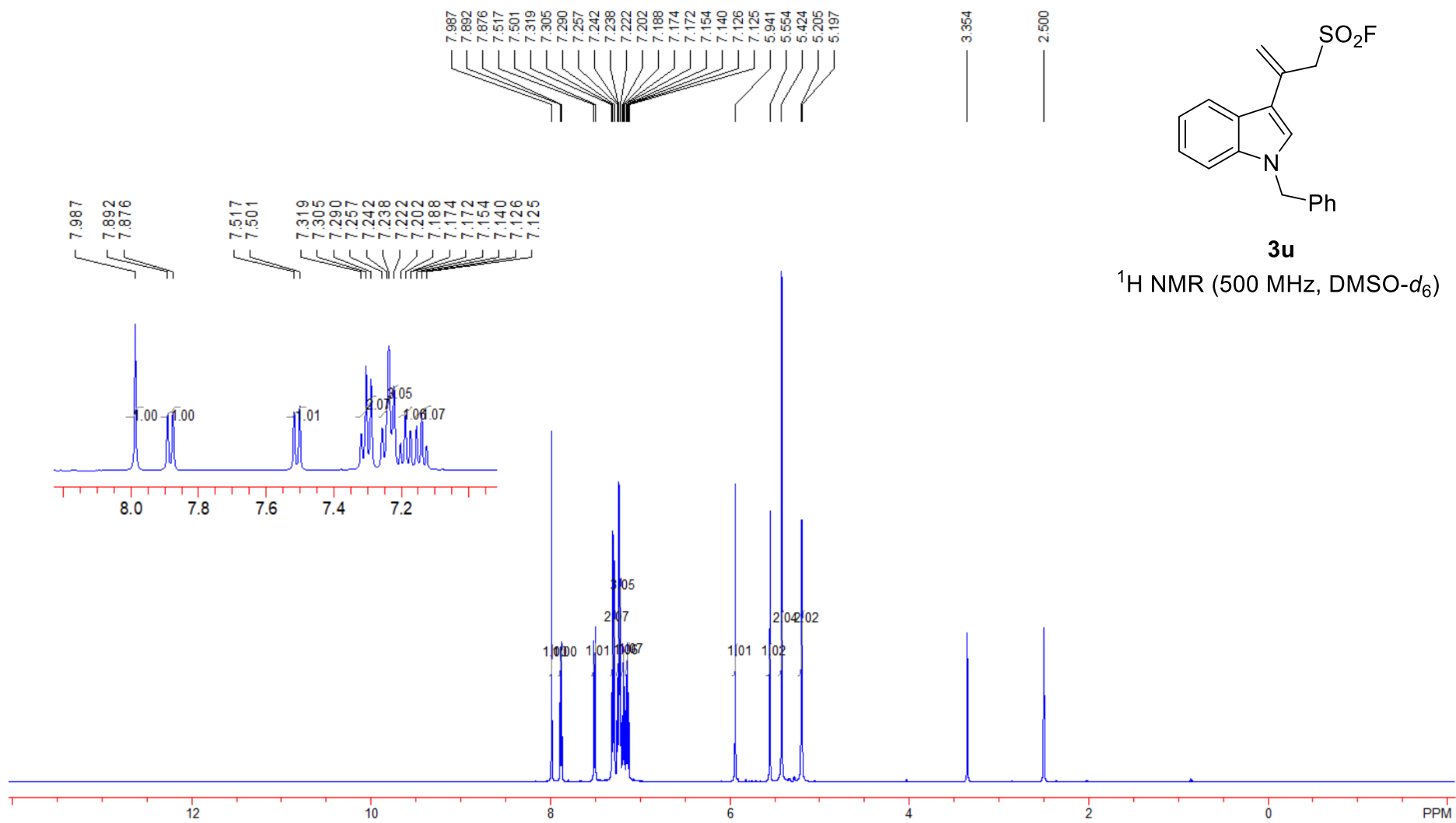


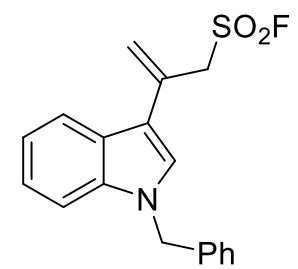


**3t**

<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)

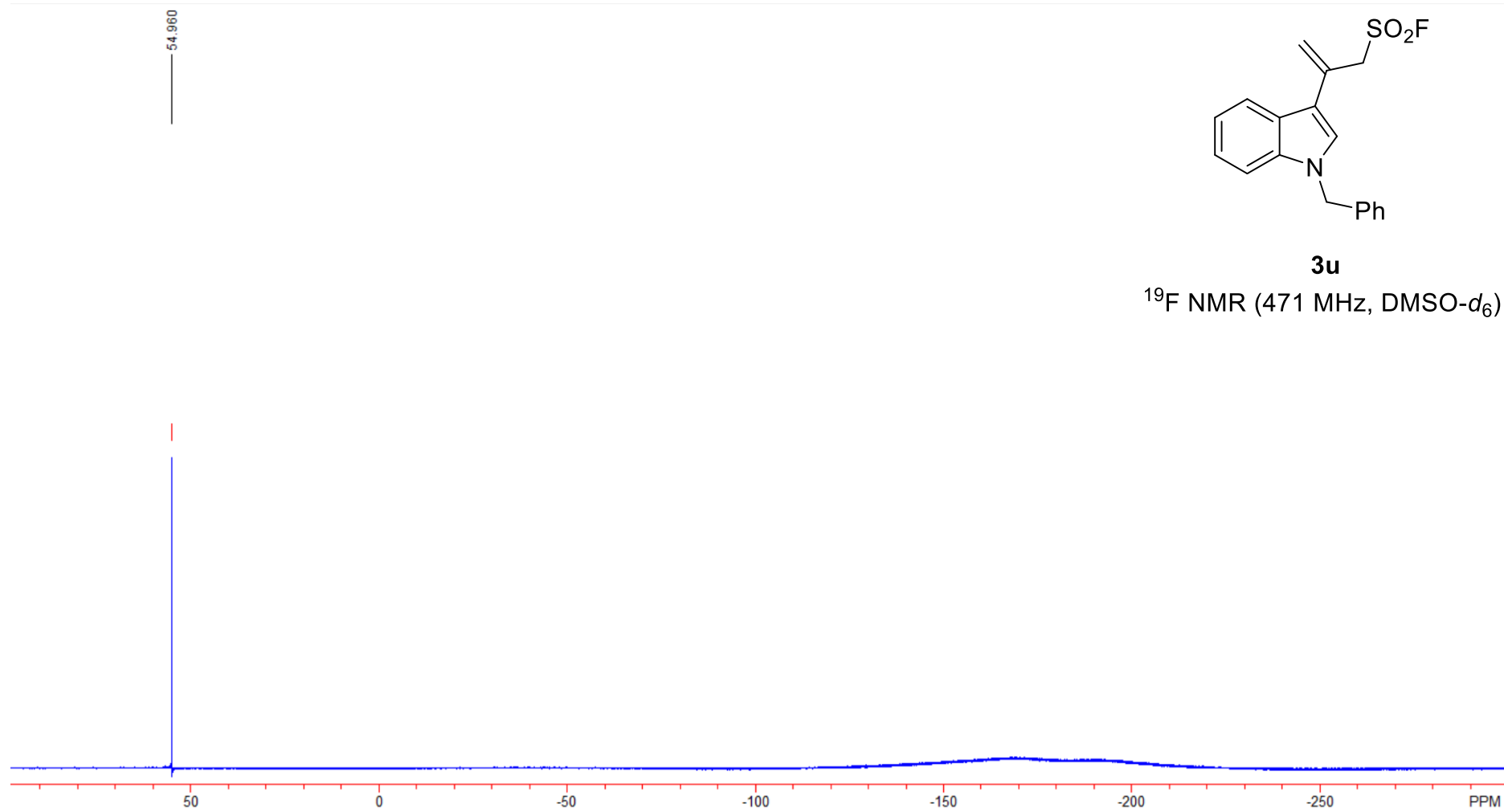


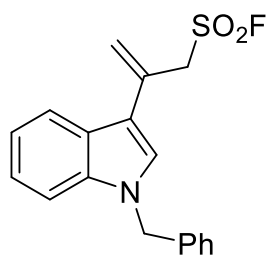




**3u**

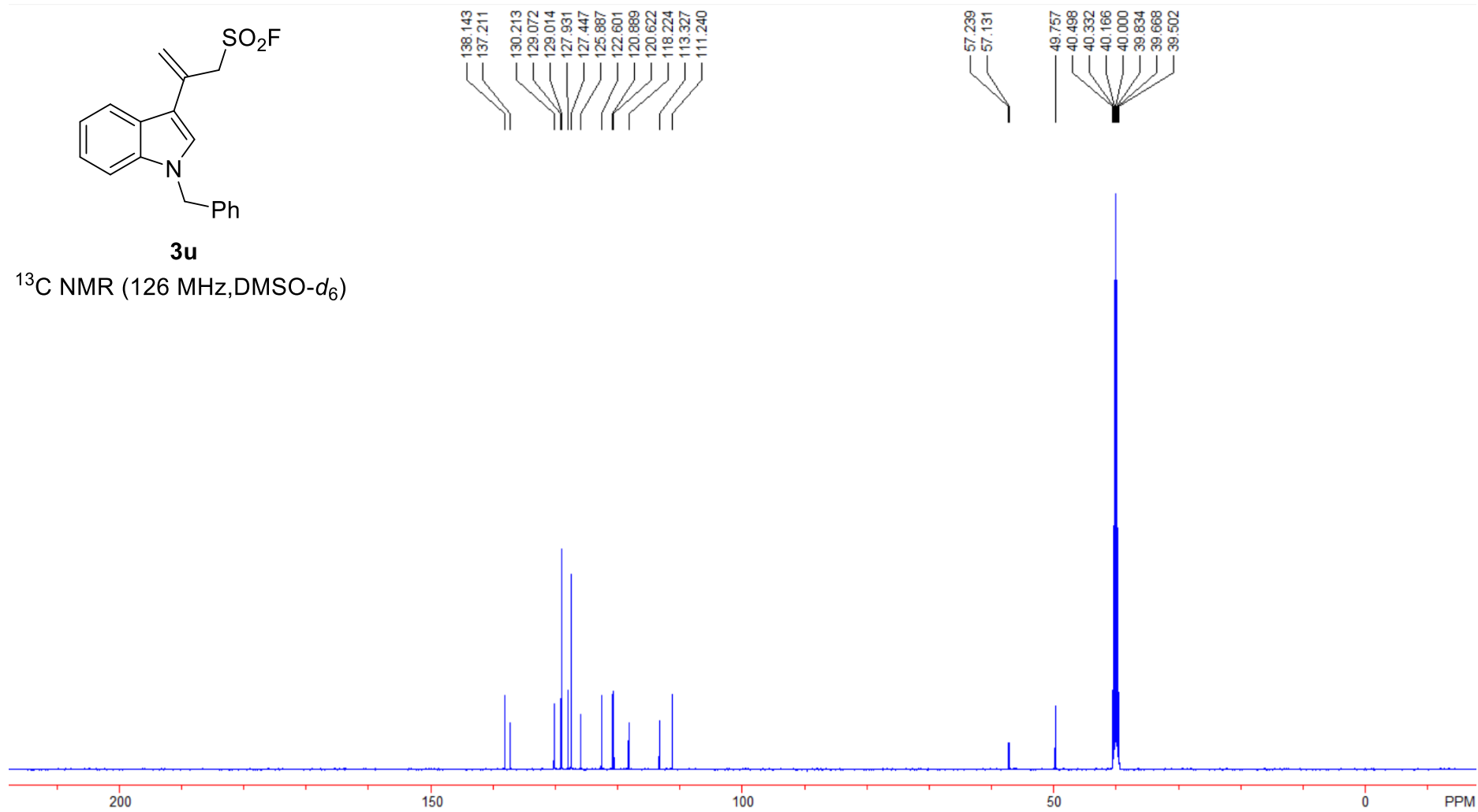
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

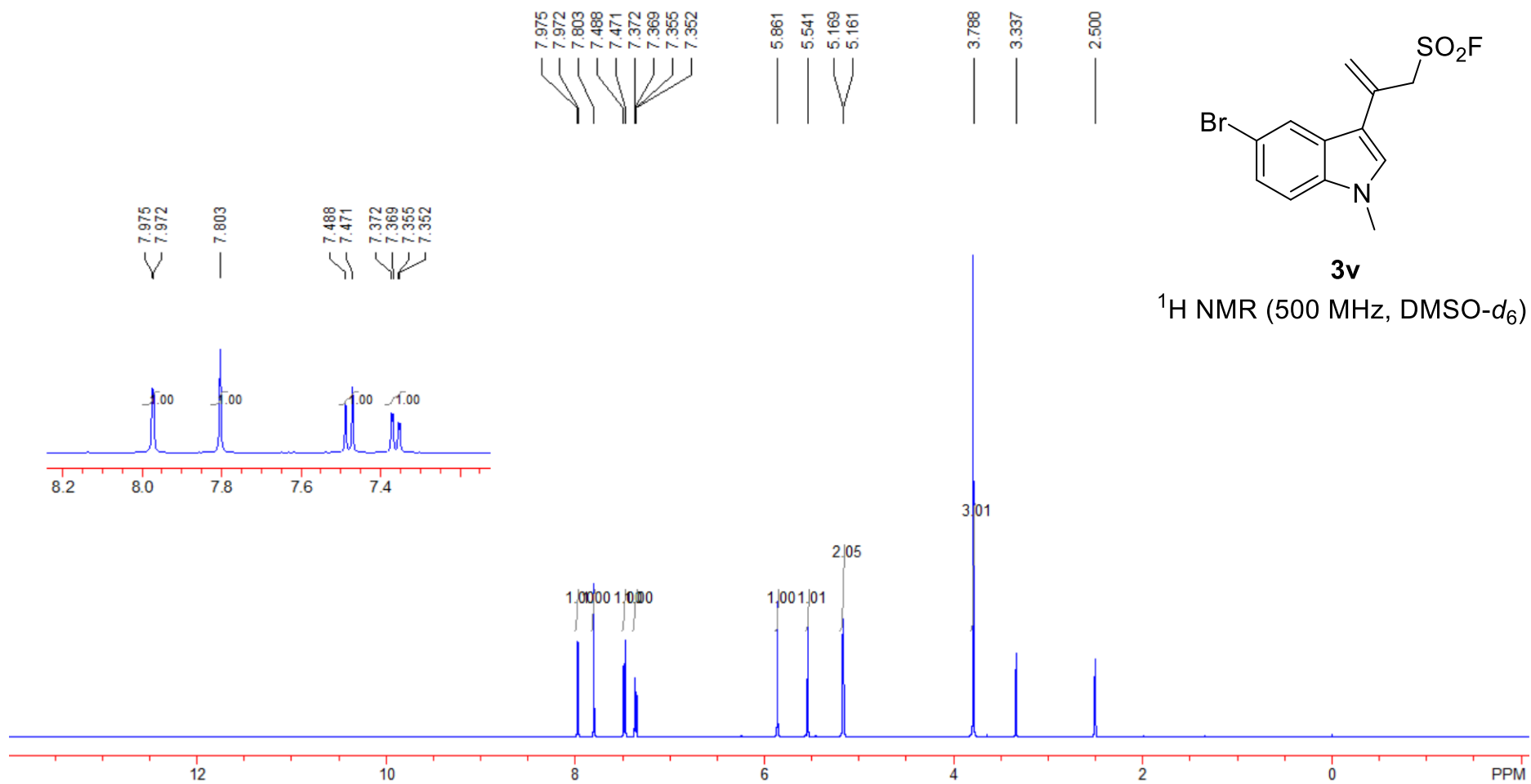


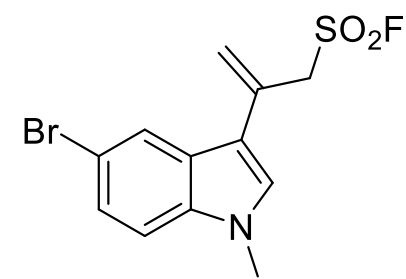


**3u**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )



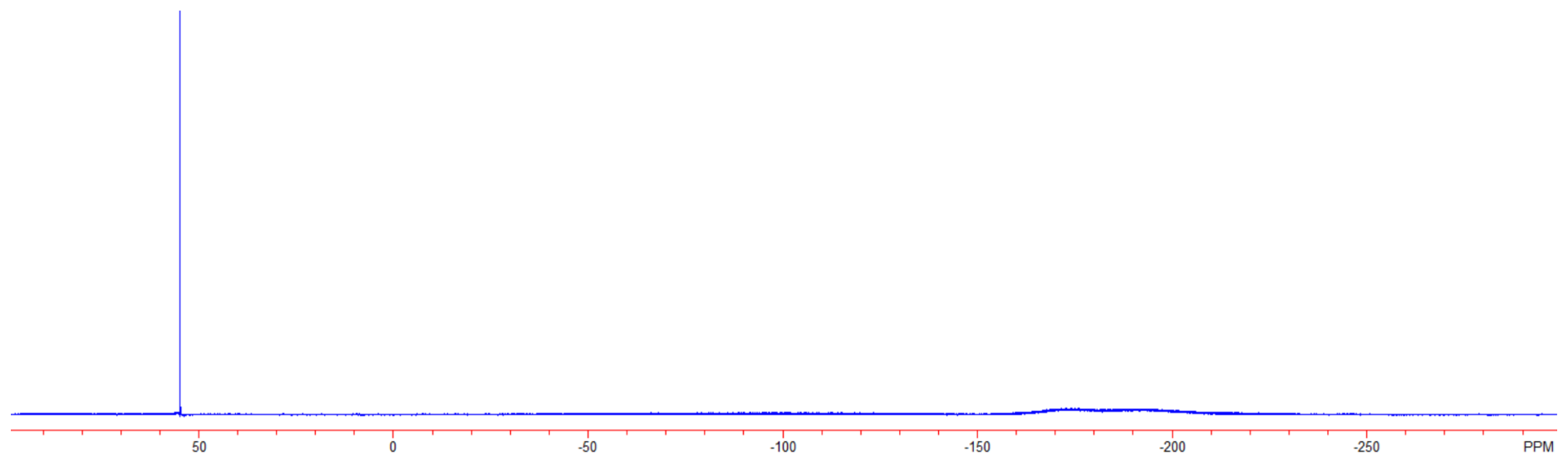


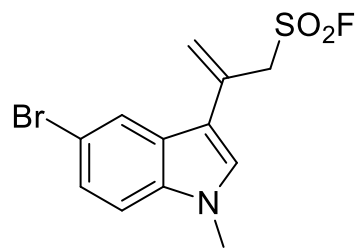


**3v**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

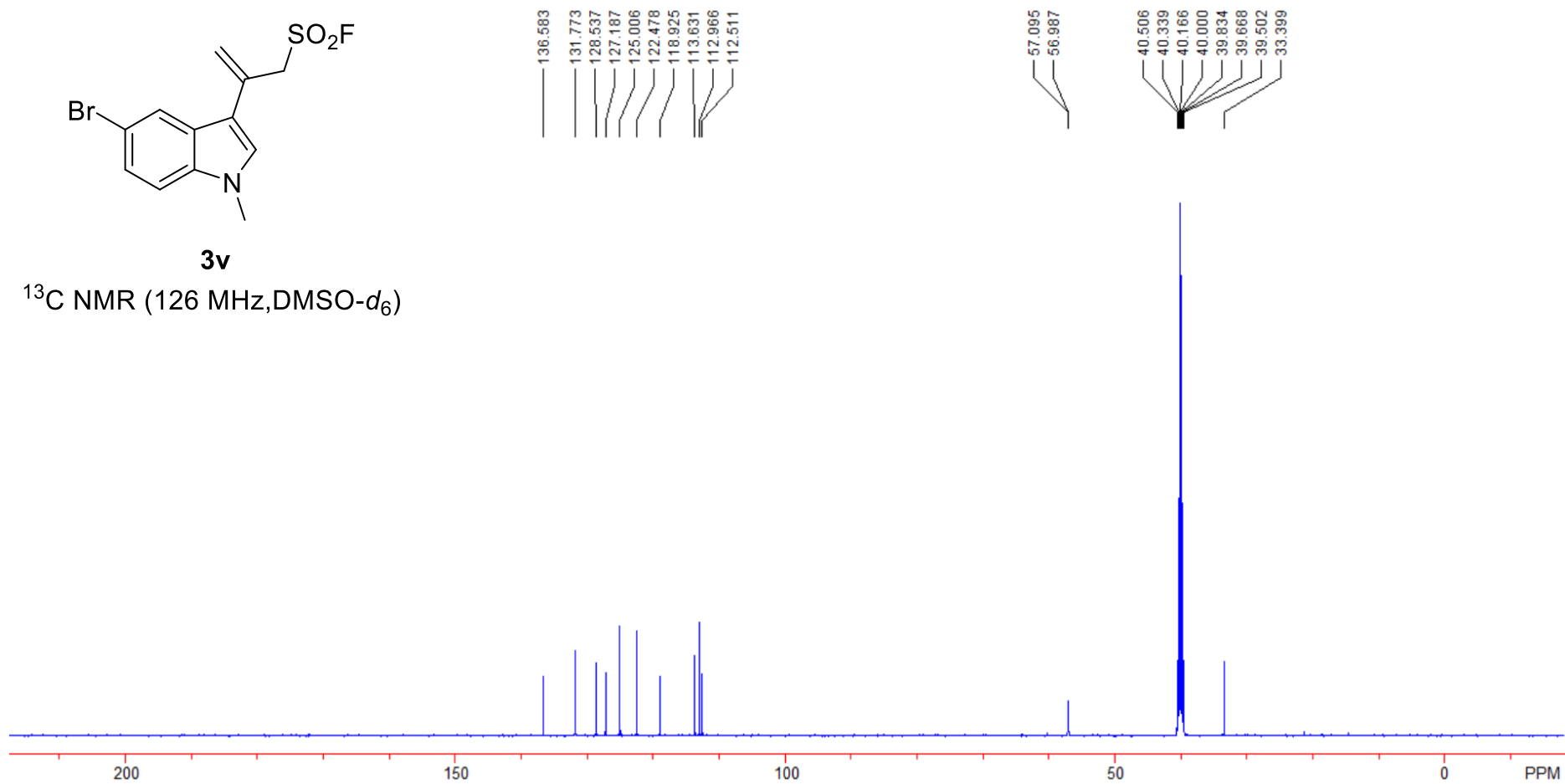
54.772



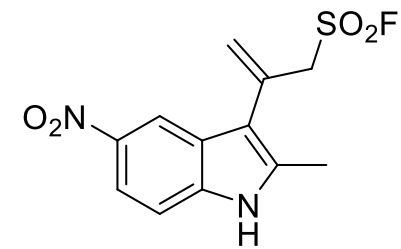


**3v**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

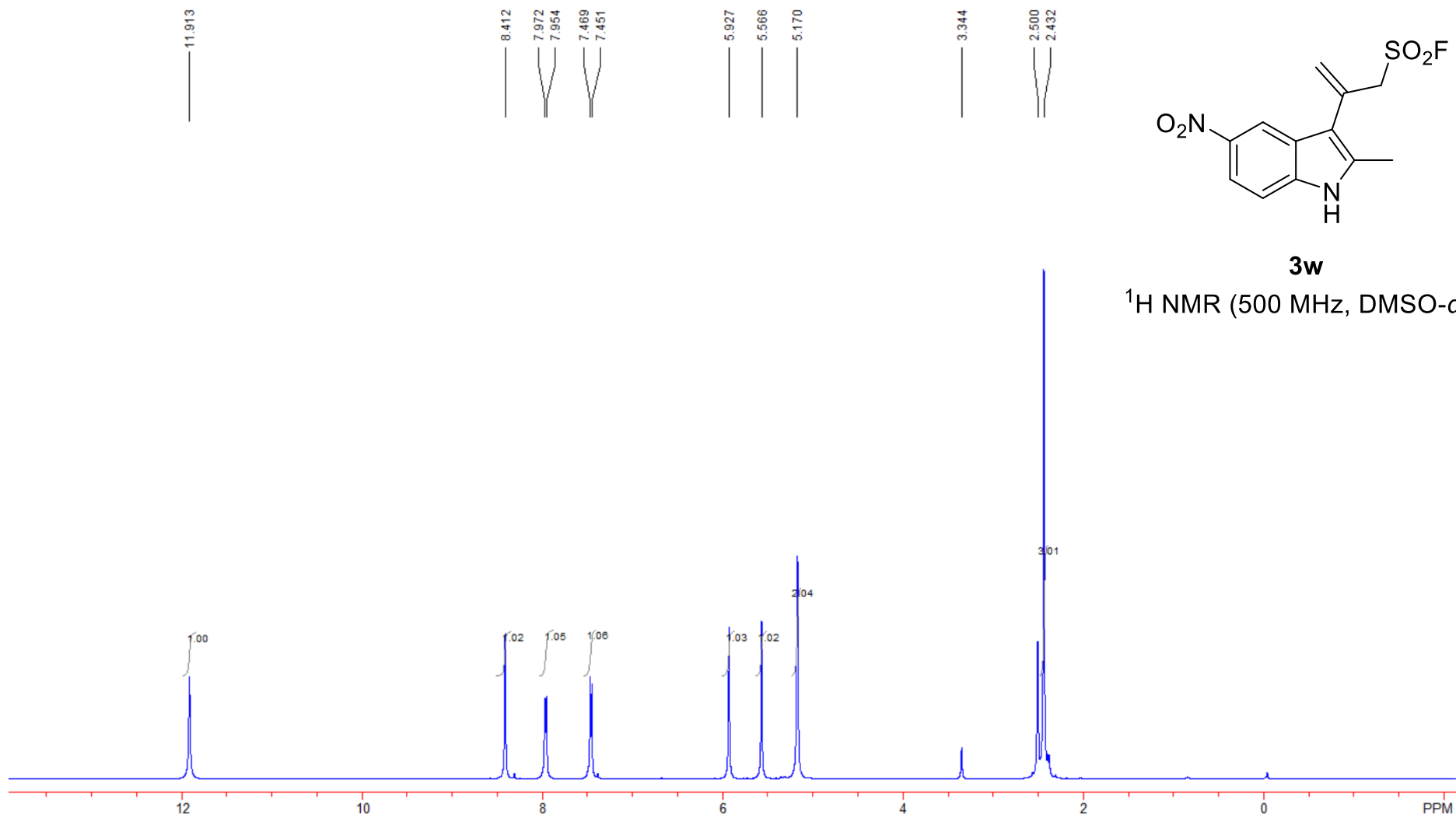




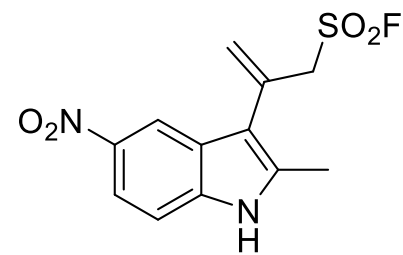


**3w**

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )

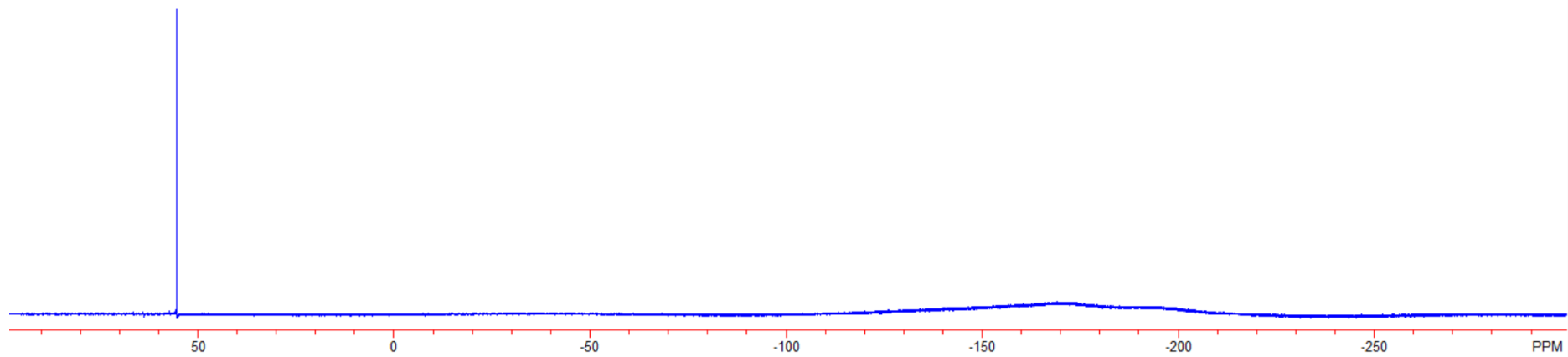


55.337

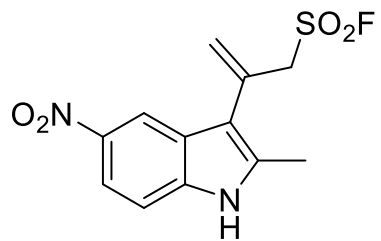


**3w**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

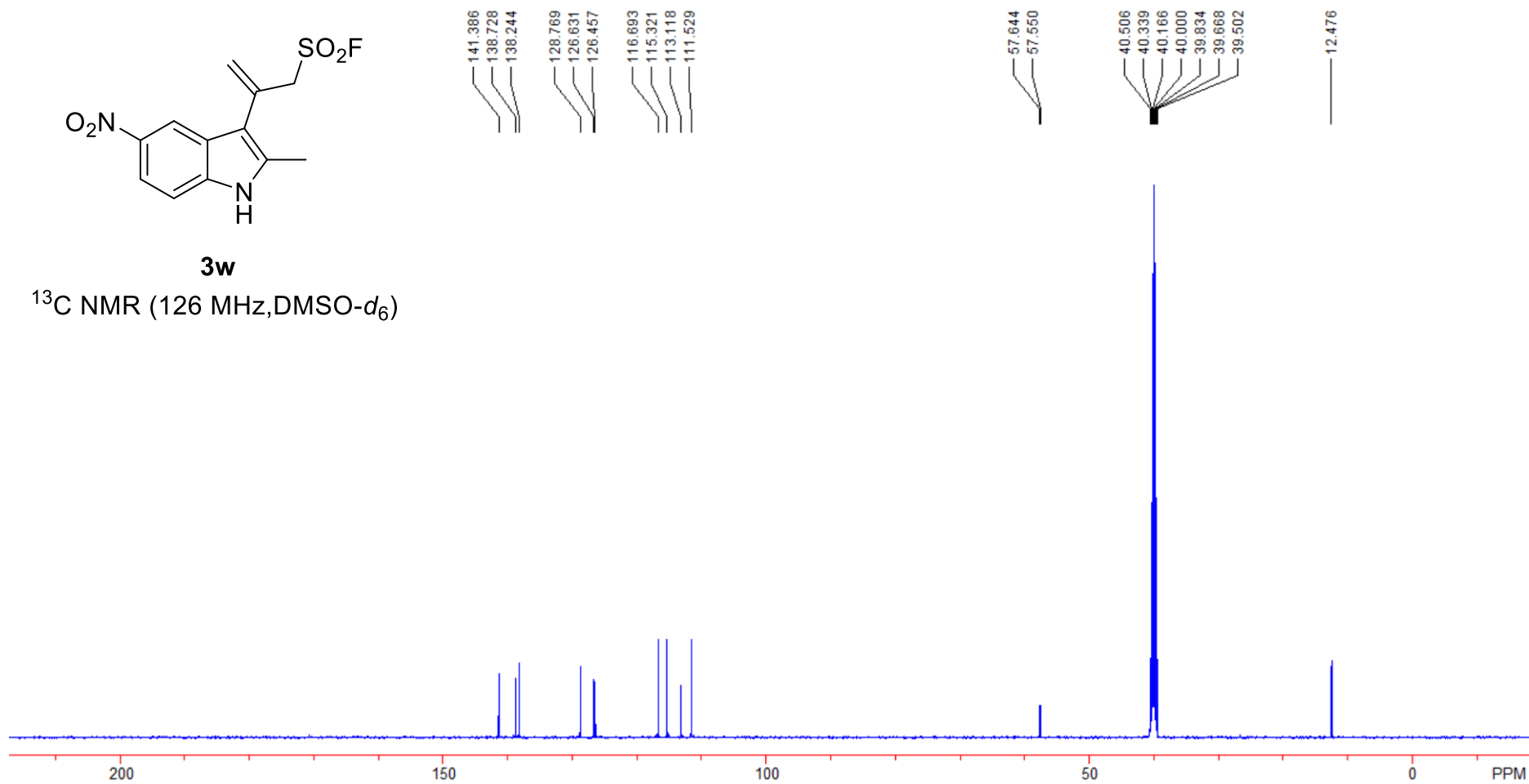


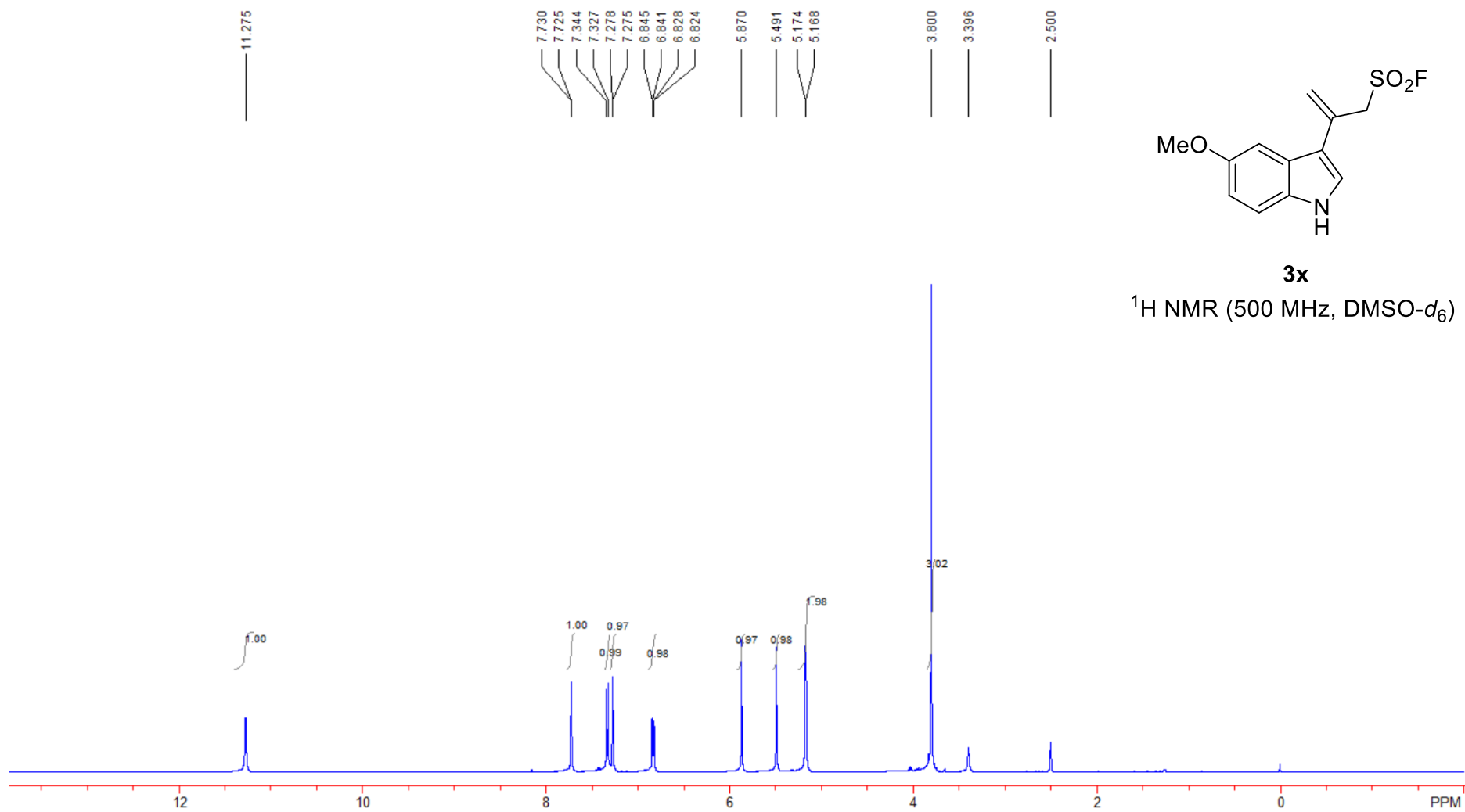
S104

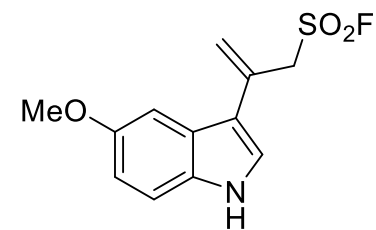


**3w**

<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)



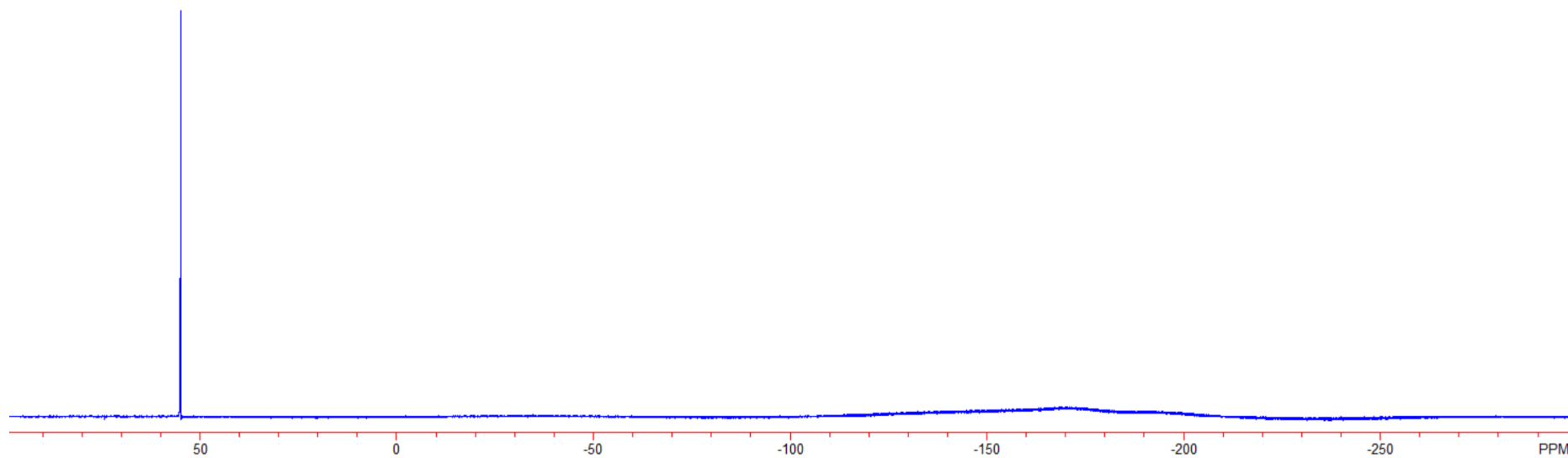




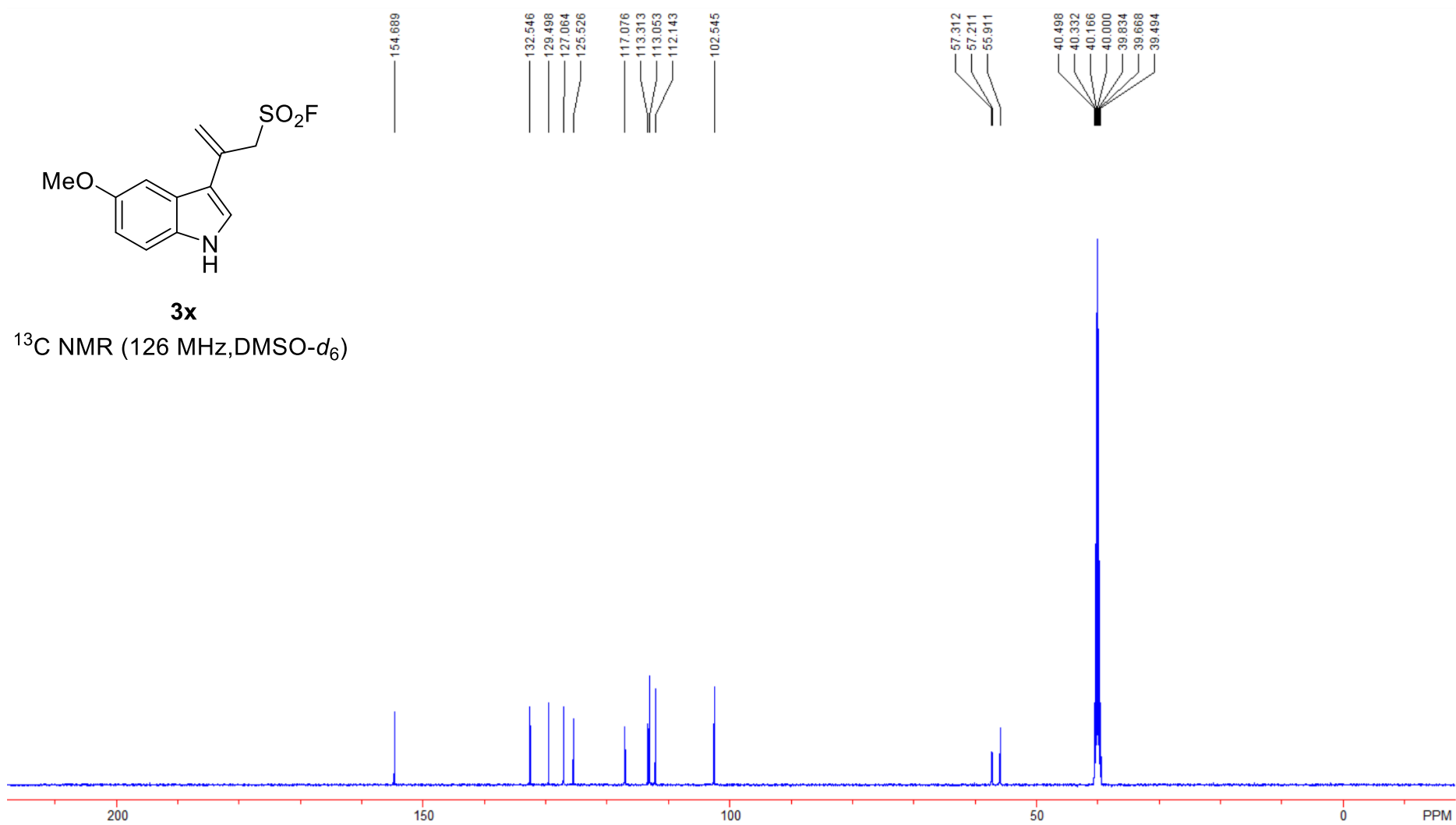
**3x**

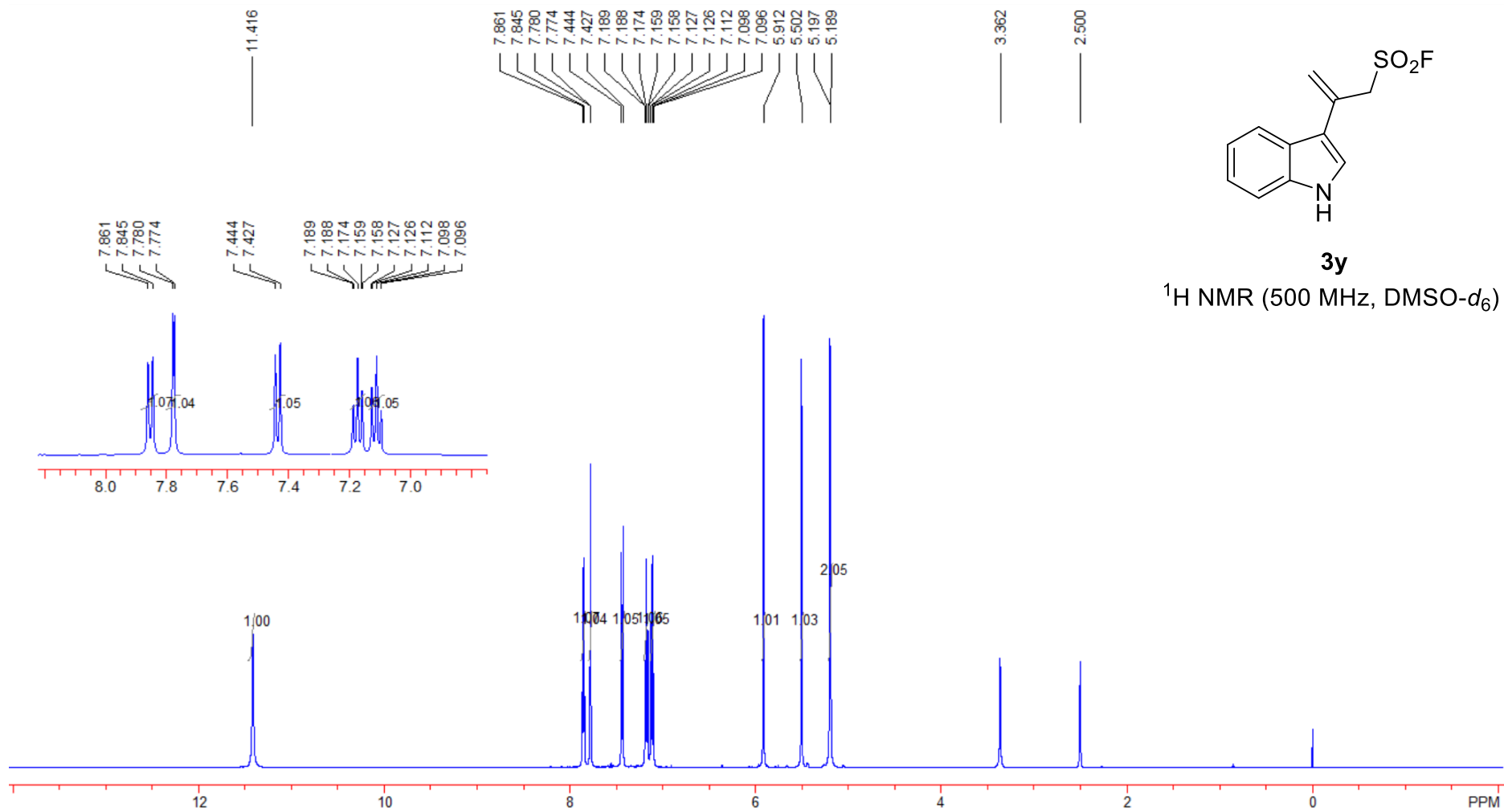
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

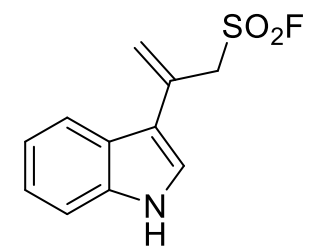
54.966



S107

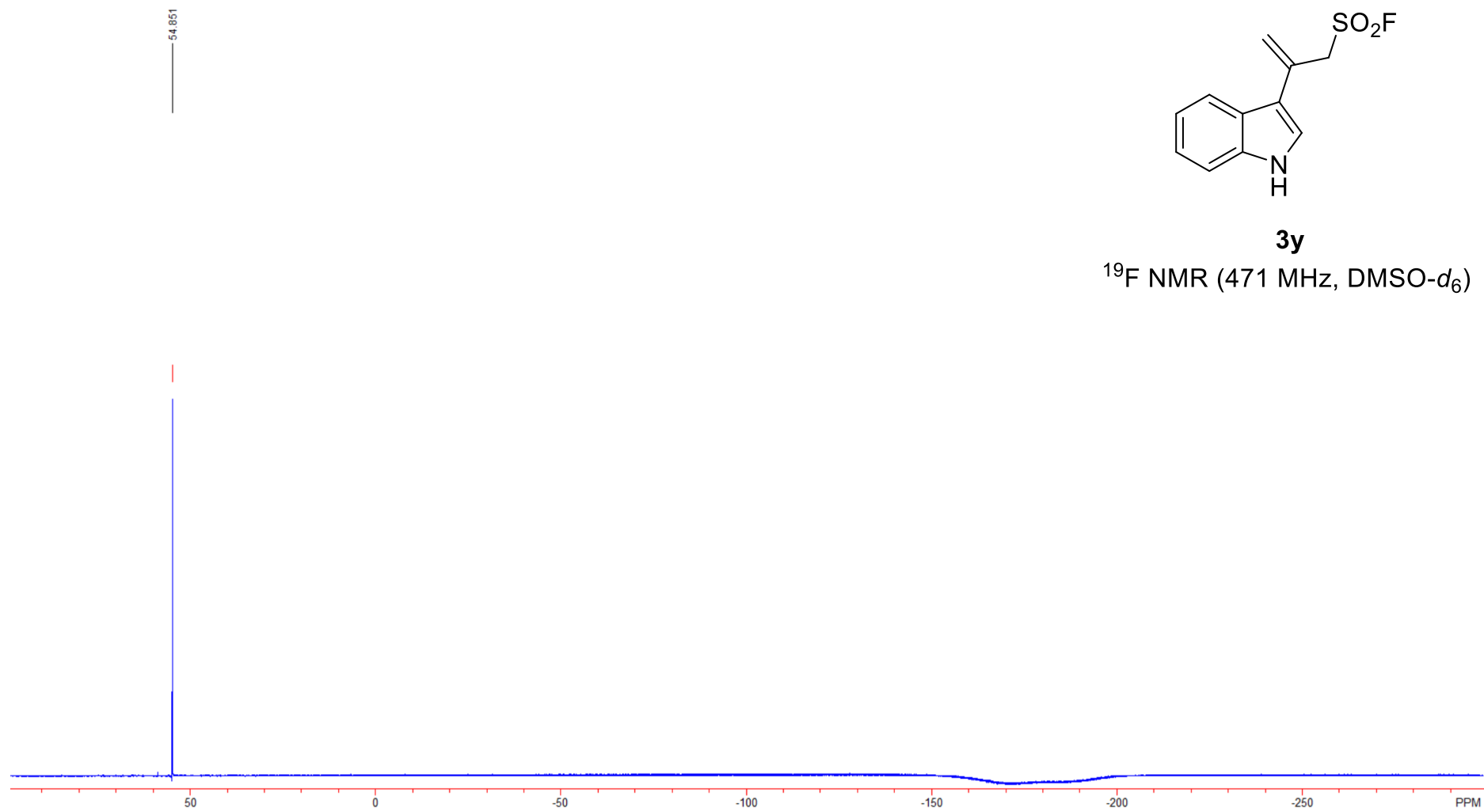






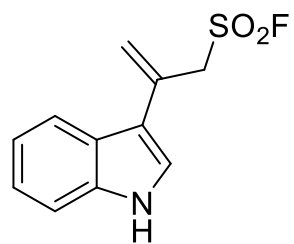
**3y**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)



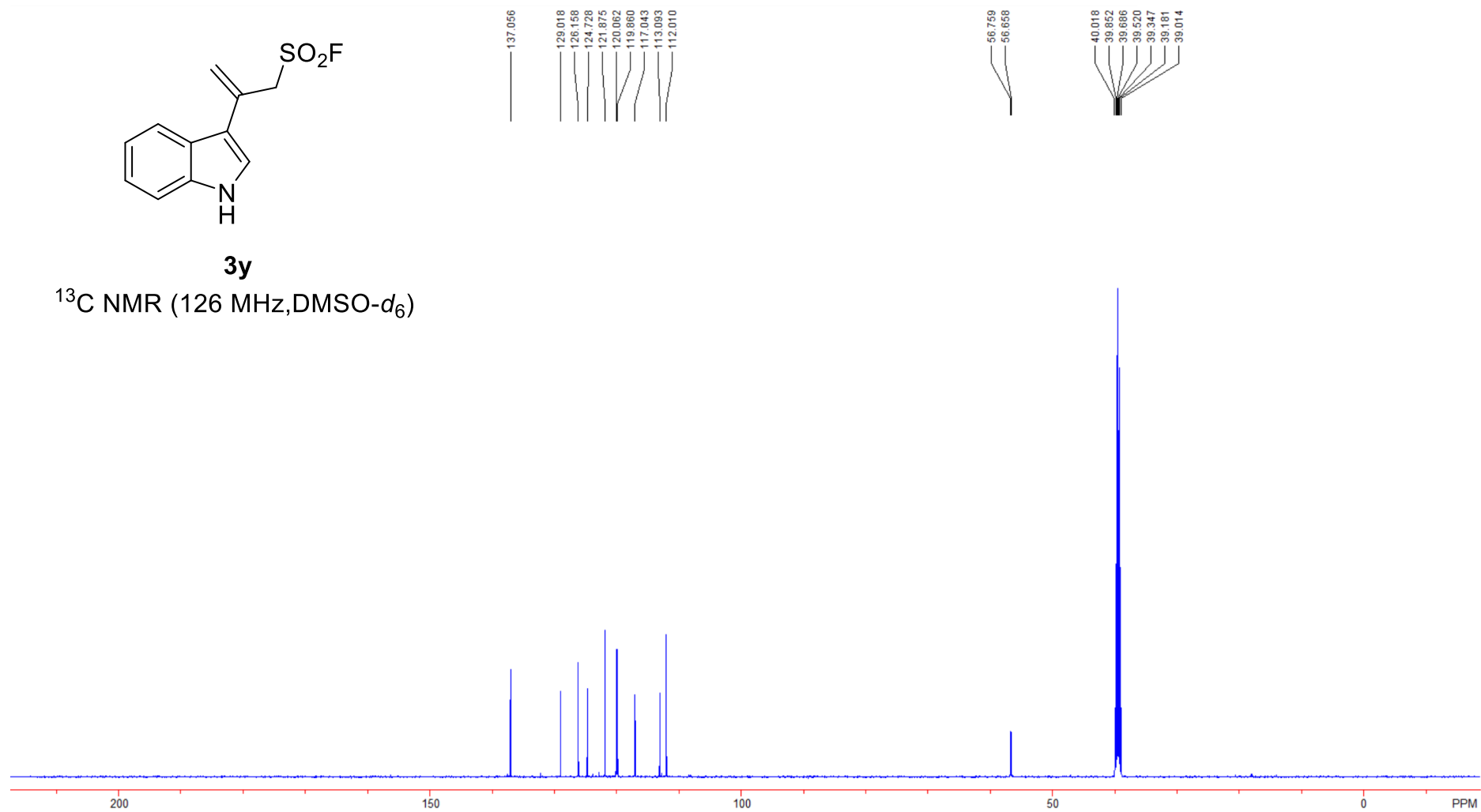
S110

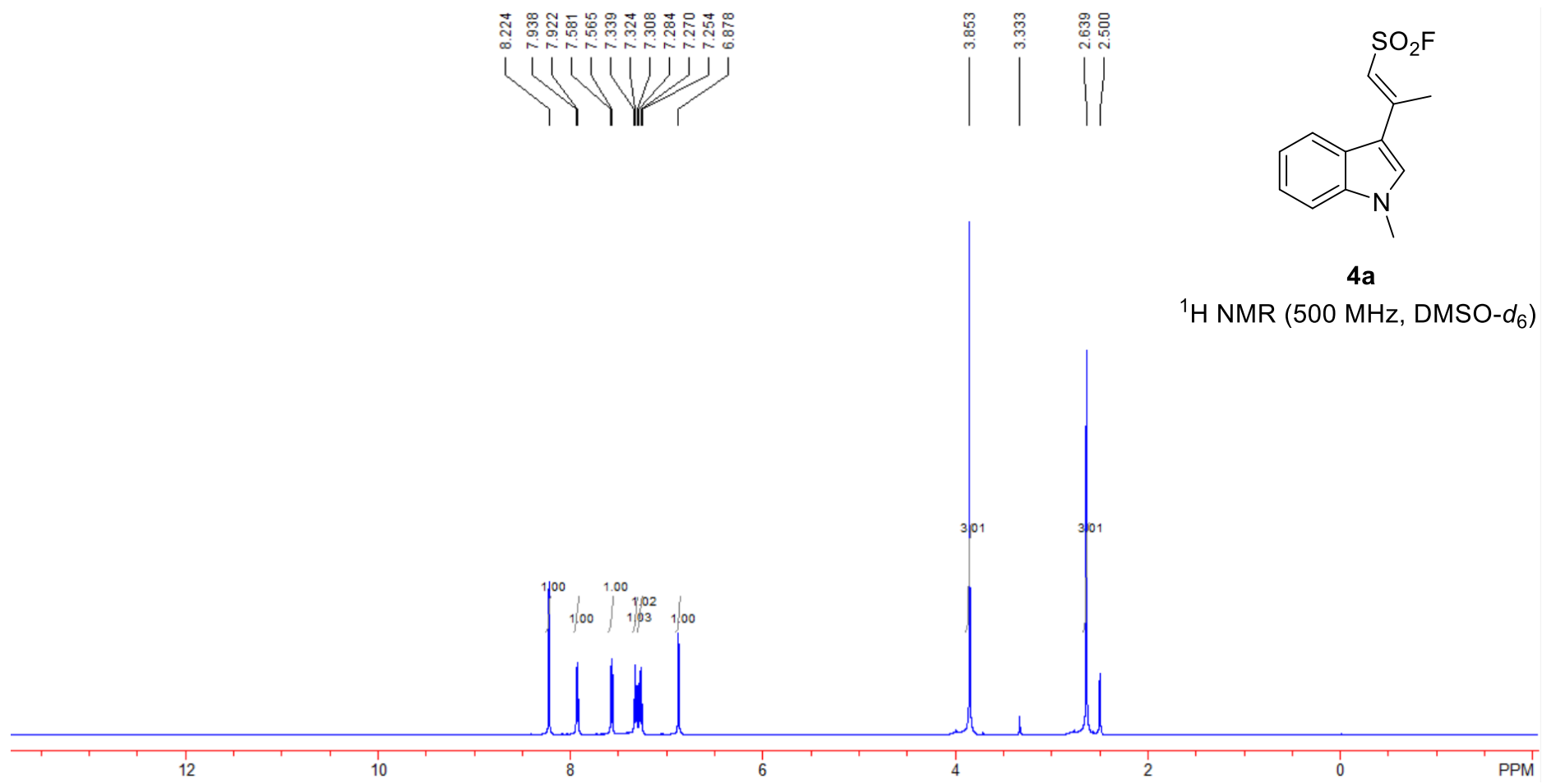


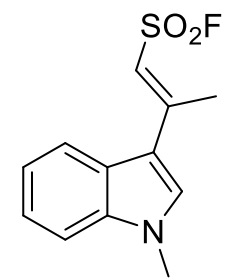


**3y**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

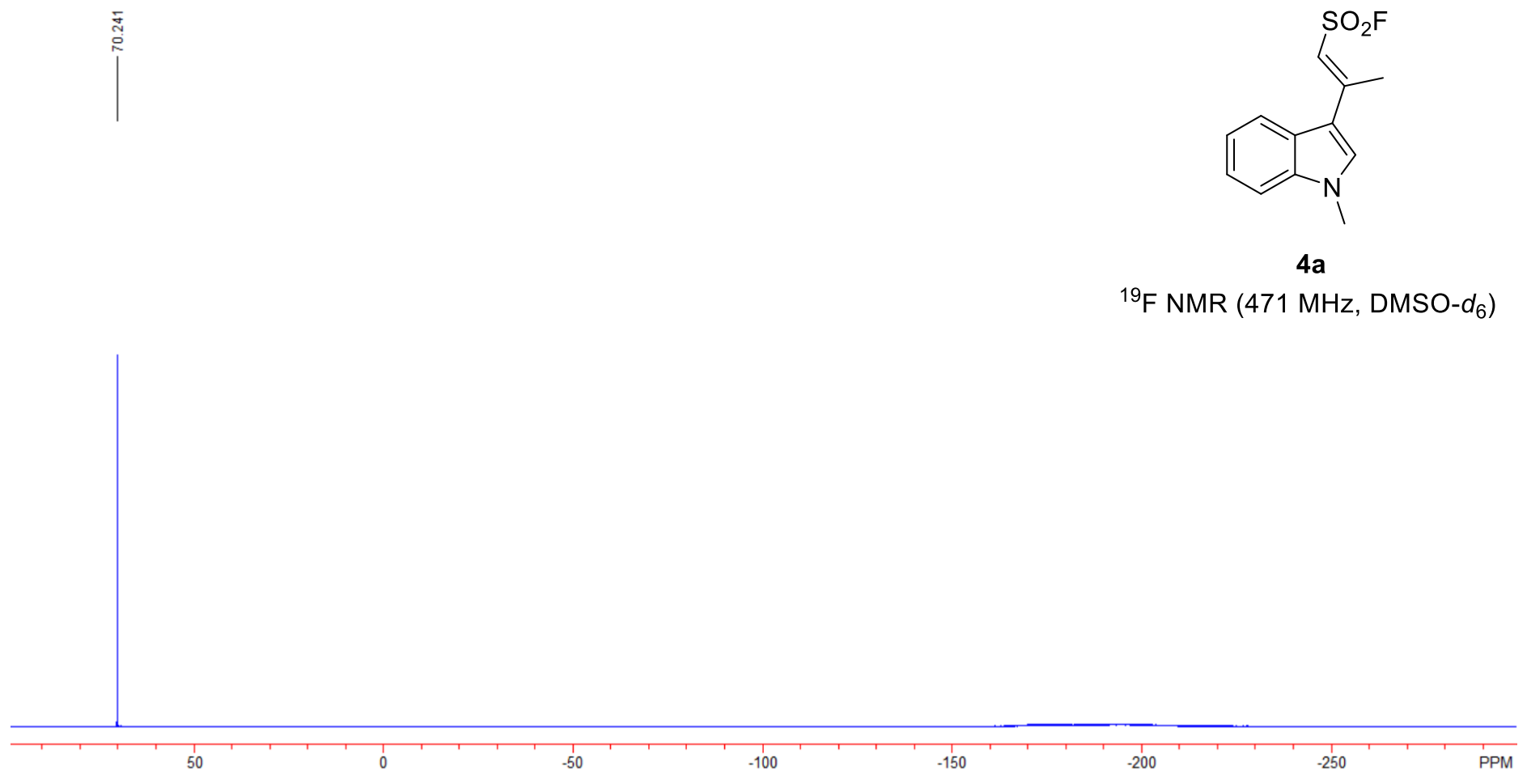


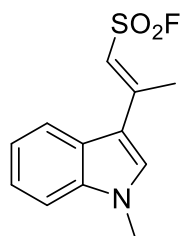




**4a**

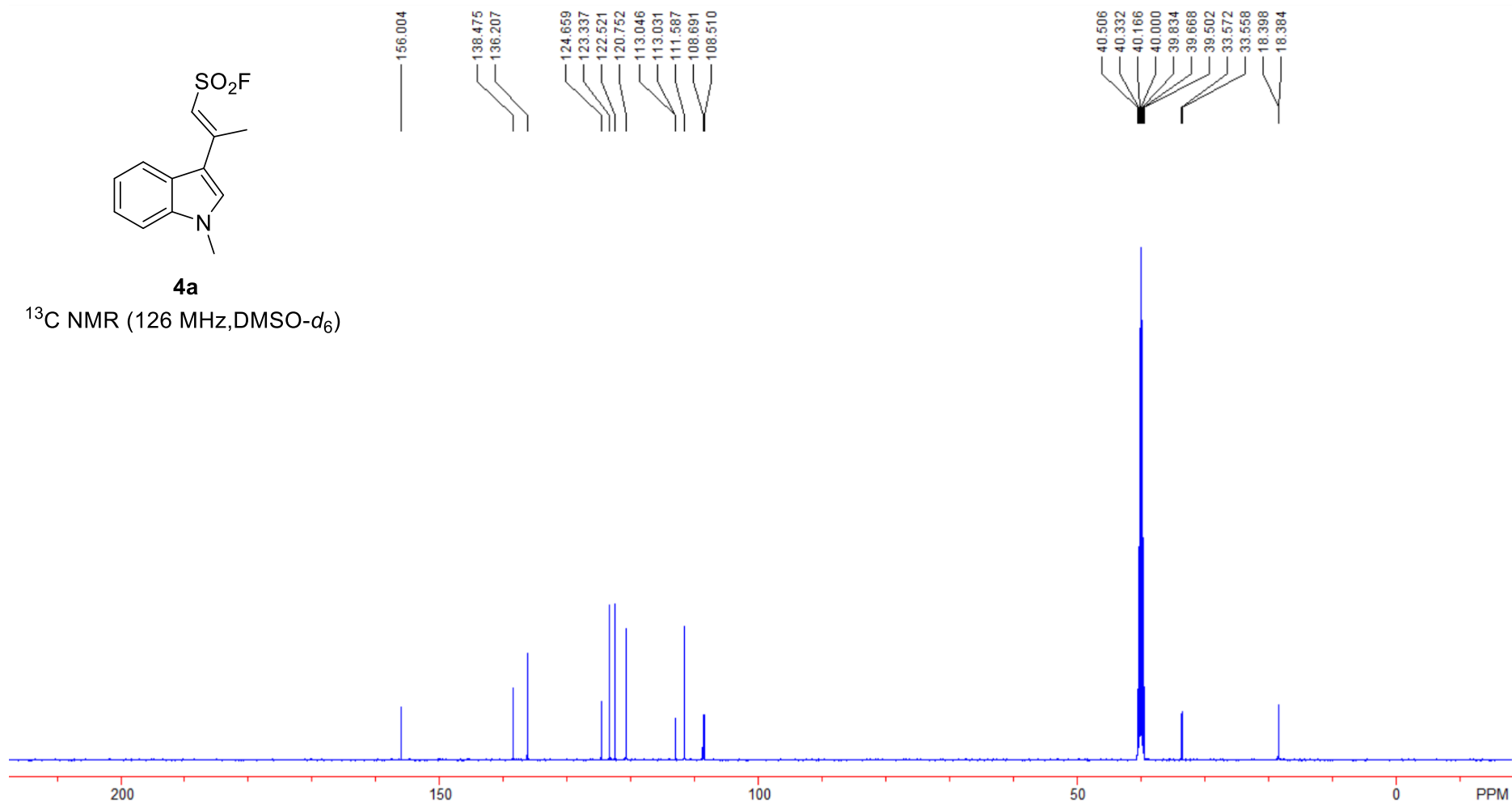
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

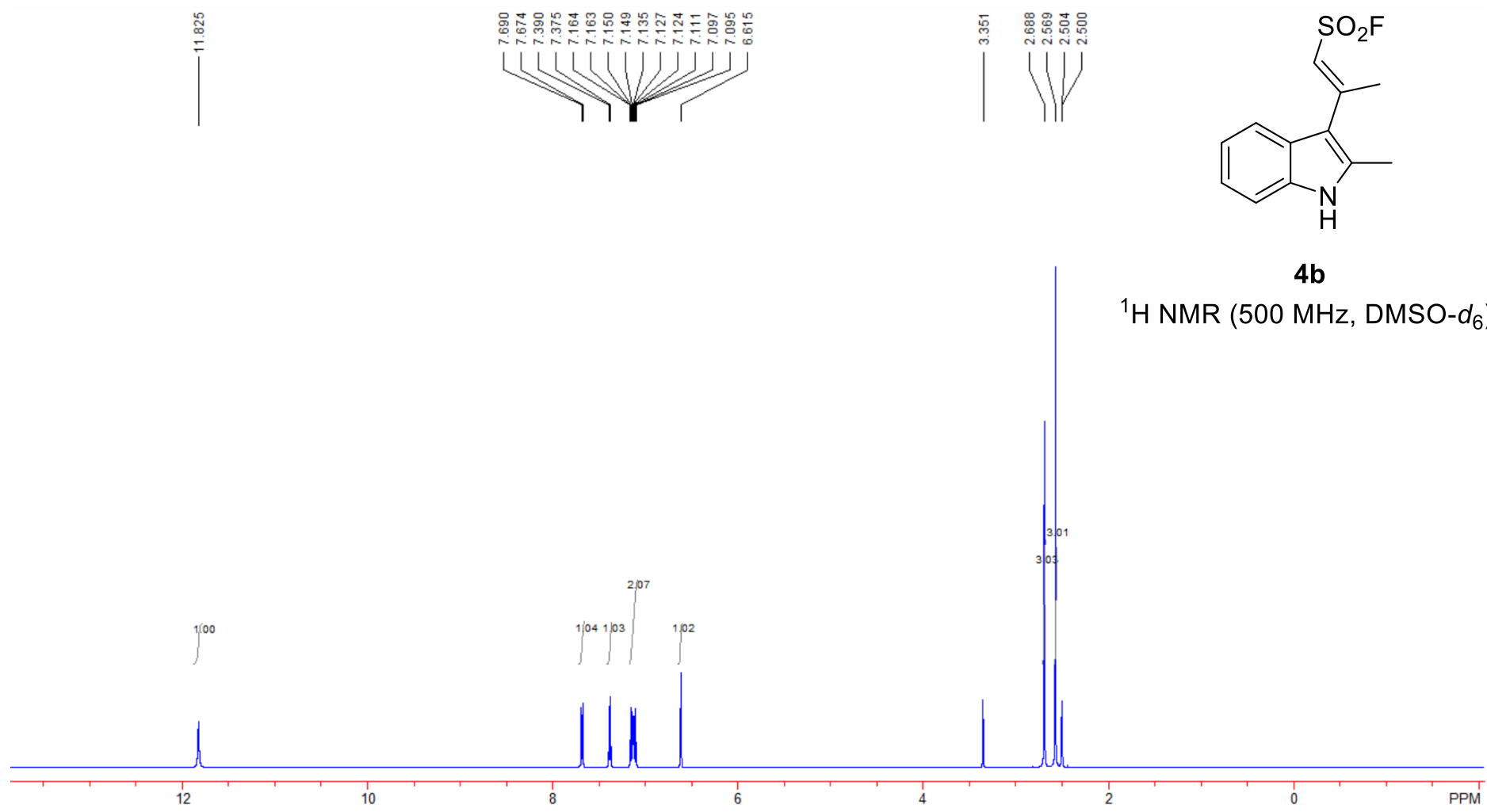


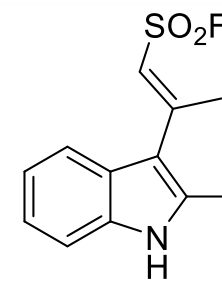


**4a**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )



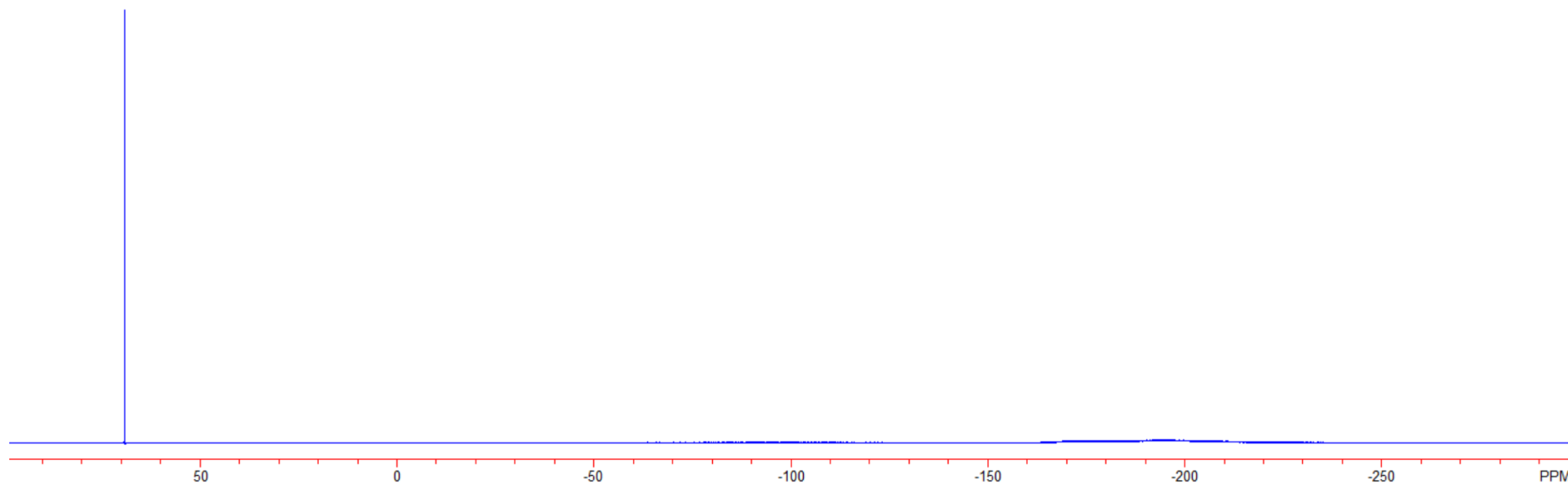


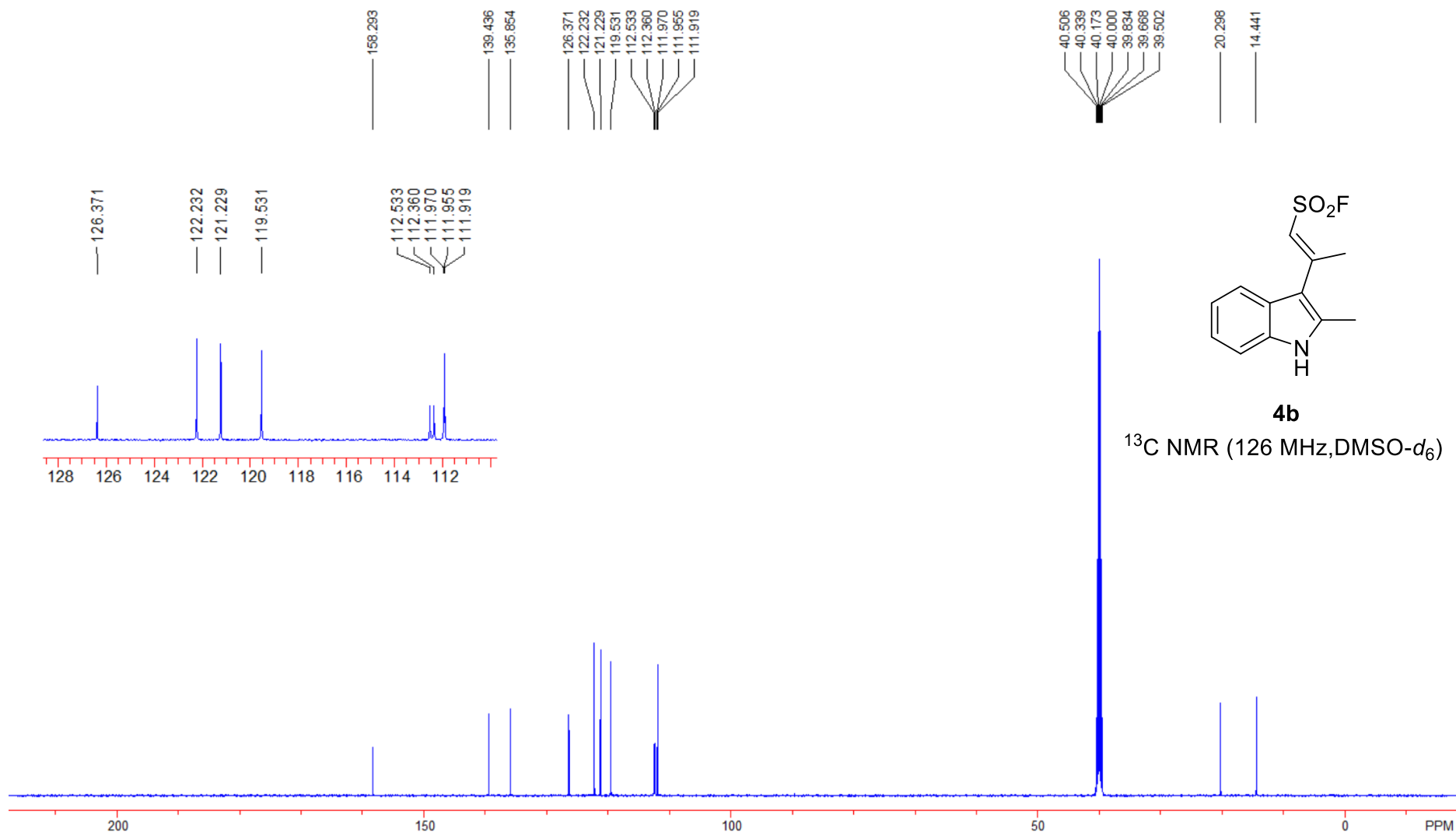


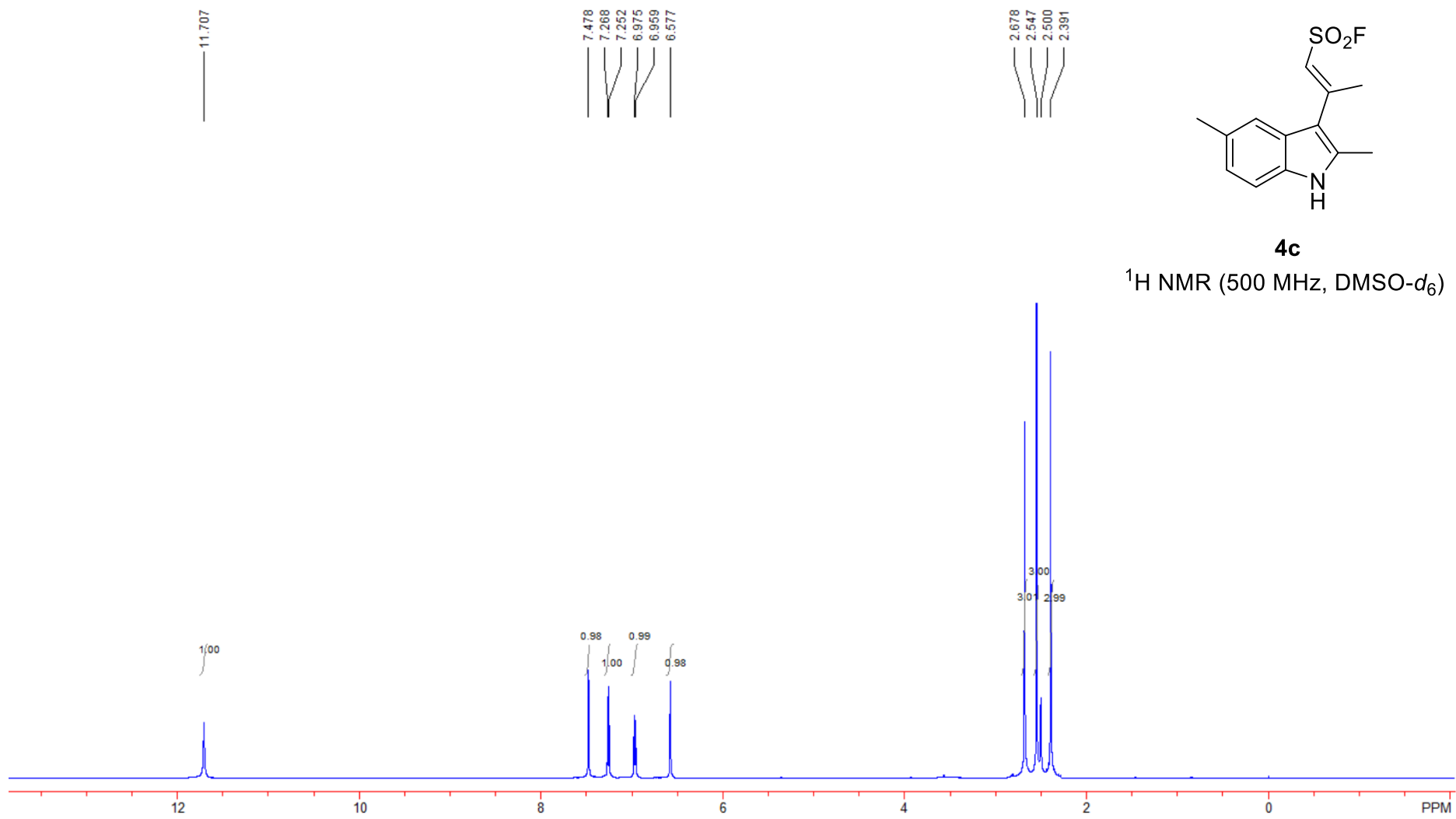
**4b**

$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

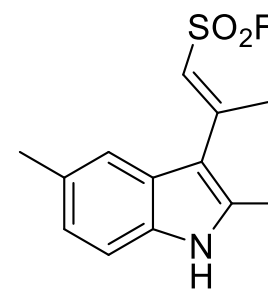
69.086







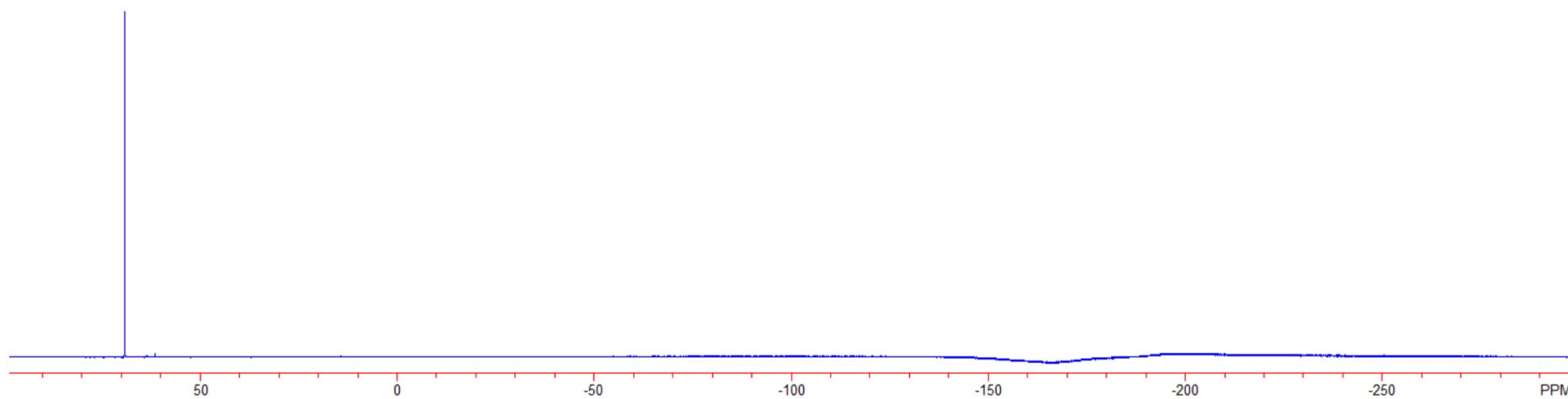


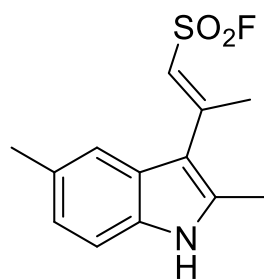


**4c**

$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

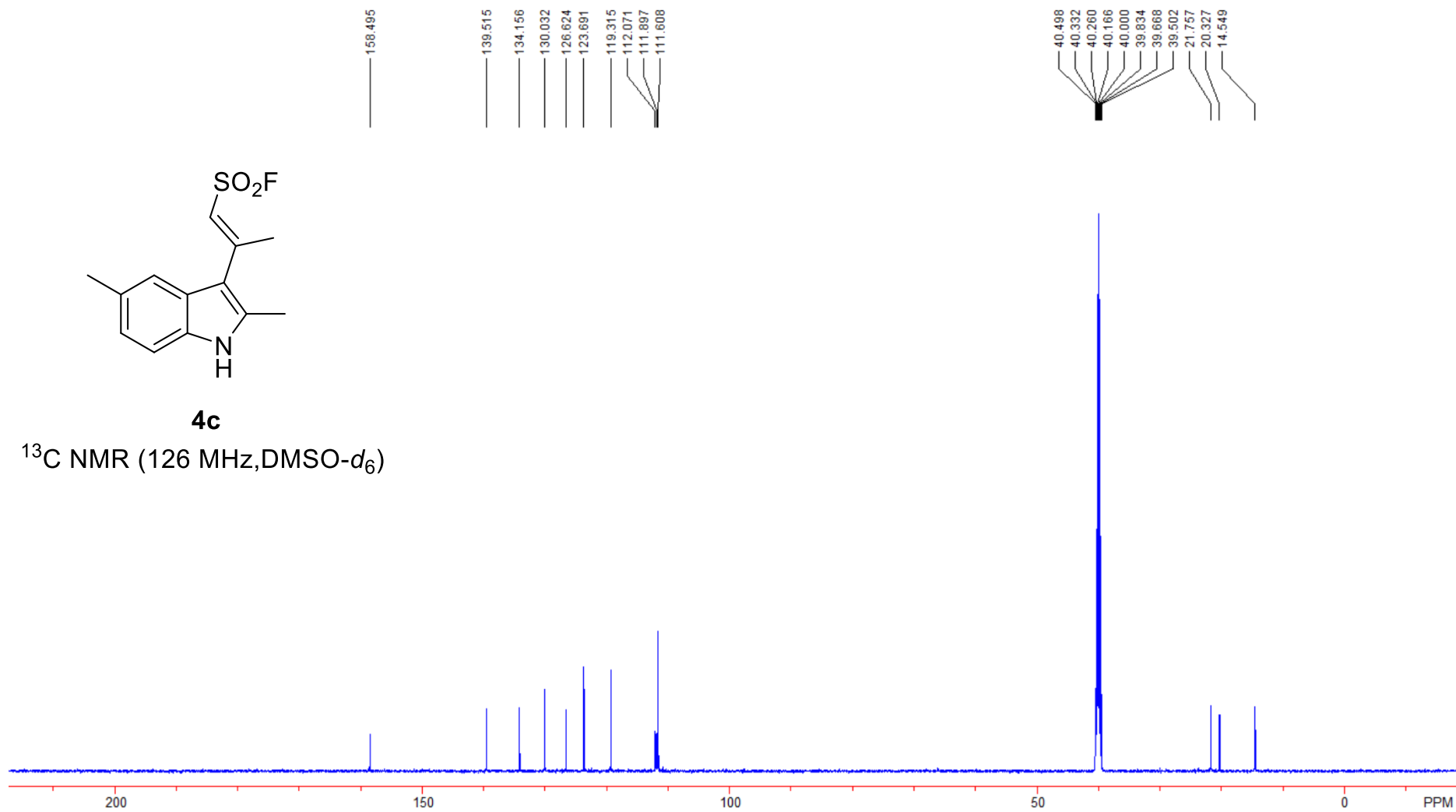
69.183

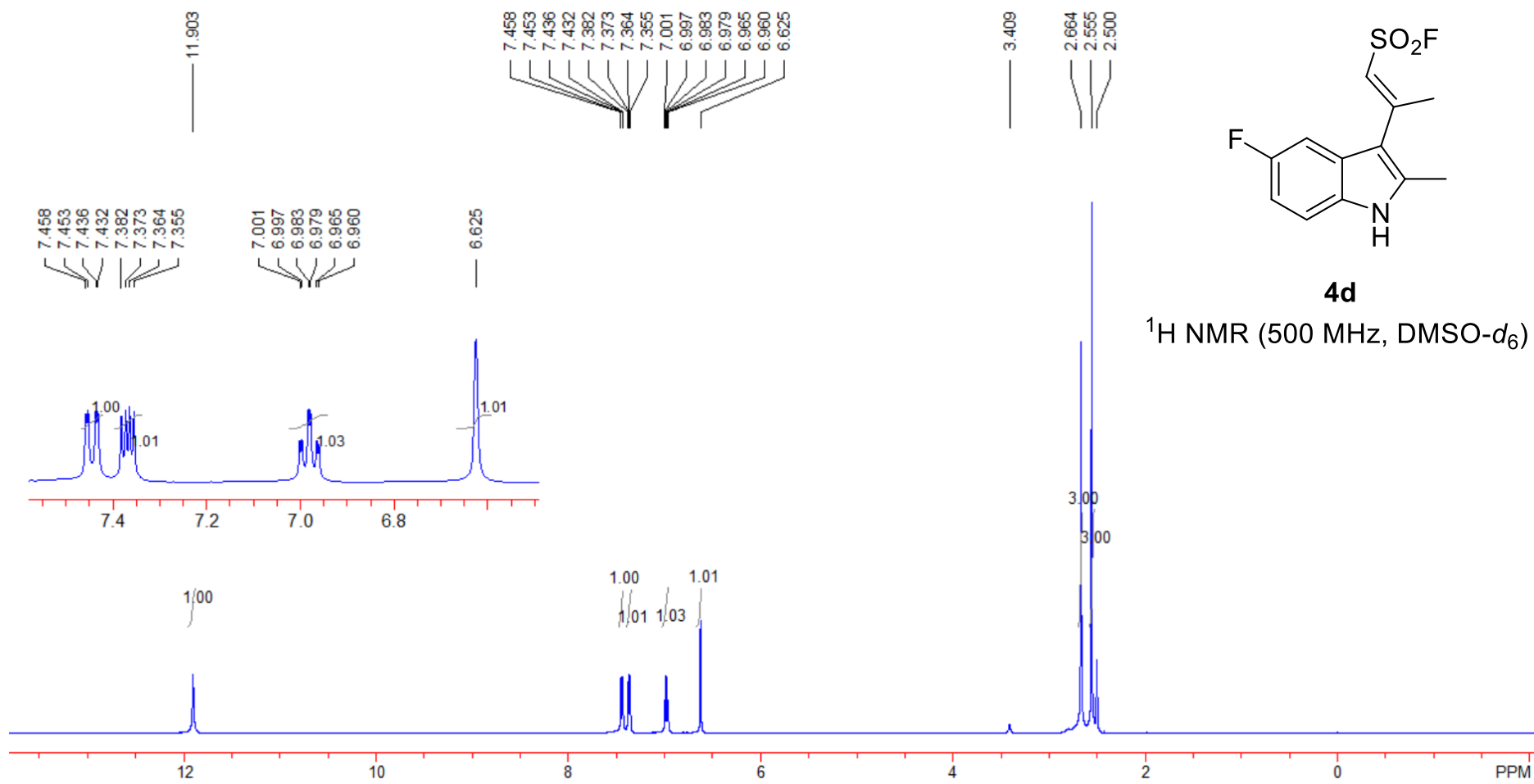


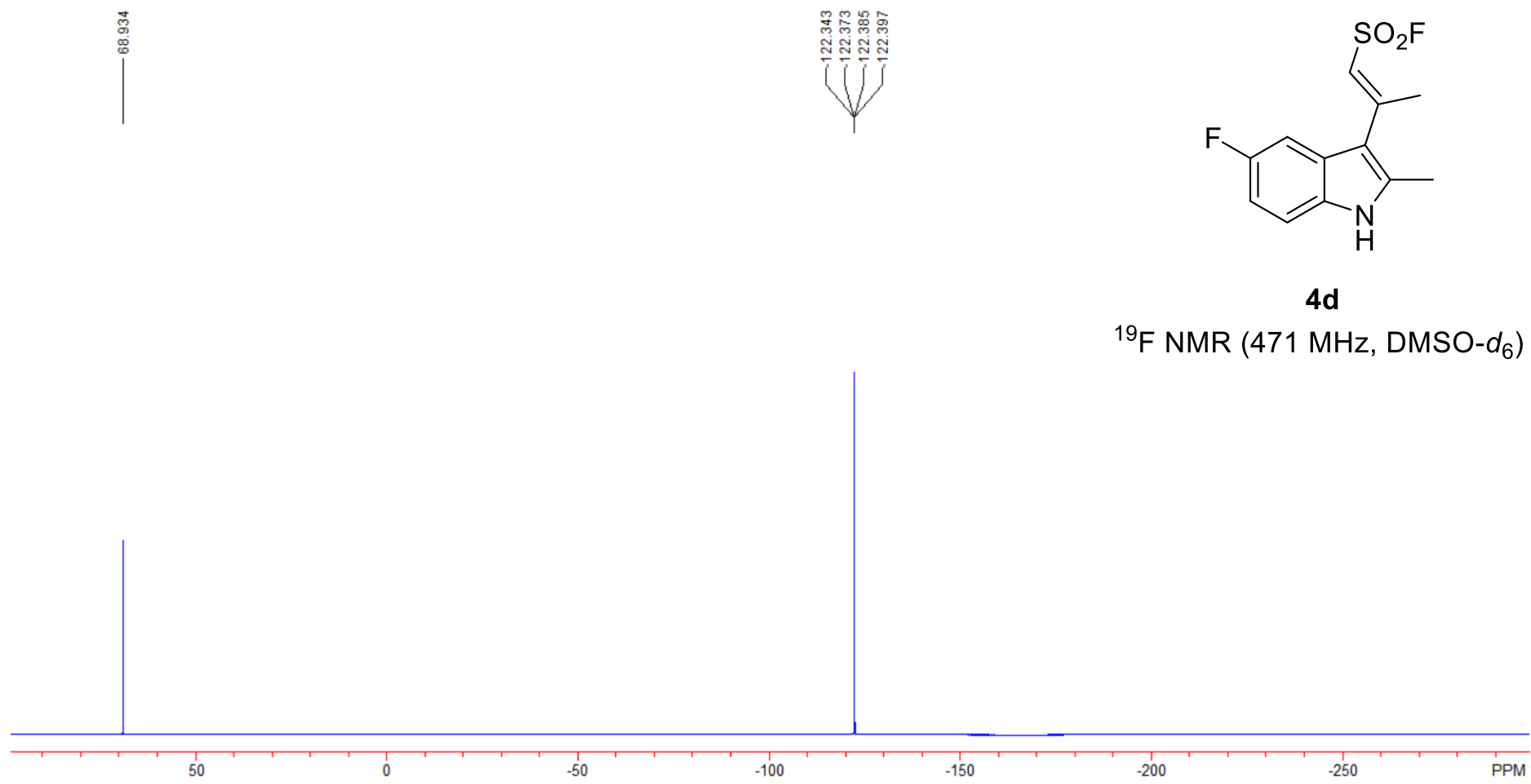


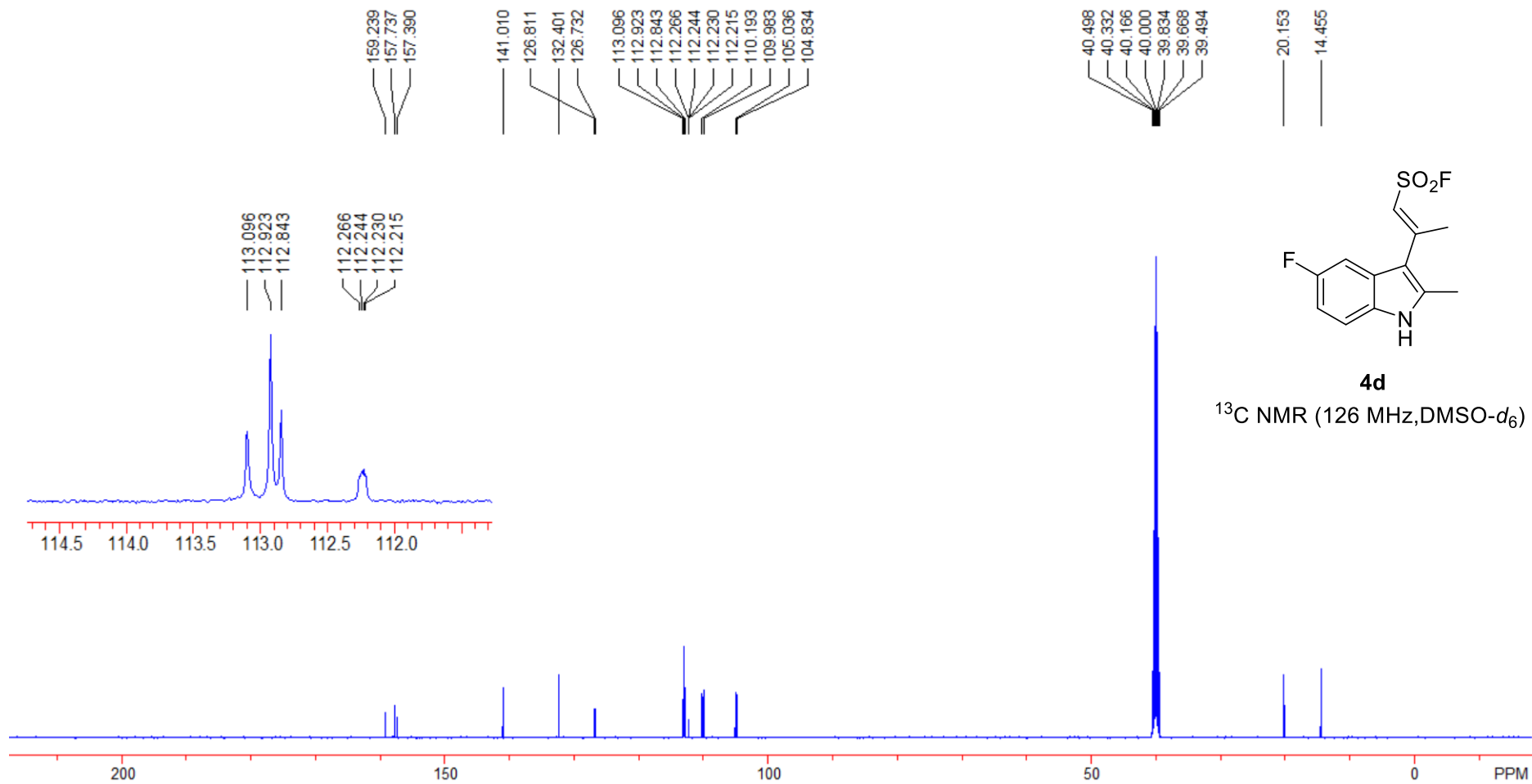
**4c**

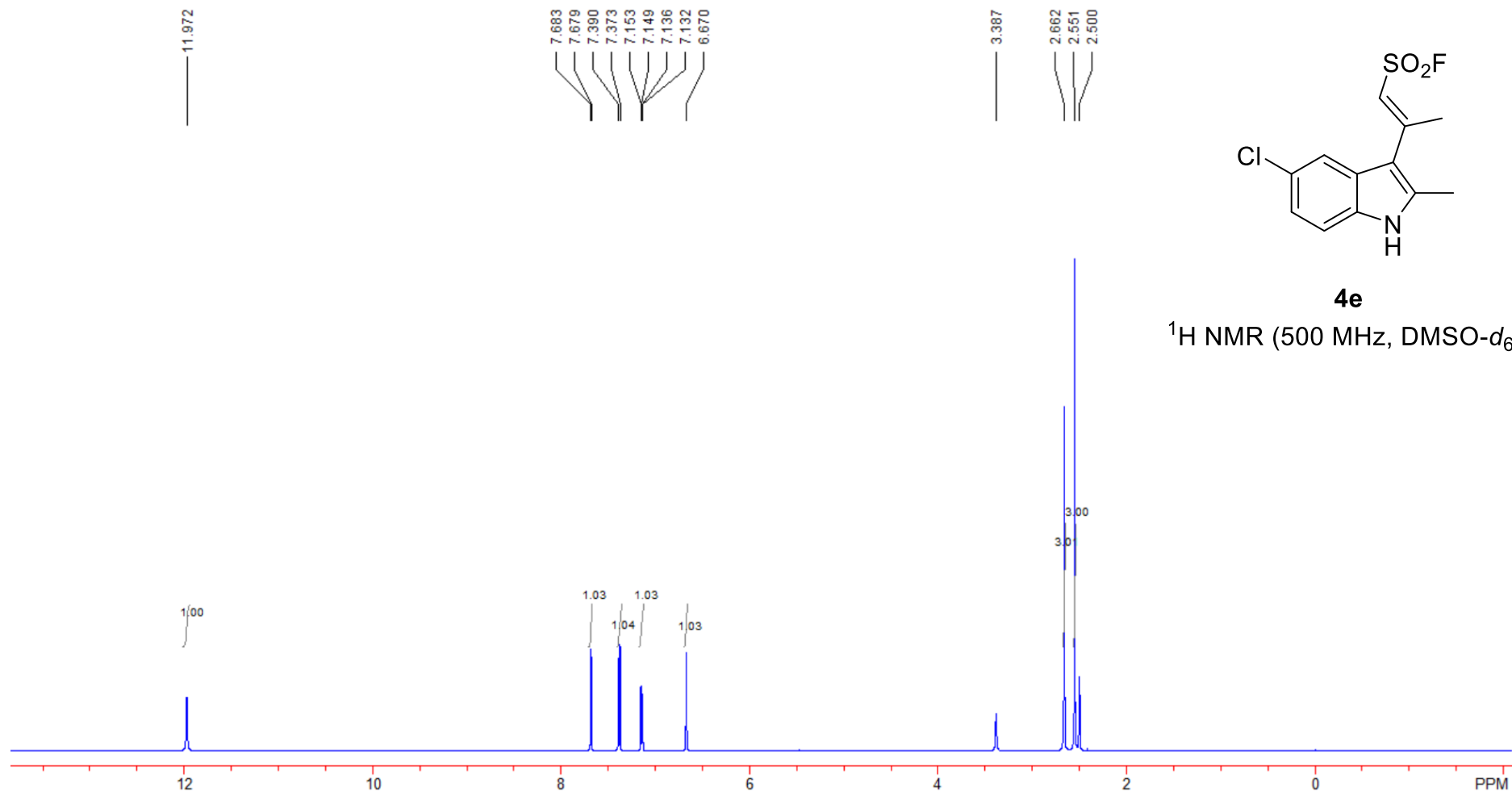
<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)



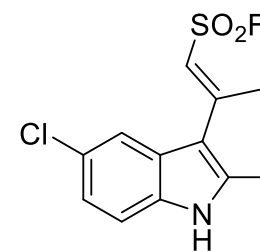






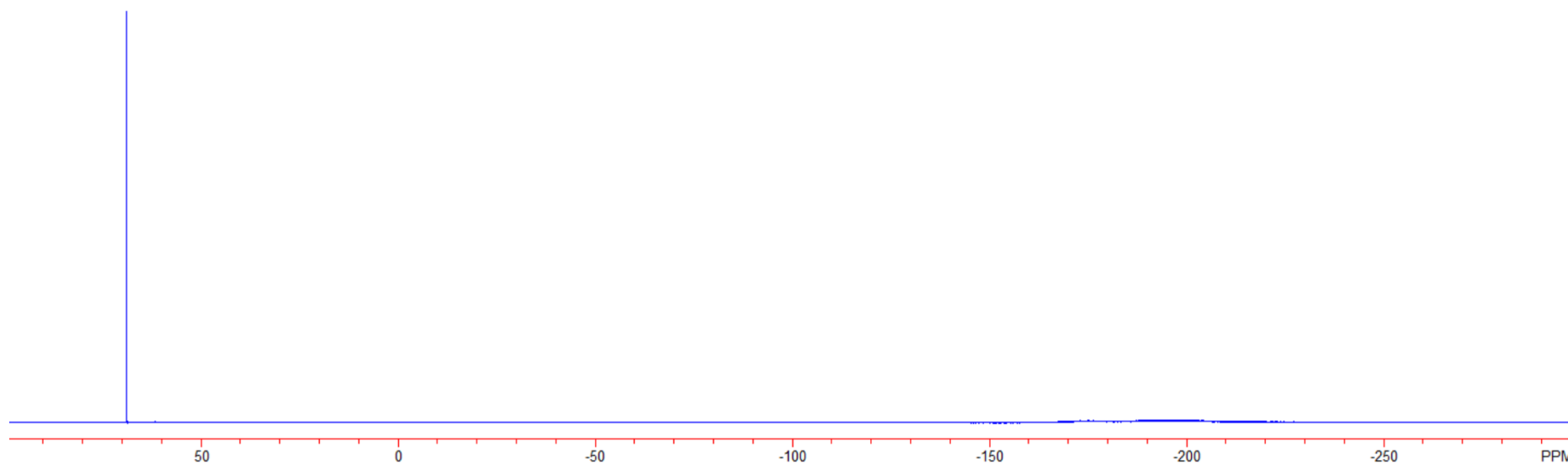


68.788

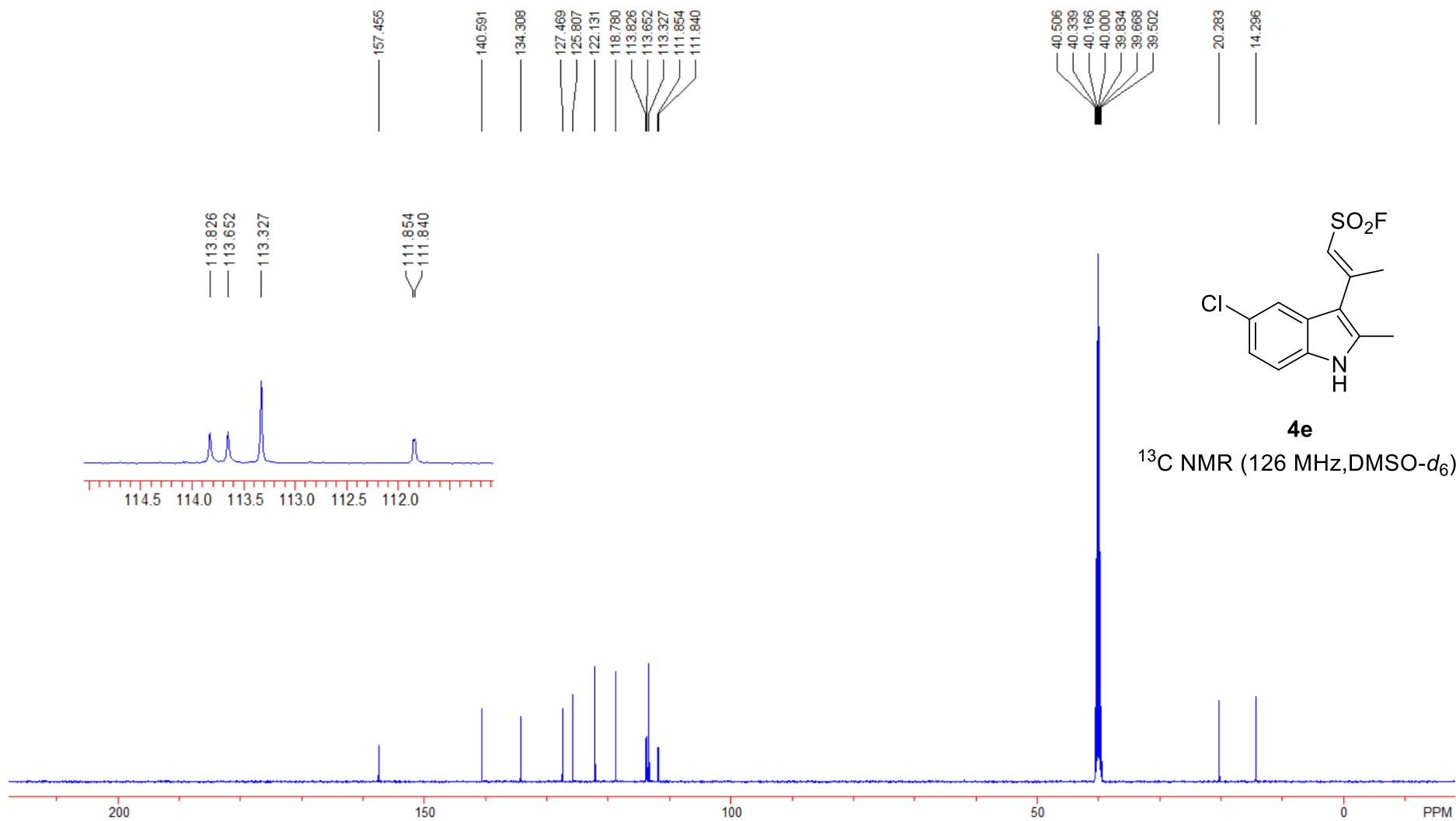


**4e**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)



S125

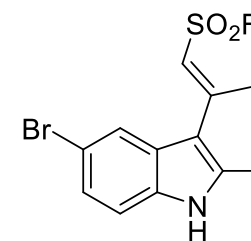




11.972

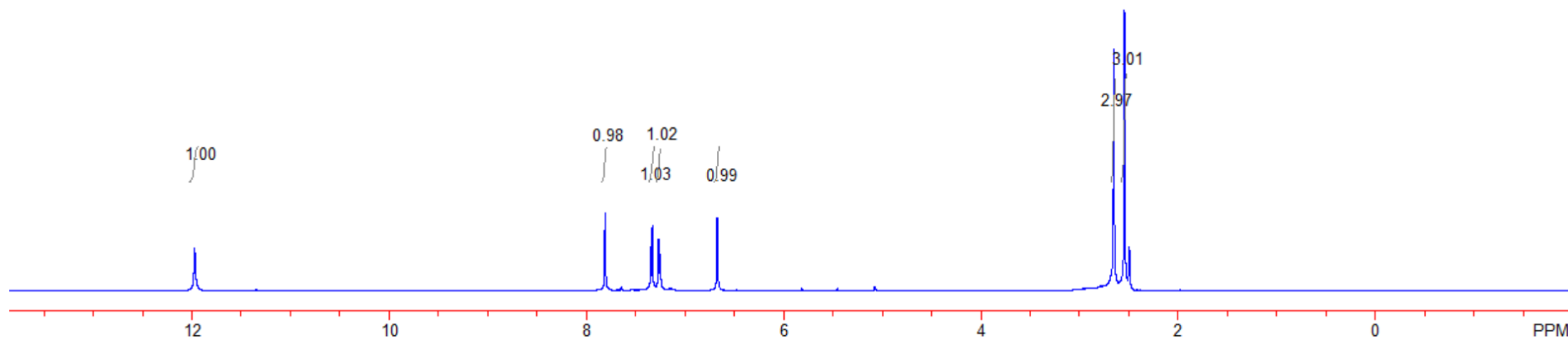
7.809  
7.348  
7.331  
7.267  
7.251  
6.674

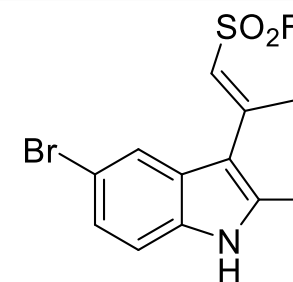
2.657  
2.549  
2.500



**4f**

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

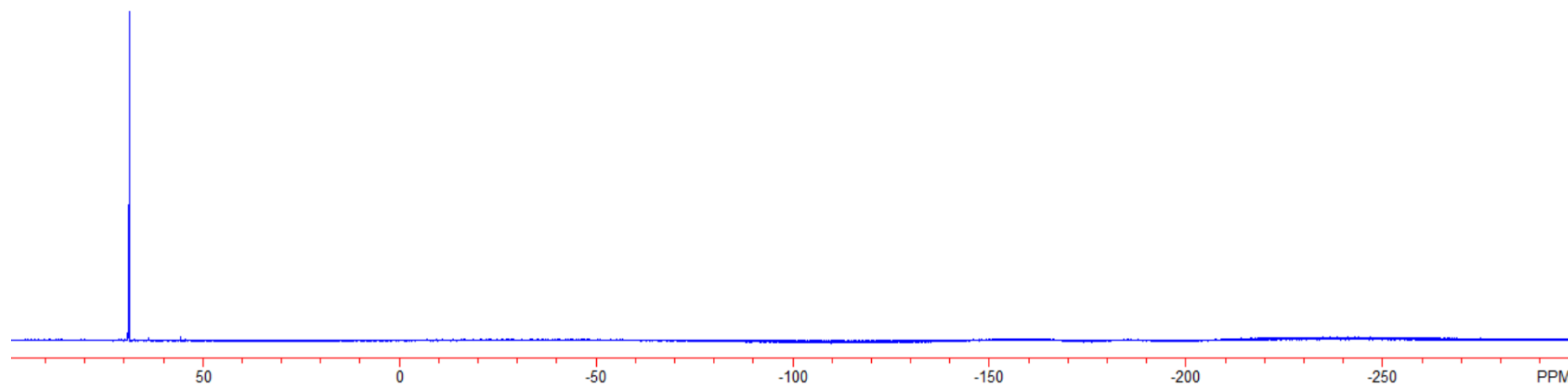


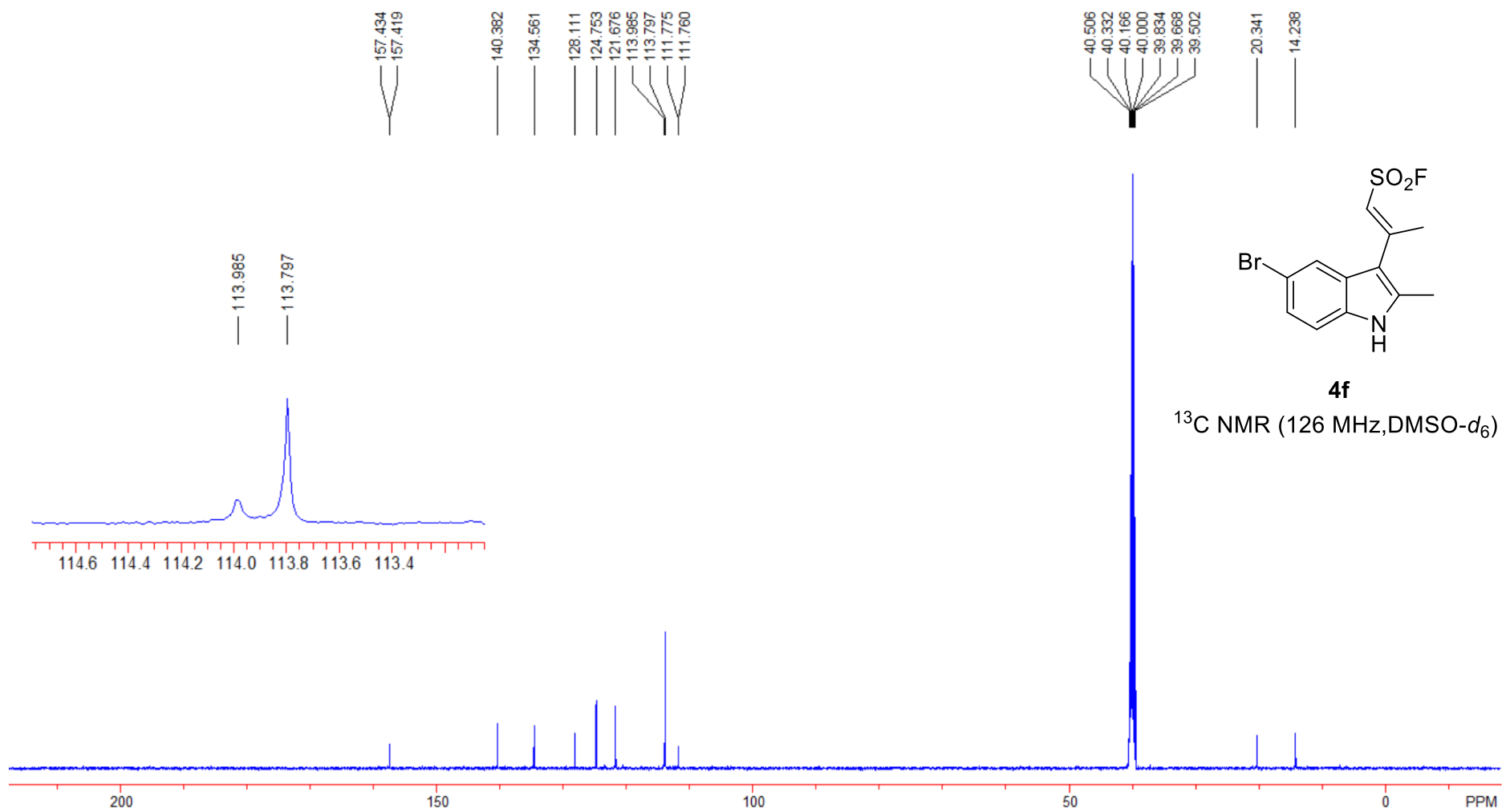


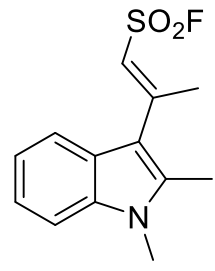
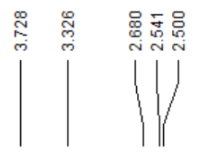
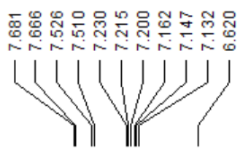
**4f**

$^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

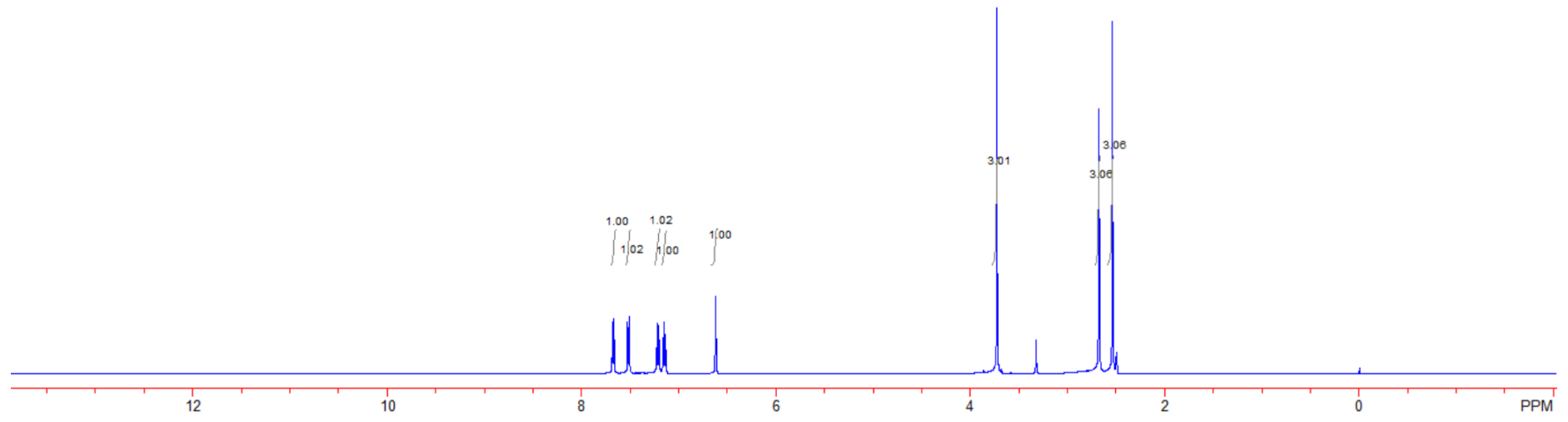
68.739

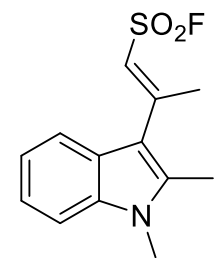






**4g**  
<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

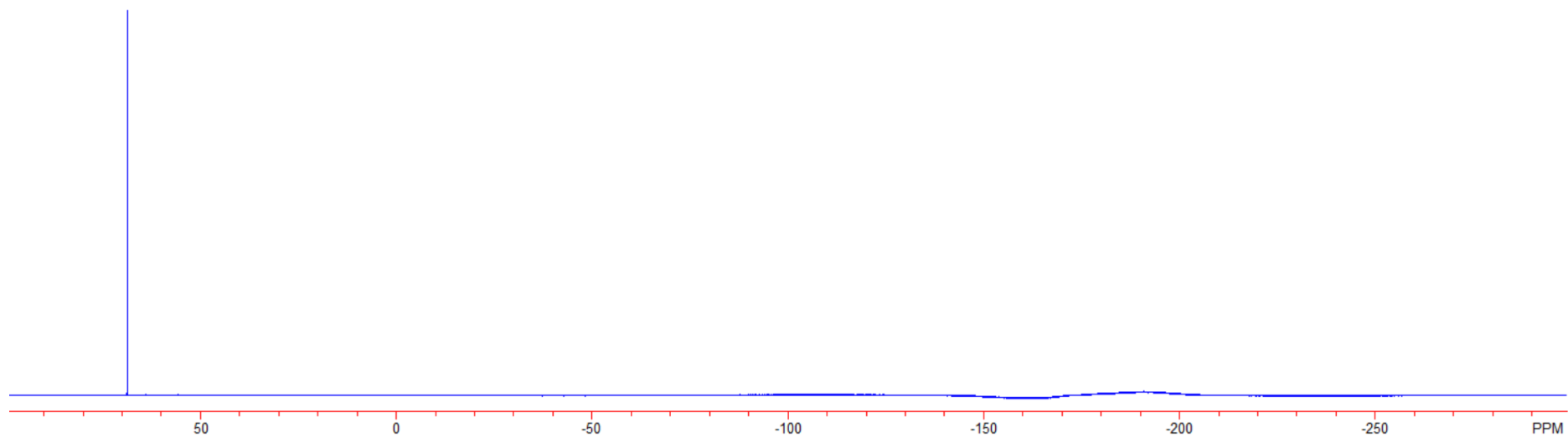


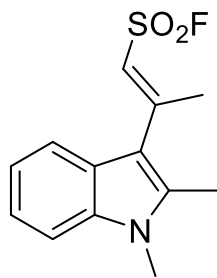


**4g**

$^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ )

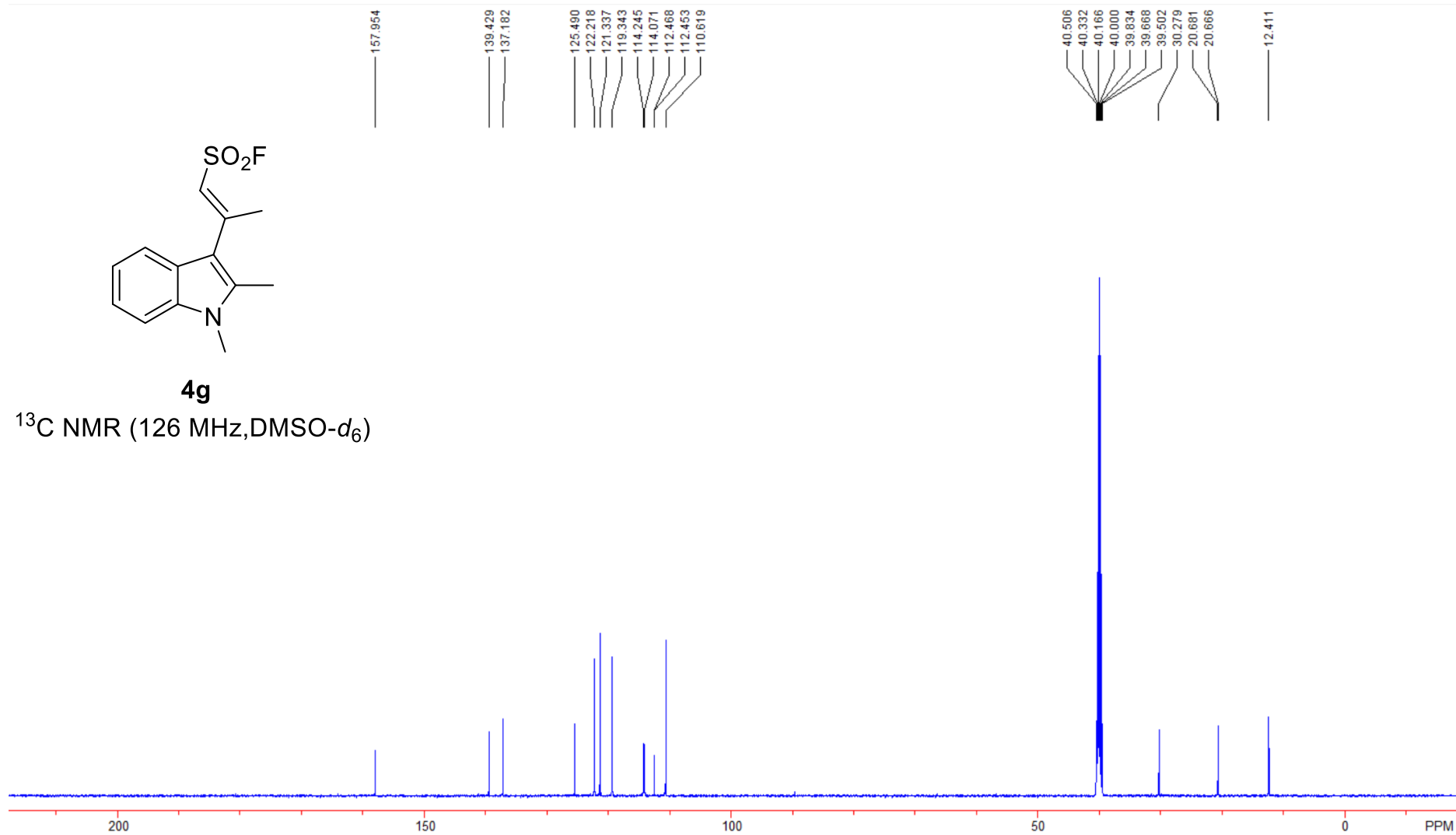
68.591

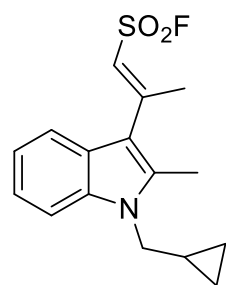




**4g**

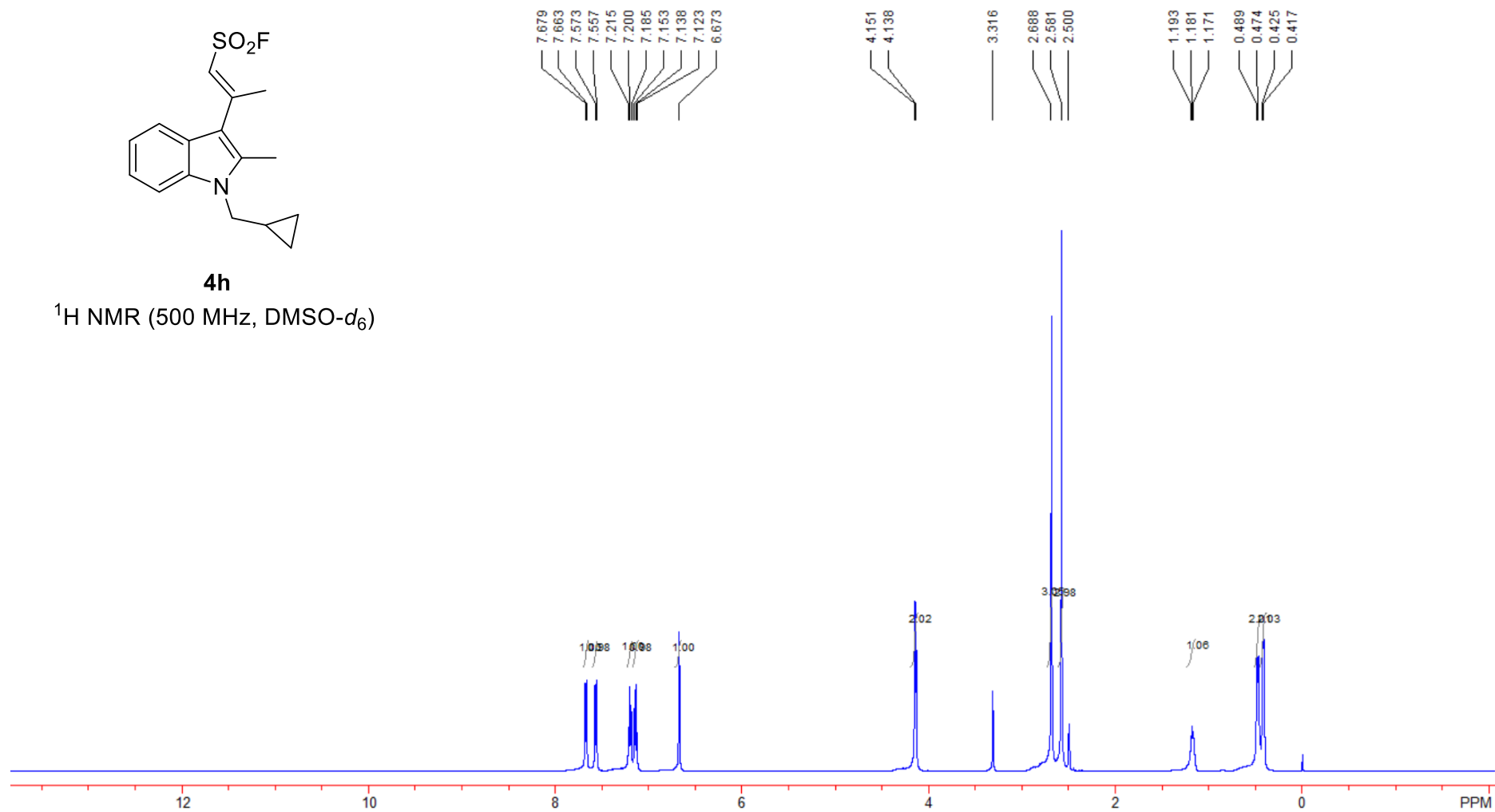
$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )



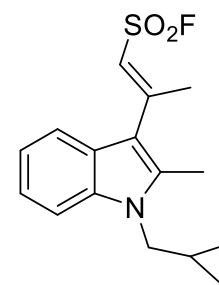


**4h**

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

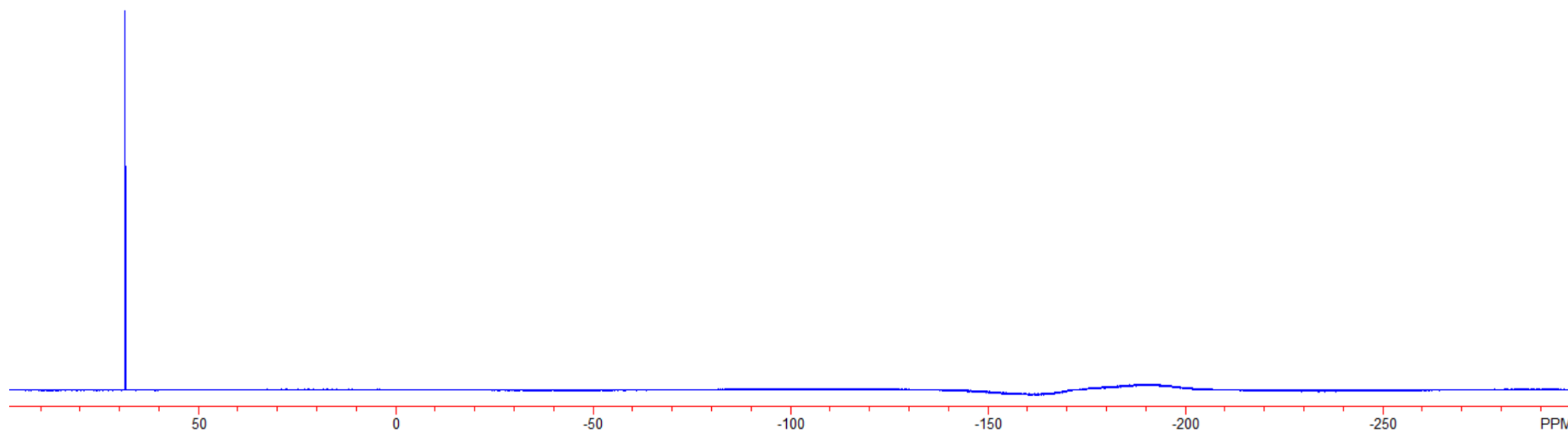


68.497



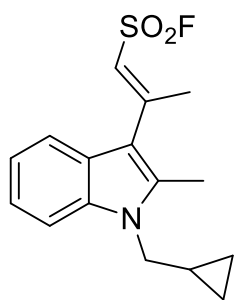
**4h**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)



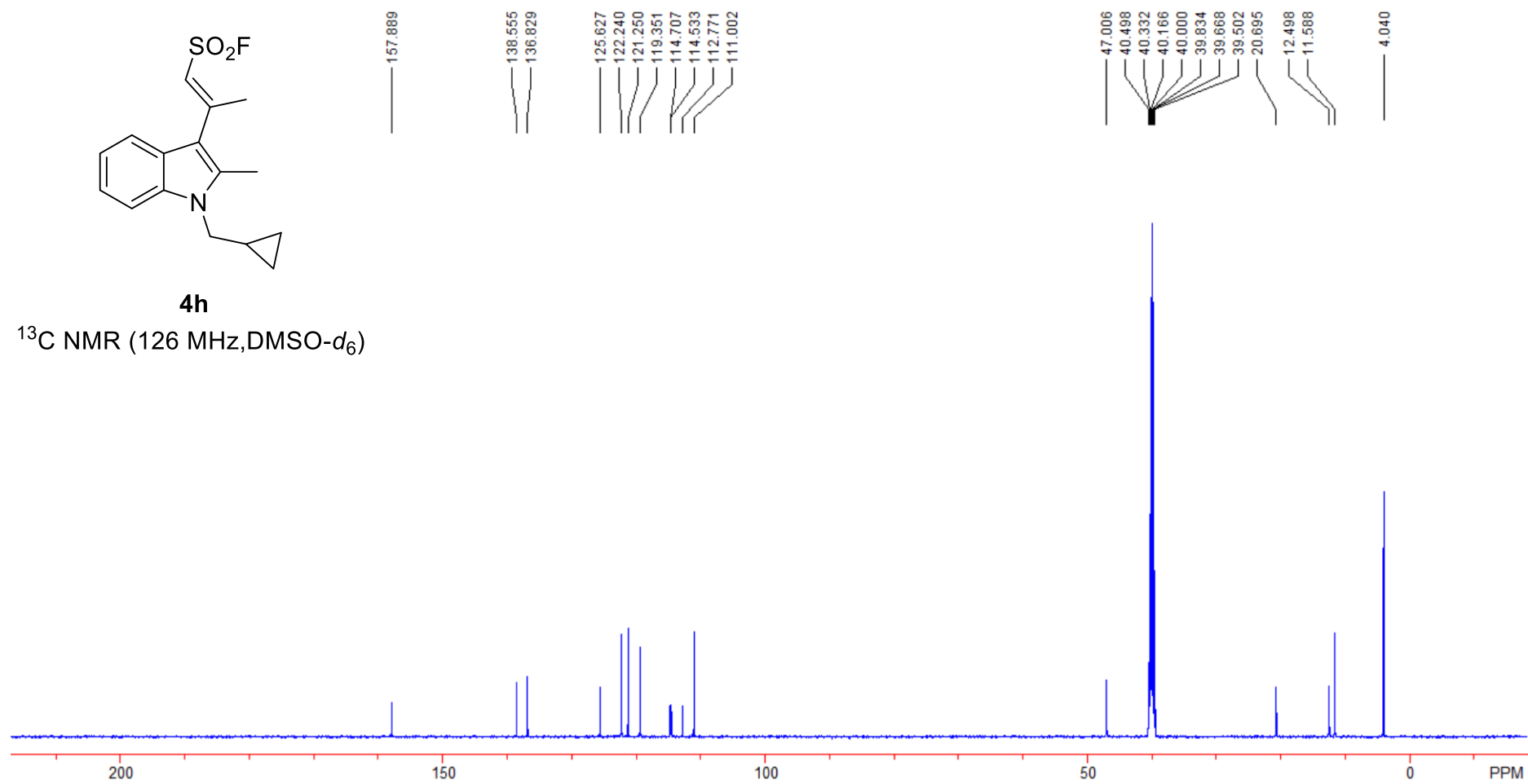
S134

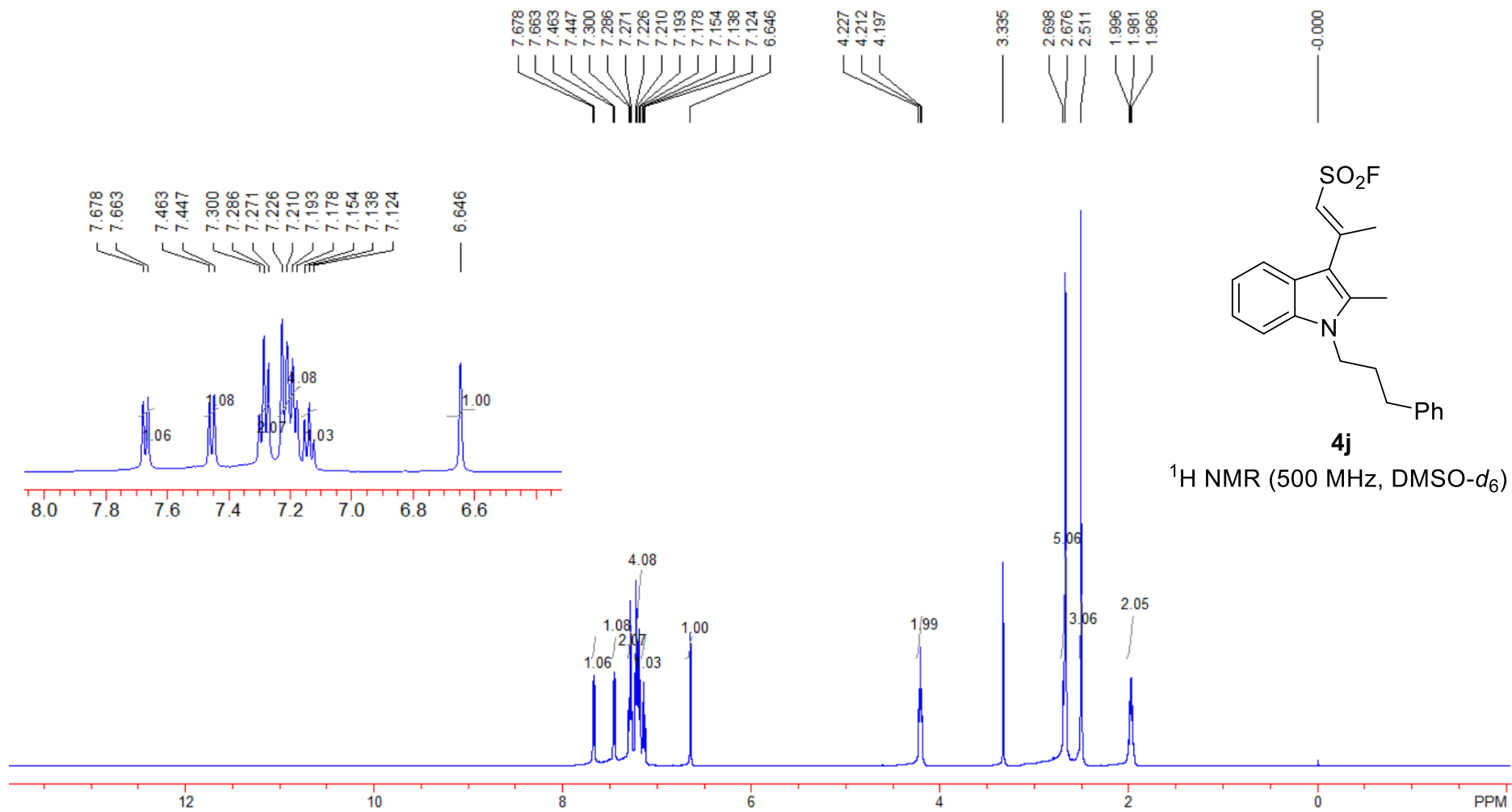


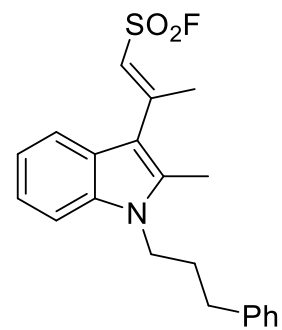


**4h**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

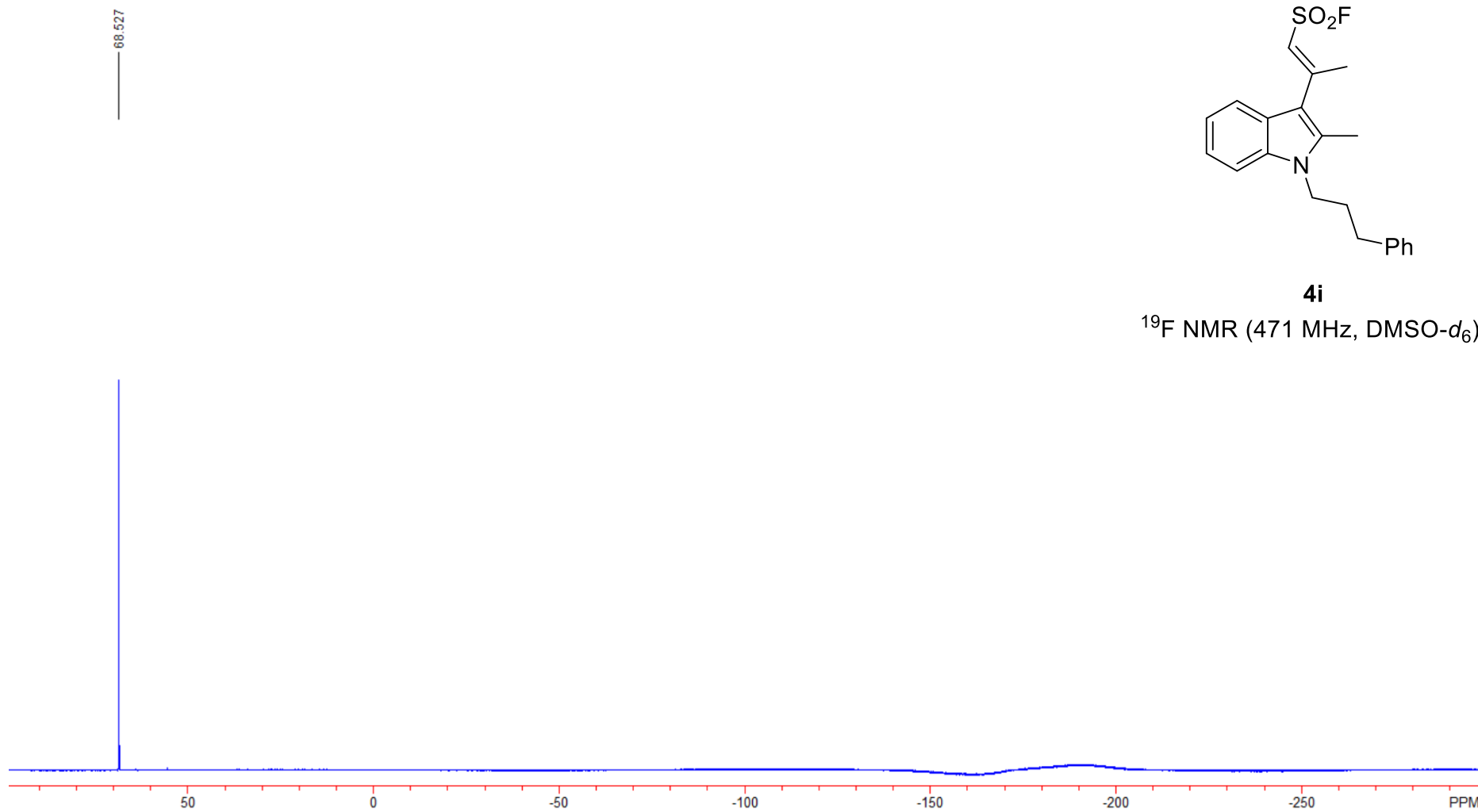


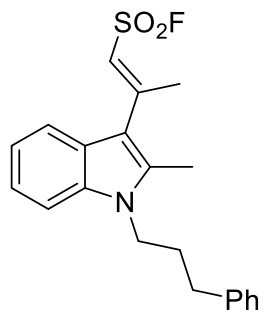




**4i**

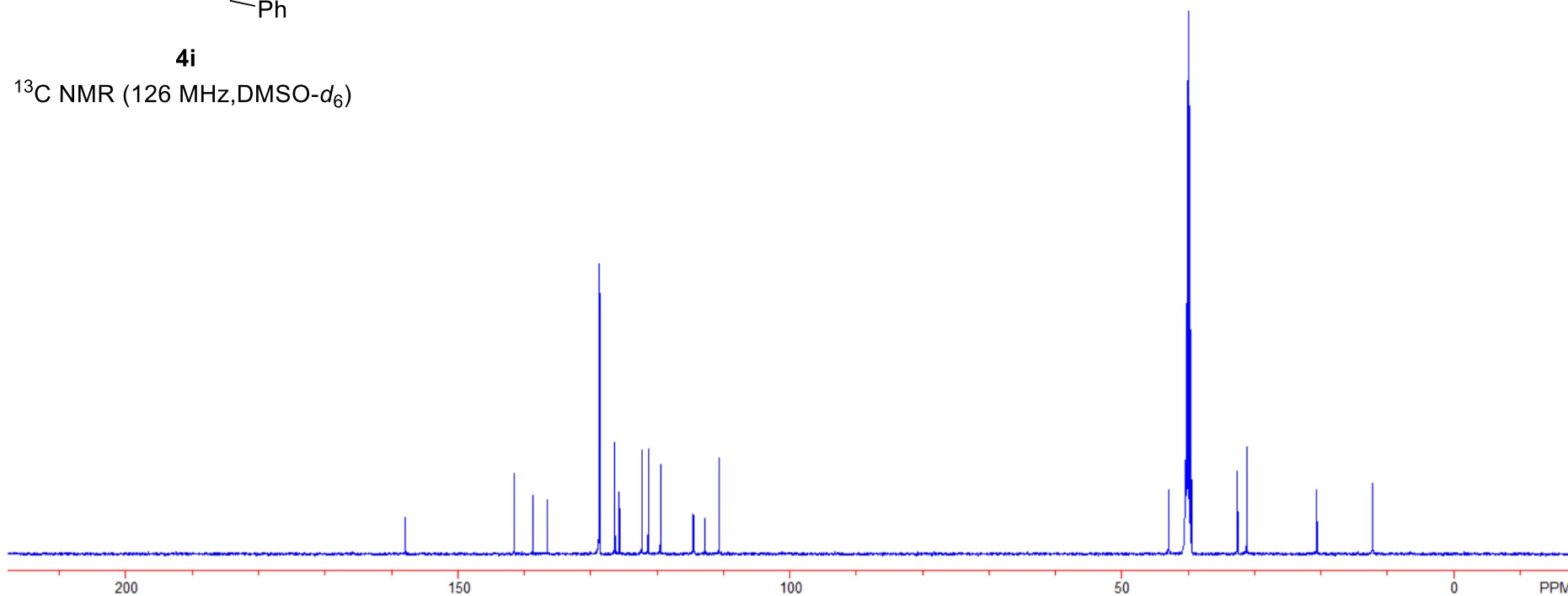
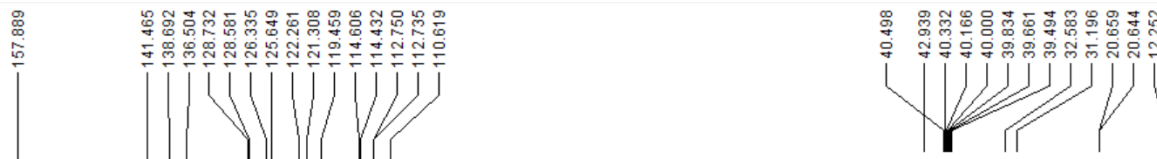
<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)

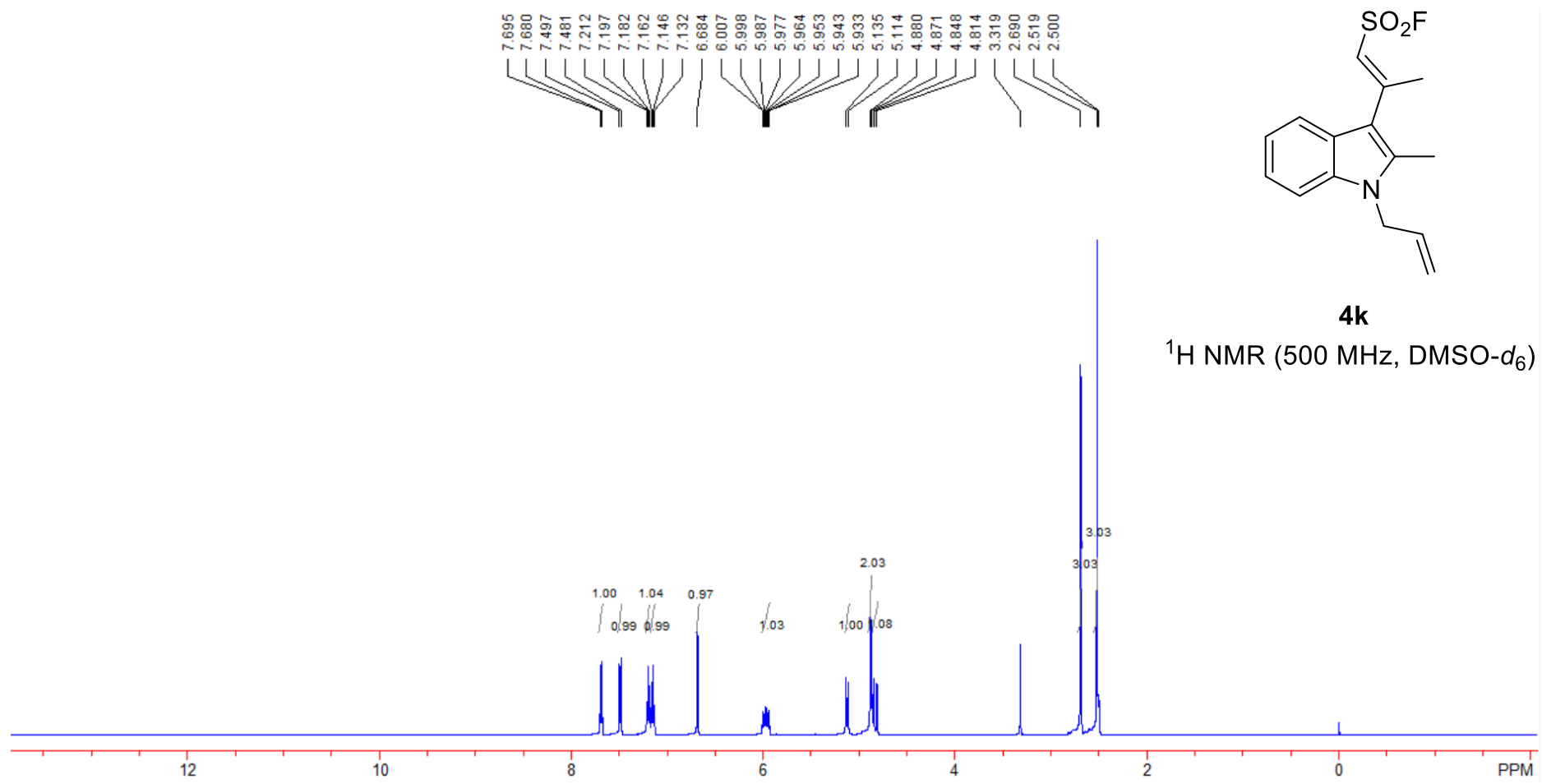


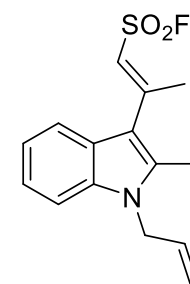


**4i**

<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)

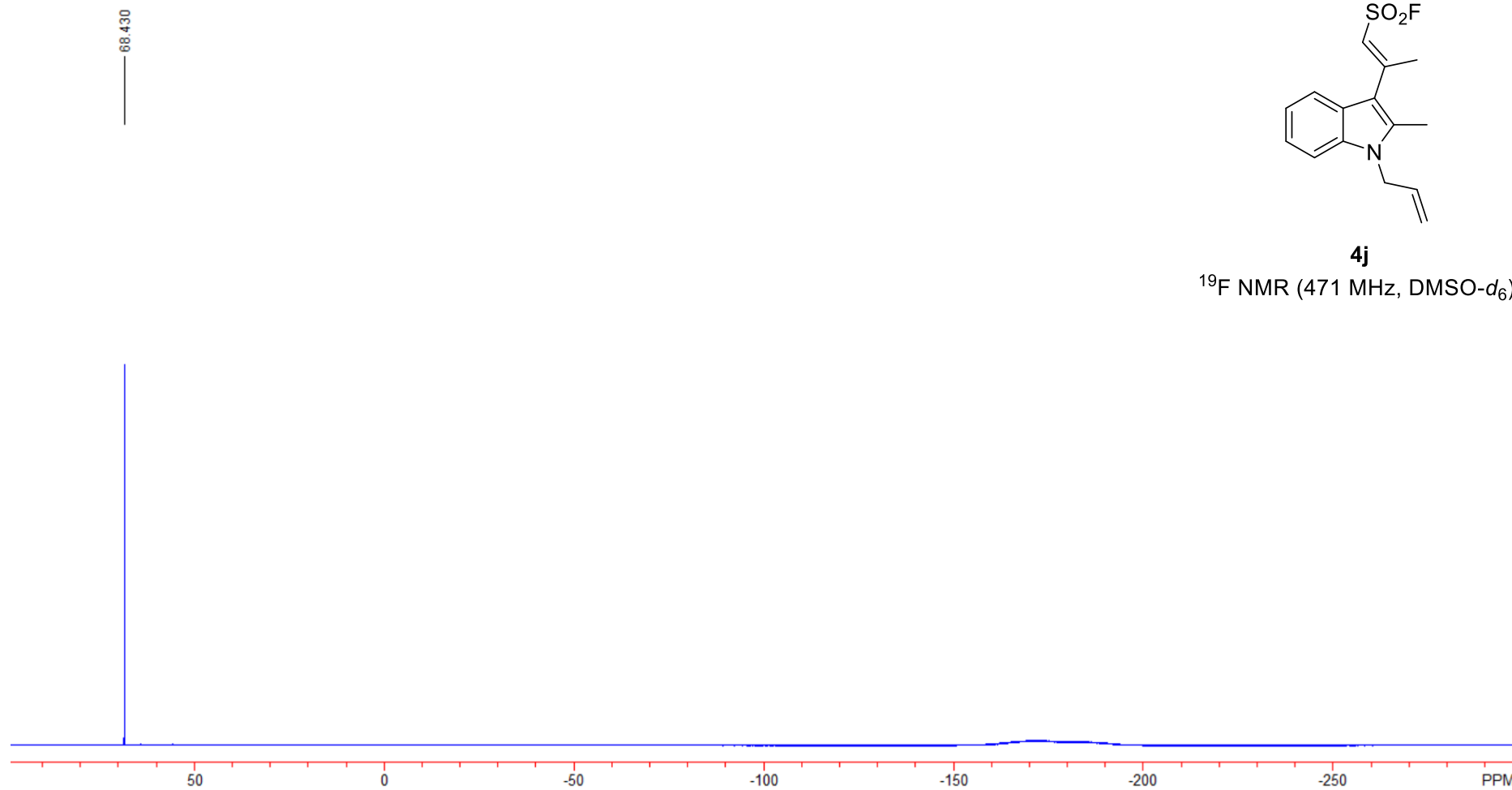


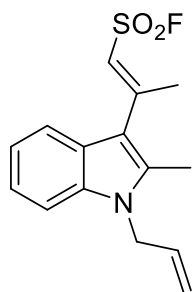




**4j**

<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>)





**4j**

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

