Electronic Supplementary Information

Silver-induced self-immolative Cl-F exchange fluorination of arylsulfur chlorotetrafluorides: Synthesis of arylsulfur pentafluorides

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1. All General Information

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. NMR spectra were recorded on a JEOL JNM-ECZ700R, Bruker Avance 500, Bruker Avance 400 and Varian Mercury 300 instruments and are calibrated using residual undeutetrated solvent ($CHCl_3$ at 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). The $CFCl_3$ [δ = 0.00 ($CDCl_3$)] was used as internal standard for ^{19}NMR. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2020 (ESI-MS). High resolution mass spectrometry were recorded on a Waters Synapt G2 HDMS (ESI-MS). Infrared spectra were recorded on a JASCOFT/IR-4100 spectrometer. Melting points were recorded on a BUCHI M-565. Commercially available chemicals were obtained from Acro Organics, Aldrich Chemical Co., Alfa Aesar, TCI, Ark Farm and used as received unless otherwise stated.

2. General Procedure for Synthesis of arylsulfur chlorotetrafluorides[1]

Procedure I

An oven-dried 30 ml FEP bottle with magnetic stirring bar was charged with disulfide (1.88 mmol), anhydrous spray dried KF (1.75 g, 30.08 mmol) and anhydrous MeCN (10 ml) inside the glove box. The bottle was cooled in an ice/water bath while chlorine gas was bubbled through the stirred reaction mixture for approximately 5 minutes. The bottle was sealed and the reaction mixture was stirred at room temperature for 12-48 h. After reaction was complete, solution was filtrated under N_2 to another 30 ml FEP bottle using a PP/ETFE filter. The residue was washed with MeCN (2 ml×2). MeCN was evaporated in vacuo to give arylsulfur chlorotetrafluorides.

Procedure II

An oven-dried 60 ml FEP bottle with magnetic stirring bar was charged with aryl sulfur (5.3 mmol), anhydrous spray dried KF (2.77 g, 47.7 mmol) and anhydrous MeCN (20 ml) inside the glove box. The bottle was cooled in an ice/water bath while chlorine gas was bubbled through the stirred reaction mixture for approximately 5 minutes. The bottle was sealed and the reaction mixture was stirred at room temperature overnight. After reaction was complete, solution was filtrated under N_2 to another 60 ml FEP bottle using a PP/ETFE filter. The residue was washed with Hexane (5 ml×2). The solvent was evaporated in vacuo to give arylsulfur chlorotetrafluorides.

3. General Method for Synthesis of arylsulfur pentafluorides

Method A:

Crude arylsulfur chlorotetrafluoride (1.0 mmol) and Ag_2CO_3 (138 mg, 0.5 mmol) were carefully weighed into FEP bottle containing a small magnetic stirrer bar in the glove box. Dry CH_2Cl_2 (5 ml) was added. The reaction was stirred at room temperature for 12 h then filtrated through a pad of Kieselguhr and washed with CH_2Cl_2. Then combined filtrate was concentrated under vacuum in the ice bath. The crude was purified by chromatography on silica gel, eluting with pentane/CH_2Cl_2 to give arylsufur pentafluoride.

Method B:

Crude arylsulfur chlorotetrafluoride (1.0 mmol) and Ag_2CO_3 (138 mg, 0.5 mmol) were carefully weighed into FEP bottle containing a small magnetic stirrer bar in the glove box. Dry CH_2Cl_2 (5 ml) was added. The reaction was stirred at 40 ^{o}C for 12-24 h then filtrated through a pad of Kieselguhr and washed with CH_2Cl_2. Then combined

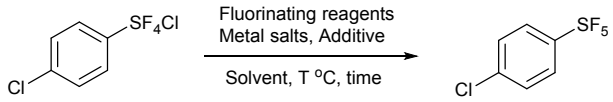
filtrate was concentrated under vacuum in the ice bath. The crude was purified by chromatography on silica gel, eluting with pentane/CH_2Cl_2 to give arylsufur pentafluoride.

Method C:

Crude arylsulfur chlorotetrafluoride (1.0 mmol) and Ag_2CO_3 (138 mg, 0.5 mmol) were carefully weighed into FEP bottle containing a small magnetic stirrer bar in the glove box. The reaction was stirred at 70 °C for 60-72 h then CH_2Cl_2 was added. The solution was filtrated through a pad of Kieselguhr and washed with CH_2Cl_2. Then combined filtrate was concentrated under vacuum in the ice bath. The crude was purified by chromatography on silica gel, eluting with pentane/CH_2Cl_2 to give arylsufur pentafluoride.

4. Optimization study of silver-indeced Cl-F exchange reaction of 2a

Table S1. Initial screening condition.



2a 3a

Entry	Metal salts (equiv)	Fluorinating reagents (equiv)	Additive (equiv)	Solvent	Time (h)	Temp. (°C)	Yield[a]
1	Ag_2CO_3 (1.0)	SelectFluor (2.0)	--	DCM	24	40	75
2	Ag_2CO_3 (1.0)	SelectFluor (2.0)	--	$CHCl_3$	24	70	70
3	Ag_2CO_3 (1.0)	TMAF (2.0)	--	DCM	24	40	0
4	Ag_2CO_3 (1.0)	DMPU·HF (2.0)	--	DCM	24	40	36
5	Ag_2CO_3 (1.0)	Py·HF (2.0)	..	DCM	24	40	35
6	Ag_2CO_3 (1.0)	TBAF (2.0)	--	DCM	24	40	25
7	Ag_2CO_3 (0.5)	DAST (2.0)	--	DCM	24	r.t	23
8	Ag_2CO_3 (0.5)	Fluolead (1.0)	--	DCM	24	40	80
9	--	Fluolead (1.0)	--	DCM	24	40	0
10	Ag_2CO_3 (1.0)	--	--	DCM	24	40	78
11	Ag_2CO_3 (0.7)	--	--	DCM	24	40	79
12	Ag_2CO_3 (0.6)	--	--	DCM	24	40	79
13	Ag_2CO_3 (0.5)	--	--	DCM	24	40	79
14	Ag_2CO_3 (0.4)	--	--	DCM	24	40	78
15	Ag_2CO_3 (0.3)	--	--	DCM	24	40	55
16	Ag_2CO_3 (0.2)	--	--	DCM	24	40	29
17	Ag_2CO_3 (0.5)	--	--	DCM	24	r.t	79
18	Ag_2CO_3 (0.5)	--	--	Hexane	24	r.t	49
19	Ag_2CO_3 (0.5)	--	--	THF	24	r.t	12
20	Ag_2CO_3 (0.5)	--	--	MeCN	24	r.t	trace
21	Ag_2CO_3 (0.5)	--	--	Dioxane	24	r.t	11
22	Ag_2CO_3 (0.5)	--	--	Toluene	24	r.t	7
23	Ag_2CO_3 (0.5)	--	--	Solkane 367/227	24	r.t	74
24	AgF (1.0)	--	--	DCM	24	r.t	29

25	AgCl (1.0)	--	--	DCM	24	r.t	0
26	AgO (1.0)	--	--	DCM	24	r.t	68
27	AgOTf (1.0)	--	--	DCM	24	r.t	32
28	Ag_2O (0.5)	--	--	DCM	24	r.t	30
29	AgOAc (1.0)	--	--	DCM	24	r.t	9
30	CuF_2 (1.0)	--	--	DCM	24	r.t	0
31	ZnF_2 (1.0)	--	--	DCM	24	r.t	0
32	CuO (1.0)	--	--	DCM	24	r.t	0
33	ZnO (1.0)	--	--	DCM	24	r.t	0
34	CuI (1.0)	--	--	DCM	24	r.t	trace
35	Na_2CO_3 (1.0)	--	--	DCM	24	r.t	0
36	Cs_2CO_3 (1.0)	--	--	DCM	24	r.t	0
37	Ag_2CO_3 (0.3)	--	Pyridine (0.3)	DCM	24	r.t	13
38	Ag_2CO_3 (0.3)	--	Et_3B (0.088)	DCM	24	r.t	58
39	Ag_2CO_3 (0.2)	--	$Na_2S_2O_8$ (2.0)	DCM	24	r.t	28
40	Ag_2CO_3 (0.5)	--	--	DCM	1	r.t	29
41	Ag_2CO_3 (0.5)	--	--	DCM	2	r.t	42
42	Ag_2CO_3 (0.5)	--	--	DCM	3	r.t	53
43	Ag_2CO_3 (0.5)	--	--	DCM	4	r.t	56
44	Ag_2CO_3 (0.5)	--	--	DCM	6	r.t	73
45	Ag_2CO_3 (0.5)	--	--	DCM	10	r.t	79
46	**Ag_2CO_3 (0.5)**	**--**	**--**	**DCM**	**12**	**r.t**	**79**
47	Ag_2CO_3 (0.5)	--	--	DCM	18	r.t	77

Conditions: **2a** (51 mg, 0.2 mmol). [a] Yield determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard.

5. ^{19}F NMR spectra of the Cl-F exchange reaction process

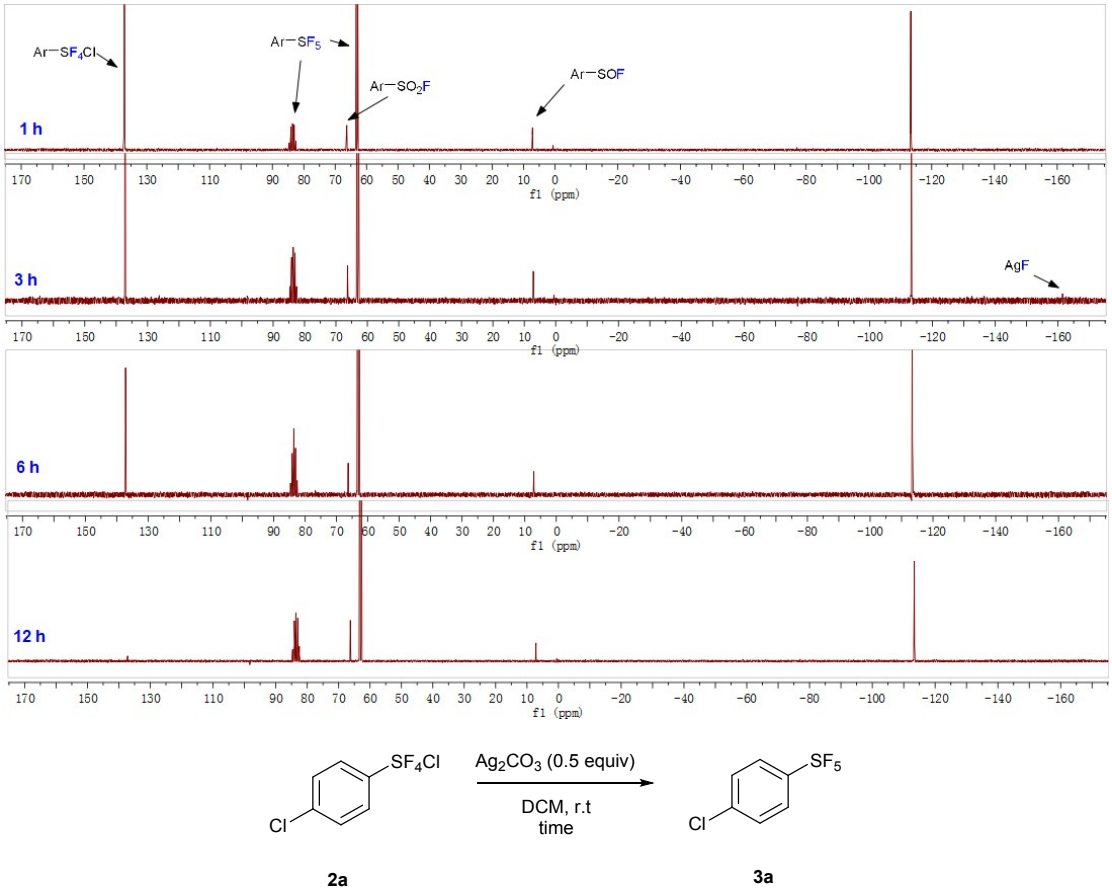
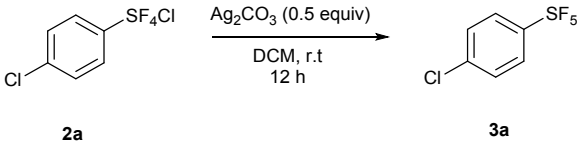


Figure S1. ^{19}F NMR spectra of the Cl-F exchange reaction process

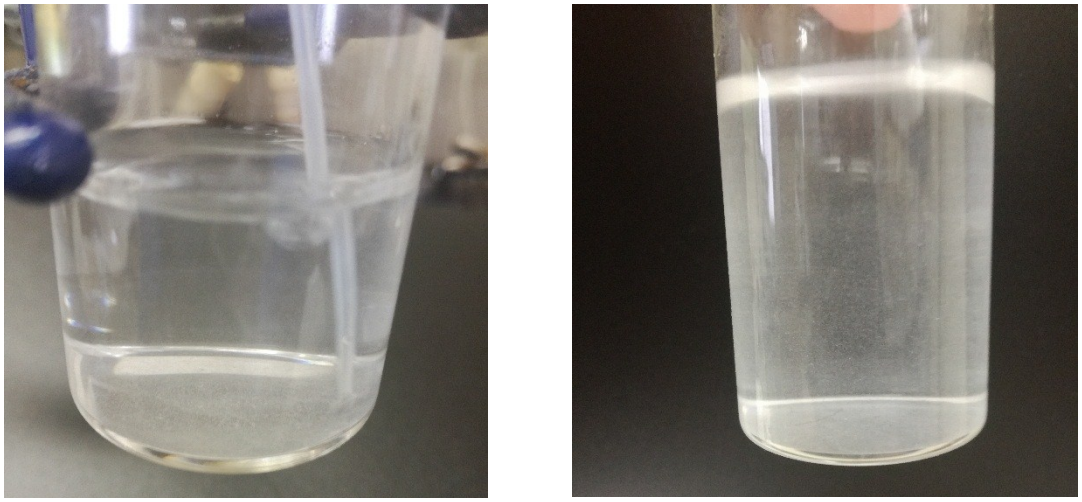
Entry	Time (h)	Yield[a] of $ArSO_2F$ (%)
1	1	5
2	3	7
3	6	11
4	12	12
5	24	12

6. Release of CO_2 in the process of silver carbonate-induced Cl-F exchange reaction



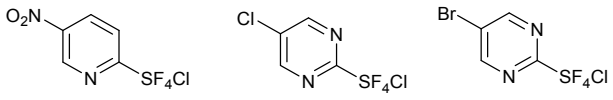
Crude 4-chlorophenylsulfur chlorotetrafluoride (51.0 mg, 0.2 mmol) and Ag_2CO_3 (27.5 mg, 0.1 mmol) were carefully weighed into FEP tube containing a small magnetic stirrer bar in the glove box. Dry CH_2Cl_2 (1 ml) was added. The reaction was stirred at room temperature for 12 h. Then, using argon gas, the generated gas was transferred slowly into another tube filled with saturated aqueous $Ca(OH)_2$. The aqueous solution became turbid, and white precipitate of $CaCO_3$ was observed in the aqueous solution. It indicates that CO_2 generated during the silver carbonate-induced Cl-F exchange reaction of $ArSF_4Cl$.

Clear, aqueous solution of $Ca(OH)_2$ (left). Transferring the gas, generated in the reaction mixture, into another tube filled with aqueous solution of $Ca(OH)_2$ (right).



After bubbling the gas generated in the reaction mixture, white precipitates were observed on the bottom of bottle (left). The precipitate was not dissolved by adding water (right). It indicates the formation of $CaCO_3$.

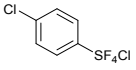
7. Examples of substrates failed for the silver salts induced Cl-F reaction.

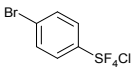
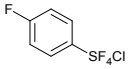
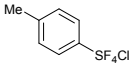
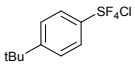
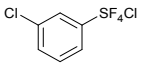
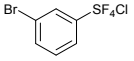
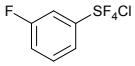
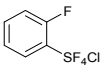
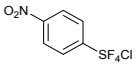
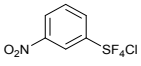
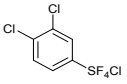
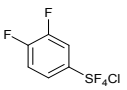


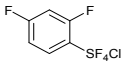
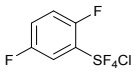
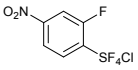
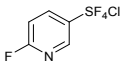
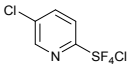
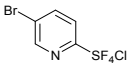
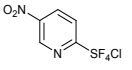
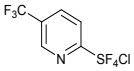
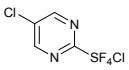
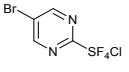
2u **2v** **2w**

Figure S2.Substrates failed for the silver salts induced Cl-F reaction, analyzed by ^{19}F NMR and GC-MS

8. Table S2. The procedure, yields, appearance and NMR data of arylsulfur chlorotetrafluorides

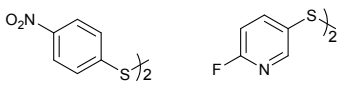
Entry	Structure	Procedure	Yield[a]	Appearance	NMR ($CDCl_3$; δ, ppm)
2a		II	81%	oil	^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.1 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.79 (s, 4F).

2b		II	75%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 137.10 (s, 4F)
2c		II	67%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.13 (t, *J* = 8.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -107.46 (s, 1F)
2d		II	71%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.39 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 137.56 (s, 4F)
2e[b]		II	80%	solid	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 1H), 7.65 (dd, *J* = 11.9, 4.4 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 1.39 – 1.27 (m, 9H). ^{19}F NMR (282 MHz, $CDCl_3$) δ135.87 (s, 4F).
2f		II	64%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.46 – 7.36 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.04 (s, 4F).
2g		II	79%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 1H), 7.73 – 7.60 (m, 2H), 7.34 (t, *J* = 8.3 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 138.11 (s, 4F).
2h		II	69%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 1H), 7.50 – 7.39 (m, 2H), 7.24 – 7.18 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.28 – 136.11 (m, 4F), -110.11 (dd, *J* = 14.3, 7.7 Hz, 1F).
2i		II	71%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 1H), 7.51 (dd, *J* = 12.5, 7.3 Hz, 1H), 7.26 – 7.13 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 140.32 (d, *J* = 24.0 Hz, 4F), -107.85 – -108.46 (m, 1F)
2j		I	87%	solid	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 134.98 (s, 4F)
2k		I	84%	solid	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.42 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 6.4 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 135.74 (s, 4F)
2l		II	80%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.3 Hz, 1H), 7.57 (dt, *J* = 16.0, 5.7 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.24 (s, 4F)
2m		II	66%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 1H), 7.58 – 7.50 (m, 1H), 7.31 – 7.20 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.88 – 136.57 (m, 4F), -130.98 – -131.50 (m, 1F), -133.92 – -134.47 (m, 1F)

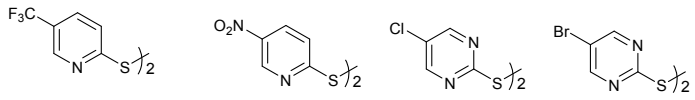
2n		II	62%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.69 (m, 1H), 7.12 (t, *J* = 8.8 Hz, 1H), 7.06 – 6.83 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 140.83 (d, *J* = 23.7 Hz, 4F), -98.60 – -112.98 (m, 2F)
2o		II	73%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 1H), 7.25 – 7.15 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 139.25 (d, *J* = 24.3 Hz, 4F), -113.40 – -114.12 (m, 1F), -116.46 (dd, *J* = 13.8, 7.5 Hz, 1F)
2p		I	79%	solid	^{1}H NMR (300 MHz, cdcl$_3$) δ 8.12 (dt, *J* = 13.5, 4.4 Hz, 2H), 7.98 (dd, *J* = 9.4, 6.4 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.07 (d, *J* = 12.3 Hz, 4F), -110.25 (d, *J* = 5.9 Hz, 4F)
2q		I	77%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.22 – 8.11 (m, 1H), 7.05 (dd, *J* = 9.0, 2.8 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 138.44 (s, 4F), -62.22 (s, 1F)
2r		I	75%	solid	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 127.99 (s, 4F).
2s		I	91%	solid	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 128.14 (s, 4F)
2t		I	82%	solid	^{1}H NMR (300 MHz, $CDCl_3$) δ 9.38 (d, *J* = 2.4 Hz, 1H), 8.70 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 127.67 (s, 4F).
2u		I	69%	solid	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 123.39 (s, 4F), -63.12 (s, 1F)
2v		I	70%	oil	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 127.17 (s, 4F).
2w		I	67%	oil	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 127.35 (s, 4F).

[a] crude yield, with purities in the range of 80-95% determined by ^{19}F NMR. [b] aryl sulfur (5.3 mmol), dried CsF (4.78 g, 53 mmol) and anhydrous MeCN (20 ml), rt, 24 h.

9. Synthesis of disulfides



1j **1q** **1r** **1s**

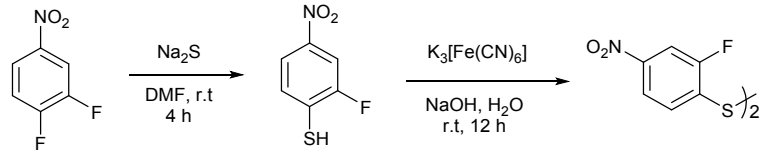


1t **1u** **1v** **1w**

Disulfides were prepared according to the literature procedures.[2]

10. Preparation of Compounds

A typical procedure (synthesis of **1q**) is shown below:

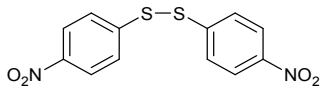


S_1 **S_2** **1p**

1,2-difluoro-4-nitrobenzene **S1** (2.22 g, 14.0 mmol) was dissolved in DMF (35 ml). Na_2S (1.20 g, 15.4 mmol) was added and the mixture was stirred at room temperature for around 4 h. After completion, the solution was acidified with HCl aqueous (2 N) to pH 2-3, and extracted with Et_2O (3×20 ml). The combined organic phases were washed with brine and dried with $MgSO_4$. The crude residue that was obtained after filtration and Et_2O was evaporated in vacuo to give 2-fluoro-4-nitrobenzenethiol **S2**. This material was used for the subsequent disulfidation without further purification.

Added the whole amount of 2-fluoro-4-nitrobenzenethiol **S2** to the solution of NaOH (0.67 g, 16.76 mmol) in water (30 ml) was stirred for 30 min. The $K_3[Fe(CN)_6]$ (5.52 g, 16.76 mmol) in water (40 ml) was dropwise added and stirred at room temperature for 12 h. The formed precipitate was filtrated ,washed with water and dried in vacuo to give 1,2-bis(2-fluoro-4-nitrophenyl)disulfane **1p** as yellow solid (1.47 g, 61% yield from **S1**); m.p = 100-102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 7.96 (m, 4H), 7.52 – 7.37 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -103.16 (t, J = 7.5 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.00 (d, J = 250.6 Hz), 148.12 (d, J = 7.8 Hz), 131.40 (d, J = 16.9 Hz), 129.09 (d, J = 1.4 Hz), 120.22 (d, J = 3.6 Hz), 111.76 (d, J = 26.2 Hz). IR (KBr, cm^{-1}): 3099, 3033, 1589, 1525, 1461, 1346, 1218, 933, 898, 879, 829, 808, 740. HRMS (TOF/EI+): Calculated for $C_{12}H_6F_2N_2O_4S_2^+$: 343.9737, found: 343.9745.

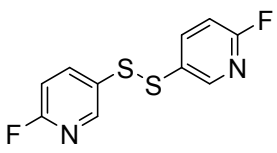
1,1′-bis(4-dinitrophenyl)disulfide



1j

Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 4H), 7.62 (d, J = 8.7 Hz, 4H).

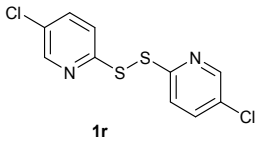
3,3′-bis(6-fluoropyridyl)disulfide



1q

White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26 (s, 2H), 7.91 (t, J = 6.6 Hz, 2H), 6.96 (dd, J = 8.0, 2.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -67.46 (s, 2F).

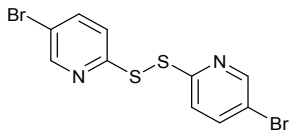
2,2′-bis(5-chloropyridyl)disulfide



1r

White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 1.5 Hz, 2H), 7.61 – 7.54 (m, 4H).

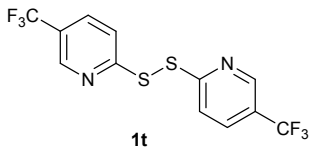
2,2′-bis(5-bromopyridyl)disulfide



1s

White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.3 Hz, 2H), 7.73 (dd, *J* = 8.6, 2.2 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H).

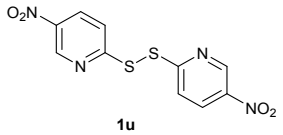
2,2′-bis(5-trifluoromethylpyridyl)disulfide



1t

White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.28 (s, 6F).

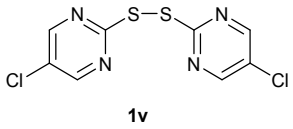
2,2′-bis(5-nitropyridyl)disulfide



1u

khaki crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (s, 2H), 8.40 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H).

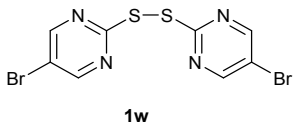
2,2′-bis(5-chloropyrimidyl)disulfide



1v

Yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.22, 156.46, 128.91, 77.41, 77.16, 76.91. IR (KBr, cm^{-1}): 3036, 1630, 1534, 1375, 1251, 1177, 759. HRMS (TOF/EI+): Calculated for $C_8H_4Cl_2N_4S_2^+$: 289.9254, found: 289.9256.

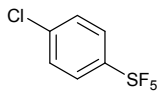
2,2′-bis(5-bromopyrimidyl)disulfide



1w

White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.71, 158.55, 117.45, 77.41, 77.16, 76.91. IR (KBr, cm^{-1}): 3023, 1637, 1529, 1383, 1178, 1165, 1108, 762. HRMS (TOF/EI+): Calculated for $C_8H_4Br_2N_4S_2^+$: 377.8244, found: 379.8231.

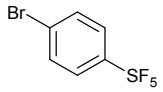
4-chlorophenylsulfur pentafluoride



3a

Prepared following method A. Flash column chromatography: pentane. Yield 0.147 g, 62%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.4 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 84.85 – 82.43 (m, 4F), 63.15 (d, *J* = 150.3 Hz, 1F).

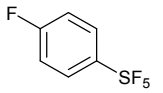
4-bromophenylsulfur pentafluoride



3b

Prepared following method A. Flash column chromatography: pentane. Yield 0.169 g, 60%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 84.85 – 82.13 (m, 1F), 63.02 (d, *J* = 150.4 Hz, 4F).

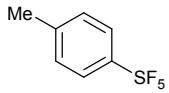
4-fluorophenylsulfur pentafluoride



3c

Prepared following method A. Flash column chromatography: pentane. Yield 0.133 g, 60%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.71 (m, 2H), 7.15 (t, *J* = 8.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 85.18 – 82.31 (m, 1F), 63.28 (d, *J* = 150.3 Hz, 4F), -107.60 (s, 1F).

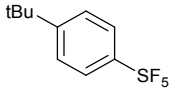
***p*-tolylsulfur pentafluoride**



3d

Prepared following method A. Flash column chromatography: pentane. Yield 0.133 g, 61%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 86.17 – 83.58 (m, 1F), 62.66 (d, *J* = 149.9 Hz, 4F).

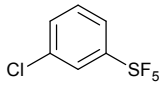
4-(*tert*-butyl)phenylsulfur pentafluoride



3e

Prepared following method A. Flash column chromatography: pentane. Yield 0.158 g, 61%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 1.32 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 86.34 – 83.33 (m, 1F), 62.64 (d, *J* = 149.9 Hz, 4F).

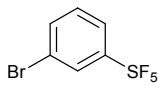
3-chlorophenylsulfur pentafluoride



3f

Prepared following method B. Flash column chromatography: pentane. Yield 0.140 g, 59%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (t, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.38 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 83.78 – 81.21 (m, 1F), 62.31 (d, *J* = 150.4 Hz, 4F).

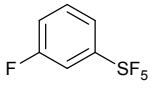
3-bromophenylsulfur pentafluoride



3g

Prepared following method B. Flash column chromatography: pentane. Yield 0.141 g, 50%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (t, *J* = 1.9 Hz, 1H), 7.74 – 7.64 (m, 2H), 7.36 (t, *J* = 8.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 83.80 – 81.01 (m, 1F), 62.34 (d, *J* = 150.5 Hz, 4F).

3-fluorophenylsulfur pentafluoride

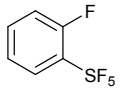


3h

Prepared following method B. Flash column chromatography: pentane. Yield 0.100 g, 45%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.41 (m, 2H), 7.29 – 7.20 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 84.31 – 81.54 (m), 62.72 (d, *J* = 150.3 Hz), -109.76 (dd, *J* = 14.2, 7.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.83 (d, *J* = 250.2 Hz), 155.27 – 154.13 (m), 130.23 (d, *J* = 7.9 Hz), 122.24 – 121.60 (m), 119.00 (d, *J* = 20.9 Hz), 114.85 – 113.77 (m). IR (KBr, cm^{-1}): 3127, 3091,

2362, 1590, 1506, 1101, 844, 809, 688, 574. HRMS (TOF/EI+): Calculated for $C_6H_4F_6S^+$: 221.9938, found: 221.9954.

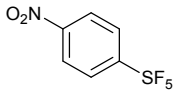
2-fluorophenylsulfur pentafluoride



3i

Prepared following method B. Flash column chromatography: pentane. Yield 0.126 g, 57%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 1H), 7.59 – 7.46 (m, 1H), 7.30 – 7.16 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 82.71 – 79.85 (m, 1F), 67.60 (dd, *J* = 150.9, 24.7 Hz, 4F), -108.32 – -109.04 (m, 1F).

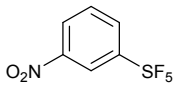
4-nitrophenylsulfur pentafluoride



3j

Prepared following method C. Flash column chromatography: Pentane/CH_2Cl_2 3/1. Yield 0.164 g, 66%. Yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 82.16 – 79.19 (m, 1F), 62.15 (d, *J* = 150.7 Hz, 4F).

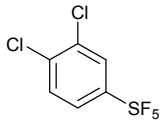
3-nitrophenylsulfur pentafluoride



3k

Prepared following method C. Flash column chromatography: pentane/CH_2Cl_2 3/1. Yield 0.127 g, 51%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 8.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 81.79 – 79.42 (m, 1F), 62.35 (d, *J* = 150.9 Hz, 4F).

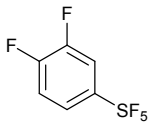
3,4-dichlorophenylsulfur pentafluoride



3l

Prepared following method C. Flash column chromatography: pentane. Yield 0.144 g, 53%. Colorless oil. m.p = 39-40 ^{o}C ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.3 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 83.67 – 80.89 (m, 1F), 63.24 (d, *J* = 150.7 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.37 (p, *J* = 19.5 Hz), 136.59 (s), 133.27 (s), 130.58 (s), 128.37 (p, *J* = 4.8 Hz), 125.39 (p, *J* = 4.6 Hz). IR (KBr, cm^{-1}): 3102, 3021, 1461, 1384, 1145, 1037, 860, 842, 765, 601, 536. HRMS (TOF/EI+): Calculated for $C_6H_3Cl_2F_5S^+$: 271.9253, found: 271.9276.

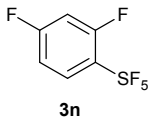
3,4-difluorophenylsulfur pentafluoride



3m

Prepared following method C. Flash column chromatography: Pentane. Yield 0.065 g, 27%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 1H), 7.60 – 7.52 (m, 1H), 7.35 – 7.22 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 83.85 – 81.25 (m, 1F), 63.59 (d, *J* = 150.8 Hz, 4F), -130.56 – -131.12 (m, 1F), -133.39 – -133.96 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.05 (dd, *J* = 256.2, 12.3 Hz), 149.60 – 149.07 (m), 149.44 (dd, *J* = 253.1, 13.4 Hz), 123.30 – 122.96 (m), 117.48 (d, *J* = 18.6 Hz), 117.05 – 116.49 (m). IR (KBr, cm^{-1}): 3141, 3099, 1617, 1517, 1427, 1286, 1083, 854, 813, 622, 597. HRMS (TOF/EI+): Calculated for $C_6H_3F_7S^+$: 239.9844, found: 239.9840.

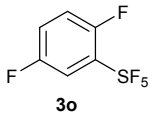
2,4-difluorophenylsulfur pentafluoride



3n

Prepared following method C. Flash column chromatography: pentane. Yield 0.115 g, 48%. Colorless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H), 7.01 – 6.91 (m, 2H). ^{19}F NMR (659 MHz, $CDCl_3$) δ 82.03 – 80.85 (m, 1F), 68.88 (dd, *J* = 152.3, 22.9 Hz, 4F), -102.52 (s, 1F), -102.62 – -102.86 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.50 (dd, *J* = 257.3, 12.8 Hz), 157.12 (dd, *J* = 261.3, 10.6 Hz), 137.32 – 135.89 (m), 130.74 – 130.10 (m), 111.72 (dd, *J* = 22.4, 3.7 Hz), 106.01 (t, *J* = 26.5 Hz). HRMS (TOF/EI+): Calculated for $C_6H_3F_7S^+$: 239.9844, found: 239.9854.

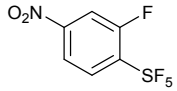
2,5-difluorophenylsulfur pentafluoride



3o

Prepared following method C. Flash column chromatography: pentane. Yield 0.098 g, 41%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 1H), 7.28 – 7.18 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 81.43 – 78.61 (m, 1F), 68.42 – 67.17 (m, 4F), -113.31 – -114.26 (m, 1F), -115.63 – -116.27 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.31 (d, *J* = 246.9 Hz), 152.39 (d, *J* = 257.1 Hz), 140.63 – 139.87 (m), 120.86 (dd, *J* = 23.6, 9.0 Hz), 119.15 (dd, *J* = 26.5, 8.1 Hz), 115.91 (dp, *J* = 28.2, 5.1 Hz). IR (KBr, cm^{-1}): 3131, 3097, 1502, 1411, 1122, 1068, 657, 605, 566. HRMS (TOF/EI+): Calculated for $C_6H_3F_7S^+$: 239.9844, found: 239.9835.

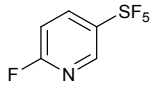
2-fluoro-4-nitrophenylsulfur pentafluoride



3p

Prepared following method C, under 100°C, reaction time for 60 h. Flash column chromatography: petane/CH_2Cl_2 10/1. Yield 0.109 g, 41%. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (t, *J* = 7.6 Hz, 2H), 8.05 – 7.95 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 79.73 – 76.86 (m, 1F), 68.60 – 67.13 (m, 4F), -101.47 – -102.42 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.75 (d, *J* = 266.4 Hz), 150.73 (d, *J* = 8.0 Hz), 145.56 – 144.48 (m), 130.74 (p, *J* = 5.0 Hz), 119.58 (d, *J* = 4.1 Hz), 114.59 (d, *J* = 28.8 Hz). IR (KBr, cm^{-1}): 3124, 3062, 1544, 1482, 1355, 1243, 1066, 863, 838, 740, 609, 582, 541. HRMS (TOF/EI+): Calculated for $C_6H_3F_6NO_2S^+$: 266.9789, found: 266.9805.

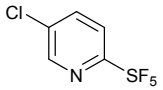
3-(6-fluoropyridyl)sulfur pentafluoride



3q

Prepared following method C, under 100°C, reaction time for 60 h. Flash column chromatography: Pentane/CH_2Cl_2 3/1. Yield 0.033 g, 15%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.29 – 8.12 (m, 1H), 7.08 (dd, *J* = 8.9, 3.1 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 82.71 – 79.80 (m, 1F), 65.36 (d, *J* = 151.4 Hz, 4F), -62.12 (s, 1F).

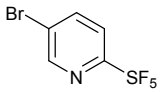
2-(5-chloropyridyl)sulfur pentafluoride



3r

Prepared following method C, under 100°C, reaction time for 60 h. Flash column chromatography: Pentane/CH_2Cl_2 3/1. Yield 0.065 g, 27%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.3 Hz, 1H), 7.95 – 7.85 (m, 1H), 7.73 (d, *J* = 8.7 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 79.06 – 76.34 (m), 53.24 (d, *J* = 150.3 Hz).

2-(5-bromopyridyl)sulfur pentafluoride

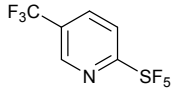


3s

Prepared following method C, under 100°C, reaction time for 60 h. Flash column

chromatography: Pentane/CH_2Cl_2 3/1. Yield 0.099 g, 35%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, *J* = 2.2 Hz, 1H), 8.11 – 8.00 (m, 1H), 7.67 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 79.03 – 76.18 (m, 1F), 53.14 (d, *J* = 150.3 Hz, 4F).

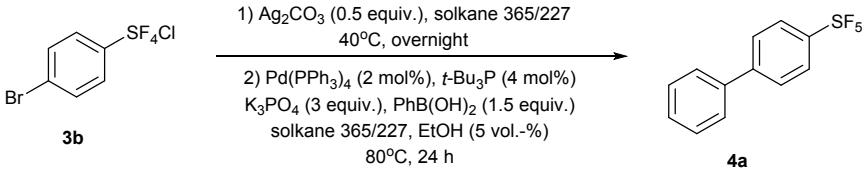
2-(5-trifluoropyridyl)sulfur pentafluoride



3t

Prepared following method C, under 100°C, reaction time for 60 h. Flash column chromatography: Pentane/CH_2Cl_2 3/1. Yield 0.057 g, 21%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 77.76 – 75.11 (m, 1F), 52.35 (d, *J* = 150.5 Hz, 4F), -62.63 (s, 1F).

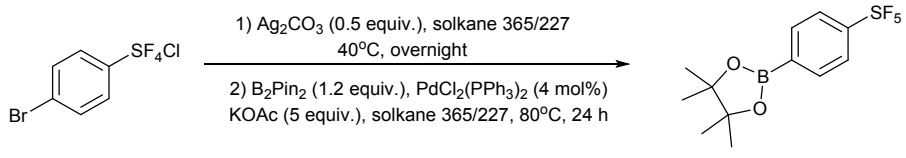
(4-biphenyl)sulfur pentafluoride[3]



3b **4a**

Crude 4-bromophenylsulfur chlorotetrafluoride (0.218 g, 0.728 mmol) and Ag_2CO_3 (0.100 g, 0.364 mmol) were carefully weighed into FEP bottle containing a small magnetic stirrer bar in the glove box. Solkane 365/227 (4 ml) was added. The reaction was stirred at 40°C for overnight, then cooled to room temperature and anhydrous EtOH (0.2 ml) was added by using a syringe. To the mixture were added $Pd(PPh_3)_4$ (16.8 mg, 0.014 mmol), *t*Bu_3P (5.9 mg, 0.029 mmol), K_3PO_4 (463.6 mg, 2.184 mmol), $PhB(OH)_2$ (133.1 mg, 1.092 mmol) in the glovebox filled with argon gas. The mixture was stirred at 80°C (oil bath temperature) for 24 h. After cooling to room temperature, to the mixture was added saturated aqueous ammonium chloride, filtrated through celite, washed with pentane. The aqueous layer was extracted with pentane. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum in the ice bath. The crude was purified by column chromatography on silica gel (pentane) to give compound (4-biphenyl)sulfur pentafluoride **4a** as white solid (0.131 g**,** 64% yield for 4-bromophenylsulfur chlorotetrafluoride) m.p = 54-56 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.50 – 7.43 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 86.34 – 83.34 (m, 1F), 63.15 (d, *J* = 150.0 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.47 – 152.62 (m), 144.67 (s), 139.22 (s), 129.20 (s), 128.90 (s), 128.59 (s), 127.42 (d, *J* = 5.2 Hz), 126.55 (p, *J* = 4.5 Hz). IR (KBr, cm^{-1}): 3077, 3033, 1569, 1482, 1398, 1106, 850, 763, 736, 597, 584. HRMS (TOF/EI+): Calculated for $C_{12}H_9F_5S^+$: 280.0345, found: 280.0354.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylsulfur pentafluoride[4]



3b **4b**

Crude 4-bromophenylsulfur chlorotetrafluoride (0.218 g, 0.728 mmol) and Ag_2CO_3 (0.100 g, 0.364 mmol) were carefully weighed into FEP bottle containing a small magnetic stirrer bar in the glove box. Solkane 365/227 (4 ml) was added. The reaction was stirred at 40 °C for overnight. Then, after cooling to room temperature, to the mixture were added B_2Pin_2 (0.221 g, 0.874 mmol), $PdCl_2((PPh_3)_2$ (20.4 mg, 0.029 mmol), KOAc (0.357 g, 3.64 mmol) in the glovebox filled with argon gas. The mixture was stirred at 80 °C (oil bath temperature) for 24 h. After cooling to

room temperature, to the mixture was added saturated aqueous ammonium chloride, filtrated through celite, washed with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum in the ice bath. The crude was purified by column chromatography on silica gel (pentane/CH_2Cl_2 1:1) to give compound 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylsulfur pentafluoride **4b** as white solid (0.122 g**,** 51% yield for 4-bromophenylsulfur chlorotetrafluoride). mp = 86-88 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 1.35 (s, 12H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 85.20 – 82.22 (m, 1F), 61.68 (d, J = 149.6 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.19 (p, J = 16.9 Hz), 135.25 (s), 125.19 (p, J = 4.5 Hz), 84.57 (s), 25.00 (s). IR (KBr, cm^{-1}): 3000, 2981, 2940, 1602, 1402, 1365, 1338, 1274, 1145, 1081, 835, 808. HRMS (TOF/EI+): Calculated for $C_{12}H_{16}BF_5O_2S^+$: 330.0884, found: 330.0898.

11. References

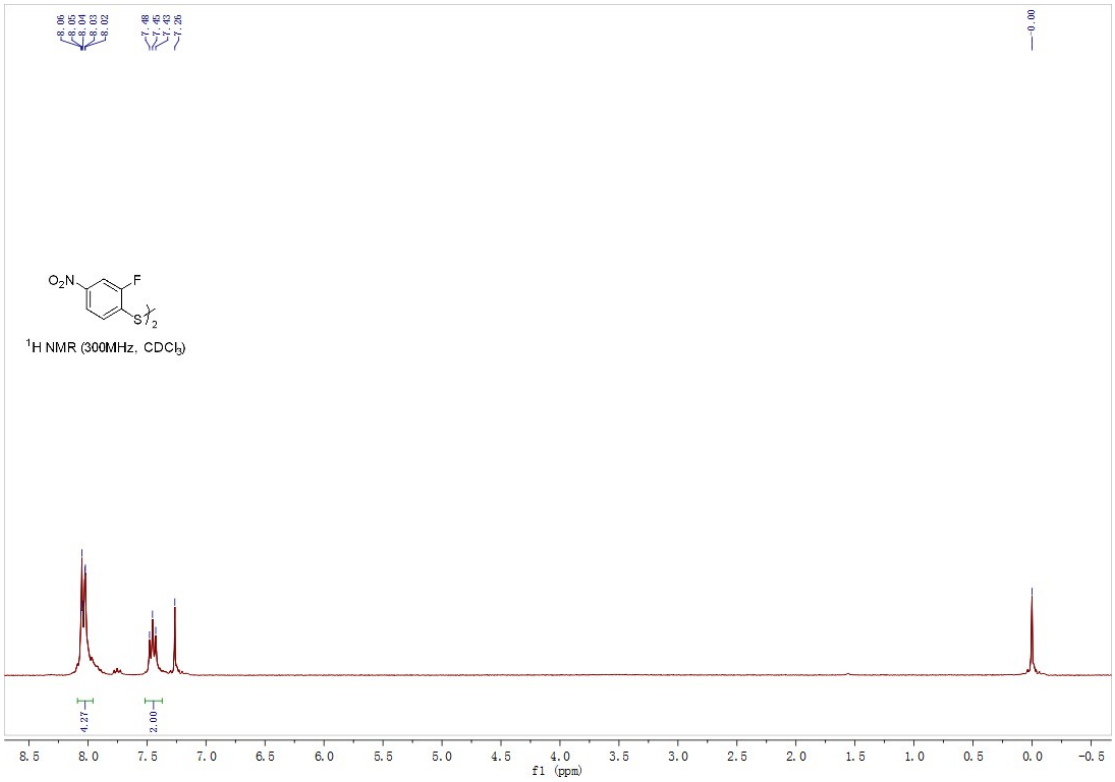
1）. T. Umemoto, L. M. Garrick, N. Saito, *Beilstein J. Org. Chem.* 2012**, 8**, 461.

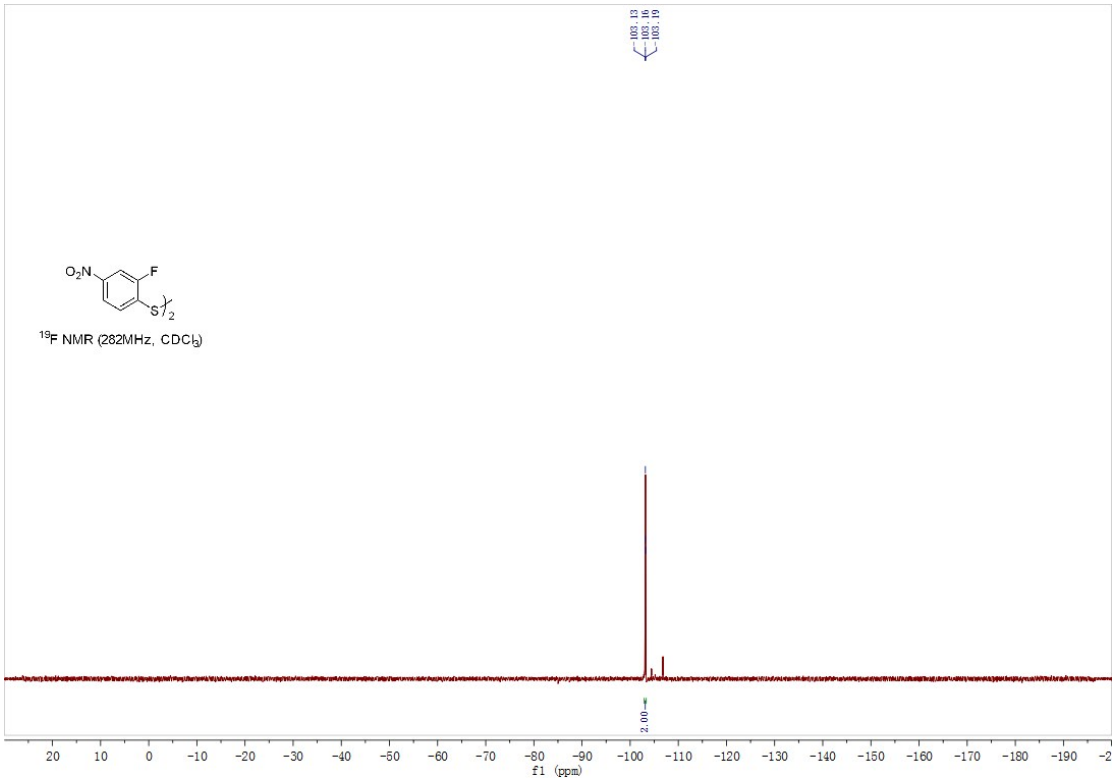
2）. a) B. Cui, M. Kosobokov, K. Matsuzaki, E. Tokunaga, N. Shibata, *Chem. Commun.* 2017**, 53**, 5997; b) M. Kosobokov, B. Cui, A. Balia, K. Matsuzaki, E. Tokunaga, N. Saito, N. Shibata, *Angew. Chem. Int. Ed.* 2016**, 55**, 10781. c) O. S. Kanishchev, W. R. Jr. Dolbier, *Angew. Chem. Int. Ed.* 2015**, 54**, 280.

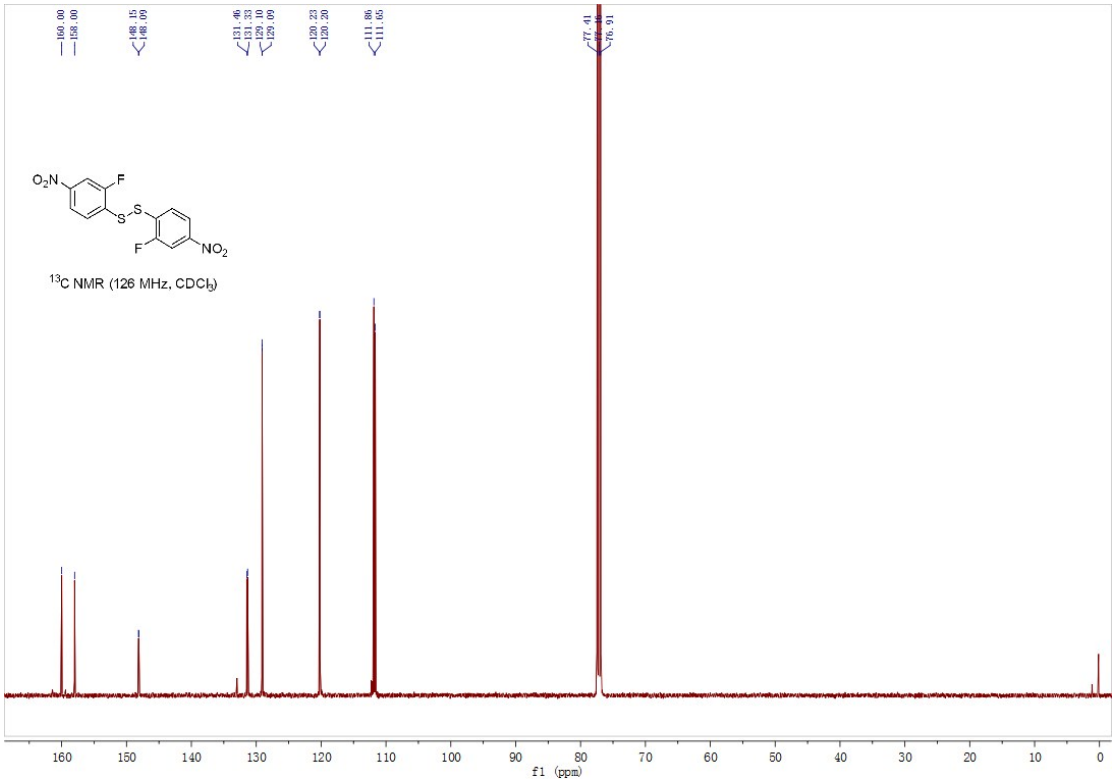
3）. X.-H. Xu, A. Azuma, A. Kusuda, E. Tokunaga, N. Shibata, *Eur. J. Org. Chem.* 2012**, 2012**, 1504.

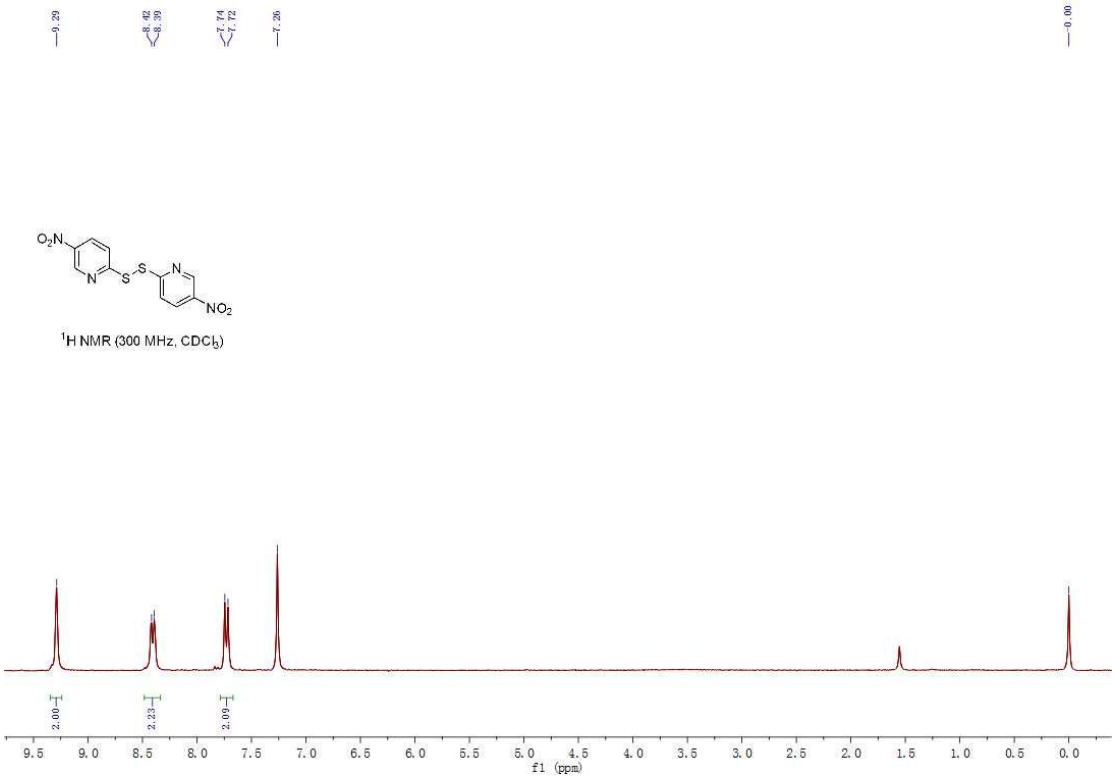
4）. T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* 1995, **60**, 7508.

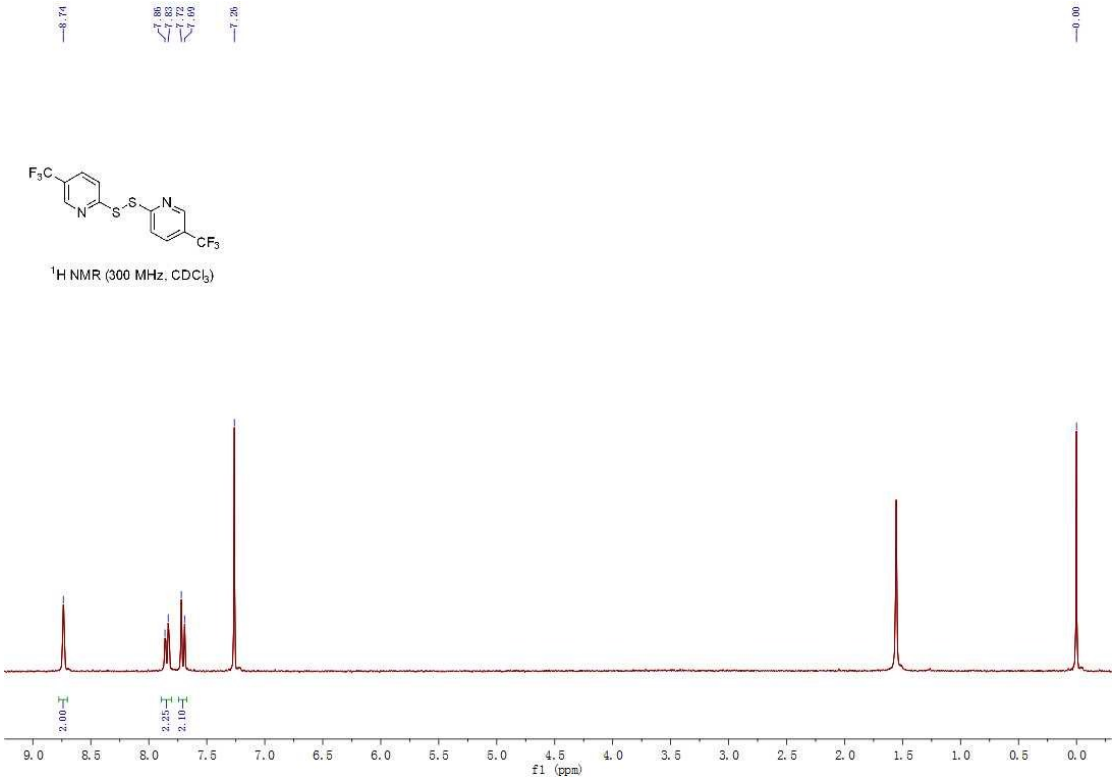
12. ^{1}H, ^{19}F and ^{13}C NMR Spectra of Products.



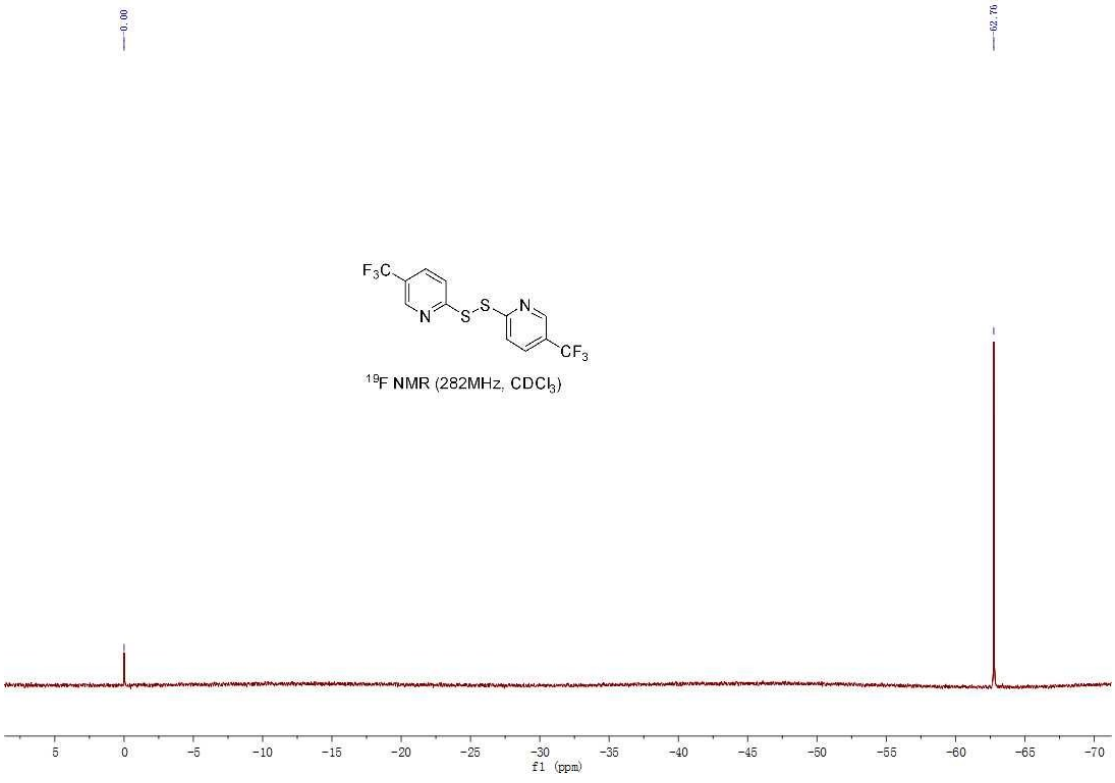



160.00
158.00
148.15
146.09
131.46
131.33
129.10
129.09
120.23
120.20
111.86
111.65
77.41
76.91
O_2N
F
S
S
F
NO_2
^{13}C NMR (126 MHz, $CDCl_3$)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

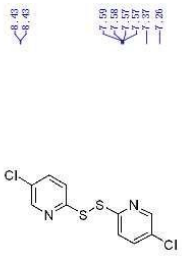

9.29
8.42
8.39
7.74
7.72
7.26
0.00
O_2N
N
S
S
N
NO_2
^{1}H NMR (300 MHz, $CDCl_3$)
2.00
2.23
2.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



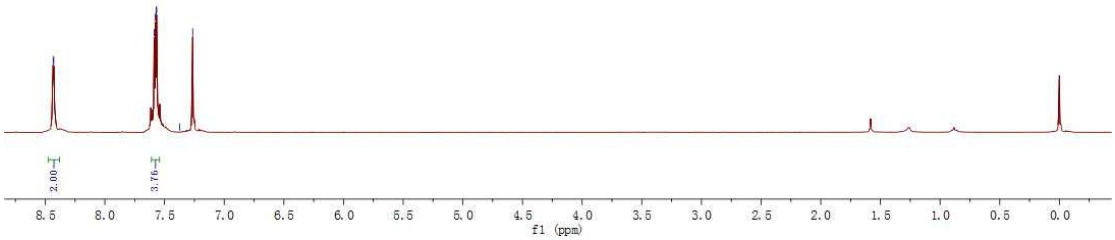
^{1}H NMR (300 MHz, $CDCl_3$)

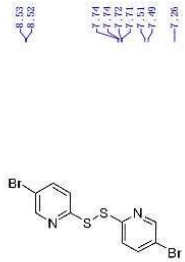


^{19}F NMR (282MHz, $CDCl_3$)

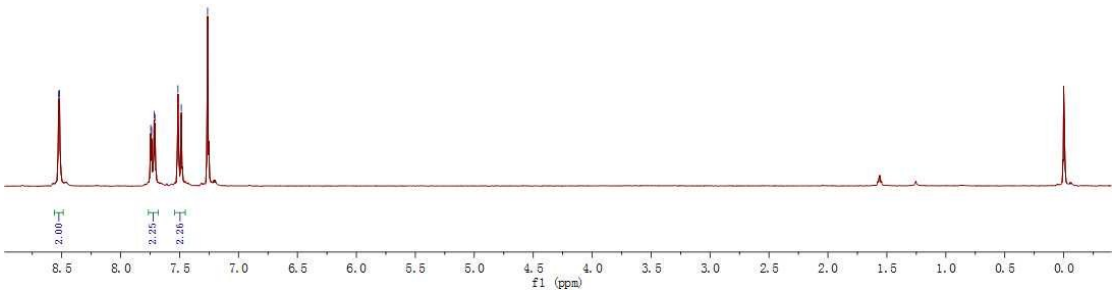


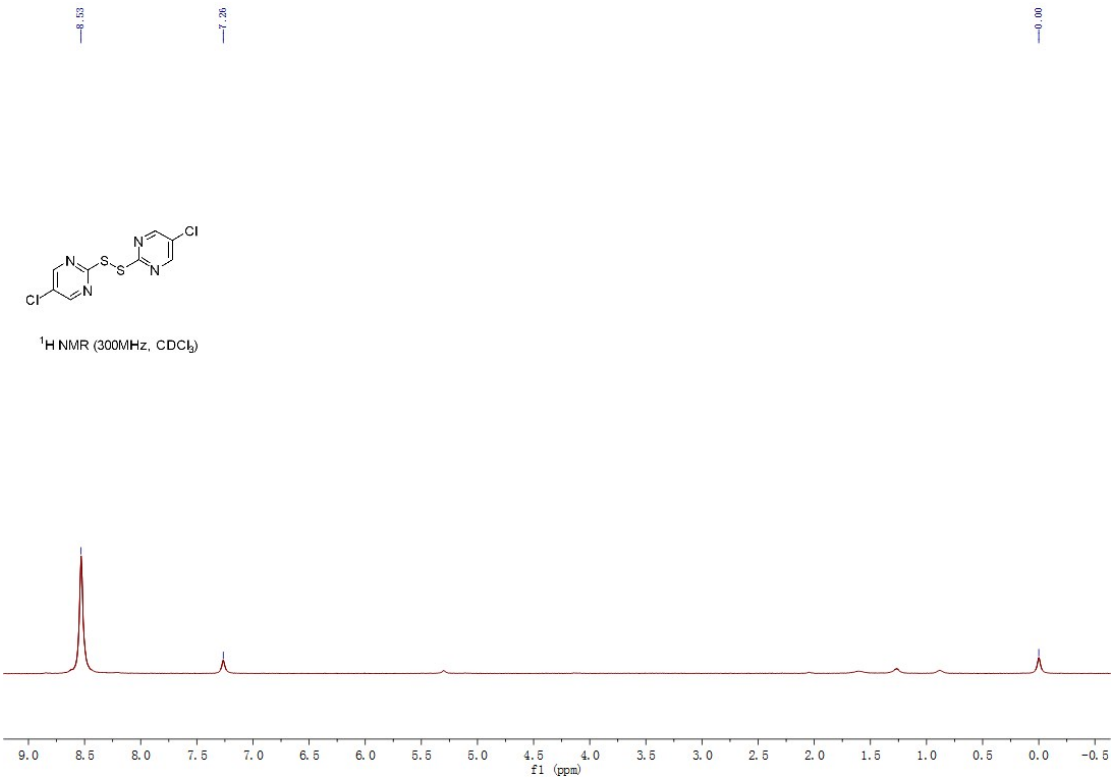
^{1}H NMR (300 MHz, $CDCl_3$)



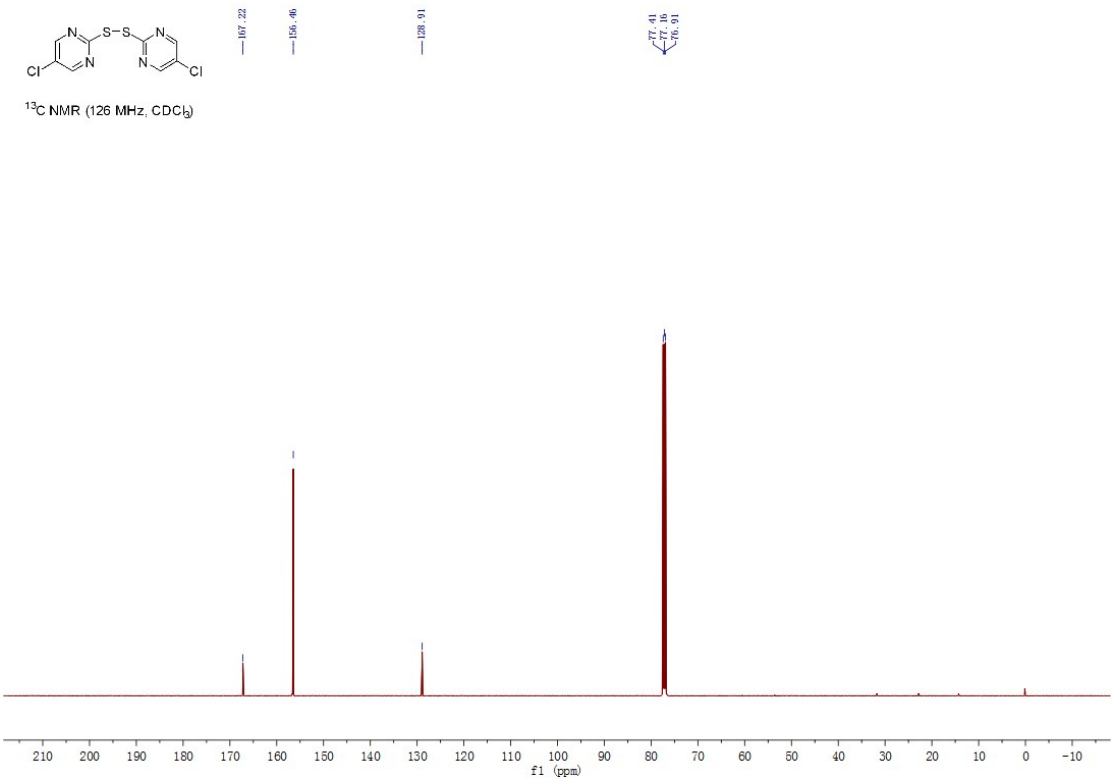


^{1}H NMR (300 MHz, $CDCl_3$)

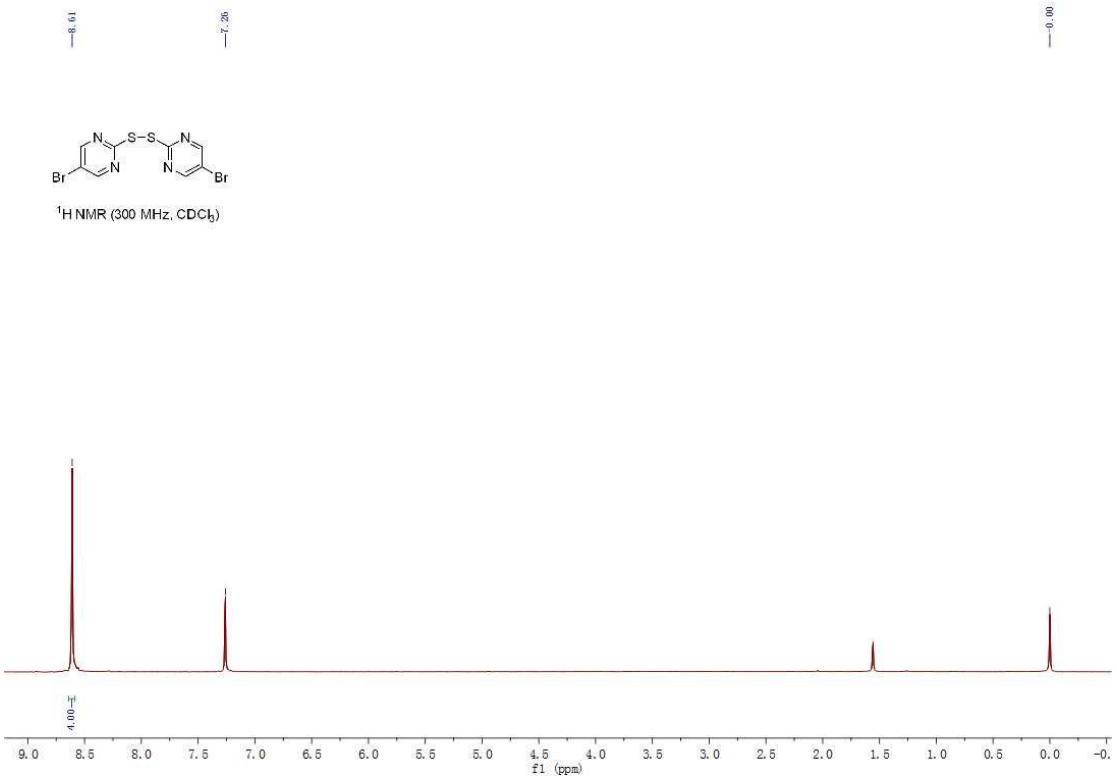


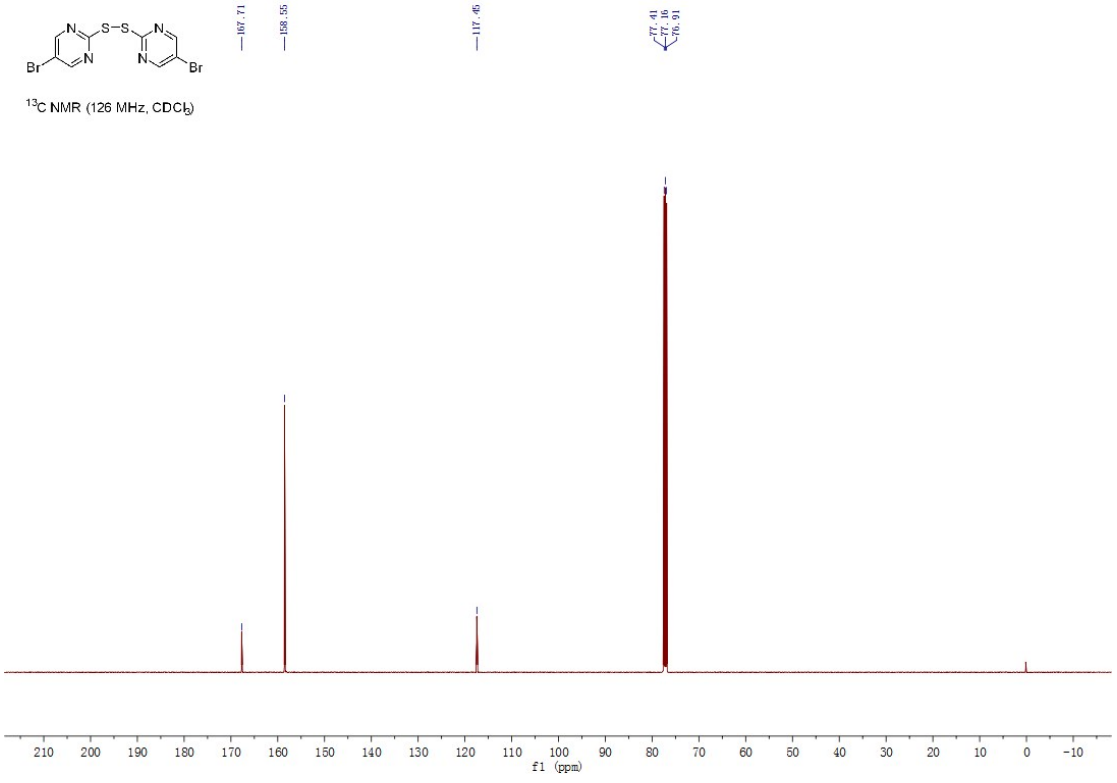


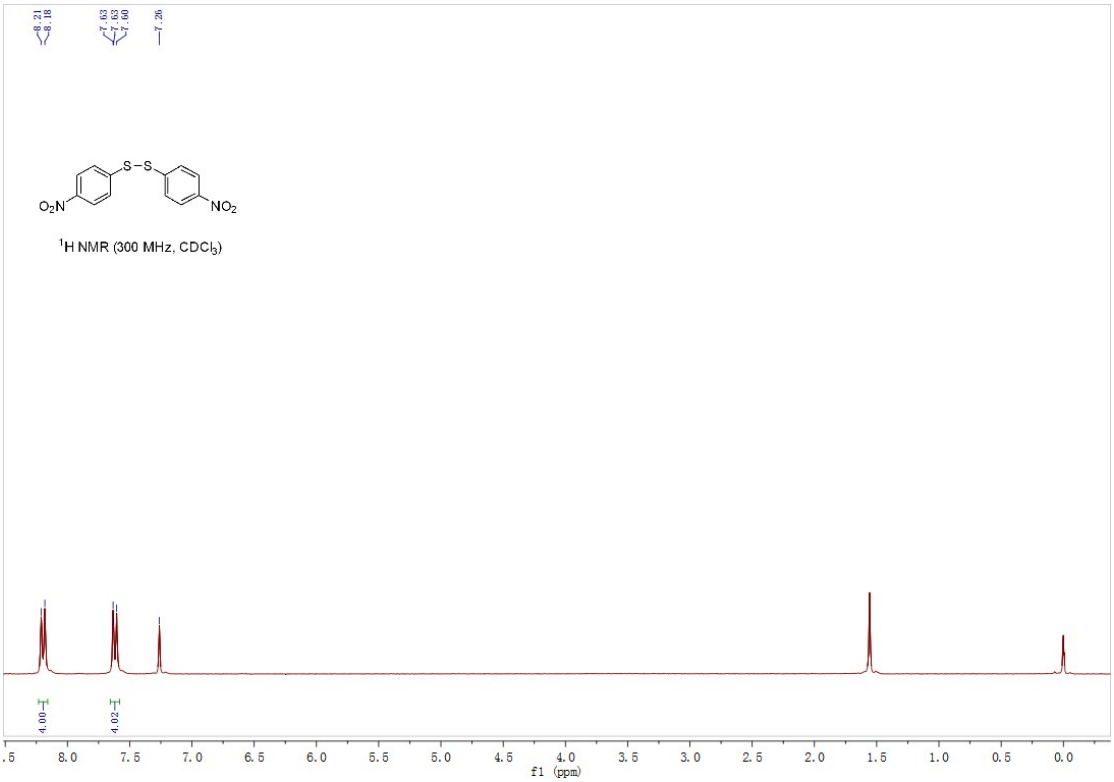
^{1}H NMR (300MHz, $CDCl_3$)

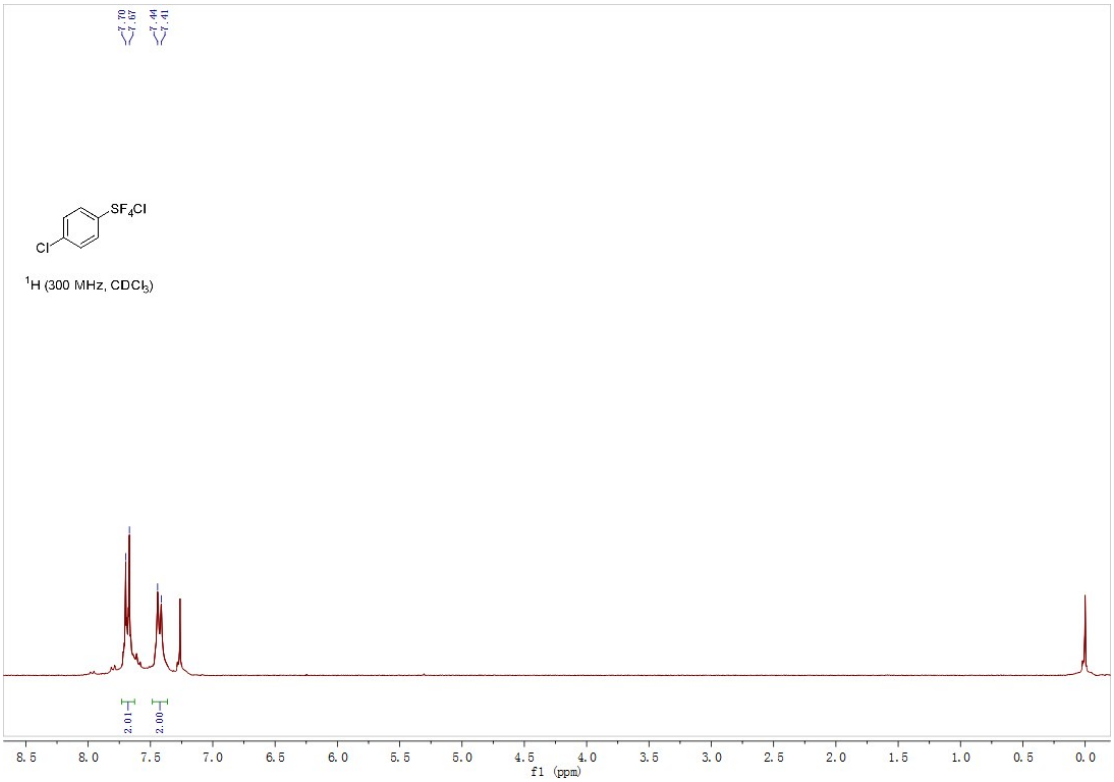


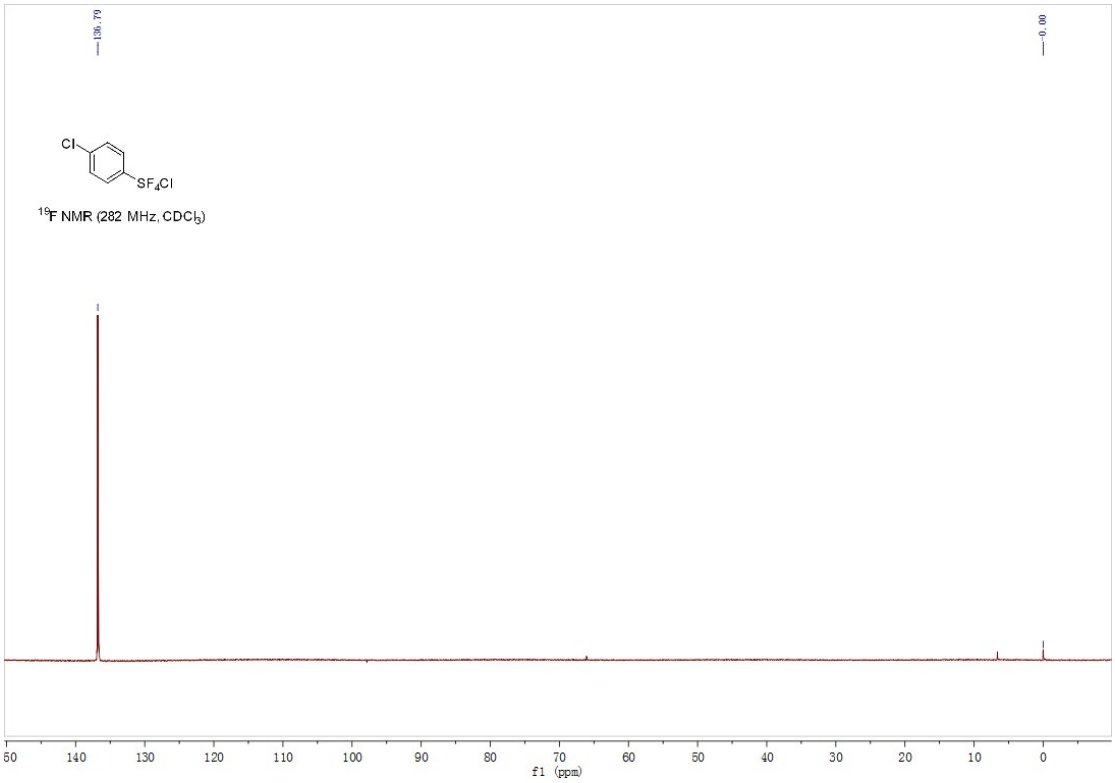
^{13}C NMR (126 MHz, $CDCl_3$)

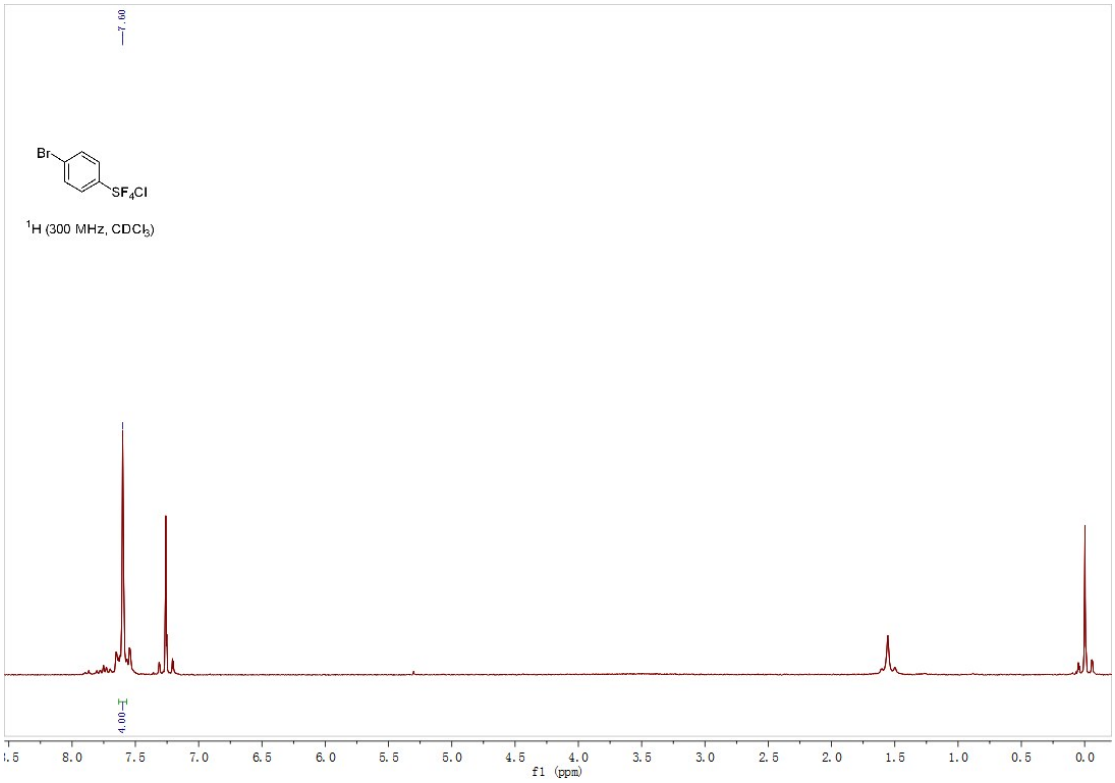

8.61
7.26
0.00
Br
S
S
N
Br
1H NMR (300 MHz, CDCl3)
4.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

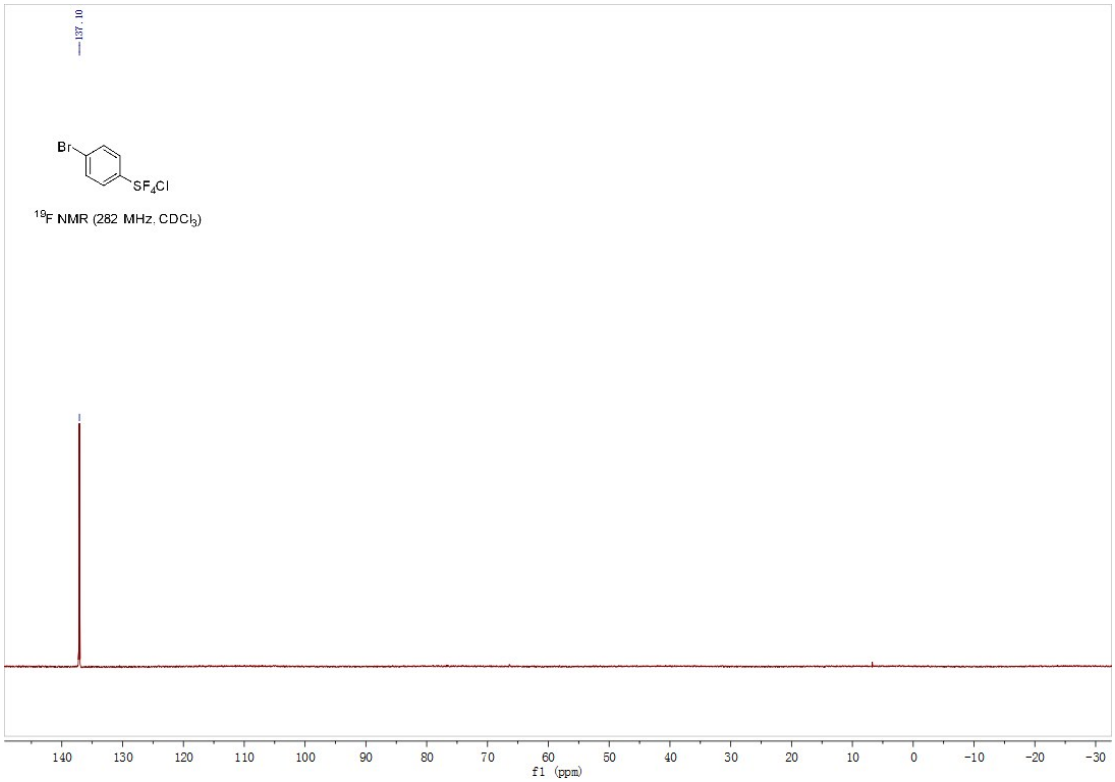

167.71
158.55
117.45
77.41
77.16
76.91
Br
S
S
N
Br
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

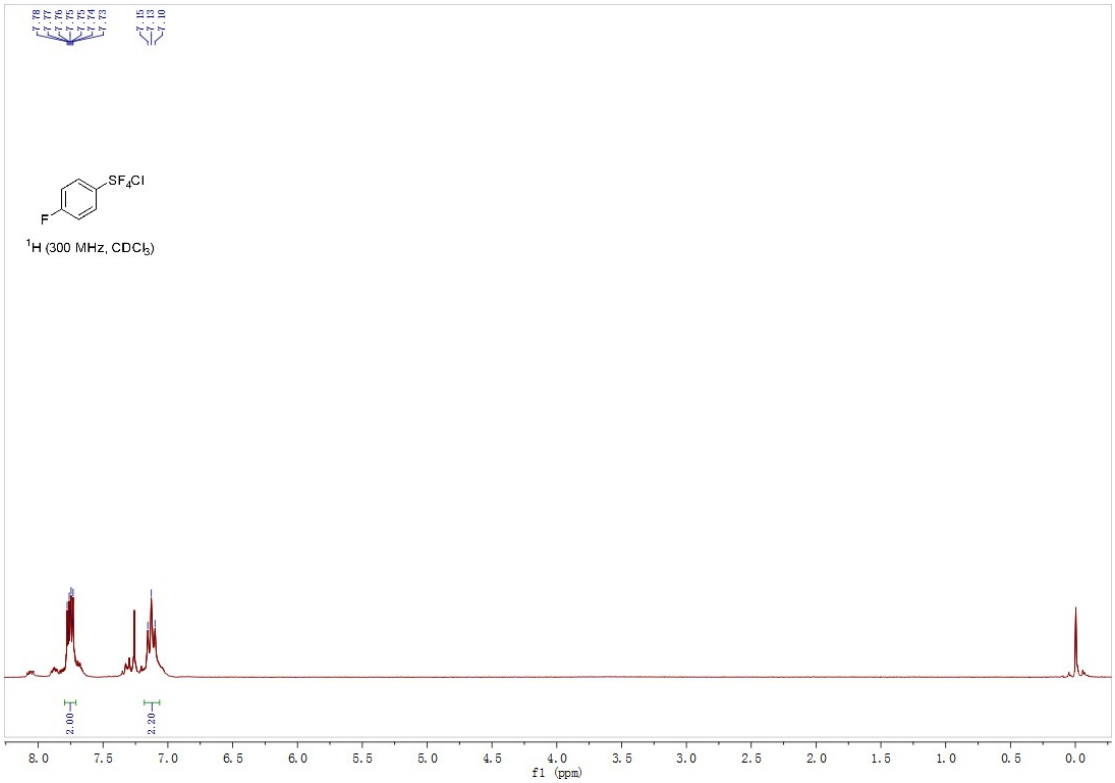

8.21
8.18
7.63
7.63
7.60
7.26
S–S
O2N
NO2
1H NMR (300 MHz, CDCl3)
4.00
4.02
f1 (ppm)

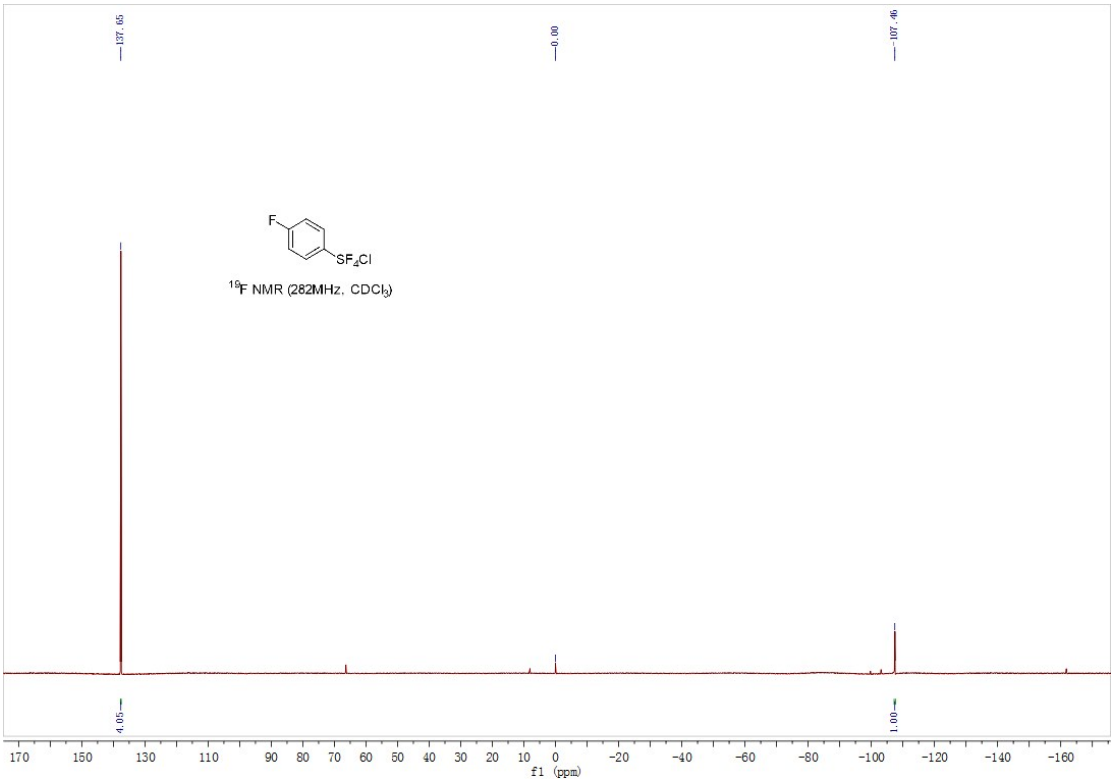

7.70
7.67
7.44
7.41
SF4Cl
Cl
1H (300 MHz, CDCl3)
2.01
2.00
f1 (ppm)

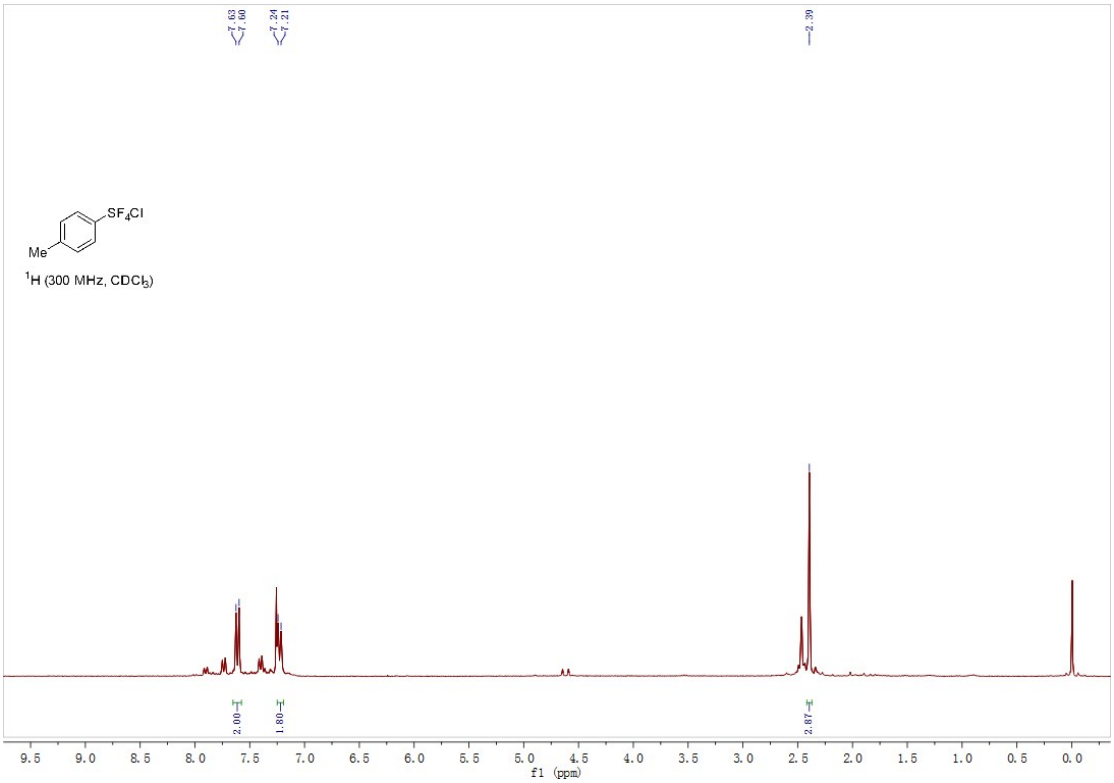

136.79
0.00
Cl
SF4Cl
19F NMR (282 MHz, CDCl3)
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

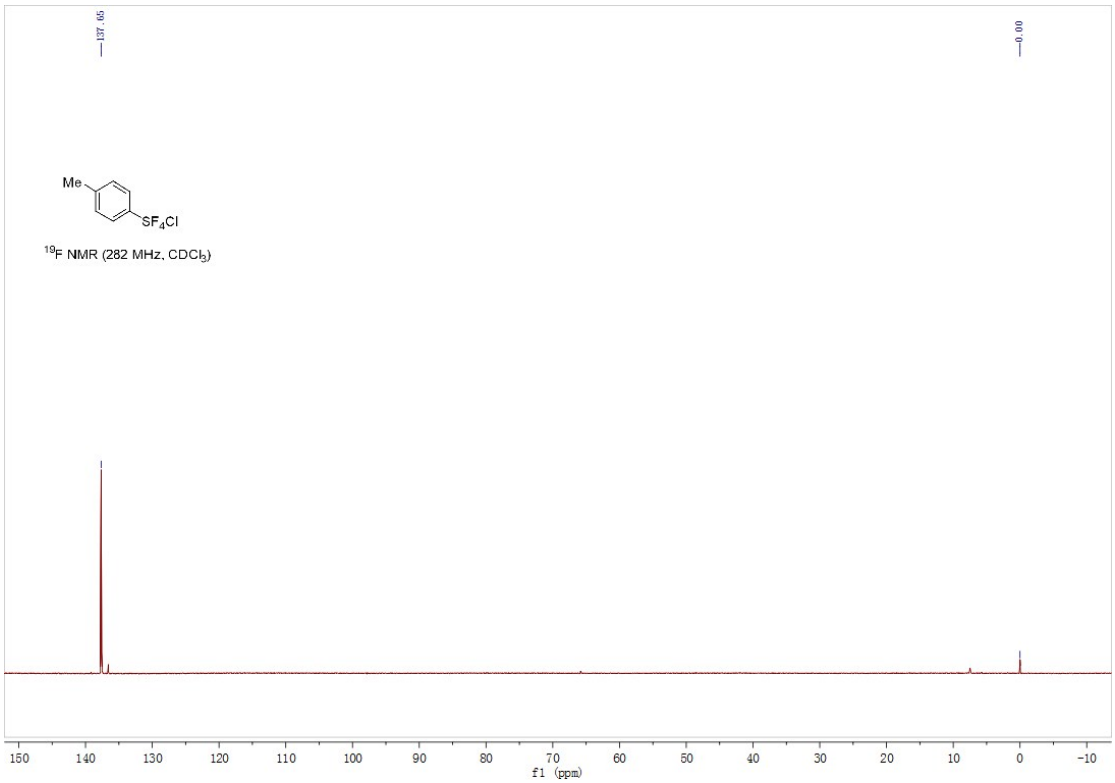

7.60
Br
SF4Cl
1H (300 MHz, CDCl3)
4.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

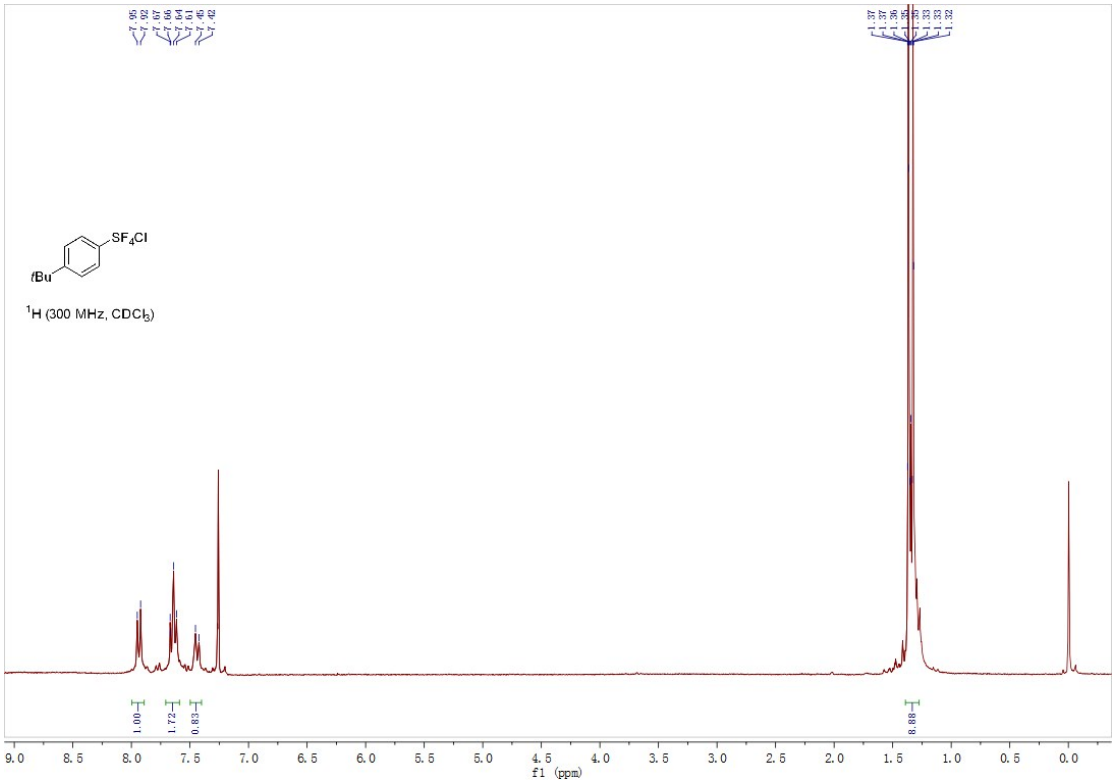

137.10
Br
SF4Cl
19F NMR (282 MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

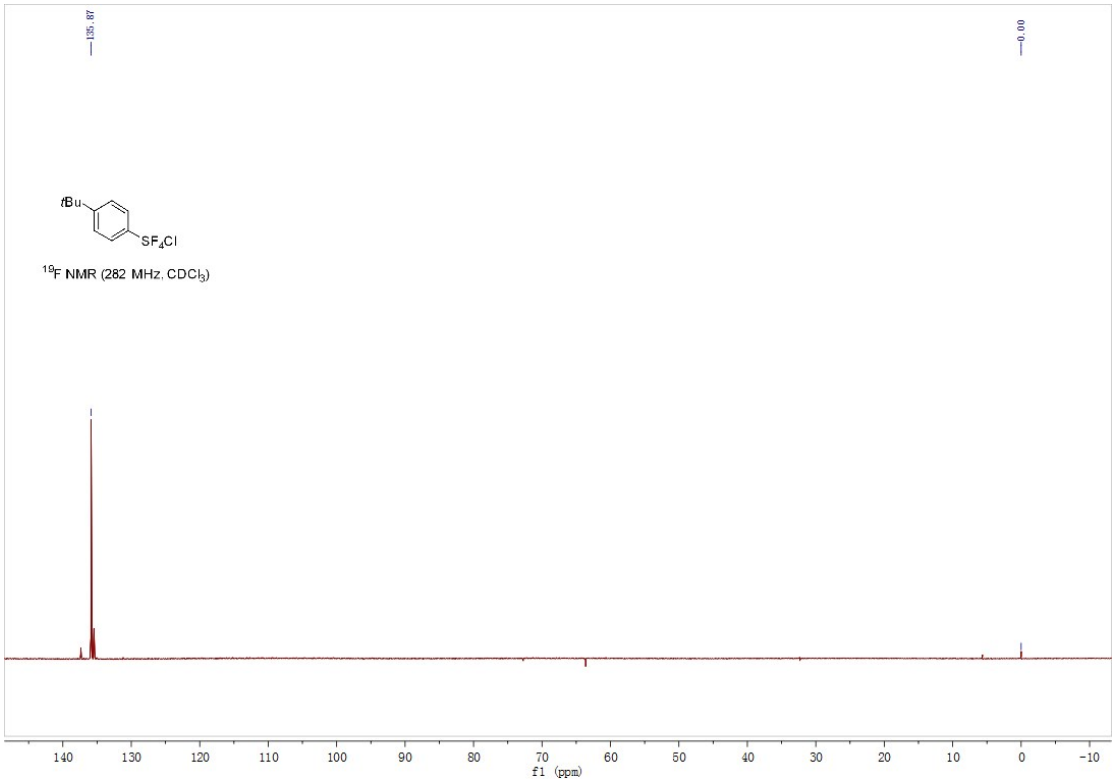

7.78 7.77 7.76 7.75 7.74 7.73
7.15 7.13 7.10
SF4Cl
F
1H (300 MHz, CDCl3)
2.00
2.20
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

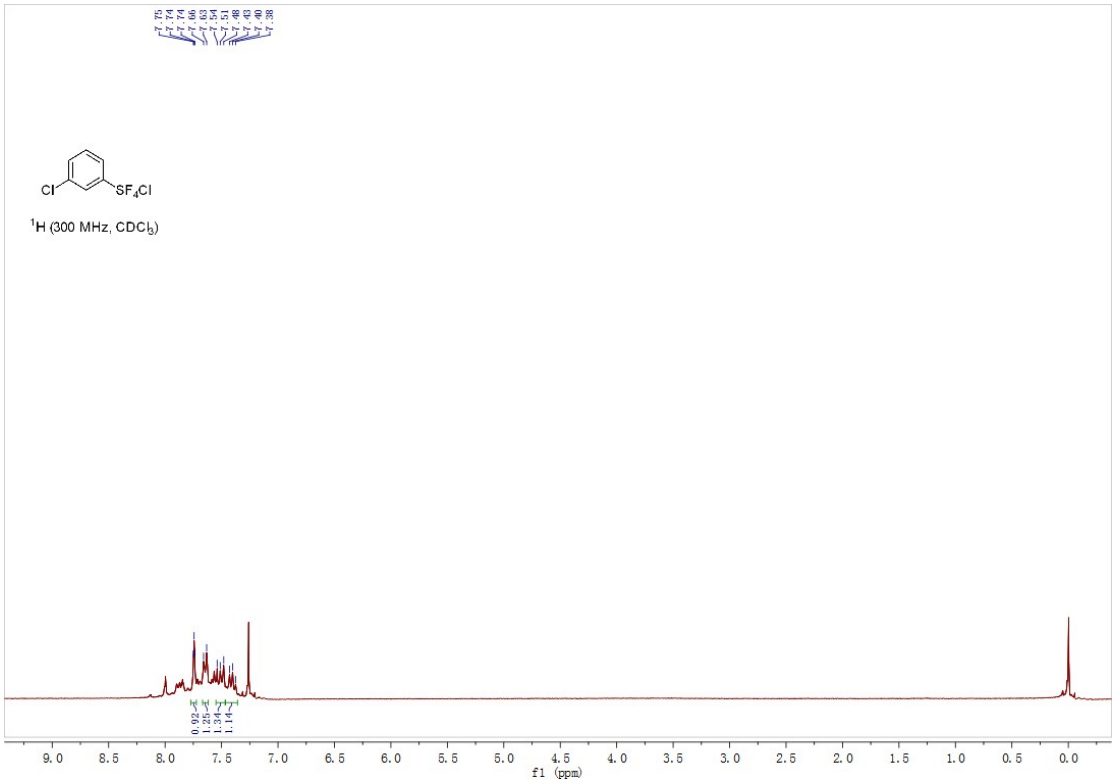

137.65
0.00
-107.46
F
SF4Cl
19F NMR (282MHz, CDCl3)
4.05
1.00
f1 (ppm)

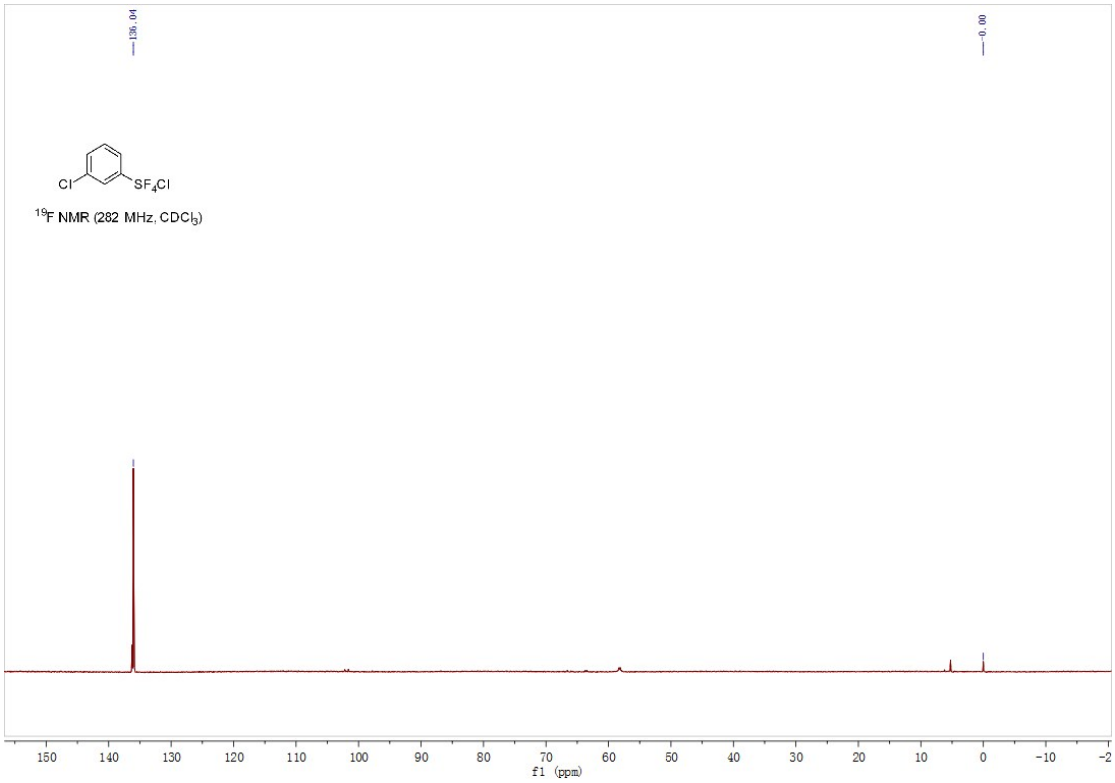

7.63
7.60
7.24
7.21
2.39
SF4Cl
Me
1H (300 MHz, CDCl3)
2.00
1.80
2.87
f1 (ppm)

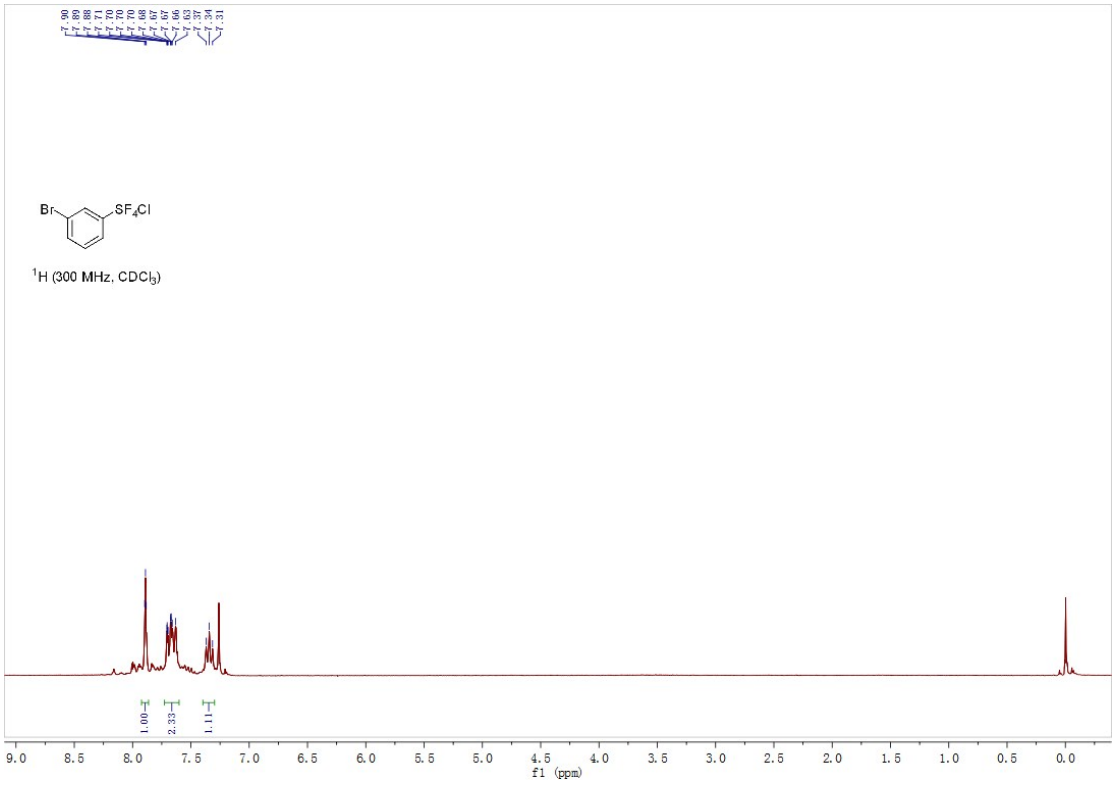

137.65
0.00
Me
SF4Cl
19F NMR (282 MHz, CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

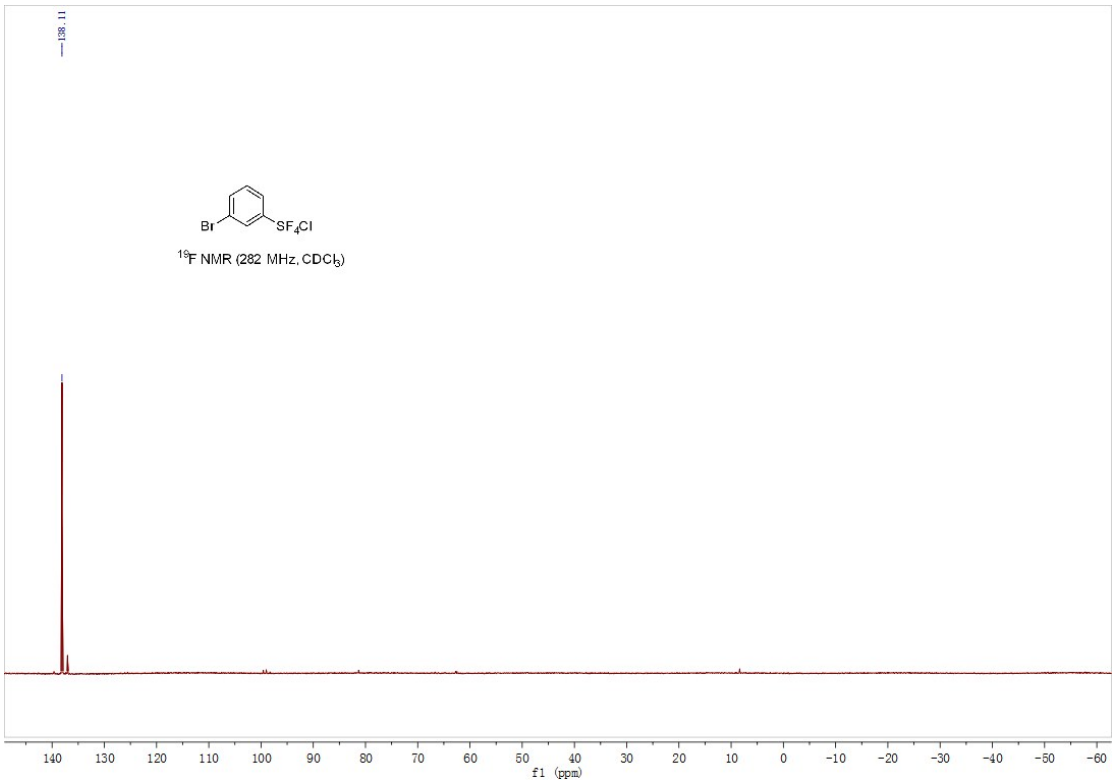

7.95
7.92
7.67
7.66
7.64
7.61
7.45
7.42
1.37
1.37
1.36
1.33
1.33
1.32
SF4Cl
tBu
1H (300 MHz, CDCl3)
1.00
1.72
0.83
8.88
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

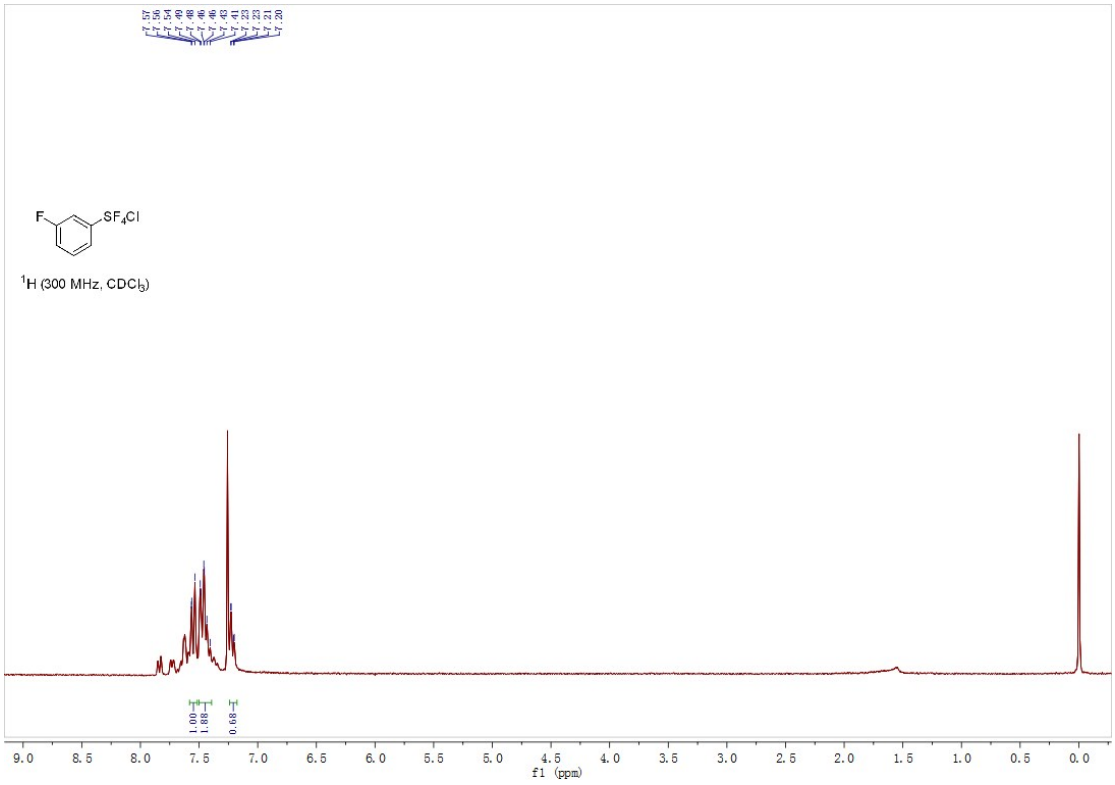

135.87
0.00
tBu
SF4Cl
19F NMR (282 MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

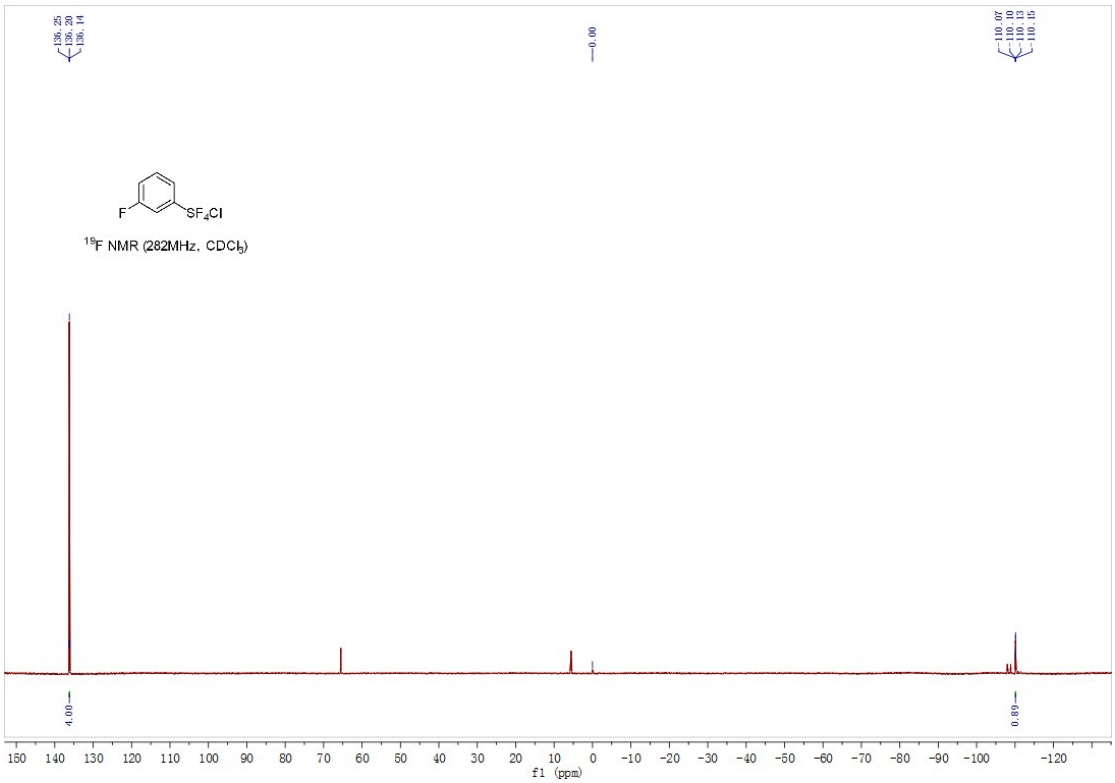

7.75
7.74
7.74
7.66
7.63
7.54
7.51
7.48
7.43
7.40
7.38
Cl
SF4Cl
1H (300 MHz, CDCl3)
0.92
1.25
1.34
1.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

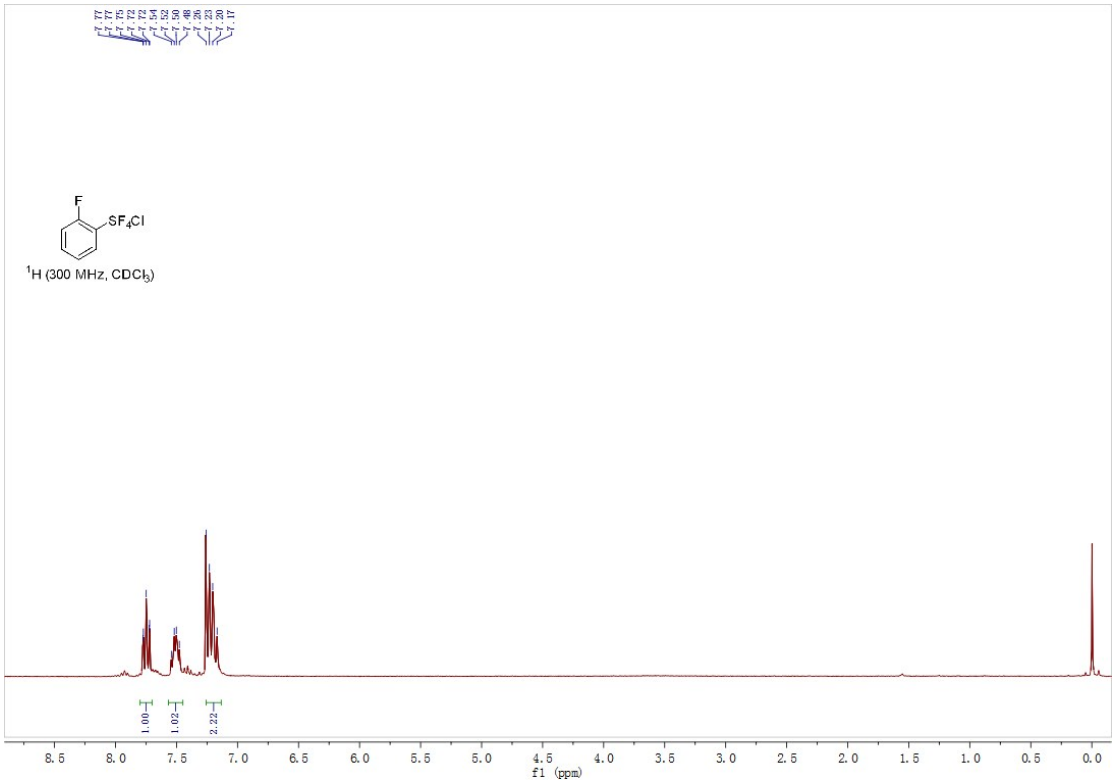

136.04
-0.00
Cl
SF4Cl
19F NMR (282 MHz, CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

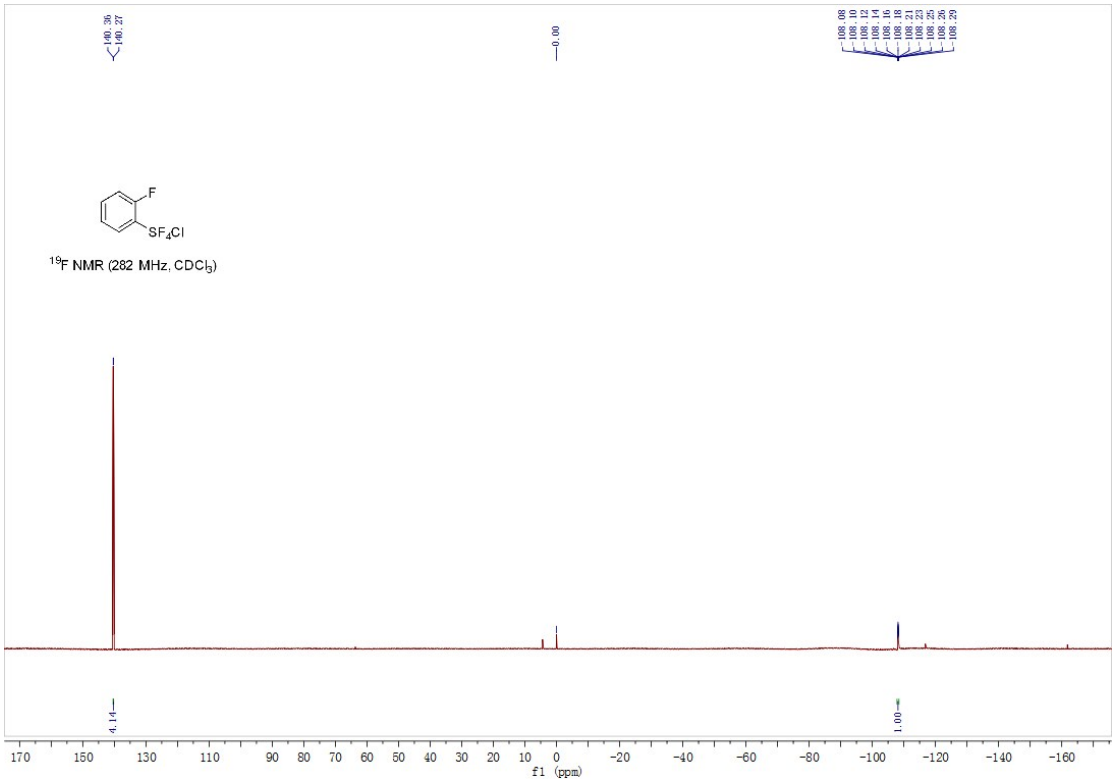

7.90
7.89
7.88
7.71
7.70
7.70
7.70
7.68
7.67
7.67
7.66
7.63
7.37
7.34
7.31
Br
SF4Cl
1H (300 MHz, CDCl3)
1.00
2.33
1.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

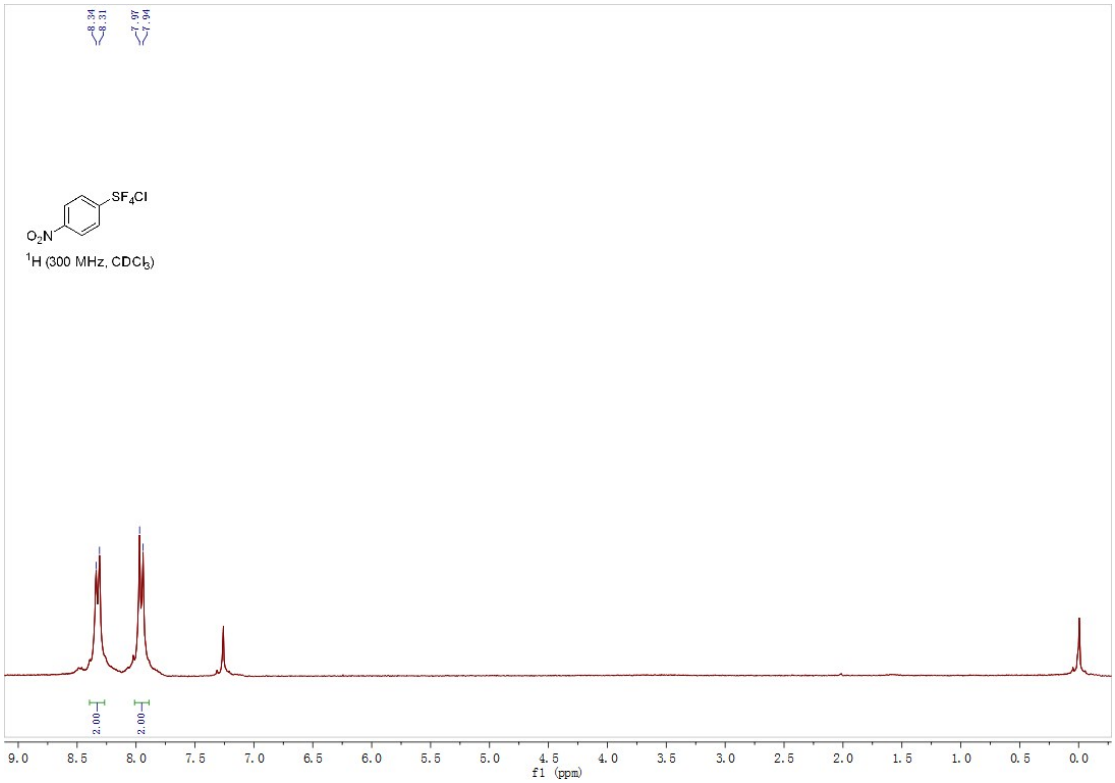

138.11
Br
SF4Cl
19F NMR (282 MHz, CDCl3)
f1 (ppm)

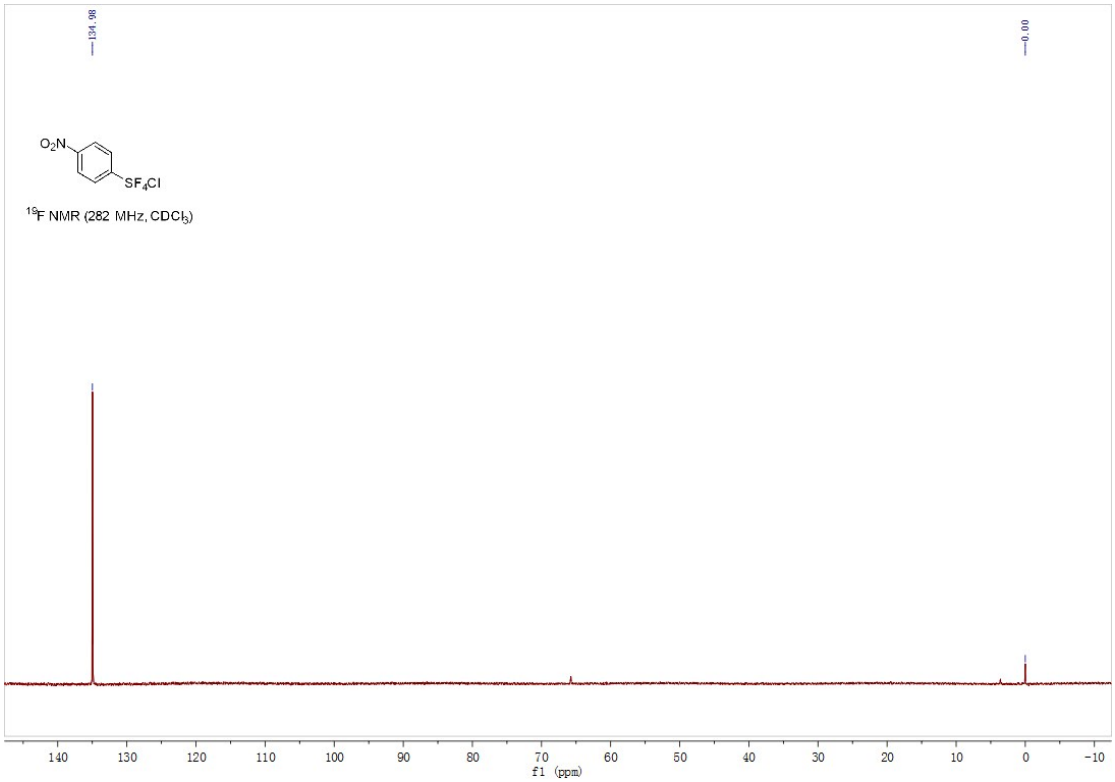

F
SF4Cl
1H (300 MHz, CDCl3)
1.00
1.88
0.68
f1 (ppm)

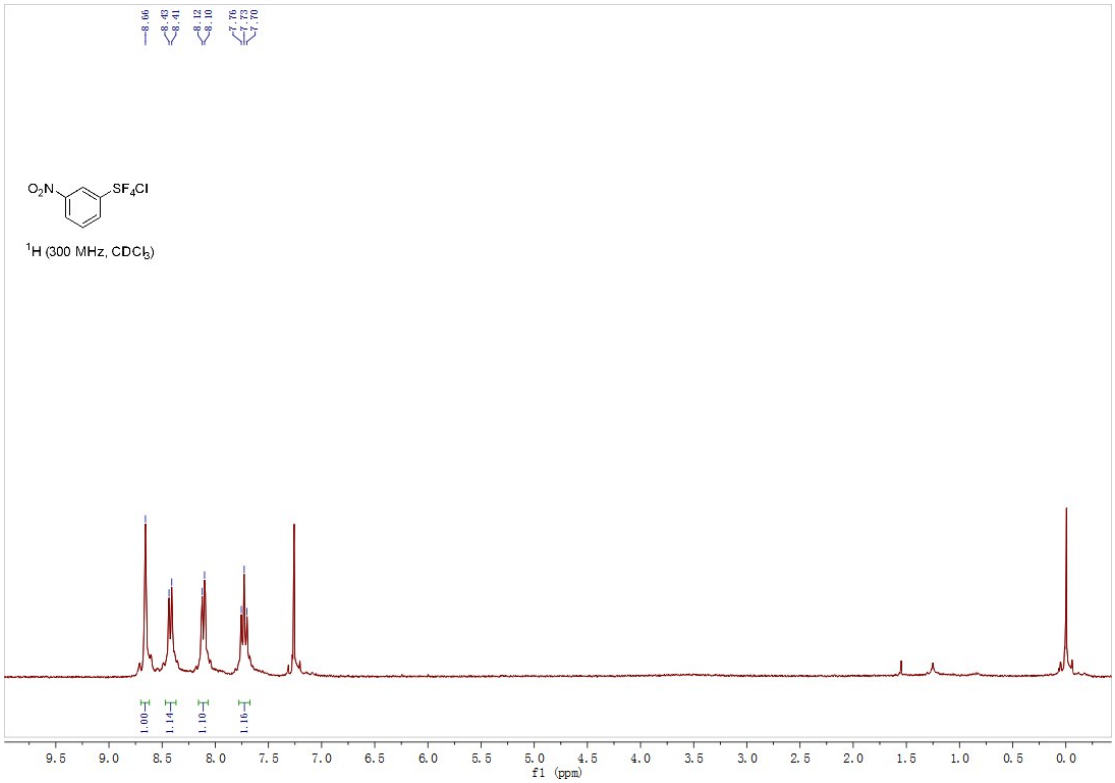

F
SF4Cl
19F NMR (282MHz, CDCl3)
f1 (ppm)

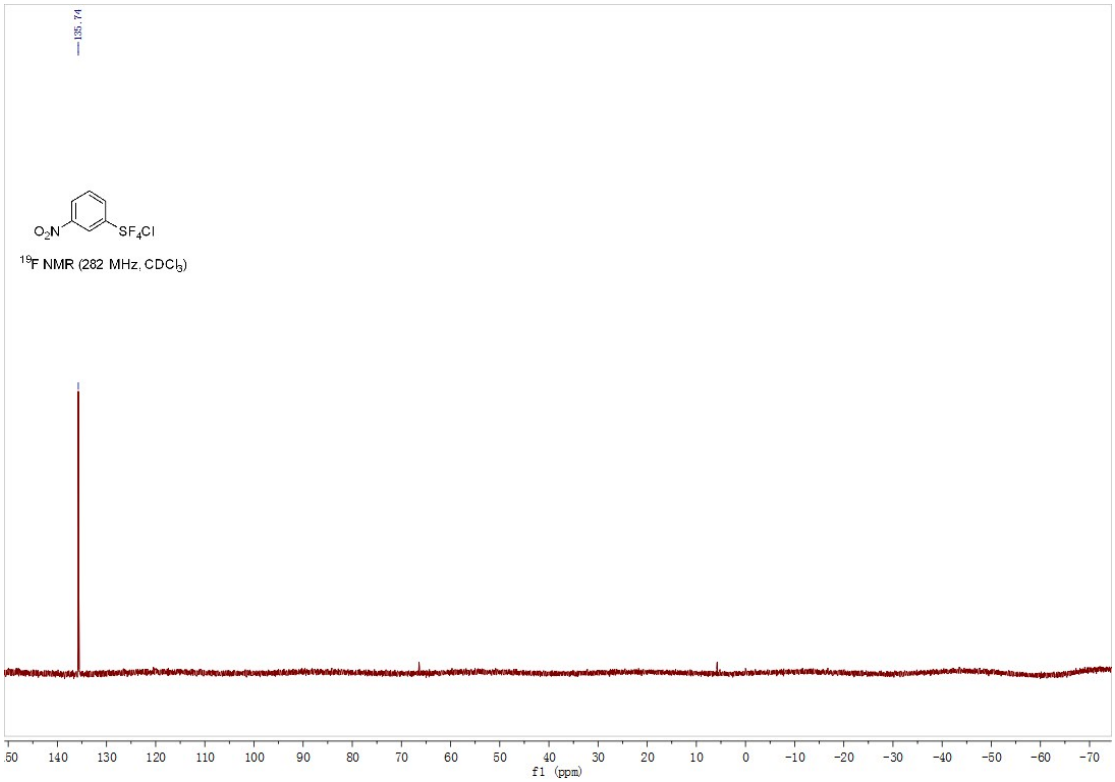

F
SF4Cl
1H (300 MHz, CDCl3)
f1 (ppm)

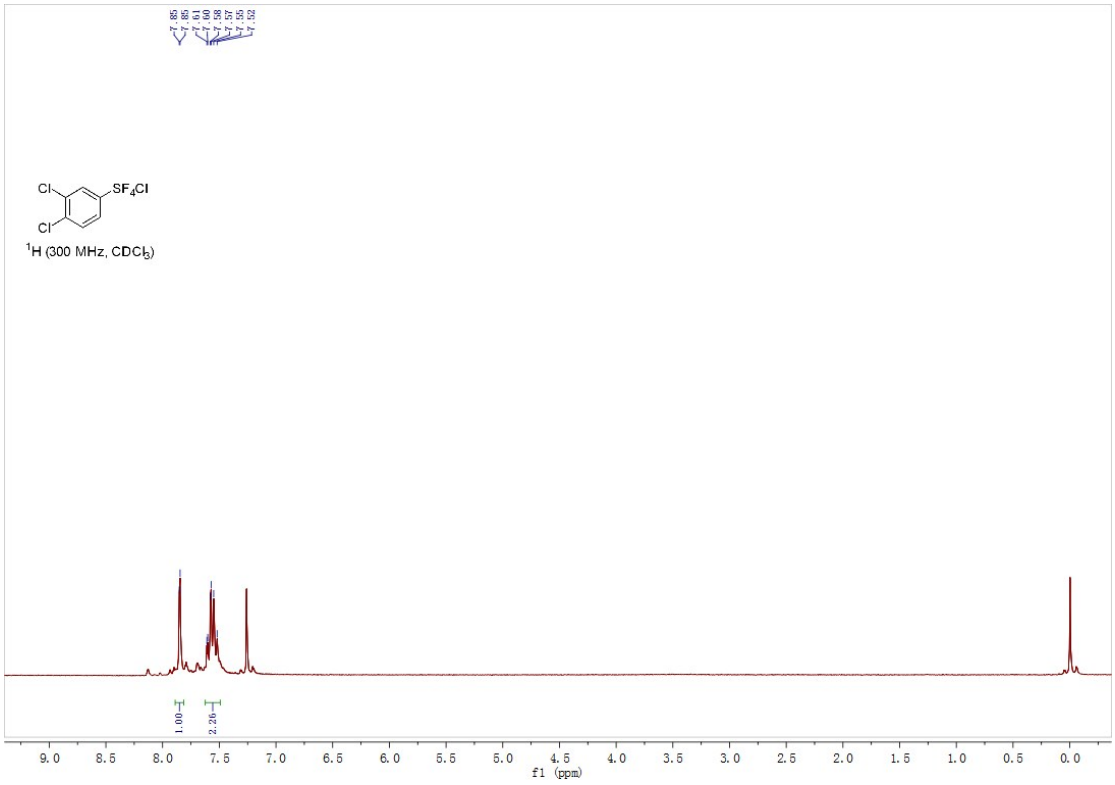

140.36
140.27
0.00
108.08
108.10
108.12
108.14
108.16
108.18
108.21
108.23
108.25
108.26
108.29
F
SF4Cl
19F NMR (282 MHz, CDCl3)
4.14
1.00
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)

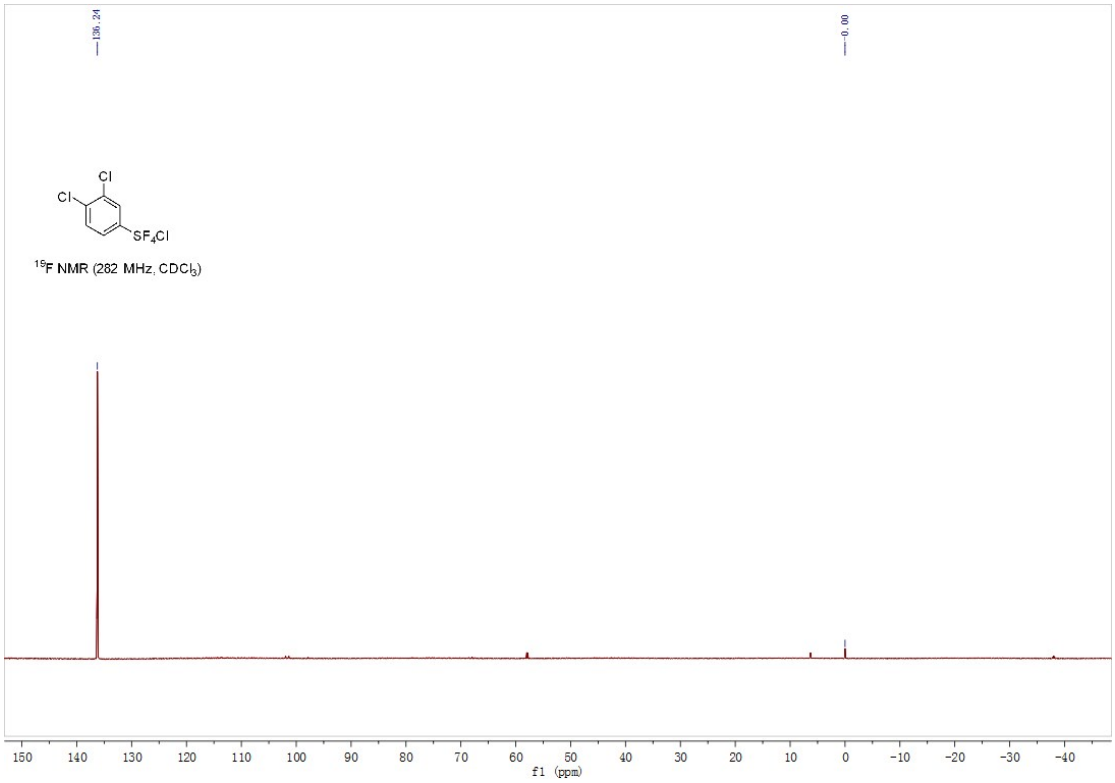

8.34
8.31
7.97
7.94
SF4Cl
O2N
1H (300 MHz, CDCl3)
2.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

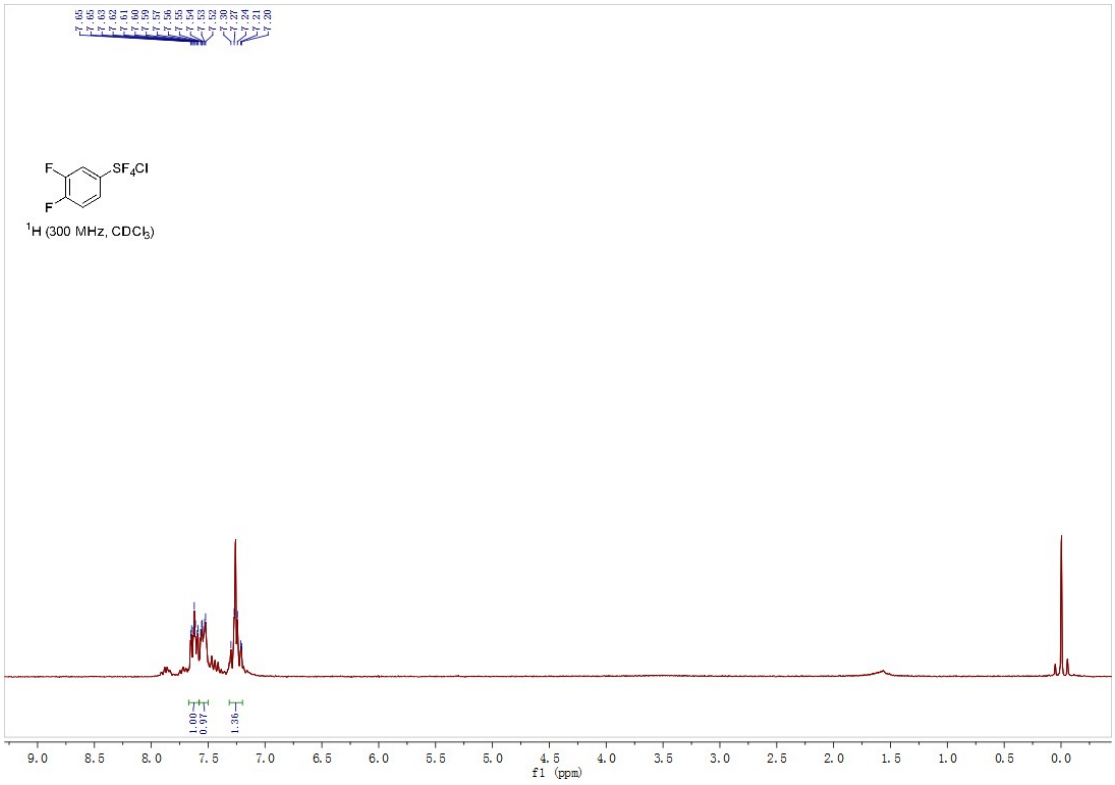

134.98
0.00
O_2N
SF_4Cl
^{19}F NMR (282 MHz, $CDCl_3$)
f1 (ppm)

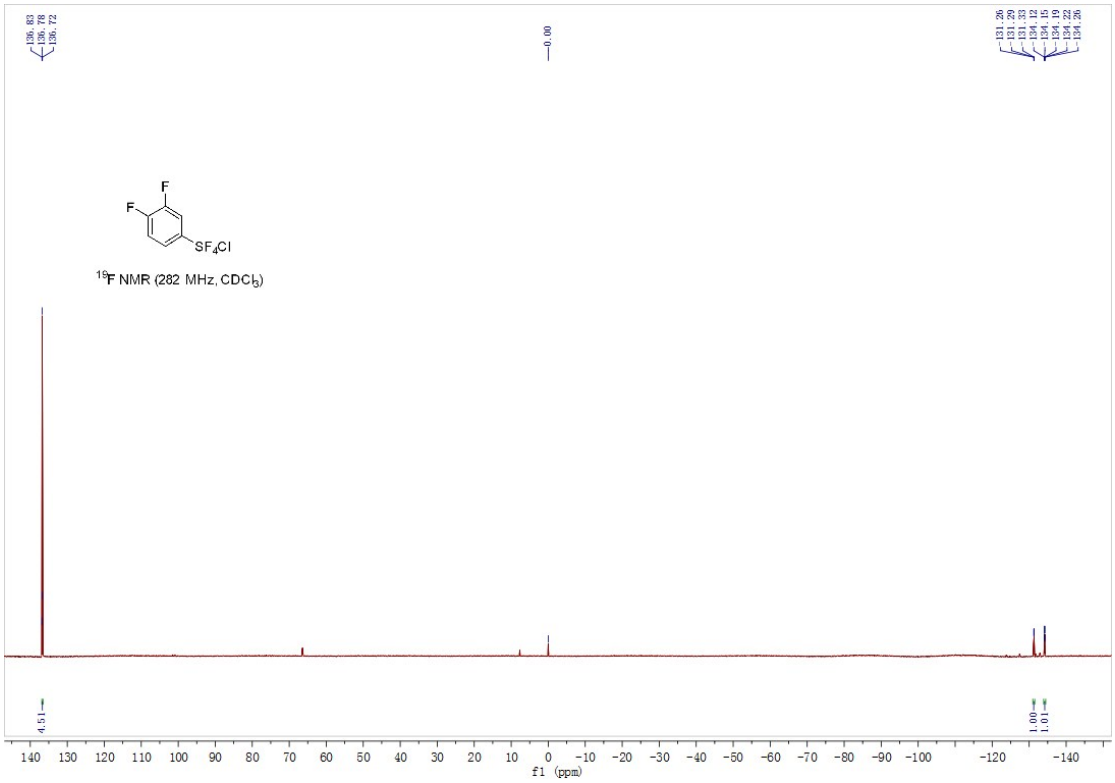

8.66
8.43
8.41
8.12
8.10
7.76
7.73
7.70
O_2N
SF_4Cl
^{1}H (300 MHz, $CDCl_3$)
1.00
1.14
1.10
1.16
f1 (ppm)

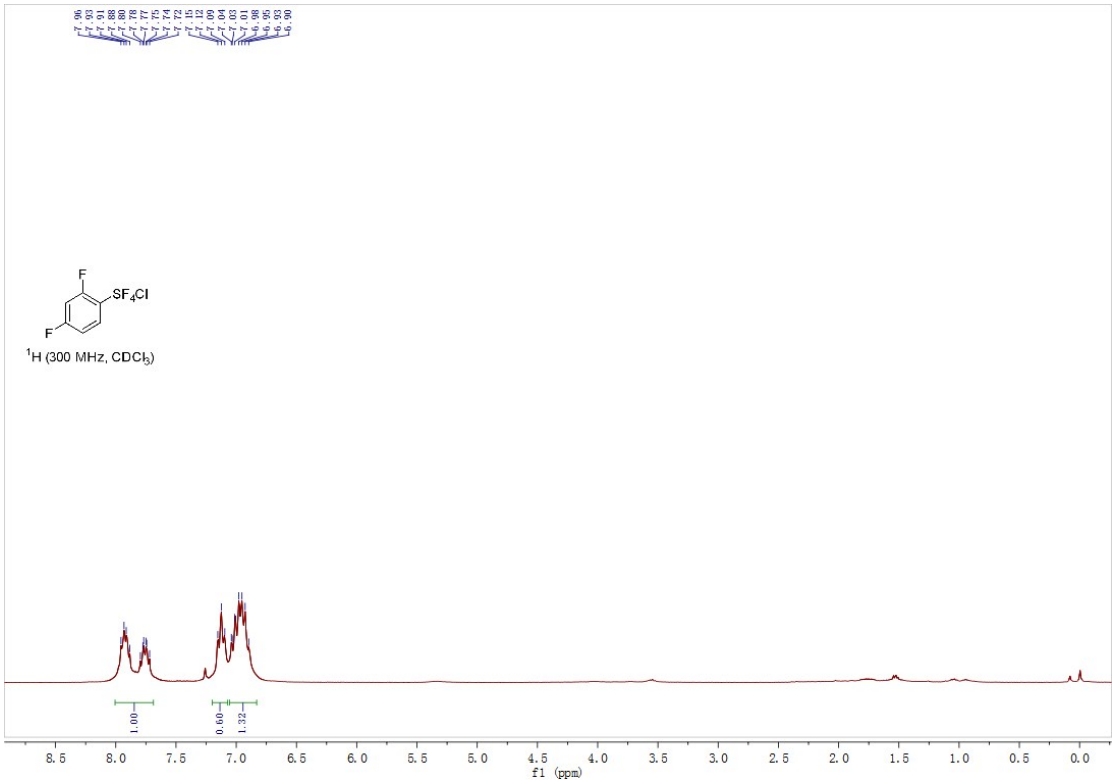

-135.74
O_2N
SF_4Cl
^{19}F NMR (282 MHz, $CDCl_3$)
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

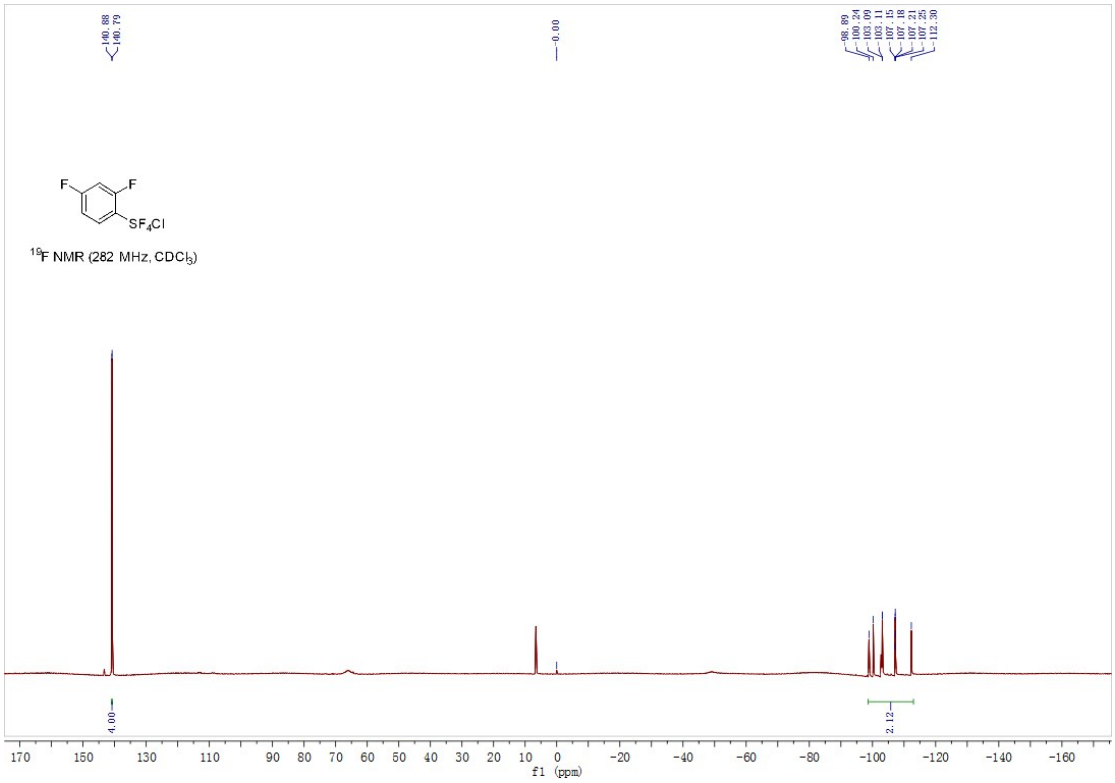

7.85
7.85
7.61
7.60
7.58
7.57
7.55
7.52
Cl
SF_4Cl
Cl
^{1}H (300 MHz, $CDCl_3$)
1.00
2.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

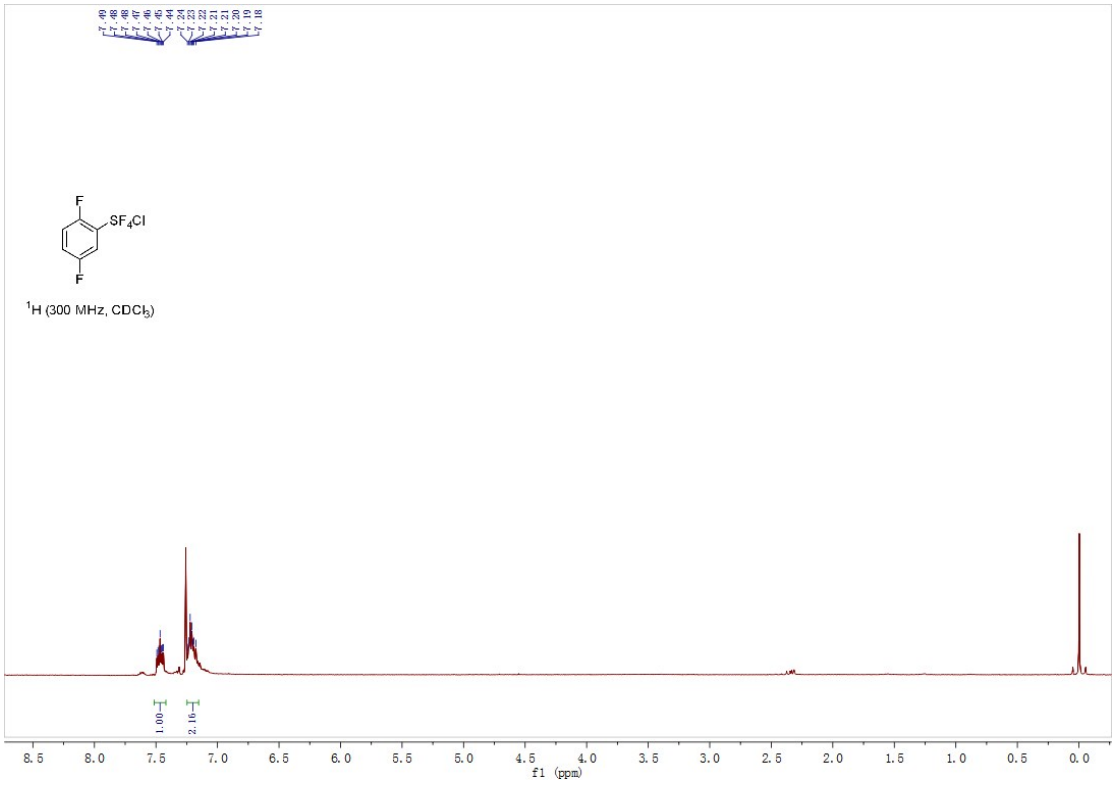

136.24
0.00
Cl
Cl
SF4Cl
19F NMR (282 MHz, CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

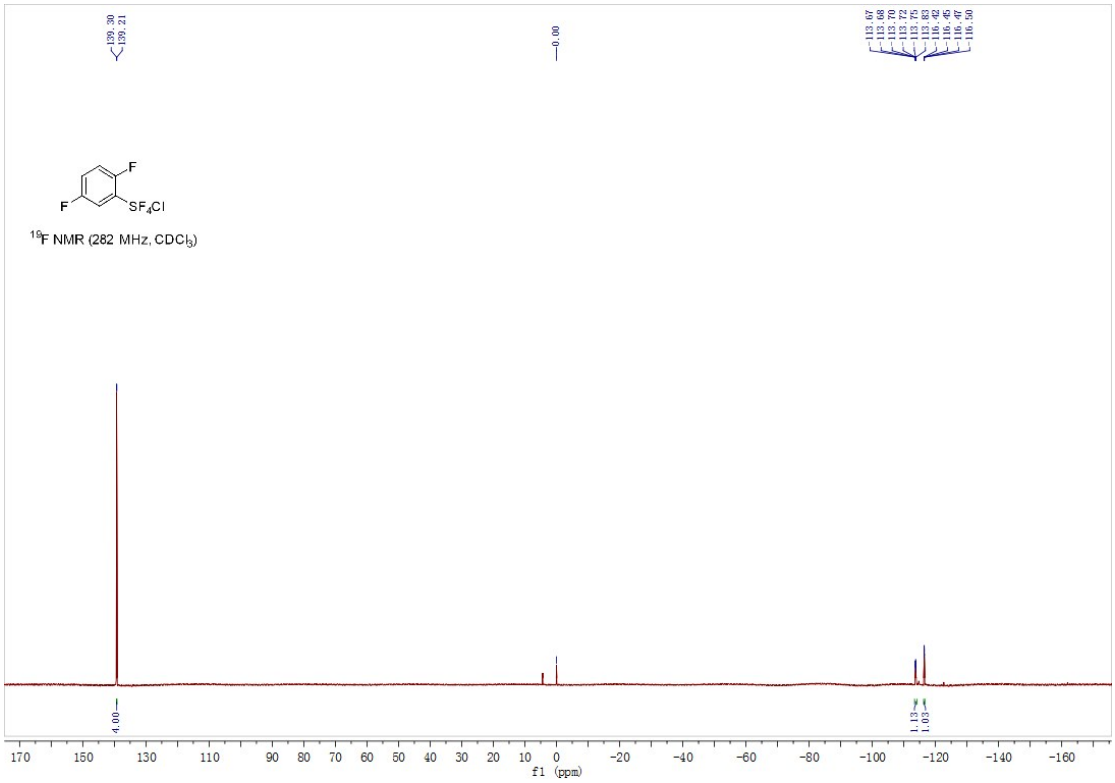

F
F
SF4Cl
1H (300 MHz, CDCl3)
1.00
0.97
1.36
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

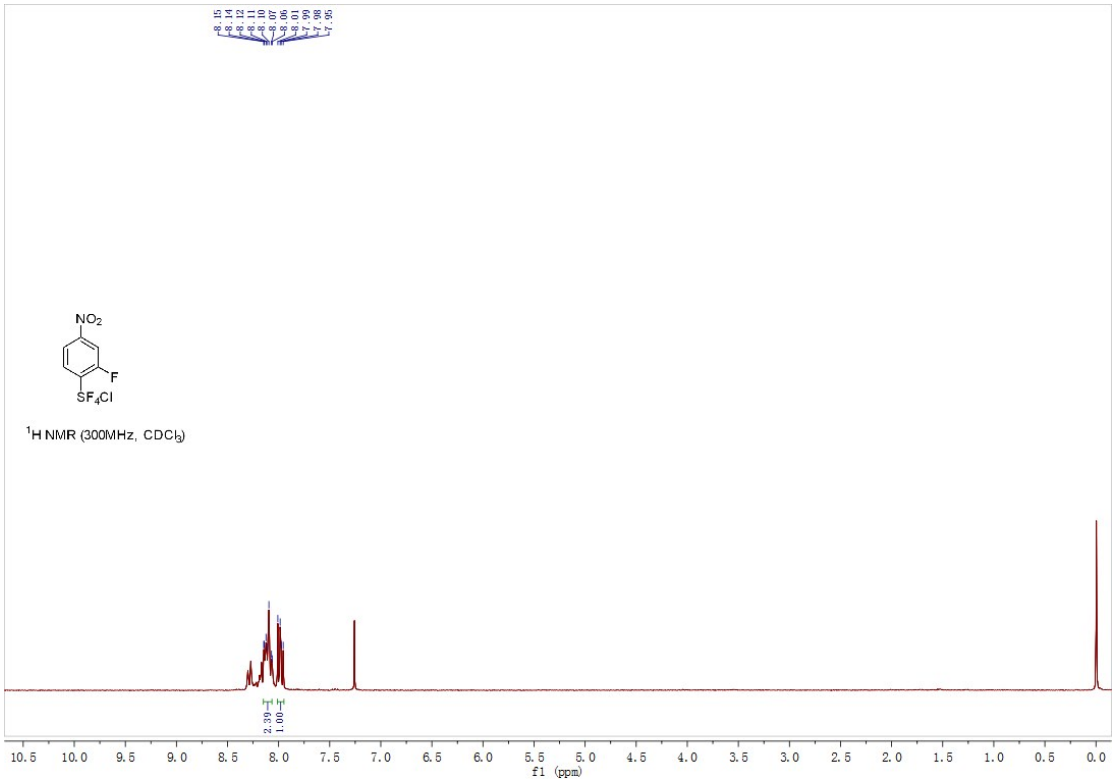

F
F
SF4Cl
19F NMR (282 MHz, CDCl3)
f1 (ppm)

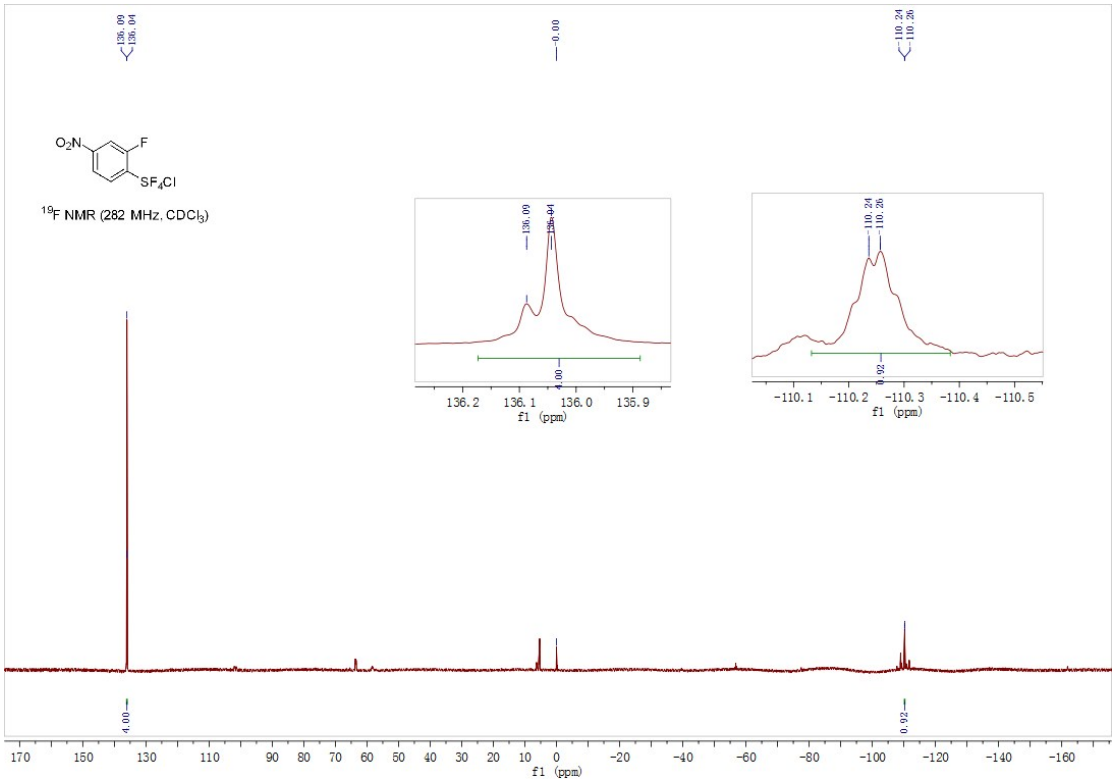

F
SF4Cl
F
1H (300 MHz, CDCl3)
f1 (ppm)

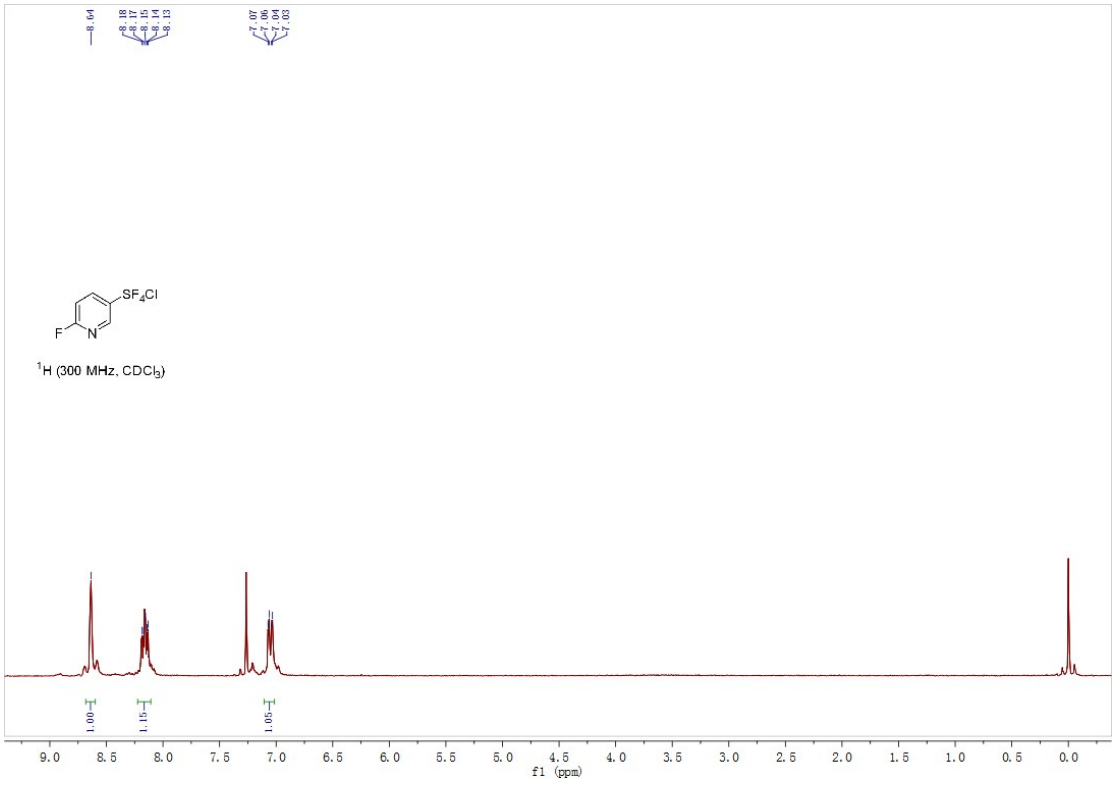

F
F
SF4Cl
19F NMR (282 MHz, CDCl3)
f1 (ppm)

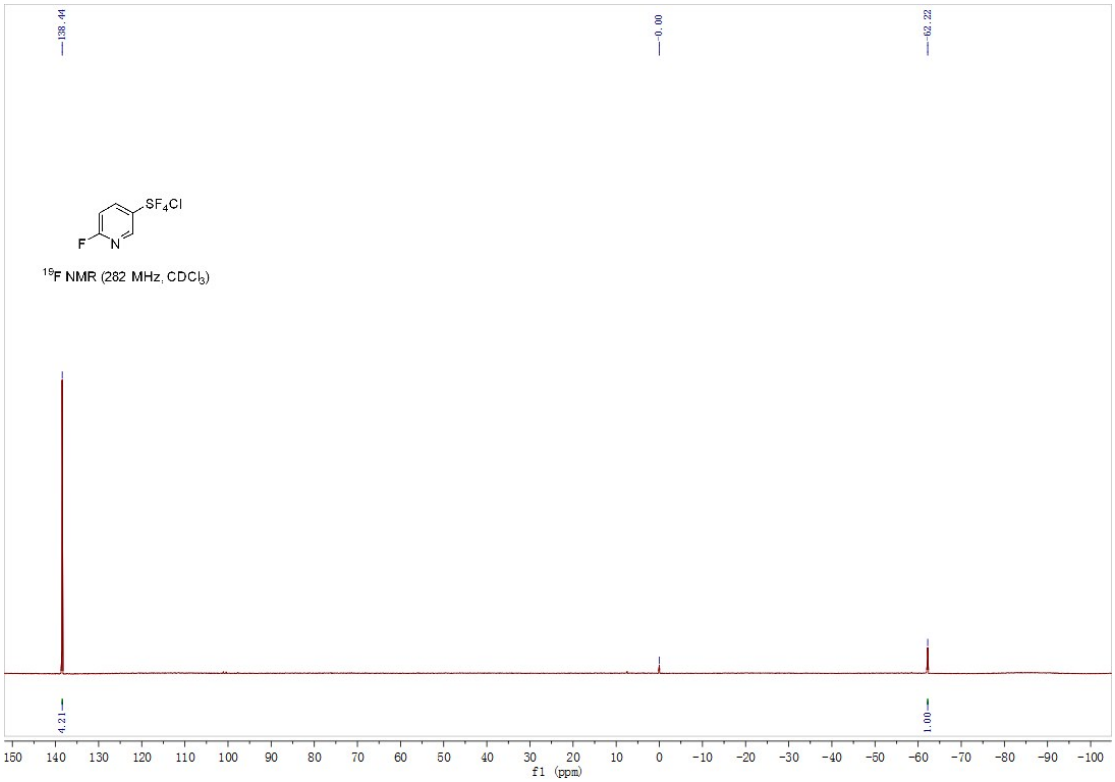

F
SF4Cl
F
1H (300 MHz, CDCl3)
f1 (ppm)

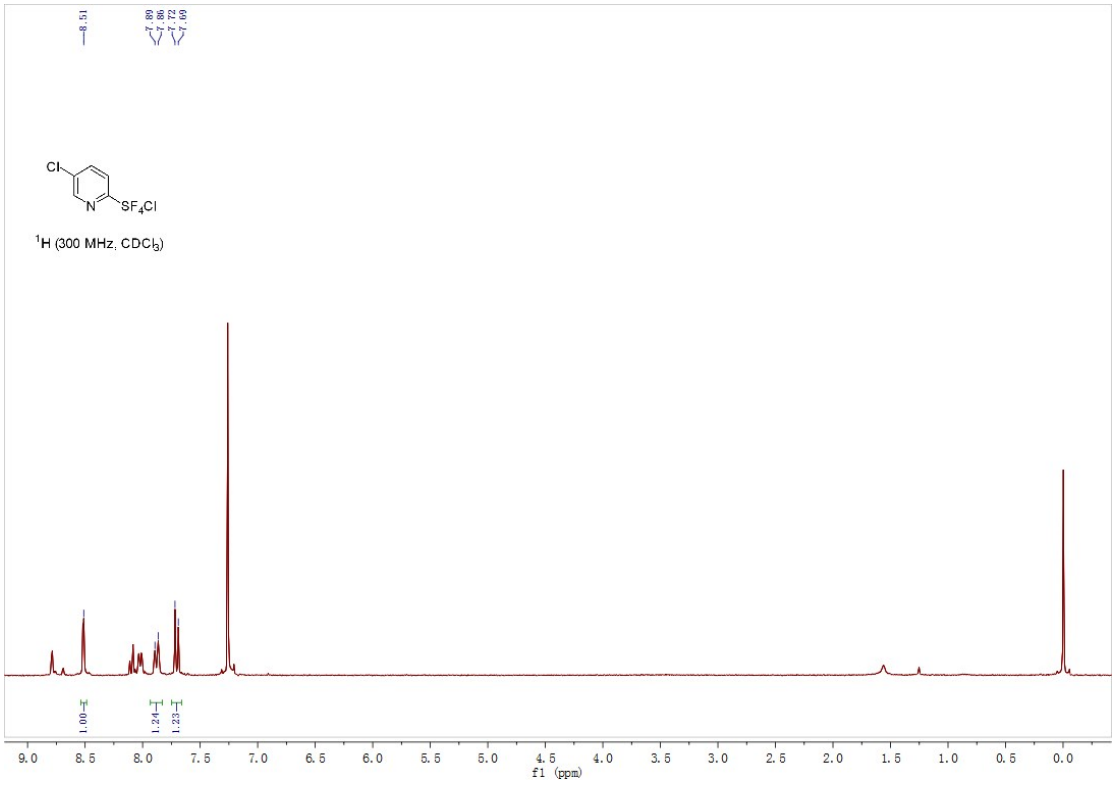

F
F
SF4Cl
19F NMR (282 MHz, CDCl3)
f1 (ppm)

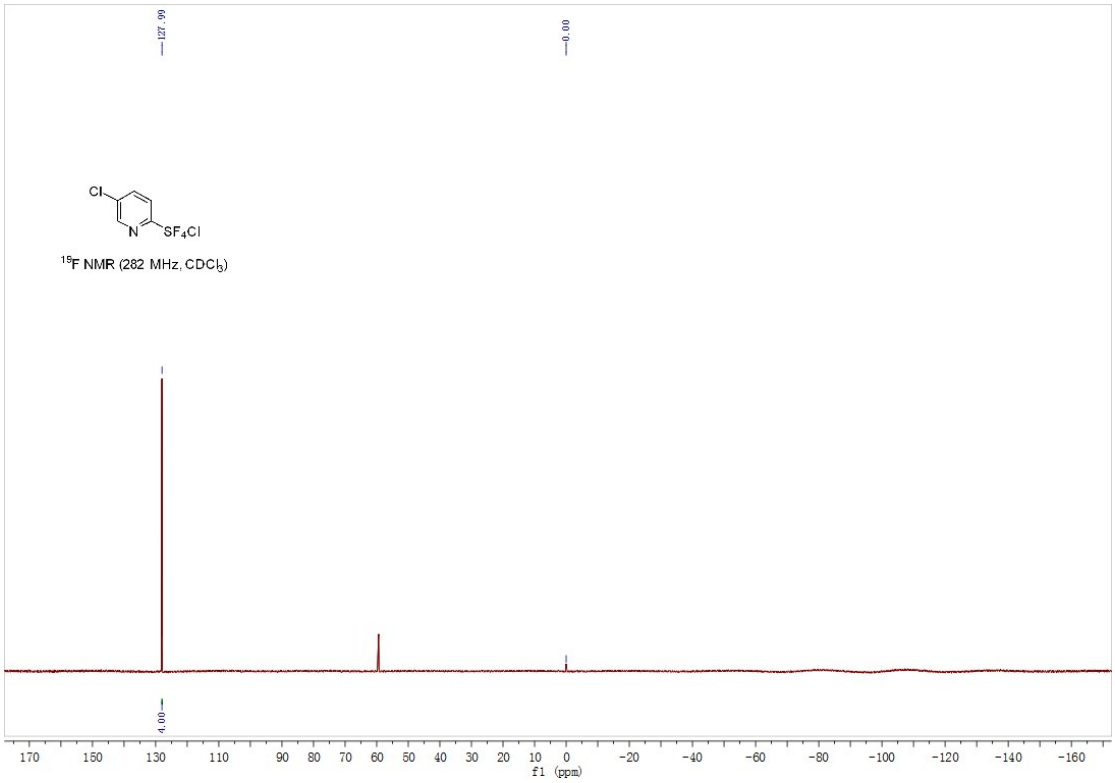

NO2
F
SF4Cl
1H NMR (300MHz, CDCl3)
f1 (ppm)

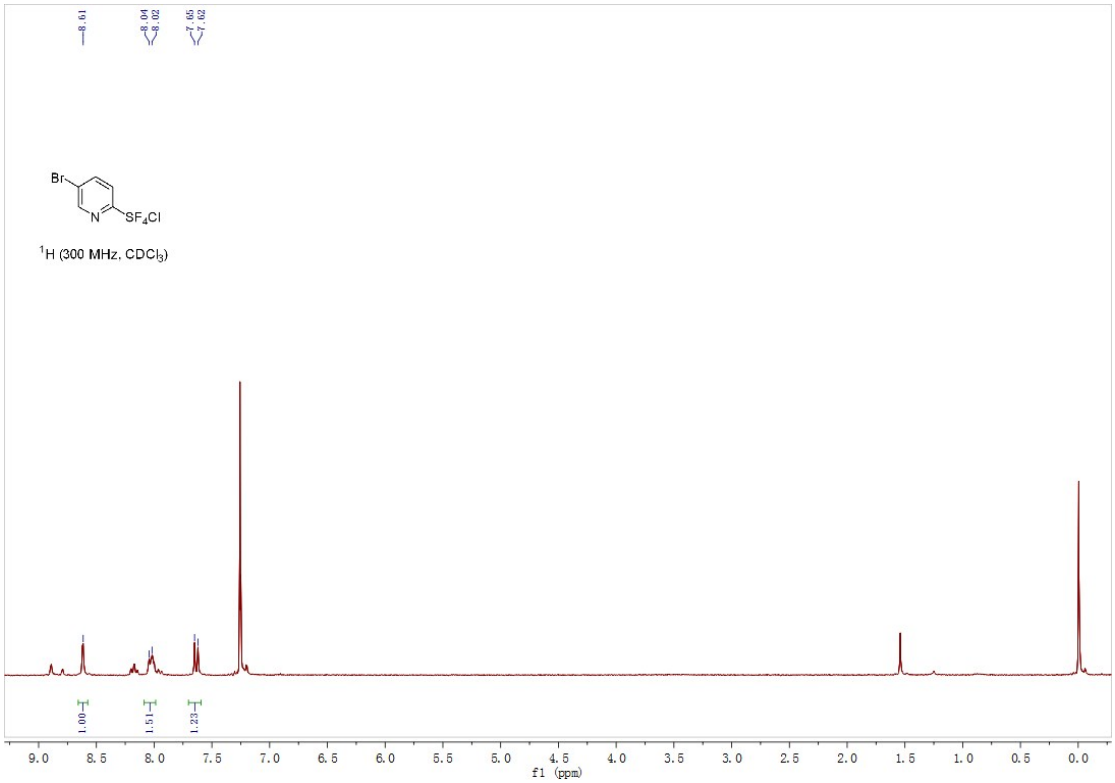

136.09
136.04
0.00
110.24
110.26
O_2N
F
SF_4Cl
^{19}F NMR (282 MHz, $CDCl_3$)
4.00
0.92
f1 (ppm)

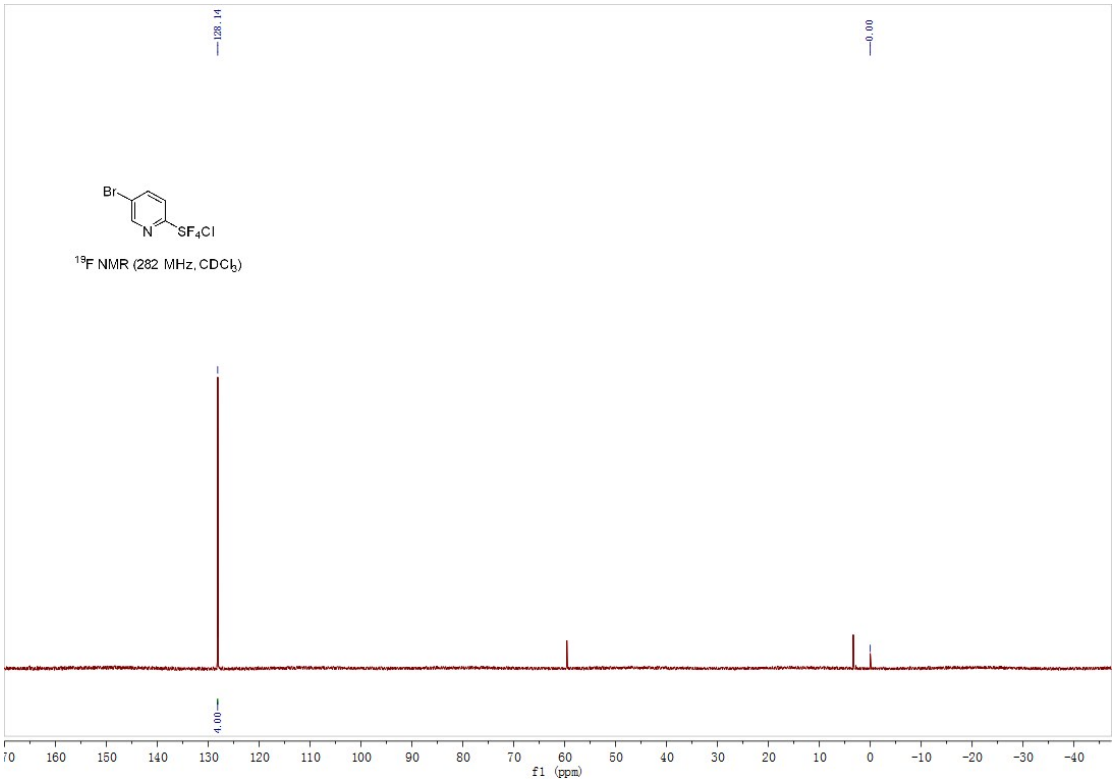

8.64
8.18
8.17
8.15
8.14
8.13
7.07
7.06
7.04
7.03
SF_4Cl
F
N
^1H (300 MHz, $CDCl_3$)
1.00
1.15
1.05
f1 (ppm)

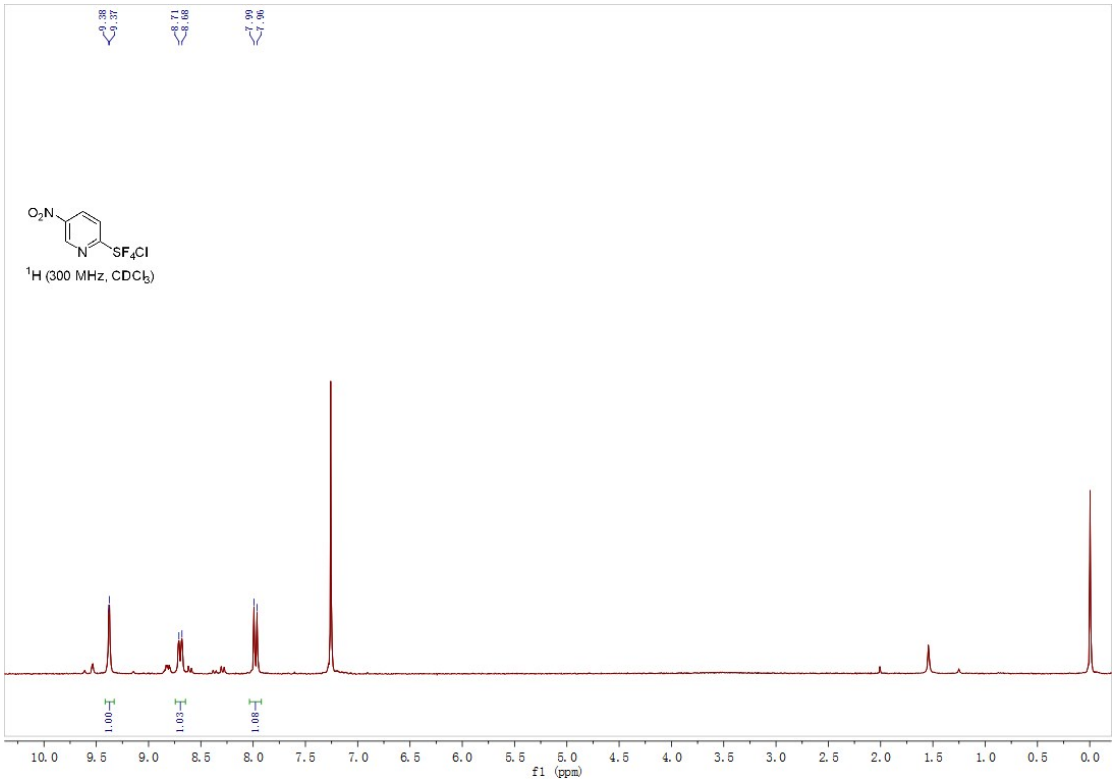

138.44
0.00
-62.22
SF4Cl
F
N
19F NMR (282 MHz, CDCl3)
4.21
1.00
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

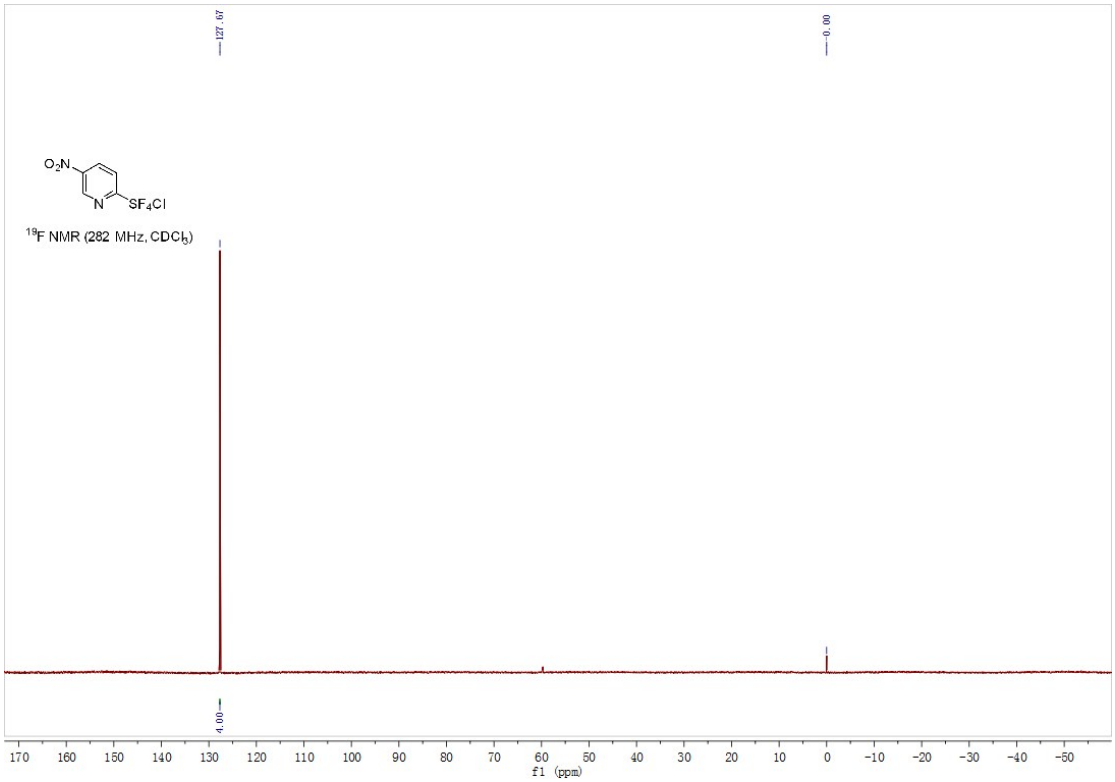

8.51
7.89
7.86
7.72
7.69
Cl
N
SF4Cl
1H (300 MHz, CDCl3)
1.00
1.24
1.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

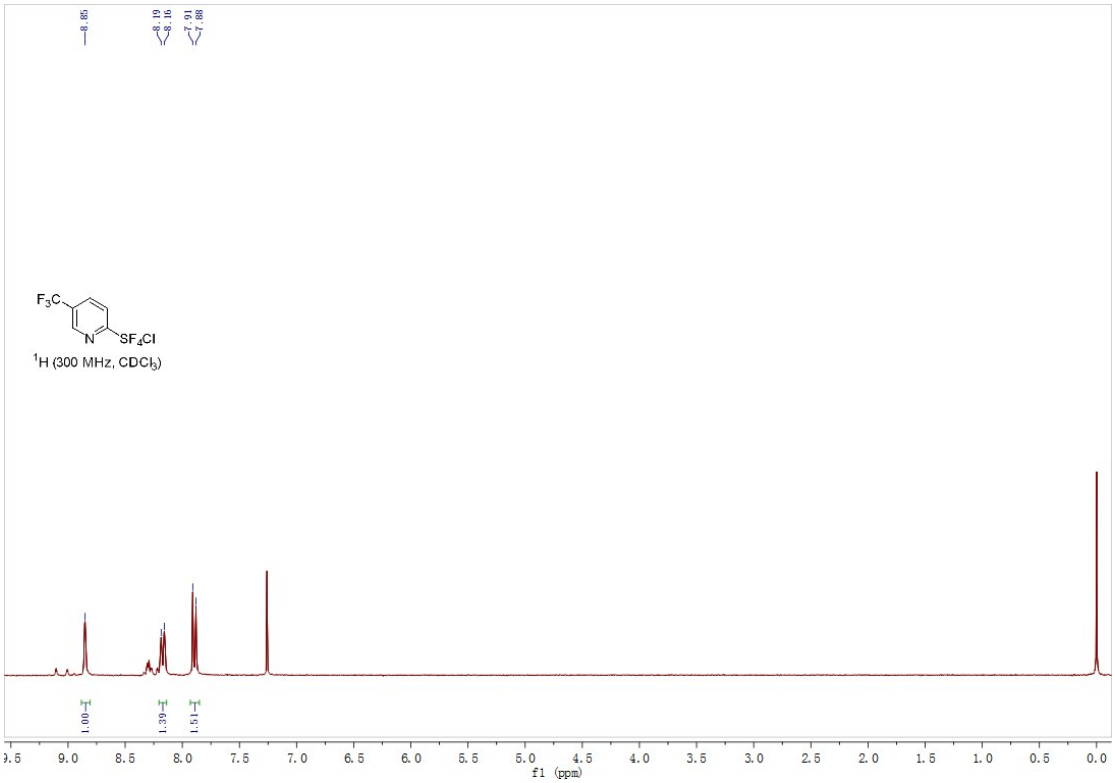

127.99
0.00
Cl
N
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)

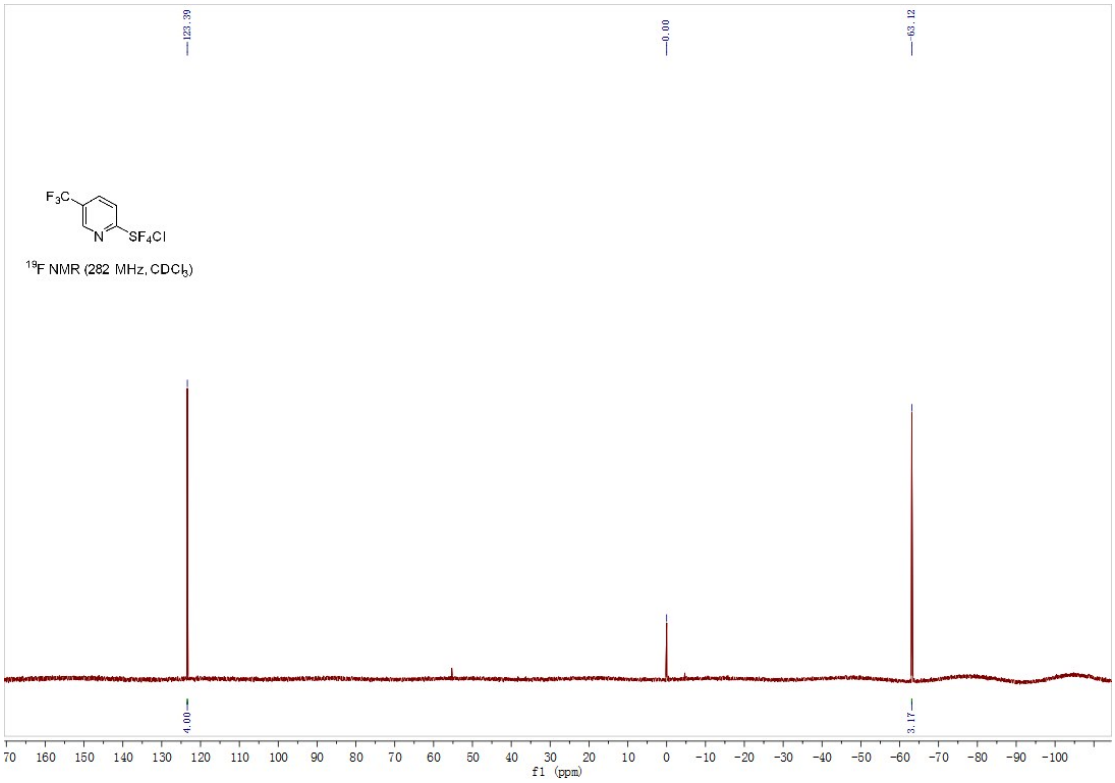

8.61
8.04
8.02
7.65
7.62
Br
N
SF4Cl
1H (300 MHz, CDCl3)
1.00
1.51
1.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

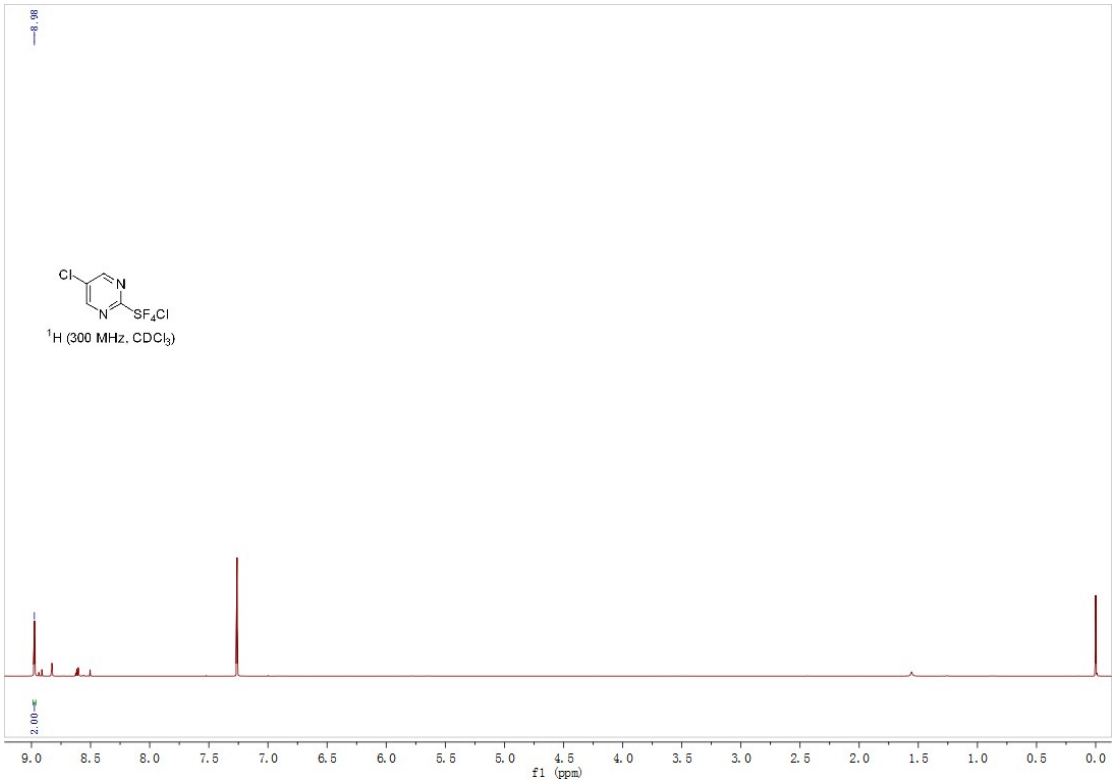

128.14
0.00
Br
N
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
f1 (ppm)

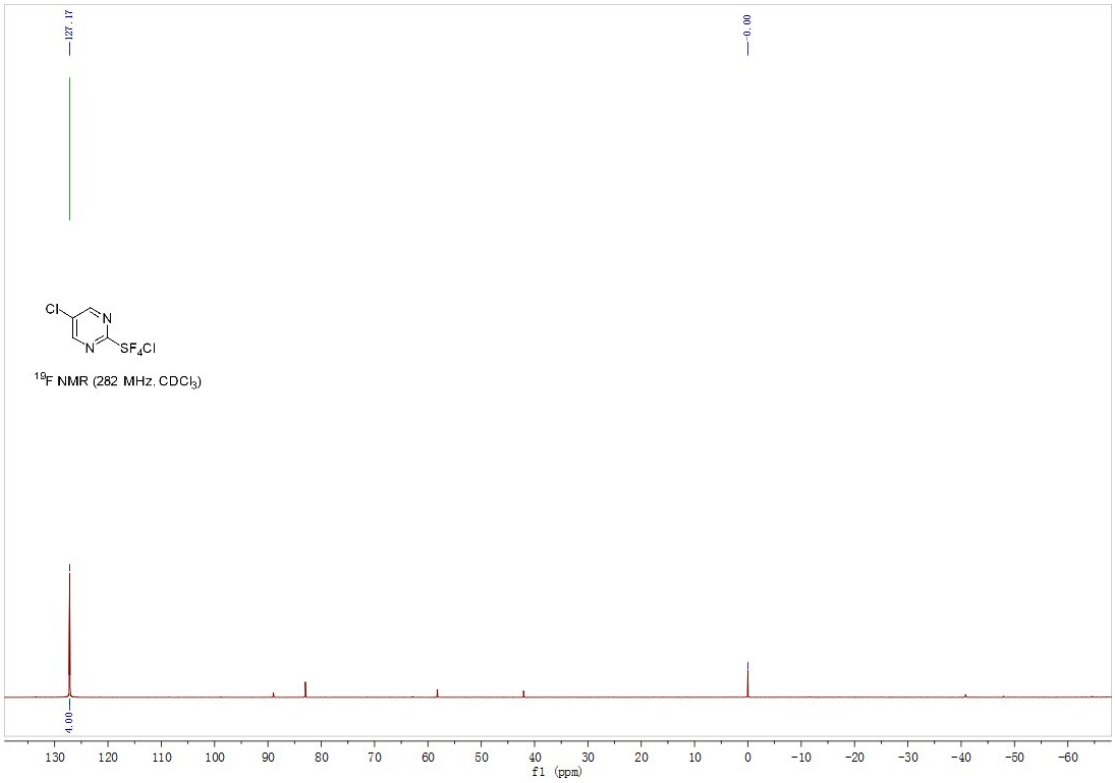

9.38
9.37
8.71
8.68
7.99
7.96
O2N
N
SF4Cl
1H (300 MHz, CDCl3)
1.00
1.03
1.08
f1 (ppm)

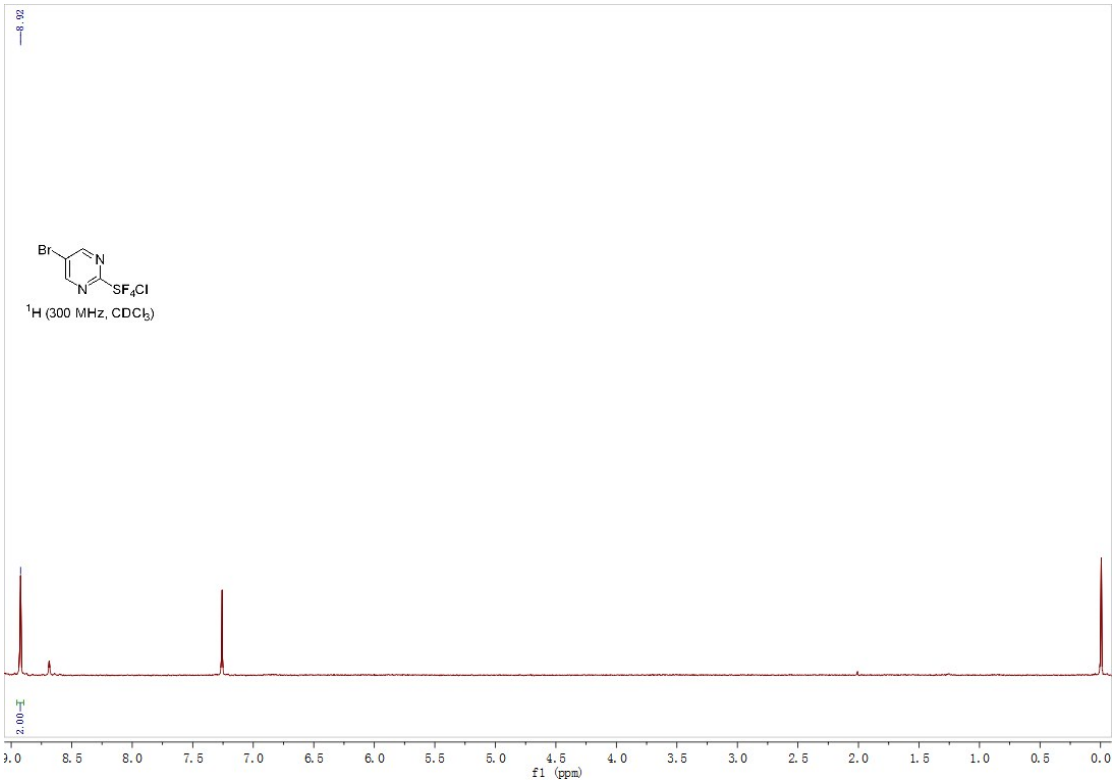

127.67
0.00
O_2N
N
SF_4Cl
^{19}F NMR (282 MHz, $CDCl_3$)
4.00
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

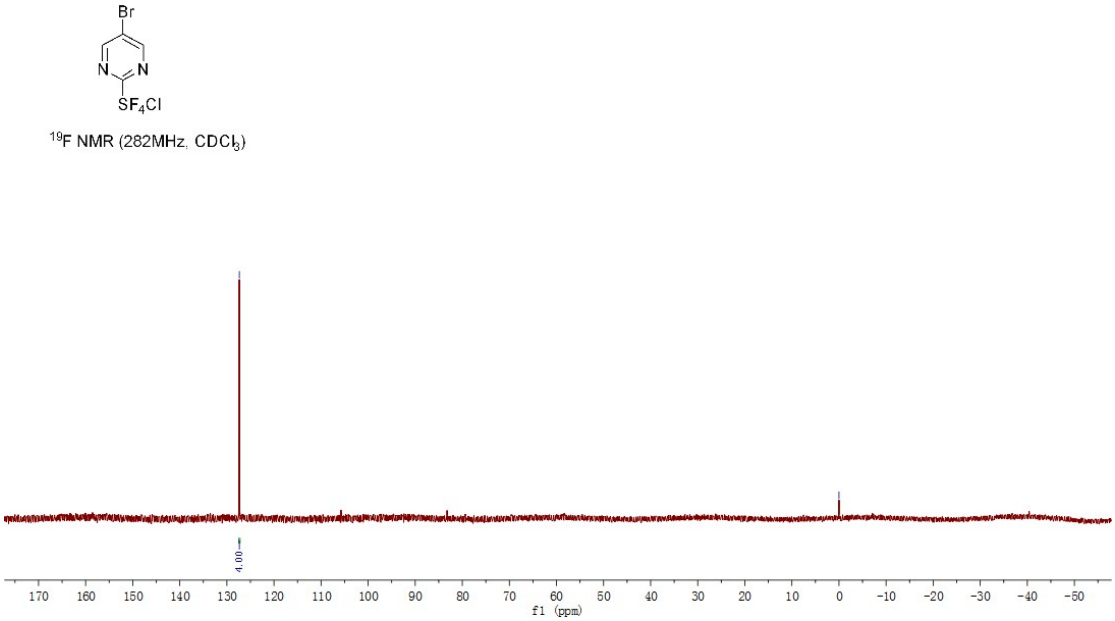

8.85
8.19
8.16
7.91
7.88
F_3C
N
SF_4Cl
^1H (300 MHz, $CDCl_3$)
1.00
1.39
1.51
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-123.39
0.00
-63.12
F3C
N
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
3.17
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

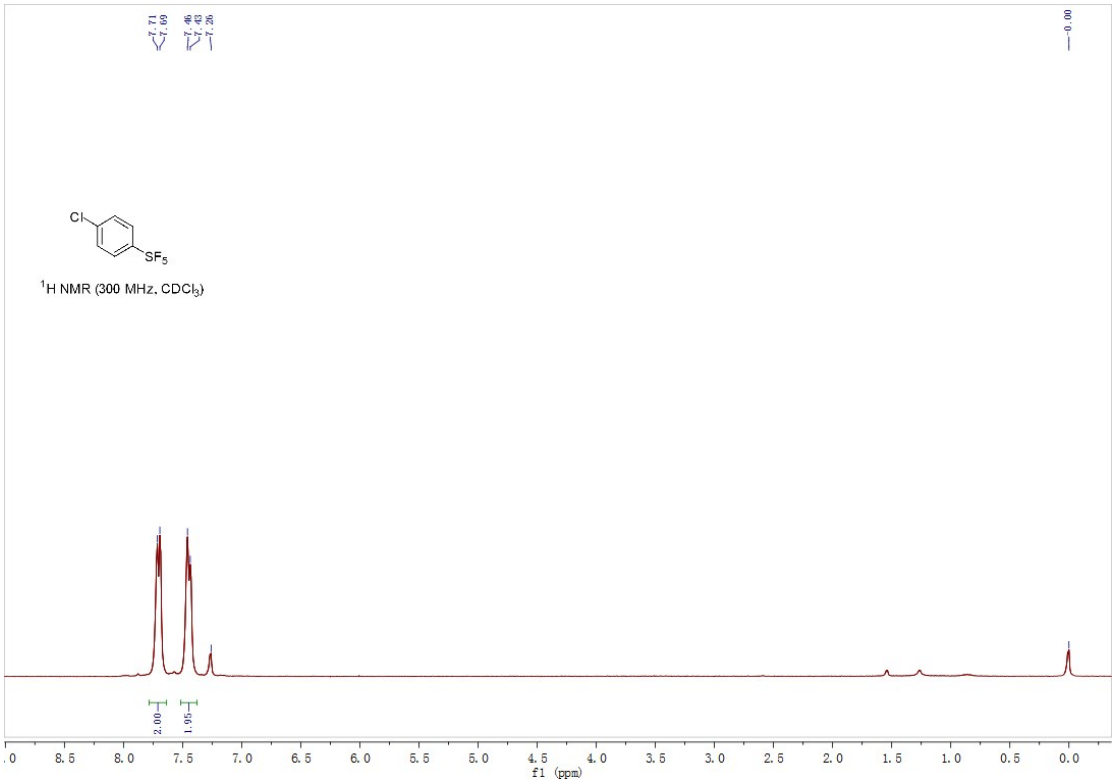

8.98
Cl
N
N
SF4Cl
1H (300 MHz, CDCl3)
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


127.17
0.00
Cl
N
N
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

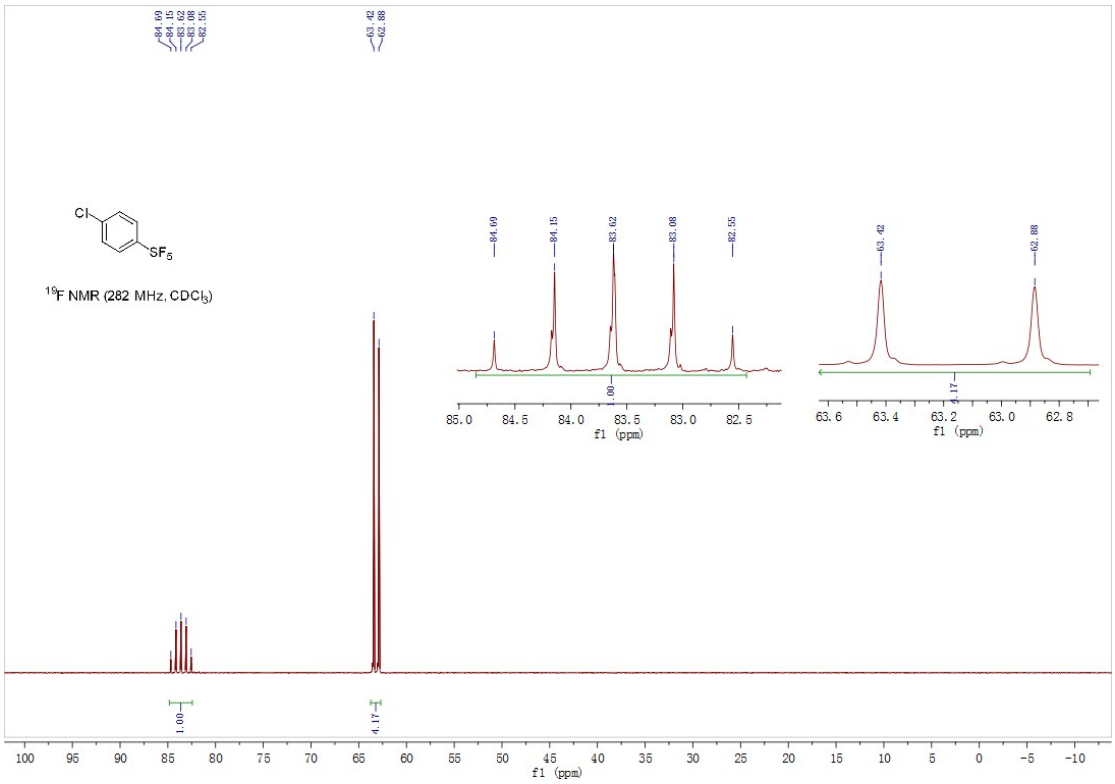

8.92
Br
N
N
SF4Cl
1H (300 MHz, CDCl3)
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

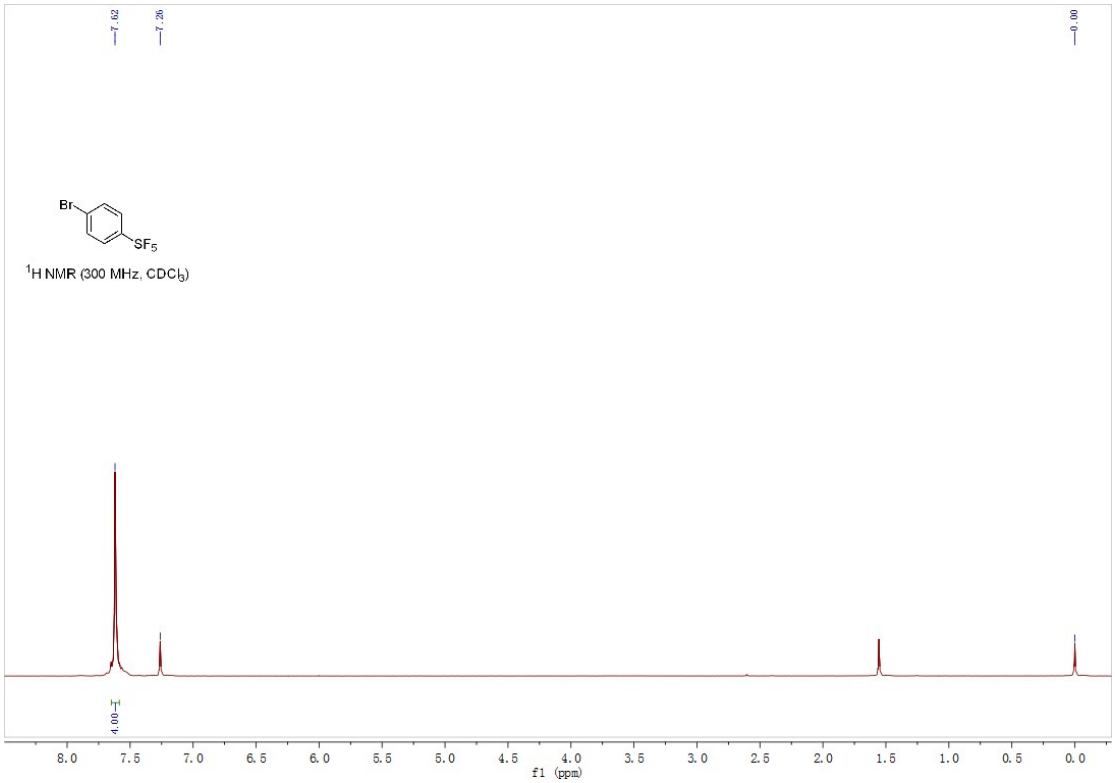


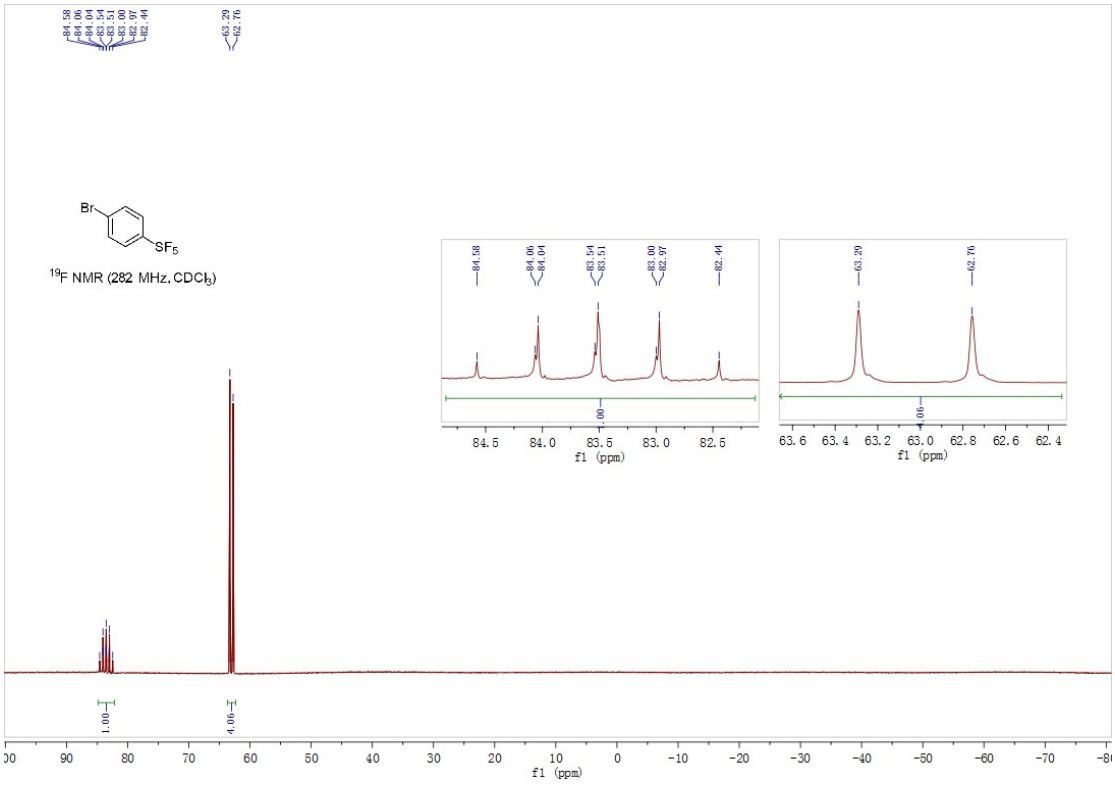
^{19}F NMR (282MHz, $CDCl_3$)

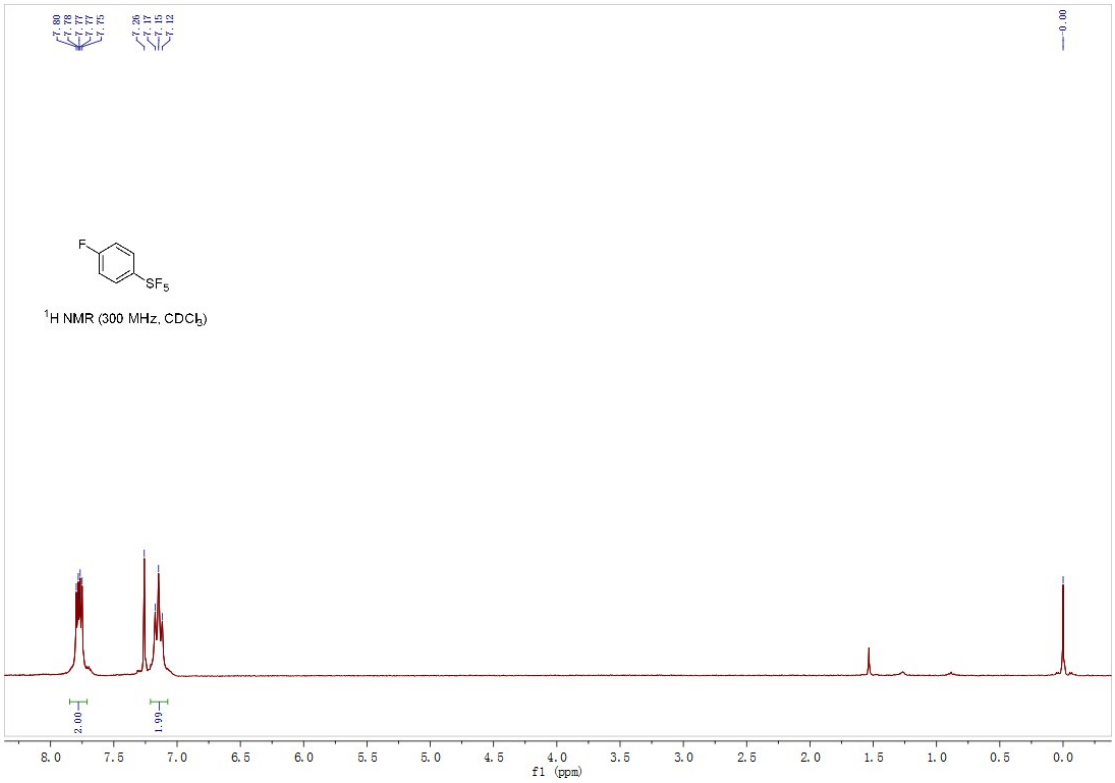


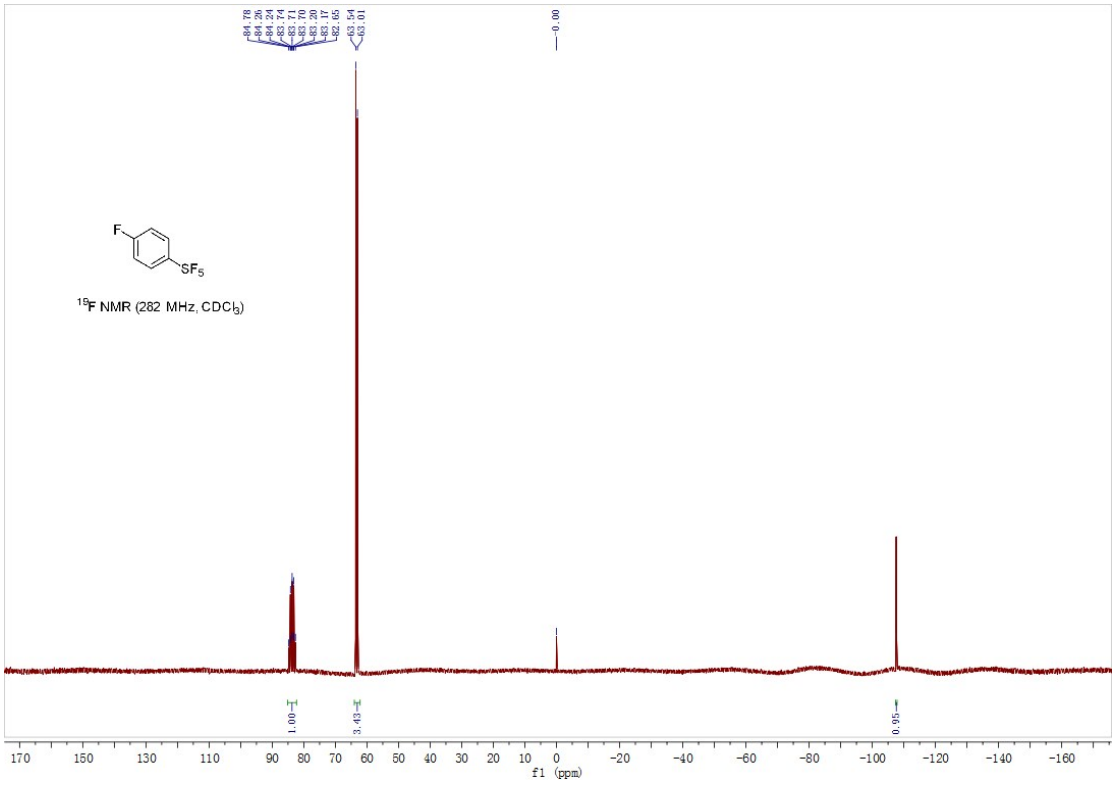
^{1}H NMR (300 MHz, $CDCl_3$)

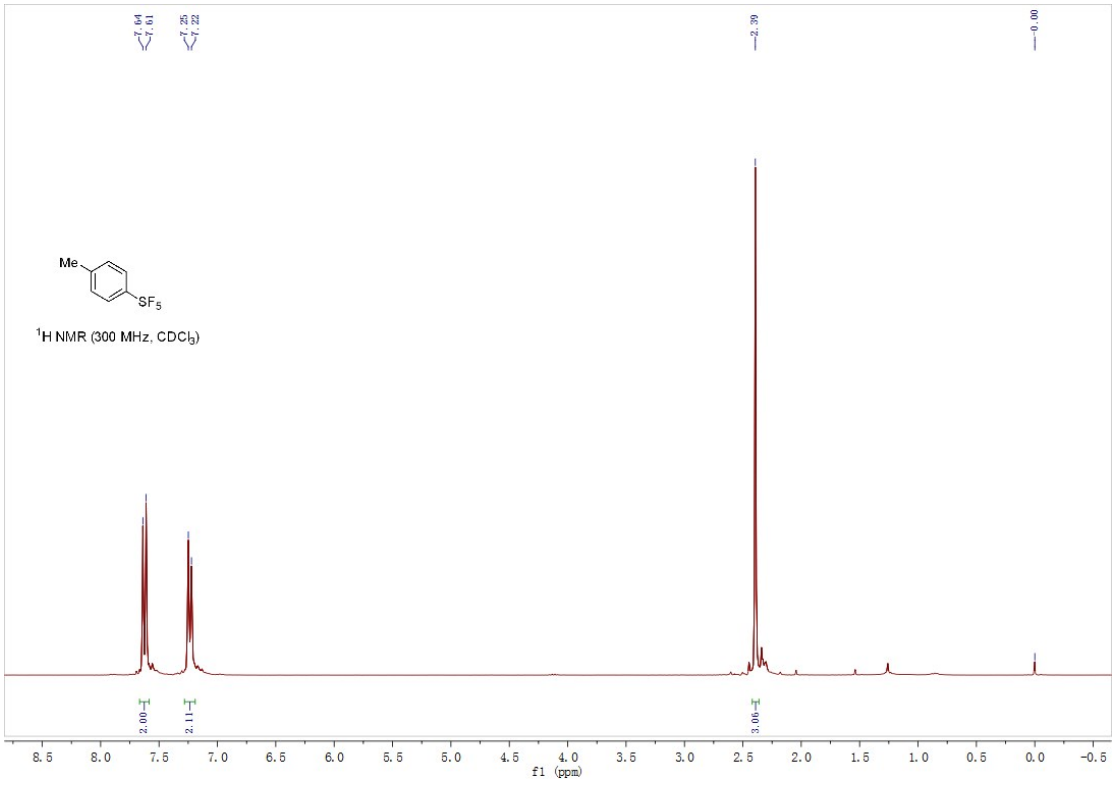

Cl
SF5
19F NMR (282 MHz, CDCl3)
84.69
84.15
83.62
83.08
82.55
63.42
62.88
1.00
4.17
f1 (ppm)

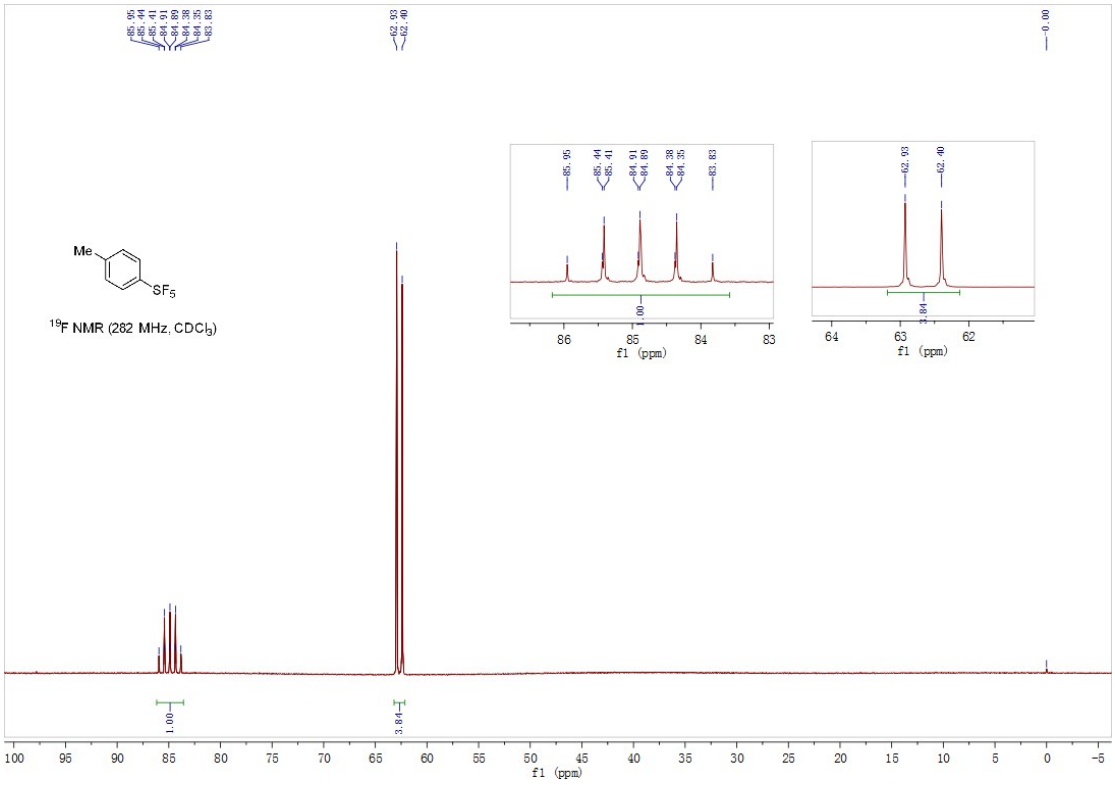

Br
SF5
1H NMR (300 MHz, CDCl3)
7.62
7.26
0.00
4.00
f1 (ppm)

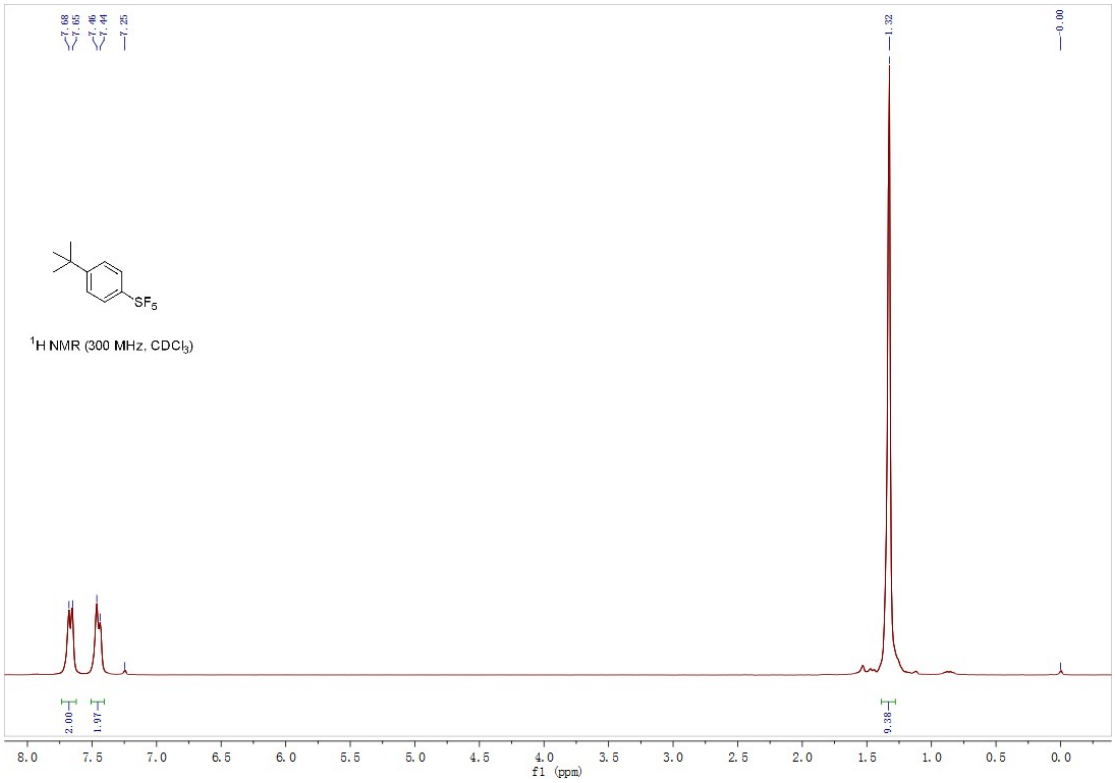

Br
SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)

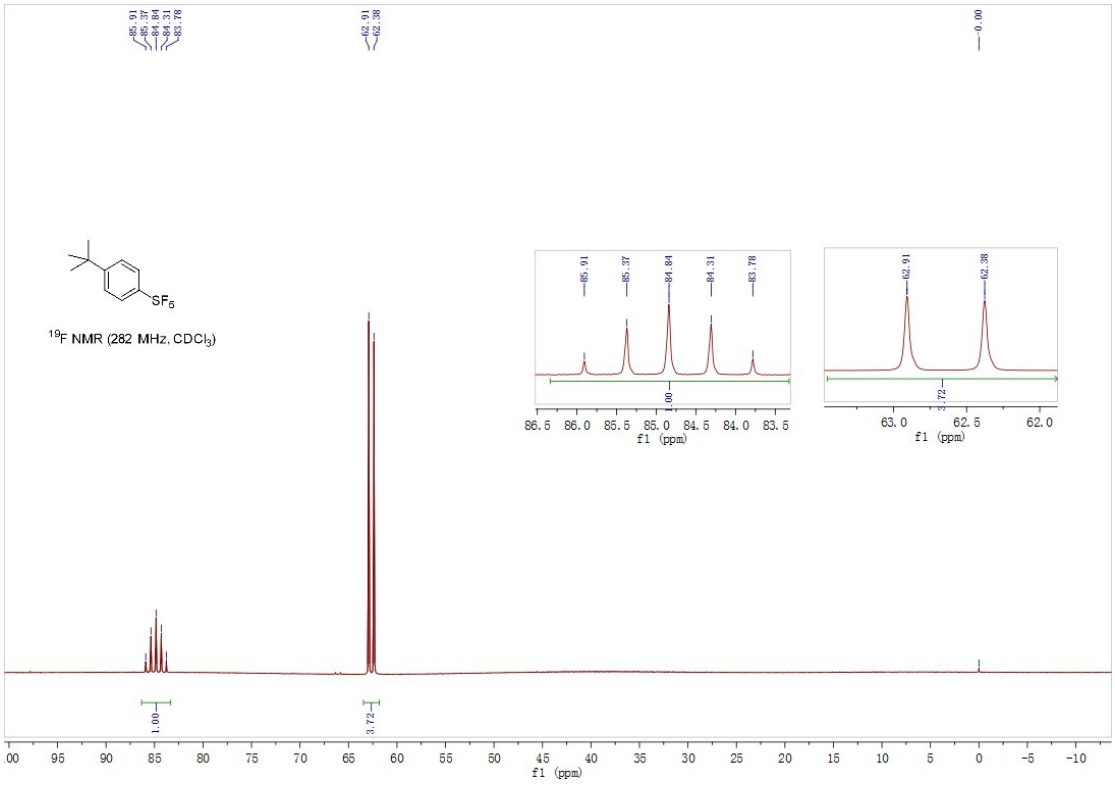

F
SF5
1H NMR (300 MHz, CDCl3)
f1 (ppm)

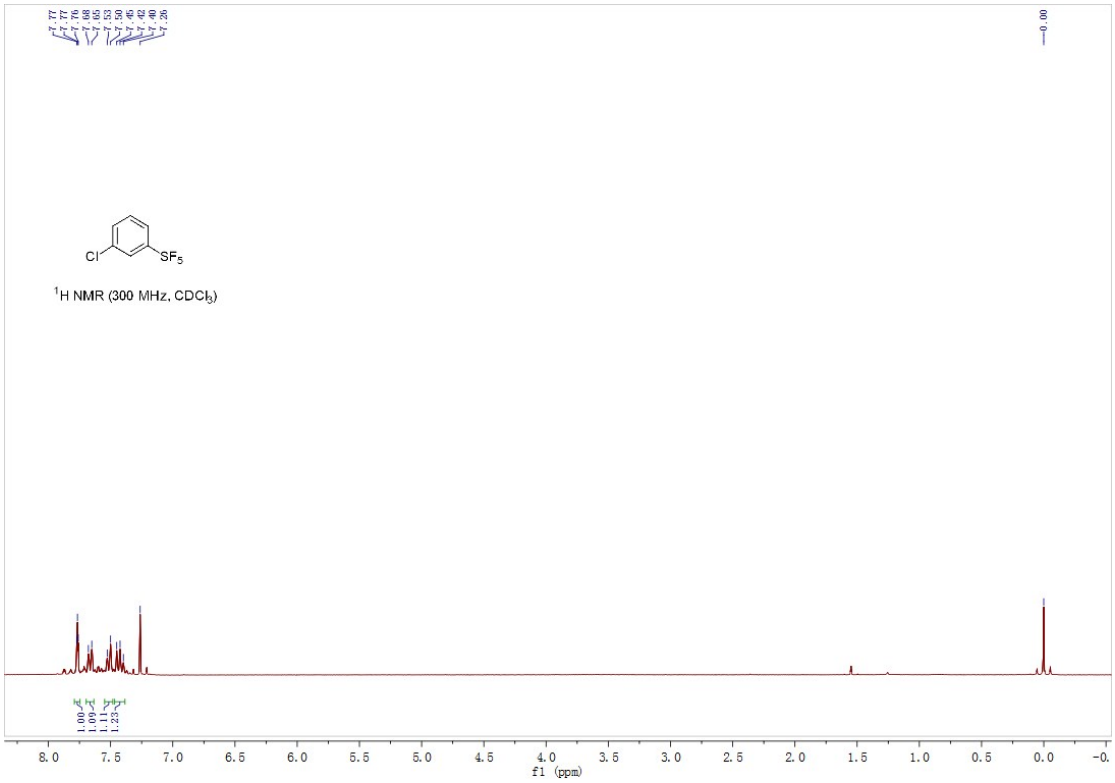

F
SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)

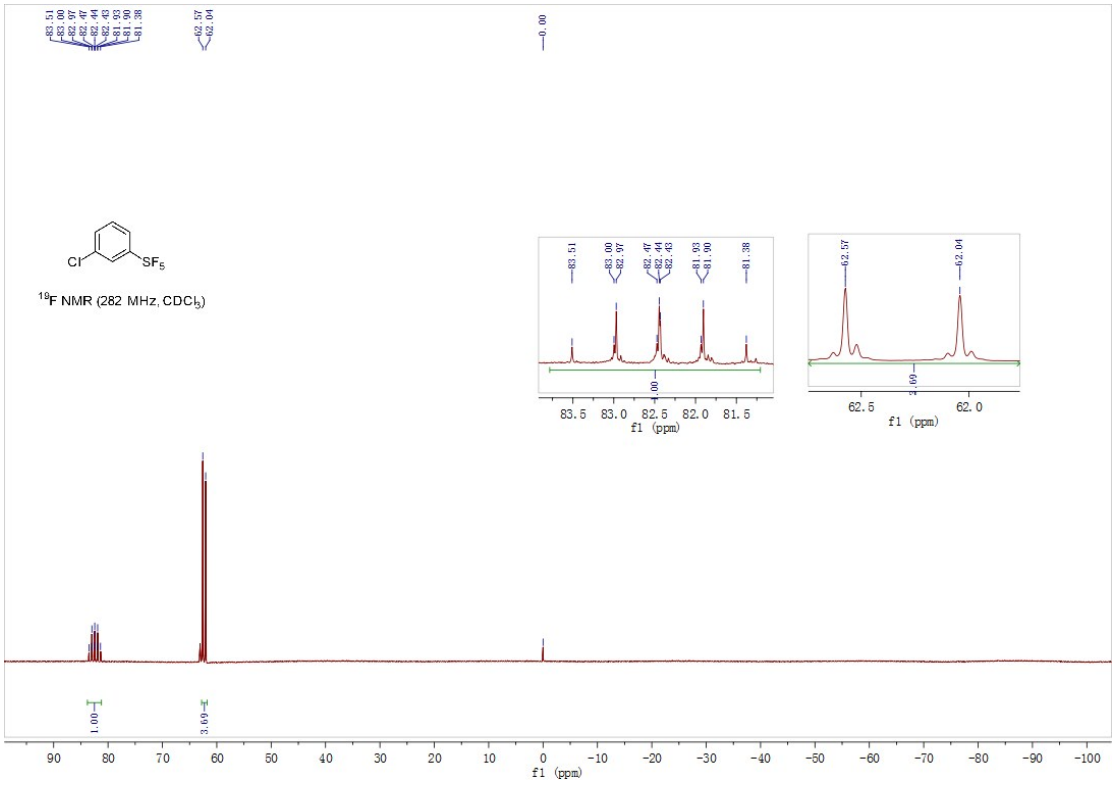

Me
SF5
1H NMR (300 MHz, CDCl3)
f1 (ppm)

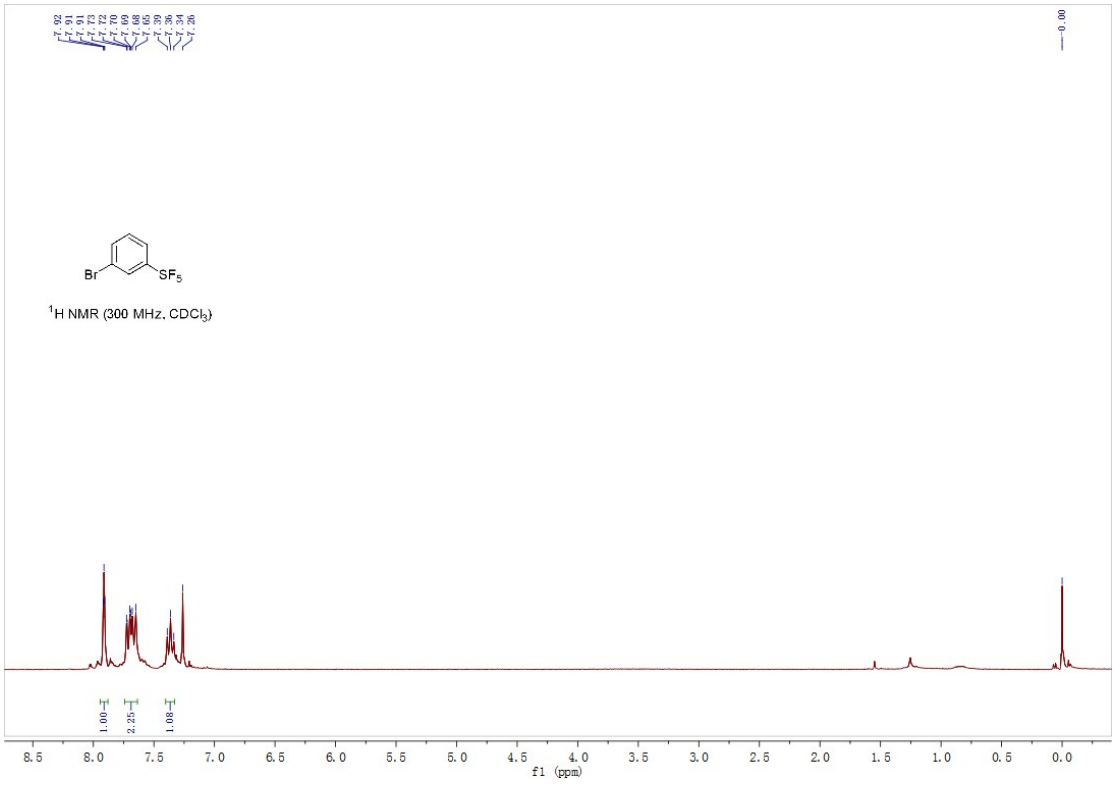

Me
SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)

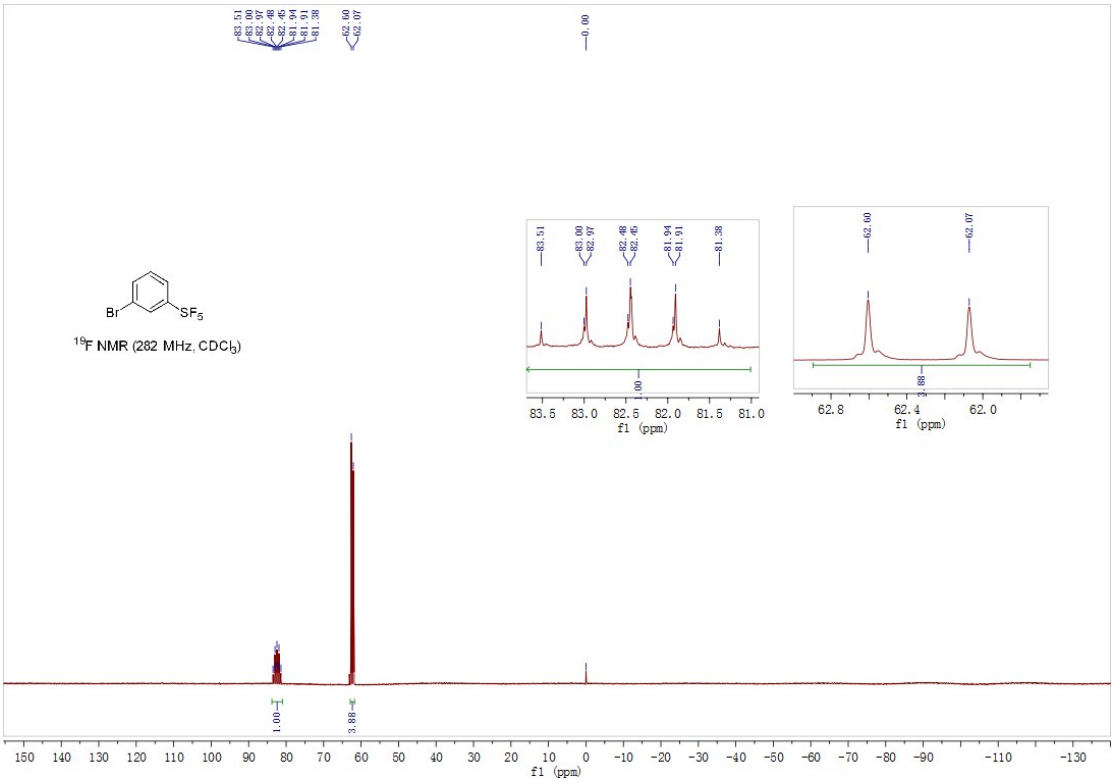

SF5
1H NMR (300 MHz, CDCl3)
f1 (ppm)

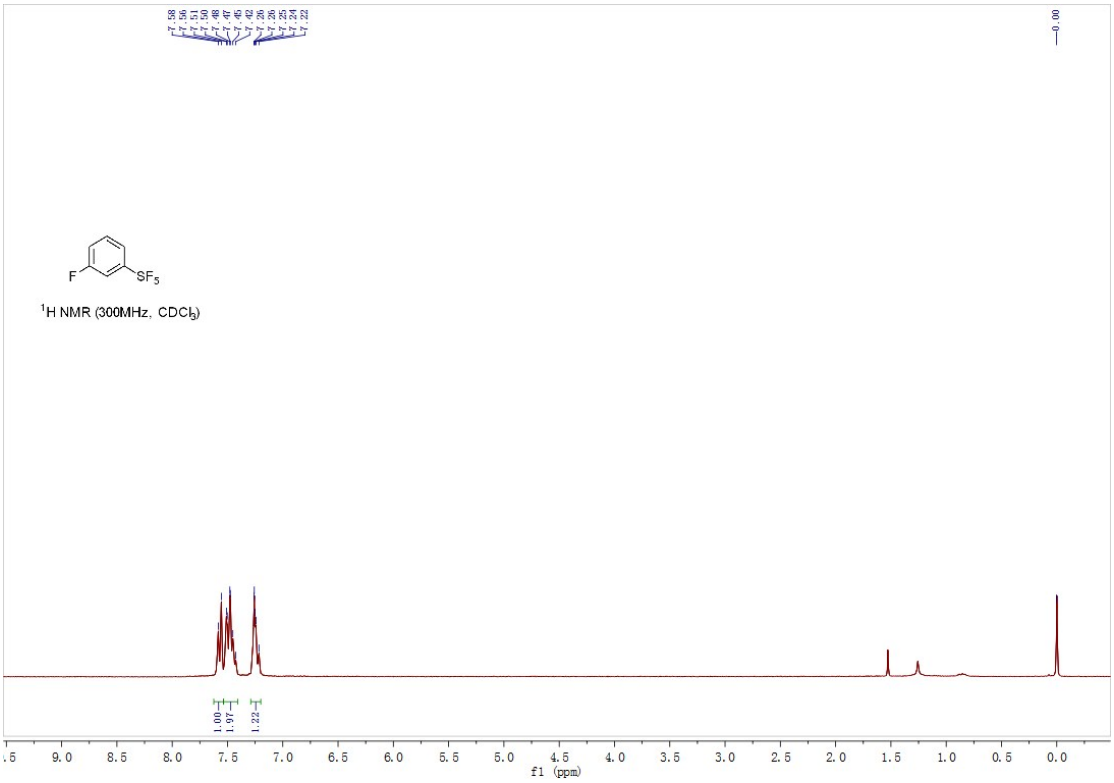

SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)

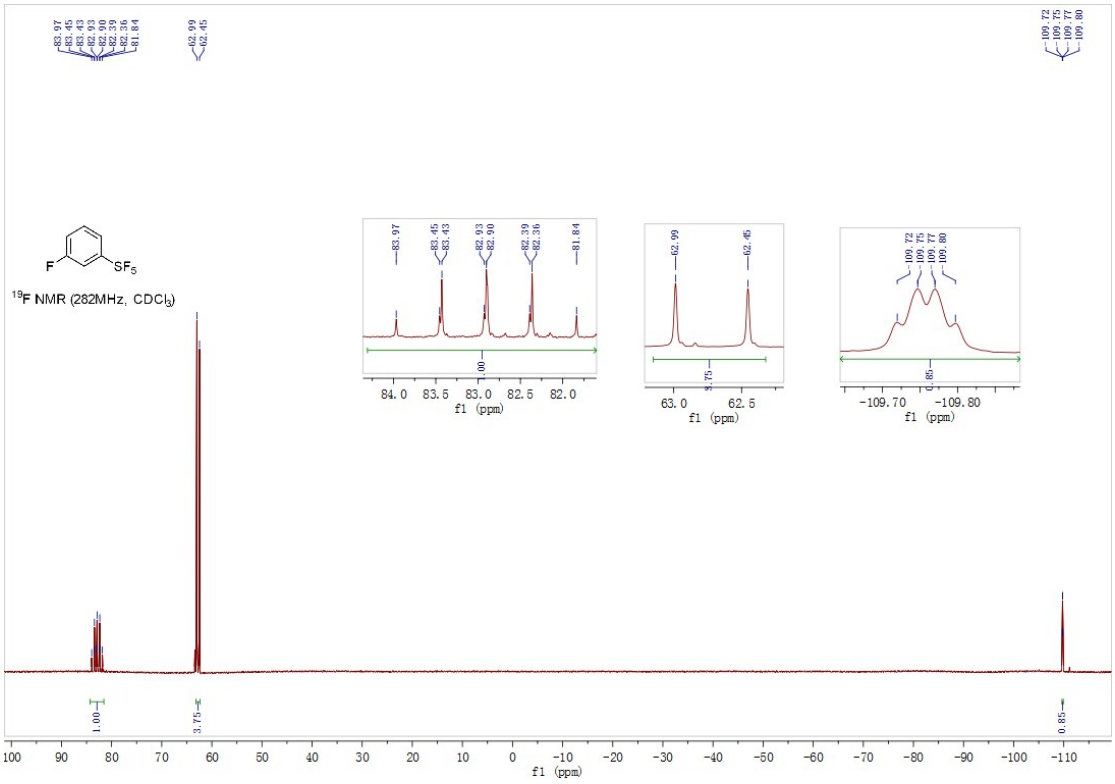

Cl
SF5
1H NMR (300 MHz, CDCl3)
f1 (ppm)

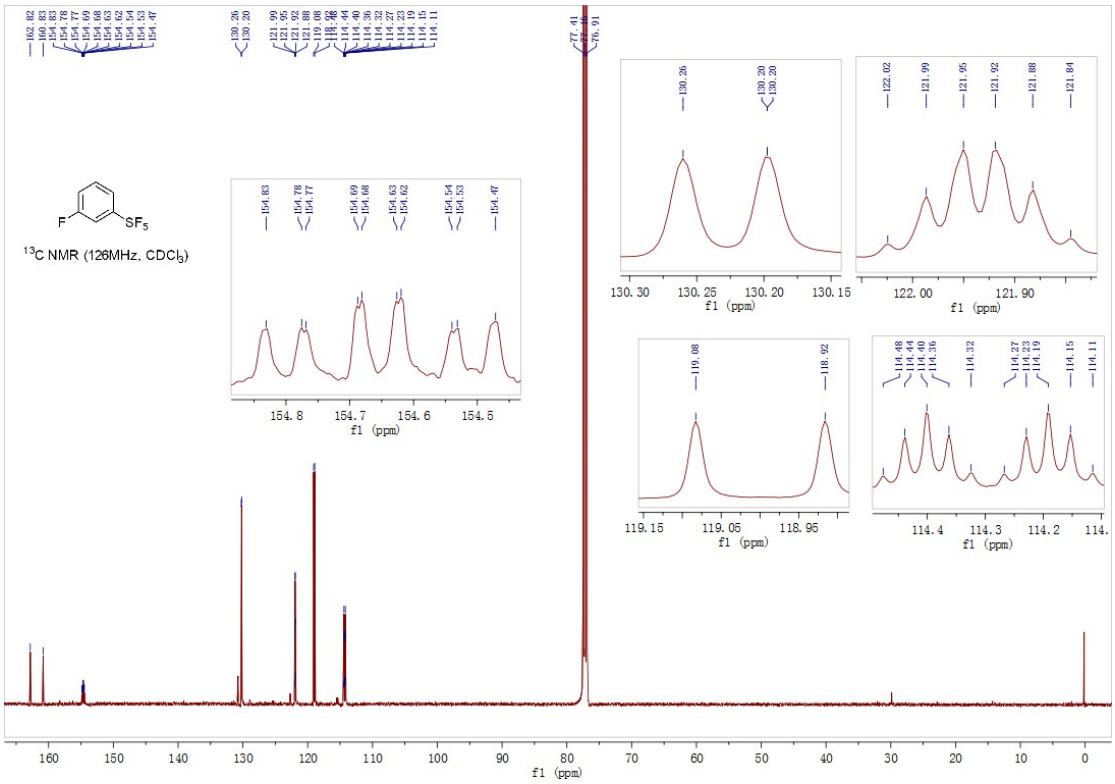

Cl
SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)

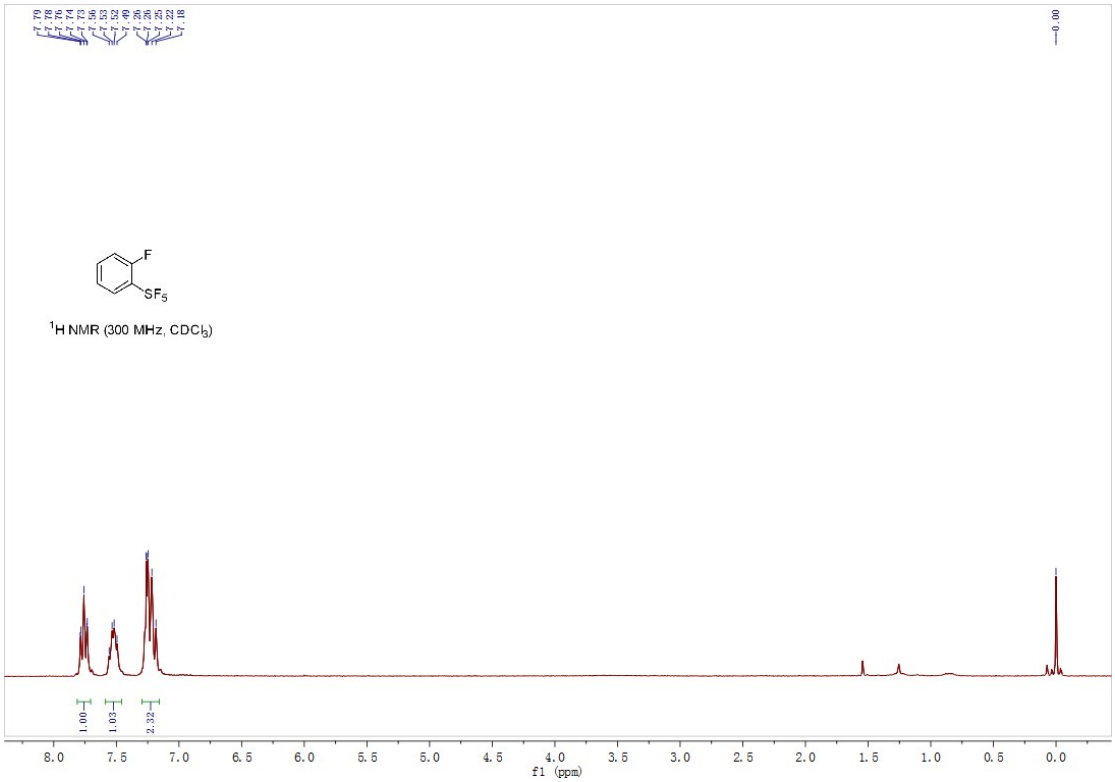

Br
SF5
1H NMR (300 MHz, CDCl3)
f1 (ppm)

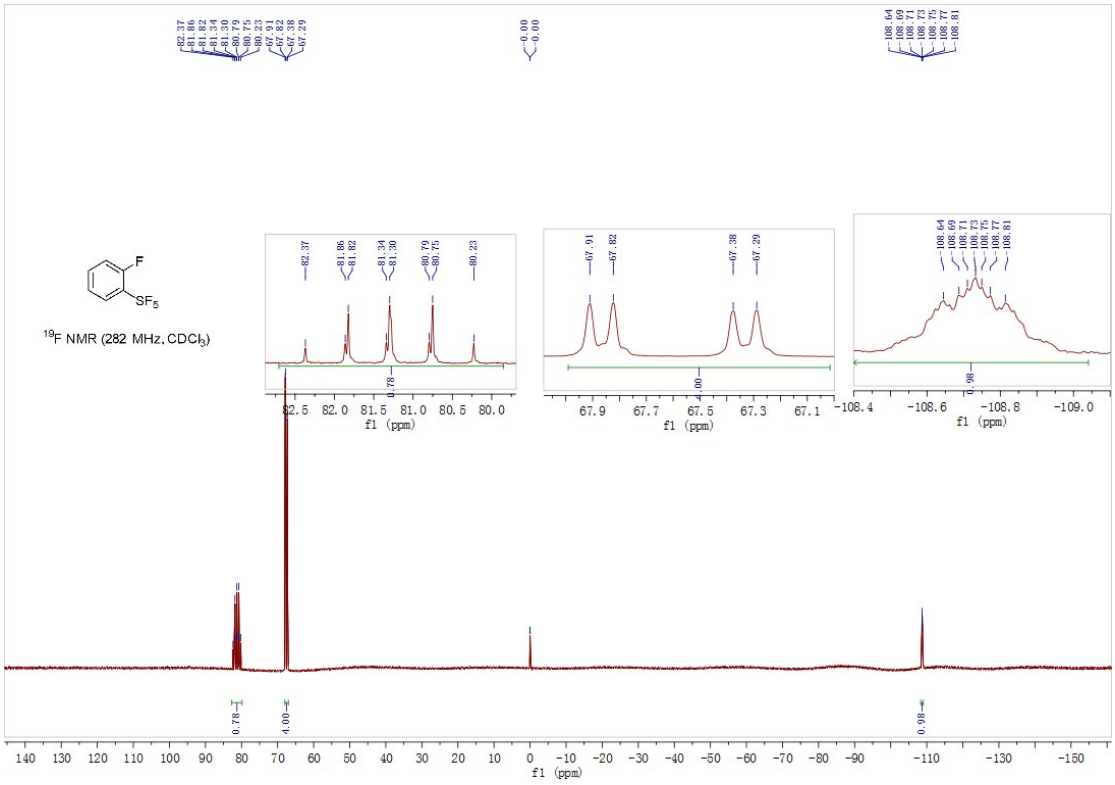

Br
SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)

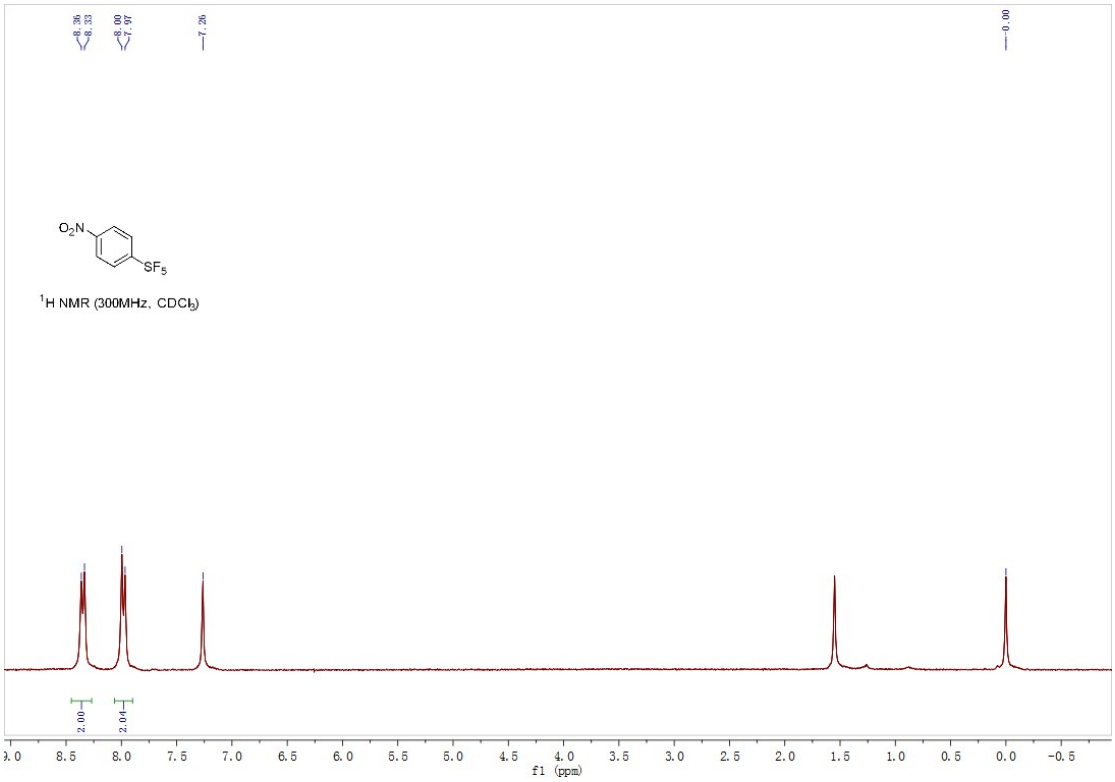

F
SF5
1H NMR (300MHz, CDCl3)
f1 (ppm)

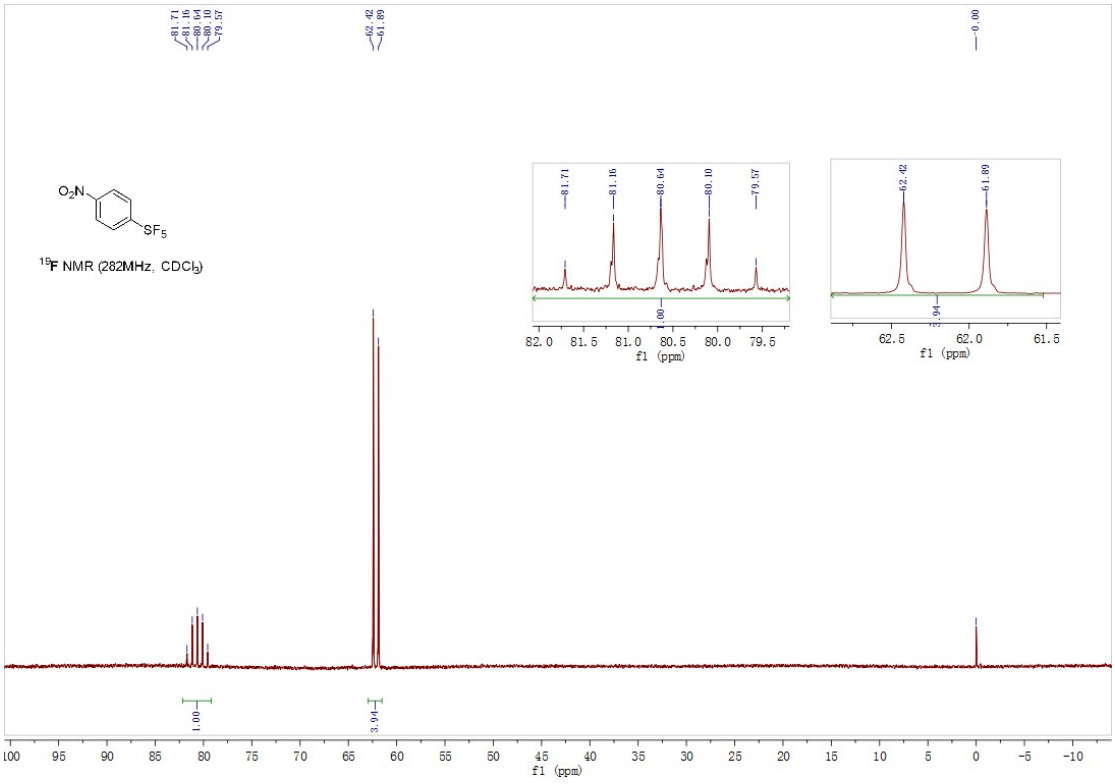

^{19}F NMR (282MHz, CDCl$_3$)
f1 (ppm)

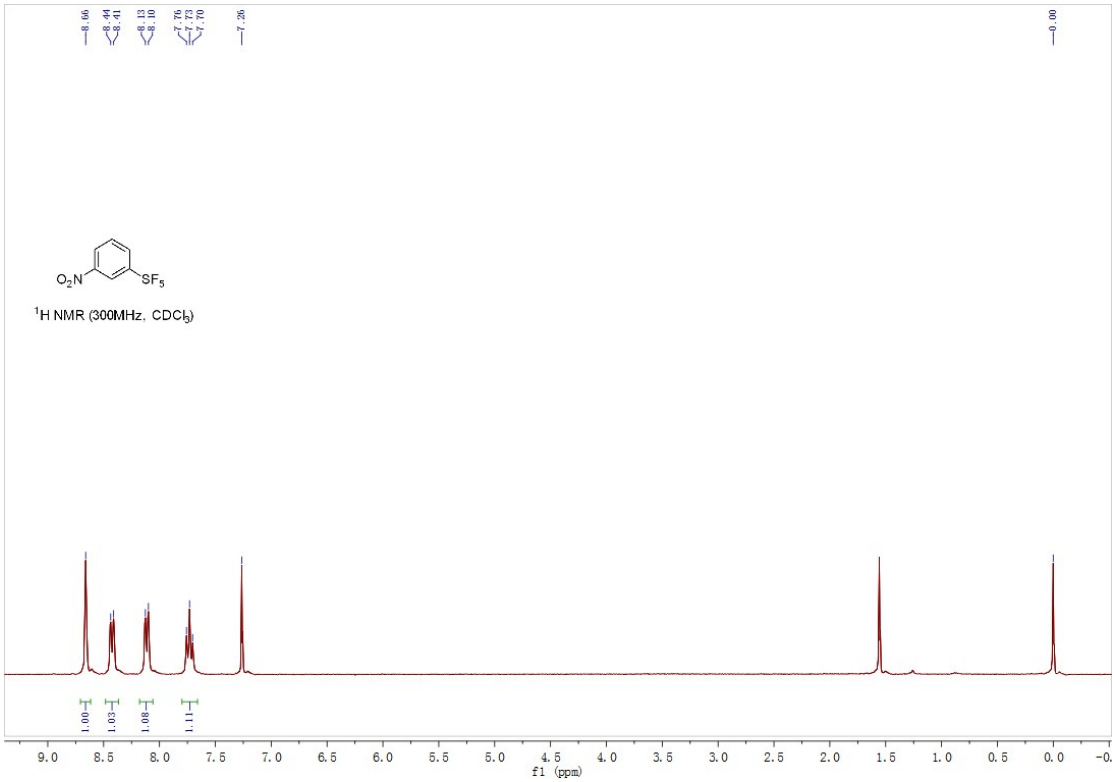

^{13}C NMR (126MHz, CDCl$_3$)
f1 (ppm)

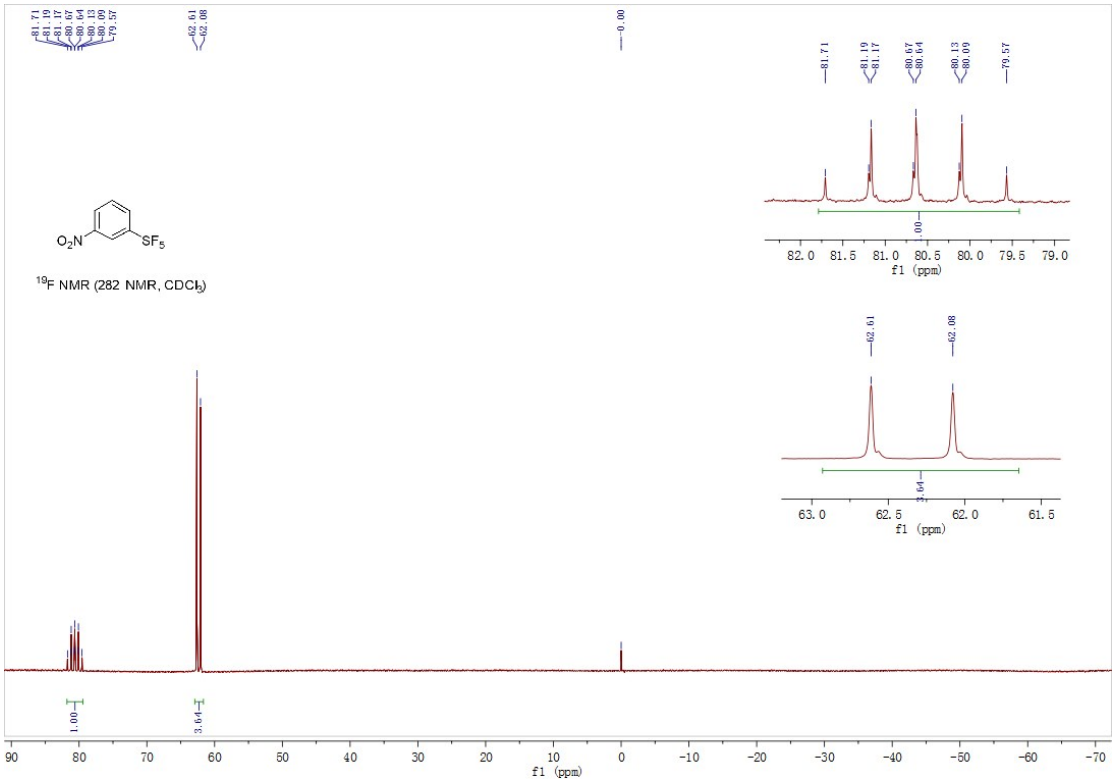

F
SF5
1H NMR (300 MHz, CDCl3)
f1 (ppm)

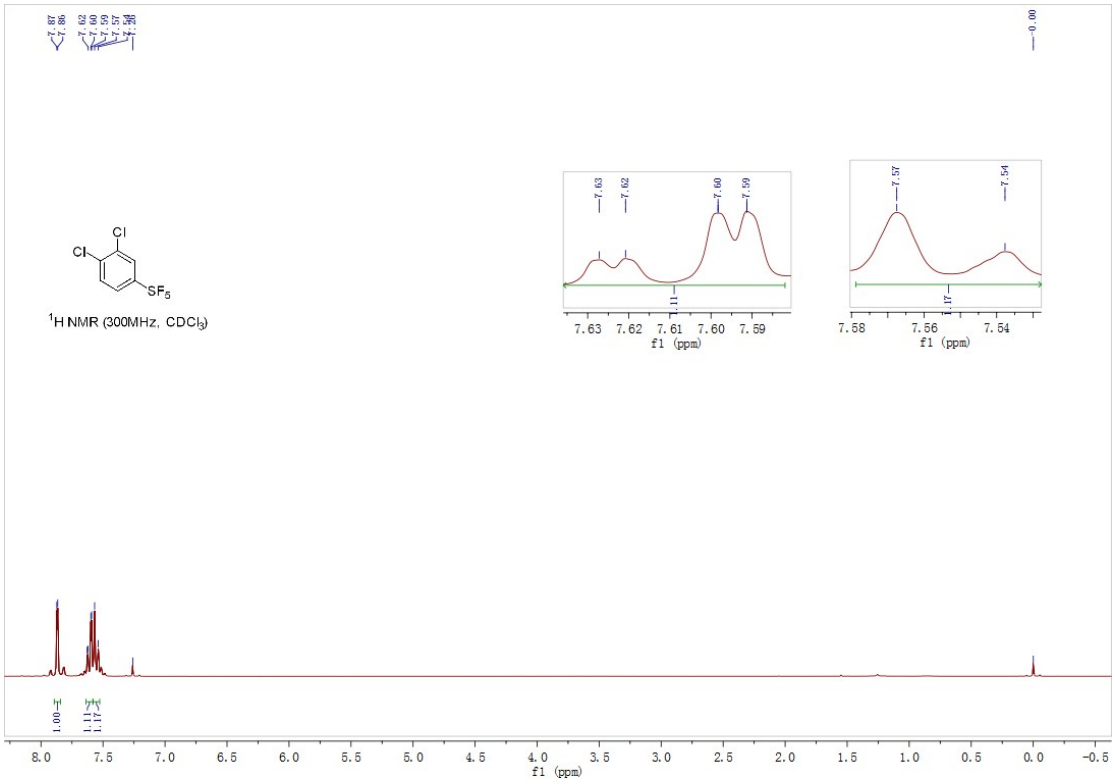

F
SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)

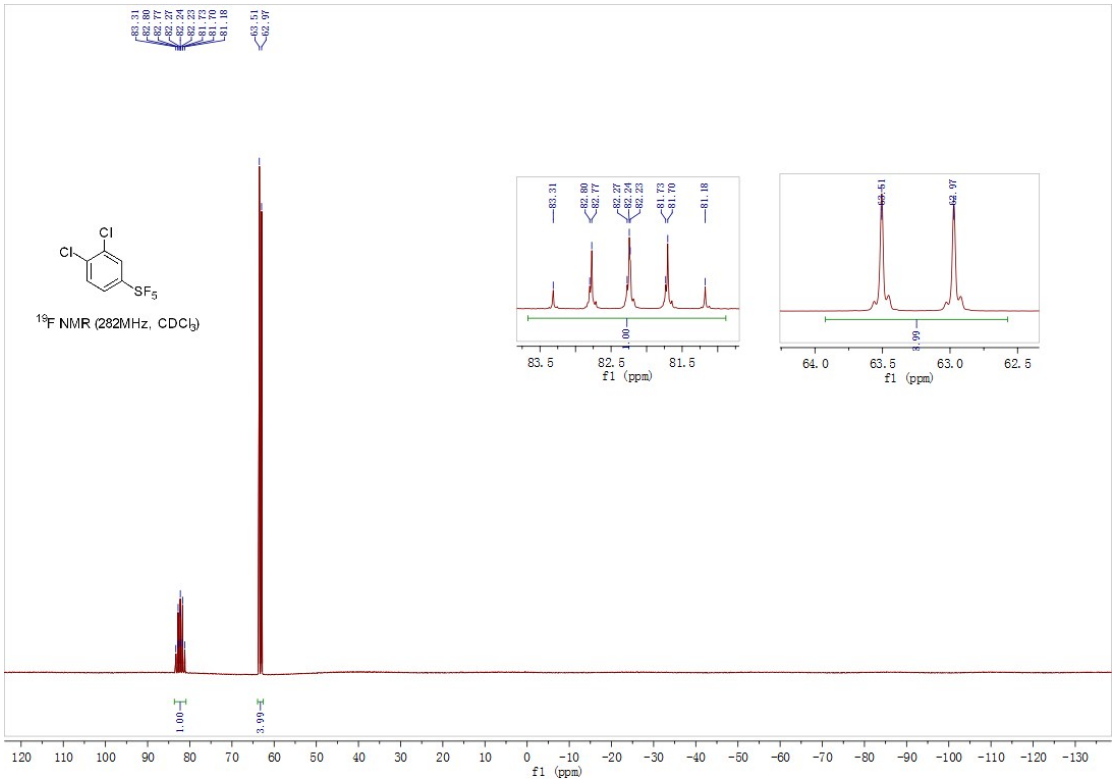

8.36
8.33
8.00
7.97
7.26
0.00
O_2N
SF_5
^{1}H NMR (300MHz, $CDCl_3$)
2.00
2.04
f1 (ppm)

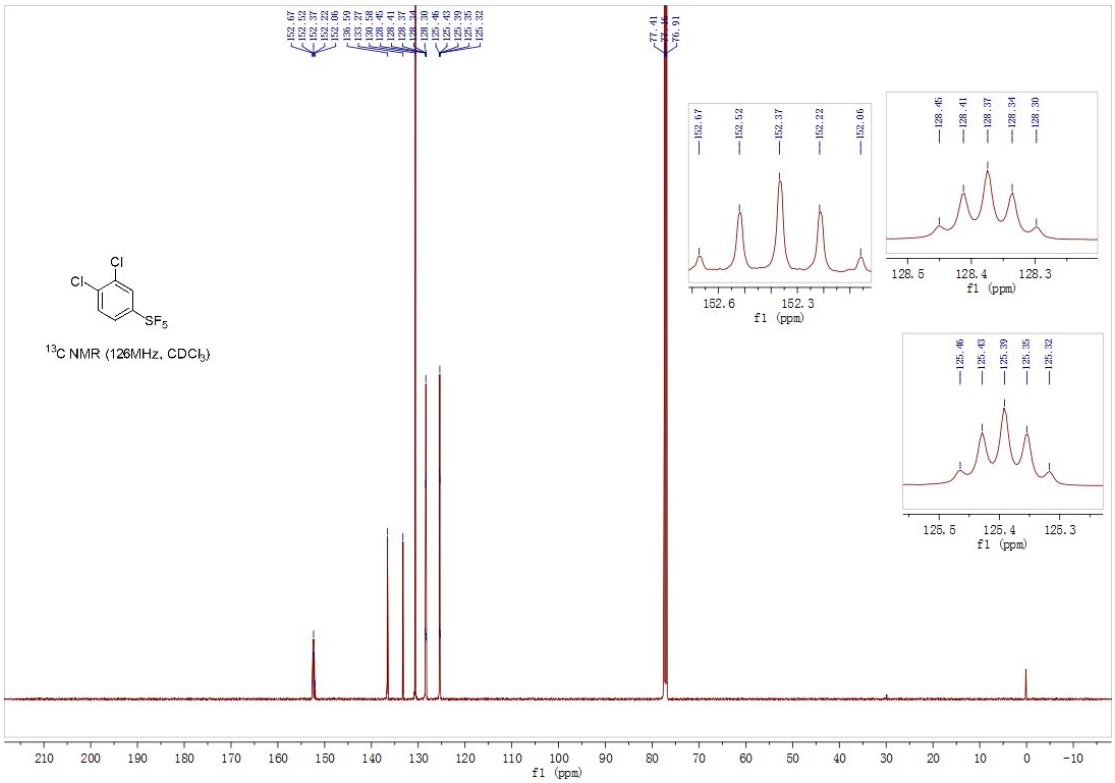

81.71
81.16
80.64
80.10
79.57
62.42
61.89
0.00
O_2N
SF_5
^{19}F NMR (282MHz, $CDCl_3$)
1.00
3.94
f1 (ppm)

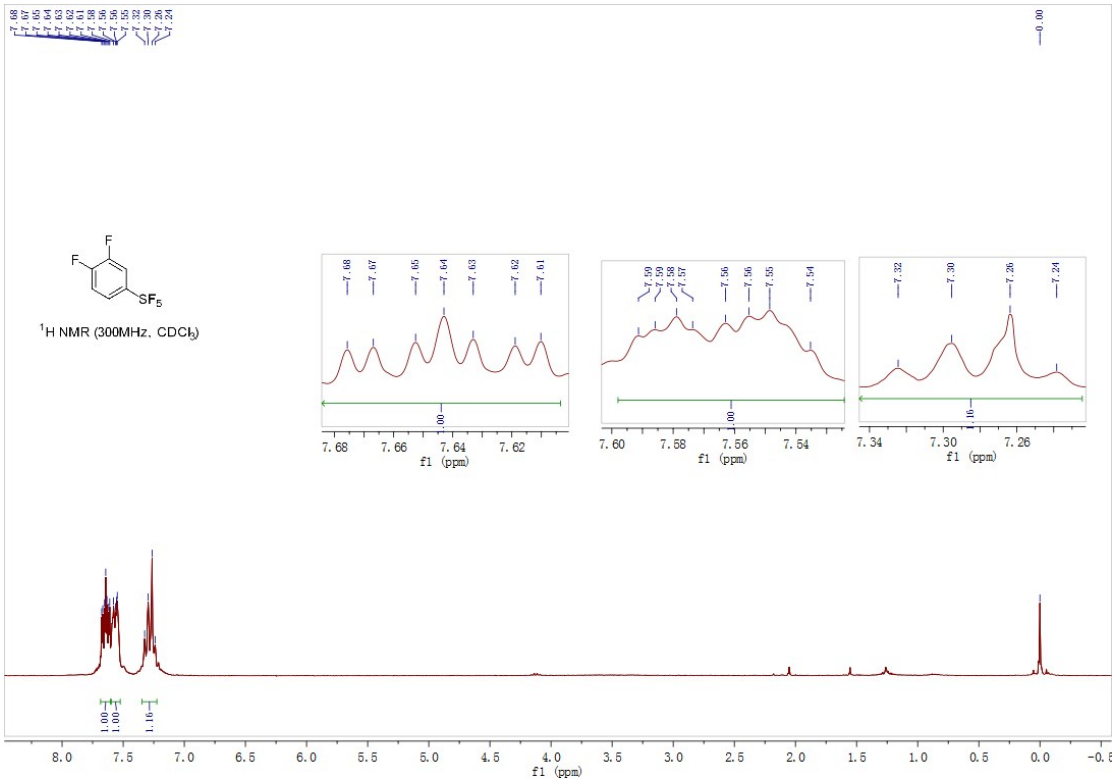

8.66
8.44
8.41
8.13
8.10
7.76
7.73
7.70
7.26
0.00
O_2N
SF_5
^{1}H NMR (300MHz, $CDCl_3$)
1.00
1.03
1.08
1.11
f1 (ppm)

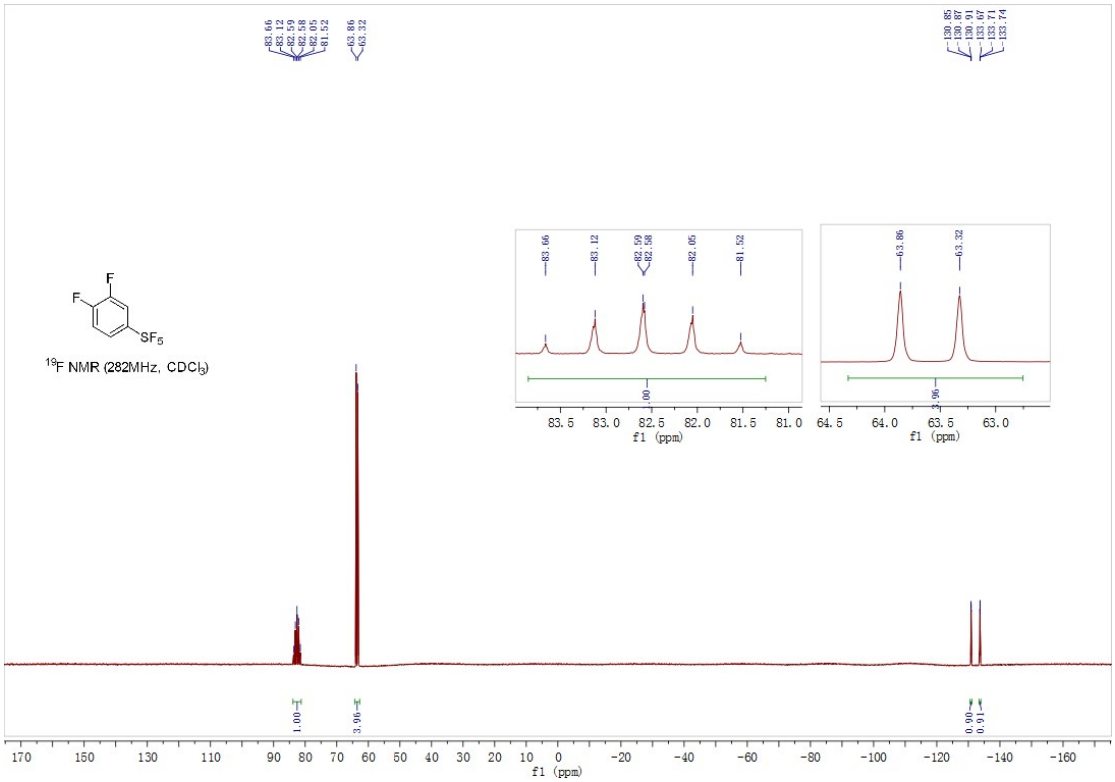

81.71
81.19
81.17
80.67
80.64
80.13
80.09
79.57
62.61
62.08
0.00
O_2N
SF_5
^{19}F NMR (282 NMR, $CDCl_3$)
1.00
3.64
f1 (ppm)

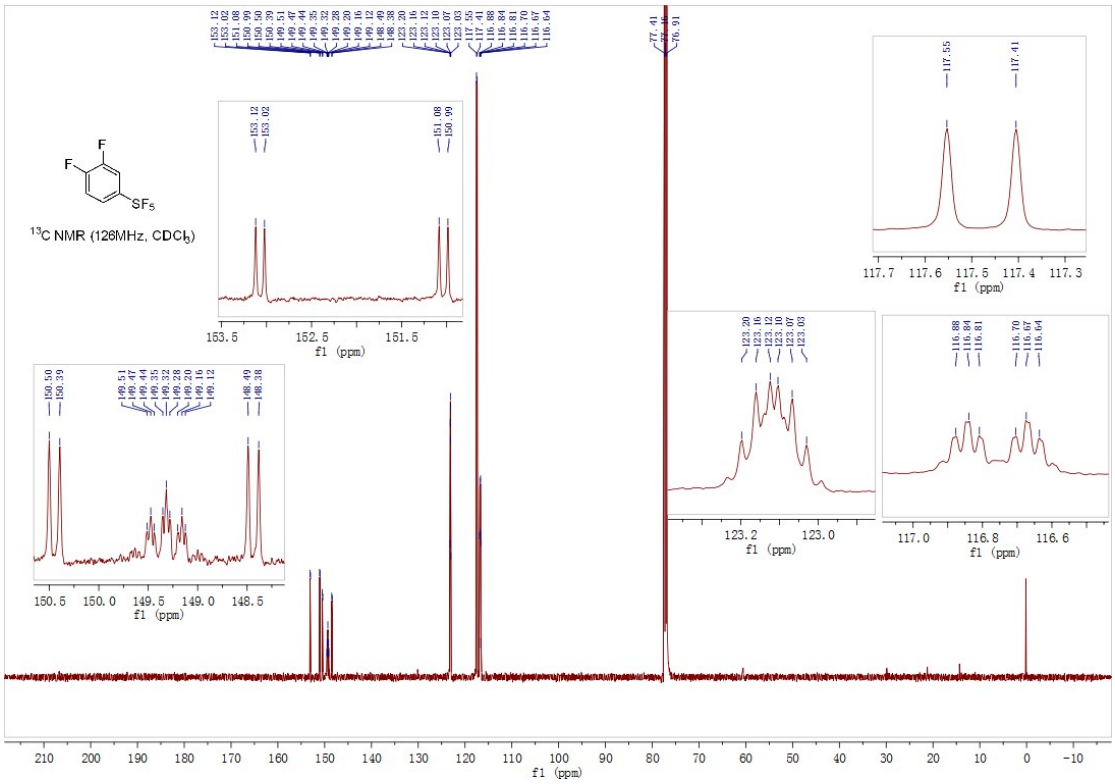

Cl
Cl
SF5
1H NMR (300MHz, CDCl3)
f1 (ppm)

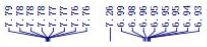

Cl
Cl
SF5
19F NMR (282MHz, CDCl3)
f1 (ppm)

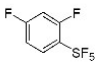

Cl
Cl
SF5
13C NMR (126MHz, CDCl3)
f1 (ppm)


F
F
SF5
1H NMR (300MHz, CDCl3)
f1 (ppm)

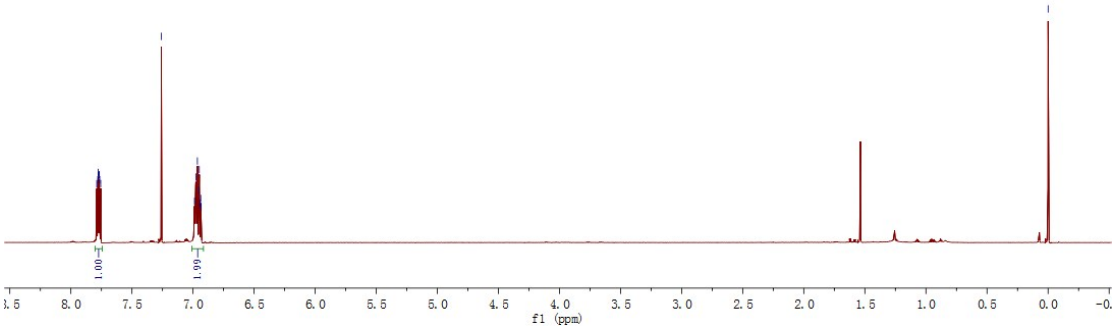

^{19}F NMR (282MHz, CDCl$_3$)

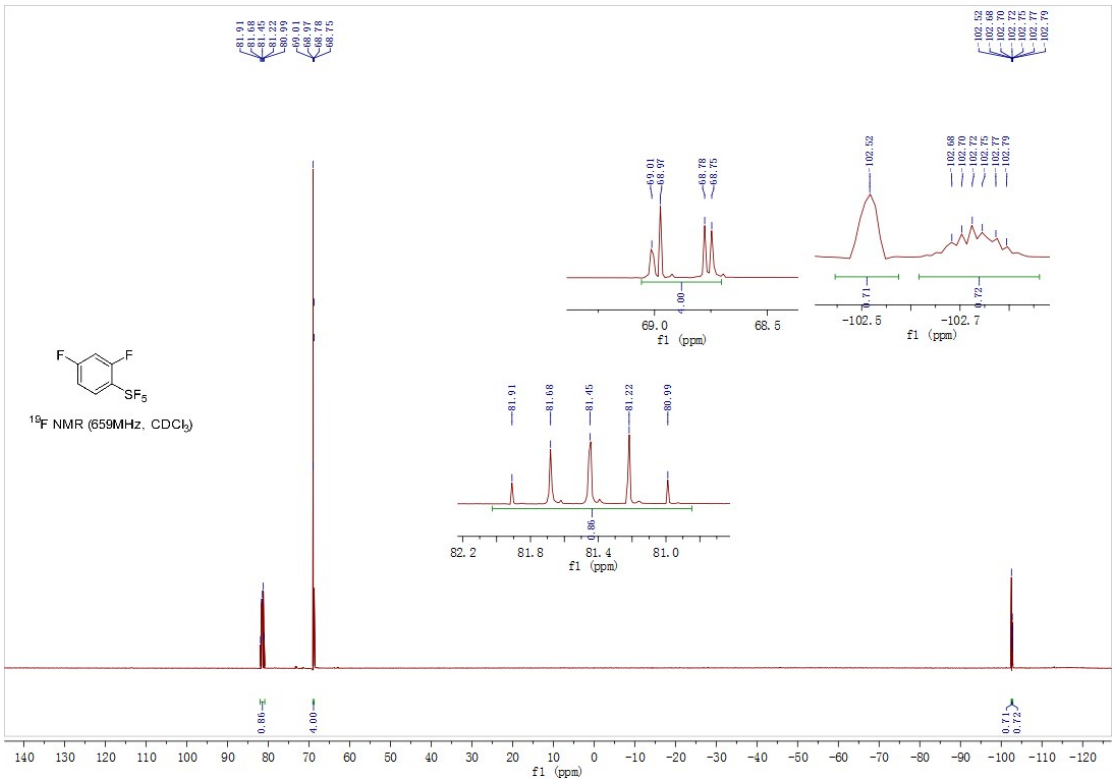

^{13}C NMR (126MHz, CDCl$_3$)



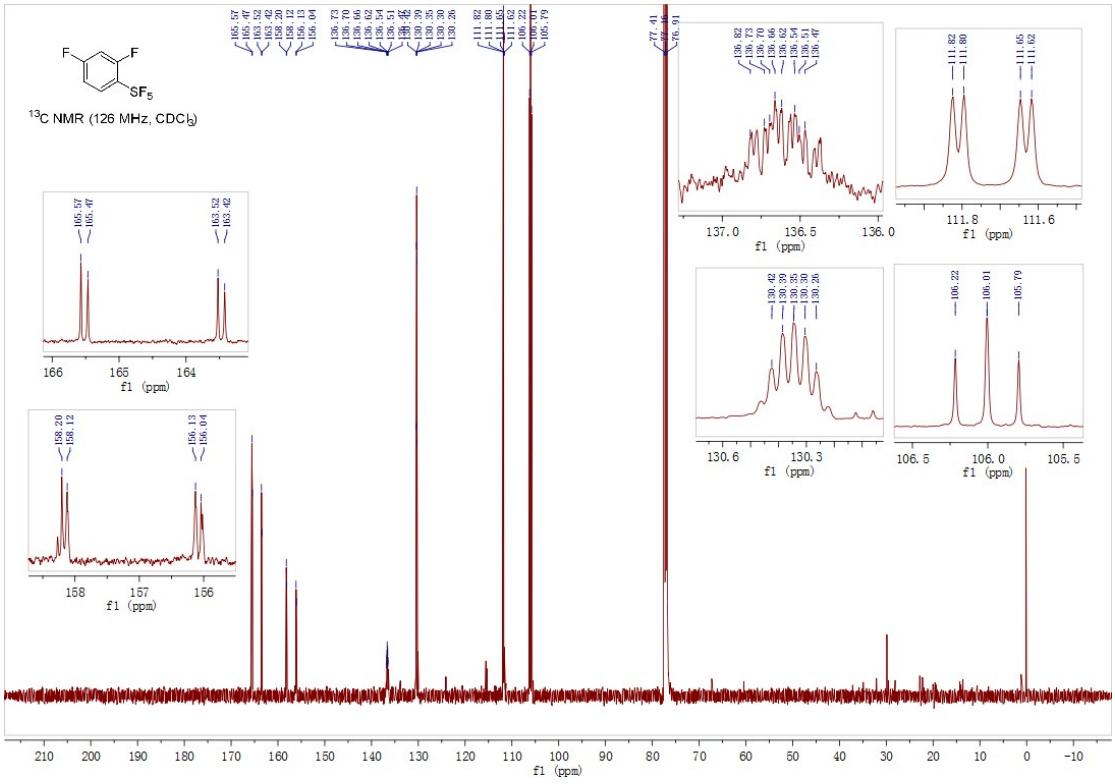


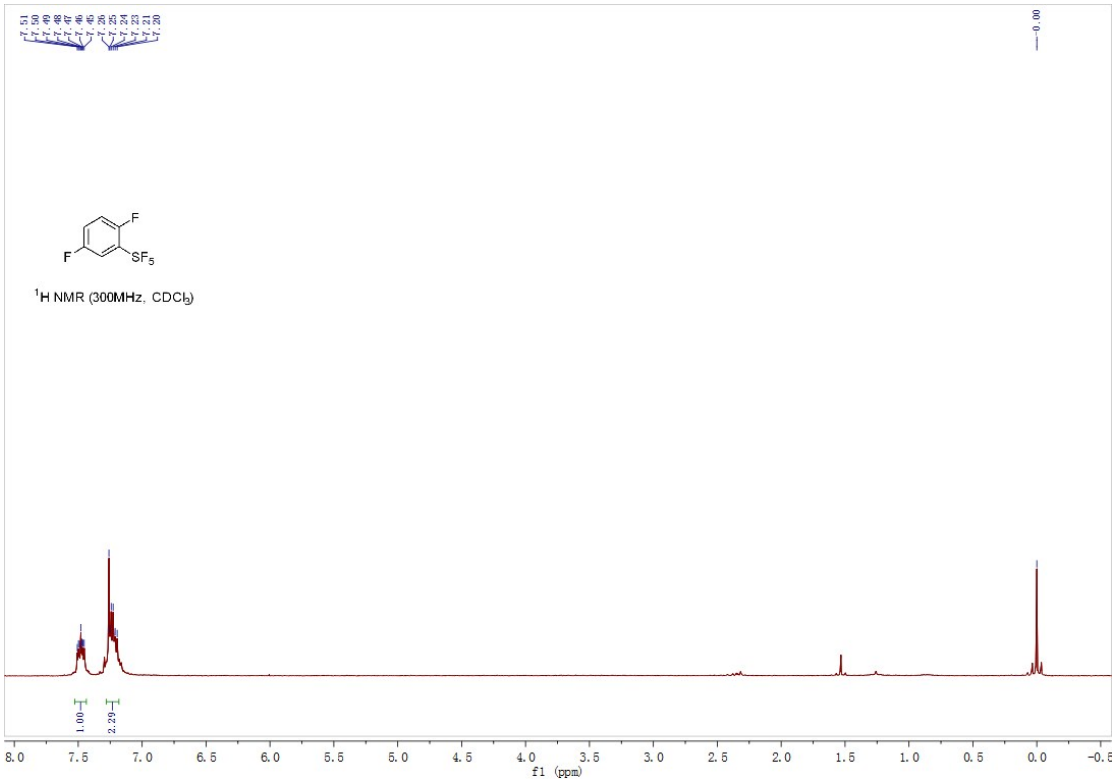
^{1}H NMR (700MHz, $CDCl_3$)

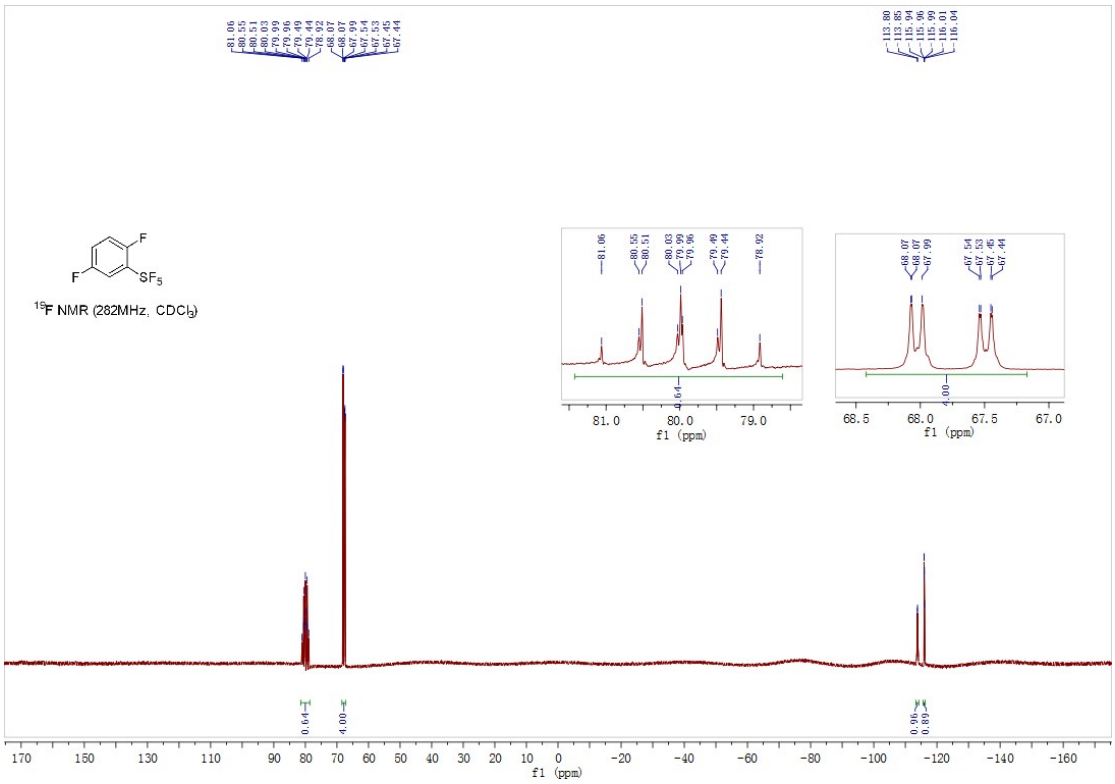


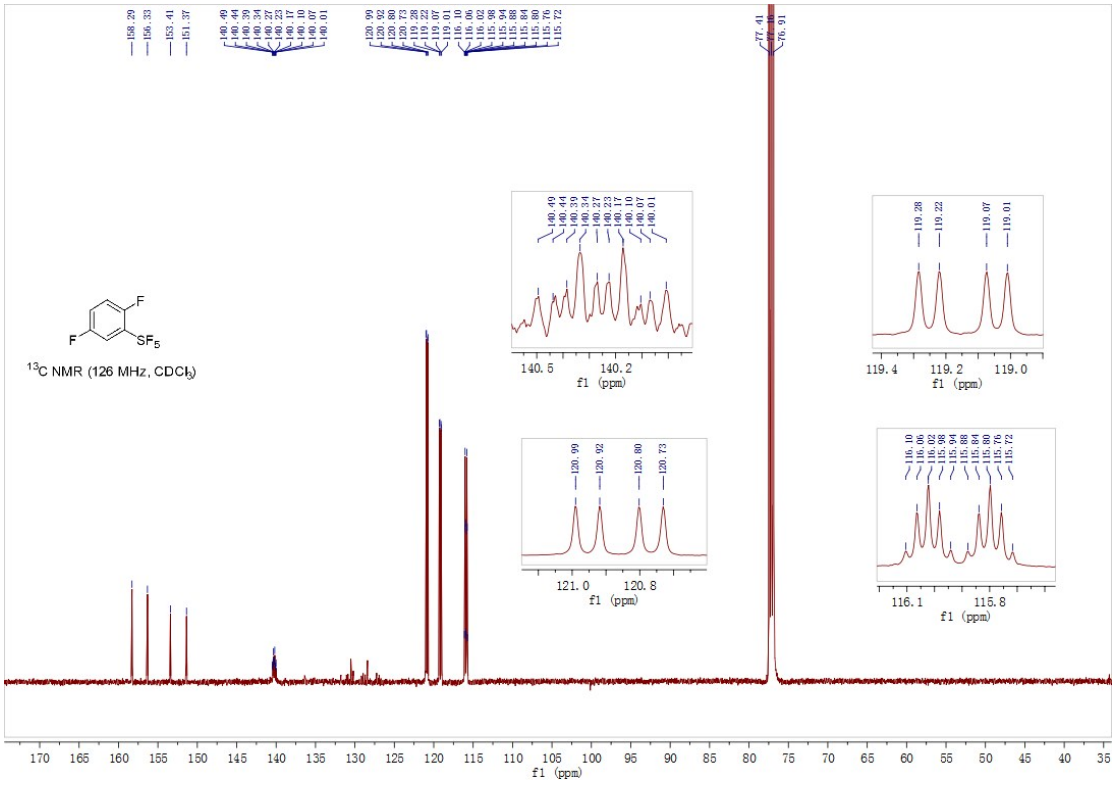


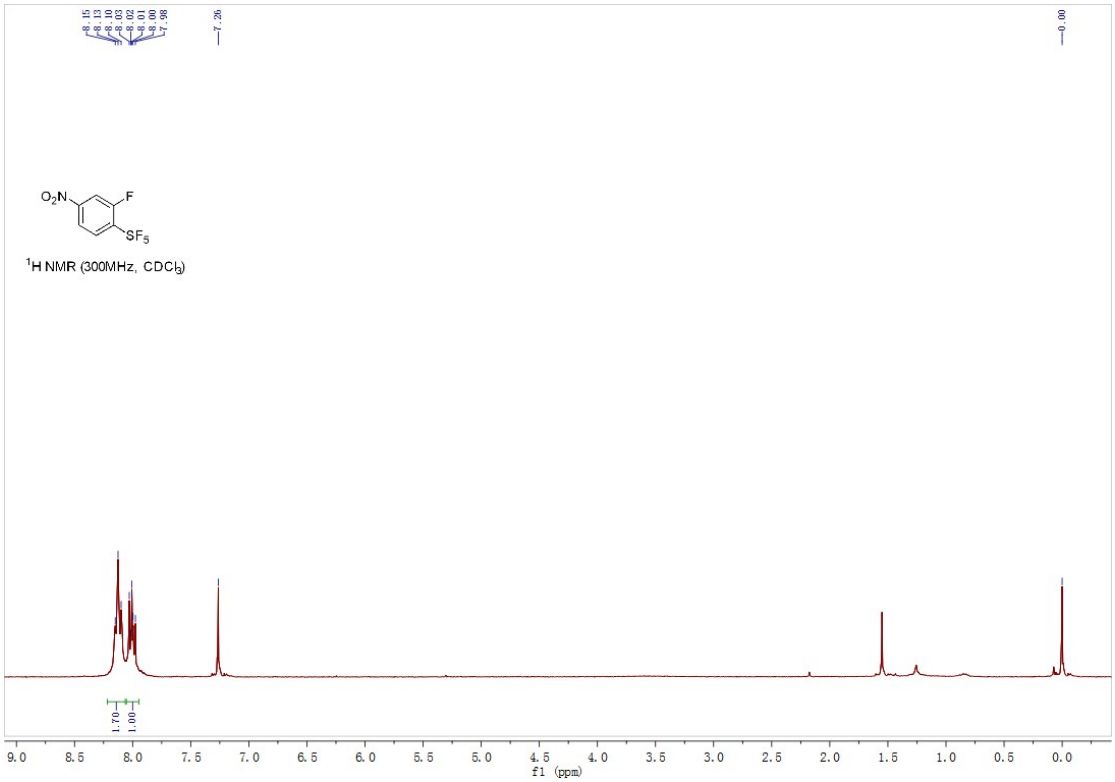
^{19}F NMR (659MHz, $CDCl_3$)

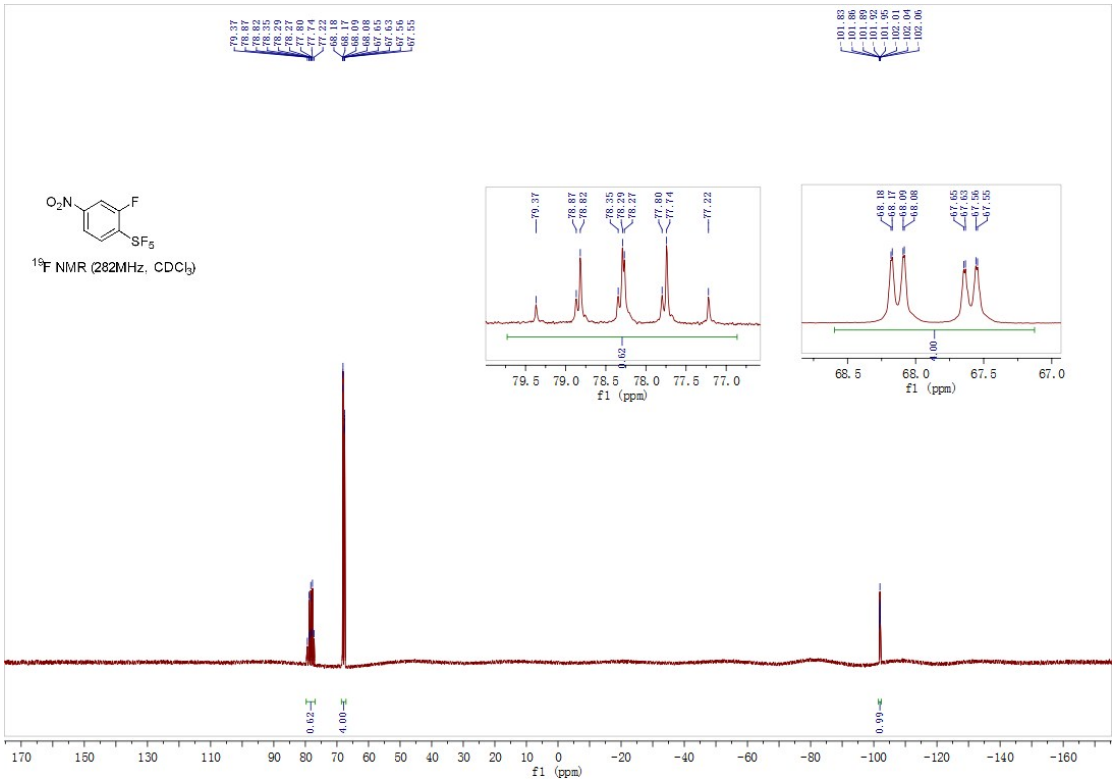

^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

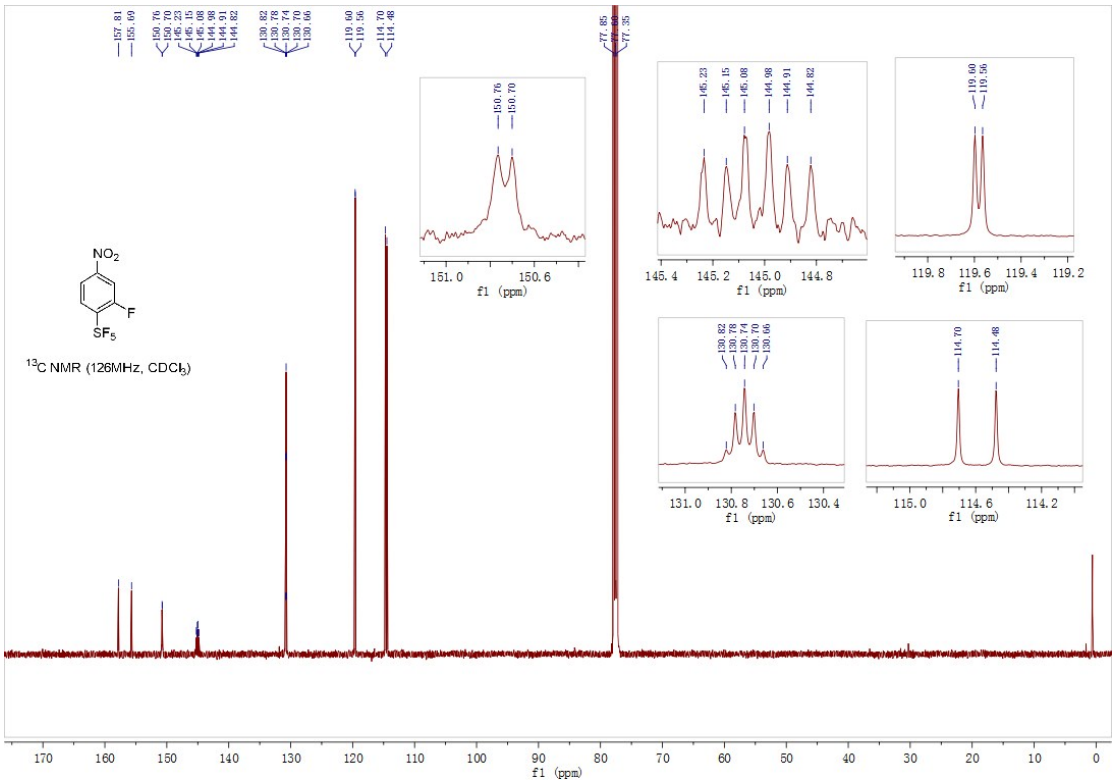

^{1}H NMR (300MHz, CDCl$_3$)
f1 (ppm)

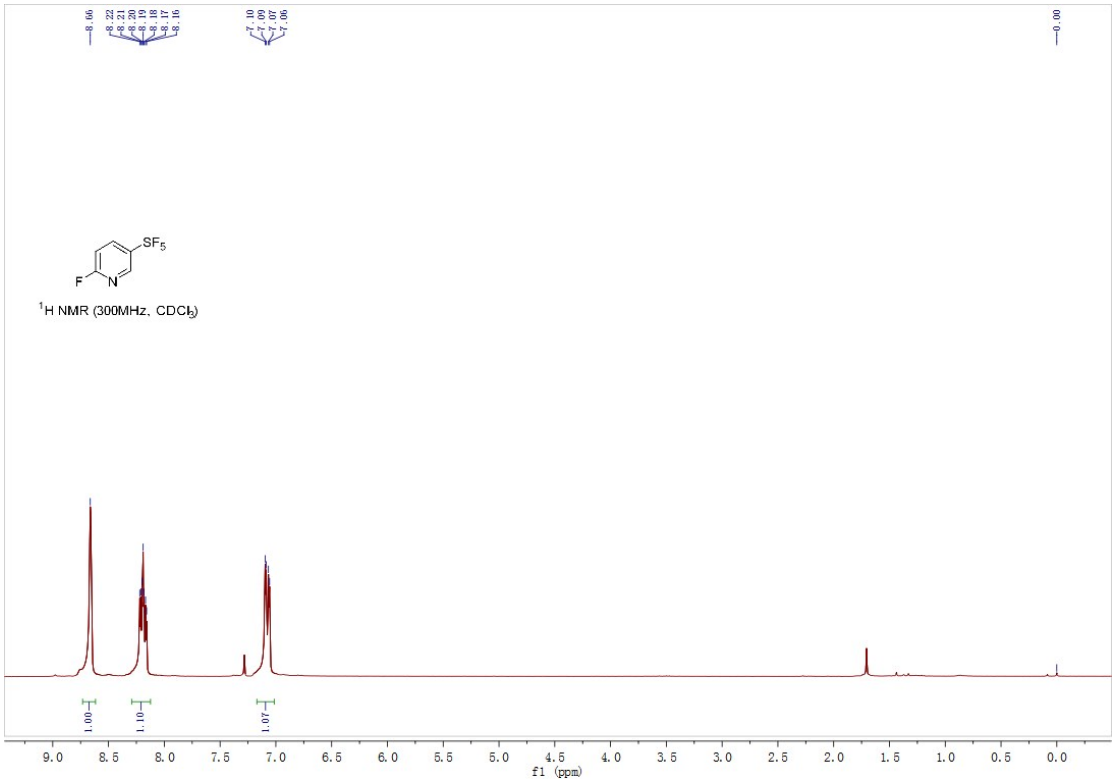

^{19}F NMR (282MHz, CDCl$_3$)
f1 (ppm)

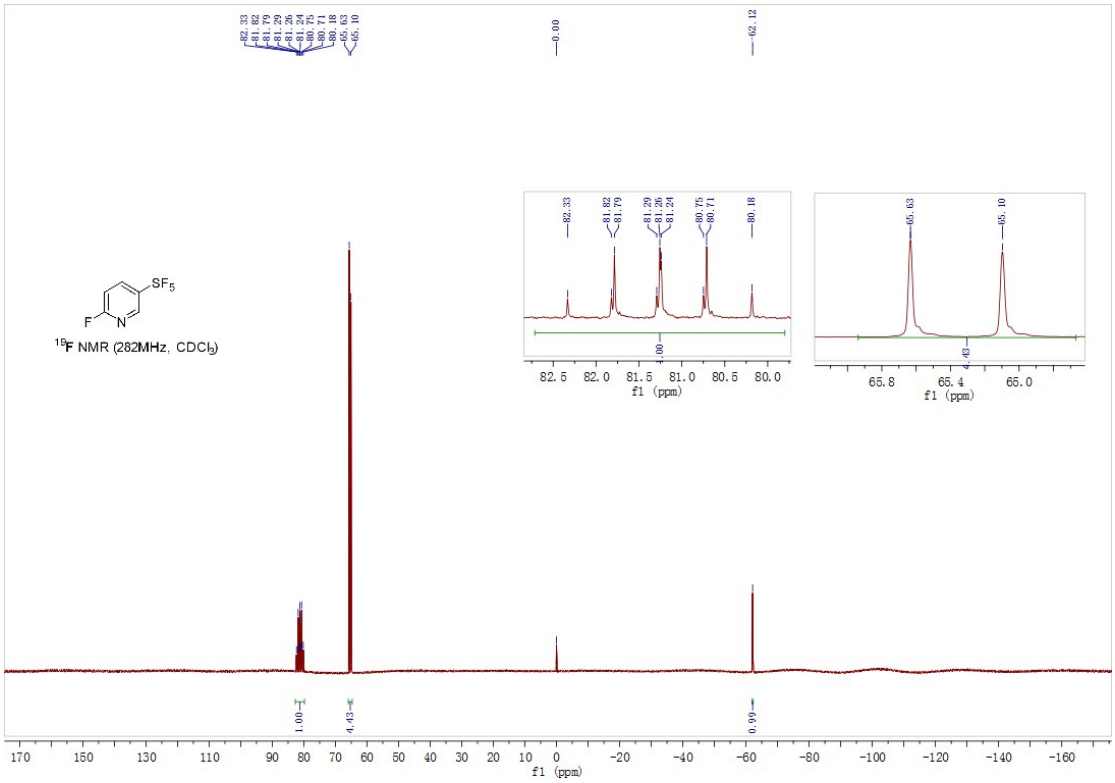

^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

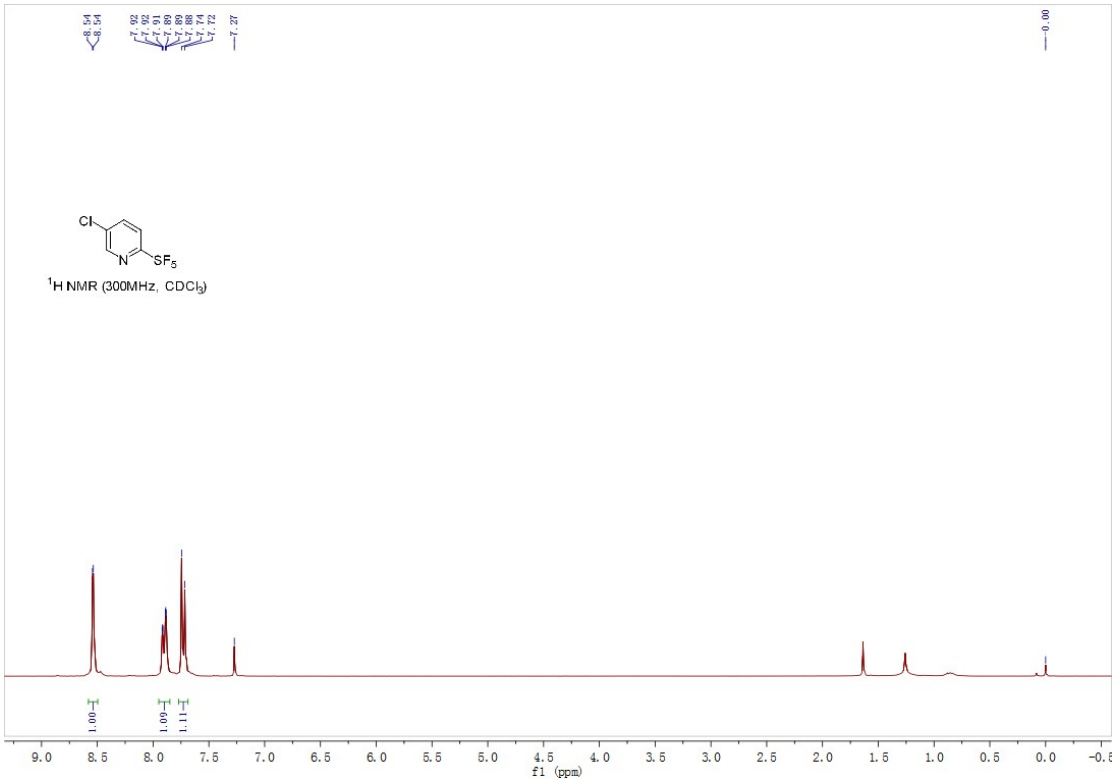

O_2N
F
SF_5
^{1}H NMR (300MHz, $CDCl_3$)
f1 (ppm)

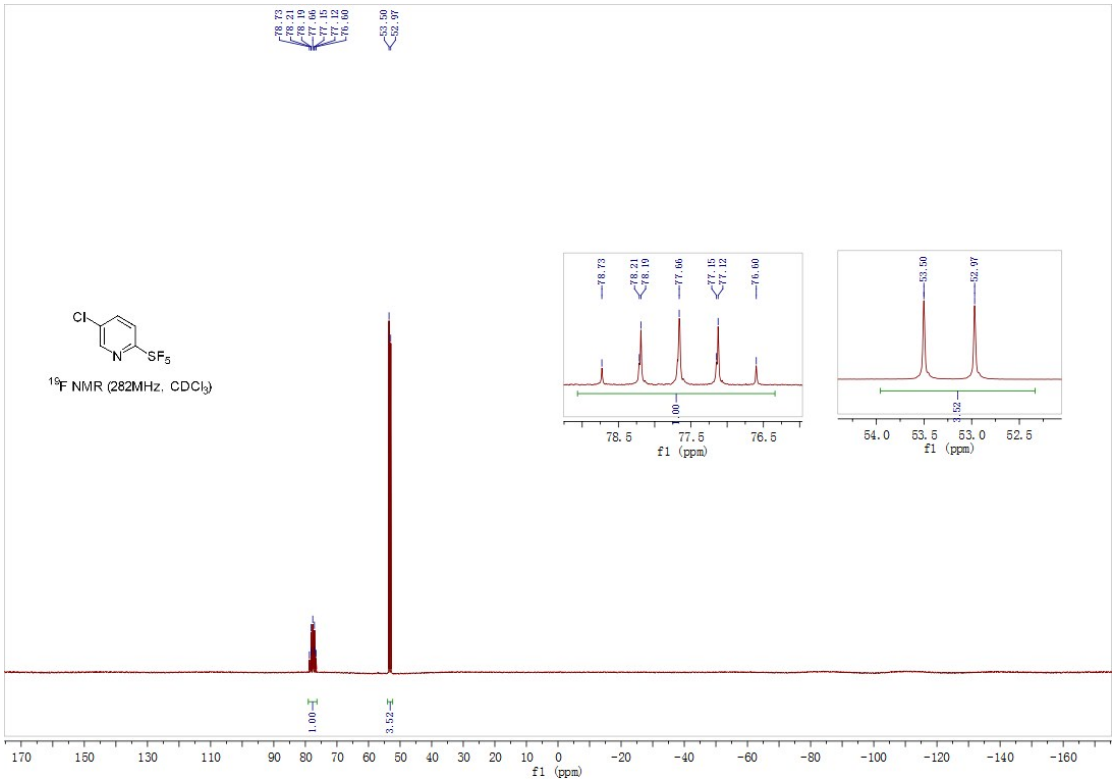

O_2N
F
SF_5
^{19}F NMR (282MHz, $CDCl_3$)
f1 (ppm)

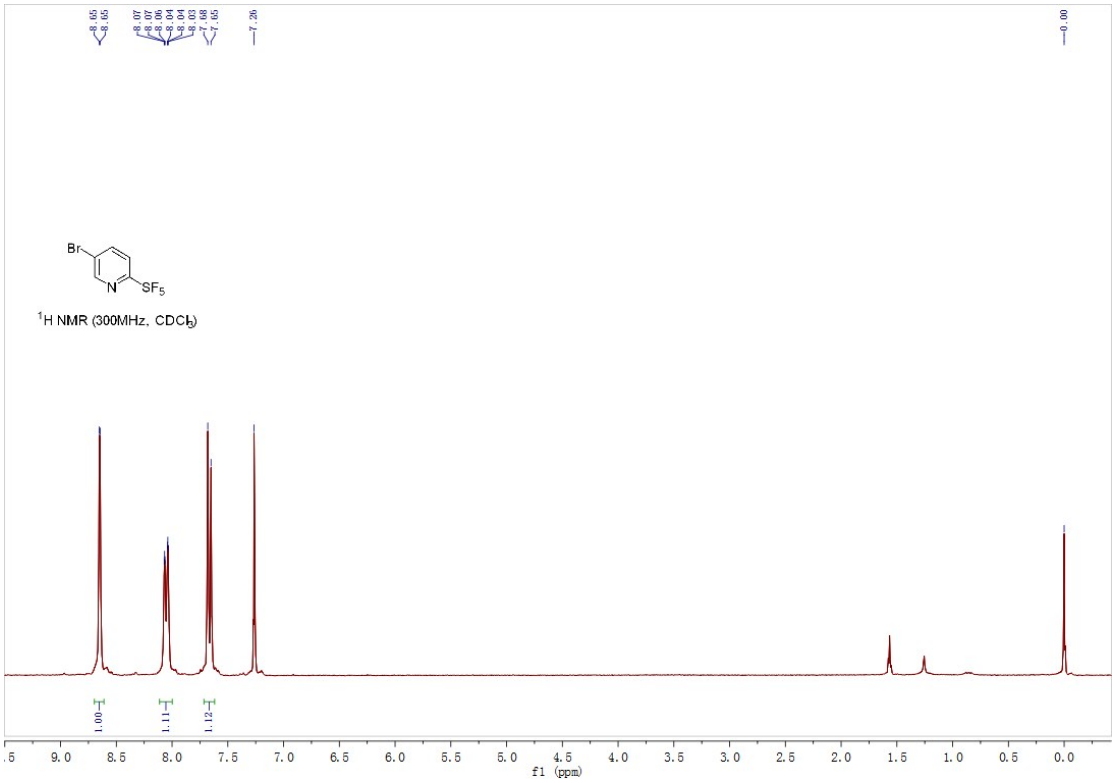

NO2
F
SF5
13C NMR (126MHz, CDCl3)
f1 (ppm)

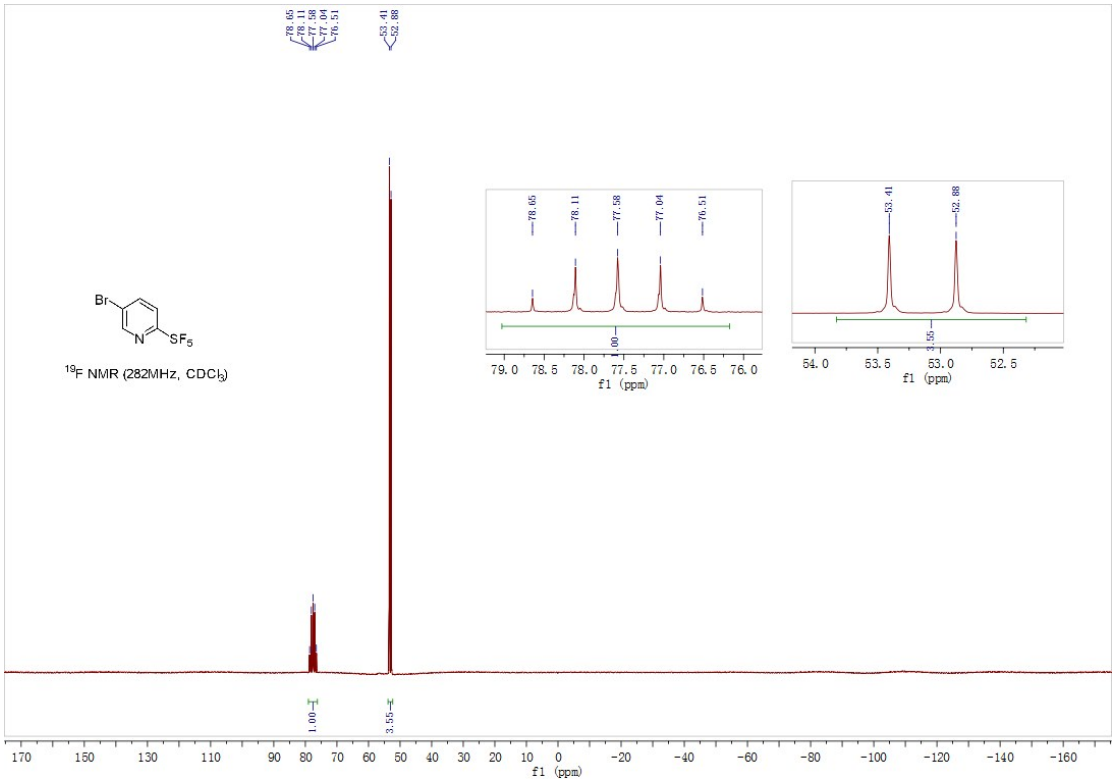

SF5
F
N
1H NMR (300MHz, CDCl3)
f1 (ppm)

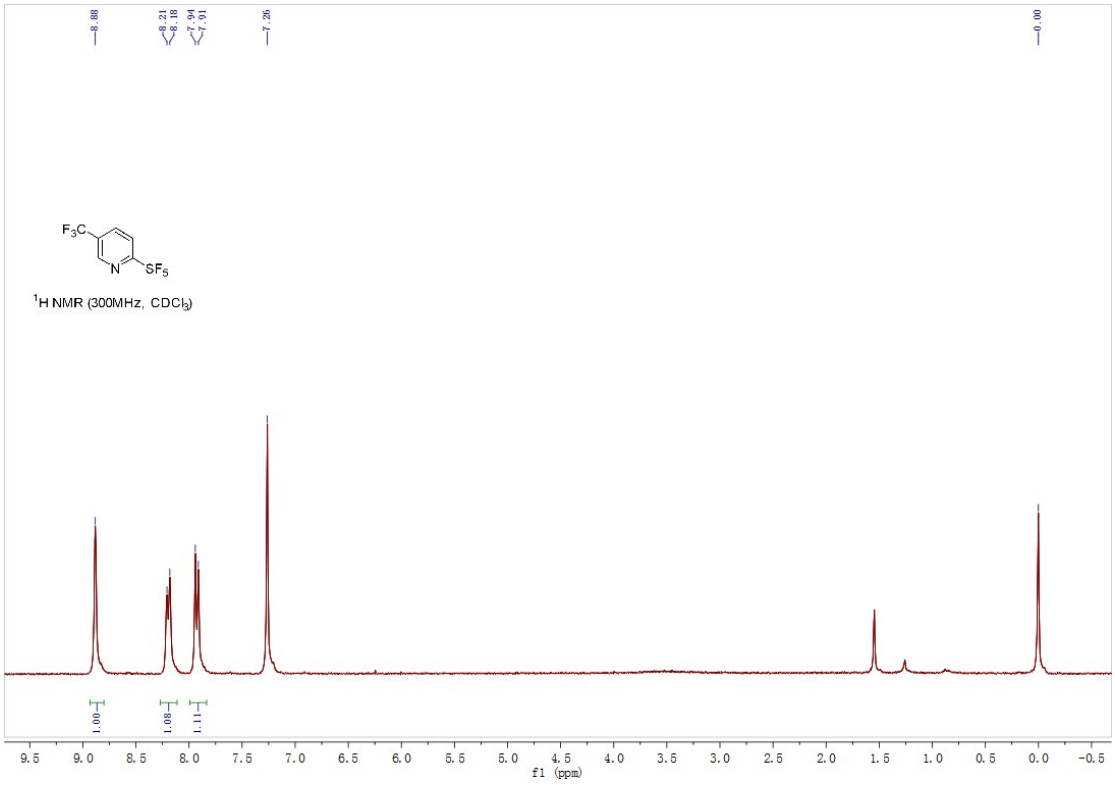

^{19}F NMR (282MHz, CDCl$_3$)
f1 (ppm)

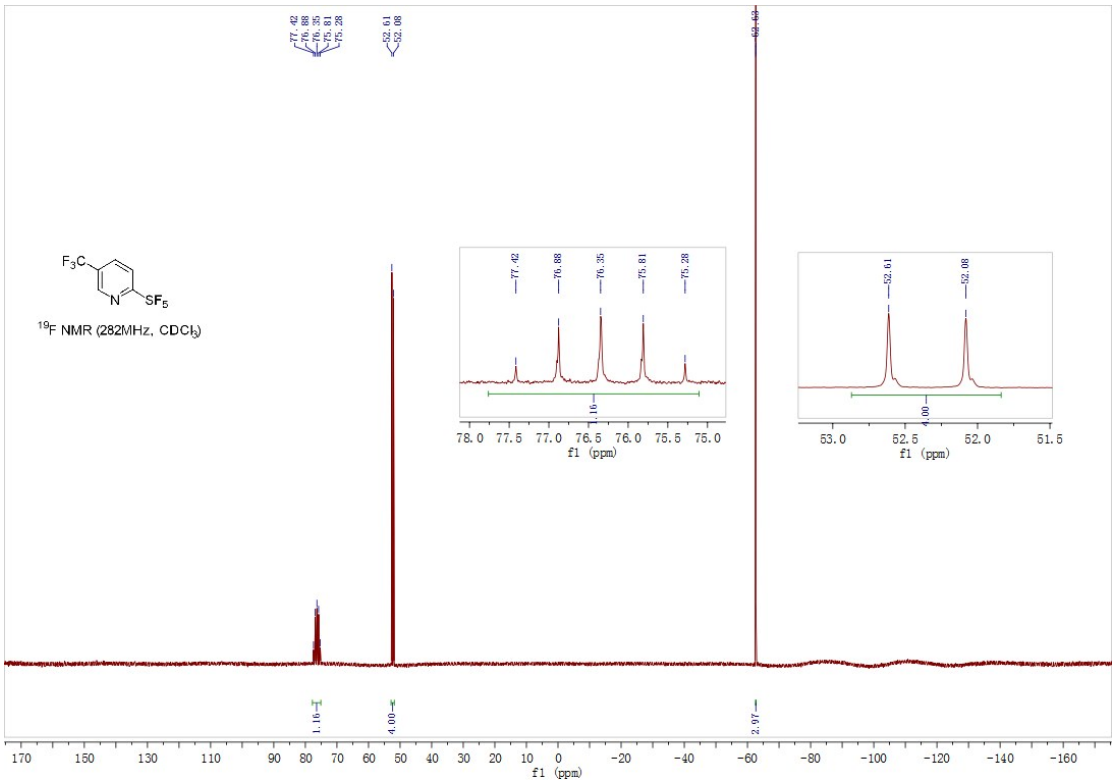

^{1}H NMR (300MHz, CDCl$_3$)
f1 (ppm)

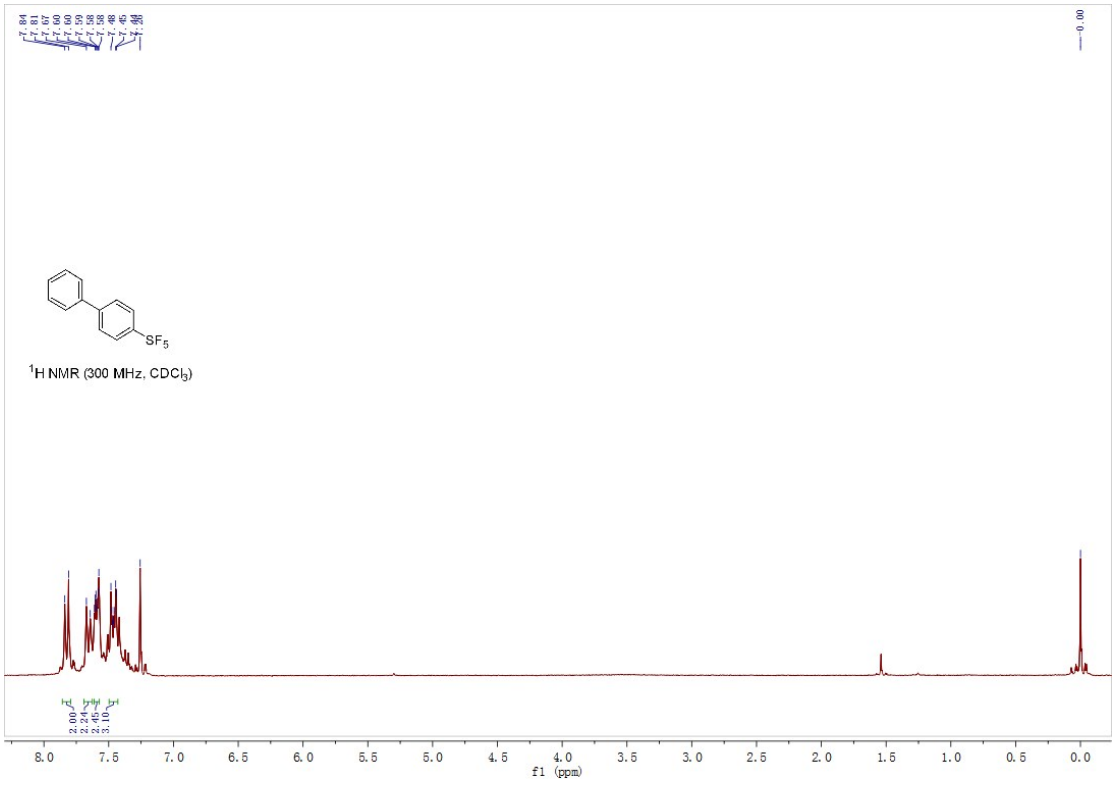

78.73
78.21
78.19
77.66
77.15
77.12
76.60
53.50
52.97
Cl
N
SF5
19F NMR (282MHz, CDCl3)
1.00
3.52
f1 (ppm)

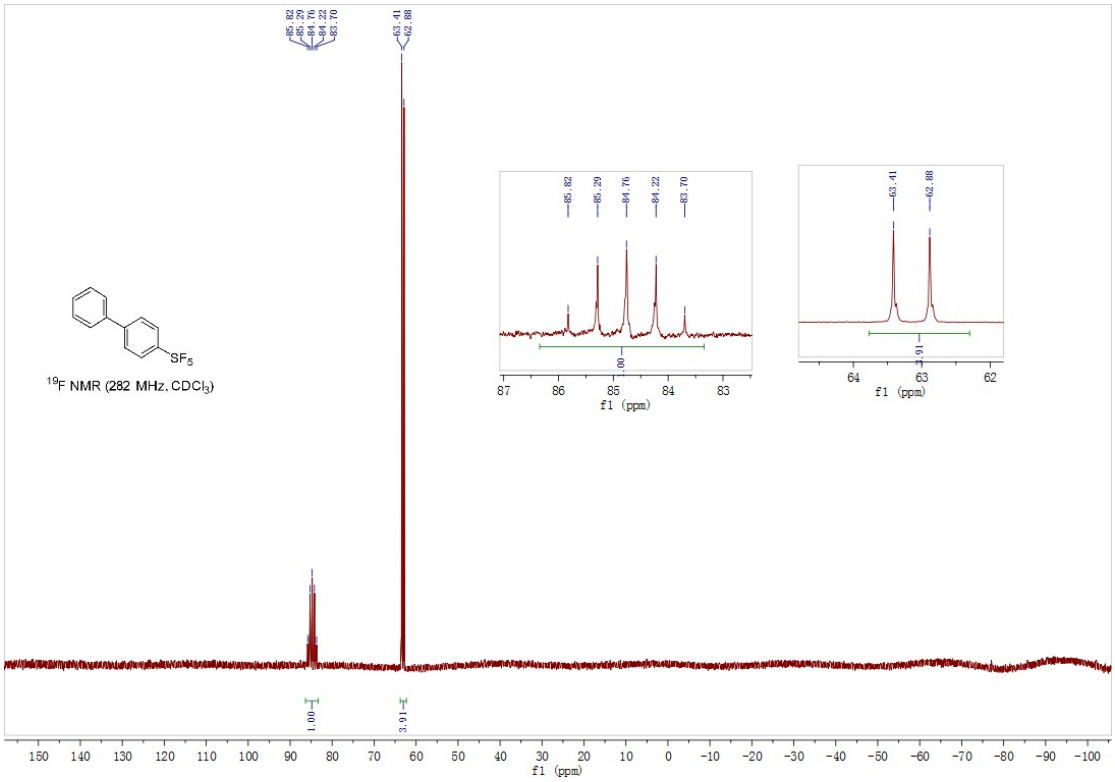

8.65
8.07
8.06
8.04
8.03
7.68
7.65
7.26
0.00
Br
N
SF5
1H NMR (300MHz, CDCl3)
1.00
1.11
1.12
f1 (ppm)

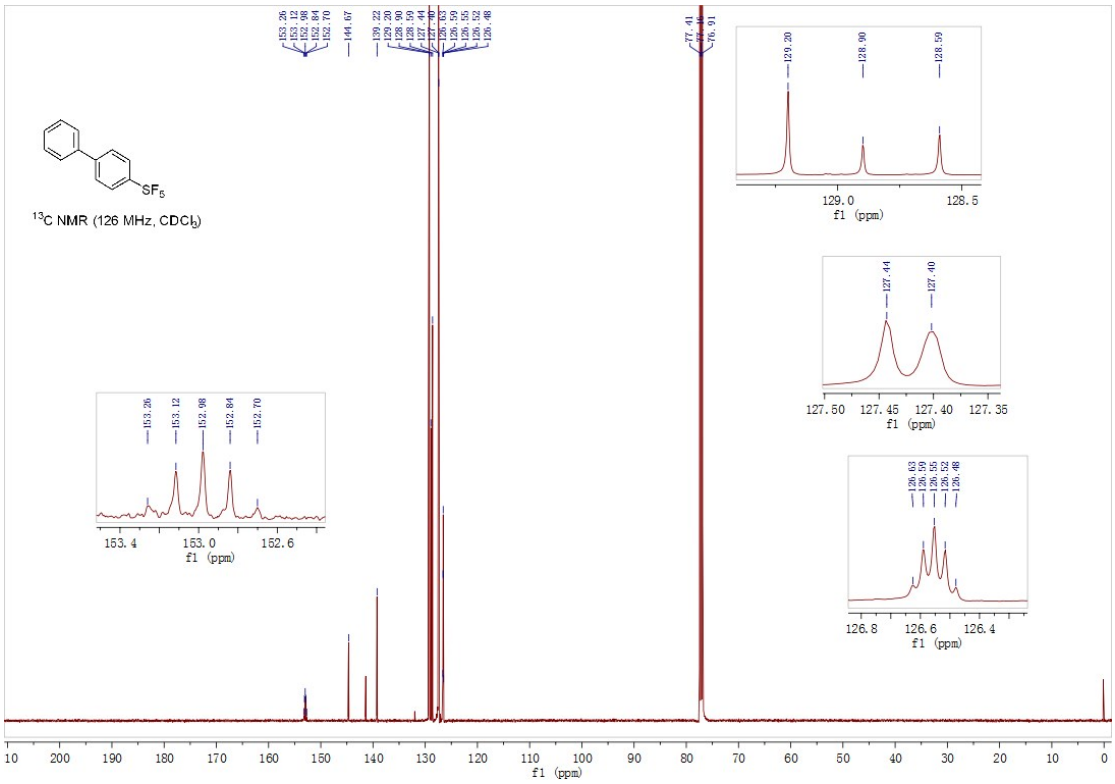

Br
N
SF5
19F NMR (282MHz, CDCl3)
78.65
78.11
77.58
77.04
76.51
53.41
52.88
1.00
3.55
f1 (ppm)

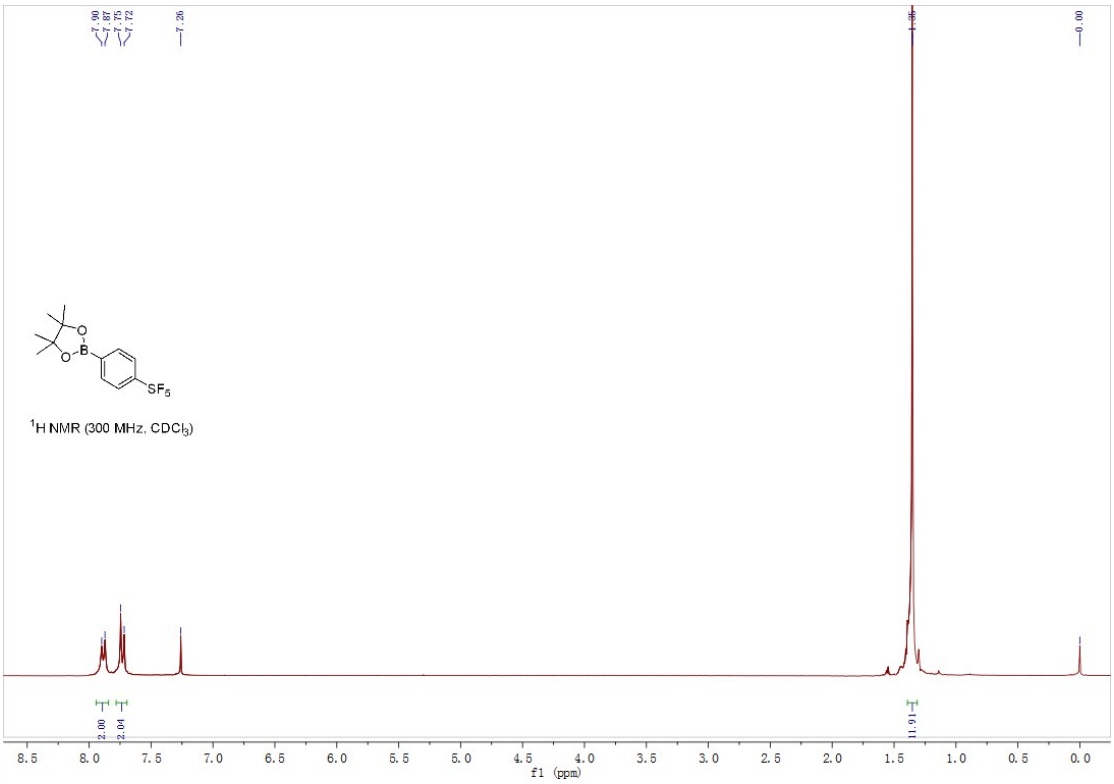

F3C
N
SF5
1H NMR (300MHz, CDCl3)
8.88
8.21
8.18
7.94
7.91
7.26
0.00
1.00
1.08
1.11
f1 (ppm)

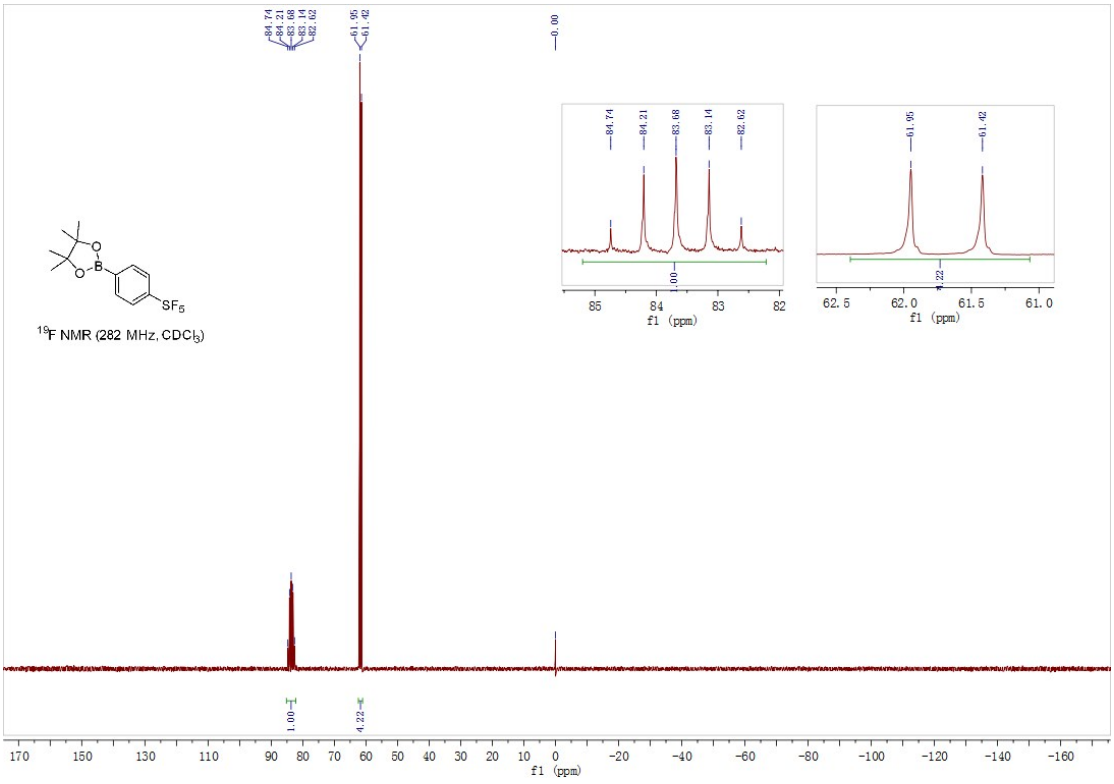

F3C
SF5
N
19F NMR (282MHz, CDCl3)
77.42
76.88
76.35
75.81
75.28
52.61
52.08
62.69
1.16
4.00
2.97
f1 (ppm)

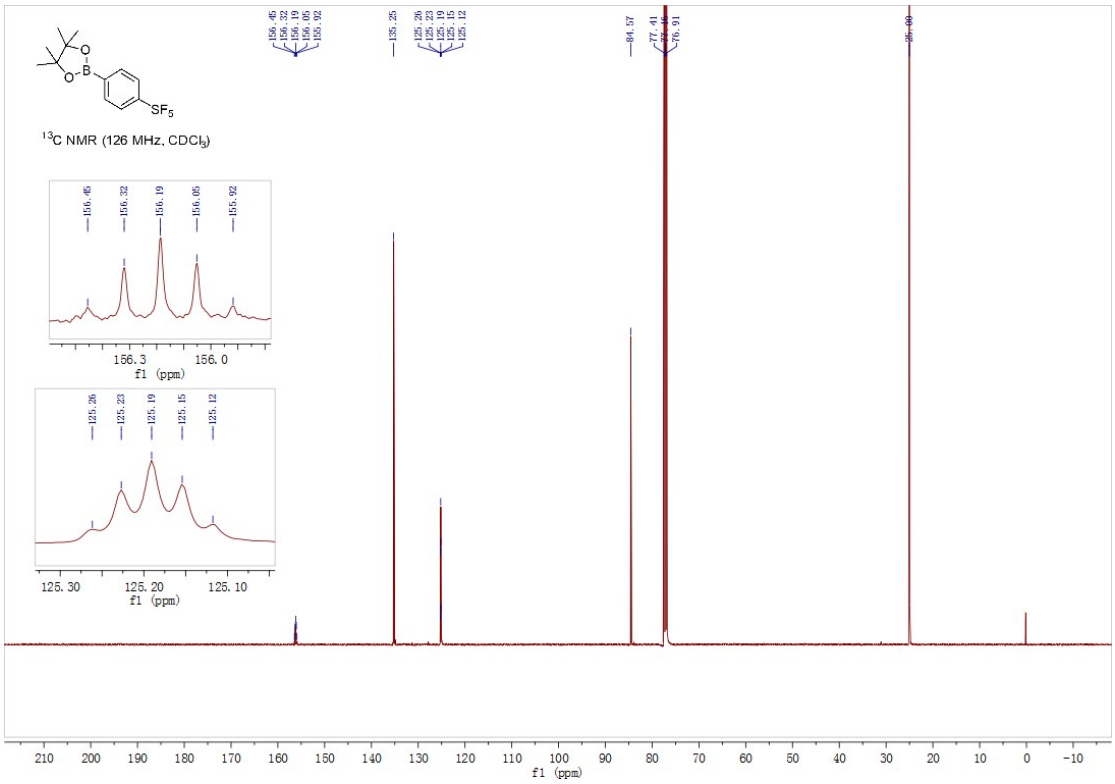

SF5
1H NMR (300 MHz, CDCl3)
0.00
2.00
2.24
2.45
3.10
f1 (ppm)


SF5
19F NMR (282 MHz, CDCl3)
f1 (ppm)


SF5
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.90
7.87
7.75
7.72
7.26
1.35
0.00
SF5
1H NMR (300 MHz, CDCl3)
2.00
2.04
11.91
f1 (ppm)


84.74
84.21
83.68
83.14
82.62
61.95
61.42
0.00
SF5
19F NMR (282 MHz, CDCl3)
1.00
4.22
f1 (ppm)


SF5
13C NMR (126 MHz, CDCl3)
156.45
156.32
156.19
156.05
155.92
156.3
156.0
f1 (ppm)
125.26
125.23
125.19
125.15
125.12
125.30
125.20
125.10
f1 (ppm)
135.25
84.57
77.41
76.91
25.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)