Supporting Information

For

N-(2,3,5,6-Tetrafluoropyridyl)sulfoximines: Synthesis, X-Ray Crystallography, and Halogen Bonding

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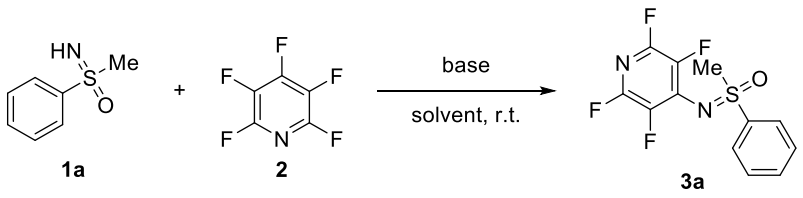
General information

If not otherwise stated all chemicals were purchased from commercial suppliers and used without further purification. Solvents for flash column chromatography purifications were of technical grade and were distilled before use. Flash column chromatography was conducted with silica 60 M (0.04–0.063 mm) as the stationary phase, which was purchased from MACHERY-NAGEL. Thin-layer chromatography (TLC) was performed with silica coated alumina plates TLC silica gel 60 F_{254} from MERCK and the products were visualized using UV-light (λ = 254 nm). Melting points (m.p.) were measured on a BÜCHI Melting Point M-560 apparatus using open-end capillaries, a heating rate of 5 °C·min^{-1} and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded either on a Varian Mercury 300, Varian VNMRS 400, Varian VNMRS 600, Bruker Avance Neo 400 or Bruker Avance Neo 600 at 25 °C, if not otherwise stated, and were processed and analyzed with the program MestReNova.[1] Chemical shifts (δ) are given in parts per million (ppm). Proton and carbon NMR spectra were referenced to the solvent residue signal of the non-deuterated solvent ($CHCl_3$: ^{1}H NMR: δ = 7.26 ppm, $CDCl_3$: $^{13}C\{^1H\}$ NMR: δ = 77.16 ppm; $(CH_3)_2SO$: ^{1}H NMR: δ = 2.50 ppm, $(CD_3)_2SO$: $^{13}C\{^1H\}$ NMR: δ = 39.52 ppm; $(CH_3)_2CO$: ^{1}H NMR: δ = 2.05 ppm, $(CD_3)_2CO$: $^{13}C\{^1H\}$ NMR: δ = 29.84, 206.26 ppm).[2] Carbon spectra were measured by proton broadband decoupling. The multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), m (multiplet), and combinations thereof. The spin-spin coupling constants (*J*) are reported in Hertz (Hz). Infrared (IR) spectra were recorded neat on a PerkinElmer Spectrum 100 FT-IR spectrometer with an attached UATR device with a KRS-5 crystal for a single reflection. IR bands are given with their corresponding wavenumber (ν) in cm^{-1} and relative intensity of transmission [strong (s), medium (m), weak (w)]. Mass spectra were recorded on a Finnigan SSQ 7000 mass spectrometer [electron ionization (EI), 70 eV; chemical ionization (CI), methane, 100 eV]. The signals are given according to their *m/z* values and corresponding relative intensities are reported in parenthesis. High-resolution mass (HRMS) spectra were recorded either as ESI (electrospray ionization, positive mode) on a ThermoFisher Scientific LTQ Orbitrap XL mass spectrometer or as EI on a Finnigan MAT 95 XP mass spectrometer. Mechanochemical reactions were performed with a RETSCH Mixer Mill MM400 and the milling containers and balls used were always of the same material. The enantiomeric ratio was determined by analytical high-performance liquid chromatography (HPLC) using an Agilent 1200 series system with chiral stationary phases (Chiralpak AD-H, 150 mm in length, 4.6 mm in internal diameter) from Chiral Technologies Inc., *n*-heptane:*iso*-propanol (97:3 *v*/*v*) as eluent with a flow rate of 0.6 mL·min^{-1} at 20 °C and using a UV-detector. To identify the enantiomers their HPLC retention times were compared with those of authentic racemates.

Optimization of the synthesis of *N*TFP-sulfoximine 3a in solution (GP1)



The depicted reaction was optimized in terms of base, equivalents thereof, equivalents of pentafluoropyridine (**2**), solvent, solvent amounts, as well as the reaction time. A sealed tube equipped with a magnetic stirring bar was charged with sulfoximine **1a** (0.30-0.50 mmol, 1.00 equiv.), base (1.05-3.00 equiv.), solvent (0.50-2.50 mL), pentafluoropyridine (**2**, 1.05-6.00 equiv.) in the given order and closed. The reaction mixture was stirred between 1 h and 24 h at room temperature. Then, it was transferred to a flask and after adding Et_2O (3 × 5 mL), the volatiles were removed under reduced pressure. The product was purified by column chromatography (silica, Et_2O).

Initial reactions

Table S1 Initial screening of the reaction conditions for the synthesis of *N*TFP-sulfoximine **3a** in solution[a]

2 (equiv.)	K_2CO_3 (equiv.)	$V_{Solvent}$ [mL]	**3a** [%]
1.05	–	2.50	traces
1.05	1.05	2.50	2
1.20	1.05	2.50	14
1.05	1.50	2.50	3
1.05	2.00	2.50	4
1.05	3.00	2.50	6
1.50	3.00	2.50	9
1.50	3.00	1.50	13
1.50	**3.00**	**0.50**	**18**

[a] **1a** (0.30-0.50 mmol, 1.00 equiv.), MeCN, overnight.

Base screening

Table S2 Base screening for the synthesis of *N*TFP-sulfoximine **3a** in solution[a]

Base (equiv.)	**3a** [%]
Na_2CO_3 (3.0)	no reaction
K_2CO_3 (3.0)	18
Cs_2CO_3 (3.0)	50
K_3PO_4 (3.0)	36
NaH (3.0) [b]	30
NEt_3 (3.0)	traces
DABCO (3.0)	traces
NaO*t*Bu (3.0)	22
KO*t*Bu (3.0)	38
LiOH (3.0)	traces
NaOH (3.0)	24
KOH (3.0)	**78**

[a] **1a** (0.30-0.50 mmol, 1.00 equiv.), **2** (1.50 equiv.), base (3.00 equiv.), MeCN (0.6 M), overnight. [b] 60% in mineral oil.

Solvent screening

Table S3 Solvent screening for the synthesis of *N*TFP-sulfoximine **3a** in solution[a]

2 (equiv.)	KOH (equiv.)	Solvent	**3a** [%]
1.5	KOH (3.0)	MeCN	78
1.5	KOH (3.0)	DMSO	88 [b]
4.5	KOH (9.0)	DMSO	90 [b]
6.0	KOH (12.0)	DMSO	98 [b]
1.5	KOH (3.0)	DMF	68 [b]
1.5	KOH (3.0)	DCM	73
1.5	KOH (3.0)	toluene	79
1.5	KOH (3.0)	EtOH	45
1.5	KOH (3.0)	Et2O	79
1.5	KOH (3.0)	DCE	68
1.5	KOH (3.0)	$CHCl_3$	44
1.5	**KOH (3.0)**	**THF**	**92**

[a] **1a** (0.30-0.50 mmol, 1.00 equiv.), solvent (0.6 M), overnight. [b] side product **4** was formed and not fully separable from **3a**.

Reaction time

Table S4 Optimization of the reaction time for the synthesis of *N*TFP-sulfoximine **3a** in solution[a]

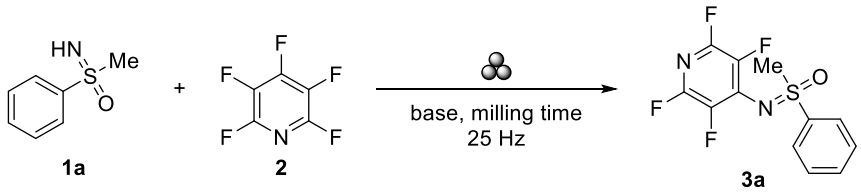
t [h]	**3a** [%]
1	82
6	83
12	83
18	92
24	**96**

[a] **1a** (0.30-0.50 mmol, 1.00 equiv.), **2** (1.50 equiv.), KOH (3.00 equiv.), THF (0.6 M).

Optimized procedure for the syntheses of *N*TFP-sulfoximines 3 in solution (GP2)

A sealed tube equipped with a magnetic stirring bar was charged with *N*H-sulfoximine **1** (0.3-0.5 mmol, 1.00 equiv.), KOH (3.00 equiv.), THF (0.6 M), pentafluoropyridine (**2**, 1.50 equiv.) in the given order. After closing the tube, the reaction mixture was stirred for 24 h at room temperature. Then, it was transferred to a flask and after adding Et_2O (3 × 5 mL), the solvent was removed under reduced pressure. Product **3** was purified by column chromatography.

Optimization of the mechanochemical synthesis of *N*TFP-sulfoximine 3a (GP3)



For the depicted reaction, the mechanochemical approach was optimized in terms of base, equivalents thereof, equivalents of pentafluoropyridine (**2**), and milling time. A stainless-steel (SS) milling container (5 mL) equipped with one milling ball (7 mm in diameter) of the same material was charged with sulfoximine **1a** (50 mg, 0.32 mmol, 1.00 equiv.), base (1.05-3.00 equiv.) and pentafluoropyridine (**2**, 1.20-1.50 equiv.) in the given order. The jar was immediately closed after reagent **2** was added, and the reaction mixture was milled at 25 Hz for the given time. After milling the product was purified by column chromatography using a dry-loaded column (silica, Et_2O).

Base screening

Table S5 Screened bases in the mechanochemical synthesis of *N*TFP-sulfoximine **3a**[a]

2 (equiv.)	Base	equiv.	**3a** [%]
1.20	–	–	3 [b]
1.20	K_2CO_3	1.50	5 [b]
1.50	–	–	1
1.20	DABCO	1.05	22
1.20	KO*t*Bu	1.05	32
1.20	NaH [c]	1.05	32
1.50	K_3PO_4	1.50	35
1.50	K_3PO_4	3.00	54
1.20	KOH	1.05	62
1.20	KOH	3.00	74
1.50	KOH	1.50	84
1.50	$LiOH·H_2O$	3.00	17
1.50	NaOH	3.00	59
1.50	**KOH**	**3.00**	**90**
1.50	$CsOH·H_2O$	3.00	85
1.50	$CsOH·H_2O$	3.00	84

[a] SS, 5 mL, 1 ball (7 mm), 90 min, 25 Hz, **1a** (50 mg, 0.32 mmol, 1.00 equiv.). [b] ZrO_2-Y, 10 mL, 1 ball (10 mm), **1a** (100 mg, 0.64 mmol, 1.00 equiv.). [c] 60% in mineral oil.

Milling time

Table S6 Optimization of the milling time in the mechanochemical synthesis of *N*TFP-sulfoximine **3a**[a]

t [min]	*Y* [%]
90	90
60	87
45	83
30	87
15	**92**
5	85

[a] SS, 5 mL, 1 ball (7 mm), 25 Hz, **1a** (50 mg, 0.32 mmol, 1.00 equiv.), KOH (3.00 equiv), **2** (1.50 equiv.).

Optimized procedure for the mechanochemical syntheses of *N*TFP-sulfoximines 3 (GP4)

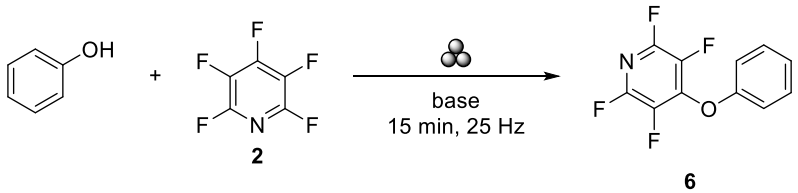
A stainless-steel milling container (5 mL) equipped with one stainless-steel ball (7 mm in diameter) was charged with *N*H-sulfoximine **3** (50–100 mg), freshly ground KOH (3.00 equiv.) and pentafluoropyridine (**2**, 1.50 equiv.) in the given order. After the addition of **2**, the jar was immediately closed. The reaction mixture was milled for 15 min at 25 Hz. After milling the reaction mixture was transferred to a flask by adding DCM (4 mL) to the jar, which was closed and shaken (3 cycles). Then, a small amount of silica was added to the flask, the volatiles were removed under reduced pressure, and product **3** was purified by column chromatography using a dry-loaded column.

Scale-up of the mechanochemical synthesis of *N*TFP-sulfoximine 3a

A stainless-steel milling container (10 mL) equipped with one stainless-steel ball (10 mm in diameter) was charged with sulfoximine **1a** (465.8 mg, 3.00 mmol, 1.00 equiv.), freshly ground KOH (506.0 mg, 9.02 mmol, 3.01 equiv.) and pentafluoropyridine [**2**, 0.49 mL (ρ = 1.54 g·mL^{-1}), 4.46 mmol, 1.49 equiv.] in the given order. The jar was immediately closed after **2** was added. The reaction mixture was milled for 15 min at 25 Hz. After milling the reaction mixture was transferred to a flask by adding DCM (8 mL) to the jar, which was closed and shaken (3 cycles). Then, a small amount of silica was added to the flask, the volatiles were removed under reduced pressure, and the product **3a** was purified by column chromatography using a dry-loaded column (silica, Et_2O). The product was obtained as a white solid (853.5 mg, 2.81 mmol, 93%).

Note: An additional up-scaling (**1a**, 4.50 mmol) was tested as well, which gave **3a** in 35% yield. The low yield was caused by an insufficient milling as the ball was stuck in the solidifying reaction mixture. This problem could be solved using more balls or a larger milling container.

Mechanochemical syntheses of 2,3,5,6-tetrafluoro-4-phenoxypyridine (6): Comparison of the standard protocol with Brittain and Cobb's method performed in a ball mill



Our Approach: A stainless-steel milling container (5 mL) equipped with one stainless-steel ball (7 mm in diameter) was charged with phenol (54.6 mg, 0.580 mmol, 1.00 equiv.), freshly ground KOH (97.8 mg, 1.743 mmol, 3.00 equiv.) and pentafluoropyridine [**2**, 95.5 μL (ρ = 1.54 g·mL^{-1}), 0.870 mmol, 1.50 equiv.] in the given order and the jar was immediately closed after reagent **2** was added. The reaction mixture was milled for 15 min at 25 Hz. After milling the reaction mixture was transferred to a flask by adding

DCM (4 mL) to the jar, which was closed and shaken (3 cycles). Then, a small amount of silica was added to the flask, the solvent was removed under reduced pressure and the product **6** was purified by running a dry-loaded column chromatography (silica, *n*-pentane).

Literature Approach[3a] **performed in a ball mill**: A stainless-steel milling container (5 mL) equipped with one stainless-steel ball (7 mm in diameter) was charged with phenol (56.0 mg, 0.595 mmol), K_2CO_3 (87.0 mg, 0.629 mmol, 1.06 equiv.) and pentafluoropyridine [**2**, 68.5 μL (ρ = 1.54 g·mL^{-1}), 0.624 mmol, 1.05 equiv.] in the given order. The reaction mixture was milled for 15 min at 25 Hz. After milling the reaction mixture was transferred to a flask by adding DCM (4 mL) to the jar, which was closed and shaken (3 cycles). Then, a small amount of silica was added to the flask, the solvent was removed under reduced pressure and the product was purified by running a dry loaded column chromatography (silica, *n*-pentane).

Table S7 Comparison of the standard protocol with the literature method[3a] performed in a ball mill

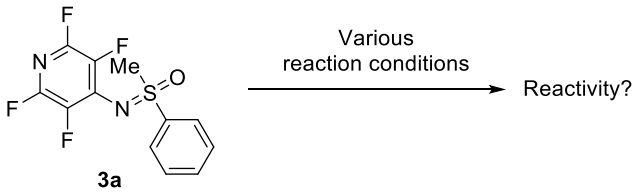
2 (equiv.)	Base	equiv.	**6** [%]
1.50	KOH	3.00	53
1.05	K_2CO_3	1.06	traces [a]

[a] Only detected by TLC, could not be isolated after column chromatography.

General procedure for growing single crystals (GP5)

Single crystals of the corresponding *N*TFP-sulfoximines **3** suitable enough for SCXRD (single crystal X-ray diffraction) analysis were obtained by slow evaporation technique. Thus, a few milligrams (5–10 mg) of the substrate were dissolved in a small amount of solvent (1–2 mL). The solvents of choice were Et_2O, DCM, acetone, or MeOH.

Stability tests of *N*-TFP-sulfoximine 3a



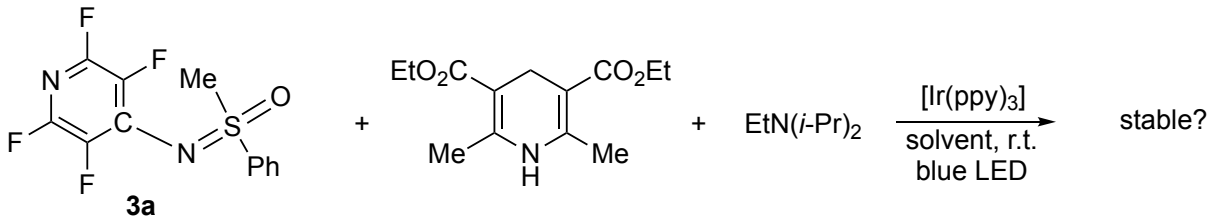
3a

The stability of *N*TFP- sulfoximine **3a** was tested under various reaction conditions. Therefore, a sealed tubed equipped with a magnetic stirring bar was charged with **3a** (15 mg) and a solvent (1 mL) was added, if not otherwise stated. Then, the reaction conditions reported below were applied, and the reaction mixture was either analyzed by TLC or NMR spectroscopy.

Table S8 Stability test of *N*TFP-sulfoximine **3a** under various reaction conditions

Reaction Conditions	Stability
TFA (0.1 mL, 27.00 equiv.), $CDCl_3$, rt, 24 h	stable
HCl (conc., 0.1 mL), $CDCl_3$, rt, 24 h	stable
$NaBH_4$ (20 mg, 18.00 equiv.), $CDCl_3$, rt, 24 h	stable
I_2 (20 mg, 3.00 equiv.), $CDCl_3$, rt, 24 h	stable
TBAF (1 M in THF, 0.5 mL, 1 equiv.), $CDCl_3$, rt, 24 h	stable
$Ba(OH)_2$ (20 mg, 2.00 equiv.), $CHCl_3$, 40 °C, 48 h	stable
$Ba(OH)_2$ (20 mg, 2.00 equiv.), MeOH, 60 °C, 48 h	stable
$Ba(OH)_2$ (20 mg, 2.00 equiv.), MeCN, 60 °C, 48 h	stable
CuI (20 mg, 2.00 equiv.), $CHCl_3$, 40 °C, 48 h	stable
CuI (20 mg, 2.00 equiv.), MeOH, 60 °C, 48 h	stable
CuI (20 mg, 2.00 equiv.), MeCN, 60 °C, 48 h	stable
CuCl (20 mg, 4.00 equiv.), $CHCl_3$, 40 °C, 48 h	stable
CuCl (20 mg, 4.00 equiv.), MeOH, 60 °C, 48 h	stable
CuCl (20 mg, 4.00 equiv.), MeCN, 60 °C, 48 h	stable
NH_3 (32% in H_2O, 4.00 equiv.), PIDA (3.00 equiv.), MeOH, 80 °C, 48 h	stable
NH_3 (7 M in MeOH, 4.00 equiv.), PIDA (3.00 equiv.), MeOH, 80 °C, 48 h	stable
$H_2NCOONH_4$ (4.00 equiv.), PIDA (3.00 equiv.), MeOH, 80 °C, 48 h	stable
S_8 (1.00 equiv.), neat, 160 °C, 48 h	stable
S_8 (20 mg, 13.00 equiv.), neat, 160 °C, 48 h	stable
Ph-S-S-Ph (1.00 equiv.), 1,2-dichlorobenzene, 60 °C, 48 h	stable
Ph-S-S-Ph (20 mg, 2 equiv.), 1,2-dichlorobenzene, 160 °C, 48 h	stable
Ph-S-S-Ph (1.00 equiv.), CCl_4, 60 °C, 48 h	stable
Ph-S-S-Ph (20 mg, 2 equiv.), CCl_4, 160 °C, 48 h	stable
$NOPF_6$ (1.50 equiv.), MeCN, 0 °C to rt, 48 h	stable
$NOPF_6$ (20 mg, 2.00 equiv.), MeCN, 60 °C, 48 h	stable
$NaNO_2$ (1.00 equiv.), HCl (half conc.), 0 °C to rt	traces of decomposition
$NaNO_2$ (20 mg, 6.00 equiv.), HCl (half conc.), 0 °C to rt	traces of decomposition
$NaNO_2$ (10.00 equiv.), HCl (half conc.), 0 °C to rt	traces of decomposition
KHF_2 (4.00 equiv.), HCl (4 M in 1,4-Dioxane), 80 °C, 3 h	traces of decomposition
3a (50 mg), H_2 (1 atm), Pd/C (5 mol%), MeOH (50 mL), rt, 48 h	stable
3a (50 mg), BH_3·THF (1 M in THF, 5.00 equiv.), THF (10 mL), 0 °C, 3 h	stable
3a (30.4 mg), SmI_2 (0.1 M in THF, 1.25 equiv.), 60 °C, 24 h	stable

Stability towards photocatalytic conditions



The depicted photocatalytic reaction was tested (in analogy to literature protocols).[3d,e] A 10 mL test tube equipped with a magnetic stirring bar was charged with **3a** (60.9 mg, 0.2 mmol, 1.00 equiv.). If used, the Hantzsch ester (101 mg, 0.4 mmol, 2.00 equiv.) and $Ir(ppy)_3$ (0.3 mg, 0.0005 mmol, 0.25 mol%) were added, and the tube was sealed with a rubber septum. Then, it was evacuated and flushed with argon (3 cycles). After the addition of *N,N*-diisopropylethylamine (51.7 mg, 0.4 mmol, 2.00 equiv.) and the solvent, the reaction mixture was stirred at room temperature for 24 h under blue LED irradiation (24 W). The reaction mixture was analyzed by TLC, and the results are given in Table S9.

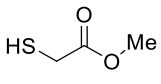
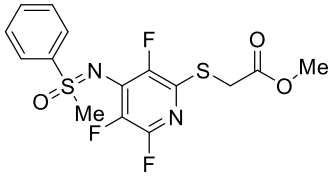
Table S9 Stability test of *N*TFP-sulfoximine **3a** under various photocatalytic conditions

Entry	Solvent [mL]	Hantzsch ester	Hünig's base	$Ir(ppy)_3$	Stability
1	*N*,*N*-Diethylacetamide (0.4)	✓	✓	–	stable
2	Dry DMSO (1.3)	✓	✓	✓	stable
3	Dry DMSO (1.3)	✓	–	✓	stable
4	Dry DMSO (1.3)	–	✓	✓	stable

Stability towards nucleophilic aromatic substitution at the pyridyl substituent

The reactivity of the *N*-(2,3,5,6-tetrafluoropyridyl) substituent towards nucleophilic aromatic substitution is described in the literature.[3] Therefore, the following protocol was applied. A reaction tube equipped with a magnetic stirring bar was charged with *N*TFP-sulfoximine **3a** (50.0 mg, 0.164 mmol, 1.00 equiv.), KF (19.1 mg, 0.329 mmol, 2.00 equiv.) and 18-crown-6 (86.9 mg, 0.329 mmol, 2.00 equiv.) in the given order. Then, MeCN (5 mL) and H_2O (0.1 mL) were added and the reaction mixture was stirred at ambient temperature for 1 h. After that time, methyl thioglycolate (10.00 equiv.) was added to the reaction mixture, which was heated to 50 °C for 13 days. Then, the reaction mixture was analyzed by TLC and possible substitution products were isolated by column chromatography.

Table S10 Result for a nucleophilic aromatic substitution reaction at the pyridyl ring of **3a**

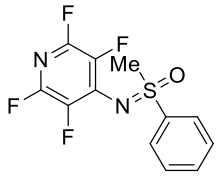
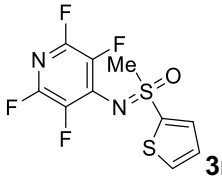
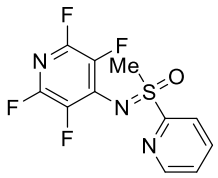
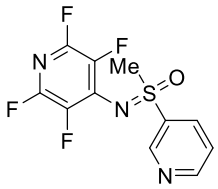
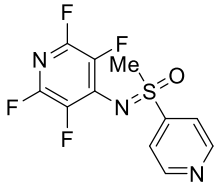
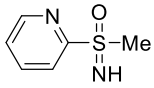
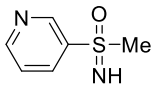
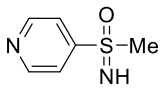
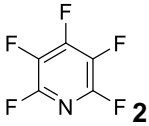
Thiole	Comment	Product **5**
	*Y* = 16% Substitution at the pyridyl ring is possible, but slow reaction	

Halogen bonding studies: NMR titrations

First experiments: Initial checking of 1:1 mixtures of *N*TFP-sulfoximines 3 and NIS for halogen bonding by ^{1}H NMR spectroscopy (in acetone-d_6)

A few milligrams of *N*TFP-sulfoximine **3** were dissolved in acetone-d_6 (600 µL, solution 1). It was fully transferred into an NMR tube, and a ^{1}H NMR spectrum (300 MHz, 25 °C) was measured of solution 1. Then, 1.00 equiv. of *N*-Iodosuccinimide (NIS) was dissolved in acetone-d_6 (400 µL, solution 2), and this solution was added to solution 1. The NMR tube was shaken, and another ^{1}H NMR experiment (300 MHz, 25 °C) was performed (solution 1+2). The spectra of solution 1 and solution 1+2 were compared, and it was investigated whether a chemical shift difference was detectable indicating the presence of halogen bonding in solution. The selected substrates, weighted samples and presence of a chemical shift are listed below (Table S11).

Table S11 Testing selected substrates for 1:1 XB-complex with NIS in acetone-d_6

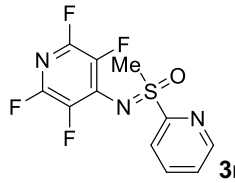
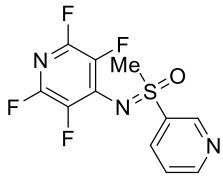
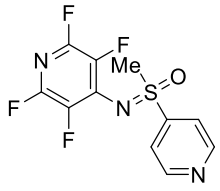
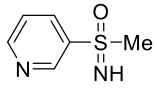
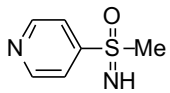
Structure of Substrate	*m* [mg] / *n* [mmol]	*m* [mg] / *n* [mmol] [a]	Substrate:NIS	Shift [b]
 **3a**	6.7 / 0.022 (1.2 / 0.004) [c]	5.0 / 0.022 (0.9 / 0.004) [c]	1.00 : 1.01 (1.0 : 1.0) [c]	N (N) [c]
 **3r**	10.1 / 0.033	7.3 / 0.032	1.00 : 1.00	N
 **3n**	3.2 / 0.010	2.4 / 0.011	1.00 : 1.02	N
 **3o**	9.6 / 0.031	7.1 / 0.032	1.00 : 1.00	Y
 **3p**	10.0 / 0.033	7.4 / 0.033	1.00 : 1.00	Y
 **1n**	0.6 / 0.004 [c]	0.8 / 0.004 [c]	1.0 : 1.0 [c]	(Y) [c,d]
 **1o**	0.6 / 0.004 [c]	0.8 / 0.004 [c]	1.0 : 1.0 [c]	Y [c]
 **1p**	0.6 / 0.004 [c]	0.8 / 0.004 [c]	1.0 : 1.0 [c]	Y [c]
	0.3 / 0.004 [c]	0.9 / 0.004 [c]	1.0 : 1.0 [c]	Y [c]
 **2**	0.7 / 0.004 [c]	0.9 / 0.004 [c]	1.0 : 1.0 [c]	N [c]

[a] For NIS. [b] Y = yes, N = no. [c] values in parenthesis: use of solution 1 for NIS in $CDCl_3$ instead of acetone-d_6 measured on a 600 MHz NMR spectrometer. [d] Showed chemical shift, but the titration and K_a value determination was unsuccessful due to signal broadening.

NMR titrations for the determination of binding constants for 1:1-XB complexes in solution

NIS (1.00 equiv.) was dissolved in $CDCl_3$ (600 µL, solution 1). A few milligrams of the selected *N*TFP-sulfoximine **3**, *N*H-sulfoximine **1** or pyridine (Table S12) were dissolved in $CDCl_3$ (400 µL, solution 2). Then, ^{1}H NMR spectra were recorded (300 MHz, 25 °C). After the first measurement of solution 1, the correct amount of solution 2 was added into the NMR tube that already contained solution 1 using an Eppendorf micropipette. The tube was shaken, and the next measurement was conducted; 0.0-1.0 equiv. of solution 2 in 0.1 equiv. steps; 1.0-2.0 equiv. of solution 2 in 0.2 equiv. steps, and 2.0-5.2 equiv. of solution 2 in 0.4 equiv. steps.

Table S12 Prepared solutions for NMR titrations

Solution 1 (NIS)			Solution 2 (*N*TFP-sulfoximine)				V (solution 2) that equals 0.1 equiv. NIS [µL]
m [mg]	*n* [mmol]	*V* ($CDCl_3$) [µL]	Structure	*m* [mg]	*n* [mmol]	*V* ($CDCl_3$) [µL]	
0.9	0.004	600	 **3n**	10.5	0.034	400	4.65
0.9	0.004	600	 **3o**	10.0	0.033	400	4.88
1.0	0.004	600	 **3p**	10.6	0.035	400	5.12
0.8	0.004	600	 **1o**	9.6	0.061	400	2.31
0.8	0.004	600	 **1p**	10.0	0.064	400	2.22
0.8	0.004	600		9.0	0.114	400	1.25

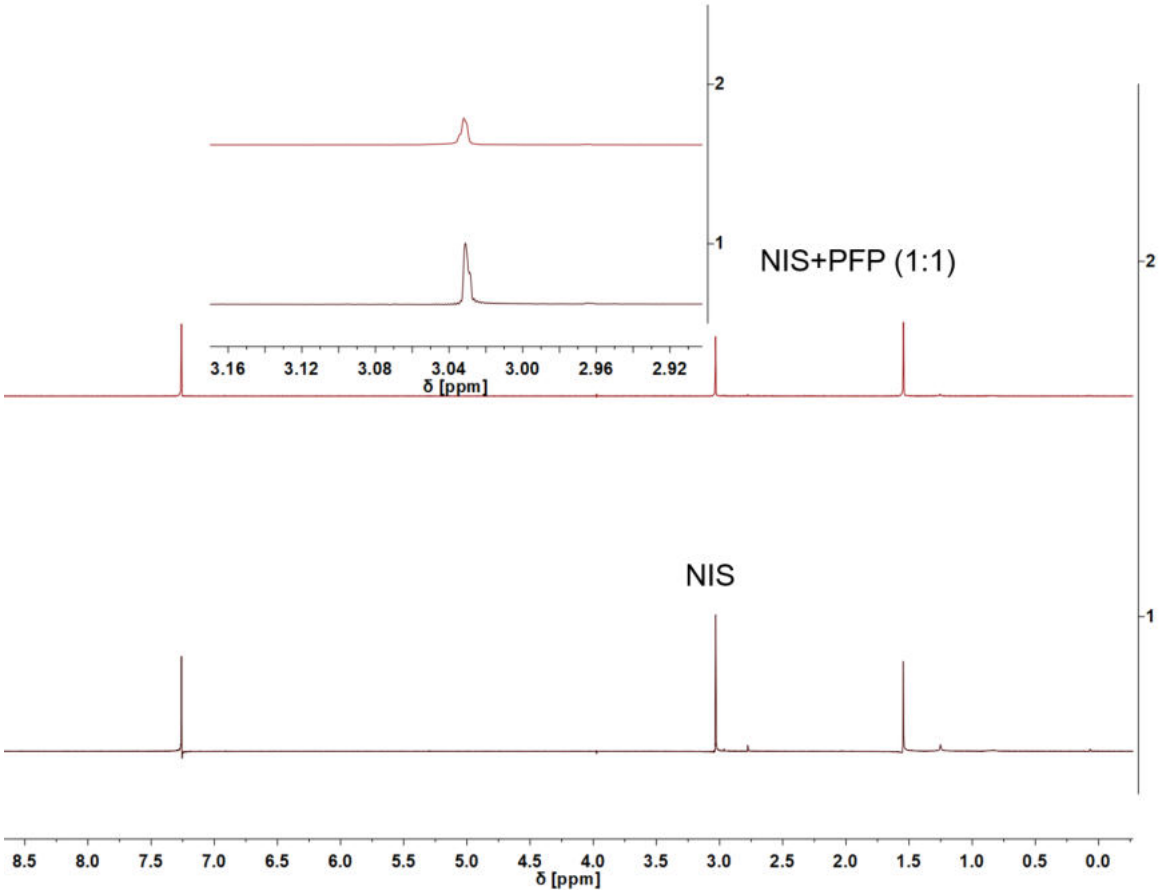
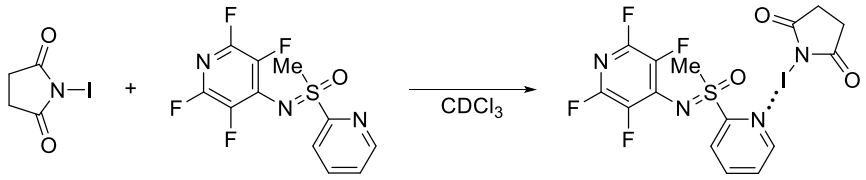


Figure S1 ^{1}H NMR (300 MHz) stack spectra of NIS and a 1:1 mixture of NIS+PFP (**2**) in $CDCl_3$.

Determination of binding constants for 1:1-XB complexes in solution

For each series of ^{1}H NMR titration, the spectra were referenced to the solvent residual signal. Then, the difference in chemical shift of the methylene protons (CH_2) of NIS was measured, and the corresponding concentration of NIS and *N*TFP-sulfoximine **3**, *N*H-sulfoximine **1** or pyridine was calculated. These raw data were analyzed using BindFit v0.5 (NMR 1:1, Nelder-Mead method).[4]

Table S13 Determined parameters for the 1:1 XB complex between NIS and **3n**[a]



Parameter (bounds)	Optimized	Error	Initial
K (0 → ∞)	7.59 M^{-1}	± 1.4123%	10.00 M^{-1}

[a] See: http://app.supramolecular.org/bindfit/view/42ecbd07-babd-4d0e-875f-5a9ed90a82a5 for BindFit v0.5 results.

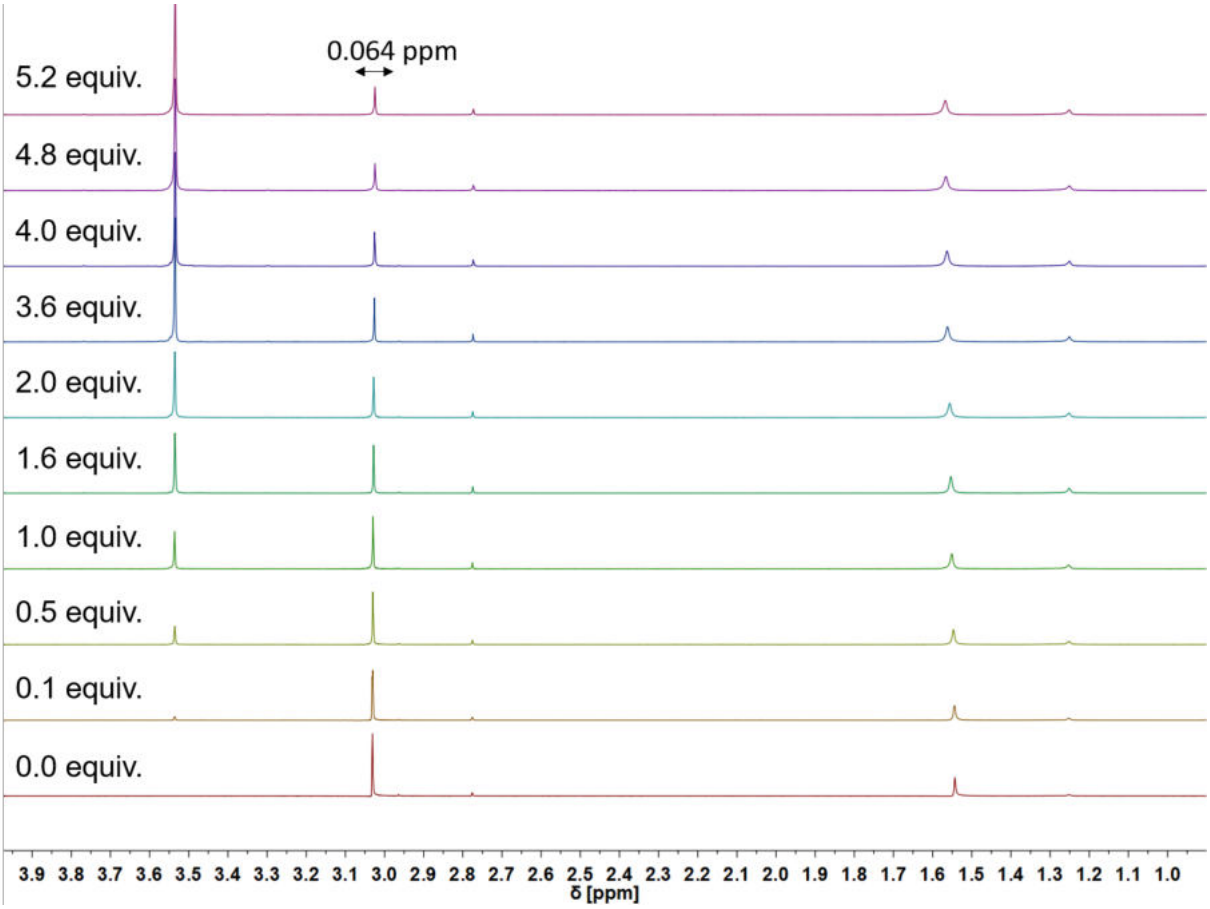
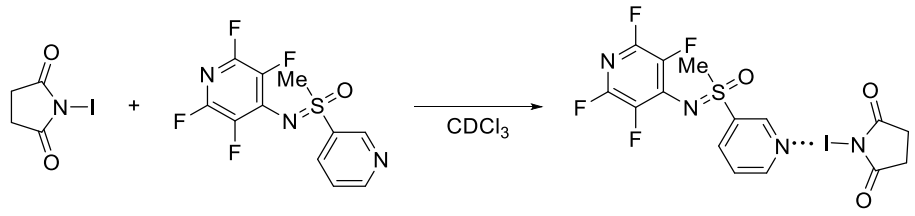


Figure S2 ^{1}H NMR (300 MHz) titration stack spectra of NIS and **3n** in $CDCl_3$.

Table S14 Determined parameters for the 1:1 XB complex between NIS and **3o**[a]



Parameter (bounds)	Optimized	Error	Initial
K (0 → ∞)	78.10 M^{-1}	± 1.4887%	100.00 M^{-1}

[a] See: http://app.supramolecular.org/bindfit/view/e3d0437e-e3be-43b0-82a4-3d5e45a986ed for BindFit v0.5 results.

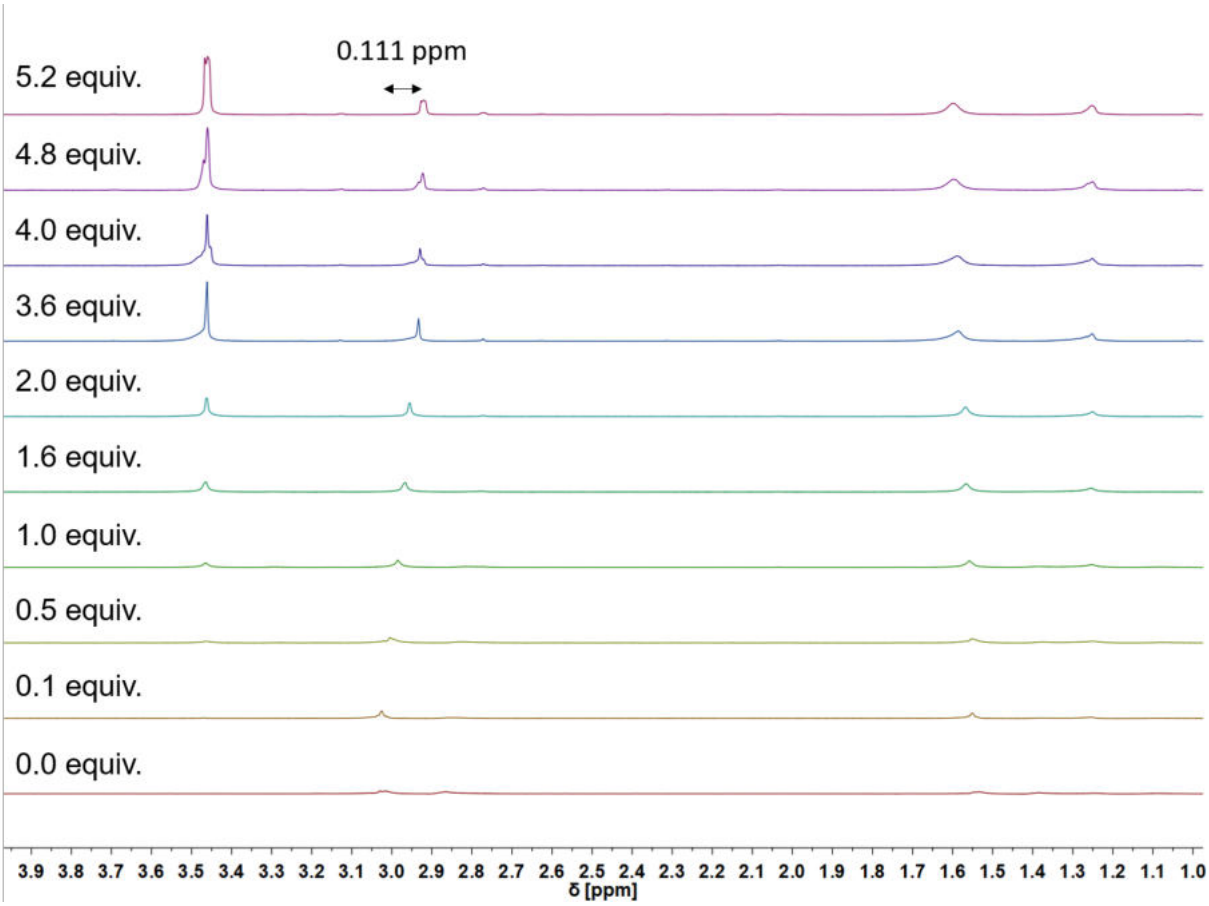
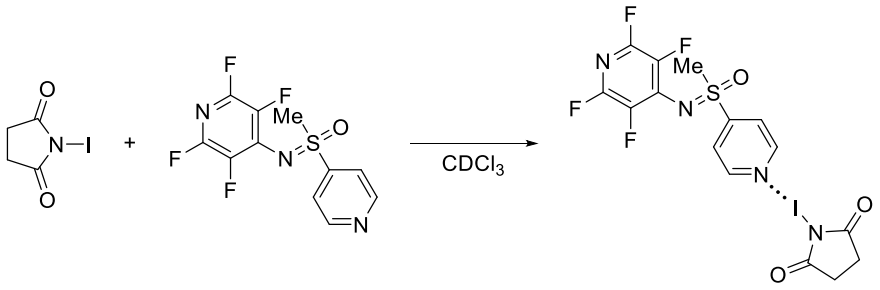


Figure S3 ^{1}H NMR (300 MHz) titration stack spectra of NIS and **3o** in $CDCl_3$.

Table S15 Determined parameters for the 1:1 XB complex between NIS and **3p**[a]



Parameter (bounds)	Optimized	Error	Initial
K (0 → ∞)	112.53 M^{-1}	± 1.3813%	100.00 M^{-1}

[a] See: http://app.supramolecular.org/bindfit/view/f8d7e3e4-3ea3-420c-a600-25860dad0367 for BindFit v0.5 results.

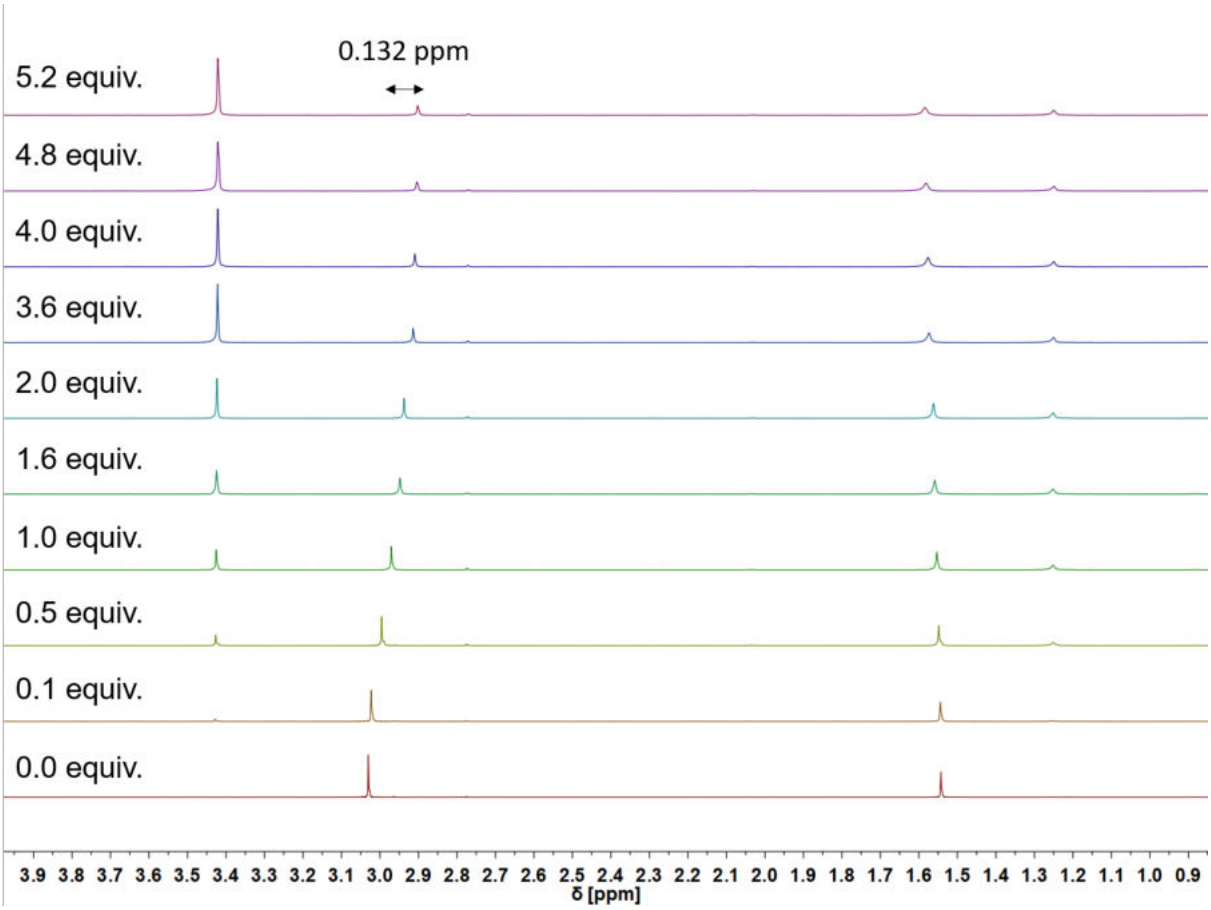
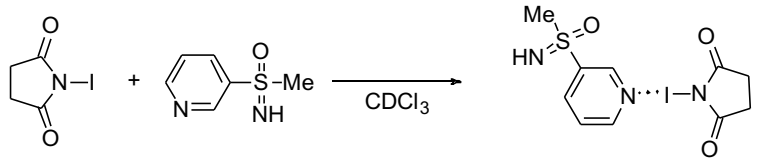


Figure S4 ^{1}H NMR (300 MHz) titration stack spectra of NIS and **3p** in $CDCl_3$.

Table S16 Determined parameters for the 1:1 XB complex between NIS and **1o**[a]



Parameter (bounds)	Optimized	Error	Initial
K (0 → ∞)	86.65 M^{-1}	± 5.5997%	100.00 M^{-1}

[a] See: http://app.supramolecular.org/bindfit/view/422f5b6e-c44c-4521-bfb4-ff7433501fba for BindFit v0.5 results.

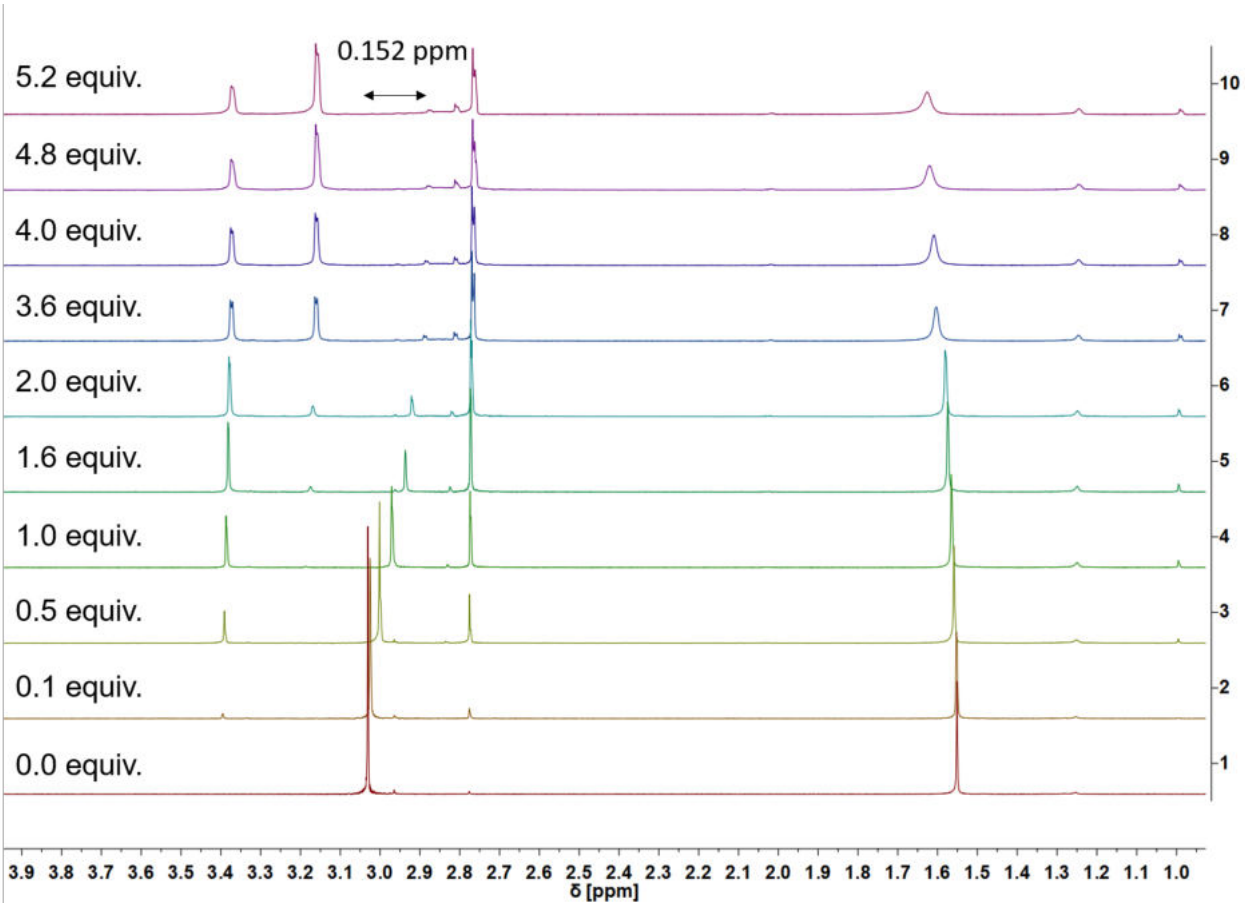
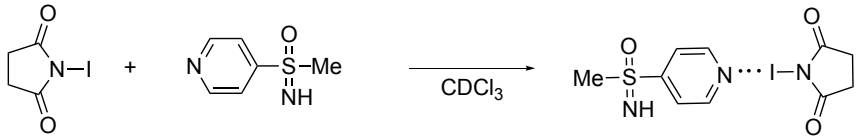


Figure S5 ^{1}H NMR (300 MHz) titration stack spectra of NIS and **1o** in $CDCl_3$.

Table S17 Determined parameters for the 1:1 XB complex between NIS and **1p**[a]



Parameter (bounds)	Optimized	Error	Initial
K (0 → ∞)	74.46 M^{-1}	± 6.5484%	100.00 M^{-1}

[a] See: http://app.supramolecular.org/bindfit/view/ec410d39-c127-4178-b0c1-b979460dd5cc for BindFit v0.5 results.

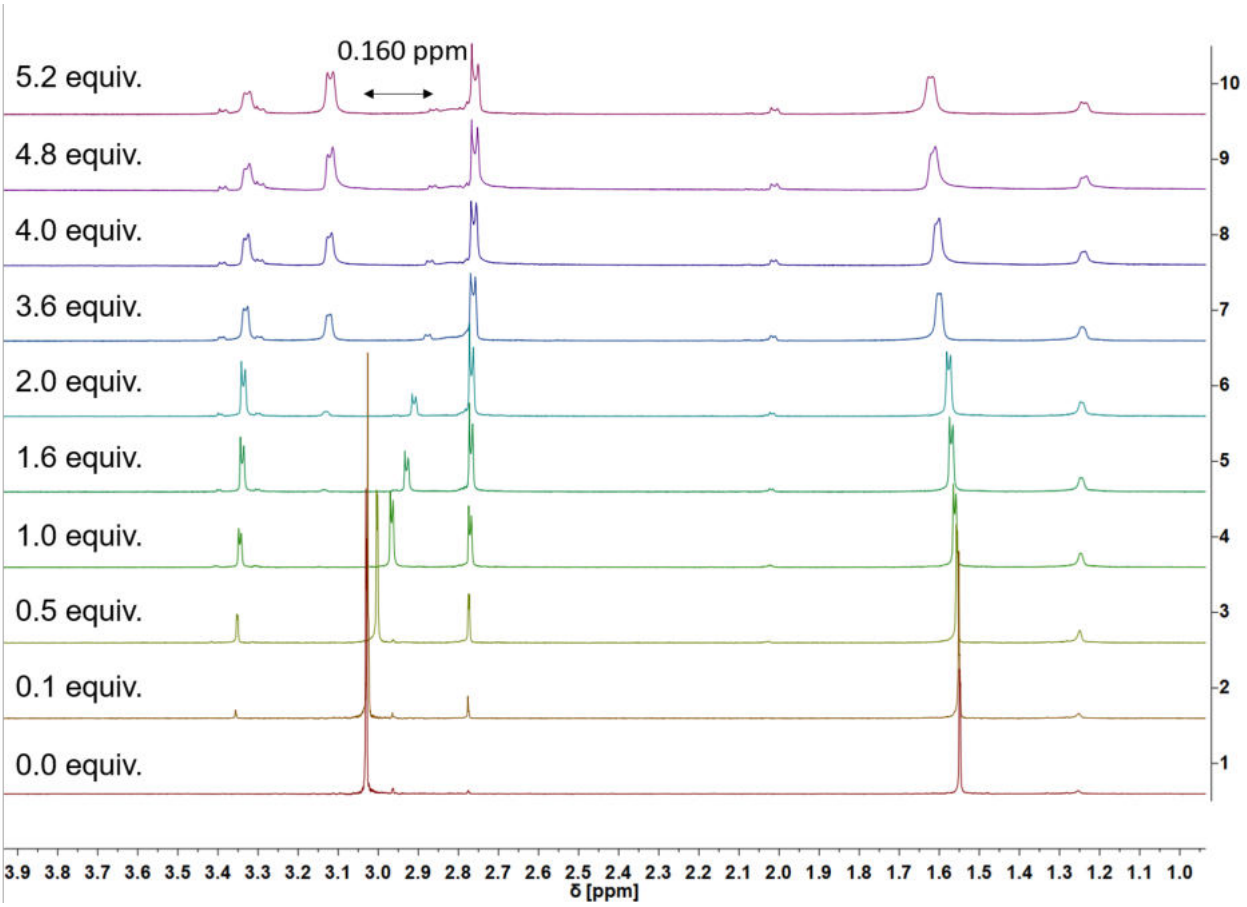
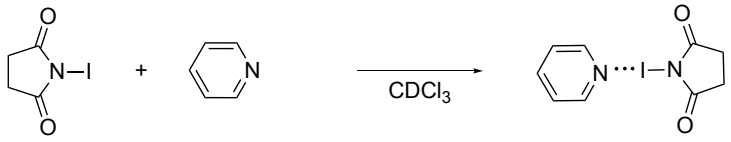


Figure S6 ^{1}H NMR (300 MHz) titration stack spectra of NIS and **1p** in $CDCl_3$.

Table S18 Determined parameters for the 1:1 XB complex between NIS and pyridine[a]



Parameter (bounds)	Optimized	Error	Initial
K (0 → ∞)	1118.95 M^{-1}	± 26.3557%	1000.00 M^{-1}

[a] See: http://app.supramolecular.org/bindfit/view/610555e6-d54f-4895-b7b5-58e82a73c153 for BindFit v0.5 results.

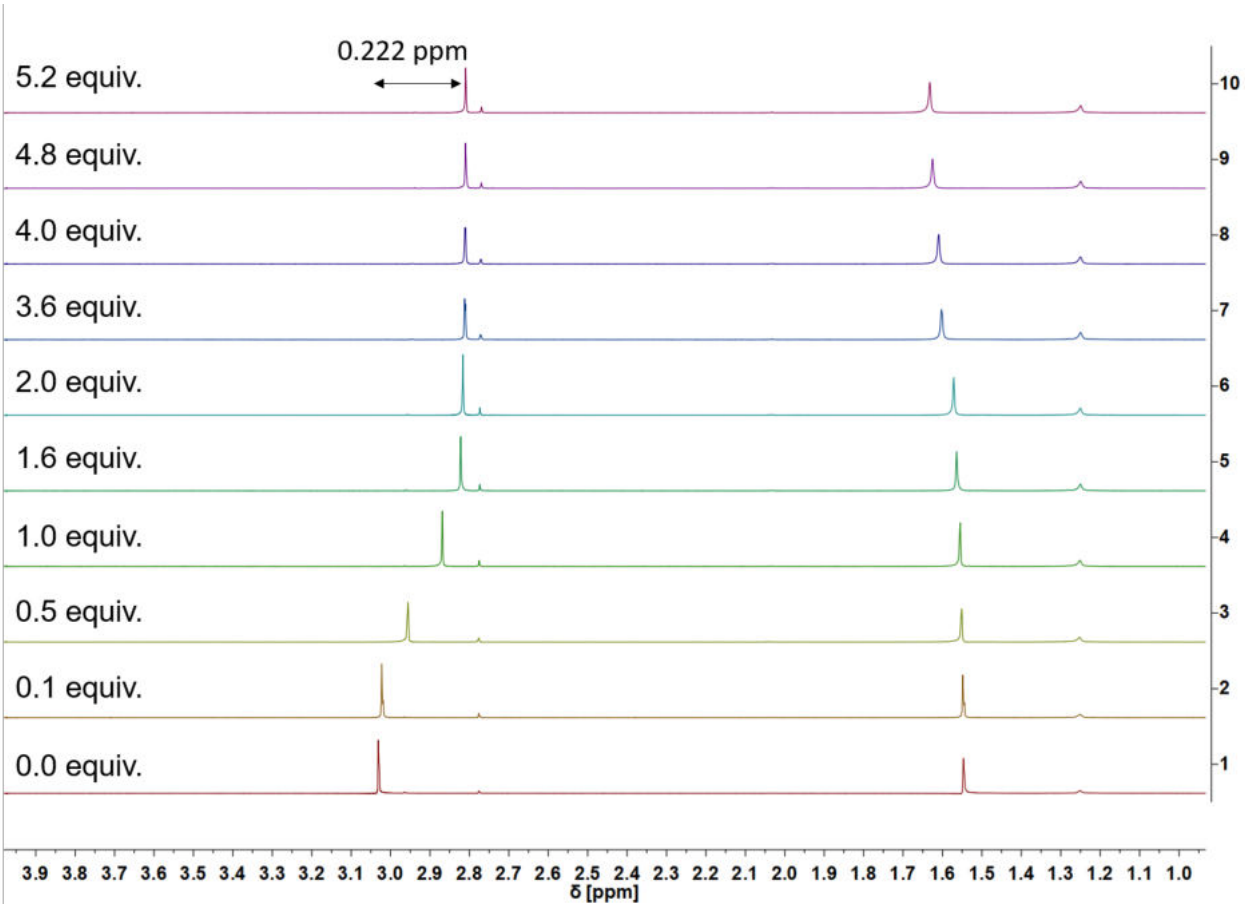
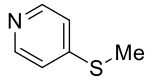


Figure S7 ^{1}H NMR (300 MHz) titration stack spectra of NIS and pyridine in $CDCl_3$.

Characterization data of starting materials

4-(Methylthio)pyridine

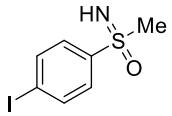


The title compound was synthesized following a modified procedure by Von Nagy-Felsobuki.[5] A round flask (50 mL) equipped with a magnetic stirring bar was charged with 4-mercaptopyridine (2.57 g, 23.1 mmol, 1.00 equiv.) and aqueous NaOH solution (1 M, 20 mL) in the given order. Then, methyl iodide (2.28 mL, 3.28 g, 23.1 mmol, 1.00 equiv.) was added dropwise while stirring over 5 min. The reaction mixture was stirred for 3 h at room temperature. Afterwards, the mixture was transferred to a separating funnel with benzene (10 mL), extracted with benzene (3 × 40 mL). The combined organic phases were dried over $MgSO_4$ and the volatiles were evaporated. The title compound was obtained as yellow liquid (2.09 g, 16.7 mmol, 72%) and was used without further purification. R_f = 0.71 (EtOAc), UV-active (254 nm); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 8.39–8.37 (m, 2H, Ar–*H*), 7.09–7.07 (m, 2H, Ar–*H*), 2.48 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 150.4, 149.2, 119.9, 13.8 ppm; **IR (ATR)**: ν = 3395 (w), 3031 (w), 2922 (w), 2852 (w), 2697 (w), 2444 (w), 2323 (w), 2096 (w), 1996 (w), 1924 (w), 1798 (w), 1648 (w), 1573 (s), 1480 (m), 1433 (m), 1407 (s), 1311 (w), 1220 (m), 1109 (m), 1066 (w), 982 (m), 855 (w), 800 (s), 727 (m), 695 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 157 (44), 126 (28) [*M*+H]$^+$, 125 (100) [*M*]+, 124 (10), 92 (31), 83 (12), 80 (10), 79 (19), 78 (19), 52 (11), 51 (32), 50 (12); **MS (CI, 100 eV, Methane)**: *m/z* (%): 126.0 (70) [*M*+H]$^+$. Data are in accordance with the literature.[5]

General procedure for the synthesis of *N*H-sulfoximines (GP6)

*N*H-Sulfoximines **1** were synthesized following a modified procedure by Bull and Luisi.[6a,b] A round flask (50 mL) equipped with a magnetic stirring bar was charged with the corresponding sulfide or sulfoxide and MeOH (0.5 M) in the given order. While stirring at room temperature, PIDA (4.00 equiv.) and ammonium carbamate (3.00 equiv.) were added portionwise and carefully, due to gas release. The reaction mixture was openly stirred at room temperature for 0.5 h-24 h until the sulphide or sulfoxide was fully consumed (as determined by TLC). Then, the mixture was concentrated *in vacuo*. The products were obtained after column chromatography (silica, EtOAc). *N*H-Sulfoximines **1** that are not listed below were either commercially available or have been in the stock in the group. Commonly, they can be prepared by GP6 or another published method.[6c,d,8]

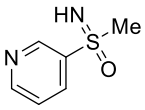
S-(4-Iodophenyl)-*S*-methyl-sulfoximine (1i)



The title compound was synthesized according to GP6 starting from *S*-(4-iodophenyl)-*S*-methyl-sulfide (1.25 g, 5.00 mmol) in 3 h reaction time and was purified by column chromatography (silica, EtOAc) to yield the product as light-yellow solid (1.08 g, 3.84 mmol, 77%). R_f = 0.32 (EtOAc), UV-active (254 nm); **m.p.:** 146.1-148.0 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.6 Hz, 2H, Ar–*H*), 7.72 (d, *J* = 8.5 Hz, 2H, Ar–*H*), 3.09 (s, 3H, CH_3), 2.50 (br s, 1H, N*H*) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 143.4, 138.7, 129.4, 100.9, 46.3 ppm; **IR (ATR)**: ν = 3851 (w), 3241 (s), 3094 (w), 3013 (w), 2923 (w), 2759 (w), 2323 (w), 2193 (w), 2162 (w), 2078 (w),

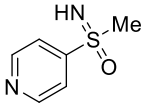
2020 (w), 1986 (w), 1918 (w), 1740 (w), 1558 (m), 1464 (m) 1379 (s), 1317 (m), 1218 (s), 1087 (s), 1051 (m), 1018 (s), 987 (s), 823 (s), 755 (s), 706 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 372 (27), 282 (50) $[M+H]^+$, 281 (49) $[M]^+$, 267 (10), 266 (33), 218 (100), 203 (21), 91 (13), 76 (15); **MS (CI, 100 eV, Methane)**: *m/z* (%): 282 (80) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_7H_8INOS+H^+$: 281.9444 $[M+H]^+$, found 281.9444.

_S_-Methyl-_S_-(3-pyridyl)-sulfoximine (1o)



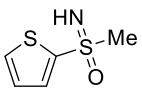
The title compound was synthesized according to GP6 starting from *S*-methyl-*S*-(3-pyridyl)-sulfoxide (0.502 g, 3.55 mmol) in 2.5 h reaction time and was purified by column chromatography (silica, EtOAc) to yield the product as brown oil (0.389 g, 2.49 mmol, 70%). R_f = 0.14 (EtOAc), UV-active (254 nm); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 9.23 (d, *J* = 2.3 Hz, 1H, Ar–*H*), 8.86 (dd, *J* = 4.8, 1.6 Hz, 1H, Ar–*H*), 8.30 (dt, *J* = 8.0, 2.0 Hz, 1H, Ar–*H*), 7.51 (dd, *J* = 8.0, 4.9 Hz, 1H, Ar–*H*), 3.17 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H}** NMR (151 MHz, $CDCl_3$): δ = 153.8, 149.1, 140.0, 135.8, 124.0, 46.6 ppm; **IR (ATR)**: ν = 3793 (w), 3577 (w), 3424 (w), 3266 (w), 3008 (w), 2924 (w), 2595 (w), 2329 (w), 2165 (w), 2085 (w), 1937 (w), 1711 (m), 1669 (m), 1572 (s), 1467 (w), 1412 (s), 1323 (w), 1222 (s), 1114 (s), 999 (s), 810 (m), 758 (s), 701 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 157 (41) $[M+H]^+$, 156 (69) $[M]^+$, 141 (60), 93 (66), 92 (72), 79 (12), 78 (100), 66 (14), 52 (11), 51 (63), 50 (22); **MS (CI, 100 eV, Methane)**: *m/z*(%): 157.0 (100) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_6H_8N_2OS+H^+$: 157.0430 $[M+H]^+$, found 157.0429. These data are in accordance with the literature.[7]

_S_-Methyl-_S_-(4-pyridyl)-sulfoximine (1p)



The title compound was synthesized according to GP6 starting from 4-(methylthio)-pyridine (1.00 g, 8.00 mmol) in 1.5 h reaction time was purified by column chromatography (silica, EtOAc) to yield the product as orange oil (1.06 g, 6.80 mmol, 85%). R_f = 0.06 (EtOAc), UV-active (254 nm); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 8.89-8.87 (m, 2H, Ar–*H*), 7.87-7.85 (m, 2H, Ar–*H*), 3.12 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 152.0, 151.4, 121.1, 45.5 ppm; **IR (ATR)**: ν = 3262 (m), 3015 (m), 2924 (m), 2344 (w), 2159 (w), 2063 (w), 1989 (w), 1952 (w), 1709 (m), 1668 (s), 1572 (s), 1493 (w), 1402 (s), 1322 (m), 1215 (s), 1110 (s), 1011 (s), 819 (s), 757 (s), 692 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 231 (10), 203 (30), 158 (11), 157 (100) $[M+H]^+$, 156 (10) $[M]^+$, 141 (58), 85 (23), 83 (28), 78 (33), 51 (15); **MS (CI, 100 eV, Methane)**: *m/z* (%): 157 (100) $[M+H]^+$, **HRMS (ESI)**: *m/z* calcd. for $C_6H_8N_2OS+H^+$: 157.0430 $[M+H]^+$, found 157.0432.

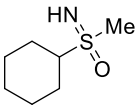
_S_-Methyl-_S_-(thiophen-2-yl)-sulfoximine (1r)



The title compound was synthesized according to GP6 starting from *S*-methyl-*S*-(thiophen-2-yl)-sulfoxide (401.7 mg, 2.75 mmol) in 3.5 h reaction time and was purified by column chromatography (silica, EtOAc) to yield the product as light-yellow solid (239 mg, 1.48 mmol, 54%). R_f = 0.37 (EtOAc), UV-active (254 nm); **m.p.:** 89.7-91.5 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.61-7.55 (m, 2H, Ar–*H*), 7.06-7.00 (m, 1H, Ar–*H*), 3.14 (s, 3H, C*H*$_3$), 3.14 (br s, 1H, N*H*) ppm; **^{13}C{^{1}H} NMR**

(151 MHz, $CDCl_3$): δ = 145.7, 133.5, 133.1, 127.8, 47.5 ppm; **IR (ATR)**: ν = 3873 (w), 3251 (s), 3062 (m), 2995 (m), 2918 (m), 2638 (s), 2291 (s), 2207 (s), 2173 (s), 2077 (s), 2027 (s), 1962 (s), 1829 (s), 1742 (s), 1592 (s), 1503 (s), 1399 (m), 1323 (m), 1219 (s), 1091 (s), 1069 (s), 1026 (s), 991 (s), 957 (s), 854 (s), 727 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z*(%): 323 (21), 164 (13), 163 (11), 162 (100) $[M+H]^+$, 98 (23); **MS (CI, 100 eV, Methane)**: *m/z*(%): 162 (100) $[M+H]^+$. These data are in accordance with the literature.[8]

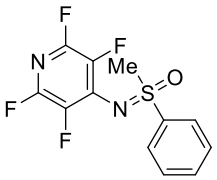
_S_-Cyclohexyl-_S_-methyl-sulfoximine (1t)



The title compound was synthesized according to GP6 starting from *S*-cyclohexyl-*S*-methyl-sulfoxide (0.627 g, 4.29 mmol) in 2.5 h reaction time and was purified by column chromatography (silica, EtOAc) to yield the product as colourless oil (0.492 g, 3.05 mmol, 71%). R_f = 0.11 (EtOAc), UV-active (254 nm); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 2.90 (s, 3H, CH_3), 2.89-2.87 (m, 1H, Cy–*H*), 2.71 (br s, 1H, N*H*), 2.27-2.20 (m, 2H, Cy–*H*), 1.98-1.93 (m, 2H, Cy–*H*), 1.74 (d, *J* = 13.1 Hz, 1H, Cy–*H*), 1.54-1.43 (m, 2H, Cy–*H*), 1.39-1.27 (m, 2H, Cy–*H*), 1.27-1.15 (m, 1H, Cy–*H*) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 64.5, 39.5, 26.1, 26.0, 25.4, 25.2 ppm; **IR (ATR)**: ν = 3849 (w), 3545 (w), 3266 (m), 3013 (w), 2930 (s), 2857 (s), 2661 (w), 2324 (w), 2177 (w), 2093 (w), 2177 (w), 2093 (w), 1994 (w), 1941 (w), 1711 (w), 1634 (w), 1450 (s), 1415 (m), 1319 (m), 1275 (w), 1194 (s), 1120 (s), 989 (s), 945 (s), 892 (m), 856 (w), 818 (w), 752 (m), 725 (m), 684 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z*(%): 162 (45) $[M+H]^+$, 146 (15), 83 (50), 82 (10), 81 (13), 80 (86), 79 (24), 67 (12), 55 (100); **MS (CI, 100 eV, Methane)**: *m/z*(%): 162 (100) $[M+H]^+$. These data are in accordance with the literature.[8]

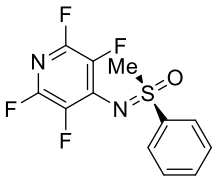
Characterization data of products

_S_-Methyl-_S_-phenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3a)



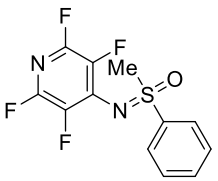
Solution: The title compound was synthesized according to GP2 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (118.9 mg, 0.391 mmol, 96%). **Mechanochemistry**: The title compound was synthesized according to the GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (90.4 mg, 0.297 mmol, 92%). R_f = 0.77 (Et_2O), UV-active (254 nm); **m.p.**: 130.3-131.1 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.96 (m, 2H, Ar–*H*), 7.70 (m, 1H, Ar–*H*), 7.62 (m, 2H, Ar–*H*), 3.40 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 144.2 (dm, $J_{C,F}$ = 239.9 Hz), 139.4, 136.5 (dm, $J_{C,F}$ = 255.8 Hz), 136.3 (m), 134.4, 130.1, 127.4, 47.8 ppm; **^{19}F NMR** (564 MHz, $CDCl_3$): δ = –93.29 (m, 2F, Py–*F*), –151.51 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3014 (w), 2925 (w), 2284 (w), 2184 (w), 2076 (w), 1983 (w), 1820 (w), 1744 (w), 1638 (s), 1459 (s), 1324 (m), 1295 (m), 1216 (s), 1149 (s), 1089 (s), 958 (s), 905 (m), 783 (m), 741 (s), 685 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 305 (27), 304 (100) $[M]^+$, 289 (20), 242 (8), 241 (65), 191 (15), 125 (30), 97 (12), 77 (39), 51 (15); **MS (CI, 100 eV, Methane)**: *m/z* (%): 305 (100) $[M+H]^+$. These data were in accordance with the literature.[9]

(*R*)-*S*-Methyl-*S*-phenyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine [(*R*)-3a]

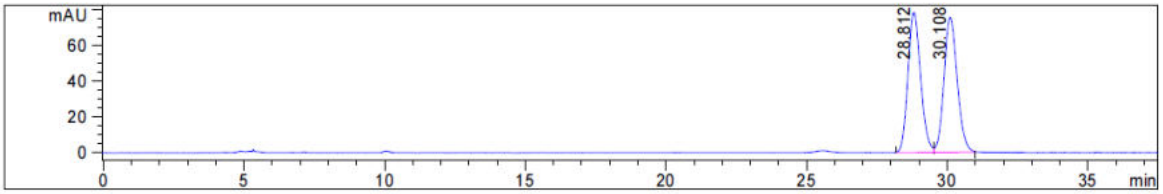


The title compound **(*R*)-3a** was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (199.4 mg, 0.655 mmol, 95%, *e.r.*: 99:1). R_f = 0.66 (Et_2O), UV-active (254 nm); **m.p.**: 74.6-76.0 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.96 (m, 2H, Ar–*H*), 7.71 (m, 1H, Ar–*H*), 7.62 (m, 2H, Ar–*H*), 3.40 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 240.6 Hz), 139.4, 136.5 (dm, $J_{C,F}$ = 253.1 Hz), 136.3 (m), 134.4, 130.1, 127.4, 47.8 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.25 (m, 2F, Py–*F*), –151.50 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3019 (w), 2926 (w), 2588 (w), 2187 (w), 1987 (w), 1817 (w), 1636 (m), 1462 (s), 1299 (m), 1219 (s), 1149 (s), 1092 (s), 956 (s), 901 (s), 783 (m), 740 (s), 686 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 305 (22), 304 (100) [*M*]$^+$, 289 (17), 241 (50), 125 (19), 77 (25); **MS (CI, 100 eV, Methane)**: *m/z* (%): 305.1 (100) [*M*+H]$^+$; **HRMS (EI)**: *m/z* calcd. for $C_{12}H_8F_4N_2OS^{\bullet+}$: 304.0288 [*M*]$^{\bullet+}$, found: 304.0281.

Sample Info: AD-H, Hep/iPrOH = 97:3, 0.6 mL/min, 20 °C



Instrument Conditions:	At Start	At Stop
Temperature in °C:	20.0	20.0
Pressure in bar:	32.5	32.8
Flow in mL/min:	0.60	0.60

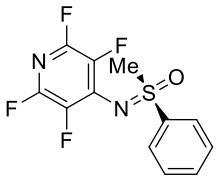


DAD1 A, Sig=254,4 Ref=360,100

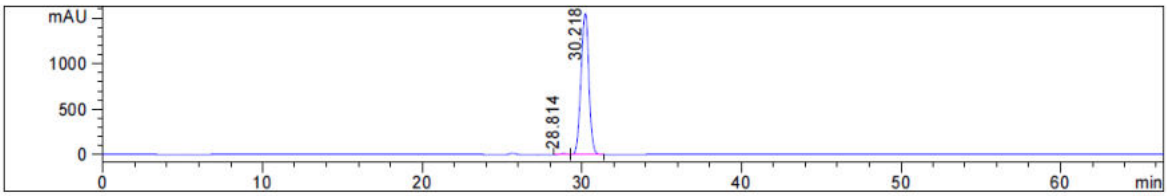
Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	28.812	0.4842	78.23409	2455.84497	49.9043
2	30.108	0.4956	75.36668	2465.26221	50.0957
Total				4921.10718	100.0000

Figure S8 Analytical HPLC chromatogram of racemic *S*-Methyl-*S*-phenyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine (**3a**).

Sample Info: AD-H, Hep/iPrOH = 97:3, 0.6 mL/min, 20 °C



Instrument Conditions:	At Start	At Stop
Temperature in °C:	20.0	20.0
Pressure in bar:	32.4	32.8
Flow in mL/min:	0.60	0.60

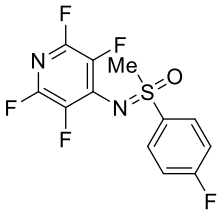


DAD1 A, Sig=254,4 Ref=360,100

Peak #	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	28.814	0.4447	12.10122	369.95169	0.6912
2	30.218	0.5326	1548.07092	53152.66406	99.3088
Total				53522.61575	100.0000

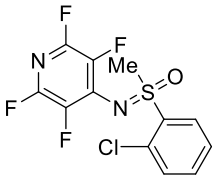
Figure S9 Analytical HPLC chromatogram of *(R)*-*S*-Methyl-*S*-phenyl-*N*-(2,3,5,6-tetrafluoropyridyl)-sulfoximine [(*R*)-**3a**].

S-4-Fluorophenyl-*S*-methyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3b)



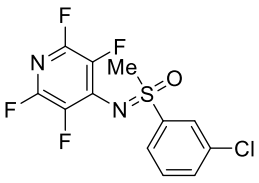
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (130.3 mg, 0.404 mmol, 71%). R_f = 0.86 (Et_2O), UV-active (254 nm); **m.p.**: 152.9-154.5 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.99 (m, 2H, Ar–*H*), 7.30 (m, 2H, Ar–*H*), 3.40 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 166.2 (d, $J_{C,F}$= 258.0 Hz), 144.2 (dm, $J_{C,F}$ = 240.4 Hz), 136.6 (dm, $J_{C,F}$ = 250.9 Hz), 135.9 (m), 135.3 (d, $J_{C,F}$ = 2.2 Hz), 130.4 (d, $J_{C,F}$ = 9.7 Hz), 117.5 (d, $J_{C,F}$ = 22.9 Hz), 47.9 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.92 (m, 2F, Py–*F*), –102.28 (m, 1F, Ar–*F*), -151.38 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3107 (w), 3078 (w), 3028 (w), 2931 (w), 2595 (w), 2399 (w), 2244 (w), 2182 (w), 2078 (w), 1993 (w), 1921 (w), 1815 (w), 1741 (w), 1638 (s), 1590 (m), 1458 (s), 1405 (s), 1325 (w), 1296 (m), 1218 (s), 1153 (s), 1091 (s), 991 (s), 958 (s), 908 (m), 839 (s), 771 (s), 733 (m), 695 (m) cm^{-1}. **MS (EI, 70 eV)**: *m/z* (%): 323 (24), 322 (100) [*M*]$^+$, 307 (15), 260 (11), 259 (73), 209 (10), 143 (33), 95 (12); **MS (CI, 100 eV, Methane)**: *m/z* (%): 323 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7F_5N_2OS$+Na$^+$: 345.0092 [*M*+Na]$^+$, found: 345.0092.

***S*-2-Chlorophenyl-*S*-methyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3c)**



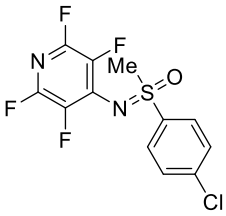
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (161.1 mg, 0.476 mmol, 90%). ***R*f** = 0.75 (Et_2O), UV-active (254 nm); **m.p.**: 96.3-97.3 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 8.26 (m, 1H, Ar–*H*), 7.62 (m, 1H, Ar–*H*), 7.56 (m, 2H, Ar–*H*), 3.60 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 240.1 Hz), 136.8, 136.4 (dm, $J_{C,F}$ = 253.4 Hz), 135.8 (m), 135.4, 132.5, 132.0, 128.3, 45.4 ppm. Ten ^{13}C signals were expected, but only nine could be detected. One quaternary carbon atom (C–Cl or C–S) could not be detected (also not by HMBC). Structure is verified by HRMS and SCXRD. **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.19 (m, 2F, Py–*F*), –151.38 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3596 (w), 3092 (w), 2935 (w), 2696 (w), 2343 (w), 2175 (w), 2085 (w), 2014 (w), 1958 (w), 1743 (w), 1639 (m), 1577 (w), 1467 (s), 1297 (m), 1231 (s), 1152 (s), 1041 (m), 960 (s), 767 (s), 732 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 341 (16), 340 (51), 339 (33) 338 (100) [*M*]$^+$, 323 (11), 277 (11), 275 (32), 241 (11), 240 (63), 159 (22); **MS (CI, 100 eV, Methane)**: *m/z* (%): 341 (42), 339 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7ClF_4N_2OS$+Na$^+$: 360.9796 [*M*+Na]$^+$, found: 360.9796.

***S*-3-Chlorophenyl-*S*-methyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3d)**



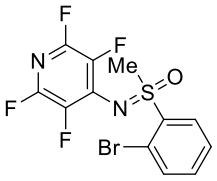
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (128.4 mg, 0.379 mmol, 72%). ***R*f** = 0.83 (Et_2O), UV-active (254 nm); **m.p.**: 90.7-92.3 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.96 (m, 1H, Ar–*H*), 7.85 (dm, *J* = 8.0 Hz, 1H, Ar–*H*), 7.67 (dm, *J* = 8.0 Hz, 1H, Ar–*H*), 7.57 (t, *J* = 8.0 Hz, 1H, Ar–*H*), 3.41 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 241.1 Hz), 141.4, 136.5 (dm, $J_{C,F}$ = 254.6 Hz), 136.4, 134.6, 131.4, 127.6, 125.5, 47.7 ppm. Ten ^{13}C signals were expected, but only nine could be detected. The quaternary carbon atom (C–N) in the perflourinated pyridine ring was not detected. Structure is verified by HRMS and SCXRD. **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.78 (m, 2F, Py–*F*), –151.25 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3600 (w), 3074 (w), 3028 (w), 2937 (w), 2699 (w), 2329 (w), 2235 (w), 2168 (w), 2015 (w), 1963 (w),1885 (w), 1742 (w), 1636 (s), 1465 (s), 1412 (s), 1296 (m), 1219 (s), 1152 (s), 962 (s), 897 (m), 794 (m), 721 (m), 672 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 341 (17), 340 (52), 339 (36), 338 (100) [*M*]$^+$, 323 (13), 277 (14), 275 (40), 240 (11), 159 (16), 111 (13); **MS (CI, 100 eV, Methane)**: *m/z* (%): 341 (43), 339 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7ClF_4N_2OS$+H$^+$: 338.9977 [*M*+H]$^+$, found: 338.9977.

***S*-4-Chlorophenyl-*S*-methyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3e)**



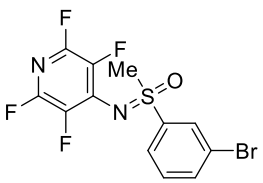
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (144.3 mg, 0.426 mmol, 79%). R_f = 0.82 (Et_2O), UV-active (254 nm); **m.p.**: 148.1-148.6 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.91 (dm, J = 8.7 Hz, 2H, Ar–*H*), 7.59 (dm, J = 8.7 Hz, 2H, Ar–*H*), 3.40 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 239.7 Hz), 141.3, 137.9, 136.6 (dm, $J_{C,F}$ = 251.4 Hz), 135.8 (m), 130.5, 129.0, 47.8 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.84 (m, 2F, Ar–*F*), –151.33 (m, 2F, Ar–*F*) ppm; **IR (ATR)**: ν = 3092 (w), 3032 (w), 2935 (w), 2769 (w), 2580 (w), 2395 (w), 2165 (w), 2088 (w), 1815 (w), 1752 (w), 1635 (s), 1577 (m), 1458 (s), 1401 (m), 1293 (m), 1213 (s), 1153 (s), 1084 (s), 956 (s), 826 (m), 775 (s), 734 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 341 (12), 340 (47), 339 (31), 338 (100) [*M*]$^+$, 323 (15), 277 (27), 276 (13), 275 (78), 240 (15), 225 (11), 161 (11), 159 (28), 111 (13), 75 (10); **MS (CI, 100 eV, Methane)**: *m/z* (%): 341 (41), 339 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7ClF_4N_2OS$+H$^+$: 338.9977 [*M*+H]$^+$, found: 338.9976.

***S*-2-Bromophenyl-*S*-methyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3f)**



The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (148.6 mg, 0.388 mmol, 90%). R_f = 0.76 (Et_2O), UV-active (254 nm); **m.p.**: 95.4-96.1 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 8.30 (dm, J = 8.0 Hz, 1H, Ar–*H*), 7.76 (dm, J = 8.0 Hz, 1H, Ar–*H*), 7.61 (m, 1H, Ar–*H*), 7.52 (td, J = 7.7, 1.6 Hz, 1H, Ar–*H*), 3.61 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 241.7 Hz), 138.6, 136.3 (dm, $J_{C,F}$ = 251.9 Hz), 136.0, 135.8 (m), 135.4, 132.2, 128.9, 120.0, 45.0 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.21 (m, 2F, Py–*F*), –151.35 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3092 (w), 2933 (w), 2349 (w), 2174 (w), 2018 (w), 1964 (w), 1740 (w), 1638 (m), 1575 (w), 1467 (s), 1297 (m), 1227 (s), 1151 (s), 1027 (m), 959 (s), 764 (s) cm^{-1}. **MS (EI, 70 eV)**: *m/z* (%): 384 (25), 382 (23) [*M*]$^+$, 240 (23), 87 (18), 85 (86), 83 (100), 47 (10); **MS (CI, 100 eV, Methane)**: *m/z* (%): 385 (98), 383 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7BrF_4N_2OS$+Na$^+$: 404.9291 [*M*+Na]$^+$, found: 404.9291.

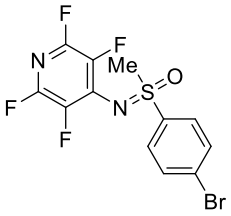
***S*-3-Bromophenyl-*S*-methyl-*N*-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3g)**



The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (118.9 mg, 0.310 mmol, 71%). R_f = 0.73 (Et_2O), UV-active (254 nm); **m.p.**: 103.0-106.5 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 8.11 (m, 1H, Ar–*H*), 7.89 (m, 1H, Ar–*H*), 7.83 (m, 1H, Ar–*H*), 7.50 (t, J = 8.0 Hz, 1H, Ar–*H*), 3.40 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 240.1 Hz), 141.5, 137.5, 136.5 (dm, $J_{C,F}$ = 255.1 Hz), 135.8 (m), 131.6, 130.4, 125.9, 124.1, 47.8 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.76 (m, 2F, Py–*F*), –151.23 (m, 2F,

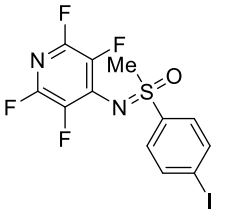
Py–*F*) ppm; **IR (ATR)**: ν = 3070 (w), 3029 (w), 2939 (w), 2321 (w), 2244 (w), 2166 (w), 2075 (w), 2034 (w), 1986 (w), 1870 (w), 1749 (w), 1637 (s), 1572 (w), 1468 (s), 1410 (s), 1364 (w), 1296 (m), 1219 (s), 1155 (s), 963 (s), 895 (s), 798 (m), 776 (m), 712 (s), 674 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 385 (21), 384 (100), 383 (24), 382 (88) $[M]^+$, 369 (14), 367 (14), 321 (16), 319 (18), 241 (13), 240 (75), 205 (18), 203 (19), 157 (15), 155 (16), 76 (11), 75 (10); **MS (CI, 100 eV, Methane)**: *m/z* (%): 385 (100), 383 (96) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7BrF_4N_2OS+K^+$: 420.9030 $[M+K]^+$, found: 420.9030.

_S_-4-Bromophenyl-_S_-methyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3h)



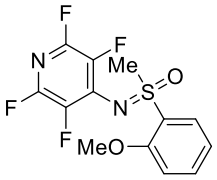
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (34.3 mg, 0.090 mmol, 21%). R_f = 0.75 (Et_2O), UV-active (254 nm); **m.p.**: 117.2-119.6 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.83 (dm, *J* = 8.5 Hz, 2H, Ar–*H*), 7.76 (dm, *J* = 8.5 Hz, 2H, Ar–*H*), 3.39 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 242.8 Hz), 138.5, 136.4 (dm, $J_{C,F}$ = 252.3 Hz), 135.8 (m), 133.5, 129.9, 129.0, 47.7 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.82 (m, 2F, Py–*F*), –151.32 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3036 (w), 2932 (w), 2587 (w), 2293 (w), 2179 (w), 1986 (w), 1813 (w), 1748 (w), 1638 (s), 1572 (m), 1494 (s), 1462 (s), 1393 (m), 1323 (w), 1296 (m), 1215 (s), 1156 (s), 1089 (m), 1069 (m), 960 (s), 908 (m), 823 (m), 775 (s), 735 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 385 (16), 384 (100) $[M]^+$, 383 (17), 382 (88), 369 (14), 367 (15), 321 (41), 319 (42), 241 (12), 240 (84), 205 (21), 203 (23), 157 (11), 155 (12), 76 (10), 75 (10); **MS (CI, 100 eV, Methane)**: *m/z* (%): 385 (100), 383 (92) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7BrF_4N_2OS+K^+$: 420.9030 $[M+K]^+$, found: 420.9030.

_S_-4-Iodophenyl-_S_-methyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3i)



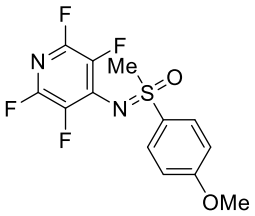
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (48.5 mg, 0.113 mmol, 63%). R_f = 0.86 (Et_2O), UV-active (254 nm); **m.p.**: 121.9-122.8 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.97 (dm, *J* = 8.6 Hz, 2H, Ar–*H*), 7.66 (dm, *J* = 8.6 Hz, 2H, Ar–*H*), 3.39 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 240.6 Hz), 139.4, 139.2, 136.5 (dm, $J_{C,F}$ = 253.5 Hz), 135.8 (m), 128.8, 102.5, 47.7 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.85 (m, 2F, Py–*F*), –151.31 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3926 (w), 3258 (w), 3031 (w), 2940 (w), 2854 (w), 2590 (w), 2241 (w), 2163 (w), 2088 (w), 2039 (w), 1996 (w), 1818 (w), 1749 (w), 1636 (s), 1567 (m), 1461 (s), 1384 (m), 1328 (w), 1300 (m), 1216 (s), 1154 (s), 1124 (s), 1089 (s), 1054 (m), 987 (s), 957 (s), 906 (m), 817 (m), 772 (s), 734 (m), 707 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 432 (17), 431 (46), 430 (67) $[M]^+$, 430 (83), 415 (36), 368 (13), 367 (93), 251 (46), 240 (100), 203 (16), 76 (25), 50 (15); **MS (CI, 100 eV, Methane)**: *m/z* (%): 431 (100) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7F_4IN_2OS+Na^+$: 452.9152 $[M+Na]^+$, found: 452.9153.

_S_-2-Methoxyphenyl-_S_-methyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3j)



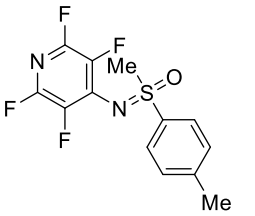
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (80.4 mg, 0.241 mmol, 87%). R_f = 0.66 (Et_2O), UV-active (254 nm); **m.p.:** 135.4-137.8 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 8.04 (d, J = 8.0 Hz, 1H, Ar–*H*), 7.63 (m, 1H, Ar–*H*), 7.16 (m, 1H, Ar–*H*), 7.02 (d, J = 8.4 Hz, 1H, Ar–*H*), 3.93 (s, 3H, OCH_3), 3.53 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 156.8, 144.1 (dm, $J_{C,F}$ = 240.1 Hz), 137.0 (m), 136.6 (dm, $J_{C,F}$ = 253.5 Hz), 136.4, 131.2, 125.7, 121.4, 112.5, 56.4, 45.5 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.79 (m, 2F, Py–*F*), –151.76 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3022 (w), 2942 (w), 2579 (w), 2404 (w), 2242 (w), 2080 (w), 2029 (w), 1987 (w), 1818 (w), 1738 (w), 1638 (m), 1592 (m), 1478 (s), 1284 (s), 1254 (m), 1212 (s), 1144 (s), 1061 (m), 1013 (m), 958 (s), 908 (m), 861 (w), 801 (m), 756 (s), 674 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 336 (20), 335 (85), 334 (100) [*M*]$^+$, 271 (13), 243 (12), 169 (31), 156 (11), 155 (22), 154 (12), 153 (25), 138 (28), 137 (12), 125 (13), 92 (11), 77 (14); **MS (CI, 100 eV, Methane)**: *m/z* (%): 335 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{13}H_{10}F_4N_2O_2S$+Na$^+$: 357.0291 [*M*+Na]$^+$, found: 357.0291.

_S_-4-Methoxyphenyl-_S_-methyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3k)



The title compound was synthesized according to general procedure GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (136.9 mg, 0.410 mmol, 75%). R_f = 0.86 (Et_2O), UV-active (254 nm); **m.p.**: 88.7-90.0 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.87 (m, 2H, Ar–*H*), 7.05 (m, 2H, Ar–*H*), 3.90 (s, 3H, OCH_3), 3.37 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 164.3, 144.2 (dm, $J_{C,F}$ = 240.7 Hz), 136.6 (dm, $J_{C,F}$ = 253.3 Hz), 136.6 (m), 130.3, 129.7, 115.3, 56.0, 48.1 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.44 (m, 2F, Py–*F*), –151.57 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3105 (w), 3021 (w), 2932 (w), 2845 (w), 2582 (w), 2395 (w), 2288 (w), 2179 (w), 2011 (w), 1903 (w), 1740 (w), 1636 (m), 1589 (m), 1460 (s), 1304 (m), 1256 (m), 1211 (s), 1149 (s), 1091 (m), 957 (s), 829 (s), 769 (m), 732 (w), 696 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 335 (13), 334 (100) [*M*]$^+$, 319 (18), 271 (93), 155 (21); **MS (CI, 100 eV, Methane)**: *m/z* (%): 335 (60), 229 (11), 195 (12), 171 (11), 167 (100), 163 (10), 155 (14), 141 (17), 109 (15); **HRMS (ESI)**: *m/z* calcd. for $C_{13}H_{10}F_4N_2O_2S$+Na$^+$: 357.0291 [*M*+Na]$^+$, found: 357.0291.

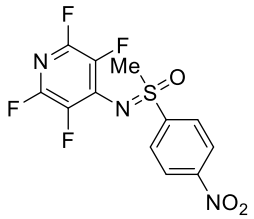
_S_-4-Methylphenyl-_S_-methyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3l)



The title compound was synthesized according to general procedure GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (145.2 mg, 0.456 mmol, 78%). R_f = 0.88 (Et_2O), UV-active (254 nm); **m.p.**: 111.8-112.5 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.82 (m, 2H, Ar–*H*), 7.40 (m, 2H, Ar–*H*), 3.37 (s, 3H, (SR_2)CH_3), 2.46 (s, 3H, Ar–CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 145.6, 144.2 (dm, $J_{C,F}$ = 240.1 Hz), 136.8 (dm, $J_{C,F}$ = 252.9 Hz), 136.5 (m), 136.3,

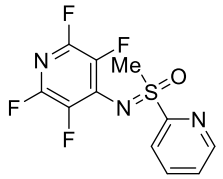
130.8, 127.5, 47.9, 21.8 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.41 (m, 2F, Py–*F*), –151.56 (m, 2F, Py-*F*) ppm; **IR (ATR)**: ν = 3028 (w), 2931 (w), 2586 (w), 2296 (w), 2181 (w), 2063 (w), 1980 (w), 1930 (w), 1737 (w), 1636 (s), 1460 (s), 1294 (m), 1213 (s), 1151 (s), 1088 (m), 1041 (w), 958 (s), 906 (m), 813 (m), 766 (m), 731 (w), 694 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 319 (15), 318 (100) [*M*]$^+$, 303 (16), 255 (55), 139 (13), 91 (10); **MS (CI, 100 eV, Methane)**: *m/z* (%): 319 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{13}H_{10}F_4N_2OS$+Na$^+$: 341.0342 [*M*+Na]$^+$, found: 341.0342.

_S_-Methyl-_S_-4-nitrophenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3m)



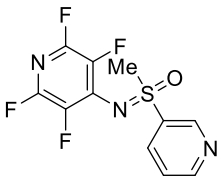
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as yellow solid (55.3 mg, 0.158 mmol, 31%). R_f = 0.66 (Et_2O), UV-active (254 nm); **m.p.**: 152.3-154.2 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 8.47 (dm, *J* = 8.7 Hz, 2H, Ar–*H*), 8.20 (dm, *J* = 8.7 Hz, 2H, Ar–*H*), 3.46 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 151.2, 145.6, 144.1 (dm, $J_{C,F}$ = 241.2 Hz), 136.5 (dm, $J_{C,F}$ = 253.8 Hz), 135.1 (m), 129.0, 125.3, 47.5 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.22 (m, 2F, Py–*F*), –151.05 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3112 (w), 3041 (w), 2934 (w), 2859 (w), 2592 (w), 2183 (w), 2073 (w), 2022 (w), 1942 (w), 1822 (w), 1638 (s), 1524 (s), 1468 (s), 1403 (m), 1344 (s), 1297 (s), 1233 (s), 1156 (s), 1109 (s), 1086 (s), 962 (s), 905 (m), 852 (s), 780 (s), 735 (s), 677 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 350 (24), 349 (100) [*M*]$^+$, 334 (13), 240 (11), 170 (11); **MS (CI, 100 eV, Methane)**: *m/z* (%): 350 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_7F_4N_3O_3S$+Na$^+$: 372.0037 [*M*+Na]$^+$, found: 372.0036.

_S_-Methyl-_S_-2-pyridyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3n)



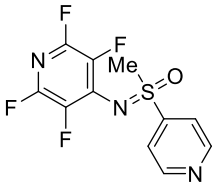
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (76.2 mg, 0.250 mmol, 64%). R_f = 0.47 (Et_2O), UV-active (254 nm); **m.p.**: 94.0-95.4 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 8.75 (d, *J* = 4.6 Hz, 1H, Py–*H*), 8.25 (d, *J* = 7.9 Hz, 1H, Py–*H*), 8.05 (td, *J* = 7.8, 1.6 Hz, 1H, Py–*H*), 7.61 (ddd, *J* = 7.7, 4.6, 0.8 Hz, 1H, Py–*H*), 3.53 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 157.6, 150.5, 144.1 (dm, $J_{C,F}$ = 240.2 Hz), 138.9, 136.6 (dm, $J_{C,F}$ = 252.8 Hz), 136.0 (m), 127.9, 122.6, 43.7 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.26 (m, 2F, Py–*F*), –151.61 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3086 (w), 3023 (w), 2935 (w), 2597 (w), 2397 (w), 2242 (w), 2203 (w), 2160 (w), 2084 (w), 2040 (w), 1942 (w), 1868 (w), 1749 (w), 1640 (s), 1578 (w), 1504 (s), 1467 (s), 1365 (w), 1308 (m), 1281 (m), 1229 (s), 1162 (s), 1121 (s), 1048 (w), 1014 (w), 962 (s), 892 (m), 787 (m), 752 (m), 705 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 307 (14), 306 (55), 305 (100) [*M*]$^+$, 242 (15), 224 (20), 211 (20), 140 (14), 78 (45), 51 (12); **MS (CI, 100 eV, Methane)**: *m/z* (%): 306 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{11}H_7F_4N_3OS$+Na$^+$: 328.0138 [*M*+Na]$^+$, found: 328.0138.

_S_-Methyl-_S_-3-pyridyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3o)



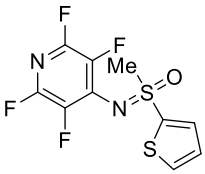
The title compound was synthesized according to GP4, but 4.02 equiv. of KOH were used instead. Purification by flash column chromatography (silica, Acetone) yield the product as a white solid (52.8 mg, 0.173 mmol, 50%). R_f = 0.80 (Acetone), UV-active (254 nm); **m.p.**: 142.6-154.1 °C; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ = 9.19 (m, 1H, Py–*H*), 8.94 (dd, *J* = 4.8, 1.6 Hz, 1H, Py–*H*), 8.29 (dt, *J* = 8.1, 2.0 Hz, 1H, Py–*H*), 7.59 (m, 1H, Py–*H*), 3.46 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)**: δ = 154.9, 148.6, 144.2 (dm, $J_{C,F}$ = 240.9 Hz),136.5 (dm, $J_{C,F}$ = 251.9 Hz), 136.5, 135.4, 135.4 (m), 124.5, 48.0 ppm; **^{19}F NMR (564 MHz, CDCl$_3$)**: δ = –92.47 (m, 2F, Py–*F*), –151.11 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3072 (w), 3016 (w), 2923 (w), 2169 (w), 2000 (w), 1863 (w), 1747 (w), 1639 (s), 1572 (m), 1488 (s), 1460 (s), 1422 (s), 1329 (m), 1299 (m), 1221 (s), 1153 (s), 1107 (s), 1033 (m), 959 (s), 906 (m), 816 (m), 773 (s), 734 (m), 699 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 307 (26), 306 (78), 305 (100) [*M*]$^+$, 290 (54), 288 (24), 286 (21), 285 (16), 270 (13), 243 (12), 242 (85), 224 (17), 223 (17), 222 (29), 196 (12), 184 (16), 179 (18), 152 (11), 141 (16), 126 (76), 124 (21), 98 (13), 94 (16), 92 (17), 79 (12), 78 (88), 66 (11), 51 (91); **MS (CI, 100 eV, Methane)**: *m/z* (%): 306 (100) [*M*+H]$^+$; **HRMS (EI)**: *m/z* calcd. for $C_{11}H_7F_4N_3OS^{\bullet+}$: 305.0241 [*M*]$^{\bullet+}$, found: 305.0250.

_S_-Methyl-_S_-4-pyridyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3p)



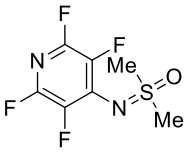
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Acetone) to yield the product as a light brown solid (137.0 mg, 0.449 mmol, 70%). R_f = 0.78 (Acetone), UV-active (254 nm); **m.p.**: 127.4-129.0 °C; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ = 8.97 (m, 2H, Py–*H*), 7.84 (m, 2H, Py–*H*), 3.42 (s, 3H, C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)**: δ = 152.0, 148.4, 144.1 (dm, $J_{C,F}$ = 240.5 Hz), 137.0 (dm, $J_{C,F}$ = 253.7 Hz), 135.2 (m), 120.5, 47.1 ppm; **^{19}F NMR (564 MHz, CDCl$_3$)**: δ = –92.35 (m, 2F, Py–*F*), –151.10 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3076 (w), 3047 (w), 3008 (w), 2924 (w), 2790 (w), 2591 (w), 2171 (w), 2038 (w), 1984 (w), 1951 (w), 1857 (w), 1747 (w), 1639 (s), 1572 (m), 1493 (s), 1465 (s), 1402 (s), 1331 (w), 1299 (m), 1236 (s), 1214 (s), 1153 (s), 1102 (s), 959 (s), 906 (m), 815 (m), 771 (s), 732 (m), 695 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 307 (35), 306 (100) [*M*+H]$^+$, 305 (62), 290 (51), 286 (12), 243 (26), 242 (39), 223 (20), 222 (17), 211 (13), 196 (14), 184 (17), 179 (15), 141 (20), 126 (27), 125 (39), 108 (13), 98 (11), 92 (12), 79 (15), 78 (82), 63 (12), 51 (85); **MS (CI, 100 eV, Methane)**: *m/z* (%): 306.0 (74) [*M*+H]$^+$, 239 (20), 230 (27), 229 (23), 207 (11), 195 (17), 192 (12), 186 (12), 184 (15), 174 (17), 168 (11), 167 (100), 166 (15), 164 (16), 163 (13), 158 (20), 156 (35), 152 (23), 150 (15), 118 (18), 116 (17), 101 (11), 85 (31), 83 (44); **HRMS (ESI)**: *m/z* calcd. for $C_{11}H_7F_4N_3OS$+Na$^+$: 328.0138 [*M*+Na]$^+$, found: 328.0146.

_S_-Methyl-_S_-2-thiopheneyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3r)



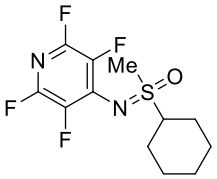
The title compound was synthesized according to GP4, but 6.06 equiv. of KOH were used instead. Purification by flash column chromatography (silica, Et_2O) to yield the product as a white solid (73.8 mg, 0.238 mmol, 54%). R_f = 0.72 (Et_2O), UV-active (254 nm); **m.p.**: 99.2-100.6 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.78 (dd, J = 5.0, 1.4 Hz, 1H, $Ar_{Het\text{-}S}$–H), 7.71 (dd, J = 3.8, 1.4 Hz, 1H, $Ar_{Het\text{-}S}$–H), 7.18 (dd, J = 5.0, 3.8 Hz, 1H, $Ar_{Het\text{-}S}$–H), 3.53 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.1 (dm, $J_{C,F}$ = 240.9 Hz), 140.0, 136.6 (dm, $J_{C,F}$ = 253.9 Hz), 135.8 (m), 135.4, 134.1, 128.7, 49.4 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.96 (m, 2F, Py–F), –150.84 (m, 2F, Py–F) ppm; **IR (ATR)**: ν = 3095 (w), 3014 (w), 2925 (w), 2259 (w), 2166 (w), 2061 (w), 1745 (w), 1638 (s), 1460 (s), 1401 (s), 1323 (w), 1295 (m), 1221 (s), 1151 (s), 1099 (s), 1020 (s), 959 (s), 905 (m), 851 (m), 769 (s), 726 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 312 (24), 311 (46), 310 (27), 310 (61) [M]$^+$, 295 (38), 249 (11), 248 (26), 247 (100), 228 (62), 203 (61), 133 (17), 131 (87), 115 (14), 103 (14), 99 (21), 71 (26), 57 (10); **MS (CI, 100 eV, Methane)**: *m/z* (%): 311 (100) [M+H]$^+$; **HRMS (EI)**: *m/z* calcd. for $C_{10}H_6F_4N_2OS_2^{\bullet+}$: 309.9852 [$M$]$^{\bullet+}$, found: 309.9852.

_S_-Methyl-_S_-methyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3s)



The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (112.8 mg, 0.466 mmol, 37%). R_f = 0.24 (Et_2O), UV-active (254 nm); **m.p.**: 105.5-107.0 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 3.35 (s, 6H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.3 (dm, $J_{C,F}$ = 239.4 Hz), 136.3 (dm, $J_{C,F}$ = 251.7 Hz), 136.2 (m), 45.4 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –92.99 (m, 2F, Py–F), –152.34 (m, 2F, Py–F) ppm; **IR (ATR)**: ν = 3023 (w), 2938 (w), 2589 (w), 2166 (w), 2075 (w), 2035 (w), 1986 (w), 1734 (w), 1642 (s), 1467 (s), 1414 (s), 1303 (m), 1220 (s), 1152 (s), 1016 (m), 962 (s), 887 (m), 767 (m), 733 (m), 687 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 243 (34), 242 (100) [M]$^+$, 227 (28), 179 (21), 78 (11), 63 (10); **MS (CI, 100 eV, Methane)**: *m/z* (%): 243 (100) [M+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_7H_6F_4N_2OS$+Na$^+$: 265.0029 [M+Na]$^+$, found: 265.0029.

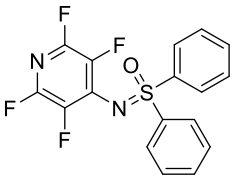
_S_-Cyclohexyl-_S_-methyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3t)



The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a yellow oil that very slowly solidifies to give a yellowish solid (41.6 mg, 0.134 mmol, 42%). R_f = 0.66 (Et_2O), UV-active (254 nm); **m.p.**: 88.3-89.4 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 3.16 (tt, J = 12.2, 3.4 Hz, 1H, Cy–H), 3.11 (s, 3H, CH_3), 2.34 (m, 2H, Cy–H), 2.01 (m, 2H, Cy–H), 1.79 (dqd, J = 13.0, 3.3, 1.6 Hz, 1H, Cy–H), 1.61 (qdd, J = 12.6, 11.0, 3.8 Hz, 2H, Cy–H), 1.38 (m, 2H, Cy–H), 1.26 (qt, J = 13.1, 3.6 Hz, 1H, Cy–H), ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 241.1 Hz), 137.0 (m), 136.5 (dm, $J_{C,F}$ = 251.4 Hz), 65.7, 39.0, 26.1, 25.6, 25.3, 25.3, 25.0 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.58 (m, 2F, Py–F), –152.33 (m, 2F, Py–F) ppm; **IR (ATR)**: ν = 2938 (m), 2862

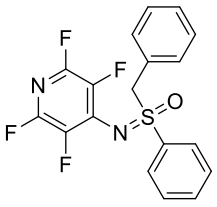
(w), 2167 (w), 1738 (w), 1636 (s), 1469 (s), 1298 (m), 1210 (s), 1151 (s), 1008 (w), 962 (s), 893 (m), 854 (w), 818 (w), 785 (w), 725 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 312 (22), 311 (51), 310 (46) $[M]^+$, 229 (48), 228 (70), 227 (12), 213 (77), 184 (17), 179 (11), 166 (41), 145 (42), 83 (68), 82 (34), 81 (17), 67 (17), 63 (11), 55 (100), 53 (14); **MS (CI, 100 eV, Methane)**: *m/z* (%): 311 (100) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{12}H_{14}F_4N_2OS^{\bullet+}$: 310.0758 $[M]^{\bullet+}$, found: 310.0754.

_S_-Phenyl-_S_-phenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3u)



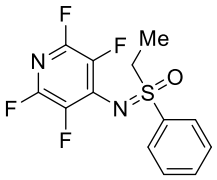
The title compound was synthesized according to general procedure GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (72.0 mg, 0.197 mmol, 84%). R_f = 0.88 (Et_2O), UV-active (254 nm); **m.p.**: 110.6-113.2 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 8.05 (m, 4H, Ar–*H*), 7.61 (m, 2H, Ar–*H*), 7.55 (m, 4H, Ar–*H*) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 240.1 Hz), 140.4, 136.9 (dm, $J_{C,F}$ = 253.6 Hz), 136.4 (m), 133.8, 129.9, 128.0 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.12 (m, 2F, Py–*F*), –150.81 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3241 (w), 3067 (w), 2926 (w), 2595 (w), 2249 (w), 2126 (w), 1987 (w), 1905 (w), 1815 (w), 1687 (w), 1638 (s), 1583 (m), 1492 (s), 1465 (s), 1364 (w), 1299 (m), 1227 (s), 1153 (s), 1128 (s), 1091 (s), 1022 (w), 998 (w), 958 (s), 906 (m), 843 (w), 725 (s), 684 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 368 (10), 367 (31), 366 (100) $[M]^+$, 241 (14), 154 (11), 125 (55), 109 (10), 97 (12), 77 (14); **MS (CI, 100 eV, Methane)**: *m/z* (%): 367 (100) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{17}H_{10}F_4N_2OS+Na^+$: 389.0342 $[M+Na]^+$, found: 389.0341.

_S_-Benzyl-_S_-phenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3v)



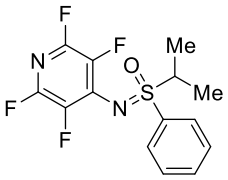
The title compound was synthesized according to GP4, but 3.61 equiv. of KOH and 1.75 equiv. of pentafluoropyridine were used instead. Purification by flash column chromatography (1st column: silica, Et_2O, 2nd column: silica, *n*-pentane:EtOAc 9:1 *v*/*v*) yield the product as a white solid (76.6 mg, 0.201 mmol, 47%). R_f = 0.89 (Et_2O), UV-active (254 nm); **m.p.**: 164.7-167.0 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.64 (m, 1H, Ar–*H*), 7.59 (m, 2H, Ar–*H*), 7.48 (m, 2H, Ar–*H*), 7.36 (m, 1H, Ar–*H*), 7.27 (m, 2H, Ar–*H*), 7.12 (m, 2H, Ar–*H*), 4.63 (m, 2H, C*H*$_2$) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 240.5 Hz), 136.7, 136.6 (m), 136.5 (dm, $J_{C,F}$ = 253.8 Hz), 134.3, 131.6, 129.6, 128.7, 128.5, 127.0, 65.8 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.48 (m, 2F, Py–*F*), –151.43 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3065 (w), 2922 (w), 2325 (w), 2245 (w), 2163 (w), 2076 (w), 1990 (w), 1816 (w), 1638 (m), 1461 (s), 1408 (m), 1300 (m), 1222 (s), 1153 (s), 1084 (s), 1009 (w), 958 (s), 905 (m), 880 (m), 827 (w), 792 (m), 754 (m), 689 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 381 (21), 380 (28) $[M]^+$, 255 (36), 125 (23), 91 (100), 65 (11); **MS (CI, 100 eV, Methane)**: *m/z* (%): 381 (100) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{18}H_{12}F_4N_2OS+Na^+$: 403.0499 $[M+Na]^+$, found: 403.0497.

_S_-Ethyl-_S_-phenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3w)



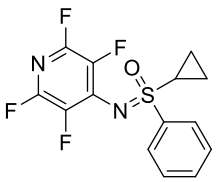
The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (118.8 mg, 0.373 mmol, 81%). R_f = 0.79 (Et_2O), UV-active (254 nm); **m.p.**: 79.1-80.7 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.89 (m, 2H, Ar–*H*), 7.70 (m, 1H, Ar–*H*), 7.61 (m, 2H, Ar–*H*), 3.51 (dq, *J* = 14.6, 7.3 Hz, 1H, (CH_3)HC–*H*), 3.43 (dq, *J* = 14.6, 7.3 Hz, 1H, (CH_3)HC–*H*), 1.38 (t, *J* = 7.4 Hz) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 240.50 Hz), 137.4, 136.6 (m), 136.4 (dm, $J_{C,F}$ = 253.1 Hz), 134.3, 130.0, 128.1, 53.9, 7.5 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.52 (m, 2F, Py–*F*), –151.60 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3073 (w), 2983 (w), 2941 (w), 2586 (w), 2396 (w), 2183 (w), 2075 (w), 1820 (w), 1637 (s), 1456 (s), 1406 (m), 1297 (m), 1207 (s), 1151 (s), 1091 (s), 1054 (s), 1001 (w), 956 (s), 905 (s), 794 (m), 770 (m), 731 (s), 683 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 320 (12), 319 (46), 318 (100) [*M*]$^+$, 289 (18), 241 (36), 126 (13), 125 (69), 78 (11), 77 (22); **MS (CI, 100 eV, Methane)**: *m/z* (%): 319 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{13}H_{10}F_4N_2OS$+Na$^+$: 341.0342 [*M*+Na]$^+$, found: 341.0342.

_S_-Isopropyl-_S_-phenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3x)



The title compound was synthesized according to general procedure GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a colorless oil (137.7 mg, 0.414 mmol, 76%). R_f = 0.76 (Et_2O), UV-active (254 nm); **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.83 (m, 2H, Ar–*H*), 7.69 (m, 1H, Ar–*H*), 7.60 (m, 2H, Ar–*H*), 3.54 (sep, *J* = 6.8 Hz, 1H, $(CH_3)_2$C*H*), 1.49 (d, *J* = 6.8 Hz, 3H, (CH_3CH)C*H*$_3$), 1.35 (d, *J* = 6.8 Hz, 3H, (CH_3CH)C*H*$_3$) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 238.6 Hz), 137.0 (m), 136.5 (dm, $J_{C,F}$ = 253.7 Hz), 135.9, 134.2, 129.9, 128.8, 59.0, 16.0, 15.6 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.80 (m, 2F, Py–*F*), –151.73 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3068 (w), 2987 (w), 2939 (w), 2593 (w), 2330 (w), 2085 (w), 1821 (w), 1636 (s), 1469 (s), 1299 (m), 1220 (s), 1151 (s), 1092 (m), 1058 (m), 1002 (w), 961 (s), 906 (m), 876 (w), 742 (m), 720 (m), 689 (m), 660 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 334 (12), 333 (61), 332 (83) [*M*]$^+$, 290 (21), 242 (20), 213 (11), 126 (19), 125 (100), 78 (14), 77 (12); **MS (CI, 100 eV, Methane)**: *m/z* (%): 333 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{14}H_{12}F_4N_2OS$+Na$^+$: 355.0499 [*M*+Na]$^+$, found: 355.0498.

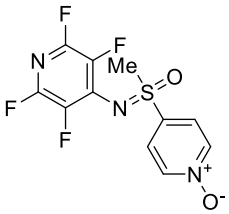
_S_-Cyclopropyl-_S_-phenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3y)



The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, Et_2O) to yield the product as a white solid (110.4 mg, 0.334 mmol, 65%). R_f = 0.85 (Et_2O), UV-active (254 nm); **m.p.**: 98.2-99.6 °C; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.89 (m, 2H, Ar–*H*), 7.68 (m, 1H, Ar–*H*), 7.59 (m, 2H, Ar–*H*), 2.74 (m, 1H, $(CH_2)_2$C*H*), 1.64 (ddt, *J* = 10.5, 7.3, 5.1 Hz, 1H, (CH_2CH)C*H*$_2$), 1.40 (ddt, *J* = 10.5, 7.3, 5.2 Hz, 1H, (CH_2CH)C*H*$_2$), 1.24 (dtd, *J* = 9.0, 7.6, 5.4 Hz, 1H, (CH_2CH)C*H*$_2$), 1.07 (dtd, *J* =

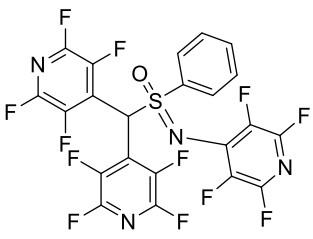
9.1, 7.6, 5.5 Hz, 1H, (CH_2CH)CH_2) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 144.2 (dm, $J_{C,F}$ = 239.8 Hz), 139.6, 136.7 (dm, $J_{C,F}$= 253.5 Hz), 136.5 (m), 134.0, 130.0, 127.6, 35.6, 7.5, 6.0 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –93.43 (m, 2F, Py–*F*), –151.41 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3056 (w), 2924 (w), 2245 (w), 2186 (w), 2075 (w), 2019 (w), 1987 (w), 1943 (w), 1901 (w), 1822 (w), 1753 (w), 1637 (s), 1463 (s), 1297 (m), 1221 (s), 1186 (m), 1150 (s), 1092 (s), 1003 (w), 957 (s), 907 (s), 882 (s), 827 (m), 765 (m), 725 (s), 680 (s) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 332 (12), 331 (40), 330 (100) [*M*]$^+$, 289 (18), 241 (29), 125 (34), 77 (20); **MS (CI, 100 eV, Methane)**: *m/z* (%): 331 (100) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{14}H_{10}F_4N_2OS$+Na$^+$: 353.0342 [*M*+Na]$^+$, found: 353.01342.

_S_-Methyl-_S_-4-pyridyl-_N_-oxide-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (3q)



N-(2,3,5,6-tetrafluoropyridyl)sulfoximine (**3p**, 101.0 mg, 0.331 mmol) was dissolved in DCM (25 mL) and oxidized using *m*CPBA (≥77%). A total of three cycles of cooling the reaction mixture in an ice bath to 0 °C, adding *m*CPBA and allowing the reaction mixture to warm up to room temperature were used. For the first cycle 1.25 equiv. of *m*CPBA (92.7 mg, 0.414 mmol) were added. The second cycle was started after 5.5 h with 1.75 equiv. of *m*CPBA (129.6 mg, 0.0.578 mmol, 1.75 equiv.). The last cycle began after 25 h and 2.00 equiv. of mCPBA (148.3 mg, 0.662 mmol) were used. After 42 h a small amount of silica was added, the solvent was removed under reduced pressure and the product was purified by running a dry loaded column chromatography (silica, EtOAc) to yield the title compound **3q** as a white solid (101.6 mg, 0.316 mmol, 96%). R_f = 0.08 (EtOAc), UV-active (254 nm); **m.p.**:182.3-183.2 °C (decomp.); **^{1}H NMR (600 MHz, $(CD_3)_2CO$)**: δ = 8.37 (m, 2H, Py–*H*), 7.99 (m, 2H, Py–*H*), 3.70 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $(CD_3)_2CO$)**: δ = 144.9 (dm, $J_{C,F}$ = 238.1 Hz), 141.1, 137.4 (dm, $J_{C,F}$ = 252.3 Hz), 134.9 (m), 126.3, 46.8 ppm; **^{19}F NMR (564 MHz, $(CD_3)_2CO$)**: δ = –95.76 (m, 2F, Py–*F*), –152.57 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3481 (w), 3113 (w), 3010 (w), 2928 (w), 2655 (w), 2543 (w), 2322 (w), 2156 (w), 2087 (w), 1998 (w), 1890 (w), 1694 (w), 1640 (m), 1594 (w), 1471 (s), 1278 (m), 1231 (s), 1154 (s), 1095 (m), 1023 (w), 967 (s), 901 (w), 842 (m), 774 (m), 743 (w), 661 (w) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 321 (34), 259 (10), 258 (100); **MS (CI, 100 eV, Methane)**: *m/z* (%): 322 (3) [*M*+H]$^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{11}H_7F_4N_3O_2S$+H$^+$: 322.0268 [*M*+H]$^+$, found: 322.0267.

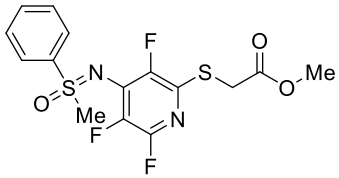
_S_-[Bis(2,3,5,6-tetrafluoropyridyl)methyl]-_S_-phenyl-_N_-(2,3,5,6-tetrafluoropyridyl)sulfoximine (4)



The title compound was obtained from collected impure mixtures of the optimization reactions with KOH in DMSO, and it was purified by flash column chromatography (silica, *n*-pentane:EtOAc 4:1 to 1:1 *v*/*v*) to yield the product as a colorless solid (155.3 mg, 0.258 mmol, 10% overall). R_f = 0.64 (*n*-pentane:EtOAc 4:1), UV-active (254 nm); **m.p.**: 176.2-182.6 °C; **^{1}H NMR (400 MHz, CD_3CN)**: δ = 7.87-7.81 (m, 3H, Ar–*H*), 7.68-7.59 (m, 2H, Ar–*H*), 6.67 (s, 1H, C*H*) ppm; **^{13}C{^{1}H, ^{19}F} NMR (101 MHz, CD_3CN)**: δ = 144.8, 144.7, 144.6, 142.0, 141.7, 137.4, 137.1, 137.0, 135.8, 131.3, 130.1, 124.1, 122.6, 61.6 ppm; **^{19}F NMR (376 MHz, CD_3CN)**:

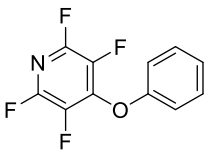
δ = –91.28 (m, 2F, Py–*F*), –92.01 (m, 2F, Py–*F*), –95.12 (m, 2F, Py–*F*), –136.07 (m, 2F, Py–*F)*, –138.67 (m, 2F, Py–*F*), –152.80 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 2931(w), 2328 (w), 2169 (w), 2067 (w), 2006 (w), 1732 (w), 1638 (m), 1470 (s), 1249 (s), 1159 (s), 1082 (w), 1050 (m), 999 (m), 958 (s), 806 (w), 743 (m), 683 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 313 (4), 290 (14), 289 (100), 241 (39), 77 (42); **MS (CI, 100 eV, Methane)**: *m/z* (%): 603 (11) $[M+H]^+$.

_S_-Methyl-_S_-phenyl-_N_-{2-[(2-methoxyl)2-ethonyl]thio-3,5,6-trifluoropyridyl}sulfoximine (5)



A reaction tube equipped with a magnetic stirring bar was charged with *N*TFP-sulfoximine **3a** (49.5 mg, 0.163 mmol, 1.00 equiv.), KF (19.1 mg, 0.329 mmol, 2.00 equiv.) and 18-crown-6 (86.9 mg, 0.329 mmol, 2.00 equiv.) in the given order. Then, MeCN (5 mL) and H_2O (0.1 mL) were added, and the reaction mixture was stirred at ambient temperature for 1 h. After that time, methyl thioglycolate [0.15 mL (ρ = 1.187 $g \cdot mL^{-1}$), 1.68 mmol, 10.31 equiv.] was added to the reaction mixture, which was heated to 50 °C for 13 days. The product was purified by column chromatography (silica, *n*-pentane:EtOAc 4:1 to 2:1 *v*/*v*) to yield the title compound as a colorless oil (34.2 mg, 0.088 mmol, 16%). R_f = 0.34 (*n*-pentane: EtOAc 2:1 *v*/*v*), UV-active (254 nm); **^{1}H NMR (600 MHz, $CDCl_3$):** δ = 7.96 (m, 2H, Ar–*H*), 7.68 (m, 1H, Ar–), 7.60 (m, 2H, Ar–*H*), 3.85 (s, 2H, CH_2), 3.72 (s, 3H, CO_2CH_3), 3.35 (s, 3H, (O)SCH_3) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 169.7, 148.1 (dm, $J_{C,F}$ = 235.2 Hz), 147.2 (dm, $J_{C,F}$ = 249.8 Hz), 139.7, 136.7 (dm, $J_{C,F}$ = 254.5 Hz), 135.3 (m), 134.2, 132.6 (m), 130.0, 127.5, 52.7, 47.7, 31.5 ppm; **^{19}F (564 MHz, $CDCl_3$)**: δ = –91.12 (t, *J* = 24.1 Hz, 1F), –131.96 (dd, *J* = 24.9, 5.2 Hz, 1F), –153.06 (dd, *J* = 23.4, 5.2 Hz, 1F) ppm; **IR (ATR)**: ν = 3475 (w), 3016 (w), 2933 (w), 2329 (w), 2173 (w), 1986 (w), 1907 (w), 1739 (s), 1604 (m), 1555 (w), 1478 (s), 1429 (s), 1298 (m), 1270 (m), 1224 (s), 1135 (s), 1091 (m), 1052 (m), 974 (m), 923 (m), 841 (m), 780 (m), 741 (s), 687 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 391 (17) $[M+H]^+$, 390 (48) $[M]^+$, 331 (100), 125 (19), 124 (14), 77 (14); **MS (CI, 100 eV, Methane)**: *m/z* (%): 391 (100) $[M+H]^+$; **HRMS (ESI)**: *m/z* calcd. for $C_{15}H_{13}F_3N_2O_4S_2+Na^+$: 413.0212 $[M+Na]^+$, found: 413.0213.

2,3,5,6-Tetrafluoro-4-phenoxypyridine (6)



The title compound was synthesized according to GP4 and was purified by flash column chromatography (silica, *n*-pentane) to yield the product as a colorless oil (74.7 mg, 0.307 mmol, 53%). R_f = 0.29 (*n*-pentane), UV-active (254 nm); **^{1}H NMR (600 MHz, $CDCl_3$)**: δ = 7.39 (m, 2H, Ar–*H*), 7.22 (m, 1H, Ar–*H*), 7.06 (d, *J* = 8.3 Hz, 2H, Ar–*H*) ppm; **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)**: δ = 156.0, 144.6 (m), 144.4 (dm, $J_{C,F}$ = 243.1 Hz), 136.4 (dm, $J_{C,F}$ = 262.3 Hz), 130.2, 125.3, 116.8 ppm; **^{19}F NMR (564 MHz, $CDCl_3$)**: δ = –88.72 (m, 2F, Py–*F*), –154.37 (m, 2F, Py–*F*) ppm; **IR (ATR)**: ν = 3066 (w), 2567 (w), 2324 (w), 2156 (w), 1847 (w), 1640 (m), 1590 (m), 1472 (s), 1418 (m), 1283 (w), 1193 (s), 1166 (m), 1069 (s), 1024 (w), 973 (s), 899 (w), 816 (w), 742 (m), 687 (m) cm^{-1}; **MS (EI, 70 eV)**: *m/z* (%): 243 (100) $[M]^+$, 77 (18), 60 (13), 49 (12); **MS (CI, 100 eV, Methane)**: *m/z* (%): 244 (100) $[M+H]^+$. There data are in accordance with the literature.[10]

Crystallographic data

All data were measured using either (a) a dual-source Rigaku SuperNova diffractometer equipped with an Atlas detector and an Oxford Cryostream cooling system using mirror-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection and reduction for the products **3c**, **3i**, **3j(120K)**, **3k, 3n**, **3o**, **3p** and **4** were performed using the program *CrysAlisPro*[11] and Gaussian face-index absorption correction method was applied;[11] or (b) a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector with graphite-monochromatized Mo-K_α (λ = 0.71073 Å) radiation. Data collection and reduction for **3a**, (*R*)-**3a**, **3b**, **3e**, **3f**, **3g**, **3h**, **3j(170K)**, **3l**, **3m**, **3q**, **3r**, **3s**, **3t**, **3u**, **3v**, **3w** and **3y** were performed using the program *COLLECT*[12] and *HKL DENZO AND SCALEPACK*,[13] respectively, and the intensities were corrected for absorption using *SADABS*.[14] All structures were solved with Direct Methods or Patterson synthesis (*SHELXS*)[6] and refined by full-matrix least squares based on F^2 using *SHELXL*-2013.[15] Non-hydrogen atoms were assigned anisotropic displacement parameters unless stated otherwise. Hydrogen atoms were placed in idealized positions and included as riding. Isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with $U_{iso}(H) = 1.2\ U_{eq}$ (parent atom). For a few reported structures, several reflections with large discrepancies between the calculated and observed structure factors have been omitted from the least-squares refinement as outliers. In addition, enhanced rigid bond restraints (RIGU)[16] with standard uncertainties of 0.001 $Å^2$ were applied for several atom pairs as well as some other constraints (EXYZ, EADP) and restraints (DFIX, FLAT) in **3j**. Positional disorders in **3j** were refined to the respective two split positions, with the sum of the site occupancies of both alternative positions constrained to unity (60.8(6)%:39.2(6)%). The X-ray single crystal data, experimental details and CCDC numbers (2027276-2027300, 2027322) are given below.

Crystal data for **3a** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027276, $C_{12}H_8F_4N_2OS$, M = 304.26 $gmol^{-1}$, colourless plate, 0.23 × 0.19 × 0.06 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 5.7581(3) Å, b = 13.2226(6) Å, c = 16.3778(8) Å, α = 90°, β = 93.070(3)°, γ = 90°, V = 1245.17(11) $Å^3$, Z = 4, D_{calc} = 1.623 gcm^{-3}, F(000) = 616, μ = 0.306 mm^{-1}, T = 170(2) K, θ_{max} = 30.508°, 9840 total reflections, 1487 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0597, 2501 data, 182 parameters, 0 restraints, GooF = 1.035, R_1 = 0.0655 and wR_2 = 0.1013 [$I_o > 2\sigma(I_o)$], R_1 = 0.1201 and wR_2 = 0.1211 (all reflections), 0.230 < dΔρ < -0.253 $eÅ^{-3}$.

Crystal data for (*R*)-**3a** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027277, $C_{12}H_8F_4N_2OS$, M = 304.26 $gmol^{-1}$, colourless plate, 0.17 × 0.15 × 0.07 mm^3, monoclinic, space group $P2_1$ (No. 4), a = 5.5411(2) Å, b = 25.4002(14) Å, c = 8.8415(5) Å, α = 90°, β = 91.752(3)°, γ = 90°, V = 1243.82(11) $Å^3$, Z = 4, D_{calc} = 1.625 gcm^{-3}, F(000) = 616, μ = 0.306 mm^{-1}, T = 170(2) K, θ_{max} = 28.283°, 6671 total reflections, 3120 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0477, 3949 data, 363 parameters, 19 restraints, GooF = 1.022, R_1 = 0.0685 and wR_2 = 0.1250 [$I_o > 2\sigma(I_o)$], R_1 = 0.0927 and wR_2 = 0.1362 (all reflections), 0.339 < dΔρ < -0.355 $eÅ^{-3}$.

Crystal data for **3b** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027278, $C_{12}H_7F_5N_2OS$, M = 322.26 $gmol^{-1}$, colourless plate, 0.32 × 0.30 × 0.11 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 5.4639(2) Å, b = 12.9237(8) Å, c = 17.7393(8) Å, α = 90°, β = 90.726(3) °, γ = 90°, V = 1252.54(11)

Å^3, Z = 4, D_{calc} = 1.709 gcm^{-3}, F(000) = 648, μ = 0.320 mm^{-1}, T = 170(2) K, θ_{max} = 28.283 °, 7441 total reflections, 1966 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0451, 2520 data, 191 parameters, 0 restraints, GooF = 1.066, R_1 = 0.0551 and wR_2 = 0.1084 [$I_o > 2\sigma(I_o)$], R_1 = 0.0753 and wR_2 = 0.1170 (all reflections), 0.322 < dΔρ < -0.356 eÅ^{-3}.

Crystal data for **3c** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027279, $C_{12}H_7ClF_4N_2OS$, M = 338.71 gmol^{-1}, colourless block, 0.173 × 0.152 × 0.105 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 16.7926(8) Å, b = 12.4383(5) Å, c = 13.0356(7) Å, α = 90°, β = 109.400(5)°, γ = 90°, V = 2568.2(2) Å^3, Z = 8, D_{calc} = 1.752 gcm^{-3}, F(000) = 1360, μ = 0.508 mm^{-1}, T = 120(2) K, θ_{max} = 28.656°, 9917 total reflections, 3925 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0296, 4623 data, 381 parameters, 0 restraints, GooF = 1.062, R_1 = 0.0447 and wR_2 = 0.0943 [$I_o > 2\sigma(I_o)$], R_1 = 0.0553 and wR_2 = 0.0999 (all reflections), 0.830 < dΔρ < -0.388 eÅ^{-3}.

Crystal data for **3e** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027280, $C_{12}H_7ClF_4N_2OS$, M = 338.71 gmol^{-1}, colourless plate, 0.34 × 0.30 × 0.16 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 5.47560(10) Å, b = 12.9051(5) Å, c = 18.9309(5) Å, α = 90°, β = 93.519(2)°, γ = 90°, V = 1335.20(7) Å^3, Z = 4, D_{calc} = 1.685 gcm^{-3}, F(000) = 680, μ = 0.488 mm^{-1}, T = 170(2) K, θ_{max} = 28.700°, 8050 total reflections, 2728 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0283, 3451 data, 191 parameters, 0 restraints, GooF = 1.074, R_1 = 0.0412 and wR_2 = 0.0948 [$I_o > 2\sigma(I_o)$], R_1 = 0.0564 and wR_2 = 0.1013 (all reflections), 0.313 < dΔρ < -0.341 e–$^{-3}$.

Crystal data for **3f** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027281,, $C_{12}H_7BrF_4N_2OS$, M = 383.17 gmol^{-1}, colourless plate, 0.38 × 0.27 × 0.18 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 16.8483(8) Å, b = 12.6532(5) Å, c = 13.1573(7) Å, α = 90°, β = 109.596(2)°, γ = 90°, V = 2642.5(2) Å^3, Z = 8, D_{calc} = 1.926 gcm^{-3}, F(000) = 1504, μ = 3.316 mm^{-1}, T = 170(2) K, θ_{max} = 28.700°, 13631 total reflections, 3779 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0572, 6790 data, 381 parameters, 0 restraints, GooF = 1.016, R_1 = 0.0600 and wR_2 = 0.1101 [$I_o > 2\sigma(I_o)$], R_1 = 0.1330 and wR_2 = 0.1315 (all reflections), 0.897 < dΔρ < -0.576 eÅ^{-3}.

Crystal data for **3g** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027282, $C_{12}H_7BrF_4N_2OS$, M = 383.17 gmol^{-1}, colourless block, 0.27 × 0.25 × 0.18 mm^3, triclinic, space group *P*-1 (No. 2), a = 7.9637(4) Å, b = 8.0951(3) Å, c = 11.7482(5) Å, α = 71.8680(10)°, β = 75.506(2)°, γ = 71.1250(10)°, V = 671.57(5) Å^3, Z = 2, D_{calc} = 1.895 gcm^{-3}, F(000) = 376, μ = 3.262 mm^{-1}, T = 170(2) K, θ_{max} = 28.700°, 6354 total reflections, 2382 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0304, 3442 data, 191 parameters, 0 restraints, GooF = 1.076, R_1 = 0.0496 and wR_2 = 0.0915 [$I_o > 2\sigma(I_o)$], R_1 = 0.0803 and wR_2 = 0.1000 (all reflections), 0.488 < dΔρ < -0.542 eÅ^{-3}.

Crystal data for **3h** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027283, $C_{12}H_7BrF_4N_2OS$, M = 383.17 gmol^{-1}, colourless plate, 0.42 × 0.20 × 0.04 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 5.4702(2) Å, b = 12.9345(8) Å, c = 19.6180(11) Å, α = 90°, β = 95.486(3)°, γ = 90°, V = 1381.70(13) Å^3, Z = 4, D_{calc} = 1.842 gcm^{-3}, F(000) = 752, μ = 3.171 mm^{-1}, T = 170(2) K, θ_{max} = 30.999°, 8941 total reflections, 2348 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0593, 4413 data, 191 parameters, 0

restraints, GooF = 1.021, R_1 = 0.0656 and wR_2 = 0.1099 [$I_o > 2\sigma(I_o)$], R_1 = 0.1488 and wR_2 = 0.1347 (all reflections), 0.640 < dΔρ < -0.451 eÅ^{-3}.

Crystal data for **3i** (obtained from recrystallization of DCM/MeOH (1:3) at –20 °C over 5 days): CCDC-2027284, $C_{12}H_7F_4IN_2OS$, M = 430.16 gmol^{-1}, colourless needle, 0.14 × 0.03 × 0.03 mm^3, triclinic, space group *P*-1 (No. 2), a = 5.2874(4) Å, b = 9.4153(8) Å, c = 14.7672(13) Å, α = 80.054(2)°, β = 85.332(3)°, γ = 79.389(2)°, V = 710.78(10) Å^3, Z = 2, D_{calc} = 2.010 gcm^{-3}, F(000) = 412, μ = 2.443 mm^{-1}, T = 120(2) K, θ_{max} = 24.9740°, 4486 total reflections, 1746 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0621, 2543 data, 191 parameters, 0 restraints, GooF = 1.037, R_1 = 0.0620 and wR_2 = 0.1155 [$I_o > 2\sigma(I_o)$], R_1 = 0.1026 and wR_2 = 0.1339 (all reflections), 1.375 < dΔρ < -0.632 eÅ^{-3}.

Crystal data for **3j(120K)** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027285, $C_{13}H_{10}F_4N_2O_2S$, M = 334.29 gmol^{-1}, colourless block, 0.252 × 0.211 × 0.072 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 12.0962(8) Å, b = 8.3321(4) Å, c = 13.6279(10) Å, α = 90°, β = 96.839(6)°, γ = 90°, V = 1363.74(15) Å^3, Z = 4, D_{calc} = 1.628 gcm^{-3}, F(000) = 680, μ = 0.293 mm^{-1}, T = 120(2) K, θ_{max} = 29.2710°, 8887 total reflections, 2208 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0336, 2749 data, 201 parameters, 0 restraints, GooF = 1.023, R_1 = 0.0357 and wR_2 = 0.0808 [$I_o > 2\sigma(I_o)$], R_1 = 0.0497 and wR_2 = 0.0887 (all reflections), 0.269 < dΔρ < -0.346 eÅ^{-3}.

Crystal data for **3j(170K)** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027286, $C_{13}H_{10}F_4N_2O_2S$, M = 334.29 gmol^{-1}, colourless block, 0.29 × 0.27 × 0.20 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 12.2106(9) Å, b = 8.3555(6) Å, c = 13.7645(8) Å, α = 90°, β = 96.208(4)°, γ = 90°, V = 1396.10(17) Å^3, Z = 4, D_{calc} = 1.590 gcm^{-3}, F(000) = 680, μ = 0.286 mm^{-1}, T = 170(2) K, θ_{max} = 28.283°, 7566 total reflections, 1385 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0722, 2794 data, 201 parameters, 0 restraints, GooF = 1.059, R_1 = 0.0726 and wR_2 = 0.1409 [$I_o > 2\sigma(I_o)$], R_1 = 0.1522 and wR_2 = 0.1689 (all reflections), 0.246 < dΔρ < -0.302 eÅ^{-3}.

Crystal data for **3k** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027287, $C_{13}H_{10}F_4N_2O_2S$, M = 334.29 gmol^{-1}, colourless plate, 0.27 × 0.20 × 0.08 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 13.3261(7) Å, b = 5.2819(2) Å, c = 19.7479(7) Å, α = 90°, β = 101.245(4)°, γ = 90°, V = 1363.31(10) Å^3, Z = 4, D_{calc} = 1.629 gcm^{-3}, F(000) = 680, μ = 0.293 mm^{-1}, T = 120(2) K, θ_{max} = 27.629°, 4062 total reflections, 2117 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0188, 2563 data, 201 parameters, 0 restraints, GooF = 1.061, R_1 = 0.0397 and wR_2 = 0.0860 [$I_o > 2\sigma(I_o)$], R_1 = 0.0519 and wR_2 = 0.0949 (all reflections), 0.267 < dΔρ < -0.364 eÅ^{-3}.

Crystal data for **3l** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027288, $C_{13}H_{10}F_4N_2OS$, M = 318.29 gmol^{-1}, colourless plate, 0.48 × 0.26 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 5.5302(2) Å, b = 13.7424(9) Å, c = 18.1828(9) Å, α = 90°, β = 91.431(3)°, γ = 90°, V = 1381.43(12) Å^3, Z = 4, D_{calc} = 1.530 gcm^{-3}, F(000) = 648, μ = 0.280 mm^{-1}, T = 170(2) K, θ_{max} = 29.131°, 7694 total reflections, 1617 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0640, 2768 data, 192 parameters, 0 restraints, GooF = 1.060, R_1 = 0.0715 and wR_2 = 0.1367 [$I_o > 2\sigma(I_o)$], R_1 = 0.1309 and wR_2 = 0.1594 (all reflections), 0.239 < dΔρ < -0.279 eÅ^{-3}.

Crystal data for **3m** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027289, $C_{12}H_7F_4N_3O_3S$, M = 349.27 gmol^{-1}, colourless plate, 0.12 × 0.12 × 0.06 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 7.8496(4) Å, b = 11.5105(5) Å, c = 14.9480(8) Å, α = 90°, β = 100.919(2)°, γ = 90°, V = 1326.14(11) Å^3, Z = 4, D_{calc} = 1.749 gcm^{-3}, F(000) = 704, μ = 0.313 mm^{-1}, T = 170(2) K, θ_{max} = 28.700°, 8081 total reflections, 1941 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0548, 3445 data, 209 parameters, 0 restraints, GooF = 1.035, R_1 = 0.0656 and wR_2 = 0.1216 [$I_o > 2\sigma(I_o)$], R_1 = 0.1339 and wR_2 = 0.1454 (all reflections), 0.469 < dΔρ < -0.360 eÅ^{-3}.

Crystal data for **3n** (obtained from slow evaporation of DCM and Acetone): CCDC-2027290, $C_{11}H_7F_4N_3OS$, M = 305.26 gmol^{-1}, colourless block, 0.425 × 0.187 × 0.117 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 10.0531(5) Å, b = 8.2642(3) Å, c = 14.0691(6) Å, α = 90°, β = 97.556(4)°, γ = 90°, V = 1158.72(9) Å^3, Z = 4, D_{calc} = 1.750 gcm^{-3}, F(000) = 616, μ = 0.331 mm^{-1}, T = 120(2) K, θ_{max} = 29.091°, 7025 total reflections, 1793 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0326, 2089 data, 182 parameters, 0 restraints, GooF = 1.042, R_1 = 0.0343 and wR_2 = 0.0825 [$I_o > 2\sigma(I_o)$], R_1 = 0.0429 and wR_2 = 0.0876 (all reflections), 0.459 < dΔρ < -0.392 eÅ^{-3}.

Crystal data for **3o** (obtained from slow evaporation of DCM and Acetone): CCDC-2027291, $C_{11}H_7F_4N_3OS$, M = 305.26 gmol^{-1}, colourless block, 0.35 × 0.32 × 0.30 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 5.7613(2) Å, b = 12.7432(3) Å, c = 15.8339(4) Å, α = 90°, β = 94.519(2)°, γ = 90°, V = 1158.87(6) Å^3, Z = 4, D_{calc} = 1.750 gcm^{-3}, F(000) = 616, μ = 0.331 mm^{-1}, T = 120(2) K, θ_{max} = 27.702°, 3644 total reflections, 1853 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0236, 2172 data, 182 parameters, 0 restraints, GooF = 1.060, R_1 = 0.0356 and wR_2 = 0.0846 [$I_o > 2\sigma(I_o)$], R_1 = 0.0429 and wR_2 = 0.0899 (all reflections), 0.492 < dΔρ < -0.323 eÅ^{-3}.

Crystal data for **3p** (obtained from slow evaporation of DCM and Acetone): CCDC-2027292, $C_{11}H_7F_4N_3OS$, M = 305.26 gmol^{-1}, yellow plate, 0.33 × 0.30 × 0.12 mm^3, orthorhombic, space group *Pbca* (No. 61), a = 8.5581(3) Å, b = 11.2534(5) Å, c = 25.1484(9) Å, α = 90°, β = 90°, γ = 90°, V = 2421.99(16) Å^3, Z = 8, D_{calc} = 1.674 gcm^{-3}, F(000) = 1232, μ = 0.317 mm^{-1}, T = 120(2) K, θ_{max} = 28.819°, 5470 total reflections, 1996 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0289, 2553 data, 182 parameters, 0 restraints, GooF = 1.058, R_1 = 0.0394 and wR_2 = 0.0864 [$I_o > 2\sigma(I_o)$], R_1 = 0.0555 and wR_2 = 0.0986 (all reflections), 0.308 < dΔρ < -0.496 eÅ^{-3}.

Crystal data for **3q** (obtained from slow evaporation of acetone): CCDC-2027300, $C_{11}H_7F_4N_3O_2S$, M = 321.26 gmol^{-1}, colourless block, 0.18 × 0.18 × 0.15 mm^3, triclinic, space group *P*-1 (No. 2), a = 7.3052(4) Å, b = 7.6862(4) Å, c = 11.7607(7) Å, α = 103.097(4)°, β = 91.929(4)°, γ = 106.247(5)°, V = 614.16(6) Å^3, Z = 2, D_{calc} = 1.737 gcm^{-3}, F(000) = 324, μ = 0.323 mm^{-1}, T = 170(2) K, θ_{max} = 28.700°, 5280 total reflections, 1748 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0420, 2477 data, 191 parameters, 0 restraints, GooF = 1.044, R_1 = 0.0585 and wR_2 = 0.1170 [$I_o > 2\sigma(I_o)$], R_1 = 0.0917 and wR_2 = 0.1320 (all reflections), 0.287 < dΔρ < -0.272 eÅ^{-3}.

Crystal data for **3r** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027293, $C_{10}H_6F_4N_2OS_2$, M = 310.29 gmol^{-1}, colourless plate, 0.31 × 0.17 × 0.06 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.1807(6) Å, b = 8.2524(5) Å, c = 13.2410(8) Å, α = 90°, β = 104.781(3)°, γ = 90°, V = 1181.29(12)

Å^3, Z = 4, D_{calc} = 1.745 gcm^{-3}, F(000) = 624, μ = 0.495 mm^{-1}, T = 170(2) K, θ_{max} = 28.283°, 8328 total reflections, 1133 with $I_o > 2\sigma(I_o)$, R_{int} = 0.1087, 2129 data, 186 parameters, 31 restraints, GooF = 1.048, R_1 = 0.0841 and wR_2 = 0.1360 [$I_o > 2\sigma(I_o)$], R_1 = 0.1614 and wR_2 = 0.1609 (all reflections), 0.370 < dΔρ < -0.348 eÅ^{-3}.

Crystal data for **3s** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027298, $C_7H_6F_4N_2OS$, M = 242.20 gmol^{-1}, colourless plate, 0.35 × 0.29 × 0.08 mm^3, monoclinic, space group *P*2$_1$/*c* (No. 14), a = 9.2463(4) Å, b = 10.7616(6) Å, c = 9.3227(4) Å, α = 90°, β = 106.151(2)°, γ = 90°, V = 891.04(7) Å^3, Z = 4, D_{calc} = 1.805 gcm^{-3}, F(000) = 488, μ = 0.401 mm^{-1}, T = 170(2) K, θ_{max} = 28.283°, 5203 total reflections, 1995 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0319, 2403 data, 138 parameters, 0 restraints, GooF = 1.029, R_1 = 0.0443 and wR_2 = 0.0968 [$I_o > 2\sigma(I_o)$], R_1 = 0.0554 and wR_2 = 0.1013 (all reflections), 0.463 < dΔρ < -0.363 eÅ^{-3}.

Crystal data for **3t** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027322, $C_{12}H_{14}F_4N_2OS$, M = 310.31 gmol^{-1}, colourless plate, 0.17 × 0.12 × 0.05 mm^3, monoclinic, space group *P*2$_1$/*c* (No. 14), a = 14.4786(9) Å, b = 20.0540(14) Å, c = 9.5173(4) Å, α = 90°, β = 107.638(3)°, γ = 90°, V = 2633.5(3) Å^3, Z = 8, D_{calc} = 1.565 gcm^{-3}, F(000) = 1280, μ = 0.291 mm^{-1}, T = 170(2) K, θ_{max} = 29.131°, 14128 total reflections, 2114 with $I_o > 2\sigma(I_o)$, R_{int} = 0.1469, 4745 data, 363 parameters, 0 restraints, GooF = 1.029, R_1 = 0.1132 and wR_2 = 0.1754 [$I_o > 2\sigma(I_o)$], R_1 = 0.2383 and wR_2 = 0.2166 (all reflections), 0.429 < dΔρ < -0.426 eÅ^{-3}.

Crystal data for **3u** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027294, $C_{17}H_{10}F_4N_2OS$, M = 366.33 gmol^{-1}, colourless rod, 0.33 × 0.11 × 0.10 mm^3, monoclinic, space group *P*2$_1$/*c* (No. 14), a = 14.0056(7) Å, b = 9.7724(6) Å, c = 11.3208(5) Å, α = 90°, β = 95.263(4)°, γ = 90°, V = 1542.93(14) Å^3, Z = 4, D_{calc} = 1.577 gcm^{-3}, F(000) = 744, μ = 0.262 mm^{-1}, T = 170(2) K, θ_{max} = 28.283°, 9996 total reflections, 1438 with $I_o > 2\sigma(I_o)$, R_{int} = 0.1191, 2348 data, 226 parameters, 0 restraints, GooF = 1.032, R_1 = 0.0794 and wR_2 = 0.1493 [$I_o > 2\sigma(I_o)$], R_1 = 0.1393 and wR_2 = 0.1736 (all reflections), 0.326 < dΔρ < -0.328 eÅ^{-3}.

Crystal data for **3v** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027295, $C_{18}H_{12}F_4N_2OS$, M = 380.36 gmol^{-1}, colourless needle, 0.31 × 0.14 × 0.13 mm^3, orthorhombic, space group *Pna*2$_1$ (No. 33), a = 17.4257(16) Å, b = 16.0239(14) Å, c = 5.7231(3) Å, α = 90°, β = 90°, γ = 90°, V = 1598.0(2) Å^3, Z = 4, D_{calc} = 1.581 gcm^{-3}, F(000) = 776, μ = 0.256 mm^{-1}, T = 170(2) K, θ_{max} = 28.700°, 9247 total reflections, 1762 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0969, 2842 data, 235 parameters, 1 restraints, GooF = 1.043, R_1 = 0.0641 and wR_2 = 0.0959 [$I_o > 2\sigma(I_o)$], R_1 = 0.1248 and wR_2 = 0.1110 (all reflections), 0.284 < dΔρ < -0.293 eÅ^{-3}.

Crystal data for **3w** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027296, $C_{13}H_{10}F_4N_2OS$, M = 318.29 gmol^{-1}, colourless plate, 0.23 × 0.22 × 0.14 mm^3, monoclinic, space group *P*2$_1$/*c* (No. 14), a = 5.5360(3) Å, b = 14.1989(11) Å, c = 17.2077(12) Å, α = 90°, β = 91.051(4)°, γ = 90°, V = 1352.39(16) Å^3, Z = 4, D_{calc} = 1.563 gcm^{-3}, F(000) = 648, μ = 0.286 mm^{-1}, T = 170(2) K, θ_{max} = 29.131°, 9865 total reflections, 1986 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0808, 3621 data, 191 parameters, 0 restraints, GooF = 1.038,

R_1 = 0.0870 and wR_2 = 0.1400 [$I_o > 2\sigma(I_o)$], R_1 = 0.1621 and wR_2 = 0.1650 (all reflections), 0.377 < dΔρ < -0.391 eÅ^{-3}.

Crystal data for **3y** (obtained from slow evaporation of DCM and Et_2O): CCDC-2027297, $C_{14}H_{10}F_4N_2OS$, M = 330.30 gmol^{-1}, colourless rod, 0.30 × 0.15 × 0.14 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 5.6040(2) Å, b = 14.6697(10) Å, c = 17.1224(11) Å, α = 90°, β = 94.862(3)°, γ = 90°, V = 1402.55(14) Å^3, Z = 4, D_{calc} = 1.564 gcm^{-3}, F(000) = 672, μ = 0.279 mm^{-1}, T = 170(2) K, θ_{max} = 29.131°, 6442 total reflections, 1437 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0800, 2525 data, 199 parameters, 0 restraints, GooF = 1.042, R_1 = 0.0833 and wR_2 = 0.1506 [$I_o > 2\sigma(I_o)$], R_1 = 0.1505 and wR_2 = 0.1786 (all reflections), 0.406 < dΔρ < -0.365 eÅ^{-3}.

Crystal data for **4** (obtained from slow evaporation of Et_2O/*n*-hexane 1:1 *v*/*v*): CCDC-2027299, $C_{22}H_6F_{12}N_4OS$, M = 602.37 gmol^{-1}, colourless block, 0.242 × 0.129 × 0.086 mm^3, orthorhombic, space group *Fdd*2 (No. 43), a = 40.6740(18) Å, b = 32.9096(15) Å, c = 6.3175(4) Å, α = 90°, β = 90°, γ = 90°, V = 8456.4(8) Å^3, Z = 16, D_{calc} = 1.893 gcm^{-3}, F(000) = 4768, μ = 0.287 mm^{-1}, T = 120(2) K, θ_{max} = 26.767°, 12983 total reflections, 3091 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0761, 3737 data, 361 parameters, 1 restraints, GooF = 1.025, R_1 = 0.0367 and wR_2 = 0.0499 [$I_o > 2\sigma(I_o)$], R_1 = 0.0521 and wR_2 = 0.0558 (all reflections), 0.206 < dΔρ < -0.257 eÅ^{-3}.

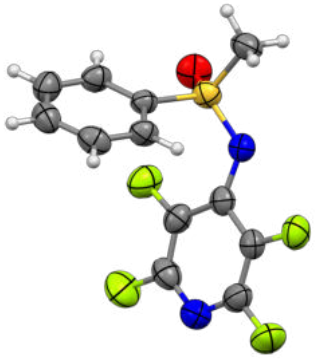


Figure S10 Displacement ellipsoid plot of **3a**. Displacement ellipsoids are drawn at the 50% probability level.

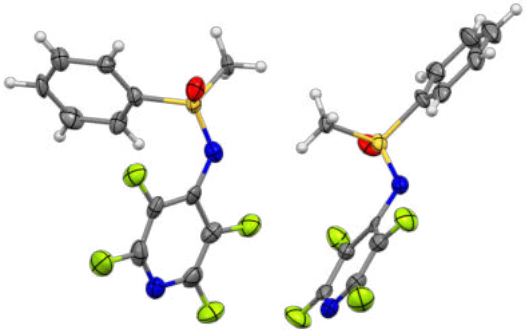


Figure S11 Displacement ellipsoid plot of (*R*)-**3a**. Displacement ellipsoids are drawn at the 50% probability level.

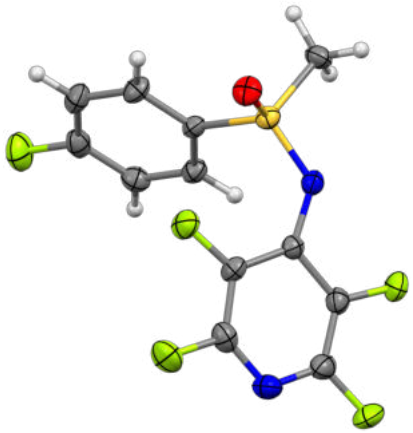


Figure S12 Displacement ellipsoid plot of **3b**. Displacement ellipsoids are drawn at the 50% probability level.

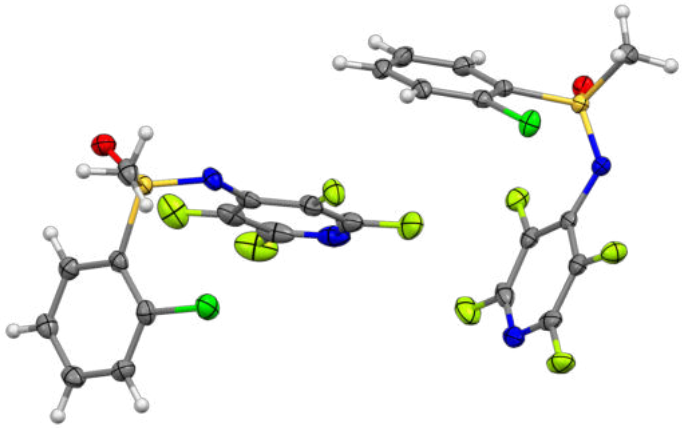


Figure S13 Displacement ellipsoid plot of **3c**. Displacement ellipsoids are drawn at the 50% probability level.

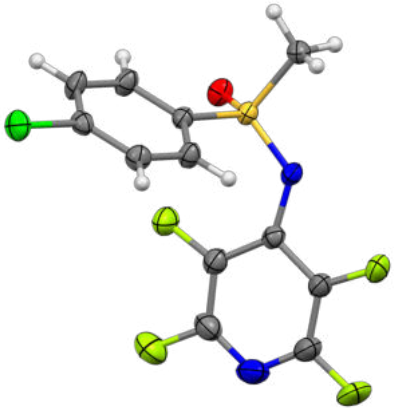


Figure S14 Displacement ellipsoid plot of **3e**. Displacement ellipsoids are drawn at the 50% probability level.

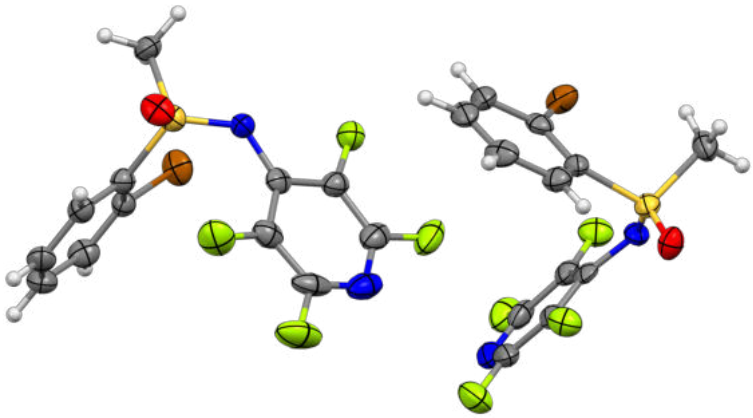


Figure S15 Displacement ellipsoid plot of **3f**. Displacement ellipsoids are drawn at the 50% probability level.

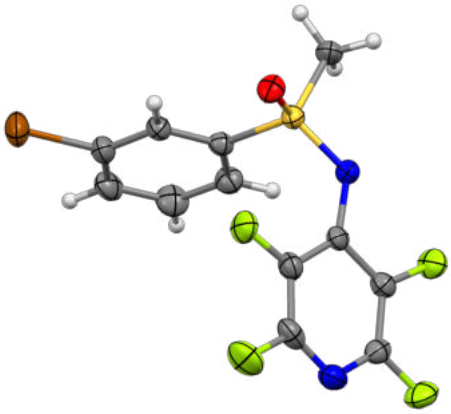


Figure S16 Displacement ellipsoid plot of **3g**. Displacement ellipsoids are drawn at the 50% probability level.

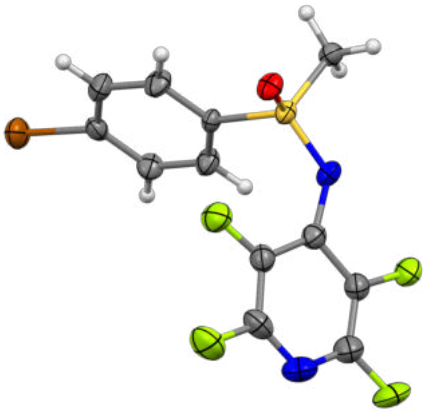


Figure S17 Displacement ellipsoid plot of **3h**. Displacement ellipsoids are drawn at the 50% probability level.

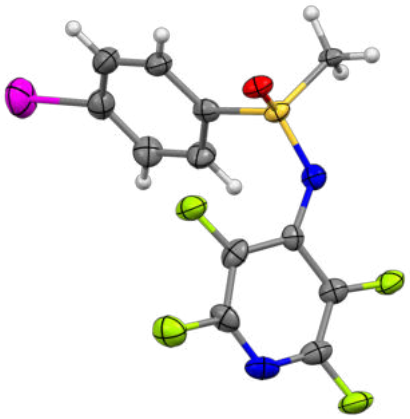


Figure S18 Displacement ellipsoid plot of **3i**. Displacement ellipsoids are drawn at the 50% probability level.

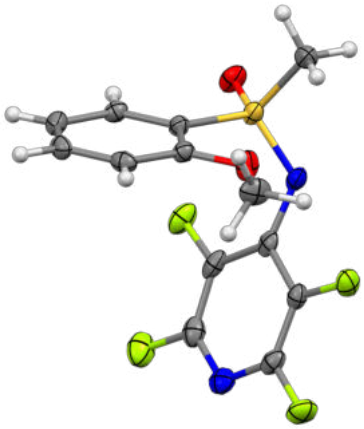


Figure S19 Displacement ellipsoid plot of **3j(120K)**. Displacement ellipsoids are drawn at the 50% probability level.

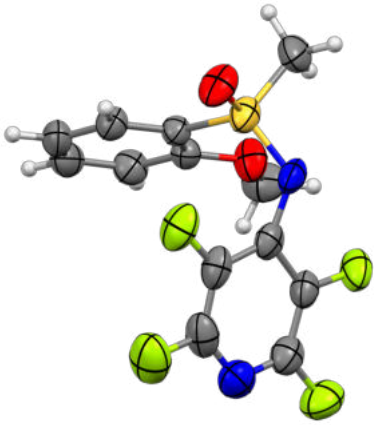


Figure S20 Displacement ellipsoid plot of **3j(170K)**. Displacement ellipsoids are drawn at the 50% probability level.

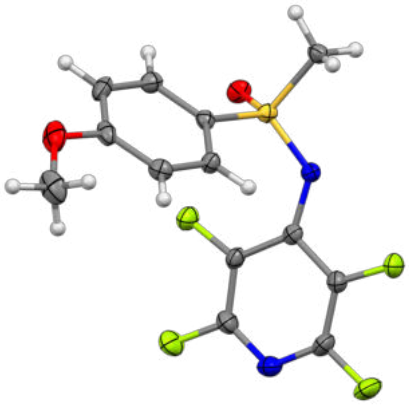


Figure S21 Displacement ellipsoid plot of **3k**. Displacement ellipsoids are drawn at the 50% probability level.

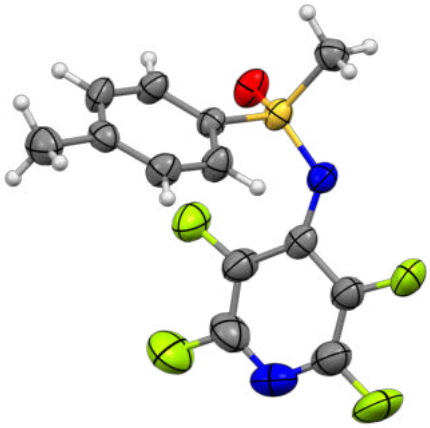


Figure S22 Displacement ellipsoid plot of **3l**. Displacement ellipsoids are drawn at the 50% probability level.

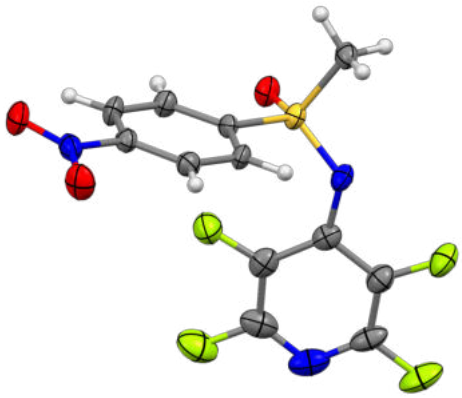


Figure S23 Displacement ellipsoid plot of **3m**. Displacement ellipsoids are drawn at the 50% probability level.

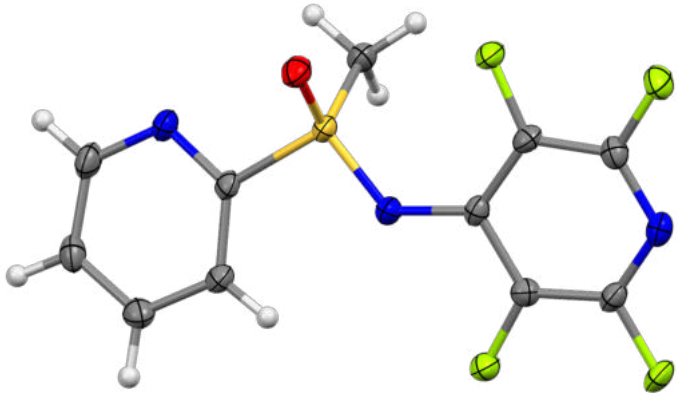


Figure S24 Displacement ellipsoid plot of **3n**. Displacement ellipsoids are drawn at the 50% probability level.

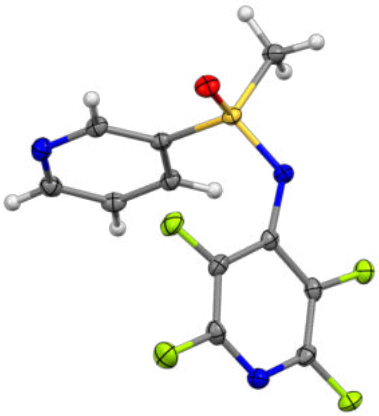


Figure S25 Displacement ellipsoid plot of **3o**. Displacement ellipsoids are drawn at the 50% probability level.

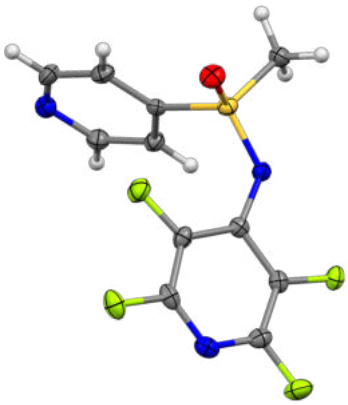


Figure S26 Displacement ellipsoid plot of **3p**. Displacement ellipsoids are drawn at the 50% probability level.

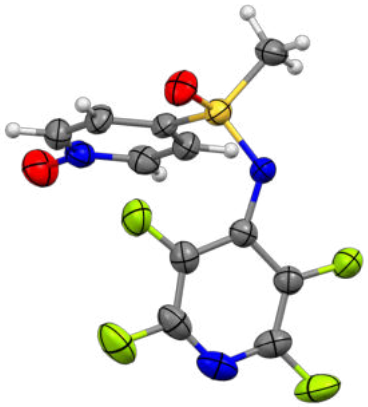


Figure S27 Displacement ellipsoid plot of **3q**. Displacement ellipsoids are drawn at the 50% probability level.

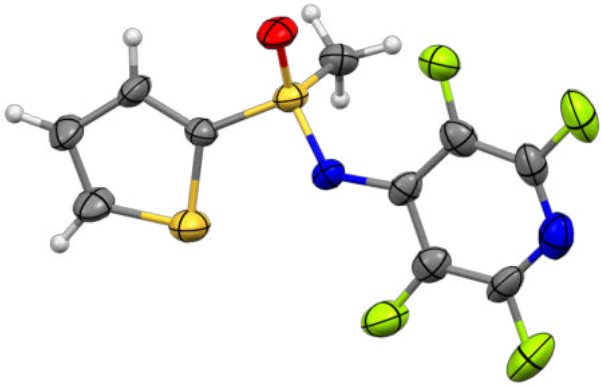


Figure S28 Displacement ellipsoid plot of **3r**. Displacement ellipsoids are drawn at the 50% probability level. The atom sites with minor occupancies (39.2(6) %) have been omitted for clarity.

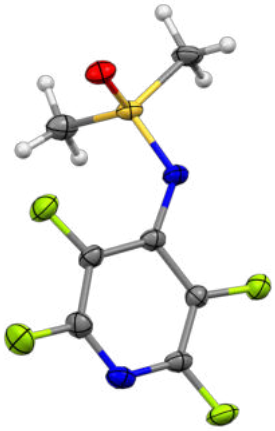


Figure S29 Displacement ellipsoid plot of **3s**. Displacement ellipsoids are drawn at the 50% probability level.

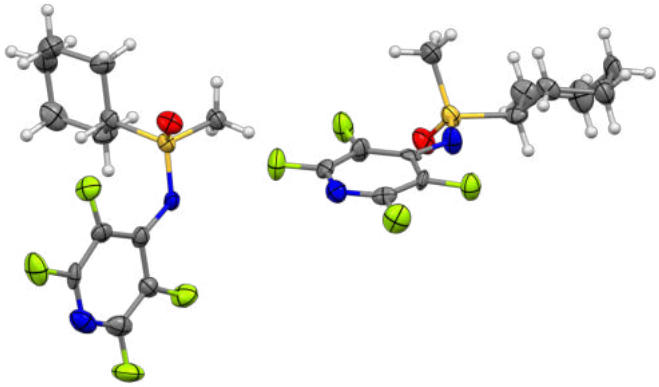


Figure S30 Displacement ellipsoid plot of **3t**. Displacement ellipsoids are drawn at the 50% probability level.

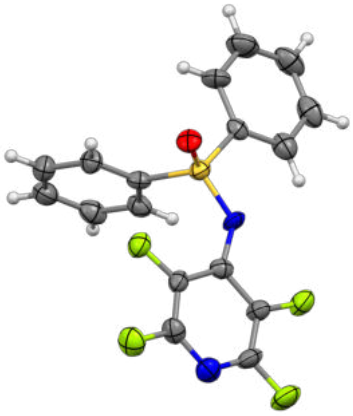


Figure S31 Displacement ellipsoid plot of **3u**. Displacement ellipsoids are drawn at the 50% probability level.

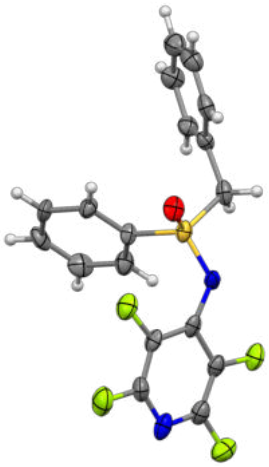


Figure S32 Displacement ellipsoid plot of **3v**. Displacement ellipsoids are drawn at the 50% probability level.

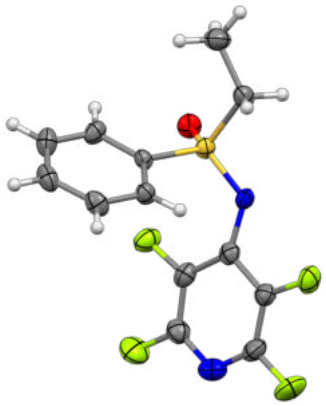


Figure S33 Displacement ellipsoid plot of **3w**. Displacement ellipsoids are drawn at the 50% probability level.

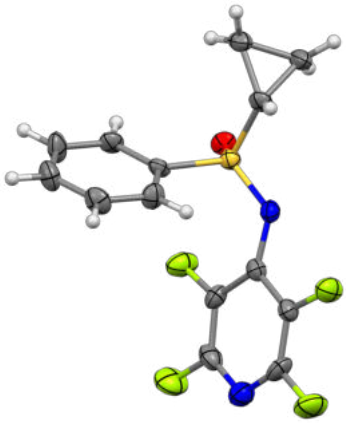


Figure S34 Displacement ellipsoid plot of **3y**. Displacement ellipsoids are drawn at the 50% probability level.

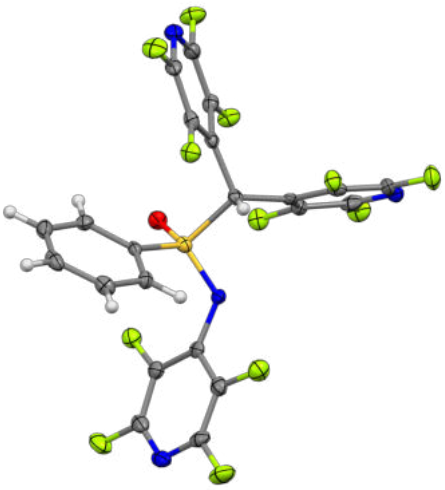


Figure S35 Displacement ellipsoid plot of **4**. Displacement ellipsoids are drawn at the 50% probability level.

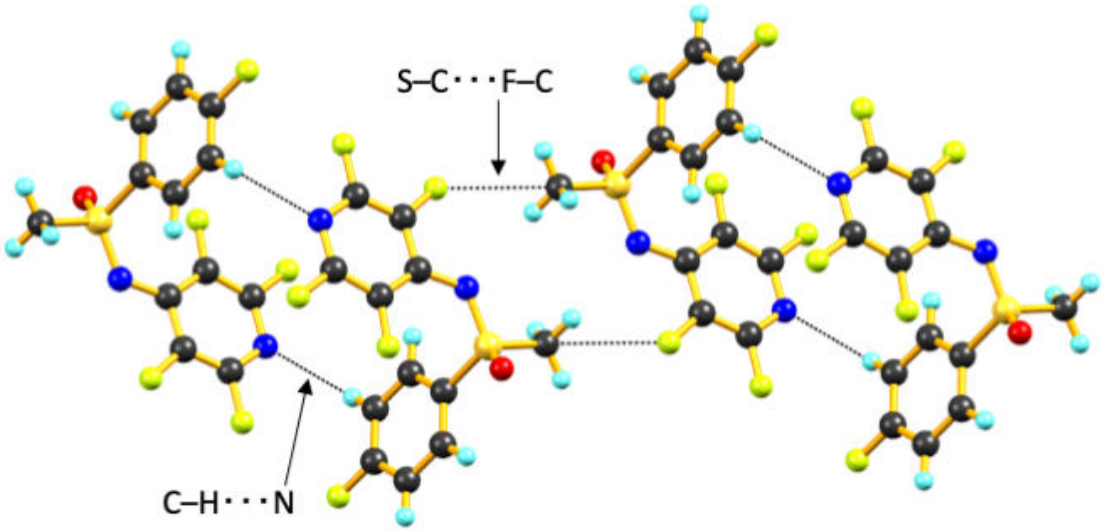


Figure S36 Partial packing view of **3b** in ball and stick model. The black dotted lines represent S–C···F–C and C–H···N interactions.

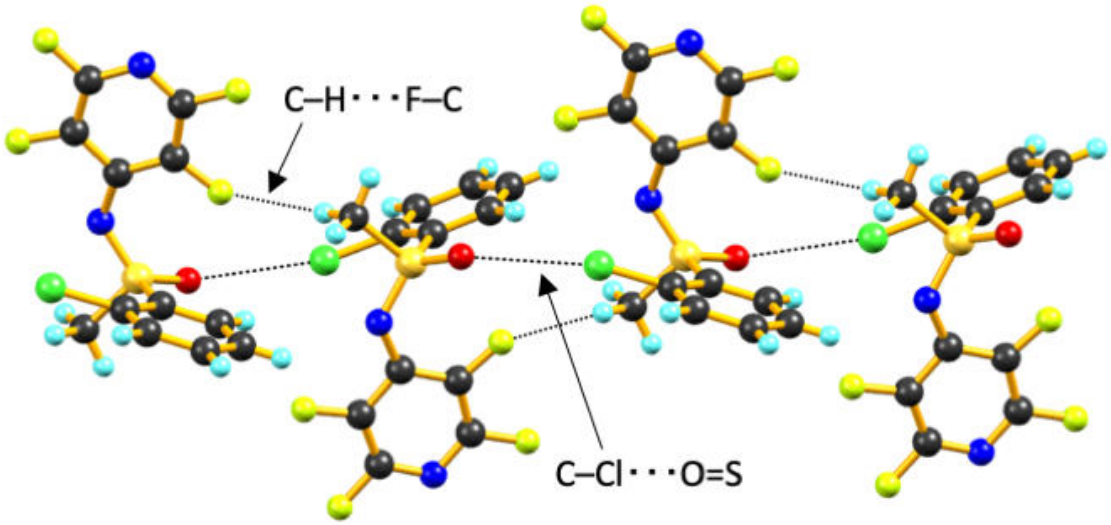


Figure S37 1D Polymeric halogen-bonded chain of **3c** in stick model. The black dotted lines represent C–Cl···O=S XB interactions.

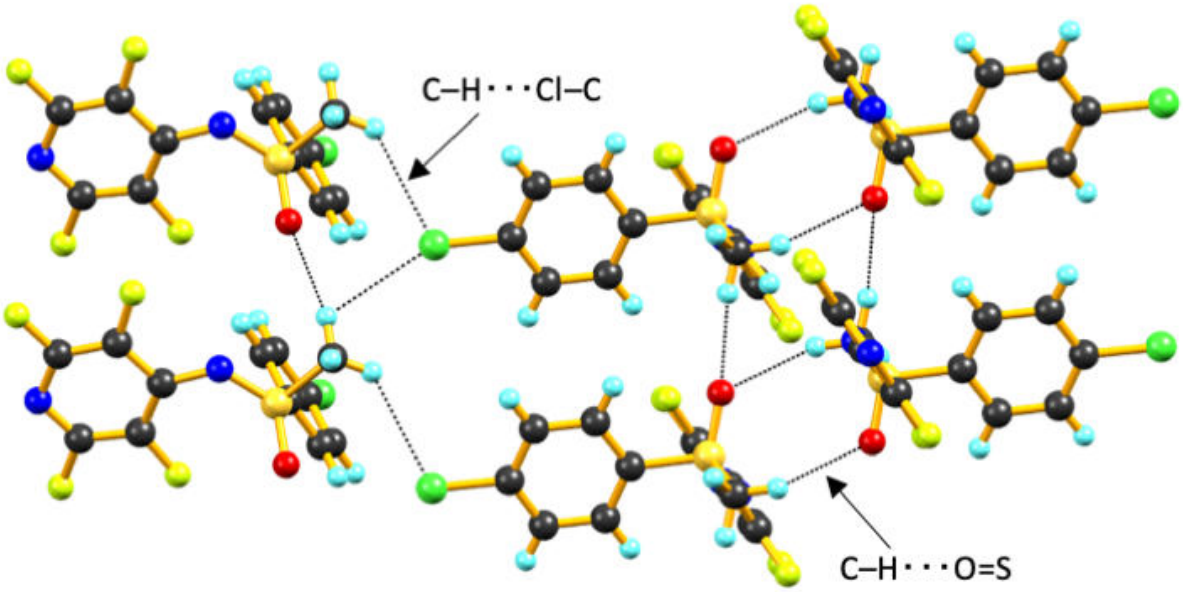


Figure S38 Partial packing view of **3e** in ball and stick model. The black dotted lines represent C–H···Cl–C and C–H···O=S interactions.

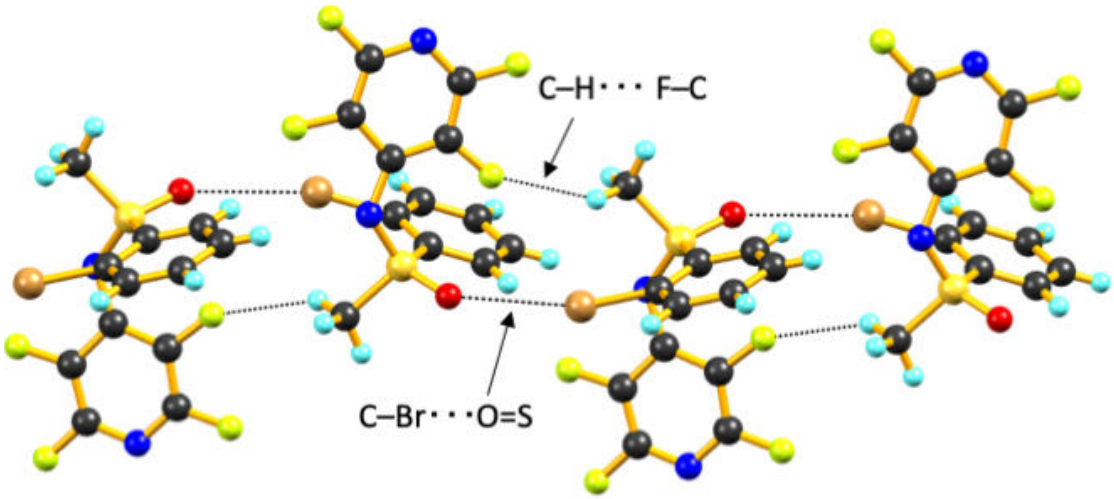


Figure S39 Partial packing view of **3f** in ball and stick model. The black dotted lines represent C–H···F–C and C–Br···O=S interactions.

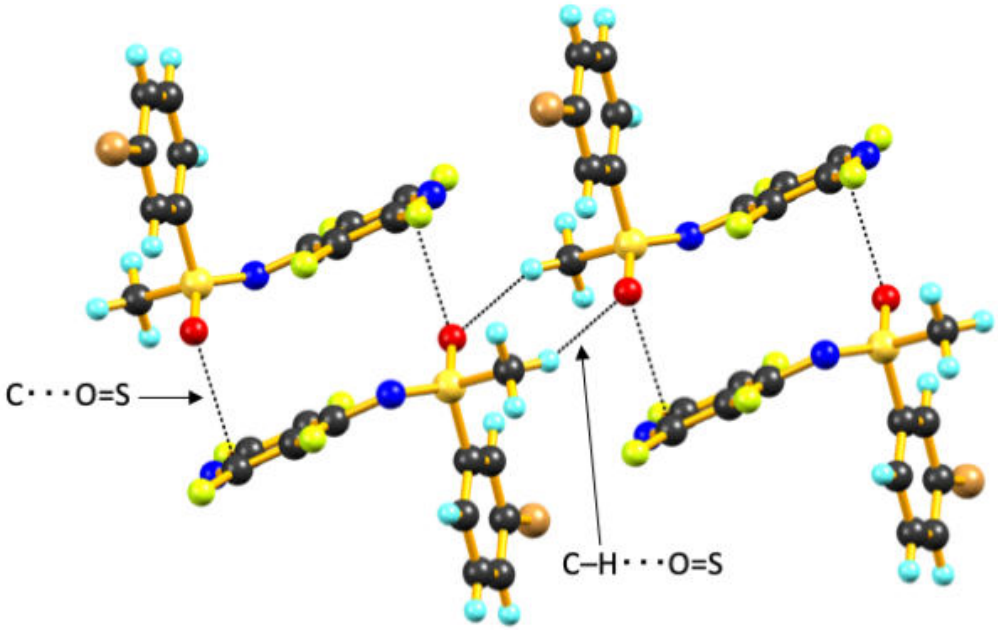


Figure S40 Partial packing view of **3g** in ball and stick model. The black dotted lines represent C···O=S and C–H···O=S interactions.

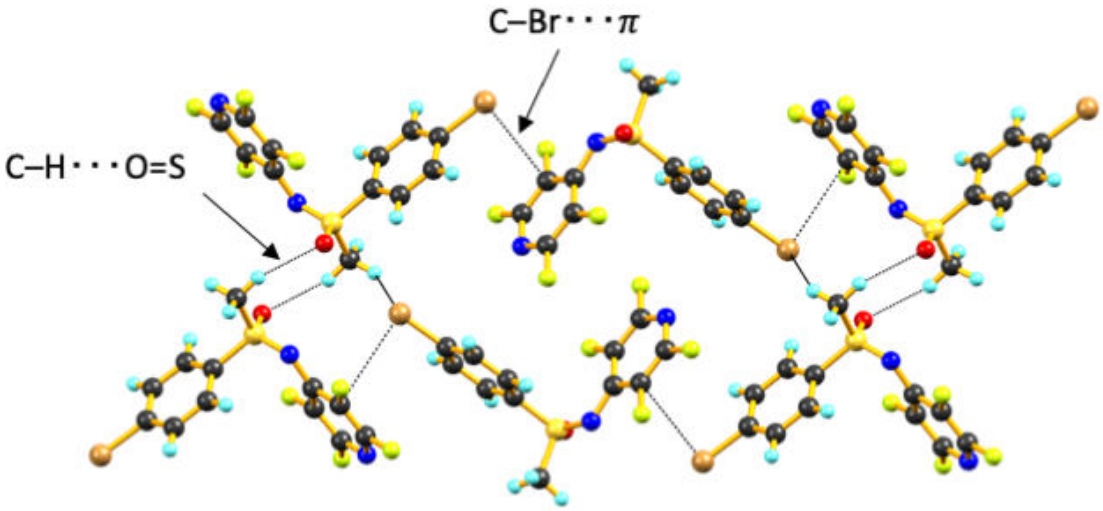


Figure S41 Partial packing view of **3h** in ball and stick model. The black dotted lines represent C–Br···π and C–H···O=S interactions.

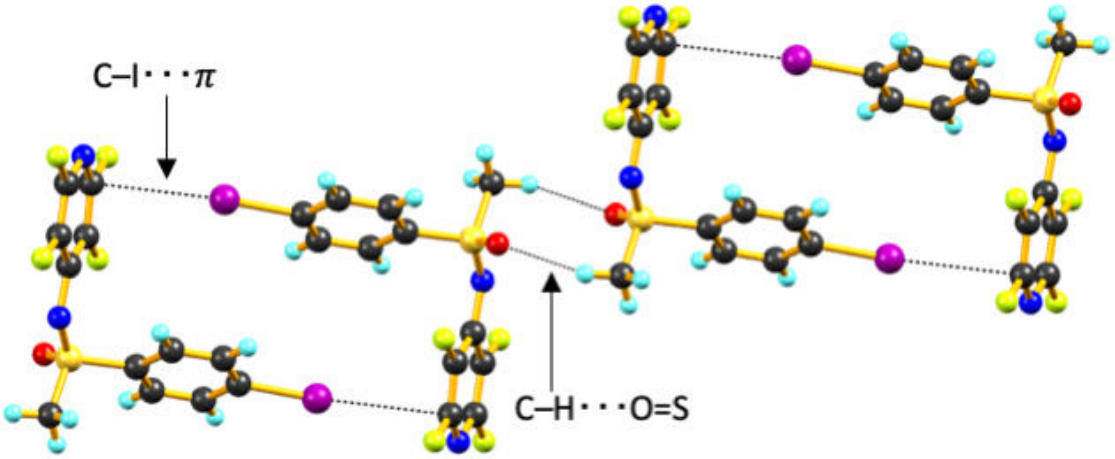
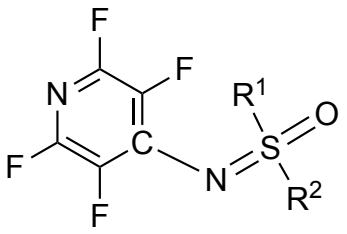


Figure S42 Partial packing view of **3i** in ball and stick model. The black dotted lines represent C–I···π and C–H···O=S interactions.

Table S19 X-Ray crystal structures bond parameters for **3a**-**y**



Substrate	S=O (Å)	S=N (Å)	N–C(TFP) (Å)
3a	1.436(3)	1.540(3)	1.385(4)
(*R*)-**3a**	1.443(6)	1.545(8)	1.371(11)
	1.444(6)	1.537(8)	1.381(11)
3b	1.446(2)	1.547(3)	1.368(4)
3c	1.448(2)	1.536(2)	1.391(4)
	1.444(2)	1.543(3)	1.379(4)
3e	1.4479(14)	1.5445(16)	1.377(2)
3f	1.445(3)	1.543(4)	1.374(6)
	1.439(3)	1.535(4)	1.389(6)
3g	1.439(2)	1.545(3)	1.385(4)
3h	1.444(3)	1.540(4)	1.378(6)
3i	1.443(5)	1.540(6)	1.379(9)
3j (120K)	1.4494(14)	1.5422(15)	1.381(3)
3j (170K)	1.443(3)	1.547(4)	1.376(6)
3k	1.4479(17)	1.5426(19)	1.374(3)
3l	1.445(3)	1.541(3)	1.368(5)
3m	1.445(2)	1.543(3)	1.386(4)
3n	1.4436(14)	1.5406(16)	1.371(2)
3o	1.4514(14)	1.5442(17)	1.380(3)
3p	1.4491(15)	1.5434(17)	1.386(3)
3q	1.444(2)	1.538(3)	1.376(4)
3r	1.446(4)	1.540(5)	1.385(7)
3s	1.4440(15)	1.5468(17)	1.381(2)
3t	1.446(6)	1.546(6)	1.388(8)
	1.442(6)	1.554(6)	1.372(8)
3u	1.450(4)	1.540(5)	1.383(7)
3v	1.451(5)	1.531(7)	1.374(10)
3w	1.446(3)	1.550(3)	1.379(5)
3y	1.446(3)	1.549(4)	1.375(7)

Hirshfeld surface analysis

General information: Hirshfeld surface plots[17] and 2D fingerprint calculations[18] were made using *CrystalExplorer17*.[19] X-Ray crystal structure files (.cif) were used for surface generation. The surfaces were generated with standard high resolution available in the *CrystalExplorer17* and mapped with the d_{norm}. The corresponding contact distances to the Hirshfeld surfaces are shown in percentage share (Table S20).

Table S20 Contribution (in %) to the Hirshfeld surface area of the various intermolecular non-covalent contacts

Code	S…S	S…F	S…N	S…O	S…C	S…H	F…F	F…O	F…N	F…C	F…H	O…O	O…N	O…C	O…H	N…N	N…C	N…H	C…C	C…H	H…H	X…X	X…F	X…O	X…N	X…C	X…H
(*R*)-**3a**	0	0	0	0	0	0	5.6	1.2	1.8	11.5	28.8	0	0.3	0	9.8	0	1	10.8	1.3	12.7	15.2						
3a	0	0	0	0	0	0	7.5	0	0.9	13.6	28.4	0	0.7	0	9.8	0	1.4	11.7	3.5	4.6	17.9						
3b	0	0	0	0	0	0	10	0.8	2.8	15.4	33.1	0.1	0.6	0	8.5	0	1.5	9	2.4	5.4	10.4						
3c	0	0	0	0	0	0	0.8	0.2	3	5.7	36.2	0	2	4.3	2	0.4	1	6.9	2.8	6	14.6	0.7	4.1	3.6	0.5	1.4	3.8
3e	0	0	0	0	0	0	6.4	0	1.4	13.8	25.5	0.1	0.4	0	8	0	1.9	8.4	1.7	5.2	9.3	0	3.3	1.1	1.5	1.5	10.5
3f	0	0	0	0	0	0	0.6	0.2	2.9	5.8	35.6	0	1.9	4.1	1.9	0.4	1	6.7	2.9	5.9	14.9	0.8	4.3	3.8	0.7	1.4	4.1
3g	0	0	0	0	0	0	4	1.4	0.9	1.6	37.7	0	0.9	3.7	3.5	0	4.2	6.6	1.6	8.1	5.2	1.4	3.2	0	1.3	6.5	8.1
3h	0	0	0	0	0	0	6.5	0	1.7	13.4	25	0	0.3	0	8	0	1.7	8.6	1.4	5.2	8.8	0	3.6	1	1.2	1.9	11.6
3i	0	0	0	0	0	0	4.4	0.4	1.1	11.5	23.5	0	0.3	0	7.9	0	0.9	8.8	0.1	8.9	9.7	0.6	8.3	0	1.2	4.6	7.9
3j(120)	0	0	0	0	0	0	2.1	0	2.6	9.6	33.7	0	0.8	0.3	9.2	0	3.4	6.7	1.6	9.3	20.6						
3j(170)	0	0	0	0	0	0	1.9	0	2.8	9.6	34.3	0	0.8	0.3	9.1	0	3.3	6.7	1.6	8.7	21						
3k	0	0	0	0	0	0	6.6	1.7	2.8	9.5	25.1	0	0.5	0	13.6	0	0	9.4	0.1	14.2	16.4						
3l	0	0	0	0	0	0	6.2	0.1	0.5	12.1	30.1	0.1	0.2	0	9	0	0.6	11.5	1.8	6.2	21.5						
3m	0	0	0	0	0	0	11.2	6.6	2.6	11.9	11.3	0.9	1.3	2.3	22.9	1.3	1.8	7.4	3.8	3.9	10.7						
3n	0	0	0	0.1	0	0	5.5	2	0.8	10	31.9	0	1.1	0.3	10.3	1	3.5	13.1	5.7	5.2	9.5						

3o	0	0	0	0	0	0	7.3	0.1	3.6	14.8	26	0	0.6	0	10.1	0.7	3.7	15.4	3	1.8	12.8							
3p	0	0	0	0	0	0	8.6	0.2	3.9	14.2	21.4	0	0.3	0.3	10	1.6	3	12.6	3.1	3.2	17.7							
3q	0	0	0	0	0	0	9.8	3.2	3.2	7	23.6	0	0	1.5	20	0.4	10.1	3.4	1.7	3.3	12.9							
3r	0	2.1	0.1	0	0.7	0.8	8.5	0.8	1.2	8.7	28.4	0	0.9	1.2	8.2	1	3.6	6.6	3.6	6.1	17.6							
3s	0	0	0	0	0	0	8.7	2.1	3.5	7.2	38.8	0	0.7	8.8	4.6	0	2	12.1	0.1	2.2	9.4							
3t	0	0	0	0	0	0	2.4	1.4	1.9	4.4	36.6	0	0.5	2.8	4.9	0.1	1	9.1	1.5	4.4	28.9							
3u	0	0	0	0	0	0	4.4	1.3	0.3	10.3	26.5	0	0	0	7.6	0	1.7	8.6	4	14.7	20.6							
3v	0	0	0	0	0	0	6.5	0.3	3	10.6	19.2	0	0	0	6.8	0	0.2	8.1	3.5	12.8	29.1							
3w	0	0	0	0	0	0	6.9	0.7	1.1	13.1	27.6	0	0.1	0	8.1	0	0.4	11.2	2.2	6.1	22.7							
3y	0	0	0	0	0	0	6.9	0	1	11.9	27.7	0	0	0	7.6	0	0.3	12.3	2.7	6.8	22.9							
4	0	0	0	0	0	0	32.4	0.8	6.8	12	21.6	0	0	0.2	3.1	0.8	9.4	3.2	2.8	3.9	3							

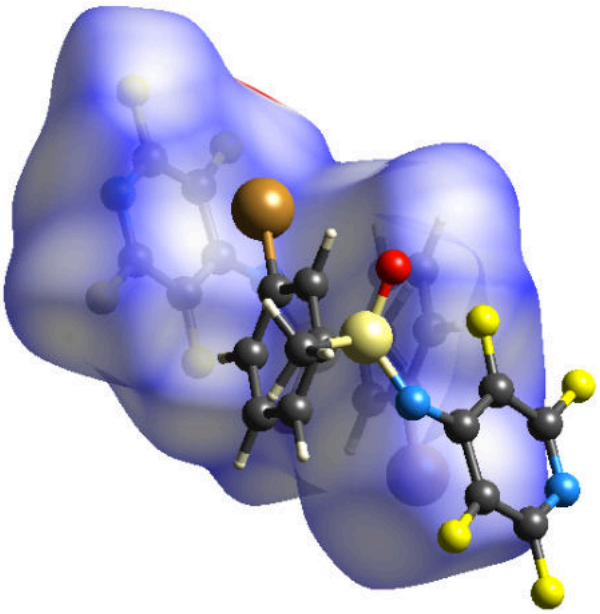


Figure S43 Hirshfeld surface for **3g** mapped with d_{norm}. Color scale is between –0.2609 (red) and 1.5434 (blue) au. The surface is generated by using the software *CrystalExplorer17.*[19]

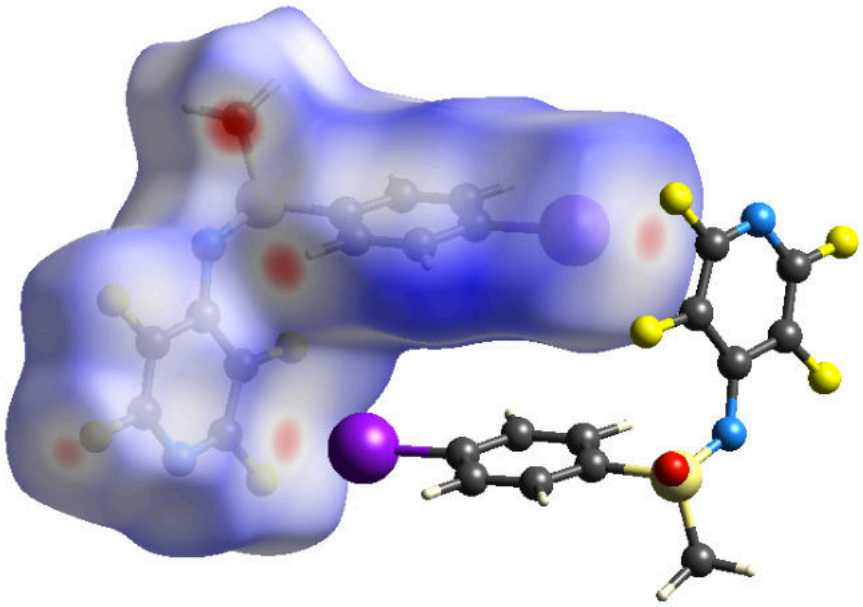


Figure S44 Hirshfeld surface for **3i** mapped with d_{norm}. Color scale is between –0.2609 (red) and 1.5434 (blue) au. The surface is generated by using the software *CrystalExplorer17.*[19]

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19 M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, CrystalExplorer17 (http://hirshfeldsurface.net), University of Western Australia, 2017.

^{1}H, ^{13}C and ^{19}F NMR spectra of synthesized compounds

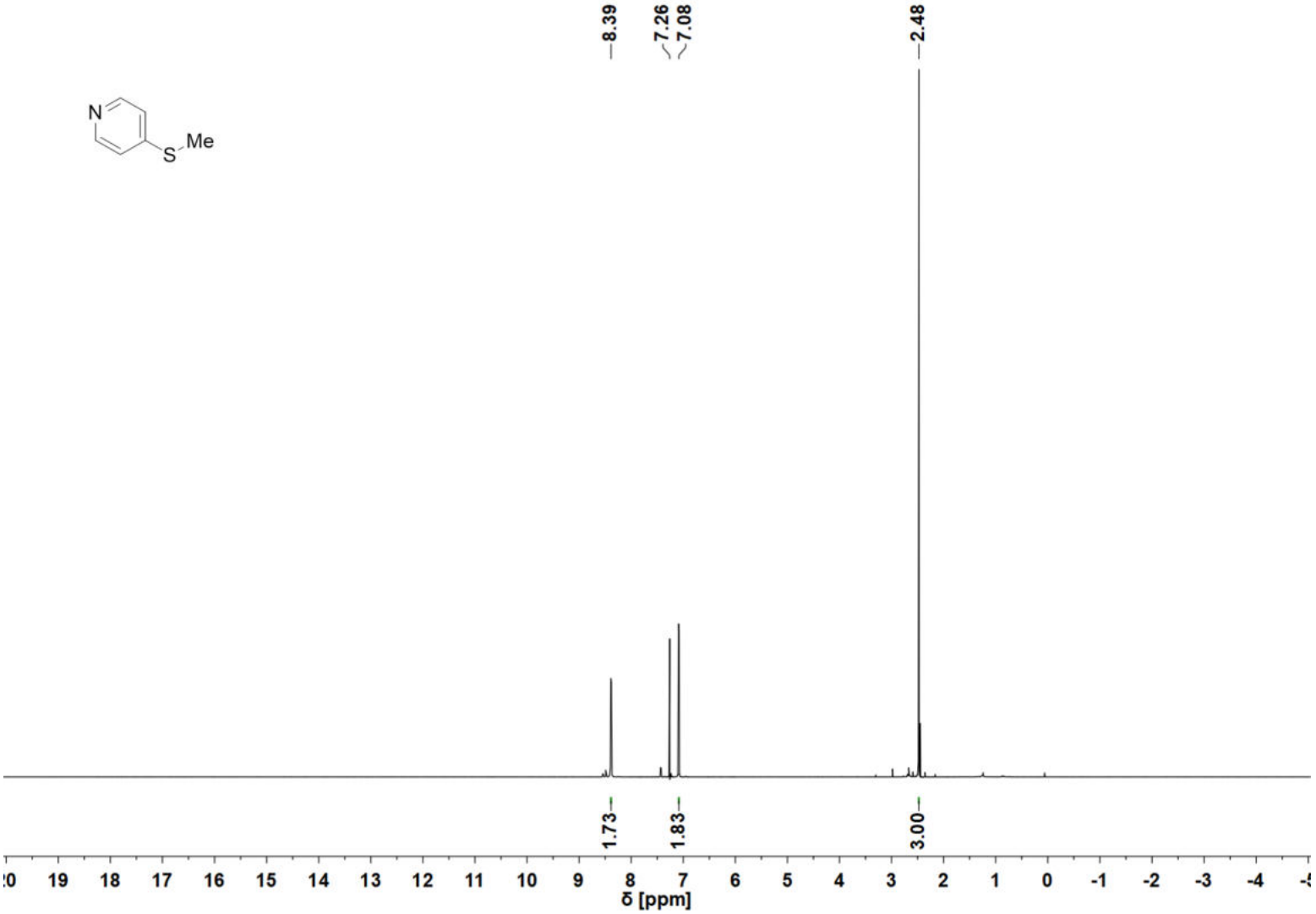

Figure S45 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of 4-(methylthio)pyridine.

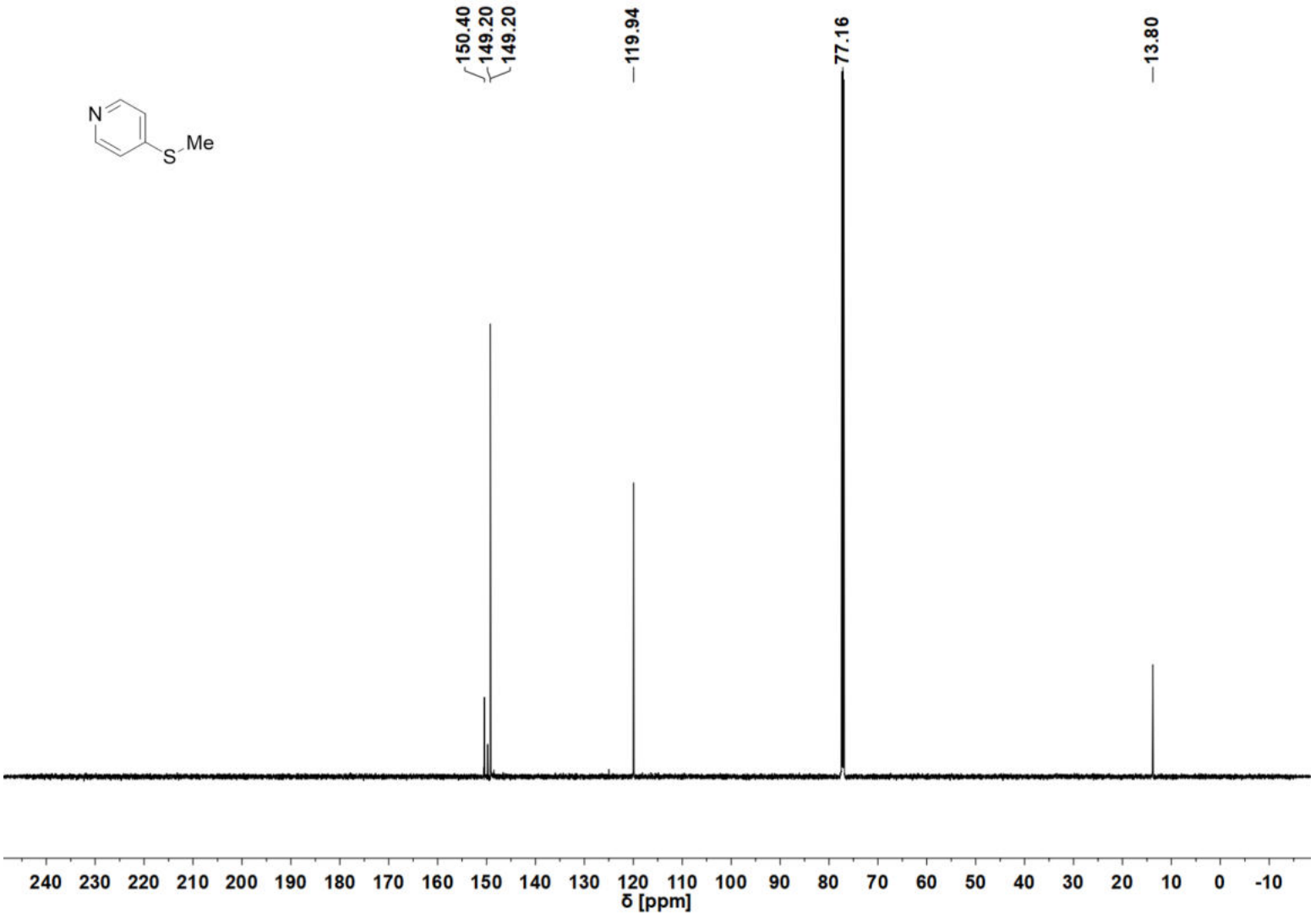

Figure S46 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of 4-(methylthio)pyridine.

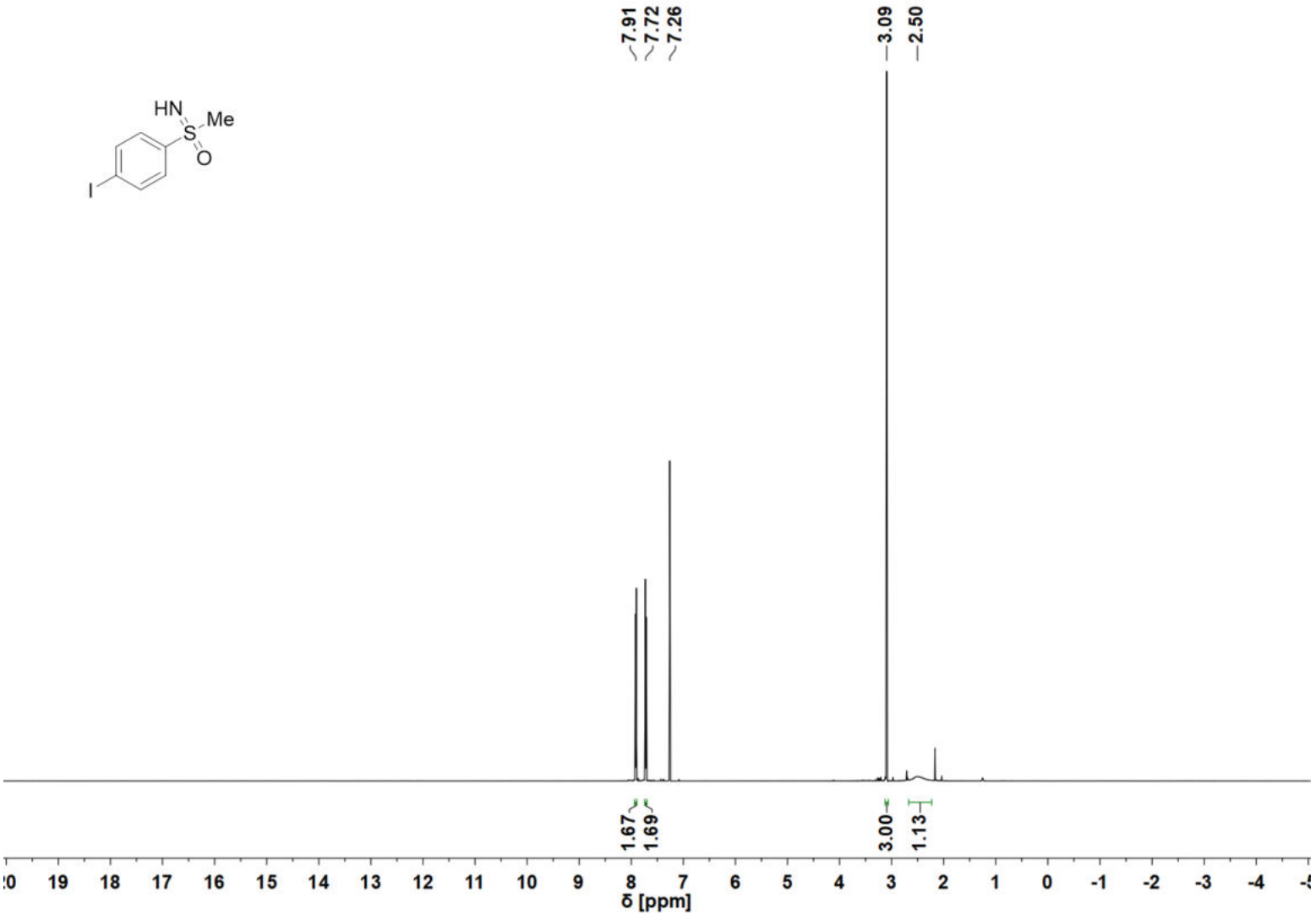

Figure S47 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1i**.

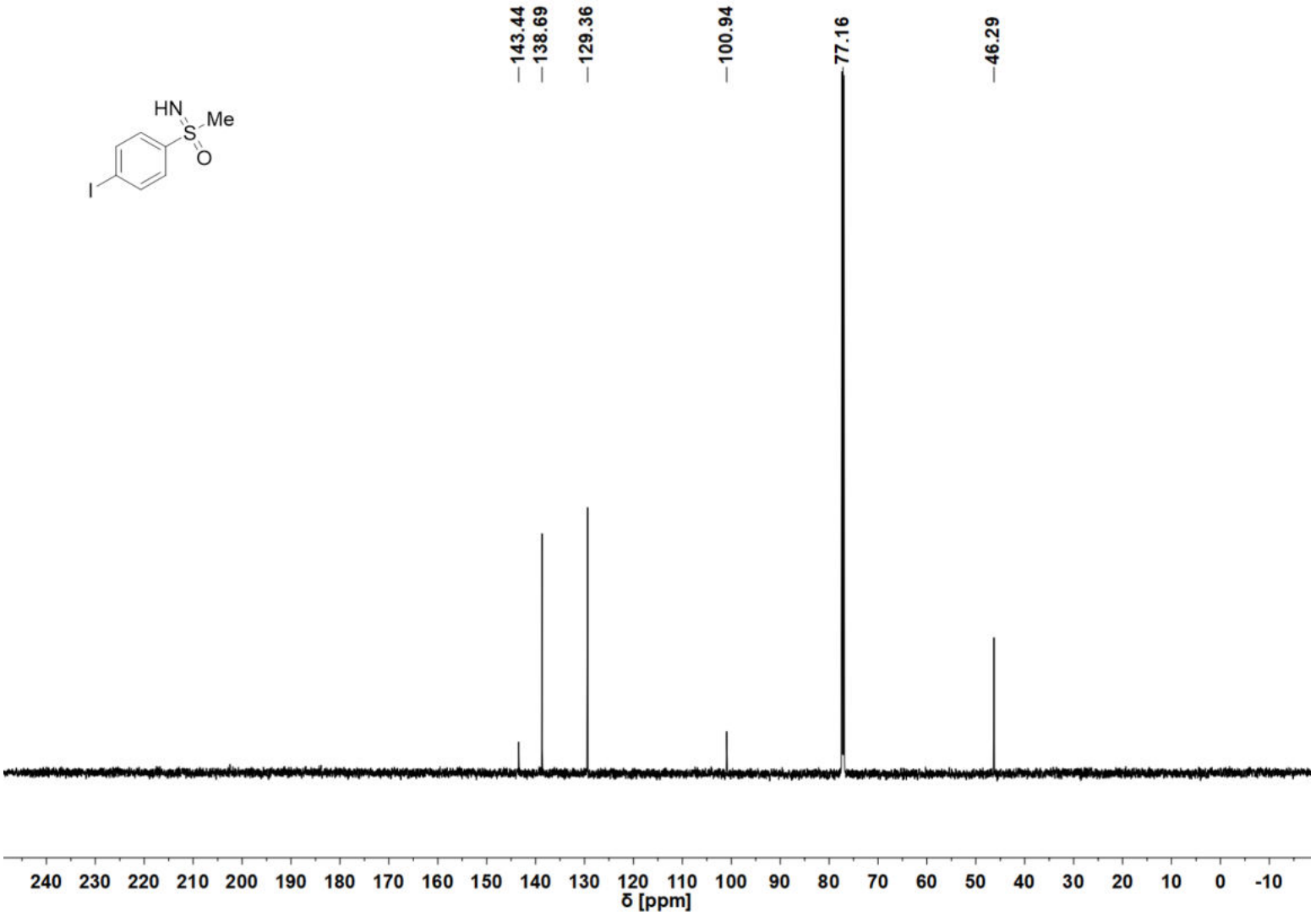

Figure S48 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **1i**.

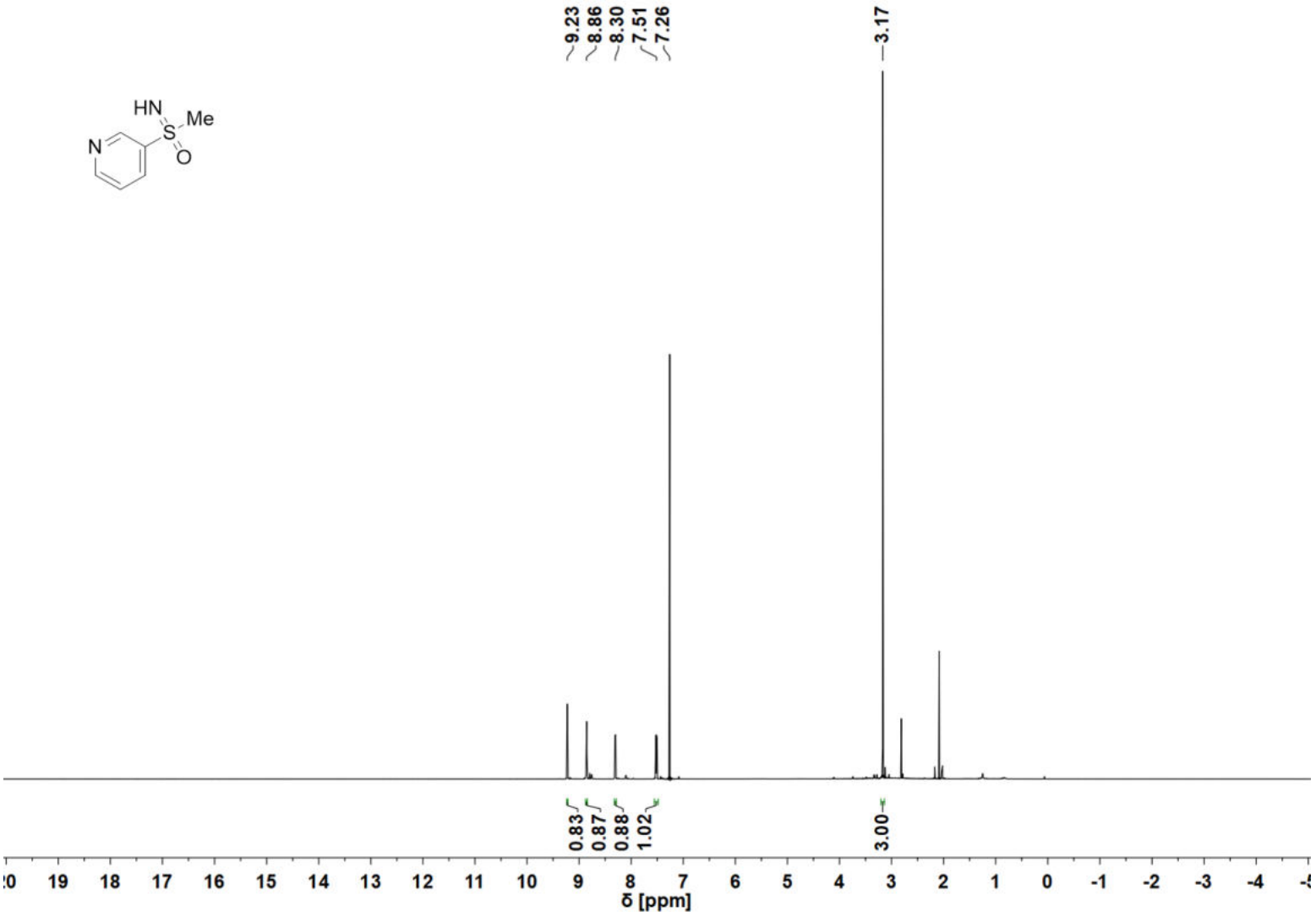

Figure S49 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1o**.

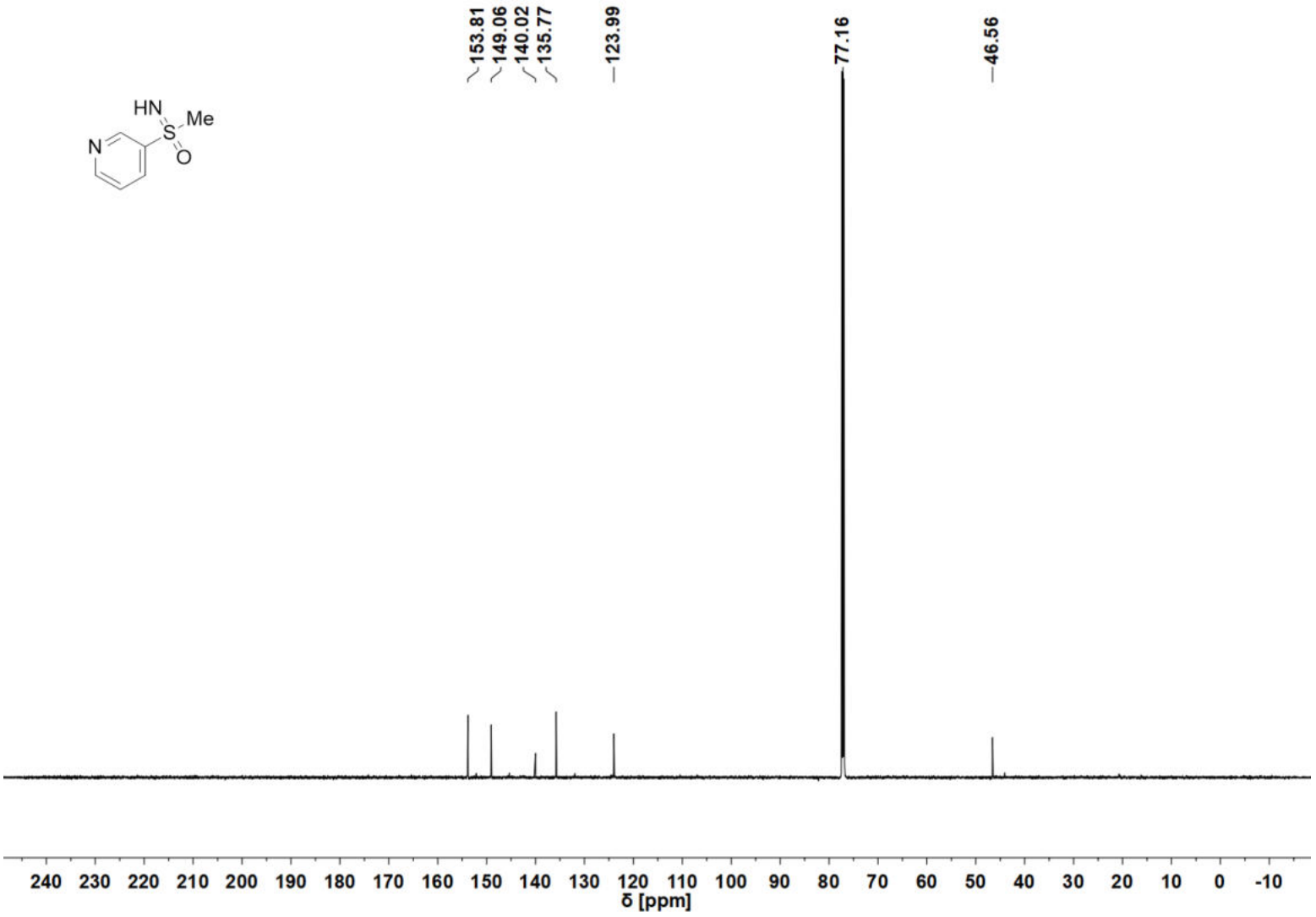

Figure S50 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **1o**.

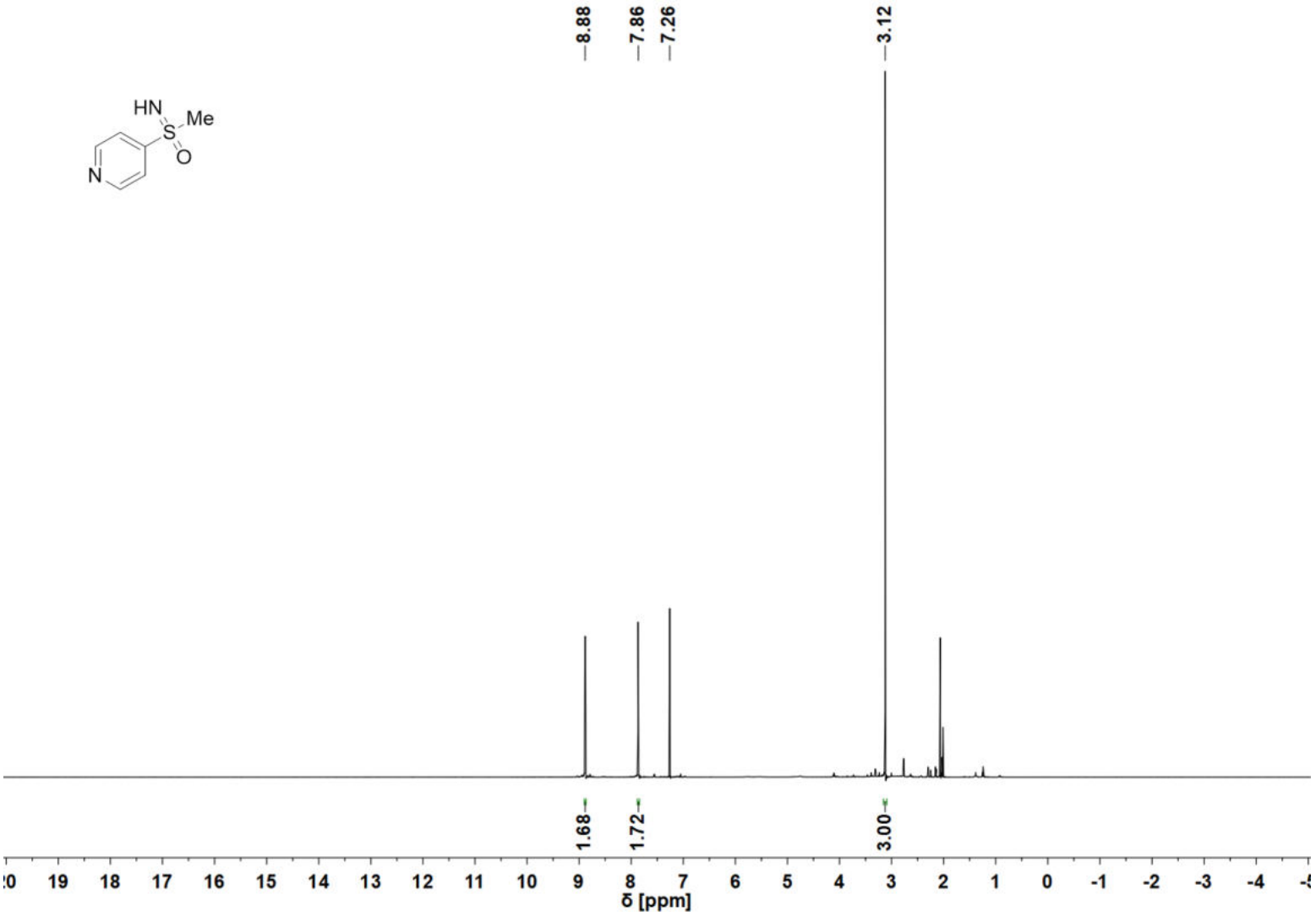

Figure S51 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1p**.

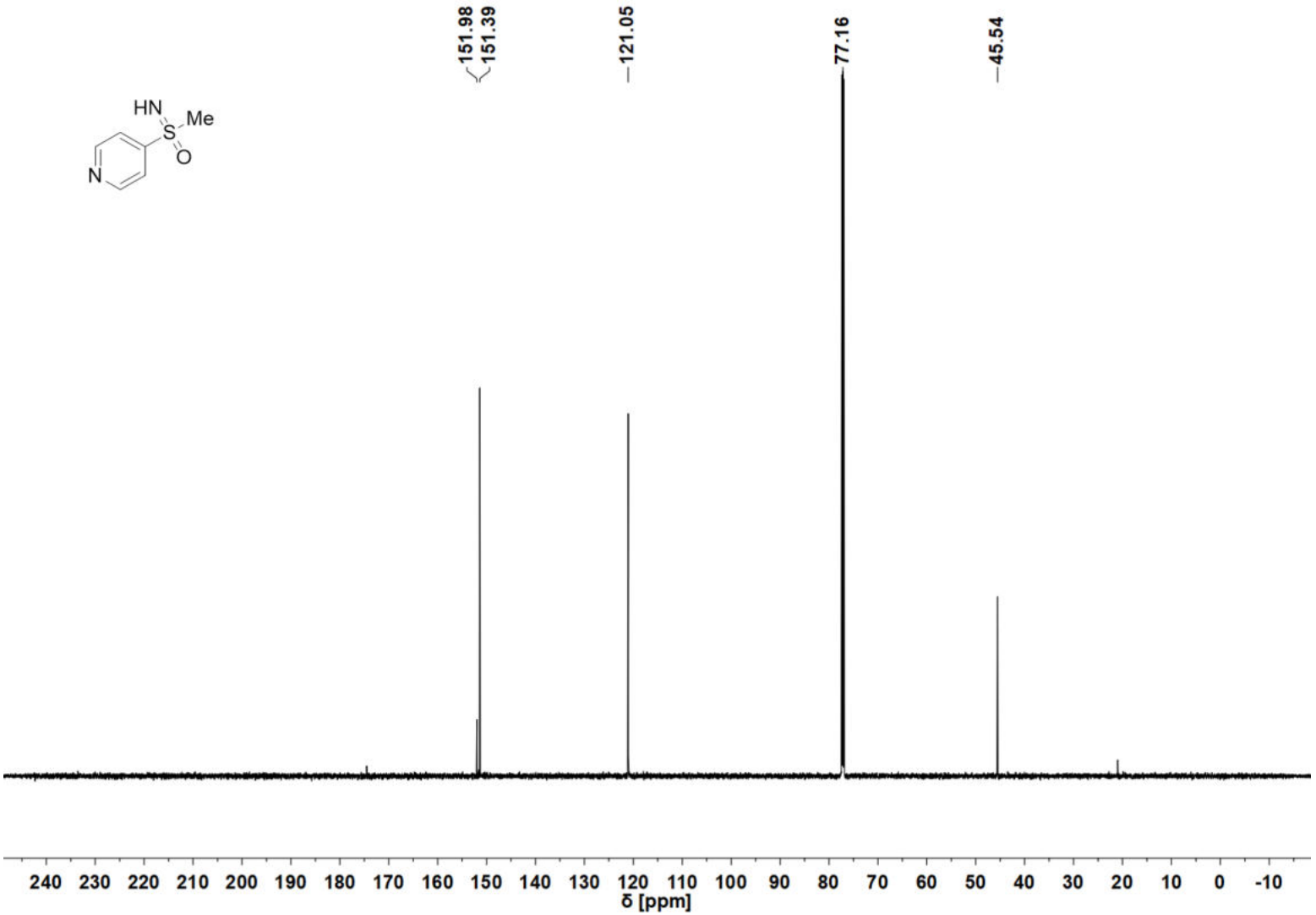

Figure S52 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **1p**.

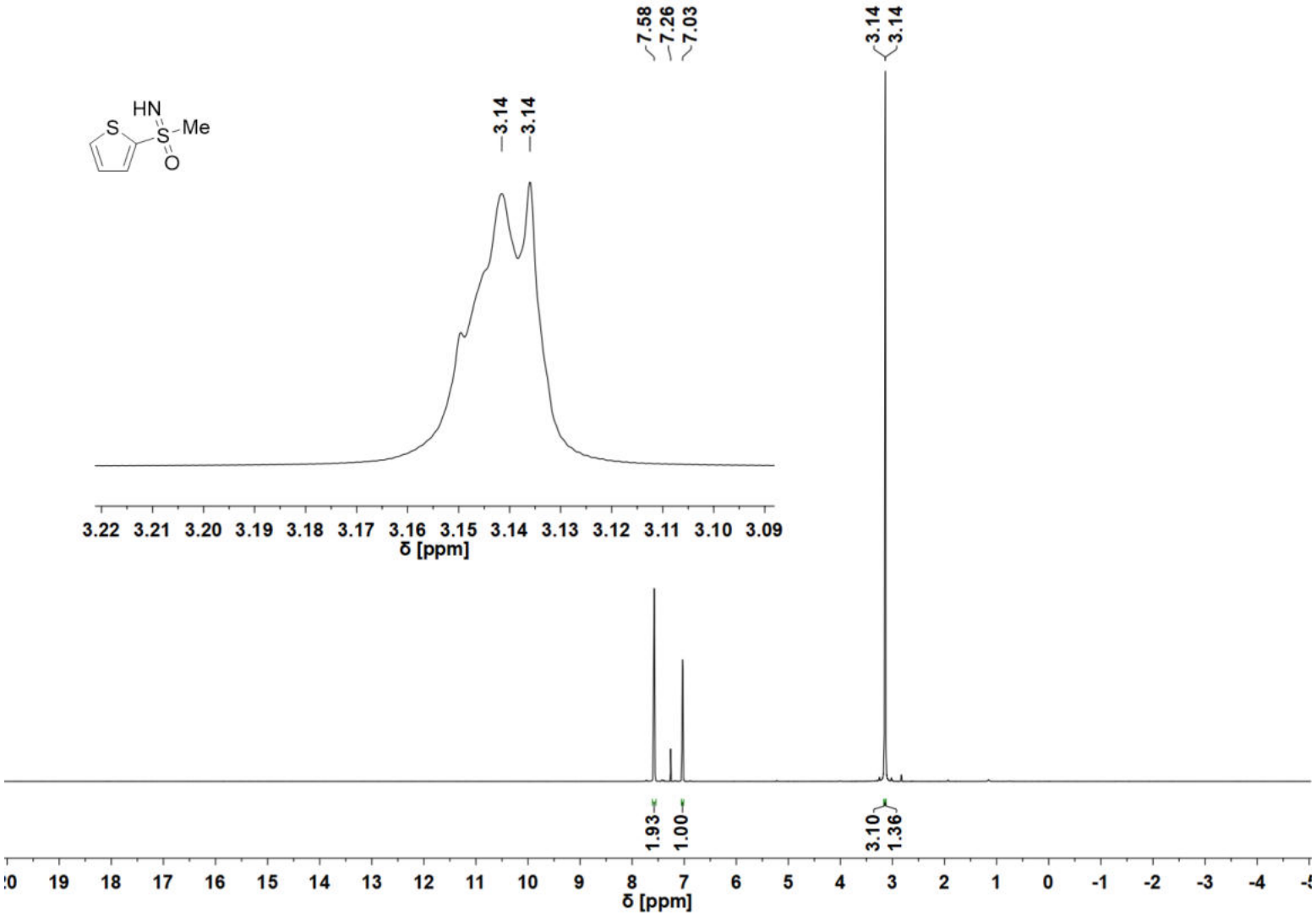

Figure S53 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1r**.

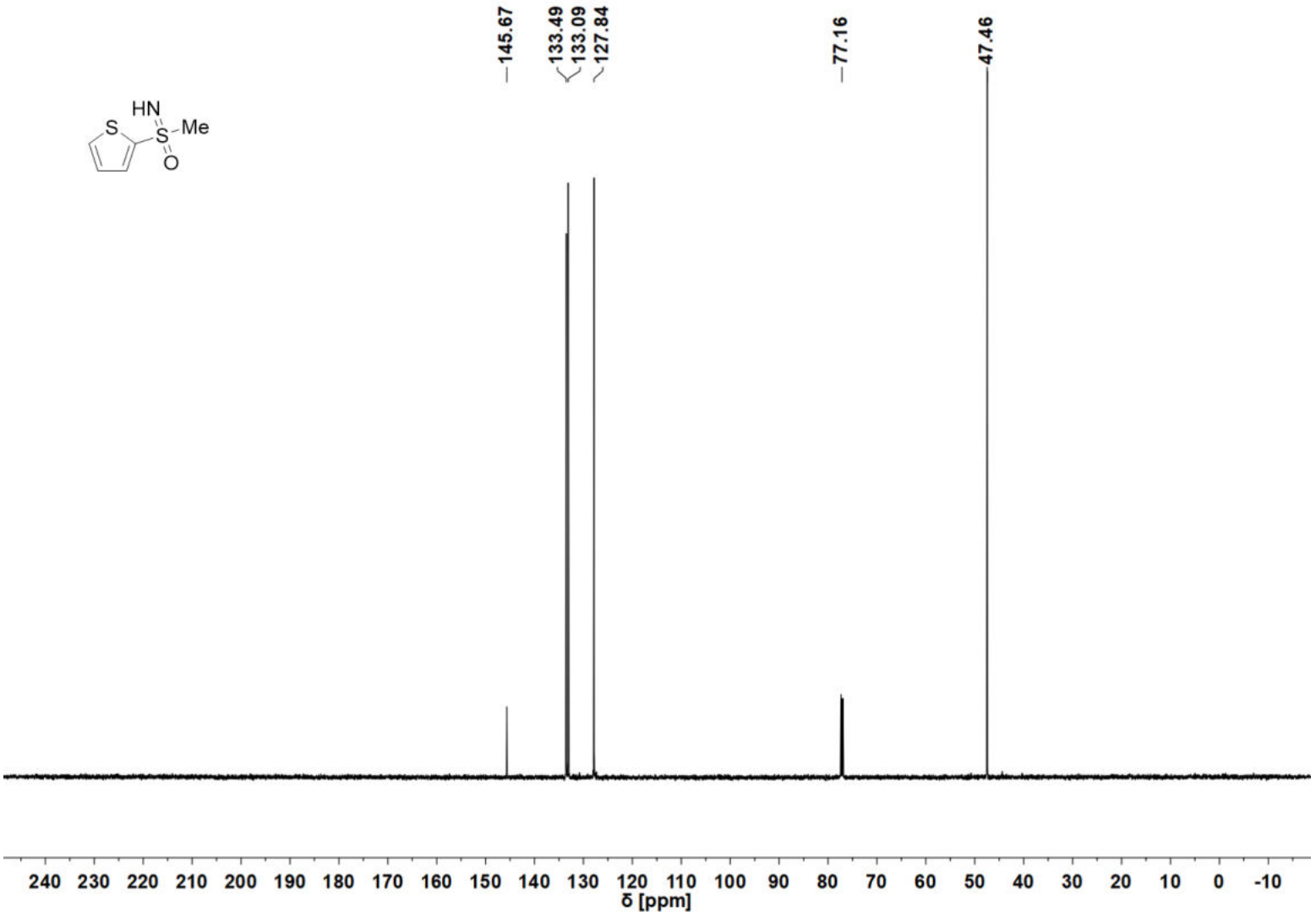

Figure S54 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **1r**.

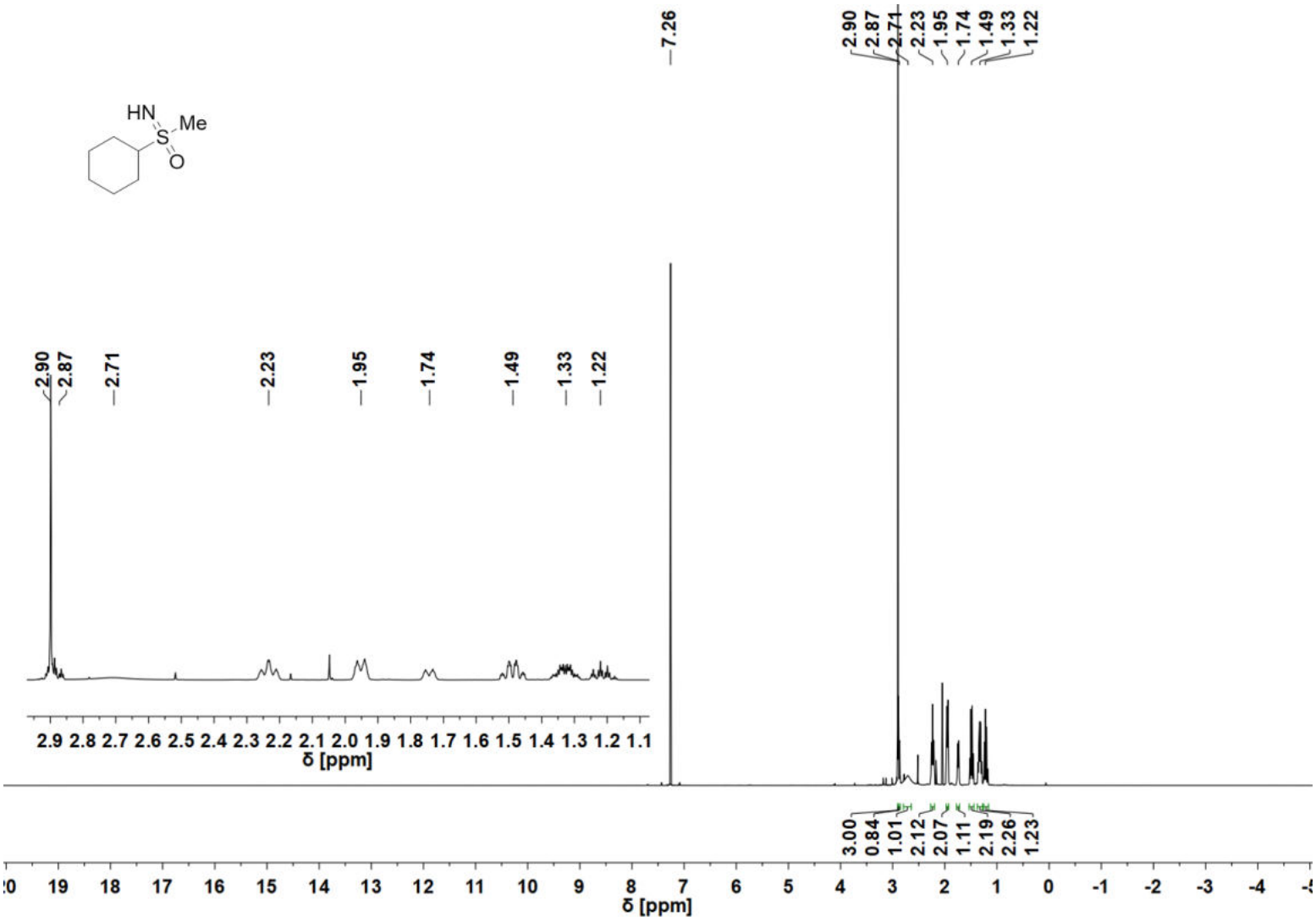

Figure S55 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1t**.

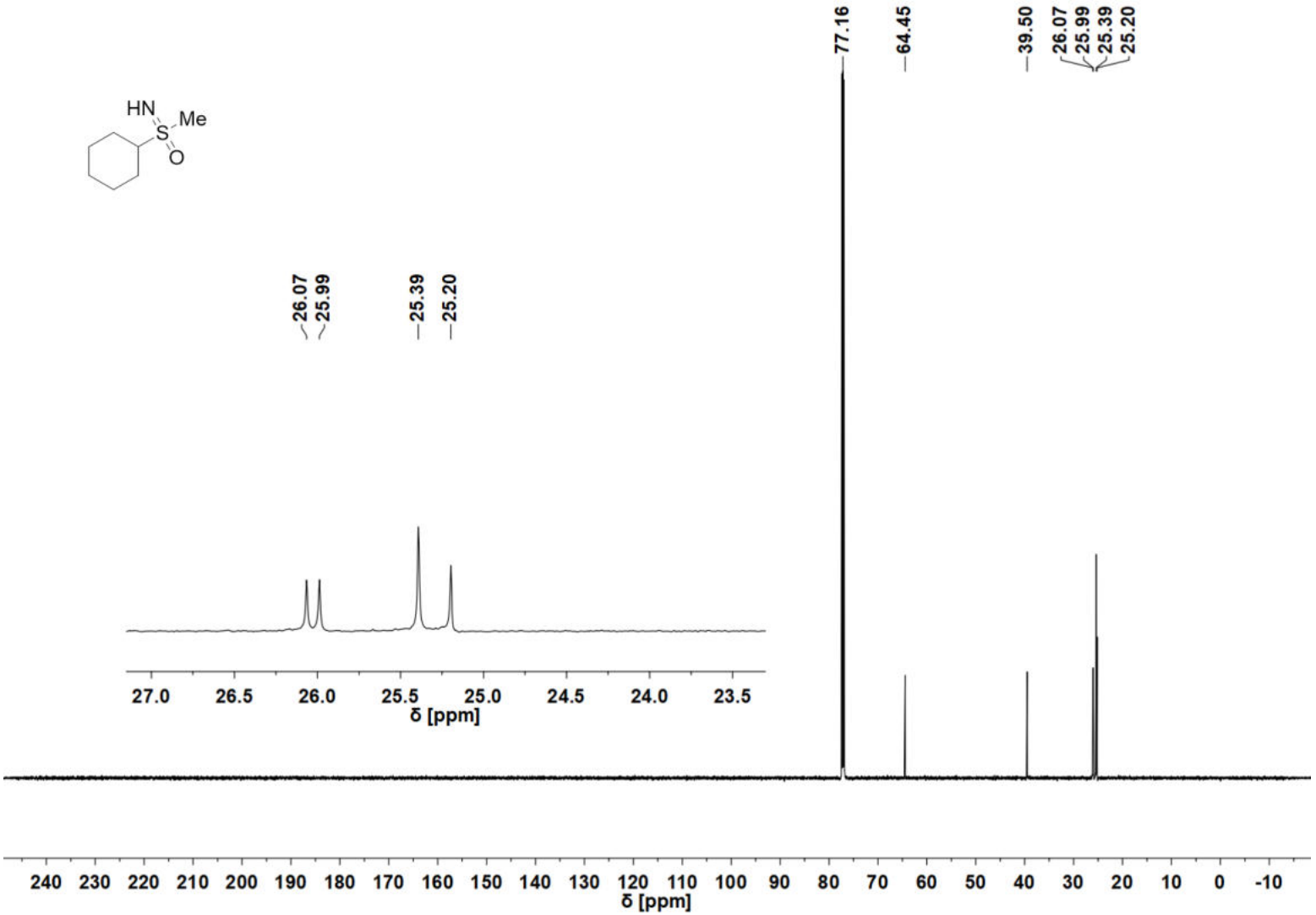

Figure S56 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **1t**.

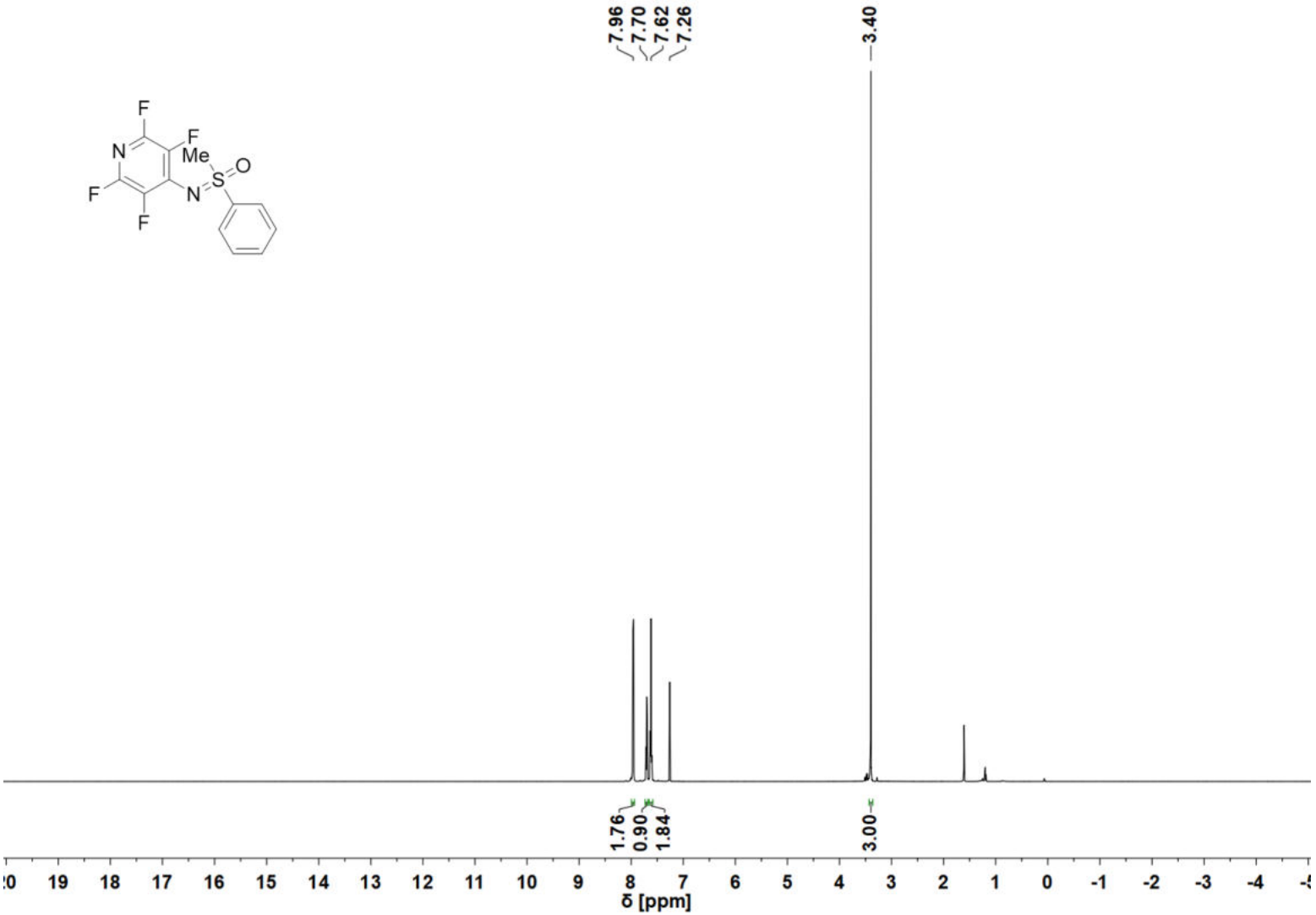

Figure S57 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3a**.

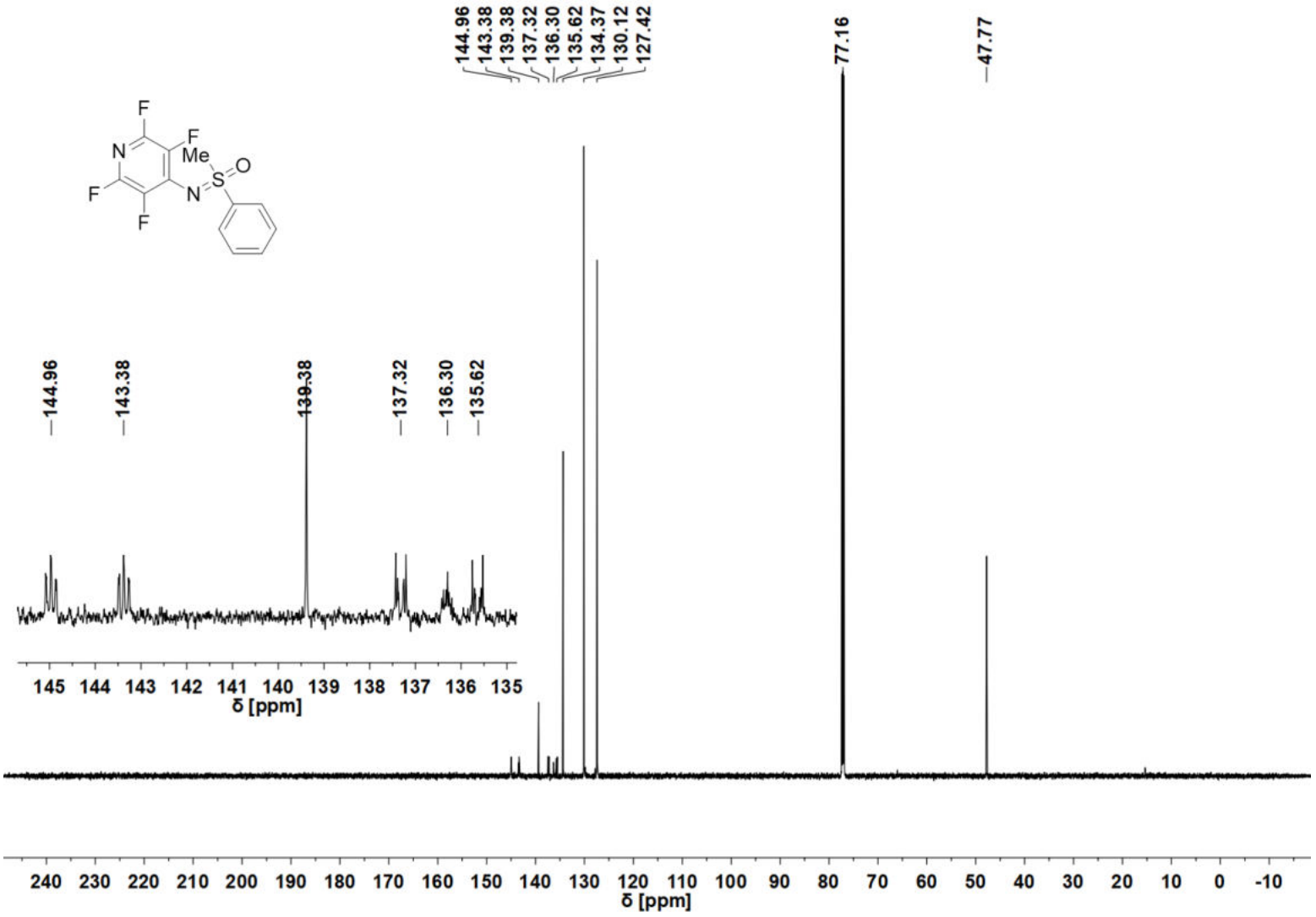

Figure S58 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3a**.

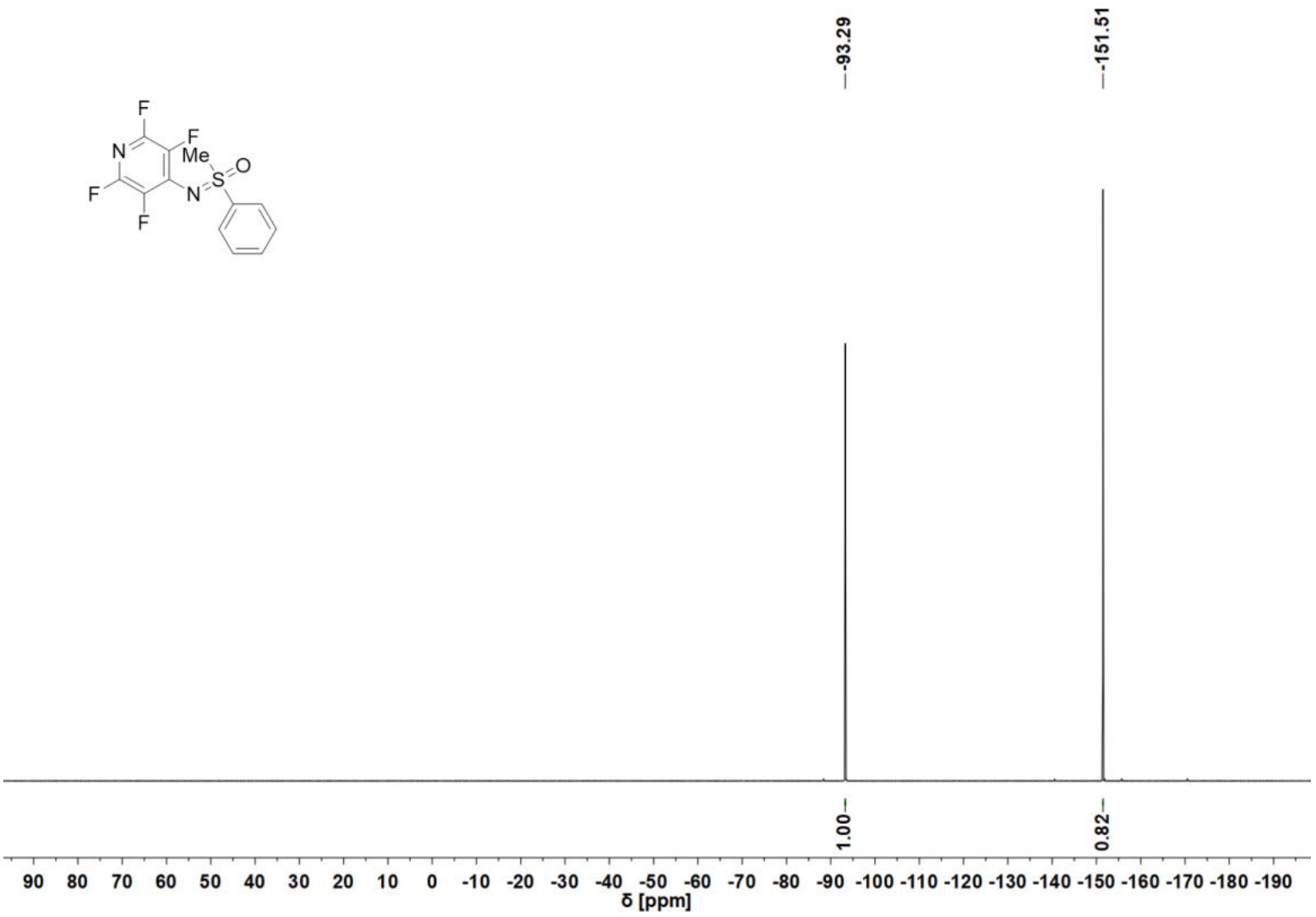

Figure S59 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3a**.

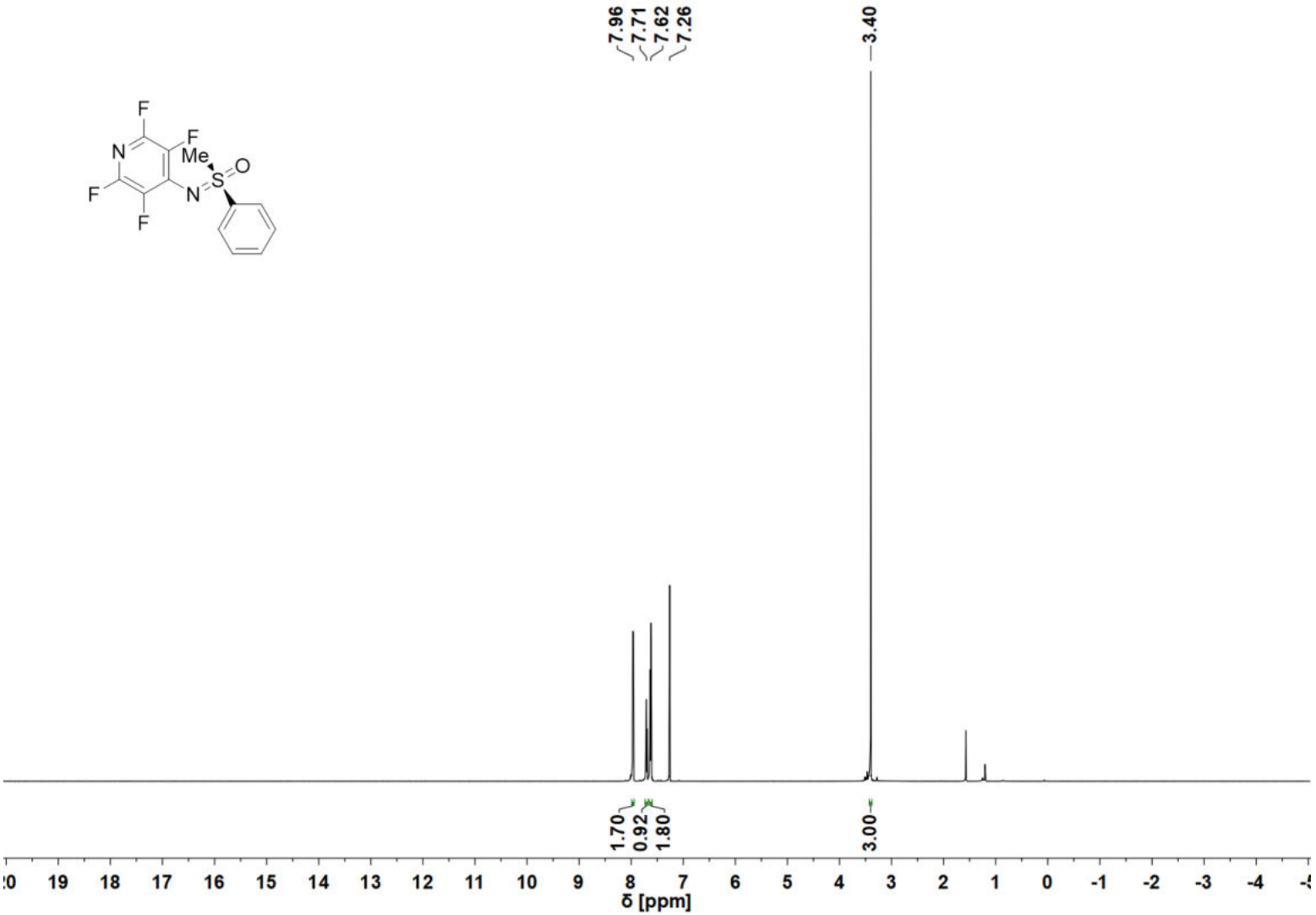

Figure S60 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of (*R*)-**3a**.

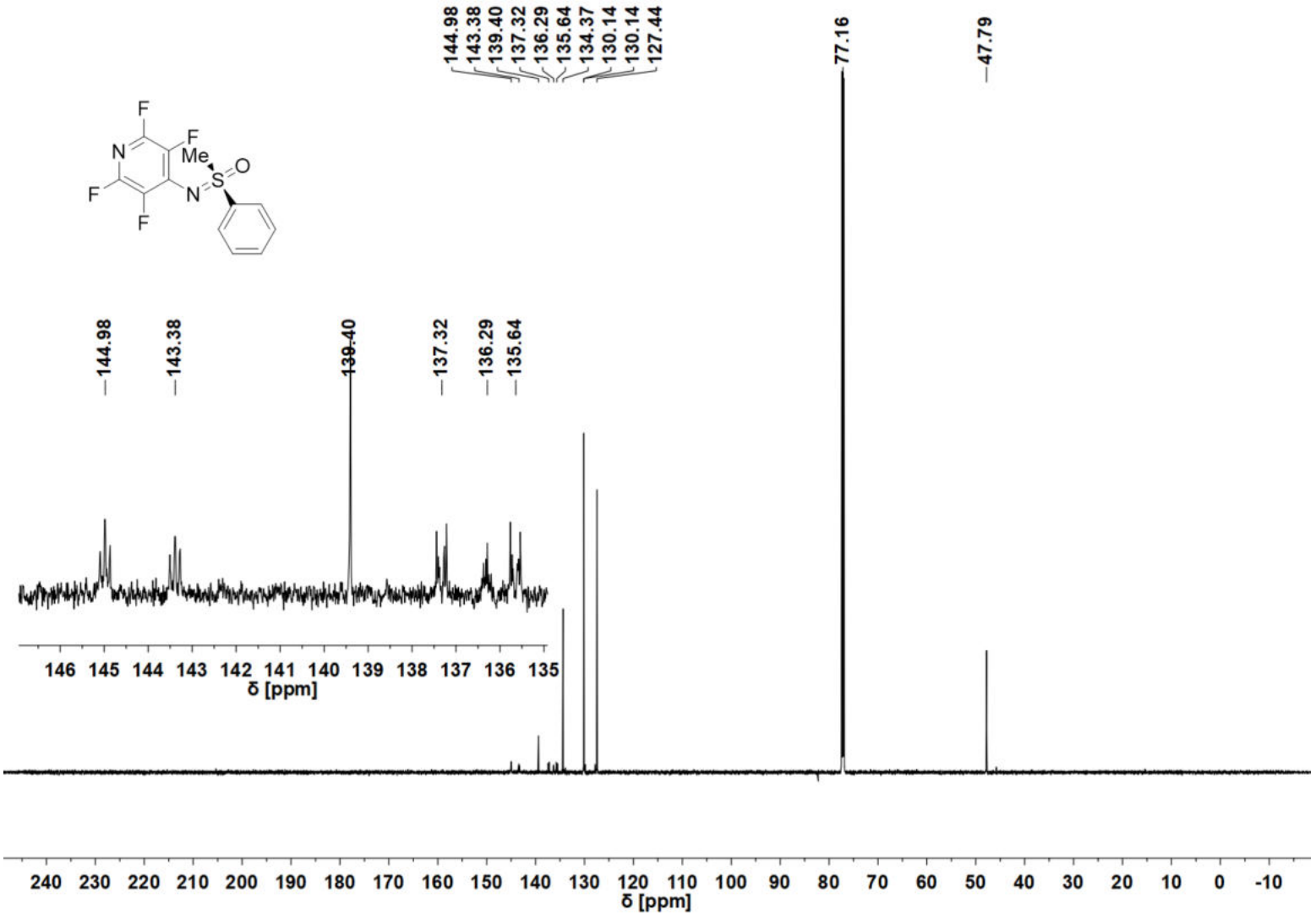

Figure S61 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of (*R*)-**3a**.

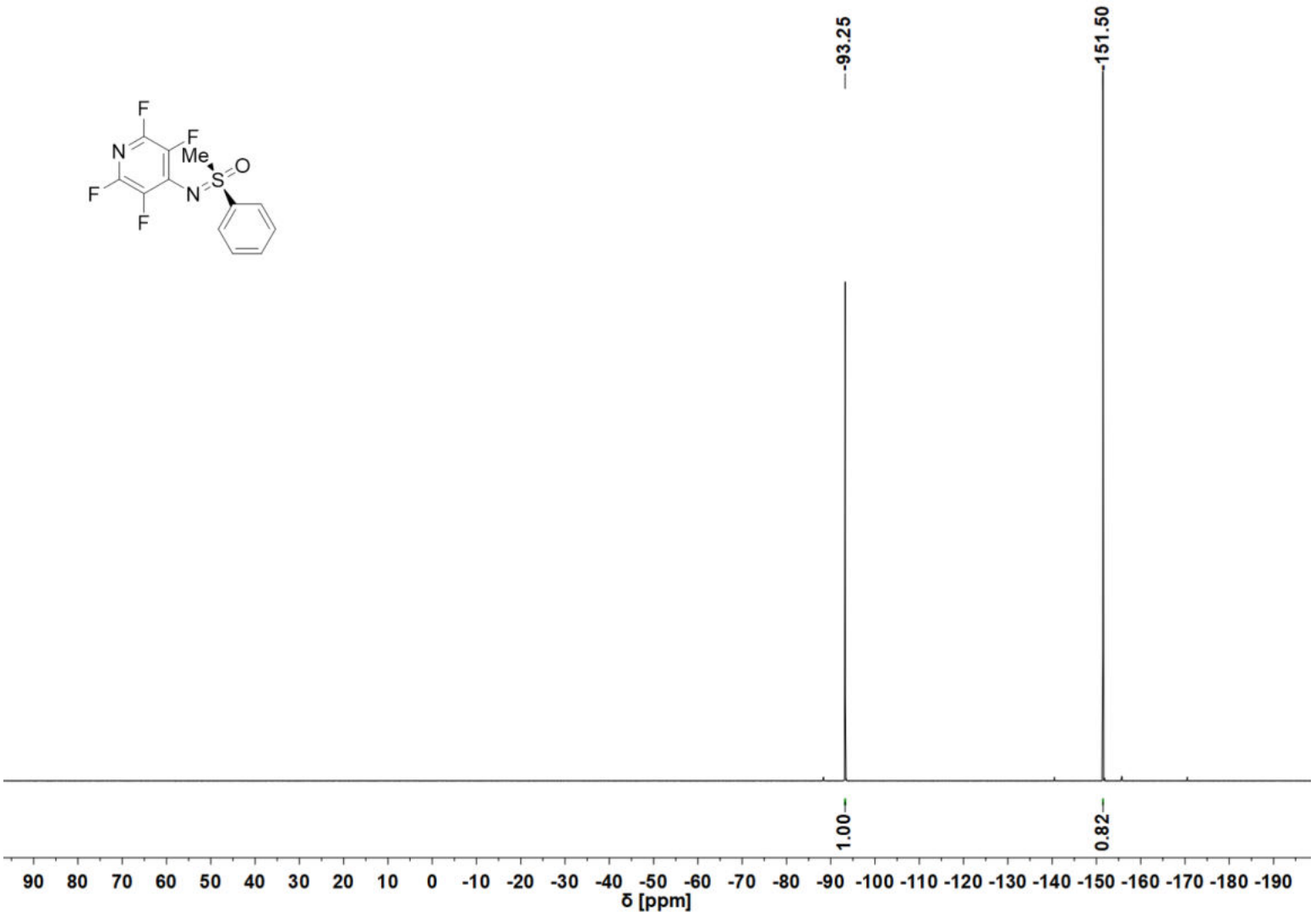

Figure S62 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of (*R*)-**3a**.

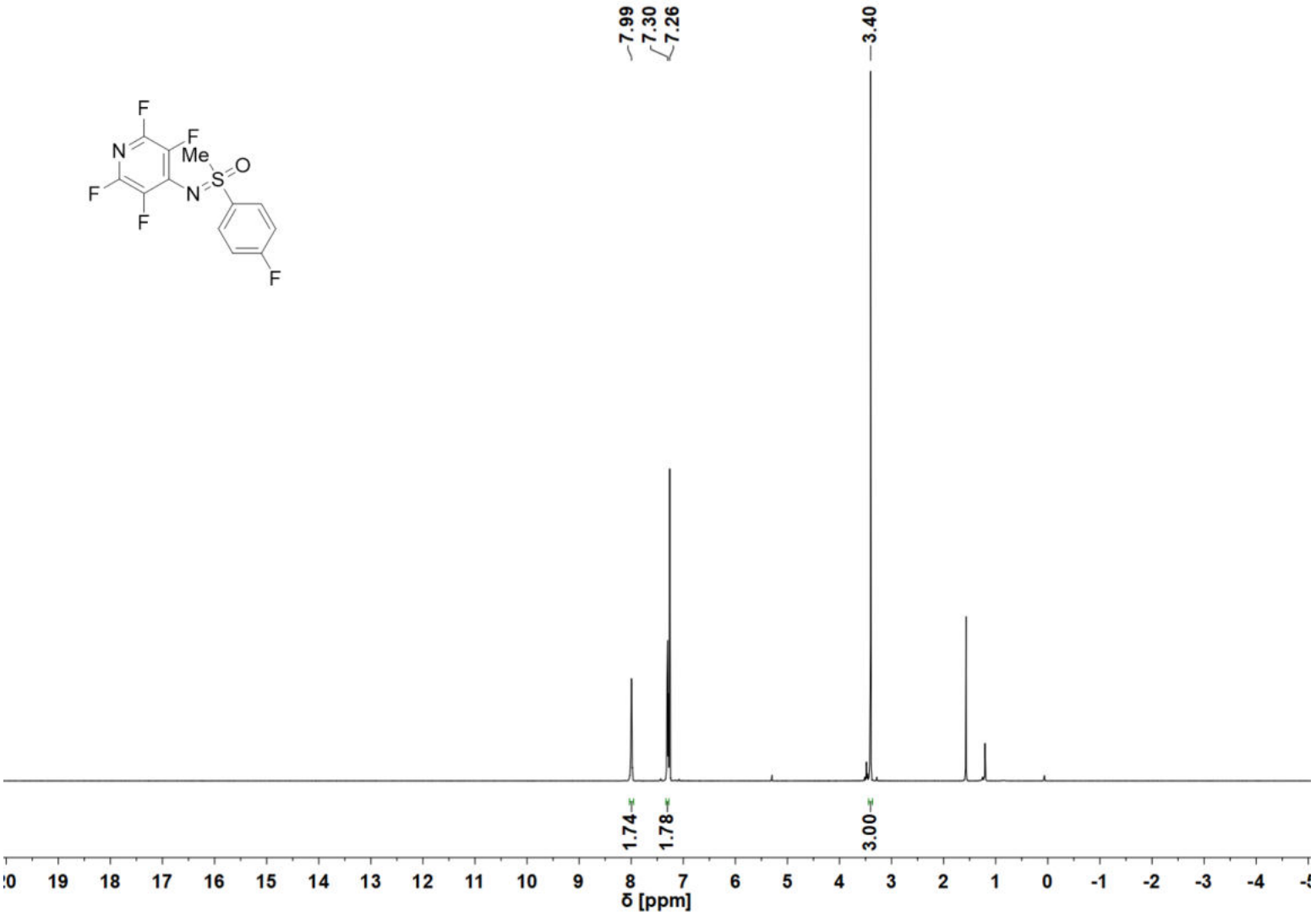

Figure S63 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3b**.

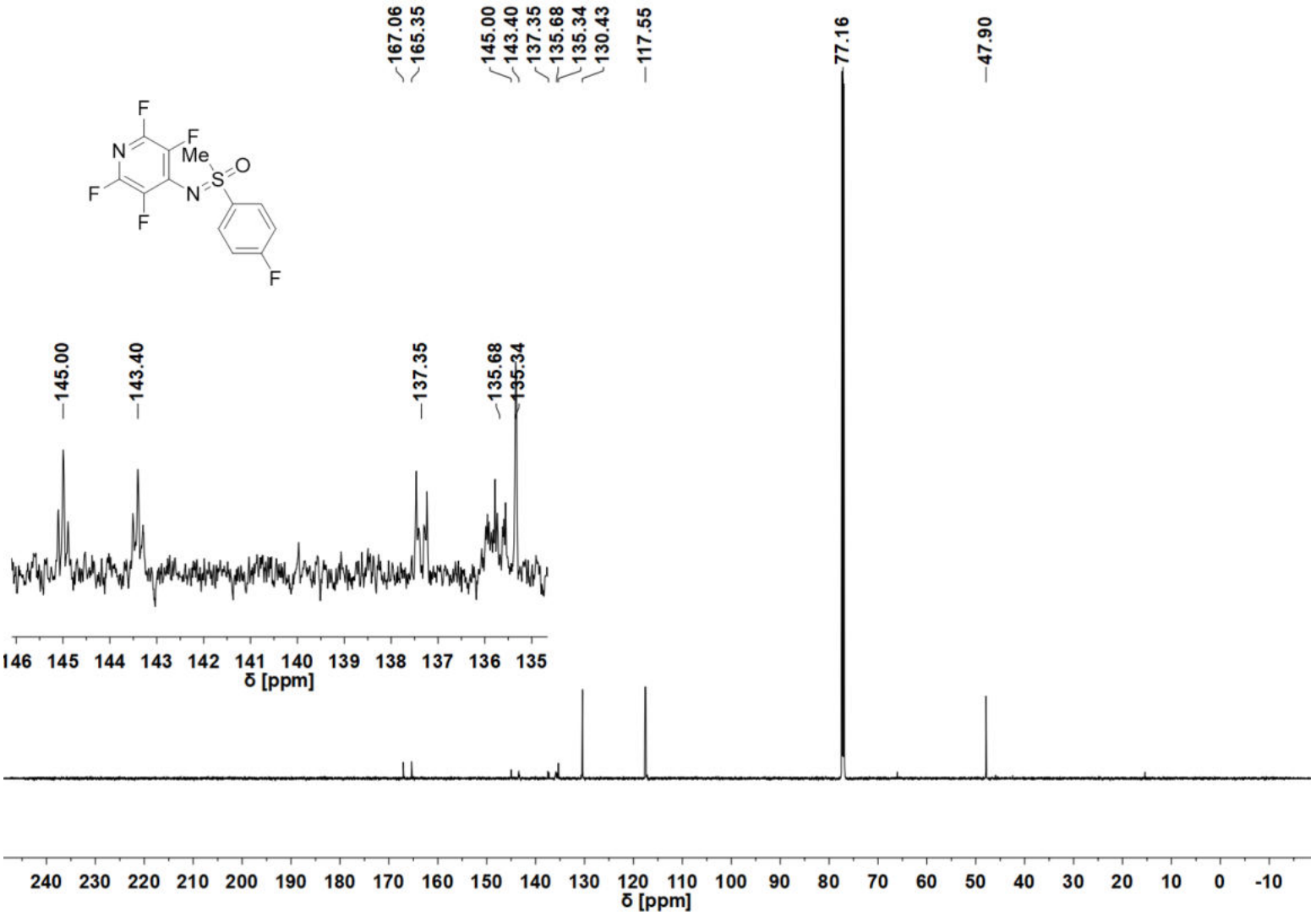

Figure S64 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3b**.

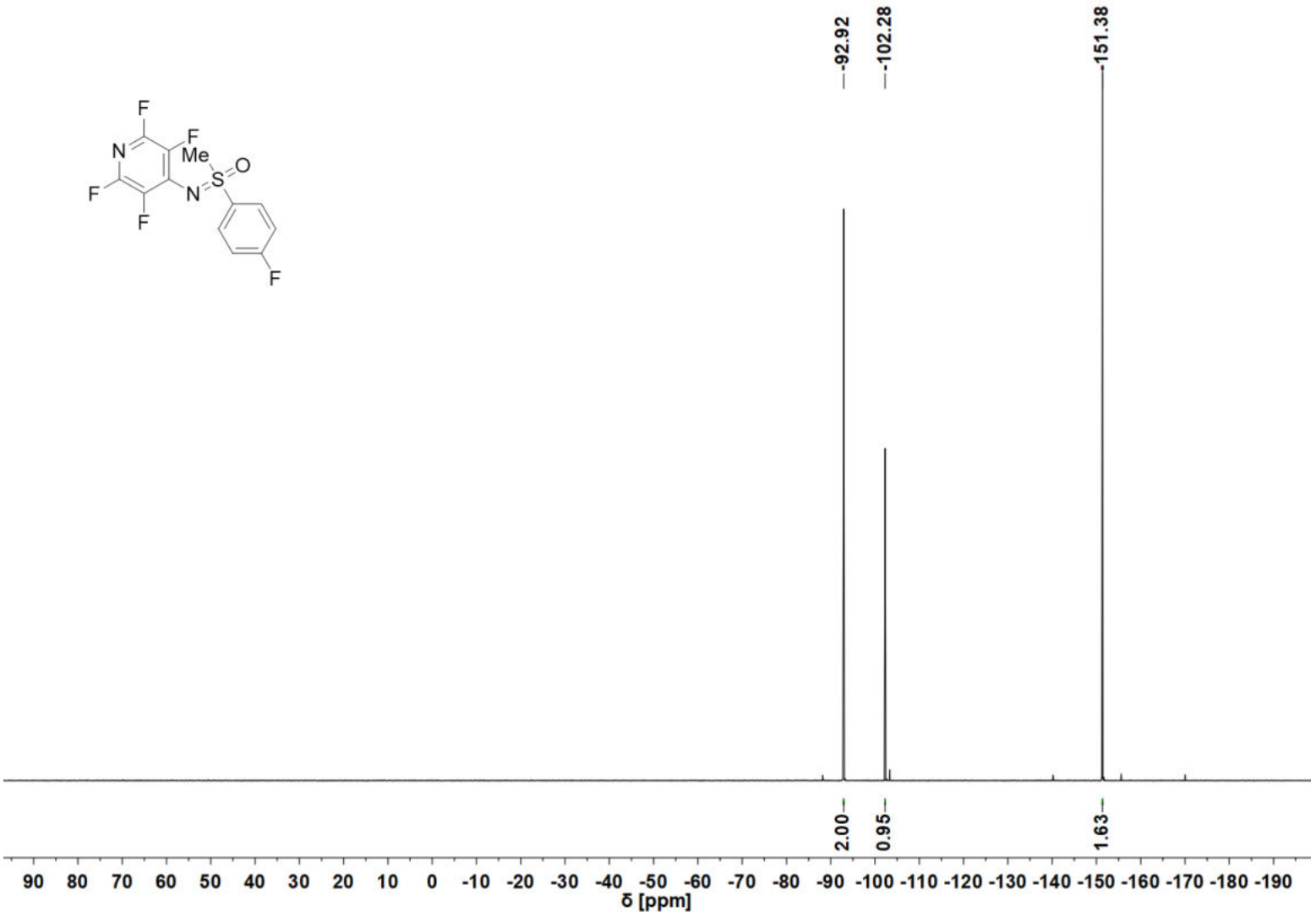

Figure S65 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3b**.

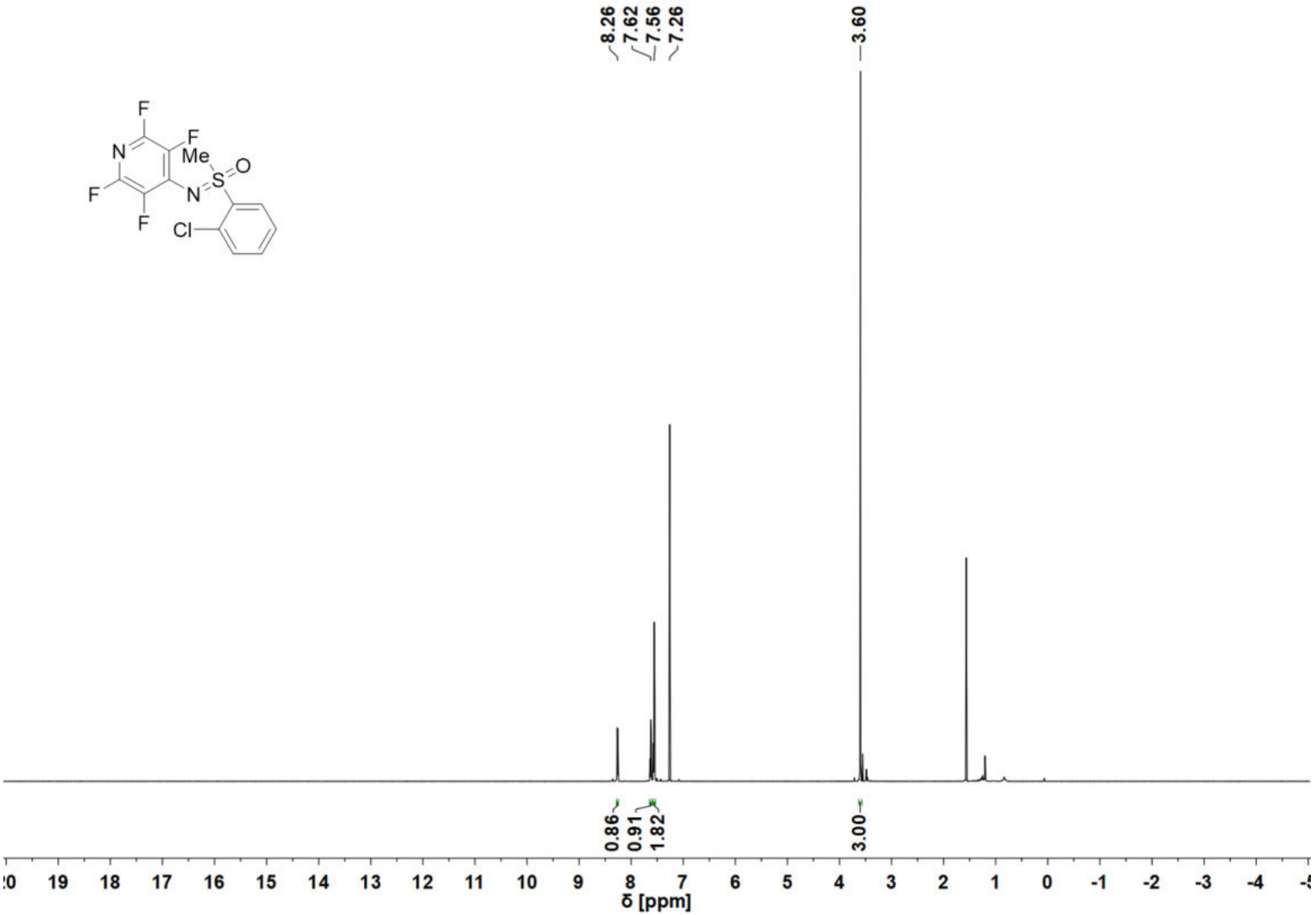

Figure S66 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3c**.

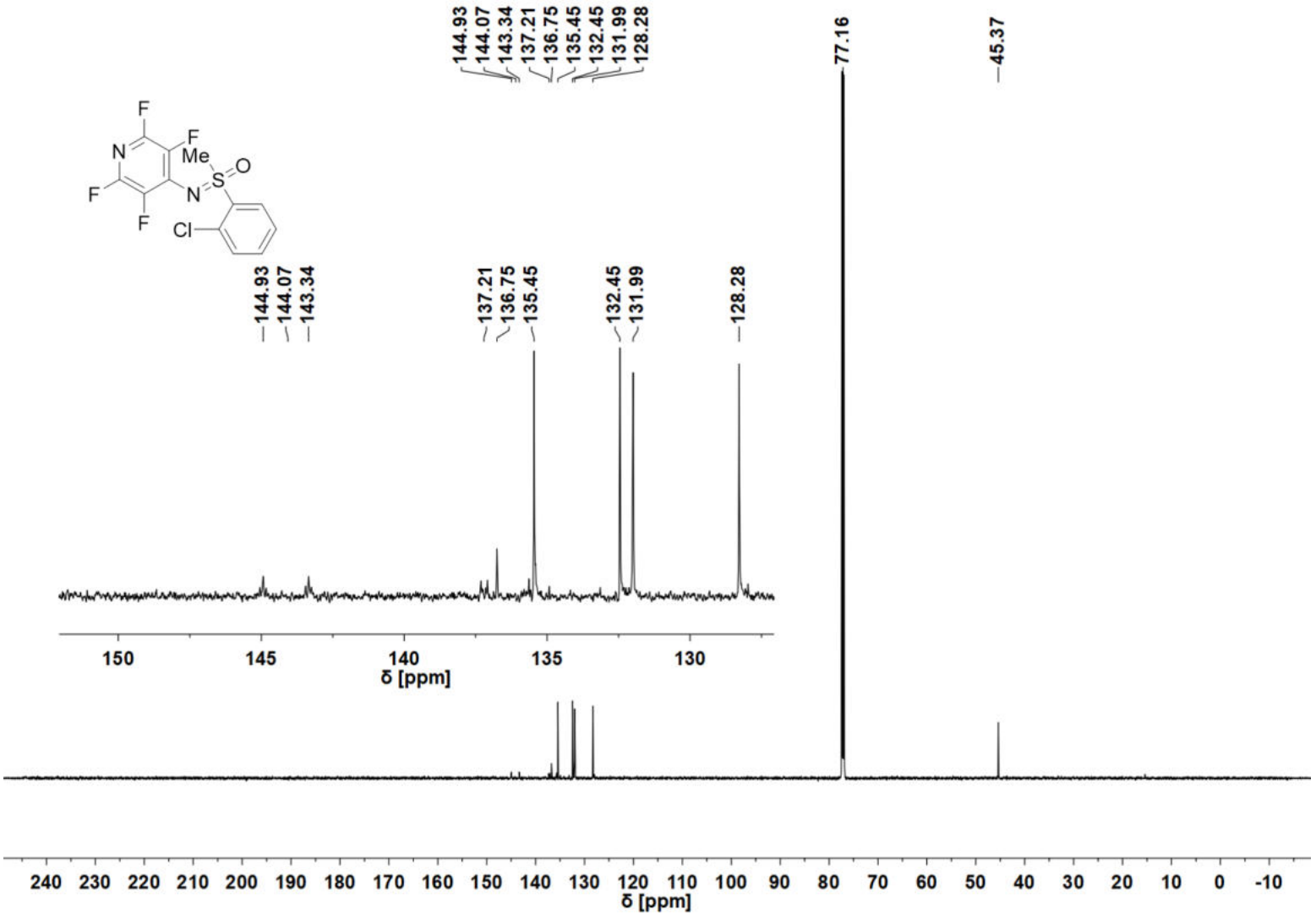

Figure S67 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3c**.

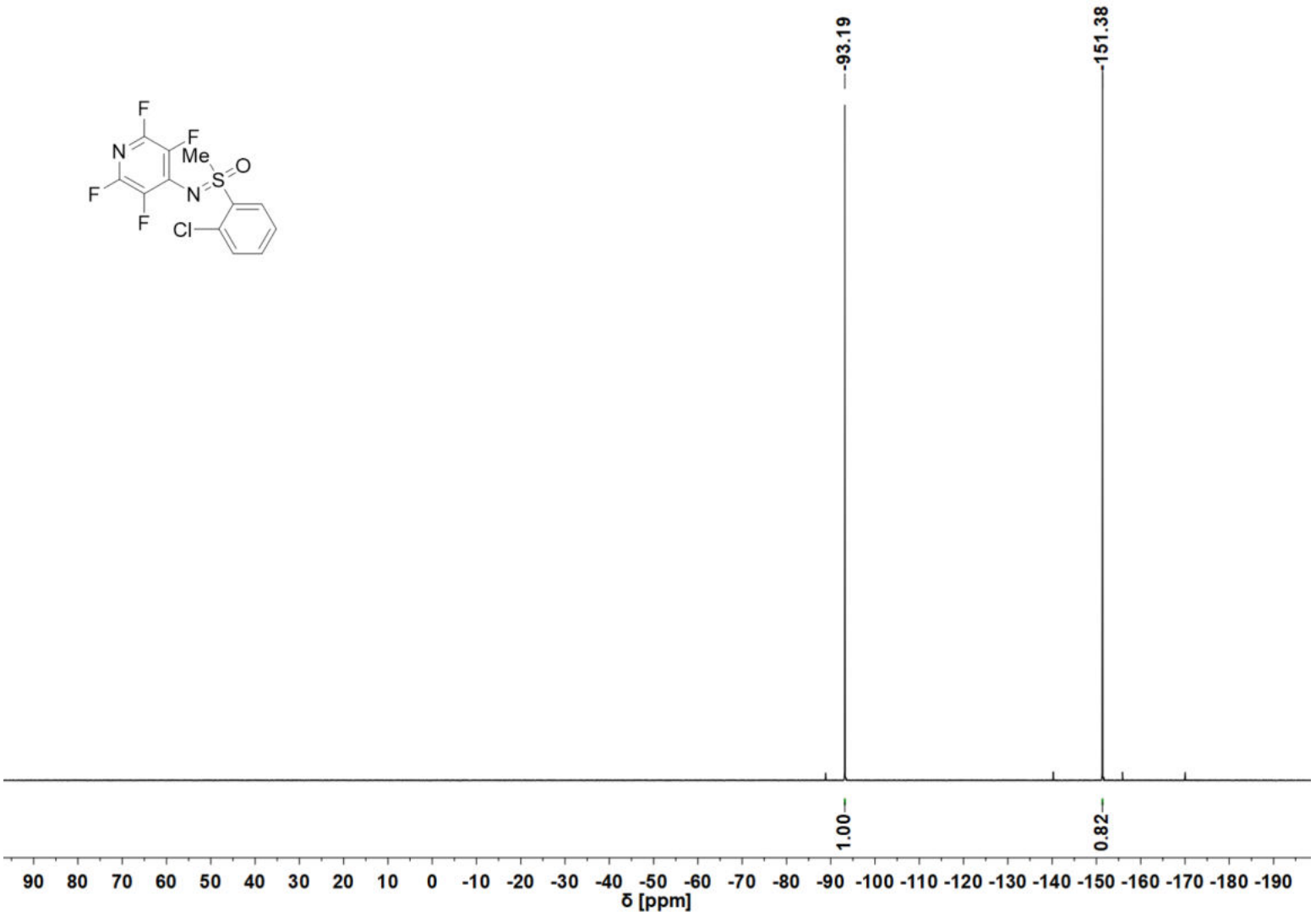

Figure S68 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3c**.

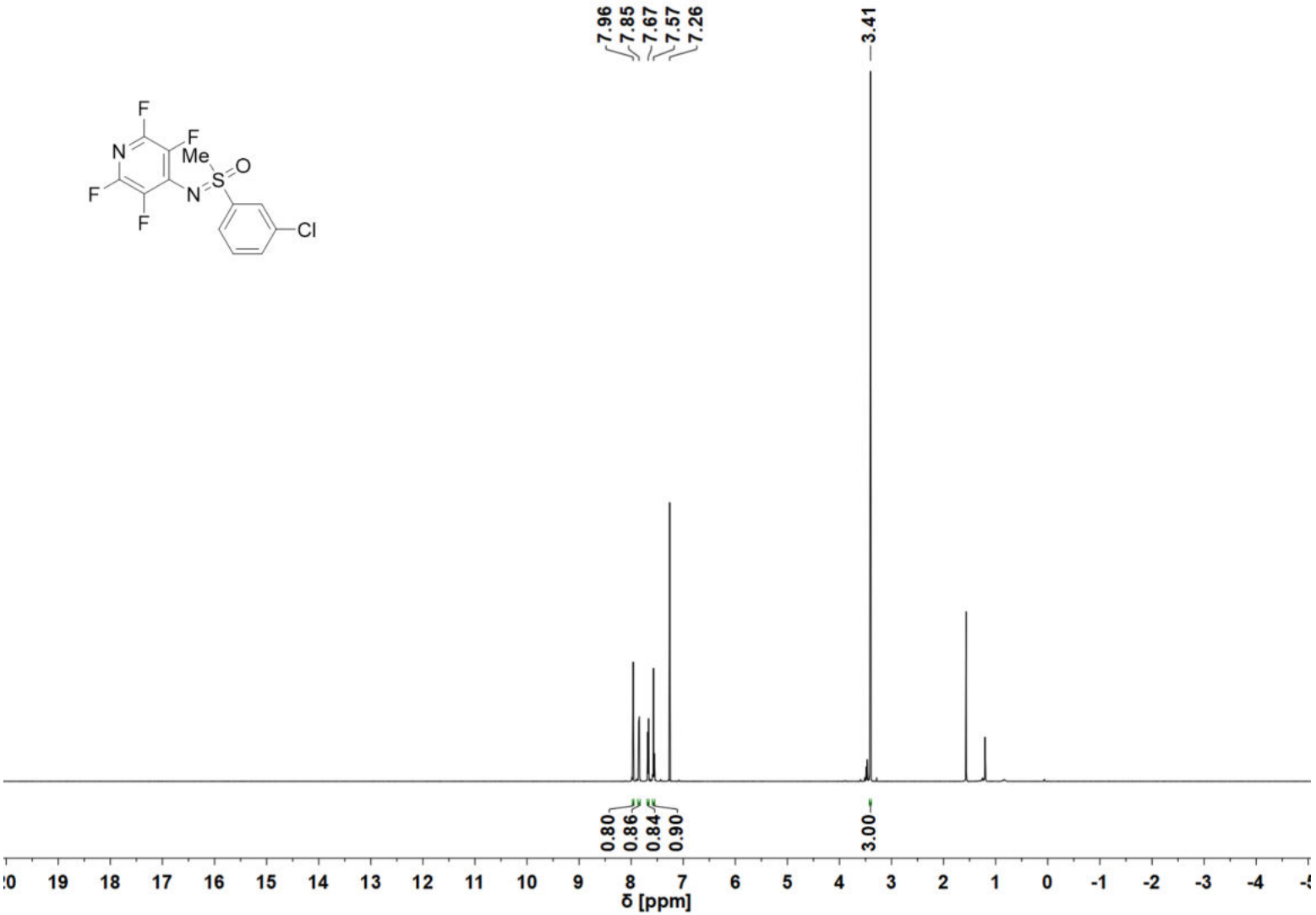

Figure S69 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3d**.

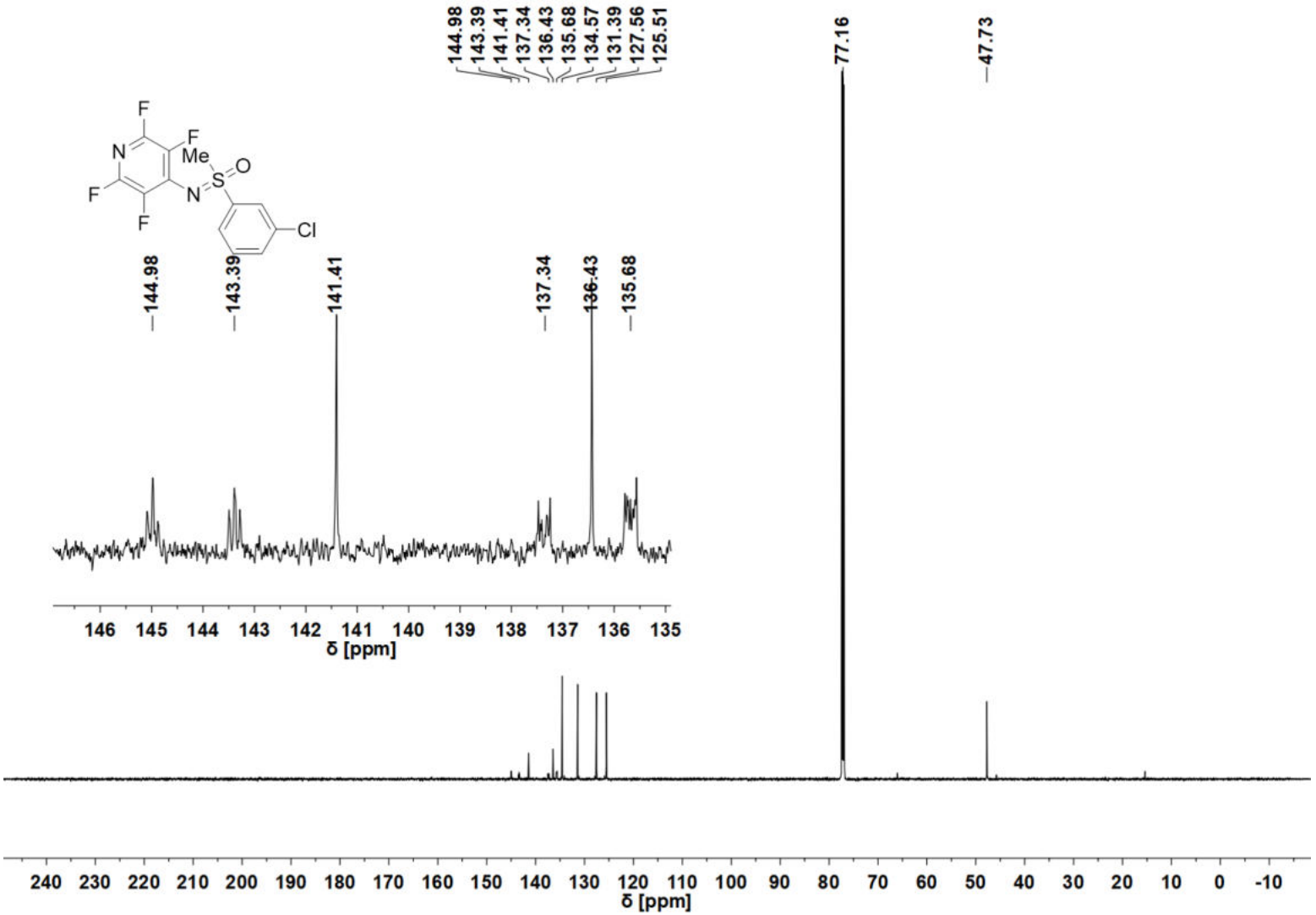

Figure S70 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3d**.

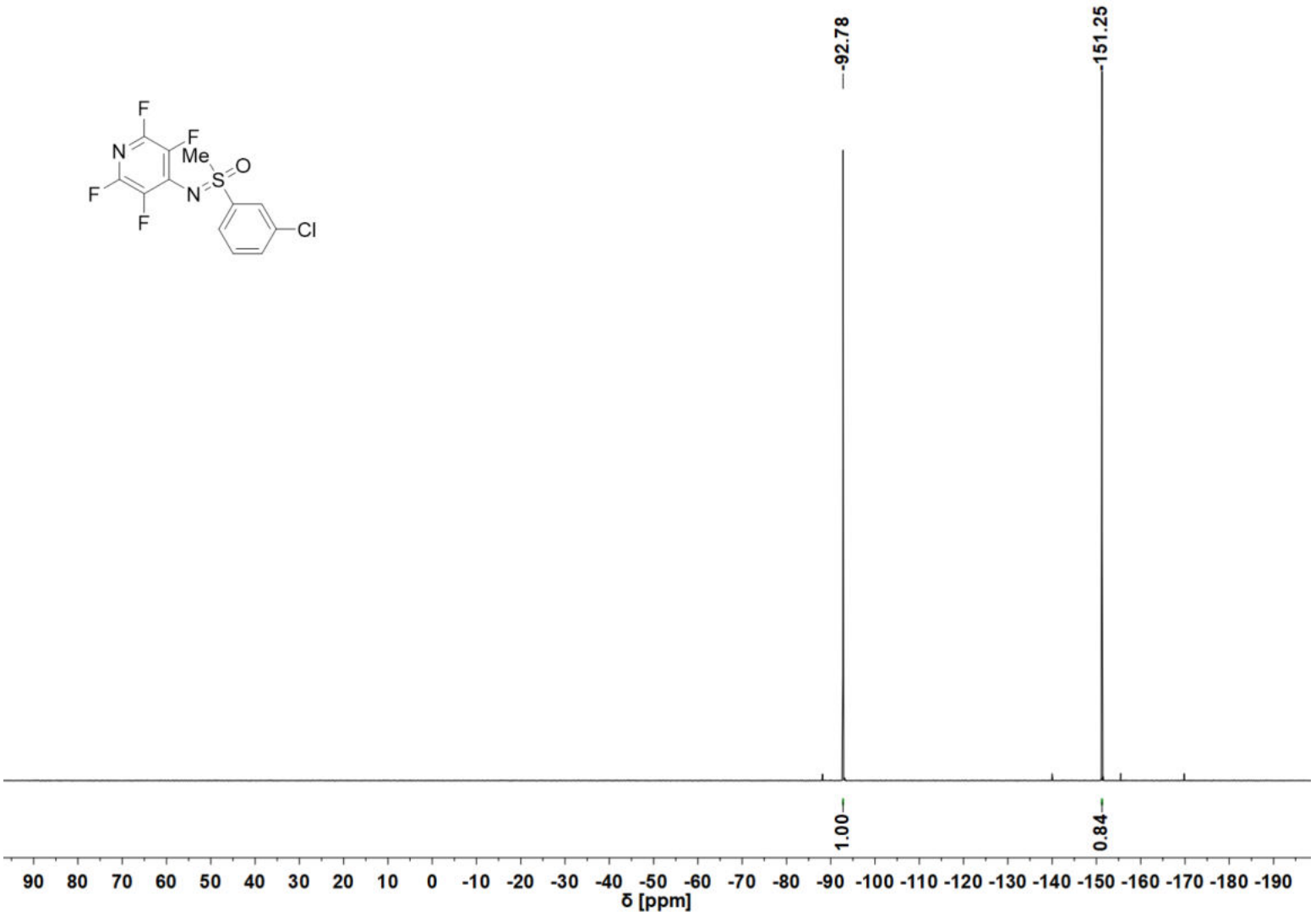

Figure S71 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3d**.

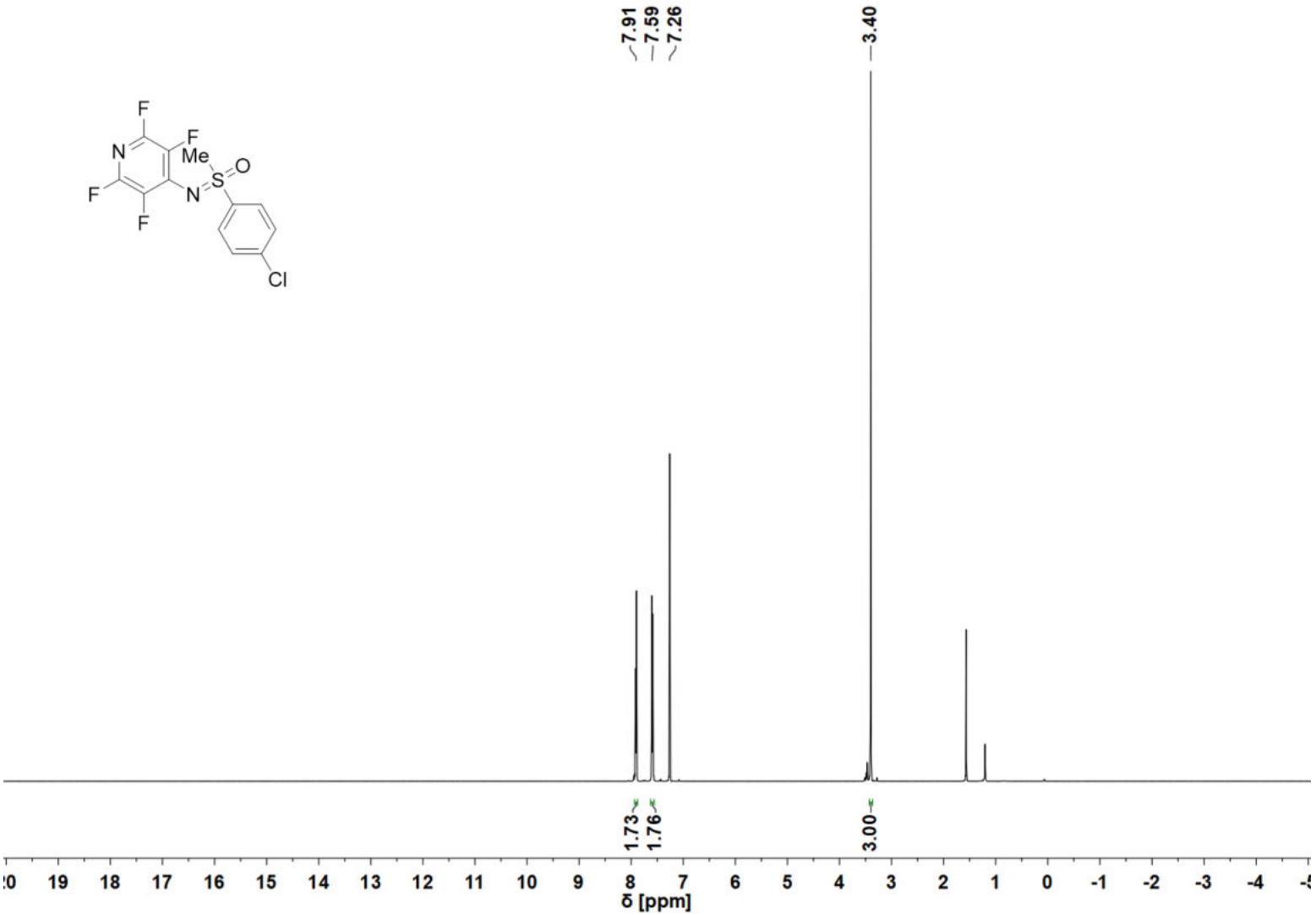

Figure S72 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3e**.

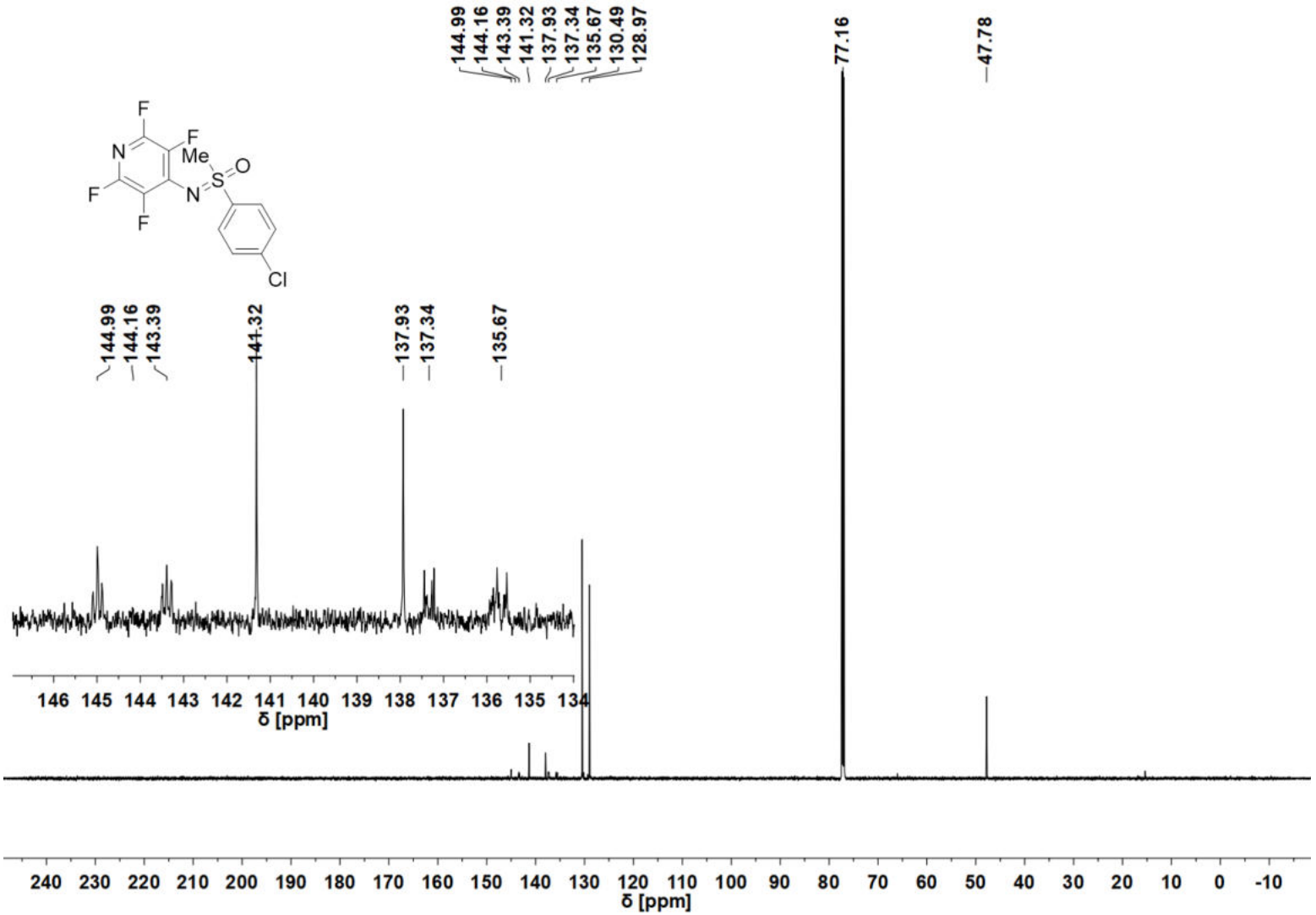

Figure S73 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3e**.

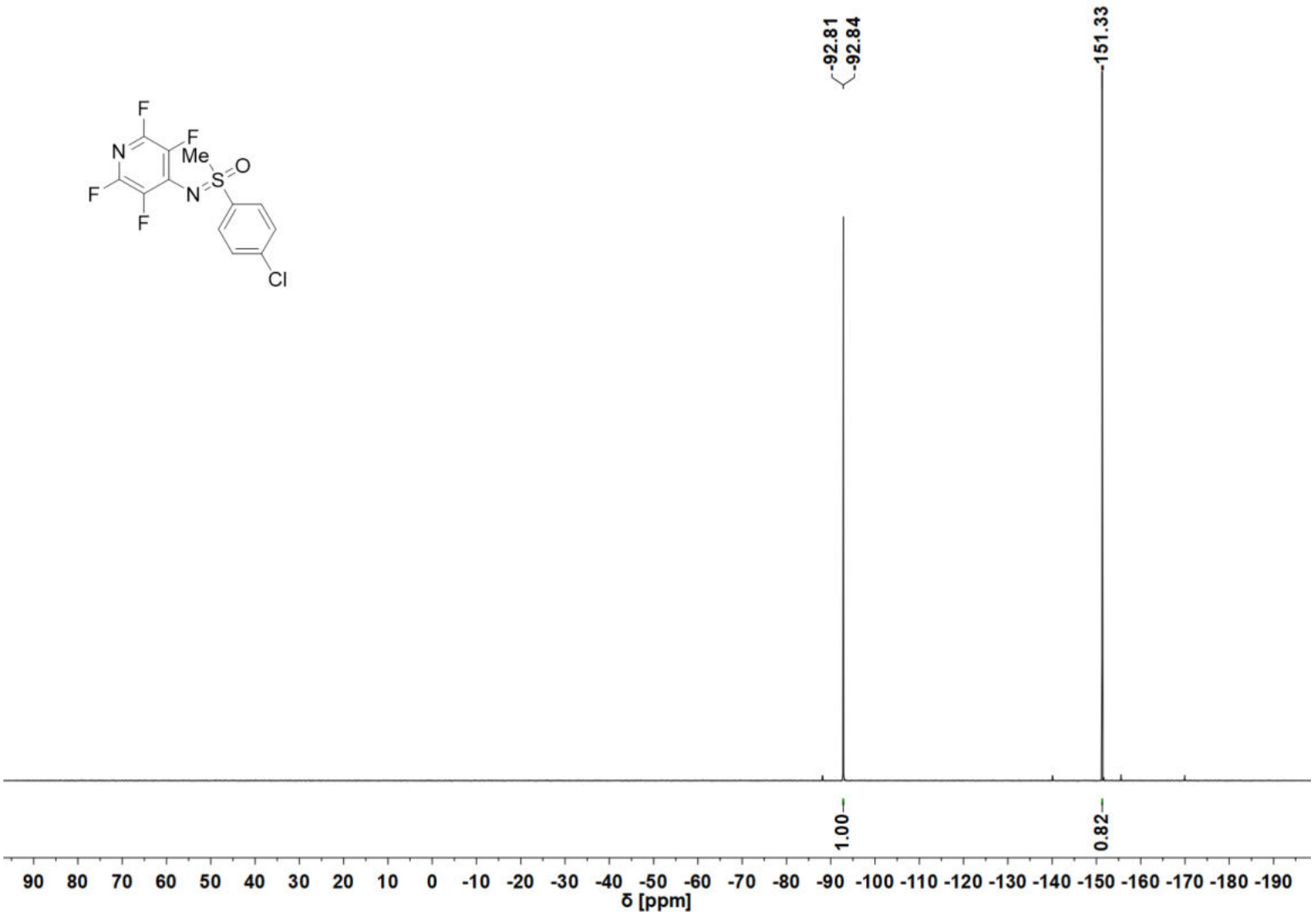

Figure S74 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3e**.

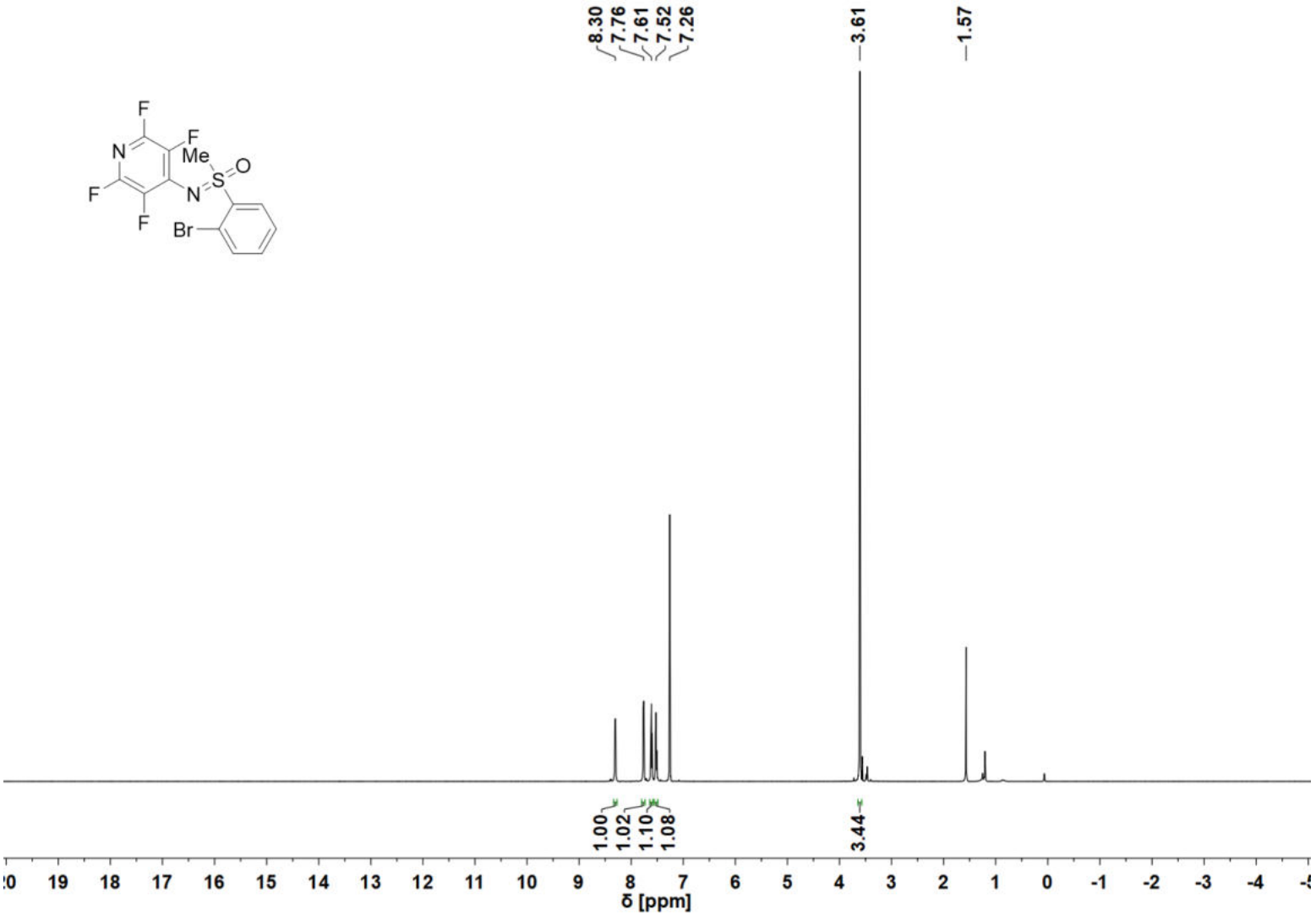

Figure S75 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3f**.

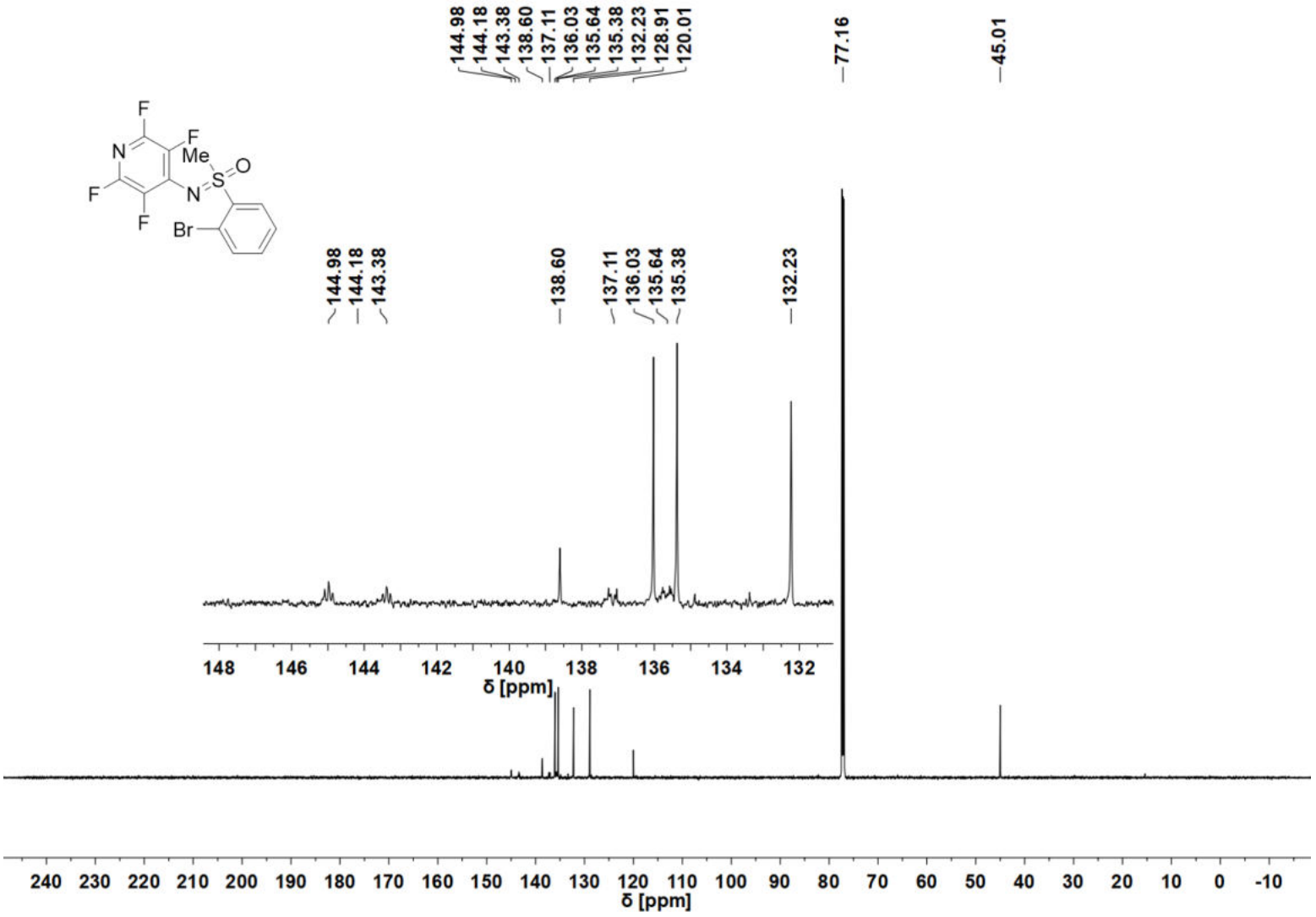

Figure S76 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3f**.

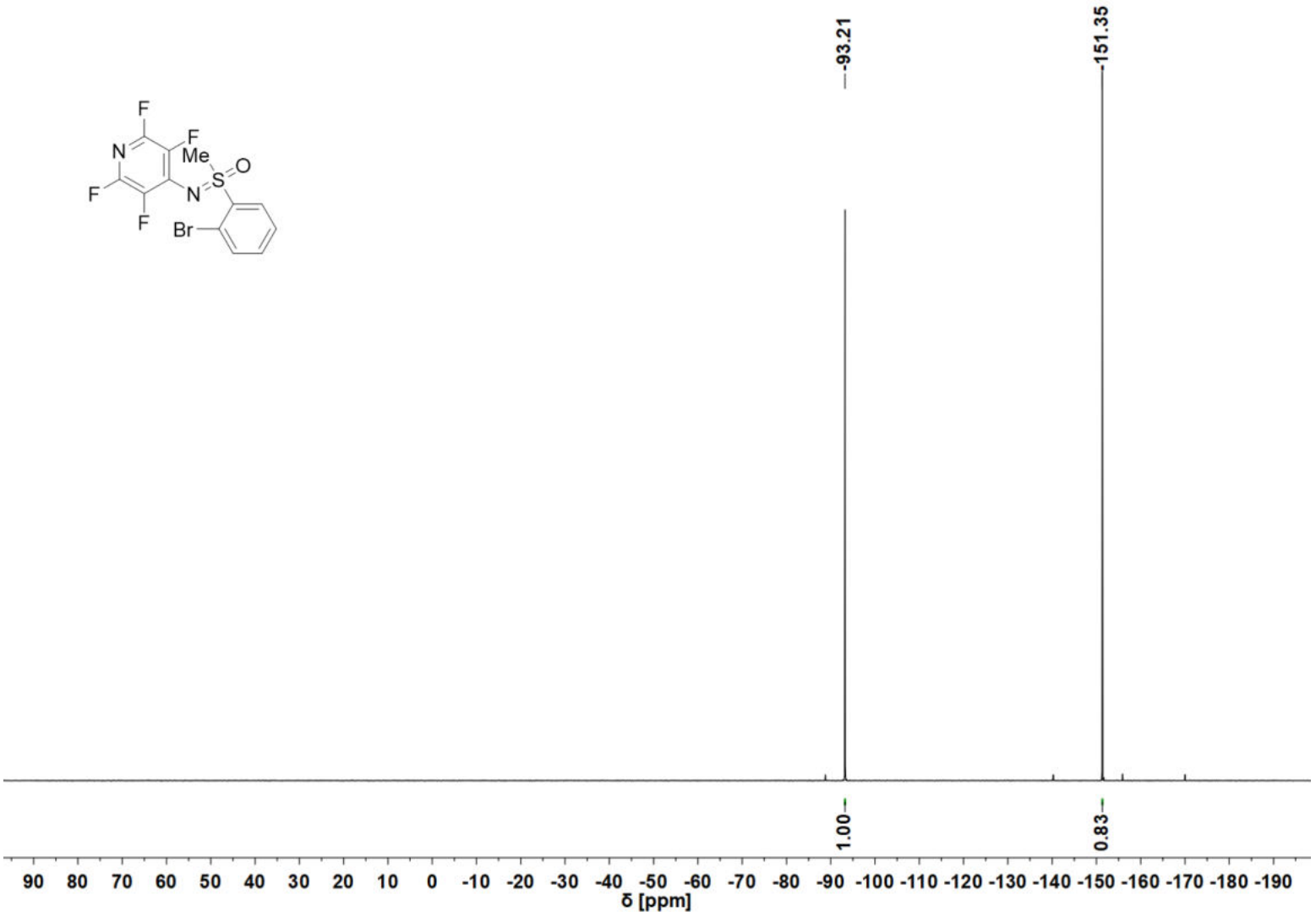

Figure S77 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3f**.

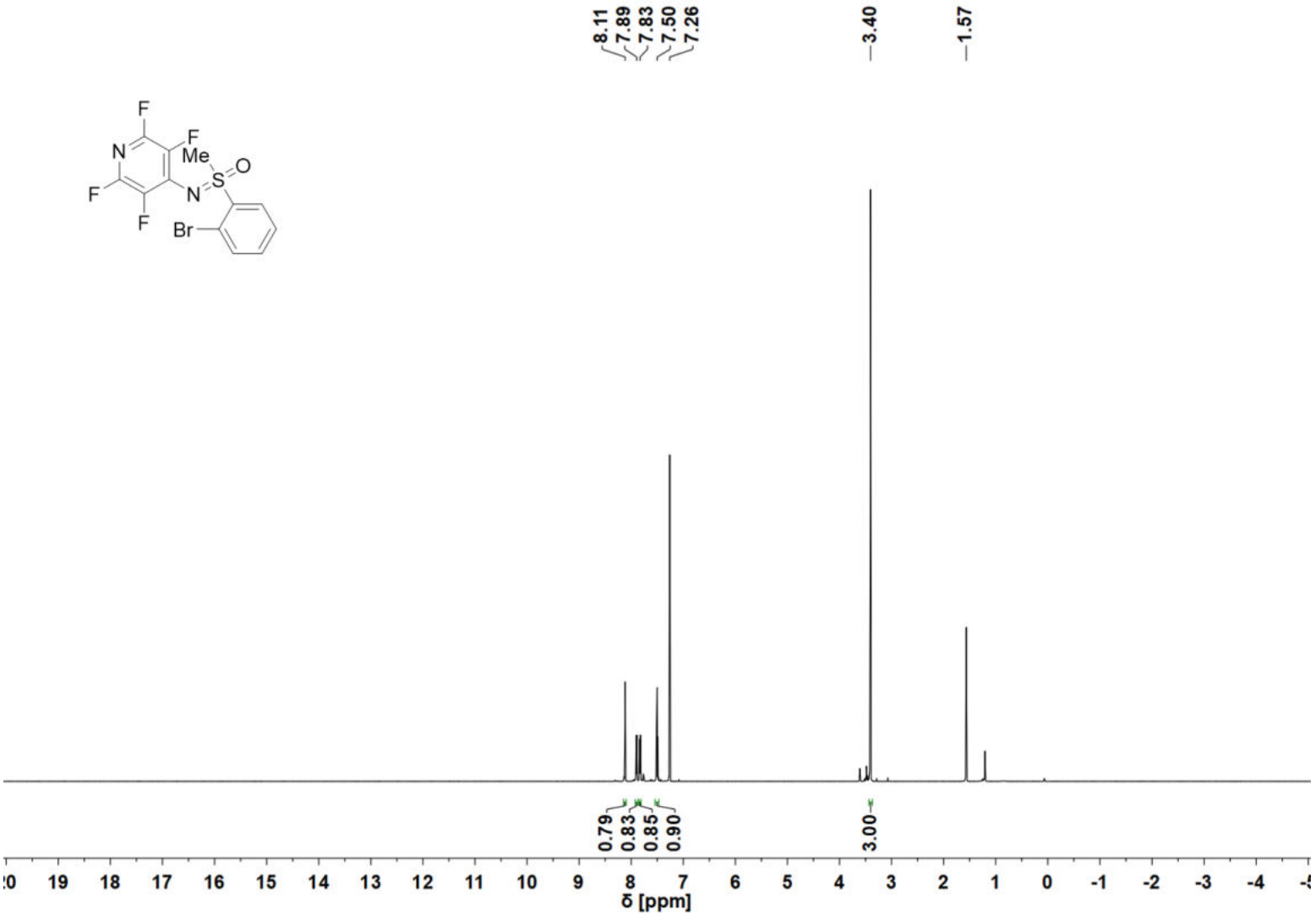

Figure S78 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3g**.

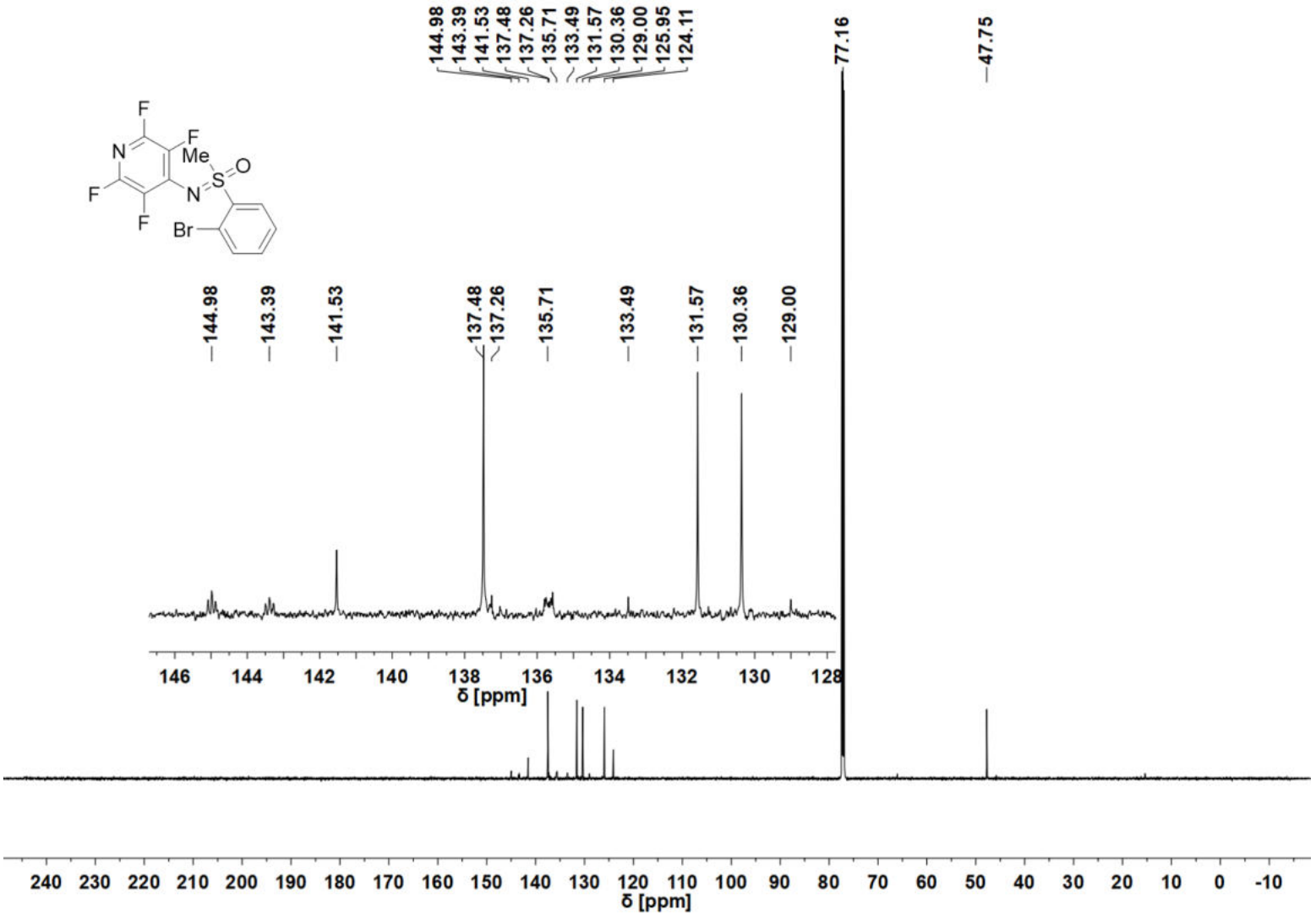

Figure S79 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3g**.

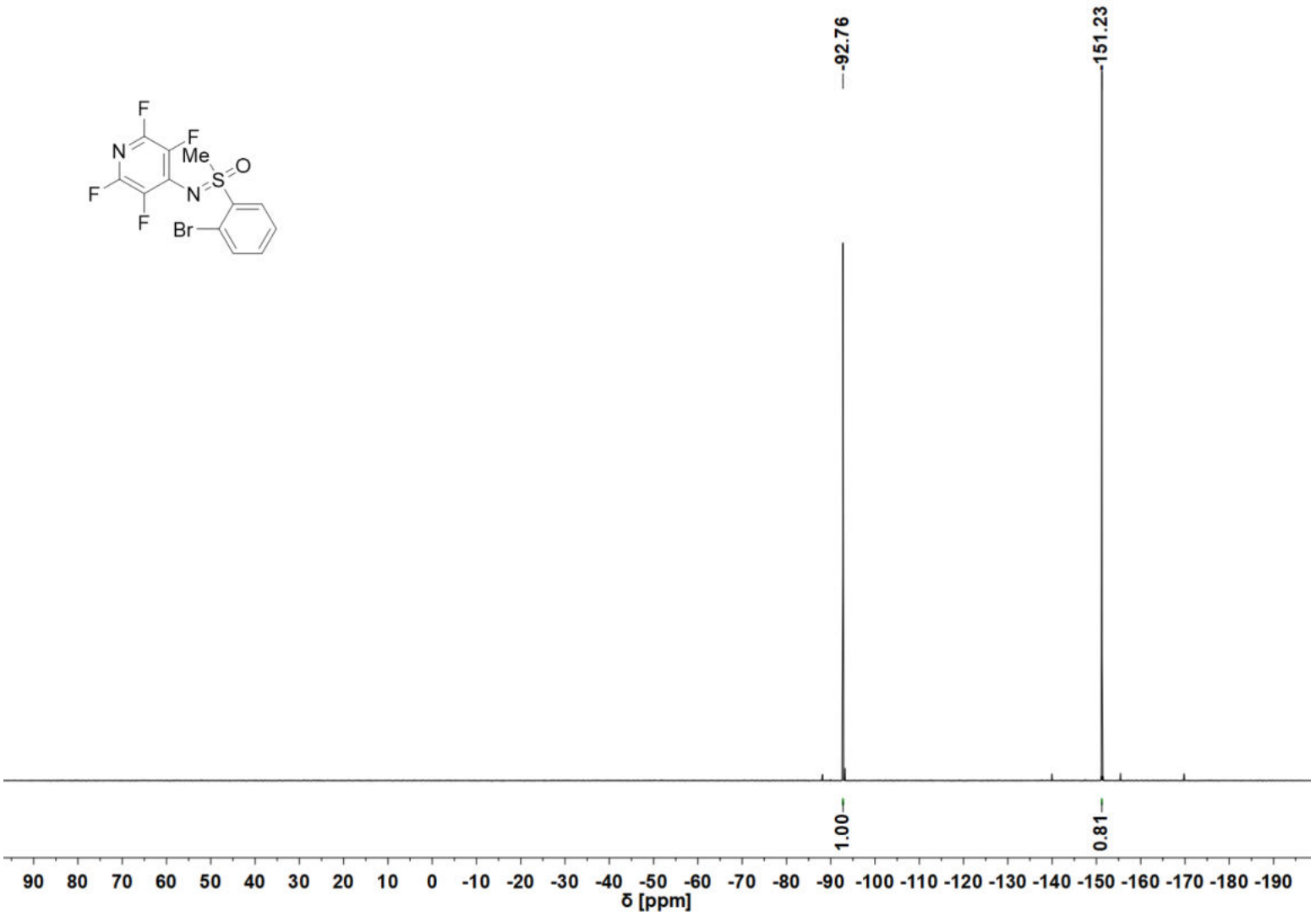

Figure S80 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3g**.

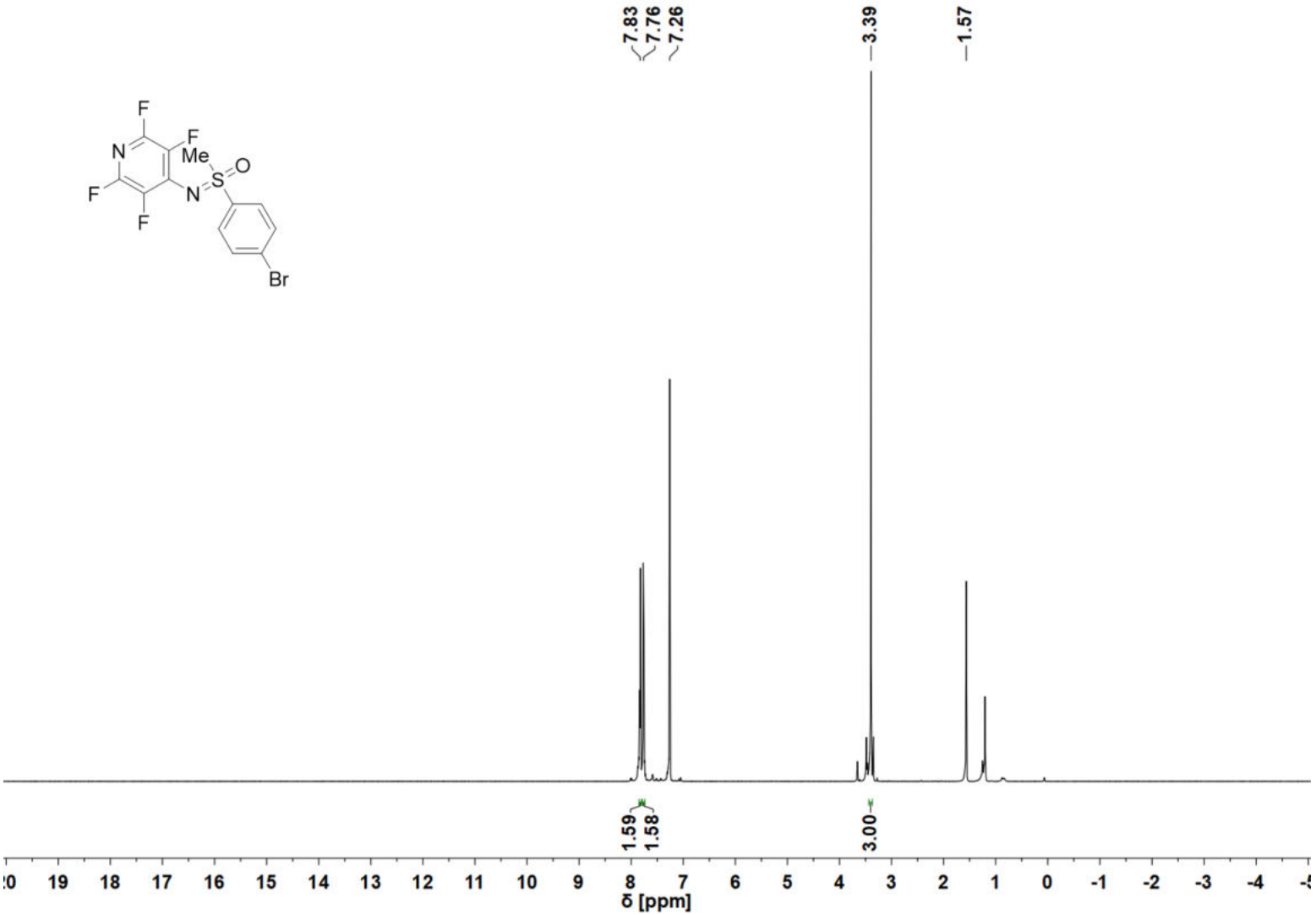

Figure S81 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3h**.

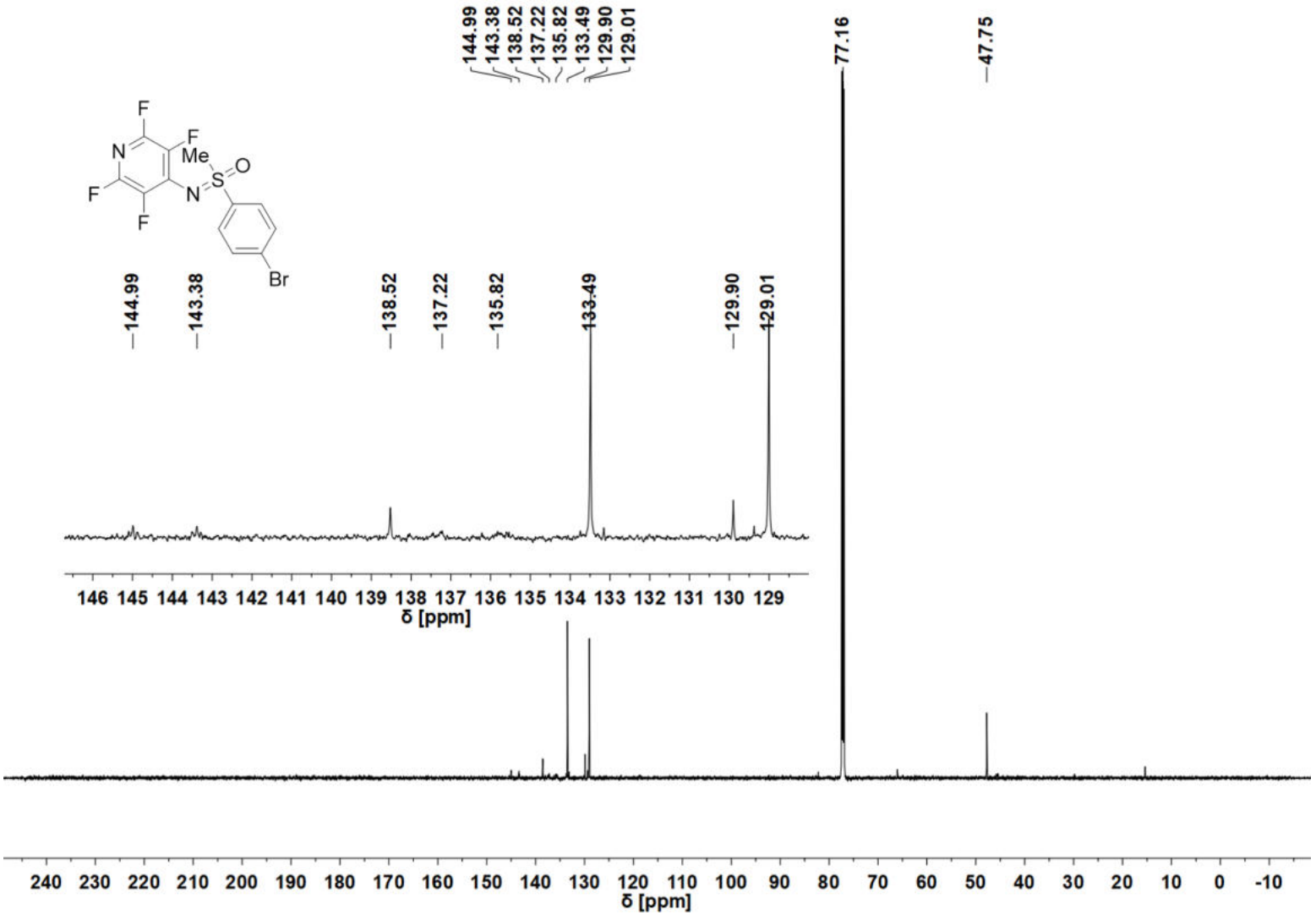

Figure S82 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3h**.

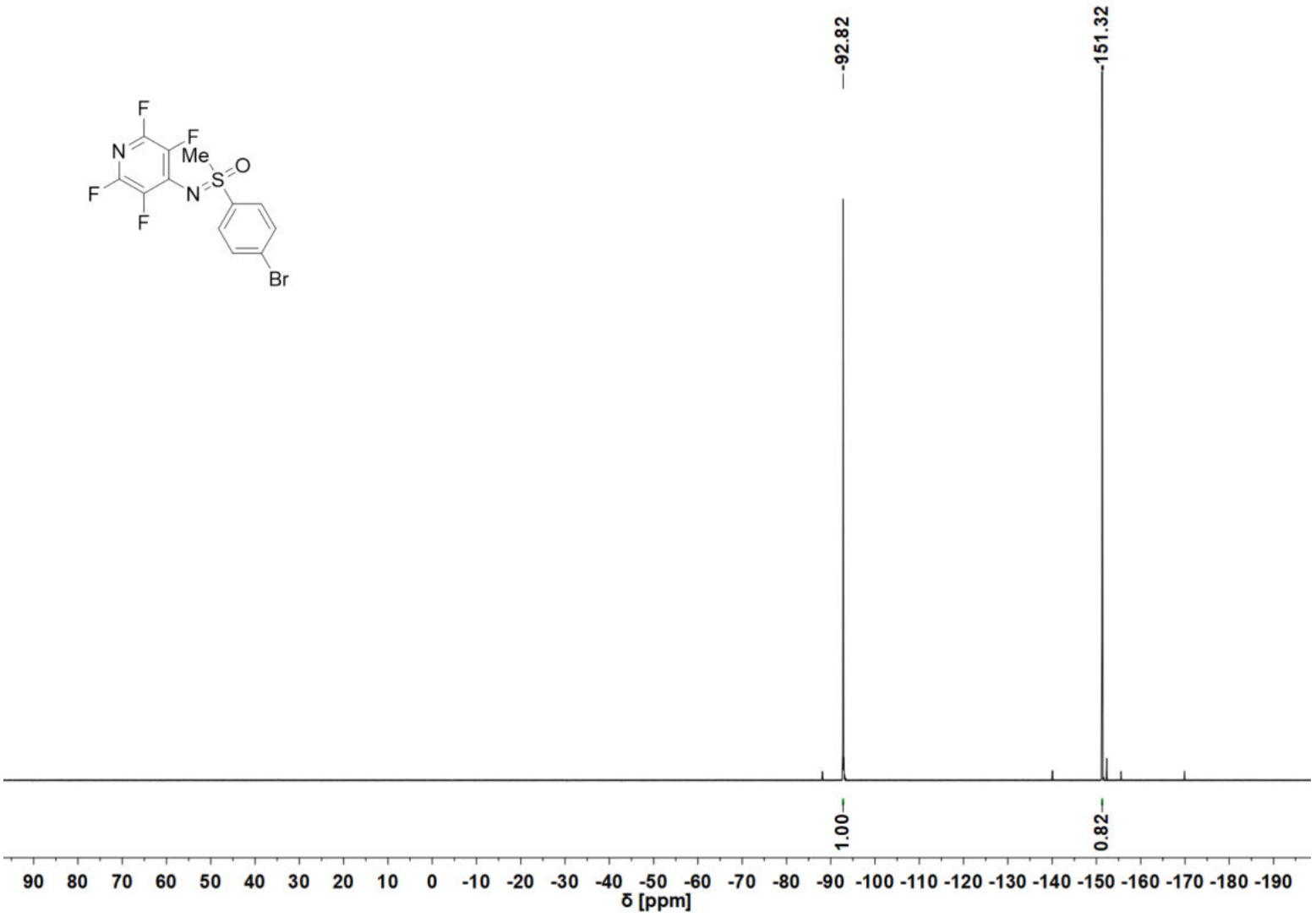

Figure S83 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3h**.

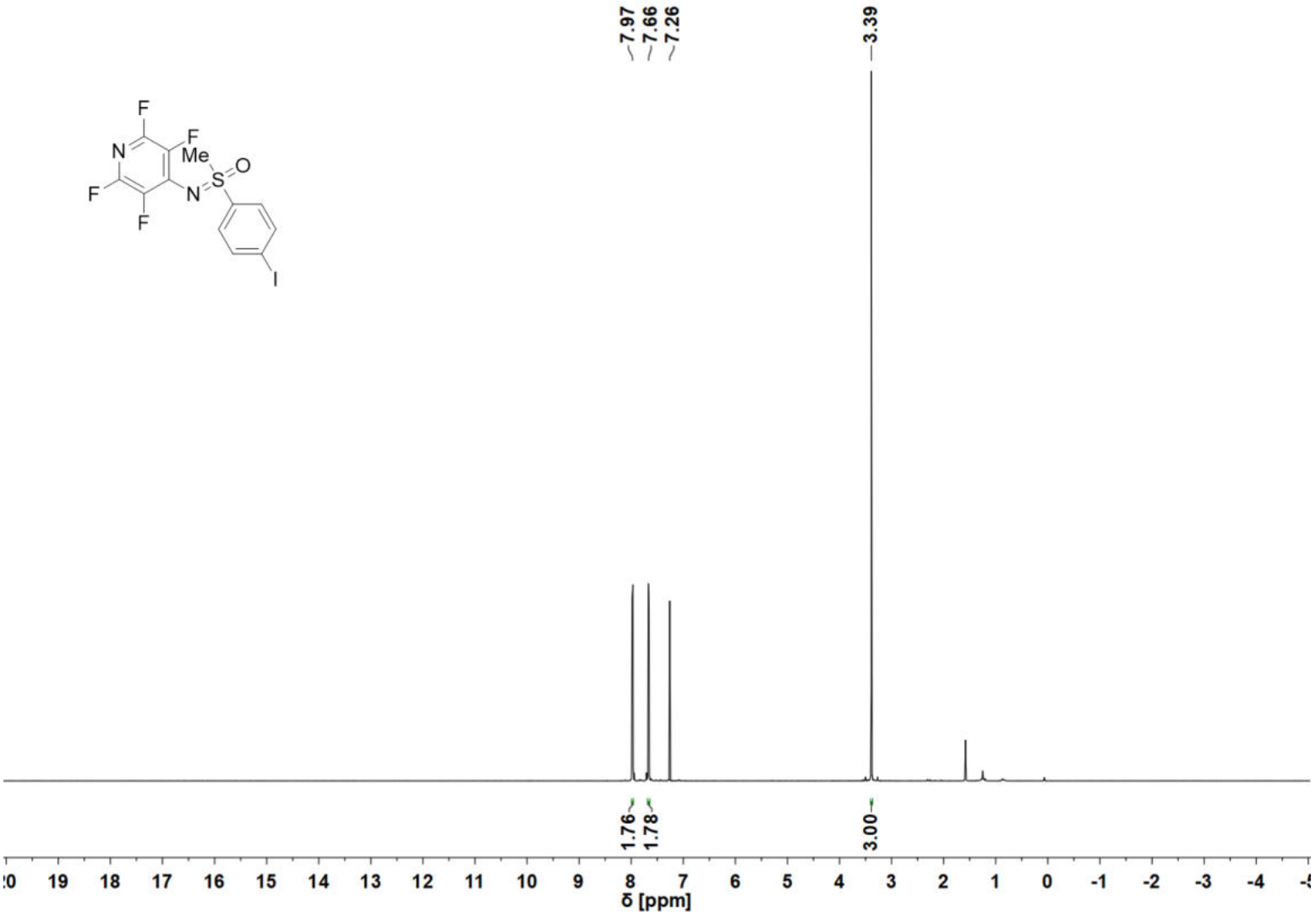

Figure S84 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3i**.

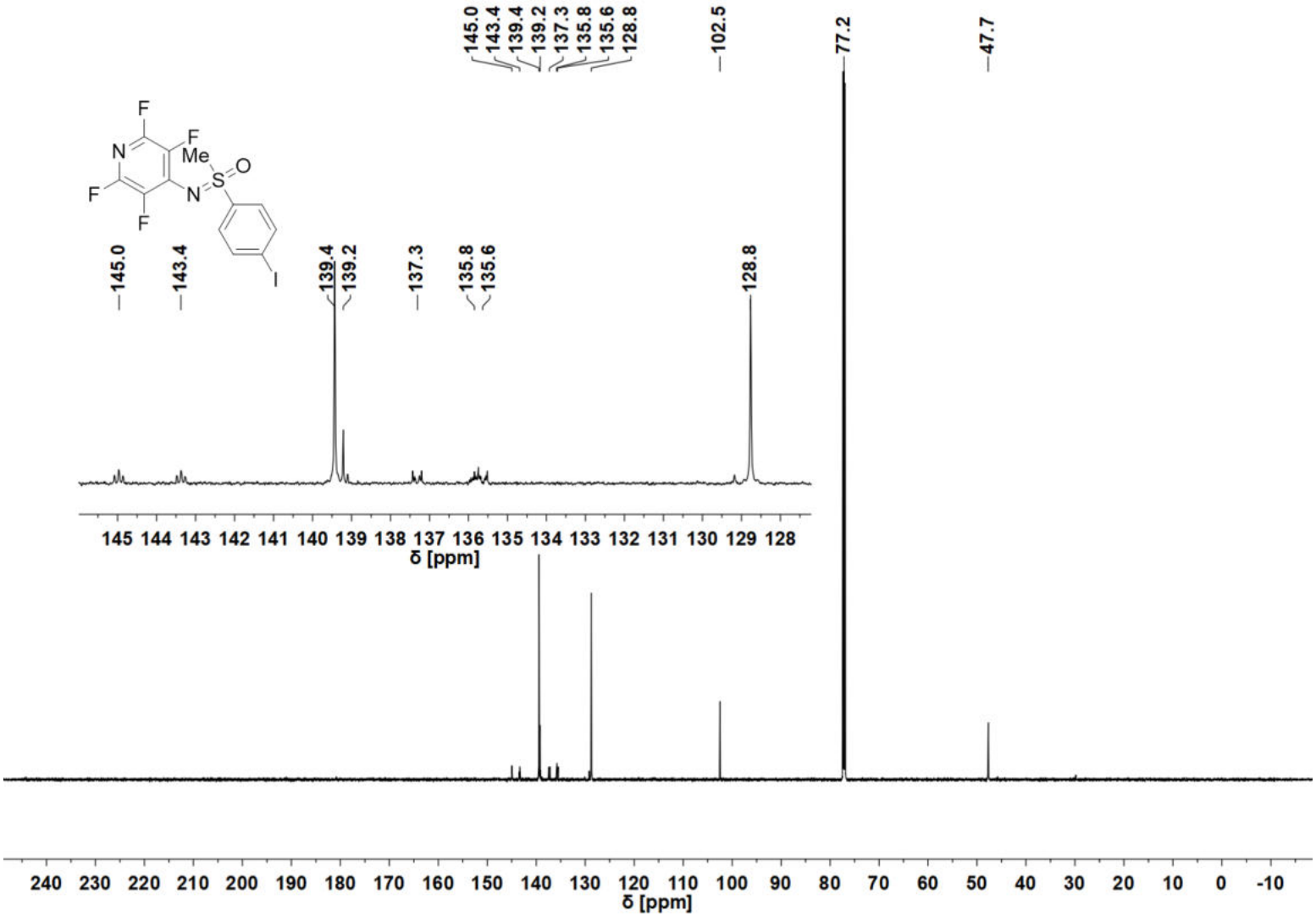

Figure S85 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3i**.

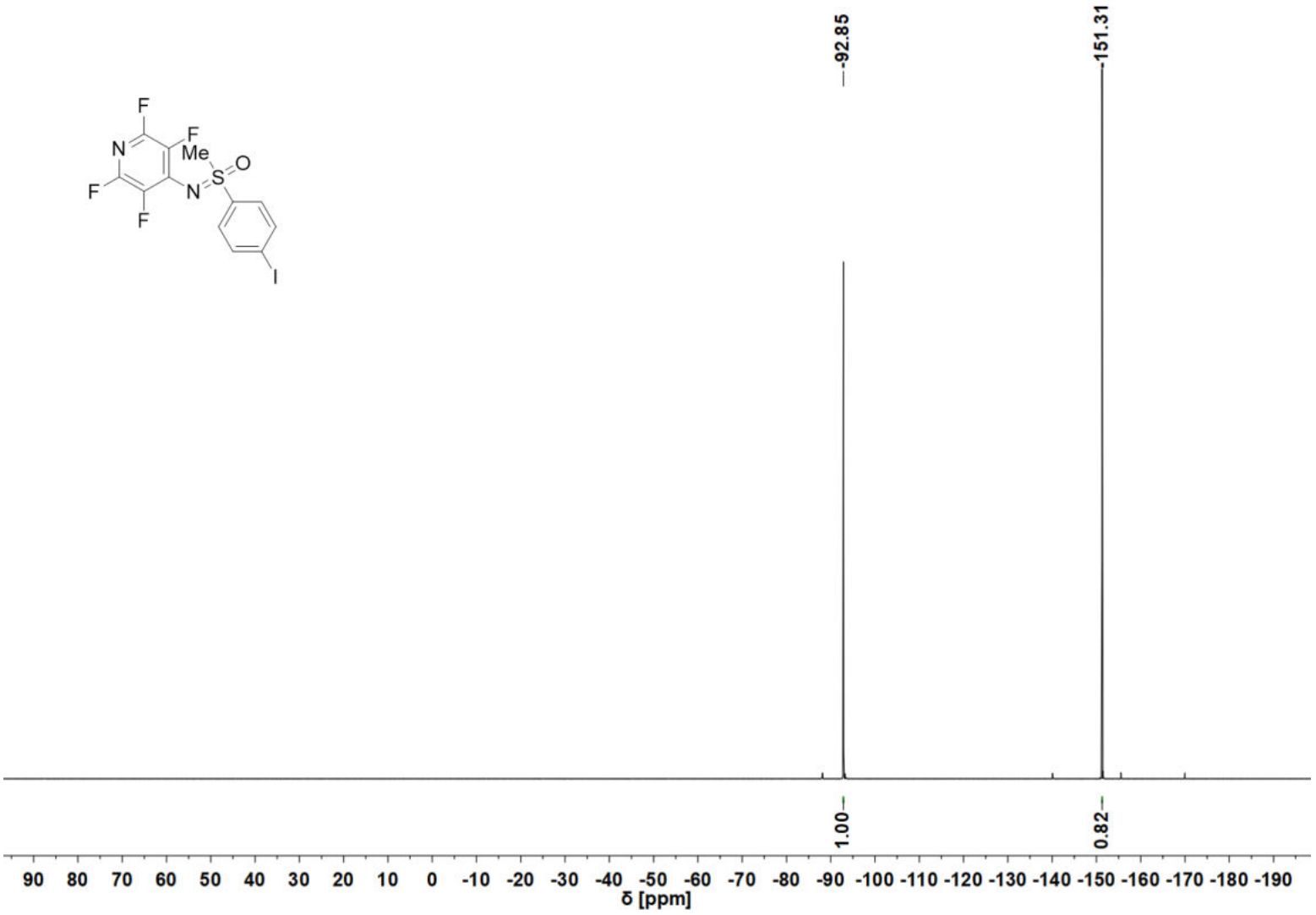

Figure S86 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3i**.

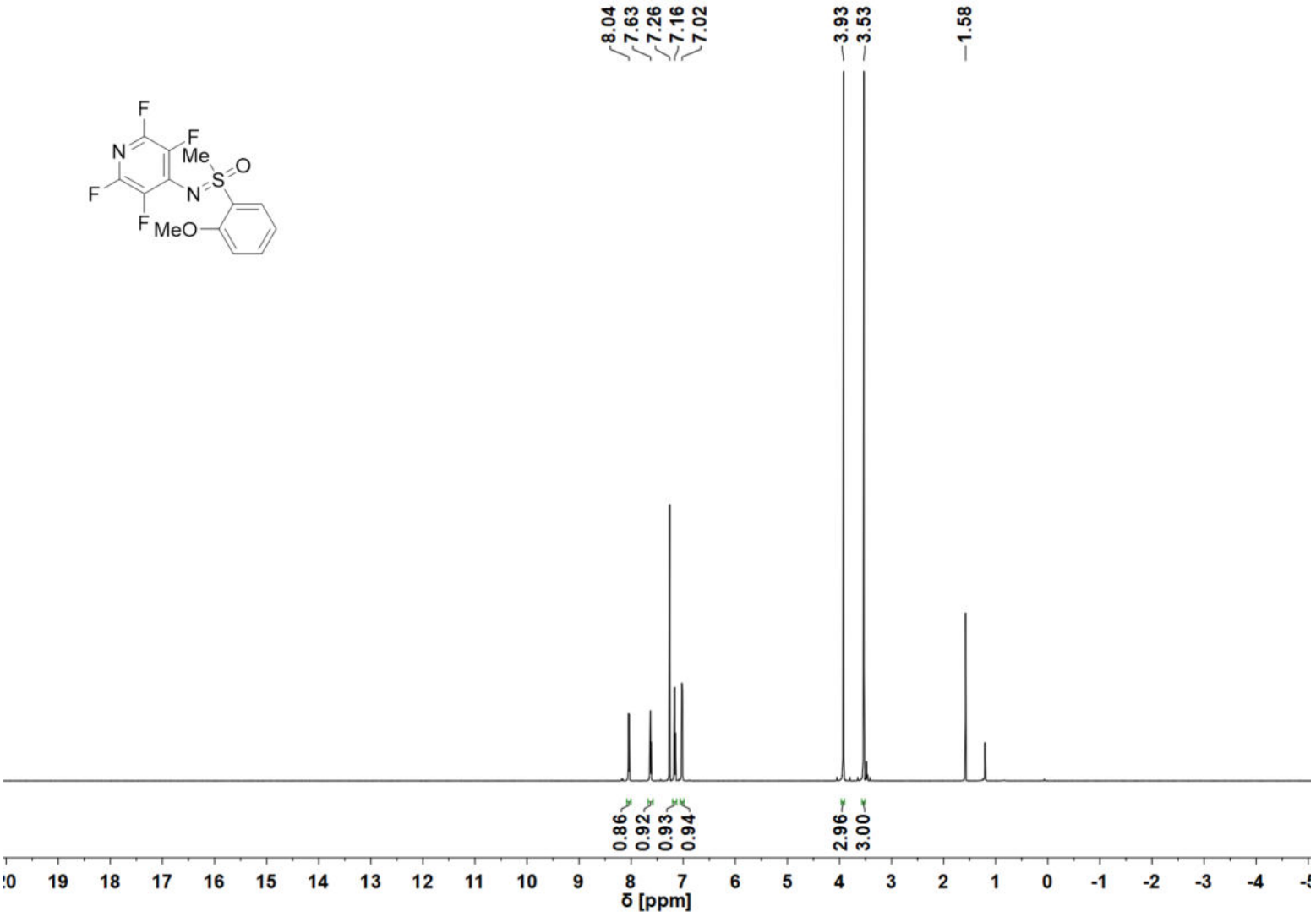

Figure S87 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3j**.

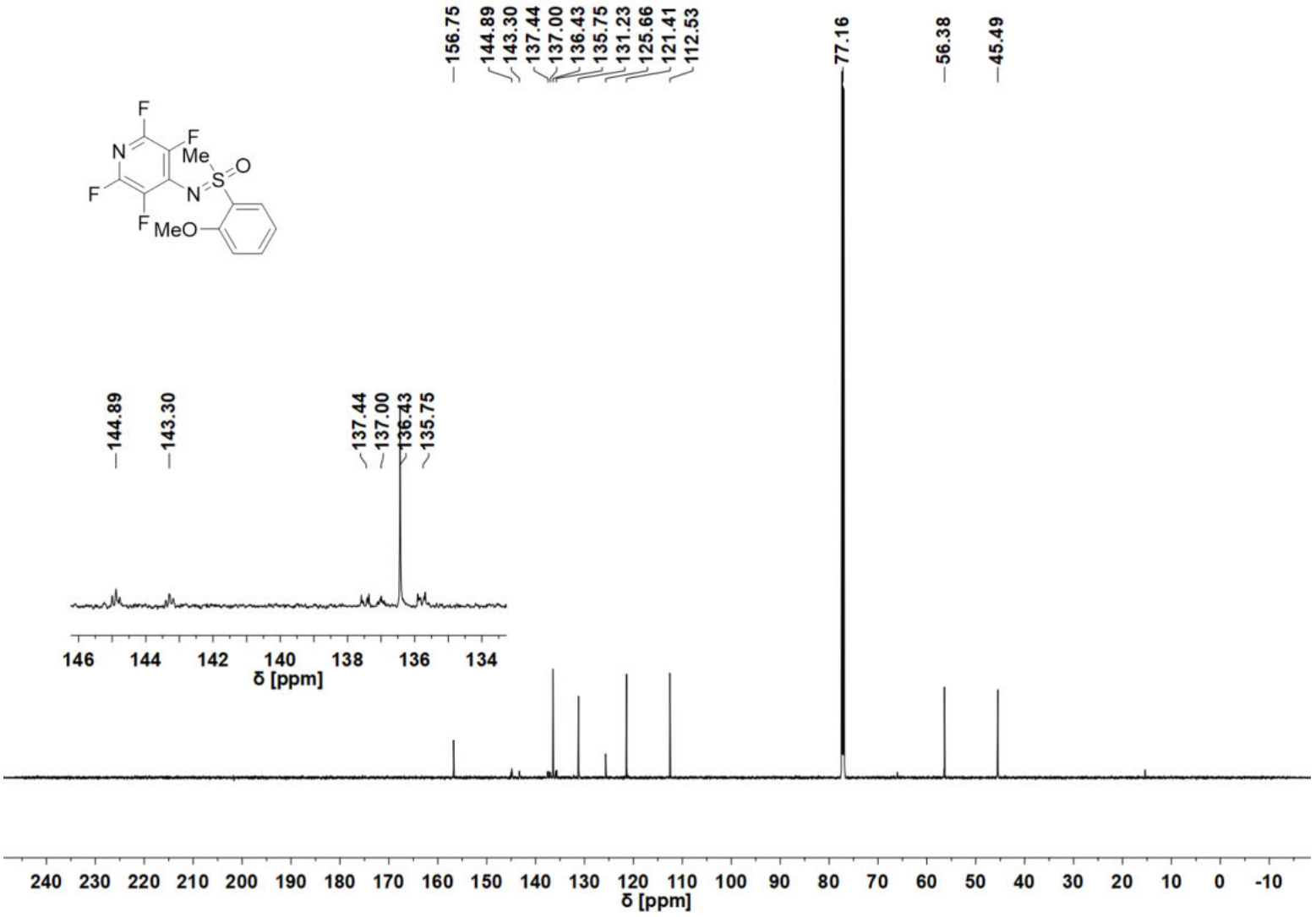

Figure S88 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3j**.

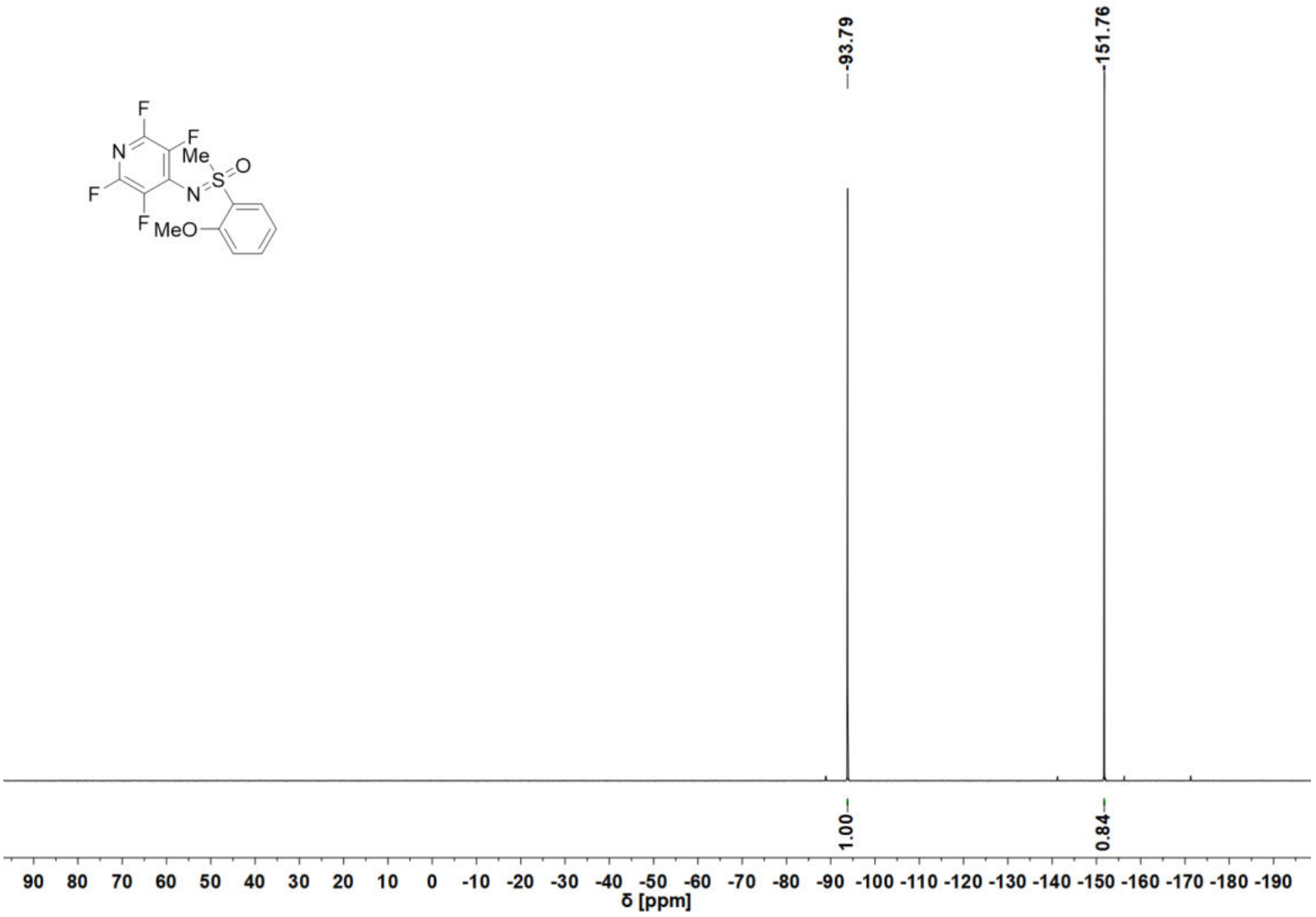

Figure S89 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3j**.

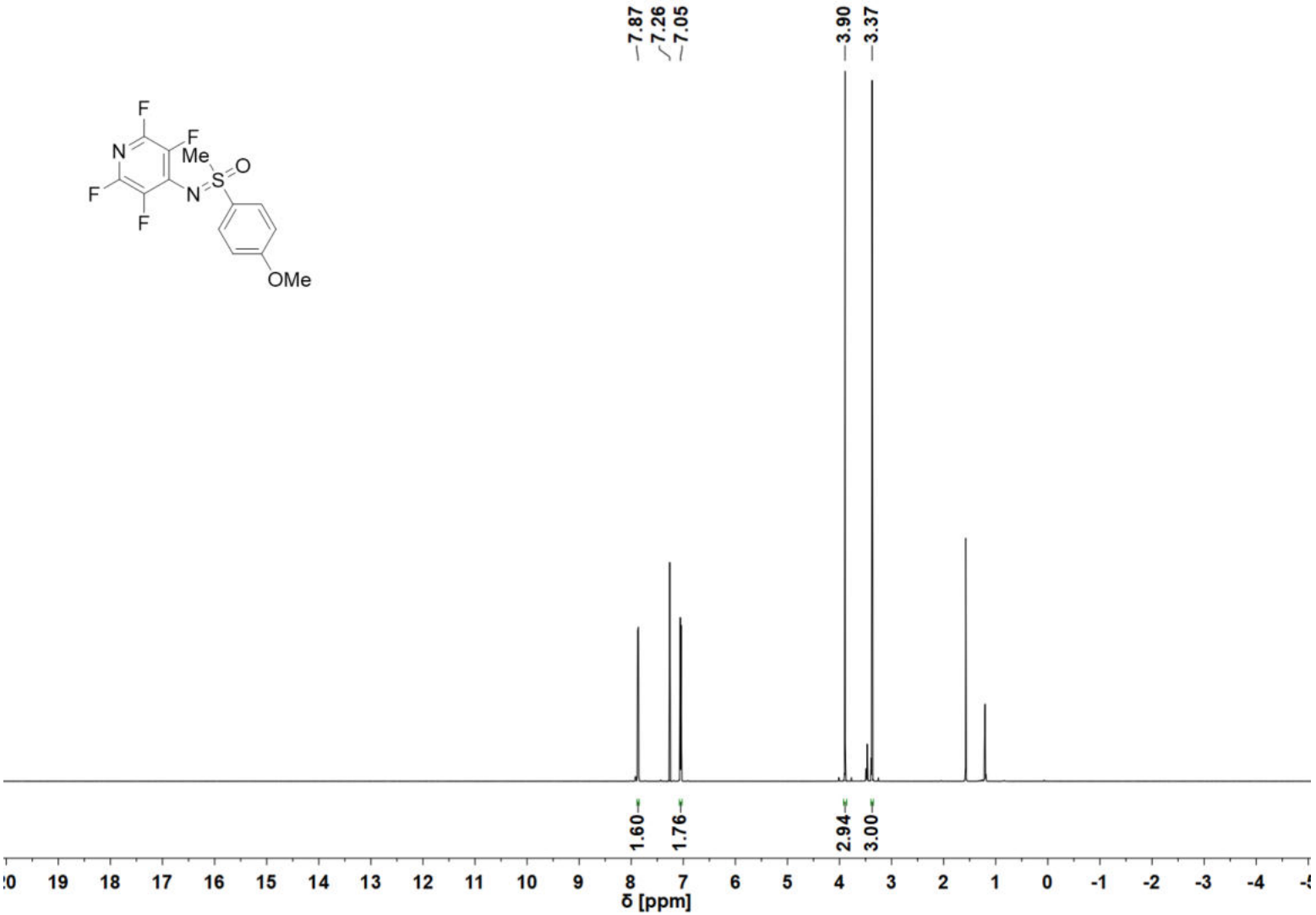

Figure S90 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3k**.

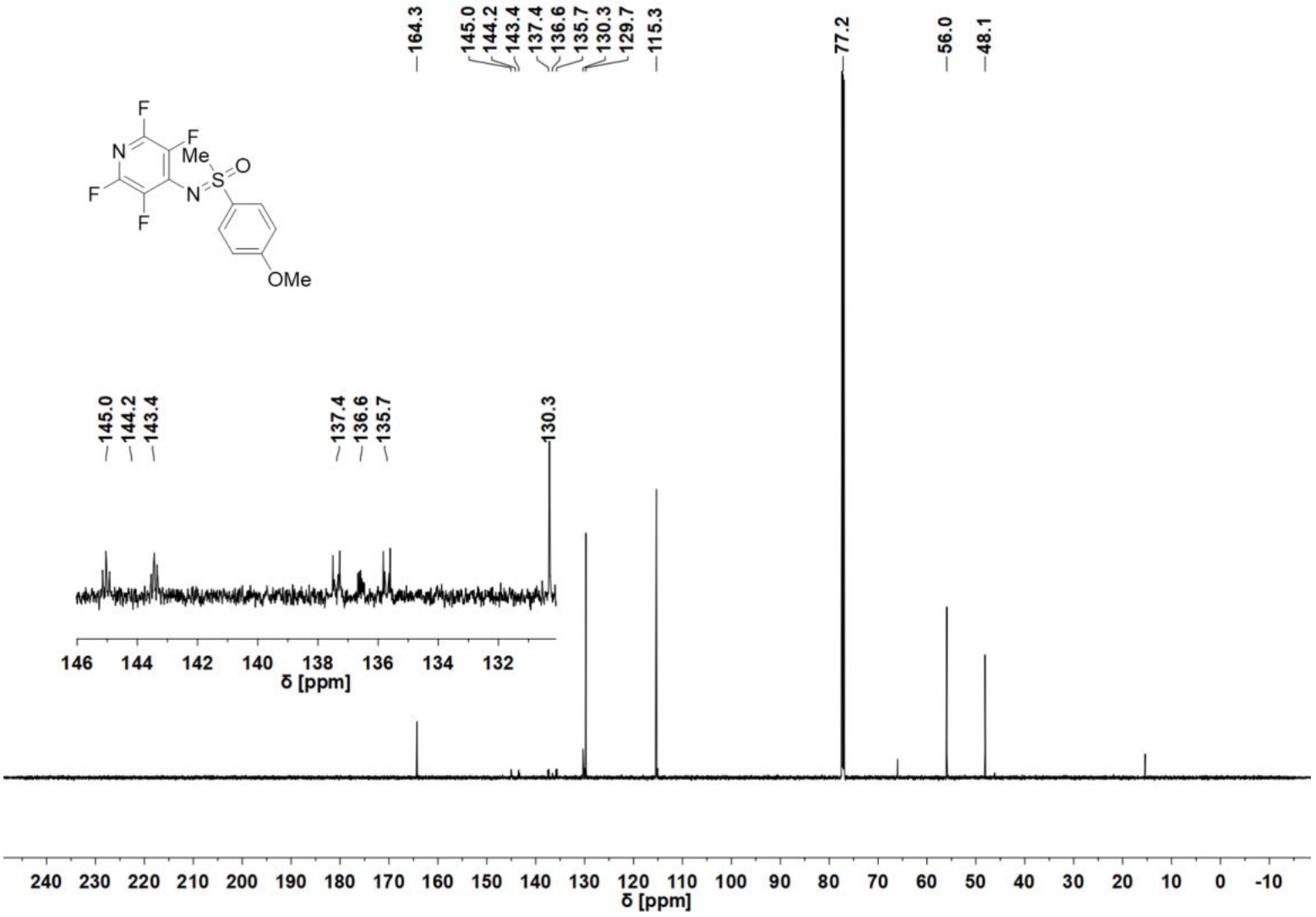

Figure S91 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3k**.

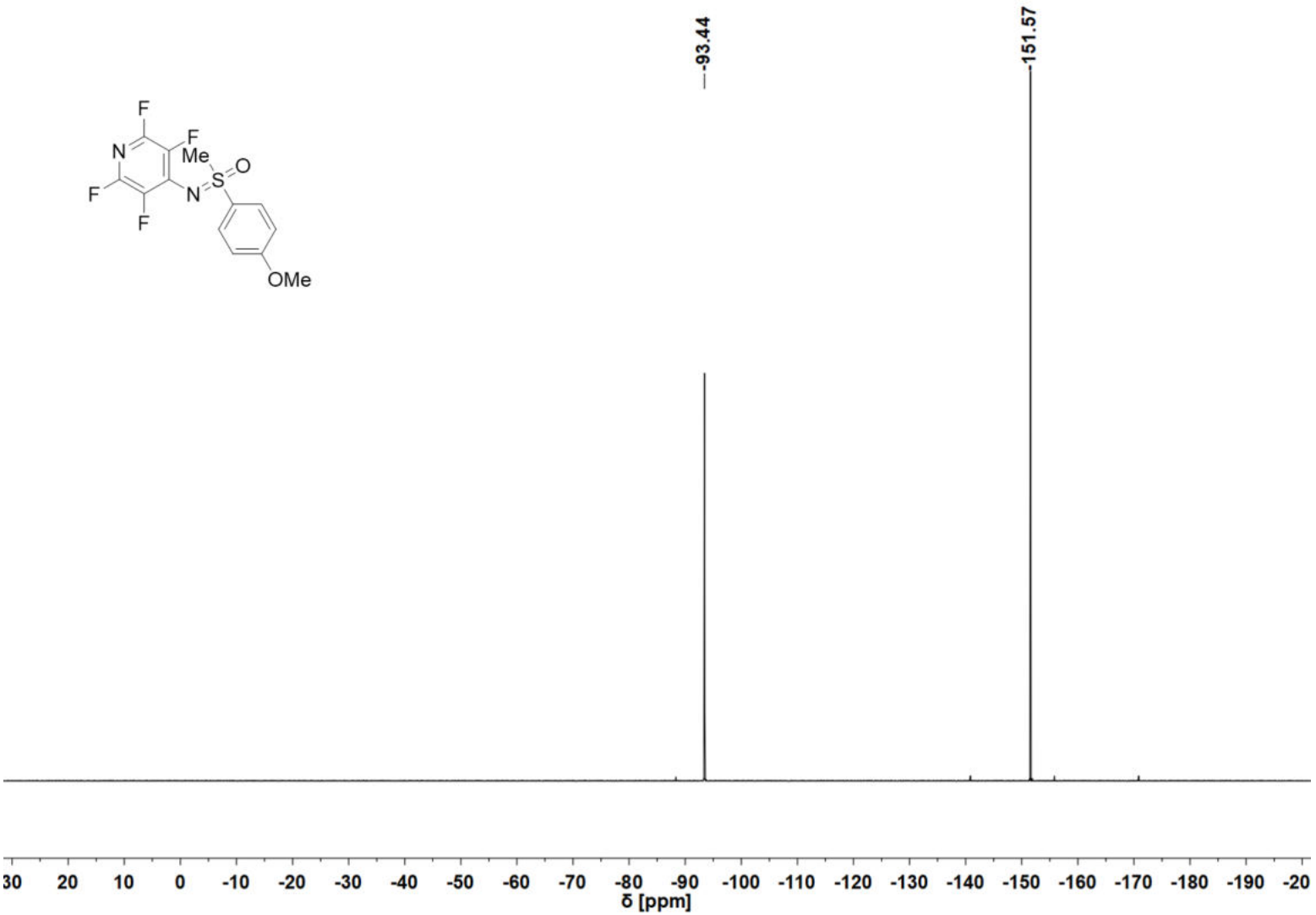

Figure S92 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3k**.

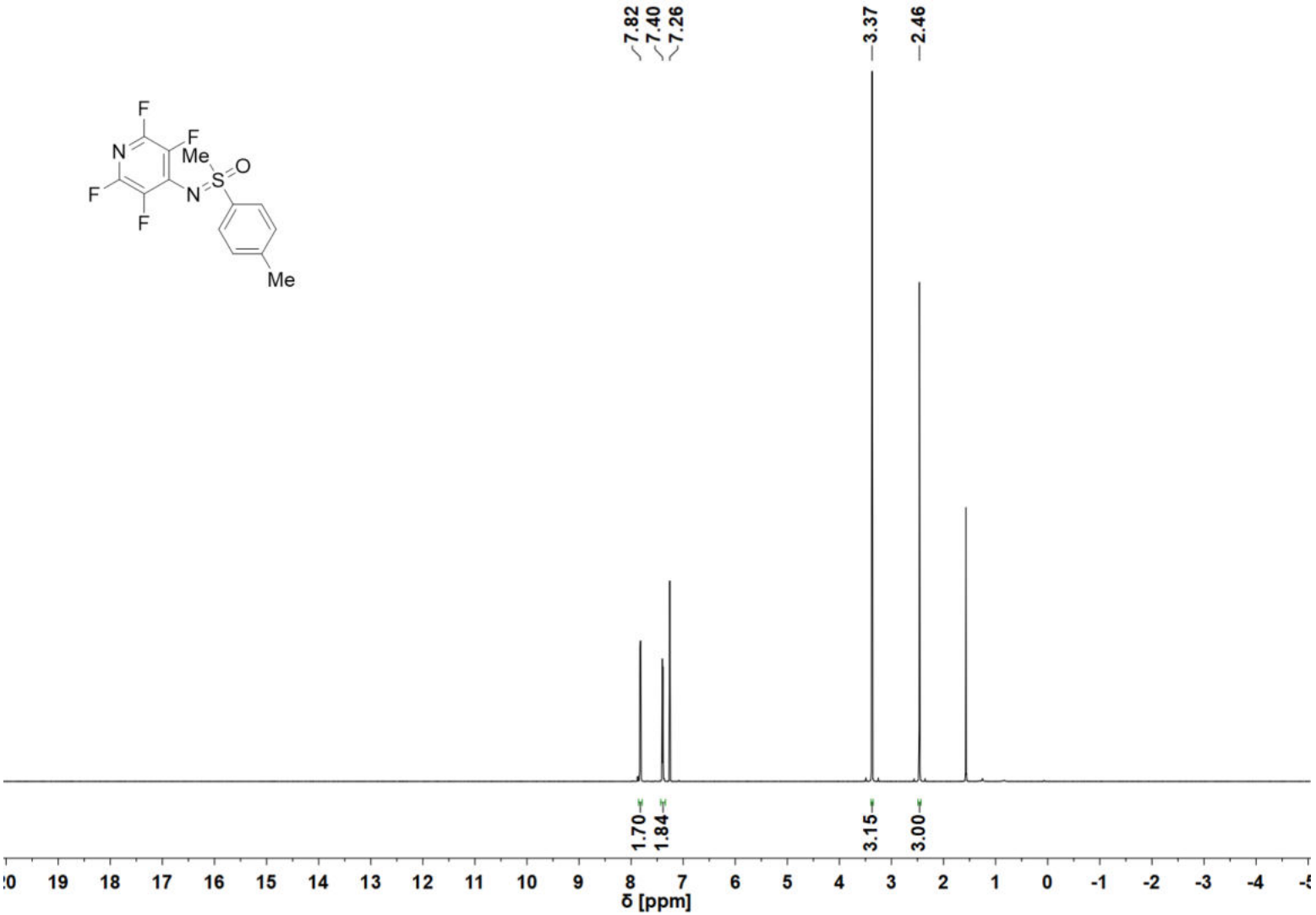

Figure S93 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3l**.

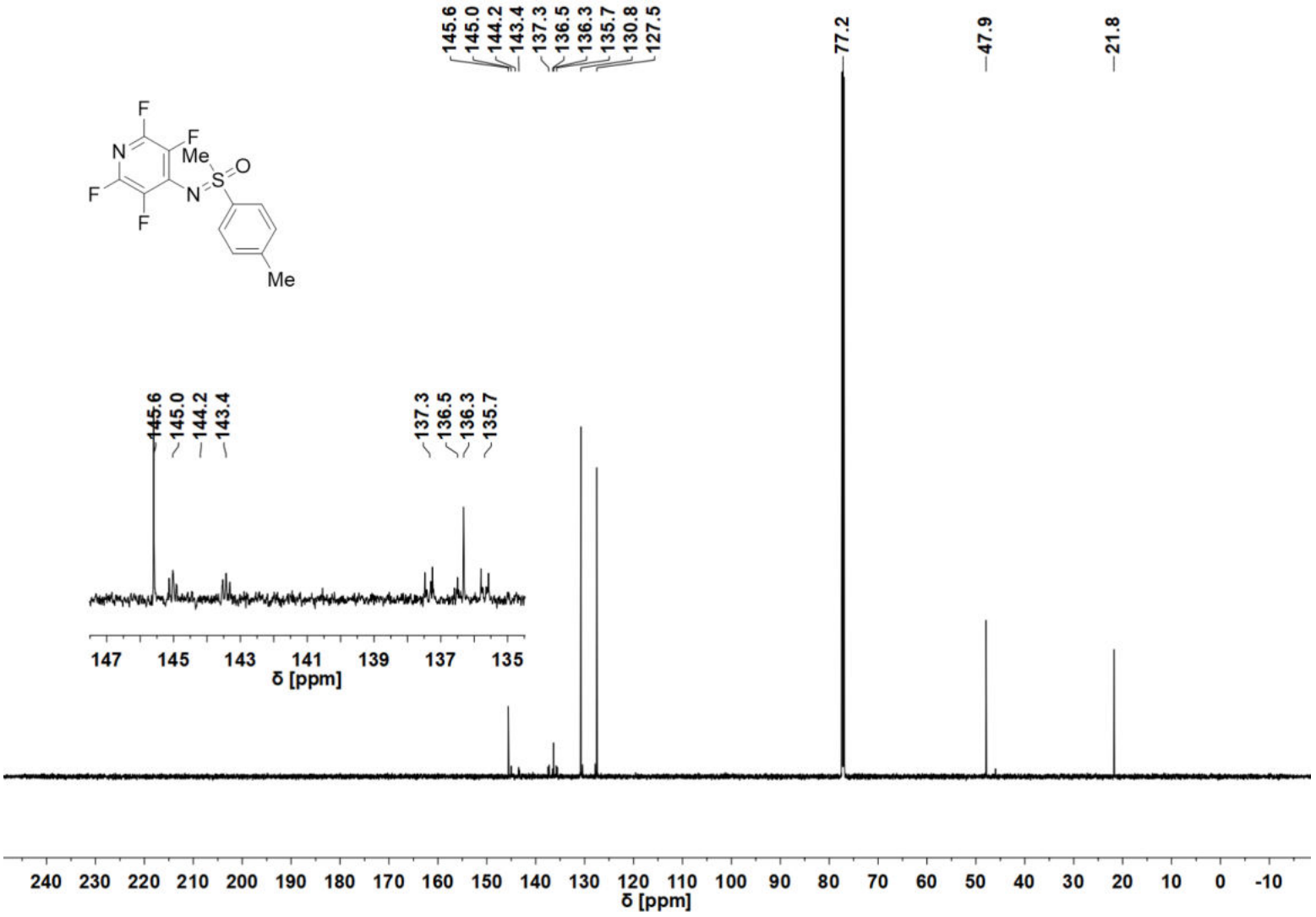

Figure S94 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3l**.

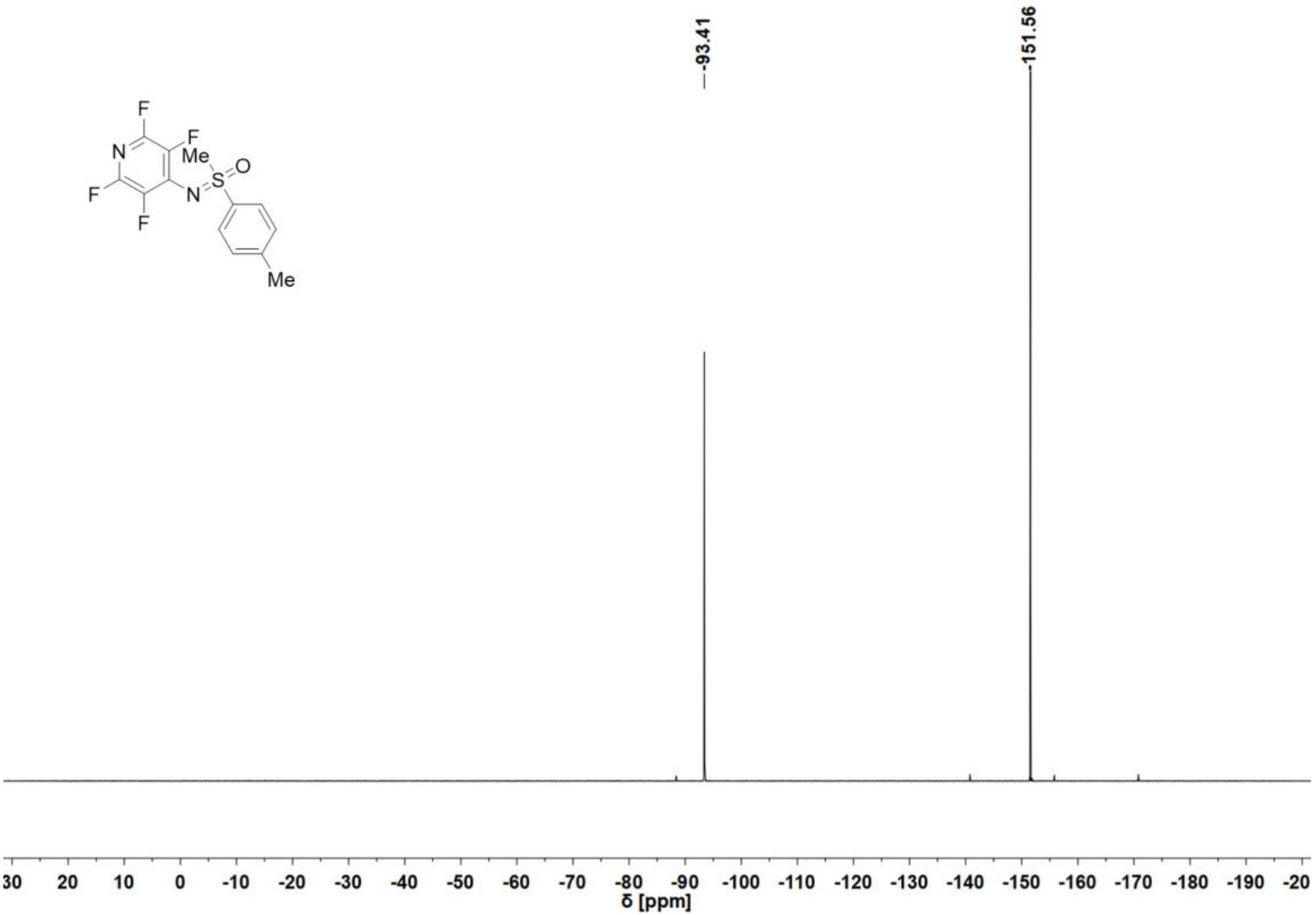

Figure S95 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3l**.

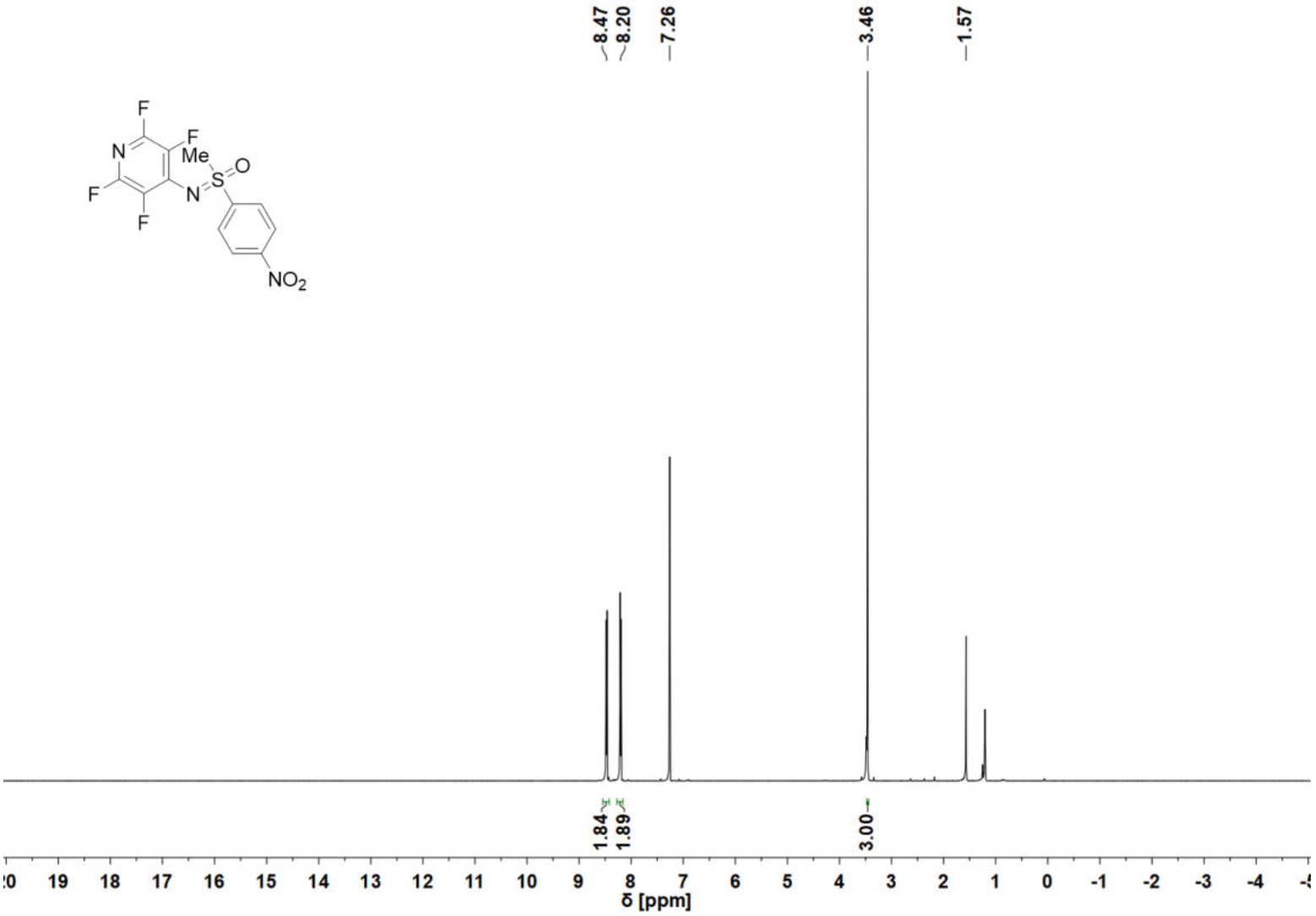

Figure S96 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3m**.

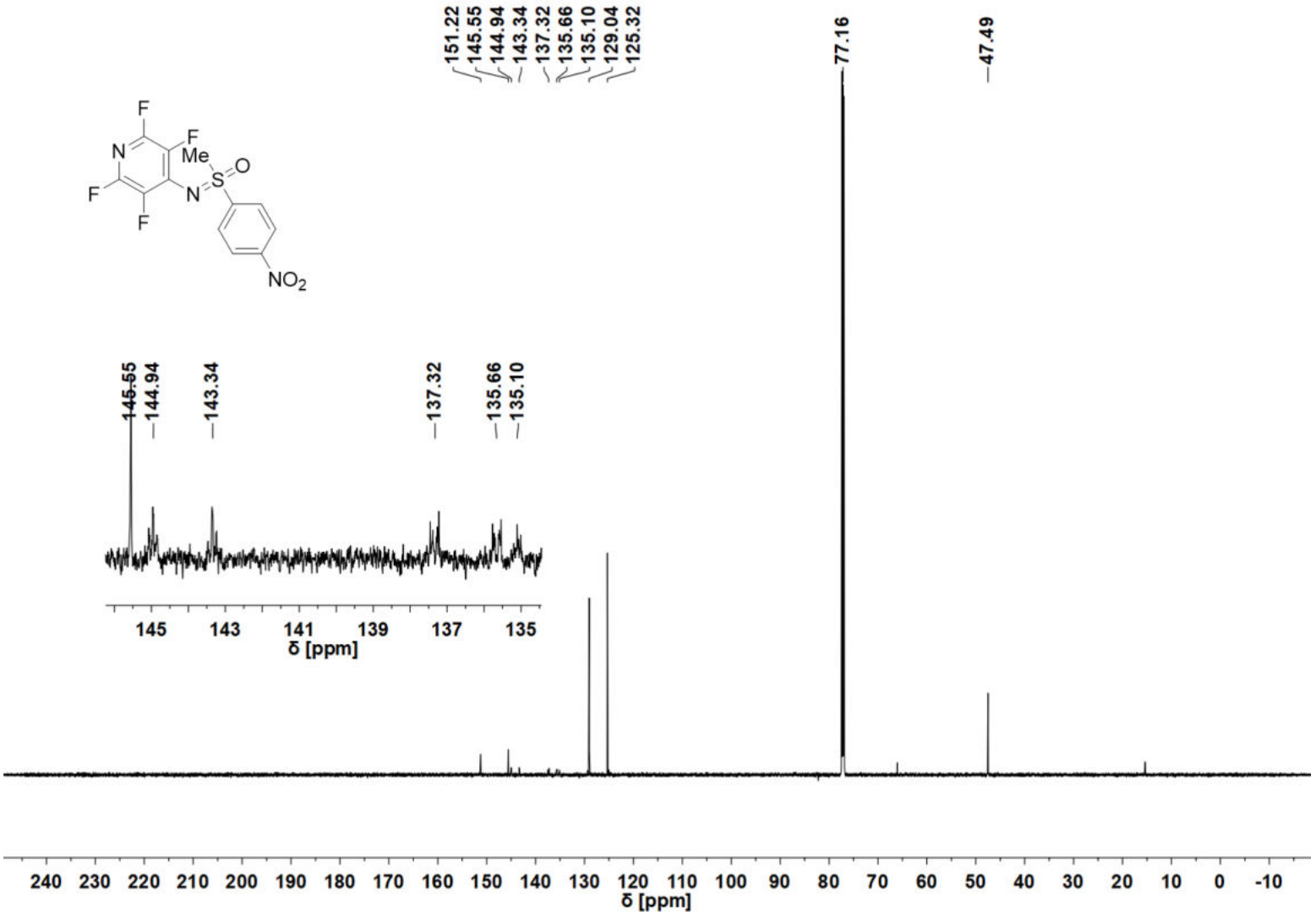

Figure S97 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3m**.

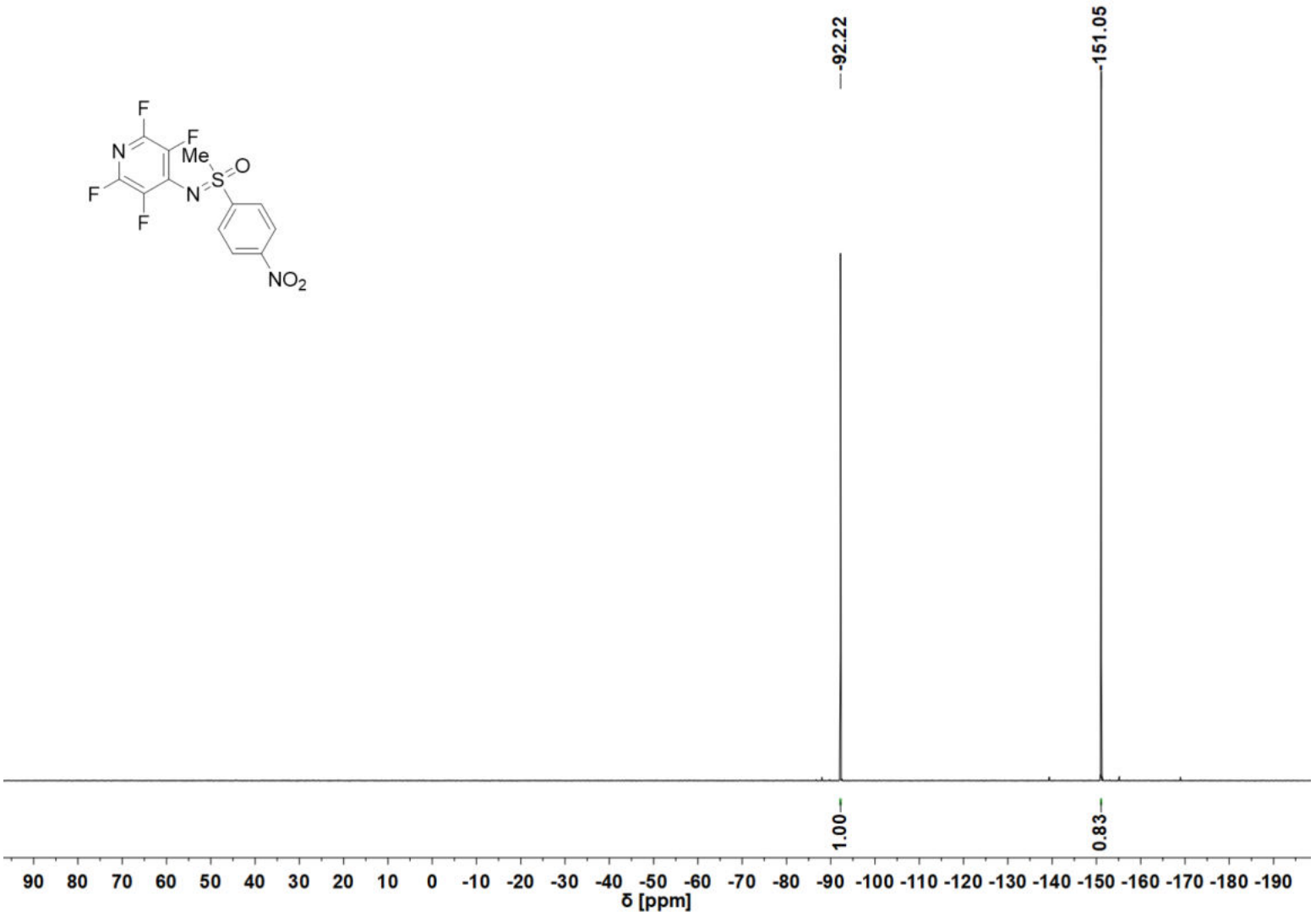

Figure S98 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3m**.

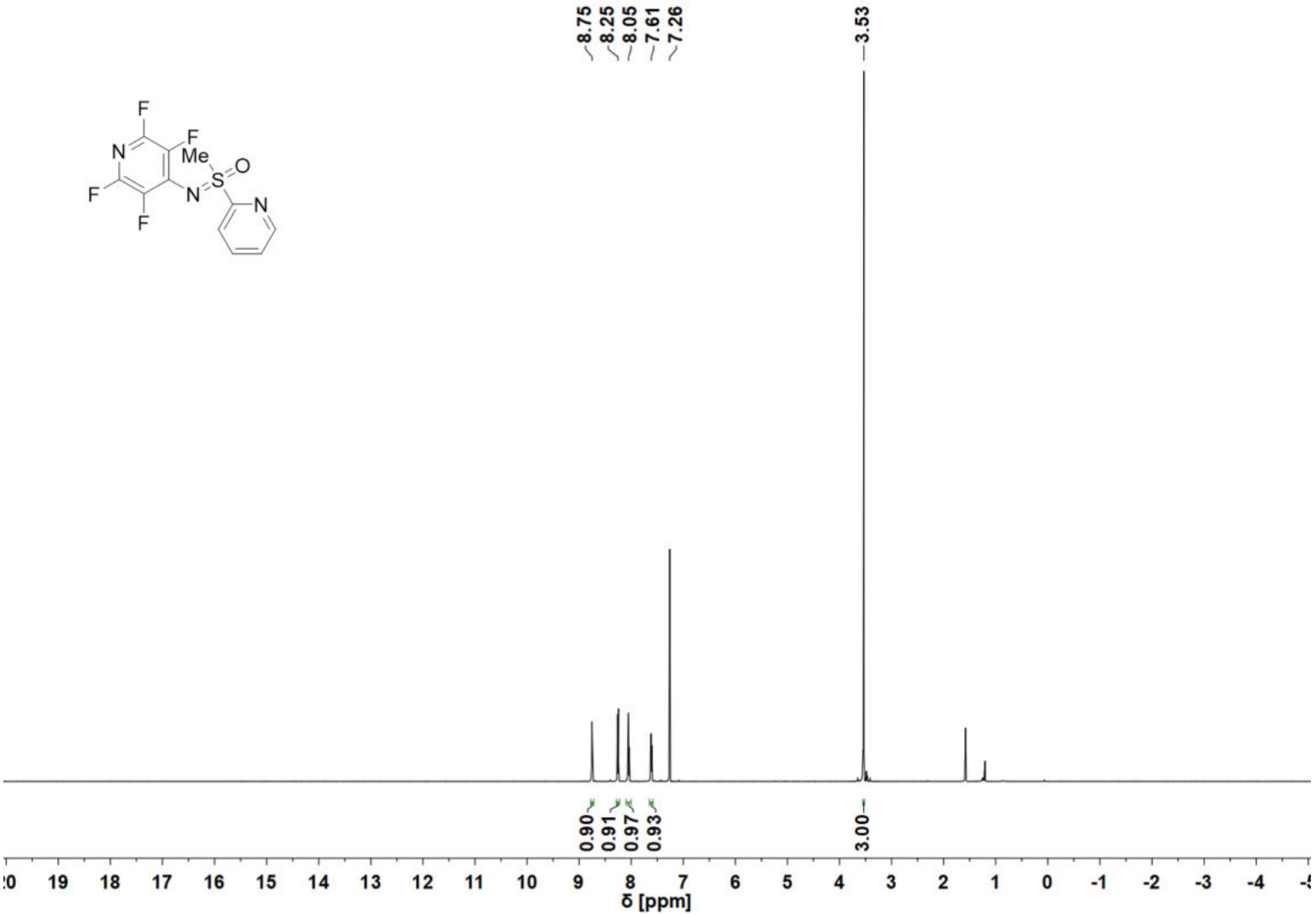

Figure S99 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3n**.

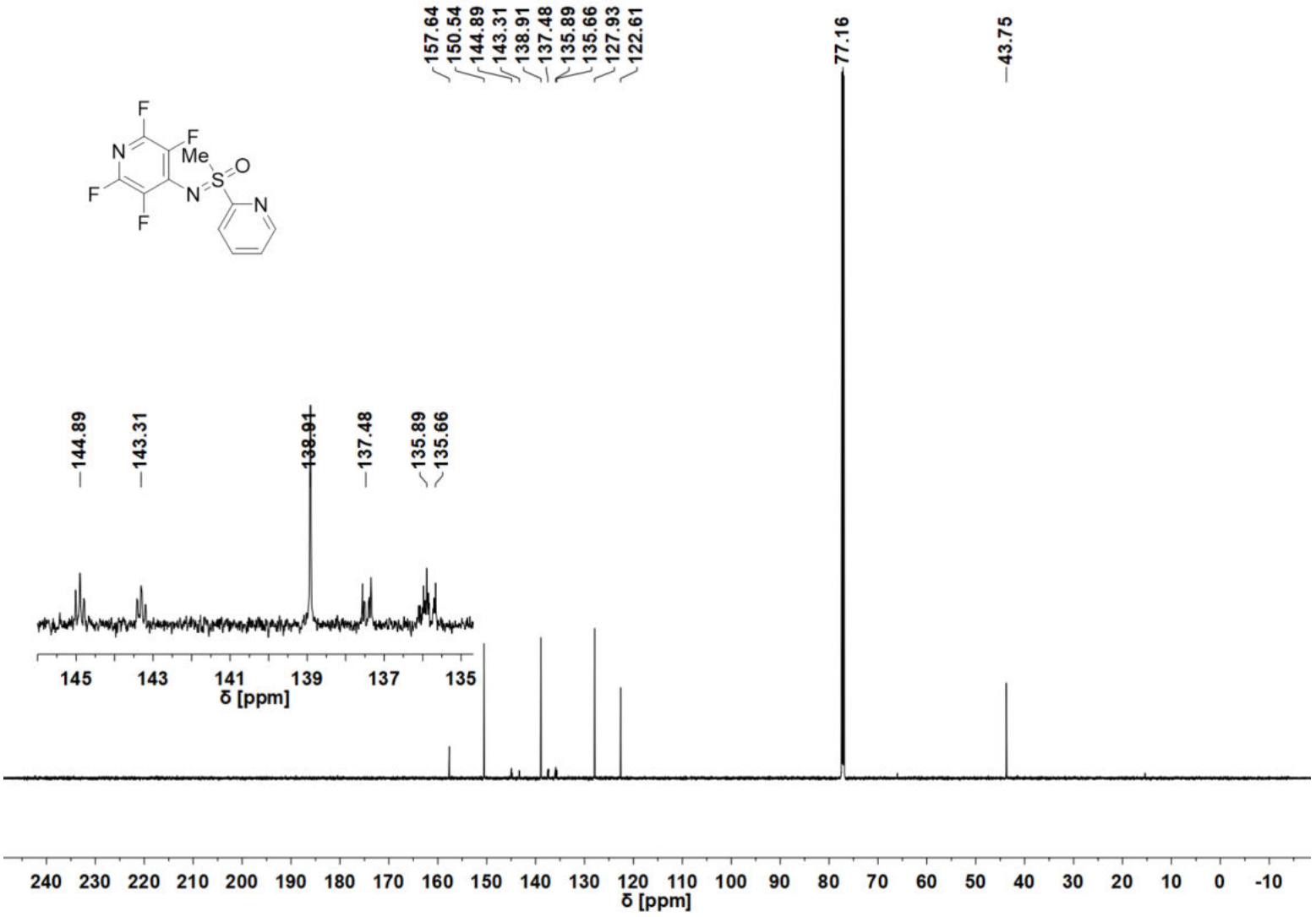

Figure S100 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3n**.

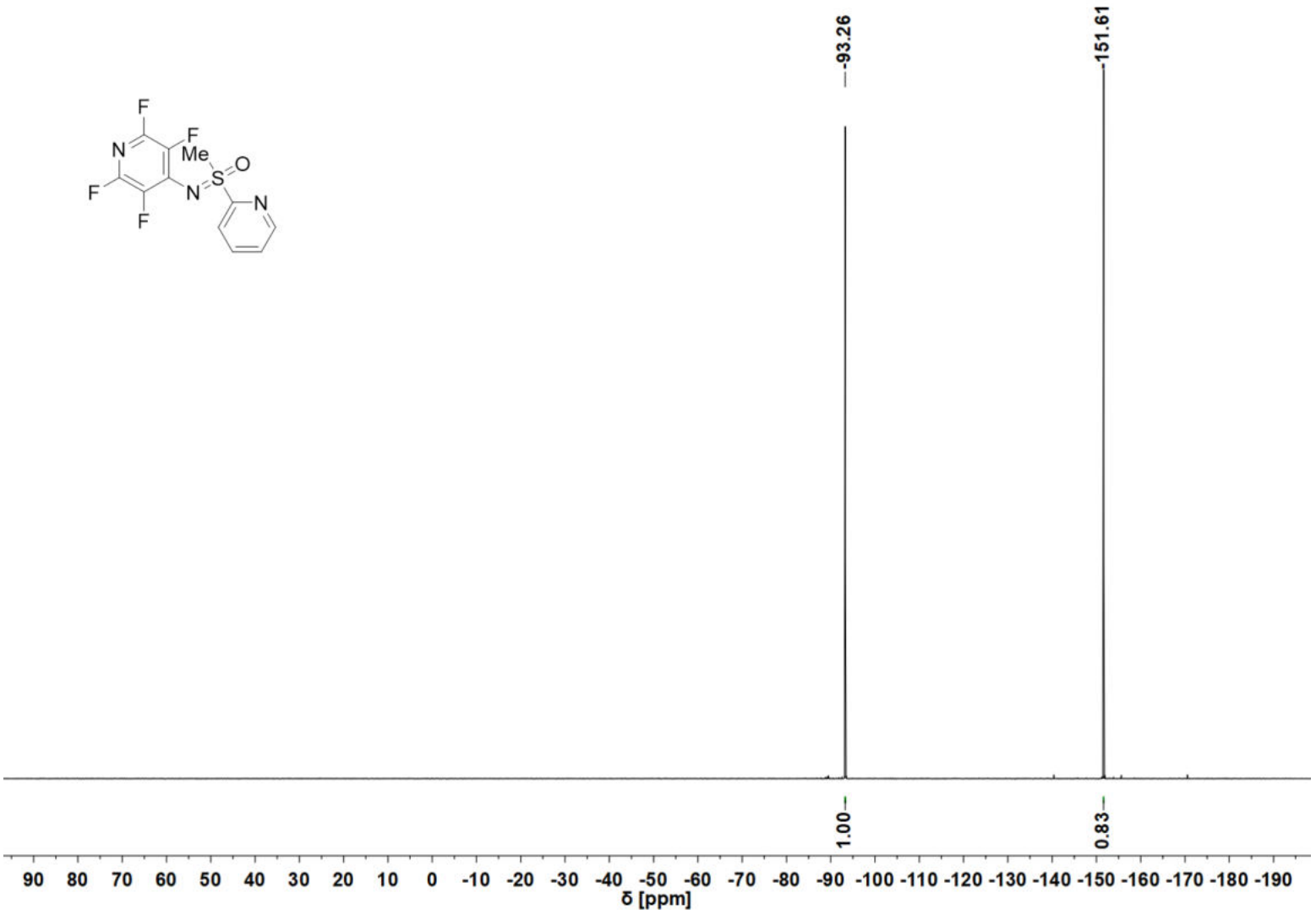

Figure S101 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3n**.

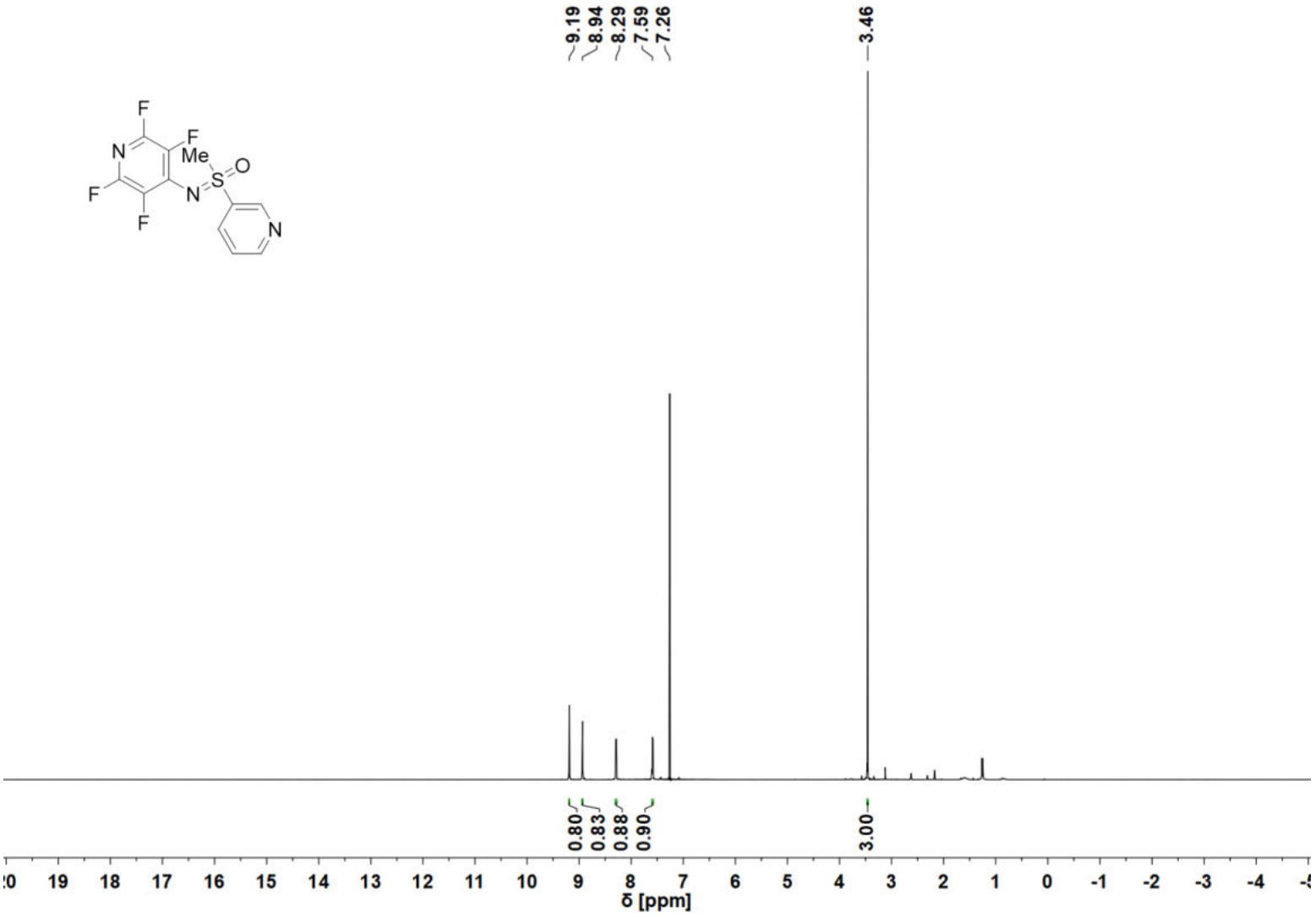

Figure S102 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3o**.

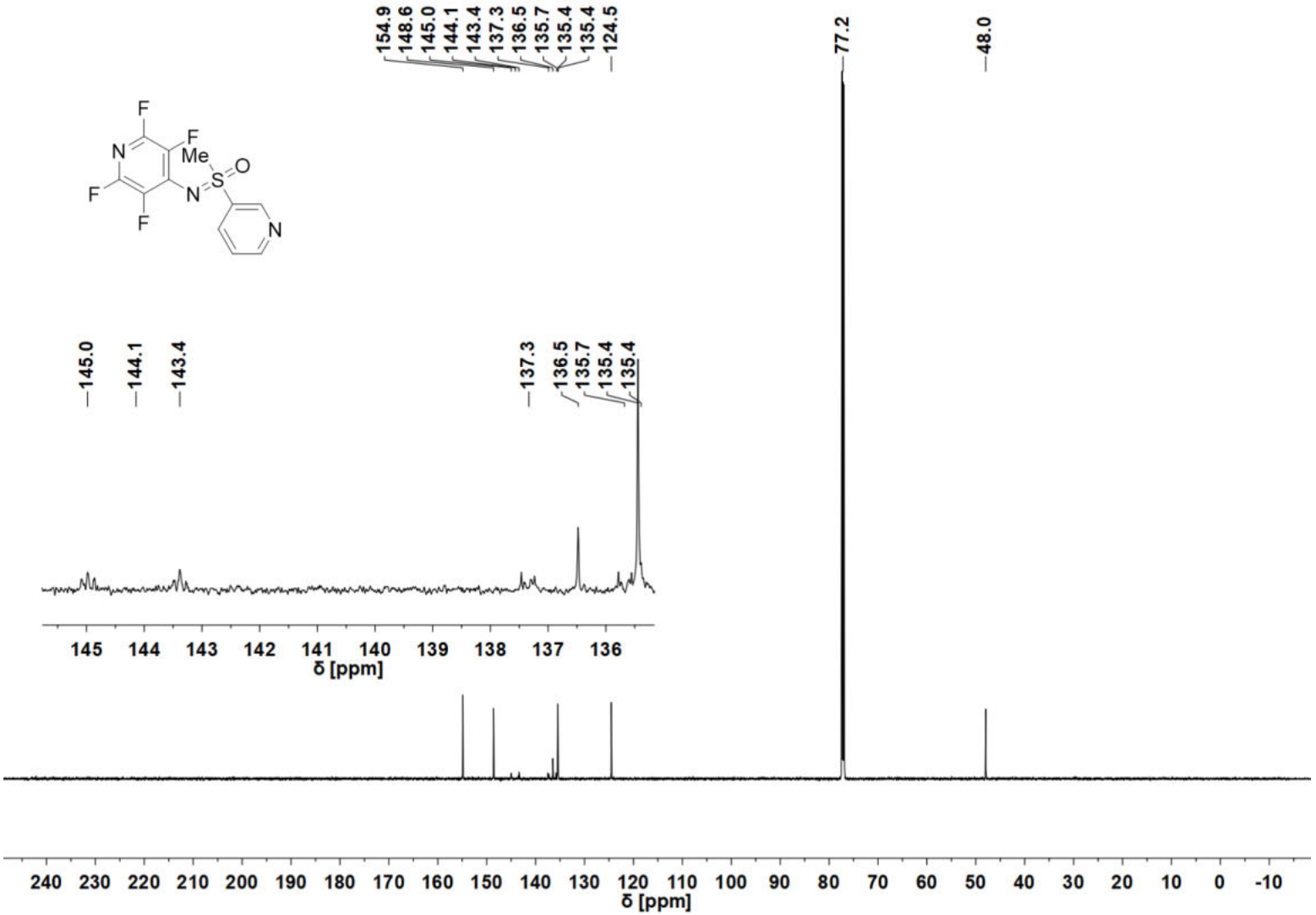

Figure S103 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3o**.

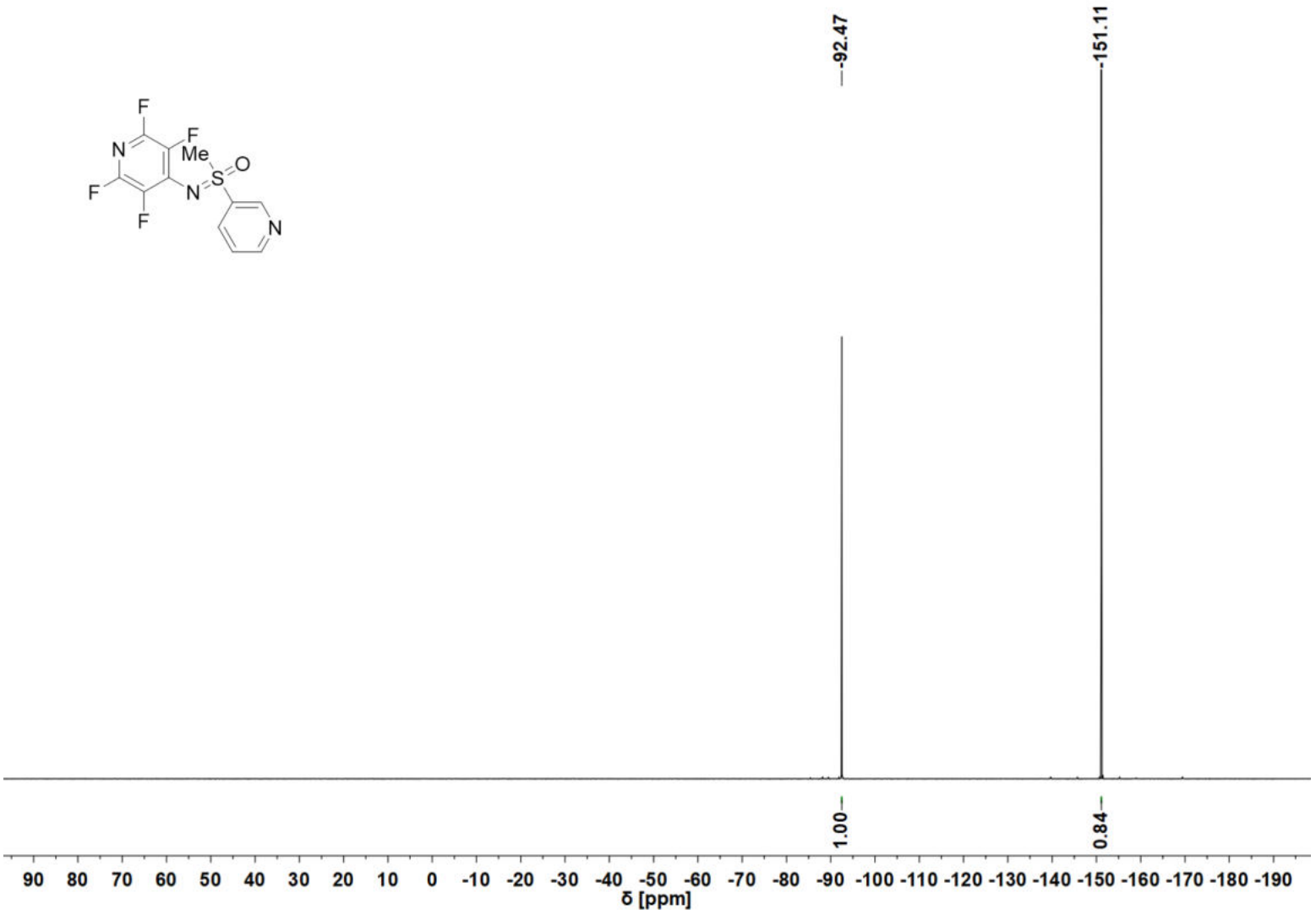

Figure S104 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3o**.

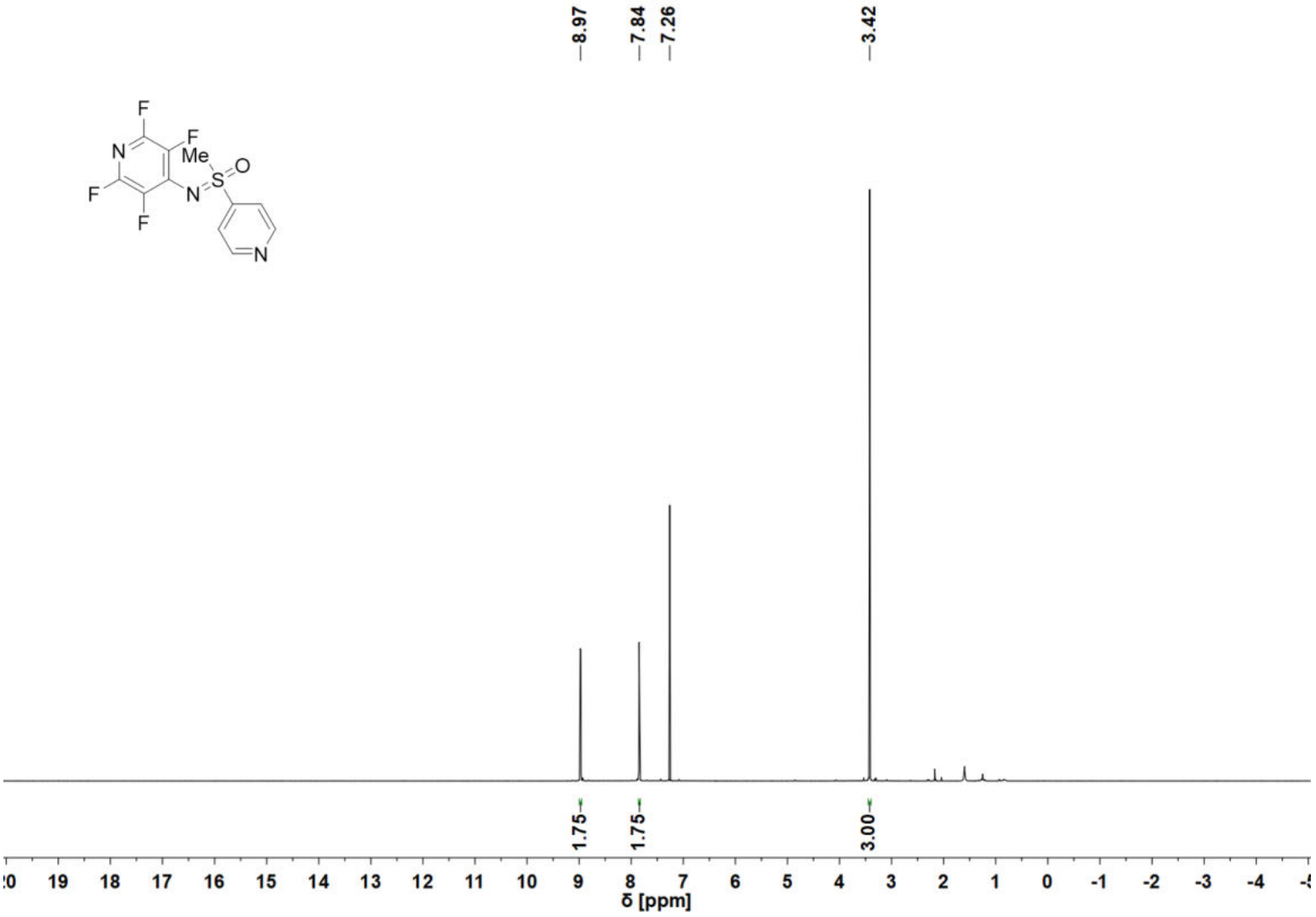

Figure S105 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3p**.

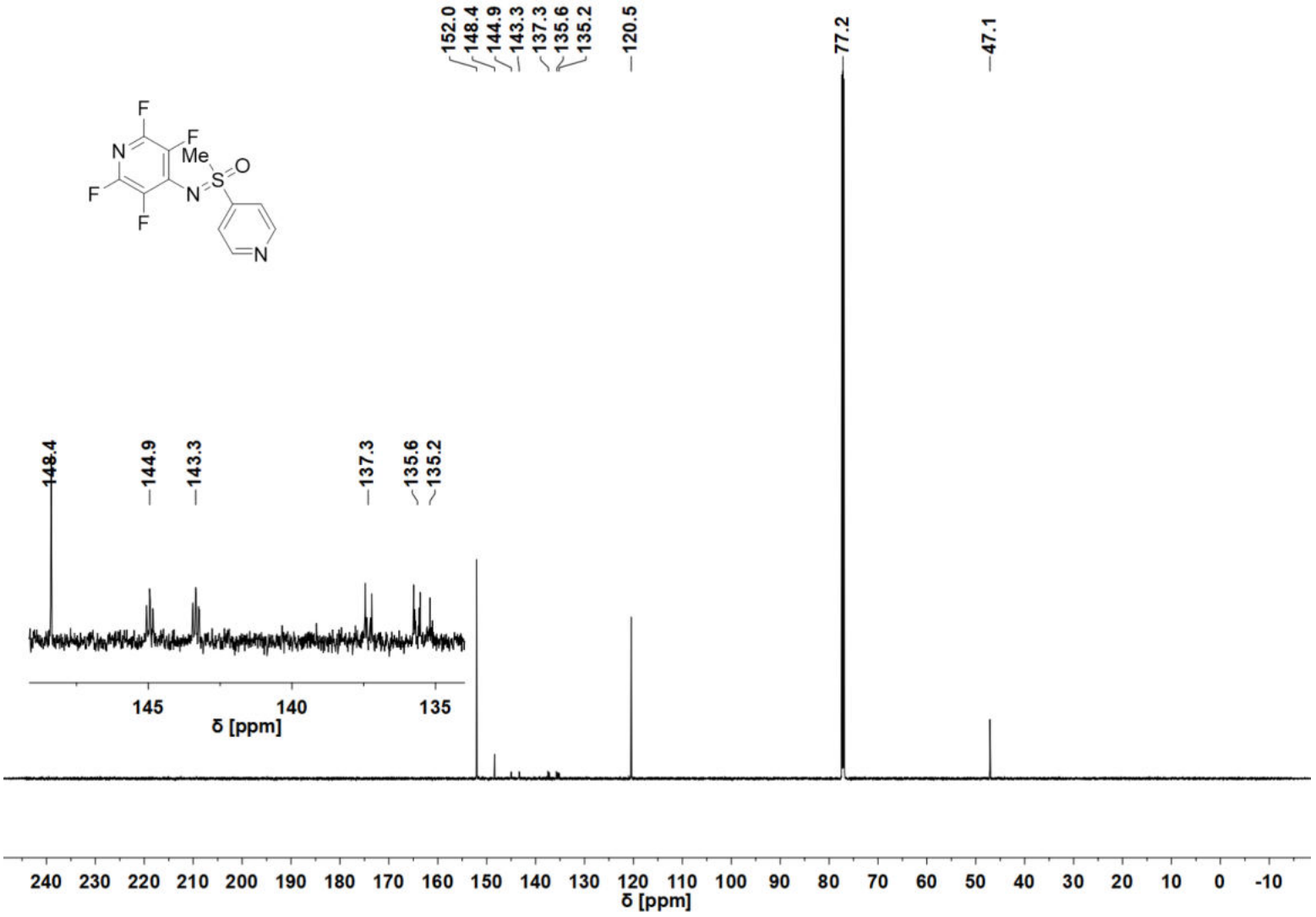

Figure S106 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3p**.

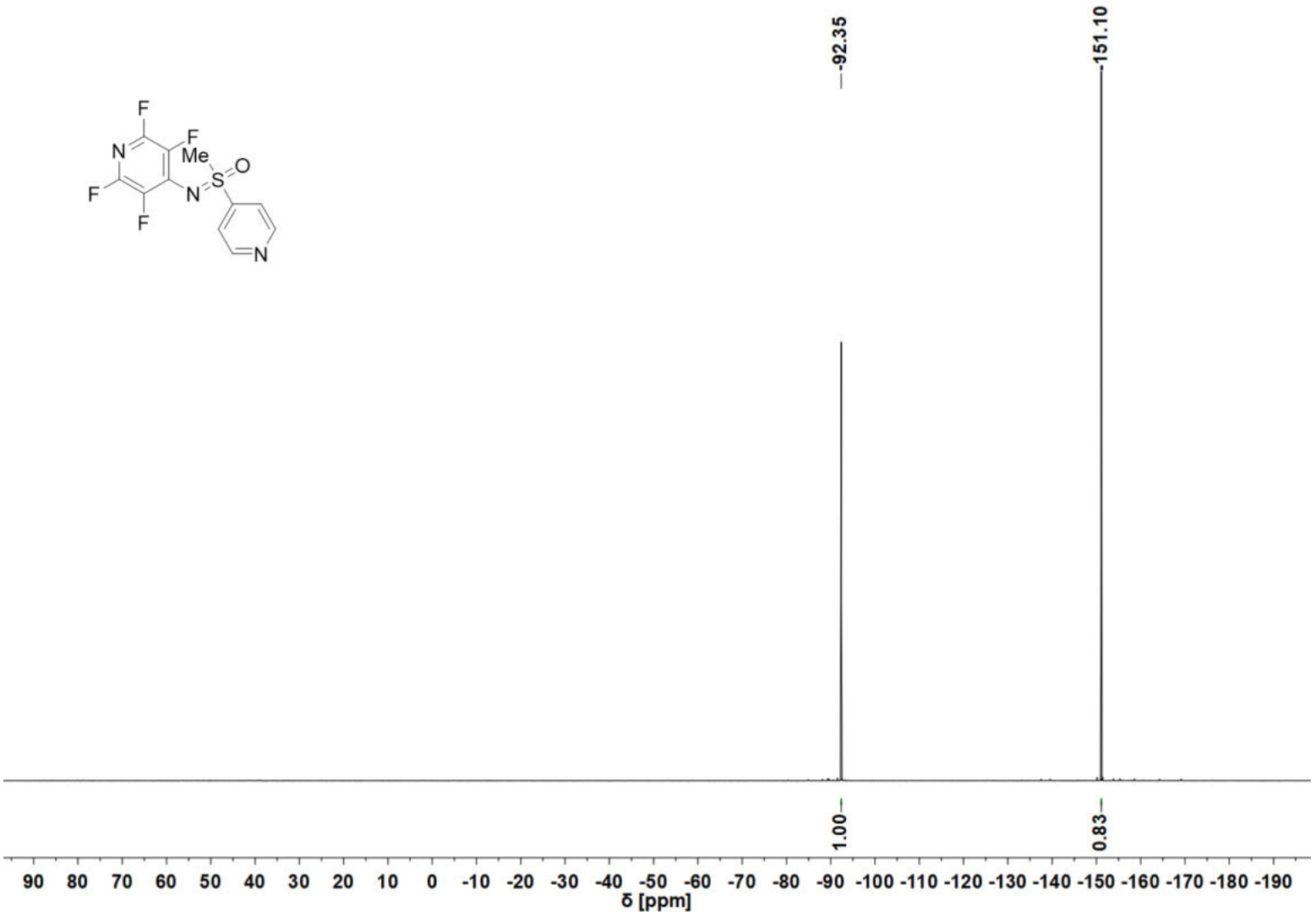

Figure S107 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3p**.

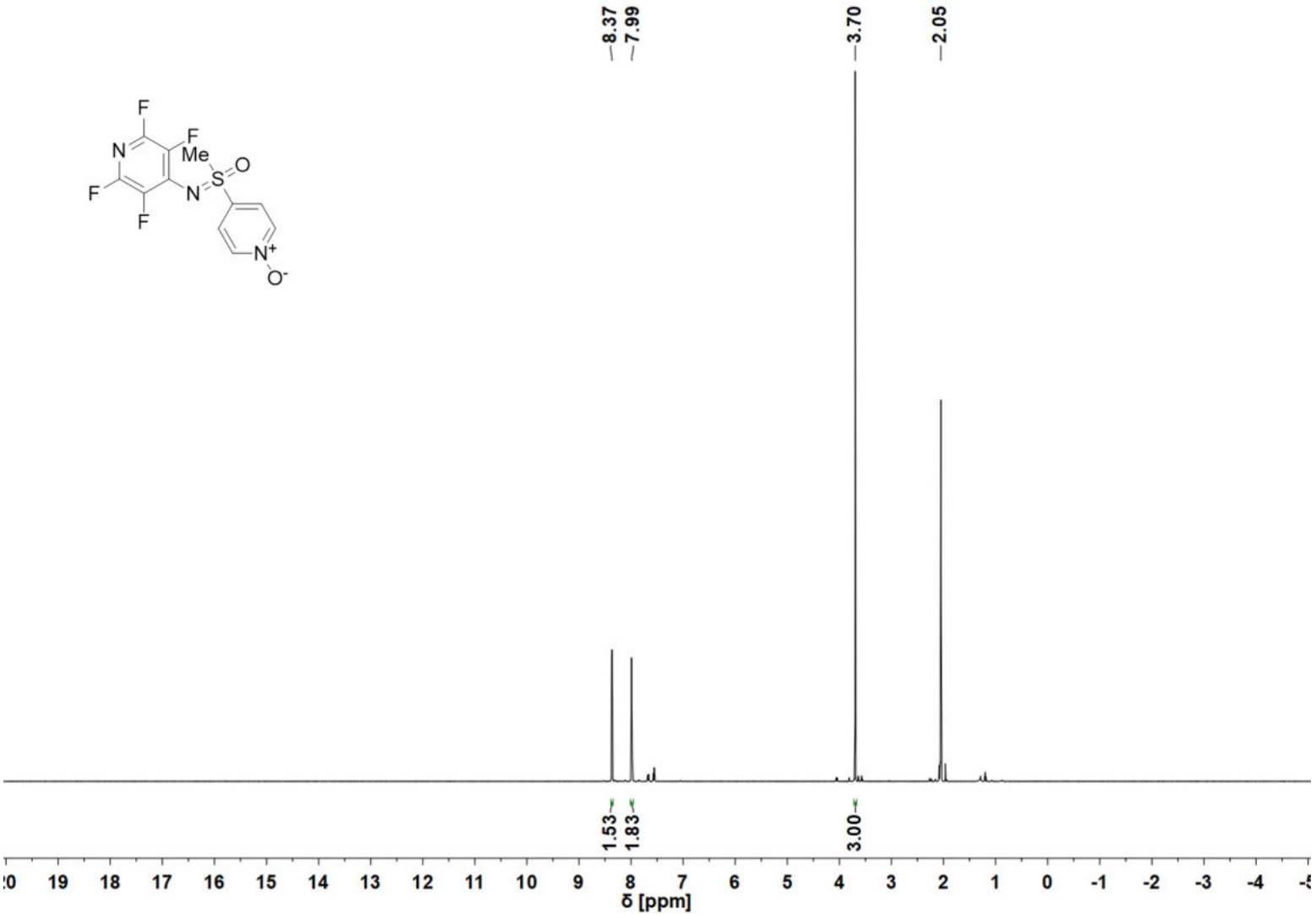

Figure S108 ^{1}H NMR spectrum ($(CD_3)_2CO$, 600 MHz) of **3q**.

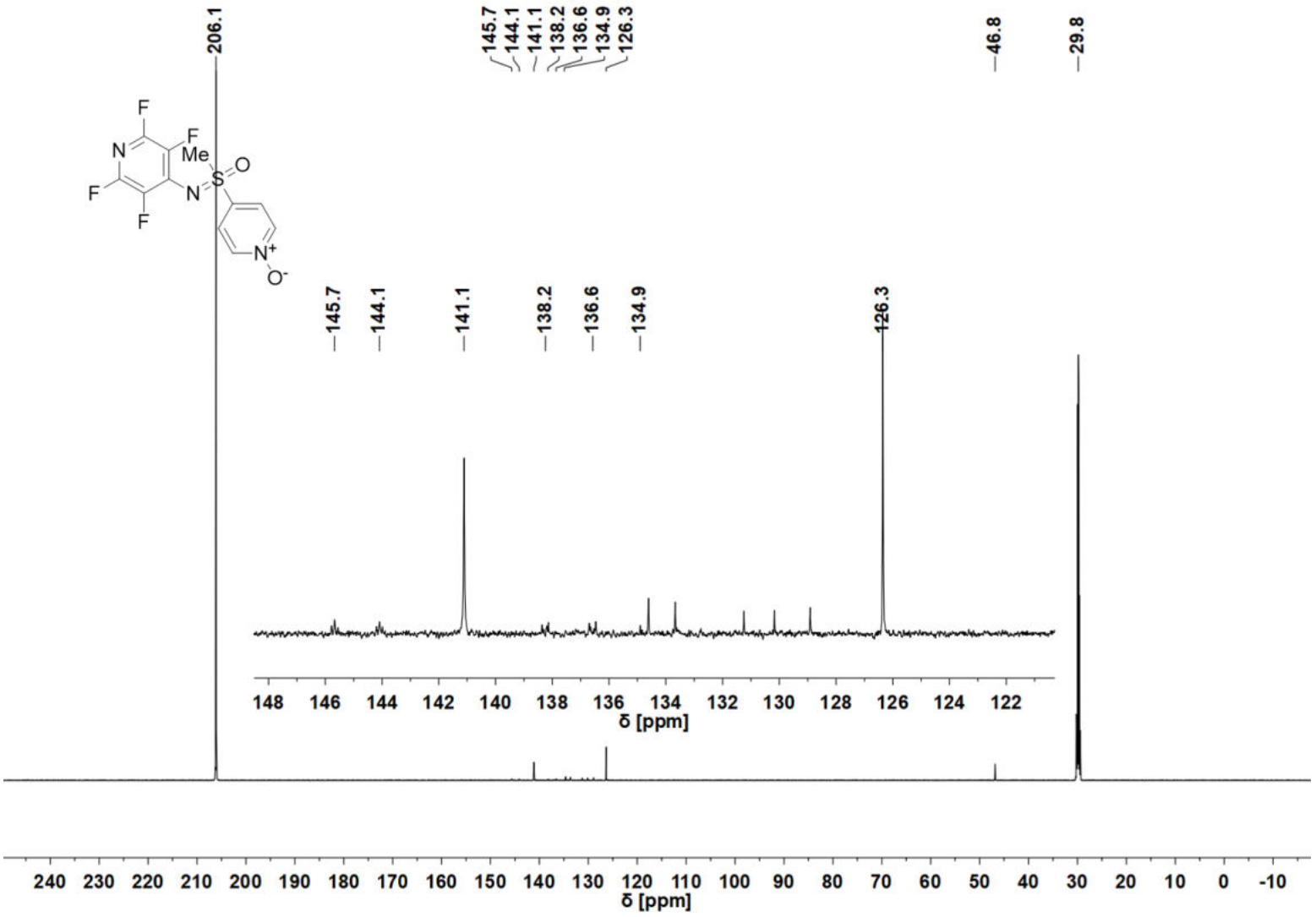

Figure S109 ^{13}C {^{1}H} NMR spectrum ($(CD_3)_2CO$, 151 MHz) of **3q**.

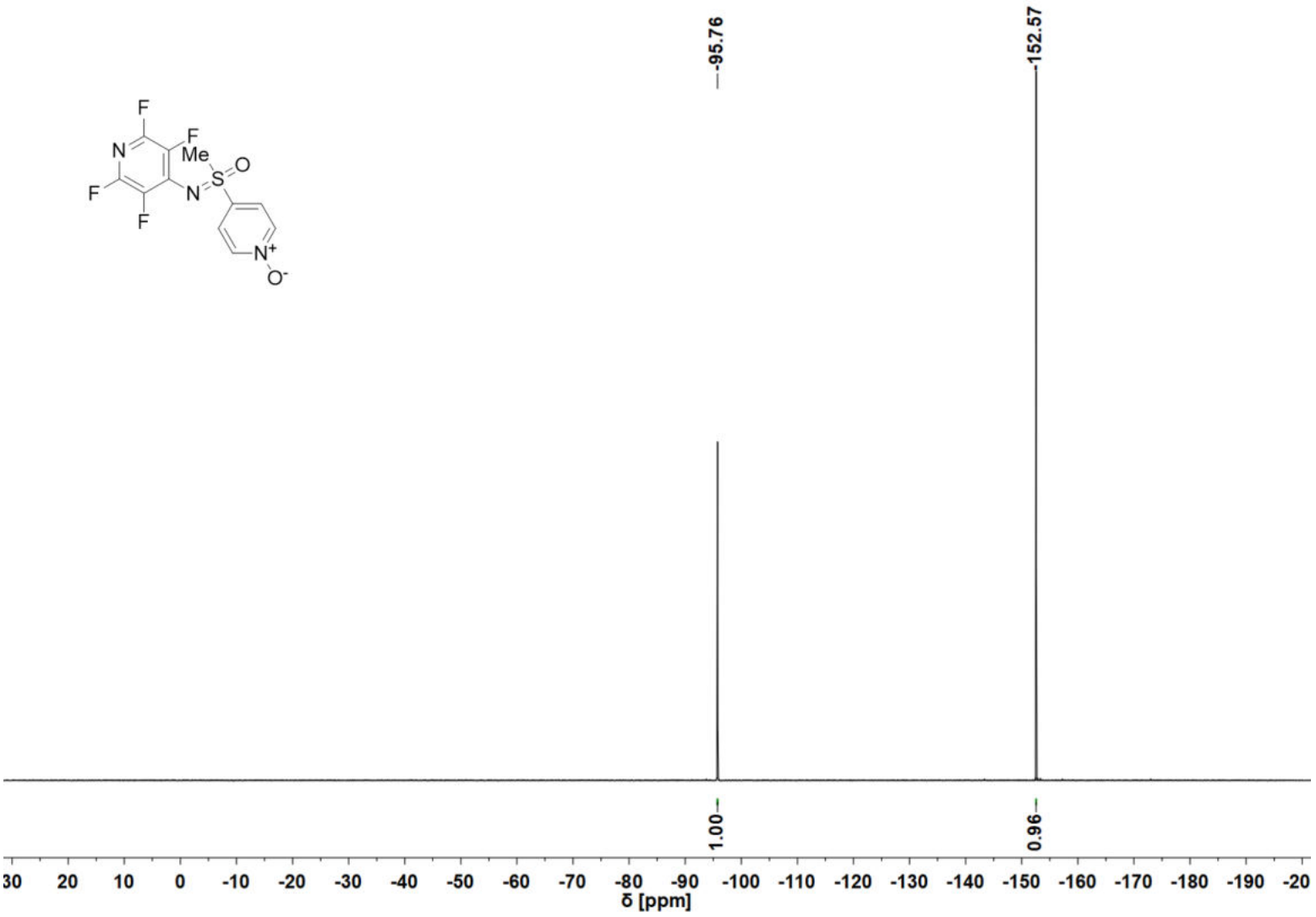

Figure S110 ^{19}F NMR spectrum ($(CD_3)_2CO$, 564 MHz) of **3q**.

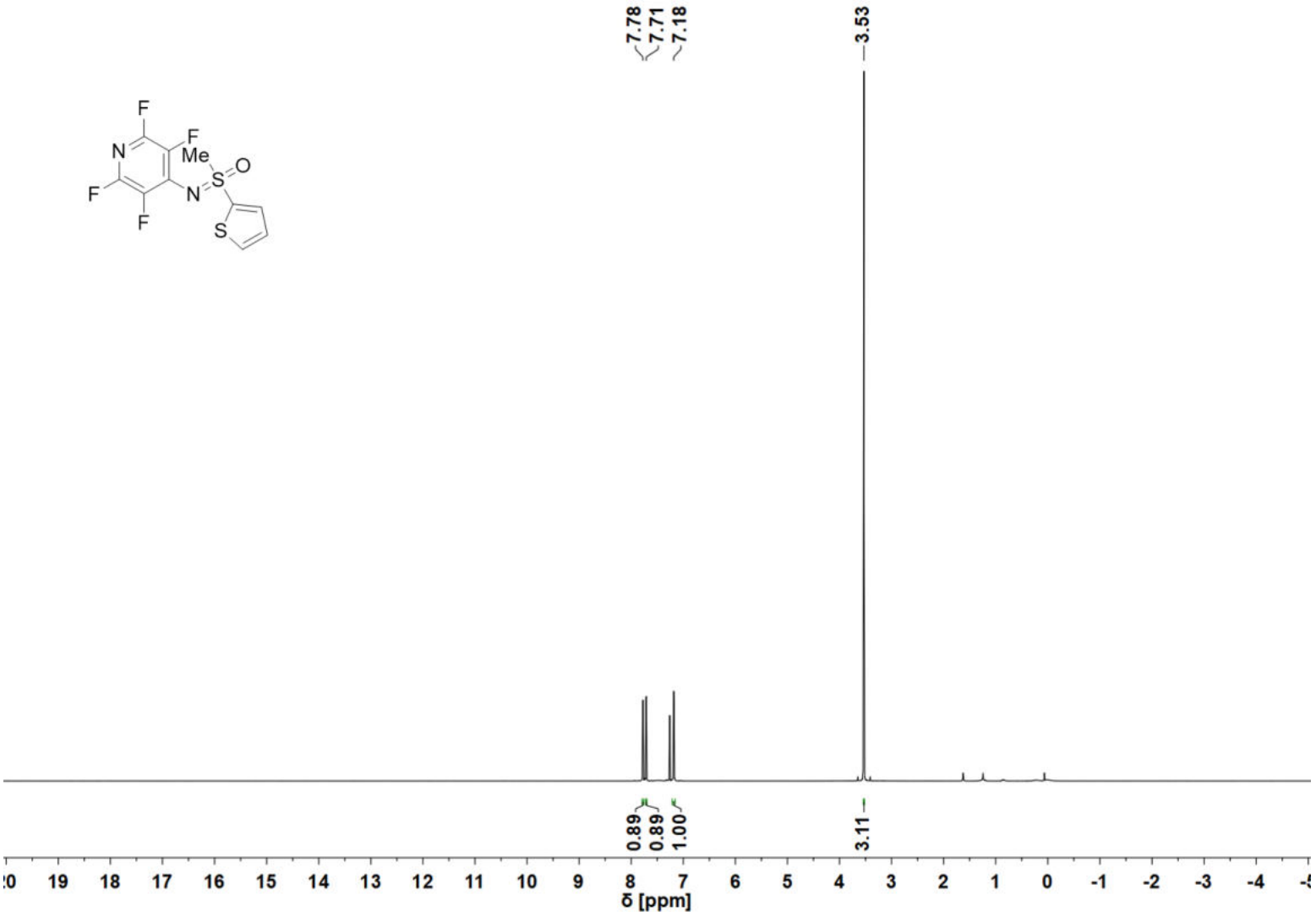

Figure S111 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3r**.

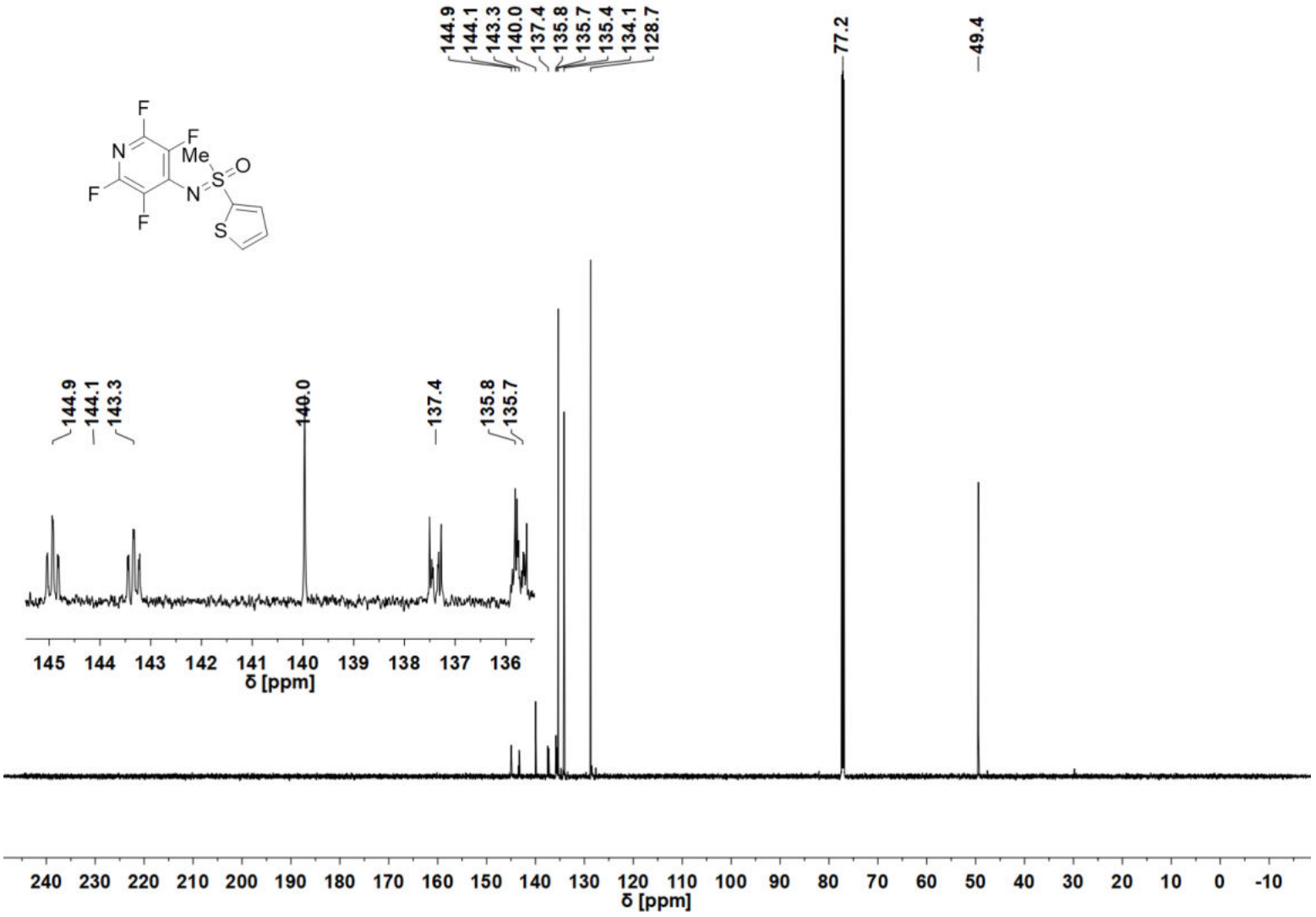

Figure S112 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3r**.

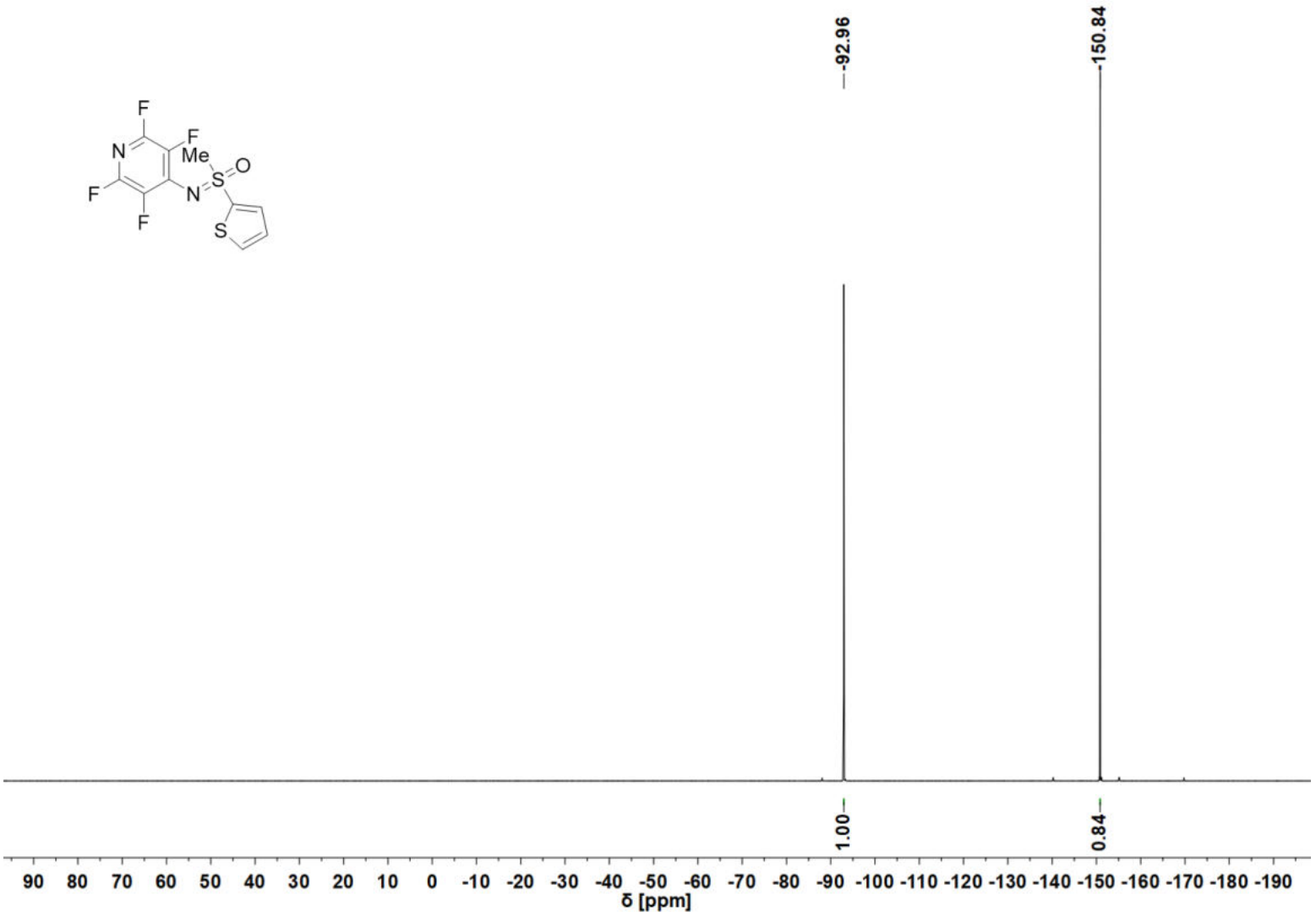

Figure S113 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3r**.

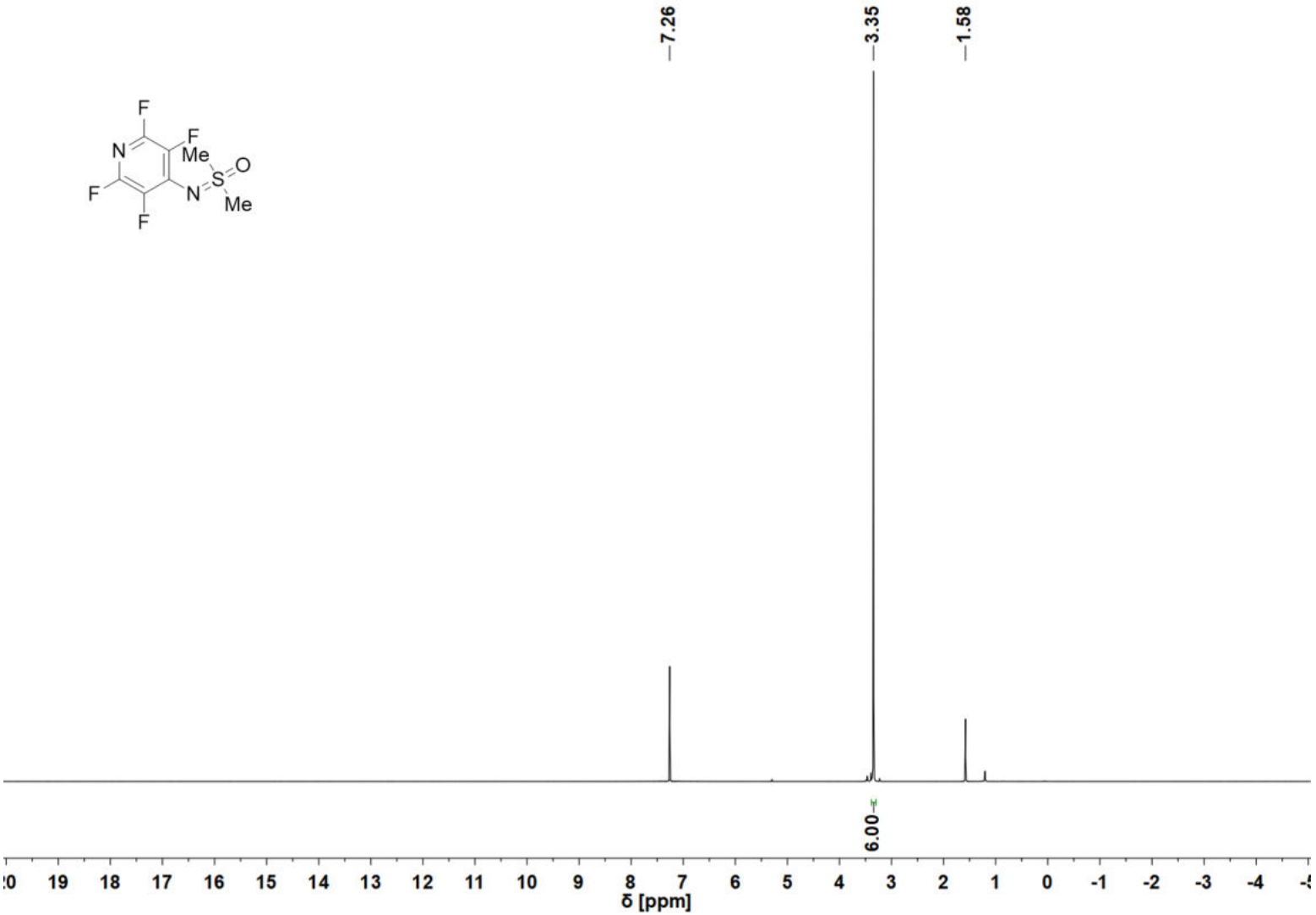

Figure S114 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3s**.

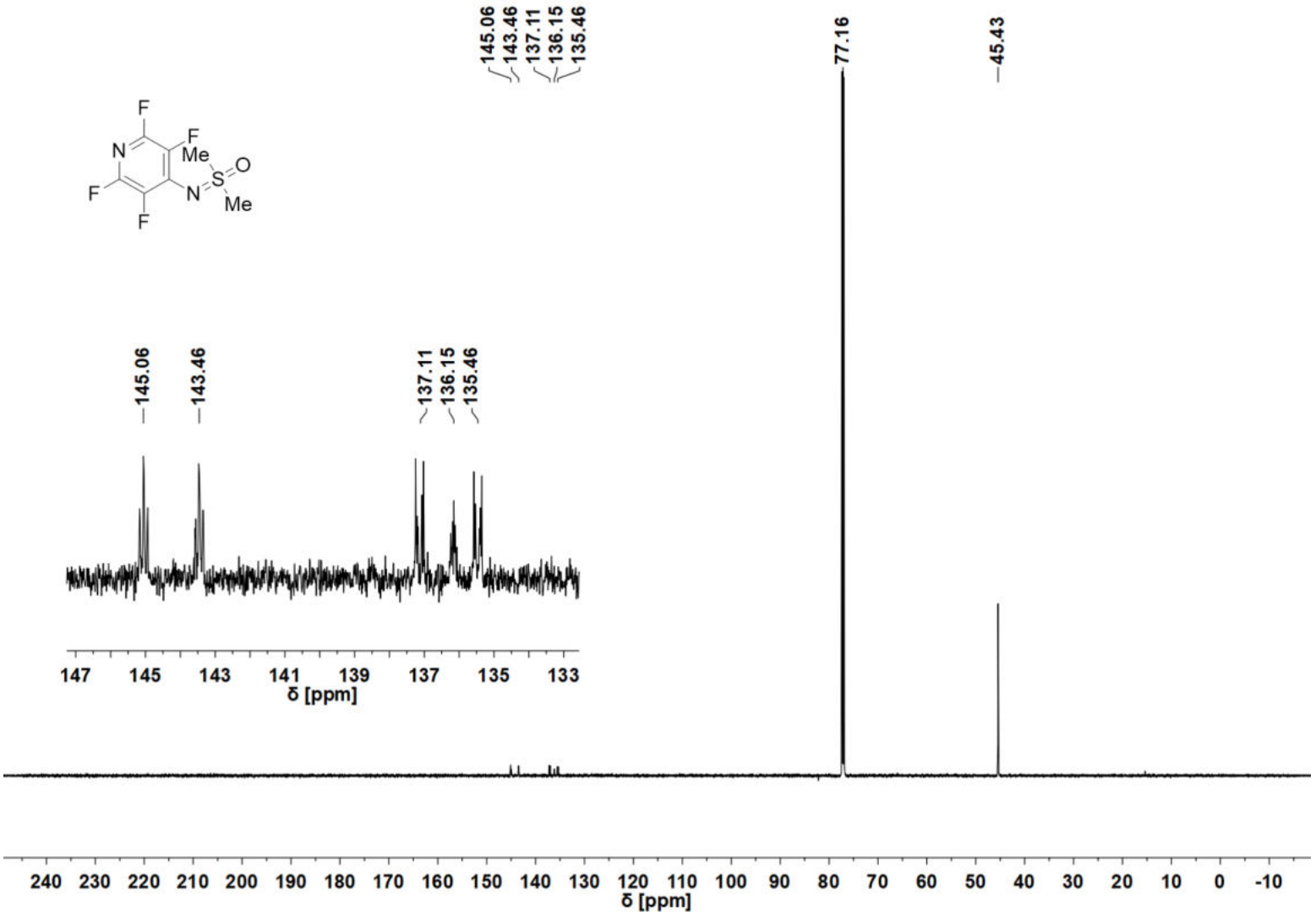

Figure S115 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3s**.

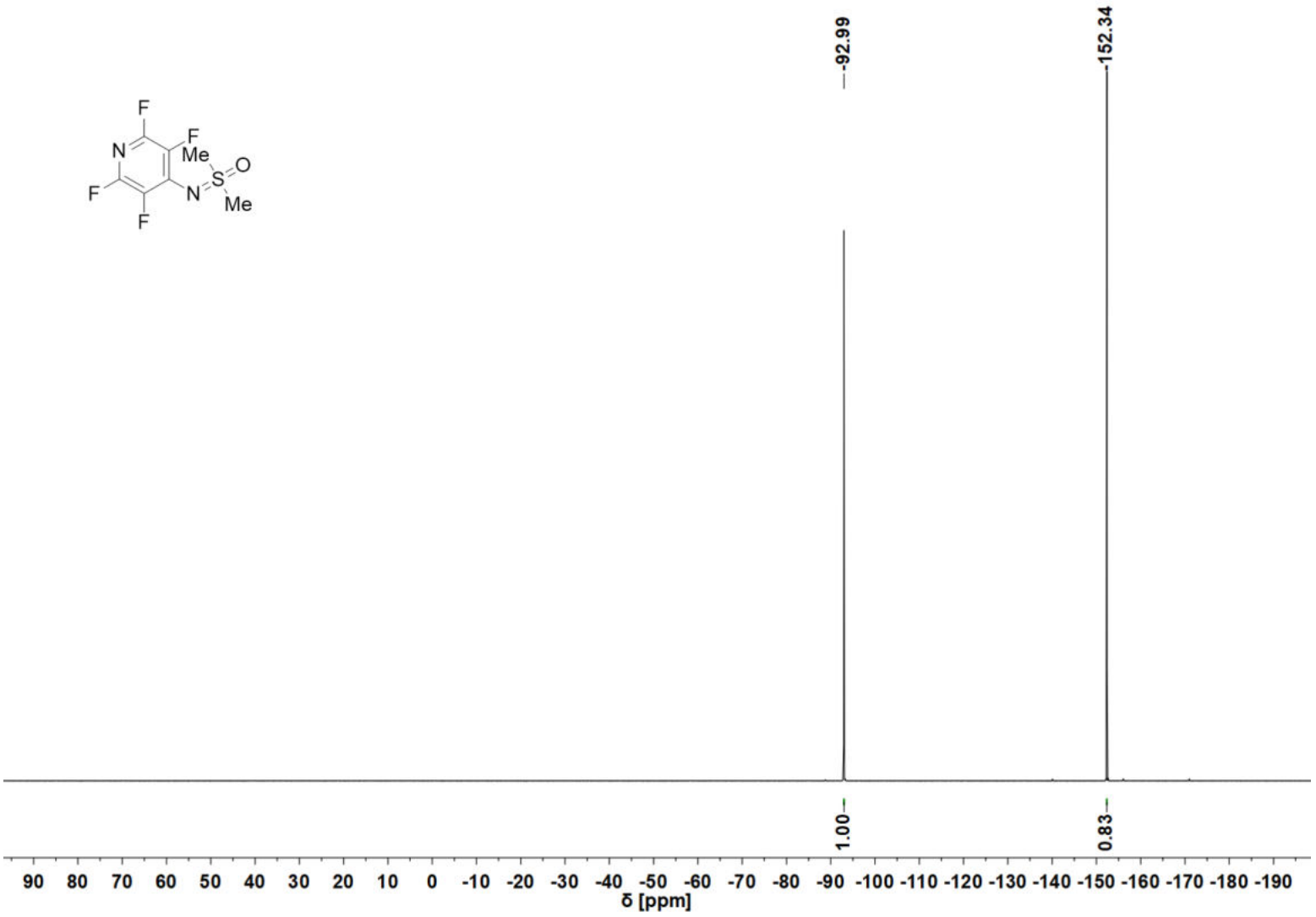

Figure S116 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3s**.

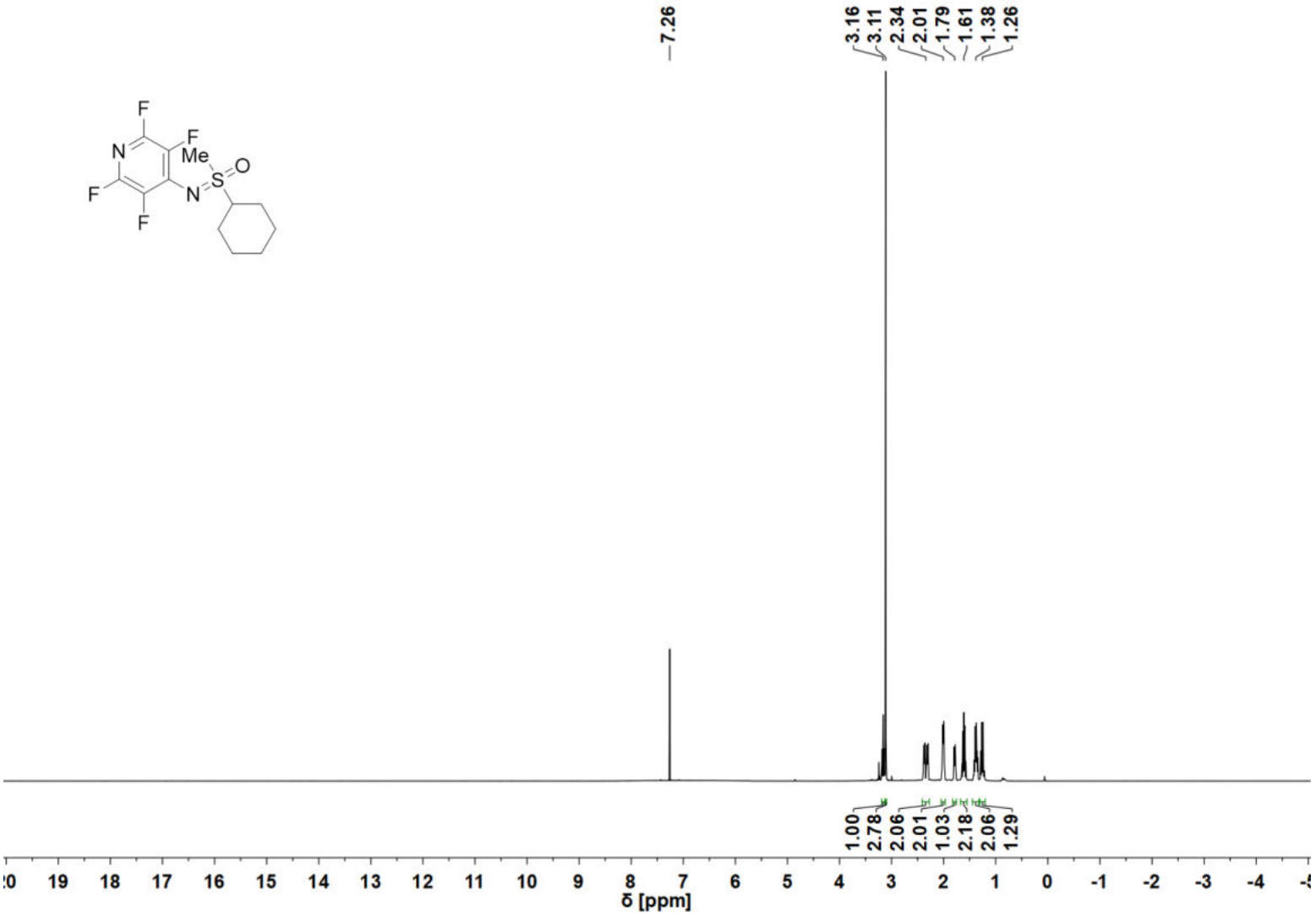

Figure S117 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3t**.

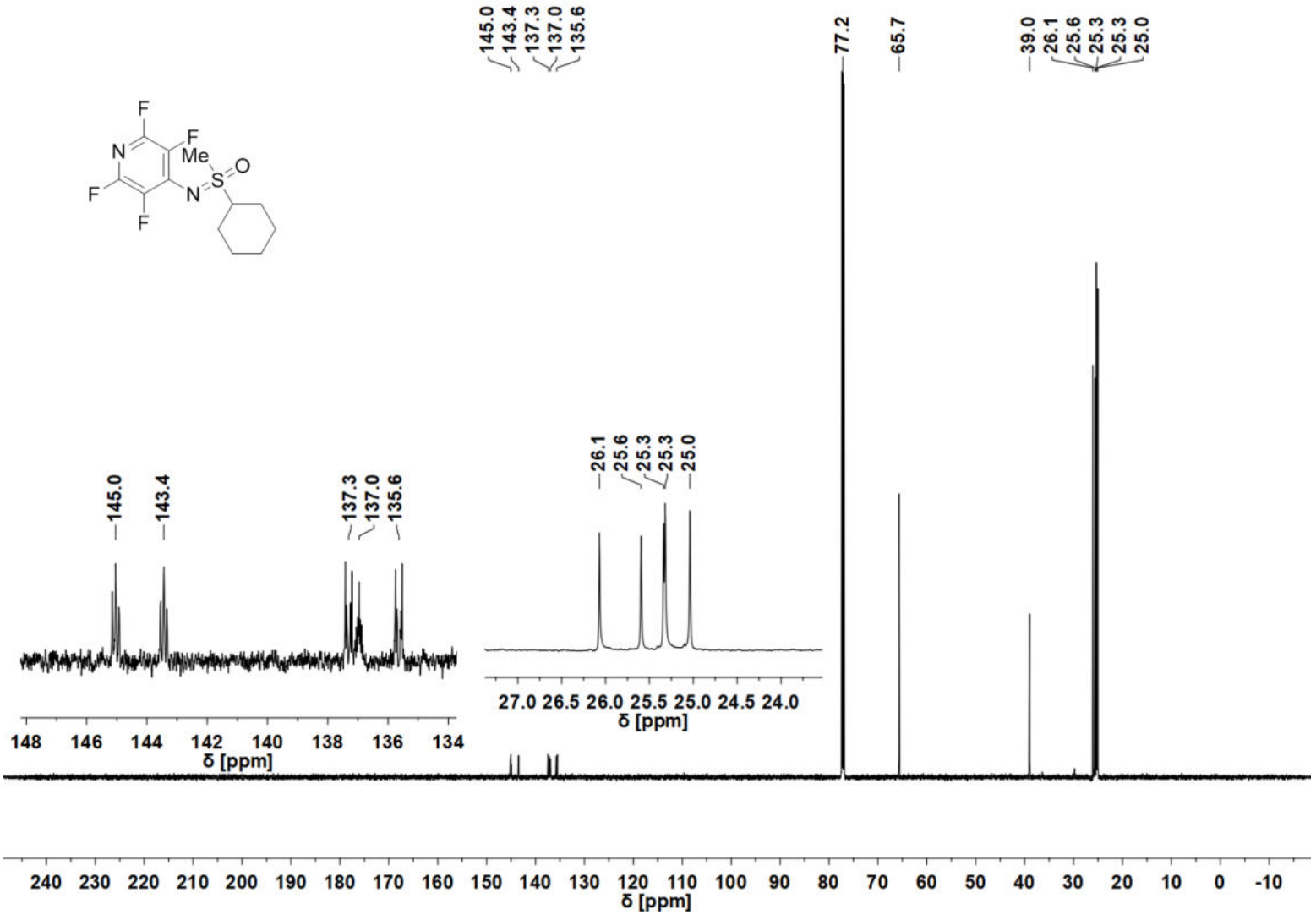

Figure S118 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3t**.

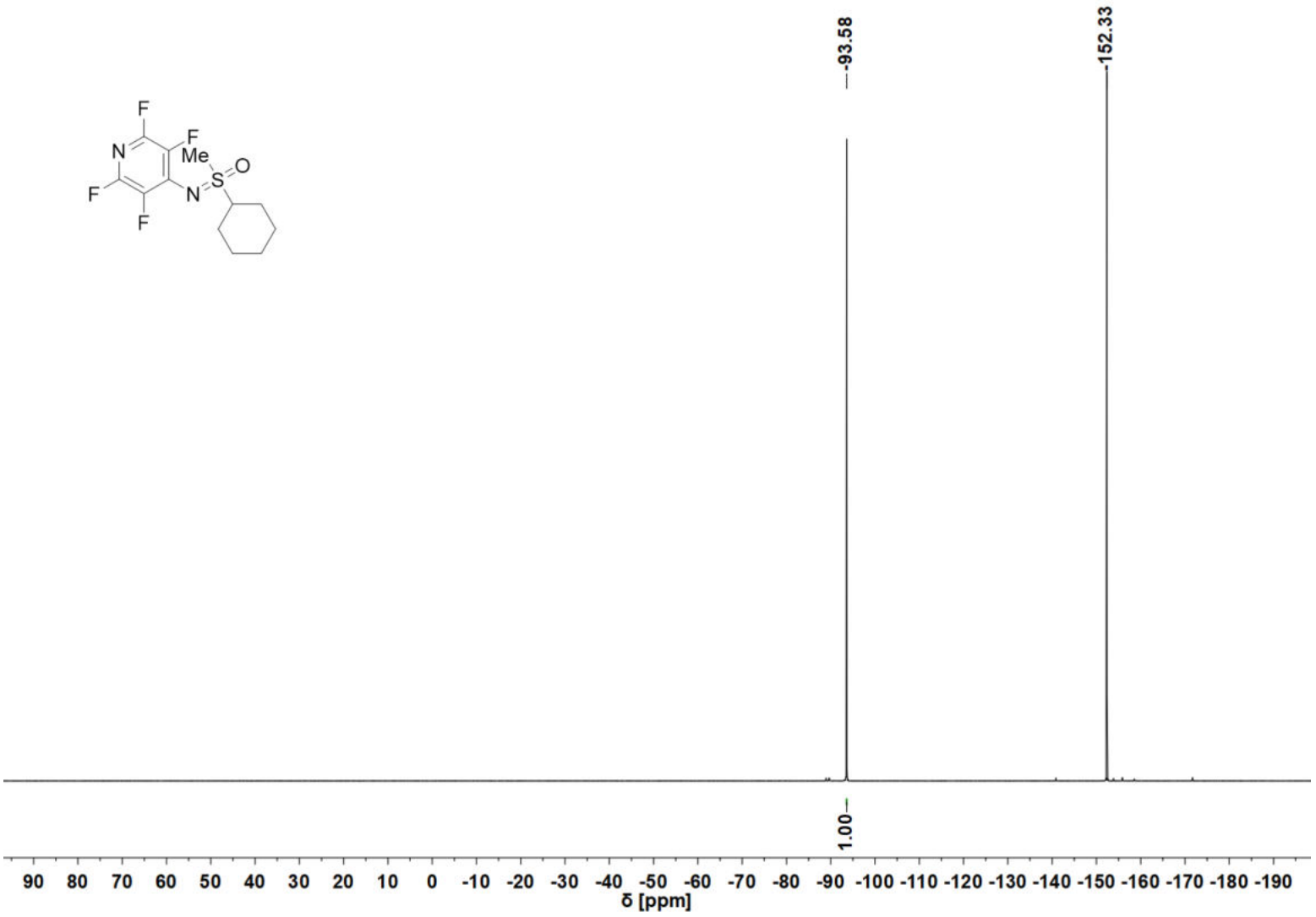

Figure S119 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3t**.

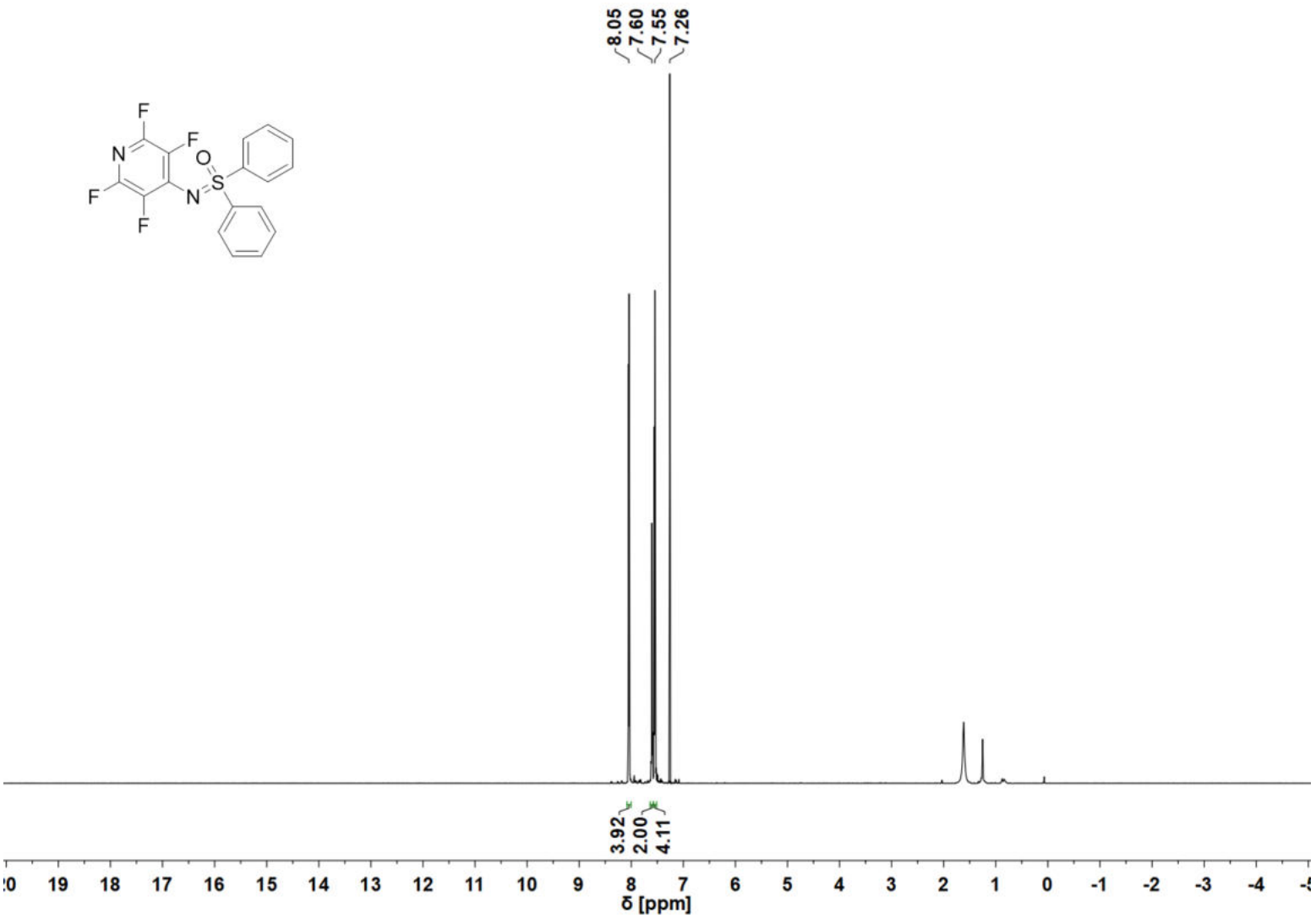

Figure S120 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3u**.

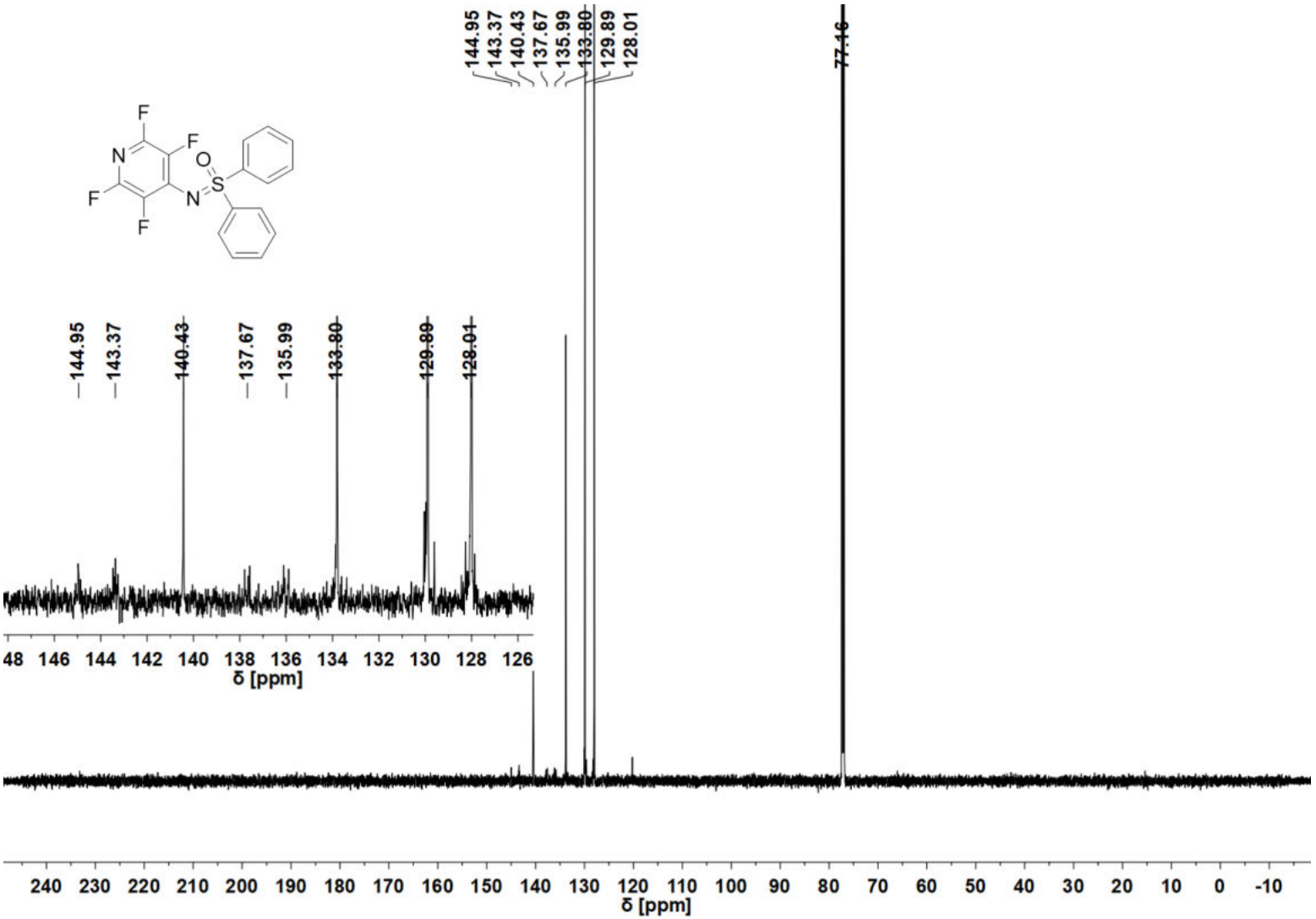

Figure S121 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of **3u**.

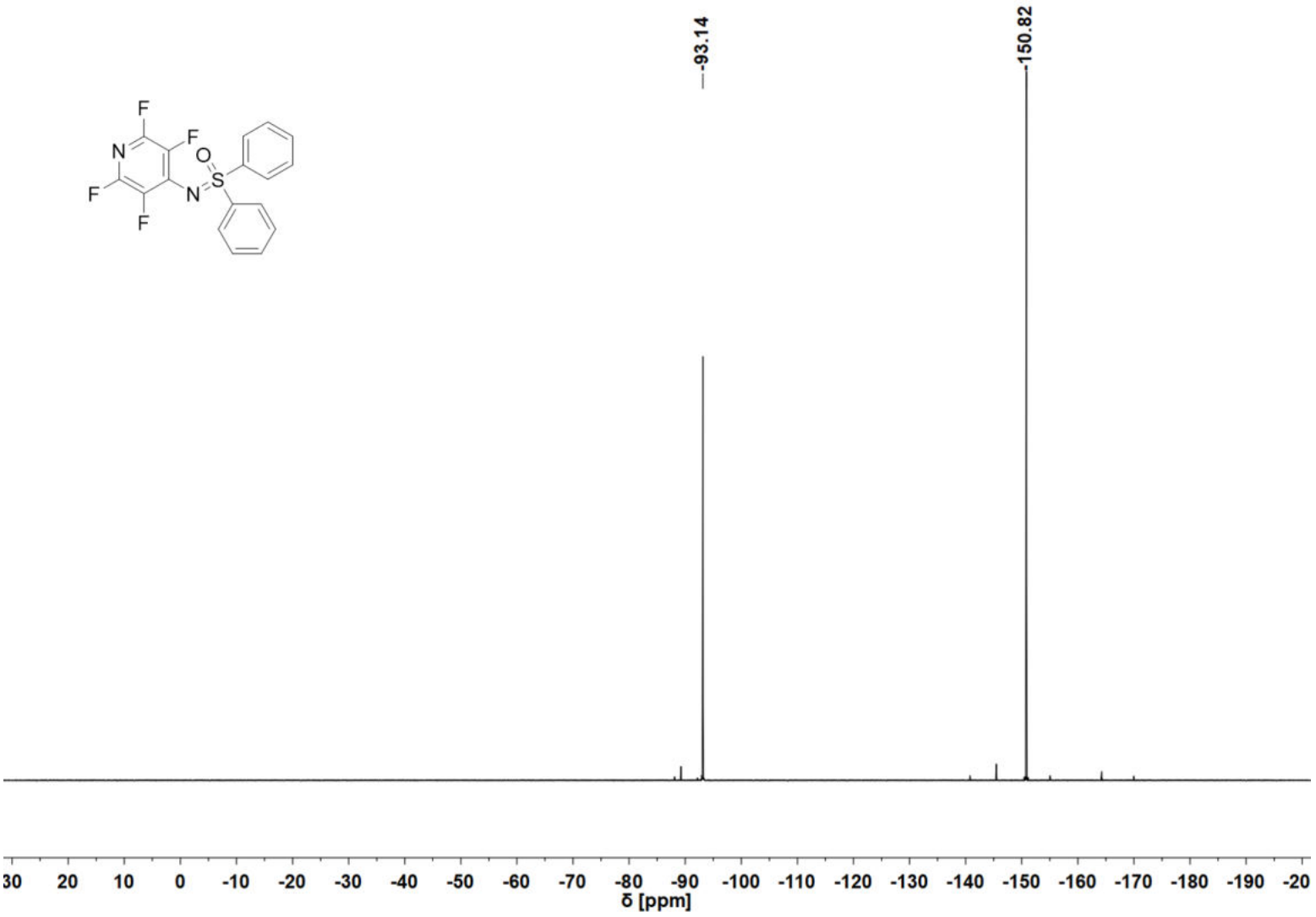

Figure S122 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3u**.

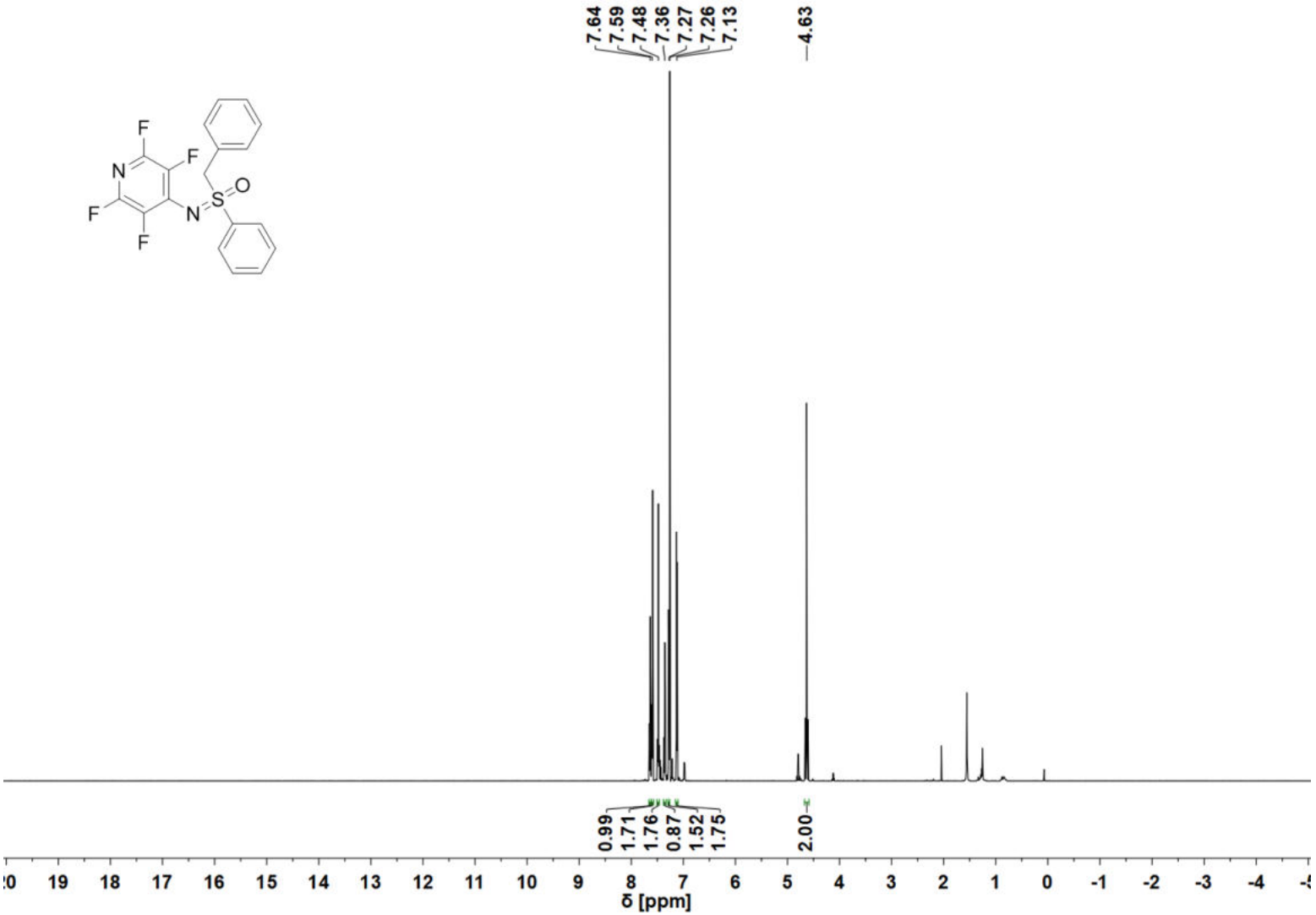

Figure S123 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3v**.

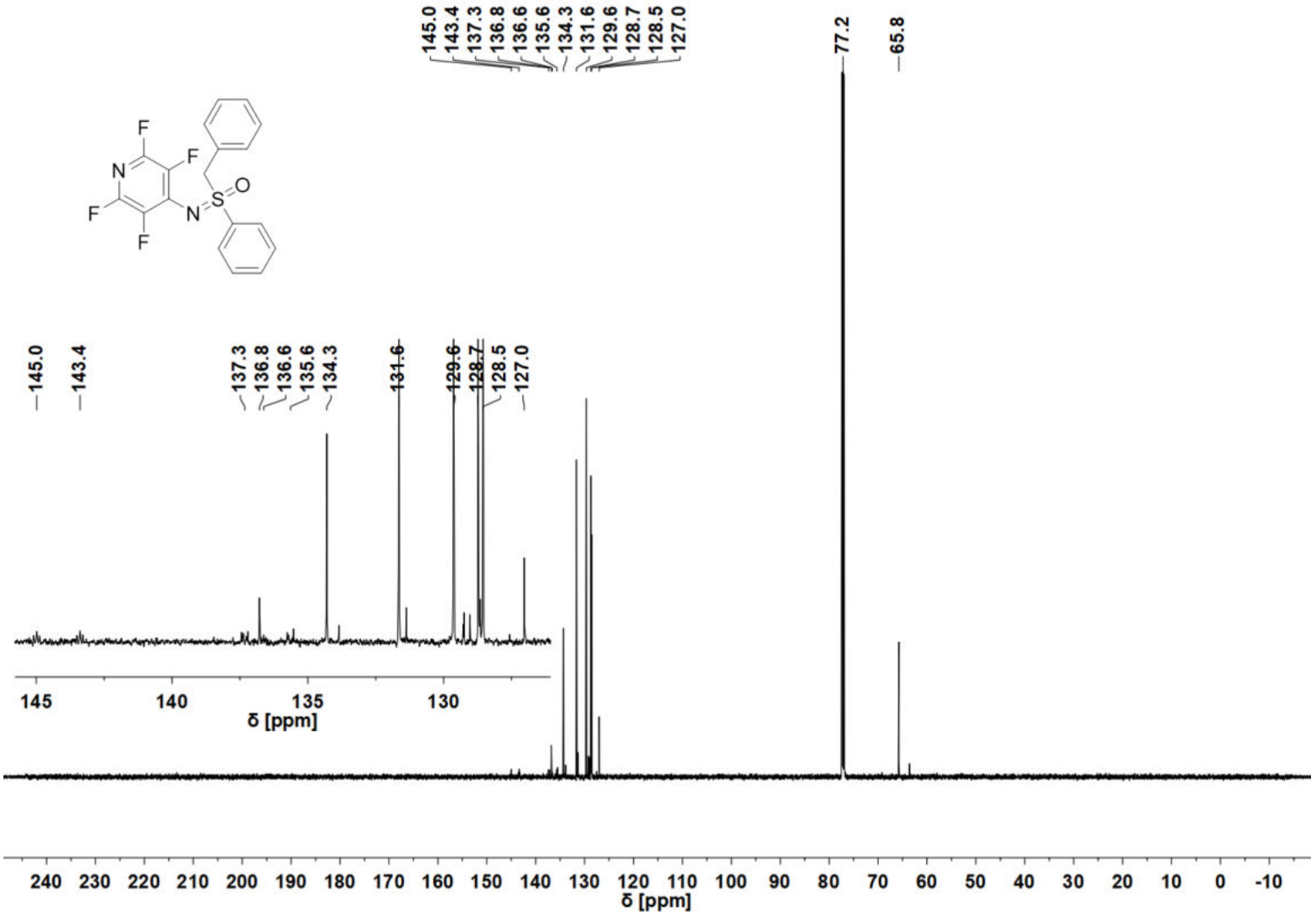

Figure S124 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3v**.

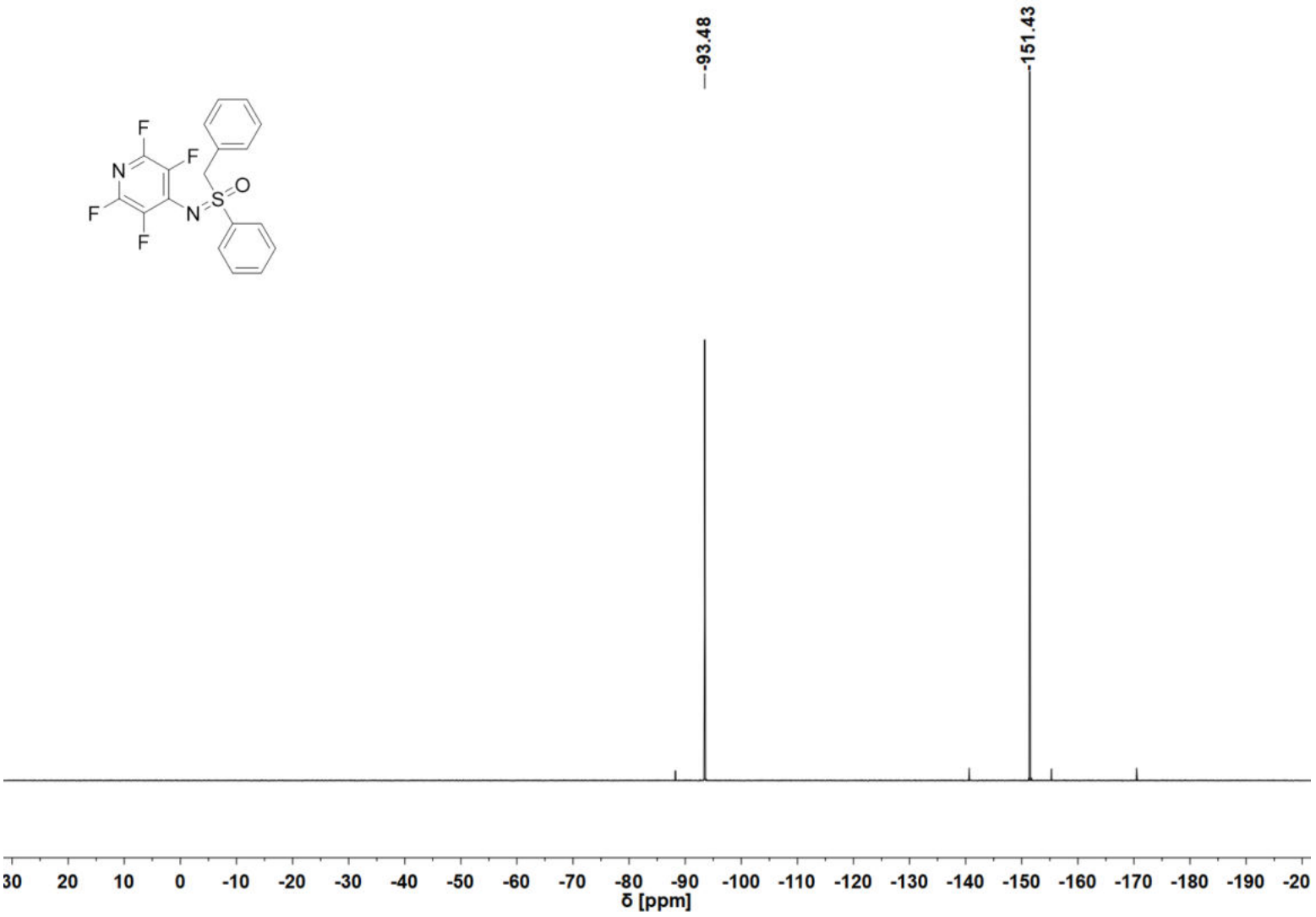

Figure S125 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3v**.

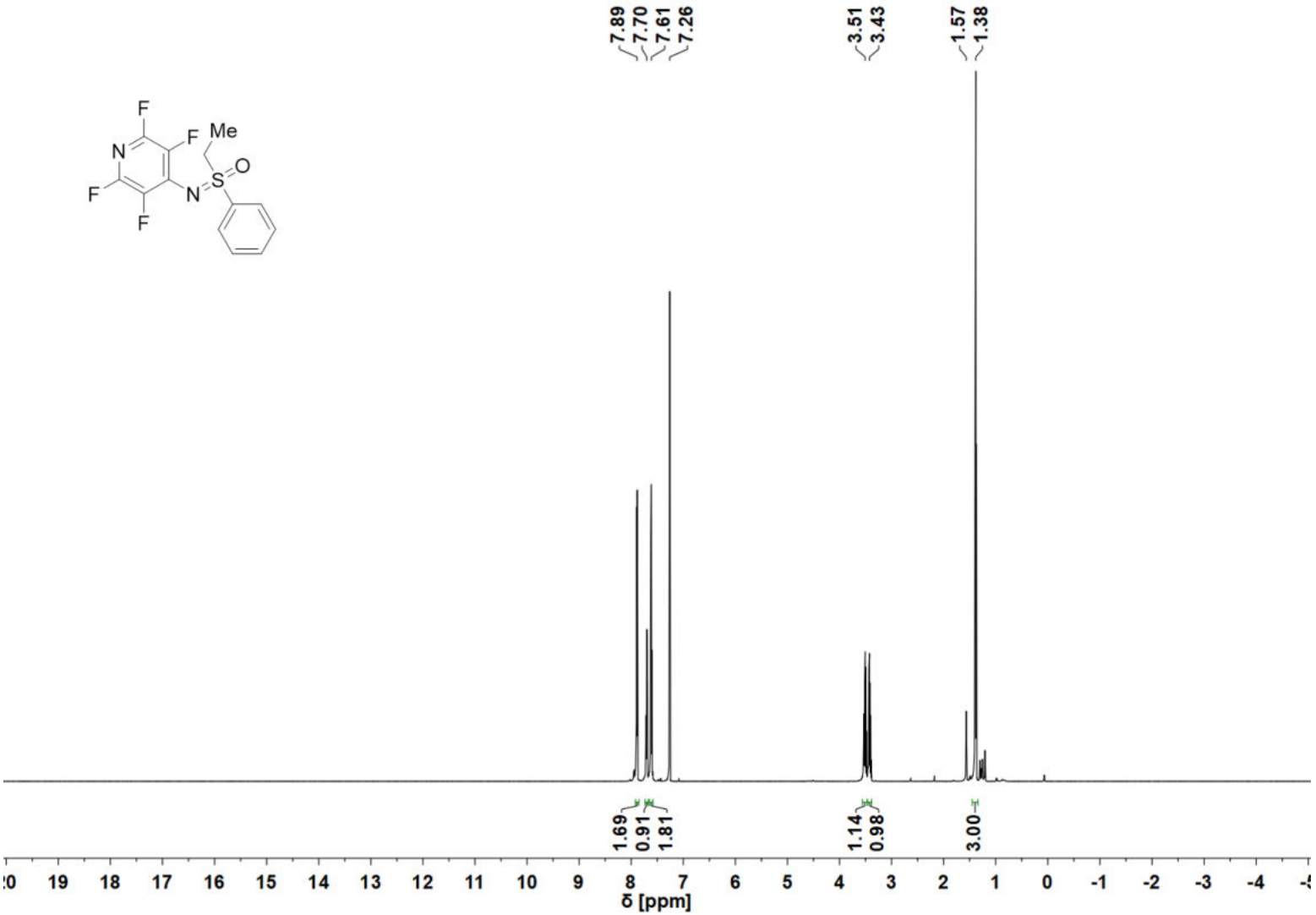

Figure S126 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3w**.

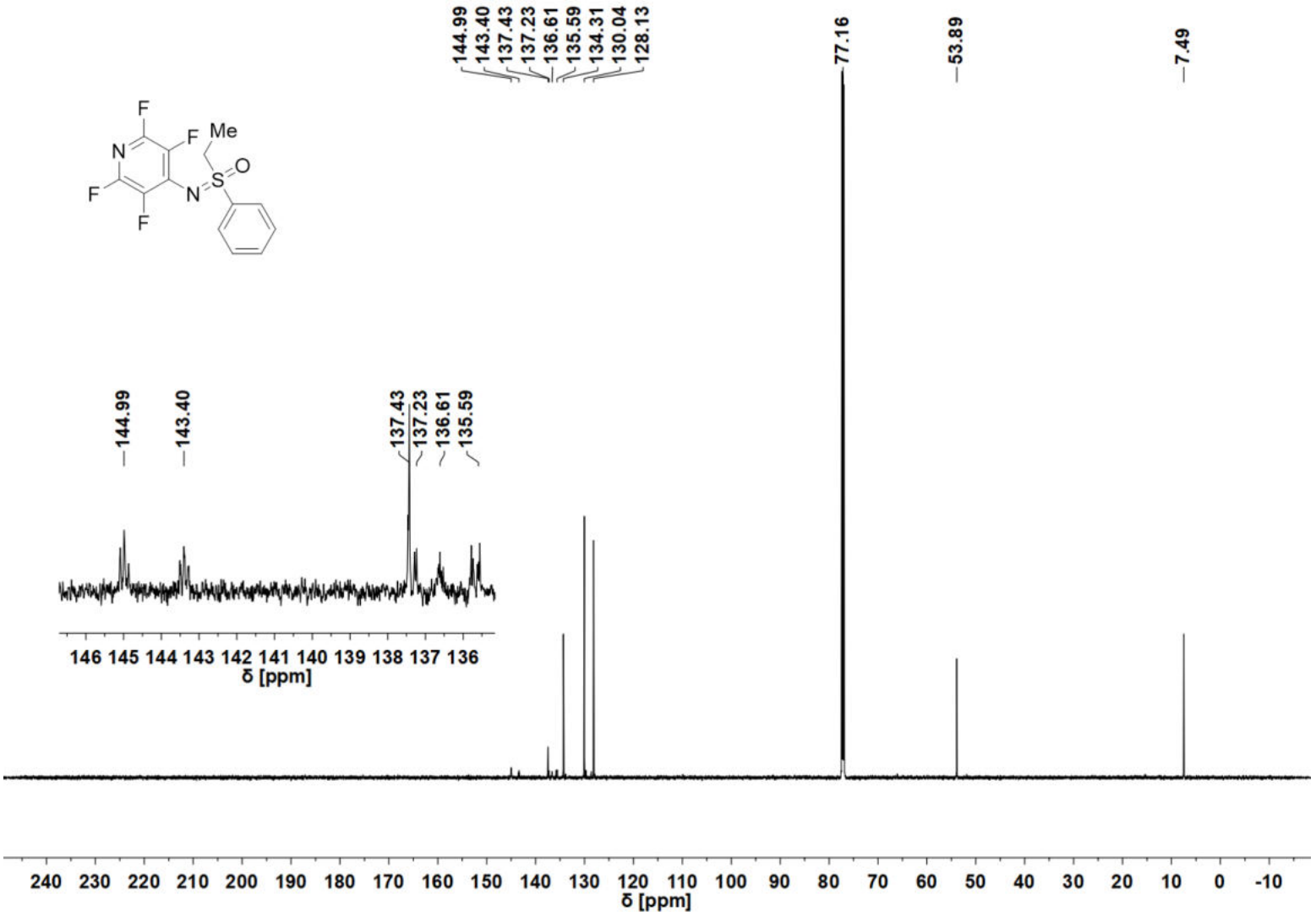

Figure S127 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of **3w**.

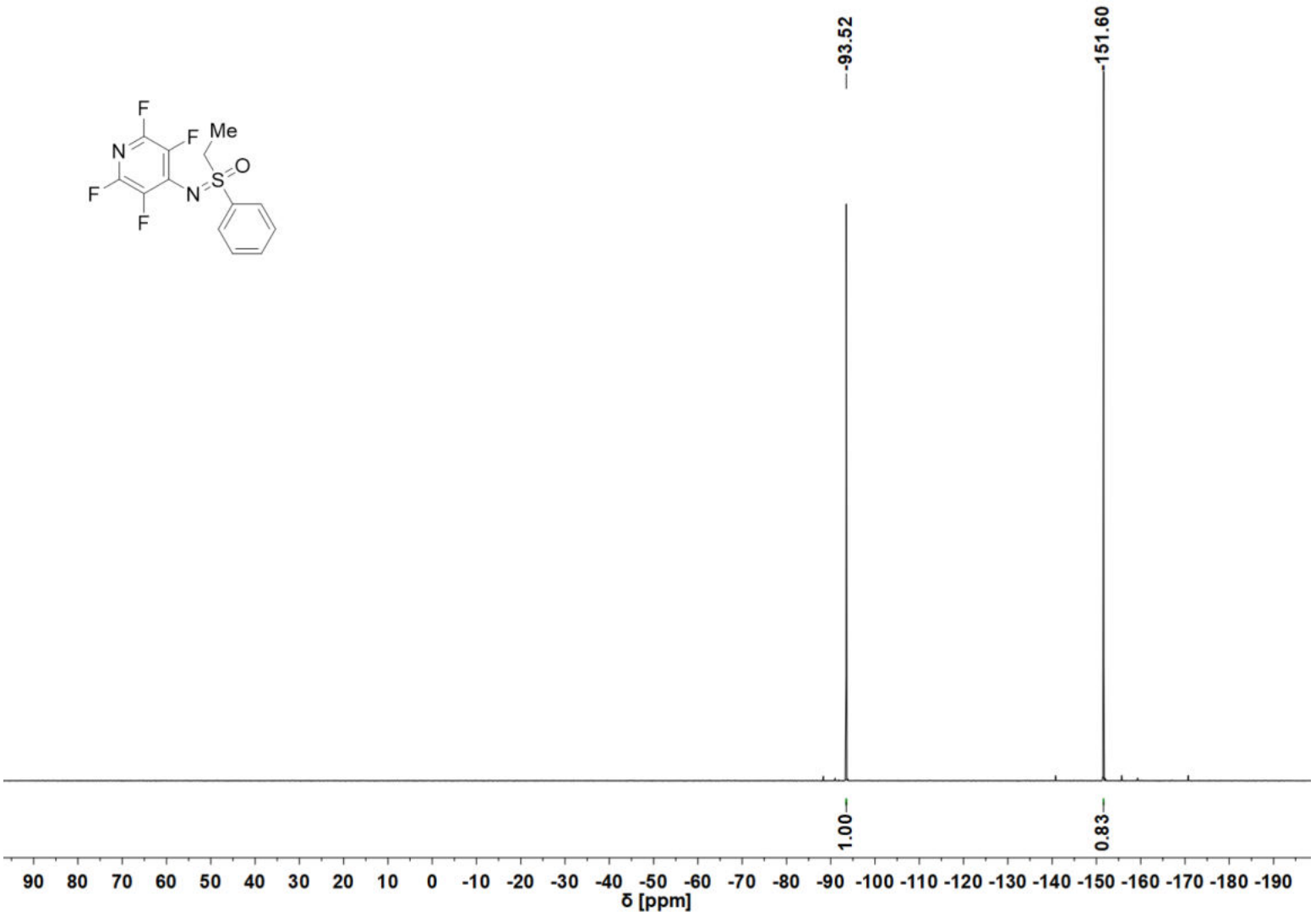

Figure S128 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3w**.

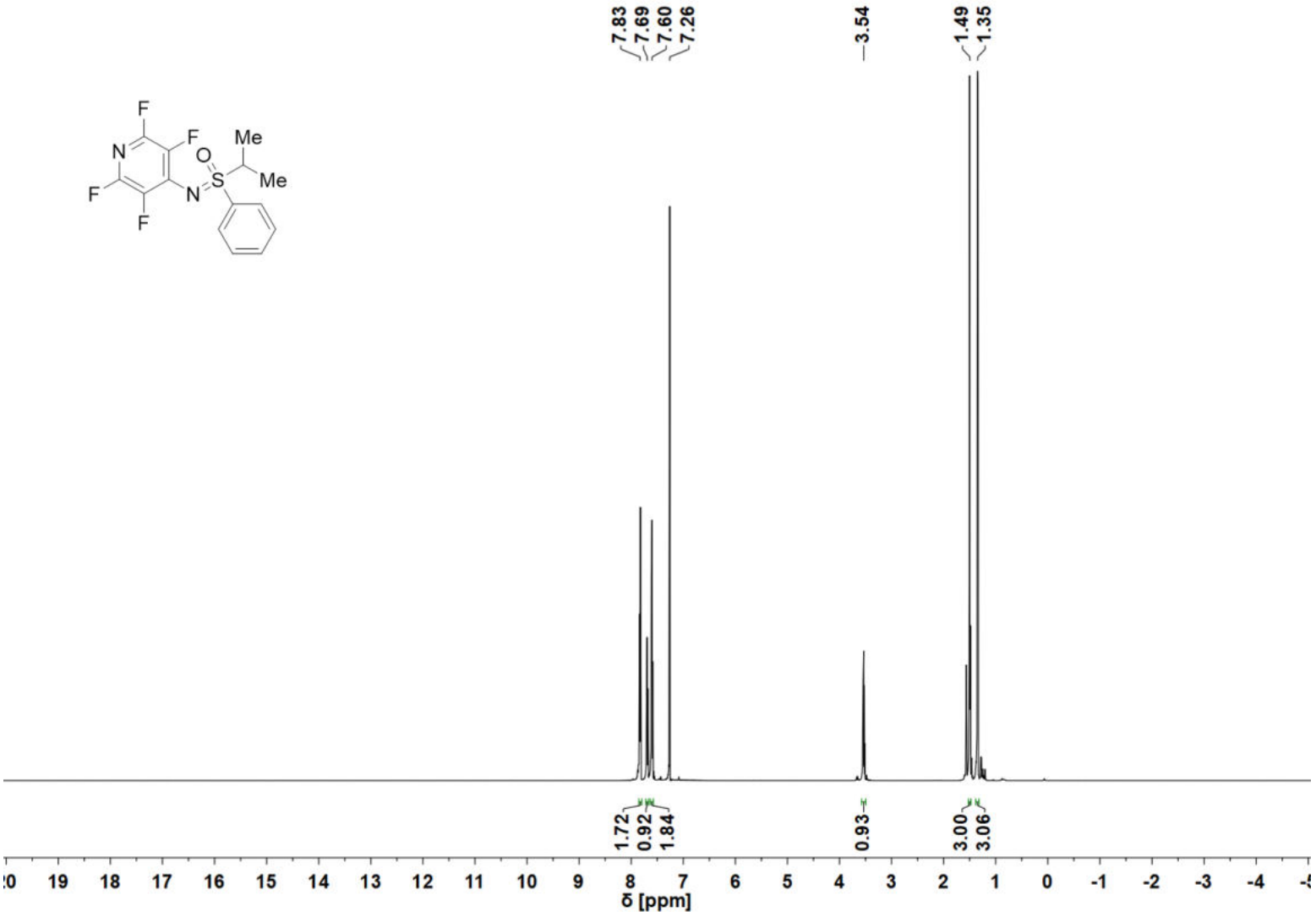

Figure S129 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3x**.

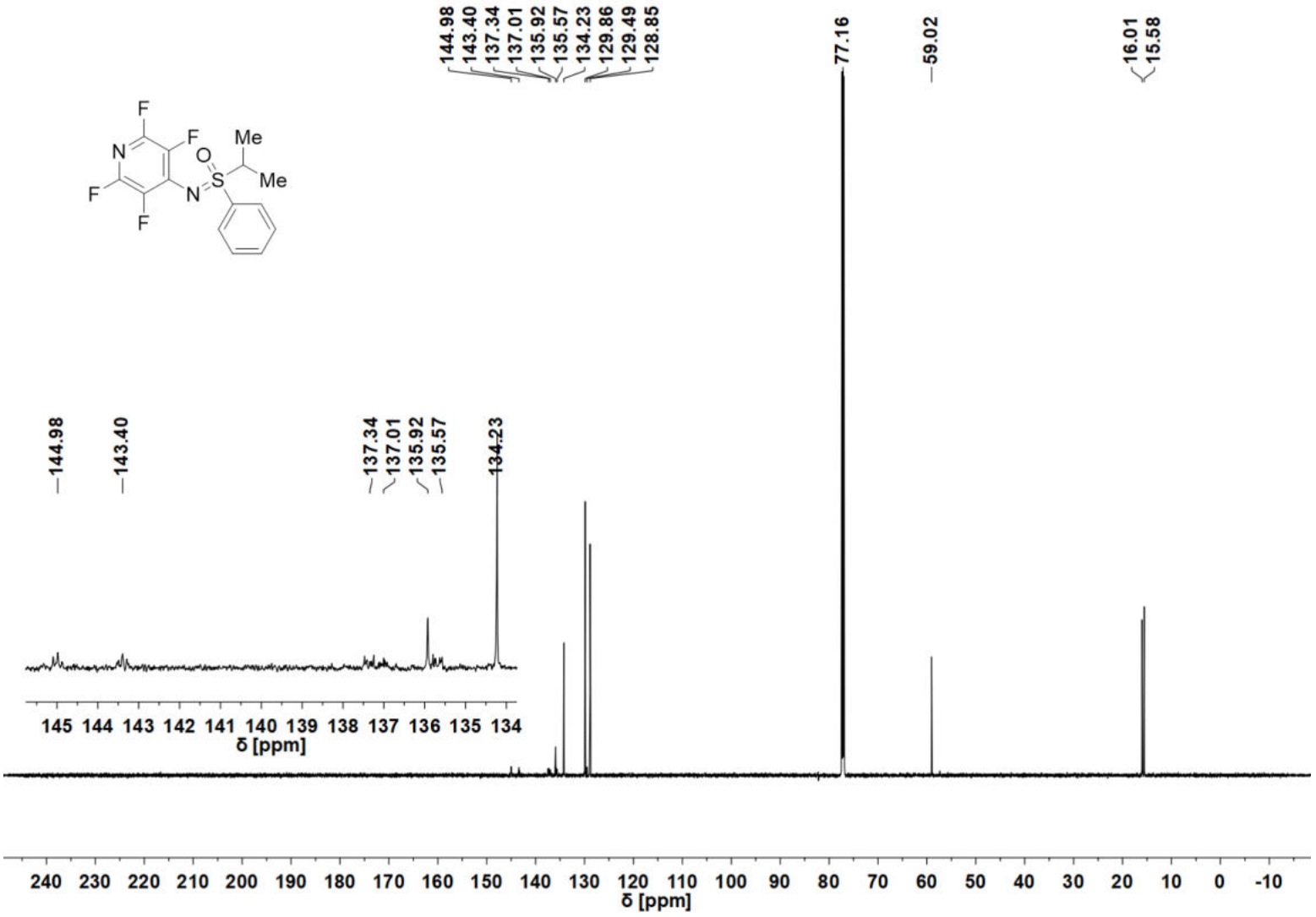

Figure S130 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3x**.

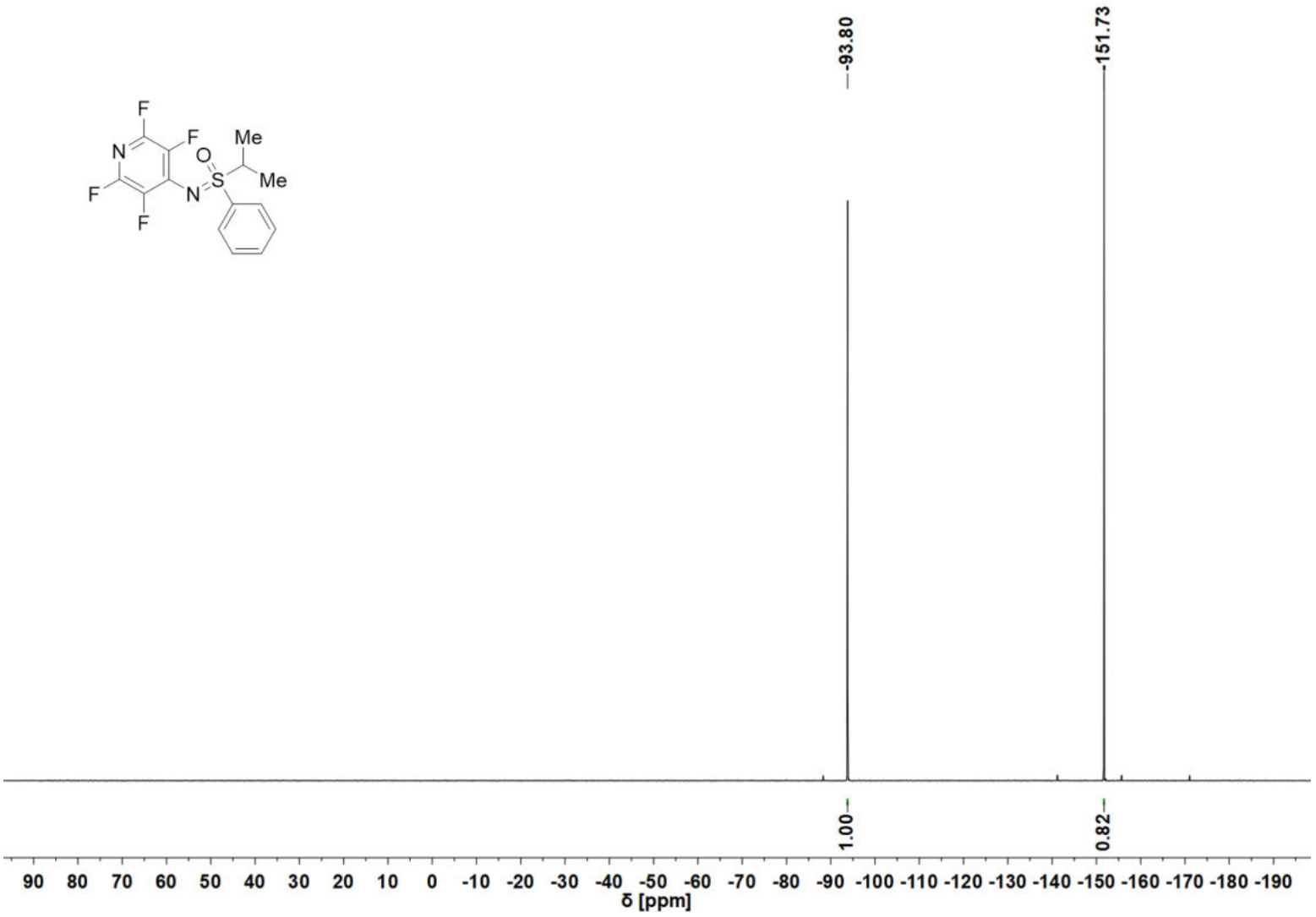

Figure S131 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3x**.

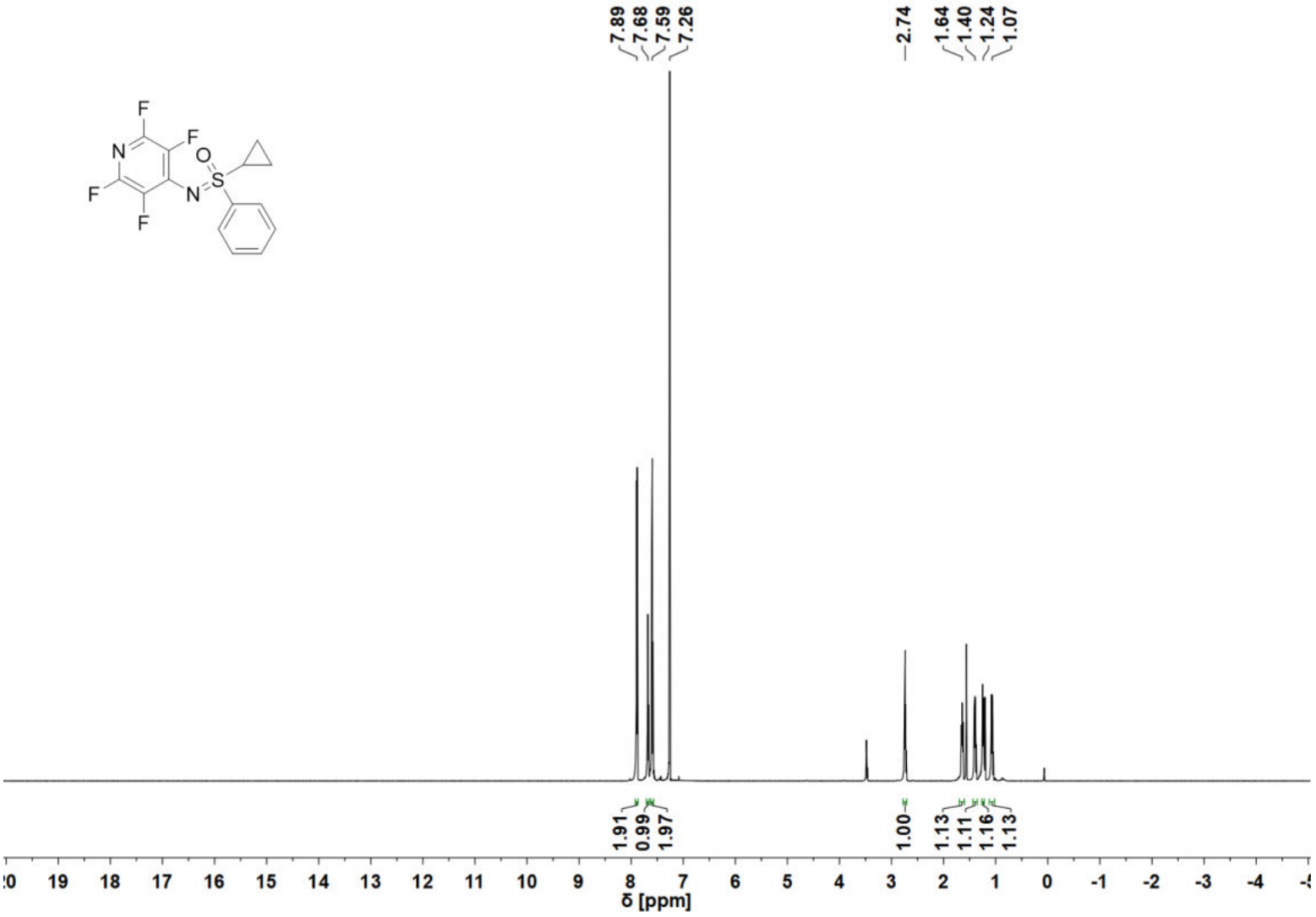

Figure S132 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **3y**.

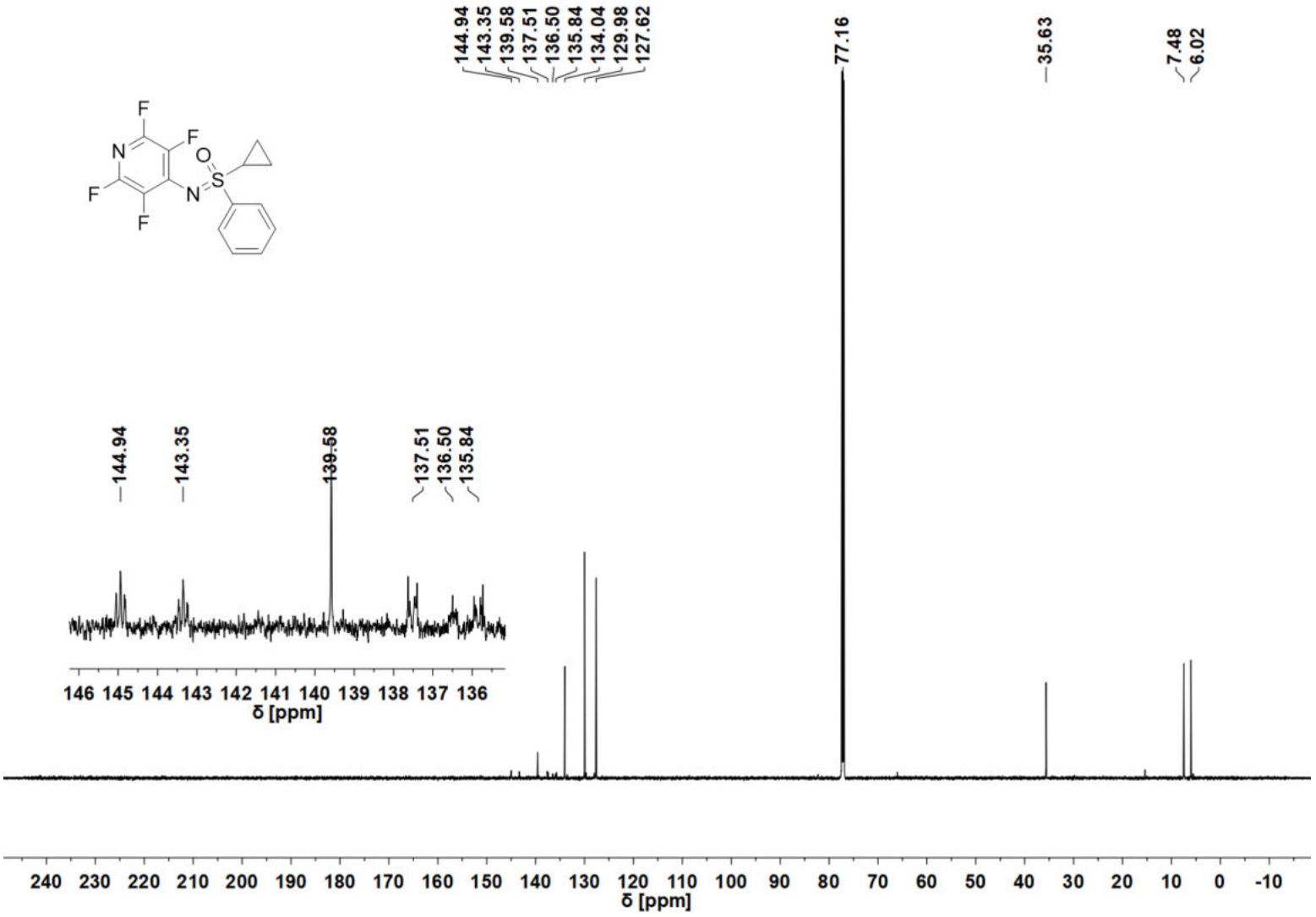

Figure S133 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **3y**.

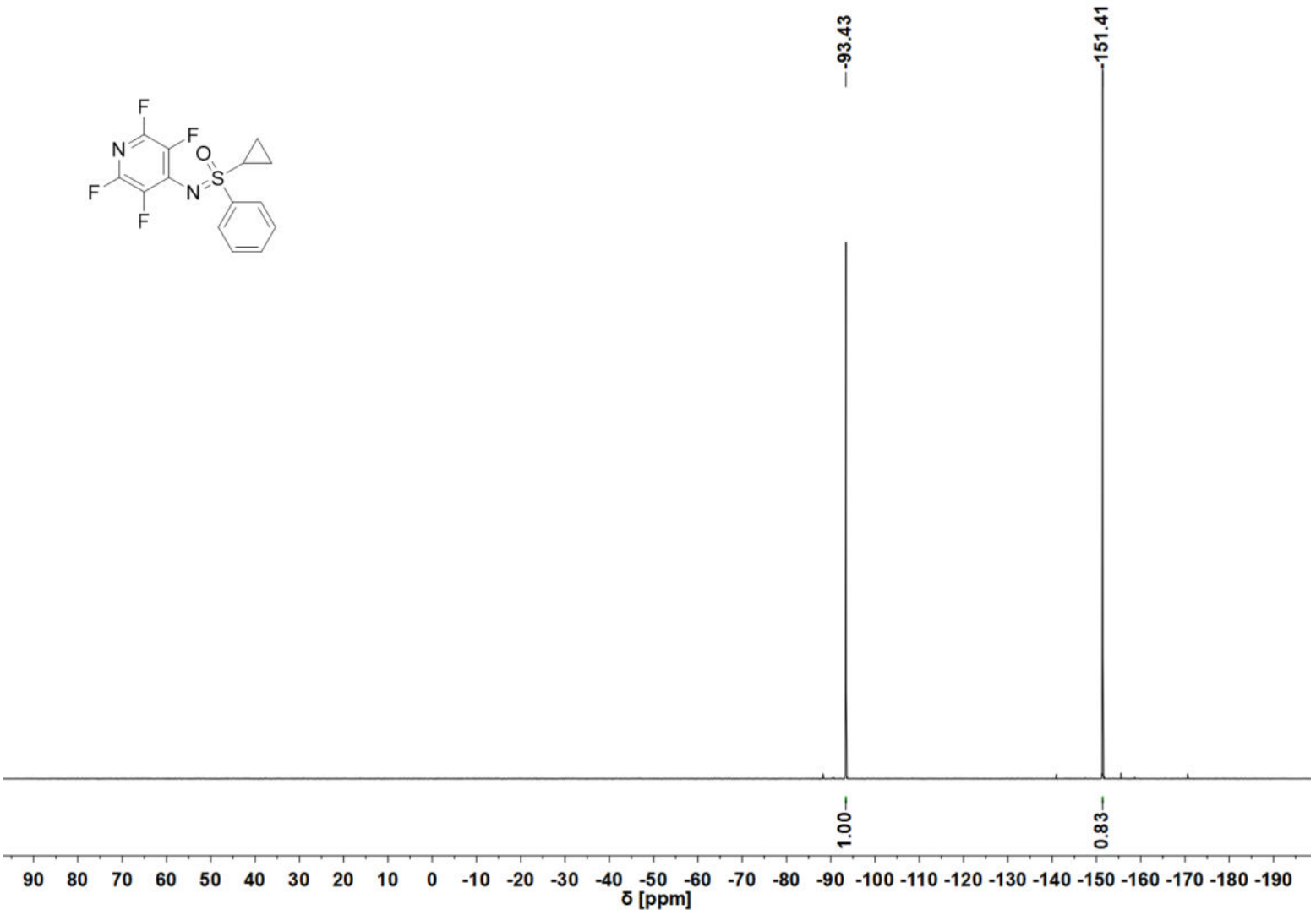

Figure S134 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **3y**.

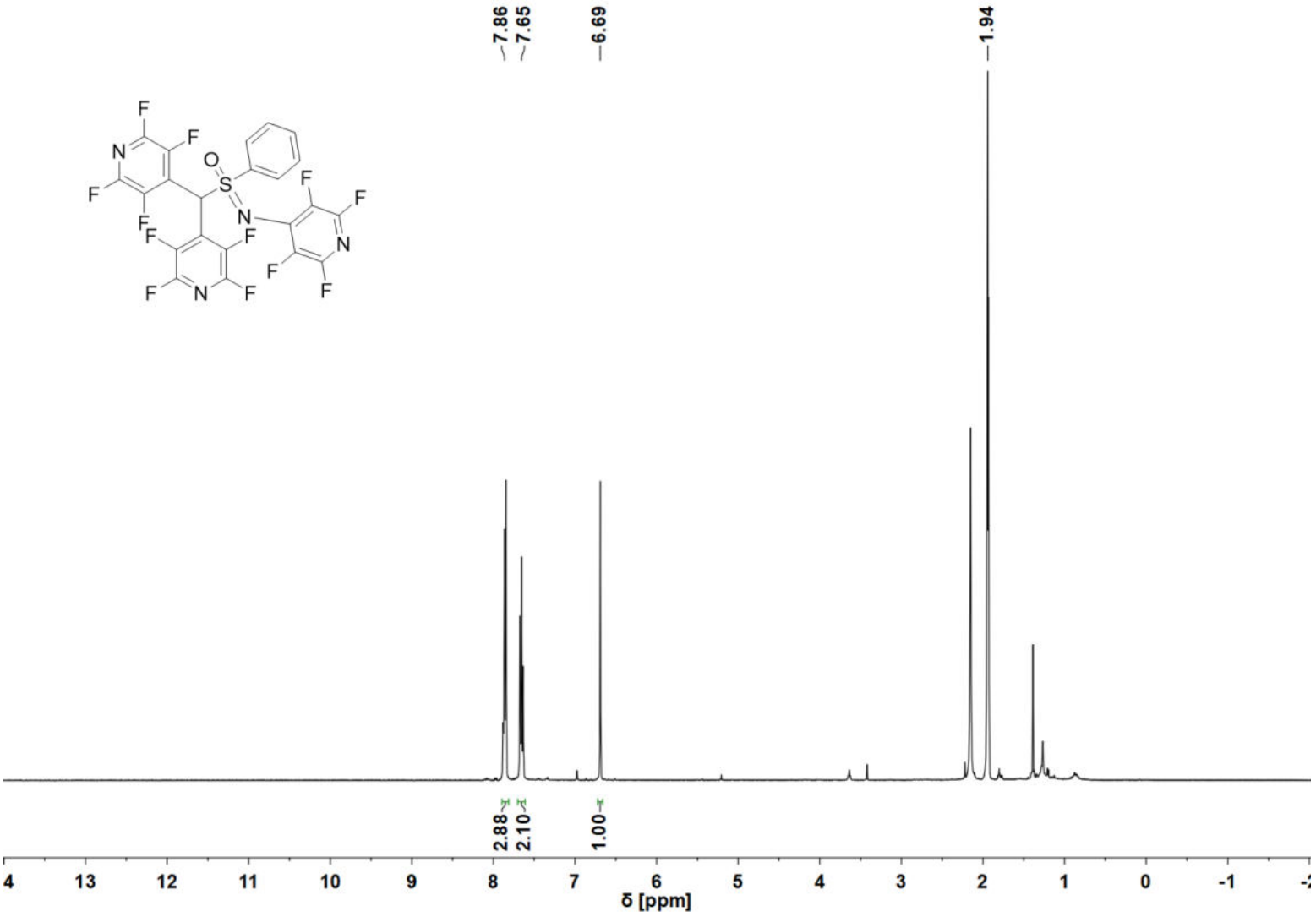

Figure S135 ^{1}H NMR spectrum (CD_3CN, 400 MHz) of **4**.

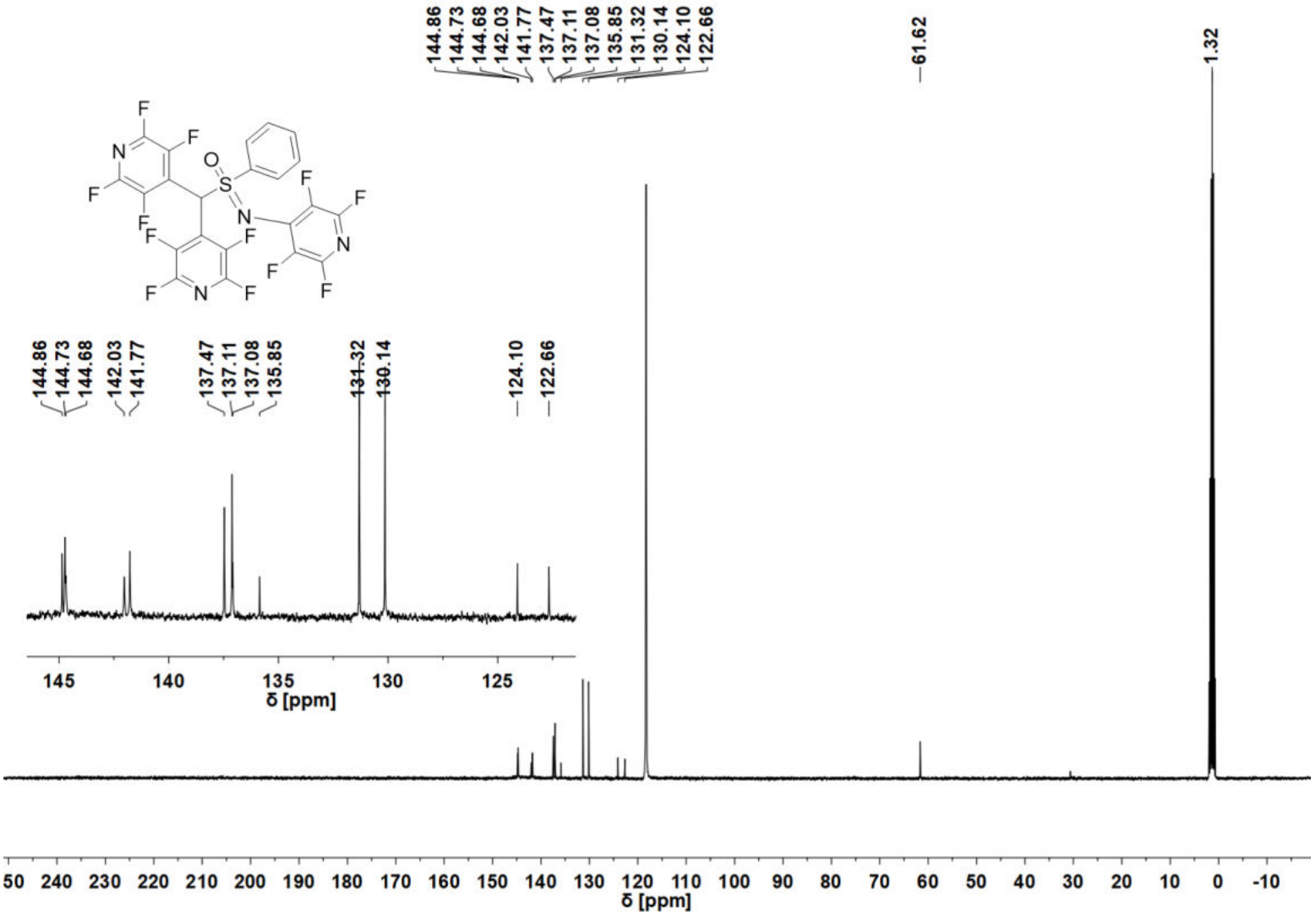

Figure S136 ^{13}C {^{1}H, ^{19}F} NMR spectrum (CD_3CN, 101 MHz) of **4**.

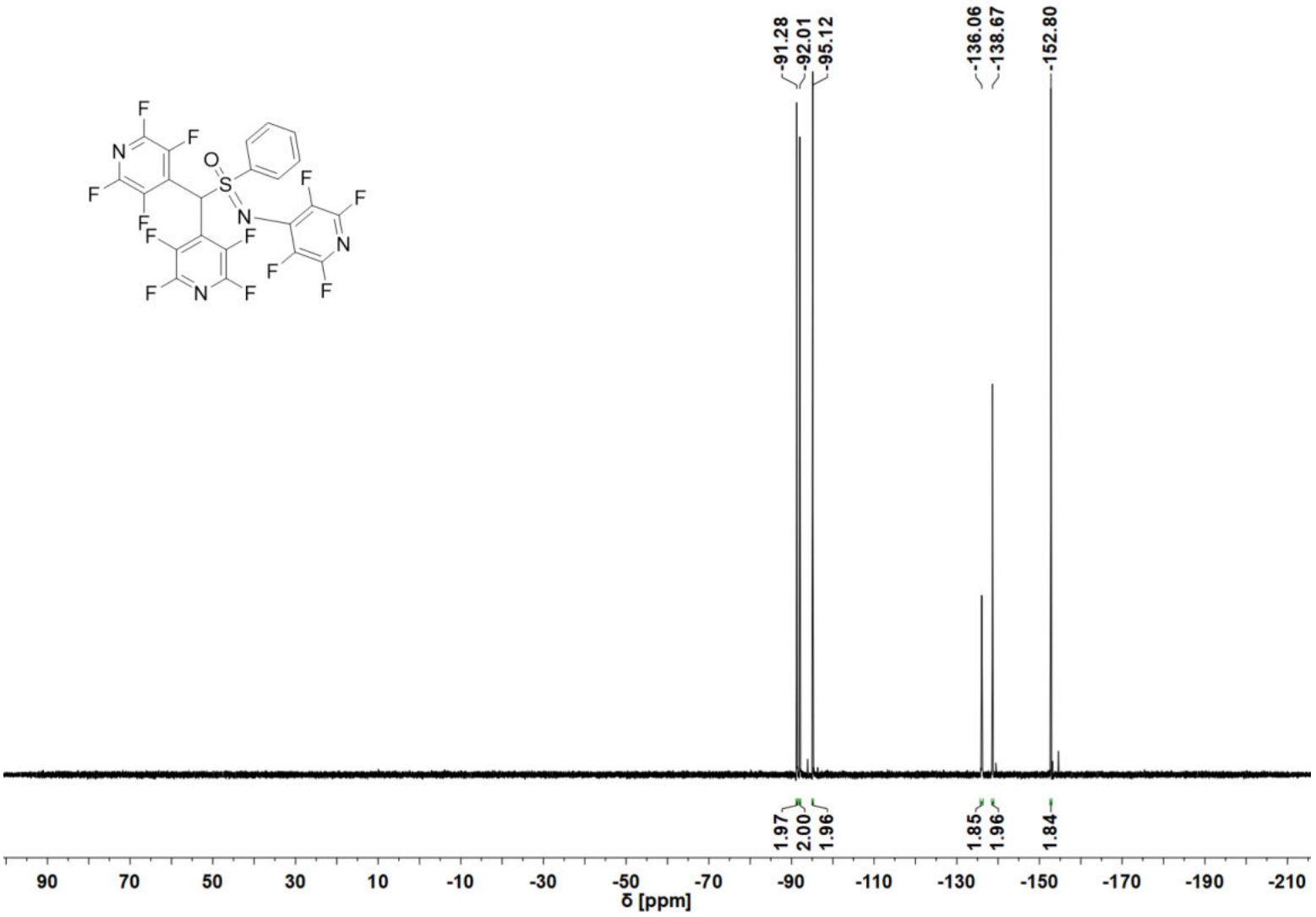

Figure S137 ^{19}F NMR spectrum (CD_3CN, 376 MHz) of **4**.

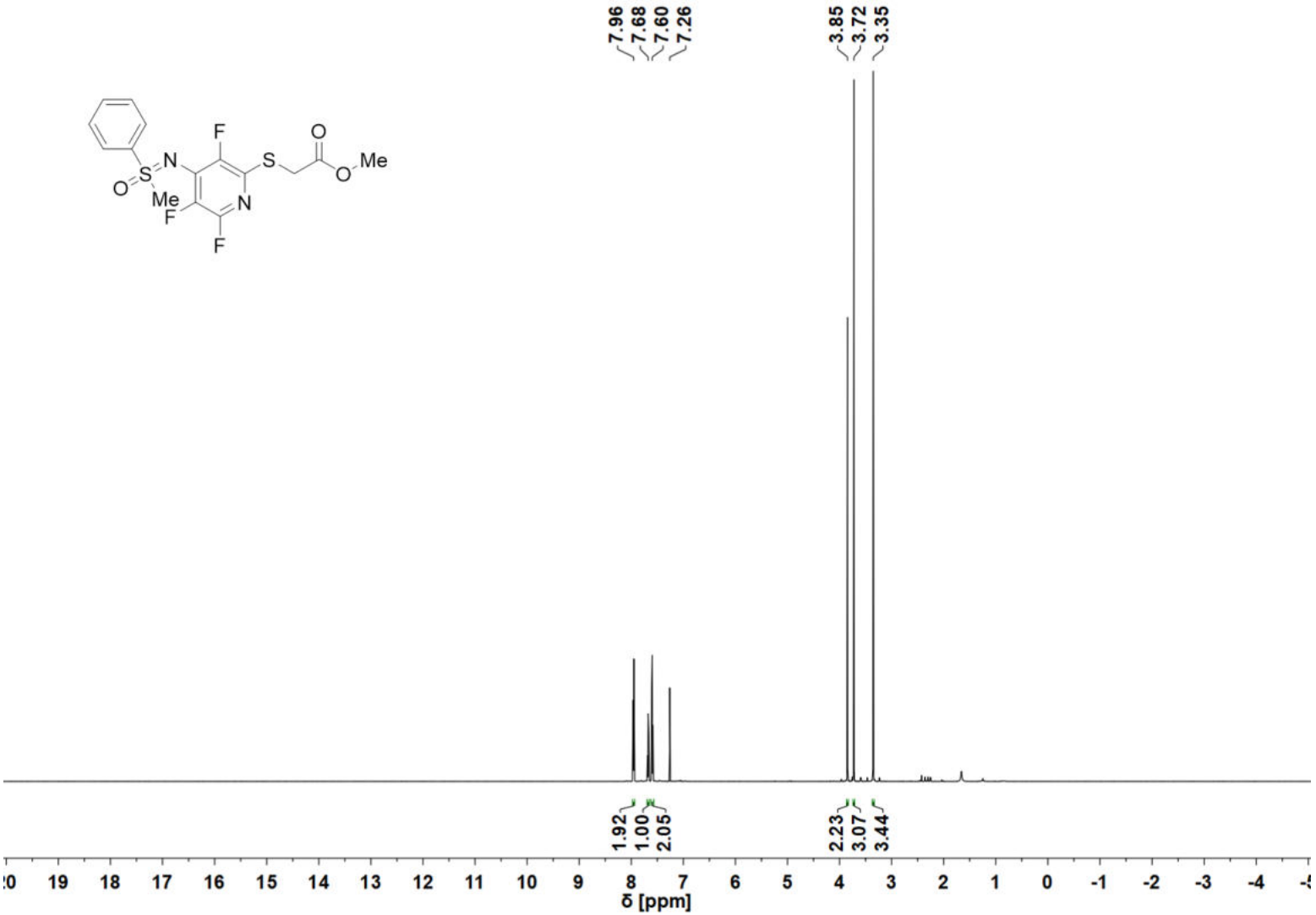

Figure S138 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **5**.

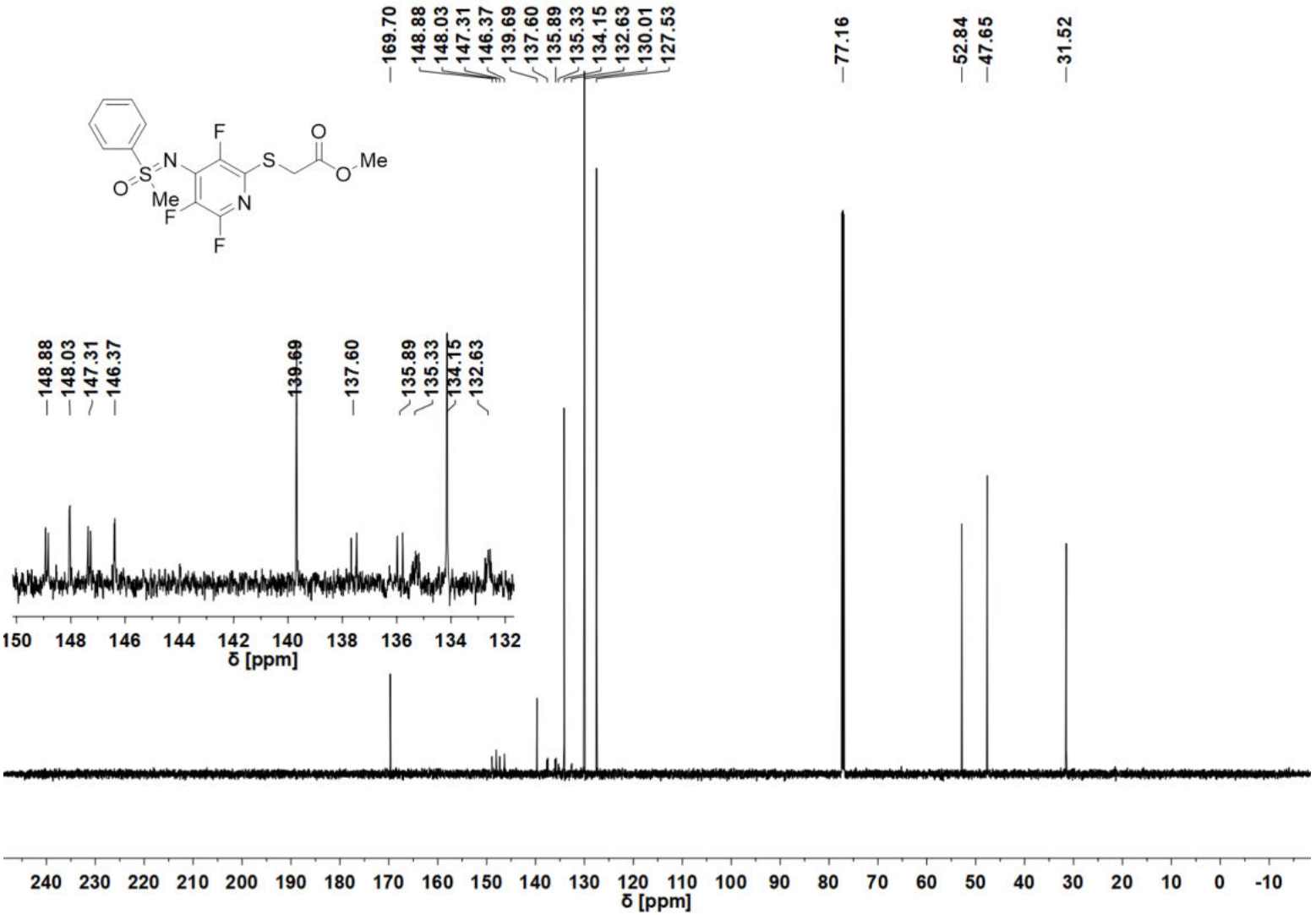

Figure S139 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **5**.

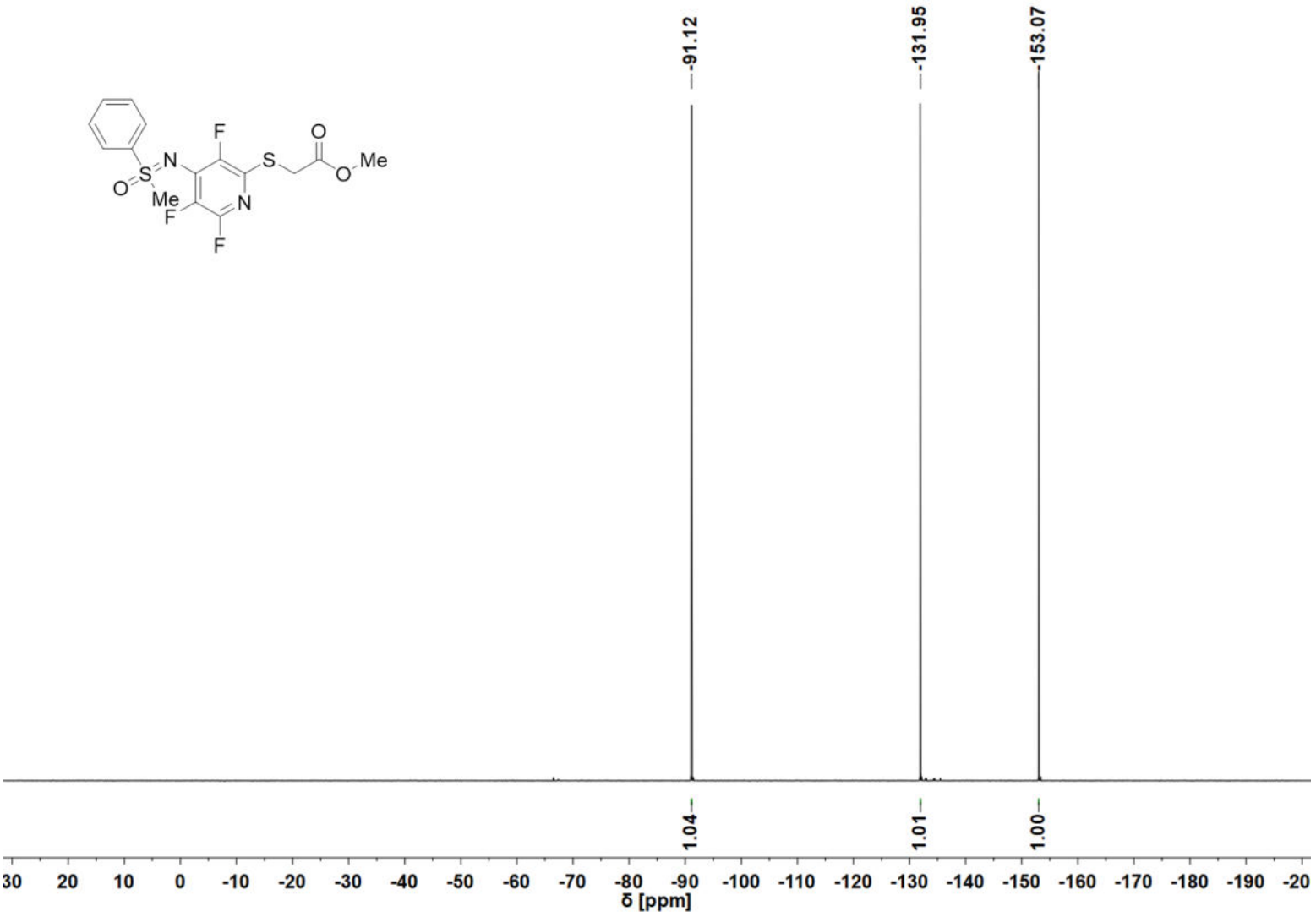

Figure S140 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **5**.

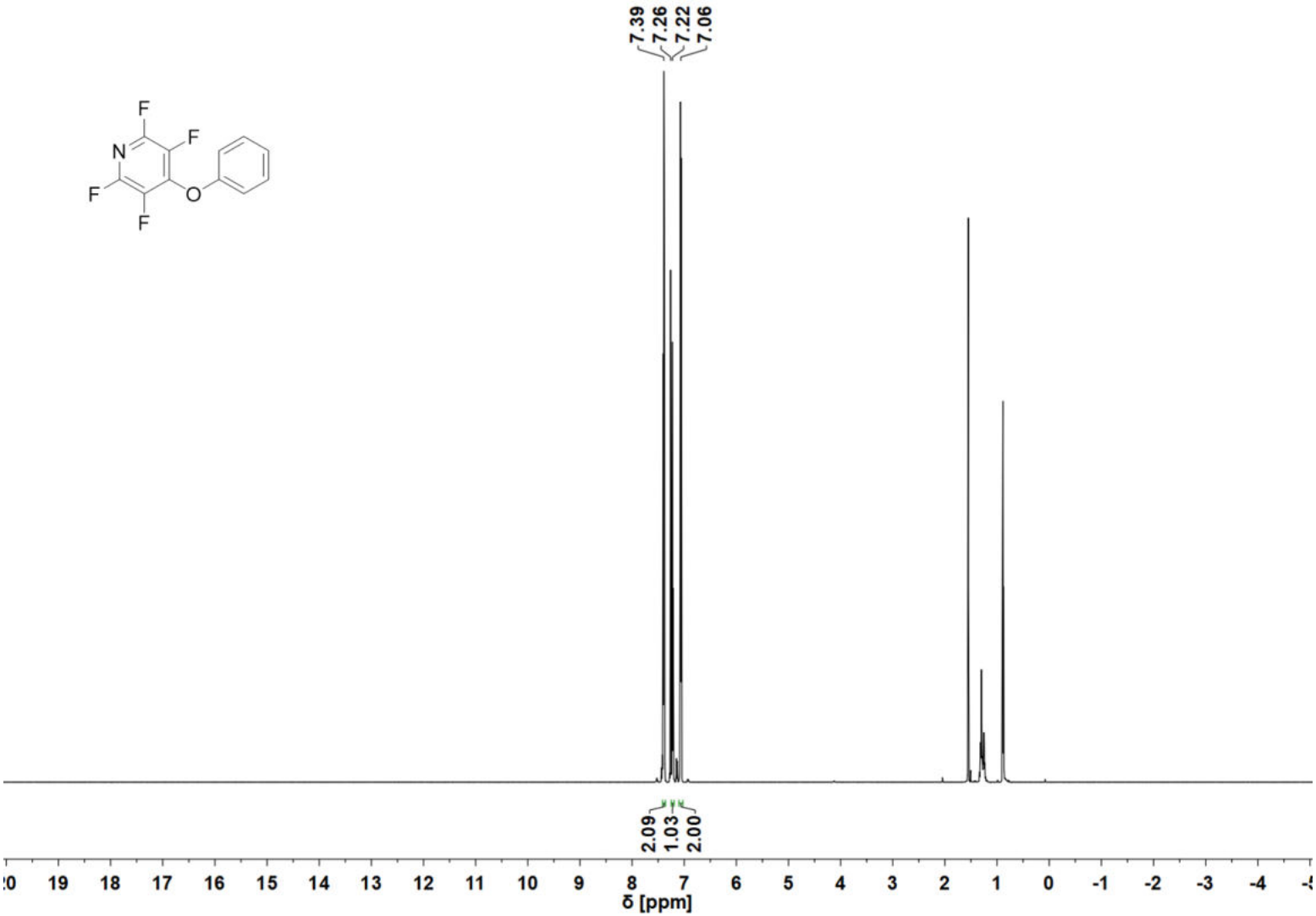

Figure S141 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **6**.

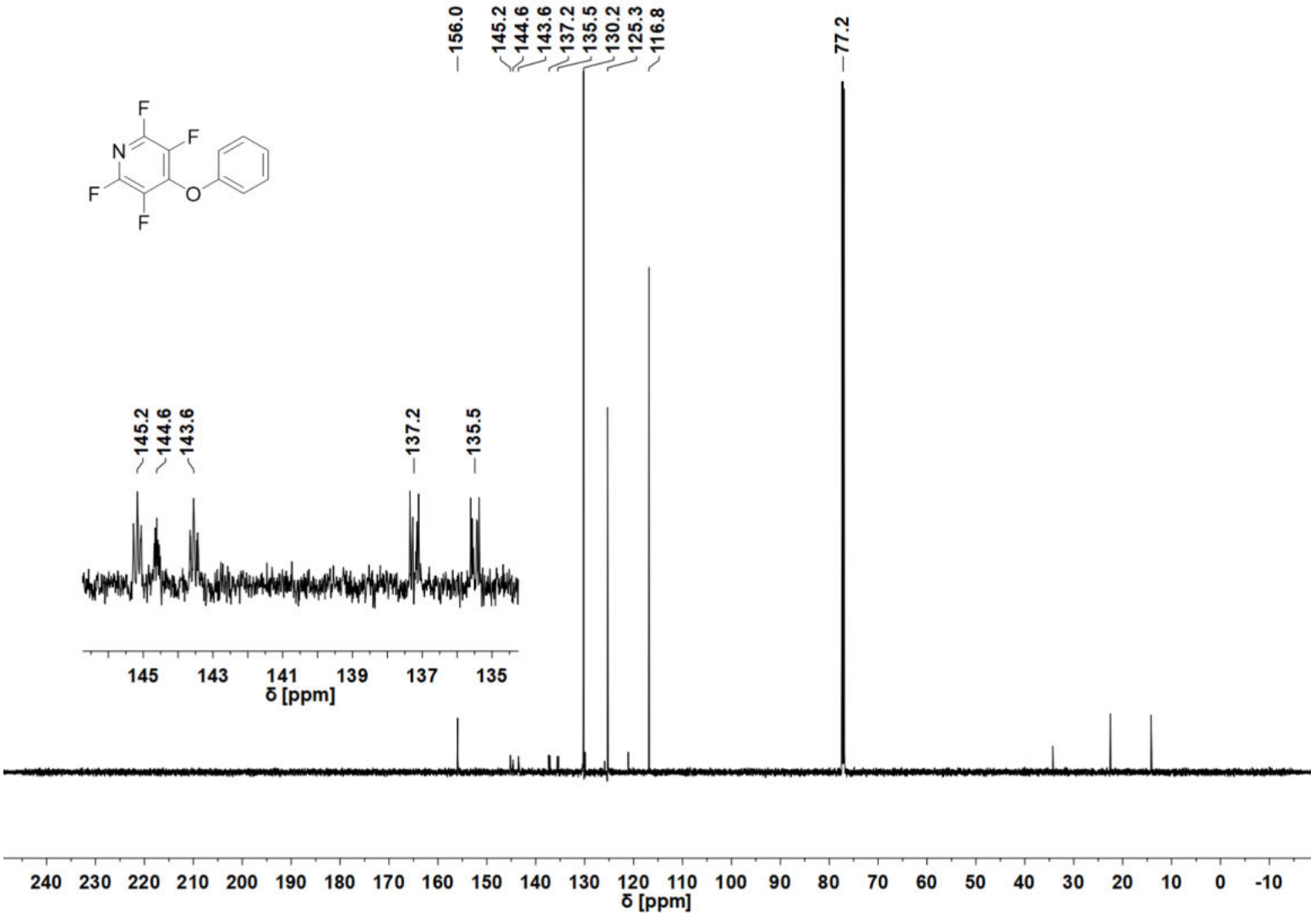

Figure S142 ^{13}C {^{1}H} NMR spectrum ($CDCl_3$, 151 MHz) of **6**.

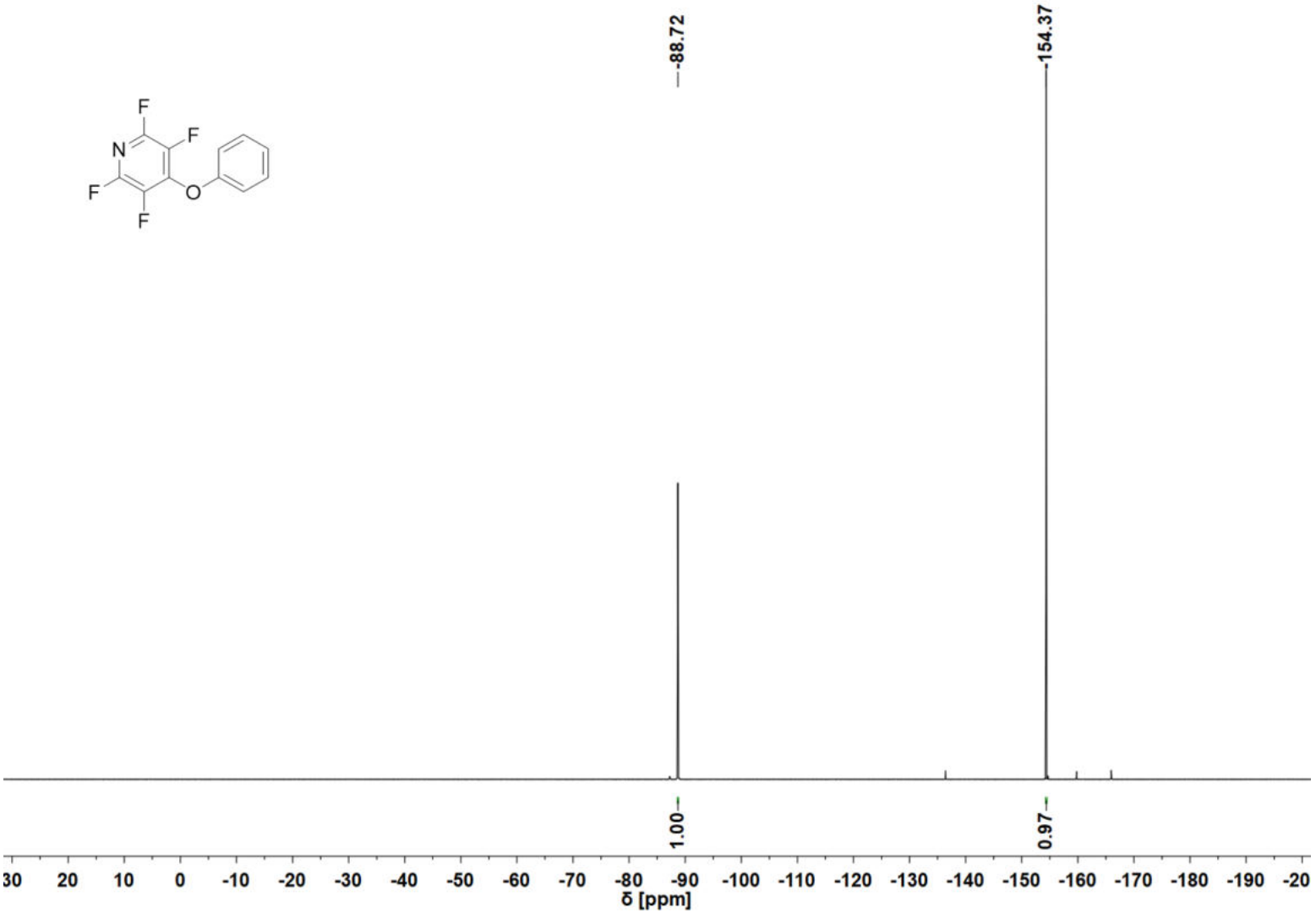

Figure S143 ^{19}F NMR spectrum ($CDCl_3$, 564 MHz) of **6**.