Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-light-mediated radical arylthiodifluoromethylation of isocyanides with fluorinated 2-pyridyl sulfones

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Supporting Information

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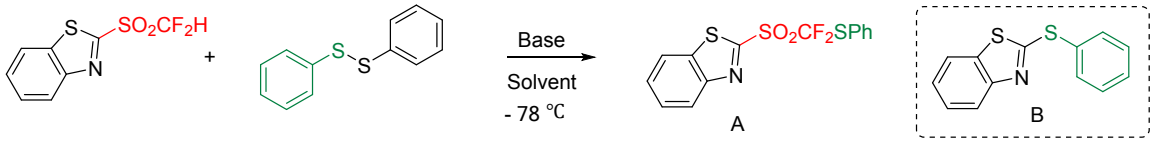
1. General information

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Reactions were monitored by thin layer chromatography purchased from commercial suppliers. Subsequent to elution, spots were visualized using UV radiation (254 nm). Flash chromatography was performed using 200-300 mesh silica gel. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance III 500 MHz. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0. High resolution MS (HRMS) were performed on an Agilent 6224 TOF LC/MS spectrometer.

$[Ru(bpy)_3Cl_2]\cdot 6H_2O$, t-BuONa, Na_2CO_3, DMF, DMSO, 6W LED bulb were commercial available. The substituted 1,2-diphenyldisulfane derivatives and the Isocyanides (**2a-2m**, **5a-5c**) were prepared according to the literature.[1][2]

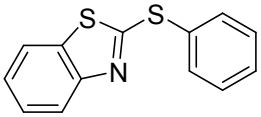
2. Variation of reaction parameters [a]



Entry	Base	Solvent	Time	Yield(%) [b]
1	*t*-BuONa	DMF	10 min	A=6, B= 65
2	LiHMDS	THF	10 min	A=7, B= 82.3
3	KHMDS	THF	10 min	A=Trace, B= 32
4	NaHMDS	THF	10 min	A=Trace, B= 34
5	LiHMDS	THF	1 second	A=12, B=62
6	LiHMDS	THF:HMPA=10:1	1 second	A=26, B=56
7	LiHMDS	THF:HMPA=5:1	1 second	A=9, B=45
8	LiHMDS	THF:HMPA=2:1	1 second	A=7, B=34

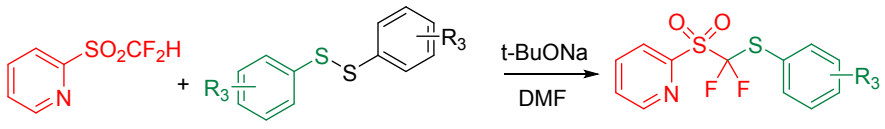
[a] Reaction condition: 2-BTSO_2CF_2H (1.0 equiv.), PhSSPh (1.5 equiv.). [b] **A**: Yields were determined by ^{19}F NMR using $PhCF_3$ as an internal standard. B:Isolated yield of **B**.

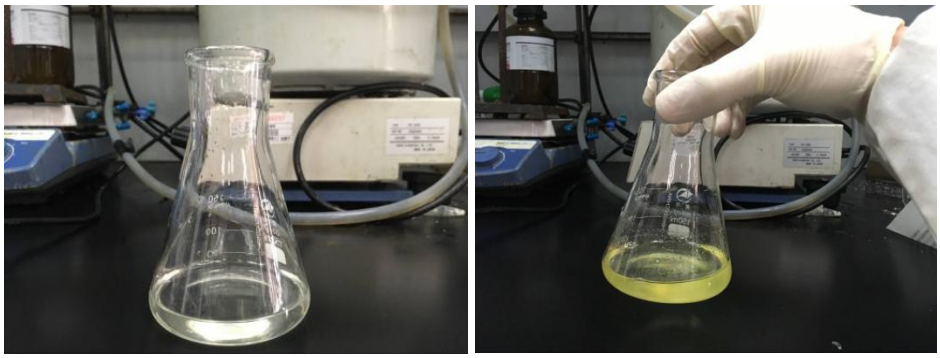
2-(phenylthio)benzo[*d*]thiazole



^{1}H NMR (400MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.40-7.36 (m, 1H), 7.24 – 7.22 (m, 1H). MS (EI, *m/z*, %): 243 (M^+).

3. Typical procedure for the synthesis of 1a-1l



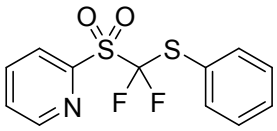


Supporting Figure 1 Left: 1,2-diphenyldisulfane and 2-(Difluoromethylsulfonyl)pyridine were dissolved in DMF; Right :slightly shook after the addition of *t*-BuONa (about 5 seconds)

t-BuONa (2.5 equiv.) was added to a solution of 1,2-diphenyldisulfane (1.2 mmol, 1.2 equiv.) and 2-(difluoromethylsulfonyl)-pyridine (1.0 mmol, 1.0 equiv.) in 10 mL DMF at room temperature. The mixture was slightly shook and the reaction completed within few seconds. Then mixture was poured into ice water and a white precipitate of compound **1a** appeared, which was filtered and dried in vacuum for direct use without further purification.

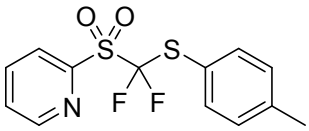
4. Characterization data of 1a-1l

2-((difluoro(phenylthio)methyl)sulfonyl)pyridine (1a)



White solid. 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (dd, *J* =1.0 Hz, 4.5 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.02 (td, *J* =2.0 Hz，8.0Hz，1H), 7.71 (d, *J* = 7.0 Hz, 2H), 7.66-7.63 (m, 1H), 7.49-7.45 (m, 1H), 7.40-7.37 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –77.0. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 151.0, 138.3, 137.3, 131.3 (t, *J* = 325.0 Hz), 131.0, 129.4, 128.7, 126.5, 123.2 (t, *J* = 2.5 Hz). HRMS (ESI): m/z calcd. for $C_{12}H_9F_2NO_2S_2$ $[M+H]^+$ 302.0115, found 302.0114.

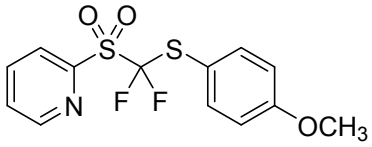
2-((difluoro(p-tolylthio)methyl)sulfonyl)pyridine (1b)



White solid, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.60 (m, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.95 (td, *J* = 1.5 Hz, 8.0Hz, 1H), 7.59-7.56 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –77.4. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4,

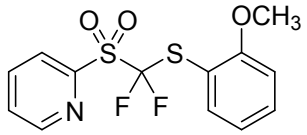
151.0, 141.7, 138.3, 137.3, 131.3 (t, *J* = 323.7 Hz), 130.2, 128.7, 126.5, 119.6 (t, *J* = 2.6 Hz), 21.4. HRMS (ESI): m/z calcd. For $C_{13}H_{11}F_2NO_2S_2$ $[M+H]^+$ 316.0272, found 316.0271.

2-((difluoro((4-methoxyphenyl)thio)methyl)sulfonyl)pyridine (1c)



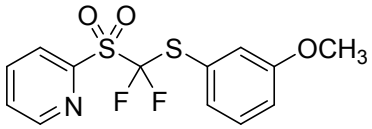
White solid, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.5 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.02 (td, *J* = 1.5, 7.5 Hz, 1H), 7.66 – 7.61 (m, 3H), 6.91-6.89 (m, 2H), 3.81 (s, 3H).^{19}F NMR (470 MHz, $CDCl_3$) δ –78.1. ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 152.5, 151.0, 139.2, 138.3, 131.1 (t, *J* = 325.0 Hz), 128.7, 126.5, 114.9, 113.4 (t, *J* = 3.3 Hz), 55.4. HRMS (ESI): m/z calcd. for $C_{13}H_{11}F_2NO_3S_2$ $[M+H]^+$ 332.0221, found 332.0222.

2-((difluoro((2-methoxyphenyl)thio)methyl)sulfonyl)pyridine (1d)



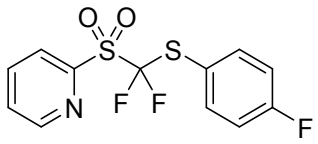
White solid, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 0.5 Hz, 4.5 Hz, 1H), 8.17 (d, *J* =8.0 Hz, 1H), 8.02 (td, *J* =1.5 Hz, 7.5 Hz, 1H), 7.68-7.63 (m, 2H), 7.47 (td, *J* =2.0 Hz, 8.0 Hz, 1H), 6.98-6.94 (m, 2H), 3.87 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –77.3. ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 152.6, 150.9, 139.6, 138.2, 133.4, 131.3 (t, *J* = 326.2 Hz), 128.6, 126.5, 121.1, 111.7, 111.2 (t, *J* = 2.6 Hz), 56.1. HRMS (ESI): m/z calcd. for $C_{13}H_{11}F_2NO_3S_2$ $[M+H]^+$ 332.0221, found 332.0221.

2-((difluoro((3-methoxyphenyl)thio)methyl)sulfonyl)pyridine (1e)



White solid, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.5 Hz, 1H), 8.19 (d, *J* =7.5 Hz, 2H), 8.06-8.02 (m, 1H), 7.69-7.67 (m, 1H), 7.34-7.29 (m, 2H), 7.26 (m, 1H), 7.04-7.02 (m, 1H), 3.84 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –76.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 152.3, 151.0, 138.3, 131.4 (t, *J* = 325.0 Hz), 130.0, 129.5, 126.5, 123.9 (t, *J* = 2.8 Hz), 122.0, 127.4, 117.4, 55.5. HRMS (ESI): m/z calcd. for $C_{13}H_{11}F_2NO_3S_2$ $[M+H]^+$ 332.0221, found 332.0220.

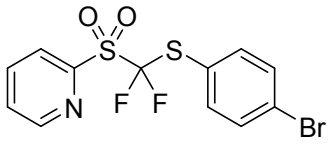
2-((difluoro((4-fluorophenyl)thio)methyl)sulfonyl)pyridine (1f)



White solid, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 – 8.84 (m, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.03 (td, *J* = 1.5Hz, 7.5 Hz, 1H), 7.73-7.70 (m, 2H), 7.67-7.65 (m, 1H), 7.14-7.05 (m, 2H).

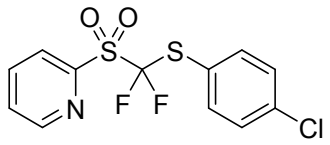
^{19}F NMR (470 MHz, $CDCl_3$) δ –77.8, –108.2. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7 (d, *J* = 252.5 Hz), 152.2, 151.1, 139.7 (d, *J* = 8.7 Hz), 138.3, 131.0 (t, *J* = 325.0 Hz), 128.8, 126.5, 118.5 (d, *J* = 3.4 Hz), 116.7 (d, *J* = 22.2 Hz). HRMS (ESI): m/z calcd. for $C_{12}H_8F_3NO_2S_2$ $[M+H]^+$ 320.0021, found 320.0020.

2-((((4-bromophenyl)thio)difluoromethyl)sulfonyl)pyridine (1g)



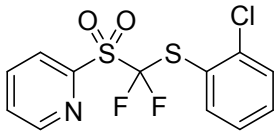
White solid, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85-8.84 (m, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.03 (td, *J* =1.5 Hz, 8.0 Hz, 1H), 7.68-7.65 (m, 1H), 7.59-7.52 (m, 4H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –77.4. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 151.1, 138.8, 138.3, 132.7, 130.9 (t, *J* = 325.0 Hz), 128.8, 126.5, 126.3, 122.3 (t, *J* = 3.3 Hz). HRMS (ESI): m/z calcd. for $C_{12}H_8BrF_2NO_2S_2$ $[M+H]^+$ 379.9221, found 379.9220.

2-((((4-chlorophenyl)thio)difluoromethyl)sulfonyl)pyridine (1h)



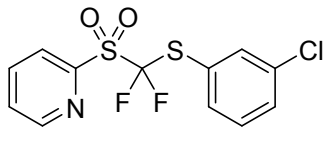
White solid, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.5 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.04 (td, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.68-7.65 (m, 3H), 7.39 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –77.5. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 151.1, 138.6, 138.3, 138.0, 131.0 (t, *J* = 325.0 Hz), 129.7, 128.8, 126.5, 121.7 (t, *J* = 4.4 Hz). HRMS (ESI): m/z calcd. for $C_{12}H_8ClF_2NO_2S_2$ $[M+H]^+$ 335.9726, found 335.9725.

2-((((2-chlorophenyl)thio)difluoromethyl)sulfonyl)pyridine (1i)



White solid. 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.5 Hz, 1H), 8.19 (d, *J*= 8.0 Hz, 1H), 8.04 (td, *J*= 1.5, 7.5 Hz, 1H), 7.86 (d, *J*= 7.5 Hz, 1H), 7.67-7.65 (m, 1H), 7.51 (d, *J*= 8.0 Hz, 1H), 7.43 (td, *J*= 1.0 , 7.5Hz, 1H), 7.32 (t, *J*= 7.5 Hz, 1H).^{19}F NMR (470 MHz, $CDCl_3$) δ –76.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2 , 151.0, 141.1, 139.8, 138.3, 132.6, 131.2 (t, *J* = 326.2 Hz), 130.6, 128.8, 127.5, 126.6, 122.9. HRMS (ESI): m/z calcd. for $C_{12}H_8ClF_2NO_2S_2$ $[M+H]^+$ 335.9726, found 335.9724.

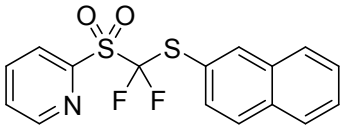
2-((((3-chlorophenyl)thio)difluoromethyl)sulfonyl)pyridine (1j)



White solid. 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.16 (d, *J* =7.5 Hz, 1H), 8.04 (t,

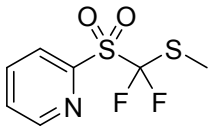
J =7.5 Hz, 1H), 7.69-7.66 (m, 2H), 7.62 (d, *J* =7.5 Hz, 1H), 7.46 (d, *J* =7.0 Hz, 1H), 7.36 (t, *J* =7.5 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –77.0. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 151.1, 138.4, 136.8, 135.4, 134.9, 131.4, 131.1 (t, *J* = 325.0 Hz), 130.4, 128.9, 126.6, 124.9 (t, *J* = 2.8 Hz). HRMS (ESI): m/z calcd. for $C_{12}H_8ClF_2NO_2S_2$ $[M+H]^+$ 335.9726, found 335.9725.

2-((difluoro(naphthalen-2-ylthio)methyl)sulfonyl)pyridine (1k)



White solid. 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82-8.81 (m, 1H), 8.25 (s, 1H), 8.15 (d, *J* =8.0 Hz, 1H), 7.99 (tt, *J* =2.0 Hz, 8.0 Hz, 1H), 7.86-7.83 (m, 3H), 7.71 (d, *J* =8.5 Hz, 1H), 7.63-7.60 (m, 1H), 7.58-7.52 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –76.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 151.0, 138.3, 138.2, 134.0, 133.3, 132.6, 131.5 (t, *J* =325.0 Hz), 129.1, 128.8, 128.3, 128.0, 127.8, 126.9, 126.5, 120.3 (t, *J* = 2.8 Hz). HRMS (ESI): m/z calcd. for $C_{16}H_{11}F_2NO_2S_2$ $[M+H]^+$ 352.0272, found 352.0274.

2-((difluoro(methylthio)methyl)sulfonyl)pyridine (1l)

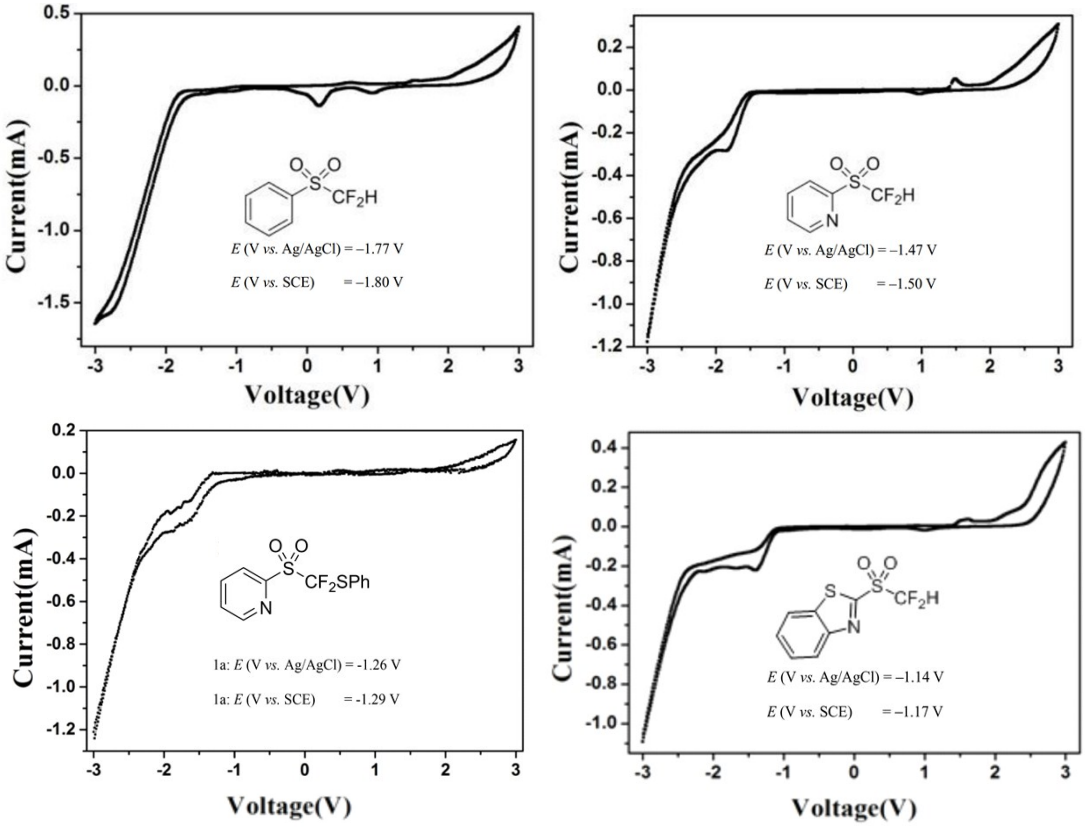


White solid. 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86(d, *J* = 4.5 Hz, 1H), 8.17 (d, *J* =7.5 Hz, 1H), 8.04 (t, *J* =8.0 Hz, 1H), 7.76-7.66 (m, 1H), 2.56 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –81.5. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 150.0, 137.3, 131.3 (t, *J* = 321.2 Hz), 127.8, 125.5, 12.2 (t, *J* =5.0 Hz). HRMS (ESI): m/z calcd. for $C_7H_7F_2NO_2S_2$ $[M+H]^+$ 239.9959, found 239.9960.

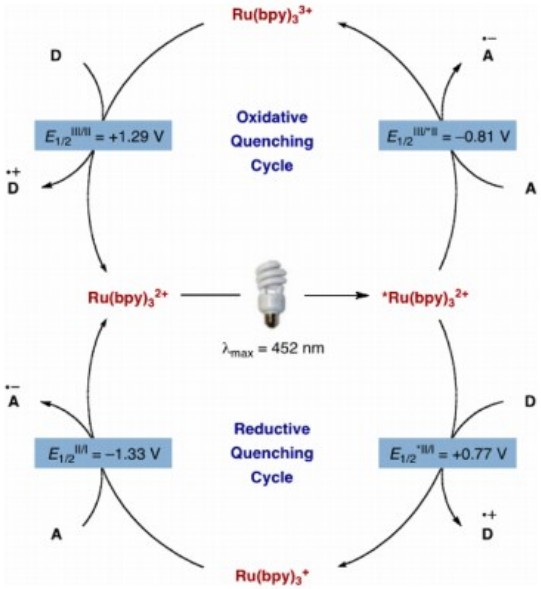
5. Cyclic voltammetry study

The cyclic voltammetry measurements were performed on an EG & G-Princeton Applied Research PARSTAT 2273 electrochemical workstation, using a standard three-electrode setup with two platinum wire electrode (a working electrode and a counter electrode) and a Ag/AgCl (3 M KCl) system in anhydrous CH_2Cl_2 as the reference electrode. All solutions of the compounds under the study were in the supporting electrolyte n-Bu_4NPF_6 0.1 M with the voltage scan rate of 0.05 V s^{-1}. Solutions (5 mL) were thoroughly bubbled with dry nitrogen for 15 min to remove oxygen before any experiment and kept under positive pressure of nitrogen. Under these experimental conditions, the $[FeCp_2]/[FeCp_2]^+$ couple was located at $E_{1/2}$ = +0.49 V in CH_2Cl_2.

The first reduction potentials of fluoroalkyl sulfones: cathodic peak potential quoted *vs*. SCE (the saturated calomel electrode). E (V *vs*. SCE) = E (V *vs*. Ag/AgCl) – 0.03 V (Potential for reference electrode: Ag/AgCl (3 M KCl): +0.21 V, SCE: +0.24 V).

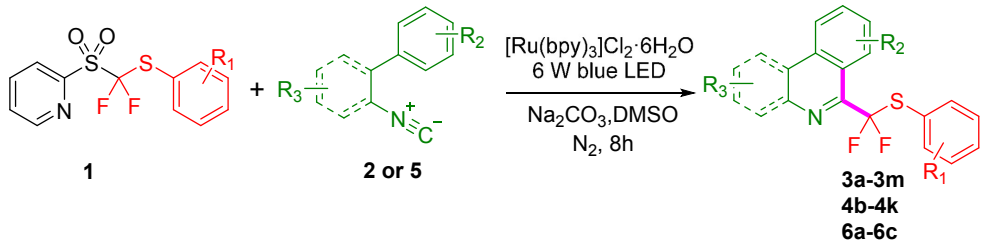


Supporting Figure 2: The cyclic voltammetry of four heteroaryl sulfone reagents.



Supporting Figure 3. Oxidative and Reductive Quenching Cycle of $Ru(bpy)_3^{2+}$. [3]

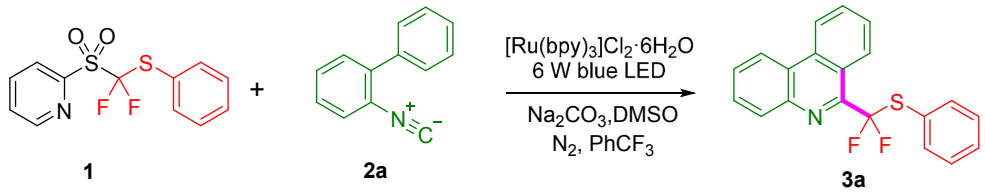
6. General procedure for the synthesis of 3a-3m, 4b-4k, 6a-6c



1 2 or 5 3a-3m 4b-4k 6a-6c

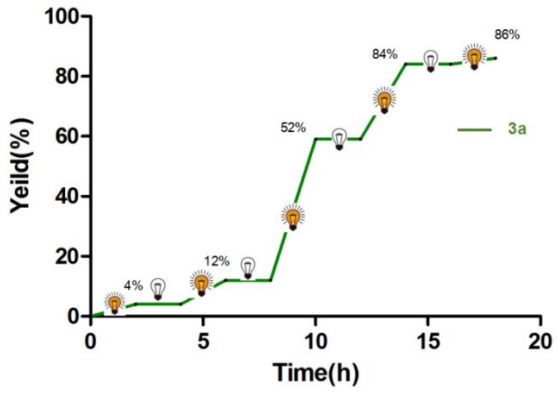
A mixture of **1** (1.2 mmol, 1.2 equiv.), **2** or **5** (1.0 mmol, 1.0 equiv.), photocatalyst (2.0 mol%) and Na_2CO_3 (3.0 equiv.), DMSO (5 mL) were added in a Schlenk tube. The tube was evacuated and backfilled with pure N_2 for 3 times. The mixture was irradiated by a 6 W blue LED for 8 h. After the reaction was complete, H_2O (20 mL) and saturated NH_4Cl solution were added. The aqueous layer was extracted with EtOAc (10 mL×3) and the organic phase was combinated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography to provide products **3a-3m**, **4b-4k** and **6a-6c**.

7. Light on/off experiment



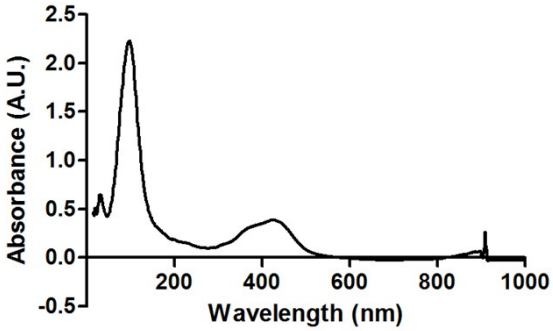
1 2a 3a

A mixture of **1a** (1.2 mmol, 1.2 equiv.), **2a** (1.0 mmol, 1.0 equiv.), photocatalyst (2 mol%), Na_2CO_3 (3.0 mmol, 3.0 equiv.) were added to a dry Schlenk tube. The flask was evacuated and backfilled with pure N_2 for 3 times. Then 5 mL DMSO and 110 mg $PhCF_3$ (internal standards) were added with syringe under N_2 atmosphere. The mixture was irradiated by a 6 W blue LED at room temperature. The blue LED was turned on (for 2 h)-off (for 2 h)-on (for 2 h)-off (for 2 h)-on (for 2 h)-off (for 2 h)-on (for 2 h)-off (for 2 h)-on (for 2 h). The reaction was monitored by ^{19}F NMR .



8. Luminescence Quenching Experiments [4]

8.1 Absorbance of Catalyst:



Absorbance of a 5.0×10^{-4} M solution of $Ru(bpy)_3Cl_2\cdot6H_2O$ in DMSO

8.2 Luminescence Quenching Experiments

Instrument

Model: Agilent Cary Eclipse FL Spectrophotometer

Instrument parameters

Measurement type: Wavelength scan

Scan mode: Emission

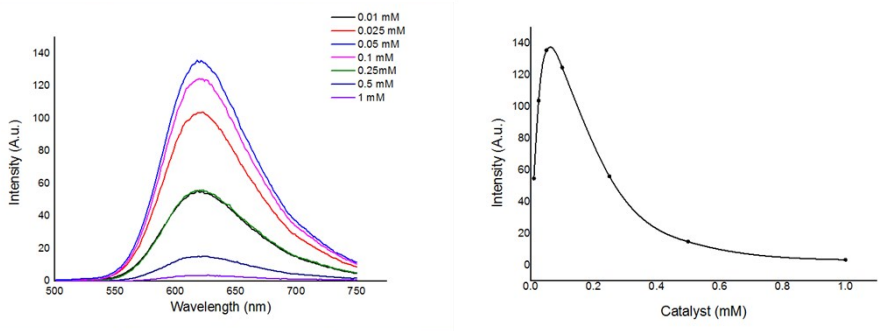
Data mode: Fluorescence

EX WL: 455.0 nm

EM Start WL: 500.0 nm

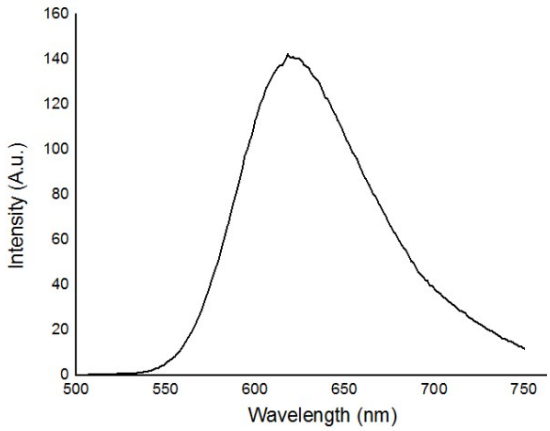
EM End WL: 750.0 nm

$\mathbf{I_0}$ is the luminescence intensity without the quencher, **I** is the intensity with the quencher.

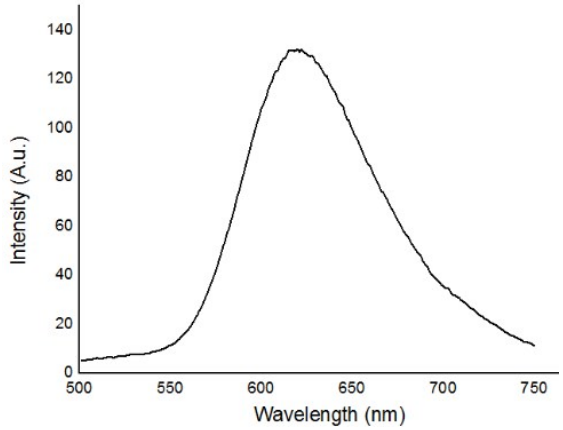


Supporting Figure 3. Relationship between concentration of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ and fluorescence intensity

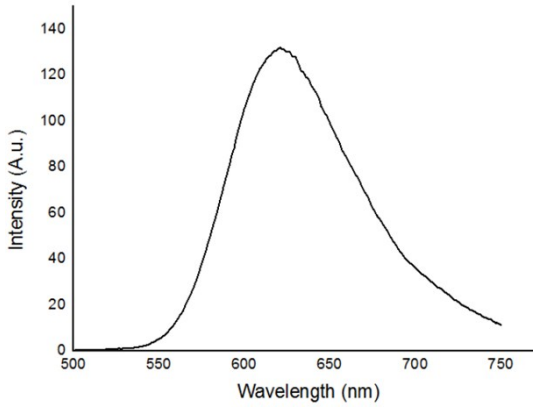
First，we tested the fluorescence value of catalyst with different concentration，and found that when the concentration exceeds 1.0×10^{-4} mol/L, the fluorescence is significantly weakened. So we deduced maybe the catalyst exist aggregation-caused quenching (ACQ) effect, which has greatly influence of the result of the fluorescence quenching experiment . With the result in hand, so we choose 5.0×10^{-5} mol/L catalyst to perform all the fluorescence quenching experiment .



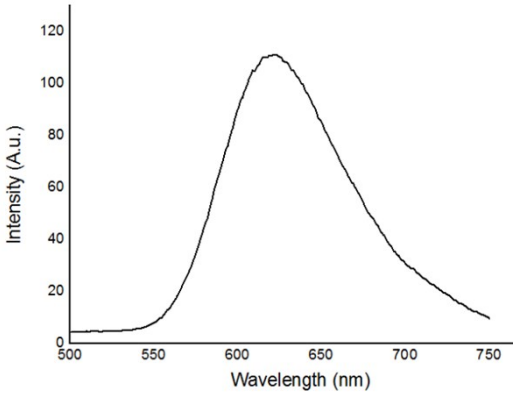
Fluorescence-emission of a 5.0×10^{-5} M solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$(without the quencher) in DMSO, $I_0 = 141.1$



Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (5.0×10^{-5} M) with **1a** (1.3×10^{-2} M) in DMSO, I = 132.7

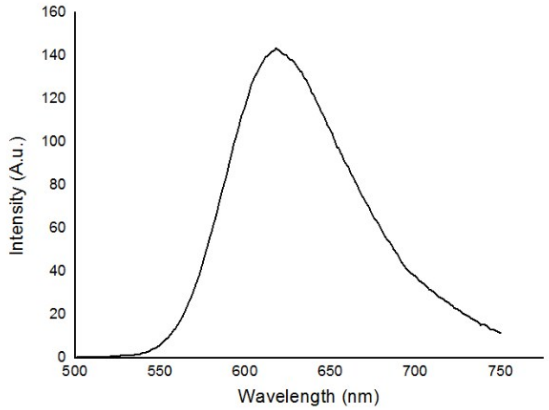


Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (5.0×10^{-5} M) with isocyanide **2a** (1.1×10^{-2} M) in DMSO, I = 131.8

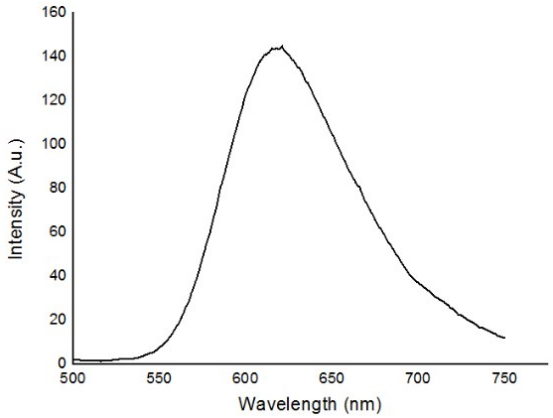


Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (5.0×10^{-5} M) with Na_2CO_3

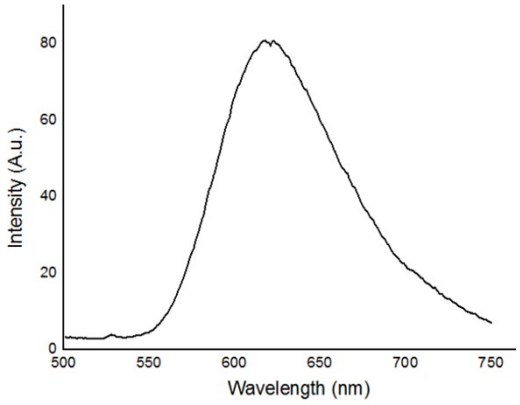
(3.2×10^{-2} M) in DMSO, I = 111.5 (Samples with Na_2CO_3 was stirred for 10 min and filtrated with a syringe filter before the luminescence measurement.)



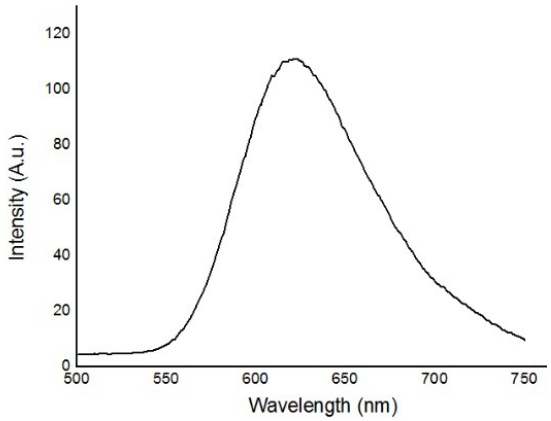
Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2•6H_2O$ (5.0×10^{-5} M) with H_2O (1.6×10^{-2} M) in DMSO, I = 142.7



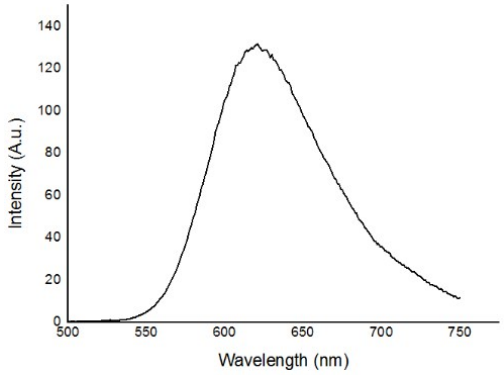
Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2•6H_2O$ (5.0×10^{-5} M) with H_2O (3.2×10^{-2} M) in DMSO, I = 144.7



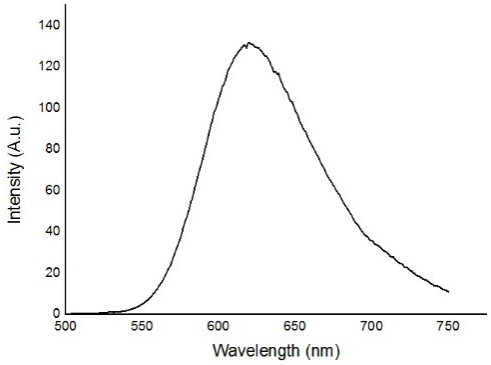
Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (5.0×10^{-5} M) with Na_2CO_3 (3.2×10^{-2} M) in DMSO, I = 80.9 (A stock solution of Na_2CO_3 (0.5 mmol) in 1 ml of H_2O was used).



Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (5.0×10^{-5} M) with $NaHCO_3$ (3.2×10^{-2} M) in DMSO, I = 112.3 (A stock solution of $NaHCO_3$ (0.5 mmol) in 1 ml of H_2O was used).



Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2•6H_2O$ ($5.0×10^{-5}$ M) with TMEDA (3.2×10^{-2} M) in DMSO, I = 131.3



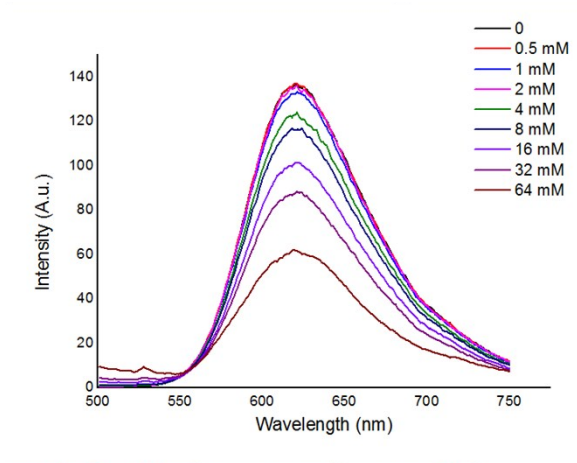
Fluorescence-emission of a solution of $Ru(bpy)_3Cl_2•6H_2O$ ($5.0×10^{-5}$ M) with 2,6-Lutidine (3.2×10^{-2} M) in DMSO, I = 132.5

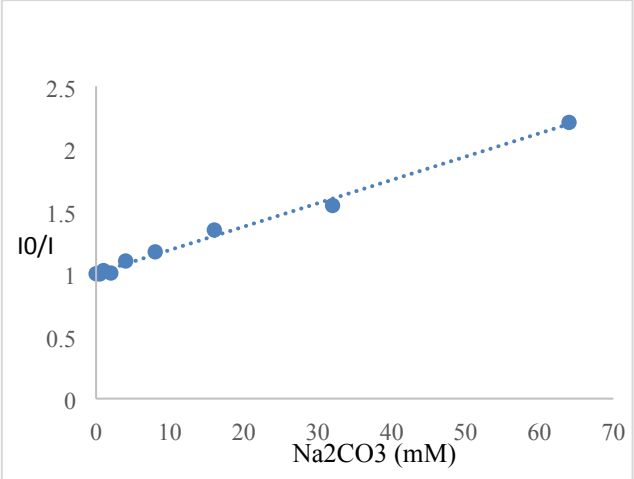
Supporting Table 1. Luminescence Quenching Experiment Results-1

Entry	Sample	Relative luminescence intensity
1	$Ru(bpy)_3Cl_2•6H_2O$ (5×10^{-5} M)	$I_0 = 1$
2	[Ru] (5×10^{-5} M) + **1a** (1.3×10^{-2} M)	$I_0/I = 1.06$
3	[Ru] (5×10^{-5} M) + isocyanide **2a** (1.1×10^{-2} M)	$I_0/I = 1.07$
4a	[Ru] (5×10^{-5} M) + Na_2CO_3 (3.2×10^{-2} M)	$I_0/I = 1.26$
5	[Ru] (5×10^{-5} M) + H_2O (1.6×10^{-2} M)	$I_0/I \approx 1$
6	[Ru] (5×10^{-5} M) + H_2O (3.2×10^{-2} M)	$I_0/I \approx 1$

7[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (3.2×10^{-2} M)	$I_0/I = 1.74$
8[b]	[Ru] (5×10^{-5} M) + $NaHCO_3$ (3.2×10^{-2} M)	$I_0/I = 1.25$
9	[Ru] (5×10^{-5} M) + TMEDA (3.2×10^{-2} M)	$I_0/I = 1.07$
10	[Ru] (5×10^{-5} M) + 2,6-Lutidine (3.2×10^{-2} M)	$I_0/I = 1.06$
11[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (5×10^{-4} M)	$I_0/I \approx 1$
12[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (1×10^{-3} M)	$I_0/I = 1.03$
13[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (2×10^{-3} M)	$I_0/I = 1.01$
14[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (4×10^{-3} M)	$I_0/I = 1.10$
15[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (8×10^{-3} M)	$I_0/I = 1.17$
16[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (16×10^{-3} M)	$I_0/I = 1.35$
17[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (32×10^{-3} M)	$I_0/I = 1.55$
18[b]	[Ru] (5×10^{-5} M) + Na_2CO_3 (64×10^{-3} M)	$I_0/I = 2.21$

[a] Samples with Na_2CO_3 was stirred for 10 min and filtrated with a syringe filter before the luminescence measurement. [b] A stock solution of the Na_2CO_3 (0.5 mmol) in 1 ml of H_2O was used.





Supporting Figure 4: Stern Volmer of Na_2CO_3

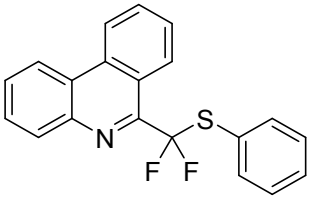
Results and Discussion.

In the luminescence quenching experiments, there was no obvious change in luminescence intensity when isocyanide **2a** or sulfone **1a** was used as a quencher to [Ru]* (entries 2 and 3). $NaHCO_3$ seemed to be a weak quencher to [Ru]*, while TMEDA and 2,6-Lutidine did not demonstrated effective quenching effect to [Ru]* (entries 8, 9 and 10). Na_2CO_3 was a weak quencher to [Ru]* due to the poor solubility in DMSO (entry 4). In order to improve the solubility, the stock solution of the Na_2CO_3 (0.5 mmol) in 1 ml of H_2O was used. While excluding the effects of water (entry 5 and 6), a significant decrease of

$Ru(bpy)_3Cl_2 \cdot 6H_2O$ luminescence was observed (entry 7), and the quenching effect of Na_2CO_3 increased with its concentration (Supporting Figure 4).

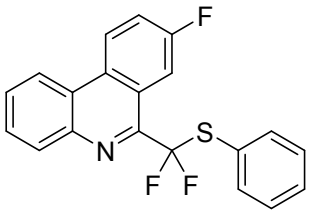
9. Characterization data of 3a-3m, 4b-4k, 6a-6c.

6-(difluoro(phenylthio)methyl)phenanthridine (3a)



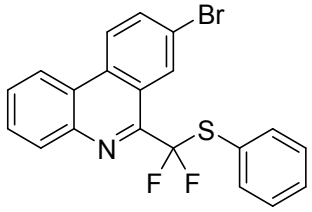
White solid, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72(d, *J* = 8.0 Hz, 1H), 8.62-8.59 (m, 2H), 8.30-8.29 (m, 1H), 7.92-7.89 (m, 1H), 7.82-7.76 (m, 4H), 7.74 (td, *J* =1.5 Hz, 7.0 Hz,1H), 7.49-7.43 (m, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.0. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3 (t, *J* = 28.0 Hz), 141.7, 137.2, 135.0, 134.1, 131.7 (d, *J* = 277.5 Hz), 131.1, 130.9, 129.9, 129.1, 129.0, 128.8, 128.6, 127.6, 127.0 (t, *J* = 5.4 Hz), 125.0, 122.3, 122.0. HRMS (CI): m/z calcd. for $C_{20}H_{13}F_2NS$ $[M+H]^+$ 338.0809, found 337.0802.

6-(difluoro(phenylthio)methyl)-8-fluorophenanthridine **(3b)**



White solid. 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67-8.64 (m, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.29-8.27 (m, 1H), 8.22 (dd, *J* = 6.5 Hz, *J* = 10.0 Hz, 1H), 7.81-7.75 (m, 4H), 7.65-7.61 (m, 1H), 7.51-7.44 (m, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.7, –110.5. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (d, *J* = 250.0 Hz), 150.6 (td, *J* =3.7, 28.7 Hz), 140.6, 138.3 (d, *J* = 8.7 Hz), 138.2, 133.0, 130.7 (t, *J* = 277.5 Hz), 130.1, 129.8, 128.1, 127.8, 126.7, 126.0 (t, *J* = 5.4 Hz), 124.0, 121.6, 121.4, 121.0, 120.8, 115.2 (d, *J* = 22.5 Hz). HRMS (CI): m/z calcd. for $C_{20}H_{12}F_3NS$ $[M+H]^+$ 356.0715, found 356.0714.

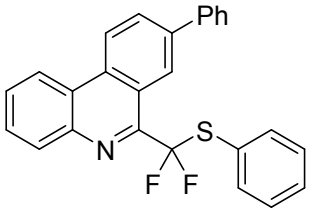
8-bromo-6-(difluoro(phenylthio)methyl)phenanthridine **(3c)**



White solid. 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.52-8.50 (m, 2H), 8.28 (d, *J* = 8.0 Hz,1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.81-7.75 (m, 4H), 7.52-7.44 (m, 3H). ^{19}F NMR (470 MHz,

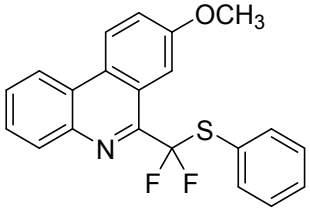
$CDCl_3$) δ –65.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2 (t, *J* = 28.7 Hz), 141.6, 137.3, 134.4, 132.7, 131.6 (t, *J* = 282.5 Hz), 131.0, 130.0, 129.5, 129.4, 129.3, 129.0, 127.0, 124.5, 124.2, 123.0, 122.0, 121.9. HRMS (CI): m/z calcd. for $C_{20}H_{12}BrF_2NS$ $[M+H]^+$ 415.9915, found 415.9913.

6-(difluoro(phenylthio)methyl)-8-phenylphenanthridine **(3d)**



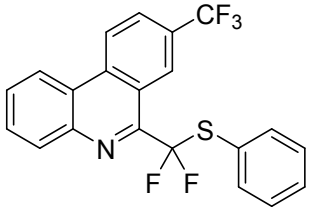
White solid. 86% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.75 (d, *J* = 8.5 Hz,1H), 8.61 (d, *J* = 7.0 Hz, 1H), 8.31 (d, *J* = 7.0 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.84-7.72 (m, 6H), 7.52-7.42 (m, 6H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2 (t, *J* = 27.5 Hz), 141.7, 140.4, 140.0, 137.3, 133.1, 132.0 (t, *J* = 277.5 Hz), 131.0, 130.4, 130.0, 129.1, 129.0, 128.9, 128.8, 128.0, 127.5, 127.4, 127.1, 123.0 (t, *J* = 5.0 Hz), 123.0, 122.3, 122.1. HRMS (CI): m/z calcd. for $C_{26}H_{17}F_2NS$ $[M+H]^+$ 414.1122, found 414.1122.

6-(difluoro(phenylthio)methyl)-8-methoxyphenanthridine **(3e)**



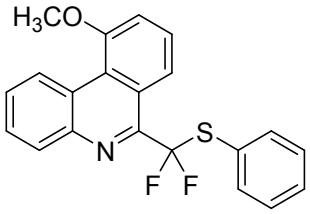
White solid. 87% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 9.0 Hz, 1H), 8.50-8.48 (m, 1H), 8.27-8.25 (m, 1H), 7.89 (d, *J* = 1.5 Hz, 1H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.74-7.71 (m, 2H), 7.52-7.44 (m, 4H), 3.94 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 150.3 (t, *J* = 28.2 Hz), 140.9, 137.3, 132.2 (t, *J* = 277.5 Hz), 130.8, 129.9, 129.0, 128.9, 128.6, 128.1, 127.5, 125.2, 124.0, 123.2, 122.4, 121.5, 106.4 (t, *J* = 5.5 Hz), 55.5. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NOS$ $[M+H]^+$ 368.0915, found 368.0914.

6-(difluoro(phenylthio)methyl)-8-(trifluoromethyl)phenanthridine **(3f)**



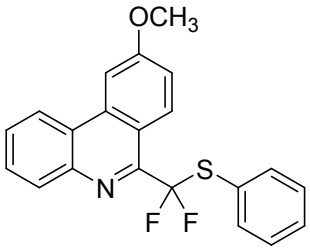
White solid. 65% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.81 (d, *J* = 8.5 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.89-7.80 (m, 4H), 7.53-7.45 (m, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.4, –65.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1 (t, *J* = 28.7 Hz), 142.3, 137.3, 136.1, 131.5 (t, *J* = 277.5 Hz), 131.1, 130.3, 130.1, 129.6, 129.5, 129.4, 129.3, 129.1, 127.0 (m), 126.8, 124.9 (q, *J* = 162.5 Hz), 124.6 (m), 124.1, 122.7. HRMS (CI): m/z calcd. for $C_{21}H_{12}F_5NS$ $[M+H]^+$ 406.0683, found 406.0682.

***6-(difluoro(phenylthio)methyl)-10-methoxyphenanthridine* (3g)**



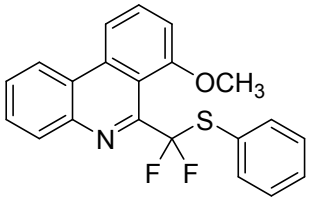
White solid. 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (dd, *J* = 1.0 Hz, *J* = 8.0 Hz, 1H), 8.30 (dd, *J* = 1.5 Hz, *J* = 8.0 Hz, 1H), 8.24-8.22 (m, 1H), 7.82-7.74 (m, 4H), 7.67 (t, *J* = 8.5 Hz, 1H), 7.49-7.43 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 4.16 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 150.9 (t, *J* = 27.8 Hz), 142.2, 137.2, 132.1 (t, *J* = 277.5 Hz), 130.7, 129.8, 128.9, 128.7, 128.4, 128.0, 127.8, 127.7, 124.9, 124.7, 123.9, 119.0 (t, *J* = 5.9 Hz), 112.0, 55.9. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NOS$ $[M+H]^+$ 368.0915, found 368.0914.

***6-(difluoro(phenylthio)methyl)-9-methoxyphenanthridine* (3h)**



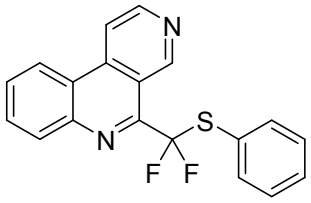
White solid. 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.5 Hz, 2H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 2.0 Hz, 1H), 7.82 (m, 4H), 7.50 (m, 3H), 7.31 (dd, *J* = 2.5, 9.5 Hz, 1H), 4.05 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 150.7 (t, *J* = 27.5 Hz), 142.0, 137.2, 136.5, 131.8 (t, *J* = 277.5 Hz) 130.9, 129.9, 129.2, 129.0, 128.9 (t, *J* = 5.0 Hz), 128.2, 127.4, 124.8, 122.0, 118.0, 116.8, 103.1, 55.6. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NOS$ $[M+H]^+$ 368.0915, found 368.0914.

***6-(difluoro(phenylthio)methyl)-7-methoxyphenanthridine* (3h')**



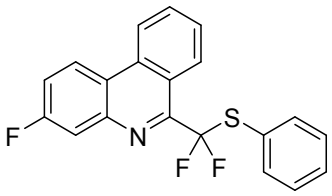
White solid. 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.26 (t, *J* = 7.5 Hz, 2H), 7.81 – 7.71 (m, 5H), 7.48 -7.41(m, 3H), 7.15 (d, *J* = 8.0 Hz, 1H), 3.97 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –68.5. ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 150.1 (t, *J* = 30.0 Hz), 141.2, 137.2, 136.4, 131.9, 131.8 (t, *J* = 272.5 Hz), 130.5, 129.7, 129.4, 129.2, 128.7, 127.3, 124.6, 122.5, 114.5, 114.4, 109.4, 56.2. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NOS$ $[M+H]^+$ 368.0915, found 368.0916.

5-(difluoro(phenylthio)methyl)benzo[c][2,7]naphthyridine (3i)



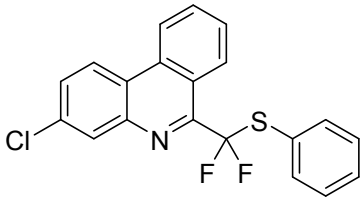
White solid, 45% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.99 (d, *J* = 5.5 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 5.5Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.92 (t, *J* = 7.5 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.43 (m, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3 (t, *J* = 28.7 Hz), 150.8 (t, *J* = 7.5 Hz), 148.6, 143.0, 138.8, 137.2, 131.4, 131.2, 130.8 (t, *J* = 276.2), 130.2, 129.5, 129.1, 126.5, 122.9, 122.6, 117.3, 115.6. HRMS (CI): m/z calcd. for $C_{19}H_{12}F_2N_2S$ $[M+H]^+$ 339.0762, found 339.0761.

6-(difluoro(phenylthio)methyl)-3-fluorophenanthridine **(3j)**



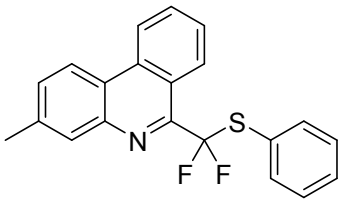
White solid. 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51-8.44 (m, 3H), 7.85 (dd, *J* = 2.0 Hz, *J* = 9.5 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.44-7.33 (m, 4H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.2, –111.1. ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7 (d, *J* = 248.0 Hz), 151.6 (t, *J* = 27.5 Hz), 141.9, 141.8, 136.1, 132.8, 130.4, 128.9, 128.2 (t, *J* = 261.2Hz), 127.9, 126.4, 126.1 – 126.0, 123.0 (d, *J* = 8.7 Hz), 121.1, 120.7, 120.4, 117.0 (d, *J* = 23.7 Hz), 114.3 (d, *J* = 20.8Hz). HRMS (CI): m/z calcd. for $C_{20}H_{12}F_3NS$ $[M+H]^+$ 356.0715, found 356.0714.

3-chloro-6-(difluoro(phenylthio)methyl)phenanthridine **(3k)**



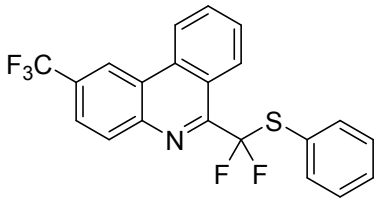
White solid, 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58-8.57 (m, 2H), 8.53 (d, *J* = 1.5 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.91 (t, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 7.0 Hz, 2H), 7.76-7.72 (m, 2H), 7.50-7.43 (m, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.3. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6 (t, *J* = 25.5 Hz), 140.1, 137.2, 135.0, 133.0, 132.3, 131.5 (t, *J* = 276.2 Hz), 131.4, 130.0, 129.7, 129.0, 128.3, 127.1 (m), 126.1, 122.4, 122.1, 121.8. HRMS (CI): m/z calcd. for $C_{20}H_{12}ClF_2NS$ $[M+H]^+$ 372.0420, found 372.0418.

6-(difluoro(phenylthio)methyl)-3-methylphenanthridine **(3l)**



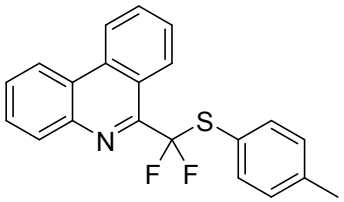
White solid. 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.5 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.09 (s, 1H), 7.86-7.81 (m, 3H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49-7.43 (m, 3H), 2.61 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0 (t, *J* = 28.5 Hz), 141.8, 139.4, 137.2, 134.1, 131.9 (t, *J* = 276.6 Hz), 131.0, 130.6, 130.4, 129.9, 129.0, 127.5, 127.2, 126.9 (t, *J* = 4.8 Hz), 122.7, 122.2, 121.8, 121.6. 21.4. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NS$ $[M+H]^+$ 352.0966, found 352.0965.

6-(difluoro(phenylthio)methyl)-2-(trifluoromethyl)phenanthridine **(3m)**



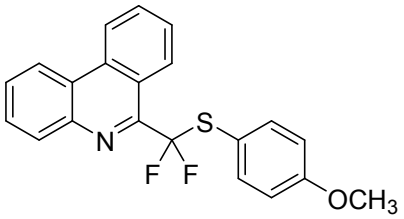
White solid, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.64 (d, *J* = 8.5 Hz, 1H), 8.64 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.00-7.94 (m, 2H), 7.80-7.77 (m, 3H), 7.51-7.43 (m, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.0, –66.5. ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5 (t, *J* = 27.5 Hz), 143.1, 137.2, 133.8, 131.8, 131.3 (t, *J* = 277.5 Hz), 130.8 (q, *J* = 32.5 Hz), 130.1, 129.0, 128.6, 127.4 (t, *J* = 5.0 Hz), 126.9, 125.2, 125.1 (q, *J* = 2.0 Hz), 124.7, 123.0, 122.4, 122.2, 119.9 (q, *J* = 3.75Hz). HRMS (CI): m/z calcd. for $C_{21}H_{12}F_5NS$ $[M+H]^+$ 406.0683, found 406.0681.

6-(difluoro(p-tolylthio)methyl)phenanthridine **(4b)**



White solid. 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.5 Hz, 1H), 8.61-8.59 (m, 2H), 8.31 (dd, *J* = 1.0 Hz, *J* = 9.5 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.81-7.75 (m, 2H), 7.73-7.69 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.5. ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4 (t, *J* = 28.0 Hz), 140.7, 139.2, 136.1, 133.0, 130.5 (t, *J* = 276.2 Hz), 130.0, 129.9, 128.8, 128.0, 127.7, 127.5, 126.6, 126.0 (t, *J* = 5.3 Hz), 124.0, 122.6, 121.3, 120.9, 20.3. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NS$ $[M+H]^+$ 352.0966, found 352.0965.

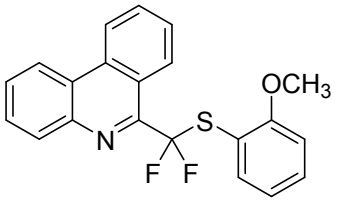
6-(difluoro((4-methoxyphenyl)thio)methyl)phenanthridine **(4c)**



White solid. 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.61 (d, *J* = 8.5 Hz, 2H), 8.30 (d, *J* = 7.5 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.81-7.70 (m, 5H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –67.1. ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 150.4 (t, *J* = 27.9 Hz), 140.7, 137.8, 133.0, 130.3 (t, *J* = 282.0 Hz), 130.0, 129.9, 128.0, 127.7, 126.6,

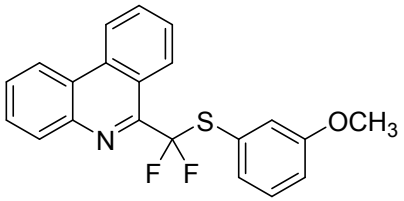
126.0 (t, *J* = 3.4 Hz), 123.9, 121.4, 121.0, 116.7, 113.5, 54.3. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NOS$ $[M+H]^+$ 368.0915, found 368.0913.

6-(difluoro((2-methoxyphenyl)thio)methyl)phenanthridine **(4d)**



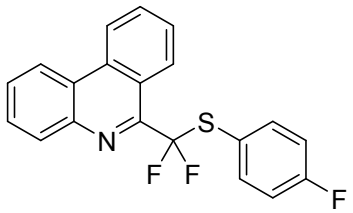
White solid. 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.60-8.58 (m, 1H), 8.28 – 8.26 (m, 1H), 7.88 (t, *J* = 7.5 Hz, 1H), 7.82-7.70 (m, 4H), 7.47-7.43 (m, 1H), 7.04 (t, *J* = 7.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –67.3. ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 150.5 (t, *J* = 27.5 Hz), 140.7, 138.7, 132.9, 131.0, 130.3 (t, *J* = 278.7Hz), 130.0, 129.9, 128.0, 127.6, 126.5, 126.1 (t, *J* = 5.0 Hz), 123.9, 121.3, 121.1, 120.9, 119.9, 114.1, 110.4, 54.9. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NOS$ $[M+H]^+$ 368.0915, found 368.0913.

6-(difluoro((3-methoxyphenyl)thio)methyl)phenanthridine **(4e)**



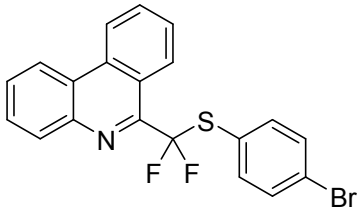
White solid. 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.0 Hz, 1H), 8.61-8.58 (m, 2H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.81-7.70 (m, 3H), 7.41-7.34 (m, 3H), 7.04-7.02 (m, 1H), 3.84 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.0. ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 150.0 (t, *J* = 27.9 Hz), 140.6, 133.0, 130.7 (t, *J* = 279 Hz), 130.1, 129.8, 128.6, 128.3, 128.0, 127.8, 127.3, 126.6, 125.9 (t, *J* = 5.2 Hz), 124.0, 121.4, 121.0, 120.9, 115.1, 54.4. HRMS (CI): m/z calcd. for $C_{21}H_{15}F_2NOS$ $[M+H]^+$ 368.0915, found 368.0916.

6-(difluoro((4-fluorophenyl)thio)methyl)phenanthridine **(4f)**



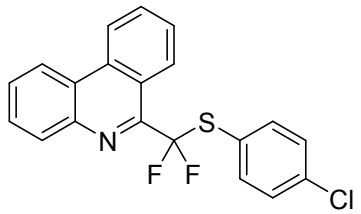
White solid. 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (d, *J* = 10.0 Hz, 1H), 8.61 (d, *J* = 7.5 Hz, 1H), 8.57 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 7.5 Hz, 1H), 7.81-7.76 (m, 4H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 8.5 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.0, –110.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (d, *J* = 250 Hz), 150.1 (t, *J* = 29.3 Hz), 140.6, 138.3 (d, *J* = 8.7 Hz), 133.0, 130.7 (t, *J* = 278 Hz), 130.1, 129.8, 128.1, 127.8, 126.7, 126.0 (t, *J* = 5.4 Hz), 124.0, 121.6, 121.4, 121.0, 120.8, 115.2 (d, *J* = 22.5Hz). HRMS (CI): m/z calcd. for $C_{20}H_{12}F_3NS$ $[M+H]^+$ 356.0715, found 356.0716.

***6-(((4-bromophenyl)thio)difluoromethyl)phenanthridine* (4g)**



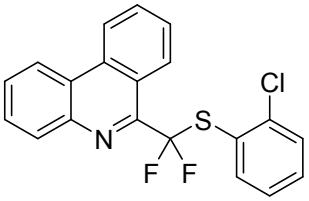
White solid. 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.61 (dd, *J* = 1.5 Hz, *J* = 7.5 Hz, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.28 (dd, *J* = 1.5 Hz, *J* = 8.0 Hz, 1H), 7.91 (td, *J* = 1.0 Hz, *J* = 7.0 Hz, 1H), 7.80-7.75 (m, 2H), 7.73-7.70 (m, 1H), 7.67-7.65 (m, 2H), 7.58-7.56 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.6. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0 (t, *J* = 28.3 Hz), 141.6, 138.6, 134.1, 132.2, 131.8 (t, *J* = 278 Hz), 131.2, 130.9, 129.2, 128.9, 127.7, 126.8 (t, *J* = 5.4 Hz), 126.6, 125.1, 124.9, 122.5, 122.1, 121.8. HRMS (CI): m/z calcd. for $C_{20}H_{12}BrF_2NS$ $[M+H]^+$ 415.9915, found 415.9914.

***6-(((4-chlorophenyl)thio)difluoromethyl)phenanthridine* (4h)**



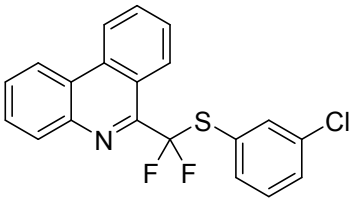
White solid. 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.61-8.59 (m, 1H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.29 (dd, *J* = 1.5 Hz, *J* = 7.5 Hz, 1H), 7.91-7.88 (m, 1H), 7.82-7.71 (m, 5H), 7.43-7.41 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8 (t, *J* = 28.1 Hz), 141.6, 138.4, 136.6, 134.1, 131.9 (t, *J* =278 Hz), 131.2, 130.9, 129.2, 129.2, 128.9, 127.7, 126.8 (t, *J* = 5.4 Hz), 126.0, 125.1, 122.5, 122.1, 121.8. HRMS (CI): m/z calcd. for $C_{20}H_{12}ClF_2NS$ $[M+H]^+$ 372.0420, found 372.0421.

***6-(((2-chlorophenyl)thio)difluoromethyl)phenanthridine* (4i)**



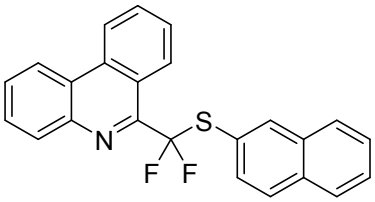
White solid. 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.0 Hz, 1H), 8.59 (t, *J* = 5.5 Hz, 2H), 8.30 (dd, *J* = 1.5 Hz, *J* = 8.5 Hz, 1H), 7.97-7.95 (m, 1H), 7.89 (t, *J* = 8.0 Hz, 1H), 7.80-7.74 (m, 2H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 1.5 Hz, *J* = 8.0 Hz, 1H), 7.44 (td, *J* = 1.5 Hz, *J* = 7.5 Hz, 1H), 7.37 (td, *J* = 1.5 Hz, *J* = 7.5 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.8. ^{13}C NMR(125 MHz, $CDCl_3$) δ 151.0 (t, *J* = 27.8 Hz), 141.6 , 140.8 , 139.7 , 134.0 , 132.1 (t, *J* = 279 Hz), 131.4 , 131.1 , 130.9 , 130.3, 129.1 , 128.9 , 127.7 , 127.1 , 127.0 , 126.8 (t, *J* = 5.3 Hz), 125.1 , 122.4 , 122.0 , 121.8. HRMS (CI): m/z calcd. for $C_{20}H_{12}ClF_2NS$ $[M+H]^+$ 372.0420, found 372.0418.

***6-(((3-chlorophenyl)thio)difluoromethyl)phenanthridine* (4j)**



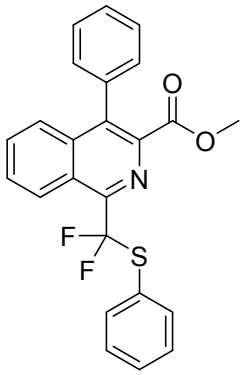
White solid. 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 7.5 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 7.0 Hz, 1H), 7.91 (t, *J* = 7.5 Hz, 1H), 7.82-7.76 (m, 3H), 7.74-7.69 (m, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.3. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0 (t, *J* = 28.3 Hz), 141.6, 136.6, 135.1, 134.5, 134.1, 132.0 (t, *J* = 279 Hz), 131.2, 130.9, 130.1, 129.9, 129.4, 129.2, 128.9, 127.8, 126.8 (t, *J* = 5.3 Hz), 125.1, 122.5, 122.1, 121.8. HRMS (CI): m/z calcd. for $C_{20}H_{12}ClF_2NS$ $[M+H]^+$ 372.0420, found 372.0419.

6-(difluoro(naphthalen-2-ylthio)methyl)phenanthridine **(4k)**



White solid. 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.5 Hz, 1H), 8.59-8.57 (m, 2H), 8.34 (s, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 7.88-7.84 (m, 5H), 7.80-7.73 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.56-7.51 (m, 2H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1 (t, *J* = 27.9 Hz), 141.7, 137.4, 134.1, 133.7, 133.5, 133.2, 132.0 (t, *J* = 278 Hz), 131.1, 130.9, 129.1, 128.8, 128.5, 128.2, 127.8, 127.7, 127.3, 127.0 (t, *J* = 5.3 Hz), 126.6, 125.1, 124.7, 122.4, 122.1, 121.9. HRMS (CI): m/z calcd. for $C_{24}H_{15}F_2NS$ $[M+H]^+$ 388.0966, found 388.0965.

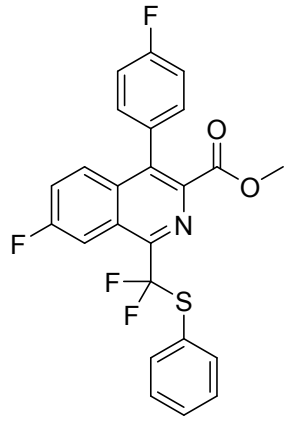
methyl 1-(difluoro(phenylthio)methyl)-4-phenylisoquinoline-3-carboxylate **(6a)**



White solid. 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.0 Hz, 2H), 7.76-7.70 (m, 3H), 7.54-7.51 (m, 3H), 7.50-7.48 (m, 1H), 7.46-7.43 (m, 2H), 7.35-7.33 (m, 2H), 3.75 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 149.5 (t, *J* = 28.7 Hz), 138.3, 136.2, 136.1, 136.1, 134.3, 130.3 (t, *J* = 276.2 Hz), 130.1, 128.9, 128.4, 128.3, 127.9, 127.3, 127.3, 126.3, 126.0, 124.7 (t, *J* = 5.0 Hz), 123.8, 51.5. HRMS (CI): m/z calcd. for $C_{24}H_{17}F_2NO_2S$ $[M+H]^+$ 422.1021, found 422.1018.

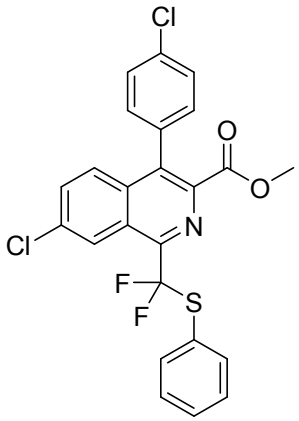
Methyl 1-(difluoro(phenylthio)methyl)-7-fluoro-4-(4-fluorophenyl)isoquinoline- 3-

***carboxylate* (6b)**



White solid. 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 2.0 Hz, *J* = 10.0 Hz, 1H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.72-7.69 (m, 1H), 7.52-7.48 (m, 2H), 7.46-7.43 (m, 2H), 7.31-7.29 (m, 2H), 7.25-7.22 (m, 2H), 3.78 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.7，–105.9，–112.6. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 163.9 (d, *J* =246.2 Hz), 163.0 (d, *J* =252.0 Hz), 150.3 (td, *J* =6.2, 28.75 Hz), 139.1, 137.2, 136.2, 134.5, 131.3 (d, *J* = 8.7 Hz), 131.0 (t, *J* = 277.5 Hz), 130.9 (d, *J* = 3.7 Hz), 130.2 (t, *J* = 5.0 Hz), 129.0, 128.7, 126.7, 126.1 (d, *J* = 10.0 Hz), 122.0 (d, *J* = 25.0 Hz), 115.8 (d, *J* = 21.2 Hz), 110.2 (td, *J* = 5.0, 23.7 Hz), 52.7. HRMS (CI): m/z calcd. for $C_{24}H_{15}F_4NO_2S$ $[M+H]^+$ 458.0832, found 458.0832.

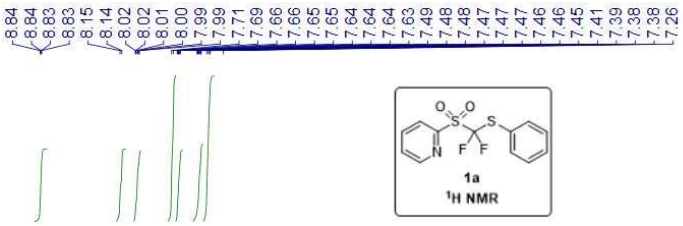
***Methyl 7-chloro-4-(4-chlorophenyl)-1-(difluoro(phenylthio)methyl)isoquinoline- 3-carboxylate* (6c)**

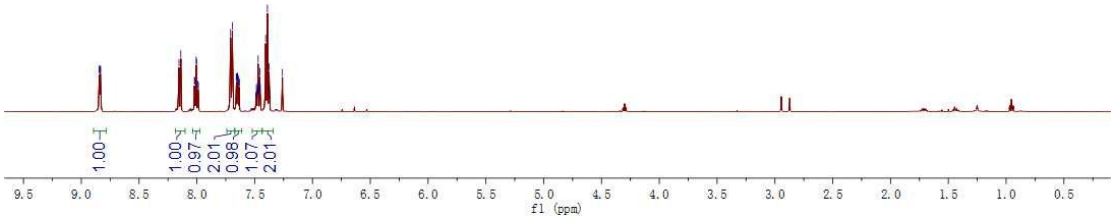


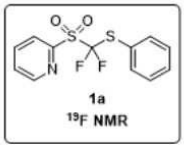
White solid. 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.66-7.59 (m, 2H), 7.52-7.44 (m, 6H), 7.26-7.24 (m, 1H), 3.79 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ –66.0. ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 150.1 (t, *J* = 28.7 Hz), 139.4, 137.2, 136.2, 136.1, 135.6 , 134.9, 133.3, 132.5, 131.1 (t, *J* = 277.5 Hz), 130.8, 130.2, 129.1, 128.8, 128.7, 126.5, 125.4, 125.0 (t, *J* = 5.0 Hz), 52.8. HRMS (CI): m/z calcd. for $C_{24}H_{15}Cl_2F_2NO_2S$ $[M+H]^+$ 490.0241, found 490.0239.

[1] S. Feng, T. Li, C. Du, P. Chen, D.Song, J. Li, X. Xie, X. She, *Chem. Commun.*, 2017, **53**, 4585-4588
[2] J. Rong, L. Deng, P. Tan, C. Ni, Y. Gu, J. Hu, *Angew. Chem. Int. Ed.* 2016, **55**, 2743-2747.
[3] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* 2013, **113**, 5322−5363
*[4] J. Liang, Z. Chen, J. Yin, G. Yu and S. Liu, Chem. Commun.,**2013**, 49, 3567*

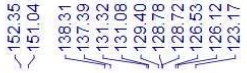
6. Copies of NMR Spectra






1a
19F NMR

-77.00
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)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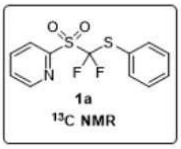
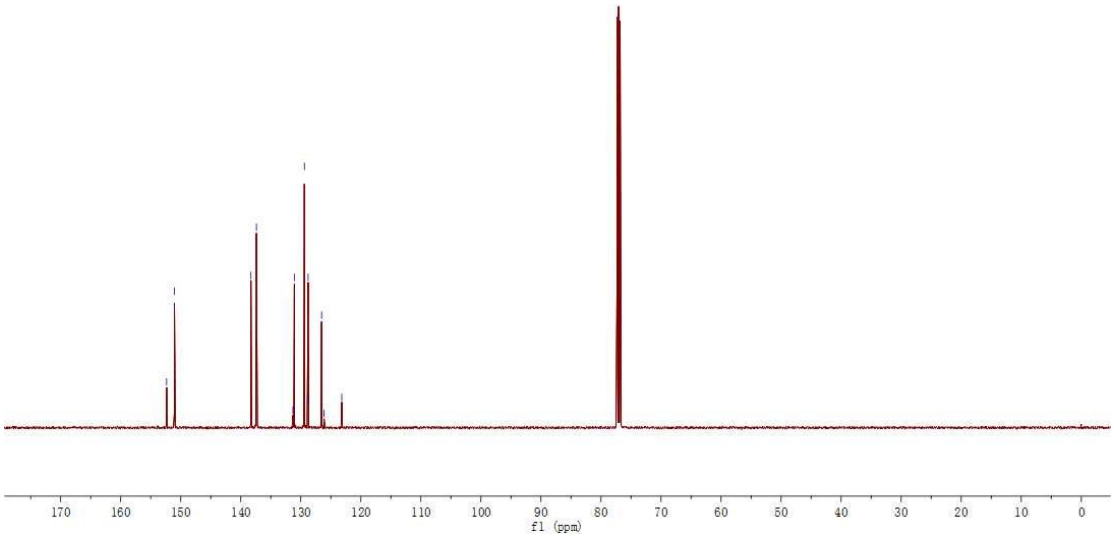
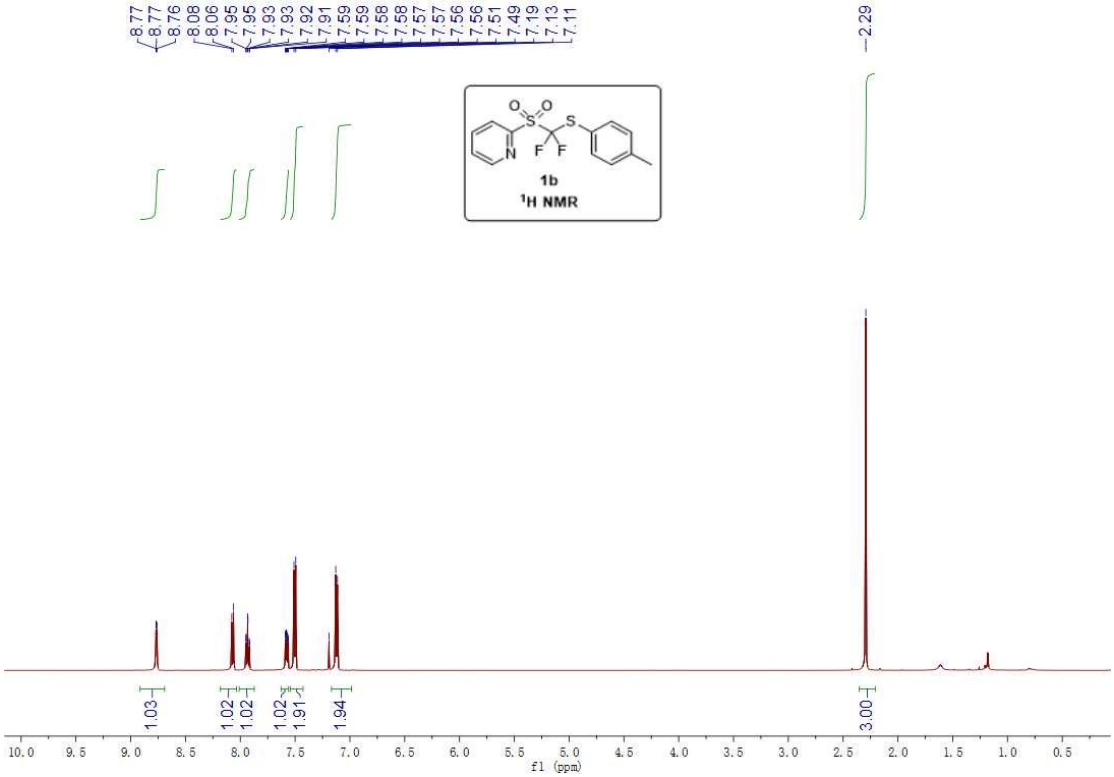
151.04
138.31
137.39
131.32
131.08
129.40
128.78
128.72
126.53
126.12
123.17


1a
13C NMR


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.08
8.06
7.95
7.95
7.93
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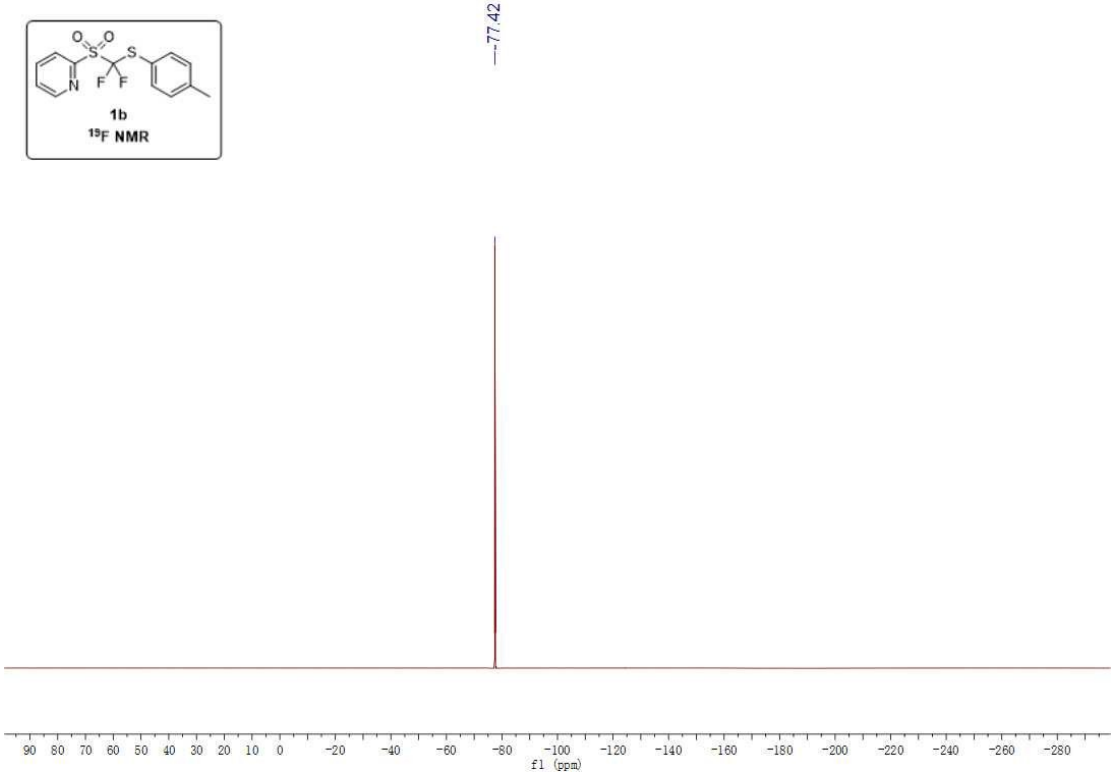
7.92
7.91
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.51
7.49
7.19
7.13
7.11
2.29
1b
1H NMR
1.03
1.02
1.02
1.02
1.91
1.94
3.00
f1 (ppm)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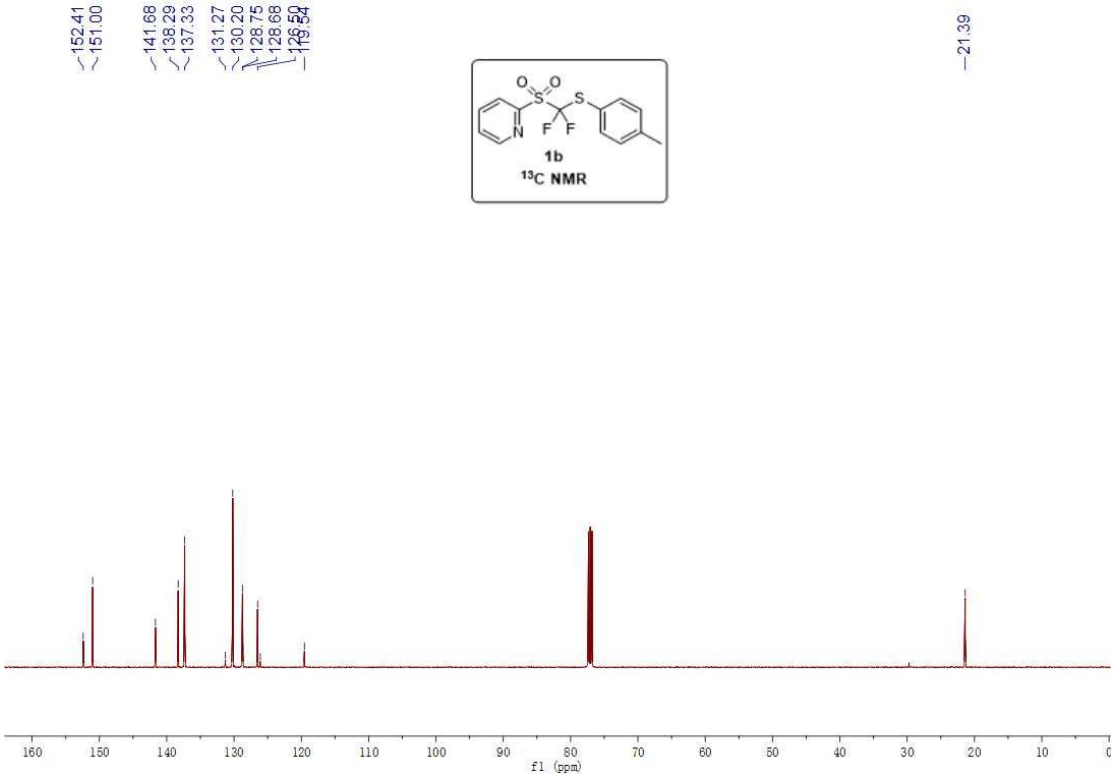
1b
19F NMR
f1 (ppm)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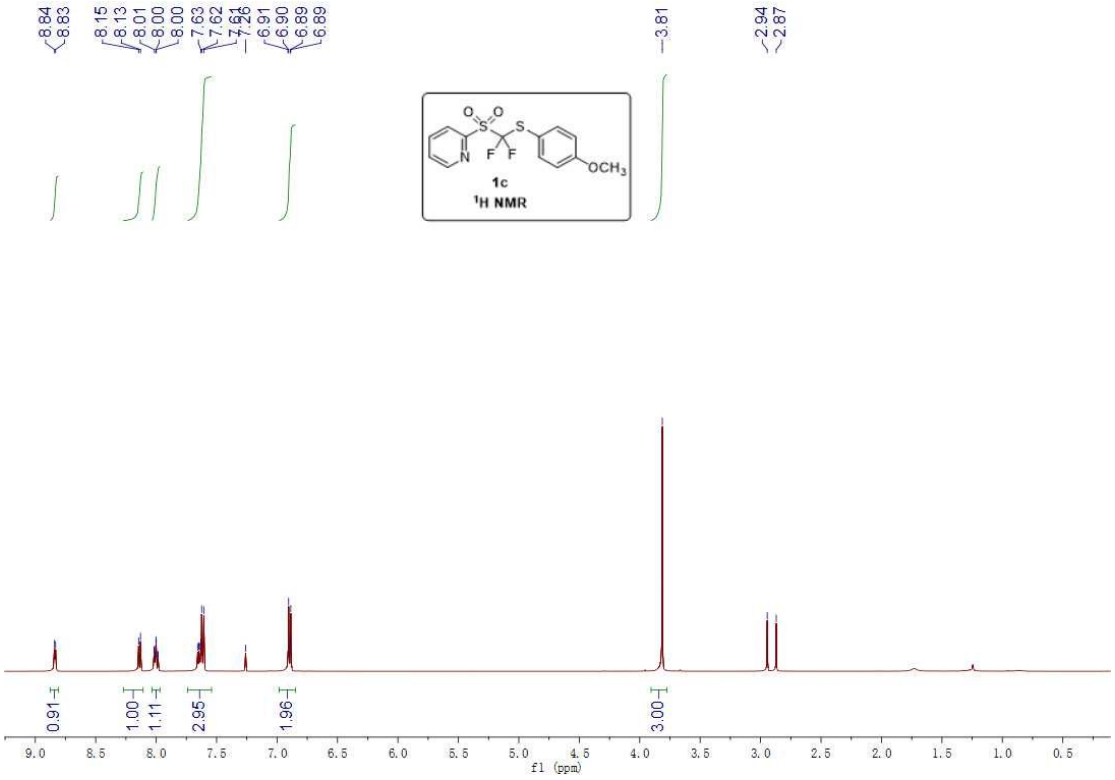
151.00
141.68
138.29
137.33
131.27
130.20
128.75
128.68
126.50
119.54
21.39
1b
13C NMR
f1 (ppm)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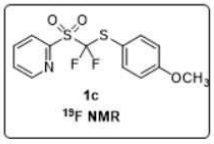
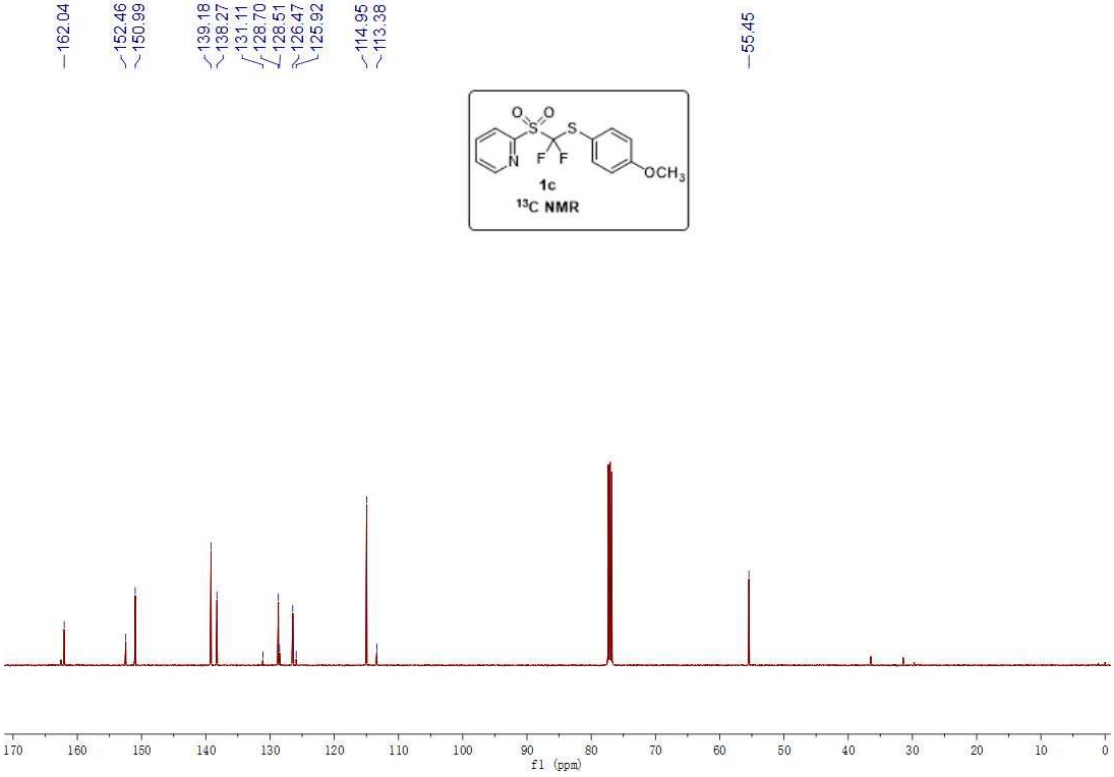
8.83
8.15
8.13
8.01
8.00
8.00
7.63
7.62
7.61
7.26
6.91
6.90
6.89
6.89
3.81
2.94
2.87
1c
1H NMR
0.91
1.00
1.11
2.95
1.96
3.00
f1 (ppm)


1c
19F NMR

-78.11
f1 (ppm)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152.46
150.99
139.18
138.27
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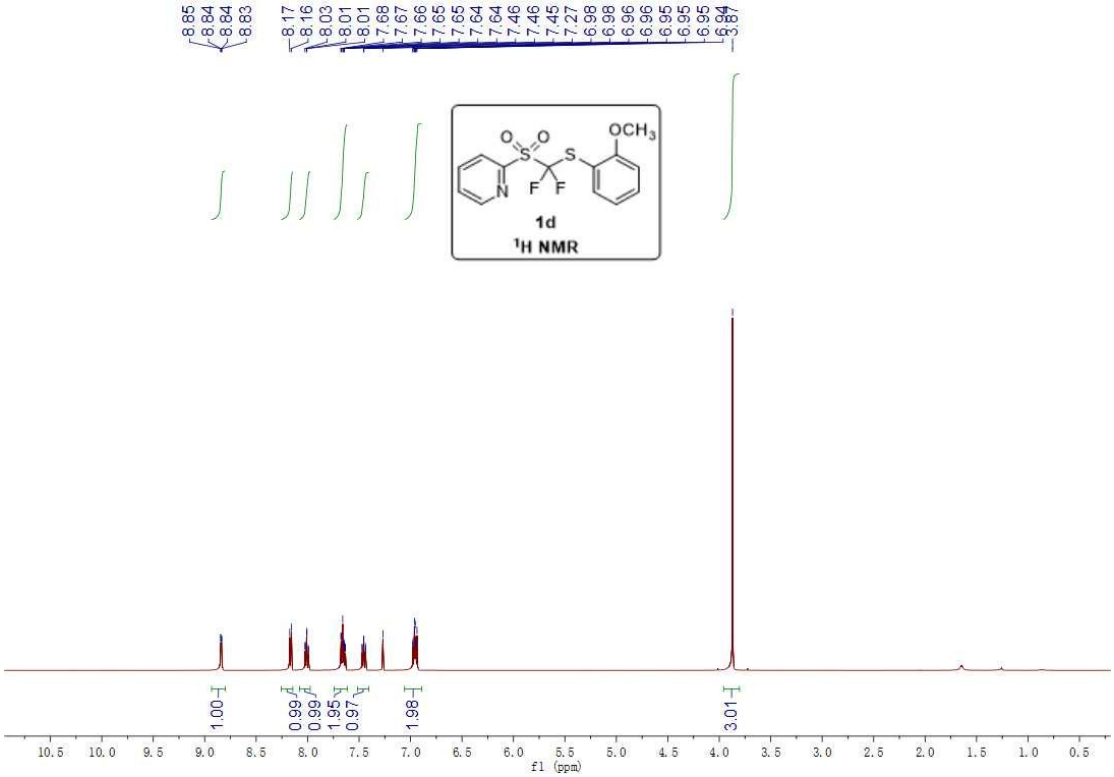
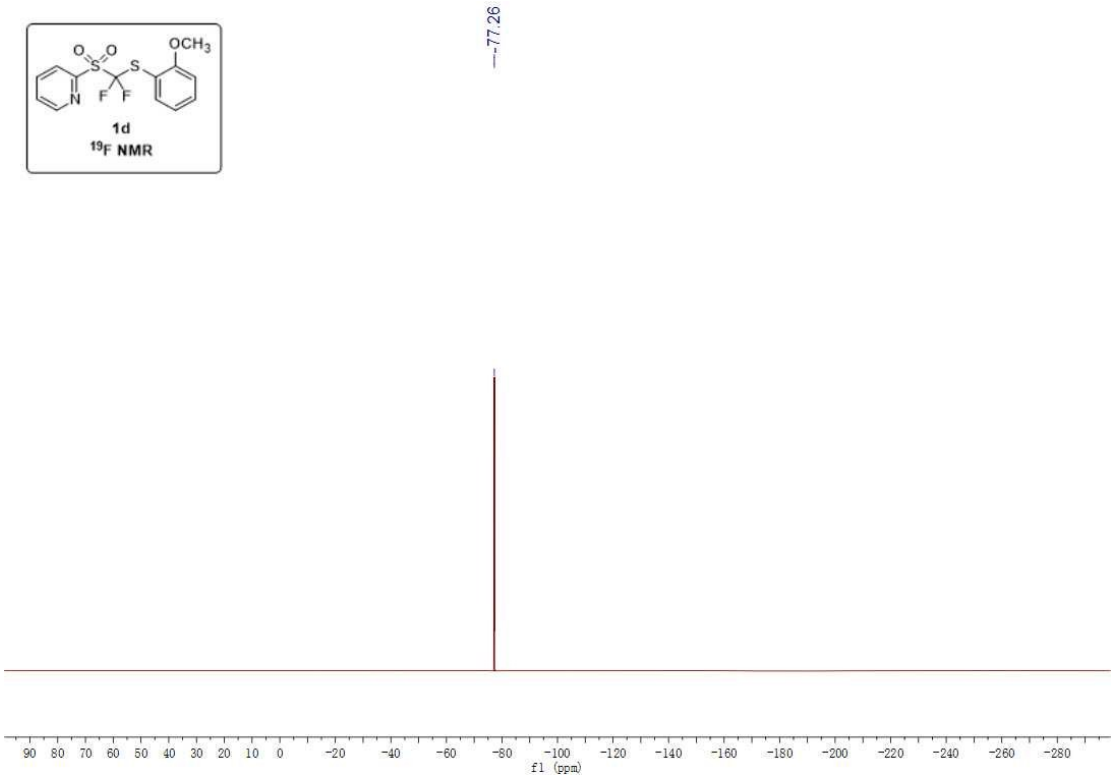
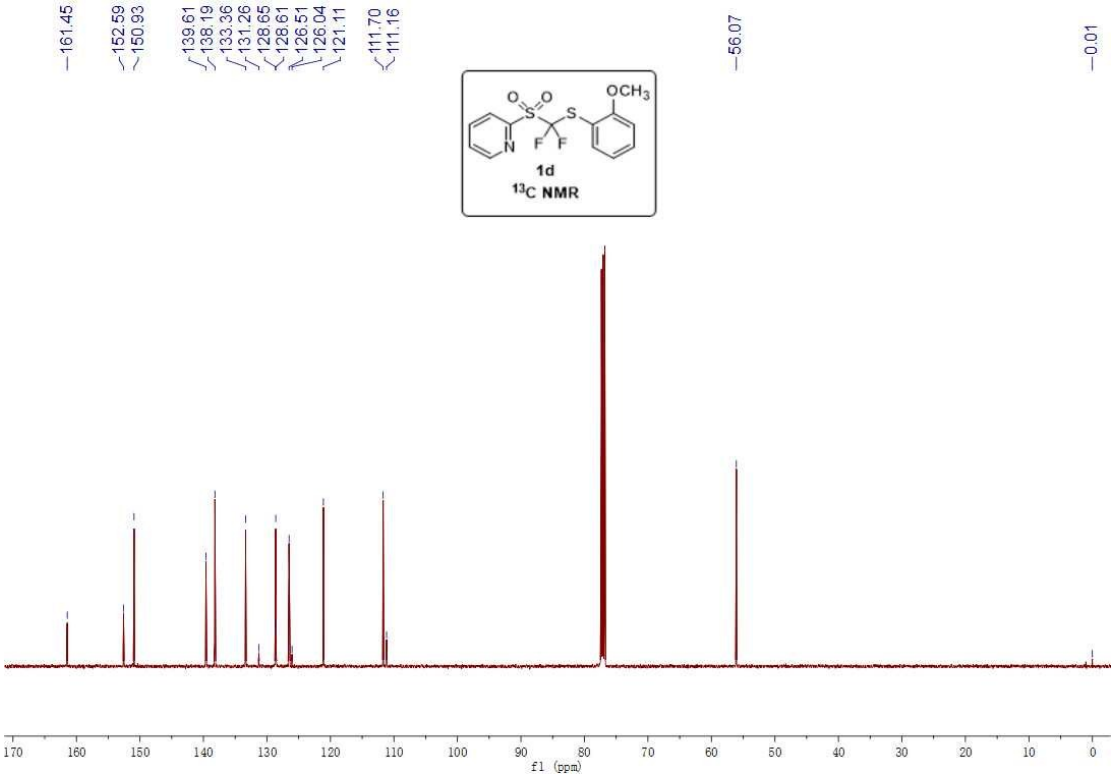
128.51
126.47
125.92
114.95
113.38
55.45
1c
13C NMR
f1 (ppm)


8.85
8.84
8.84
8.83
8.17
8.16
8.03
8.01
8.01
7.68
7.67
7.66
7.65
7.65
7.64
7.64
7.46
7.46
7.45
7.27
6.98
6.98
6.96
6.96
6.95
6.95
6.95
6.94
3.87
1d
1H NMR
1.00
0.99
0.99
1.95
0.97
1.98
3.01
f1 (ppm)


-77.26
1d
19F NMR
f1 (ppm)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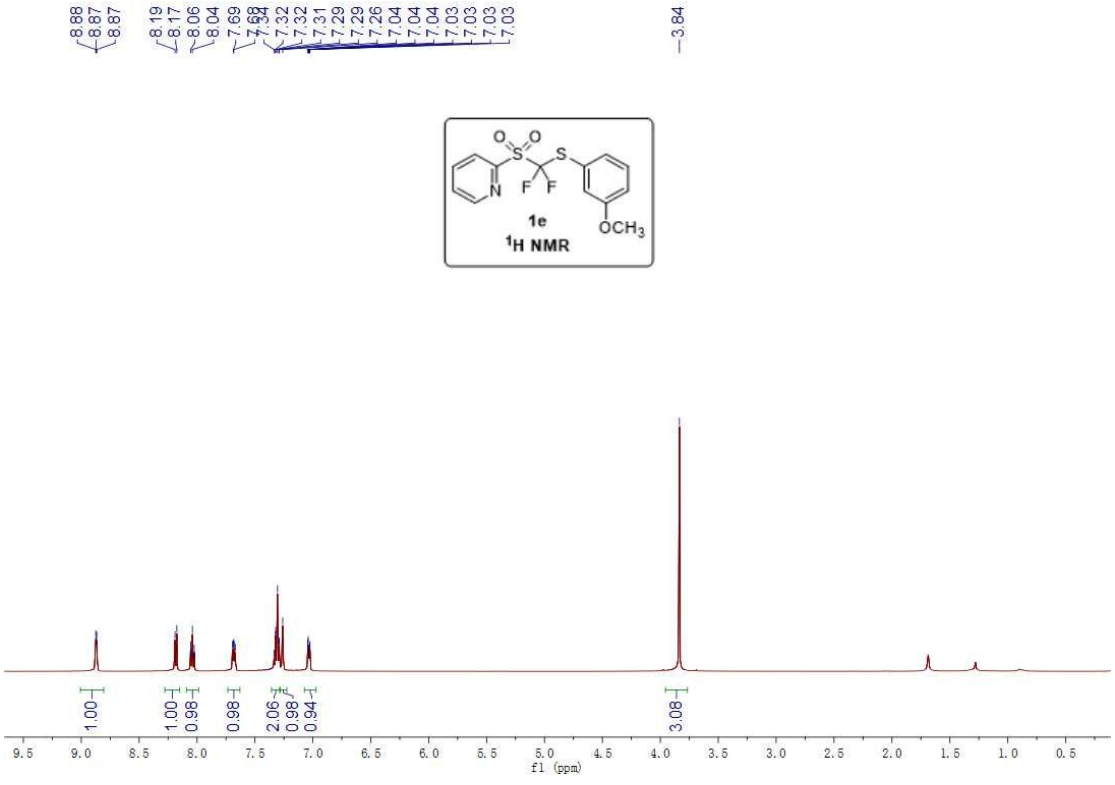
152.59
150.93
139.61
138.19
133.36
131.26
128.65
128.61
126.51
126.04
121.11
111.70
111.16
56.07
0.01
1d
13C NMR
f1 (ppm)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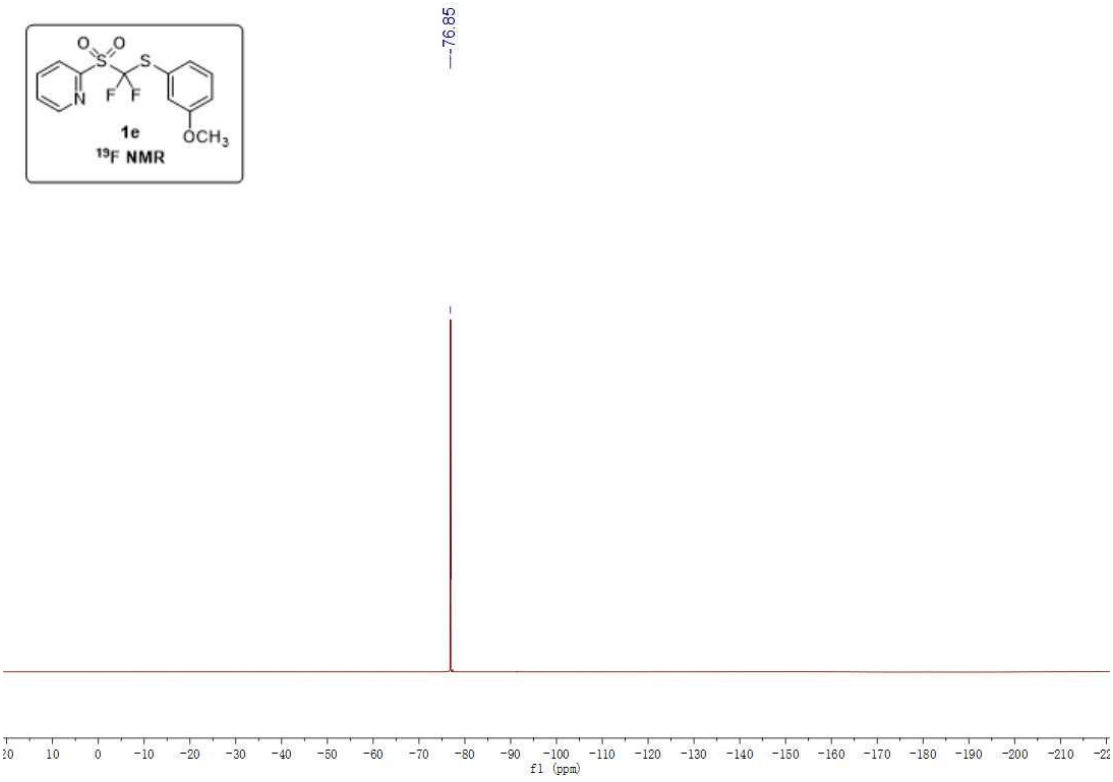
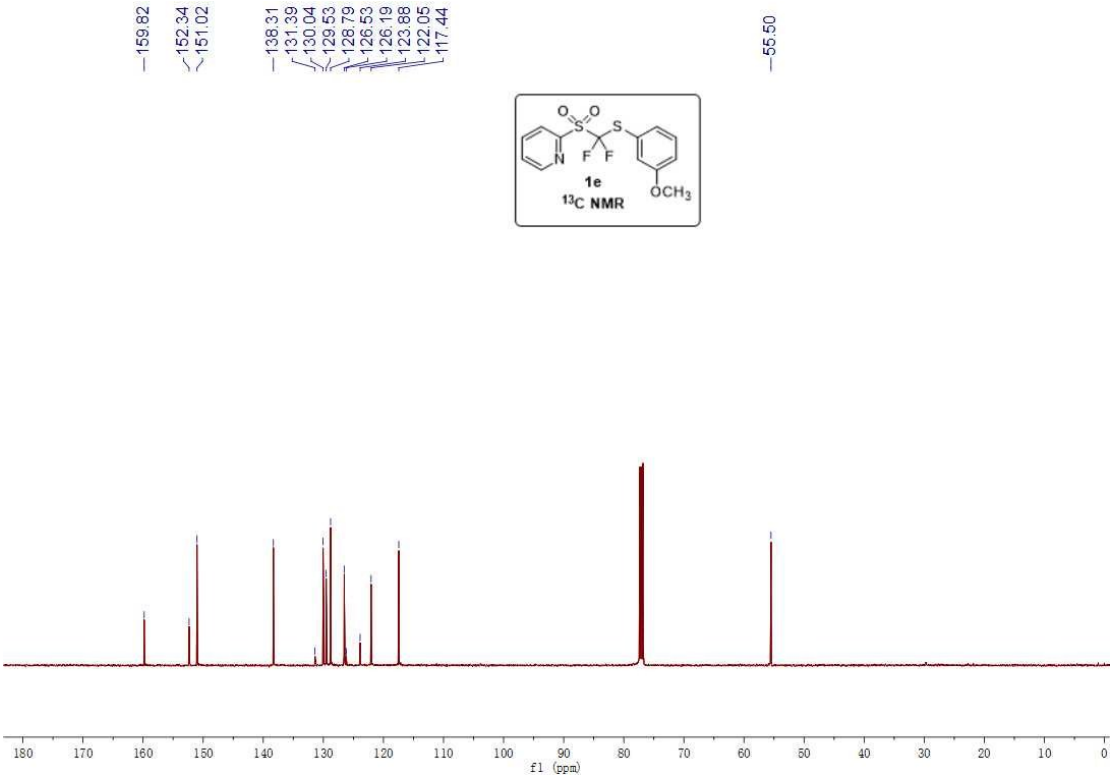
8.06
8.04
7.69
7.68
7.34
7.32
7.31
7.29
7.29
7.26
7.04
7.04
7.04
7.03
7.03
7.03
7.03
3.84
1e
1H NMR
OCH3
1.00
1.00
0.98
0.98
2.06
0.98
0.94
3.08
f1 (ppm)


1e
19F NMR
-76.85
f1 (ppm)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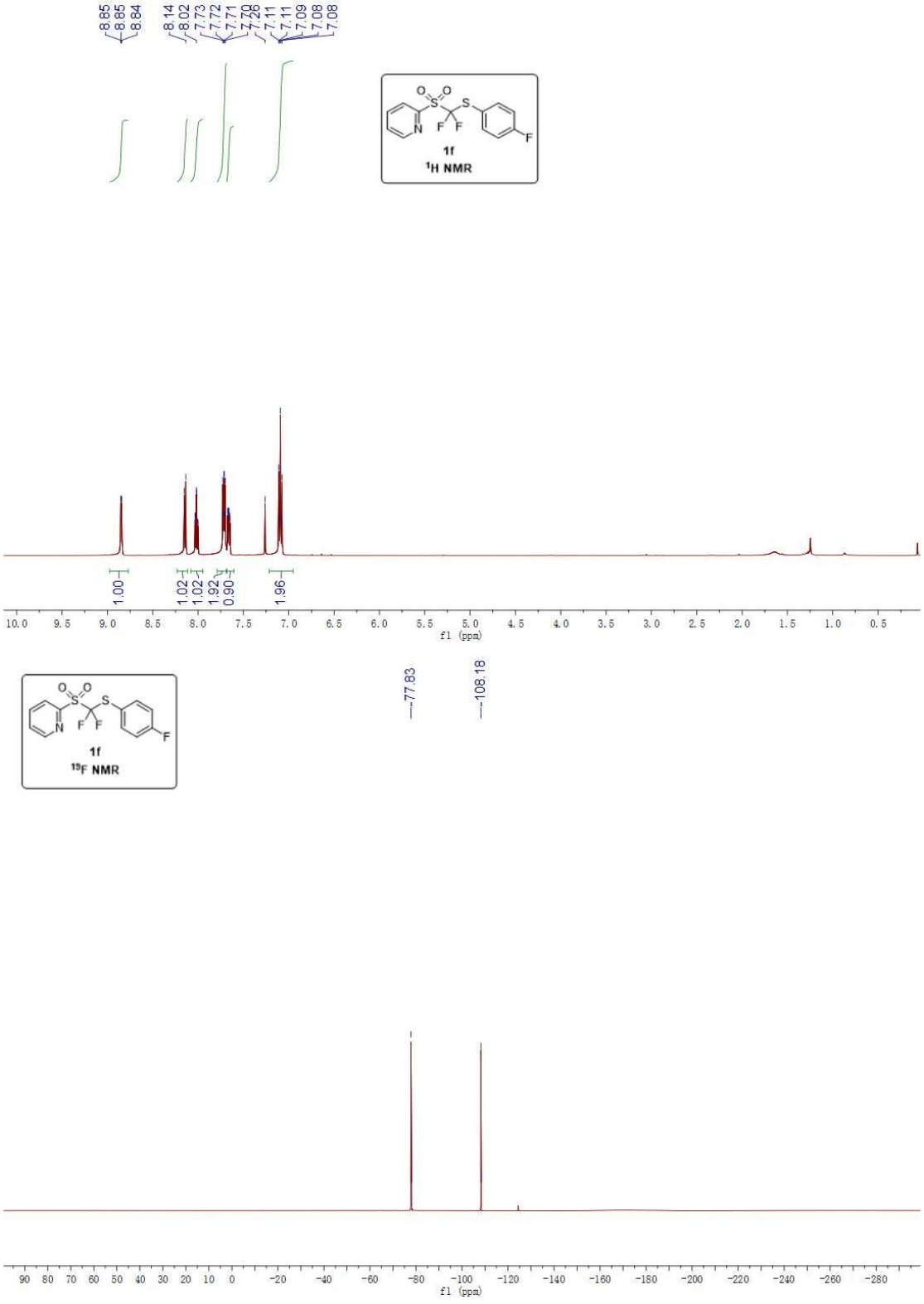
138.31
131.39
130.04
129.53
128.79
126.53
126.19
123.88
122.05
117.44
55.50
1e
13C NMR
f1 (ppm)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8.02
7.73
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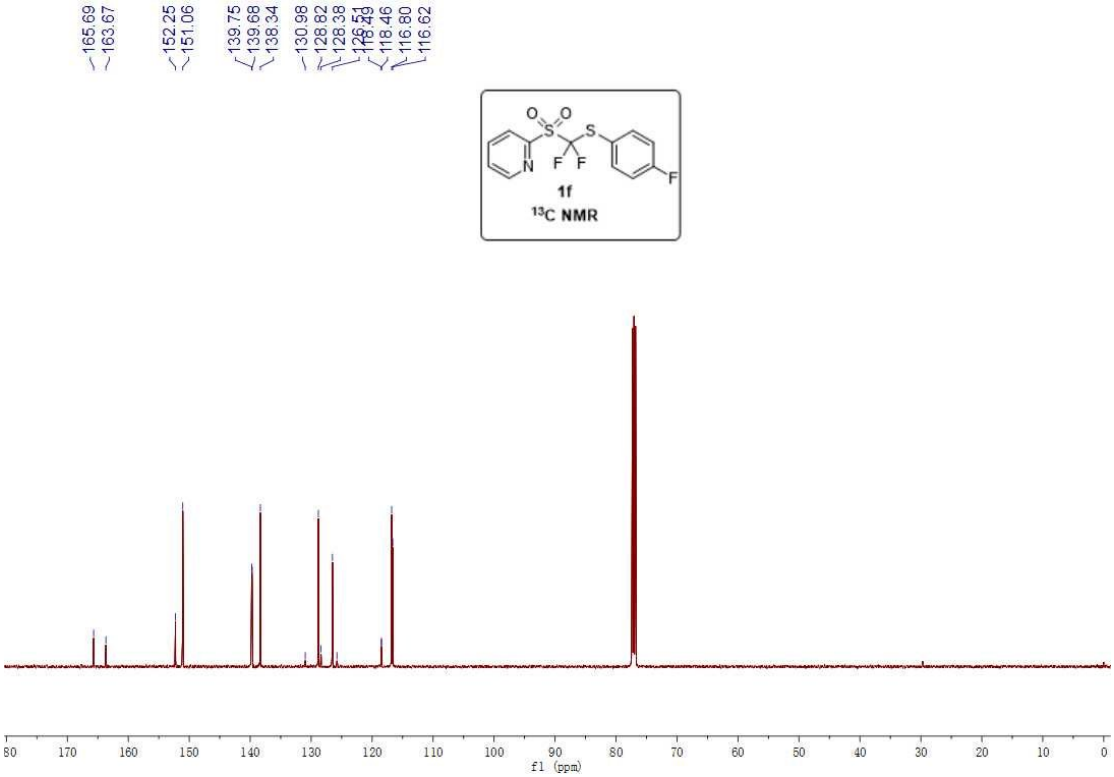
7.71
7.70
7.20
7.11
7.11
7.09
7.08
7.08
1f
1H NMR
1.00
1.02
1.02
1.92
0.90
1.96
f1 (ppm)
1f
19F NMR
-77.83
-108.18
f1 (ppm)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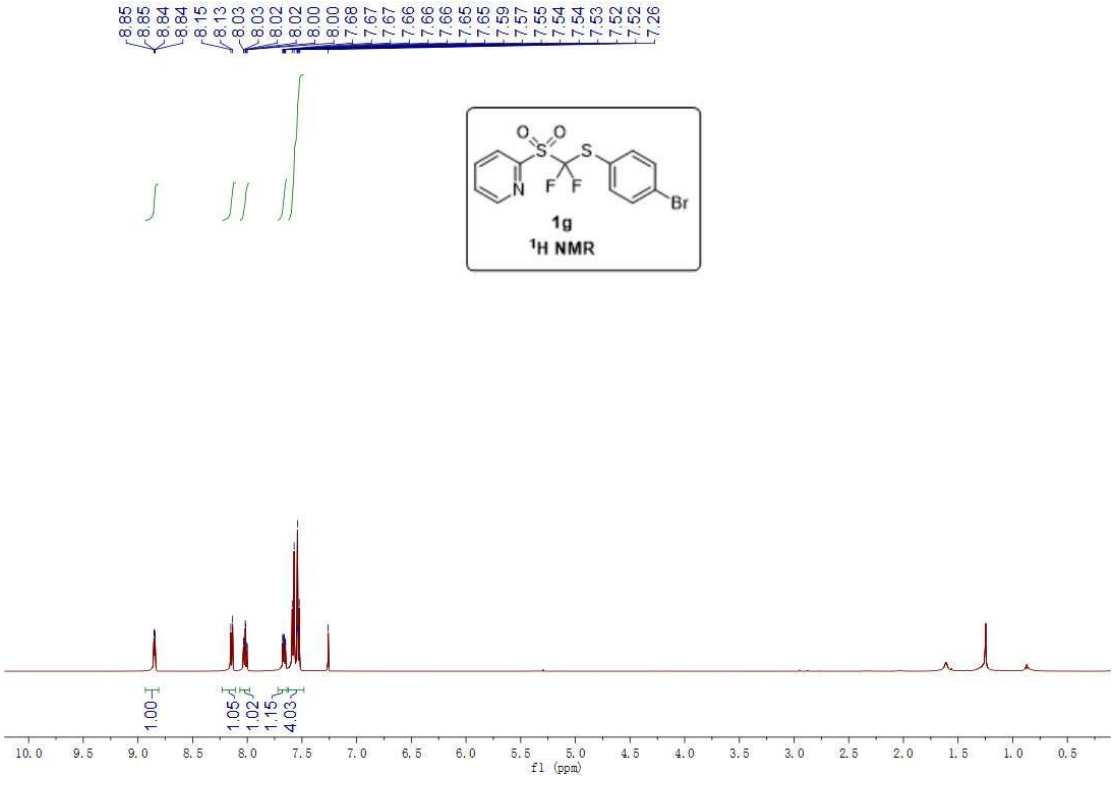
126.49
118.46
116.80
116.62
1f
13C NMR
f1 (ppm)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8.84
8.15
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8.03
8.02
8.02
8.00
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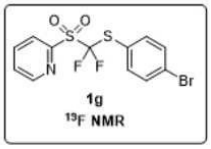
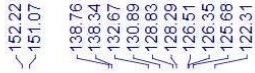
7.67
7.67
7.66
7.66
7.66
7.65
7.65
7.59
7.57
7.55
7.54
7.54
7.53
7.52
7.52
7.26
1g
1H NMR
1.00
1.05
1.02
1.15
4.03
f1 (ppm)


1g
^{19}F NMR

-77.44
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)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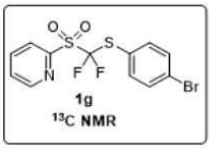
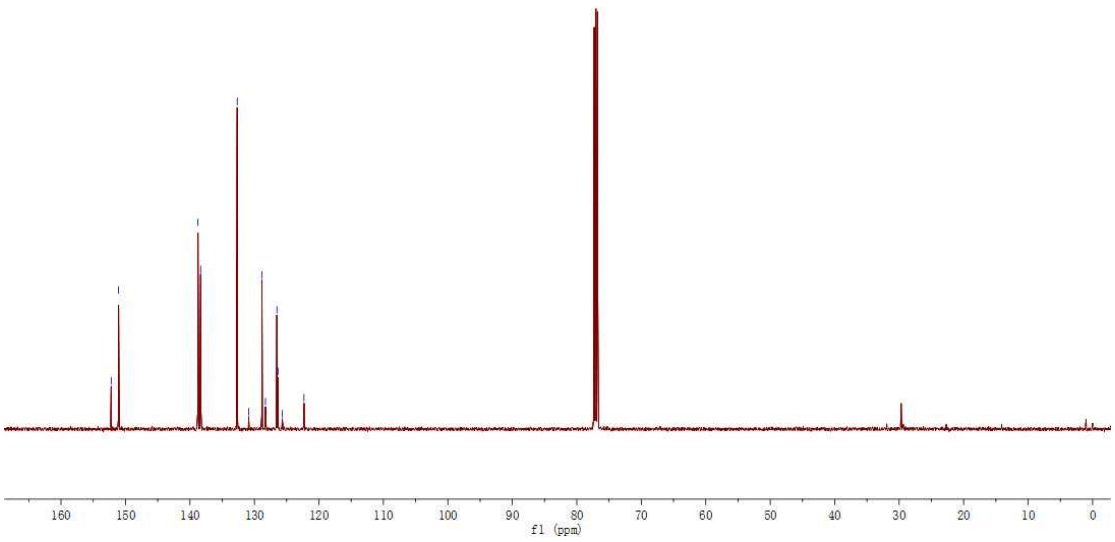
126.51
126.35
125.68
122.31


1g
^{13}C NMR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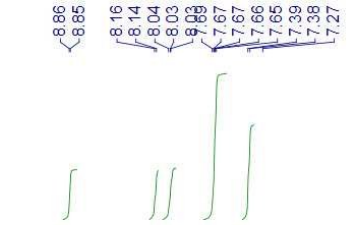
f1 (ppm)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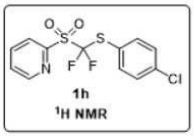
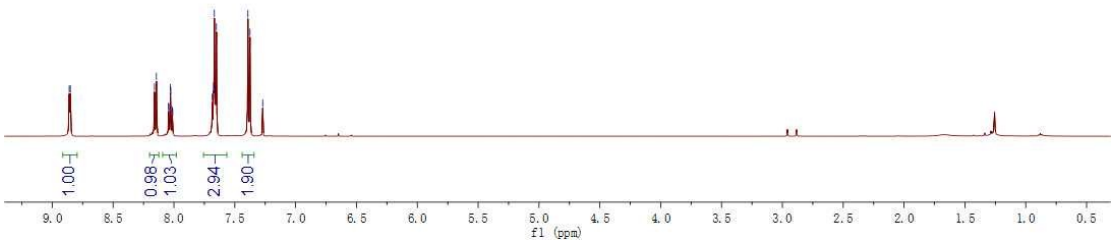
7.67
7.66
7.65
7.39
7.38
7.27


1h
1H NMR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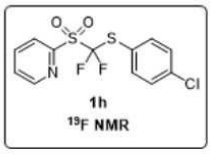
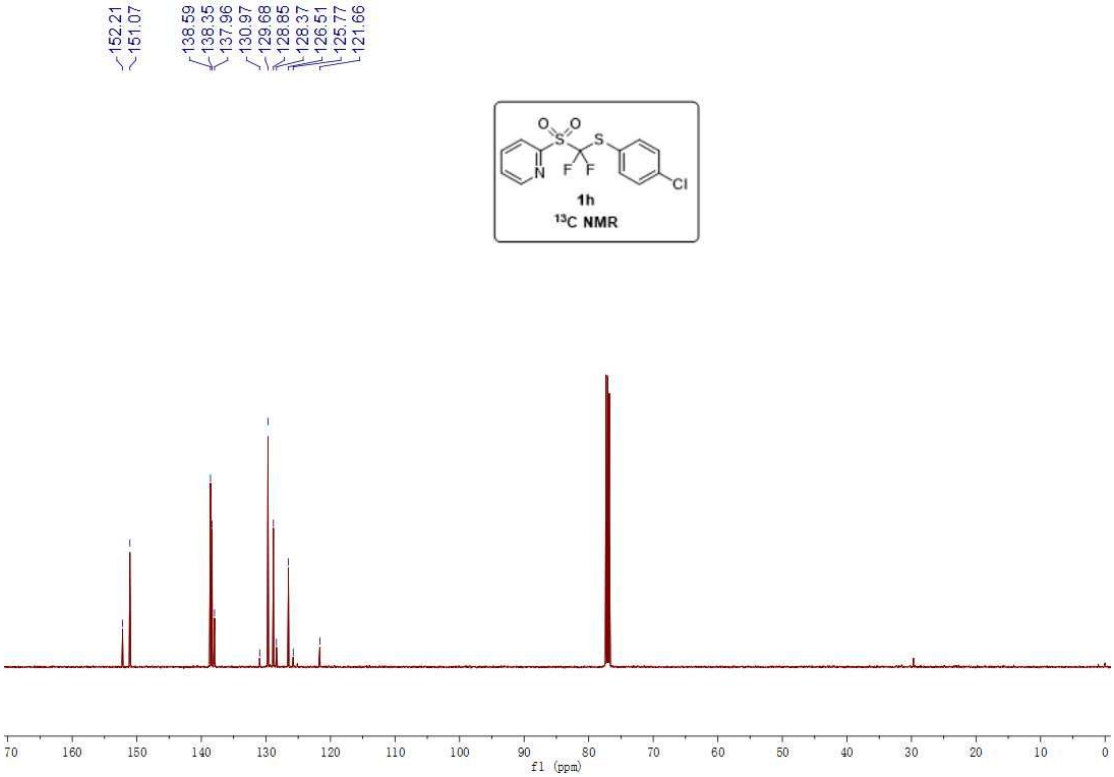
0.98
1.03
2.94
1.90
f1 (ppm)


1h
19F NMR

-77.51
f1 (ppm)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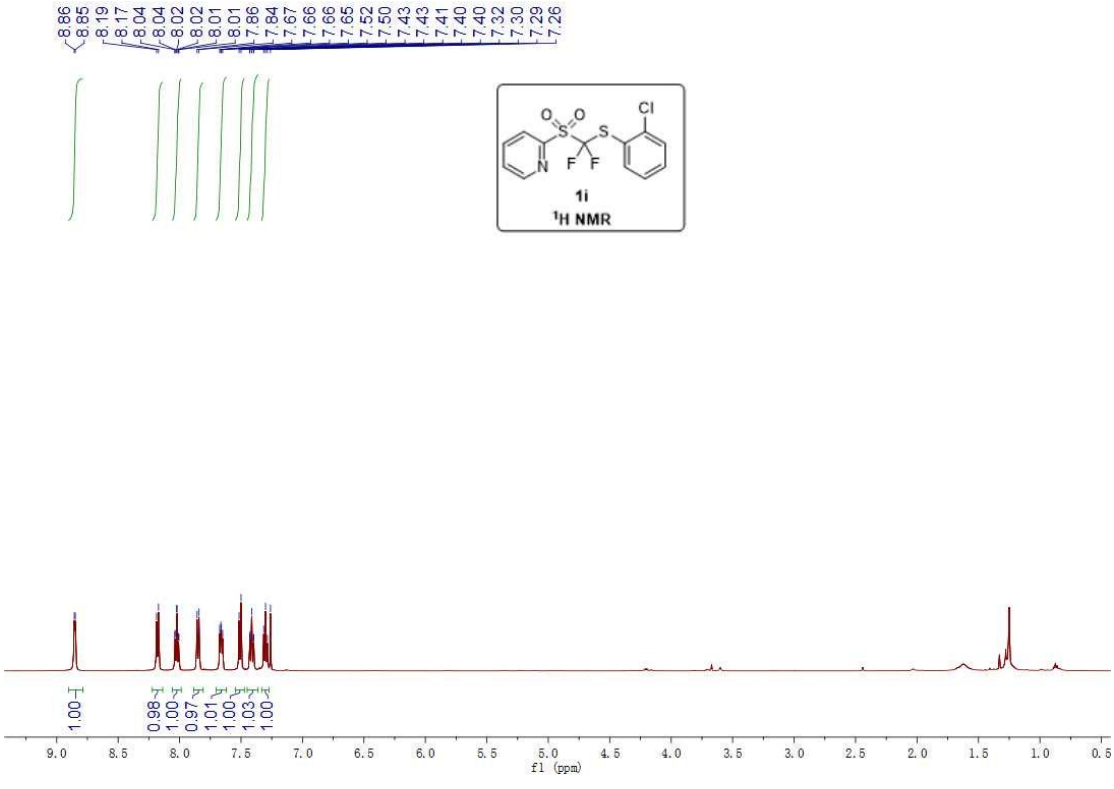
151.07
138.59
138.35
137.96
130.97
129.68
128.85
128.37
126.51
125.77
121.66
1h
13C NMR
f1 (ppm)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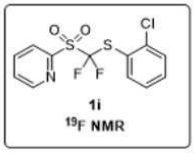
8.85
8.19
8.17
8.04
8.04
8.02
8.02
8.01
8.01
7.86
7.84
7.67
7.66
7.66
7.65
7.52
7.50
7.43
7.43
7.41
7.40
7.40
7.32
7.30
7.29
7.26
1i
1H NMR
1.00
0.98
1.00
0.97
1.01
1.00
1.03
1.00
f1 (ppm)


1i
19F NMR

-76.80
f1 (ppm)


152.22
151.04
141.15
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132.65
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128.56
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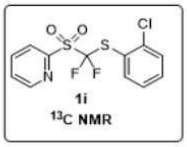
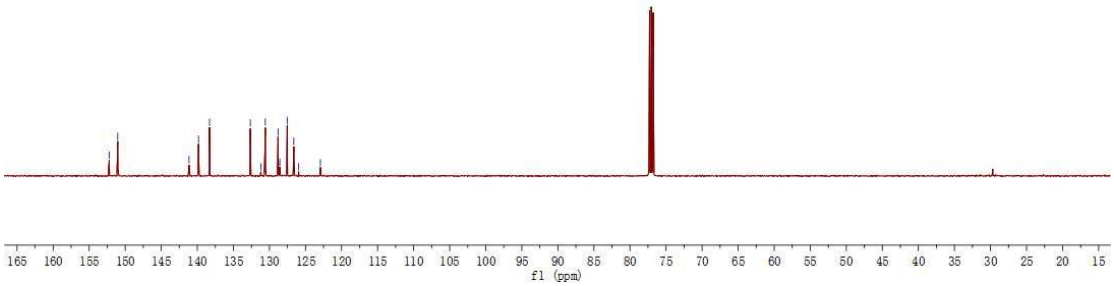
126.62
125.94
122.93


1i
13C NMR


f1 (ppm)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8.16
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8.02
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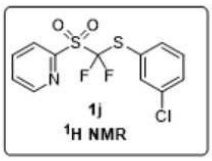
7.46
7.45
7.36
7.34
7.33
7.26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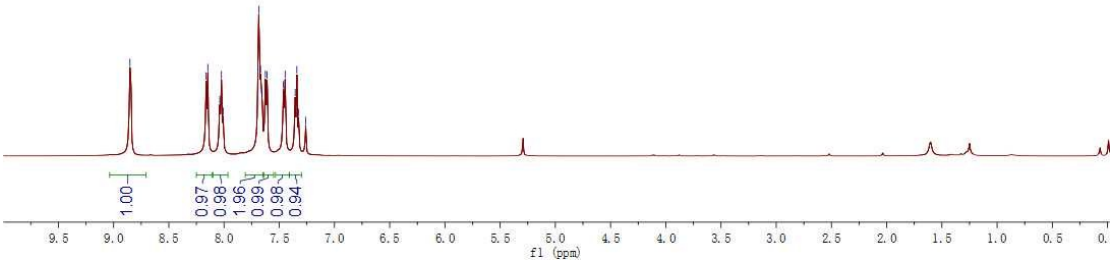
1H NMR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1.96
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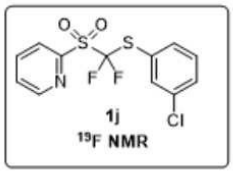
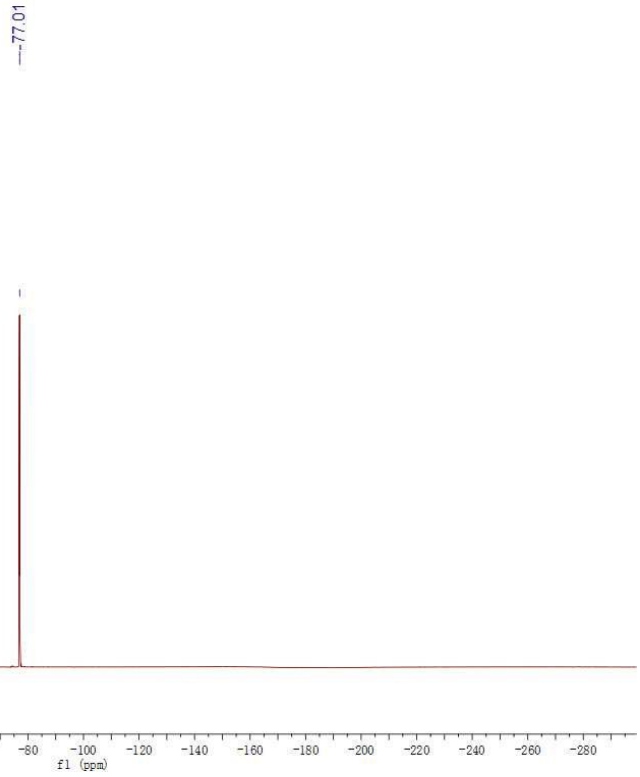
0.98
0.94
f1 (ppm)


1j
19F NMR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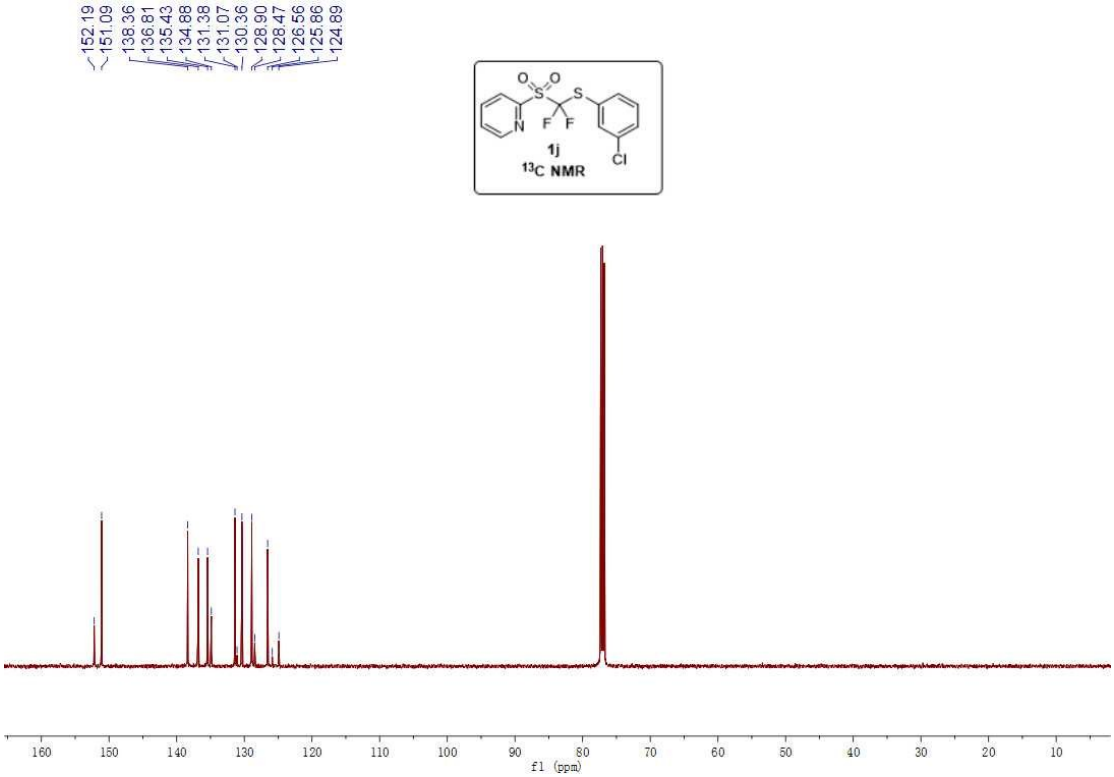
f1 (ppm)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151.09
138.36
136.81
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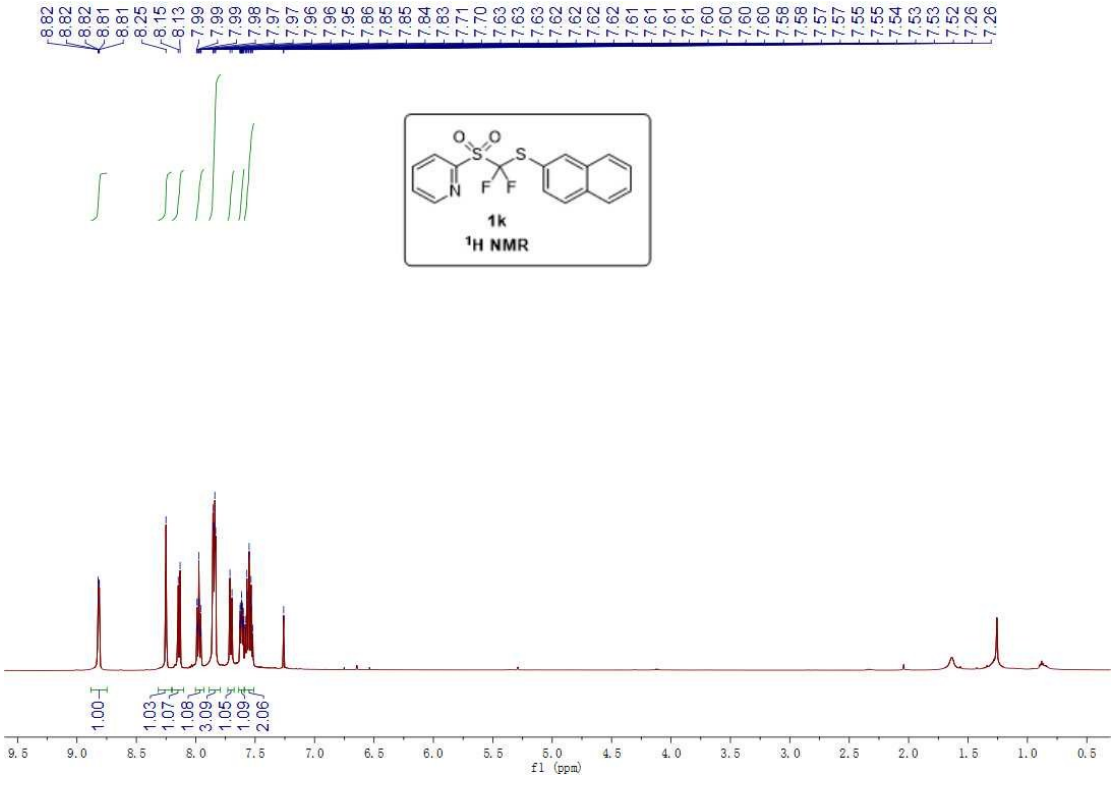
131.38
131.07
130.36
128.90
128.47
126.56
125.86
124.89
1j
13C NMR
f1 (ppm)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8.82
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8.81
8.25
8.15
8.13
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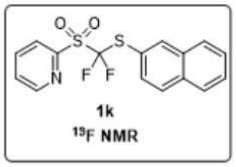
7.99
7.99
7.98
7.97
7.97
7.96
7.96
7.95
7.86
7.85
7.85
7.84
7.83
7.71
7.70
7.63
7.63
7.63
7.62
7.62
7.62
7.62
7.62
7.61
7.61
7.61
7.61
7.60
7.60
7.60
7.60
7.58
7.58
7.57
7.57
7.55
7.55
7.54
7.53
7.53
7.52
7.26
7.26
1k
1H NMR
1.00
1.03
1.07
1.08
3.09
1.05
1.09
2.06
f1 (ppm)


1k
19F NMR

-76.86
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


152.37
151.01
138.28
138.23
134.01
133.35
132.62
131.47
129.06
128.87
128.76
128.28
128.05
127.77
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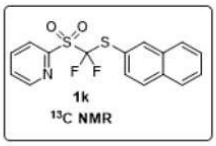
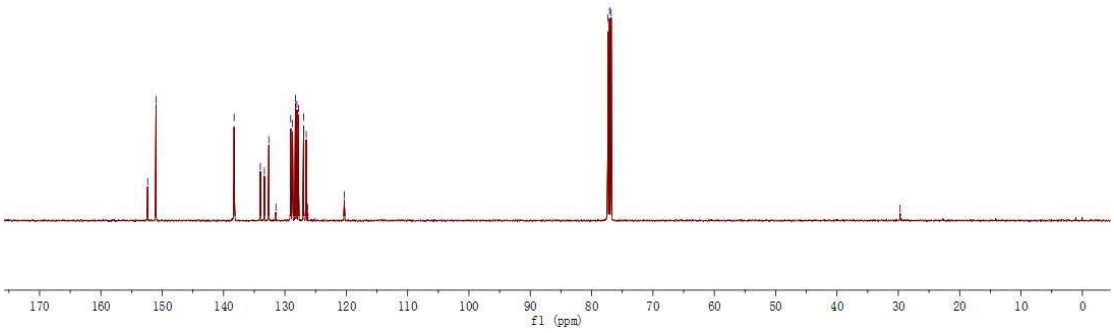
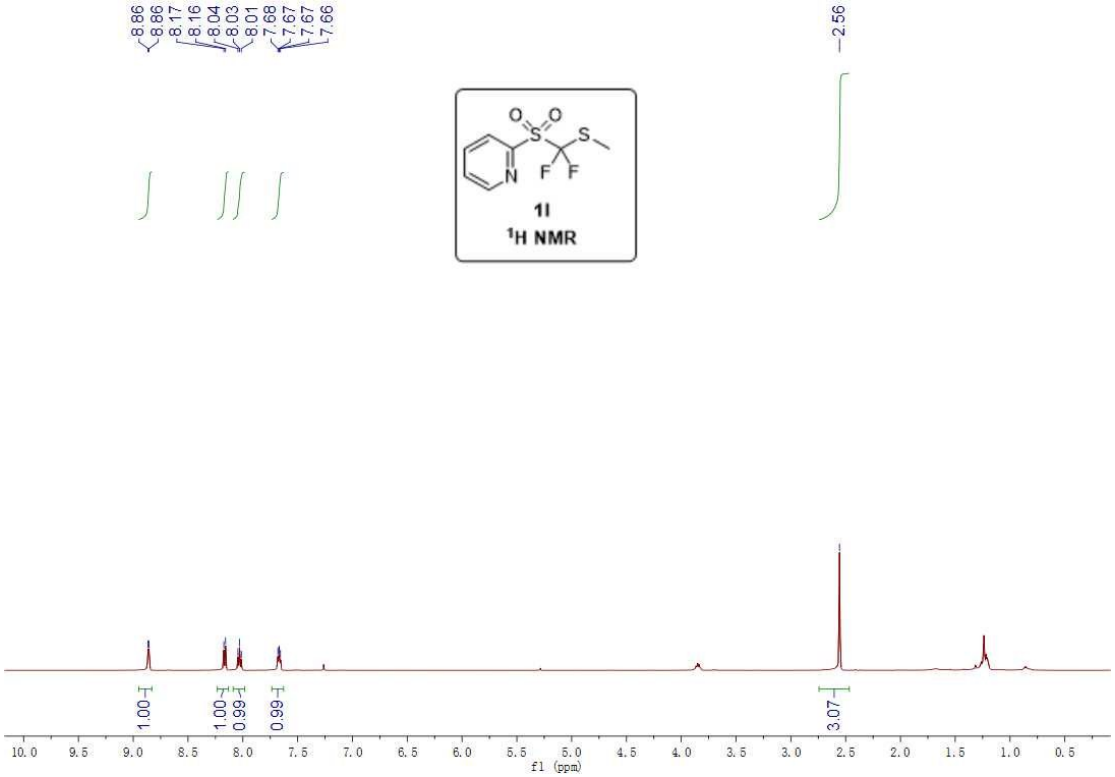
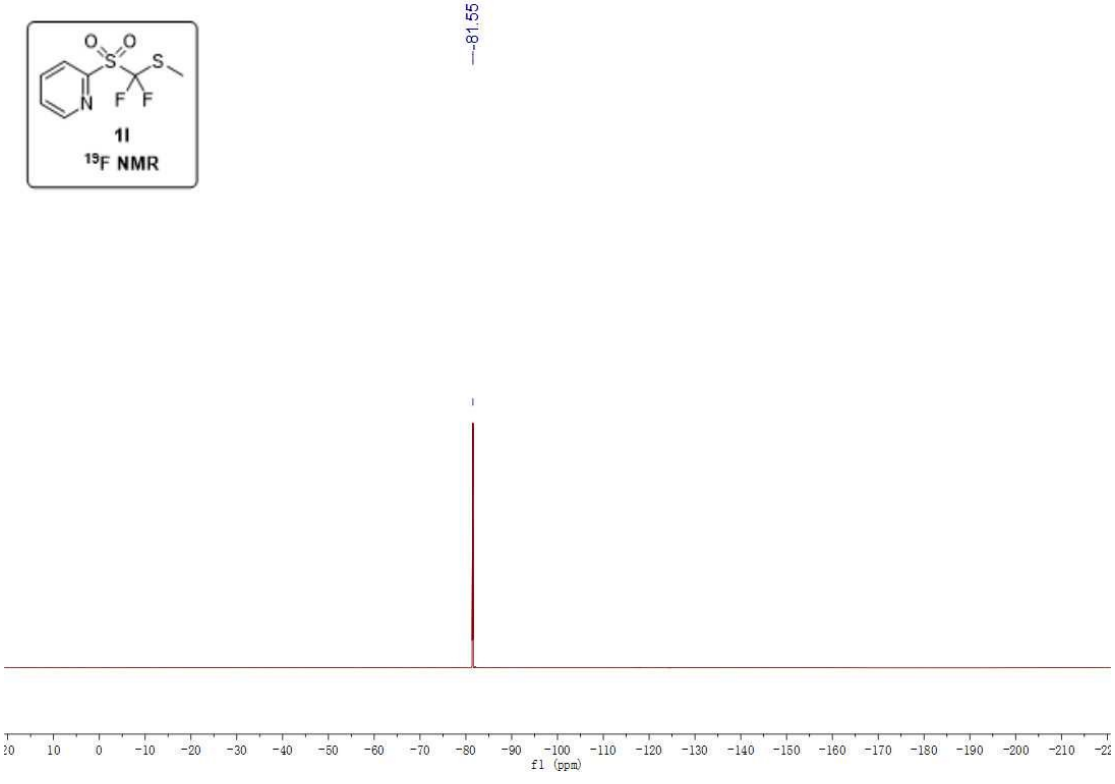
126.27
120.30
77.33
77.07
76.82
29.72


1k
13C NMR


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.86
8.86
8.17
8.16
8.04
8.03
8.01
7.68
7.67
7.67
7.66
2.56
1l
1H NMR
1.00
1.00
0.99
0.99
3.07
f1 (ppm)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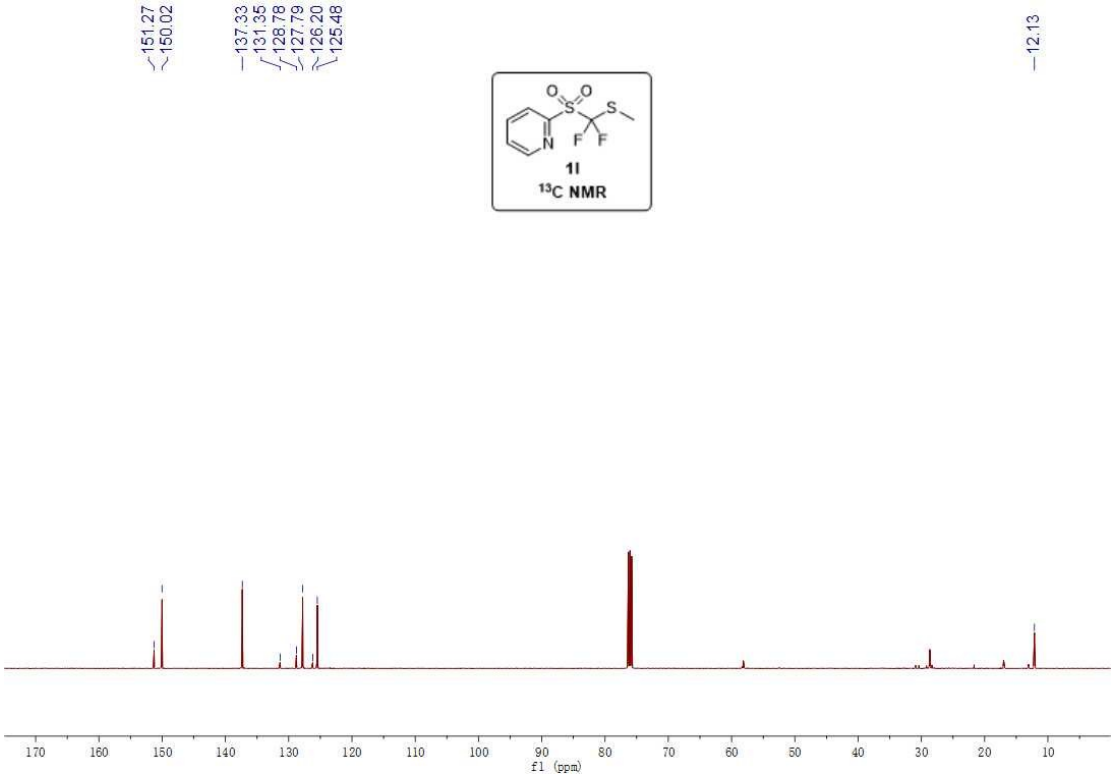
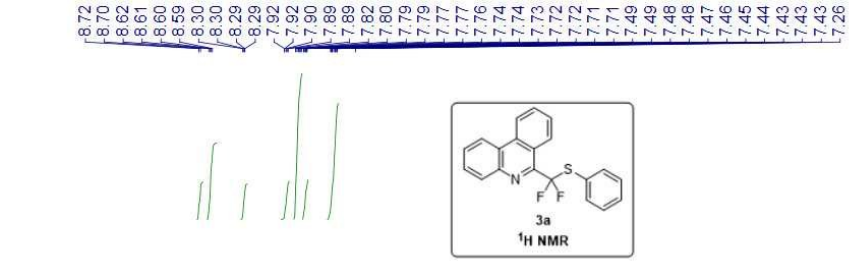
1l
19F NMR
f1 (ppm)


151.27
150.02
137.33
131.35
128.78
127.79
126.20
125.48
12.13
1l
13C NMR
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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8.59
8.30
8.30
8.29
8.29
7.92
7.92
7.90
7.89
7.89
7.82
7.80
7.79
7.79
7.77
7.77
7.76
7.74
7.74
7.73
7.72
7.72
7.71
7.71
7.49
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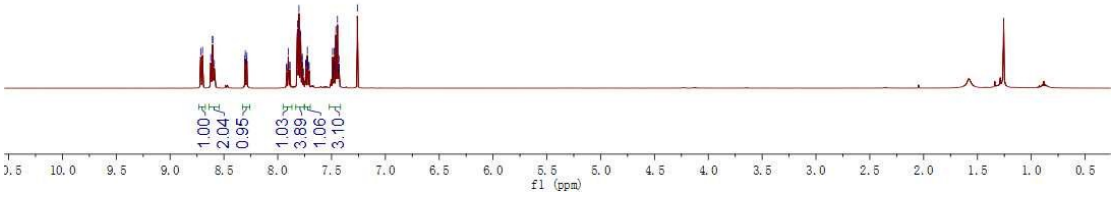
7.44
7.43
7.43
7.26
3a
1H NMR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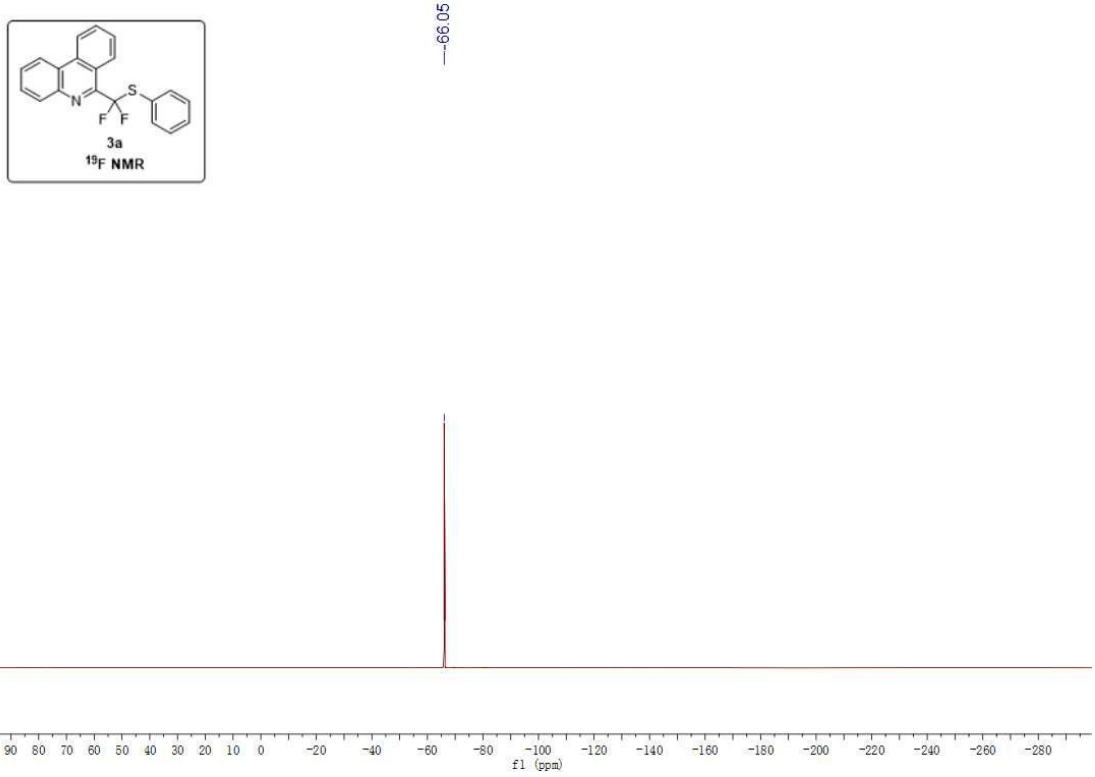
2.04
0.95
1.03
3.89
1.06
3.10
f1 (ppm)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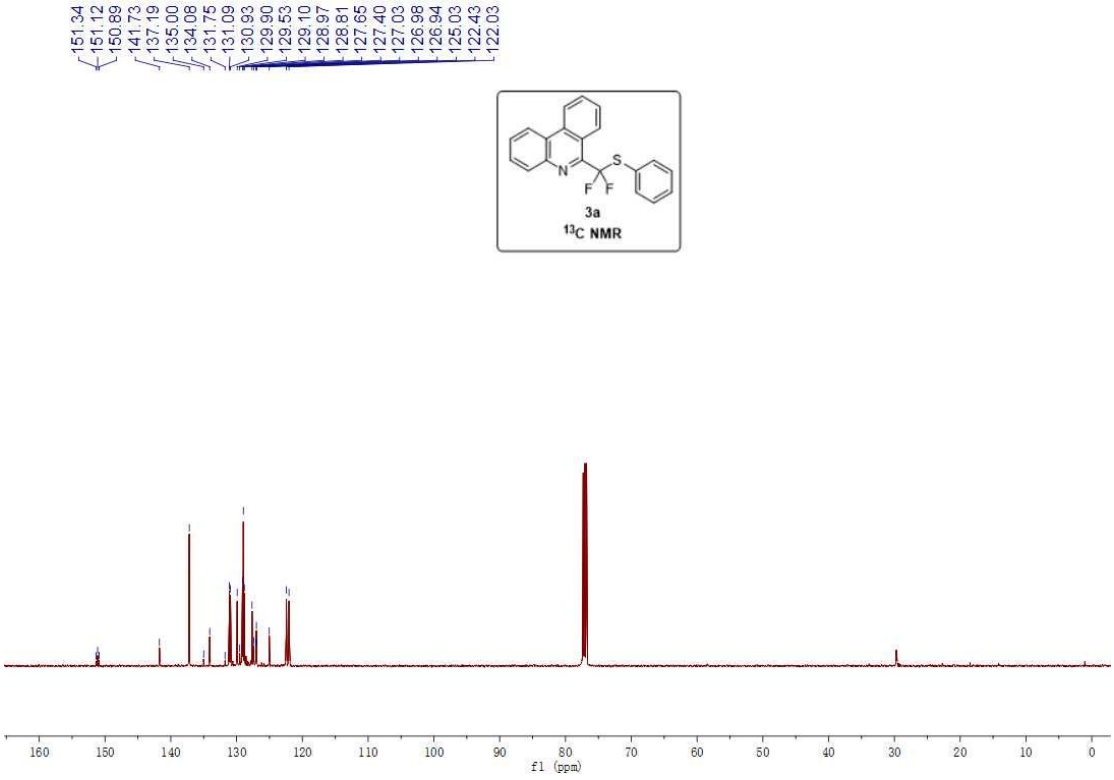
3a
19F NMR
f1 (ppm)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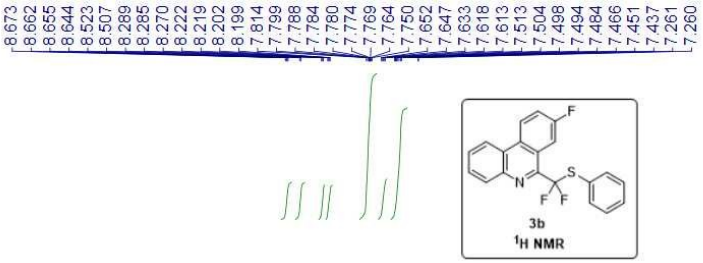
151.12
150.89
141.73
137.19
135.00
134.08
131.75
131.09
130.93
129.90
129.53
129.10
128.97
128.81
127.65
127.40
127.03
126.98
126.94
125.03
122.43
122.03
N
S
F
F
3a
13C NMR
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.222
8.219
8.202
8.199
7.814
7.799
7.788
7.784
7.780
7.774
7.769
7.764
7.750
7.652
7.647
7.633
7.618
7.613
7.513
7.504
7.498
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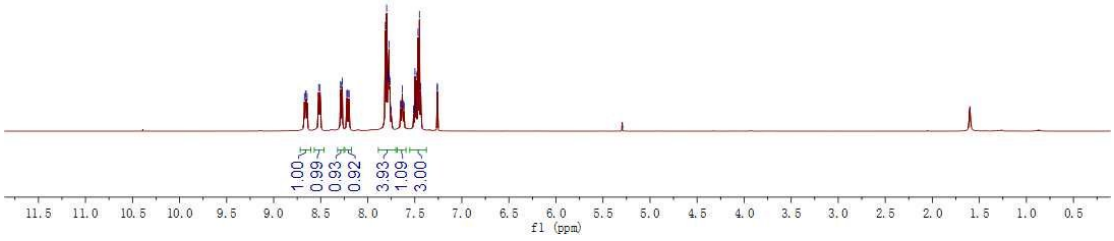
7.466
7.451
7.437
7.261
7.260
F
S
N
F F
3b
1H NMR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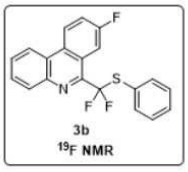
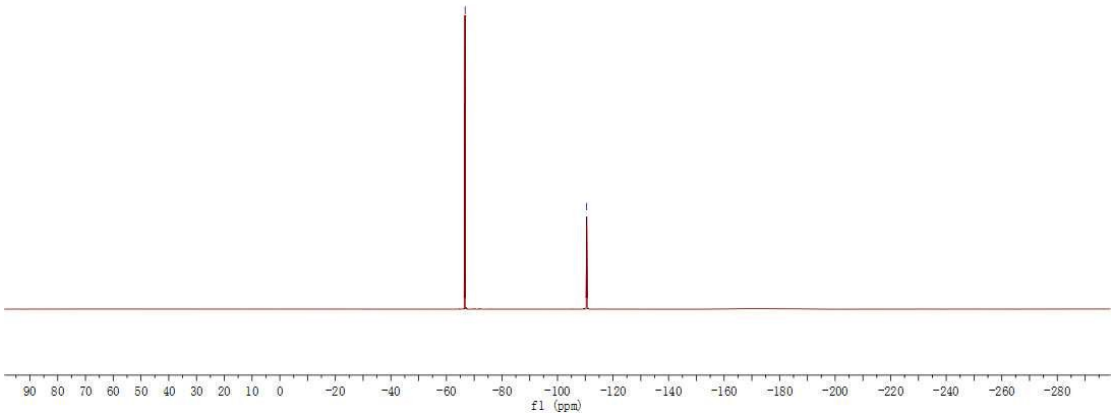
0.99
0.93
0.92
3.93
1.09
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


F
S
N
F F
3b
19F NMR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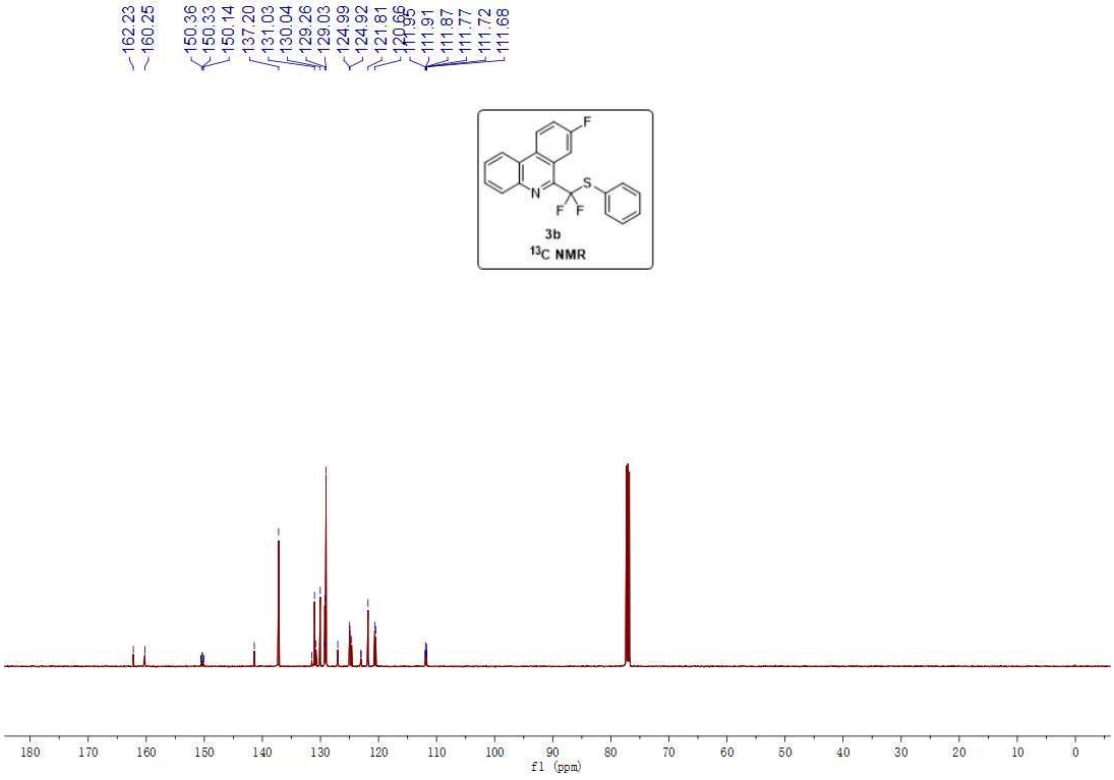
-110.50
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)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137.20
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130.04
129.26
129.03
124.99
124.92
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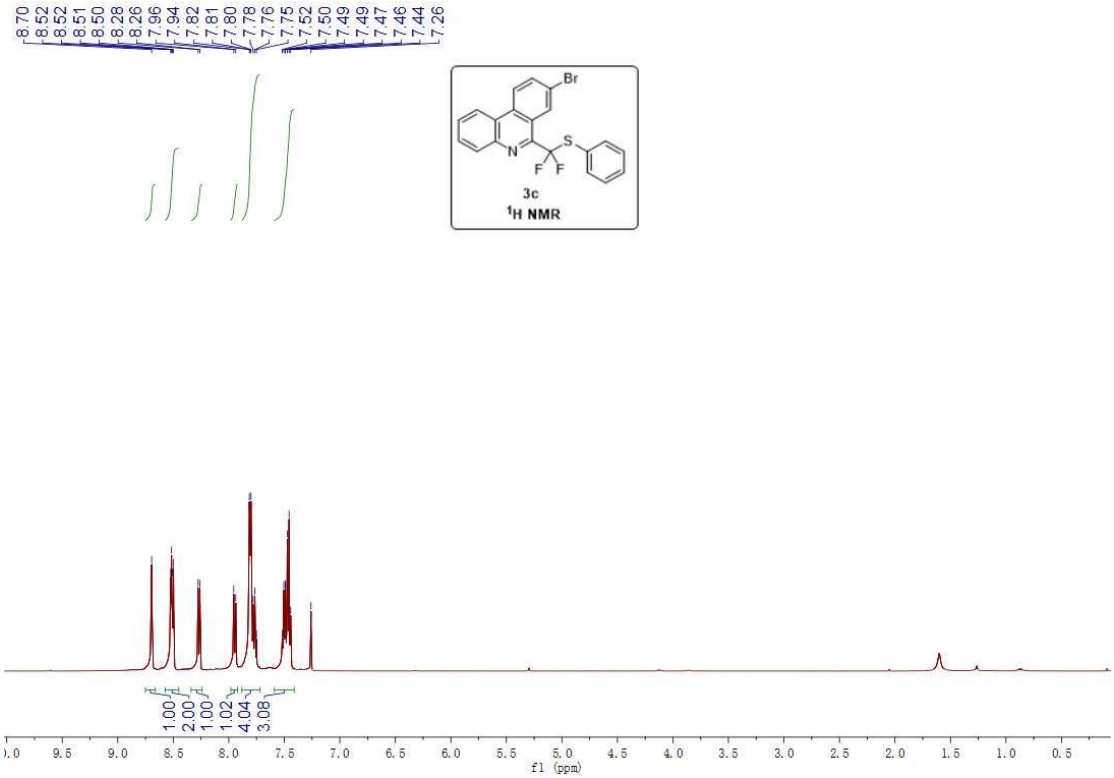
F
N
S
F F
3b
13C NMR
f1 (ppm)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7.82
7.81
7.80
7.78
7.76
7.75
7.52
7.50
7.49
7.49
7.47
7.46
7.44
7.26
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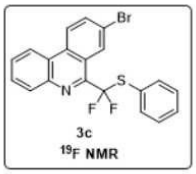
N
S
F F
3c
1H NMR
1.00
2.00
1.00
1.02
4.04
3.08
f1 (ppm)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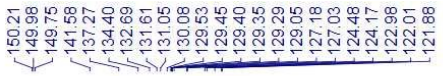
N
S
F F
3c
19F NMR

-65.83
f1 (ppm)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129.53
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129.29
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127.18
127.03
124.48
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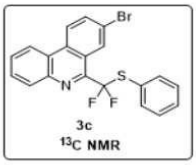
122.01
121.88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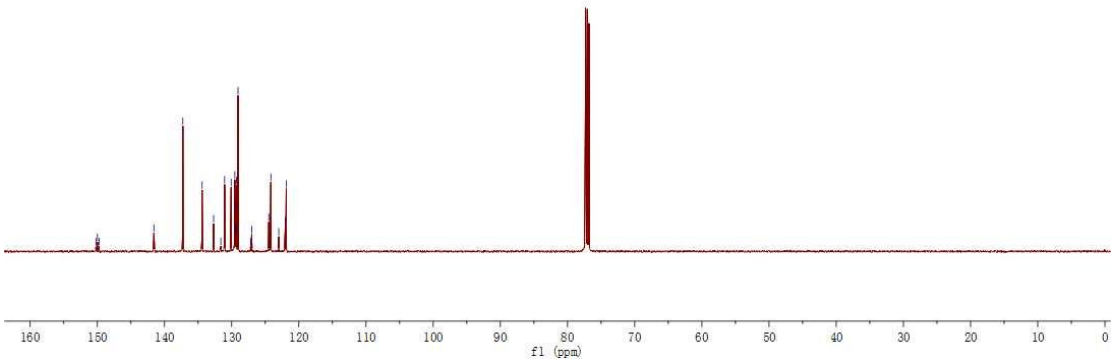
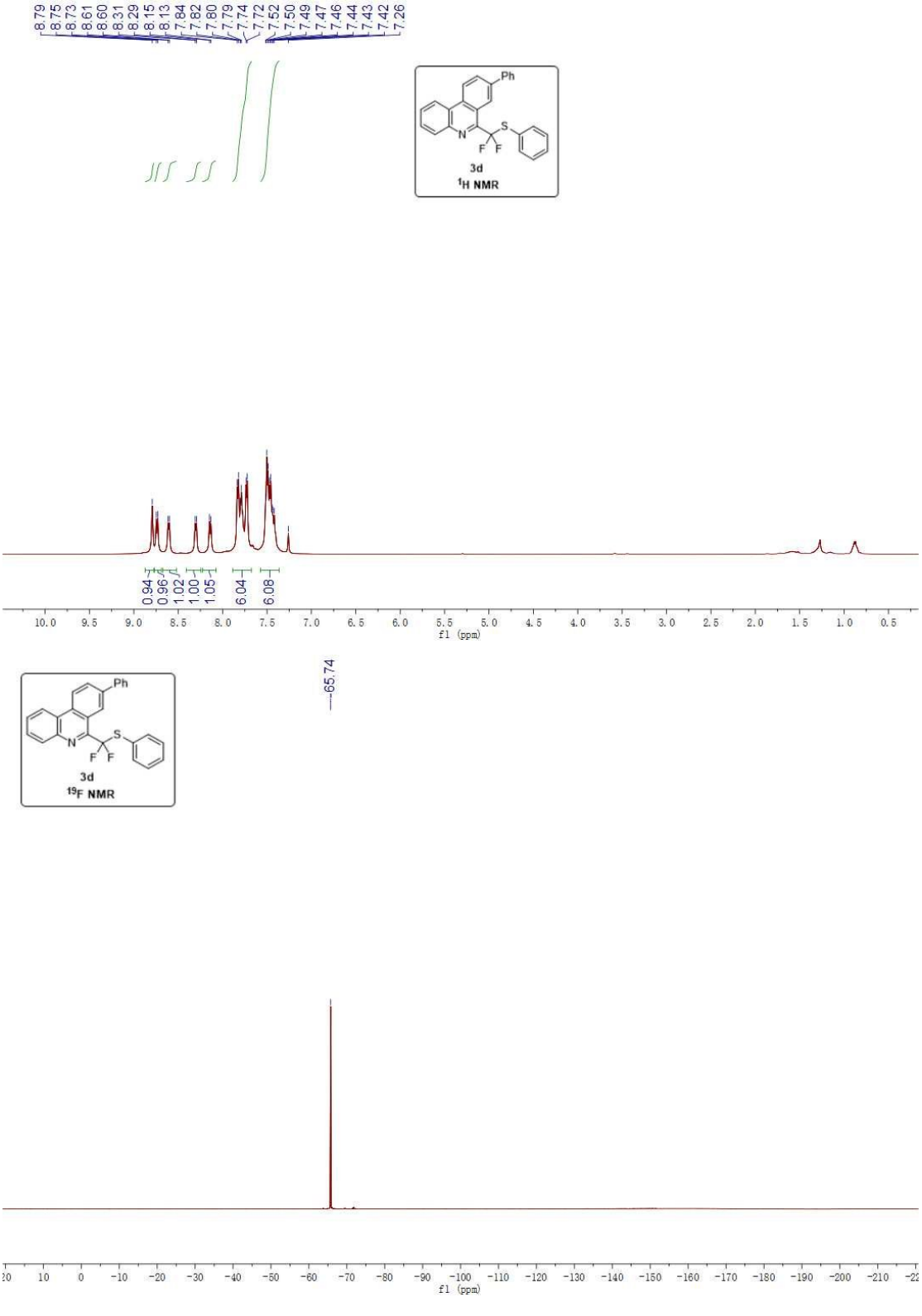
N
S
F F
3c
13C NMR


f1 (ppm)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8.15
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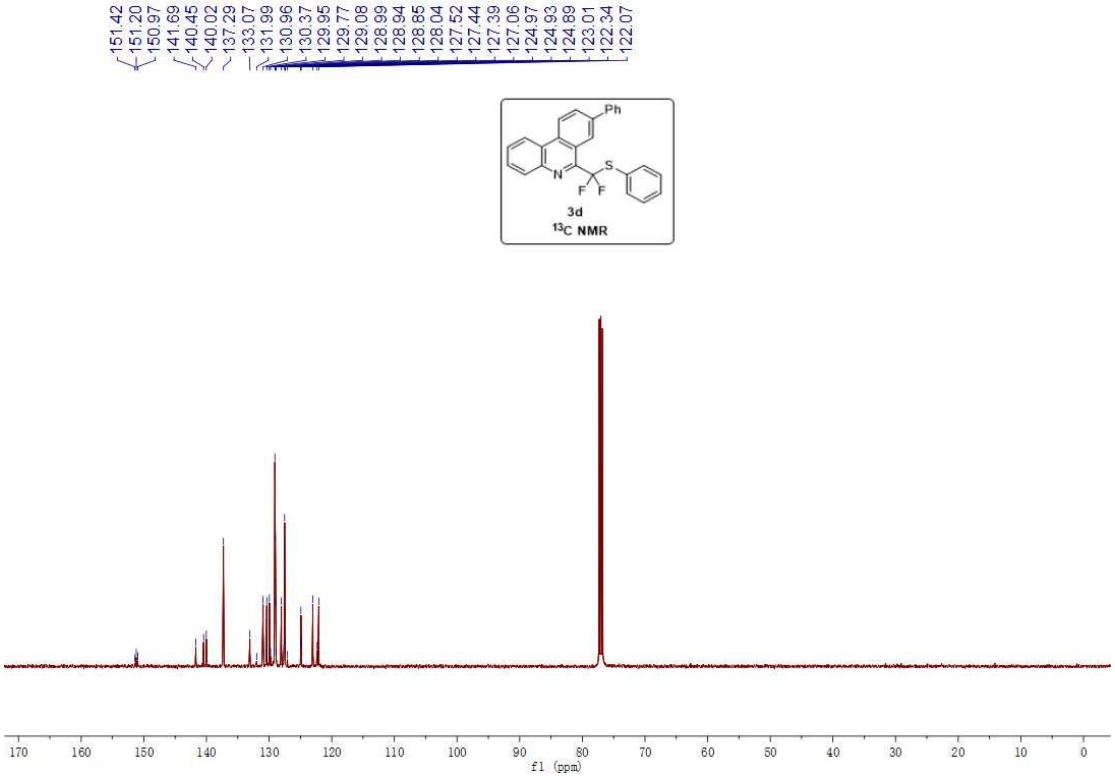
7.82
7.80
7.79
7.74
7.72
7.52
7.50
7.49
7.47
7.46
7.44
7.43
7.42
7.26
Ph
N
S
F F
3d
1H NMR
0.94
0.96
1.02
1.00
1.05
6.04
6.08
f1 (ppm)
Ph
N
S
F F
3d
19F NMR
-65.74
f1 (ppm)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129.08
128.99
128.94
128.85
128.04
127.52
127.44
127.39
127.06
124.97
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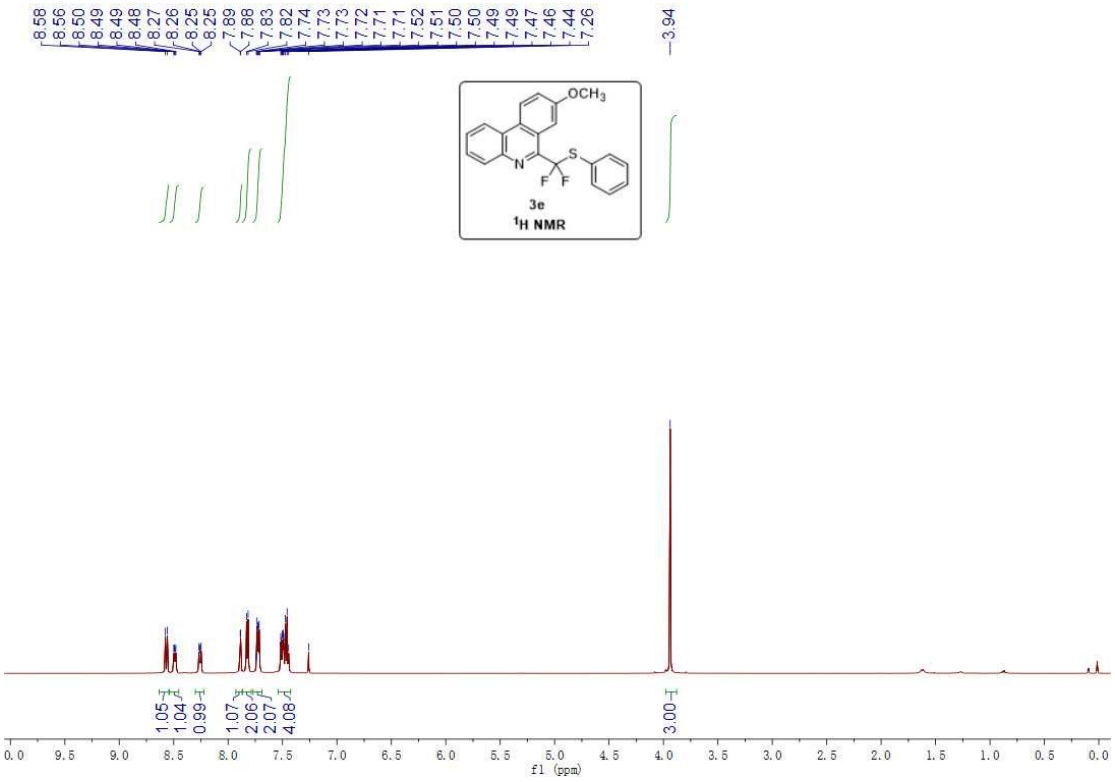
123.01
122.34
122.07
Ph
N
S
F F
3d
13C NMR
f1 (ppm)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8.49
8.48
8.27
8.26
8.25
8.25
7.89
7.88
7.83
7.82
7.74
7.73
7.73
7.72
7.71
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7.52
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7.50
7.50
7.49
7.49
7.47
7.46
7.44
7.26
3.94
OCH3
N
S
F F
3e
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1.04
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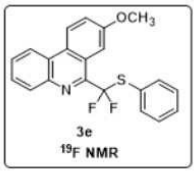
1.07
2.06
2.07
4.08
3.00
f1 (ppm)


OCH3
S
N
F F
3e
19F NMR

-66.69
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


158.68
150.30
150.08
149.85
140.93
137.29
130.84
129.92
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128.86
128.58
128.09
125.21
123.98
122.41
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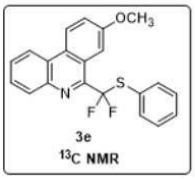
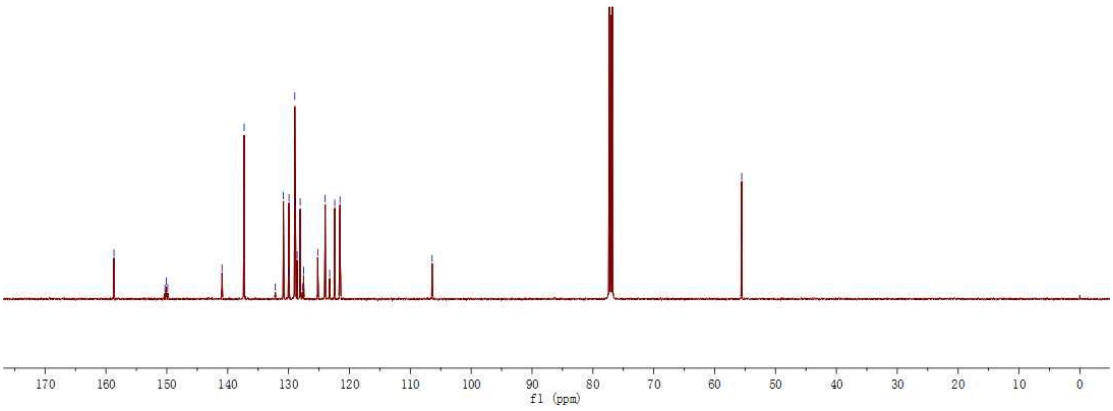
-55.55


OCH3
S
N
F F
3e
13C NMR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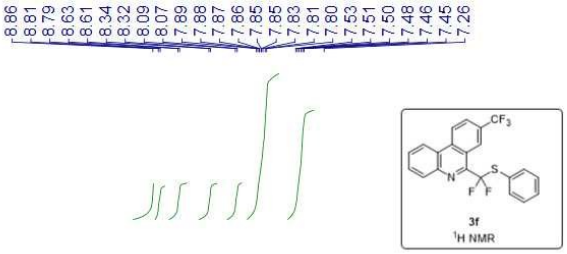
f1 (ppm)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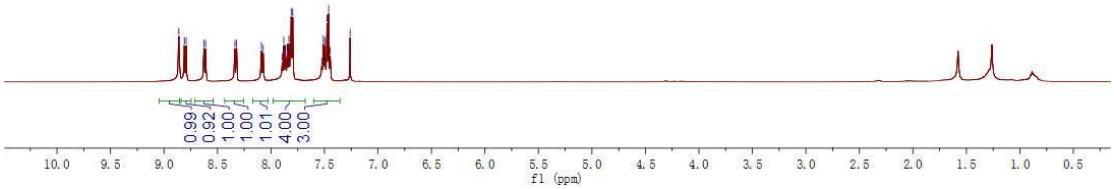
7.85
7.85
7.83
7.81
7.80
7.53
7.51
7.50
7.48
7.46
7.45
7.26
CF3
S
F F
N
3f
1H NMR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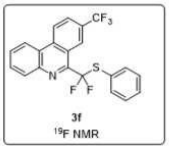
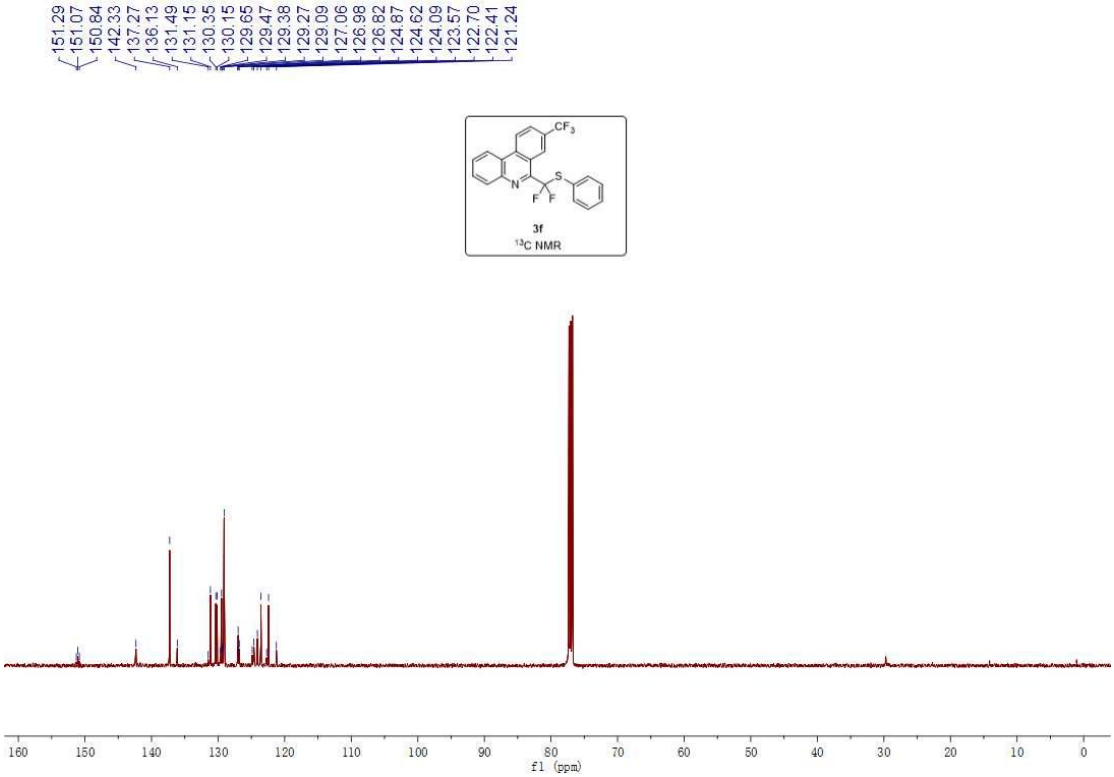
0.92
1.00
1.00
1.01
4.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


CF3
S
F F
N
3f
19F NMR

-62.43
-65.67
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)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131.49
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129.38
129.27
129.09
127.06
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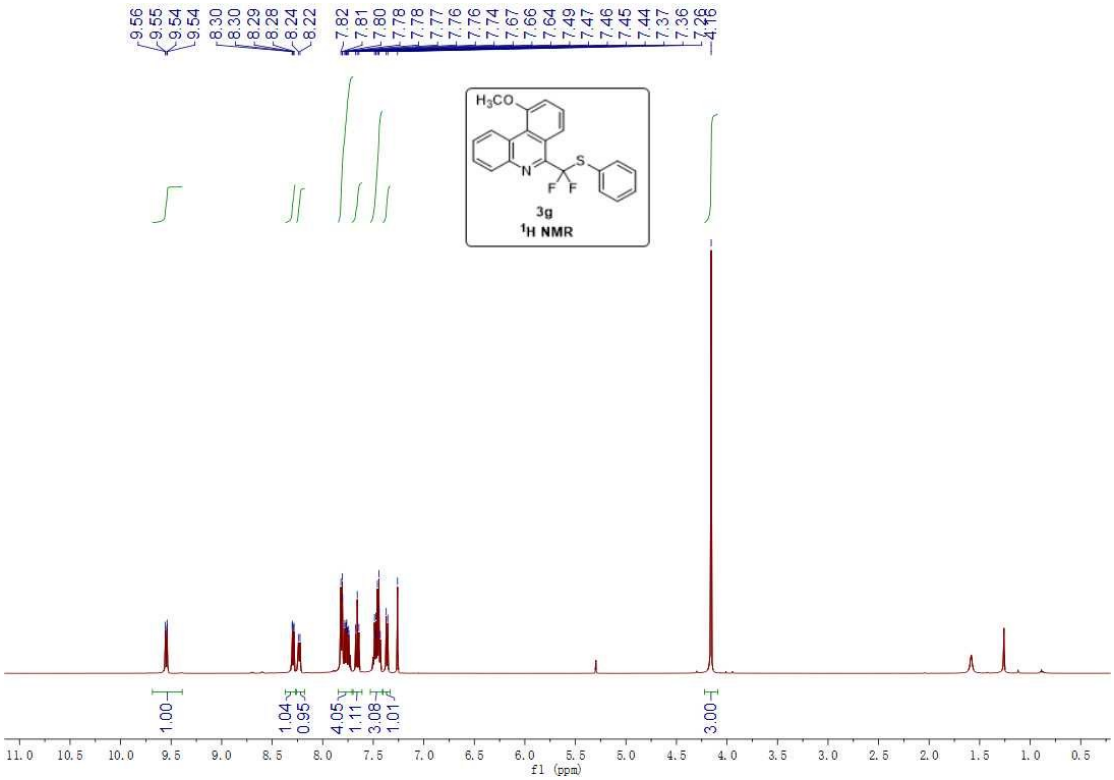
124.62
124.09
123.57
122.70
122.41
121.24
3f
13C NMR
f1 (ppm)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9.54
9.54
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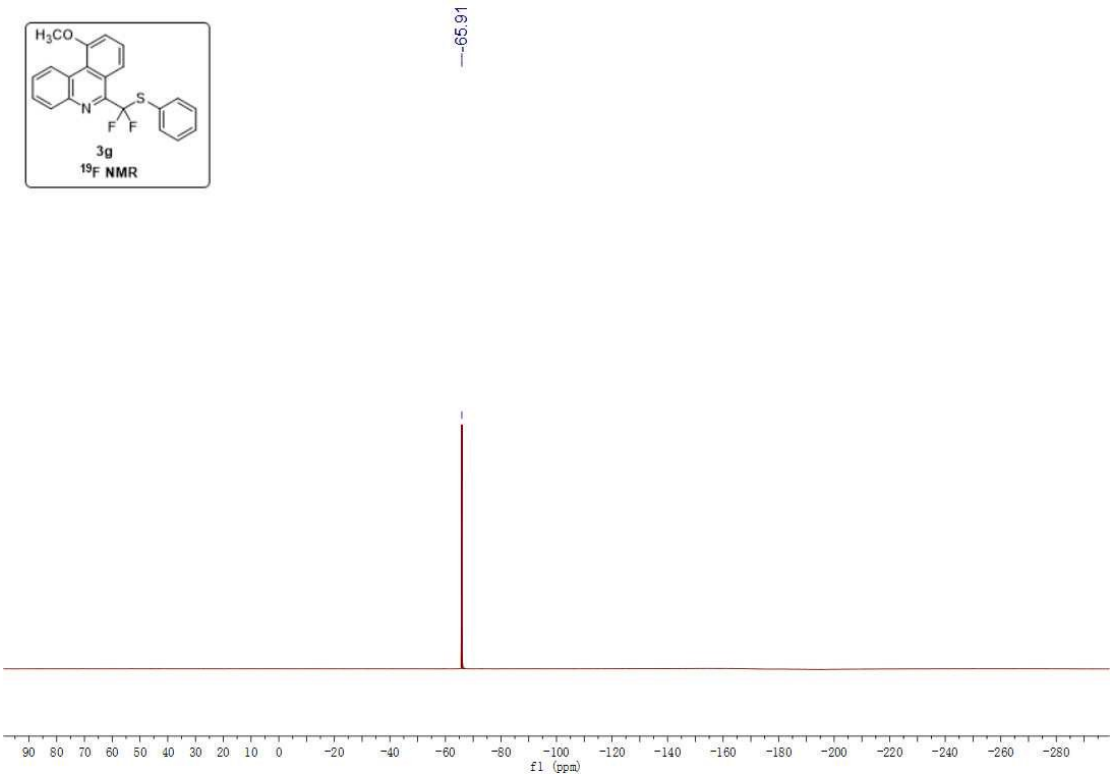
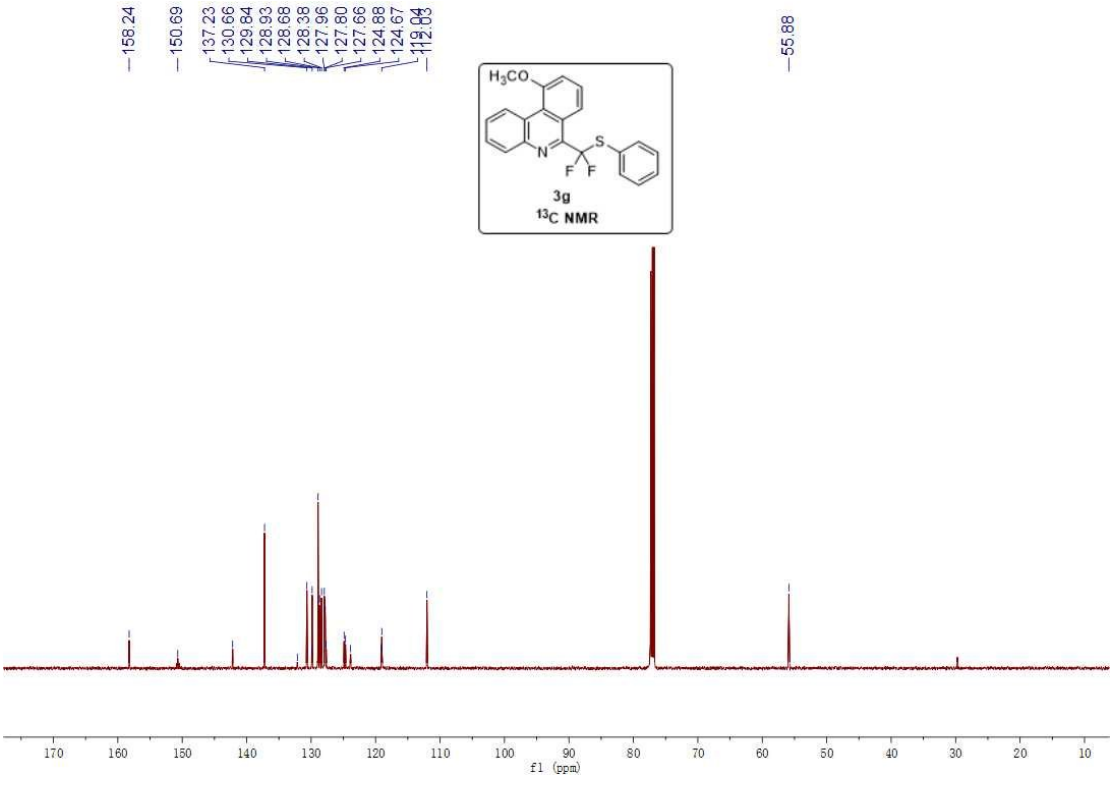
8.30
8.29
8.28
8.24
8.22
7.82
7.81
7.80
7.78
7.78
7.77
7.76
7.76
7.74
7.67
7.66
7.64
7.49
7.47
7.46
7.45
7.44
7.37
7.36
7.26
4.16
3g
1H NMR
1.00
1.04
0.95
4.05
1.11
3.08
1.01
3.00
f1 (ppm)


H3CO
N
S
F F
3g
19F NMR
-65.91
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)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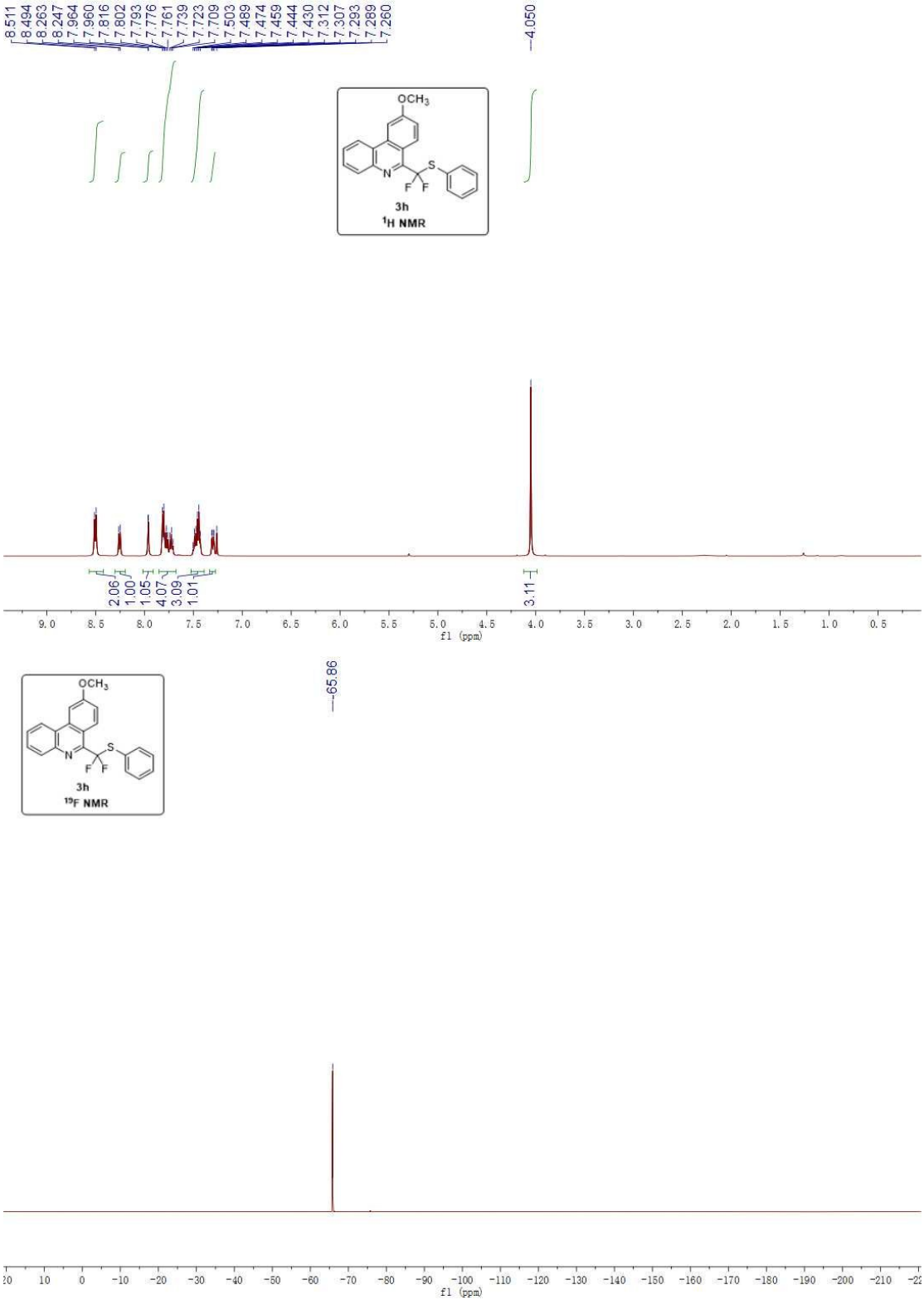
137.23
130.66
129.84
128.93
128.68
128.38
127.96
127.80
127.66
124.88
124.67
119.04
112.03
55.88
H3CO
N
S
F F
3g
13C NMR
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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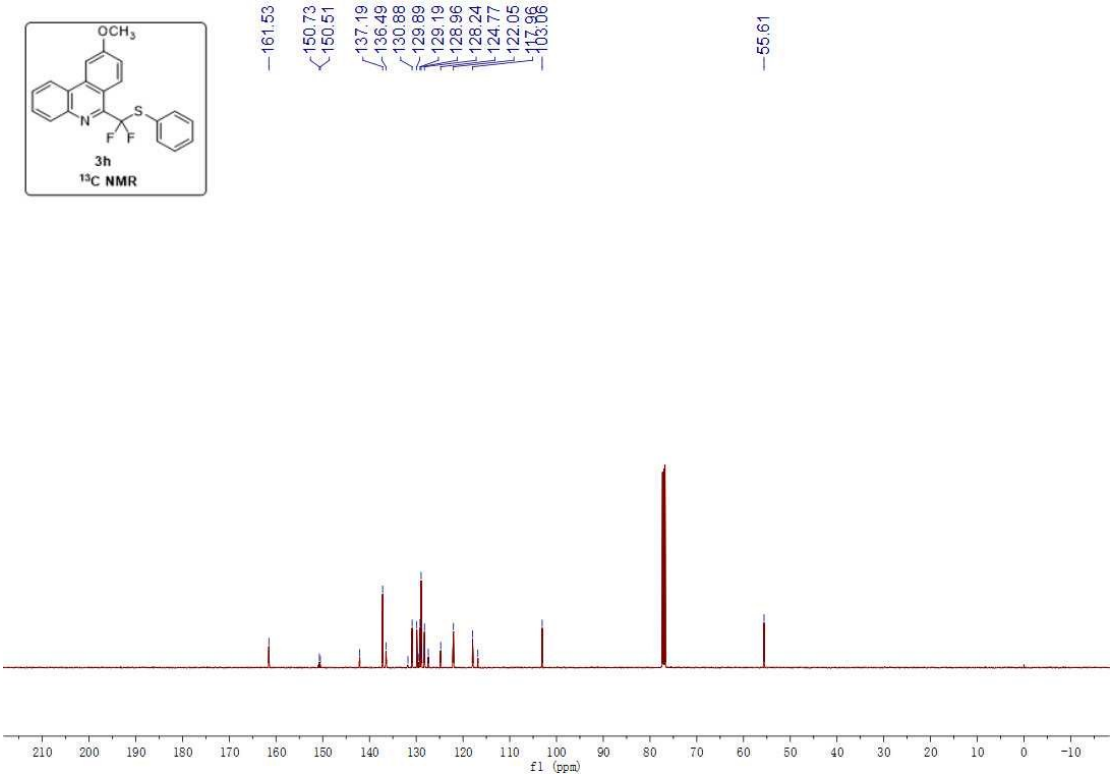
8.247
7.964
7.960
7.816
7.802
7.793
7.776
7.761
7.739
7.723
7.709
7.503
7.489
7.474
7.459
7.444
7.430
7.312
7.307
7.293
7.289
7.260
4.050
OCH3
S
N
F F
3h
1H NMR
2.06
1.00
1.05
4.07
3.09
1.01
3.11
f1 (ppm)
-65.86
3h
19F NMR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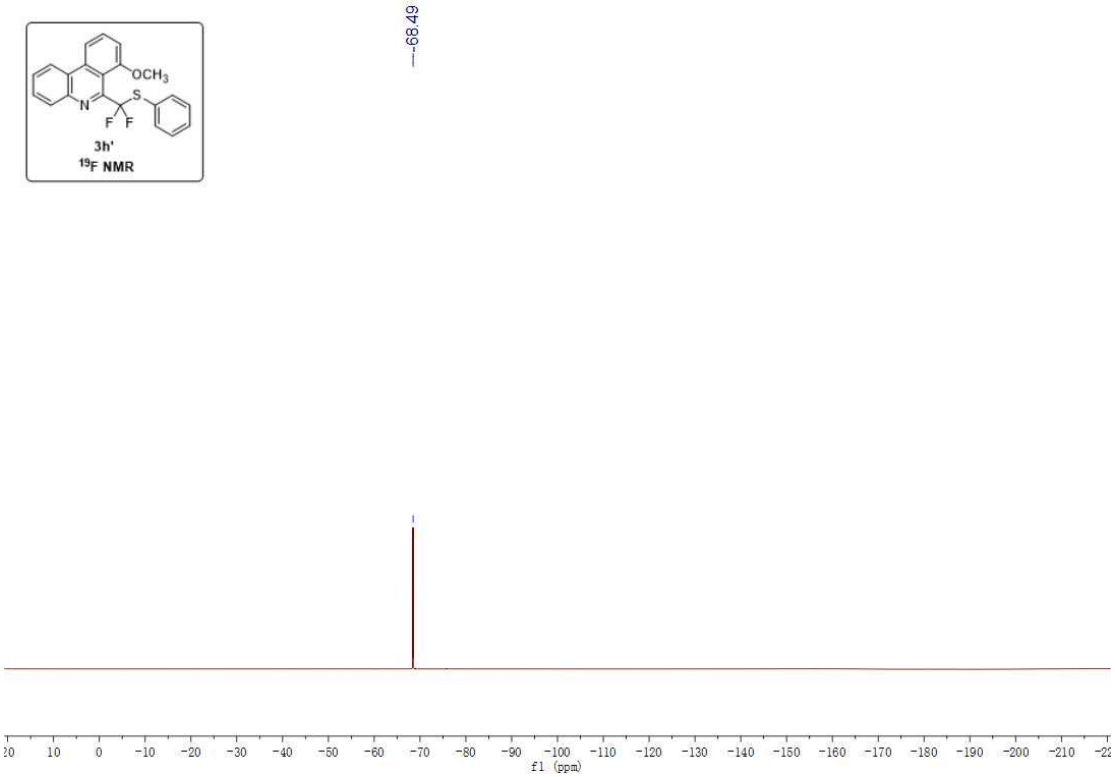
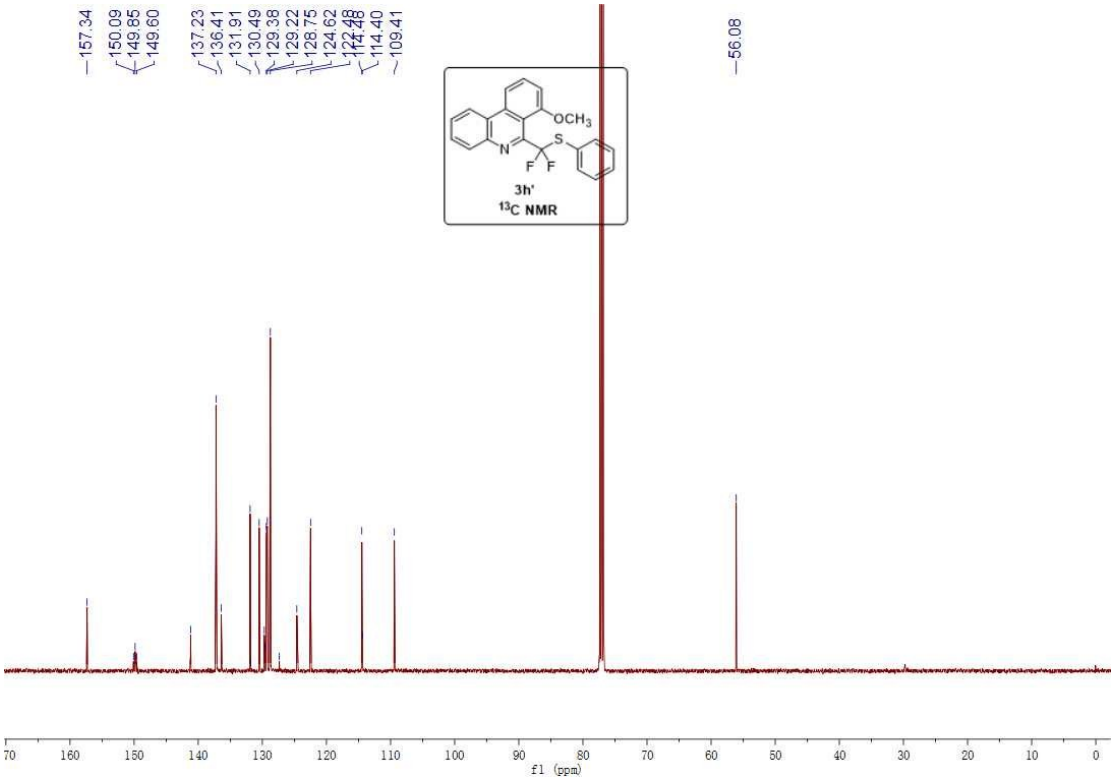
N
S
F F
3h
13C NMR
161.53
150.73
150.51
137.19
136.49
130.88
129.89
129.19
128.96
128.24
124.77
122.05
117.96
103.08
55.61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
8.55
8.53
8.26
8.25
8.23
7.81
7.80
7.78
7.76
7.74
7.73
7.71
7.48
7.46
7.46
7.45
7.44
7.42
7.41
7.26
7.15
7.14
3.97
OCH3
N
S
F F
3h'
1H NMR
1.02
2.03
5.08
3.06
1.01
3.00
10.0 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
f1 (ppm)


3h'
19F NMR
-68.49
f1 (ppm)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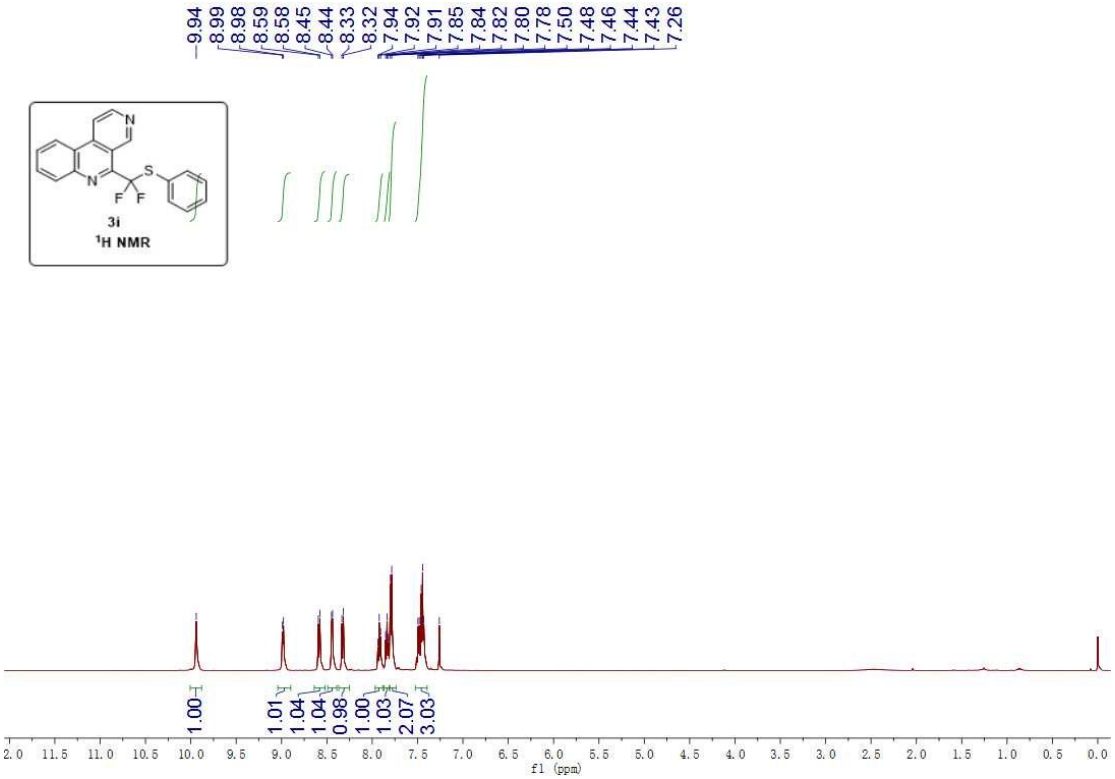
150.09
149.85
149.60
137.23
136.41
131.91
130.49
129.38
129.22
128.75
124.62
122.48
114.40
109.41
56.08
3h'
13C NMR
f1 (ppm)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8.98
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8.45
8.44
8.33
8.32
7.94
7.92
7.91
7.85
7.84
7.82
7.80
7.78
7.50
7.48
7.46
7.44
7.43
7.26
3i
1H NMR
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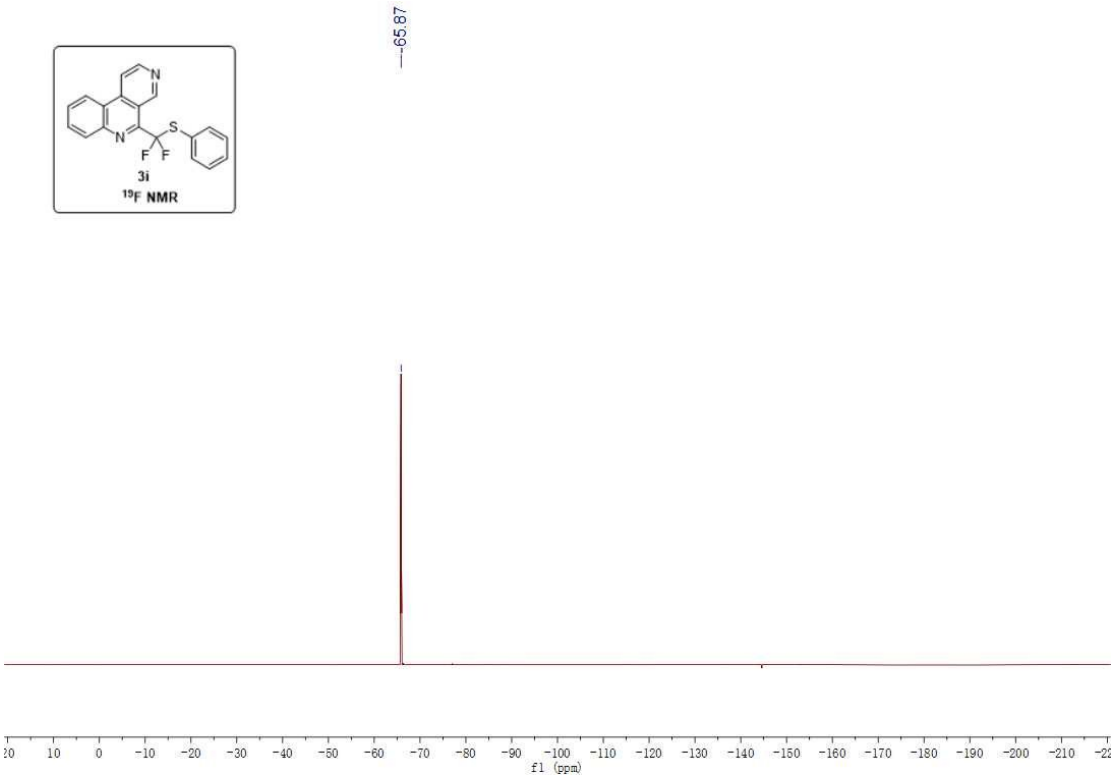
1.01
1.04
1.04
0.98
1.00
1.03
2.07
3.03
f1 (ppm)


-65.87
3i
19F NMR
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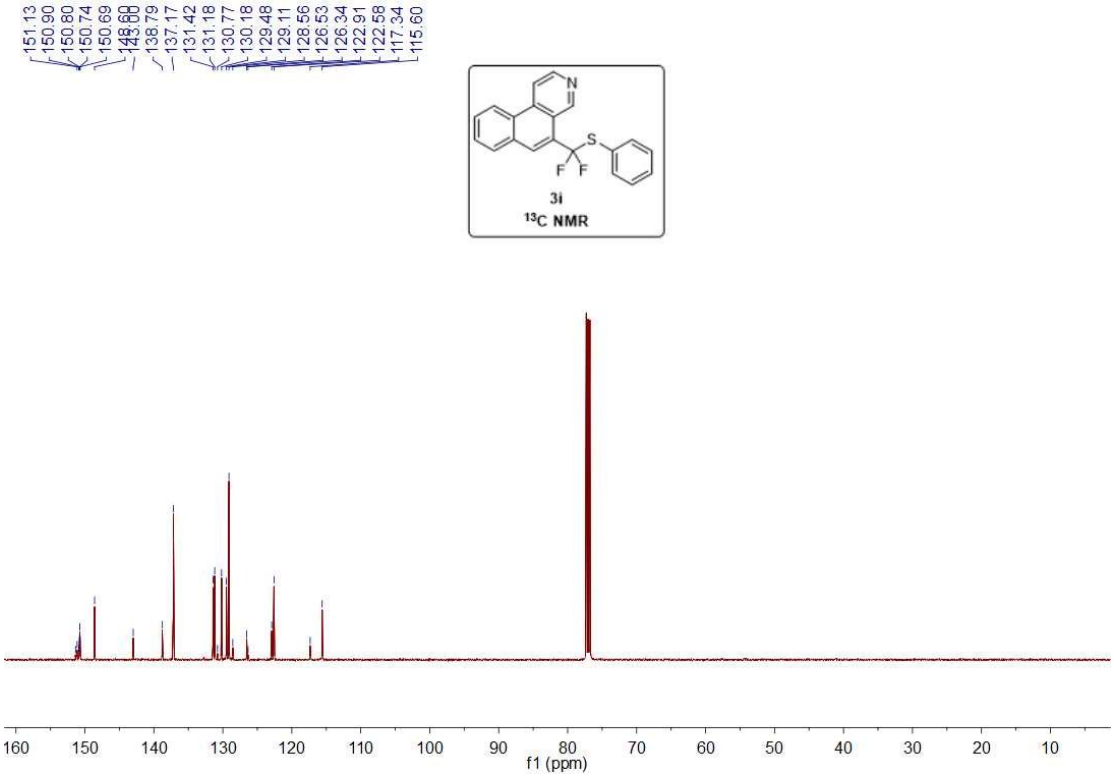
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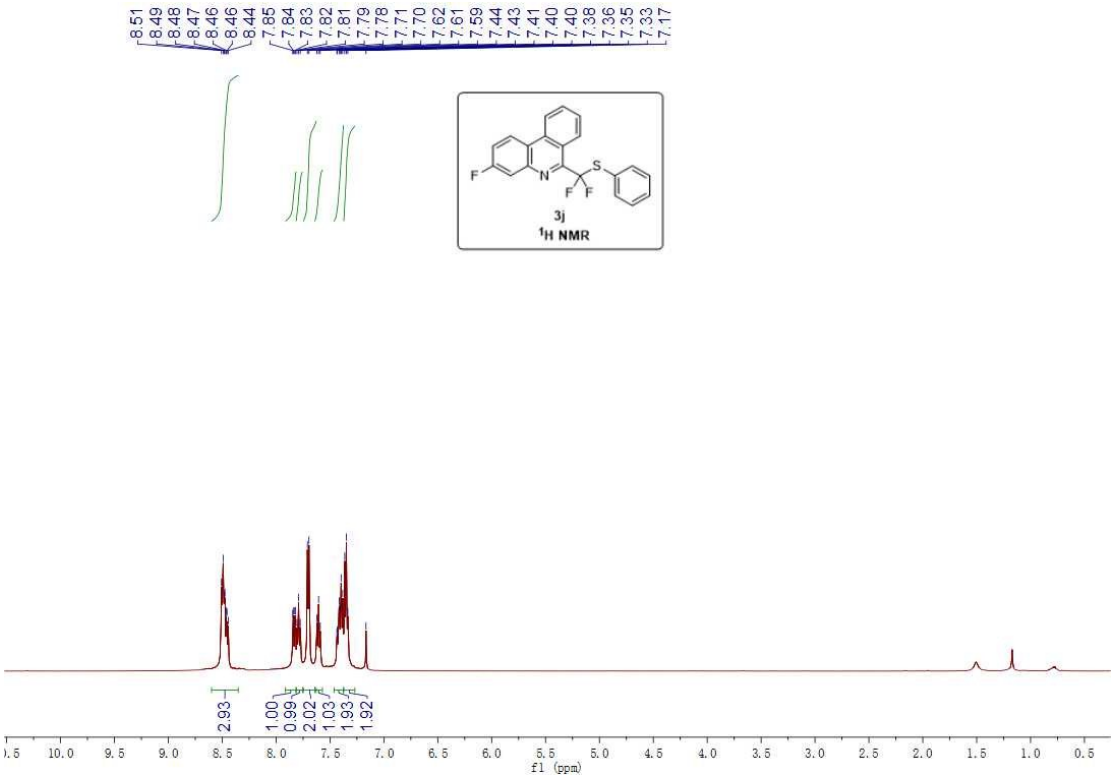
131.18
130.77
130.18
129.48
129.11
128.56
126.53
126.34
122.91
122.58
117.34
115.60
N
S
F F
3i
13C NMR
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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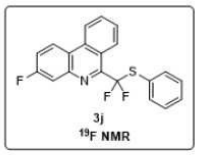
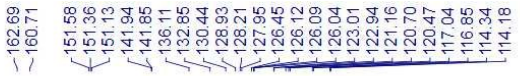
8.46
8.44
7.85
7.84
7.83
7.82
7.81
7.79
7.78
7.71
7.70
7.62
7.61
7.59
7.44
7.43
7.41
7.40
7.40
7.38
7.36
7.35
7.33
7.17
F
N
S
F F
3j
1H NMR
2.93
1.00
0.99
2.02
1.03
1.93
1.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


3j
19F NMR

-66.27
-111.06
f1 (ppm)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136.11
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128.93
128.21
127.95
126.45
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123.01
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120.47
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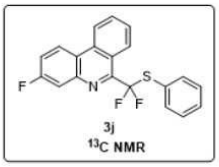
114.34
114.18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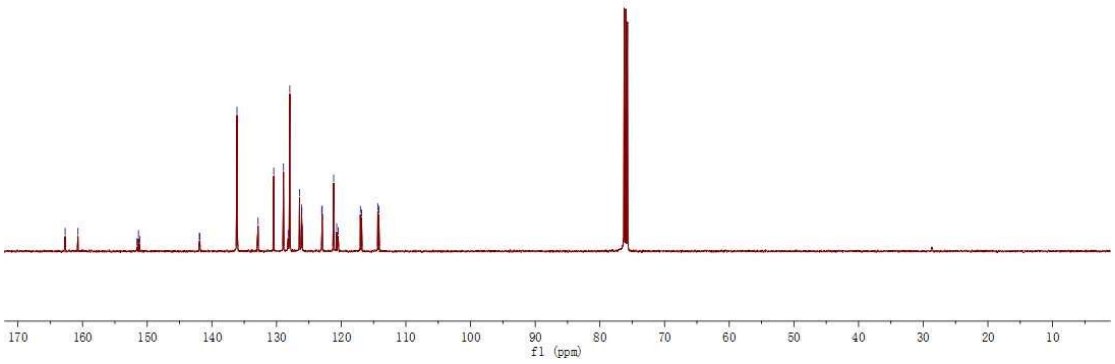
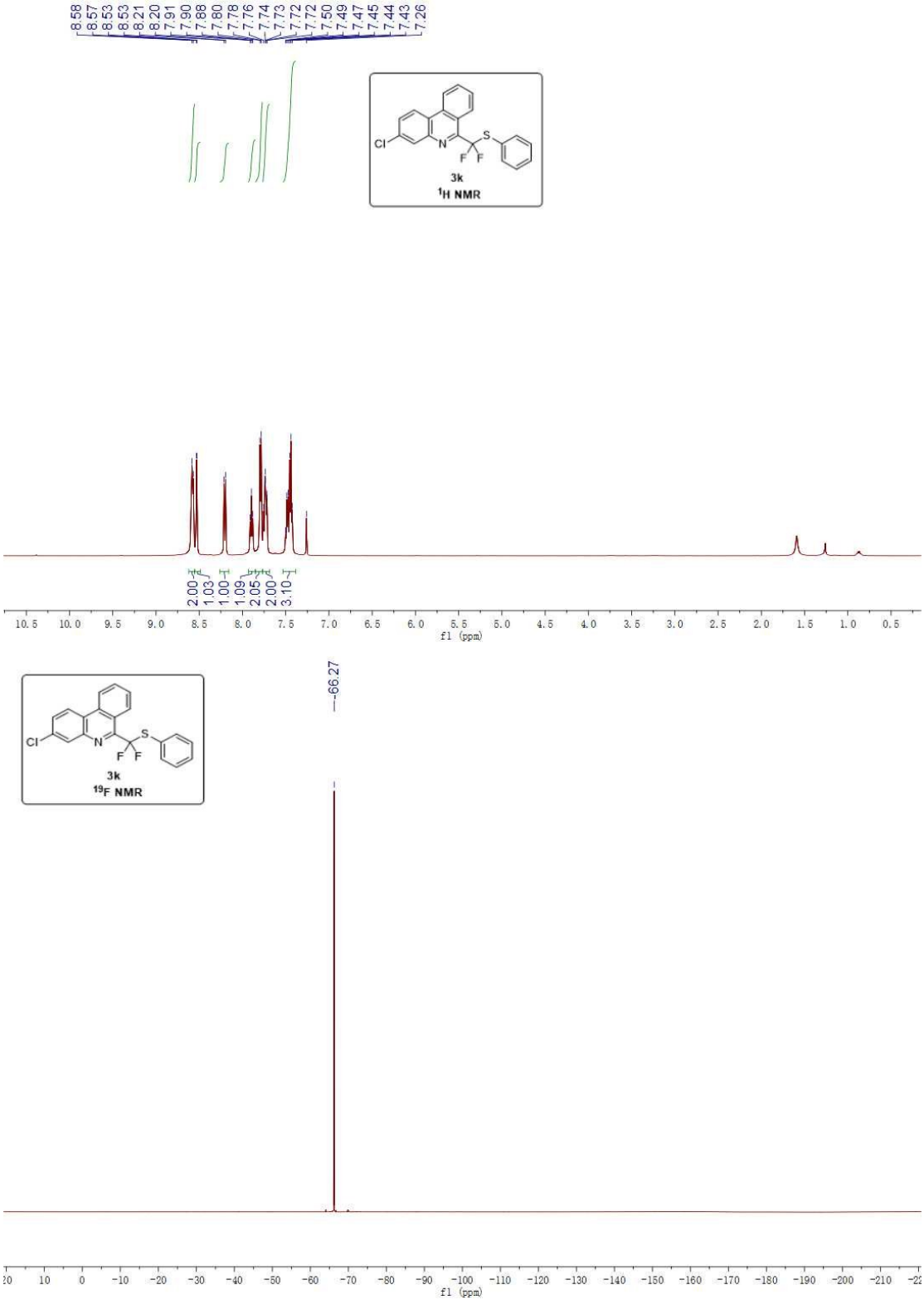
13C NMR


f1 (ppm)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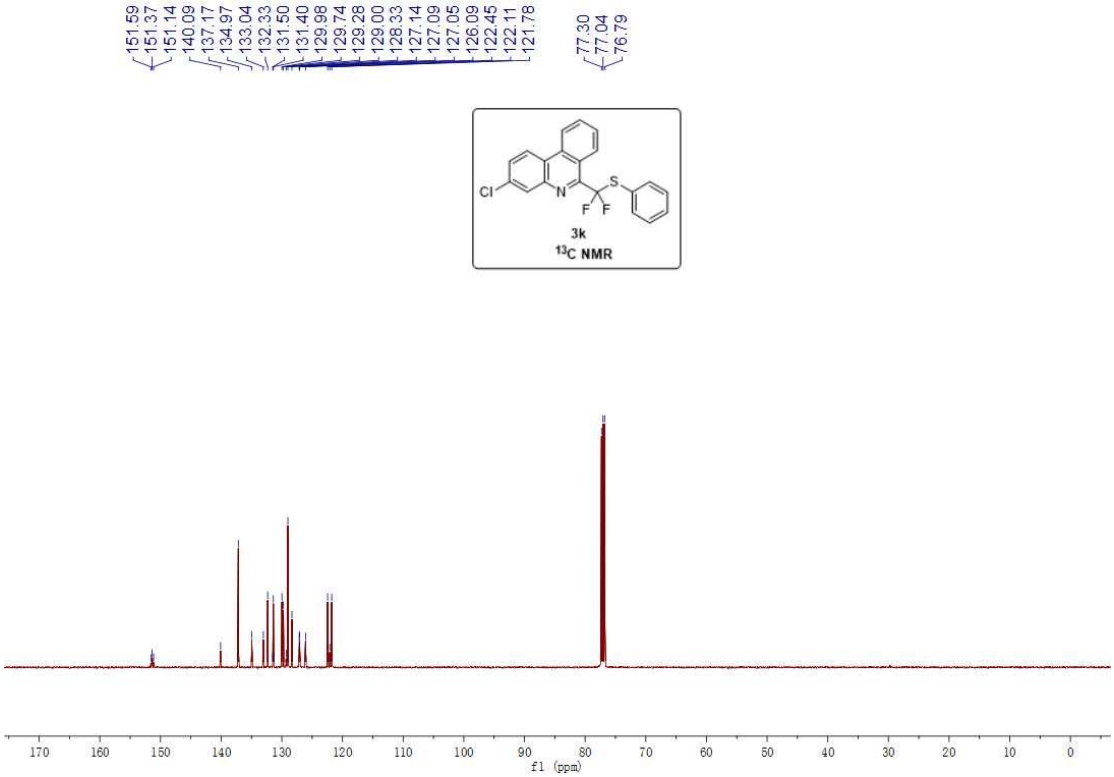
7.90
7.88
7.80
7.78
7.76
7.74
7.73
7.72
7.72
7.50
7.49
7.47
7.45
7.44
7.43
7.26
Cl
N
S
F
F
3k
1H NMR
2.00
1.03
1.00
1.09
2.05
2.00
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
Cl
N
S
F
F
3k
19F NMR
-66.27
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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129.98
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129.28
129.00
128.33
127.14
127.09
127.05
126.09
122.45
122.11
121.78
77.30
77.04
76.79
Cl
N
S
F
F
3k
13C NMR
f1 (ppm)
8.63
8.62
8.57
8.55
8.46
8.45
8.09
7.86
7.85
7.83
7.81
7.68
7.67
7.65
7.58
7.57
7.49
7.48
7.46
7.45
7.44
7.26
2.61
N
S
F
F
3l
1H NMR
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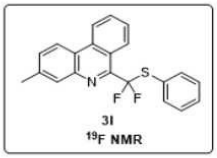
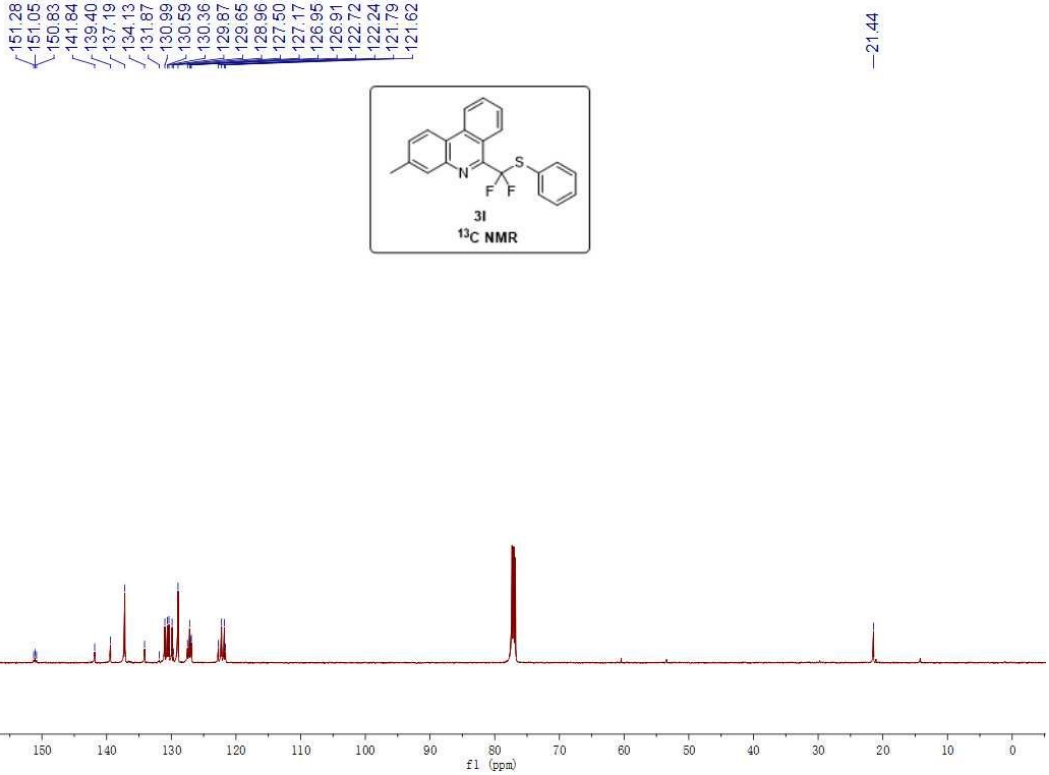
1.09
1.02
3.06
1.06
1.00
2.93
3.05
f1 (ppm)


3l
19F NMR

-65.89
f1 (ppm)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128.96
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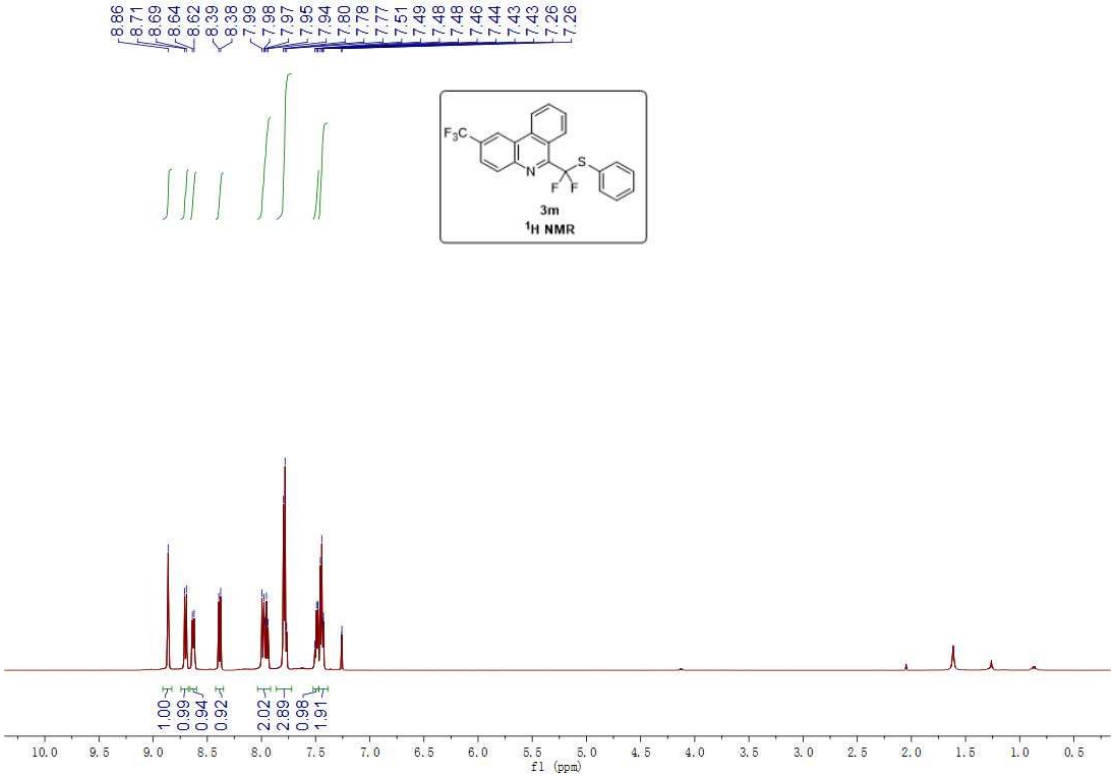
122.72
122.24
121.79
121.62
-21.44
3l
13C NMR
f1 (ppm)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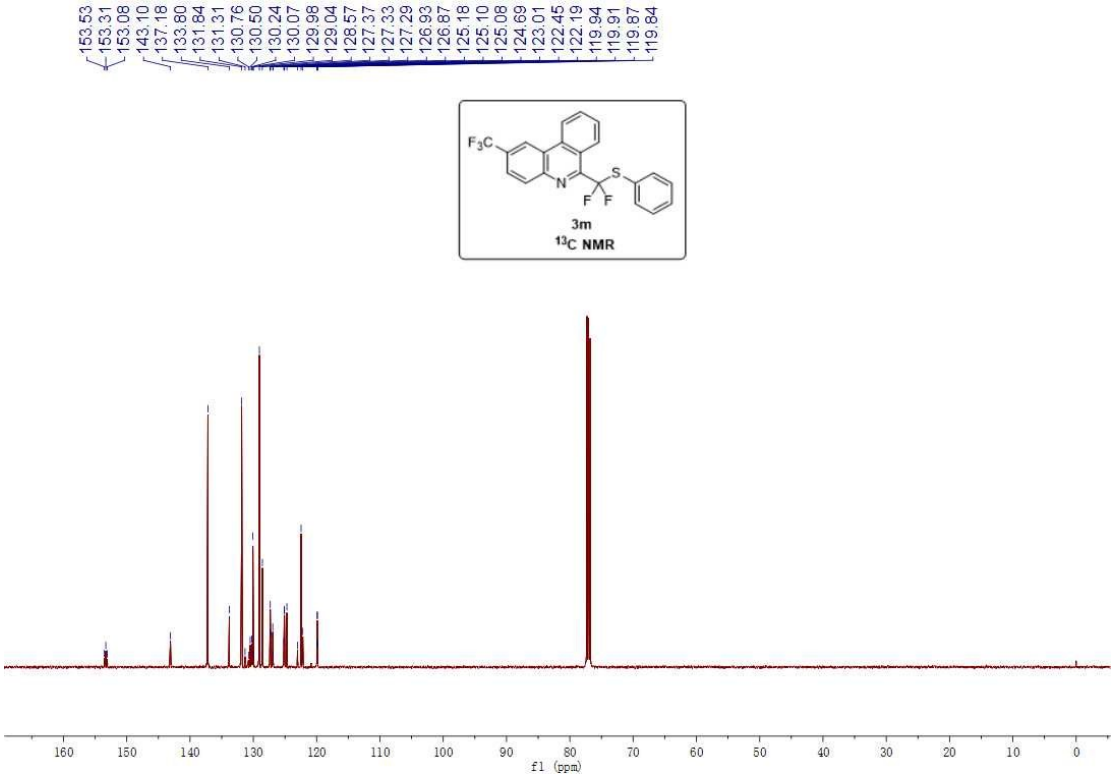
7.97
7.95
7.94
7.80
7.78
7.77
7.51
7.49
7.48
7.48
7.46
7.44
7.43
7.43
7.26
7.26
F3C
N
S
F F
3m
1H NMR
1.00
0.99
0.94
0.92
2.02
2.89
0.98
1.91
f1 (ppm)
F3C
N
S
F F
3m
19F NMR
-62.02
-66.54
f1 (ppm)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143.10
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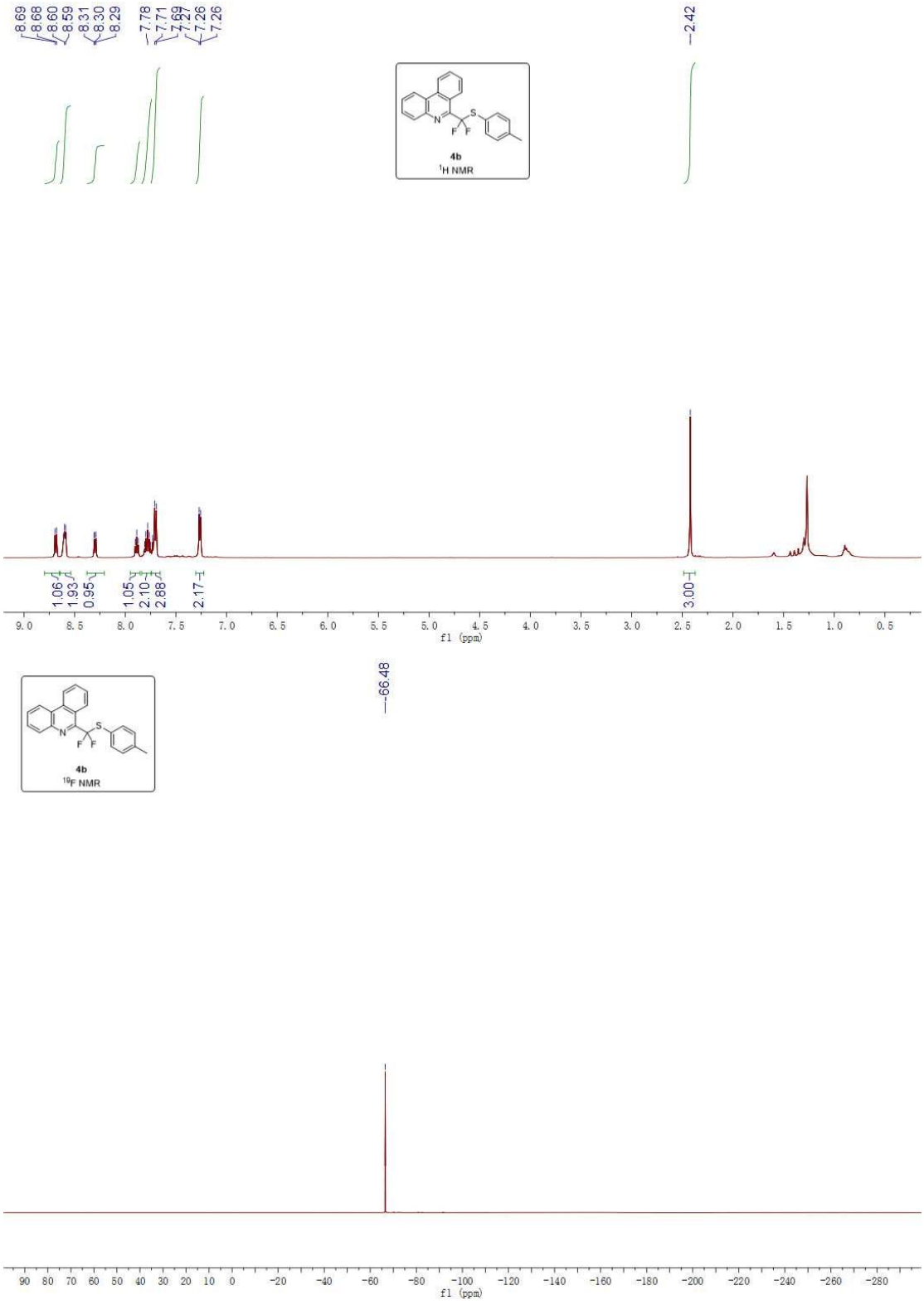
130.07
129.98
129.04
128.57
127.37
127.33
127.29
126.93
126.87
125.18
125.10
125.08
124.69
123.01
122.45
122.19
119.94
119.91
119.87
119.84
F3C
N
S
F F
3m
13C NMR
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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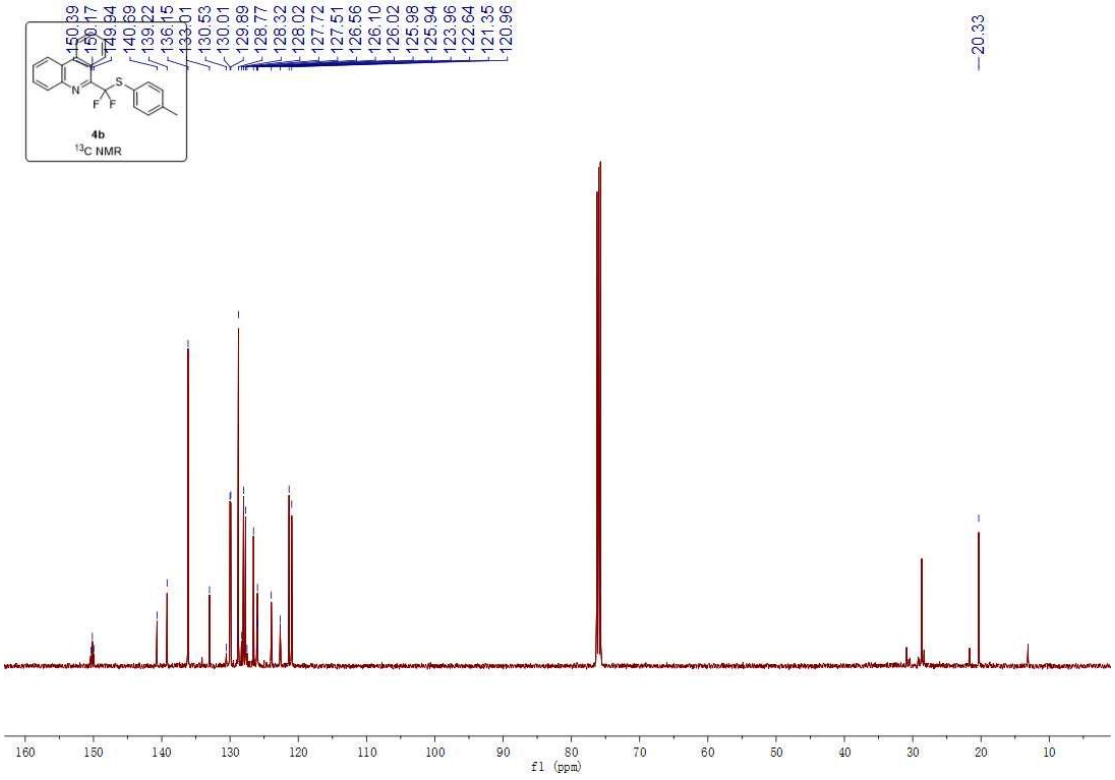
8.29
7.78
7.71
7.69
7.27
7.26
7.26
2.42
4b
1H NMR
1.06
1.93
0.95
1.05
2.10
2.88
2.17
3.00
f1 (ppm)
-66.48
4b
19F NMR
f1 (ppm)


4b
13C NMR
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150.17
149.94
140.69
139.22
136.15
133.01
130.53
130.01
129.89
128.77
128.32
128.02
127.72
127.51
126.56
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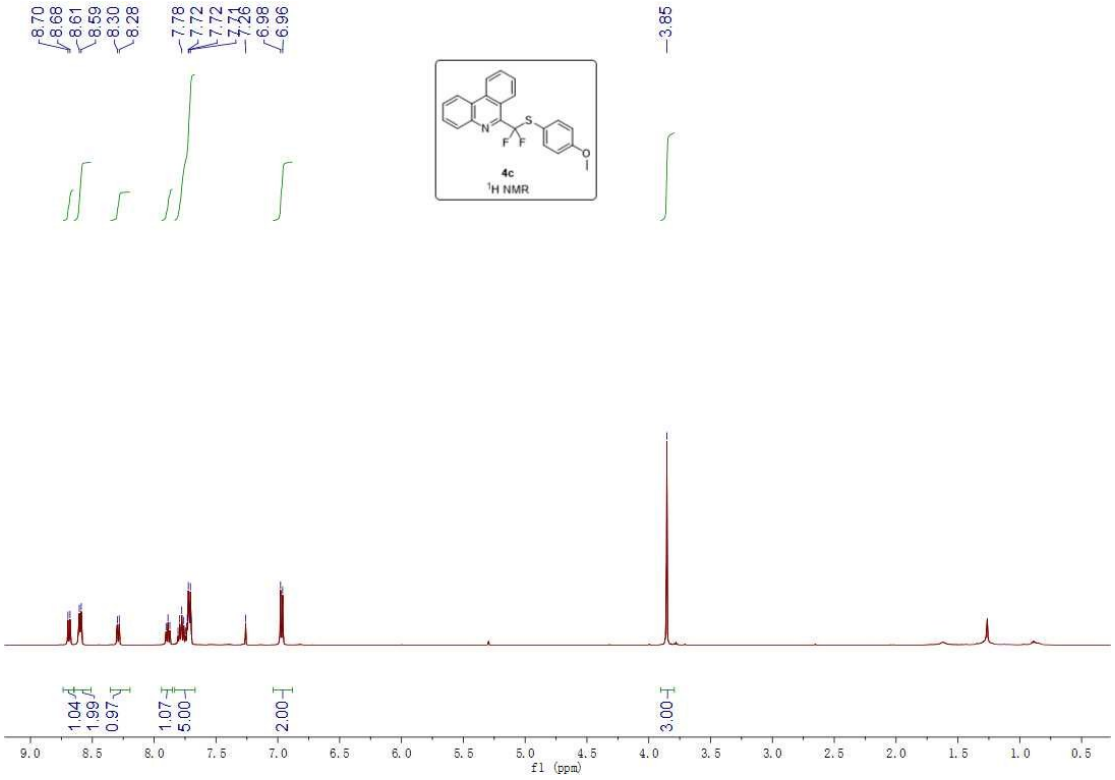
126.02
125.98
125.94
123.96
122.64
121.35
120.96
20.33
f1 (ppm)


4c
1H NMR
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8.30
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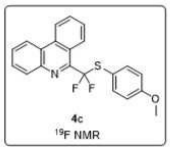
7.72
7.72
7.71
7.26
6.98
6.96
3.85
1.04
1.99
0.97
1.07
5.00
2.00
3.00
f1 (ppm)


4c
19F NMR

-67.12
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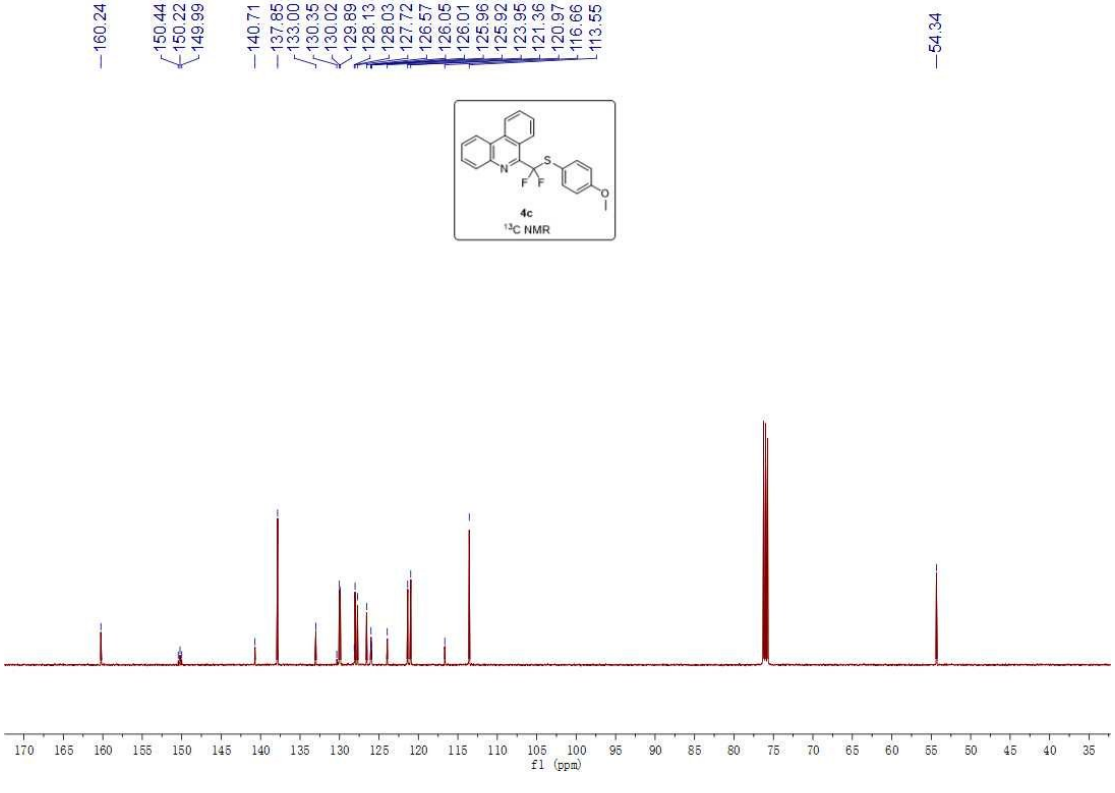
f1 (ppm)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150.22
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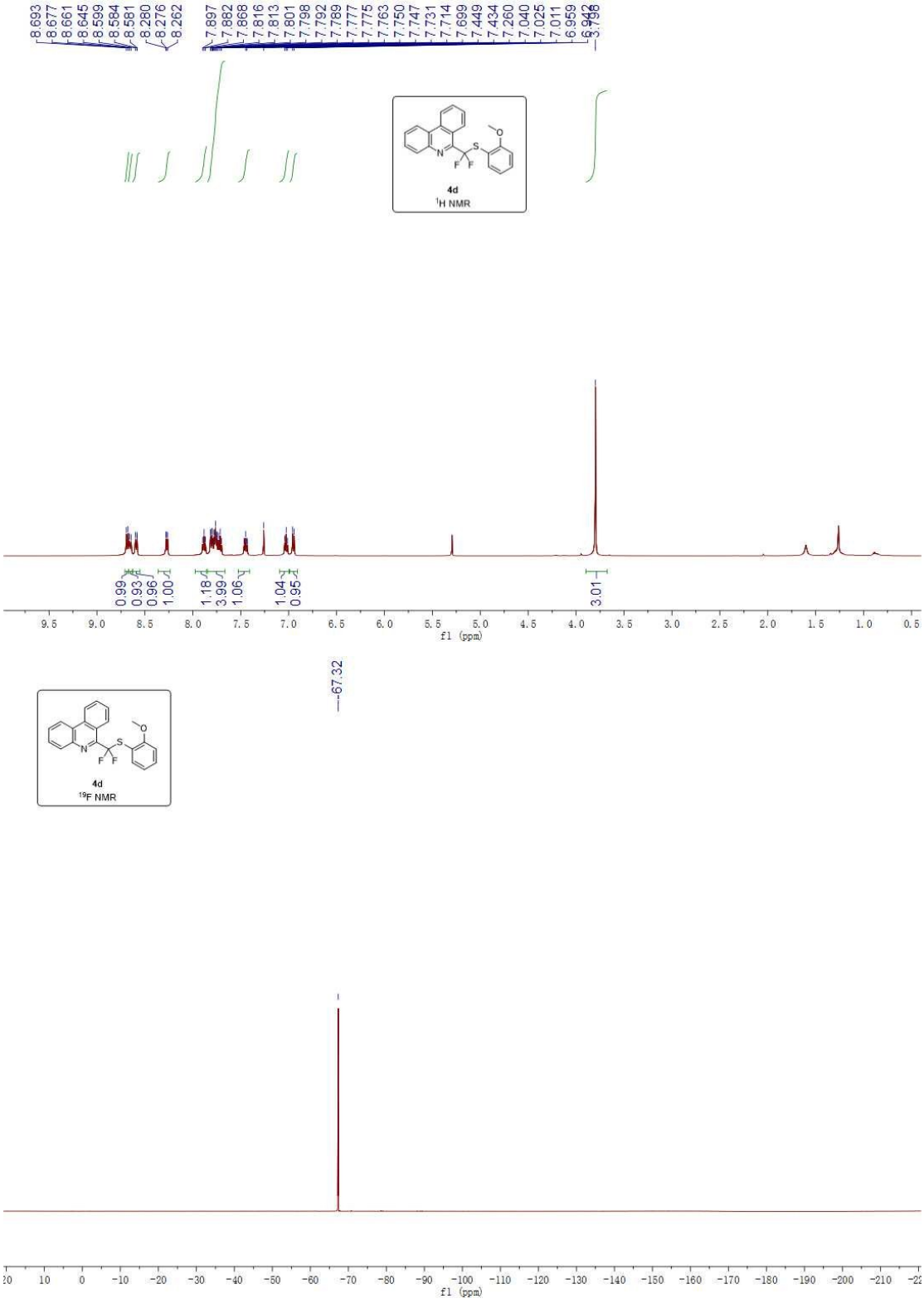
133.00
130.35
130.02
129.89
128.13
128.03
127.72
126.57
126.05
126.01
125.96
125.92
123.95
121.36
120.97
116.66
113.55
54.34
4c
13C NMR
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)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8.677
8.661
8.645
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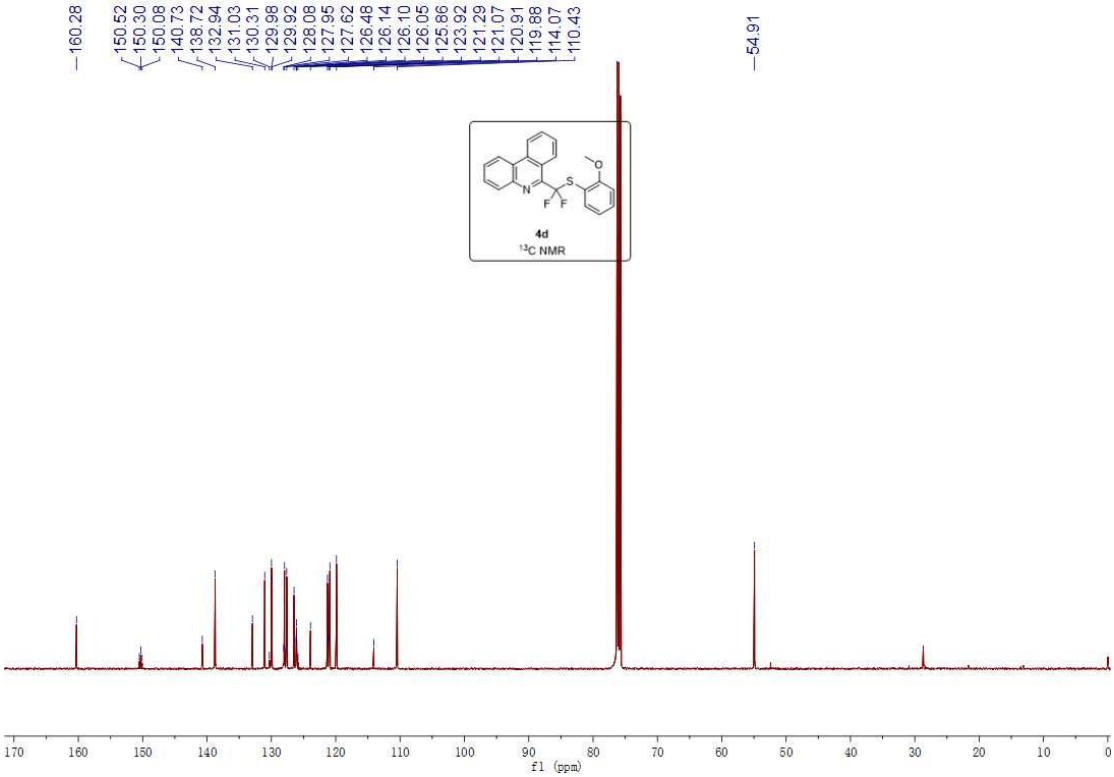
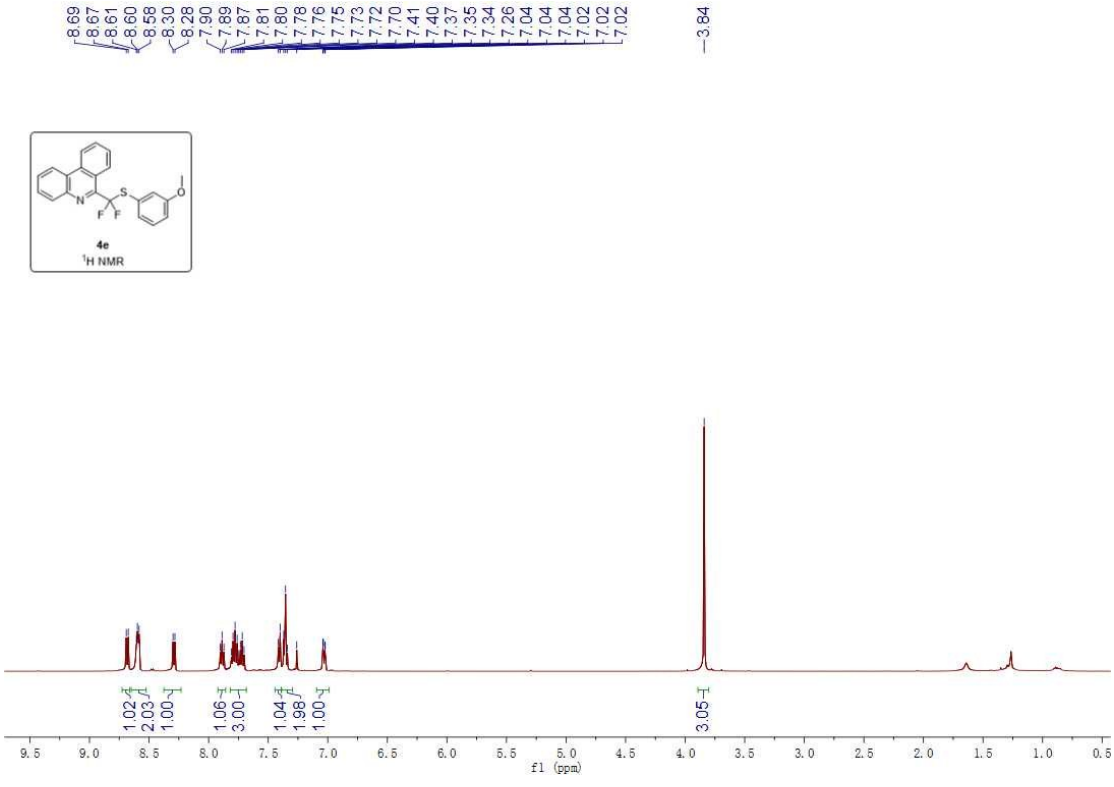
8.584
8.581
8.280
8.276
8.262
7.897
7.882
7.868
7.816
7.813
7.801
7.798
7.792
7.789
7.777
7.775
7.763
7.750
7.747
7.731
7.714
7.699
7.449
7.434
7.260
7.040
7.025
7.011
6.959
3.998
4d
1H NMR
0.99
0.93
0.96
1.00
1.18
3.99
1.06
1.04
0.95
3.01
f1 (ppm)
-67.32
4d
19F NMR
f1 (ppm)


160.28
150.52
150.30
150.08
140.73
138.72
132.94
131.03
130.31
129.98
129.92
128.08
127.95
127.62
126.48
126.14
126.10
126.05
125.86
123.92
121.29
121.07
120.91
119.88
114.07
110.43
54.91
4d
13C NMR
f1 (ppm)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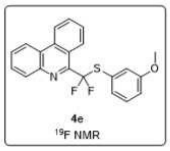
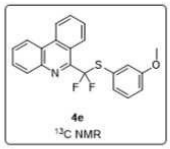
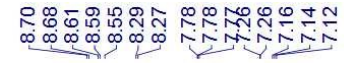
8.30
8.28
7.90
7.89
7.87
7.81
7.80
7.78
7.76
7.75
7.73
7.72
7.70
7.41
7.40
7.37
7.35
7.34
7.26
7.04
7.04
7.04
7.02
7.02
7.02
3.84
4e
1H NMR
1.02
2.03
1.00
1.06
3.00
1.04
1.98
1.00
3.05
f1 (ppm)


4e
19F NMR

-65.99
f1 (ppm)


4e
13C NMR

158.59
150.26
150.04
149.82
140.65
133.01
130.74
130.06
129.85
128.60
128.51
128.27
128.05
127.77
127.28
126.61
126.30
125.95
125.91
125.87
123.97
121.38
120.98
120.88
115.09
54.36
f1 (ppm)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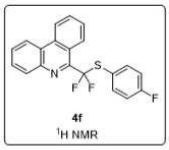
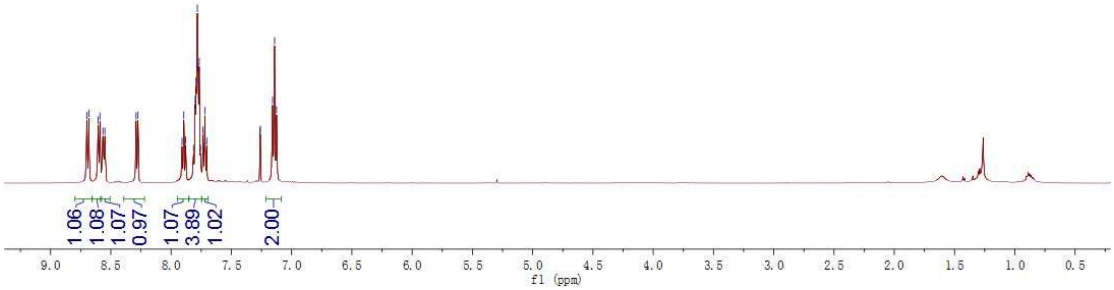
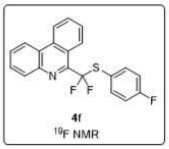
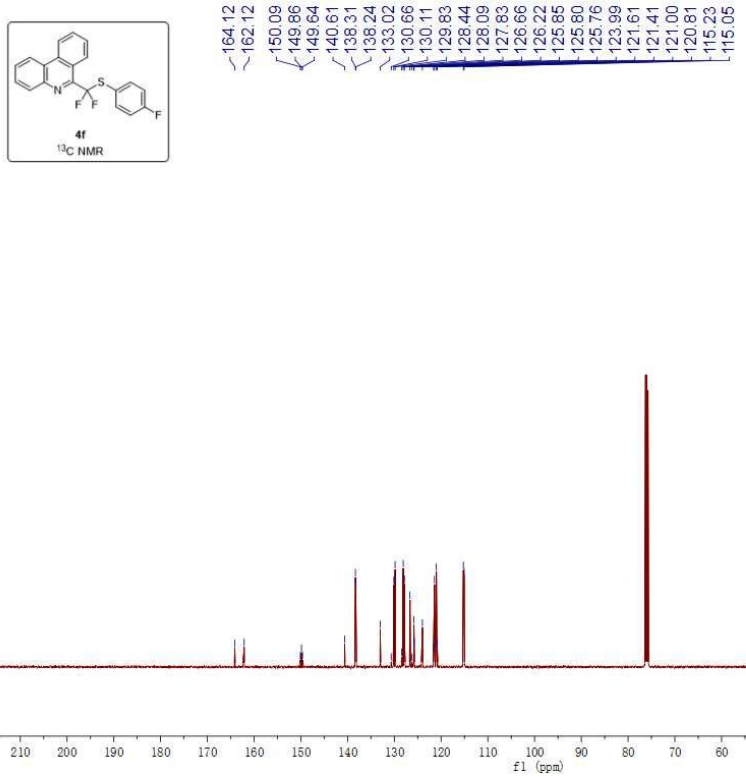
8.68
8.61
8.59
8.55
8.29
8.27
7.78
7.78
7.26
7.16
7.14
7.12

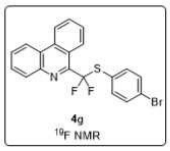

4f
^{1}H NMR


1.06
1.08
1.07
0.97
1.07
3.89
1.02
2.00
f1 (ppm)

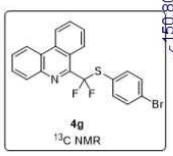

4f
^{19}F NMR

-66.23
-110.77
f1 (ppm)


164.12
162.12
150.09
149.86
149.64
140.61
138.31
138.24
133.02
130.66
130.11
129.83
128.44
128.09
127.83
126.66
126.22
125.85
125.80
125.76
123.99
121.61
121.41
121.00
120.81
115.23
115.05
4f
13C NMR
f1 (ppm)
8.70
8.68
8.61
8.59
8.28
8.28
8.26
7.91
7.91
7.89
7.88
7.88
7.81
7.81
7.80
7.80
7.78
7.78
7.77
7.77
7.75
7.75
7.73
7.73
7.72
7.70
7.70
7.67
7.65
7.58
7.58
7.57
7.56
7.56
7.25
4g
1H NMR
1.00
0.99
0.93
0.91
1.04
2.01
1.00
1.94
1.93
f1 (ppm)


4g
19F NMR

-65.63
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


4g
13C NMR


150.80
150.57
141.64
138.60
134.09
132.21
131.83
131.19
130.87
129.61
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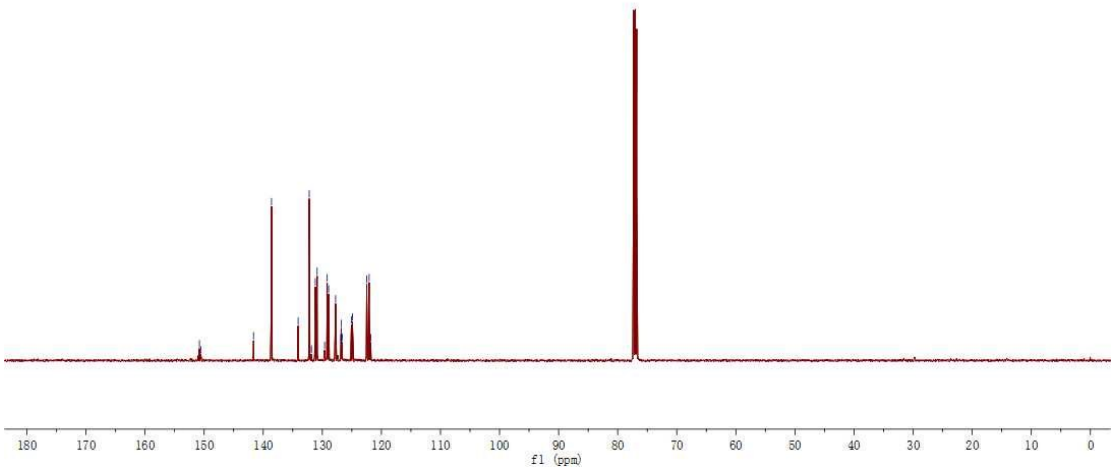
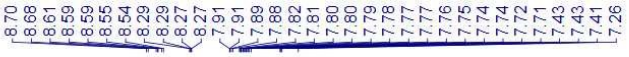
127.75
126.85
126.80
126.76
126.64
125.08
124.90
122.48
122.07
121.81


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.70
8.68
8.61
8.59
8.59
8.55
8.54
8.29
8.29
8.27
8.27
7.91
7.91
7.89
7.88
7.82
7.81
7.80
7.80
7.79
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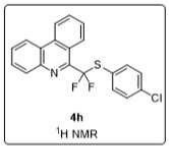
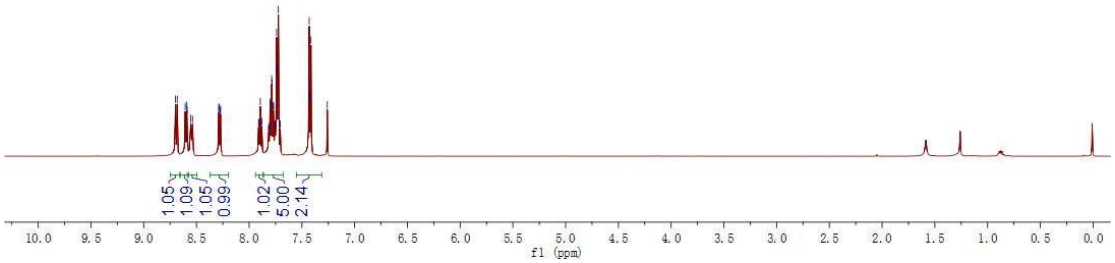
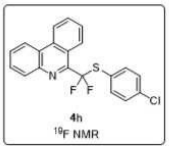
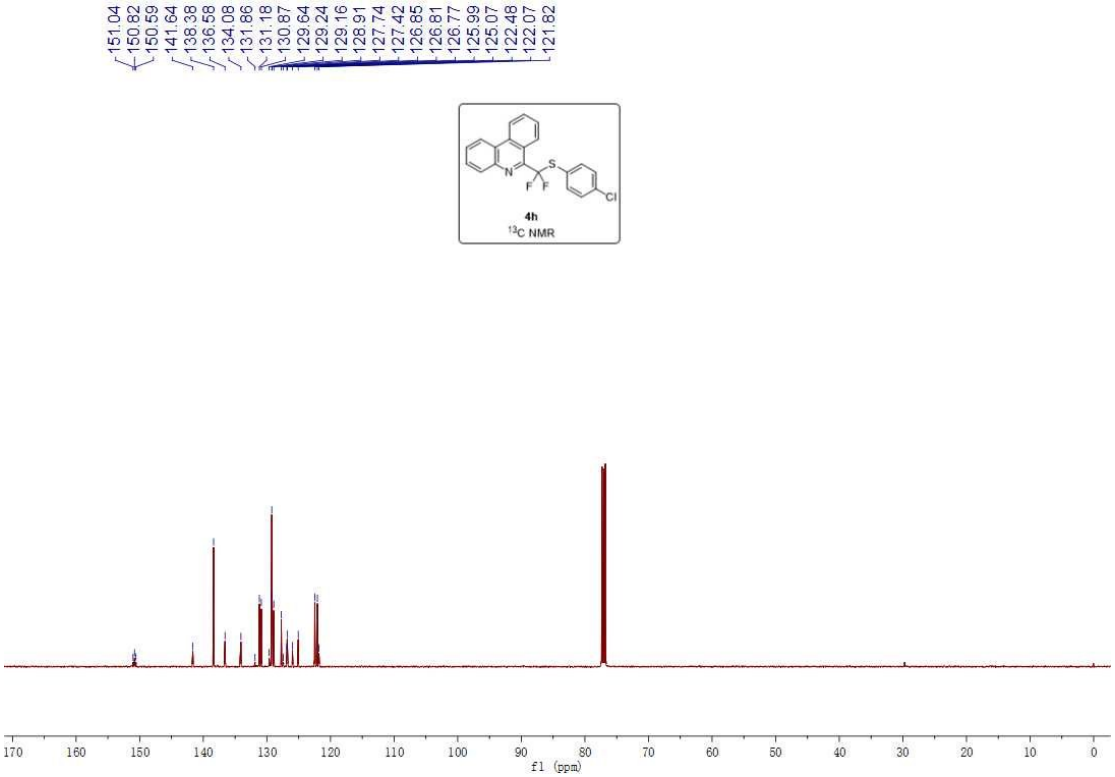
7.72
7.71
7.43
7.41
7.26

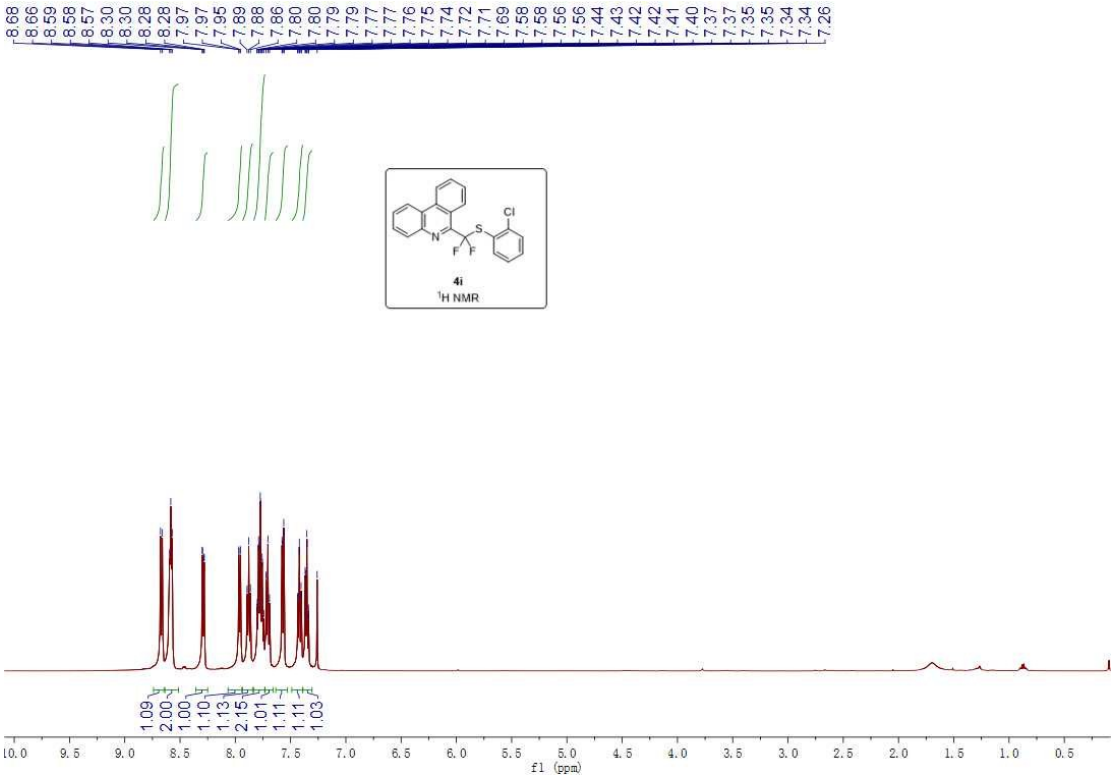

4h
^{1}H NMR


1.05
1.09
1.05
0.99
1.02
5.00
2.14
10.0 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
f1 (ppm)


4h
^{19}F NMR

-65.71
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


151.04
150.82
150.59
141.64
138.38
136.58
134.08
131.86
131.18
130.87
129.64
129.24
129.16
128.91
127.74
127.42
126.85
126.81
126.77
125.99
125.07
122.48
122.07
121.82
4h
13C NMR
f1 (ppm)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8.58
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8.30
8.28
8.28
7.97
7.97
7.95
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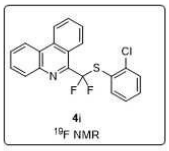
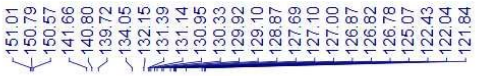
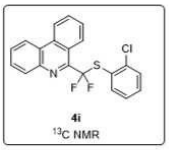
7.88
7.86
7.80
7.80
7.79
7.79
7.77
7.77
7.76
7.75
7.74
7.72
7.71
7.69
7.58
7.58
7.56
7.44
7.43
7.42
7.42
7.41
7.40
7.37
7.37
7.35
7.35
7.34
7.34
7.26
4i
1H NMR
1.09
2.00
1.00
1.10
1.13
2.15
1.01
1.11
1.11
1.03
f1 (ppm)

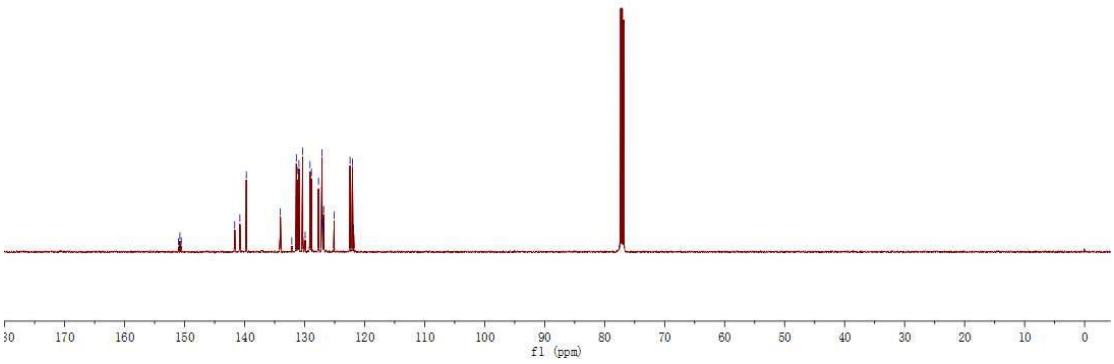


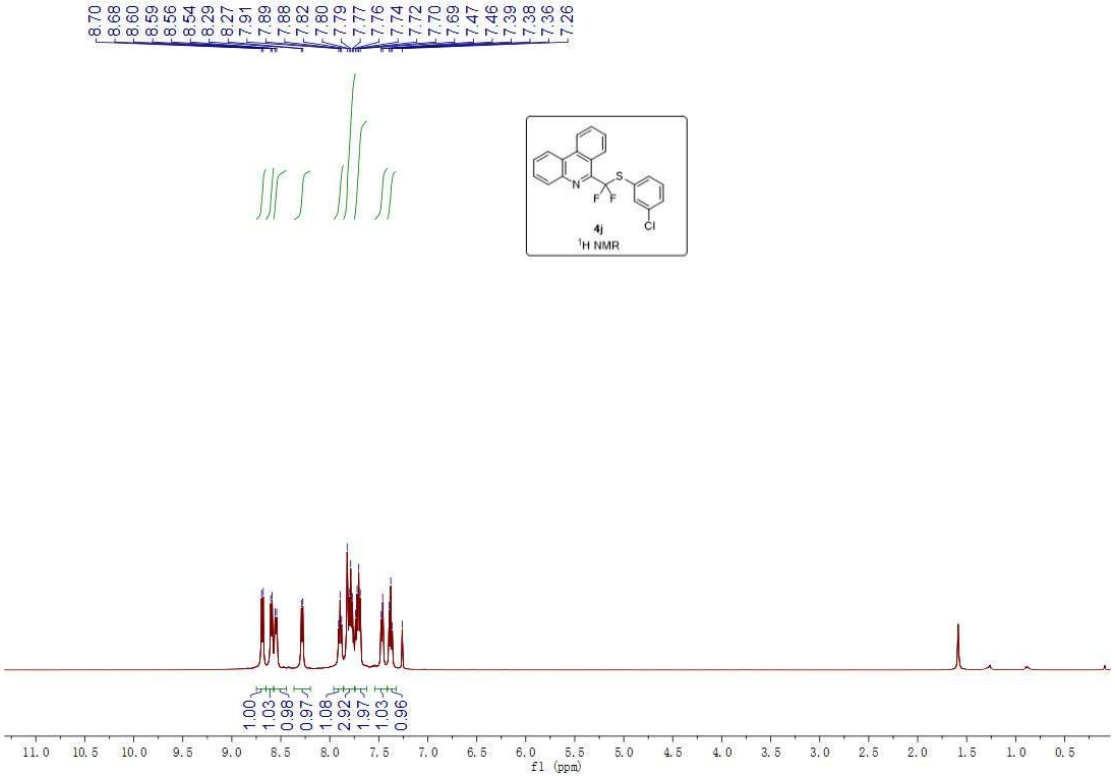
4i
^{19}F NMR





4i
^{13}C NMR

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8.27
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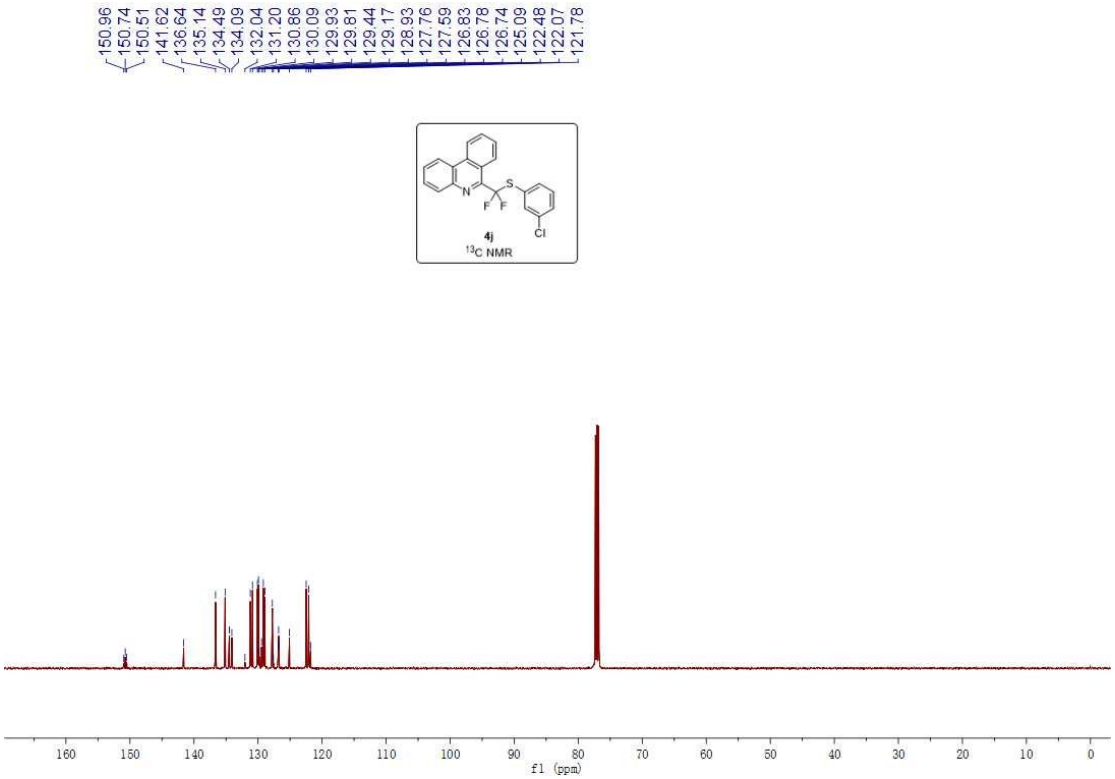
7.79
7.77
7.76
7.74
7.72
7.70
7.69
7.47
7.46
7.39
7.38
7.36
7.26
4j
1H NMR
1.00
1.03
0.98
0.97
1.08
2.92
1.97
1.03
0.96
f1 (ppm)
4j
19F NMR
-65.30
f1 (ppm)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135.14
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129.81
129.44
129.17
128.93
127.76
127.59
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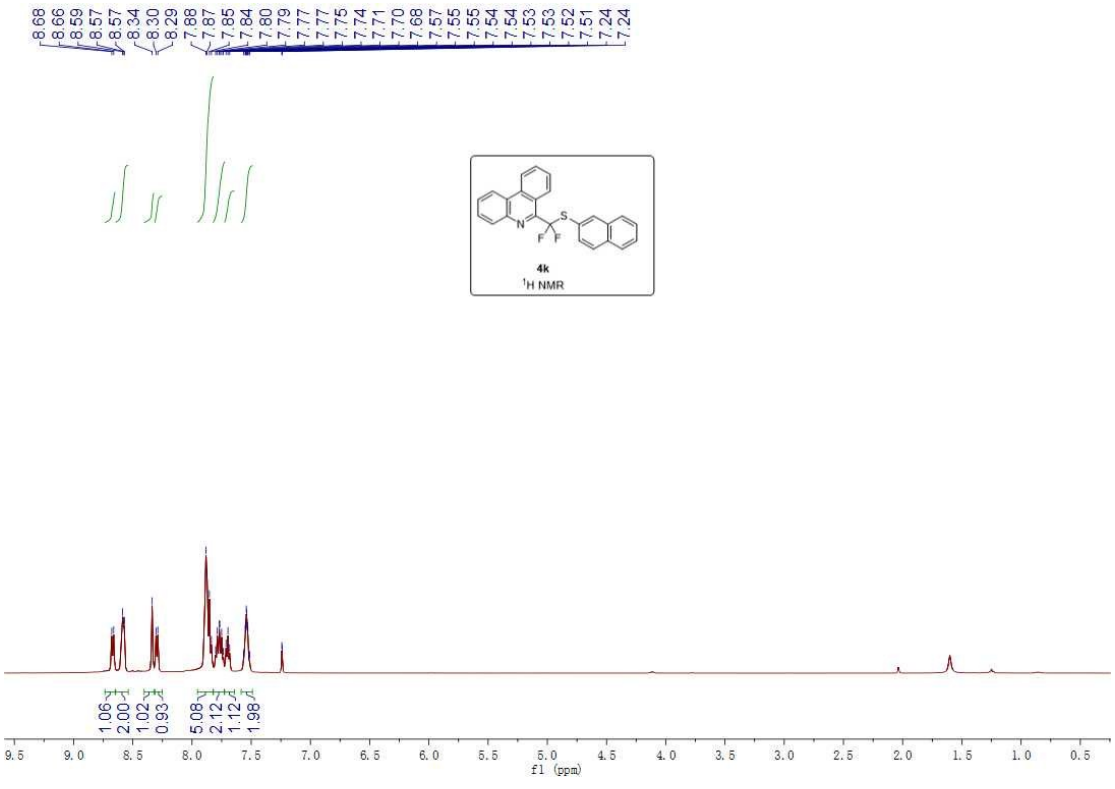
126.78
126.74
125.09
122.48
122.07
121.78
4j
13C NMR
f1 (ppm)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8.34
8.30
8.29
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7.87
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7.79
7.77
7.77
7.75
7.74
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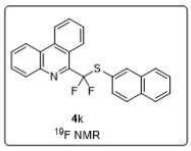
7.68
7.57
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.24
7.24
4k
1H NMR
1.06
2.00
1.02
0.93
5.08
2.12
1.12
1.98
f1 (ppm)


4k
19F NMR

-65.76
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


151.37
151.15
141.75
137.43
134.10
133.68
133.50
133.19
131.97
131.12
130.95
129.75
129.13
128.84
128.49
128.17
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126.58
125.07
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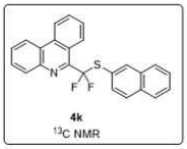
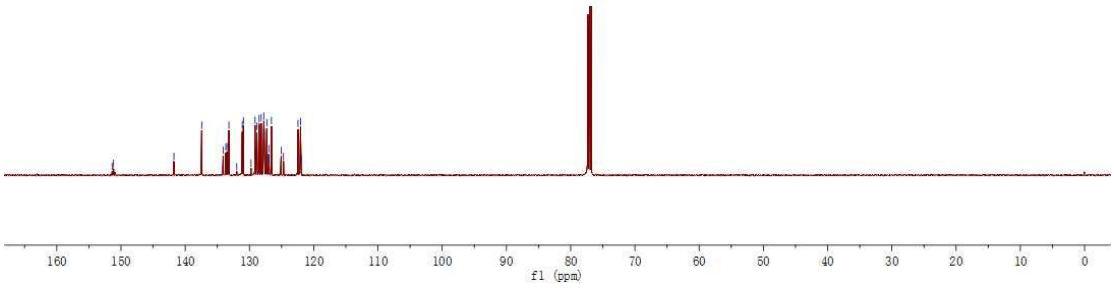
122.06
121.95


4k
13C NMR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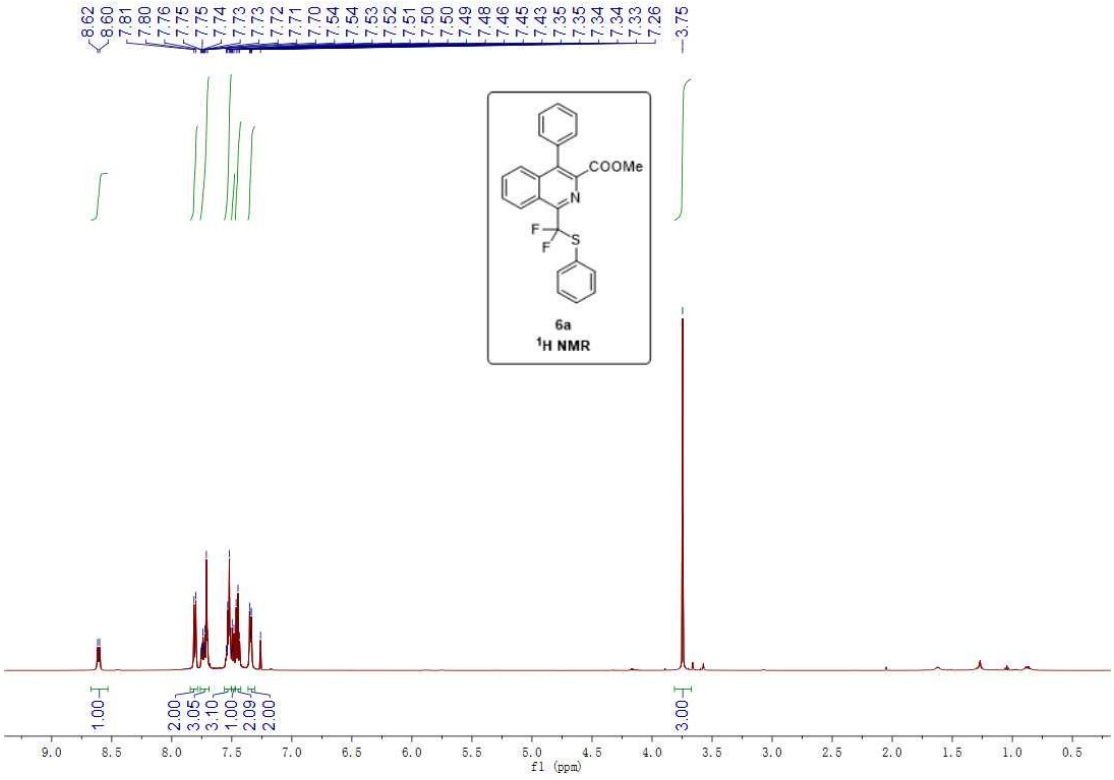
f1 (ppm)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7.54
7.53
7.52
7.51
7.50
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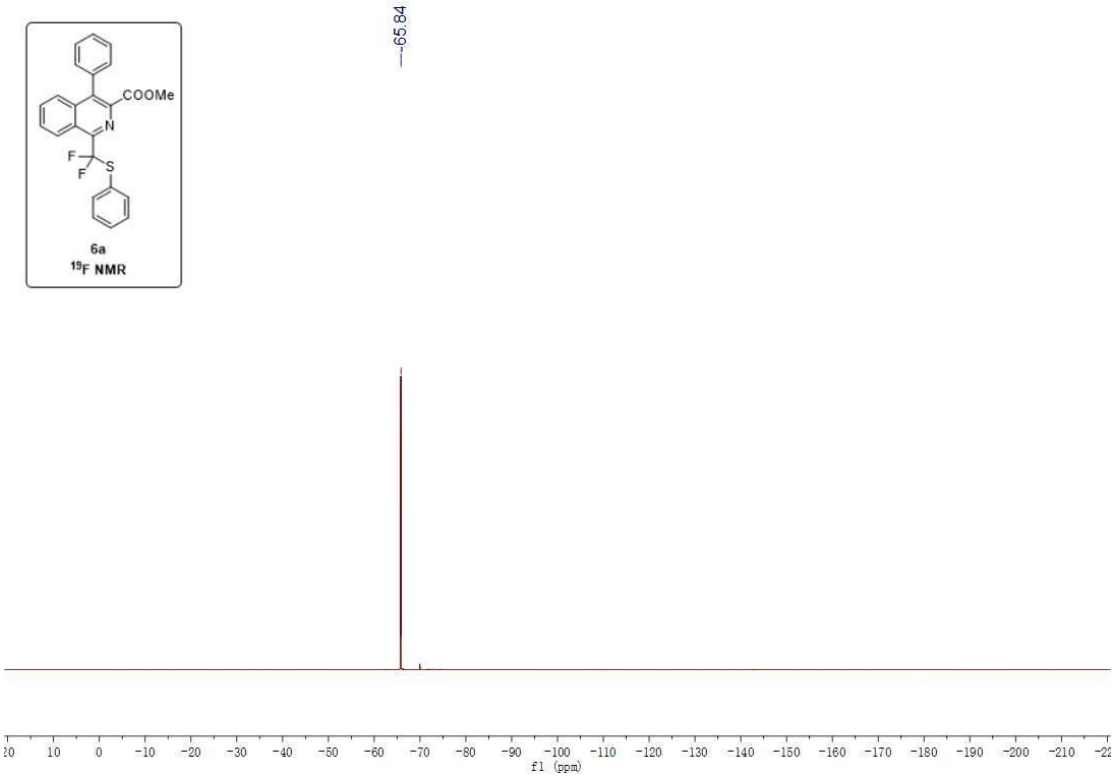
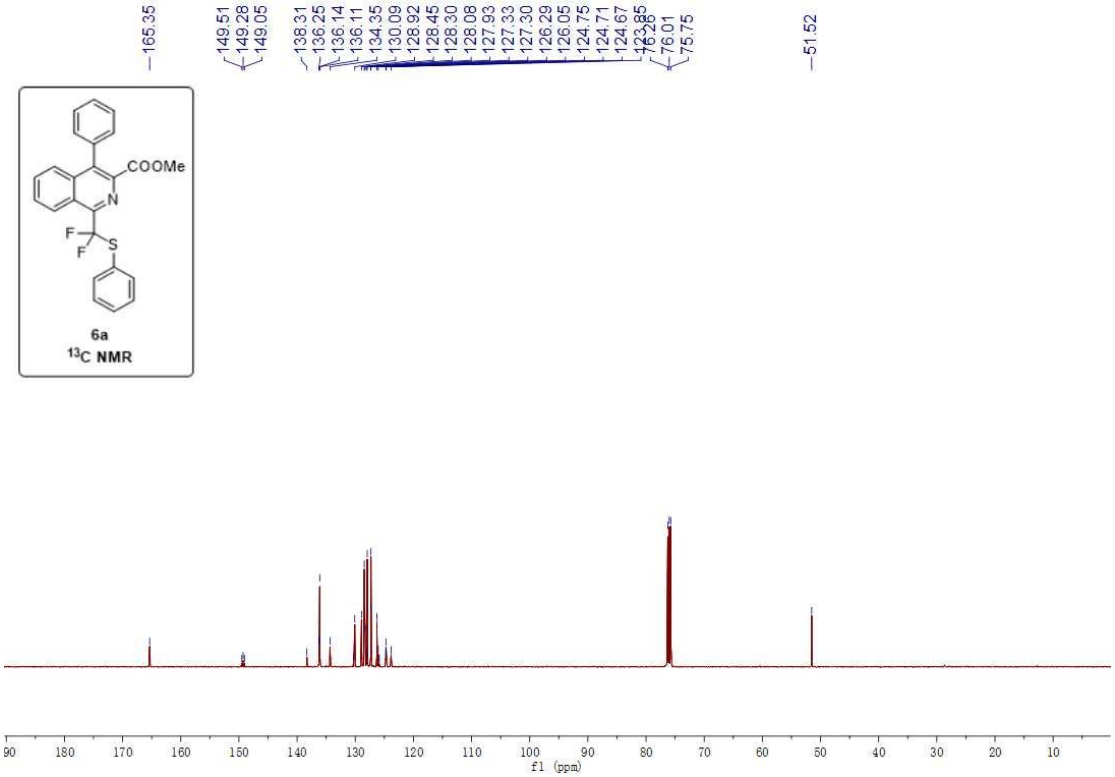
7.49
7.48
7.46
7.45
7.43
7.35
7.35
7.34
7.34
7.33
7.26
3.75
COOMe
N
F
F
S
6a
1H NMR
1.00
2.00
3.05
3.10
1.00
2.09
2.00
3.00
f1 (ppm)


-65.84
COOMe
N
F
F
S
6a
19F NMR
f1 (ppm)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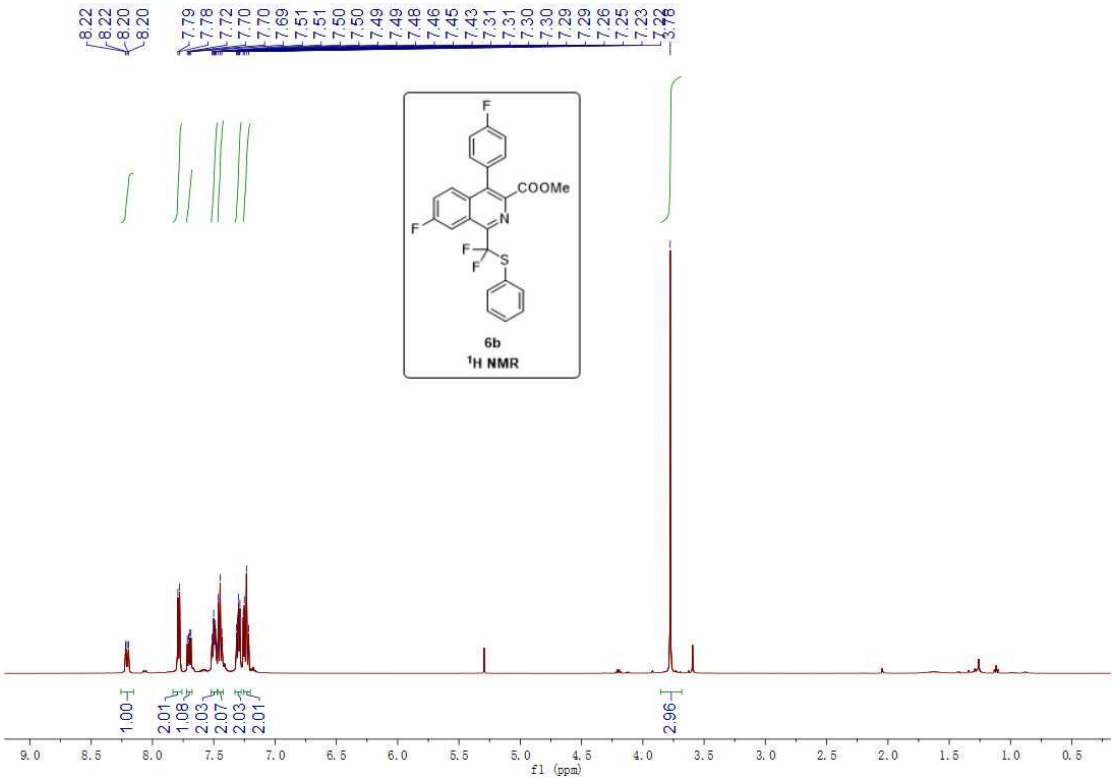
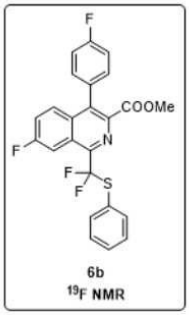
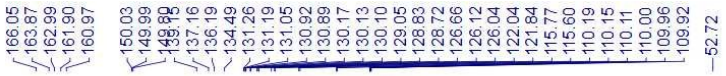
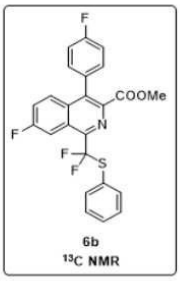
128.30
128.08
127.93
127.33
127.30
126.29
126.05
124.75
124.71
124.67
123.85
76.26
76.01
75.75
51.52
COOMe
N
F
F
S
6a
13C NMR
f1 (ppm)

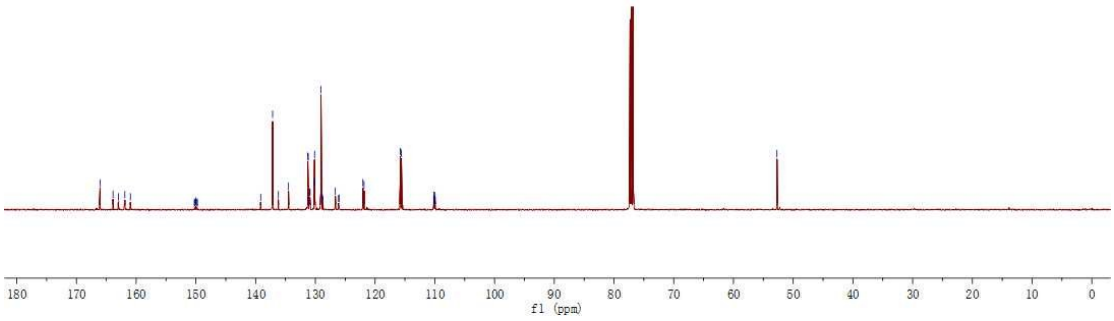

8.22
8.22
8.20
8.20
7.79
7.78
7.72
7.70
7.70
7.69
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.46
7.45
7.43
7.31
7.31
7.30
7.30
7.29
7.29
7.26
7.25
7.23
7.22
3.76
F
COOMe
N
F
F
S
6b
1H NMR
1.00
2.01
1.08
2.03
2.07
2.03
2.01
2.96
f1 (ppm)

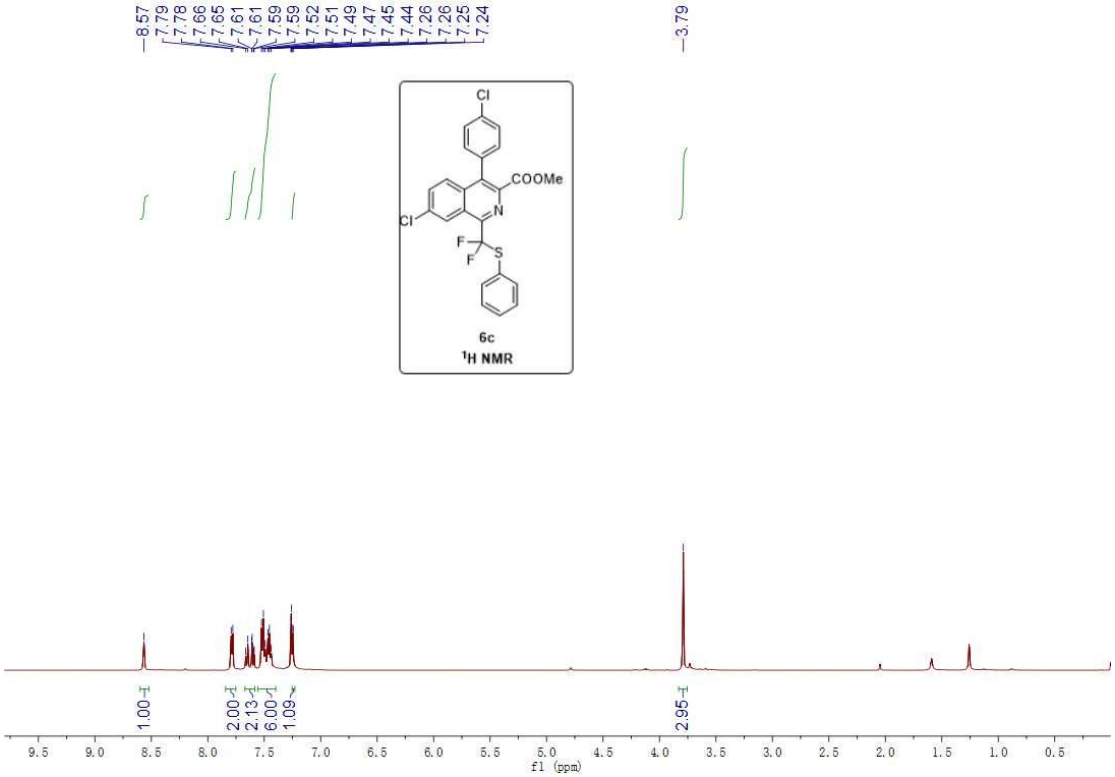

F
COOMe
F
N
F
F
S
6b
19F NMR

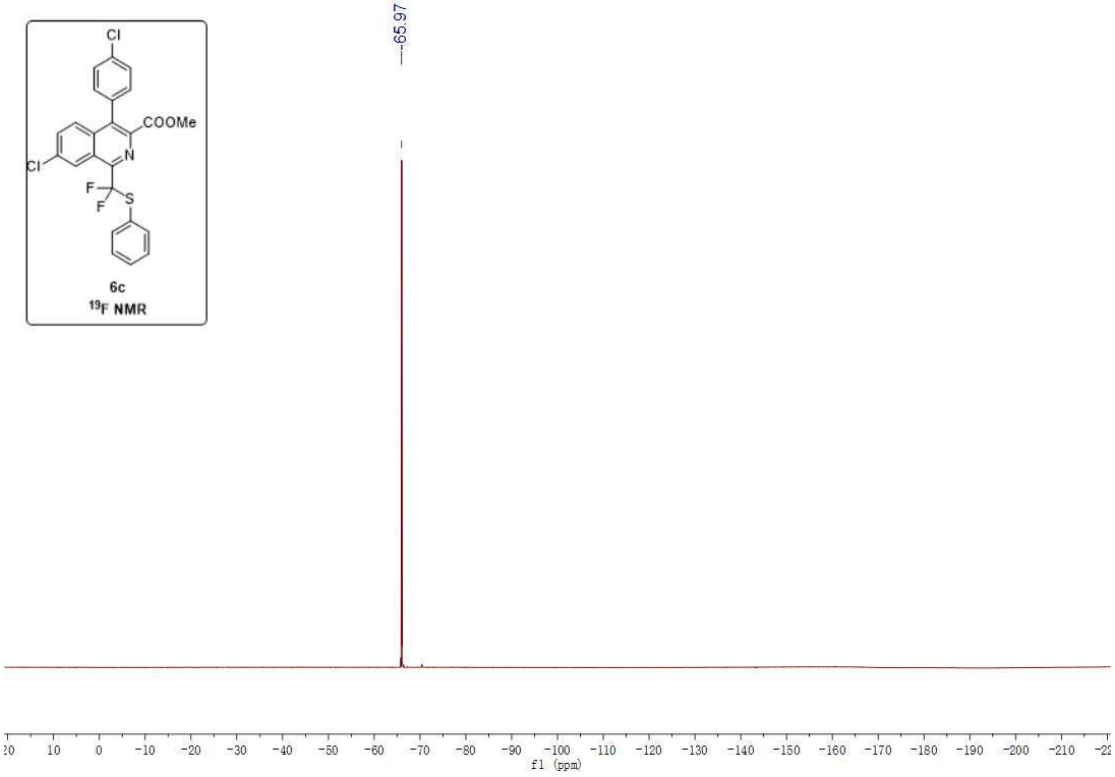
-66.68
-105.94
-112.62
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

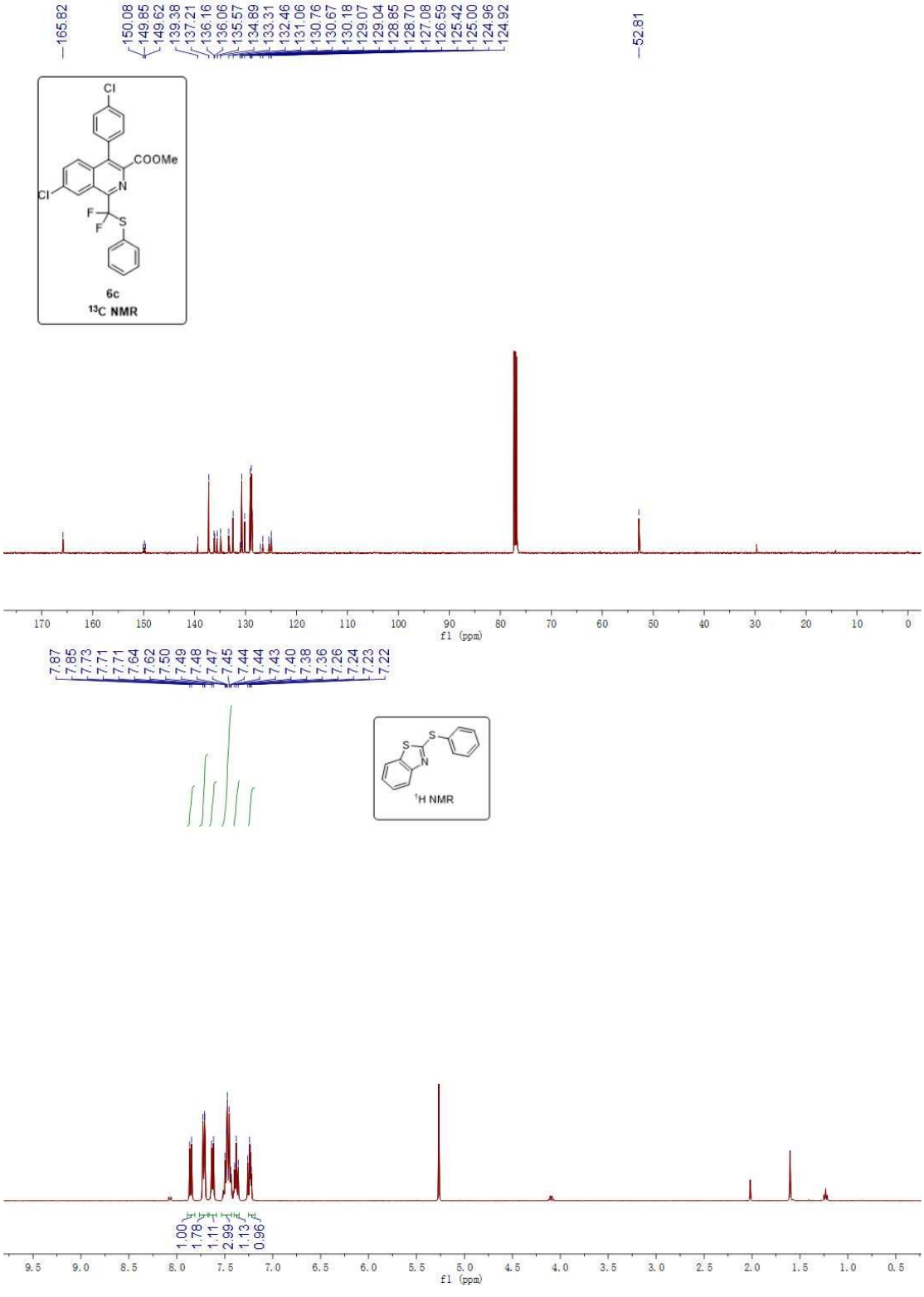

166.05
163.87
162.99
161.90
160.97
150.03
149.99
137.16
136.19
134.49
131.26
131.19
131.05
130.92
130.89
130.17
130.13
130.10
129.05
128.83
128.72
126.66
126.12
126.04
122.04
121.84
115.77
115.60
110.19
110.15
110.11
110.00
109.96
109.92
52.72


F
COOMe
F
N
F
F
S
6b
13C NMR


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.57
7.79
7.78
7.66
7.65
7.61
7.61
7.59
7.59
7.52
7.51
7.49
7.47
7.45
7.44
7.26
7.26
7.25
7.24
3.79
Cl
COOMe
Cl
N
F
F
S
6c
1H NMR
1.00
2.00
2.13
6.00
1.09
2.95
f1 (ppm)


Cl
COOMe
Cl
N
F
F
S
6c
19F NMR
-65.97
f1 (ppm)


165.82
150.08
149.85
149.62
139.38
137.21
136.16
136.06
135.57
134.89
133.31
132.46
131.06
130.76
130.67
130.18
129.07
129.04
128.85
128.70
127.08
126.59
125.42
125.00
124.96
124.92
52.81
Cl
COOMe
Cl
N
F
F
S
6c
13C NMR
f1 (ppm)
7.87
7.85
7.73
7.71
7.71
7.64
7.62
7.50
7.49
7.48
7.47
7.45
7.44
7.44
7.43
7.40
7.38
7.36
7.26
7.24
7.23
7.22
S
S
N
1H NMR
1.00
1.78
1.11
2.99
1.13
0.96
f1 (ppm)