Supporting Information

A cascade reaction for regioselective construction of pyrazole-containing aliphatic sulfonyl fluorides

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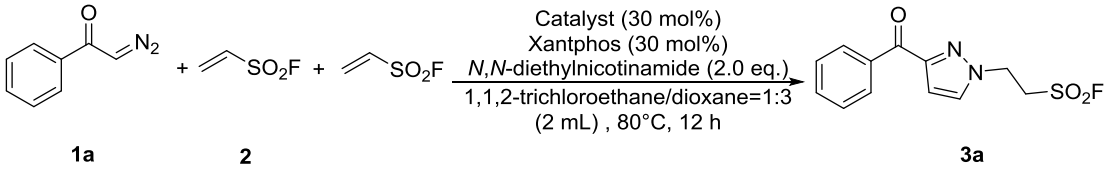
1. General Information

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 all chemical shifts are reported in ppm relative to TMS (0 ppm) as an internal standard. 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. Other reagents used in the reactions were all purchased from commercial sources and used without further purification. The product spots on the thin layer chromatography (TLC) were visualized under ultraviolet light (254 nm or 365 nm) followed by staining with potassium permanganate or phosphomolybdic acid.

2. Optimization of the Reaction Conditions

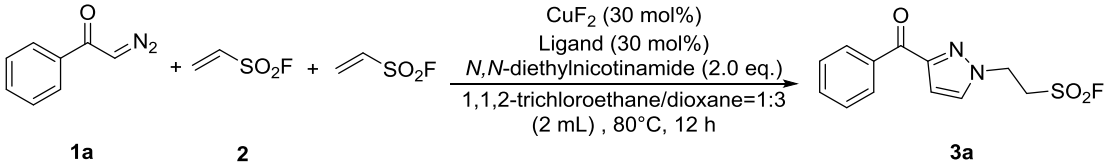
Table S1 Screening of the catalytic system[a]



Entry	Catalyst (30 mol%)	Yield (**3a**,%)[b]
1	CuBr	15
2	CuCl	Trace
3	CuI	Trace
4	Cu_2O	27
5	**CuF_2**	**70**
6	$CuBr_2$	17
7	$Cu(acac)_2$	19
8	$Cu(PF_6)(CH_3CN)_4$	21
9	/	N.D.

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), *N,N*-diethylnicotinamide (71 mg, 0.4 mmol, 2.0 equiv.), Cu catalyst (30 mol%) and Xantphos (30 mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at 80 °C for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

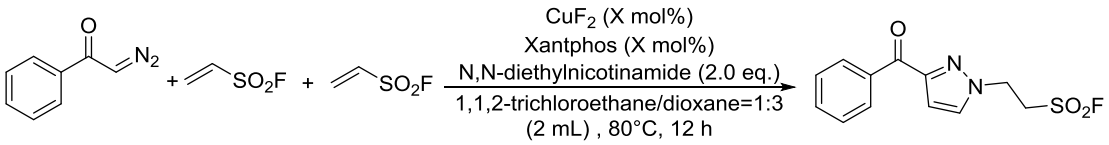
Table S2 Screening of the ligand[a]



Entry	Ligand (30 mol%)	Yield (**3a**,%)[b]
1	/	20
2	DPPF	27
3	DPPB	36
4	DPPP	Trace
5	DPPE	Trace
6	**Xantphos**	**70**
7	DPE-phos	Trace
8	X-phos	38
9	Ph_3P	20

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), *N,N*-diethylnicotinamide (71 mg, 0.4 mmol, 2.0 equiv.), CuF_2 (30 mol%) and ligand (30 mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at 80 °C for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

Table S3 Screening the loading amount of Cu catalyst and Ligand[a]

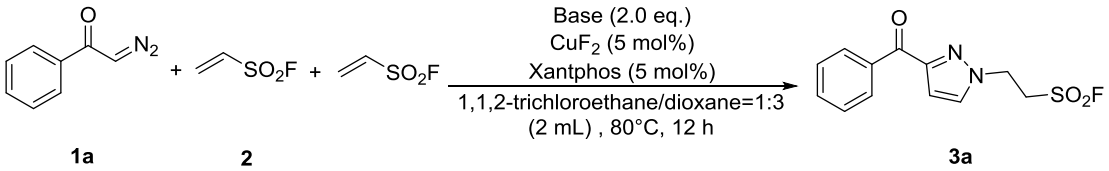


1a **2** **3a**

Entry	CuF_2 (X mol%)	Xantphos (X mol%)	Yield (**3a**,%)[b]
1	/	/	N.D.
2	3	3	59
3	**5**	**5**	**71**
4	10	10	68
5	20	20	70
6	30	30	70
7	40	40	73

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), *N,N*-diethylnicotinamide (71 mg, 0.4 mmol, 2.0 equiv.), CuF_2 (X mol%) and Xantphos (X mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at 80 °C for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

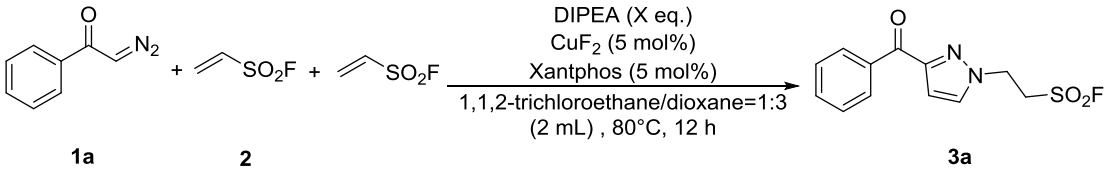
Table S4 Screening of the Base[a]



Entry	Base	Yield (**3a**,%)[b]
1	Et_3N	76
2	**DIPEA**	**89**
3	TMEDA	67
4	DBU	18
5	Pyridine	82
6	K_2CO_3	62
7	Na_2CO_3	50
8	$NaHCO_3$	75
9	NaOH	35
10	Cs_2CO_3	69
11	NaOAc	44
12	Na_3PO_4	57
12	KF	40

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), base (0.4 mmol, 2.0 equiv.), CuF_2 (5 mol%) and Xantphos (5 mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at 80 ^oC for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

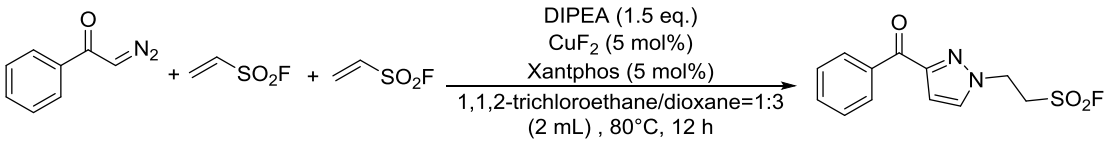
Table S5 Screening the base equivalent[a]



Entry	DIPEA (X equiv.)	Yield (**3a**,%)[b]
1	1	40
2	1.3	66
3	**1.5**	**92**
4	2.0	89
5	2.5	67
6	3.0	64

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), DIPEA (X equiv.), CuF_2 (5 mol%) and Xantphos (5 mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at 80 ^{o}C for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

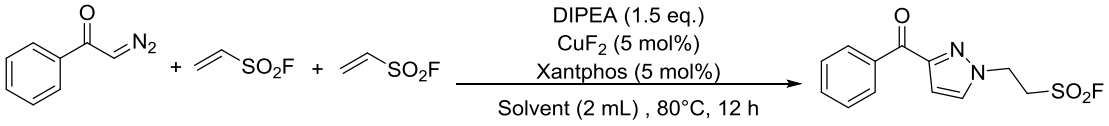
Table S6 Screening the ESF equivalent[a]



Entry	ESF (X equiv.)	Yield (**3a**,%)[b]
1	2	38
2	3	65
3	**4**	**92**
4	5	96
5	6	97

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, X equiv.), DIPEA (39 mg, 0.3 mmol, 1.5 equiv.), CuF_2 (5 mol%) and Xantphos (5 mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at 80 ^{o}C for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

Table S7 Screening of the solvent[a]

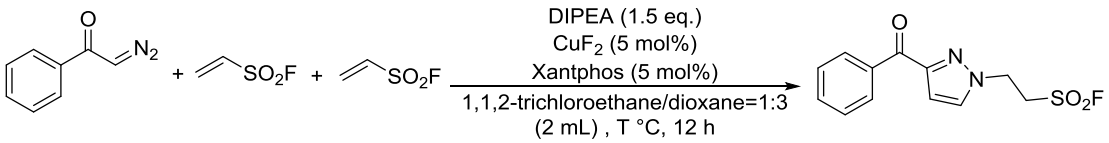


1a **2** **3a**

entry	Solvent	Yield(**3a**,%)[b]
1	Dioxane	79
2	**1,1,2-trichloroethane/dioxane (v/v = 1:3)**	**92**
3	1,1,2-trichloroethane/ dioxane (v/v = 1:2)	78
4	1,1,2-trichloroethane/ dioxane (v/v = 1:1)	74
5	1,1,2-trichloroethane/ dioxane (v/v = 2:1)	71
6	1,1,2-trichloroethane/ dioxane (v/v = 3:1)	68
7	1,1,2-trichloroethane	61
8	THF	62
9	DMF	trace
10	Toluene	70
11	DCE	60
12	MeCN	14
13	DMSO	trace
14	1,3-Dichloropropane	67

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), DIPEA (39 mg, 0.3 mmol, 1.5 equiv.), CuF_2 (5 mol%) and Xantphos (5 mol%) dissolved in solvent was stirred at 80 °C for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

Table S8 Screening of the reaction temperature[a]

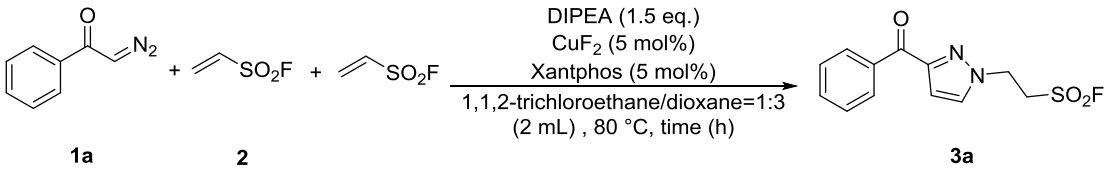


1a **2** **3a**

Entry	Temperature (^{o}C)	Yield(**3a**,%)[b]
1	r.t.	32
2	40	65
3	60	70
4	**80**	**92**
5	100	59

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), DIPEA (39 mg, 0.3 mmol, 1.5 equiv.), CuF_2 (5 mol%) and Xantphos (5 mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at the corresponding temperature for 12 h under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v)).

Table S9 Screening the reaction time[a]

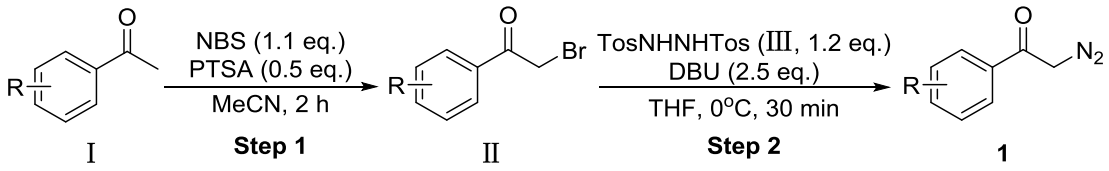


Entry	Time (h)	Yield(**3a**,%)[b]
1	1	58
2	3	74
3	**6**	**90**
4	9	93
5	12	92

[a]Reaction conditions：a mixture of α-diazoacetophenone (**1a**, 29 mg, 0.2 mmol, 1.0 equiv.), ethenesulfonyl fluoride (ESF, **2**, 0.8 mmol, 4.0 equiv.), DIPEA (39 mg, 0.3 mmol, 1.5 equiv.), CuF_2 (5 mol%) and Xantphos (5 mol%) dissolved in co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 2 mL) was stirred at 80 °C for the corresponding time under air atmosphere. [b]HPLC yield ($t_{R,\mathbf{3a}}$ = 4.5 min, $\lambda_{max,\mathbf{3a}}$ = 258.3 nm, water/methanol = 30 : 70 (v/v))

3. Experimental Procedures

3.1 General procedure for preparation of α-diazocarbonyl compounds (**1**)



3.1.1 Preparation of the substituted 2-bromoacetophenones.[1]

Step 1: An oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar was charged with substituted acetophenone (**I**, 10 mmol), *p*-toluenesulfonic acid (PTSA, 0.95 g, 5 mmol, 0.5 equiv), NBS (1.96 g, 11 mmol, 1.1 equiv) and acetonitrile (40 mL). The resulting mixture was stirred at room temperature for five minutes and then refluxed for 3 h. When the reaction reached its completion, the reaction mixture was diluted with water and the aqueous phrase was

extracted with dichloromethane (30 mL×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. Then the organic solvent was removed under vacuum on a rotary evaporator and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent to afford the substituted 2-bromoacetophenones (**II**).

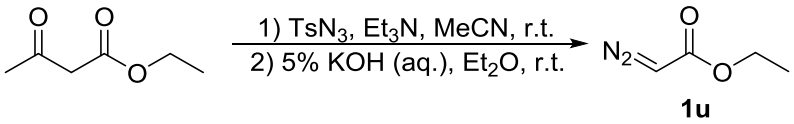
3.1.2 Preparation of *N*, *N*′-Bis(*p*-toluenesulfonyl)hydrazine (**III**).[2]

A mixture of *p*-toluenesulfonyl hydrazide (9.5 g, 50 mmol, 1.0 equiv.) and *p*-toluenesulfonyl chloride (12.4 g, 65 mmol, 1.3 equiv.) in DCM (50 mL) was cooled to 0 ^oC before the slow addition of pyridine (5.1 g, 65 mmol, 1.3 equiv.). The reaction mixture became homogenous and turned yellow gradually with the generation of white precipitates during the addition. The reaction mixture was further stirred for 1 h, then n-Hexane (50 mL) and H_2O (70 mL) were added, and the stirring lasted for 15 min under the ice bath. The white precipitates were collected by filtration and washed with ice-cooled Et_2O (100 mL), then dried under air to afford the product *N*,*N*'-ditosylhydrazine (**III**, 12.7 g, 75%)

3.1.3 Preparation of α-diazocarbonyl compounds (**1**).[2]

Step 2: A mixture of the substituted 2-bromoacetophenones (**II**, 10 mmol), *N*, *N*'-ditosylhydrazine (3.74 g, 11 mmol, 1.1 equiv.) in THF (40 mL) was stirred at 0 ^oC for 5 min, then DBU (3.8 g, 25 mmol, 2.5 equiv.) was added dropwise. After the addition was complete, the resulting mixture was allowed to stir at 0 °C for 0.5 h. The reaction mixture was poured into saturated aqueous solution of sodium bicarbonate (20 mL) and stirred for several minutes. The organic layer was separated and the aqueous phrase was extracted with ethyl acetate (50 mL×3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The organic solvent was removed under vacuum on a rotary evaporator and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent to afford the α-diazocarbonyl compounds (**1**).

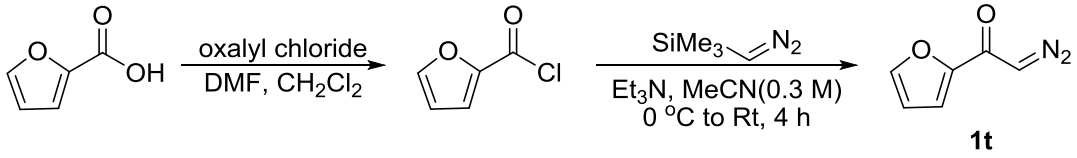
3.2 Preparation of ethyl diazoacetate (**1u**).[3]



1u

To a mixture of ethyl acetoacetate (9.11 g, 70 mmol) and Et_3N (9.19 g, 91 mmol, 1.3 equiv.) in MeCN (84 mL) slowly added a solution of *p*-toluenesulfonyl azide (15.19 g, 77 mmol, 1.1 equiv) dissolved in MeCN (84 mL) under the ice bath. After the completion of the addition, the reaction mixture was warmed to room temperature and the stirring lasted overnight. The solvent was evaporated with a rotary evaporator and the residue re-dissolved with ethyl ether (420 mL), then 5% aqueous solution of potassium hydroxide (350 mL) was added. The reaction mixture was left to stir at room temperature for 1 hour. The organic layer was separated and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel chromatography to give a final yellow liquid (**1u**) with the yield of (85%, 6.78 g)

3.3 Preparation of 2-diazo-1-(furan-2-yl)ethan-1-one (**1t**).[4]



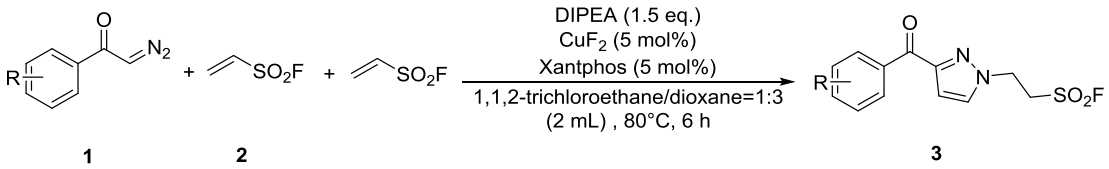
1t

An oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar was charged with furan-2-carboxylic acid (1.12 g, 10 mmol), CH_2Cl_2 (133 mL) and DMF (18.33 mg, 0.25 mL), and the mixture was cooled to 0 ^oC with an ice bath. Oxalyl chloride (1.27 g, 20 mmol, 2.0 equiv) was subsequently introduced dropwise and the mixture reacted at room temperature for 3 h. The organic solvent was removed under vacuum to obtain the crude furan-2-carbonyl chloride, which was used for next step without further purification.

To a solution of trimethylsilyl diazomethane (2M in Et_2O) (1.37 g, 12 mmol, 1.2

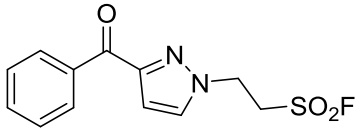
equiv,) and triethylamine (1.01 g, 10 mmol, 1.0 equiv) in acetonitrile (20 mL) added the crude furan-2-carbonyl chloride dropwise at 0 °C under Argon atmosphere. Then the mixture reacted at room temperature until the furan-2-carbonyl chloride was completely consumed (Monitored by TLC). The desired product (**1t,** 544 mg, 40%) was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1, v/v) as eluent.

3.4 General procedure for preparation of **3a-3u**



An oven-dried reaction tube equipped with a magnetic stirring bar was charged with α-diazocarbonyl compounds (**1**, 1 mmol), CuF_2 (5 % mol, 5 mg), Xantphos (5 % mol, 30 mg), DIPEA (1.5 mmol, 1.5 equiv, 194 mg), ethenesulfonyl fluoride (ESF, 4.0 mmol, 4.0 equiv, 440 mg) and co-solvent 1,1,2-trichloroethane/dioxane (v/v = 1:3, 10 mL). Then the mixture reacted at 80 °C for 6 h under air atmosphere. The organic solvent was removed under vacuum and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent to afford the title products **3**.

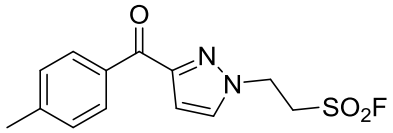
4. Characterization



3a

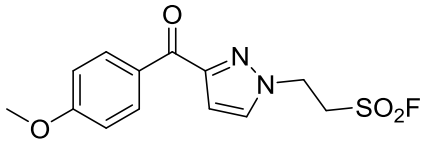
2-(3-benzoyl-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3a**). Yellow viscous liquid, 257 mg, 91 % yield. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, J = 7.4 Hz, 2H), 7.61-7.58 (m, 2H), 7.49 (t, J = 7.6 Hz, 2H), 6.94 (d, J = 2.3 Hz, 1H), 4.76 (t, J = 6.3 Hz, 2H), 4.07 (q, J = 5.9 Hz, 2H). **^{19}F NMR** (471 MHz,

$CDCl_3$) δ 57.5 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.6, 152.2, 137.1, 132.9, 131.8, 130.4, 128.3, 109.9, 50.4 (d, J = 17.2 Hz), 46.4. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{11}FN_2O_3S]^+$ ($[M+H]^+$): 283.0545, found: 283.0547.



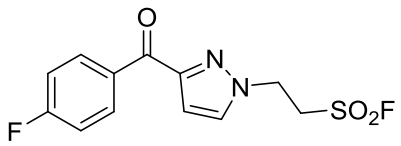
3b

2-(3-(4-methylbenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3b**). Light yellow powder, 263 mg, 89 % yield. M.p. 93-95 ^{o}C. Purified 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 8.09 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 2.2 Hz, 1H), 7.29 (d, J = 7.9 Hz, 2H), 6.92 (d, J = 2.3 Hz, 1H), 4.76 (t, J = 6.5 Hz, 2H), 4.06 (q, J = 5.8 Hz, 2H), 2.43 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.6 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.3, 152.3, 143.8, 134.5, 131.6, 130.5, 129.0, 109.8, 50.4 (d, J = 17.2 Hz), 46.4, 21.7. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{13}FN_2O_3S]^+$ ($[M+H]^+$): 297.0765, found: 297.0766.



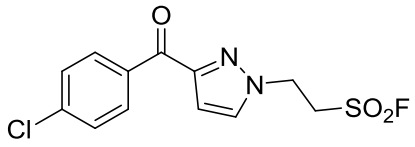
3c

2-(3-(4-methoxybenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3c**). Light yellow solid, 284 mg, 91 % yield. M.p. 60-62 ^{o}C. Purified 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 8.25 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 1.9 Hz 1H), 6.97 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 1.9 Hz, 1H), 4.76 (t, J = 6.5 Hz, 2H), 4.07 (q, J = 5.9 Hz, 2H), 3.89 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.6 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.9, 163.6, 152.5, 132.8, 131.6, 129.8, 113.6, 109.8, 55.5, 50.5 (d, J =17.3 Hz), 46.3. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{13}FN_2O_4S]^+$ ($[M+H]^+$): 313.0720, found: 313.0723.



3d

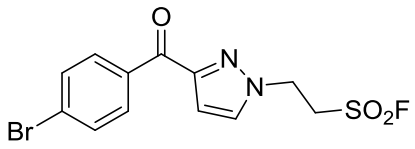
2-(3-(4-fluorobenzoyl)-1H-pyrazol-1-yl)ethane-1-sulfonyl fluoride (**3d**). Light yellow solid, 264 mg, 88 % yield. M.p. 54-56 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30-8.27 (m, 2H), 7.58 (d, J = 2.5 Hz, 1H), 7.19-7.15 (m, 2H), 6.97 (d, J = 2.5 Hz, 1H), 4.78 (t, J = 6.5 Hz, 2H), 4.07 (q, J = 5.9 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.8 (s, 1F), −105.38—−105.44 (m, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.7, 165.8 (d, J = 254.4 Hz), 152.1, 133.3 (d, J = 2.8 Hz), 133.1 (d, J = 9.1 Hz), 131.8, 115.4 (d, J = 21.8 Hz), 110.0, 50.5 (d, J = 18.1 Hz), 46.4. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{10}F_2N_2O_3S]^+$ ($[M+H]^+$): 301.0545, found: 301.0547.



3e

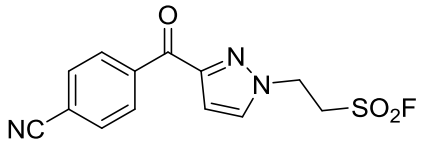
2-(3-(4-chlorobenzoyl)-1H-pyrazol-1-yl)ethane-1-sulfonyl fluoride (**3e**). Light yellow solid, 284 mg, 90 % yield. M.p. 83-85 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.24 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 2.1 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 1.9 Hz, 1H), 4.85 (t, J = 6.1 Hz, 2H), 4.64 (q, J = 6.0 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.8 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.1, 152.0, 139.4, 135.3, 131.9, 128.6, 110.0, 50.4 (d, J = 17.2 Hz), 46.4. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{10}ClFN_2O_3S]^+$ ($[M+H]^+$): 317.0260, found: 317.0258.

Note: In the ^{13}C NMR spectrum of **3e**, theoretically, there should be ten peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



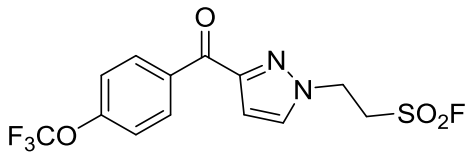
3f

2-(3-(4-bromobenzoyl)-1H-pyrazol-1-yl)ethane-1-sulfonyl fluoride (**3f**). Yellowish solid, 317 mg, 88 % yield. M.p. 92-94 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.15 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 2.3 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 2.1 Hz, 1H), 4.85 (t, J = 6.2 Hz, 2H), 4.63 (q, J = 6.1 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.8 (s, 1F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 186.1, 150.6, 136.3, 133.5, 132.7, 131.9, 127.5, 109.4, 50.4 (d, J = 14.5 Hz), 46.6. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{10}BrFN_2O_3S]^+$ ($[M+H]^+$): 360.9760, found: 360.9763.



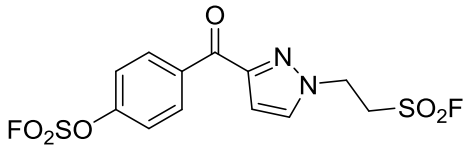
3g

2-(3-(4-cyanobenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3g**). Light yellow powder, 236 mg, 77 % yield. M.p. 111-113 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.30 (d, J = 8.2 Hz, 2H), 8.08 (d, J = 2.2 Hz, 1H), 8.00 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 2.1 Hz, 1H), 4.85 (t, J = 6.2 Hz, 2H), 4.63 (q, J = 6.1 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 58.0 (s, 1F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 186.2, 150.3, 140.8, 133.8, 132.8, 131.2, 118.8, 115.3, 109.5, 50.4 (d, J = 14.5 Hz), 46.6. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{10}FN_3O_3S]^+$ ($[M+H]^+$): 308.0570, found: 308.0570.



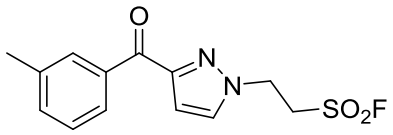
3h

2-(3-(4-(trifluoromethoxy) benzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3h**). Yellowish solid, 302 mg, 82 % yield. M.p. 46-48 ^{o}C. Purified 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 8.30 (d, J = 9.0 Hz, 2H), 7.59 (d, J = 2.4 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 2.5 Hz, 1H), 4.78 (t, J = 6.5 Hz, 2H), 4.07 (q, J = 5.9 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.8 (s, 1F), -57.5 (s, 3F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.7, 152.6, 152.0, 135.2, 132.5, 131.9, 120.4 (q, J = 258.9 Hz), 120.1, 110.0, 50.5 (d, J = 17.3 Hz), 46.5. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{10}F_4N_2O_4S]^+$ ($[M+H]^+$): 367.0466, found: 367.0464.



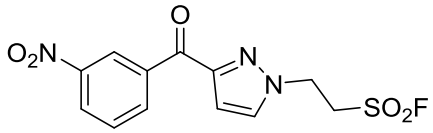
3i

4-(1-(2-(fluorosulfonyl) ethyl)-1H-pyrazole-3-carbonyl) phenyl sulfurofluoridate (**3i**). Light yellow solid, 287 mg, 76 % yield. M.p. 73-75 ^{o}C. Purified 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 8.38 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 2.3 Hz, 1H), 7.46 (d, J = 6.8 Hz, 2H), 7.00 (d, J = 2.4 Hz, 1H), 4.78 (t, J = 6.4 Hz, 2H), 4.07 (q, J = 5.6 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.9 (s, 1F), 38.8 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.3, 152.6, 151.7, 137.1, 132.9, 132.1, 120.7, 110.1, 50.4 (d, J = 17.3 Hz), 46.5. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{10}F_2N_2O_6S_2]^+$ ($[M+H]^+$): 380.9995, found: 381.0095.



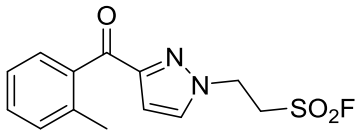
3j

2-(3-(3-methylbenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3j**). Yellow viscous liquid, 289 mg, 98 % yield. Purified 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 7.97 (d, J = 7.5 Hz, 1H), 7.93 (s, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.42-7.36 (m, 2H), 6.93 (d, J = 2.2 Hz, 1H), 4.76 (t, J = 6.4 Hz, 2H), 4.06 (q, J = 5.9 Hz, 2H), 2.43 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.7 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.0, 152.1, 138.1, 137.2, 133.7, 131.7, 130.7, 128.1, 127.7, 109.9, 50.4 (d, J = 17.2 Hz), 46.4, 21.4. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{13}FN_2O_3S]^+$ ($[M+H]^+$): 297.0765, found: 297.0771.



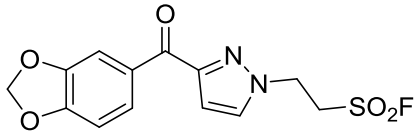
3k

2-(3-(3-nitrobenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3k**). Light brown solid, 245 mg, 75 % yield. M.p. 109-111 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.91 (s, 1H), 8.65 (d, J = 7.8 Hz, 1H), 8.49 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 2.1 Hz, 1H), 7.85 (t, J = 8.1 Hz, 1H), 7.01 (d, J = 2.3 Hz, 1H), 4.88 (t, J = 6.1 Hz, 2H), 4.64 (q, J = 6.0 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.9 (s, 1F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 185.1, 150.2, 148.1, 138.3, 136.8, 133.8, 130.6, 127.6, 125.1, 109.6, 50.4 (d, J = 14.5 Hz), 46.7. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_{10}FN_3O_5S]^+$ ($[M+H]^+$): 328.0490, found: 328.0493.



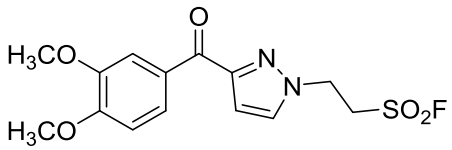
3l

2-(3-(2-methylbenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3l**). Yellow viscous liquid, 269 mg, 91 % yield. Purified 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 7.56-7.55 (m, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.29-7.24 (m, 2H), 6.84 (d, J = 1.8 Hz, 1H), 4.70 (t, J = 6.3 Hz, 2H), 4.00 (q, J = 5.8 Hz, 2H), 2.41 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.6 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 191.1, 152.7, 137.9, 137.5, 132.1, 131.2, 130.9, 129.6, 125.1, 109.6, 50.4 (d, J = 17.3 Hz), 46.4, 20.2. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{13}FN_2O_3S]^+$ ($[M+H]^+$): 297.0765, found: 297.0758.



3m

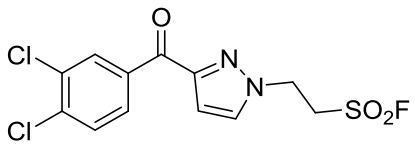
2-(3-(benzo[d] [1,3] dioxole-5-carbonyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3m**). Yellow viscous liquid, 287 mg, 88 % yield. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.01 (d, J = 2.3 Hz, 1H), 7.96 (dd, J_1 = 1.3 Hz, J_2 = 6.9 Hz, 1H), 7.73 (d, J = 1.4 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 2.3 Hz, 1H), 6.15 (s, 2H), 4.85 (t, J = 6.2 Hz, 2H), 4.62 (q, J = 5.9 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.7 (s,1F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 185.0, 151.9, 151.1, 147.9, 133.1, 131.5, 127.4, 110.1, 109.4, 108.4, 102.4, 50.5 (d, J = 14.6 Hz), 46.5. **HRMS-ESI** (m/z) calcd. for $[C_{13}H_{11}FN_2O_5S]^+$ ($[M+H]^+$): 327.0540, found: 327.0540.



3n

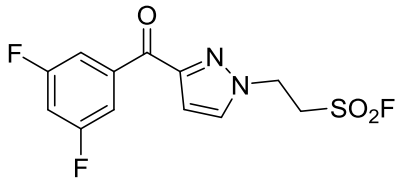
2-(3-(3,4-dimethoxybenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3n**). White

solid, 300 mg, 88 % yield. M.p. 109-111 ^{o}C. Purified 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 8.00 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.57 (d, J = 1.6 Hz, 1H), 6.95-6.93 (m, 2H), 4.77 (t, J = 6.4 Hz, 2H), 4.07 (q, J = 5.9 Hz, 2H), 3.96 (s, 3H). 3.95 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.7 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.9, 153.4, 152.5, 148.9, 131.5, 129.9, 125.8, 112.3, 110.0, 109.9, 56.1, 56.0, 50.4 (d, J = 18.1 Hz), 46.3. **HRMS-ESI** (m/z) calcd. for $[C_{14}H_{15}FN_2O_5S]^+$ ($[M+H]^+$): 343.0850, found: 343.0852.



3o

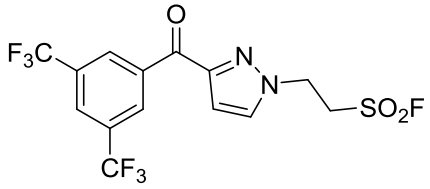
2-(3-(3,4-dichlorobenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3o**). Yellow solid, 284 mg, 81 % yield. M.p. 77-79 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, J = 1.9 Hz, 1H), 8.09 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 4.79 (t, J = 6.3 Hz, 2H), 4.06 (q, J = 5.9 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.9 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.7, 151.7, 137.4, 136.5, 132.8, 132.4, 132.0, 130.4, 129.5, 110.1, 50.4 (d, J = 18.1 Hz), 46.5. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_9Cl_2FN_2O_3S]^+$ ($[M+H]^+$): 350.9870, found: 350.9873.



3p

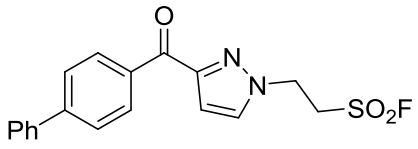
2-(3-(3,5-difluorobenzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3p**). Yellow lumpy solid, 277 mg, 87 % yield. M.p. 70-72 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, J = 6.4 Hz, 2H), 7.60 (d, J = 1.7 Hz, 1H), 7.04 (t, J = 8.4 Hz,

1H), 6.99 (d, J = 1.8 Hz, 1H), 4.79 (t, J = 6.4 Hz, 2H), 4.07 (q, J = 5.8 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.9 (s, 1F). −108.68— −108.72 (m, 2F) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.3, 162.6 (dd, J_1 = 249.8 Hz, J_2 = 11.8 Hz), 151.6, 139.6 (t, J = 8.2 Hz), 132.1, 113.5 (dd, J_1 = 20.9 Hz, J_2 = 6.4 Hz), 110.1, 108.1 (t, J = 25.5 Hz), 50.4 (d, J = 18.2 Hz), 46.5. **HRMS-ESI** (m/z) calcd. for $[C_{12}H_9F_3N_2O_3S]^+$ ($[M+H]^+$): 319.0457, found: 319.0455.



3q

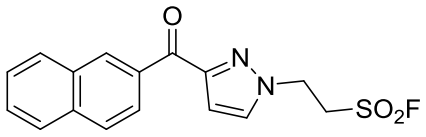
2-(3-(3,5-bis(trifluoromethyl)benzoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3q**). Yellow viscous liquid, 315 mg, 75 % yield. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (s, 2H), 8.09 (s, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.07 (d, J = 1.7 Hz, 1H), 4.80 (t, J = 6.2 Hz, 2H), 4.05 (q, J = 5.6 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.9 (s, 1F), −62.9 (s, 6F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.1, 151.2, 138.4, 132.4, 131.8 (q, J = 33.6 Hz), 130.67-130.65 (m), 125.9-125.8 (m), 123.1 (q, J = 272.5 Hz), 110.2, 50.2 (d, J = 18.2 Hz), 46.6. **HRMS-ESI** (m/z) calcd. for $[C_{14}H_9F_7N_2O_3S]^+$ ($[M+H]^+$): 419.0406, found: 419.0406.



3r

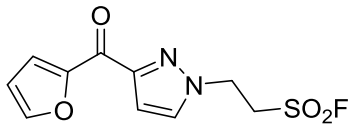
2-(3-([1,1'-biphenyl]-4-carbonyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3r)**. Off-white lumpy solid, 293 mg, 82 % yield. M.p. 120-122 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 2.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.1 Hz, 1H), 6.99 (d, J = 2.0 Hz, 1H), 4.79 (t, J = 6.4 Hz, 2H), 4.09 (q, J = 5.9

Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.7 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.0, 152.3, 145.6, 140.1, 135.8, 131.7, 131.0, 129.0, 128.2, 127.3, 127.0, 109.9, 50.5 (d, J = 17.3 Hz), 46.4. **HRMS-ESI** (m/z) calcd. for $[C_{18}H_{15}FN_2O_3S]^+$ ($[M+H]^+$): 359.0930, found: 359.0929.



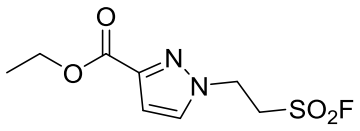
3s

2-(3-(2-naphthoyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3s)**. Yellow solid, 294 mg, 88 % yield. M.p. 93-95 ^oC. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.19 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.94-7.88 (m, 2H), 7.62-7.59 (m, 2H), 7.57-7.54 (m, 1H), 6.99 (d, J = 2.1 Hz, 1H), 4.78 (t, J = 6.4 Hz, 2H), 4.08 (q, J = 5.8 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.9 (s, 1F). **^{13}C NMR** (126 MHz, DMSO) δ 187.5, 152.3, 135.6, 134.4, 132.6, 132.4, 131.7, 129.8, 128.5, 128.1, 127.8, 126.7, 125.7, 110.0, 50.5 (d, J = 18.2 Hz), 46.4. **HRMS-ESI** (m/z) calcd. for $[C_{16}H_{13}FN_2O_3S]^+$ ($[M+H]^+$): 333.0780, found: 333.0779.



3t

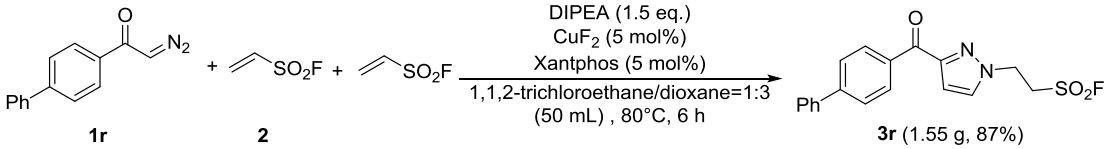
2-(3-(furan-2-carbonyl)-1H-pyrazol-1-yl) ethane-1-sulfonyl fluoride (**3t)**. White powder, 217 mg, 80 % yield. M.p. 148-150 ^oC. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.09-8.03 (m, 3H), 6.90-6.77 (m, 2H), 4.85-4.68 (m, 4H). **^{19}F NMR** (471 MHz, DMSO-d_6) δ 57.5 (s, 1F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 173.6, 151.0, 150.1, 148.9, 133.4, 123.1, 113.1, 108.5, 50.4 (d, J = 14.5 Hz), 46.5. **HRMS-ESI** (m/z) calcd. for $[C_{10}H_9FN_2O_4S]^+$ ($[M+H]^+$): 273.0420, found: 273.0421.



3u

ethyl 1-(2-(fluorosulfonyl)ethyl)-1H-pyrazole-3-carboxylate (**3u)**. Off-white powder, 165 mg, 66 % yield. M.p. 94-96 ^{o}C. Purified 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 7.53 (d, J = 2.0 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 4.73 (t, J = 6.5 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 4.04 (q, J = 6.0 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ 57.5 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8, 145.5, 132.1, 109.4, 61.2, 50.5 (d, J = 18.2 Hz), 46.5, 14.3. **HRMS-ESI** (m/z) calcd. for $[C_8H_{11}FN_2O_4S]^+$ ($[M+H]^+$): 251.0610, found: 251.0612.

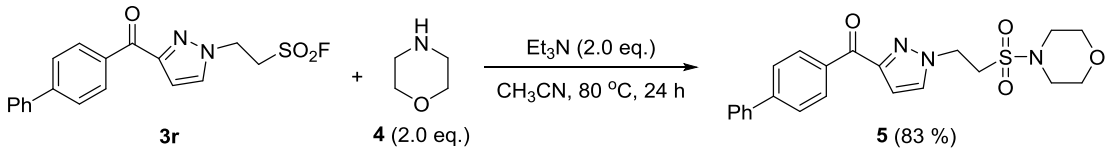
5. Procedure for Scale-up Reaction of 3r



1r **2** **3r** (1.55 g, 87%)

An oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar was charged with diazo (**1r**, 5 mmol, 1.11 g), CuF_2 (5 % mol, 25 mg), Xantphos (5 % mol, 145 mg), DIPEA (7.5 mmol, 1.5 equiv, 970 mg), ethenesulfonyl fluoride (ESF, **2**, 20.0 mmol, 4.0 equiv, 2.2 g) and co-solvent 1,1,2-trichloroethane/dioxane (v/v =1:3, 50 mL). Then the mixture reacted at 80 ^{o}C for 6 h under air atmosphere. The organic solvent was removed under vacuum on a rotary evaporator and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE : EA = 5 : 1 (v/v)) as eluent to afford the title product **3r** as off-white lumpy solid (87% yield, 1.55 g).

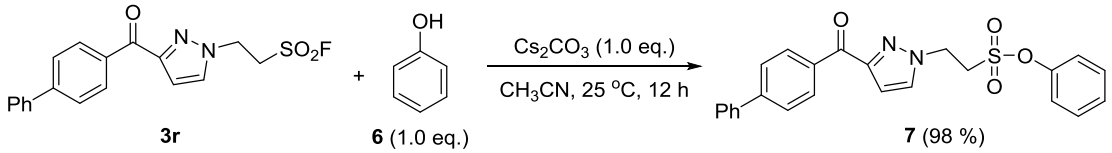
6. SuFEx Reactions of compound 3r



3r **4** (2.0 eq.) **5** (83 %)

A mixture of compound **3r** (179 mg, 0.5 mmol), morpholine (**4**, 87 mg, 1.0 mmol, 2.0 eq.), triethylamine (101 mg, 1.0 mmol, 2.0 eq.) and acetonitrile (2 mL) was agitated at 80°C for 24 h under air atmosphere. The organic solvent was removed under vacuum and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE : EA = 5:1 (v/v)) as eluent to afford the title product **5**.

[1,1'-biphenyl]-4-yl(1-(2-(morpholinosulfonyl)ethyl)-1H-pyrazol-3-yl)methanone **(5)**. White solid, 177 mg, 83 % yield. M.p. 49-51 °C. Purified 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 8.30 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.4 Hz, 2H), 7.58 (d, J = 1.1 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 6.97 (d, J = 1.3 Hz, 1H). 4.71 (t, J = 6.8 Hz, 2H). 3.70 (t, J = 4.4 Hz, 4H). 3.57 (t, J = 6.8 Hz, 2H). 3.21 (t, J = 4.4 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.1, 151.8, 145.5, 140.1, 135.9, 131.6, 131.0, 129.0, 128.2, 127.3, 126.9, 109.7, 66.3, 48.5, 46.7, 45.5. **HRMS-ESI** (m/z) calcd. for $[C_{22}H_{23}N_3O_4S]^+$ ($[M+H]^+$): 426.1460, found: 426.1463.

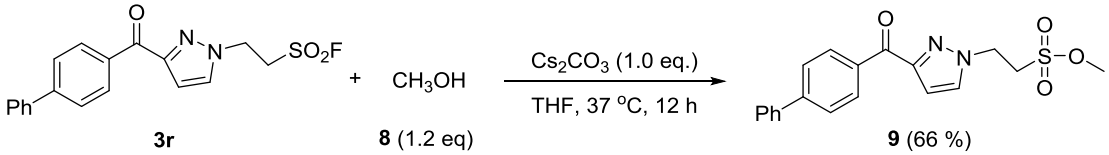


3r **6** (1.0 eq.) **7** (98 %)

To a solution of **3r** (179 mg, 0.5 mmol) and phenol (**6**, 47 mg, 0.5 mmol, 1.0 eq.) dissolved in acetonitrile (1 mL) added Cs_2CO_3 (163 mg, 0.5 mmol, 1.0 eq.), and the resulting mixture was stirred at room temperature for 12 h. The organic solvent was removed under vacuum and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE:EA = 3:1 (v/v)) as eluent to afford the title product **7**.

Phenyl 2-(3-([1,1'-biphenyl]-4-carbonyl)-1H-pyrazol-1-yl) ethane-1-sulfonate **(7)**.

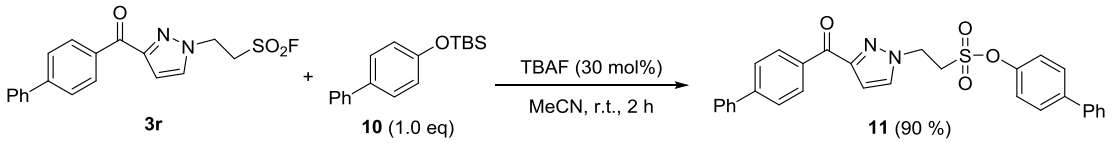
White solid, 212 mg, 98 % yield. M.p. 103-105 °C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 7.9 Hz, 2H), 7.67-7.64 (m, 3H), 7.49 (t, J = 7.4 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H). 7.18 (d, J = 7.9 Hz, 2H). 6.99 (d, J = 1.7 Hz, 1H). 4.83 (t, J = 6.5 Hz, 2H). 3.92 (t, J = 6.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.0, 152.1, 148.8, 145.5, 140.1, 135.9, 131.9, 131.1, 130.1, 129.0, 128.2, 127.6, 127.3, 126.9, 121.8, 109.8, 50.0, 47.0. **HRMS-ESI** (m/z) calcd. for $[C_{24}H_{20}N_2O_4S]^+$ ($[M+H]^+$): 433.1300, found: 433.1302.



3r **8** (1.2 eq) **9** (66 %)

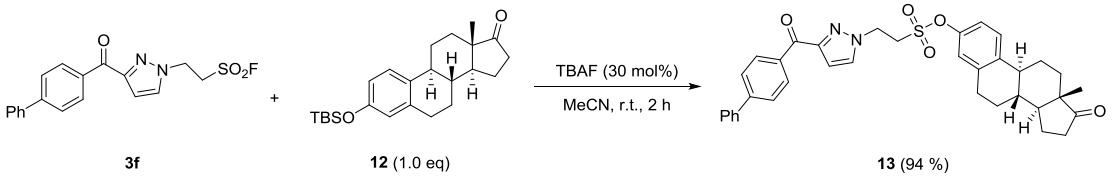
To a solution of **3r** (179 mg, 0.5 mmol) and methanol (**8**, 19 mg, 0.6 mmol, 1.2 eq.) dissolved in THF (2 mL) added Cs_2CO_3 (163 mg, 0.5 mmol, 1.0 eq.), and the resulting mixture was stirred at 37 °C for 12 h. The organic solvent was removed under vacuum and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE : EA = 5:1 (v/v)) as eluent to afford the title product **9**.

Methyl 2-(3-([1,1'-biphenyl]-4-carbonyl)-1H-pyrazol-1-yl)ethane-1-sulfonate **(9)**. Yellow viscous liquid, 122 mg, 66 % yield. Purified 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 8.31 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 1.2 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 6.97 (d, J = 1.5 Hz, 1H), 4.71 (t, J = 6.4 Hz, 2H), 3.79-3.77 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.0, 151.9, 145.5, 140.1, 135.9, 131.8, 131.0, 129.0, 128.2, 127.3, 127.0, 109.6, 55.9, 49.1, 47.0. **HRMS-ESI** (m/z) calcd. for $[C_{19}H_{18}N_2O_4S]^+$ ($[M+H]^+$): 371.1170, found: 371.1170.



To a solution of **3r** (107 mg, 0.3 mmol) and TBS-protected phenol (**10**, 85 mg, 0.3 mmol, 1.0 eq.) dissolved in anhydrous MeCN (2 mL) added catalytic amount (30 mol%, 90 μL) of TBAF solution (tetrabutylammonium fluoride, 1 M in anhydrous THF), and the resulting mixture was stirred at room temperature for 2 h. The organic solvent was removed under vacuum and the residue was purified by flash silica gel chromatography using a mixture of petroleum ether and ethyl acetate (PE:EA = 3:1 (v/v)) as eluent to afford the title product **11**.

[1,1'-biphenyl]-4-yl 2-(3-([1,1'-biphenyl]-4-carbonyl)-1H-pyrazol-1-yl) ethane-1-sulfonate **(11)**. White solid, 137 mg, 90 % yield. M.p. 151-153 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.30 (d, J = 8.2 Hz, 2H), 8.11 (d, J = 2.1 Hz, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.44-7.36 (m, 6H), 6.95 (d, J = 2.1 Hz, 1H), 4.90 (t, J = 6.4 Hz, 2H). 4.28 (t, J = 6.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.0, 152.1, 148.2, 145.5, 140.9, 140.1, 139.5, 135.9, 131.9, 131.1, 129.0, 128.9, 128.8, 128.2, 127.8, 127.3, 127.1, 126.9, 122.1, 109.8, 50.0, 47.0. **HRMS-ESI** (m/z) calcd. for $[C_{30}H_{24}N_2O_4S]^+$ ($[M+H]^+$): 509.1660, found: 509.1663.



To a solution of **3r** (72 mg, 0.2 mmol) and TBS-protected estrone (**12**, 77 mg, 0.2 mmol, 1.0 eq.) dissolved in anhydrous MeCN (2 mL) added catalytic amount (30 mol%, 60 μL) of TBAF solution (tetrabutylammonium fluoride, 1 M in anhydrous THF), and the resulting mixture was stirred at room temperature for 2 h. The organic solvent was removed under vacuum and the residue was purified by flash silica gel

chromatography using a mixture of petroleum ether and ethyl acetate (PE:EA = 3:1 (v/v)) as eluent to afford the title product **13**.

(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 2-(3-([1,1'-biphenyl]-4-carbonyl)-1H-pyrazol-1-yl) ethane-1-sulfonate **(13).** White solid, 114 mg, 94 % yield. M.p. 131-133 ^{o}C. Purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 7.9 Hz, 2H), 7.66-7.65 (m, 3H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 1.4 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.83 (s, 1H), 4.83 (t, J = 6.4 Hz, 2H), 3.90 (t, J = 6.4 Hz, 2H), 2.81-2.80 (m, 2H), 2.52-2.46 (m, 1H), 2.31-2.29 (m, 1H), 2.19-1.90 (m, 5H), 1.60-1.36 (m, 6H), 0.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.6, 187.0, 152.0, 146.8, 145.5, 140.0, 139.4, 139.0, 135.9, 132.0, 131.1, 129.0, 128.3, 127.3, 127.0, 126.9, 121.7, 118.8, 109.8, 50.3, 49.7, 47.8, 47.0, 44.0, 37.8, 35.8, 31.5, 29.3, 26.1, 25.7, 21.5, 13.8. **HRMS-ESI** (m/z) calcd. for $[C_{36}H_{36}N_2O_5S]^+$ ($[M+H]^+$): 609.2398, found: 609.2399.

7. References

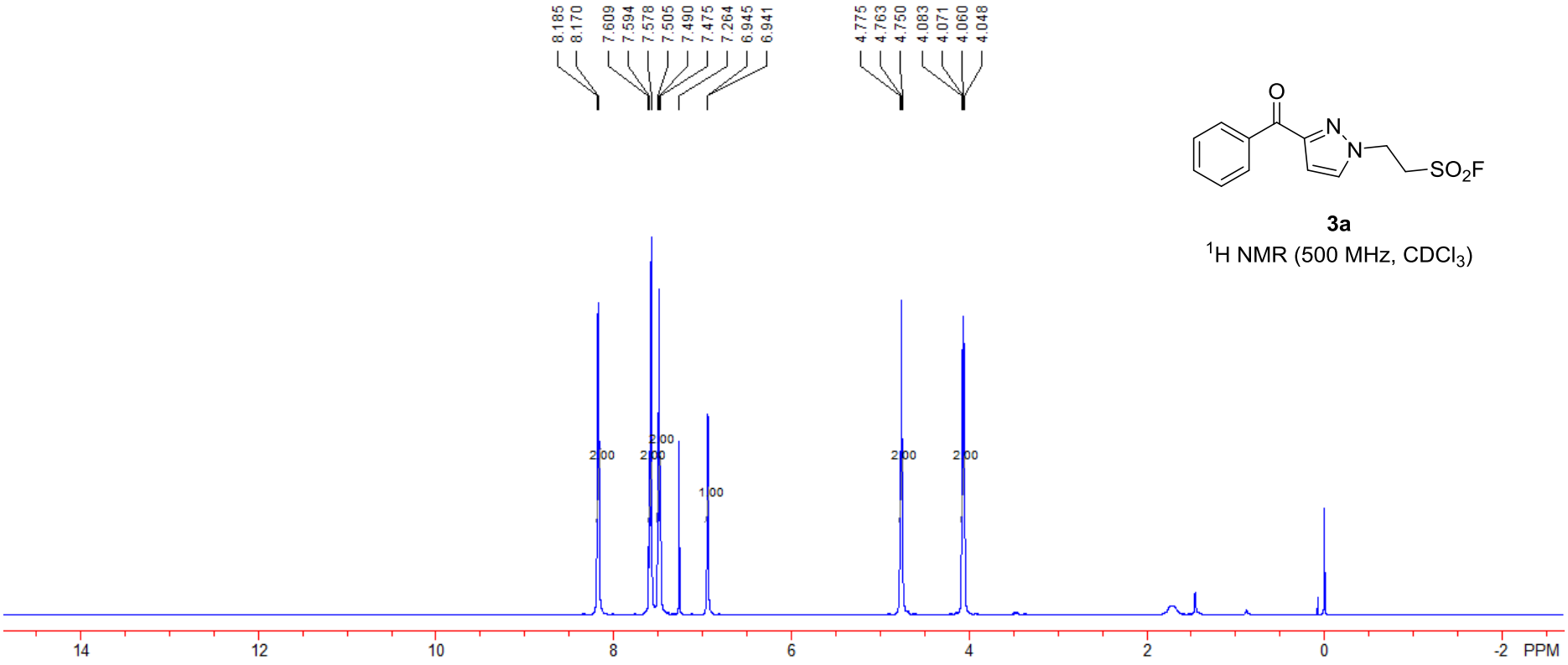
[1] J. C. Rodríguez, R. A. Maldonado, G. Ramírez-García, E. D. Cervantes and F. N. de la Cruz, *J Heterocyclic Chem*., 2020, **57**, 2279.

[2] Z.-L. Xia, J.-D. Hu, Y.-Q. Gao, Q.-Z. Yao and W.-Q. Xie, *Chem. Commun.,* 2017, **53**, 7485.

[3] R.-X. Chen, Y.-W. Zhao, H.-M. Sun, Y. Shao, Y.-D. Xu, M.-H. Ma, L. Ma and X.-B. Wan, *J. Org. Chem.,* 2017, **82**, 9291.

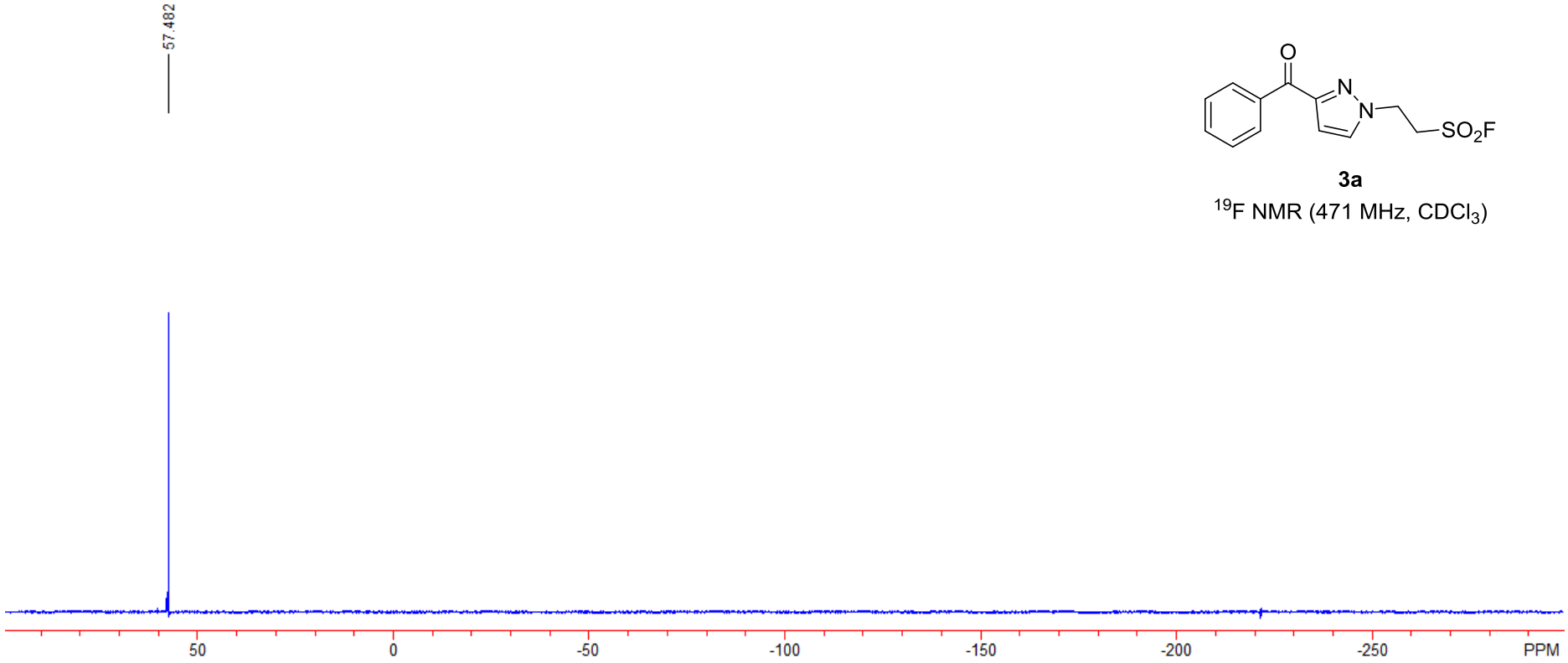
[4] (a) M.-M. Sun, W.-D. Chen, H.-J. Wu, X.-Y. Xia, J.-G. Yang, L. Wang, G.-D. Shen and Z.-M. Wang, *Org. Lett.,* 2020, **22**, 8313. (b) M. A. Cortes Gonzalez, X.-G. Jiang, P. Nordeman, G. Antonib and K. J. Szabo, *Chem. Commun.,* 2019, **55**, 13358

8. NMR spectra



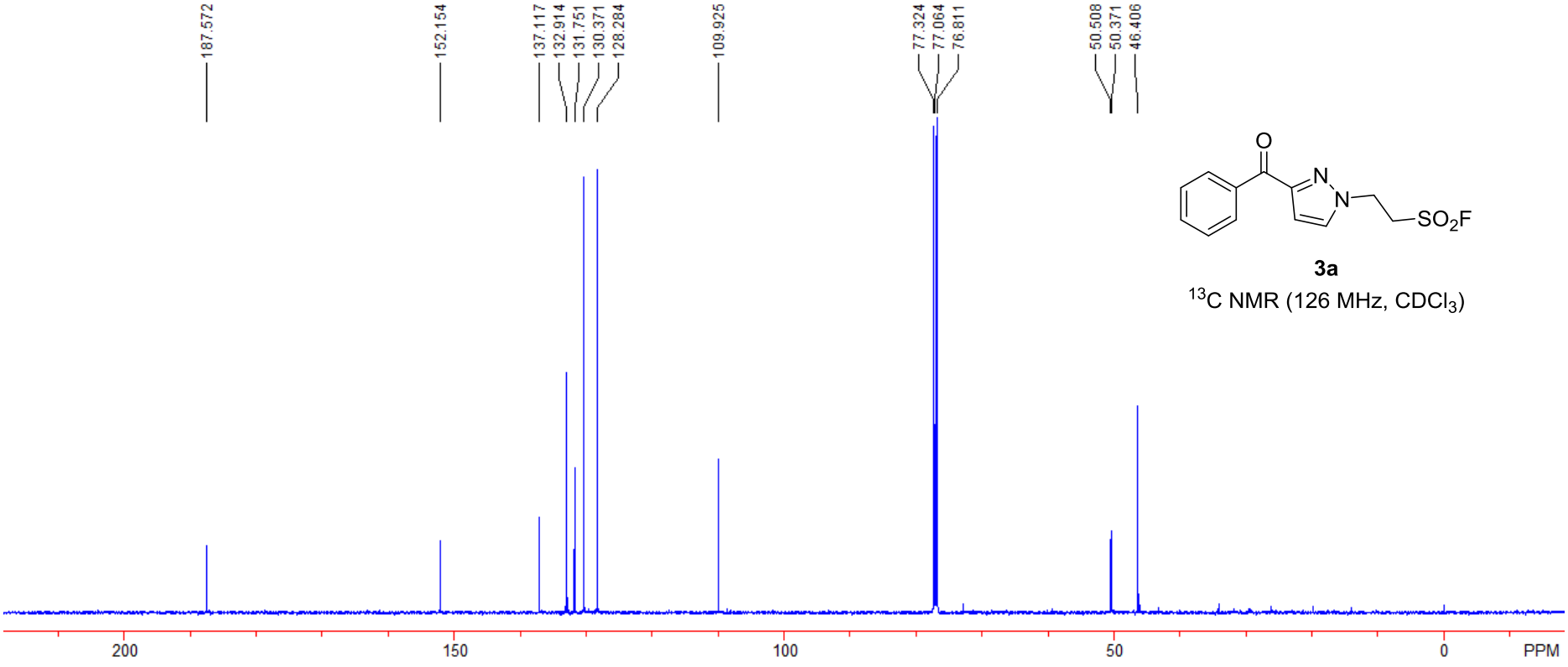
3a

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



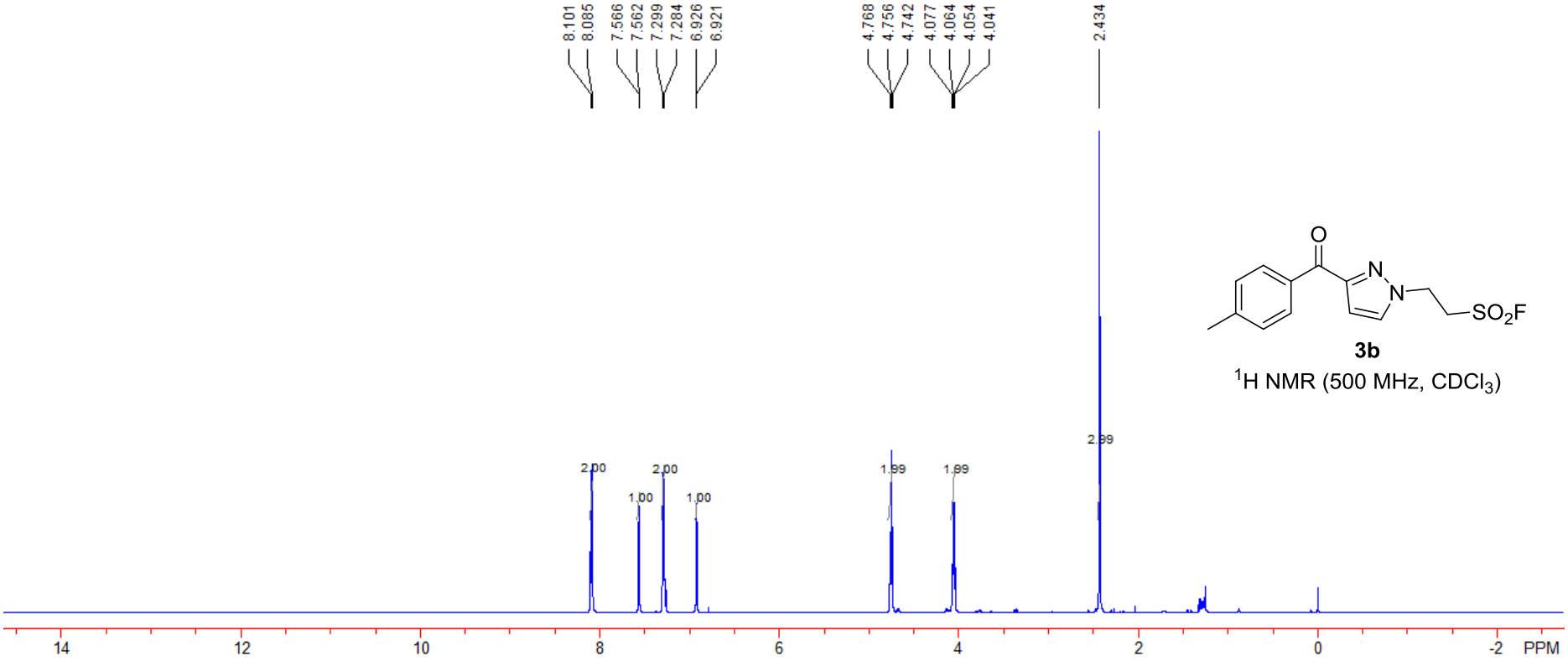
3a

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



3a

^{13}C NMR (126 MHz, $CDCl_3$)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1.99
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10
8
6
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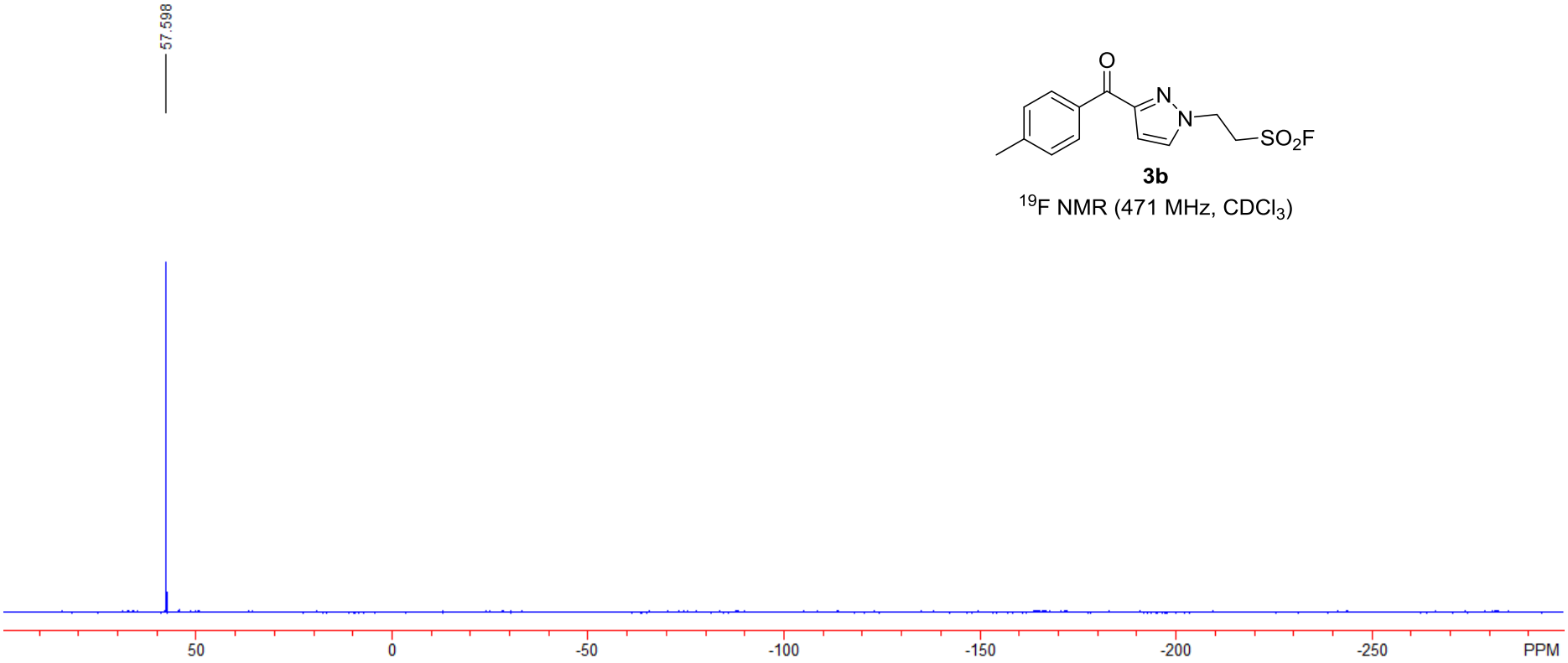
PPM



3b

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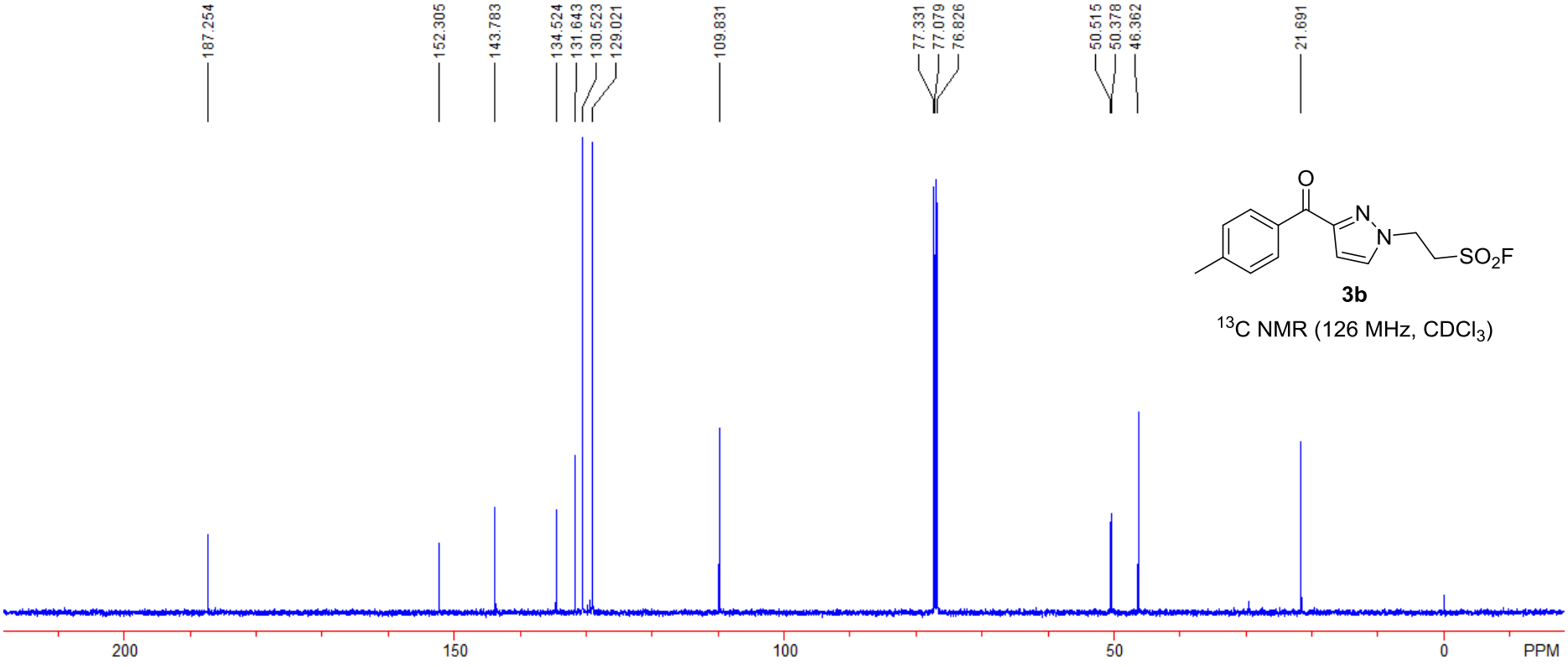
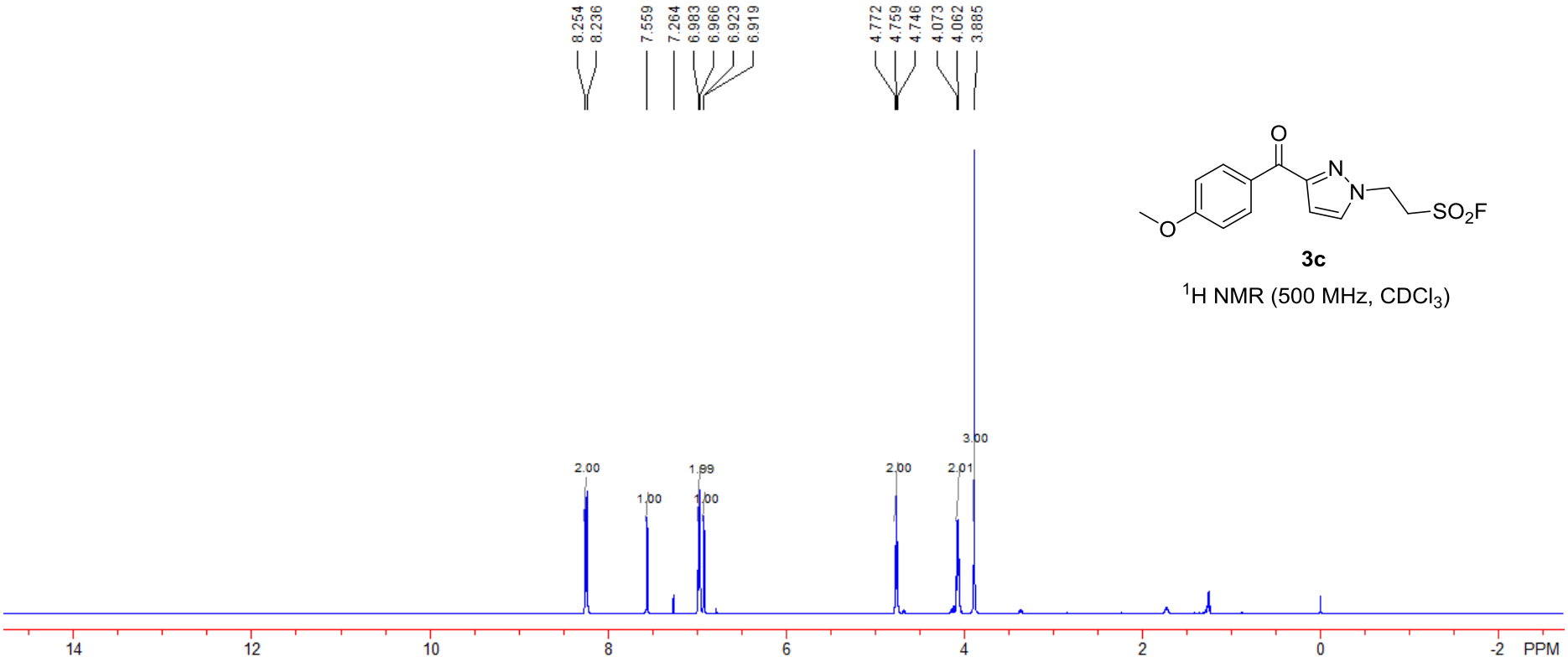


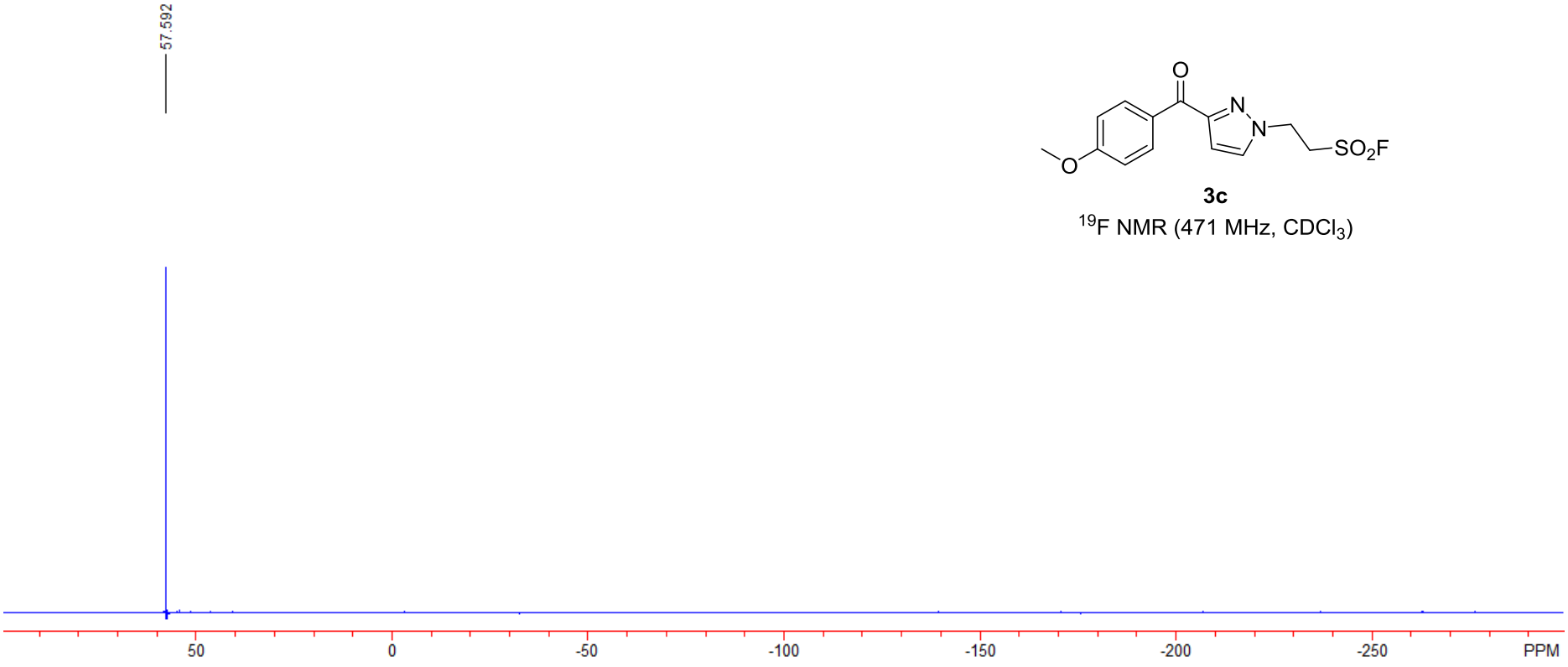
3b

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



3c

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



3c

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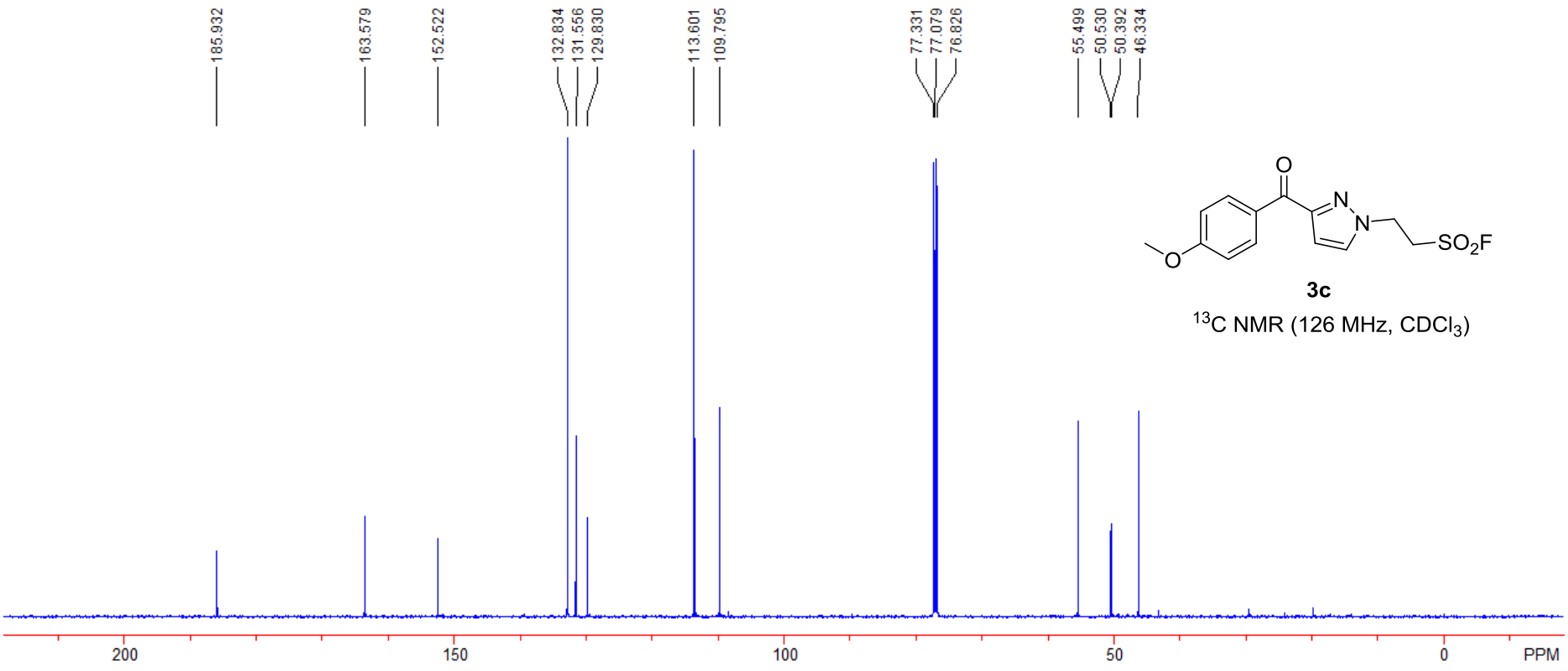
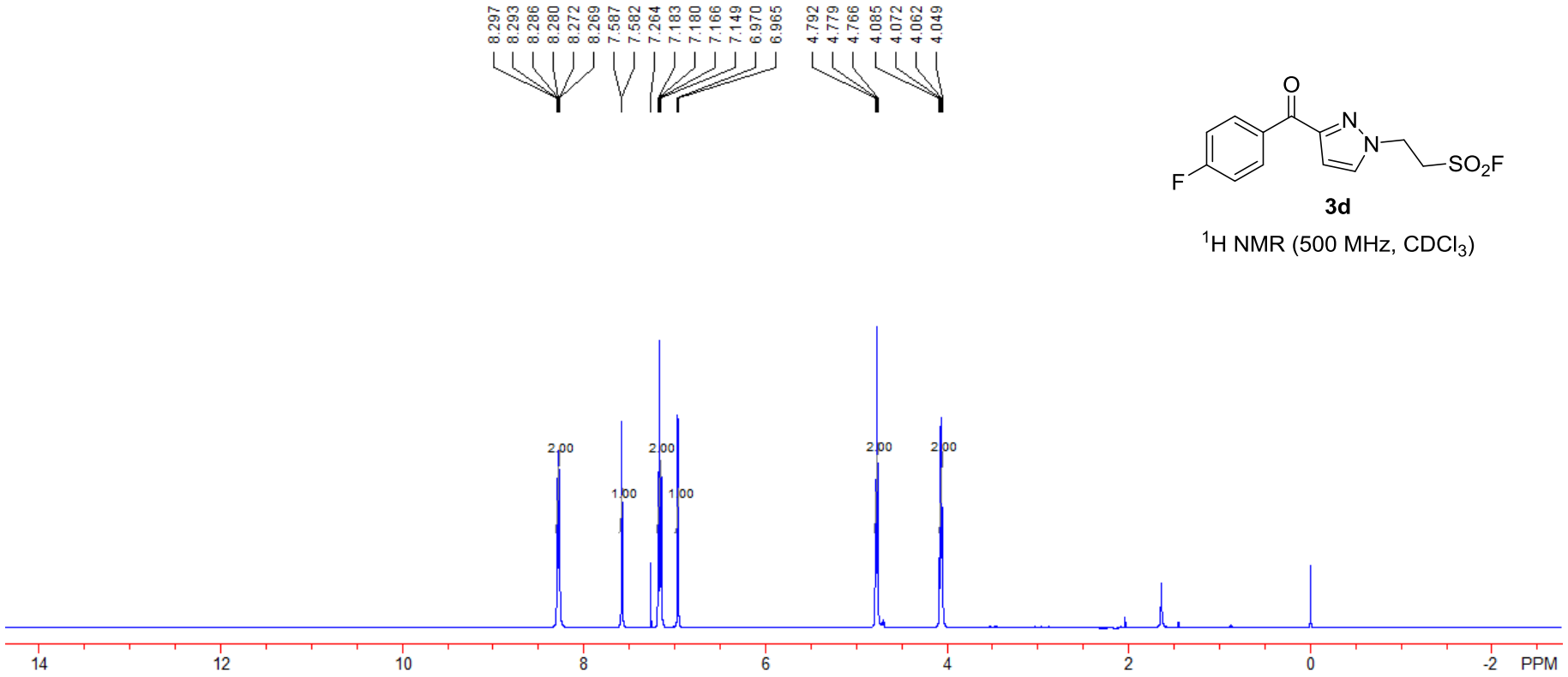


3c

^{13}C NMR (126 MHz, $CDCl_3$)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6.970
6.965
4.792
4.779
4.766
4.085
4.072
4.062
4.049
O
N
N
F
SO2F
3d
1H NMR (500 MHz, CDCl3)
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10
8
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4
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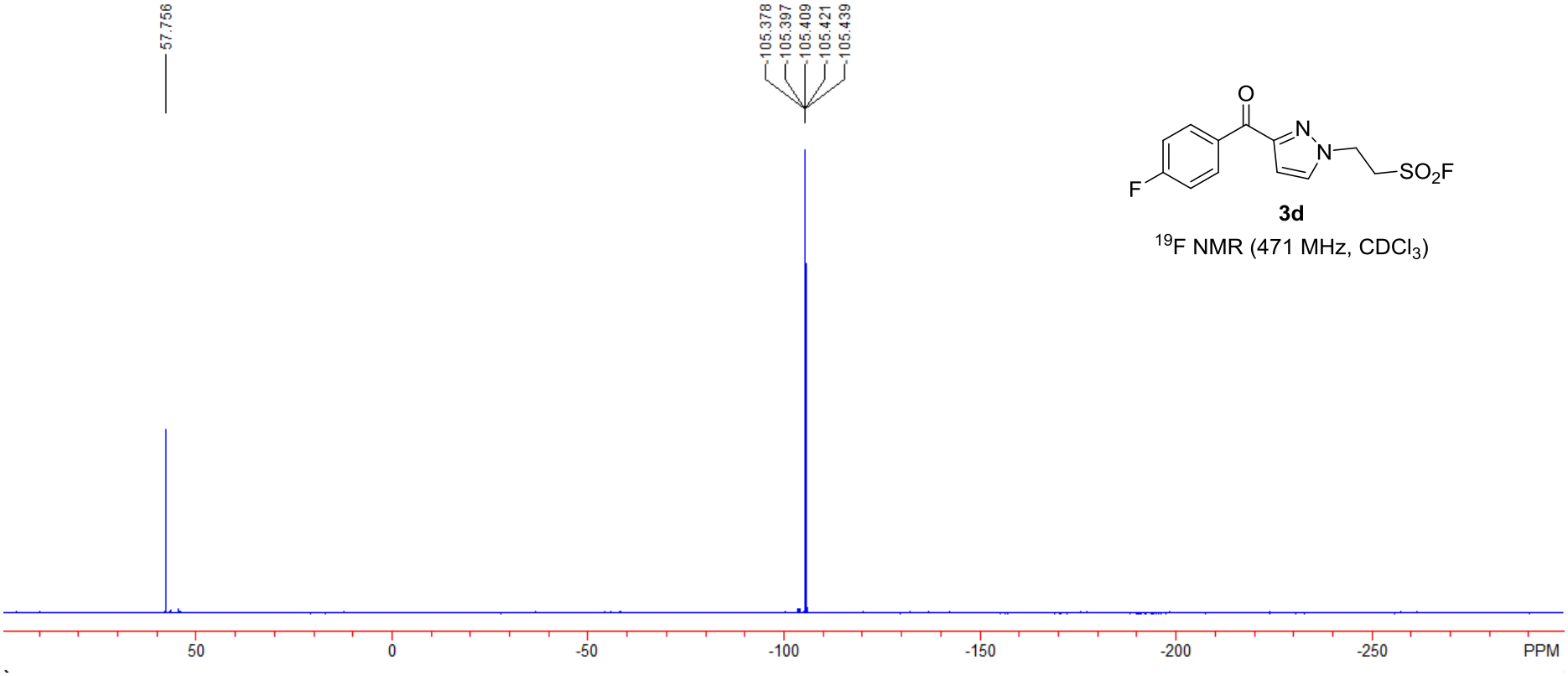
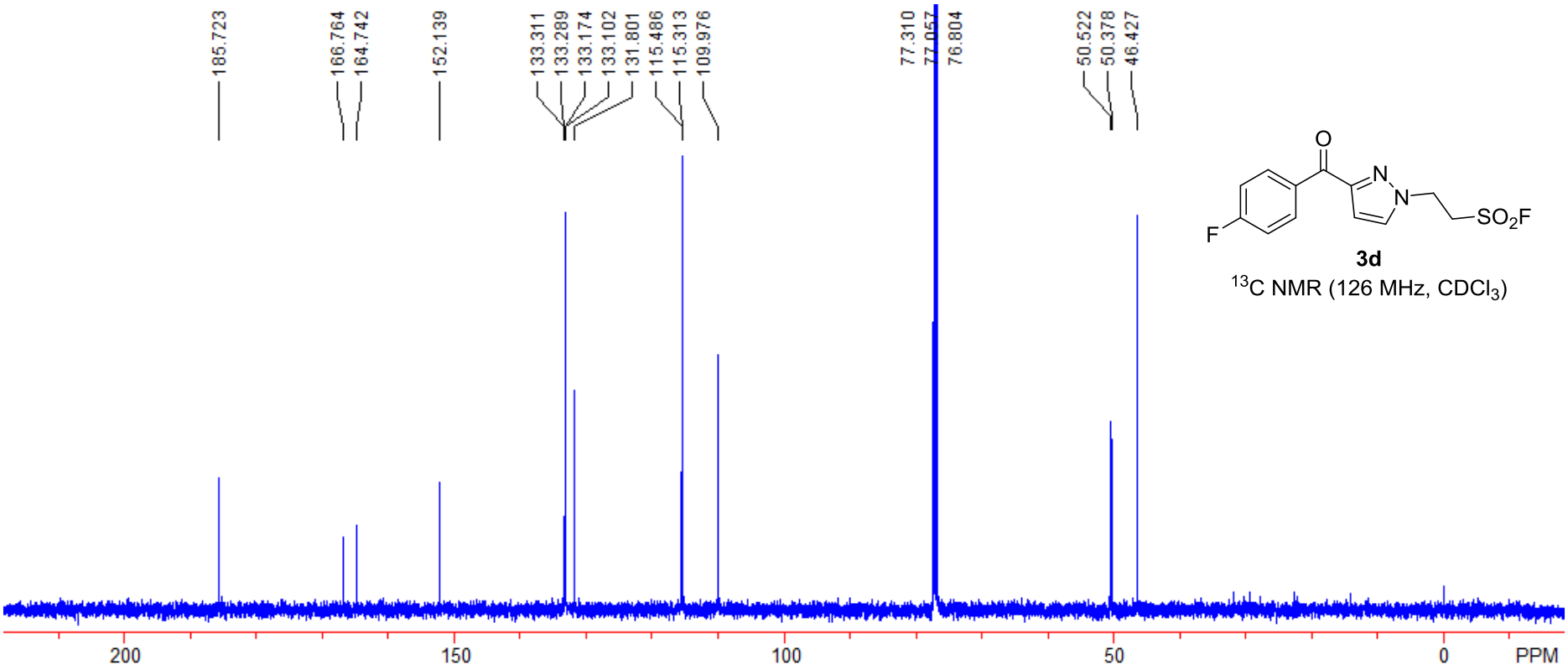
PPM



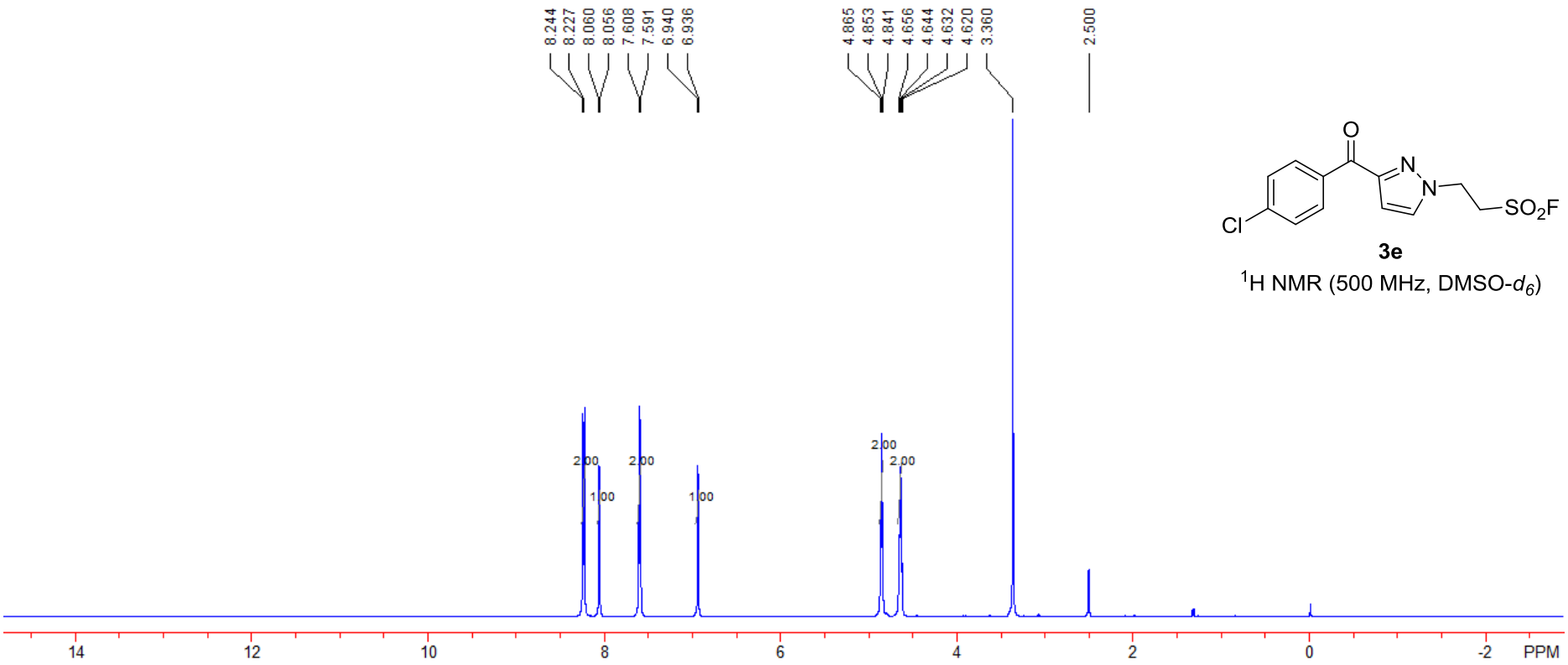
3d

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



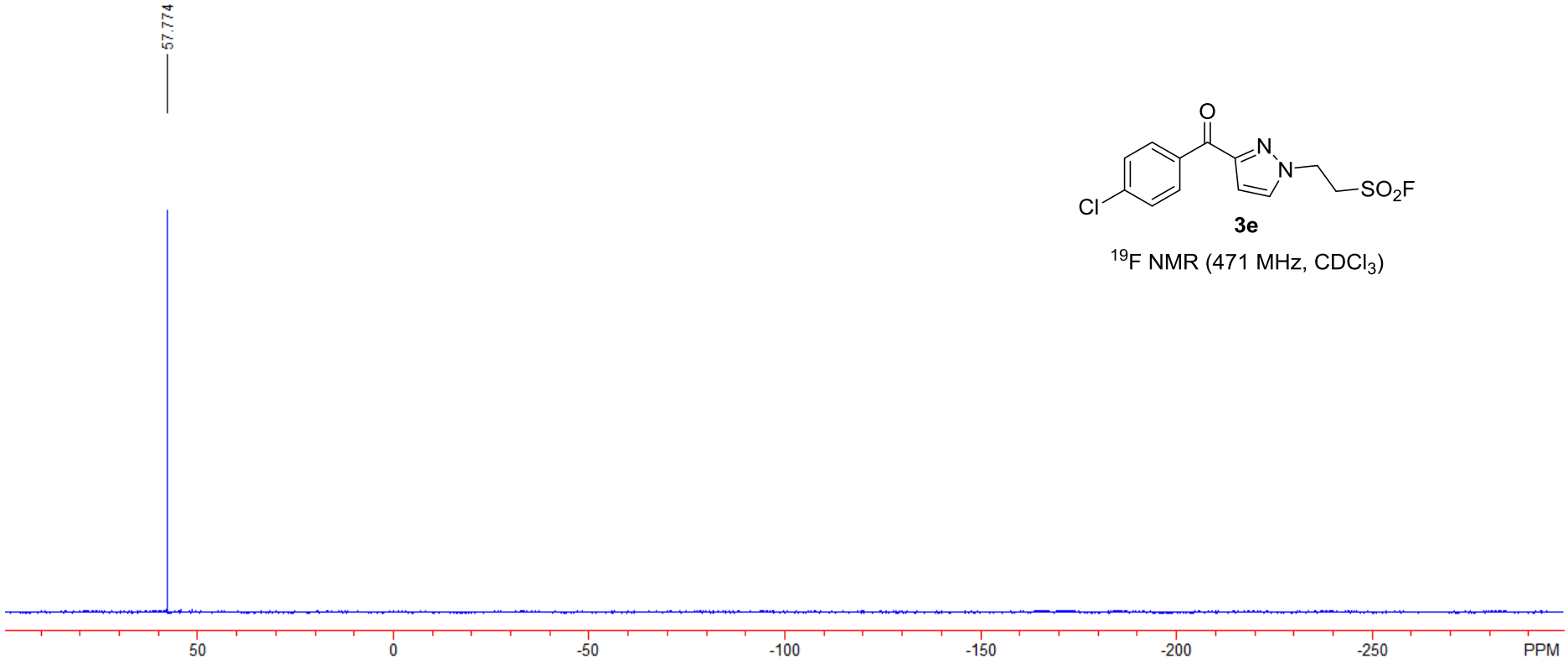
3d

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



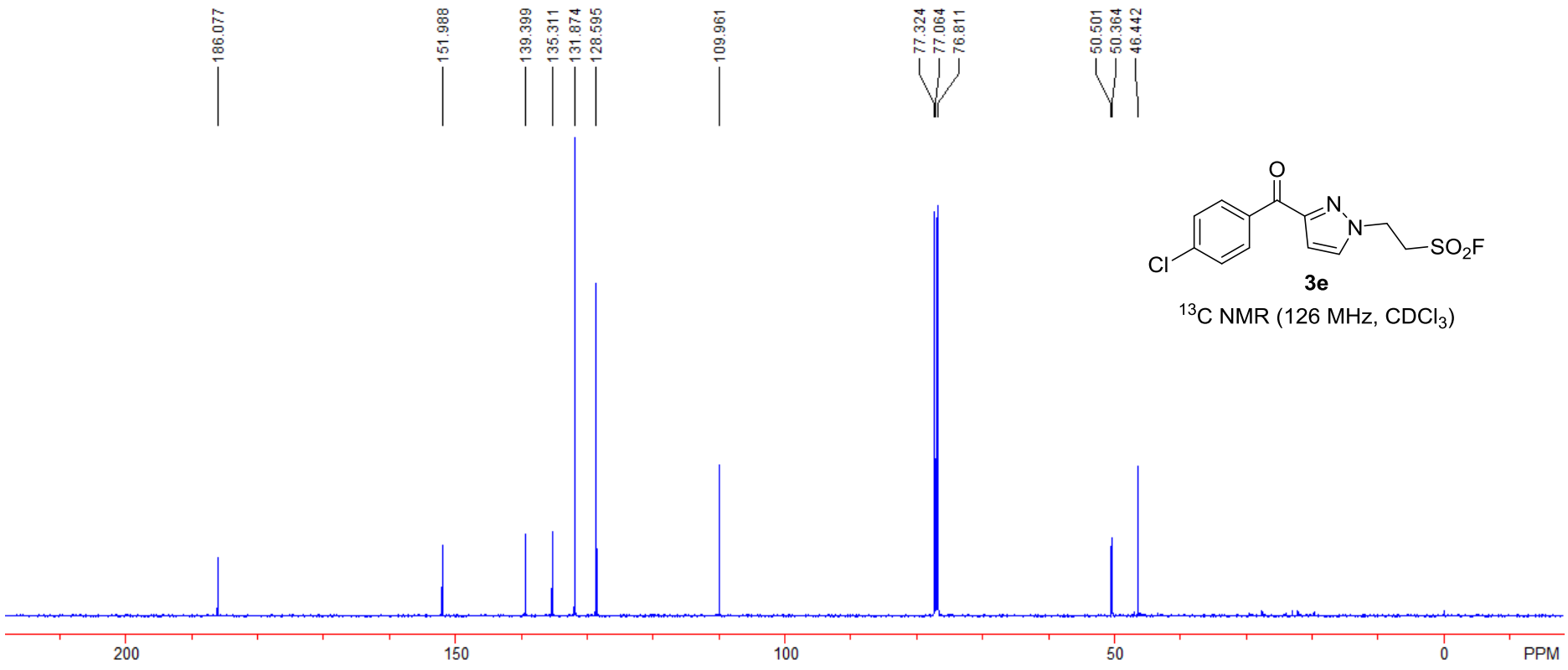
3e

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



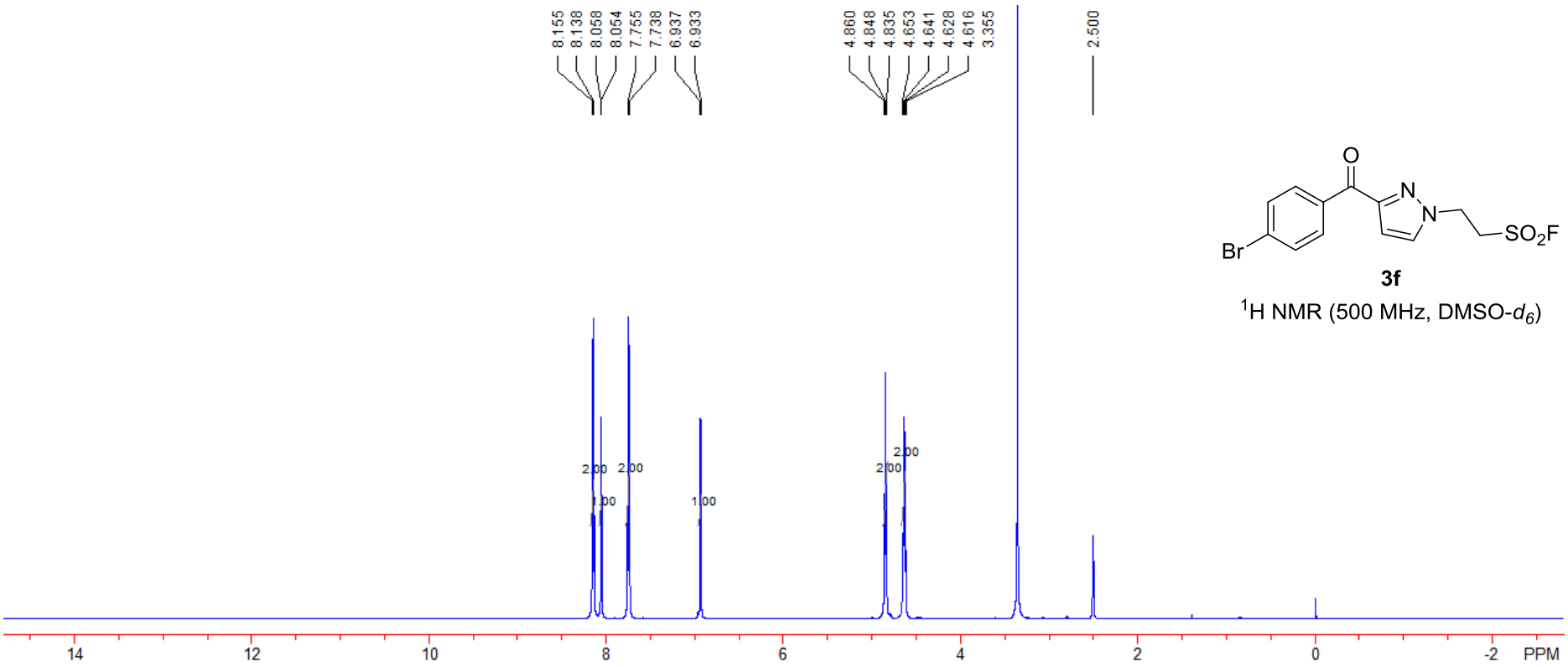
3e

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



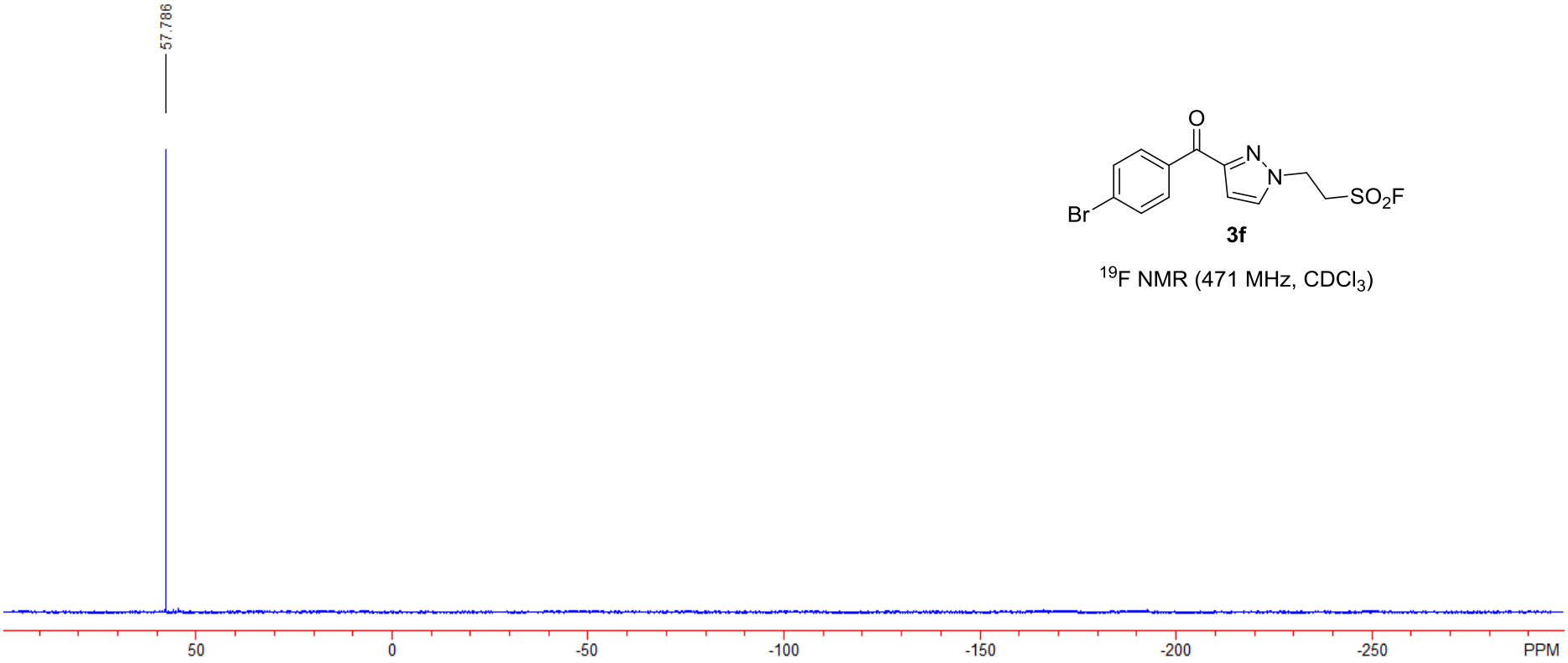
3e

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



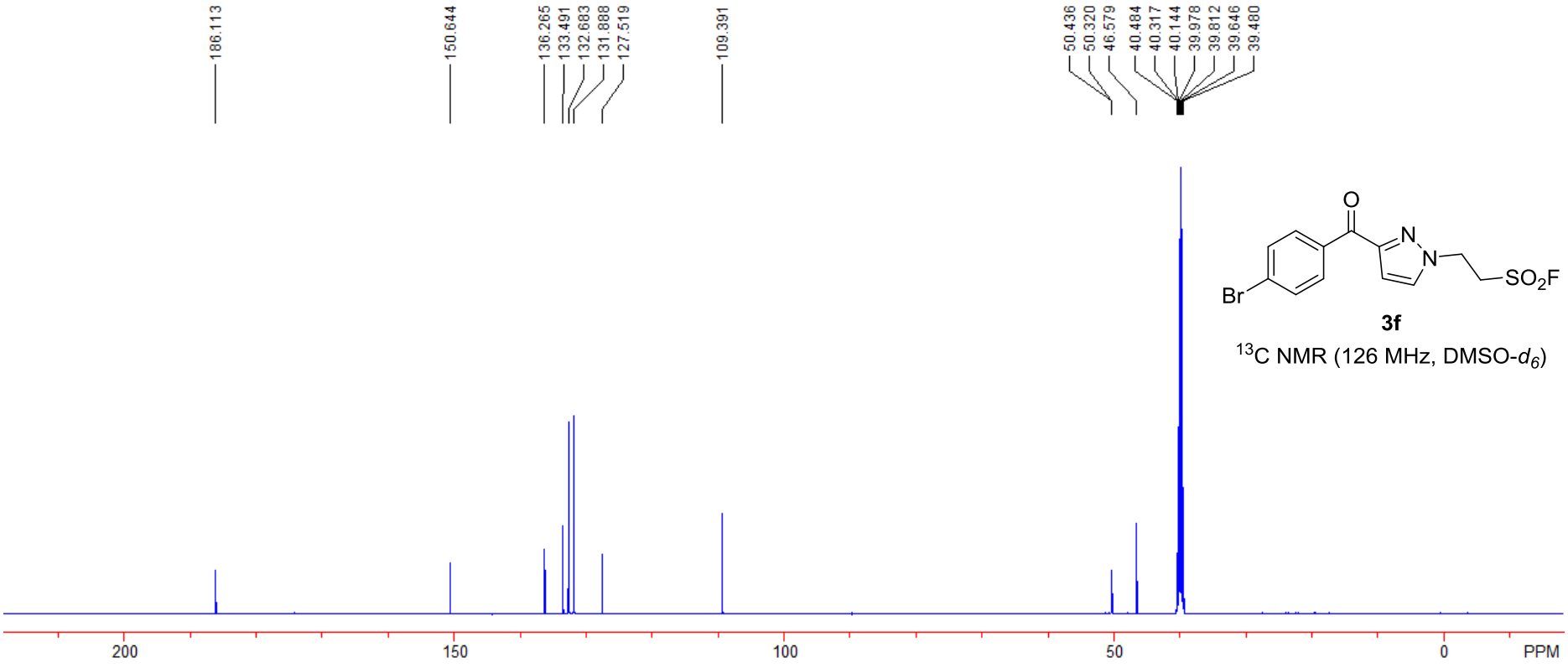
3f

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



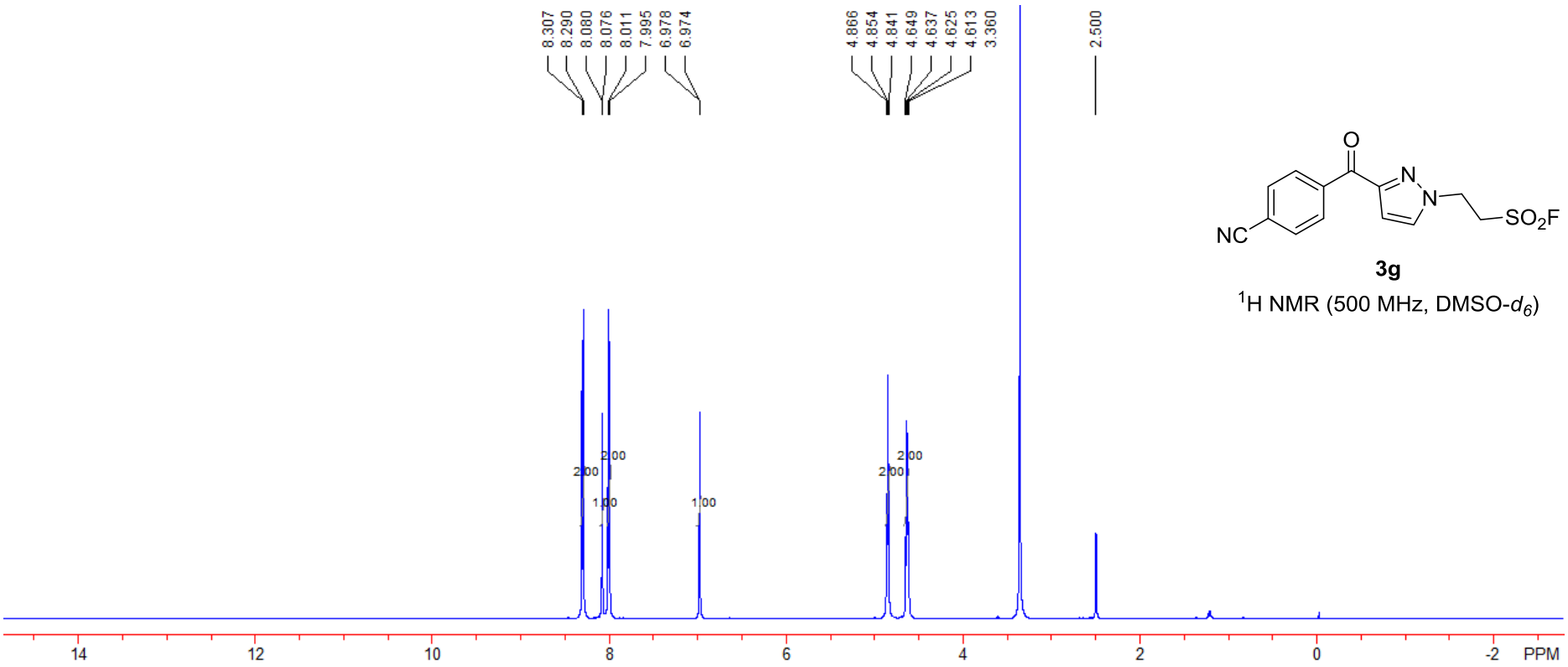
3f

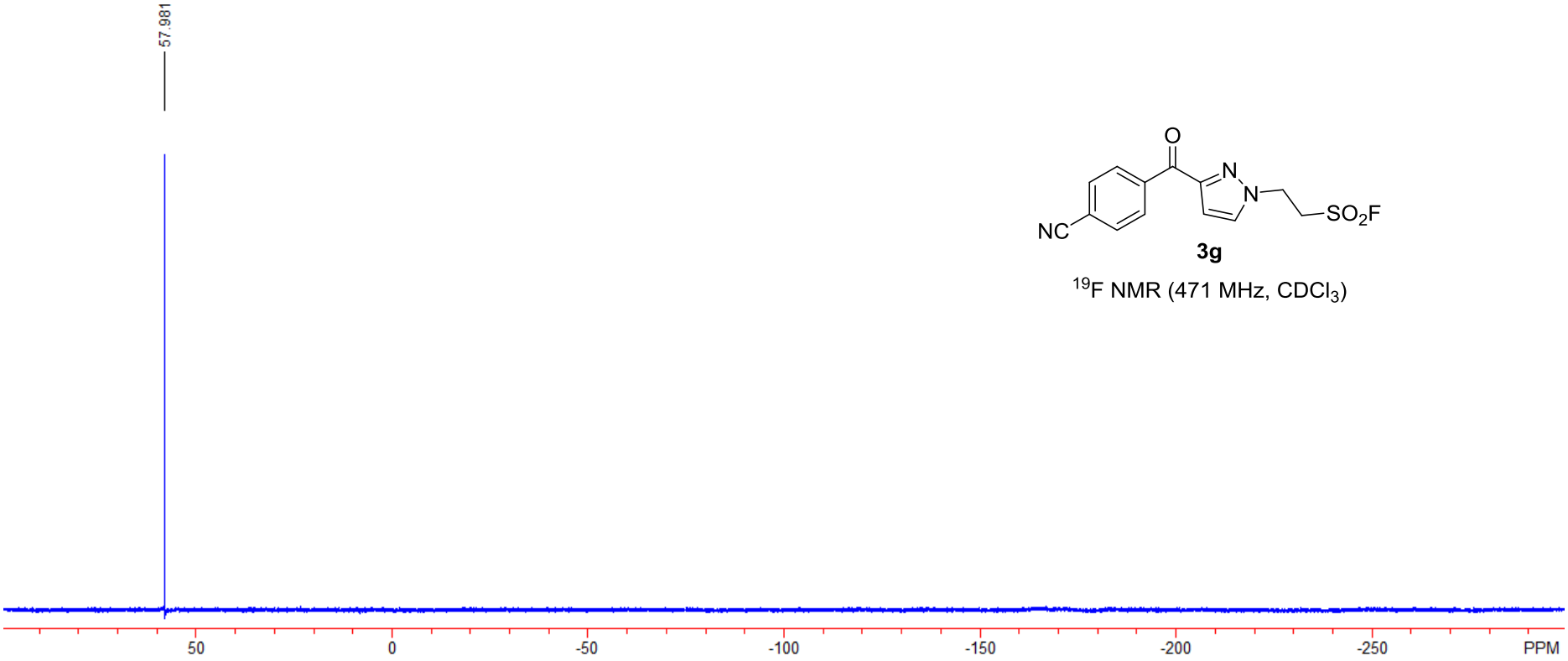
^{19}F NMR (471 MHz, $CDCl_3$)



3f

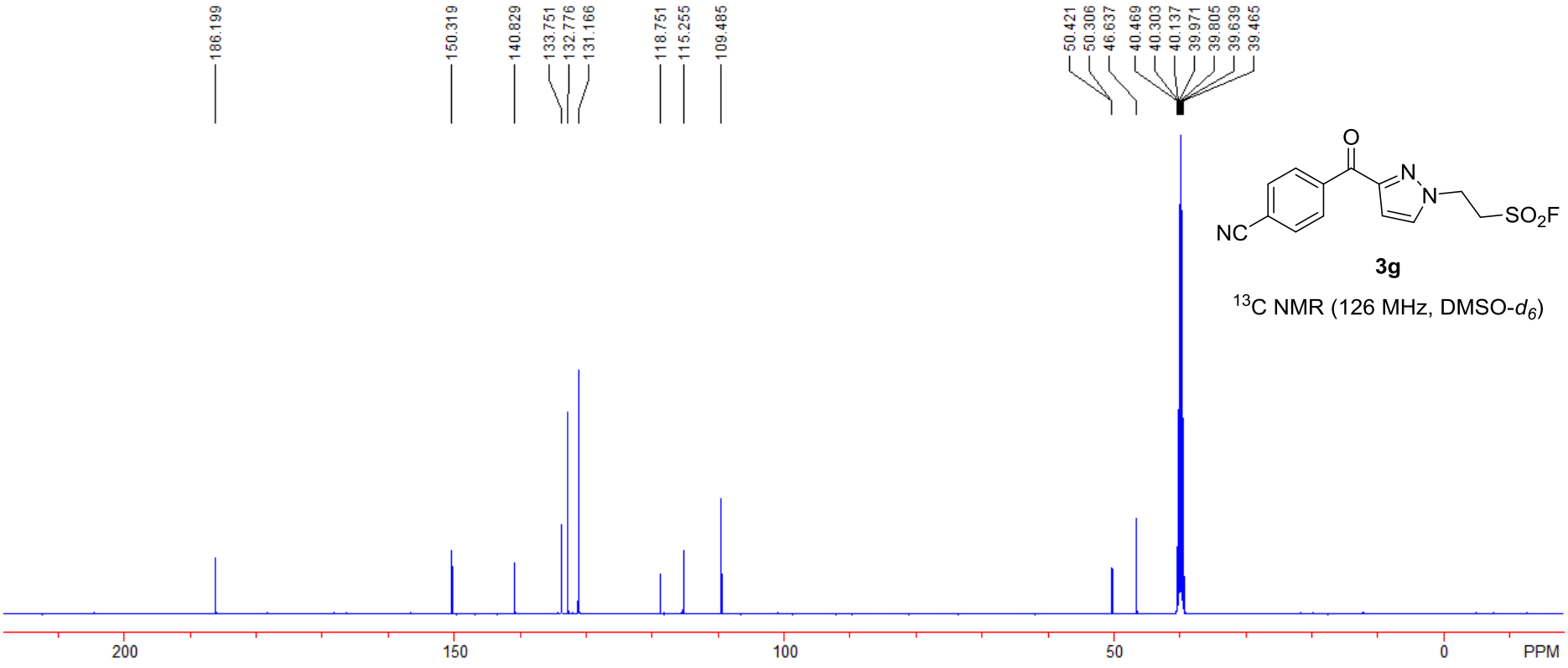
^{13}C NMR (126 MHz, DMSO-d_6)

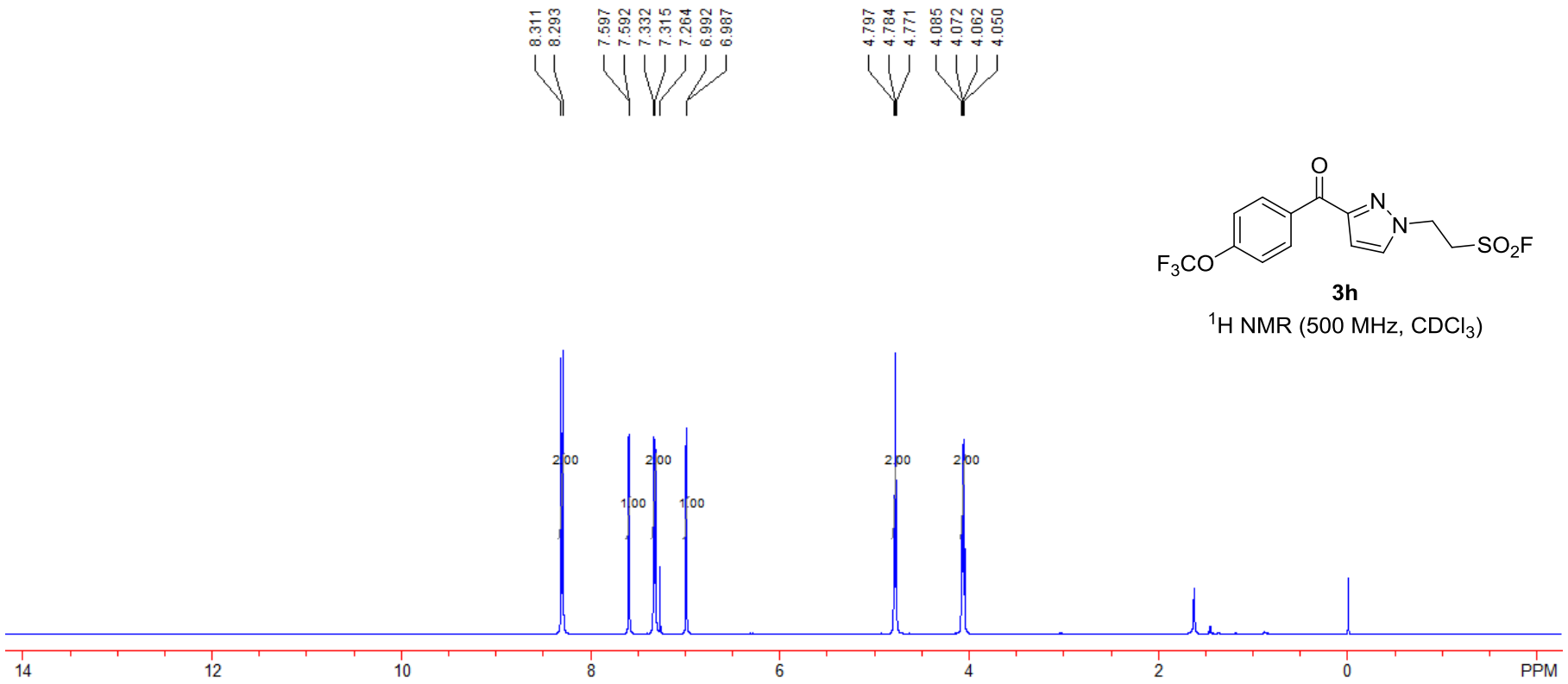

8.307
8.290
8.080
8.076
8.011
7.995
6.978
6.974
4.866
4.854
4.841
4.649
4.637
4.625
4.613
3.360
2.500
2.00
2.00
1.00
1.00
2.00
2.00
O
N
N
NC
SO2F
3g
1H NMR (500 MHz, DMSO-d6)
14
12
10
8
6
4
2
0
-2
PPM

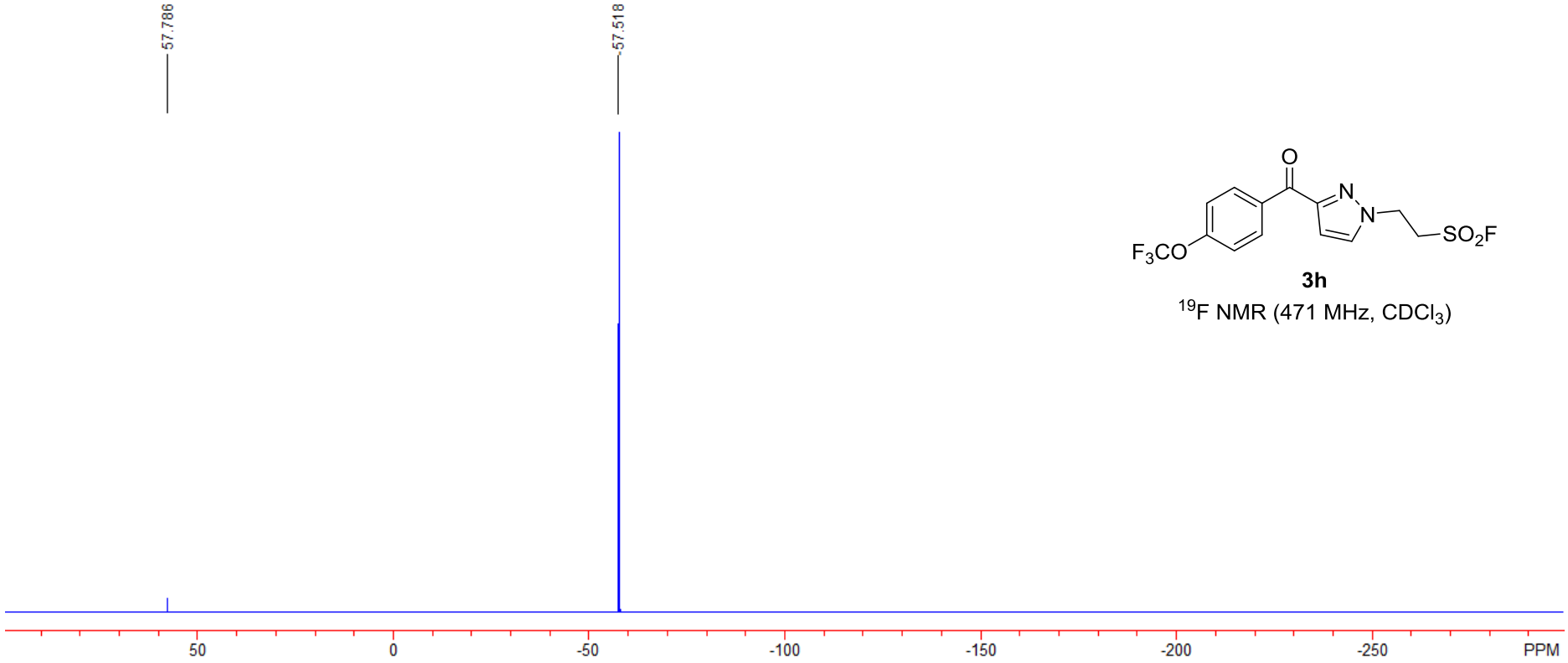


3g

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

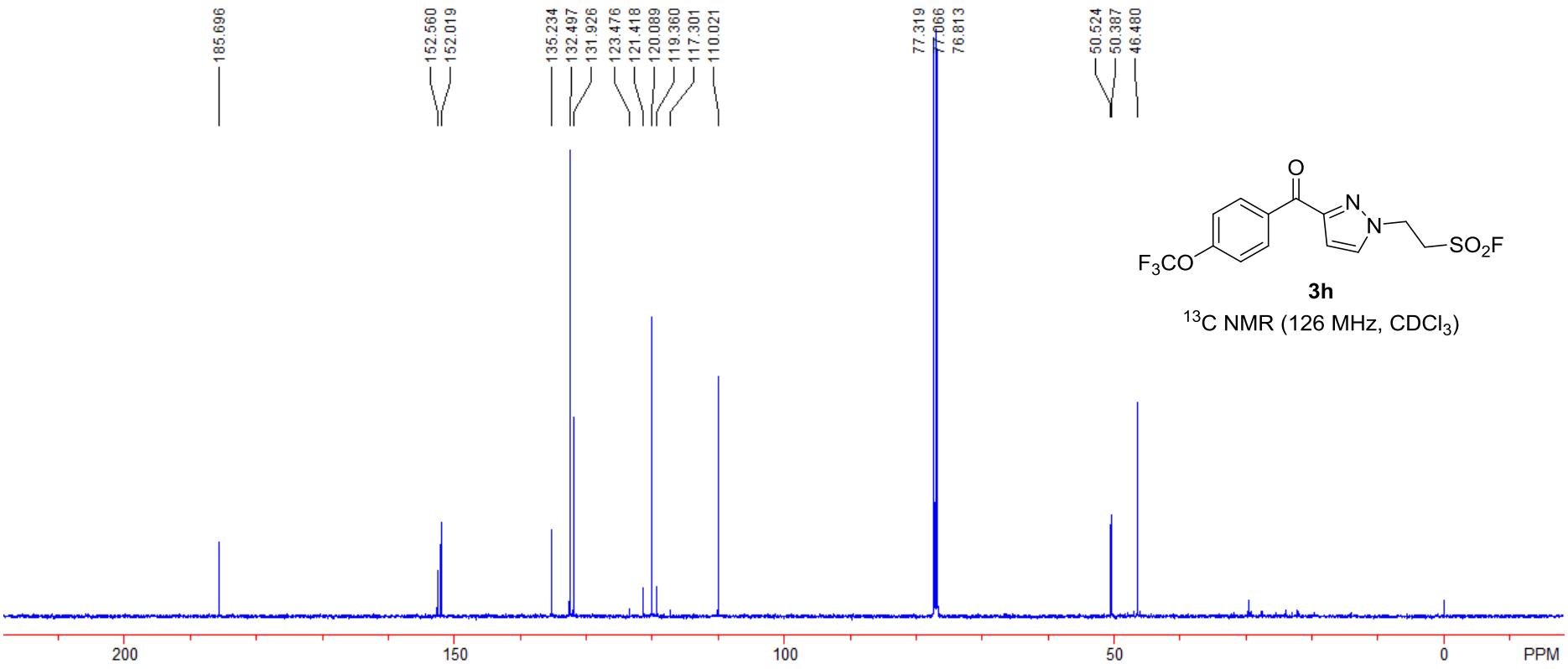

186.199
150.319
140.829
133.751
132.776
131.166
118.751
115.255
109.485
50.421
50.306
46.637
40.469
40.303
40.137
39.971
39.805
39.639
39.465
O
N
N
NC
SO2F
3g
13C NMR (126 MHz, DMSO-d6)
200
150
100
50
0
PPM


8.311
8.293
7.597
7.592
7.332
7.315
7.264
6.992
6.987
4.797
4.784
4.771
4.085
4.072
4.062
4.050
O
N
N
F3CO
SO2F
3h
1H NMR (500 MHz, CDCl3)
2.00
2.00
1.00
1.00
2.00
2.00
14
12
10
8
6
4
2
0
PPM



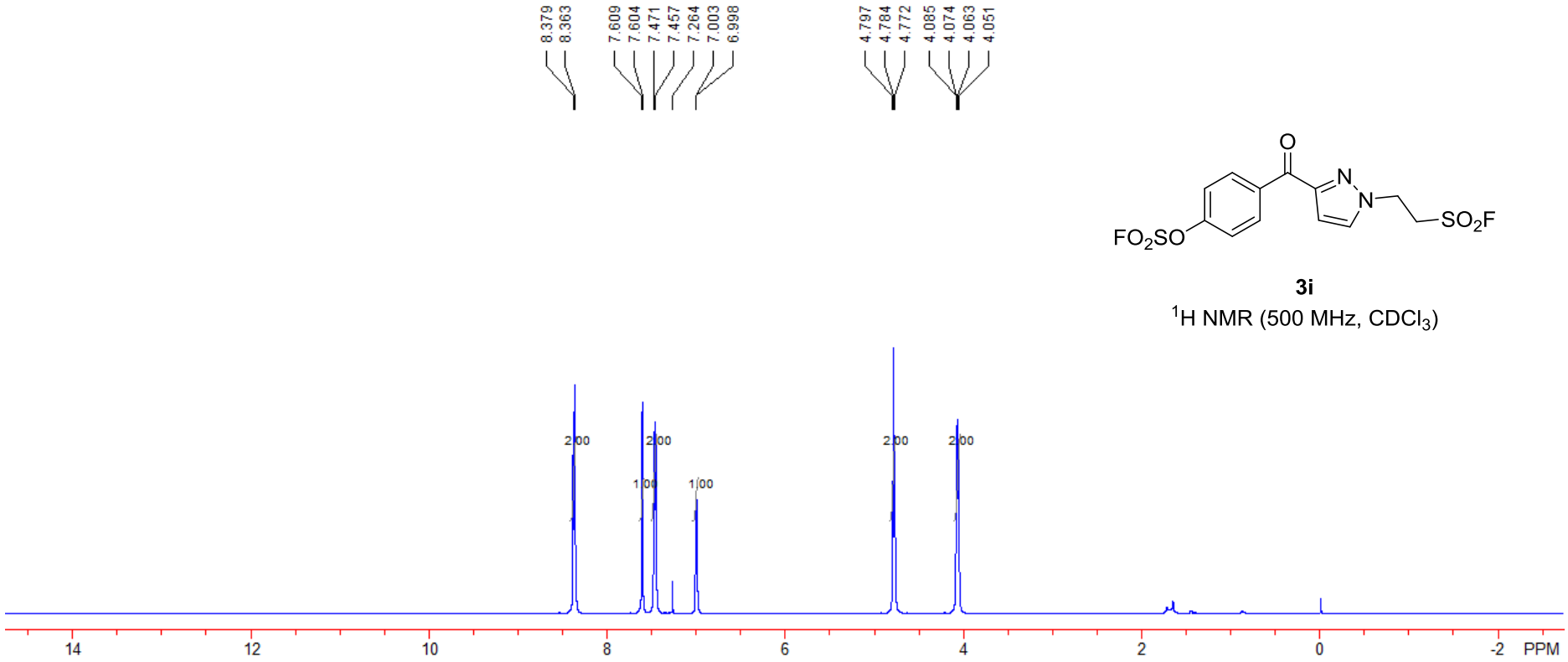
3h

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



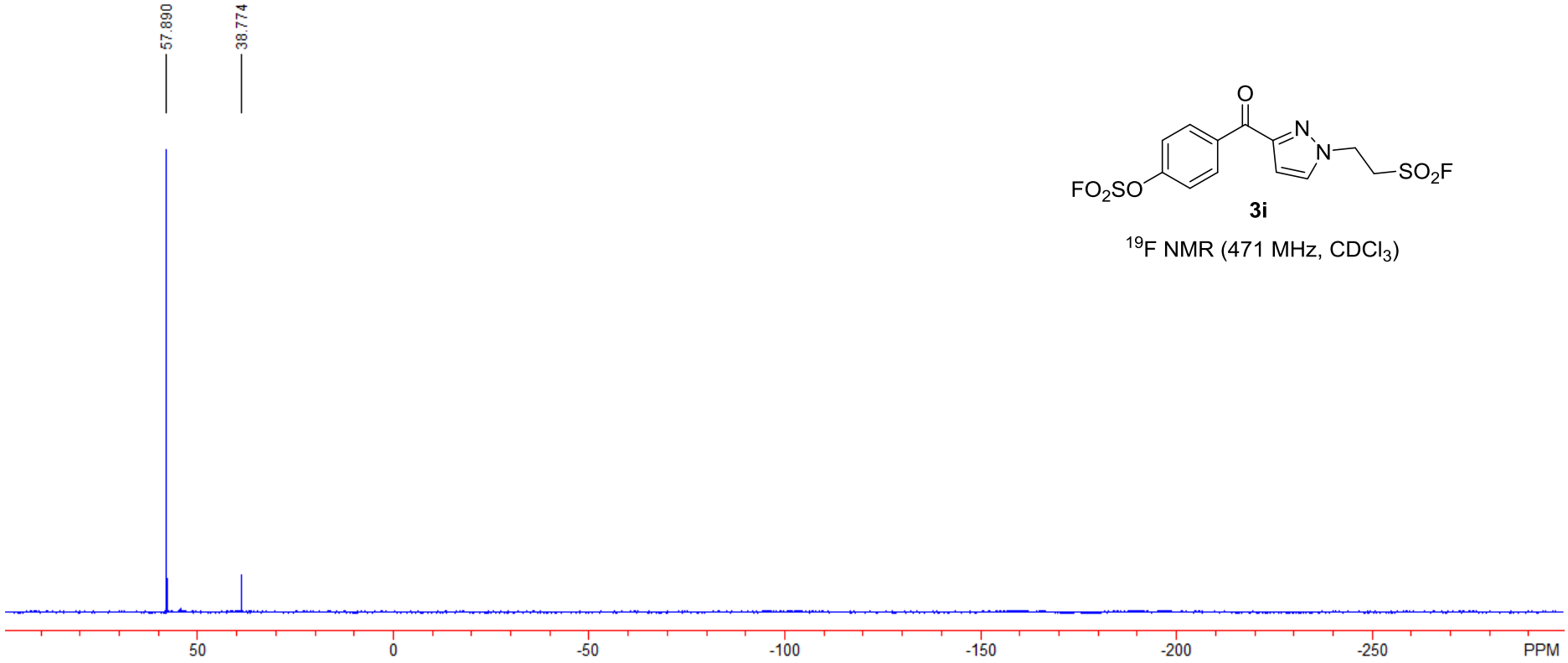
3h

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



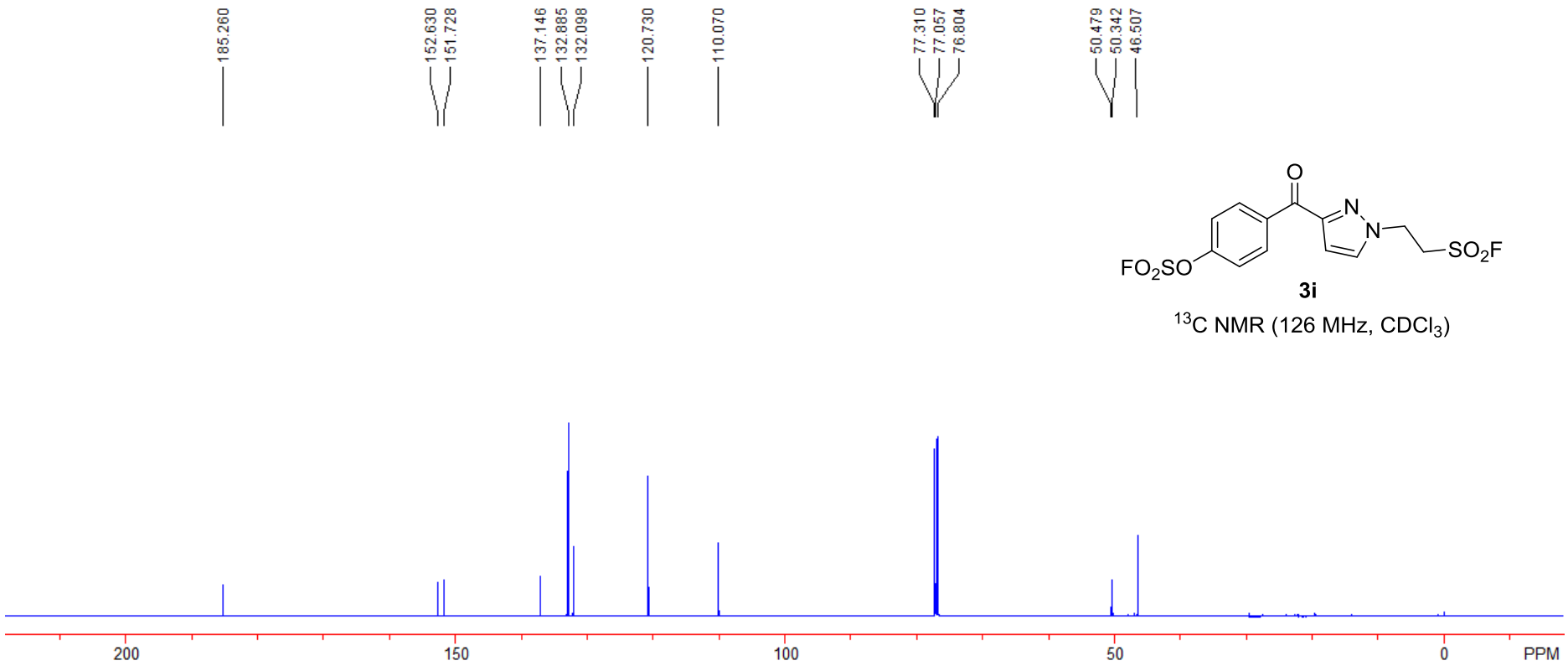
3i

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



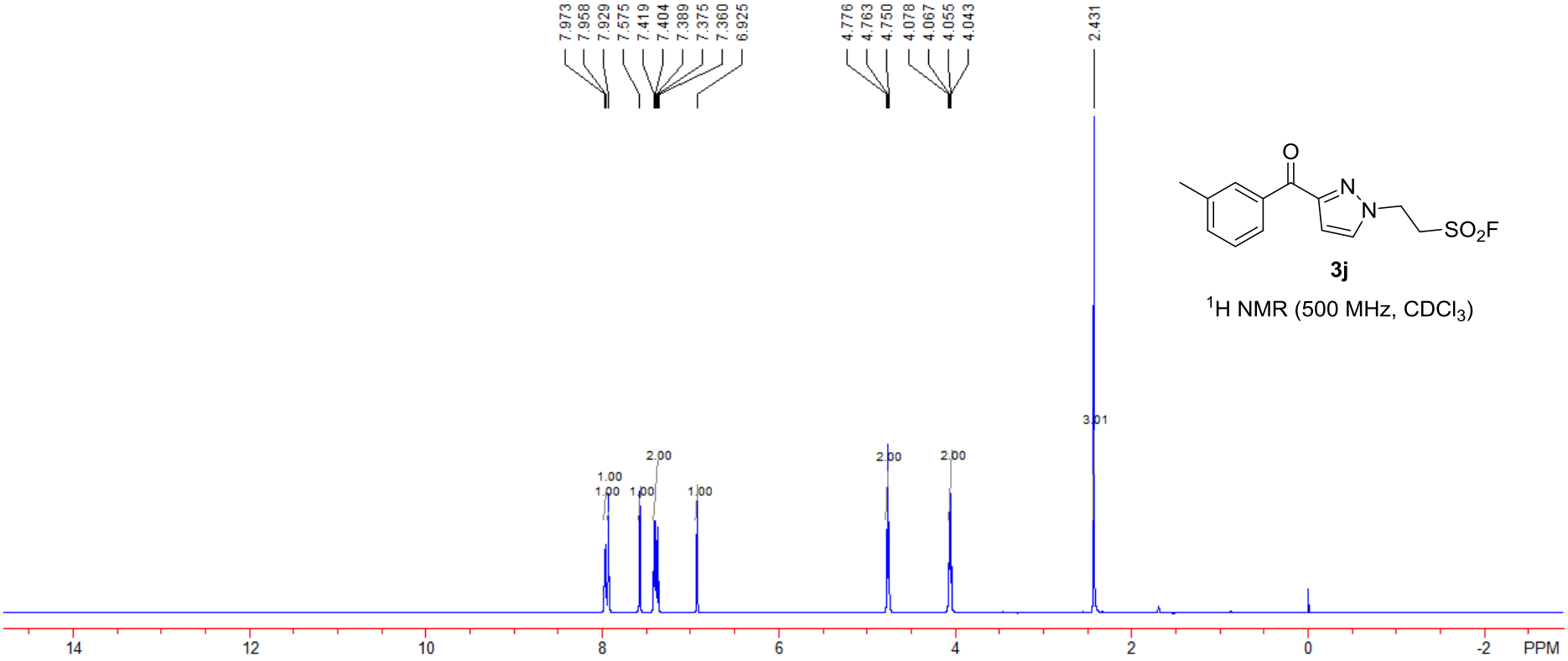
3i

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



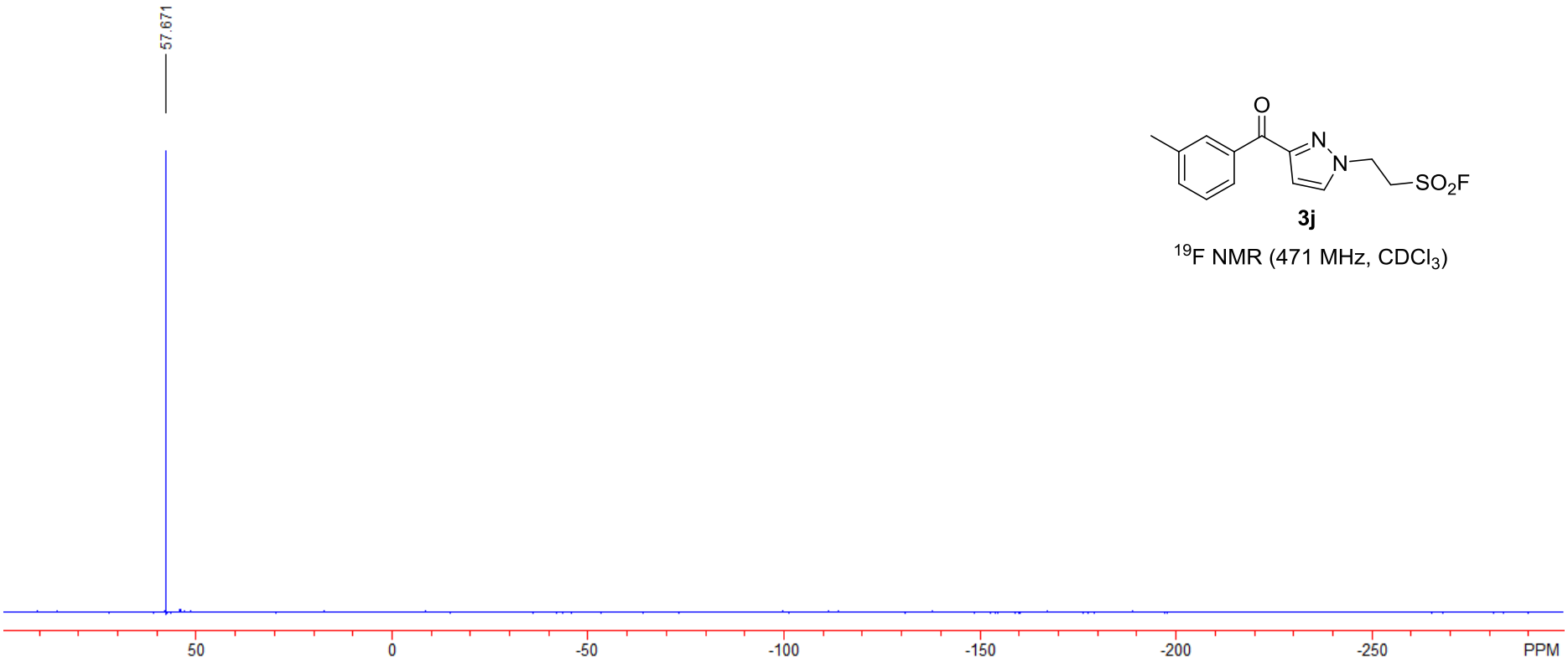
3i

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



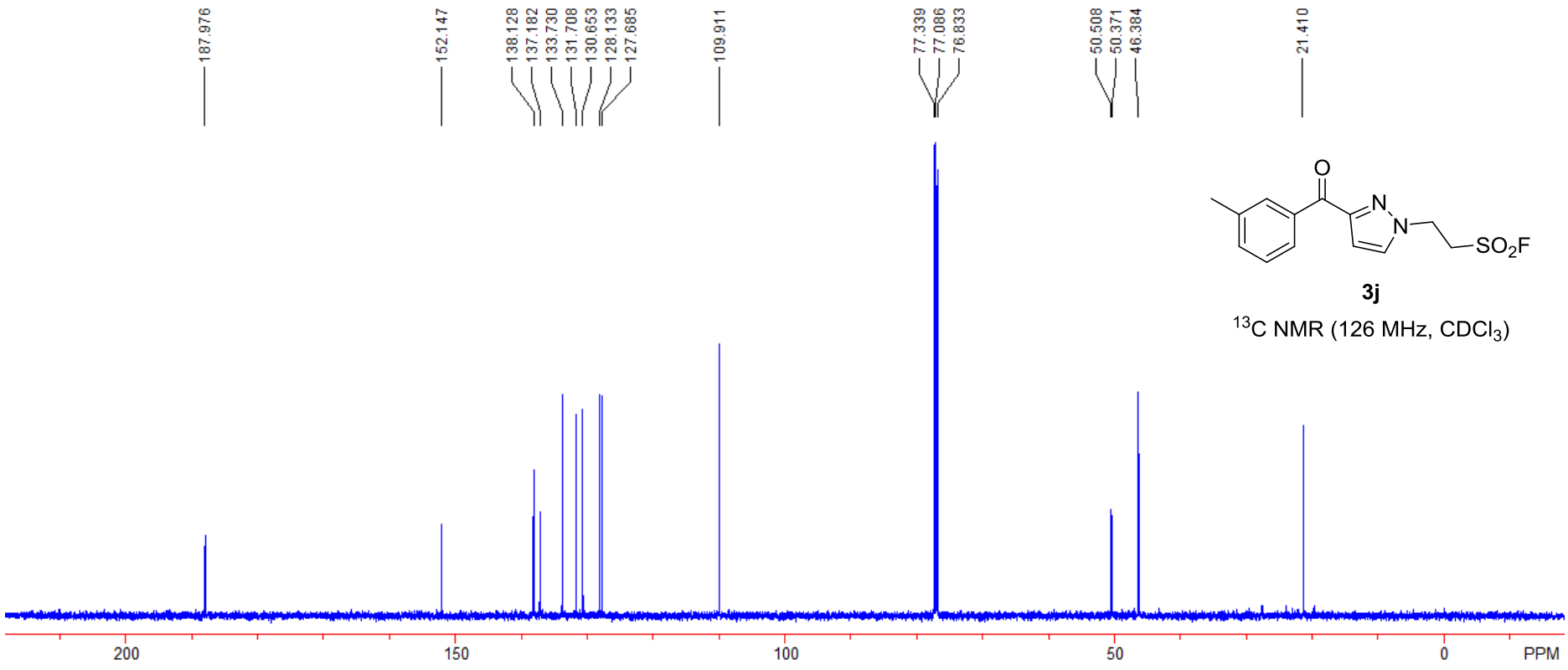
3j

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



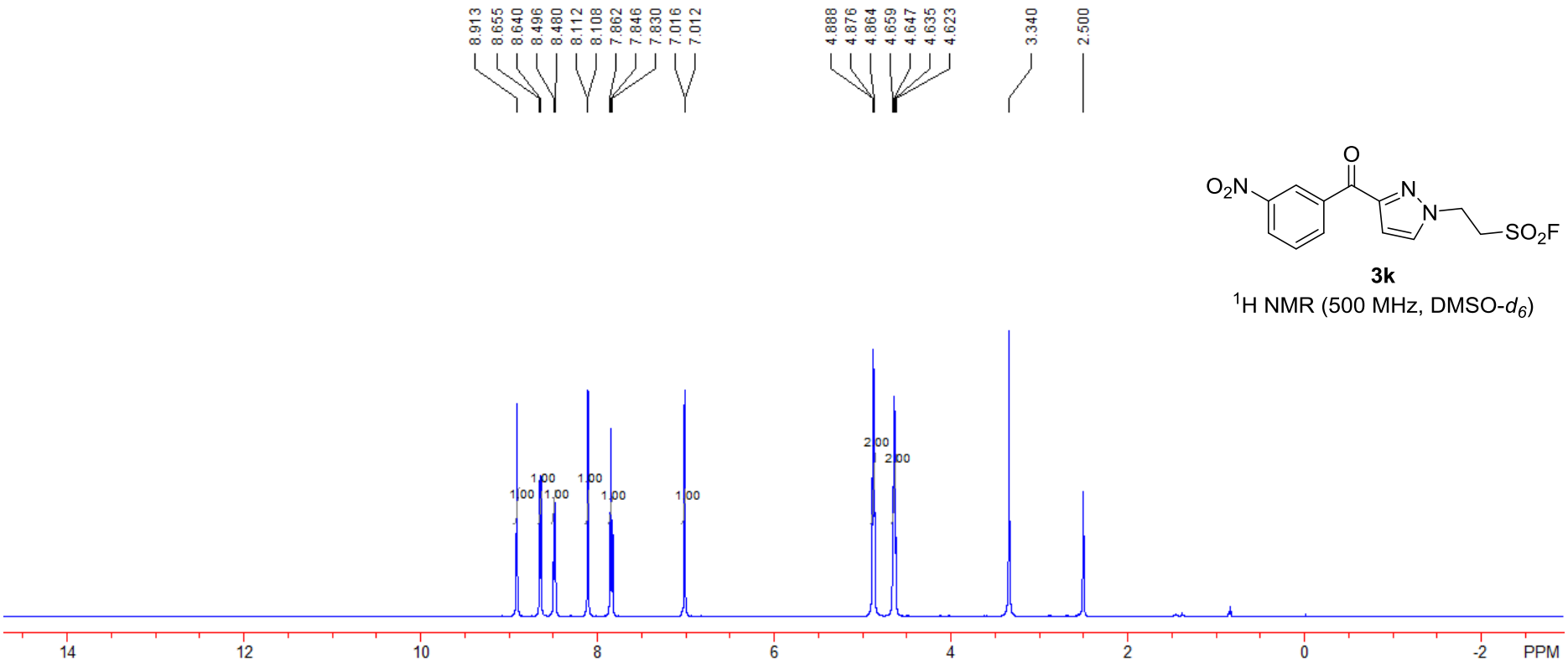
3j

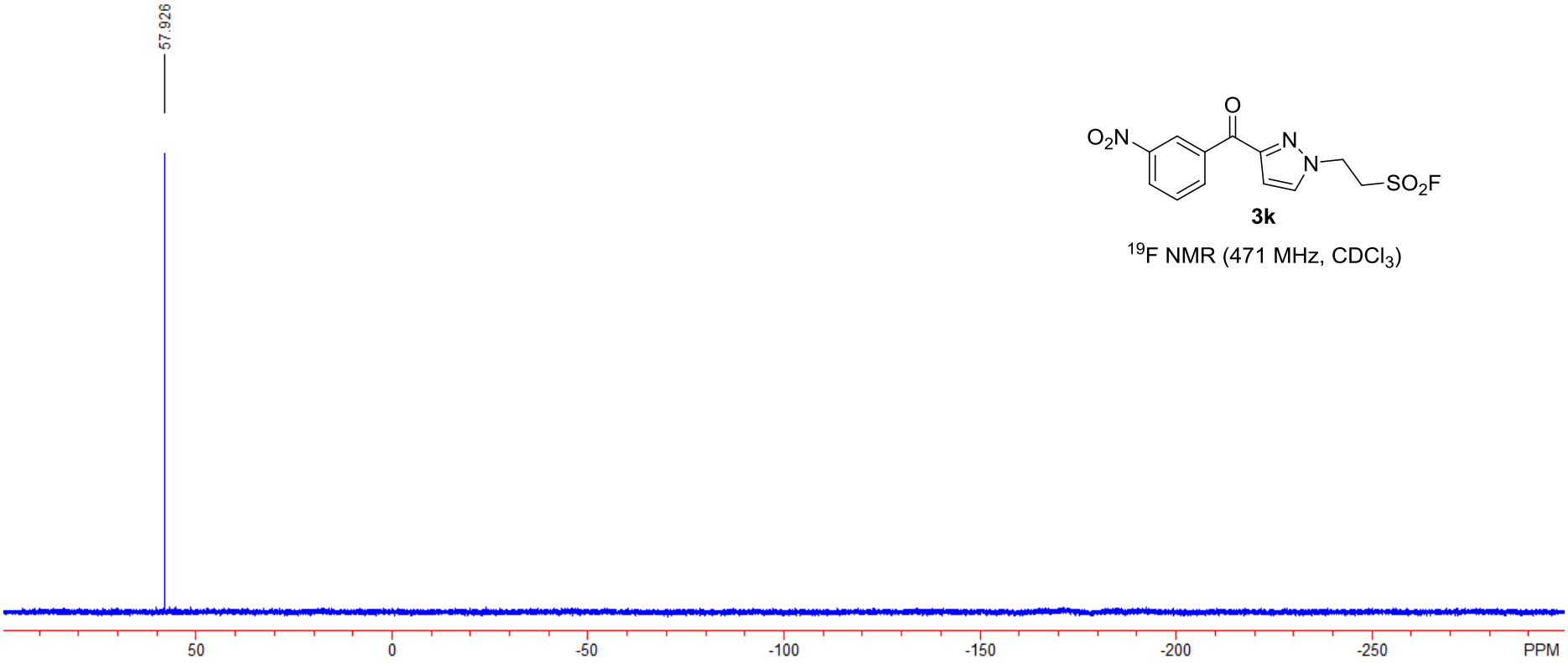
^{19}F NMR (471 MHz, $CDCl_3$)



3j

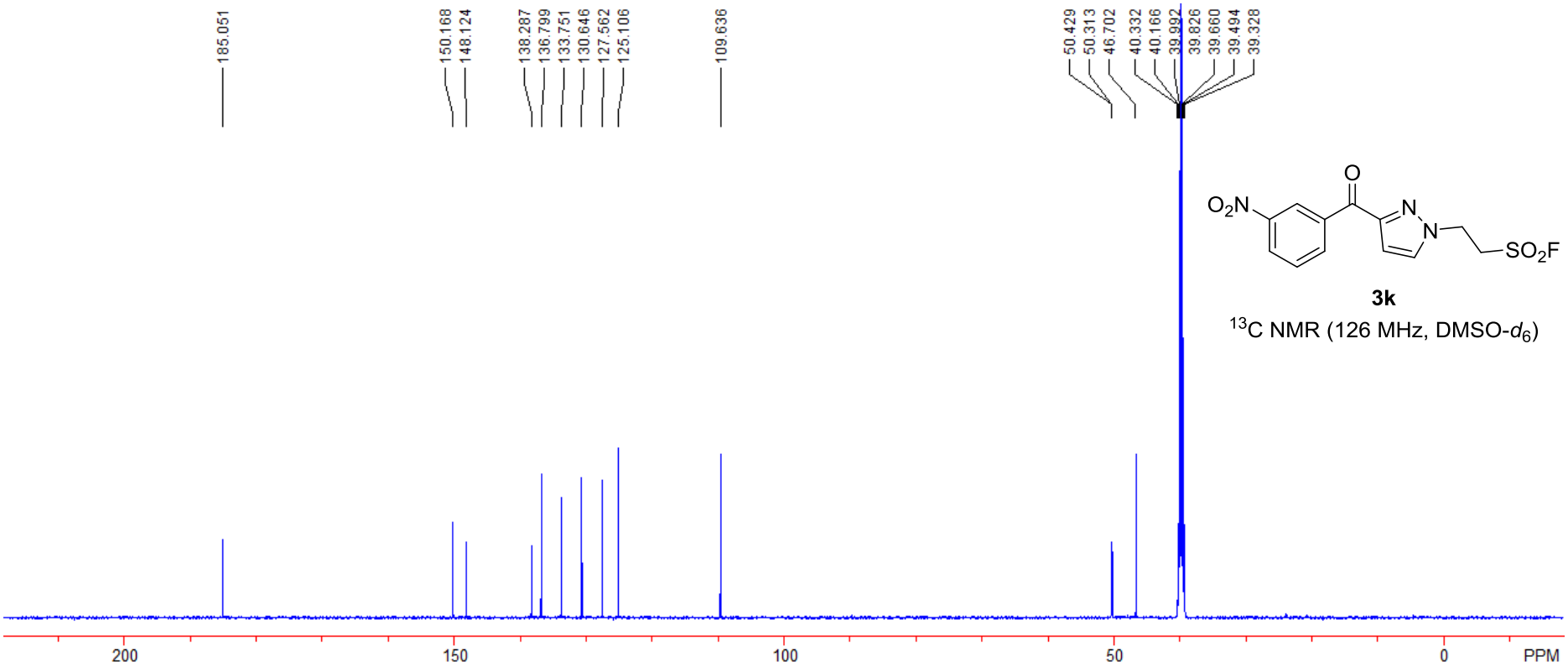
^{13}C NMR (126 MHz, $CDCl_3$)


8.913
8.655
8.640
8.496
8.480
8.112
8.108
7.862
7.846
7.830
7.016
7.012
4.888
4.876
4.864
4.659
4.647
4.635
4.623
3.340
2.500
O
O2N
N
N
SO2F
3k
1H NMR (500 MHz, DMSO-d6)
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
14
12
10
8
6
4
2
0
-2
PPM



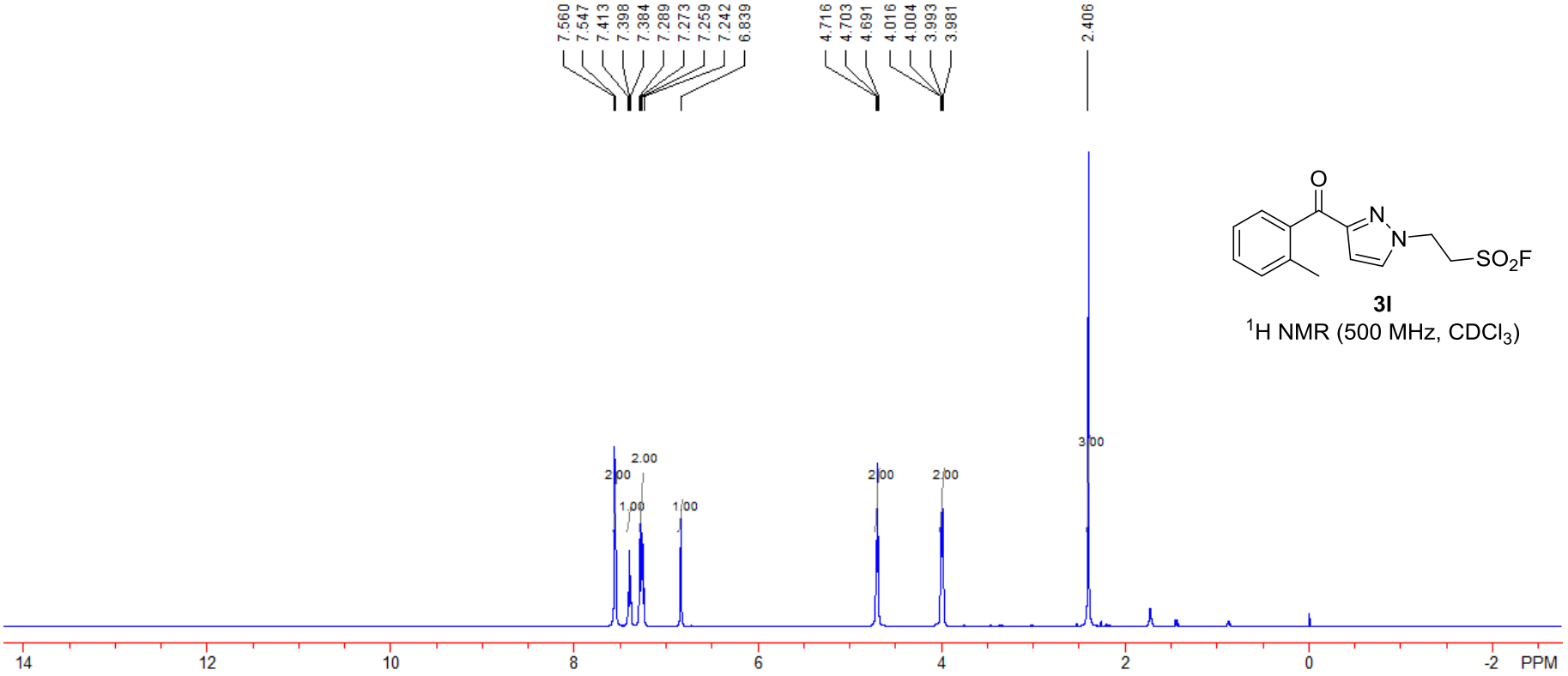
3k

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



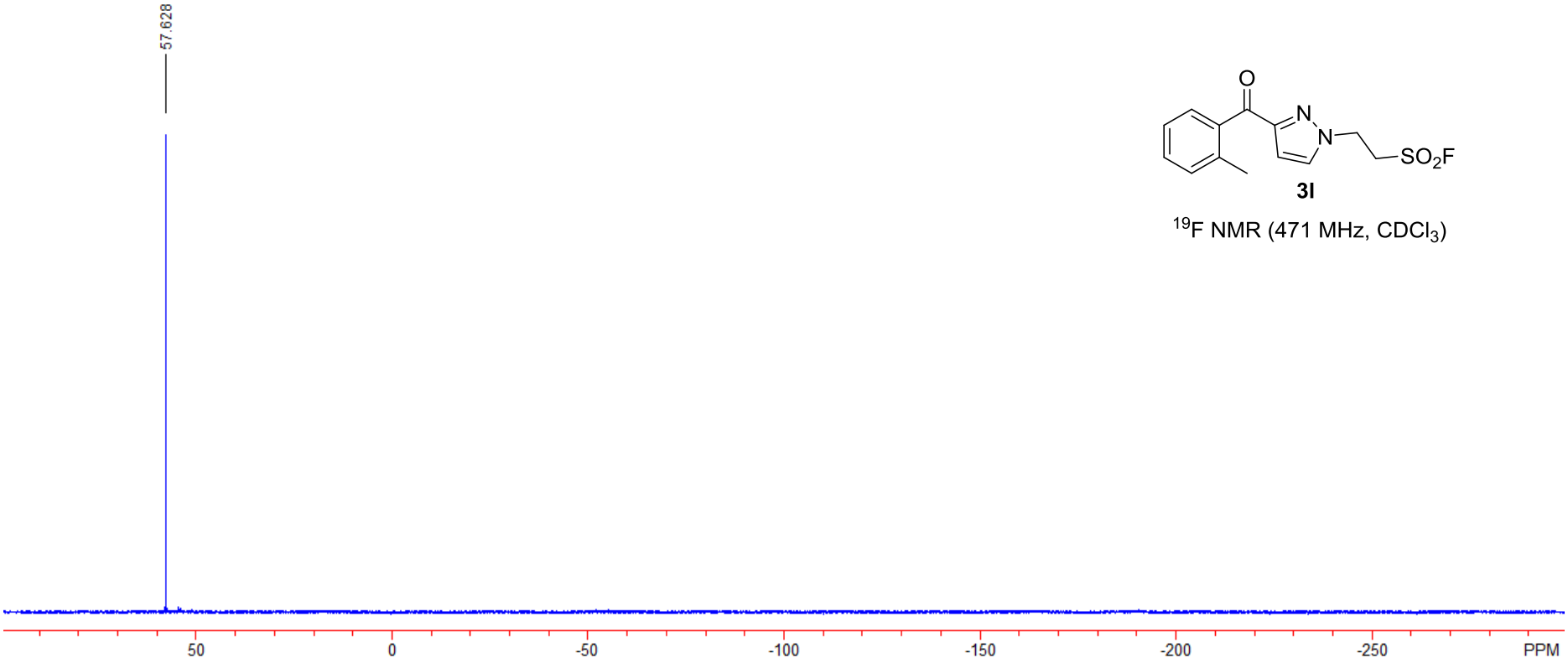
3k

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



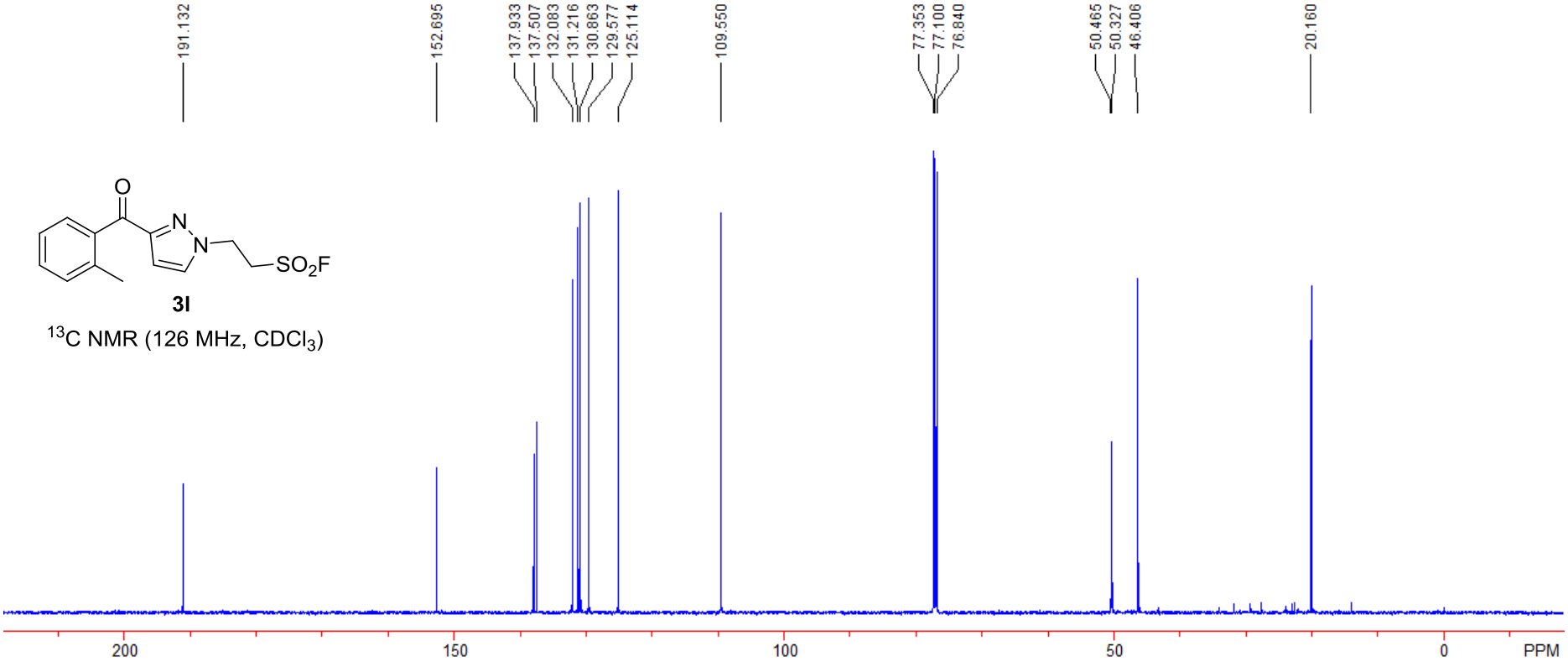
3l

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



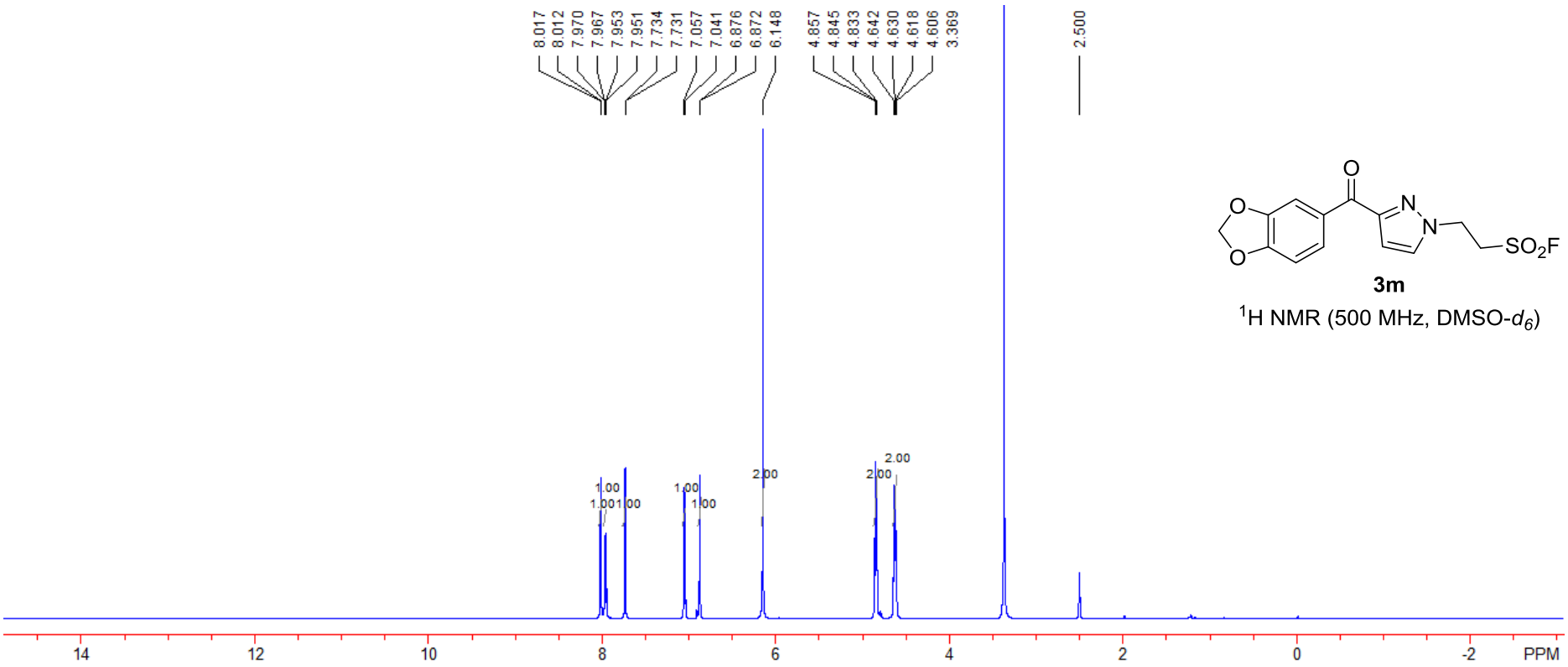
3l

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



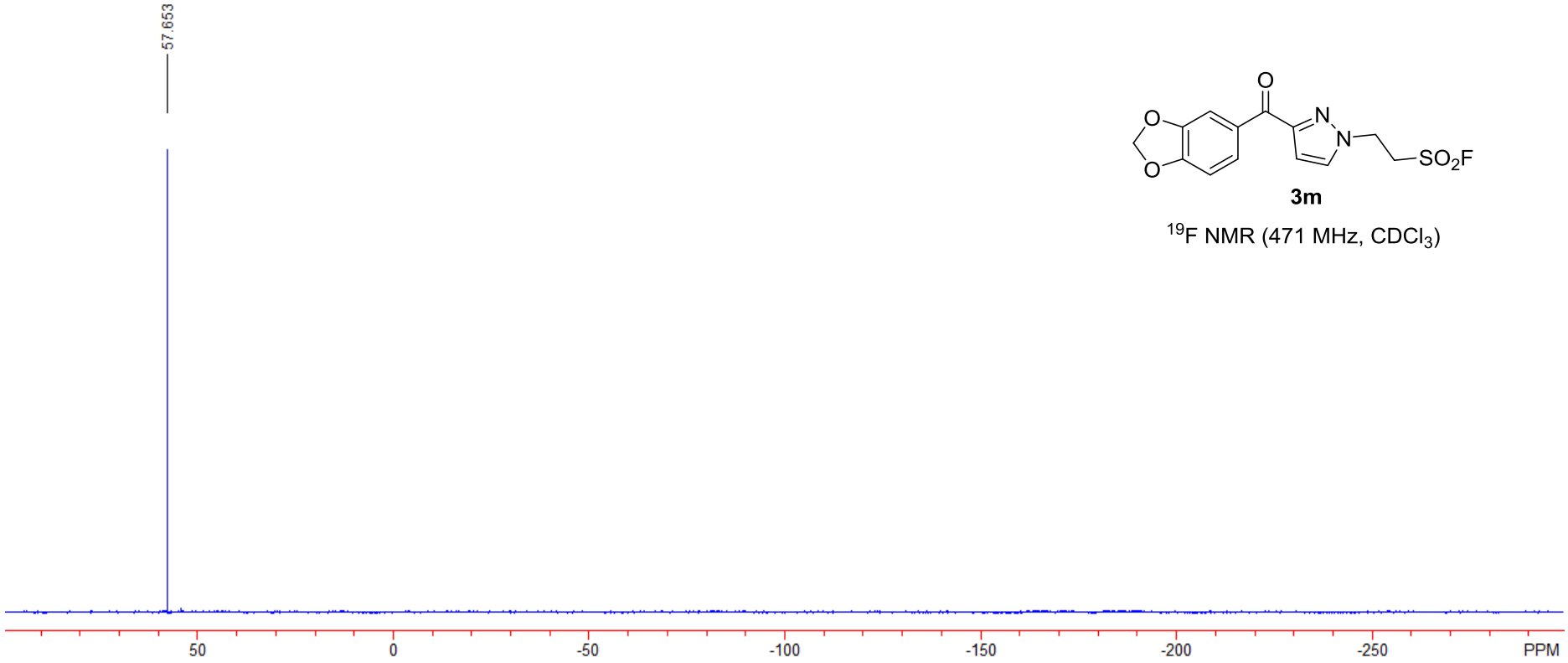
3l

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



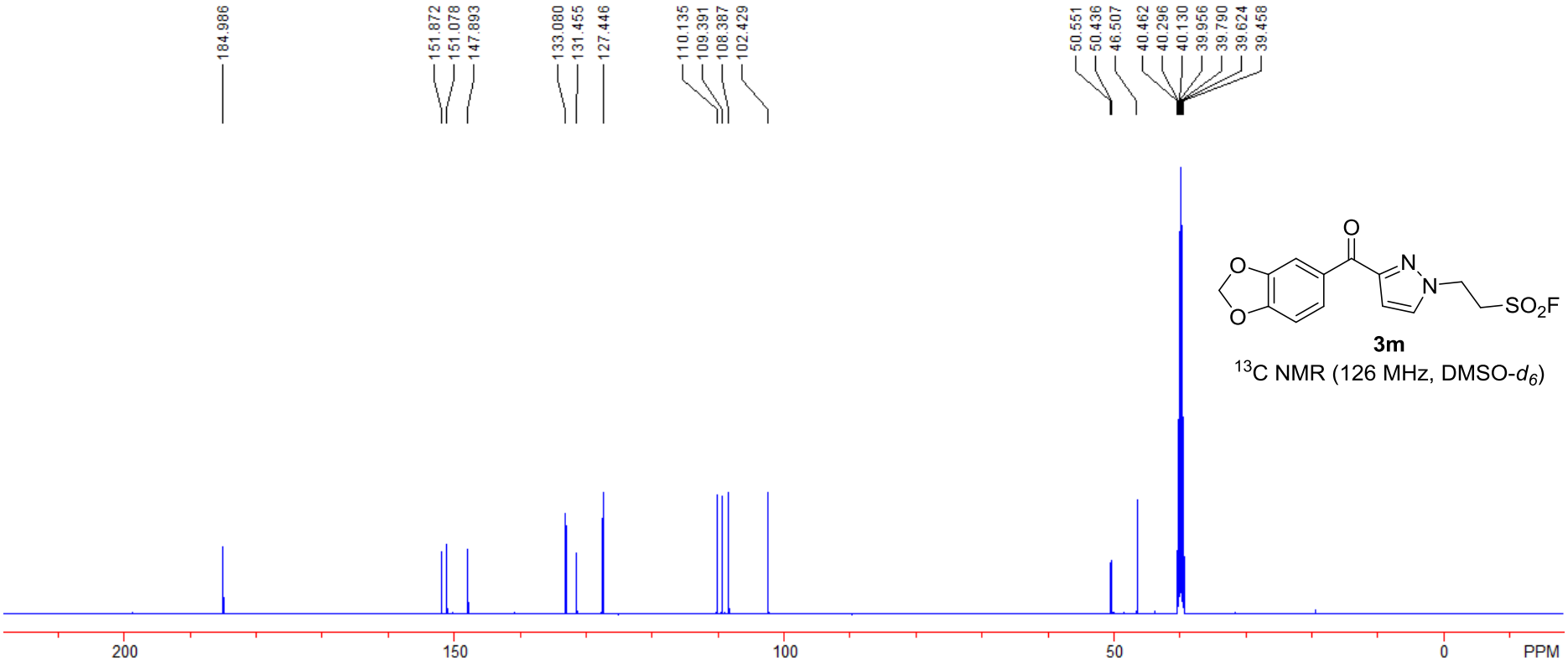
3m

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



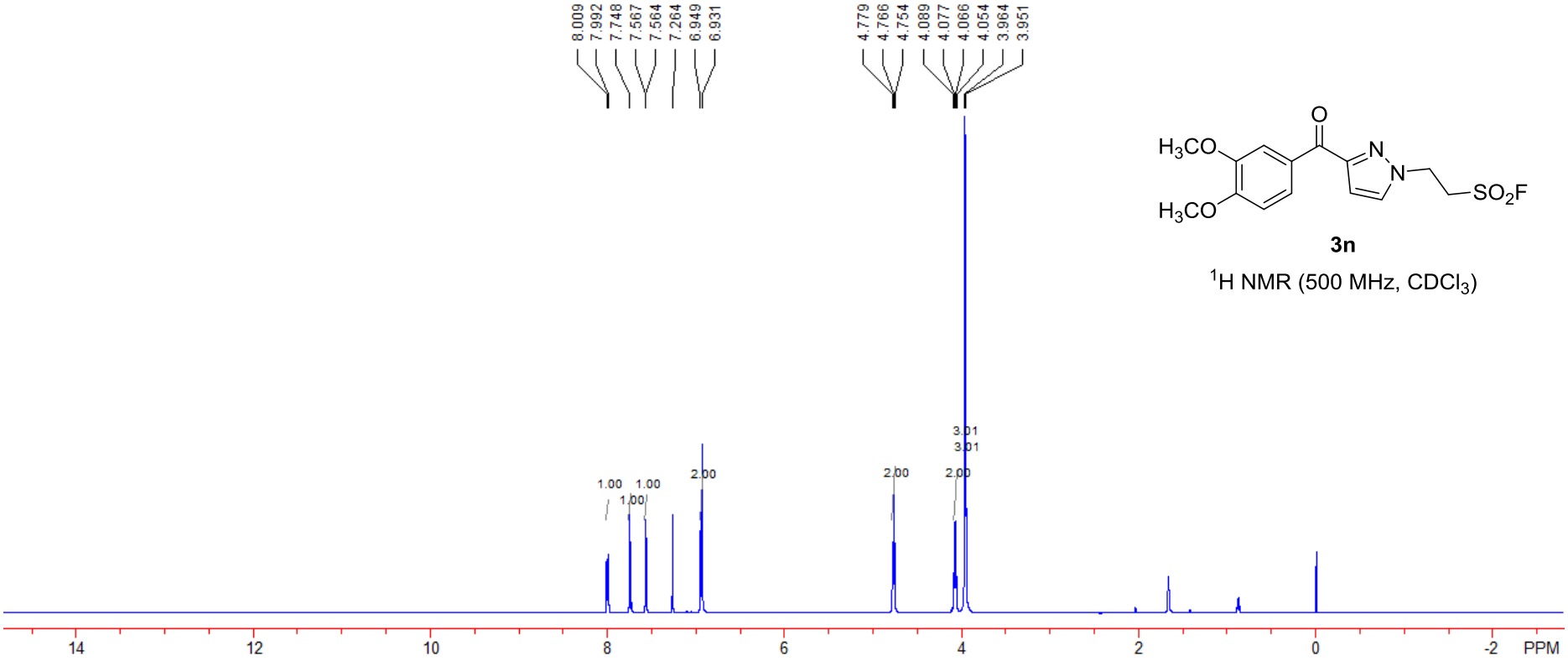
3m

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



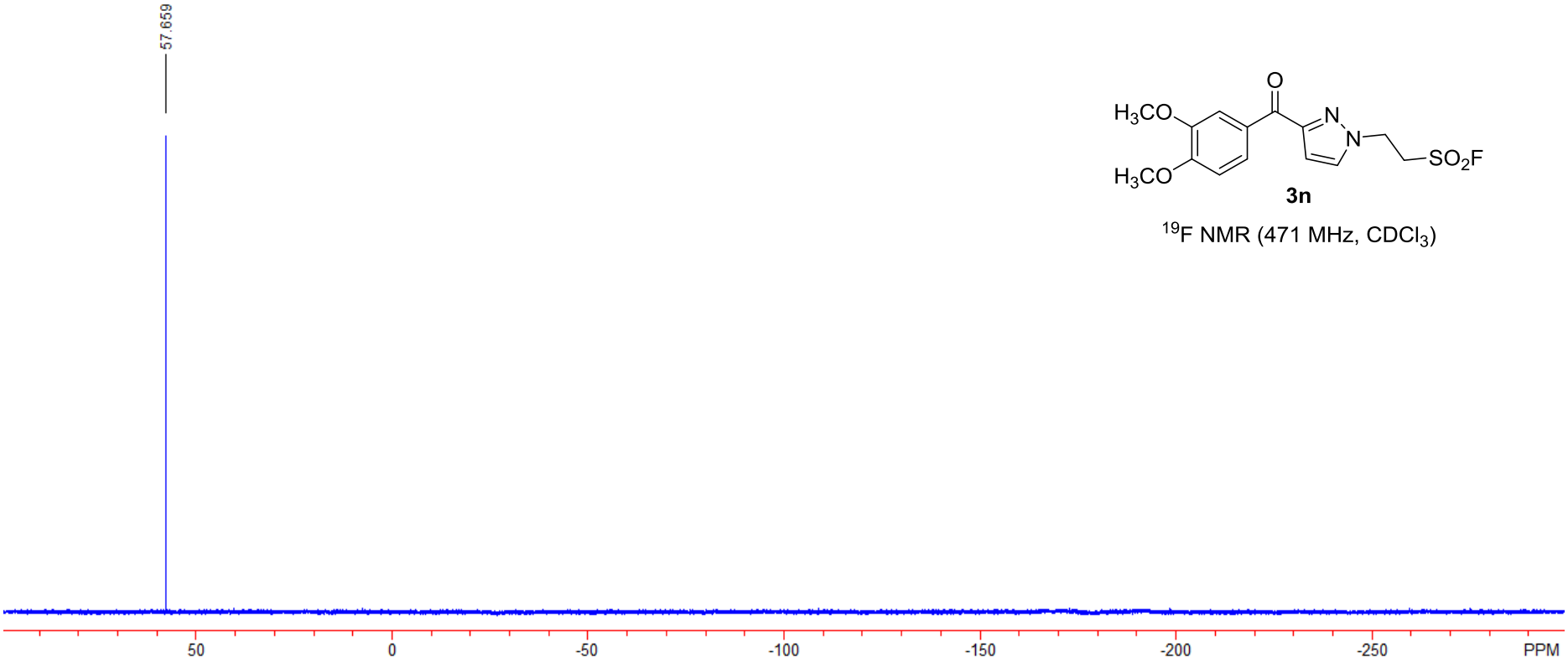
3m

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



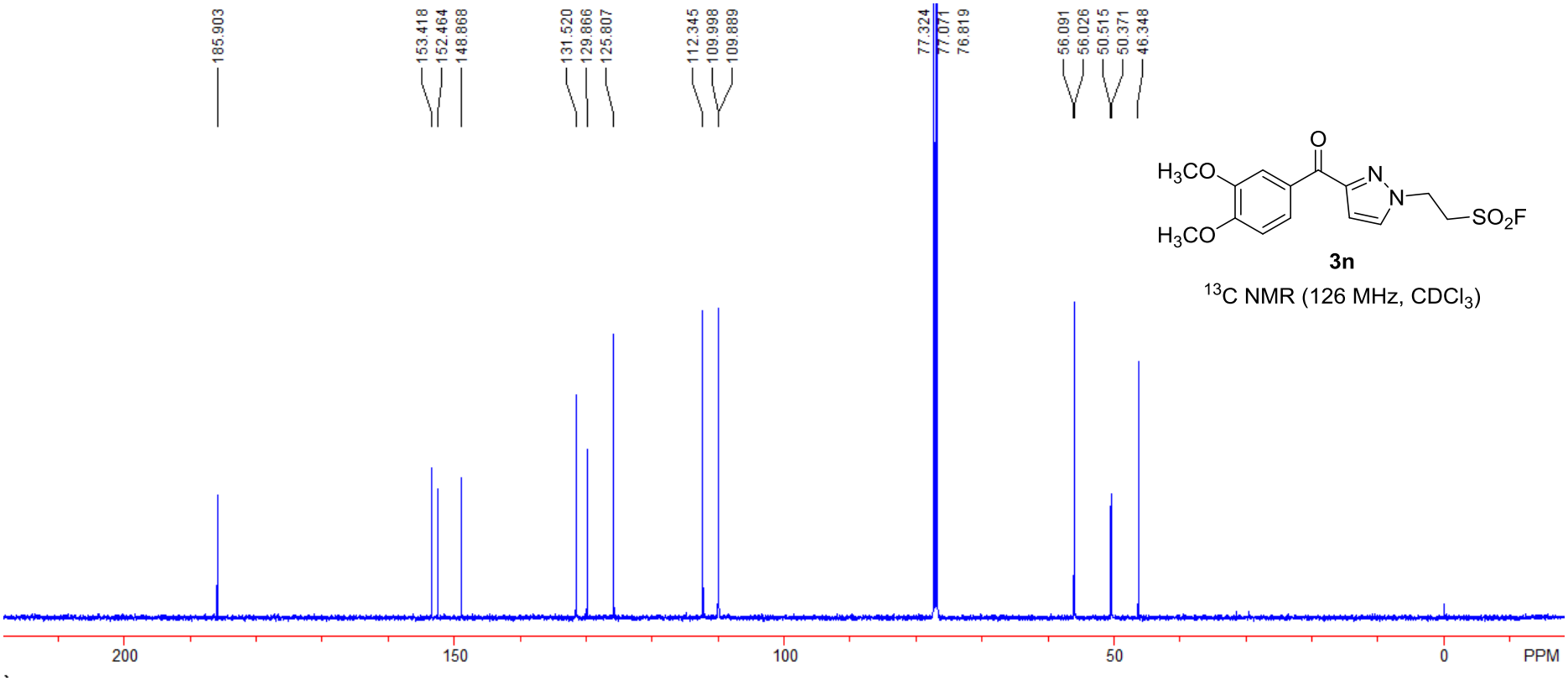
3n

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



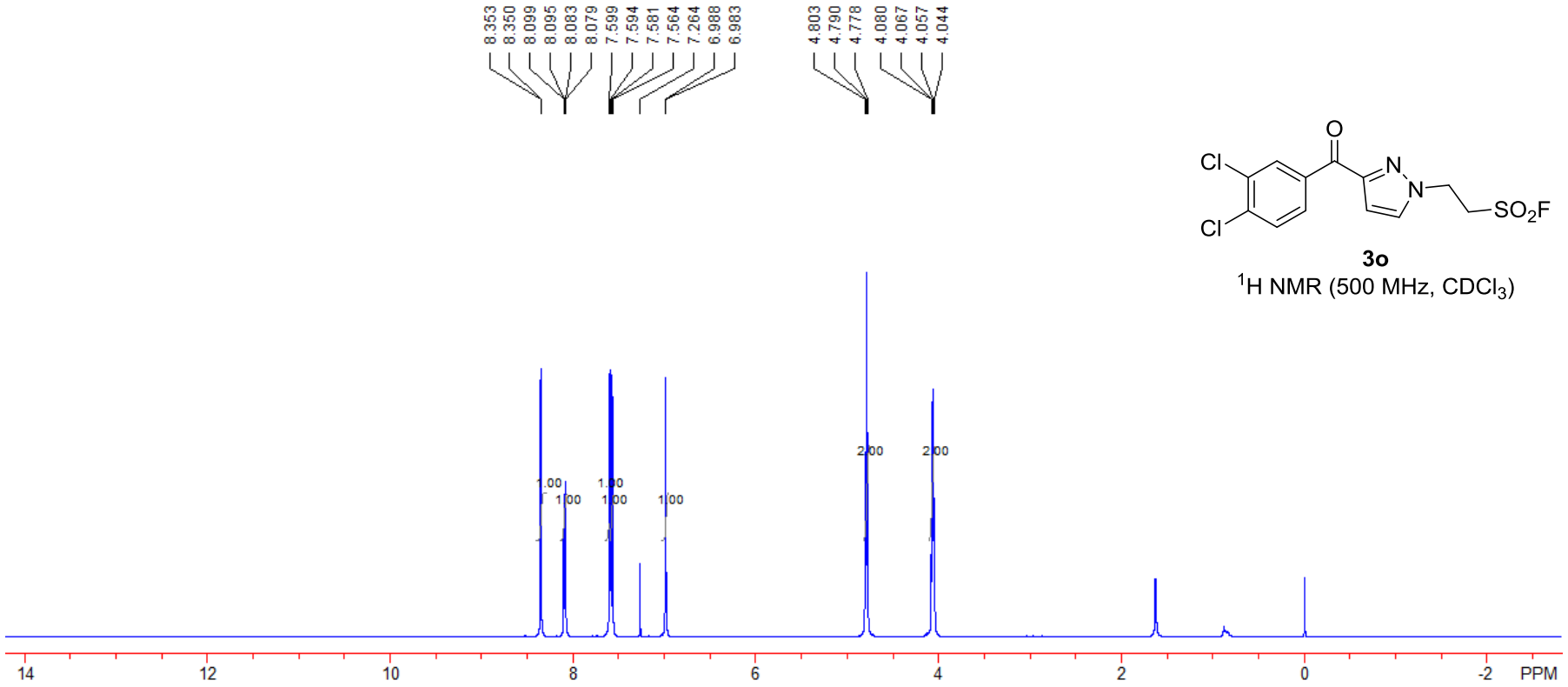
3n

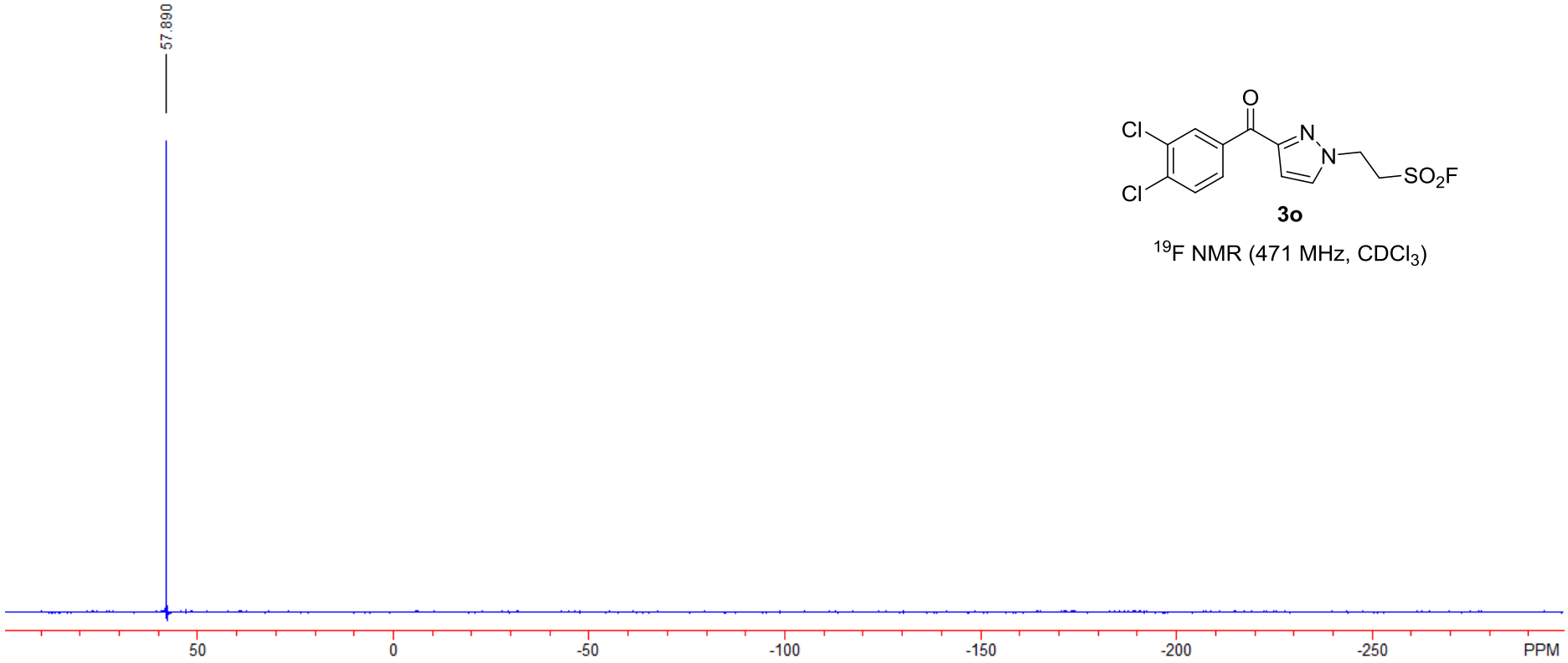
^{19}F NMR (471 MHz, $CDCl_3$)



3n

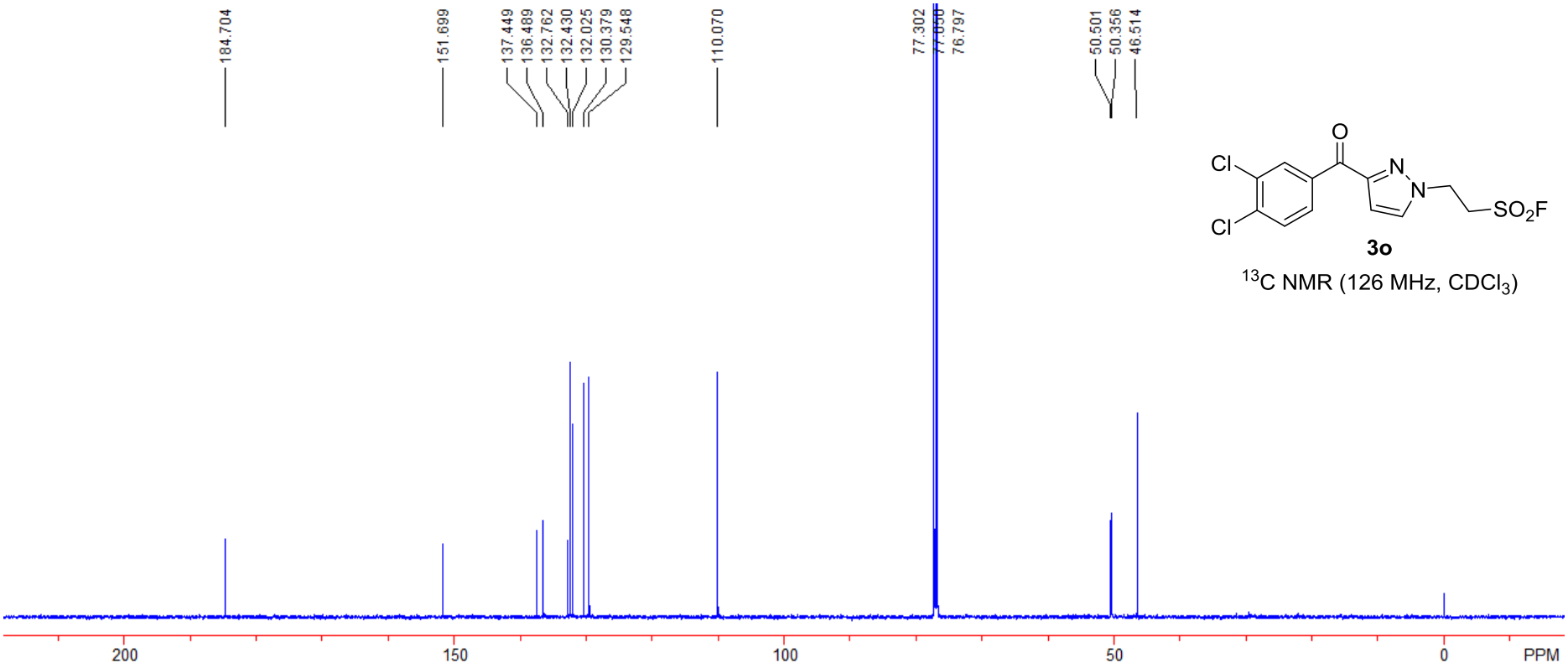
^{13}C NMR (126 MHz, $CDCl_3$)


8.353
8.350
8.099
8.095
8.083
8.079
7.599
7.594
7.581
7.564
7.264
6.988
6.983
4.803
4.790
4.778
4.080
4.067
4.057
4.044
Cl
Cl
O
N
N
SO2F
3o
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.00
1.00
1.00
2.00
2.00
14
12
10
8
6
4
2
0
-2
PPM



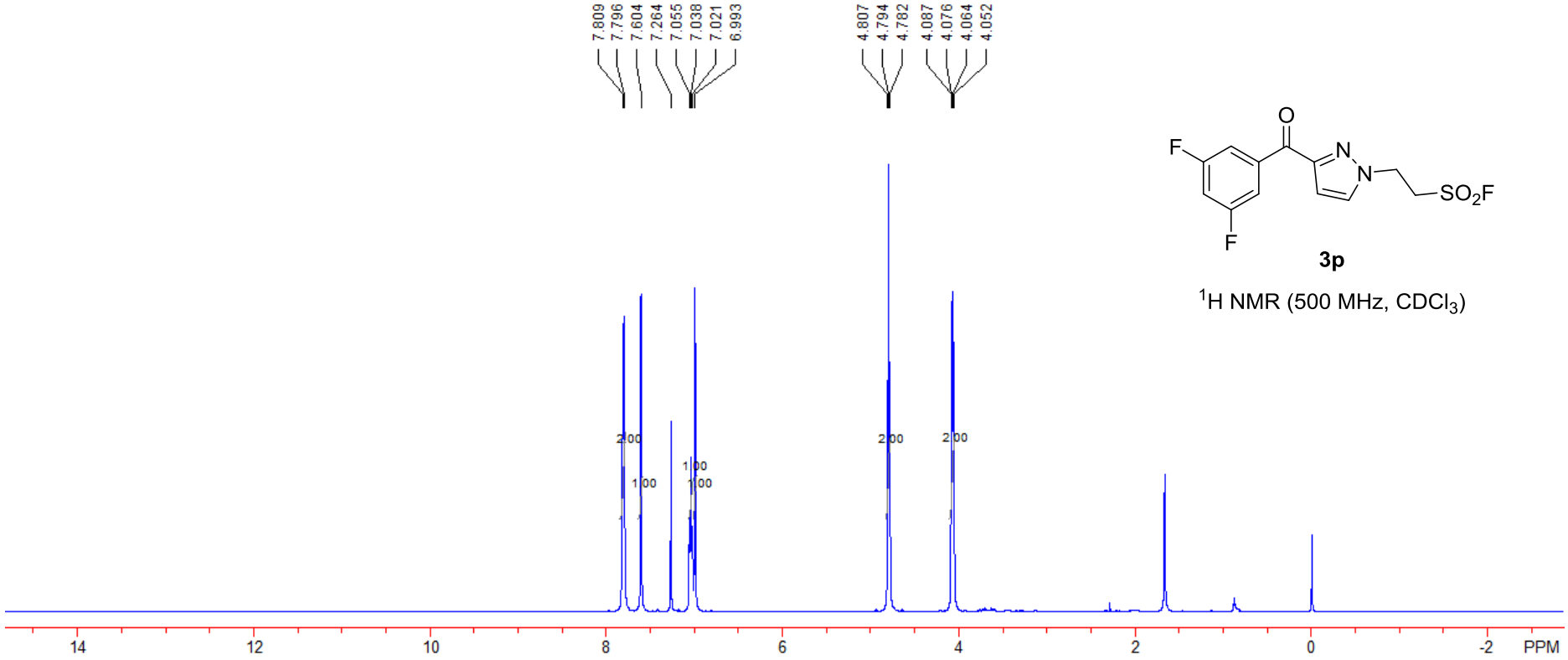
3o

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



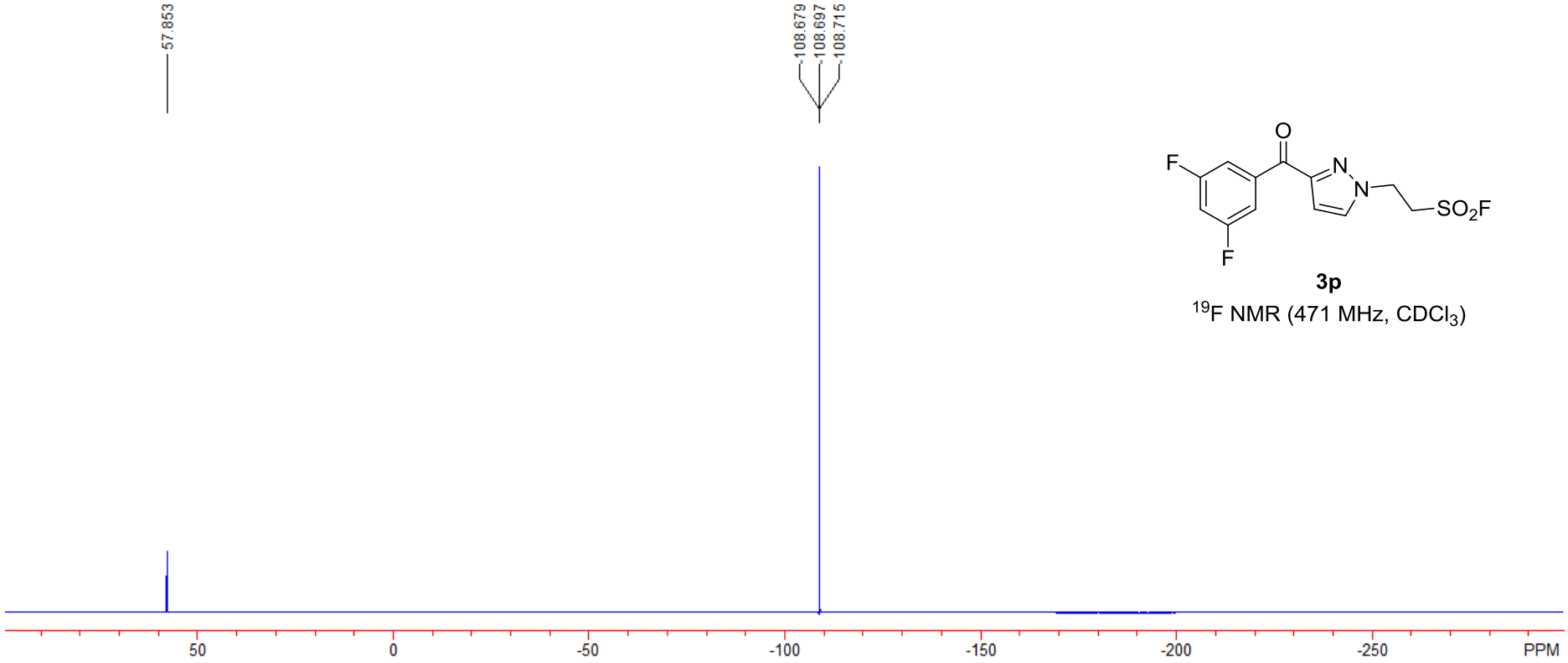
3o

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



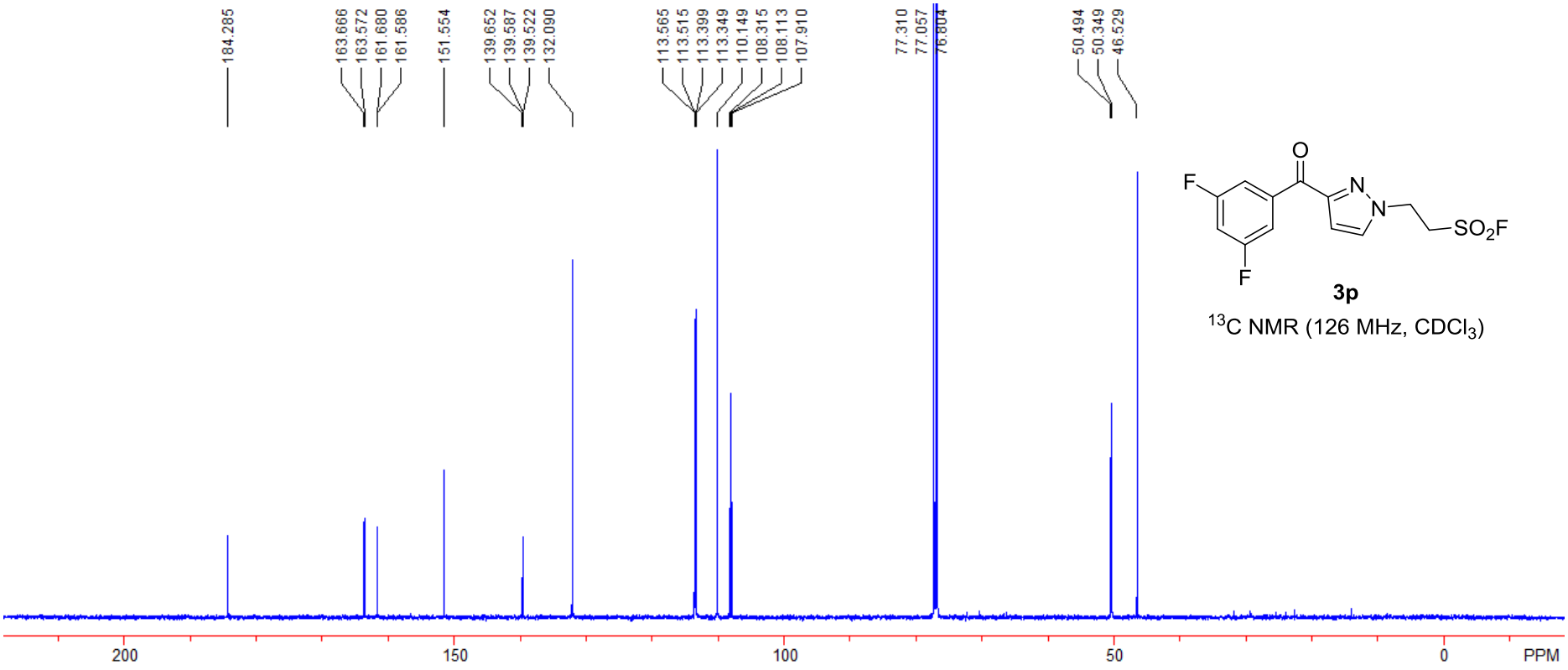
3p

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



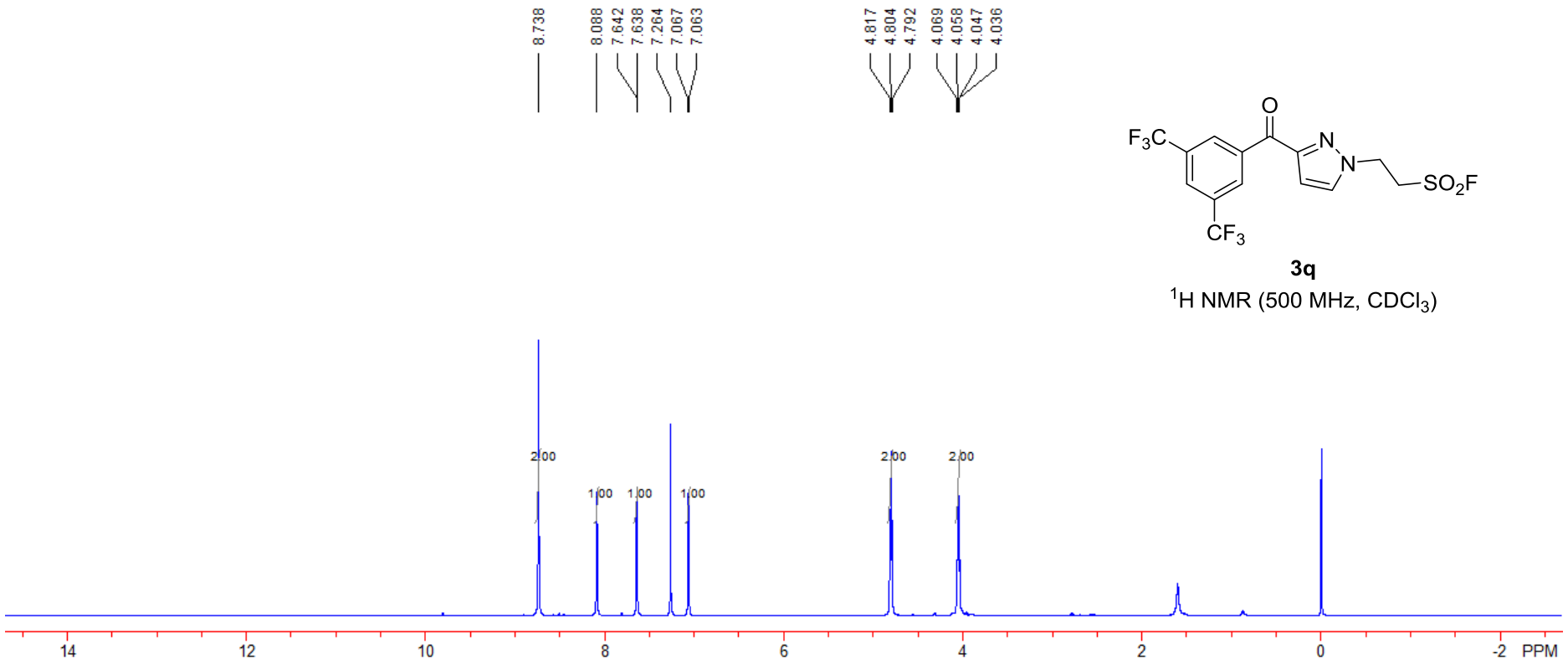
3p

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



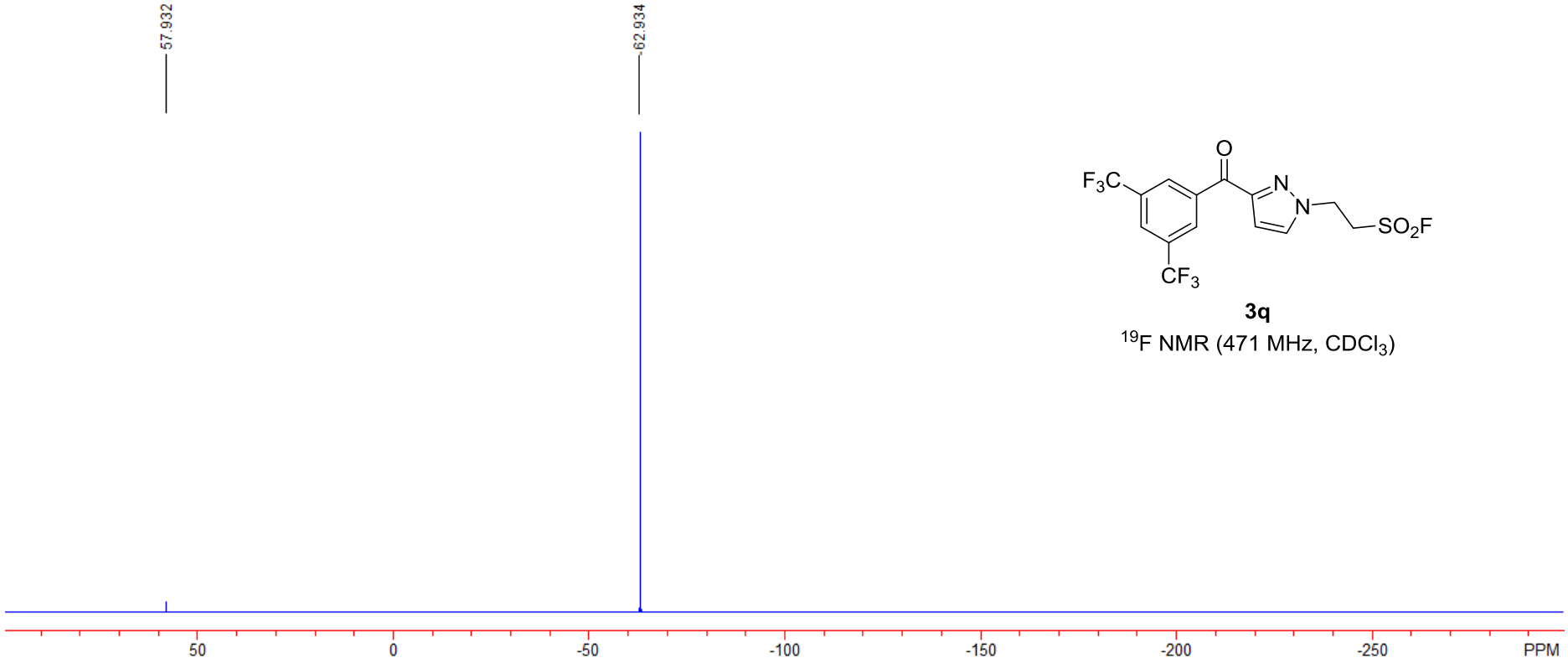
3p

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



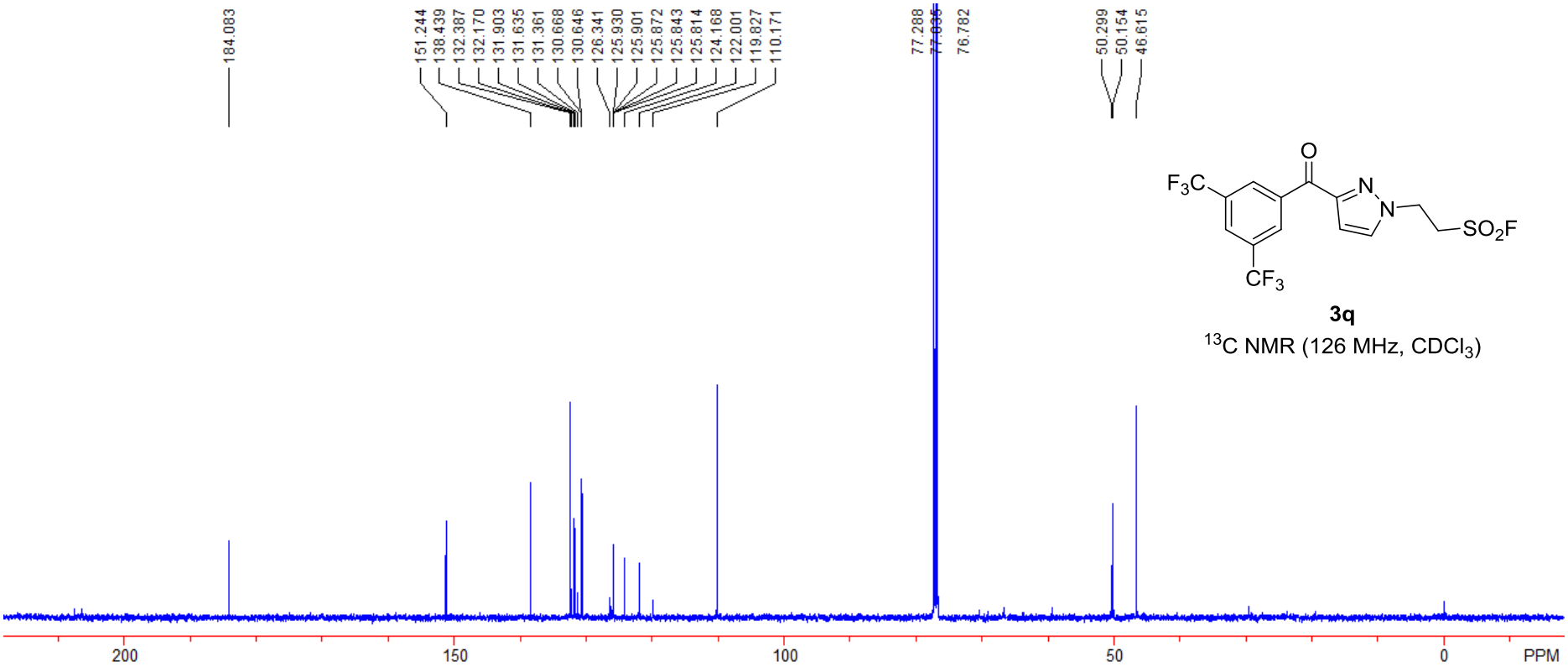
3q

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



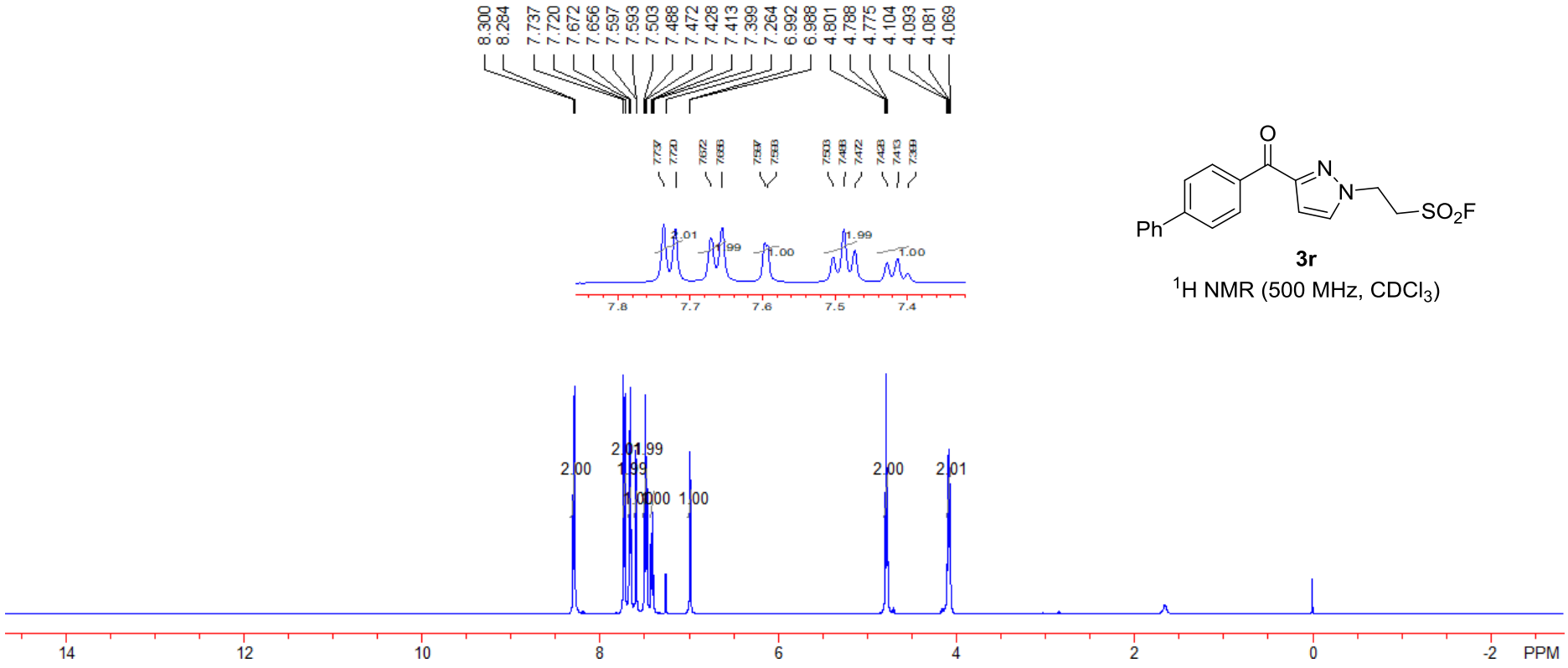
3q

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



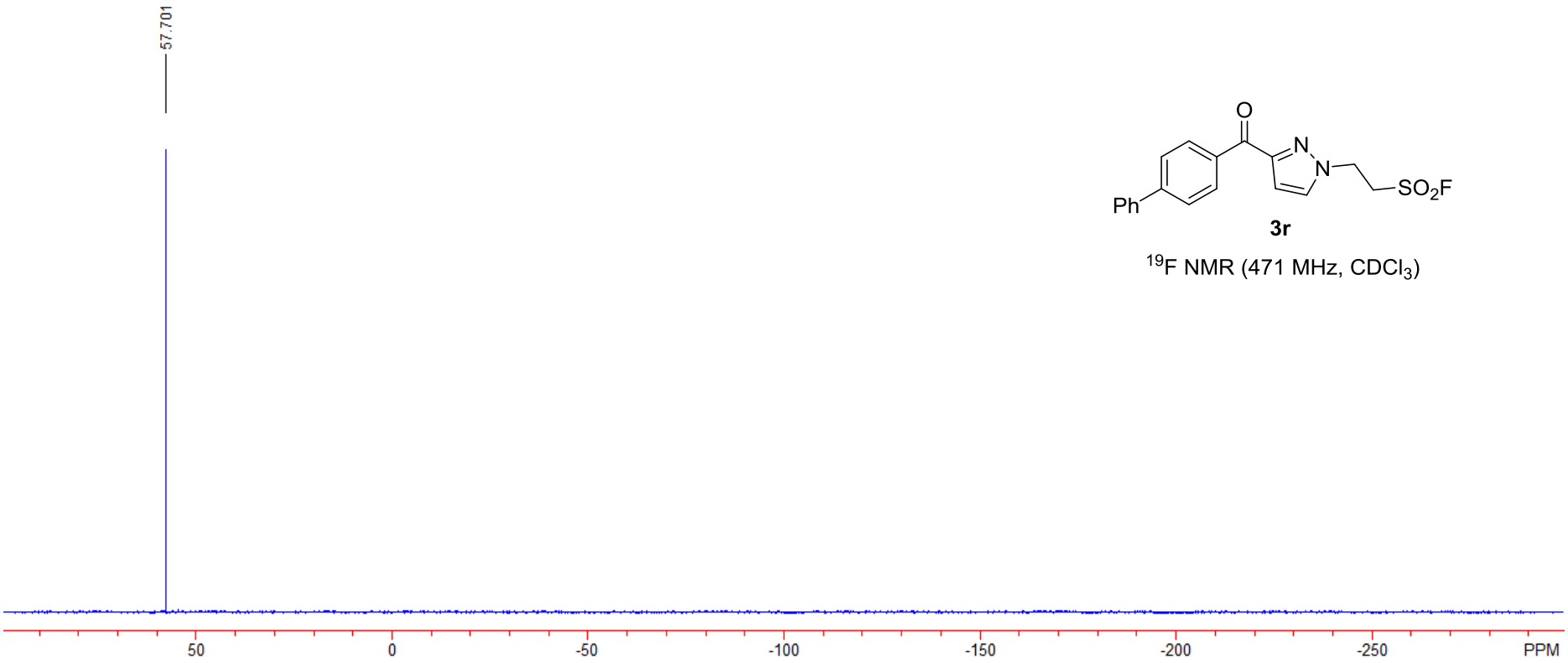
3q

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



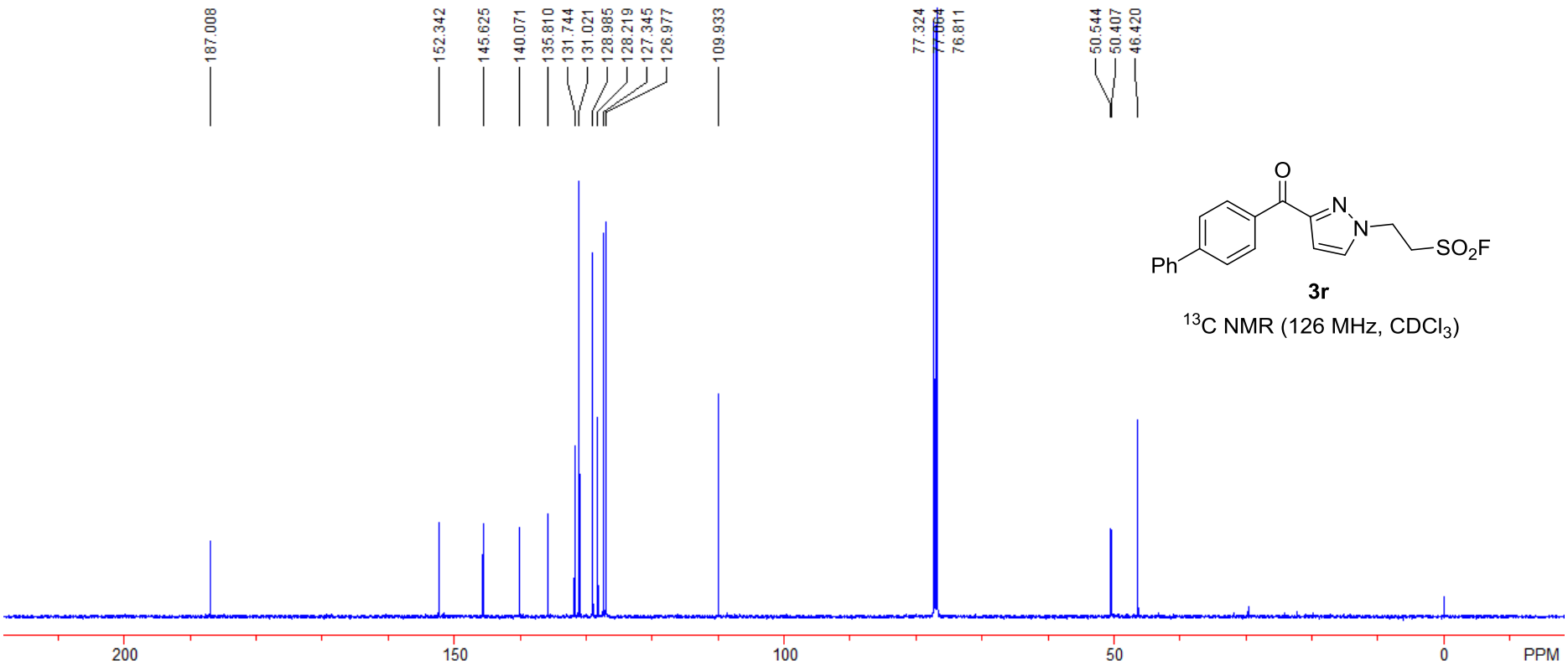
3r

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



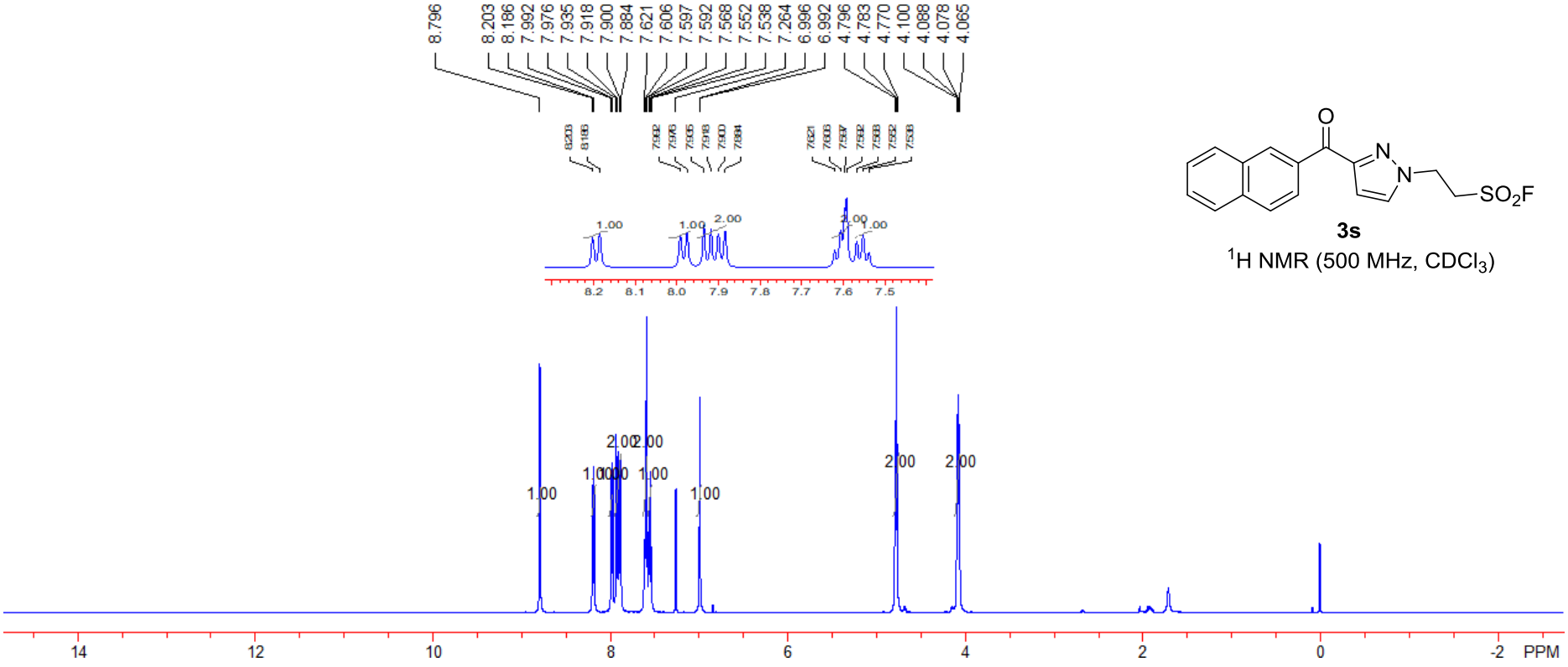
3r

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



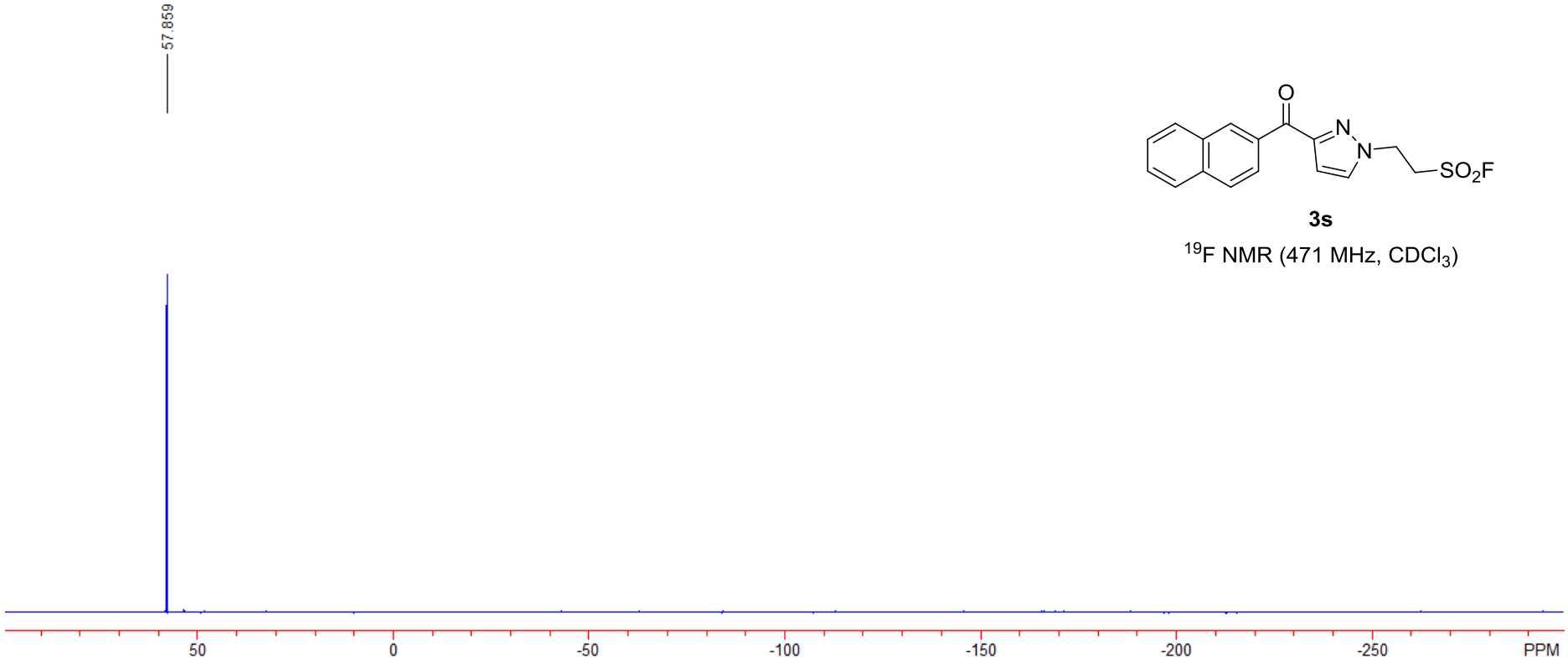
3r

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



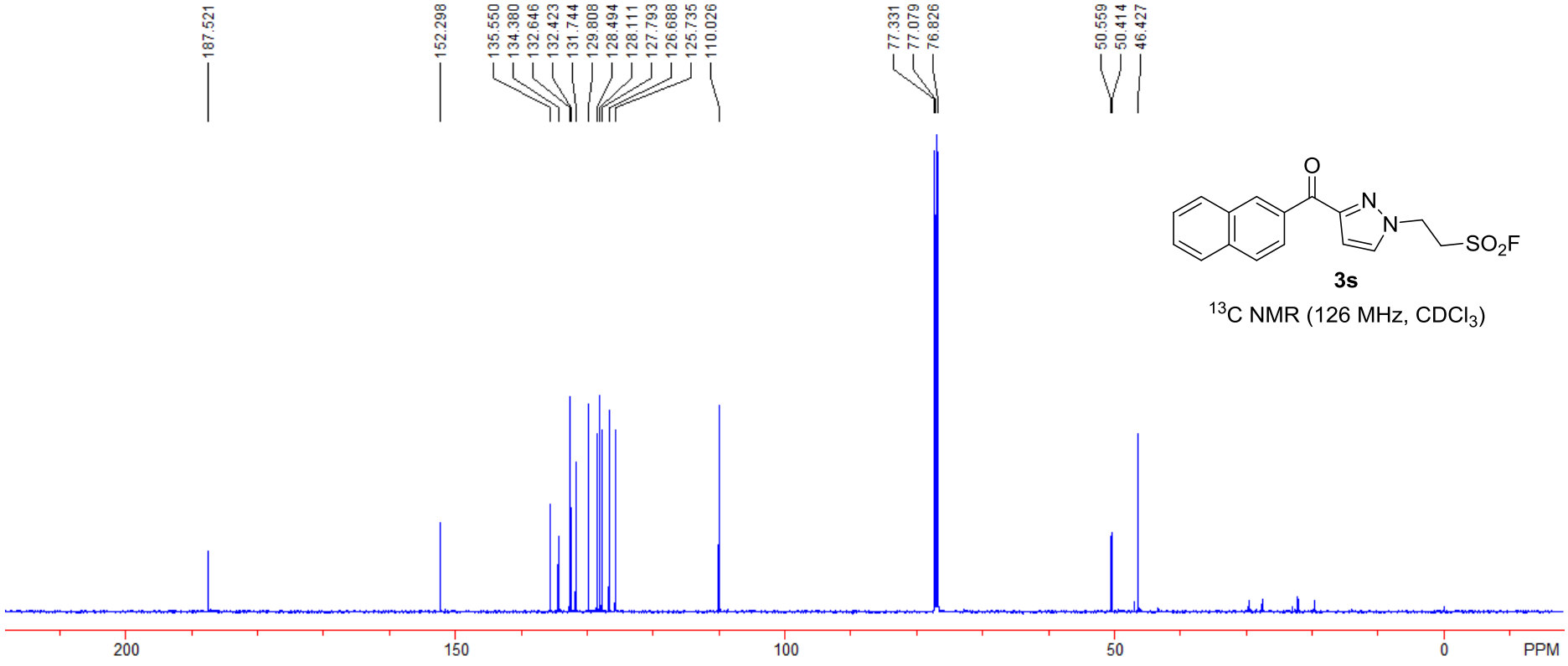
3s

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



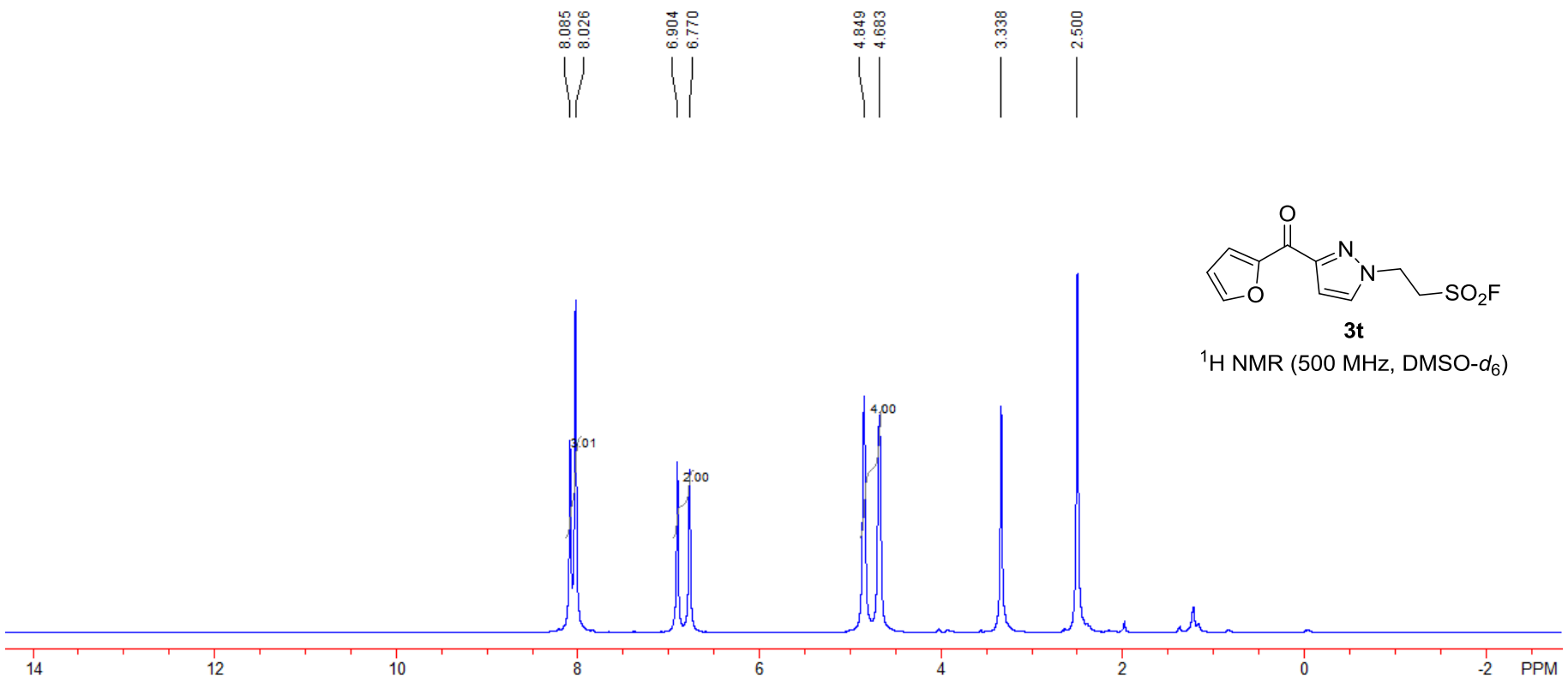
3s

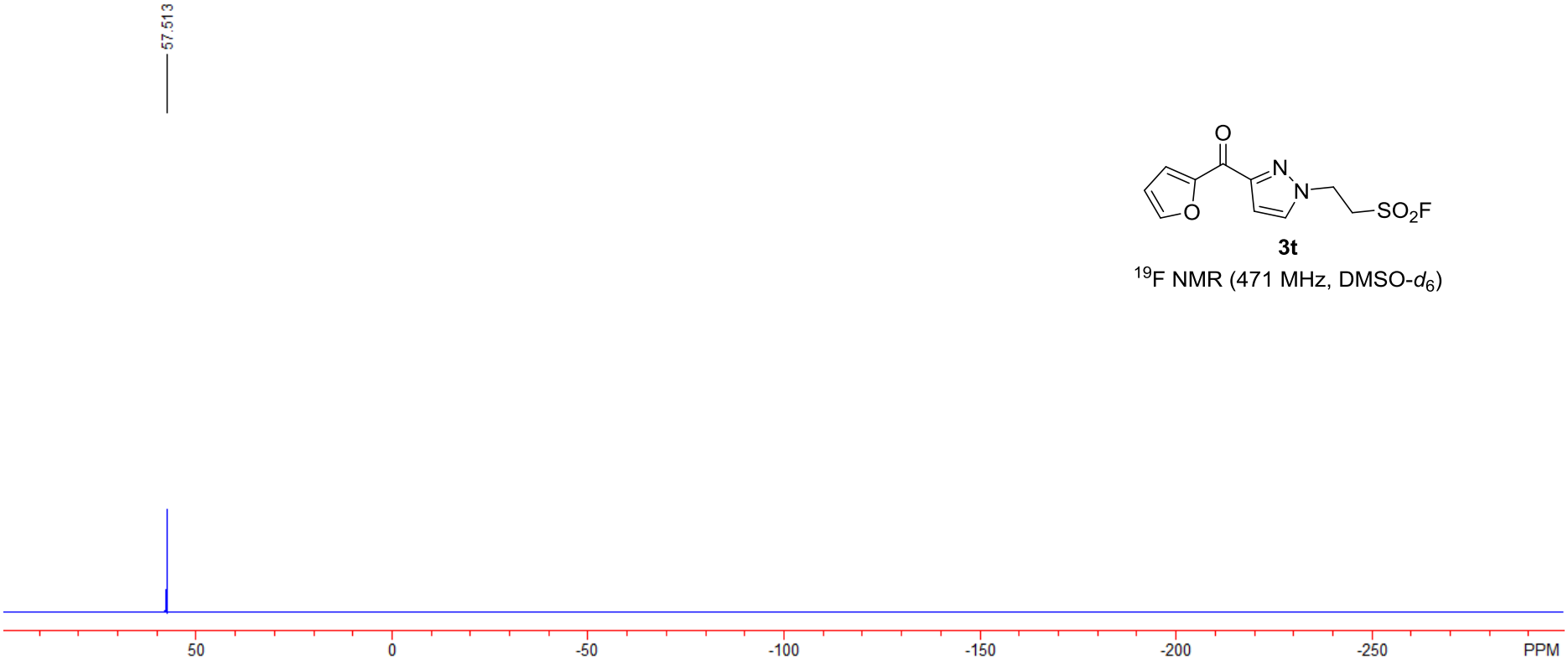
^{19}F NMR (471 MHz, $CDCl_3$)



3s

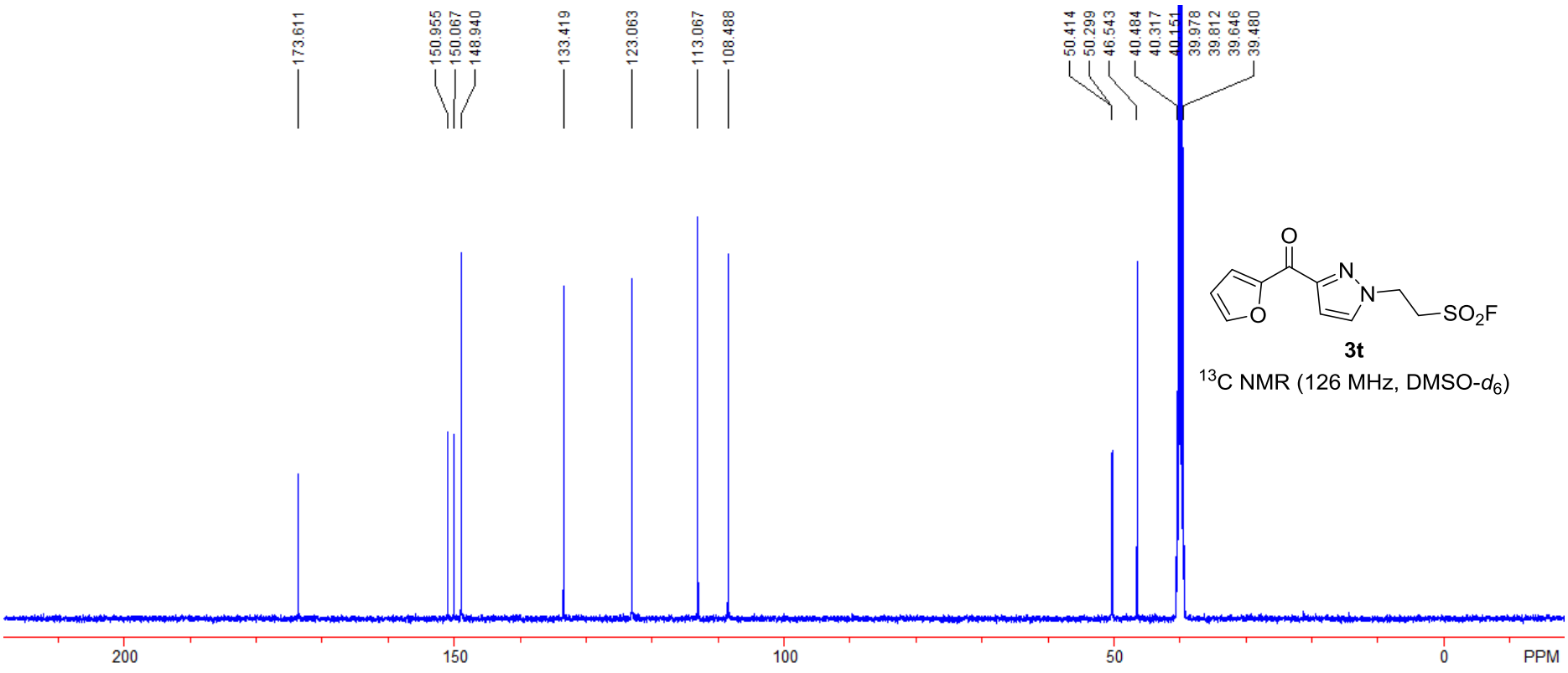
^{13}C NMR (126 MHz, $CDCl_3$)


8.085
8.026
6.904
6.770
4.849
4.683
3.338
2.500
O
N
N
O
SO2F
3t
1H NMR (500 MHz, DMSO-d6)
4.00
3.01
2.00
14
12
10
8
6
4
2
0
-2
PPM



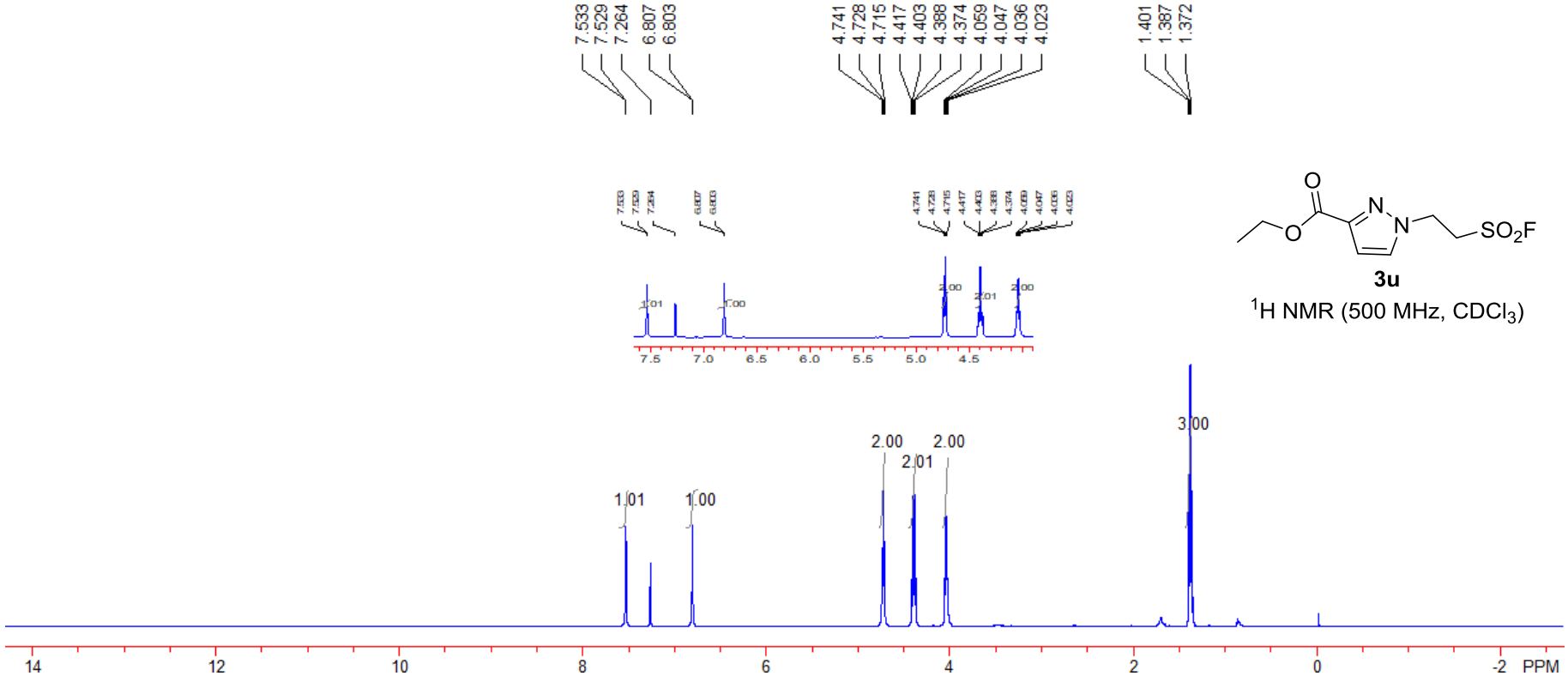
3t

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



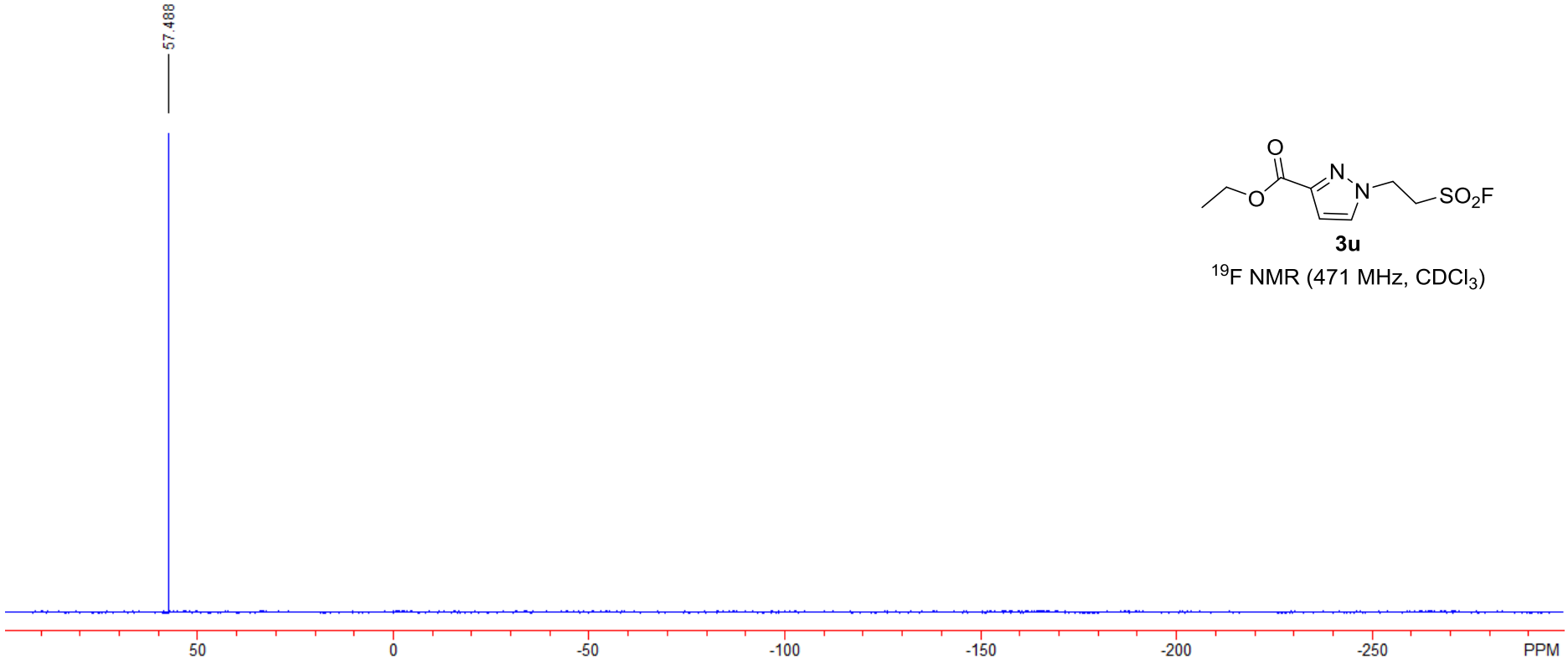
3t

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



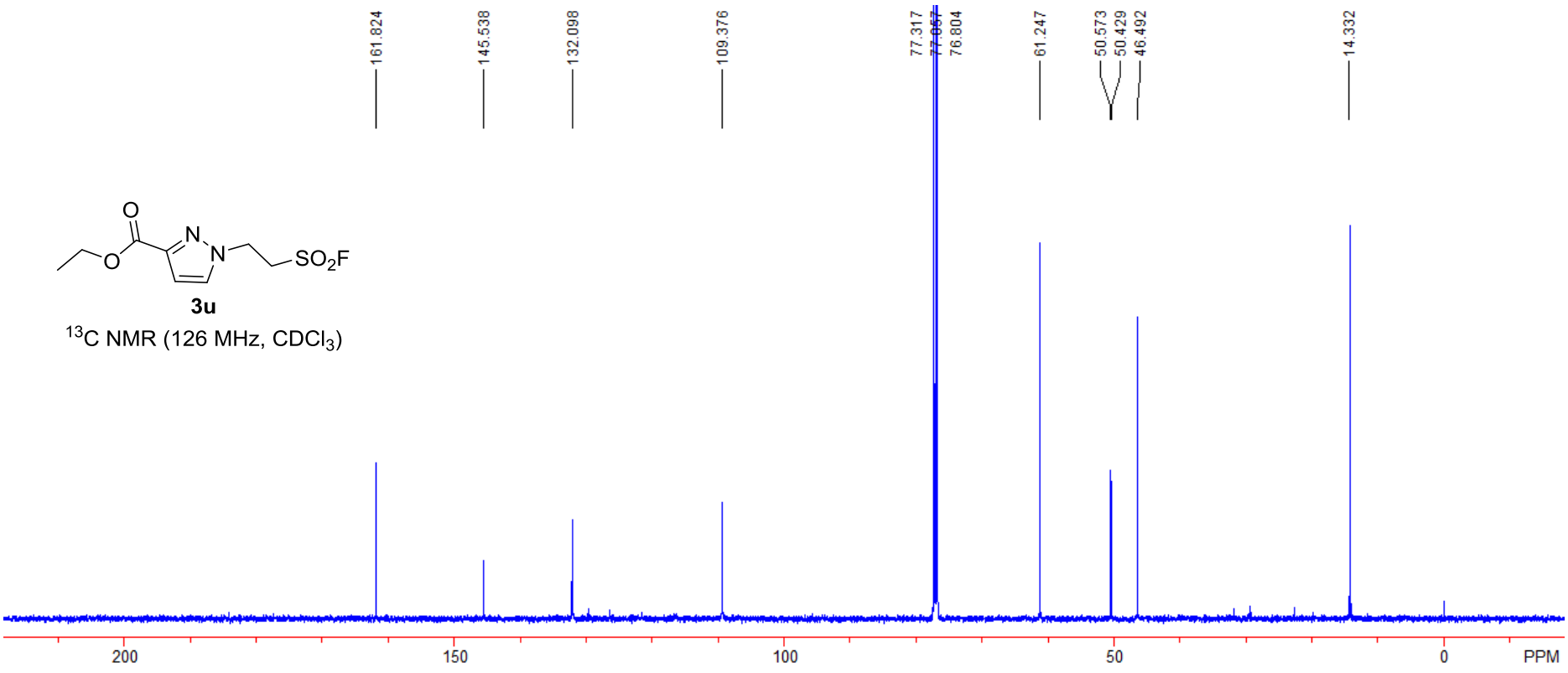
3u

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



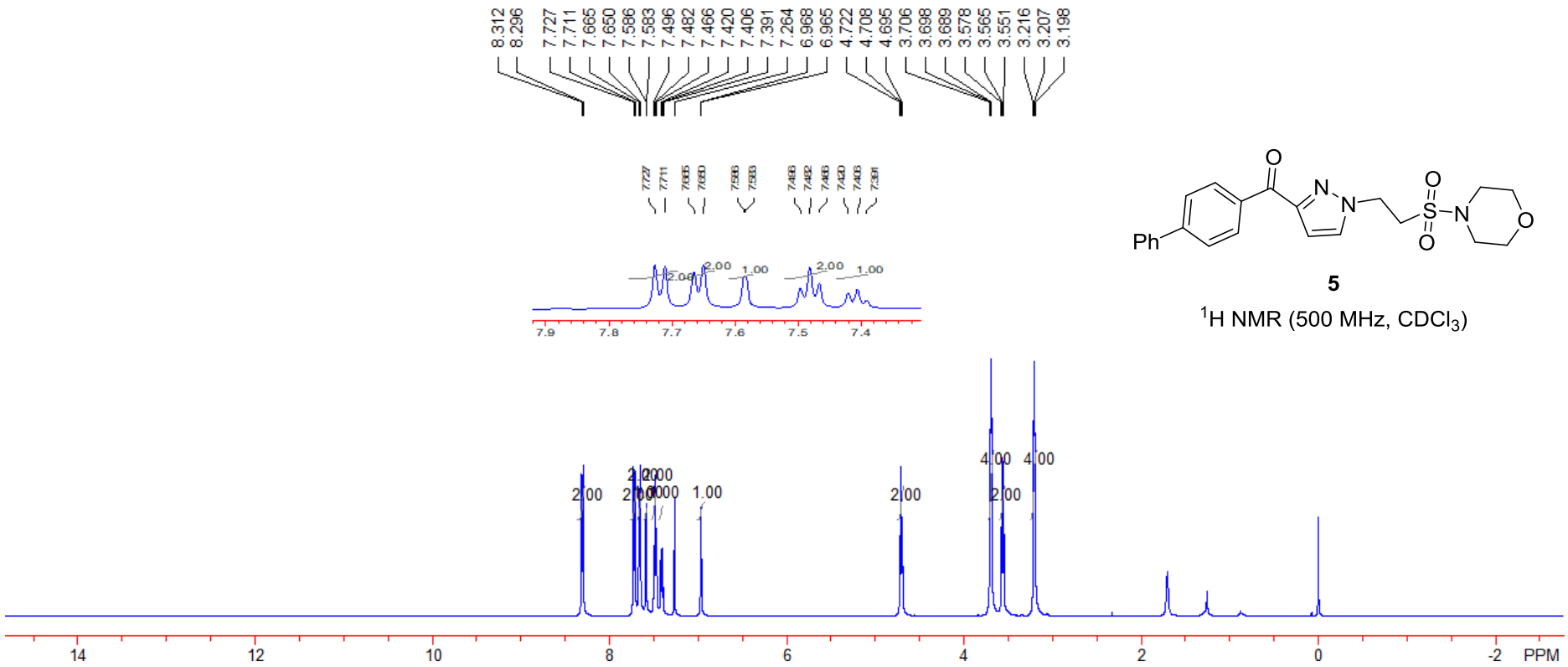
3u

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



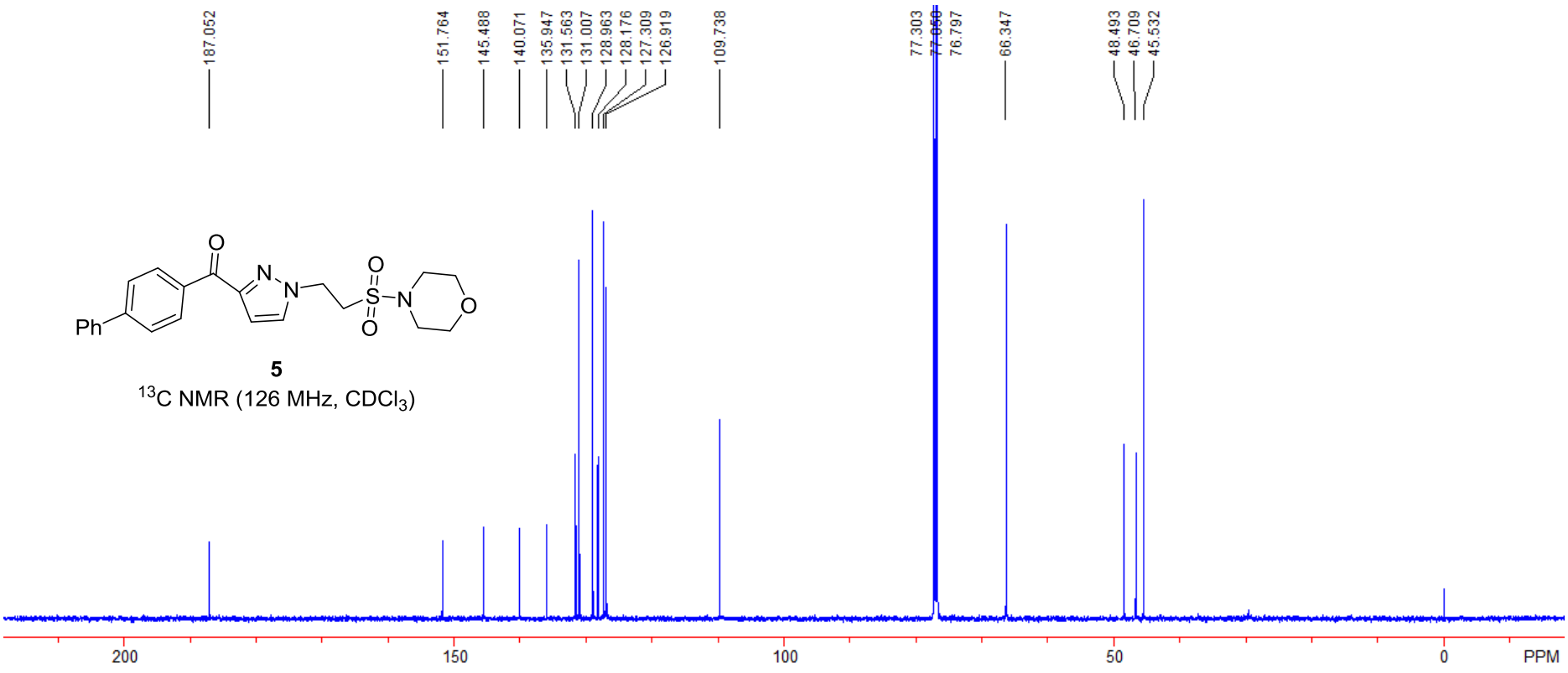
3u

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



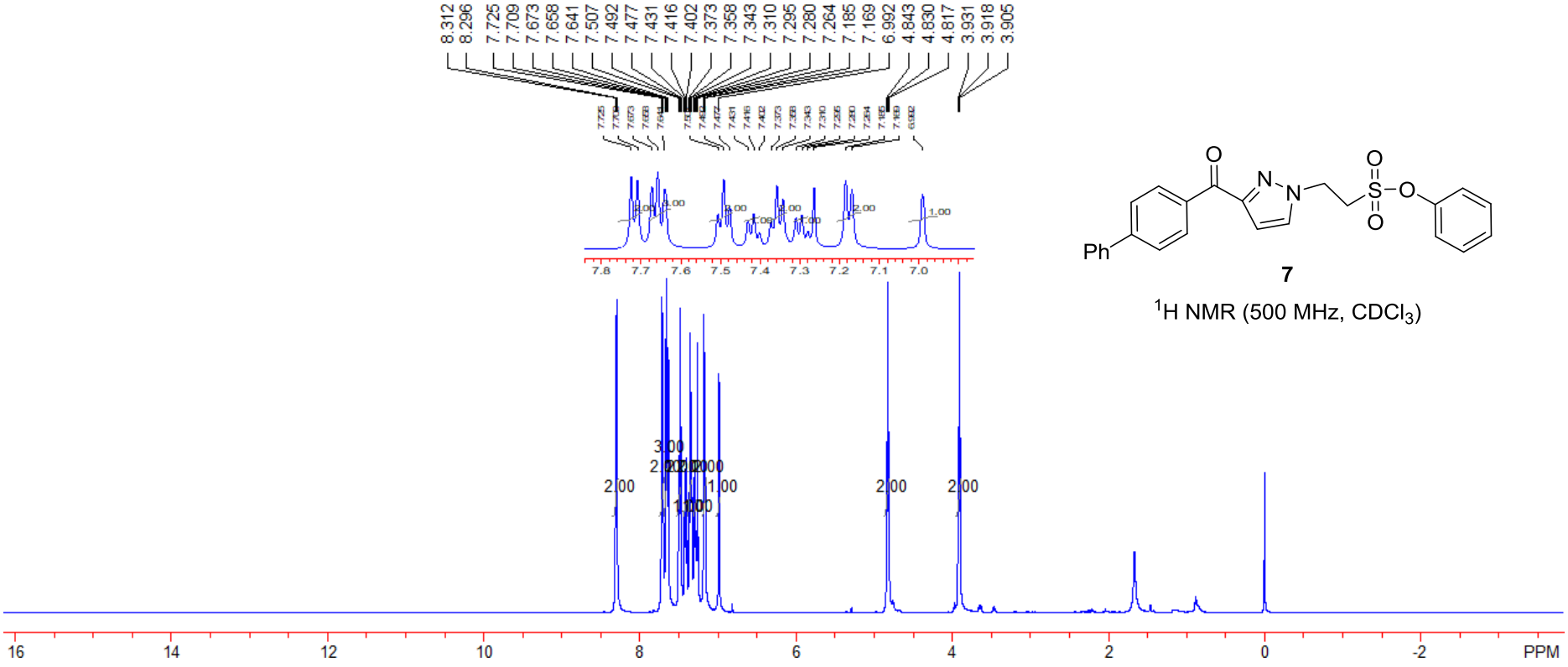
5

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



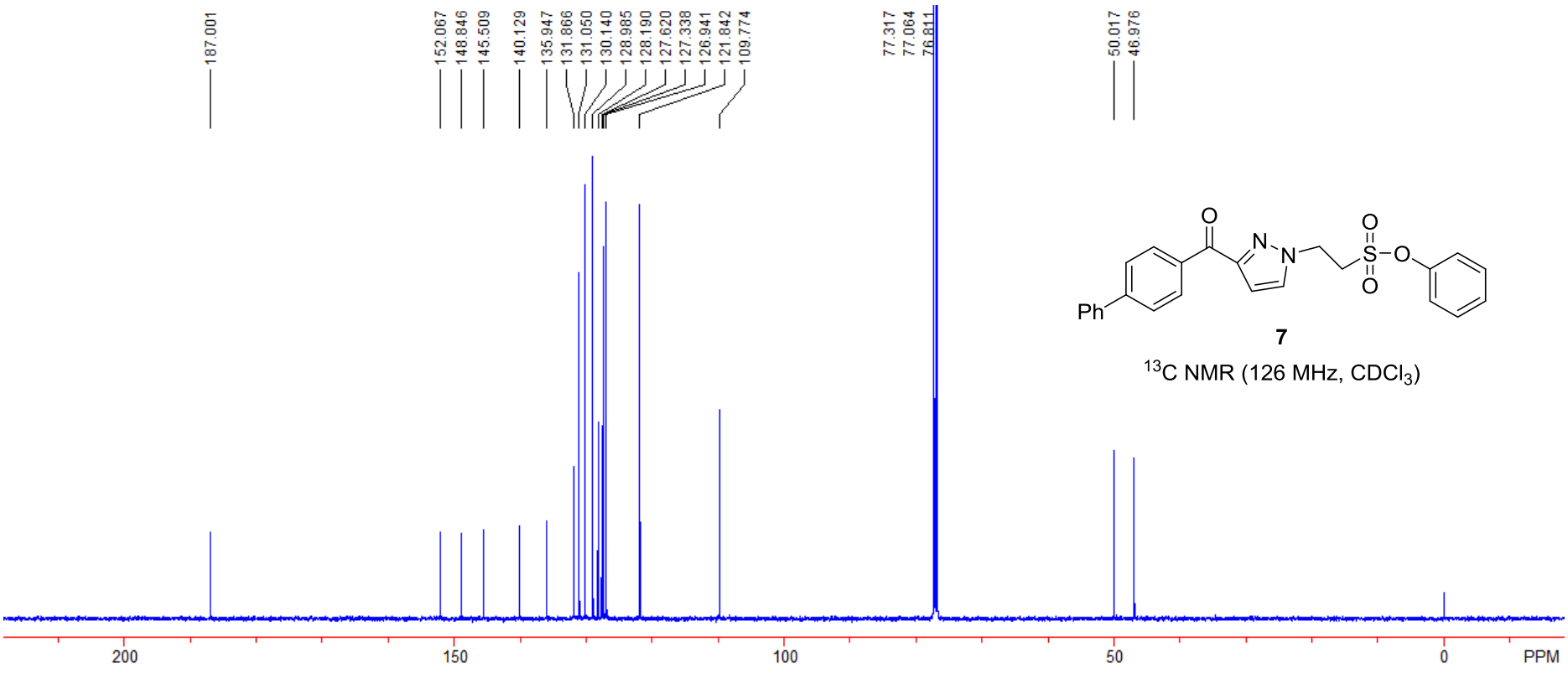
5

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



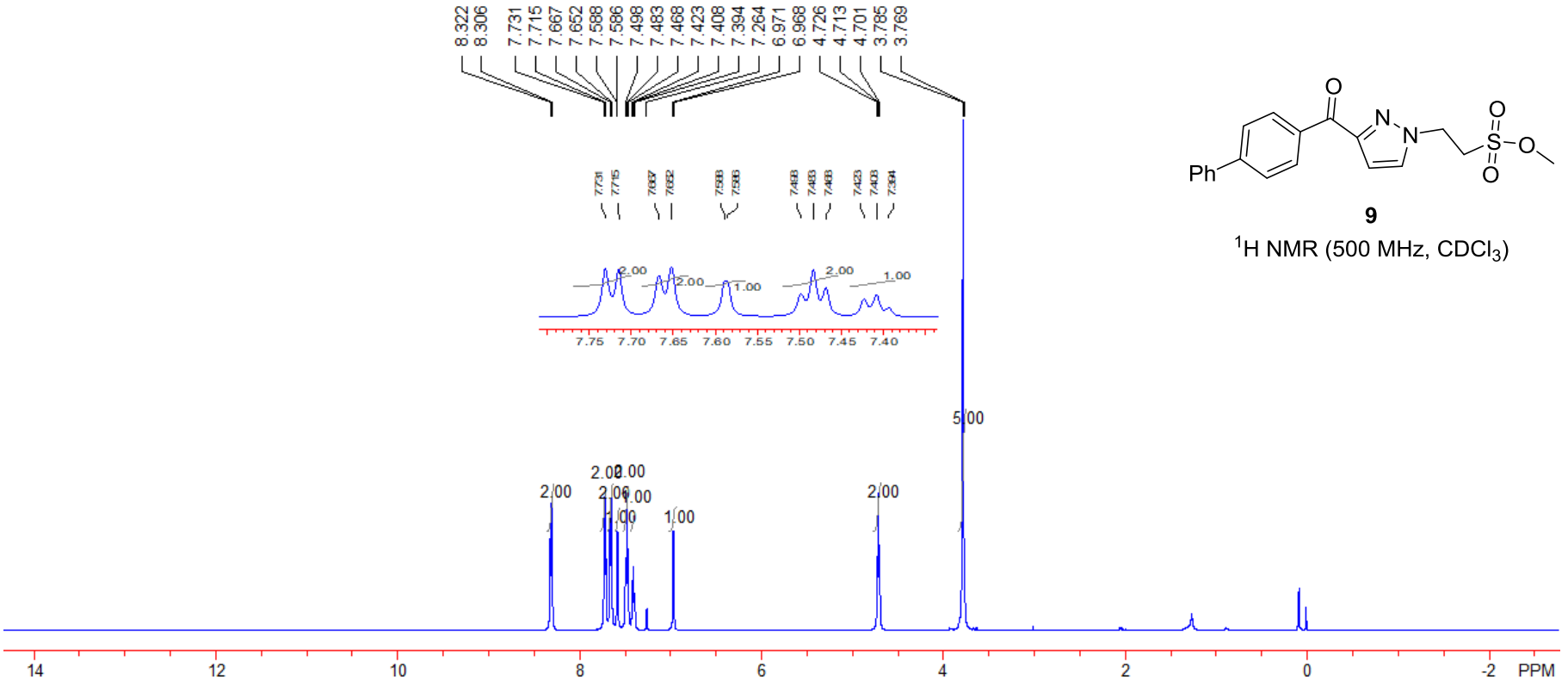
7

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



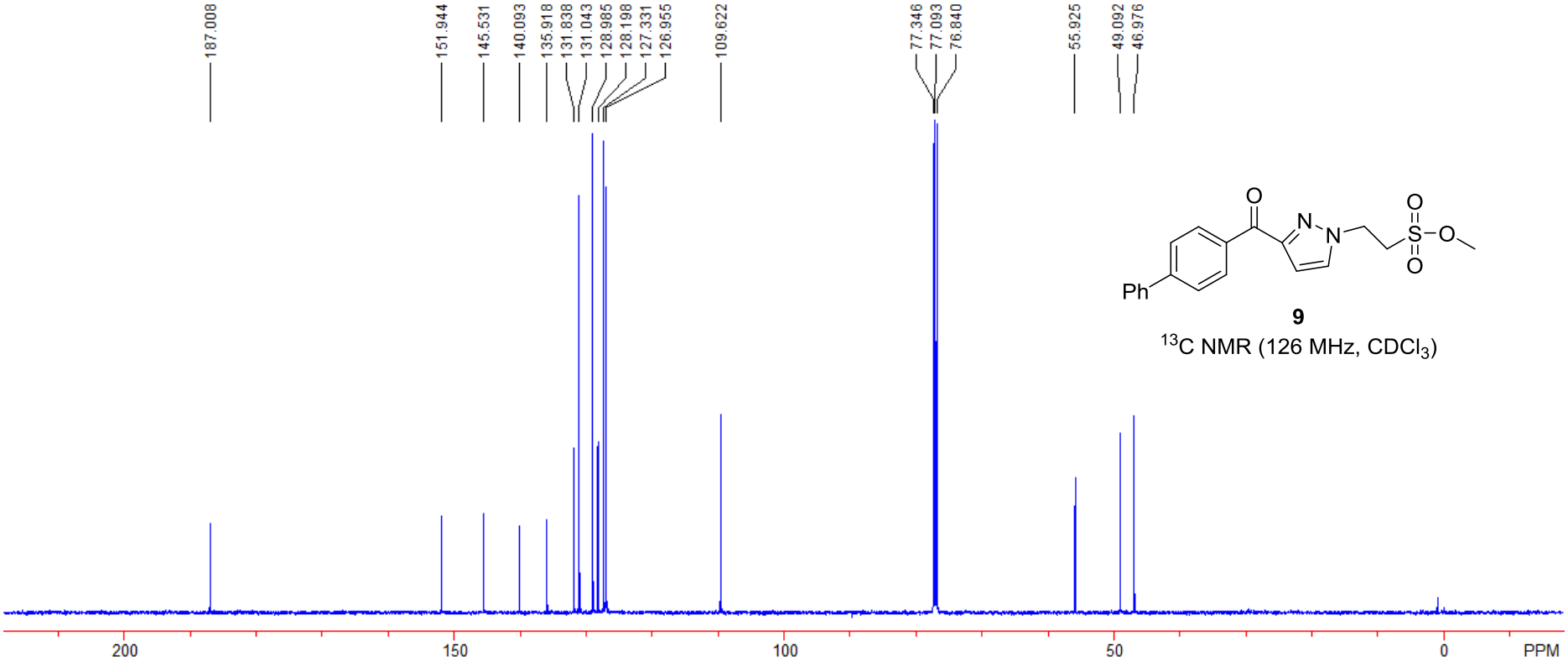
7

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



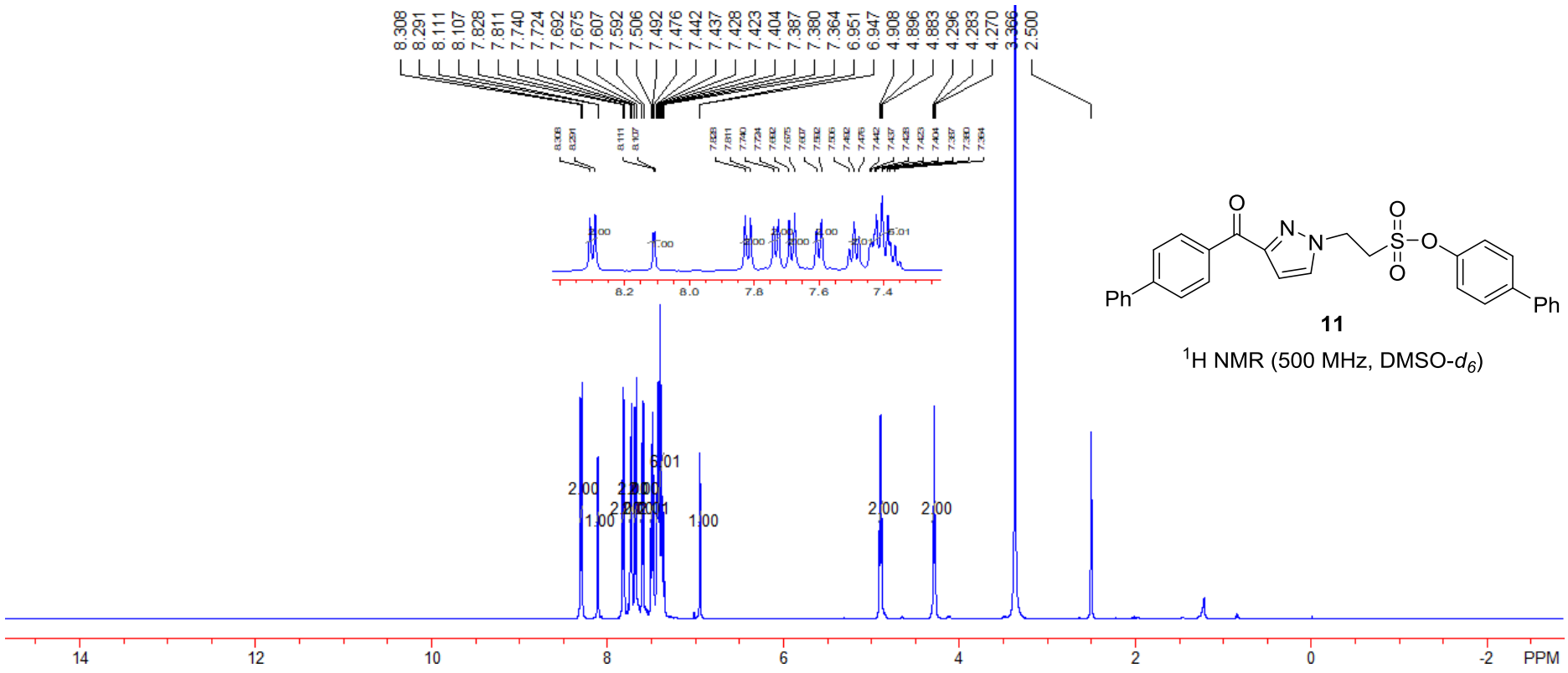
9

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



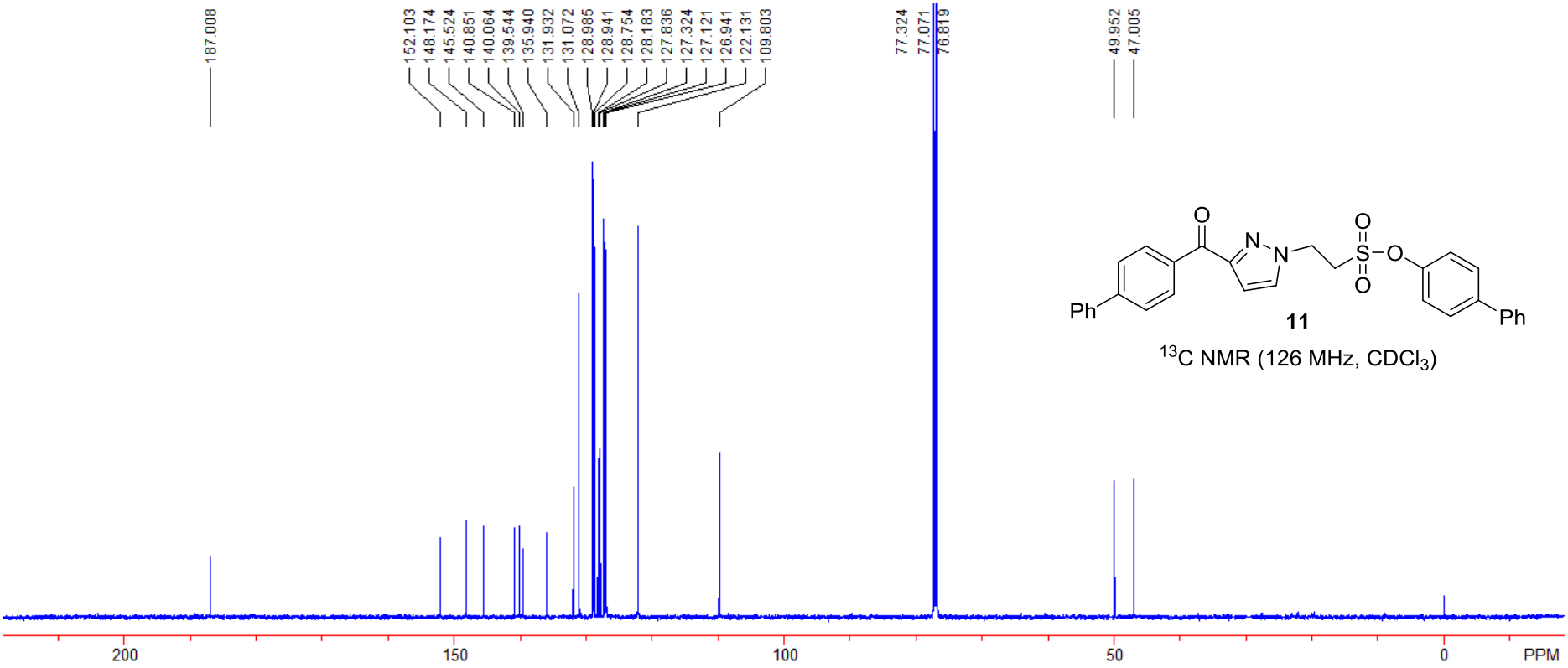
9

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



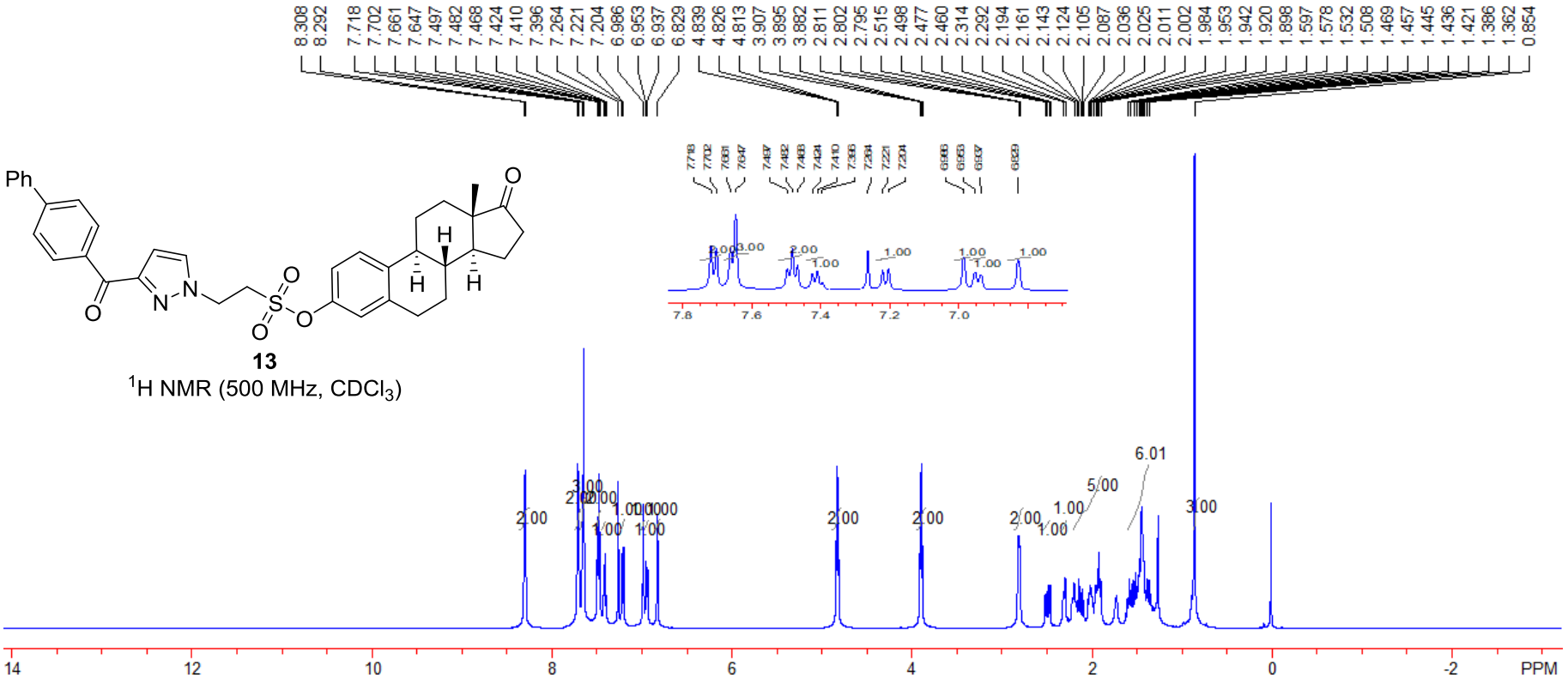
11

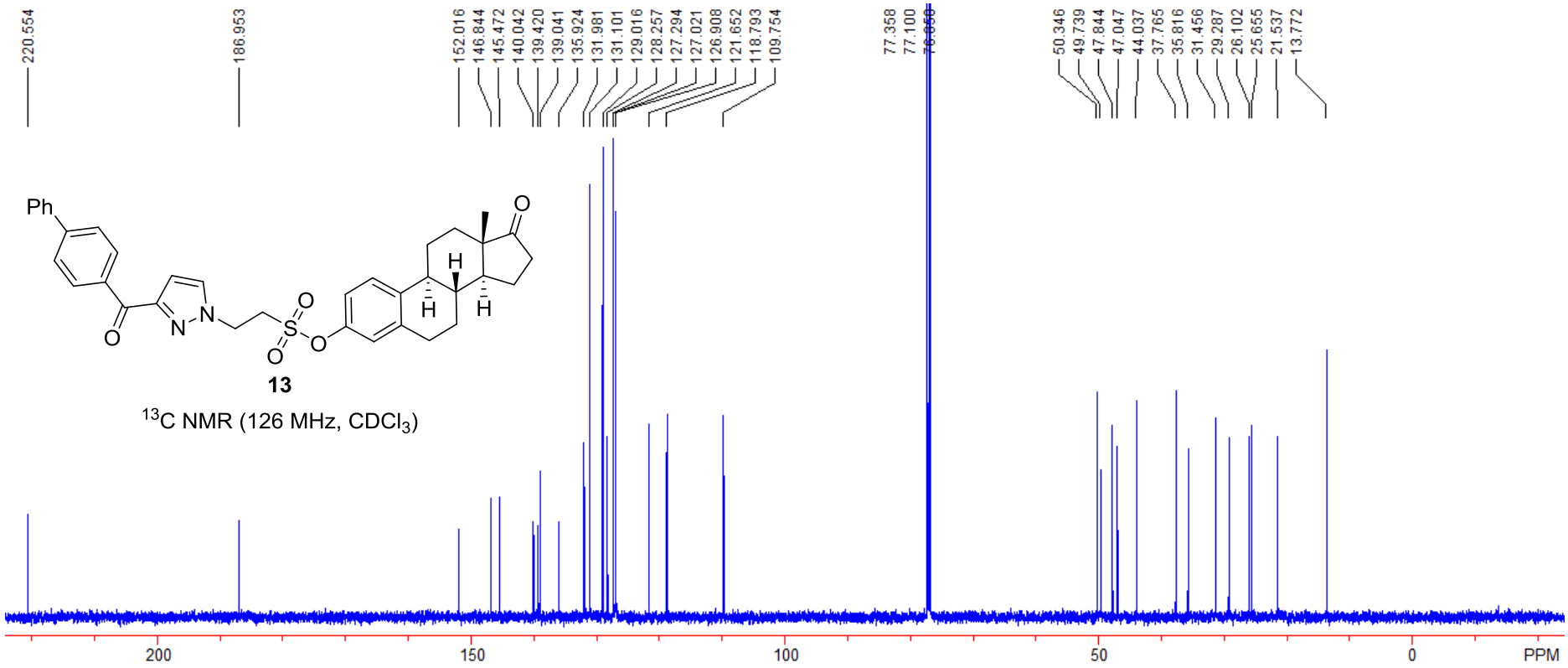
^{1}H NMR (500 MHz, DMSO-d_6)



11

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

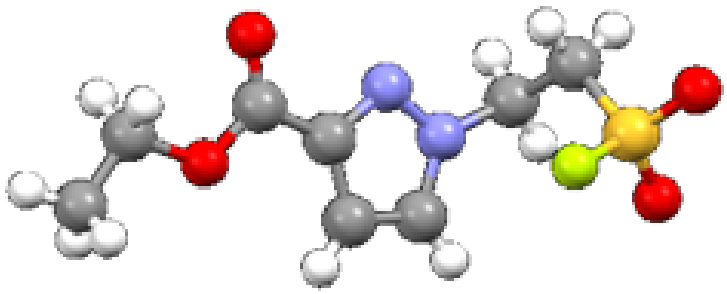

Ph
O
N
N
O
S
O
O
O
H
H
H
O
13
1H NMR (500 MHz, CDCl3)
14
12
10
8
6
4
2
0
-2
PPM



13

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

9 Data of crystal structure of 3u



Approximately 136 mg of the purified compound **3u** was dissolved in dichloroethane and placed under dark conditions to evaporate slowly. After several days, a colorless bulk crystal is obtained. The X-ray crystal-structure determinations were obtained on a Bruker Smart-1000 CDCC diffractometer (graphite-monochromated Mo Kα radiation, λ=0.71073 nm) at 298(2) K. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2106085). The ellipsoid contour probability level in the caption is 50 %.

Table S10. Crystal data and structure refinement for 201110b.

Identification code	201110b
Empirical formula	C8 H11 F N2 O4 S
Formula weight	250.25
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 20.3525(18) A alpha = 90 deg. b = 5.1265(6) A beta = 111.209(4) deg. c = 23.391(2) A gamma = 90 deg.
Volume	2275.3(4) A^3
Z, Calculated density	8, 1.461 Mg/m^3
Absorption coefficient	0.299 mm^-1
F(000)	1040

Crystal size	0.27 x 0.15 x 0.04 mm
Theta range for data collection	1.87 to 25.02 deg.
Limiting indices	-23<=h<=24, -6<=k<=5, -27<=l<=22
Reflections collected / unique	5292 / 2003 [R(int) = 0.1089]
Completeness to theta = 25.02	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9881 and 0.9235
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2003 / 0 / 147
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0740, wR2 = 0.1857
R indices (all data)	R1 = 0.1260, wR2 = 0.2077
Extinction coefficient	0.0010(5)
Largest diff. peak and hole	0.269 and -0.267 e.A^-3

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 201110b.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	879(2)	10621(6)	10483(2)	136(1)
N(1)	1217(2)	7629(7)	9478(2)	66(1)
N(2)	1688(2)	9162(7)	9372(2)	66(1)
O(1)	1225(2)	13597(7)	8156(2)	88(1)
O(2)	2267(2)	13026(7)	8872(2)	99(1)
O(3)	507(2)	6526(7)	10676(2)	112(1)
O(4)	1414(3)	8758(10)	11457(2)	142(2)
S(1)	1089(1)	8206(3)	10825(1)	87(1)
C(1)	1655(3)	12527(9)	8652(3)	70(1)
C(2)	1309(2)	10637(9)	8903(2)	65(1)
C(3)	594(3)	10046(11)	8723(2)	83(2)
C(4)	559(3)	8085(11)	9098(3)	83(2)
C(5)	1447(2)	5706(9)	9961(2)	73(1)
C(6)	1717(2)	6839(10)	10587(2)	71(1)
C(7)	1536(3)	15439(12)	7850(3)	107(2)
C(8)	977(4)	16519(16)	7346(3)	158(3)

Table S12. Bond lengths [A] and angles [deg] for 201110b.

F(1)-S(1)	1.452(4)
N(1)-N(2)	1.331(4)
N(1)-C(4)	1.334(6)
N(1)-C(5)	1.443(6)
N(2)-C(2)	1.327(5)
O(1)-C(1)	1.296(6)
O(1)-C(7)	1.461(6)
O(2)-C(1)	1.190(5)
O(3)-S(1)	1.402(4)
O(4)-S(1)	1.412(5)
S(1)-C(6)	1.718(4)
C(1)-C(2)	1.442(6)
C(2)-C(3)	1.393(6)
C(3)-C(4)	1.352(7)
C(3)-H(3)	0.9300
C(4)-H(4)	0.9300
C(5)-C(6)	1.485(6)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.422(8)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600

N(2)-N(1)-C(4)	112.9(4)
N(2)-N(1)-C(5)	119.9(4)
C(4)-N(1)-C(5)	127.2(4)
C(2)-N(2)-N(1)	104.3(3)
C(1)-O(1)-C(7)	116.1(4)
O(3)-S(1)-O(4)	114.7(3)
O(3)-S(1)-F(1)	109.4(3)
O(4)-S(1)-F(1)	109.8(3)
O(3)-S(1)-C(6)	109.2(2)
O(4)-S(1)-C(6)	107.3(3)
F(1)-S(1)-C(6)	106.0(2)
O(2)-C(1)-O(1)	123.9(5)
O(2)-C(1)-C(2)	124.0(5)

O(1)-C(1)-C(2)	112.1(4)
N(2)-C(2)-C(3)	110.9(4)
N(2)-C(2)-C(1)	119.7(4)
C(3)-C(2)-C(1)	129.4(5)
C(4)-C(3)-C(2)	105.2(5)
C(4)-C(3)-H(3)	127.4
C(2)-C(3)-H(3)	127.4
N(1)-C(4)-C(3)	106.6(4)
N(1)-C(4)-H(4)	126.7
C(3)-C(4)-H(4)	126.7
N(1)-C(5)-C(6)	113.8(4)
N(1)-C(5)-H(5A)	108.8
C(6)-C(5)-H(5A)	108.8
N(1)-C(5)-H(5B)	108.8
C(6)-C(5)-H(5B)	108.8
H(5A)-C(5)-H(5B)	107.7
C(5)-C(6)-S(1)	115.1(3)
C(5)-C(6)-H(6A)	108.5
S(1)-C(6)-H(6A)	108.5
C(5)-C(6)-H(6B)	108.5
S(1)-C(6)-H(6B)	108.5
H(6A)-C(6)-H(6B)	107.5
C(8)-C(7)-O(1)	107.4(5)
C(8)-C(7)-H(7A)	110.2
O(1)-C(7)-H(7A)	110.2
C(8)-C(7)-H(7B)	110.2
O(1)-C(7)-H(7B)	110.2
H(7A)-C(7)-H(7B)	108.5
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters (A^2 x 10^3) for 201110b.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	157(3)	80(2)	216(4)	23(2)	121(3)	27(2)
N(1)	68(2)	67(2)	72(3)	-1(2)	37(2)	-5(2)
N(2)	57(2)	73(3)	76(3)	1(2)	35(2)	-6(2)
O(1)	81(2)	108(3)	77(3)	21(2)	31(2)	-1(2)
O(2)	80(2)	93(3)	122(3)	28(2)	33(2)	-12(2)
O(3)	102(2)	81(3)	199(4)	-13(2)	110(3)	-21(2)
O(4)	173(4)	178(5)	92(3)	-33(3)	68(3)	-6(4)
S(1)	97(1)	84(1)	101(1)	-4(1)	63(1)	4(1)
C(1)	66(3)	80(3)	71(4)	-3(3)	32(3)	-5(3)
C(2)	62(3)	72(3)	66(3)	-4(2)	31(2)	2(2)
C(3)	64(3)	103(4)	79(4)	12(3)	22(3)	5(3)
C(4)	68(3)	97(4)	93(4)	2(3)	40(3)	-12(3)
C(5)	78(3)	65(3)	93(4)	2(3)	50(3)	1(2)
C(6)	60(3)	82(3)	76(4)	5(3)	32(2)	6(2)
C(7)	109(4)	115(5)	97(5)	34(4)	38(4)	-9(4)
C(8)	197(7)	155(7)	125(7)	50(5)	60(6)	-1(6)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 201110b.

	x	y	z	U(eq)
H(3)	222	10830	8413	99
H(4)	154	7224	9092	100
H(5A)	1815	4652	9905	88
H(5B)	1054	4561	9925	88
H(6A)	2063	8165	10603	85
H(6B)	1958	5477	10875	85
H(7A)	1784	16808	8132	128
H(7B)	1869	14551	7707	128
H(8A)	689	15137	7106	237
H(8B)	1169	17513	7095	237
H(8C)	696	17636	7495	237

Table S15. Torsion angles [deg] for 201110b.

C(4)-N(1)-N(2)-C(2)	-0.3(5)
C(5)-N(1)-N(2)-C(2)	179.0(4)
C(7)-O(1)-C(1)-O(2)	2.5(8)
C(7)-O(1)-C(1)-C(2)	-176.8(4)
N(1)-N(2)-C(2)-C(3)	1.1(5)
N(1)-N(2)-C(2)-C(1)	-178.7(4)
O(2)-C(1)-C(2)-N(2)	-6.6(7)
O(1)-C(1)-C(2)-N(2)	172.7(4)
O(2)-C(1)-C(2)-C(3)	173.7(5)
O(1)-C(1)-C(2)-C(3)	-7.0(7)
N(2)-C(2)-C(3)-C(4)	-1.5(6)
C(1)-C(2)-C(3)-C(4)	178.3(5)
N(2)-N(1)-C(4)-C(3)	-0.7(6)
C(5)-N(1)-C(4)-C(3)	-179.9(4)
C(2)-C(3)-C(4)-N(1)	1.2(6)
N(2)-N(1)-C(5)-C(6)	69.1(5)
C(4)-N(1)-C(5)-C(6)	-111.7(5)
N(1)-C(5)-C(6)-S(1)	71.3(5)
O(3)-S(1)-C(6)-C(5)	45.0(5)
O(4)-S(1)-C(6)-C(5)	169.9(4)
F(1)-S(1)-C(6)-C(5)	-72.8(4)
C(1)-O(1)-C(7)-C(8)	-176.1(6)

Symmetry transformations used to generate equivalent atoms:

Table S16. Hydrogen bonds for 201110b [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)