Supporting Information

Visible-Light-Initiated Catalyst-Free Trifluoromethylselenolation of Arylsulfonium Salts with $[Me_4N][SeCF_3]$

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1. General information

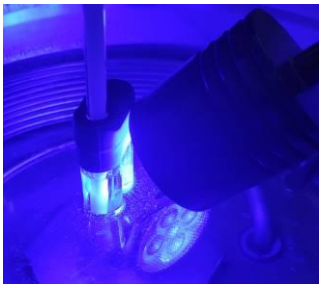
All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$, CD_3CN, or acetone-d_6 on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), 126 MHz (for ^{13}C), and 114 MHz (for ^{77}Se) spectroscopy. All chemical shifts were reported in ppm relative to TMS (0 ppm for ^1H NMR), $PhOCF_3$ (-58.0 ppm for ^{19}F NMR), or PhSeBr (880.5 ppm for ^{77}Se NMR) as an internal or external standard. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the yields of product were determined by using the corresponding pure compound as an external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI or EI instrument. Thianthrene 5-oxide (TTO)[1], 2,3,7,8-tetrafluorothianthrene 5-oxide (TFTO)[1], dibenzo[*b*,*d*]thiophene 5-oxide (DBTO)[2], 3,7-di-*tert*-butyldibenzo[*b*,*d*]thiophene 5-oxide (2TB-DBTO)[2], and arylsulfonium salts **1a**[3] and **1h**[4] were prepared according to the literature. Solvents were dried before use according to the literature.[5] Other reagents in the reactions were all purchased from the commercial sources and used without further purification.

2. The light source and equipments of the reaction



The reaction vial for 0.10-0.20 mmol scales (left).

The table lamp equipped with two 5 W blue LED (right).

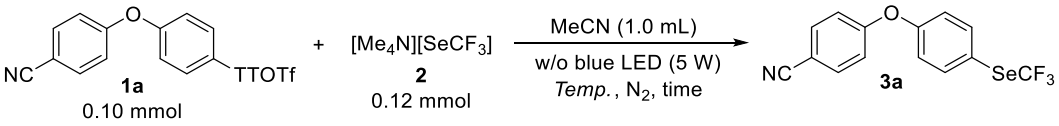



The reaction vial was parallel to a blank vial that was only equipped with solvent and a thermometer to monitor the temperature (left)

The vials were placed in a cooler to keep the reaction temperature at around 0 °C and were irradiated with the blue LED (5 W) (right).

3. Screening of optimal reaction conditions for the trifluoromethylselenolation of arylsulfonium salt (1a) with [Me$_4$N][SeCF$_3$]

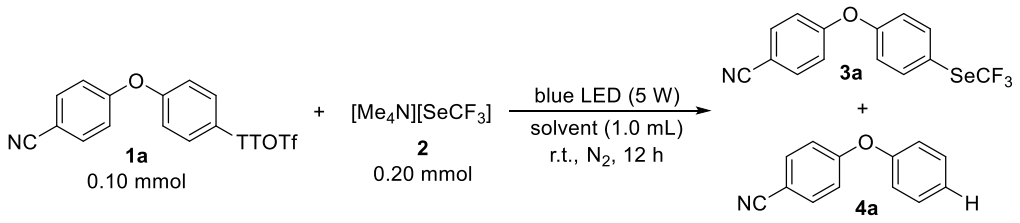
Table S1. Reactions of **1a** and [Me$_4$N][SeCF$_3$] without light irradiation.



Entry [a]	*Temp.*	Time (h)	**3a** (Yield, %)
1	r.t.	5	trace
2	40 °C	5	trace
3	60 °C	5	trace
4 [b]	r.t.	24	trace

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.12 mmol), MeCN (1.0 mL), N_2. Yields of **3a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**, t_R = 7.8 min) as an external standard. [b] **1a** (0.10 mmol), **2** (0.16 mmol), MeCN (1 mL), N_2.

Table S2. Blue-LED-irradiated trifluoromethylselenolation of **1a** with [Me$_4$N][SeCF$_3$] in different solvents at room temperature.



Entry [a]	Solvent	**3a** (Yield, %)	**4a** (Yield, %)

1	MeCN	62	8
2 [b]	MeCN	62	7
3	acetone	66	16
4	DMF	34	51
5	DMSO	9	<1
6	$PhCF_3$	53	trace
7	PhCl	50	3

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.20 mmol), solvent (1.0 mL), blue LED (5 W), room temperature, N_2, 12 h. Yields of **3a** and **4a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl)-phenoxy)benzonitrile (**3a**, t_R = 7.8 min) and 4-phenoxybenzonitrile (**4a**, t_R = 5.5 min) as external standards. [b] Purple LED (5 W) was used instead of blue LED (5 W).

Table S3. Blue-LED-irradiated trifluoromethylselenolation of **1a** with $[Me_4N][SeCF_3]$ in MeCN at room temperature with different concentrations.

Entry [a]	Concentration (M)	**3a** (Yield, %)	**4a** (Yield, %)
1	0.4	57	trace
2	0.2	65	1
3	0.1	62	8
4	0.067	51	4
5 [b]	0.4	66	9
6 [b]	0.2	66	12

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.20 mmol), MeCN (0.25, 0.5, 1.0, or 1.5 mL), blue LED (5 W), room temperature, N_2, 12 h. Yields of **3a** and **4a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**, t_R = 7.8 min) and 4-phenoxy-benzonitrile (**4a**, t_R = 5.5 min) as external standards. [b] Acetone (0.25 or 0.5 mL) was used as the solvent.

Table S4. Blue-LED-irradiated trifluoromethylselenolation of **1a** with $[Me_4N][SeCF_3]$ at room temperature within different times.

Entry [a]	Time (h)	**3a** (Yield, %)	**4a** (Yield, %)
1	4	48	< 1
2	6	64	1
3	8	63	1
4	12	65	1

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.20 mmol), MeCN (0.5 mL), blue LED (5 W), room temperature, N_2. Yields of **3a** and **4a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl) phenoxy)benzonitrile (**3a**, t_R = 7.8 min) and 4-phenoxybenzonitrile (**4a**, t_R = 5.5 min) as external standards.

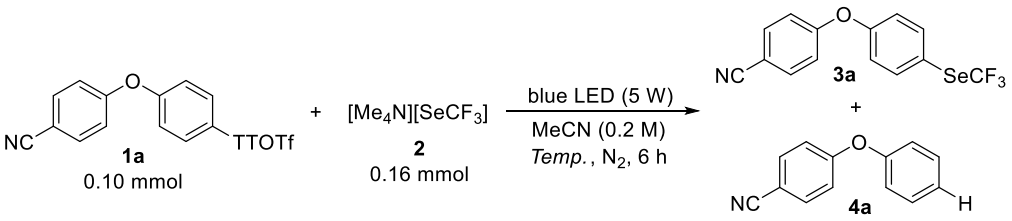
Table S5. Blue-LED-irradiated trifluoromethylselenolation of **1a** with $[Me_4N][SeCF_3]$ at room temperature with different reactant ratios.

Entry [a]	Ratio (x : y)	**3a** (Yield, %)	**4a** (Yield, %)
1	1 : 1	50	7
2	1 : 1.2	59	4
3	1 : 1.4	62	4
4	1 : 1.6	64	3
5	1 : 1.8	60	3
6	1 : 2	64	1
7	1 : 2.4	67	< 1

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.10, 0.12, 0.14, 0.16, 0.18, 0.20, or 0.24

mmol), MeCN (0.5 mL), blue LED (5 W), room temperature, N_2, 6 h. Yields of **3a** and **4a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**, t_R = 7.8 min) and 4-phenoxybenzonitrile (**4a**, t_R = 5.5 min) as external standards.

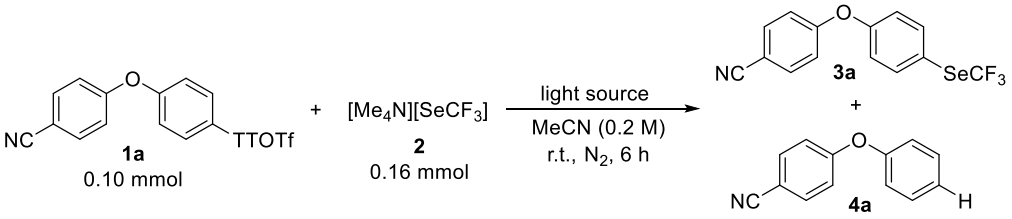
Table S6. Blue-LED-irradiated trifluoromethylselenolation of **1a** with $[Me_4N][SeCF_3]$ at different temperatures.



Entry [a]	*Temp.*	**3a** (Yield, %)	**4a** (Yield, %)
1	0 °C	42	< 1
2	r.t.	64	3
3	50 °C	50	6

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.16 mmol), MeCN (0.5 mL), blue LED (5 W), 0 °C or room temperature or 50 °C, N_2, 6 h. Yields of **3a** and **4a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**, t_R = 7.8 min) and 4-phenoxybenzonitrile (**4a**, t_R = 5.5 min) as external standards.

Table S7. Trifluoromethylselenolation of **1a** with $[Me_4N][SeCF_3]$ under different light irradiation.



Entry [a]	Light source	**3a** (Yield, %)	**4a** (Yield, %)
1	blue LED (5 W)	64	3
2	purple LED (5 W)	64	4
3	green LED (5 W)	44	4
4	380-385 nm LED (50 W)	65	5

5 [b]	380-385 nm LED (50 W)	63	4

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.16 mmol), MeCN (0.5 mL), light source, room temperature, N_2, 6 h. Yields of **3a** and **4a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl) phenoxy)benzonitrile (**3a**, t_R = 7.8 min) and 4-phenoxybenzonitrile (**4a**, t_R = 5.5 min) as external standards. [b] **1a** (0.10 mmol), **2** (0.20 mmol), acetone (1.0 mL), light source, 5 h.

Table S8. The effect of counteranions on the trifluoromethylselenolation.

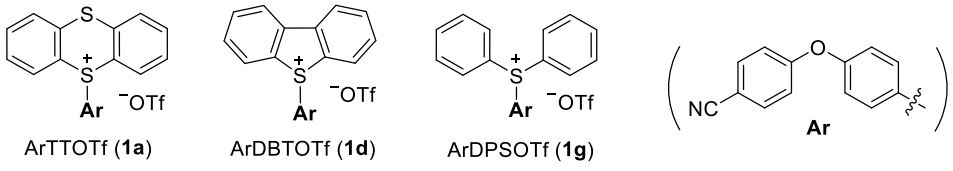
Entry	Anion (X)	**3a** (Yield, %)	**4a** (Yield, %)
1	OTf	64	3
2	BF_4	61	5

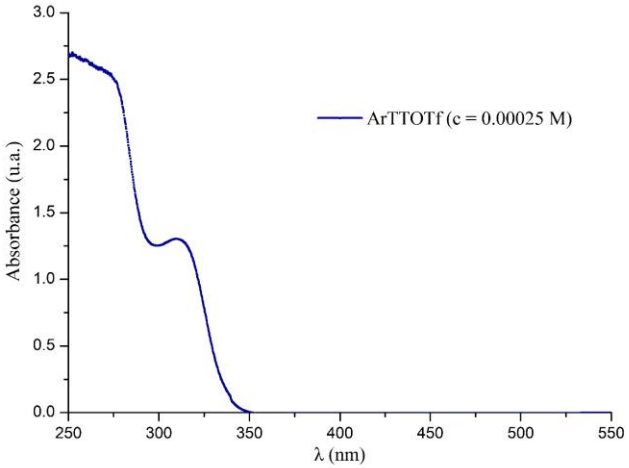
[a] Reaction conditions: **1** (0.10 mmol), **2** (0.16 mmol), MeCN (0.5 mL), blue LED (5 W), room temperature, N_2, 6 h. Yields of **3a** and **4a** were determined by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl) phenoxy)benzonitrile (**3a**, t_R = 7.8 min) and 4-phenoxybenzonitrile (**4a**, t_R = 5.5 min) as external standards.

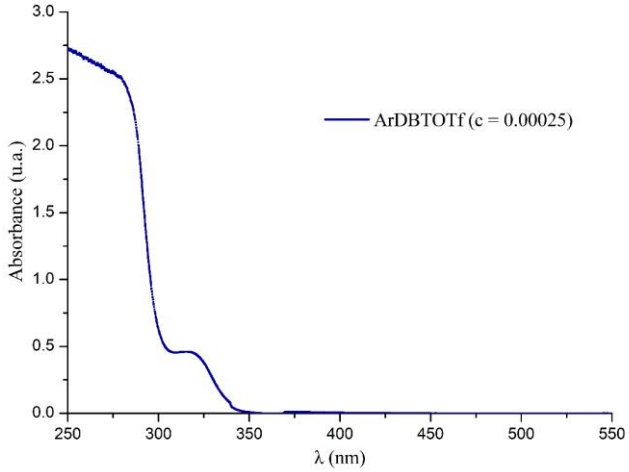
4. The UV-vis absorption spectra of the mixtures of arylsulfonium salts and [Me4N][SeCF3].

All solutions of arylsulfonium salt and [Me_4N][$SeCF_3$] in MeCN were prepared in a nitrogen-filled glove-box, and were placed in sealed standard quartz cuvettes (*l* = 1.0 cm) for UV-vis absorption measurement.

Figure 1. The UV-vis absorption spectra of ArTTOTf (**1a**), ArDBTOTf (**1d**), and ArDPSOTf (**1g**) in MeCN (c = 0.00025 M).




ArTTOTf (c = 0.00025 M)
Absorbance (u.a.)
λ (nm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
250
300
350
400
450
500
550


ArDBTOTf (c = 0.00025)
Absorbance (u.a.)
λ (nm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
250
300
350
400
450
500
550

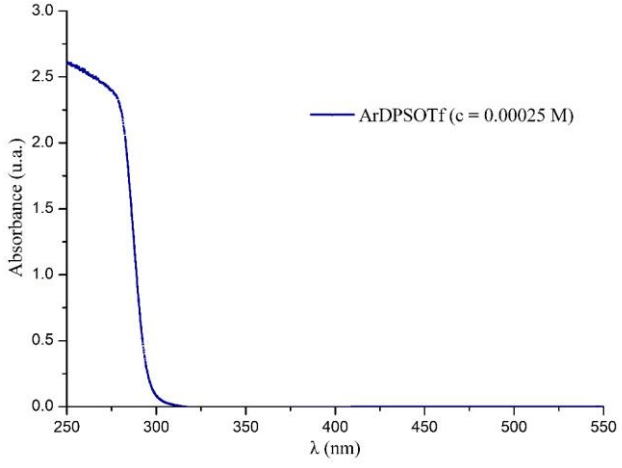

ArDPSOTf (c = 0.00025 M)
Absorbance (u.a.)
λ (nm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
250
300
350
400
450
500
550

Figure 2. The combined UV-vis absorption spectra of $[Me_4N][SeCF_3]$, ArTTOTf (**1a**), and the 1 : 1 mixture of $[Me_4N][SeCF_3]$ and ArTTOTf (**1a**) in MeCN (c = 0.05 M).

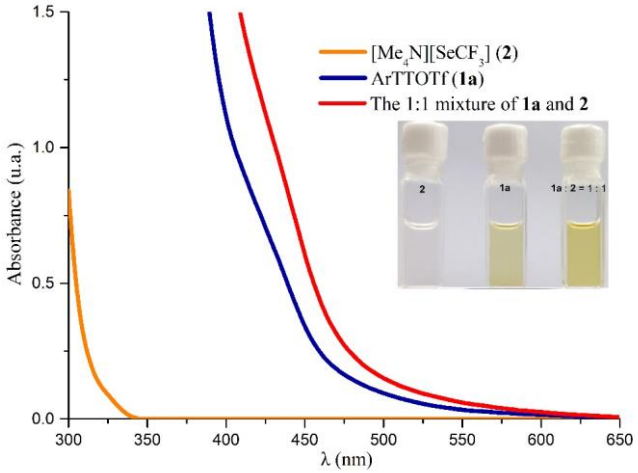


Figure 3. The combined UV-vis absorption spectra of $[Me_4N][SeCF_3]$, ArDBTOTf (**1d**), and the 1 : 1 mixture of $[Me_4N][SeCF_3]$ and ArDBTOTf (**1d**) in MeCN (c = 0.05 M).

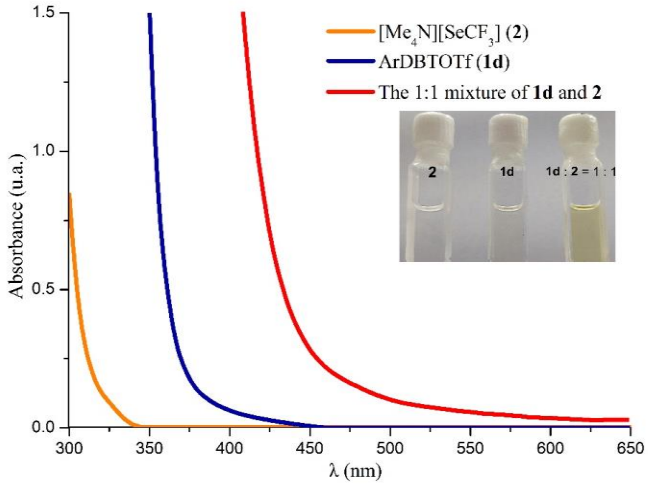


Figure 4. The combined UV-vis absorption spectra of $[Me_4N][SeCF_3]$, ArDPSOTf (**1g**), and the 1 : 1 mixture of $[Me_4N][SeCF_3]$ and ArDPSOTf (**1g**) in MeCN (c = 0.05 M).

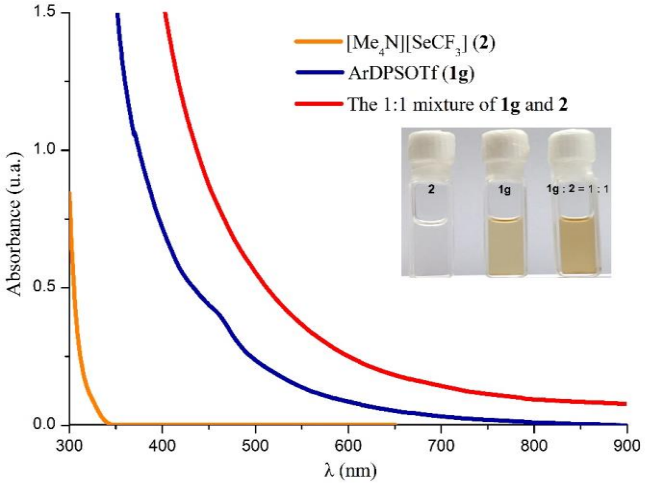


Figure 5. The combined UV-vis absorption spectra of ArDBTOTf (**1d**) and the mixtures of ArDBTOTf (**1d**) and $[Me_4N][SeCF_3]$ in MeCN (c = 0.00025M (**1d**)).

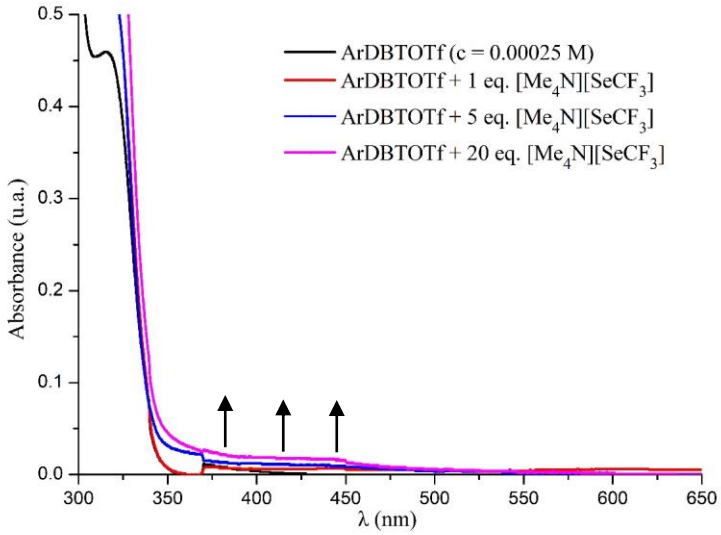


Figure 6. The combined UV-vis absorption spectra of ArDBTOTf (**1d**) and the mixtures of ArDBTOTf (**1d**) and $[Me_4N][SeCF_3]$ in MeCN (c = 0.0005M (**1d**)).

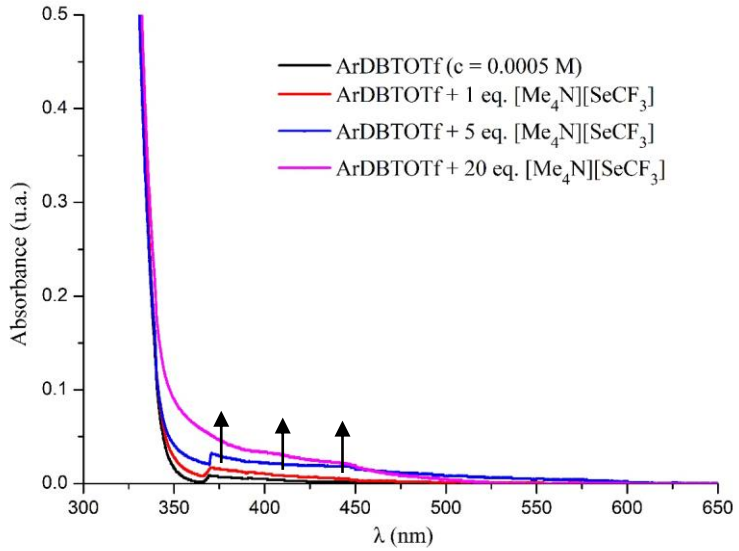


Figure 7. The combined UV-vis absorption spectra of the 1 : 1 mixtures of $[Me_4N][SeCF_3]$ and ArDBTOTf (**1d**) in MeCN at different concentrations (0.00025 to 0.01 M (for both)).

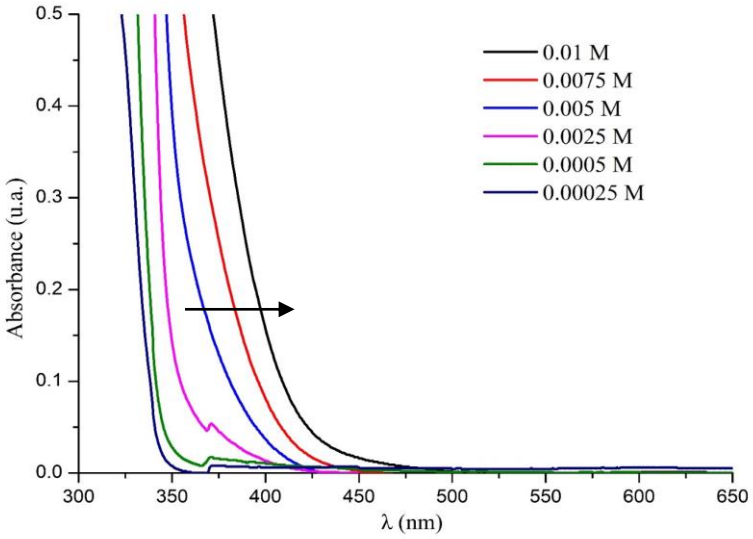
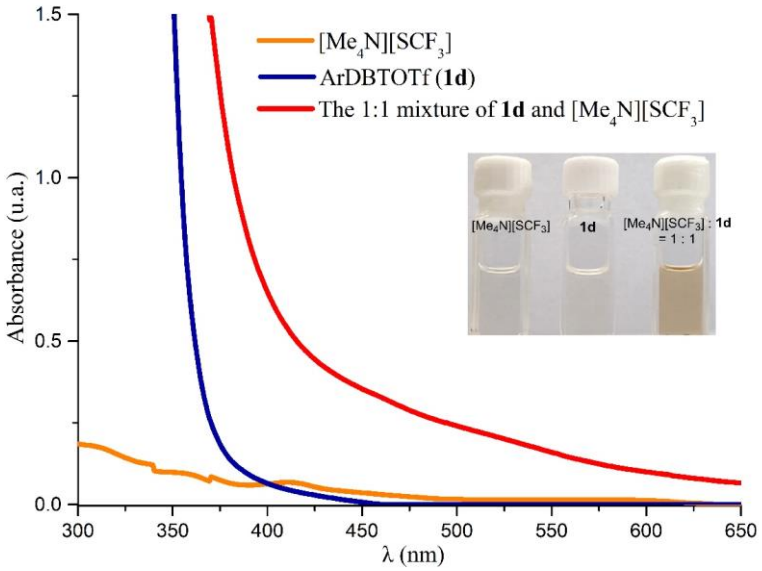


Figure 8. The combined UV-vis absorption spectra of $[Me_4N][SCF_3]$, ArDBTOTf (**1d**), and the 1 : 1 mixture of $[Me_4N][SCF_3]$ and ArDBTOTf (**1d**) in MeCN (c = 0.05 M).



5. The CV experiments

The electrochemical studies were performed by using a CHI660E electrochemical workstation with a three-electrode one-compartment cell fitted with a glassy-carbon working electrode (2.0 mm diameter), a Pt wire counter electrode, and a Ag/AgCl reference electrode (Ag wire dipped in saturated KCl aqueous solution). The General Purpose Electrochemical Software (GPES) was utilized to record and process the data. The dry MeCN from commercial source was degassed by bubbling nitrogen gas before use. All experiments were performed at ambient temperature with a scan rate of 0.05 $V \bullet s^{-1}$ in MeCN solutions containing 2.0 mmol/L analyte and 0.1 mol/L [*n*Bu$_4$N][PF$_6$] supporting electrolyte. All data were referenced to an external ferrocene/ferrocenium reference redox couple. *Note*: the half-wave potentials ($E^{1/2}$) are reported based on the midpoint between the peaks of the anodic and cathodic waves. For irreversible reduction or oxidation waves, the inflection-point potentials (E^i) are calculated by the known literature.[6,7]

Figure 9. The cyclic voltammogram of [Me$_4$N][SeCF$_3$] (2.0 mmol/L) in MeCN containing [*n*Bu$_4$N][PF$_6$] supporting electrolyte (0.1 mol/L).

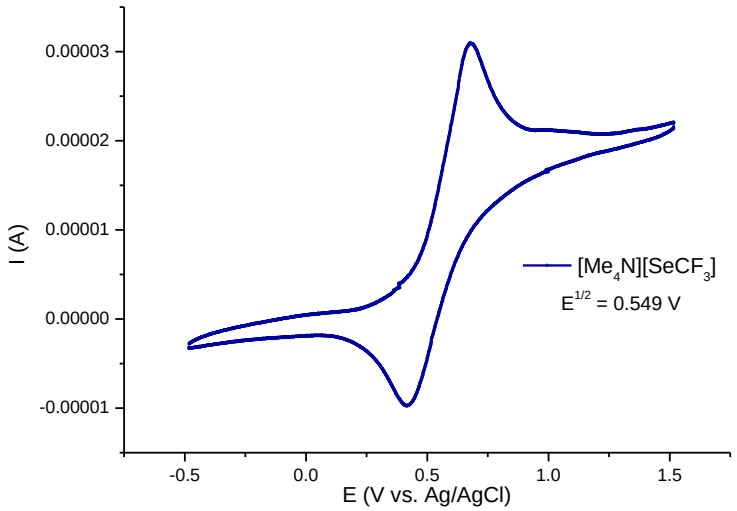


Figure 10. The cyclic voltammogram of $[Me_4N][SCF_3]$ (2.0 mmol/L) in MeCN containing $[nBu_4N][PF_6]$ supporting electrolyte (0.1 mol/L).

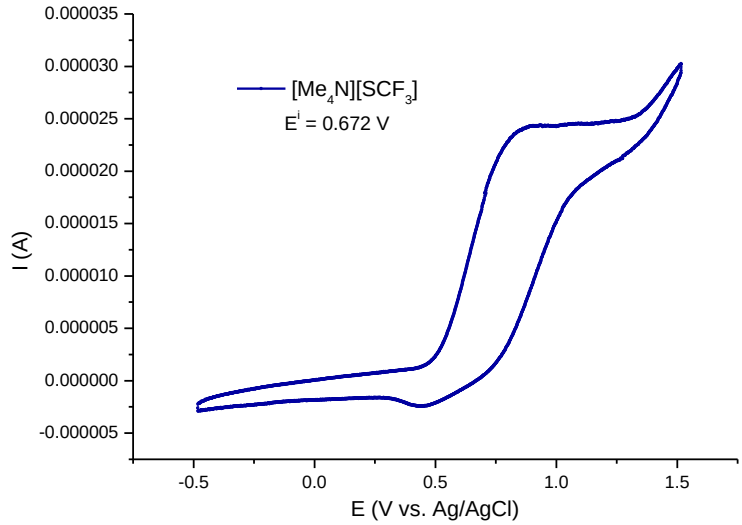


Figure 11. The cyclic voltammogram of ArTTOTf (**1a**, 2.0 mmol/L) in MeCN containing $[nBu_4N][PF_6]$ supporting electrolyte (0.1 mol/L).

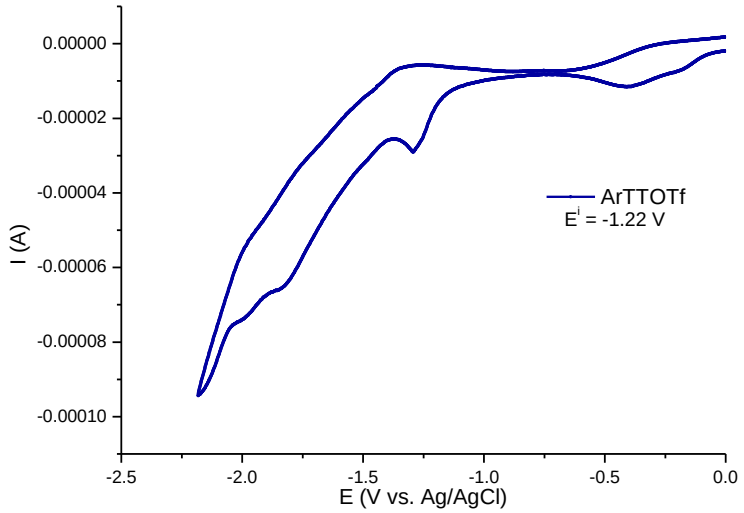


Figure 12. The cyclic voltammogram of ArDBTOTf (**1d**, 2.0 mmol/L) in MeCN containing [*n*Bu$_4$N][PF$_6$] supporting electrolyte (0.1 mol/L).

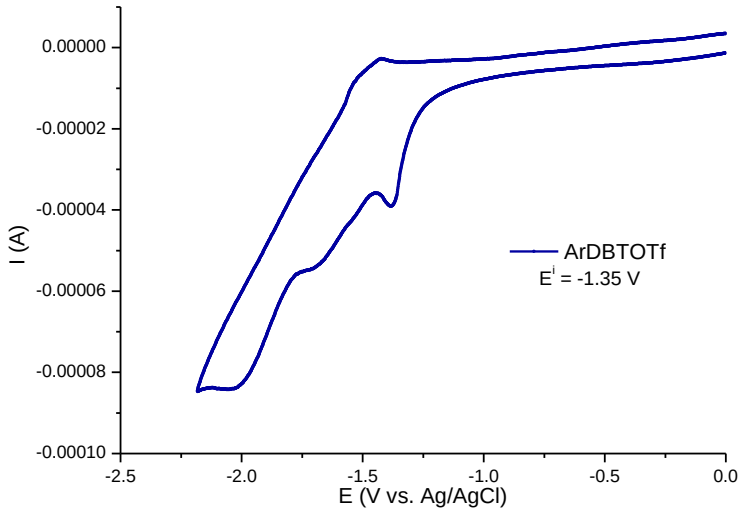
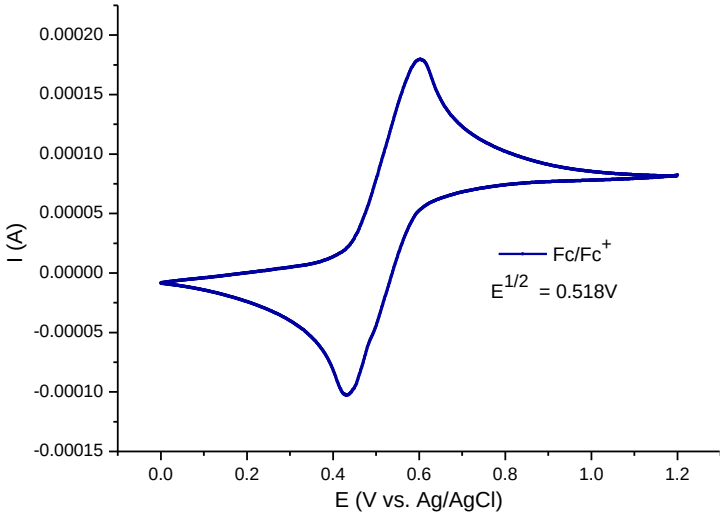


Figure 13. The cyclic voltammogram of ferrocene (2.0 mmol/L) in MeCN containing [*n*Bu$_4$N][PF$_6$] supporting electrolyte (0.1 mol/L).



6. The NMR spectra of the mixtures of arylsulfonium salt and [Me$_4$N][SeCF$_3$] in acetonitrile

Figure 14. The combined ^{19}F NMR spectra of [Me$_4$N][SeCF$_3$] and the mixtures of **1d** and [Me$_4$N][SeCF$_3$] in CD$_3$CN (0.6 mL) without light irradiation (using PhOCF$_3$ (24.5 mg, 0.15 mmol) as an internal standard).

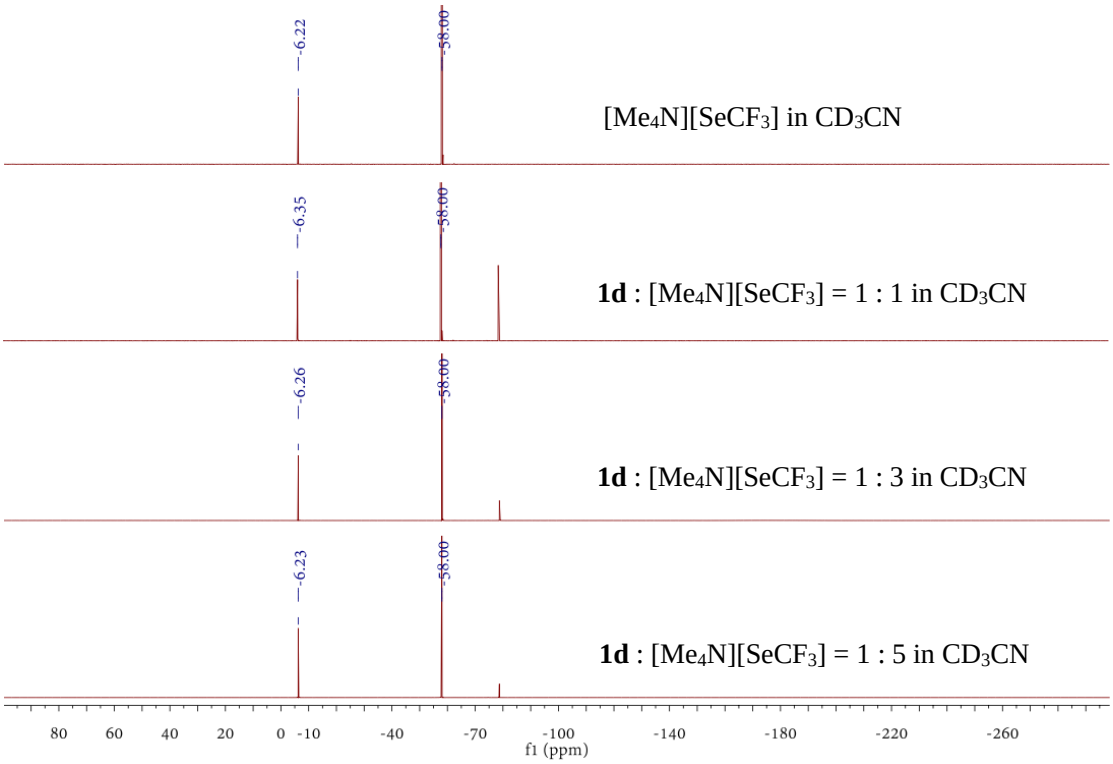


Figure 15. The ^{19}F NMR spectrum of the reaction mixture of **1d** (10.5 mg, 0.02 mmol) and [Me$_4$N][SeCF$_3$] (4.5 mg, 0.02 mmol) in CD$_3$CN (0.6 mL) at room temperature

under blue LED (5 W) irradiation for 5 minutes (using $PhOCF_3$ (24.5 mg, 0.15 mmol) as an internal standard). 13% of **3a** was determined according to the internal standard.

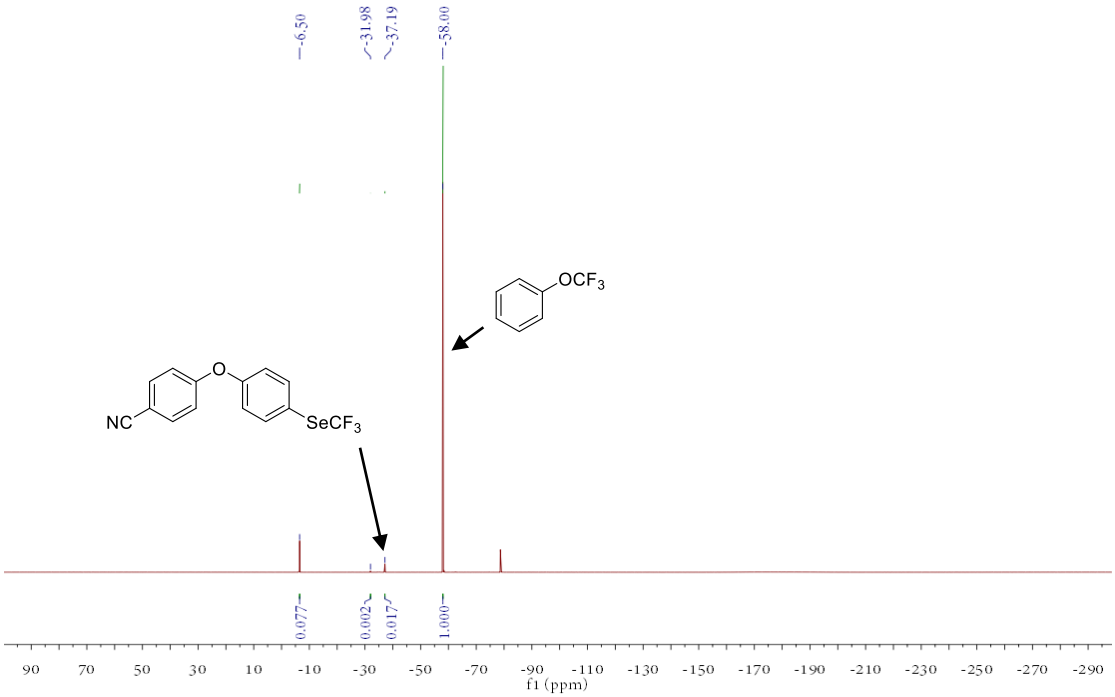


Figure 16. The ^{19}F NMR spectrum of the reaction mixture of **1d** (10.5 mg, 0.02 mmol) and $[Me_4N][SeCF_3]$ (4.5 mg, 0.02 mmol) in CD_3CN (0.6 mL) at room temperature under blue LED (5 W) irradiation for 20 minutes (using $PhOCF_3$ (24.5 mg, 0.15 mmol) as an internal standard). 25% of **3a** was determined according to the internal standard.

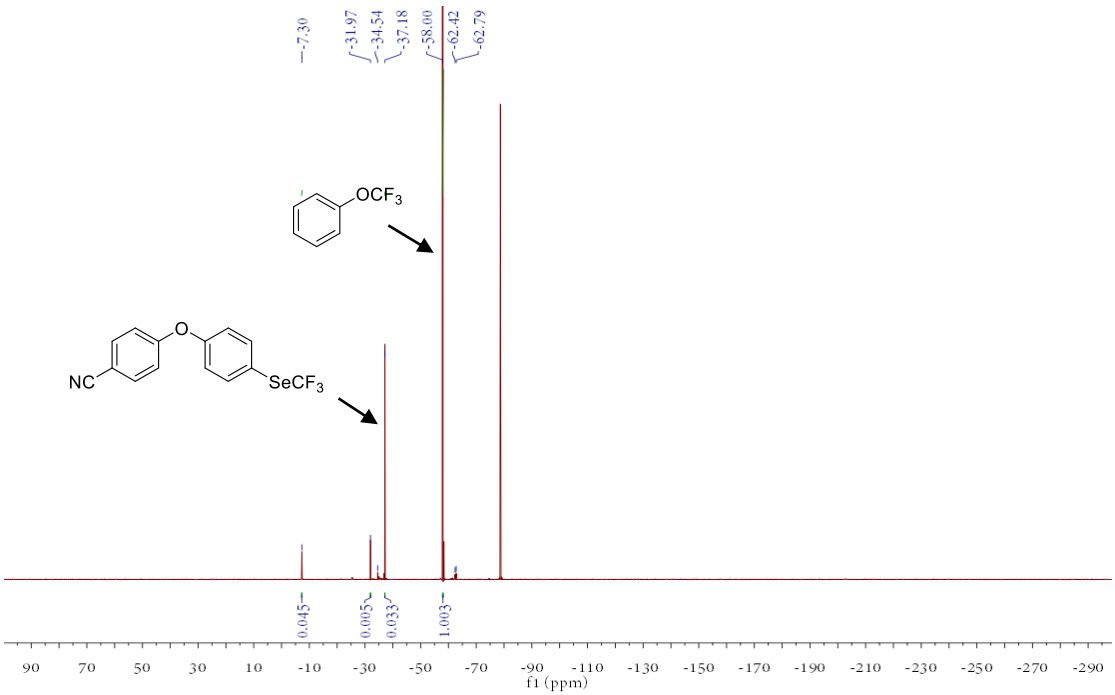


Figure 17. The ^{19}F NMR spectrum of the reaction mixture of **1d** (10.5 mg, 0.02 mmol) and $[Me_4N][SeCF_3]$ (4.5 mg, 0.02 mmol) in CD_3CN (0.6 mL) at room temperature under blue LED (5 W) irradiation for 1 hour (using $PhOCF_3$ (24.5 mg, 0.15 mmol) as an internal standard). 32% of **3a** was determined according to the internal standard.

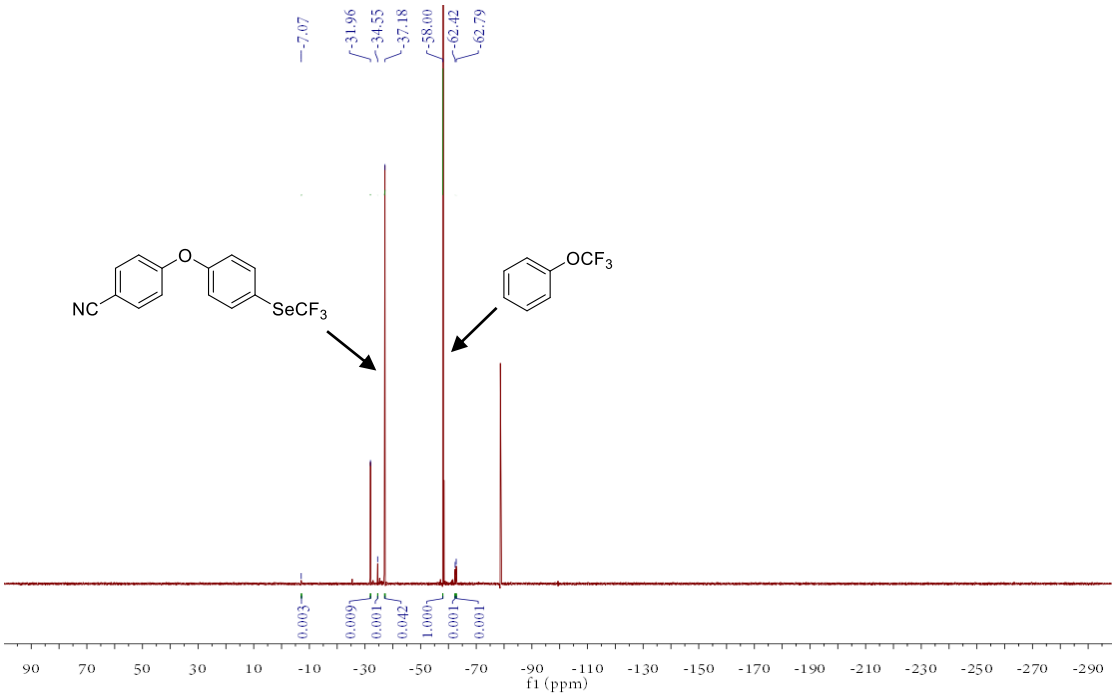


Figure 18. The combined ^{19}F NMR spectra of the above reaction mixtures (**Figures 15-17**).

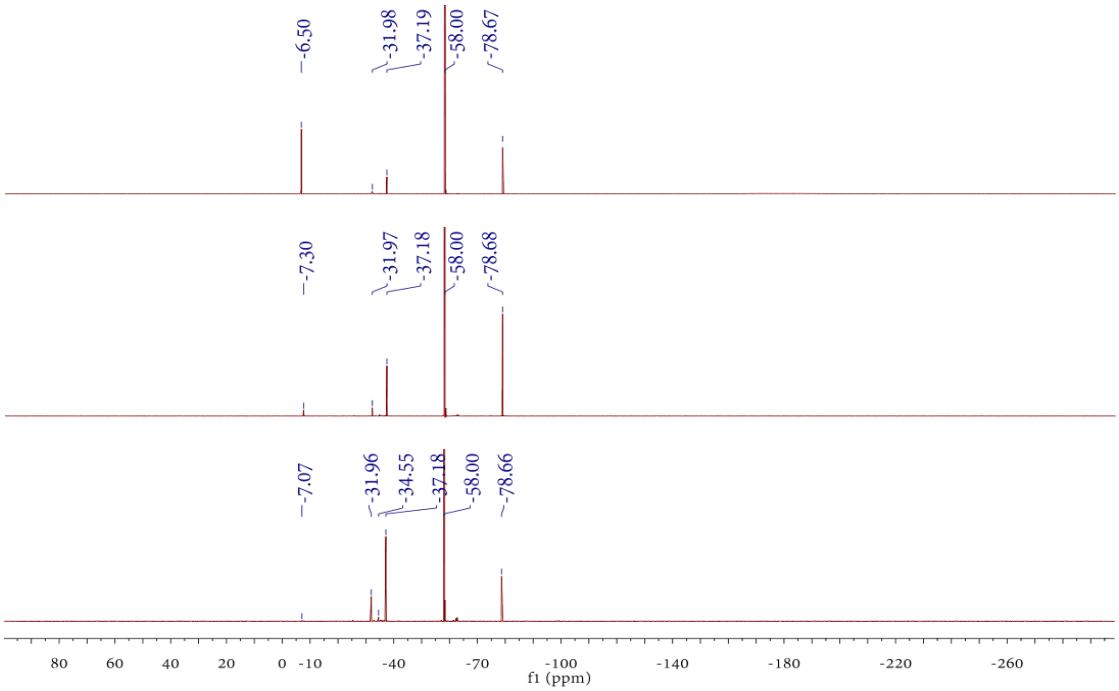


Figure 19. The ^{19}F NMR analysis of the below reaction mixture of **1d** and $[Me_4N][SeCF_3]$ using $PhOCF_3$ (14.5 mg, 0.0895 mmol) as an internal standard.

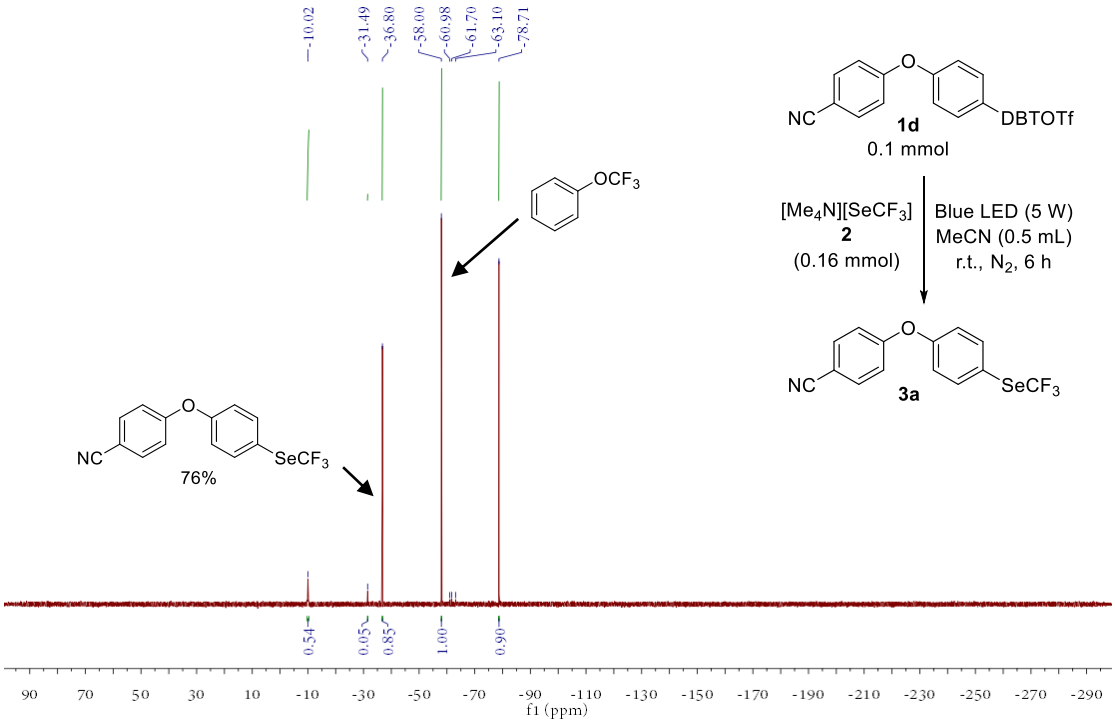


Figure 20. The ^{19}F NMR analysis of the below reaction mixture of **1d** and $[Me_4N][SeCF_3]$ using $PhOCF_3$ (20.5 mg, 0.127 mmol) as an internal standard.

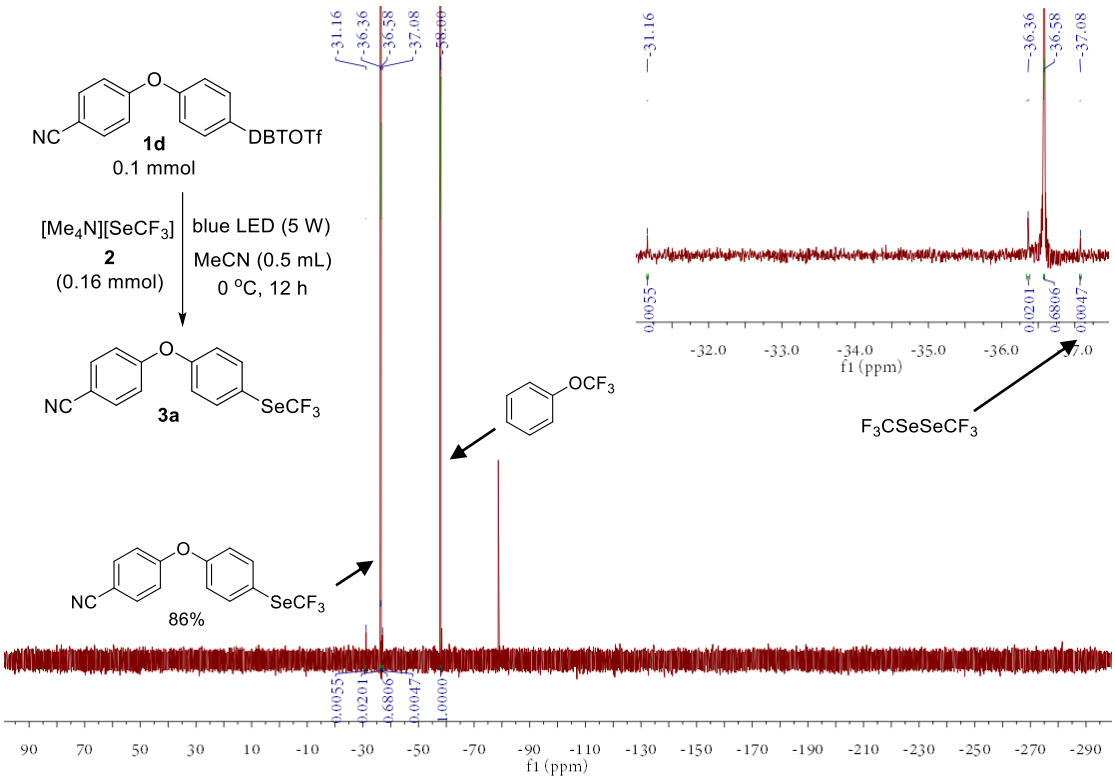


Figure 21. The ^{19}F NMR analysis of the below reaction mixture of **1g** and $[Me_4N][SeCF_3]$ using $PhOCF_3$ (12.2 mg, 0.075 mmol) as an internal standard.

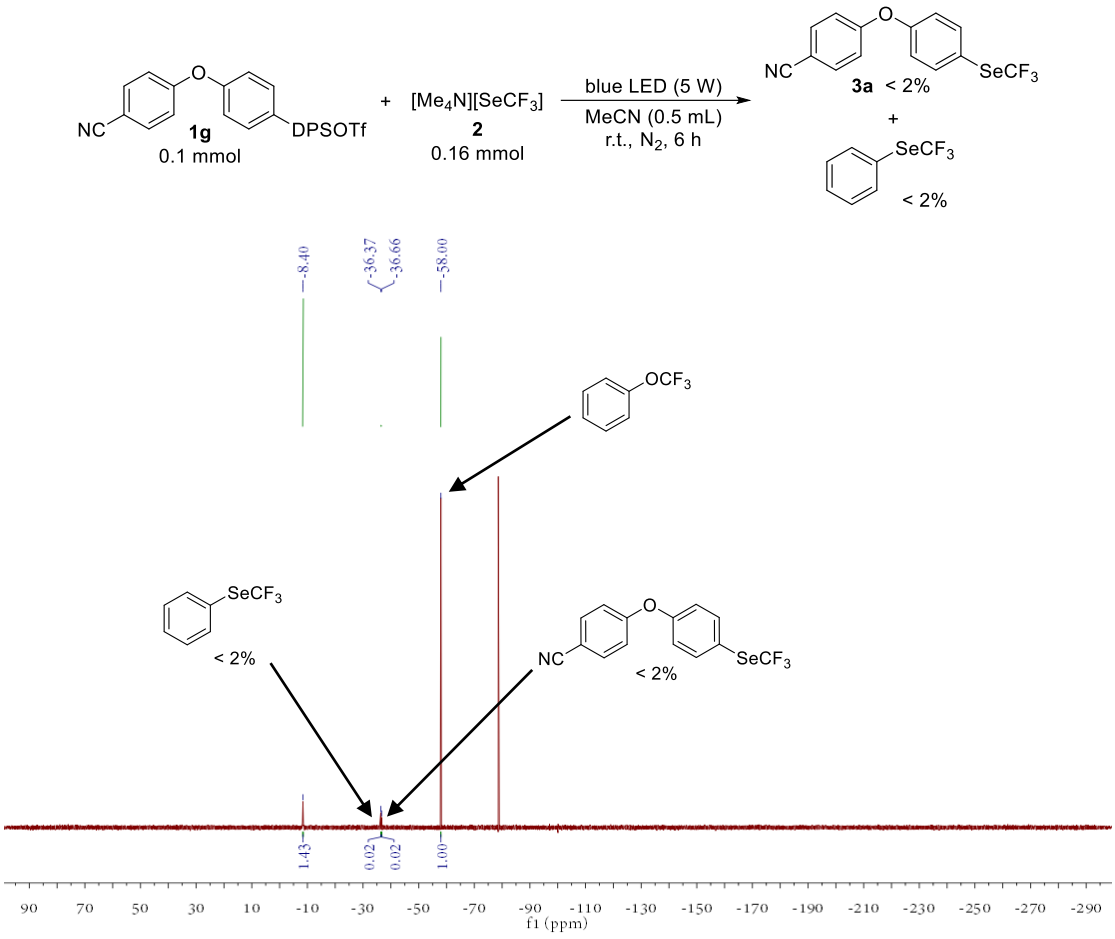


Figure 22. The ^{77}Se NMR spectrum of 4-(4-((trifluoromethyl)selanyl)phenoxy)-benzonitrile (**3a**, δ 555.4) in CD_3CN.

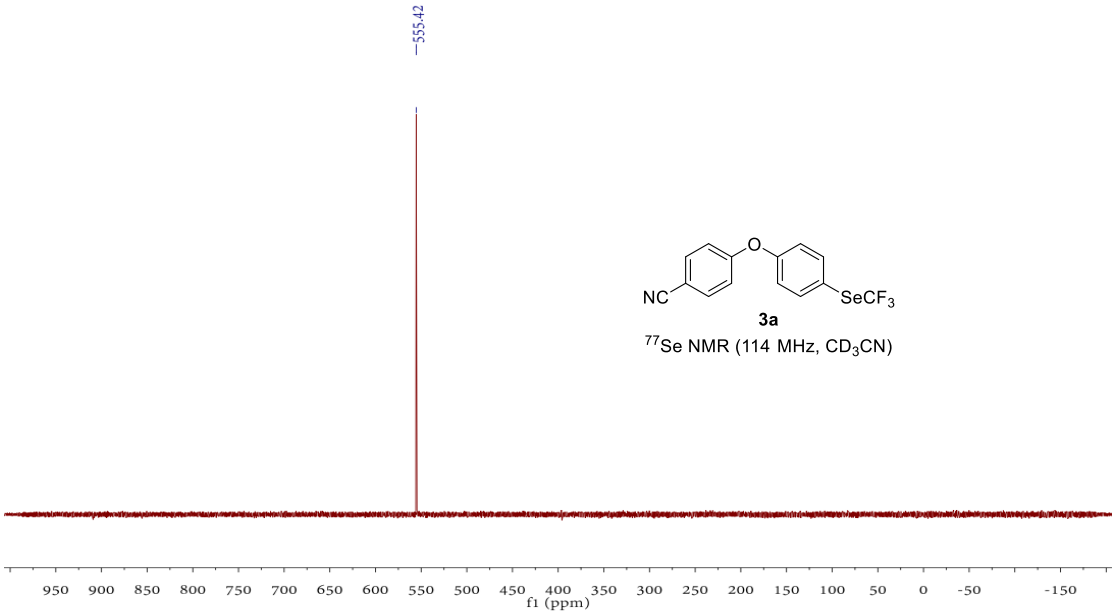


Figure 23. The ^{77}Se NMR spectrum of [Me_4N][$SeCF_3$] (δ 159.5 (q, J = 76.4 Hz)) in CD_3CN.

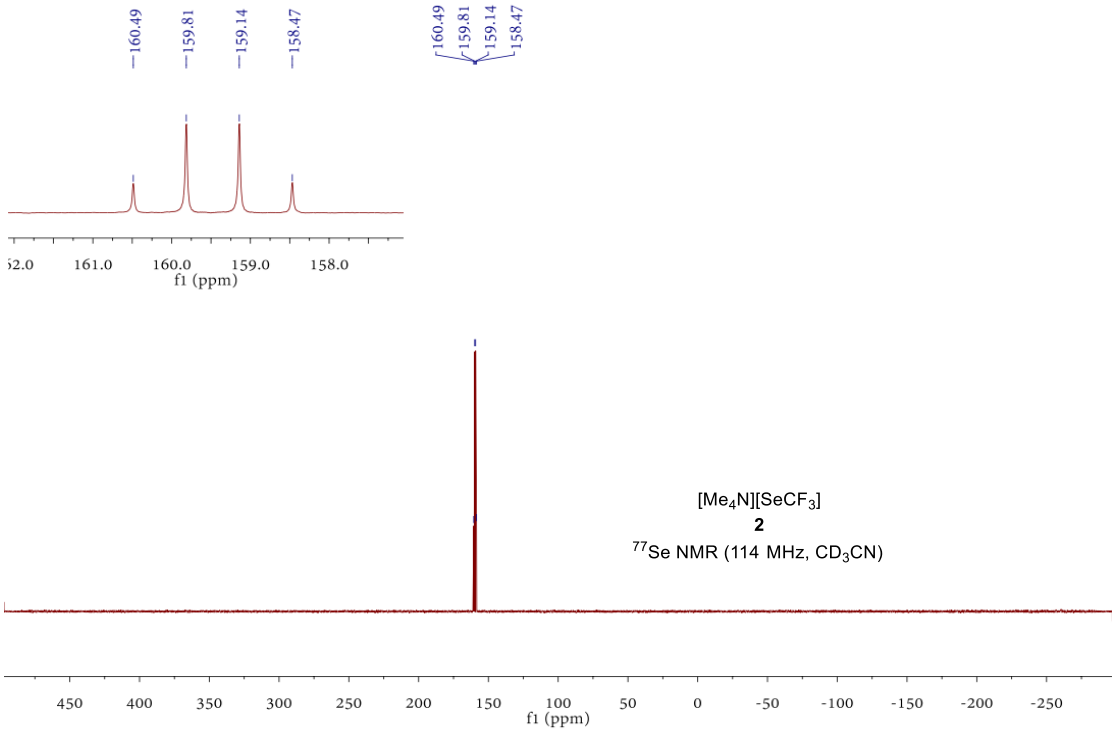


Figure 24. The ^{77}Se NMR spectrum of the mixture of [Me_4N][$SeCF_3$] (0.06 mmol) and ArDBTOTf (**1d**, 0.02 mmol) in CD_3CN (0.6 mL) without irradiation.

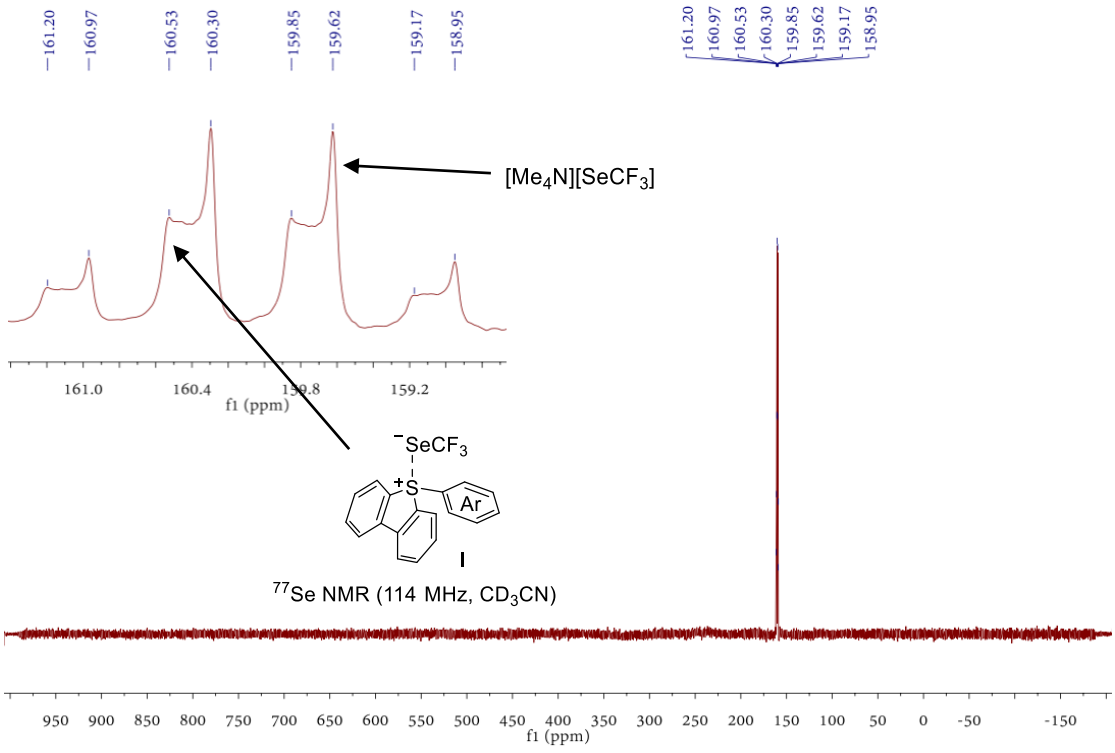
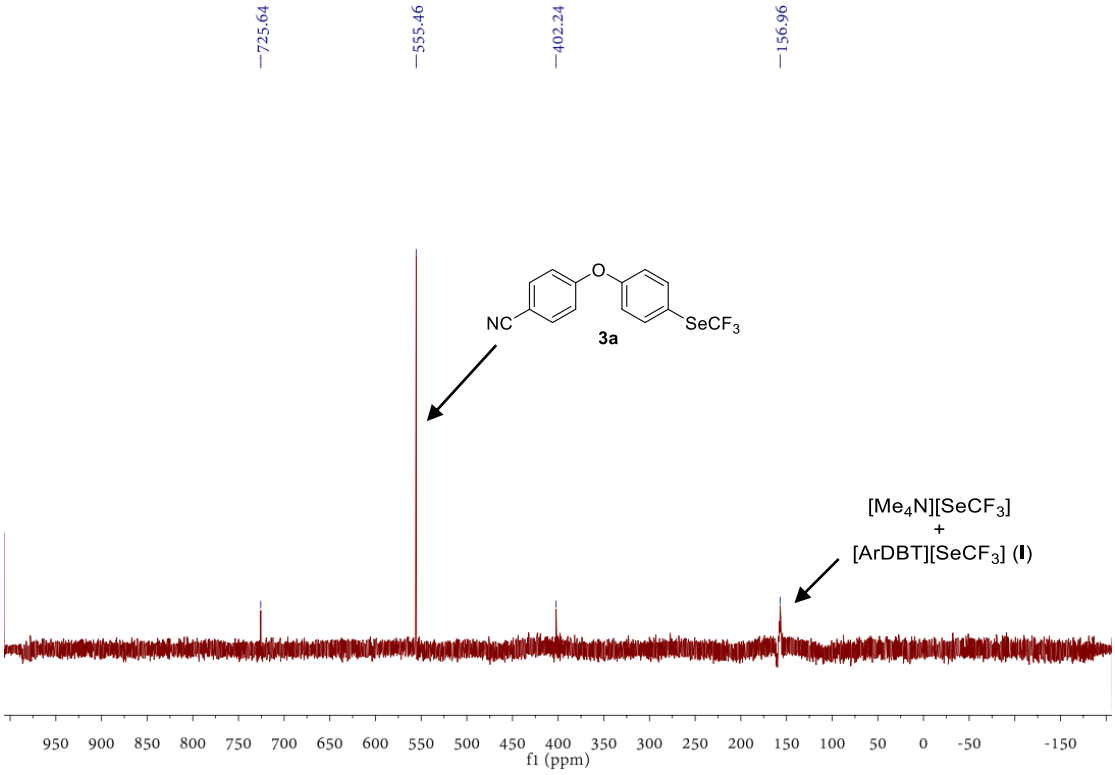


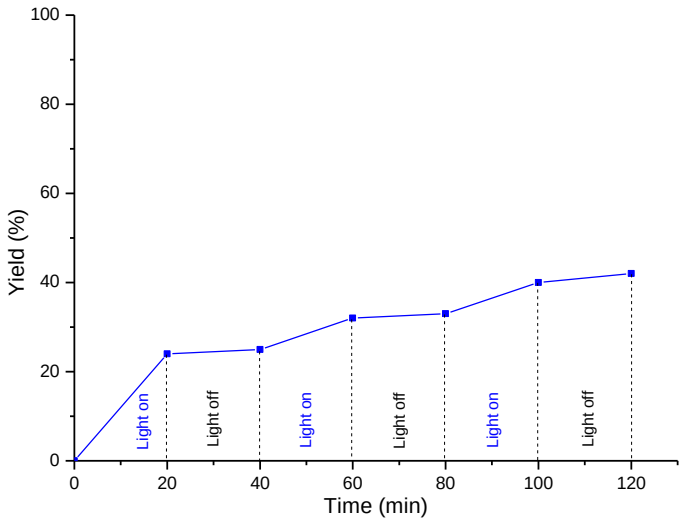
Figure 25. The ^{77}Se NMR spectrum of the reaction mixture of [Me_4N][$SeCF_3$] (0.06 mmol) and ArDBTOTf (**1d**, 0.02 mmol) in CD_3CN (0.6 mL) under blue LED (5 W) irradiation for 20 minutes.



7. The light on-off experiment

The light on-off experiments were carried out under the standard reaction conditions using a mixture of **1d** (0.20 mmol), [Me_4N][$SeCF_3$] (0.32 mmol) and MeCN (5.0 mL). Light was switched on and off with the intervals of 20 minutes, and the reaction mixture was monitored by HPLC after each period.

Time (min)	20	40	60	80	100	120
On\Off	On	Off	On	Off	On	Off
Yield	24	25	32	33	40	42



8. Measurement of the quantum yield

The photo flux of the blue LED (5 W, λ_{max} = 450 nm) was determined by the standard ferrioxalate actinometry according to the literature.[8-10]

Procedure: A 0.15 M ferrioxalate solution was prepared by dissolving 2.21 g of potassium ferrioxalate trihydrate in 30 mL of aqueous H_2SO_4 solution (0.05 M). A buffered phenanthroline solution was prepared by dissolving 5.0 mg of 1,10-phenanthroline and 1.13 g of NaOAc•3H_2O in 5.0 mL of aqueous H_2SO_4 solution (0.5 M). Both solutions were stored in the dark environment. The ferrioxalate solution (2.0 mL) was placed in a standard cuvette tube (l = 1.00 cm) and its absorbances at 450 and 510 nm were measured. Subsequently, the quartz cuvette was irradiated by the blue LED (5 W) for 90 seconds (the distance between the quartz cuvette and blue LED is 2-3 cm). After irradiation, the phenanthroline solution (0.35 mL) was added to the quartz cuvette immediately, and the mixture was stand in the dark for 30 minutes to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. The above procedure was repeated twice to obtain the corresponding absorbances. The data were summarized in the following tables.

A	1st	2nd	3rd
$A_{510\ nm}$-non-irradiation	0.094	0.074	0.066
$A_{510\ nm}$-irradiation	1.586	1.586	1.600
$\Delta A_{510\ nm}$	1.492	1.512	1.534

Average $\Delta A_{510\ nm}$	1.513

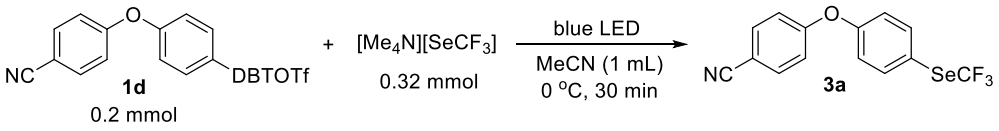
$$\text{mol of } Fe^{2+} = \frac{V \cdot \Delta A_{510\ nm}}{l \cdot \varepsilon} = \frac{(0.00235\ L) \cdot (1.513)}{(1.00\ cm) \cdot (11100\ L \cdot mol^{-1}cm^{-1})} = 3.20 \times 10^{-7} mol$$

A	1st	2nd	3rd
$A_{450\ nm}$-non-irradiation	1.725	1.699	1.699
Average $A_{450\ nm}$-non-irradiation		1.708	
$f = 1 - 10^{-A}$		0.980	

$$\text{Photon flux} = \frac{\text{mol of } Fe^{2+}}{\phi \cdot t \cdot f} = \frac{3.20 \times 10^{-7} mol}{(1.0) \cdot (90s) \cdot (0.980)} = 3.63 \times 10^{-9} einstein/s$$

Note: V is the total volume of the solution after addition of phenanthroline (0.00235 L). $\Delta A_{510\ nm}$ is the difference absorbance at 510 nm between the irradiated and non-irradiated solution. l is the path length (1.00 cm). ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11100 L•mol^{-1}•cm^{-1}).[8] Φ is the quantum yield for the ferrioxalate actinometer (1.0 for a 0.15 M solution at λ = 450 nm).[8-9] t is the irradiation time. f is the fraction of light absorbed at λ = 450 nm, where $f = 1 - 10^{-A}$.

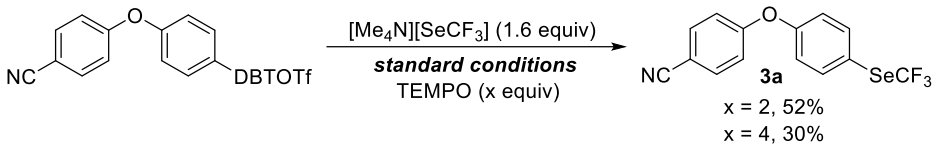
Determination of the quantum yield:



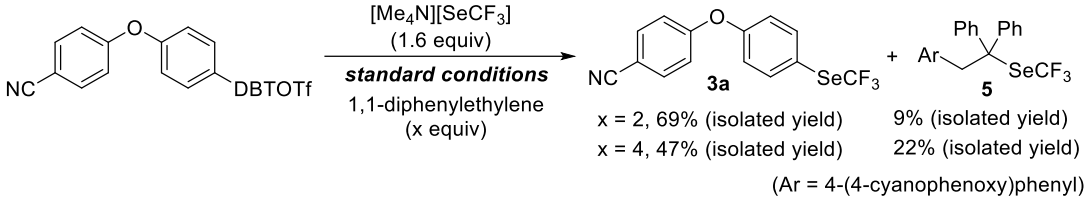
In a nitrogen-filled glove box, **1d** (105.4 mg, 0.20 mmol), [Me$_4$N][SeCF$_3$] (71.4 mg, 0.32 mmol), MeCN (1.0 mL), and a teflon magnetic stir bar were added to a standard quartz cuvette (l = 1.00 cm). The quartz cuvette was sealed and taken out of the glove box, and its absorbance at 450 nm was measured ($A_{450\ nm}$ = 1.096, $f = 1 - 10^{-A}$ = 0.920). Then, the mixture was placed into a cooling tank to keep the reaction temperature at around 0 °C. After 30 minutes of the irradiation with a 5 W blue LED, the mixture was filtrated through a celite pad and washed with MeCN (2 × 0.5 mL). The yield of **3a** (7.8%, 0.16 × 10^{-4} mol) was determined by HPLC using pure 4-(4-((trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**) as an external standard.

$$\phi = \frac{\text{mol of product}}{\text{photon flux} \cdot t \cdot f} = \frac{0.16 \times 10^{-4}}{3.63 \times 10^{-9} einstein \cdot s^{-1} \cdot 1800s \cdot 0.92} = 2.66$$

9. The control experiments for mechanistic insights.

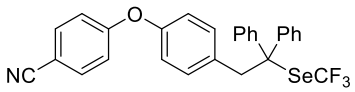


In a nitrogen-filled glove box, a sealed reaction vial was charge with 5-(4-(4-cyanophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1d**, 105.4 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, 62.5 mg (0.40 mmol) or 125 mg (0.80 mmol)), MeCN (1.0 mL), and a teflon magnetic stir bar. The reaction vial was taken out from the glove box and placed into a cooling tank to keep the reaction temperature at around 0 ^oC. After irradiation with a 5 W blue LED for 12 h, the reaction mixture was analyzed by HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) using pure 4-(4-((trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**, t_R = 7.8 min) as an external standard. The yield of the product (**3a**) was determined to be 52% and 30%, respectively.

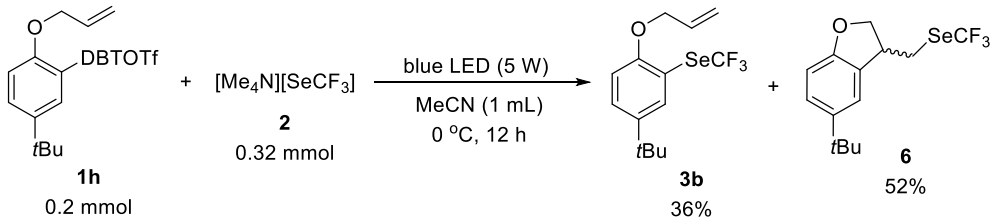


In a nitrogen-filled glove box, a sealed reaction vial was charge with 5-(4-(4-cyanophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1d**, 105.4 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), 1,1-diphenylethylene (72 mg (0.40 mmol) or 144 mg (0.80 mmol)), MeCN (1.0 mL), and a teflon magnetic stir bar. The reaction vial was taken out from the glove box and placed into a cooling tank to keep the reaction temperature at around 0 ^oC. After irradiation with a 5 W blue LED for 12 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate (40/0 to 50/1 (v/v)) as eluents to give **3a** (47.8 mg, 69% yield from the reaction with 0.4 mmol of 1,1-diphenylethylene; 32.1 mg, 47% yield from the reaction with 0.8 mmol of 1,1-diphenylethylene) and **5** (9.8 mg, 9% yield from the reaction with 0.4 mmol of 1,1-diphenylethylene; 23.0 mg, 22% yield from the reaction with 0.8 mmol of 1,1-diphenylethylene).

4-(4-(2,2-Diphenyl-2-((trifluoromethyl)selanyl)ethyl)phenoxy)benzonitrile (**5**)

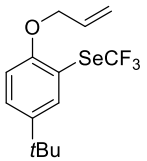


White solid. M.p.: 163-165 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.32-7.29 (m, 10H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -32.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 153.7, 143.7, 134.1, 133.1, 133.0, 129.1, 128.0, 127.6, 122.6 (q, *J* = 333.9 Hz), 119.2, 118.8, 117.9, 105.8, 66.0, 47.1. IR (KBr): 3097, 3060, 3029, 2223, 1593, 1491, 1444, 1415, 1245, 1206, 1163, 1095, 1073, 1002, 958, 873, 838, 758, 736, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{28}H_{20}F_3NNaOSe]^+$ ([M + Na]$^+$): 546.0554; found: 546.0554.



In a nitrogen-filled glove box, a sealed reaction vial was charge with 5-(2-(allyloxy)-5-(*tert*-butyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium (**1h**, 104.4 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), MeCN (1.0 mL), and a teflon magnetic stir bar. The reaction vial was taken out from the glove box and placed into a cooling tank to keep the reaction temperature at around 0 °C. After irradiation with a 5 W blue LED for 12 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate (40/0 to 50/1 (v/v)) as eluents to give 24.6 mg of **3b** (36% yield) and 34.9 mg of **6** (52% yield).

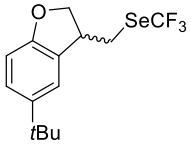
(2-(Allyloxy)-5-(*tert*-butyl)phenyl)(trifluoromethyl)selane (**3b**)



Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.3 Hz, 1H), 7.39 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.04 (m, 1H), 5.46 (dm, *J* = 17.3 Hz, 1H),

5.29 (dm, *J* = 10.6 Hz, 1H), 4.60 (dt, *J* = 5.0, 1.6 Hz, 2H), 1.31 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 144.7, 134.7, 132.8, 128.5, 122.7 (q, *J* = 335.2 Hz), 117.5, 112.5, 112.3, 69.6, 34.2, 31.4. IR (KBr): 3085, 2965, 2870, 1650, 1598, 1498, 1462, 1364, 1290, 1264, 1129, 1099, 1050, 997, 928, 814, 738 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{14}H_{17}F_3O^{74}Se$ ([M]): 332.0456; found: 332.0451.

5-(*Tert*-butyl)-3-(((trifluoromethyl)selanyl)methyl)-2,3-dihydrobenzofuran (**6**)

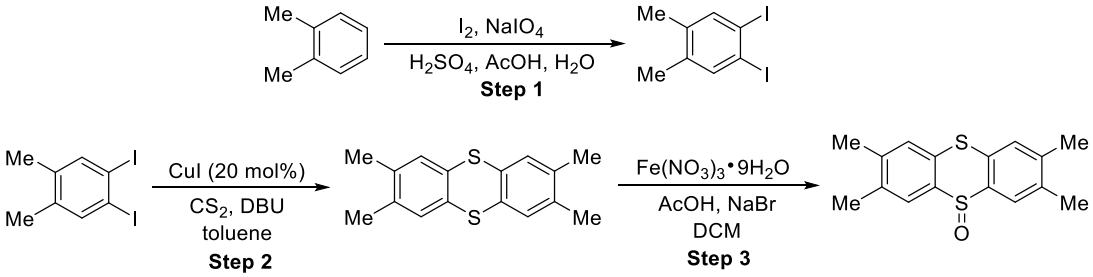


Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.9 Hz, 1H), 7.22 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.68 (t, *J* = 8.9 Hz, 1H), 4.38 (dd, *J* = 9.3, 5.1 Hz, 1H), 3.79 (m, 1H), 3.37 (dd, *J* = 12.6, 5.4 Hz, 1H), 3.14 (dd, *J* = 12.6, 9.0 Hz, 1H), 1.31 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -33.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 144.0, 128.3, 126.2, 122.5 (q, *J* = 331.4 Hz), 121.3, 109.3, 76.6, 42.4, 34.4, 31.7, 29.9. IR (KBr): 3058, 2964, 2872, 2216, 1614, 1494, 1365, 1293, 1236, 1204, 1099, 970, 887, 822, 739, 692 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{14}H_{17}F_3O^{74}Se$ ([M]): 332.0456; found: 332.0451.

10. Procedures for the synthesis of arylsulfonium salts

10.1. Procedures for the synthesis of aryl sulfoxides

2,3,7,8-Tetramethylthianthrene 5-oxide (TMTO)



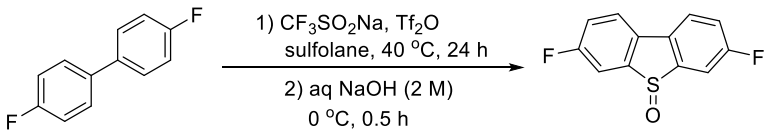
Step 1: Under an ambient atmosphere, concentrated H_2SO_4 (1.5 mL) was added slowly to a mixture of *o*-xylene (5.3 g, 50 mmol), $NaIO_4$ (4.3 g, 20 mmol), H_2O (10 mL), AcOH (50 mL), and I_2 (11.4 g, 45 mmol) at 0 °C with vigorous stirring. The mixture was reacted at 70 °C overnight, cooled to room temperature, diluted with DCM (150 mL), washed with an aqueous solution of sodium bisulfite (2 × 200 mL),

and neutralized by an aqueous solution of Na_2CO_3. The organic phase was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure to give a yellow crude product, which was recrystallized from methanol to afford 1,2-diiodo-4,5-dimethylbenzene (10.5 g, 58%) as a white solid.

Step 2: Under a N_2 atmosphere, CS_2 (2.4 mL, 40 mmol) and DBU (11.95 mL, 80 mmol) were added to a mixture of 1,2-diiodo-4,5-dimethylbenzene (7.16 g, 20 mmol), CuI (760 mg, 4 mmol), and toluene (60 mL) with vigorous stirring. The mixture was heated at 100 ^oC for 24 h, cooled to room temperature, diluted with ethyl acetate (100 mL), and washed with H_2O (200 mL × 2). The aqueous phase was extracted with ethyl acetate (30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether as an eluent to give 2,3,7,8-tetramethylthianthrene (680 mg, 25%) as white solid.

Step 3: Under an ambient atmosphere, $Fe(NO_3)_3$•$9H_2O$ (1.0 g, 2.5 mmol) was added to a mixture of DCM (30 mL), AcOH (0.11 mL, 1.84 mmol), NaBr (12.8 mg, 0.125 mmol), and 2,3,7,8-tetramethylthianthrene (680 mg, 2.5 mmol) with stirring. The mixture was reacted at room temperature for 4 h, washed with an aqueous Na_2CO_3 solution, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10/1 to 7/1 (v/v)) as eluents to give 2,3,7,8-tetramethylthianthrene 5-oxide (TMTO, 354 mg, 49%) as a white solid. M.p.: 181-183 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.37 (s, 2H), 2.32 (s, 6H), 2.28 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 138.7, 137.5, 130.0, 125.7, 125.3, 19.6, 19.5. IR (KBr): 2918, 2850, 2116, 1588, 1455, 1382, 1357, 1229, 1128, 1066, 882, 868, 813, 754, 719 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}OS_2]^+$ ([M + H]$^+$): 289.0715; found: 289.0722.

3,7-Difluorodibenzo[*b*,*d*]thiophene 5-oxide (2F-DBTO)

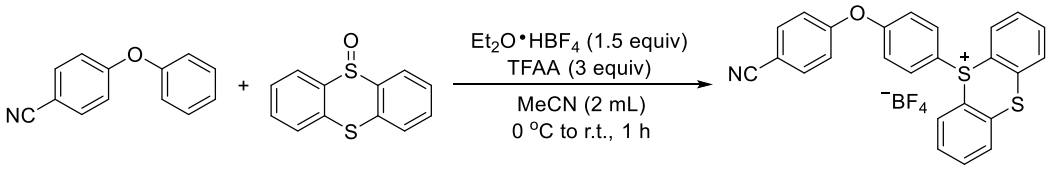


Under a N_2 atmosphere, Tf_2O (6.05 mL, 36 mmol) was added to a mixture of CF_3SO_2Na (4.68 g, 30 mmol), 4,4'-difluoro-1,1'-biphenyl (1.9 g, 10 mmol), and sulfolane (10 mL) with vigorous stirring. The mixture was reacted at 40 ^oC for 24 h

and was then slowly poured into an aqueous NaOH solution (2 M, 500 mL) at 0 °C for 0.5 h. The resulting solid was filtrated, washed with H_2O (2 × 200 mL), and extracted with ethyl acetate (4 × 50 mL). The aqueous phases were extracted with ethyl acetate (100 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate/dichloromethane (10/1/1 (v/v/v)) as eluents to give 3,7-difluorodibenzo-[*b*,*d*]thiophene 5-oxide (2F-DBTO, 1.08 g, 46%) as a white solid. M.p.: 194-196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.6, 4.4 Hz, 2H), 7.69 (dd, *J* = 7.0, 2.4 Hz, 2H), 7.31 (td, *J* = 8.6, 2.4 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.1 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0 (d, *J* = 253.3 Hz), 147.0 (d, *J* = 8.7 Hz), 132.4 (d, *J* = 2.0 Hz), 123.1 (d, *J* = 8.7 Hz), 120.2 (d, *J* = 22.4 Hz), 115.3 (d, *J* = 25.0 Hz). IR (KBr): 3050, 3030, 1592, 1465, 1419, 1255, 1208, 1053, 1020, 857, 824, 703, 678 cm^{-1}. HRMS-ESI (m/z) calcd. For $[C_{12}H_7F_2OS]^+$ ($[M + H]^+$): 237.0180; found: 237.0192.

10.2. Procedures for the synthesis of arylsulfonium salts

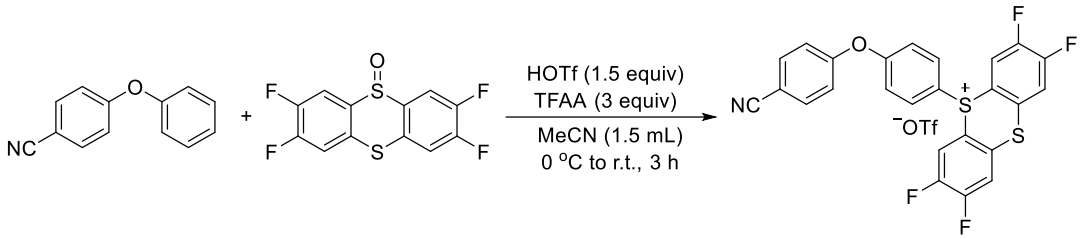
5-(4-(4-Cyanophenoxy)phenyl)-5*H*-thianthren-5-ium tetrafluoroborate (**1a**-BF_4)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and $Et_2O{\cdot}HBF_4$ (0.2 mL, 1.5 mmol) were successively added to a mixture of 4-phenoxybenzonitrile (195 mg, 1.0 mmol) and thianthrene 5-oxide (232 mg, 1.0 mmol) in MeCN (2 mL) at 0 °C with stirring. The mixture was reacted at room temperature for 1 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM (5 mL) / Et_2O (40 mL) system to afford 5-(4-(4-cyanophenoxy)phenyl)-5*H*-thianthren-5-ium tetrafluoroborate as a white solid (347 mg, 70%). M.p.: 154-156 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.10 (d, *J* = 8.0, 2H), 8.58 (d, *J* = 8.0 Hz, 2H), 8.46 (m, 2H), 8.38 (t, *J* = 7.7 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.4

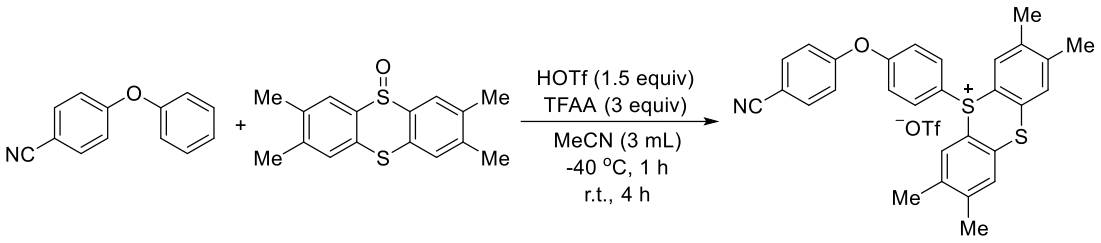
Hz, 2H). ^{19}F NMR (471 MHz, acetone-d_6) δ -151.5 (m, 4F). ^{13}C NMR (126 MHz, acetone-d_6) δ 159.9, 159.0, 136.4, 135.2, 135.2, 134.7, 131.0, 130.7, 130.1, 120.8, 120.1, 119.3, 118.7, 118.0, 108.1. IR (KBr): 3083, 2993, 2925, 2226, 1606, 1579, 1485, 1449, 1292, 1248, 1172, 1055, 873, 835, 759, 701 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{16}NOS_2]^+$ ([M]$^+$): 410.0668; found: 410.0671.

5-(4-(4-Cyanophenoxy)phenyl)-2,3,7,8-tetrafluoro-5*H*-thianthren-5-ium trifluoromethanesulfonate (**1b**)



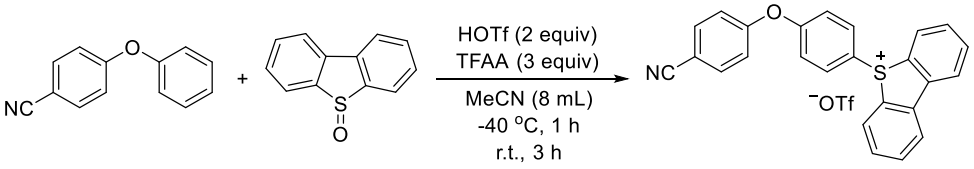
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.46 mL, 3.3 mmol) and HOTf (0.14 mL, 1.65 mmol) was successively added to a mixture of 4-phenoxybenzonitrile (215 mg, 1.1 mmol) and 2,3,7,8-tetrafluorothianthrene 5-oxide (340 mg, 1.1 mmol) in MeCN (1.5 mL) at 0 °C with stirring. The mixture was reacted at room temperature for 3 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solution (3 × 25 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to give 5-(4-(4-cyanophenoxy)phenyl)-2,3,7,8-tetrafluoro-5*H*-thianthren-5-ium trifluoromethanesulfonate as a white solid (237 mg, 34%). M.p.:140-142 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.86 (m, 2H), 8.27 (dd, *J* = 10.0, 7.2 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR (471 MHz, acetone-d_6) δ -78.9 (s, 3F), -126.1 (m, 2F), -134.3 (m, 2F). ^{13}C NMR (126 MHz, acetone-d_6) δ 160.0, 159.0, 153.7 (dd, *J* = 261.2, 13.7 Hz), 150.5 (dd, *J* = 255.6, 13.4 Hz), 134.7, 134.3 (dd, *J* = 8.7 Hz, 3.8 Hz), 131.3, 125.0 (dd, *J* = 22.3 Hz, 1.6 Hz), 120.7, 120.1, 120.1 (d, *J* = 21.9 Hz), 117.9, 117.5, 115.5 (dd, *J* = 7.2, 3.4 Hz), 108.2. IR (KBr): 3095, 3039, 2228, 1698, 1578, 1482, 1408, 1383, 1286, 1250, 1172, 1029, 967, 873, 836, 798 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{12}F_4NOS_2]^+$ ([M]$^+$): 482.0291; found: 482.0298.

5-(4-(4-Cyanophenoxy)phenyl)-2,3,7,8-tetramethyl-5*H*-thianthren-5-ium trifluoromethanesulfonate (**1c**)



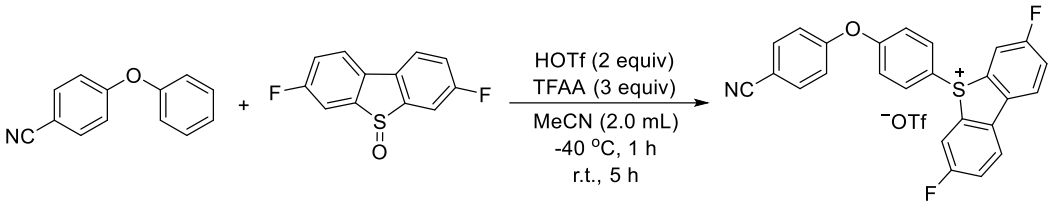
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.13 mL, 1.5 mmol) were successively added to a mixture of 4-phenoxybenzonitrile (195 mg, 1.0 mmol) and 2,3,7,8-tetramethylthianthrene 5-oxide (288 mg, 1.0 mmol) in MeCN (3 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 4 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic layers were washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) to afford 5-(4-(4-cyanophenoxy)phenyl)-2,3,7,8-tetramethyl-5*H*-thianthren-5-ium trifluoromethanesulfonate as a white solid (533 mg, 87%). M.p.: 121-123 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.39 (s, 2H), 7.85 (s, 2H), 7.82 (dm, *J* = 9.1 Hz, 2H), 7.46 (dm, *J* = 9.2 Hz, 2H), 7.24 (d, *J* = 9.1 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H), 2.47 (m, 12H). ^{19}F NMR (471 MHz, acetone-d_6) δ -78.7 (s, 3F). ^{13}C NMR (126 MHz, acetone-d_6) δ 159.6, 159.2, 145.8, 139.7, 135.0, 134.7, 133.6, 131.0, 130.7, 121.5 (q, *J* = 322.6 Hz), 120.8, 120.2, 120.0, 118.0, 115.8, 108.0, 19.2, 18.5. IR (KBr) 3092, 3064, 2878, 2227, 1606, 1580, 1486, 1406, 1387, 1248, 1152, 1030, 947, 873, 836, 754, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{29}H_{24}NOS_2]^+$ ($[M]^+$): 466.1294; found: 466.1297.

5-(4-(4-Cyanophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1d**)[11]



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.84 mL, 6.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.35 mL, 4.0 mmol) were successively added to a solution of 4-phenoxybenzonitrile (390 mg, 2.0 mmol) in MeCN (8 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (600 mg, 3.0 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 3 h, diluted with DCM (40 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was washed with aqueous NaOTf solution (3 × 40 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to afford 5-(4-(4-cyanophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (870 mg, 83%). M.p.: 263-265 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.55 (d, *J* = 7.9 Hz, 2H), 8.40 (d, *J* = 8.1 Hz, 2H), 8.05 (t, *J* = 7.7 Hz, 2H), 7.87-7.83 (m, 6H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (471 MHz, acetone-d_6) δ -78.8 (s, 3F). ^{13}C NMR (126 MHz, acetone-d_6) δ 161.5, 158.6, 139.5, 134.8, 134.5, 133.5, 132.9, 131.7, 128.3, 124.6, 121.5 (q, *J* = 322.6 Hz), 121.1, 121.0, 120.6, 117.9, 108.5.

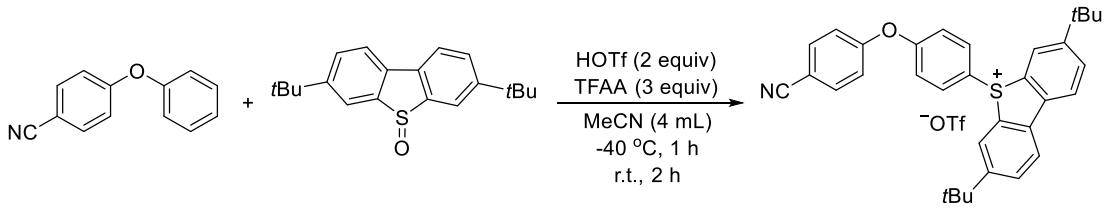
5-(4-(4-Cyanophenoxy)phenyl)-3,7-difluoro-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1e**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.21 mL, 1.5 mmol) and trifluoromethanesulfonic acid (TfOH, 0.09 mL, 1.0 mmol) were successively added to a solution of 4-phenoxybenzonitrile (98 mg, 0.5 mmol) in MeCN (2 mL) at -40 °C with stirring. Then, 3,7-difluorodibenzo[*b*,*d*]thiophene 5-oxide (177 mg, 0.75 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 5 h, diluted with DCM (10 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was washed with aqueous NaOTf solution (3 × 10 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column

chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 to 20/1 (v/v)) as eluents to afford 5-(4-(4-cyanophenoxy)phenyl)-3,7-difluoro-5*H*-dibenzo [*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (242 mg, 86%). M.p.: 235-237 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.58 (dd, *J* = 8.8, 4.6 Hz, 2H), 8.30 (dd, *J* = 7.6, 2.4 Hz, 2H), 7.90 (dm, *J* = 9.1 Hz, 2H), 7.89-7.83 (m, 4H), 7.34-7.31 (m, 4H). ^{19}F NMR (471 MHz, acetone-d_6) δ -78.8 (s, 3F), -108.6 (m, 2F). ^{13}C NMR (126 MHz, acetone-d_6) δ 163.2 (d, *J* = 253.3 Hz), 161.8, 158.6, 135.3 (d, *J* = 1.7 Hz), 134.9 (d, *J* = 12.2 Hz), 134.8, 133.9, 126.2 (d, *J* = 9.4 Hz), 122.2 (d, *J* = 22.9 Hz), 121.5 (q, *J* = 322.2 Hz), 121.1, 120.7, 119.9, 117.9, 115.9 (d, *J* = 28.3 Hz), 108.6. IR (KBr): 3086, 3044, 2230, 1597, 1577, 1487, 1417, 1397, 1266, 1250, 1214, 1156, 1031, 875, 832, 756, 740, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{14}F_2NOS]^+$ ($[M]^+$): 414.0759; found: 414.0758.

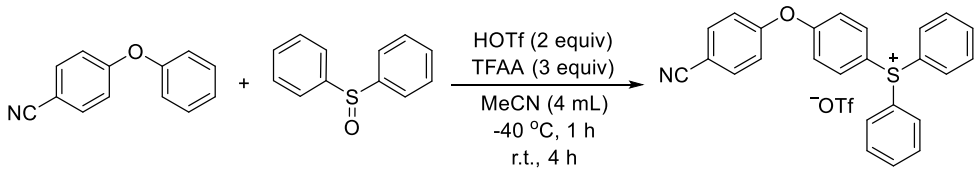
3,7-Di-*tert*-butyl-5-(4-(4-cyanophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1f**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.17 mL, 2.0 mmol) were successively added to a solution of 4-phenoxybenzonitrile (195 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, 3,7-di-*tert*-butyldibenzo[*b*,*d*]thiophene 5-oxide (468 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 2 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 to 20/1 (v/v)) as eluents to afford 3,7-di-*tert*-butyl-5-(4-(4-cyanophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a red solid (614 mg, 96%). M.p.: 121-123 °C ^{1}H NMR (500 MHz, CD_3CN) δ 8.21 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 1.6 Hz, 2H), 7.98 (d, *J* = 8.3, 1.7 Hz, 2H), 7.78 (dm, *J* = 8.9 Hz, 2H), 7.61 (dm, *J* =

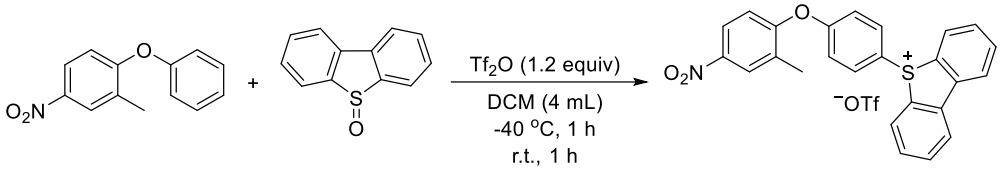
9.1 Hz, 2H), 7.20-7.16 (m, 4H), 1.34 (s, 18H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.2 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 161.5, 158.6, 155.6, 136.7, 134.9, 133.4, 132.6, 131.9, 124.8, 123.9, 121.1, 120.7, 120.5, 118.2, 108.3, 35.5, 30.3. IR (KBr): 3066, 2964, 2227, 1605, 1579, 1486, 1398, 1366, 1252, 1155, 1108, 1030, 873, 836, 754, 715 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{33}H_{32}NOS]^+$ ($[M]^+$): 490.2199; found: 490.2206.

(4-(4-Cyanophenoxy)phenyl)diphenylsulfonium trifluoromethanesulfonate (**1g**)



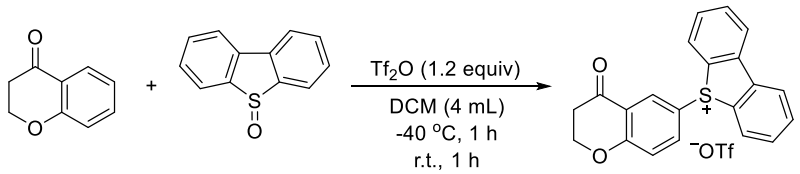
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.17 mL, 2.0 mmol) were successively added to a solution of 4-phenoxybenzonitrile (195 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, diphenyl sulfoxide (303 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 4 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 to 20/1 (v/v)) to afford (4-(4-cyanophenoxy)phenyl) diphenylsulfonium trifluoromethanesulfonate as a yellow solid (520 mg, 98%). M.p.: 128-130 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.04 (d, J = 8.9 Hz, 2H), 7.95 (d, J = 8.1 Hz, 4H), 7.92-7.83 (m, 8H), 7.50 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H). ^{19}F NMR (471 MHz, acetone-d_6) δ -78.8 (s, 3F). ^{13}C NMR (126 MHz, acetone-d_6) δ 161.3, 158.8, 134.8, 134.7, 134.3, 131.6, 131.2, 125.5, 121.6 (q, J = 322.6), 121.4, 120.5, 118.6, 117.9, 108.5. IR (KBr): 3093, 3063, 3048, 2228, 1584, 1492, 1448, 1373, 1260, 1206, 1177, 1153, 1030, 998, 876, 838, 748, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{18}NOS]^+$ ($[M]^+$): 380.1104; found: 380.1110.

5-(4-(2-Methyl-4-nitrophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1i**)



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of 2-methyl-4-nitro-1-phenoxybenzene (229 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) to give 5-(4-(2-methyl-4-nitrophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a pale solid (532 mg, 95%). M.p.: 261-263 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.34 (d, *J* = 7.9 Hz, 2H), 8.21 (d, *J* = 2.5 Hz, 1H), 8.09-8.06 (m, 3H), 7.95 (t, *J* = 7.7 Hz, 2H), 7.74 (t, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 1H), 2.25 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 161.9, 157.9, 144.8, 139.3, 134.5, 133.5, 132.4, 131.9, 131.7, 127.9, 127.1, 124.6, 123.4, 121.1 (q, *J* = 321.3 Hz), 120.3, 120.2, 119.5, 15.2. IR (KBr): 3094, 3009, 2926, 1576, 1513, 1482, 1448, 1347, 1282, 1252, 1152, 1090, 1027, 1001, 930, 861, 831, 803, 757, 720, 706 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{18}NO_3S]^+$ ($[M]^+$): 412.1002; found: 412.1009.

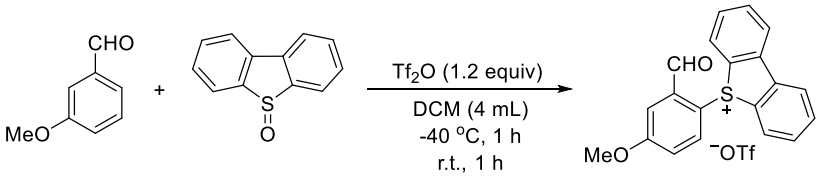
5-(4-Oxochroman-6-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1j**)[11]



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of chroman-4-one (148 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$

solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to give 5-(4-oxochroman-6-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (440 mg, 92%). M.p.: 240-242 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.35 (dm, *J* = 7.9 Hz, 2H), 8.33 (d, *J* = 2.6 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.95 (tm, *J* = 7.7 Hz, 2H), 7.73 (m, 2H), 7.24 (dd, *J* = 9.2 Hz, 2.6 Hz, 1H), 7.10 (d, *J* = 9.1 Hz, 1H), 4.64 (t, *J* = 6.5 Hz, 2H), 2.84 (t, *J* = 6.5 Hz, 2H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 189.5, 166.3, 139.4, 135.4, 134.6, 132.3, 132.1, 131.8, 127.9, 124.7, 122.7, 122.4, 117.5, 68.0, 36.4.

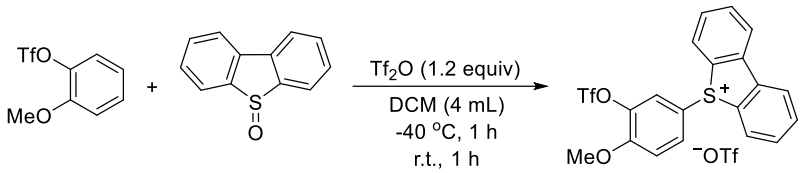
5-(2-Formyl-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1k**)



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of 3-methoxybenzaldehyde (136 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to give 5-(2-formyl-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (392 mg, 84%). M.p.: 128-130 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 10.31 (s, 3H), 8.33 (d, *J* = 7.8 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.95 (t, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 2.9 Hz, 1H), 7.72 (tm, *J* = 7.8 Hz, 2H), 7.11 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 193.6, 164.6, 139.6, 138.2, 134.5, 131.6, 131.3, 130.4, 128.2, 124.6, 122.4, 121.1, 115.4, 56.5. IR (KBr) 3107, 2983, 1778, 1724, 1682, 1607, 1484, 1438, 1392, 1360, 1308, 1232, 1157, 1100,

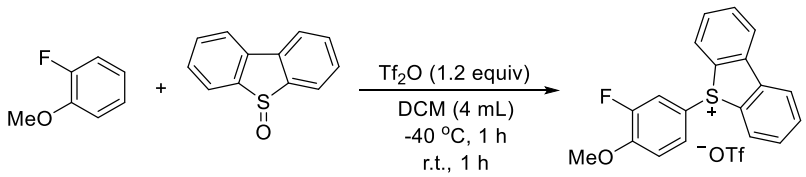
1036, 1004, 946, 900, 852, 755, 708 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{15}O_2S]^+$ ($[M]^+$): 319.0787; found: 319.0789.

5-(4-Methoxy-3-((trifluoromethyl)sulfonyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1l**)



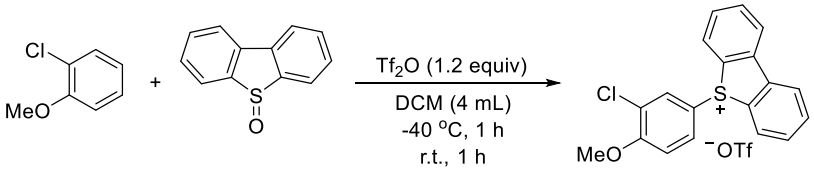
Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of 1-methoxy-2-((trifluoromethyl)sulfonyl)benzene (256 mg, 1 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to give 5-(4-methoxy-3-((trifluoromethyl)sulfonyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethane-sulfonate as a white solid (450 mg, 77%). M.p.: 150-152 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.34 (d, *J* = 7.8 Hz, 2H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.96 (t, *J* = 7.7 Hz, 2H), 7.74 (tm, *J* = 7.8 Hz, 2H), 7.63 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 9.1 Hz, 1H), 3.97 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -74.5 (s, 3F), -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 156.8, 139.4, 139.0, 134.7, 133.3, 132.0, 131.8, 127.9, 125.4, 124.7, 121.2 (q, *J* = 321.3 Hz), 121.1 (q, *J* = 320.0 Hz), 116.5, 116.3, 57.3. IR (KBr) 3102, 2989, 2953, 2854, 2602, 2280, 1601, 1499, 1447, 1428, 1319, 1263, 1221, 1143, 1072, 1032, 1018, 922, 874, 808, 754, 717, 706 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{14}F_3O_4S_2]^+$ ($[M]^+$): 439.0280; found: 439.0283.

5-(3-Fluoro-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1m**)



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of 1-fluoro-2-methoxybenzene (126 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (60/0 to 60/1 to 30/1 (v/v)) to give 5-(3-fluoro-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (440 mg, 96%). M.p.: 161-163 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.33 (d, *J* = 7.7 Hz, 2H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.95 (t, *J* = 7.7 Hz, 2H), 7.72 (tm, *J* = 7.8 Hz, 2H), 7.58 (dm, *J* = 8.9 Hz, 1H), 7.28 (m, 1H), 7.18 (dd, *J* = 10.3, 2.4 Hz, 1H), 3.93 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.28 (s, 3F), -123.0 (m, 1F). ^{13}C NMR (126 MHz, CD_3CN) δ 153.8 (d, *J* = 10.3 Hz), 152.6 (d, *J* = 253.3 Hz), 139.3, 134.5, 132.2, 131.7, 129.9 (d, *J* = 3.6 Hz), 127.9, 124.7, 117.5, 115.6 (d, *J* = 2.3 Hz), 115.2 (d, *J* = 7.1 Hz), 56.7. IR (KBr) 3091, 3057, 2981, 2950, 1602, 1505, 1465, 1441, 1321, 1261, 1223, 1143, 1076, 1029, 954, 875, 806, 756, 706 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}FOS]^+$ ($[M]^+$): 309.0744; found: 309.0751.

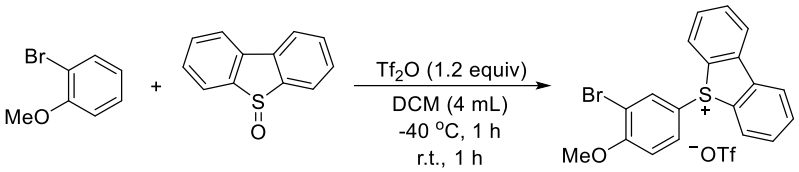
5-(3-Chloro-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1n**)



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of 1-chloro-2-methoxybenzene (142.5 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1

h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to give 5-(3-chloro-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (442 mg, 93%). M.p.: 173-175 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.33 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.95 (t, *J* = 7.7 Hz, 2H), 7.73 (m, 2H), 7.55-7.53 (m, 2H), 7.21 (d, *J* = 9.6 Hz, 1H), 3.94 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 160.6, 139.3, 134.6, 132.2, 132.1, 131.8, 131.7, 127.9, 124.8, 124.7, 115.9, 114.8, 57.0. IR (KBr): 3108, 3090, 2960, 1578, 1491, 1471, 1449, 1396, 1306, 1265, 1158, 1088, 1061, 1028, 1003, 943, 890, 811, 757, 705 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}ClOS]^+$ ($[M]^+$): 325.0448; found: 325.0450.

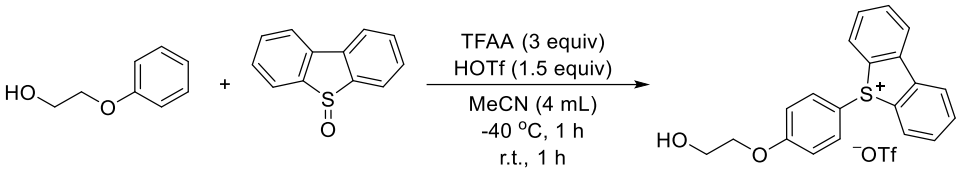
5-(3-Bromo-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1o**)



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of 1-bromo-2-methoxybenzene (142.5 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to give 5-(3-bromo-4-methoxyphenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a light yellow solid (462 mg, 89%). M.p.: 196-198 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.33 (d, *J* = 7.8 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.94 (t, *J* = 7.4 Hz, 2H), 7.74-7.71 (m, 3H), 7.56 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 3.92 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 161.5, 139.3, 135.0, 134.5, 132.6, 132.3, 131.7, 127.9, 124.7,

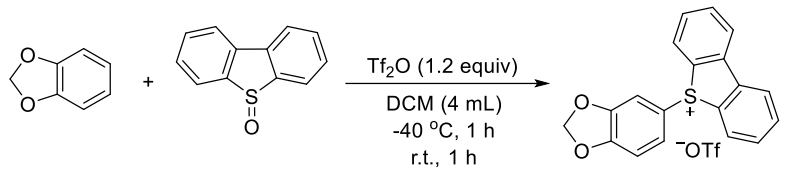
121.2 (q, J = 321.3 Hz), 116.3, 114.6, 113.5, 57.1. IR (KBr): 3088, 3026, 2947, 1576, 1483, 1451, 1398, 1273, 1221, 1156, 1083, 1051, 1030, 962, 874, 812, 761, 707, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}BrOS]^+$ ($[M]^+$): 368.9943; found: 368.9950.

5-(4-(2-Hydroxyethoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1p**)



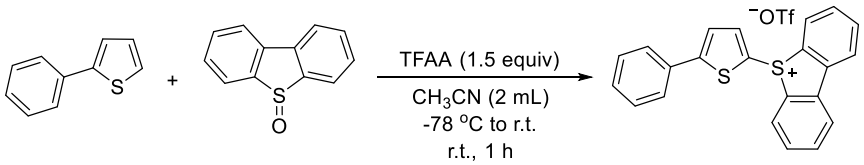
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.13 mL, 1.5 mmol) were successively added to a solution of 2-phenoxyethan-1-ol (138 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (40/0 to 40/1 to 20/1 (v/v)) as eluents to give 5-(4-(2-hydroxyethoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (346 mg, 74%). M.p.: 159-161 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.33 (d, J = 7.5 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 7.94 (tm, J = 7.7 Hz, 2H), 7.72 (tm, J = 7.8 Hz, 2H), 7.49 (dm, J = 9.1 Hz, 2H), 7.09 (dm, J = 9.1 Hz, 2H), 4.09 (t, J = 4.7 Hz, 2H), 3.79 (m, 2H), 3.05 (m, 1H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 164.6, 139.2, 134.3, 133.1, 132.8, 131.6, 127.7, 124.5, 117.6, 114.9, 70.6, 59.9. IR (KBr): 3462, 3091, 3011, 2944, 2924, 1590, 1573, 1496, 1448, 1429, 1250, 1224, 1182, 1158, 1031, 916, 833, 759, 708 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{17}O_2S]^+$ ($[M]^+$): 321.0944; found: 321.0948.

5-(Benzo[*d*][1,3]dioxol-5-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1q**)[11]



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of benzo[*d*][1,3]dioxole (136 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to give 5-(benzo[*d*][1,3]dioxol-5-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (404 mg, 89%). M.p.: 165-167 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8,32 (d, *J* = 7.9 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.94 (t, *J* = 7.7 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.54 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 1.5 Hz, 1H), 6.07 (s, 2H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.2 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 154.3, 150.5, 139.3, 134.4, 132.3, 131.6, 129.4, 127.7, 124.6, 116.2, 109.9, 107.6, 103.9.

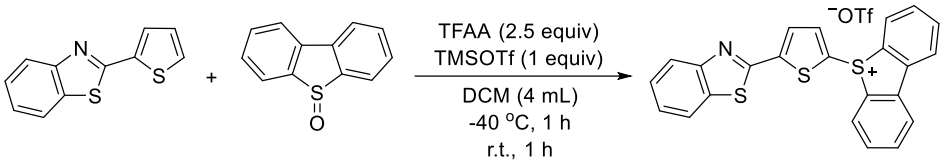
5-(5-Phenylthiophen-2-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1r**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.21 mL, 1.5 mmol) was added to a mixture of dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) and 2-phenylthiophene (160 mg, 1.0 mmol) in MeCN (2 mL) at -78 °C with stirring. The mixture was slowly warmed to room temperature, reacted at room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to afford

5-(5-phenylthiophen-2-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as white solid (440 mg, 89%). M.p.: 148-150 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.32 (d, *J* = 7.9 Hz, 2H), 8.28 (d, *J* = 4.2 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 2H), 7.95 (tm, *J* = 7.6 Hz, 2H), 7.74 (tm, *J* = 7.8 Hz, 2H), 7.52 (m, 1H), 7.49-7.46 (m, 2H), 7.37-7.36 (m, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.2 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 157.2, 143.6, 138.5, 134.8, 133.4, 131.8, 131.5, 130.3, 129.4, 127.9, 126.3, 125.2, 124.6, 121.2 (q, *J* = 322.6 Hz), 119.2. IR (KBr): 3084, 3023, 1631, 1576, 1486, 1450, 1421, 1267, 1224, 1151, 1030, 997, 952, 811, 758, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{15}S_2]^+$ ($[M]^+$): 343.0610; found: 343.0612.

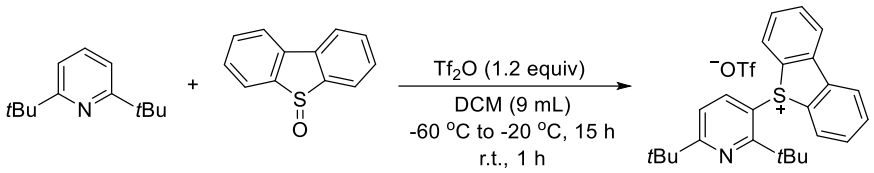
5-(5-(Benzo[*d*]thiazol-2-yl)thiophen-2-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1s**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.35 mL, 2.5 mmol) and TMSOTf (0.18 mL, 1.0 mmol) were successively added to a mixture of dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) and 2-(thiophen-2-yl)benzo[*d*]thiazole (217 mg, 1.0 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with an aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) to afford 5-(5-(benzo[*d*]thiazol-2-yl)thiophen-2-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a yellow solid (406 mg, 74%). M.p.: 219-221 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.33 (d, *J* = 7.9 Hz, 2H), 8.25 (d, *J* = 4.1 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 2H), 8.00-7.96 (m, 3H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.78-7.75 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.46 (m, 1H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 159.1, 153.6, 148.6, 142.7, 139.3, 136.0, 135.6, 133.6, 132.5, 129.8, 128.6, 127.8, 127.3, 125.6, 125.4, 123.8, 122.9, 121.8 (q, *J* = 321.8 Hz). IR (KBr): 3085, 3060, 3009, 1591, 1556, 1477, 1449, 1419, 1258, 1222, 1156, 1029,

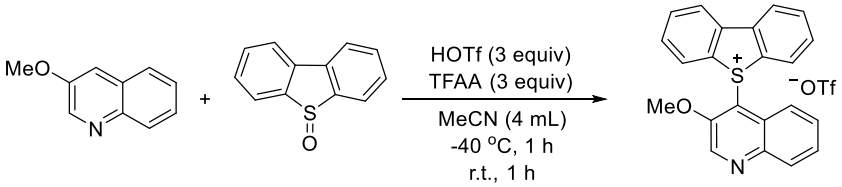
1000, 906, 808, 758, 726, 702 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{23}H_{14}NS_3]^+$ ($[M]^+$): 400.0283; found: 400.0287.

5-(2,6-Di-*tert*-butylpyridin-3-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1t**)[12]



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (9 mL) at -60 °C with stirring. After 20 minutes, 2,6-di-*tert*-butylpyridine (191 mg, 1.0 mmol) was added. The mixture was slowly warmed to -20 °C over 15 h, reacted at room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel with a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to give 5-(2,6-di-*tert*-butylpyridin-3-yl)-5*H*-dibenzo [*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (183 mg, 35%). M.p.: 265-267 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.39 (d, *J* = 7.9 Hz, 2H), 7.98 (tm, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.73 (tm, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 1.85 (s, 9H), 1.30 (s, 9H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 174.4, 169.5, 139.5, 139.3, 134.7, 132.5, 131.9, 127.5, 125.0, 120.6, 117.5, 40.3, 38.4, 31.3, 28.9.

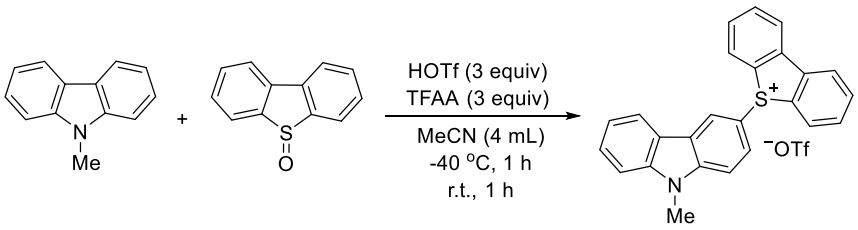
5-(3-Methoxyquinolin-4-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1u**)[2]



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of 3-methoxyquinoline (159 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with

stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 40 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents followed by recrystallization from DCM/MTBE to afford 5-(3-methoxyquinolin-4-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (446 mg, 91%). M.p.: 228-230 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 9.16 (d, *J* = 8.3 Hz, 1H), 9.04 (s, 1H), 8.51 (d, *J* = 9.4 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 2H), 7.94-7.88 (m, 5H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 9.3 Hz, 1H), 3.28 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 160.9, 150.8, 144.4, 141.2, 140.8, 134.2, 131.8, 131.6, 131.5, 129.7, 127.5, 124.9, 124.5, 121.8 (q, *J* = 321.3 Hz), 118.5, 101.6, 57.5.

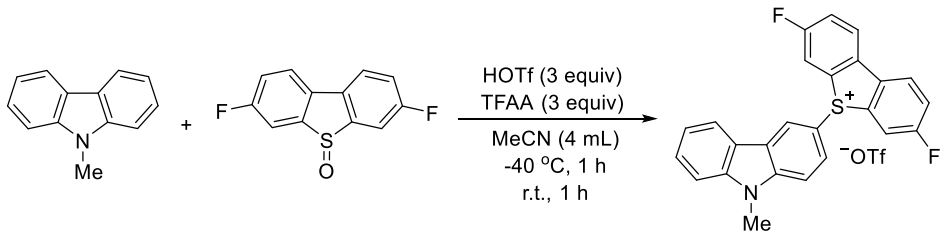
5-(9-Methyl-9*H*-carbazol-3-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1v**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of 9-methyl-9*H*-carbazole (271.5 mg, 1.5 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (200 mg, 1.0 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (40 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (60/0 to 60/1 to 30/1 (v/v)) as eluents to afford 5-(9-methyl-9*H*-carbazol-3-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a pale solid (285 mg, 56%). M.p.: 250-252 °C. ^{1}H NMR

(500 MHz, CD_3CN) δ 8.54 (d, *J* = 1.9 Hz, 1H), 8.37 (d, *J* = 7.9 Hz, 2H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.95 (tm, *J* = 7.7 Hz, 2H), 7.70 (tm, *J* = 7.7 Hz, 2H), 7.64-7.59 (m, 3H), 7.39 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.34 (tm, *J* = 7.0 Hz, 1H), 3.87 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 144.0, 142.0, 139.0, 134.2, 133.6, 131.6, 127.9, 127.7, 126.5, 125.3, 124.5, 124.3, 121.3, 121.0, 120.9, 112.2, 111.6, 110.1, 29.3. IR (KBr): 3059, 3013, 2949, 1586, 1505, 1474, 1449, 1427, 1327, 1265, 1223, 1150, 1048, 1031, 818, 752, 705 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{18}NS]^+$ ($[M]^+$): 364.1154; found: 364.1160.

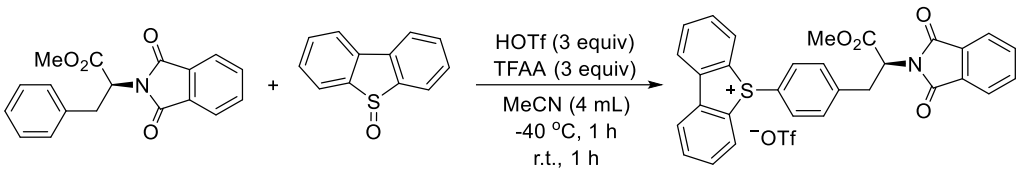
3,7-Difluoro-5-(9-methyl-9*H*-carbazol-3-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1w**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of 9-methyl-9*H*-carbazole (271.5 mg, 1.5 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, 3,7-difluorodibenzo[*b*,*d*]thiophene 5-oxide (236 mg, 1 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (40 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (60/0 to 60/1 to 30/1 (v/v)) as eluents to give 3,7-difluoro-5-(9-methyl-9*H*-carbazol-3-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as an off-white solid (408 mg, 74%). M.p.: 256-258 °C. ^1H NMR (500 MHz, CD_3CN) δ 8.52 (s, 1H), 8.34 (dd, *J* = 8.7, 4.6 Hz, 2H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.84 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.72-7.66 (m, 3H), 7.64-7.60 (m, 2H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.36 (m, 1H), 3.89 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.29 (s, 3F), -108.8 (m, 2F). ^{13}C NMR (126 MHz, CD_3CN) δ 163.2 (d, *J* = 252.3 Hz), 144.3, 142.0, 135.3, 135.2, 134.7 (d, *J* = 1.8 Hz), 128.0, 127.1, 126.0 (d, *J* = 9.4 Hz), 125.7, 124.4, 122.1 (d, *J* = 23.1 Hz), 121.3, 121.0 (d, *J* = 16.1 Hz), 121.2 (q, *J* =

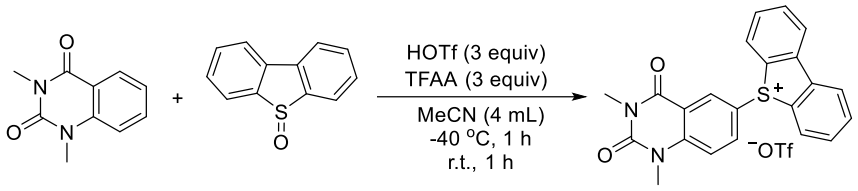
321.3 Hz), 115.4 (d, *J* = 28.0 Hz), 112.1, 110.1, 110.1, 29.3. IR (KBr): 3085, 3039, 2989, 2947, 1597, 1505, 1470, 1327, 1254, 1212, 1158, 1064, 1029, 881, 833, 754, 725, 695 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{25}H_{16}F_2NS]^+$ ($[M]^+$): 400.0966; found: 400.0974.

(*S*)-5-(4-(2-(1,3-Dioxoisoindolin-2-yl)-3-methoxy-3-oxopropyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1x**)



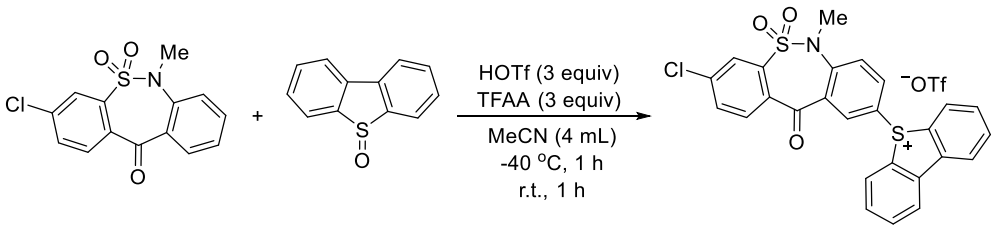
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of methyl (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanoate (309 mg, 1 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (40/0 to 40/1 to 20/1 (v/v)) as eluents to give (*S*)-5-(4-(2-(1,3-dioxoisoindolin-2-yl)-3-methoxy-3-oxopropyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (530 mg, 83%, the molar ratio of the *para*-/*ortho*-isomers was > 7.7:1). M.p.: 160-162 °C. ^{1}H NMR (500 MHz, CD_3CN, for the *para*-isomer) δ 8.29 (dd, *J* = 7.9 Hz, 2H), 7.94 (t, *J* = 7.5 Hz, 2H), 7.92 (t, *J* = 7.5 Hz, 2H), 7.80-7.77 (m, 2H), 7.75-7.72 (m, 2H), 7.70-7.65 (m, 2H), 7.38 (m, 4H), 5.12 (dd *J* = 11.0, 5.2 Hz, 1H), 3.68 (s, 3H), 3.60 (dd, *J* = 14.2, 5.2 Hz, 1H), 3.43 (dd, *J* = 14.2, 11.0 Hz, 1H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN, for the *para*-isomer) δ 168.8, 167.2, 145.7, 139.4, 134.8, 134.4, 132.3, 132.0, 131.7, 131.2, 130.5, 127.7, 124.9, 124.5, 123.3, 52.6, 52.2, 34.2. IR (KBr): 3090, 3065, 3013, 2956, 2927, 1776, 1745, 1716, 1613, 1592, 1468, 1450, 1389, 1263, 1157, 1089, 1031, 975, 922, 885, 834, 764, 724, 707 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{30}H_{22}NO_4S]^+$ ($[M]^+$): 492.1264; found: 492.1270.

5-(1,3-Dimethyl-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl)-5*H*-dibenzo[*b*,*d*]thioph en-5-ium trifluoromethanesulfonate (**1y**)[2]



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of 1,3-dimethylquinazoline-2,4(1*H*,3*H*)-dione (198 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (40/0 to 40/1 to 20/1 (v/v)) as eluents to give 5-(1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydroquinazolin-6-yl) -5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (423 mg, 81%). M.p.: 260-262 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.58 (s, 1H), 8.37 (d, *J* = 7.8 Hz, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.96 (t, *J* = 7.7 Hz, 2H), 7.73 (tm, *J* = 7.8 Hz, 2H), 7.45 (m, 1H), 7.40 (d, *J* = 9.1 Hz, 1H), 3.49 (s, 3H), 3.34 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 160.7, 151.2, 146.0, 140.0, 135.3, 135.3, 133.5, 132.7, 132.4, 128.6, 125.3, 121.7 (q, *J* = 321.3 Hz), 119.2, 118.8, 117.6, 31.5, 28.7.

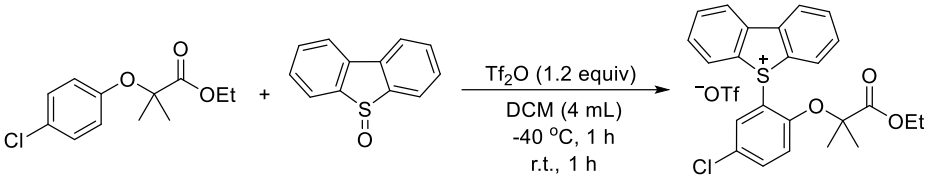
5-(3-Chloro-6-methyl-5,5-dioxido-11-oxo-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepin-9-y l)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1z**)[2]



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and

trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of 3-chloro-6-methyldibenzo[*c*,*f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide (308 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (40/0 to 40/1 to 20/1 (v/v)) as eluents to give 5-(3-chloro-6-methyl-5,5-dioxido-11-oxo-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepin-9-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (592 mg, 93%). M.p.: 230-232 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.64 (s, 1H), 8.37 (d, *J* = 7.9 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H), 7.98 (t, *J* = 7.7 Hz, 2H), 7.94 (s, 1H), 7.85-7.80 (m, 2H), 7.75 (t, *J* = 7.8 Hz, 2H), 7.54-7.50 (m, 2H), 3.39 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 188.7, 146.5, 139.6, 138.8, 137.7, 135.5, 134.8, 134.5, 134.4, 133.8, 132.8, 131.9, 131.7, 131.1, 128.1, 126.6, 124.8, 122.44, 121.2 (q, *J* = 321.3 Hz), 38.1.

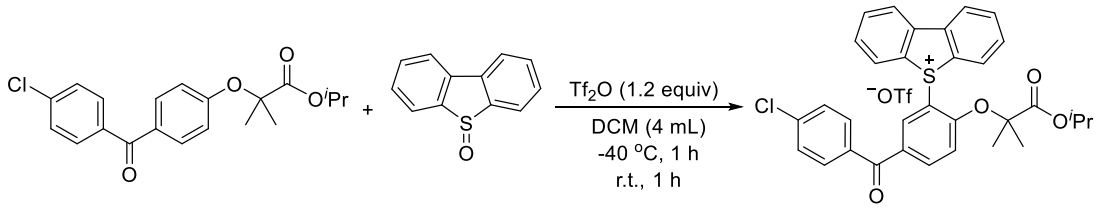
5-(5-Chloro-2-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1aa**)[11]



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of ethyl 2-(4-chlorophenoxy)-2-methylpropanoate (Clofibrate, 242 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to give 5-(5-chloro-2-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)

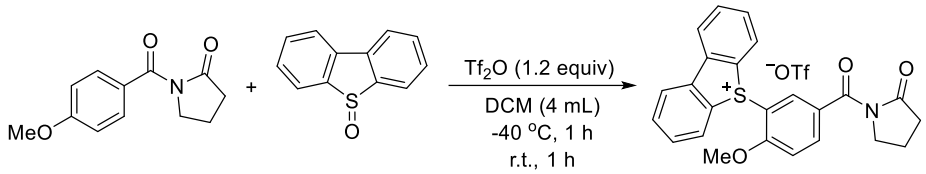
phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (543 mg, 95%). M.p.: 151-153 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.33 (d, *J* = 7.9 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.96 (t, *J* = 7.7 Hz, 2H), 7.76 (tm, *J* = 7.8 Hz, 2H), 7.63 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.45 (brs, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.18 (s, 6H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 172.2, 155.0, 140.6, 137.2, 135.0, 132.1, 129.8, 128.4, 127.8, 125.1, 121.8 (q, *J* = 321.3 Hz), 119.4, 118.1, 83.0, 62.7, 24.8, 13.8.

5-(5-(4-Chlorobenzoyl)-2-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1ab**)[11]



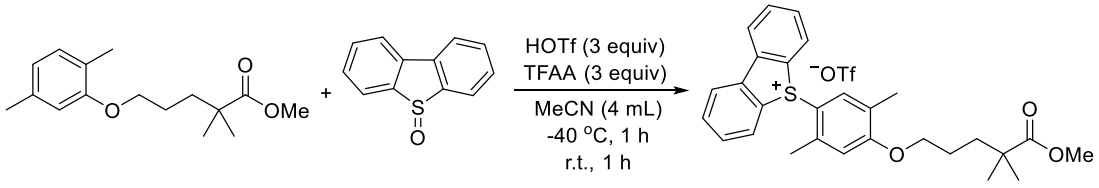
Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of ethyl isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (Fenofibrate, 360.1 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to give 5-(5-(4-chlorobenzoyl)-2-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (564 mg, 82%). M.p.: 197-199 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.31 (d, *J* = 7.7 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.06 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.96-7.93 (m, 3H), 7.76 (t, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 4.94 (m, 1H), 1.39 (s, 6H), 1.09 (d, *J* = 6.2 Hz, 6H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 191.5, 170.7, 158.3, 140.0, 138.6, 138.3, 135.2, 134.3, 131.5, 131.3, 131.2, 129.3, 128.8, 127.8, 124.5, 121.2 (q, *J* = 321.3 Hz), 116.9, 82.7, 70.2, 24.1, 20.7.

5-(2-Methoxy-5-(2-oxopyrrolidine-1-carbonyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1ac**)



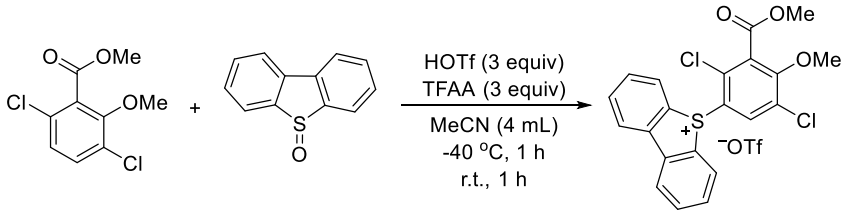
Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol) was added to a mixture of 1-(4-methoxybenzoyl)pyrrolidin-2-one (Aniracetam, 219 mg, 1.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to give 5-(2-methoxy-5-(2-oxopyrrolidine-1-carbonyl) phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (438 mg, 79%). M.p.: 109-111 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.32 (d, *J* = 7.9 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H), 7.95 (t, *J* = 7.6 Hz, 2H), 7.91 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 1.7 Hz, 1H), 4.05 (s, 3H), 3.73 (t, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 8.0 Hz, 2H), 2.00 (m, 2H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 175.7, 167.5, 161.9, 140.5, 138.4, 135.1, 132.1, 131.4, 130.1, 129.8, 128.8, 125.1, 121.8 (q, *J* = 322.6 Hz), 113.7, 113.6, 58.2, 46.8, 33.3, 17.6. IR (KBr): 3090, 2992, 2955, 1740, 1668, 1599, 1567, 1498, 1463, 1450, 1401, 1361, 1318, 1259, 1224, 1150, 1030, 1007, 961, 920, 844, 760, 706 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{24}H_{20}NO_3S]^+$ ($[M]^+$): 402.1158; found: 402.1160.

5-(4-((5-Methoxy-4,4-dimethyl-5-oxopentyl)oxy)-2,5-dimethylphenyl)-5*H*-dibenzo[*b*, *d*]thiophen-5-ium trifluoromethanesulfonate (**1ad**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (Gemfibrozil methyl ester, 264 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 to 20/1 (v/v)) as eluents to give 5-(4-((5-methoxy-4,4-dimethyl-5-oxopentyl)oxy)-2,5-dimethylphenyl)-5*H*-dibenzo[*b*, *d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (405 mg, 68%). M.p.: 143-145 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.34 (d, *J* = 7.8 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.93 (tm, *J* = 7.7 Hz, 2H), 7.71 (tm, *J* = 7.8 Hz, 2H), 7.03 (s, 1H), 6.45 (s, 1H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.57 (s, 3H), 2.83 (s, 3H), 1.90 (s, 3H), 1.72-1.63 (m, 4H), 1.15 (s, 6H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 177.7, 162.5, 144.1, 139.2, 134.2, 132.5, 131.5, 129.4, 127.6, 124.6, 121.2 (q, *J* = 321.3 Hz), 114.7, 112.1, 69.0, 51.2, 41.7, 36.5, 24.4, 24.4, 19.3, 14.6. IR (KBr): 3088, 3062, 2988, 2937, 1725, 1603, 1559, 1500, 1485, 1467, 1450, 1388, 1369, 1328, 1260, 1222, 1199, 1144, 1031, 986, 895, 867, 785, 770, 718, 707 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{28}H_{31}O_3S]^+$ ($[M]^+$): 447.1988; found: 447.1990.

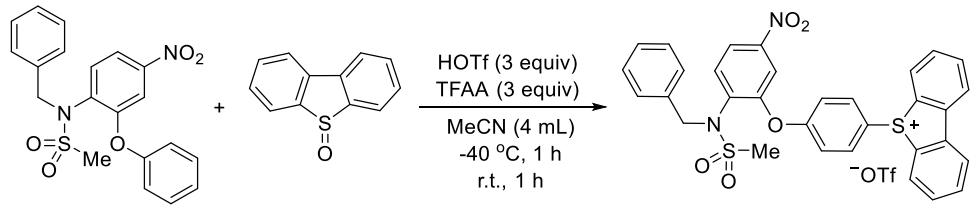
5-(2,5-Dichloro-4-methoxy-3-(methoxycarbonyl)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1ae**)[2]



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of methyl 3,6-dichloro-2-methoxybenzoate (Dicamba methyl ester, 234 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene

5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 to 20/1 (v/v)) as eluents to give 5-(2,5-dichloro-4-methoxy-3-(methoxycarbonyl) phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (393 mg, 69%). M.p.: 217-219 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.35 (d, *J* = 7.9 Hz, 2H), 8.15 (d, *J* = 8.1 Hz, 2H), 8.00 (tm, *J* = 7.7 Hz, 2H), 7.78 (tm, *J* = 7.8 Hz, 2H), 7.03 (s, 1H), 4.01 (s, 3H), 3.93 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 163.1, 158.8, 140.0, 135.2, 133.2, 132.0, 129.8, 129.2, 128.4, 125.1, 122.0 (q, *J* = 322.5 Hz), 62.5, 53.6.

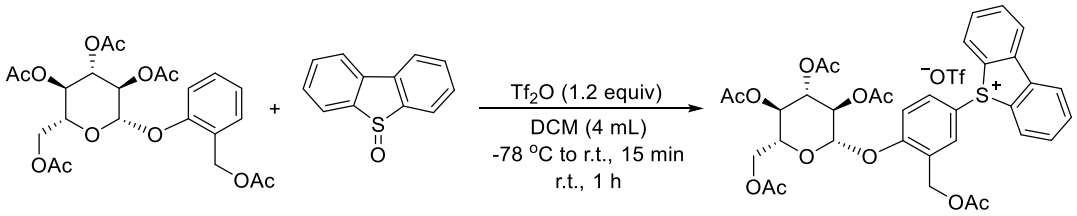
5-(4-(2-(*N*-Benzylmethylsulfonamido)-5-nitrophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiop hen-5-ium trifluoromethanesulfonate (**1af**)[2]



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of *N*-benzyl-*N*-(4-nitro-2-phenoxyphenyl)methanesulfonamide (*N*-benzyl-Nimesulide, 398 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 to 20/1 (v/v)) as eluents to give 5-(4-(2-(*N*-benzylmethylsulfonamido)-5-nitrophenoxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiop hen-5-ium trifluoromethanesulfonate as a light yellow solid (424 mg, 58%). M.p.:

214-216 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.36 (d, *J* = 7.6 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 8.00-7.95 (m, 3H), 7.76 (tm, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.19 (dm, *J* = 7.8 Hz, 2H), 7.15-7.07 (m, 3H), 7.05 (d, *J* = 9.0 Hz, 2H), 4.79 (s, 2H), 3.05 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 161.2, 153.0, 148.0, 139.4, 136.9, 135.6, 134.6, 133.3, 132.9, 132.3, 131.8, 128.8, 128.5, 128.0, 128.0, 124.7, 120.8, 120.3, 120.0, 115.5, 54.0, 39.3.

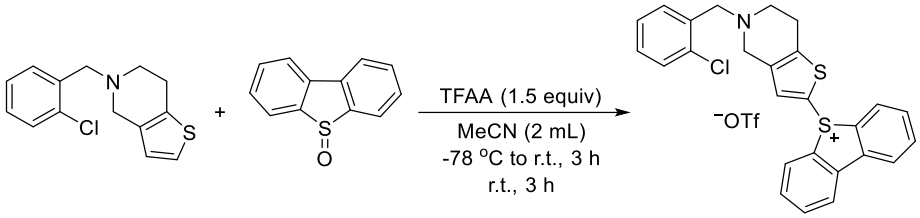
5-(3-(Acetoxymethyl)-4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1ag**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.21 mL, 1.5 mmol) was added to a mixture of 3,7-difluorodibenzo[*b*,*d*]thiophene 5-oxide (260 mg, 1.1 mmol) and (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(2-(acetoxymethyl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (Salicin pentaacetate, 496 mg, 1.0 mmol) in DCM (4 mL) at -78 °C with stirring. The mixture was warmed to room temperature over 15 minutes, reacted at room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (50/0 to 50/1 to 30/1 (v/v)) as eluents to afford 5-(3-(acetoxymethyl)-4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a gray solid (299 mg, 36%). M.p.: 106-108 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.34 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.95 (t, *J* = 7.7 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.52 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 5.39 (d, *J* = 7.7 Hz, 1H), 5.35 (t, *J* = 9.5 Hz, 1H), 5.22 (dd, *J* = 9.5, 7.9 Hz, 1H), 5.11 (t, *J* = 9.7 Hz, 1H), 4.91 (s, 2H), 4.20 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.11 (dd, *J* = 12.5, 2.1 Hz, 1H), 4.05 (m, 1H), 1.99 (s, 3H), 1.99 (s, 3H),

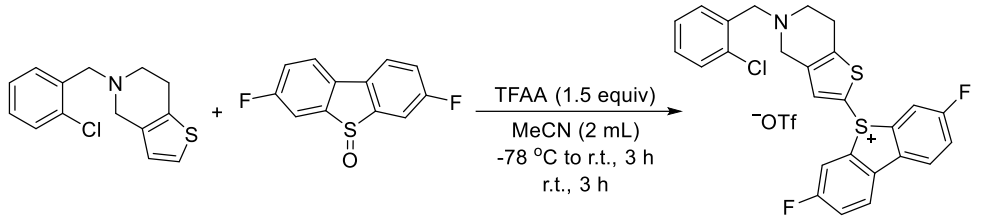
1.98 (s, 3H), 1.97 (s, 3H), 1.92 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 170.7, 170.7, 170.5, 170.1, 170.0, 159.3, 139.9, 135.1, 133.0, 132.9, 132.3, 131.5, 130.3, 128.5, 125.2, 119.4, 117.6, 98.1, 72.7, 72.2, 71.0, 68.5, 62.0, 60.2, 20.5, 20.5, 20.5, 20.4, 20.4. IR (KBr): 3090, 2956, 1752, 1598, 1489, 1450, 1379, 1225, 1148, 1075, 1030, 907, 817, 762, 736, 706 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{35}H_{35}O_{12}S]^+$ ($[M]^+$): 679.1844; found: 679.1846.

5-(5-(2-Chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1ah**)



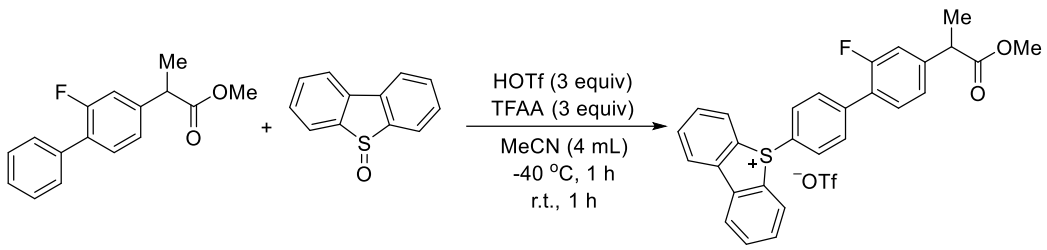
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.21 mL, 1.5 mmol) was added to a mixture of dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol), 5-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine (Ticlopidine, 263 mg, 1.0 mmol) in MeCN (2 mL) at -78 °C with stirring. The mixture was slowly warmed to room temperature over 3 h, reacted at room temperature for another 3 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (50/0 to 50/1 to 30/1 (v/v)) as eluents to give 5-(5-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a light yellow solid (533 mg, 90%). M.p.: 175-177 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.30 (d, *J* = 7.8 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.95-7.92 (m, 3H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.32-7.26 (m, 2H), 3.78 (s, 2H), 3.60 (s, 2H), 2.78 (m, 4H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.2 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 149.3, 140.5, 138.4, 137.2, 135.8, 134.7, 134.0, 133.5, 131.8, 131.0, 129.5, 128.8, 127.8, 127.0, 124.6, 121.2 (q, *J* = 321.3 Hz), 57.8, 51.8, 49.3, 26.0. IR (KBr): 3089, 3068, 2928, 2832, 1593, 1572, 1466, 1426, 1354, 1265, 1152, 1030, 958, 861, 756, 707, 682 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{26}H_{21}ClNS_2]^+$ ($[M]^+$): 446.0798; found: 446.0802.

5-(5-(2-Chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl)-3,7-difluoro-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1ai**)



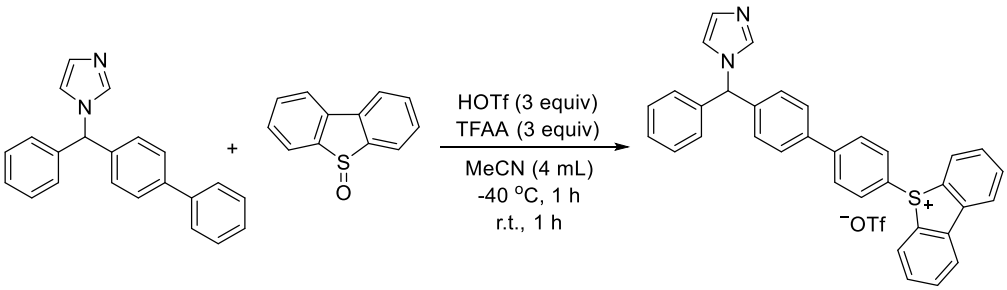
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.21 mL, 1.5 mmol) was added to a mixture of 3,7-difluorodibenzo[*b*,*d*]thiophene 5-oxide (260 mg, 1.1 mmol) and 5-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine (Ticlopidine, 263 mg, 1.0 mmol) in MeCN (2 mL) at -78 °C with stirring. The mixture was slowly warmed to room temperature over 3 h, reacted at room temperature for 3 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (50/0 to 50/1 to 30/1 (v/v)) as eluents to give 5-(5-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl)-3,7-difluoro-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a light yellow solid (318 mg, 50%). M.p.: 213-215 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.26 (dd, *J* = 8.7, 4.5 Hz, 2H), 7.90-7.89 (m, 3H), 7.70 (td, *J* = 8.7, 1.8 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33-7.27 (m, 2H), 3.80 (s, 2H), 3.61 (s, 2H), 2.83 (m, 4H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.2 (s, 3F), -108.1 (m, 2F). ^{13}C NMR (126 MHz, CD_3CN) δ 163.2 (d, *J* = 253.3 Hz), 150.3, 141.1, 137.7, 137.4, 135.7 (d, *J* = 2.0 Hz), 135.2 (d, *J* = 11.2 Hz), 134.1, 134.0, 131.0, 129.5, 128.8, 127.0, 126.1 (d, *J* = 9.3 Hz), 122.5 (d, *J* = 22.9 Hz), 115.4 (d, *J* = 28.2 Hz), 57.8, 51.7, 49.3, 26.1. IR (KBr): 3074, 2927, 2833, 1596, 1468, 1354, 1263, 1215, 1167, 1100, 1030, 972, 877, 840, 756, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{26}H_{19}ClF_2NS_2]^+$ ($[M]^+$): 482.0610; found: 482.0612.

5-(2'-Fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-[1,1'-biphenyl]-4-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1aj**)[2]



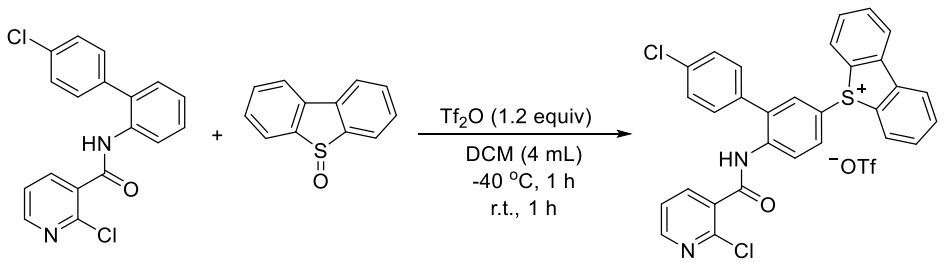
Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of methyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (Flurbiprofen methyl ester, 258 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 to 20/1 (v/v)) as eluents to give 5-(2'-fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-[1,1'-biphenyl]-4-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (508 mg, 86%). M.p.: 174-176 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.37 (d, *J* = 7.8 Hz, 2H), 8.12 (d, *J* = 8.1 Hz, 2H), 7.97 (t, *J* = 7.8 Hz, 2H), 7.77-7.73 (m, 4H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.45 (t, *J* = 8.1 Hz, 1H), 7.23-7.18 (m, 2H), 3.83 (q, *J* = 7.2 Hz, 1H), 3.63 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.2 (s, 3F), -118.8 (m, 1F). ^{13}C NMR (126 MHz, CD_3CN) δ 174.6, 160.0 (d, *J* = 248.2 Hz), 145.4 (d, *J* = 8.1 Hz), 142.8, 140.1, 135.2, 132.6, 132.4 (d, *J* = 3.4 Hz), 132.4, 131.5 (d, *J* = 3.1 Hz), 131.3, 128.6, 126.4, 125.4, 125.3, 124.9 (d, *J* = 3.3 Hz), 121.8 (d, *J* = 322.6 Hz), 116.0 (d, *J* = 23.4 Hz), 52.3, 45.1, 18.3.

5-(4'-((1*H*-Imidazol-1-yl)(phenyl)methyl)-[1,1'-biphenyl]-4-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1ak**)[2]



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.42 mL, 3.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.26 mL, 3.0 mmol) were successively added to a solution of 1-([1,1'-biphenyl]-4-yl(phenyl)methyl)-1*H*-imidazole (Bifonazole, 310 mg, 1.0 mmol) in MeCN (4 mL) at -40 °C with stirring. Then, dibenzo[*b*,*d*]thiophene 5-oxide (300 mg, 1.5 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), neutralized by a saturated aqueous $NaHCO_3$ solution, and washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (40/0 to 40/1 to 30/1 (v/v)) as eluents to give 5-(4'-((1*H*-imidazol-1-yl)(phenyl)methyl)-[1,1'-biphenyl]-4-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (411 mg, 64%). M.p.: 106-108 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.36 (d, *J* = 7.9 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.96 (t, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.74 (tm, *J* = 7.7 Hz, 2H), 7.66-7.63 (m, 4H), 7.52 (s, 1H), 7.42-7.37 (m, 3H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.18-7.17 (m, 2H), 7.00 (d, *J* = 11.5 Hz, 2H), 6.76 (s, 1H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 147.7, 141.9, 140.4, 140.3, 138.7, 138.2, 135.5, 133.0, 132.7, 132.5, 132.1, 130.8, 129.8, 129.6, 129.3, 129.0, 128.9, 128.7, 126.2, 125.6, 122.1 (q, *J* = 321.4 Hz), 120.3, 64.9.

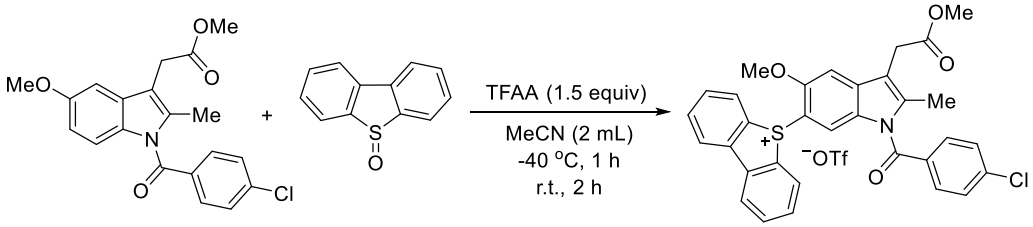
5-(4'-Chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1al**)



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.2 mL, 1.2 mmol)

was added to a mixture of dibenzo[*b*,*d*]thiophene 5-oxide (220 mg, 1.1 mmol) in DCM (4 mL) at -40 °C with stirring. Then, 2-chloro-*N*-(4'-chloro-[1,1'-biphenyl]-2-yl) nicotinamide (Boscalid, 342 mg, 1.0 mmol) was slowly added. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 1 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to give 5-(4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a light yellow solid (504 mg, 75%). M.p.: 124-126 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.53 (brs, 1H), 8.42 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.38 (d, *J* = 8.9 Hz, 1H), 8.34 (d, *J* = 7.9 Hz, 2H), 8.12 (d, *J* = 8.1 Hz, 2H), 7.96 (tm, *J* = 7.7 Hz, 2H), 7.84 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.75 (tm, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.50-7.47 (m, 3H), 7.40-7.35(m, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 164.2, 151.1, 146.7, 140.9, 139.5, 138.2, 135.7, 134.6, 134.5, 134.4, 133.4, 132.0, 131.8, 131.7, 131.1, 130.3, 129.2, 128.0, 125.5, 124.7, 122.9, 121.3, 121.2 (q, *J* = 321.3 Hz). IR (KBr): 3371, 3230, 3087, 3060, 3003, 1674, 1574, 1513, 1449, 1400, 1257, 1223, 1153, 1090, 1066, 1029, 898, 832, 757, 705 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{30}H_{19}Cl_2N_2OS]^+$ ($[M]^+$): 525.0590; found: 525.0598.

5-(1-(4-Chlorobenzoyl)-5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1*H*-indol-6-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1am**)



Under a N_2 atmosphere, trifluoroacetic anhydride (TFAA, 0.21 mL, 1.5 mmol) was added to a mixture of dibenzo[*b*,*d*]thiophene 5-oxide (110 mg, 0.55 mmol) and methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (Indometacin methyl ester, 186 mg, 0.5 mmol) in MeCN (2 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 2 h, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer

was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / MeOH (30/0 to 30/1 (v/v)) as eluents to give 5-(1-(4-chlorobenzoyl)-5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1*H*-indol-4-yl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate as a white solid (200 mg, 57%). M.p.: 211-213 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.91 (t, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.8 Hz, 2H), 7.37 (s, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.23 (s, 1H), 4.11 (s, 3H), 3.77 (s, 2H), 3.67 (s, 3H), 2.35 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 171.4, 167.9, 155.5, 142.9, 139.8, 139.8, 137.0, 134.9, 133.2, 132.0, 131.7, 131.2, 131.0, 129.7, 128.5, 124.8, 121.8 (q, *J* = 321.3 Hz), 114.6, 113.6, 108.6, 103.0, 58.1, 52.3, 29.5, 13.1. IR (KBr): 3094, 3014, 2958, 2932, 1742, 1695, 1588, 1466, 1428, 1400, 1355, 1313, 1266, 1225, 1170, 1088, 1030, 939, 842, 765, 717, 686 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{32}H_{25}ClNO_4S]^+$ ($[M]^+$): 554.1187; found: 554.1196.

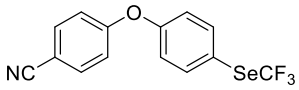
11. General procedures for the trifluoromethylselenolation of arylsulfonoium salts with $[Me_4N][SeCF_3]$.

Procedure A: In a nitrogen-filled glove box, a sealed reaction vial was charge with arylsulfonium salts (**1**, 0.10 mmol), $[Me_4N][SeCF_3]$ (**2**, 35.7 mg, 0.16 mmol, 1.6 equiv), MeCN (0.5 mL), and a teflon magnetic stir bar. The reaction vial was taken out from the glove box and placed into a cooling tank to keep the reaction temperature at around 0 °C. After irradiated with a 5 W blue LED for 12 h, the reaction mixture was concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using mixtures of petroleum ether/ethyl acetate, hexane/THF, or petroleum ether/dichloromethane as eluents to give the corresponding trifluoromethylselenolated product (**3**).

Procedure B: In a nitrogen-filled glove box, a sealed reaction vial was charge with arylsulfonium salts (**1**, 0.10 mmol), $[Me_4N][SeCF_3]$ (**2**, 35.7 mg, 0.16 mmol, 1.6 equiv), MeCN (0.5 mL), and a teflon magnetic stir bar. The reaction vial was taken out from the glove box and irradiated with a 5 W blue LED for 6 h. The reaction mixture was concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using mixtures of petroleum ether/ethyl

acetate, hexane/THF, or petroleum ether/dichloromethane as eluents to give the corresponding trifluoromethylselenolated product (**3**).

4-(4-((Trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**)



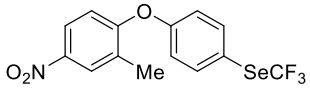
28.2 mg, 82% yield from **Procedure A** using **1d** (52.7 mg, 0.10 mmol), $[Me_4N][SeCF_3]$ (35.7 mg, 0.16 mmol), and MeCN (0.5 mL).

23.2 mg, 69% from **Procedure B** using **1d** (52.7 mg, 0.10 mmol), $[Me_4N][SeCF_3]$ (35.7 mg, 0.16 mmol), and MeCN (0.5 mL).

A mixture of hexane/THF = 50/0 to 50/1 (v/v) as eluents for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dm, *J* = 8.7 Hz, 2H), 7.65 (dm, *J* = 8.9 Hz, 2H), 7.09-7.04 (m, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 157.4, 139.3, 134.4, 122.4 (q, *J* = 333.9 Hz), 120.8, 119.0, 118.5, 118.4, 107.1. IR (KBr): 3098, 3060, 2230, 1604, 1579, 1499, 1482, 1404, 1282, 1244, 1170, 1106, 1070, 1005, 964, 873, 835, 816, 738, 701 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_9F_3NOSe]^+$ ($[M + H]^+$): 343.9796; found: 343.9802.

(4-(2-Methyl-4-nitrophenoxy)phenyl)(trifluoromethyl)selane (**3c**)

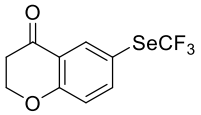


64.1 mg, 85% yield from **Procedure A** using **1i** (112.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 50/0 to 50/1 (v/v) as eluents for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dm, *J* = 2.8 Hz, 1H), 8.05 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.76 (dm, *J* = 8.7 Hz, 2H), 7.01 (dm, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 157.9, 143.6, 139.4, 130.6, 127.0, 123.2, 122.4 (q, *J* = 333.9 Hz), 119.9, 117.8, 117.3, 16.3. IR (KBr): 3075, 2930, 2857, 1724, 1618, 1579, 1521, 1483, 1345, 1281, 1212, 1130, 1096, 1068, 1012, 932, 900, 828, 774, 746, 715, 705 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_{11}F_3NO_3Se]^+$ ($[M + H]^+$): 377.9851; found: 377.9857.

6-((Trifluoromethyl)selanyl)chroman-4-one (**3d**)[13]

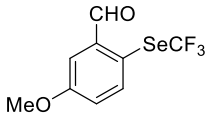


46.7 mg, 79% yield from **Procedure A** using **1j** (96.0 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 40/0 to 40/1 (v/v) as eluents for column chromatography.

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.79 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 4.58 (t, *J* = 6.5 Hz, 2H), 2.84 (t, *J* = 6.5 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 163.2, 144.2, 136.6, 122.3 (q, *J* = 333.9 Hz), 122.0, 119.7, 114.4, 67.2, 37.4.

5-Methoxy-2-((trifluoromethyl)selanyl)benzaldehyde (**3e**)

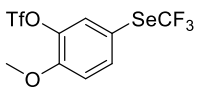


48.7 mg, 86% yield from **Procedure A** using **1k** (93.6 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 50/0 to 50/1 (v/v) as eluents for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 3.0 Hz, 1H), 7.17 (dd, *J* = 8.6, 3.0 Hz, 1H), 3.90 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 161.4, 138.7, 138.1, 122.2 (q, *J* = 333.9 Hz), 121.7, 118.1, 114.9, 55.8. IR (KBr): 3073, 3014, 2943, 2846, 1703, 1588, 1563, 1476, 1384, 1281, 1193, 1100, 1020, 932, 873, 822, 783, 738 cm^{-1}. HRMS-EI (m/z) calcd. for $[C_9H_7F_3O_2{}^{74}Se]$ ([M]): 277.9623; found: 277.9619.

2-Methoxy-5-((trifluoromethyl)selanyl)phenyl trifluoromethanesulfonate (**3f**)



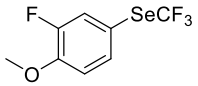
57.2 mg, 71% yield from **Procedure A** using **1l** (117.6 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 50/0 to 50/1 (v/v) as eluents for column

chromatography.

Light yellow solid. M.p.: 60-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 3.96 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.8 (s, 3F), -73.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 138.7, 138.5, 131.3, 122.2 (q, *J* = 333.9 Hz), 118.7 (q, *J* = 320.0 Hz), 113.9, 112.8, 56.4. IR (KBr): 3091, 3022, 2990, 2953, 2851, 2228, 1597, 1499, 1445, 1414, 1302, 1259, 1219, 1154, 1075, 1017, 909, 808, 770, 747, 719 cm^{-1}. HRMS-EI (m/z) calcd. for [$C_9H_6F_6O_4S^{74}Se$] ([M]): 397.9116; found: 397.9110.

(3-Fluoro-4-methoxyphenyl)(trifluoromethyl)selane (**3g**)

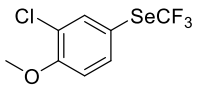


31.7 mg, 58% yield from **Procedure A** using **1m** (91.6 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

Petroleum ether as eluent for column chromatography.

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 6.96 (m, 1H), 3.92 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.9 (s, 3F), -132.8 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9 (d, *J* = 252.0 Hz), 150.0 (d, *J* = 10.1 Hz), 134.1 (d, *J* = 3.8 Hz), 124.8 (q, *J* = 18.9 Hz), 122.4 (q, *J* = 333.9 Hz), 113.9 (d, *J* = 1.3 Hz), 112.5 (d, *J* = 7.6 Hz), 56.2. IR (KBr): 3081, 3019, 2937, 2846, 1602, 1580, 1506, 1444, 1408, 1302, 1272, 1215, 1134, 1096, 1026, 878, 808, 762, 738 cm^{-1}. HRMS-EI (m/z) calcd. for [$C_8H_6F_4O^{74}Se$] ([M]): 267.9580; found: 267.9574.

(3-Chloro-4-methoxyphenyl)(trifluoromethyl)selane (**3h**)[13]

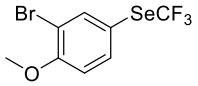


42.0 mg, 72% yield from **Procedure A** using **1n** (94.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

Petroleum ether as eluent for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 138.7, 137.2, 123.4, 122.3 (q, *J* = 333.9 Hz), 113.2, 112.7, 56.3.

(3-Bromo-4-methoxyphenyl)(trifluoromethyl)selane (**3i**)

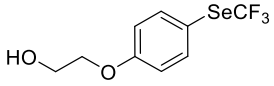


52.3 mg, 78% yield from **Procedure A** using **1o** (103.6 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

Petroleum ether as eluent for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.0 Hz, 1H), 7.65 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 141.6, 137.9, 122.4 (q, *J* = 333.9 Hz), 113.7, 112.6, 112.4, 56.4. IR (KBr): 3068, 3016, 2941, 2844, 1579, 1557, 1482, 1439, 1373, 1293, 1257, 1128, 1099, 1021, 886, 809, 738, 710 cm^{-1}. HRMS-EI (m/z) calcd. for $[C_8H_6BrF_3O^{74}Se]$ ([M]): 327.8779; found: 327.8773.

2-(4-((Trifluoromethyl)selanyl)phenoxy)ethan-1-ol (**3j**)

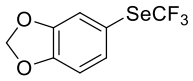


26.4 mg, 46% yield from **Procedure A** using **1p** (109.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 50/0 to 50/1 (v/v) as eluents for column chromatography.

White solid. M.p.: 69-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.11 (t, *J* = 4.5 Hz, 2H), 3.99 (m, 2H), 2.00 (t, *J* = 6.2 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 139.0, 122.5 (q, *J* = 333.9 Hz), 115.7, 113.5, 69.4, 61.3. IR (KBr): 3451, 2935, 2856, 1592, 1571, 1493, 1456, 1382, 1303, 1247, 1180, 1144, 1094, 1005, 942, 894, 836, 812, 735 cm^{-1}. HRMS-EI (m/z) calcd. for $[C_9H_9F_3O_2{}^{74}Se]$ ([M]): 279.9779; found: 279.9774.

5-((Trifluoromethyl)selanyl)benzo[*d*][1,3]dioxole (**3k**)[14]



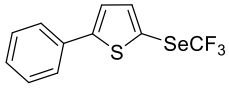
30.0 mg, 56% yield from **Procedure A** using **1q** (90.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 50/0 to 50/1 (v/v) as eluents for column

chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.19 (d, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.02 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 148.4, 132.1, 122.5 (q, *J* = 333.9 Hz), 117.1, 113.7, 109.4, 101.8.

2-Phenyl-5-((trifluoromethyl)selanyl)thiophene (**3l**)

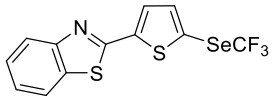


53.0 mg, 86% yield from **Procedure A** using **1r** (98.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

Hexane as eluent for column chromatography.

Light yellow solid. M.p.: 44-46 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dm, *J* = 7.3 Hz, 2H), 7.43-7.40 (m, 3H), 7.35 (tm, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 3.8 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 140.9, 133.3, 129.1, 128.6, 126.1, 124.3, 121.9 (q, *J* = 336.4 Hz), 114.5. IR (KBr): 3094, 2924, 1595, 1489, 1447, 1423, 1326, 1234, 1207, 1166, 1095, 999, 945, 835, 804, 758, 736 cm^{-1}. HRMS-EI (m/z) calcd. for $[C_{11}H_7F_3S^{74}Se]$ ([M]): 301.9445; found: 301.9440.

2-(5-((Trifluoromethyl)selanyl)thiophen-2-yl)benzo[*d*]thiazole (**3m**)



37.8 mg, 52% yield from **Procedure A** using **1s** (109.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), MeCN (1 mL).

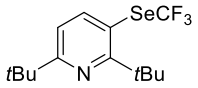
45.7 mg, 63% yield from **Procedure B** using **1s** (109.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 40/0 to 40/1 (v/v) as eluents for column chromatography.

Light yellow solid. M.p.: 120-122 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 3.8 Hz, 1H), 7.50 (tm, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 3.8 Hz, 1H), 7.40 (tm, *J* = 7.6 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 153.6, 145.5, 140.3, 134.8, 128.9,

126.7, 125.8, 123.4, 121.7 (q, J = 336.4 Hz), 121.6, 119.6. IR (KBr): 3085, 3057, 1536, 1475, 1435, 1413, 1313, 1231, 1200, 1140, 1100, 1014, 904, 832, 813, 755, 727, 703 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_7F_3NS_2Se]^+$ ($[M + H]^+$): 365.9132; found: 365.9140.

2,6-Di-*tert*-butyl-3-((trifluoromethyl)selanyl)pyridine (**3n**)



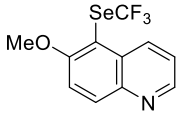
23.7 mg, 47% yield from **Procedure A** using **1t** (78.5 mg, 0.15 mmol), $[Me_4N][SeCF_3]$ (53.5 mg, 0.24 mmol), and MeCN (1 mL).

21.5 mg, 42% yield from **Procedure B** using **1t** (78.5 mg, 0.15 mmol), $[Me_4N][SeCF_3]$ (53.5 mg, 0.24 mmol), MeCN (1 mL).

Hexane as eluent for column chromatography.

Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 1.50 (s, 9H), 1.35 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 167.9, 147.7, 122.4 (q, J = 333.9 Hz), 117.0, 114.7, 40.6, 37.9, 30.5, 30.0. IR (KBr): 3056, 2966, 2930, 2870, 1568, 1478, 1420, 1365, 1262, 1204, 1151, 1096, 1009, 932, 833, 739, 692 cm^{-1}. HRMS-EI (m/z) calcd. for $[C_{14}H_{20}F_3N^{74}Se]$ ([M]): 333.0773; found: 333.0767.

6-Methoxy-5-((trifluoromethyl)selanyl)quinolone (**3o**)



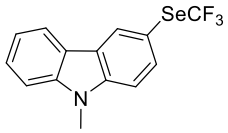
53.1 mg, 86% yield from **Procedure A** using **1u** (98.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 50/0 to 50/1 (v/v) as eluents for column chromatography.

White solid. M.p.: 76-78 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (dd, J = 4.2, 1.5 Hz, 1H), 8.76 (d, J = 8.7 Hz, 1H), 8.26 (d, J = 9.3 Hz, 1H), 7.57 (d, J = 9.3 Hz, 1H), 7.46 (dd, J = 8.6, 4.2 Hz, 1H), 4.04 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -34.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 148.7, 144.3, 135.6, 135.2, 132.3, 122.7, 122.3 (q, J = 336.4 Hz), 116.1, 106.5, 57.0. IR (KBr): 3069, 2969, 2943, 2844, 1605, 1586, 1499, 1463, 1322, 1260, 1188, 1101, 1059, 966, 894, 808, 768, 735, 720 cm^{-1}.

HRMS-EI (m/z) calcd. for [$C_{11}H_8F_3NO^{74}Se$] ([M]): 300.9783; found: 300.9777.

9-Methyl-3-((trifluoromethyl)selanyl)-9*H*-carbazole (**3p**)



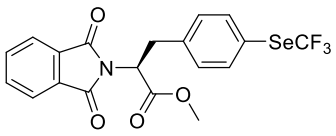
20.2 mg, 31% yield from **Procedure A** using **1v** (102.6 mg, 0.20 mmol), [Me_4N][$SeCF_3$] (71.4 mg, 0.32 mmol), MeCN (2 mL), 24 hours.

38.7 mg, 59% yield from **Procedure B** using **1w** (109.8 mg, 0.20 mmol), [Me_4N][$SeCF_3$] (71.4 mg, 0.32 mmol), MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 40/0 to 40/1 (v/v) as eluents for column chromatography.

White solid. M.p.: 106-108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.5 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.82 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.53 (tm, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.30 (tm, *J* = 7.5 Hz, 1H), 3.86 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 141.3, 134.5, 130.1, 126.6, 124.0, 122.7 (q, *J* = 335.2 Hz), 122.1, 120.6, 119.8, 111.1, 109.5, 108.8, 29.2. IR (KBr): 3054, 2940, 2874, 1589, 1496, 1458, 1355, 1315, 1274, 1244, 1157, 1100, 1006, 883, 801, 749, 734 cm^{-1}. HRMS-EI (m/z) calcd. for [$C_{14}H_{10}F_3N^{74}Se$] ([M]): 322.9990; found: 322.9985.

Methyl (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-((trifluoromethyl)selanyl)phenyl)propanoate (**3q**)



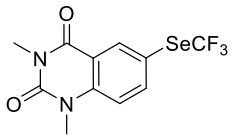
52.9 mg, 58% yield from **Procedure A** using **1x** (128.2 mg, 0.20 mmol), [Me_4N][$SeCF_3$] (71.4 mg, 0.32 mmol), and MeCN (1 mL). The molar ratio of the *para*-/*ortho*-isomers was found to be > 7.7:1 according to the NMR data.

A mixture of petroleum ether/methyl *t*-butyl ether = 30/1 to 10/1 (v/v) as eluents for column chromatography.

Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, for the *para*-isomer) δ 7.80 (m, 2H), 7.72 (m, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.18 (m, 1H), 3.80 (s, 3H),

3.66-3.56 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$, for the *para*-isomer) δ -36.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$, for the *para*-isomer) δ 169.0, 167.4, 139.5, 137.3, 134.3, 134.2, 131.5, 130.2, 123.6, 122.4 (q, *J* = 333.9 Hz), 53.0, 52.8, 34.5. IR (KBr): 3062, 3031, 2955, 2926, 2849, 1777, 1749, 1717, 1614, 1594, 1469, 1437, 1388, 1309, 1246, 1202, 1101, 1071, 1015, 919, 884, 808, 738, 720, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{15}F_3NO_4Se]^+$ ($[M + H]^+$): 458.0113; found: 458.0120.

1,3-Dimethyl-6-((trifluoromethyl)selanyl)quinazoline-2,4(1*H*,3*H*)-dione (**3r**)

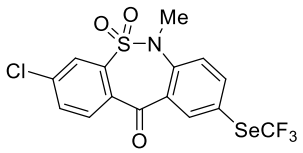


62.9 mg, 93% yield from **Procedure A** using **1y** (104.4 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), MeCN (1 mL).

A mixture of petroleum ether/THF = 10/1 to 6/1 (v/v) as eluents for column chromatography.

Light yellow solid. M.p.: 103-105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (m, 1H), 7.99 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 3.61 (s, 3H), 3.47 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 150.9, 143.3, 141.9, 137.9, 122.3 (q, *J* = 333.9 Hz), 116.3, 116.1, 114.9, 31.0, 28.7. IR (KBr): 3087, 3045, 2959, 2892, 1709, 1662, 1601, 1581, 1493, 1424, 1363, 1312, 1241, 1129, 1001, 871, 821, 781, 738, 719, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_9F_3N_2NaO_2Se]^+$ ($[M + Na]^+$): 360.9674; found: 360.9673.

3-Chloro-6-methyl-9-((trifluoromethyl)selanyl)dibenzo[*c*,*f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide (**3s**)



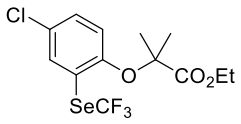
82.0 mg, 90% yield from **Procedure B** using **1z** (127.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 40/1 to 30/1 (v/v) as eluents for column chromatography.

Yellow solid. M.p.: 125-127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.5 Hz,

1H), 7.97 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.70 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 3.42 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.6, 143.0, 142.6, 140.5, 139.0, 138.3, 134.1, 133.6, 133.2, 131.0, 125.1, 124.8, 122.3 (q, *J* = 332.6 Hz), 119.7, 38.6. IR (KBr): 3091, 2959, 2871, 1661, 1585, 1469, 1431, 1364, 1287, 1231, 1137, 1088, 950, 890, 820, 770, 737, 702, 681 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_9ClF_3NNaO_3SSe]^+$ ([M + Na])$^+$: 477.9001; found: 477.9002.

Ethyl 2-(4-chloro-2-((trifluoromethyl)selanyl)phenoxy)-2-methylpropanoate (**3t**)

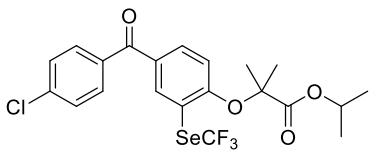


57.4 mg, 74% yield from **Procedure A** using **1aa** (114.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/THF = 60/0 to 60/1 (v/v) as eluents for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.4 Hz, 1H), 7.23 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.63 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -34.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 153.5, 135.1, 130.3, 127.4, 122.5 (q, *J* = 333.9 Hz), 121.8, 117.6, 80.8, 61.8, 25.1, 14.0. IR (KBr): 3074, 2990, 2876, 1739, 1579, 1470, 1385, 1283, 1243, 1138, 1099, 1023, 969, 910, 816, 768, 738, 721 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{14}ClF_3NaO_3Se]^+$ ([M + Na]$^+$): 412.9641; found: 412.9641.

Isopropyl
2-(4-(4-chlorobenzoyl)-2-((trifluoromethyl)selanyl)phenoxy)-2-methylpropanoate
(**3u**)

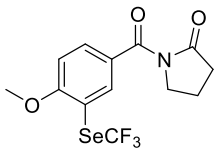


86.7 mg, 85% yield from **Procedure A** using **1ab** (138.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/THF = 30/0 to 30/1 (v/v) as eluents for column chromatography.

Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.8 Hz, 1H), 7.79 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 1H), 5.08 (m, 1H), 1.71 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -34.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 172.5, 159.0, 139.2, 138.9, 135.7, 133.1, 131.2, 130.9, 128.7, 122.5 (q, *J* = 333.9 Hz), 115.4, 115.0, 81.0, 69.6, 25.2, 21.5. IR (KBr): 3068, 2985, 2877, 1734, 1659, 1589, 1482, 1387, 1269, 1148, 1098, 1015, 944, 848, 760, 739, 700 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{21}ClF_3O_4Se]^+$ ($[M + H]^+$): 509.0240; found: 509.0245.

1-(4-Methoxy-3-((trifluoromethyl)selanyl)benzoyl)pyrrolidin-2-one (**3v**)

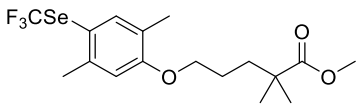


46.9 mg, 64% yield from **Procedure A** using **1ac** (112.0 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/dichloromethane = 1/10 to 1/20 (v/v) as eluents for column chromatography.

Light yellow solid. M.p.: 76-78 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 3.95-3.92 (m, 5H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.14 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 168.8, 162.2, 139.4, 134.0, 127.2, 122.4 (q, *J* = 333.9 Hz), 111.8, 110.2, 56.4, 46.7, 33.3, 17.7. IR (KBr): 3088, 2989, 2844, 1745, 1660, 1595, 1562, 1491, 1397, 1360, 1232, 1124, 1101, 1015, 919, 834, 767, 736, 694 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{13}F_3NO_3Se]^+$ ($[M + H]^+$): 368.0007; found: 368.0009.

Methyl 5-(2,5-dimethyl-4-((trifluoromethyl)selanyl)phenoxy)-2,2-dimethylpentanoate (**3w**)



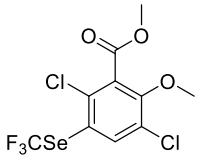
55.7 mg, 68% yield from **Procedure A** using **1ad** (119.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), MeCN (1 mL).

A mixture of petroleum ether/dichloromethane = 10/1 to 2/1 (v/v) as eluents for

column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 6.73 (s, 1H), 3.95 (t, *J* = 5.9 Hz, 2H), 3.66 (s, 3H), 2.51 (s, 3H), 2.18 (s, 3H), 1.78-1.69 (m, 4H), 1.22 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 159.3, 142.7, 141.1, 125.6, 122.7 (q, *J* = 335.2 Hz), 113.3, 112.7, 68.0, 51.8, 42.1, 37.0, 25.2, 25.0, 23.5, 15.5. IR (KBr): 2981, 2953, 2928, 2874, 1732, 1601, 1563, 1497, 1474, 1386, 1366, 1309, 1249, 1198, 1124, 1097, 1018, 991, 843, 802, 774, 737 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{23}F_3NaO_3Se]^+$ ($[M + Na]^+$): 435.0657; found: 435.0666.

Methyl 2,5-dichloro-6-methoxy-3-((trifluoromethyl)selanyl)benzoate (**3x**)



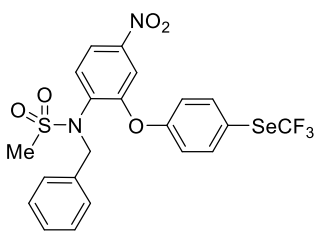
31.0 mg, 41% yield from **Procedure A** using **1ae** (113.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

24.9 mg, 33% yield from **Procedure B** using **1ae** (113.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/ethyl acetate = 40/0 to 40/1 (v/v) as eluents for column chromatography.

Light yellow solid. M.p.: 58-60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -34.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 155.6, 139.9, 134.9, 131.5, 127.3, 122.2 (q, *J* = 333.9 Hz), 120.0, 62.4, 53.2. IR (KBr): 3079, 3019, 2960, 2951, 2883, 2848, 1745, 1560, 1461, 1404, 1266, 1168, 1126, 1098, 1008, 965, 894, 862, 795, 736 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{10}H_8Cl_2F_3O_3Se]^+$ ($[M + H]^+$): 382.8962; found: 382.8970.

N-Benzyl-*N*-(4-nitro-2-(4-((trifluoromethyl)selanyl)phenoxy)phenyl)methanesulfonamide (**3y**)



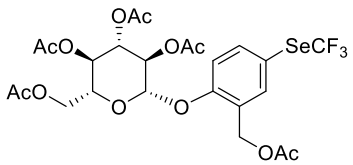
12.4 mg, 11% yield from **Procedure A** using **1af** (146.0 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

78.4 mg, 72% yield from **Procedure A** using **1af** (146.0 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (2 mL), and the reaction run for 24 h.

A mixture of petroleum ether/ethyl acetate = 10/1 to 5/1 (v/v) as eluents for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.81 (m, 3H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.26 (m, 5H), 7.05 (dm, *J* = 7.4 Hz, 2H), 4.87 (s, 2H), 3.04 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 154.4, 147.9, 139.7, 135.2, 135.1, 134.1, 128.8, 128.4, 122.4 (q, *J* = 333.9 Hz), 120.5, 118.8, 118.8, 118.7, 113.4, 54.2, 40.6. IR (KBr): 3089, 3034, 2935, 2860, 2259, 1734, 1583, 1528, 1486, 1418, 1347, 1247, 1215, 1153, 1099, 1012, 911, 843, 795, 737, 702 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{18}F_3N_2O_5SSe]^+$ ($[M + H]^+$): 547.0048; found: 547.0059.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(Acetoxymethyl)-6-(2-(acetoxymethyl)-4-((trifluoromethyl)selanyl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3z**)



30.2 mg, 47% yield from **Procedure A** using **1ag** (82.8 mg, 0.10 mmol), $[Me_4N][SeCF_3]$ (35.7 mg, 0.16 mmol), MeCN (0.5 mL).

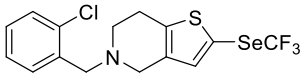
30.5 mg, 47% yield from **Procedure B** using **1ag** (82.8 mg, 0.10 mmol), $[Me_4N][SeCF_3]$ (35.7 mg, 0.16 mmol), MeCN (0.5 mL).

A mixture of petroleum ether/ethyl acetate/dichloromethane = 10/3/0 to 10/3/2 (v/v/v) as eluents for column chromatography.

Light yellow solid. M.p.: 74-76 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.9 Hz, 1H), 7.64 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 5.33-5.28 (m, 2H), 5.21-5.10 (m, 3H), 5.02 (d, *J* = 13.4 Hz, 1H), 4.27 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.18 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.89 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 170.5, 170.2, 169.4, 169.3, 155.9, 138.4, 138.0, 127.8, 122.4 (q, *J* =

332.6 Hz), 116.2, 116.2, 98.7, 72.5, 72.2, 70.9, 68.2, 61.8, 60.3, 20.9, 20.6, 20.6. IR (KBr): 3019, 2964, 2947, 2893, 2848, 1743, 1647, 1594, 1579, 1486, 1434, 1379, 1229, 1127, 1097, 1046, 982, 922, 895, 827, 726, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{24}H_{27}F_3NaO_{12}Se]^+$ ([M + Na]$^+$): 667.0512; found: 667.0518.

5-(2-Chlorobenzyl)-2-((trifluoromethyl)selanyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine (**3aa**)



25.2 mg, 31% yield from **Procedure A** using **1ah** (119.0 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

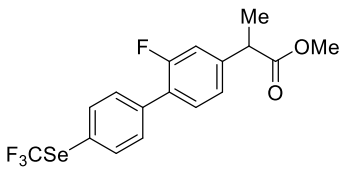
25.8 mg, 31% yield from **Procedure B** using **1ah** (119.0 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

60.5 mg, 74% yield from **Procedure B** using **1ai** (126.2 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/dichloromethane = 5/1 to 2/1 (v/v) as eluents for column chromatography.

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.27-7.19 (m, 2H), 7.04 (s, 1H), 3.83 (s, 2H), 3.63 (s, 2H), 2.93 (t, *J* = 5.2 Hz, 2H), 2.87 (t, *J* = 5.3 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 138.2, 135.8, 135.8, 134.3, 130.7, 129.6, 128.4, 126.8, 121.8 (q, *J* = 336.4 Hz), 112.5, 58.5, 52.5, 50.3, 25.8. IR (KBr): 3066, 2925, 2839, 1682, 1572, 1462, 1443, 1362, 1290, 1234, 1137, 1097, 1036, 947, 906, 844, 753, 738 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}ClF_3NSSe]^+$ ([M + H]$^+$): 411.9647; found: 411.9647.

Methyl 2-(2-fluoro-4'-((trifluoromethyl)selanyl)-[1,1'-biphenyl]-4-yl)propanoate (**3ab**)

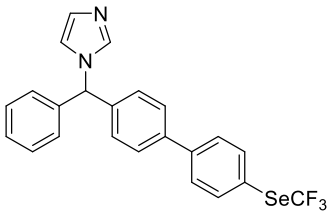


64.0 mg, 79% yield from **Procedure A** using **1aj** (118.0 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/THF = 40/0 to 40/1 (v/v) as eluents for column chromatography.

Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.55 (dm, *J* = 8.2 Hz, 2H), 7.39 (m, 1H), 7.19-7.14 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.9 (s, 3F), -117.2 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 159.7 (d, *J* = 250.7 Hz), 142.8 (d, *J* = 7.6 Hz), 137.7, 137.0, 130.7 (d, *J* = 3.8 Hz), 130.1 (d, *J* = 2.5 Hz), 126.5 (d, *J* = 12.6 Hz), 123.8 (d, *J* = 3.8 Hz), 122.6 (q, *J* = 333.9 Hz), 121.8, 115.5 (d, *J* = 22.7 Hz), 52.3, 45.0, 18.4. IR (KBr): 3064, 3034, 2985, 2954, 2880, 2845, 1739, 1625, 1574, 1515, 1485, 1462, 1429, 1392, 1334, 1199, 1101, 1007, 921, 876, 843, 739, 723 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{14}F_4NaO_2Se]^+$ ($[M + Na]^+$): 428.9987; found: 428.9987.

1-(Phenyl(4'-((trifluoromethyl)selanyl)-[1,1'-biphenyl]-4-yl)methyl)-1*H*-imidazole (**3ac**)



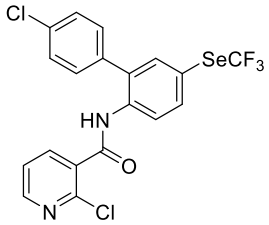
51.0 mg, 56% yield from **Procedure A** using **1ak** (128.4 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/dichloromethane/ethyl acetate = 10/10/3 as eluents for column chromatography.

Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) 7.81 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 4H), 7.54 (s, 1H), 7.41-7.37 (m, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.16-7.14 (m, 3H), 6.90 (m, 1H), 6.58 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 140.0, 138.7, 138.6, 137.5, 129.1, 128.7, 128.6, 128.2, 128.1, 127.7, 122.5 (q, *J* = 328.9 Hz), 121.8, 121.8, 119.5, 65.0. IR (KBr): 3060, 3031, 2958, 2926, 1706, 1589, 1485, 1453, 1390, 1224, 1100, 1073, 1004, 905, 822, 738, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{23}H_{18}F_3N_2Se]^+$ ($[M + H]^+$): 459.0582; found: 459.0585.

2-Chloro-*N*-(4'-chloro-5-((trifluoromethyl)selanyl)-[1,1'-biphenyl]-2-yl)nicotinamide

(**3ad**)

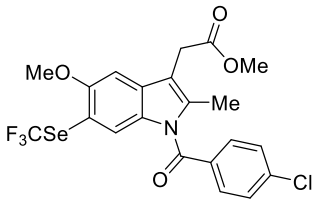


69.7 mg, 71% yield from **Procedure A** using **1al** (134.8 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (1 mL).

A mixture of petroleum ether/dichloromethane = 1/1 to 2/3 (v/v) as eluents for column chromatography.

Pale solid. M.p.: 164-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) 8.56 (d, *J* = 8.6 Hz, 1H), 8.43 (dd, *J* = 4.7, 2.0 Hz, 1H), 8.35 (brs, 1H), 8.15 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.81 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.46 (dm, *J* = 8.5 Hz, 2H), 7.37-7.32 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 151.6, 146.6, 140.4, 138.6, 137.7, 136.7, 135.2, 134.7, 132.9, 130.8, 130.6, 129.6, 123.0, 122.4 (q, *J* = 332.6 Hz), 122.3, 118.1. IR (KBr): 3222, 3084, 3002, 2924, 1669, 1574, 1558, 1512, 1470, 1405, 1381, 1308, 1275, 1148, 1101, 1078, 1011, 899, 853, 779, 737, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{12}Cl_2F_3N_2OSe]^+$ ([M + H]$^+$): 490.9439; found: 490.9441.

Methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-6-((trifluoromethyl)selanyl)-1*H*-indol-3-yl)acetate (**3ae**)



17.8 mg, 17% yield from **Procedure A** using **1am** (140.6 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (2 mL).

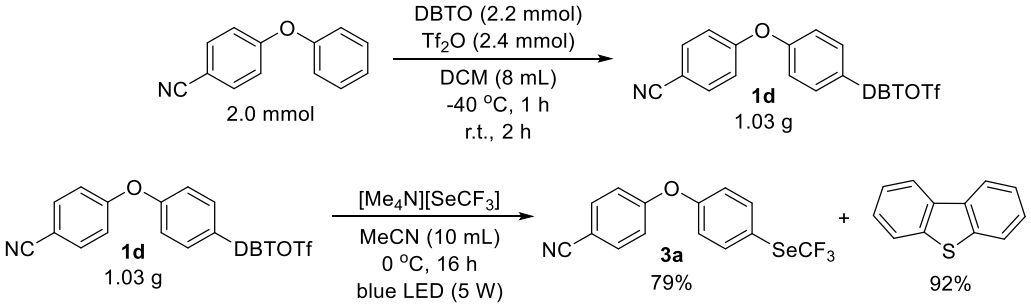
55.0 mg, 53% yield from **Procedure B** using **1am** (140.6 mg, 0.20 mmol), $[Me_4N][SeCF_3]$ (71.4 mg, 0.32 mmol), and MeCN (2 mL).

A mixture of petroleum ether/ethyl acetate = 20/1 to 15/1 (v/v) as eluents for column chromatography.

Light yellow solid. M.p.: 129-131 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 7.64 (d, *J* = 8.5

Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.36 (s, 1H), 7.14 (s, 1H), 3.89 (s, 3H), 3.73 (s, 2H), 3.67 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -37.2 (s, 3F). ^{13}C NMR (126 MHz, CD_3CN) δ 171.7, 168.6, 156.1, 139.3, 138.6, 134.5, 133.8, 131.8, 131.1, 129.7, 124.0, 123.3 (q, *J* = 332.6 Hz), 113.4, 107.7, 101.1, 56.8, 52.2, 29.7, 13.4. IR (KBr): 2994, 2965, 2952, 2928, 2849, 1732, 1684, 1598, 1464, 1418, 1398, 1344, 1305, 1264, 1225, 1126, 1100, 1014, 976, 910, 875, 843, 756, 712 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{17}ClF_3NNaO_4Se]^+$ ($[M + Na]^+$): 541.9856; found: 541.9856.

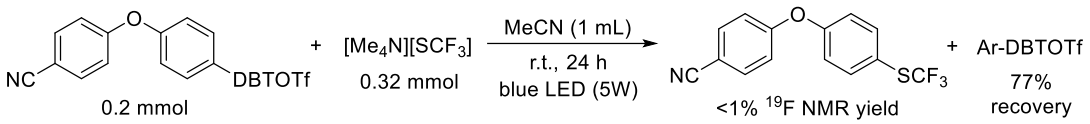
12. An example of the scale-up C-H trifluoromethylselenolation



Under a N_2 atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 0.40 mL, 2.4 mmol) was added to a mixture of 4-phenoxybenzonitrile (390 mg, 2.0 mmol) and dibenzo[*b*,*d*]thiophene 5-oxide (440 mg, 2.2 mmol) in DCM (8 mL) at -40 °C with stirring. The mixture was reacted at -40 °C for 1 h, warmed to room temperature for 2 h, diluted with DCM (40 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of DCM / MeOH (20/0 to 20/1 (v/v)) as eluents to give 1.03 g of **1d** as a white solid.

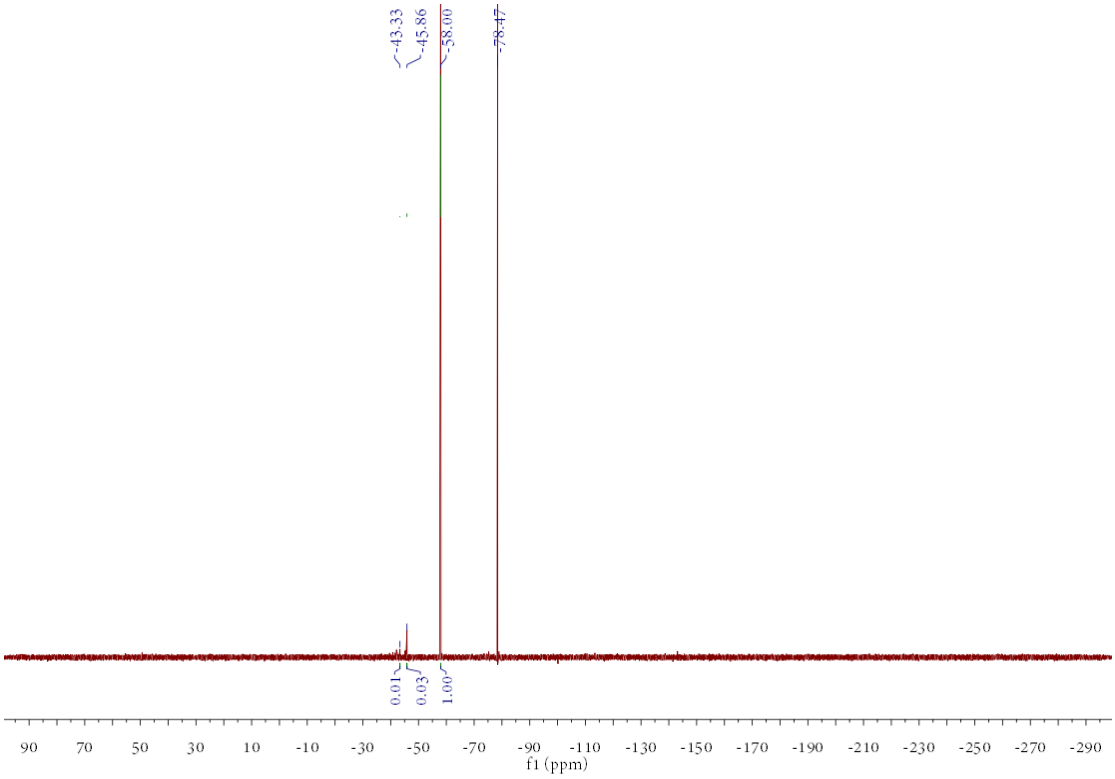
In a nitrogen-filled glove box, a sealed round bottom flask was charge with **1d** (1.03 g), $[Me_4N][SeCF_3]$ (713.6 mg, 3.2 mmol), MeCN (10 mL), and a teflon magnetic stir bar. The flask was taken out from the glove box and placed into a cooling tank to keep the reaction temperature at around 0 °C. After irradiated with a 5 W blue LED for 16 h, the mixture was concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether as eluent to give 542 mg of 4-(4-((trifluoromethyl)selanyl)phenoxy)benzonitrile (**3a**, 79%) with recovery of 340 mg of dibenzo[*b*,*d*]thiophene (92%).

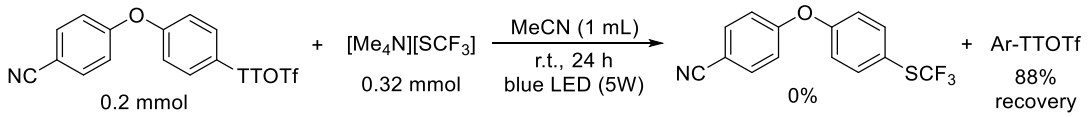
13. Experiments for the catalyst-free trifluoromethylthiolation of arylsulfonium salt with [Me$_4$N][SCF$_3$]



Only trace amount of 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile was detected by both ^{19}F NMR and HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) analysis of the reaction mixture using pure 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile (δ -43.1 ppm, t_R = 12.46 min) as an external standards.

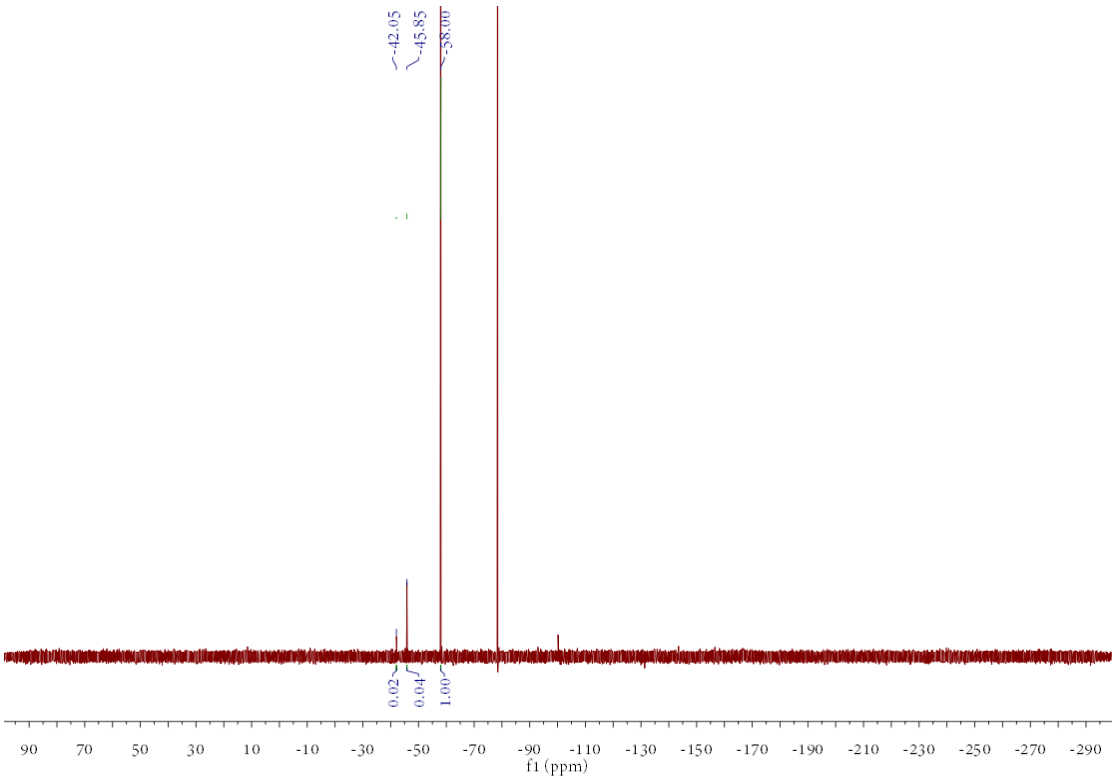
The ^{19}F NMR spectrum of the above reaction mixture using PhOCF$_3$ (29.1 mg, 0.18 mmol) as an internal standard.



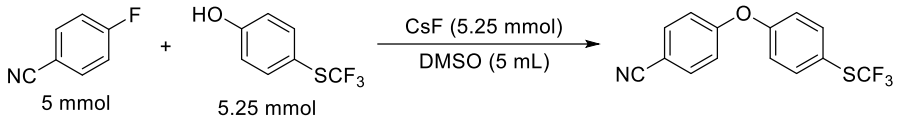


None of 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile (0%) was detected by both ^{19}F NMR and HPLC (λ = 250 nm, water / methanol = 20 / 80 (v / v)) analysis of the reaction mixture using pure 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile (δ -43.1 ppm, t_R = 12.46 min) as an external standards.

The ^{19}F NMR spectrum of the above reaction mixture using $PhOCF_3$ (28.0 mg, 0.17 mmol) as an internal standard.



Synthesis of 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile by other method



Under an ambient atmosphere, CsF (798 mg, 5.25 mmol) was added to a mixture of 4-fluorobenzonitrile (605 mg, 5.00 mmol) and 4-((trifluoromethyl)thio)phenol (1.02 g, 5.25 mmol) in DMSO (5 mL). The mixture was reacted at 110 ^oC overnight, cooled to room temperature, diluted with ethyl acetate (20 mL), and washed with water (3 × 50 mL). The aqueous phases were extracted with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether/ethyl acetate = 40/1 (v/v) as eluents to give 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile as a white solid (1.4 g, 95%). M.p.: 72-74 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.69-7.65 (m, 4H), 7.09 (d, J = 8.6 Hz, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 157.8, 138.6, 134.4, 129.4 (q, J = 308.7 Hz), 120.5, 119.9, 119.1, 118.5, 107.3. IR (KBr): 3098, 3061, 3048, 2230, 1605, 1582, 1500, 1484, 1410, 1282, 1245, 1119,

1007, 874, 837, 755, 740, 713 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_8F_3NNaOS]^+$ ($[M + Na]^+$): 318.0171; found: 318.0170.

Note: The product obtained from this procedure was used as a standard reference for the analysis of the above reaction mixtures.

Reference

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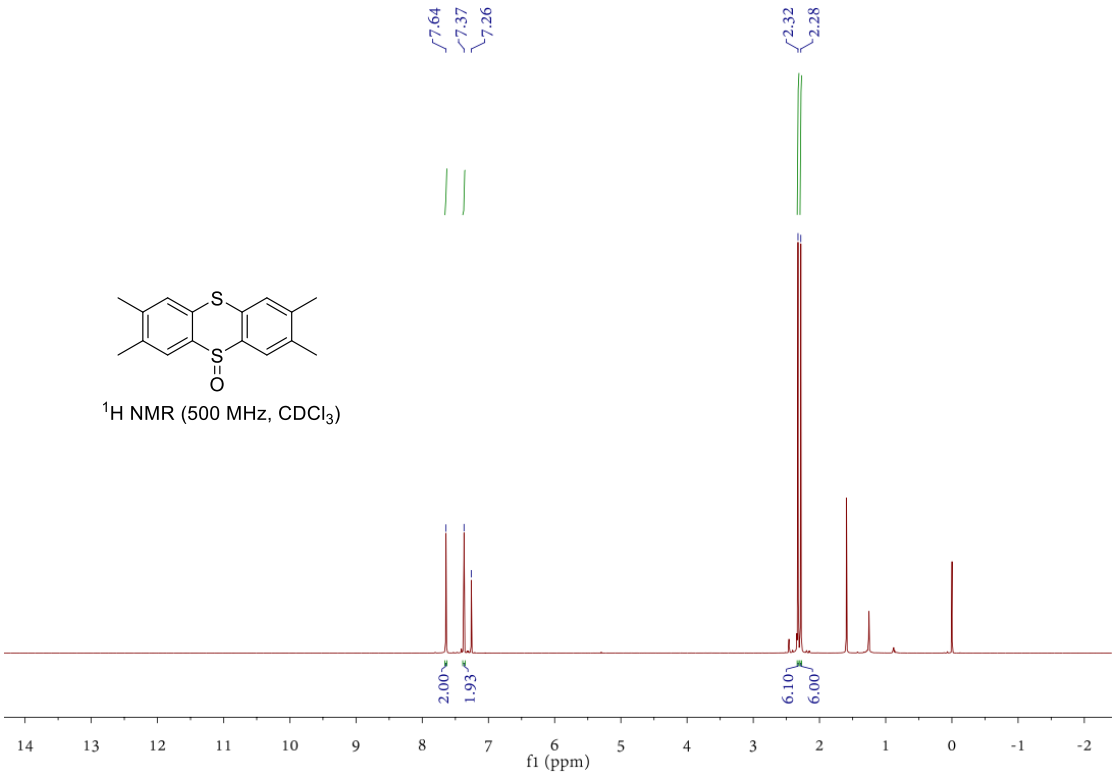
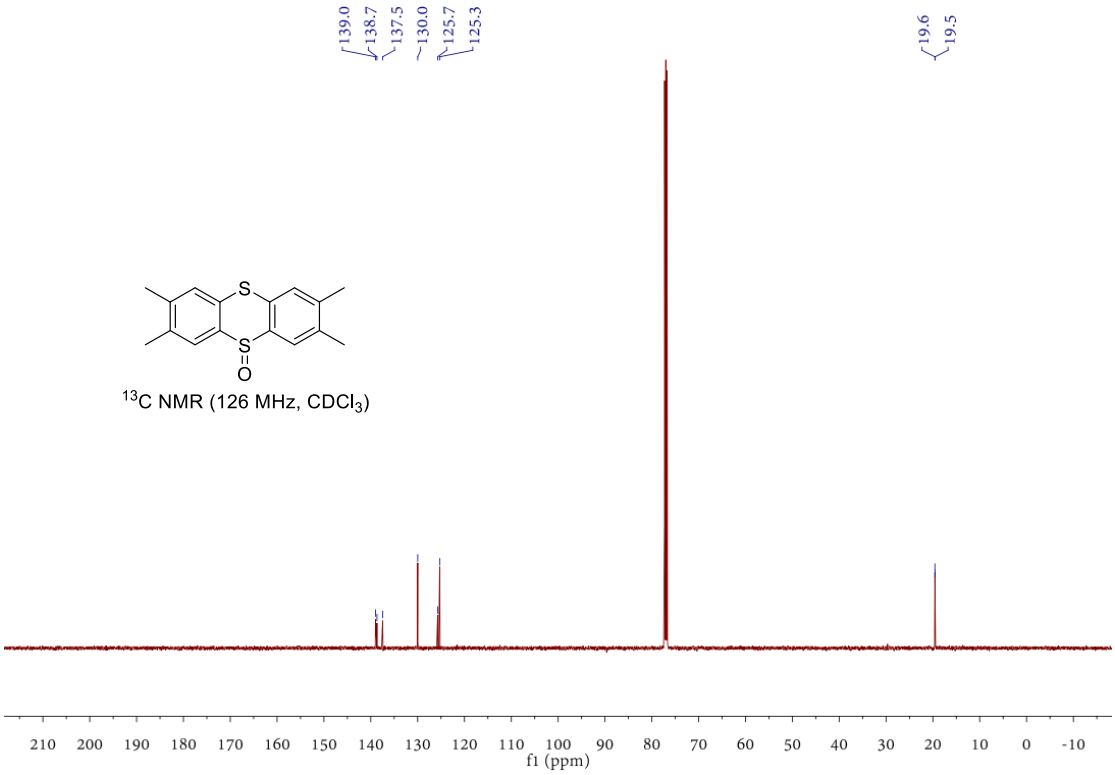
14. NMR spectra of the products

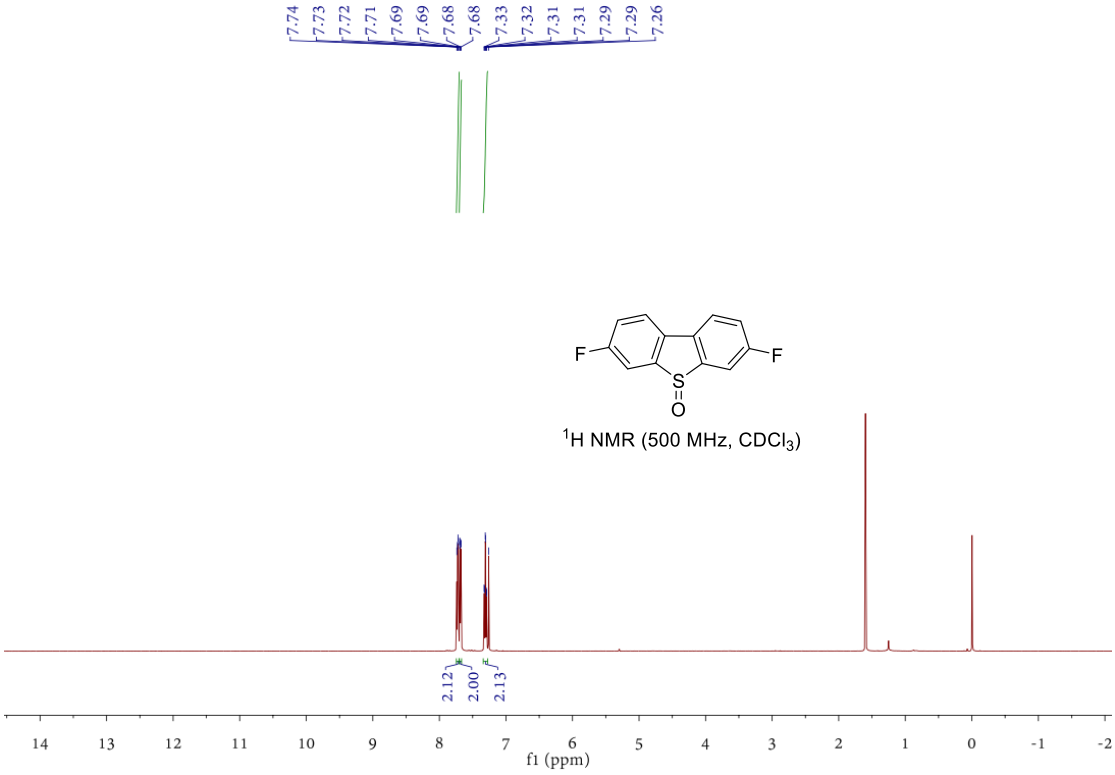
^{1}H NMR spectrum of 2,3,7,8-tetramethylthianthrene 5-oxide (TMTO)



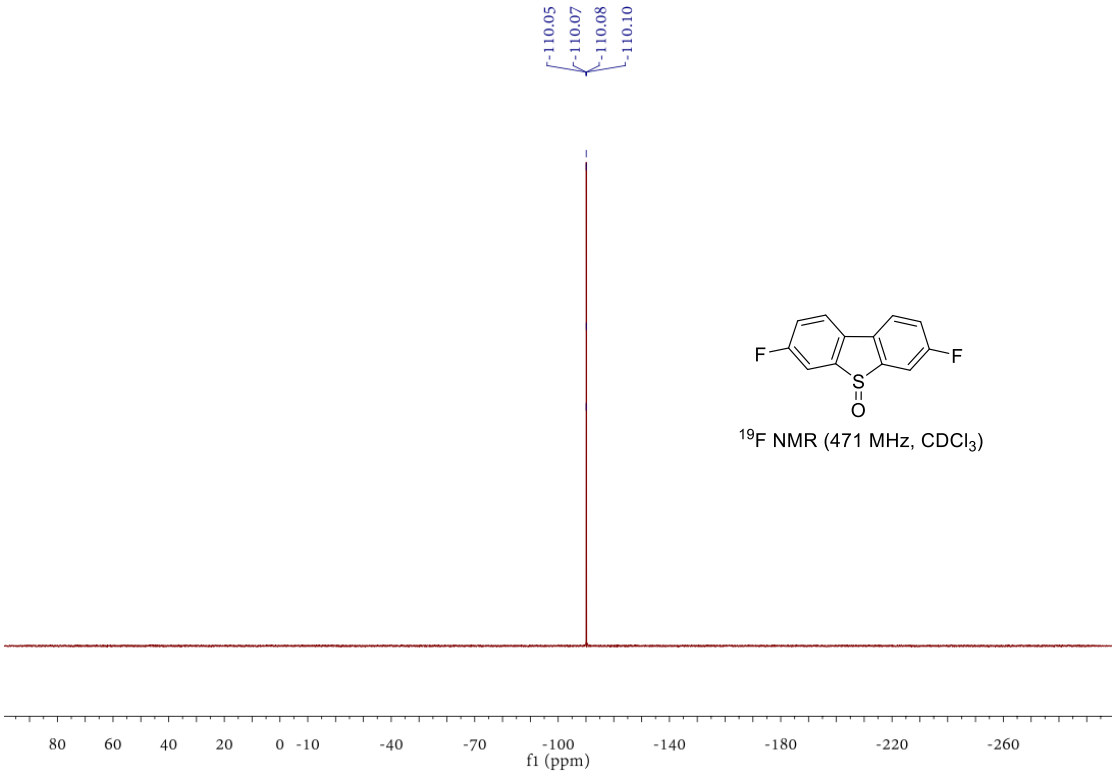
^{13}C NMR spectrum of 2,3,7,8-tetramethylthianthrene 5-oxide (TMTO)



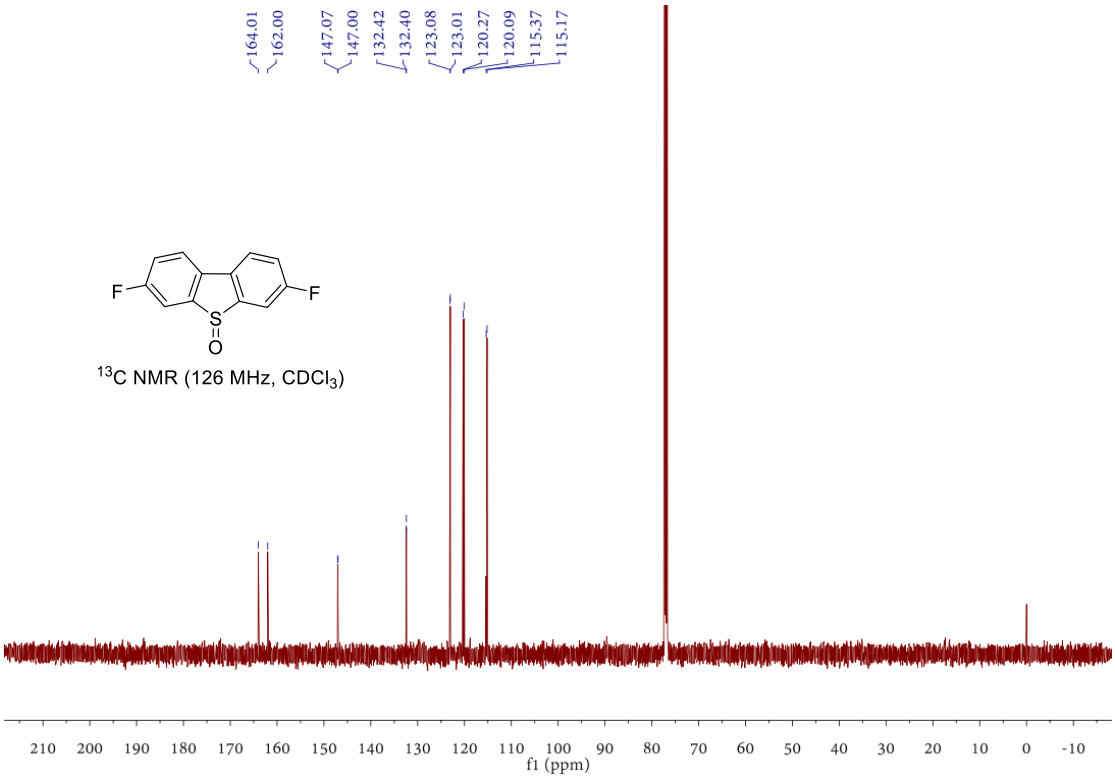
^{1}H NMR spectrum of 3,7-difluorodibenzo-[*b*,*d*]thiophene 5-oxide (2F-DBTO)



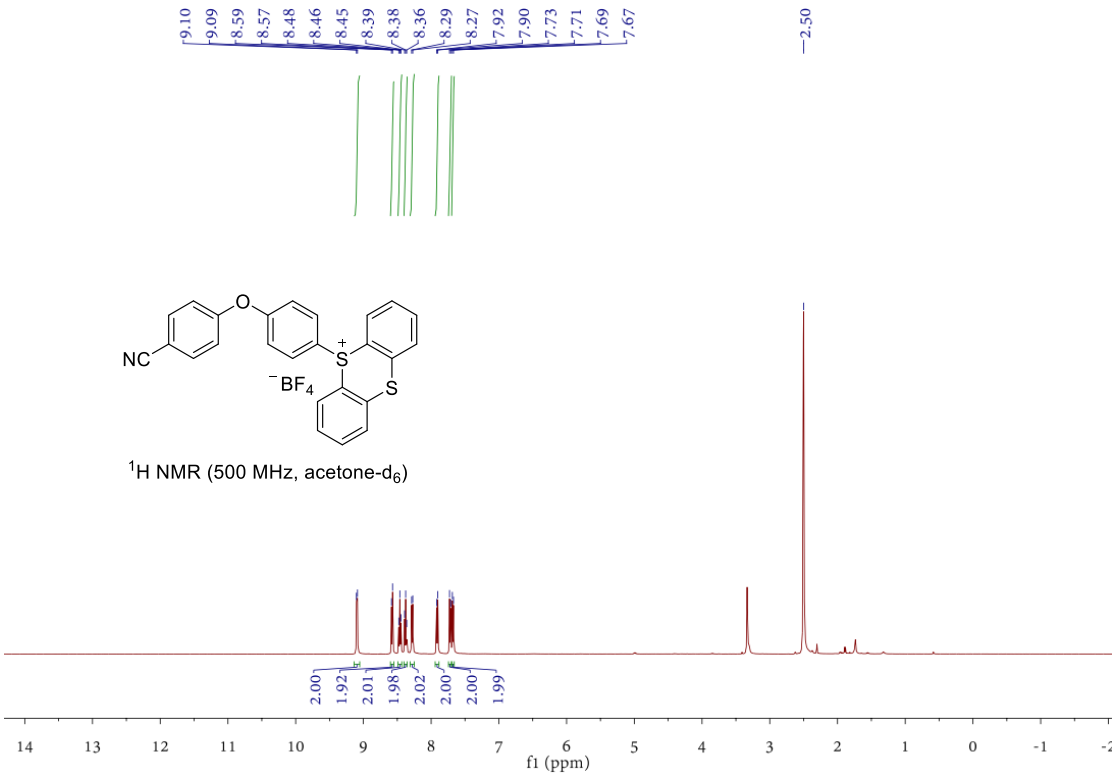
^{19}F NMR spectrum of 3,7-difluorodibenzo-[*b*,*d*]thiophene 5-oxide (2F-DBTO)



^{13}C NMR spectrum of 3,7-difluorodibenzo-[*b*,*d*]thiophene 5-oxide (2F-DBTO)



^{1}H NMR spectrum of **1a**-BF_4



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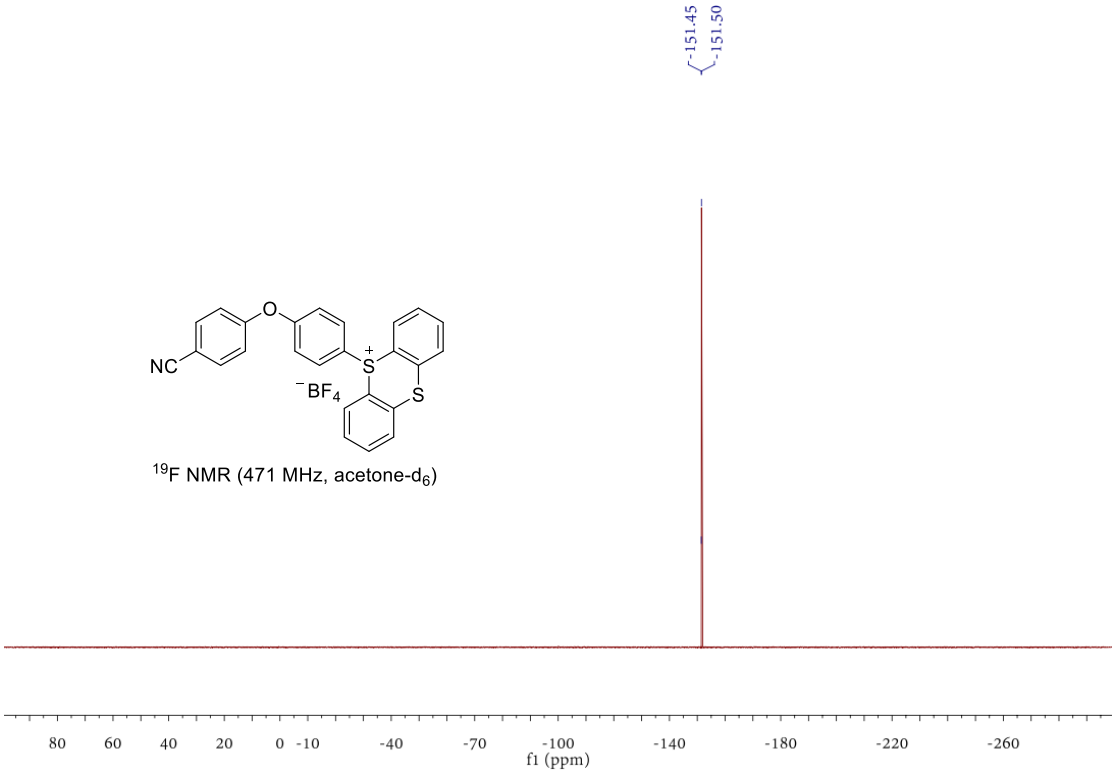
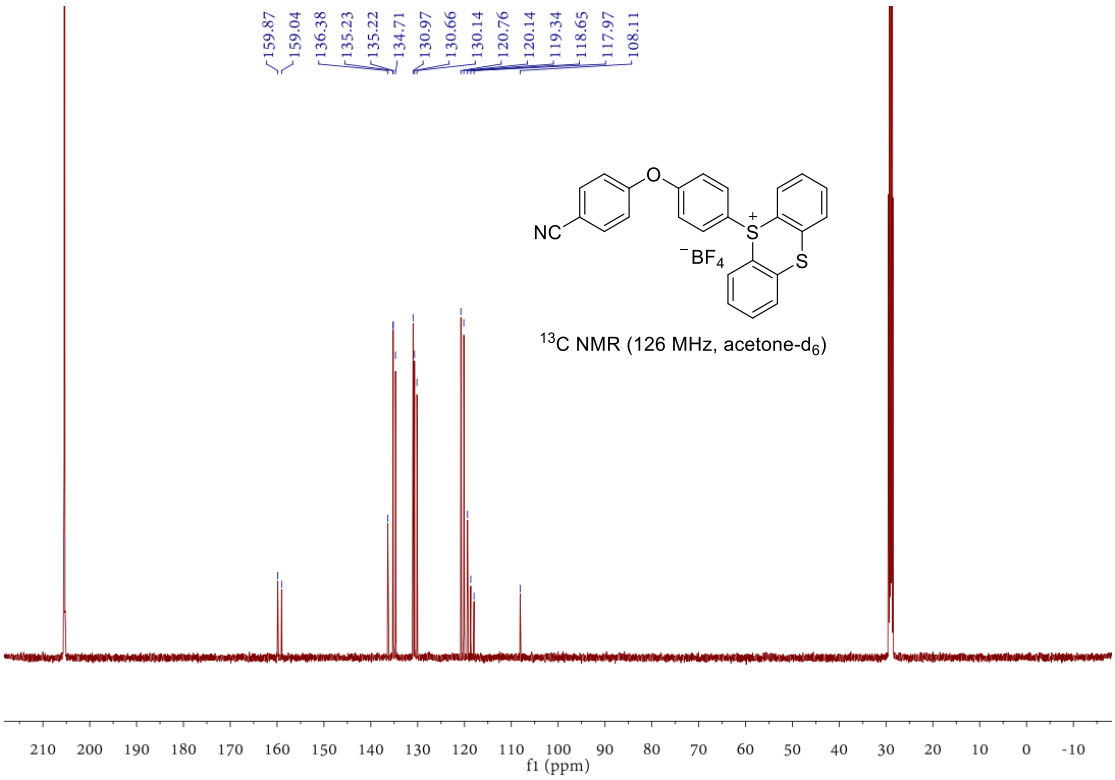
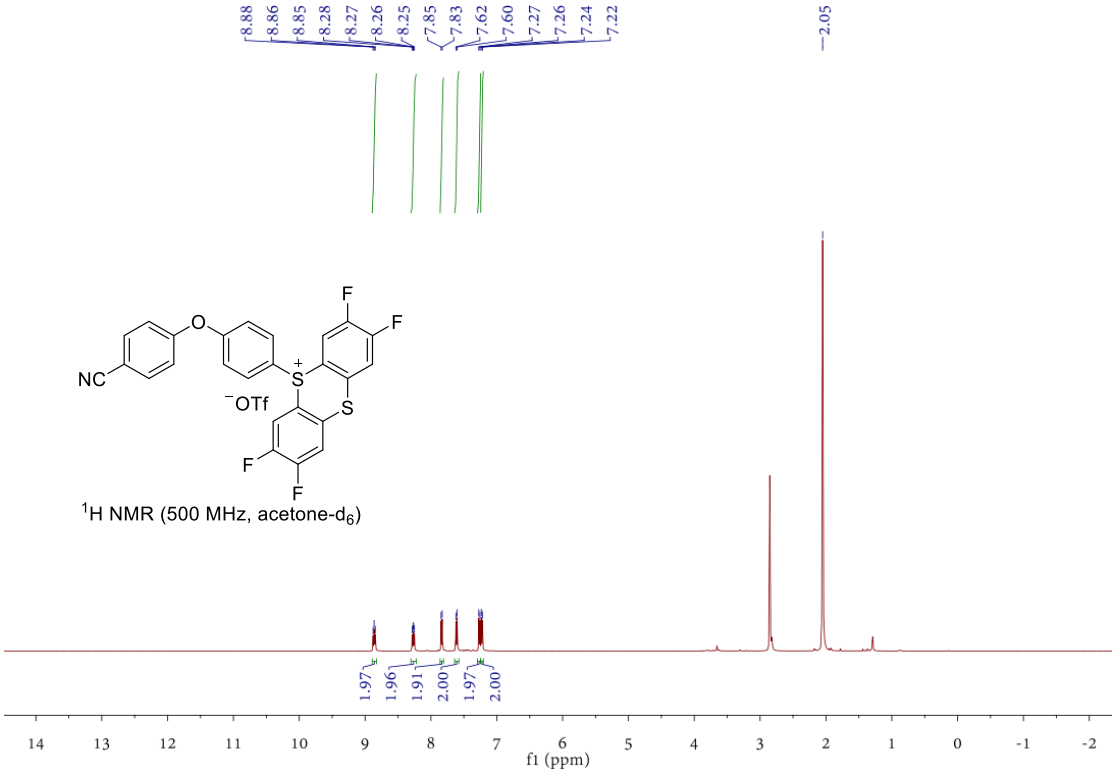


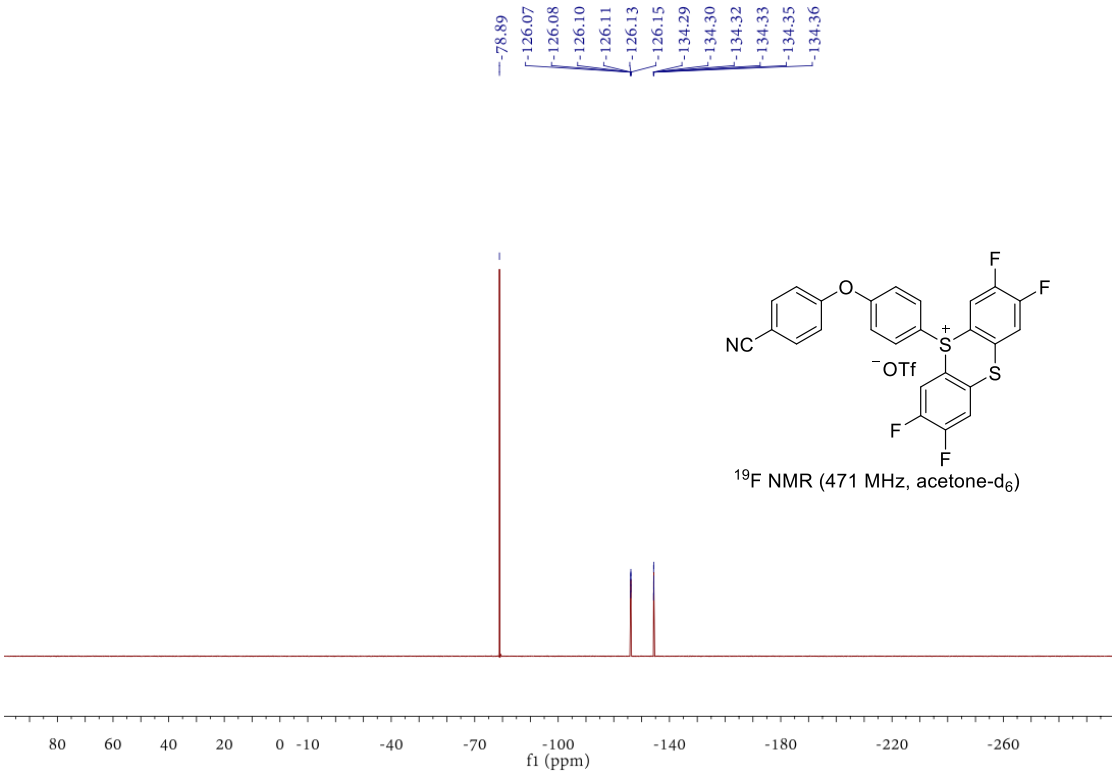
^{13}C NMR spectrum of **1a**-BF_4



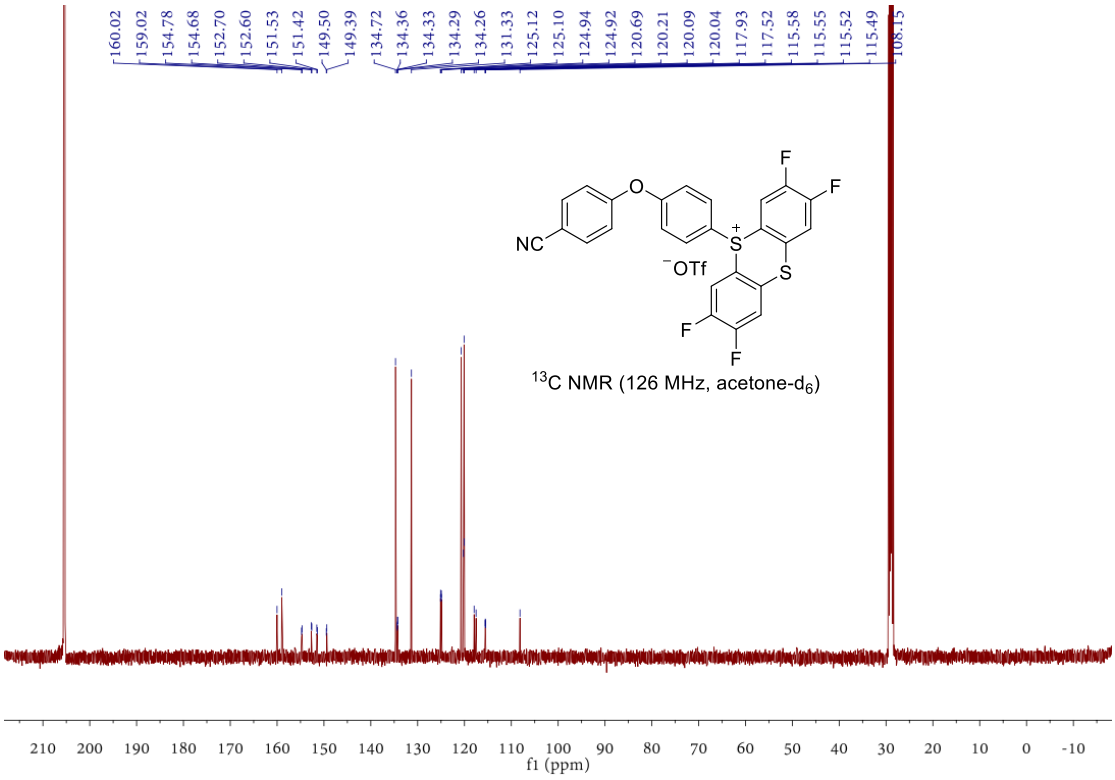
^{1}H NMR spectrum of **1b**



^{19}F NMR spectrum of **1b**



^{13}C NMR spectrum of **1b**



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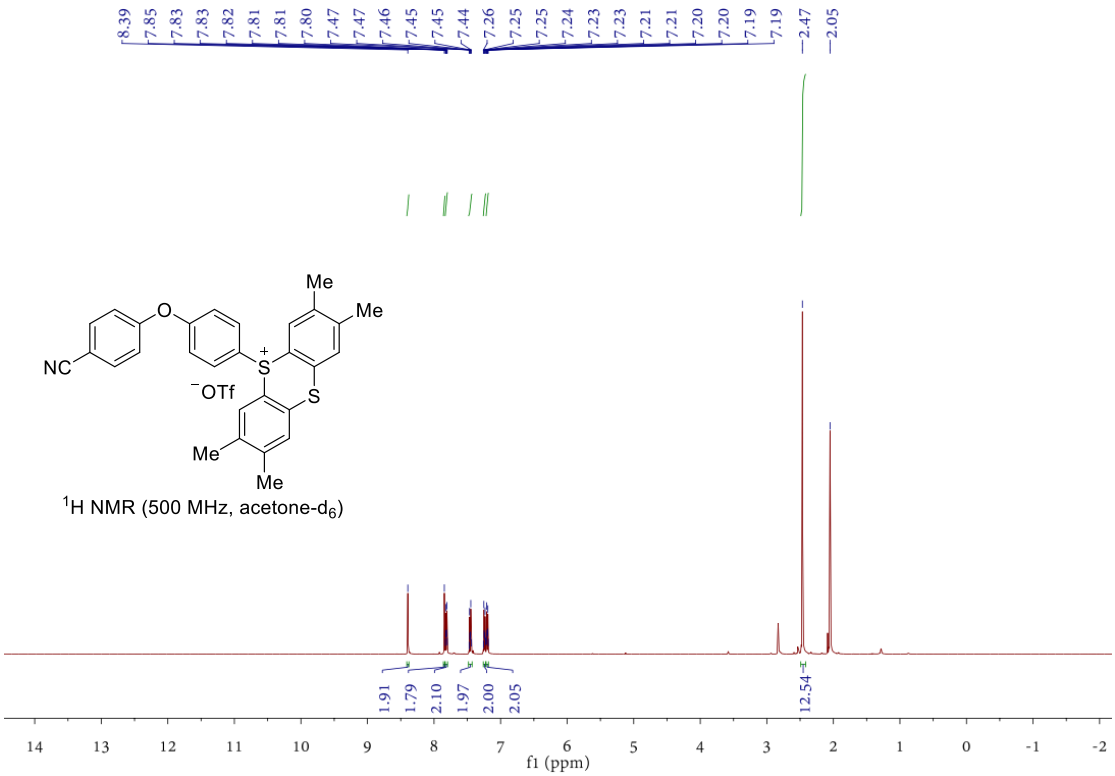
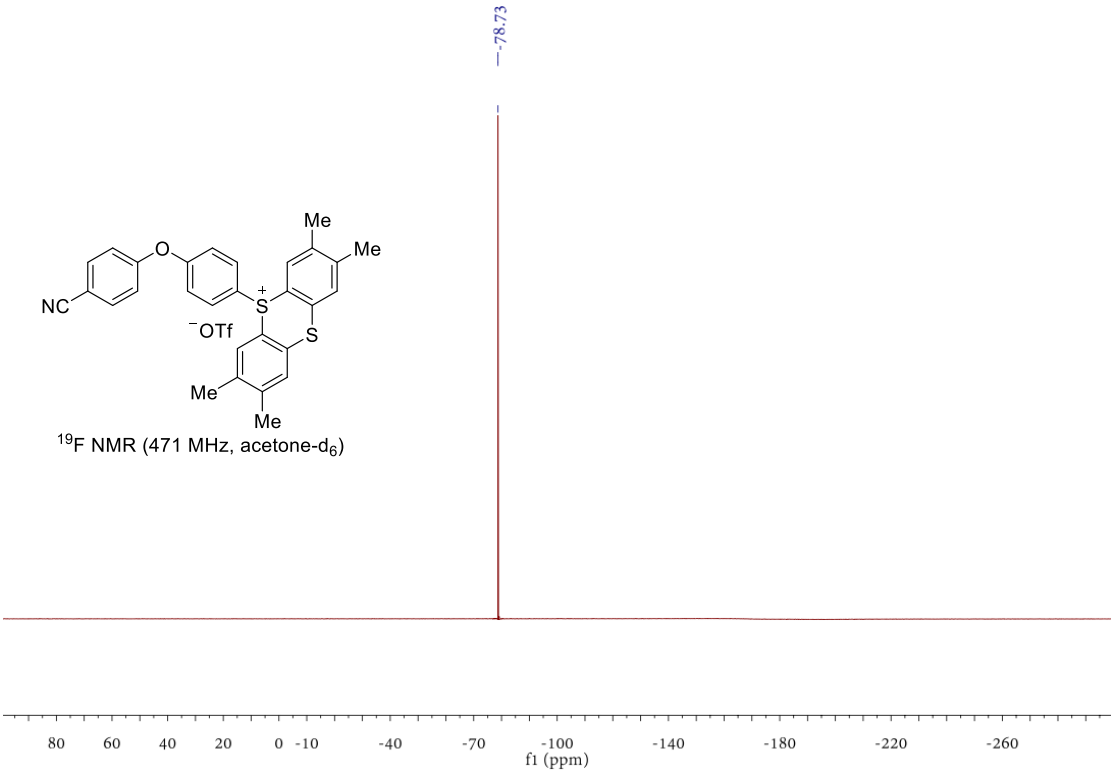
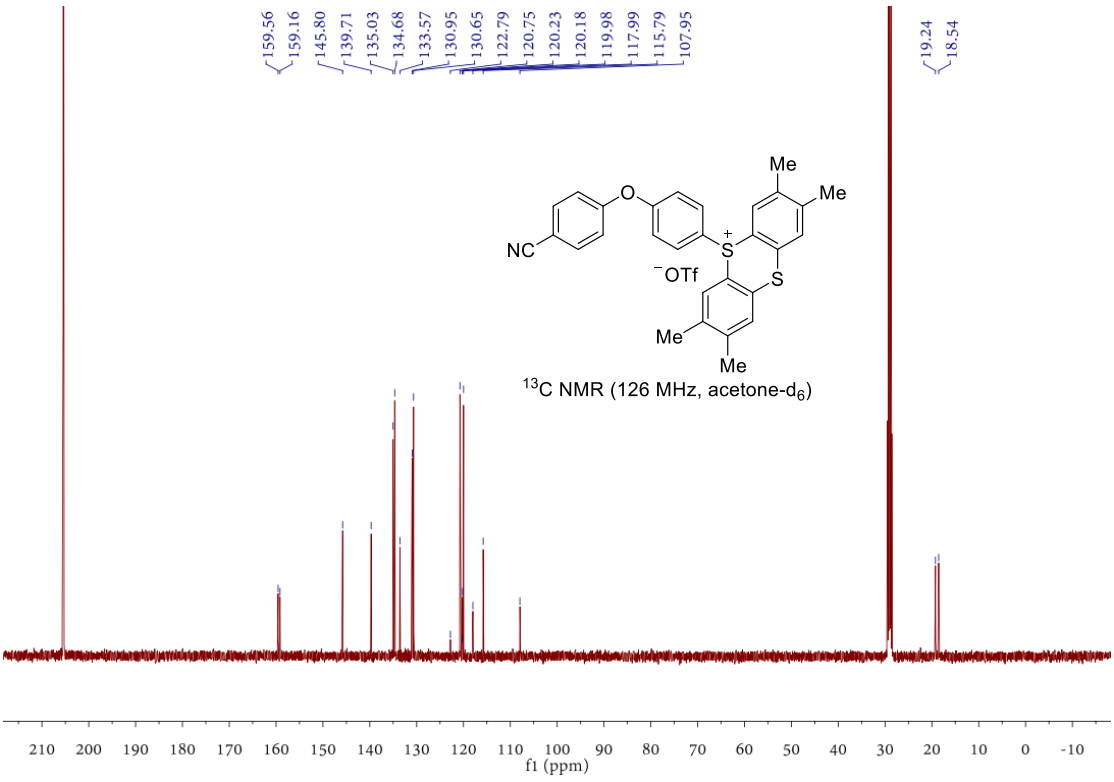


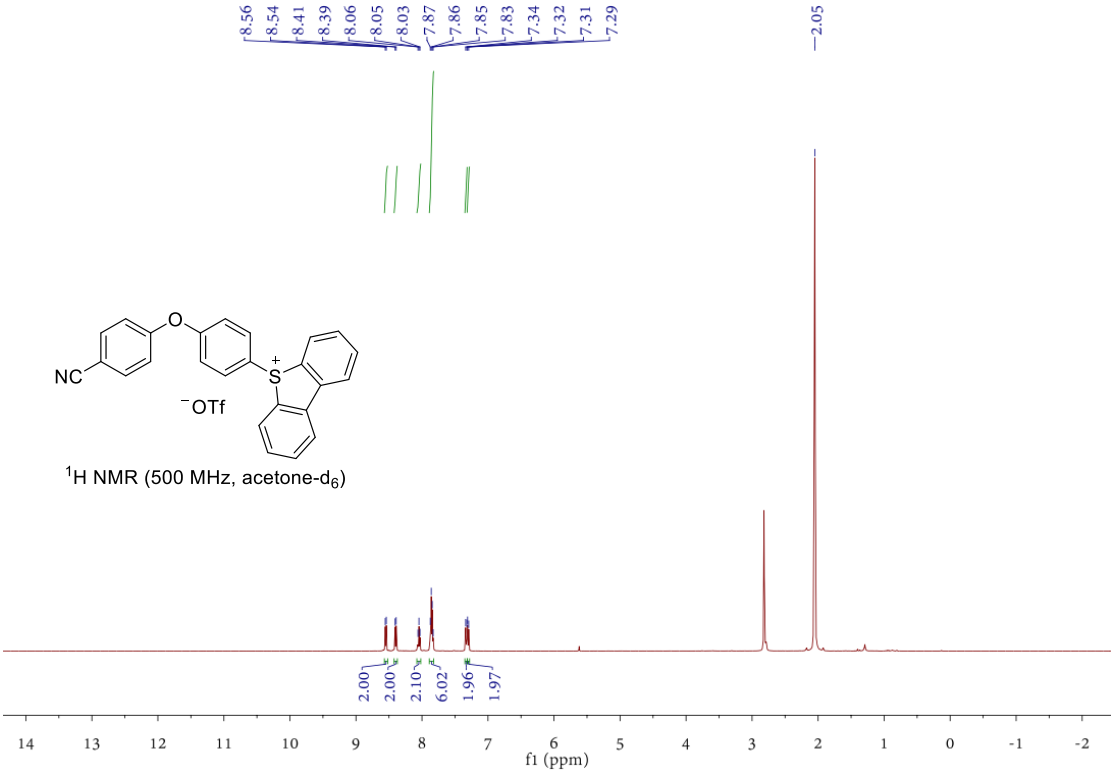
^{19}F NMR spectrum of **1c**



^{13}C NMR spectrum of **1c**

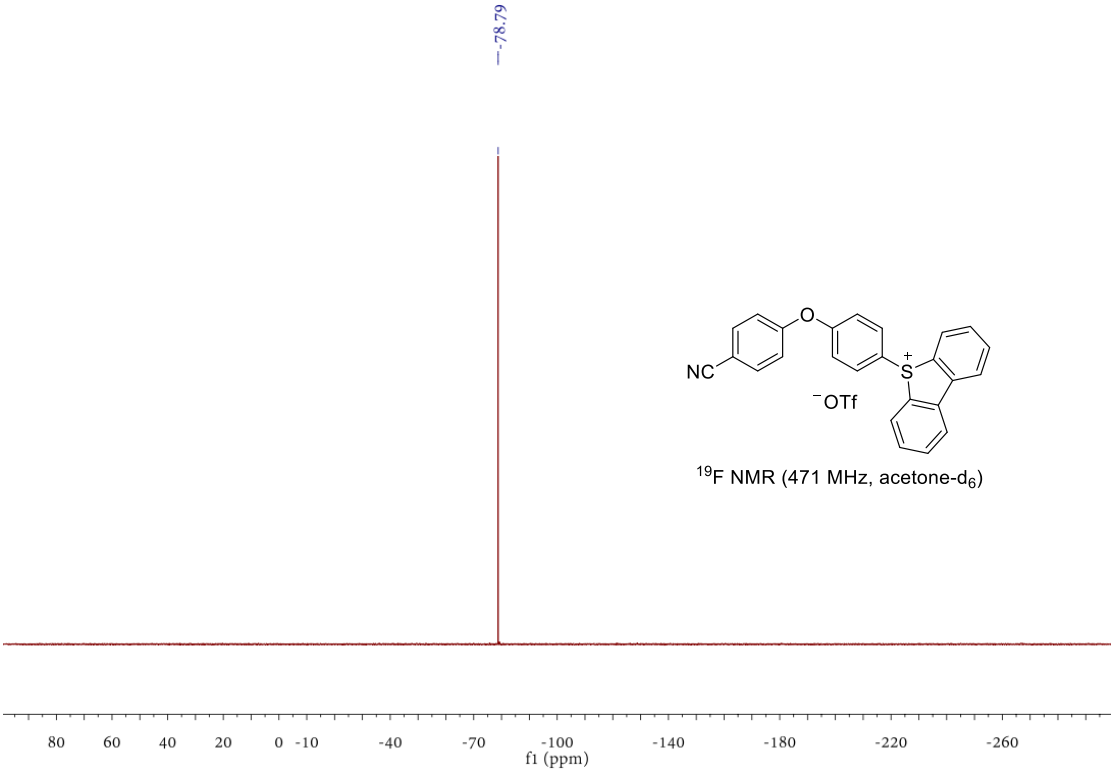


^{1}H NMR spectrum of **1d**



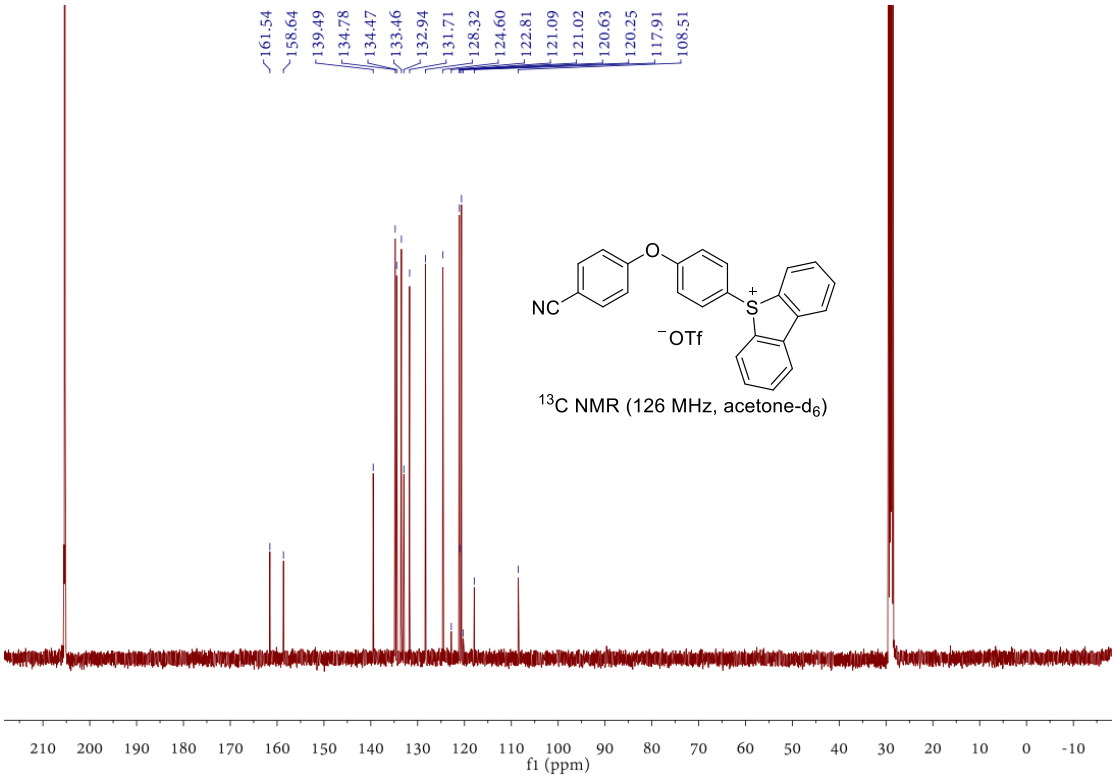
^{1}H NMR (500 MHz, acetone-d_6)

^{19}F NMR spectrum of **1d**

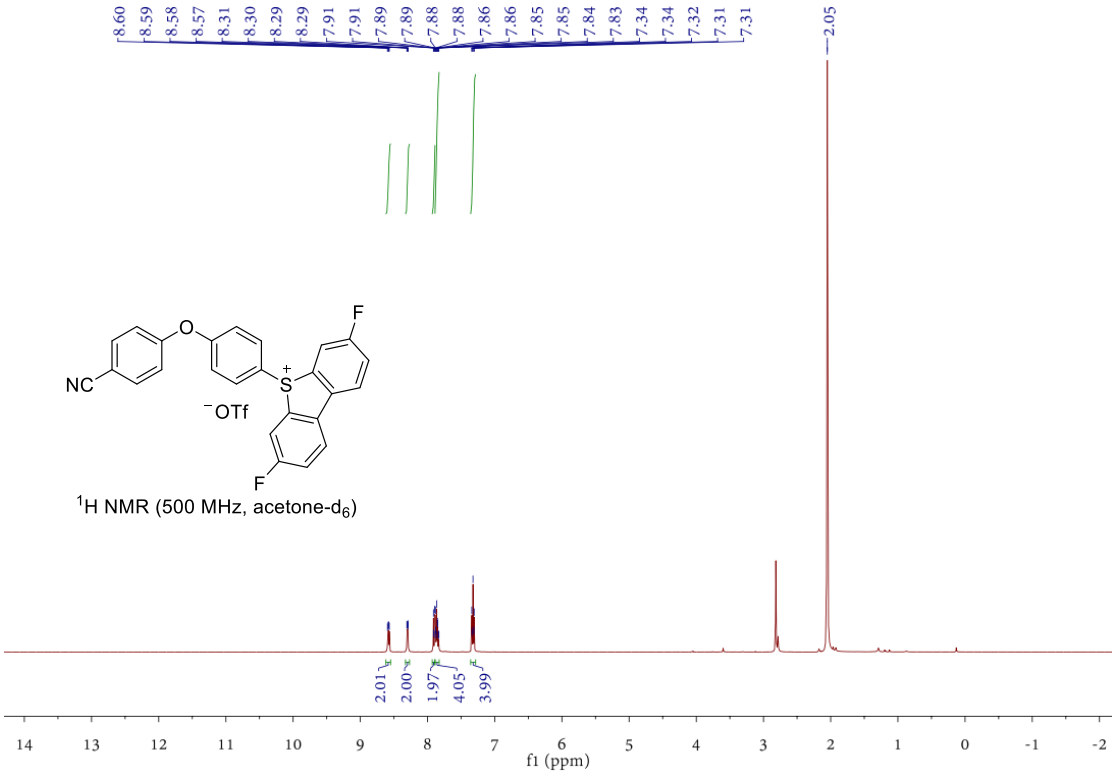


^{19}F NMR (471 MHz, acetone-d_6)

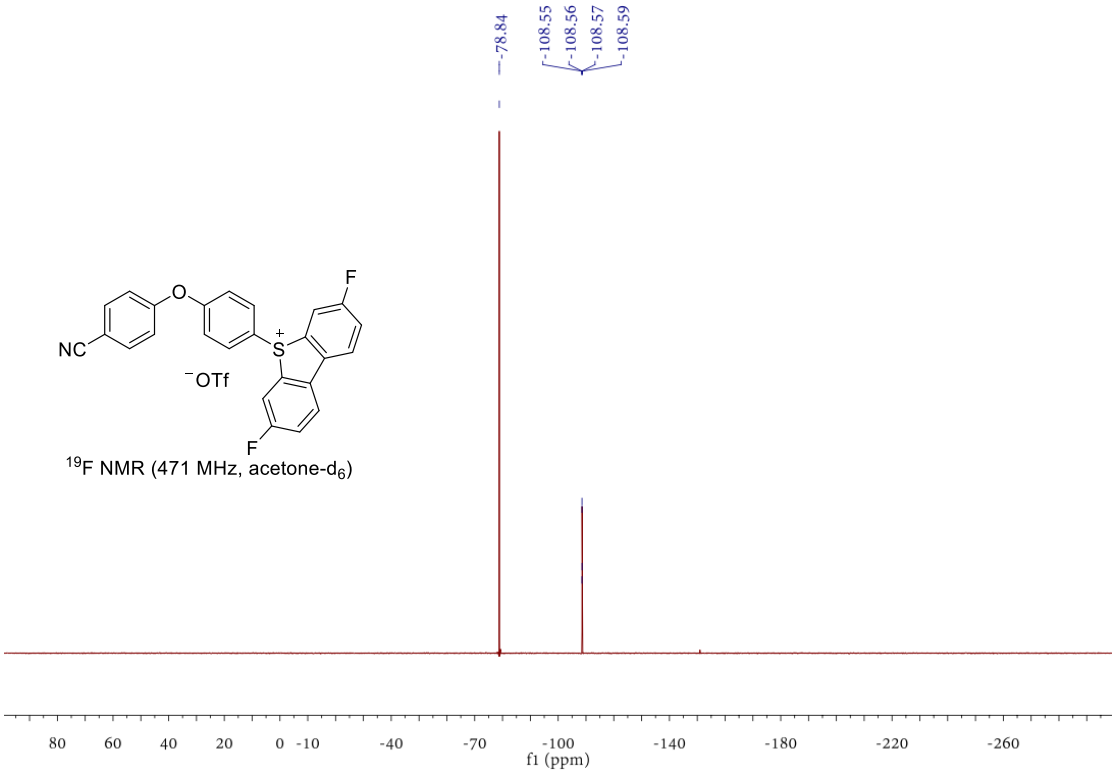
^{13}C NMR spectrum of **1d**



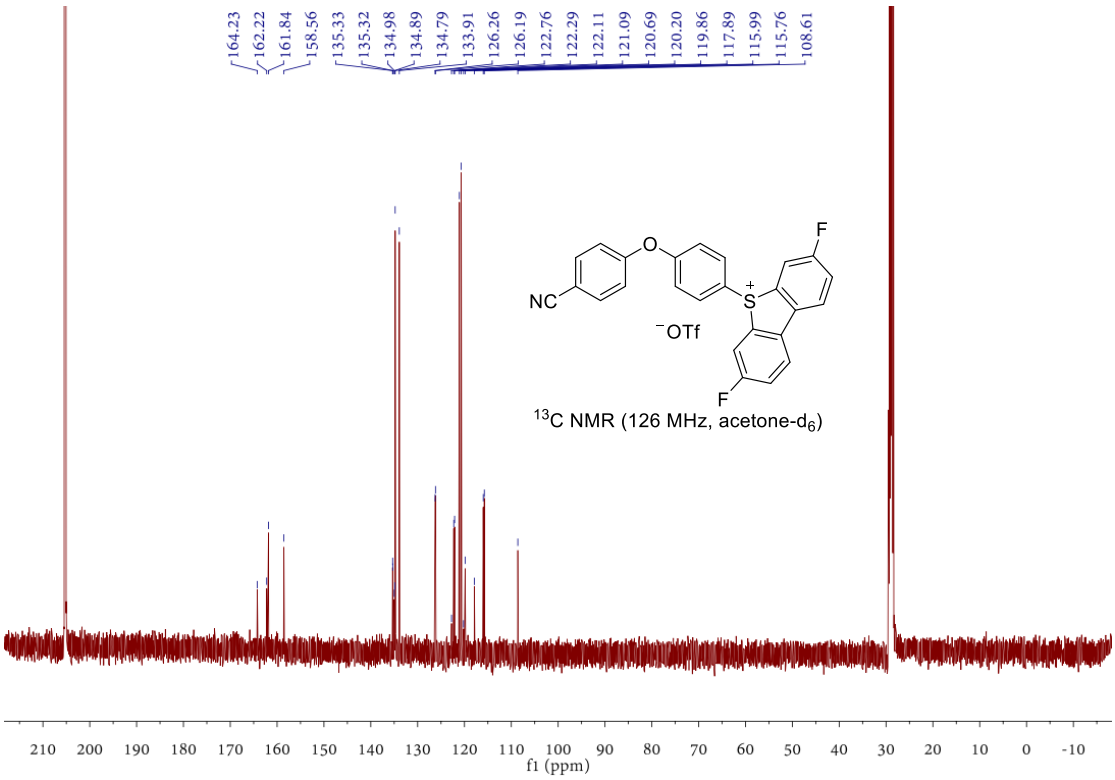
^{1}H NMR spectrum of **1e**



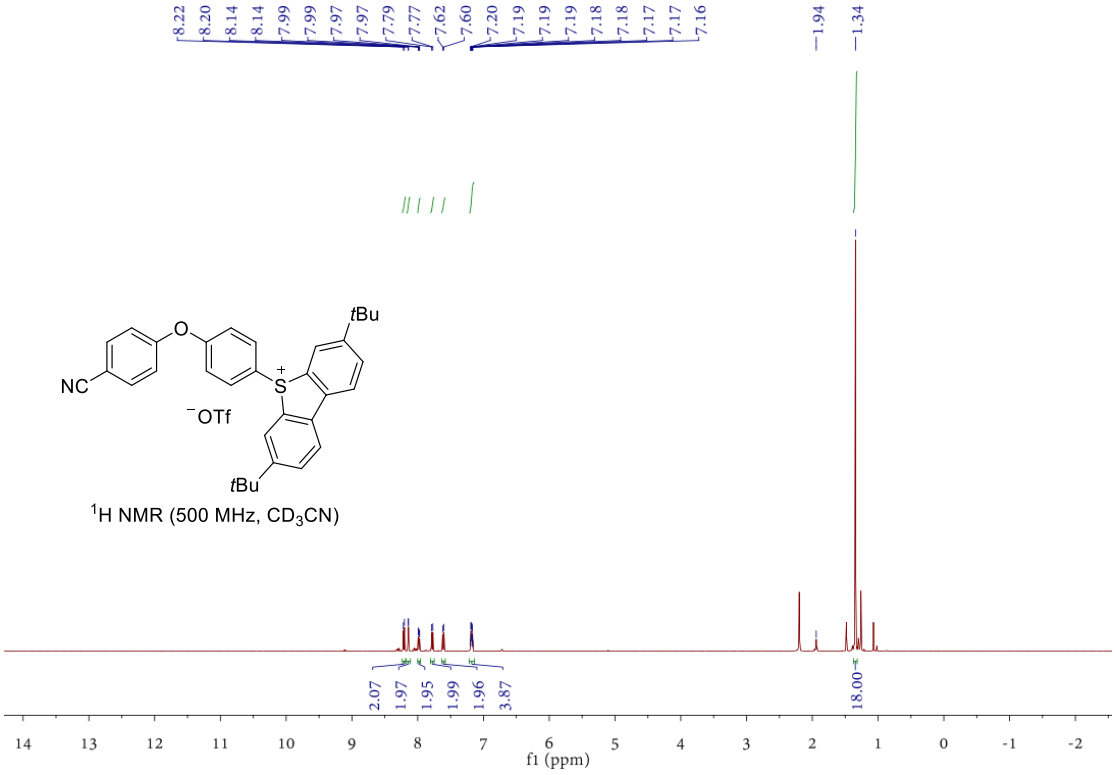
^{19}F NMR spectrum of **1e**



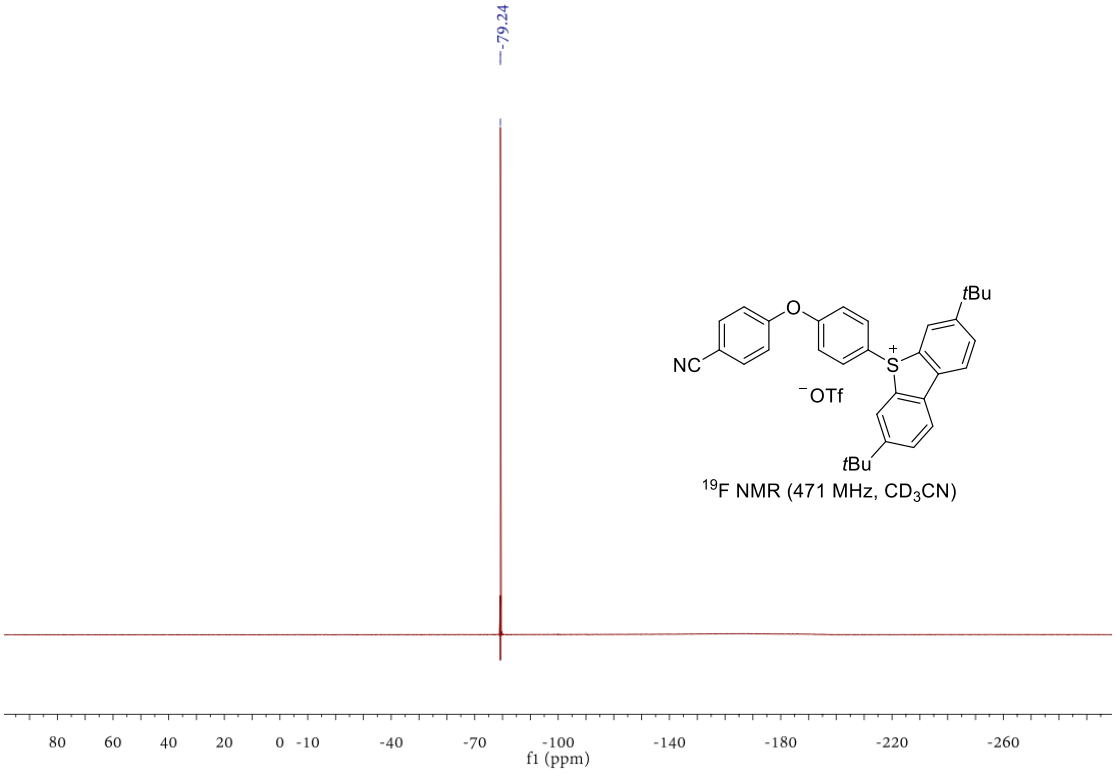
^{13}C NMR spectrum of **1e**



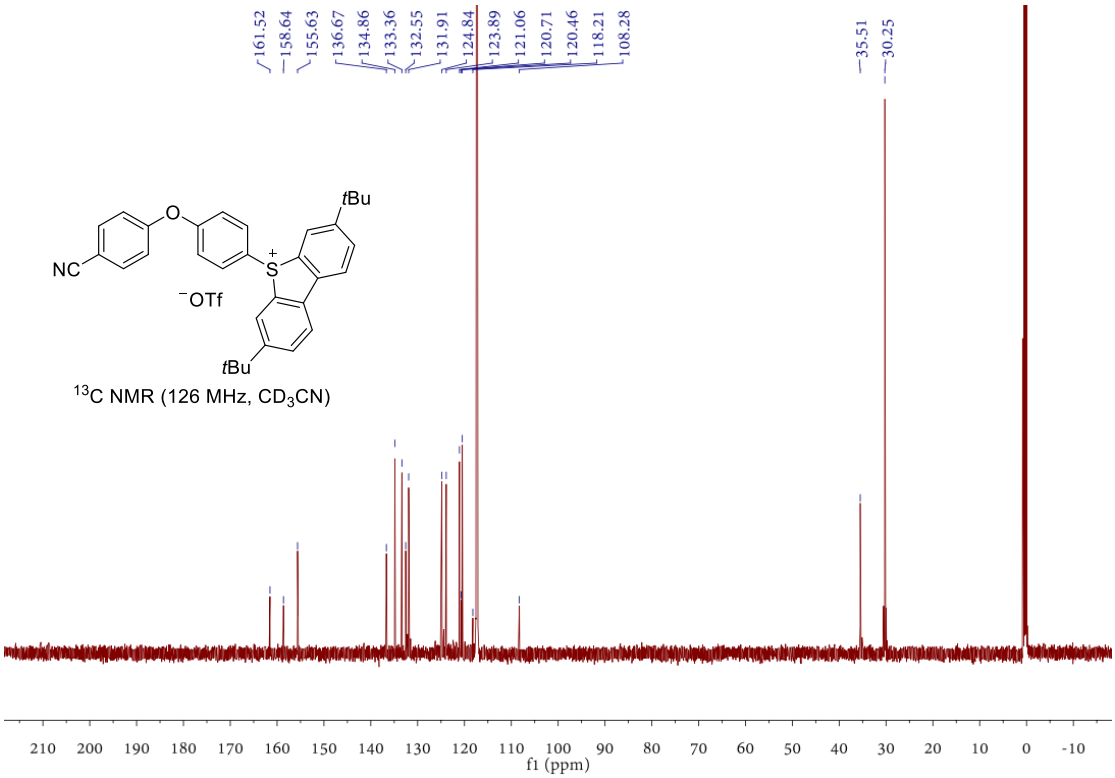
^{1}H NMR spectrum of **1f**



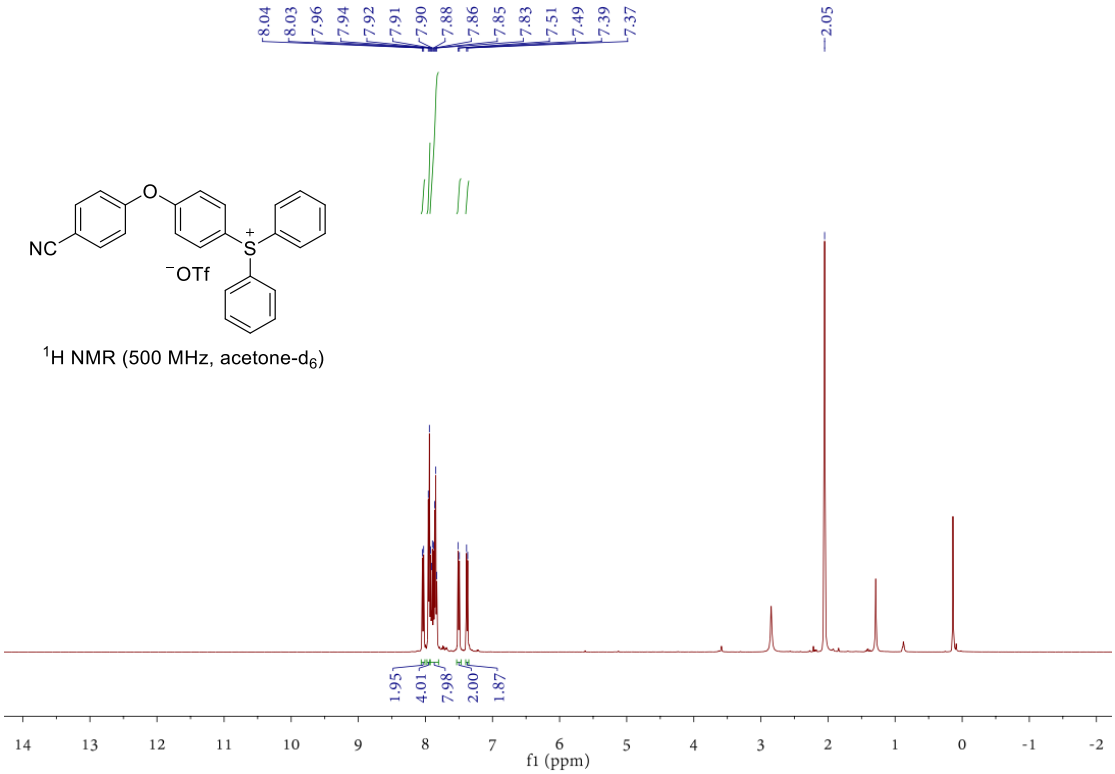
^{19}F NMR spectrum of **1f**



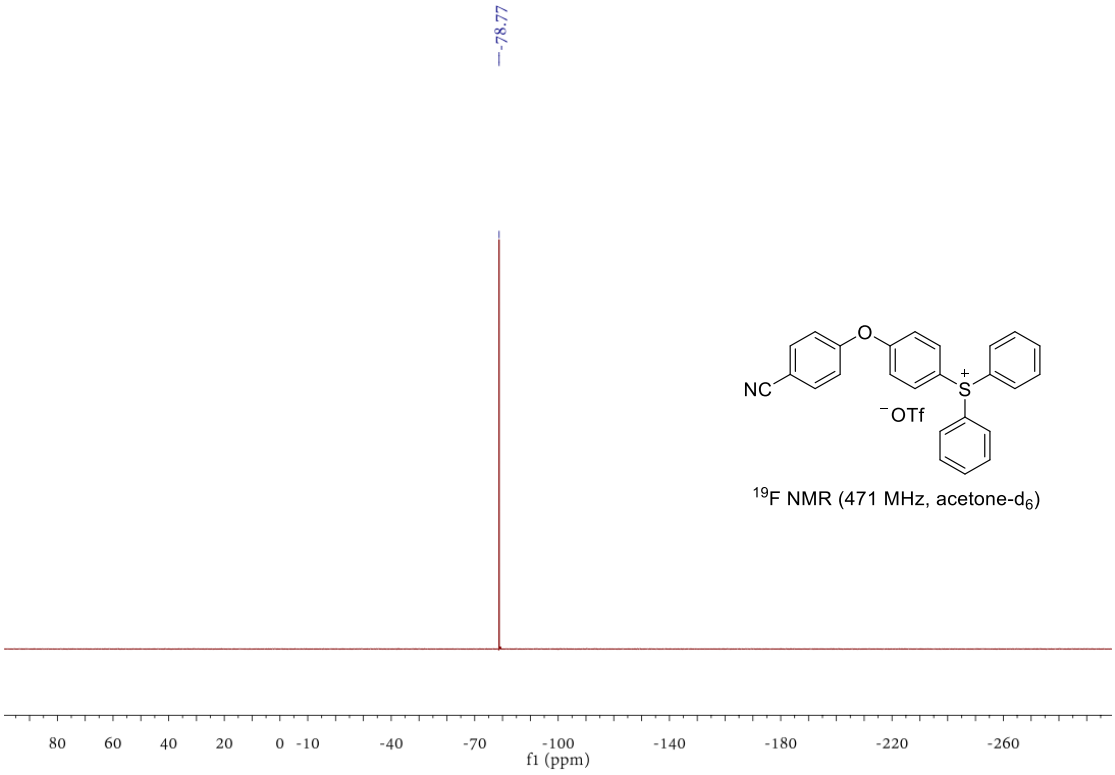
^{13}C NMR spectrum of **1f**



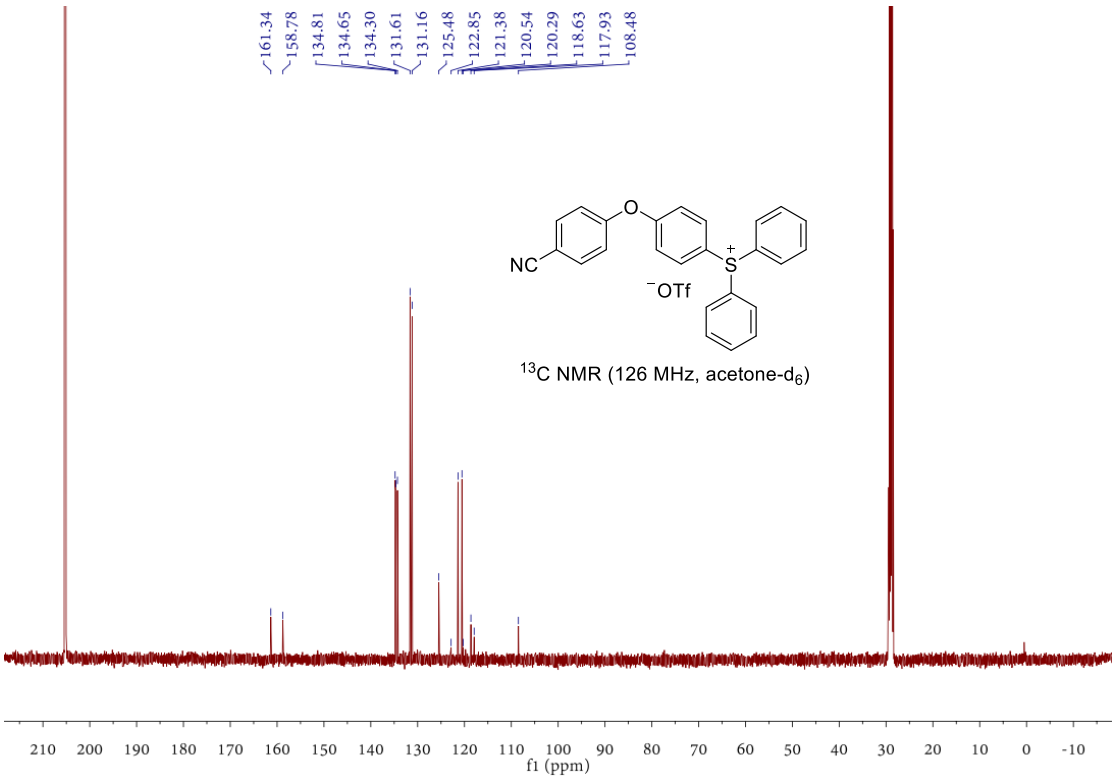
^{1}H NMR spectrum of **1g**



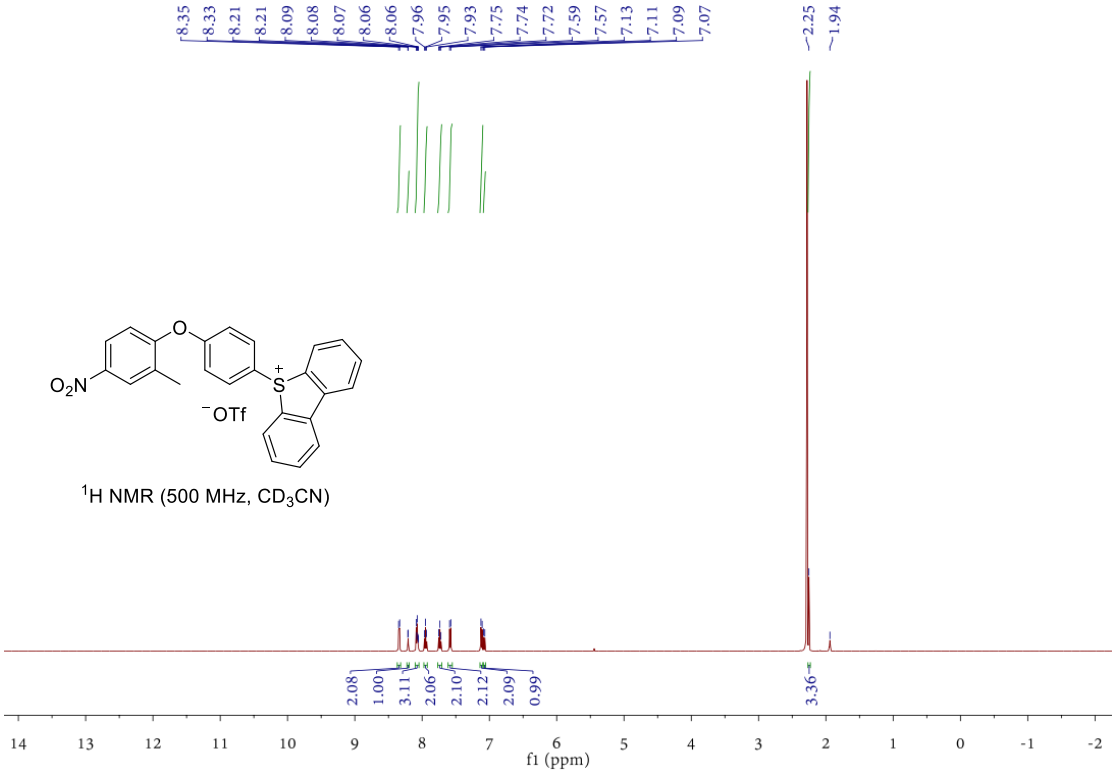
^{19}F NMR spectrum of **1g**



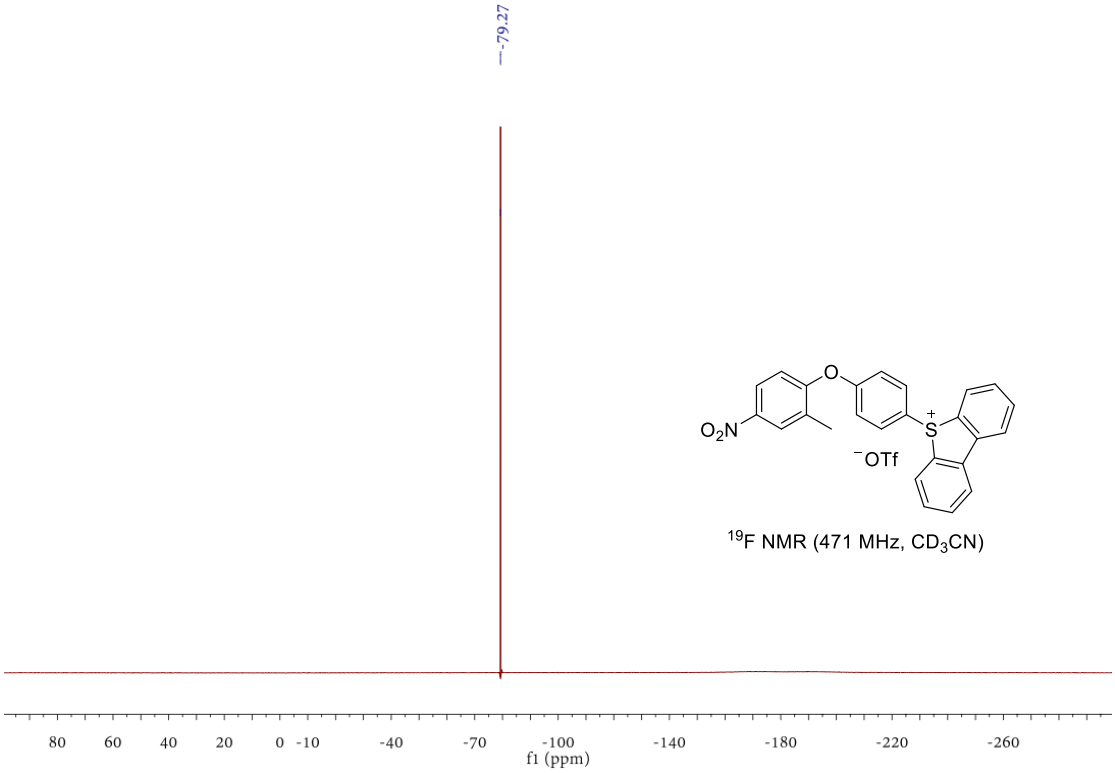
^{13}C NMR spectrum of **1g**



^{1}H NMR spectrum of **1i**



^{19}F NMR spectrum of **1i**



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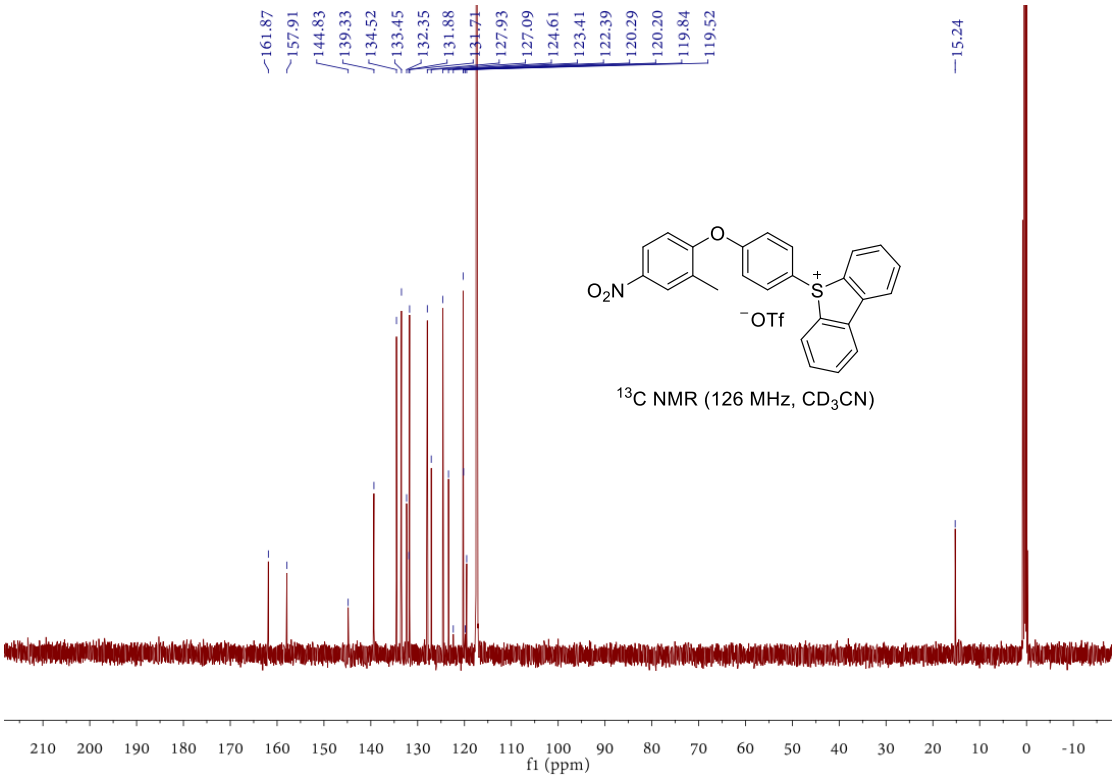

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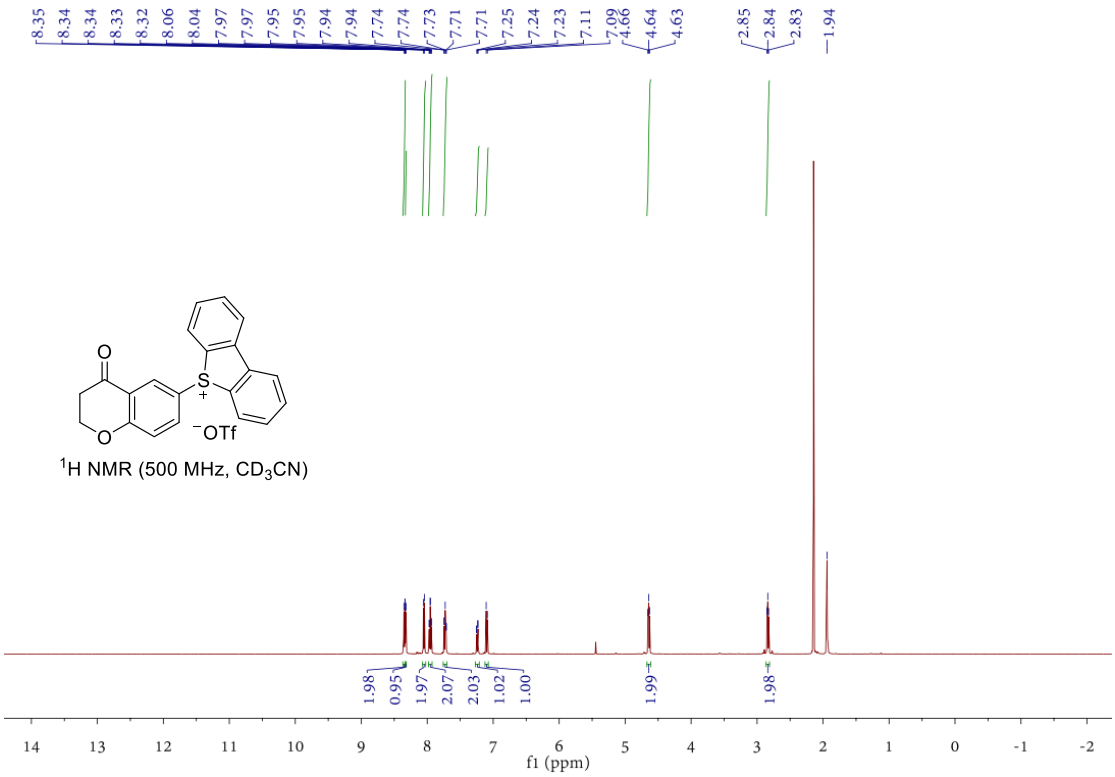

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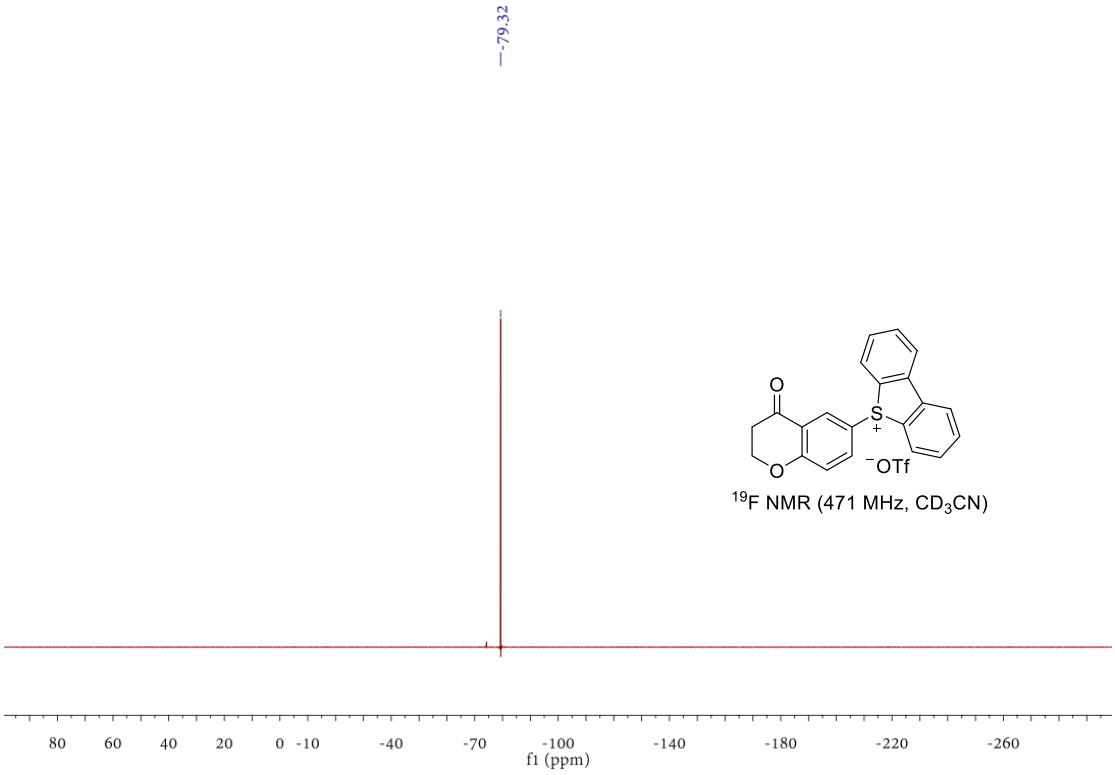
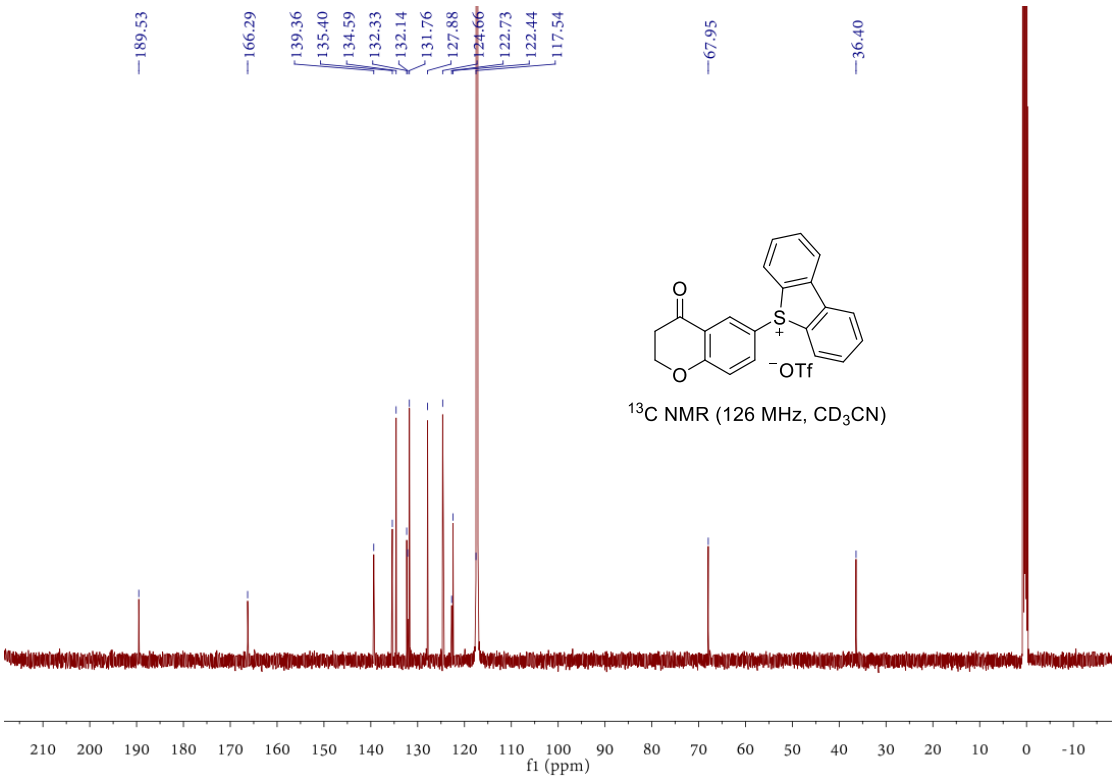


^{13}C NMR spectrum of **1j**



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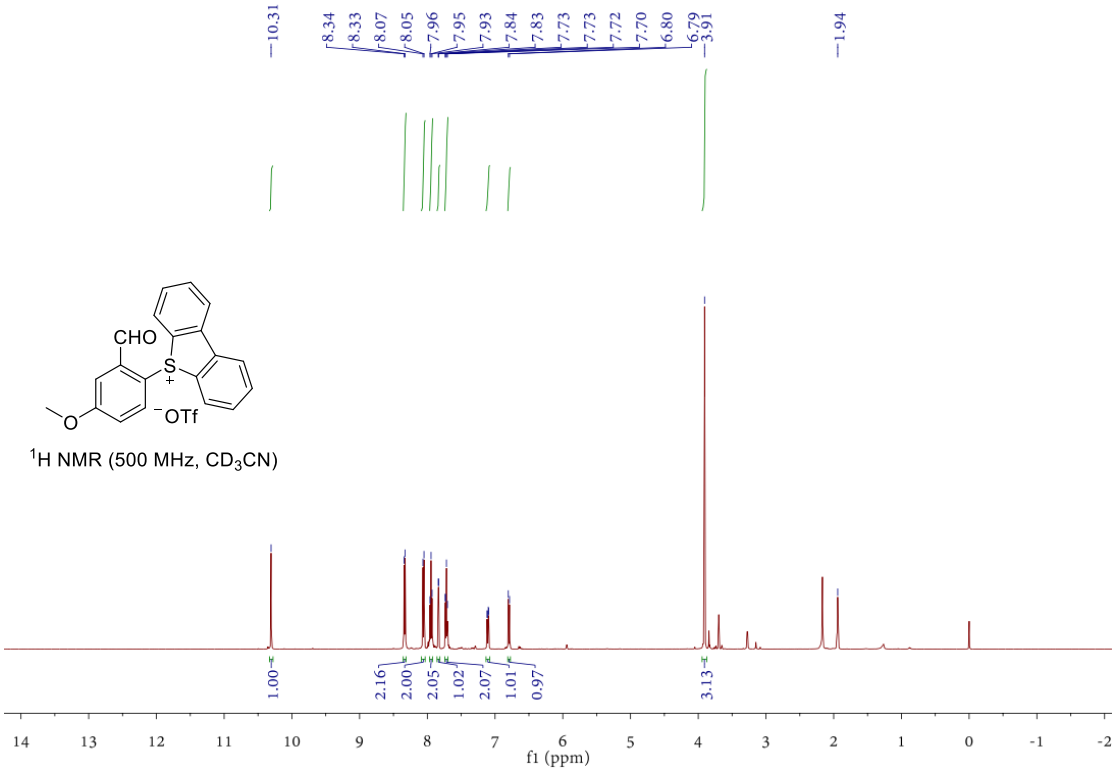

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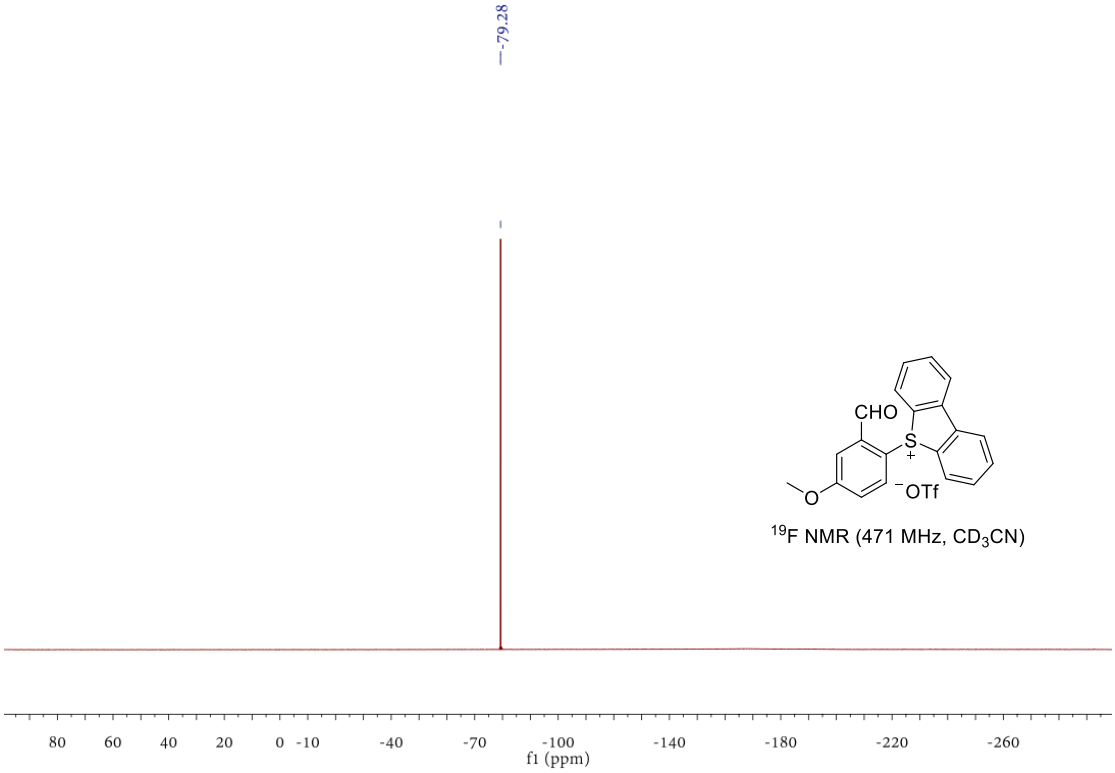

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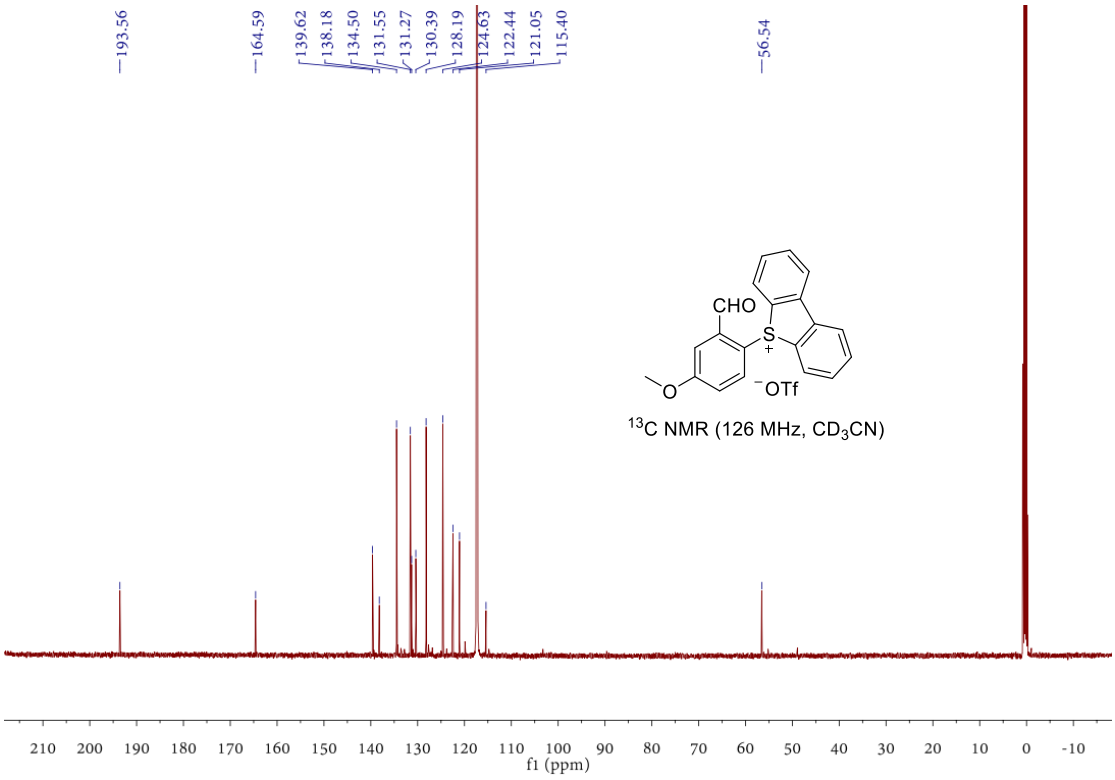

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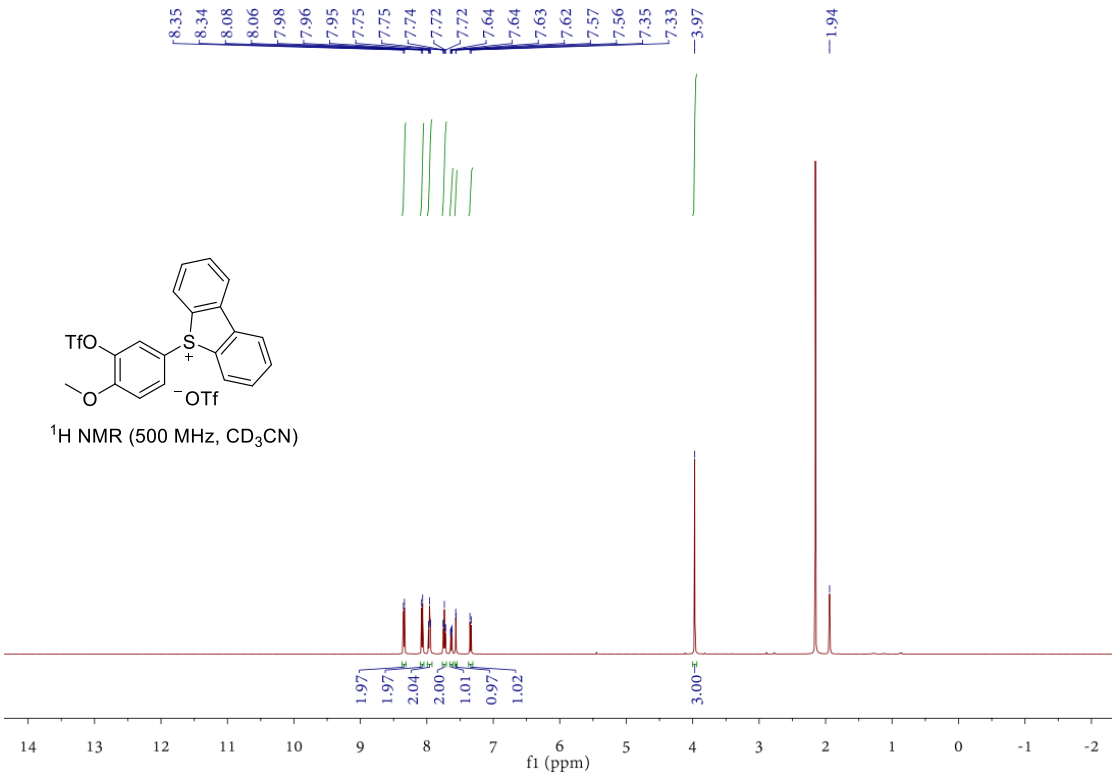

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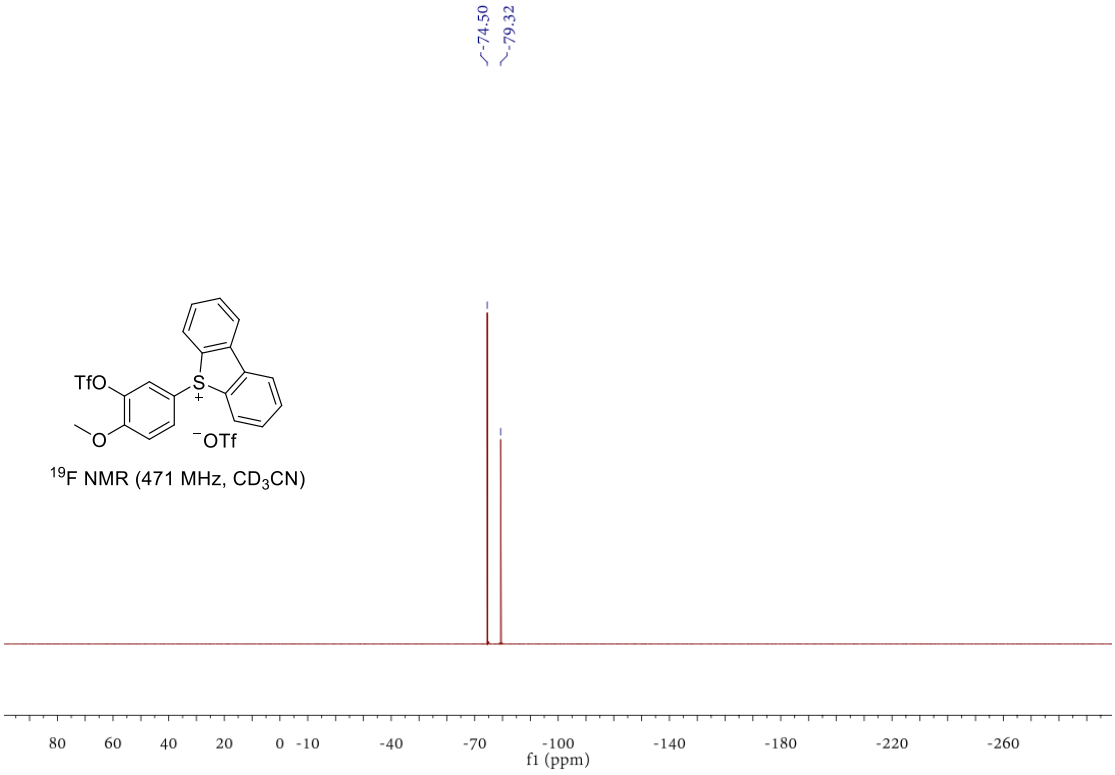

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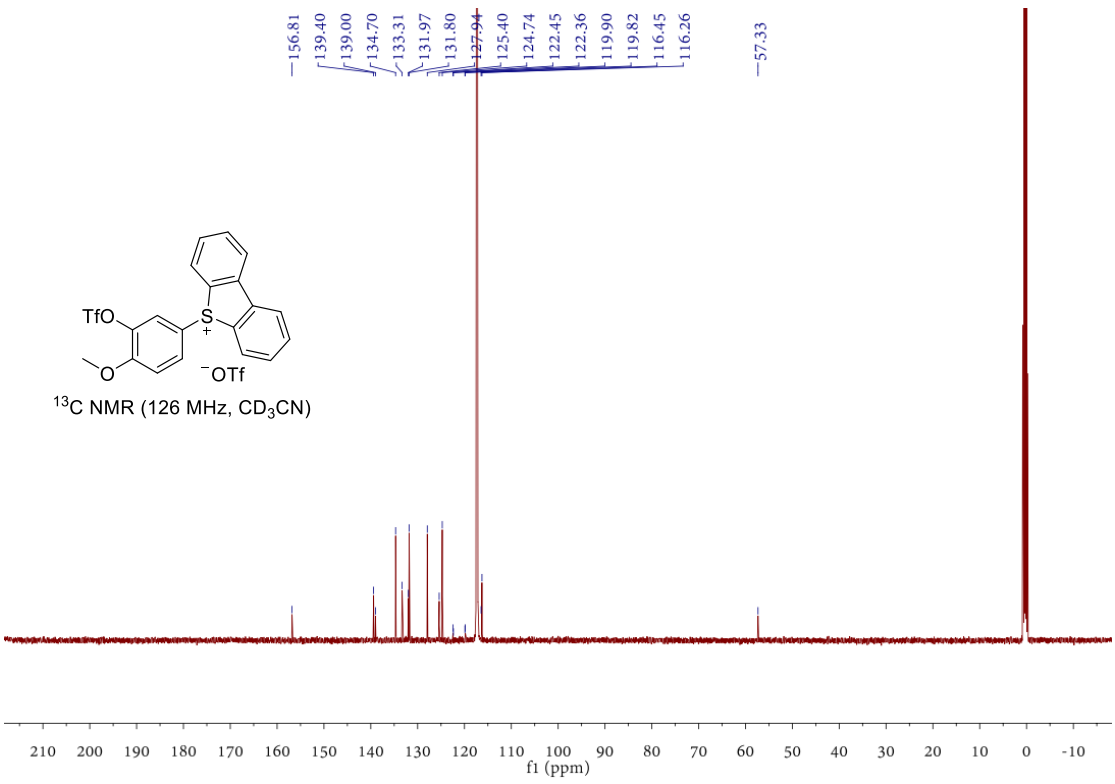

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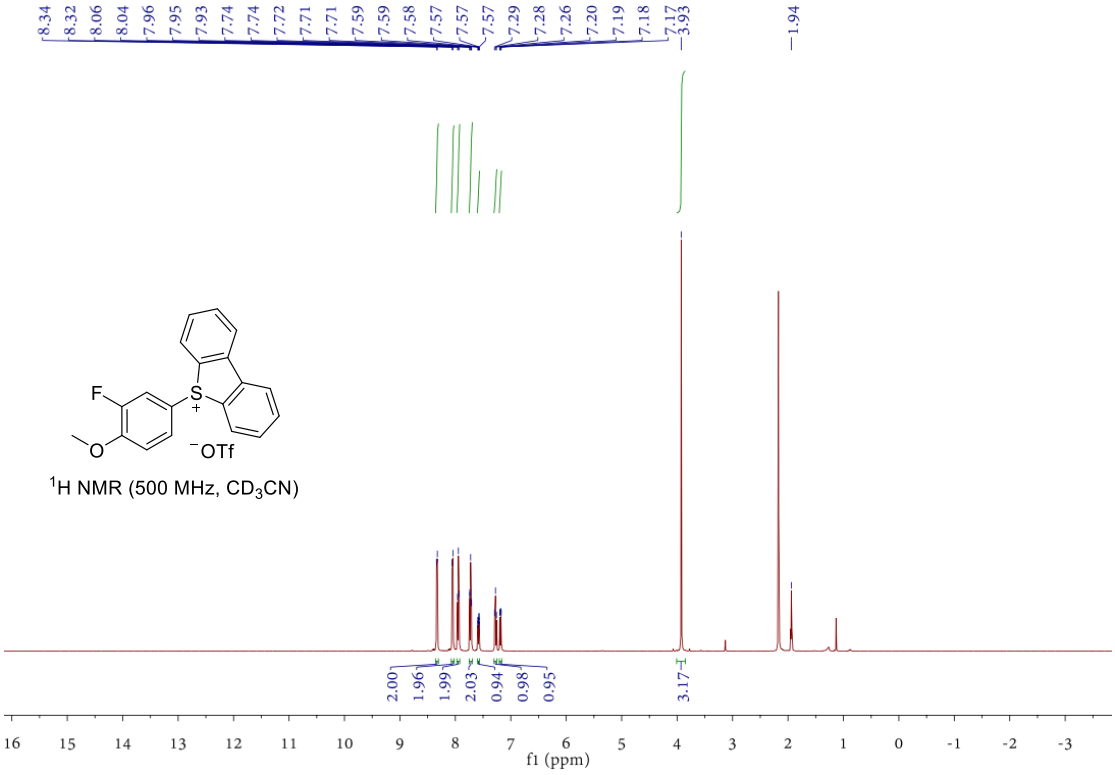

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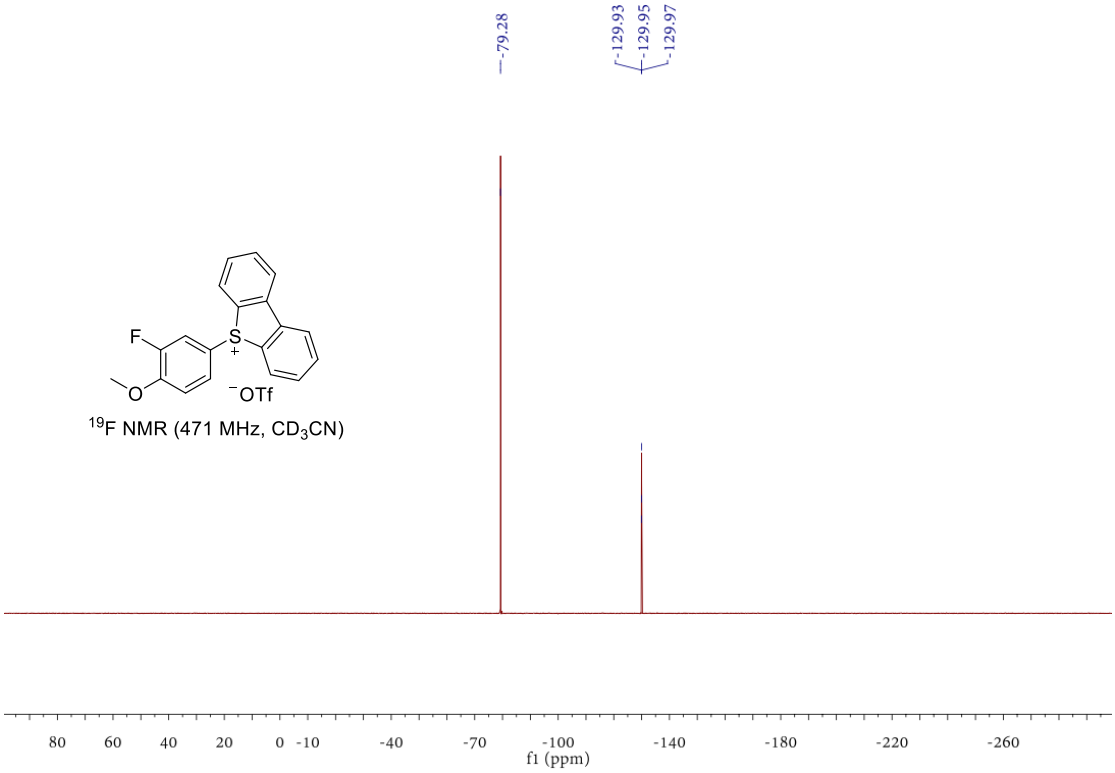

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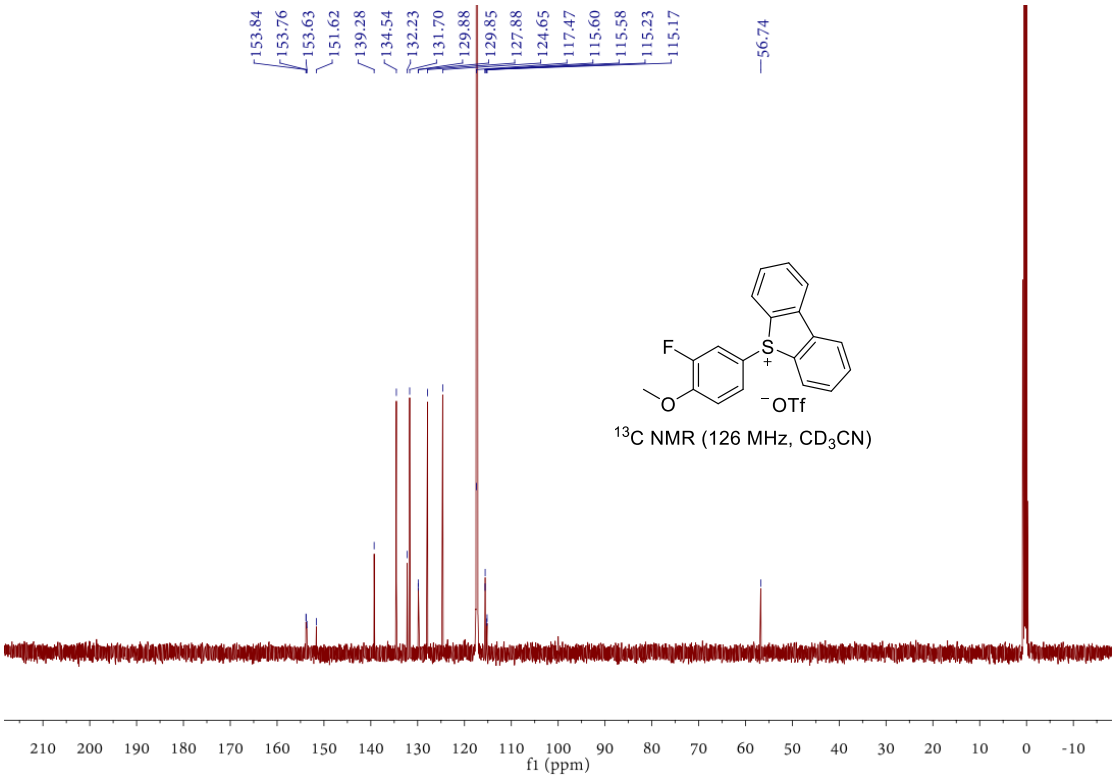

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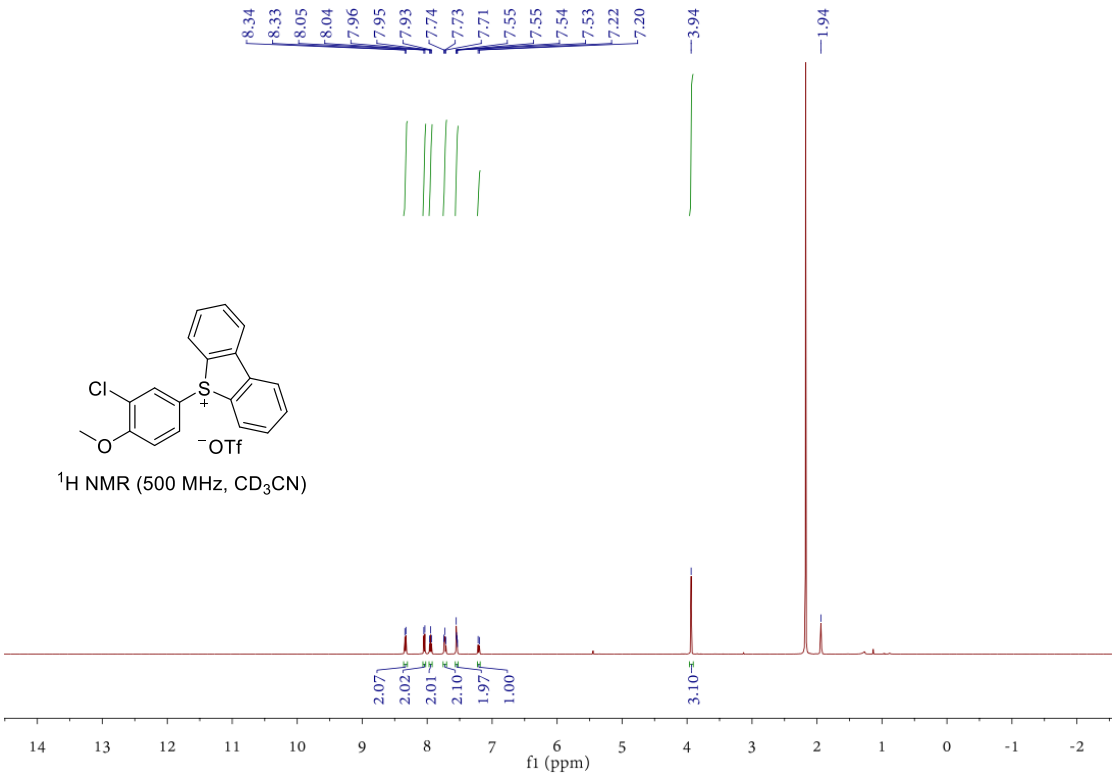

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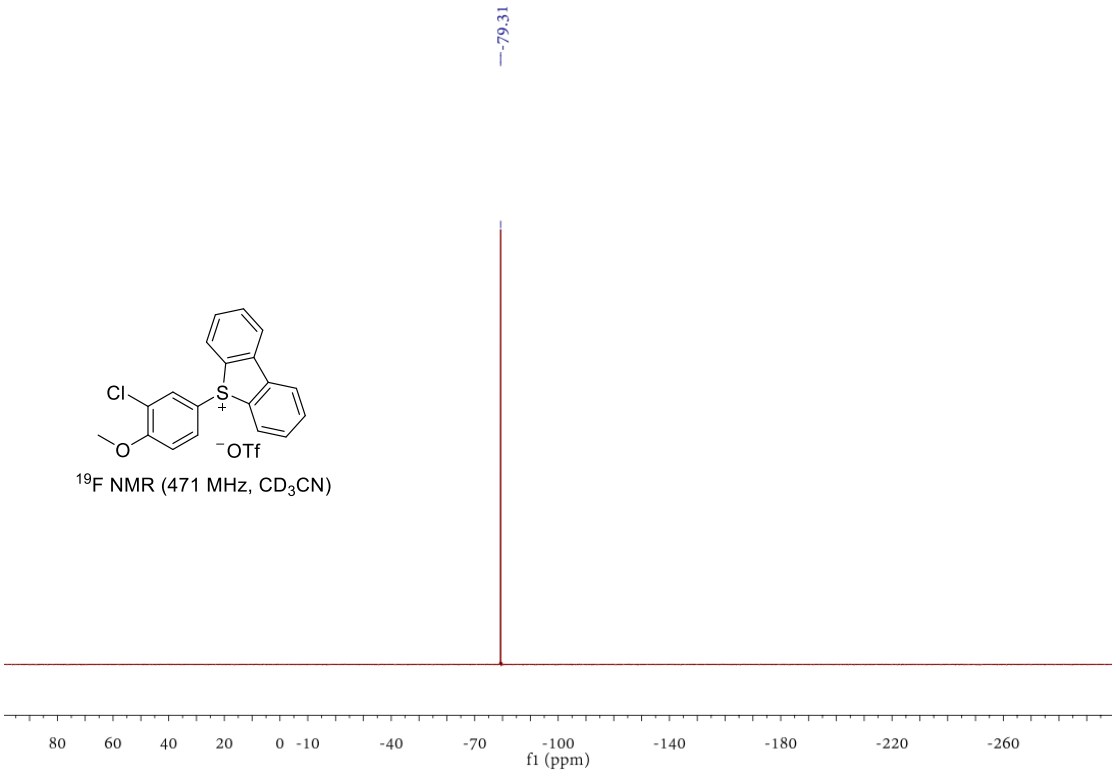

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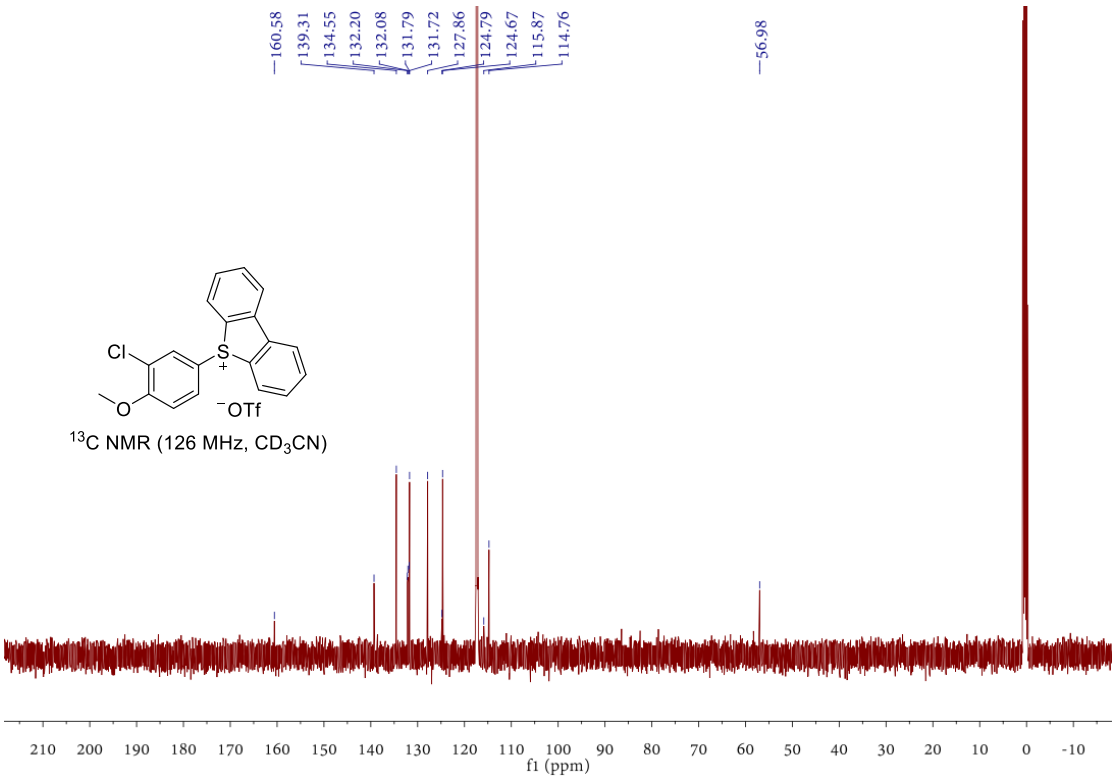

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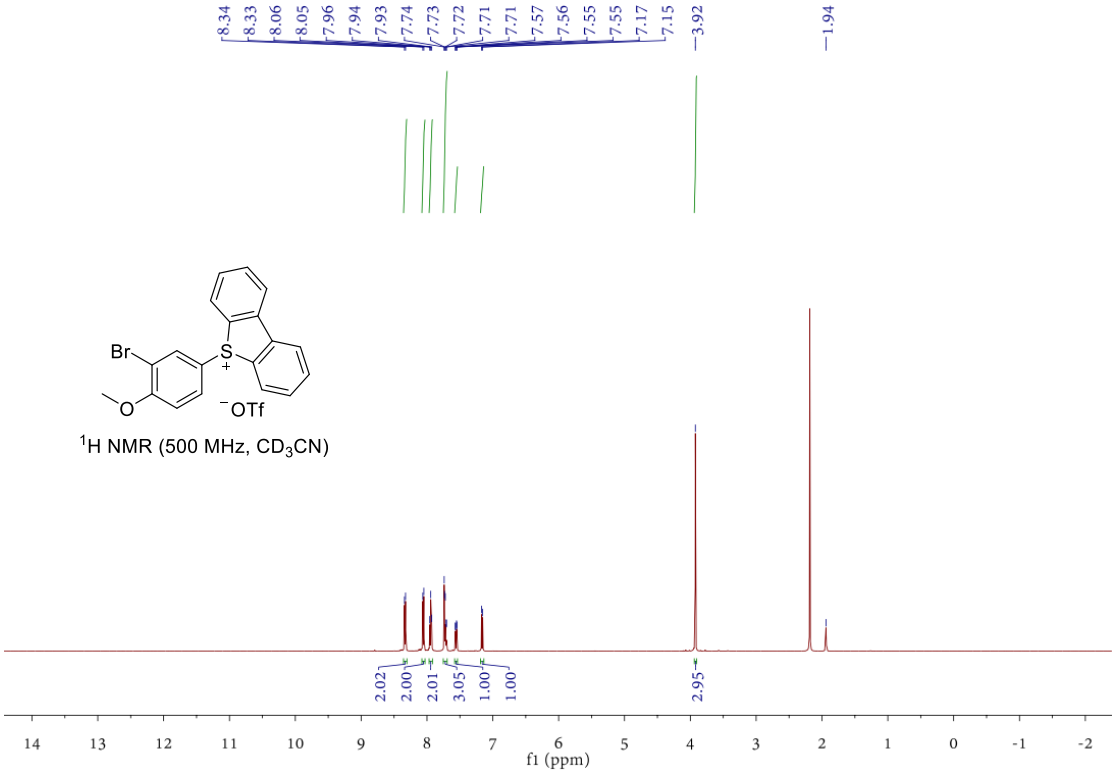

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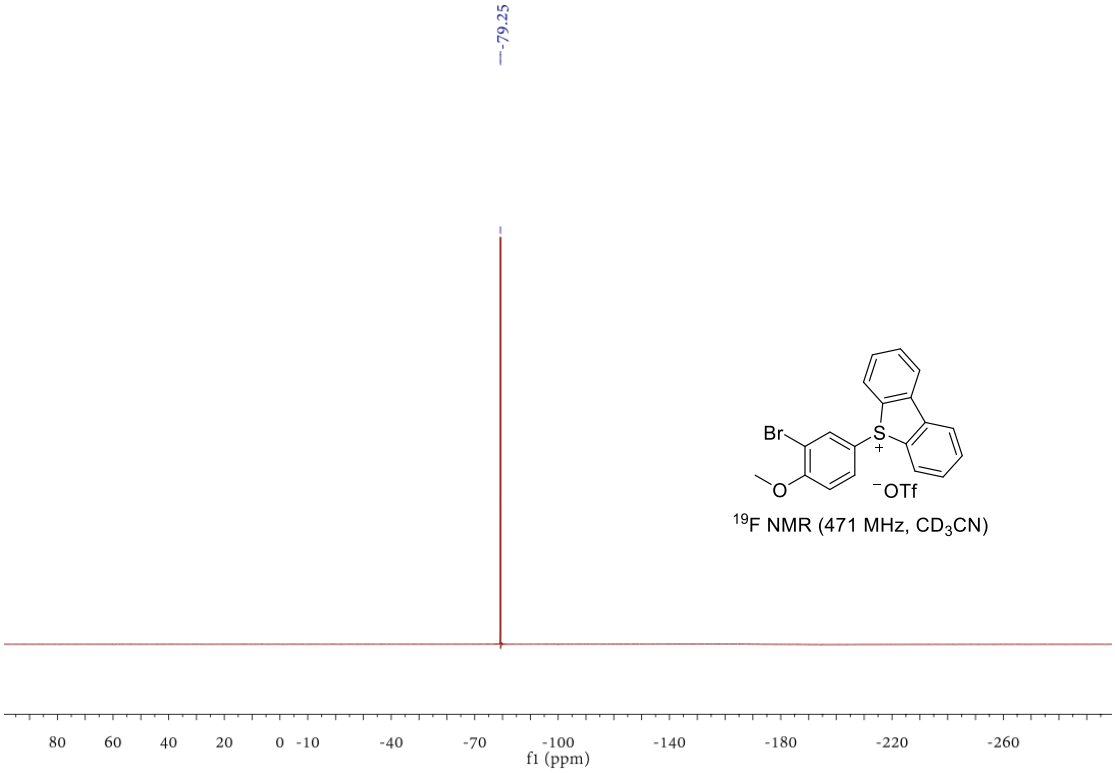

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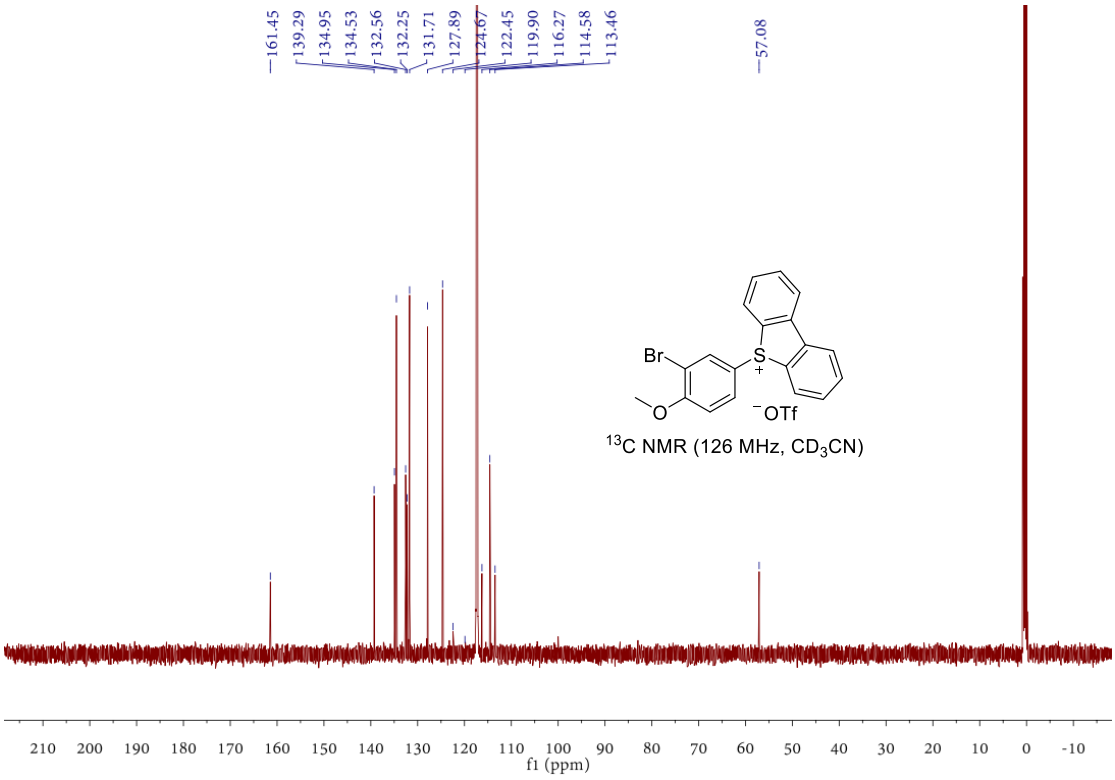

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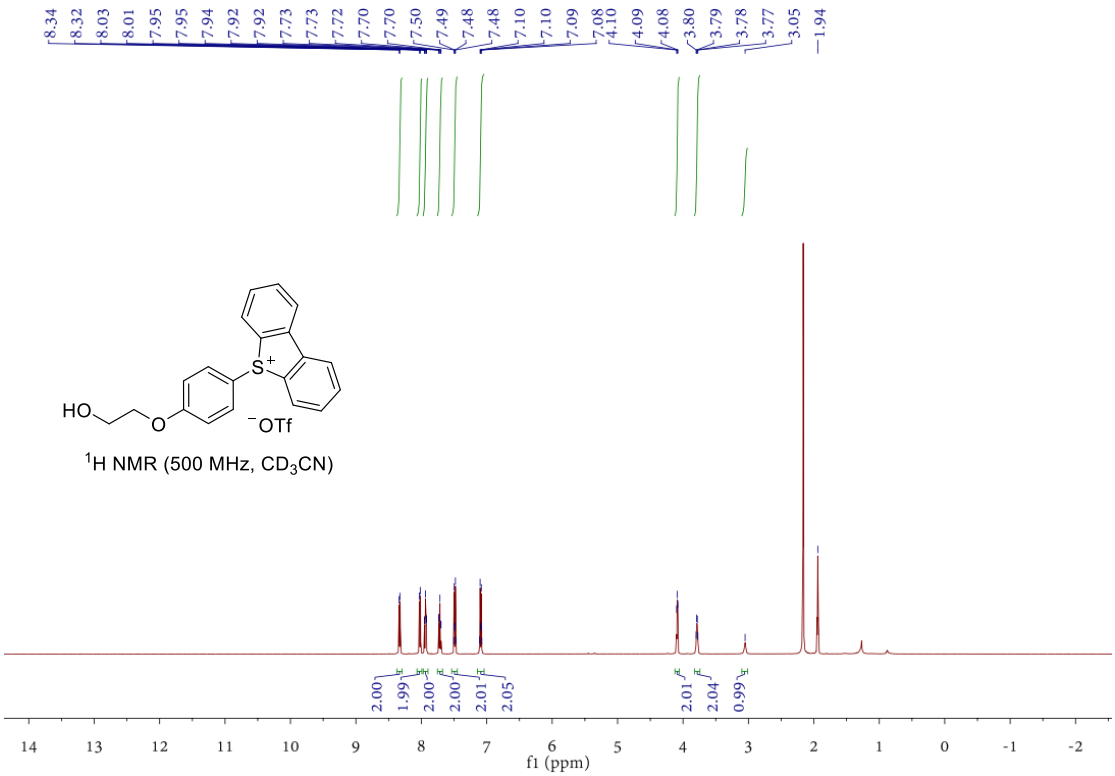
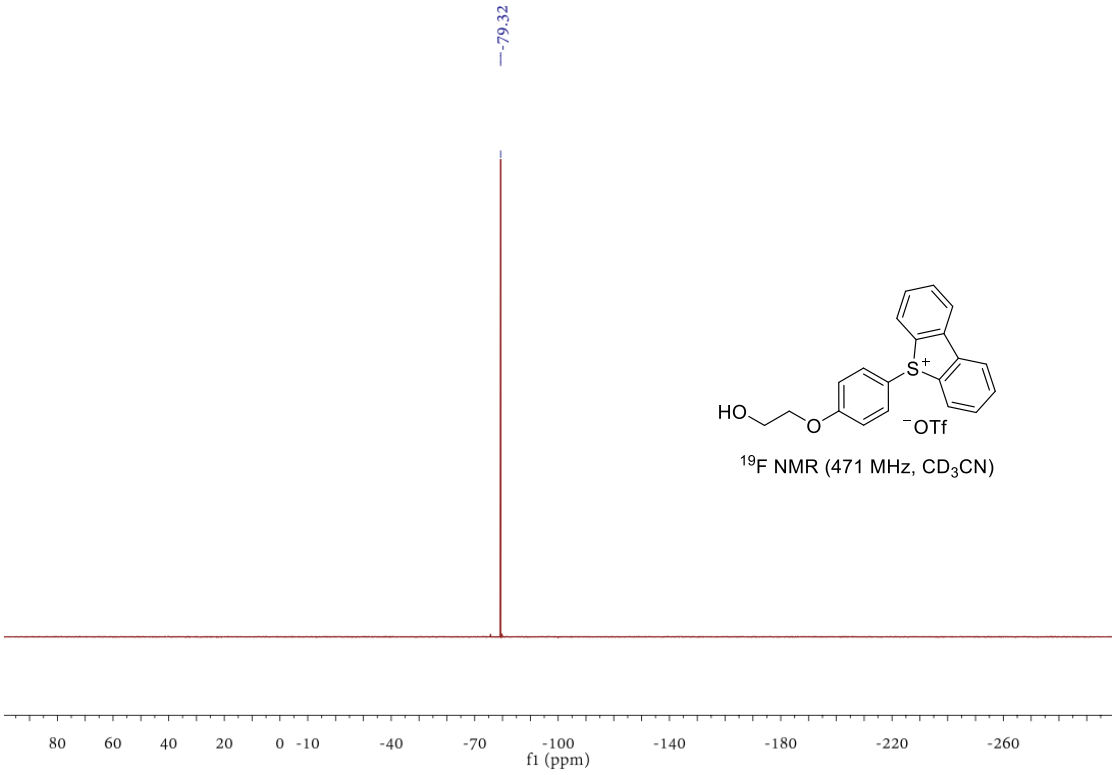
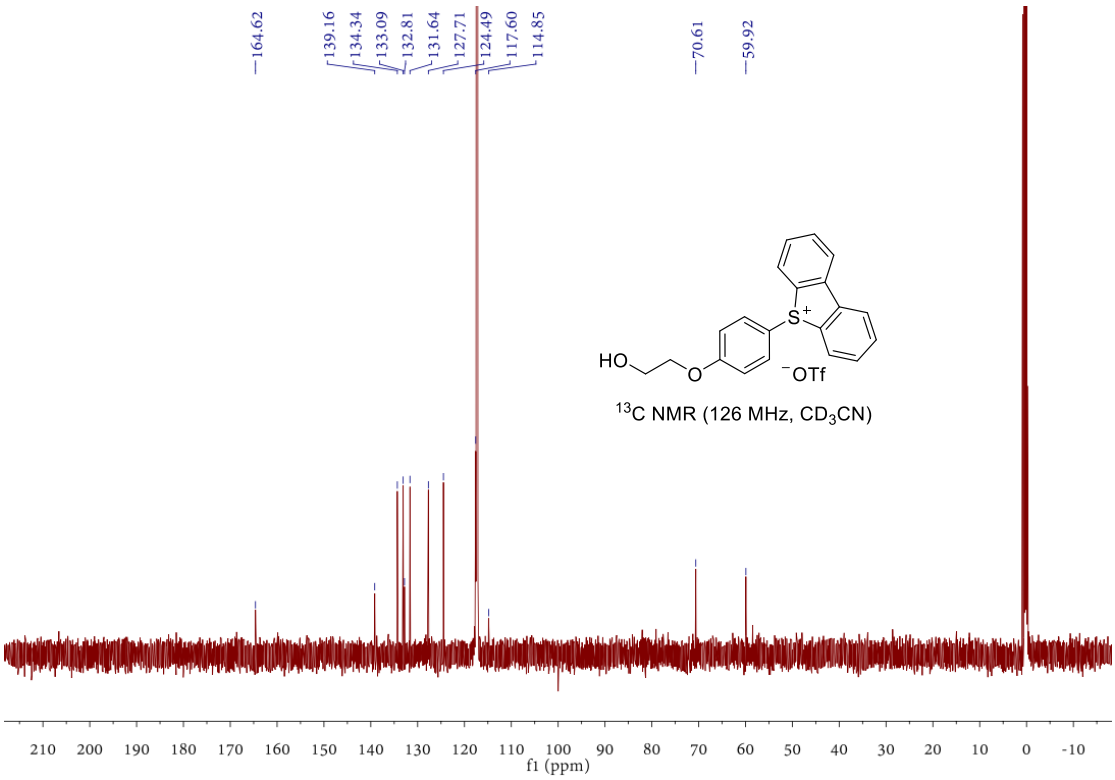


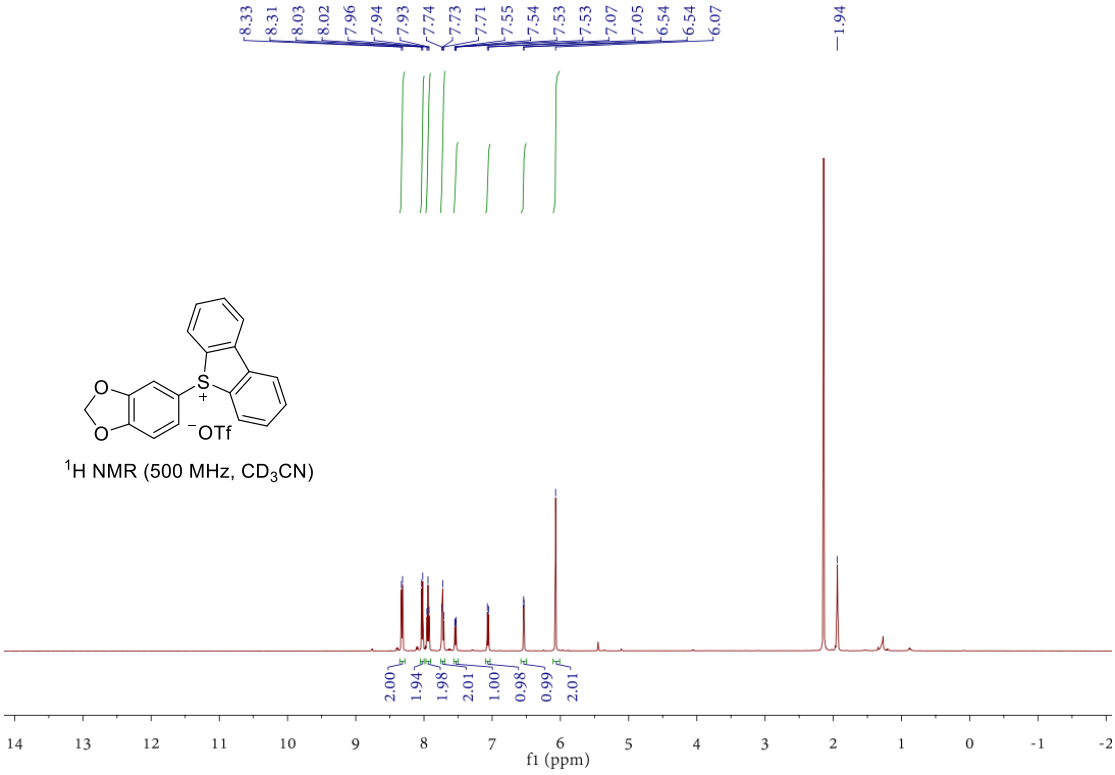
^{19}F NMR spectrum of **1p**



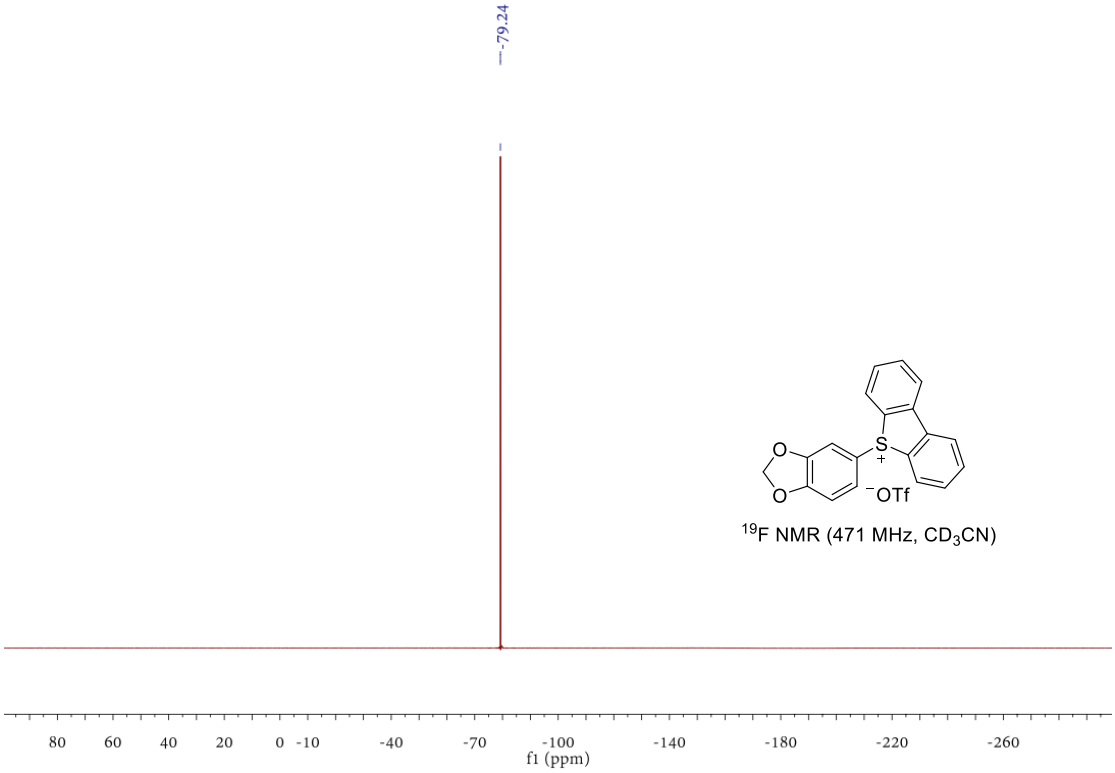
^{13}C NMR spectrum of **1p**



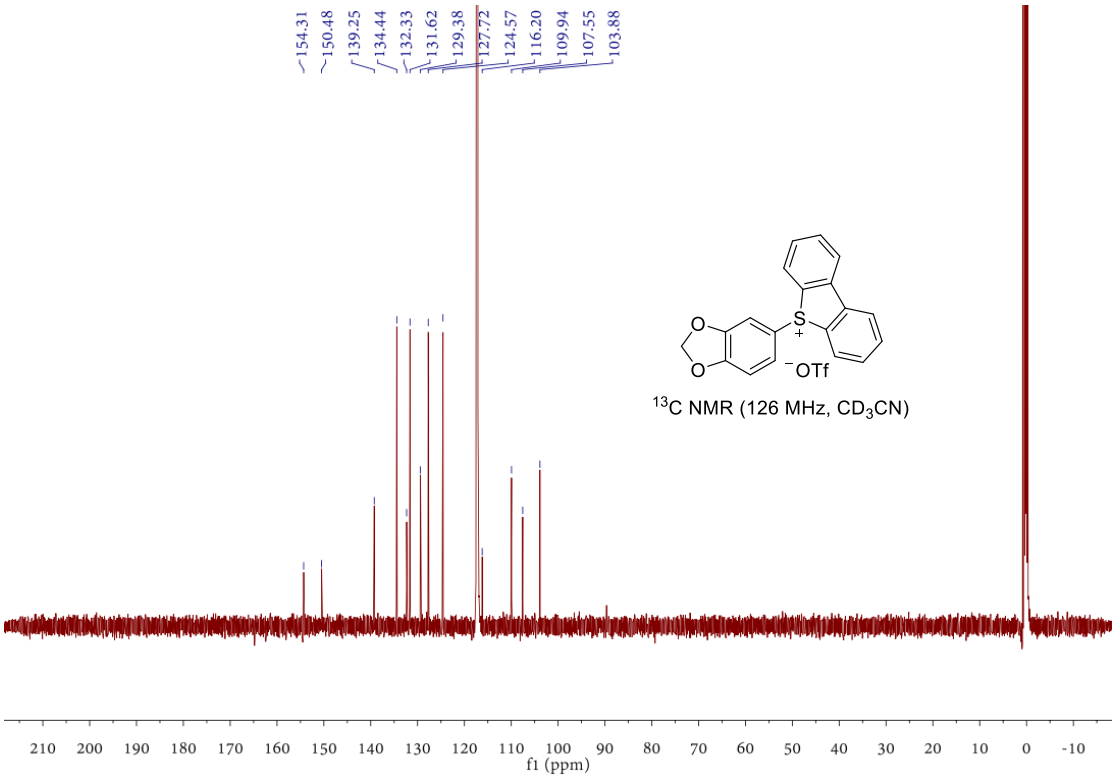
^{1}H NMR spectrum of **1q**



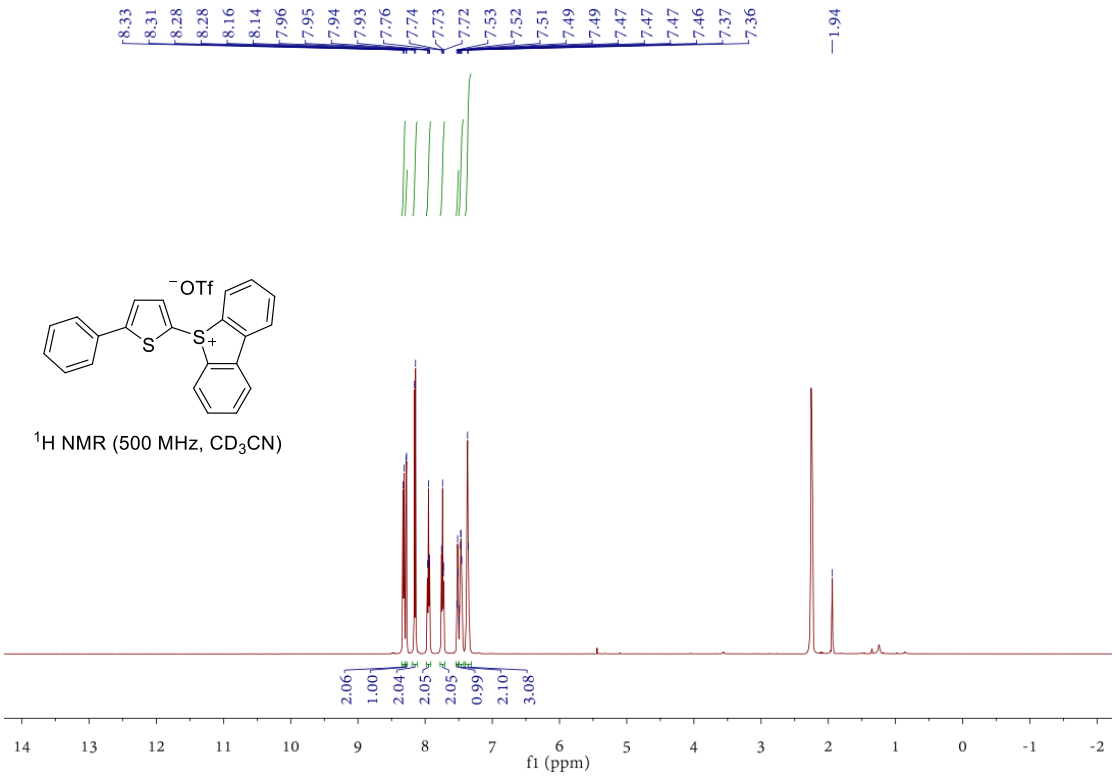
^{19}F NMR spectrum of **1q**



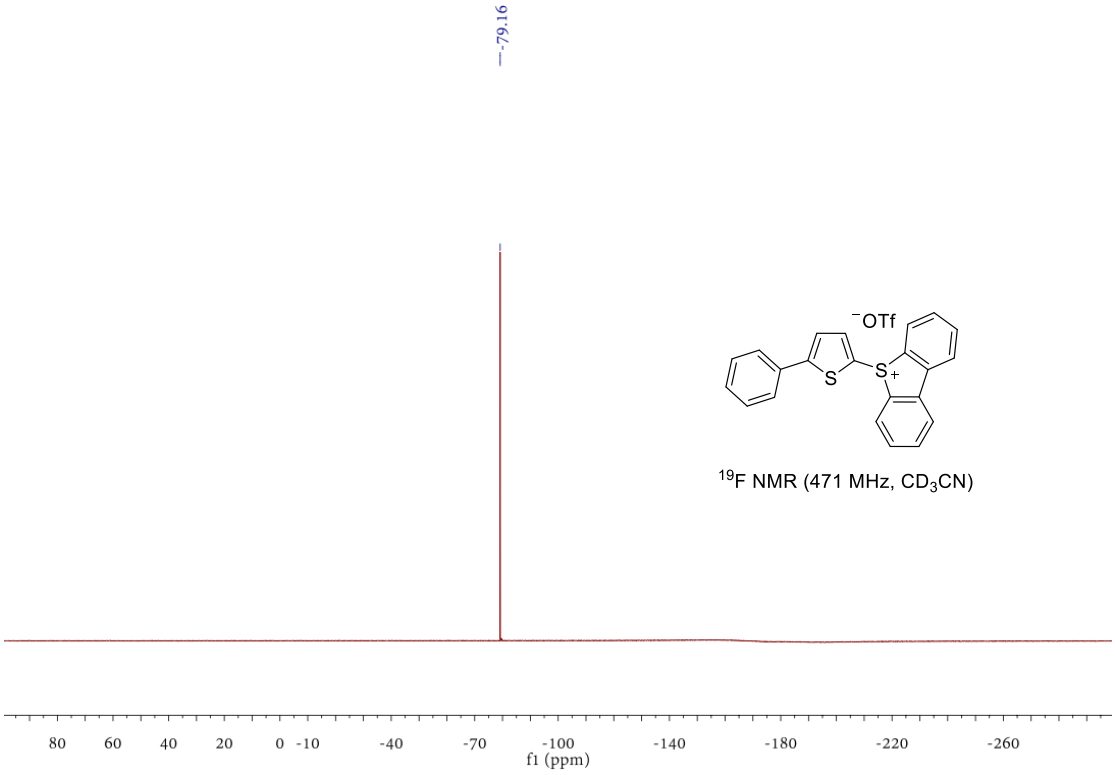
^{13}C NMR spectrum of **1q**



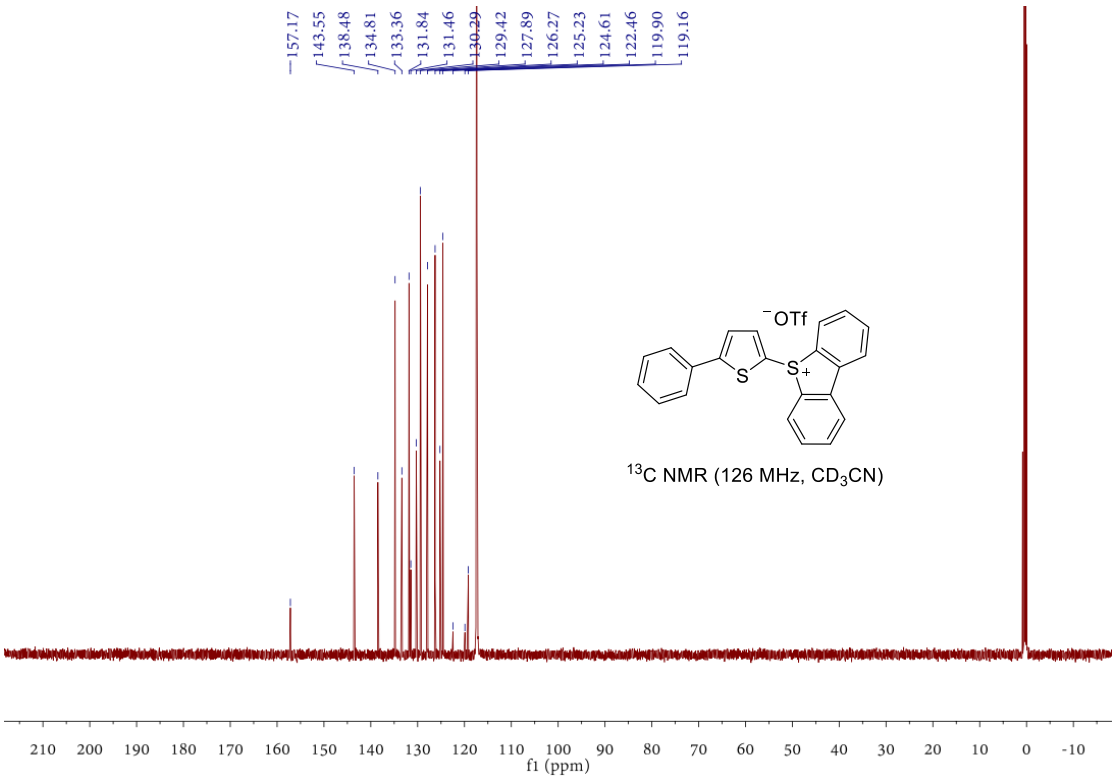
^{1}H NMR spectrum of **1r**



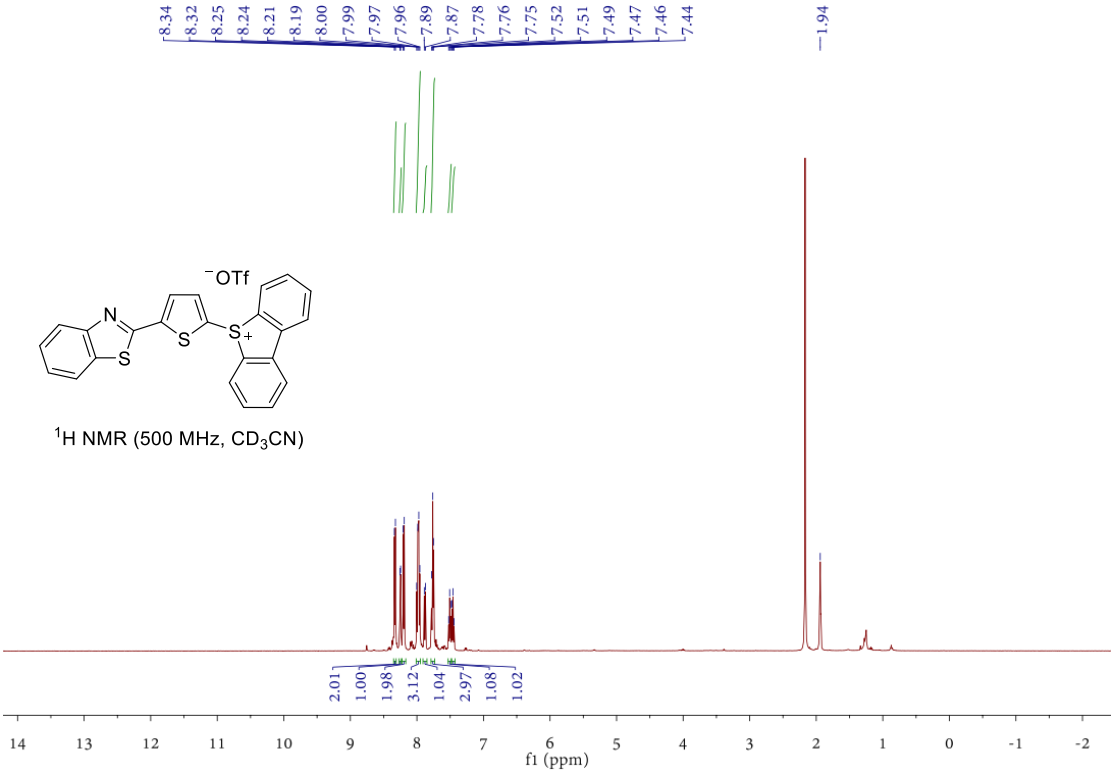
^{19}F NMR spectrum of **1r**



^{13}C NMR spectrum of **1r**

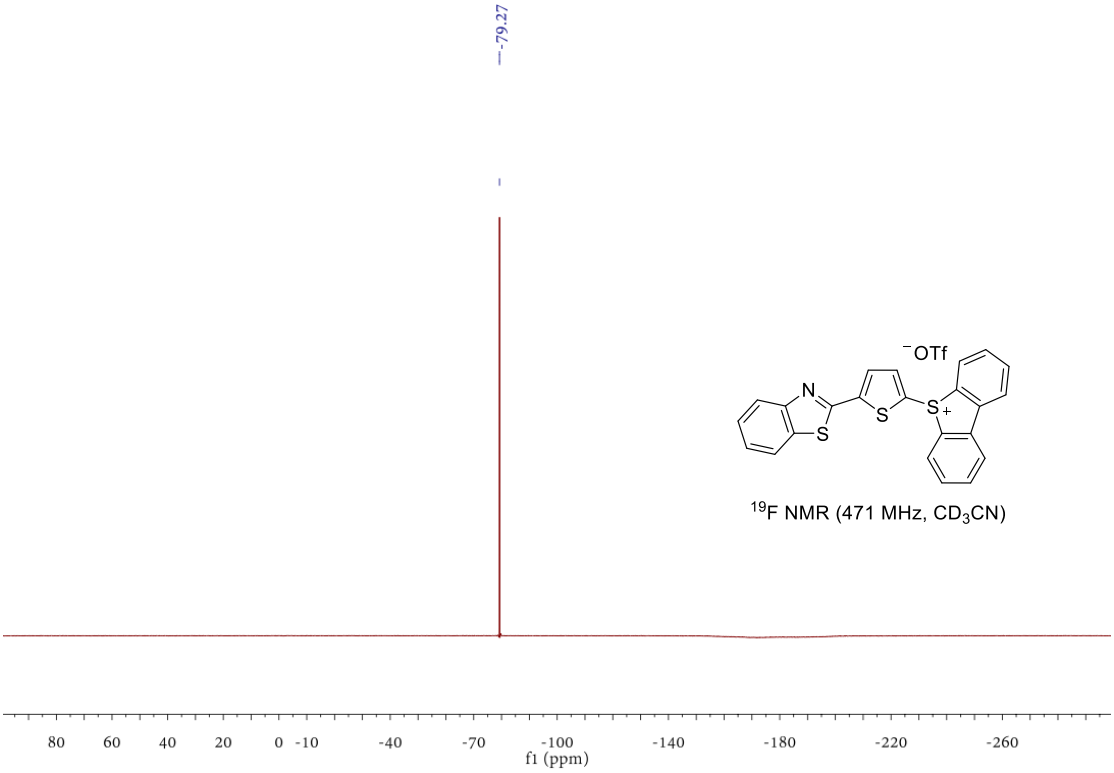


^{1}H NMR spectrum of **1s**



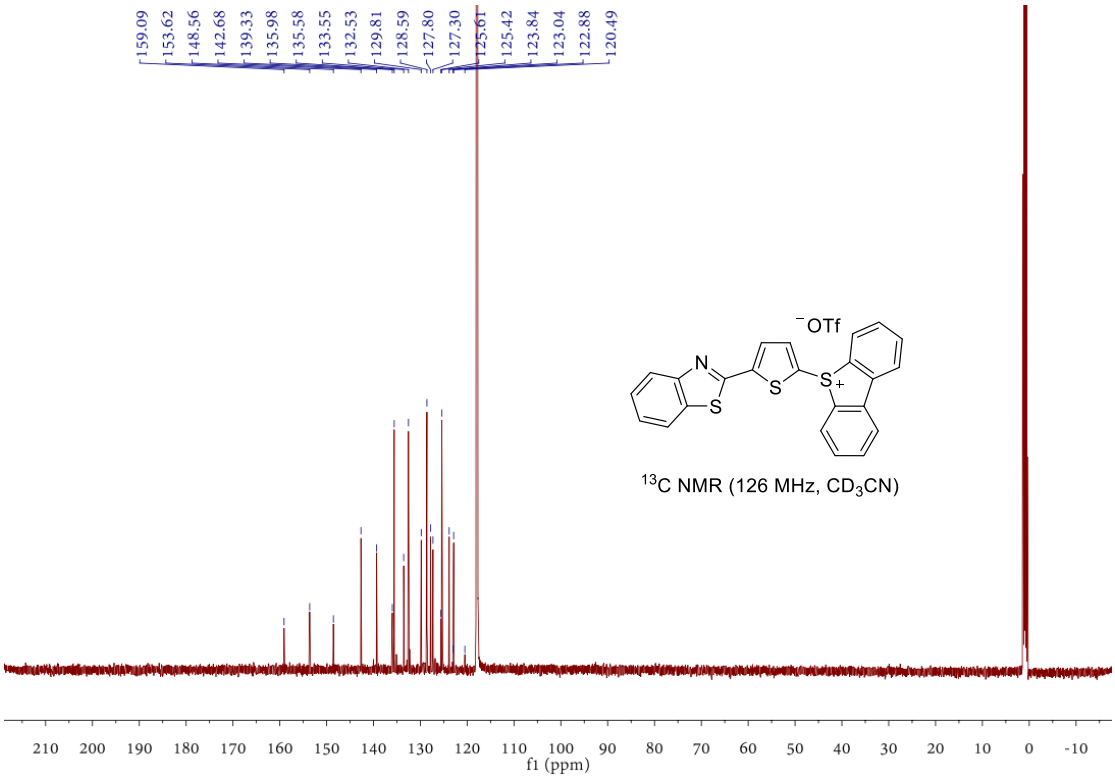
^{1}H NMR (500 MHz, CD_3CN)

^{19}F NMR spectrum of **1s**

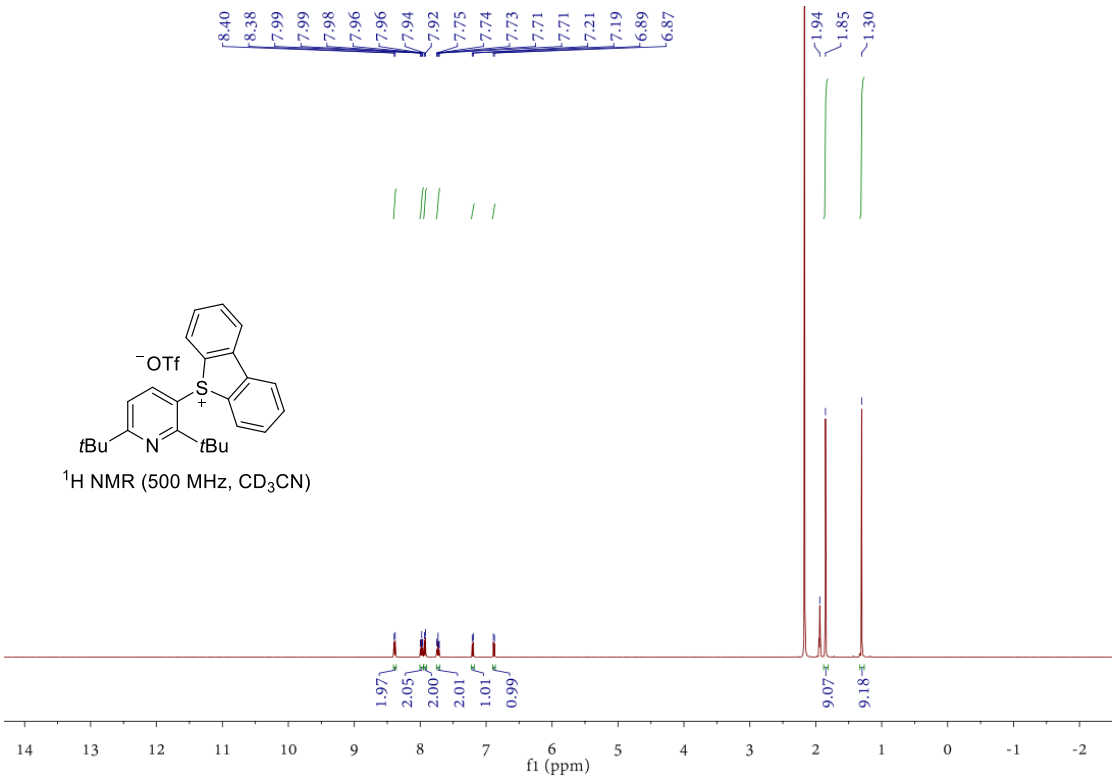


^{19}F NMR (471 MHz, CD_3CN)

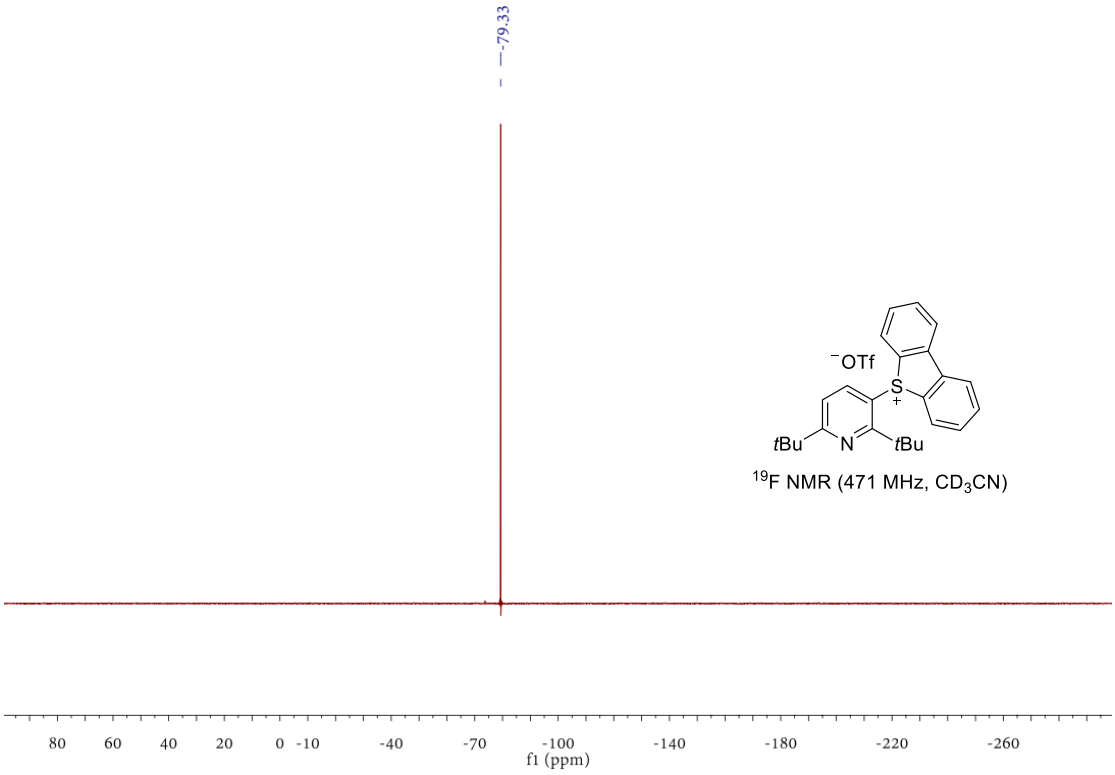
^{13}C NMR spectrum of **1s**



^{1}H NMR spectrum of **1t**

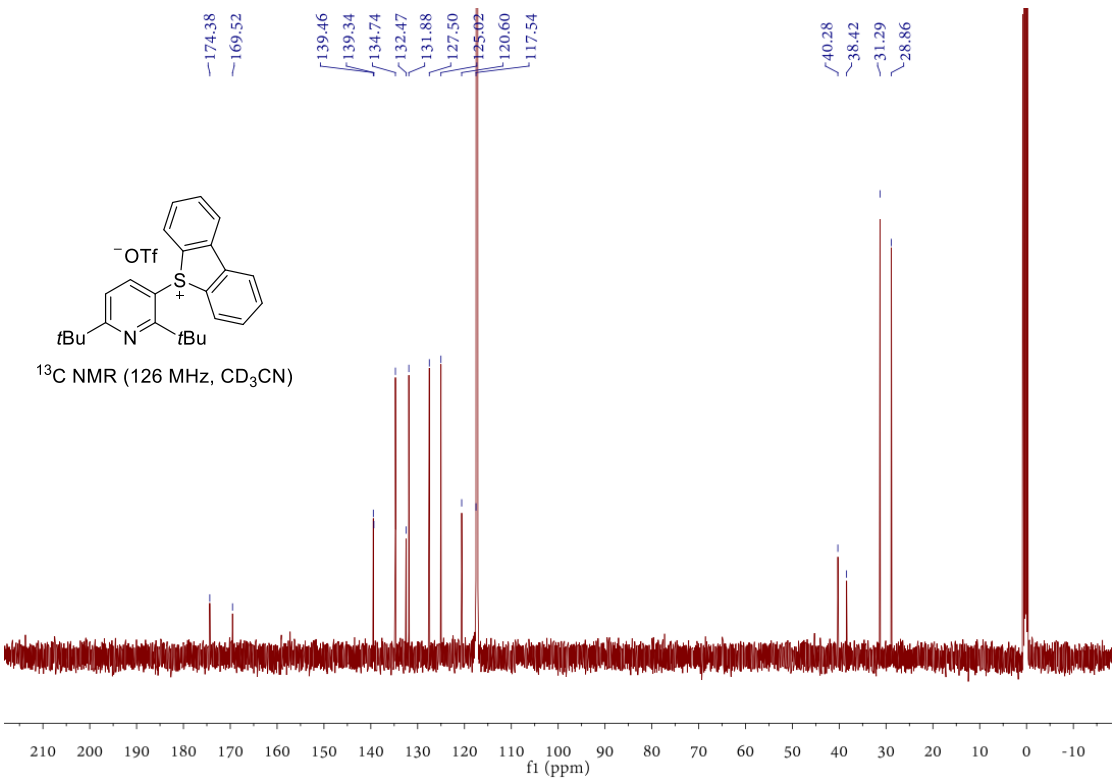


^{19}F NMR spectrum of **1t**



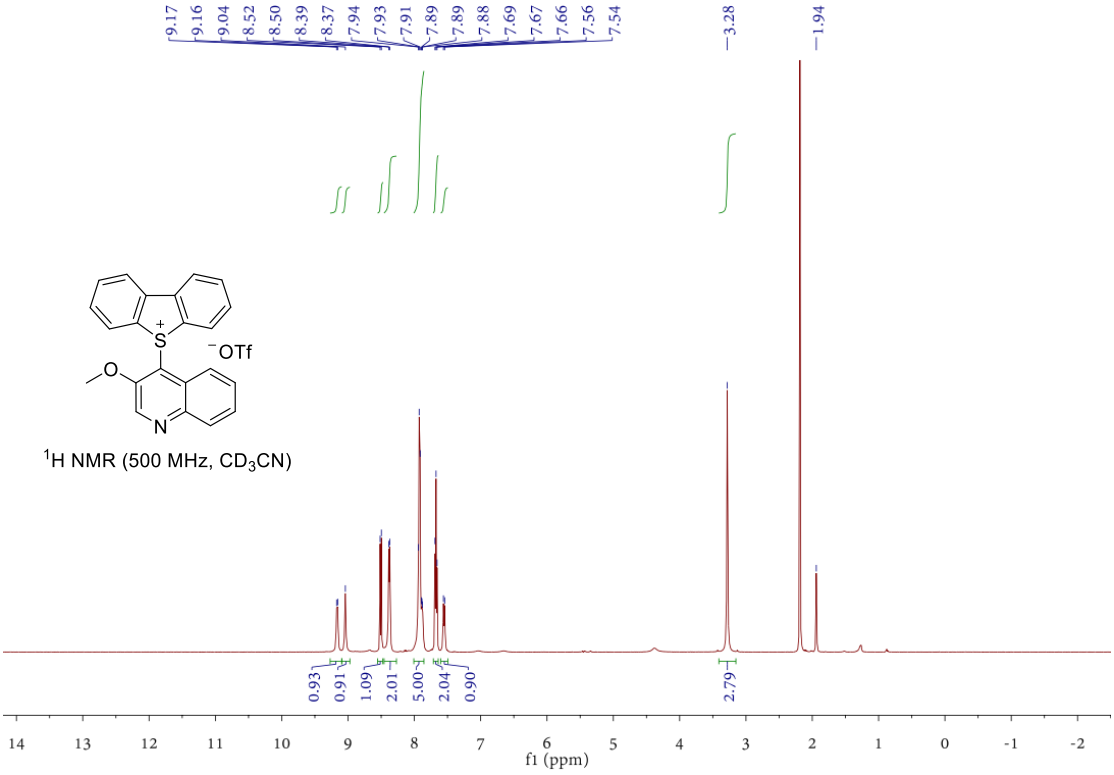
^{19}F NMR (471 MHz, CD_3CN)

^{13}C NMR spectrum of **1t**

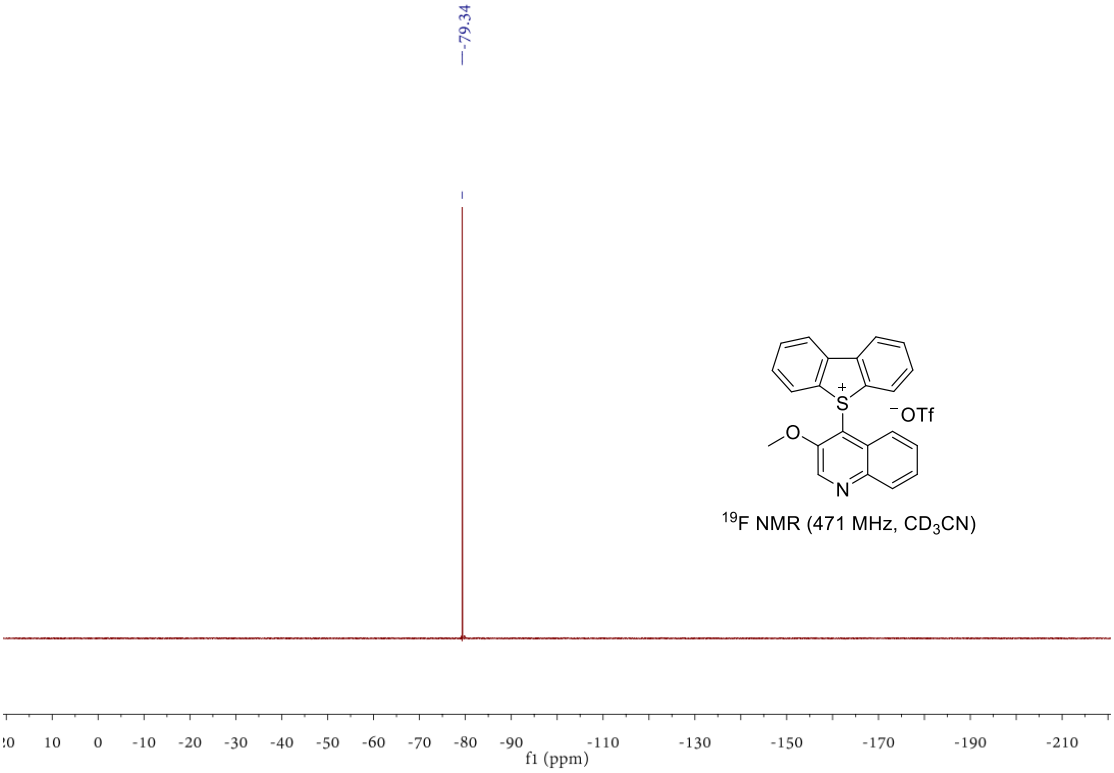


^{13}C NMR (126 MHz, CD_3CN)

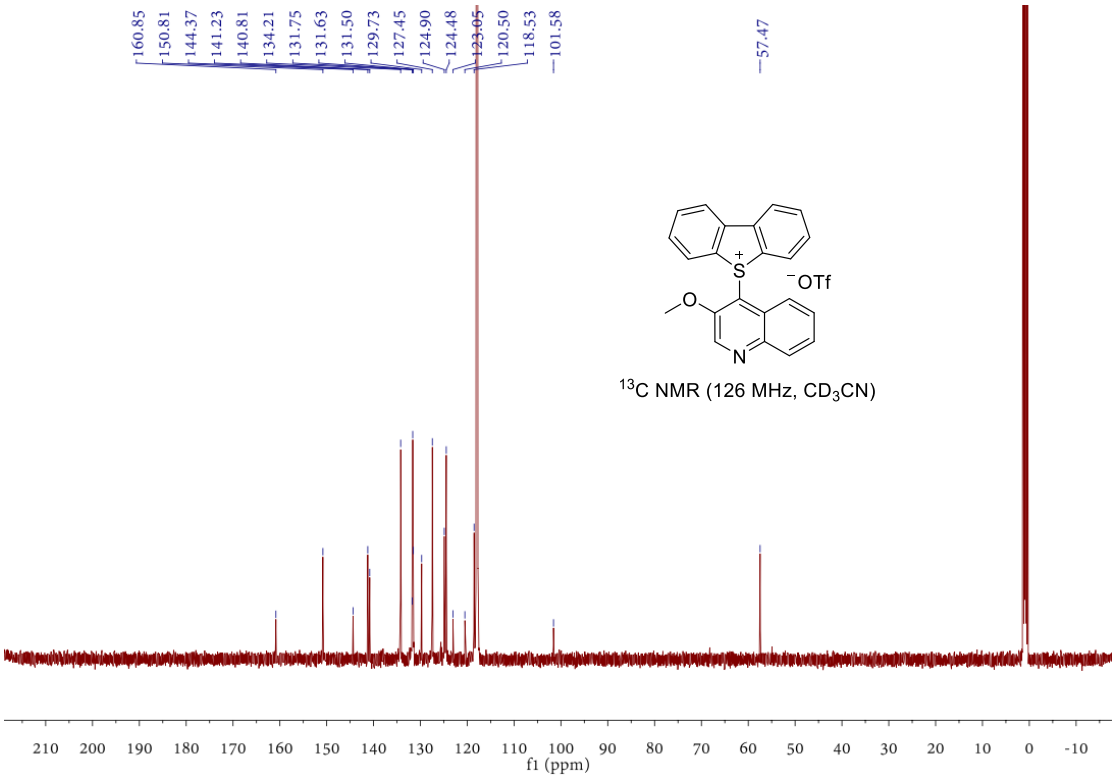
^{1}H NMR spectrum of **1u**



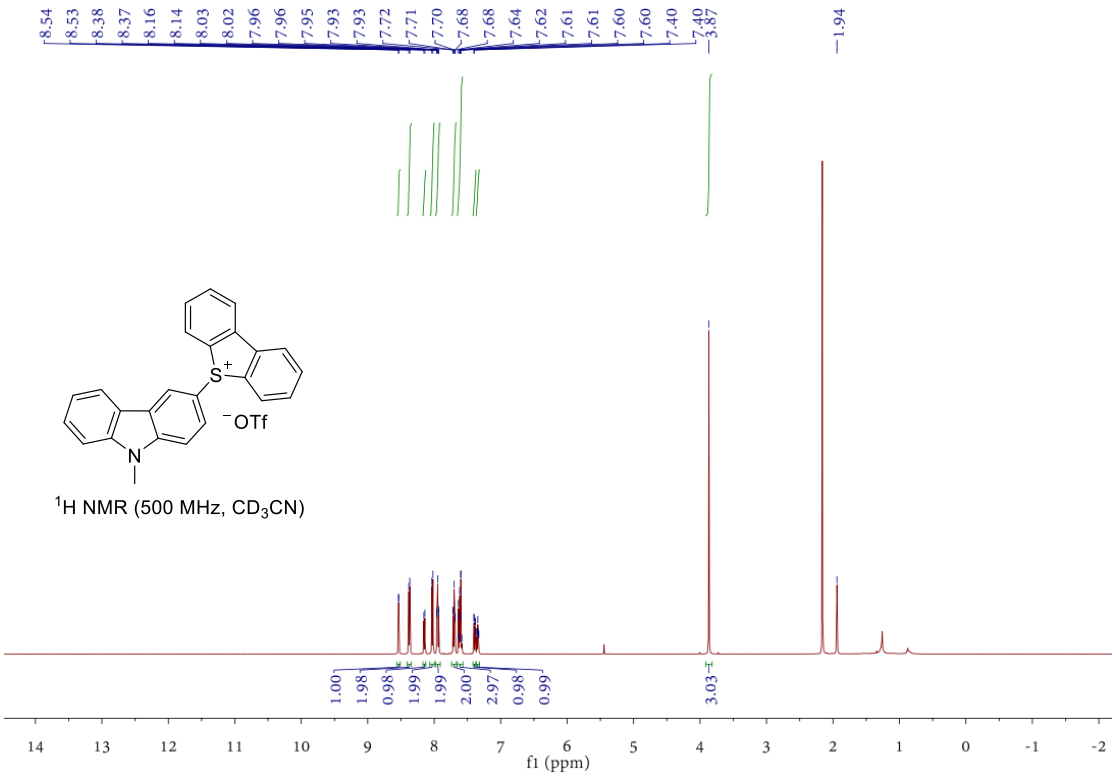
^{19}F NMR spectrum of **1u**



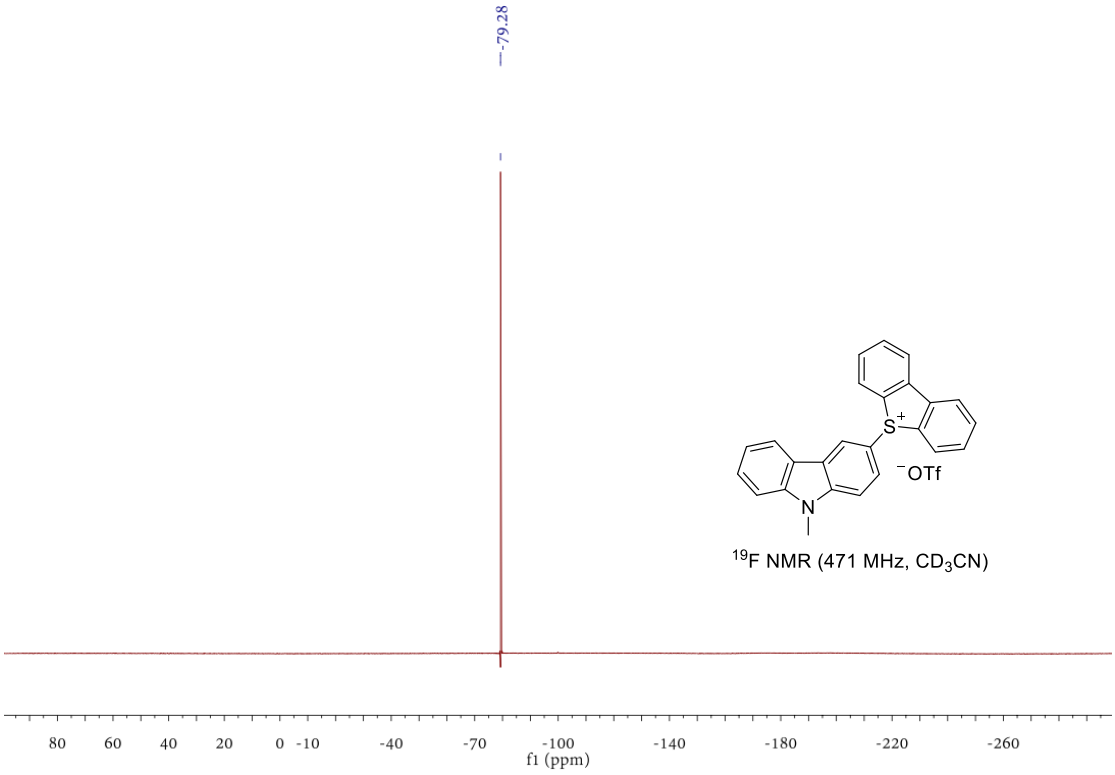
^{13}C NMR spectrum of **1u**



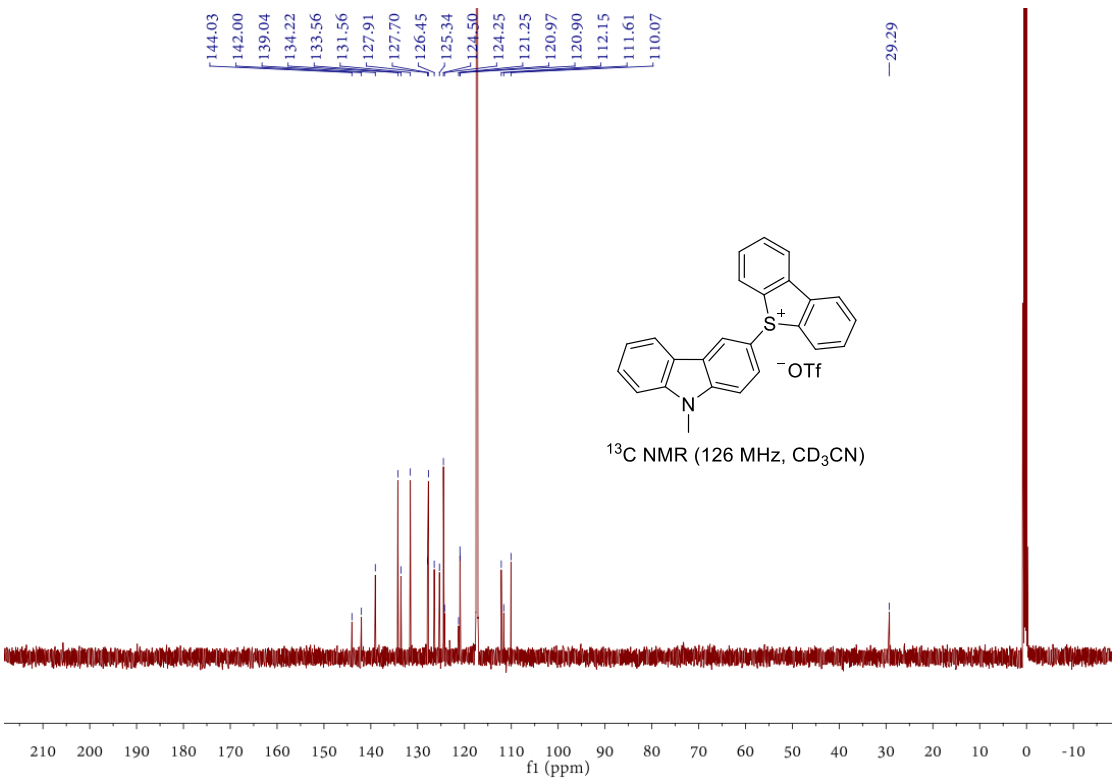
^{1}H NMR spectrum of **1v**



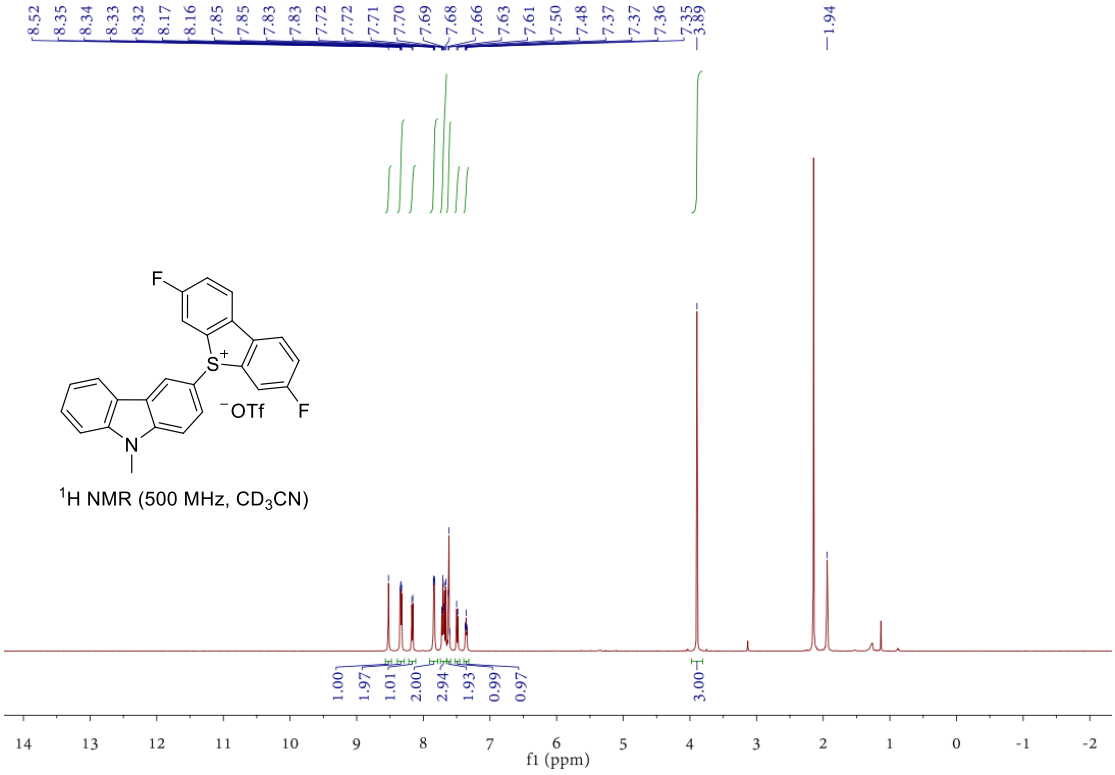
^{19}F NMR spectrum of **1v**



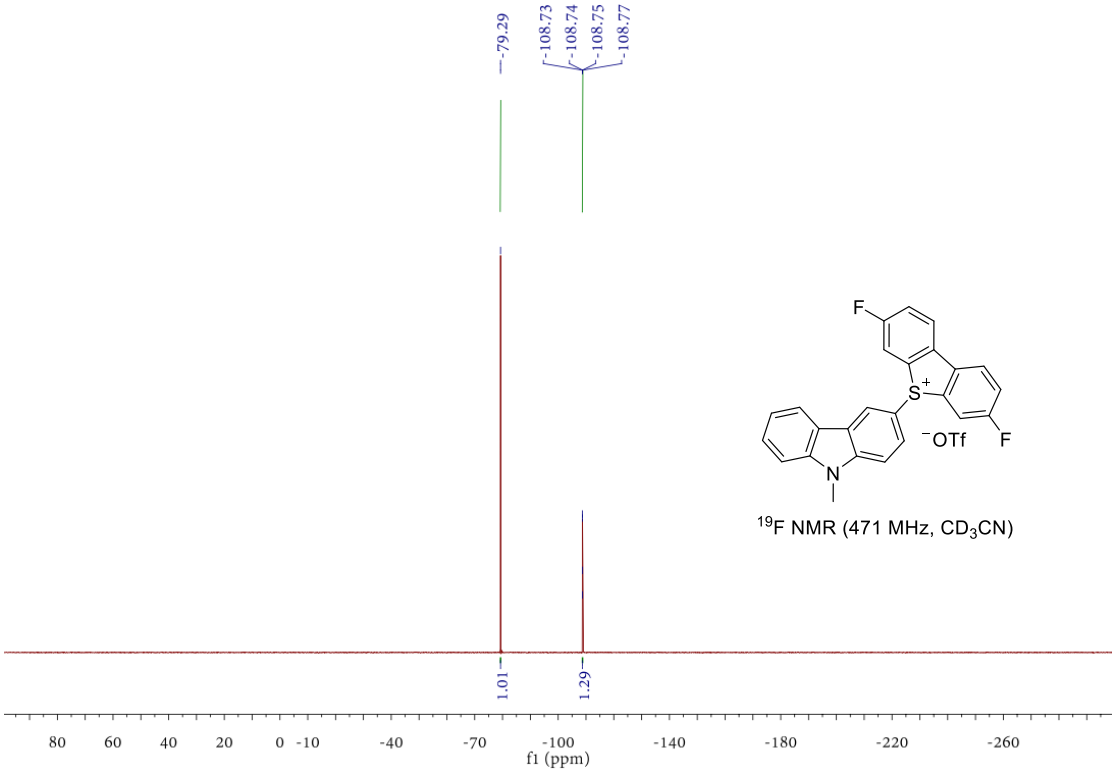
^{13}C NMR spectrum of **1v**



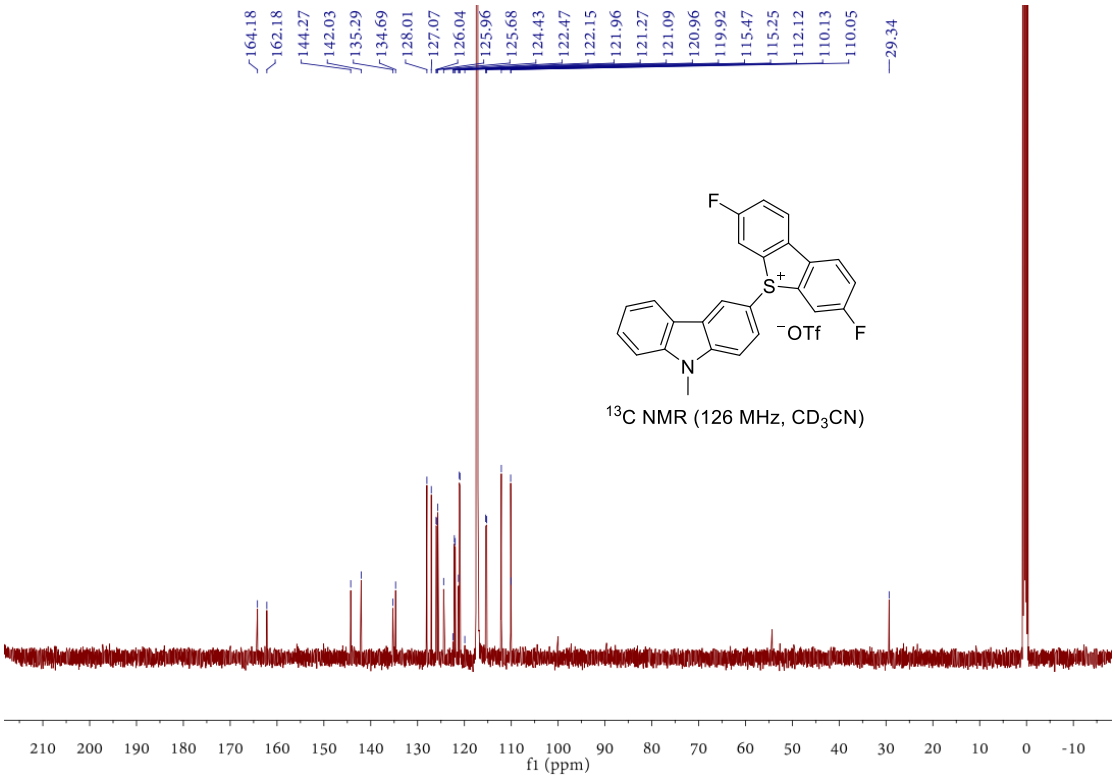
^{1}H NMR spectrum of **1w**



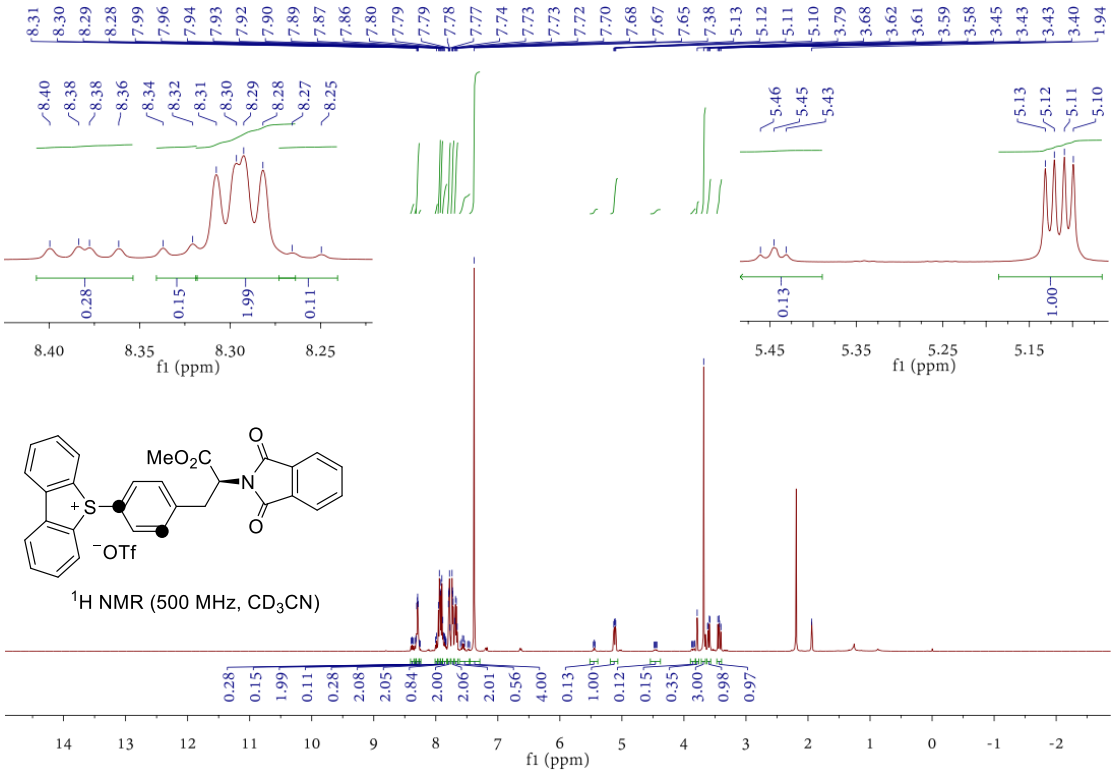
^{19}F NMR spectrum of **1w**



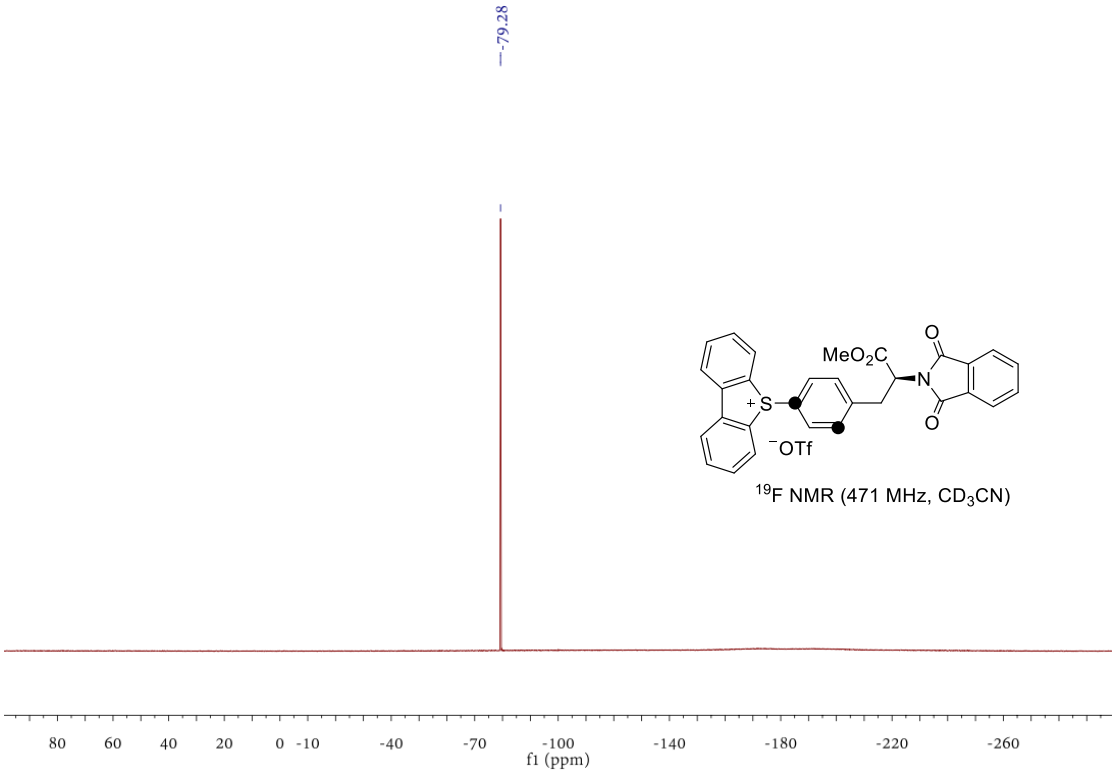
^{13}C NMR spectrum of **1w**



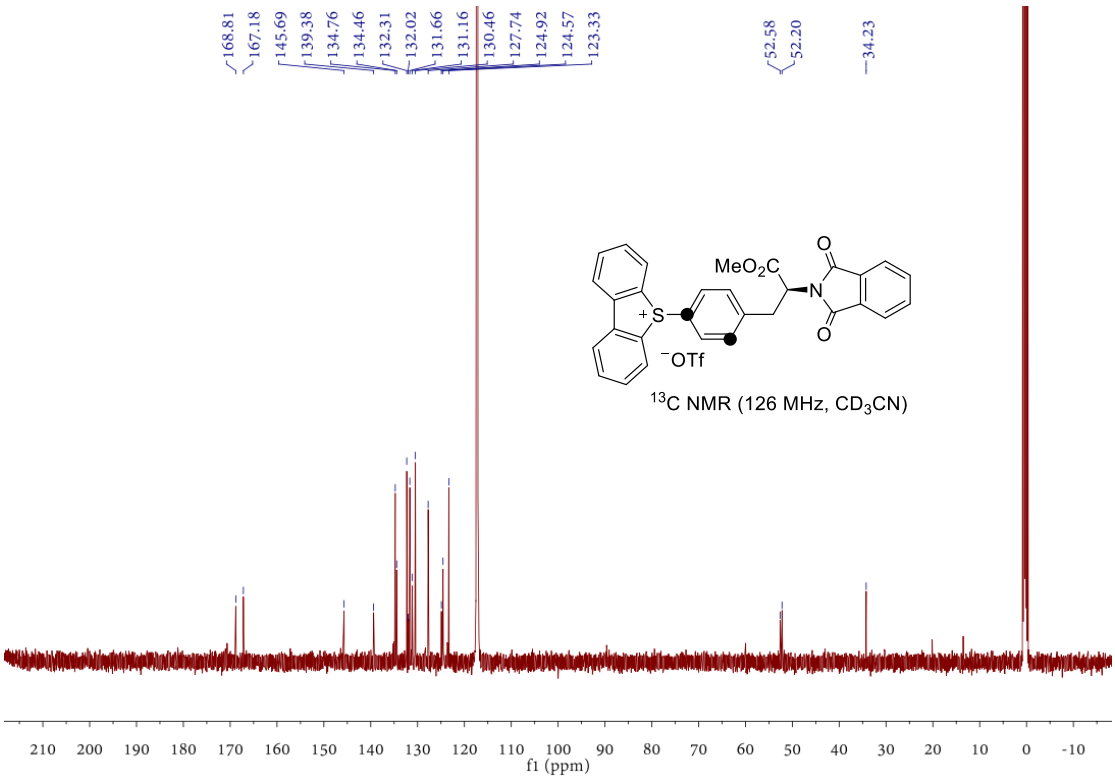
^{1}H NMR spectrum of **1x**



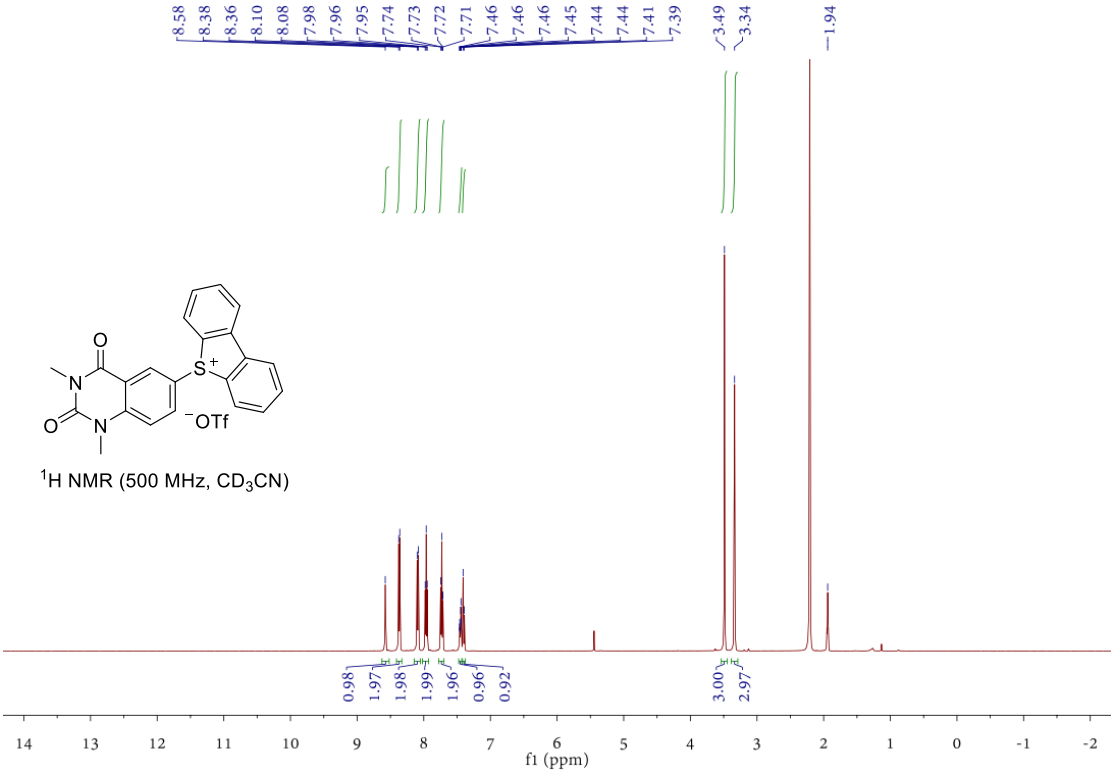
^{19}F NMR spectrum of **1x**



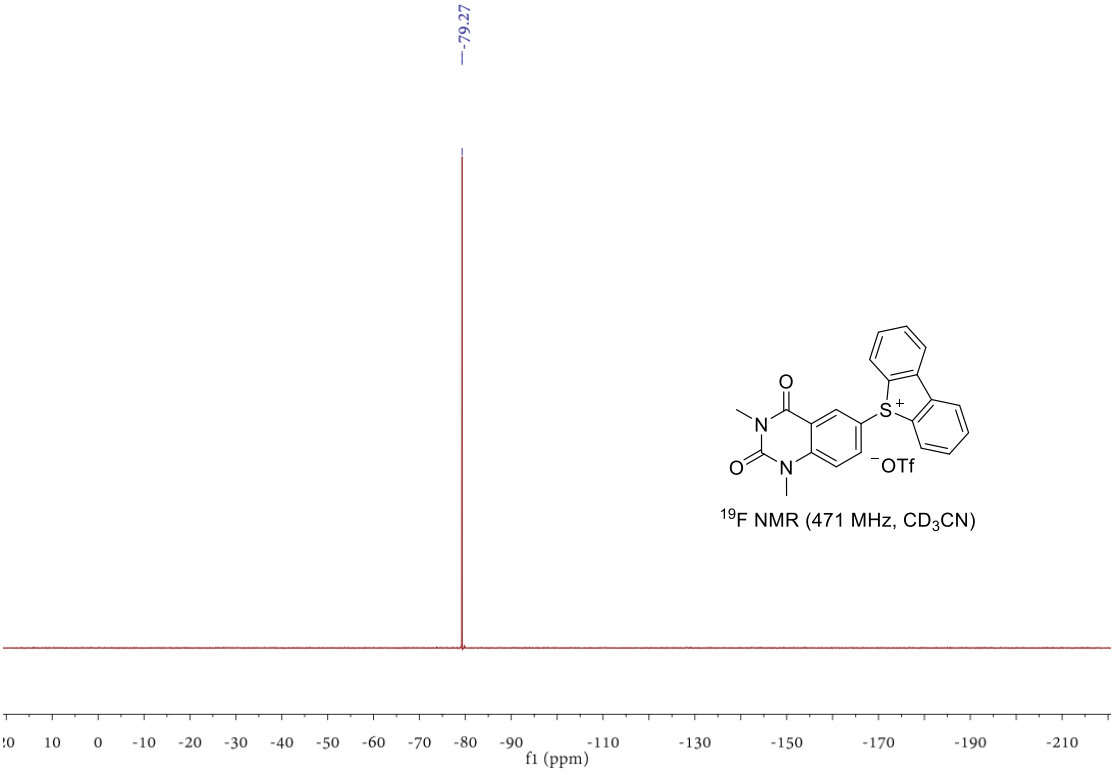
^{13}C NMR spectrum of **1x**



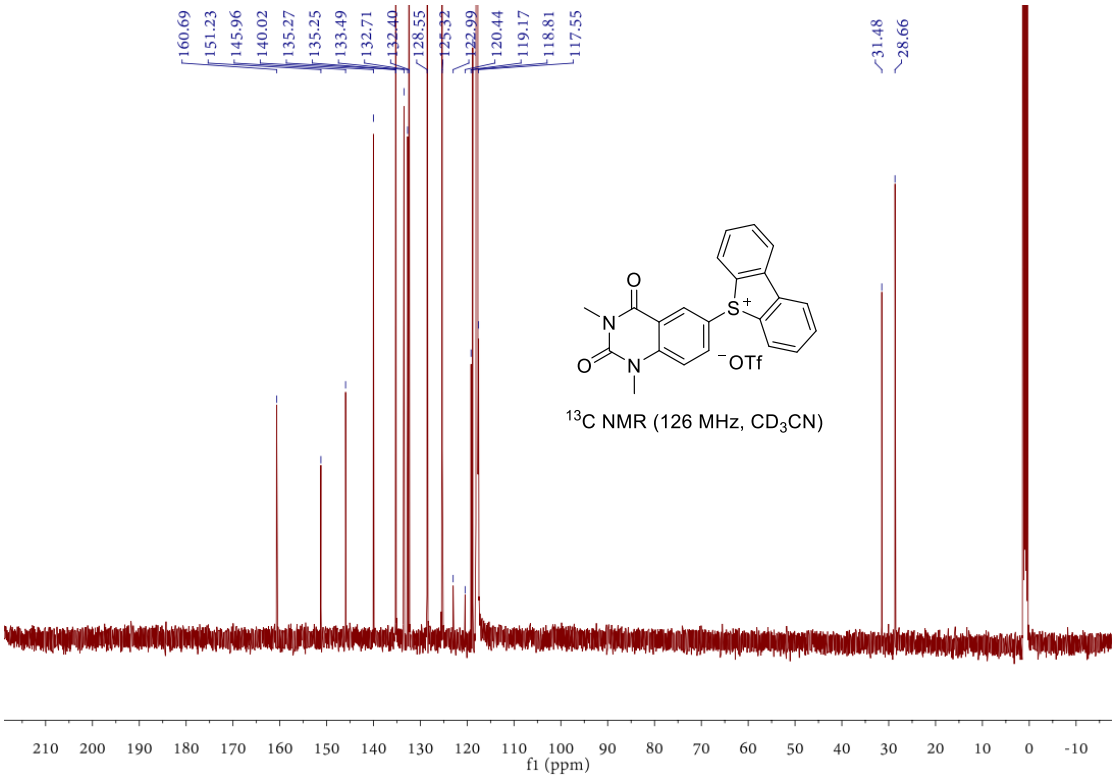
^{1}H NMR spectrum of **1y**



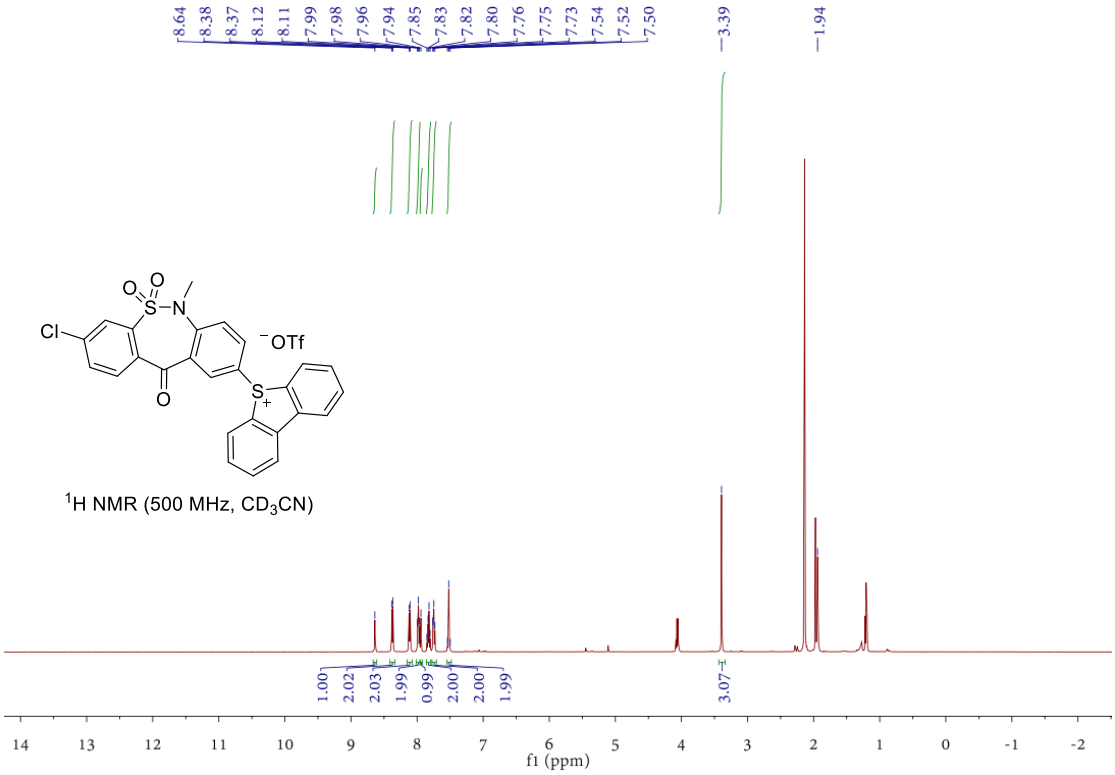
^{19}F NMR spectrum of **1y**



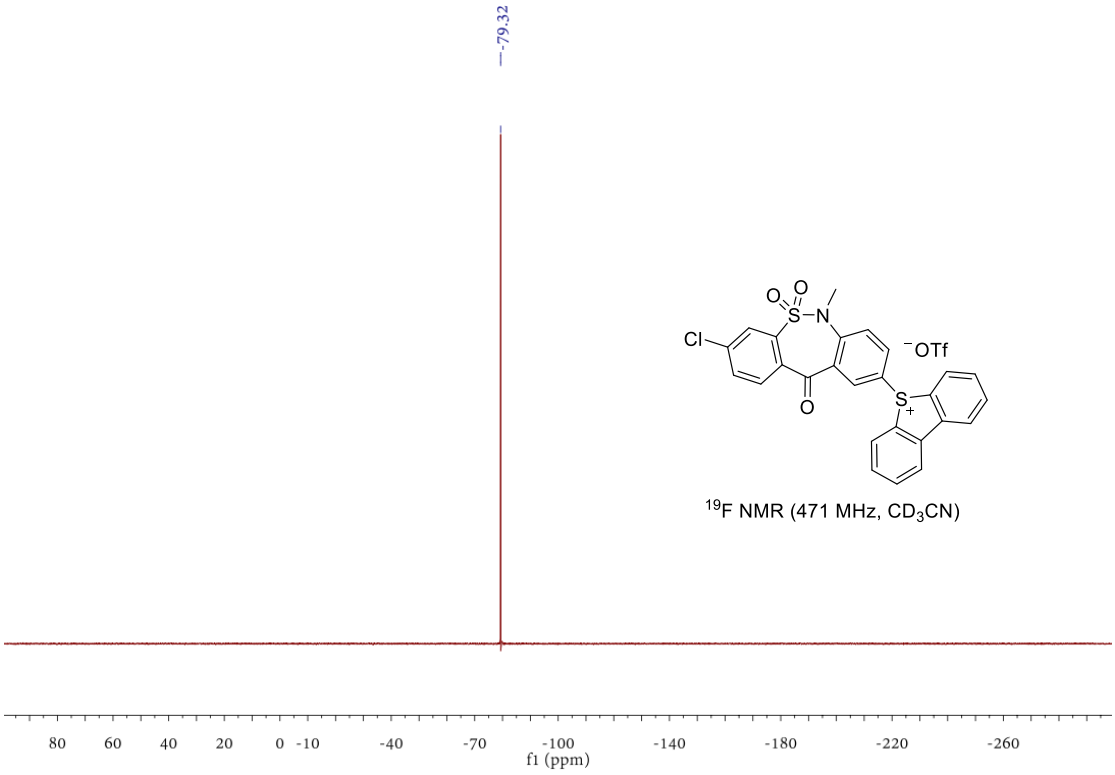
^{13}C NMR spectrum of **1y**



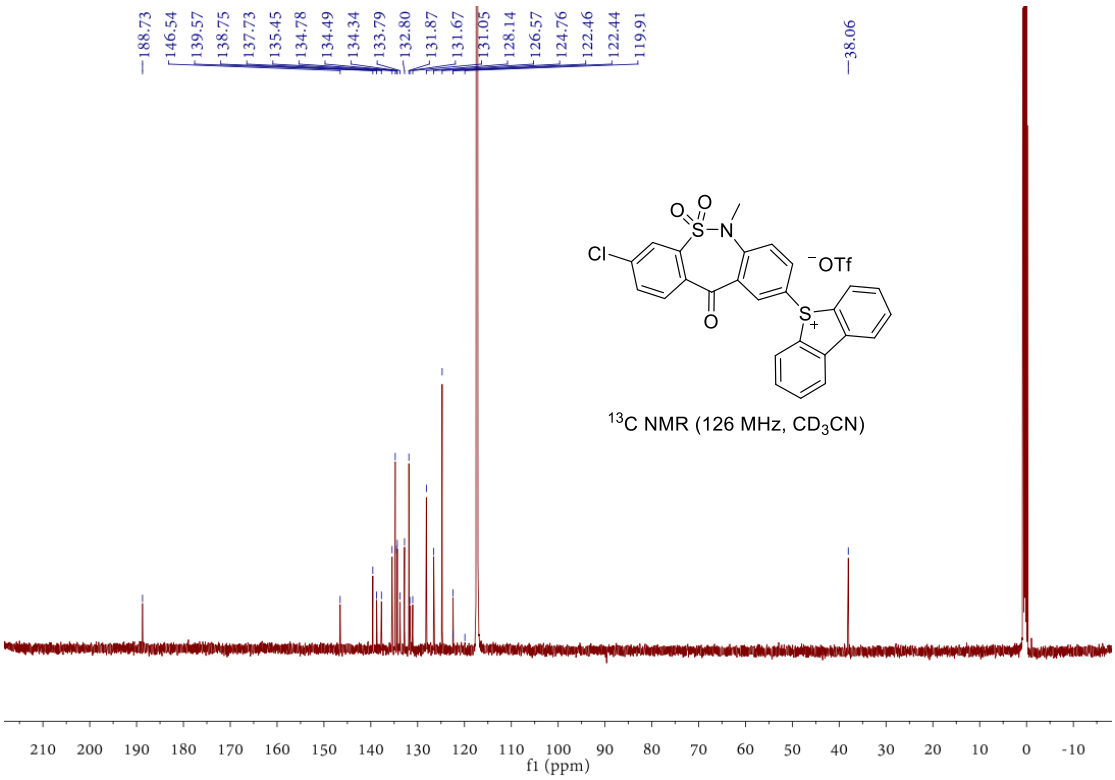
^{1}H NMR spectrum of **1z**



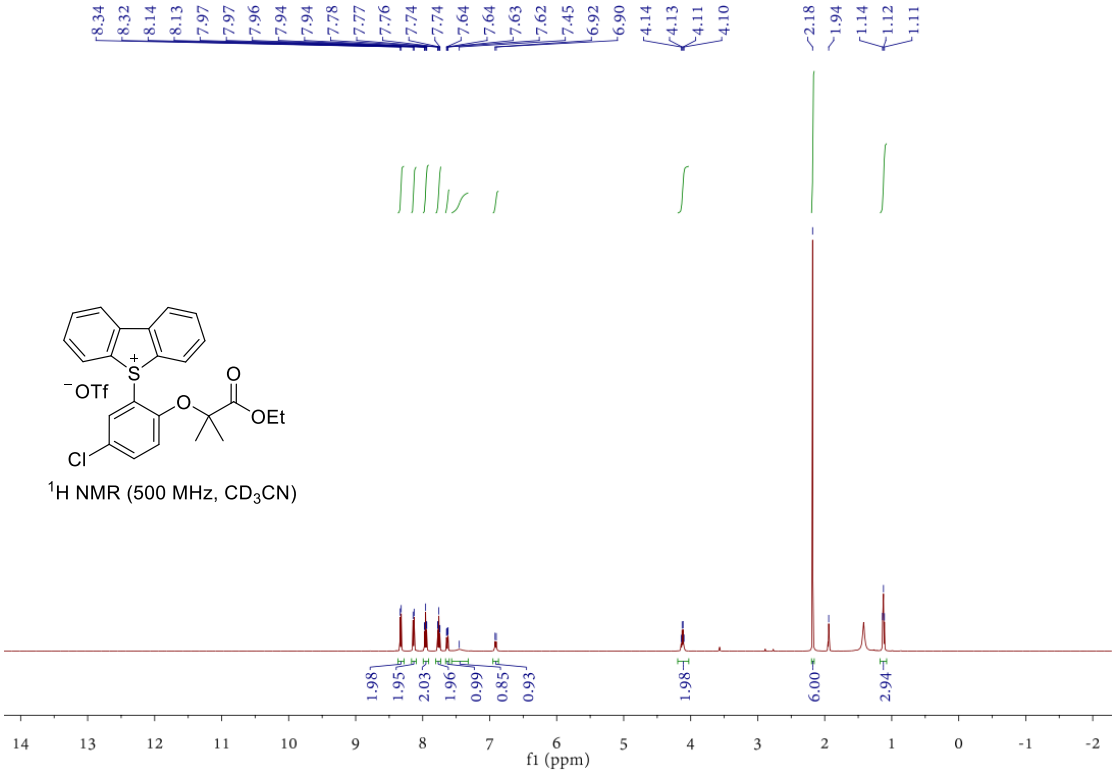
^{19}F NMR spectrum of **1z**



^{13}C NMR spectrum of **1z**

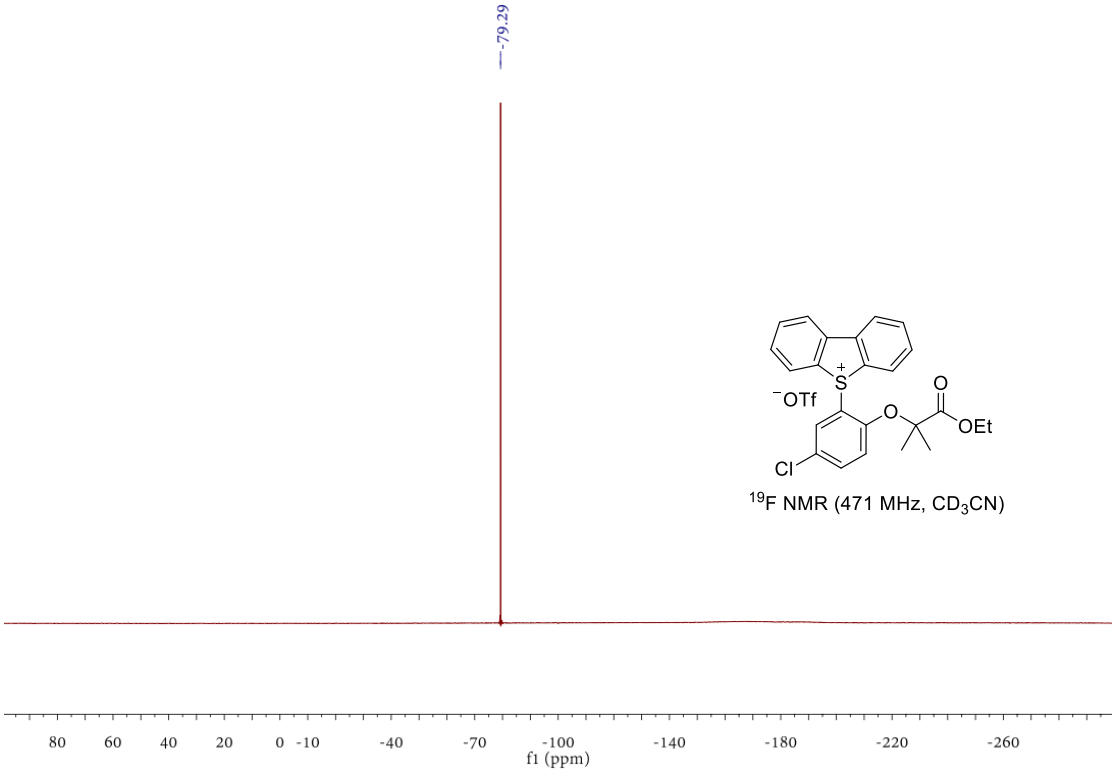


^{1}H NMR spectrum of **1aa**



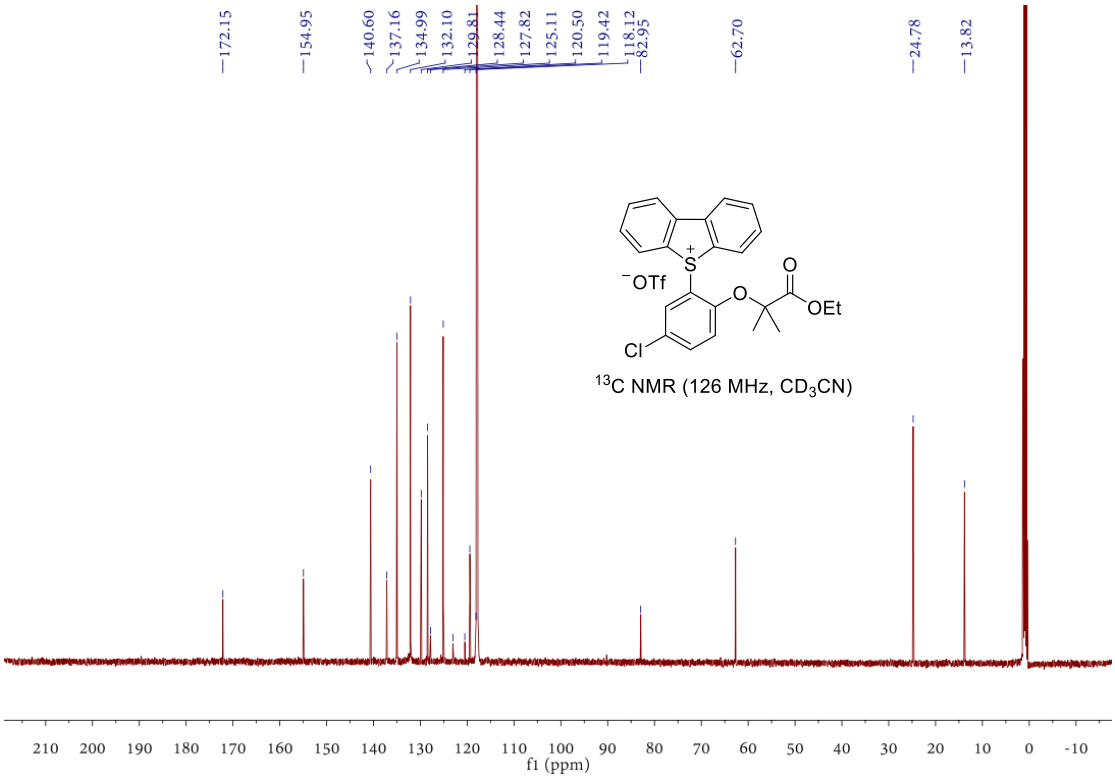
^{1}H NMR (500 MHz, CD_3CN)

^{19}F NMR spectrum of **1aa**

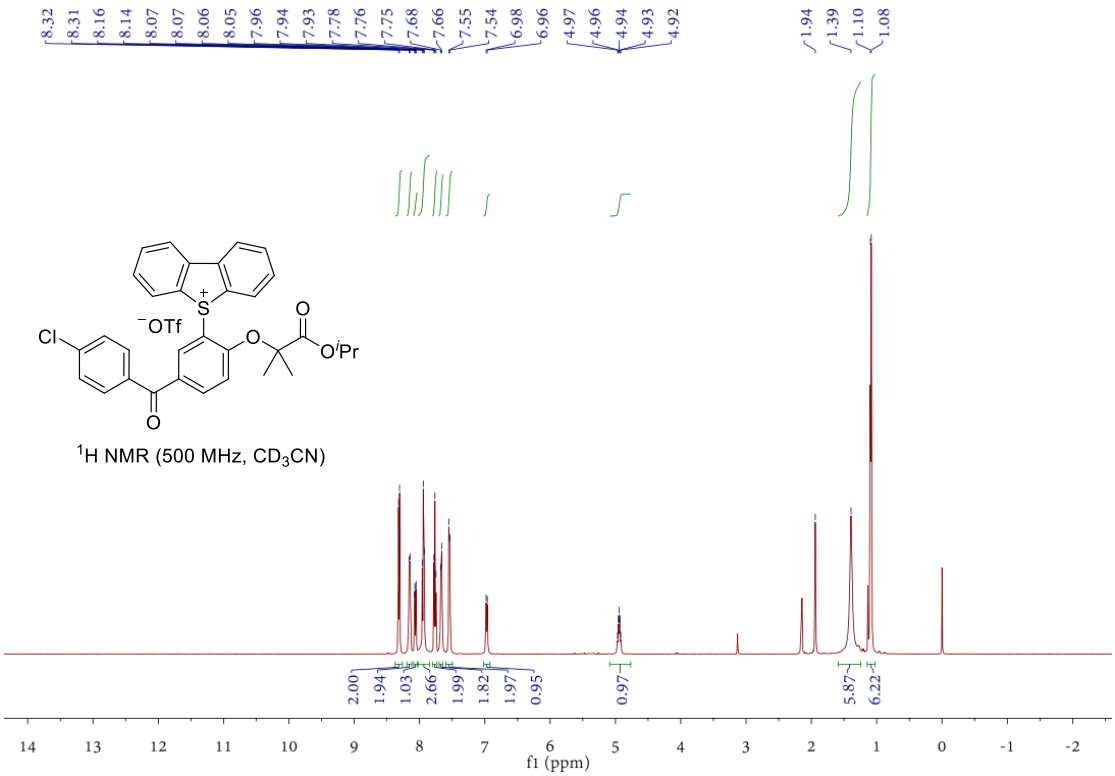


^{19}F NMR (471 MHz, CD_3CN)

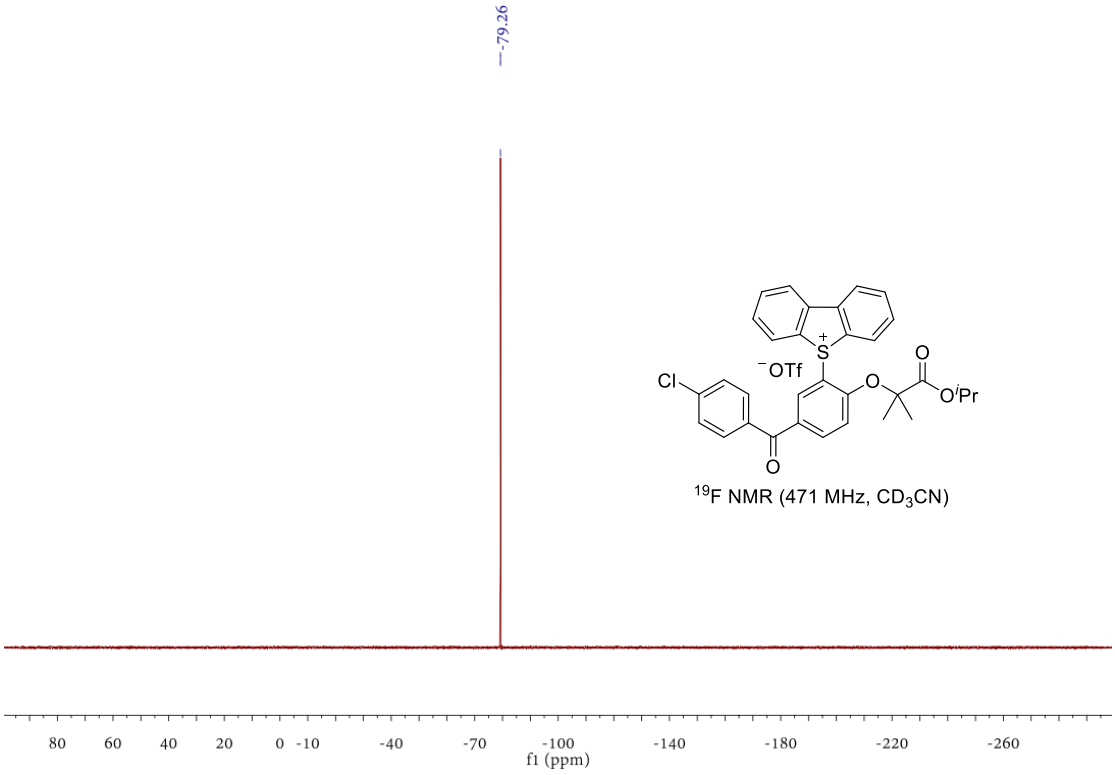
^{13}C NMR spectrum of **1aa**



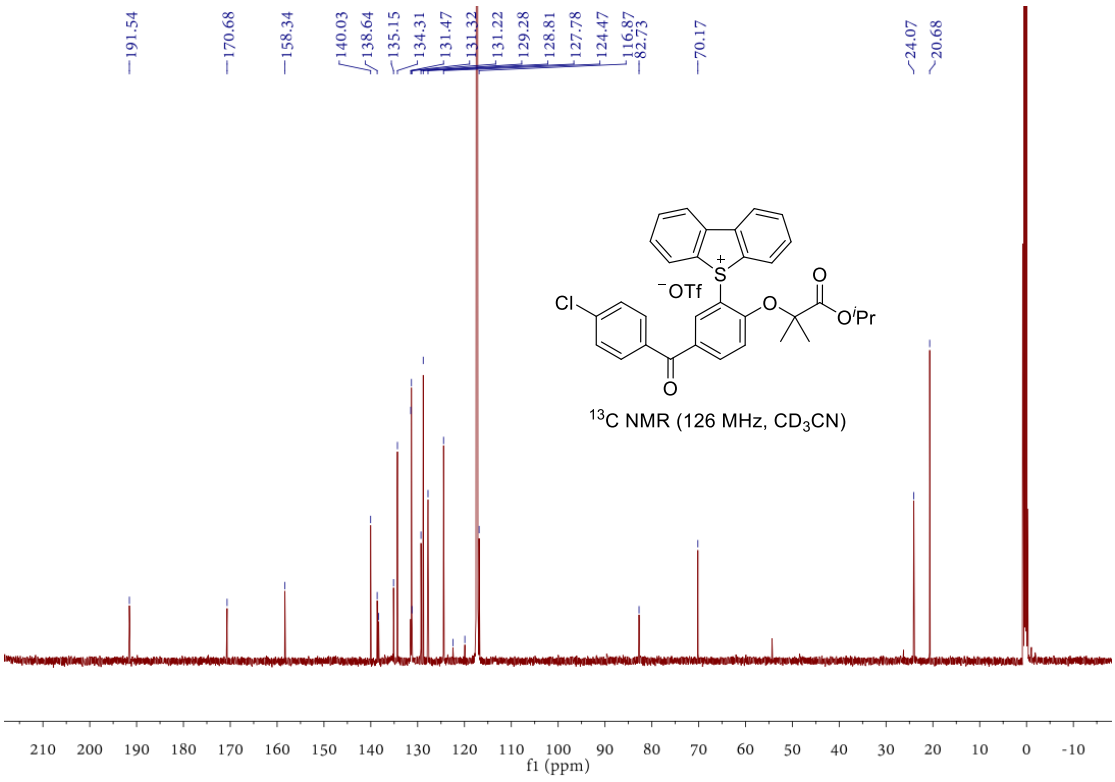
^{1}H NMR spectrum of **1ab**



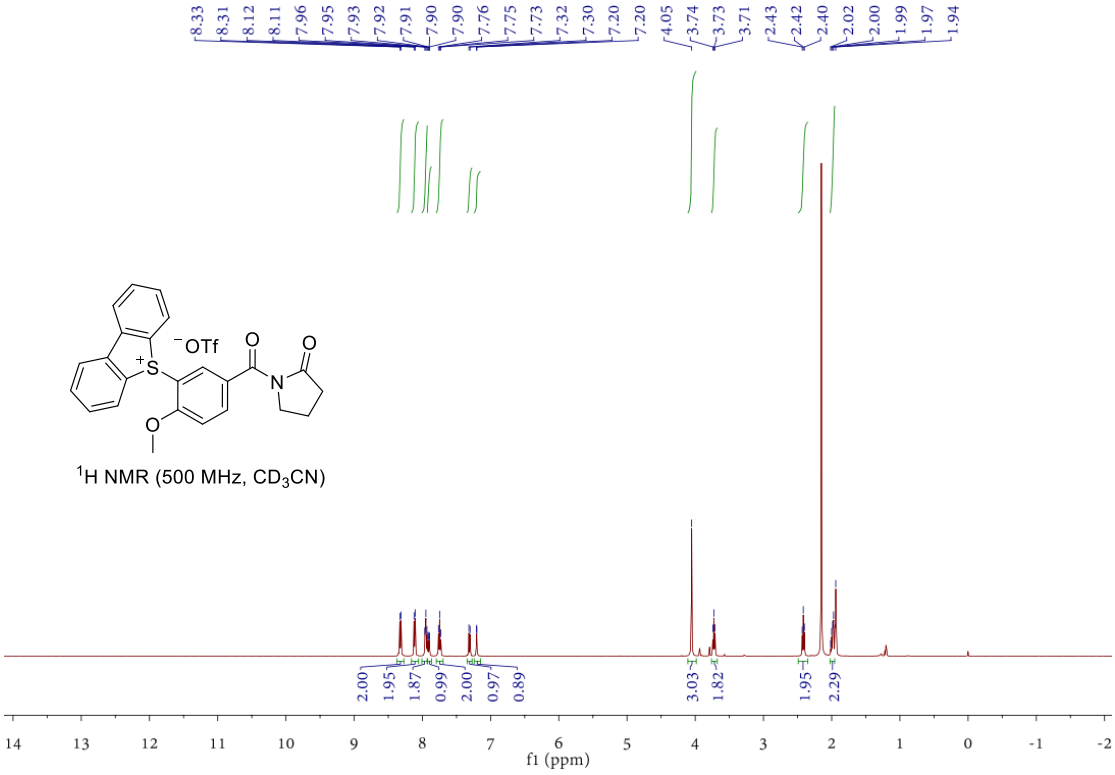
^{19}F NMR spectrum of **1ab**



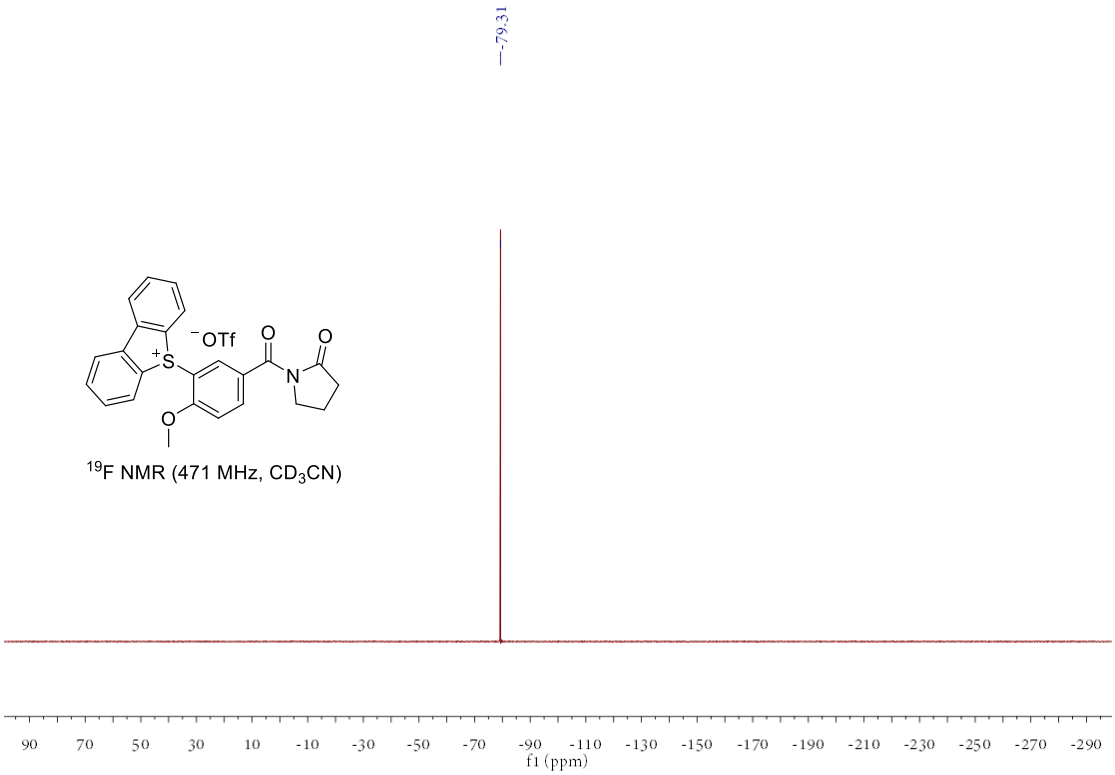
^{13}C NMR spectrum of **1ab**



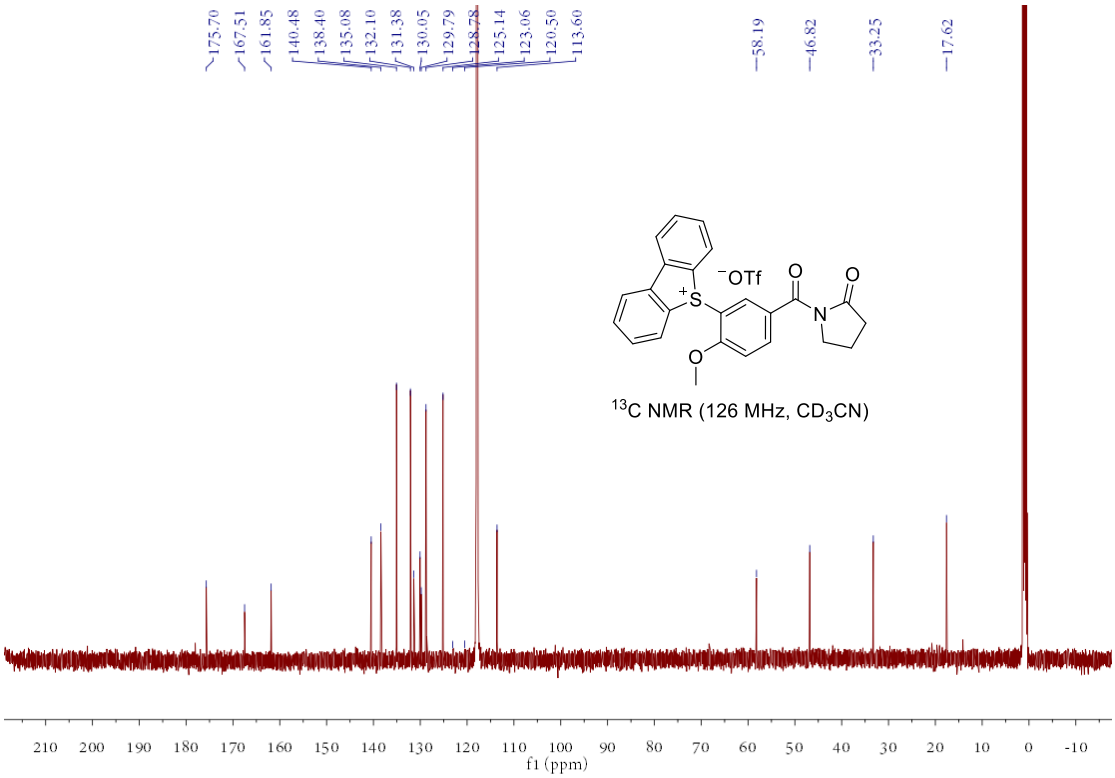
^{1}H NMR spectrum of **1ac**



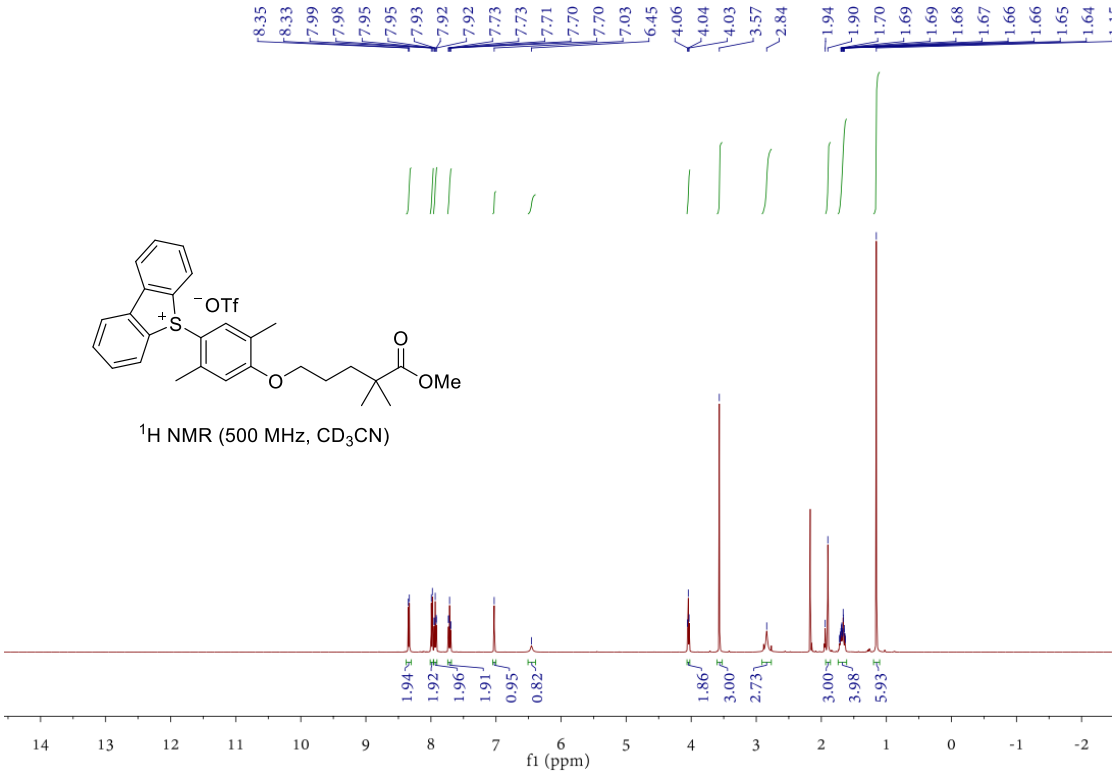
^{19}F NMR spectrum of **1ac**



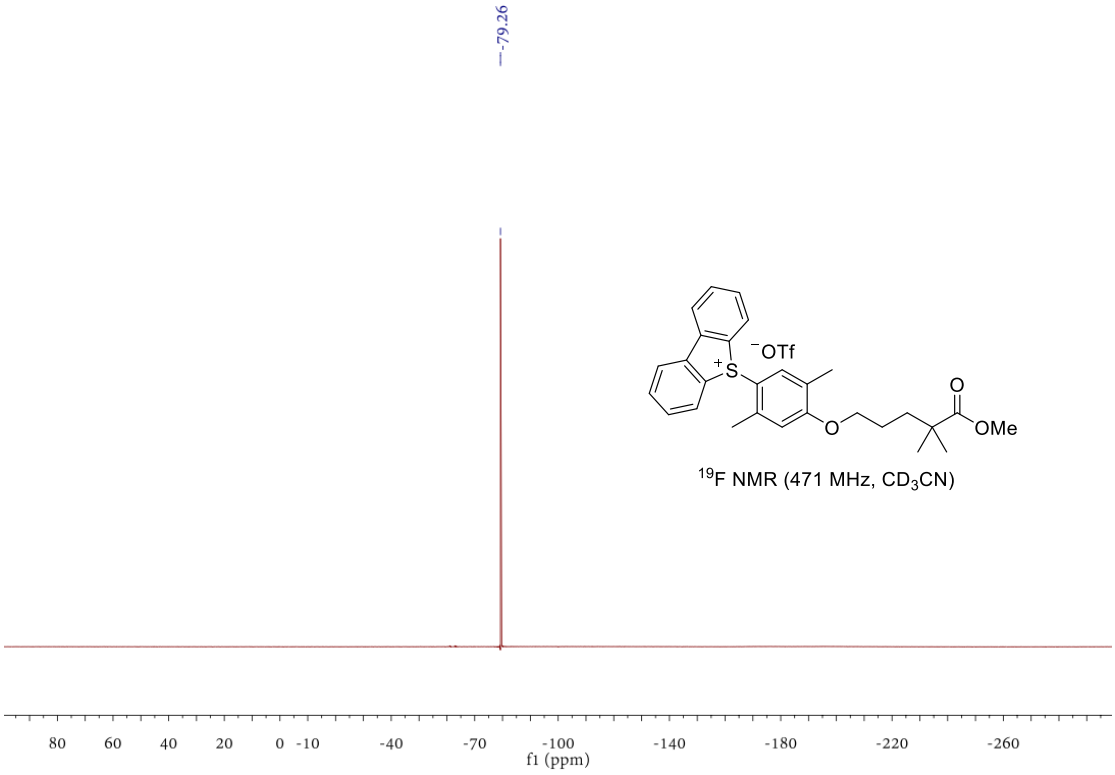
^{13}C NMR spectrum of **1ac**



^{1}H NMR spectrum of **1ad**

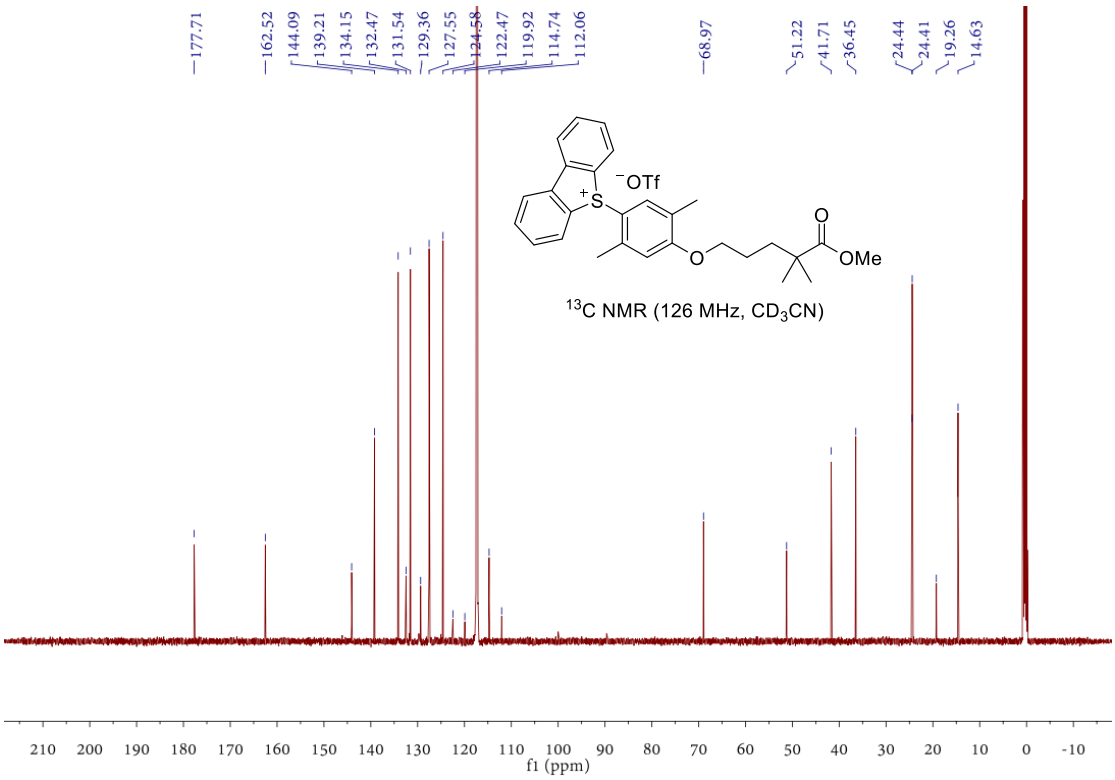


^{19}F NMR spectrum of **1ad**



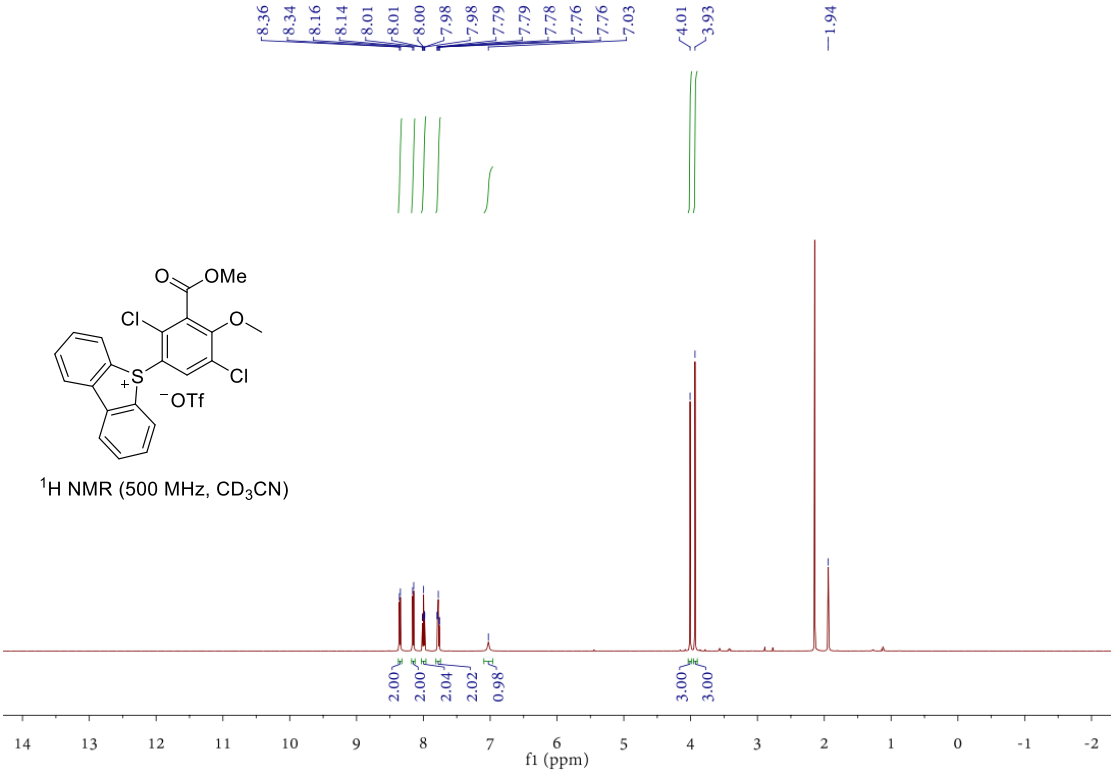
^{19}F NMR (471 MHz, CD_3CN)

^{13}C NMR spectrum of **1ad**



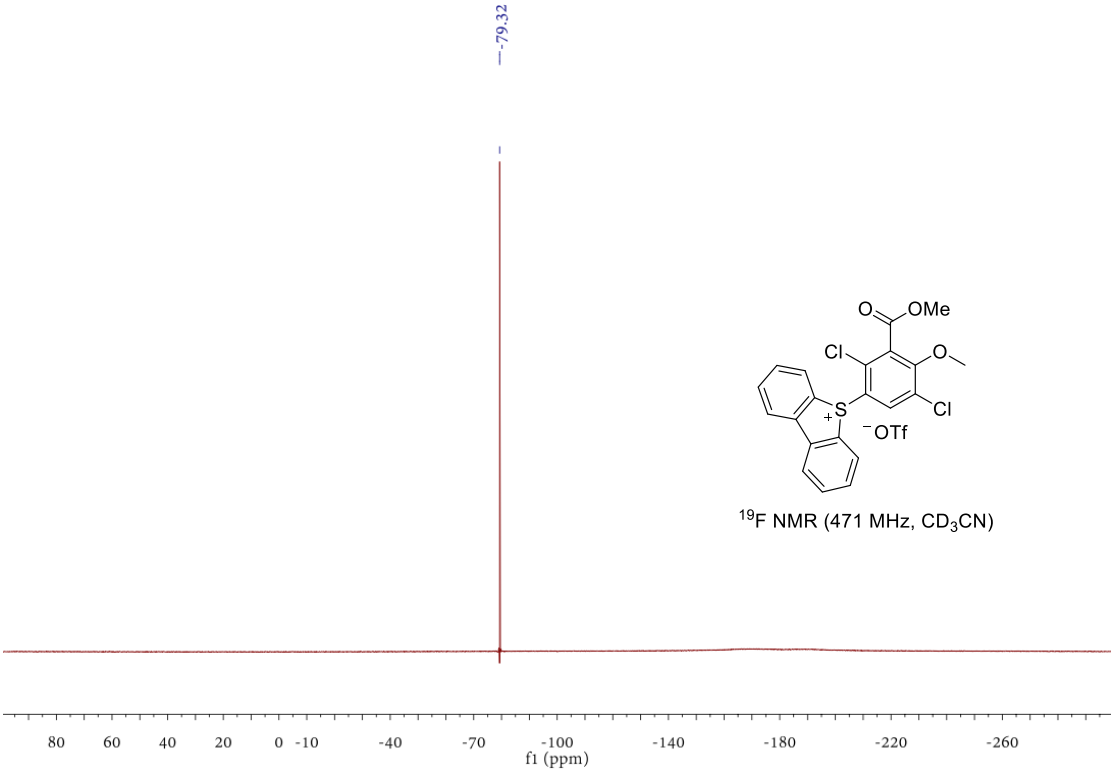
^{13}C NMR (126 MHz, CD_3CN)

^{1}H NMR spectrum of **1ae**



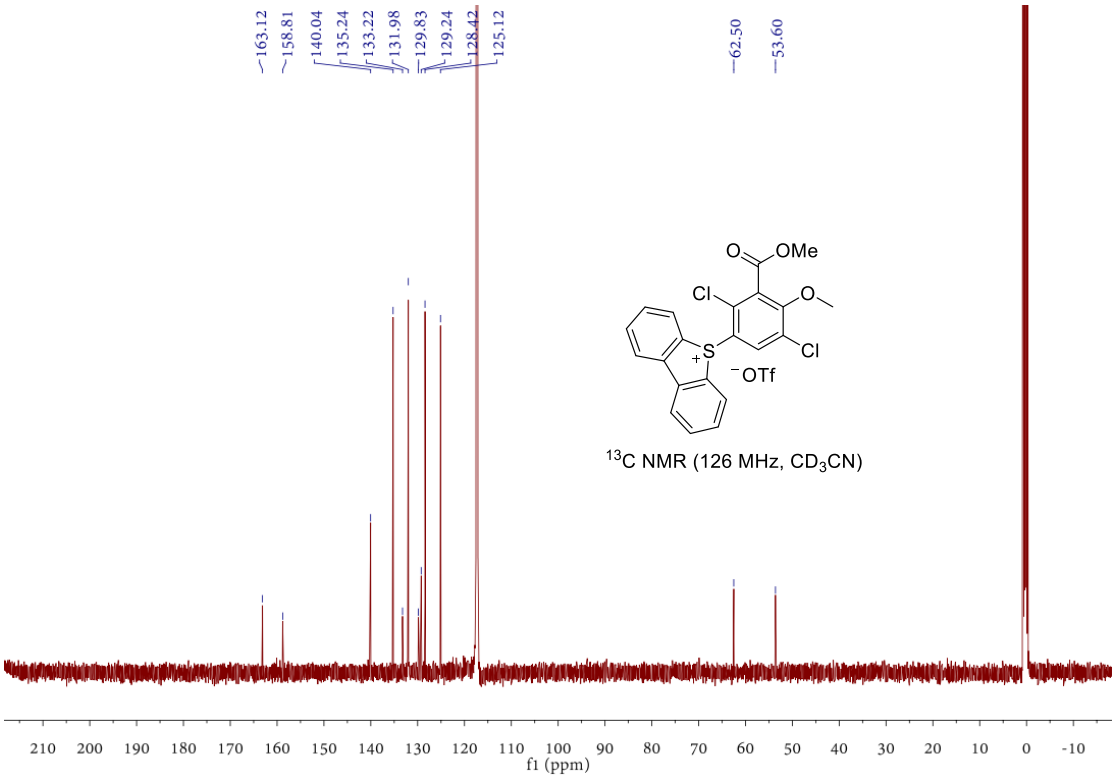
^{1}H NMR (500 MHz, CD_3CN)

^{19}F NMR spectrum of **1ae**

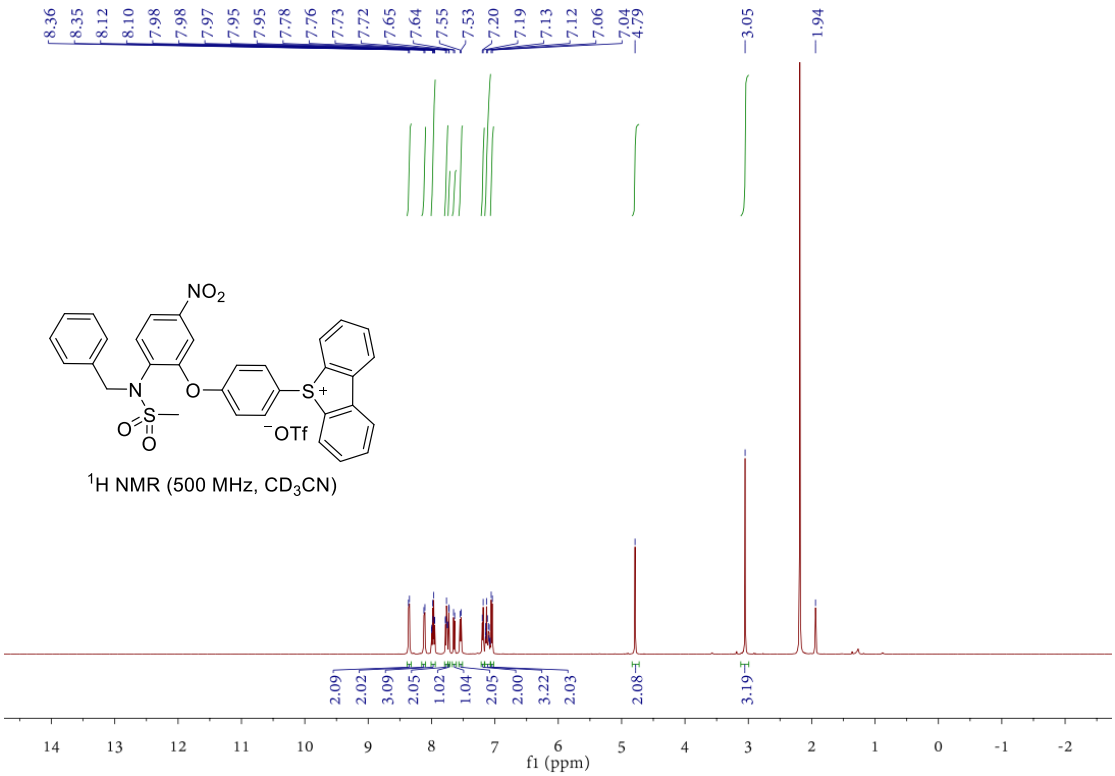


^{19}F NMR (471 MHz, CD_3CN)

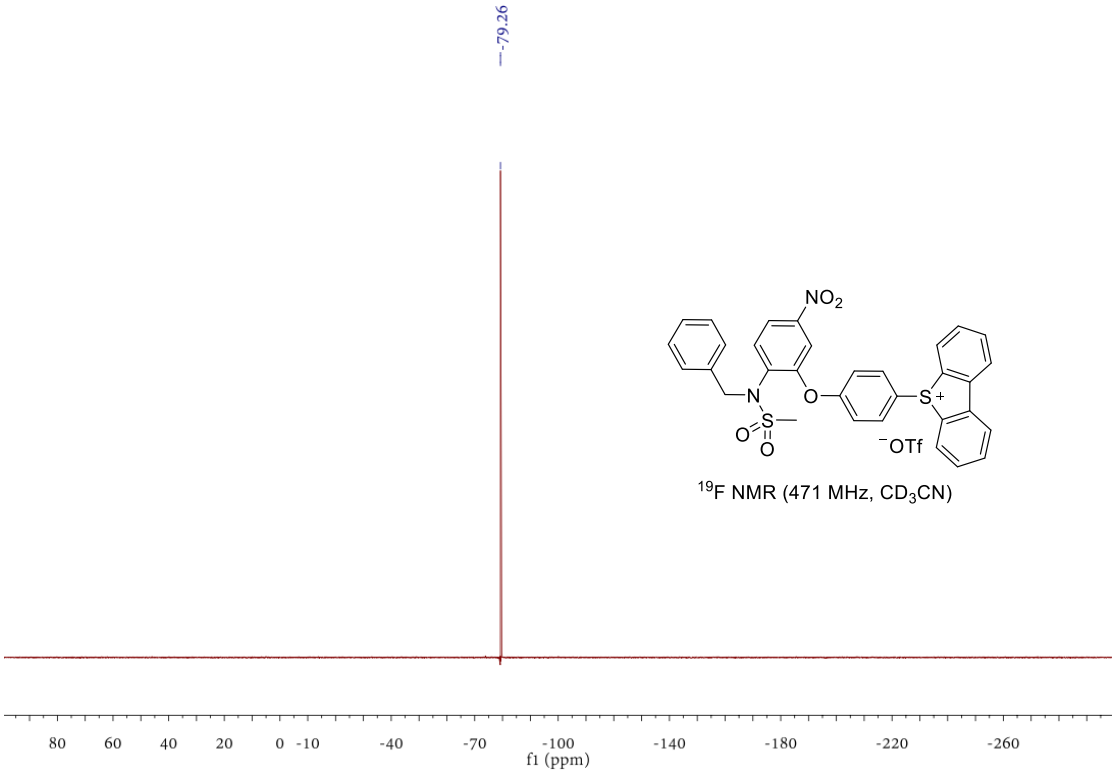
^{13}C NMR spectrum of **1ae**



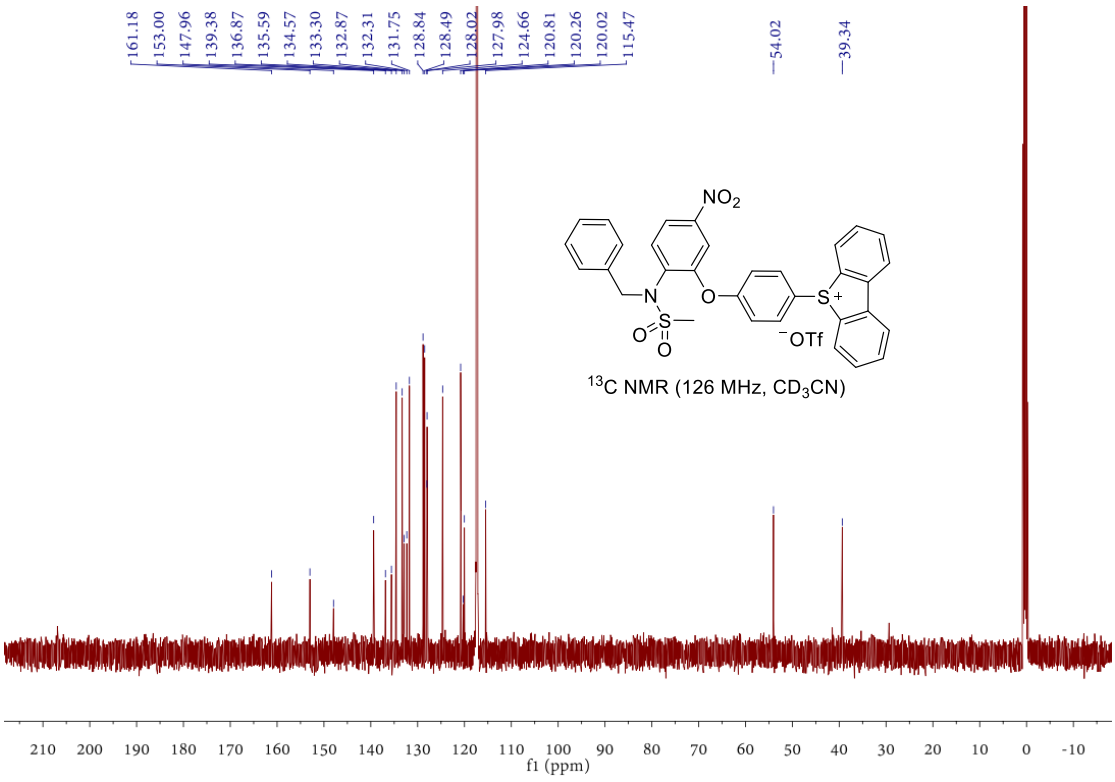
^{1}H NMR spectrum of **1af**



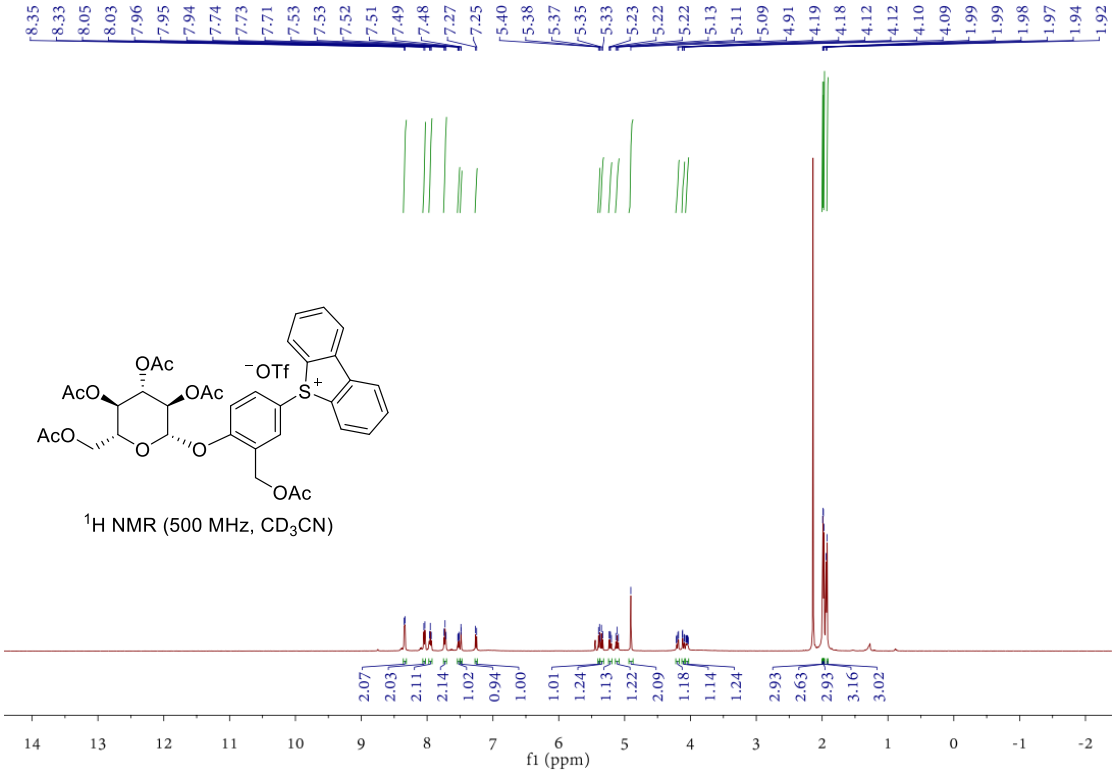
^{19}F NMR spectrum of **1af**



^{13}C NMR spectrum of **1af**

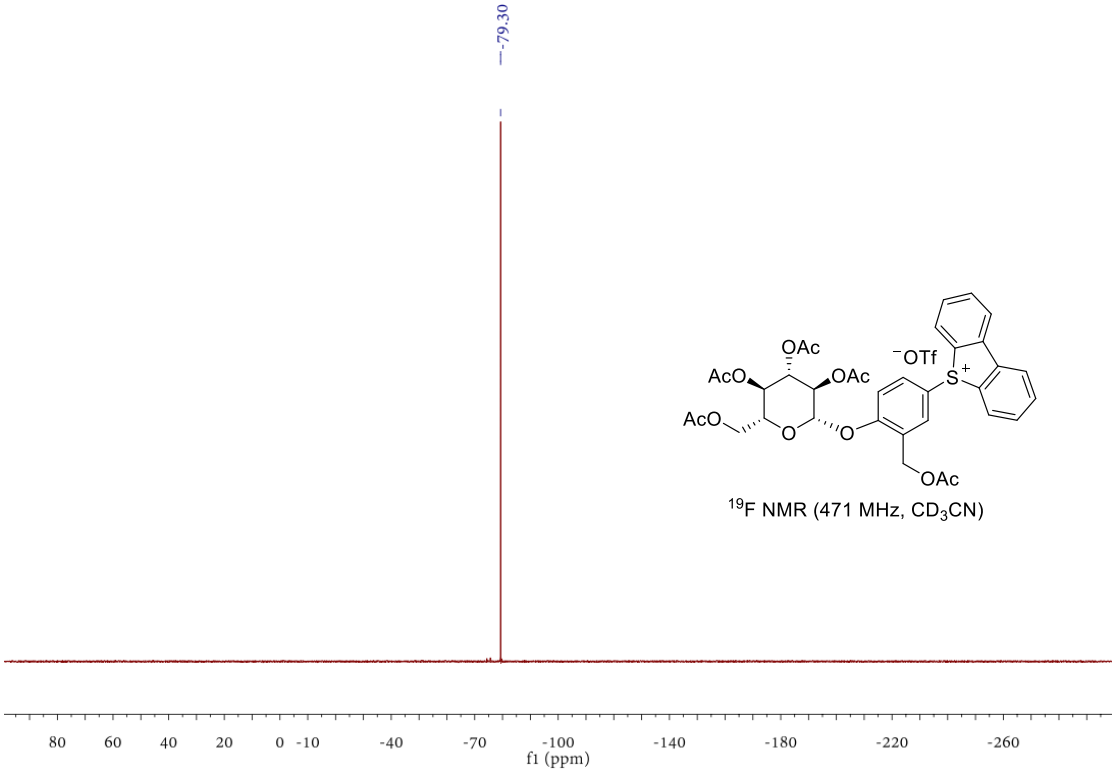


^{1}H NMR spectrum of **1ag**



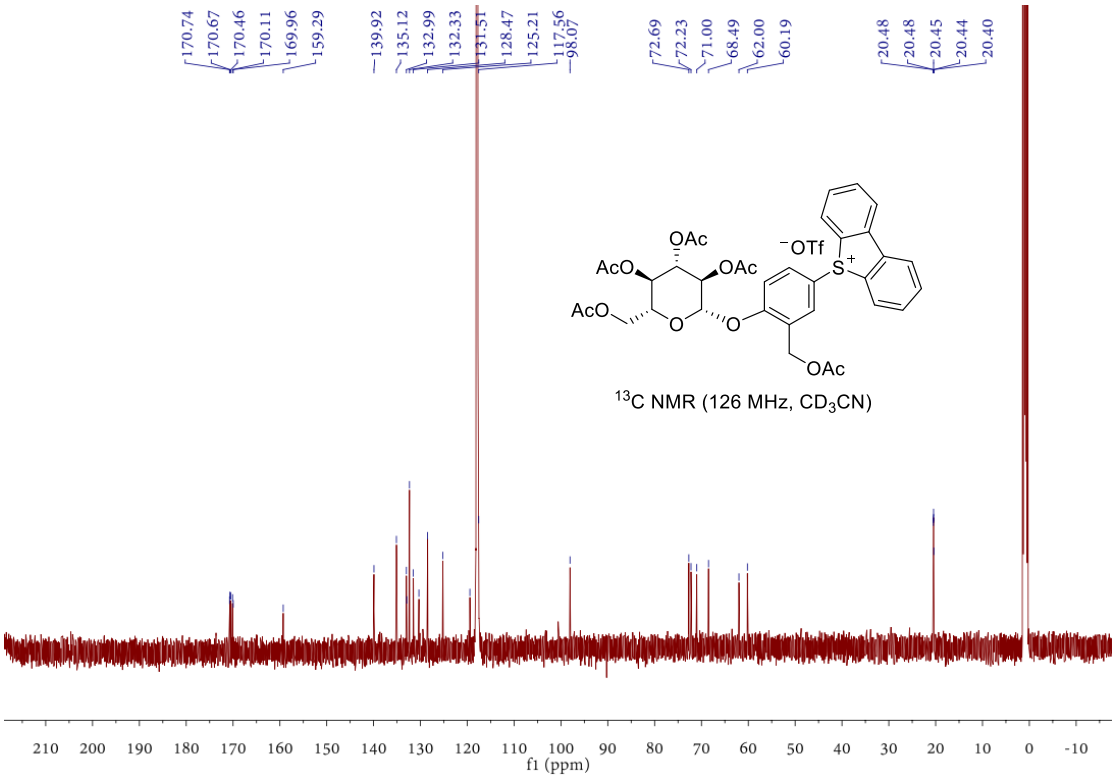
^{1}H NMR (500 MHz, CD_3CN)

^{19}F NMR spectrum of **1ag**

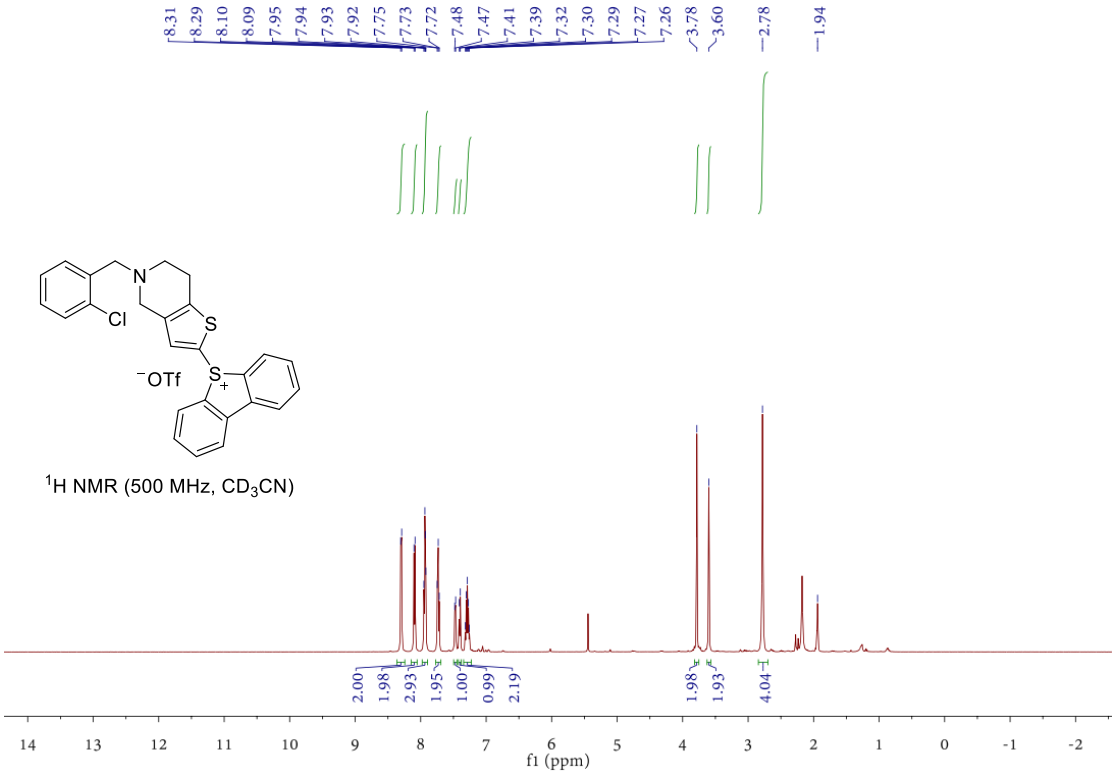


^{19}F NMR (471 MHz, CD_3CN)

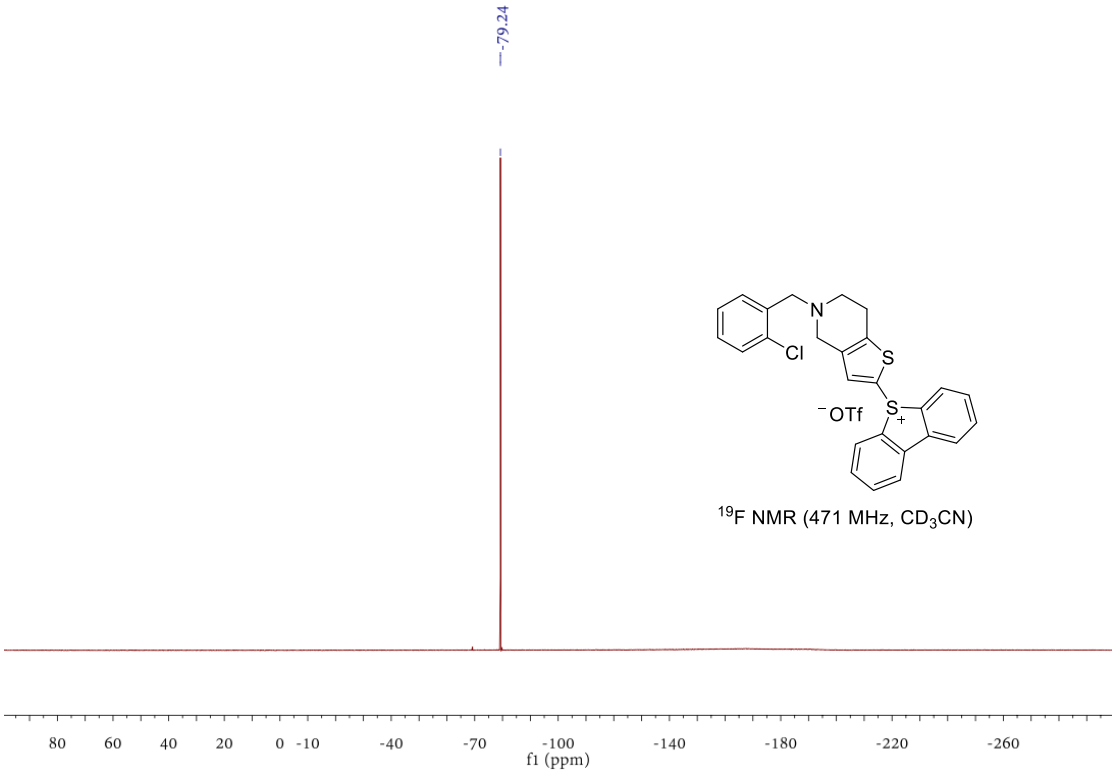
^{13}C NMR spectrum of **1ag**



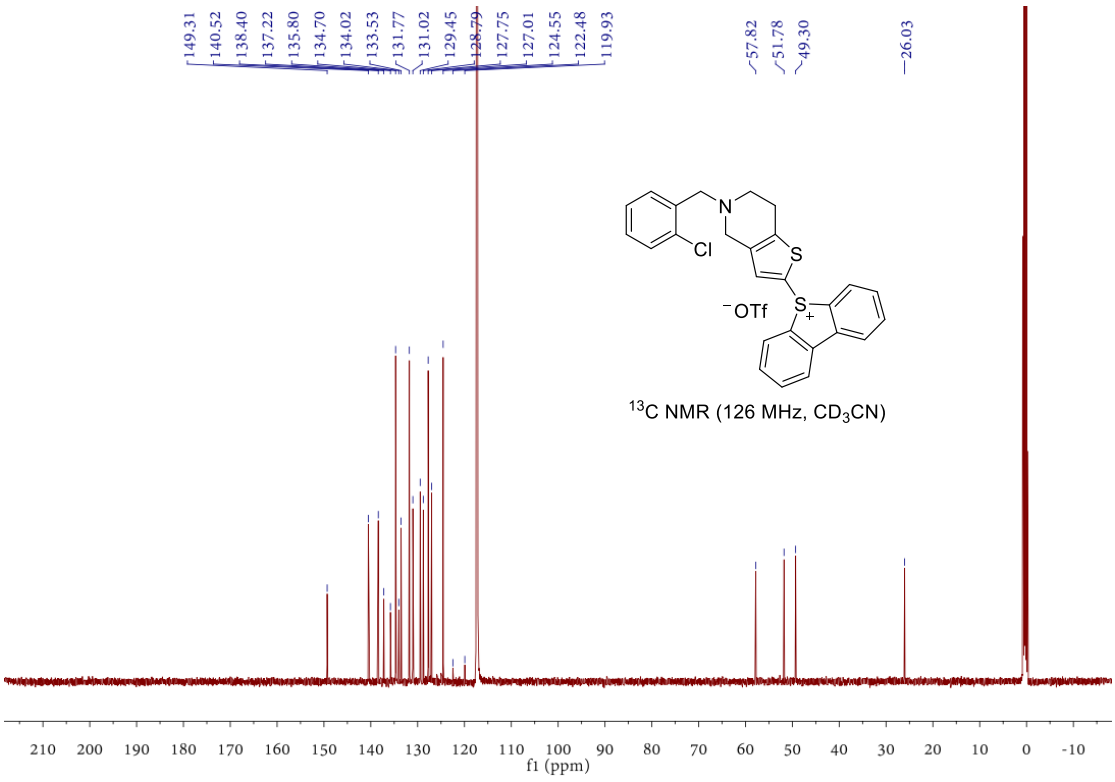
^{1}H NMR spectrum of **1ah**



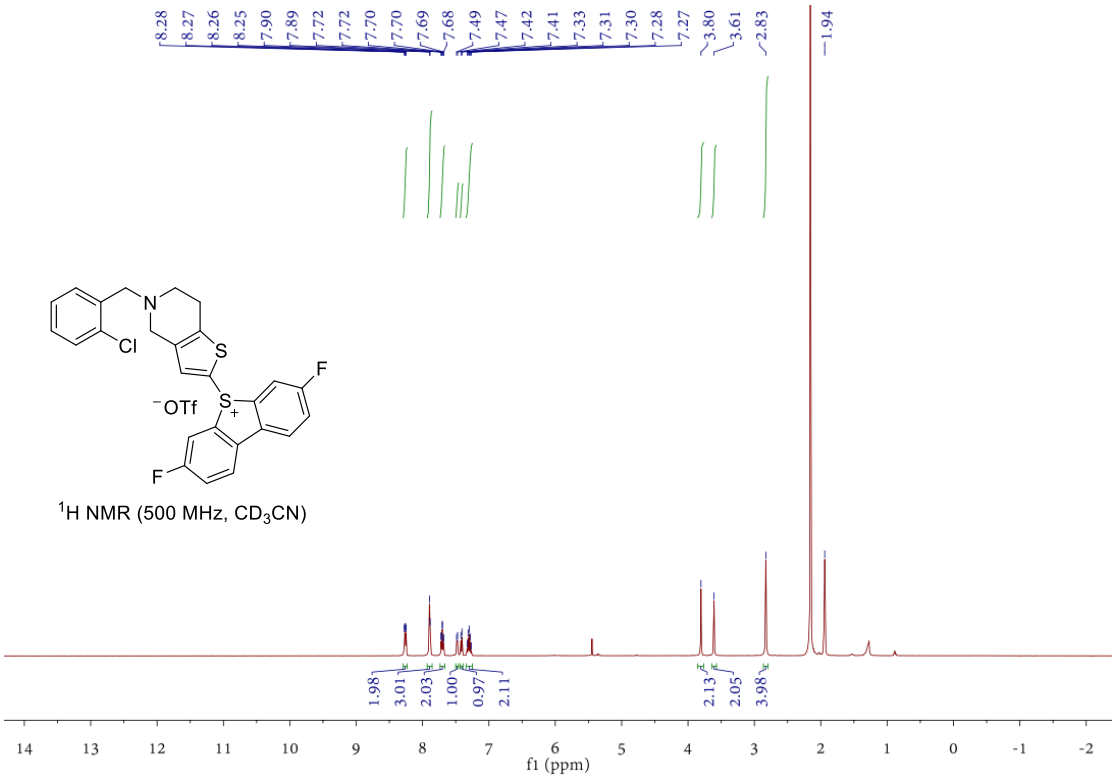
^{19}F NMR spectrum of **1ah**



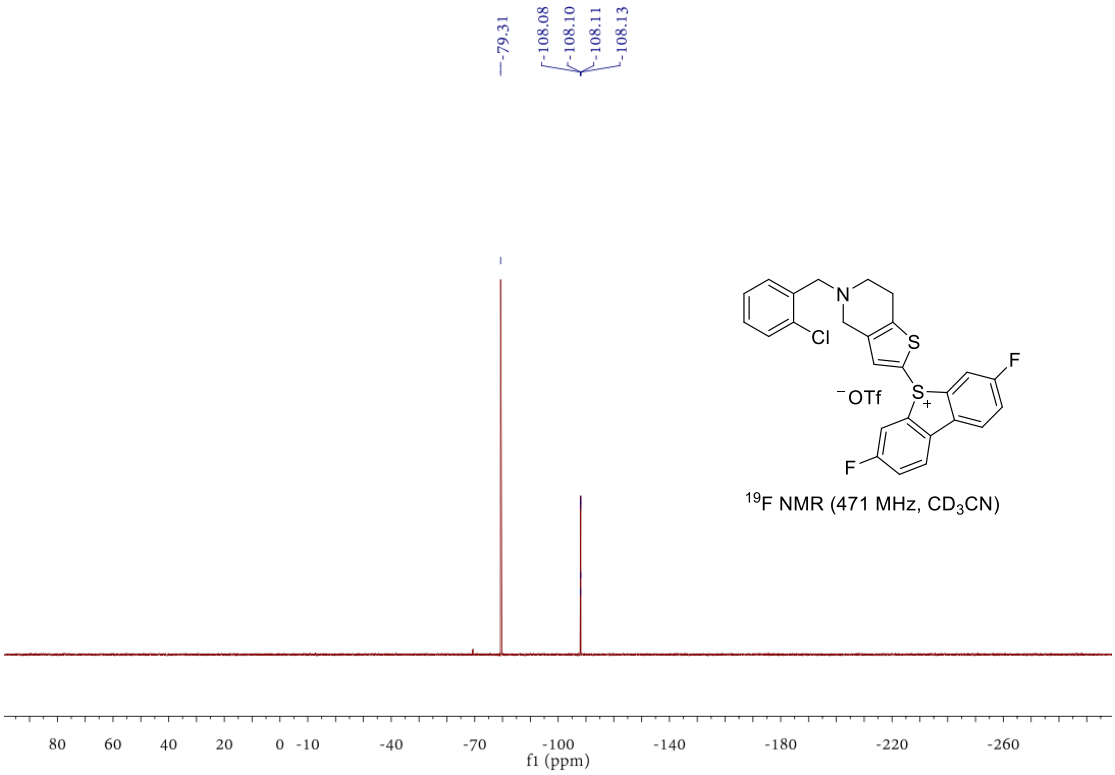
^{13}C NMR spectrum of **1ah**



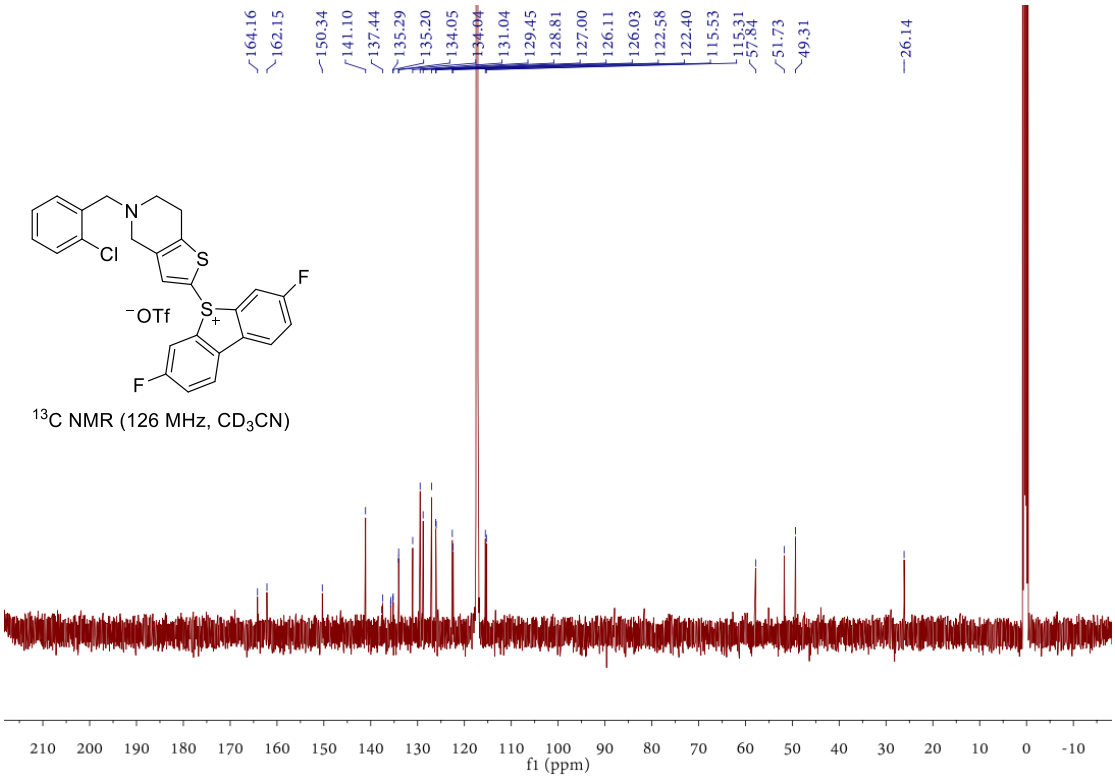
^{1}H NMR spectrum of **1ai**



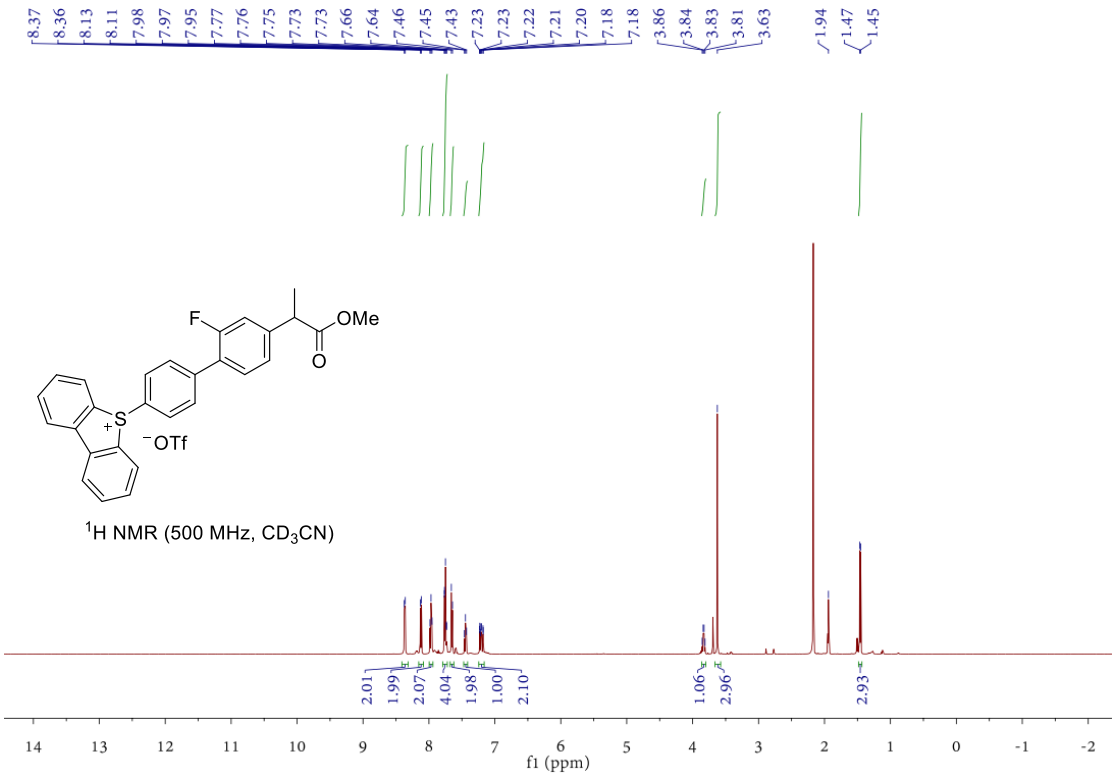
^{19}F NMR spectrum of **1ai**



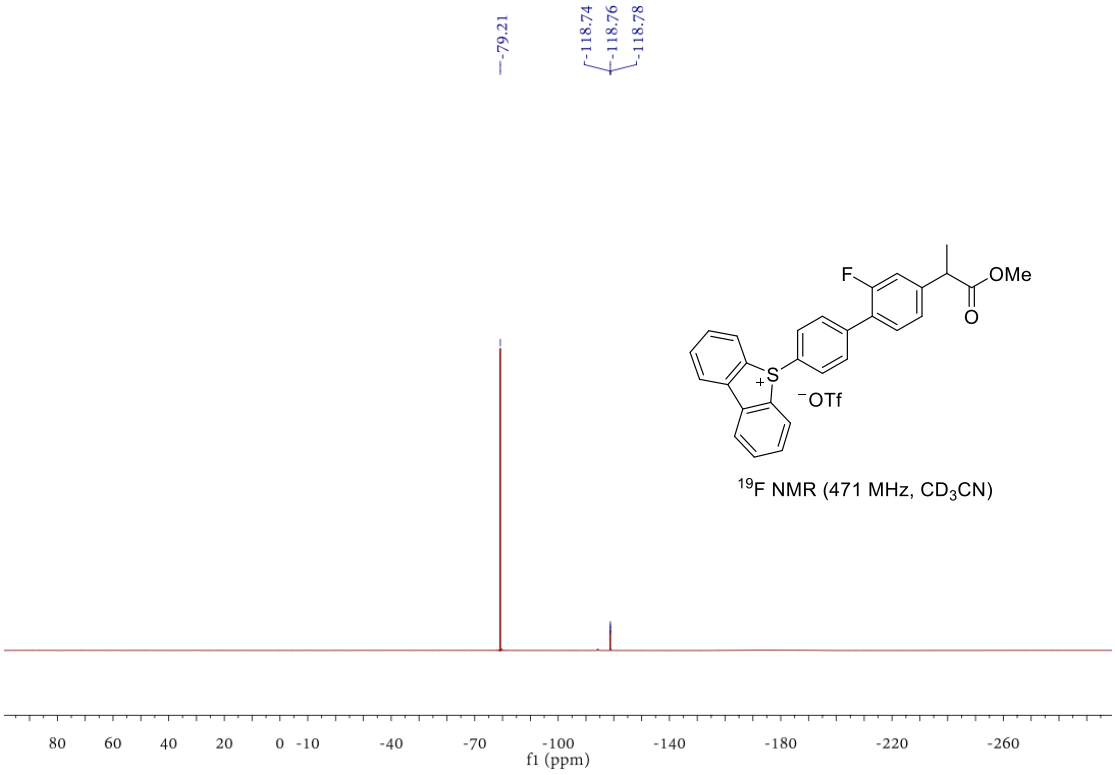
^{13}C NMR spectrum of **1ai**



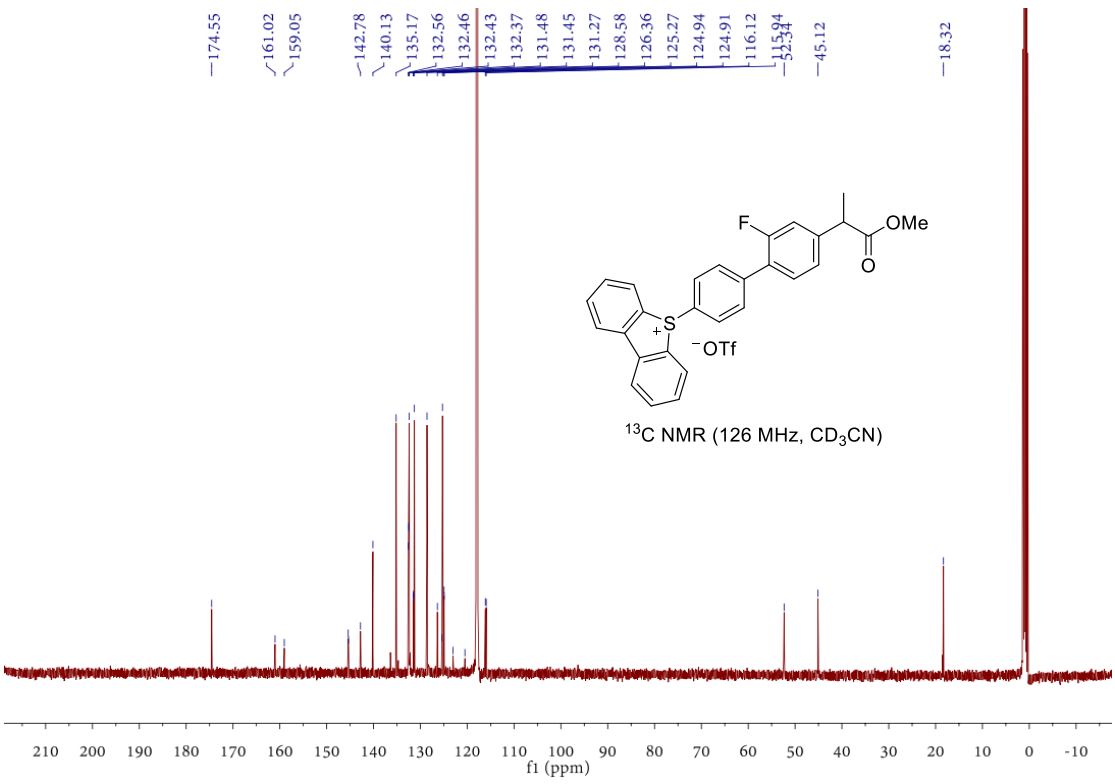
^{1}H NMR spectrum of **1aj**



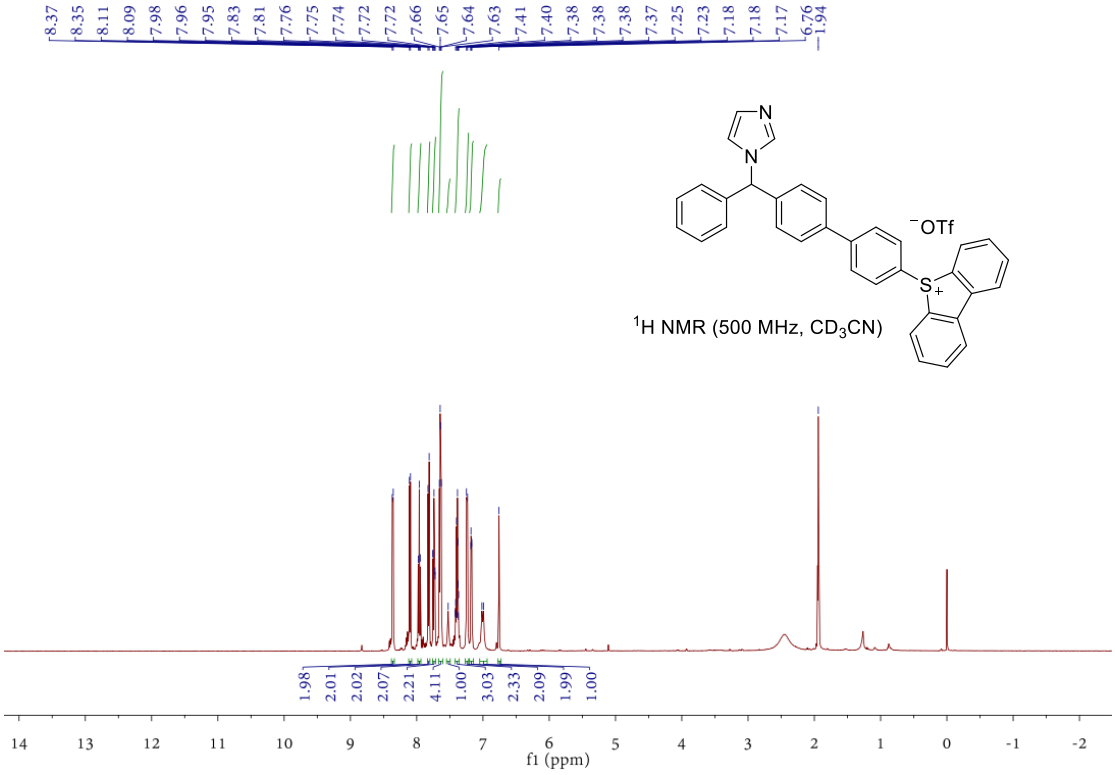
^{19}F NMR spectrum of **1aj**



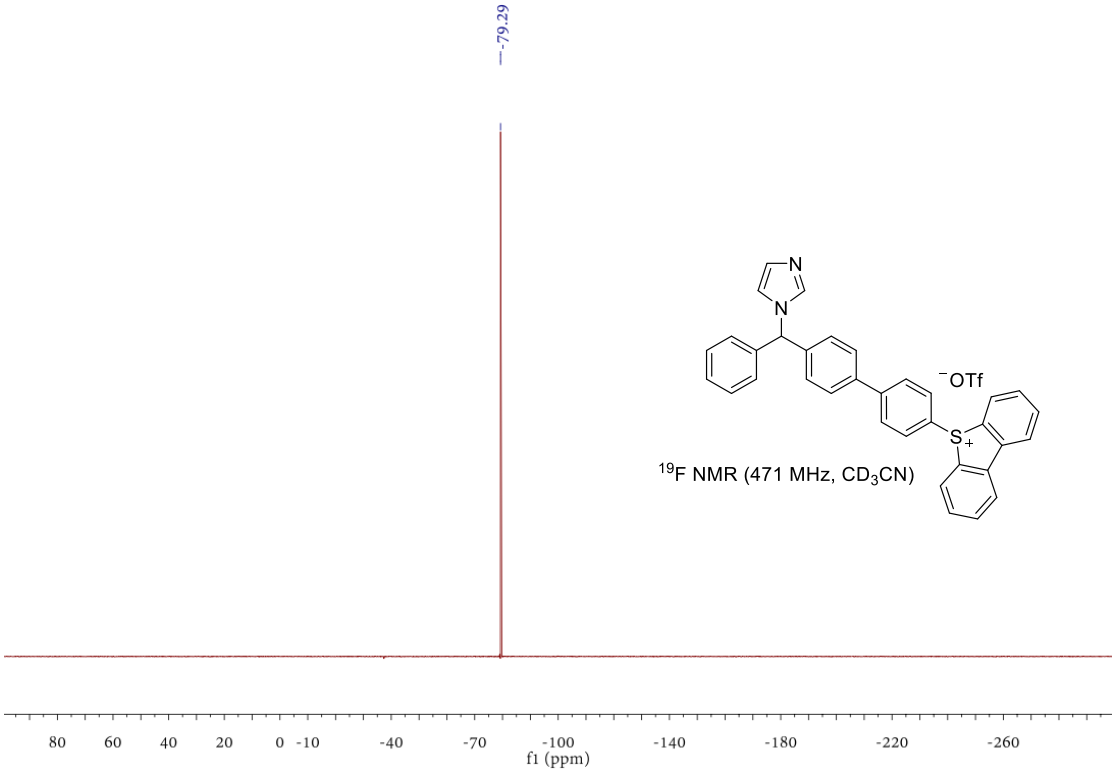
^{13}C NMR spectrum of **1aj**



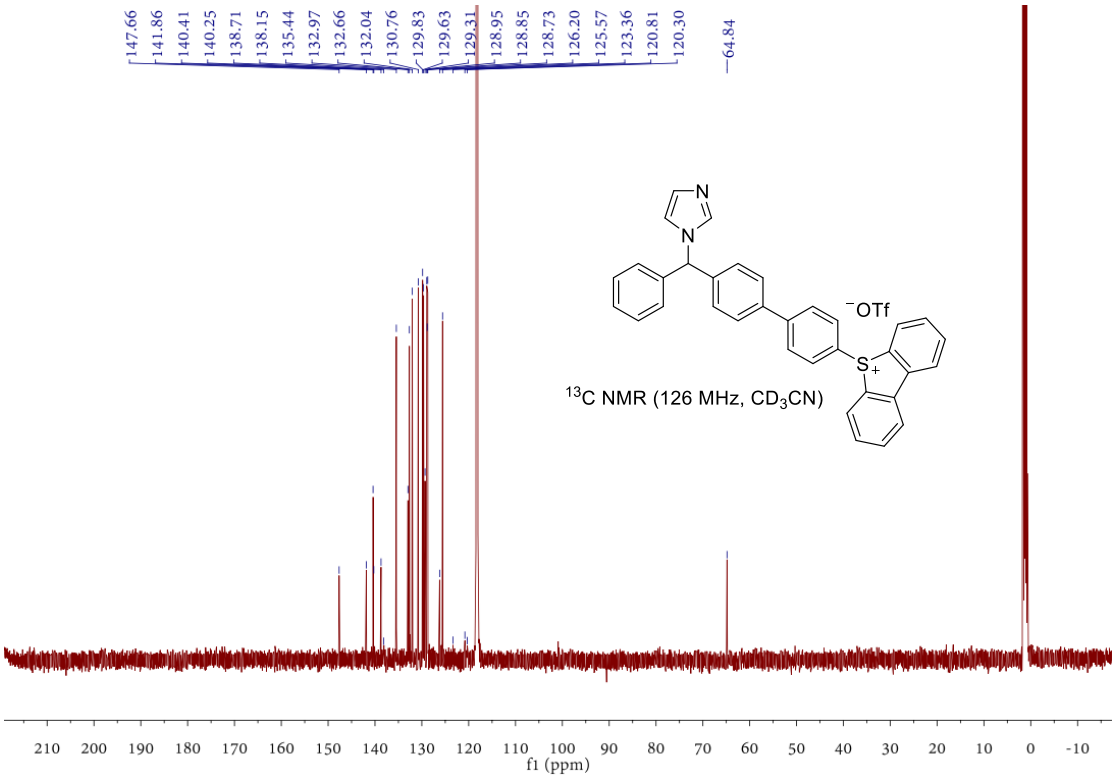
^{1}H NMR spectrum of **1ak**



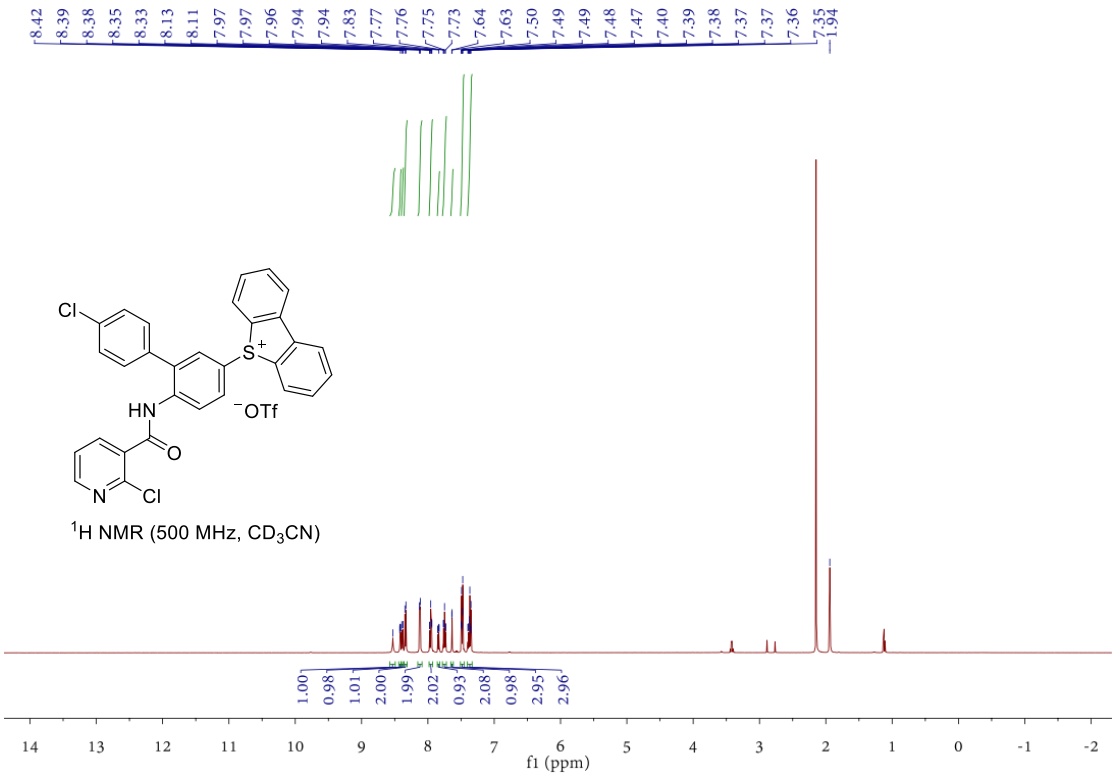
^{19}F NMR spectrum of **1ak**



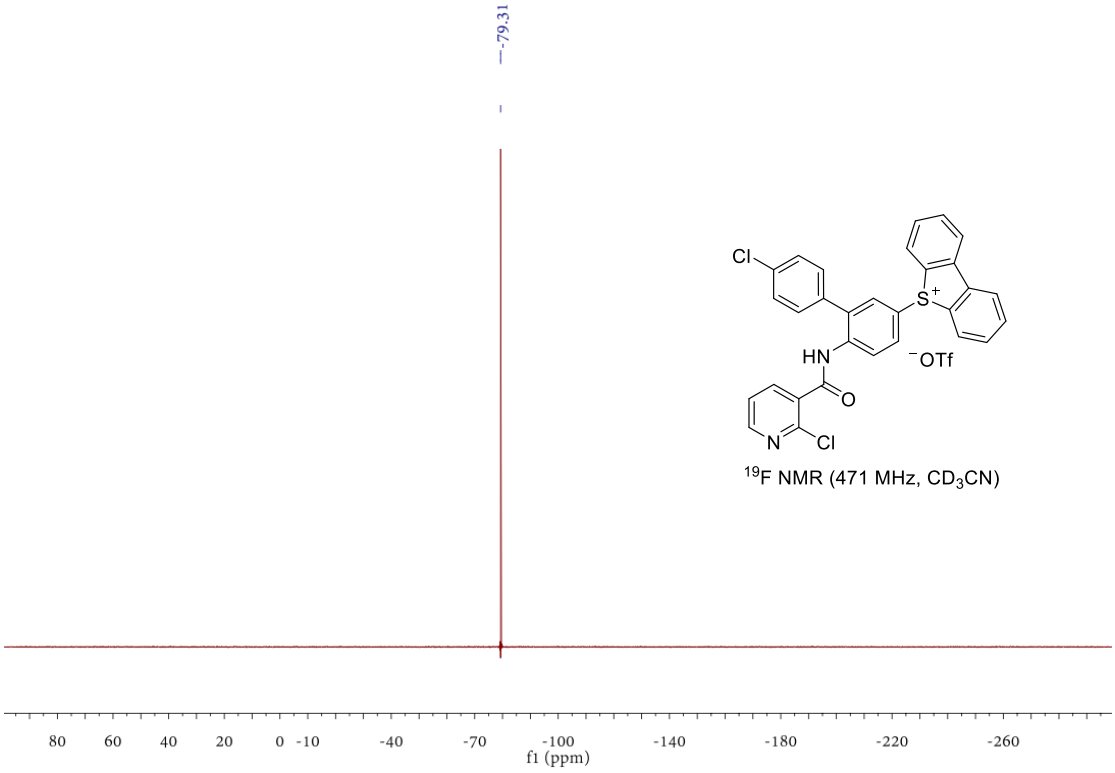
^{13}C NMR spectrum of **1ak**



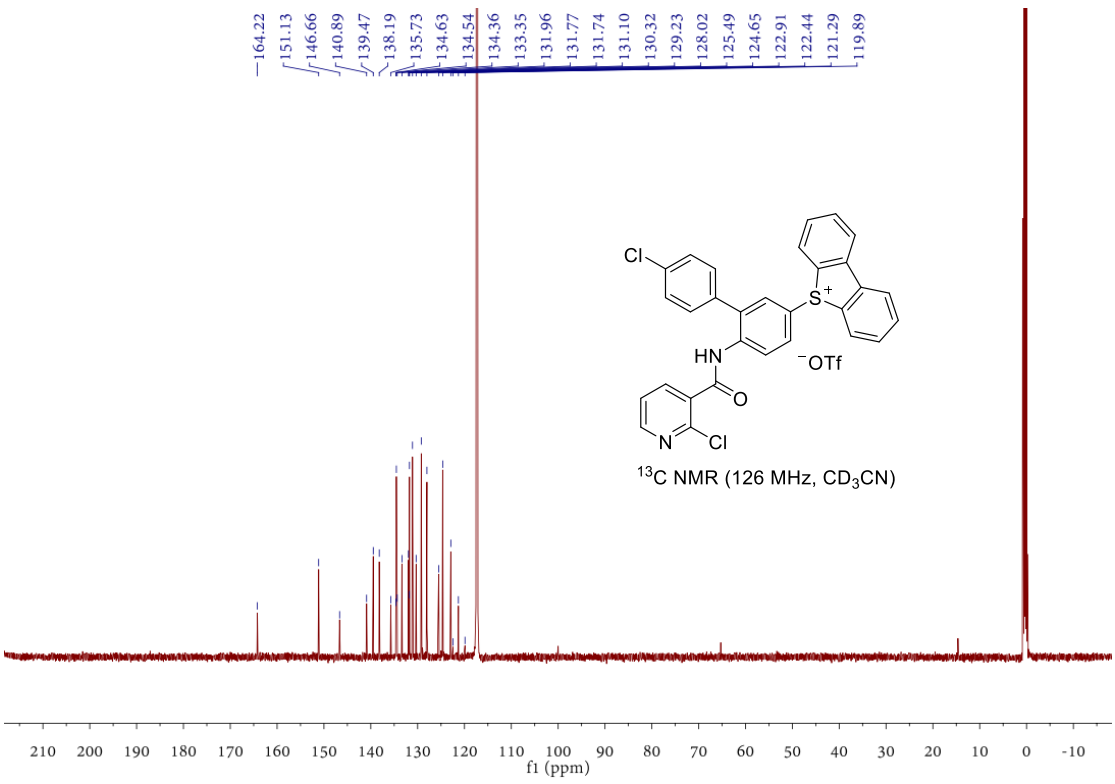
^{1}H NMR spectrum of **1al**



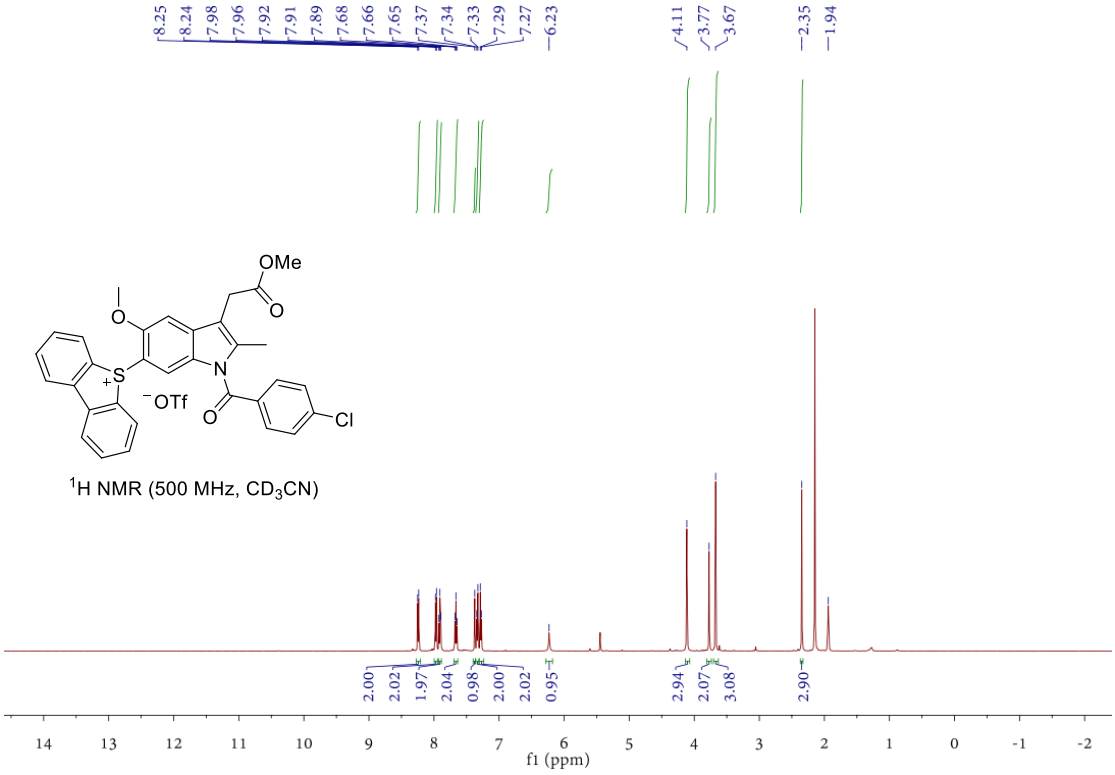
^{19}F NMR spectrum of **1al**



^{13}C NMR spectrum of **1al**

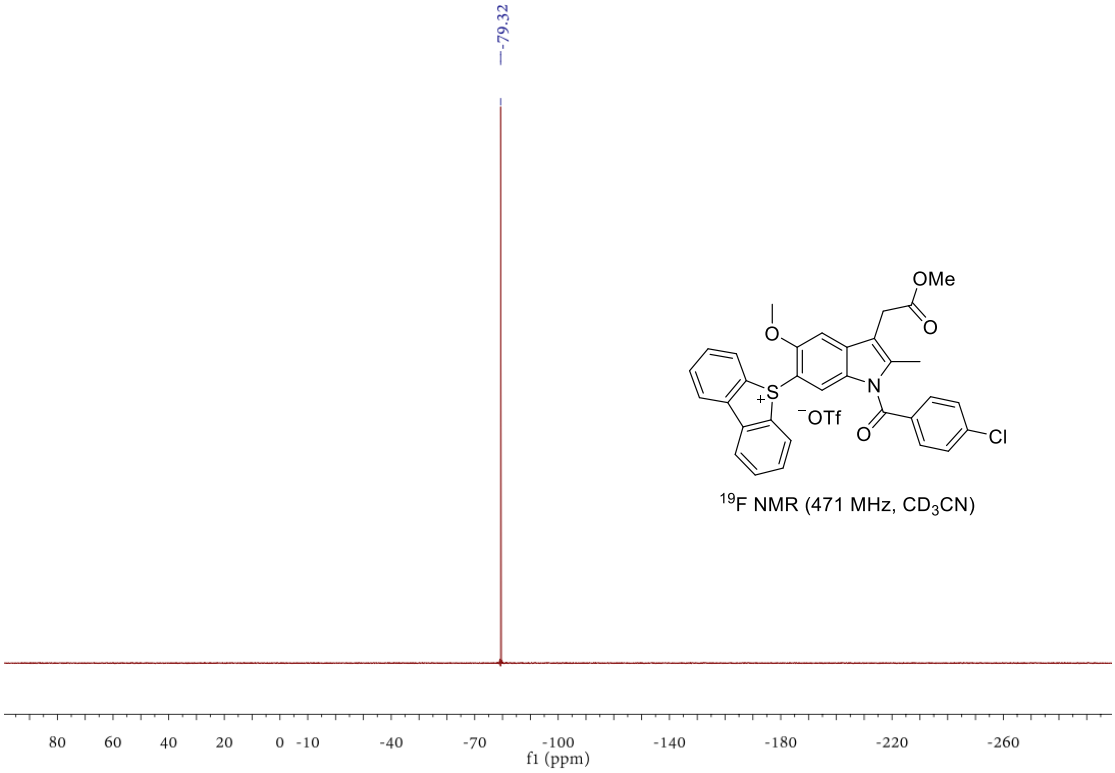


^{1}H NMR spectrum of **1am**



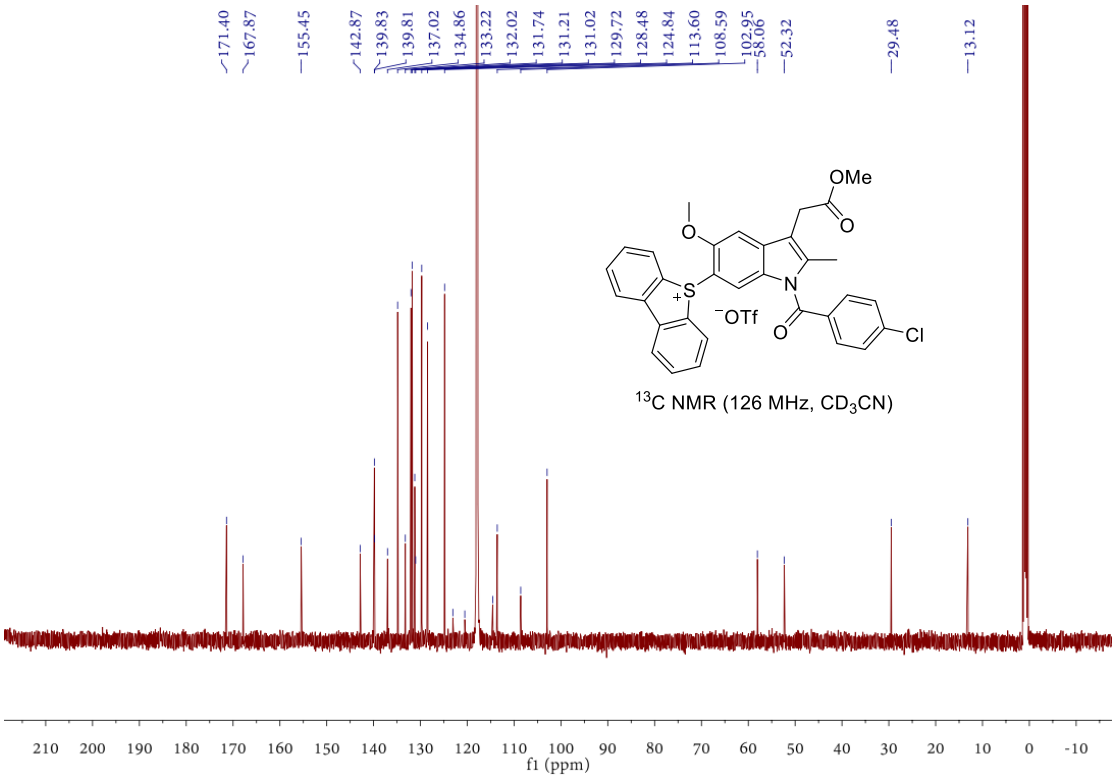
^{1}H NMR (500 MHz, CD_3CN)

^{19}F NMR spectrum of **1am**

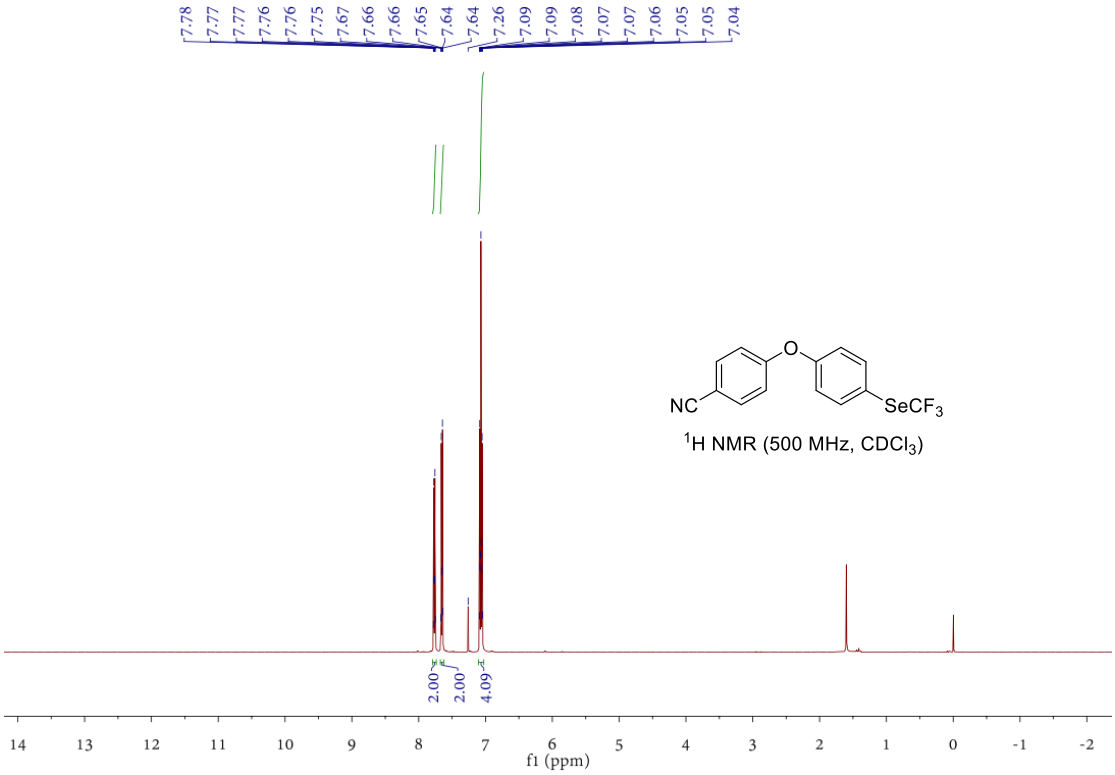


^{19}F NMR (471 MHz, CD_3CN)

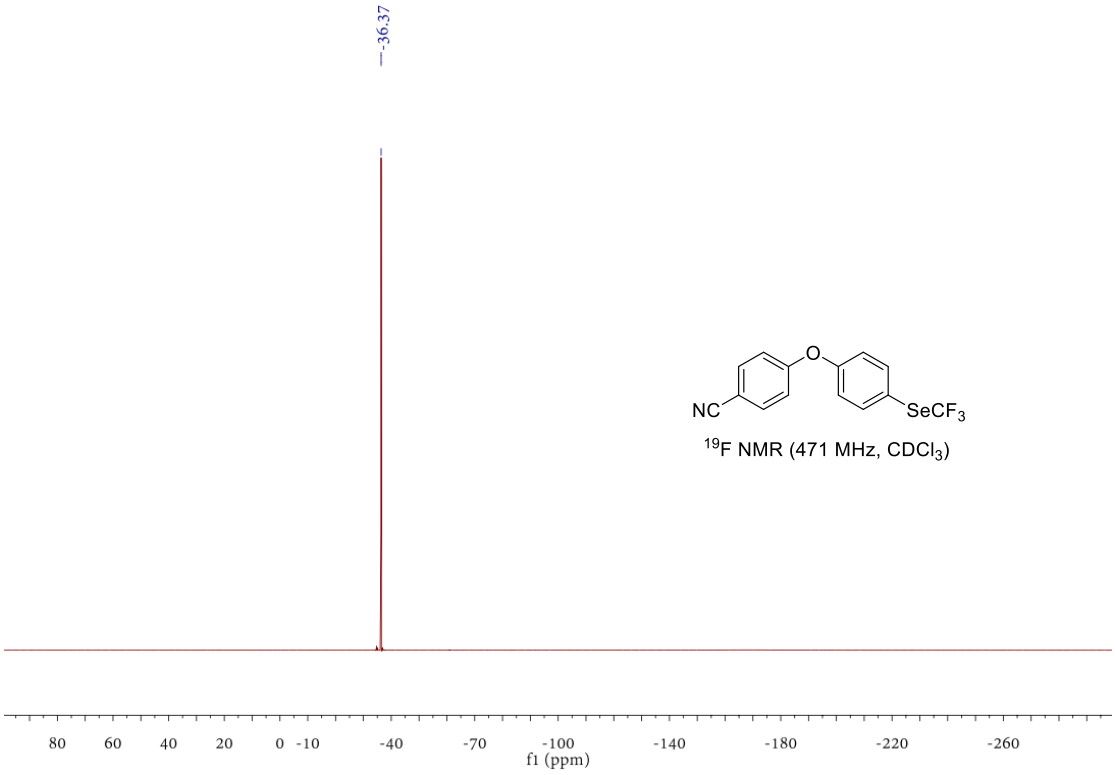
^{13}C NMR spectrum of **1am**



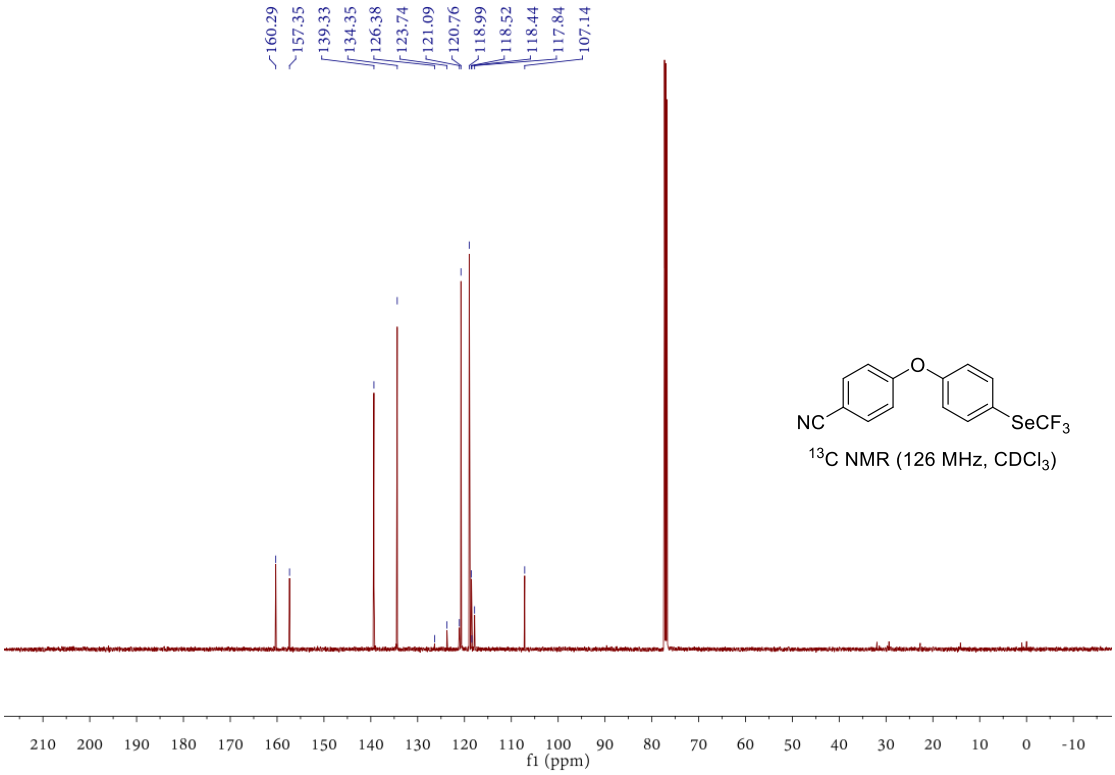
^{1}H NMR spectrum of **3a**



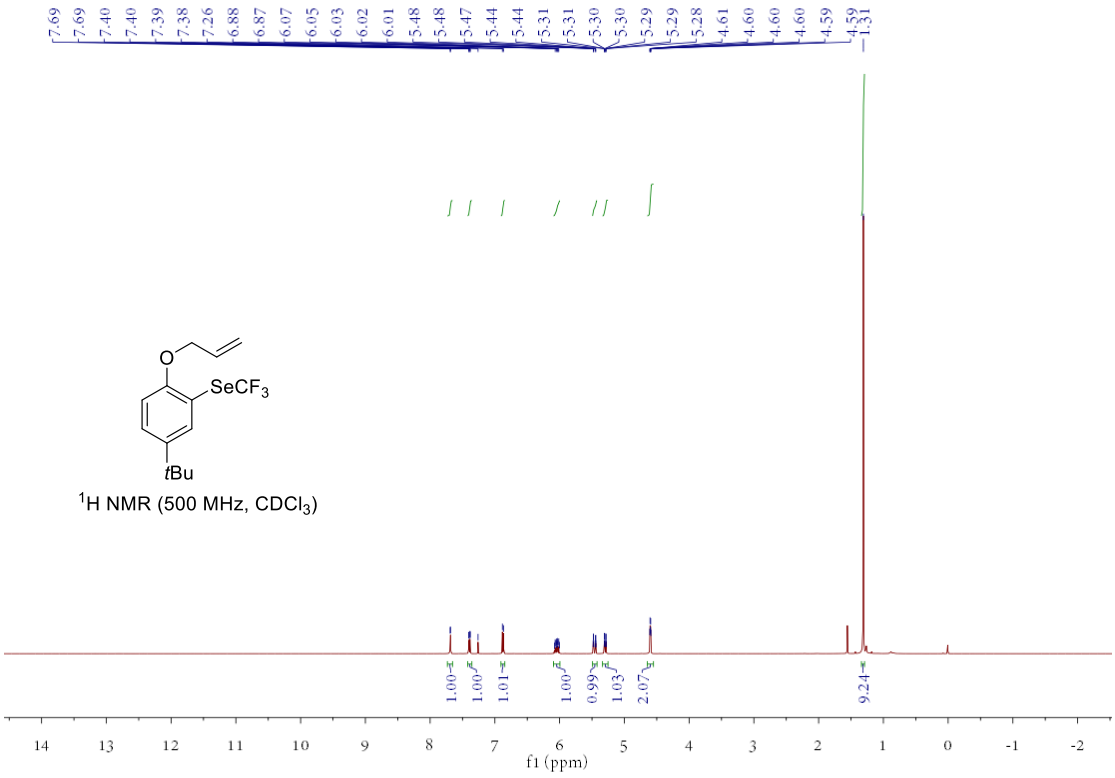
^{19}F NMR spectrum of **3a**



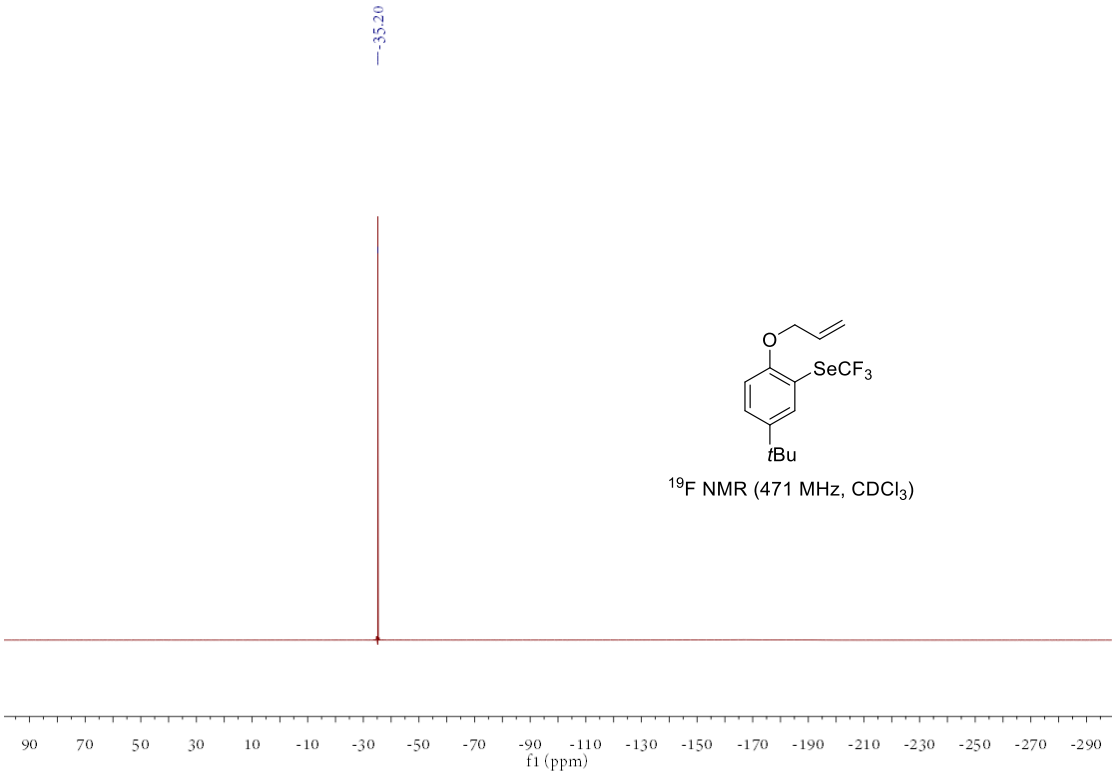
^{13}C NMR spectrum of **3a**



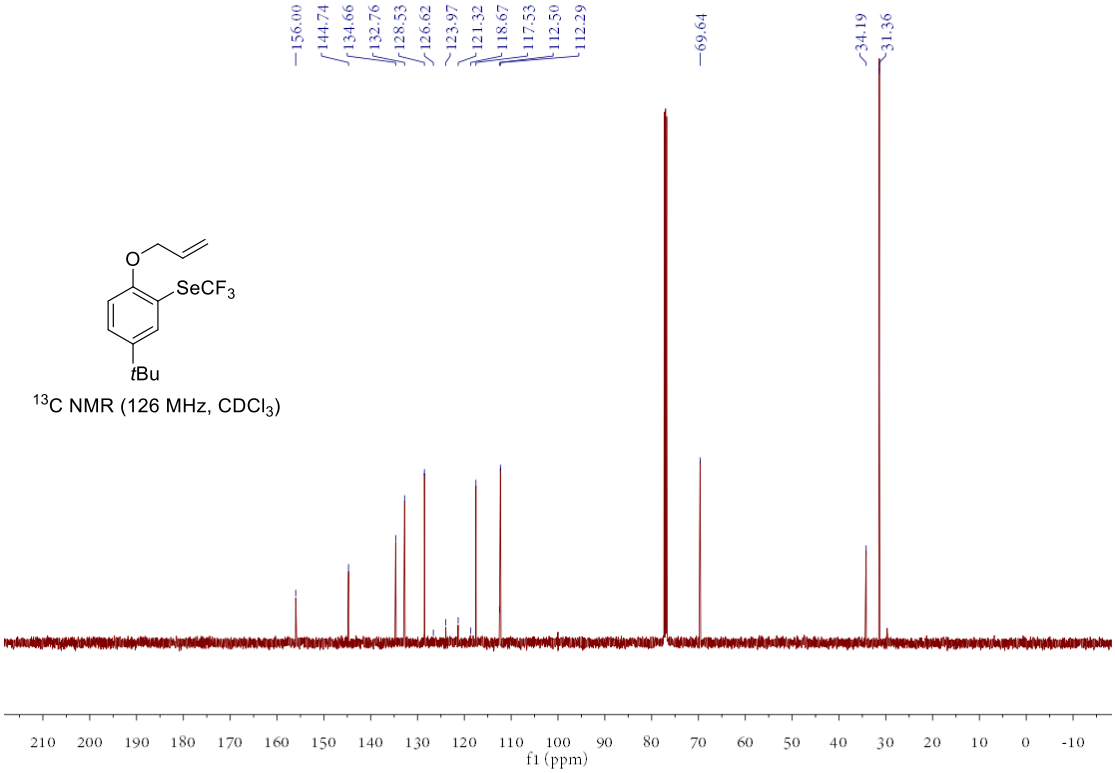
^{1}H NMR spectrum of **3b**



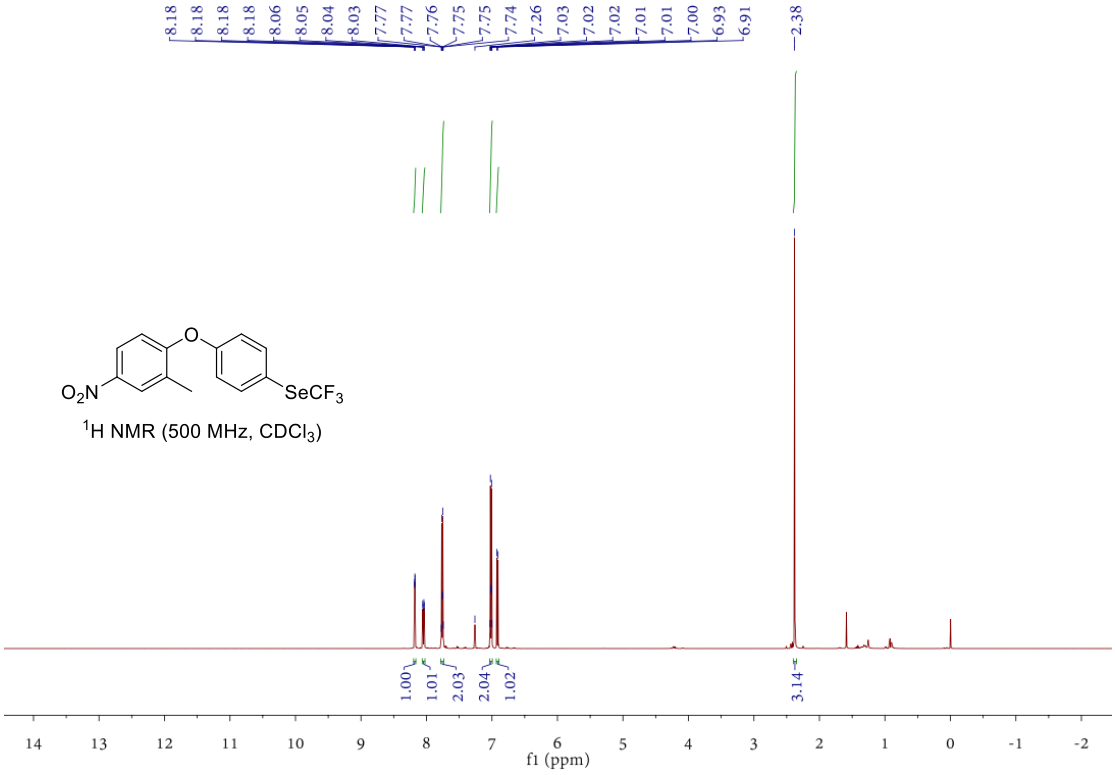
^{19}F NMR spectrum of **3b**



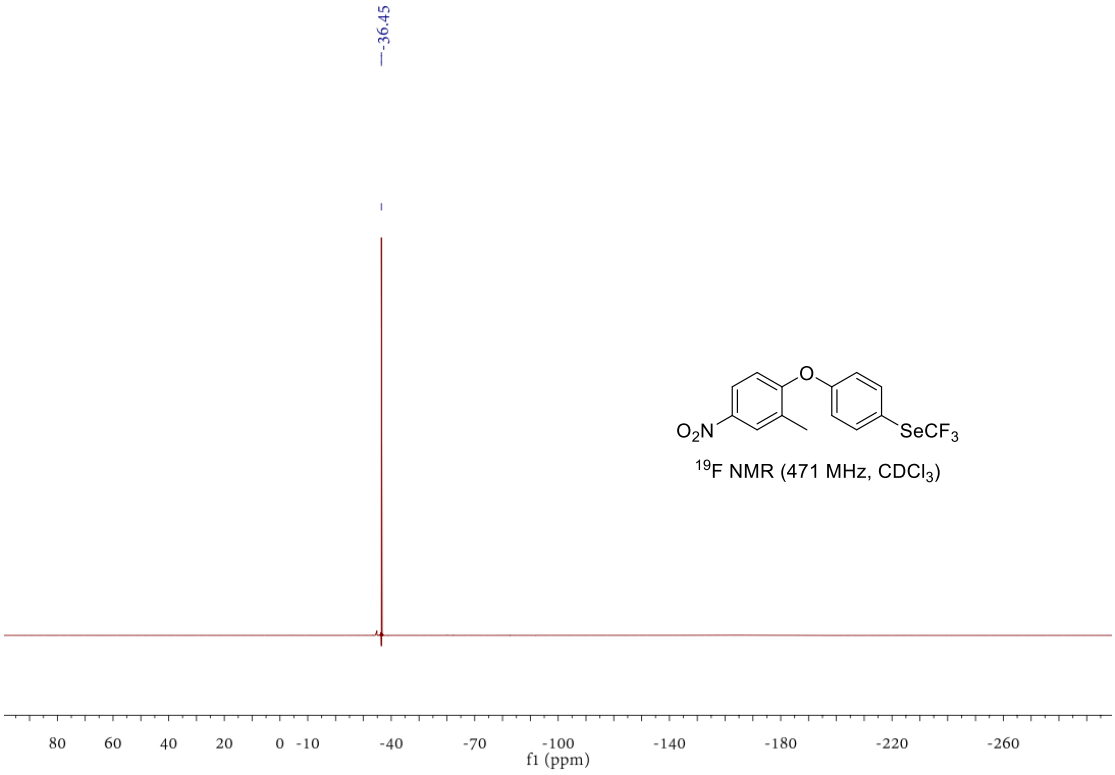
^{13}C NMR spectrum of **3b**



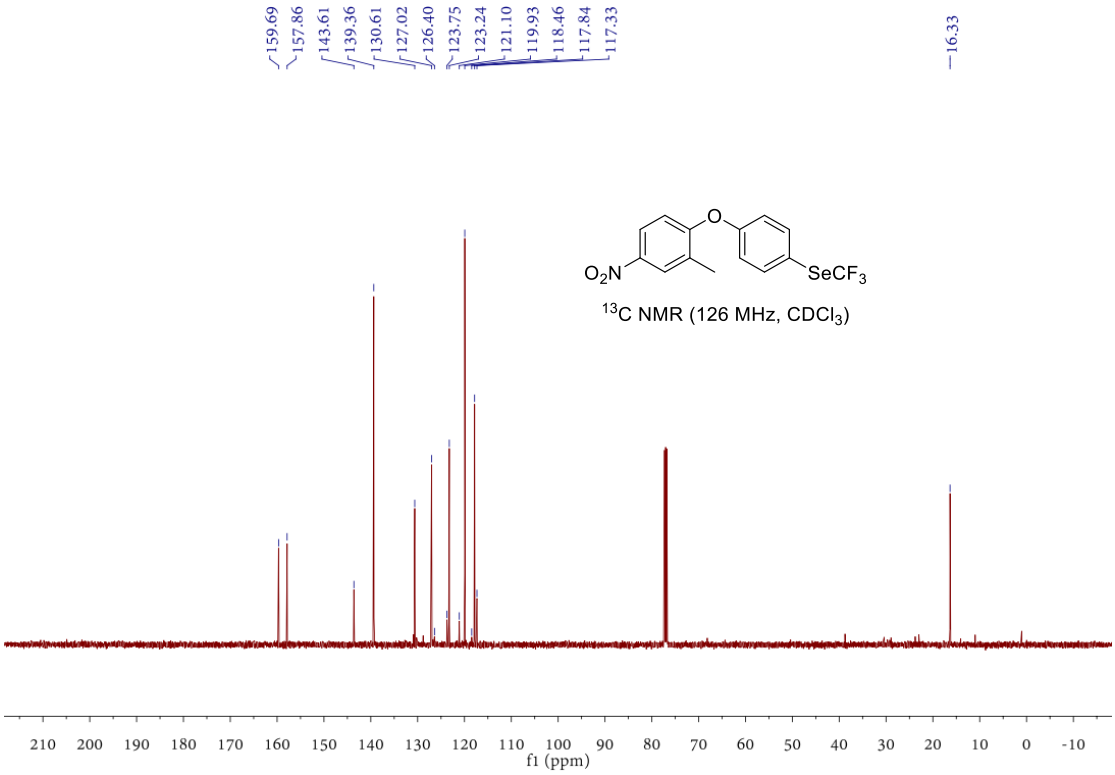
^{1}H NMR spectrum of **3c**



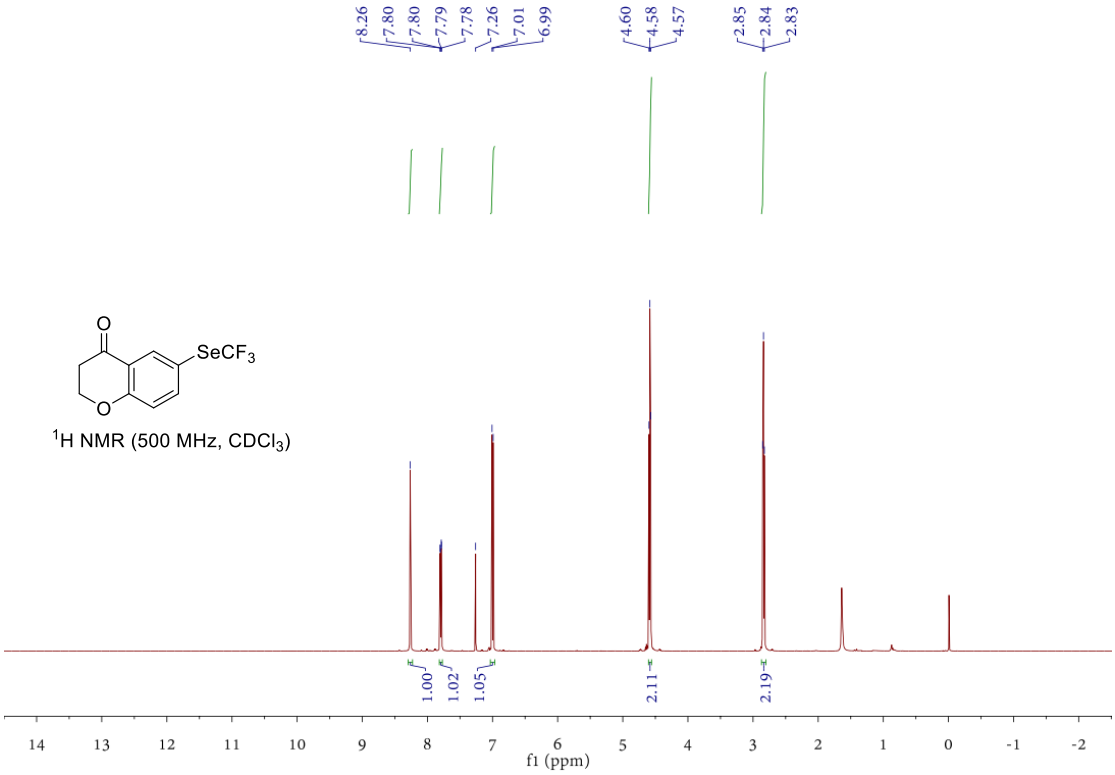
^{19}F NMR spectrum of **3c**



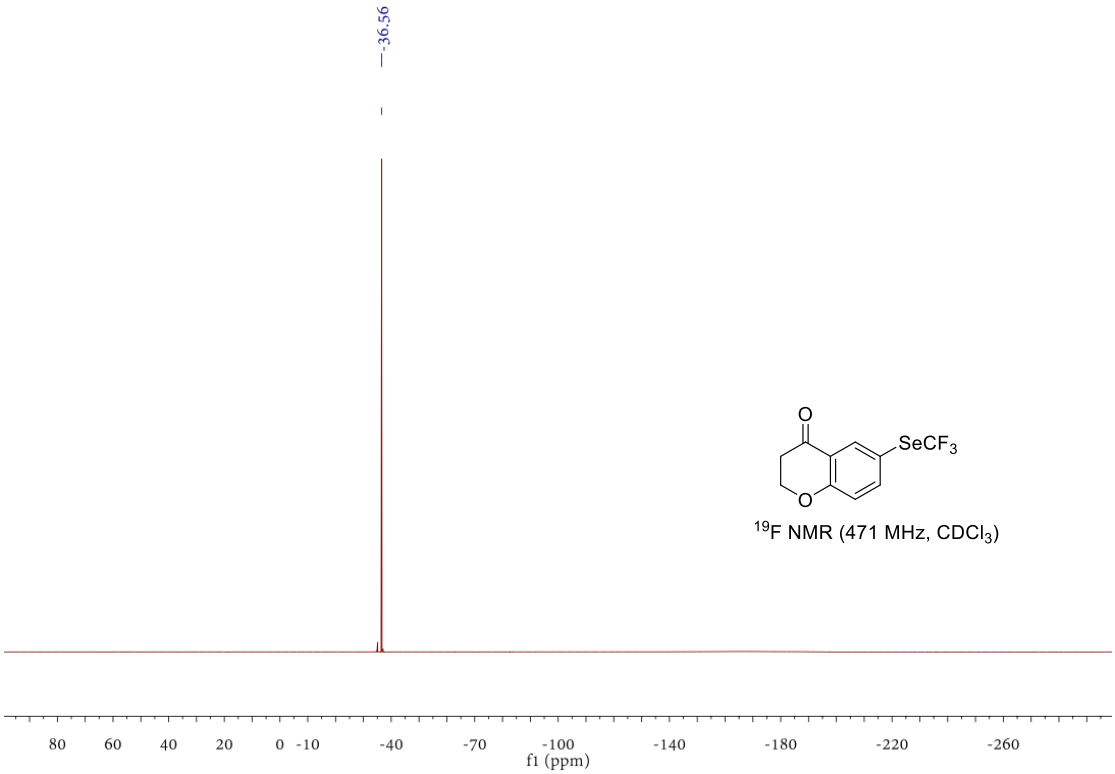
^{13}C NMR spectrum of **3c**



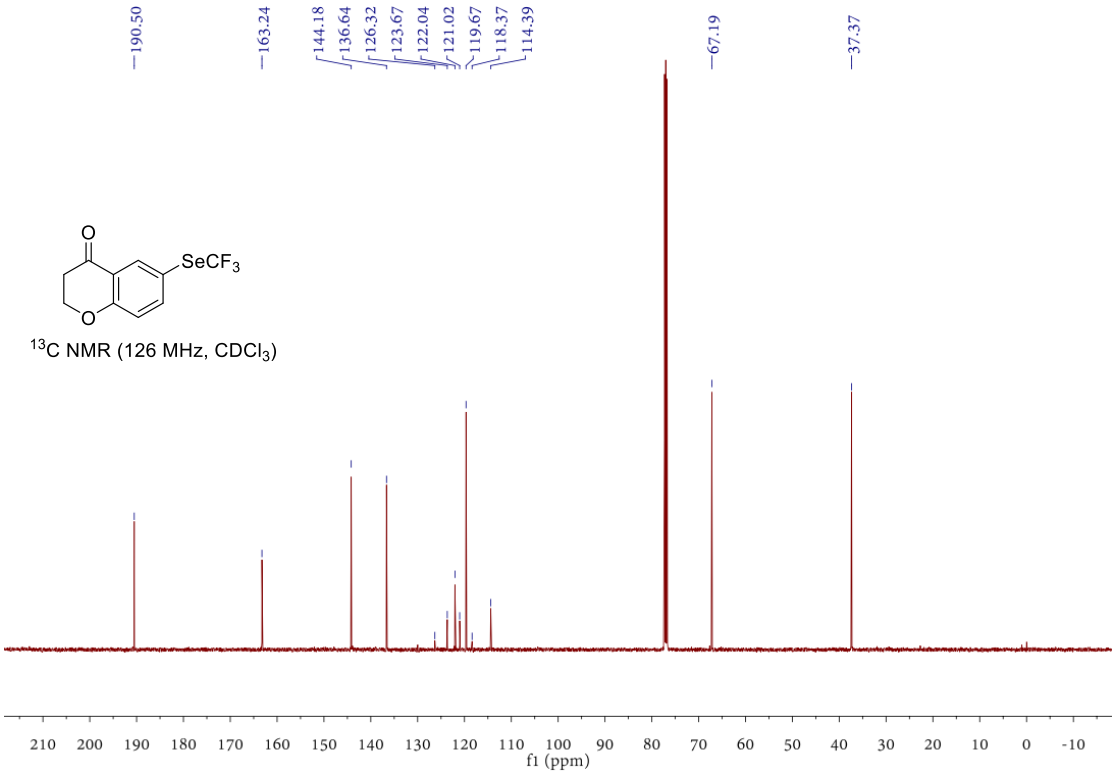
^{1}H NMR spectrum of **3d**



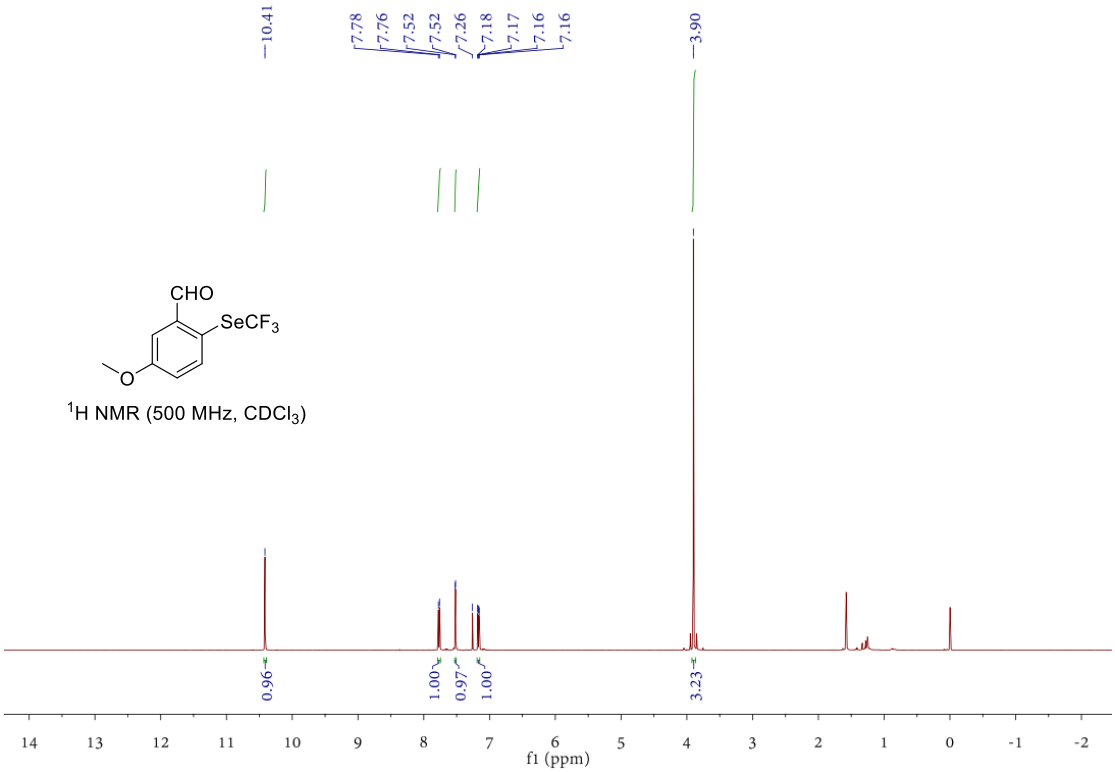
^{19}F NMR spectrum of **3d**



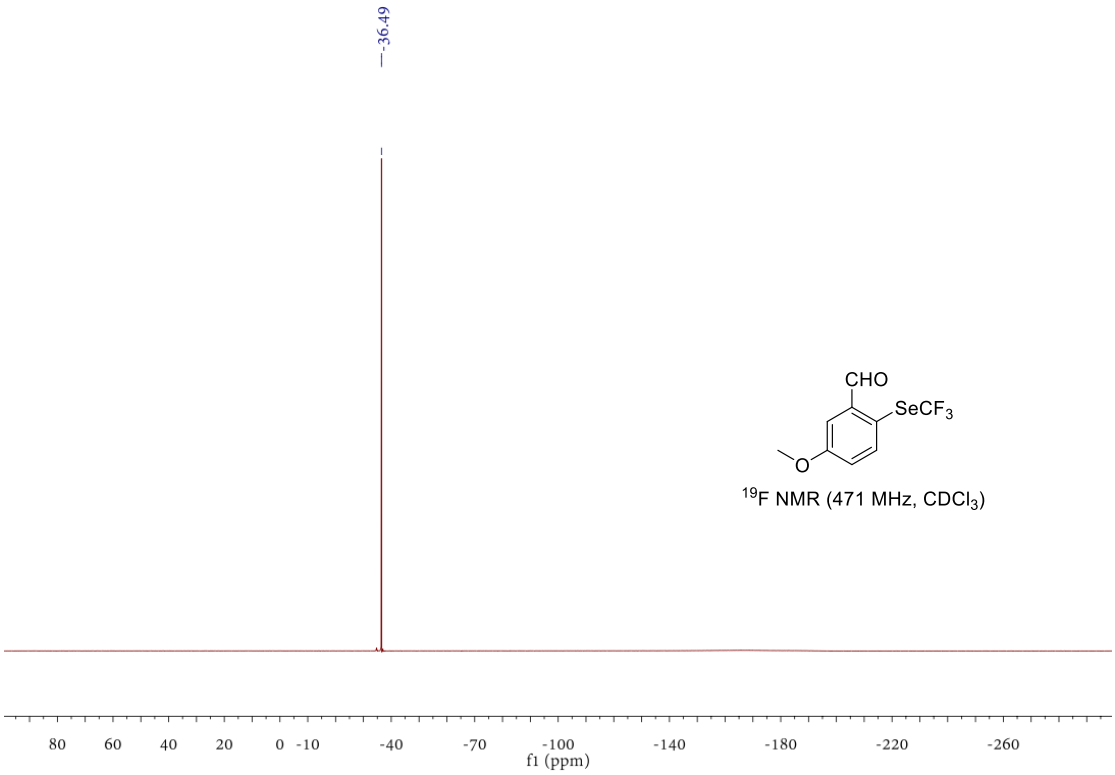
^{13}C NMR spectrum of **3d**



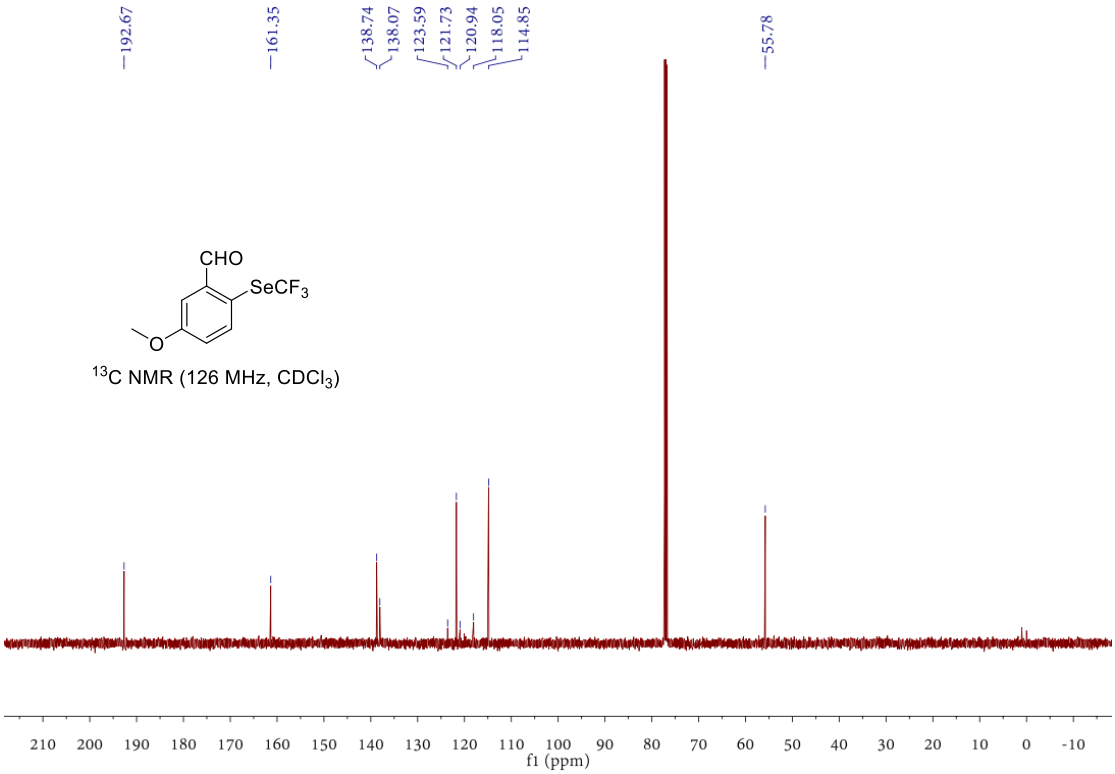
^{1}H NMR spectrum of **3e**



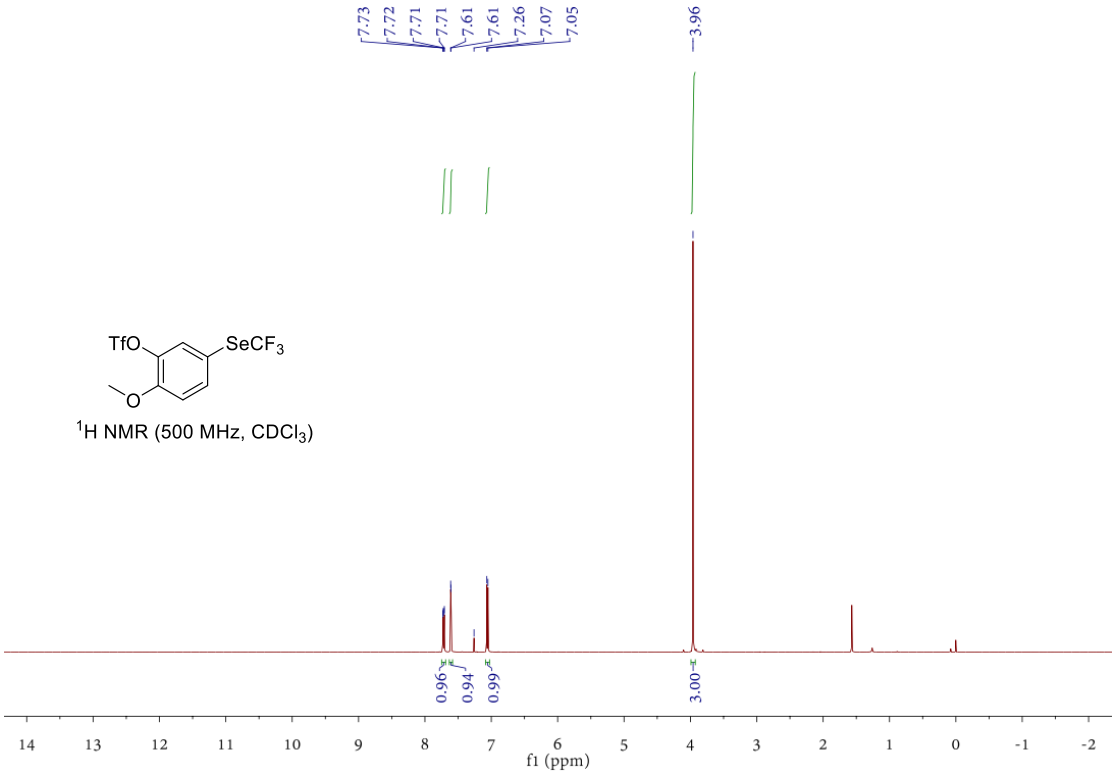
^{19}F NMR spectrum of **3e**



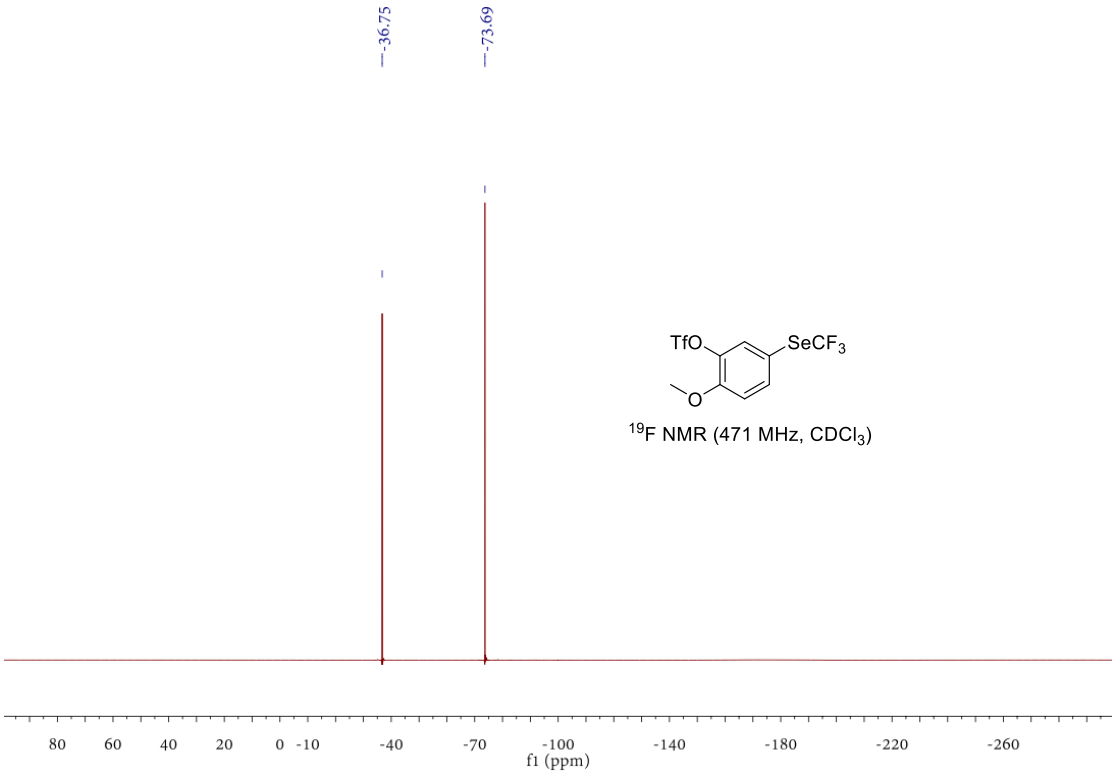
^{13}C NMR spectrum of **3e**



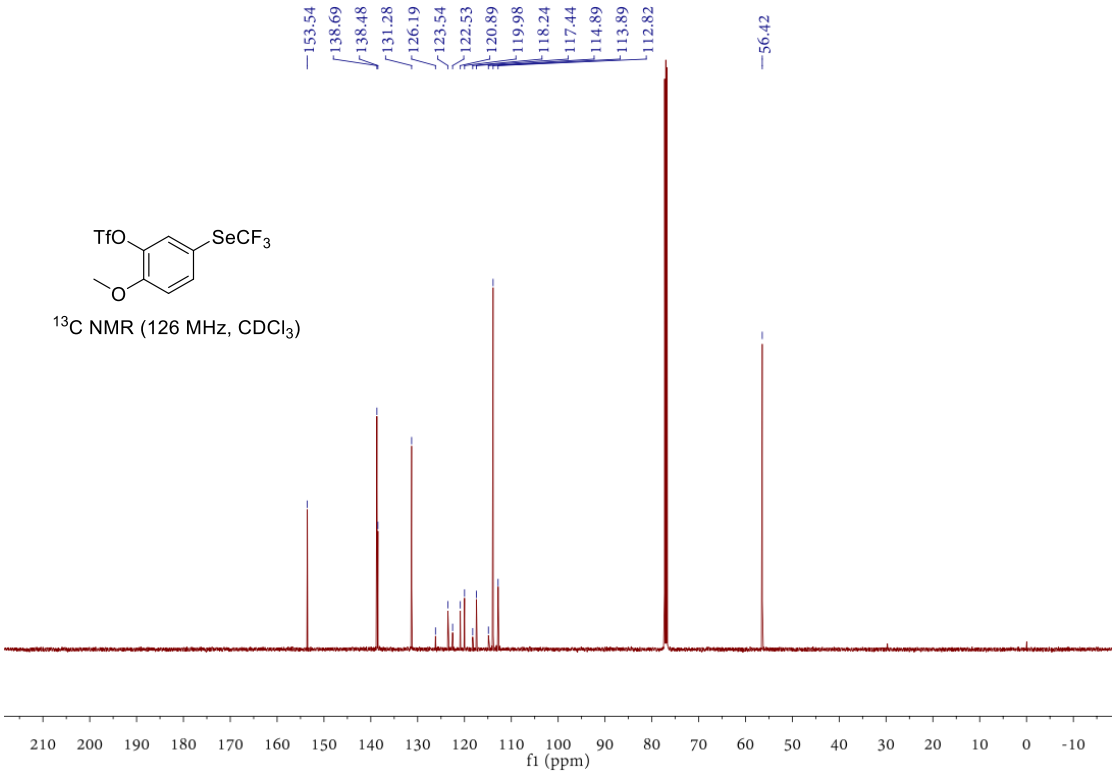
^{1}H NMR spectrum of **3f**



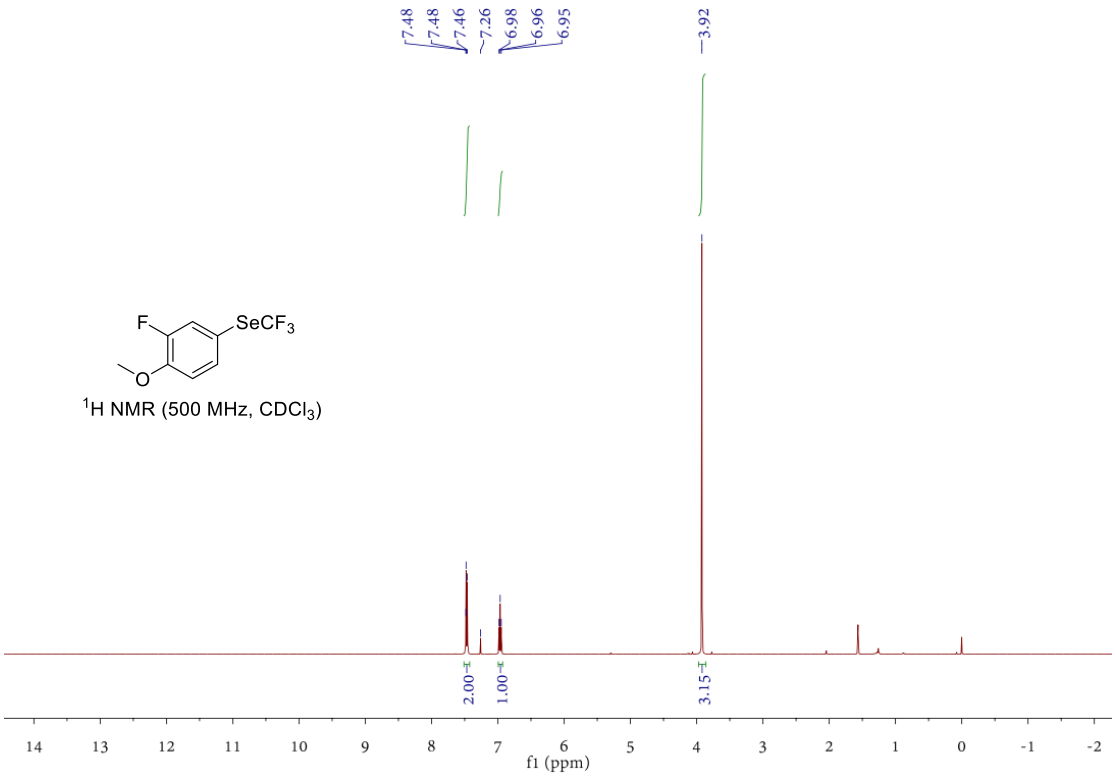
^{19}F NMR spectrum of **3f**



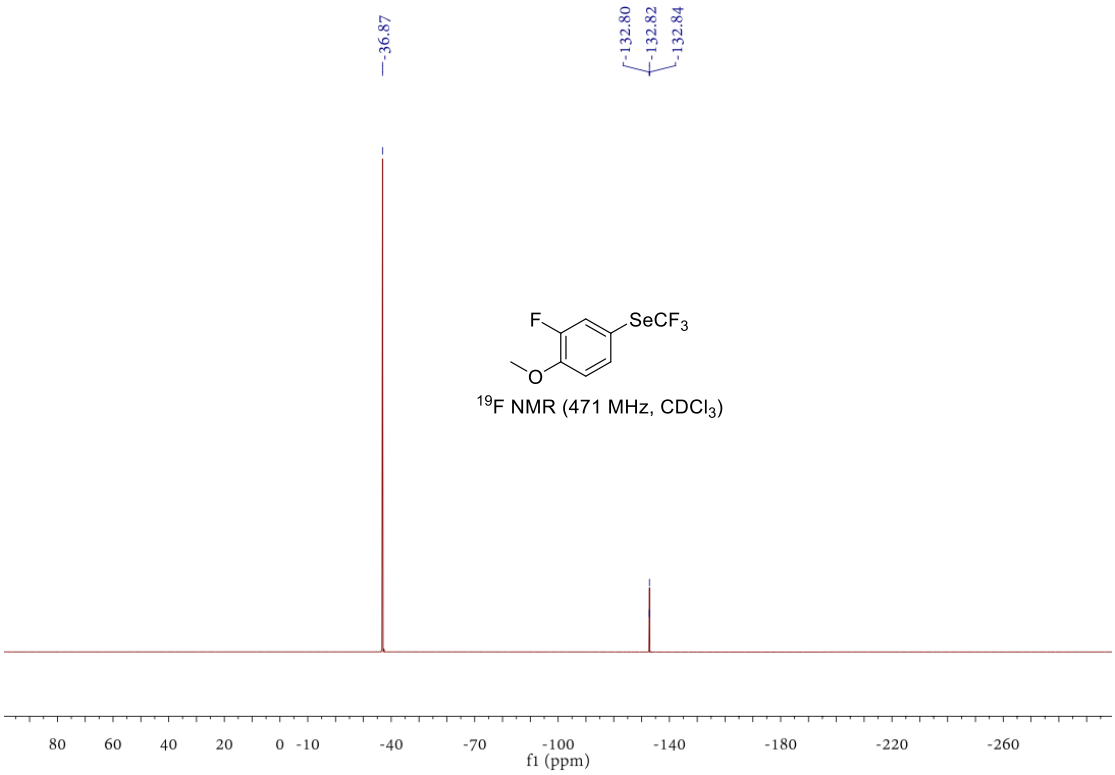
^{13}C NMR spectrum of **3f**



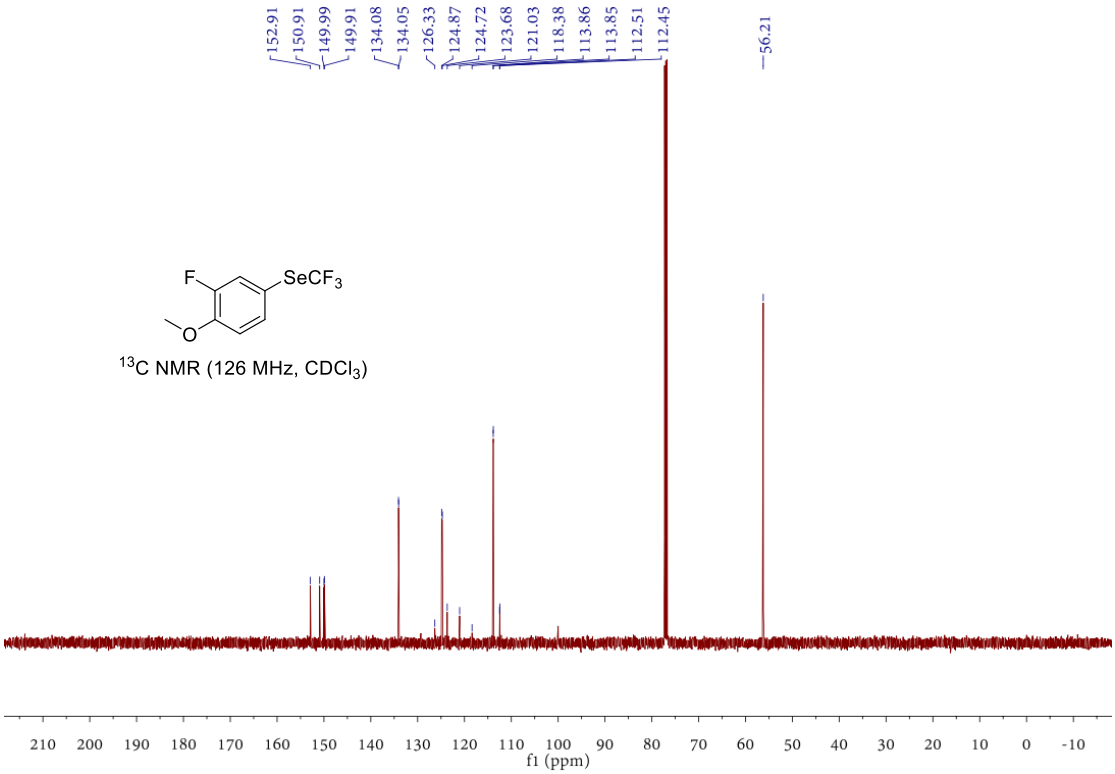
^{1}H NMR spectrum of **3g**



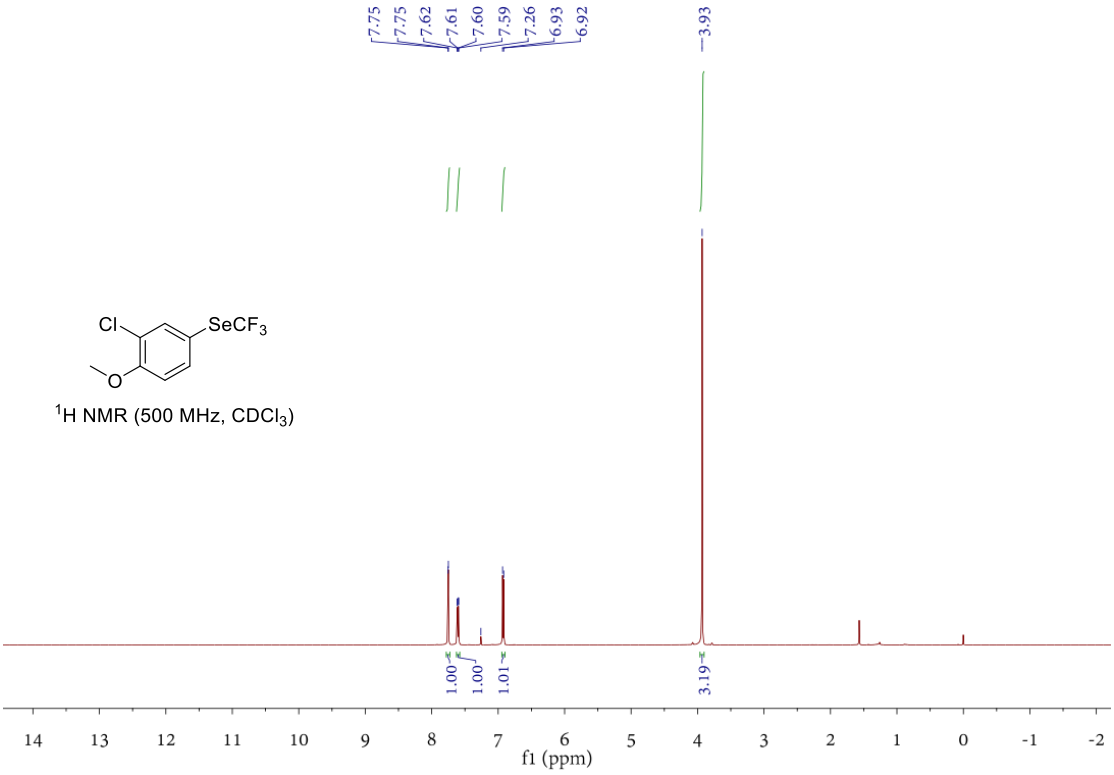
^{19}F NMR spectrum of **3g**



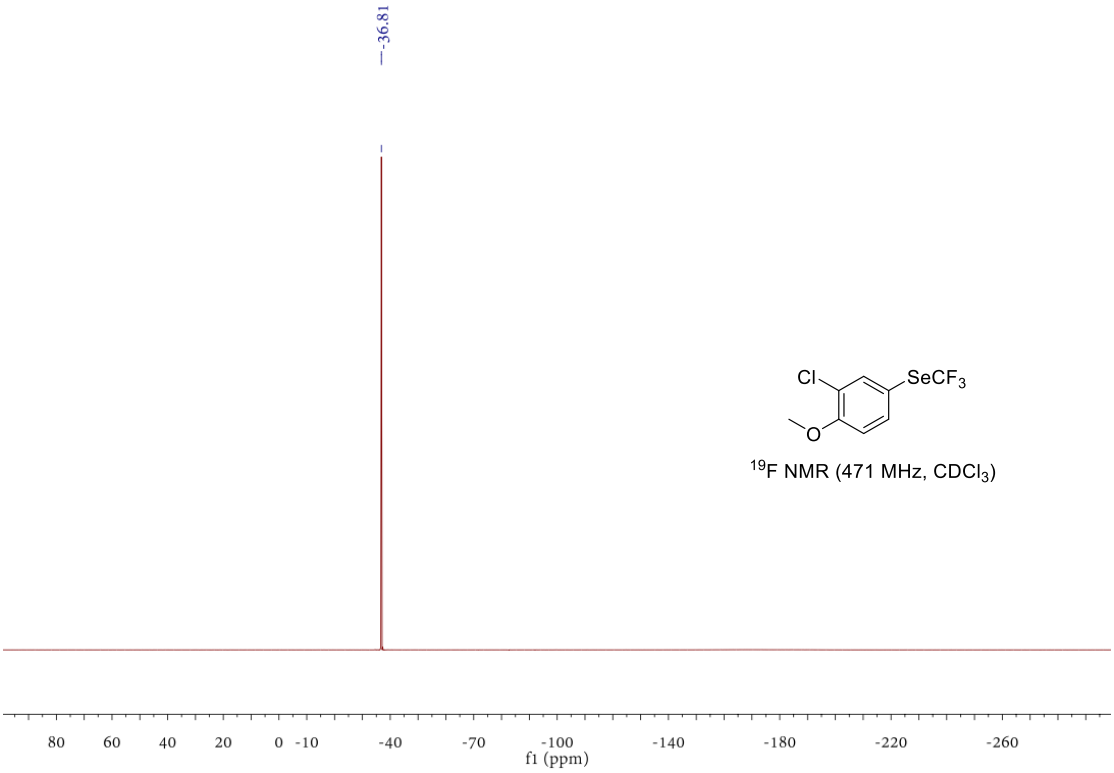
^{13}C NMR spectrum of **3g**



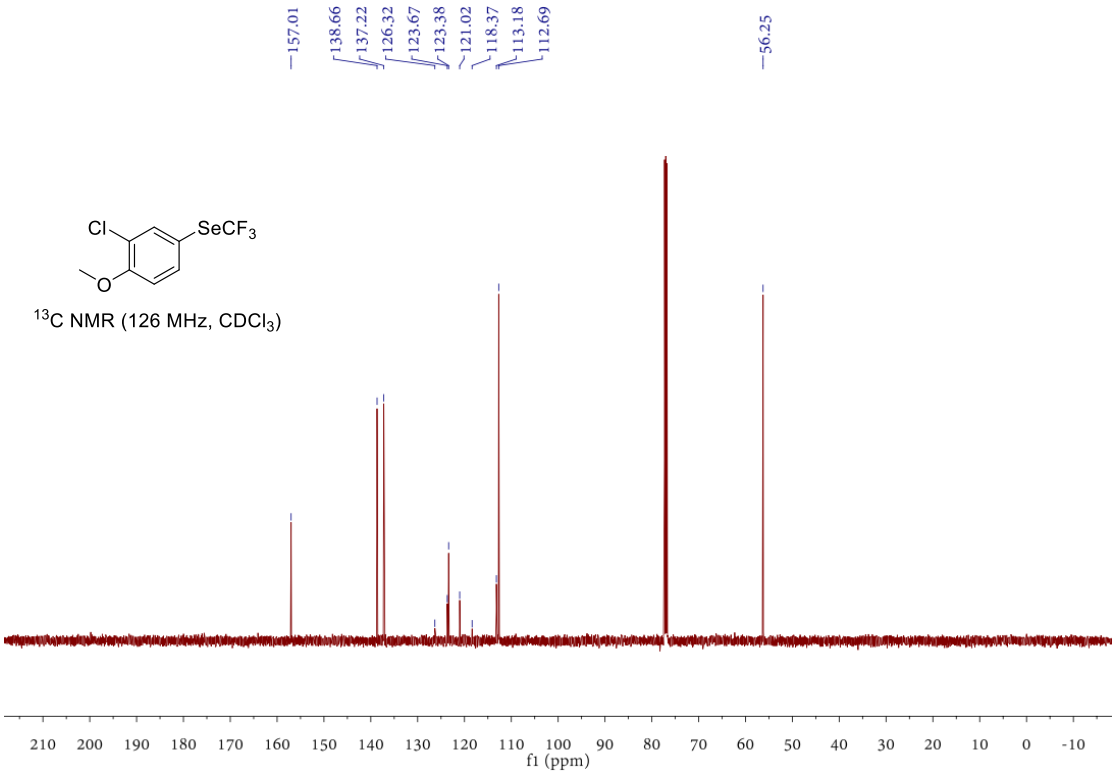
^{1}H NMR spectrum of **3h**



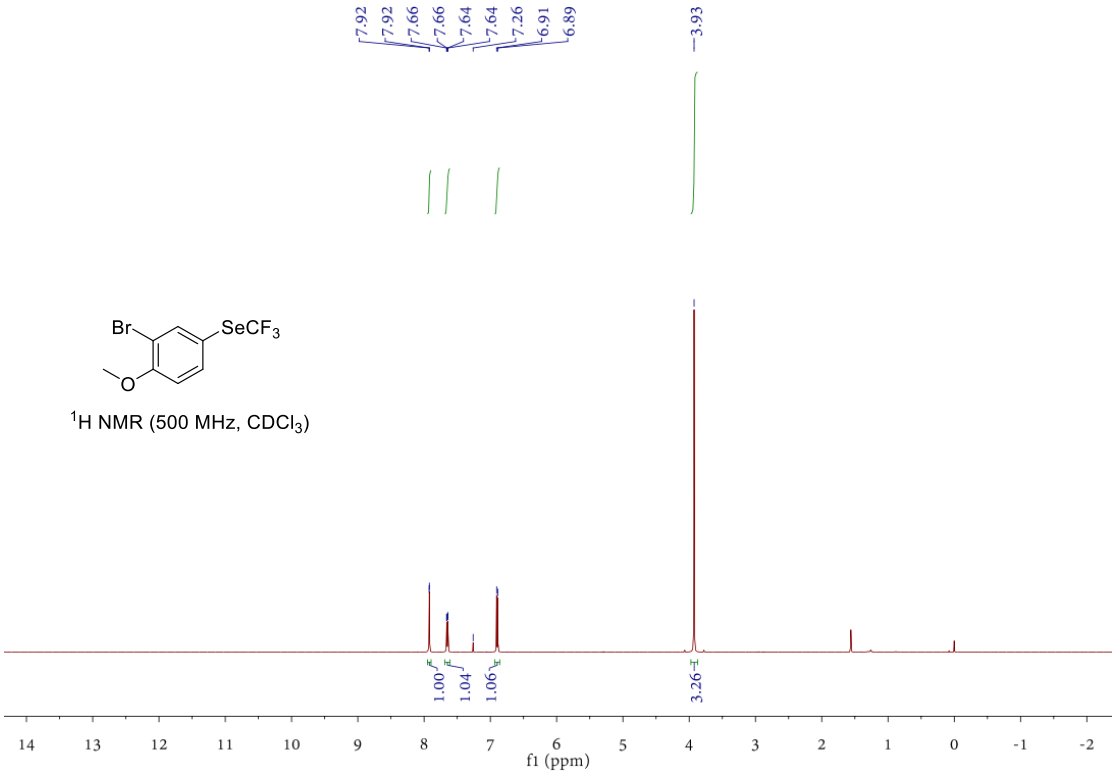
^{19}F NMR spectrum of **3h**



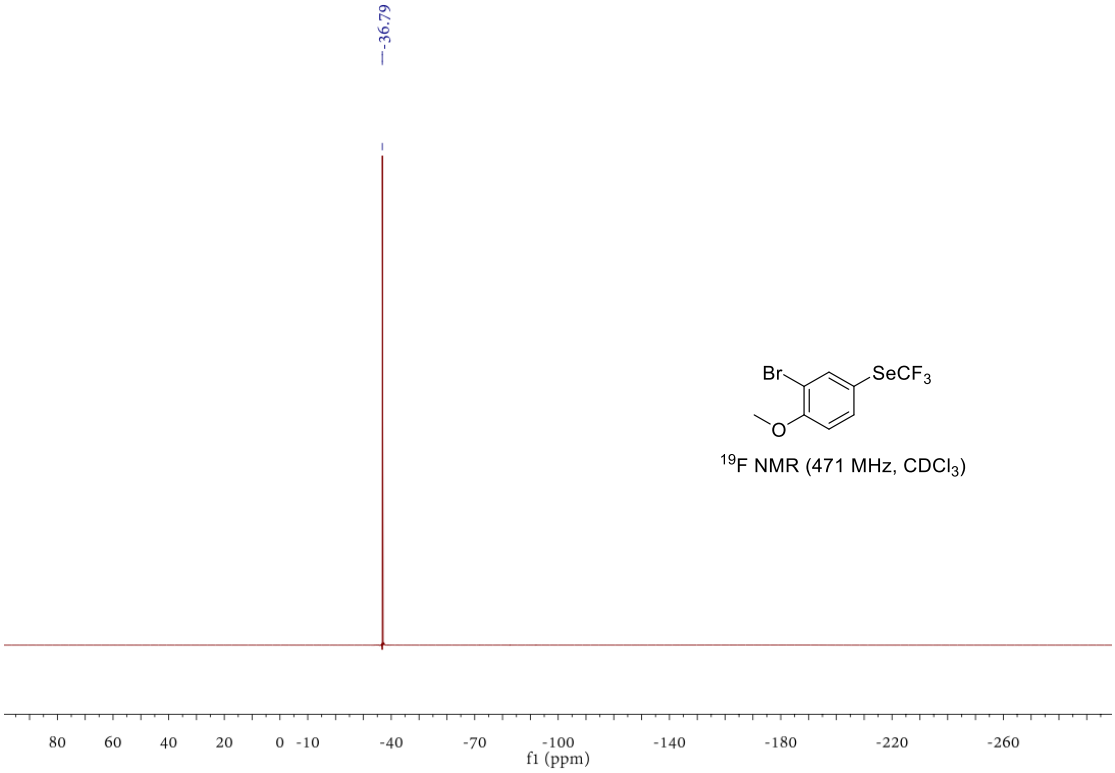
^{13}C NMR spectrum of **3h**



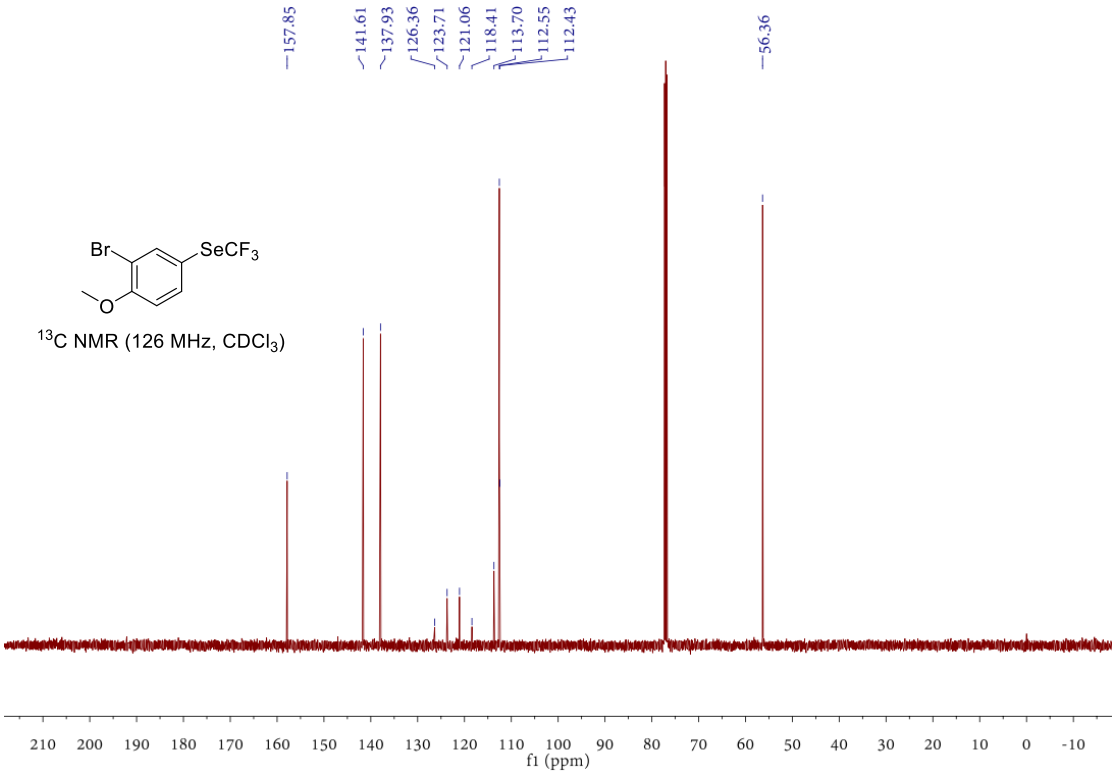
^{1}H NMR spectrum of **3i**



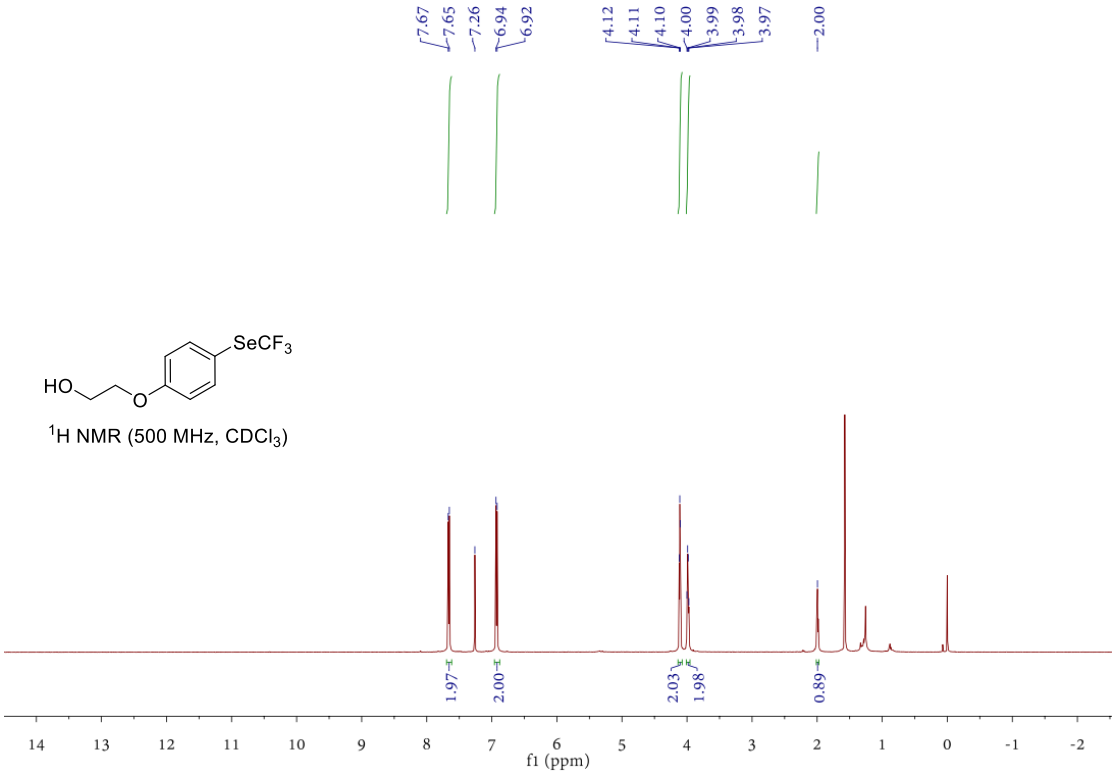
^{19}F NMR spectrum of **3i**



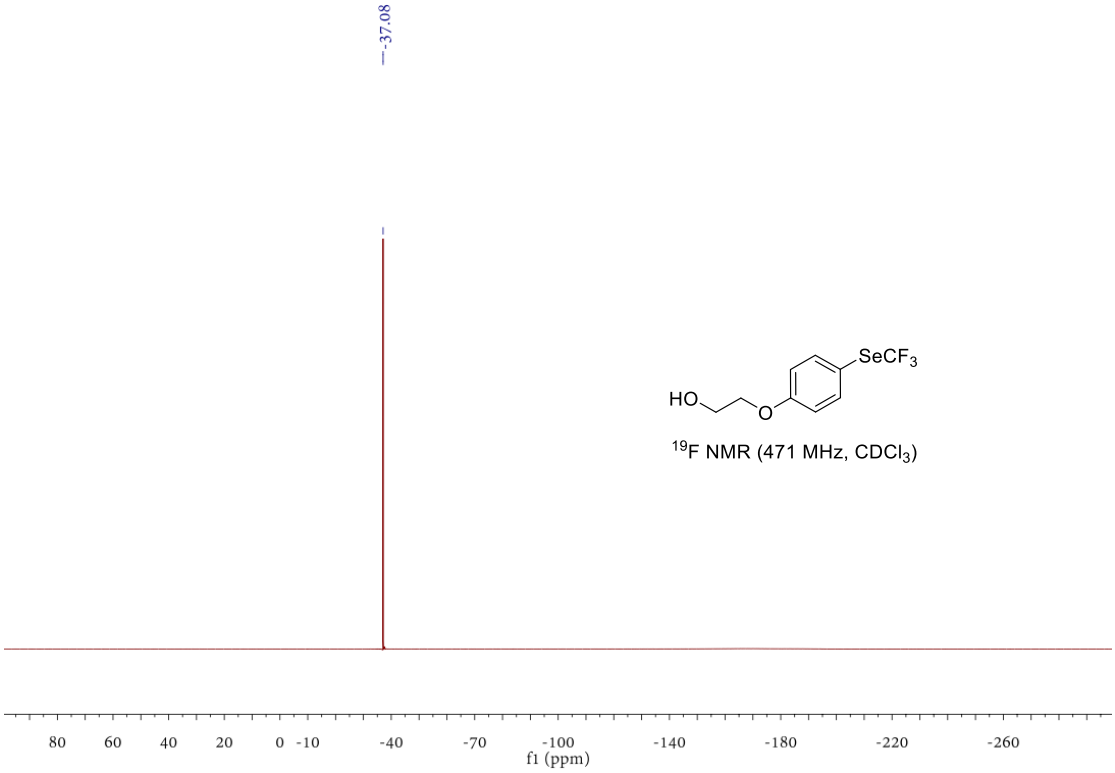
^{13}C NMR spectrum of **3i**



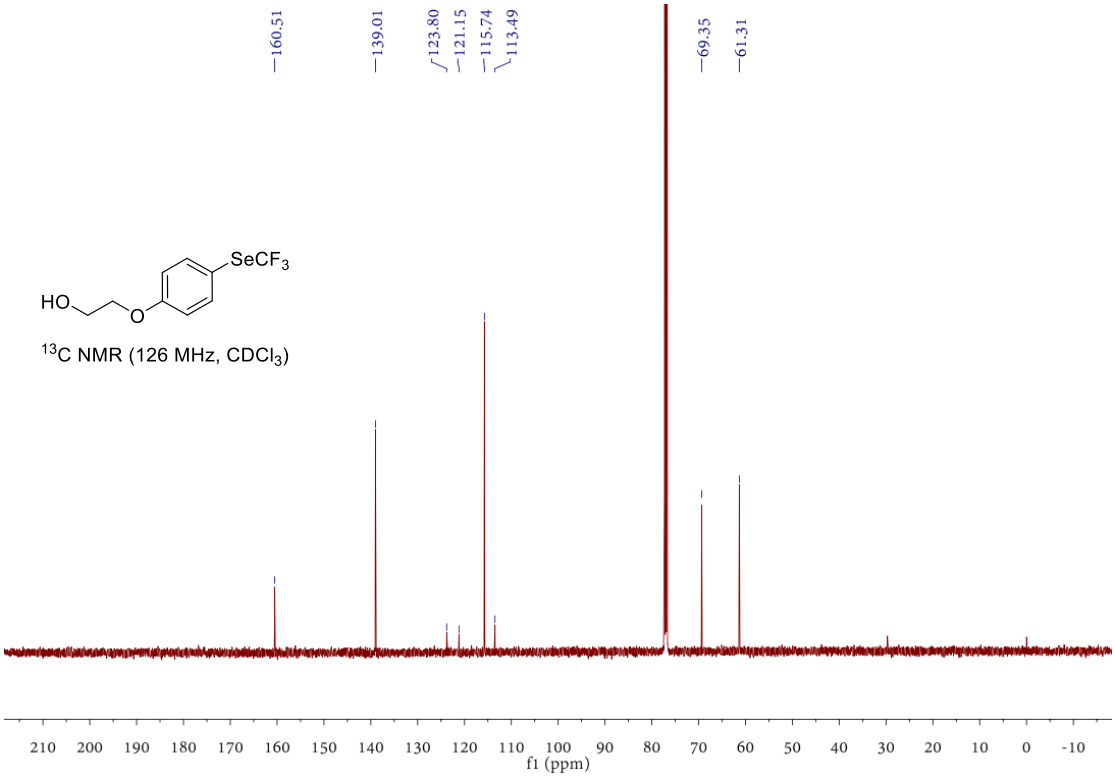
^{1}H NMR spectrum of **3j**



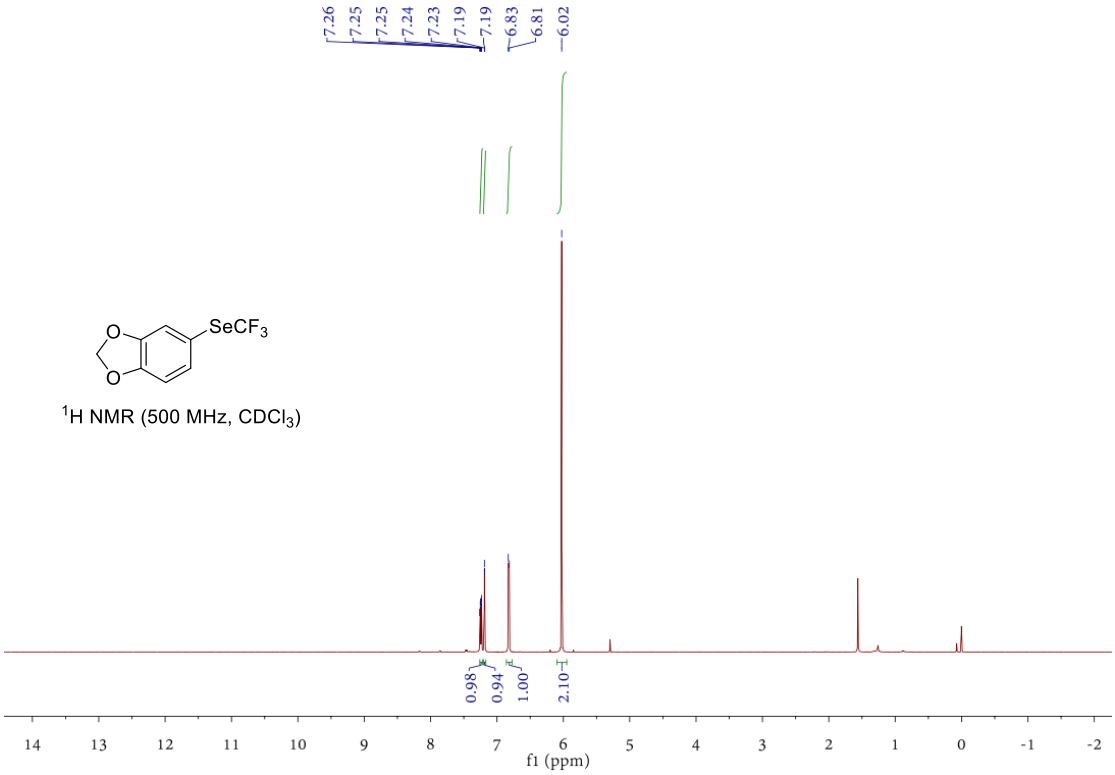
^{19}F NMR spectrum of **3j**



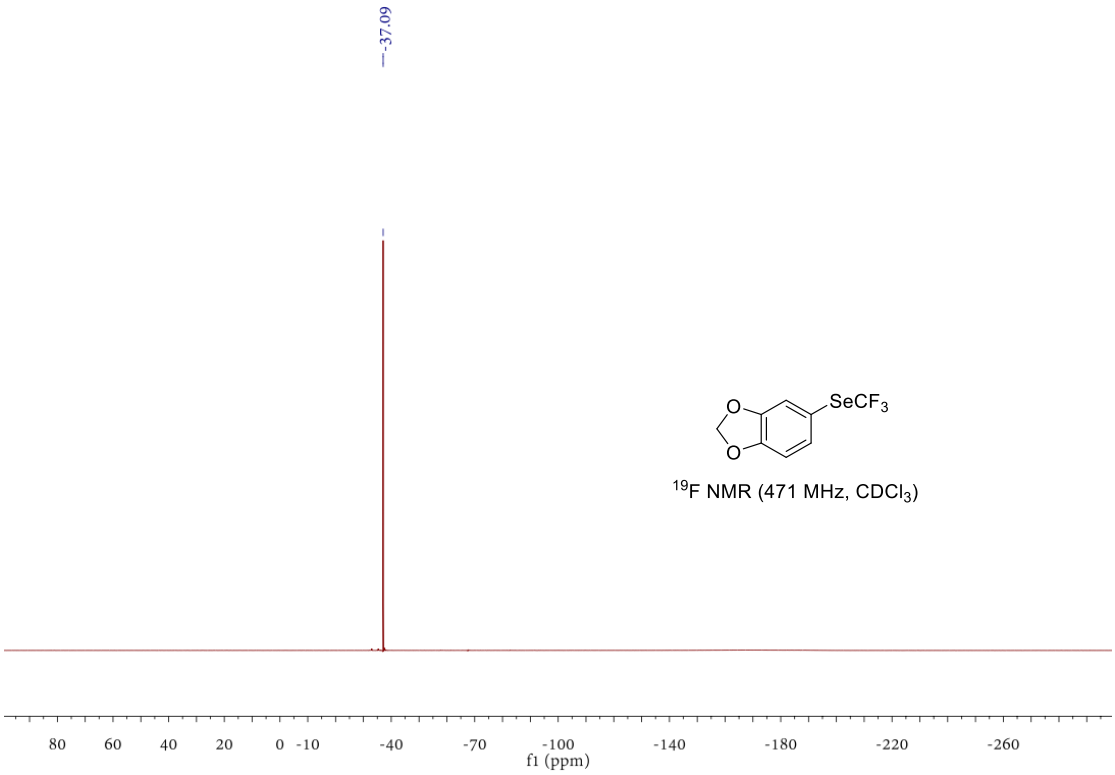
^{13}C NMR spectrum of **3j**



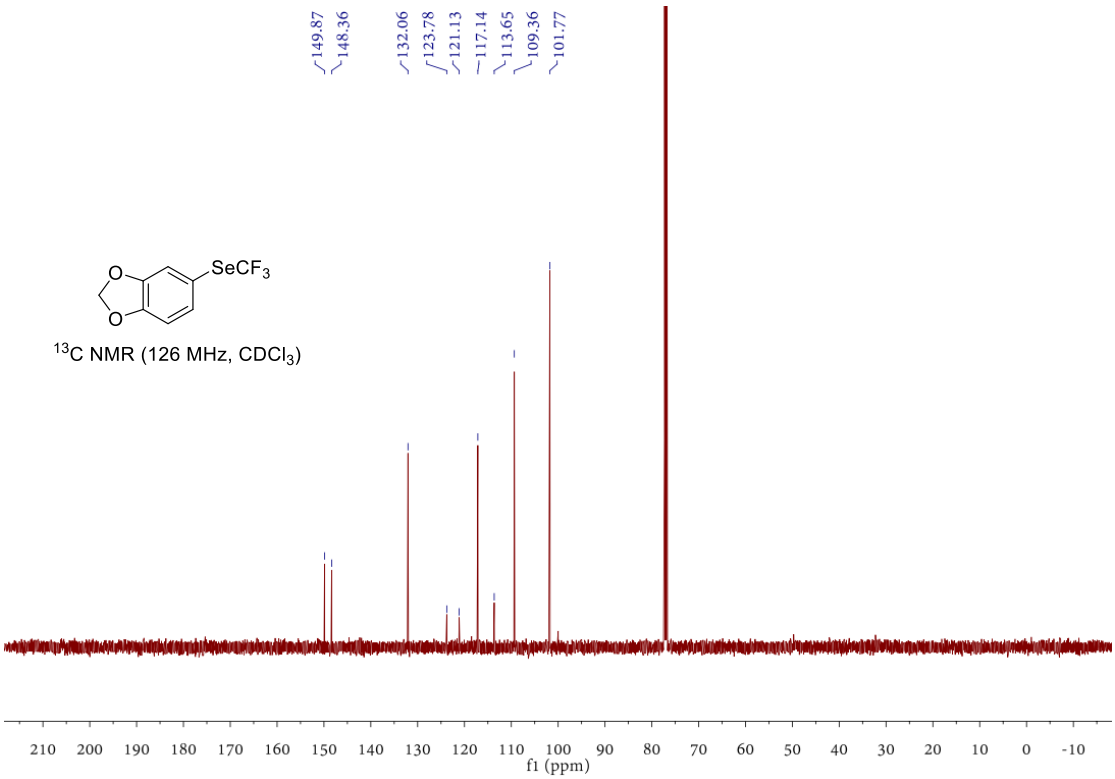
^{1}H NMR spectrum of **3k**



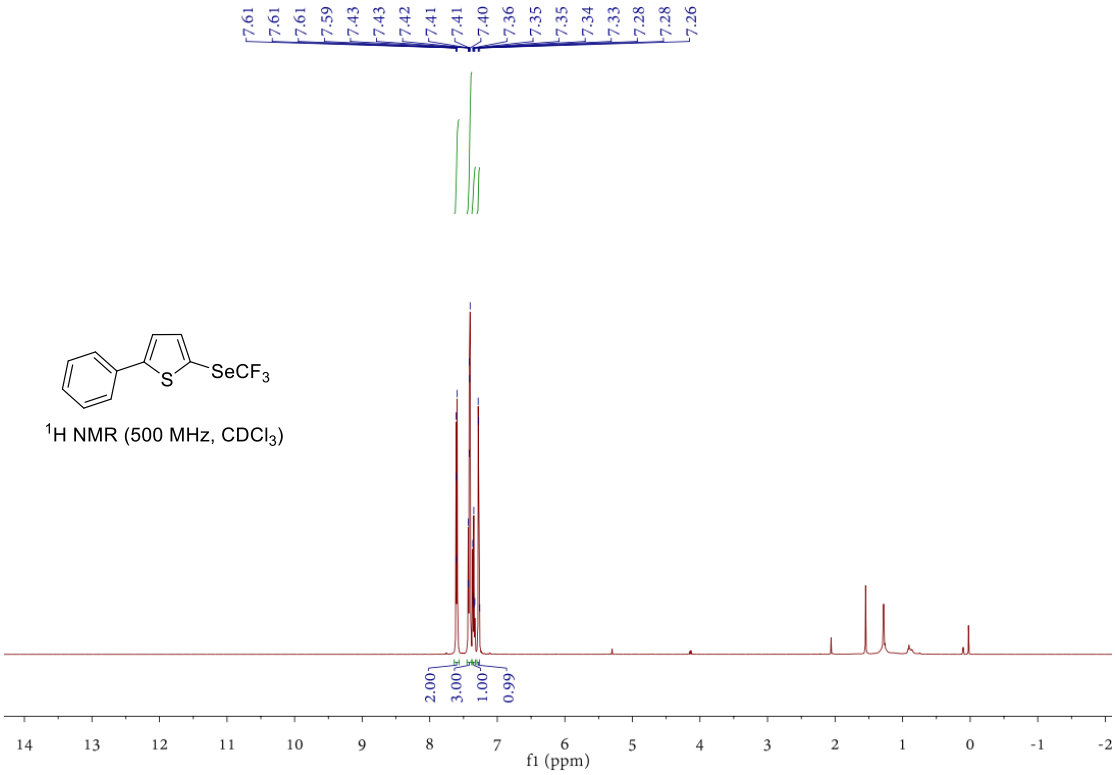
^{19}F NMR spectrum of **3k**



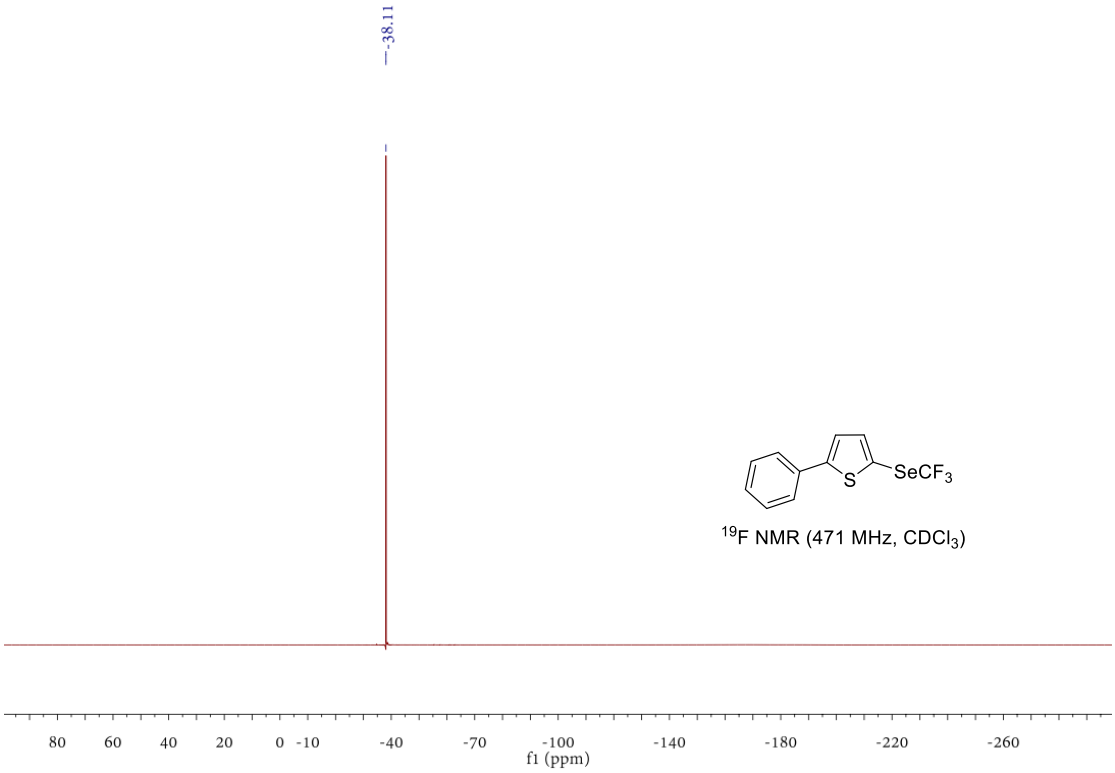
^{13}C NMR spectrum of **3k**



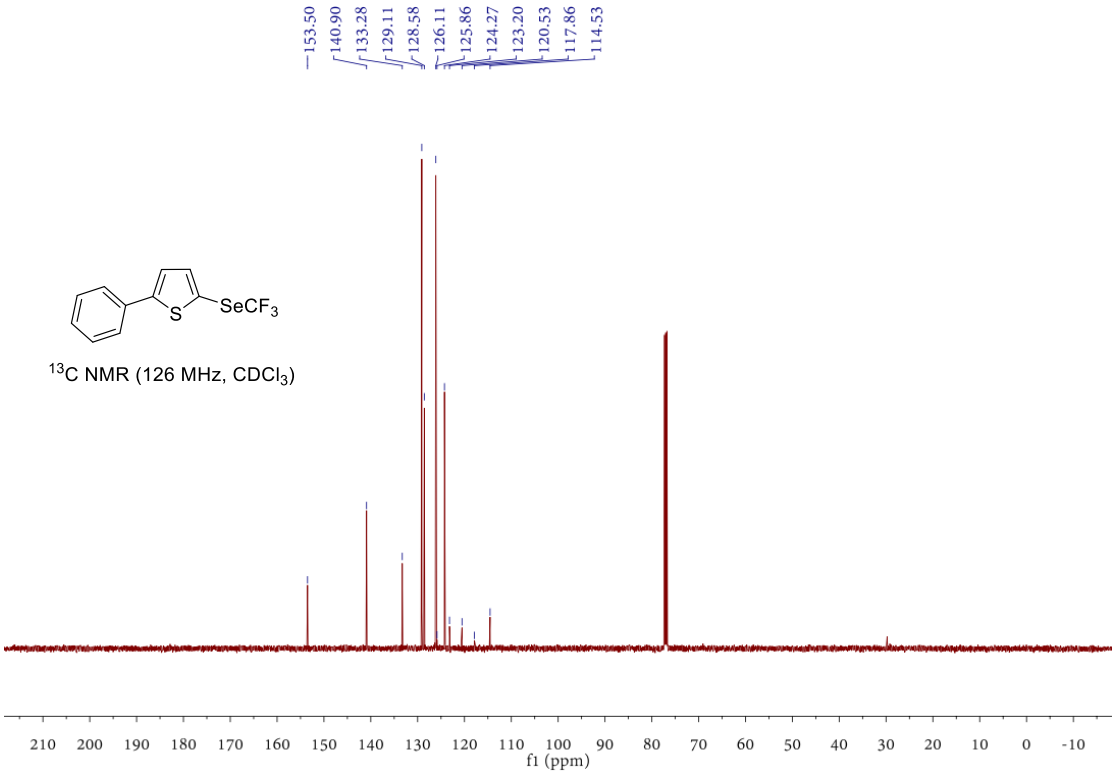
^{1}H NMR spectrum of **3l**



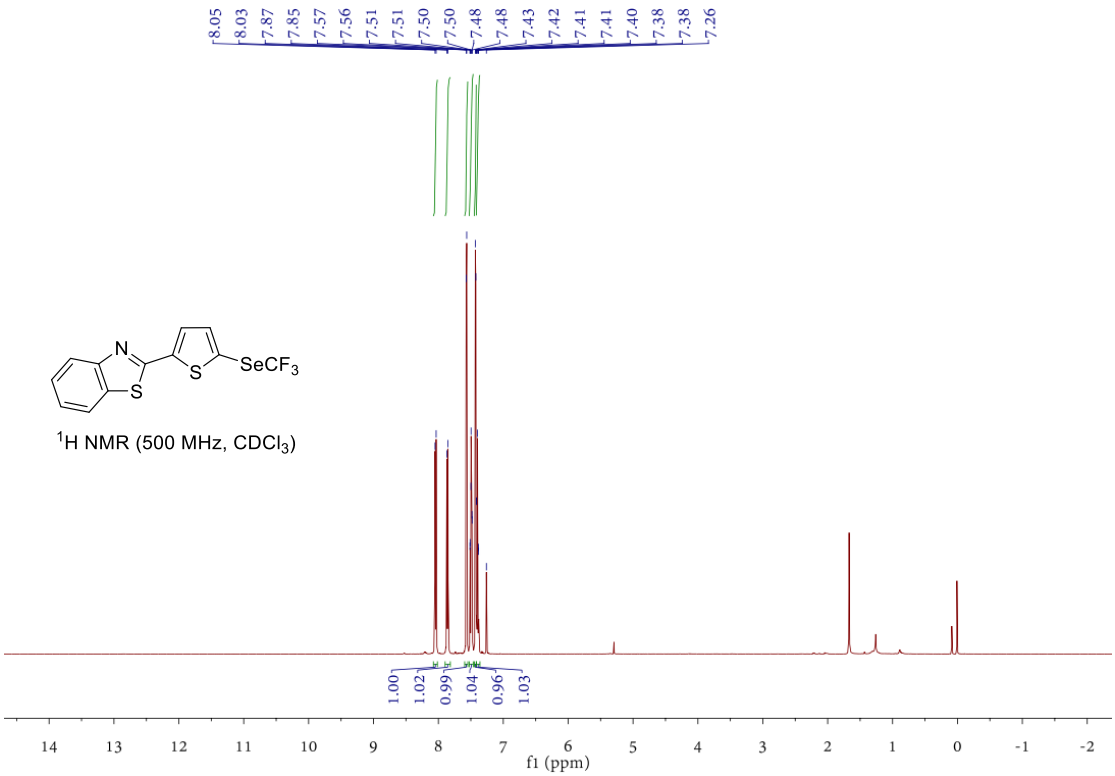
^{19}F NMR spectrum of **3l**



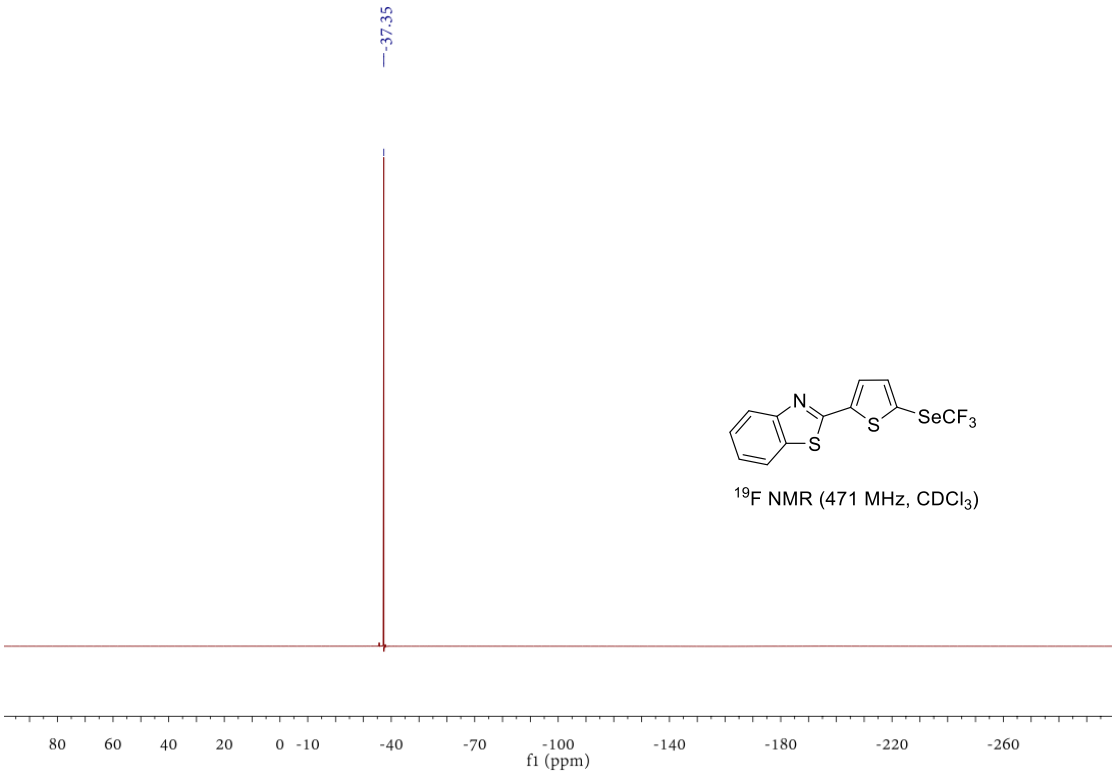
^{13}C NMR spectrum of **3l**



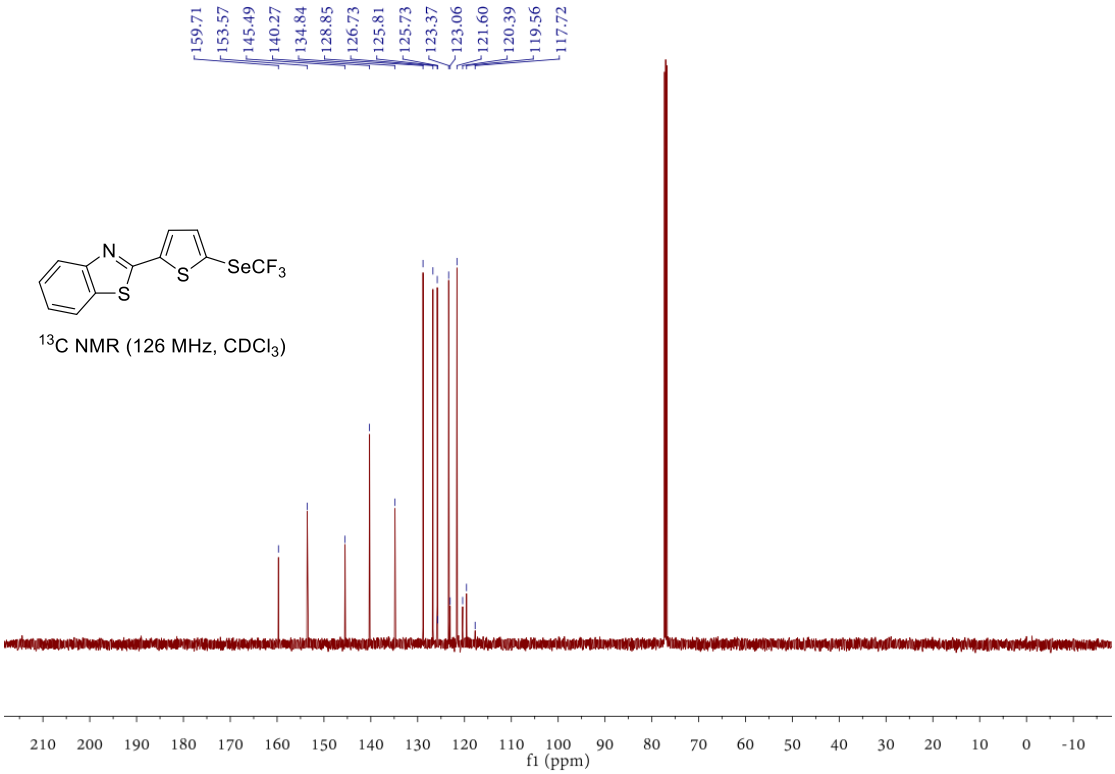
^{1}H NMR spectrum of **3m**



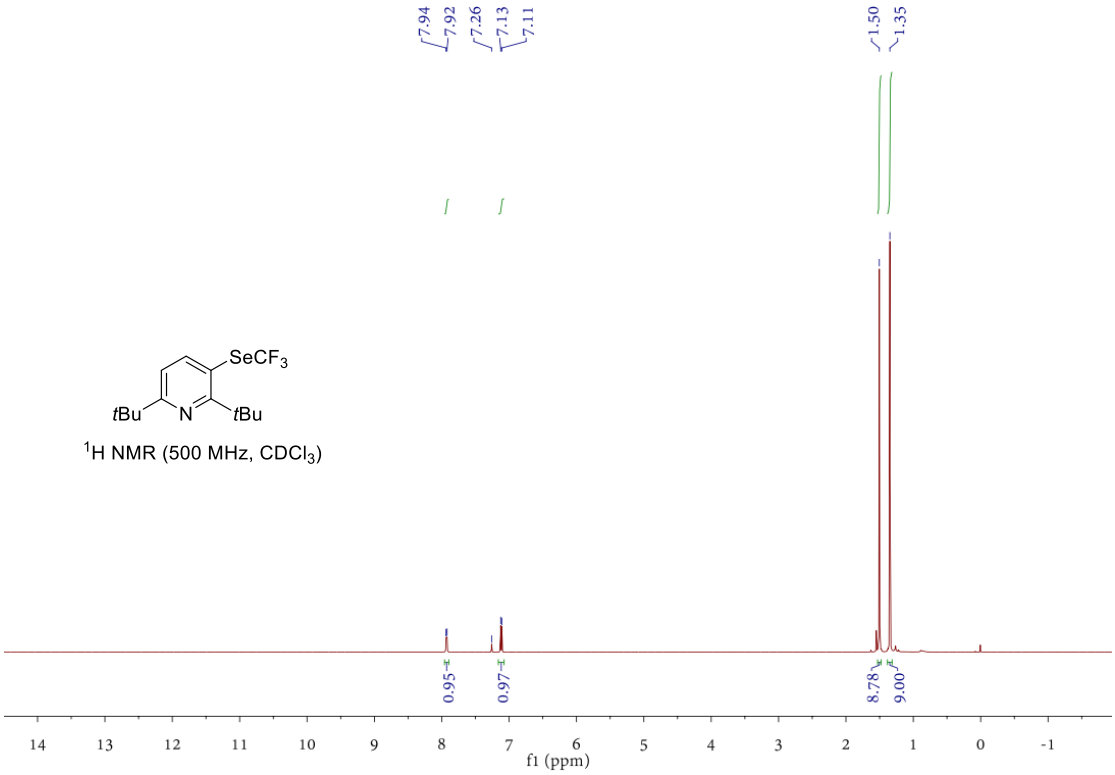
^{19}F NMR spectrum of **3m**



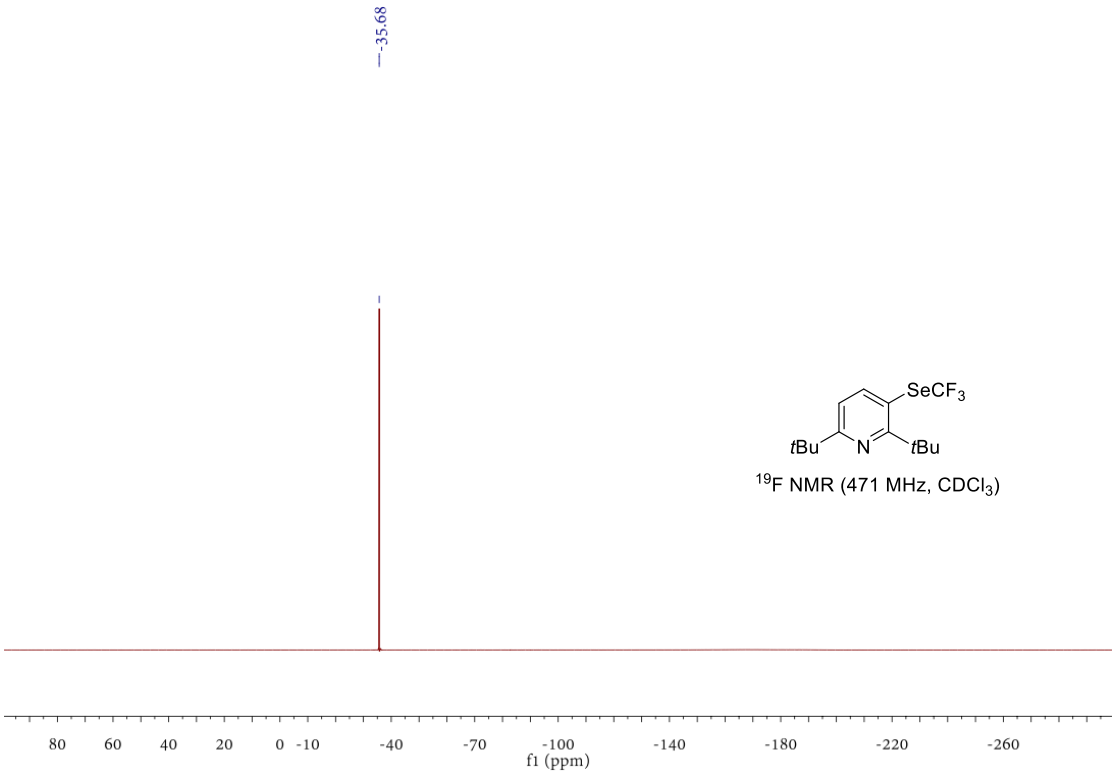
^{13}C NMR spectrum of **3m**



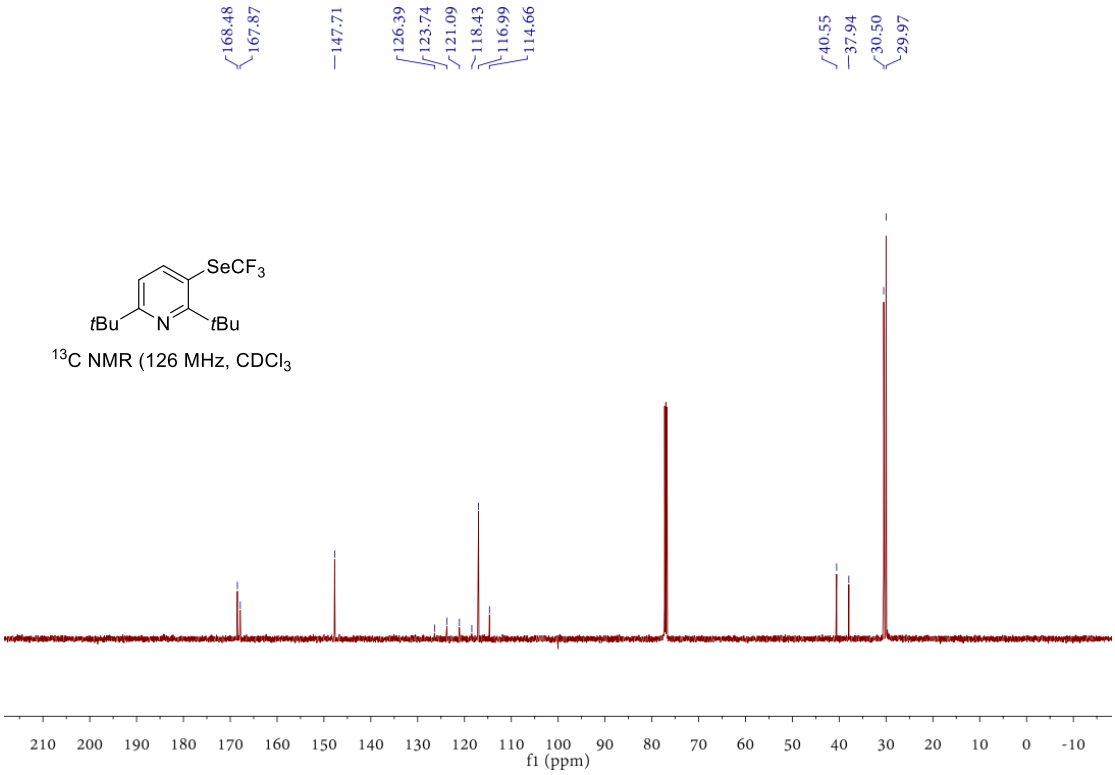
^{1}H NMR spectrum of **3n**



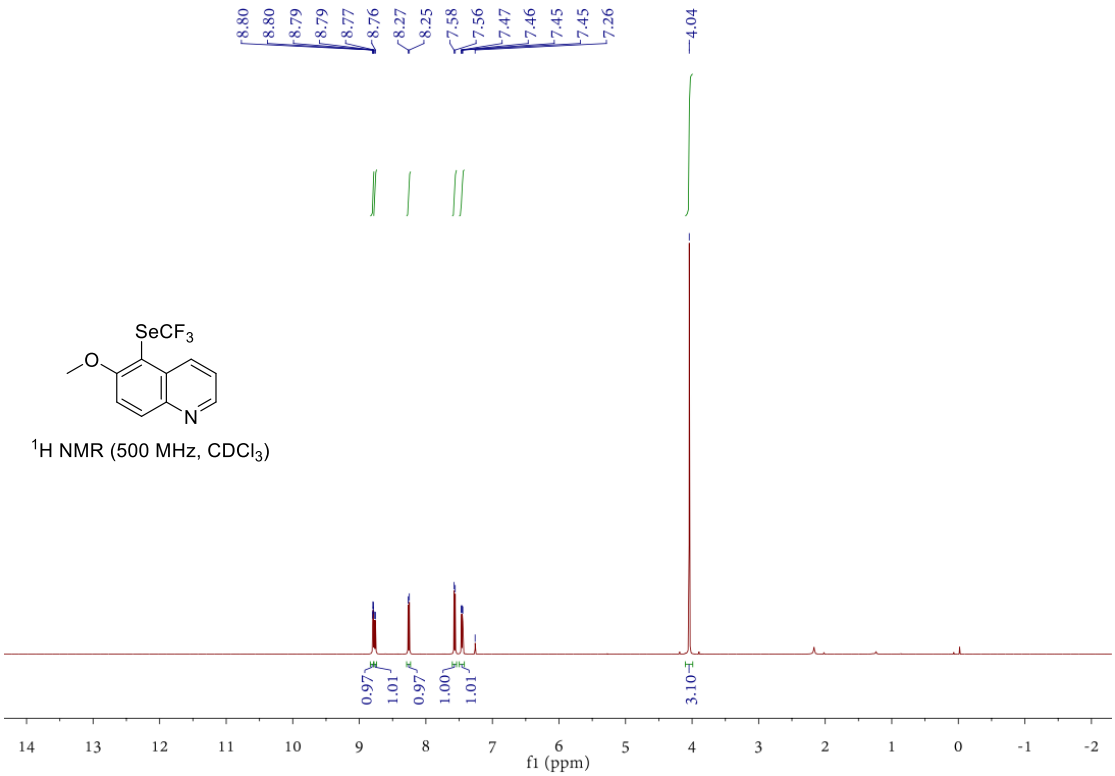
^{19}F NMR spectrum of **3n**



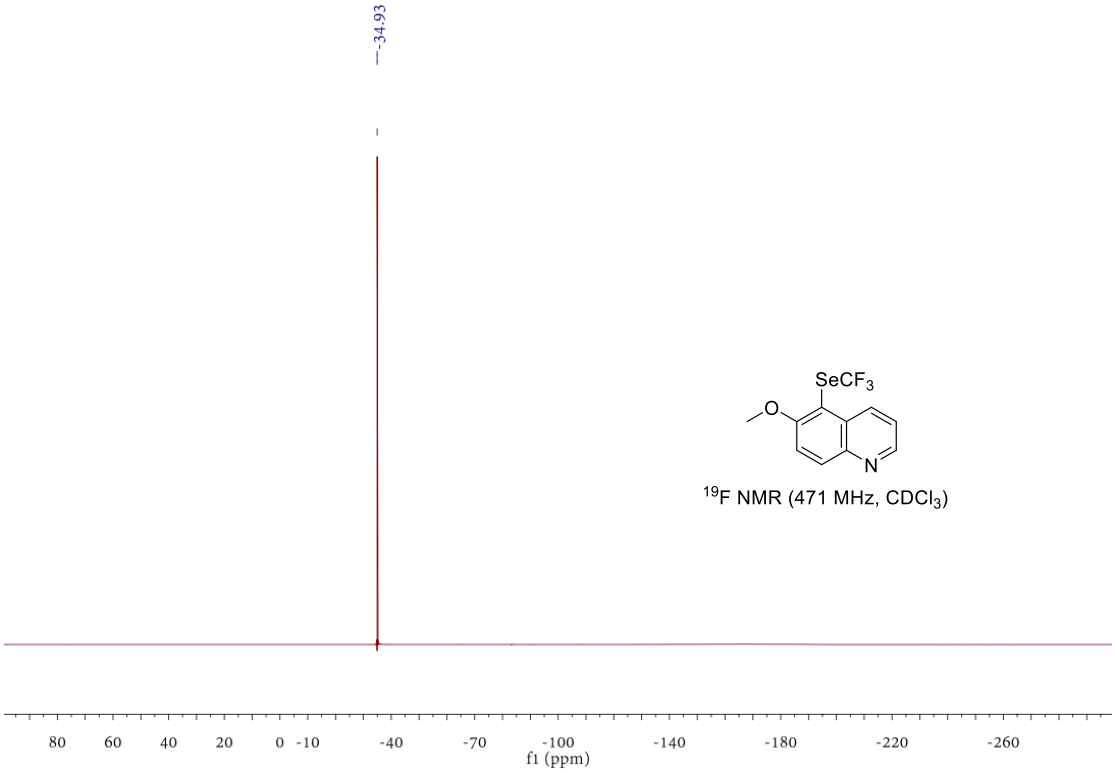
^{13}C NMR spectrum of **3n**



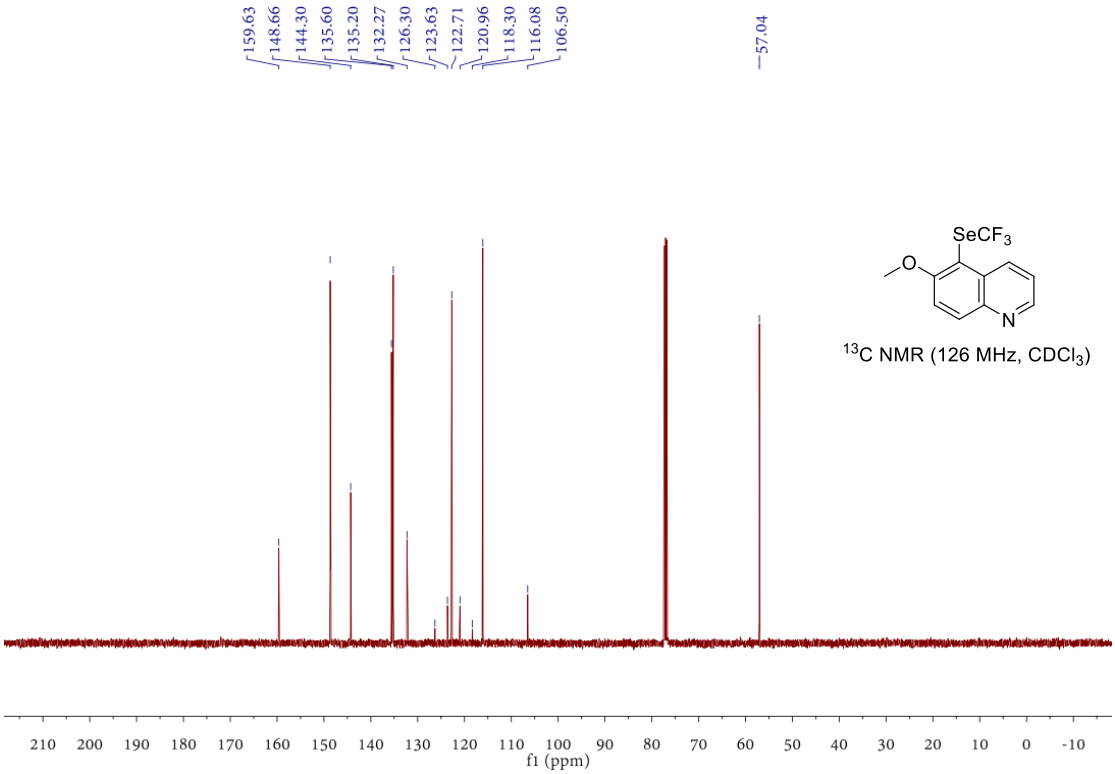
^{1}H NMR spectrum of **3o**



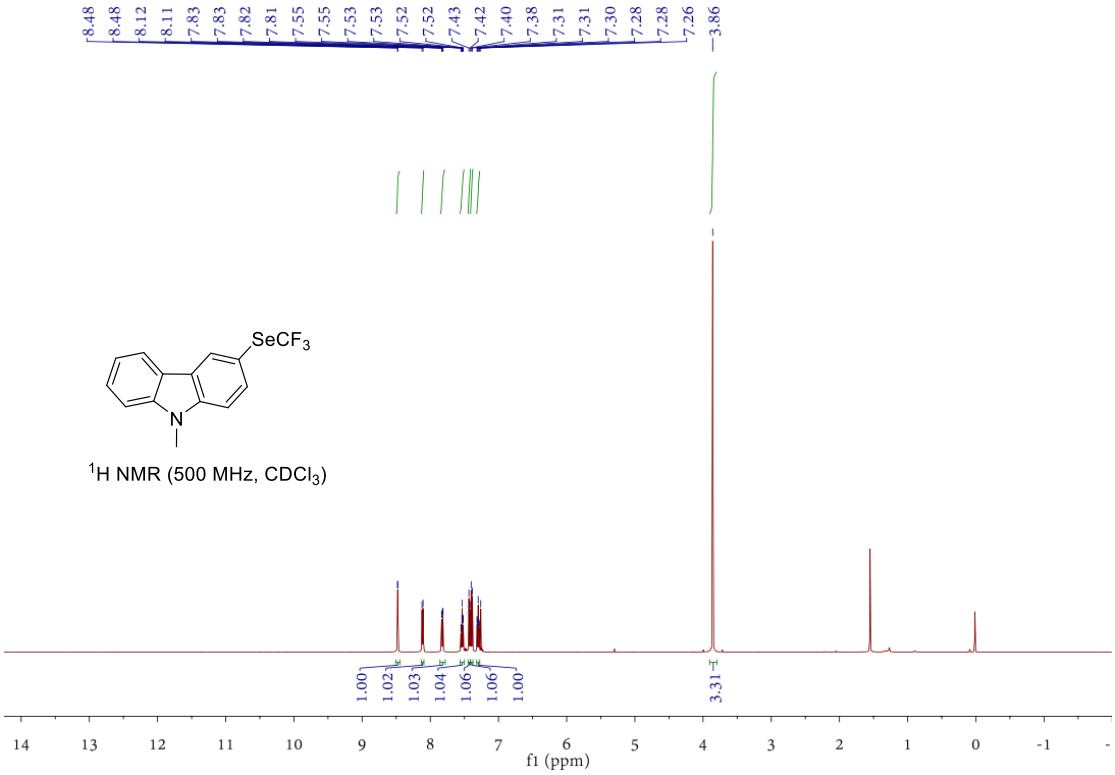
^{19}F NMR spectrum of **3o**



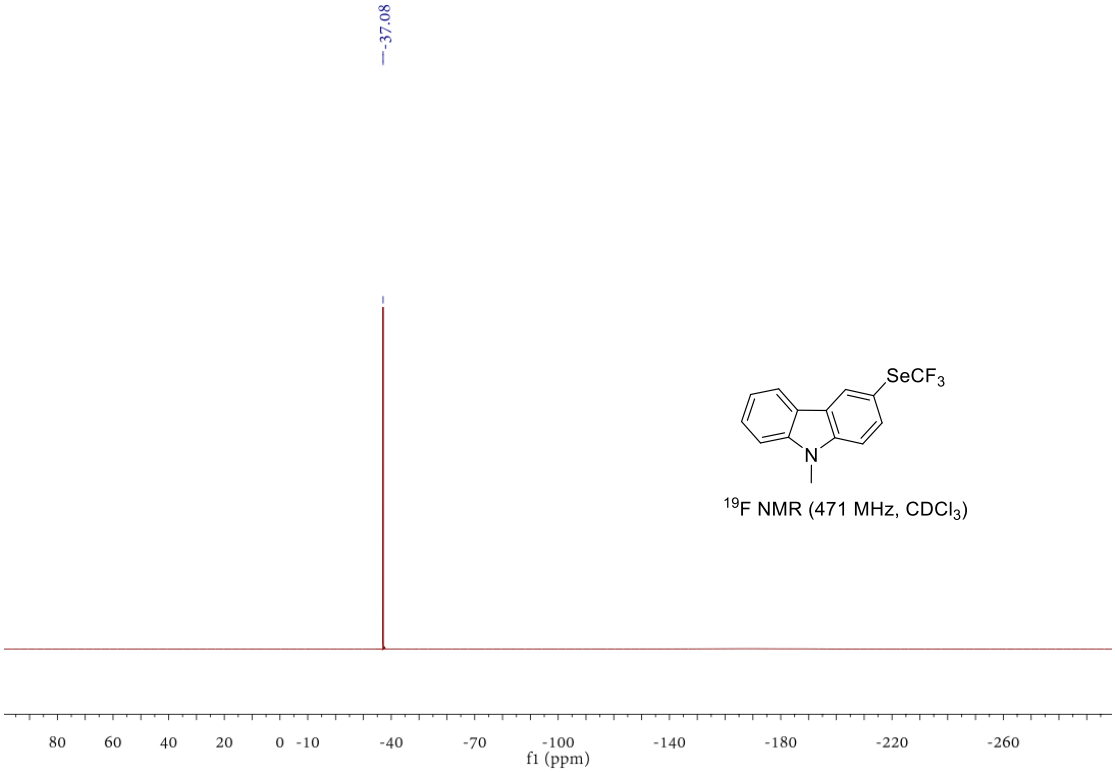
^{13}C NMR spectrum of **3o**



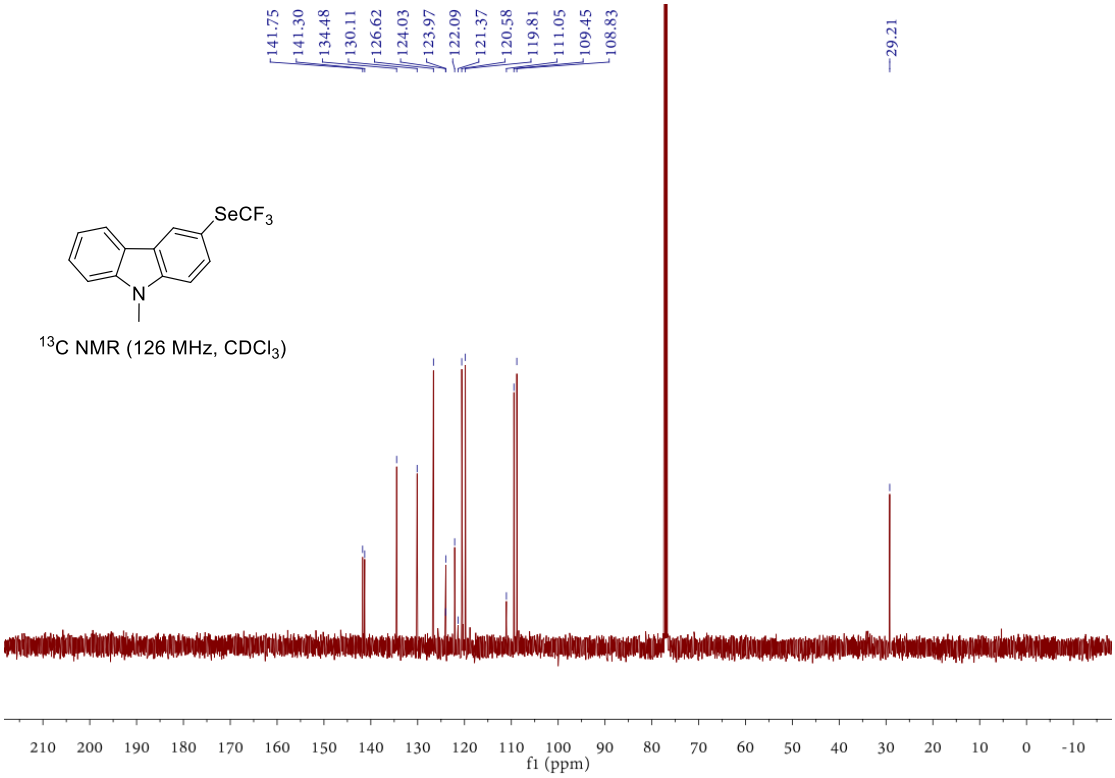
^{1}H NMR spectrum of **3p**



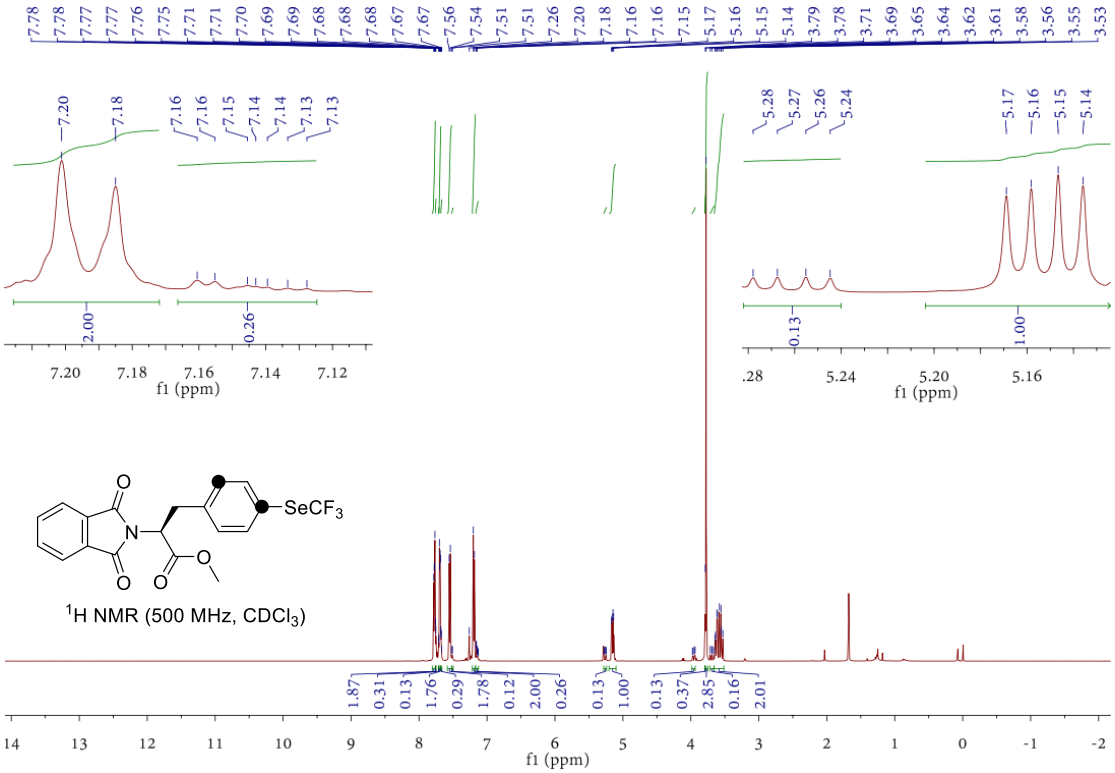
^{19}F NMR spectrum of **3p**



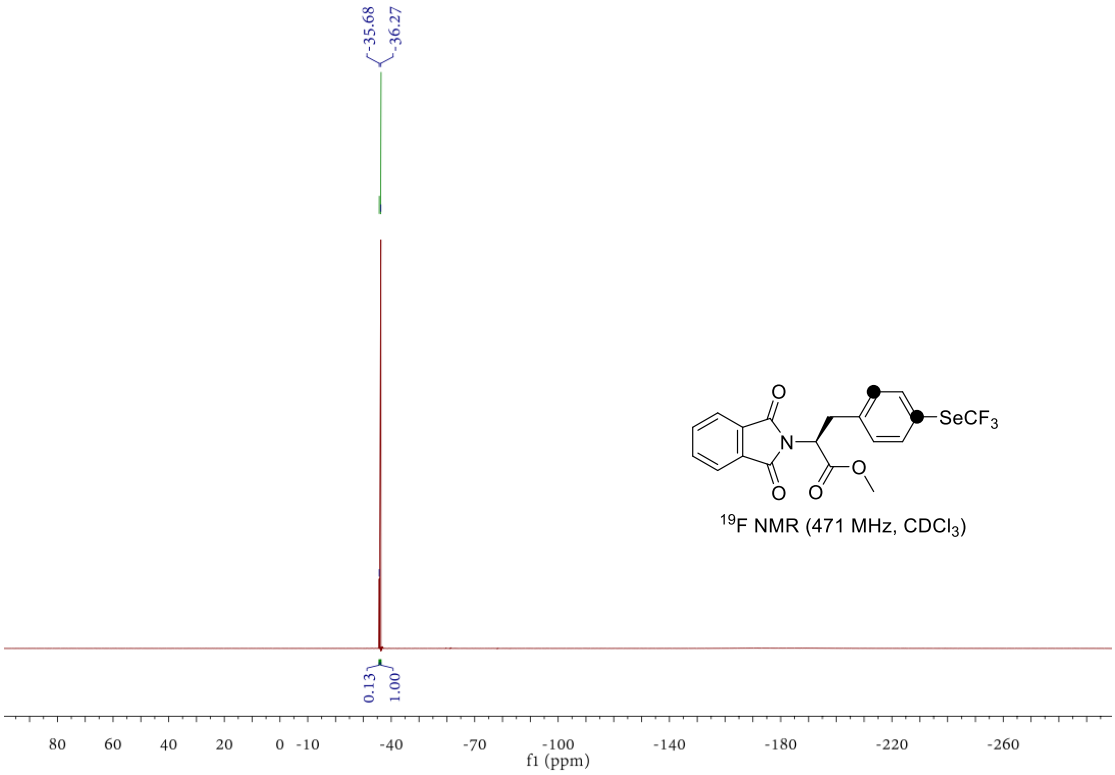
^{13}C NMR spectrum of **3p**



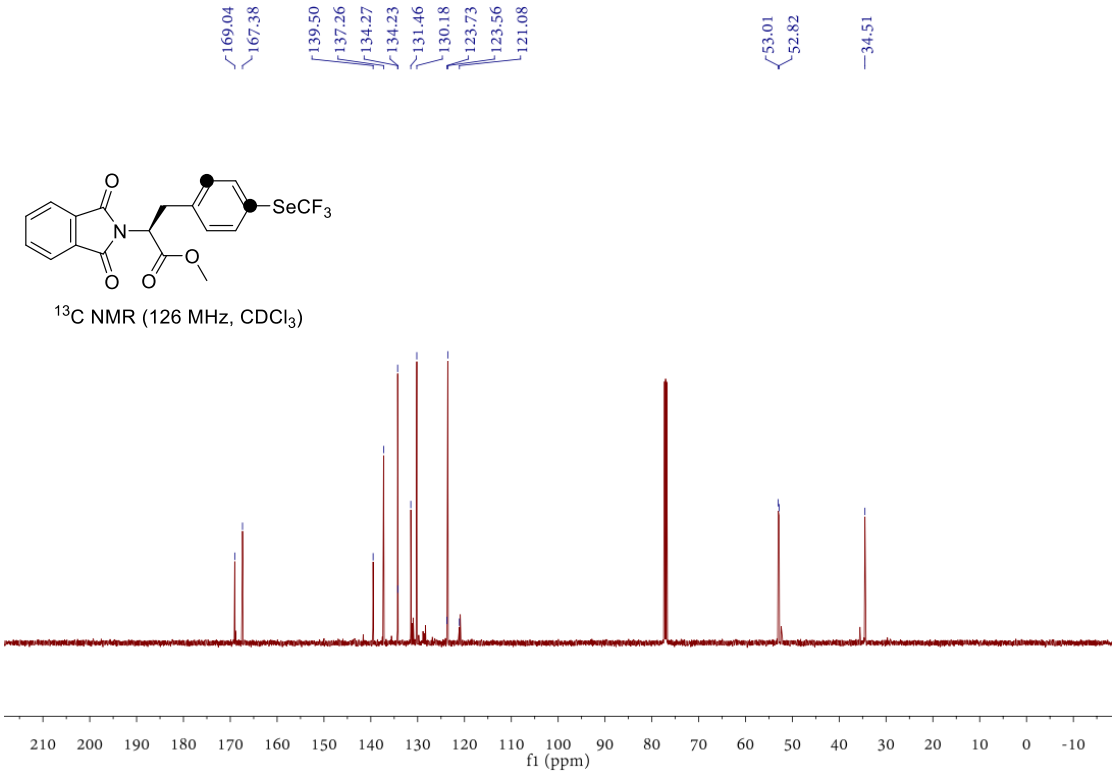
^{1}H NMR spectrum of **3q**



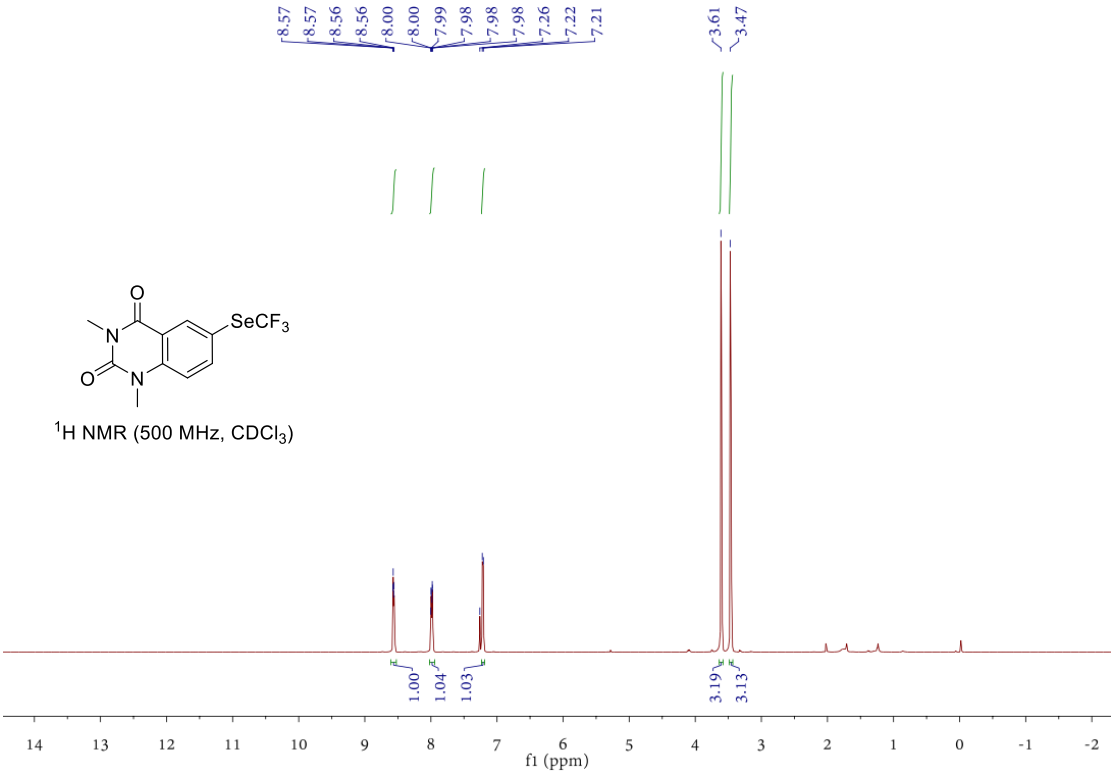
^{19}F NMR spectrum of **3q**



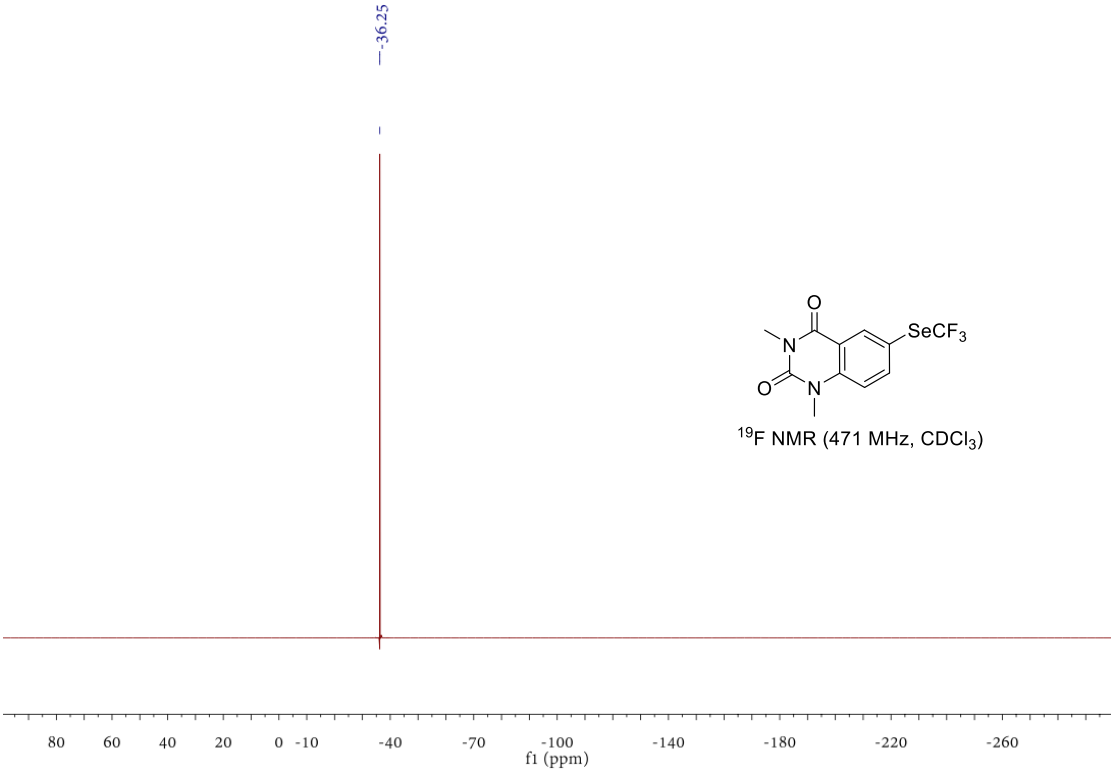
^{13}C NMR spectrum of **3q**



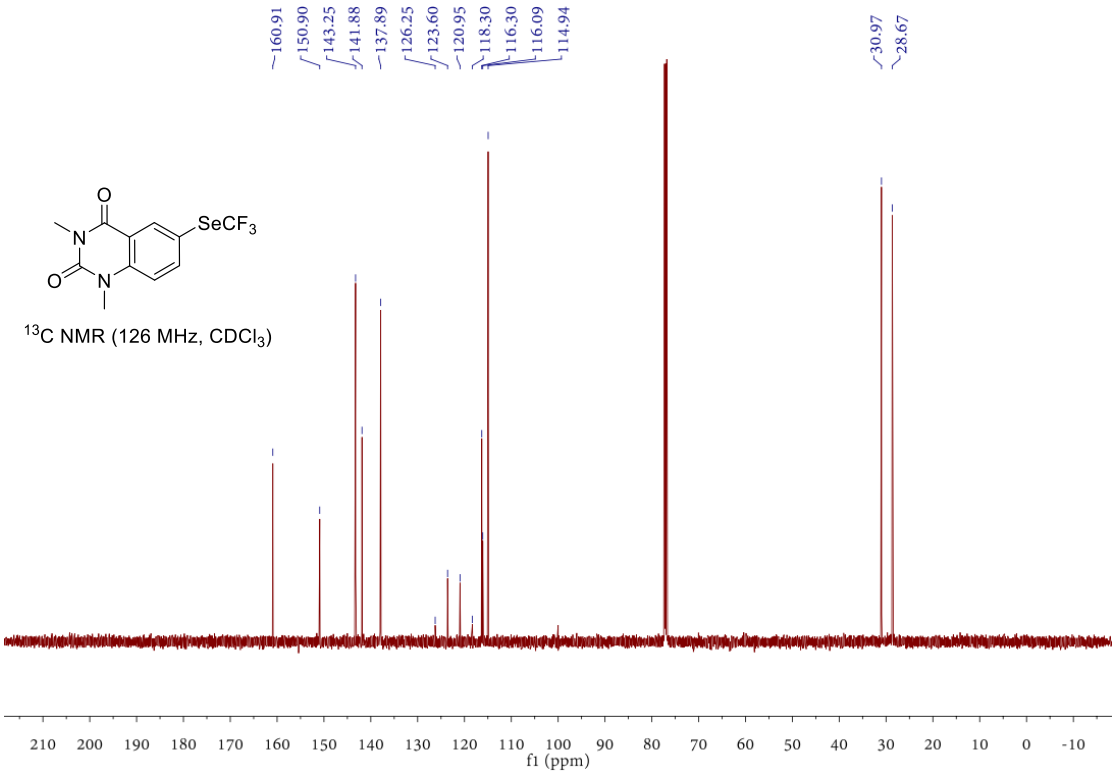
^{1}H NMR spectrum of **3r**



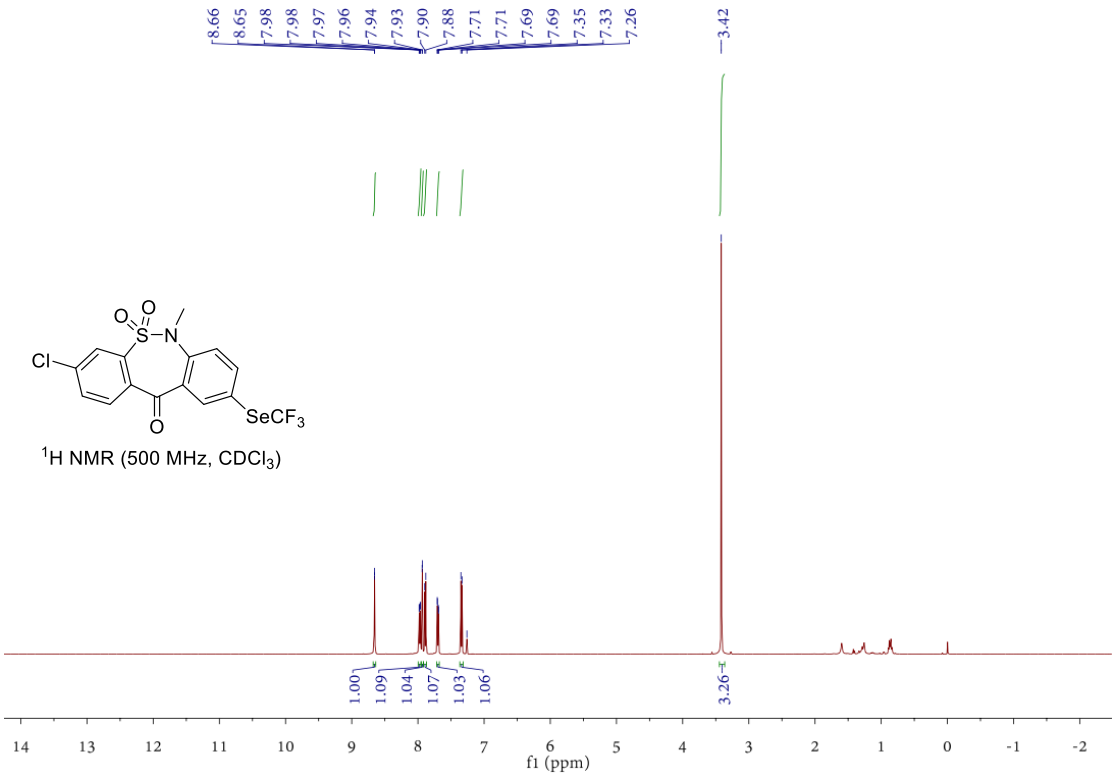
^{19}F NMR spectrum of **3r**



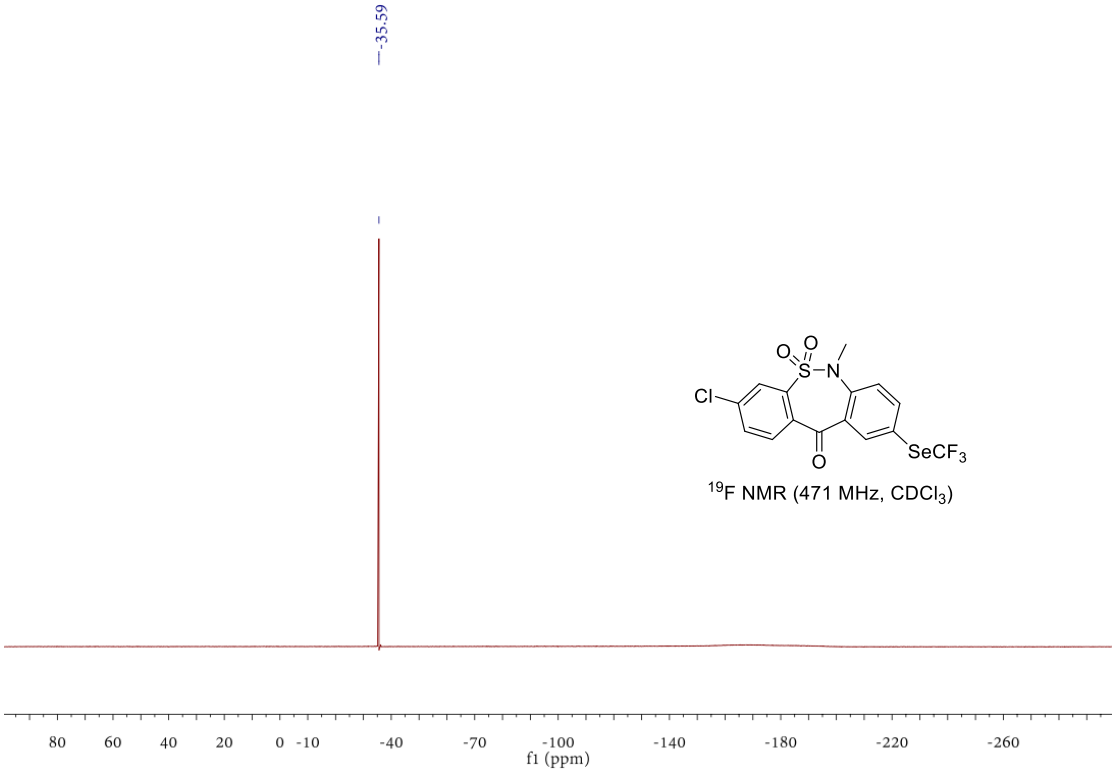
^{13}C NMR spectrum of **3r**



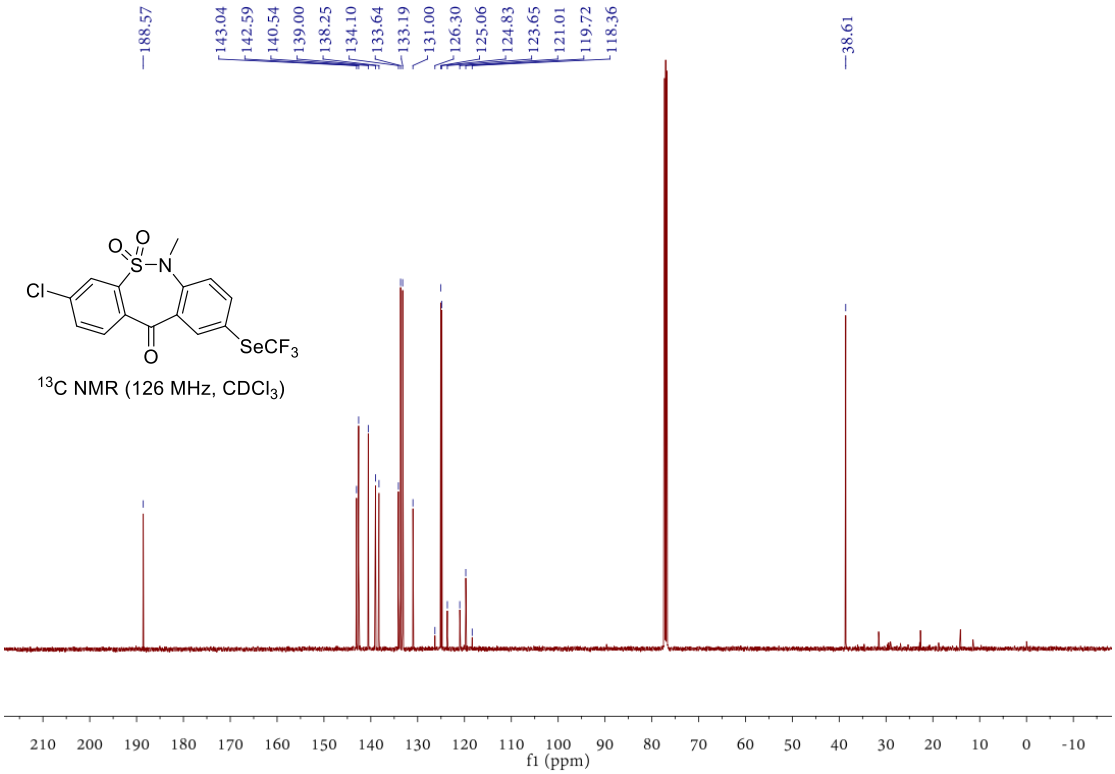
^{1}H NMR spectrum of **3s**



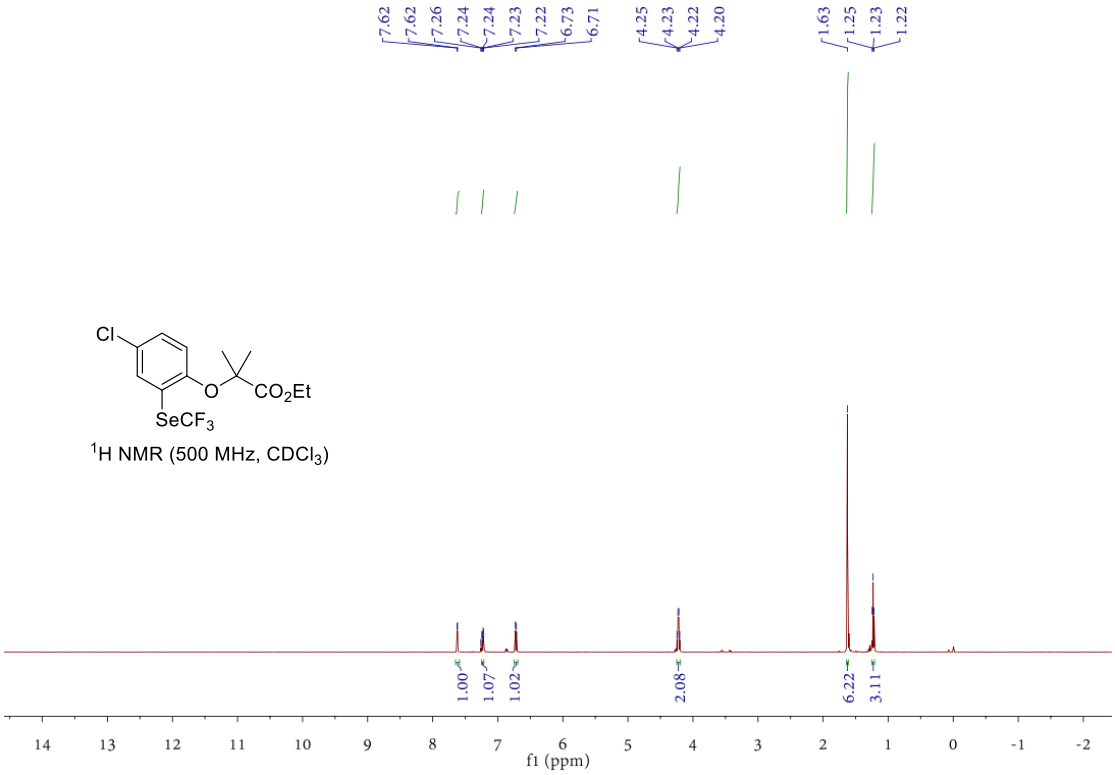
^{19}F NMR spectrum of **3s**



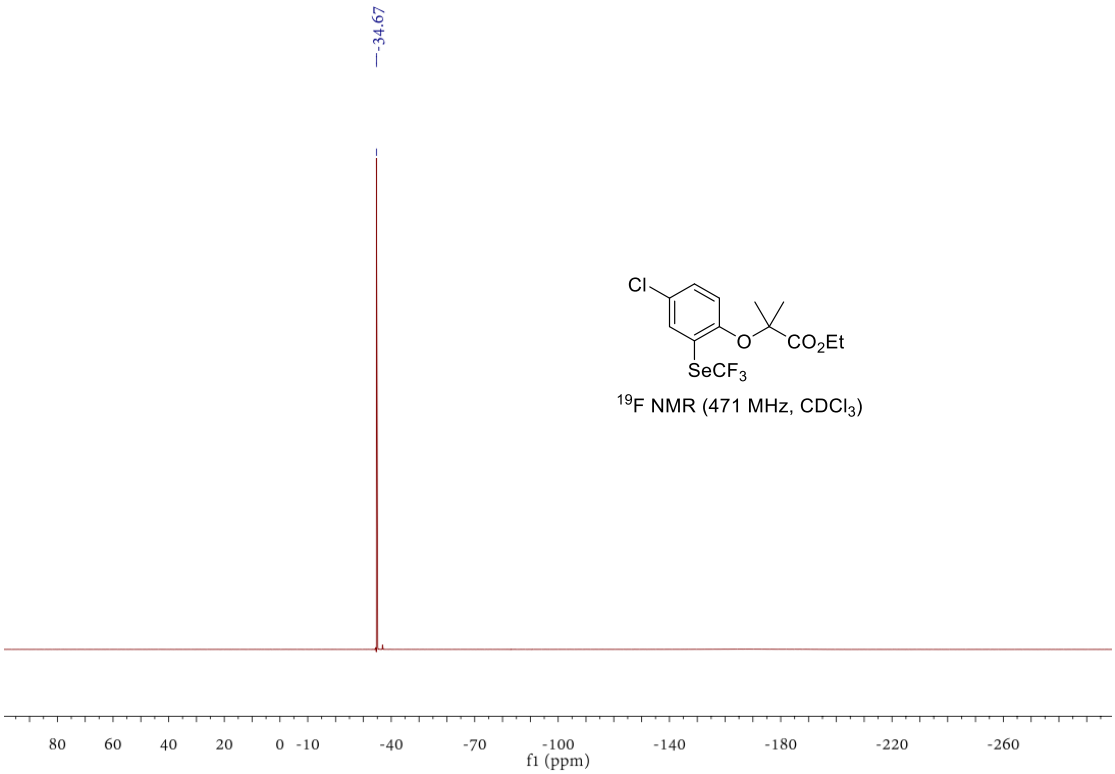
^{13}C NMR spectrum of **3s**



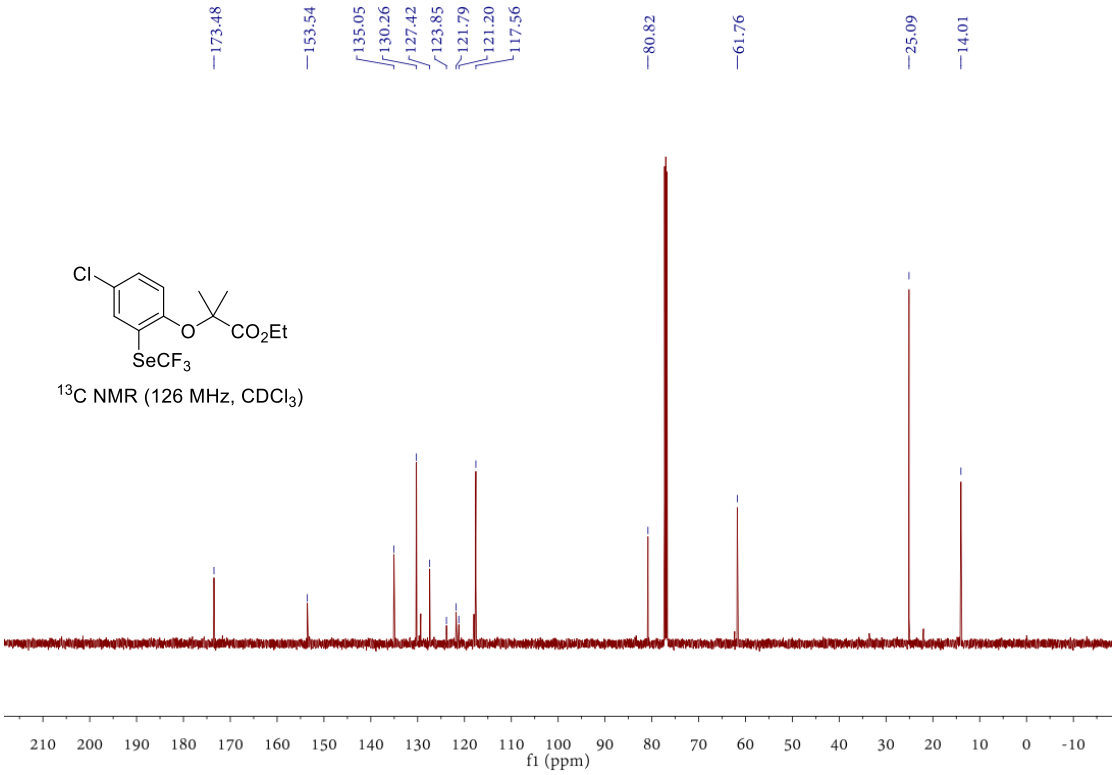
^{1}H NMR spectrum of **3t**



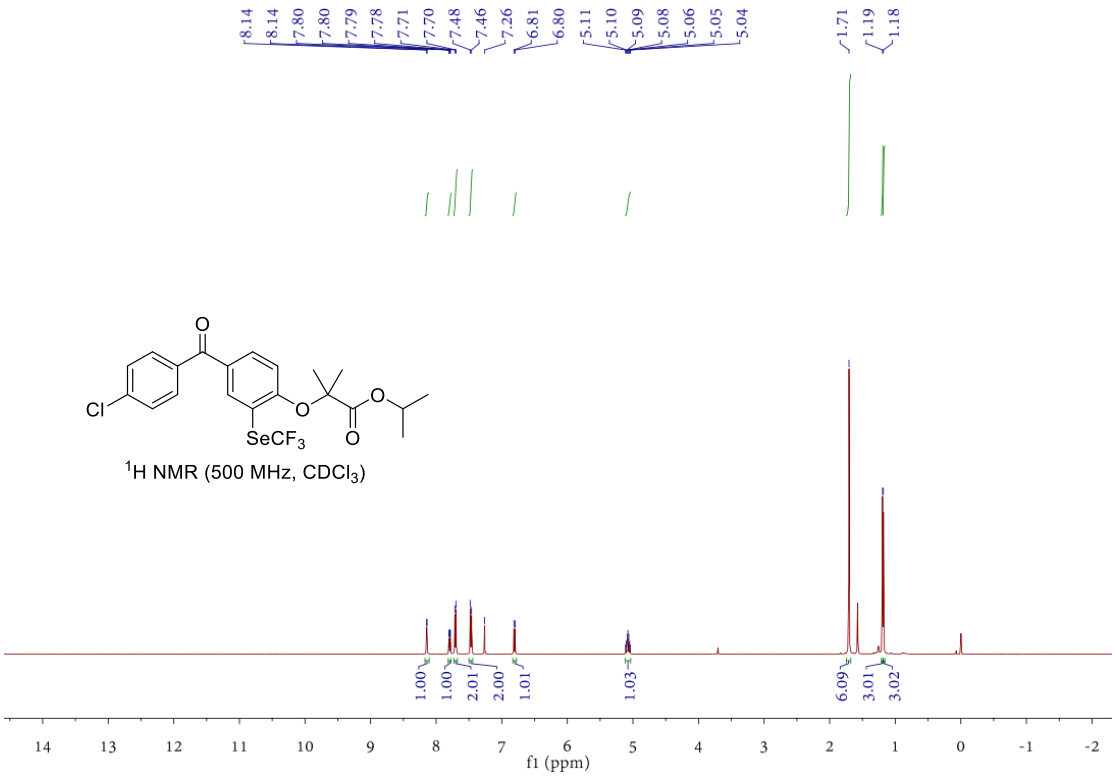
^{19}F NMR spectrum of **3t**



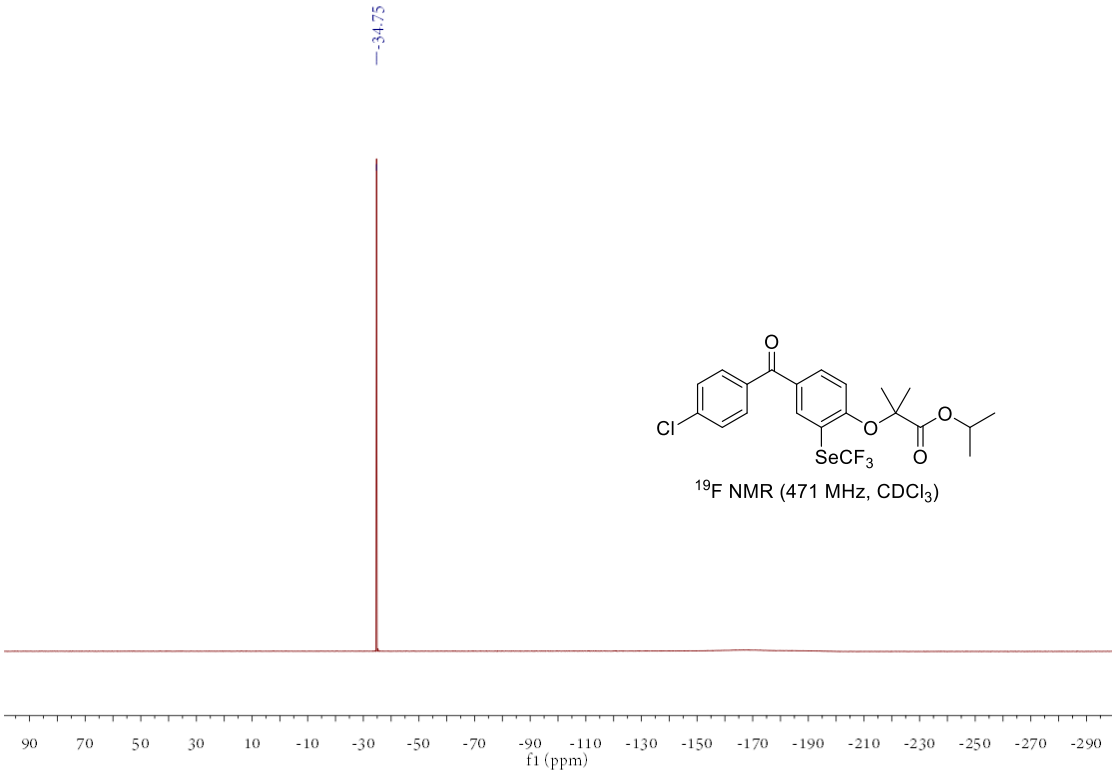
^{13}C NMR spectrum of **3t**



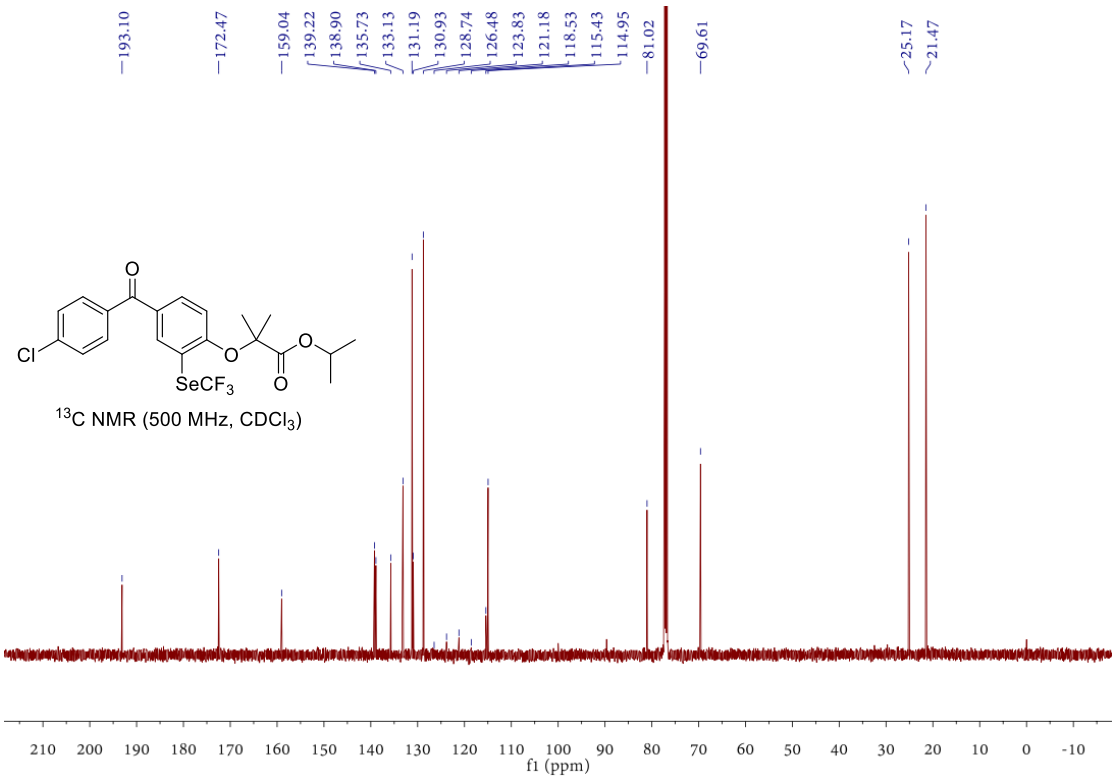
^{1}H NMR spectrum of **3u**



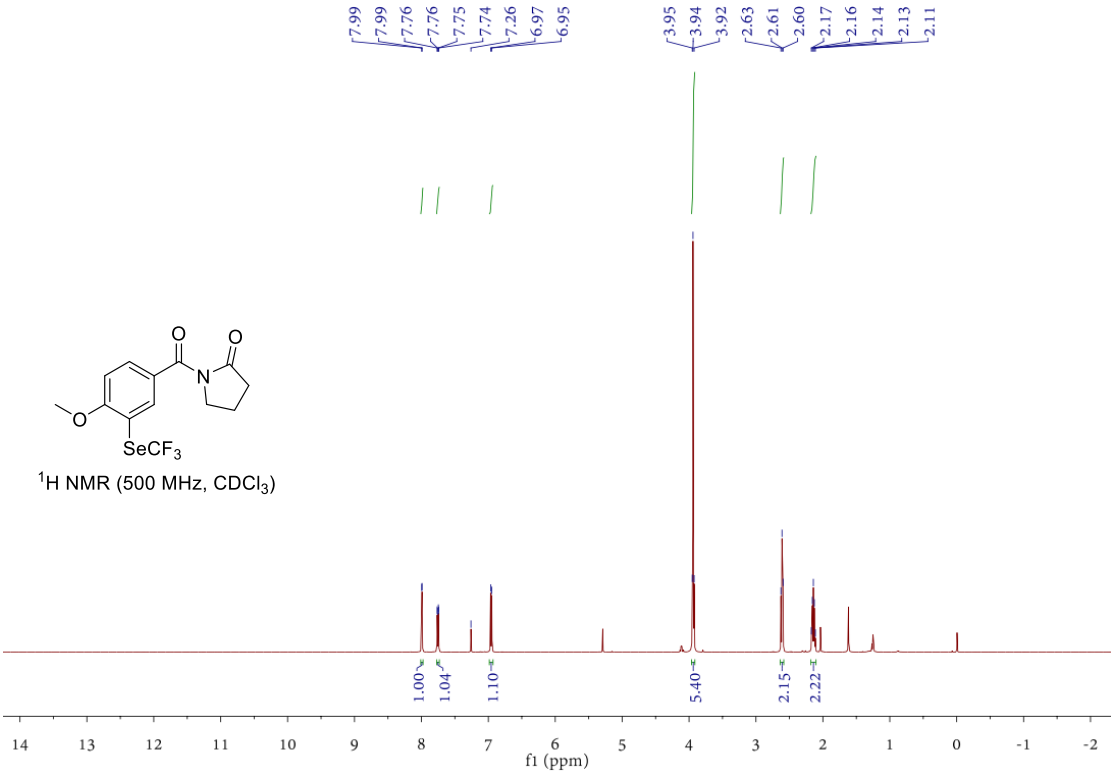
^{19}F NMR spectrum of **3u**



^{13}C NMR spectrum of **3u**

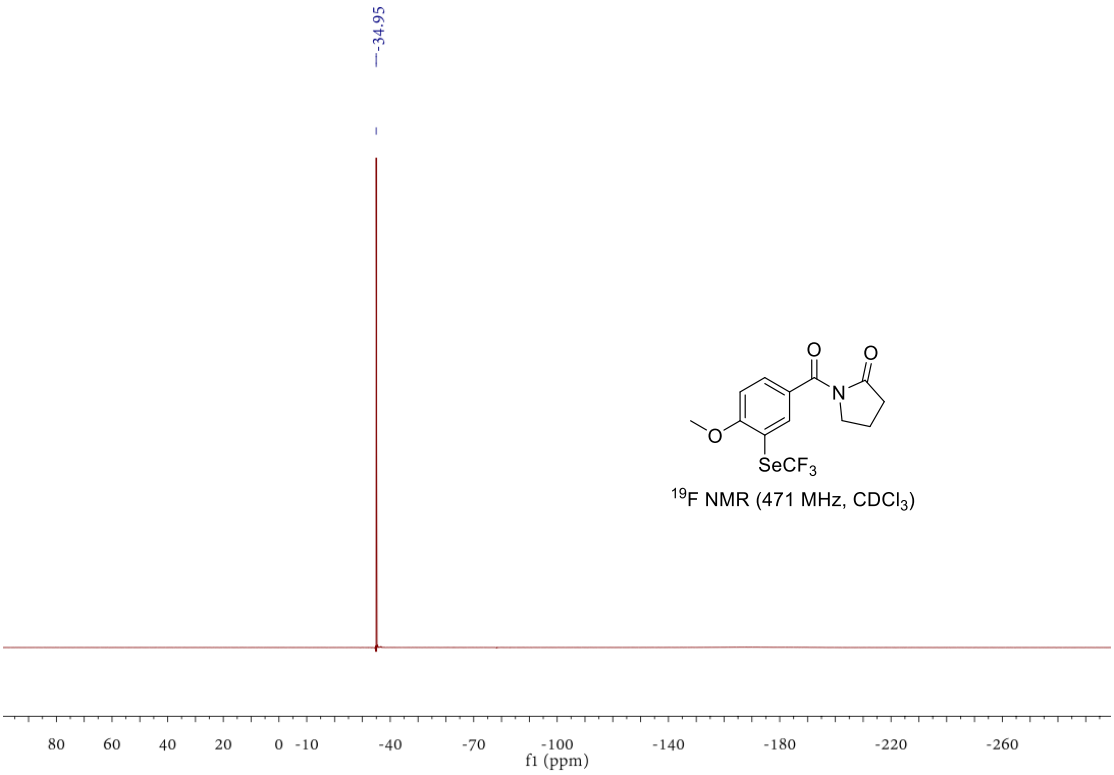


^{1}H NMR spectrum of **3v**



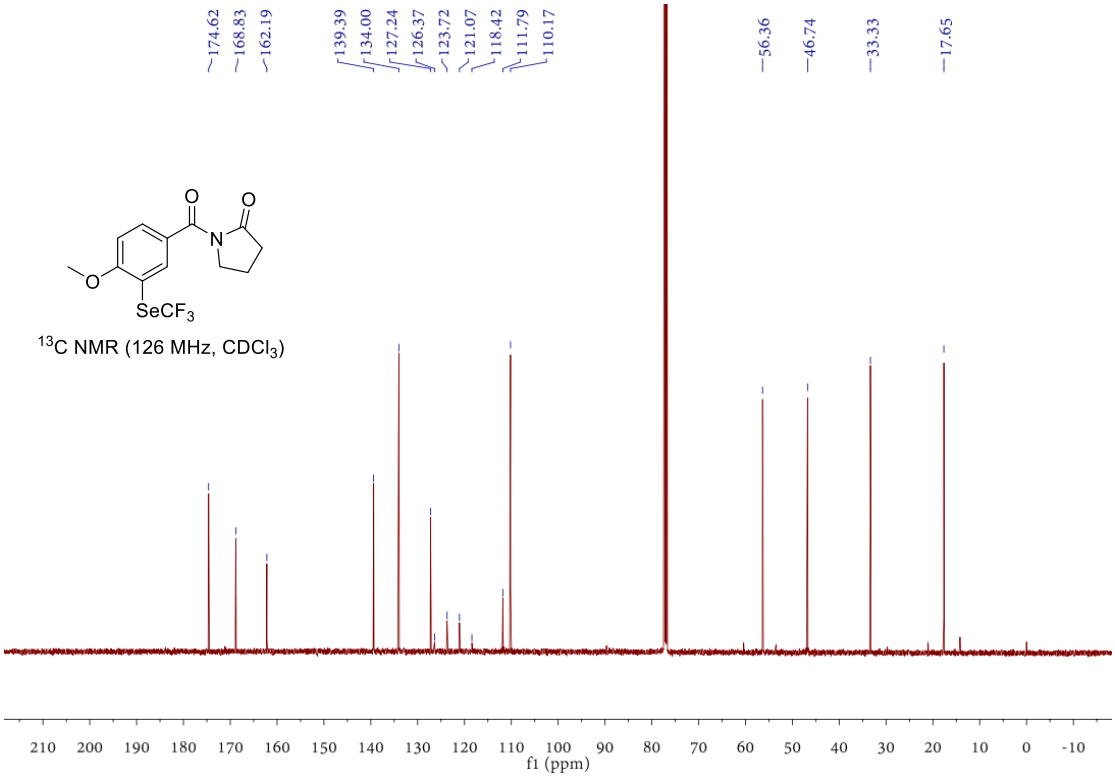
^{1}H NMR (500 MHz, $CDCl_3$)

^{19}F NMR spectrum of **3v**

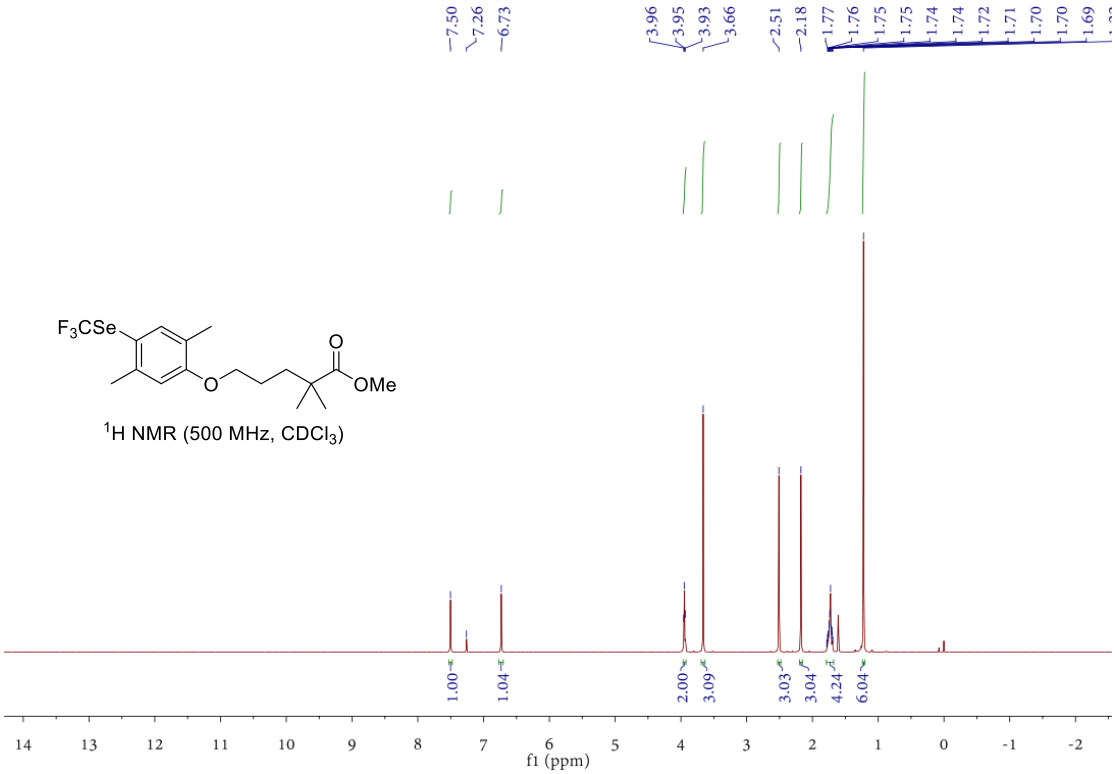


^{19}F NMR (471 MHz, $CDCl_3$)

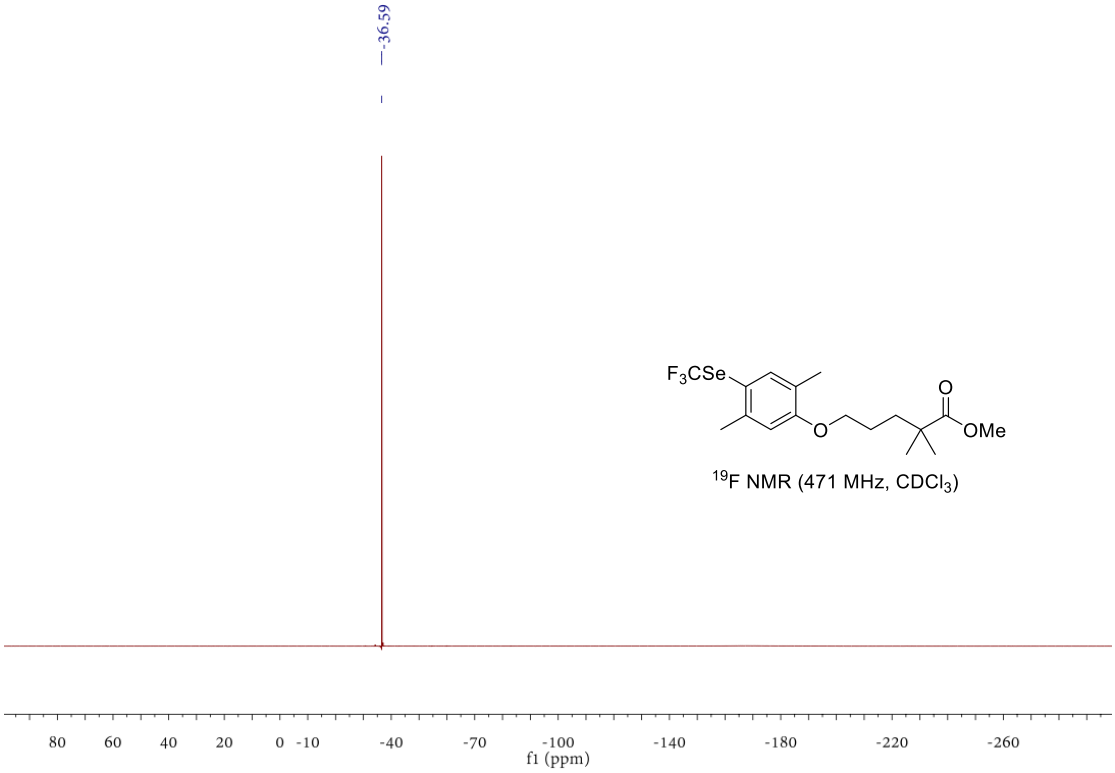
^{13}C NMR spectrum of **3v**



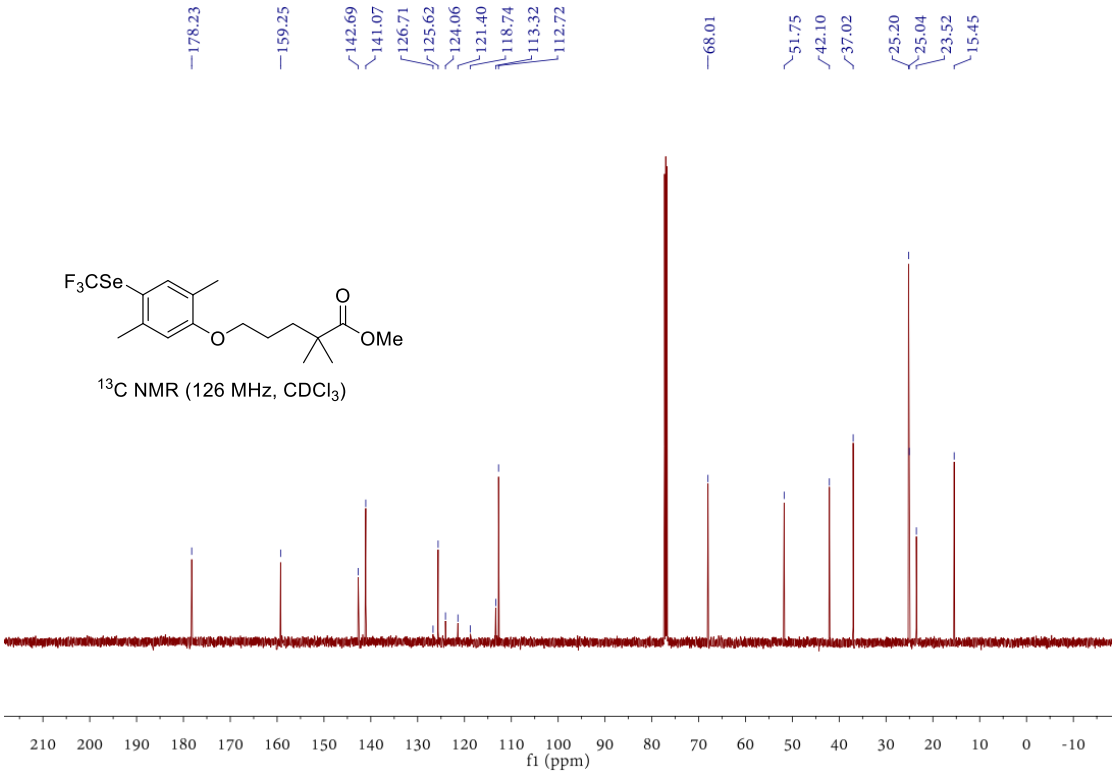
^{1}H NMR spectrum of **3w**



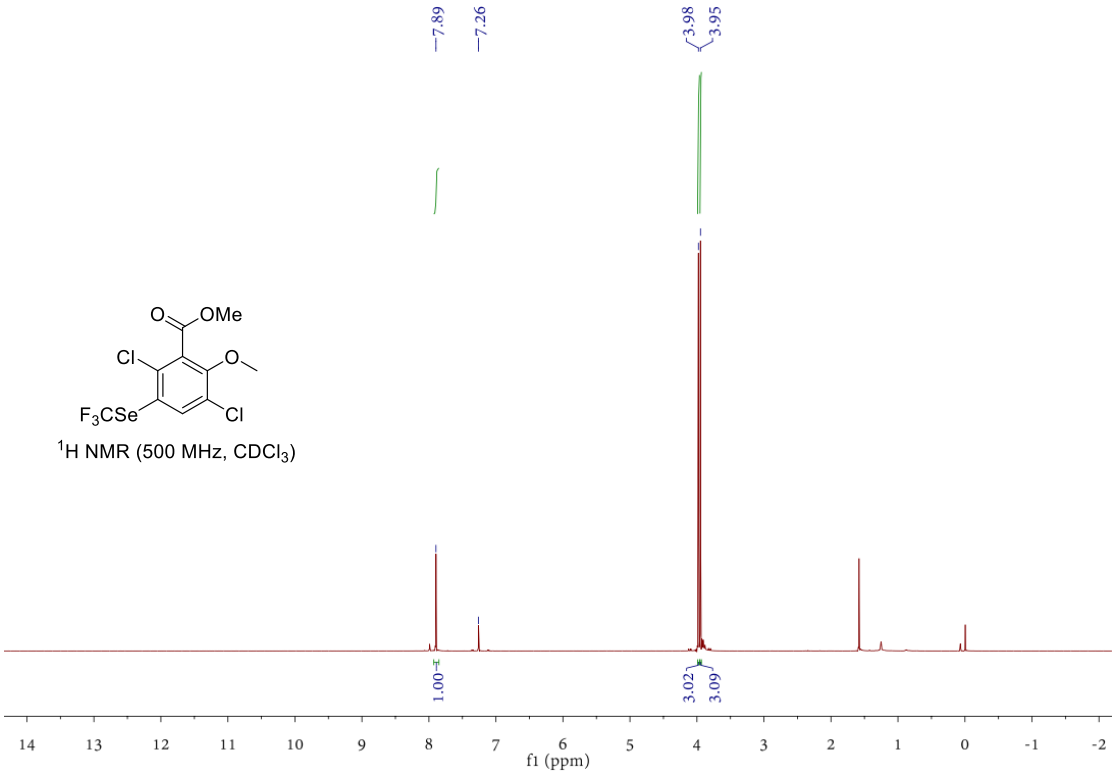
^{19}F NMR spectrum of **3w**



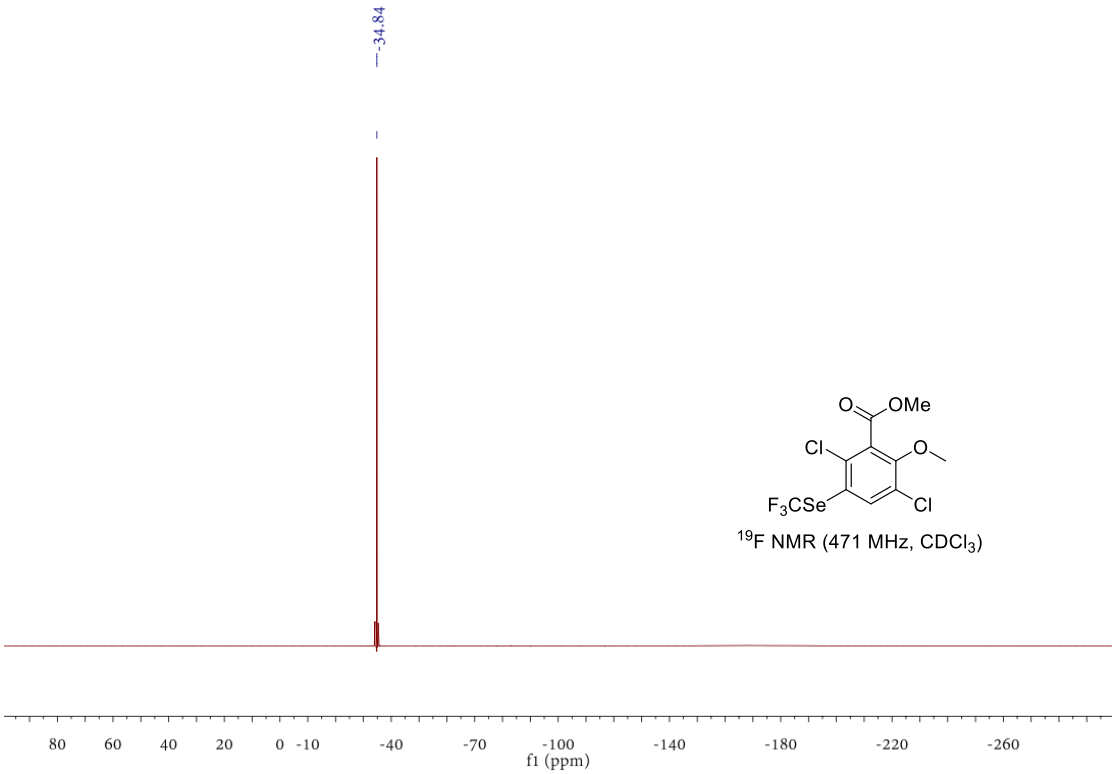
^{13}C NMR spectrum of **3w**



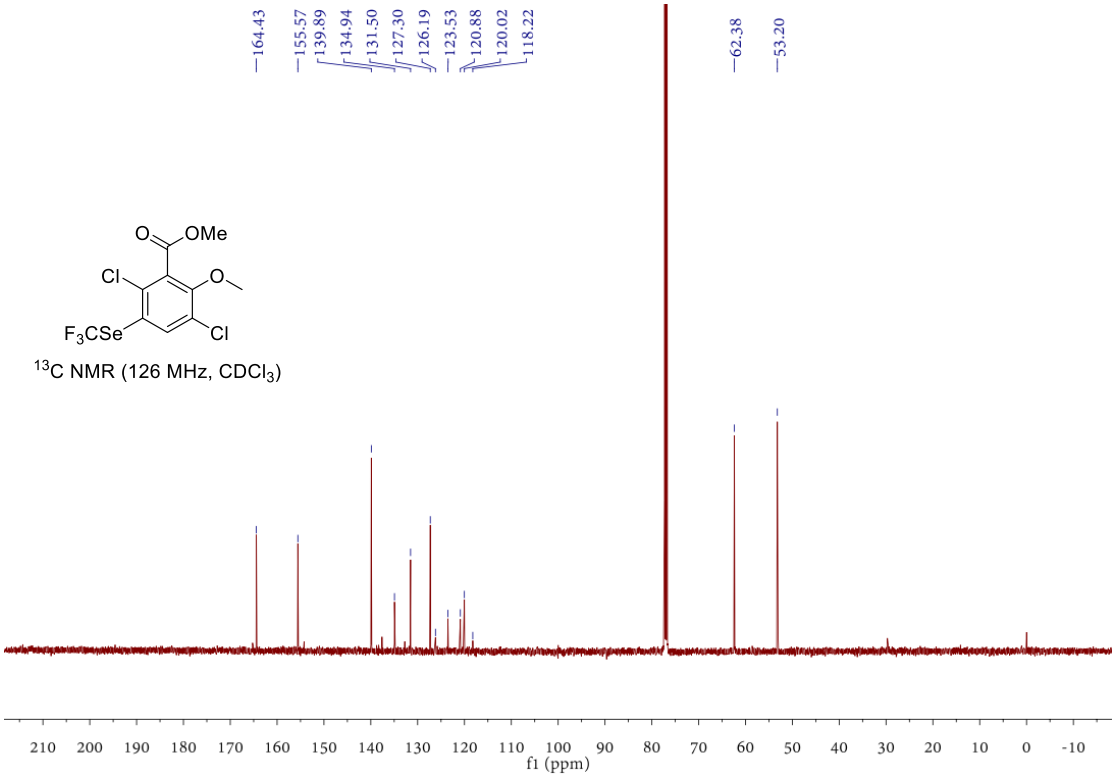
^{1}H NMR spectrum of **3x**



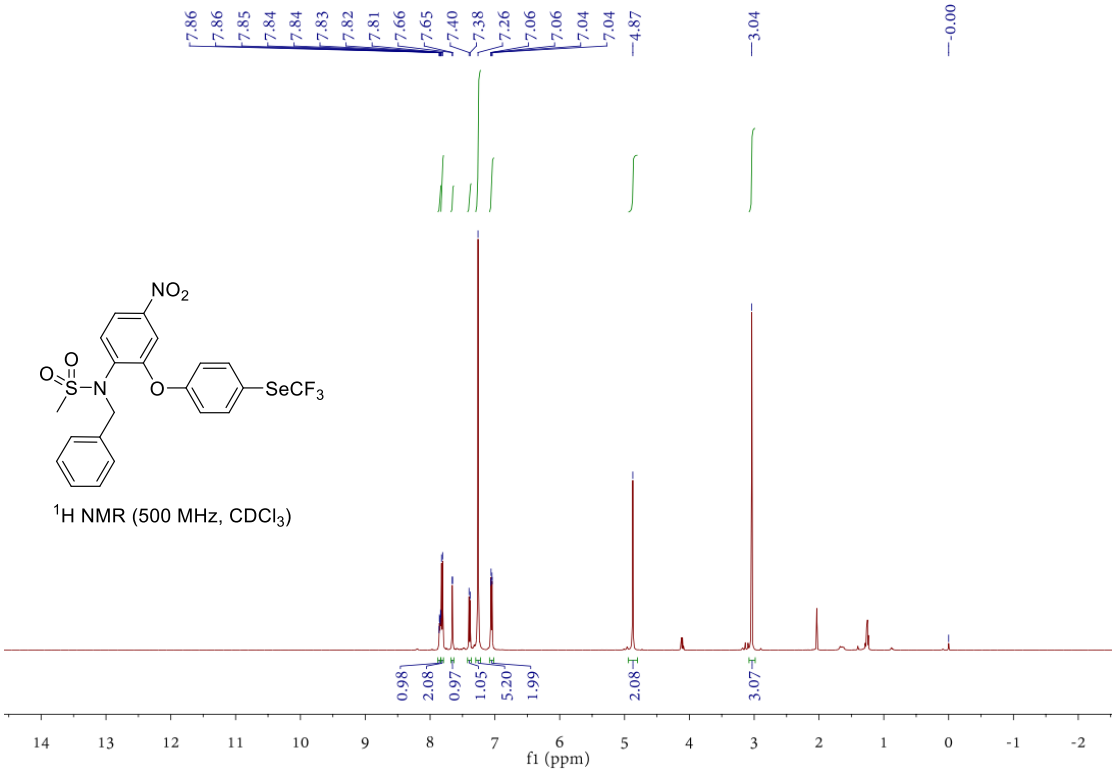
^{19}F NMR spectrum of **3x**



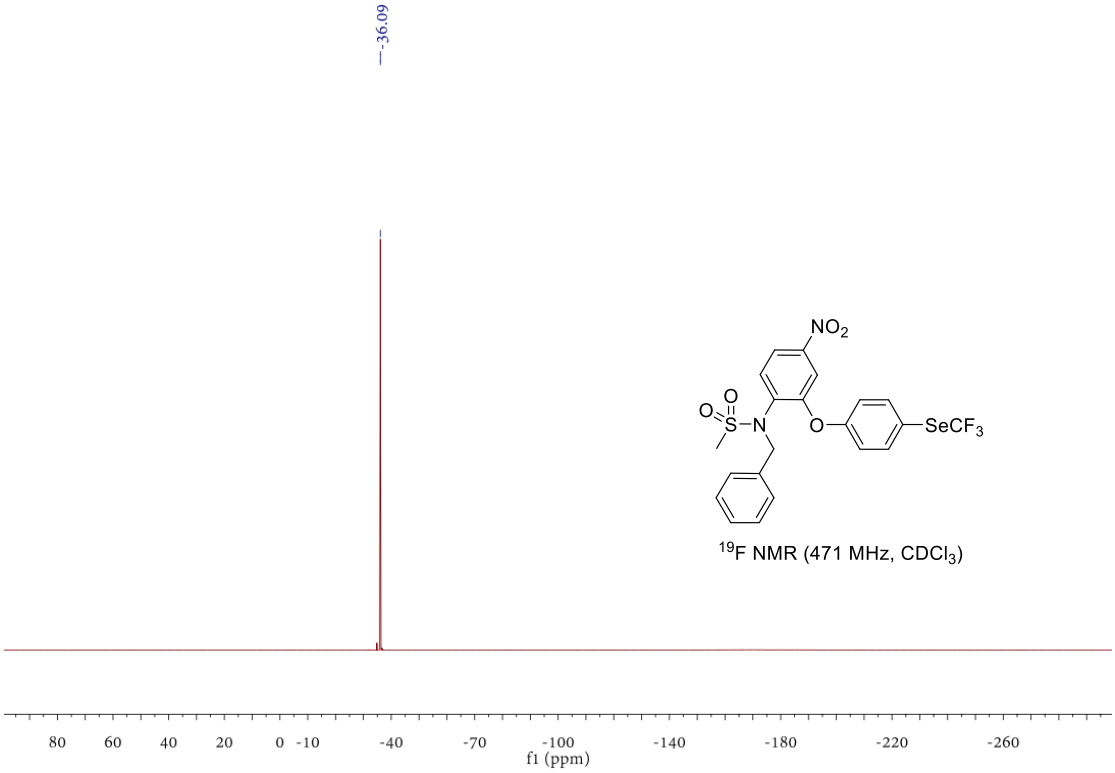
^{13}C NMR spectrum of **3x**



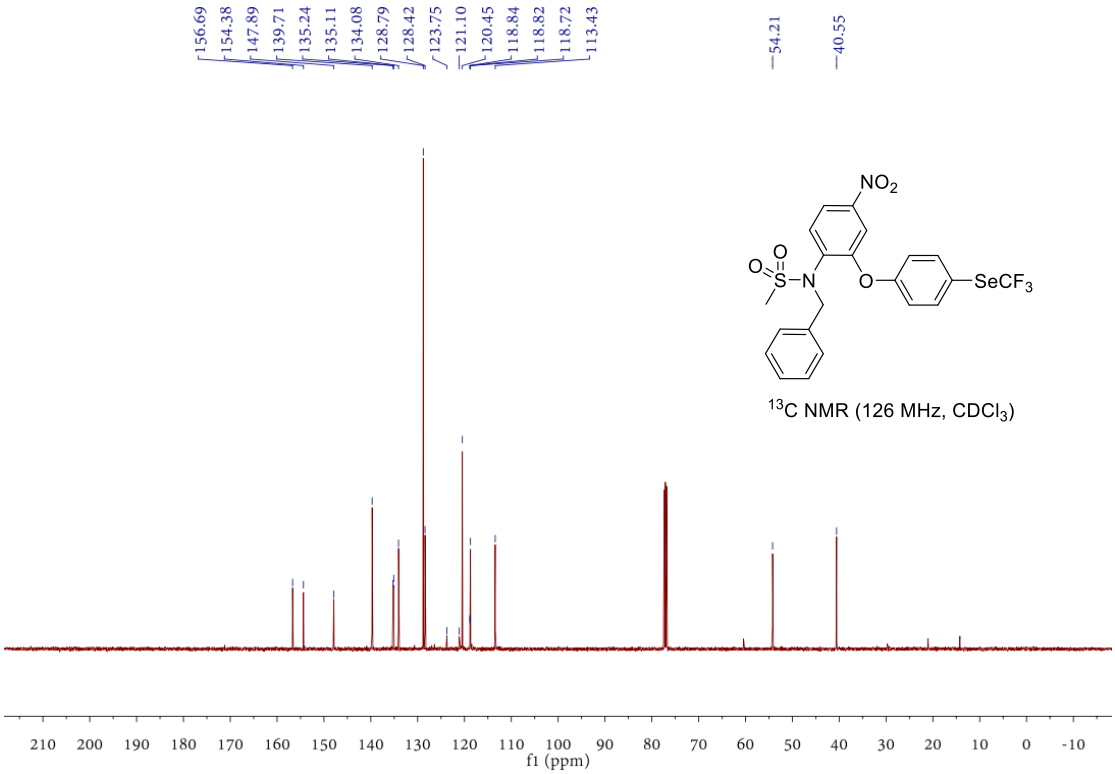
^{1}H NMR spectrum of **3y**



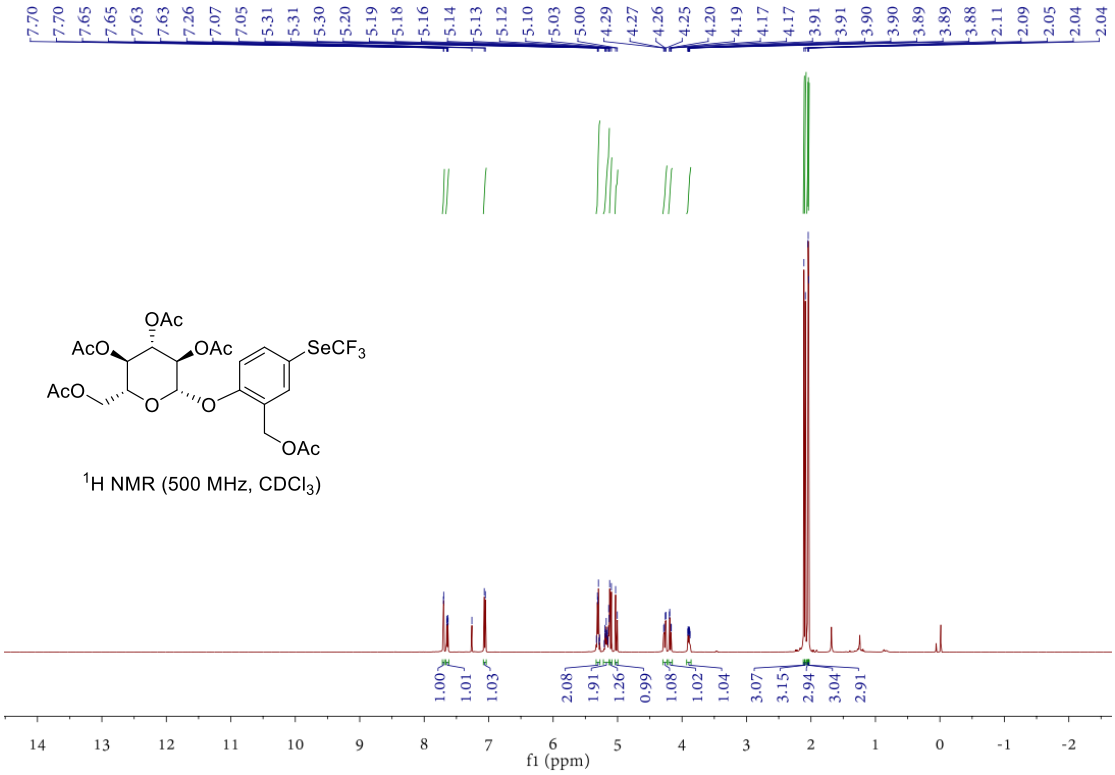
^{19}F NMR spectrum of **3y**



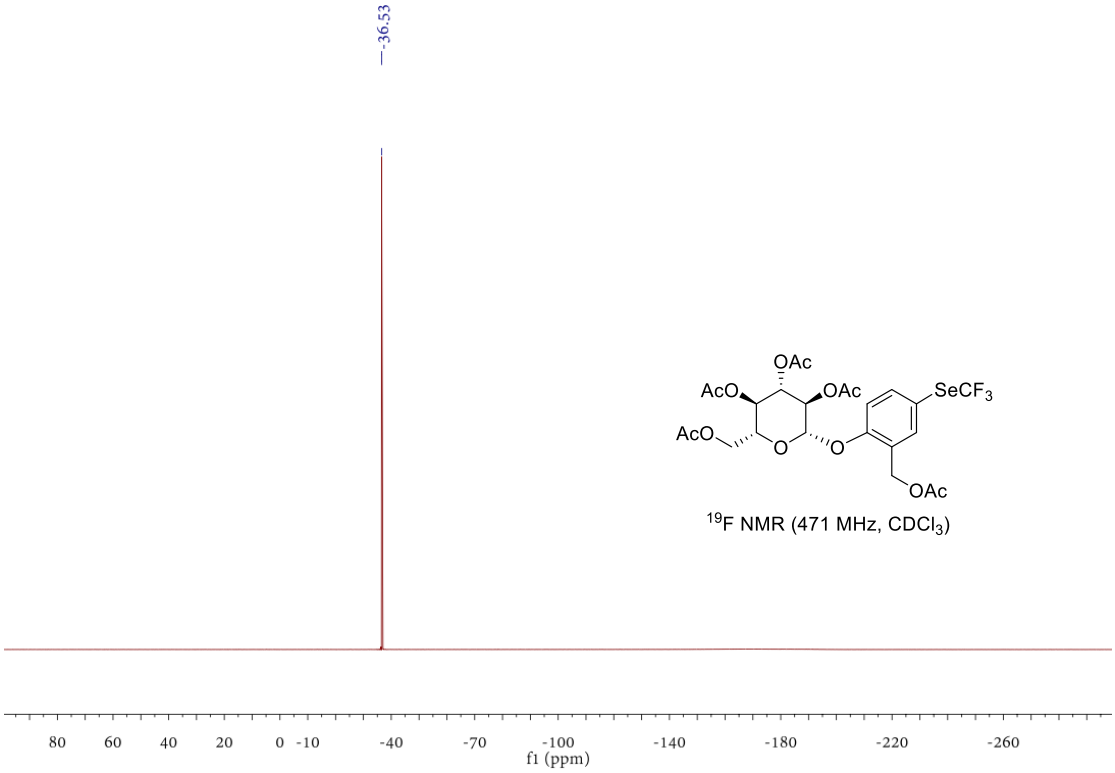
^{13}C NMR spectrum of **3y**



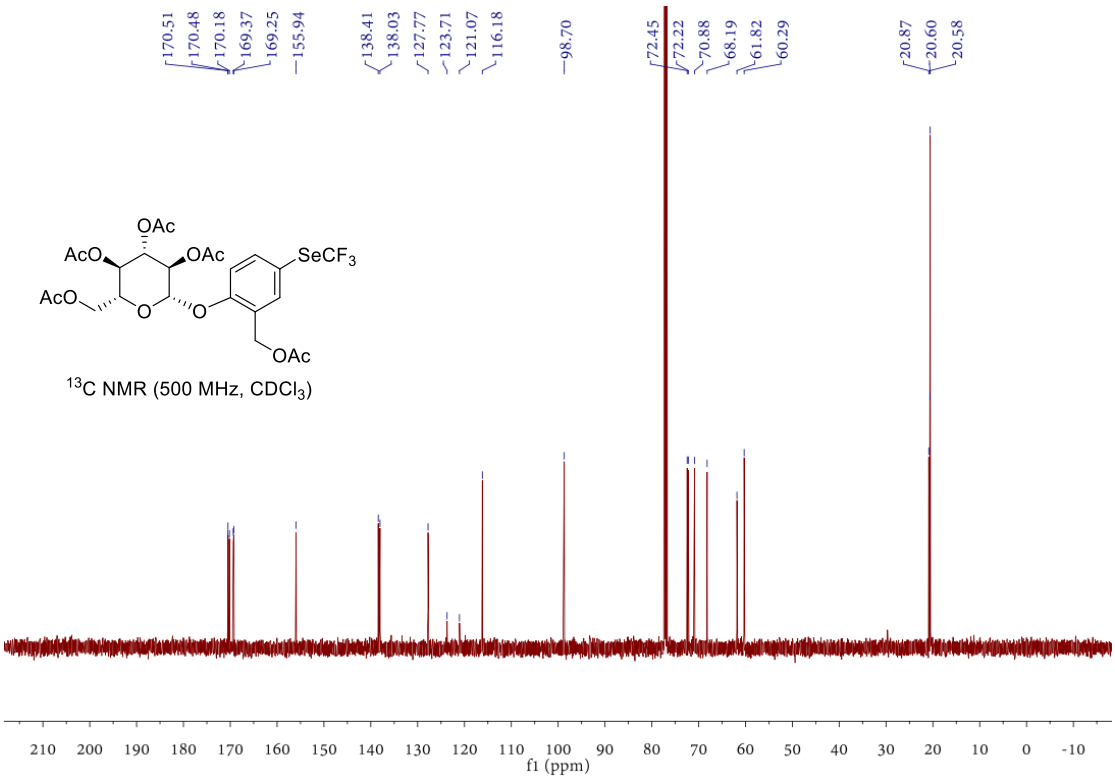
^{1}H NMR spectrum of **3z**



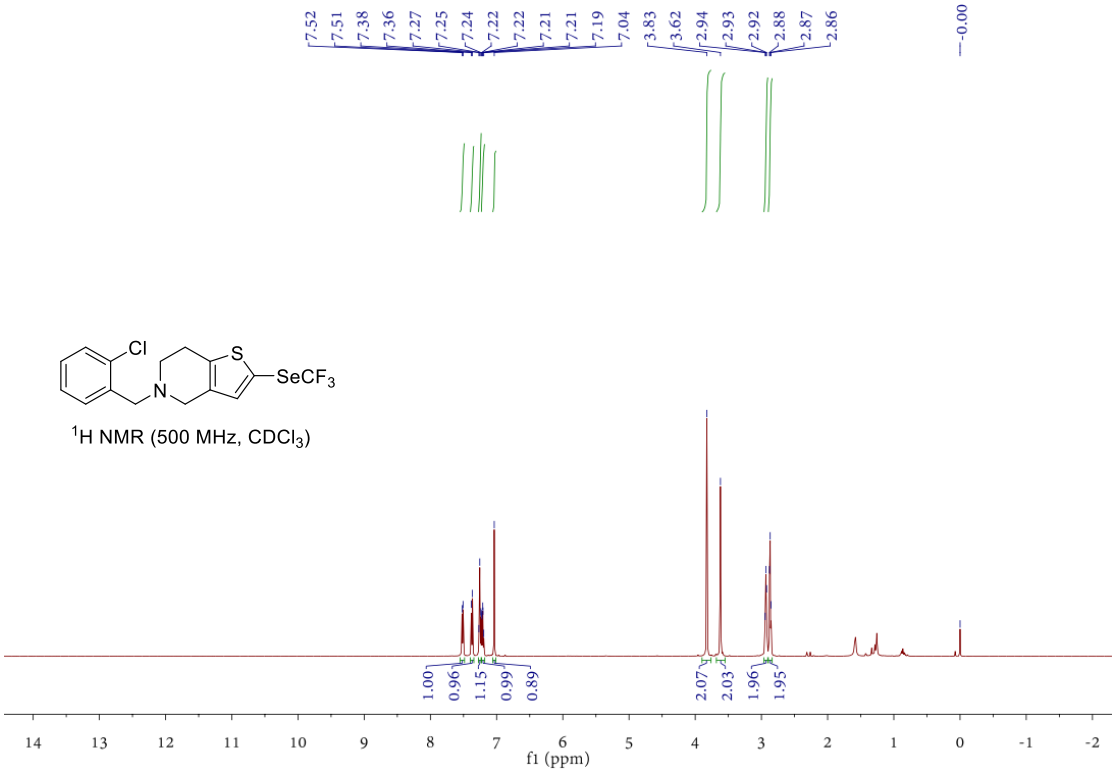
^{19}F NMR spectrum of **3z**



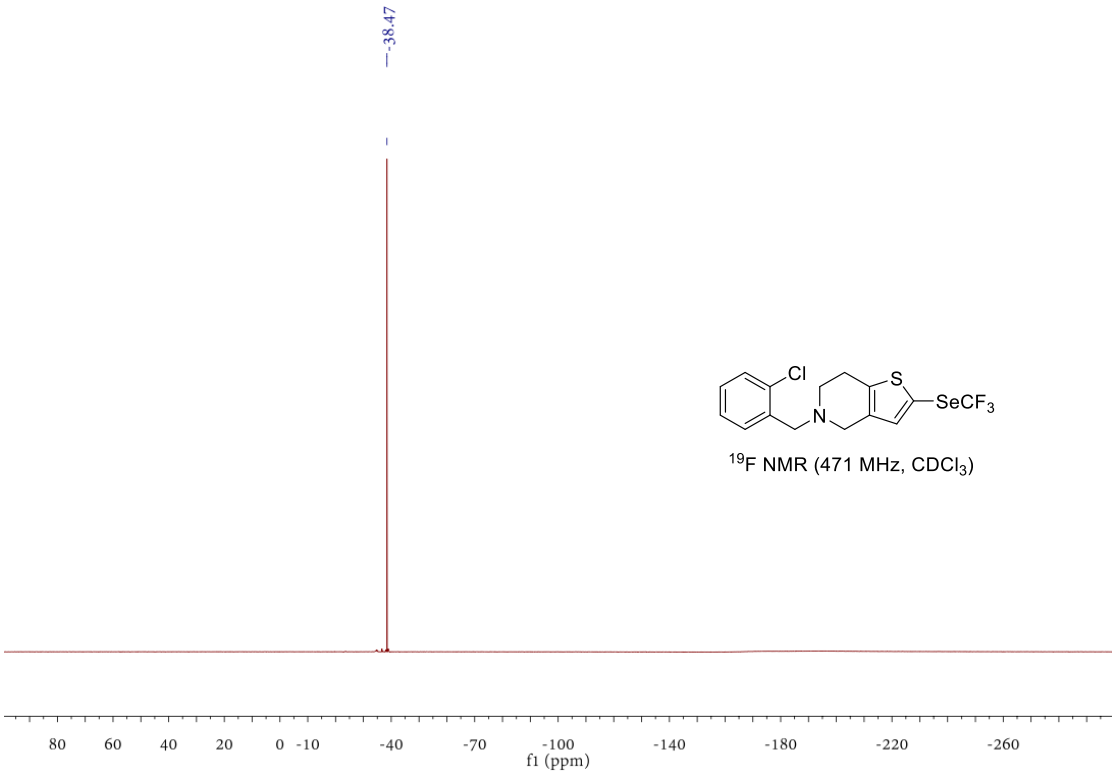
^{13}C NMR spectrum of **3z**



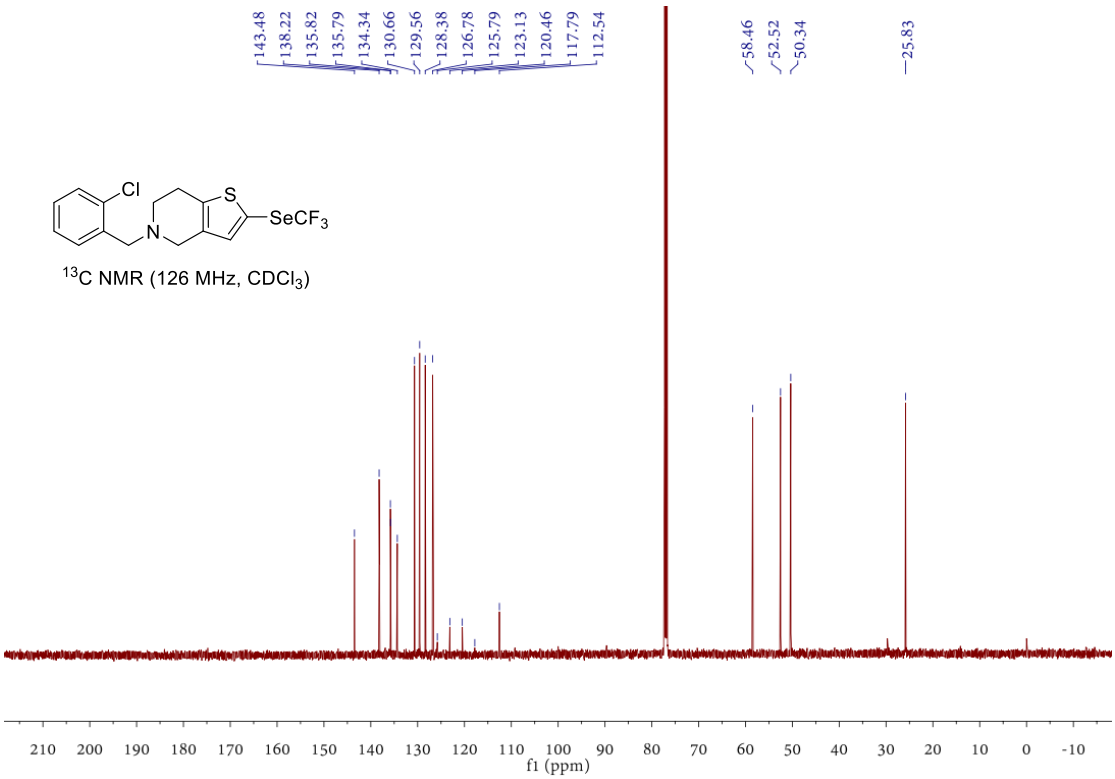
^{1}H NMR spectrum of **3aa**



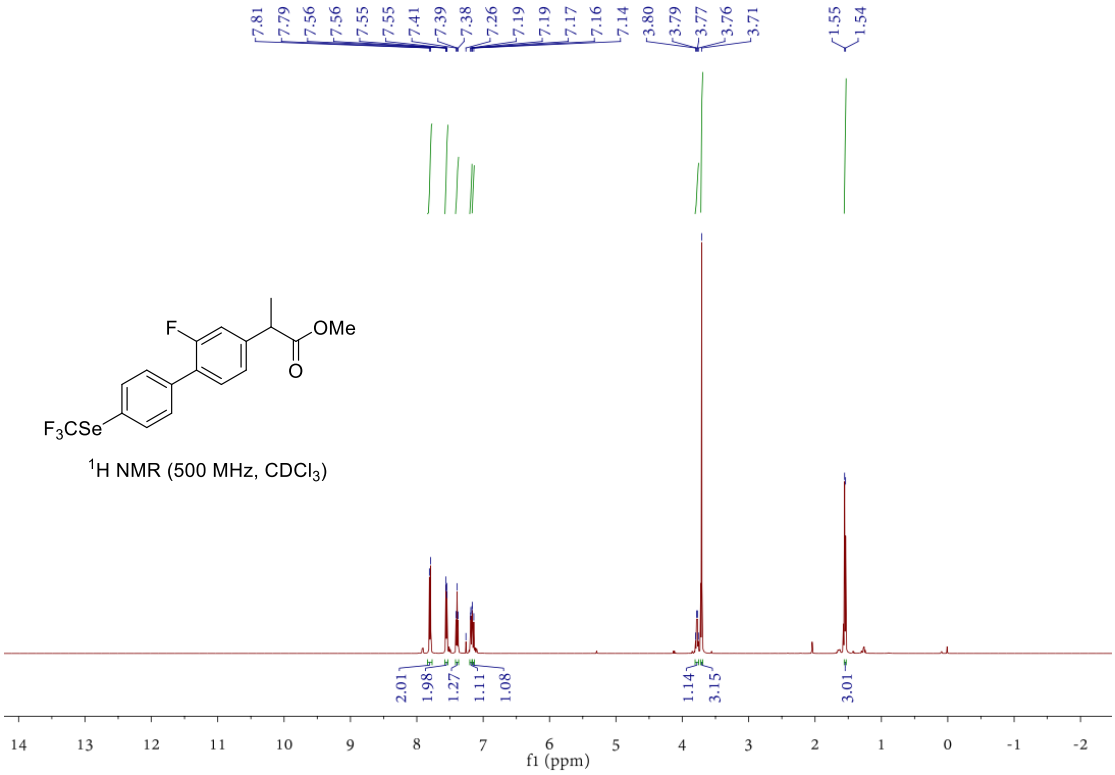
^{19}F NMR spectrum of **3aa**



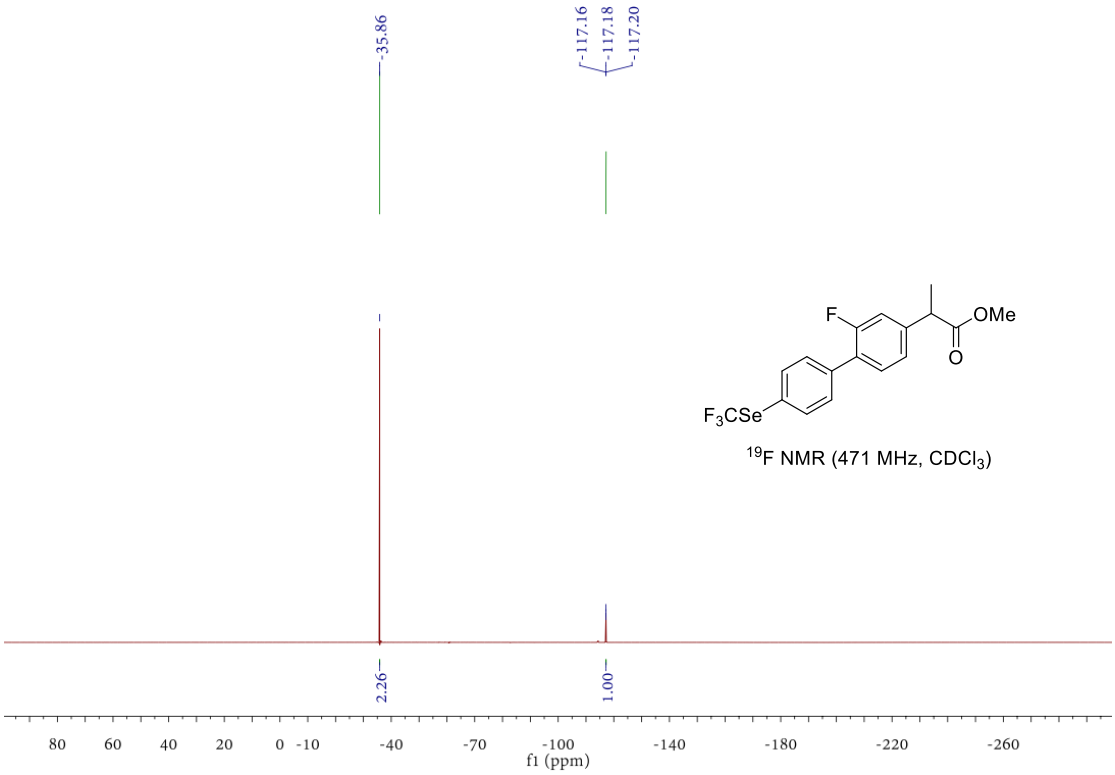
^{13}C NMR spectrum of **3aa**



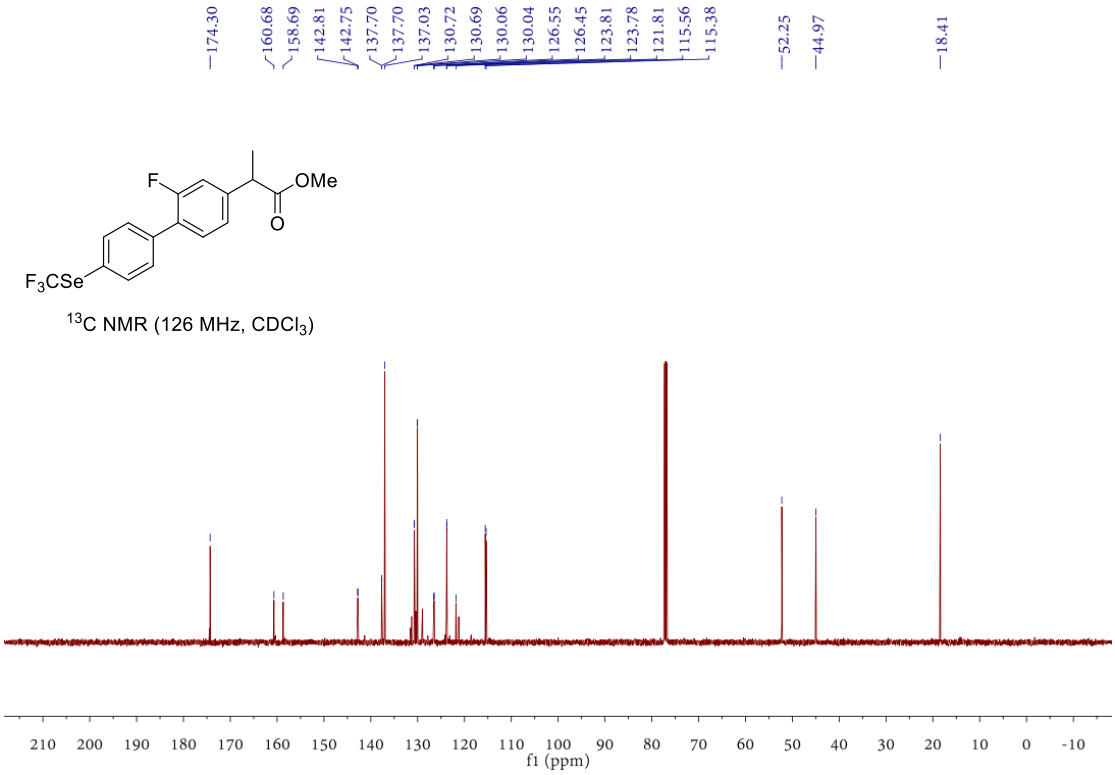
^{1}H NMR spectrum of **3ab**



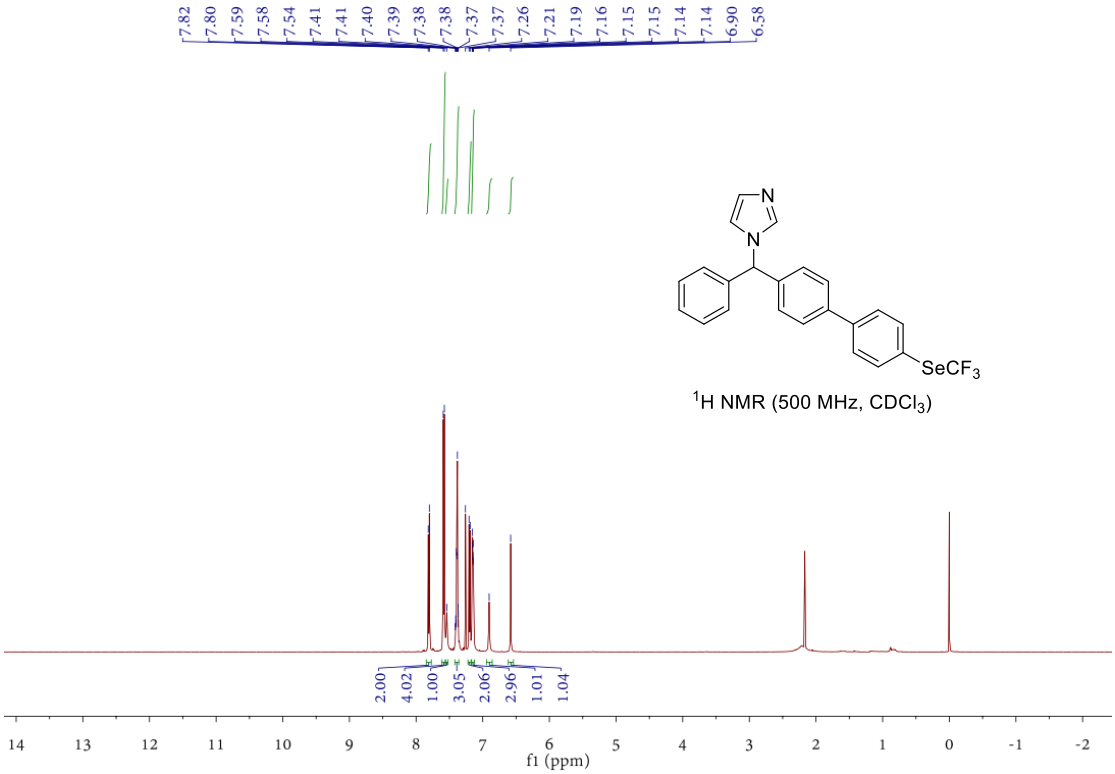
^{19}F NMR spectrum of **3ab**



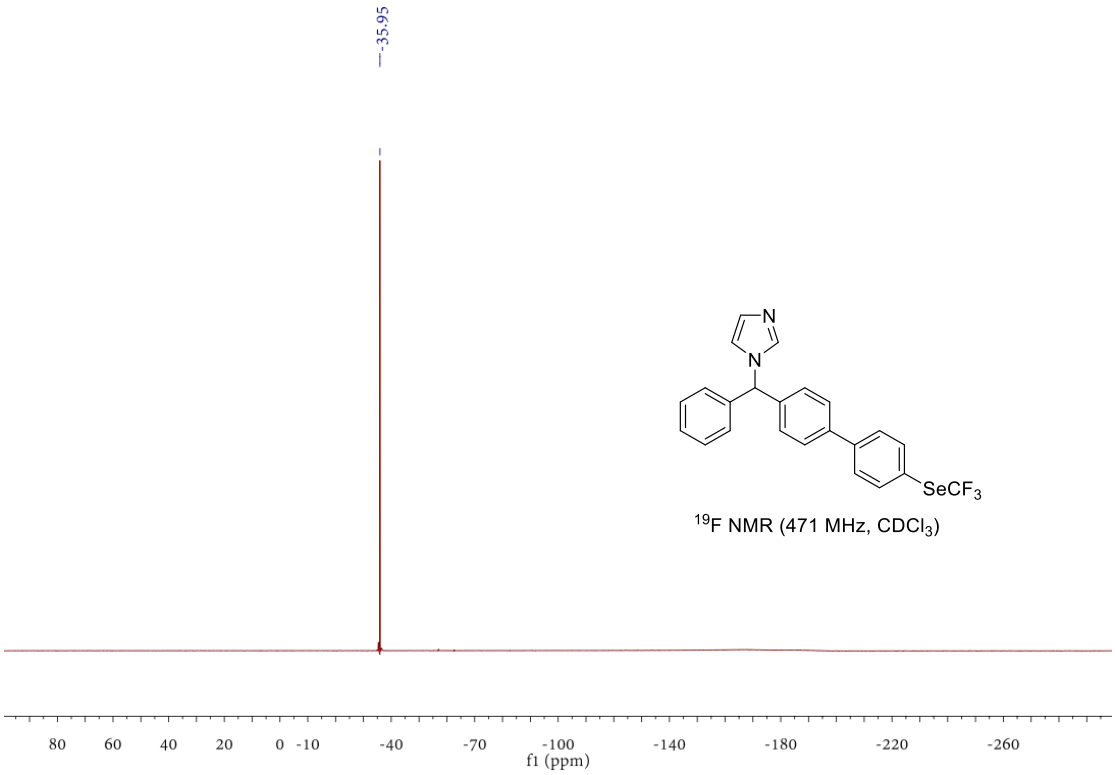
^{13}C NMR spectrum of **3ab**



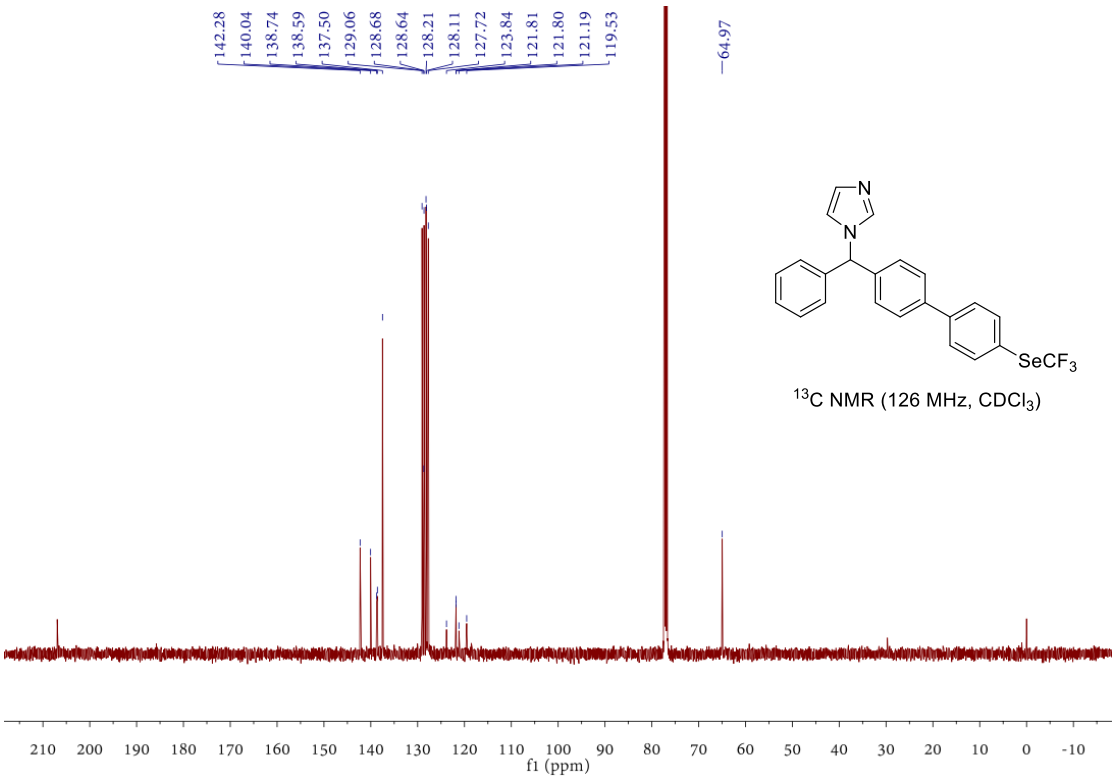
^{1}H NMR spectrum of **3ac**



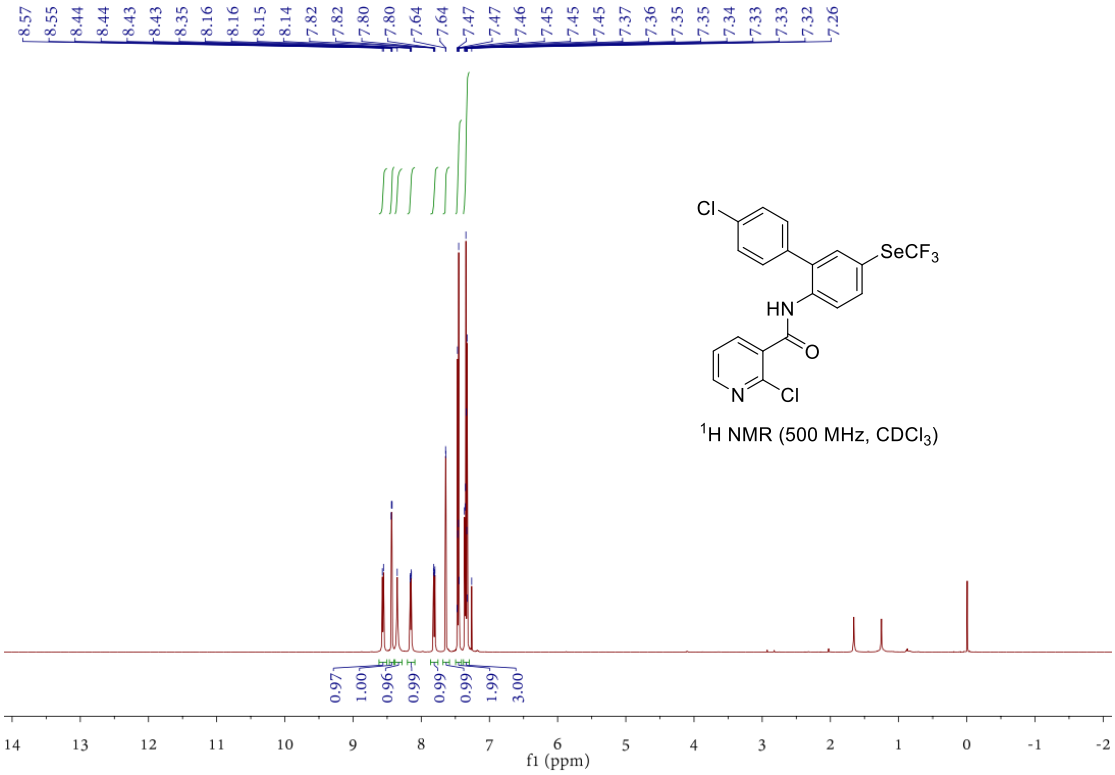
^{19}F NMR spectrum of **3ac**



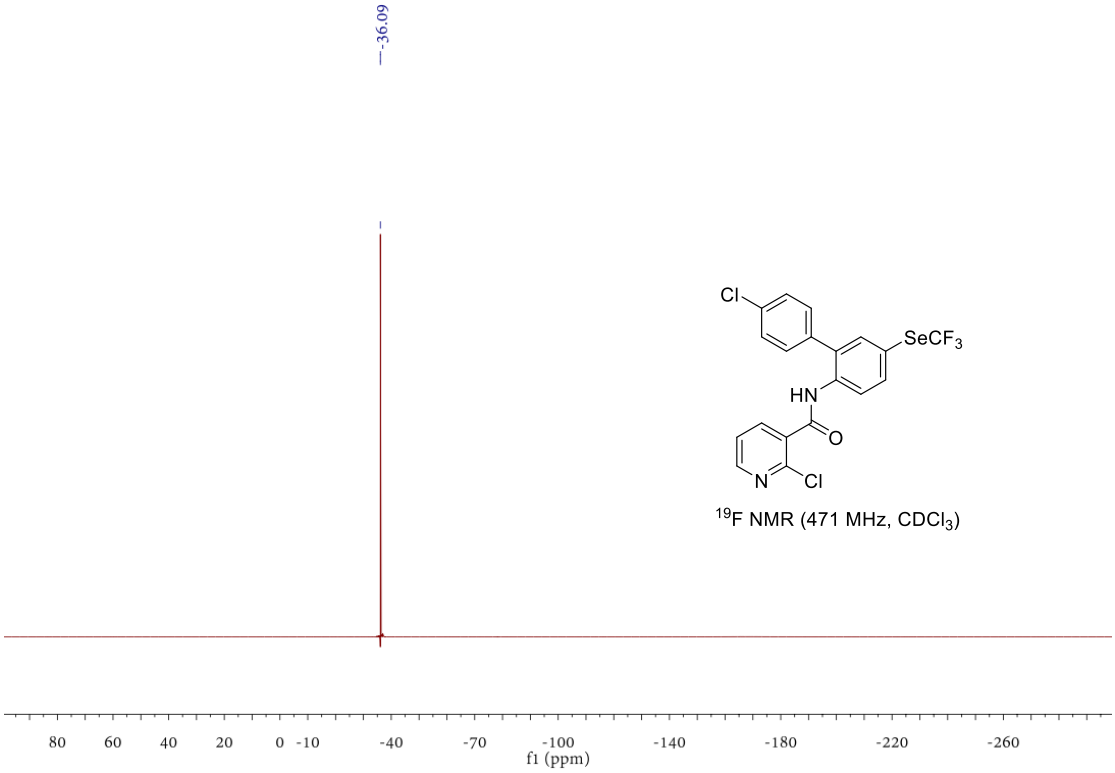
^{13}C NMR spectrum of **3ac**



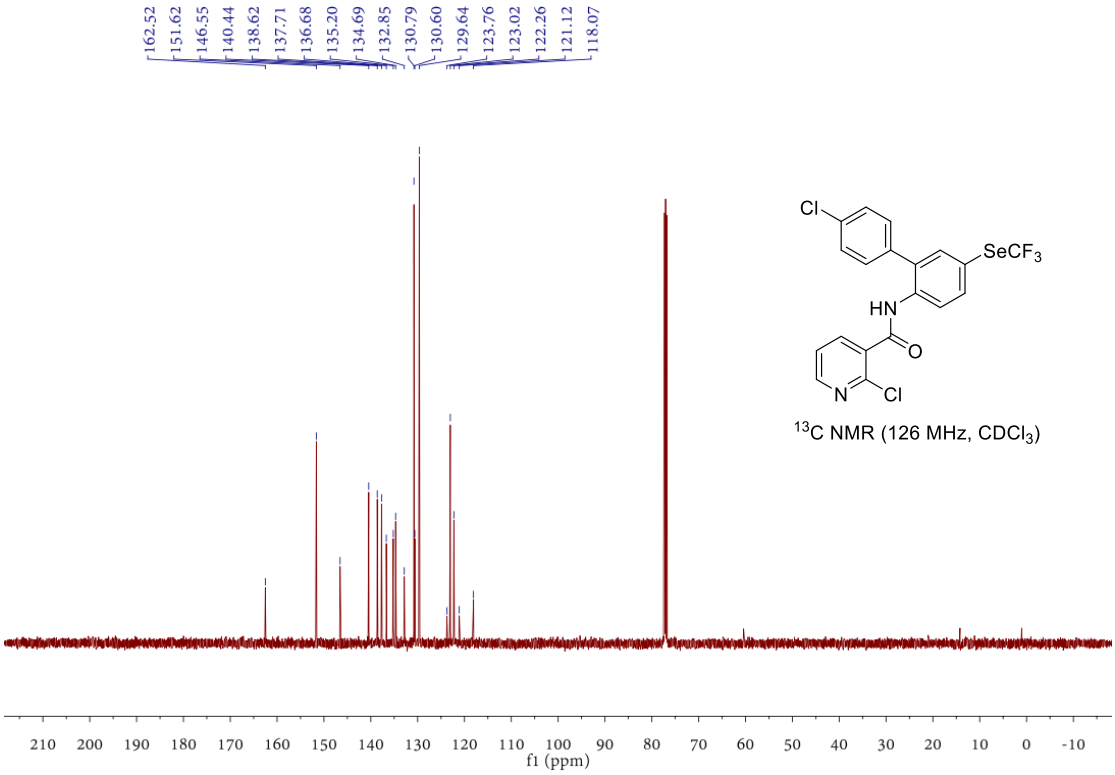
^{1}H NMR spectrum of **3ad**



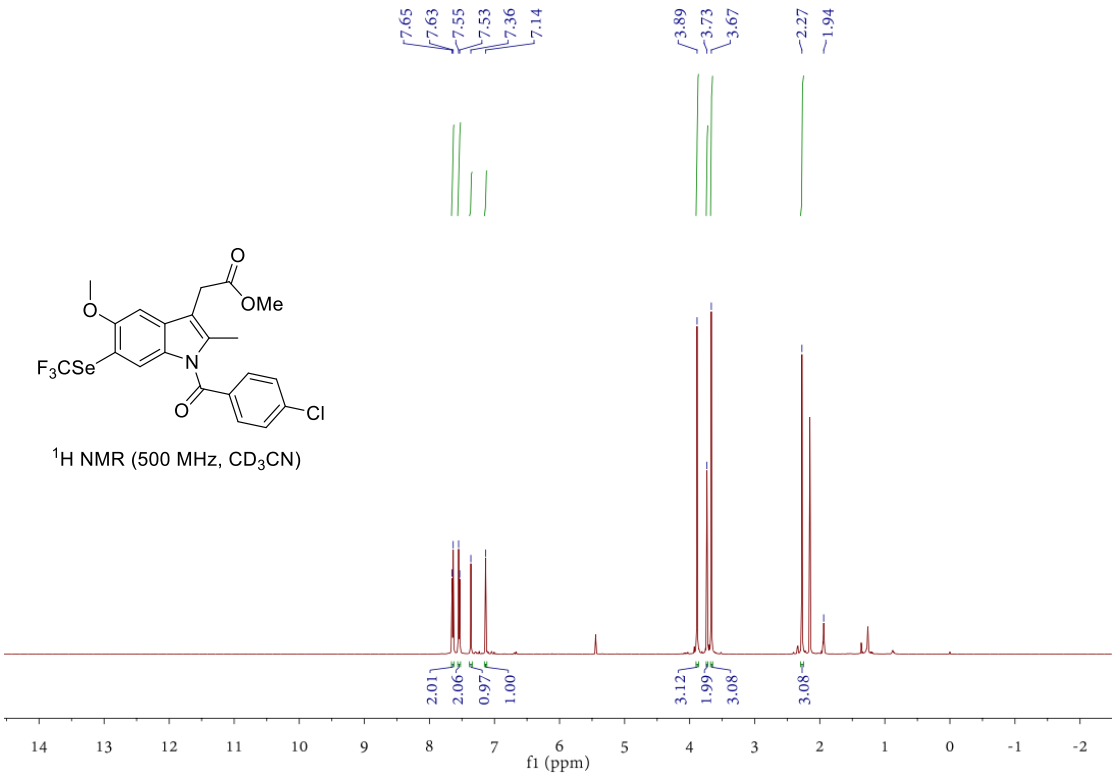
^{19}F NMR spectrum of **3ad**



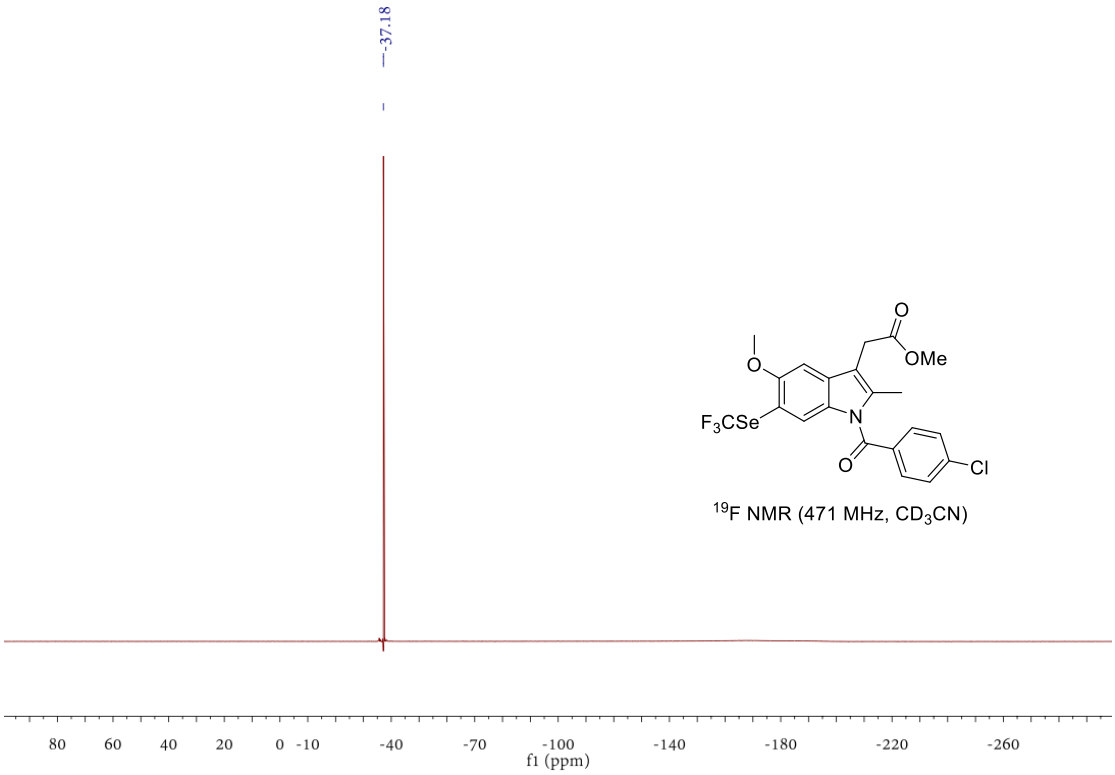
^{13}C NMR spectrum of **3ad**



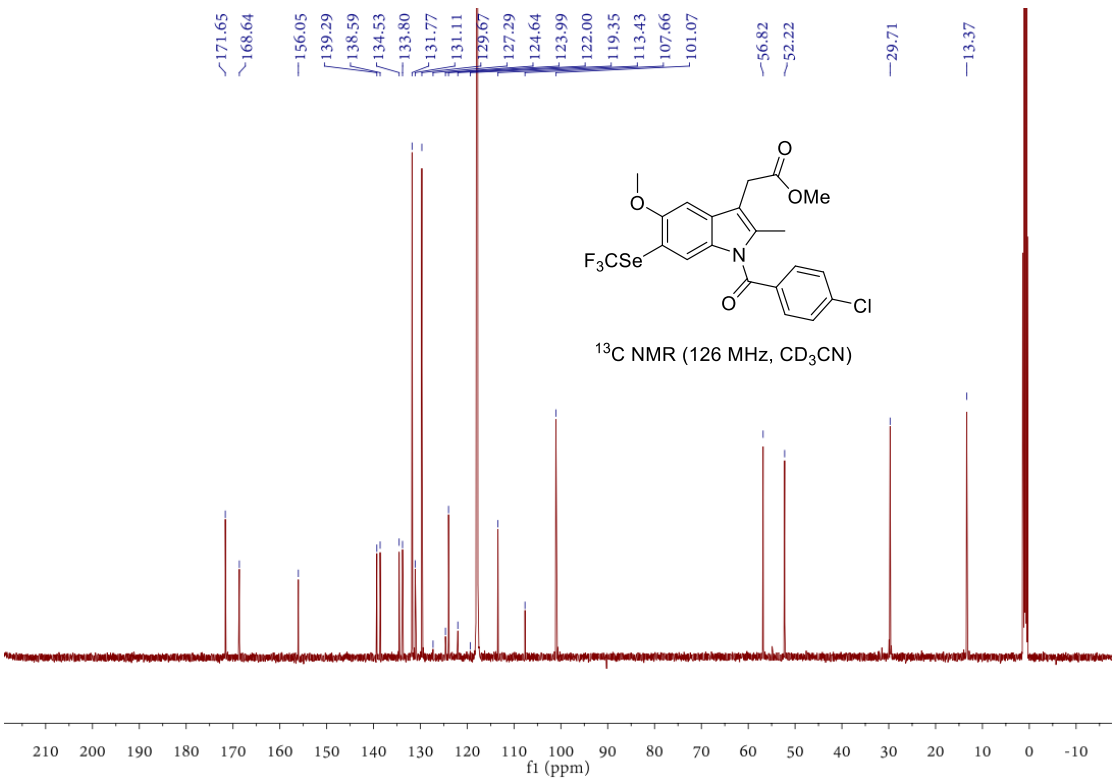
^{1}H NMR spectrum of **3ae**



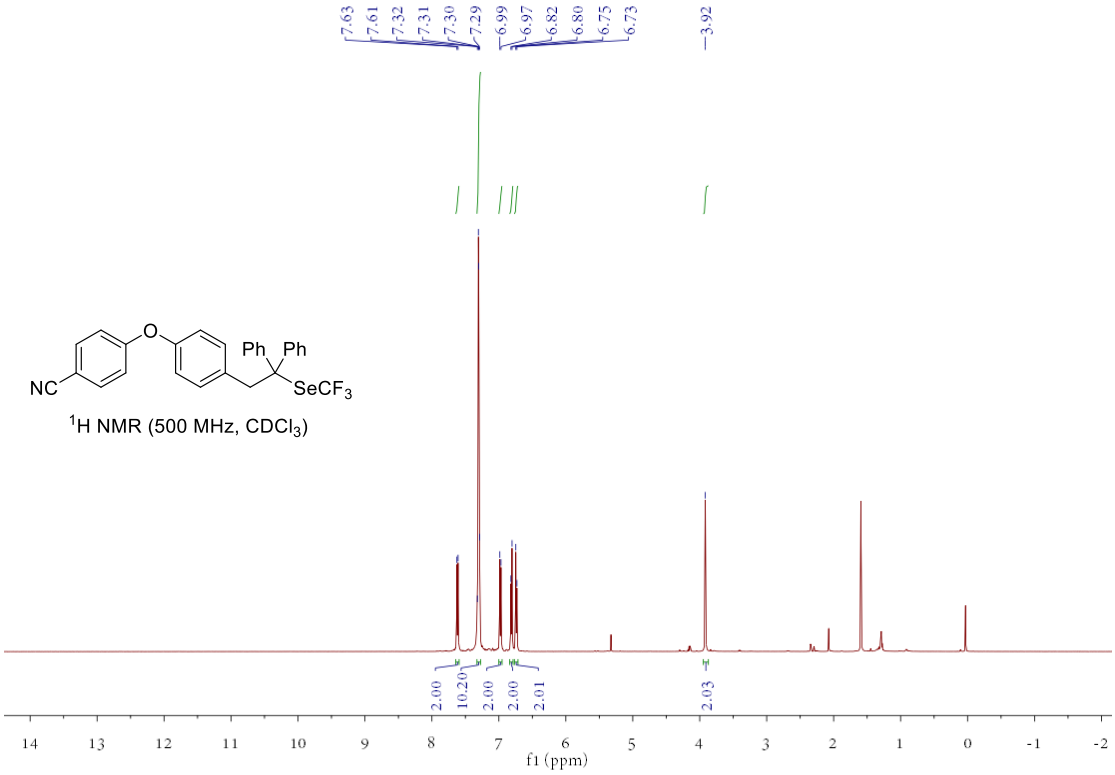
^{19}F NMR spectrum of **3ae**



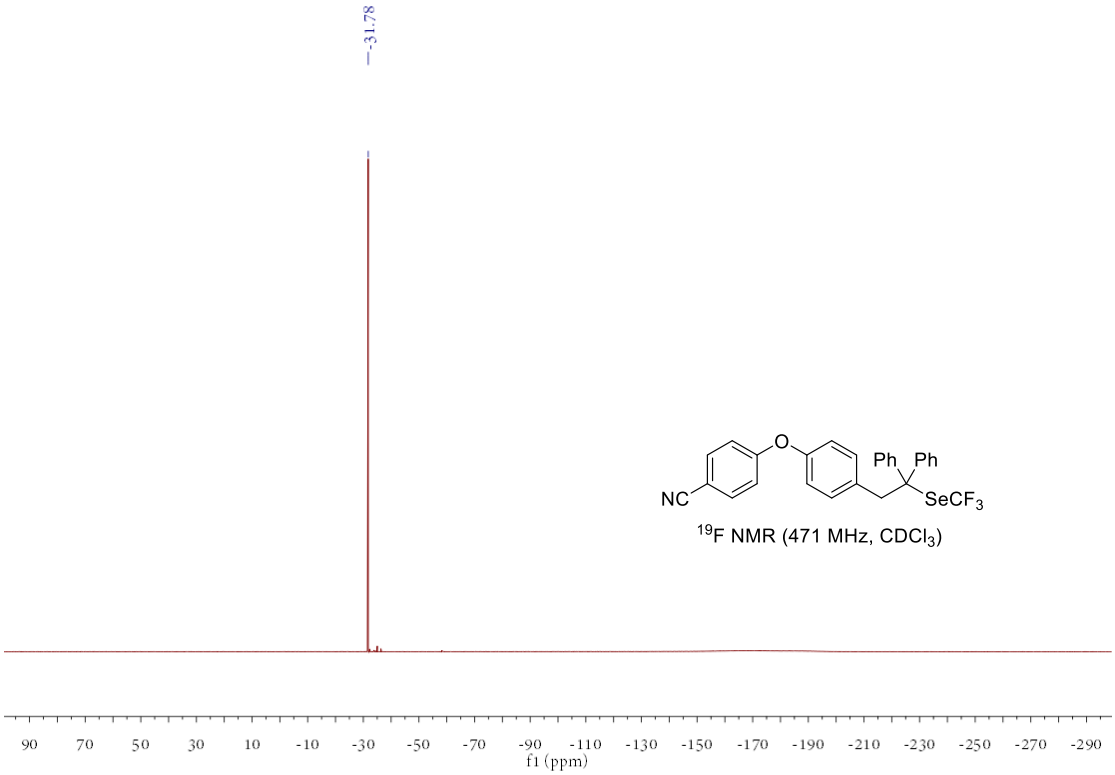
^{13}C NMR spectrum of **3ae**



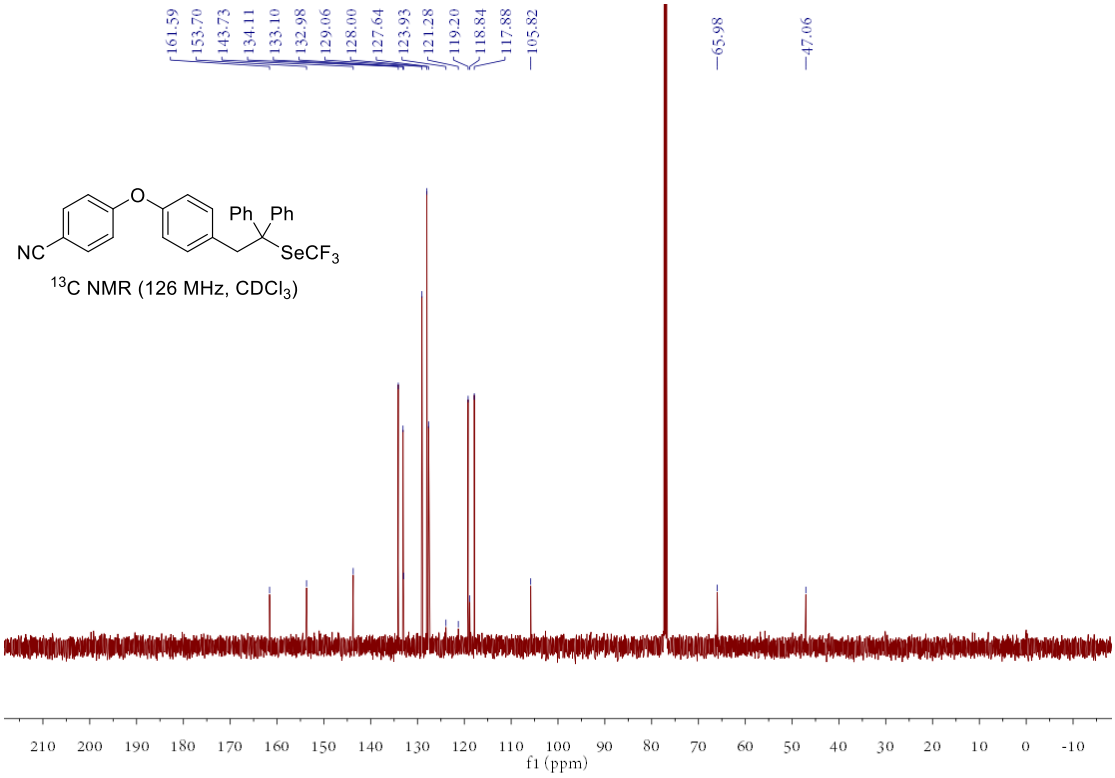
^{1}H NMR spectrum of **5**



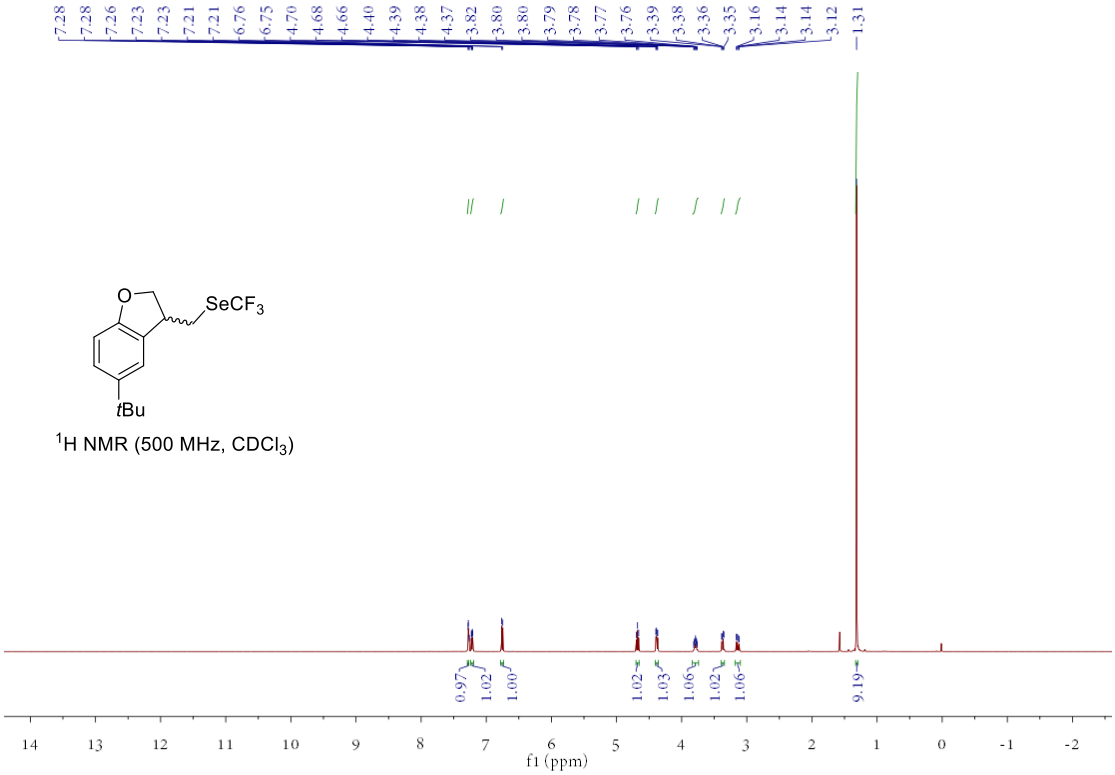
^{19}F NMR spectrum of **5**



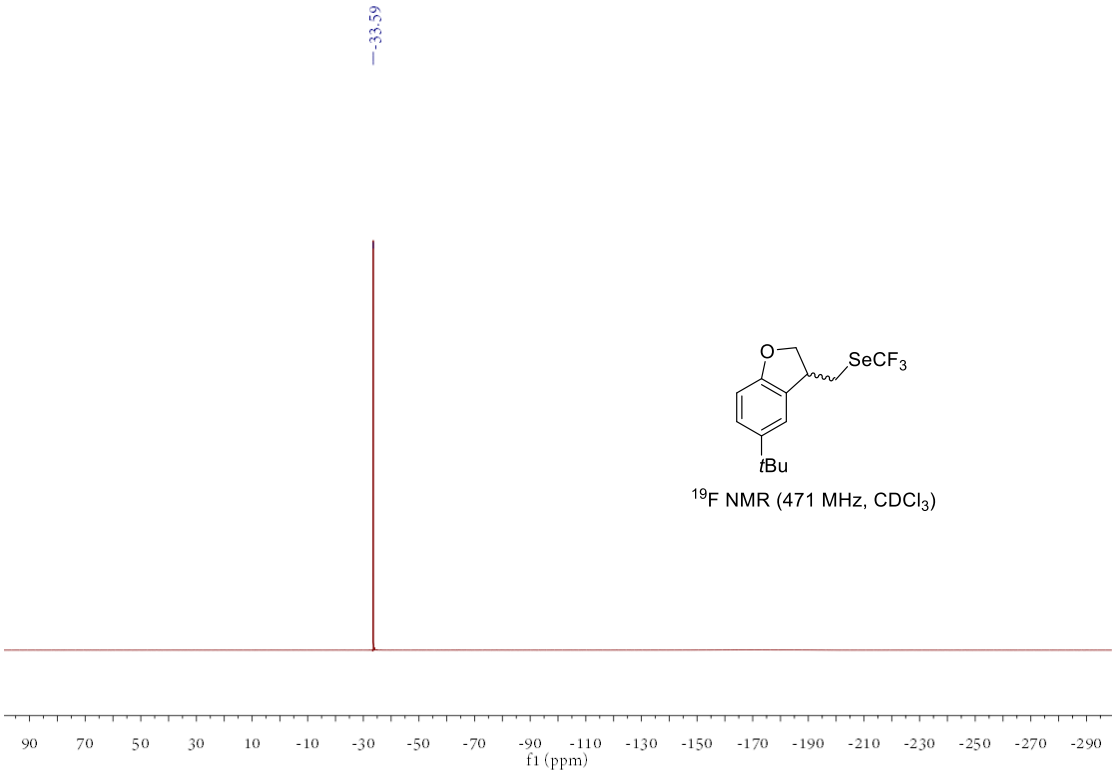
^{13}C NMR spectrum of **5**



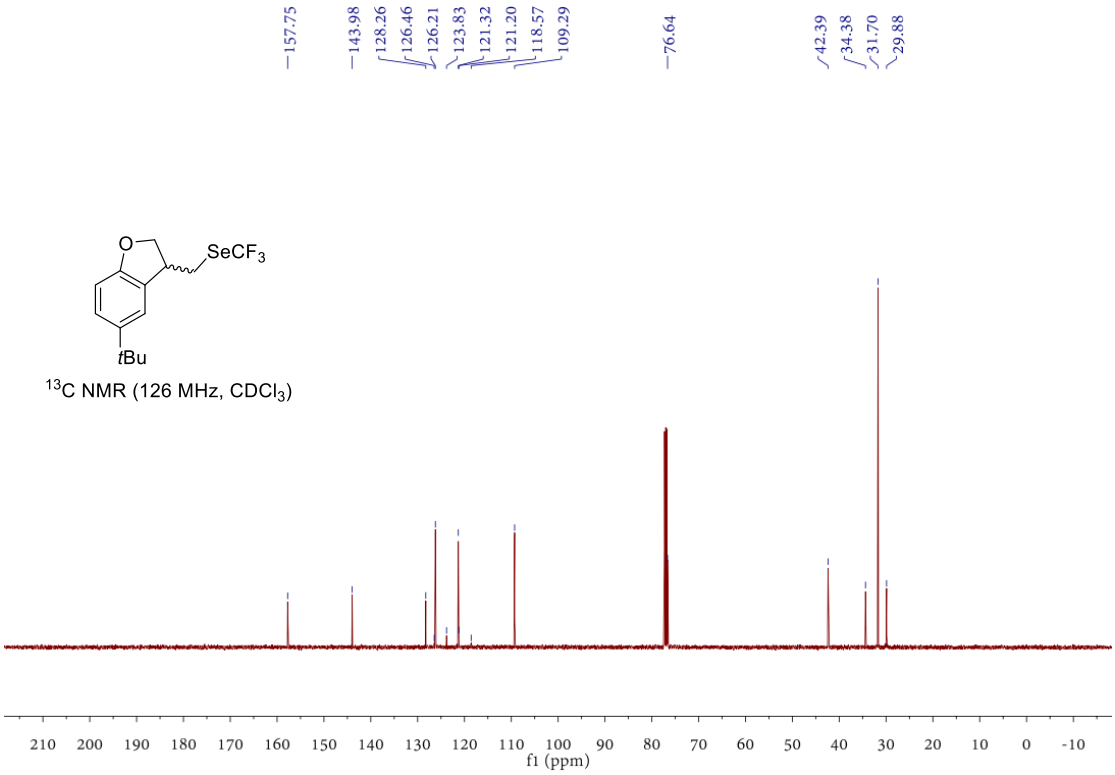
^{1}H NMR spectrum of **6**



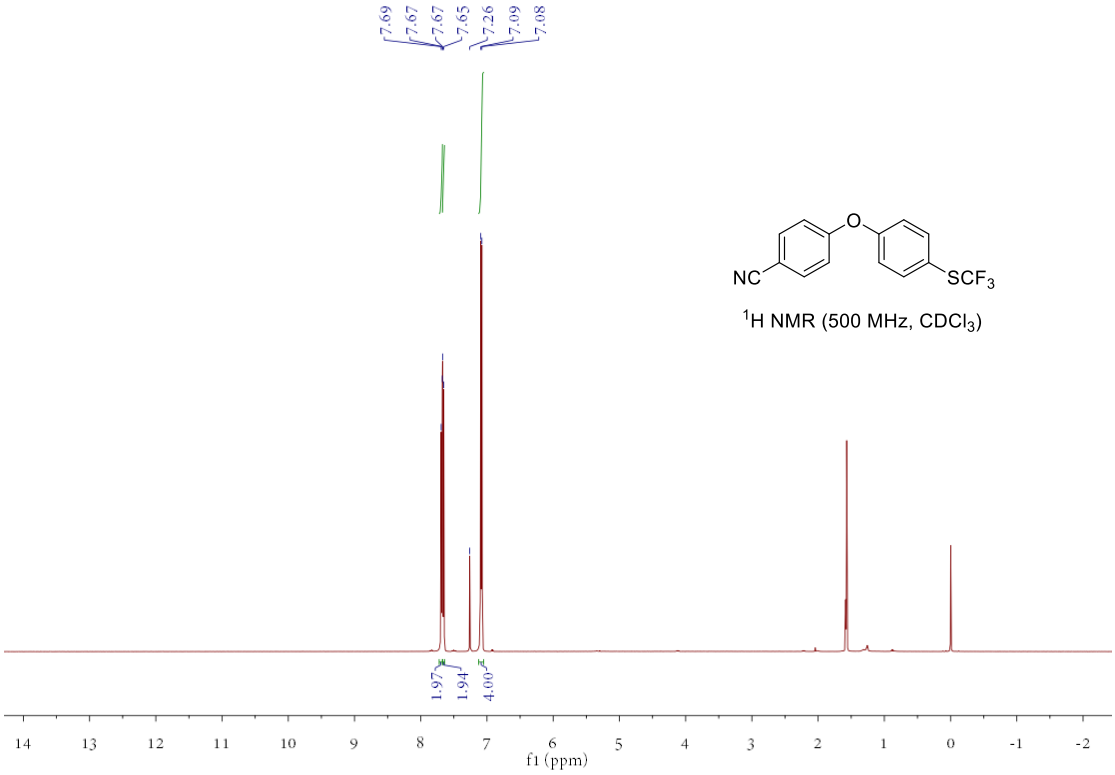
^{19}F NMR spectrum of **6**



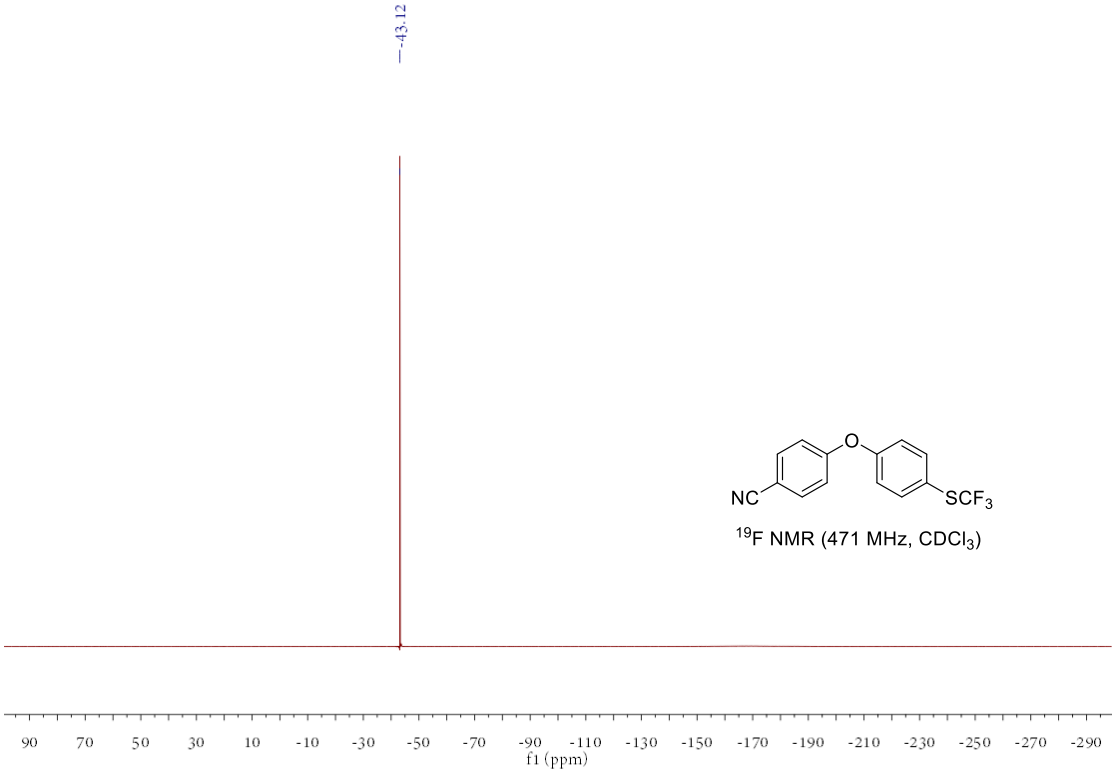
^{13}C NMR spectrum of **6**



^{1}H NMR spectrum of 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile



^{19}F NMR spectrum of 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile



^{13}C NMR spectrum of 4-(4-((trifluoromethyl)thio)phenoxy)benzonitrile