

Supporting Information

The Construction of Novel Pyrrole-4H-Chromene-Embed Vinyl Sulfonyl Fluorides *via* a Three-Component Process

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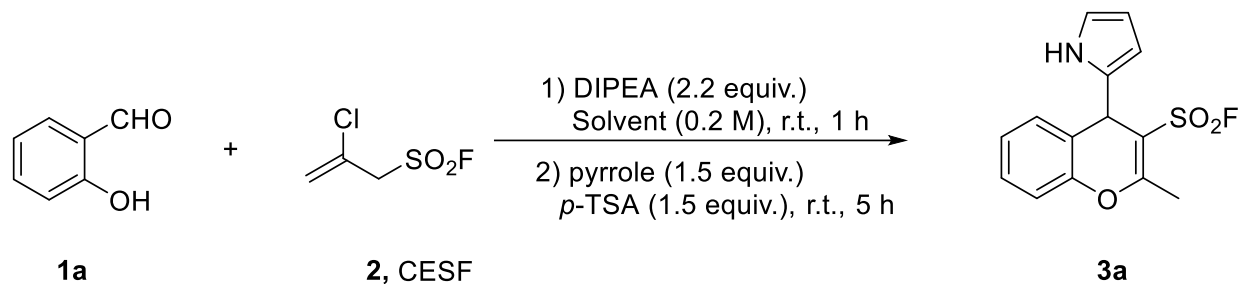
1. General Information

Instrumentation:

The reactions were conducted in standard glassware under ambient air conditions unless otherwise specified. Room temperature (r.t) was maintained at 20-25 °C, while temperatures of 0 °C were achieved using an ice/water bath, and higher temperatures were attained using an oil bath equipped with a contact thermometer. NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ on a Bruker Advance spectrometer operating at 500 MHz (for ¹H), 471 MHz (for ¹⁹F), and 126 MHz (for ¹³C), with internal referencing to solvent residual signals (CDCl₃: δ H = 7.264 ppm, δ C = 77.16 ppm; DMSO-*d*₆: δ H = 2.500 ppm, δ C = 39.52 ppm). Chemical shifts were reported in ppm relative to TMS (1H NMR, 0 ppm) as internal standards. HPLC experiments were conducted using a Waters e2695 instrument with a J&K RP-C18 column (5 μm, 4.6 × 150 mm), and product yields were determined using corresponding pure compounds as external standards. Coupling constants were expressed in Hertz (Hz), with abbreviations such as s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptet, m = multiplet, br s = broad singlet, dd = doublet of doublets. Compound numbering for NMR spectra assignment was arbitrary and not based on IUPAC numbering. Chemical structures were named using Chemdraw software. Electrospray ionization (ESI) HRMS experiments were conducted on a TOF-Q EI instrument. Melting points were measured and reported without correction. Reagents used were commercially sourced and utilized without additional purification. Column chromatography was performed using silica gel (60–120 mesh and 100–200 mesh) packed in glass columns. Product spots on thin-layer chromatography (TLC) plates were visualized under ultraviolet light (254 nm or 365 nm) and stained with potassium permanganate or phosphomolybdic acid. Salicylaldehydes, pyrroles, morpholine, 4-methoxyphenol, and 4-(benzyloxy)phenol were purchased commercially and used as received. 2-chloroprop-2-ene-1-sulfonyl fluoride (CESF, **2**) was synthesized following an established procedure.¹

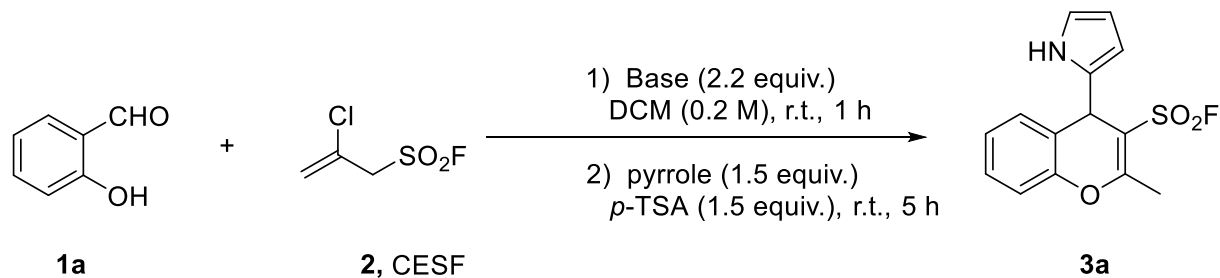
2. Optimization of the Reaction Conditions

Table S1 Screening the Solvent. ^a



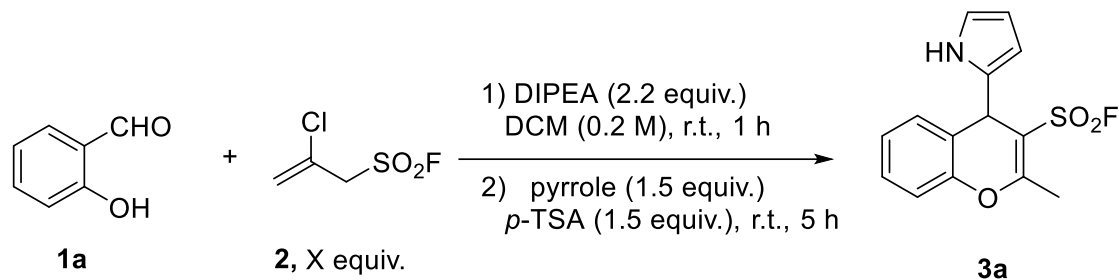
Entry	Solvent	Yield (3a , %) ^b
1	DCM	56
2	DCE	48
3	DMSO	30
4	CH ₃ CN	14
5	EA	28
6	DMF	27
7	THF	18
8	NMP	31
9	1,4-Dioxane	32
10	EtOH	36
11	CH ₃ OH	10
12	Acetone	29

^aReaction conditions: a mixture of 2-hydroxybenzaldehyde (**1a**, 24 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 48 mg, 0.3 mmol, 1.5 equiv.) and DIPEA (57 mg, 0.44 mmol, 2.2 equiv.) in solvent (1.0 mL) was stirred at r.t. for 1 h in a sealed tube. After 1 h of maintaining the same continuous one-pot reaction conditions, then pyrrole (20 mg, 0.3 mmol, 1.5 equiv.) and *p*-TSA (52 mg, 0.3 mmol, 1.5 equiv.) were added to the same reaction tube under air at r.t. for additional 5 h. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.067$ min, $\lambda_{max} = 209.9$ nm, water/methanol = 30:70 (v/v)).

Table S2. Screening the base.^a

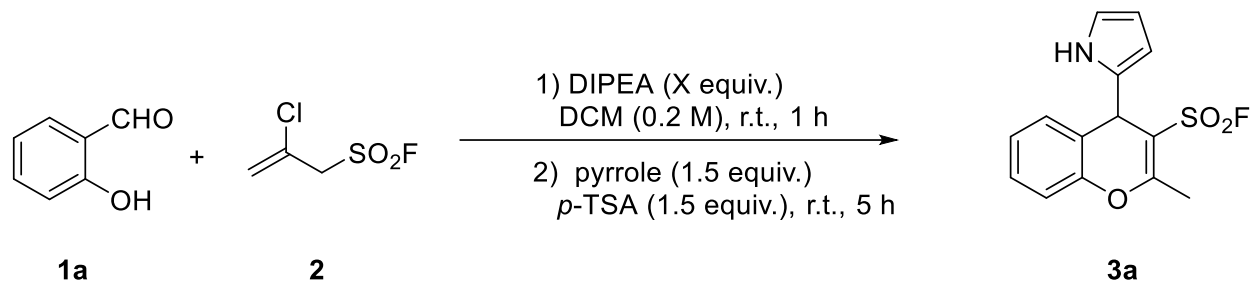
Entry	Base (2.2 equiv.)	Yield (3a , %) ^b
1	NaHCO ₃	N.D.
2	K ₂ CO ₃	N.D.
3	KF	N.D.
4	MgO	N.D.
5	TEA	12
6	DBU	31
7	CsF	N.D.
8	DIPEA	56
9	NaOH	N.D.
10	Na ₂ CO ₃	N.D.

^aReaction conditions: a mixture of 2-hydroxybenzaldehyde (**1a**, 24 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 48 mg, 0.3 mmol, 1.5 equiv.) and base (0.44 mmol, 2.2 equiv.) in solvent (1.0 mL) was stirred at r.t. for 1 h in a sealed tube, After 1 h of maintaining the same reaction conditions under the same continuous one-pot reaction, then pyrrole (20 mg, 0.3 mmol, 1.5 equiv.) and *p*-TSA (52 mg, 0.3 mmol, 1.5 equiv.) were added under air at r.t. for additional 5 h. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.067$ min, $\lambda_{max} = 209.9$ nm, water/methanol =30:70 (v/v)). N.D. = Not detected.

Table S3 Screening the loading of CESF (**2**)^a

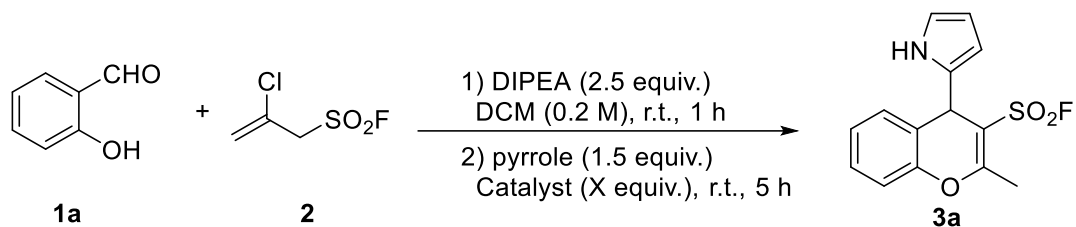
Entry	X equiv.	Yield (3a , %) ^b
1	1.0	46
2	1.5	56
3	2.0	56
4	2.5	45
5	3.0	49

^aReaction conditions: a mixture of 2-hydroxybenzaldehyde (**1a**, 24 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, X equiv.) and DIPEA (57 mg, 0.44 mmol, 2.2 equiv.) in solvent (1.0 mL) was stirred at r.t. for 1 h in a sealed tube, under the same continuous one-pot reaction, then pyrrole (20 mg, 0.3 mmol, 1.5 equiv.) and *p*-TSA (52 mg, 0.3 mmol, 1.5 equiv.) were added under air at r.t. for additional 5 h. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.067$ min, $\lambda_{max} = 209.9$ nm, water/methanol = 30:70 (v/v)).

Table S4. Screening the loading of base.^a

Entry	DIPEA (x equiv.)	Yield (3a , %) ^b
1	1.0	15
2	1.5	33
3	2.0	54
4	2.2	56
5	2.5	71
6	3.0	61
7	3.5	59
8	4.0	25
9	4.5	19
10	5.0	15

^aReaction conditions: a mixture of 2-hydroxybenzaldehyde (**1a**, 24 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 48 mg, 0.3 mmol, 1.5 equiv.) and base (X equiv.) in solvent (1.0 mL) was stirred at r.t. for 1 h in a sealed tube, under the same continuous one-pot reaction, then pyrrole (20 mg, 0.3 mmol, 1.5 equiv.) and *p*-TSA (52 mg, 0.3 mmol, 1.5 equiv.) were added under air at r.t. for additional 5 h. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.067$ min, $\lambda_{max} = 209.9$ nm, water/methanol = 30:70 (v/v)).

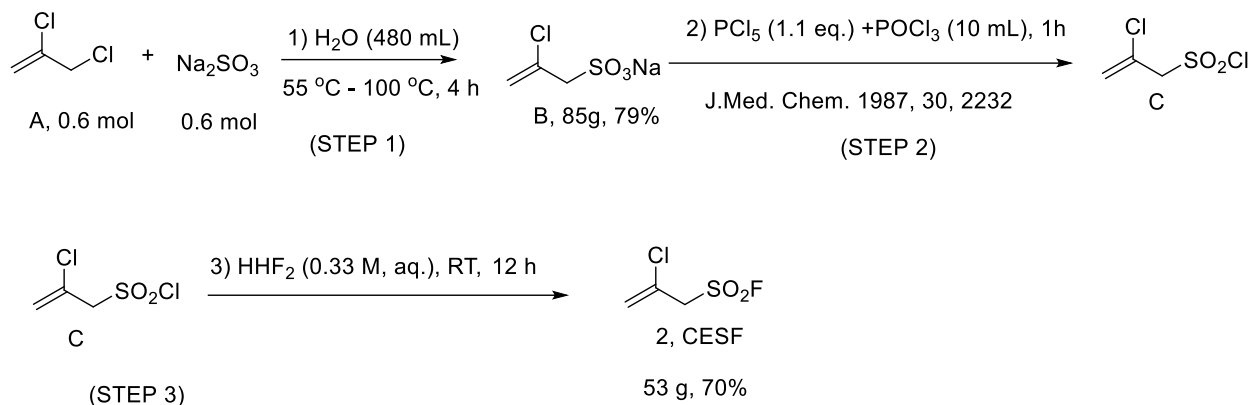
Table S6. Screening the catalysts. ^a

Entry	Catalyst (x equiv.)	Yield (3a , %) ^b
1	C ₆ H ₅ CO ₂ H (1.5)	N.D.
2	HCO ₂ H (1.5)	N.D.
3	CH ₃ CO ₂ H (1.5)	N.D.
4	MeSO ₃ H (1.5)	66
5	<i>p</i>-TSA (1.5)	71
6	<i>p</i> -TSA (2.0)	58
7	<i>p</i> -TSA (3.0)	43
8	TFA (2.0)	70

^aReaction conditions: a mixture of 2-hydroxybenzaldehyde (**1a**, 24 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 48 mg, 0.3 mmol, 1.5 equiv.) and DIPEA (65 mg, 0.5 mmol, 2.5 equiv.) in solvent (1.0 mL) was stirred at r.t. for 1 h in a sealed tube, under the same continuous one-pot reaction, then pyrrole (20 mg, 0.3 mmol, 1.5 equiv.) and catalyst (X equiv.) were added under air at r.t. for additional 5 h. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.067$ min, $\lambda_{max} = 209.9$ nm, water/methanol = 30:70 (v/v)). N.D. = Not detected.

3. Experimental Procedures

3.1 Preparation of 2-chloroprop-2-ene-1-sulfonyl fluoride (CESF).¹



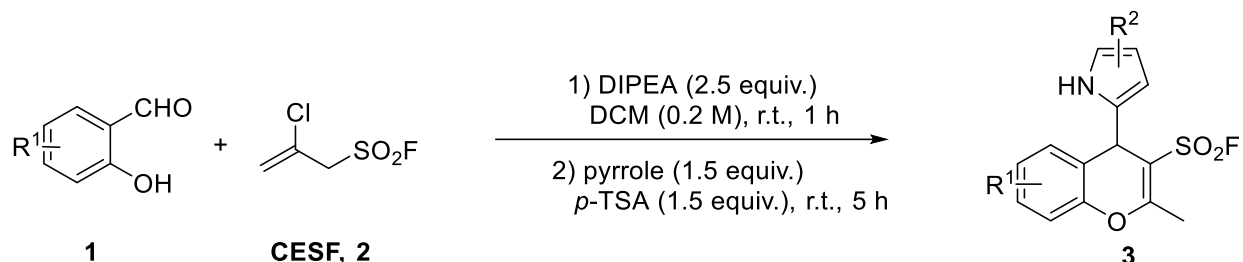
Step 1: 1,2-Dichloro-2-propene (**A**, 0.6 mol) was gradually added to a solution containing Na₂SO₃ (0.6 mol) in 480 mL of water with stirring, and the resulting mixture was maintained at 55 °C on an oil bath. Subsequently, the mixture was refluxed for 4 hours, followed by removal of the solvent under vacuum. To the residue, 500 mL of ethanol (EtOH) was added, and the mixture was refluxed with stirring for 10 minutes. Upon filtration of the hot mixture to remove insoluble material, the filtrate was cooled. The resulting crystalline product, sodium 2-chloro-2-propene-1-sulfonate, was obtained by filtration, yielding 85.0 g (**B**, 0.476 mol, 79% yield).

Step 2: A blend of the sodium salt (**B**, 0.476 mol, 85.0 g) and PCl₅ (1.1 equivalents, 0.474 mol, 99 g) was vigorously stirred until the mixture liquefied, which induced an exothermic reaction lasting approximately 10 minutes. Subsequently, any residual solids on the bottle wall were rinsed with 10 mL of phosphorus oxychloride, and the mixture was swiftly heated on an oil bath at 120°C for 1 hour. After cooling, the mixture was poured onto ice with vigorous stirring and allowed to stand for 30 minutes at ambient temperature.

Step 3: The evaporated 2-chloro-2-propenesulfonyl chloride (**C**) was reacted directly in a solution containing KHF₂ (112 g, 0.33 M) for 12 hours. The resulting mixture underwent extraction with CH₂Cl₂, followed by drying and subsequent evaporation under vacuum. The obtained 2-chloroprop-2-ene-1-sulfonyl fluoride (CESF) was distilled under reduced pressure, yielding 53 g of colorless oil (**2**, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ 5.75 (dd, *J*₁ = 19.6 Hz, *J*₂ = 2.3 Hz, 2H), 4.33 (d, *J* = 3.6 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ 56.4 (s, 1F). ¹³C NMR (126 MHz,

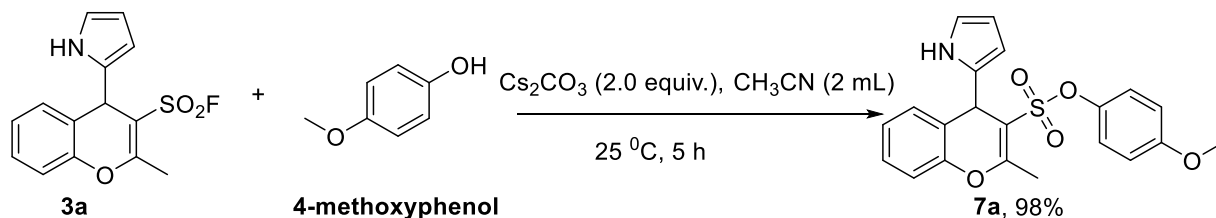
CDCl₃) δ 126.6, 123.6 (d, J = 1.6 Hz), 59.34(d, J = 19.4 Hz). HRMS-ESI (m/z) calcd. for [C₃H₅ClFO₂S]⁺ ([M+H]⁺): 158.9677, found: 158.9674.

3.2 Procedure for the Synthesis of 3 and 4 (indole).



A 20 mL reaction sealed tube, dried in an oven and fitted with a magnetic stirring bar, was loaded with salicylaldehydes (**1**, 1.0 mmol, 1.0 equiv.), 2-chloroprop-2-ene-1-sulfonyl fluoride (CESF, **2**, 1.5 mmol, 1.5 equiv.), DIPEA (2.5 mmol, 2.5 equiv.), and DCM (0.2 M, 5 mL). The mixture was then allowed to react at room temperature for 1 hour. After maintaining the same reaction conditions for an additional hour, pyrrole (101 mg, 1.5 mmol, 1.5 equiv.) and *p*-TSA (258 mg, 1.5 mmol, 1.5 equiv.) were introduced into the reaction tube under ambient air, and the reaction was continued for another 5 hours. Upon completion, the resulting mixture was diluted with ethyl acetate, followed by washing with water (30 mL \times 3). The aqueous phase was further extracted with ethyl acetate (30 mL \times 2). The combined organic layers were then dried over anhydrous sodium sulfate and concentrated to yield a residue. Purification of the residue was accomplished via column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (or dichloromethane) as eluent, leading to the isolation of pure sulfonyl fluoride-substituted pyrrolyl chromenes **3**.

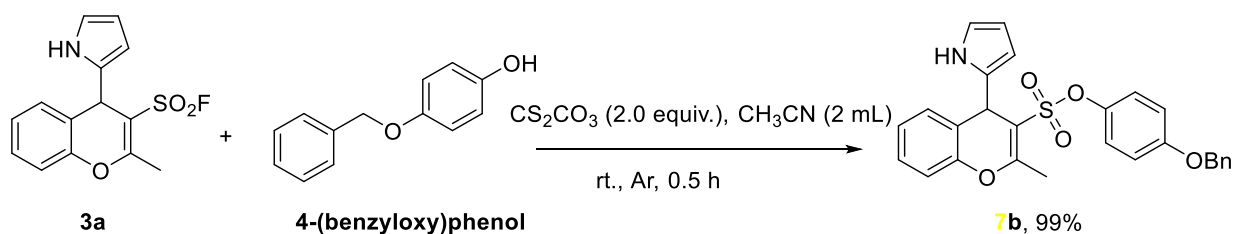
3.3 General procedure for synthesis of vinyl sulfonate from 4-methoxyphenol.²



2-methyl-4-(1H-pyrrol-2-yl)-4H chromene-3-sulfonyl fluoride (**3a**, 0.5 mmol, 147 mg), 4-methoxyphenol (1.0 mmol, 2.0 eq., 124.1 mg), cesium carbonate (1.0 mmol, 2.0 eq., 326.8 mg)

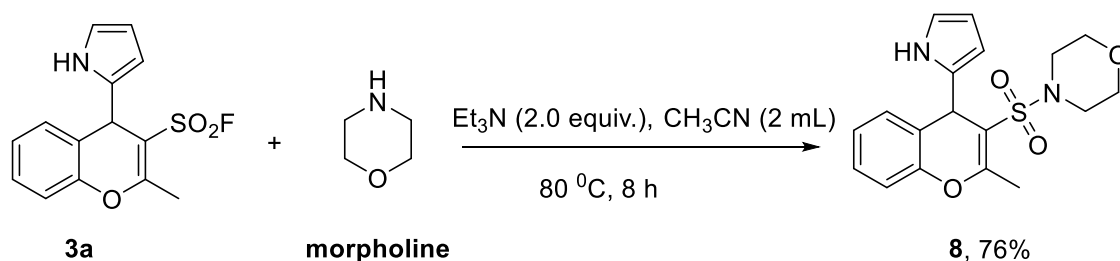
were added in a solution of acetonitrile (2 mL) and reacted at room temperature for 5 h. The reaction mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layers was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel by gradient elution with petroleum ether/ethyl acetate (20:1 to 10:1, v/v) as eluent to obtain pure vinyl sulfonate **7a** as white solid (194 mg, 98% yield).

3.4 procedure for synthesis of vinyl sulfonate from 4-(benzyloxy)phenol under argon atmosphere.



2-methyl-4-(1H-pyrrol-2-yl)-4H chromene-3-sulfonyl fluoride (**3a**, 0.5 mmol, 147 mg), 4-(benzyloxy)phenol (1.0 mmol, 2.0 eq., 200.2 mg), cesium carbonate (1.0 mmol, 2.0 eq., 326.8 mg) were added in a solution of acetonitrile (2 mL) and reacted at room temperature in an argon atmosphere for 0.5 h. The reaction mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layers was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel by gradient elution with petroleum ether/ethyl acetate (20:1 to 10:1, v/v) as eluent to obtain pure vinyl sulfonate **7b** as light yellow solid (234 mg, 99% yield).

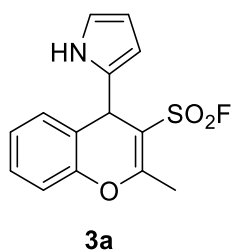
3.5 General procedure for synthesis of vinyl sulfonamide from morpholine.



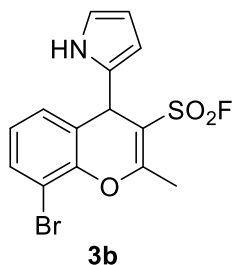
Morpholine (1.0 mmol, 2.0 eq., 87.1 mg) and triethylamine (1.0 mmol, 2.0 eq., 101.2 mg) were added to a stirred solution of 2-methyl-4-(1H-pyrrol-2-yl)-4H chromene-3-sulfonyl fluoride (**3a**,

Morpholine (0.6 mmol, 2.0 eq., 52.3 mg) and triethylamine (0.6 mmol, 2.0 eq., 60.7 mg) were added to a stirred solution of 4-(5-(2-fluorophenyl)-3-formyl-1H-pyrrol-2-yl)-2-methyl-4H-chromene-3-sulfonyl fluoride (**3s**, 0.3 mmol, 125 mg) dissolved in acetonitrile (1.2 mL) and the resulting mixture reacted at 80 °C for 8 h. The reaction was concentrated to dryness and the residue was further purified by column chromatography on silica gel by gradient elution with petroleum ether/ethyl acetate (10:1 to 5:1, v/v) as eluent to obtain pure vinyl sulfonamide **10** as light yellow solid (113 mg, 78% yield).

4. Characterization

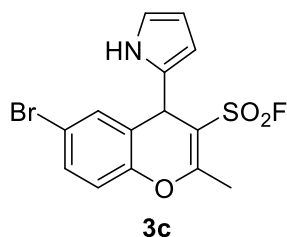


2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3a). Colorless solid, 179 mg, 61% yield. M.p. 95–96 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.41 (s, 1H), 7.31 (ddd, $J_1 = 8.5$ Hz, $J_2 = 6.9$ Hz, $J_3 = 2.1$ Hz, 1H), 7.20 (qd, $J_1 = 7.7$ Hz, $J_2 = 4.4$ Hz, 2H), 7.14 (d, $J = 8.2$ Hz, 1H), 6.70 (q, $J = 2.3$ Hz, 1H), 6.07 (q, $J = 3.0$ Hz, 1H), 5.64 (d, $J = 3.5$ Hz, 1H), 5.19 (s, 1H), 2.49 (s, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.3 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 164.5, 149.4, 133.2, 129.5, 128.9, 126.1, 121.8, 118.2, 116.7, 109.6 (d, $J = 20.0$ Hz), 108.7, 107.2, 35.2, 19.9. **HRMS-ESI** (m/z) calcd. for [C₁₄H₁₃FN₃O₃S]⁺ ([M+H]⁺): 294.0595, found: 294.0595.

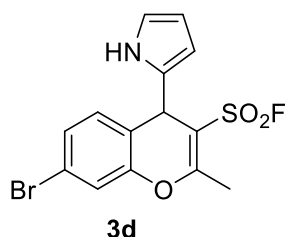


8-bromo-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3b). Colorless solid, 231 mg, 62% yield. M.p. 118–119 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.40 (s, 1H),

7.53 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.5$ Hz, 1H), 7.16 (dd, $J_1 = 7.8$, $J_2 = 1.5$ Hz, 1H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.71 (q, $J = 2.3$ Hz, 1H), 6.07 (q, $J = 2.9$ Hz, 1H), 5.68 (d, $J = 3.5$ Hz, 1H), 5.19 (s, 1H), 2.56 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 69.3 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 164.3, 146.4, 132.7, 132.5, 128.6, 126.8, 123.7, 118.5, 110.8, 110.5 (d, $J = 20.5$ Hz), 108.9, 107.5, 35.7, 19.7. HRMS-ESI (m/z) calcd. for $[\text{C}_{14}\text{H}_{12}\text{BrFNO}_3\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 371.9700, found: 371.9699.

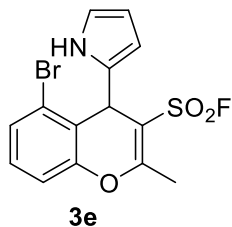


6-bromo-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3c). Colorless solid, 253 mg, 68% yield. M.p. 114–115 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 8.43 (s, 1H), 7.41 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.4$ Hz, 1H), 7.34 (d, $J = 2.3$ Hz, 1H), 7.02 (d, $J = 8.7$ Hz, 1H), 6.72 (q, $J = 2.3$ Hz, 1H), 6.09 (q, $J = 2.9$ Hz, 1H), 5.67 (d, $J = 3.4$ Hz, 1H), 5.13 (s, 1H), 2.48 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 69.4 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 164.1, 148.4, 132.5, 132.1, 132.0, 123.85, 118.5, 118.5, 118.4, 109.7 (d, $J = 20.4$ Hz), 108.9, 107.6, 35.1, 19.8. HRMS-ESI (m/z) calcd. for $[\text{C}_{14}\text{H}_{12}\text{BrFNO}_3\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 371.9700, found: 371.9701.

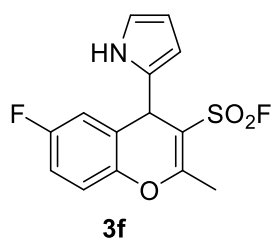


7-bromo-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3d). Colorless solid, 206 mg, 55% yield. M.p. 101–102 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 8.42 (s, 1H), 7.34 – 7.28 (m, 2H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.71 (td, $J_1 = 2.7$, $J_2 = 1.5$ Hz, 1H), 6.07 (q, $J = 2.9$ Hz, 1H), 5.63 (ddd, $J_1 = 3.7$, $J_2 = 2.5$, $J_3 = 1.5$ Hz, 1H), 5.13 (s, 1H), 2.48 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 69.3 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 164.0, 149.8, 132.5, 130.7, 129.3,

121.7, 120.92, 120.0, 118.4, 110.1 (d, $J = 20.3$ Hz), 108.9, 107.5, 34.9, 19.7. **HRMS-ESI** (m/z) calcd. for $[C_{14}H_{12}BrFNO_3S]^+$ ($[M+H]^+$): 371.9700, found: 371.9699.

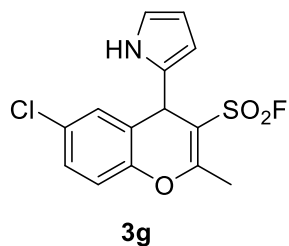


5-bromo-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3e). Colorless solid, 229 mg, 62% yield. M.p. 141–142 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **1H NMR** (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.47 – 7.40 (m, 1H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 8.2$ Hz, 1H), 6.75 – 6.68 (m, 1H), 6.07 (q, $J = 3.3$ Hz, 1H), 5.61 (d, $J = 3.1$ Hz, 1H), 5.32 (s, 1H), 2.50 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 69.5 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.2, 150.6, 131.3, 130.2, 129.6, 123.9, 122.8, 118.1, 116.2, 110.6 (d, $J = 20.5$ Hz), 108.8, 107.3, 35.8, 19.4. **HRMS-ESI** (m/z) calcd. for $[C_{14}H_{12}BrFNO_3S]^+$ ($[M+H]^+$): 371.9700, found: 371.9702.

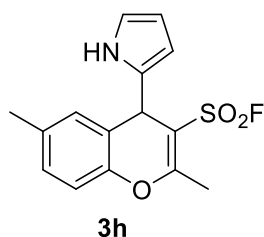


6-fluoro-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3f). White solid, 173 mg, 58% yield. M.p. 105–106 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **1H NMR** (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.12 (dd, $J_1 = 9.0$ Hz, $J_2 = 4.6$ Hz, 1H), 7.01 (td, $J_1 = 8.4$ Hz, $J_2 = 3.0$ Hz, 1H), 6.91 (dd, $J_1 = 8.2$ Hz, $J_2 = 3.0$ Hz, 1H), 6.71 (q, $J = 2.4$ Hz, 1H), 6.09 (q, $J = 2.9$ Hz, 1H), 5.69 (d, $J = 3.6$ Hz, 1H), 5.15 (s, 1H), 2.49 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 69.5 (s, 1F), -115.80 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.4, 161.0, 159.0, 145.5 (d, $J = 2.6$ Hz), 132.5, 123.5 (d, $J = 8.0$ Hz), 118.4,

118.2 (d, $J = 8.6$ Hz), 115.8 (dd, $J_1 = 71.6$ Hz, $J_2 = 23.9$ Hz), 109.0 (d, $J = 20.4$ Hz), 108.9, 107.4, 35.5, 19.8. **HRMS-ESI** (m/z) calcd. for $[C_{14}H_{12}F_2NO_3S]^+$ ($[M+H]^+$): 312.0500, found: 312.0500.

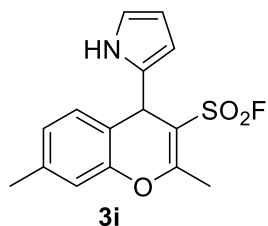


6-chloro-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3g). Colorless solid, 234 mg, 72% yield. M.p. 116–117 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **1H NMR** (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.37 – 7.31 (m, 1H), 7.27 (s, 1H), 7.15 (d, $J = 8.8$ Hz, 1H), 6.79 (q, $J = 2.3$ Hz, 1H), 6.16 (q, $J = 2.9$ Hz, 1H), 5.75 (q, $J = 2.5$ Hz, 1H), 5.21 (s, 1H), 2.56 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 69.4 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.2, 147.9, 132.5, 131.1, 129.1, 129.1, 123.5, 118.5, 118.1, 109.6 (d, $J = 20.5$ Hz), 108.9, 107.5, 35.2, 19.8. **HRMS-ESI** (m/z) calcd. for $[C_{14}H_{12}ClFNO_3S]^+$ ($[M+H]^+$): 328.0205, found: 328.0206.

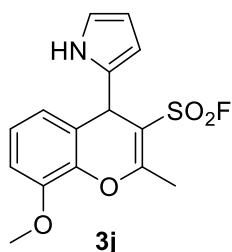


2,6-dimethyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3h). Colorless solid, 178 mg, 58% yield. M.p. 86–87 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **1H NMR** (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.11 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.07 – 6.98 (m, 2H), 6.73 – 6.67 (m, 1H), 6.09 (q, $J = 3.1$ Hz, 1H), 5.72 (q, $J = 2.2$ Hz, 1H), 5.15 (s, 1H), 2.49 (s, 3H), 2.32 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 69.4 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.5, 147.4, 135.9, 133.3, 129.6, 129.5, 121.4, 118.1,

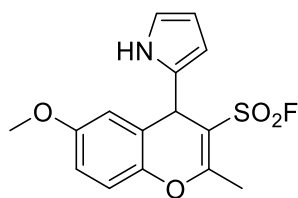
116.4, 109.3 (d, $J = 19.8$ Hz), 108.7, 107.1, 35.3, 20.9, 19.9. **HRMS-ESI** (m/z) calcd. for $[C_{15}H_{15}FNO_3S]^+$ ($[M+H]^+$): 308.0751, found: 308.0751.



2,7-dimethyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3i). Colorless solid, 138 mg, 45% yield. M.p. 79–80 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **1H NMR** (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.08 (d, $J = 7.8$ Hz, 1H), 7.00 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.7$ Hz, 1H), 6.95 (d, $J = 1.7$ Hz, 1H), 6.69 (td, $J_1 = 2.7$, $J_2 = 1.5$ Hz, 1H), 6.06 (q, $J = 2.9$ Hz, 1H), 5.65 (td, $J_1 = 3.1$ Hz, $J_2 = 1.7$ Hz, 1H), 5.15 (s, 1H), 2.48 (s, 3H), 2.37 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 69.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.5, 149.3, 139.3, 133.4, 129.1, 127.0, 118.7, 118.1, 116.9, 109.7 (d, $J = 19.6$ Hz), 108.7, 107.1, 35.0, 21.2, 19.9. **HRMS-ESI** (m/z) calcd. for $[C_{15}H_{15}FNO_3S]^+$ ($[M+H]^+$): 308.0751, found: 308.0751.

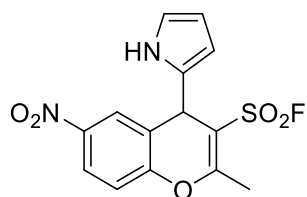


8-methoxy-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3j). Colorless solid, 219 mg, 68% yield. M.p. 174–175 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **1H NMR** (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.11 (t, $J = 8.0$ Hz, 1H), 6.87 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.4$ Hz, 1H), 6.77 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.3$ Hz, 1H), 6.68 (q, $J = 2.4$ Hz, 1H), 6.07 (q, $J = 2.9$ Hz, 1H), 5.73 (q, $J = 2.0$ Hz, 1H), 5.17 (s, 1H), 3.92 (s, 3H), 2.53 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 69.3 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.3, 147.9, 139.1, 133.0, 126.0, 123.0, 120.5, 118.1, 111.0, 109.7 (d, $J = 20.0$ Hz), 108.8, 107.2, 56.2, 35.3, 19.8. **HRMS-ESI** (m/z) calcd. for $[C_{15}H_{15}FNO_4S]^+$ ($[M+H]^+$): 324.0700, found: 324.0705.



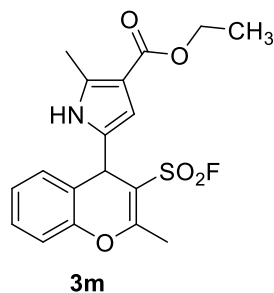
3k

6-methoxy-2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3k). Colorless solid, 280 mg, 87% yield. M.p. 120–121 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.40 (s, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 6.85 (dd, *J*₁ = 9.0 Hz, *J*₂ = 3.0 Hz, 1H), 6.69 (t, *J* = 2.9 Hz, 2H), 6.08 (q, *J* = 2.9 Hz, 1H), 5.73 (dq, *J*₁ = 3.2 Hz, *J*₂ = 1.8 Hz, 1H), 5.16 (s, 1H), 3.76 (s, 3H), 2.48 (s, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.5 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 164.7, 157.5, 143.6, 133.0, 122.5, 118.2, 117.6, 115.3, 112.9, 108.7, 108.6, 107.2, 55.9, 35.6, 19.9. **HRMS-ESI** (m/z) calcd. for [C₁₅H₁₅FNO₄S]⁺ ([M+H]⁺): 324.0700, found: 324.0704.

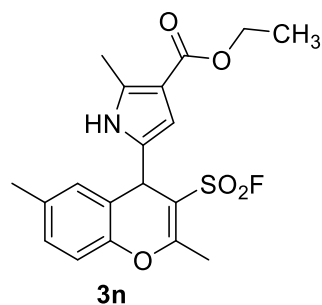


3l

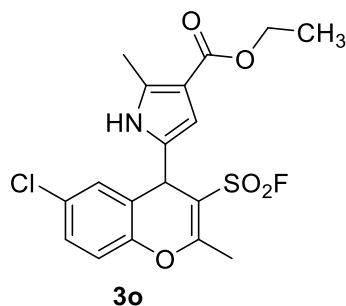
2-methyl-6-nitro-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonyl fluoride (3l). Yellow solid, 211 mg, 62% yield. M.p. 147–148 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.53 (s, 1H), 8.19 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.6 Hz, 1H), 8.14 (d, *J* = 2.7 Hz, 1H), 7.28 (s, 1H), 6.74 (q, *J* = 2.3 Hz, 1H), 6.09 (q, *J* = 3.0 Hz, 1H), 5.62 (d, *J* = 3.5 Hz, 1H), 5.23 (s, 1H), 2.54 (s, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.5 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 163.4, 153.1, 145.4, 131.9, 125.7, 124.6, 123.4, 118.9, 117.8, 110.7 (d, *J* = 21.0 Hz), 109.2, 107.9, 35.3, 19.6. **HRMS-ESI** (m/z) calcd. for [C₁₄H₁₂FN₂O₅S]⁺ ([M+H]⁺): 339.0445, found: 339.0443.



ethyl 5-(3-(fluorosulfonyl)-2-methyl-4H-chromen-4-yl)-2-methyl-1H-pyrrole-3-carboxylate (3m). Light yellow solid, 339 mg, 89% yield. M.p. 134–135 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.44 – 7.31 (m, 2H), 7.26 (s, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.00 (d, *J* = 2.9 Hz, 1H), 5.15 (s, 1H), 4.27 (t, *J* = 7.1 Hz, 2H), 2.55 (d, *J* = 13.7 Hz, 6H), 1.35 (d, *J* = 7.1 Hz, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.4 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 164.88, 149.3, 135.6, 131.4, 129.3, 129.1, 126.3, 121.2, 116.8, 112.3, 109.1, 108.9, 59.6, 35.0, 19.9, 14.6, 13.5. **HRMS-ESI** (m/z) calcd. for [C₁₈H₁₉FNO₅S]⁺ ([M+H]⁺): 380.0962, found: 380.0963.

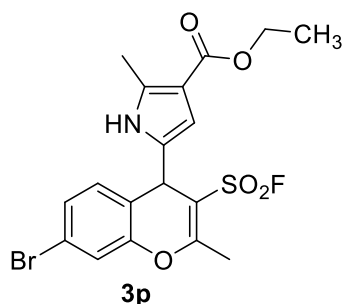


ethyl 5-(3-(fluorosulfonyl)-2,6-dimethyl-4H-chromen-4-yl)-2-methyl-1H-pyrrole-3-carboxylate (3n). Light yellow solid, 286 mg, 73% yield. M.p. 148–149 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.40 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.96 (s, 1H), 5.96 (d, *J* = 2.9 Hz, 1H), 5.02 (s, 1H), 4.20 (dt, *J*₁ = 7.4 Hz, *J*₂ = 3.7 Hz, 2H), 2.47 (d, *J* = 3.4 Hz, 6H), 2.30 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.4 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 165.0, 147.4, 136.1, 135.6, 131.5, 129.8, 129.4, 120.8, 116.5, 112.3, 109.0, 108.7 (d, *J* = 19.9 Hz), 59.6, 35.0, 20.9, 19.9, 14.6, 13.5. **HRMS-ESI** (m/z) calcd. for [C₁₉H₂₁FNO₅S]⁺ ([M+H]⁺): 394.1119, found: 394.1120.

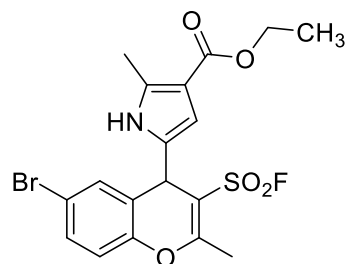


ethyl 5-(6-chloro-3-(fluorosulfonyl)-2-methyl-4H-yl)-2-methyl-1H-pyrrole-3-carboxylate (3o).

Light yellow solid, 362 mg, 87% yield. M.p. 169–170 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.67 (s, 1H), 7.38 – 7.35 (m, 1H), 7.27 (s, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.07 (d, *J* = 2.9 Hz, 1H), 5.12 (s, 1H), 4.38 – 4.30 (m, 2H), 2.58 (d, *J* = 7.7 Hz, 6H), 1.40 (t, *J* = 7.1 Hz, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.6 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 164.6, 147.8, 135.8, 131.2, 130.7, 129.3, 129.0, 122.9, 118.3, 112.5, 109.4, 109.0 (d, *J* = 20.7 Hz), 59.7, 35.0, 19.8, 14.6, 13.5. **HRMS-ESI** (m/z) calcd. for [C₁₈H₁₈ClFNO₅S]⁺ ([M+H]⁺): 414.0573, found: 414.0575.

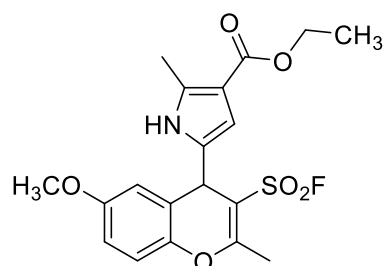


ethyl 5-(7-bromo-3-(fluorosulfonyl)-2-methyl-4H-chromen-4-yl)-2-methyl-1H-pyrrole-3-carboxylate (3p). Light yellow solid, 414 mg, 90% yield. M.p. 140–141 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.67 (s, 1H), 7.25 (d, *J* = 2.2 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 5.96 (d, *J* = 2.9 Hz, 1H), 4.99 (s, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 2.44 (d, *J* = 18.4 Hz, 6H), 1.27 (t, *J* = 7.2 Hz, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.5 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 165.4, 164.5, 149.7, 135.9, 130.8, 130.6, 129.5, 122.0, 120.3, 120.1, 112.4, 109.5 (d, *J* = 20.6 Hz), 109.3, 59.6, 34.7, 19.8, 14.6, 13.4. **HRMS-ESI** (m/z) calcd. for [C₁₈H₁₈BrFNO₅S]⁺ ([M+H]⁺): 458.0068, found: 458.0070.



3q

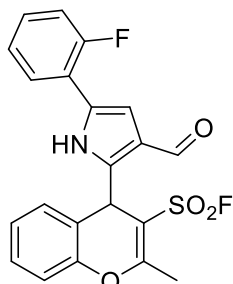
ethyl 5-(6-bromo-3-(fluorosulfonyl)-2-methyl-4H-chromen-4-yl)-2-methyl-1H-pyrrole-3-carboxylate (3q). Light yellow solid, 424 mg, 93% yield. M.p. 143–144 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.54 (s, 1H), 7.41 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.3$ Hz, 1H), 7.31 (d, $J = 2.3$ Hz, 1H), 7.01 (d, $J = 8.6$ Hz, 1H), 5.98 (d, $J = 2.9$ Hz, 1H), 5.01 (s, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 2.47 (d, $J = 7.0$ Hz, 6H), 1.30 (t, $J = 7.1$ Hz, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.5 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 164.5, 148.3, 135.8, 132.2, 131.9, 130.7, 118.7, 118.6, 112.5, 110.7, 109.4, 109.2 (d, $J = 20.6$ Hz), 59.7, 34.9, 19.8, 14.6, 13.5. **HRMS-ESI** (m/z) calcd. for [C₁₈H₁₈BrFNO₅S]⁺ ([M+H]⁺): 458.0068, found: 458.0071.



3r

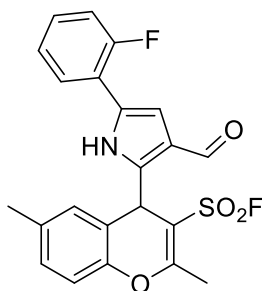
ethyl 5-(3-(fluorosulfonyl)-6-methoxy-2-methyl-4H-chromen-4-yl)-2-methyl-1H-pyrrole-3-carboxylate (3r). yellow solid, 284 mg, 69% yield. M.p. 172–173 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.43 (s, 1H), 7.06 (d, $J = 9.0$ Hz, 1H), 6.85 (dd, $J_1 = 9.0$ Hz, $J_2 = 3.0$ Hz, 1H), 6.64 (d, $J = 2.9$ Hz, 1H), 5.98 (d, $J = 2.9$ Hz, 1H), 5.04 (s, 1H), 4.20 (qd, $J_1 = 7.1$, $J_2 = 2.0$ Hz, 2H), 3.75 (s, 3H), 2.47 (d, $J = 2.9$ Hz, 6H), 1.29 (t, $J = 7.1$ Hz, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.5 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 165.1, 157.6, 143.5, 135.6, 131.2, 121.9, 117.8,

115.4, 112.9, 112.3, 109.1, 108.0 (d, $J = 20.0$ Hz), 59.6, 55.9, 35.4, 19.9, 14.6, 13.5. **HRMS-ESI** (m/z) calcd. for $[C_{19}H_{21}FNO_6S]^+$ ($[M+H]^+$): 410.1068, found: 410.1069.



3s

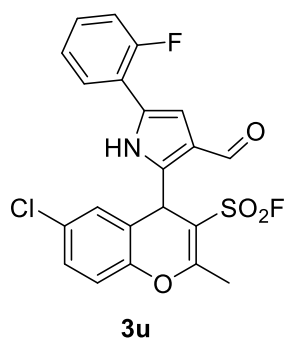
4-(5-(2-fluorophenyl)-3-formyl-1H-pyrrol-2-yl)-2-methyl-4H-chromene-3-sulfonyl fluoride (3s). White solid, 263 mg, 87% yield. M.p. 181–182 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. 1H NMR (500 MHz, DMSO- d_6) δ 12.11 (s, 1H), 9.91 (s, 1H), 7.73 – 7.68 (m, 1H), 7.33 – 7.27 (m, 4H), 7.23 – 7.15 (m, 3H), 6.88 (t, $J = 2.7$ Hz, 1H), 5.97 (s, 1H), 2.54 (s, 3H). ^{19}F NMR (471 MHz, DMSO- d_6) δ 70.1 (s, 1F), -115.1 (m, 1F). ^{13}C NMR (126 MHz, DMSO- d_6) δ 186.12, 165.6, 159.9, 157.9, 147.7, 141.7, 129.5 (d, $J = 2.5$ Hz), 129.2 (d, $J = 8.3$ Hz), 128.1 (d, $J = 3.1$ Hz), 126.7, 126.31, 125.1 (d, $J = 3.4$ Hz), 123.1, 120.6, 119.7 (d, $J = 12.4$ Hz), 117.1, 116.6 (d, $J = 21.8$ Hz), 111.2 (d, $J = 8.5$ Hz), 105.8 (d, $J = 20.4$ Hz), 33.3, 20.2. **HRMS-ESI** (m/z) calcd. for $[C_{21}H_{16}F_2NO_4S]^+$ ($[M+H]^+$): 416.0763, found: 416.0773.



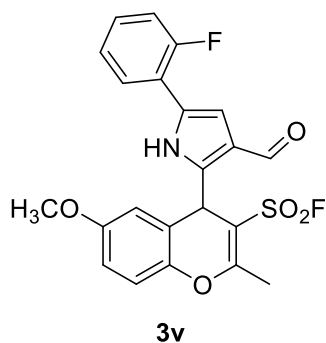
3t

4-(5-(2-fluorophenyl)-3-formyl-1H-pyrrol-2-yl)-2,6-dimethyl-4H-chromene-3-sulfonyl fluoride (3t). White solid, 377 mg, 88% yield. M.p. 173–174 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. 1H NMR (500 MHz,

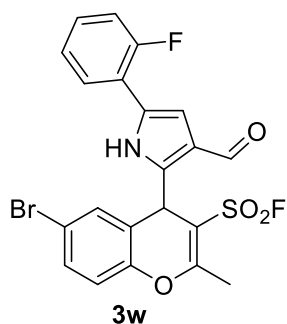
DMSO-*d*₆) δ 12.09 (s, 1H), 9.91 (s, 1H), 7.71 (td, $J_1 = 7.8$ Hz, $J_2 = 1.7$ Hz, 1H), 7.36 – 7.25 (m, 3H), 7.11 (d, $J = 1.2$ Hz, 2H), 6.96 (s, 1H), 6.87 (t, $J = 2.8$ Hz, 1H), 5.91 (s, 1H), 2.52 (s, 3H), 2.19 (s, 3H). **¹⁹F NMR** (471 MHz, DMSO-*d*₆) δ 70.1 (s, 1F), -115.1 (dd, 1F). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 186.1, 165.6, 159.9, 157.9, 145.76, 141.8, 135.6, 130.2, 129.3 (d, $J = 10.0$ Hz), 128.1 (d, $J = 3.2$ Hz), 126.7, 125.1 (d, $J = 3.2$ Hz), 123.1, 120.2, 119.7 (d, $J = 12.3$ Hz), 116.9, 116.6 (d, $J = 21.7$ Hz), 111.1 (d, $J = 8.4$ Hz), 105.5 (d, $J = 20.4$ Hz), 33.3, 20.74, 20.2. **HRMS-ESI** (m/z) calcd. for [C₂₂H₁₈F₂NO₄S]⁺ ([M+H]⁺): 430.0919, found: 430.0920.



6-chloro-4-(5-(2-fluorophenyl)-3-formyl-1H-pyrrol-2-yl)-2-methyl-4H-chromene-3-sulfonyl fluoride (3u). Light yellow solid, 326 mg, 72% yield. M.p. 141–142 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, DMSO-*d*₆) δ 12.14 (s, 1H), 9.89 (s, 1H), 7.74 – 7.66 (m, 1H), 7.39 – 7.25 (m, 5H), 7.18 (d, $J = 2.5$ Hz, 1H), 6.91 (t, $J = 2.6$ Hz, 1H), 5.94 (s, 1H), 2.52 (s, 3H). **¹⁹F NMR** (471 MHz, DMSO-*d*₆) δ 70.2 (s, 1F), -115.2 (d, 1F). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 186.6, 165.5, 159.9, 157.9, 146.6, 141.8, 135.1, 131.6, 129.5 (dd, $J_1 = 34.1$ Hz, $J_2 = 8.7$ Hz), 128.4 (d, $J = 76.8$ Hz), 125.2 (d, $J = 3.2$ Hz), 123.2, 122.5, 121.1, 119.5 (d, $J = 12.3$ Hz), 119.2, 116.7 (d, $J = 21.7$ Hz), 111.6, 105.4 (d, $J = 20.9$ Hz), 33.3, 20.2. **HRMS-ESI** (m/z) calcd. for [C₂₁H₁₅ClF₂NO₄S]⁺ ([M+H]⁺): 450.0373, found: 450.0373.

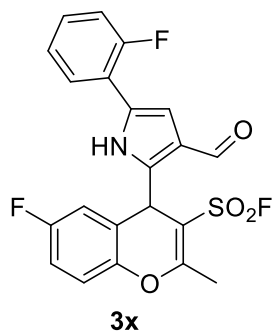


4-(5-(2-fluorophenyl)-3-formyl-1H-pyrrol-2-yl)-6-methoxy-2-methyl-4H-chromene-3-sulfonyl fluoride (3v). Light yellow solid, 204 mg, 46% yield. M.p. 195–196 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, DMSO-*d*₆) δ 12.11 – 12.07 (m, 1H), 9.91 (s, 1H), 7.70 (td, *J*₁ = 7.8, *J*₂ = 1.6 Hz, 1H), 7.36 – 7.25 (m, 3H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.70 (d, *J* = 3.0 Hz, 1H), 5.91 (s, 1H), 3.65 (s, 3H), 2.52 (s, 3H). **¹⁹F NMR** (471 MHz, DMSO-*d*₆) δ 70.2 (s, 1F), -115.1 (d, 1F) (d, *J* = 8.2 Hz). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 186.3, 165.9, 159.9, 157.9, 157.0, 141.7 (d, *J* = 23.6 Hz), 129.3 (d, *J* = 8.3 Hz), 128.1 (d, *J* = 3.1 Hz), 126.7, 125.1 (d, *J* = 3.2 Hz), 123.1, 121.5, 119.6 (d, *J* = 12.3 Hz), 118.3, 116.7 (d, *J* = 21.7 Hz), 115.0, 113.7, 111.2 (d, *J* = 8.4 Hz), 104.6 (d, *J* = 20.3 Hz), 55.9, 33.6, 20.3. **HRMS-ESI** (m/z) calcd. for [C₂₂H₁₈F₂NO₅S]⁺ ([M+H]⁺): 446.0868, found: 446.0868.

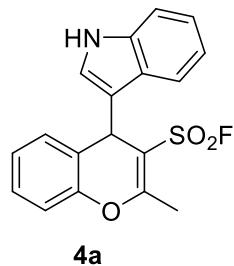


6-bromo-4-(5-(2-fluorophenyl)-3-formyl-1H-pyrrol-2-yl)-2-methyl-4H-chromene-3-sulfonyl fluoride (3w). Light yellow solid, 338 mg, 68% yield. M.p. 130–131 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, DMSO-*d*₆) δ 12.14 (s, 1H), 9.90 (s, 1H), 7.70 (td, *J*₁ = 7.8 Hz, *J*₂ = 1.6 Hz, 1H), 7.48 (dd, *J*₁ = 8.7 Hz, *J*₂ = 2.4 Hz, 1H), 7.35 – 7.25 (m, 4H), 7.21 (d, *J* = 8.7 Hz, 1H), 6.92 (t, *J* = 2.7 Hz, 1H), 5.94 (s, 1H), 2.52 (s, 3H). **¹⁹F NMR** (471 MHz, DMSO-*d*₆) δ 70.2 (s, 1F), -115.14 (m,

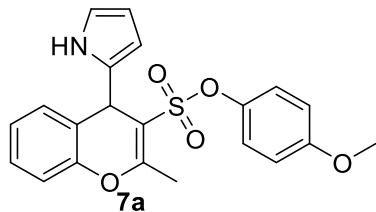
1F). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 186.6, 165.4, 159.9, 157.9, 147.1, 141.8, 140.6, 134.5 (d, *J* = 7.8 Hz), 132.0 (d, *J* = 105.7 Hz), 129.4 (d, *J* = 8.3 Hz), 128.1 (d, *J* = 3.1 Hz), 126.8, 125.2 (d, *J* = 3.5 Hz), 123.0 (d, *J* = 32.5 Hz), 119.5 (d, *J* = 6.2 Hz), 117.6, 116.7 (d, *J* = 21.7 Hz), 111.6, 105.5 (d, *J* = 20.4 Hz), 33.1, 20.2. **HRMS-ESI** (*m/z*) calcd. for [C₂₁H₁₅BrF₂NO₄S]⁺ ([M+H]⁺): 493.9868, found: 493.9871.



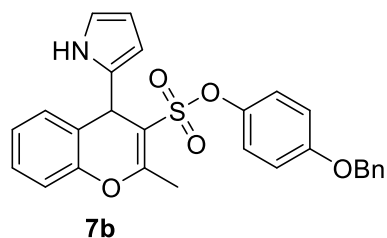
6-fluoro-4-(5-(2-fluorophenyl)-3-formyl-1H-pyrrol-2-yl)-2-methyl-4H-chromene-3-sulfonyl fluoride (3x). Colorless solid, 273 mg, 63% yield. M.p. 164–165 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, DMSO-*d*₆) δ 12.13 (s, 1H), 9.89 (s, 1H), 7.70 (td, *J*₁ = 7.8 Hz, *J*₂ = 1.6 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.18 (td, *J*₁ = 8.5 Hz, *J*₂ = 3.0 Hz, 1H), 6.97 (dd, *J*₁ = 8.8 Hz, *J*₂ = 3.0 Hz, 1H), 6.90 (t, *J* = 2.7 Hz, 1H), 5.95 (s, 1H), 2.52 (s, 3H). **¹⁹F NMR** (471 MHz, DMSO-*d*₆) δ 70.2 (s, 1F), -115.20 (t, 1F), -116.4 (s, 1F). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 186.5, 165.7, 160.1 (d, *J* = 54.2 Hz), 158.1 (d, *J* = 59.5 Hz), 144.2 (d, *J* = 2.2 Hz), 140.7, 129.3 (d, *J* = 8.5 Hz), 128.1 (d, *J* = 3.1 Hz), 126.8, 125.1 (d, *J* = 3.4 Hz), 123.2, 122.5 – 122.1 (m), 121.3 (d, *J* = 8.9 Hz), 119.4 (dd, *J*₁ = 43.0 Hz, *J*₂ = 10.5 Hz), 118.1 (d, *J* = 25.0 Hz), 116.7 (dd, *J*₁ = 22.7 Hz, *J*₂ = 8.4 Hz), 115.2 (d, *J* = 24.4 Hz), 111.5, 104.9 (d, *J* = 20.5 Hz), 33.5, 20.2. **HRMS-ESI** (*m/z*) calcd. for [C₂₁H₁₅F₃NO₄S]⁺ ([M+H]⁺): 434.0668, found: 434.0669.



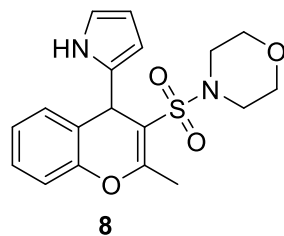
4-(1H-indol-3-yl)-2-methyl-4H-chromene-3-sulfonyl fluoride (4a). Colorless solid, 280 mg, 82% yield. Mp 143-145 °C. Purification by column chromatography on silica gel using petroleum ether/ethyl acetate = 10:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 8.06 (s, 1H), 7.34 (dd, *J* = 15.3, 8.1 Hz, 2H), 7.22 – 7.11 (m, 5H), 7.07 – 7.03 (m, 2H), 5.39 (s, 1H), 2.57 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ 70.1 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 163.2, 148.7, 136.8, 129.3, 128.3, 125.9, 125.3, 123.4, 122.9, 122.4, 120.1, 118.6, 116.4, 111.7, 110.1 (d, *J* = 19.5 Hz), 34.1, 19.8. Note: In the ¹³C NMR spectrum of **4a**, there should theoretically be eighteen peaks. However, due to the close proximity of these peaks, distinguishing the overlapping ones is challenging.



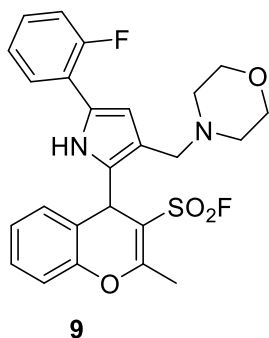
4-methoxyphenyl 2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonate (7a). White solid, 194 mg, 98% yield. M.p. 104–105 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 8.74 (s, 1H), 7.30 (ddd, *J*₁ = 8.4 Hz, *J*₂ = 6.9 Hz, 2.0 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.09 (dd, *J*₁ = 8.1 Hz, *J*₂ = 1.2 Hz, 1H), 6.81 – 6.75 (m, 3H), 6.65 (td, *J*₁ = 2.7 Hz, *J*₂ = 1.6 Hz, 1H), 6.02 (q, *J* = 2.9 Hz, 1H), 5.45 (dq, *J*₁ = 3.0 Hz, *J*₂ = 1.8 Hz, 1H), 5.17 (s, 1H), 3.77 (d, *J* = 1.2 Hz, 4H), 2.07 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 162.8, 158.5, 153.9, 150.2, 149.6, 142.6, 133.7, 129.5, 128.6, 125.6, 123.7, 122.3, 117.7, 116.2 (d, *J* = 17.5 Hz), 114.8 (d, *J* = 36.8 Hz), 110.5, 108.3, 107.0, 55.7, 35.4, 19.2. HRMS-ESI (m/z) calcd. for [C₂₁H₂₀NO₅S]⁺ ([M+H]⁺): 398.1057, found: 398.1057.



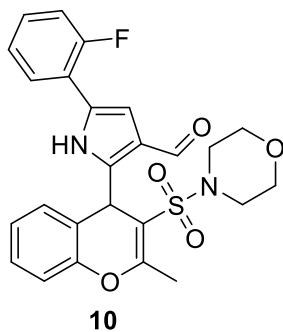
4-(benzyloxy)phenyl 2-methyl-4-(1H-pyrrol-2-yl)-4H-chromene-3-sulfonate (7b). Light yellow solid, 234 mg, 99% yield. M.p. 118–119 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.75 – 8.71 (m, 1H), 7.43 – 7.27 (m, 6H), 7.22 – 7.13 (m, 2H), 7.09 (dd, *J*₁ = 8.2 Hz, *J*₂ = 1.2 Hz, 1H), 6.85 – 6.76 (m, 4H), 6.64 (td, *J*₁ = 2.7, *J*₂ = 1.5 Hz, 1H), 6.01 (q, *J* = 2.9 Hz, 1H), 5.47 – 5.41 (m, 1H), 5.17 (s, 1H), 5.02 (s, 2H), 2.05 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 162.8, 157.7, 150.1, 142.8, 136.6, 133.7, 129.5, 128.8, 128.6, 128.3, 127.6, 125.6, 123.7, 122.2, 117.7, 116.3, 115.7, 110.5, 108.3, 107.0, 70.5, 35.4, 19.2. **HRMS-ESI** (m/z) calcd. for [C₂₇H₂₄NO₅S]⁺ ([M+H]⁺): 474.1370, found: 474.1373.



4-((2-methyl-4-(1H-pyrrol-2-yl)-4H-chromen-3-yl)sulfonyl)morpholine (8). Light yellow solid, 137 mg, 76% yield. M.p. 117–178 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 9.00 (s, 1H), 7.30 (ddd, *J*₁ = 8.5, *J*₂ = 7.2, *J*₃ = 1.8 Hz, 1H), 7.21 (dd, *J*₁ = 7.6 Hz, *J*₂ = 1.8 Hz, 1H), 7.19 – 7.09 (m, 2H), 6.68 (td, *J*₁ = 2.7 Hz, *J*₂ = 1.5 Hz, 1H), 5.98 (q, *J* = 2.8 Hz, 1H), 5.38 – 5.32 (m, 1H), 4.99 (s, 1H), 3.65 (t, *J* = 4.8 Hz, 4H), 3.13 – 2.98 (m, 4H), 2.42 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.2, 150.8, 133.9, 129.1, 128.5, 125.3, 122.8, 117.7, 116.4, 111.9, 108.2, 106.5, 66.3, 45.3, 36.0, 19.4. **HRMS-ESI** (m/z) calcd. for [C₁₈H₂₁N₂O₄S]⁺ ([M+H]⁺): 361.1217, found: 361.1219.



4-(5-(2-fluorophenyl)-3-(morpholinomethyl)-1H-pyrrol-2-yl)-2-methyl-4H-chromene-3-sulfonyl fluoride (9). Light yellow solid, 202 mg, 83% yield. M.p. 189–190 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 8.85 – 8.77 (m, 1H), 7.56 – 7.49 (m, 1H), 7.31 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.7 Hz, 1H), 7.25 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.7 Hz, 1H), 7.15 – 7.03 (m, 5H), 6.46 (d, *J* = 2.8 Hz, 1H), 5.39 (s, 1H), 3.71 – 3.61 (m, 4H), 3.16 (dd, *J*₁ = 90.9 Hz, *J*₂ = 12.9 Hz, 2H), 2.57 (s, 3H), 2.45 – 2.20 (m, 4H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 69.3 (s, 1F), -118.8 (d, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 163.5, 159.6, 157.7, 148.8, 131.5, 129.6, 128.8, 127.2 (d, *J* = 8.7 Hz), 126.4 (d, *J* = 4.5 Hz), 126.1, 125.7, 124.8 (d, *J* = 3.0 Hz), 121.6, 119.8 (d, *J* = 10.9 Hz), 116.5, 116.4 (d, *J* = 22.8 Hz), 110.8 (d, *J* = 2.4 Hz), 108.6 (d, *J* = 20.1 Hz), 67.1, 55.0, 53.8, 34.4, 20.1. **HRMS-ESI** (m/z) calcd. for [C₂₅H₂₅F₂N₂O₄S]⁺ ([M+H]⁺): 487.1498, found: 487.1498.



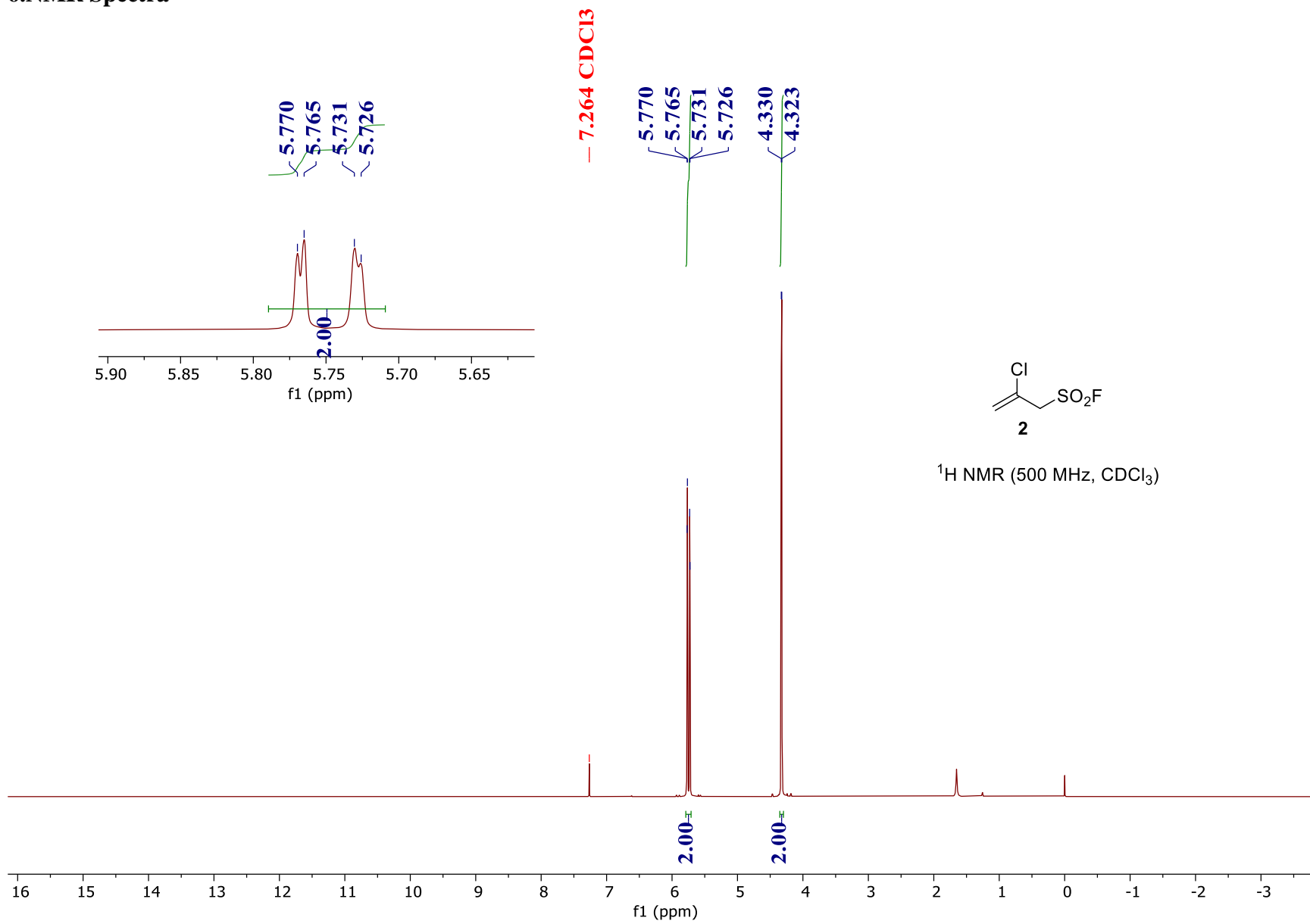
5-(2-fluorophenyl)-2-(2-methyl-3-(morpholinylsulfonyl)-4H-chromen-4-yl)-1H-pyrrole-3-carbaldehyde (10). Colorless solid, 113 mg, 78% yield. M.p. 190–191 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 9.81 (s, 1H), 9.28 (s, 1H), 7.55 (td, *J*₁ = 7.9, *J*₂ = 1.8 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.06 (m, 6H), 6.93 (d, *J* = 2.8 Hz, 1H), 5.80 (s, 1H), 3.50 (t, *J* = 4.8 Hz, 4H), 3.03 (tq,

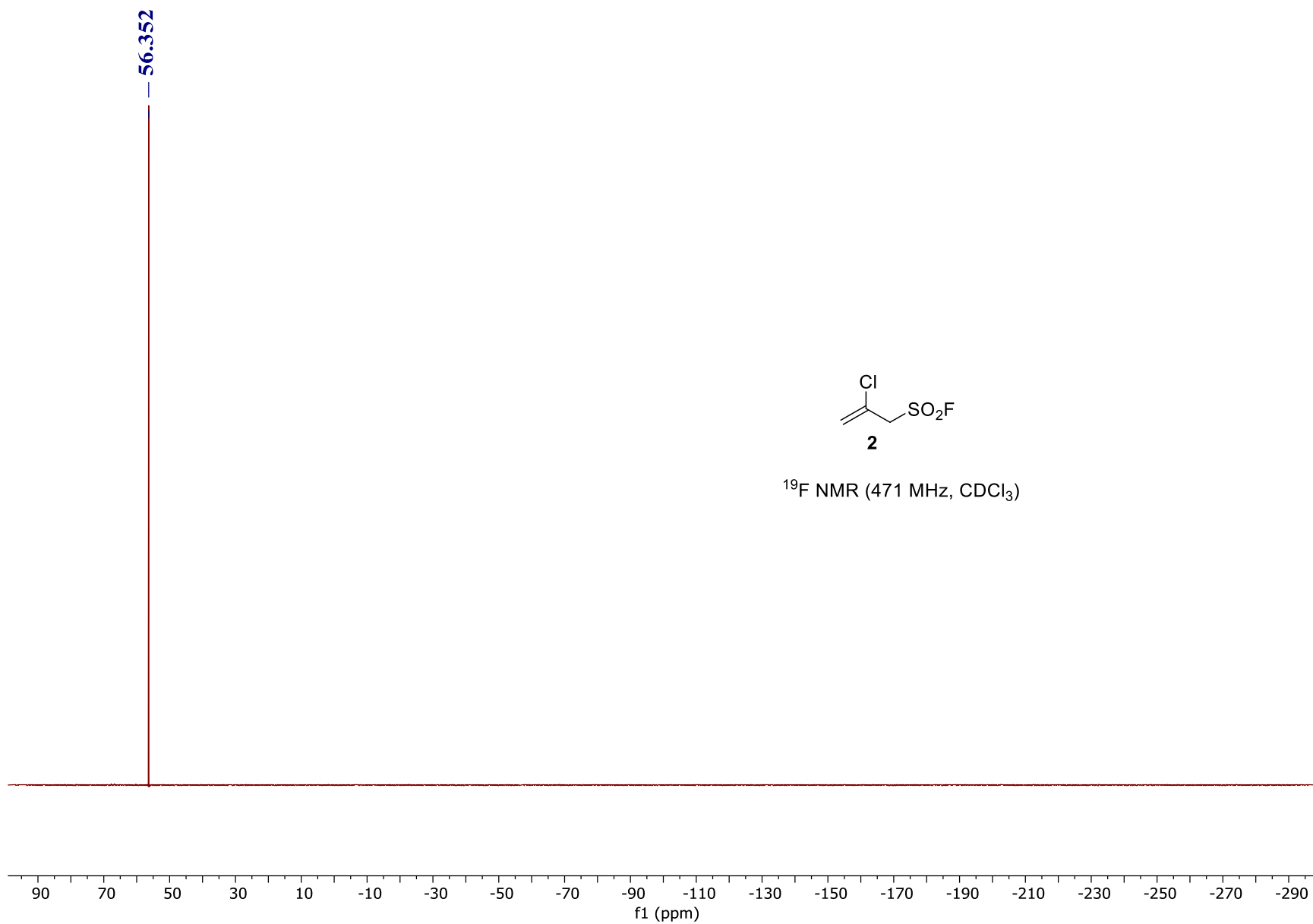
$J_1 = 12.1$ Hz, $J_2 = 6.0$ Hz, 4H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.0, 161.2, 159.8, 157.9, 149.3, 142.0 (d, $J = 2.5$ Hz), 129.0, 128.9, 128.8 (d, $J = 8.8$ Hz), 127.5 (d, $J = 1.9$ Hz), 127.0 (d, $J = 3.9$ Hz), 125.9, 125.2 (d, $J = 3.1$ Hz), 122.0 (d, $J = 27.7$ Hz), 118.6 (d, $J = 11.0$ Hz), 116.7, 116.5 (d, $J = 22.7$ Hz), 110.7, 108.93 (d, $J = 2.2$ Hz), 66.2, 44.9, 34.5, 19.4. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{25}\text{H}_{24}\text{FN}_2\text{O}_5\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 483.1384, found: 483.1385.

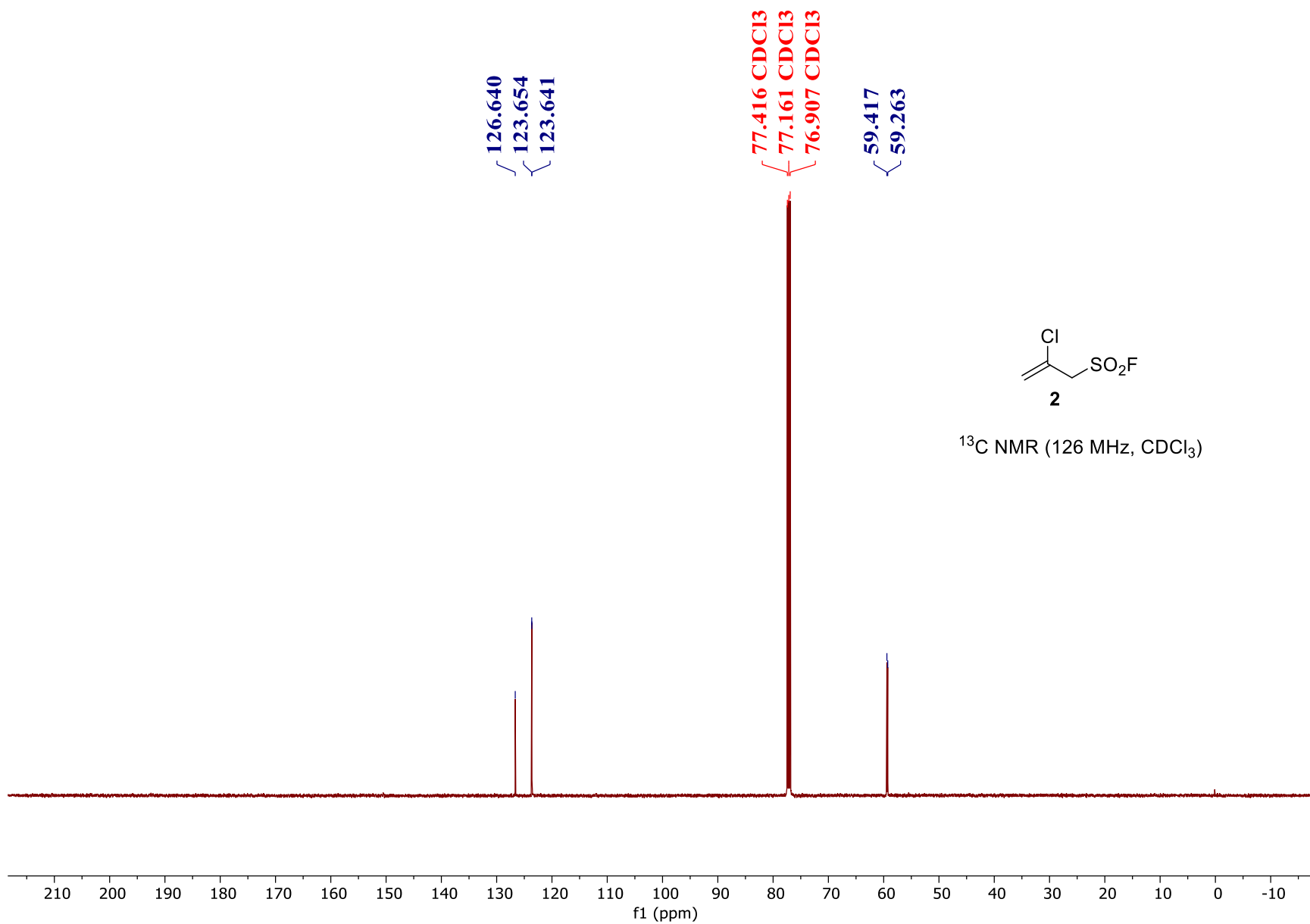
5. References.

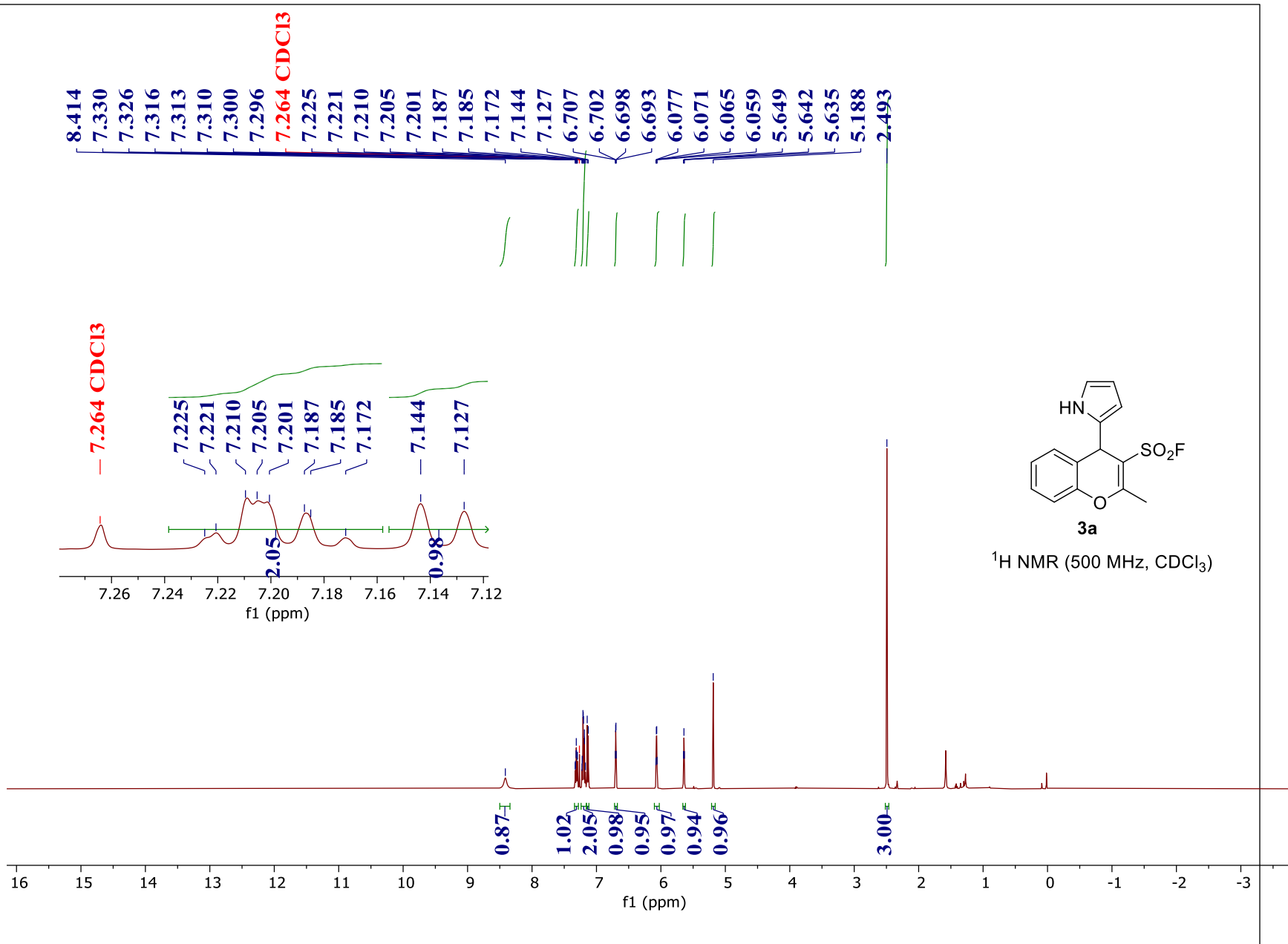
- 1 M. J. Brienne, D. Varech, M. Leclercq, J. Jacques, N. Radembino, C. Dessalles, G. Mahuzier, C. Gueyouche and C. Bories, *J. Med. Chem.*, 1987, **30**, 2232–2239.
- 2 X. Zhang, W. Fang, R. Lekkala, W. Tang and H. Qin, *Adv. Synth. Catal.*, 2020, **362**, 3358–3363.
- 3 A. F. Abdel-Magid, K. G. Carson, B. D. Harris, C. A. Maryanoff and R. D. Shah, *J. Org. Chem.*, 1996, **61**, 3849–3862.

6.NMR Spectra

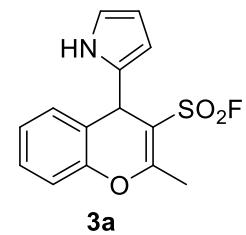




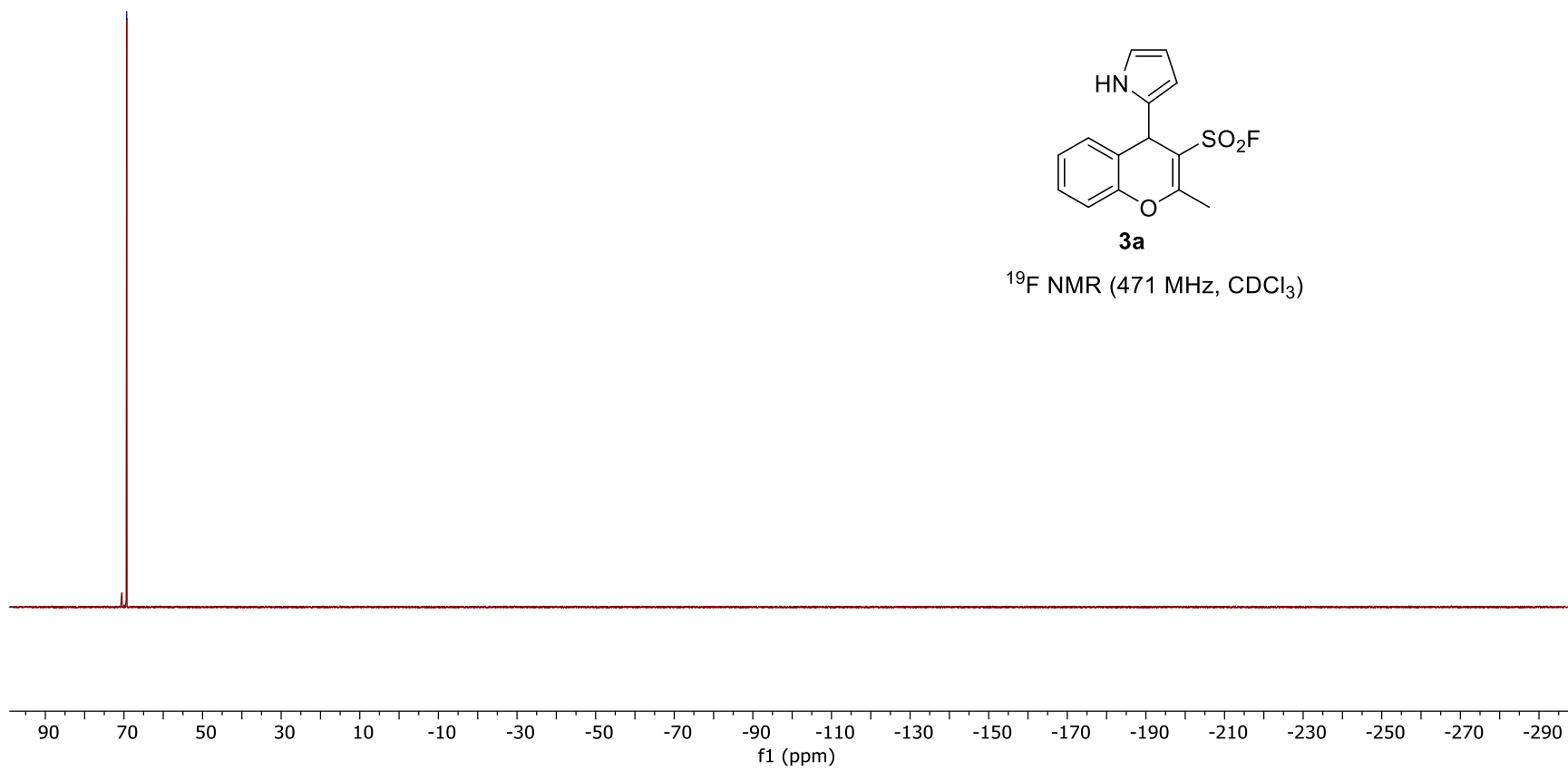


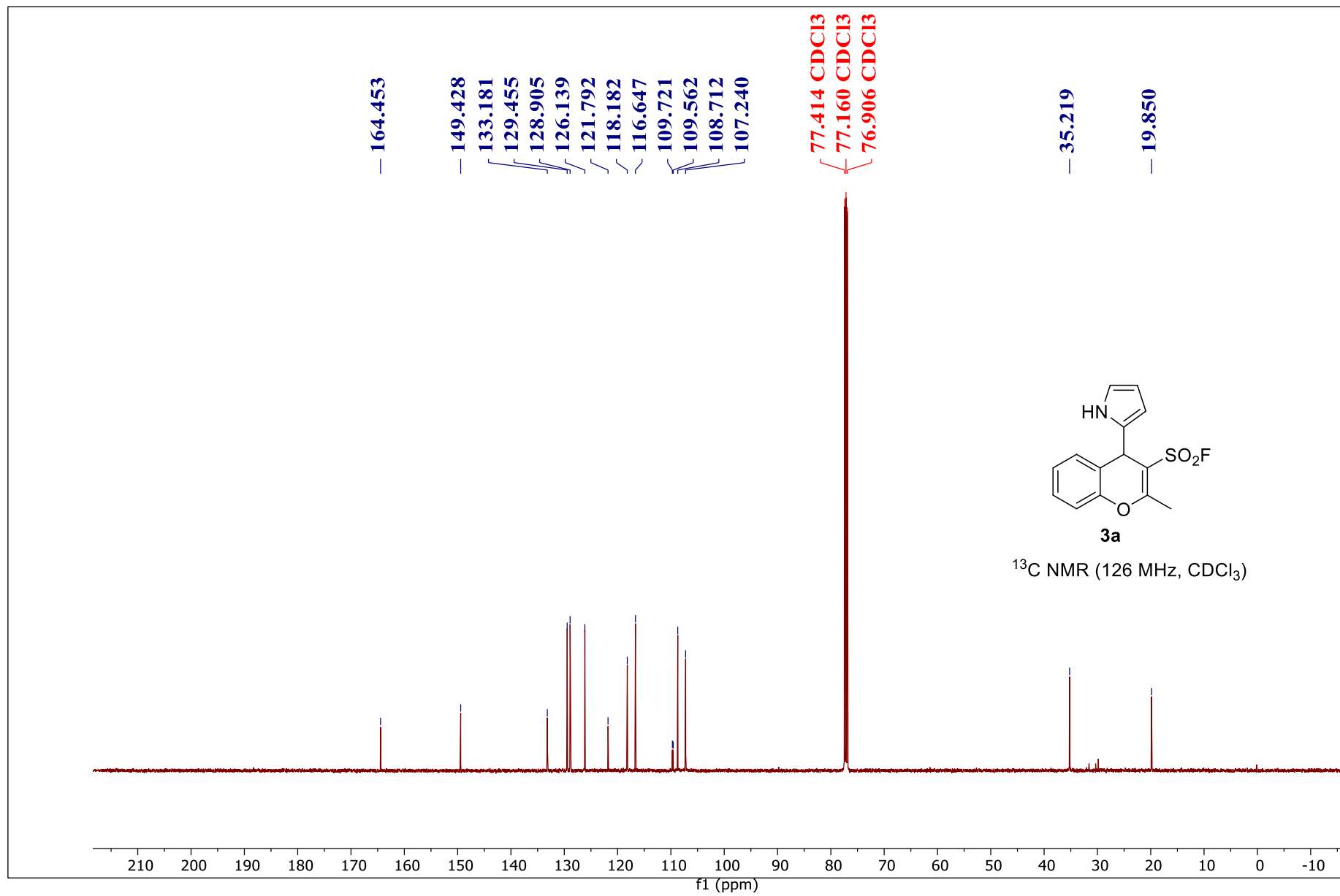


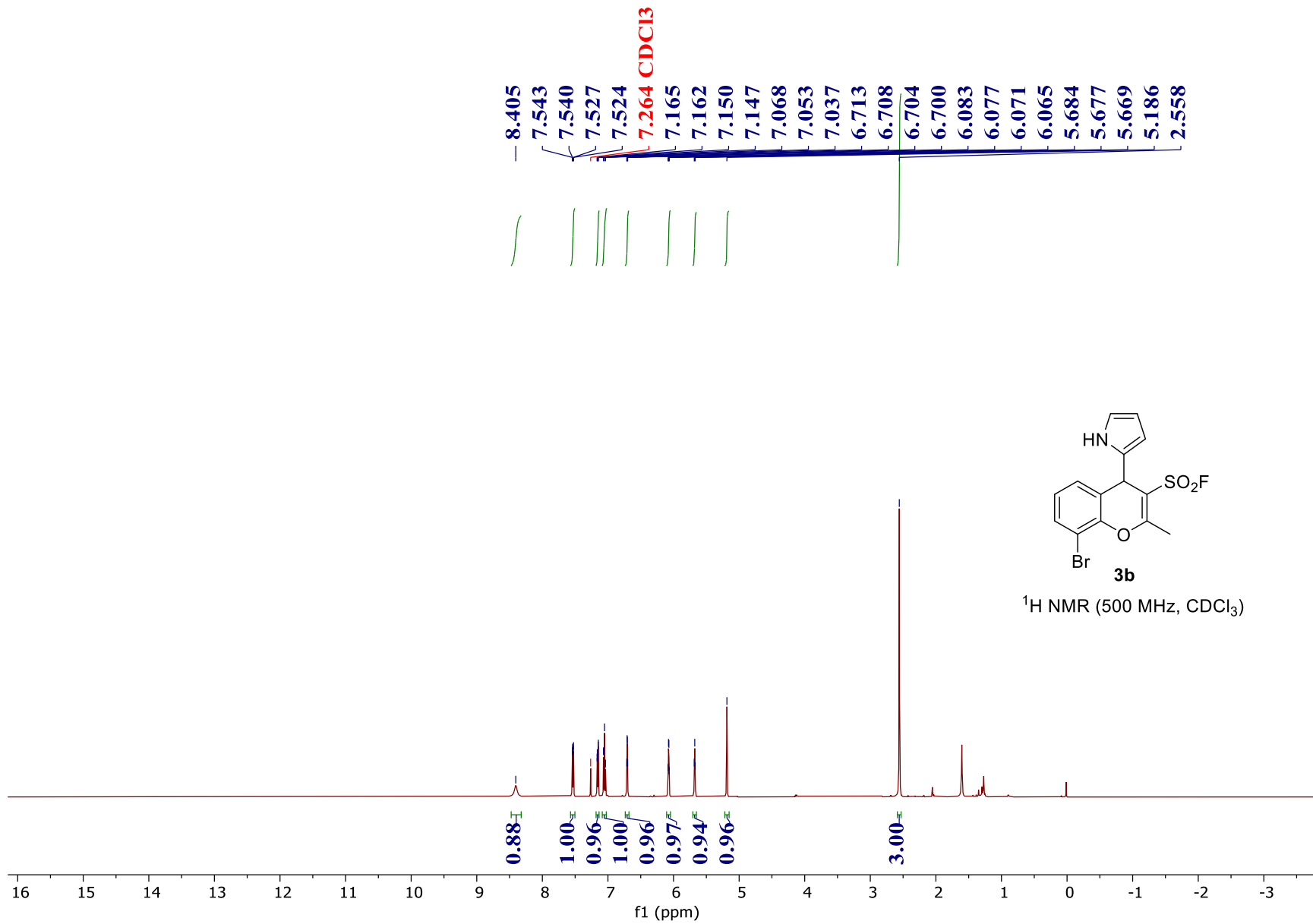
— 69.297

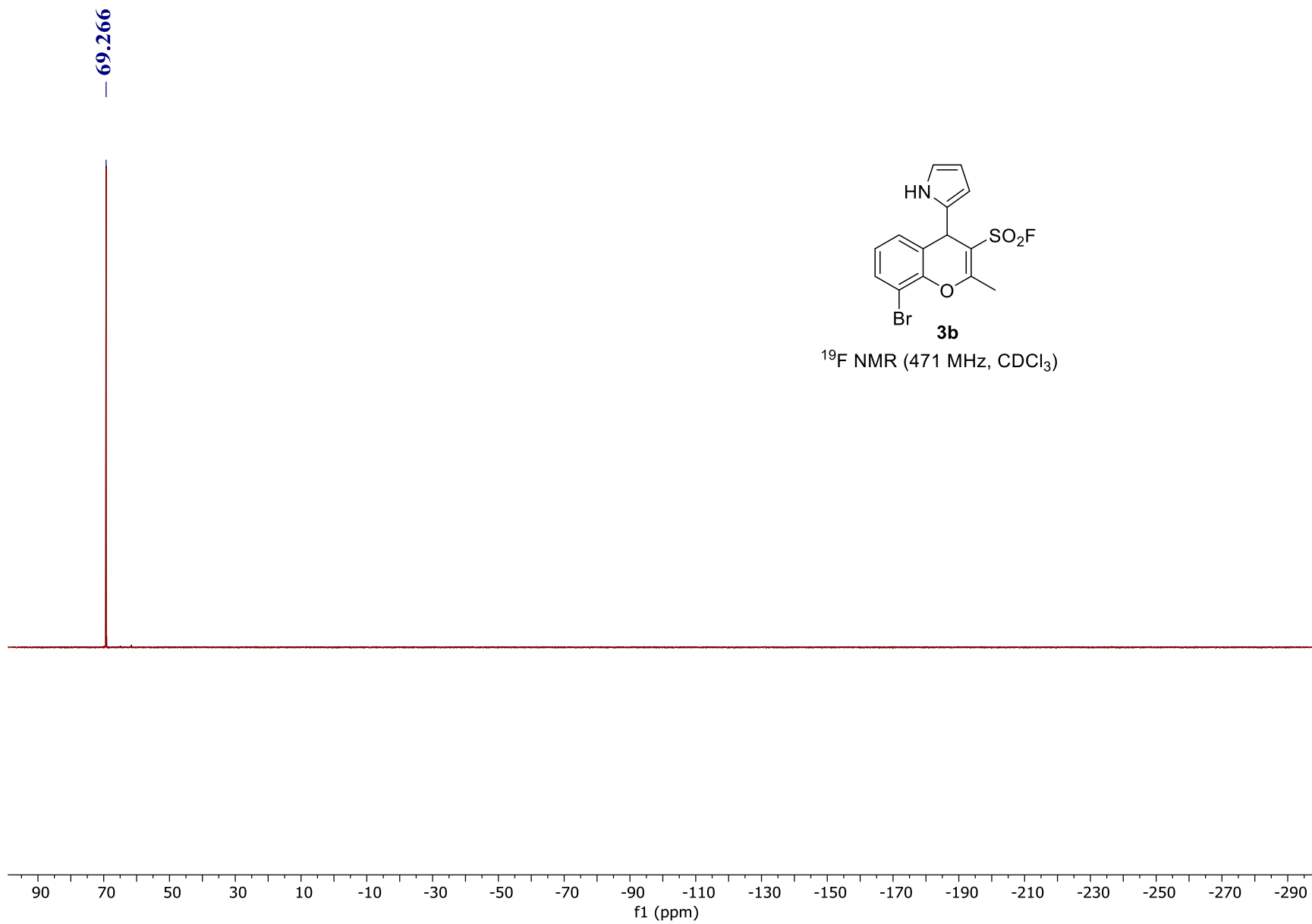


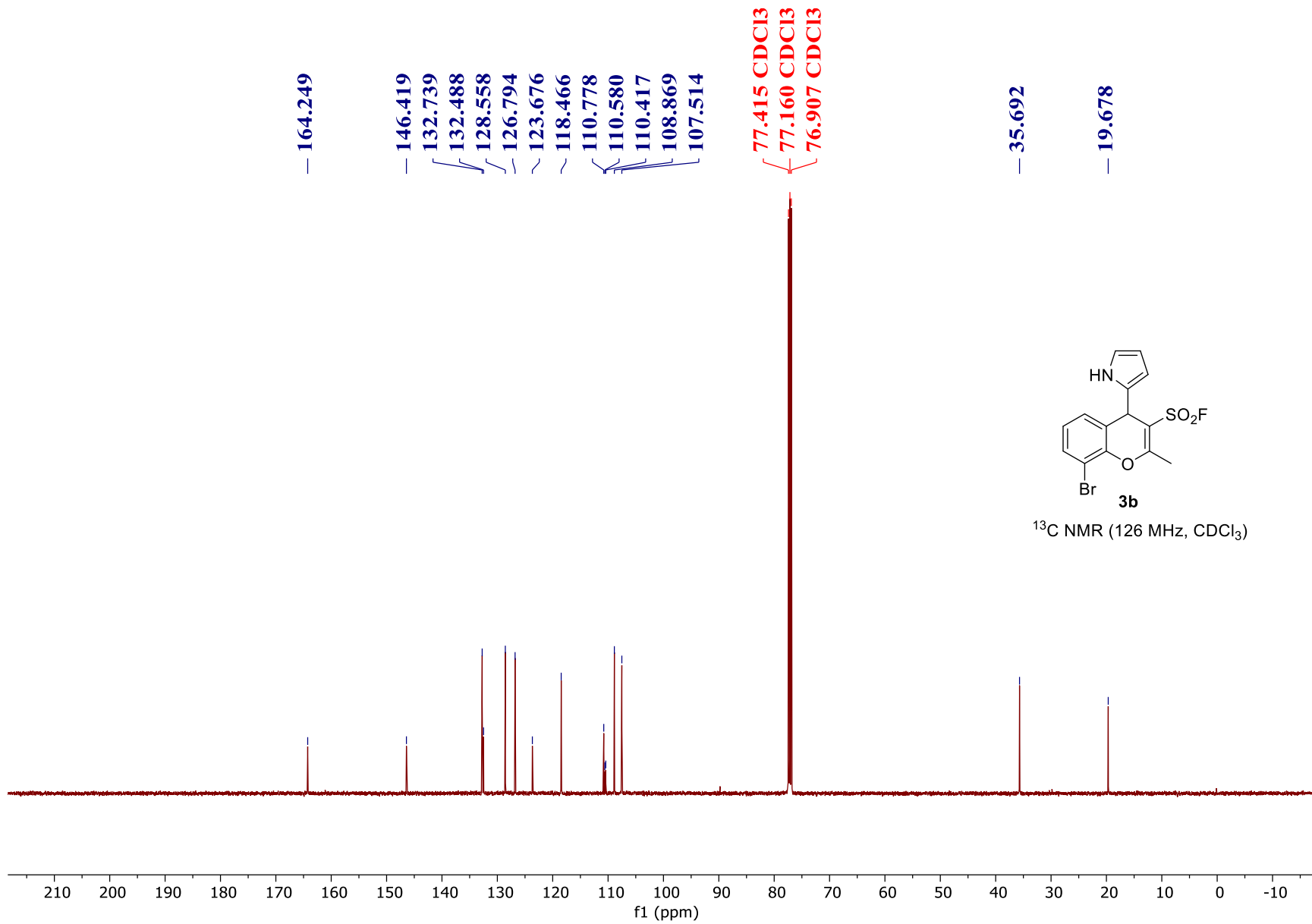
¹⁹F NMR (471 MHz, CDCl₃)

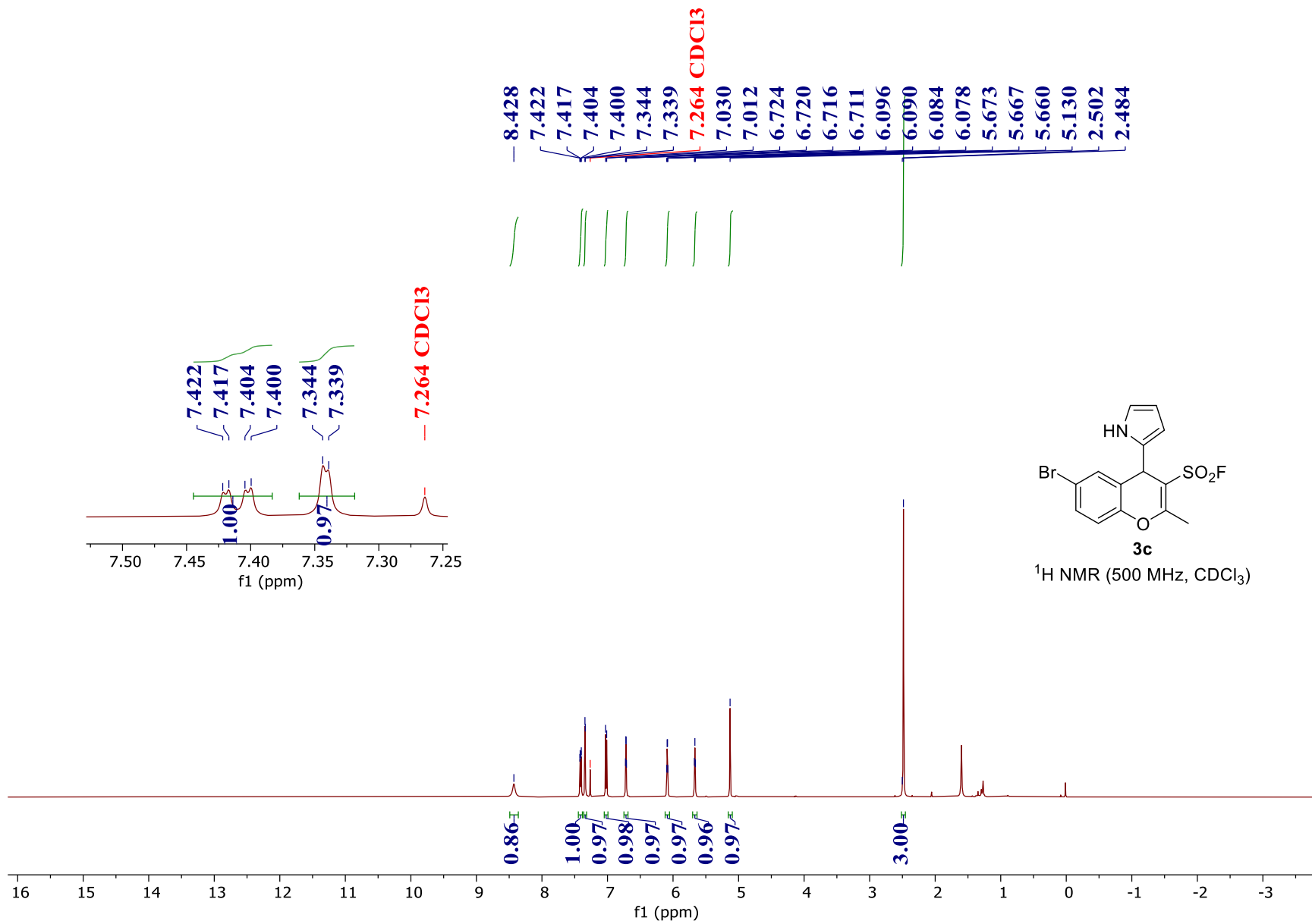




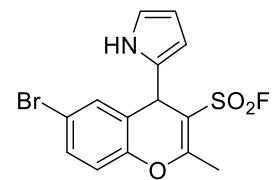






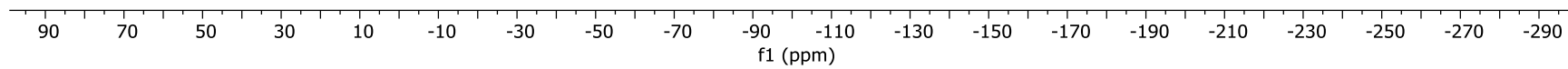


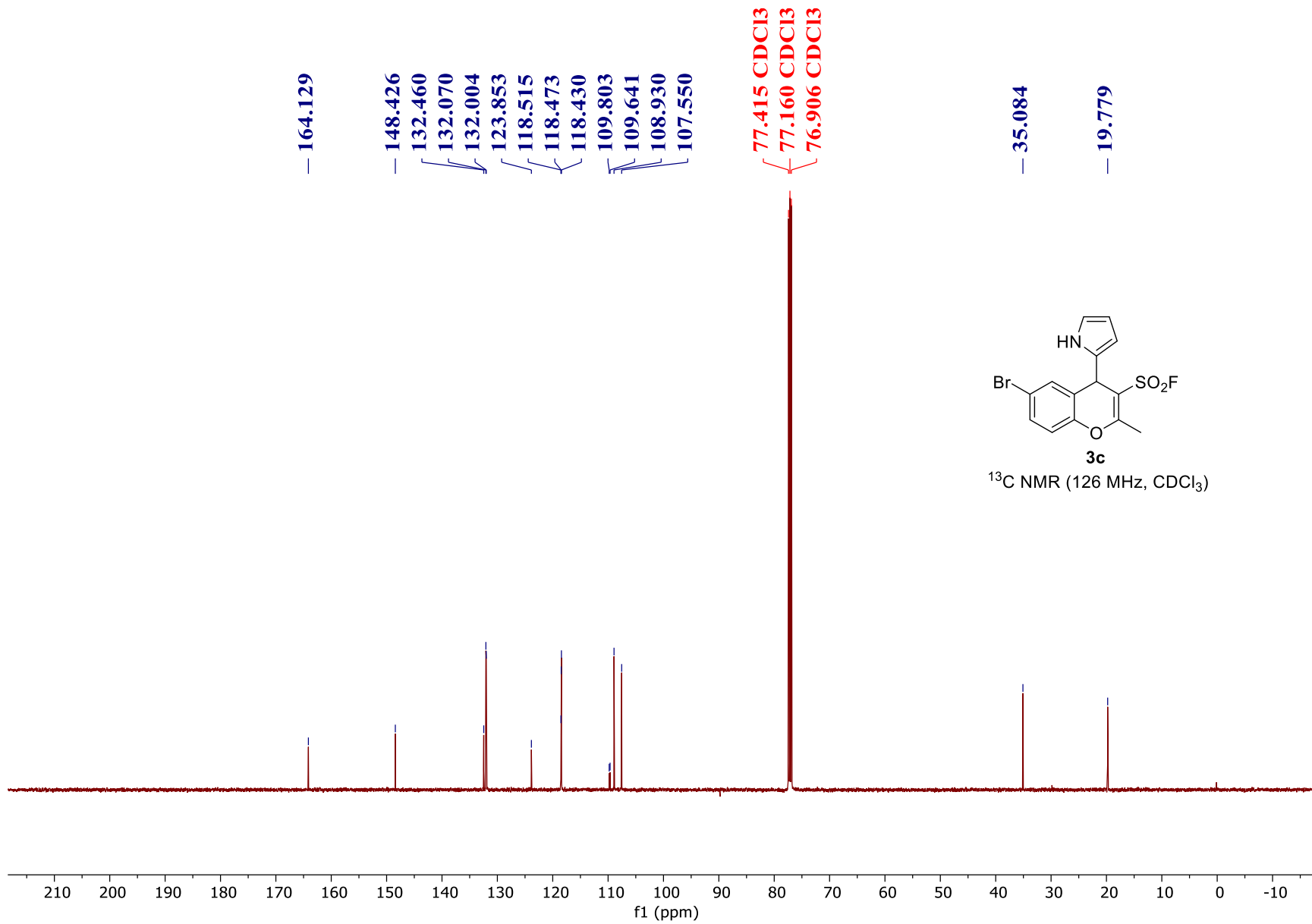
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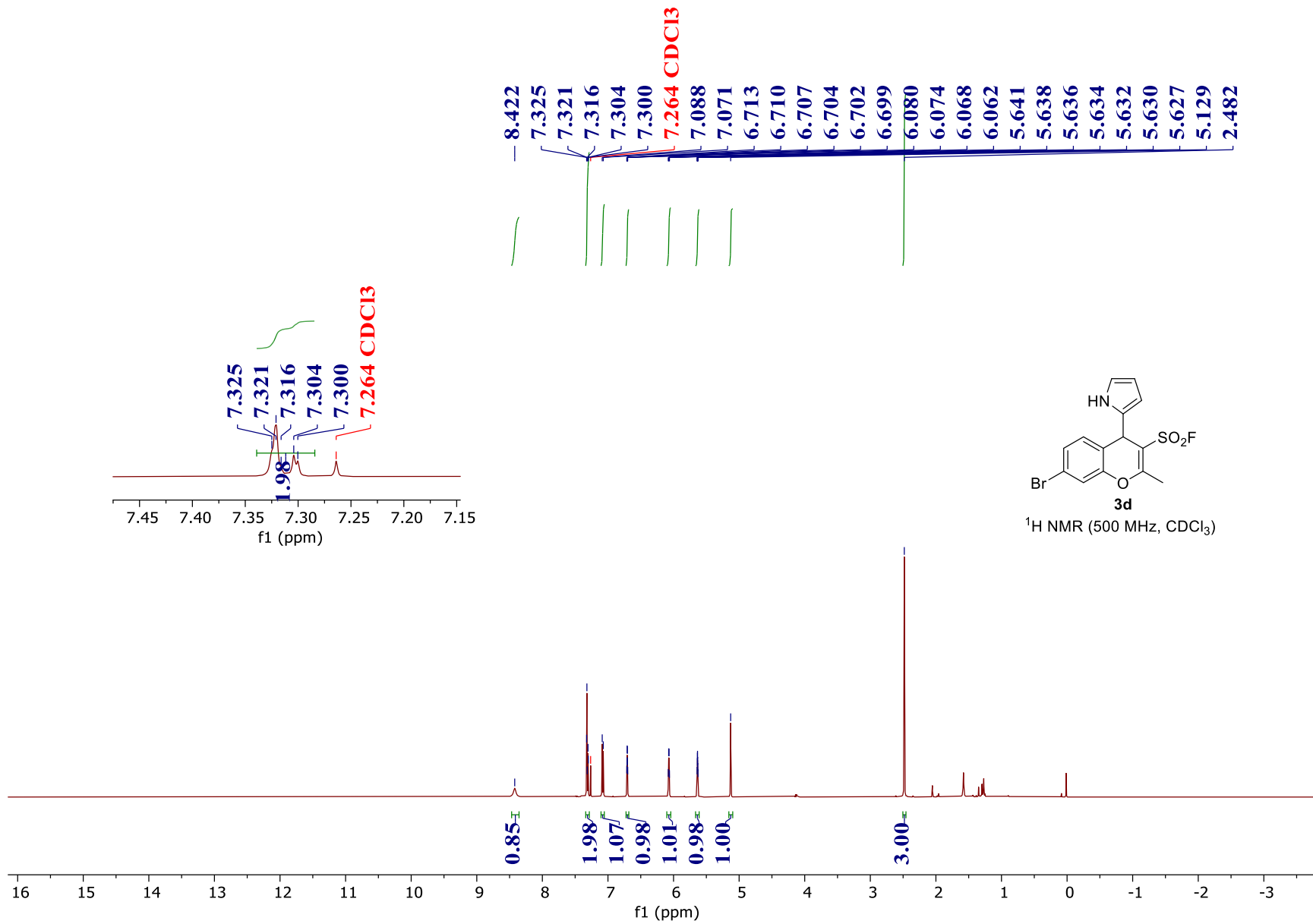


3c

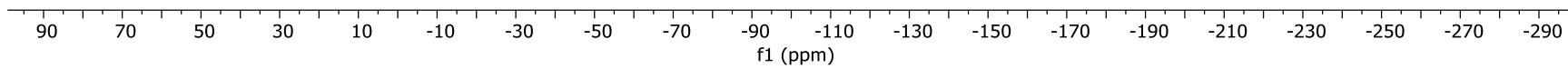
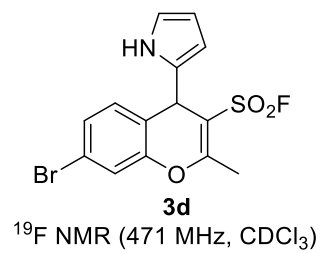
¹⁹F NMR (471 MHz, CDCl₃)

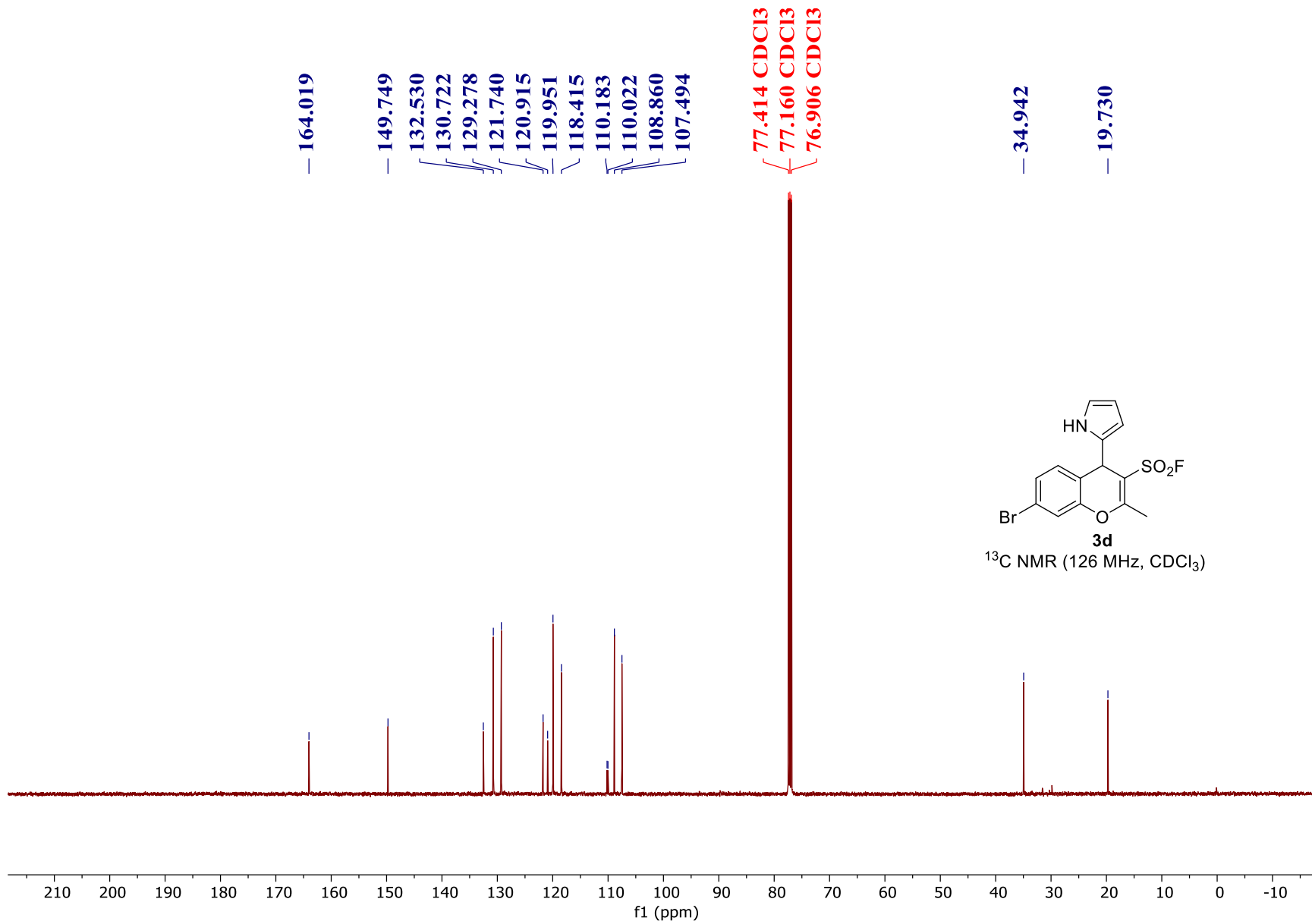


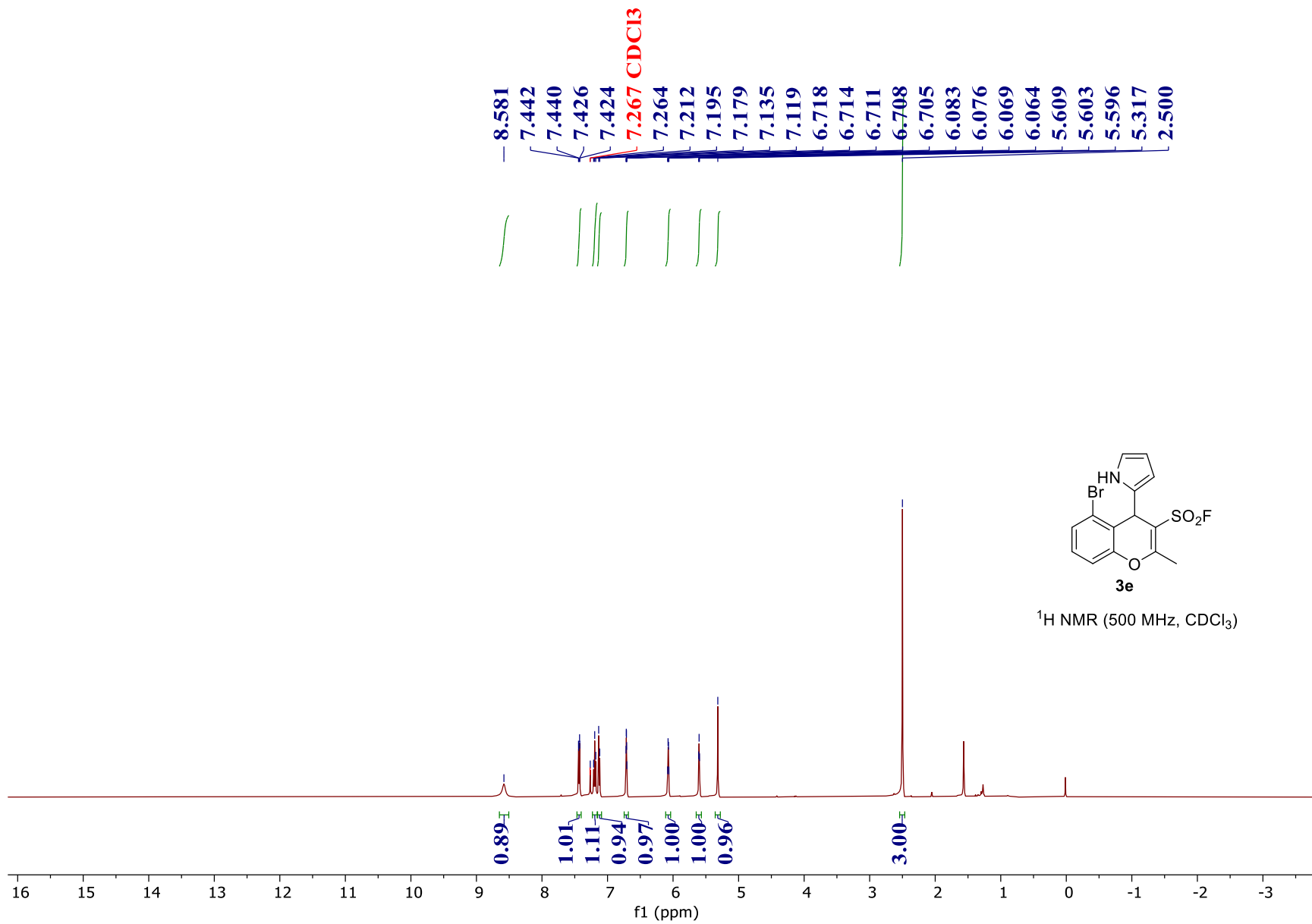


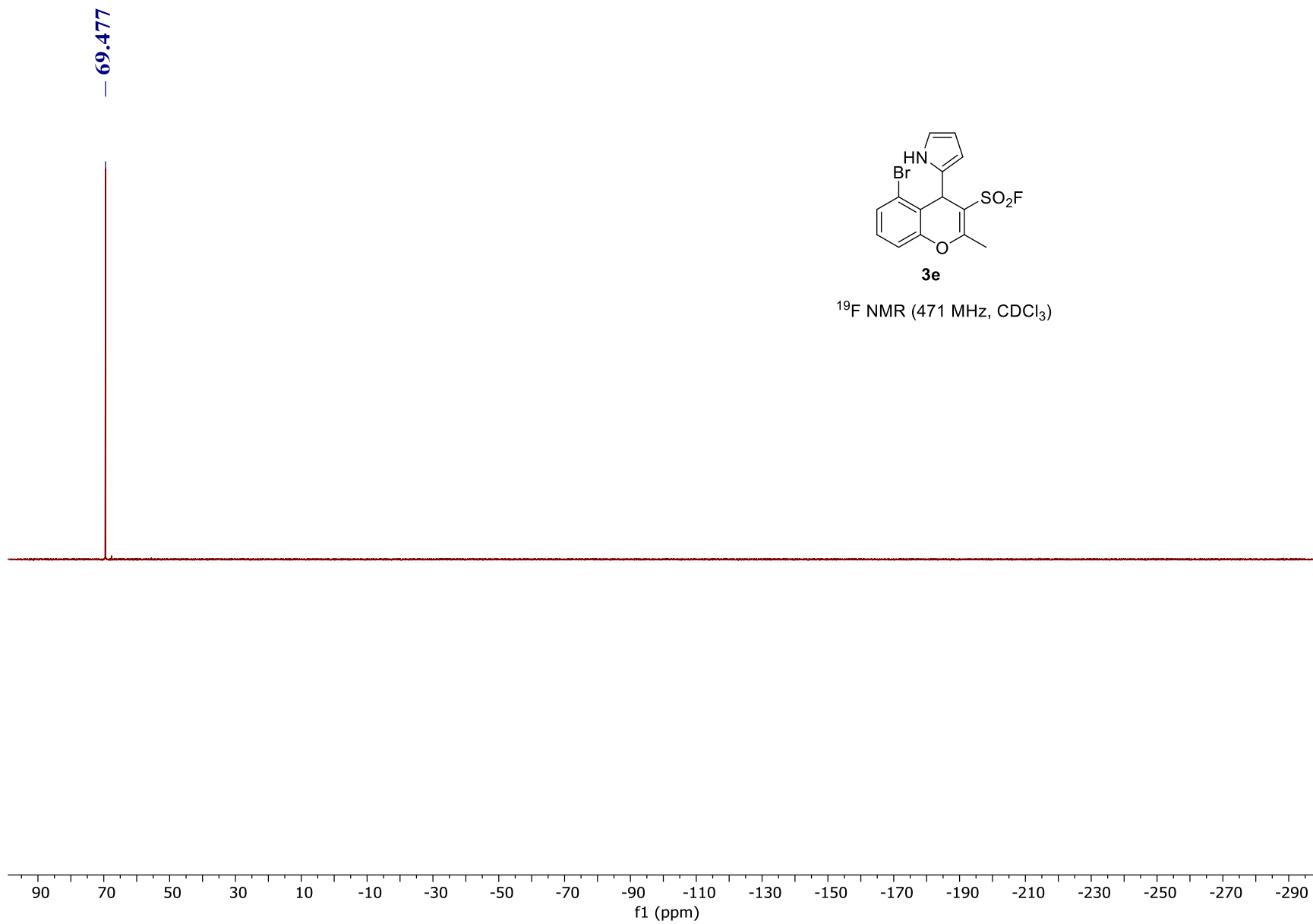


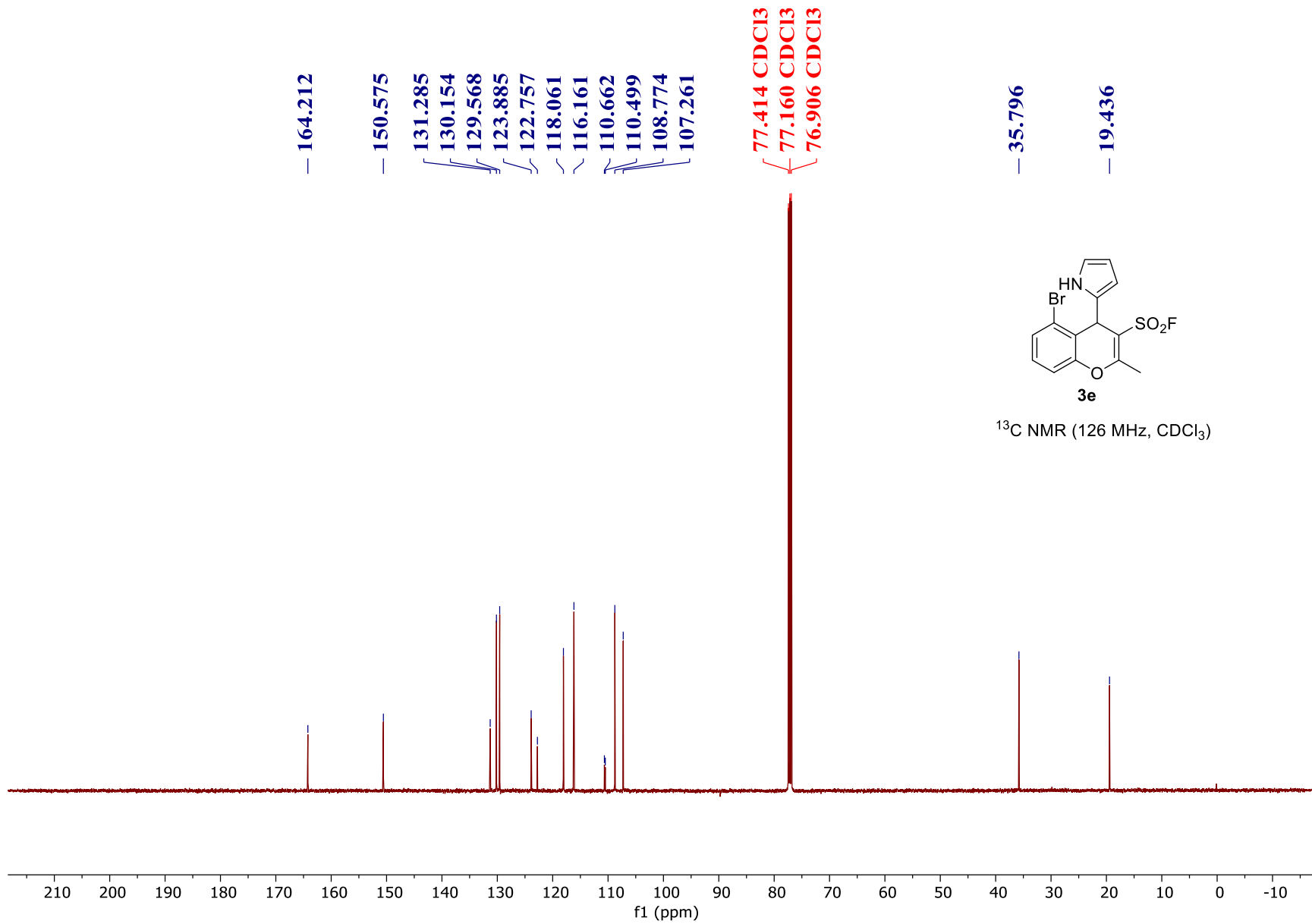
— 69.348

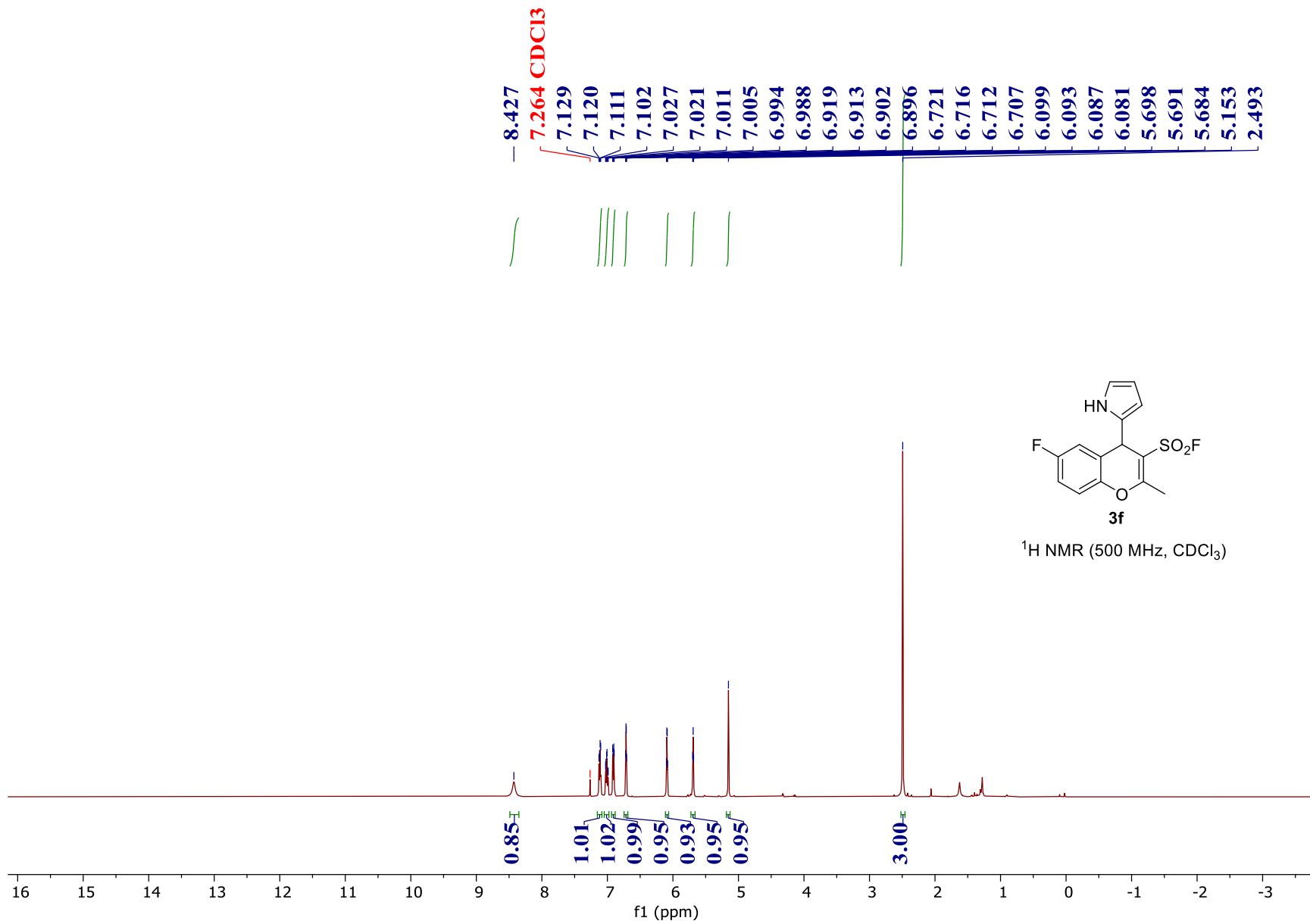


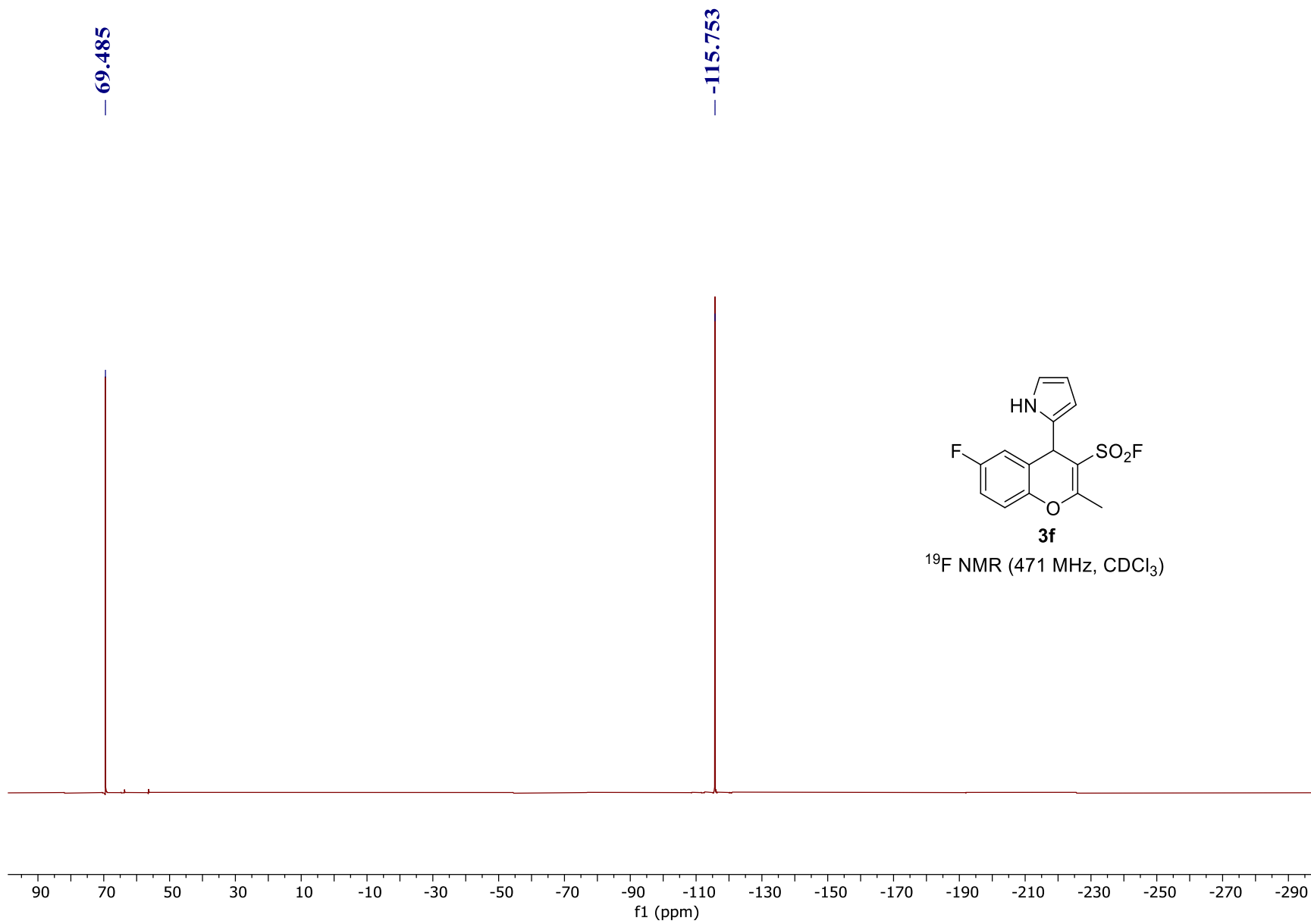


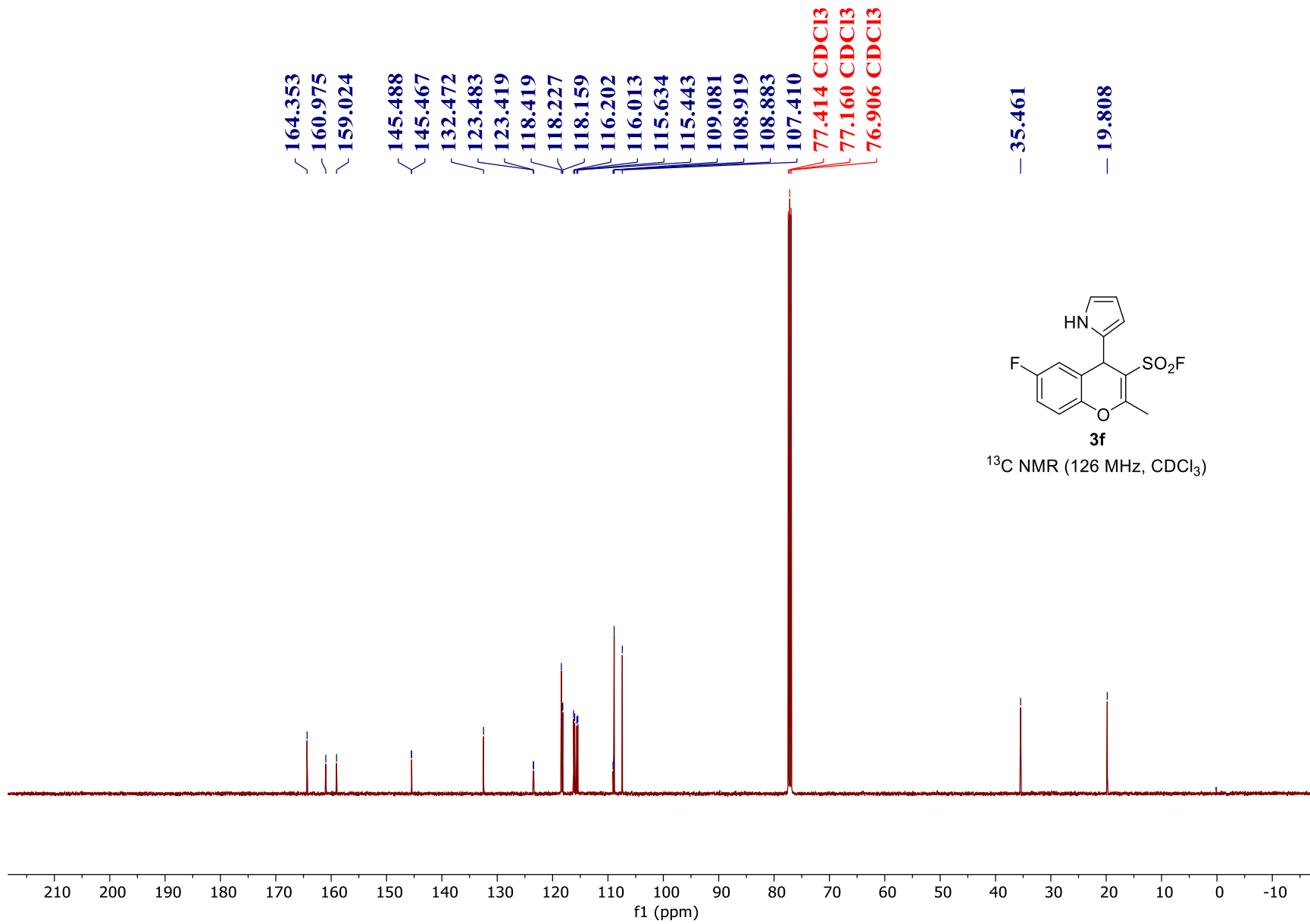


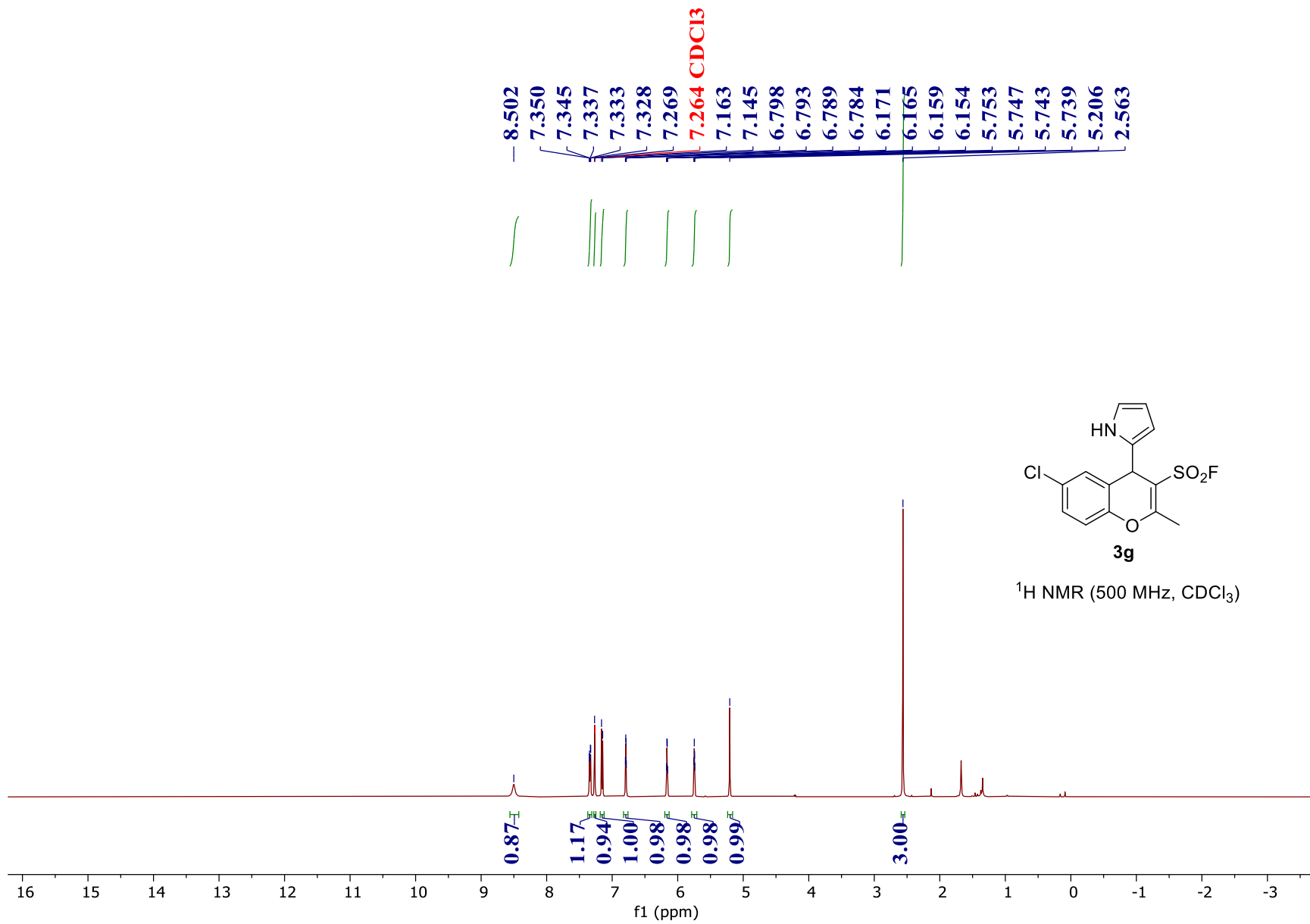




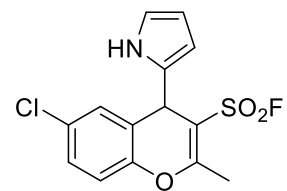






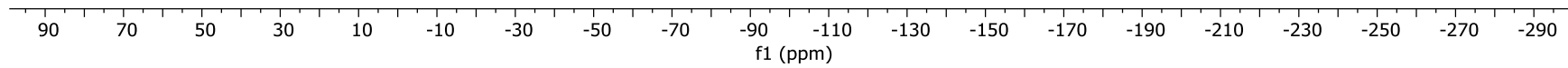


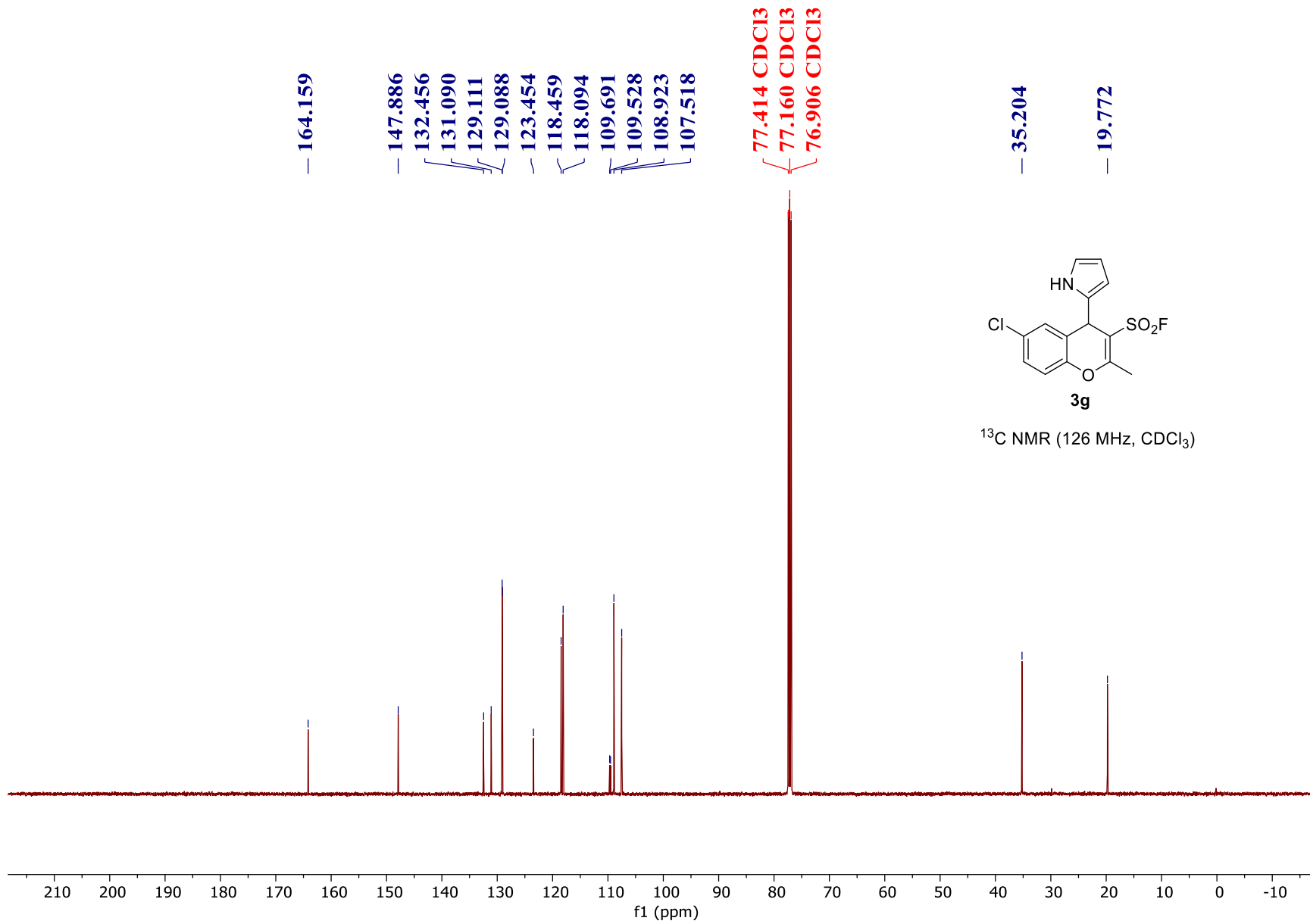
— 69.430

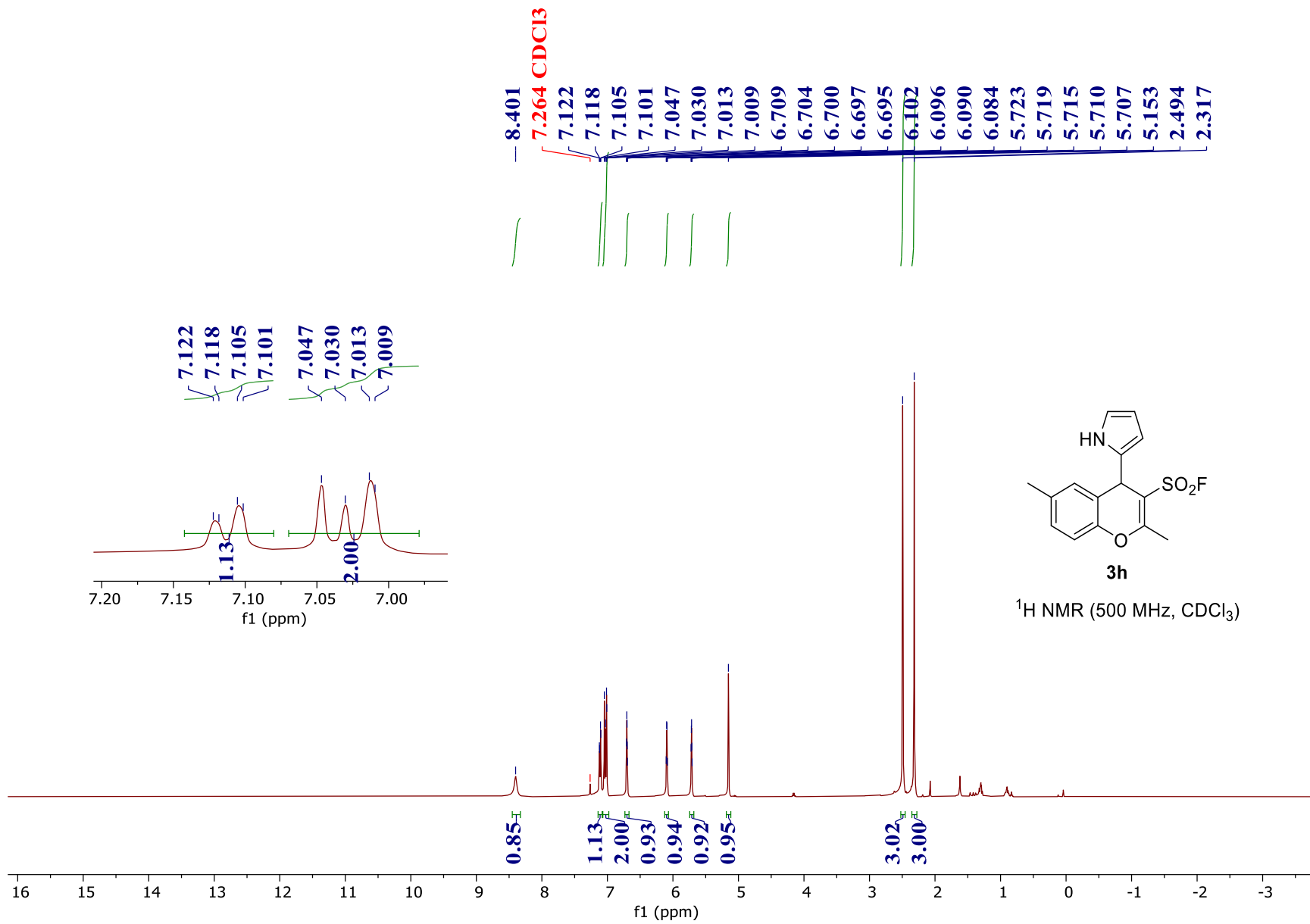


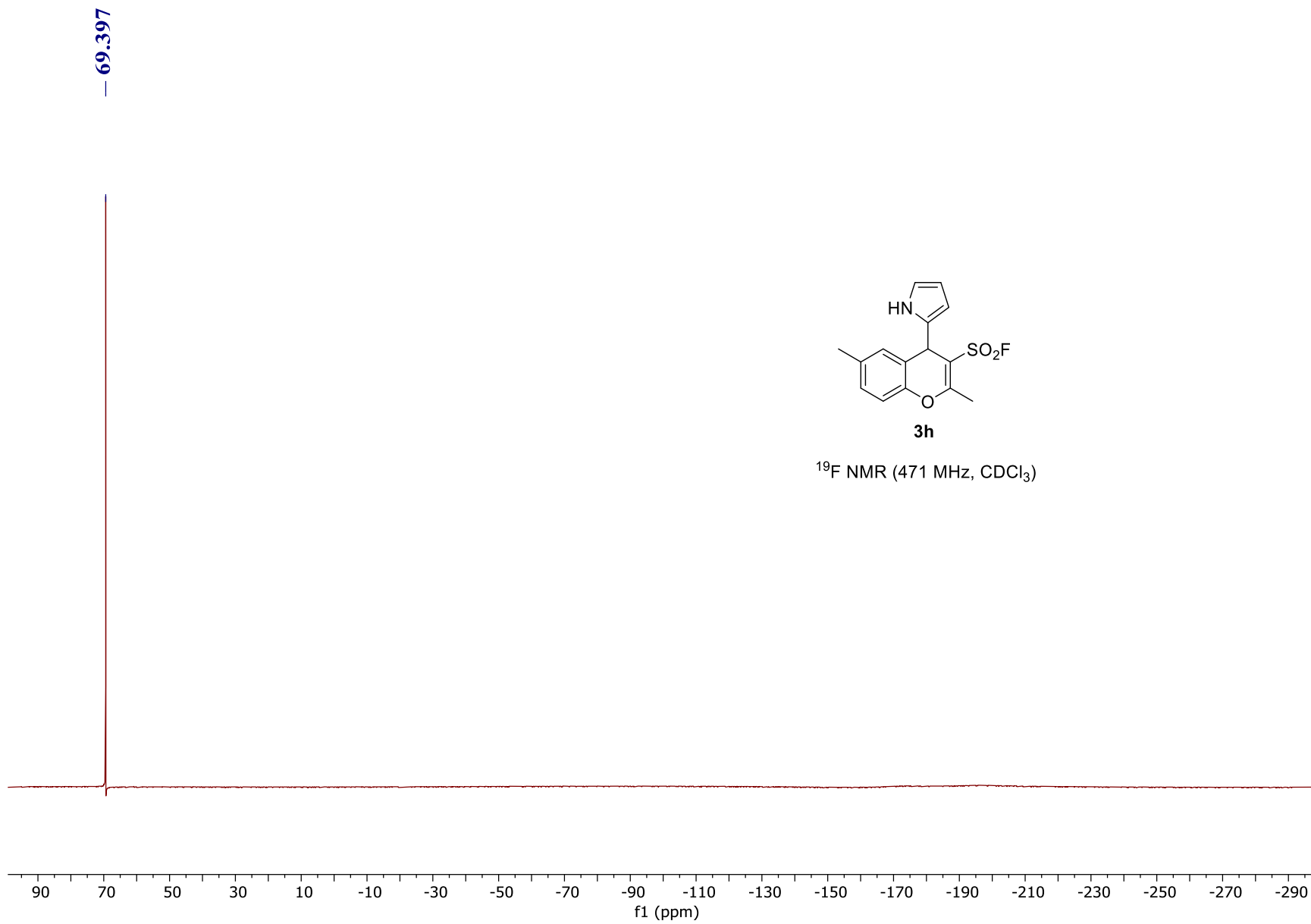
3g

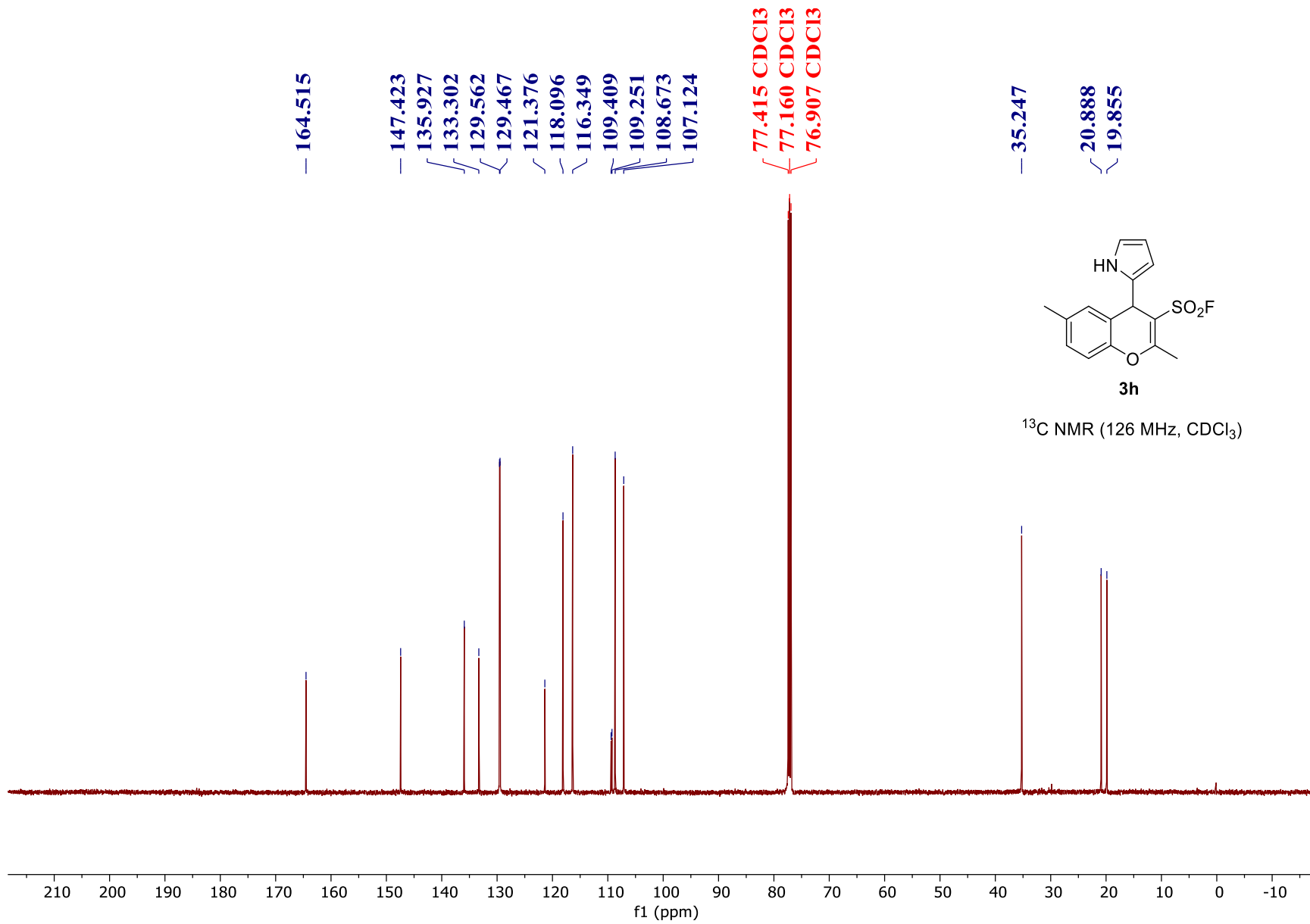
^{19}F NMR (471 MHz, CDCl_3)

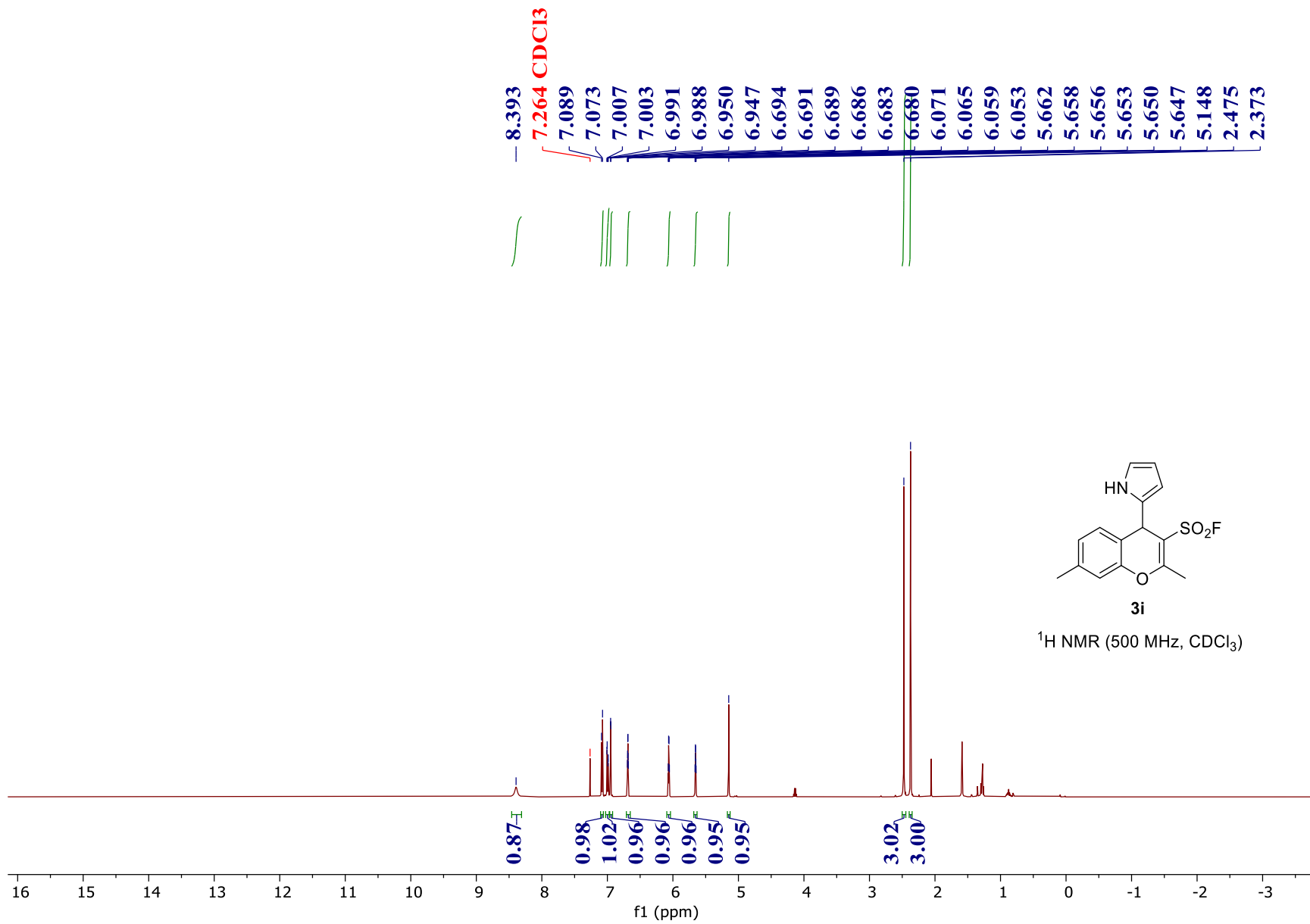




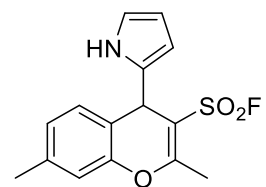






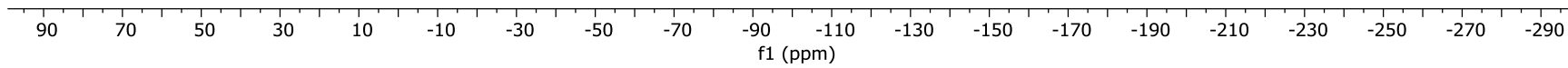


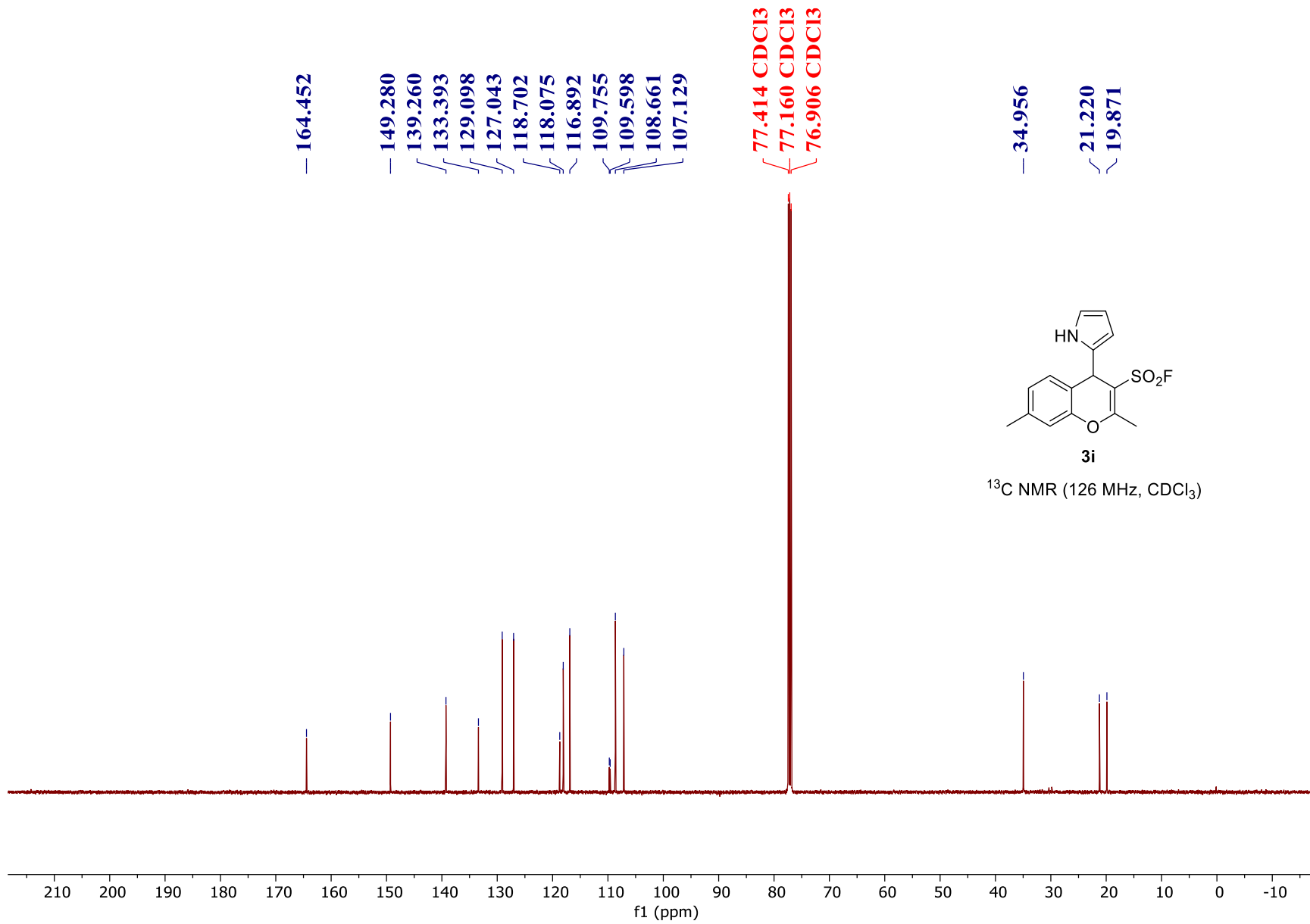
— 69.294

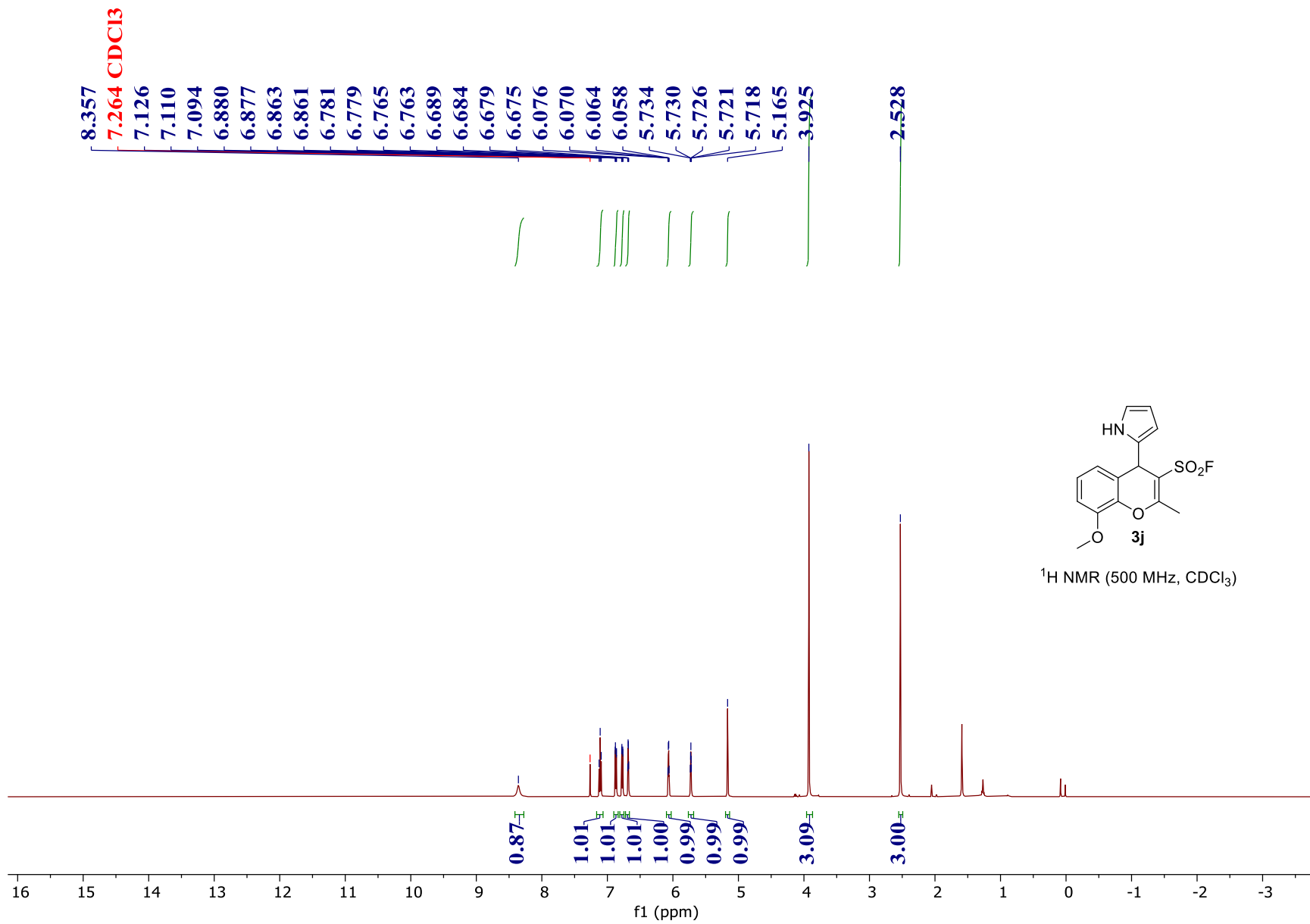


3i

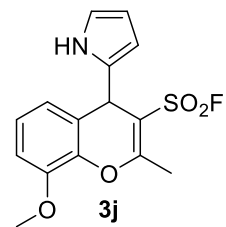
¹⁹F NMR (471 MHz, CDCl₃)



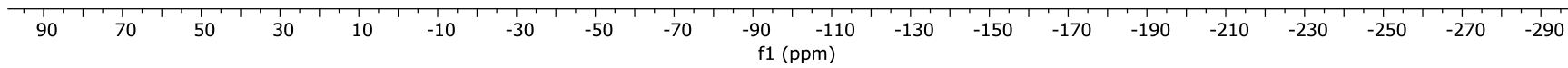


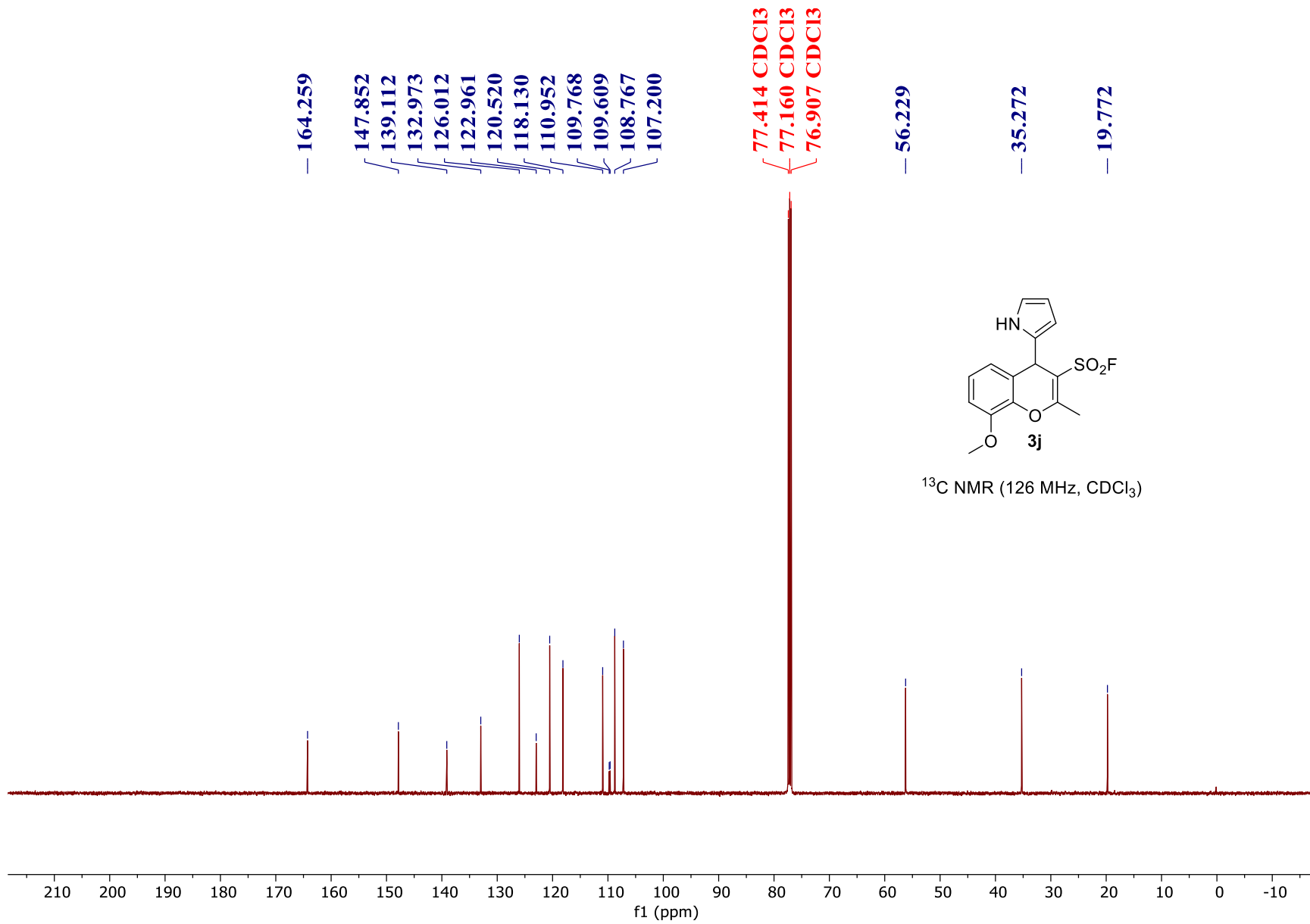


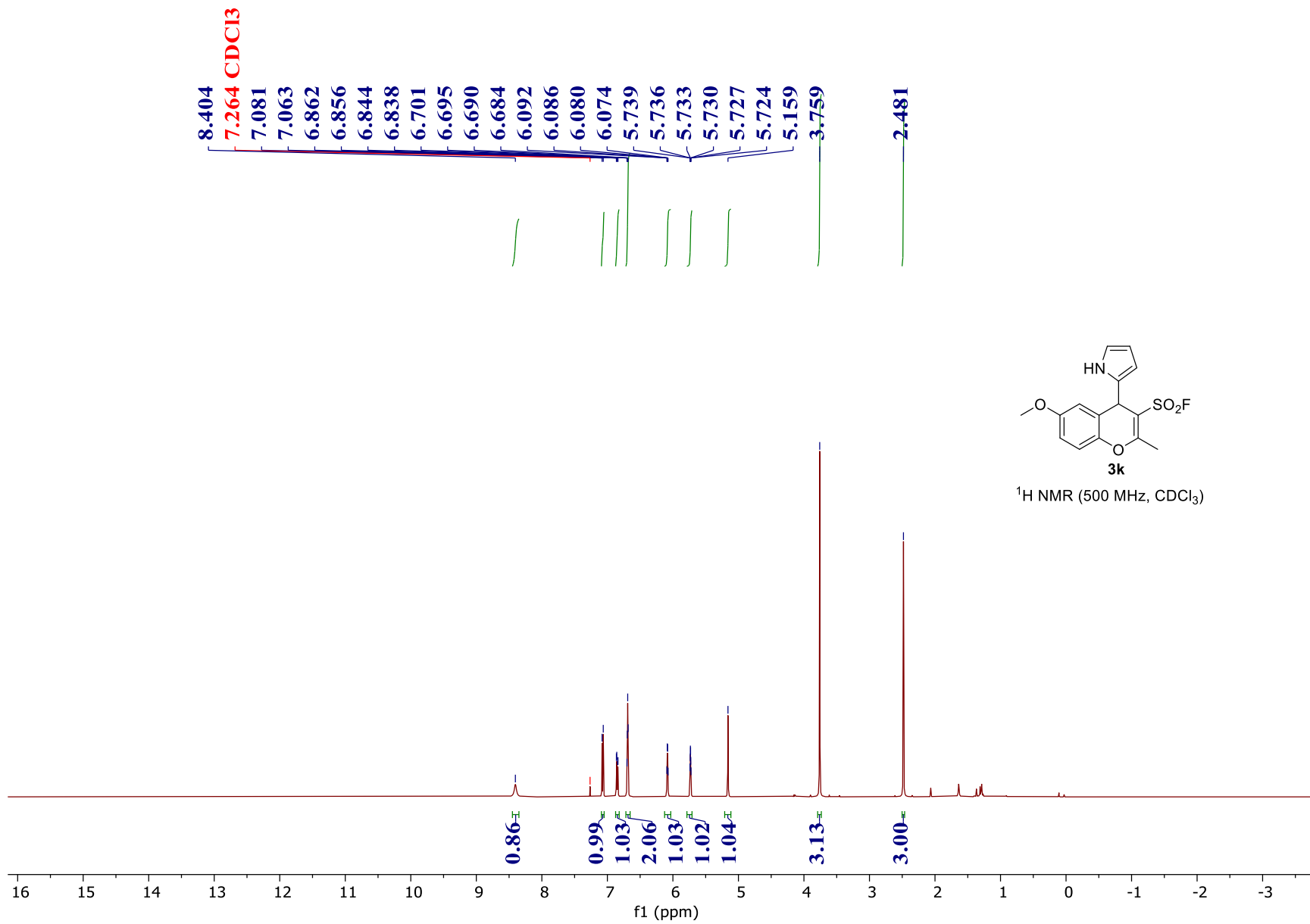
— 69.349



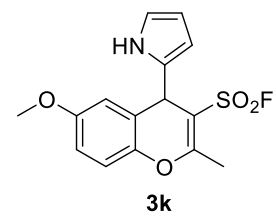
¹⁹F NMR (471 MHz, CDCl₃)



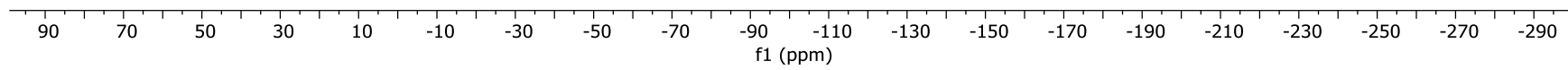


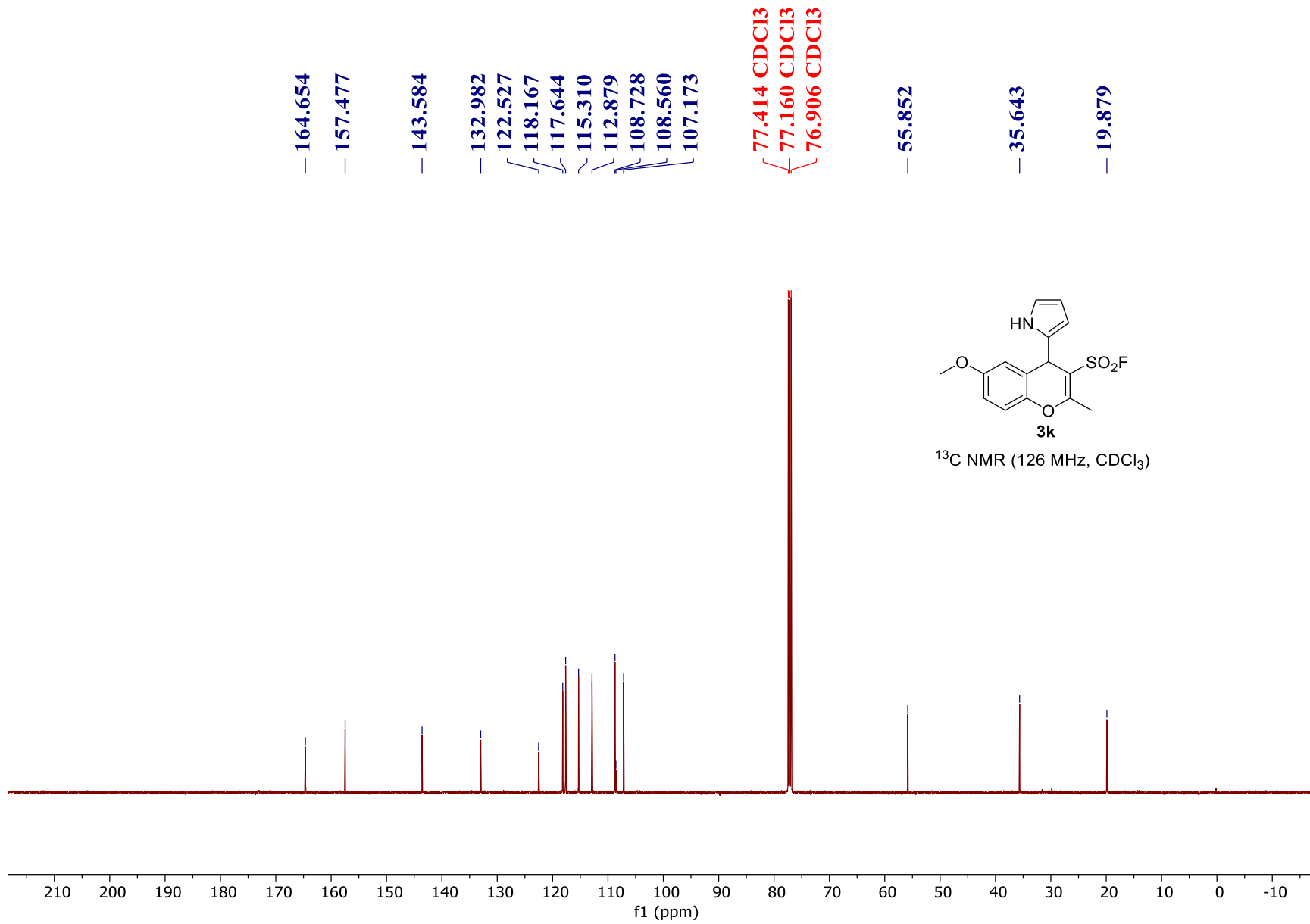


— 69.504



¹⁹F NMR (471 MHz, CDCl₃)





— 164.654

— 157.477

— 143.584

— 132.982

— 122.527

— 118.167

— 117.644

— 115.310

— 112.879

— 108.728

— 108.560

— 107.173

77.414 CDCl₃

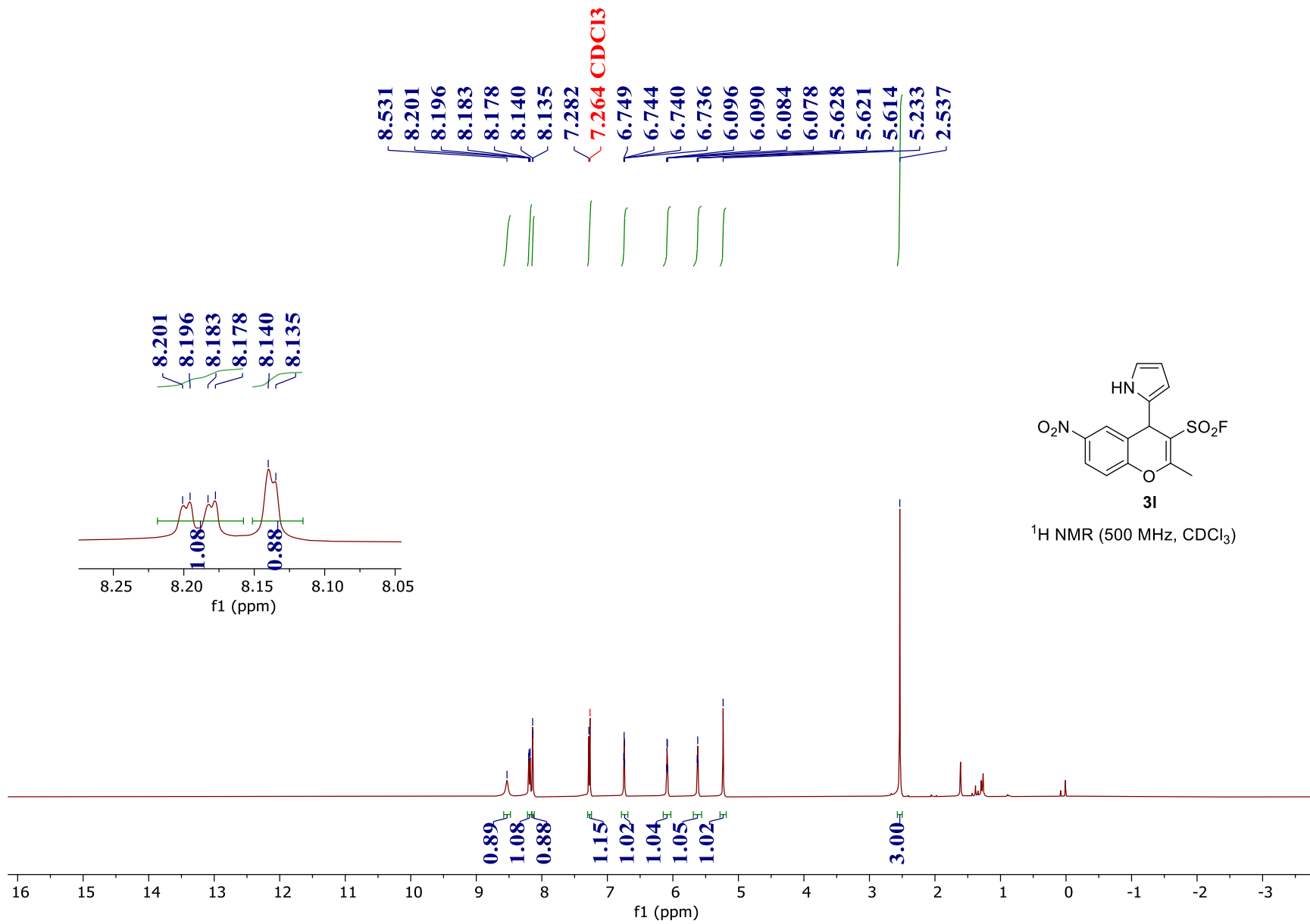
77.160 CDCl₃

76.906 CDCl₃

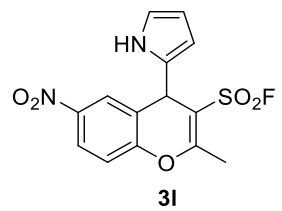
— 55.852

— 35.643

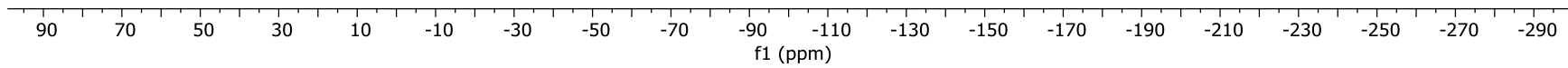
— 19.879

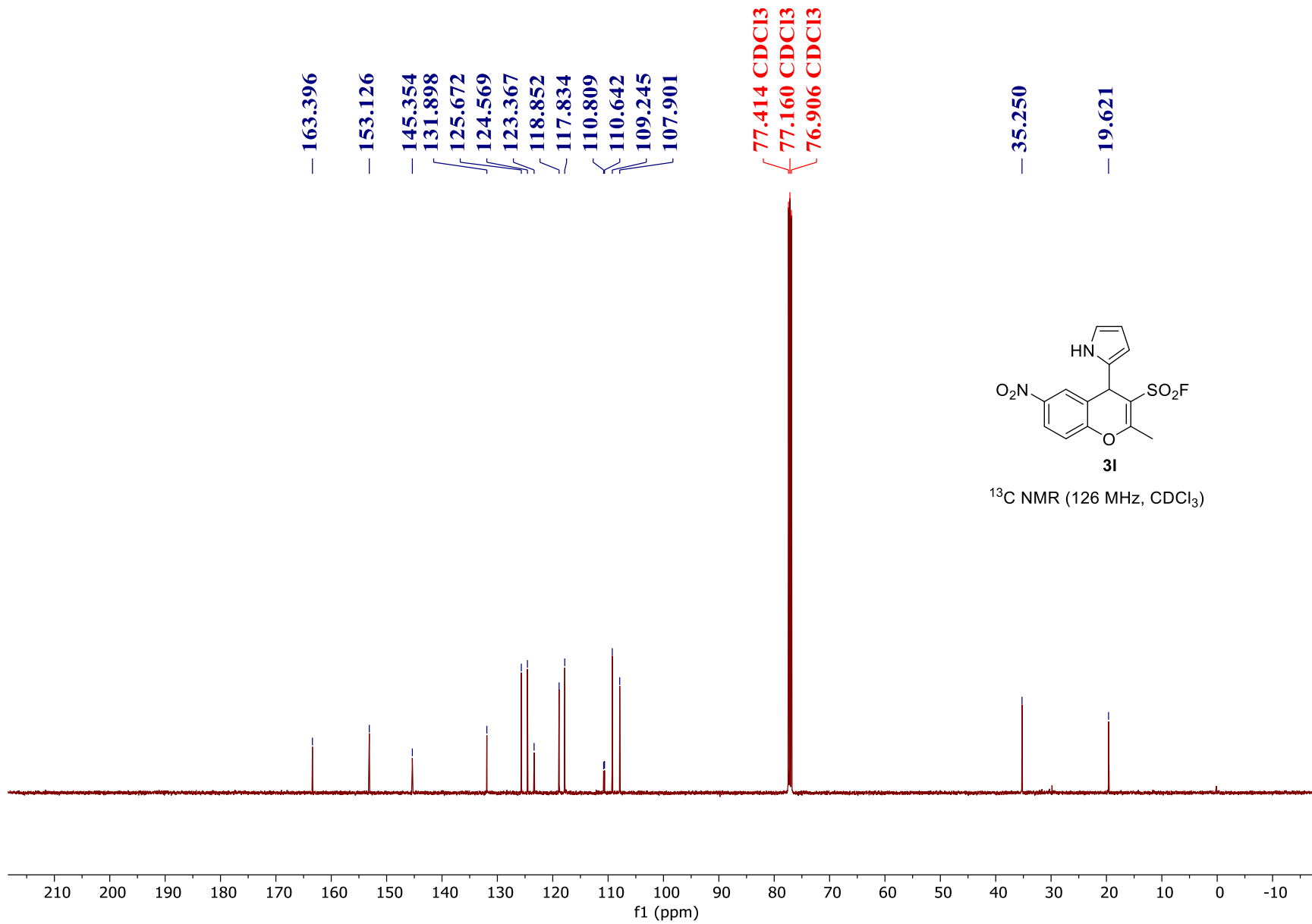


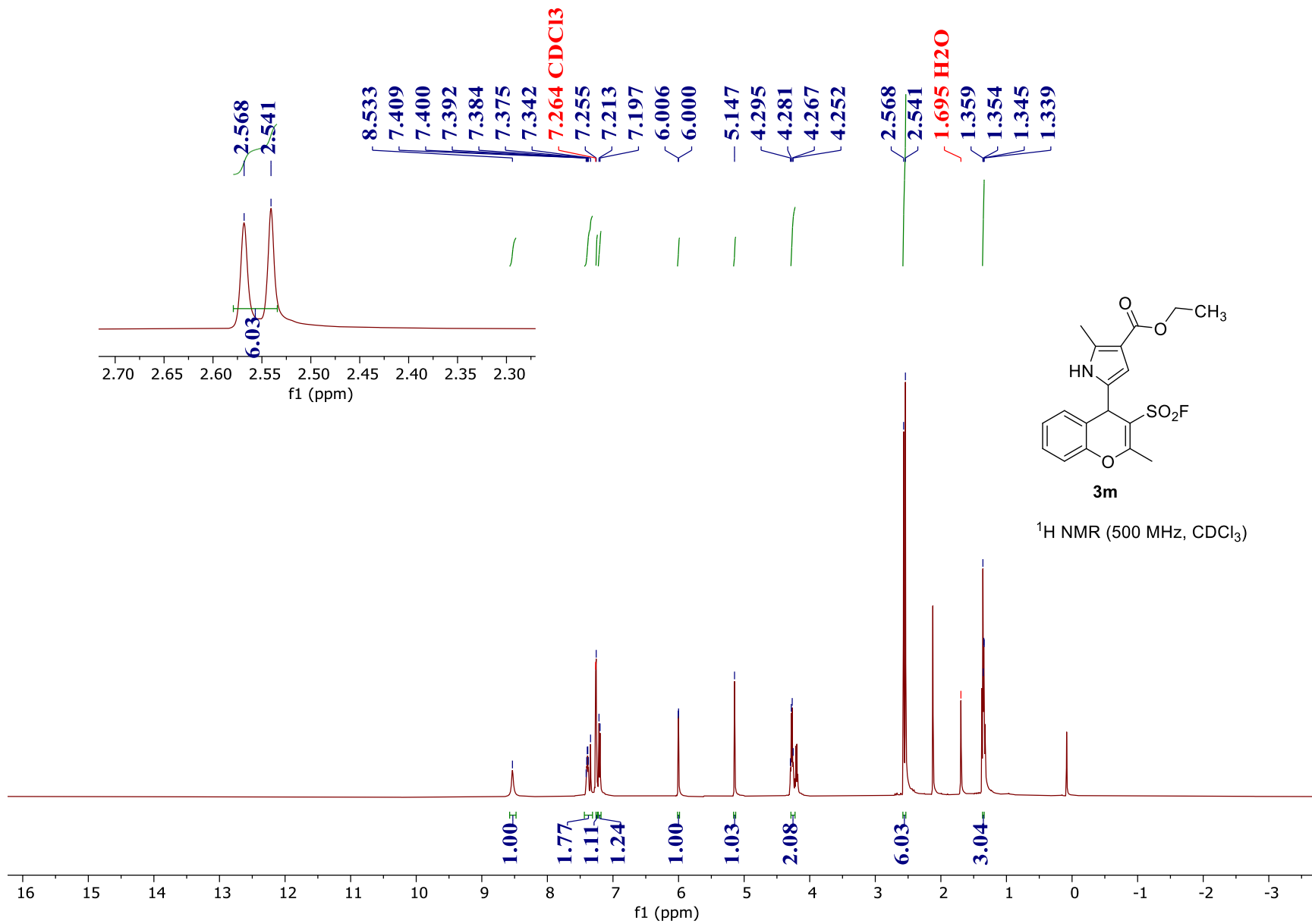
- 69.531



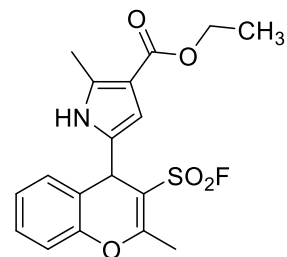
¹⁹F NMR (471 MHz, CDCl₃)





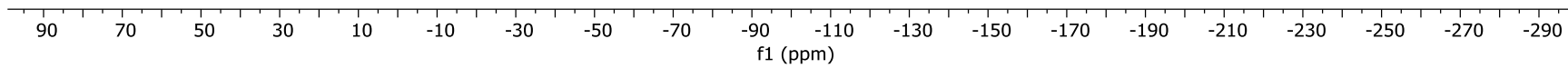


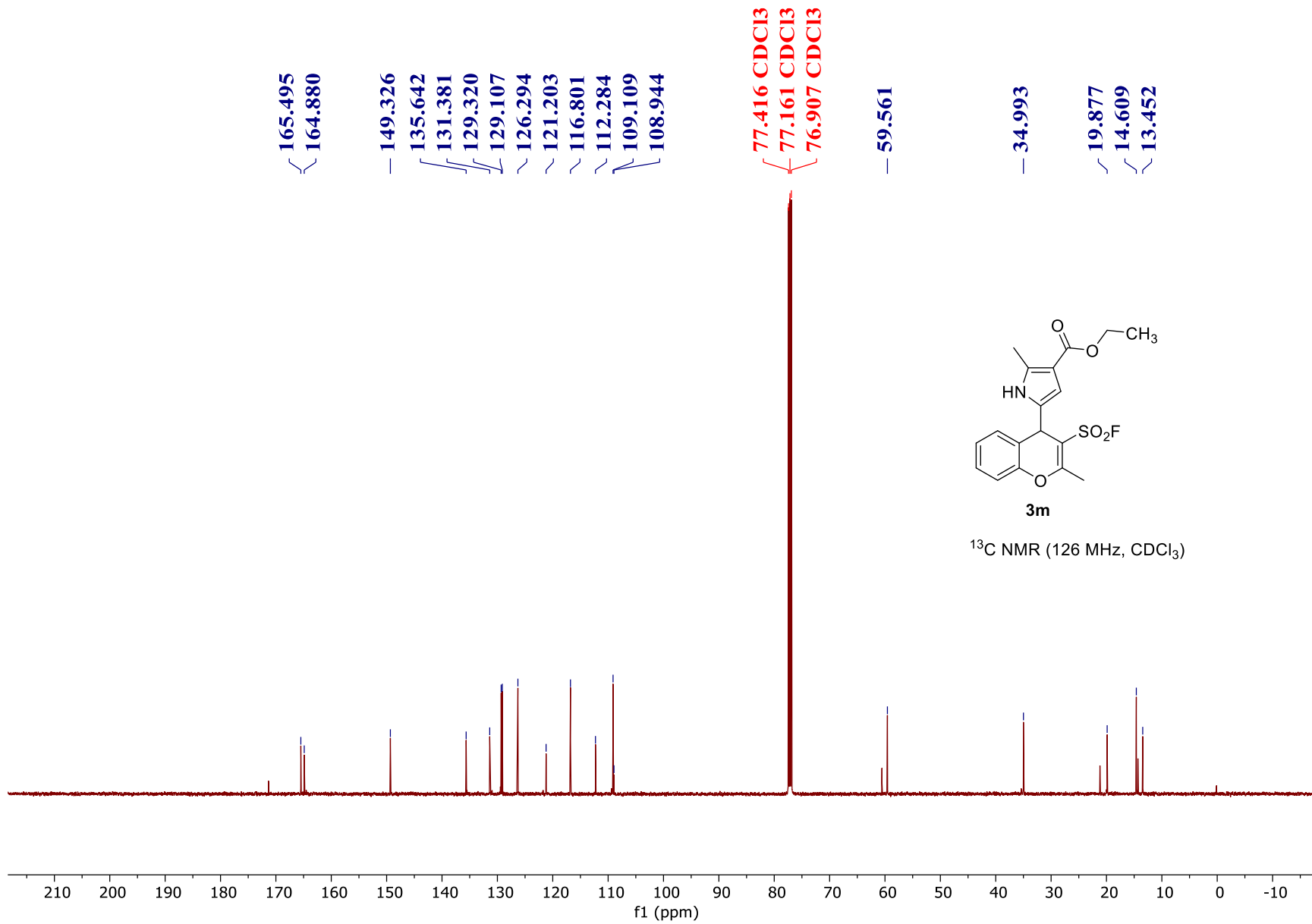
— 69.366

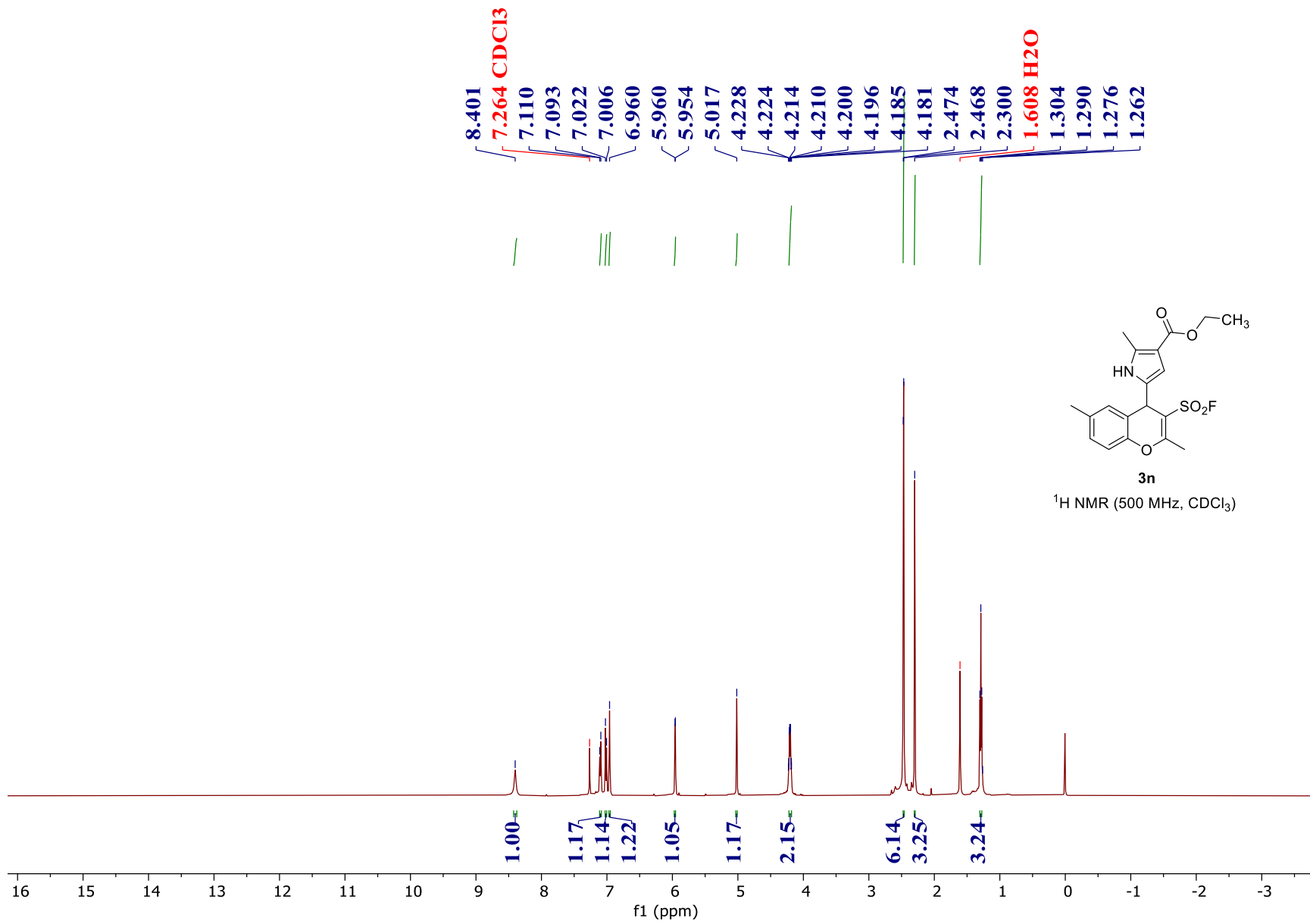


3m

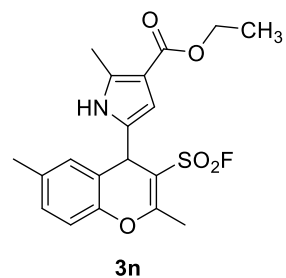
¹⁹F NMR (471 MHz, CDCl₃)



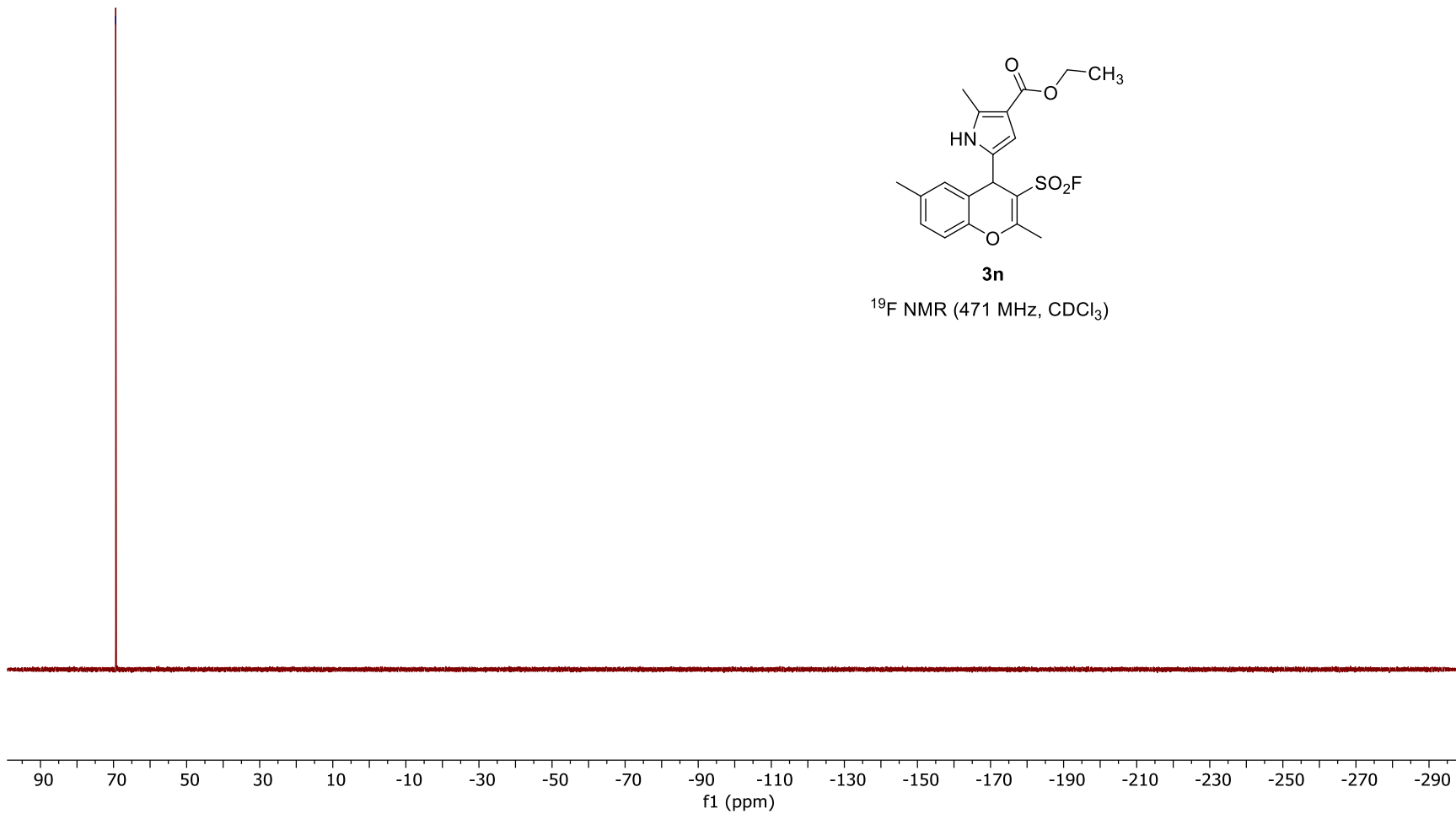


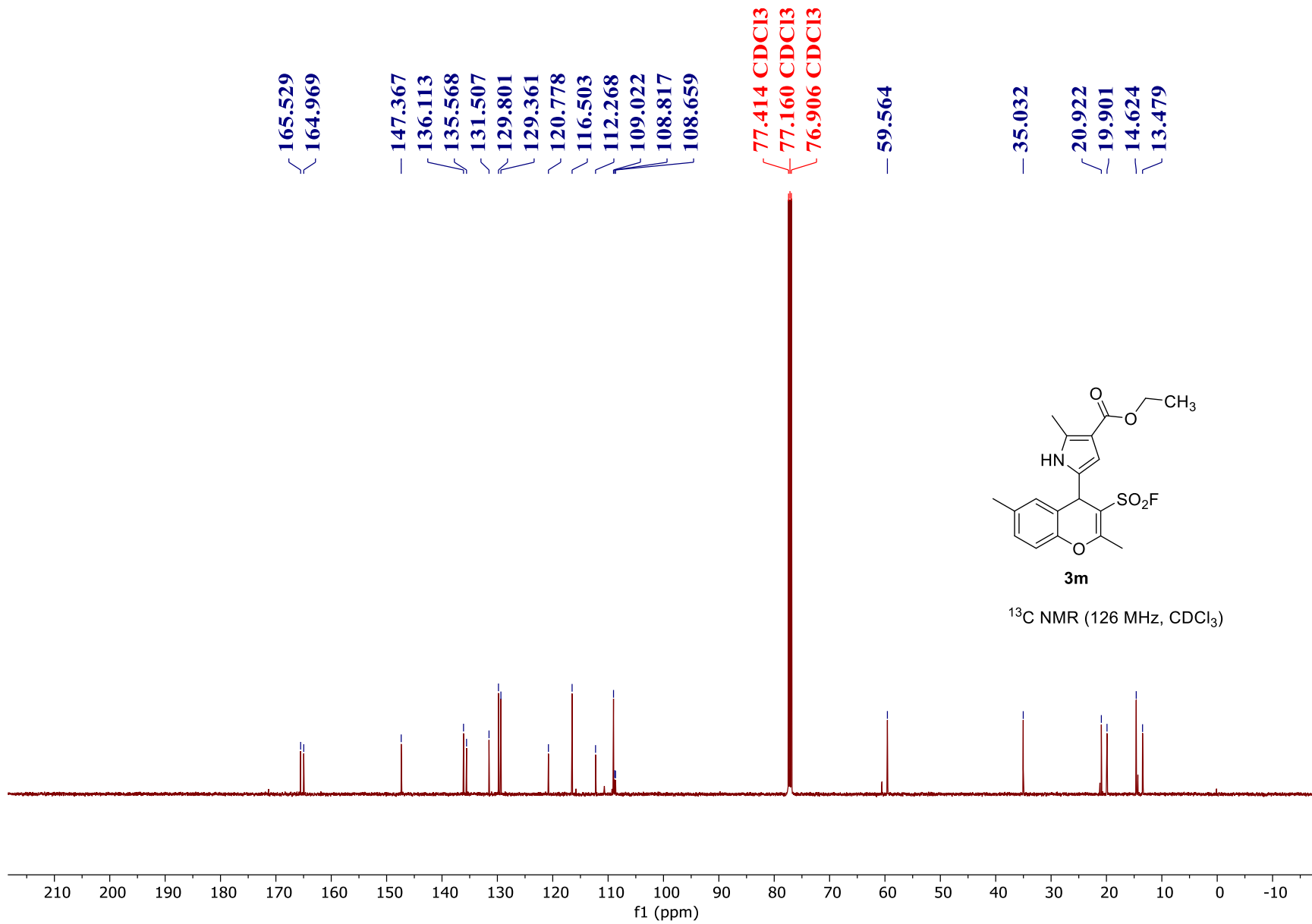


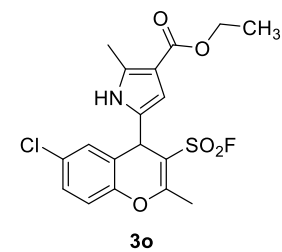
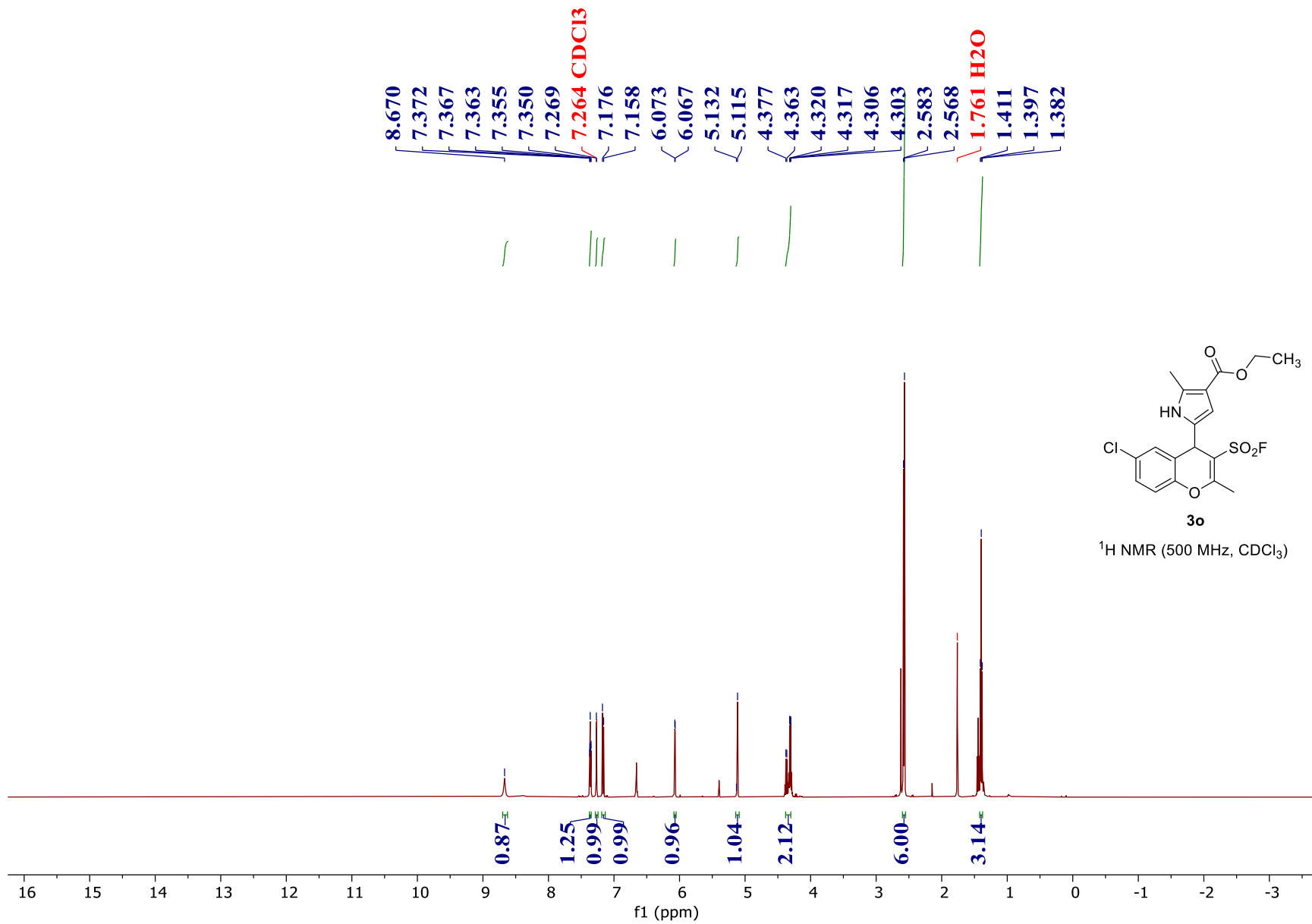
— 69.397



¹⁹F NMR (471 MHz, CDCl₃)

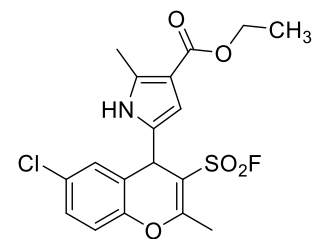






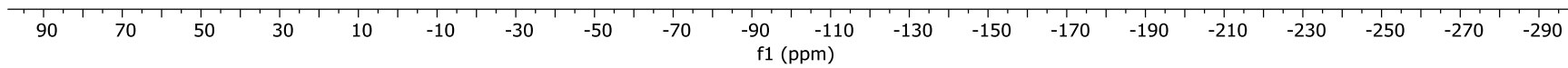
¹H NMR (500 MHz, CDCl₃)

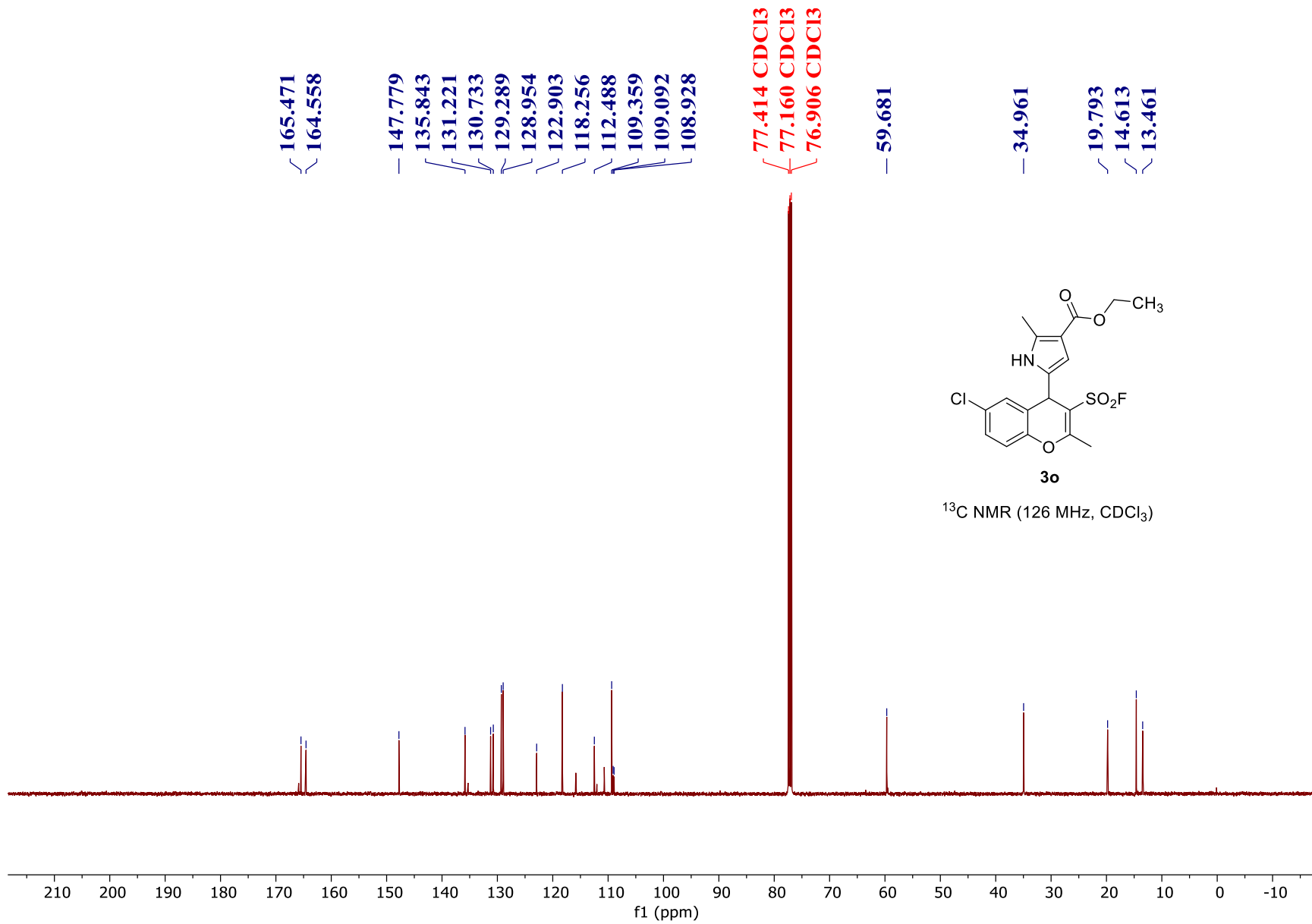
— 69.558

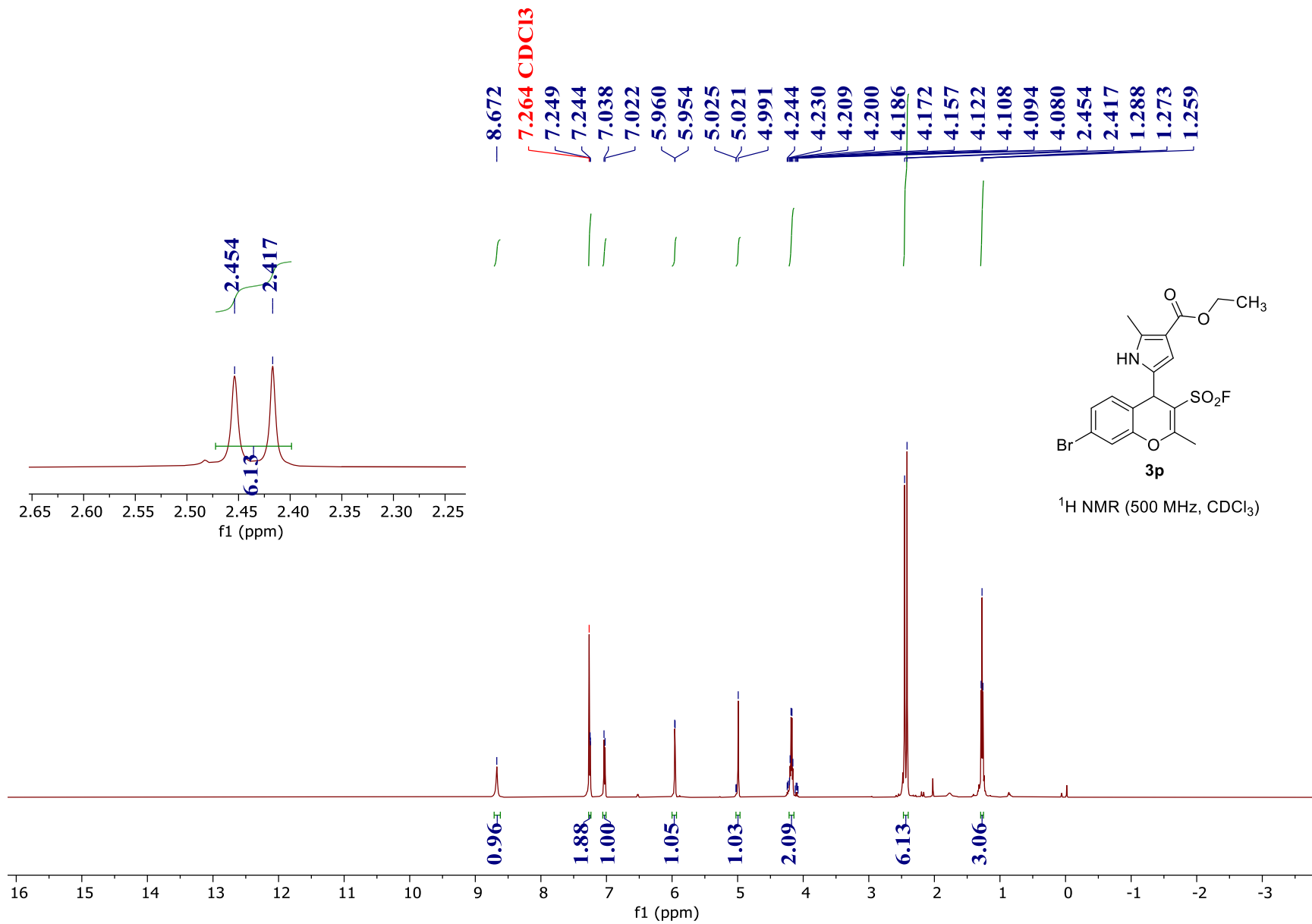


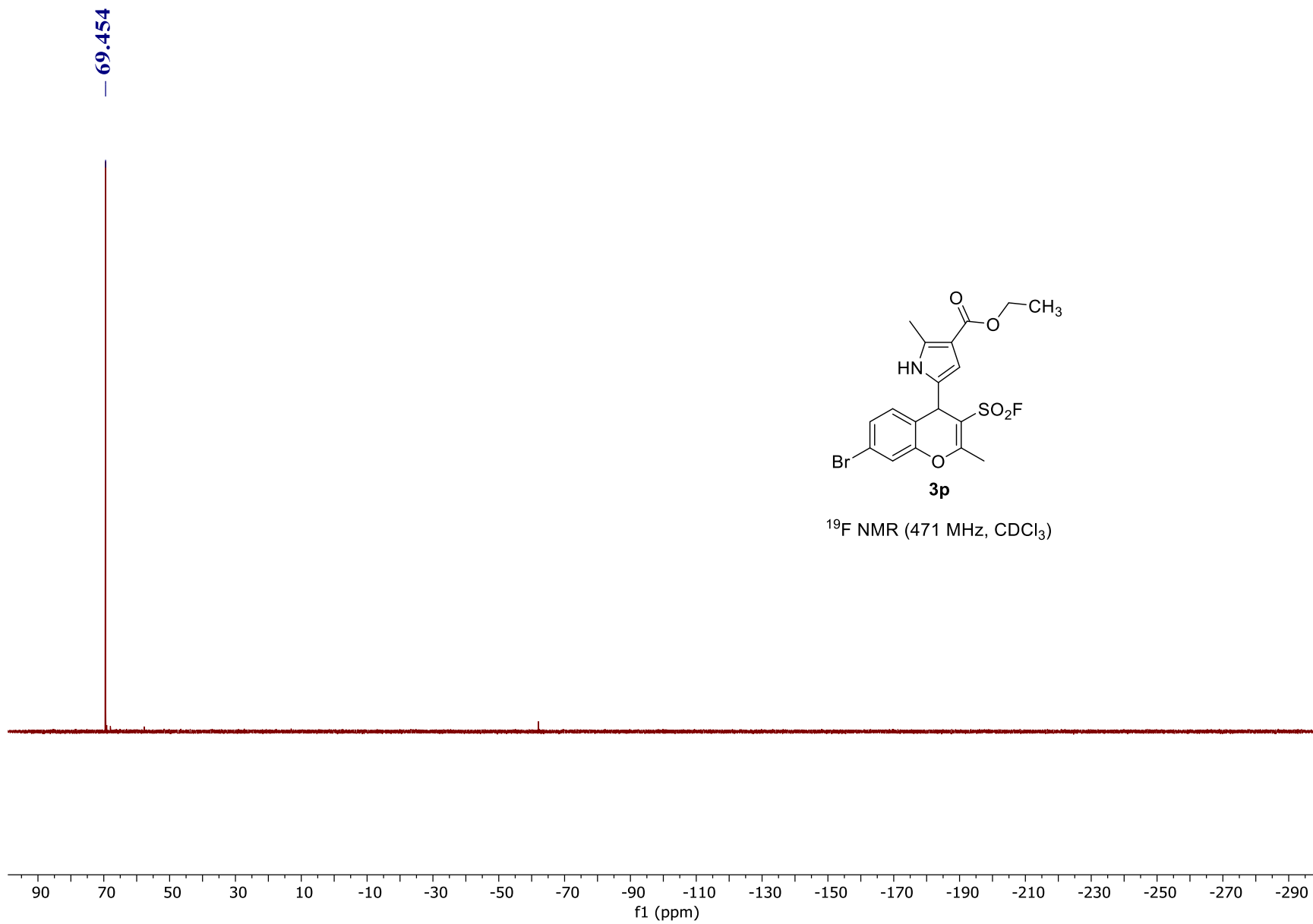
3o

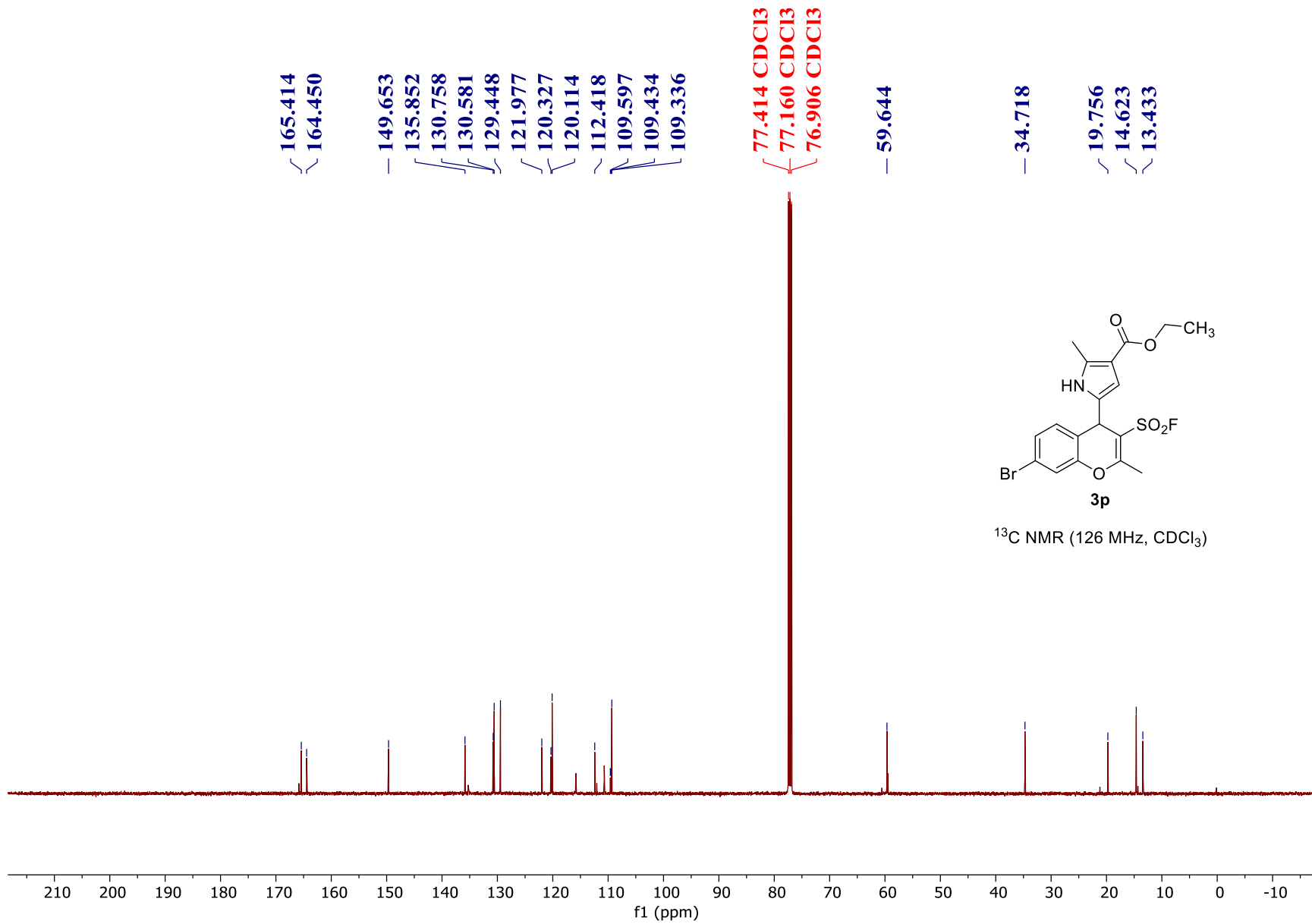
¹⁹F NMR (471 MHz, CDCl₃)

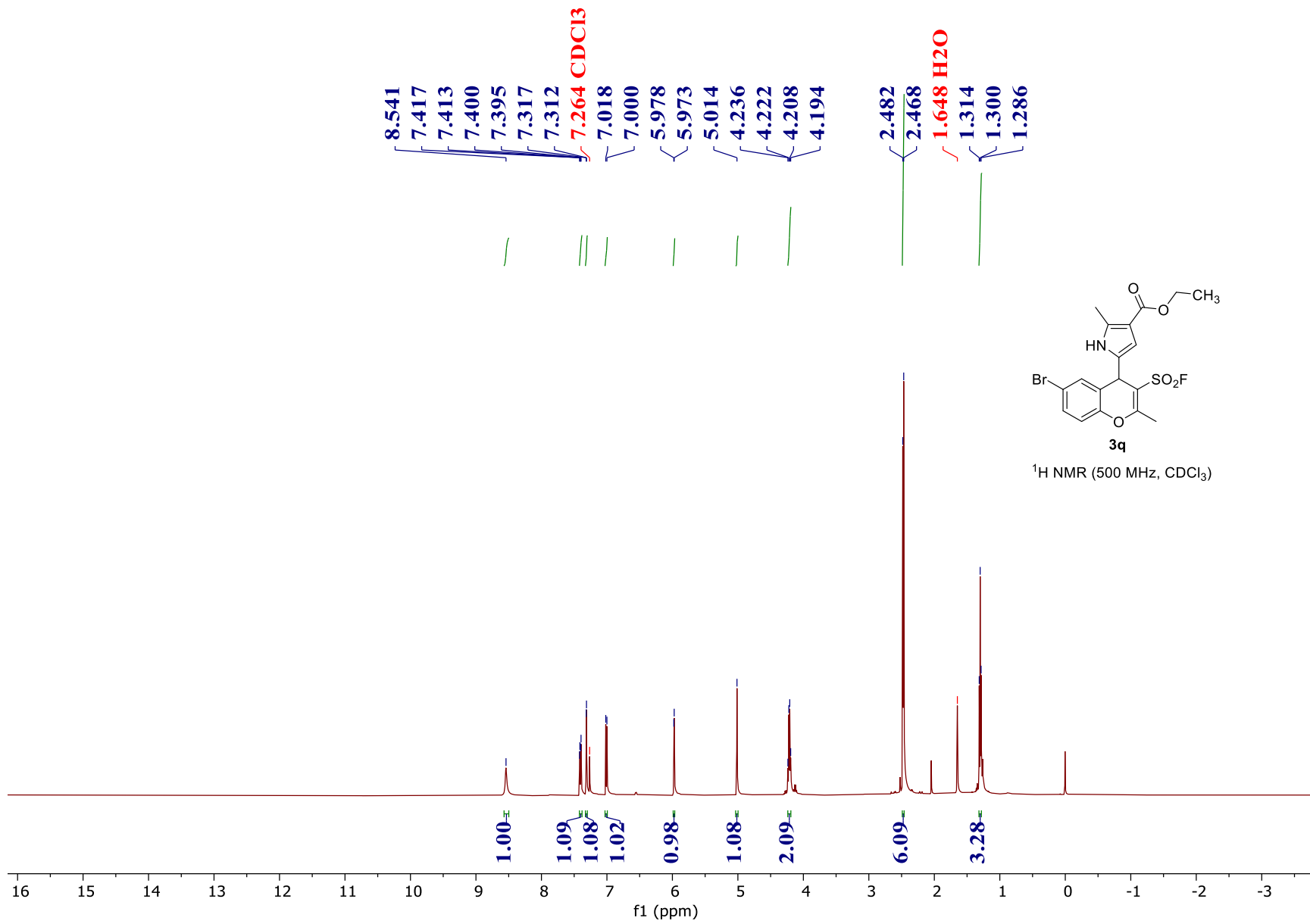


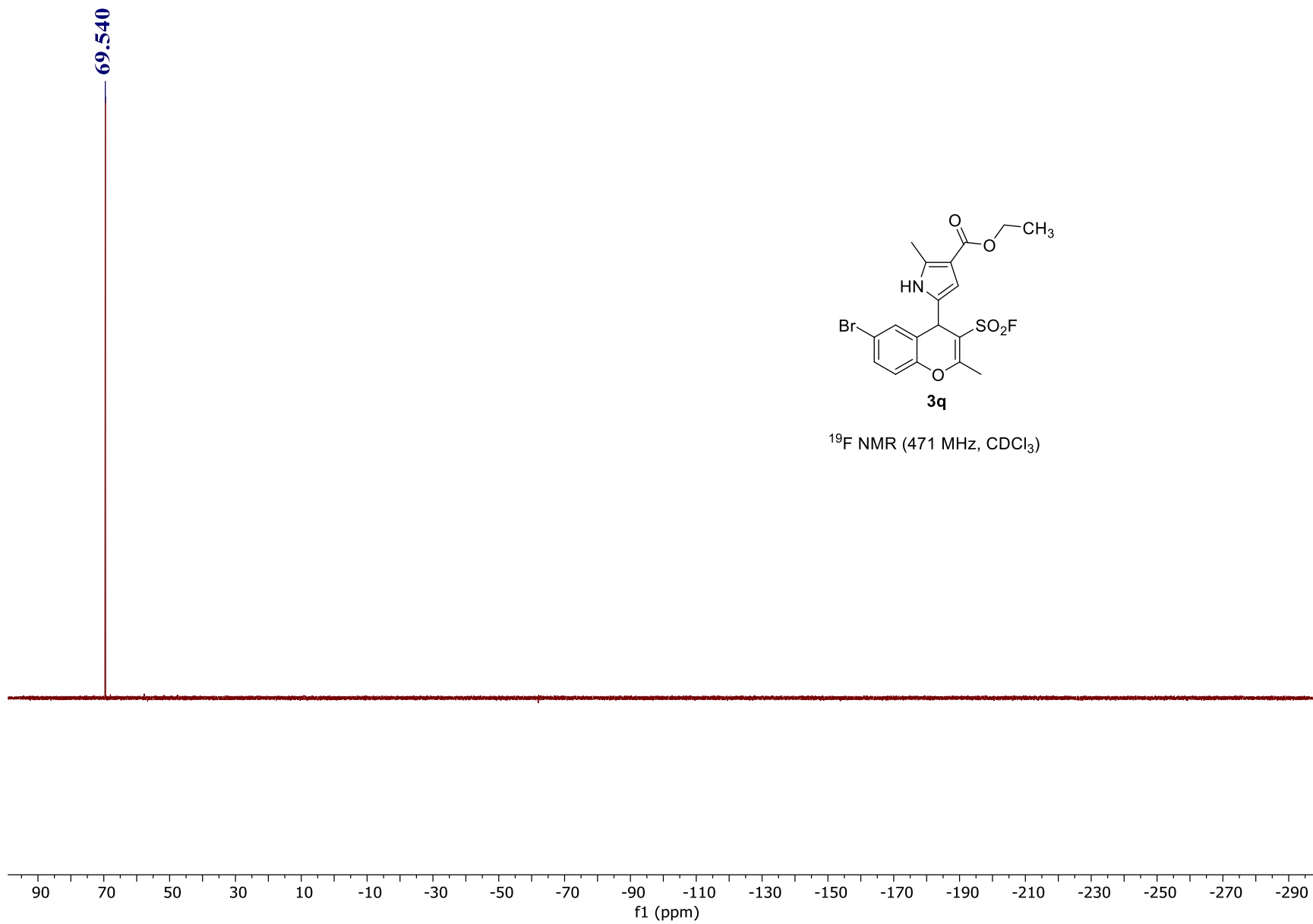


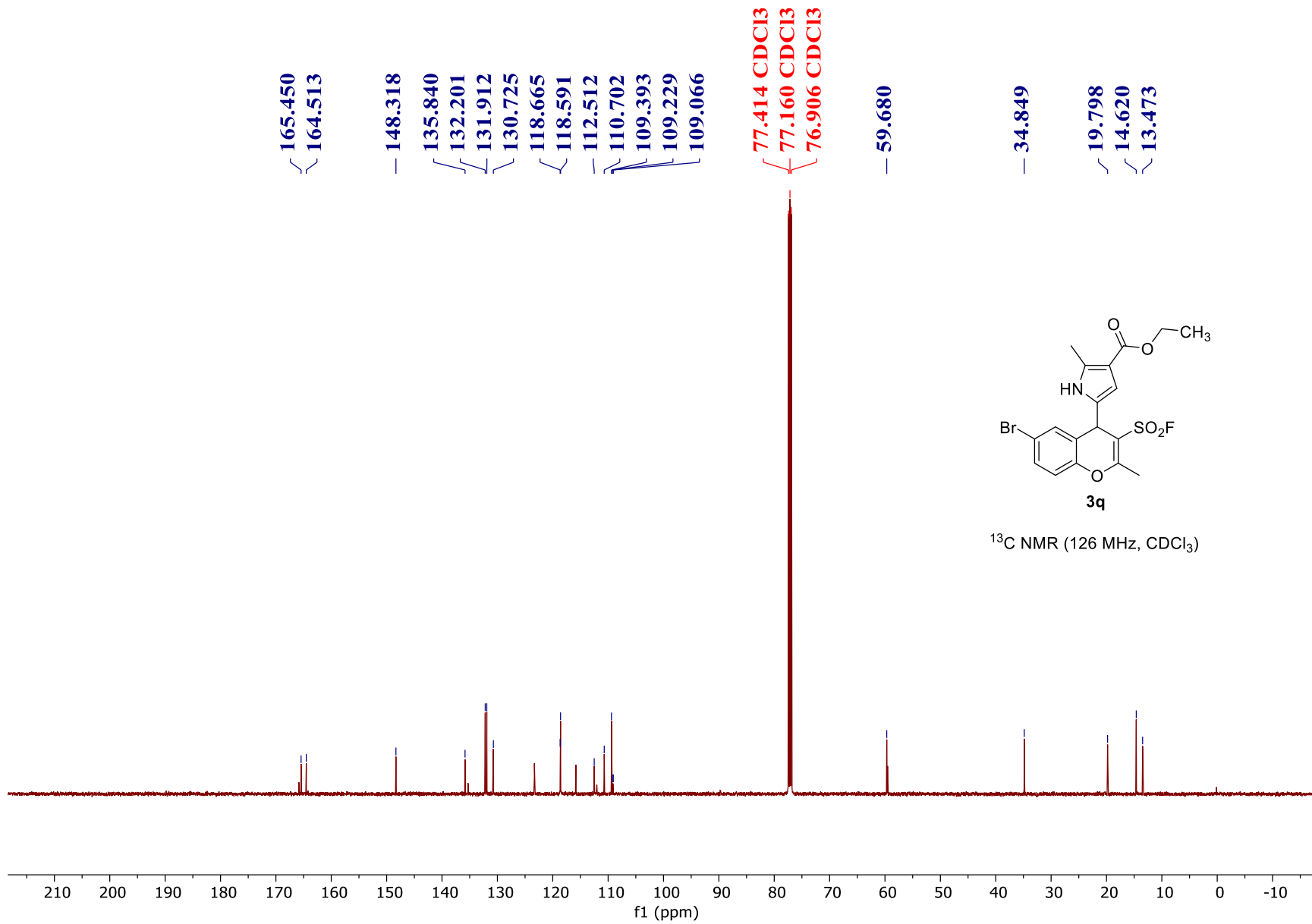


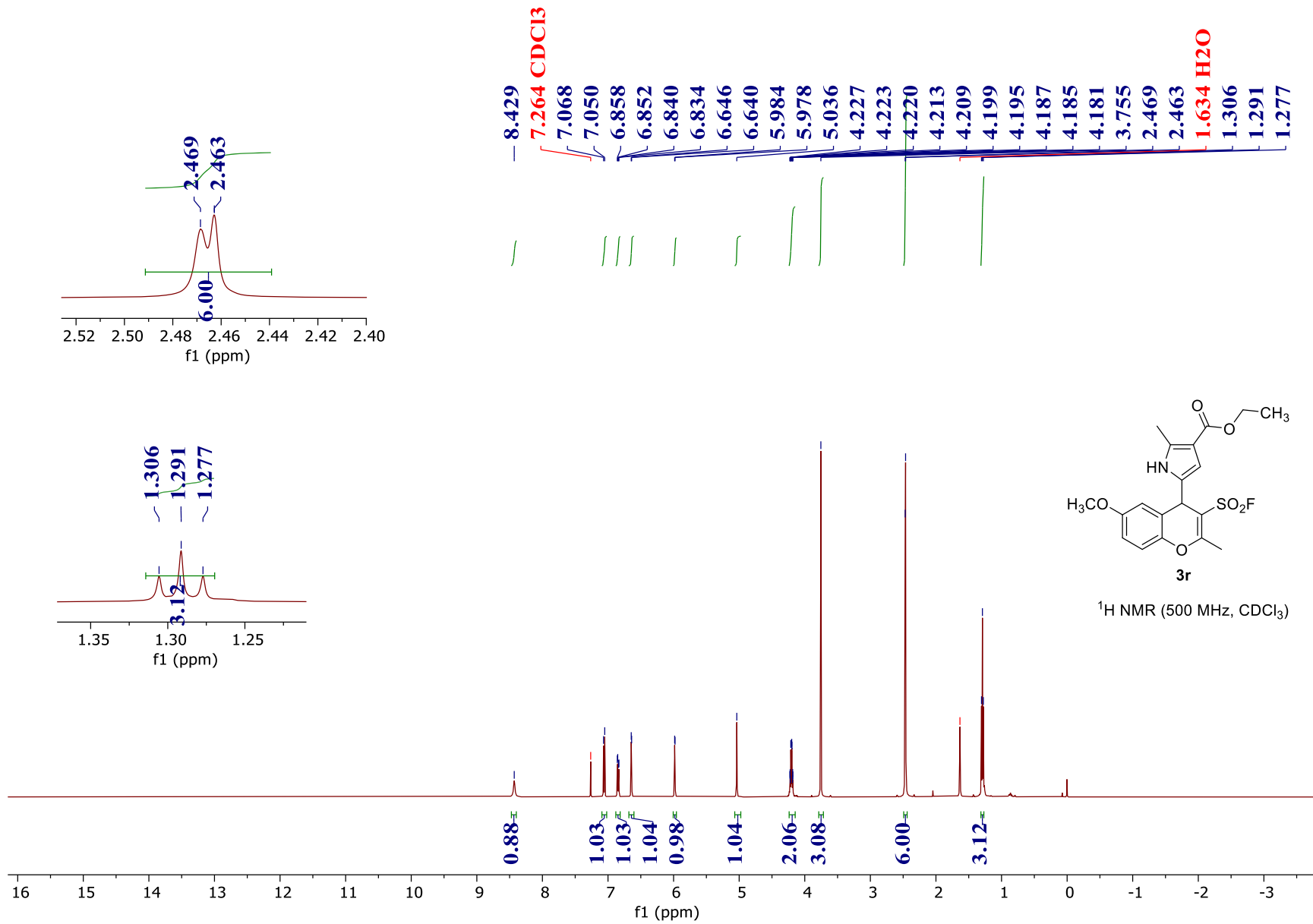




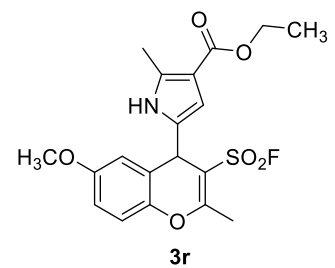








— 69.540



¹⁹F NMR (471 MHz, CDCl₃)

