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Electronic Supplementary Information

IF_5 affects the final stage of the Cl-F exchange fluorination in the synthesis of pentafluoro-λ^6-sufanyl-pyridines, pyrimidines and benzenes with electron-withdrawing substituents

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1. General Information

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. The ^{1}H-NMR (300 MHz), ^{13}C-NMR (125.8 MHz), ^{19}F-NMR (282 MHz) spectra for solution in $CDCl_3$ were recorded on a Buruker Avance 500, Buruker Avance 400 and a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS (δ = 0.00). The residual solvent signals were used as references (TMS: δ H = 0.00 ppm, δ C = 77.16 ppm; and $CFCl_3$: δ F = 0.00 ppm). 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. IF_5 in a stainless-steel cylinder was supplied by Kanto Denka Kogyo Co Ltd.

2. General Procedure for Synthesis of arylsulfur pentafluorides

Method A

Crude arylsulfur chlorotetrafluoride (0.72 mmol) was placed into FEP bottle in the glove box. From a cylinder, IF_5 was transferred through a Teflon tube into a FEP bottle under an N_2 atmosphere. It should be carefully handled with Teflon equipment in a bench hood. Measured the amount of IF_5 (0.25 ml, 3.6 mmol) in the PFA syringe was quickly transferred into the bottle of starting material and added slowly under N_2 protected at room temperature. The mixture was stirred at 65 ^{o}C for 14 h, then poured into cooled water, neutralized with aq. $NaHCO_3$, and extracted with CH_2Cl_2 (5 ml × 3). The combined organic phase was dried over $MgSO_4$, filtered and evaporated under vacuum in the ice bath. The crude was purified by silico chromatography, eluting with pentane/CH_2Cl_2 to give arylsufur pentafluoride.

Method B

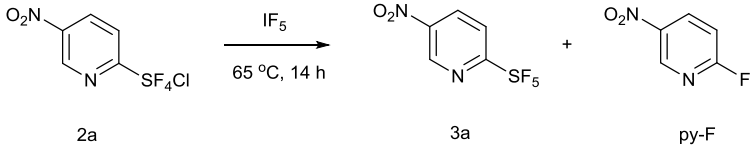
Crude arylsulfur chlorotetrafluoride (0.72 mmol) was placed into FEP bottle in the glove box. From a cylinder, IF_5 was transferred through a Teflon tube into a FEP bottle under an N_2 atmosphere. It should be carefully handled with Teflon equipment in a bench hood. Measured the amount of IF_5 (0.15 ml, 2.16 mmol) in the PFA syringe was quickly transferred into the bottle of starting material and added slowly under N_2 protected at room temperature. The mixture was stirred at 65 ^{o}C for 14 h, then poured into cooled water, neutralized with aq. $NaHCO_3$, and extracted with CH_2Cl_2 (5 ml × 3). The combined organic phase was dried over $MgSO_4$, filtered and evaporated under vacuum in the ice bath. The crude was purified by silico chromatography, eluting with pentane/CH_2Cl_2 to give arylsufur pentafluoride.

Method C

Crude arylsulfur chlorotetrafluoride (0.72 mmol) was placed into FEP bottle in the glove box. From a cylinder, IF_5 was transferred through a Teflon tube into a FEP bottle under an N_2 atmosphere. It should be carefully handled with Teflon equipment in a bench hood. Measured the amount of IF_5 (0.010 ml, 0.144 mmol) in the PFA syringe was quickly transferred into the bottle of starting material and added slowly under N_2 protected at room temperature. The mixture was stirred at room

temperature for 5 – 24 h, then poured into cooled water, neutralized with aq. $NaHCO_3$, and extracted with CH_2Cl_2 (5 ml × 3). The combined organic phase was dried over $MgSO_4$, filtered and evaporated under vacuum in the ice bath. The crude was purified by silico chromatography, eluting with pentane/CH_2Cl_2 to give arylsufur pentafluoride.

3. Table S1. Competitive relationship between 3a and Py-F by-product



2a 3a py-F

Entry	IF_5 (equiv)	Yield[a]	
		3a	Py-F
1	2	12	41
2	3	43	26
3	4	57	13
4	5	97	trace

Condition: 2a (192 mg, 0.72 mmol), 65 °C, 14 h. [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard.

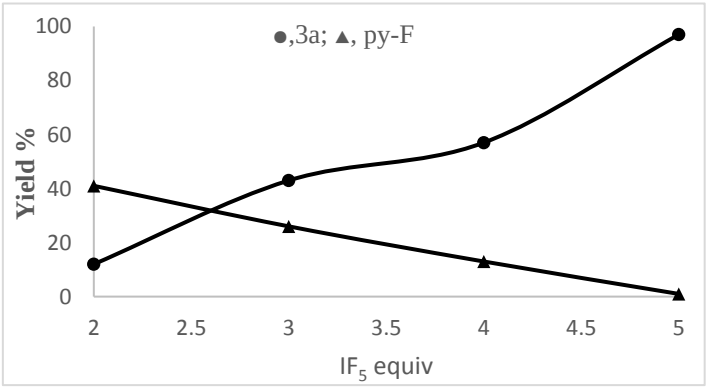


Figure S1. Competitive relationship between 3a and Py-F byproduct

4. General Procedure for Synthesis of arylsulfur chlorotetrafluorides

Procedure I[1, 2, 3]

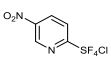
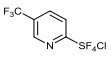
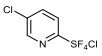
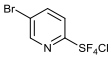
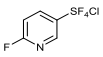
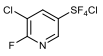
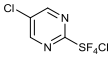
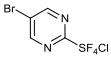
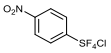
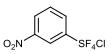
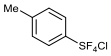
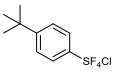
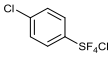
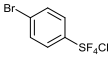
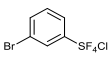
An oven-dried 30 ml FEP bottle with magnetic stirring bar was charged with disulfide (1.88 mmol), anhydrous spray dried KF (1.75 g, 30.08 mmol) and anhydrous MeCN (10 ml) inside the glove box. The bottle was cooled in an ice/water bath while chlorine gas was bubbled through the stirred reaction mixture for approximately 5 minutes. The bottle was sealed and the reaction mixture was stirred at room temperature for 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[1, 2, 3]

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

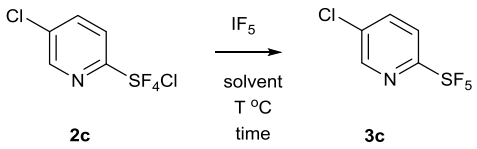
to another 60 ml FEP bottle using a PP/ETFE filter. The residue was washed with Hexane (5 ml×2). The solvent was evaporated in vacuo to give arylsulfur chlorotetrafluorides.

5. Table S2. The procedure, yields, appearance and ^{19}F NMR data of arylsulfur chlorotetrafluorides 2a-p[1,2]

Entry	Structure	Procedure	Yield[a]	Appearance	^{19}F NMR ($CDCl_3$; δ_F, ppm)
2a		I	82%	solid	127.99 (s, 4F).
2b		I	69%	solid	123.39 (s, 4F), -63.12 (s, 3F)
2c		I	75%	solid	127.99 (s, 4F)
2d		I	91%	solid	128.14 (s, 4F)
2e		I	77%	oil	138.96 (s, 4F), -61.70 (s, 1F)
2f		I	73%	oil	134.63 (s, 4F), -68.35 (s, 1F)
2g		I	90%	oil	132.28 (s, 4F), -63.35 (s, 2F)
2h		I	70%	oil	120.05 (s, 4F)
2i		I	67%	oil	127.35 (s, 4F)
2j		I[b]	87%	solid	134.98 (s, 4F)
2k		I[b]	84%	solid	135.75 (s, 4F)
2l		II	71%	oil	137.56 (s, 4F)
2m		II[c]	80%	solid	135.88 (s, 4F).
2n		II	81%	oil	δ 136.79 (s, 4F)
2o		II	75%	oil	137.11 (s, 4F)
2p		II	79%	oil	136.04 (s, 4F)

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

6. Table S3. Optimizing of the Cl-F exchange reactions of 2c.

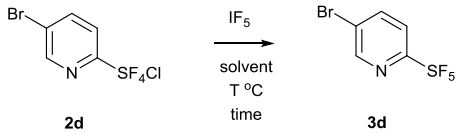


2c **3c**

Entry	IF_5 (equiv)	T (^oC)	Time (h)	Solvent	Yield[a]
1	0.5	65	24	neat	trace
2	1	65	24	neat	trace
3	2	65	24	neat	51
4[b]	3	65	14	neat	70

Condition: 2c (69 mg, 0.288 mmol). [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard. [b] Using 2c (148 mg, 0.72 mmol).

7. Table S4. Optimizing of the Cl-F exchange reactions of 2d.

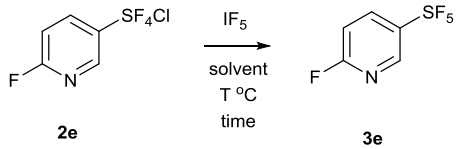


2d **3d**

Entry	IF_5 (equiv)	T (^oC)	Time (h)	Solvent	Yield[a]
1	0.5	65	24	neat	trace
2	1	65	24	neat	trace
3	2	65	48	neat	63
4[b]	3	65	14	neat	80

Condition: 2d (87 mg, 0.288 mmol). [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard. [b] Using 2d (216 mg, 0.72 mmol).

8. Table S5. Optimizing of the Cl-F exchange reactions of 2e.

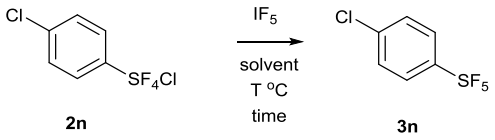


2e **3e**

Entry	IF_5 (equiv)	T (^oC)	Time (h)	Solvent	Yield[a]
1	0.5	70	24	neat	2
2	1.2	70	24	neat	60
3	2	70	48	neat	81
4	3	65	14	neat	97

Condition: 2e (173 mg, 0.72 mmol). [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard.

9. Table S6. Optimizing of the Cl-F exchange reactions of 2n.

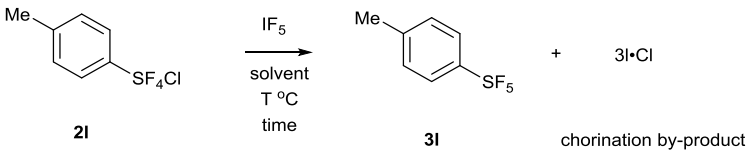


2n 3n

Entry	IF_5 (equiv)	T (^oC)	Time (h)	Solvent	Yield[a]
1[b]	3	65	1	neat	19
2[b]	1	rt	2	neat	70
3[b]	0.5	rt	2	neat	86
4[b]	0.3	rt	2	neat	93
5	0.2	rt	12	neat	92

Condition: 2n (184 mg, 0.72 mmol). [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard. [b] Excess IF_5 induced chlorination of 3n.

10. Table S7. Optimizing of the Cl-F exchange reaction of 2l

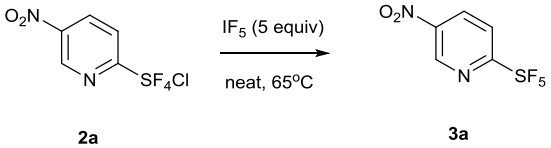


2l 3l chorination by-product

entry	IF_5 (equiv)	T (^oC)	Time (h)	Solvent	Yield[a]	
					3l	3l:3l·Cl
1	0.2	rt	5	neat	35	23
2	0.2	rt	12	neat	42	2.3
3	0.2	0	4	neat	27	22
4	0.2	0	8	neat	49	8

Condition: 2l (170 mg, 0.72 mmol). [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard.

11. Table S8. Time course of the reaction process of 2a.

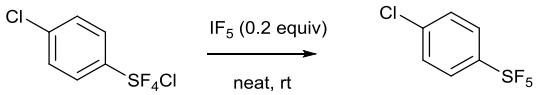


2a 3a

Entry	Time (h)	Yield[a]
1	1	12
2	3	21
3	4	73
4	6	95
5	8	97

Condition: 2a (38 mg, 0.144 mmol), IF_5 (0.05 ml, 0.721 mmol), 65 ^oC. [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard.

12. Table S9. Time course of the reaction process of 2n.



2n **3n**

Entry	Time (h)	Yield[a]
1	3	2
2	6	6
3	9	68
4	11	88
5	12	92

Condition: 2n (184 mg, 0.72 mmol), IF_5 (10 µl, 0.144 mmol), rt. [a] Yield determined by ^{19}F NMR with fluorobenzene as internal standard.

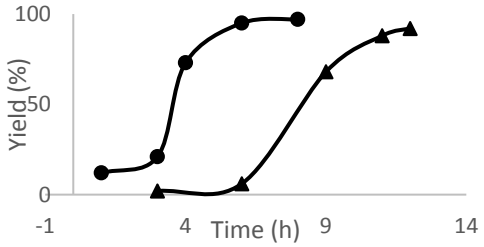


Figure S2. Time course of the yields of **3a** and **3n** in the reaction of IF_5 with **2a** and **2n** (●,**3a**;▲,**3n**).

13. EPS of IF_5 and Py-*o*-SF_4Cl by DFT computation

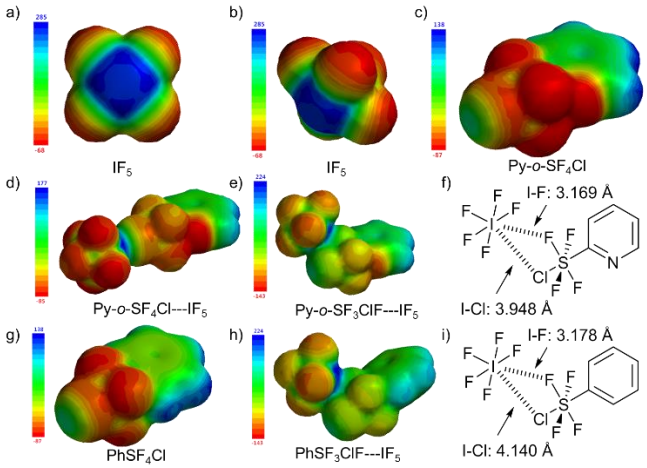
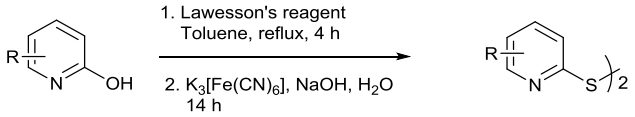


Figure S3. DFT calculations of IF_5 (a,b), py-*o*-SF_4Cl (c), a complex [IF_5/Py-*o*-SF_4Cl] (e), $PhSF_4Cl$ (g) and a complex [IF_5/Ph-SF_4Cl] (h) by B3LYP/6-311+G(*d*,*p*) except a complex [IF_5/Py-*o*-SF_4Cl] (d) by B3LYP/6-31G(d).

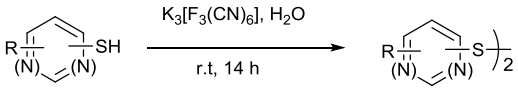
14. General Procedure for Synthesis of disulfides

Method E[1]



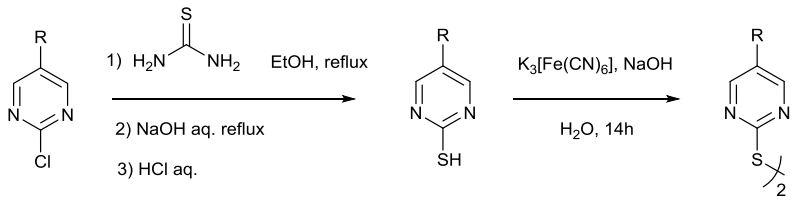
The solution of 2-pyridone (21.5 mmol) and Lawesson's reagent (5.22 g, 12.9 mmol) in anhydrous toluene (107 ml) was stirred at reflux for 14 h. After cooling, NaOH (5N, 10 ml) solution was added to the reaction mixture. The aqueous layer was separated and washed with Et_2O (30 ml). The organic phases were discarded, and the aqueous phase was acidified with HCl aqueous (2N) to pH 2-3, and extracted with CH_2Cl_2 (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 CH_2Cl_2 was evaporated in vacuo to give pyridine-2-thiol. Not further purify and directly continue the next step. Added crude pyridine-2-thiol to the solution of NaOH (1.03g, 25.5 mmol) in water (43 ml) was stirred for 30 min. Then $K_3[Fe(CN)_6]$ (8.49 g, 25.8 mmol) in water (57 ml) was dropwise added and stirred at room temperature for overnight. The formed precipitate was filtered, washed with water and dried in vacuo to give disulfide.

Method F[1]



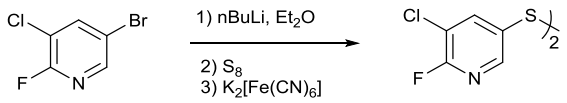
To aromatic thiol (9.7 mmol) was added solution of NaOH (0.46 g, 11.6 mmol) in water (19 ml) and it was stirred for 30 minutes and after a solution of $K_3[Fe(CN)_6]$ (3.82 g, 11.6 mmol) in water (25 ml) was added to it. The reaction mixture was stirred for 14 h, precipitate formed was filtered, washed with water and dried in vacuo to give disulfide.

Method G



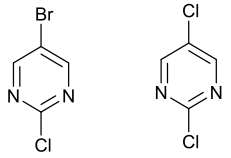
The solution of substituted 2-chloropyrimidine (2.4 mmol) and thiocarbamide (0.365 g, 4.8 mmol) in ethanol (5 ml) was stirred and heated at reflux overnight. Upon completion, aqueous NaOH (0.24 g, 6.0 mmol) solution was added and heated at reflux for 2 h. Cooling to room temperature, the ethanol was evaporated in vacuo and the residue was washed with Et_2O (2 ml×3). The aqueous was acidified with HCl aqueous (2 N) to pH 2-3, precipitate formed was filtered, washed with water and dried in vacuo to give 5-substituded pyrimidine-2-thiol. Not further purify and directly continue the next step. Added crude 5-substituded pyrimidine-2-thiol to the solution of NaOH (0.115 g, 2.88 mmol) in water (3 ml) was stirred for 30 min. Then $K_3[Fe(CN)_6]$ (0.948 g, 2.88 mmol) in water (5 ml) was added dropwise and stirred at room temperature overnight. The formed precipitate was filtered, washed with water and dried in vacuo to give pure disulfide as a crystalline solid.

Method H



To solution of 2-fluoro-3-chloro-5-bromopyridine (1.96 g, 9.3 mmol) in Et_2O (45 ml), *n*BuLi (6.4ml, 9.3 mmol, 1.45 M solution in Hexene) was added drop wise at -78 °C, after which it was stirred for an additional half hour. Powdered elemental sulfur (0.328 g, 10.23 mmol) in Toluene (16 ml) was then added in portions and maintained at -78 ^oC for 30 min. It was then allowed to room temperature with stirring under nitrogen overnight. Reaction mixture was poured to a solution of $K_3[Fe(CN)_6]$ (3.67 g, 11.16 mmol) in water (50 ml) and stirred at room temperature over 2 h. For workup, organic layer was separated and aqueous phase was extracted with EtOAc (3×30 ml). Combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and solvent was evaporated. The crude was purified by flash column chromatography (hexane/EtOAC, 50/1) to give white solid.

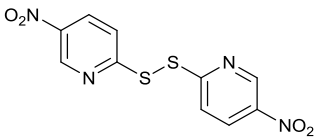
15. General Procedure of synthesis of 2-chloropyrimidines



2-chloropyrimidines were prepared according to the literature procedures.[4]

16. Preparation of Compounds

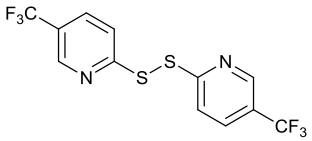
2,2`-bis(5-nitropyridyl)disulfide



1a

Prepared following Method E. Recrystallized from ethanol. Yield 2.668 g, 80%. khaki crystalline solid. Mp 133-135 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.41 (d, *J* = 6.9 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.10, 145.48, 142.81, 132.27, 119.95, 77.41, 77.16, 76.91. IR (KBr, cm^{-1}): 3088, 1590, 1563, 1519, 1343, 1100, 855, 748. HRMS (TOF/EI+): Calculated for $C_{10}H_6N_4O_4S_2^+$: 309.9830, found: 309.9820.

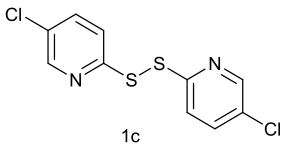
2,2`-bis(5-trifluoromethylpyridyl)disulfide



1b

Prepared following Method E. Flash column chromatography: Hexane/AcOEt 6:1. Yield 2.834 g, 74%. White solid. ^1H 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).

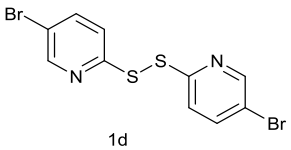
2,2`-bis(5-chloropyridyl)disulfide



1c

Prepared following Method E. Flash column chromatography: Hexane/AcOEt 6:1. Yield 2.332 g, 75%. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 1.5 Hz, 2H), 7.57 (dd, *J* = 4.5, 1.5 Hz, 4H).

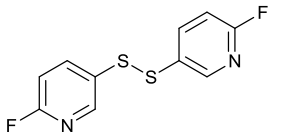
2,2`-bis(5-bromopyridyl)disulfide



1d

Prepared following Method E. Flash column chromatography: Hexane/AcOEt 6:1. Yield 2.723 g, 67%. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.3 Hz, 2H), 7.73 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H).

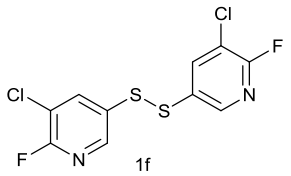
3,3`-bis(6-fluoropyridyl)disulfide



1e

1e was prepared according to the literature procedures[3]. Yield 1.46 g, 57%. 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).

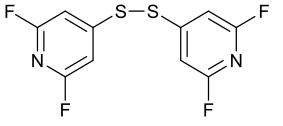
3,3`-bis(5-chloro-6-fluoropyridyl)disulfide



1f

Prepared following Method H. Flash column chromatography: Hexane/AcOEt 50:1. Yield 0.76 g, 50%. White solid. Mp 79-81 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14-8.13 (m, , 2H), 7.95 (dd, *J* = 8.1, 2.3 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.20 (d, *J* = 7.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.12 (s), 158.20 (s), 146.18 (d, *J* = 14.0 Hz), 142.35 (d, *J* = 2.5 Hz), 131.55 (d, *J* = 5.2 Hz), 118.58 (d, *J* = 35.3 Hz). IR (KBr, cm^{-1}): 3040, 1564, 1441, 1366, 1258, 1071, 727. HRMS (TOF/EI+): Calculated for $C_{10}H_4Cl_2F_2N_2S_2^+$: 323.9161, found: 323.9182.

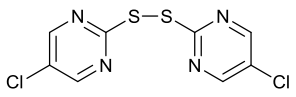
4,4`-bis(2,6-difluoropyridyl)disulfide



1g

1h was prepared according to the literature procedures[3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.69 (s, 4F).

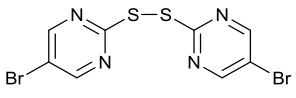
2,2`-bis(5-chloropyrimidyl)disulfide



1h

Prepared following Method G. Yield 0.22 g, 63%. Yellowish solid. Mp 201-204 ºC. ^{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.

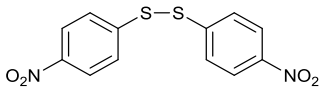
2,2`-bis(5-bromopyrimidyl)disulfide



1i

Prepared following Method G. Yield 0.237 g, 52%. 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.

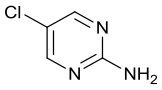
1,1`-bis(4-dinitrophenyll)disulfide



1j

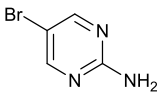
Prepared following Method F. Yield 1.435 g, 96%. Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 4H), 7.62 (d, *J* = 8.7 Hz, 4H).

5-chloro-2-pyrimidinamine



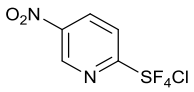
To a solution of 2-aminopyridine (3 g, 31.5 mmol) in MeCN (60 ml) cooled in an ice bath was added *N*-chlorosuccinimide, then the reaction mixture was heated reflux overnight. The solution was evaporated after the completion of reaction. The residue obtained was washed with $NaHCO_3$ aqueous and water, filtered and dried under vacuum to give 3.85 g, 94% yield of 5-chloro-2-pyrimidinamine as white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 2H), 5.05 (s, 2H).

5-bromo-2-pyrimidinamine



To a solution of 2-aminopyridine (5 g, 53.1 mmol) in MeCN (80 ml) cooled in an ice bath was added *N*-bromosuccinimide, then the reaction mixture was stirred at room temperature overnight. The solution was evaporated after the completion of reaction. The residue obtained was washed with $NaHCO_3$ aqueous and water, filtered and dried under vacuum to give 8.64 g, 94% yield of 5-bromo-2-pyrimidinamine as white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 2H).

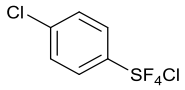
2-(chlorotetrafluoro-λ^6-sulfanyl)-5-nitropyridine



2a

Prepared following Procedure I. Yield 0.792 g, 79%. Yellow 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 127.99 (s, 4F).

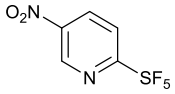
(4-chlorophenyl)chlorotetrafluoro-λ^6-sulfane



2n

Prepared following Procedure II. Yield 1.974 g, 73%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.0 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.79 (s, 4F).

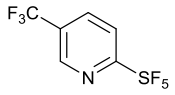
5-nitro-2-(pentafluoro-λ^6-sulfanyl)pyridine



3a

Prepared following Method A. Flash column chromatography: Pentane/DCM 3:1. Yield 0.158 g, 88%. Yellow solid. Mp 43-45 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 76.15 – 73.79 (m, 1F), 52.51 (d, *J* = 150.9 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.16 (p, *J* = 25.2 Hz), 145.37 (s), 144.03 (s), 134.25 (s), 122.52 (p, *J* = 3.9 Hz). IR (KBr, cm^{-1}): 3061, 1982, 1602, 1528, 1455, 1369, 1297, 1018, 835. HRMS (TOF/EI+): Calculated for $C_5H_3F_5N_2O_2S^+$: 249.9835, found: 249.9842.

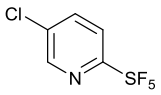
2-(pentafluoro-λ^6-sulfanyl)-5-(trifluoromethyl)pyridine



3b

Prepared following Method A. Flash column chromatography: Pentane/DCM 3:1. Yield 0.159 g, 81%. 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 77.10 – 74.48 (m, 1F), 51.87 (d, *J* = 150.4 Hz, 4F), -63.14 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.92 – 166.99 (m), 145.54 (d, *J* = 1.9 Hz), 136.30 (d, *J* = 3.3 Hz), 129.71 (q, *J* = 33.9 Hz), 122.34 (d, *J* = 273.2 Hz), 121.94 – 121.44 (m). IR (KBr, cm^{-1}): 3125, 3082, 1603, 1580, 1471, 1386, 1329, 1180, 1147, 1080, 1014, 854. HRMS (TOF/EI+): Calculated for $C_6H_3F_8NS^+$: 272.9858, found: 272.9857.

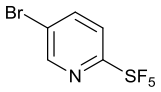
5-chloro-2-(pentafluoro-λ^6-sulfanyl)pyridine



3c

Prepared following Method B. Flash column chromatography: Pentane/DCM 3:1. Yield 97 mg, 56%. 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 78.80 – 76.44 (m, 1F), 53.24 (d, *J* = 150.3 Hz, 4F).

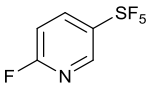
5-bromo-2-(pentafluoro-λ^6-sulfanyl)pyridine



3d

Prepared following Method B. Flash column chromatography: Pentane/DCM 3:1. Yield 0.139 g, 68%. 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 78.89 – 76.25 (m, 1F), 53.14 (d, *J* = 150.3 Hz, 4F).

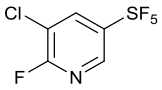
2-fluoro-5-(pentafluoro-λ^6-sulfanyl)pyridine



3e

Prepared following Method B. Yield 0.114 g, 71%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.34 – 8.09 (m, 1H), 7.05 (dd, *J* = 8.9, 3.1 Hz, 1H). ^{19}F NMR (282 MHz, $cdcl_3$) δ 83.43 – 79.55 (m), 65.36 (d, *J* = 151.4 Hz), -62.12 (s).

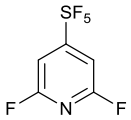
3-chloro-2-fluoro-5-(pentafluoro-λ^6-sulfanyl)pyridine



3f

Prepared following Method B. Flash column chromatography: Pentane/DCM 1:1. Yield 83 mg, 45%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.22 (dd, *J* = 7.6, 2.4 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 81.55 – 79.30 (m, 1F), 66.12 (d, *J* = 151.9 Hz, 4F), -64.26 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.48 (d, *J* = 255.6 Hz), 148.49 – 147.74 (m), 143.49 – 143.10 (m), 139.10 – 138.78 (m), 118.07 (d, *J* = 35.3 Hz). IR (KBr, cm^{-1}): 1713, 1578, 1458, 1392, 1269, 1129, 1076, 825. HRMS (TOF/EI+): Calculated for $C_5H_2ClF_6NS^+$: 256.9501, found: 256.9490.

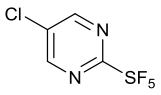
2,6-difluoro-4-(pentafluoro-λ^6-sulfanyl)pyridine



3g

Crude pyridylsulfur chlorotetrafluoride (1.26 g, 4.9 mmol) was placed into FEP bottle in the glove box. From a cylinder, IF_5 was transferred through a Teflon tube into a FEP bottle under an N_2 atmosphere. Measured the amount of IF_5 (0.51 ml, 7.35 mmol) in the PFA syringe was quickly transferred into the bottle of starting material and added slowly under N_2 protected at room temperature. The mixture was stirred at 65 ^{o}C for 14 h. Workup was conducted as it is shown in Method B. Flash column chromatography: Pentane/DCM 1:1. Yield 0.236 g, 20%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 78.86 – 75.42 (m, 1F), 60.91 (d, *J* = 151.4 Hz, 4F), -63.14 (s, 2F).

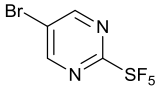
5-chloro-2-(pentafluoro-λ^6-sulfanyl)pyrimidine



3h

Prepared following Method A. Flash column chromatography: Pentane/DCM 3:1. Yield 47 mg, 27%. White solid. Mp 57-60 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 74.75 – 71.58 (m, 1F), 48.47 (d, *J* = 152.1 Hz, 4F).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.08 – 165.56 (m), 157.03 (s), 134.04 (s). IR (KBr, cm^{-1}): 2960, 1676, 1554, 1449, 1397, 1368, 1134, 855, 774. Calculated for $C_4H_2ClF_5N_2S^+$: 239.9547, found: 239.9572.

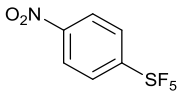
5-bromo-2-(pentafluoro-λ^6-sulfanyl)pyrimidine



3i

Prepared following Method A. Flash column chromatography: Pentane/DCM 3:1. Yield 86 mg, 42%. White solid. Mp 78-79 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 74.57 – 71.71 (m, 1F), 48.41 (d, *J* = 152.0 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.38 – 167.48 (m), 159.29 (s), 123.02 (s). IR (KBr, cm^{-1}): 2913, 1553, 1394, 1367, 1270, 1188, 840. HRMS (TOF/EI+): Calculated for $C_4H_2BrF_5N_2S^+$: 283.9042, found: 283.9056.

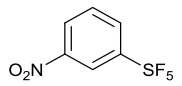
(4-nitrophenyl)pentafluoro-λ^6-sulfane



3j

Prepared following Method B. Flash column chromatography: Pentane/DCM 3:1. Yield 0.134 g, 75%. 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 81.96 – 79.35 (m, 1F), 62.15 (d, *J* = 150.7 Hz, 4F).

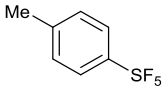
(3-nitrophenyl]pentafluoro-λ^6-sulfane



3k

Prepared following Method B. Flash column chromatography: Pentane/DCM 3:1. Yield 0.147 g, 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.42 (d, *J* = 8.0 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), 62.35 (d, *J* = 150.9 Hz).

***p*-tolylpentafluoro-λ^6-sulfane**

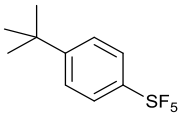


3l

Prepared following Method C, reaction time for 5 h, yield 44 mg, 28%. Flash column chromatography: Pentane. 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 87.42 – 82.88 (m), 62.66 (d, *J* = 149.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.38 – 149.00 (m), 142.19 (s), 129.32 (s), 125.95 (p, *J* =

4.6 Hz), 21.28 (s). HRMS (TOF/EI+): Calculated for $C_7H_7F_5S^+$: 218.0189, found: 218.0201.

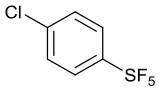
[4-(*tert*-butyl)phenyl]pentafluoro-λ^6-sulfane



3m

Prepared following Method C, reaction time for 24 h. Flash column chromatography: Pentane. Yield 77 mg, 41%. 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 86.72 – 83.82 (m, 1F), 63.12 (d, *J* = 149.9 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.21 (s), 151.56 (p, *J* = 16.9 Hz), 125.94 – 125.67 (m), 35.07 (s), 31.20 (s). IR (KBr, cm^{-1}): 2967, 2909, 2872, 1596, 1499, 1477, 1463, 1402, 1366, 1268, 1091, 840. HRMS (TOF/EI+): Calculated for $C_{10}H_{13}F_5S^+$: 260.0658, found: 260.0673.

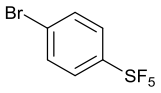
(4-chlorophenyl]pentafluoro-λ^6-sulfane



3n

Prepared following Method C, reaction time for 12 h. Flash column chromatography: Pentane. Yield 0.140 g, 82%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H). ^{19}F NMR (282 MHz, $cdcl_3$) δ 84.85 – 82.43 (m), 63.15 (d, *J* = 150.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.84 – 151.58 (m), 137.94 (s), 129.05 (s), 127.57 (p, *J* = 4.6 Hz). IR (KBr, cm^{-1}) 3016, 1583, 1490, 1475, 1402, 1093, 831. HRMS (TOF/EI+): Calculated for $C_6H_4ClF_5S^+$: 237.9642, found: 237.9653.

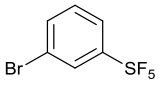
(4-bromophenyl]pentafluoro-λ^6-sulfane



3o

Prepared following Method C, reaction time for 12 h. Flash column chromatography: Pentane. Yield 0.157 g, 77%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 85.00 – 82.18 (m, 1F), 63.02 (d, *J* = 150.4 Hz, 4F).

(3-bromophenyl]pentafluoro-λ^6-sulfane



3p

Prepared following Method C, under 65^{o}C, reaction time for 12 h. Flash column chromatography: Pentane. Yield 145.0 mg, 71%. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (t, *J* = 1.9 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.36 (t, *J* = 8.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ 83.58 – 81.18 (m), 62.34 (d, *J* = 150.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.14 – 154.20 (m), 134.91 (s), 130.26 (s), 129.31 (p, *J* = 4.8 Hz), 124.79 (p, *J* = 4.7 Hz), 122.38 (s). IR (KBr, cm^{-1}): 3109, 3078, 1579, 1465, 1422, 1113, 1098, 1080, 852. HRMS (TOF/EI+): Calculated for $C_6H_4BrF_5S^+$: 281.9137, found: 281.9143.

17. References

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

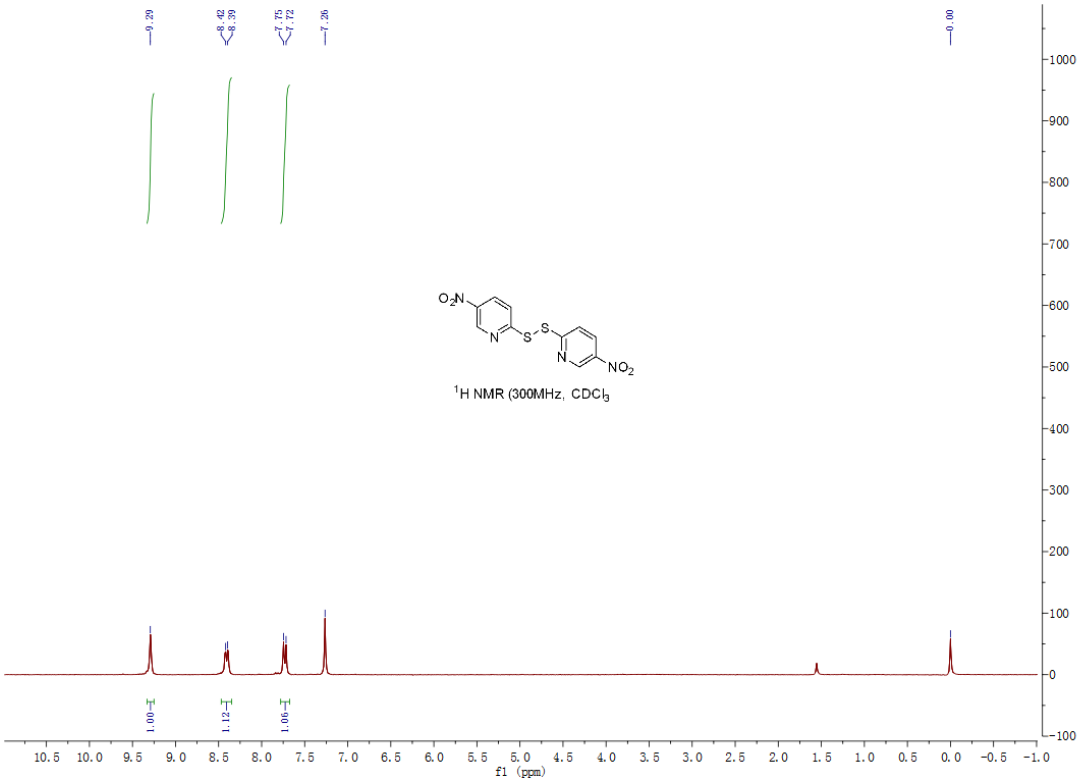
[2]. O. S. Kanishchev, W. R. Dolbier, Jr., *Angew. Chem. Int. Ed*. 2015, **54**, 280.

[3]. M. Kosobokov, B. Cui, A. balia, K. Matsuzaki, E. Tokunaga, N. Saito, N. Shibata, *Angew.*

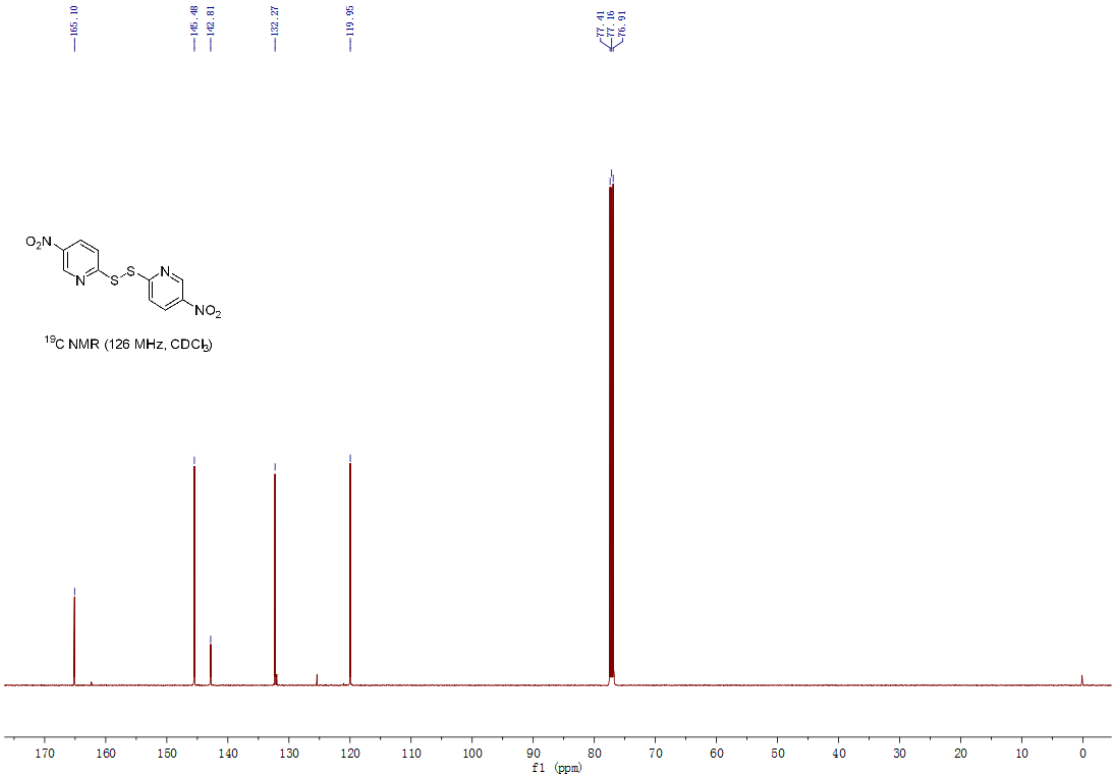
Chem. Int. Ed. 2016, **55**, 10781.

[4]. S. J. Nara, M. Jha, J. Brinkhorst, T. J. Zemanek, D. A. Pratt, *J. Org. Chem*. 2008, **73**, 9326.

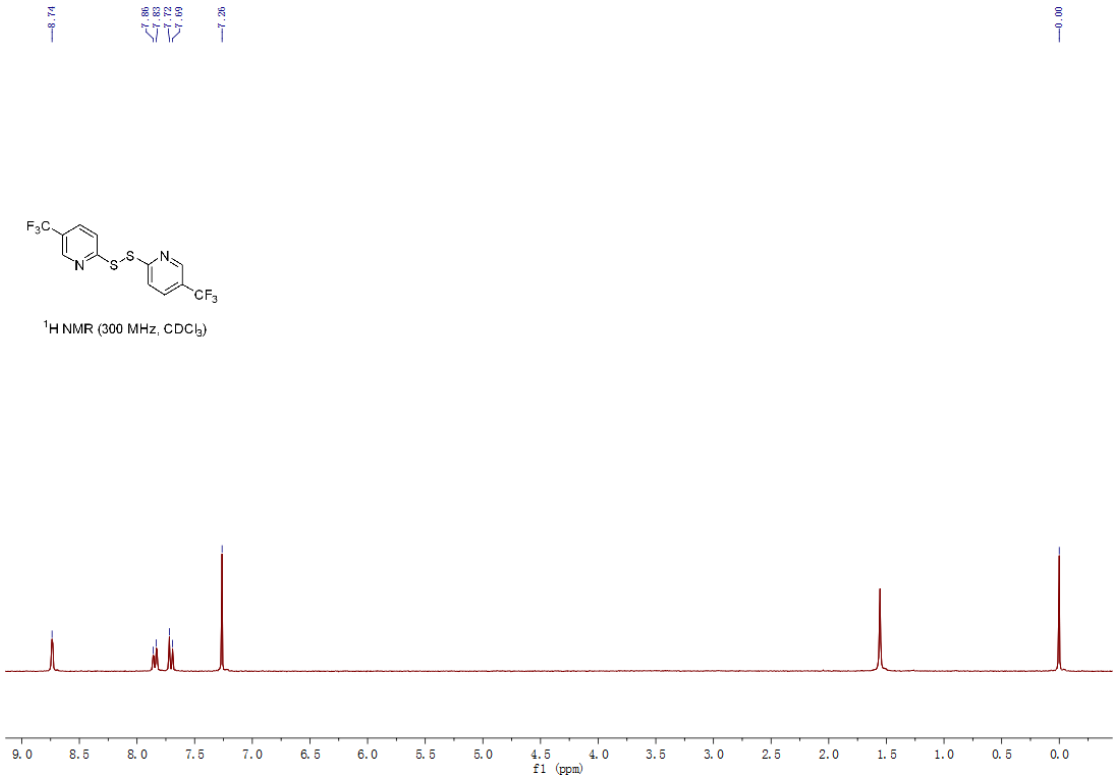
18. ^{1}H, ^{19}F and ^{13}C NMR Spectra of Products.

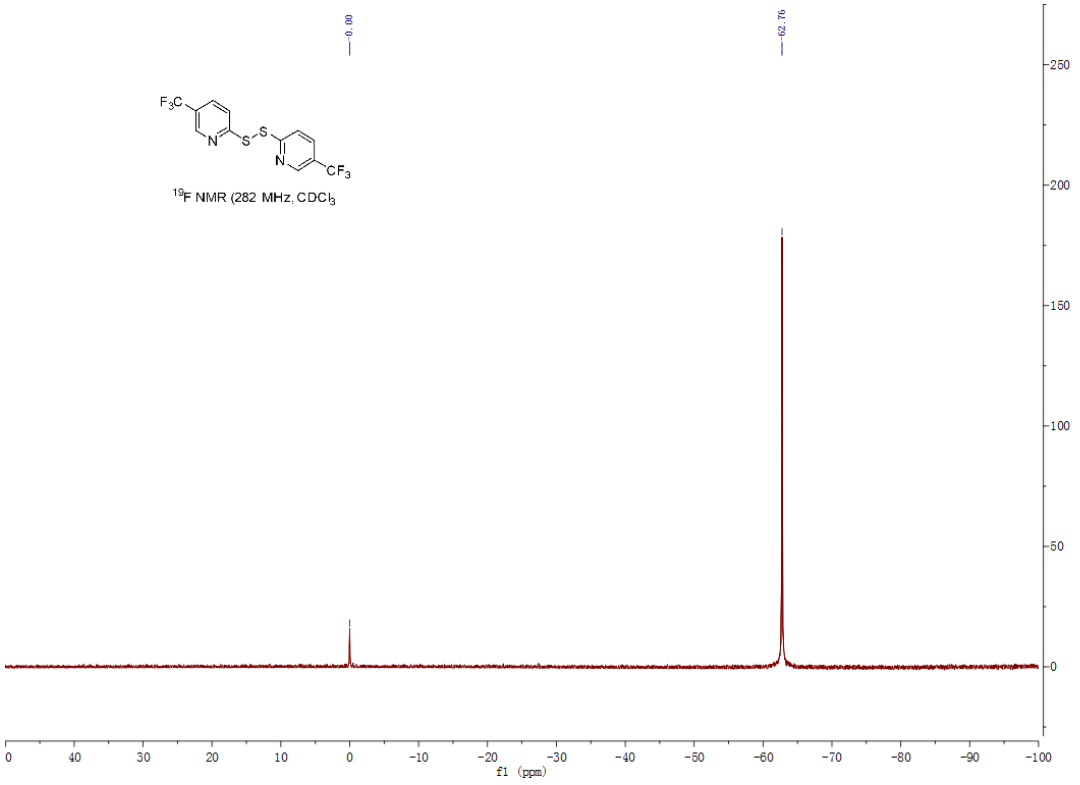


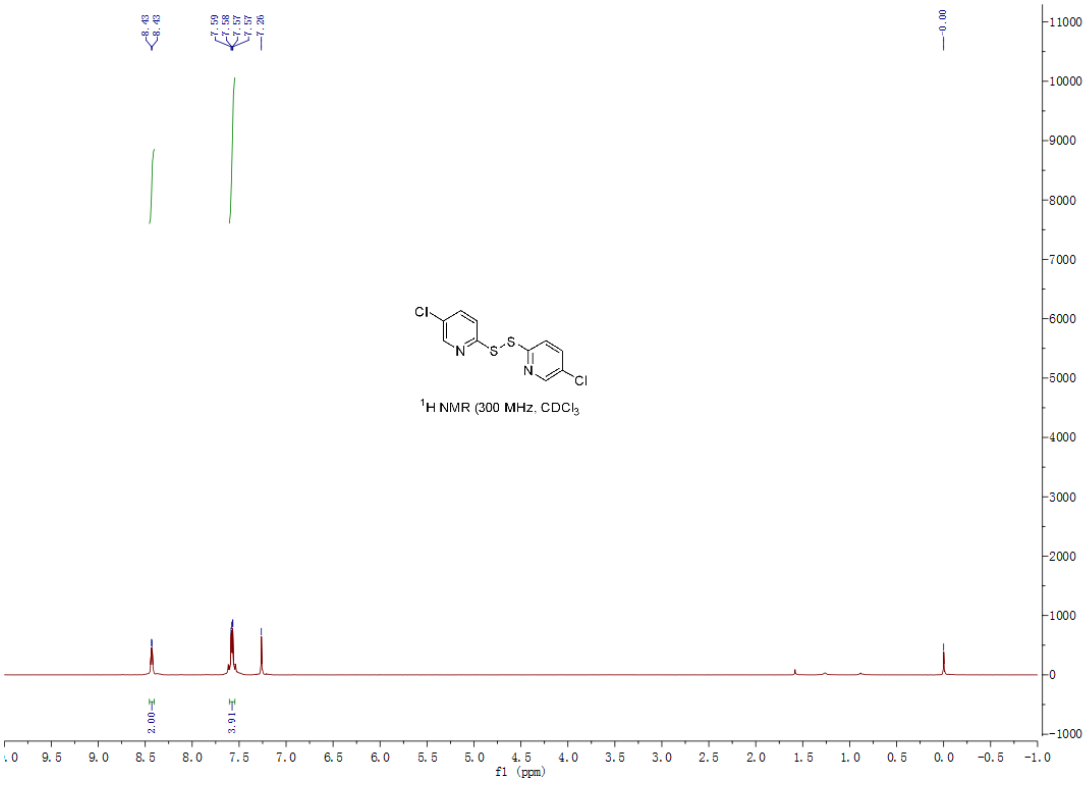
^{1}H NMR (300MHz, $CDCl_3$)



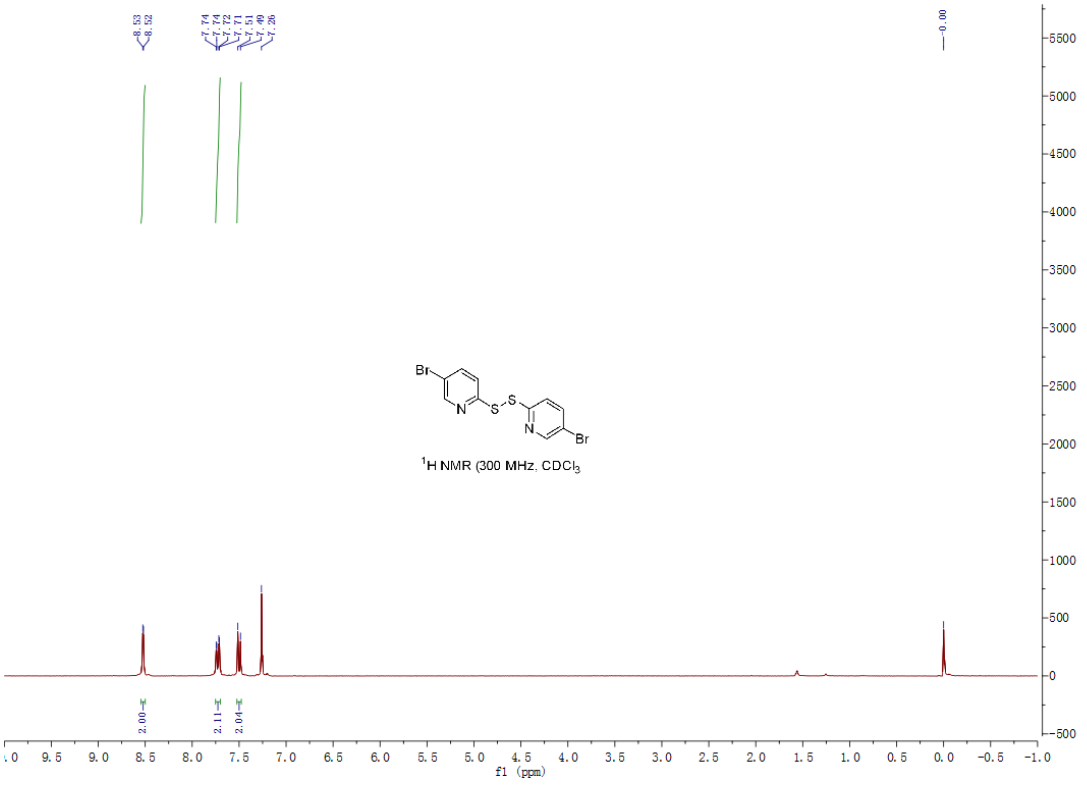
^{19}C NMR (126 MHz, $CDCl_3$)


8.74
7.86
7.82
7.72
7.69
7.26
0.00
F3C
N
S
S
N
CF3
1H NMR (300 MHz, CDCl3)
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)

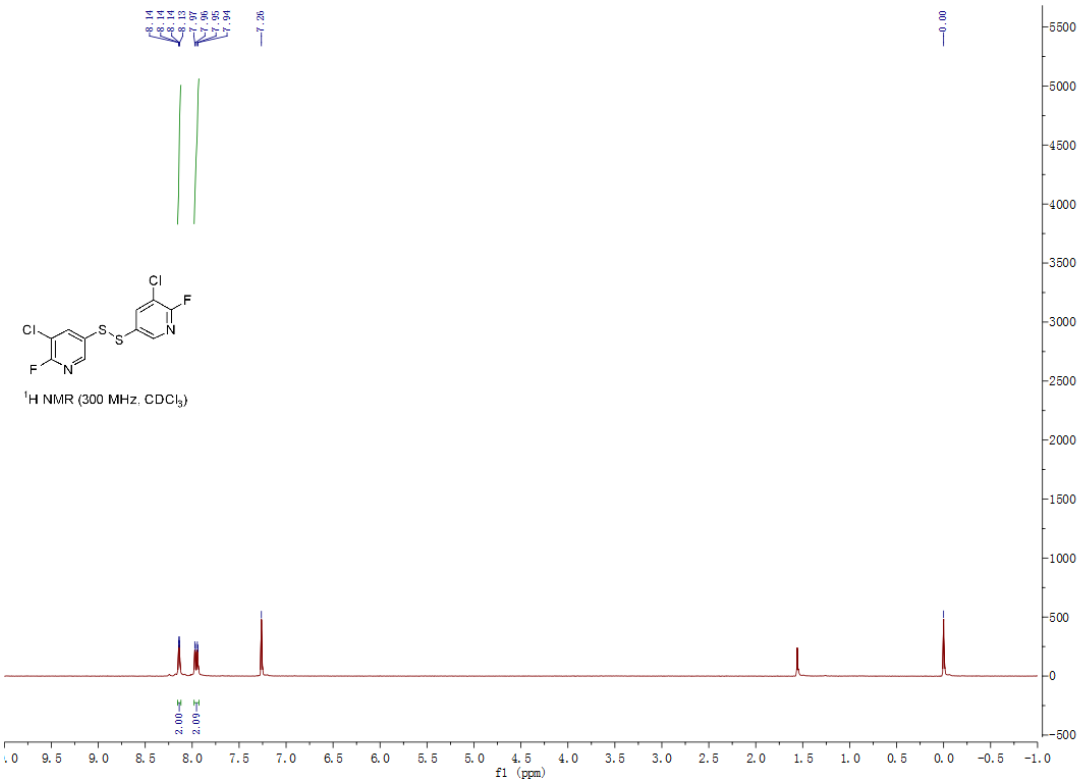

0.00
-62.76
F3C
N
S
S
N
CF3
19F NMR (282 MHz, CDCl3)
250
200
150
100
50
0
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)



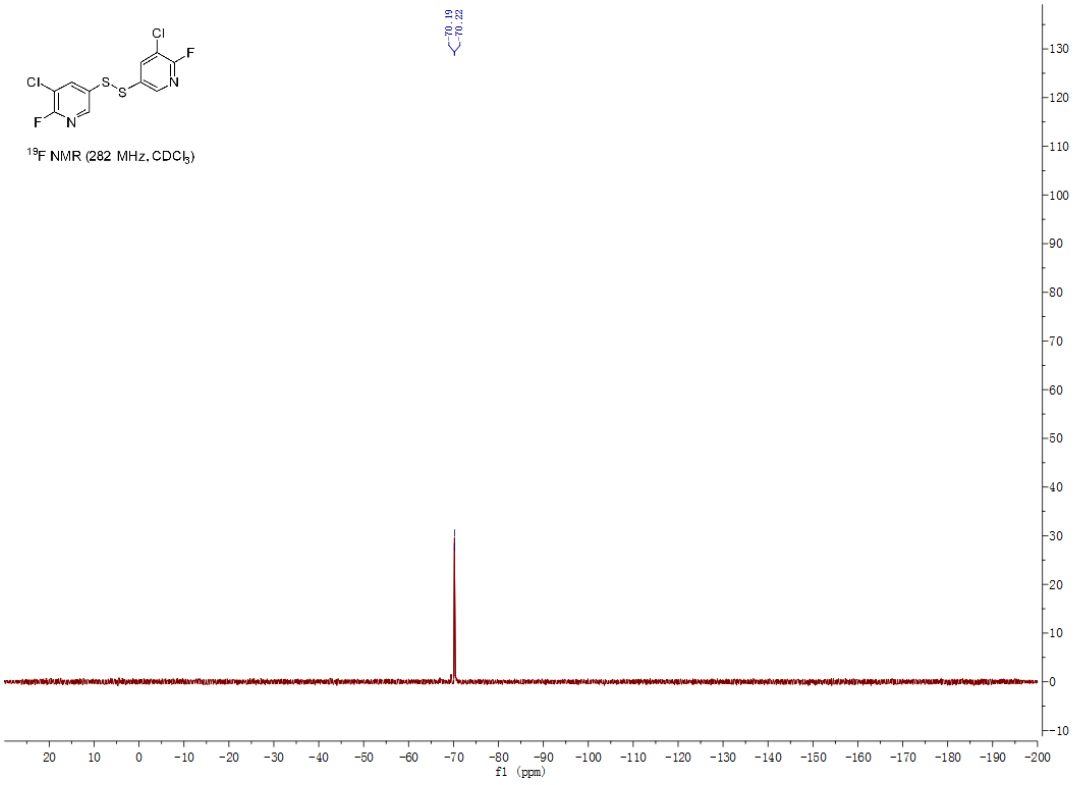
^{1}H NMR (300 MHz, $CDCl_3$)



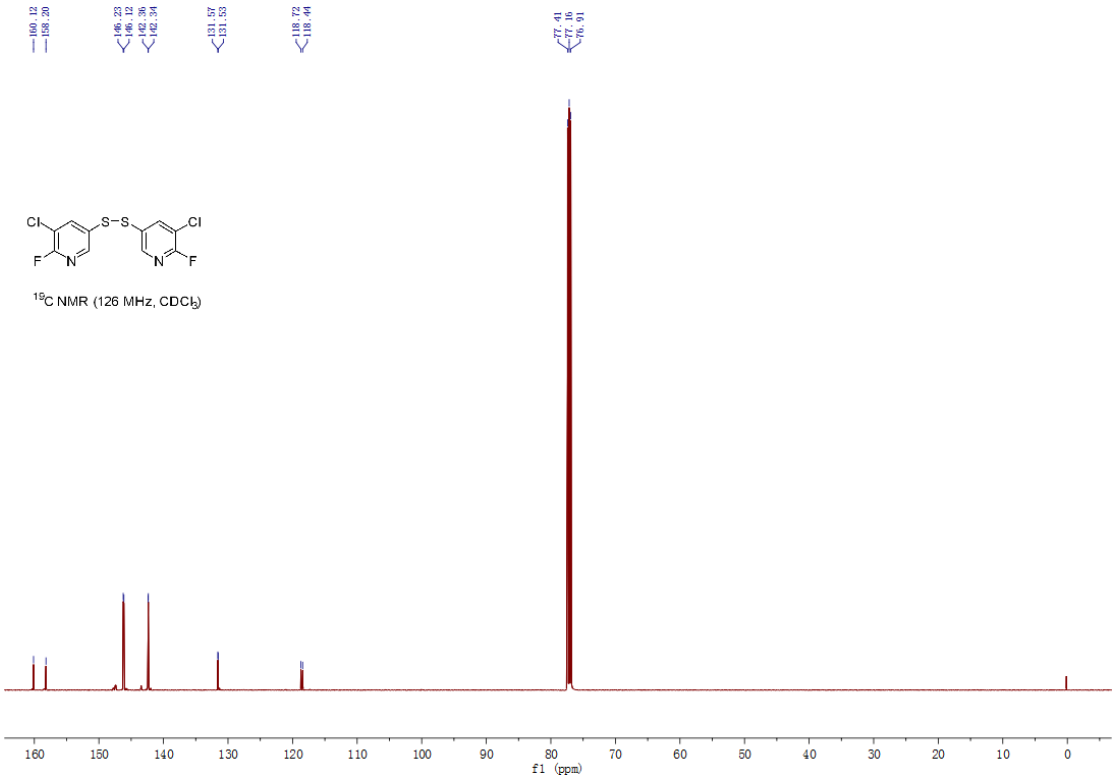
^{1}H NMR (300 MHz, $CDCl_3$)



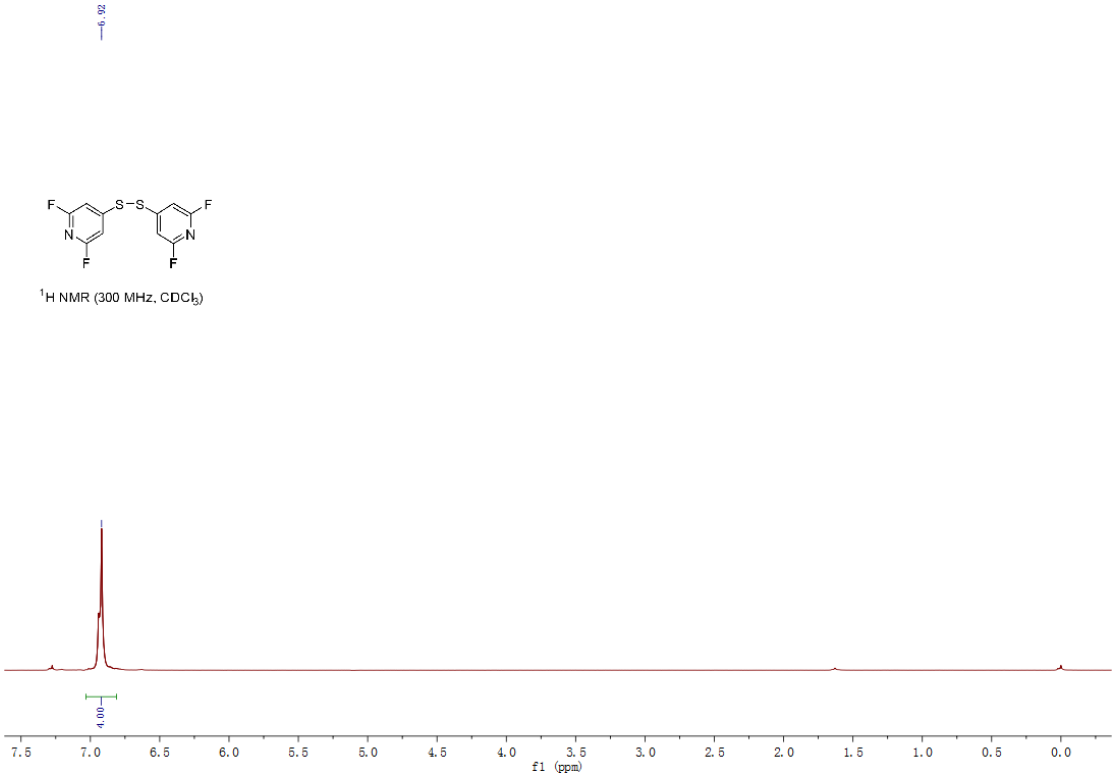
^{1}H NMR (300 MHz, $CDCl_3$)



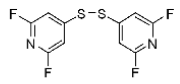
^{19}F NMR (282 MHz, $CDCl_3$)



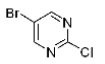
^{19}C NMR (126 MHz, $CDCl_3$)



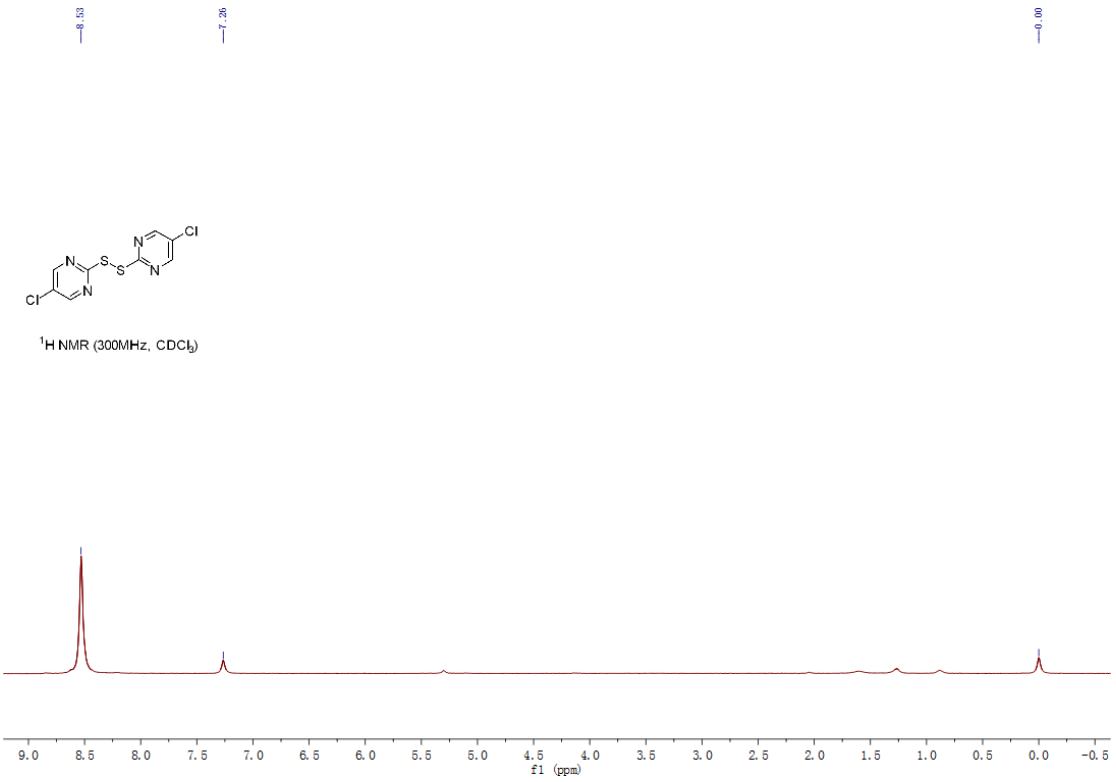
^{1}H NMR (300 MHz, $CDCl_3$)



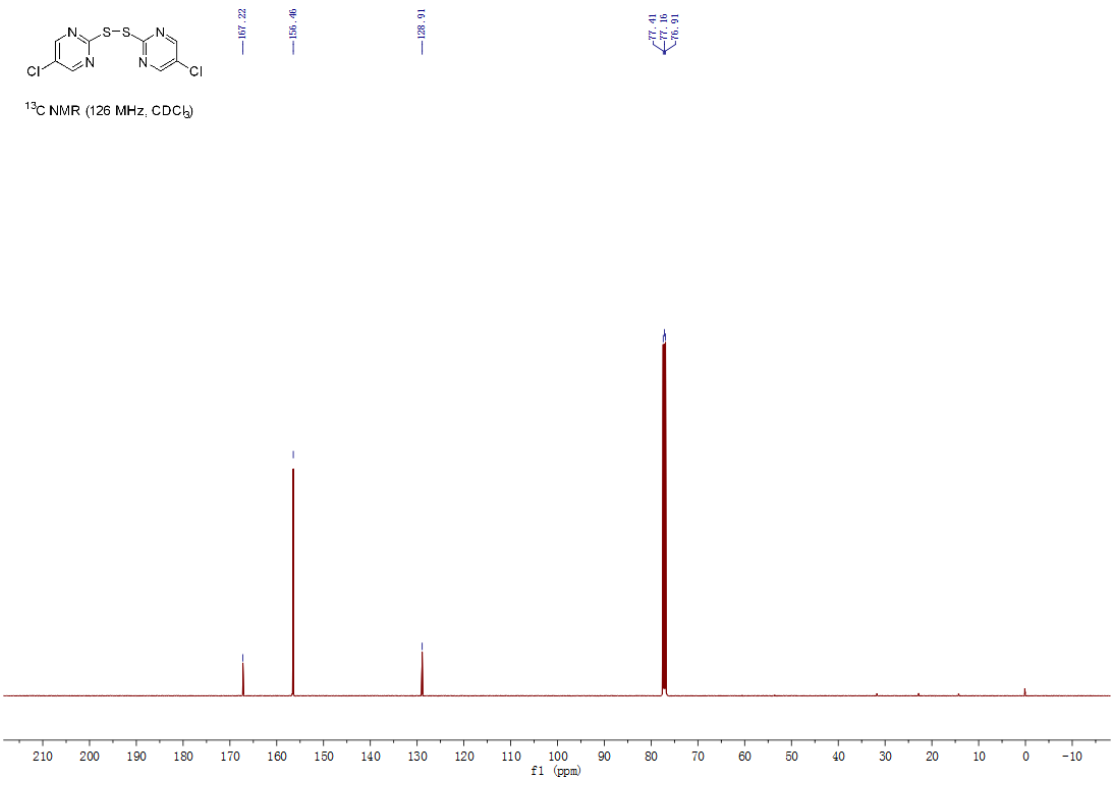
^{19}F NMR (282 MHz, $CDCl_3$)



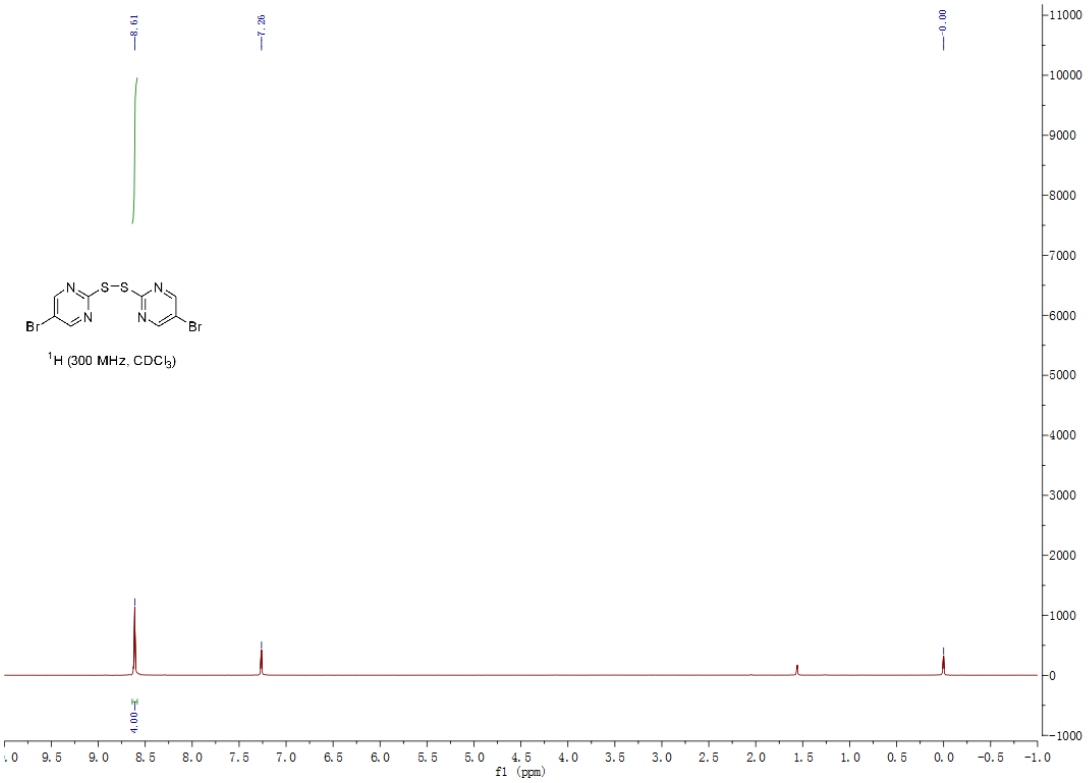
^{1}H NMR (300 MHz, $CDCl_3$)



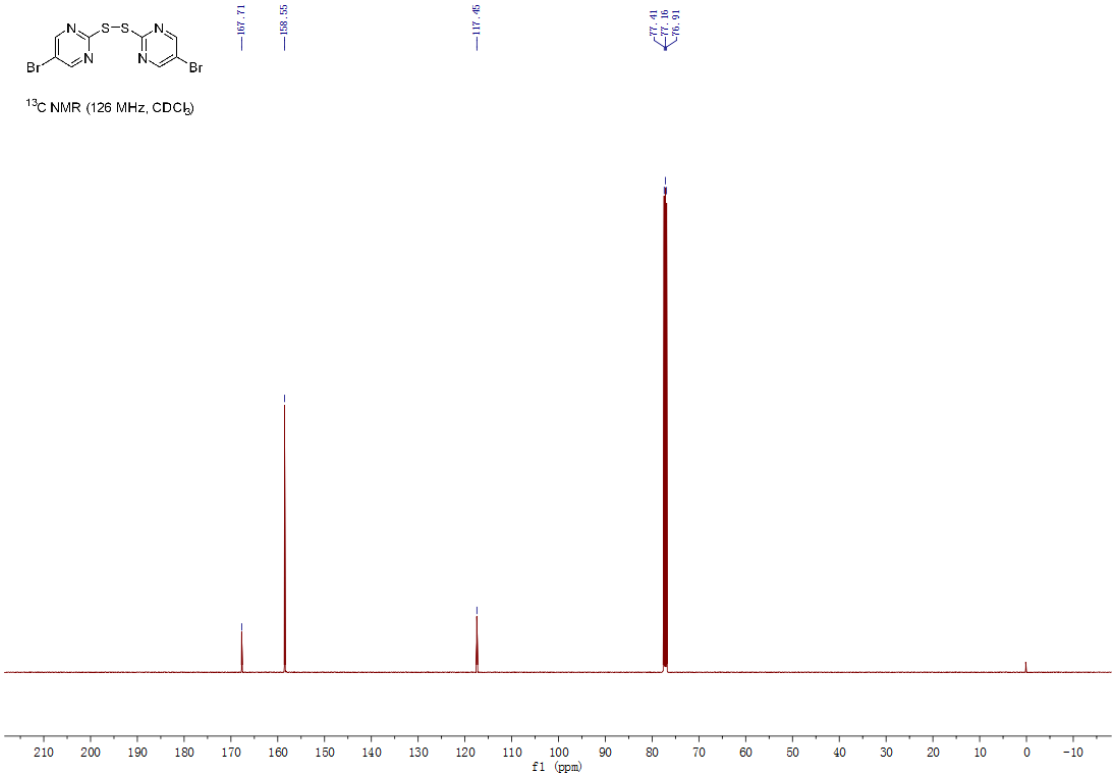
^{1}H NMR (300MHz, $CDCl_3$)



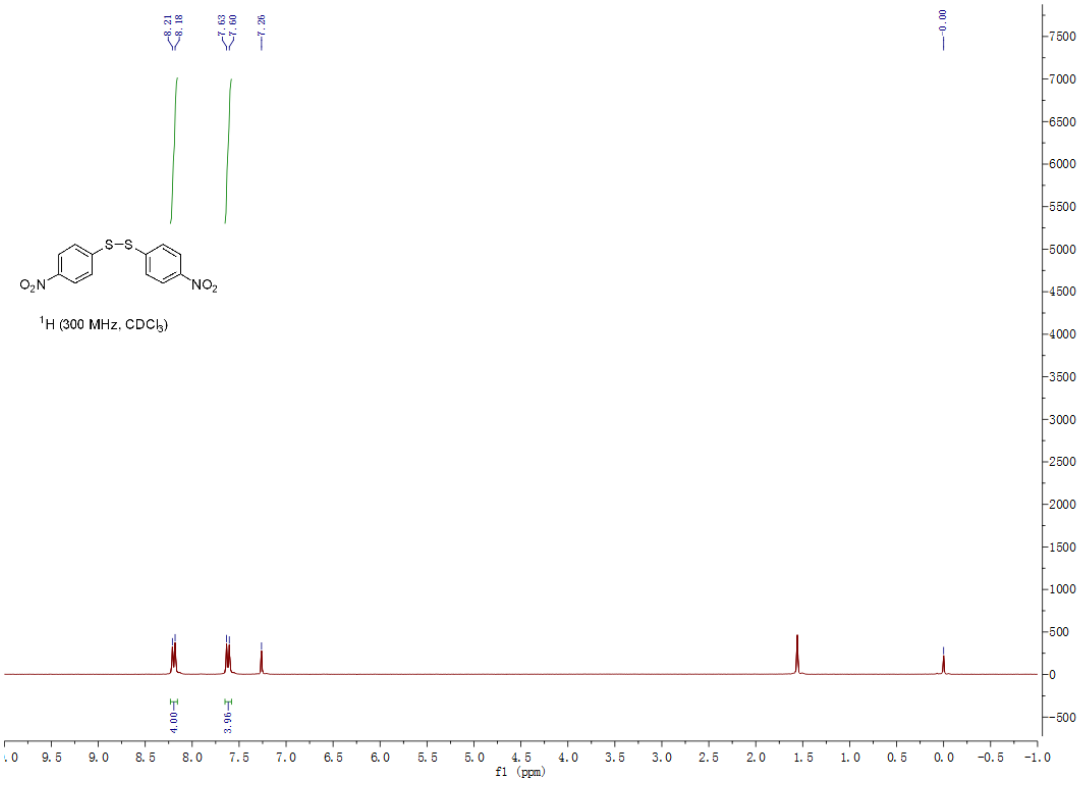
^{13}C NMR (126 MHz, $CDCl_3$)

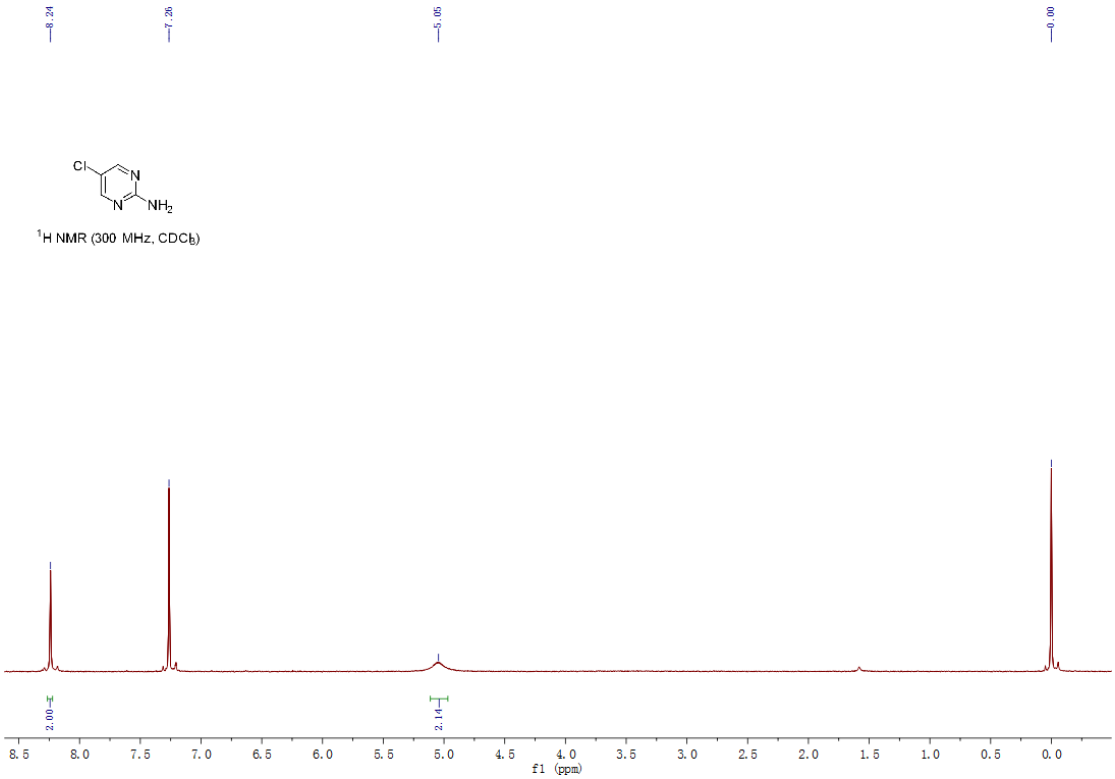


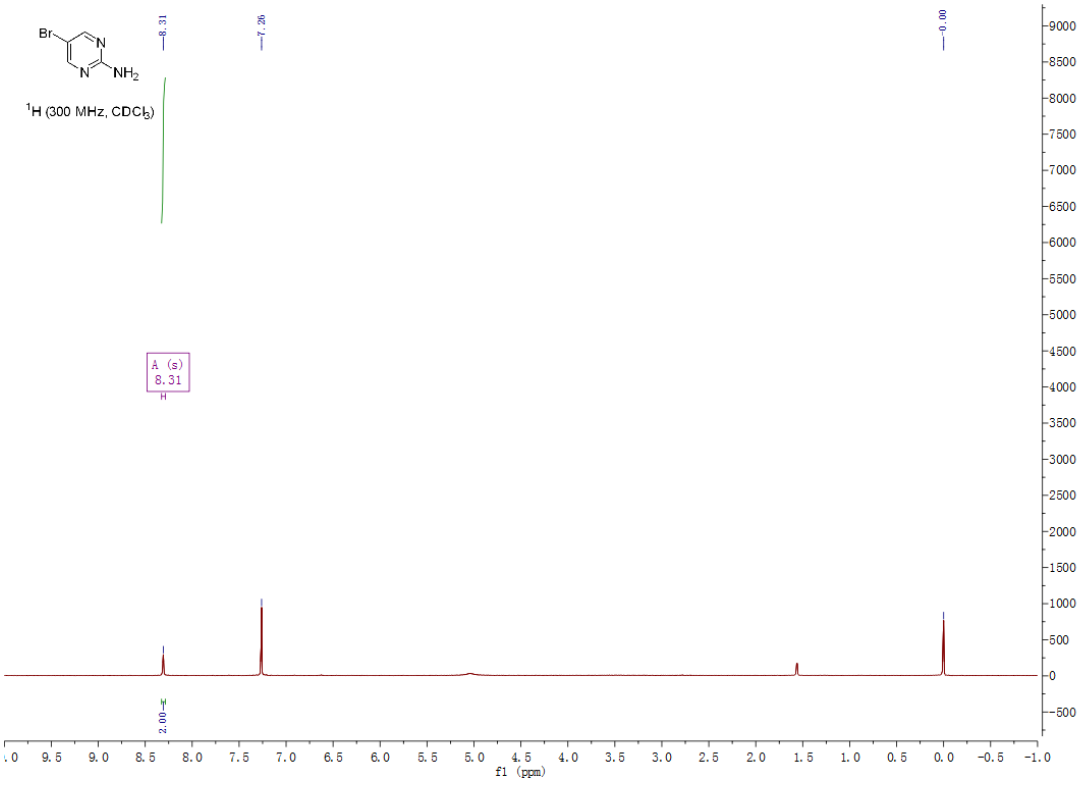
^{1}H (300 MHz, $CDCl_3$)

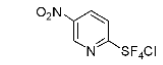


^{13}C NMR (126 MHz, $CDCl_3$)

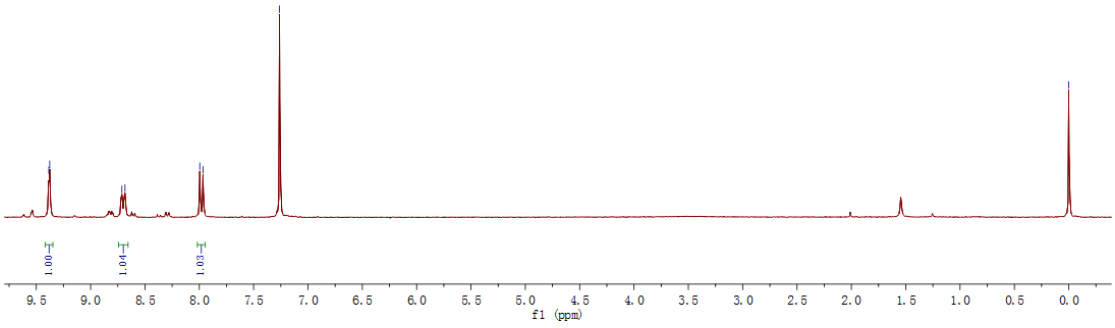

8.21
8.18
7.63
7.60
7.26
0.00
S–S
O_2N
NO_2
^{1}H (300 MHz, $CDCl_3$)
4.00
3.96
f1 (ppm)

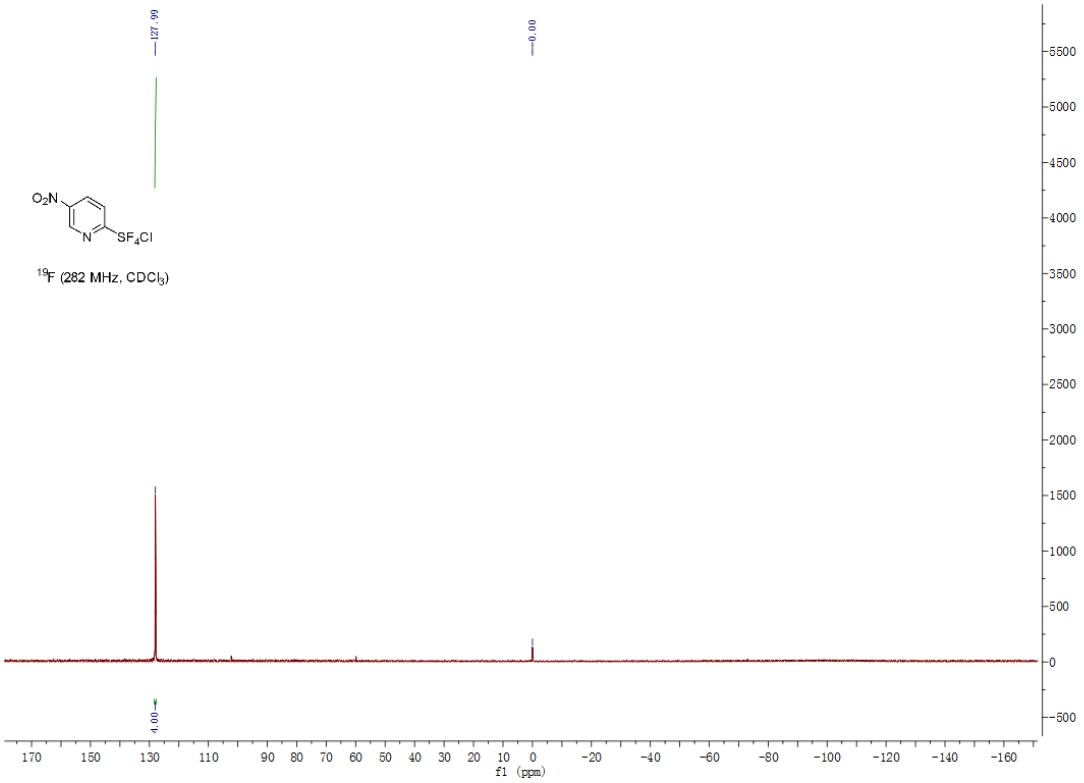

8.24
7.26
5.05
0.00
Cl
N
N
NH_2
^{1}H NMR (300 MHz, $CDCl_3$)
2.00
2.14
f1 (ppm)



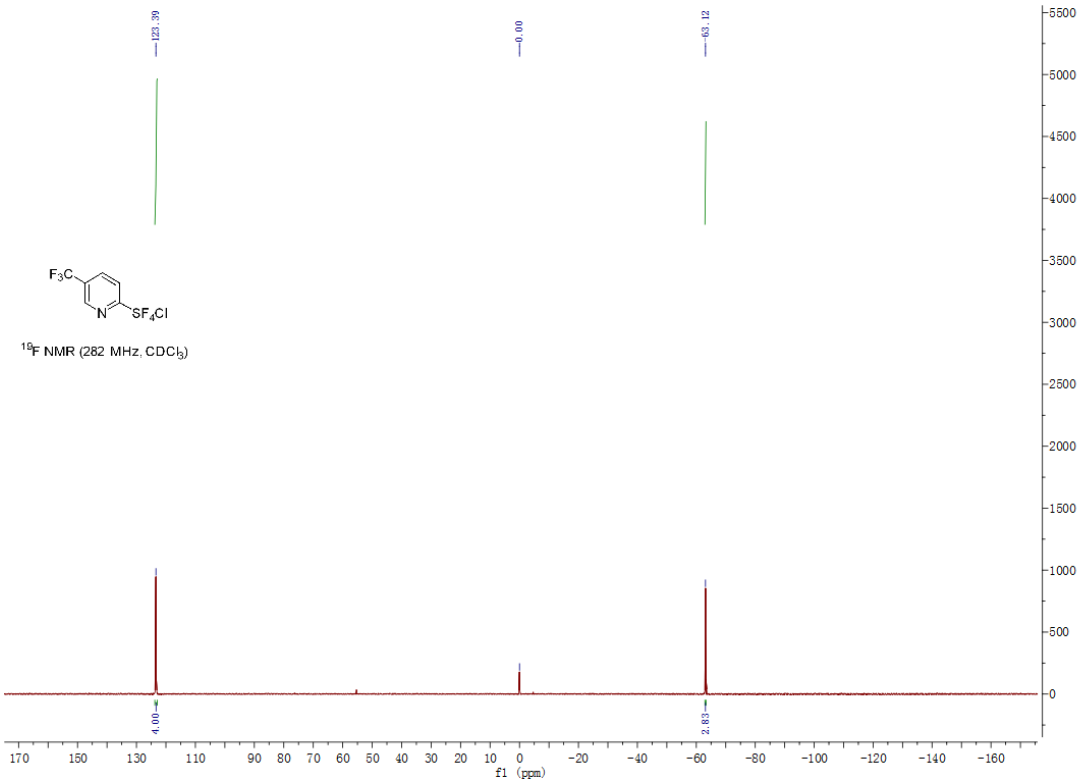


1H NMR (300MHz, $CDCl_3$)

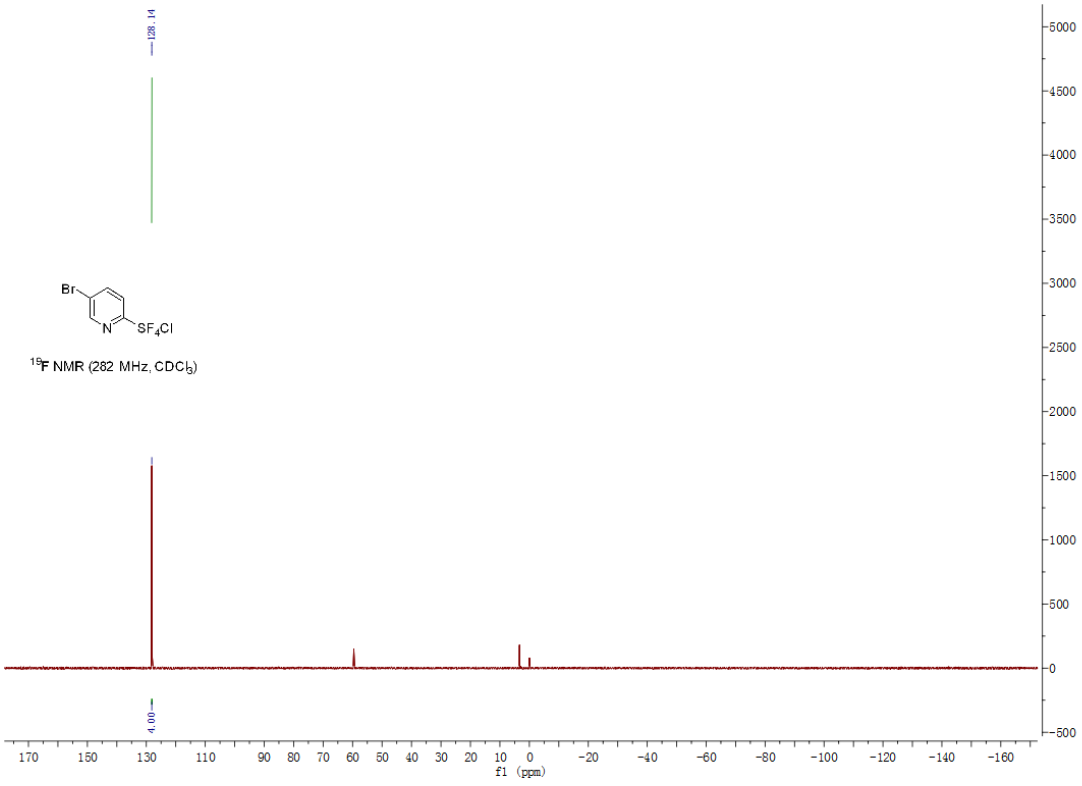


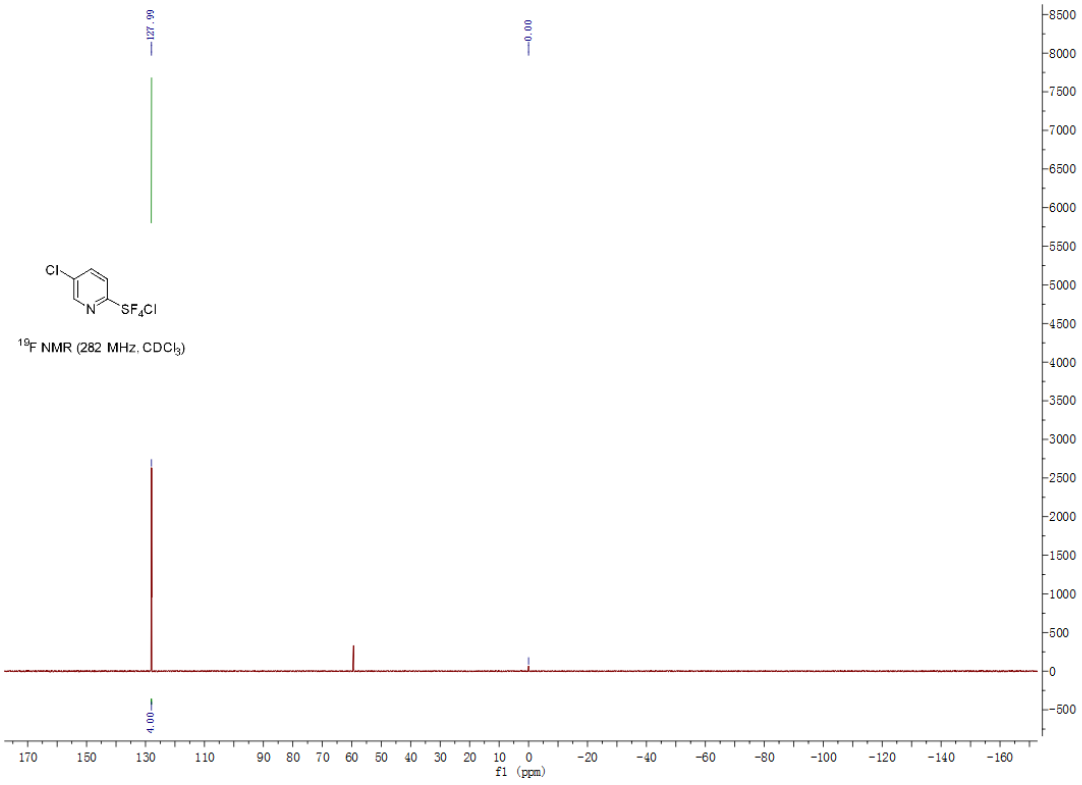


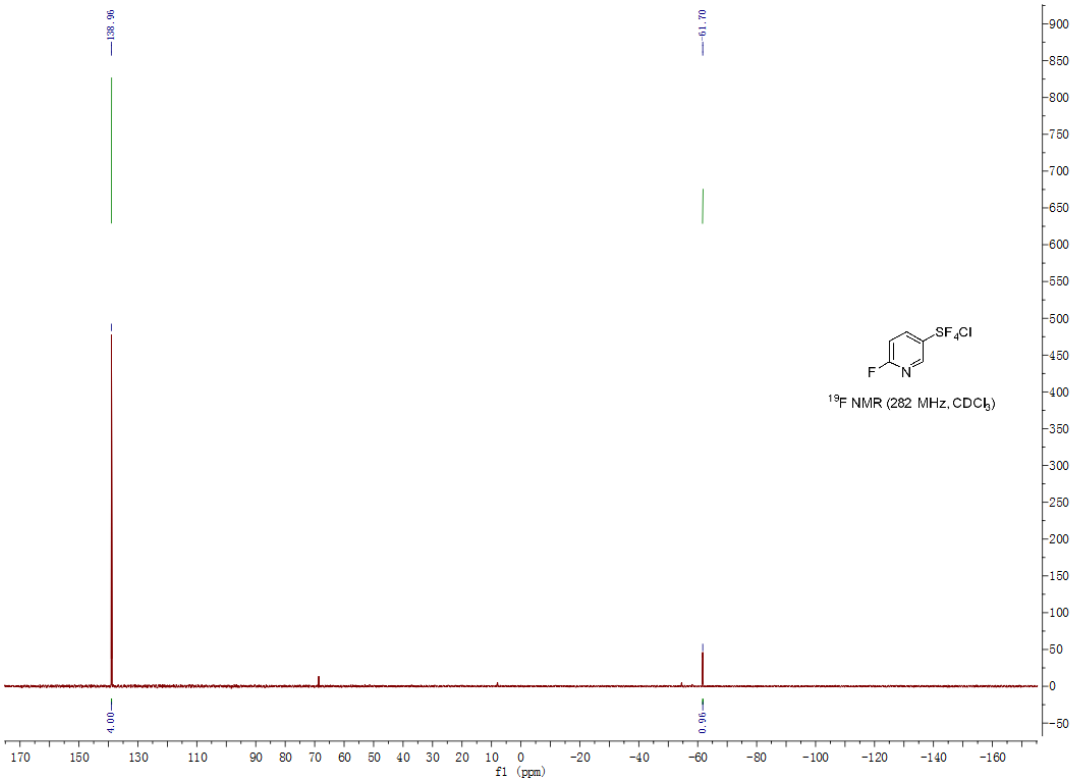
^{19}F (282 MHz, $CDCl_3$)

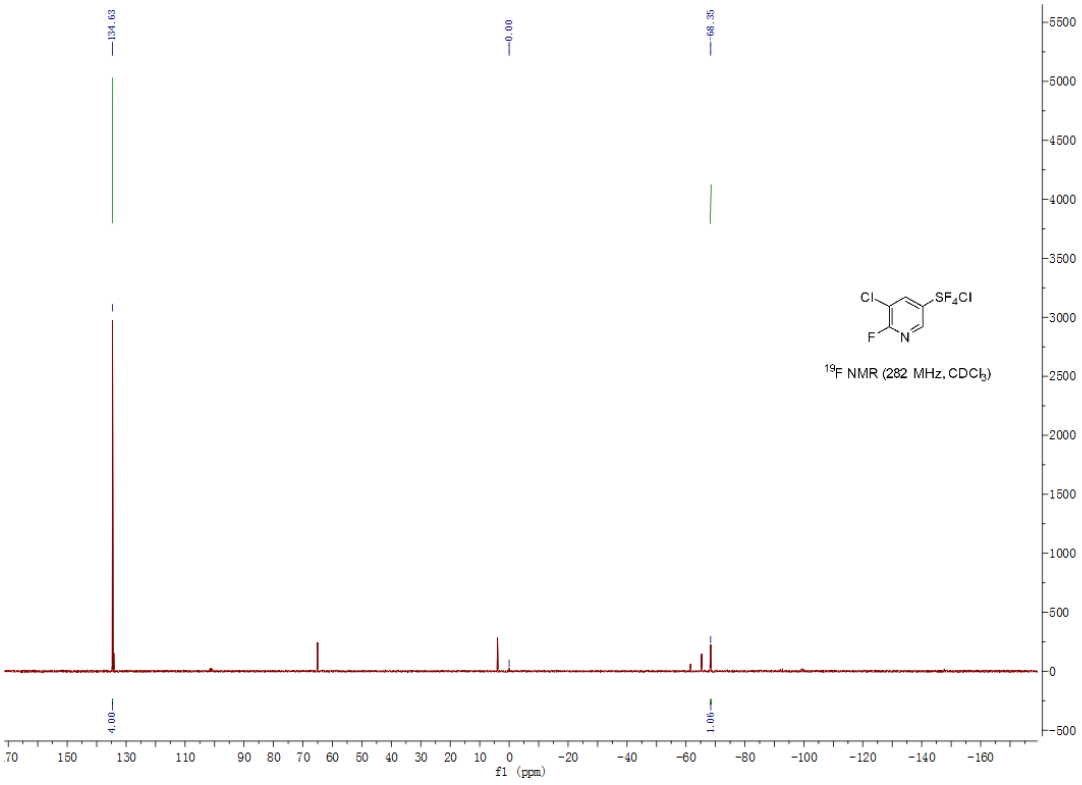


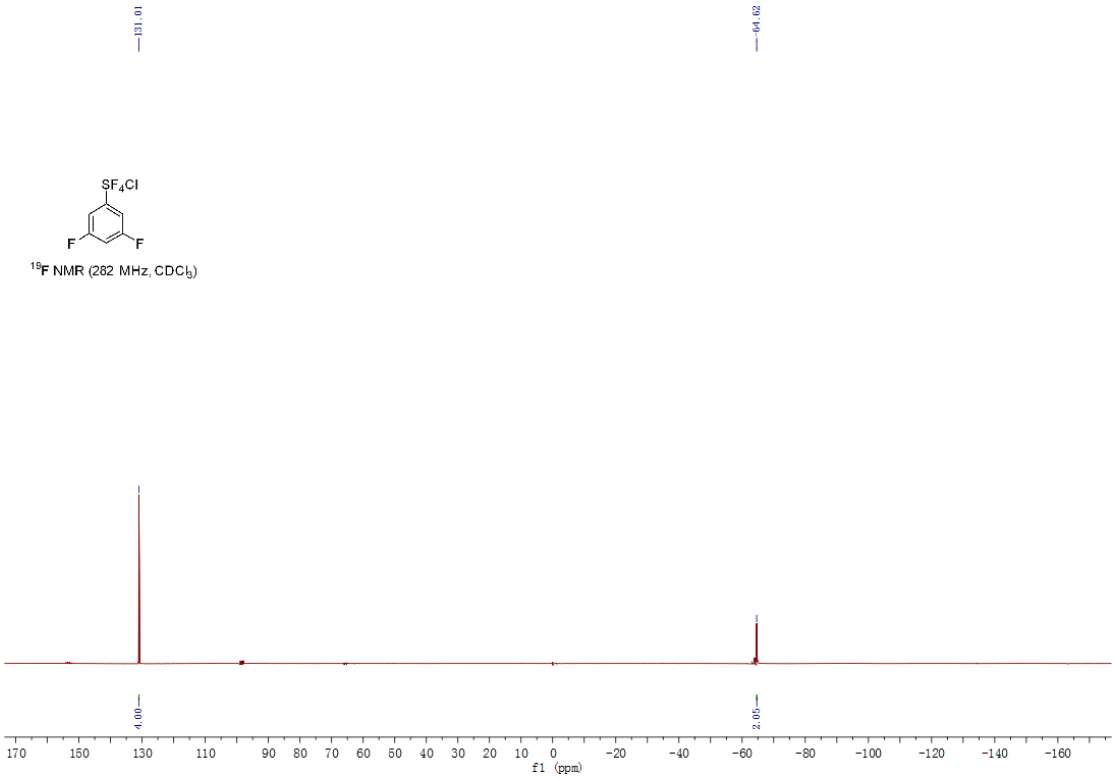
^{19}F NMR (282 MHz, $CDCl_3$)


128.14
Br
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)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

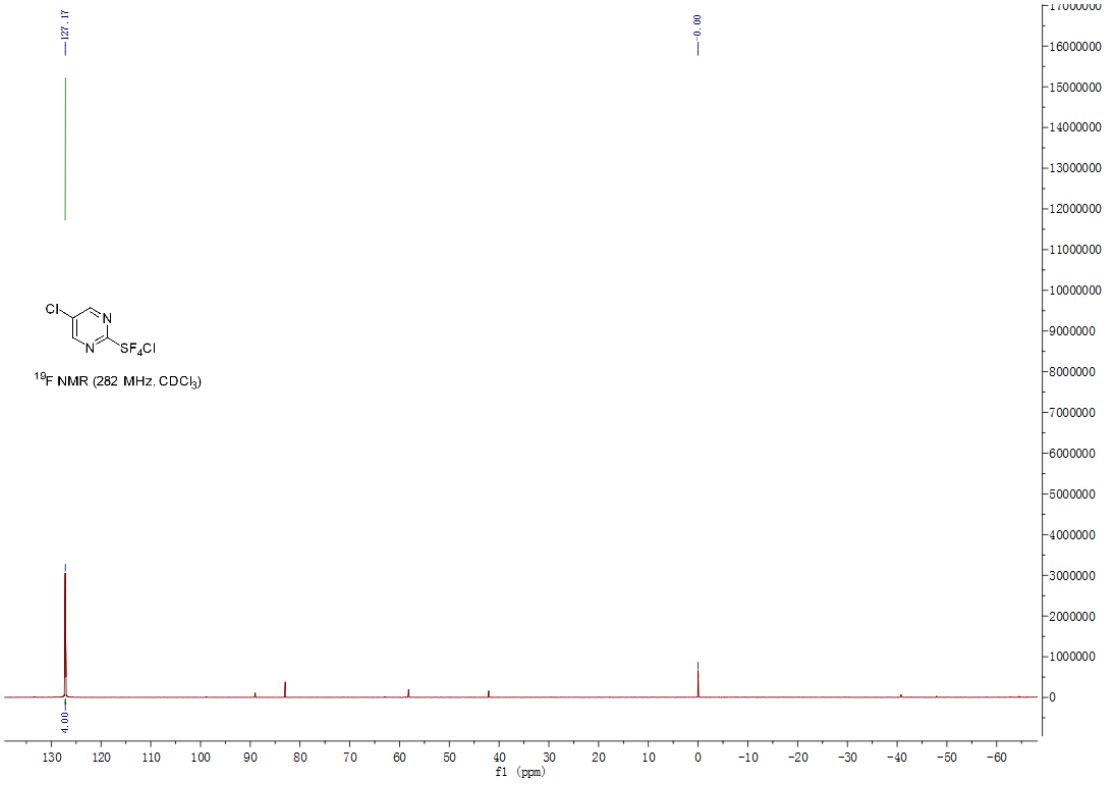

127.99
0.00
Cl
N
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


138.96
61.70
4.00
0.96
f1 (ppm)
^{19}F NMR (282 MHz, CDCl$_3$)

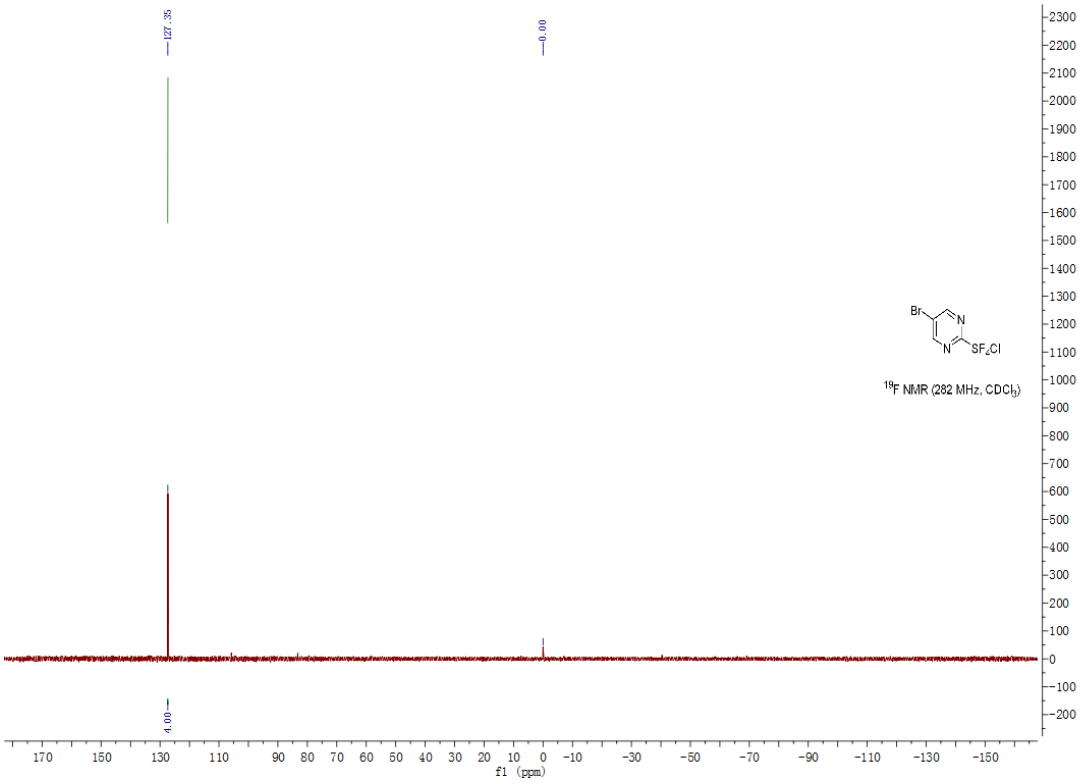

134.63
0.00
68.35
4.00
1.06
f1 (ppm)
^{19}F NMR (282 MHz, CDCl$_3$)

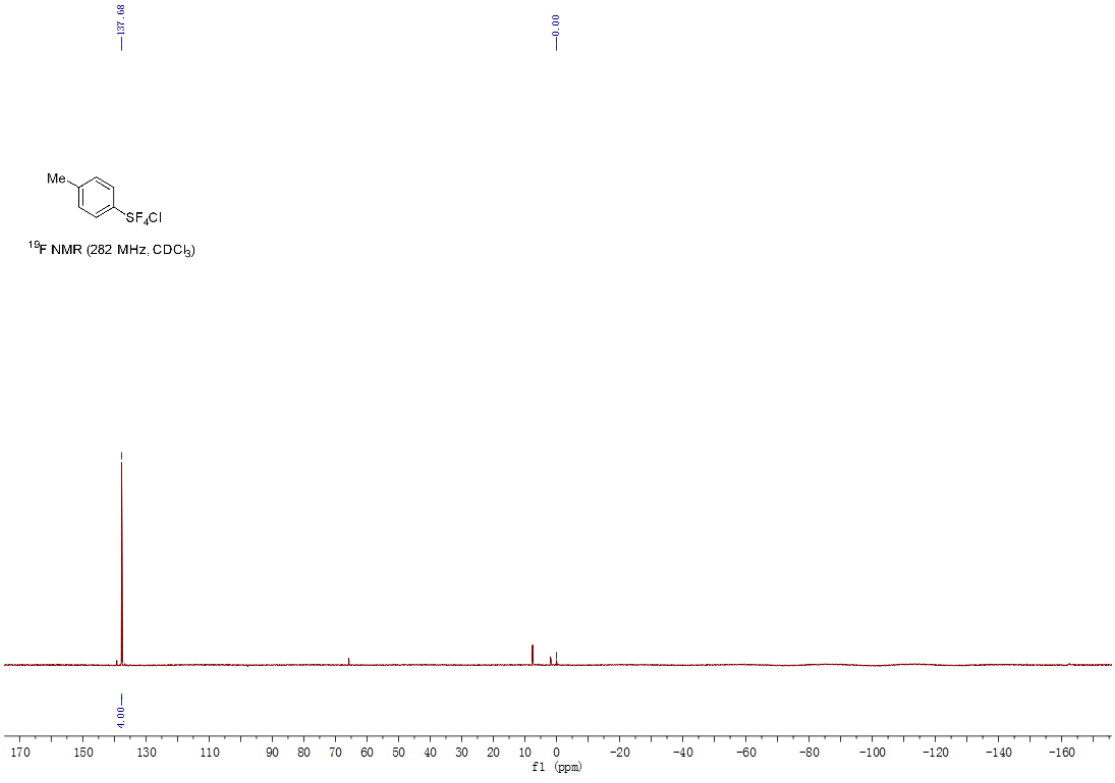


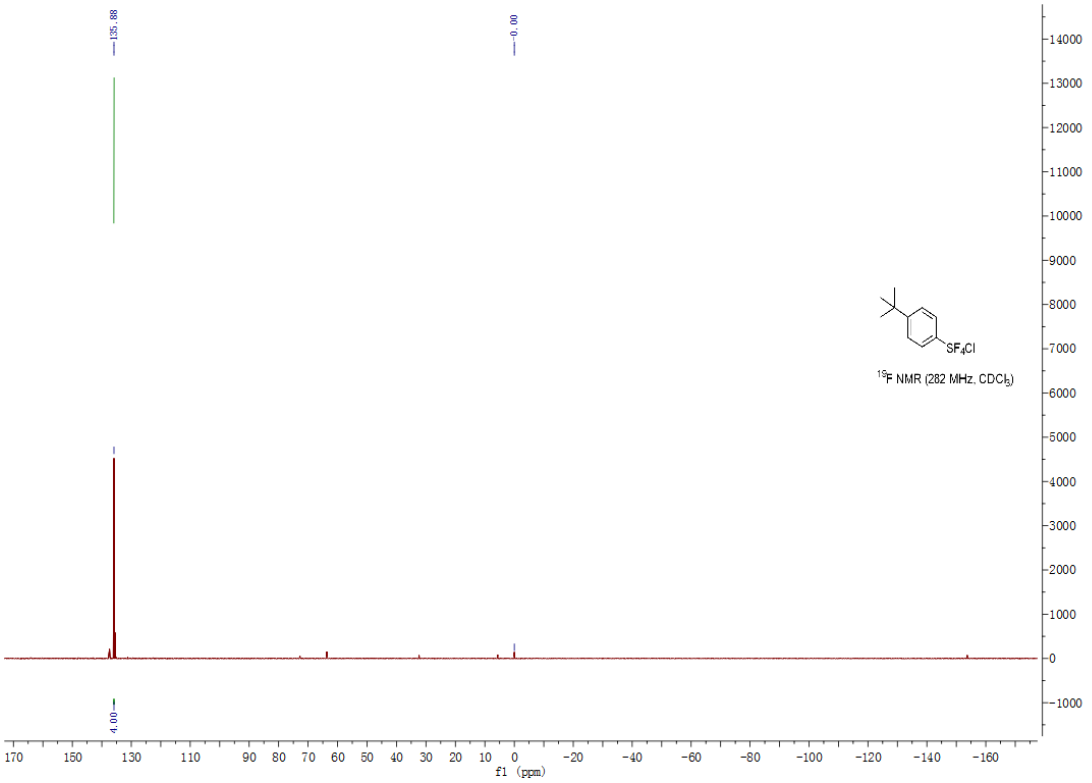
^{19}F NMR (282 MHz, $CDCl_3$)

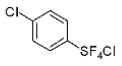


^{19}F NMR (282 MHz, $CDCl_3$)

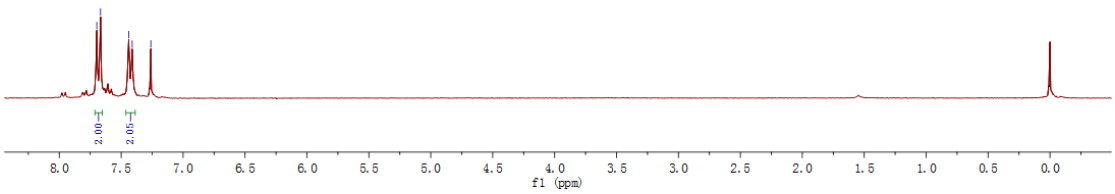

127.35
0.00
Br
N
N
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
f1 (ppm)

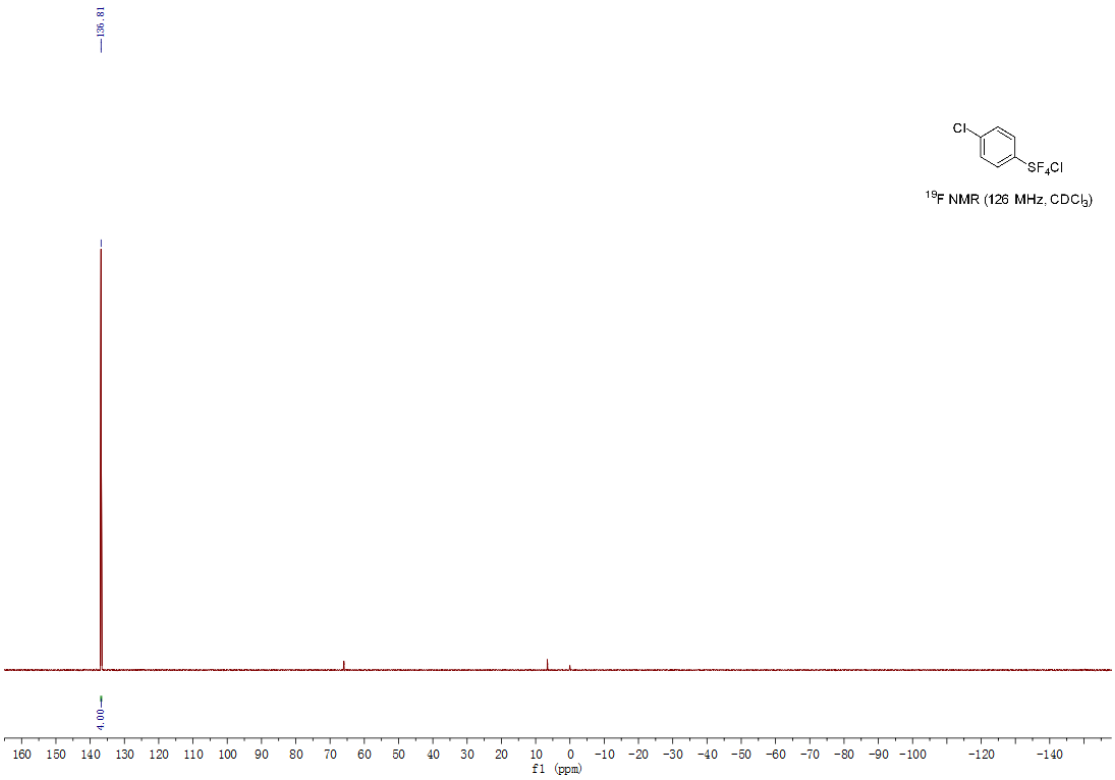

137.68
0.00
Me
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
f1 (ppm)

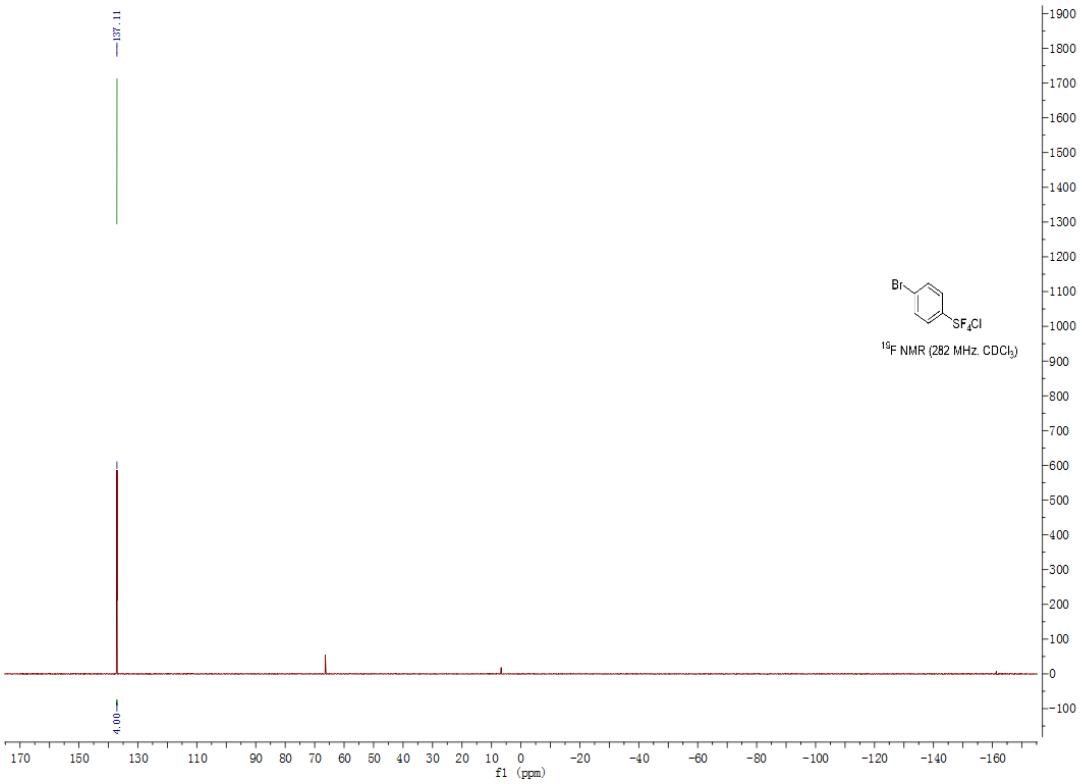


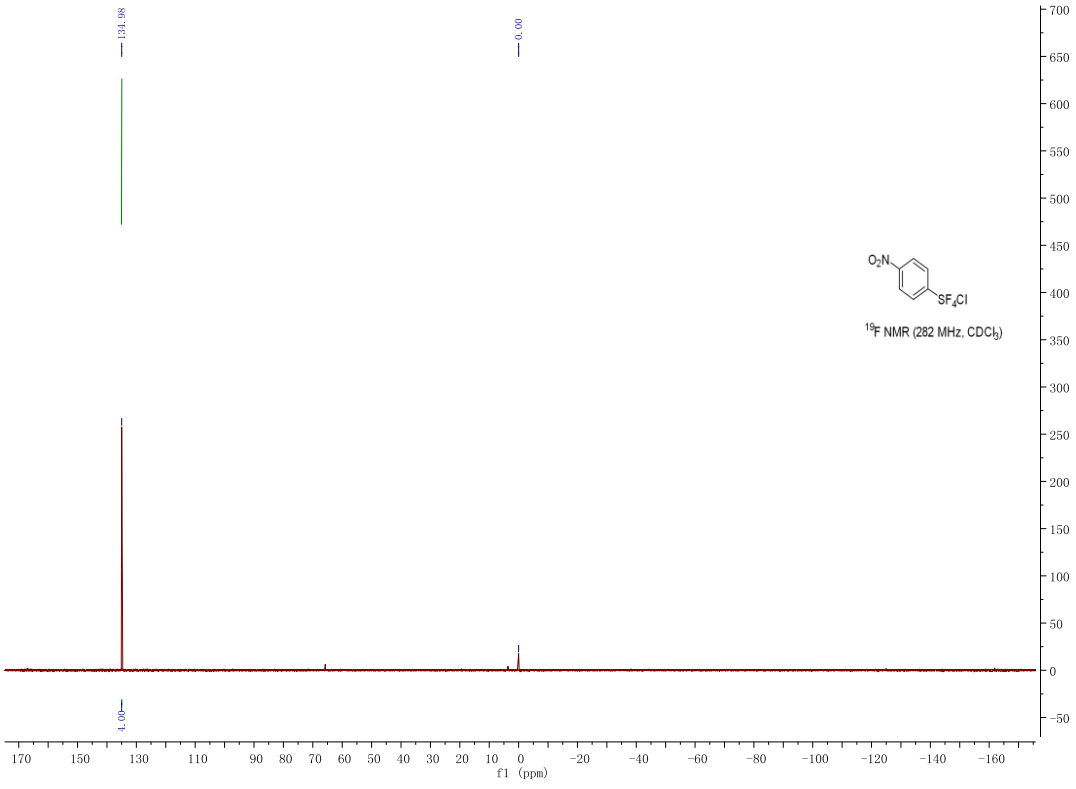


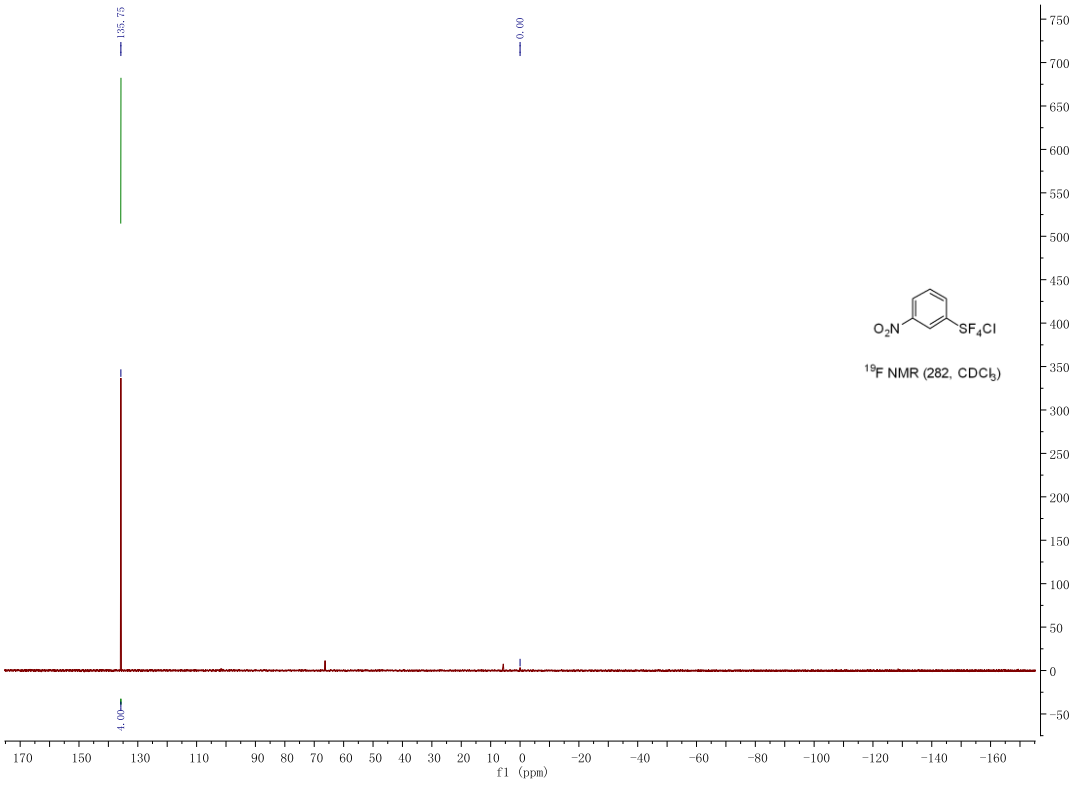
^{1}H NMR (300MHz, $CDCl_3$)

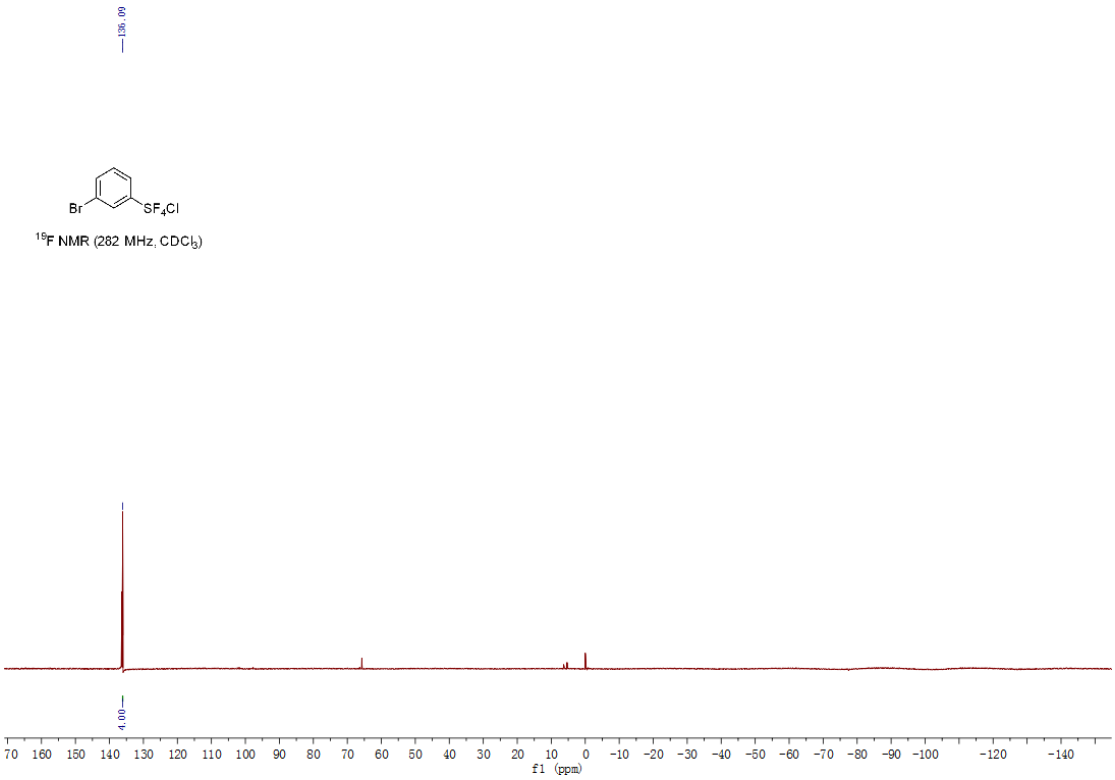


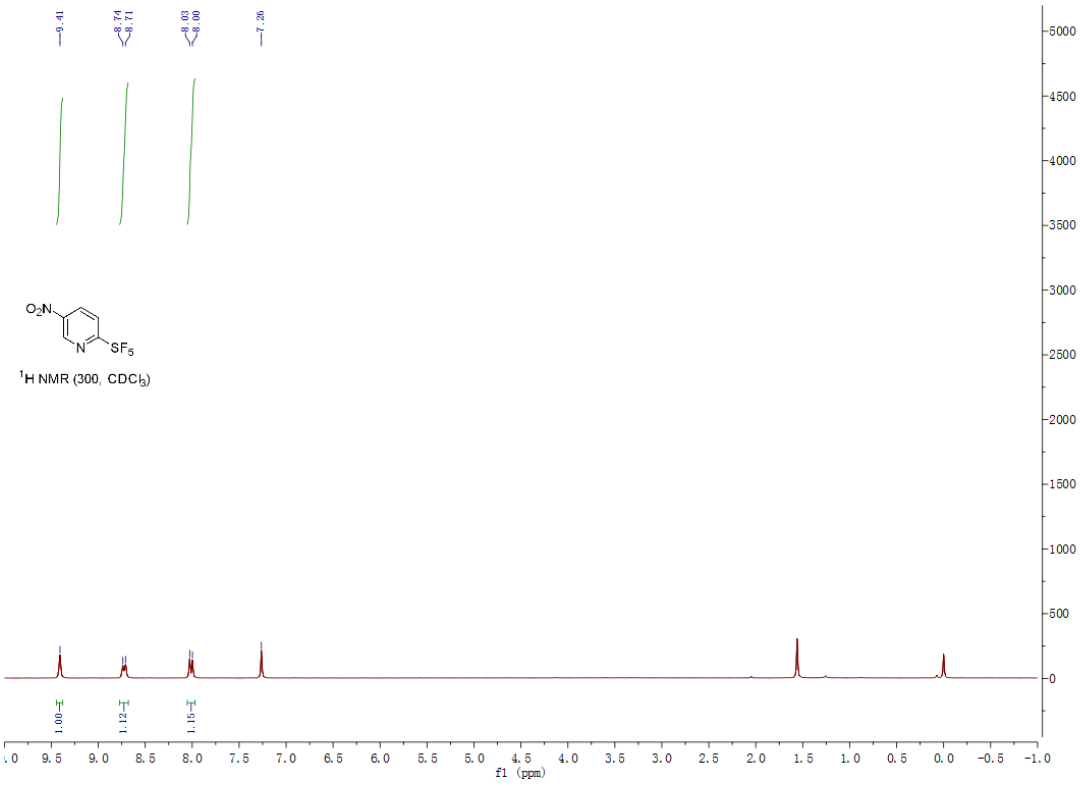

136.81
Cl
SF4Cl
19F NMR (126 MHz, CDCl3)
4.00
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
f1 (ppm)

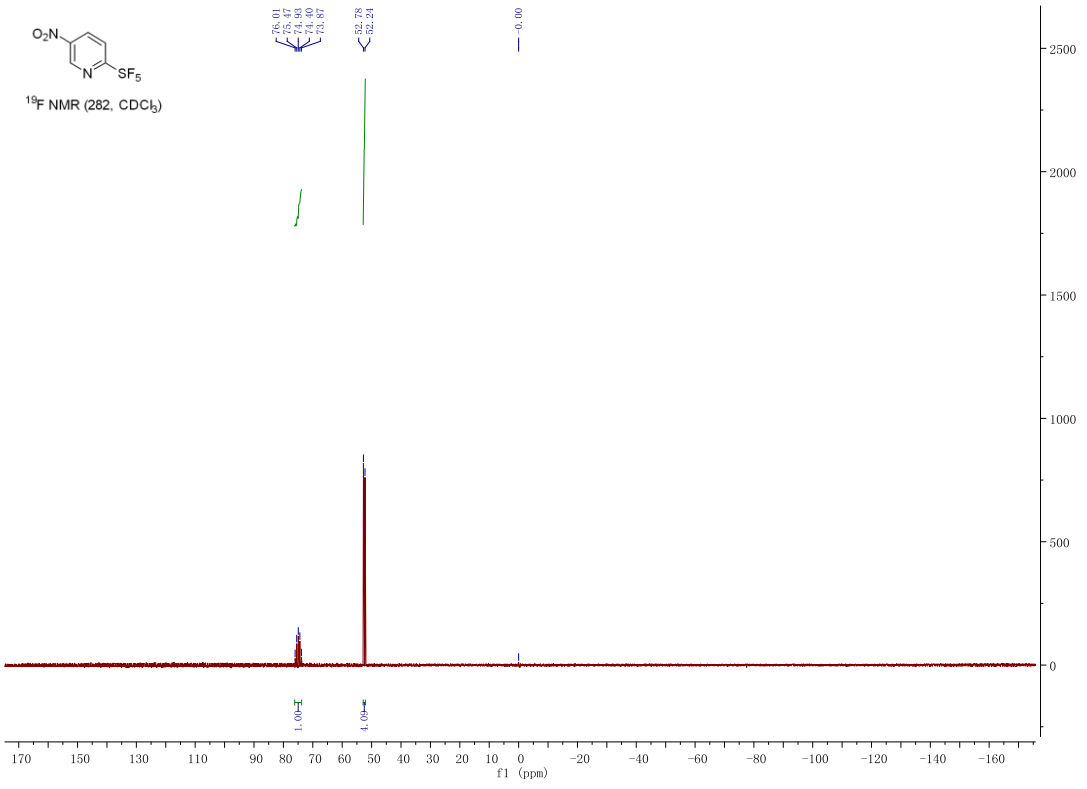

137.11
Br
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)

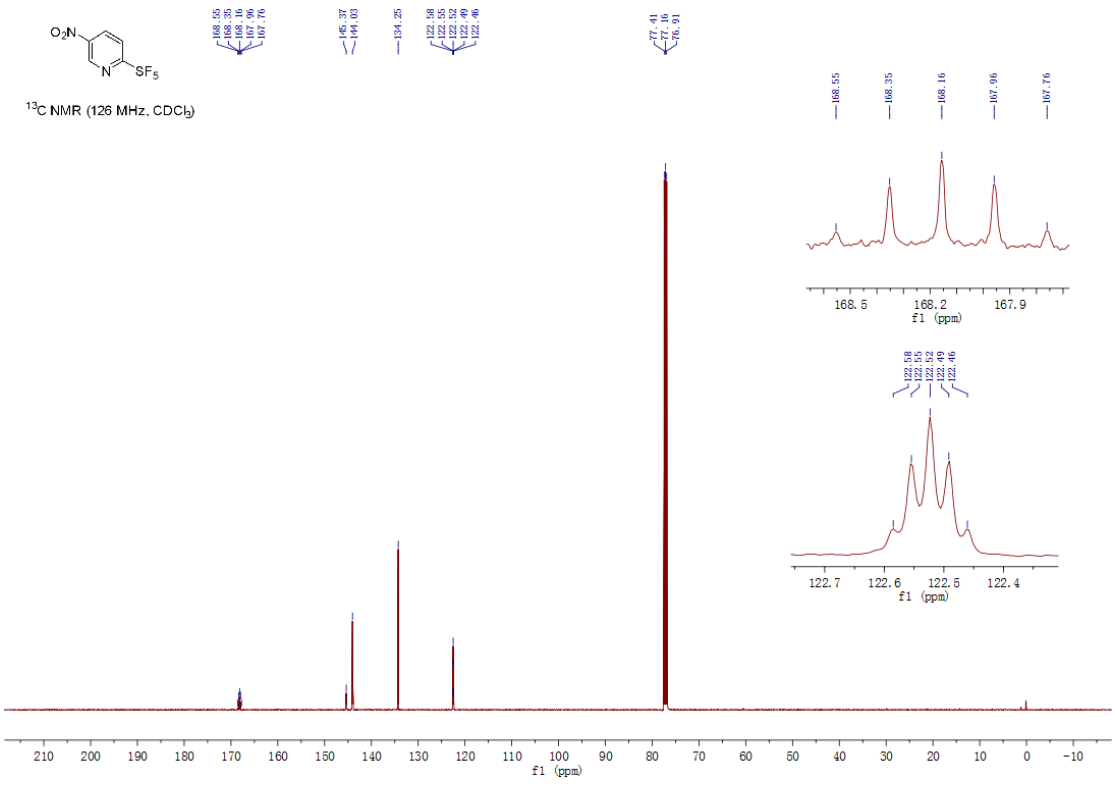

134.98
0.00
4.00
O2N
SF4Cl
19F NMR (282 MHz, CDCl3)
f1 (ppm)

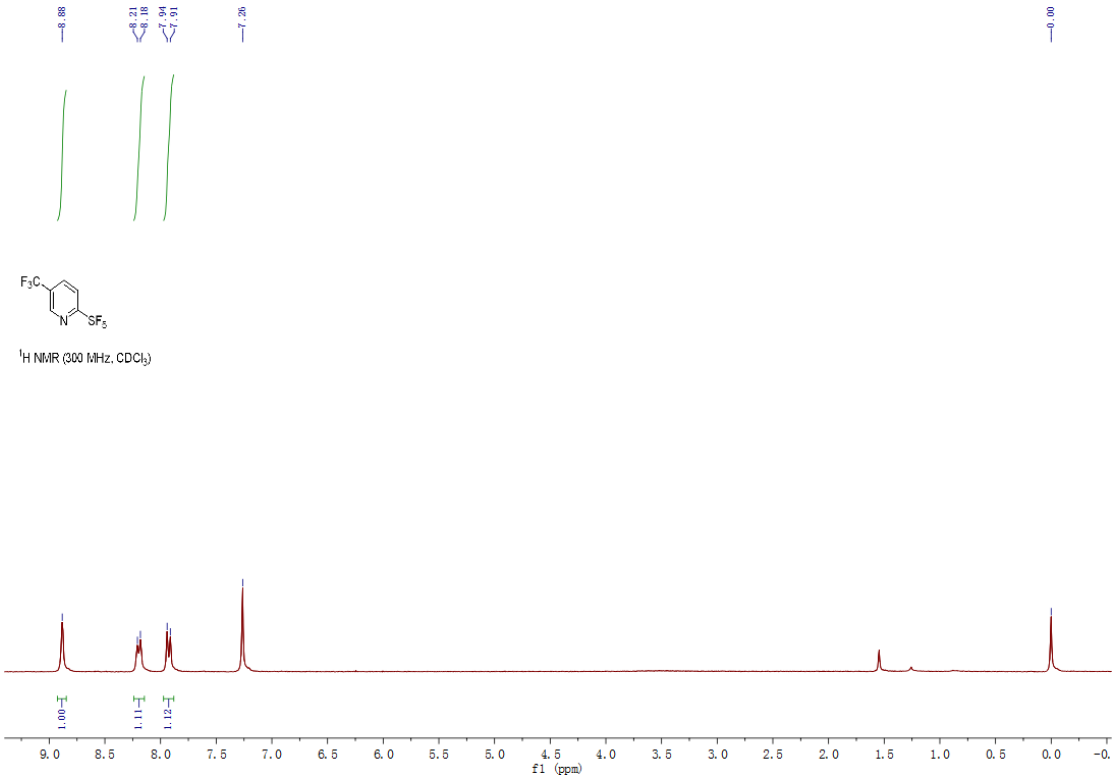

135.75
0.00
4.00
O2N
SF4Cl
19F NMR (282, CDCl3)
f1 (ppm)

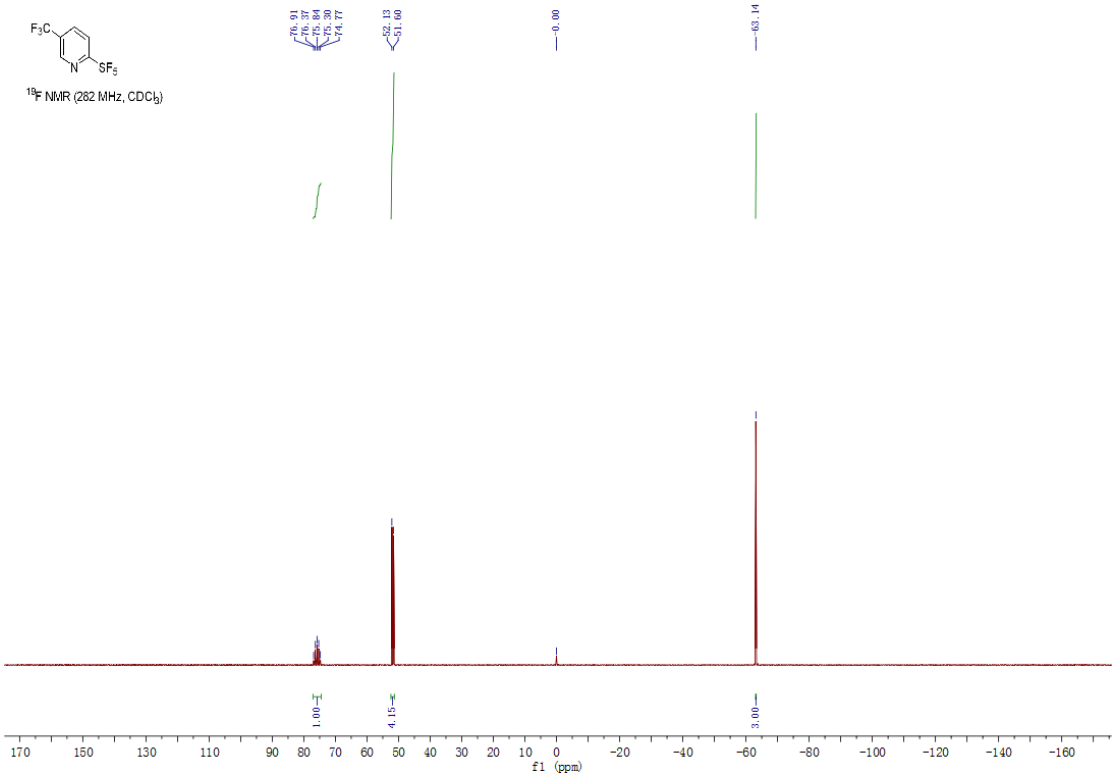

136.09
Br
SF4Cl
19F NMR (282 MHz, CDCl3)
4.00
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
f1 (ppm)

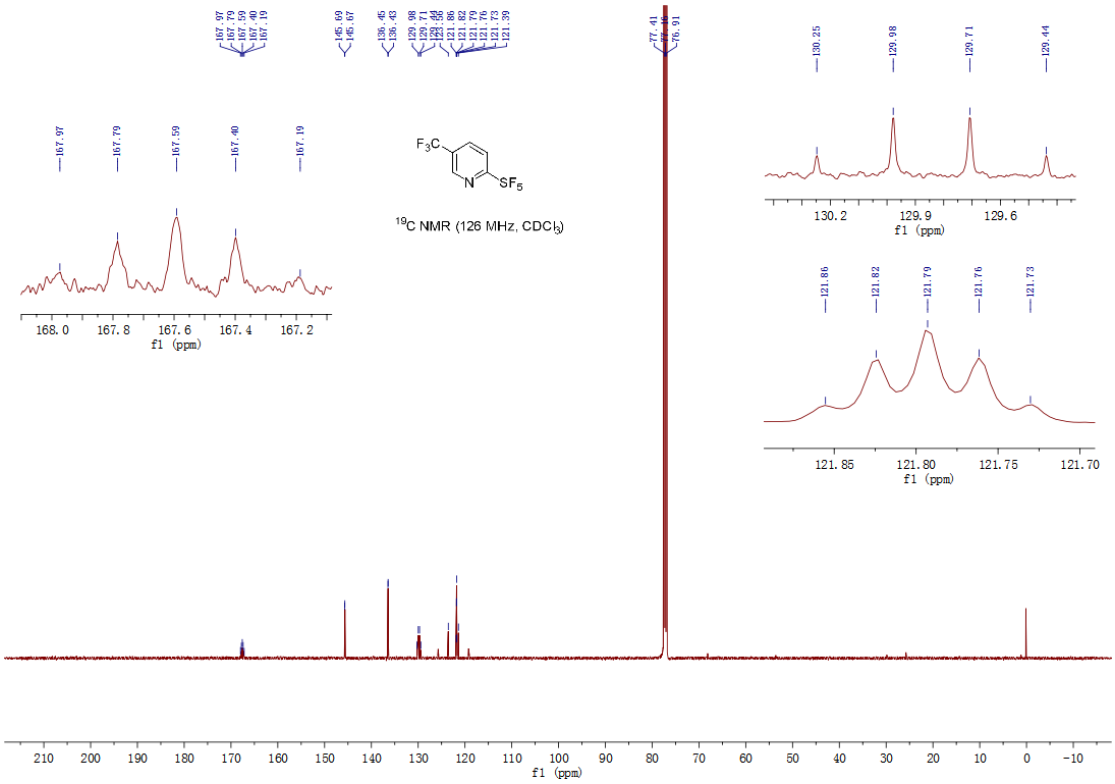

9.41
8.74
8.71
8.03
8.00
7.26
O2N
N
SF5
1H NMR (300, CDCl3)
1.00
1.12
1.15
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

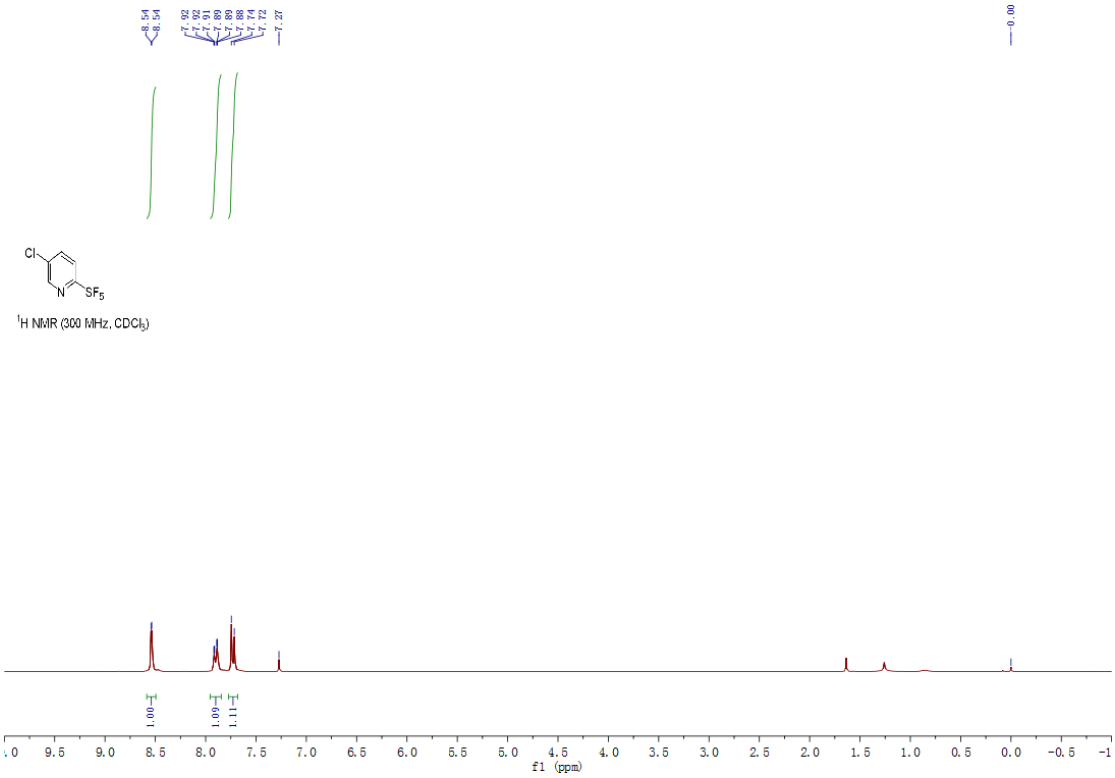

^{19}F NMR (282, CDCl$_3$)
76.01
75.47
74.93
74.40
73.87
52.78
52.24
-0.00
1.00
4.00
f1 (ppm)

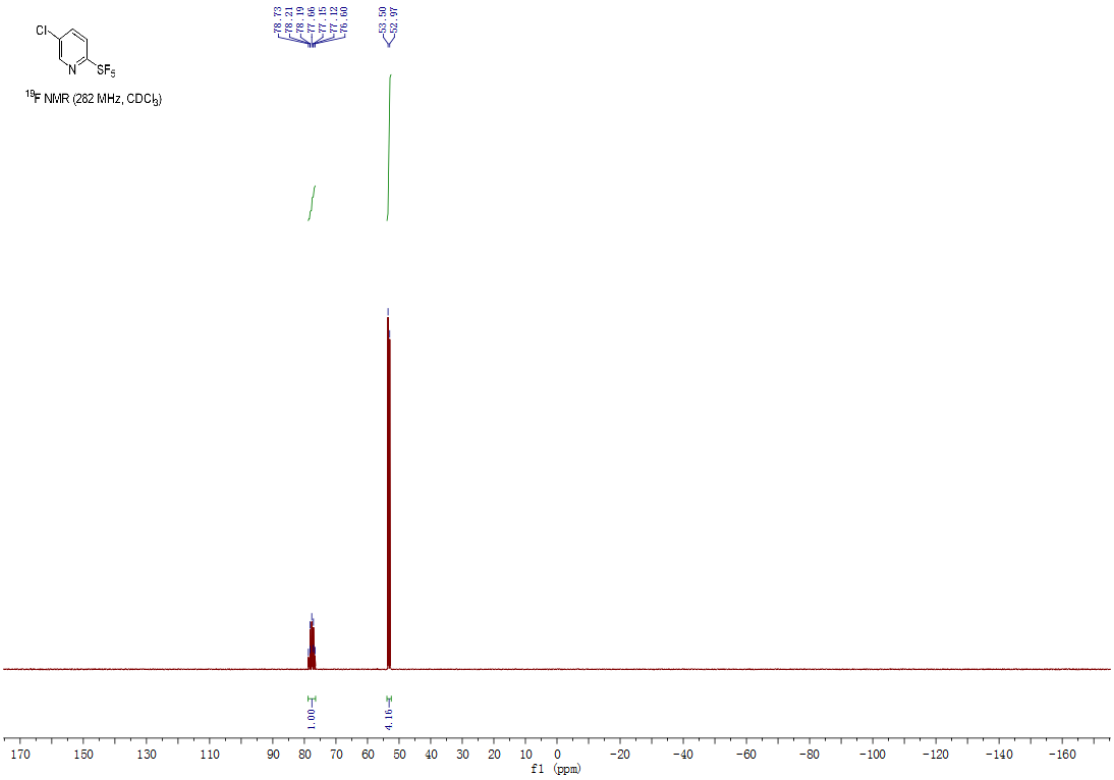

^{13}C NMR (126 MHz, CDCl$_3$)
168.55
168.35
168.16
167.96
167.76
145.37
144.03
134.25
122.58
122.55
122.52
122.49
122.46
77.41
77.16
76.91
f1 (ppm)


8.88
8.21
8.18
7.94
7.91
7.26
0.00
F3C
N
SF5
1H NMR (300 MHz, CDCl3)
1.00
1.11
1.12
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 -0.
f1 (ppm)

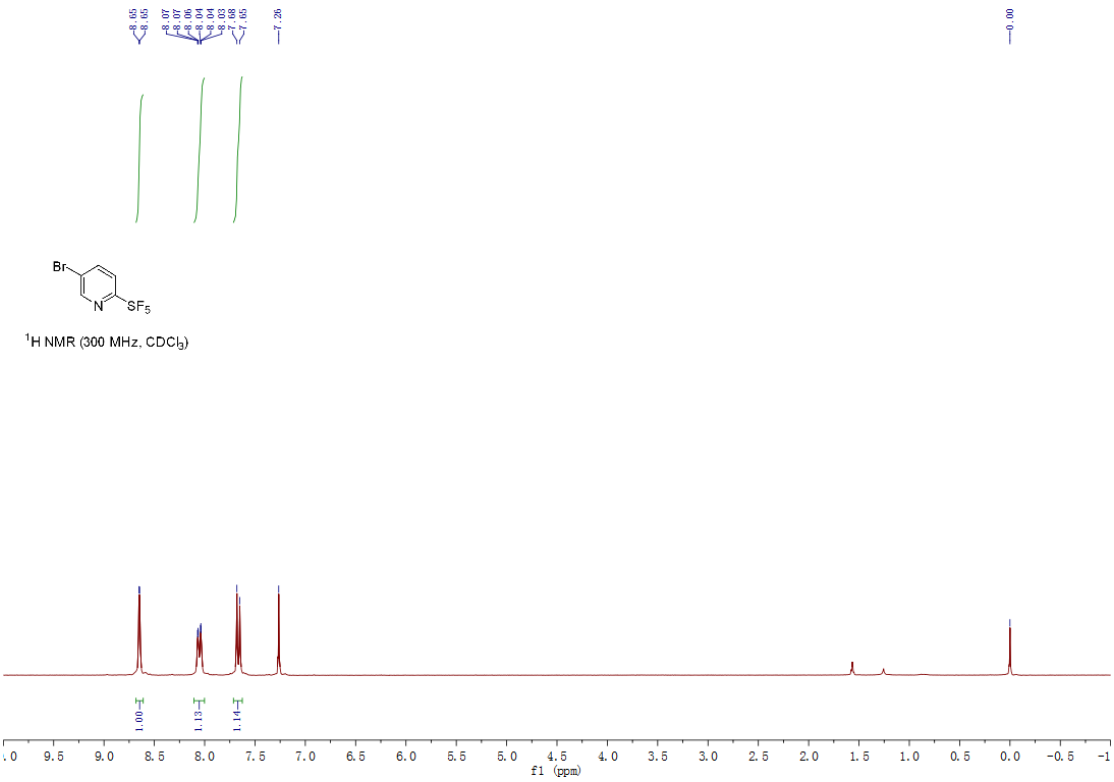

F3C
N
SF5
19F NMR (282 MHz, CDCl3)
76.91
76.37
75.84
75.30
74.77
62.13
61.60
0.00
-63.14
1.00
4.15
3.00
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)


^{19}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

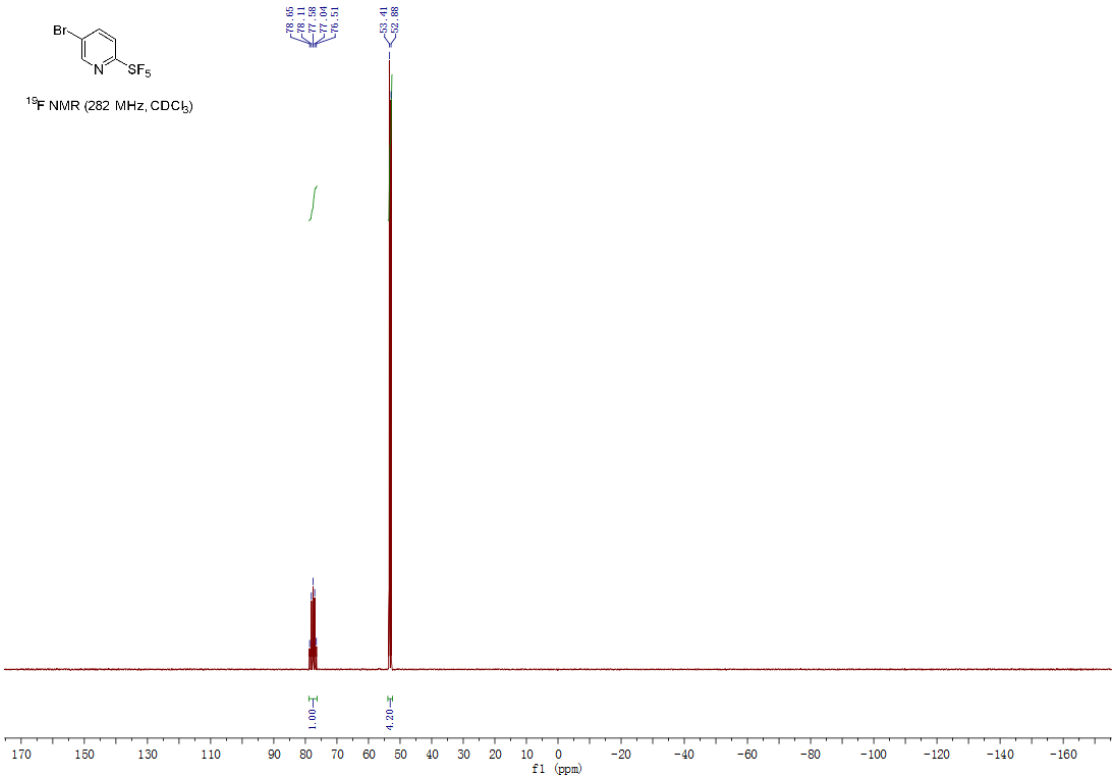

^{1}H NMR (300 MHz, CDCl$_3$)
f1 (ppm)

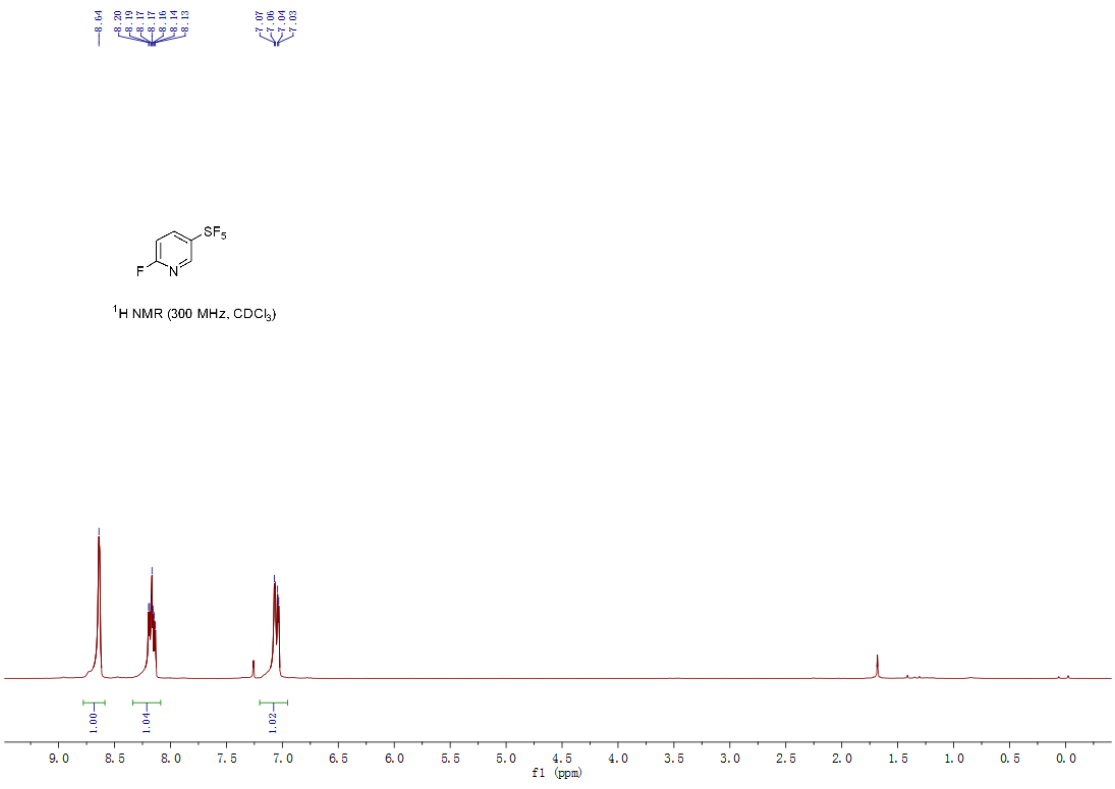


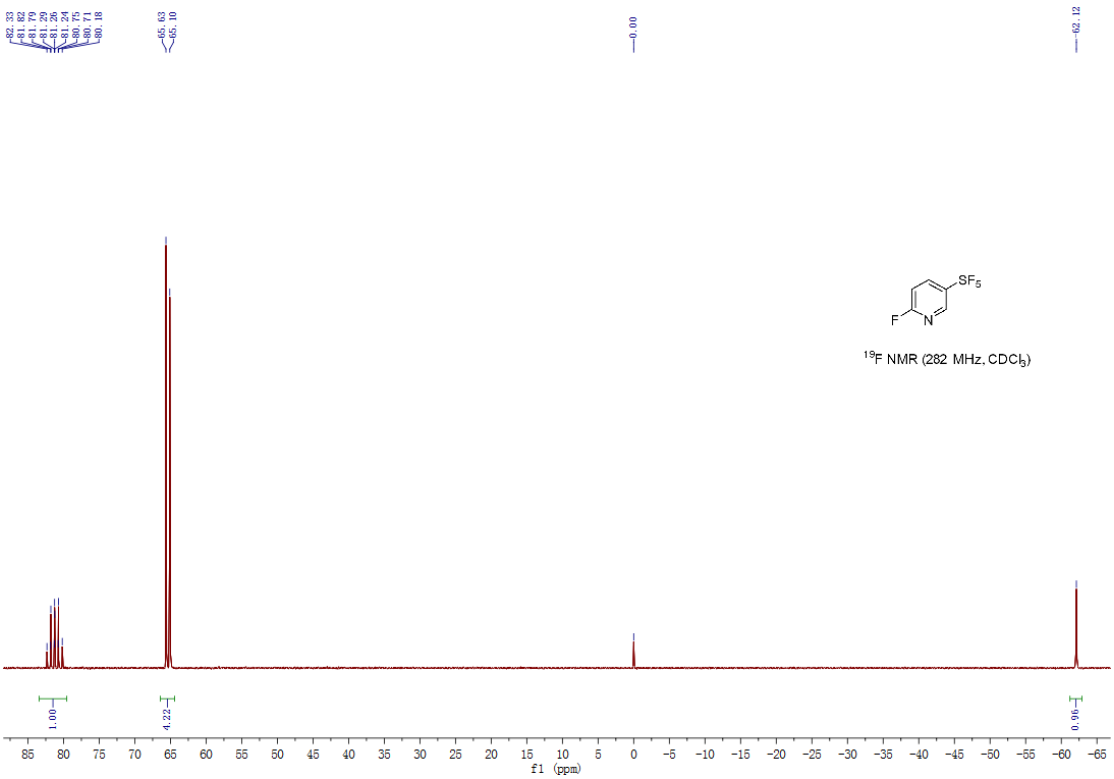
^{19}F NMR (282 MHz, $CDCl_3$)



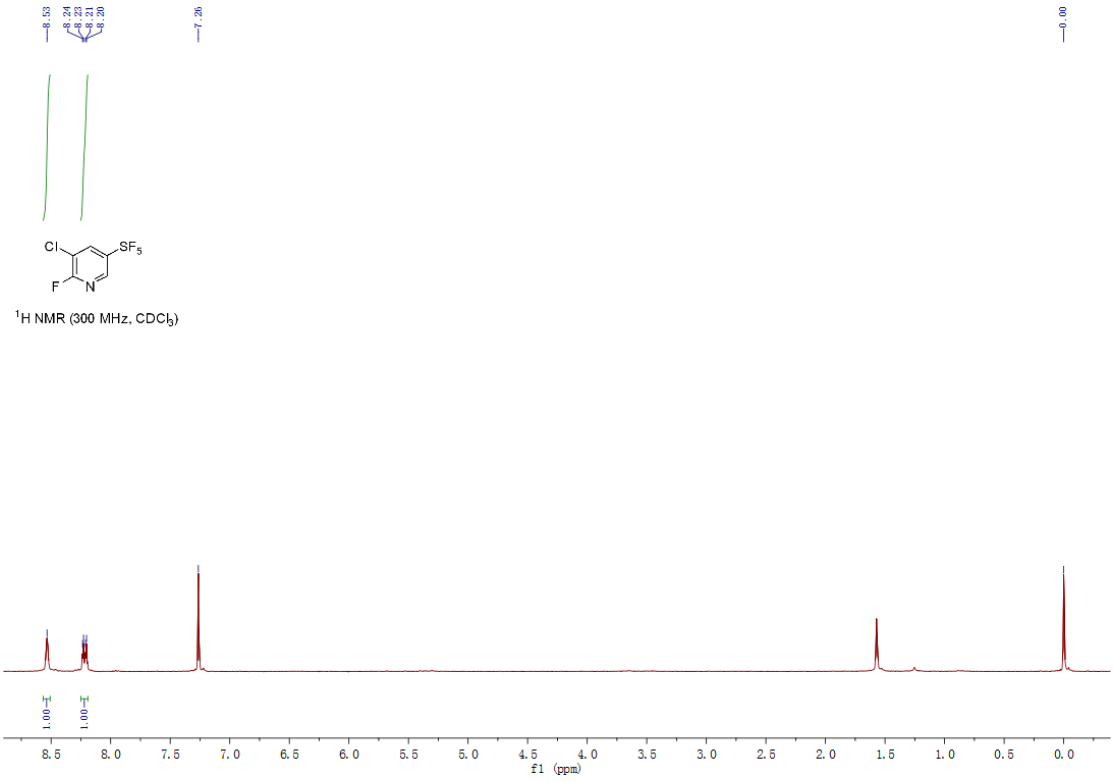
^{1}H NMR (300 MHz, $CDCl_3$)


Br
N
SF5
19F NMR (282 MHz, CDCl3)
78.65
78.11
77.58
77.04
76.51
53.41
52.88
1.00
4.20
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)

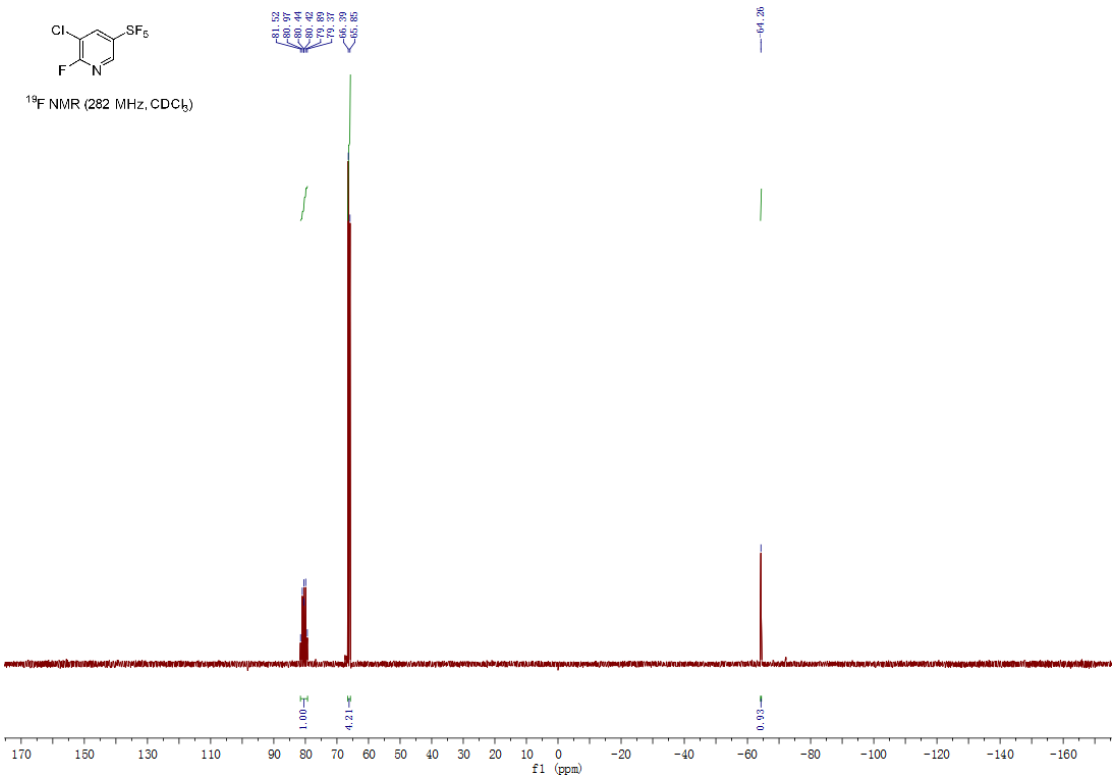

8.64
8.20
8.19
8.17
8.17
8.16
8.14
8.13
7.07
7.06
7.04
7.03
SF5
F
N
1H NMR (300 MHz, CDCl3)
1.00
1.04
1.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

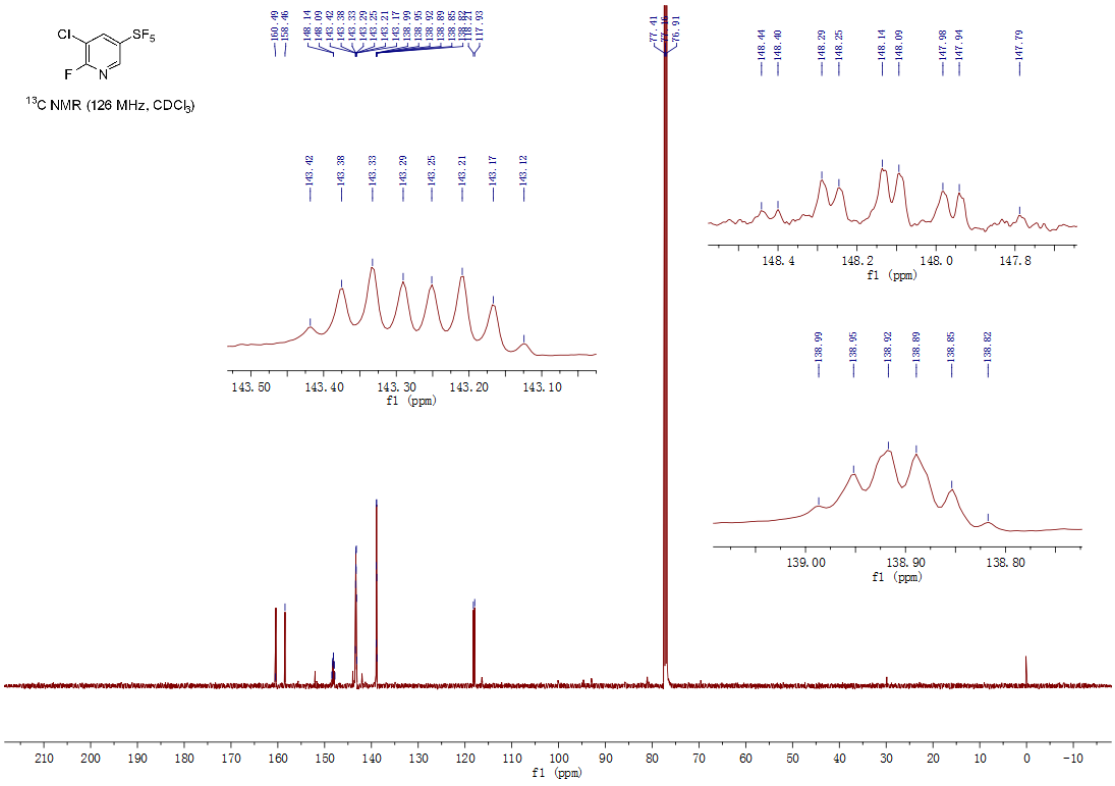


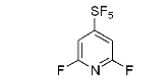
^{19}F NMR (282 MHz, $CDCl_3$)



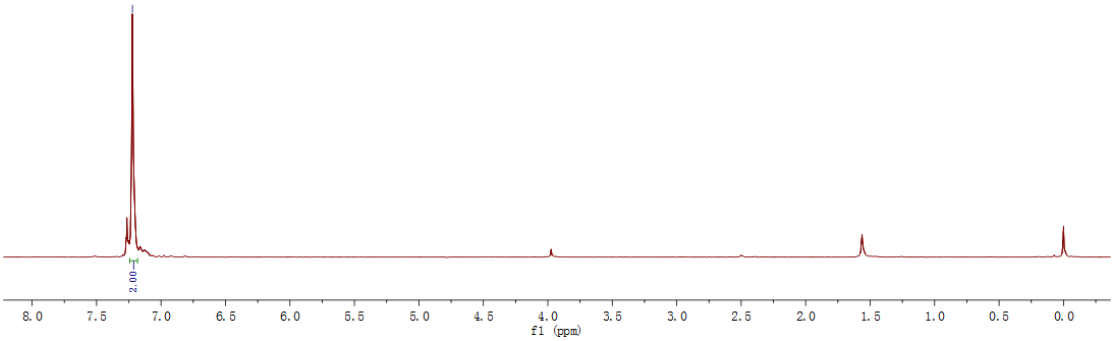
^{1}H NMR (300 MHz, $CDCl_3$)

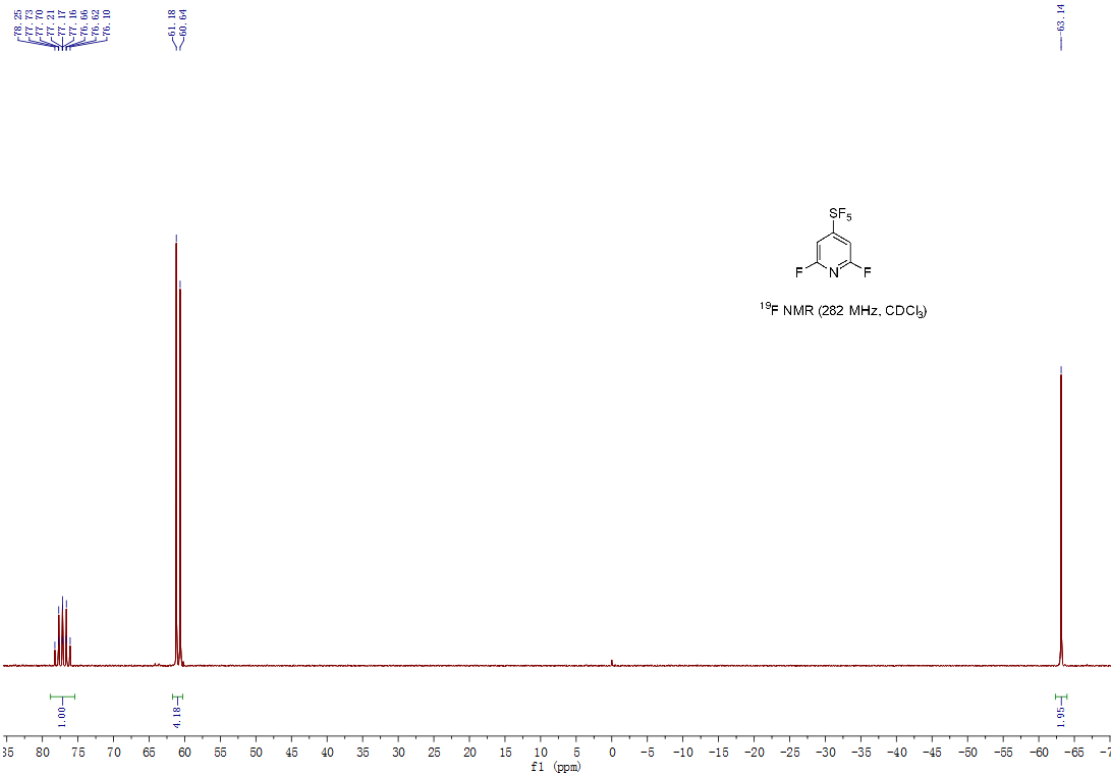

Cl
SF5
F
N
19F NMR (282 MHz, CDCl3)
81.52
80.97
80.44
80.07
79.89
79.37
66.39
65.85
64.26
1.00
4.21
0.93
f1 (ppm)


Cl
SF5
F
N
13C NMR (126 MHz, CDCl3)
160.49
158.46
148.14
148.09
143.42
143.38
143.33
143.29
143.25
143.21
143.17
138.99
138.95
138.92
138.89
138.85
138.82
117.93
77.41
77.16
76.91
148.44
148.40
148.29
148.25
148.14
148.09
147.98
147.94
147.79
143.42
143.38
143.33
143.29
143.25
143.21
143.17
143.12
138.99
138.95
138.92
138.89
138.85
138.82
f1 (ppm)



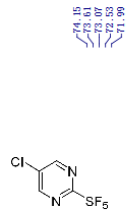
^{1}H NMR (300 MHz, $CDCl_3$)



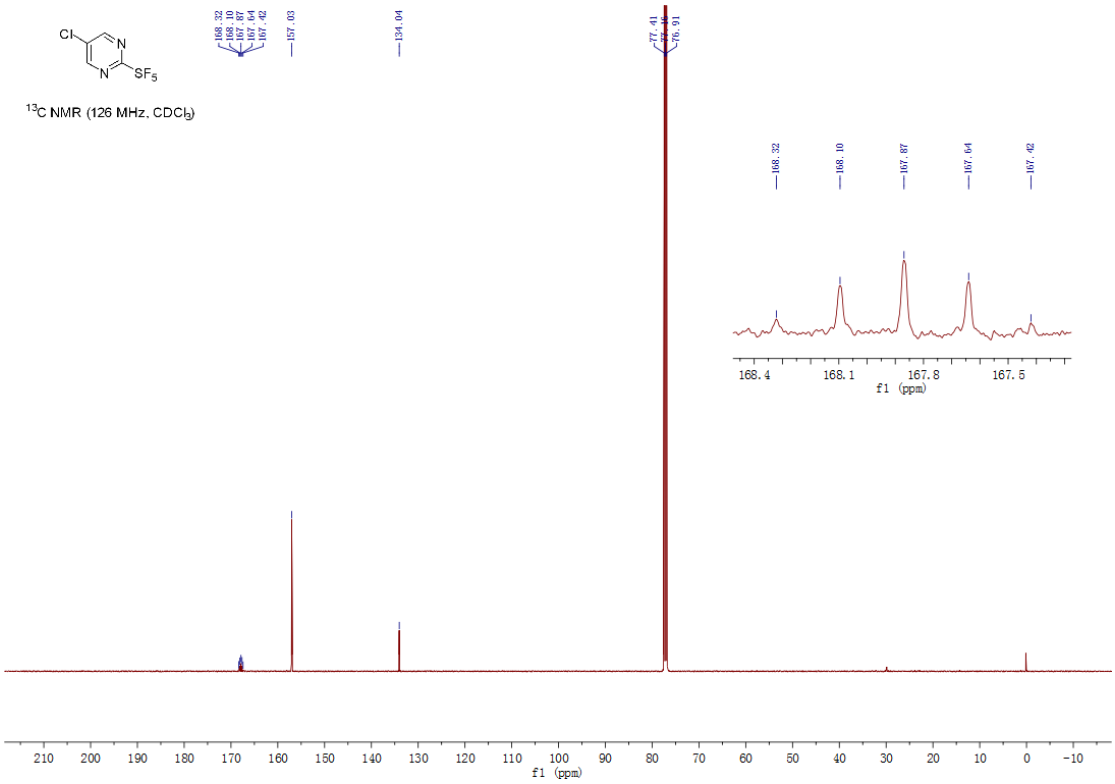


^{19}F NMR (282 MHz, $CDCl_3$)

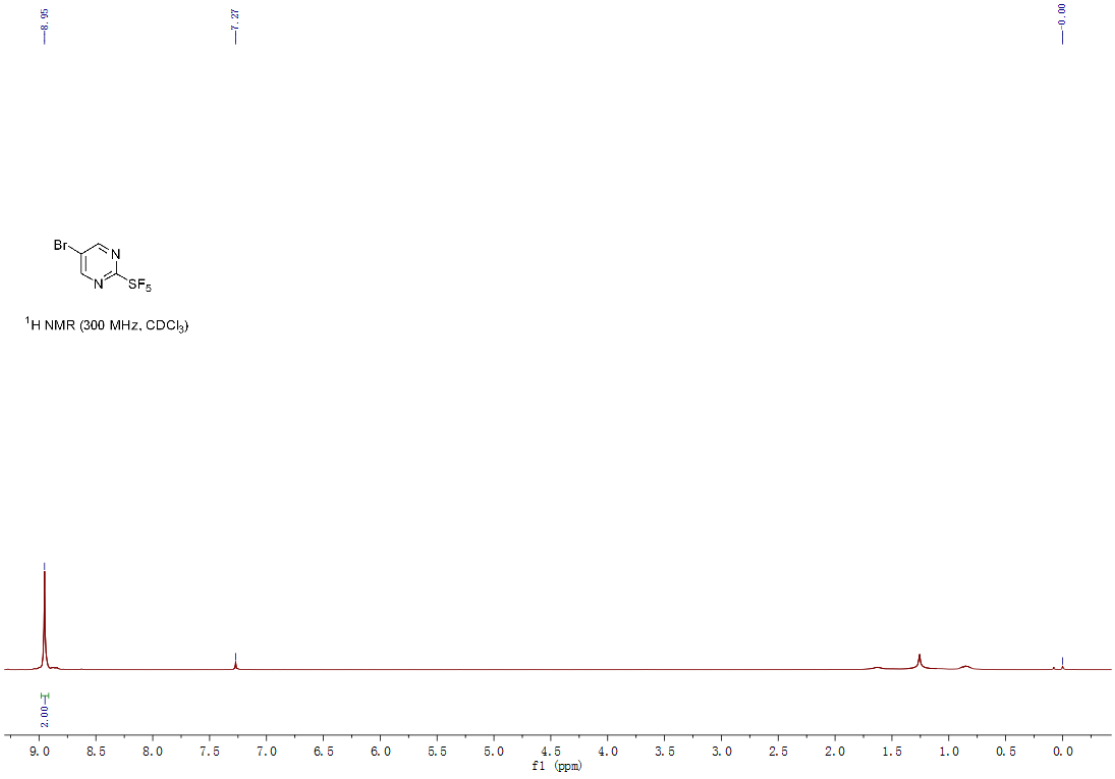
^{1}H NMR (300 MHz, $CDCl_3$)



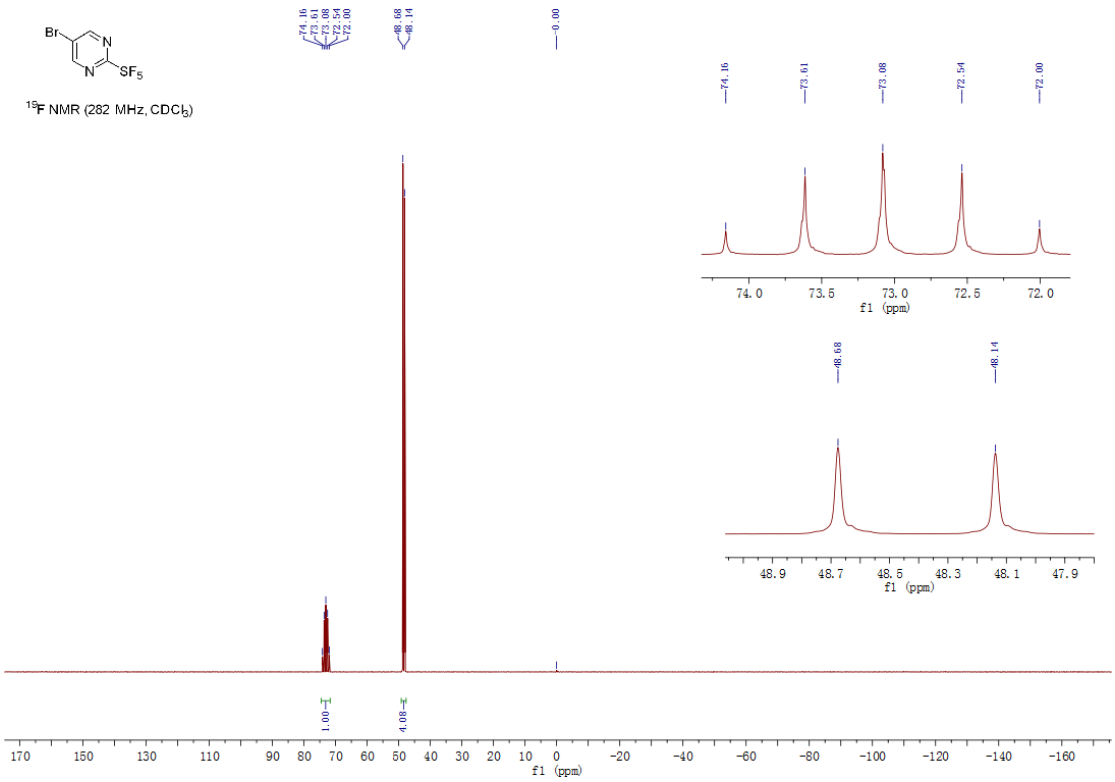
^{19}F NMR (282 HMz, $CDCl_3$)

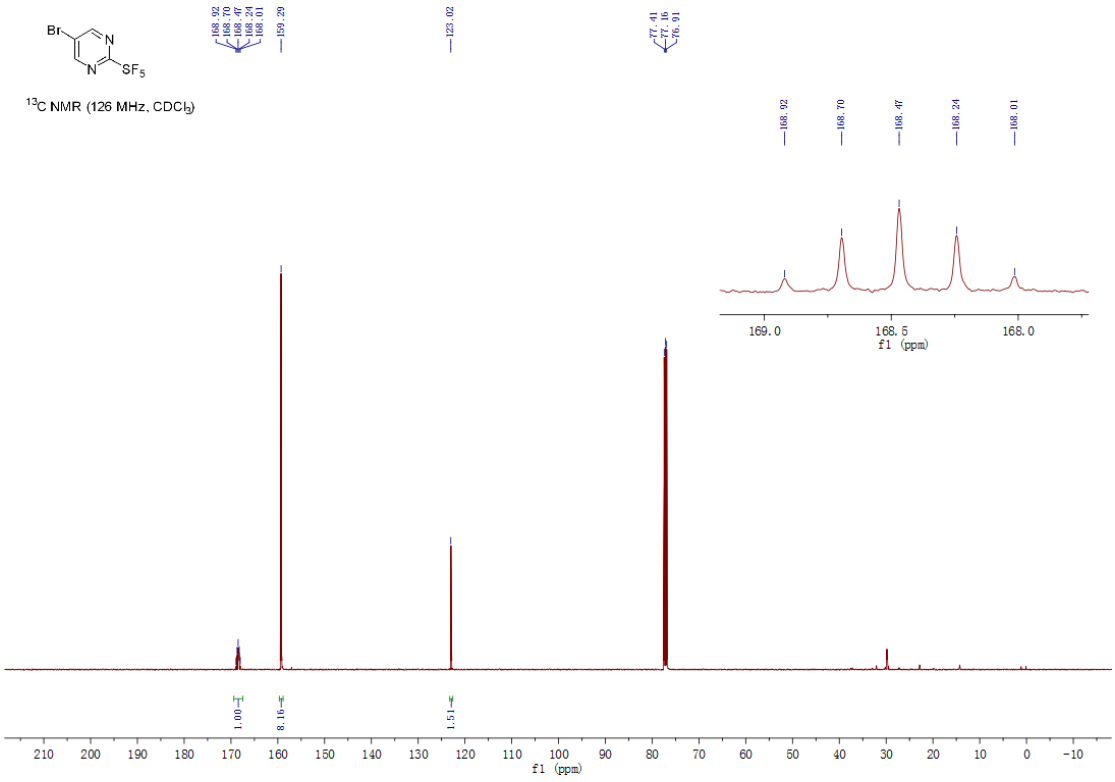


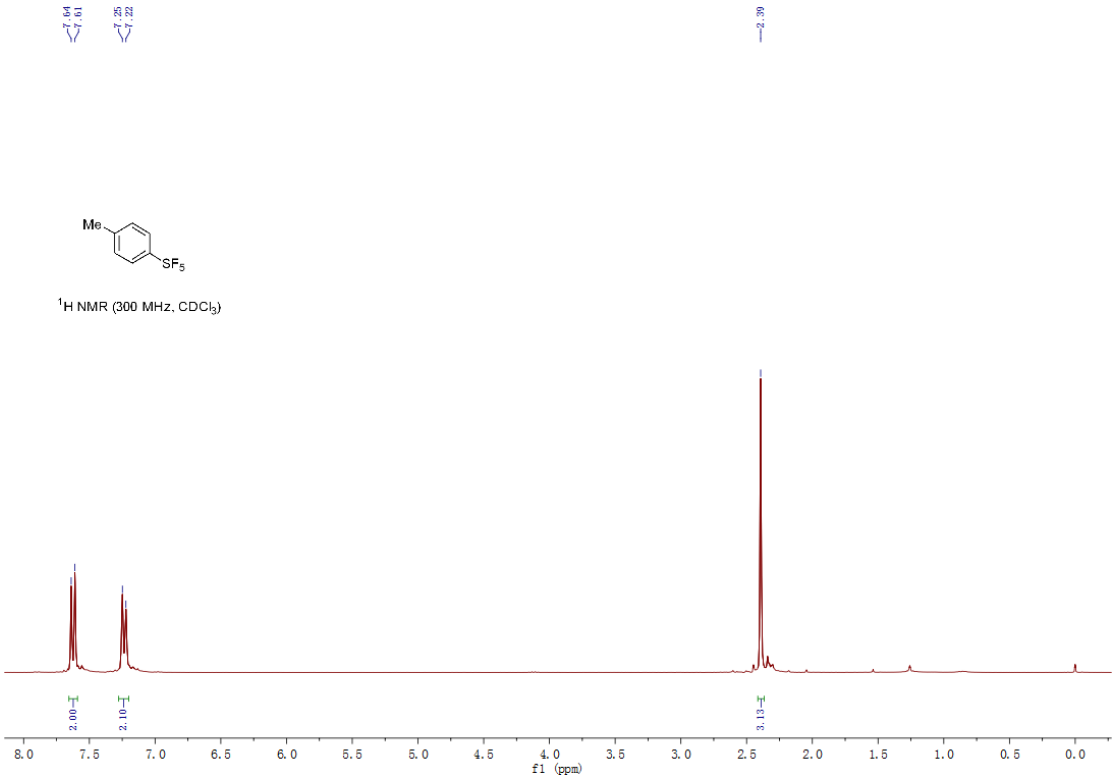
^{13}C NMR (126 MHz, $CDCl_3$)



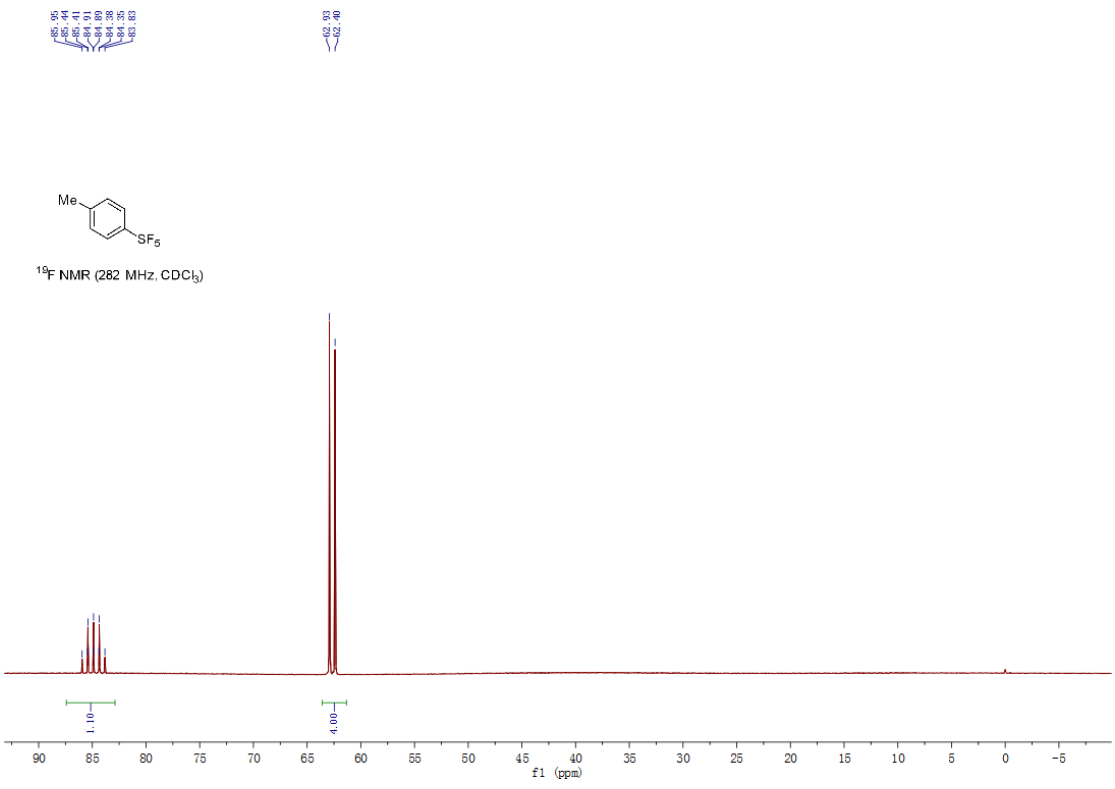
^{1}H NMR (300 MHz, $CDCl_3$)


Br
N
N
SF5
19F NMR (282 MHz, CDCl3)
74.16
73.61
73.08
72.54
72.00
48.68
48.14
0.00
1.00
4.08
f1 (ppm)

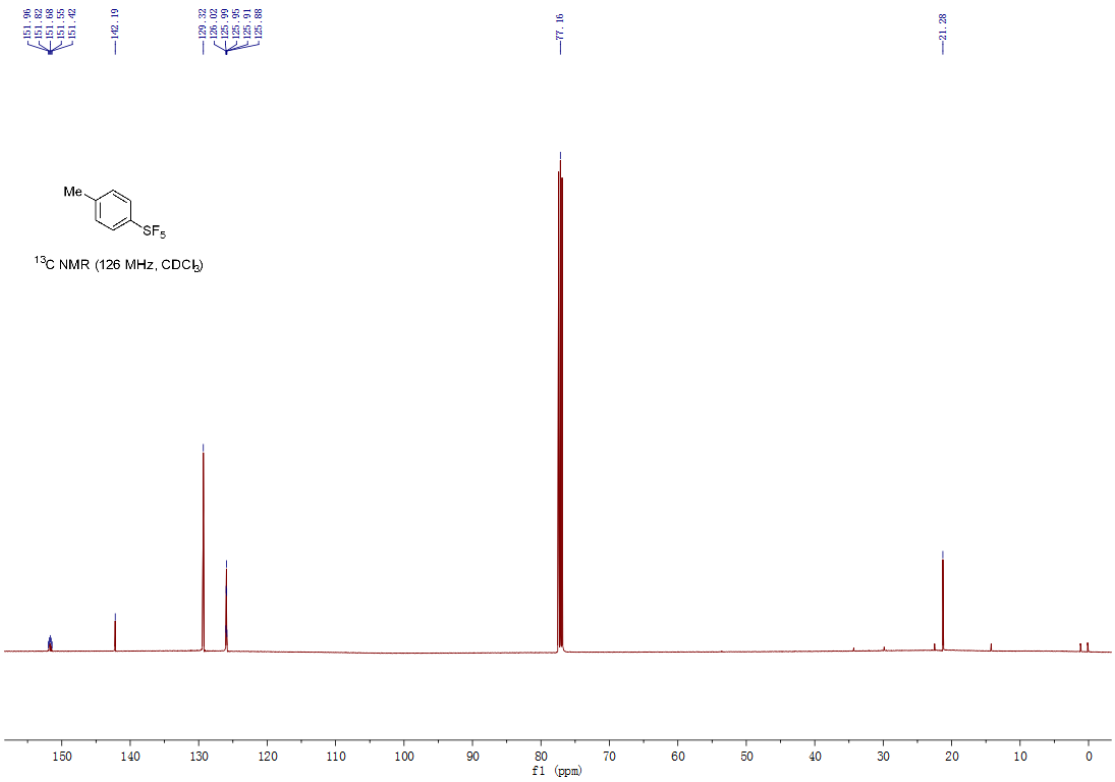

Br
N
N
SF5
13C NMR (126 MHz, CDCl3)
168.92
168.70
168.47
168.24
168.01
159.29
123.02
77.41
77.16
76.91
1.00
8.16
1.51
f1 (ppm)

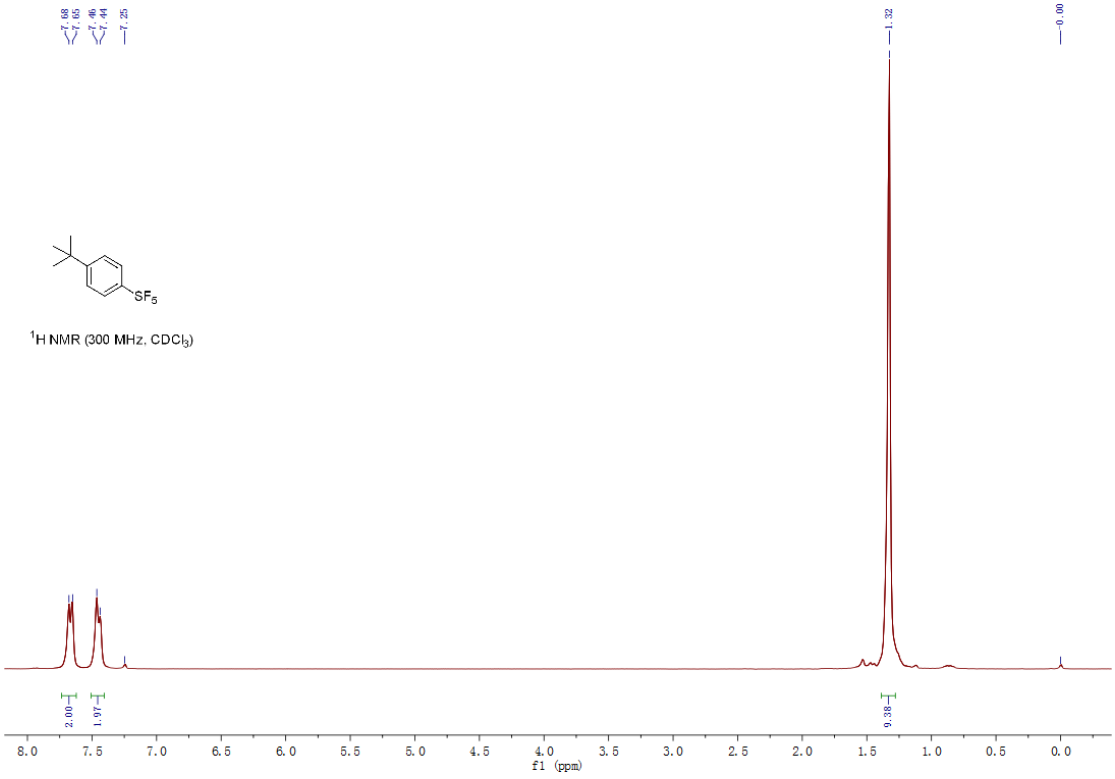


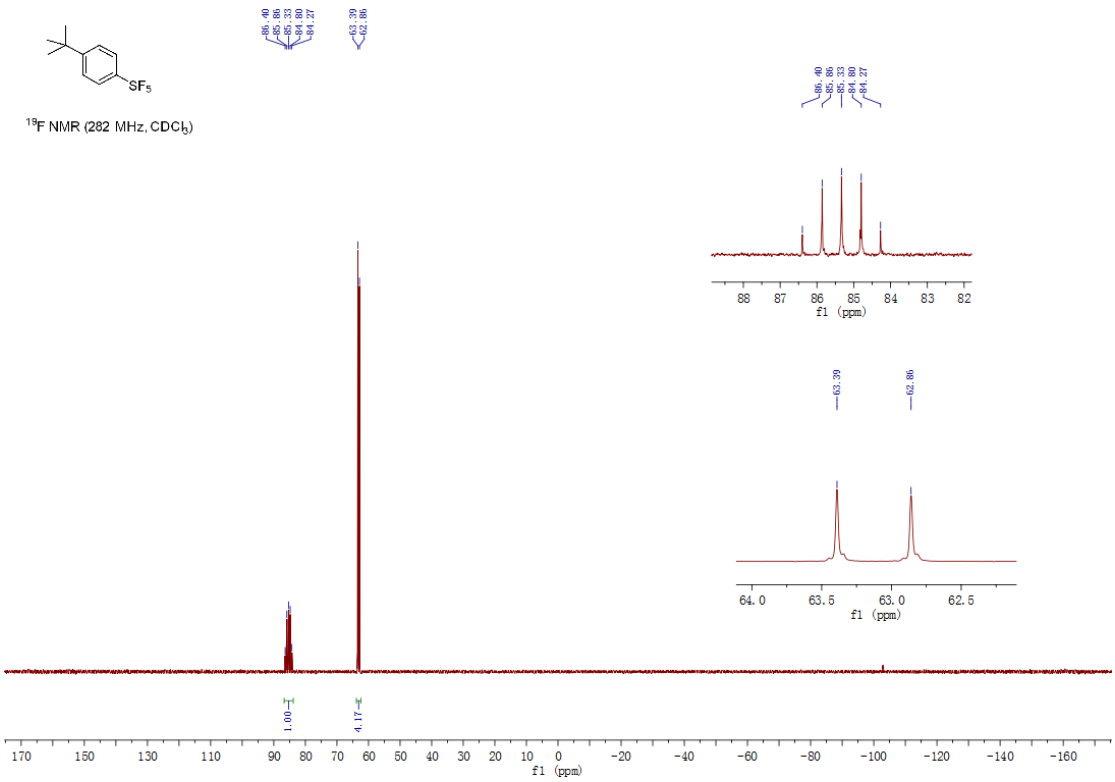
^{1}H NMR (300 MHz, $CDCl_3$)

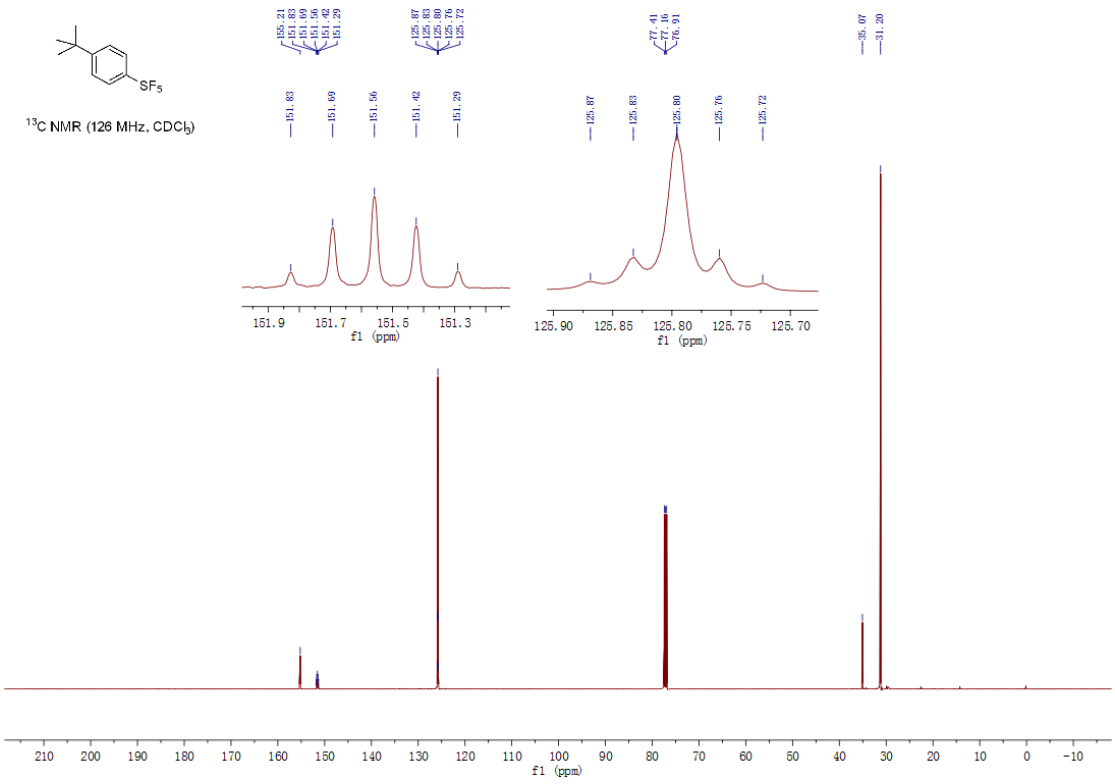


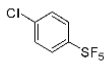
^{19}F NMR (282 MHz, $CDCl_3$)


151.96
151.82
151.68
151.55
151.42
142.19
129.32
126.02
125.99
125.95
125.91
125.88
77.16
21.28
Me
SF5
13C NMR (126 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

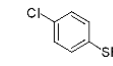

7.68
7.65
7.46
7.44
7.25
1.32
0.00
SF5
1H NMR (300 MHz, CDCl3)
2.00
1.97
9.38
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


SF5
19F NMR (282 MHz, CDCl3)
86.40
85.86
85.33
84.80
84.27
63.39
62.86
1.00
4.17
f1 (ppm)

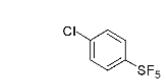

SF5
13C NMR (126 MHz, CDCl3)
155.21
151.83
151.69
151.56
151.42
151.29
125.87
125.83
125.80
125.76
125.72
77.41
77.16
76.91
35.07
31.20
f1 (ppm)



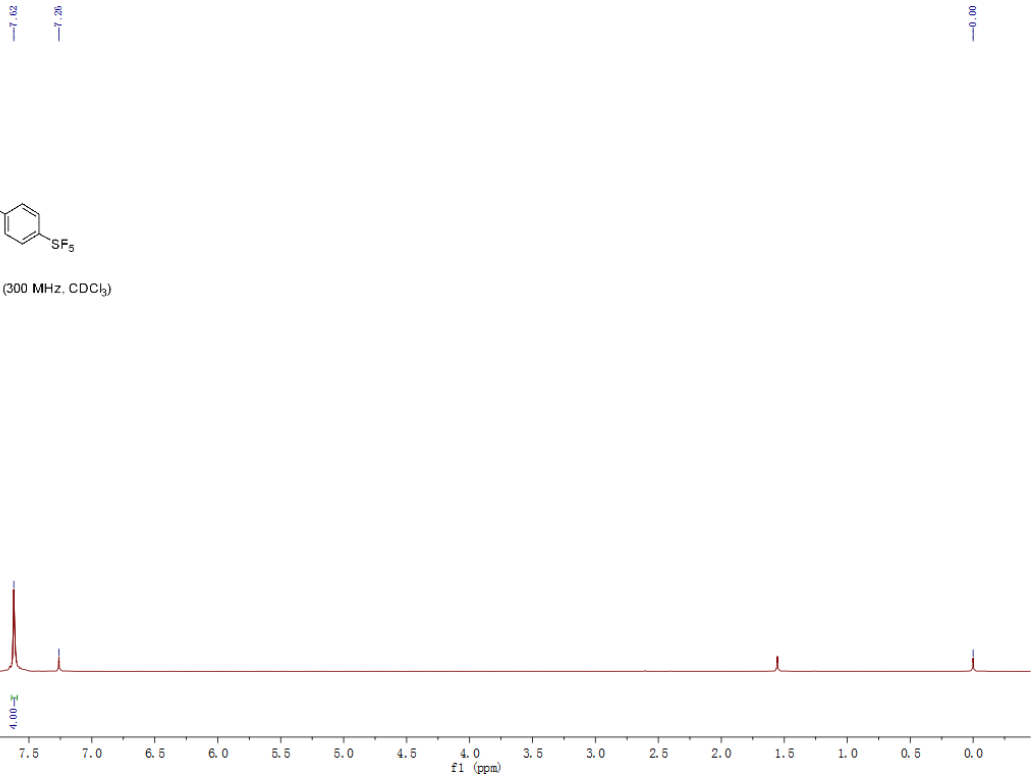
^{1}H NMR (300 MHz, $CDCl_3$)



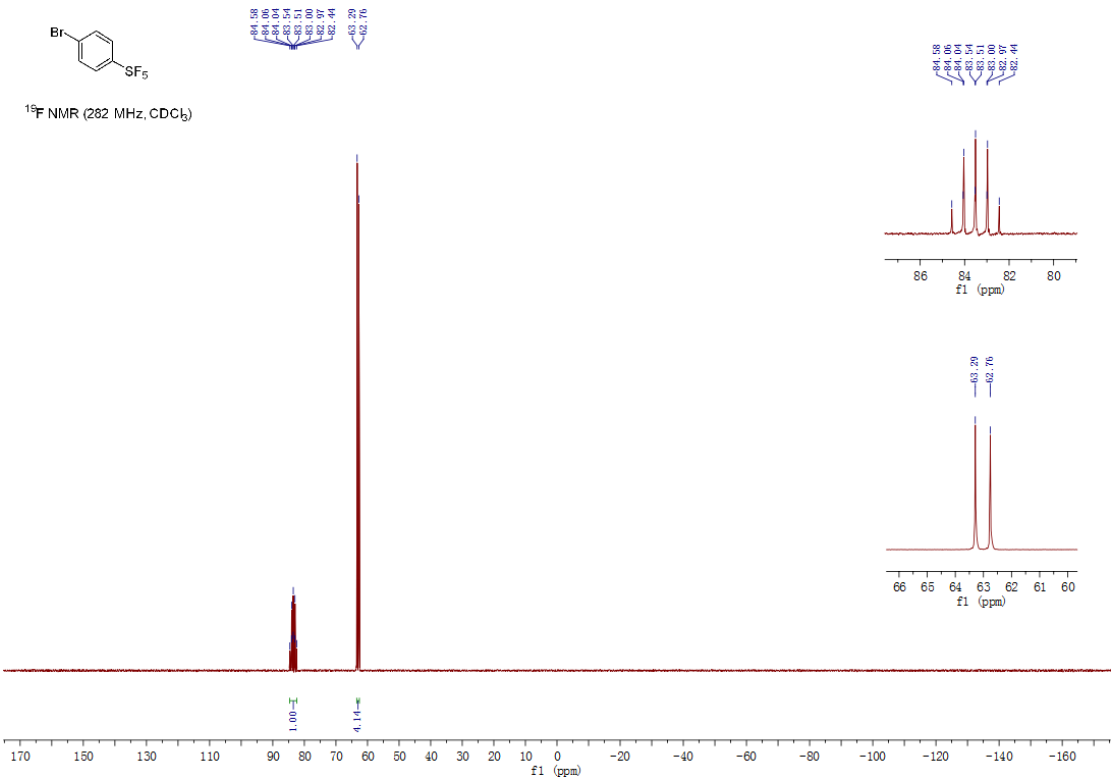
^{19}F NMR (282 MHz, $CDCl_3$)

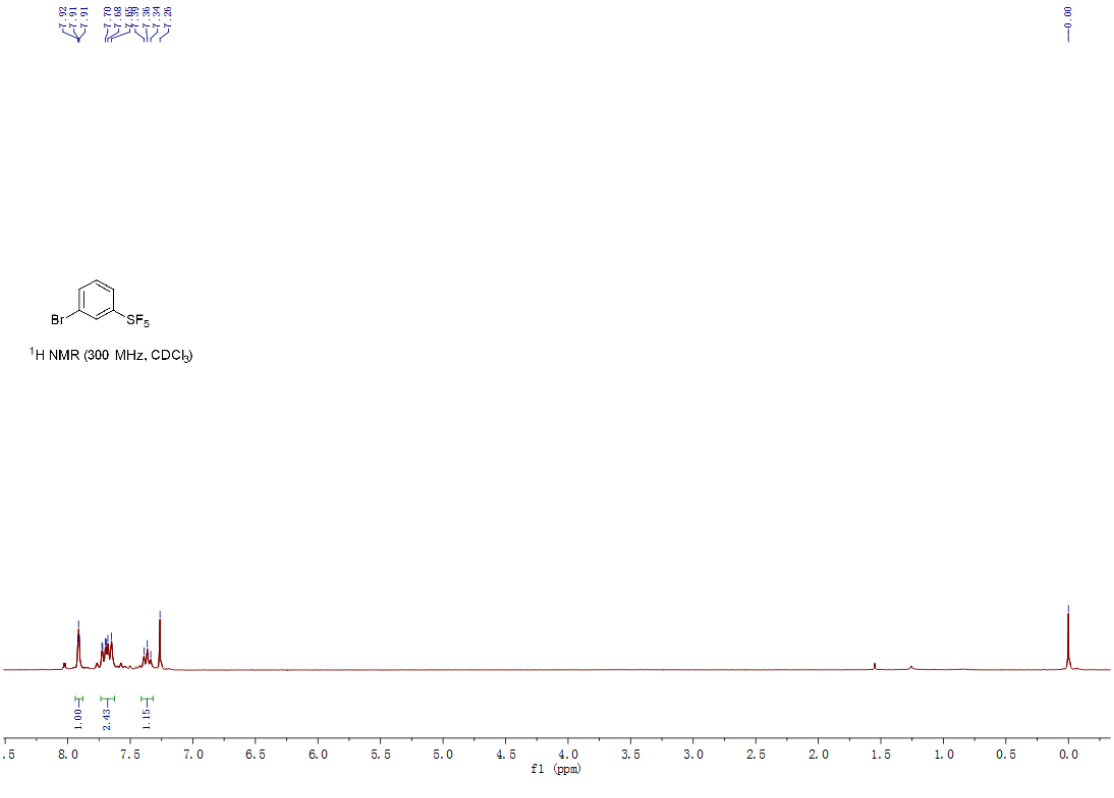


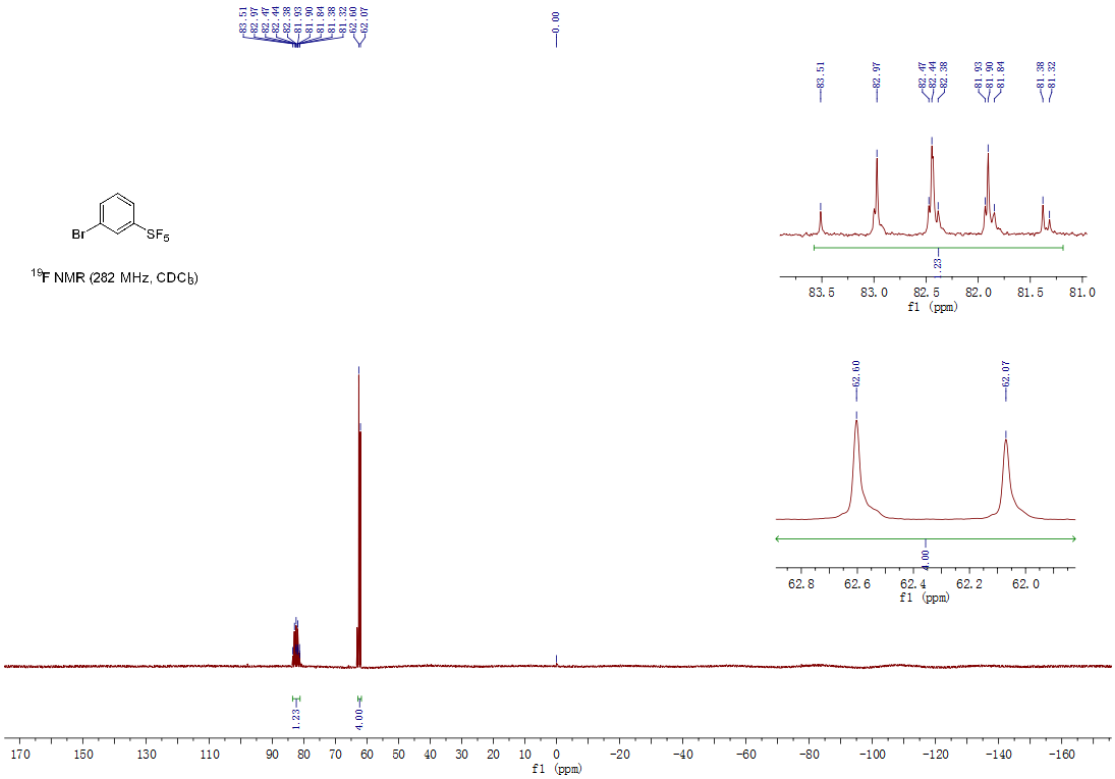
^{13}C NMR (126 MHz, $CDCl_3$)

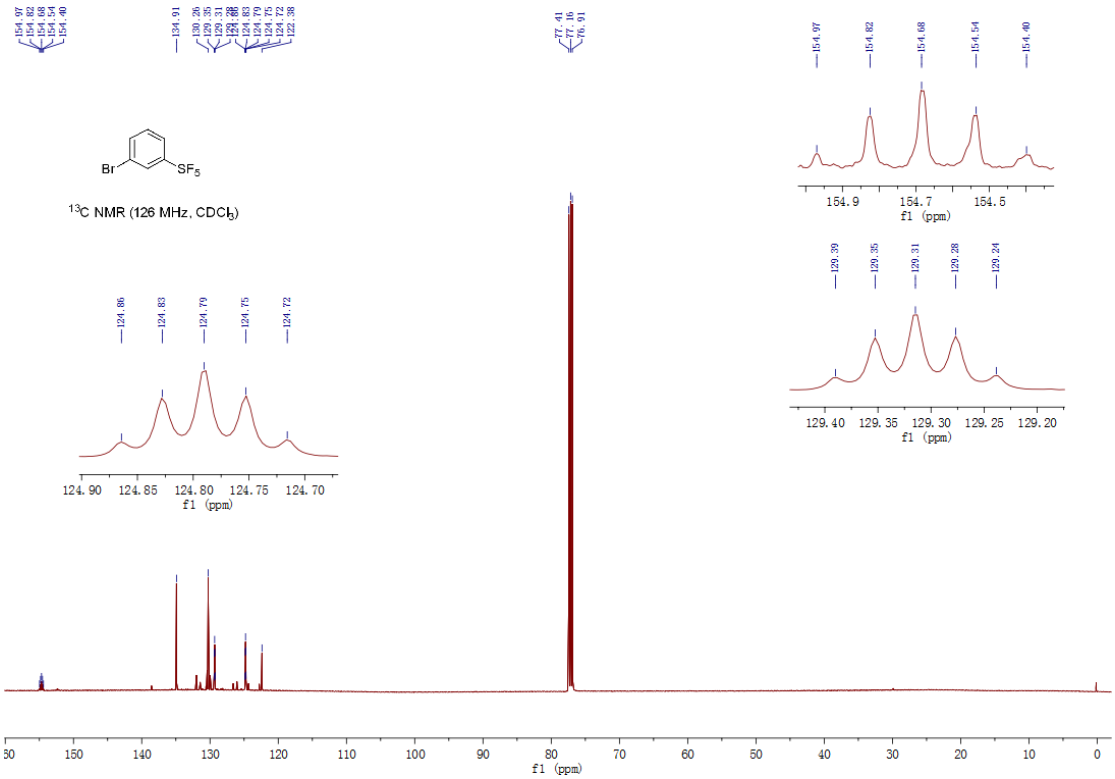


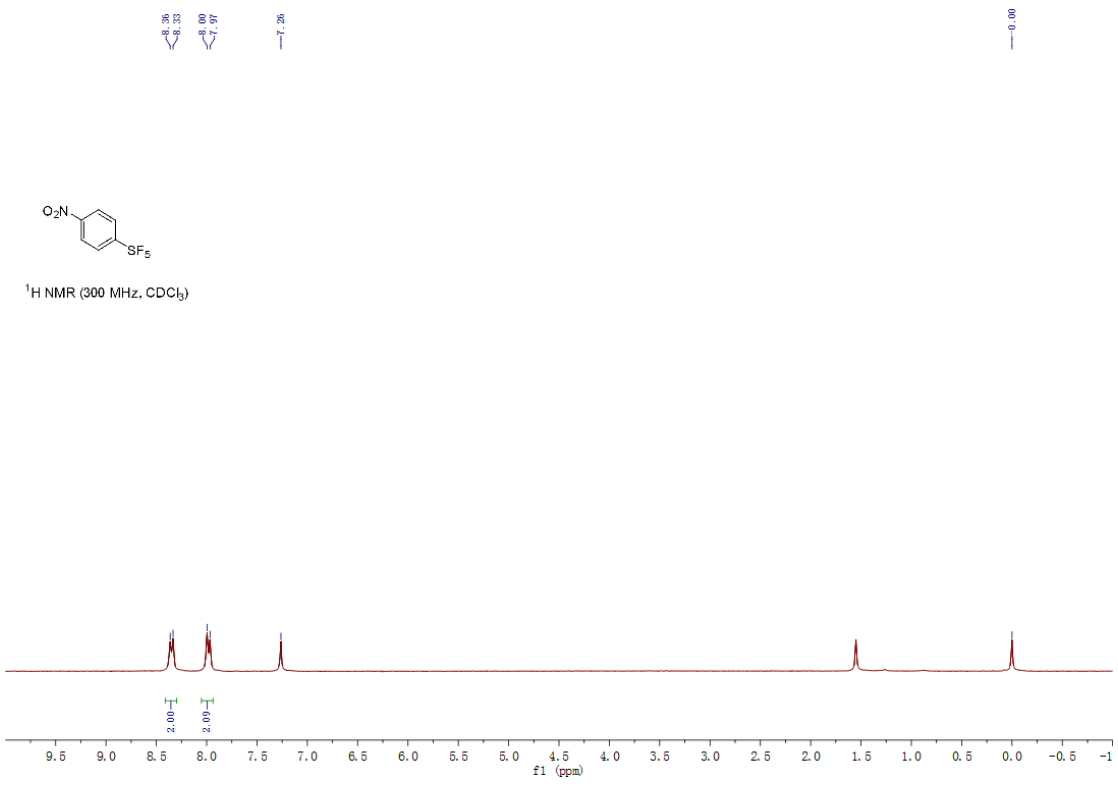
^{1}H NMR (300 MHz, $CDCl_3$)


Br
SF5
19F NMR (282 MHz, CDCl3)
-84.58
-84.06
-84.04
-83.54
-83.51
-83.00
-82.97
-82.44
-63.29
-62.76
1.00
4.14
f1 (ppm)

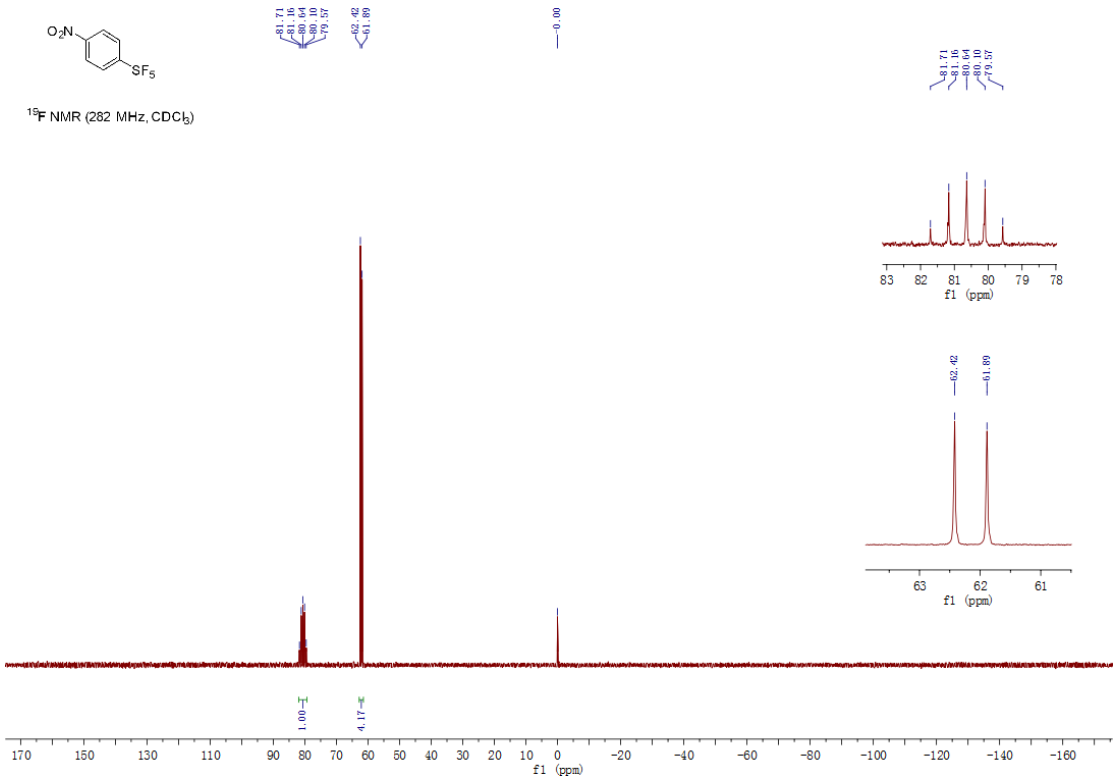

7.92
7.91
7.91
7.70
7.68
7.55
7.55
7.36
7.34
7.26
0.00
Br
SF5
1H NMR (300 MHz, CDCl3)
1.00
2.43
1.15
f1 (ppm)


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

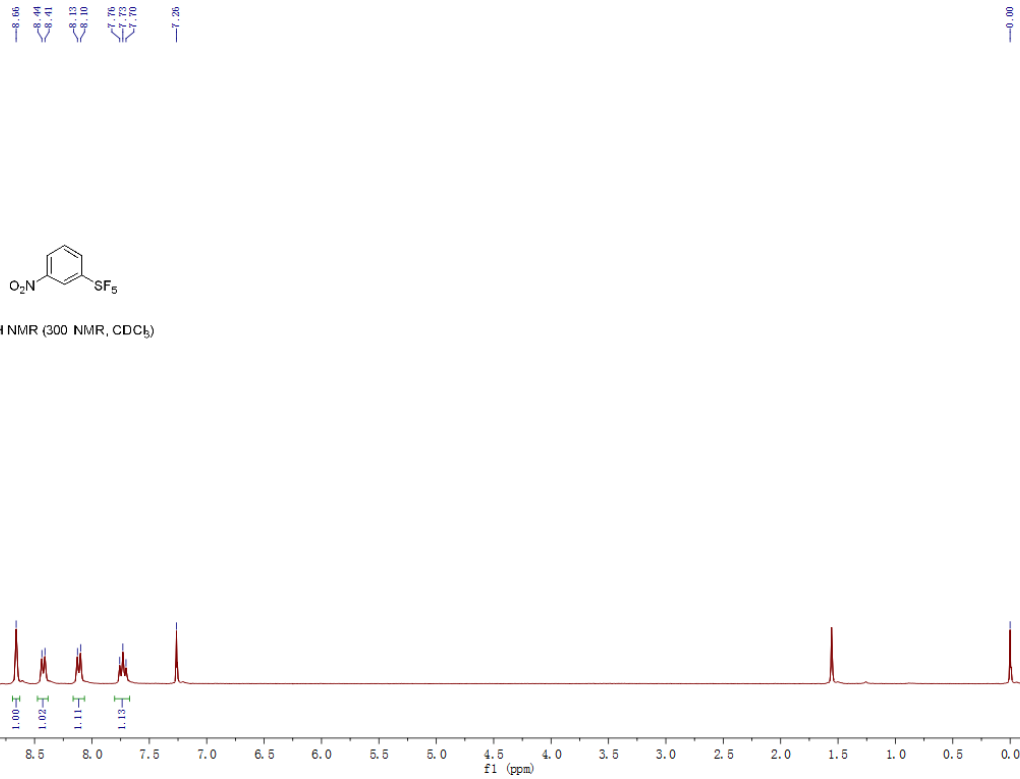

Br
SF5
13C NMR (126 MHz, CDCl3)
f1 (ppm)

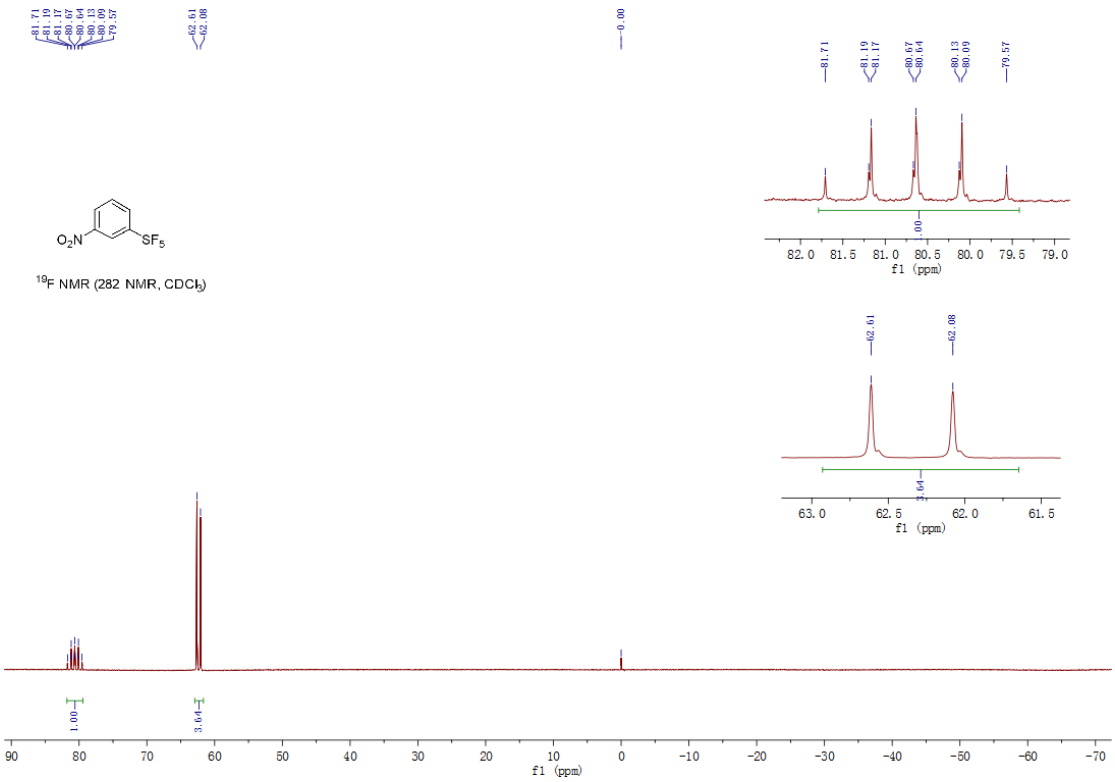


^{1}H NMR (300 MHz, $CDCl_3$)



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


8.66
8.44
8.41
8.13
8.10
7.76
7.73
7.70
7.26
0.00
O2N
SF5
1H NMR (300 NMR, CDCl3)
1.00
1.02
1.11
1.13
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)


81.71
81.19
81.17
80.67
80.64
80.13
80.09
79.57
62.61
62.08
0.00
O2N
SF5
19F NMR (282 NMR, CDCl3)
1.00
3.64
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)
82.0
81.5
81.0
80.5
80.0
79.5
79.0
63.0
62.5
62.0
61.5