Supporting Information

A reductive dehalogenative process for chemo- and stereoselective synthesis of 1,3-dienylsulfonyl fluorides

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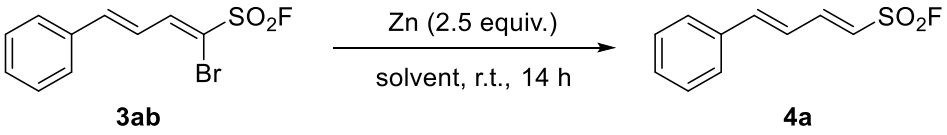
1. General Information

All reactions were carried out under an air atmosphere unless otherwise specified. Oil bath was used for the heating reactions. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), and 126 MHz (for ^{13}C) Bruker Avance spectrometer, and were internally referenced to solvent residual signals (note: $CDCl_3$: δ H = 7.264 ppm, δ C = 77.16 ppm; DMSO-d_6: δ H = 2.500 ppm, δ C = 39.52 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. The coupling constants were reported in Hertz (Hz). The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the HPLC yields of the products were determined by using the corresponding pure compounds as the external standards. Melting points were measured and uncorrected. HRMS experiments were performed on a TOF-Q ESI instrument. Reagents used in the reactions were all purchased from commercial sources and used without further purification.

2. Optimization of the Reaction Conditions

Table S1 Screening of the solvent[a]

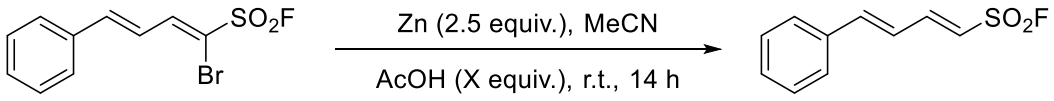


3ab **4a**

Entry	Solvent (v: v)	Yield (**4a**, %)[b]
1	DCM: AcOH (1: 1)	82
2	Acetone: AcOH (1: 1)	97
3	THF: AcOH (1: 1)	96
4	1,4-Dioxane: AcOH (1: 1)	91
5	**MeCN: AcOH (1: 1)**	**98**
6	EA: AcOH (1: 1)	85
7	EtOH: AcOH (1: 1)	90
8	H_2O: AcOH (1: 1)	65

[a]Reaction conditions: a mixture of (1*Z*,3*E*)-1-bromo-4-phenylbuta-1,3-diene-1-sulfonyl fluoride (**3ab,** 58 mg, 0.2 mmol, 1.0 equiv.) and Zn powder (33 mg, 0.5 mmol, 2.5 equiv.) in co-solvent (1.0 mL) was stirred at room temperature for 14 h. [b]HPLC yield ($t_{R,\mathbf{4a}}$ = 3.716 min, $\lambda_{max,\ \mathbf{4a}}$ = 308.2 nm; acetonitrile/water = 80: 20 (v/v)).

Table S2 Screening of the AcOH loading[a]

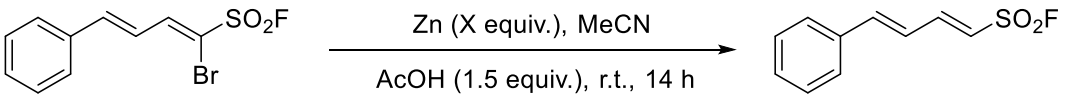


3ab **4a**

Entry	AcOH (X equiv.)	Yield (**4a**, %)[b]
1	1.0	92
2	**1.5**	**99**
3	2.0	98
4	2.5	96
5	3.0	97
6	4.0	99
7	5.0	96

[a]Reaction conditions: a mixture of (1*Z*,3*E*)-1-bromo-4-phenylbuta-1,3-diene-1-sulfonyl fluoride (**3ab,** 58 mg, 0.2 mmol, 1.0 equiv.), Zn powder (33 mg, 0.5 mmol, 2.5 equiv.) and AcOH (X equiv.) in MeCN (1.0 mL) was stirred at room temperature for 14 h. [b]HPLC yield ($t_{R,\mathbf{4a}}$ = 3.716 min, $\lambda_{max,\mathbf{4a}}$ = 308.2 nm; acetonitrile/water = 80: 20 (v/v)).

Table S3 Screening of the Zn loading[a]

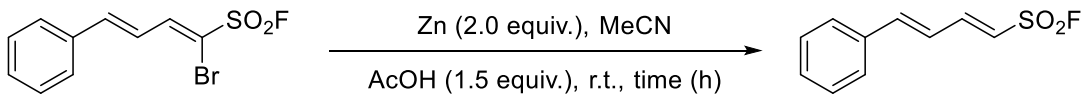


3ab **4a**

Entry	Zn (X equiv.)	Yield (**4a**, %)[b]
1	1.0	78
2	1.5	93
3	**2.0**	**98**
4	2.5	98

[a]Reaction conditions: a mixture of (1*Z*,3*E*)-1-bromo-4-phenylbuta-1,3-diene-1-sulfonyl fluoride (**3ab,** 58 mg, 0.2 mmol, 1.0 equiv.), Zn powder (X equiv.) and AcOH (18 mg, 0.3 mmol, 1.5 equiv.) in MeCN (1.0 mL) was stirred at room temperature for 14 h. [b]HPLC yield ($t_{R,\mathbf{4a}}$ = 3.716 min, $\lambda_{max,\ \mathbf{4a}}$ = 308.2 nm; acetonitrile/water = 80: 20 (v/v)).

Table S4 Screening of the reaction time[a]

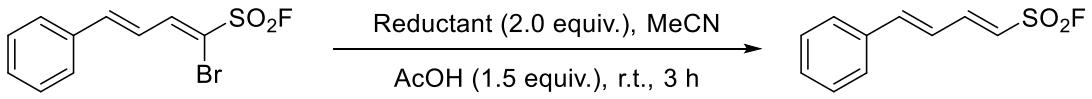


3ab **4a**

Entry	Time (h)	Yield (**4a**, %)[b]
1	0.5	92
2	1	94
3	2	95
4	**3**	**98**
5	4	97
6	5	98

[a]Reaction conditions: a mixture of (1*Z*,3*E*)-1-bromo-4-phenylbuta-1,3-diene-1-sulfonyl fluoride (**3ab,** 58 mg, 0.2 mmol, 1.0 equiv.), Zn powder (26 mg, 0.4 mmol, 2.0 equiv.) and AcOH (18 mg, 0.3 mmol, 1.5 equiv.) in MeCN (1.0 mL) was stirred at room temperature for the corresponding time. [b]HPLC yield ($t_{R,\mathbf{4a}}$ = 3.716 min, $\lambda_{max,\,\mathbf{4a}}$ = 308.2 nm; acetonitrile/water = 80: 20 (v/v)).

Table S5 Screening of the reductant[a]



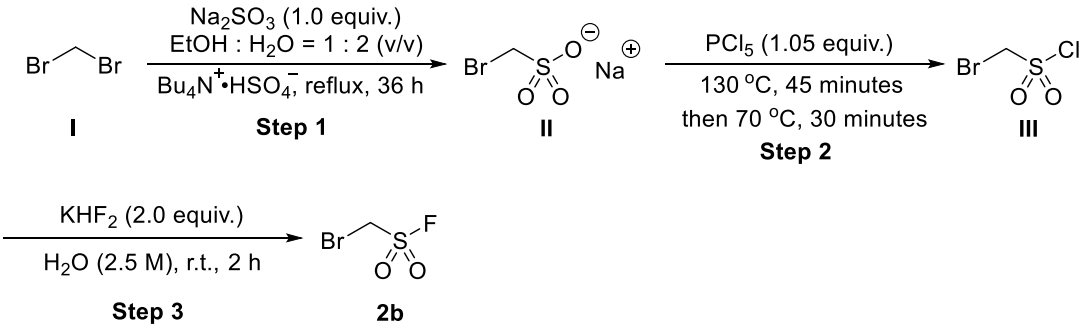
3ab **4a**

Entry	Reductant (2.0 equiv.)	Yield (**4a**, %)[b]
1	Mg	trace
2	Mn	trace
3	Et_3SiH	trace
4	**Zn**	**98**

[a]Reaction conditions: a mixture of (1*Z*,3*E*)-1-bromo-4-phenylbuta-1,3-diene-1-sulfonyl fluoride (**3ab,** 58 mg, 0.2 mmol, 1.0 equiv.), reductant (2.0 equiv.) and AcOH (18 mg, 0.3 mmol, 1.5 equiv.) in MeCN (1.0 mL) was stirred at room temperature for 3 h. [b]HPLC yield ($t_{R,\mathbf{4a}}$ = 3.716 min, $\lambda_{max,\ \mathbf{4a}}$ = 308.2 nm; acetonitrile/water = 80: 20 (v/v)).

3. Experimental Procedures

3.1 Preparation of bromomethanesulfonyl fluoride (2b)[1]



Step 1: A 1000 mL round bottom flask equipped with a magnetic stirring bar was charged with CH_2Br_2 (**I**, 343.7 g, 2 mol), Na_2SO_3 (252.1 g, 2 mol), tetrabutylammonium hydrogen sulfate (10.0 g, 0.03 mol) and co-solvent EtOH / H_2O (v/v = 1:2, 600 mL), then the mixture was refluxed for 36 h with vigorous stirring. The solvent was evaporated under vacuum and the resulting solid residue was dissolved in a warm mixture of H_2O (320 mL) and EtOH (1800 mL). After filtration of some insoluble materials, the filtrate was cooled at -20 ℃. The crystalline sodium salt was collected by filtration: 298.6 g (76% yield).

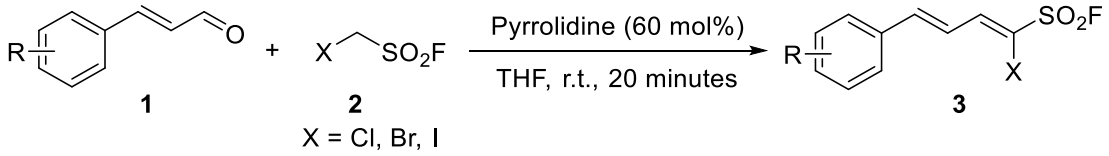
Step 2: A 500 mL three-necked flask, equipped with a magnetic stirring bar, a glass stopper and a reflux condenser, was charged with sodium bromomethanesulfonate (**II**, 195.9 g, 1 mol), and cooled with an ice bath. Phosphorus pentachloride (218.6 g, 1.05 mol) was added cautiously to the sulfonate with vigorous stirring. It liquified immediately and the reddish brown solution was heated at 130 ℃ for 45 minutes and then at 70 ℃ for 30 minutes. The solution was then poured into 500 mL of ice water and allowed to stand for 1 h in order to hydrolyze the phosphorus oxychloride. Bromomethanesulfonyl chloride (**III**) was extracted with methylene chloride (150 mL×3). The combined methylene chloride extracts were washed with 200 mL of water, two 200 mL portions of 5% sodium bicarbonate, and finally with 150 mL of water. The solvent was evaporated to give crude bromomethanesulfonyl chloride (**III**), which was used directly in the next step.

Step 3: KHF_2 (156.2 g, 2 mol) was added to 400 mL water and a nearly saturated KHF_2 solution formed after 1 h, when the solution approached to room temperature. At

this point, the crude bromomethanesulfonyl chloride generated from the previous step was all added to KHF_2 solution, then the mixture was allowed to stir at room temperature for 2 h. After the reaction got its completion, the stationary mixture separates into two phases. The upper phase is an aqueous solution of salts, and the lower phase is bromomethanesulfonyl fluoride. Bromomethanesulfonyl fluoride was extracted with methylene chloride (100 mL×3), and the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated using a rotary evaporator to give crude bromomethanesulfonyl fluoride. Further reduced pressure distillation to provide the pure bromomethanesulfonyl fluoride (**2b**) as colorless liquid (97.3 g, 55% yield over two steps).

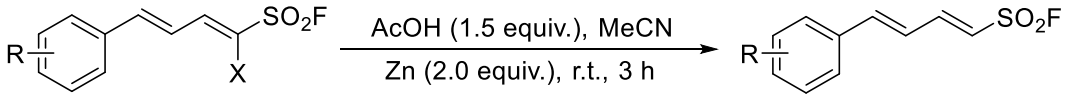
Iodomethanesulfonyl fluoride (**2a**) and chloromethanesulfonyl fluoride (**2c**) were prepared following the similar procedures as described above according to the literature[1].

3.2 General procedure for synthesis of *α*-halo-1,3-dienylsulfonyl fluorides (3)[1]



Aldehyde (**1**, 1.0 mmol, 1.0 equiv.), pyrrolidine (60 mol%, 50 μL) and THF (5 mL, 0.2 M) were added to an oven-dried reaction tube equipped with a magnetic stirring bar, and the stirring was lasted for 5 minutes before the subsequent addition of halomethylsulfonyl fluoride (**2**, 3.0 mmol, 3.0 equiv.). Then, the resulting mixture was allowed to stir at room temperature for about 20 minutes, until the aldehyde was completely consumed monitored by TLC. The mixture was diluted with ethyl acetate (10 mL) and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluent to afford the target product **3**.

3.3 General procedure for synthesis of 1,3-dienylsulfonyl fluorides (4)

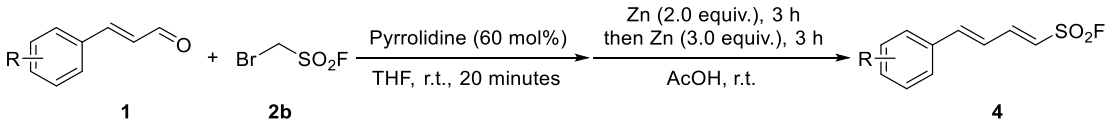


3
X = Cl, Br, I

4

An oven-dried reaction tube equipped with a magnetic stirring bar was charged with *α*-halo-1,3-dienylsulfonyl fluorides (**3**, 1.0 mmol, 1.0 equiv.), Zn powder (2.0mmol, 2.0 equiv.), AcOH (1.5 mmol, 1.5 equiv.) and MeCN (5 mL, 0.2 M), then the mixture reacted at room temperature for 3 h. When the reaction reached its completion, the mixture was diluted with ethyl acetate (10 mL) and filtered, then the filtrate was concentrated to dryness under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (or dichloromethane) as eluent to afford the target product **4**.

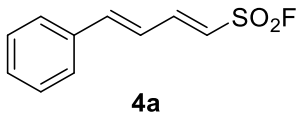
3.4 One-pot procedure for synthesis of 1,3-dienylsulfonyl fluorides (4)



1 **2b** **4**

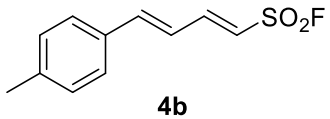
An oven-dried reaction tube equipped with a magnetic stirring bar was charged with aldehyde (**1**, 1.0 mmol, 1.0 equiv.), pyrrolidine (60 mol%, 50 μL) and THF (5 mL, 0.2 M) and the stirring was lasted for 5 minutes before the subsequent addition of bromomethanesulfonyl fluoride (**2b**, 3.0 mmol, 3.0 equiv.). Then, the mixture reacted at room temperature for about 20 minutes, until the aldehyde was completely consumed monitored by TLC. Zn powder (2.0 mmol, 2.0 equiv.) and AcOH (5 mL) were added to the crude reaction mixture, then the stirring was lasted for 3 h before the subsequent addition of another portion of Zn powder (3.0 mmol, 3.0 equiv.). After the addition was over, the resulting mixture was allowed to stir at room temperature for 3 h. Once the reaction reached its completion, the mixture was diluted with water and extracted with methylene chloride (3×20 mL), then the combined organic phase was washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluent to afford the target product **4**.

4. Characterization



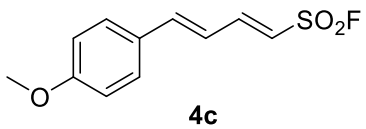
4a

(1E,3E)-4-phenylbuta-1,3-diene-1-sulfonyl fluoride (**4a**). Yellow solid, 206 mg, 97% isolated yield from *α*-iodo-1,3-dienylsulfonyl fluoride (**3aa**); 204 mg, 96% isolated yield from *α*-bromo-1,3-dienylsulfonyl fluoride (**3ab**); 49 mg, 23% isolated yield, 72% (The yield was based on the recovery of the starting material) from *α*-chloro-1,3-dienylsulfonyl fluoride (**3ac**); 148 mg, 70% isolated yield from cinnamaldehyde (**1a**). Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (dd, J_1 = 14.7 Hz, J_2 = 11.2 Hz, 1H), 7.53-7.51 (m, 2H), 7.44-7.41 (m, 3H), 7.12 (d, J = 15.6 Hz, 1H), 6.87 (dd, J_1 = 15.5 Hz, J_2 = 11.2 Hz 1H), 6.45 (dd, J_1 = 14.8 Hz, J_2 = 1.9 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.0 (s, 1F).



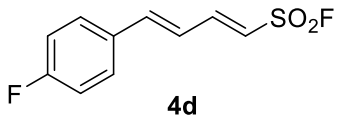
4b

(1E,3E)-4-(p-tolyl)buta-1,3-diene-1-sulfonyl fluoride (**4b**). Yellow solid, 213 mg, 94% isolated yield from *α*-iodo-1,3-dienylsulfonyl fluoride (**3ba**); 221 mg, 97% isolated yield from *α*-bromo-1,3-dienylsulfonyl fluoride (**3bb**); 151 mg, 67% isolated yield from (*E*)-3-(*p*-tolyl)acrylaldehyde (**1b**). Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (dd, J_1 = 14.6 Hz, J_2 = 11.4 Hz, 1H), 7.41 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 15.5 Hz, 1H), 6.82 (dd, J_1 = 15.3 Hz, J_2 = 11.2 Hz, 1H), 6.41 (d, J = 14.7 Hz, 1H), 2.40 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.1 (s, 1F).



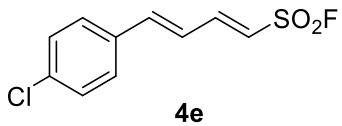
4c

(1E,3E)-4-(4-methoxyphenyl)buta-1,3-diene-1-sulfonyl fluoride (**4c**). Light yellow solid, 231 mg, 95% isolated yield from *α*-iodo-1,3-dienylsulfonyl fluoride (**3ca**); 226 mg, 93% isolated yield from *α*-bromo-1,3-dienylsulfonyl fluoride (**3cb**); 184 mg, 76% isolated yield from (*E*)-3-(4-methoxyphenyl)acrylaldehyde (**1c**). M.p. 91-92 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 14.7 Hz, J_2 = 11.3 Hz, 1H), 7.46 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 15.4 Hz, 1H), 6.93 (d, J = 8.9 Hz, 2H), 6.74 (dd, J_1 = 15.4 Hz, J_2 = 11.2 Hz, 1H), 6.37 (dd, J_1 = 14.7 Hz, J_2 = 2.0 Hz, 1H), 3.85 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8, 149.3 (d, J = 2.8 Hz), 146.4, 129.8, 127.6, 120.2, 117.5 (d, J = 27.2 Hz), 114.7, 55.5. **HRMS-ESI** (m/z) calcd. for $[C_{11}H_{12}FO_3S]^+$ ($[M+H]^+$): 243.0486, found: 243.0489.



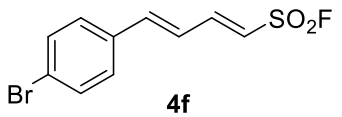
4d

(1E,3E)-4-(4-fluorophenyl)buta-1,3-diene-1-sulfonyl fluoride (**4d**). White solid, 220 mg, 95% isolated yield. M.p. 50-52 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57-7.49 (m, 3H), 7.12-7.07 (m, 3H), 6.79 (dd, J_1 = 15.3 Hz, J_2 = 11.2 Hz, 1H), 6.45 (d, J = 14.8 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.9 (s, 1F), -108.8 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.1 (d, J = 252.5 Hz), 148.5 (d, J = 2.8 Hz), 145.1, 131.1 (d, J = 3.6 Hz), 129.9 (d, J = 8.2 Hz), 122.2 (d, J = 1.8 Hz), 119.4 (d, J = 27.2 Hz), 116.4 (d, J = 21.8 Hz). **HRMS-ESI** (m/z) calcd. for $[C_{10}H_9F_2O_2S]^+$ ($[M+H]^+$): 231.0286, found: 231.0288.



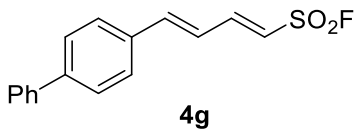
4e

(1E,3E)-4-(4-chlorophenyl)buta-1,3-diene-1-sulfonyl fluoride (**4e**). Yellow solid, 230 mg, 93% isolated yield from *α*-iodo-1,3-dienylsulfonyl fluoride (**3ea**); 226 mg, 92% isolated yield from *α*-bromo-1,3-dienylsulfonyl fluoride (**3eb**); 153 mg, 62% isolated yield from (*E*)-3-(4-chlorophenyl)acrylaldehyde (**1e**). Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 14.6 Hz, J_2 = 11.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 15.6 Hz, 1H), 6.84 (dd, J_1 = 15.5 Hz, J_2 = 11.2 Hz, 1H), 6.47 (d, J = 14.8 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.9 (s, 1F).



4f

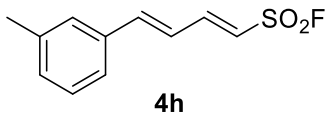
(1E,3E)-4-(4-bromophenyl)buta-1,3-diene-1-sulfonyl fluoride (**4f**). Yellow solid, 268 mg, 92% isolated yield. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56-7.51 (m, 3H), 7.37 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 15.4 Hz, 1H), 6.86 (dd, J_1 = 15.4 Hz, J_2 = 11.2 Hz, 1H), 6.47 (d, J = 14.8 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.8 (s, 1F).



4g

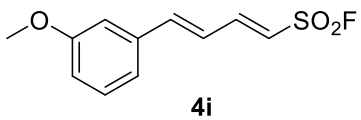
(1E,3E)-4-([1,1'-biphenyl]-4-yl)buta-1,3-diene-1-sulfonyl fluoride (**4g**). Light yellow solid, 270 mg, 93% isolated yield. M.p. 191-193 ℃. Purification by column chromatography on silica gel using petroleum ether / dichloromethane = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.62 (m, 4H), 7.61-7.56 (m, 3H), 7.49-7.46 (m, 2H), 7.41-7.38 (m, 1H), 7.16 (d, J = 15.5 Hz, 1H), 6.91 (dd, J_1 = 15.5 Hz, J_2 = 11.2

Hz, 1H), 6.46 (dd, J_1 = 14.8 Hz, J_2 = 1.8 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.1 (s, 1F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 149.7 (d, J = 2.7 Hz), 146.0, 141.8, 139.1, 134.0, 129.0, 128.6, 128.0, 127.2, 126.7, 123.2, 118.9 (d, J = 25.5 Hz). **HRMS-ESI** (m/z) calcd. for $[C_{16}H_{14}FO_2S]^+$ ($[M+H]^+$): 289.0693, found: 289.0690.



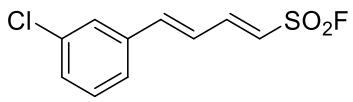
4h

(1E,3E)-4-(m-tolyl)buta-1,3-diene-1-sulfonyl fluoride (**4h**). Yellow solid, 215 mg, 95% isolated yield. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 30:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (dd, J_1 = 14.7 Hz, J_2 = 11.2 Hz, 1H), 7.33-7.29 (m, 3H), 7.23-7.20 (m, 1H), 7.09 (d, J = 15.4 Hz, 1H), 6.86 (dd, J_1 = 15.4 Hz, J_2 = 11.1 Hz, 1H), 6.43 (dd, J_1 = 14.8 Hz, J_2 = 2.0 Hz, 1H), 2.39 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.0 (s, 1F).



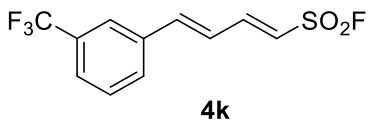
4i

(1E,3E)-4-(3-methoxyphenyl)buta-1,3-diene-1-sulfonyl fluoride (**4i**). Light yellow solid, 202 mg, 83% isolated yield. M.p. 64-66 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 14.8 Hz, J_2 = 11.3 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.11-7.06 (m, 2H), 7.02 (s, 1H), 6.96 (dd, J_1 = 8.2 Hz, J_2 = 2.4 Hz, 1H), 6.85 (dd, J_1 = 15.4 Hz, J_2 = 11.1 Hz, 1H), 6.44 (dd, J_1 = 14.8 Hz, J_2 = 1.4 Hz, 1H), 3.85 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.9 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.2, 148.6 (d, J = 2.8 Hz), 146.4, 136.2, 130.2, 122.7, 120.7, 119.4 (d, J = 27.2 Hz), 116.4, 113.1, 55.5. **HRMS-ESI** (m/z) calcd. for $[C_{11}H_{12}FO_3S]^+$ ($[M+H]^+$): 243.0486, found: 243.0484.



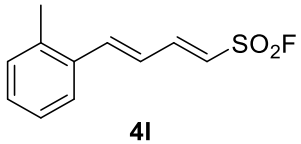
4j

(1E,3E)-4-(3-chlorophenyl)buta-1,3-diene-1-sulfonyl fluoride (**4j**). Light yellow solid, 219 mg, 89% isolated yield. M.p. 47-49 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 40:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 14.7 Hz, J_2 = 11.2 Hz, 1H), 7.49 (s, 1H), 7.38-7.33 (m, 3H), 7.04 (d, J = 15.5 Hz, 1H), 6.86 (dd, J_1 = 15.5 Hz, J_2 = 11.0 Hz, 1H), 6.49 (dd, J_1 = 14.8 Hz, J_2 = 1.4 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.8 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0 (d, J = 2.7 Hz), 144.6, 136.6, 135.2, 130.47, 130.44, 127.7, 126.2, 123.7, 120.4 (d, J = 28.2 Hz). **HRMS-ESI** (m/z) calcd. for $[C_{10}H_9ClFO_2S]^+$ ($[M+H]^+$): 246.9990, found: 246.9985.



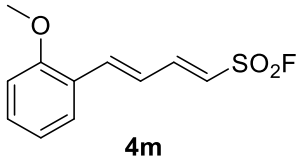
4k

(1E,3E)-4-(3-(trifluoromethyl)phenyl)buta-1,3-diene-1-sulfonyl fluoride (**4k**). White solid, 270 mg, 96% isolated yield from *α*-iodo-1,3-dienylsulfonyl fluoride (**3ka**); 251 mg, 89% isolated yield from *α*-bromo-1,3-dienylsulfonyl fluoride (**3kb**). M.p. 52-54 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.59-7.54 (m, 2H), 7.14 (d, J = 15.5 Hz, 1H), 6.94 (dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz, 1H), 6.53 (dd, J_1 = 14.8 Hz, J_2 = 1.2 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.6 (s, 1F), -62.9 (s, 3F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.8 (d, J = 2.7 Hz), 144.3, 135.6, 131.8 (q, J = 32.7 Hz), 131.0, 129.8, 127.0 (q, J = 3.6 Hz), 124.4 (q, J = 3.6 Hz), 124.2, 123.9 (q, J = 272.5 Hz), 120.9 (d, J = 28.2 Hz). **HRMS-ESI** (m/z) calcd. for $[C_{11}H_9F_4O_2S]^+$ ($[M+H]^+$): 281.0254, found: 281.0257.



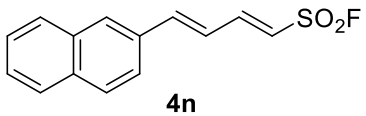
4l

(1E,3E)-4-(o-tolyl)buta-1,3-diene-1-sulfonyl fluoride (**4l**). Yellow liquid, 206 mg, 91% isolated yield. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.38 (d, J = 15.2 Hz, 1H), 7.30-7.28 (m, 1H), 7.25-7.21 (m, 2H), 6.79 (dd, J_1 = 15.4 Hz, J_2 = 11.3 Hz, 1H), 6.43 (dd, J_1 = 14.8 Hz, J_2 = 1.3 Hz, 1H), 2.41 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.0 (s, 1F).



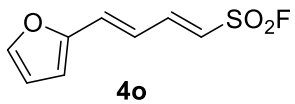
4m

(1E,3E)-4-(2-methoxyphenyl)buta-1,3-diene-1-sulfonyl fluoride (**4m**). Light yellow solid, 235 mg, 97% isolated yield from α-iodo-1,3-dienylsulfonyl fluoride (**3ma**); 233 mg, 96% isolated yield from α-bromo-1,3-dienylsulfonyl fluoride (**3mb**); 189 mg, 78% isolated yield from (*E*)-3-(2-methoxyphenyl)acrylaldehyde (**1m**). M.p. 39-41 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (dd, J_1 = 14.8 Hz, J_2 = 11.3 Hz, 1H), 7.50 (dd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H), 7.44 (d, J = 15.8 Hz, 1H), 7.38 (td, J_1 = 8.6 Hz, J_2 = 1.5 Hz, 1H), 7.01-6.92 (m, 3H), 6.39 (dd, J_1 = 14.8 Hz, J_2 = 2.0 Hz, 1H), 3.90 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.2 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.3, 149.9 (d, J = 2.8 Hz), 142.2, 132.0, 128.6, 123.8, 123.0, 121.0, 118.2 (d, J = 27.2 Hz), 111.4, 55.7. **HRMS-ESI** (m/z) calcd. for $[C_{11}H_{12}FO_3S]^+$ ($[M+H]^+$): 243.0486, found: 243.0481.



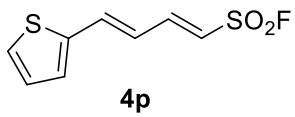
4n

(1E,3E)-4-(naphthalen-2-yl)buta-1,3-diene-1-sulfonyl fluoride (**4n**). Yellow solid, 227 mg, 86% isolated yield. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.88-7.84 (m, 3H), 7.65 (dd, J_1 = 8.7 Hz, J_2 = 1.6 Hz, 1H), 7.61 (dd, J_1 = 14.7 Hz, J_2 = 11.2 Hz, 1H), 7.56-7.52 (m, 2H), 7.26 (d, J = 15.5 Hz, 1H), 6.97 (dd, J_1 = 15.6 Hz, J_2 = 11.3 Hz, 1H), 6.47 (dd, J_1 = 14.7 Hz, J_2 = 1.9 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.1 (s, 1F).



4o

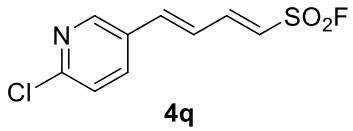
(1E,3E)-4-(furan-2-yl)buta-1,3-diene-1-sulfonyl fluoride (**4o**). Light brown solid, 183 mg, 90% isolated yield from α-bromo-1,3-dienylsulfonyl fluoride (**3ob**); 143 mg, 71% isolated yield from (*E*)-3-(furan-2-yl)acrylaldehyde (**1o**). M.p. 55-57 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 6.86 (d, J = 15.3 Hz, 1H), 6.75 (dd, J_1 = 15.3 Hz, J_2 = 11.5 Hz, 1H), 6.63 (d, J = 3.4 Hz, 1H), 6.51-6.50 (m, 1H), 6.40 (d, J = 14.8 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.2 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.2, 148.2 (d, J = 2.8 Hz), 145.4, 132.1, 120.5, 118.7 (d, J = 27.2 Hz), 115.2, 112.8. **HRMS-ESI** (m/z) calcd. for $[C_8H_8FO_3S]^+$ ($[M+H]^+$): 203.0173, found: 203.0169.



4p

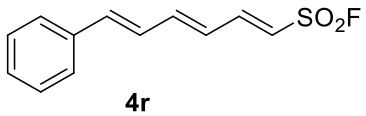
(1E,3E)-4-(thiophen-2-yl)buta-1,3-diene-1-sulfonyl fluoride (**4p**). Yellow solid, 205 mg, 94% isolated yield. M.p. 112-114 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (dd, J_1 = 14.7 Hz, J_2 = 11.5 Hz, 1H), 7.43 (d, J = 4.9 Hz, 1H), 7.25-7.21

(m, 2H), 7.09-7.07 (m, 1H), 6.65 (dd, J_1 = 15.1 Hz, J_2 = 11.3 Hz, 1H), 6.39 (d, J = 14.6 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.2 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.3 (d, J = 2.7 Hz), 140.2, 138.6, 131.1, 129.2, 128.5, 121.6, 118.4 (d, J = 27.2 Hz). **HRMS-ESI** (m/z) calcd. for $[C_8H_6FO_2S_2]^-$ ([M–H]$^-$): 216.9799, found: 216.9795.



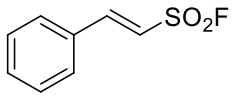
4q

(1E,3E)-4-(6-chloropyridin-3-yl)buta-1,3-diene-1-sulfonyl fluoride (**4q**). Light yellow solid, 211 mg, 85% isolated yield. M.p. 146-148 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 7:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (d, J = 2.3 Hz, 1H), 7.79 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.54 (dd, J_1 = 14.8 Hz, J_2 = 11.1 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.08 (d, J = 15.7 Hz, 1H), 6.91 (dd, J_1 = 15.5 Hz, J_2 = 11.0 Hz, 1H), 6.54 (dd, J_1 = 14.8 Hz, J_2 = 1.2 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.6 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.9, 149.4, 147.3 (d, J = 3.6 Hz), 140.6, 136.5, 129.6, 124.88, 124.86, 121.5 (d, J = 28.1 Hz). **HRMS-ESI** (m/z) calcd. for $[C_9H_8ClFNO_2S]^+$ ([M+H]$^+$): 247.9943, found: 247.9951.



4r

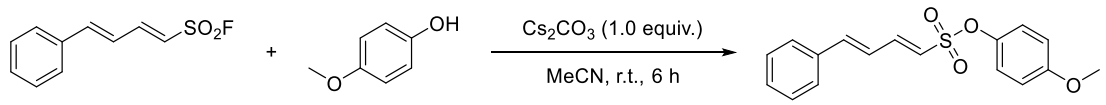
(1E,3E,5E)-6-phenylhexa-1,3,5-triene-1-sulfonyl fluoride (**4r**). Light yellow solid, 208 mg, 87% isolated yield. M.p. 121-123 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50-7.44 (m, 3H), 7.40-7.32 (m, 3H), 6.95-6.86 (m, 3H), 6.46-6.39 (m, 1H), 6.35 (dd, J_1 = 14.8 Hz, J_2 = 1.0 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 63.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.5 (d, J = 2.7 Hz), 146.6, 140.7, 136.0, 129.5, 129.0, 127.4, 126.9, 126.0, 118.3 (d, J = 27.2 Hz). **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{12}FO_2S]^+$ ([M+H]$^+$): 239.0537, found: 239.0542.



6

(E)-2-phenylethene-1-sulfonyl fluoride (**6**). White solid, 181 mg, 97% isolated yield. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 20:1 (v/v) as eluent. The NMR data is identical to that reported in literature.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, J = 15.5 Hz, 1H), 7.57-7.52 (m, 3H), 7.50-7.47 (m, 2H), 6.88 (dd, J_1 = 15.4 Hz, J_2 = 2.6 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 62.3 (s, 1F).

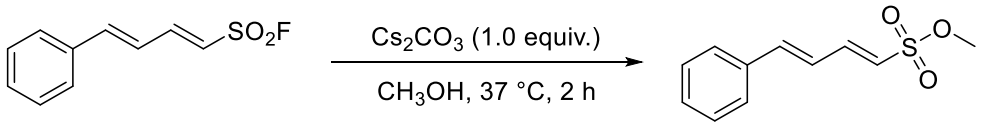
5. SuFEx Reactions of 1,3-Dienylsulfonyl Fluoride (4a)



4a **7** (1.1 equiv.) **8**, 94% yield

A mixture of compound **4a** (106 mg, 0.5 mmol, 1.0 equiv.), 4-methoxyphenol (**7**, 68 mg, 0.55 mmol, 1.1 equiv.), Cs_2CO_3 (163 mg, 0.5 mmol, 1.0 equiv.) and acetonitrile (2.5 mL) was stirred at room temperature for 6 h. The organic solvent was removed under vacuum and the residue was purified through silica gel chromatography using a mixture of petroleum ether and dichloromethane (PE: DCM = 1:2 (v/v)) as eluent to provide the final product sulfonate **8**.

4-methoxyphenyl (1E,3E)-4-phenylbuta-1,3-diene-1-sulfonate **(8)**. White solid, 149 mg, 94% yield. M.p. 100-102 ℃. Purification by column chromatography on silica gel using petroleum ether / dichloromethane = 1:2 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.40-7.35 (m, 3H), 7.25 (dd, J_1 = 14.8 Hz, J_2 = 11.0 Hz, 1H), 7.19-7.16 (m, 2H), 6.95 (d, J = 15.6 Hz, 1H), 6.89-6.87 (m, 2H), 6.82 (dd, J_1 = 15.5 Hz, J_2 = 10.9 Hz, 1H), 6.42 (d, J = 14.8 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.4, 146.1, 144.2, 143.1, 135.2, 130.1, 129.1, 127.7, 123.6, 123.1, 122.3, 114.8, 55.7. **HRMS-ESI** (m/z) calcd. for $[C_{17}H_{17}O_4S]^+$ ($[M+H]^+$): 317.0842, found: 317.0842.

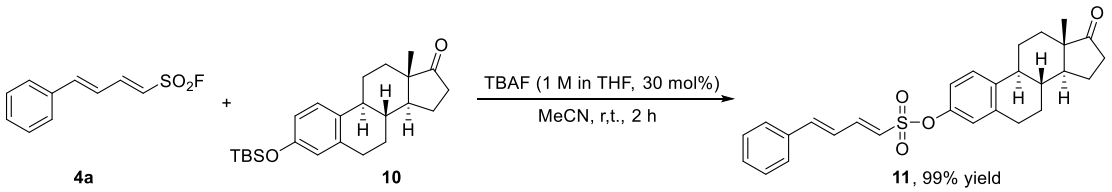


4a **9**, 87% yield

A mixture of compound **4a** (212 mg, 1.0 mmol, 1.0 equiv.), Cs_2CO_3 (326 mg, 1.0 mmol, 1.0 equiv.) and methanol (5 mL) was stirred at 37 ℃ for 2 h. The reaction mixture was diluted with water and the aqueous phrase was extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 before being concentrated to dryness under vacuum. The residue was purified through silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE: EA = 5:1 (v/v)) as eluent to provide the final product sulfonate **9**.

Methyl (1E,3E)-4-phenylbuta-1,3-diene-1-sulfonate **(9)**. White solid, 195 mg, 87%

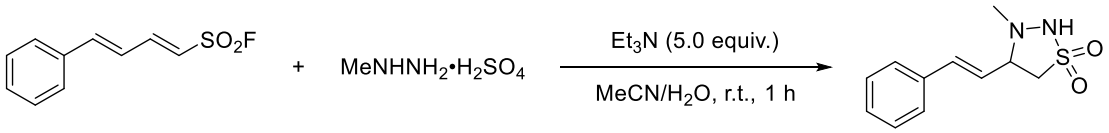
yield. M.p. 63-65 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 6.8 Hz, 2H), 7.41-7.36 (m, 4H), 7.01 (d, J = 15.5 Hz, 1H), 6.85 (dd, J_1 = 15.6 Hz, J_2 = 11.0 Hz, 1H), 6.31 (d, J = 14.8 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.4, 143.7, 135.3, 130.0, 129.1, 127.7, 123.2, 122.0, 56.1. **HRMS-ESI** (m/z) calcd. for $[C_{11}H_{13}O_3S]^+$ ($[M+H]^+$): 225.0580, found: 225.0582.



To a solution of compound **4a** (106 mg, 0.5 mmol, 1.0 equiv.) and TBS-protected estrone (**10**, 192 mg, 0.5 mmol, 1.0 equiv.) dissolved in acetonitrile (5 mL) was added catalytic amount (30 mol%, 150 μL) of TBAF solution (tetrabutylammonium fluoride, 1 M in anhydrous THF), and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with water and the aqueous phrase was extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 before being concentrated to dryness under vacuum. The residue was purified through silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE: EA = 2:1 (v/v)) as eluent to provide the final product sulfonate **11**.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (1E,3E)-4-phenylbuta-1,3-diene-1-sulfonate **(11)**. White solid, 229 mg, 99 % yield. M.p. 72-74 ℃. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 2:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.40 (m, 2H), 7.34-7.29 (m, 3H), 7.24-7.20 (m, 2H), 6.95-6.88 (m, 3H), 6.77 (dd, J_1 = 15.6 Hz, J_2 = 11.0 Hz, 1H), 6.39 (d, J = 14.8 Hz, 1H), 2.86-2.84 (m, 2H), 2.47-2.41 (m, 1H), 2.33-2.30 (m, 1H), 2.23-2.18 (m, 1H), 2.11-2.04 (m, 1H), 2.02-1.88 (m, 3H), 1.60-1.35 (m, 6H), 0.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.7, 147.6, 145.8, 144.1, 139.0, 138.7, 135.2, 130.1, 129.1, 127.7, 126.8,

123.1, 122.6, 122.5, 119.5, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.5, 26.3, 25.8, 21.7, 13.9. **HRMS-ESI** (m/z) calcd. for $[C_{28}H_{31}O_4S]^+$ ($[M+H]^+$): 463.1938, found: 463.1939.

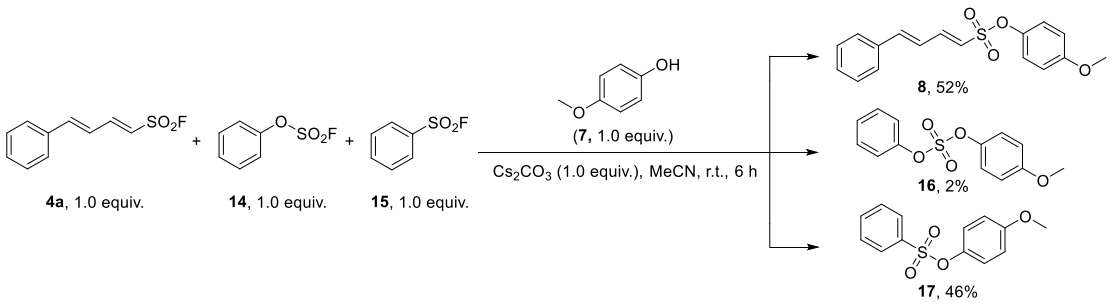


4a **12** (2.0 equiv.) **13**, 75% yield

A mixture of compound **4a** (212 mg, 1.0 mmol, 1.0 equiv.), methylhydrazine sulfate (**12**, 288 mg, 2.0 mmol, 2.0 equiv.), triethylamine (506 mg, 5.0 mmol, 5.0 equiv.), acetonitrile (4.2 mL) and H_2O (0.8 mL) were stirred at room temperature for 1 h. The reaction mixture was diluted with water and the aqueous phrase was extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 before being concentrated to dryness under vacuum. The residue was purified through silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE: EA = 2:1 (v/v)) as eluent to provide the final product **13**.

(E)-3-methyl-4-styryl-1,2,3-thiadiazolidine 1,1-dioxide **(13)**. Light yellow liquid, 179 mg, 75% yield. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 2:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 2H), 7.37-7.34 (m, 2H), 7.32-7.29 (m, 1H), 6.69 (d, J = 15.9 Hz, 1H), 6.14 (dd, J_1 = 15.8 Hz, J_2 = 7.4 Hz, 1H), 5.72 (s, 1H), 4.09 (dd, J_1 = 16.2 Hz, J_2 = 7.3 Hz, 1H), 3.55 (dd, J_1 = 12.9 Hz, J_2 = 6.9 Hz, 1H), 3.19 (dd, J_1 = 12.8 Hz, J_2 = 9.3 Hz, 1H), 2.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.5, 134.6, 128.9, 128.7, 126.8, 124.7, 71.4, 52.6, 44.0. **HRMS-ESI** (m/z) calcd. for $[C_{11}H_{14}N_2NaO_2S]^+$ ($[M+Na]^+$): 261.0668, found: 261.0665.

6. SuFEx Reactivity of 1,3-Dienylsulfonyl Fluoride Comparing to Other Sulfonyl Fluoride Counterparts



A mixture of compound **4a** (106 mg, 0.5 mmol, 1.0 equiv.), 4-methoxyphenol (**7**, 62 mg, 0.5mmol, 1.0 equiv.), fluorosulfate (**14**, 88 mg, 0.5 mmol, 1.0 equiv.), benzenesulfonyl fluoride (**15**, 80 mg, 0.5 mmol, 1.0 equiv.), Cs_2CO_3 (163 mg, 0.5 mmol, 1.0 equiv.) and acetonitrile (2.5 mL) was stirred at room temperature for 6 h. The reaction mixture was detected by HPLC and the corresponding sulfonates **8**, **16** and **17** were obtained in 52%, 2%, and 46% HPLC yields respectively.

4-methoxyphenyl phenyl sulfate (**16**). Colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.35-7.31 (m, 3H), 7.25-7.22 (m, 2H), 6.92-6.88 (m, 2H), 3.80 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.7, 150.6, 144.0, 130.2, 127.7, 122.4, 121.2, 115.0, 55.8. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{12}NaO_5S]^+$ ($[M+Na]^+$): 303.0298, found: 303.0293.

4-methoxyphenyl benzenesulfonate (**17**). Light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.68-7.64 (m, 1H), 7.54-7.50 (m, 2H), 6.89-6.86 (m, 2H), 6.78-6.76 (m, 2H), 3.76 (s, 3H). The NMR data is identical to that reported in literature.[3]

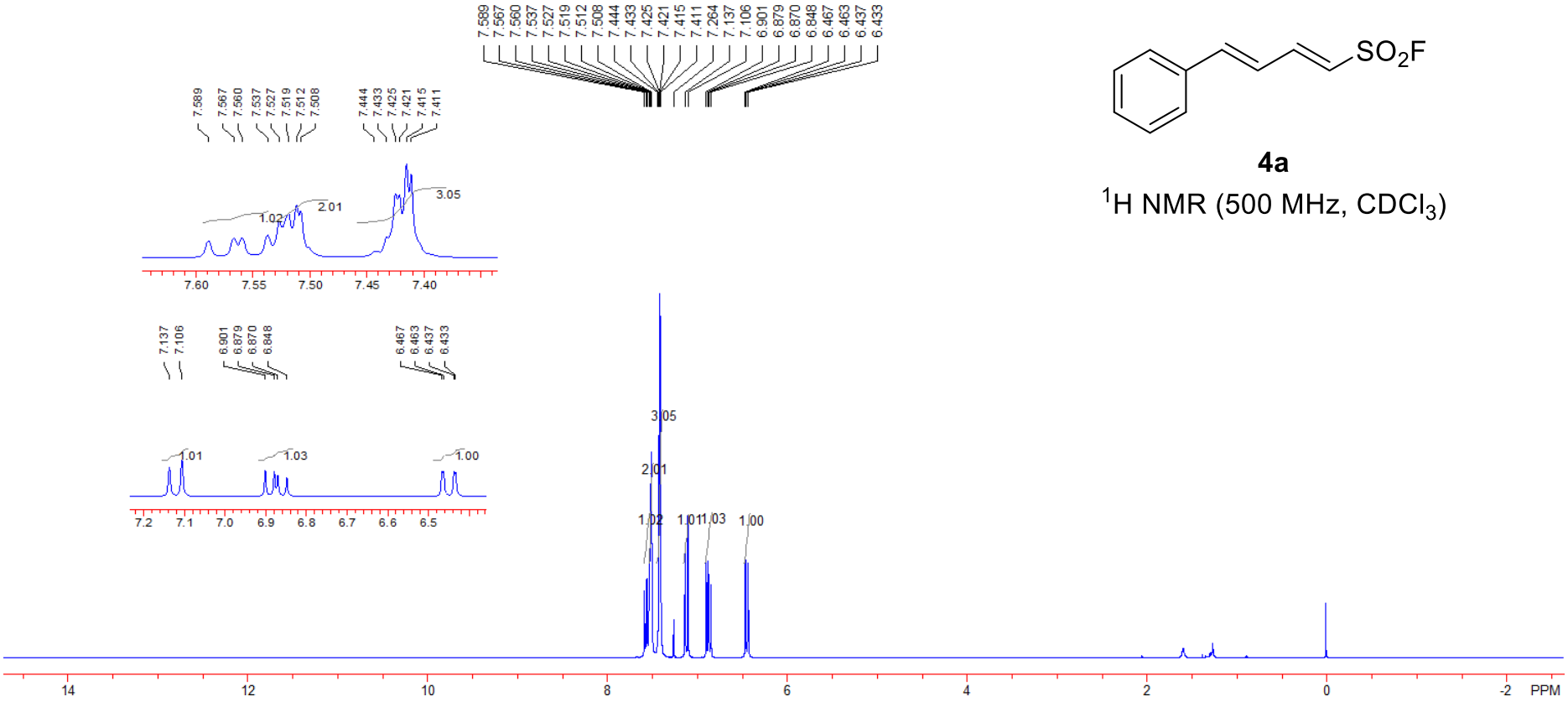
7. References

[1] Z.-W. Zhang, S.-M. Wang, W.-Y. Fang, R. Lekkala and H.-L. Qin, *J. Org. Chem.*, 2020, **85**, 13721-13734.

[2] G.-F. Zha, Q. Zheng, J. Leng, P. Wu, H.-L. Qin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2017, **56**, 4849-4852.

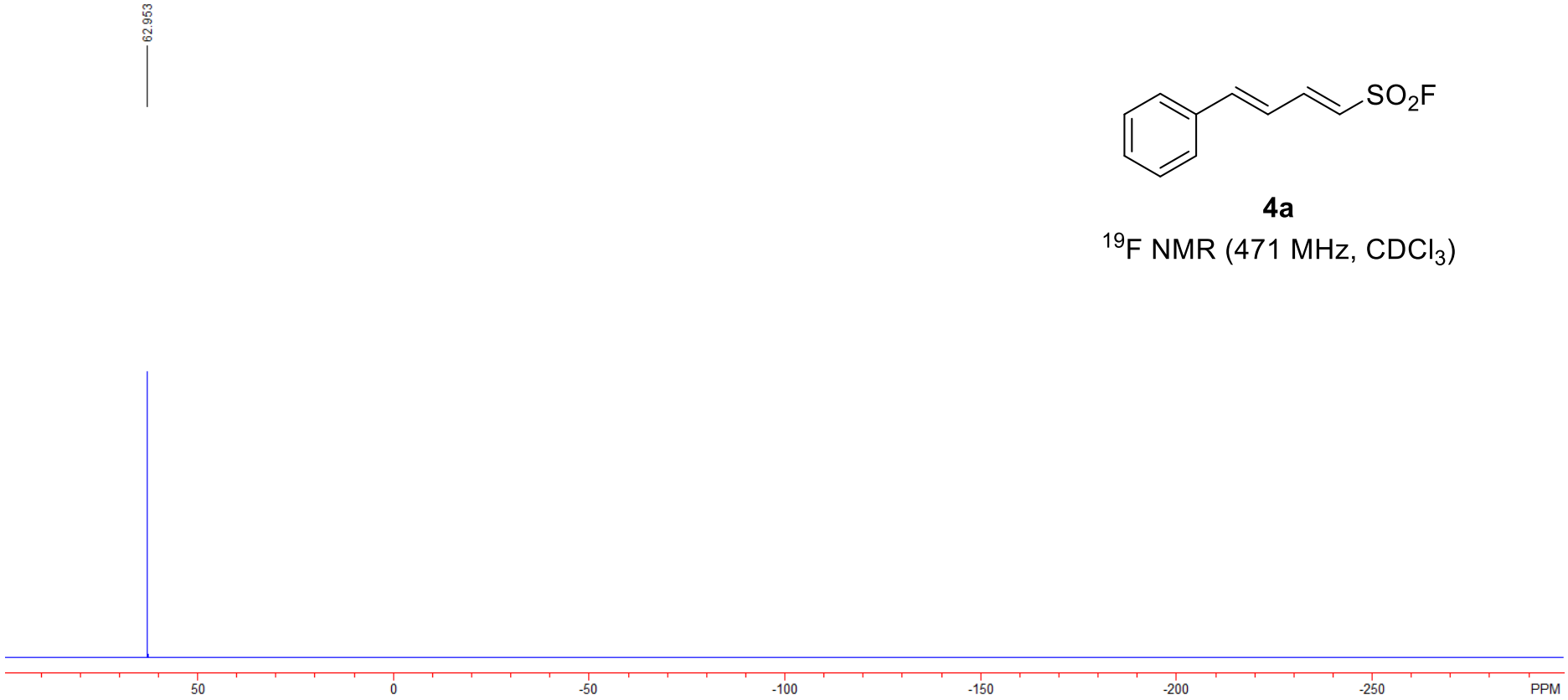
[3] Z.-Y. Tang and Q.-S. Hu, *J. Am. Chem. Soc.*, 2004, **126**, 3058-3059.

8. NMR Spectra



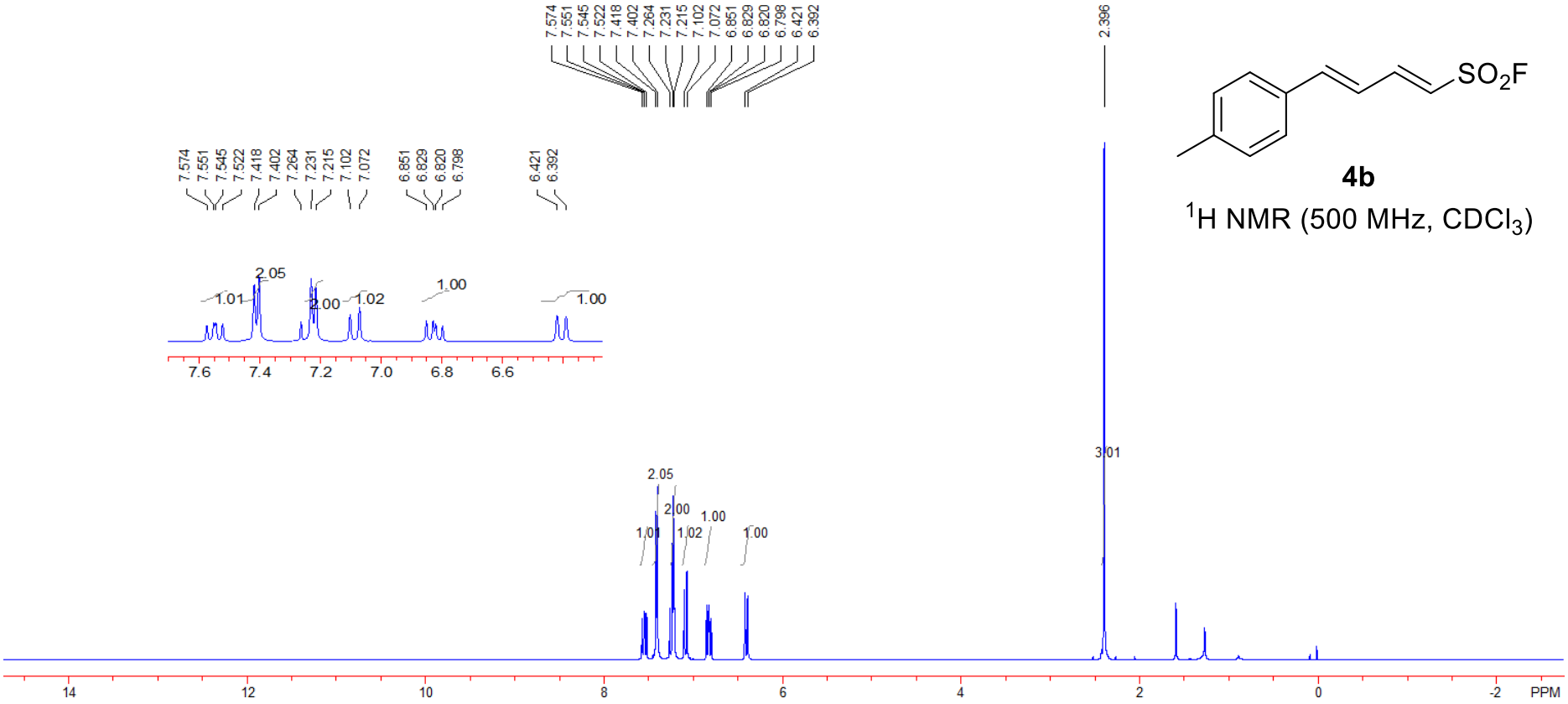
4a

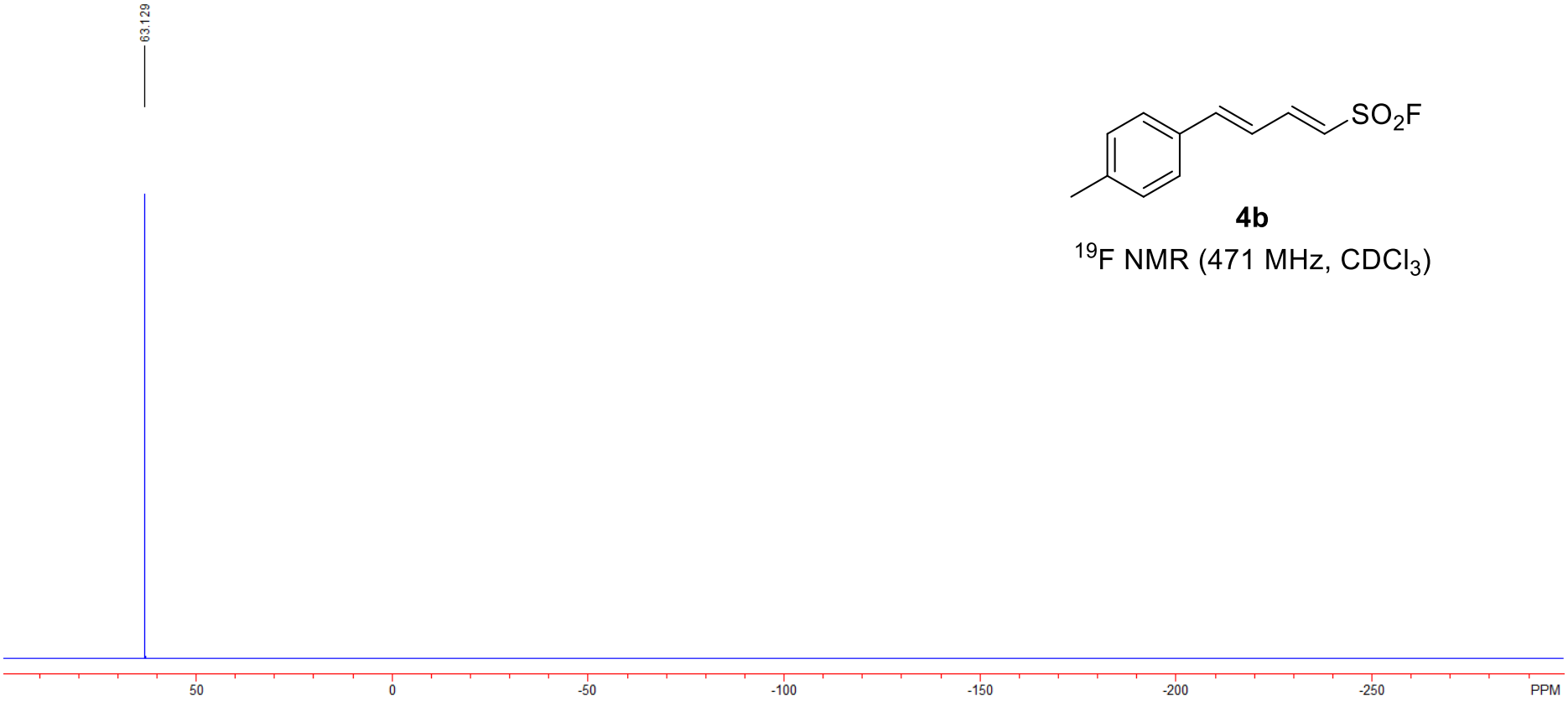
^{1}H NMR (500 MHz, $CDCl_3$)



4a

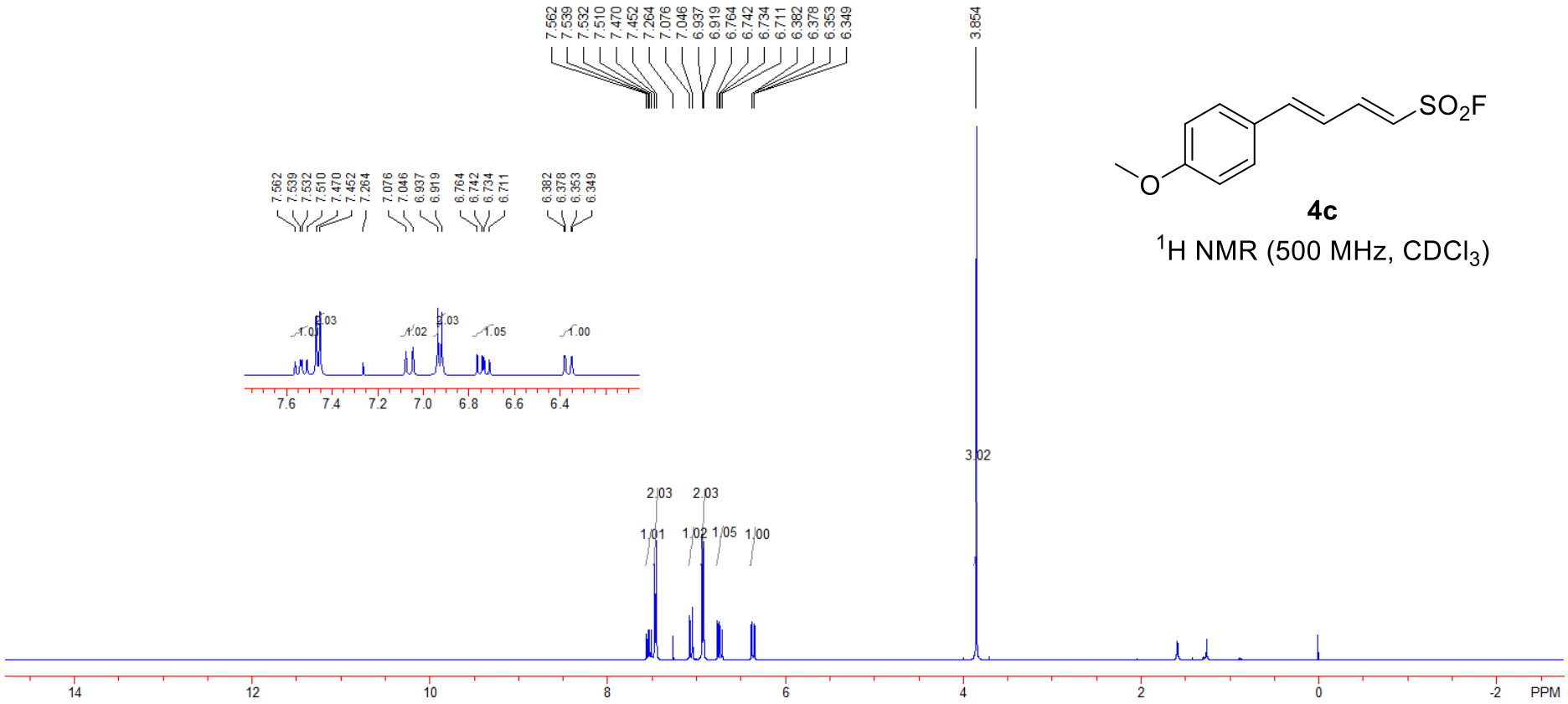
^{19}F NMR (471 MHz, $CDCl_3$)


7.574
7.551
7.545
7.522
7.418
7.402
7.264
7.231
7.215
7.102
7.072
6.851
6.829
6.820
6.798
6.421
6.392
2.396
SO2F
4b
1H NMR (500 MHz, CDCl3)
2.05
1.01
2.00
1.02
1.00
1.00
3.01
14
12
10
8
6
4
2
0
-2
PPM



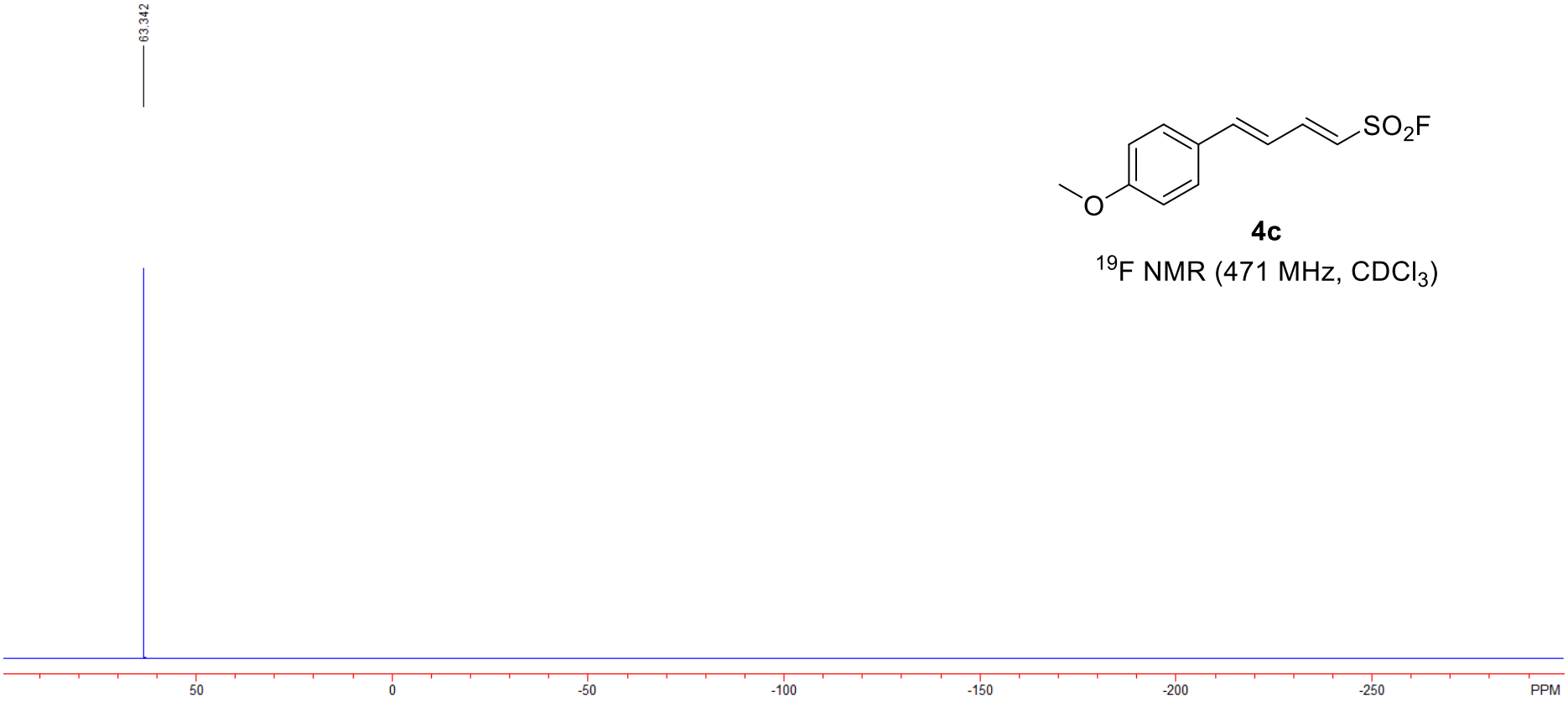
4b

^{19}F NMR (471 MHz, $CDCl_3$)



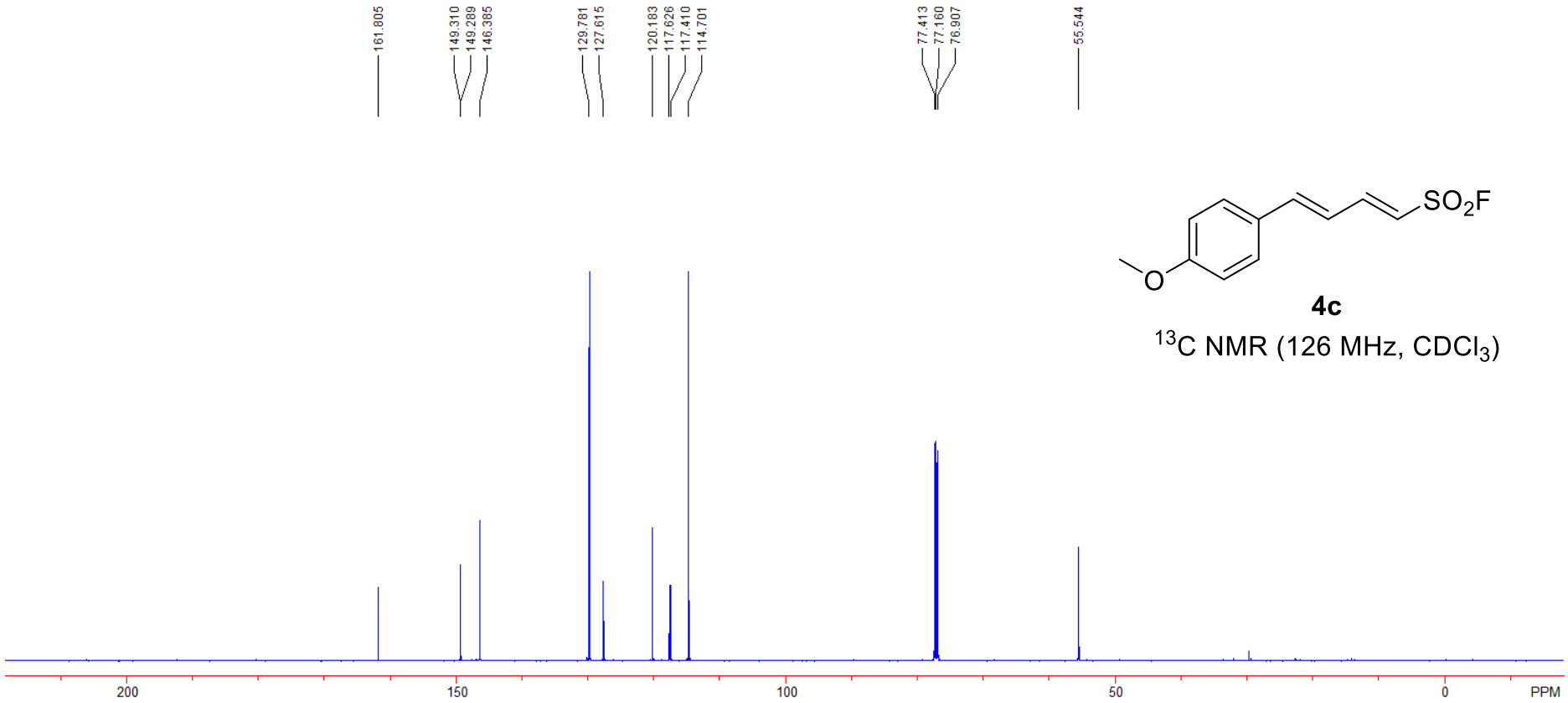
4c

^{1}H NMR (500 MHz, $CDCl_3$)



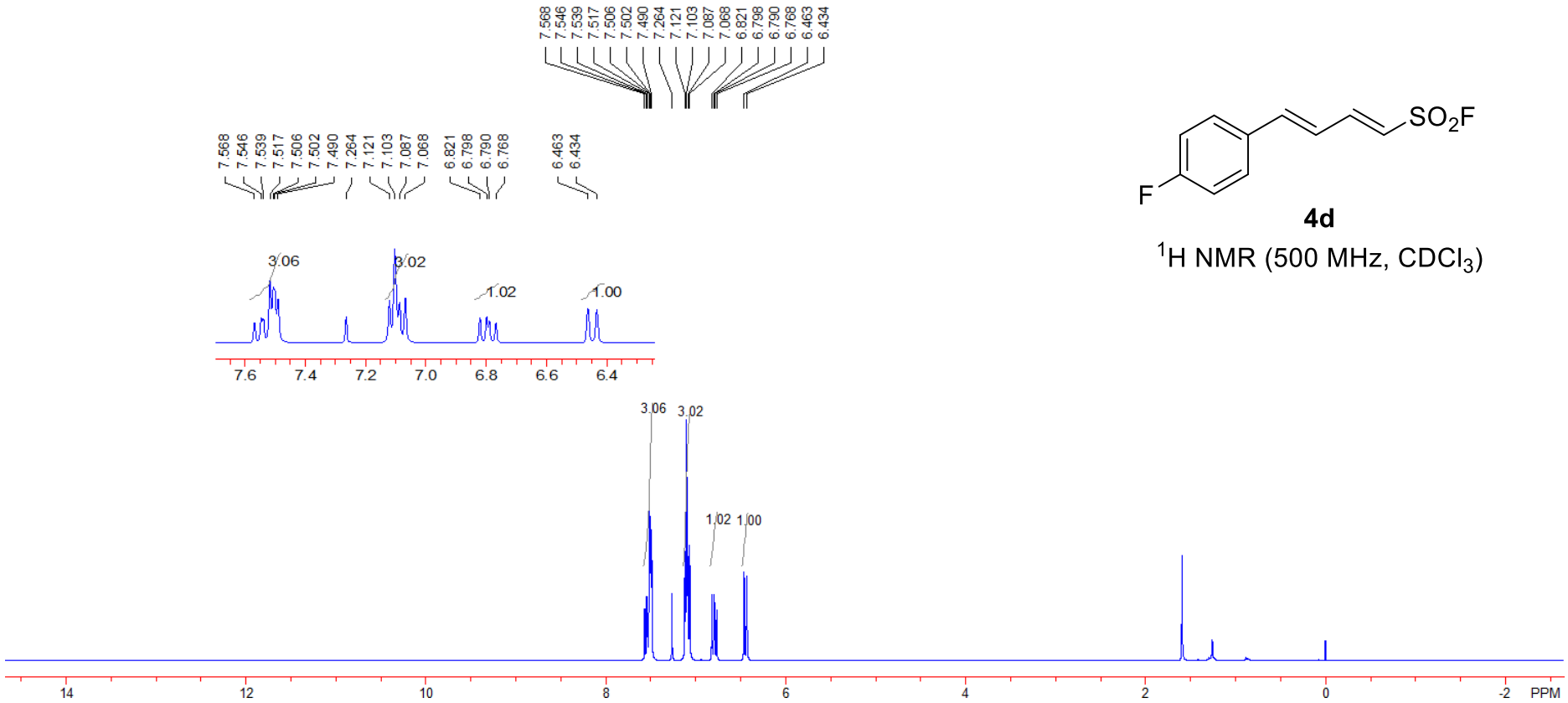
4c

^{19}F NMR (471 MHz, $CDCl_3$)



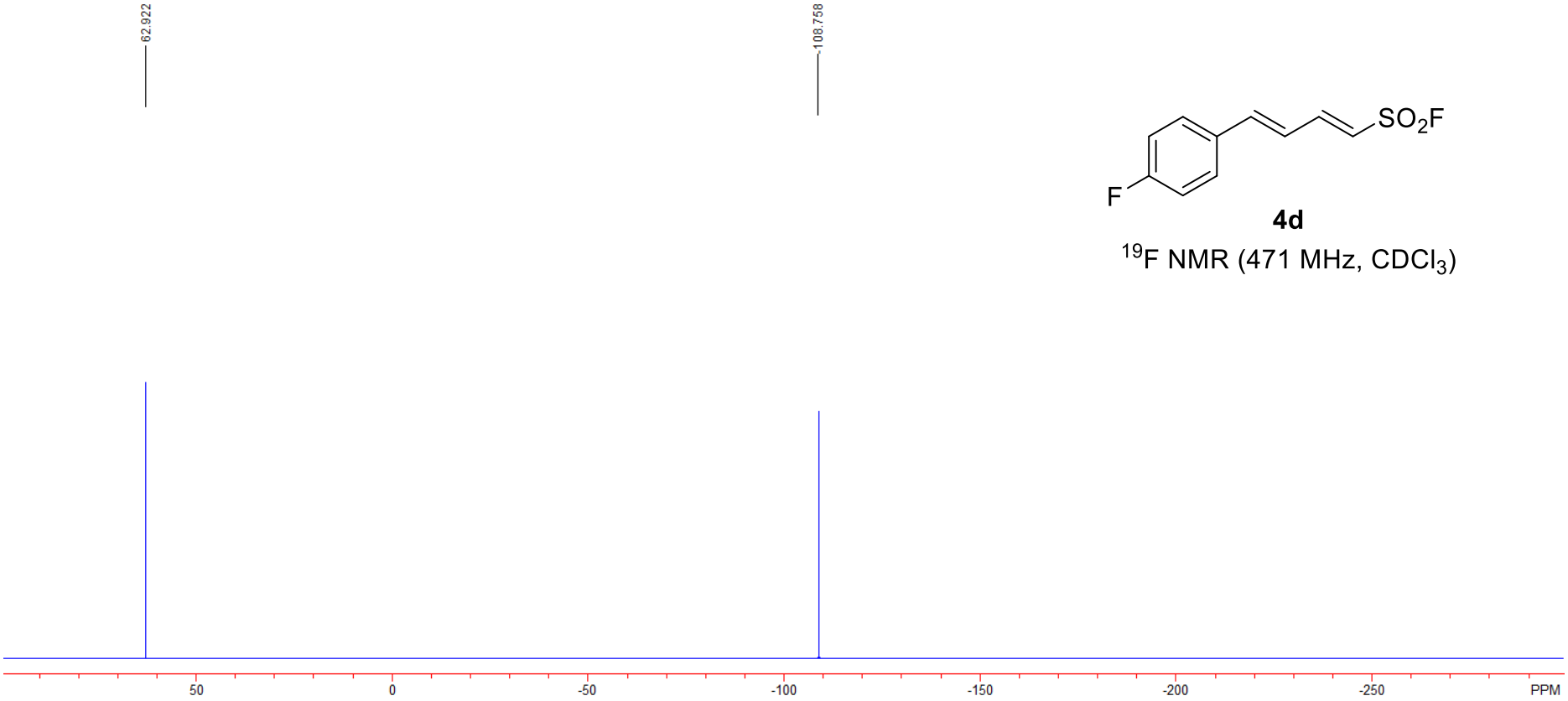
4c

^{13}C NMR (126 MHz, $CDCl_3$)



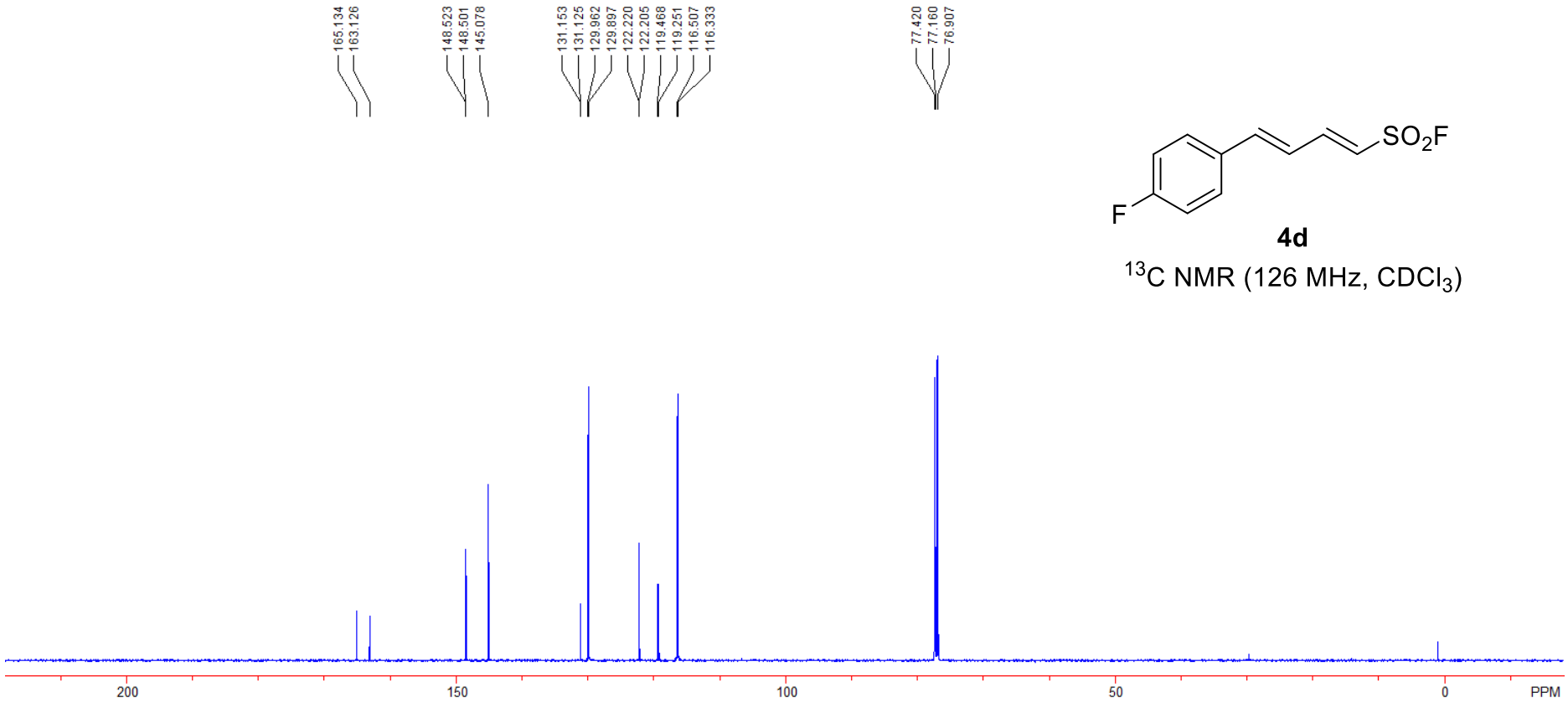
4d

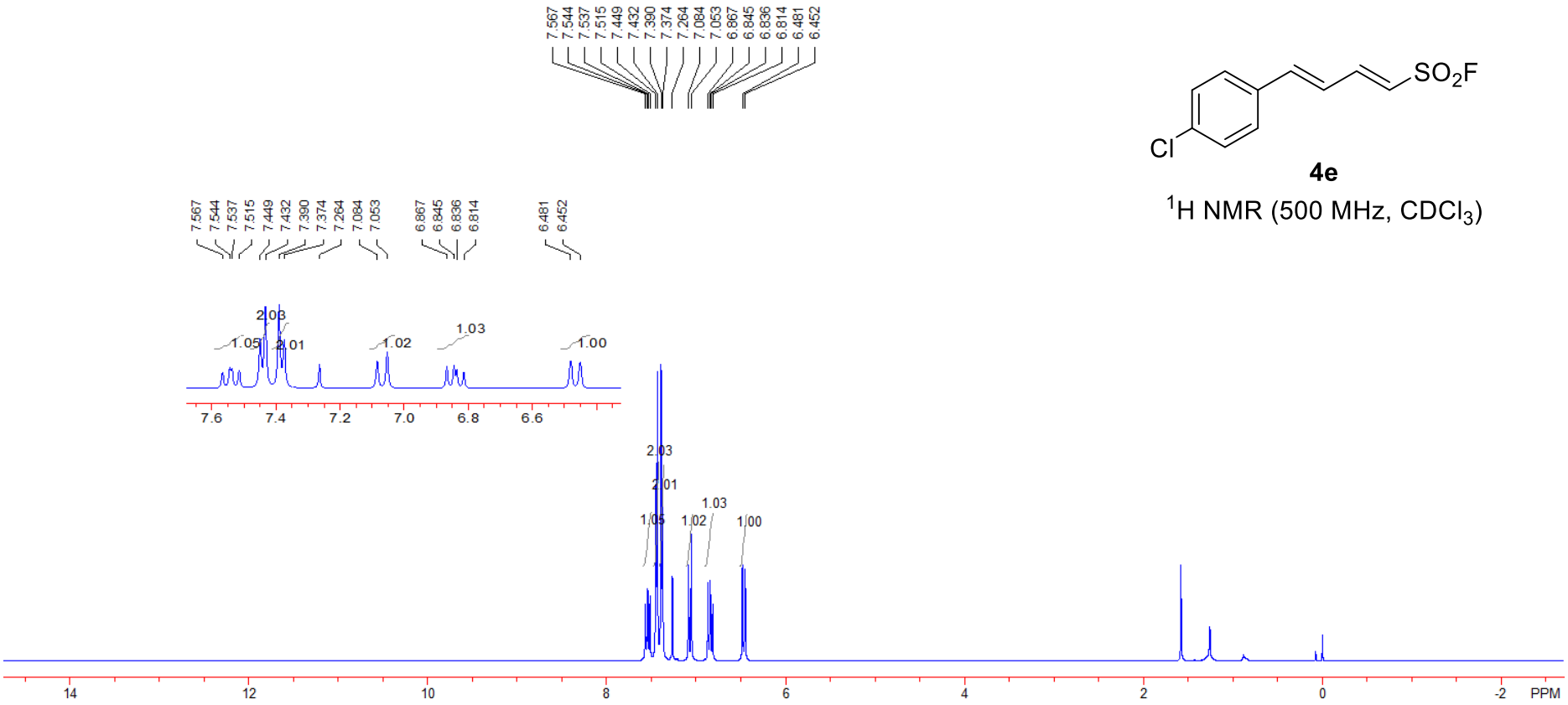
^{1}H NMR (500 MHz, $CDCl_3$)



4d

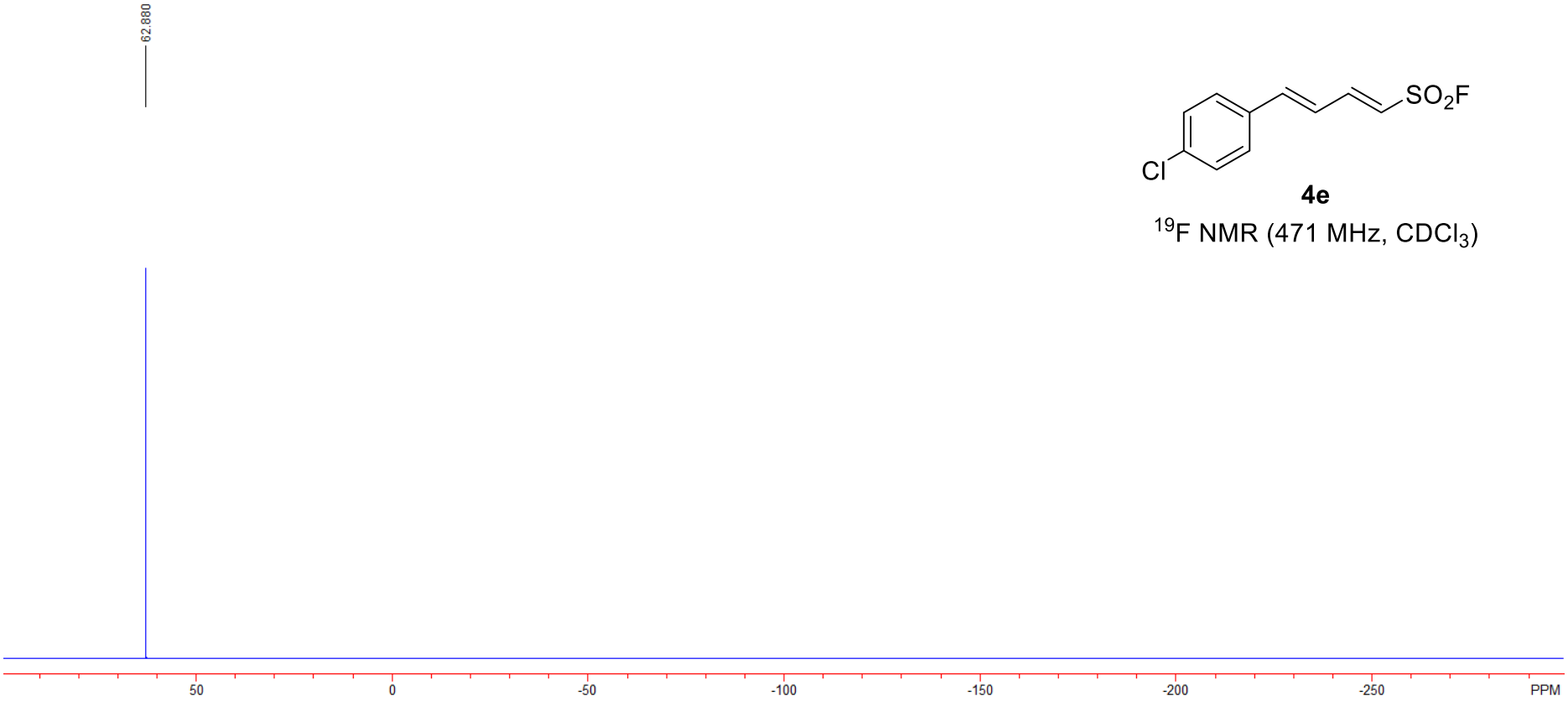
^{19}F NMR (471 MHz, $CDCl_3$)


165.134
163.126
148.523
148.501
145.078
131.153
131.125
129.962
129.897
122.220
122.205
119.468
119.251
116.507
116.333
77.420
77.160
76.907
SO2F
F
4d
13C NMR (126 MHz, CDCl3)
200
150
100
50
0
PPM



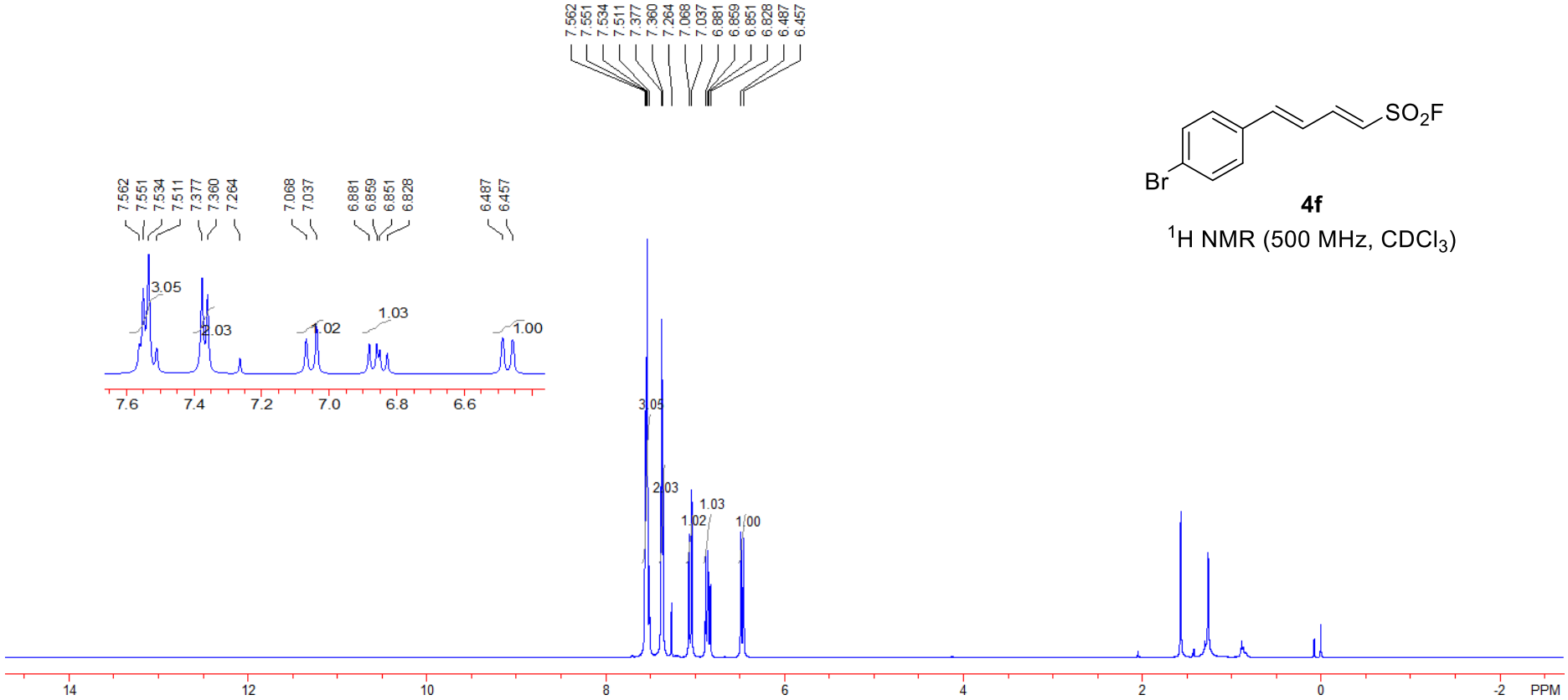
4e

^{1}H NMR (500 MHz, $CDCl_3$)



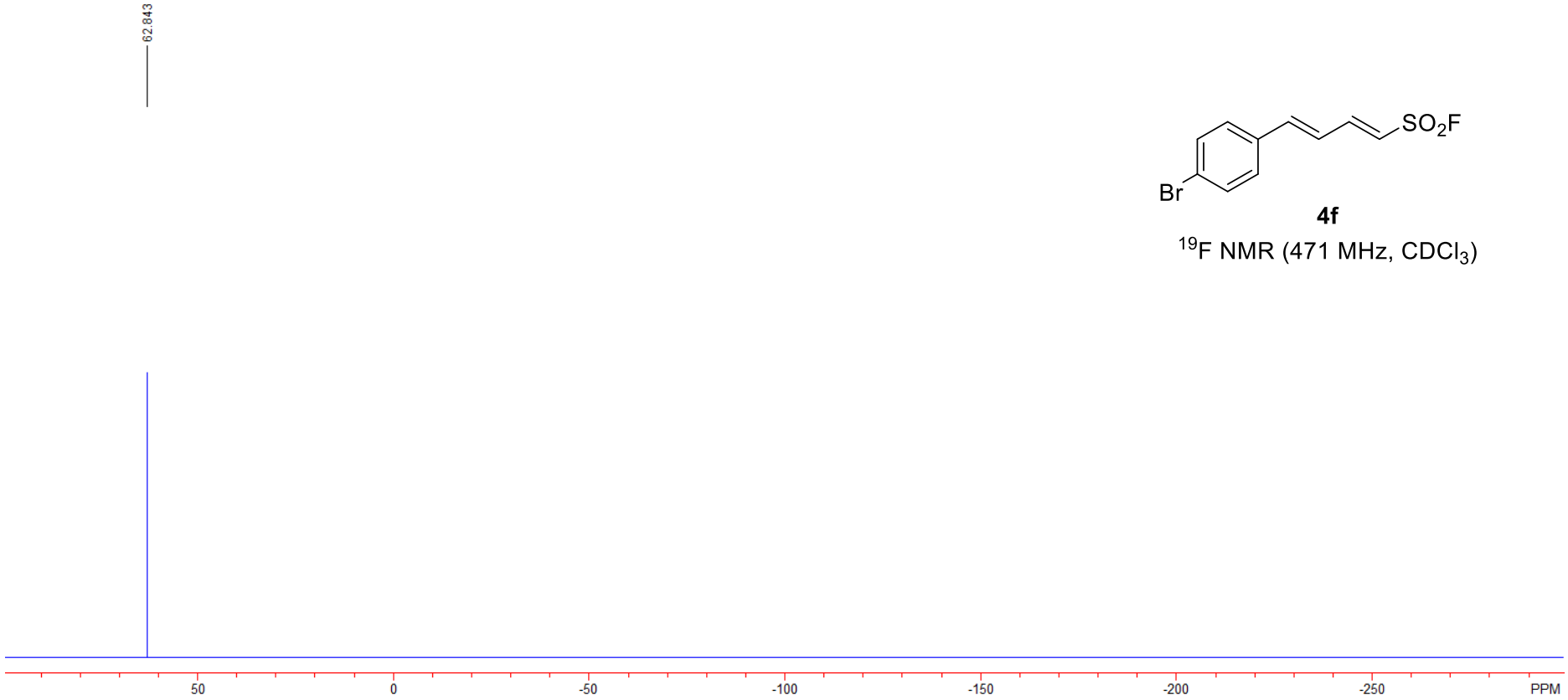
4e

^{19}F NMR (471 MHz, $CDCl_3$)



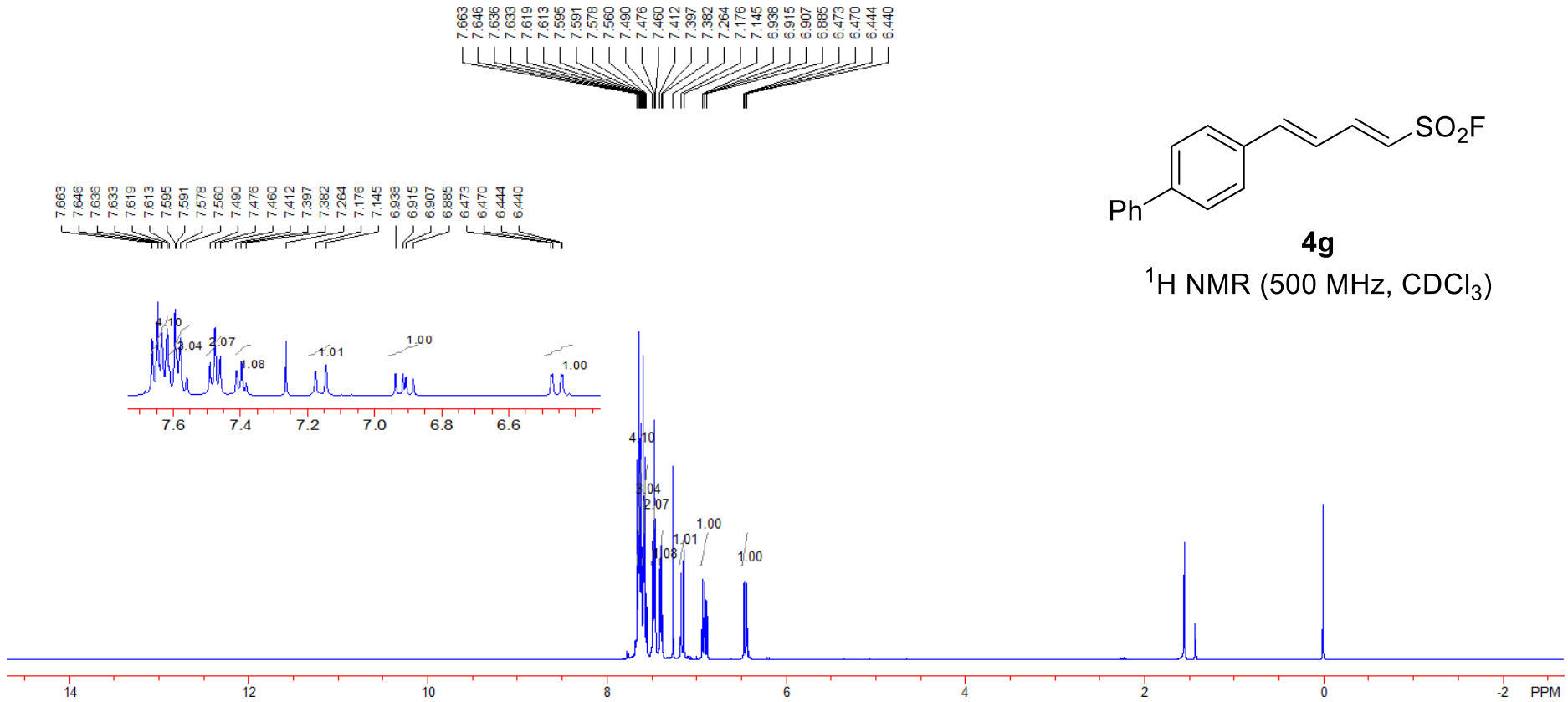
4f

^{1}H NMR (500 MHz, $CDCl_3$)



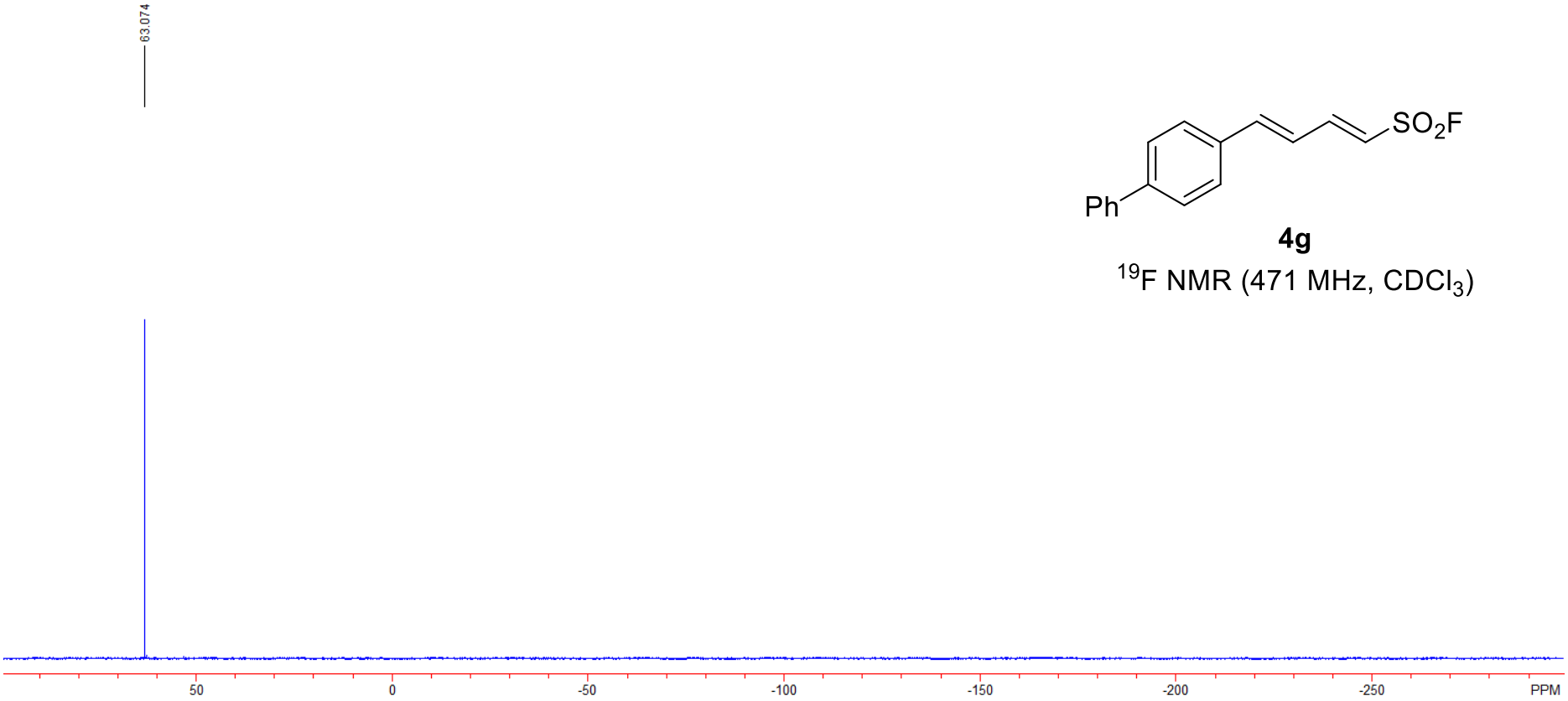
4f

^{19}F NMR (471 MHz, $CDCl_3$)



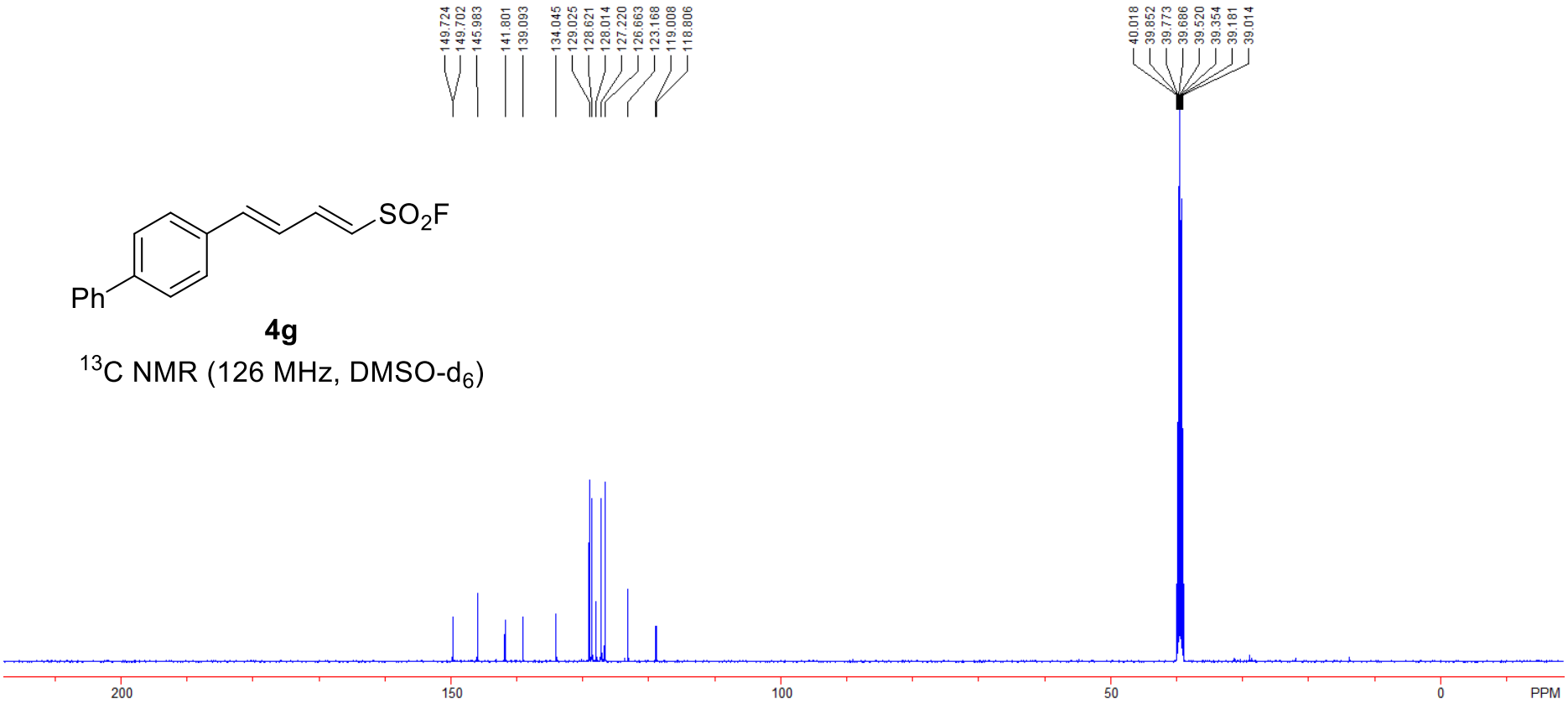
4g

^{1}H NMR (500 MHz, $CDCl_3$)



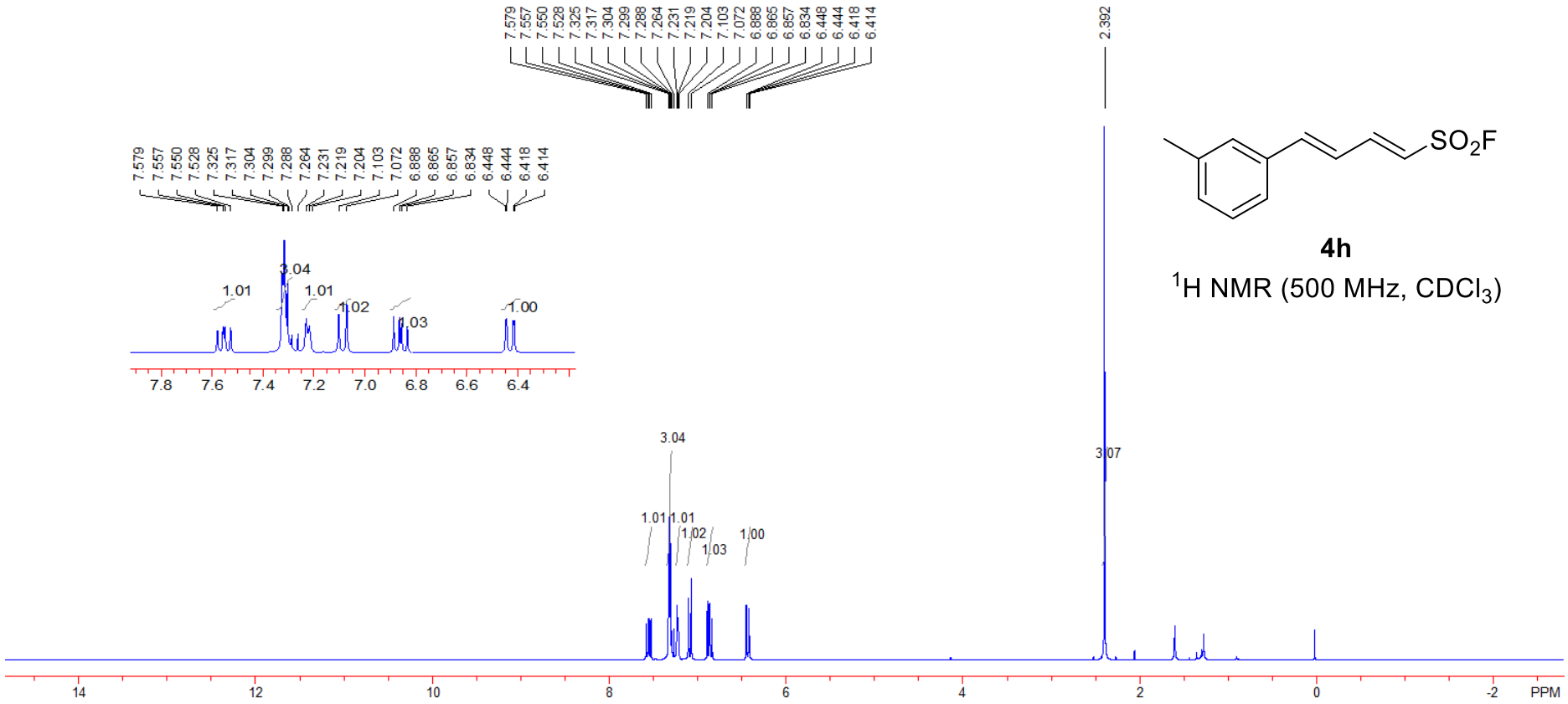
4g

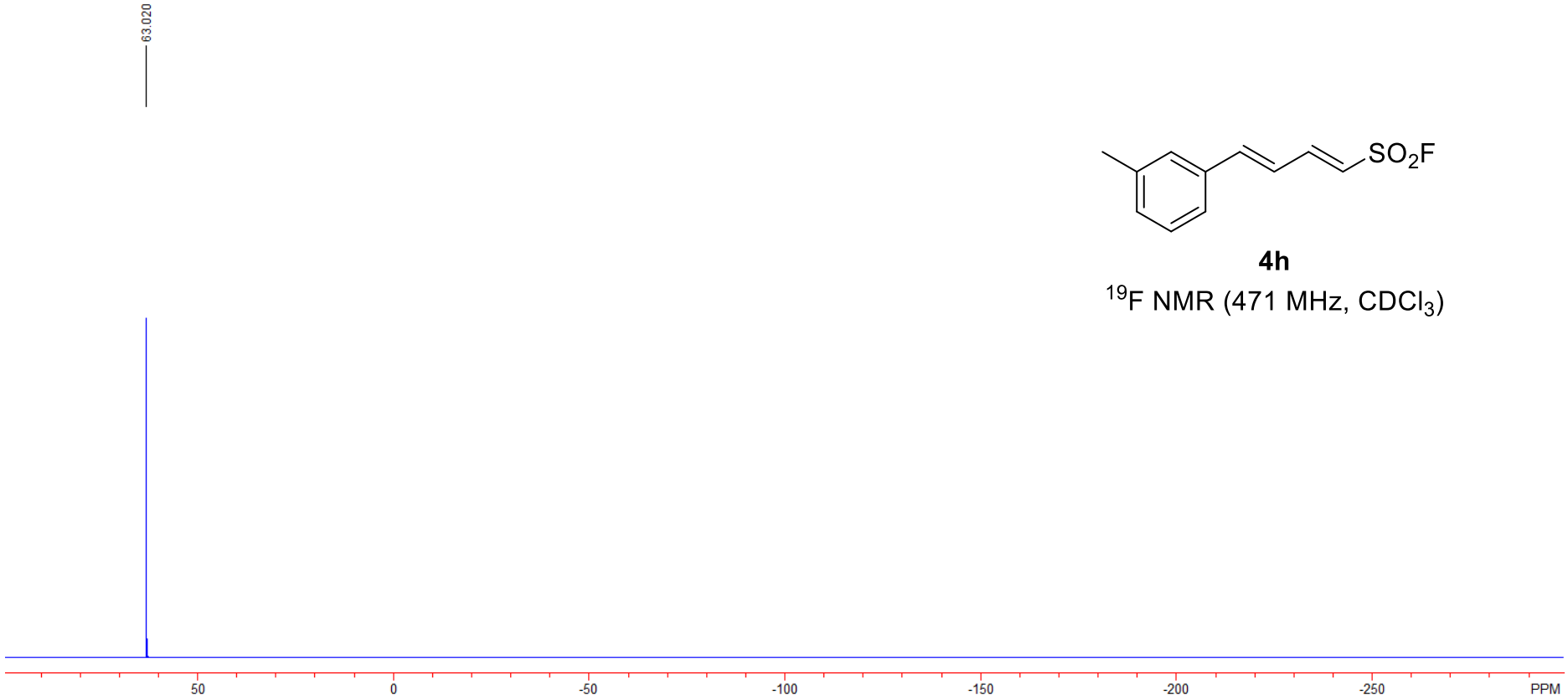
^{19}F NMR (471 MHz, $CDCl_3$)



4g

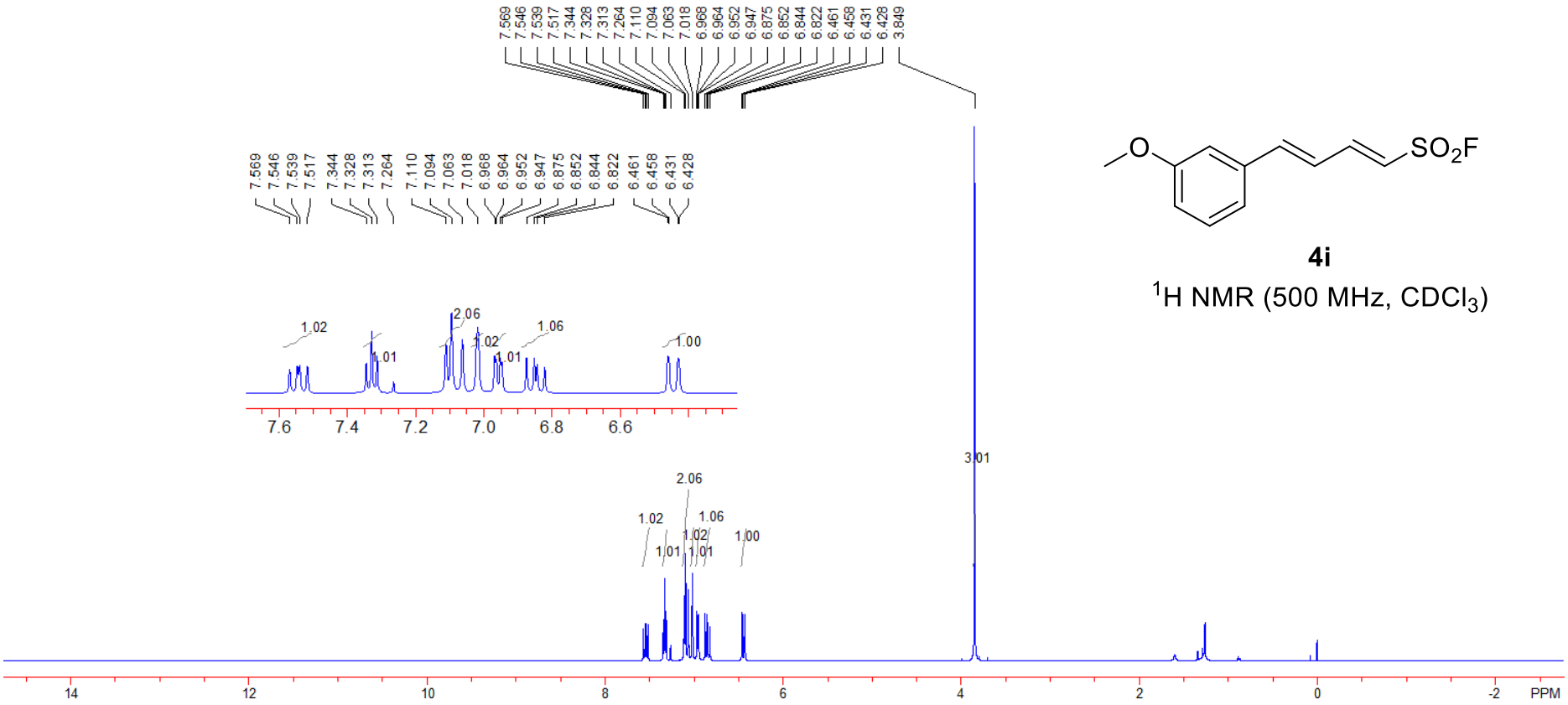
^{13}C NMR (126 MHz, DMSO-d_6)


7.579
7.557
7.550
7.528
7.325
7.317
7.304
7.299
7.288
7.264
7.231
7.219
7.204
7.103
7.072
6.888
6.865
6.857
6.834
6.448
6.444
6.418
6.414
2.392
3.04
1.01
1.01
1.02
1.03
1.00
3.07
14
12
10
8
6
4
2
0
-2
PPM
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
SO2F
4h
1H NMR (500 MHz, CDCl3)



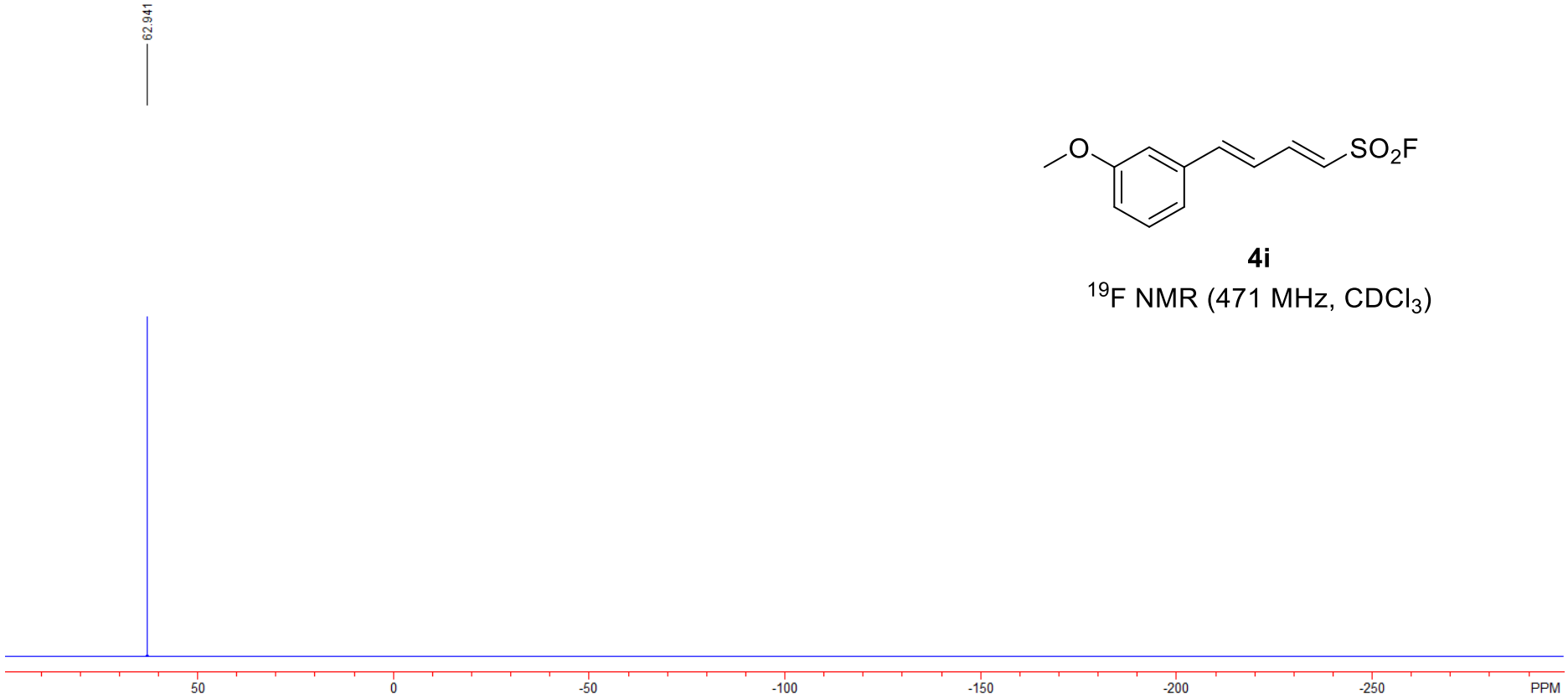
4h

^{19}F NMR (471 MHz, $CDCl_3$)



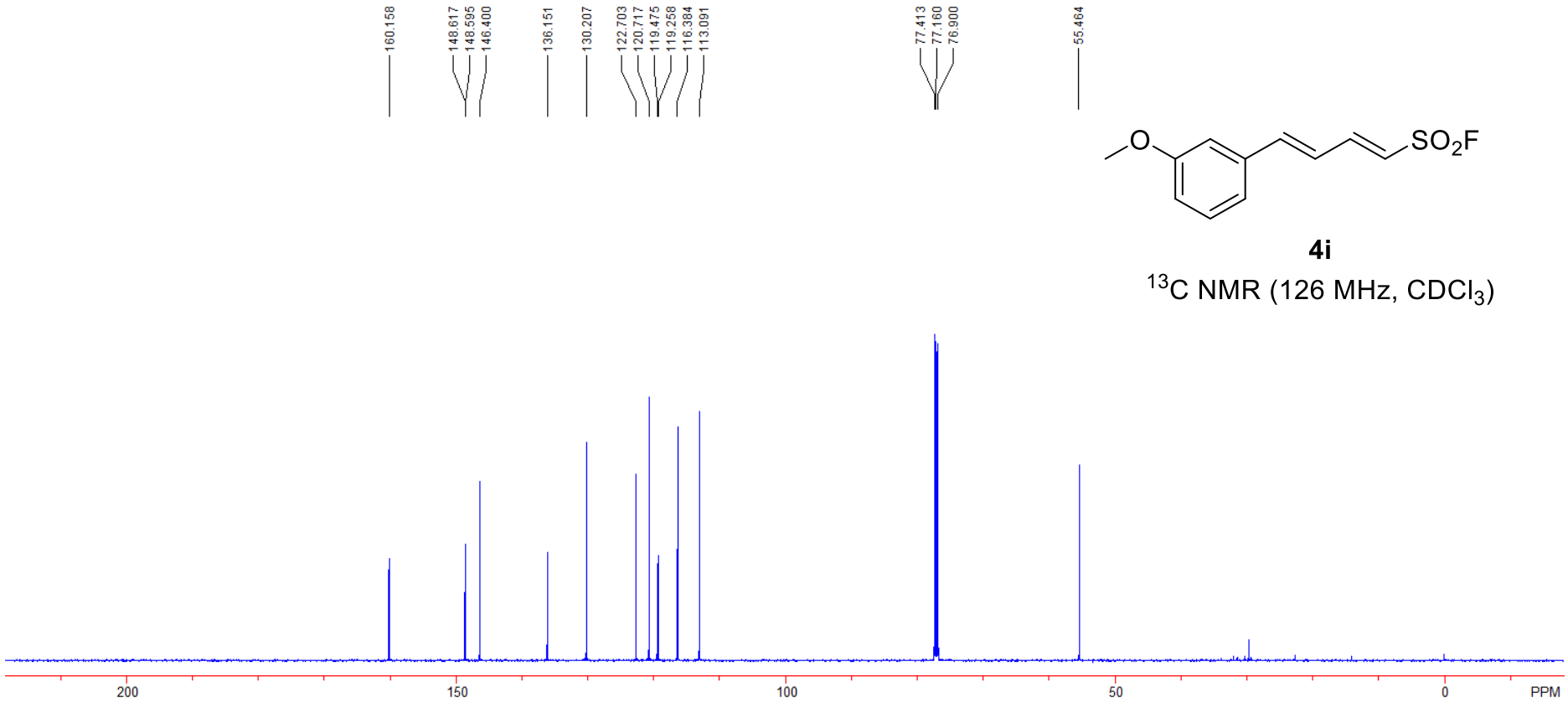
4i

^{1}H NMR (500 MHz, $CDCl_3$)



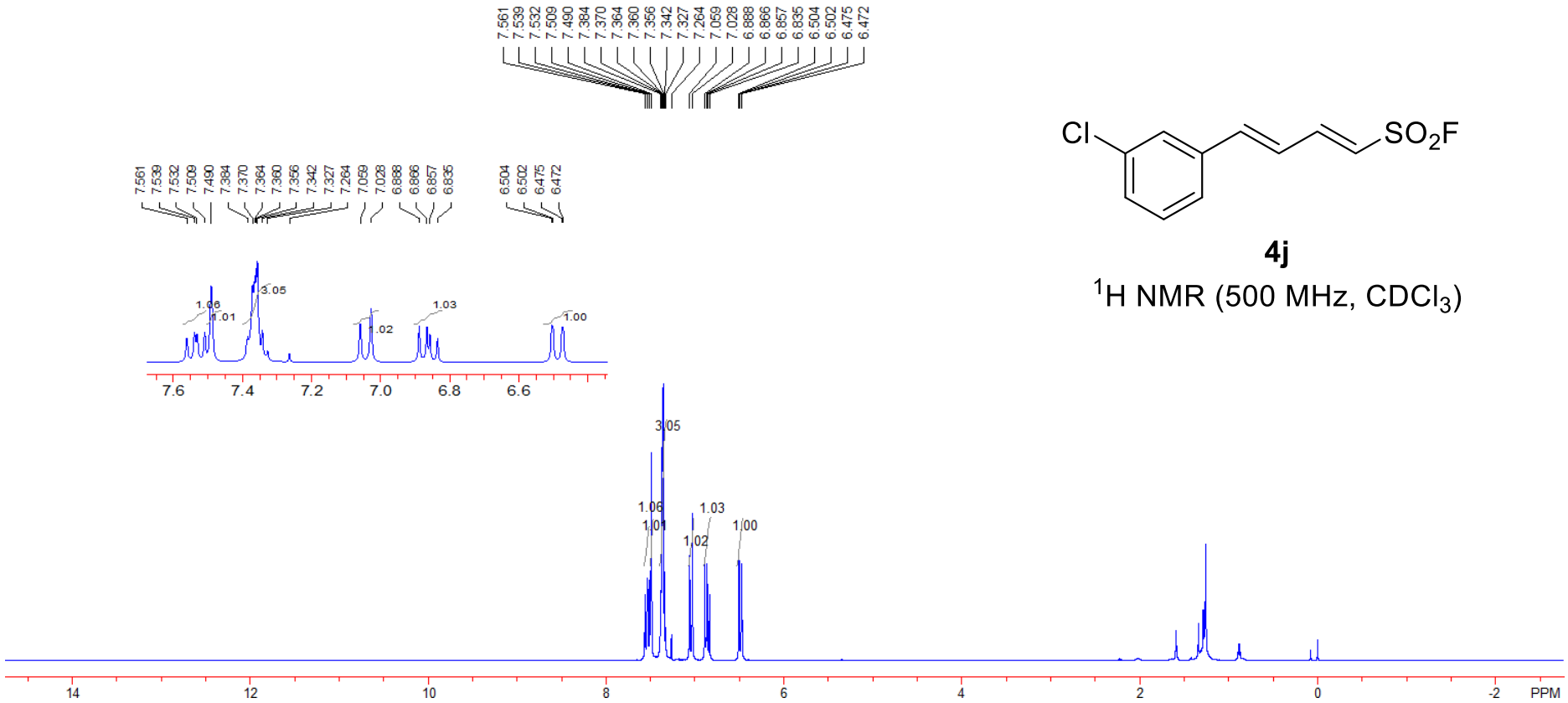
4i

^{19}F NMR (471 MHz, $CDCl_3$)



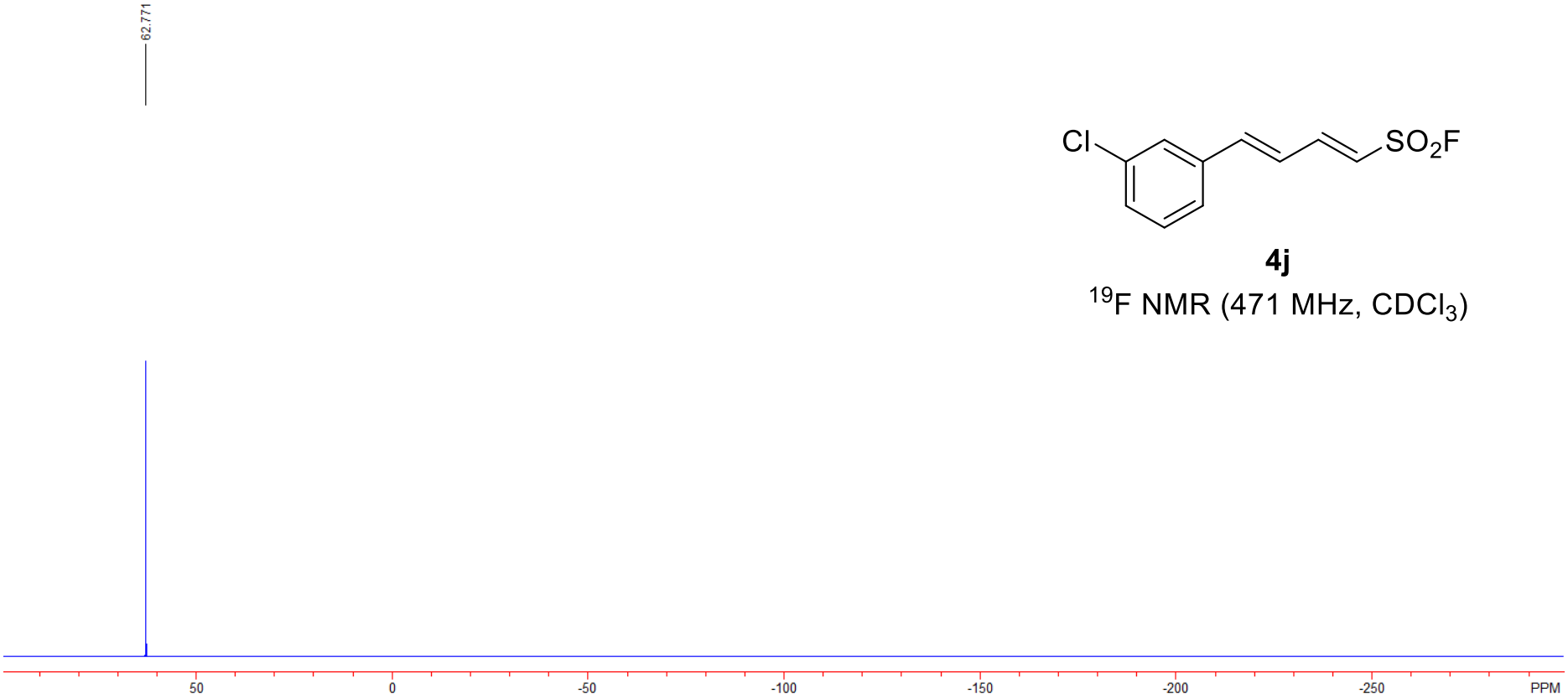
4i

^{13}C NMR (126 MHz, $CDCl_3$)



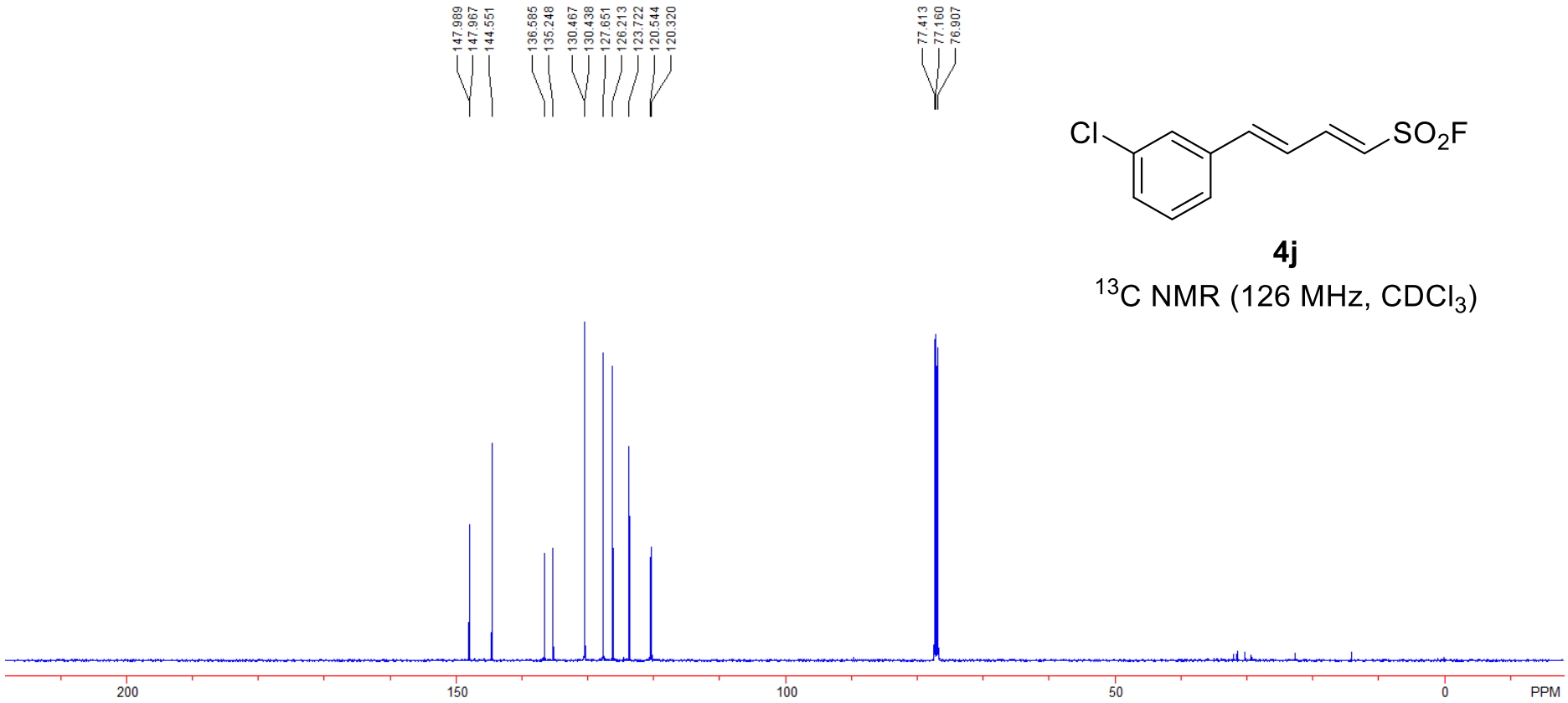
4j

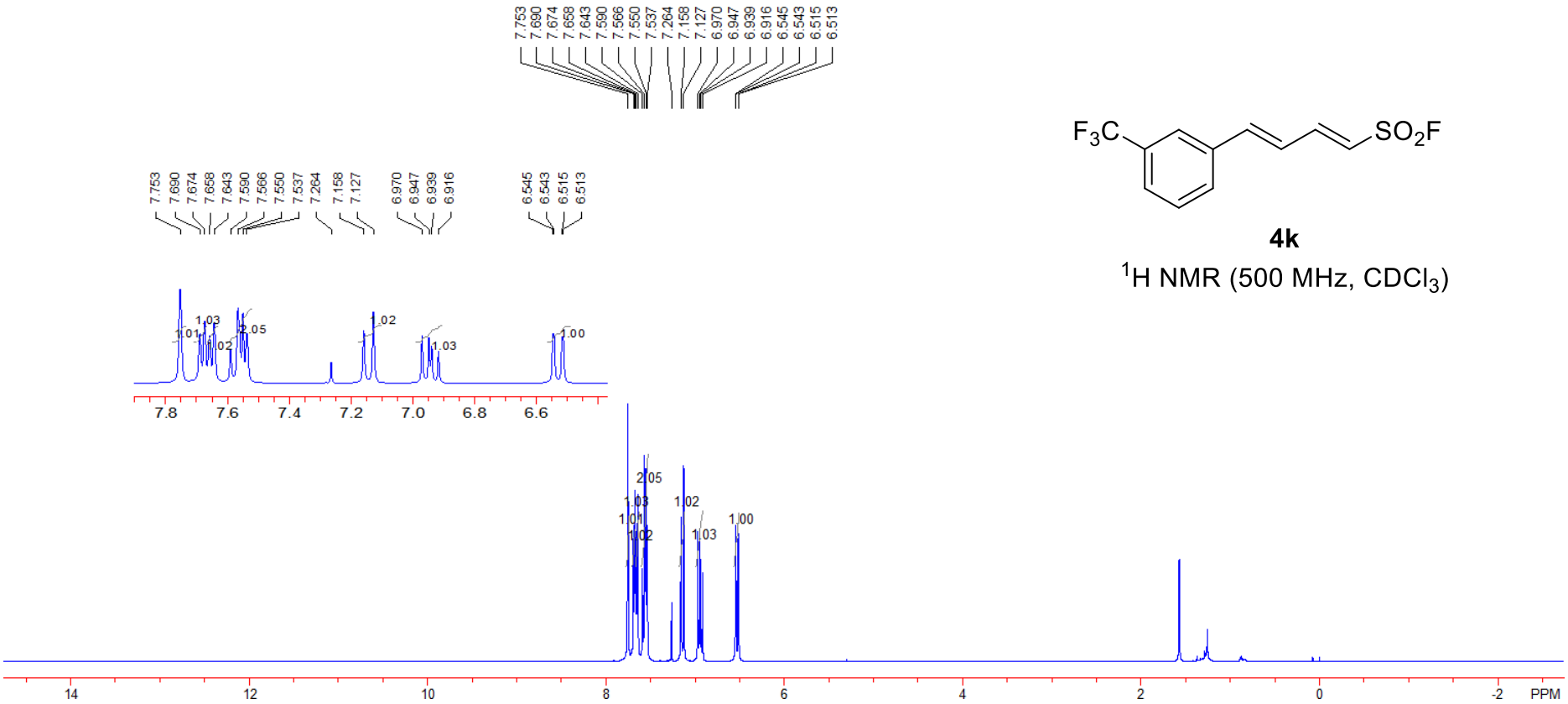
^{1}H NMR (500 MHz, $CDCl_3$)



4j

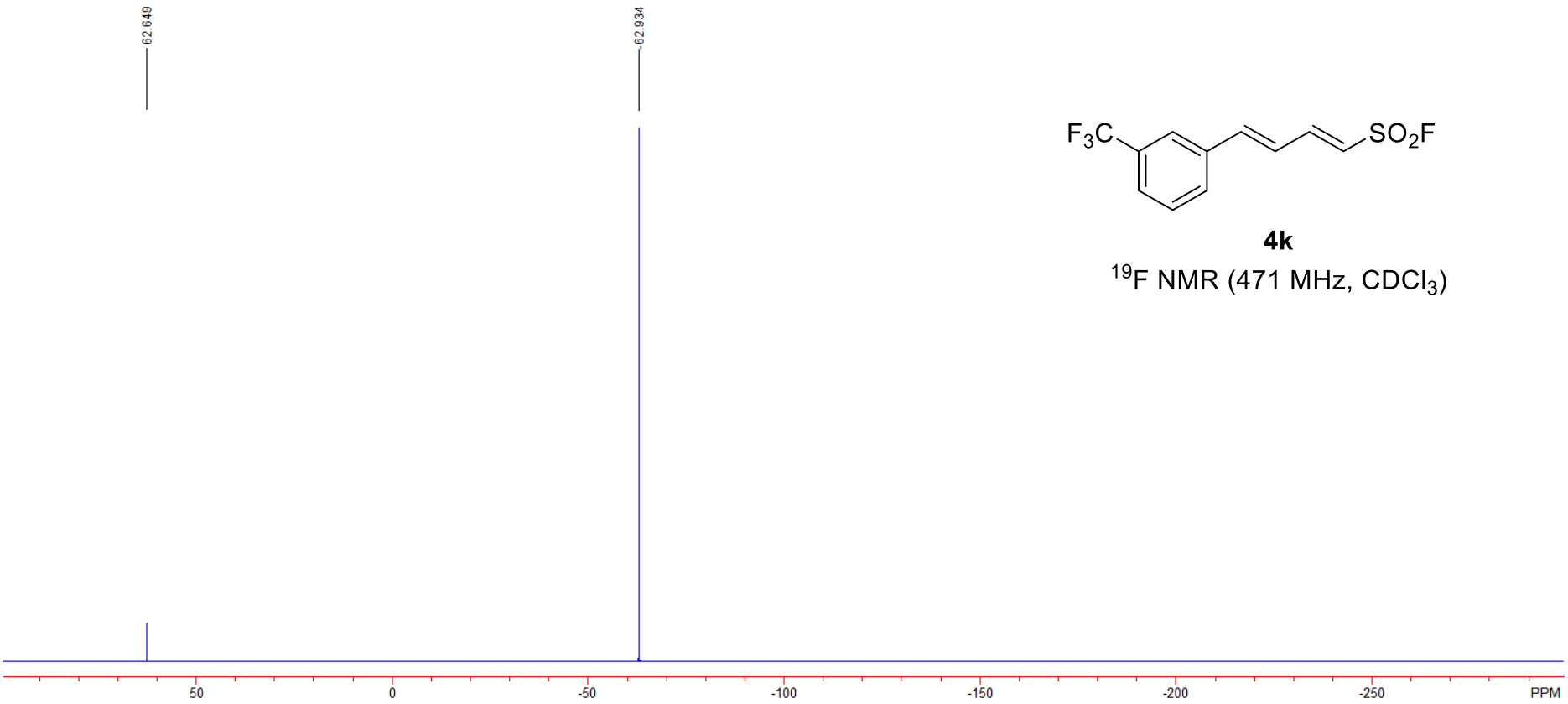
^{19}F NMR (471 MHz, $CDCl_3$)


147.989
147.967
144.551
136.585
135.248
130.467
130.438
127.651
126.213
123.722
120.544
120.320
77.413
77.160
76.907
Cl
SO2F
4j
13C NMR (126 MHz, CDCl3)
200
150
100
50
0
PPM



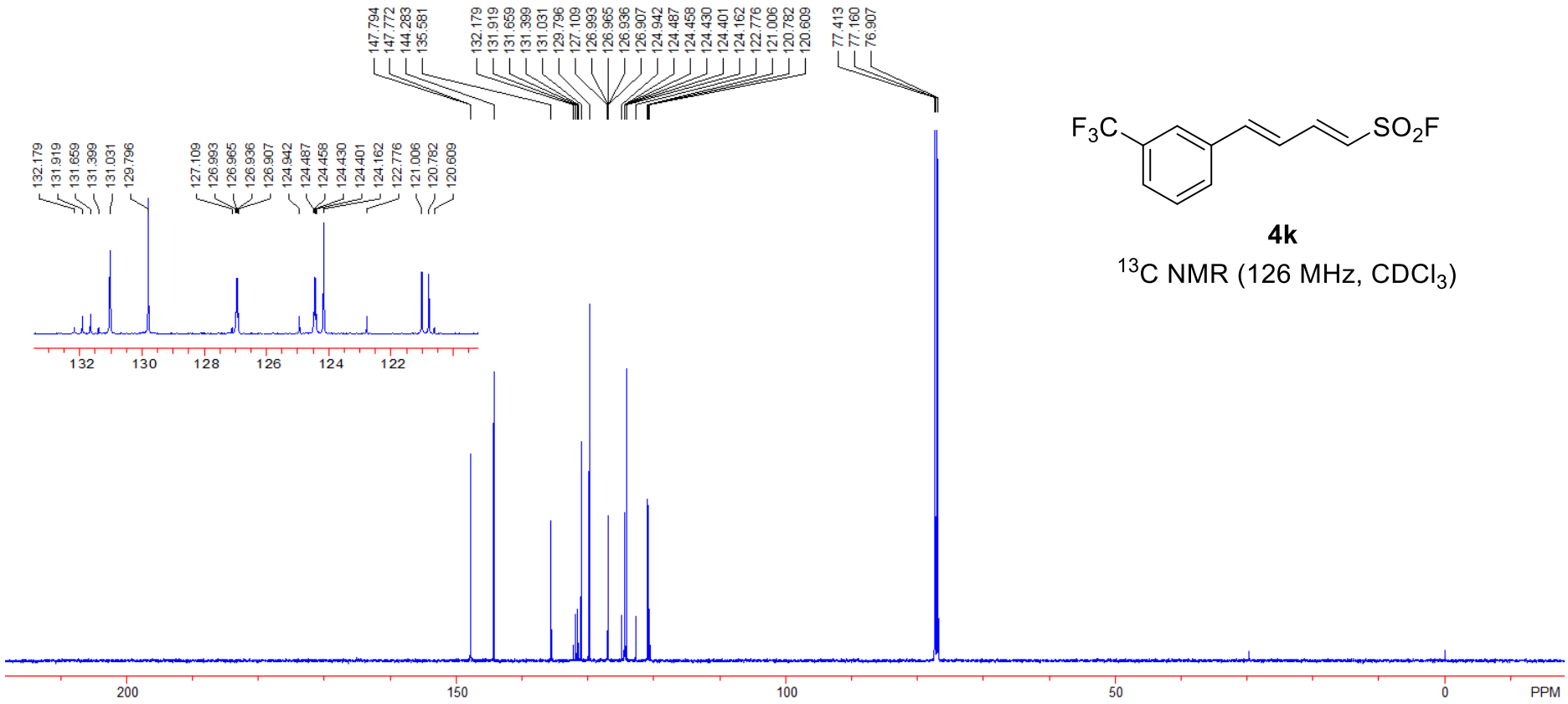
4k

^{1}H NMR (500 MHz, $CDCl_3$)



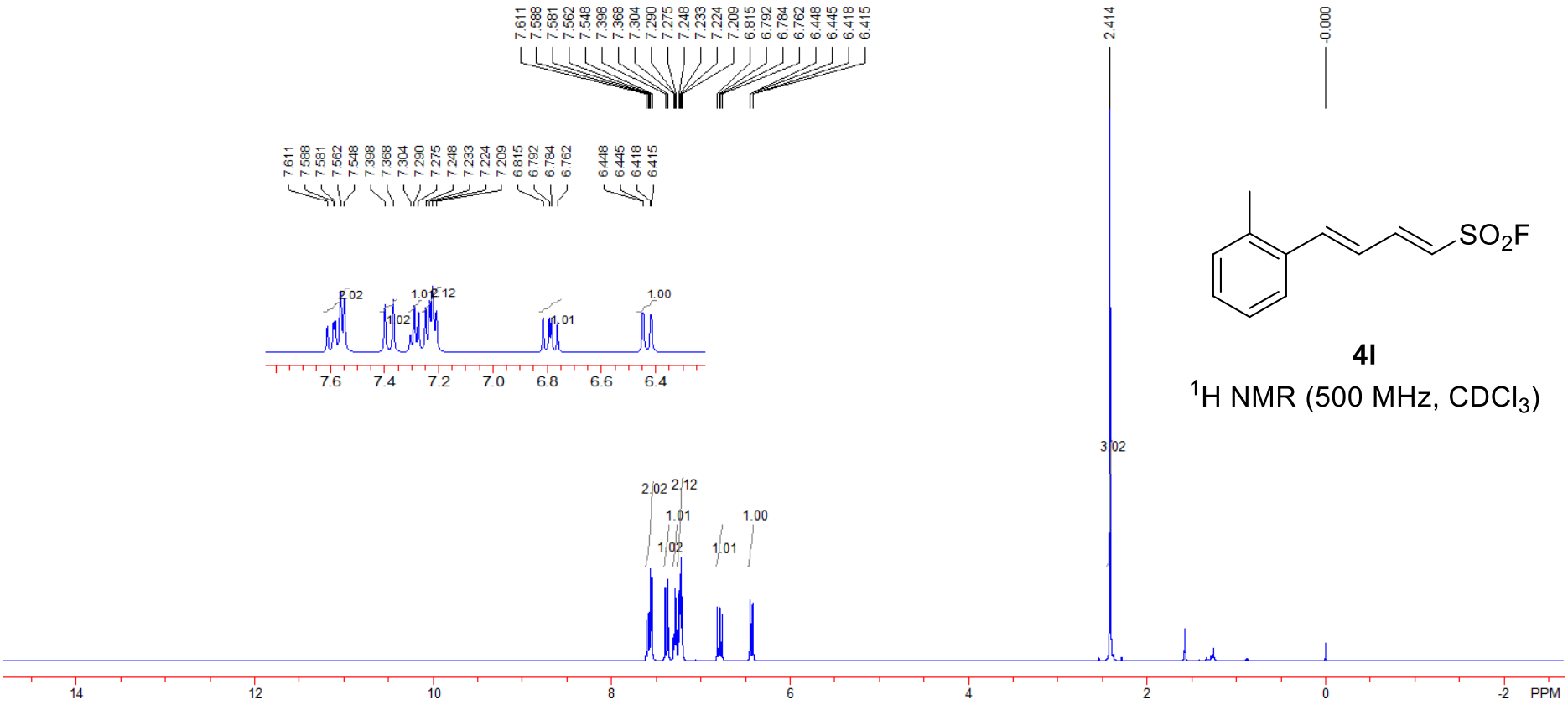
4k

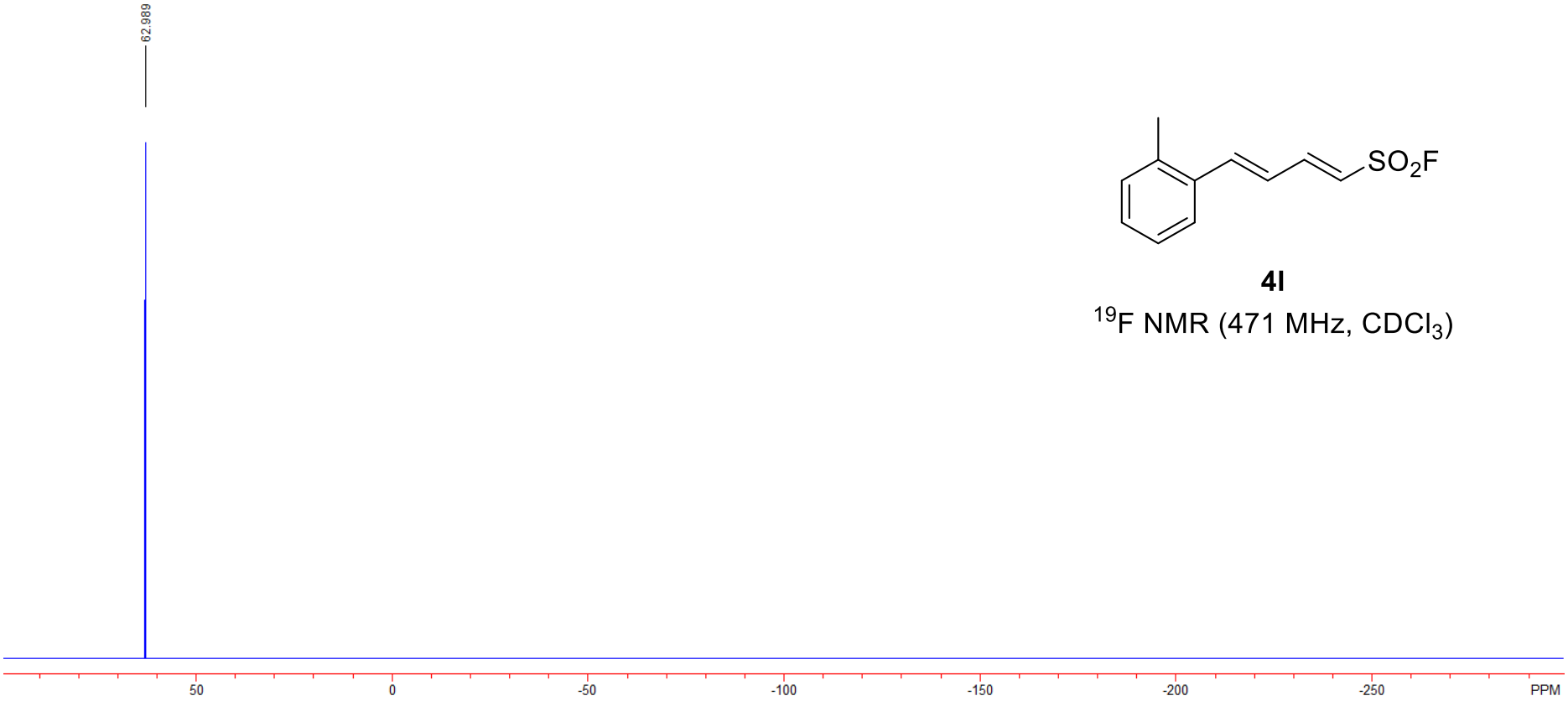
^{19}F NMR (471 MHz, $CDCl_3$)



4k

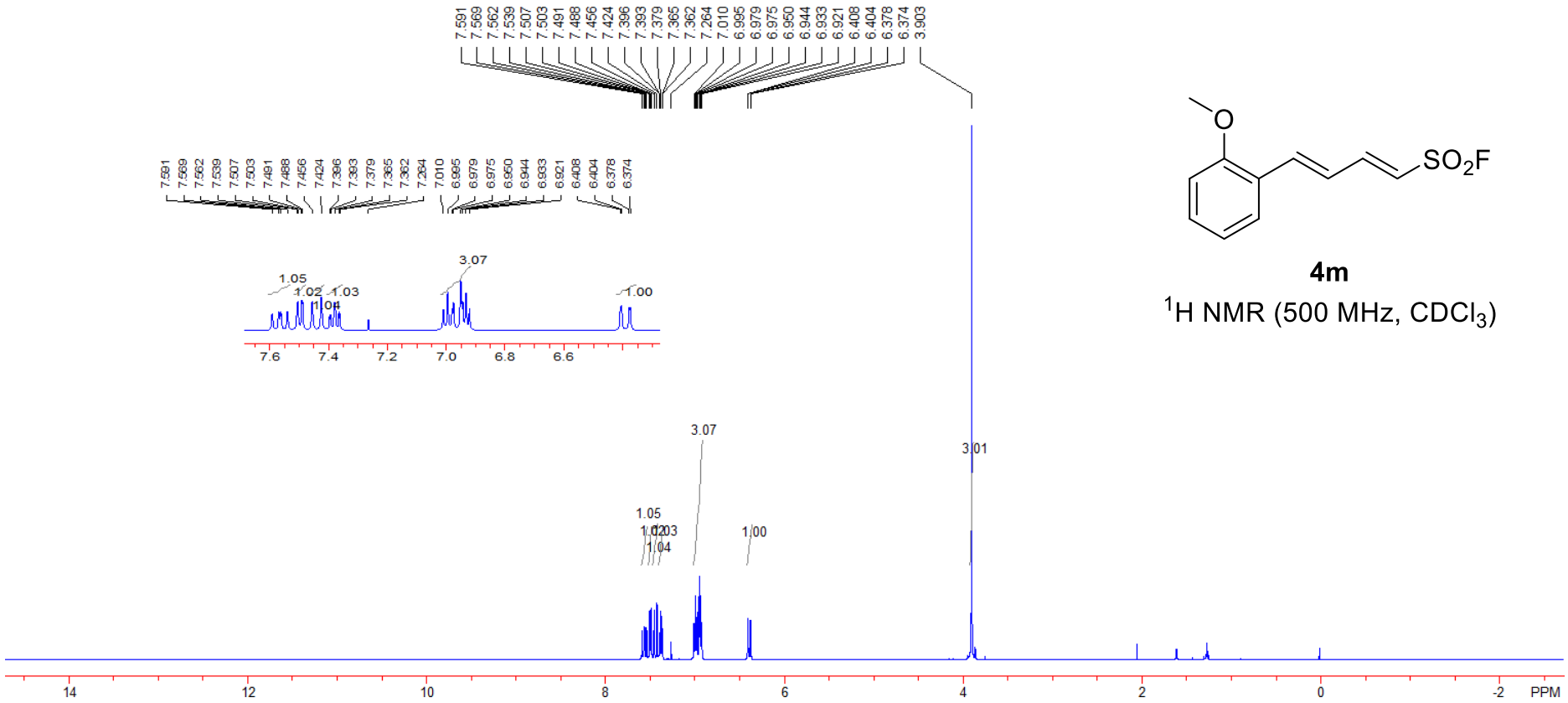
^{13}C NMR (126 MHz, $CDCl_3$)


7.611
7.588
7.581
7.562
7.548
7.398
7.368
7.304
7.290
7.275
7.248
7.233
7.224
7.209
6.815
6.792
6.784
6.762
6.448
6.445
6.418
6.415
2.414
-0.000
2.02
2.12
1.02
1.01
1.01
1.00
3.02
7.6
7.4
7.2
7.0
6.8
6.6
6.4
14
12
10
8
6
4
2
0
-2
PPM
SO_2F
4l
^{1}H NMR (500 MHz, $CDCl_3$)



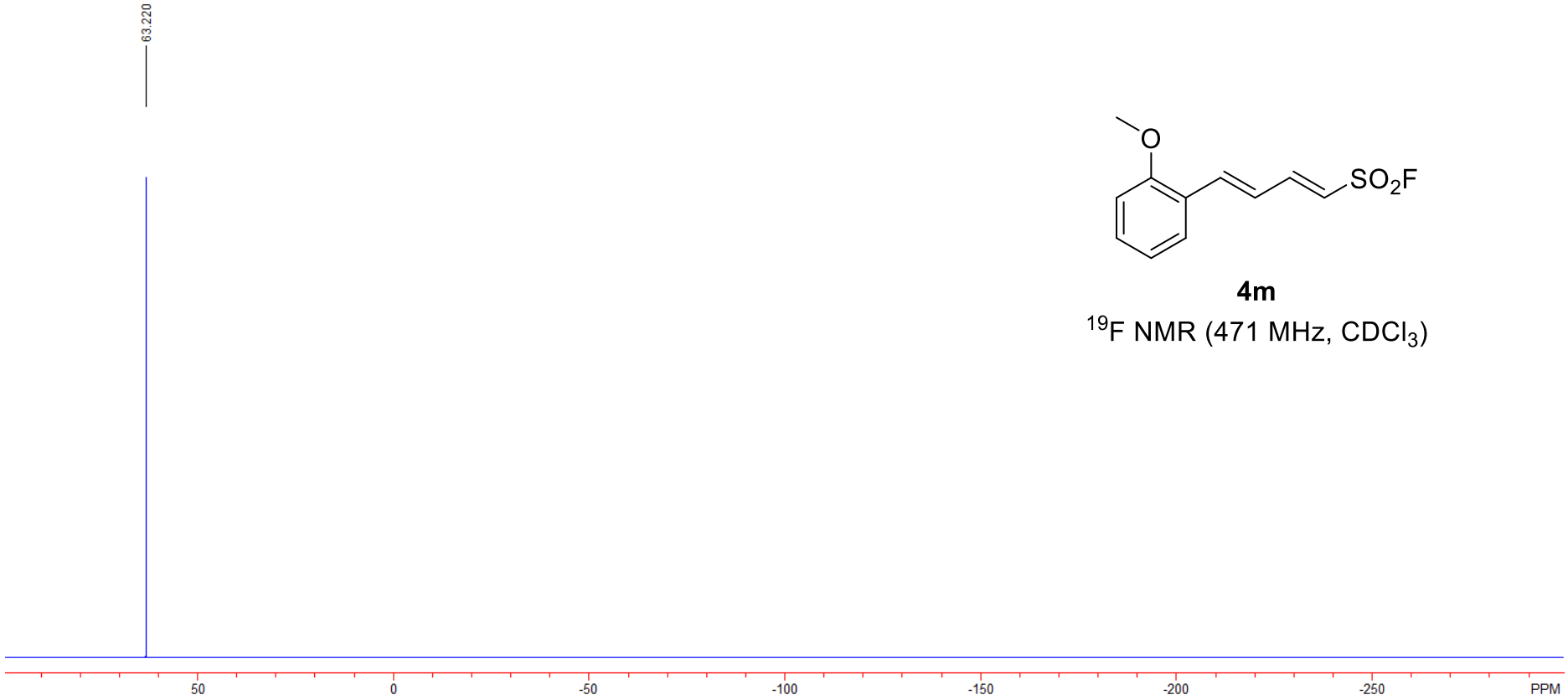
4l

^{19}F NMR (471 MHz, $CDCl_3$)



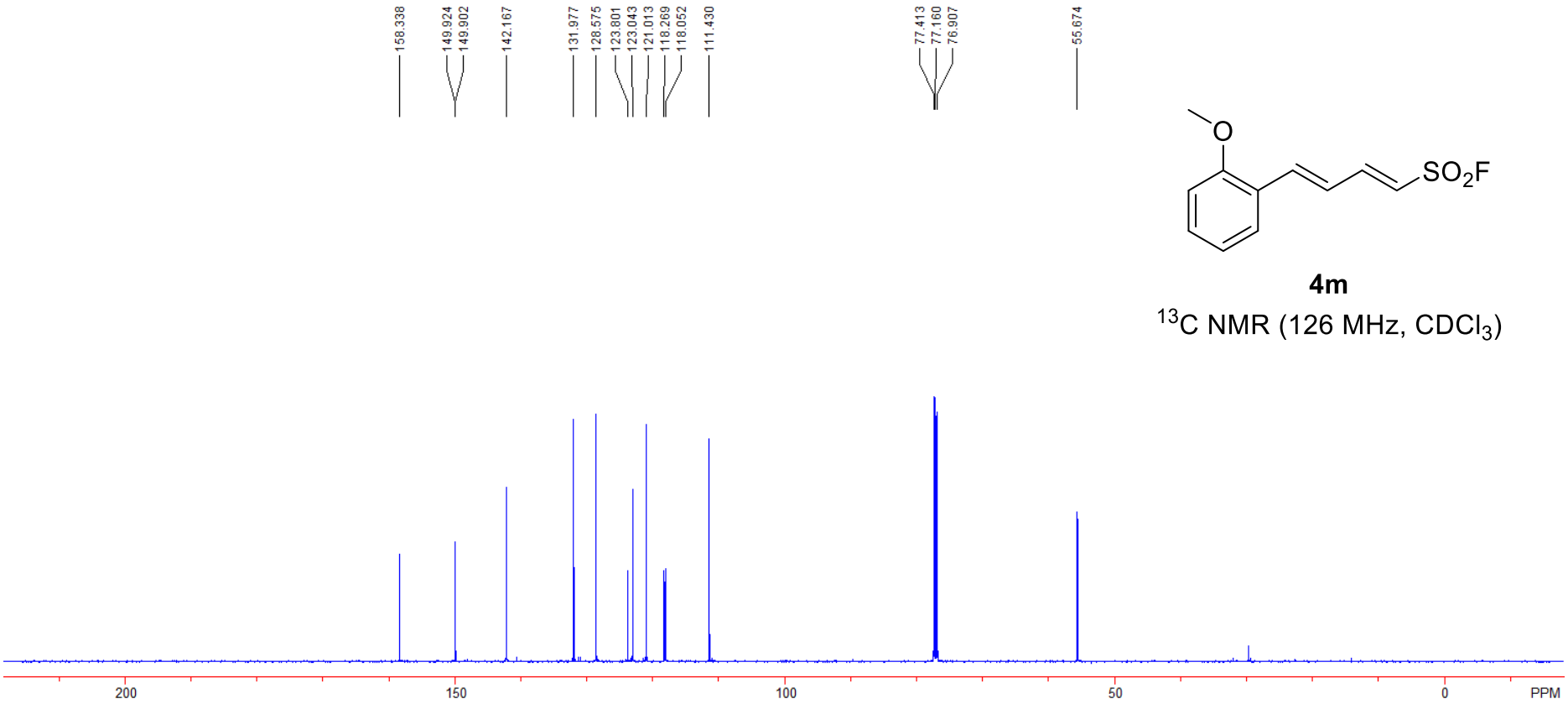
4m

^{1}H NMR (500 MHz, $CDCl_3$)



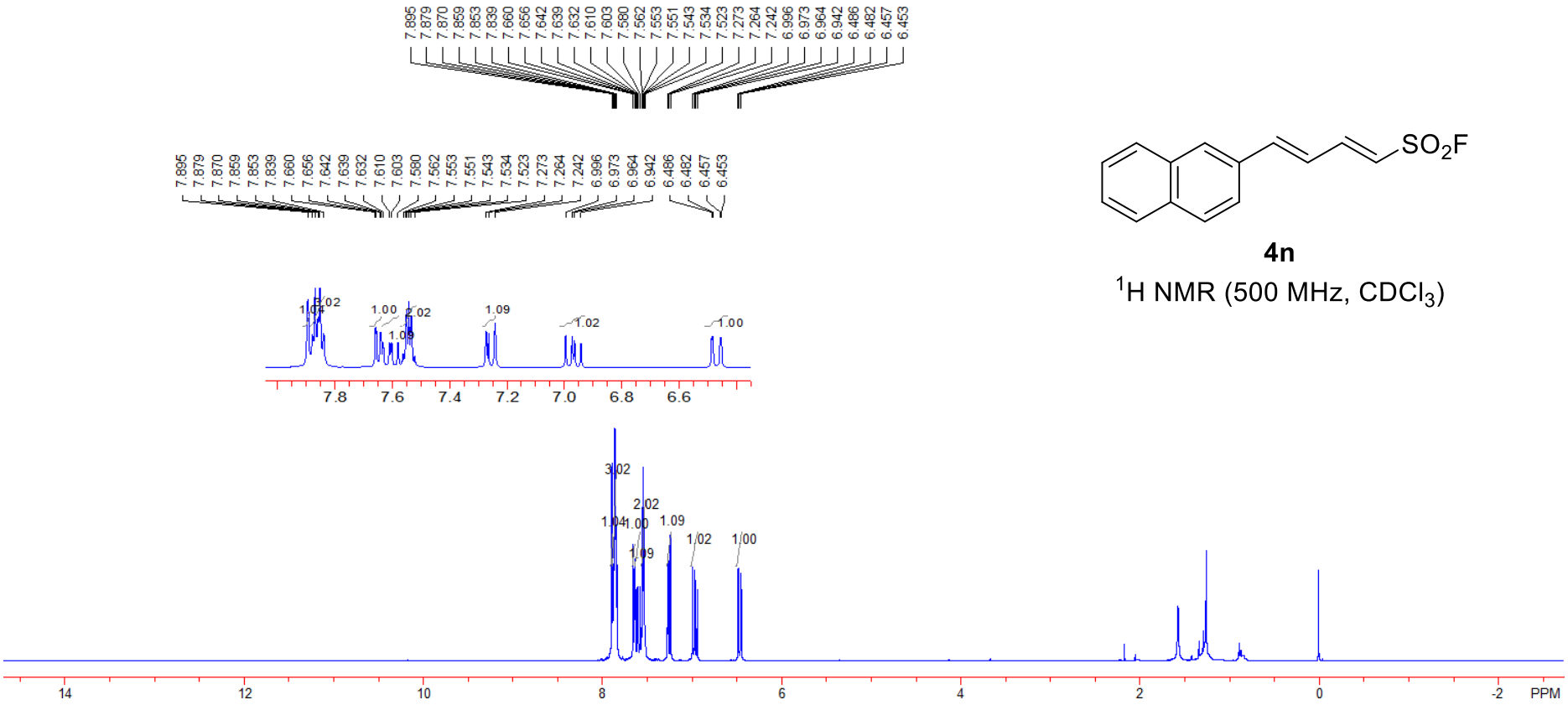
4m

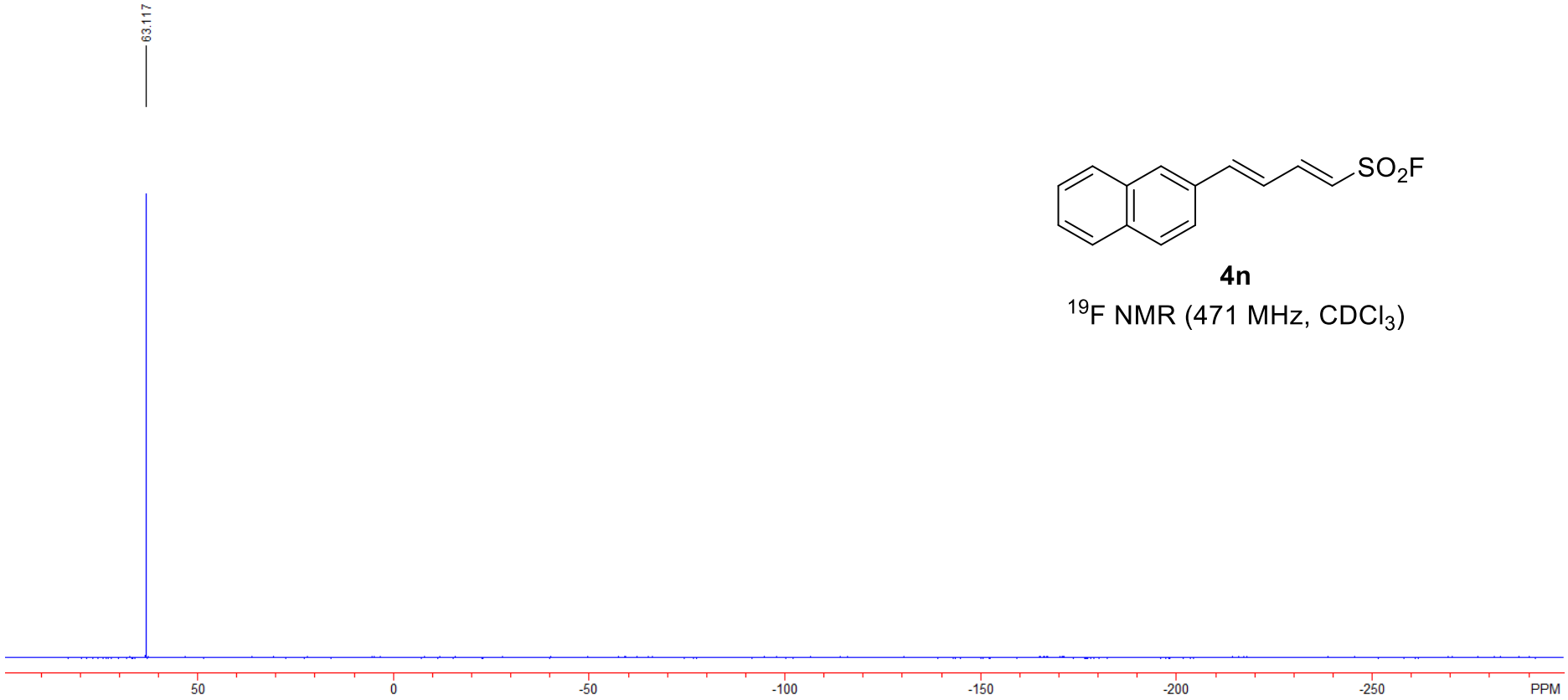
^{19}F NMR (471 MHz, $CDCl_3$)



4m

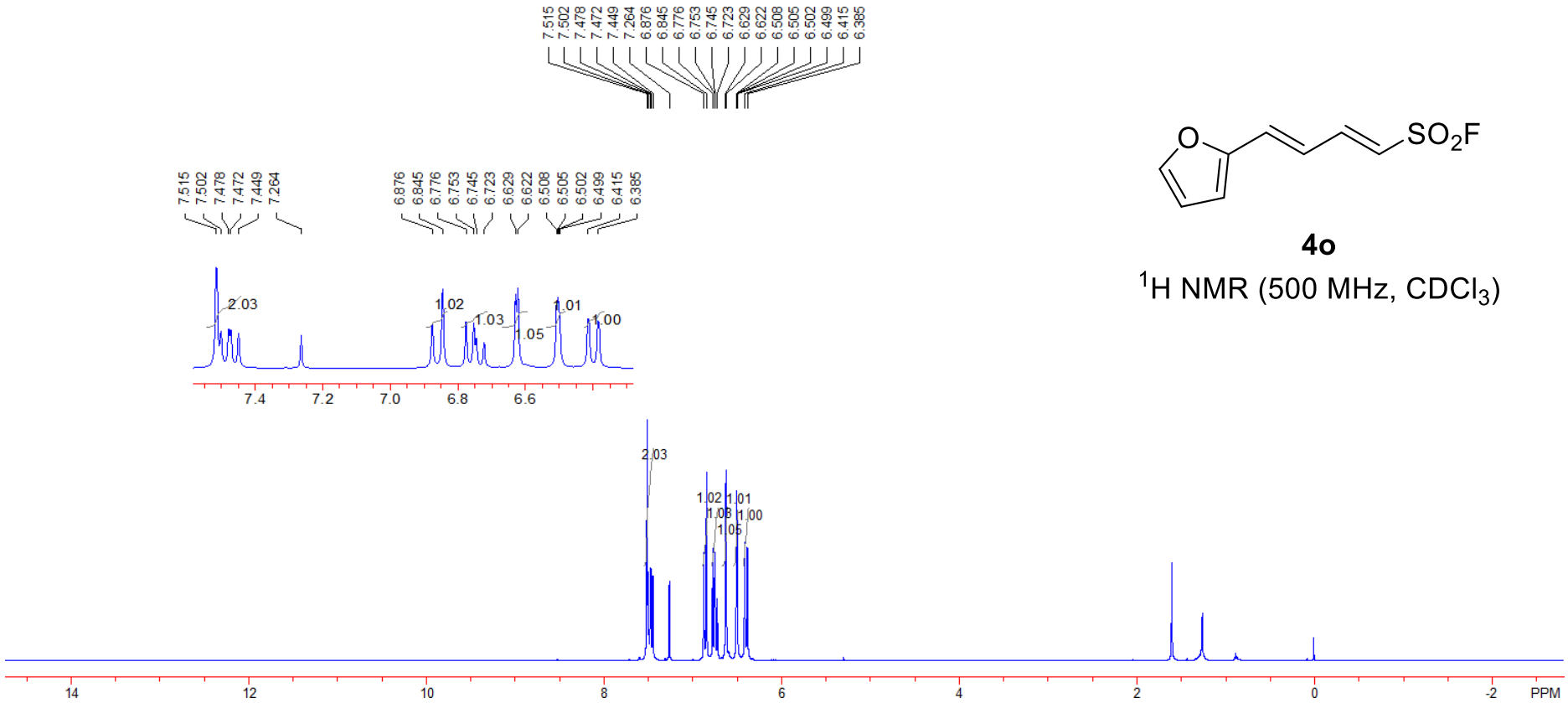
^{13}C NMR (126 MHz, $CDCl_3$)


7.895
7.879
7.870
7.859
7.853
7.839
7.660
7.656
7.642
7.639
7.632
7.610
7.603
7.580
7.562
7.553
7.551
7.543
7.534
7.523
7.273
7.264
7.242
6.996
6.973
6.964
6.942
6.486
6.482
6.457
6.453
SO2F
4n
1H NMR (500 MHz, CDCl3)
3.02
1.00
2.02
1.09
1.02
1.00
7.8
7.6
7.4
7.2
7.0
6.8
6.6
14
12
10
8
6
4
2
0
-2
PPM



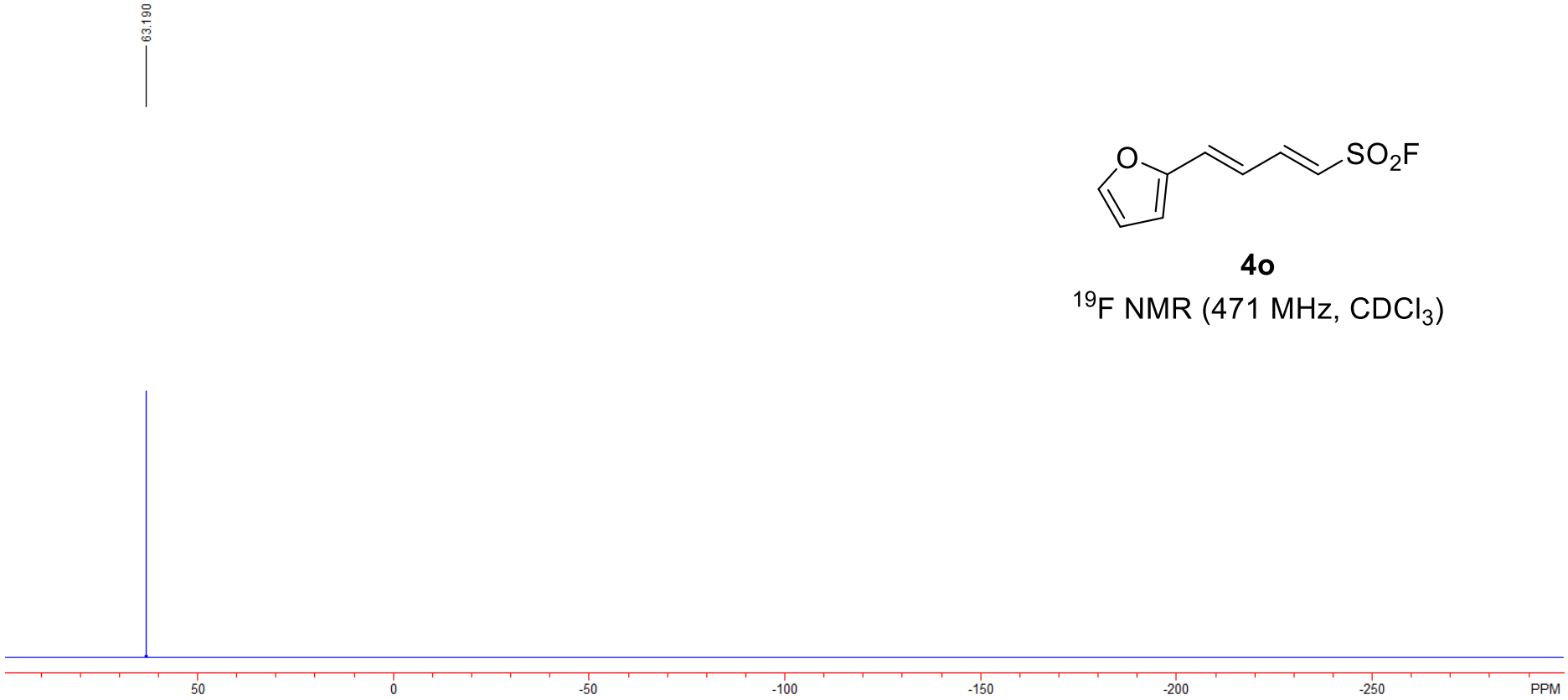
4n

^{19}F NMR (471 MHz, $CDCl_3$)



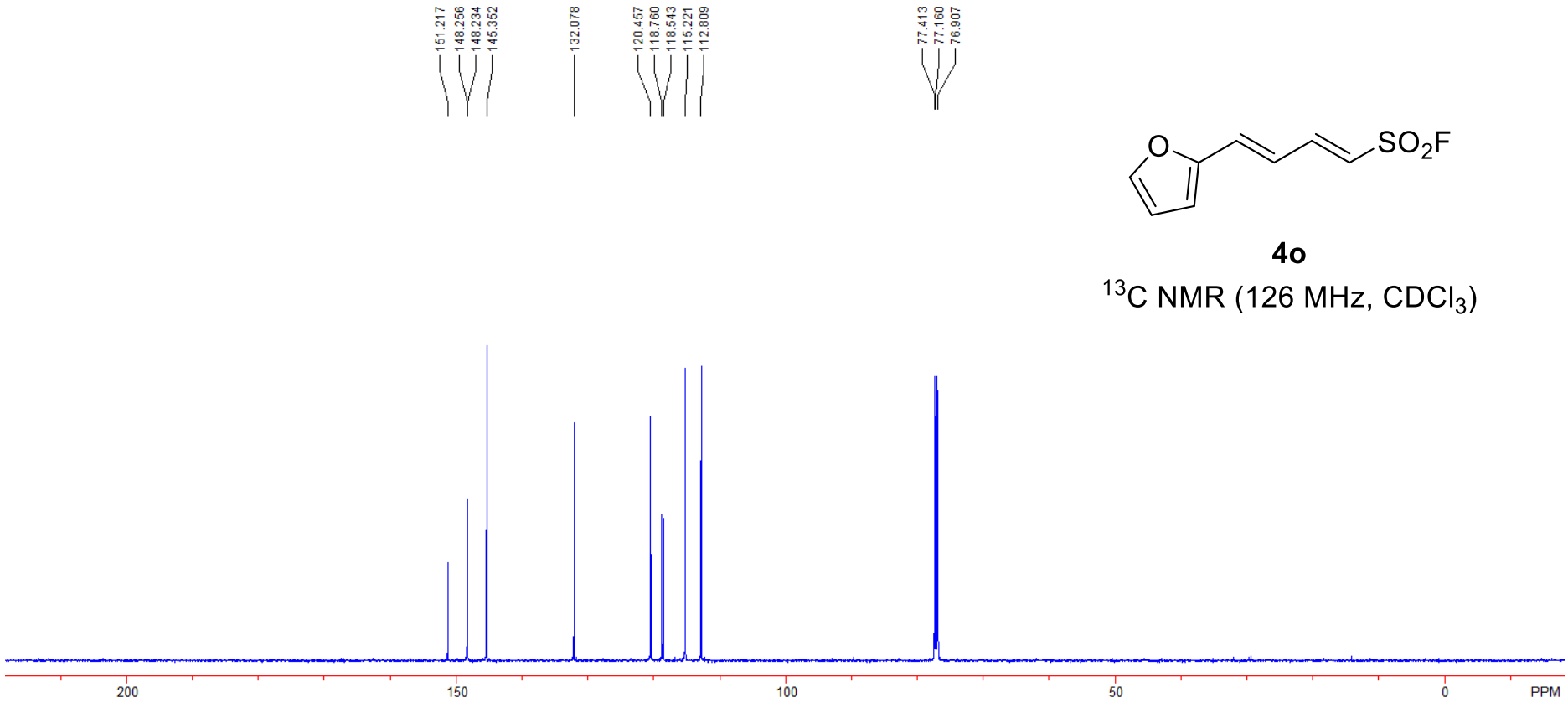
4o

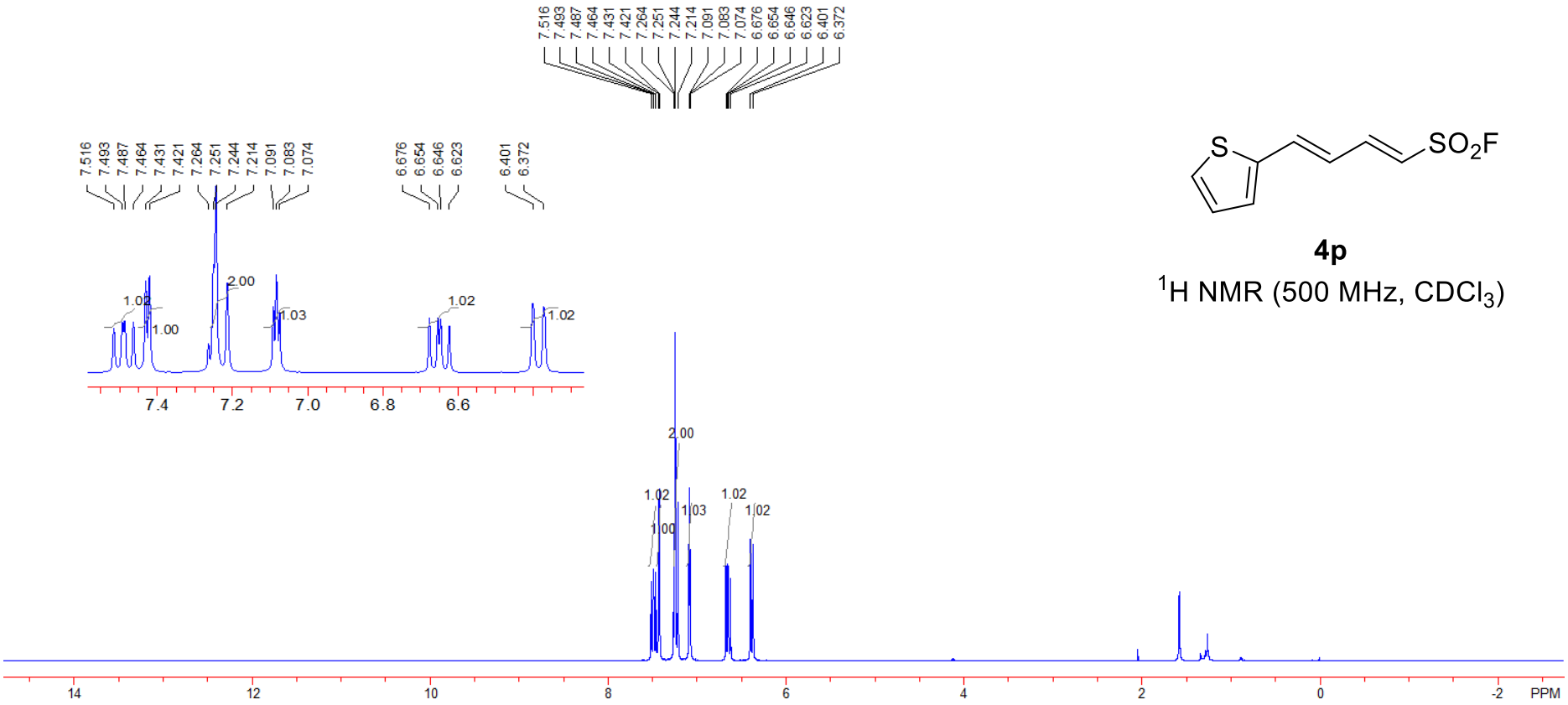
^{1}H NMR (500 MHz, $CDCl_3$)

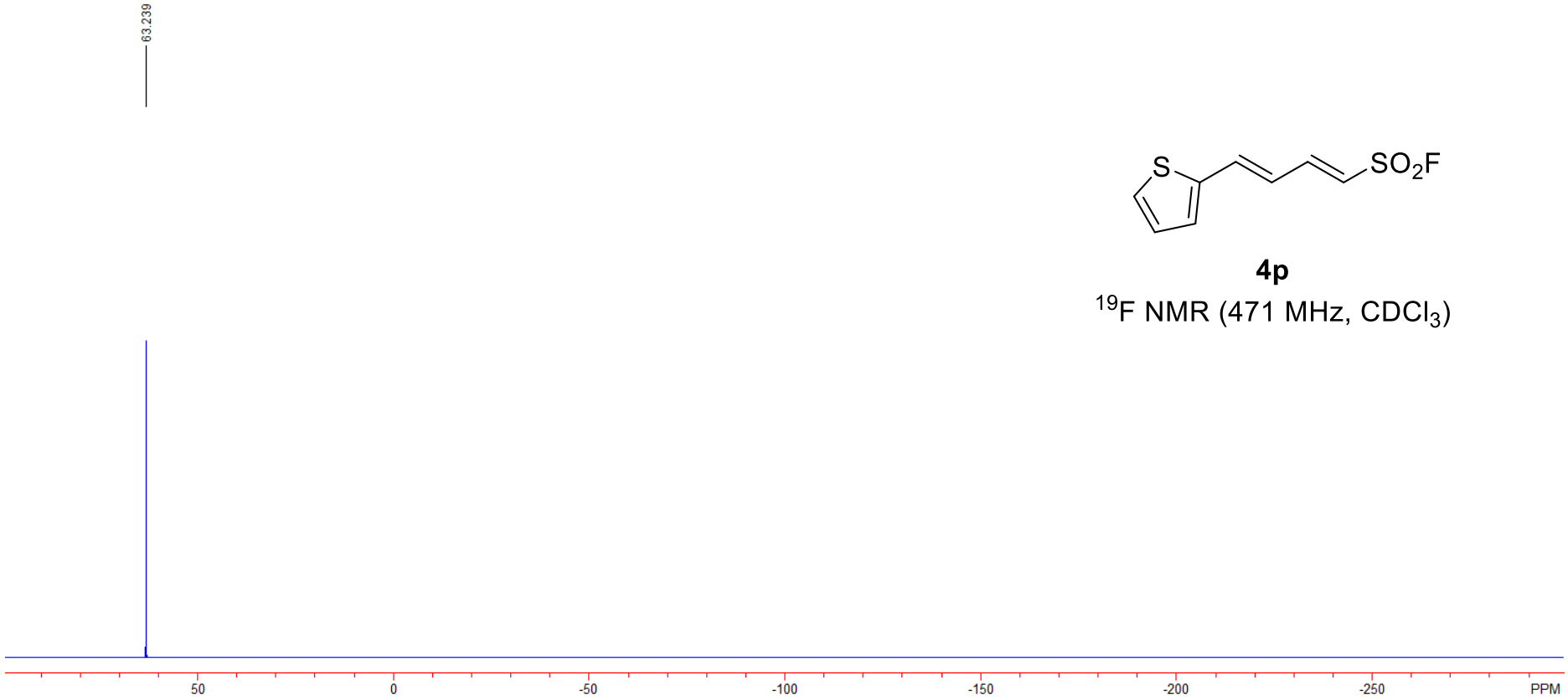


4o

^{19}F NMR (471 MHz, $CDCl_3$)

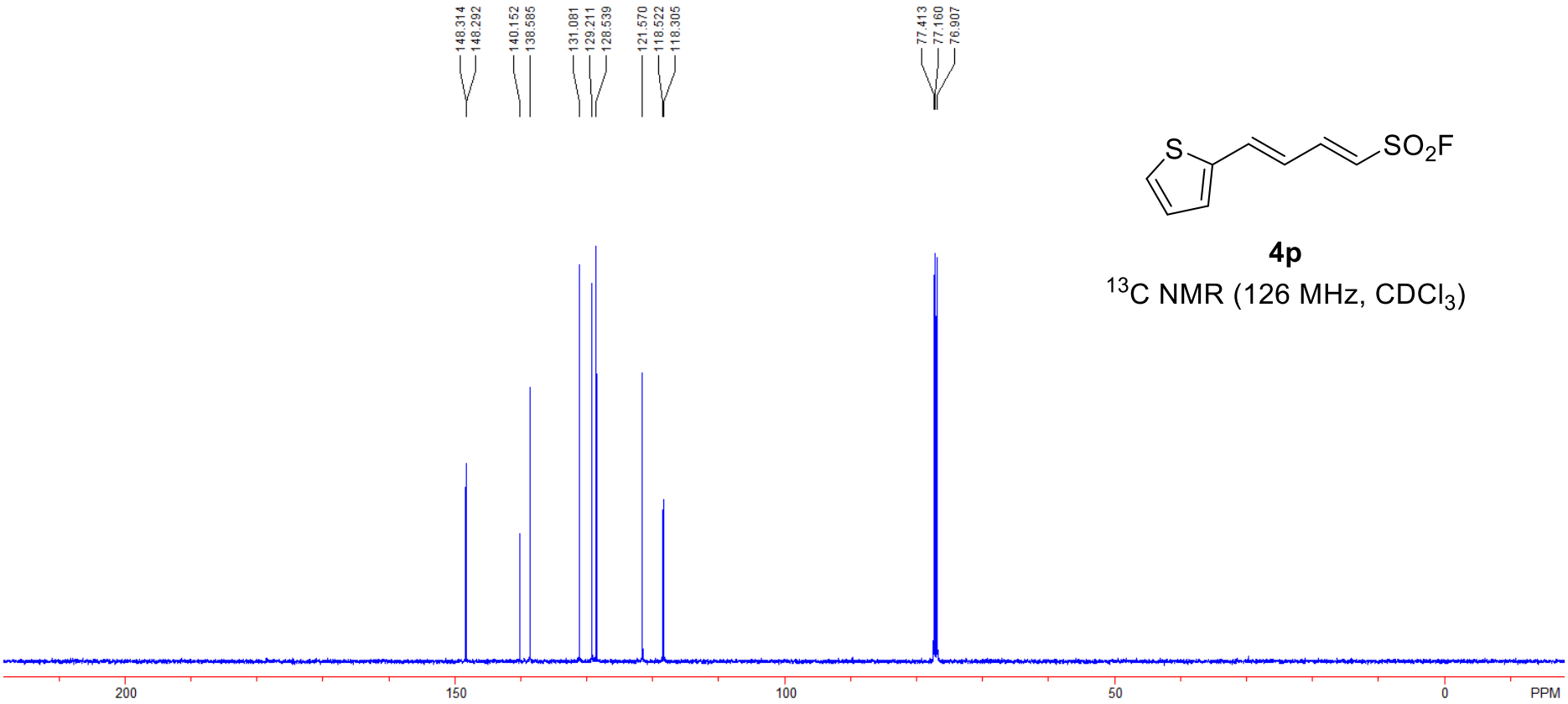

151.217
148.256
148.234
145.352
132.078
120.457
118.760
118.543
115.221
112.809
77.413
77.160
76.907
O
SO2F
4o
13C NMR (126 MHz, CDCl3)
200
150
100
50
0
PPM


7.516
7.493
7.487
7.464
7.431
7.421
7.264
7.251
7.244
7.214
7.091
7.083
7.074
6.676
6.654
6.646
6.623
6.401
6.372
1.02
1.00
2.00
1.03
1.02
1.02
7.4
7.2
7.0
6.8
6.6
S
SO2F
4p
1H NMR (500 MHz, CDCl3)
14
12
10
8
6
4
2
0
-2
PPM



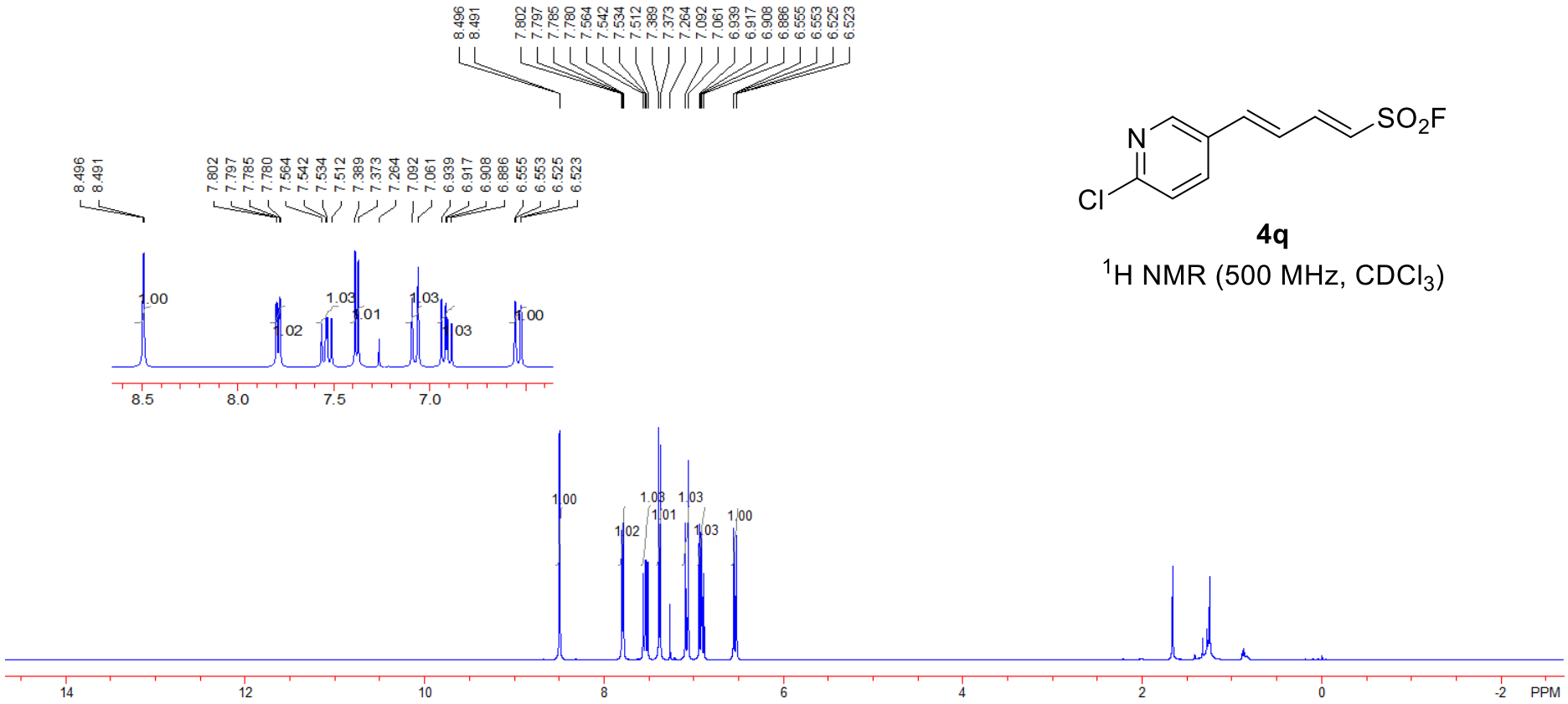
4p

^{19}F NMR (471 MHz, $CDCl_3$)



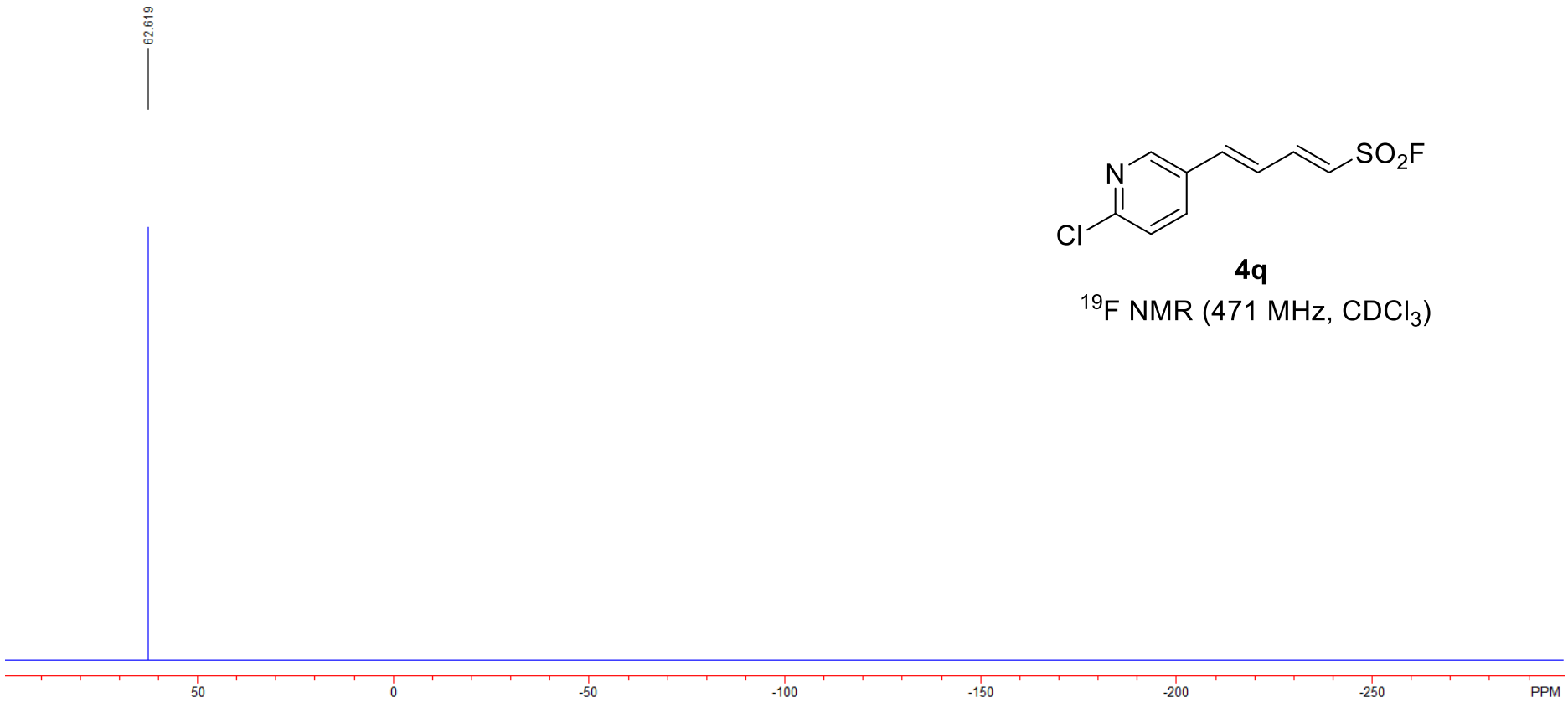
4p

^{13}C NMR (126 MHz, $CDCl_3$)



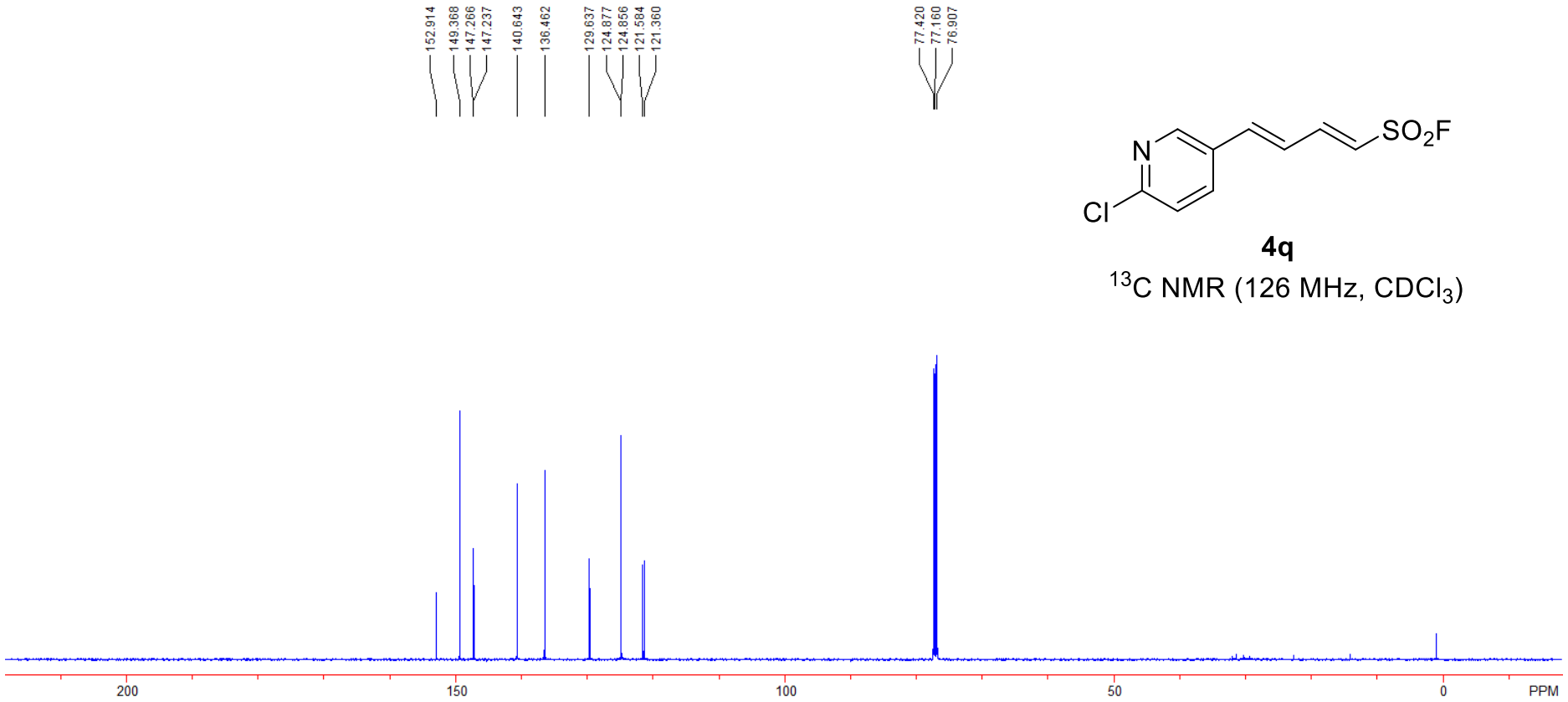
4q

^{1}H NMR (500 MHz, $CDCl_3$)



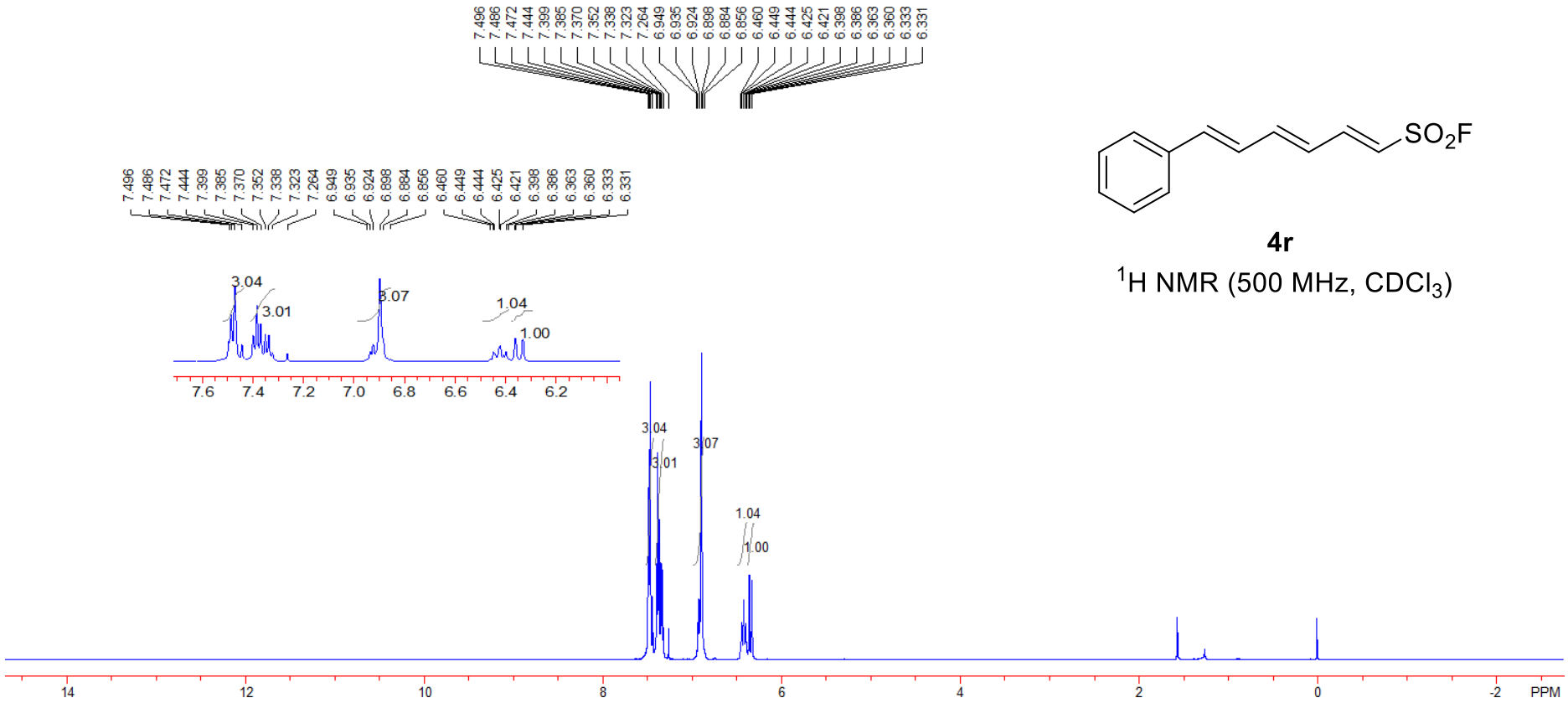
4q

^{19}F NMR (471 MHz, $CDCl_3$)



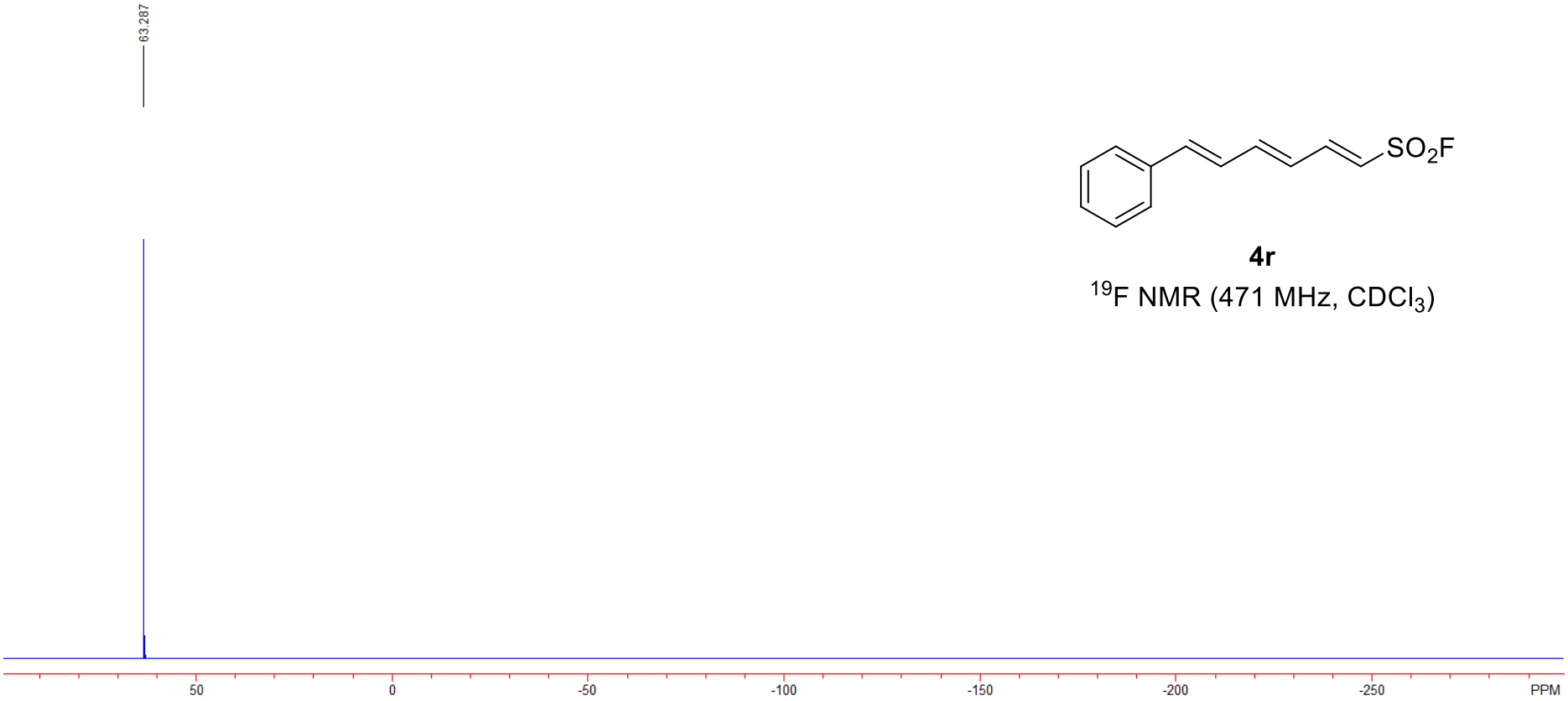
4q

^{13}C NMR (126 MHz, $CDCl_3$)



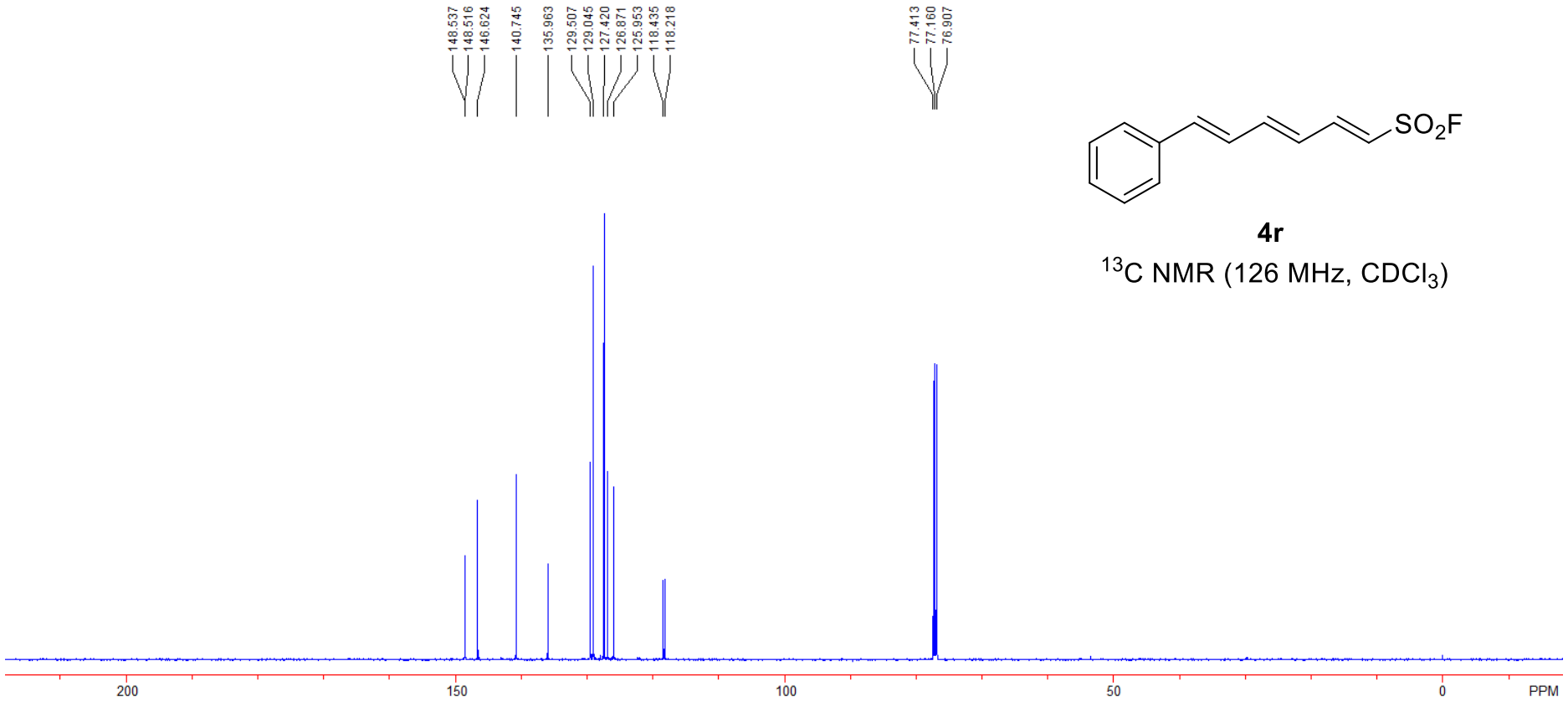
4r

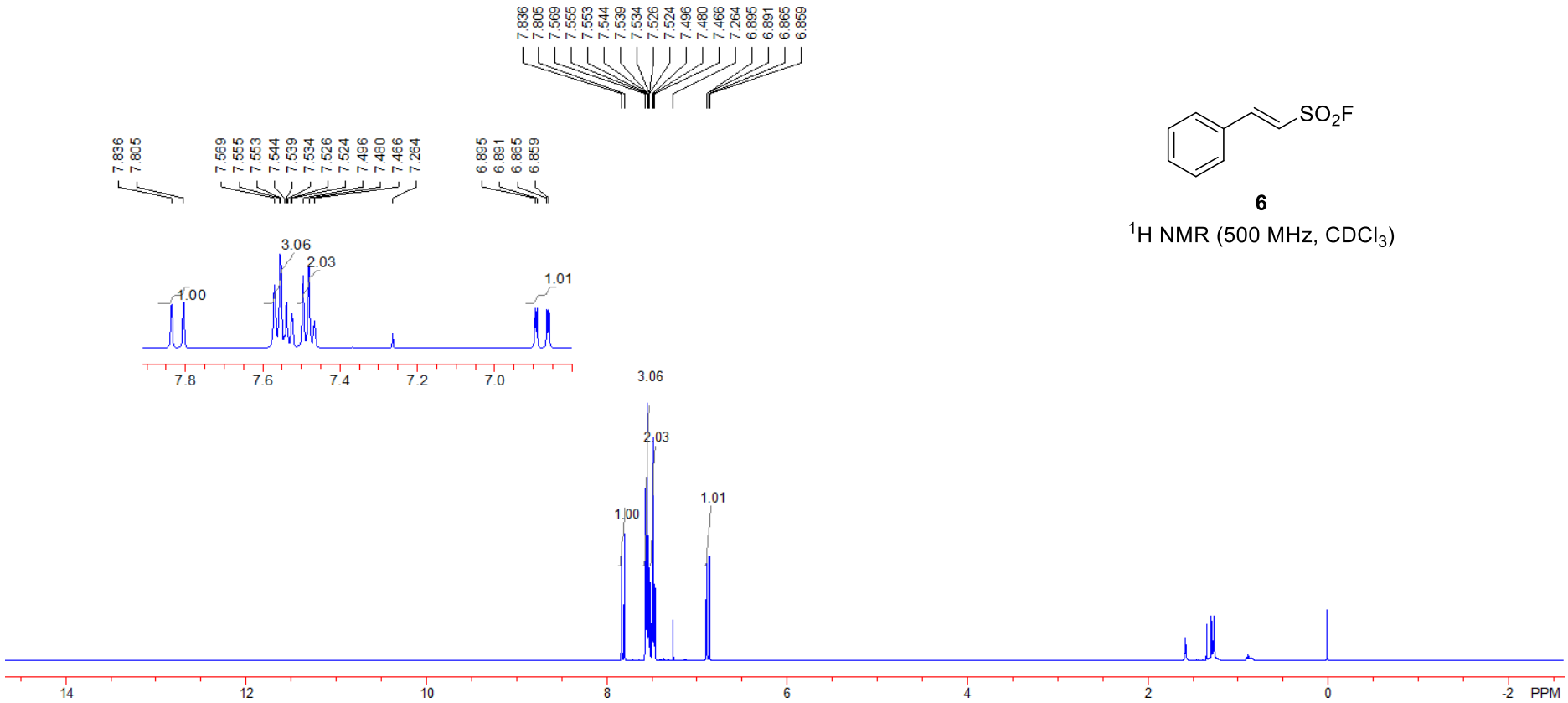
^{1}H NMR (500 MHz, $CDCl_3$)



4r

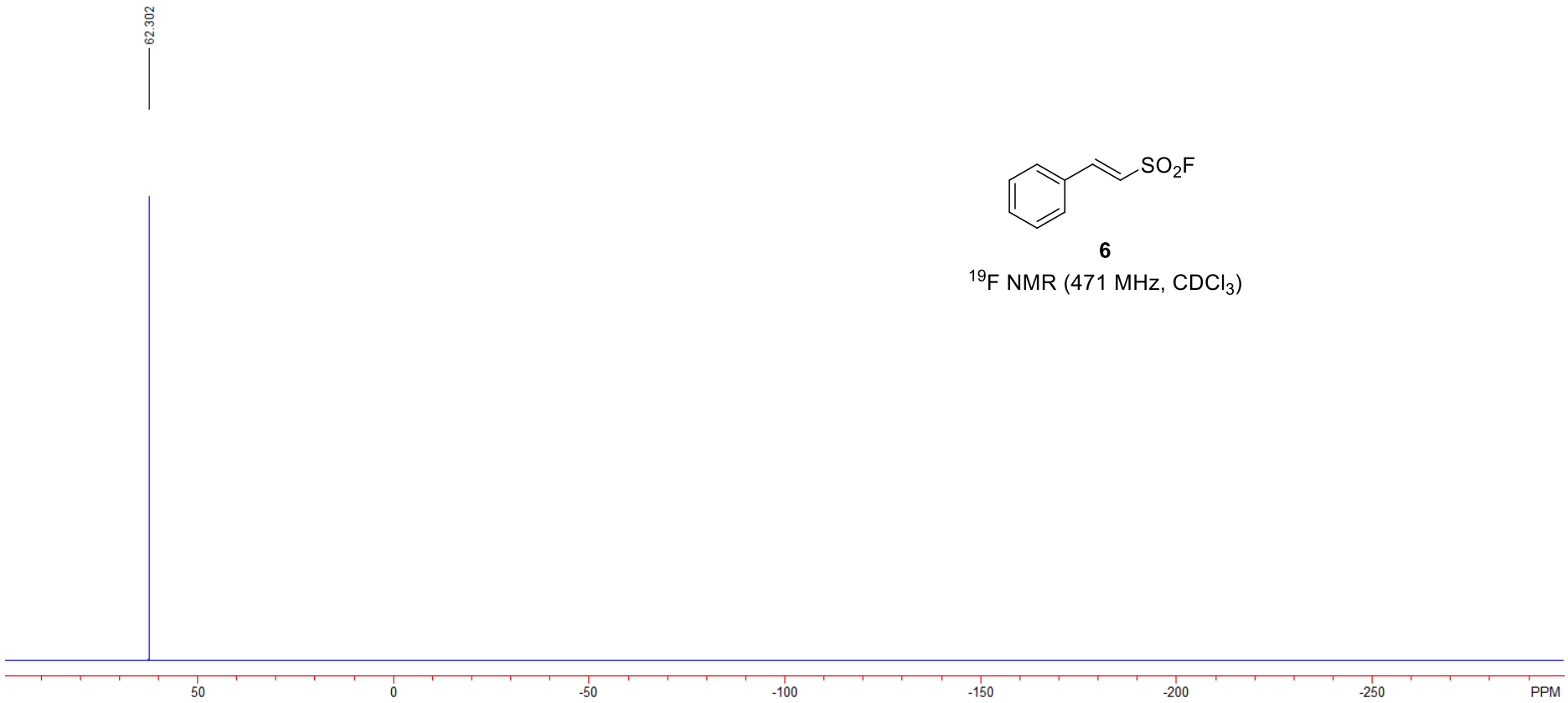
^{19}F NMR (471 MHz, $CDCl_3$)


148.537
148.516
146.624
140.745
135.963
129.507
129.045
127.420
126.871
125.953
118.435
118.218
77.413
77.160
76.907
SO2F
4r
13C NMR (126 MHz, CDCl3)
200
150
100
50
0
PPM



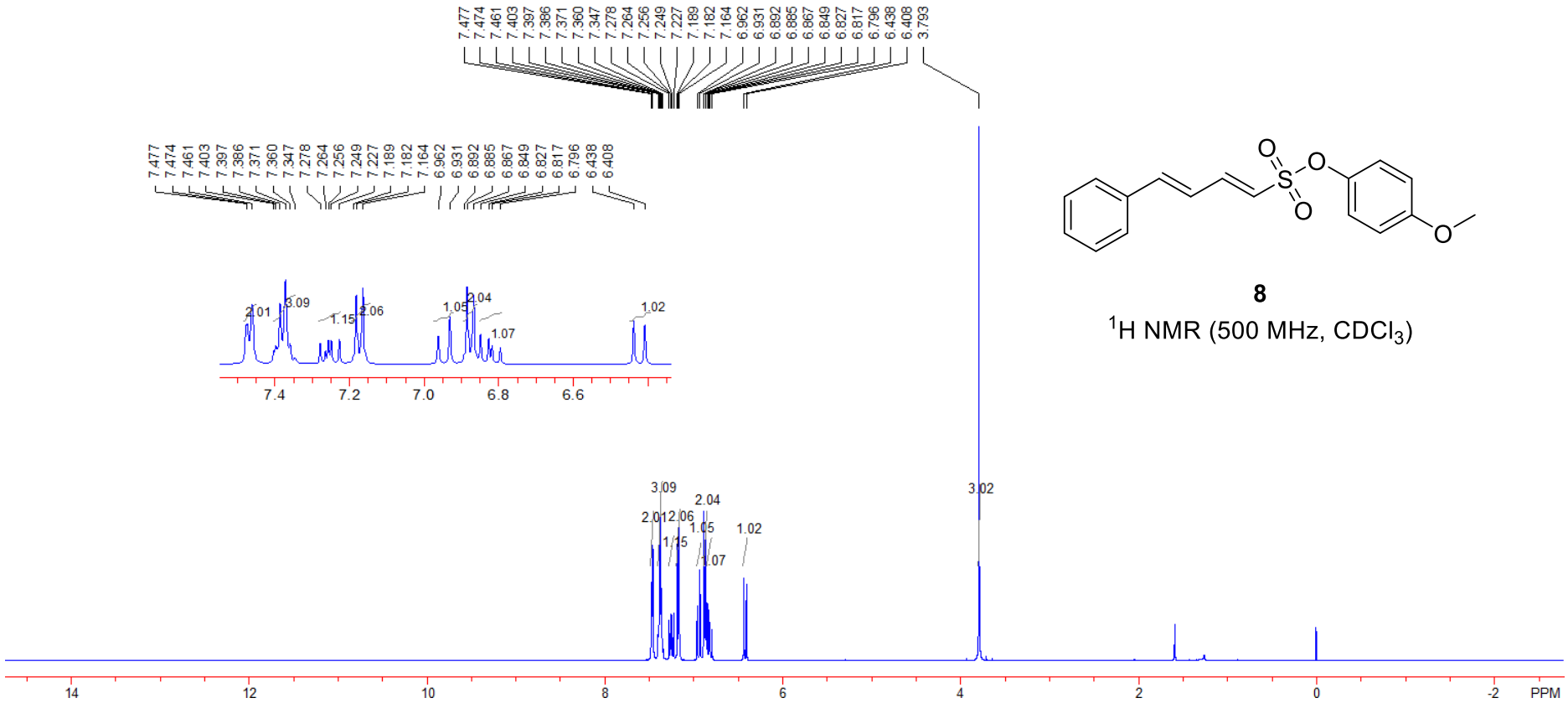
6

^{1}H NMR (500 MHz, $CDCl_3$)



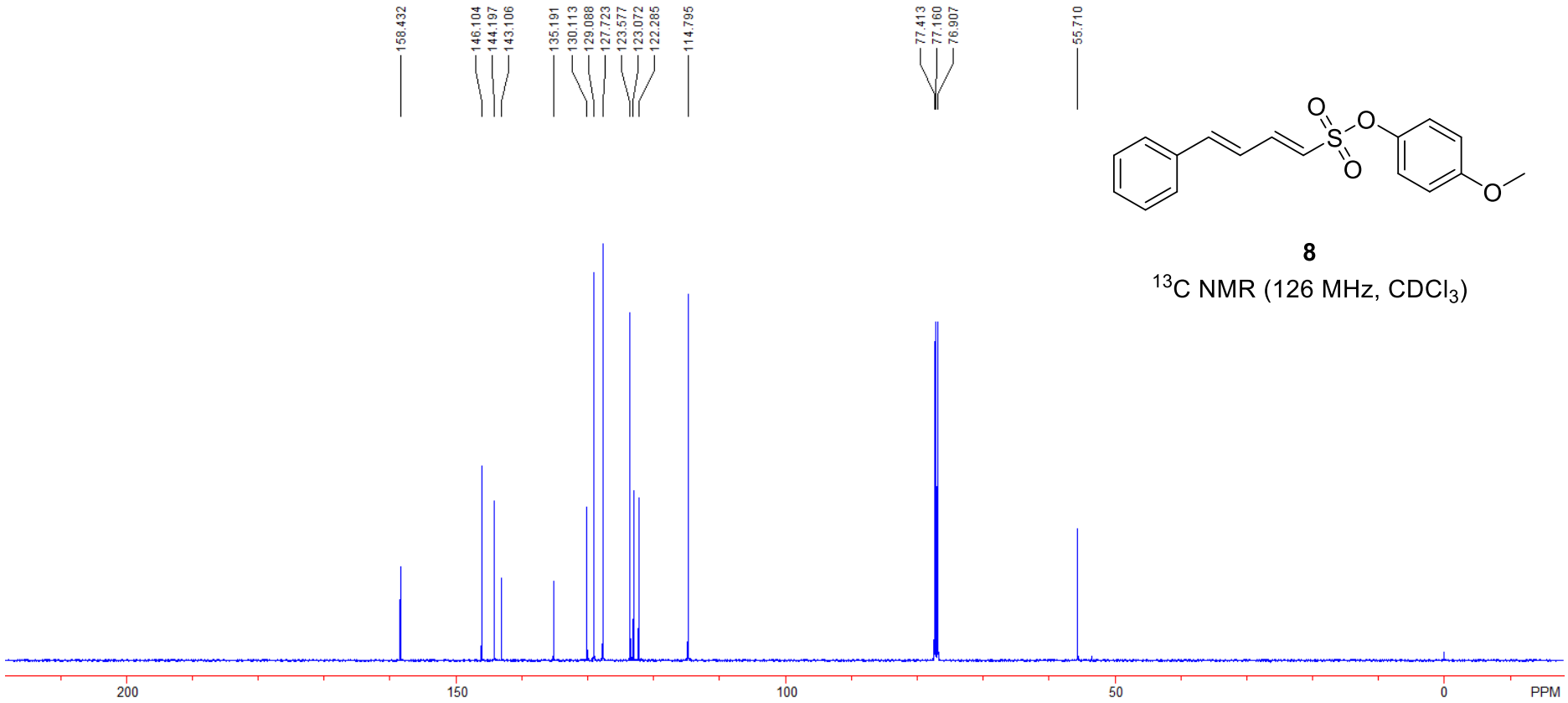
6

^{19}F NMR (471 MHz, $CDCl_3$)



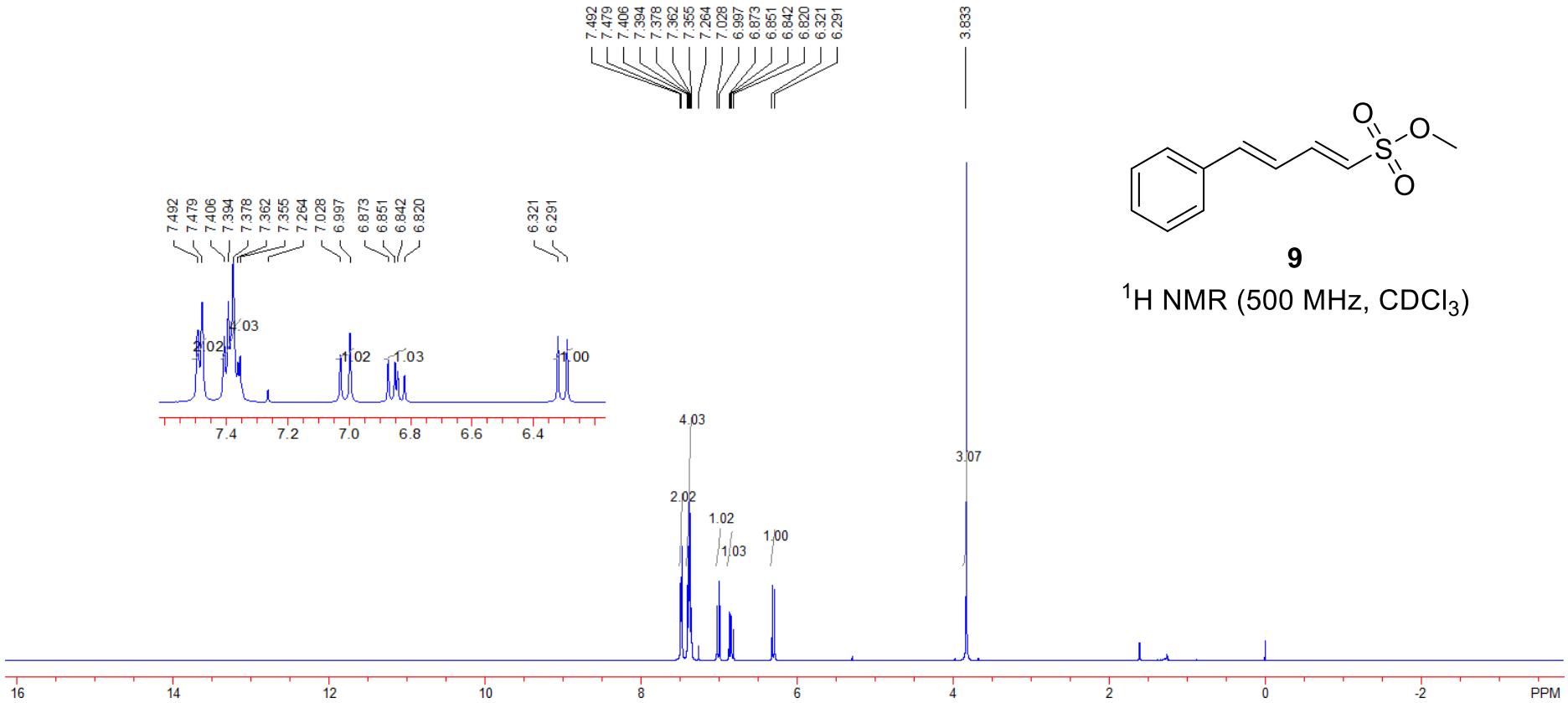
8

^{1}H NMR (500 MHz, $CDCl_3$)



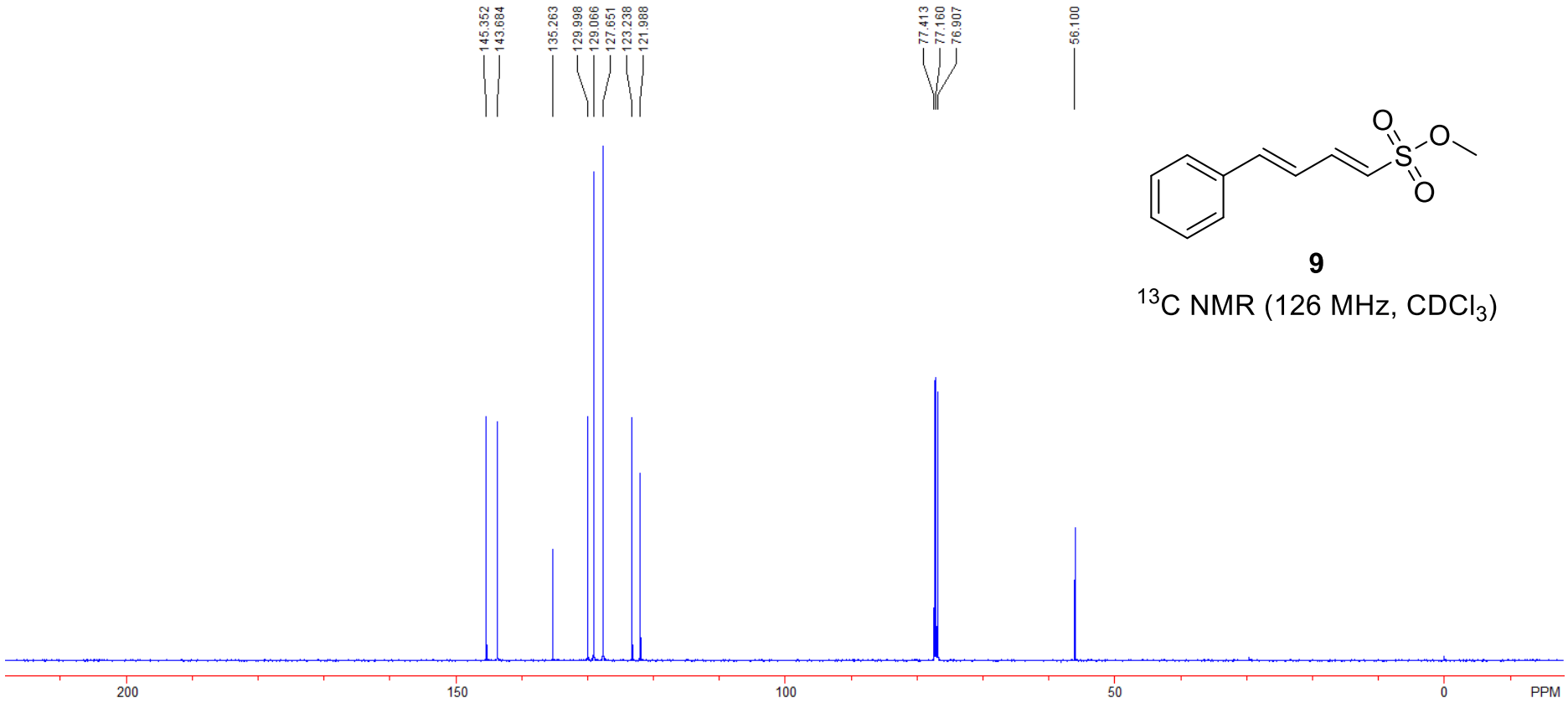
8

^{13}C NMR (126 MHz, $CDCl_3$)



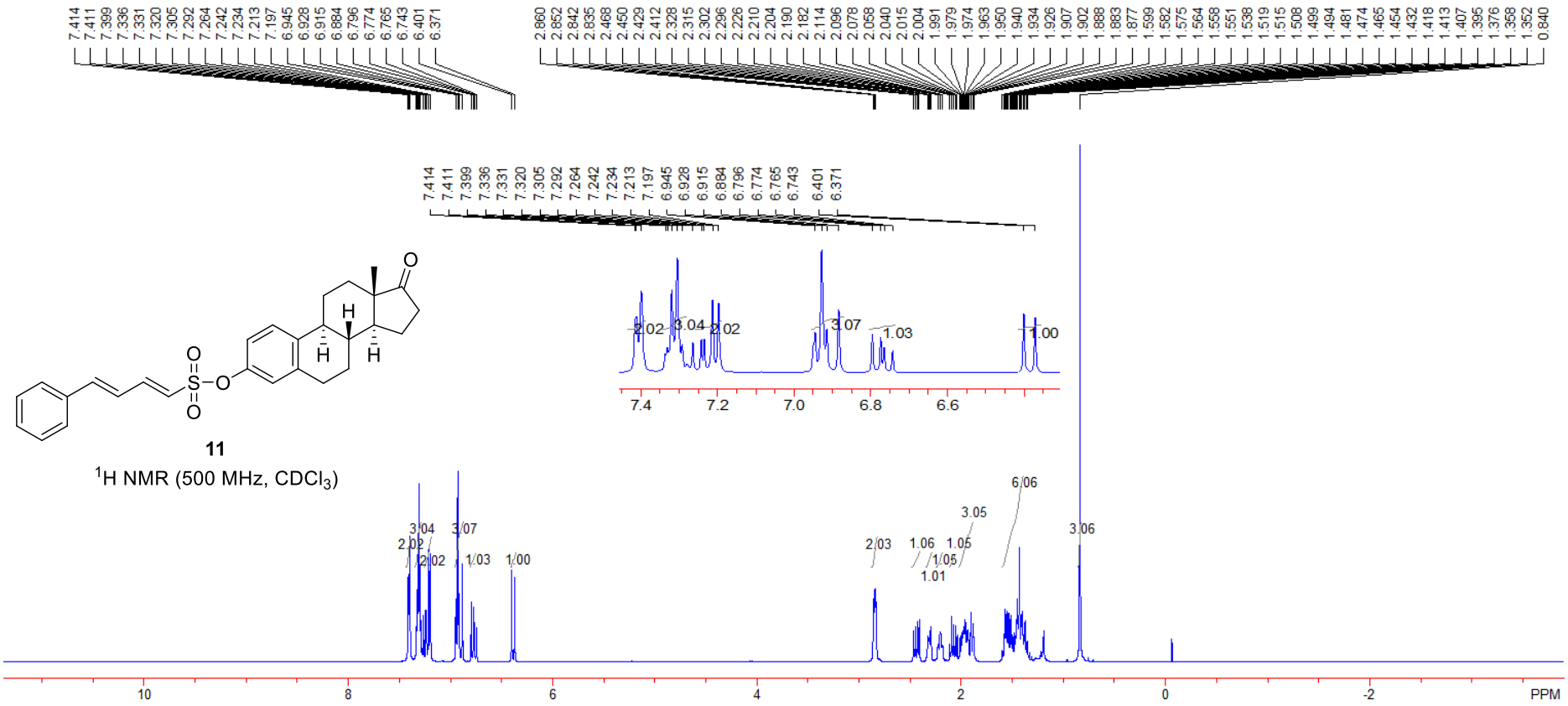
9

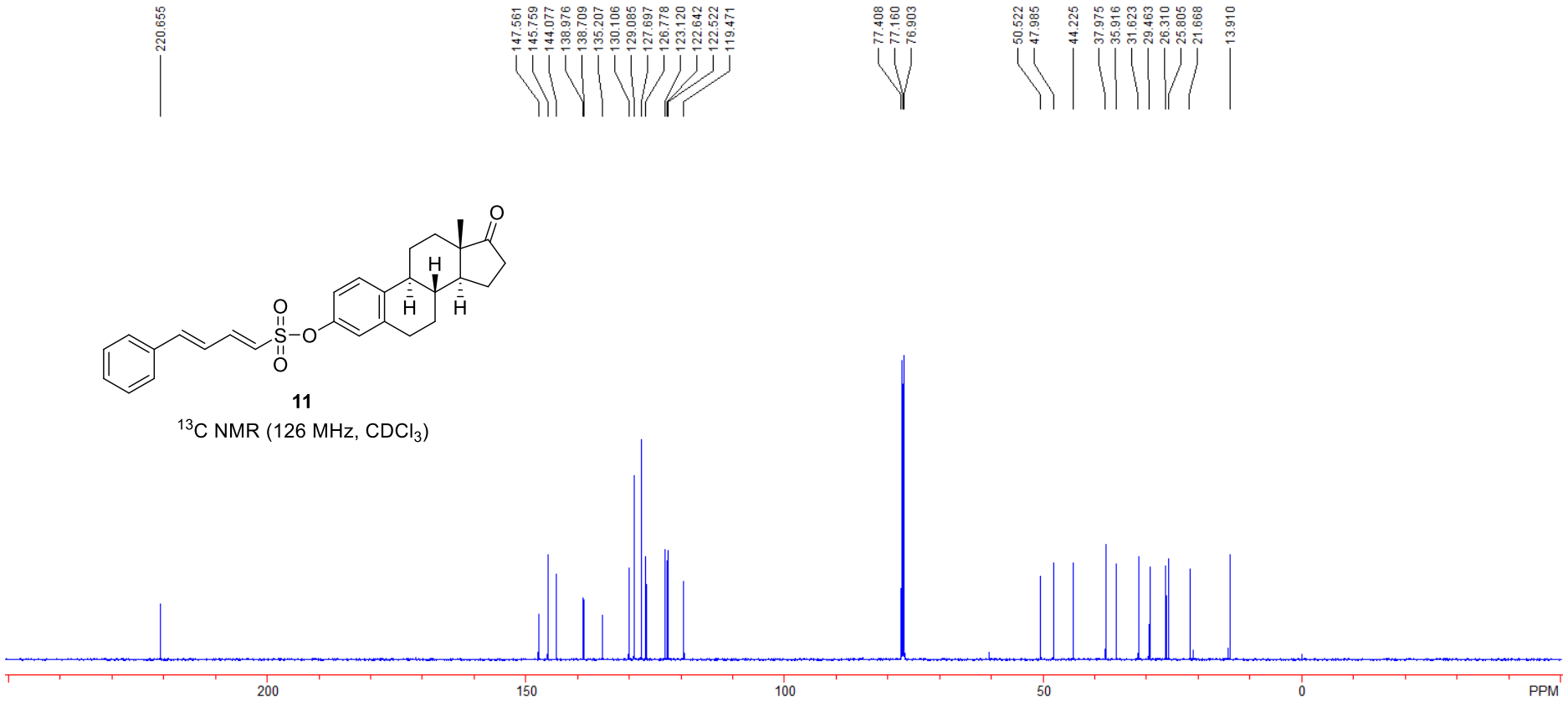
^{1}H NMR (500 MHz, $CDCl_3$)



9

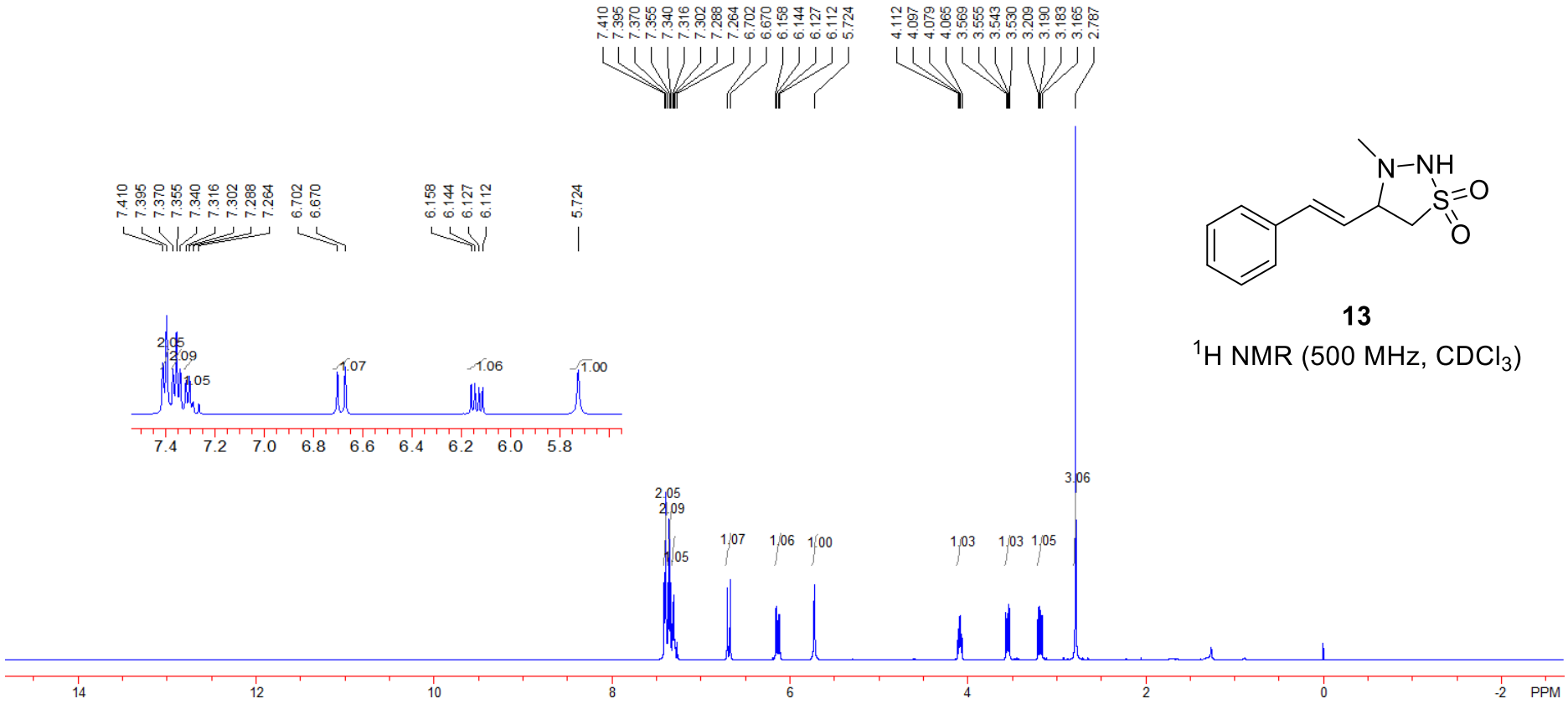
^{13}C NMR (126 MHz, $CDCl_3$)


7.414
7.411
7.399
7.336
7.331
7.320
7.305
7.292
7.264
7.242
7.234
7.213
7.197
6.945
6.928
6.915
6.884
6.796
6.774
6.765
6.743
6.401
6.371
2.860
2.852
2.842
2.835
2.468
2.450
2.429
2.412
2.328
2.315
2.302
2.296
2.226
2.210
2.204
2.190
2.182
2.114
2.096
2.078
2.058
2.040
2.015
2.004
1.991
1.979
1.974
1.963
1.950
1.940
1.934
1.926
1.907
1.902
1.888
1.883
1.877
1.599
1.582
1.575
1.564
1.558
1.551
1.538
1.519
1.515
1.508
1.499
1.494
1.481
1.474
1.465
1.454
1.432
1.418
1.413
1.407
1.395
1.376
1.358
1.352
0.840
O
H
H
H
O
S
O
O
11
1H NMR (500 MHz, CDCl3)
2.02
3.04
2.02
3.07
1.03
1.00
7.4
7.2
7.0
6.8
6.6
2.02
3.04
2.02
3.07
1.03
1.00
2.03
1.06
1.05
1.05
1.01
3.05
6.06
3.06
10
8
6
4
2
0
-2
PPM



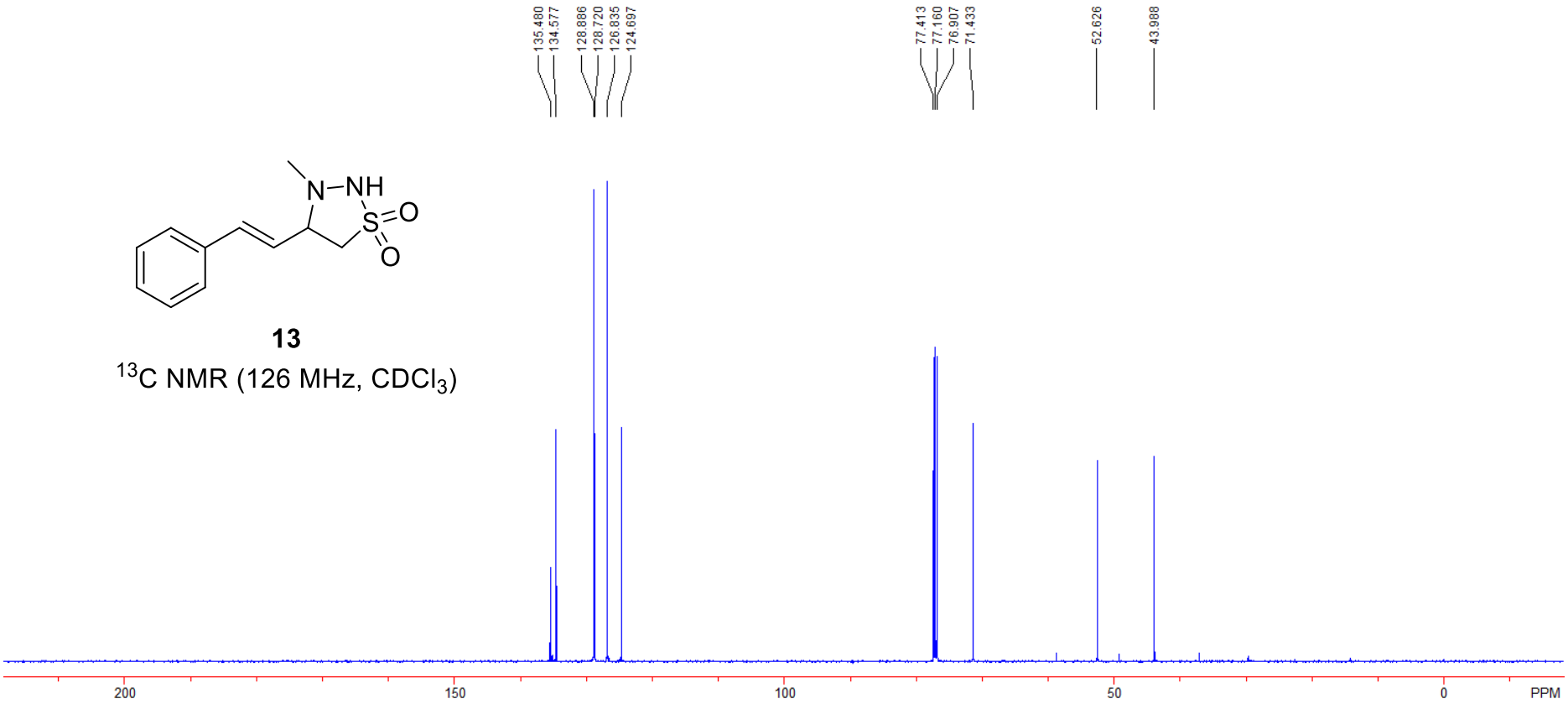
11

^{13}C NMR (126 MHz, $CDCl_3$)



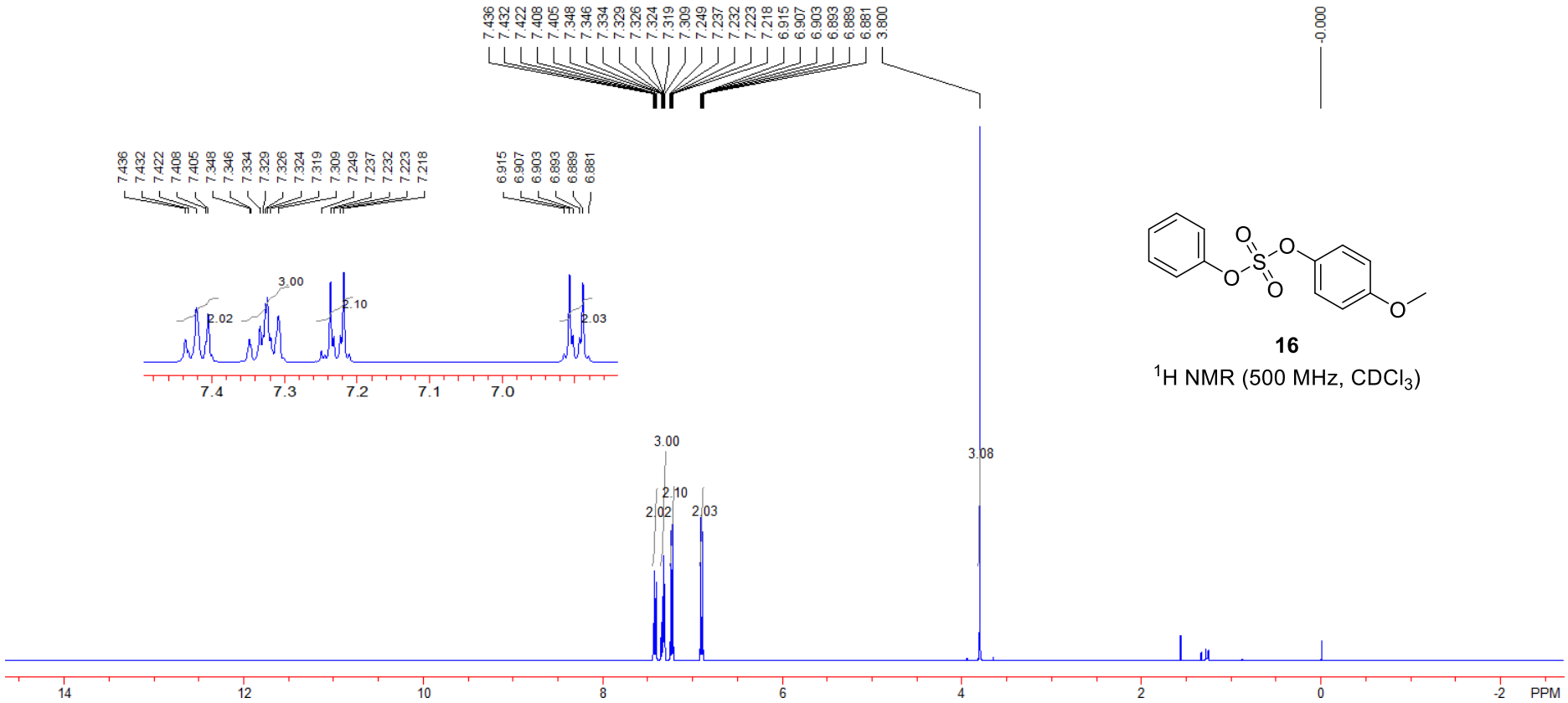
13

^{1}H NMR (500 MHz, $CDCl_3$)



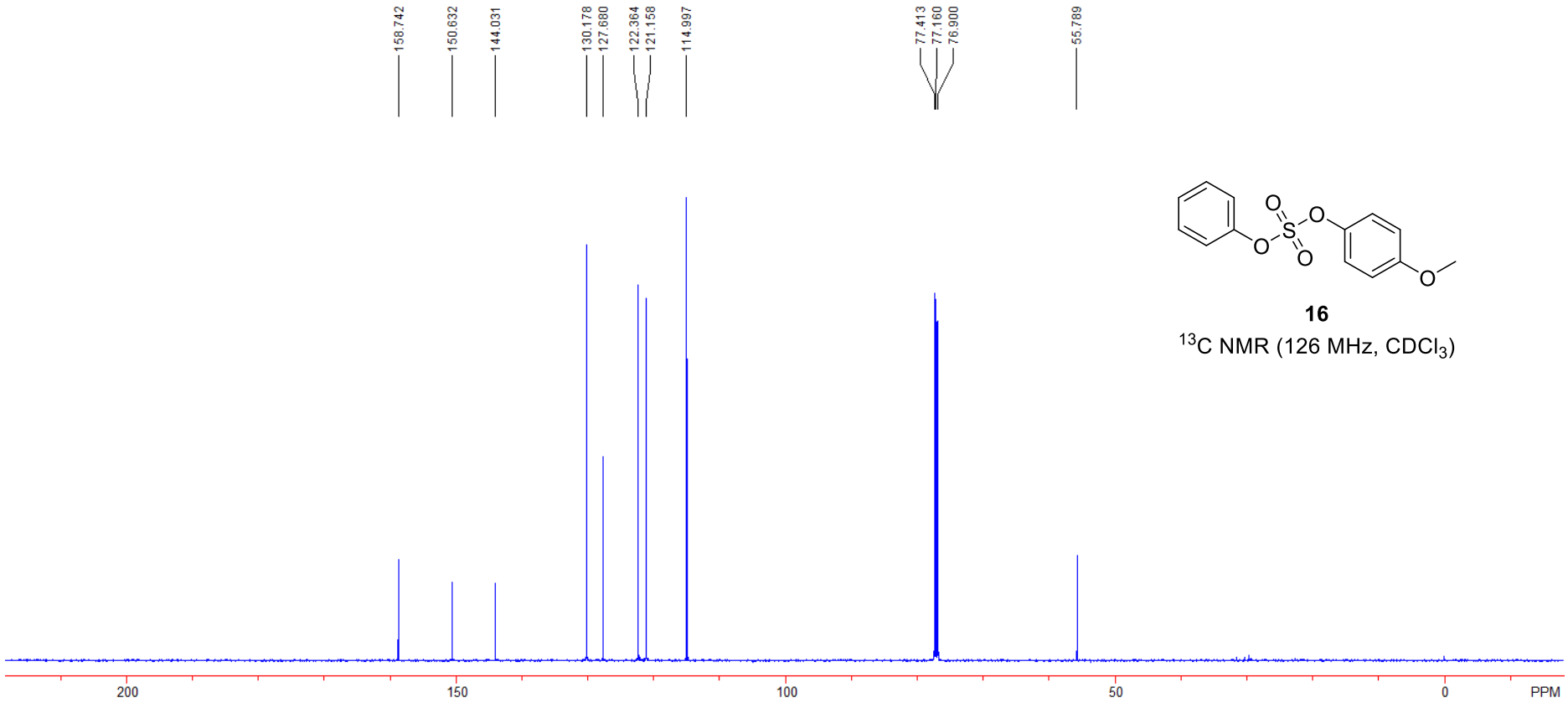
13

^{13}C NMR (126 MHz, $CDCl_3$)



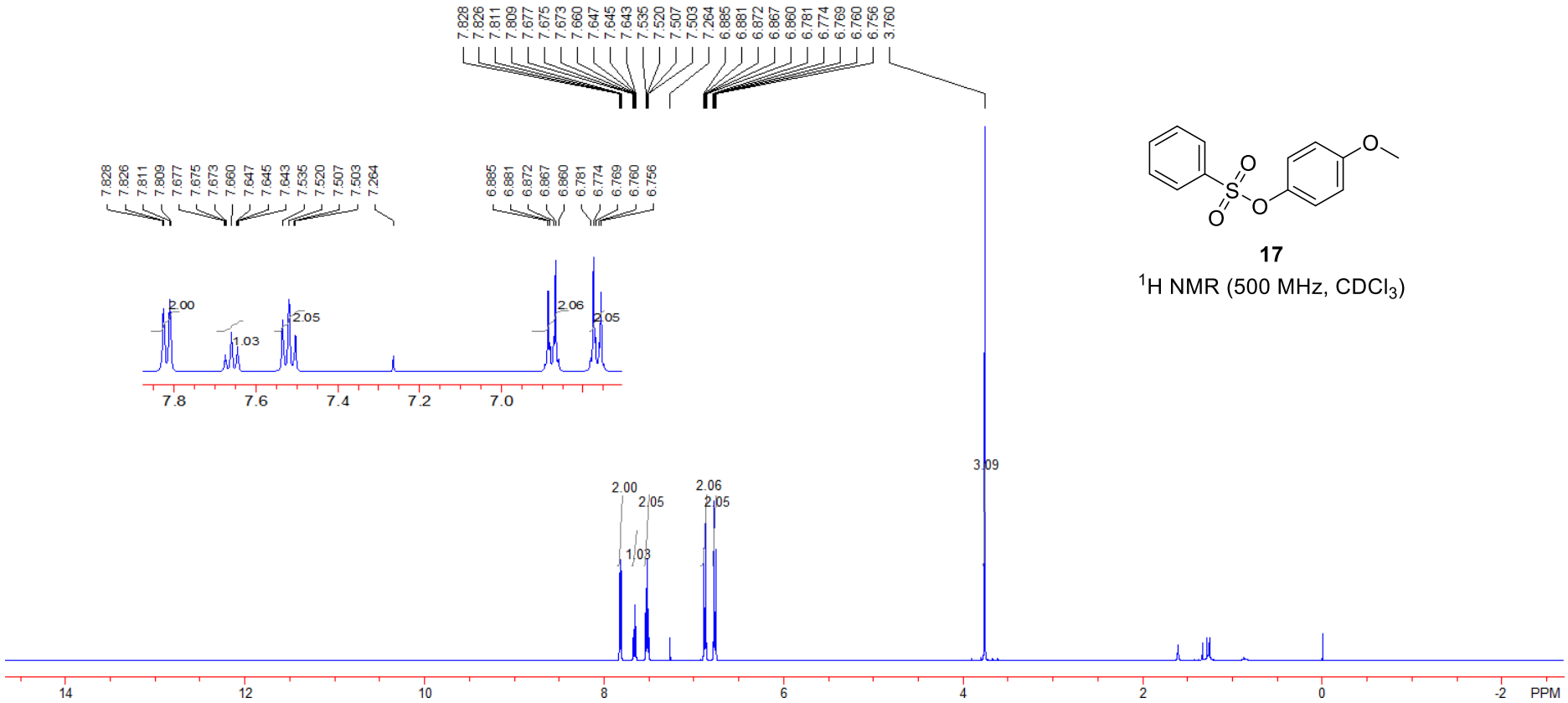
16

^{1}H NMR (500 MHz, $CDCl_3$)



16

^{13}C NMR (126 MHz, $CDCl_3$)



17

^{1}H NMR (500 MHz, $CDCl_3$)