# Supporting Information

## Aryl sulfonyl fluoride synthesis via palladium-catalyzed fluorosulfonylation of aryl thianthrenium salts

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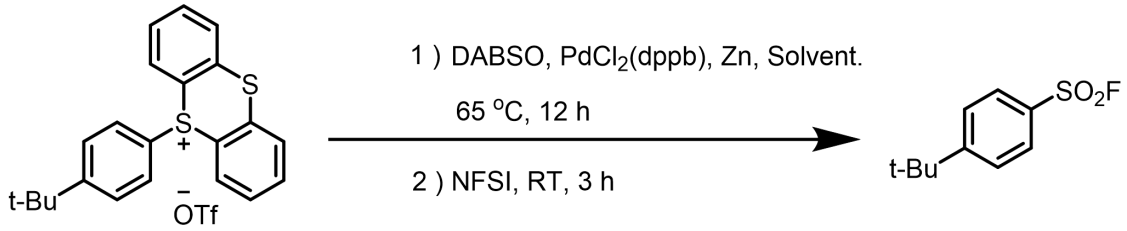
## Tables of cotents

## Ⅰ. General information

The solvents were dried and distilled by the standard methods, other commercially available reagents were purchased and used without further purification. $^{1}H$ NMR ($(CH_3)_4Si$ (TMS) as the internal standard) and $^{19}F$ NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a 400MHz spectrometer. $^{13}C$ NMR also was recorded on 400MHz spectrometer. Data for $^{1}H$ NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The NMR yield was determined by $^{19}F$ NMR using 1-methoxy-4-(trifluoromethoxy) benzene ($^{19}F$ NMR: δ -58.4 ppm) as an internal standard before working up the reaction. GC-MS (EI) data were determined on an Agilent 5975C. LRMS (ESI / EI) and HRMS (ESI / EI) data were tested on a Waters Micromass GCT Premier.

## Ⅱ. Screening reaction conditions

**Table S1. Screening the solvents[a]**

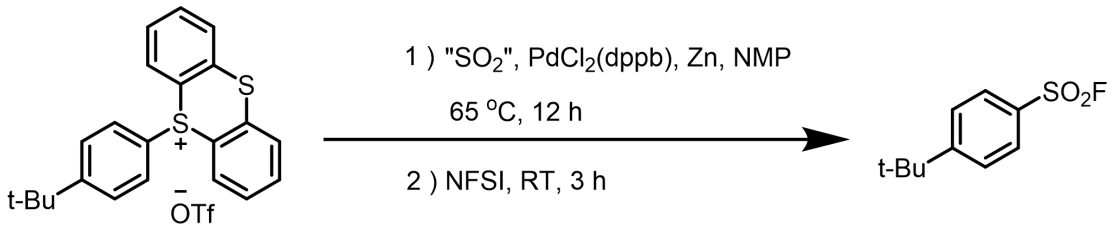



**1a** **2a**

| Entry | Solvent | Yield (%)[b] |
|---|---|---|
| 1 | MeCN | 5 |
| 2 | DMF | 41 |
| 3 | DMAC | 3 |
| **4** | **NMP** | **60** |
| 5 | DMSO | 38 |
| 6 | EtOH/Dioxane (1:1) | 58 |
| 7 | EtOH | 39 |
| 8 | Dioxane | 22 |
| 9 | DCE | 18 |
| 10 | MeOH | 12 |
| 11 | Acetone | 5 |
| 12 | NMP/EtOH (1:1) | 36 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.24 mmol, 1.2 equiv.), $PdCl_2$(dppb) (0.01 mmol, 5.0 mol %), Zinc (0.4 mmol, 2.0 equiv.), Solvent (2.0 mL), Ar atmosphere, 65 °C, 12 h and then NFSI (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy) benzene as an internal standard.

## Table S2. Screening the "$SO_2$"source[a]

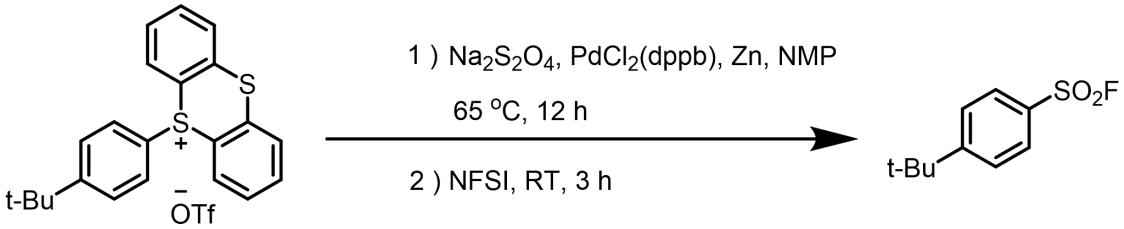



**1a** **2a**

| Entry | "$SO_2$" source | Yield (%)[b] |
|---|---|---|
| 1 | DABSO | 60 |
| **2** | **$Na_2S_2O_4$** | **64** |
| 3 | $K_2S_2O_5$ | 53 |
| 4 | $Na_2S_2O_5$ | 32 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), "$SO_2$" (0.24 mmol, 1.2 equiv.), $PdCl_2$(dppb) (0.01 mmol, 5.0 mol %), Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, 65 ℃, 12 h and then NFSI (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy) benzene as an internal standard.

## Table S3. Screening the $Na_2S_2O_4$ equivalent[a]

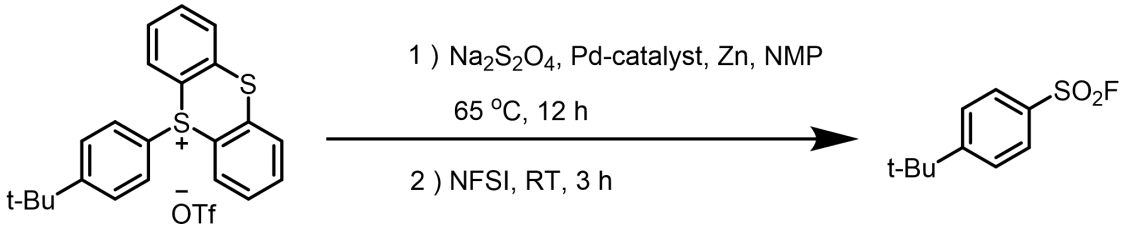



**1a** **2a**

| Entry | $Na_2S_2O_4$ (equiv.) | Yield (%)[b] |
|---|---|---|
| 1 | 1.2 | 66 |
| **2** | **1.5** | **69** |
| 3 | 2.0 | 59 |
| 4 | 3.0 | 54 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$, $PdCl_2$(dppb) (0.01 mmol, 5.0 mol %), Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, 65 ℃, 12 h and then NFSI (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

## Table S4. Screening the different Pd-catalyst[a]

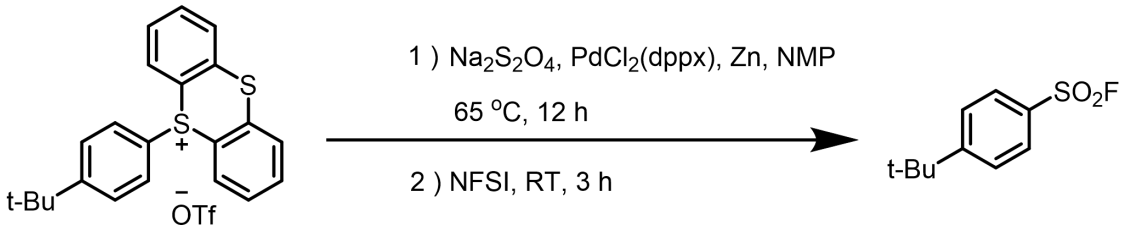



**1a** **2a**

| Entry | Pd-catalyst | Yield (%)[b] |
|---|---|---|
| 1 | $PdCl_2$(dppb) | 69 |
| 2 | $Pd(PPh_3)_4$ | 55 |
| 3 | $PdCl_2(PPh_3)_2$ | 68 |
| 4 | $PdCl_2(PhCN)_2$ | 15 |
| 5 | $PdCl_2[P(t\text{-}Bu)_2Ph]_2$ | 82 |
| 6 | $PdCl_2$(dppf) | 76 |
| **7** | **$PdCl_2$(dppx)** | **90** |
| 8 | $PdCl_2$(dppf)·$CH_2Cl_2$ | 84 |
| 9 | Pd(aMphos)$Cl_2$ | 84 |
| 10 | $PdCl_2$ | 46 |
| 11 | $PdCl_2$+2,2'-bipyridine | 41 |
| 12 | / | 5 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), Pd-catalyst (0.01 mmol, 5.0 mol %), Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, 65 ℃, 12 h and then NFSI (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

## Table S5. Screening the equivalent of $PdCl_2(dppx)$[a]

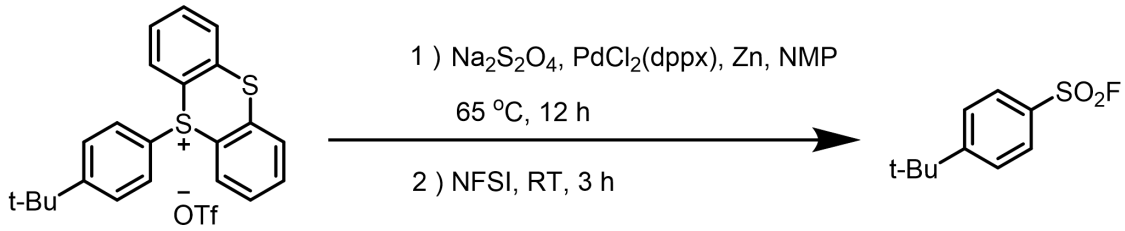



**1a** **2a**

| Entry | $PdCl_2(dppx)$（mol %) | Yield (%)[b] |
|---|---|---|
| 1 | 0 | 5 |
| **2** | **2.5** | **91** |
| 3 | 5 | 85 |
| 4 | 10 | 86 |
| 5 | 15 | 91 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), $PdCl_2(dppx)$, Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, 65 °C, 12 h and then NFSI (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

## Table S6. Survey on the amount of Zinc[a]



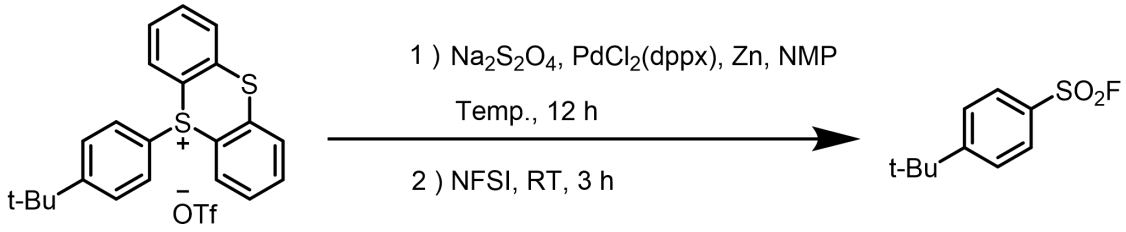

**1a** **2a**

| Entry | Zinc (equiv.) | Yield (%)[b] |
|---|---|---|
| 1 | 0 | 25 |
| 2 | 1.0 | 78 |

| | | |
|---|---|---|
| **3** | **2.0** | **87** |
| 4 | 3.0 | 87 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.005 mmol, 2.5 mol %), Zinc, NMP (2.0 mL), Ar atmosphere, 65 °C, 12 h and then NFSI (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

## Table S7. Survey on the reaction temperatures[a]

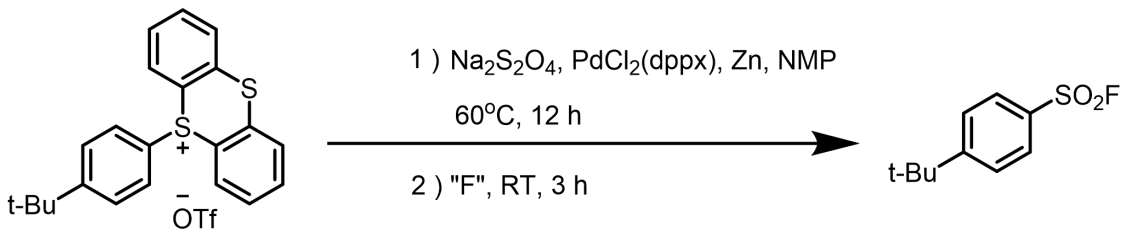



**1a** **2a**

| Entry | Temp. (°C) | Yield (%)[b] |
|---|---|---|
| 1 | 40 | 37 |
| **2** | **60** | **98** |
| 4 | 80 | 85 |
| 5 | 100 | 83 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.005 mmol, 2.5 mol %), Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, Temp., 12 h and then NFSI (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

## Table S8. Survey on the "F" source[a]

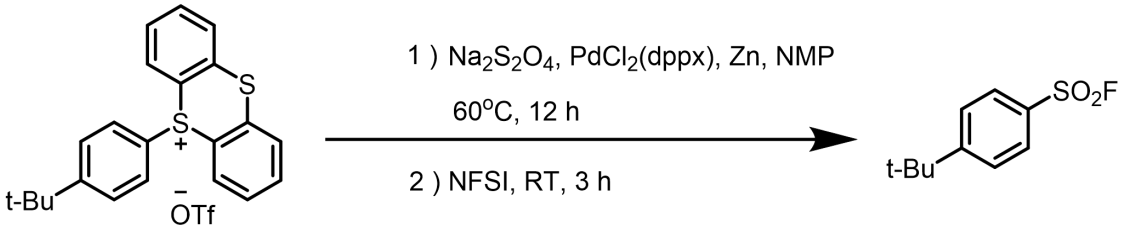



**1a** **2a**

| Entry | "F" source | Yield (%)[b] |
|---|---|---|
| **1** | **NFSI** | **91** |
| 2 | $KHF_2$ | 0 |
| 3 | KF | 0 |
| 4 | Tetrabutylammonium Difluorotriphenylsilicate | 0 |
| 5 | Selectfiour | 81 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.005 mmol, 2.5 mol %), Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, 60 °C, 12 h and then "F" Source (0.6 mmol, 3.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

## Table S9. Survey on the amount of "F" source[a]

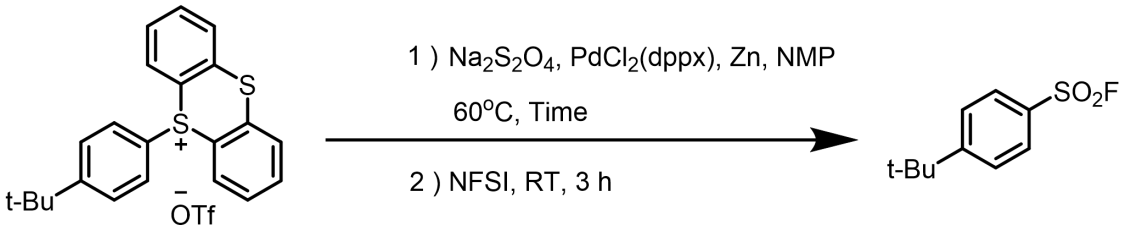



**1a** **2a**

| Entry | NFSI (equiv.) | Yield (%)[b] |
|---|---|---|
| 1 | 1.0 | 62 |
| **2** | **2.0** | **94** |
| 3 | 3.0 | 91 |
| 5 | 4.0 | 94 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.005 mmol, 2.5 mol %), Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, 60 °C, 12 h, and then NFSI, RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

## Table S10. Survey on the reaction time[a]



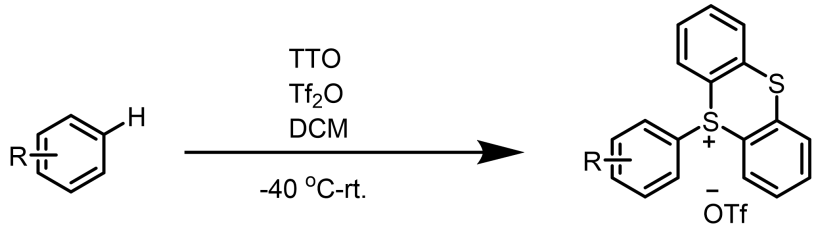

**1a** **2a**

| Entry | Time (h) | Yield (%)[b] |
|---|---|---|
| 1 | 4 | 99 |
| 2 | 8 | 99 |
| 3 | 12 | 98 |
| 4 | 24 | 95 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.005 mmol, 2.5 mol %), Zinc (0.4 mmol, 2.0 equiv.), NMP (2.0 mL), Ar atmosphere, 60 °C, time (h) and then NFSI (0.4 mmol, 2.0 equiv.), RT, 3 h. [b]Yields were determined by $^{19}F$ NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

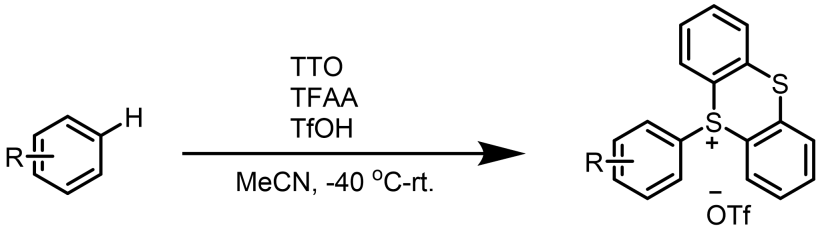
## Ⅲ. Procedures for the synthesis of aryl thianthrenium salts

### Method A :




Various aryl thianthrenium salts were prepared according to the known procedures.[1] S-oxide (6.0 mmol, 1.2 equiv.), DCM (50 mL), arenes (5.0 mmol, 1.0 equiv.) was added to a 250 mL round-bottomed flask equipped with a magnetic stirring bar under Ar atmosphere, and cooled the mixture to -40 ℃, then $Tf_2O$ (6.0 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at the same temperature for 1.0 h, and then warmed up to room temperature until the arenes was completely consumed. After the reaction, wash the organic layer with water for three times and dry it with anhydrous sodium sulfate. Then, the solvent is removed under vacuum, the resulting mixture is dissolved in a small amount of anhydrous dichloromethane, and anhydrous ether is slowly dropped into the system to precipitate a solid. Aryl thianthracene salts are obtained by collecting solids through filtration and washing with ether, or the crude product was purified by column chromatography on silica gel (eluents: DCM/MeOH = 30/0 to 30/1 (v/v)).

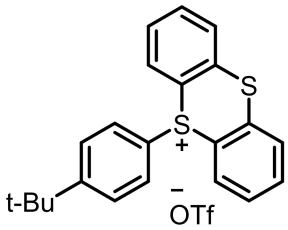
### Method B[2] :



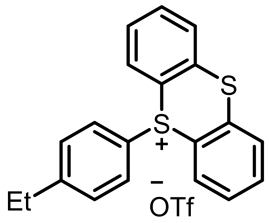

S-oxide (6.0 mmol, 1.0 equiv), MeCN (50 mL), arenes (6.0 mmol, 1.0 equiv.) was added to a round-bottomed flask under Ar atmosphere, and cooled the mixture to

-40 ℃, trifluoroacetic anhydride (TFAA, 18 mmol, 3.0 equiv.) and trifluoromethanesulfonic acid (TfOH, 9.0 mmol, 1.5 equiv.) were added dropwise to the round-bottomed flask. The reaction mixture was stirred at the same temperature for 1.0 h, and then the mixture was reacted at room temperature overnight. The mixture was 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 (eluents: DCM/MeOH = 30/0 to 30/1 (v/v)).

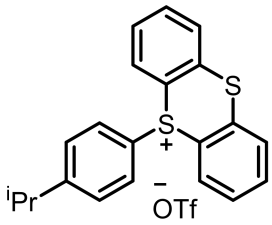
## Ⅳ. Analytical data for compounds 1a-1v



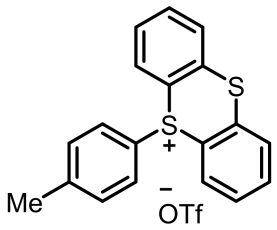

**5-(4-(tert-butyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1a):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 8.0 Hz, 2H), 7.84-7.73 (m, 6H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 1.24 (s, 9H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 157.4, 136.6, 135.5, 134.9, 130.3 (d, *J* = 4.0 Hz), 128.1 (d, *J* = 6.0 Hz), 120.5, 119.1, 35.3, 31.0 ppm. HRMS-ESI (m/z) calcd. for $[C_{22}H_{21}S_2]^+$ ($[M]^+$): 349.1079; found: 349.1076.



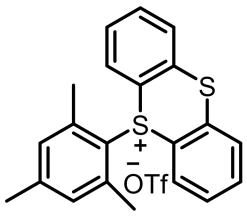

**5-(4-ethylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1b):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 8.0 Hz, 2H), 7.84-7.73 (m, 6H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.63 (q, *J* = 8.0 Hz, 2H), 1.17 (t, *J* = 8.0 Hz, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 150.5, 136.6, 135.5, 134.9, 130.4, 130.3 (d, *J* = 4.0 Hz), 128.3, 120.7, 119.2, 28.7, 14.9 ppm. HRMS-ESI (m/z) calcd. for $[C_{20}H_{17}S_2]^+$ ($[M]^+$): 321.0766; found: 321.0764.



**5-(4-isopropylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1c):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.0 Hz, 2H), 7.84-7.73 (m, 6H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.88 (m, 1H), 1.17 (d, *J* = 8.0 Hz, 6H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s,3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.1, 136.6, 135.5, 134.9, 130.3 (d, *J* = 3.0 Hz), 129.1, 128.4, 120.7, 119.1, 34.1, 23.5 ppm. HRMS-ESI (m/z) calcd. for $[C_{21}H_{19}S_2]^+$ ($[M]^+$): 335.0923; found: 335.0919.

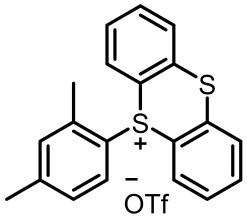



**5-(p-tolyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1d):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.0 Hz, 2H), 7.83-7.74 (m, 6H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.3 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 144.5, 136.6, 135.6 (d, *J* = 3.0 Hz), 134.9, 131.5, 130.3 (d, *J* = 4.0 Hz), 128.1, 120.5, 119.2 (d, *J* = 2.0 Hz), 21.5 ppm. HRMS-ESI (m/z) calcd. for $[C_{19}H_{15}S_2]^+$ ($[M]^+$): 307.0610; found: 307.0607.

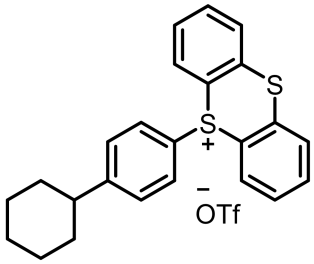



**5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1e):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): 7.86 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 8.0 Hz, 2H), 7.40 (s, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.52 (s, 3H), 2.29 (s, 6H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 149.5, 145.6,

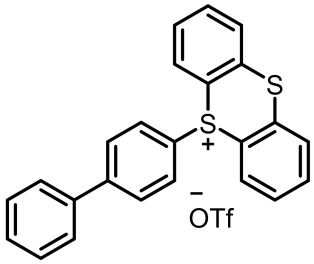
134.0, 133.7, 130.8, 130.5, 130.2, 126.9, 124.4, 110.4, 22.1, 21.8 ppm. HRMS-ESI (m/z) calcd. for $[C_{21}H_{19}S_2]^+$ ($[M]^+$): 335.0966; found: 335.0965.



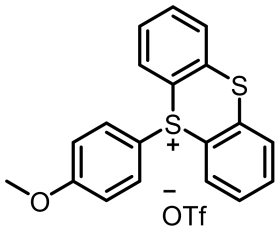

**5-(2,4-dimethylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1f):** According to the Method **B**, white solid. $^1$H NMR (400 MHz, acetone-$d_6$): δ 8.46 (d, *J* = 8.0 Hz, 2H), δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.97 (t, *J* = 8.0 Hz, 2H), 7.88 (t, *J* = 8.0 Hz, 2H), 7.43 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 2.74 (s, 3H), 2.36 (s, 3H). $^{19}$F NMR (376 MHz, acetone-$d_6$): δ -84.0 (s, 3F) ppm. $^{13}$C NMR (101 MHz, acetone-$d_6$): δ 145.4, 140.2, 136.7, 134.6, 134.2 (d, *J* = 8.8 Hz), 130.7, 130.0, 129.7, 128.6, 118.9, 118.3, 20.1, 19.6 ppm. HRMS-ESI (m/z) calcd. for $[C_{20}H_{17}S_2]^+$ ($[M]^+$): 321.0766; found: 321.0763.



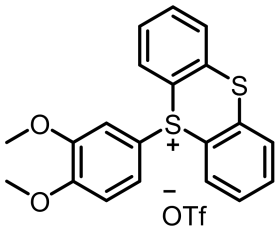

**(4-cyclohexylphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1g):** According to the Method **A**, white solid. $^1$H NMR (400 MHz, $CDCl_3$): 8.58 (d, *J* = 8.0 Hz, 2H), 7.84-7.72 (m, 6H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.47 (t, *J* = 12.0 Hz, 1H), 1.77-1.69 (m, 5H), 1.38-1.16 (m, 5H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 154.2, 136.6, 135.5, 134.9, 130.3 (d, *J* = 2.0 Hz), 129.4, 128.3, 120.6, 119.1, 44.4, 34.0, 26.6, 25.9 ppm. HRMS-ESI (m/z) calcd. for $[C_{24}H_{23}S_2]^+$ ($[M]^+$): 375.1236; found: 375.1232.




**5-([1,1'-biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (1h):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): 8.62 (d, *J* = 8.0 Hz, 2H), 7.85-7.75 (m, 6H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.47-7.38 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 146.2, 138.2, 136.7, 129.2 (d, *J* = 3.0 Hz), 129.1, 128.7, 127.3, 122.3, 119.0 ppm. HRMS-ESI (m/z) calcd. for $[C_{24}H_{17}S_2]^+$ ($[M]^+$): 369.0766; found: 369.0763.

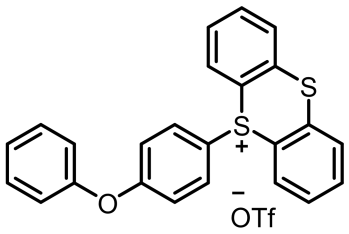



**(4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1i):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 2H), 7.83-7.70 (m, 6H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 163.8, 136.2, 134.8 (d, *J* = 12.0 Hz), 130.8, 130.3 (d, *J* = 7.0 Hz), 119.7, 116.6, 113.6, 56.0 ppm. HRMS-ESI (m/z) calcd. for $[C_{19}H_{15}OS_2]^+$ ($[M]^+$): 323.0569; found: 323.0567.

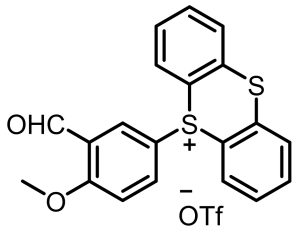



**5-(3,4-dimethoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1j):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CD_3CN$): 8.21 (d, *J* =

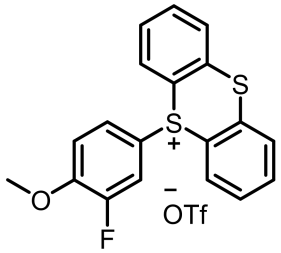
8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.85 (t, *J* = 8.0 Hz, 2H), 7.76 (t, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.89 (q, *J* = 4.0 Hz, 1H), 6.76 (s, 1H), 3.83 (s, 3H), 3.65 (s, 3H). $^{19}$F NMR (376 MHz, $CD_3CN$): δ -84.6 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CD_3CN$): δ 154.8, 151.9, 136.8, 135.7, 134.9, 131.5, 130.9, 124.4, 120.9, 113.9, 113.5, 112.0, 56.9, 57.0 ppm. HRMS-ESI (m/z) calcd. for $[C_{20}H_{17}O_2S_2]^+$ ($[M]^+$): 353.0664; found: 353.0662.



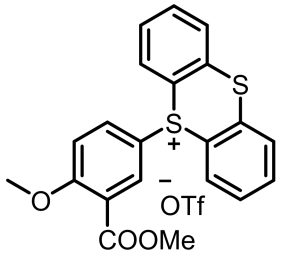

**5-(4-phenoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1k):** According to the Method **A**, white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 8.0 Hz, 2H), 7.83-7.71 (m, 6H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.23-7.17 (m, 3H), 6.99-6.93 (m, 4H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 162.5, 154.4, 136.4 (d, *J* = 27.3 Hz), 130.4 (d, *J* = 4.0 Hz), 130.3, 125.7, 120.6, 119.4, 119.2, 115.8 ppm. HRMS-ESI (m/z) calcd. for $[C_{24}H_{17}OS_2]^+$ ($[M]^+$): 385.0715; found: 385.0713.



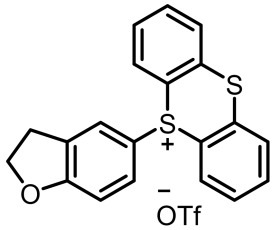

**(3-formyl-4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1l):** According to the Method **A**, Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, 1H), 8.59 (d, *J* = 8.0 Hz, 2H), 7.88-7.75 (m, 7H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.3 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 187.2, 164.8, 136.5 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 11.0 Hz), 130.5 (d, *J* = 3.0 Hz), 128.0, 125.6, 118.9, 115.5, 115.2, 56.9 ppm. HRMS-ESI (m/z) calcd. for $[C_{20}H_{15}O_2S_2]^+$ ($[M]^+$): 351.0508; found: 351.0503.



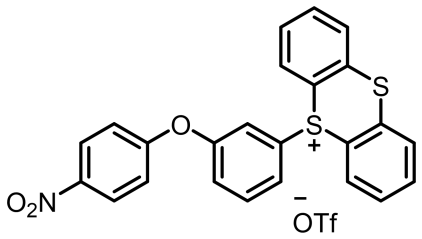

**(3-fluoro-4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1m):** According to the Method **A**, Yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): 8.56 (d, *J* = 8.0 Hz, 2H), 7.86-7.79 (m, 4H), 7.75 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F), -128.04 (t, *J* = 7.5 Hz, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 153.8, 152.3 (d, *J* = 10.0 Hz), 151.3, 136.4, 135.3, 135.1, 130.4 (d, *J* = 5.0 Hz), 126.6 (d, *J* = 4.0 Hz), 119.0, 116.1, 115.8, 115.0 (d, *J* = 2.0 Hz), 114.1 (d, *J* = 7.0 Hz), 56.8 ppm. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}OFS_2]^+$ ($[M]^+$): 341.0465; found: 341.0461.



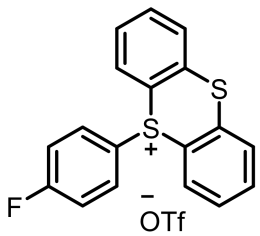

**5-(4-methoxy-3-(methoxycarbonyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1n):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): 8.57 (d, *J* = 4.0 Hz, 2H), 7.85-7.72 (m, 6H), 7.59-7.55 (m, 2H), 7.12 (d, *J* = 12.0 Hz, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -72.9 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 164.5, 162.7, 136.4, 135.1, 134.5, 131.7, 130.4, 122.2, 119.1, 114.9, 113.8, 56.9, 52.8 ppm. HRMS-ESI (m/z) calcd. for $[C_{21}H_{17}O_3S_2]^+$ ($[M]^+$): 381.0614; found: 381.0612.



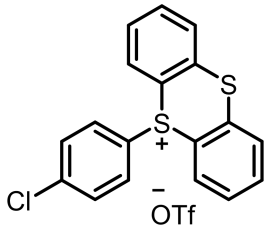

**5-(2,3-dihydrobenzofuran-5-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (1o):** According to the Method **B**, white solid. $^{1}$H NMR (400 MHz, acetone-$d_6$): δ 8.52 (d, *J* = 4.0 Hz, 2H), 8.09-8.06 (m, 2H), 7.96 (t, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 6.91-6.88 (m, 1H), 4.68-4.63 (m, 2H), 3.21 (t, *J* = 8.0 Hz, 2H). $^{19}$F NMR (376 MHz, acetone-$d_6$): δ -83.9 (s, 3F) ppm. $^{13}$C NMR (101 MHz, acetone-$d_6$): δ 165.7, 136.7, 135.7, 135.2, 132.7, 131.3, 131.2, 131.0, 126.8, 121.0, 114.0, 112.0, 73.7 ppm. HRMS-ESI (m/z) calcd. for $[C_{20}H_{15}OS_2]^+$ ($[M]^+$): 335.0559; found: 335.0564.



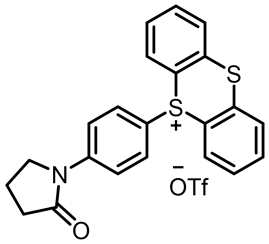

**5-(3-(4-nitrophenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1p):** According to the Method **B**, white solid. $^{1}$H NMR (400 MHz, acetone-$d_6$): 8.68 (d, *J* = 8.0 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 8.01 (t, *J* = 8.0 Hz, 2H), 7.93 (t, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H). $^{19}$F NMR (376 MHz, acetone-$d_6$): δ -83.9 (s, 3F) ppm. $^{13}$C NMR (101 MHz, acetone-$d_6$): δ 161.7, 160.4, 137.145.1, 137.3, 136.1 (d, *J* = 5.0 Hz), 131.9, 131.5, 131.0, 127.0, 122.0, 120.3, 120.2, 120.0 ppm. HRMS-ESI (m/z) calcd. for $[C_{24}H_{16}O_3NS_2]^+$ ($[M]^+$): 430.0566; found: 430.0563.



**5-(4-fluorophenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1q):** According to the Method **A**, Yellow solid. $^{1}$H NMR (400 MHz, dmso-$d_6$): δ 8.58 (d, *J* = 12.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.93 (t, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.31 (m, 2H). $^{19}$F NMR (376 MHz, dmso-$d_6$): δ -82.5 (s, 3F), -111.10 (m, 1F) ppm. $^{13}$C NMR (101 MHz, dmso-$d_6$): δ 135.6, 135.3, 134.8, 131.1, (d, *J* = 10.1 Hz), 130.3, 129.6, 120.4 (d, *J* = 3.3 Hz), 119.5, 117.9, 117.7 ppm. HRMS-ESI (m/z) calcd. for $[C_{18}H_{12}FS_2]^+$ ($[M]^+$): 311.0358; found: 311.0355.

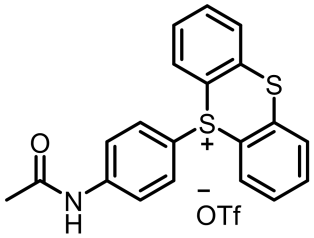



**(4-chlorophenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1r):** According to the Method **B**, Yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.62 (br, 2H), 7.84-7.77 (m, 6H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 144.5, 136.6, 135.5, 134.9, 131.5, 130.3 (d, *J* = 4.0 Hz), 128.1, 120.5, 119.2 ppm. HRMS-ESI (m/z) calcd. for $[C_{18}H_{12}ClS_2]^+$ ($[M]^+$): 327.0064; found: 327.0063.

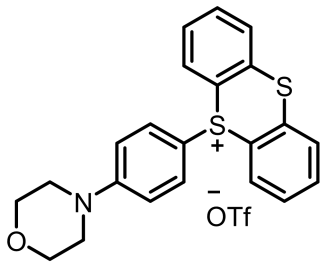



**5-(4-(2-oxopyrrolidin-1-yl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1s):** According to the Method **A**, white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): 8.52 (d, *J* = 8.0 Hz, 2H), 7.83-7.71 (m, 8H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.79 (t, *J* = 8.0 Hz, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 2.13 (m, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 175.2, 143.9, 136.4, 135.0 (d, *J* = 11.0 Hz), 130.3 (d, *J* = 8.0 Hz), 129.2 120.8, 119.1, 116.8, 48.4,

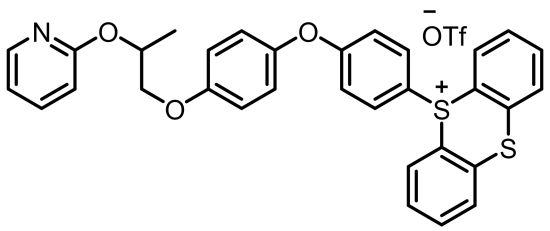
32.8, 17.7 ppm. HRMS-ESI (m/z) calcd. for $[C_{22}H_{18}ONS_2]^+$ ($[M]^+$): 376.0824; found: 376.0821.




**5-(4-acetamidophenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1t):** According to the Method **B**, white solid. $^1$H NMR (400 MHz, acetone-$d_6$): δ 9.81 (s, 1H), 8.59 (d, *J* = 4.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.98 (t, *J* = 8.0 Hz, 2H), 7.92-7.85 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.08 (s, 3H). $^{19}$F NMR (376 MHz, acetone-$d_6$): δ -84.1 (s, 3F) ppm. $^{13}$C NMR (101 MHz, acetone-$d_6$): δ 170.0, 145.1, 137.1, 135.7, 131.4, 130.9, 130.4, 121.2, 120.6, 116.5, 24.33 ppm. HRMS-ESI (m/z) calcd. for $[C_{20}H_{16}ONS_2]^+$ ($[M]^+$): 350.0668; found: 350.0669.

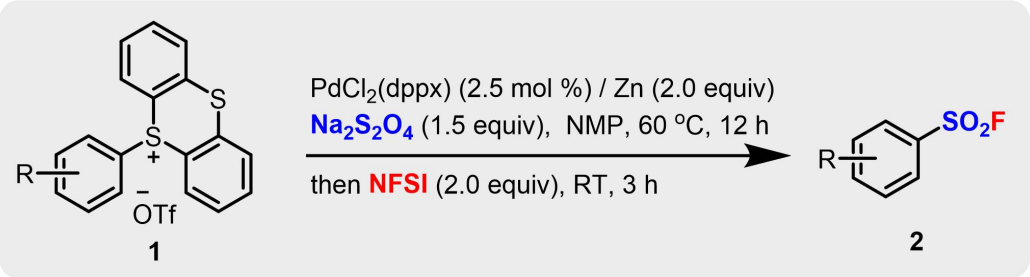



**(4-morpholinophenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1u):** According to the Method **A**, white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.76-7.67 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.79 (t, *J* = 8.0 Hz, 4H), 3.26 (t, *J* = 8.0 Hz, 4H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 154.5, 135.3, 134.1 (d, *J* = 27.3 Hz), 131.4, 130.2 (d, *J* = 24.2 Hz), 121.2, 115.6, 108.1, 47.0 ppm. HRMS-ESI (m/z) calcd. for $[C_{22}H_{20}ONS_2]^+$ ($[M]^+$): 378.0981; found: 378.0978.



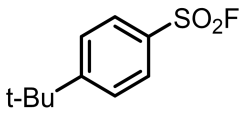

**(5-5-(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (1v) :** According to the Method **B**, Yellow solid. $^{1}$H NMR (400 MHz, acetone-$d_6$): δ 8.35 (d, *J* = 8.0 Hz, 2H), 7.81-7.76 (m, 6H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.79 (t, *J* = 8.0 Hz, 4H), 3.26 (t, *J* = 8.0 Hz, 4H). $^{19}$F NMR (376 MHz, acetone-$d_6$): δ -78.2 (s, 3F) ppm. $^{13}$C NMR (101 MHz, acetone-$d_6$): δ 154.5, 135.3, 134.1 (d, *J* = 27.3 Hz), 131.4, 130.2 (d, *J* = 24.2 Hz), 121.2, 115.6, 108.1, 47.0 ppm. HRMS-ESI (m/z) calcd. for $[C_{32}H_{26}O_3NS_2]^+$ ($[M]^+$): 536.1349; found: 536.1346.

## Ⅴ. General procedures for the fluorosulfonylation of various aryl thianthrenium salts

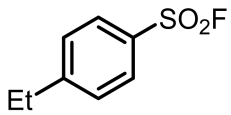



Aryl thianthrenium salts **1** (0.4 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.6 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.01 mmol, 2.5 mol %), Zinc (0.8 mmol, 2 equiv.) were added to an oven-dried sealed tube (25 mL) equipped with a magnetic stirring bar. The tube was evacuated and backfilled with Ar (3 times), and then NMP (4.0 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at 60 ℃ for 12 h. After cooled to room temperature, NFSI (0.8 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at room temperature for 3 h. Yields of the desired product were measured by $^{19}F$ NMR spectroscopy before working-up. Then the reaction mixture was filtered through a pad of celite, diluted with DCM (20 mL) and $H_2O$ (50 mL). The resulting mixture was extracted with DCM (2 × 20 mL). The organic layers were combined, washed with brine (50 mL), dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by silica gel column chromatography to give the desired product.

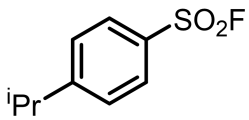
## Ⅵ. Analytical data for compounds 2a-2v.




**4-(tert-butyl)benzenesulfonyl fluoride (2a):** Obtained as a white solid in 86% yield (74.3 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 8:1v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 1.37 (s, 9H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.2 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 160.1, 130.1 (d, *J* = 24.2 Hz), 128.5, 126.8, 35.7, 31.1 ppm. GC-MS (EI) m/z = 216.1 ($M^+$). The analytical data are consistent with literature values.[3]

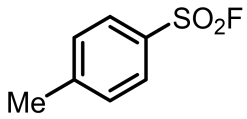



**4-ethylbenzenesulfonyl fluoride (2b):** Obtained as colorless oil in 80% yield (60.2 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 8:1 v/v.. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 2.78 (q, *J* = 8.0 Hz, 2H), 1.28 (t, *J* = 8.0 Hz, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.2 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 153.2, 130.2 (d, *J* = 24.2 Hz), 129.2, 128.6, 29.0, 14.9 ppm. GC-MS (EI) m/z = 188.0 ($M^+$). The analytical data are consistent with literature values.[4]

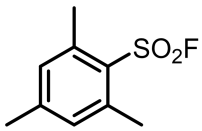



**4-isopropylbenzenesulfonyl fluoride (2c):** Obtained as colorless oil in 90% yield (72.8 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 8:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 3.04 (m, *J* = 8.0 Hz, 1H), 1.29 (d, *J* = 8.0 Hz, 6H).$^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.2 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 157.8, 130.4

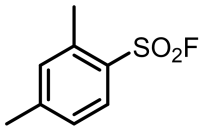
(d, $J$ = 24.2 Hz), 128.7, 127.9, 34.6, 23.6 ppm. GC-MS (EI) m/z = 202.1 ($M^+$). The analytical data are consistent with literature values.[4]




**4-methylbenzenesulfony (2d):** Obtained as colorless oil in 78% yield (54.3 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 10:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, $J$ = 8.0 Hz, 2H), 7.41 (d, $J$ = 8.0 Hz, 2H), 2.48 (s, 3H).$^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.2 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 147.3, 130.4, 130.2 (d, $J$ = 24.2 Hz), 128.5, 21.9 ppm. GC-MS (EI) m/z = 174.0 ($M^+$). The analytical data are consistent with literature values.[3]

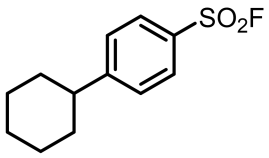



**2,4,6-trimethylbenzenesulfonyl fluoride (2e):** Obtained as white solid in 40% yield (32.3 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 8:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.03 (s, 2H), 2.64 (s, 6H), 2.35 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 68.2 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 145.2, 140.2, 132.0, 129.4 (d, $J$ = 40.4 Hz), 22.5, 21.3 ppm. GC-MS (EI) m/z = 202.0 ($M^+$). The analytical data are consistent with literature values.[5]

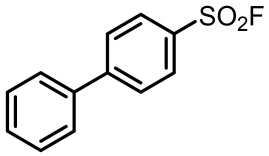



**2,4-dimethylbenzenesulfonyl fluoride (2f):** Obtained as colorless oil in 74% yield (55.6 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 8:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, $J$ = 8.0 Hz, 1H), 7.22 (s, 1H), 7.19 (d, $J$ = 8.0 Hz, 1H), 2.64 (s, 3H), 2.42 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 60.8 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 146.8, 139.0, 133.7,

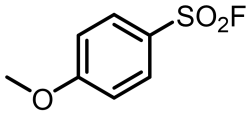
130.3, 129.4 (d, $J$ = 22.2 Hz), 127.3, 21.7, 20.3 ppm. GC-MS (EI) m/z = 188.0 ($M^+$). The analytical data are consistent with literature values.[4]




**4-cyclohexylbenzenesulfonyl fluoride (2g):** Obtained as colorless oil in 85% yield (82.3 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 8:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.45 (d, $J$ = 8.0 Hz, 2H), 2.63 (br, 1H), 1.87 (m, 4H), 1.42 (m, 4H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.2 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 156.9, 130.3 (d, $J$ = 24.2 Hz), 128.7, 128.3, 44.9, 34.1, 26.7, 26.0 ppm. GC-MS (EI) m/z = 242.1 ($M^+$). The analytical data are consistent with literature values.[4]

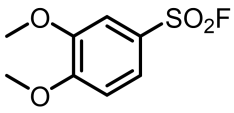



**[1,1'-biphenyl]-4-sulfonyl fluoride (2h):** Obtained as white solid in 80% yield (75.5 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 5:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, $J$ = 8.0 Hz, 2H), 7.83 (d, $J$ = 8.0 Hz, 2H) 7.64 (d, $J$ = 8.0 Hz, 2H), 7.55-7.46 (m, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.5 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 148.7, 138.6, 131.5 (d, $J$ = 25.3 Hz), 129.4, 129.3, 129.1, 128.3, 127.6 ppm. GC-MS (EI) m/z = 236.0 ($M^+$). The analytical data are consistent with literature values.[3]

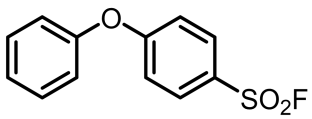



**4-methoxybenzenesulfonyl fluoride (2i):** Obtained as colorless oil in 75% yield (57.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 3:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, $J$ = 8.0 Hz, 2H), 7.06 (d, $J$ = 8.0 Hz, 2H), 3.91 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.3 (s, 1F)

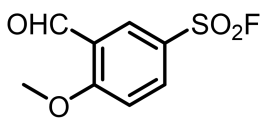
ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 165.4, 131.0, 124.2 (d, *J* = 24.7 Hz), 115.0, 56.0 ppm. GC-MS (EI) m/z = 190.0 ($M^+$). The analytical data are consistent with literature values.[3]




**3,4-dimethoxybenzenesulfonyl fluoride (2j):** Obtained as white solid in 80% yield (70.4 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 5:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 8.0, 0 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 72.4 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.1, 149.6, 123.9 (d, *J* = 24.2 Hz), 123.3, 110.9, 110.3,56.5, 56.4 ppm. GC-MS (EI) m/z = 220.0 ($M^+$). The analytical data are consistent with literature values.[3]

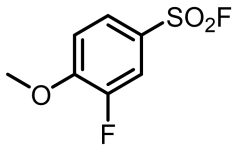



**4-phenoxybenzenesulfonyl fluoride (2k):** Obtained as colorless oil in 76% yield (76.6 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 4:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H) 7.27 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 12.0 Hz, 4H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.1 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 164.3, 154.4, 131.0, 125.9 (d, *J* = 25.3 Hz), 125.8, 120.8, 117.8 ppm. GC-MS (EI) m/z = 252.0 ($M^+$). The analytical data are consistent with literature values.[3]

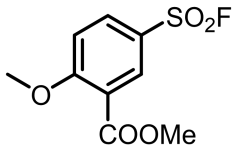



**formyl-4-methoxybenzenesulfonyl fluoride (2l):** Obtained as yellow solid (m.p. 77-79 ℃) in 70% yield (61.1 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 4:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 10.46 (s,1H), 8.45 (d, *J* = 0 Hz, 1H), 8.18 (dd, *J* = 0, 4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H),

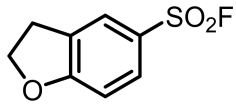
4.12 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 70.9 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 187.2, 166.3, 135.6, 129.9, 125.2 (d, *J* = 5.0 Hz), 125.0, 113.2, 56.9 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_8H_7FO_4S$ 218.0044; Found 218.0042.



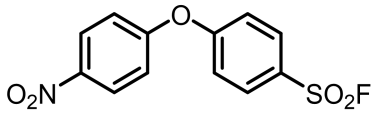

**3-fluoro-4-methoxybenzenesulfonyl fluoride (2m):** Obtained as white solid (m.p. 46-48 ℃) in 82% yield (68.2 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethan = 3:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, *J* =0, 4 Hz, 1H), 7.14 (t, *J* =8 Hz, 1H), 4.01 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.3 (s, 1F), -130.1 (t, *J* = 7.5 Hz, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 154.2 (d, *J* = 10.0 Hz), 153.1, 150.5, 126.5 (d, *J* = 4.0 Hz), 116.5 (d, *J* = 21.2 Hz), , 113.4 (d, *J* = 2.0 Hz), 56.8 ppm. HRMS (Dart positive) m/z: $[M+NH_4]^+$ Calcd for $C_8H_7FO_4S$ 226.0344; Found 226.0346. The analytical data are consistent with literature values.[4]



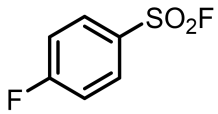

**methyl 5-(fluorosulfonyl)-2-methoxybenzoate (2n):** Obtained as yellow solid (m.p. 48-50 ℃) in 74% yield (73.4 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 3:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* =0 Hz, 1H), 8.06 (q, *J* =4 Hz, 1H), 7.16 (d, *J* =8 Hz, 1H), 4.01 (s, 3H), 3.90 (s, 3H).$^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.3 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 164.3 (d, *J* = 10.1 Hz), 133.9, 132.8, 124.4 (d, *J* = 25.3 Hz), 121.3, 112.5, 56.9, 52.7 ppm. HRMS (Dart positive) m/z: $[M+H]^+$ Calcd for $C_8H_7FO_4S$ 249.0227; Found 249.0227.



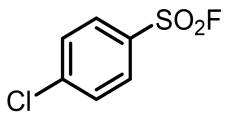
**2,3-dihydrobenzofuran-5-sulfonyl fluoride (2o):** Obtained as white solid in 65% yield (52.5 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethan = 2:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 4.74 (t, *J* = 8.0 Hz, 2H), 3.31 (t, *J* = 8.0 Hz, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.4 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 166.4, 130.7, 129.4, 125.8, 123.8 (d, *J* = 23.2 Hz), 110.2, 72.9, 28.9 ppm. GC-MS (EI) m/z=202.0 ($M^+$). The analytical data are consistent with literature values.[4]




**4-(4-nitrophenoxy)benzenesulfonyl fluoride (2p):** Obtained in 11% $^{19}$F NMR yield. Characterization of **2p** in reaction solution: Crude $^{19}$F NMR (376 MHz, unlocked): δ 66.3 (s, 1F) ppm. GC-MS (EI) m/z = 297.1 ($M^+$). Due to its lower yield, it was not purified by silica gel flash column chromatography from impurities. No further characterization data were provided. The compound was reported in the literature (B. R. Baker, G. J. Lourens, J. Med. Chem. 1969, 12, 95-101.), but no corresponding analytical data are available.

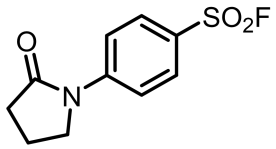



**4-fluorobenzenesulfonyl fluoride (2q):** Obtained in 84% $^{19}$F NMR yield. Due to its low boiling point, it can not be purified by silica gel flash column chromatography from impurities.

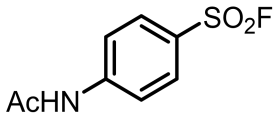



**4-chlorobenzenesulfonyl fluoride (2r):** Obtained as white solid in 57% yield (44.2 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethan = 8:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.5 (s, 1F) ppm. $^{13}$C NMR

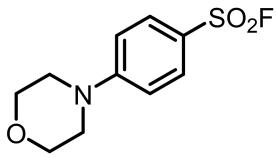
(101 MHz, $CDCl_3$): δ 142.8, 131.5 (d, *J* = 26.3 Hz), 130.3, 130.0 ppm. GC-MS (EI) m/z = 194.0 ($M^+$). The analytical data are consistent with literature values.[3]




4-**(2-oxopyrrolidin-1-yl)benzenesulfonyl fluoride (2s):** Obtained as yellow solid (m.p. 104-106 ℃) in 73% yield (71.0 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 2:1 v/v). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 4H), 3.86 (t, *J* =8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.21-2.13 (m, 2H). $^{19}F$ NMR (376 MHz, $CDCl_3$): δ 66.9 (s, 1F) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 175.2, 145.7, 129.4, 126.4 (d, *J* = 26.3 Hz), 119.0, 48.2, 32.7, 17.6 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{10}H_{10}FNO_3S$ 243.0360; Found 243.0364.

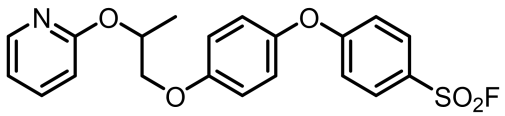



**4-acetamidobenzenesulfonyl fluoride (2t):** Obtained as white solid in 78% yield (67.7 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 1:1 v/v. $^1H$ NMR (400 MHz, $CD_3CN$): δ 8.83 (br, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 2.12 (s, 3H). $^{19}F$ NMR (376 MHz, $CD_3CN$): δ 65.6 (s, 1F) ppm. $^{13}C$ NMR (101 MHz, $CD_3CN$): δ 170.5,147.0, 130.9, 126.2 (d, *J* = 24.2 Hz), 120.0, 24.6 ppm. GC-MS (EI) m/z = 217.0 ($M^+$). The analytical data are consistent with literature values.[3]




**4-morpholinobenzenesulfonyl fluoride (2u):** Obtained as yellow solid (m.p. 98-100 ℃) in 45% yield (44.1 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 3:1 v/v. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.82 (q, *J* =12.0 Hz, 2H), 6.92 (d, *J* =8.0 Hz, 2H), 3.85 (t, *J* =8.0 Hz, 4H), 3.36 (t, *J* =8.0 Hz,

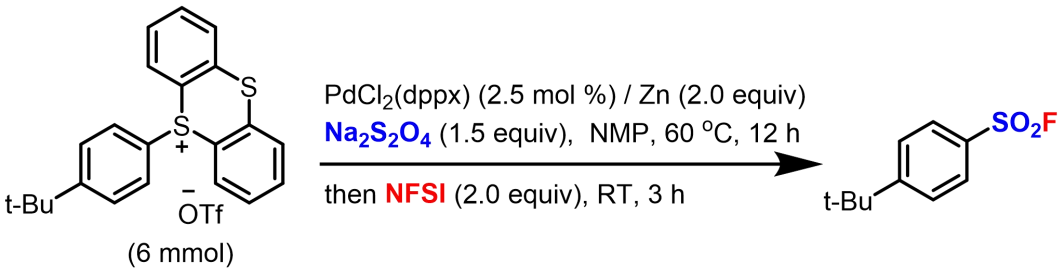
4H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.8 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.6, 130.6, 120.1 (d, *J* = 30.0 Hz),113.4, 66.4, 47.0 ppm. HRMS (FI) m/z: [M] $^+$ Calcd for $C_{10}H_{12}FNO_3S$ 245.0516; Found 245.0515.




**4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)benzenesulfonyl fluoride (2v):** Obtained as white solid (m.p. 58-60 ℃) in 65% yield (104.8 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 10:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* =4.0 Hz, 1H), 7.89 (d, *J* =8.0 Hz, 2H), 7.54 (d, *J* =8.0 Hz, 2H), 7.40 (t, *J* =8.0 Hz, 1H), 6.99 (s, 4H), 6.85 (t, *J* =8.0 Hz, 1H), 6.74 (d, *J* =8.0 Hz, 1H), 5.60 (m, 1H), 4.20 (m, 1H), 4.10 (m, 1H), 1.48 (d, *J* =4.0 Hz, 3H).$^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.2 (s, 1F) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): δ 164.9, 163.1, 156.7, 147.7, 146.8, 141.4, 138.8, 130.9, 129.9, 129.0, 128.4, 124.5, 121.9, 117.1, 116.9, 116.3, 111.7, 71.0, 69.2, 17.0 ppm. HRMS (Dart positive) m/z: [M+ H] $^+$ Calcd for $C_{20}H_{18}FNO_5S$ 404.0962; Found 404.0962.

## Ⅶ. Scale-up and derivatization reactions of 2a

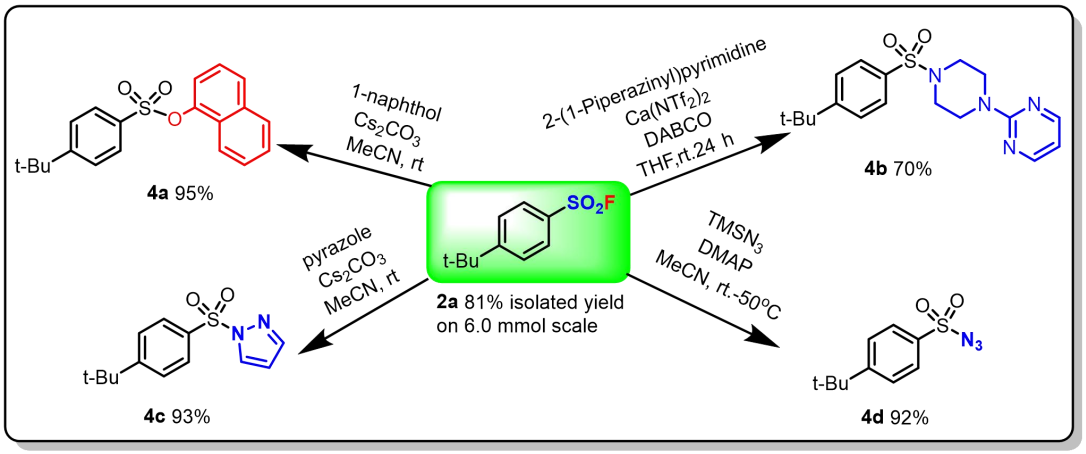
### 1. Gram-scale synthesis of 4-(tert-butyl)benzenesulfonyl fluoride (2a)




**1a** **2a**

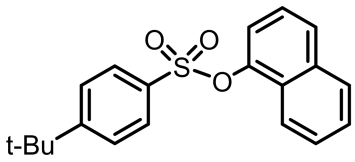
To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added tert-butylthianthrenium salt **1a** (6.0 mmol, 1.0 equiv.), $Na_2S_2O_4$ (9 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.15 mmol, 2.5 mol %), Zinc (12 mmol, 2.0 equiv.). The tube was then evacuated and backfilled with Ar (3 times) and NMP (N-Methyl-2-pyrrolidinone) (4.0 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at 60 ℃ for 12 h. NFSI (12 mmol, 2.0 equiv.) was added when the mixture is cooled to room temperature, and then stirred at room temperature for 3 h. The reaction mixture was filtered through a pad of celite, diluted with DCM (20 mL) and $H_2O$ (50 mL). The resulting mixture was extracted with DCM (2 × 20 mL). The organic layers were combined, washed with brine (50 mL), dried over $Na_2SO_4$. filtered and concentrated. The crude product was purified by silica gel chromatography to give the desired product **2a** (1.05 g, 81%).

## 2. Derivatization of 4-(tert-butyl)benzenesulfonyl fluoride 2a with various O- or N-nucleophiles.




### (a) The procedure for the preparation of 4a[6]

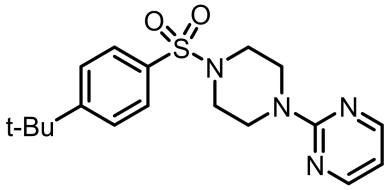
A 10 mL sealed tube equipped with a magnetic stirring bar was charged with **2a** (0.3 mmol, 1.0 equiv.), 1-naphthalenol (0.6 mmol, 2.0 equiv.), $Cs_2CO_3$ (0.33 mmol, 1.1 equiv.) and anhydrous MeCN (3 mL). The reaction mixture was stirred vigorously at room temperature under Ar atmosphere for 12 h. The resulting mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.



**naphthalen-1-yl 4-(tert-butyl)benzenesulfonate:** Obtained as white solid in 95% yield (96.9 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethan = 2:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.85-7.80 (m, 4H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.48-7.41 (m, 3H), 7.39-7.37 (m, 2H),7.28 (d, *J* = 8.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 158.5, 145.8, 134.7, 132.6, 128.3, 127.7, 127.3, 127.1, 126.6 (d, *J* = 5.0 Hz), 126.2, 125.2, 121.7, 118.7, 35.3, 31.0 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{20}O_3S$ 340.1128; Found 340.1127.

**(b) The procedure for the preparation of 4b[7]**

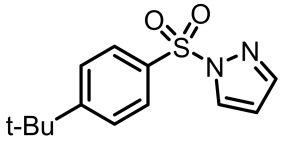
A 10 mL sealed tube equipped with a magnetic stirring bar was charged with **2a** (0.4 mmol, 1.0 equiv.), 2-(1-Piperazinyl)pyrimidine (0.44 mmol, 1.1 equiv.), $Ca(NTf_2)_2$ (0.44 mmol, 1.1 equiv.), DABCO (0.6 mmol, 1.5 equiv.) and anhydrous THF (4 mL). The reaction mixture was stirred vigorously at room temperature under Ar atmosphere for 24 h. The resulting mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.




**2-(4-((4-(tert-butyl)phenyl)sulfonyl)piperazin-1-yl)pyrimidine:** Obtained as white solid (m.p. 188-190 ℃) in 70% yield (100.8 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 3:1 v/v. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 4.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 6.46 (t, *J* = 4.0 Hz, 1H), 3.90 (t, *J* = 4.0 Hz, 4H), 3.04 (t, *J* = 4.0 Hz, 4H), 1.29 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 161.2, 157.8, 156.7, 132.4, 127.7, 126.1, 110.5, 46.0, 43.0, 35.2, 31.1 ppm. HRMS (Dart positive) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}FN_4O_2S$ 361.1693; Found 361.1693.

**(c) The procedure for the preparation of 4c[6]**

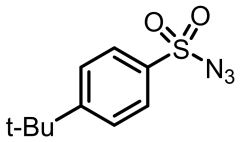
A 10 mL sealed tube equipped with a magnetic stirring bar was charged with **2a** (0.3 mmol, 1.0 equiv.), Pyrazole (0.6 mmol, 2.0 equiv.), $Cs_2CO_3$ (0.33 mmol, 1.1 equiv.) and anhydrous MeCN (3 mL). The reaction mixture was stirred vigorously at room temperature under Ar atmosphere for 12 h. The resulting mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.




**1-((4-(tert-butyl)phenyl)sulfonyl)-1H-pyrazole:** Obtained as white solid (m.p. 98-100 ℃) in 93% yield (73.6 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 10:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 4.0 Hz, 1H), 7.92 (d, *J* = 12.0 Hz, 2H), 7.72 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 6.39 (s, 1H), 1.30 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 158.8, 145.3, 134.0, 131.2, 128.1, 126.6, 108.8, 35.4, 31.0 ppm. HRMS (Dart positive) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}N_2O_2S$ 265.1005; Found 265.1005.

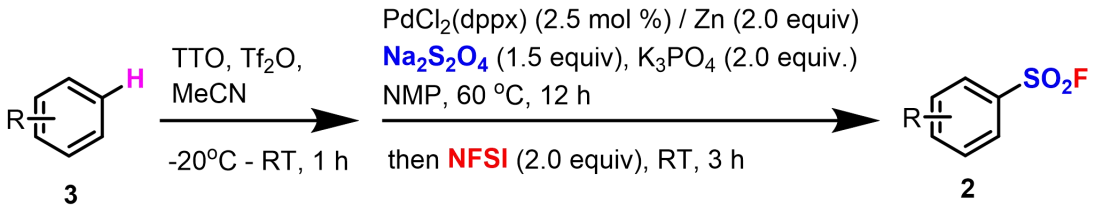
**(d) The procedure for the preparation of 4d[8]**

A 10 mL sealed tube equipped with a magnetic stirring bar was charged with **2a** (0.4 mmol, 1.0 equiv.), Azidotrimethylsilane (0.6 mmol, 1.5 equiv.), DMAP (0.6 mmol, 1.5 equiv.) and anhydrous MeCN (4 mL). The reaction mixture was stirred vigorously at 50℃ under Ar atmosphere for 8 h. The resulting mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.



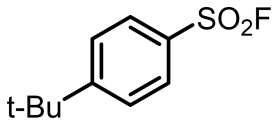

**(tert-butyl)benzenesulfonyl azide:** Obtained as colorless oil in 92% yield (88.0 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 4:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 1.36 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 159.2, 135.5, 127.5, 126.8, 35.5, 31.0 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{10}H_{13}N_3O_2S$ 239.0723; Found 239.0726.

## Ⅷ. General procedure for one-pot fluorosulfonylation starting from arenes

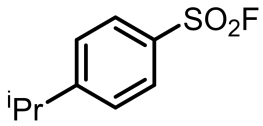



**General Procedure**: A 25 mL Schlenk tube was charged with thianthrene S-oxide (111.4 mg, 0.48 mmol, 1.2 equiv.), $CH_3CN$ (1.0 mL) and **3** (0.4 mmol, 1.0 equiv.) under Ar atmosphere. The reaction mixture was then cooled to -20 °C, followed by the addition of $Tf_2O$ (80 μL, 0.48 mmol, 1.2 equiv.) dropwise. The reaction mixture was stirred at the same temperature for 30 min, and then allowed to stir at room temperature for another 30 minutes. $K_3PO_4$ (170.0 mg, 0.8 mmol, 2.0 equiv.) was added to neutralize the reaction mixture for 2.0 h. After that, NMP (4.0 mL), $Na_2S_2O_4$ (174.1 mg, 0.6 mmol, 1.5 equiv.), $PdCl_2$(dppx) (7.6 mg, 0.01 mmol, 2.5 mol %), zinc (52.3 mg, 0.8 mmol, 2.0 equiv.) were added under Ar atmosphere. The reaction mixture was stirred in preheated oil bath (60 ℃) for 12 hours. Then NFSI (252.3 mg, 0.8 mmol, 2.0 equiv.) was added and the reaction mixture was stirred smoothly at room temperature for 3 h. Upon completion, the reaction mixture was filtered through a pad of celite, diluted with DCM (20 mL) and $H_2O$ (50 mL). The resulting mixture was extracted with DCM (2 × 20 mL). The organic layers were combined, washed with brine (50 mL), dried over $Na_2SO_4$. filtered and concentrated. The crude product was purified by silica gel chromatography to give the desired product **2**.

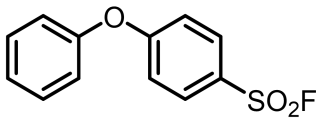
## Ⅸ. Analytical data for compounds 2a, 2c, 2k, 2n



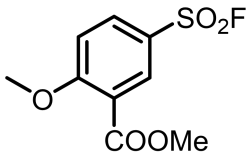

**4-(tert-butyl)benzenesulfonyl fluoride (2a):** Obtained as white solid in 81% yield (70.0 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 8:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 1.37 (s, 9H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.2 (s, 1F) ppm.




**4-isopropylbenzenesulfonyl fluoride (2c):** Obtained as colorless oil in 80% yield (64.6 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 8:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 3.04 (m, *J* = 8.0 Hz, 1H), 1.29 (d, *J* = 8.0 Hz, 6H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 66.2 (s, 1F) ppm.



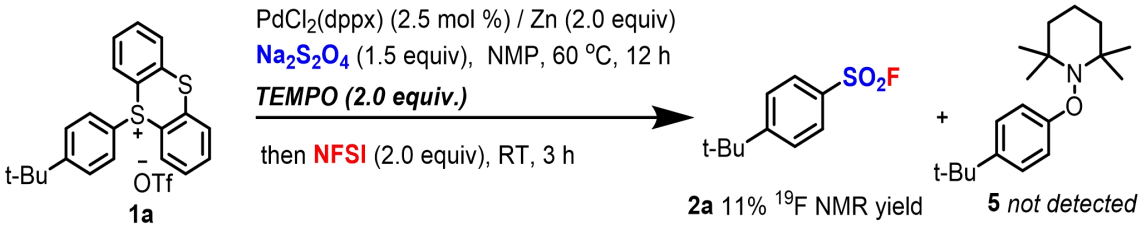

**4-phenoxybenzenesulfonyl fluoride (2k):** Obtained as colorless oil in 70% yield (70.6 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 4:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H) 7.27 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 12.0 Hz, 4H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.1 (s, 1F) ppm.



**methyl 5-(fluorosulfonyl)-2-methoxybenzoate (2n):** Obtained as yellow solid in 86% yield (85.3 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 3:1 v/v. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* =0 Hz, 1H), 8.06 (q, *J* =4 Hz, 1H), 7.16 (d, *J* =8 Hz, 1H), 4.01 (s, 3H), 3.90 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$): δ 67.3 (s, 1F) ppm.

# Ⅹ. Preliminary mechanistic studies

## 1. Radical inhibition experiments




To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added tert-butylthianthrenium salt **1a** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), $PdCl_2$(dppx) (0.005 mmol, 2.5 mol %), Zinc (0.4 mmol, 2 equiv.), TEMPO (0.4 mmol, 2 equiv.). The tube was then evacuated and backfilled with Ar (3 times) and NMP (N-Methyl-2-pyrrolidinone) (2.0 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at 60 ℃ for 12 h. Then NFSI (0.4 mmol, 2.0 equiv.) was added and the reaction mixutre was stirred smoothly at room temperature for 3 h. The crude reaction mixture was then analyzed by $^{19}F$ NMR spectroscopy and HRMS.

## XI. Reference


[1] X.-X. Nie, Y.-H. Huang and P. Wang, Thianthrenation-Enabled α-Arylation of Carbonyl Compounds with Arenes. *Org. Lett*. **2020** *22* (19), 7716-7720.

[2] Z.-Y. Tian, Z.-H. Lin, and C.-P. Zhang, Pd/Cu-Catalyzed C-H/C-H Cross Coupling of (Hetero)Arenes with Azoles through Arylsulfonium Intermediates. *Org. Lett.* **2021**, *23* (11), 4400-4405.

[3] Y. Liu, D. Yu, Y. Guo, J.-C. Xiao, Q.-Y. Chen, and C. Liu, Arenesulfonyl Fluoride Synthesis via Copper-Catalyzed Fluorosulfonylation of Arenediazonium Salts. *Org. Lett*. **2020**, *22* (6), 2281-2286.

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[5] Q. Pan, Y. Liu, W. Pang, J. Wu, X. Ma, X. Hu, Y. Guo, Q.-Y. Chen and C. Liu, Copper-catalyzed three-component reaction of arylhydrazine hydrochloride, DABSO, and NFSI for the synthesis of arenesulfonyl fluorides. *Org. Biomol. Chem*. **2021**,*19*, 8999-9003.

[6] A. L. Tribby, I. Rodríguez, S. Shariffudin, and N. D. Ball, Pd-Catalyzed Conversion of Aryl Iodides to Sulfonyl Fluorides Using $SO_2$ Surrogate DABSO and Selectfluor. *J. Org. Chem*. **2017**, *82*, 2294−2299.

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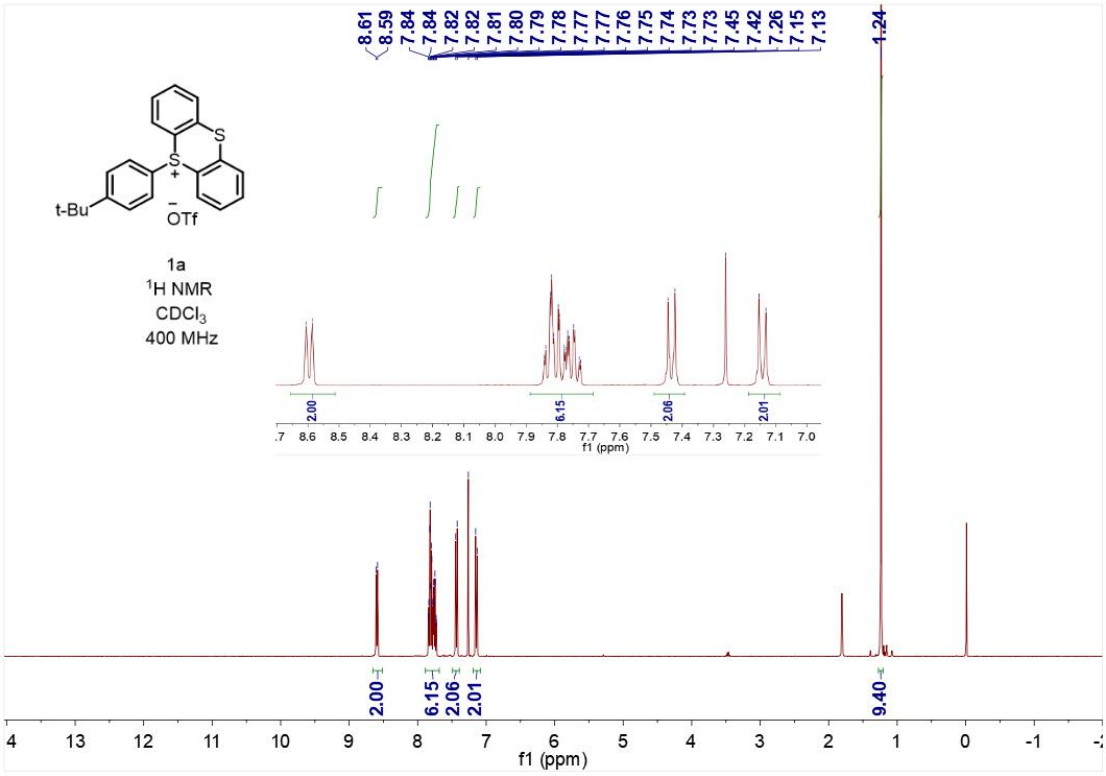
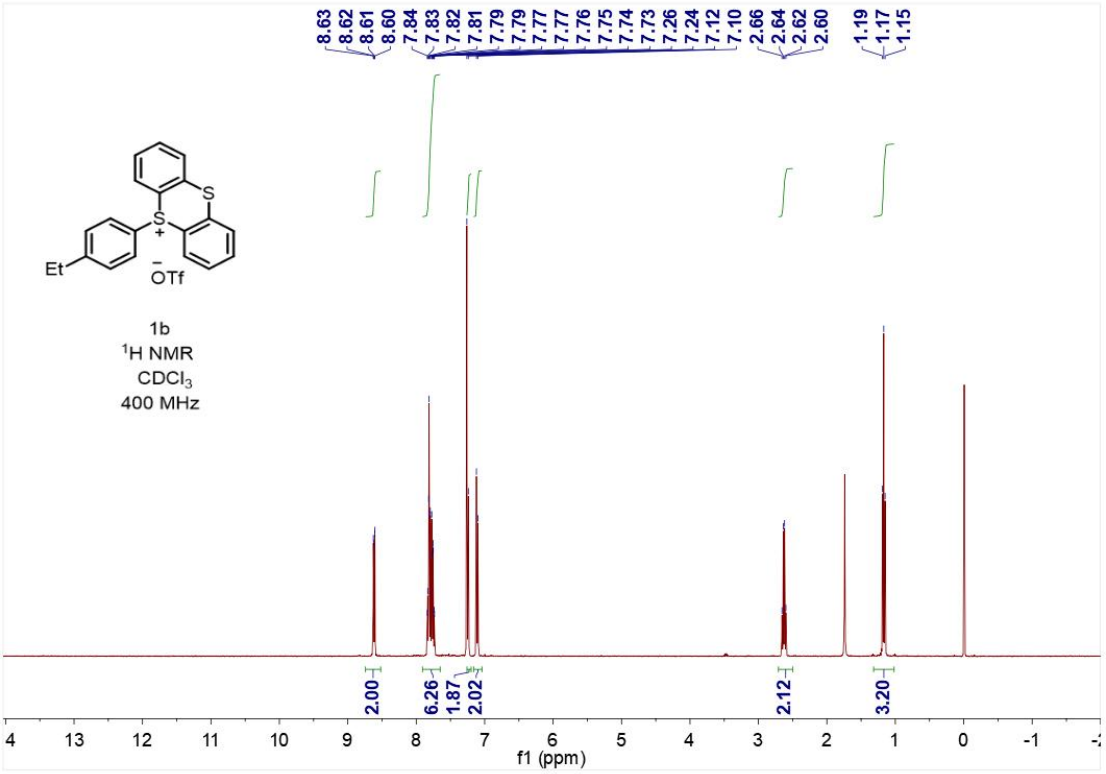
[8] A. S. Barrow and J. E. Moses, Synthesis of Sulfonyl Azides via Lewis Base Activation of Sulfonyl Fluorides and Trimethylsilyl Azide. *Synlett.* **2016**, *27*, 1840−1843.

# Ⅻ. Copies of $^{1}H$, $^{19}F$, and $^{13}C$ NMR spectra

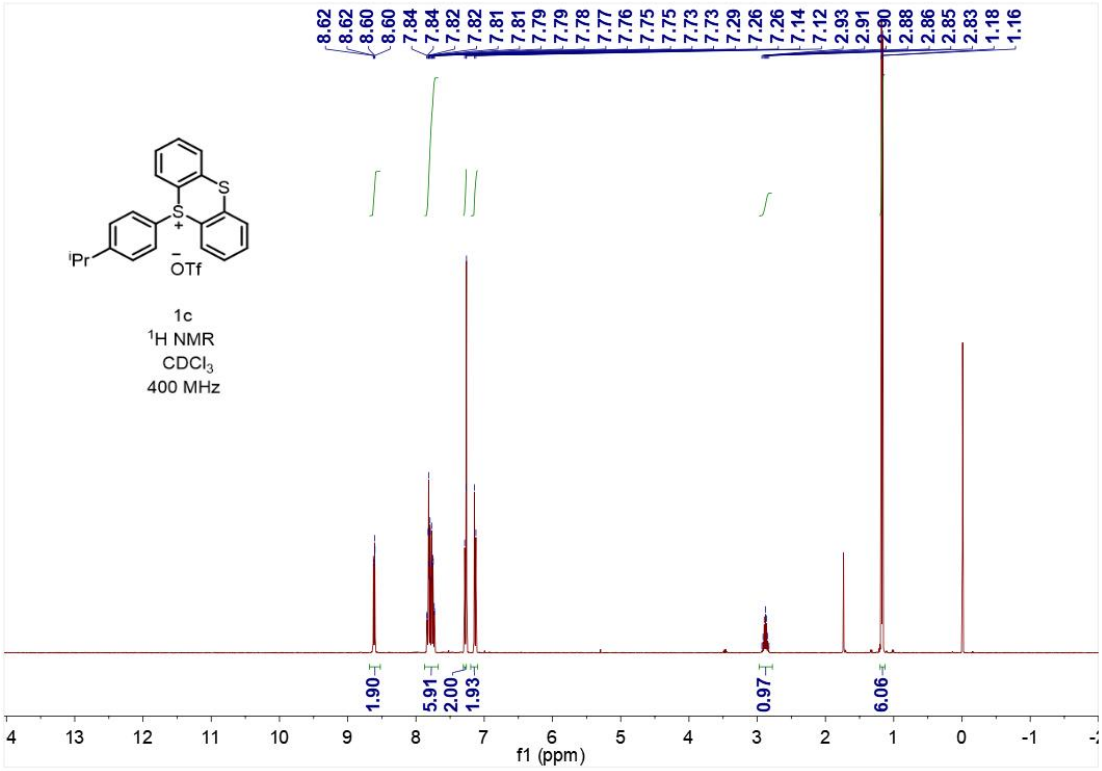
$^{1}$H NMR spectrum of **1a**



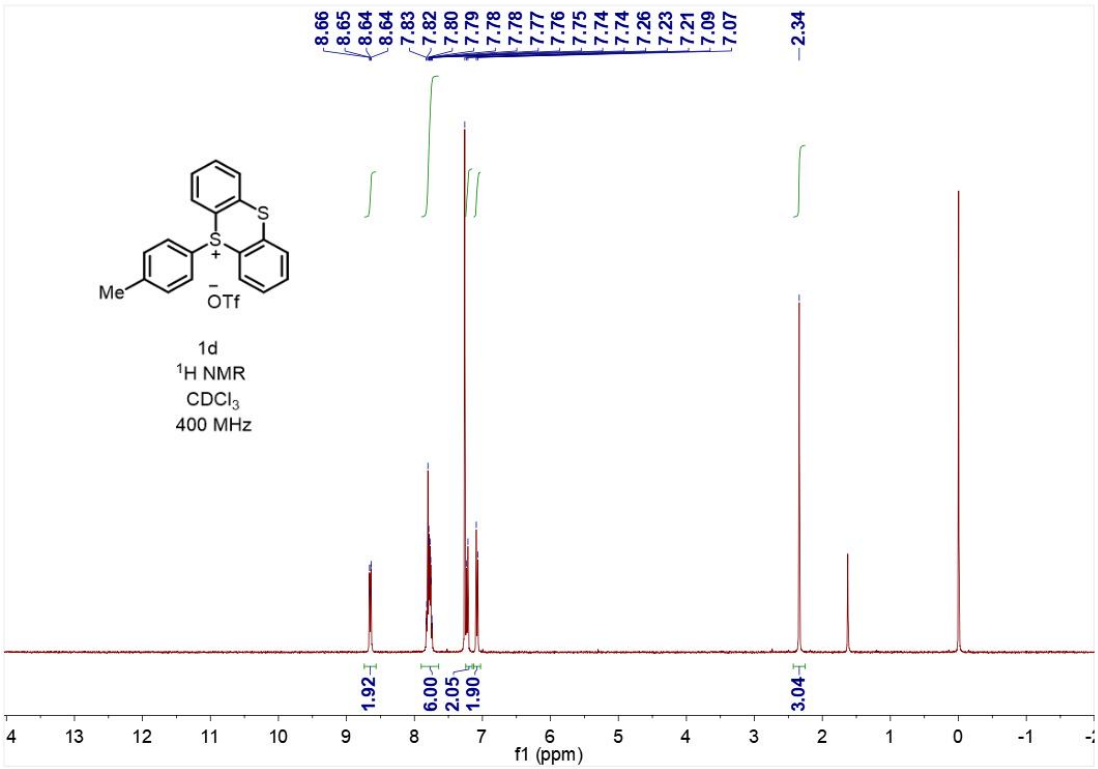

$^{1}$H NMR spectrum of **1b**



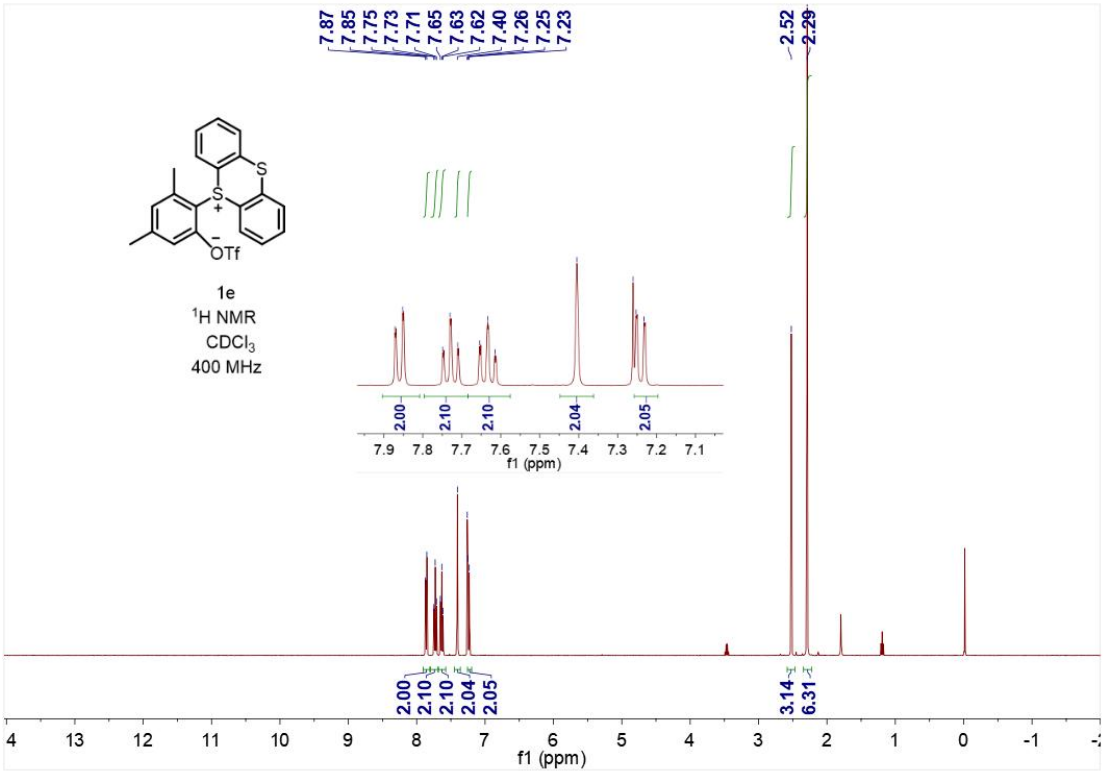
[1] H NMR spectrum of **1c**



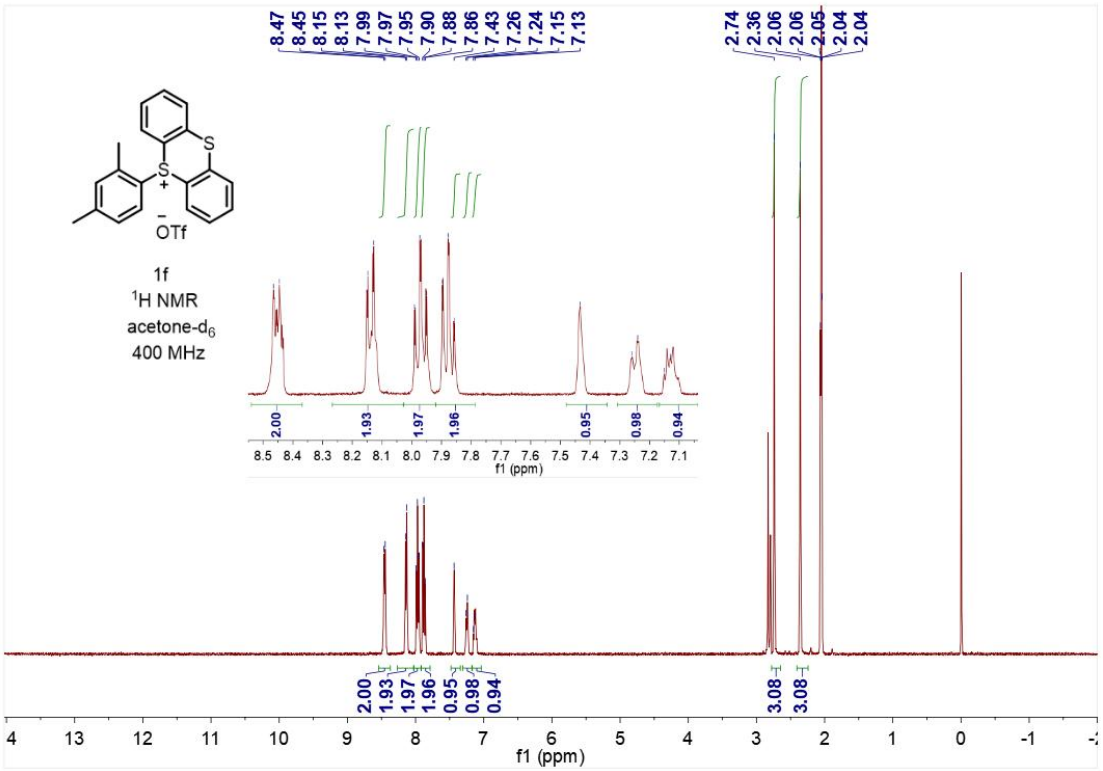

[1] H NMR spectrum of **1d**



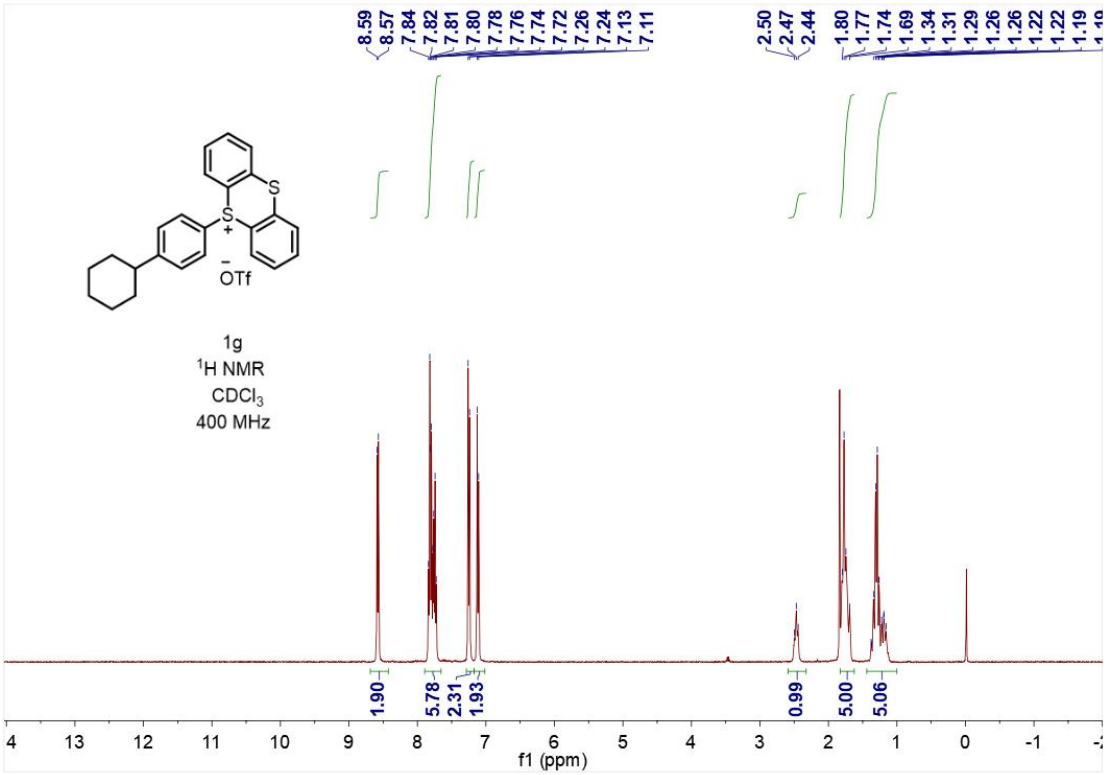
[1] H NMR spectrum of **1e**



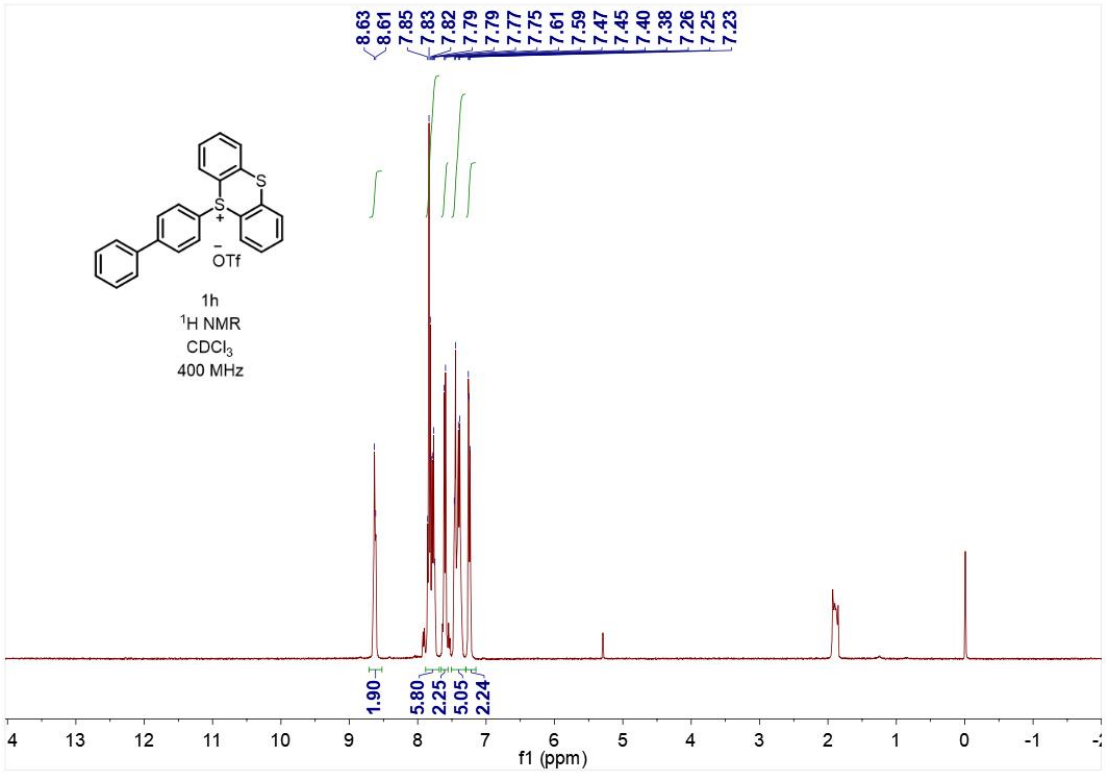

[1] H NMR spectrum of **1f**



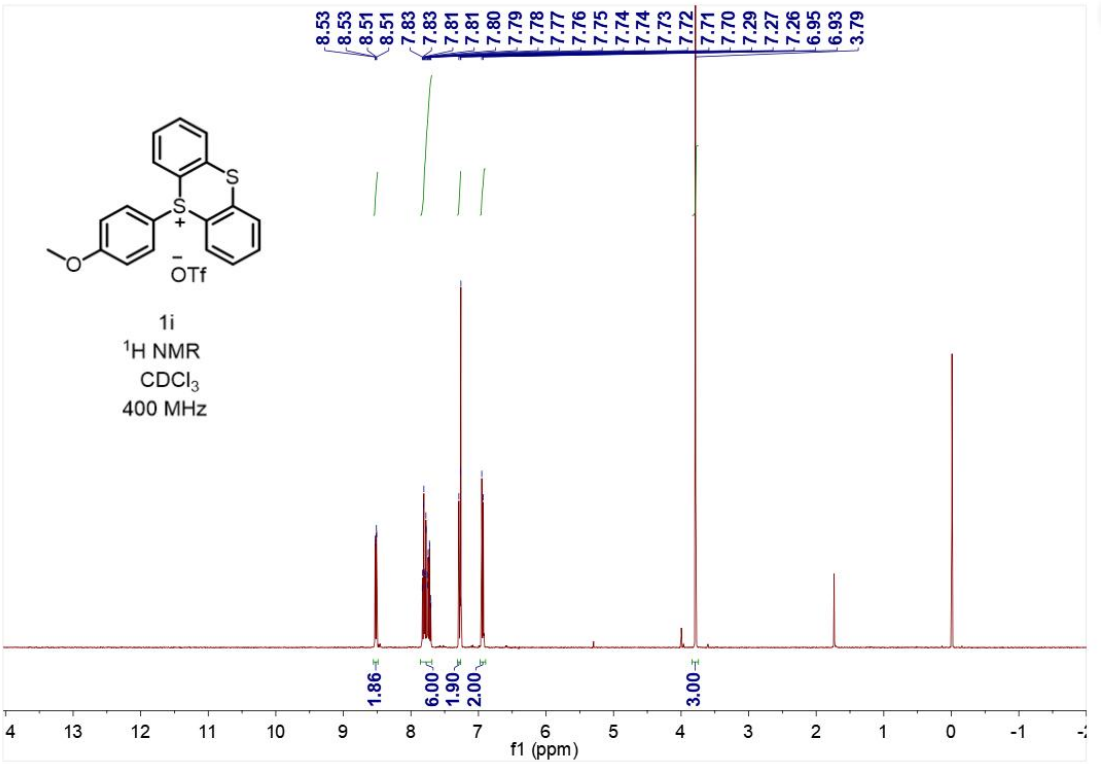
[1] H NMR spectrum of **1g**



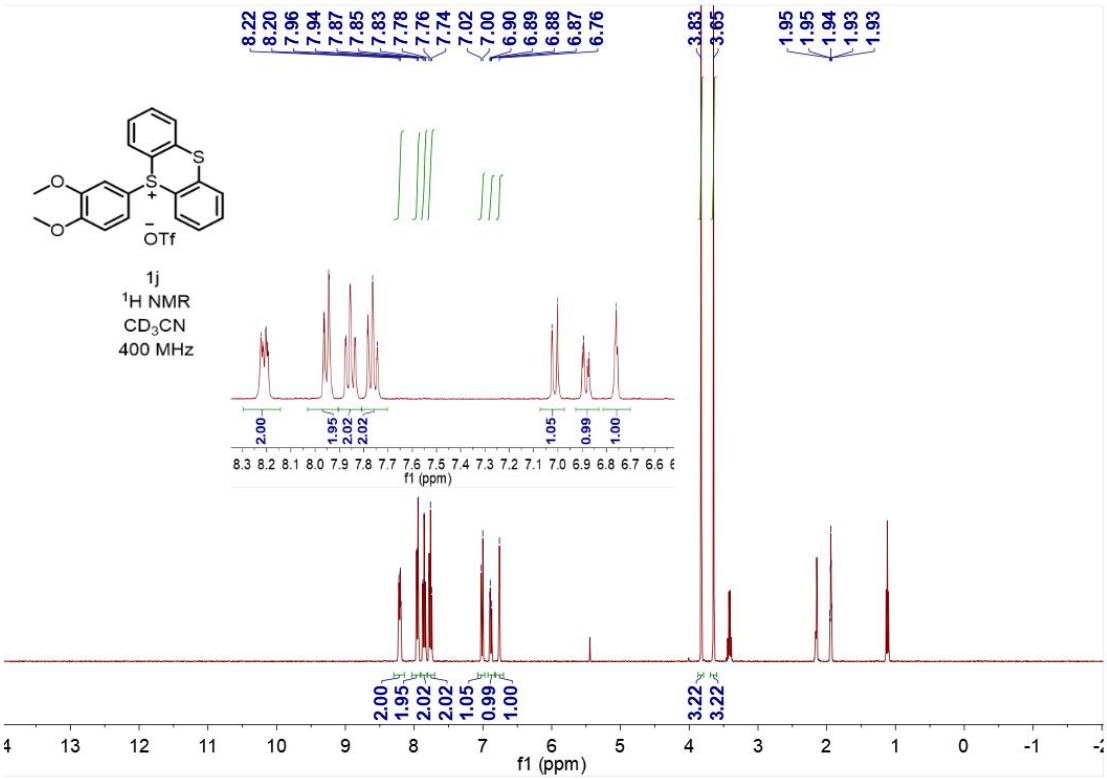

[1] H NMR spectrum of **1h**



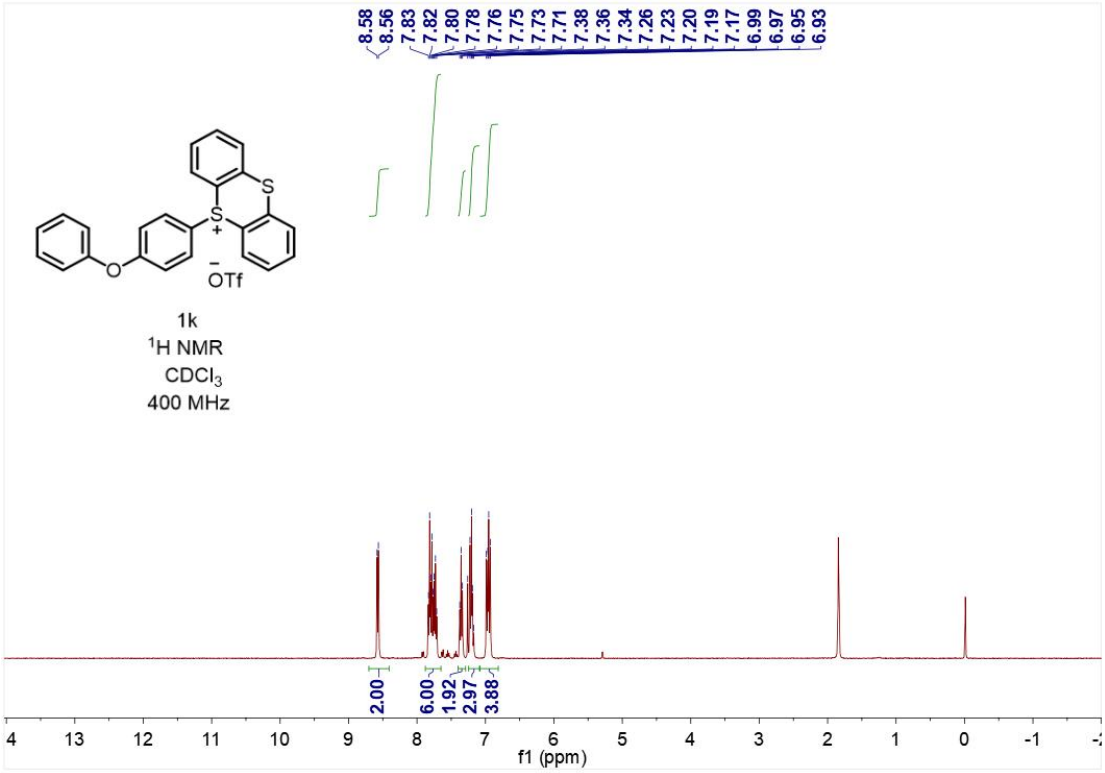
[1] H NMR spectrum of **1i**



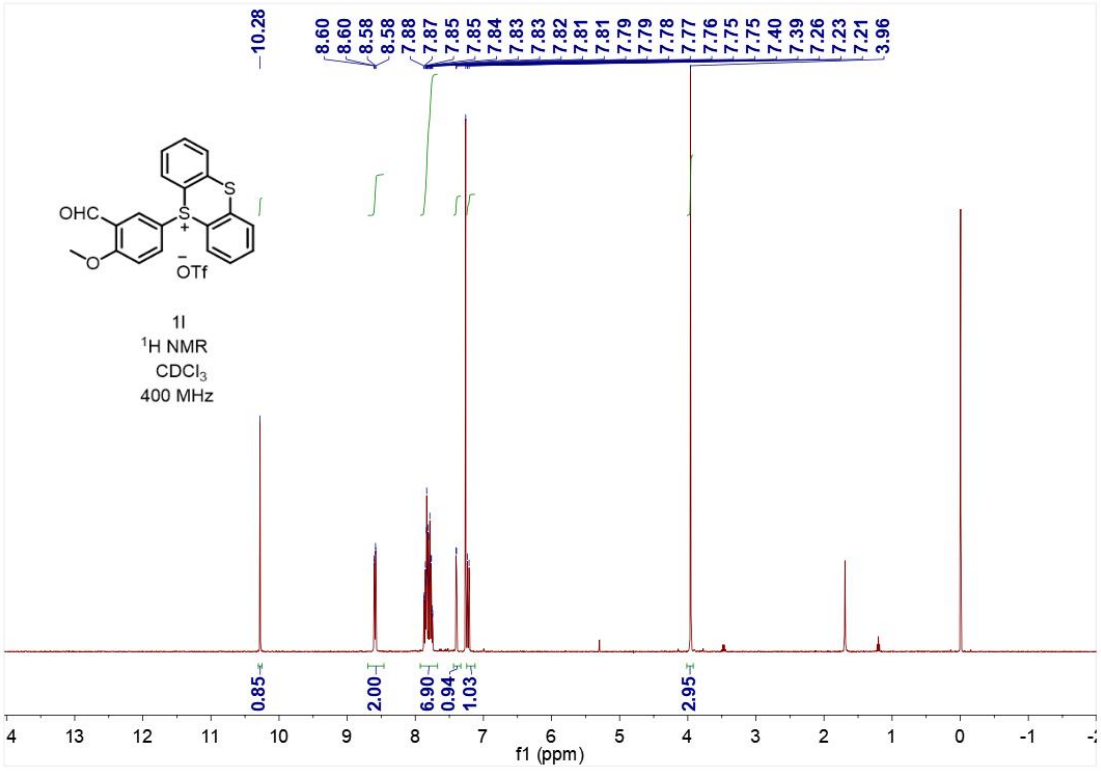

[1] H NMR spectrum of **1j**



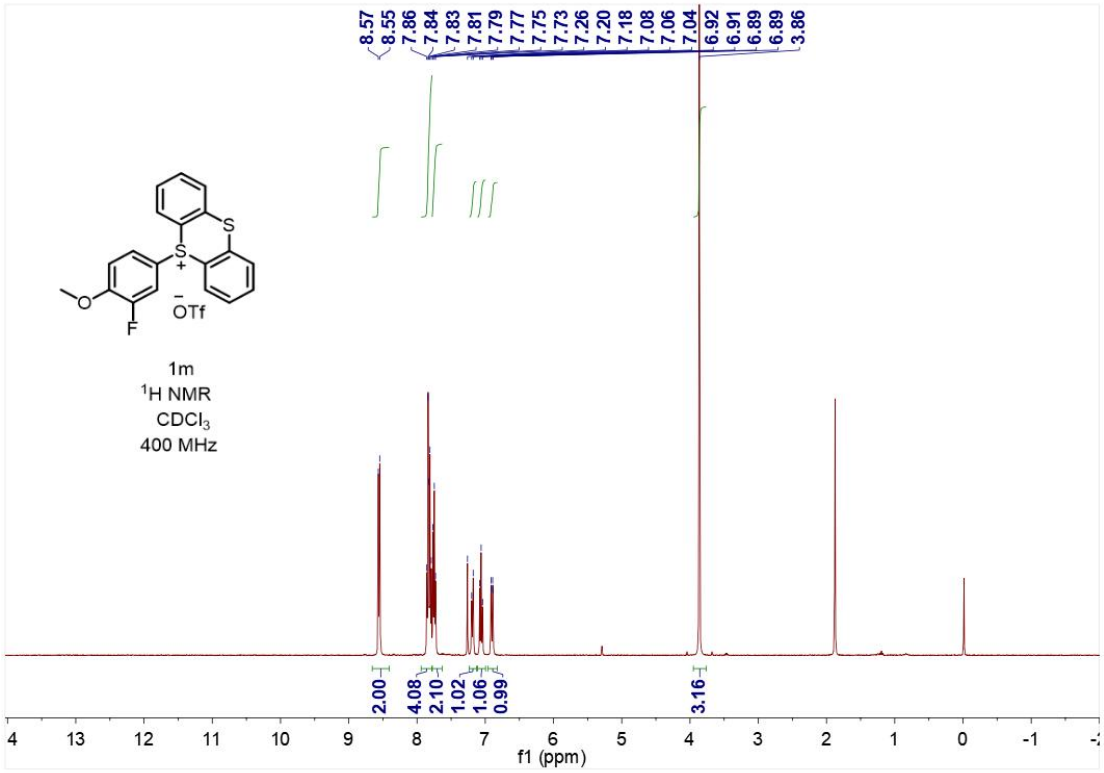
$^{1}$H NMR spectrum of **1k**



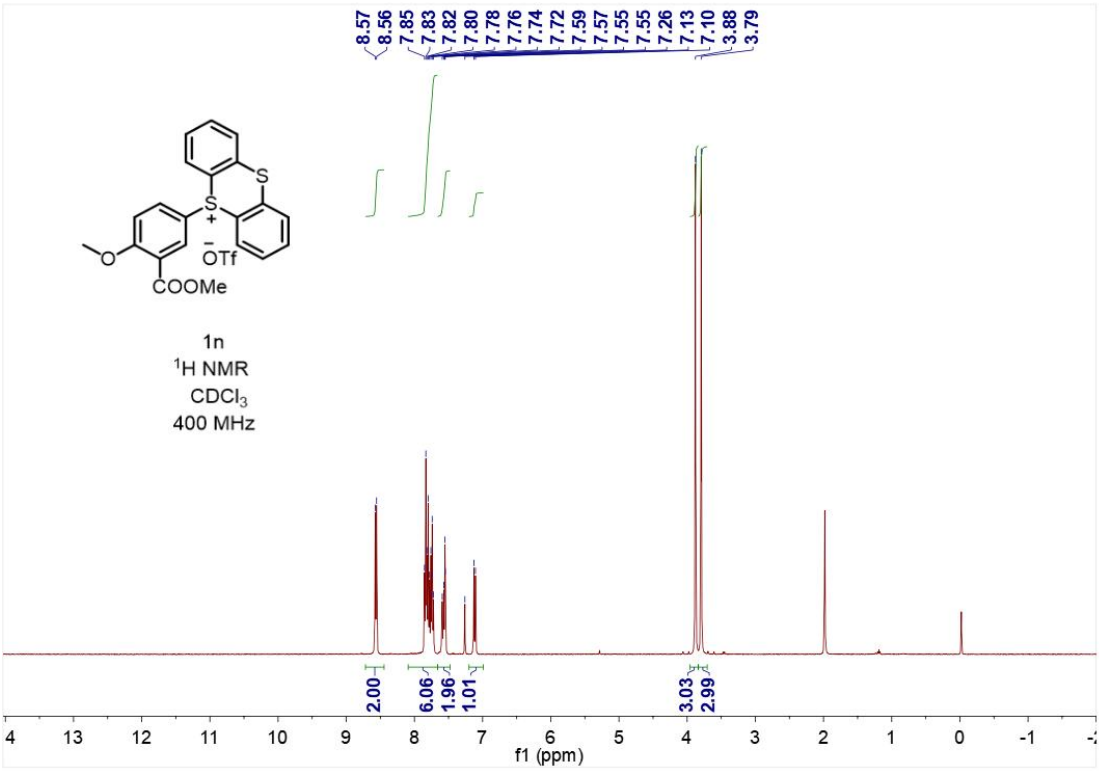

$^{1}$H NMR spectrum of **1l**



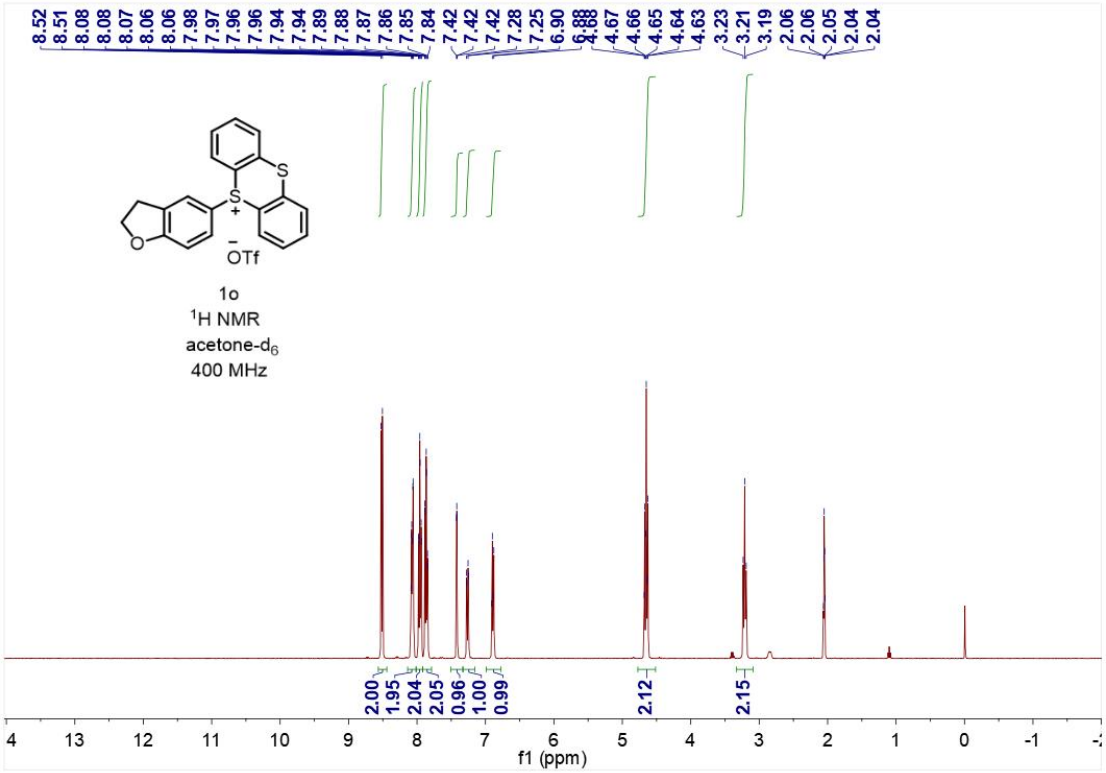
[1] H NMR spectrum of **1m**



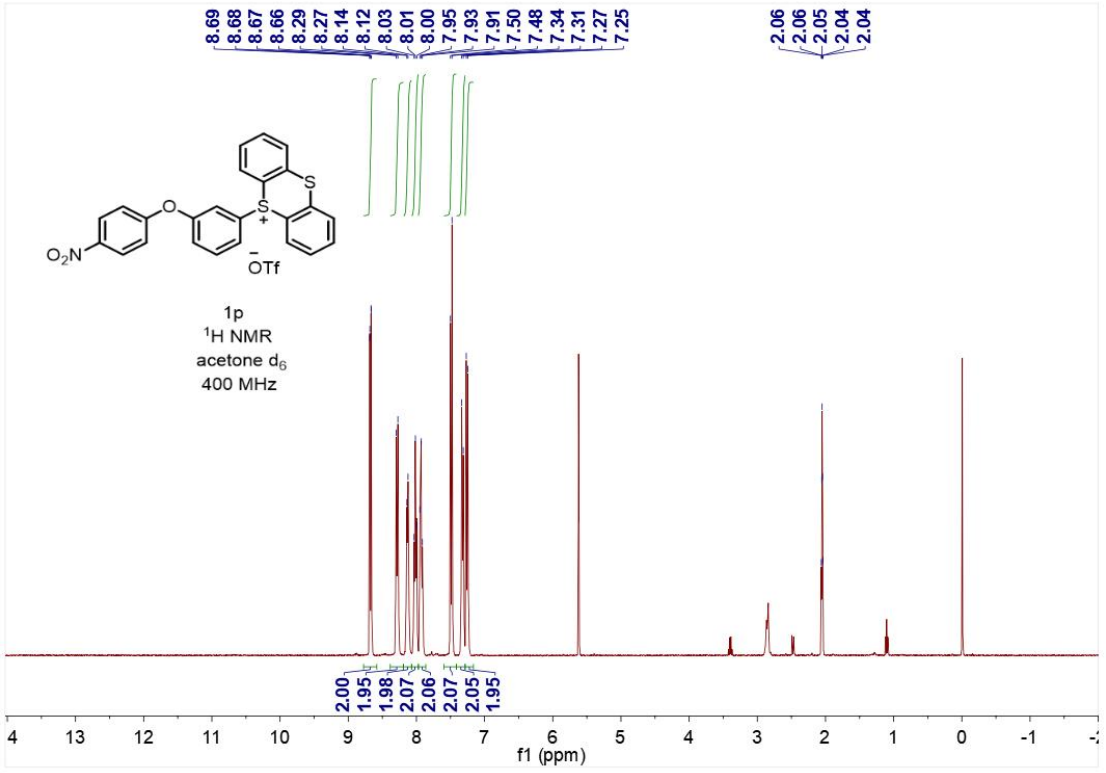

[1] H NMR spectrum of **1n**



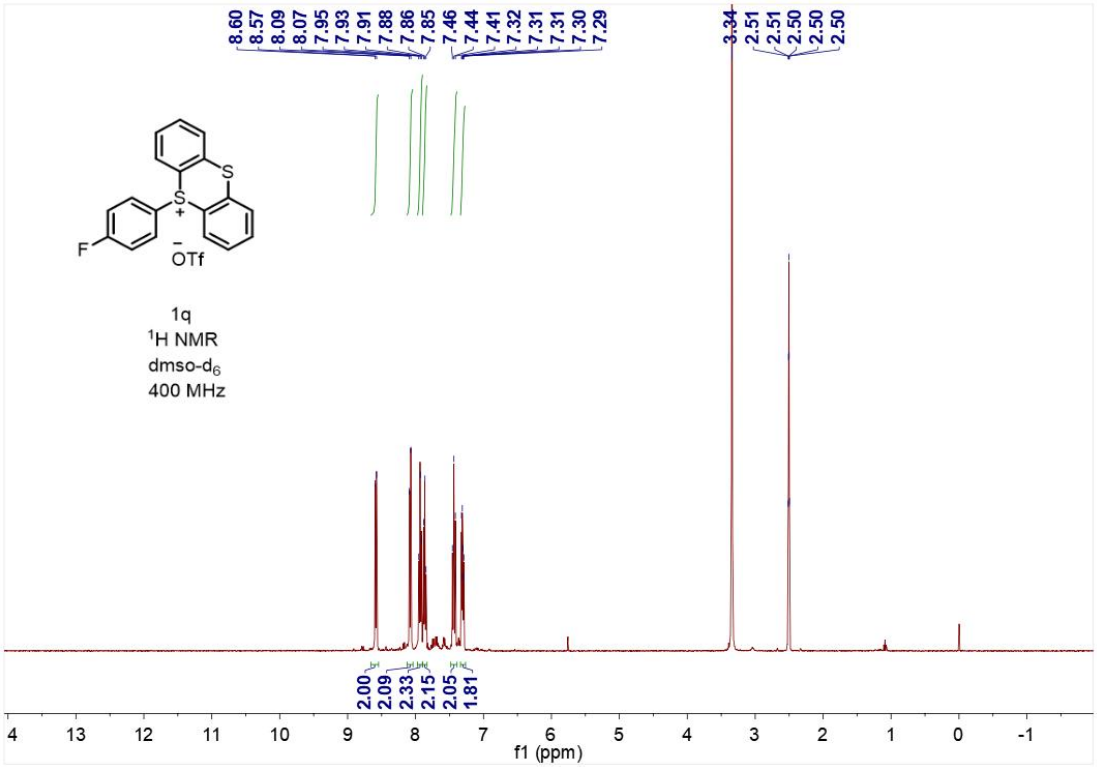
[1] H NMR spectrum of **1o**



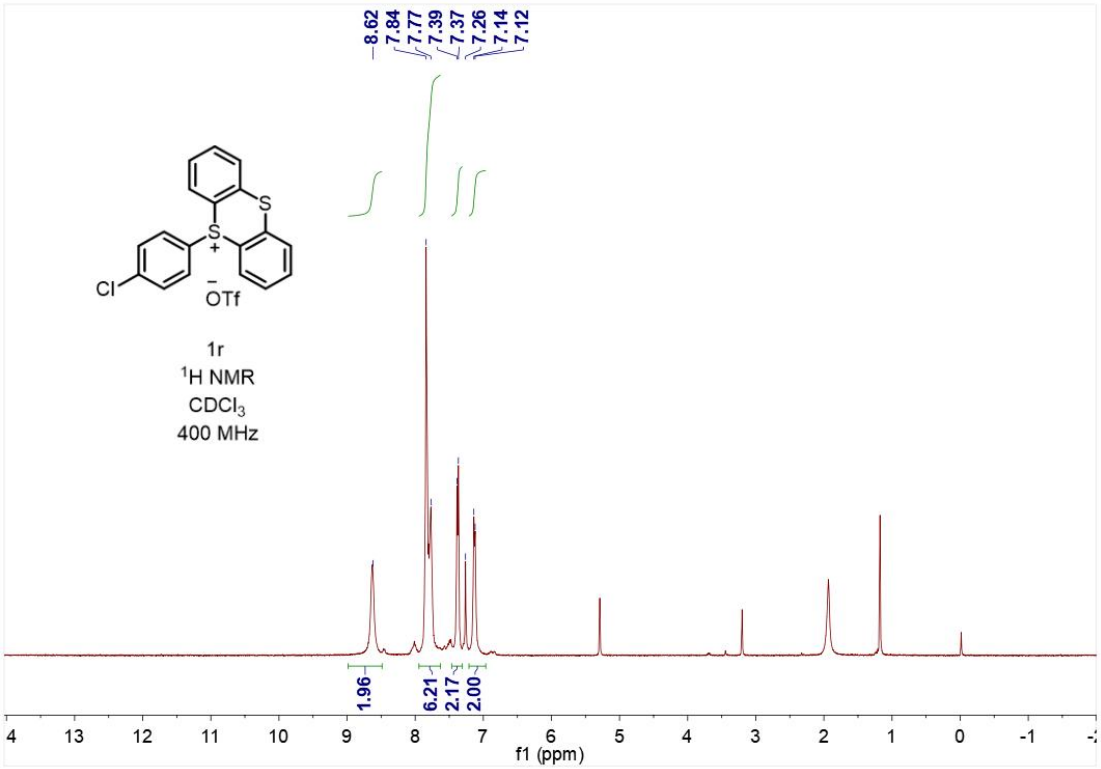

[1] H NMR spectrum of **1p**



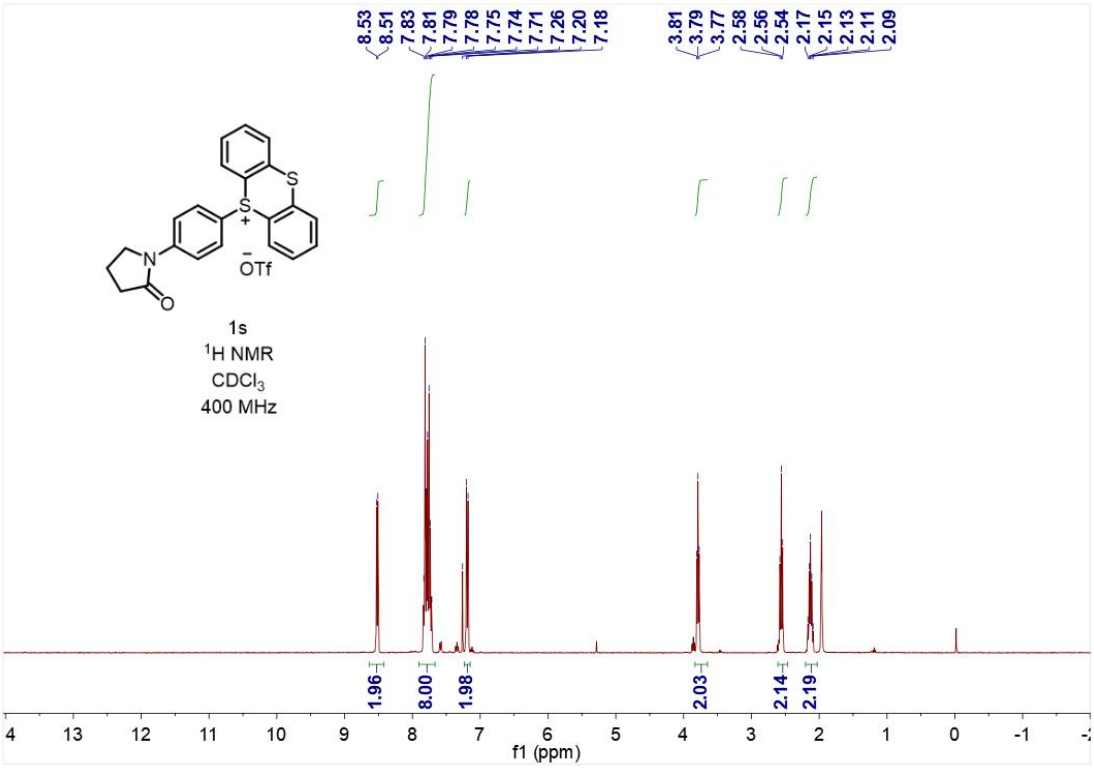
[1] H NMR spectrum of **1q**



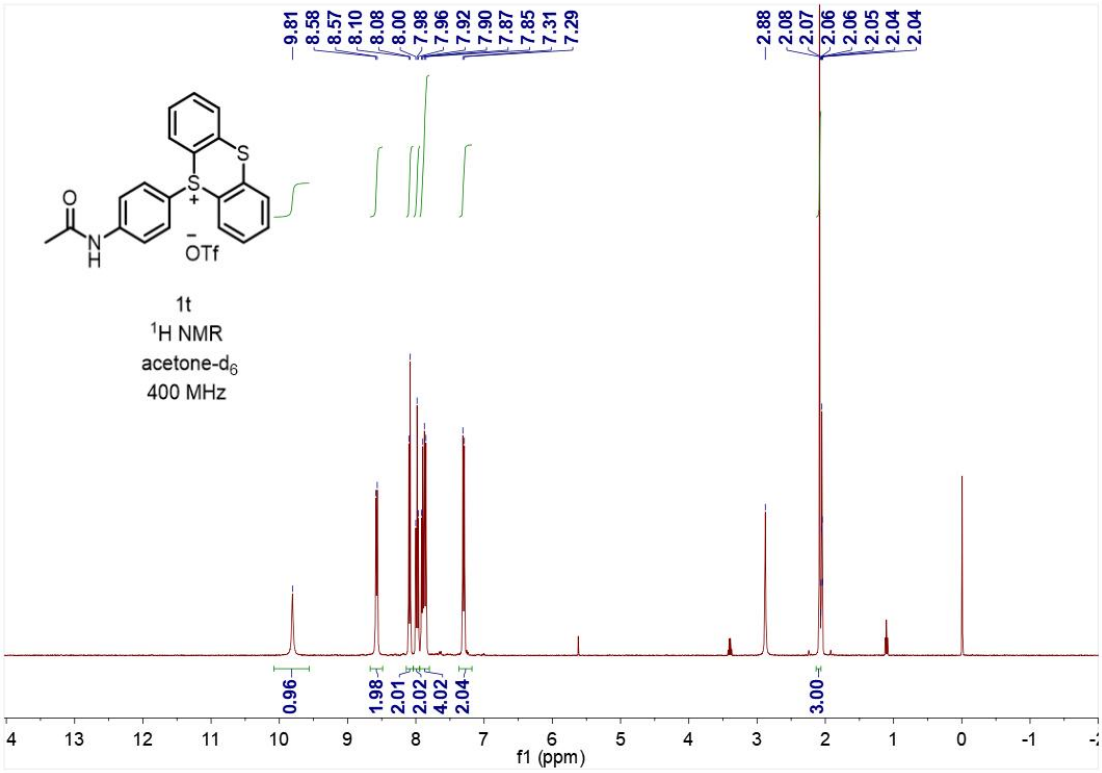

[1] H NMR spectrum of **1r**



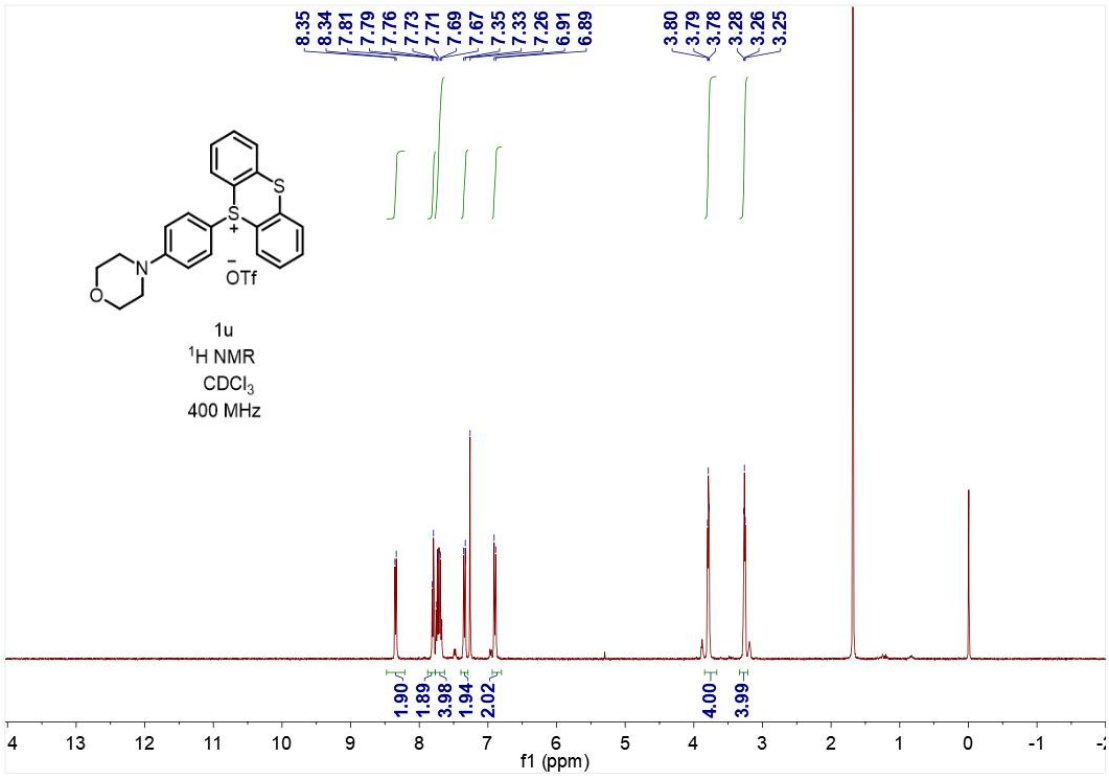
[1] H NMR spectrum of **1s**



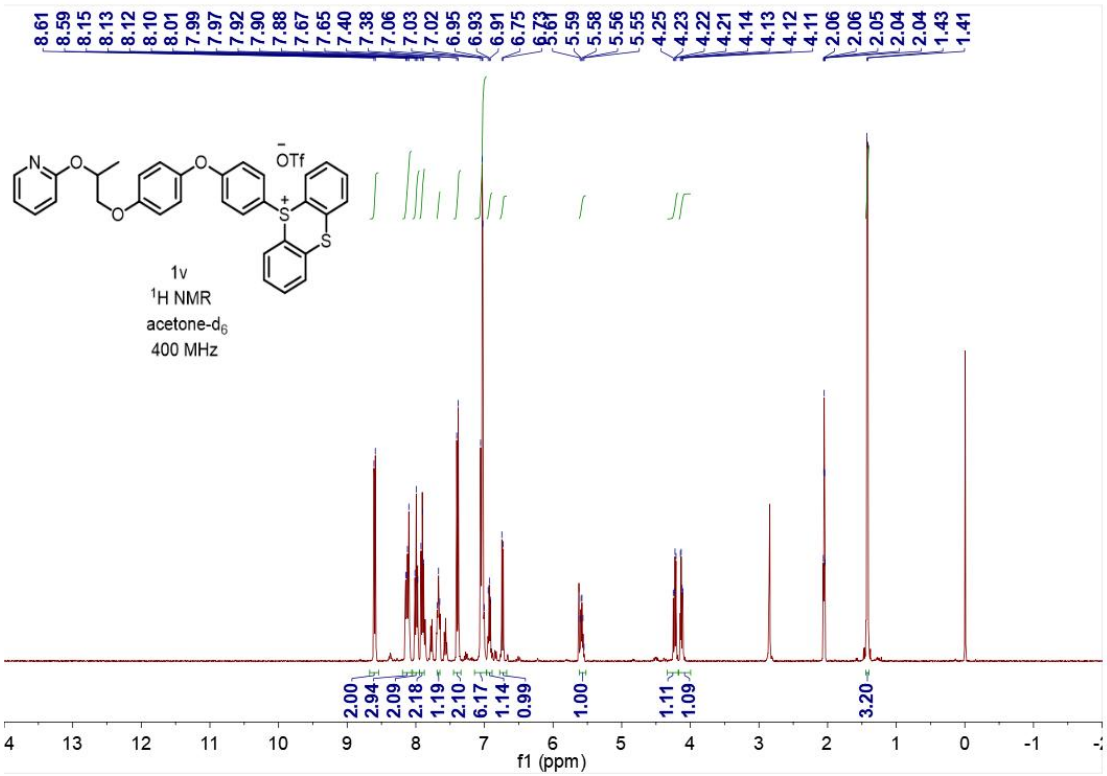

[1] H NMR spectrum of **1t**



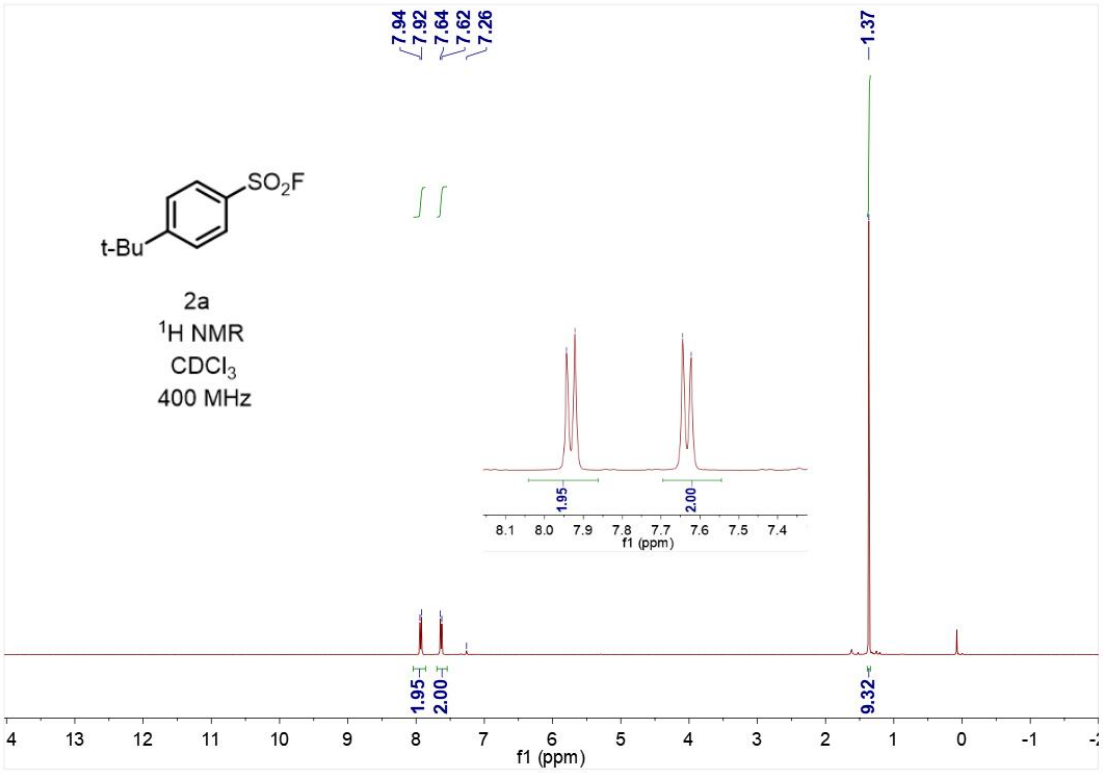
[1] H NMR spectrum of **1u**



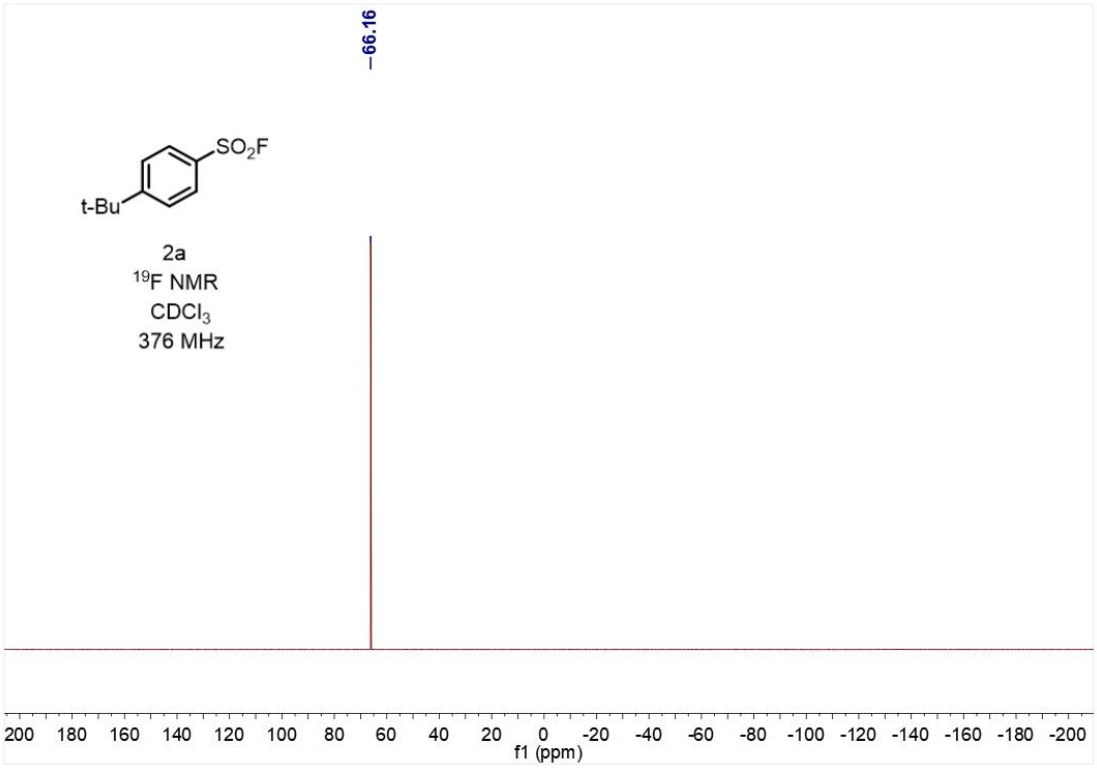

[1] H NMR spectrum of **1v**



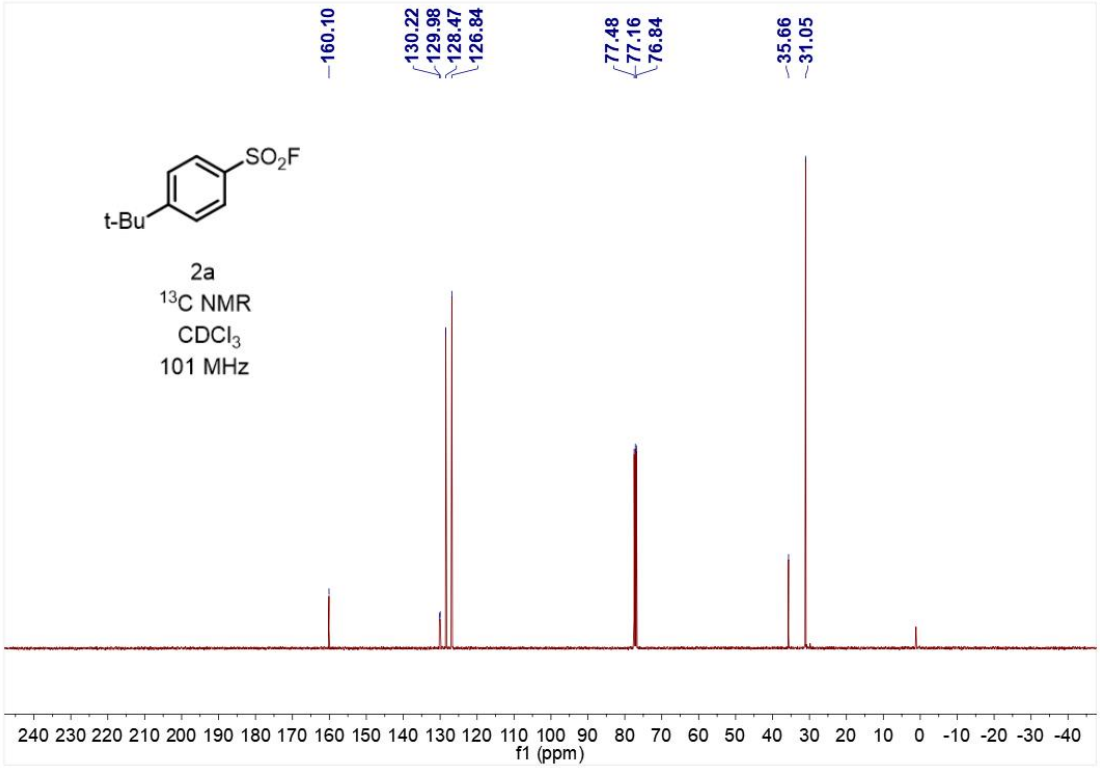
[1] H NMR spectrum of **2a**



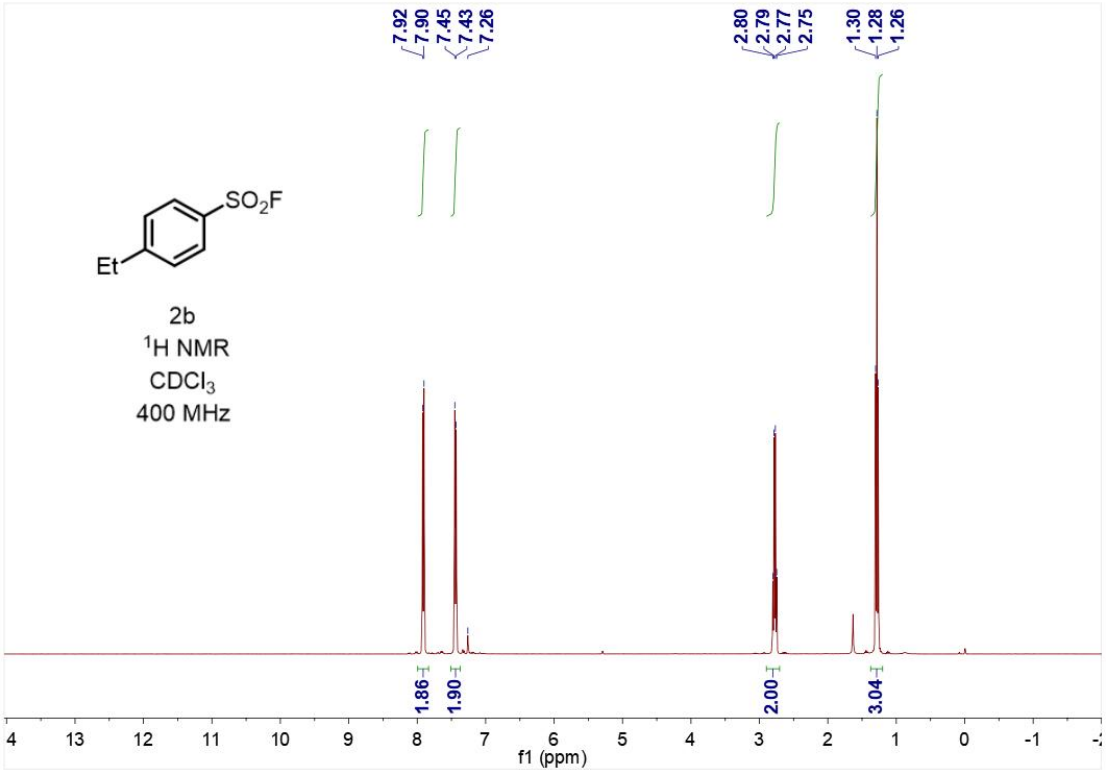

[19] F NMR spectrum of **2a**



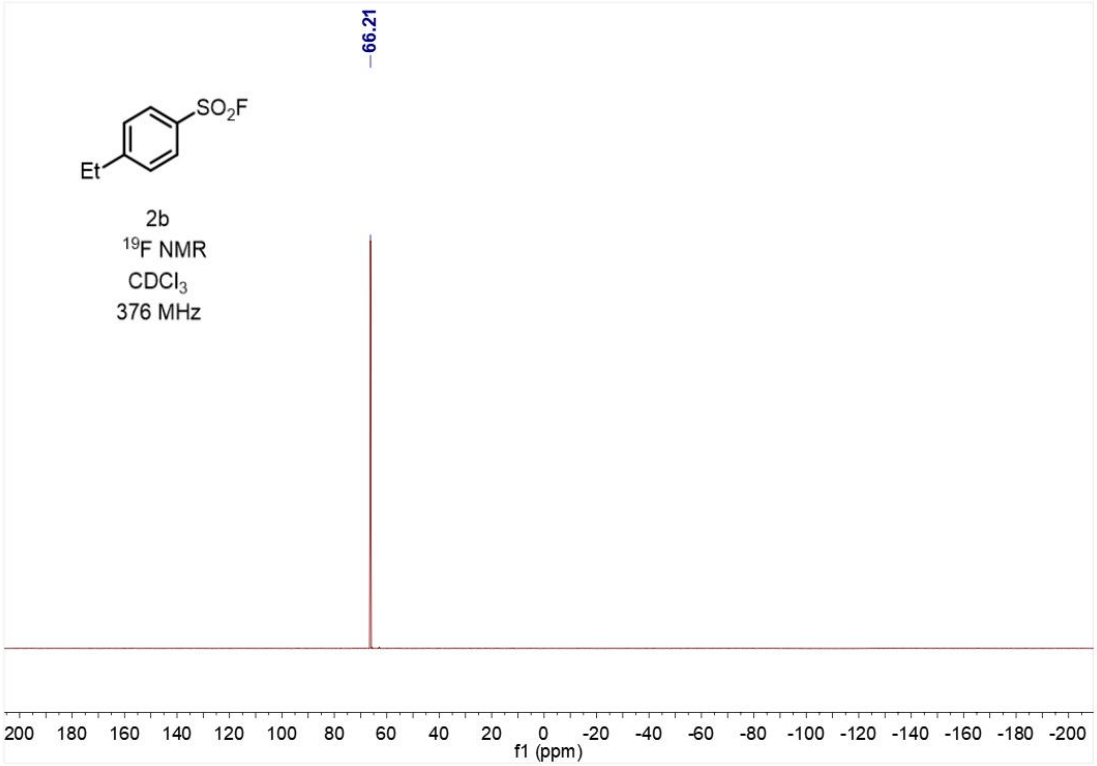
$^{13}$C NMR spectrum of **2a**



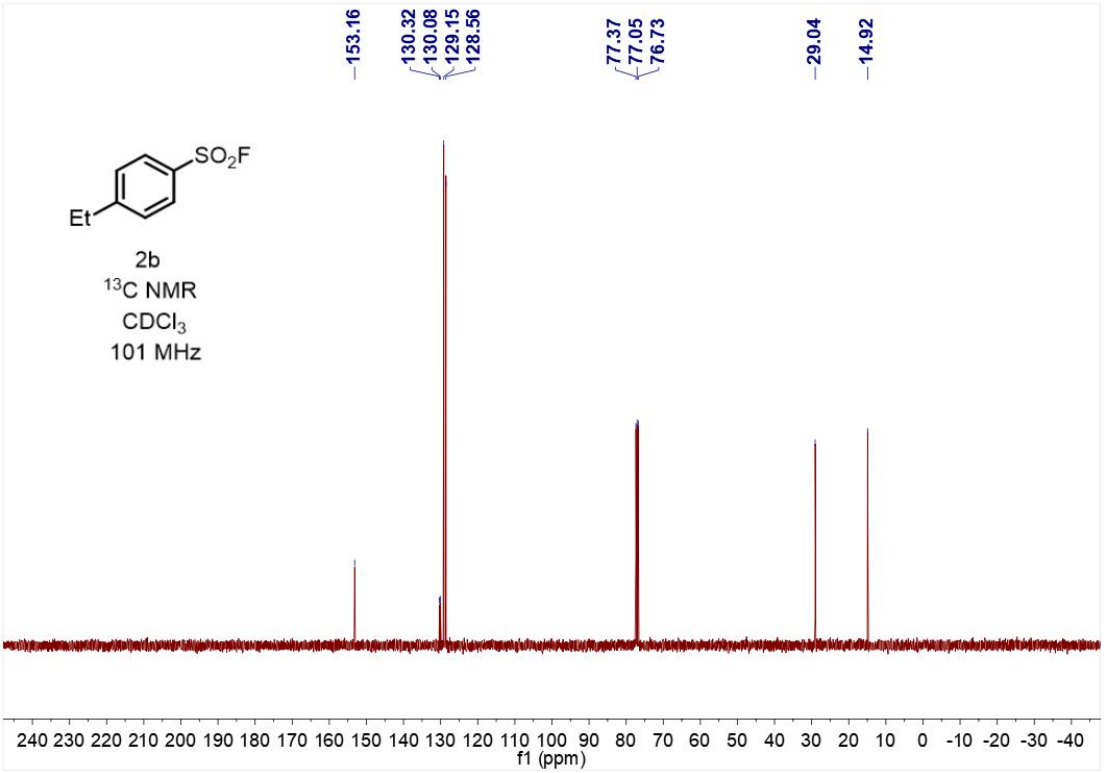

$^{1}$H NMR spectrum of **2b**



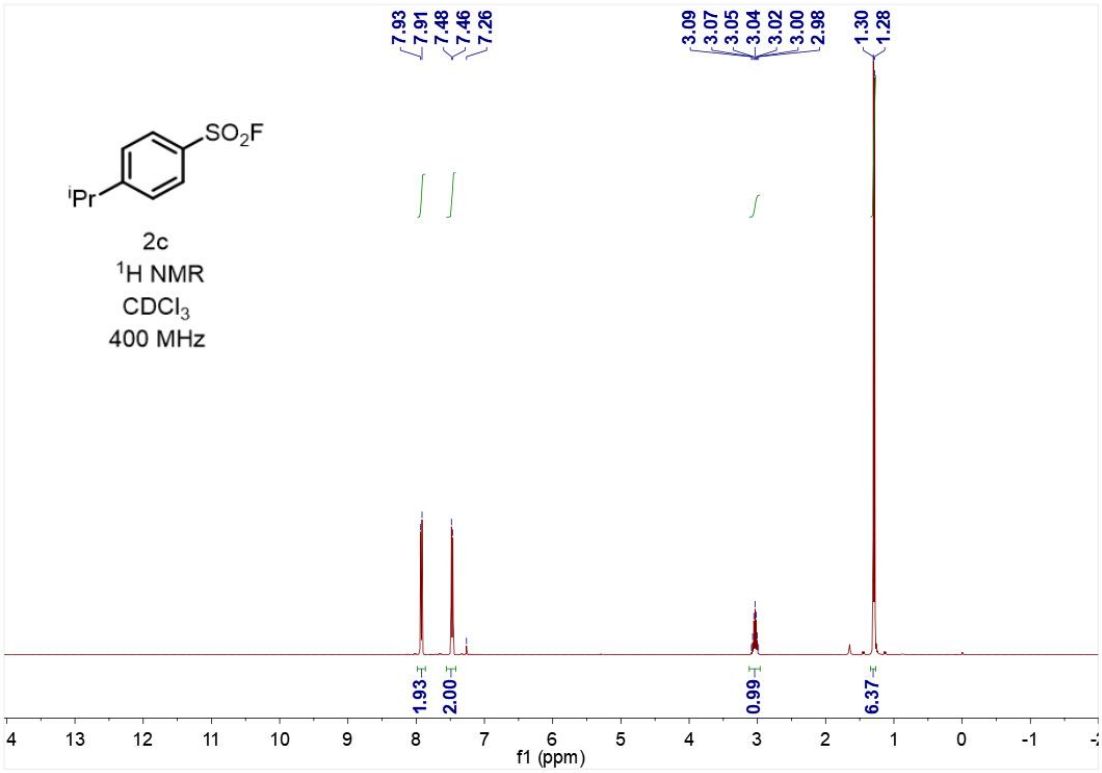
$^{19}$F NMR spectrum of **2b**



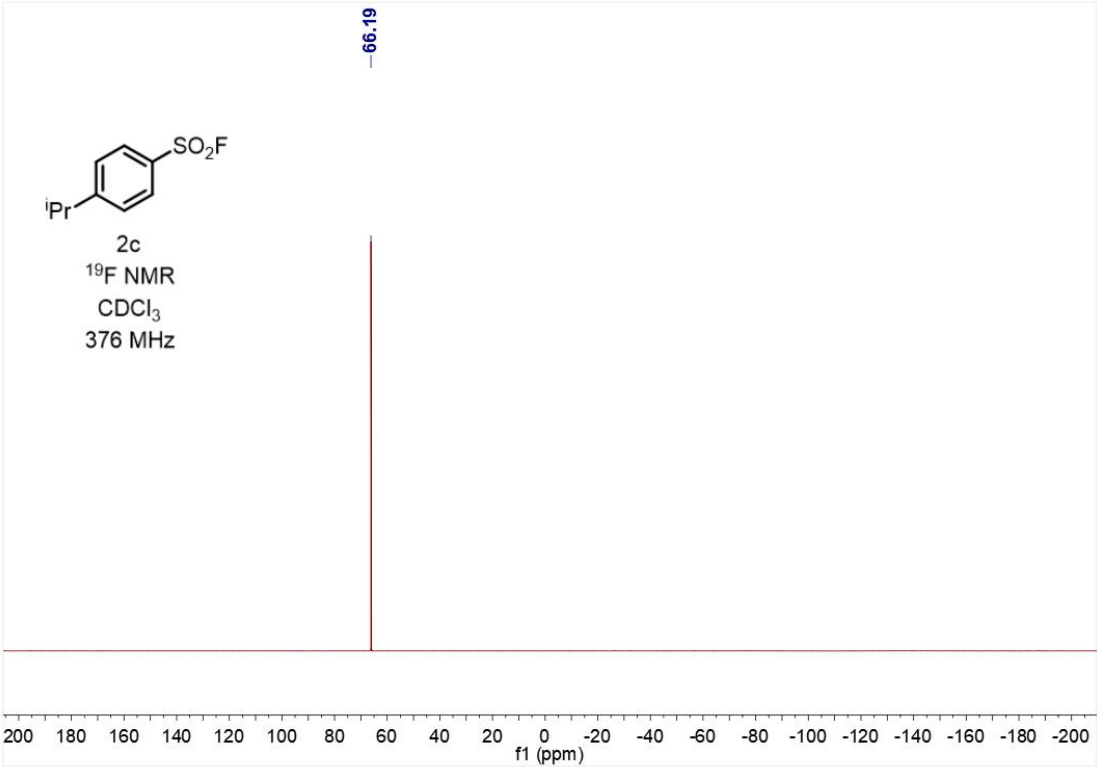

$^{13}$C NMR spectrum of **2b**



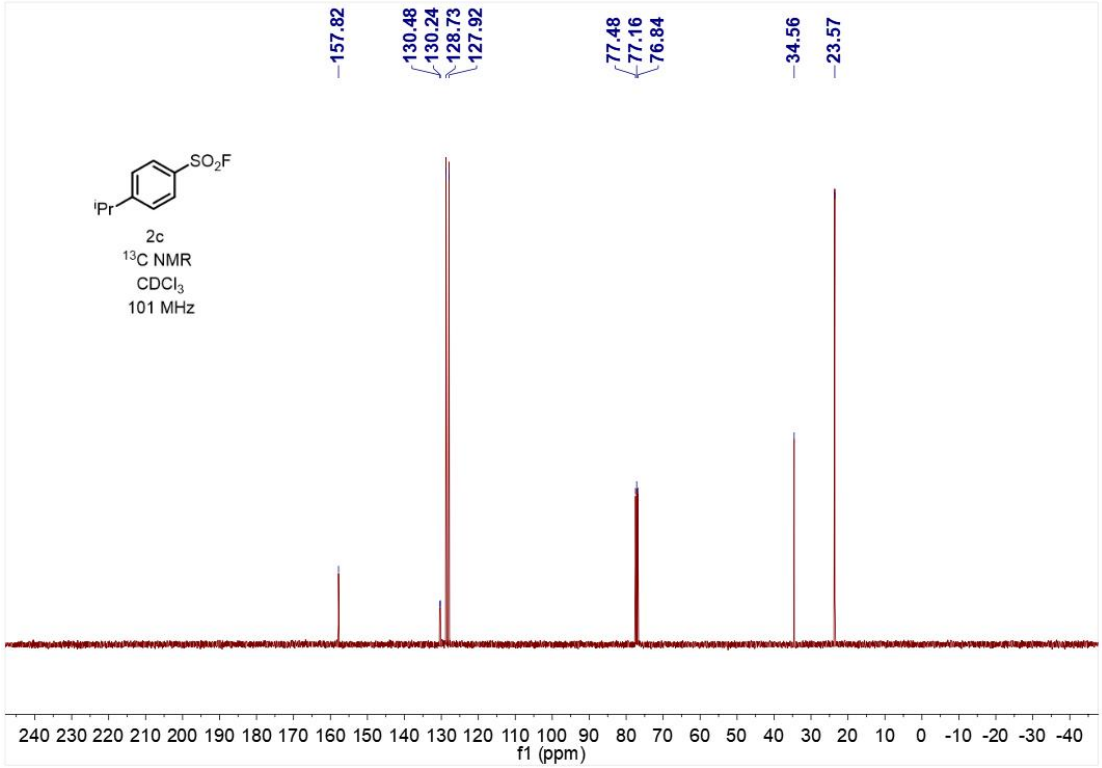
[1] H NMR spectrum of **2c**



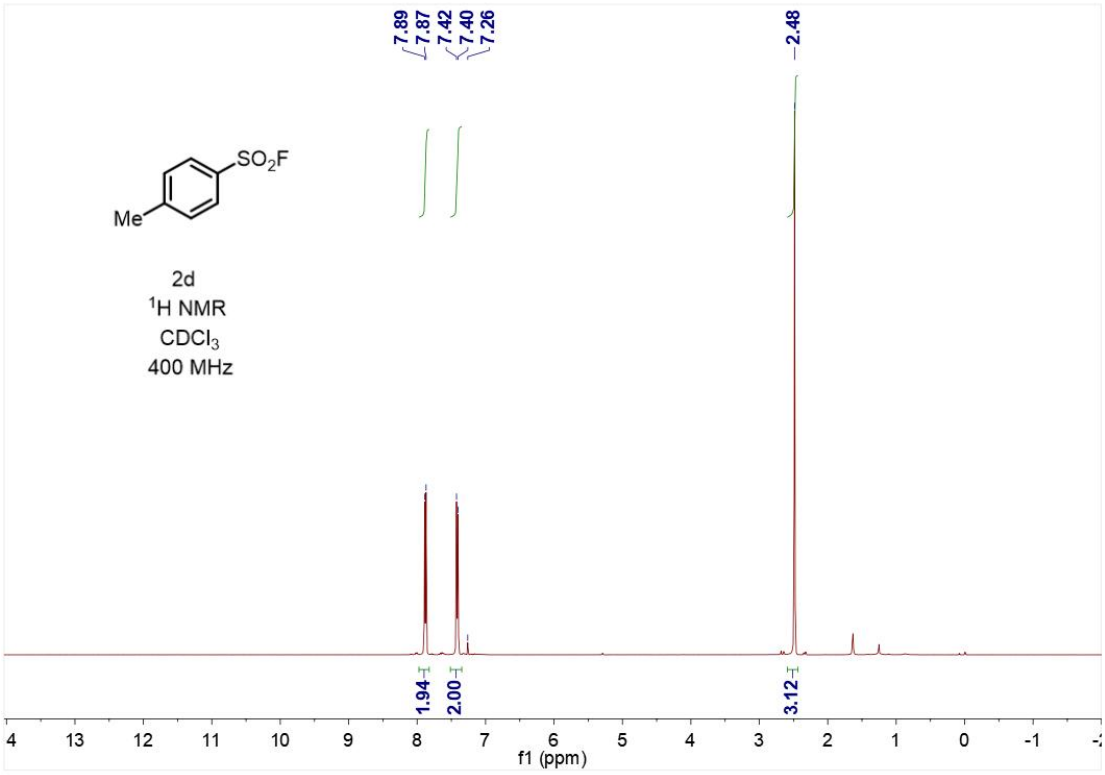

[19] F NMR spectrum of **2c**



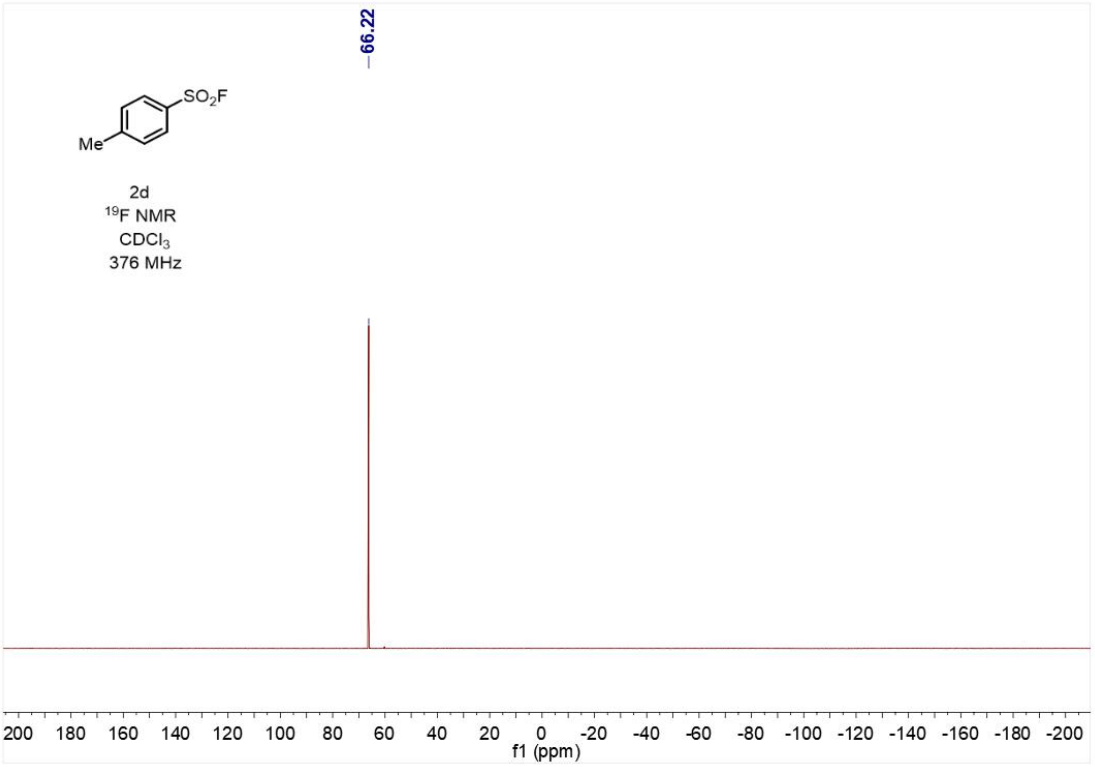
$^{13}$C NMR spectrum of **2c**



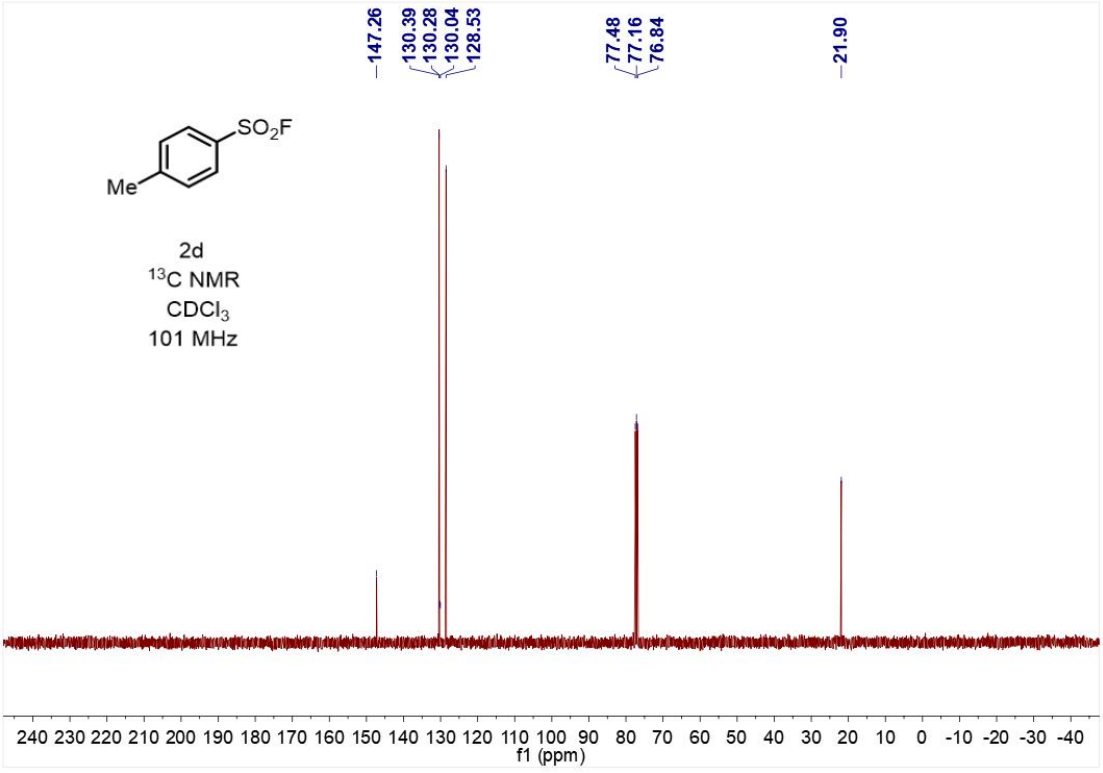

$^{1}$H NMR spectrum of **2d**



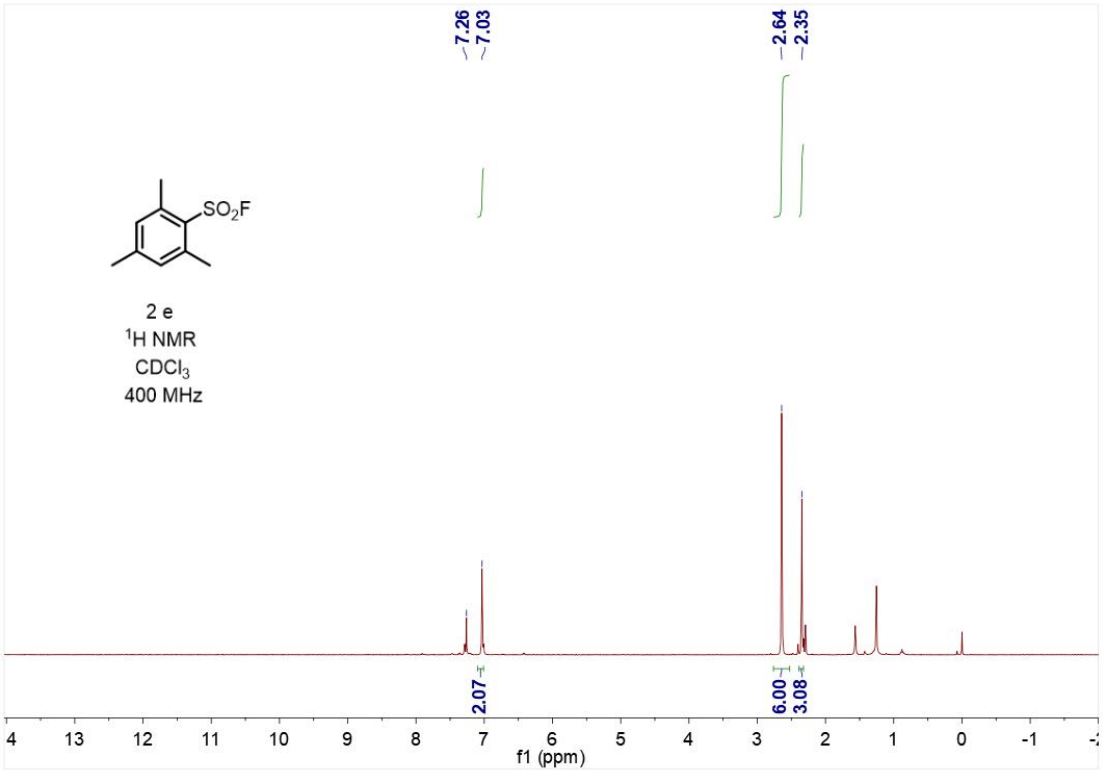
$^{19}$F NMR spectrum of **2d**



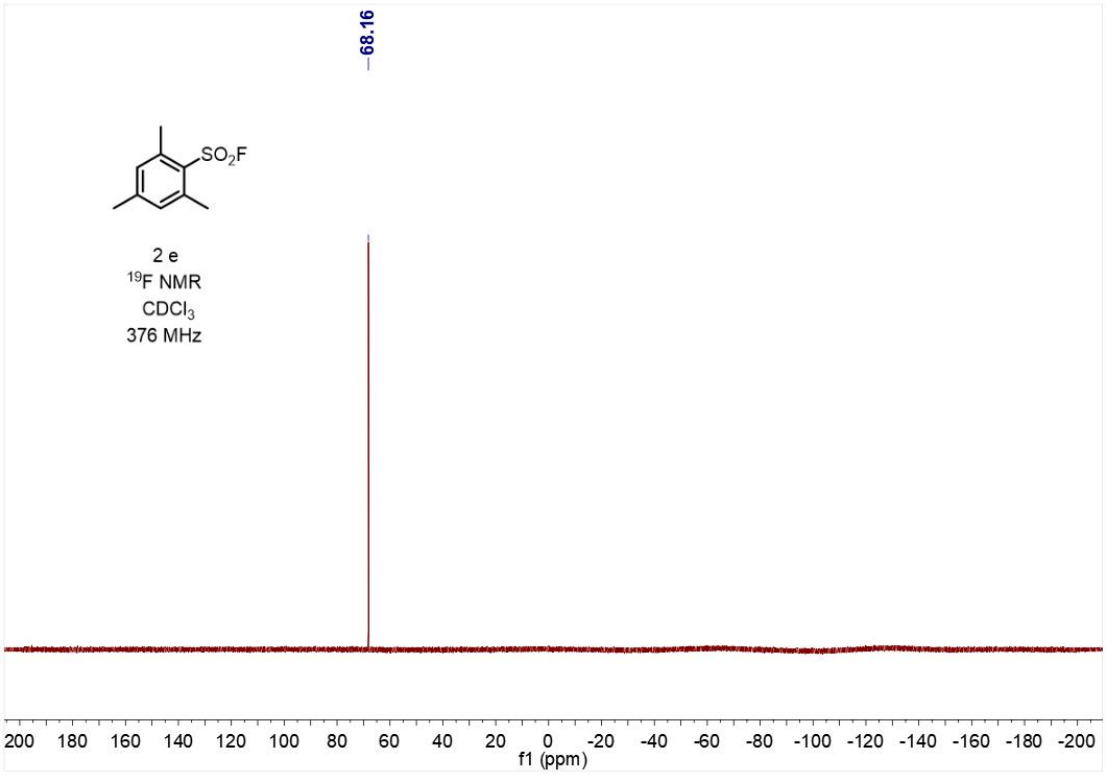

$^{13}$C NMR spectrum of **2d**



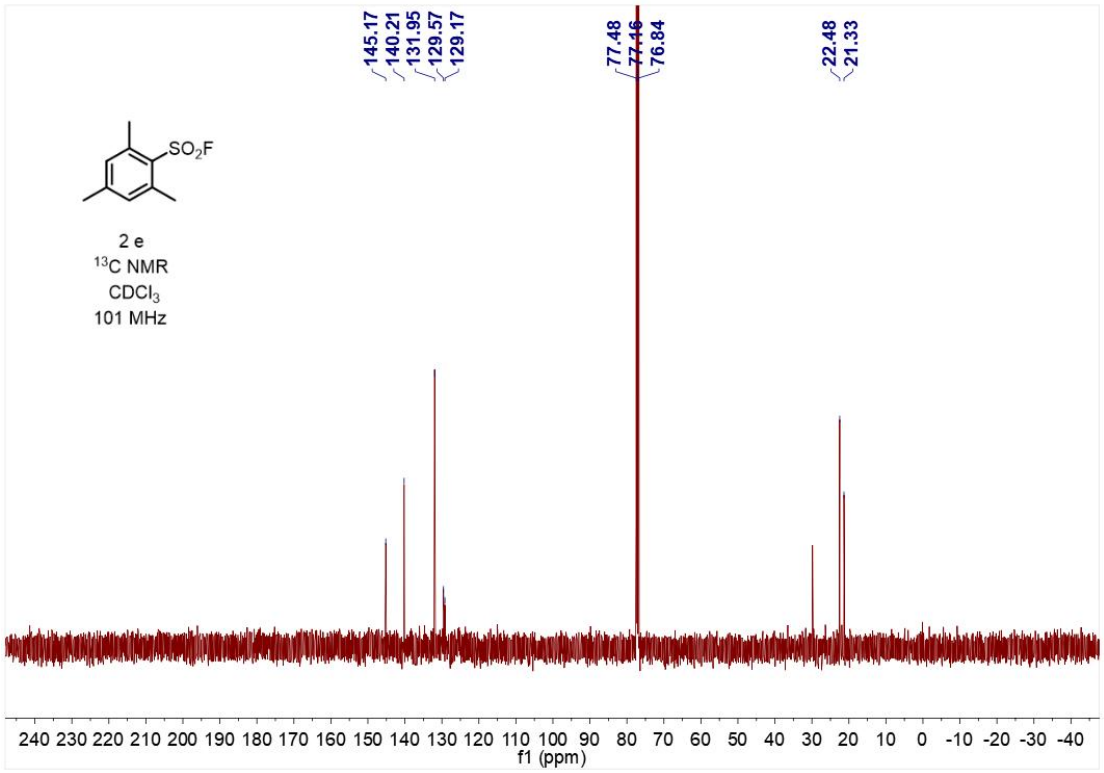
[1] H NMR spectrum of **2e**



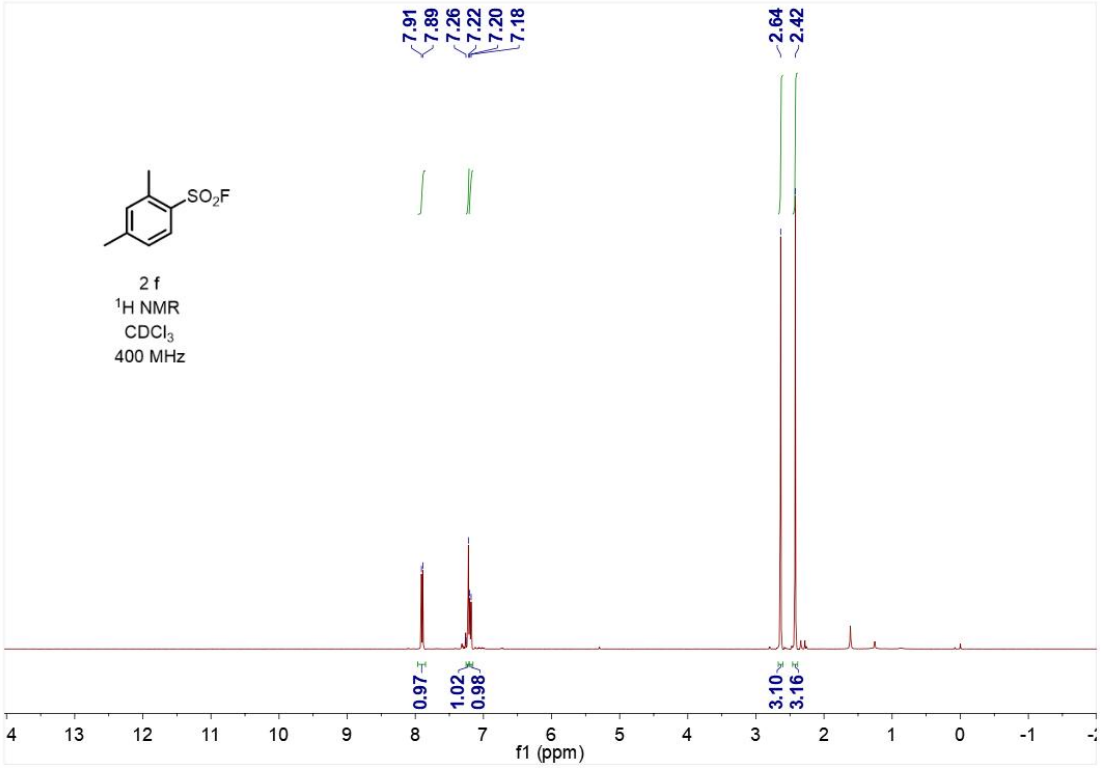

[19] F NMR spectrum of **2e**



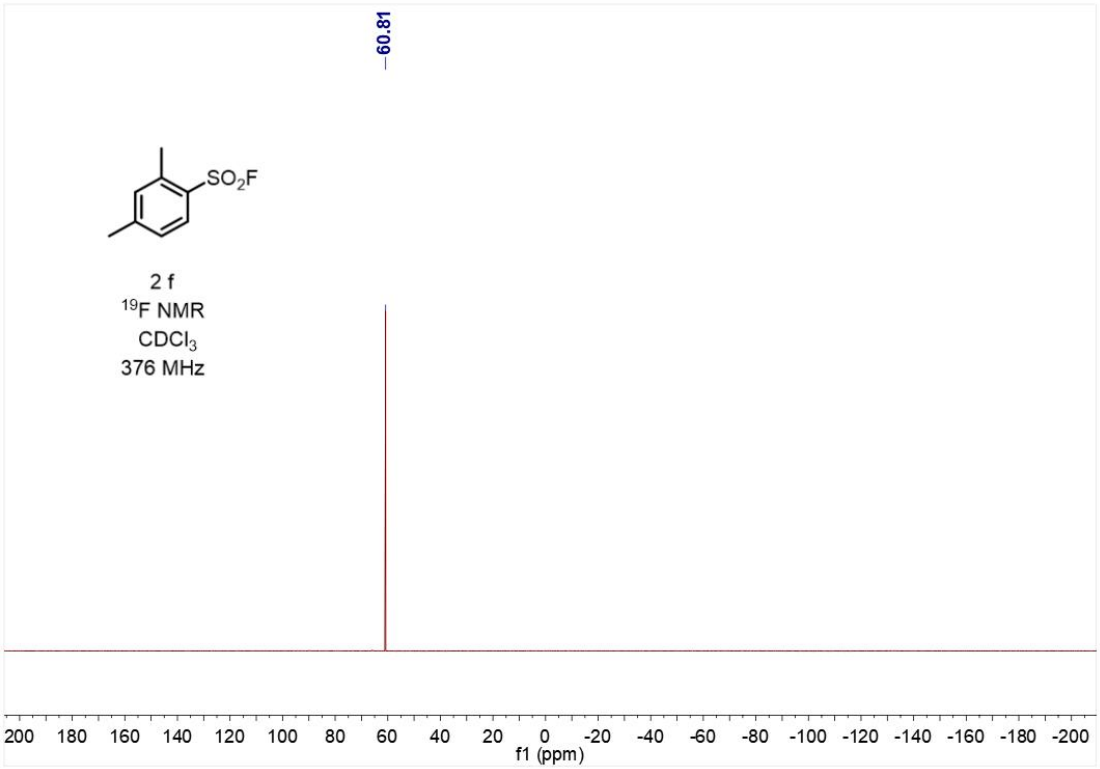
[13] C NMR spectrum of **2e**



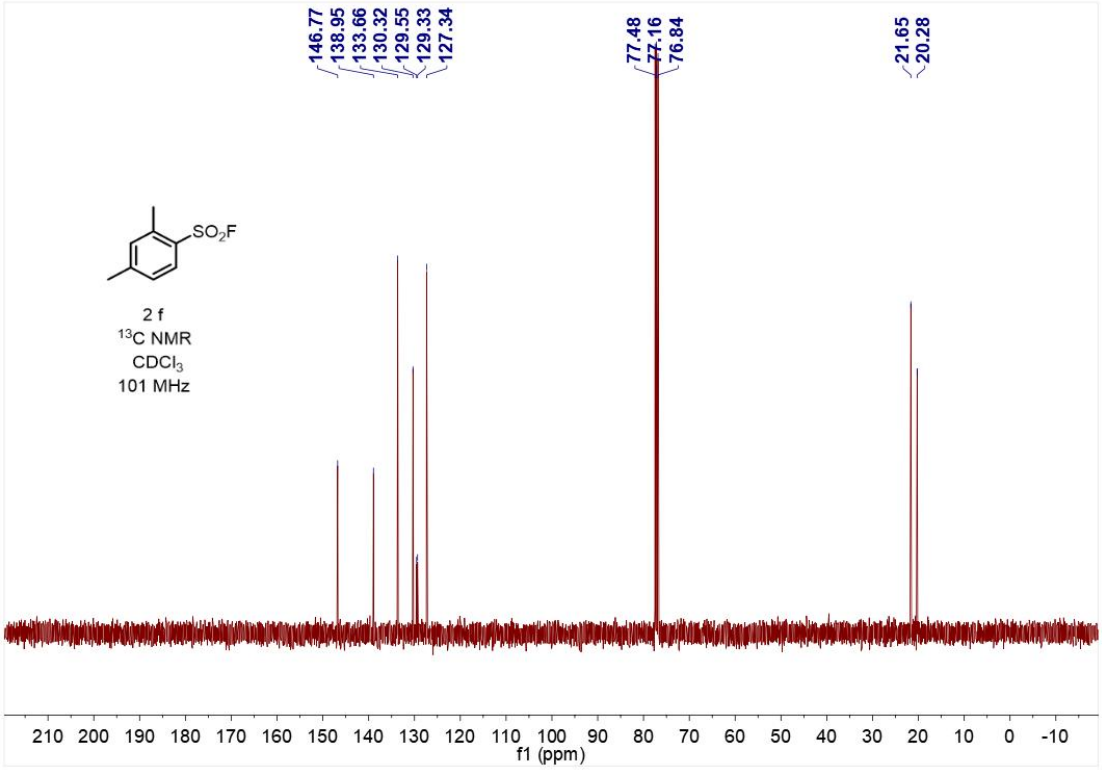

[1] H NMR spectrum of **2f**



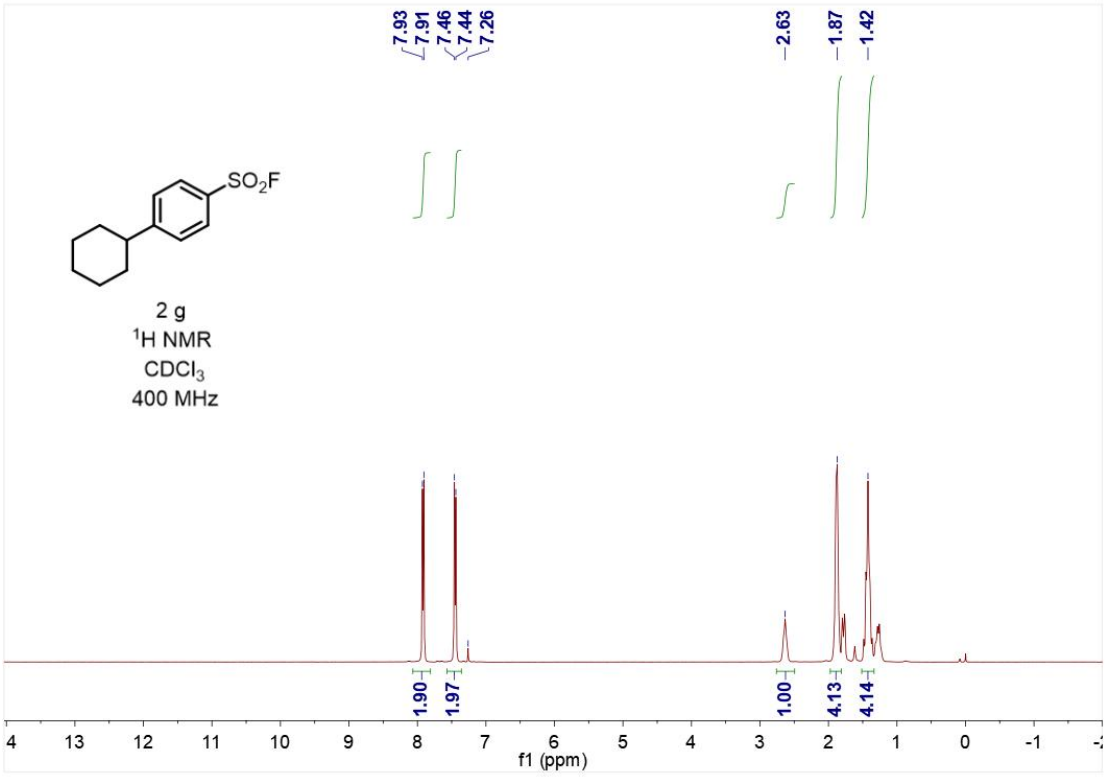
$^{19}$F NMR spectrum of **2f**



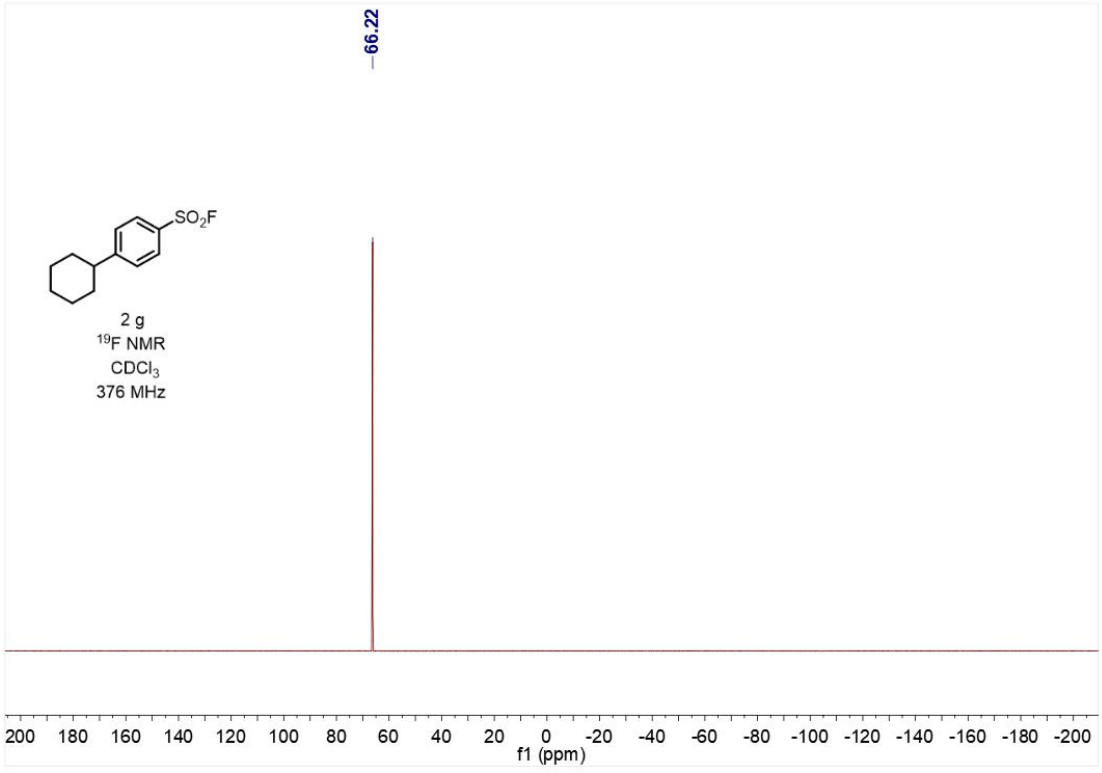

$^{13}$C NMR spectrum of **2f**



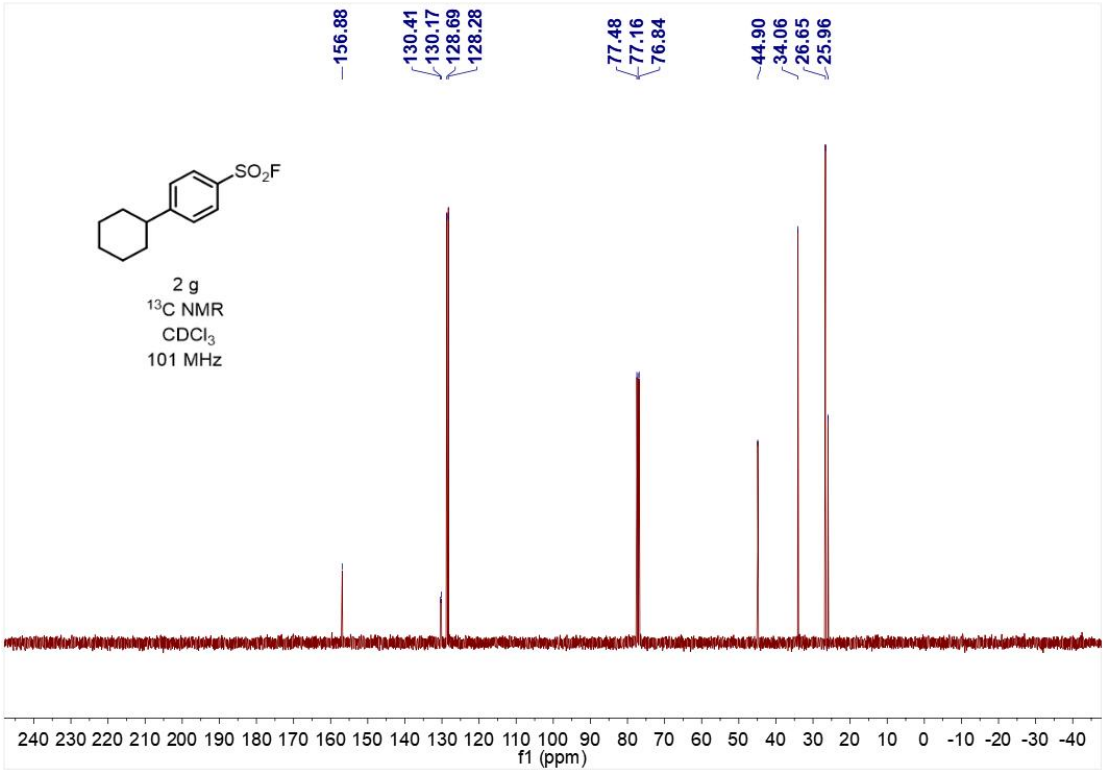
[1] H NMR spectrum of **2g**



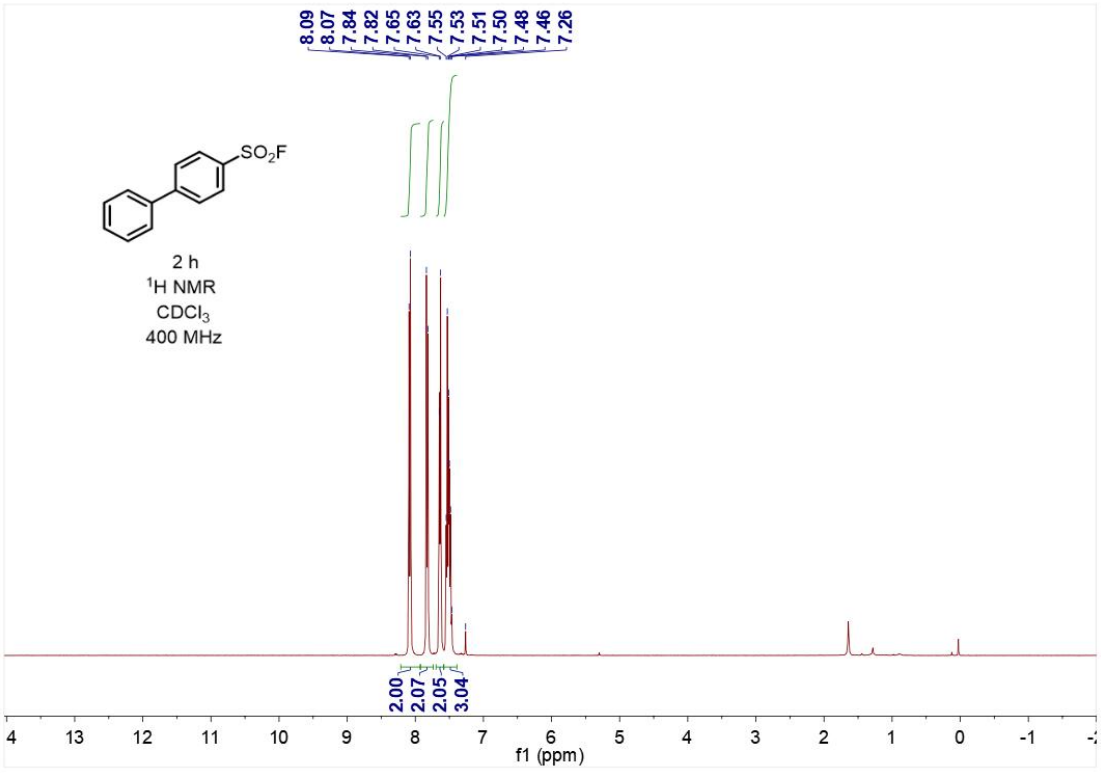

[19] F NMR spectrum of **2g**



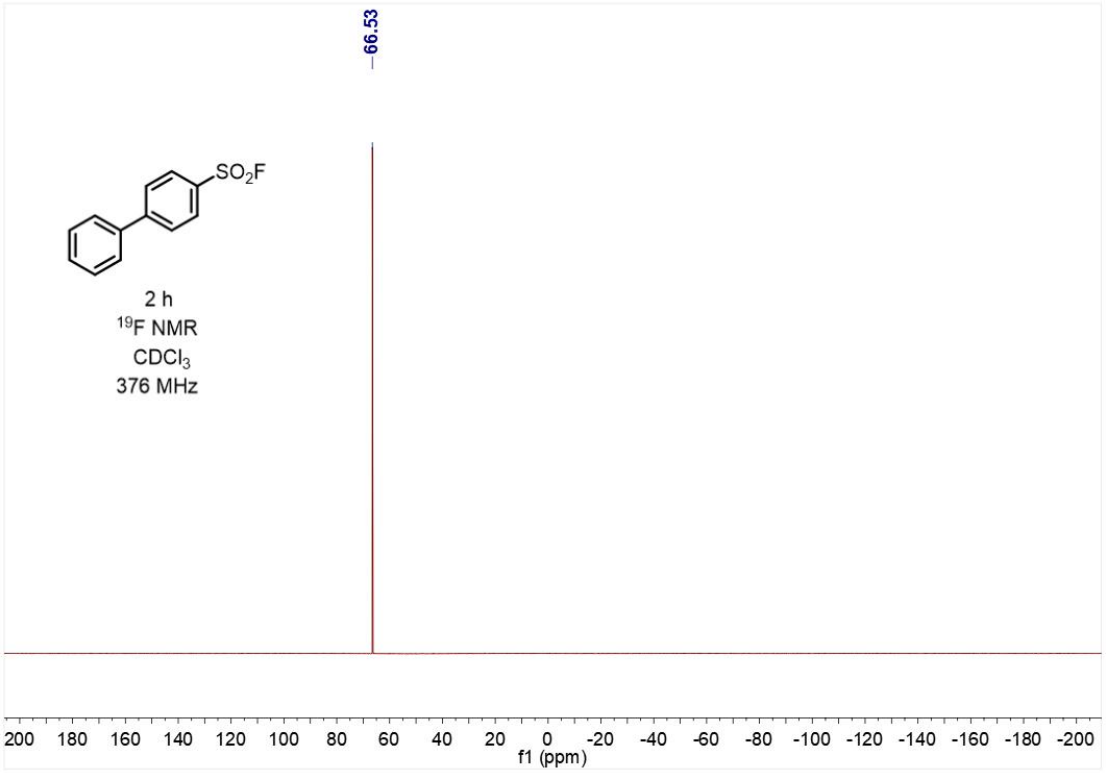
$^{13}$C NMR spectrum of **2g**



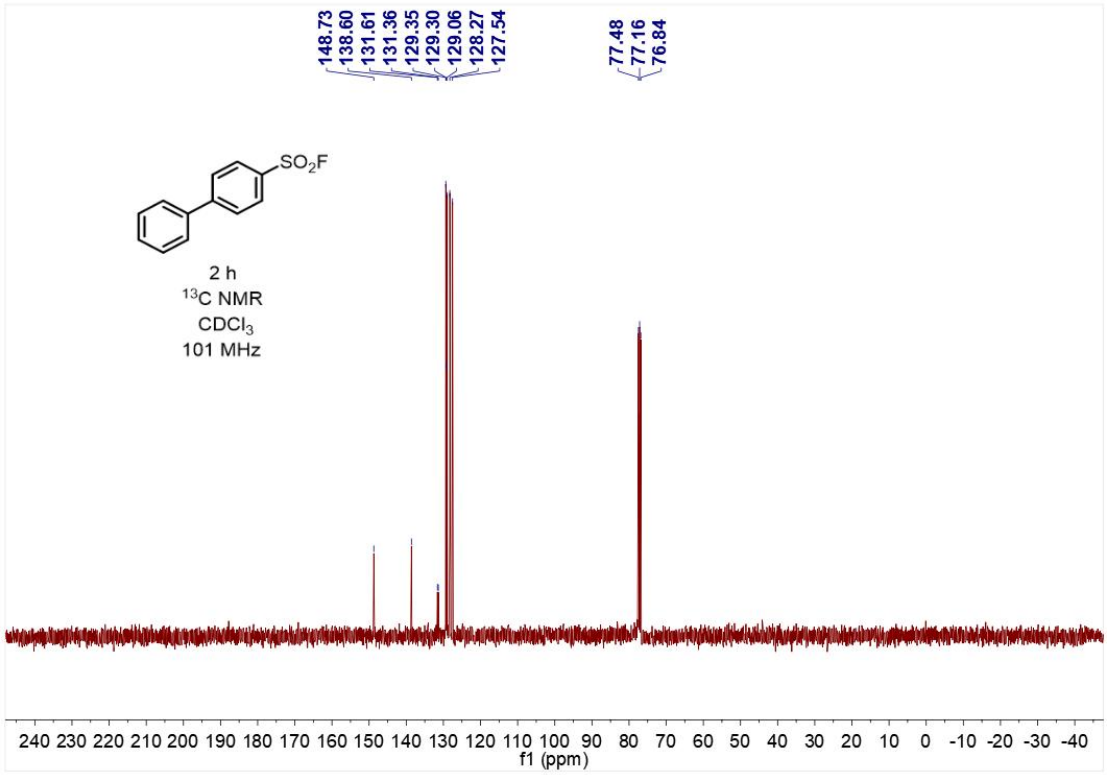

$^{1}$H NMR spectrum of **2h**



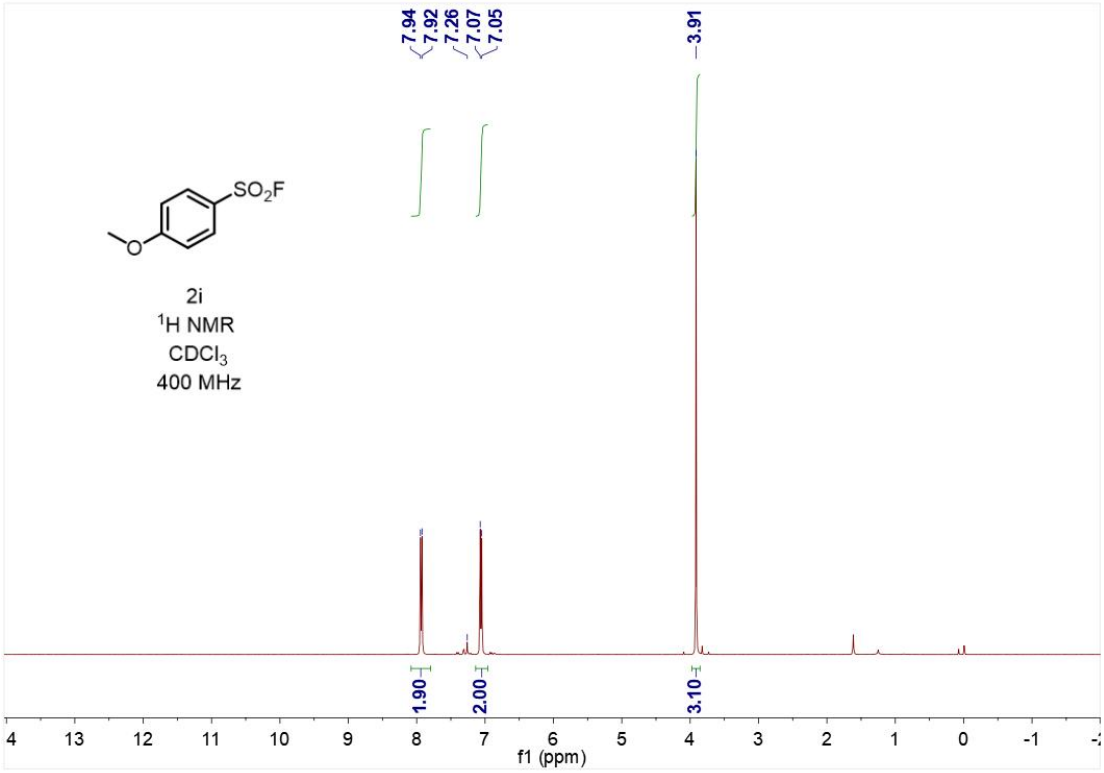
$^{19}$F NMR spectrum of **2h**



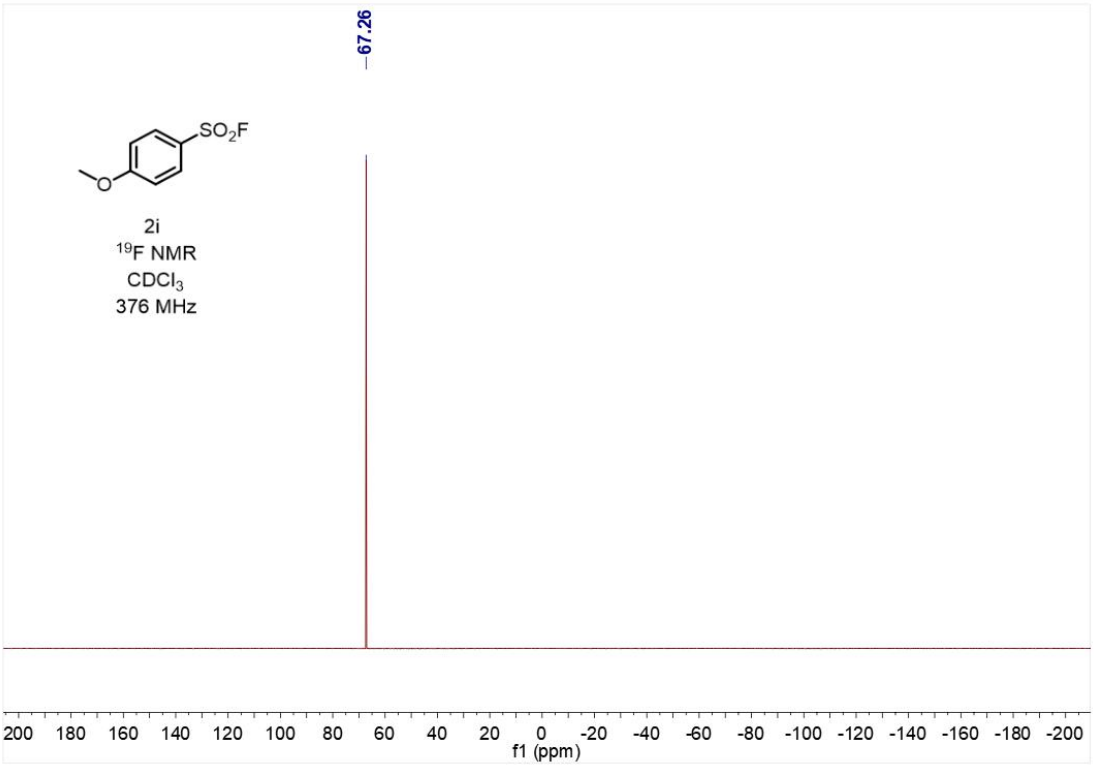

$^{13}$C NMR spectrum of **2h**



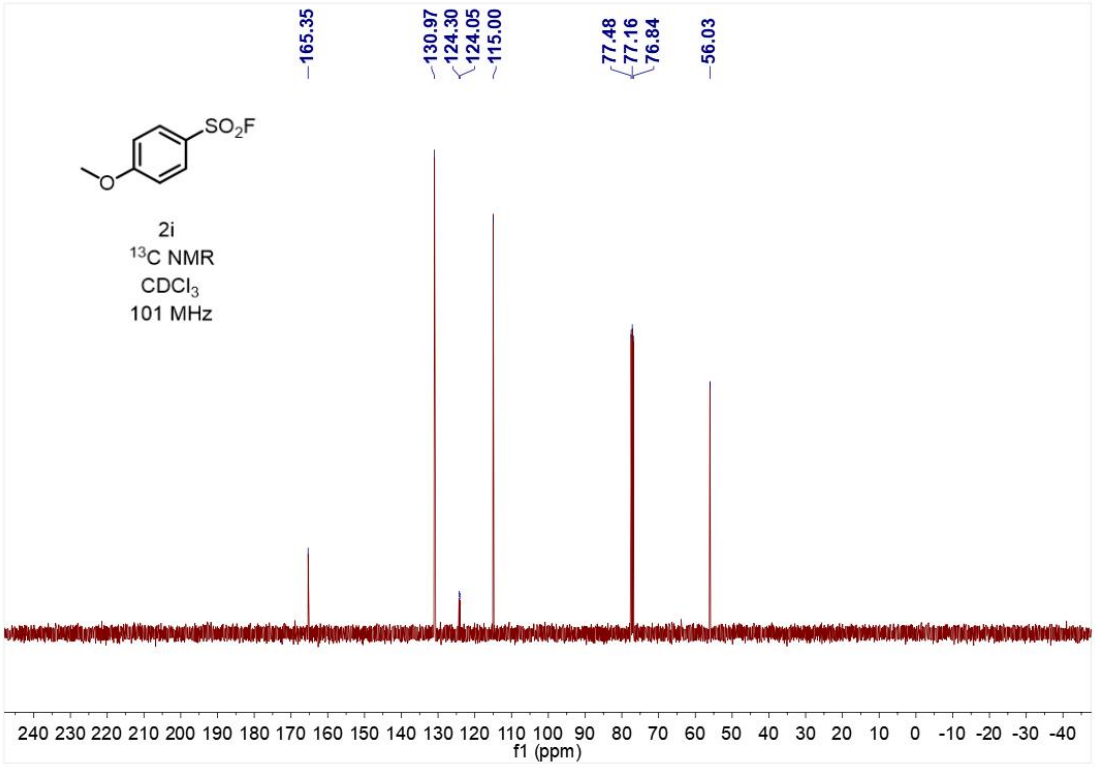
[1] H NMR spectrum of **2i**



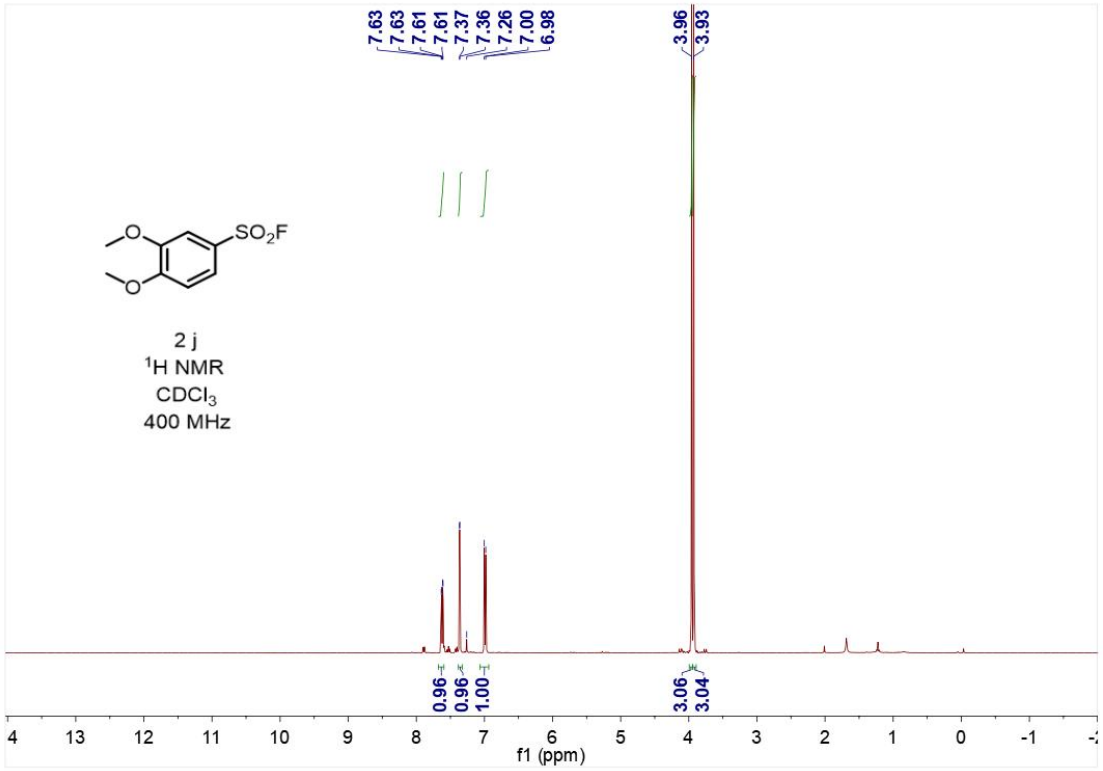

[19] F NMR spectrum of **2i**



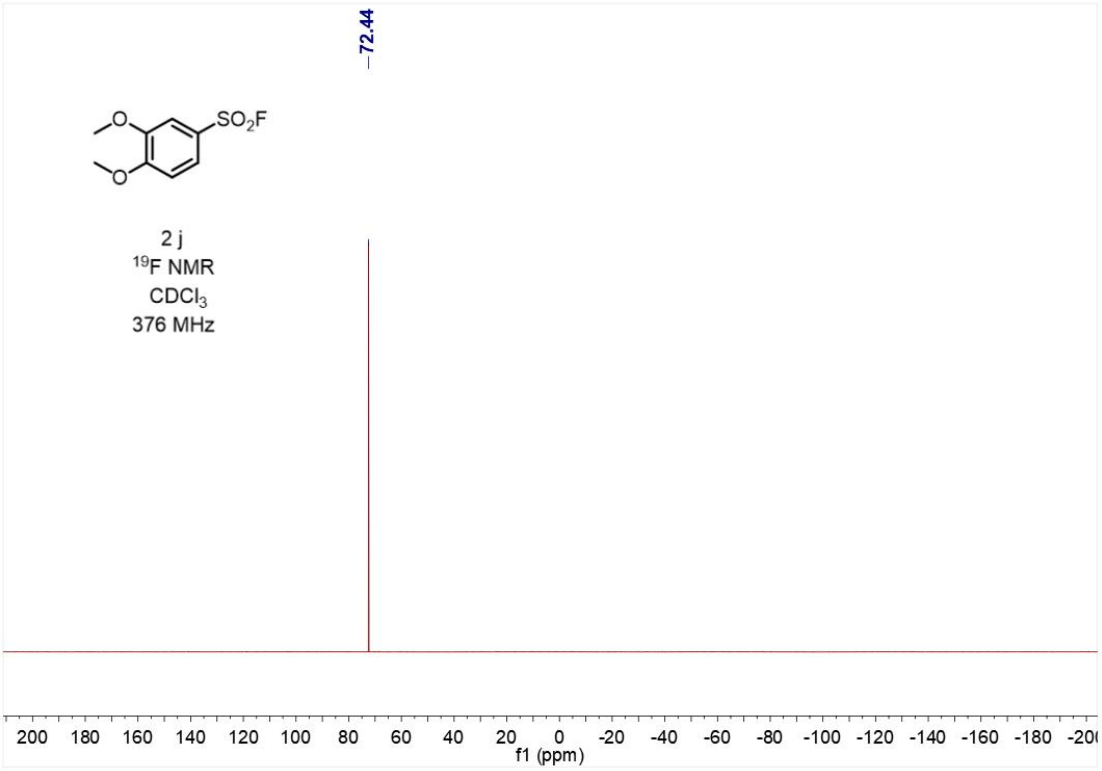
$^{13}$C NMR spectrum of **2i**



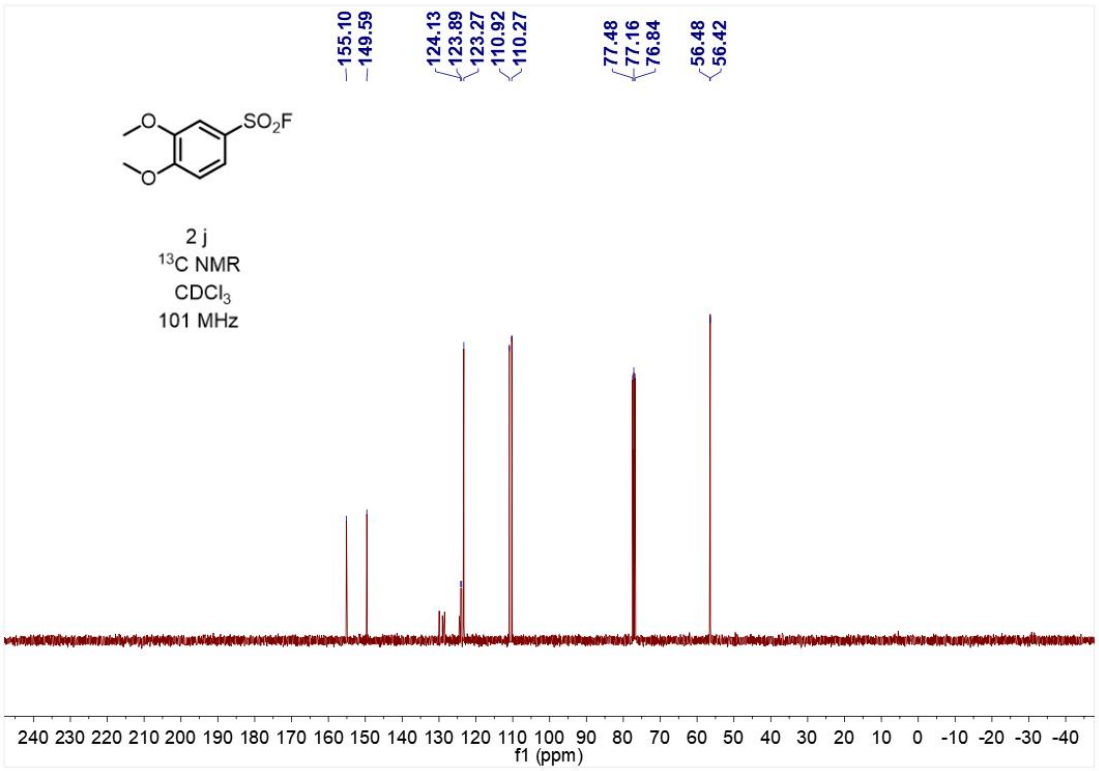

$^{1}$H NMR spectrum of **2j**



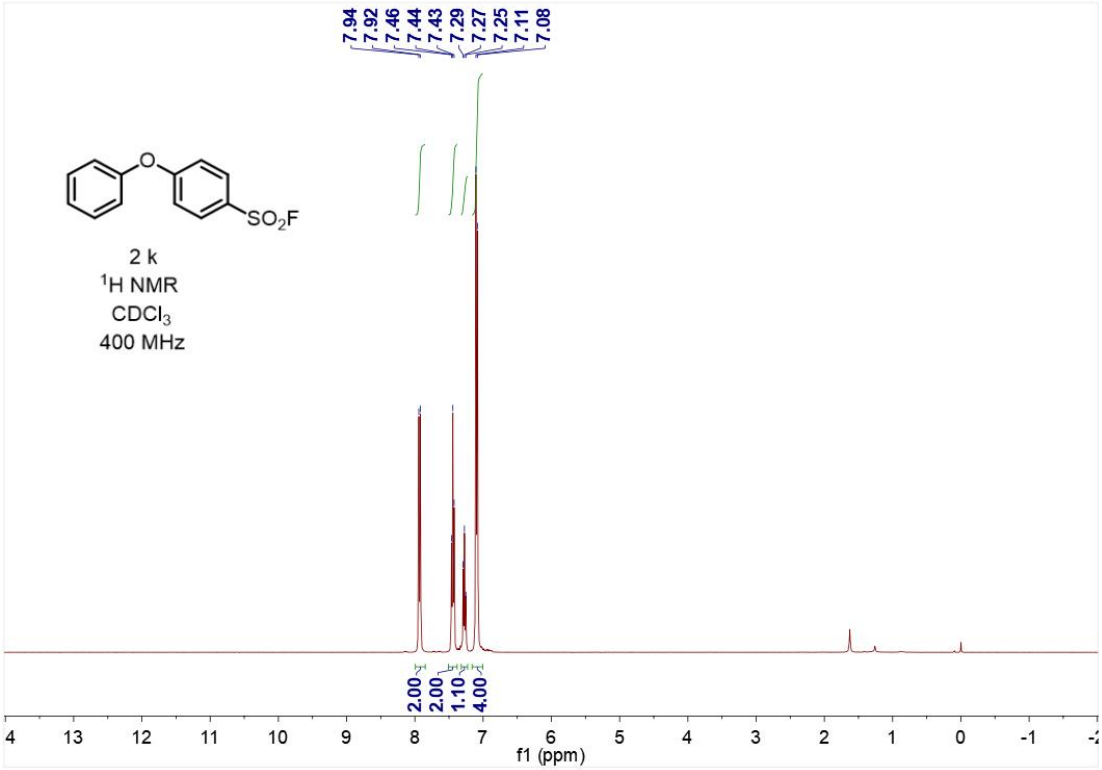
$^{19}$F NMR spectrum of **2j**



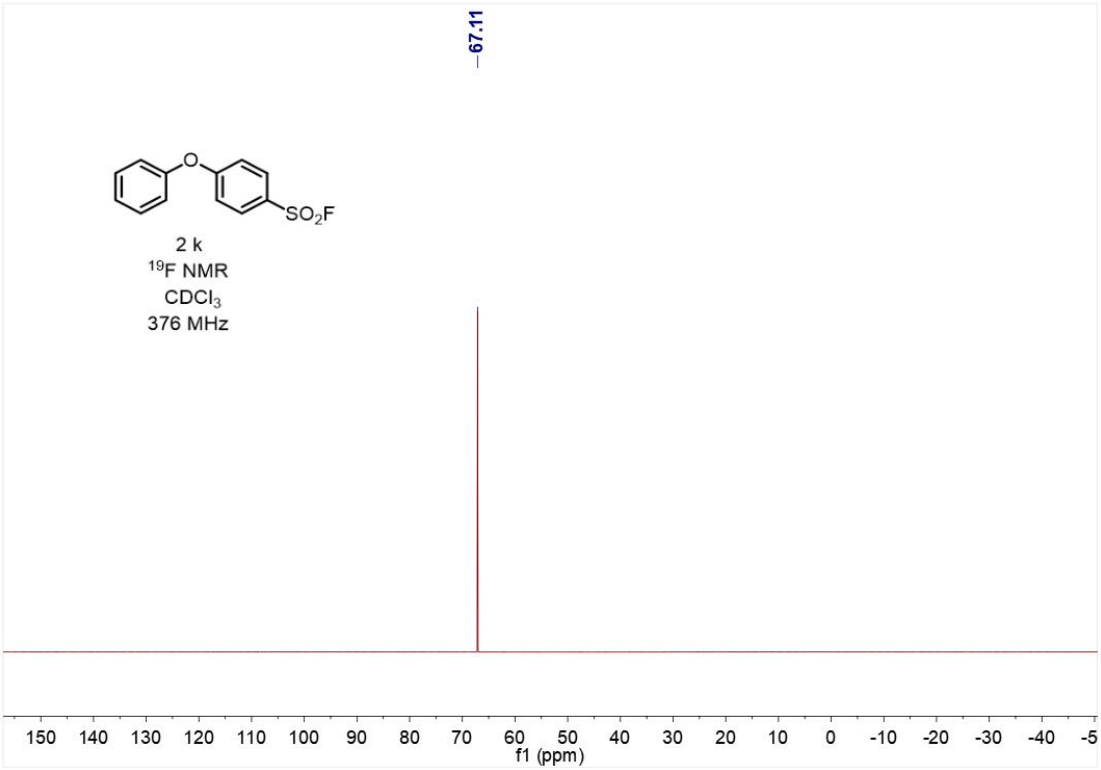

$^{13}$C NMR spectrum of **2j**



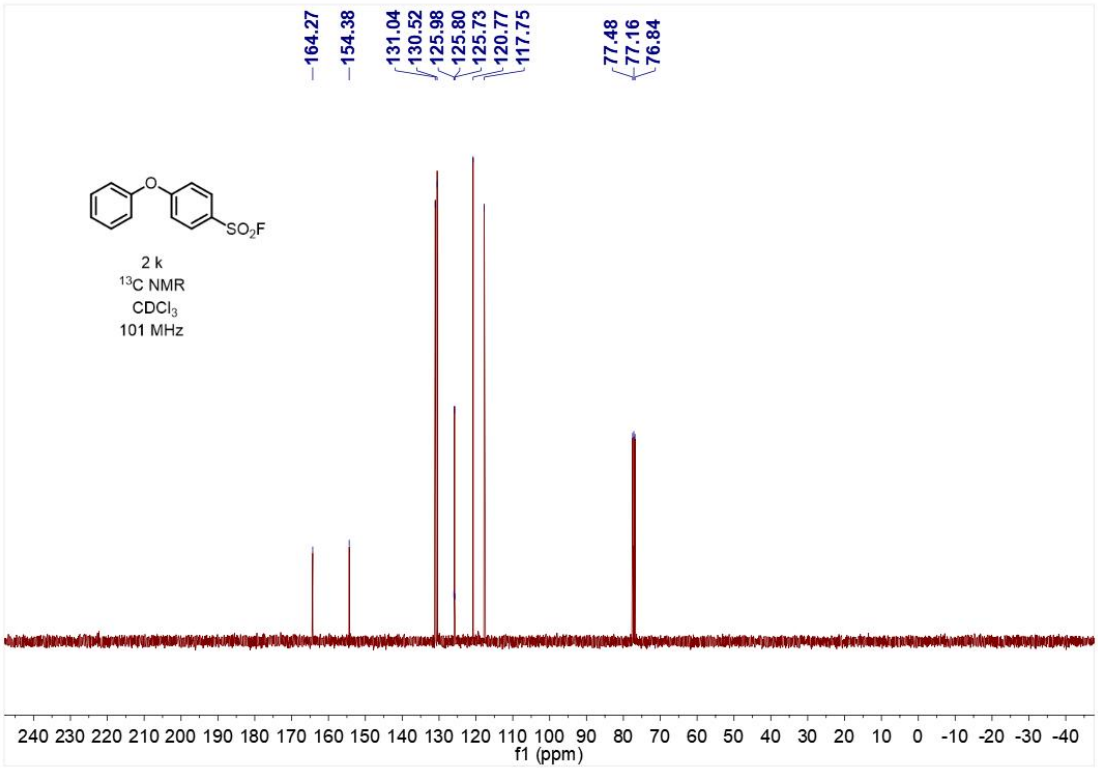
[1] H NMR spectrum of **2k**



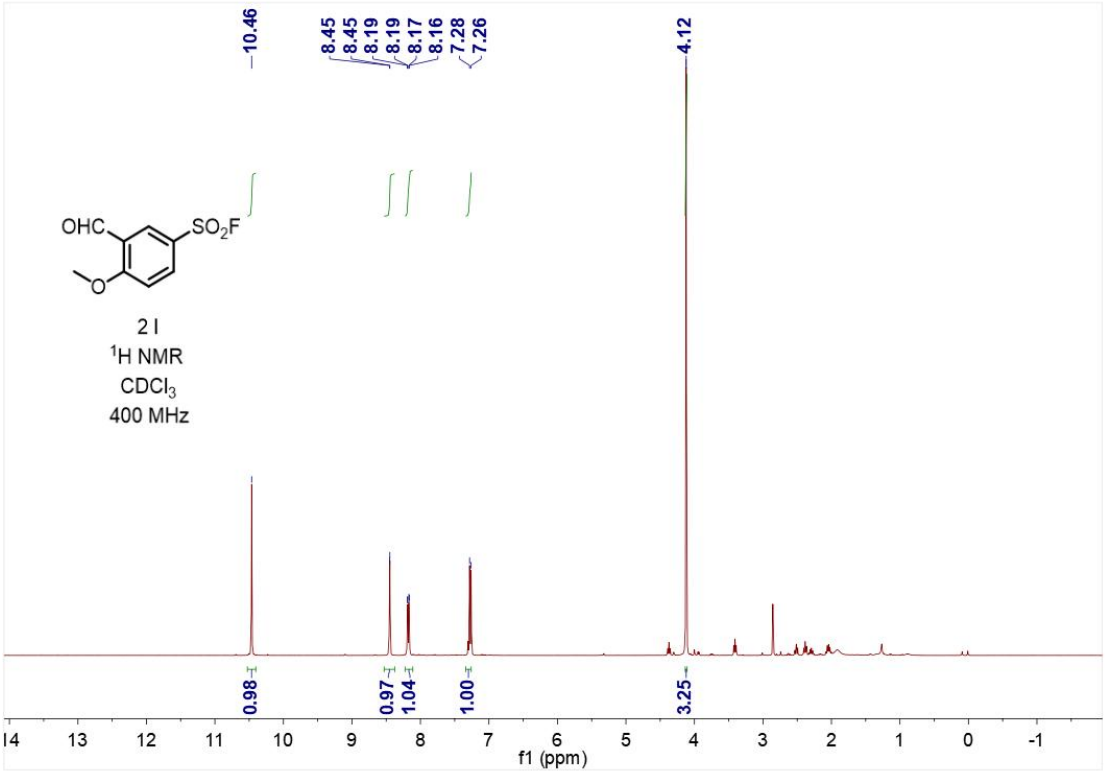

[19] F NMR spectrum of **2k**



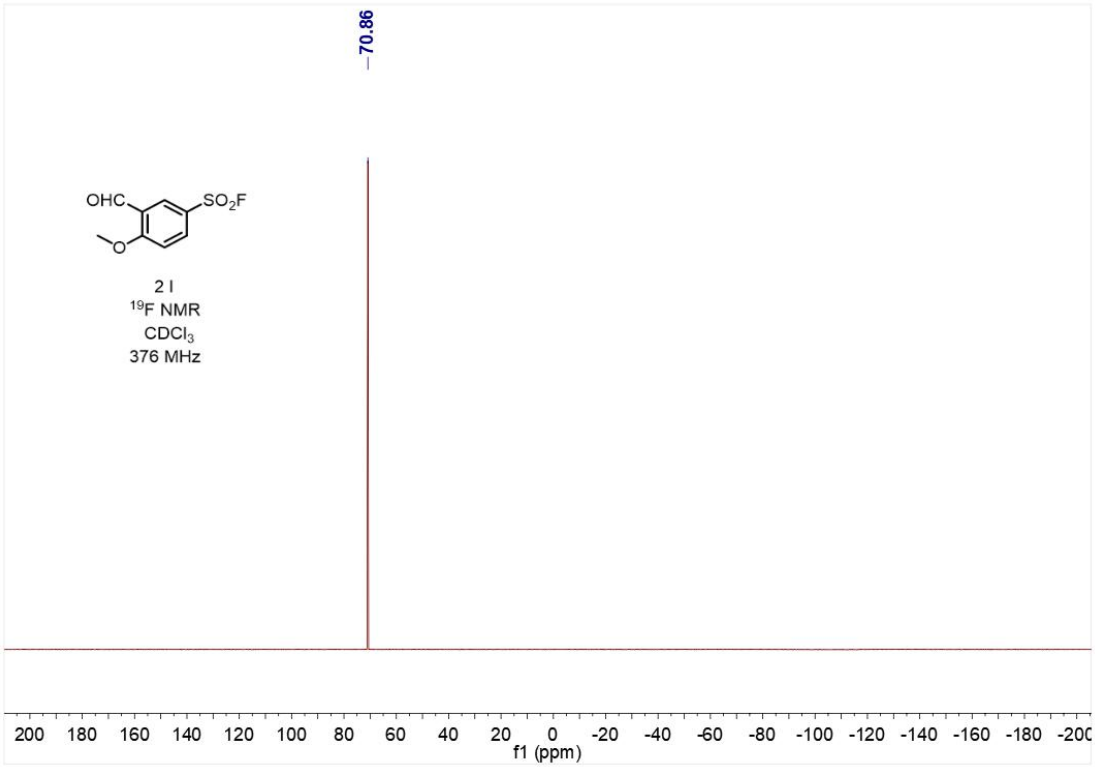
$^{13}$C NMR spectrum of **2k**



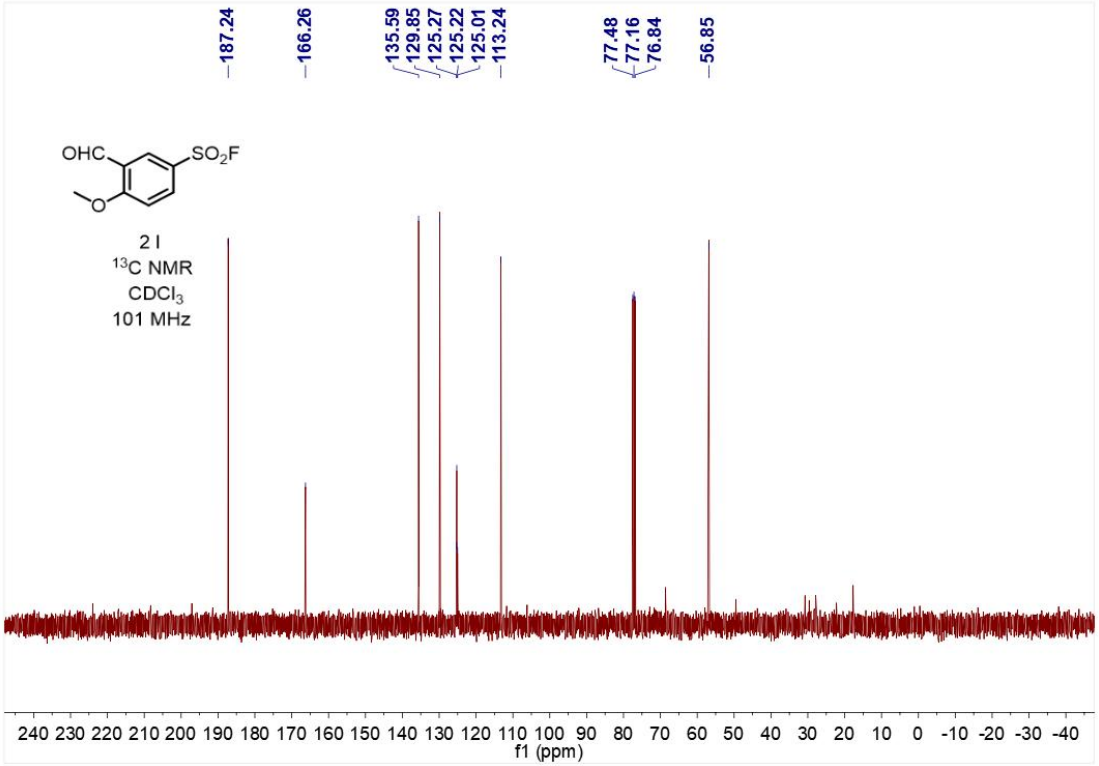

$^{1}$H NMR spectrum of **2l**



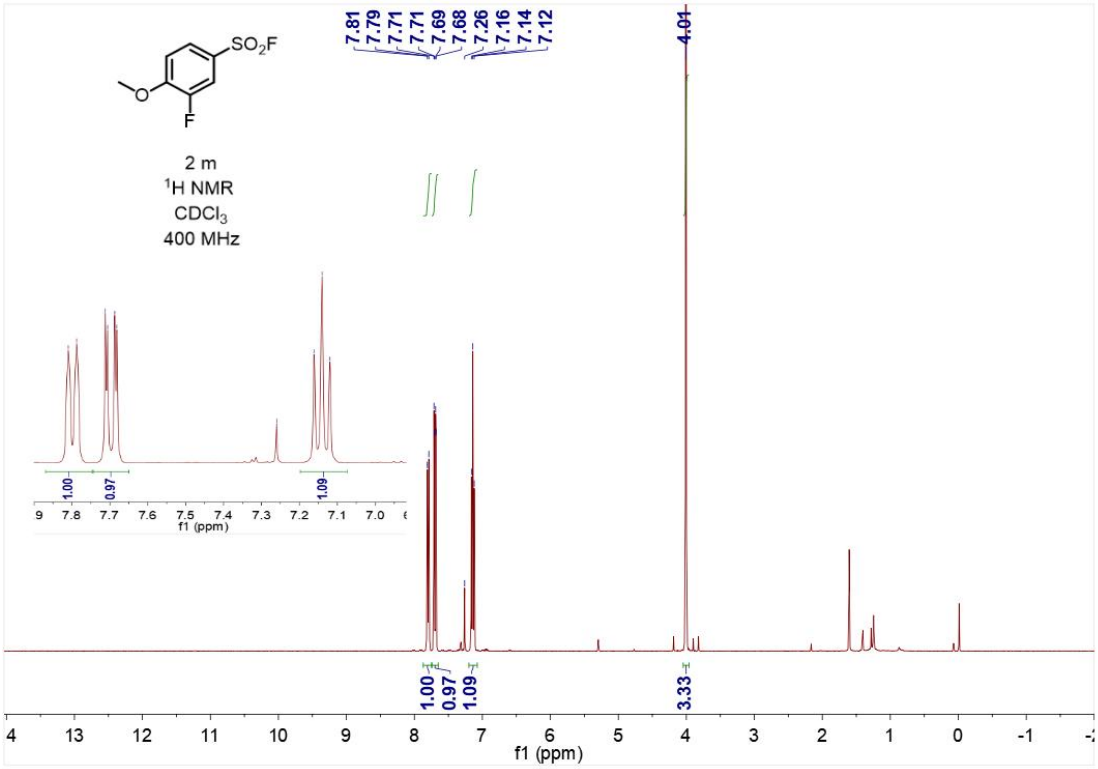
$^{19}$F NMR spectrum of **2l**



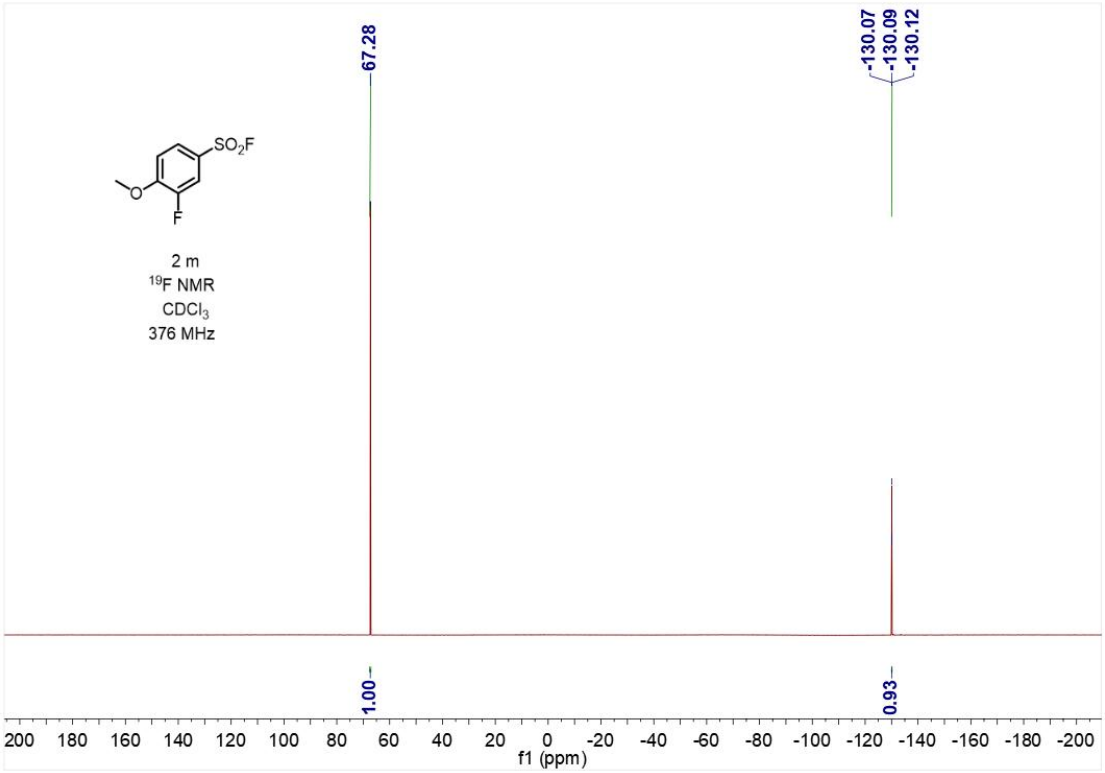

$^{13}$C NMR spectrum of **2l**



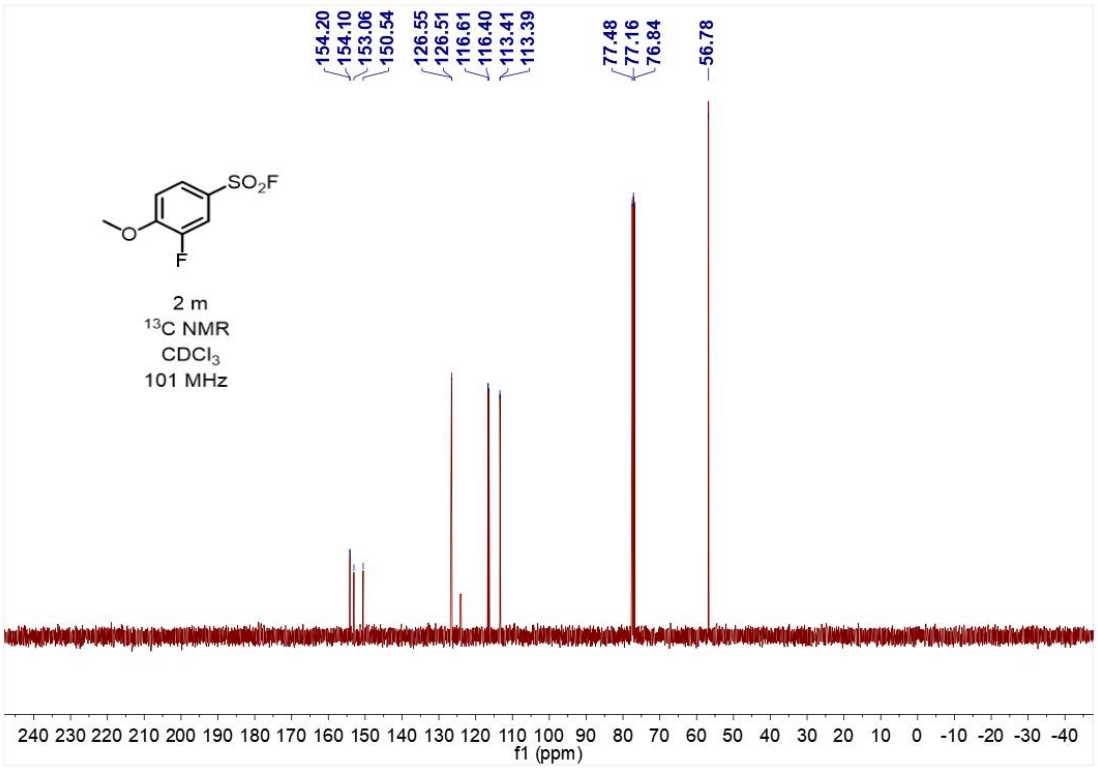
[1] H NMR spectrum of **2m**



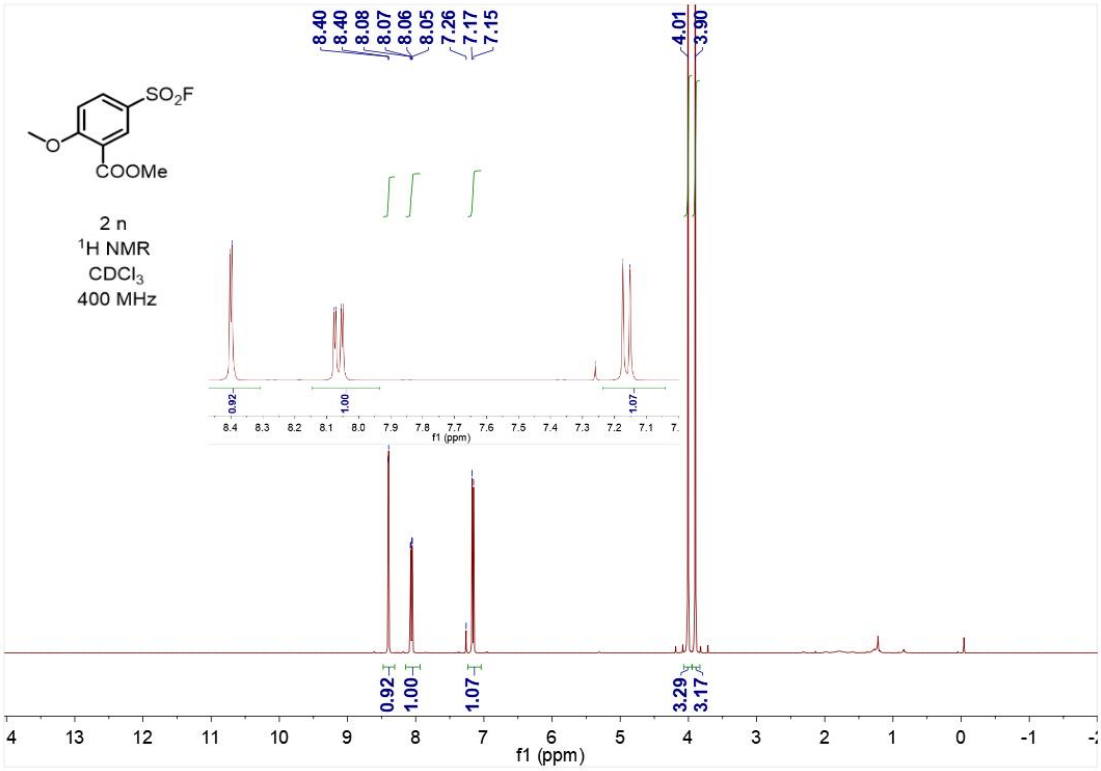

[19] F NMR spectrum of **2m**



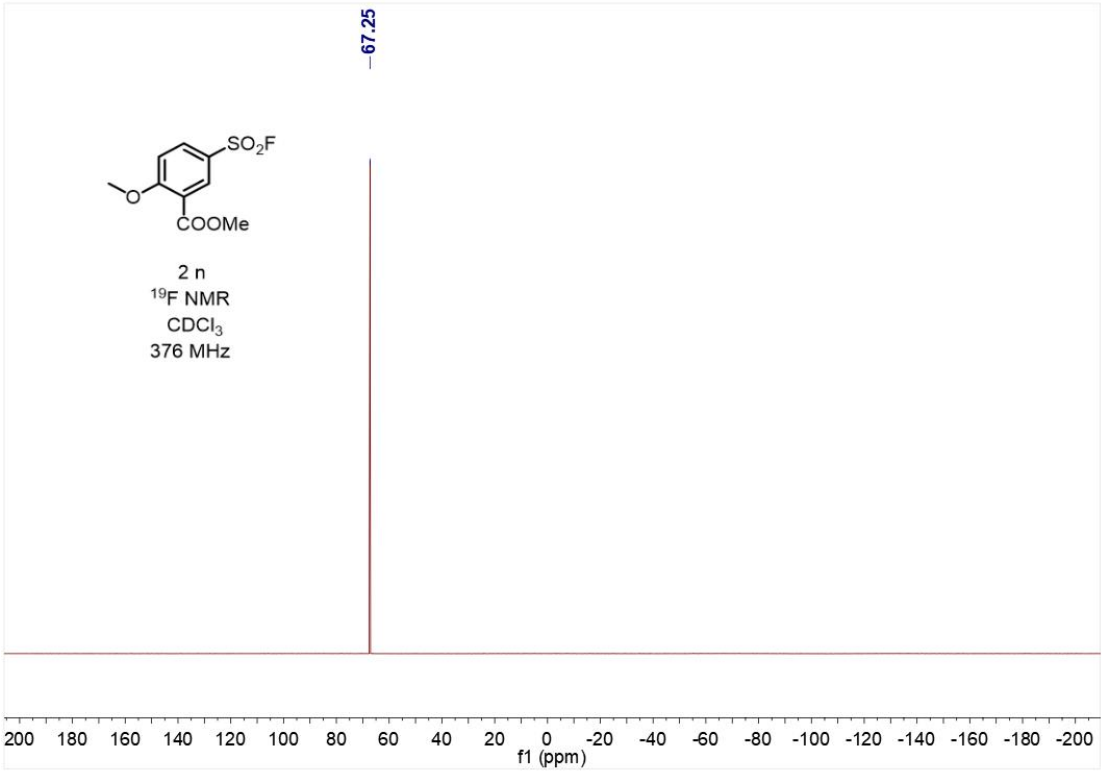
$^{13}$C NMR spectrum of **2m**



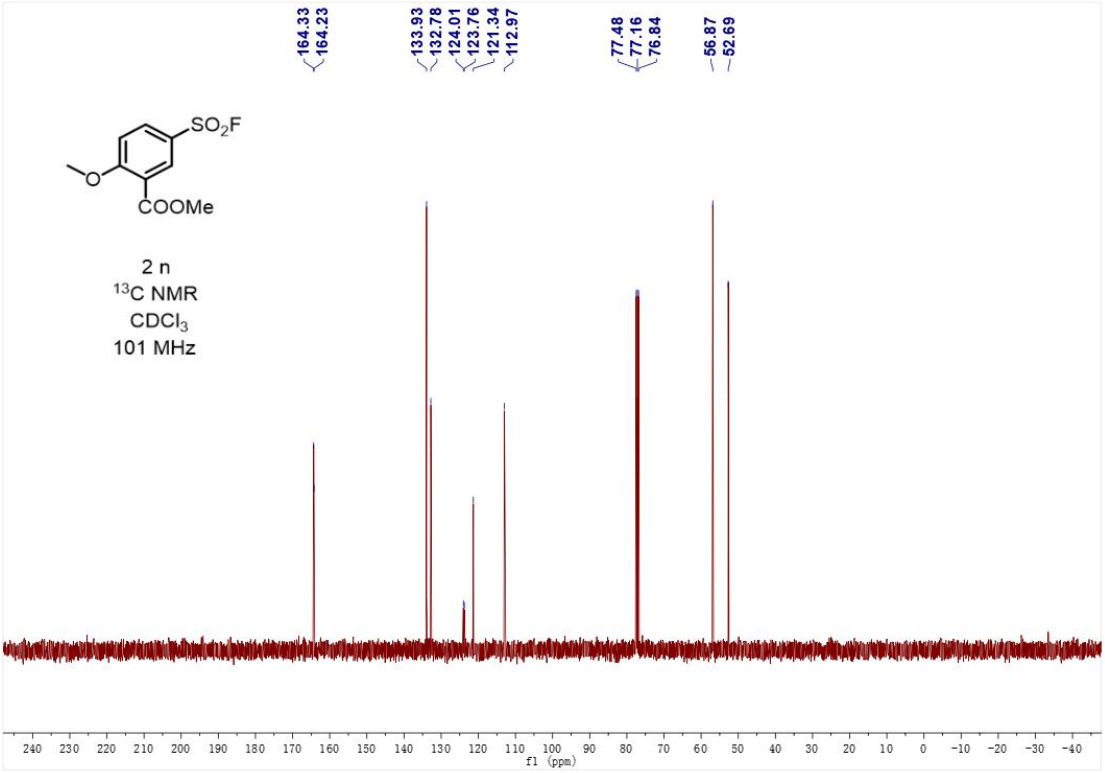

$^{1}$H NMR spectrum of **2n**



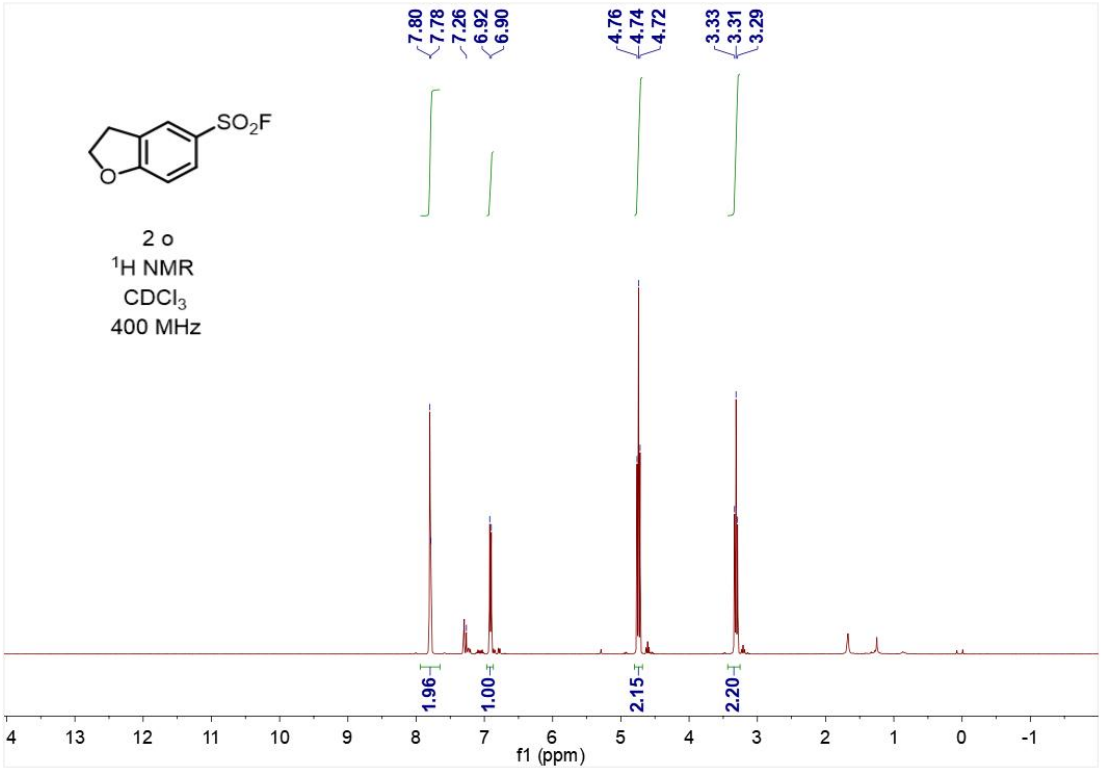
$^{19}$F NMR spectrum of **2n**



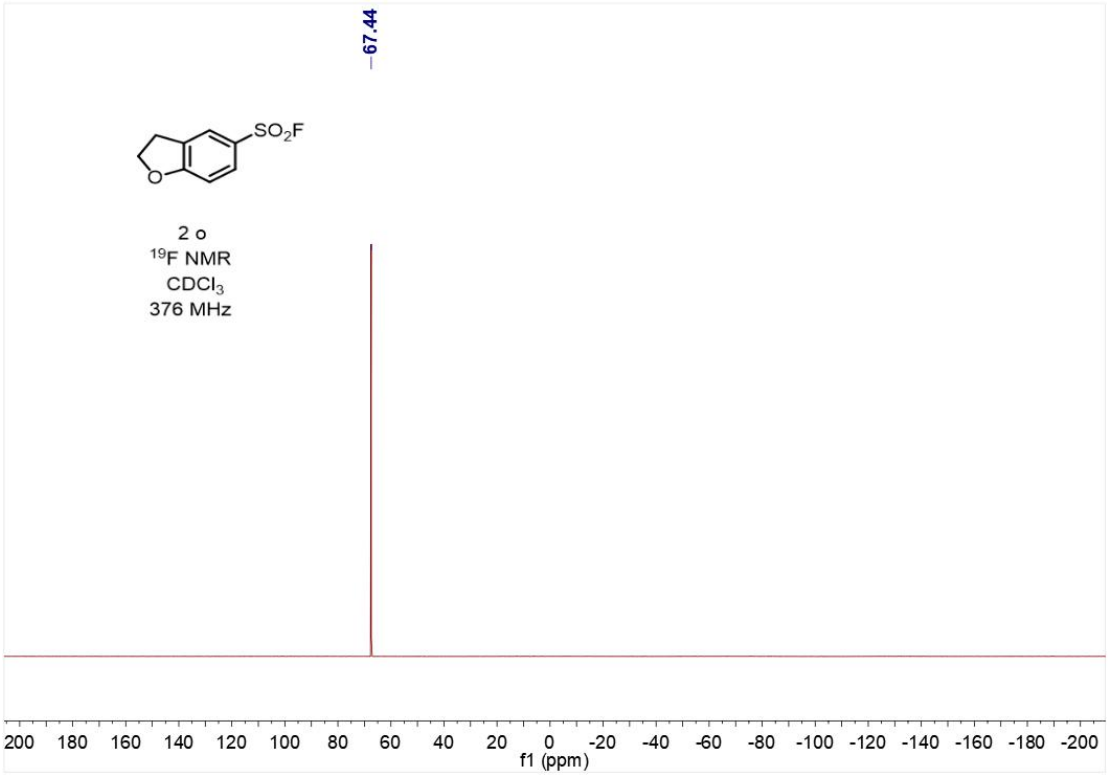

$^{13}$C NMR spectrum of **2n**



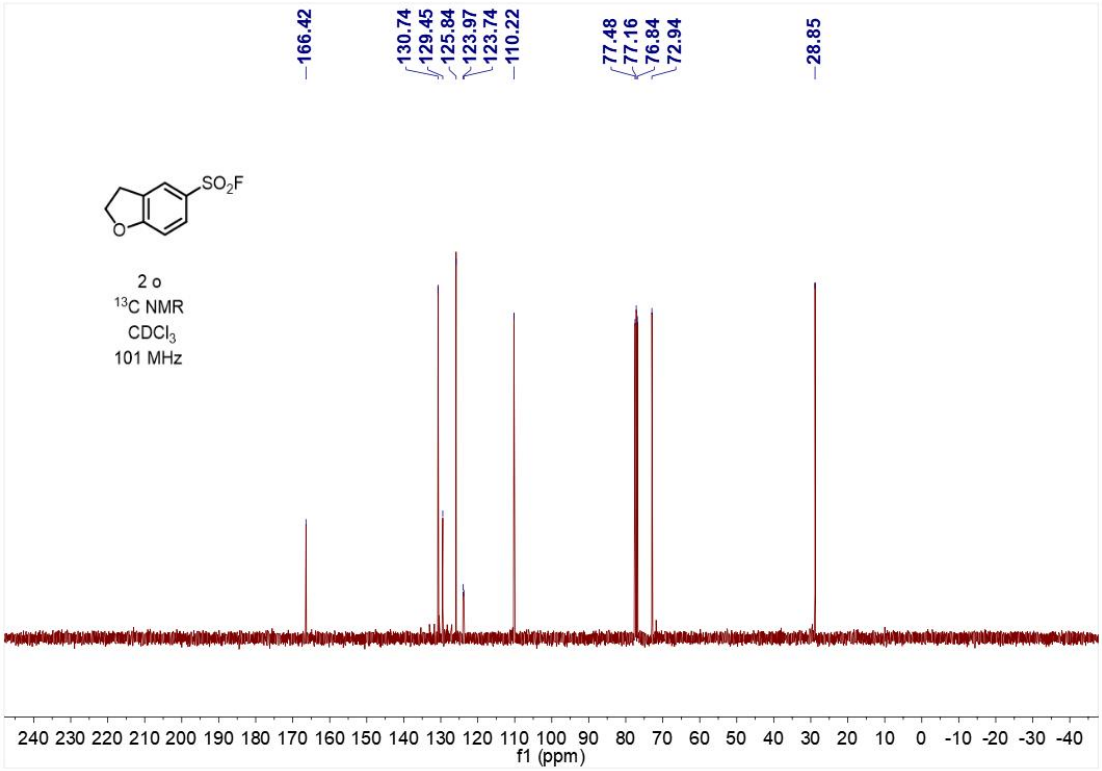
[1] H NMR spectrum of **2o**



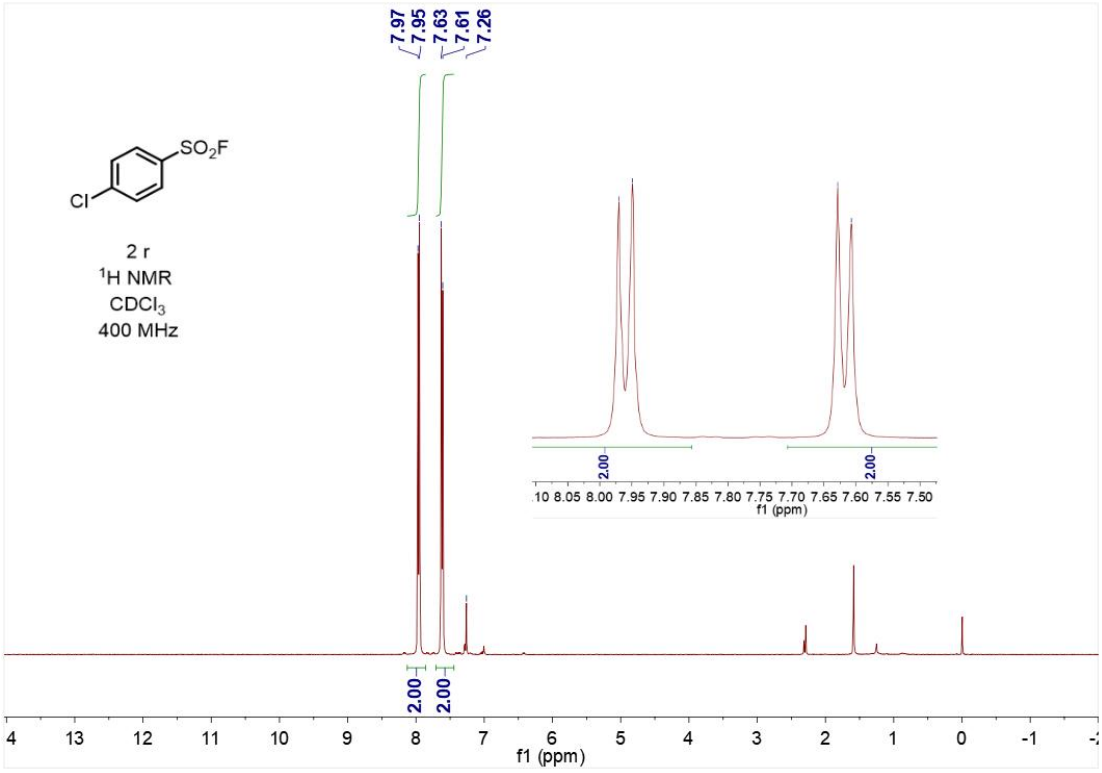

[19] F NMR spectrum of **2o**



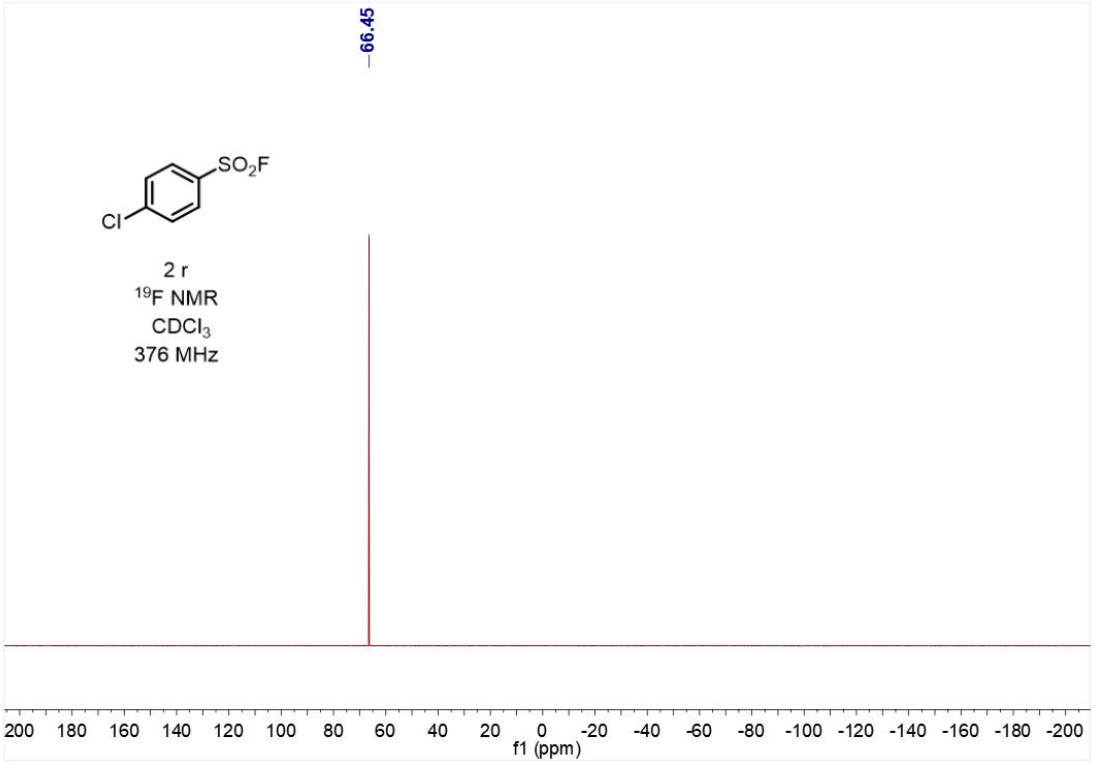
$^{13}$C NMR spectrum of **2o**



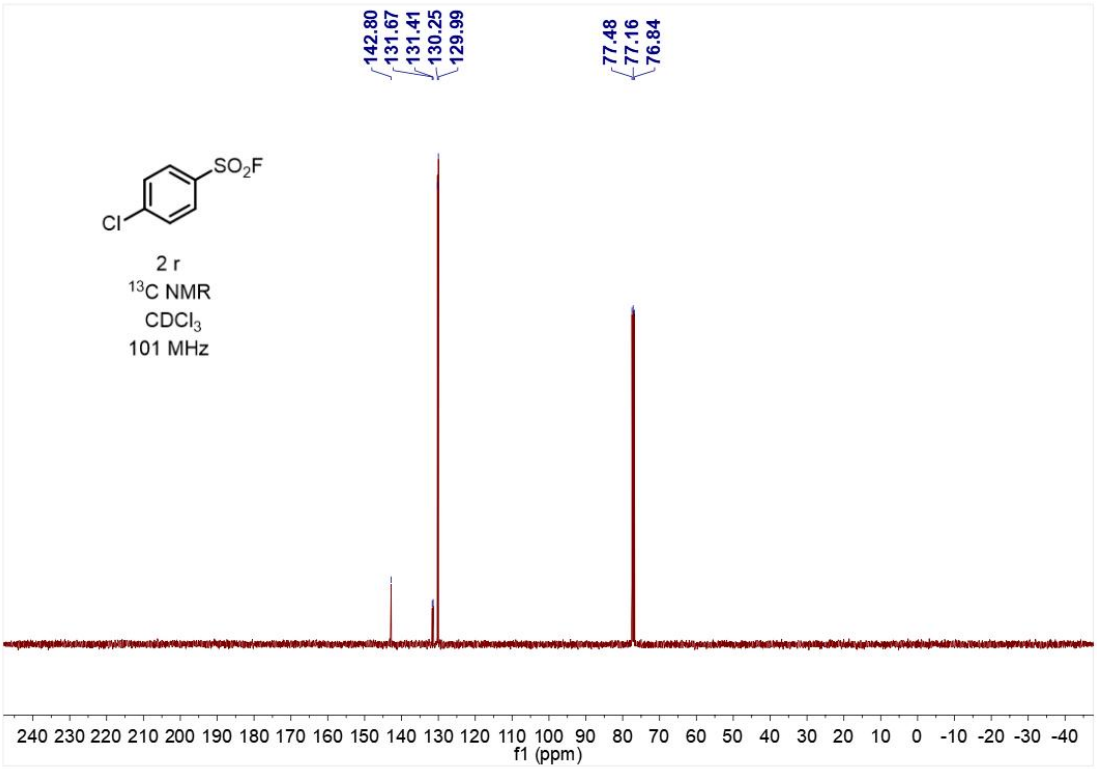

$^{1}$H NMR spectrum of **2r**



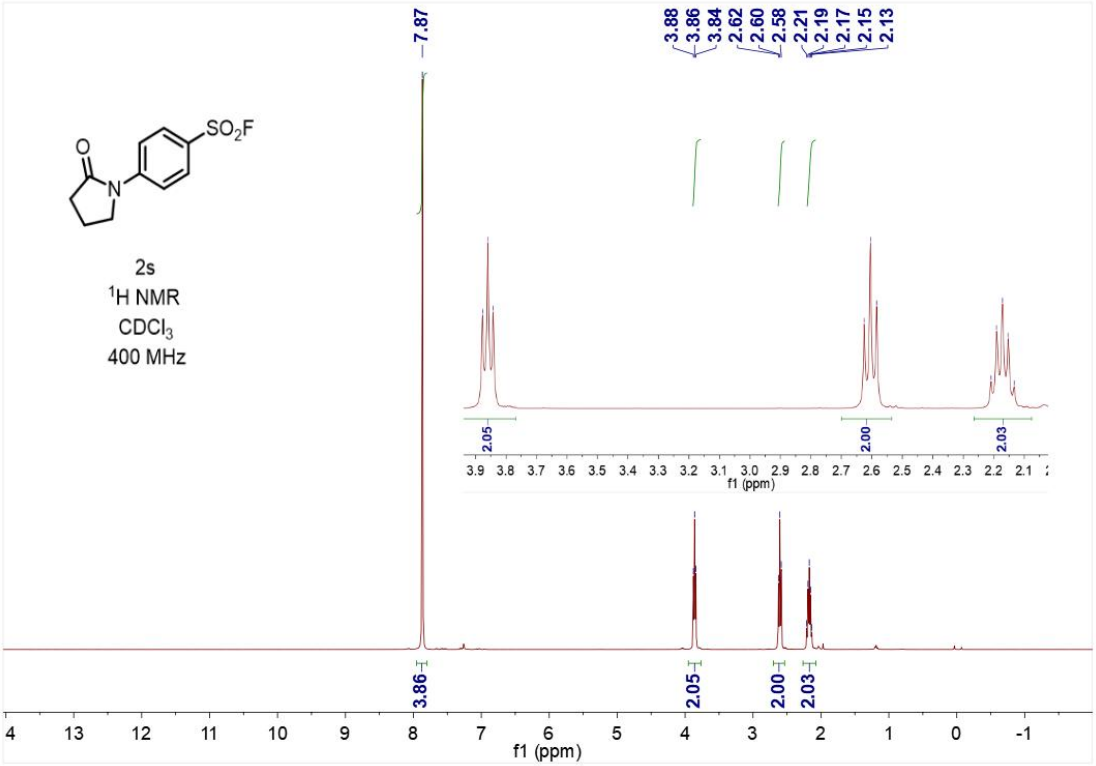
$^{19}$F NMR spectrum of **2r**



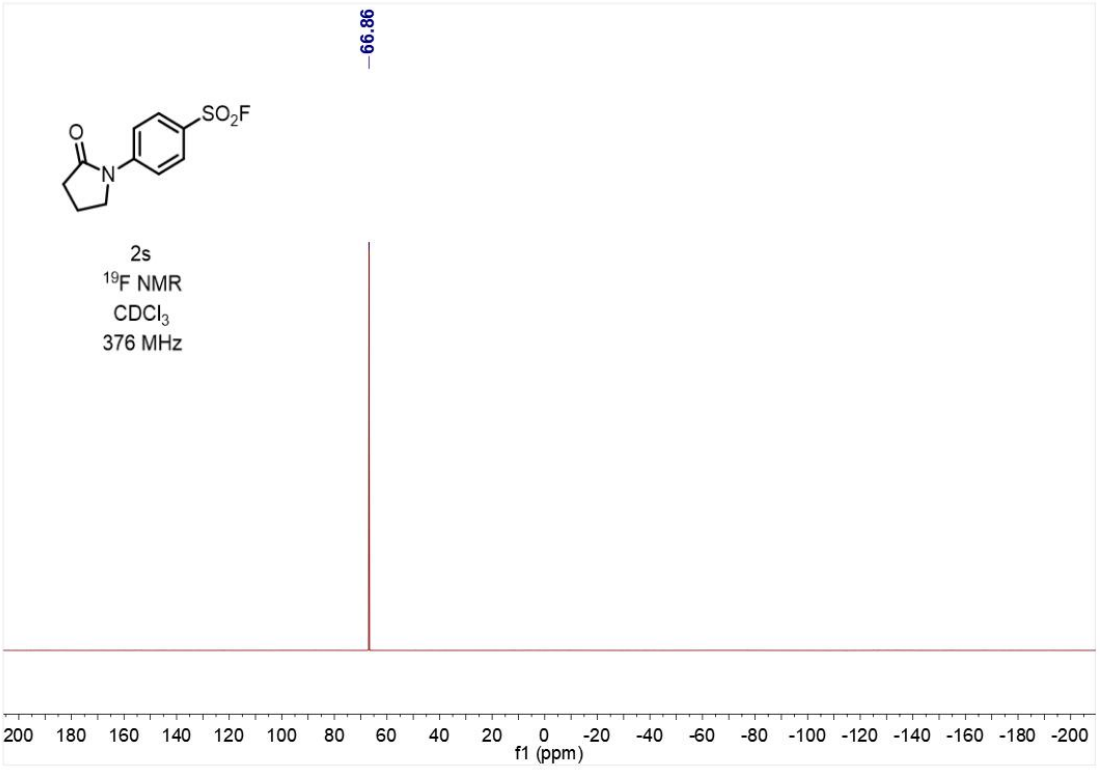

$^{13}$C NMR spectrum of **2r**



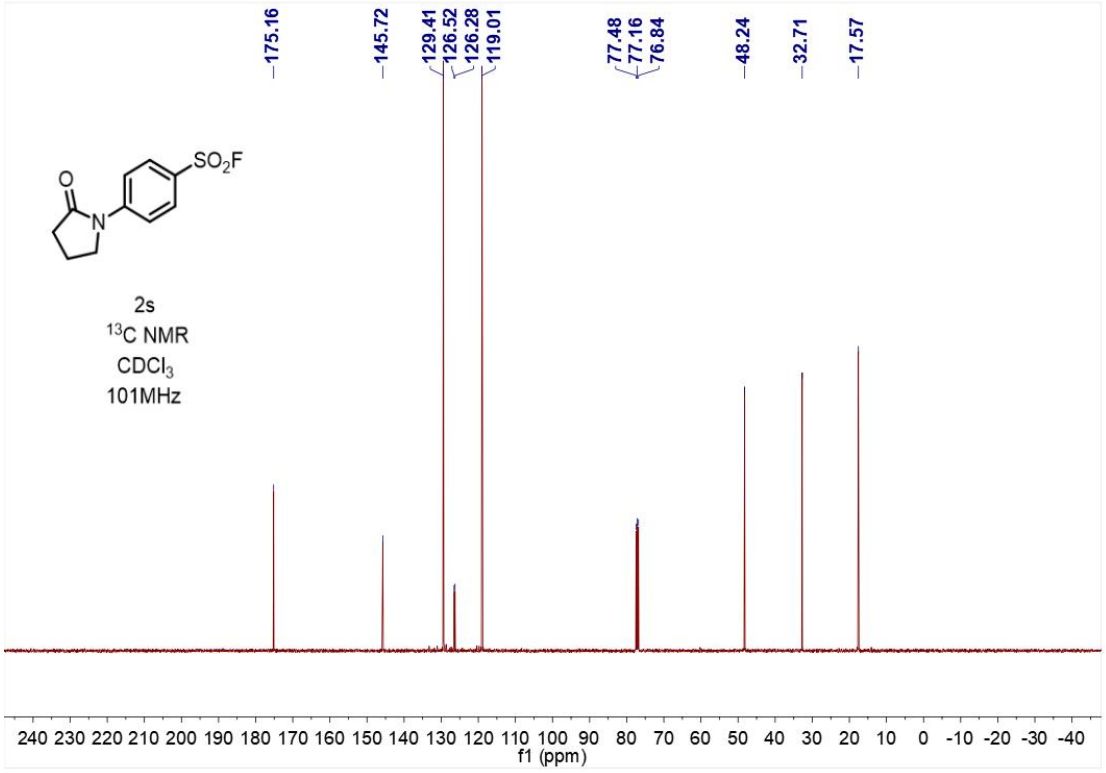
[1] H NMR spectrum of **2s**



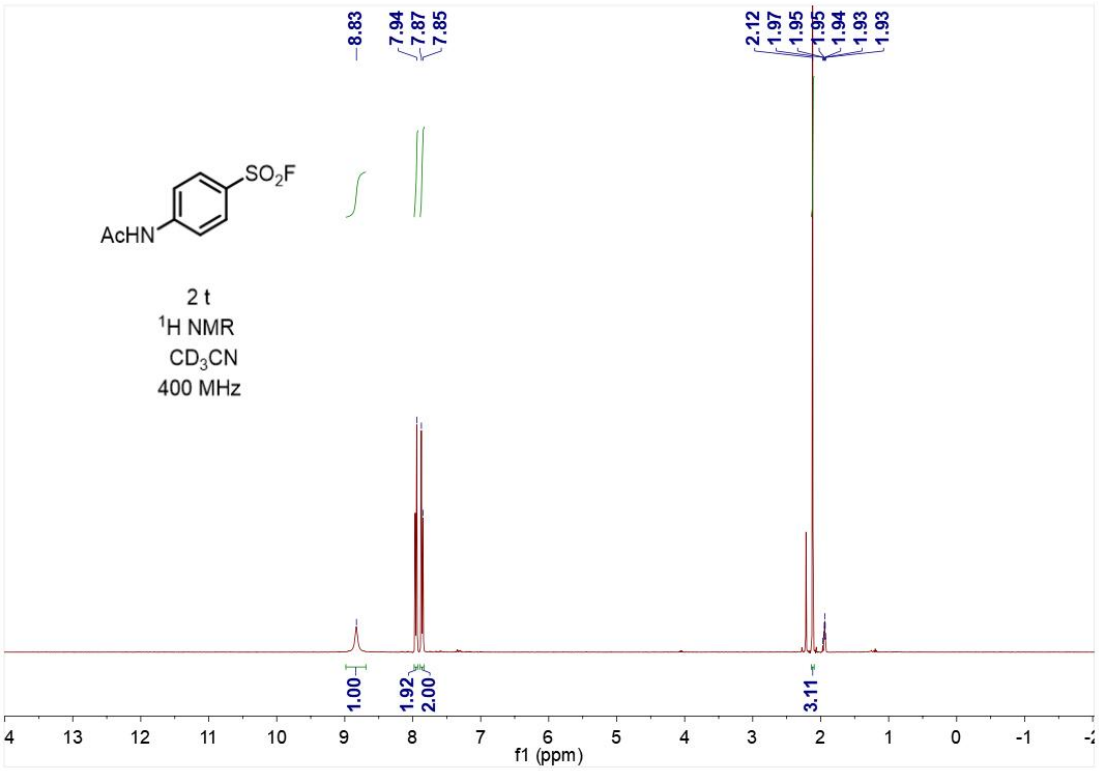

[19] F NMR spectrum of **2s**



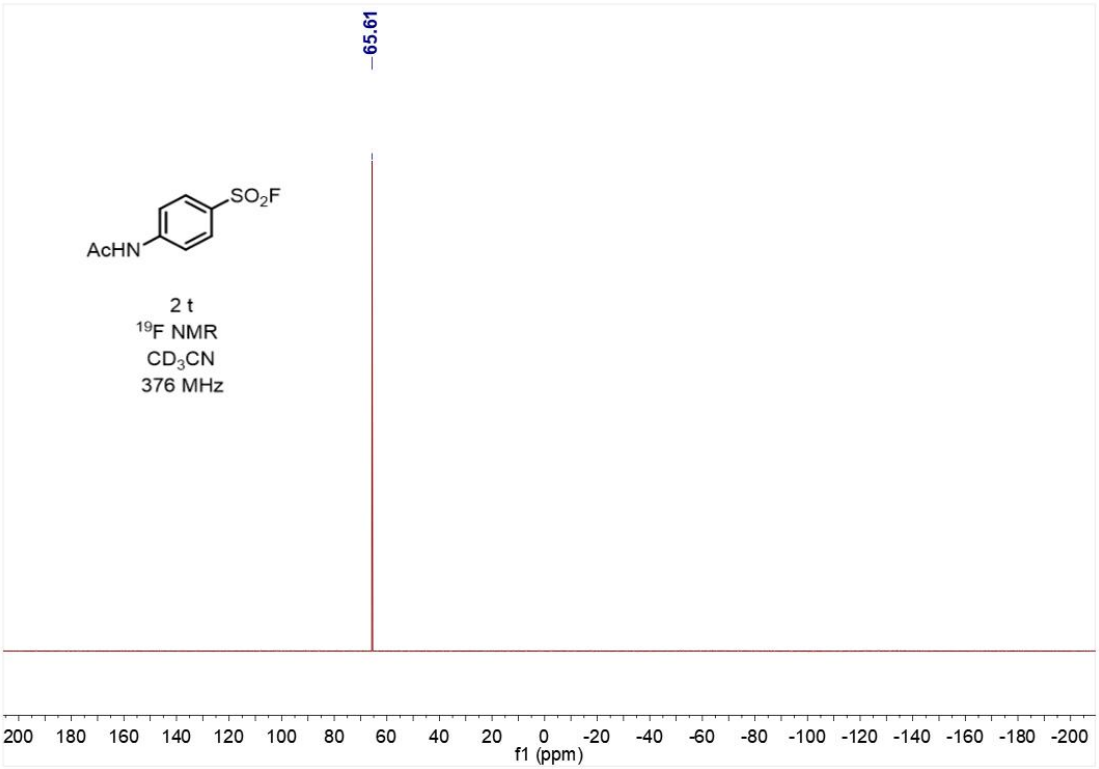
$^{13}$C NMR spectrum of **2s**



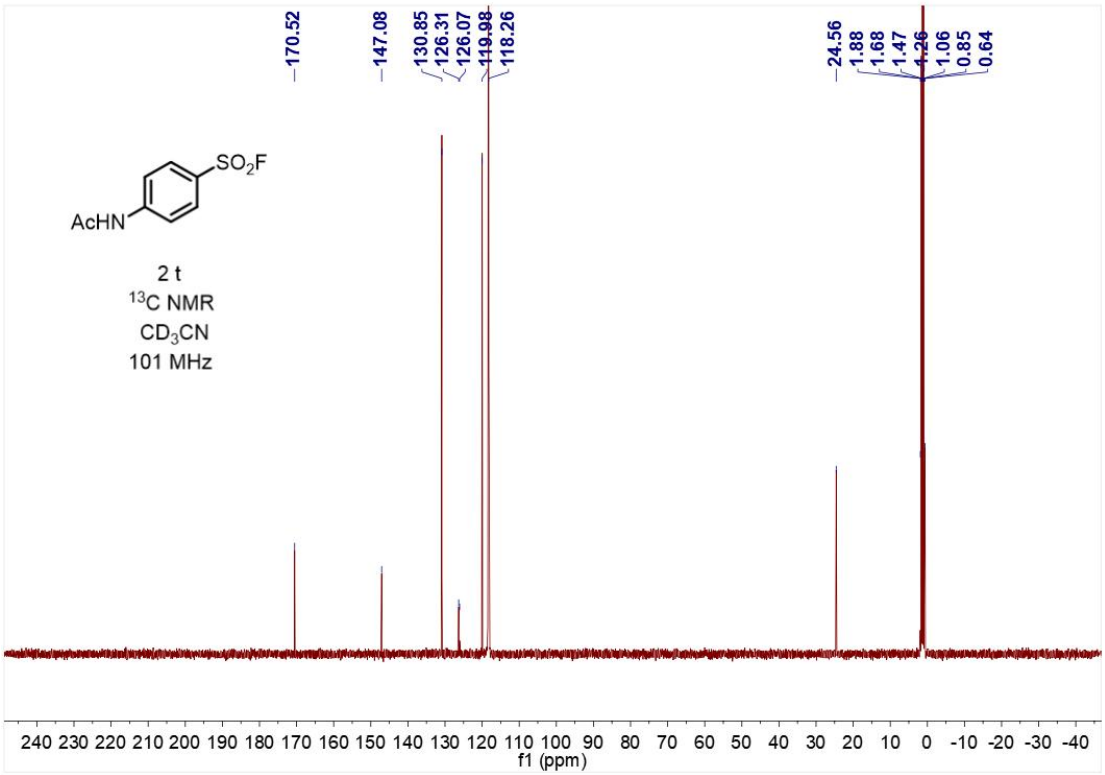

$^{1}$H NMR spectrum of **2t**



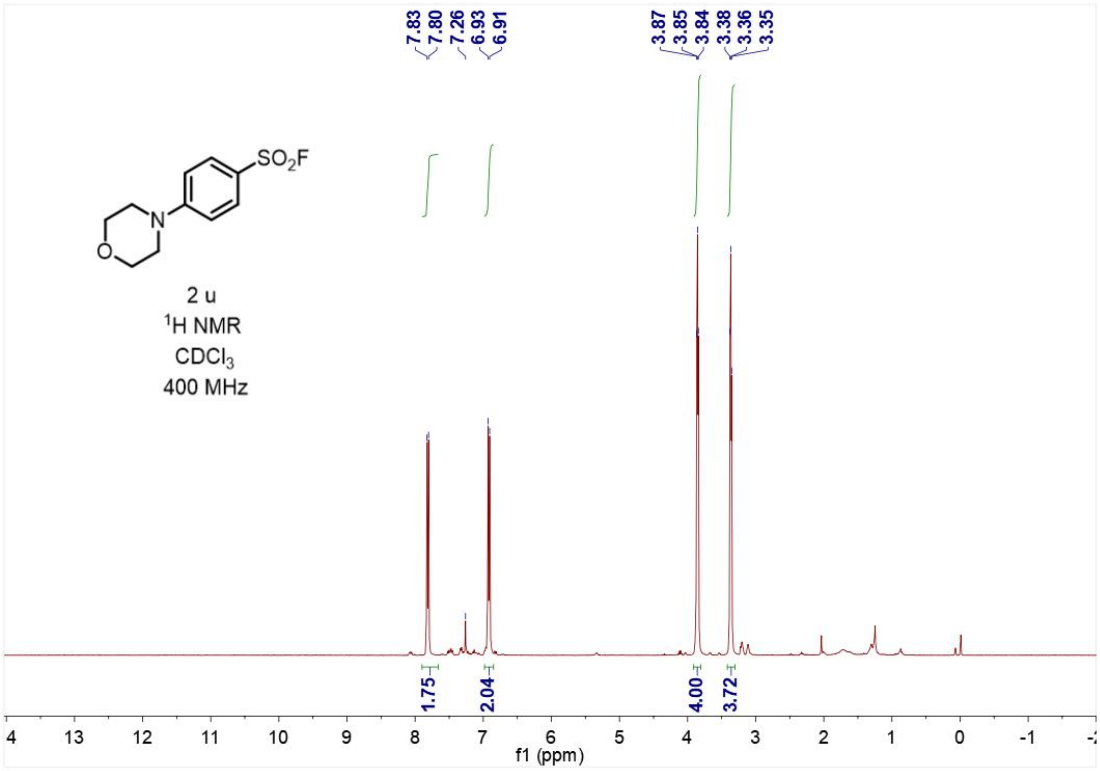
$^{19}$F NMR spectrum of **2t**



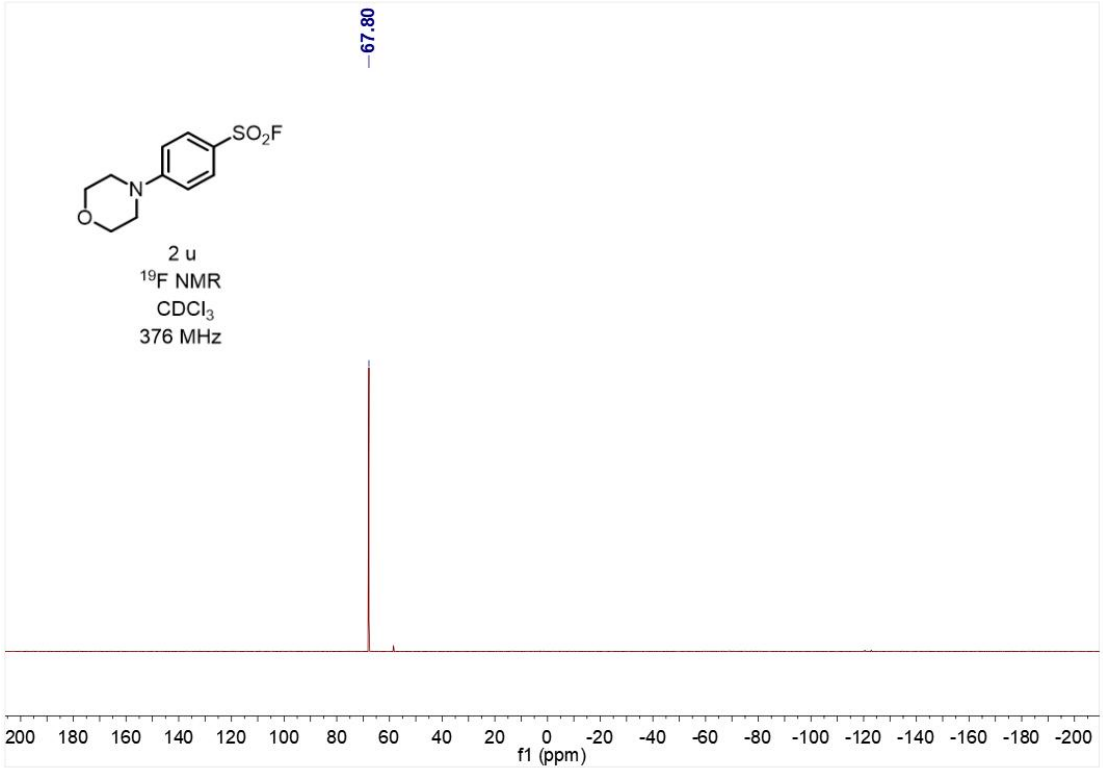

$^{13}$C NMR spectrum of **2t**



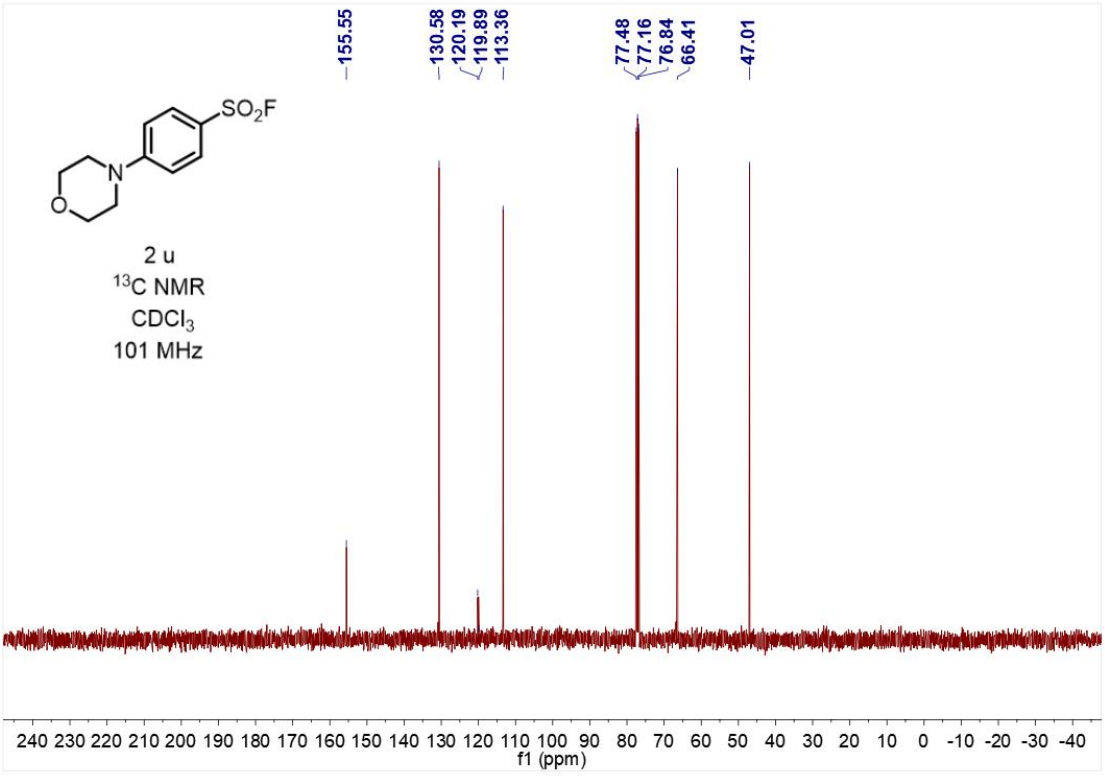
[1] H NMR spectrum of **2u**



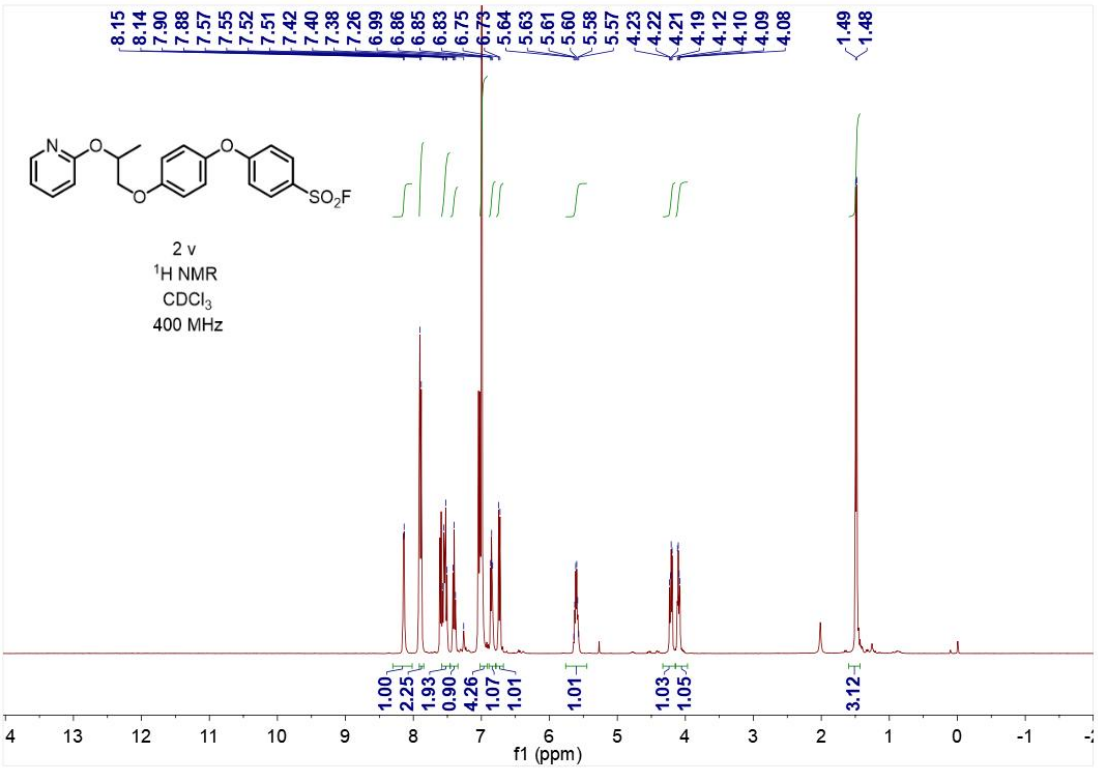

[19] F NMR spectrum of **2u**



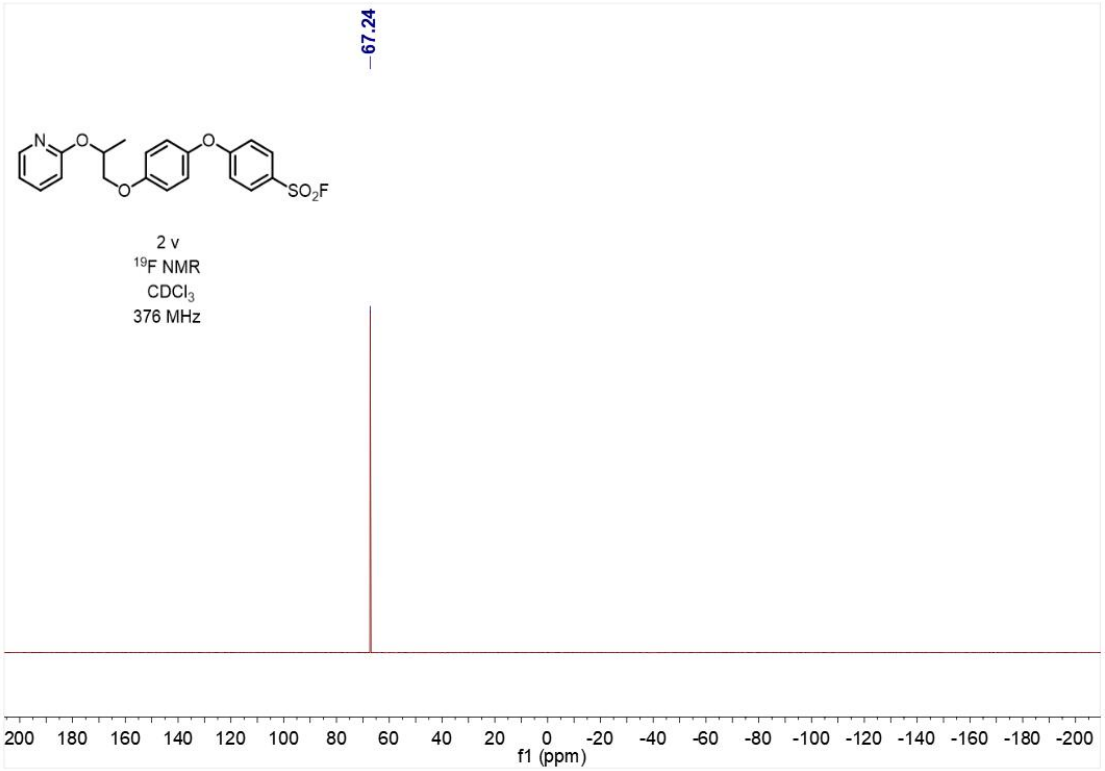
$^{13}$C NMR spectrum of **2u**



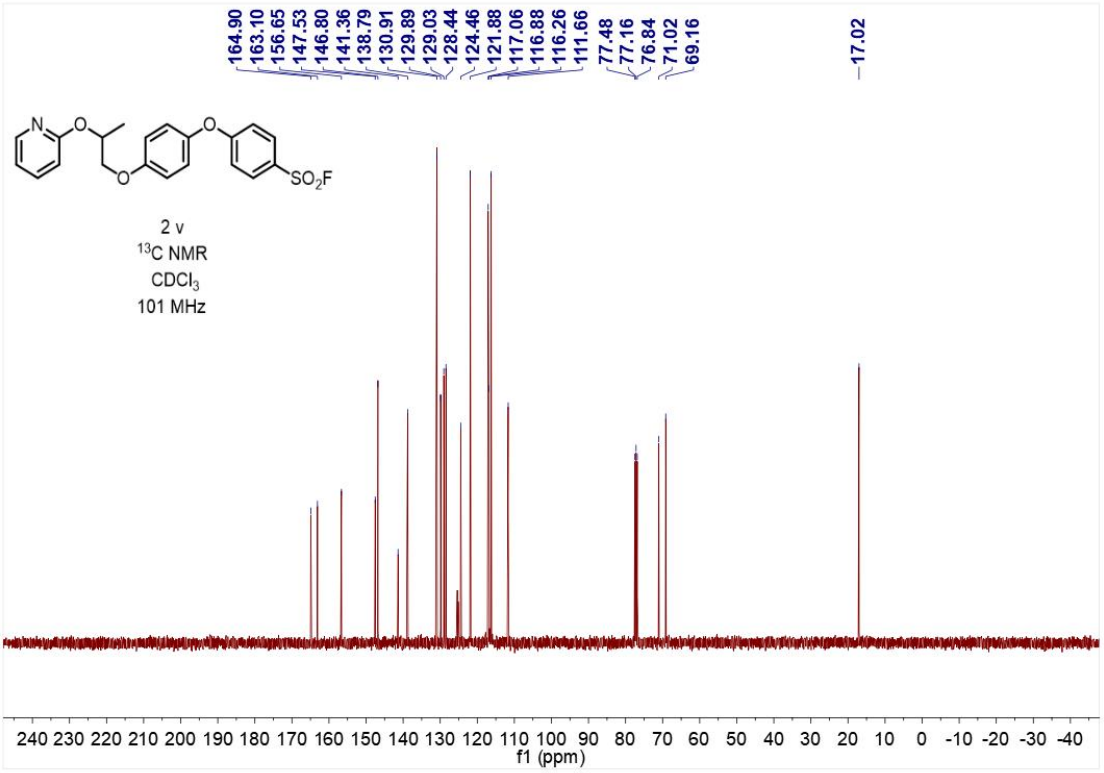

$^{1}$H NMR spectrum of **2v**



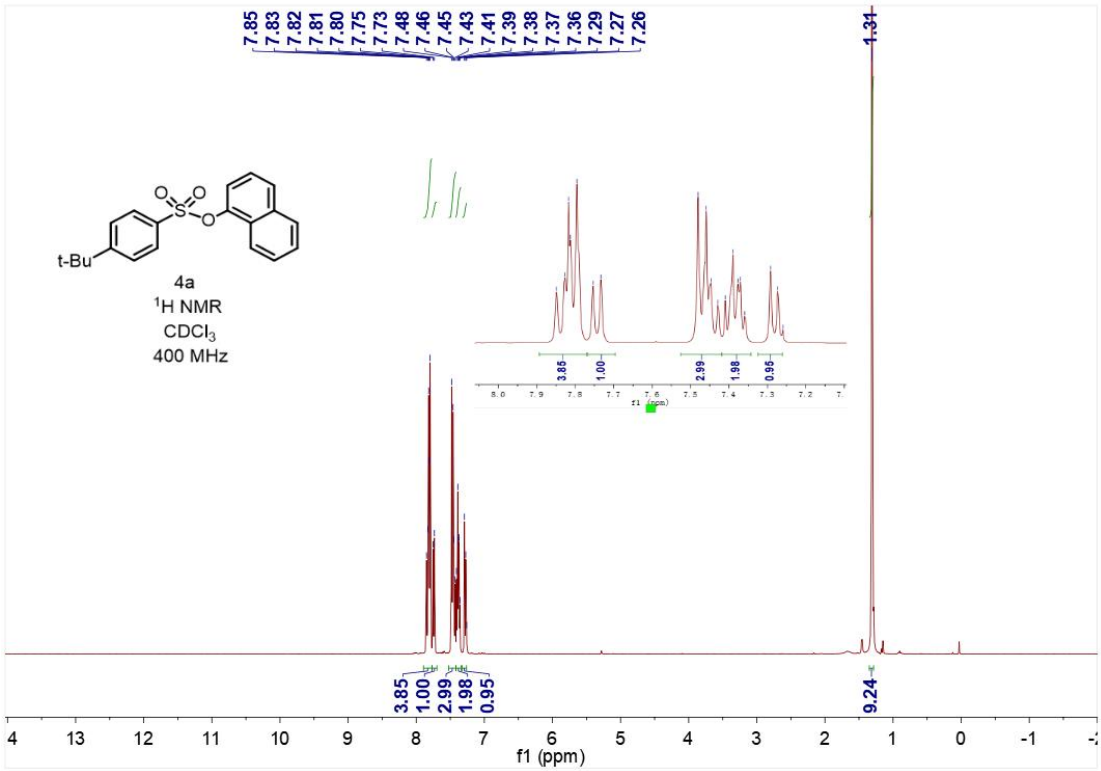
$^{19}$F NMR spectrum of **2v**



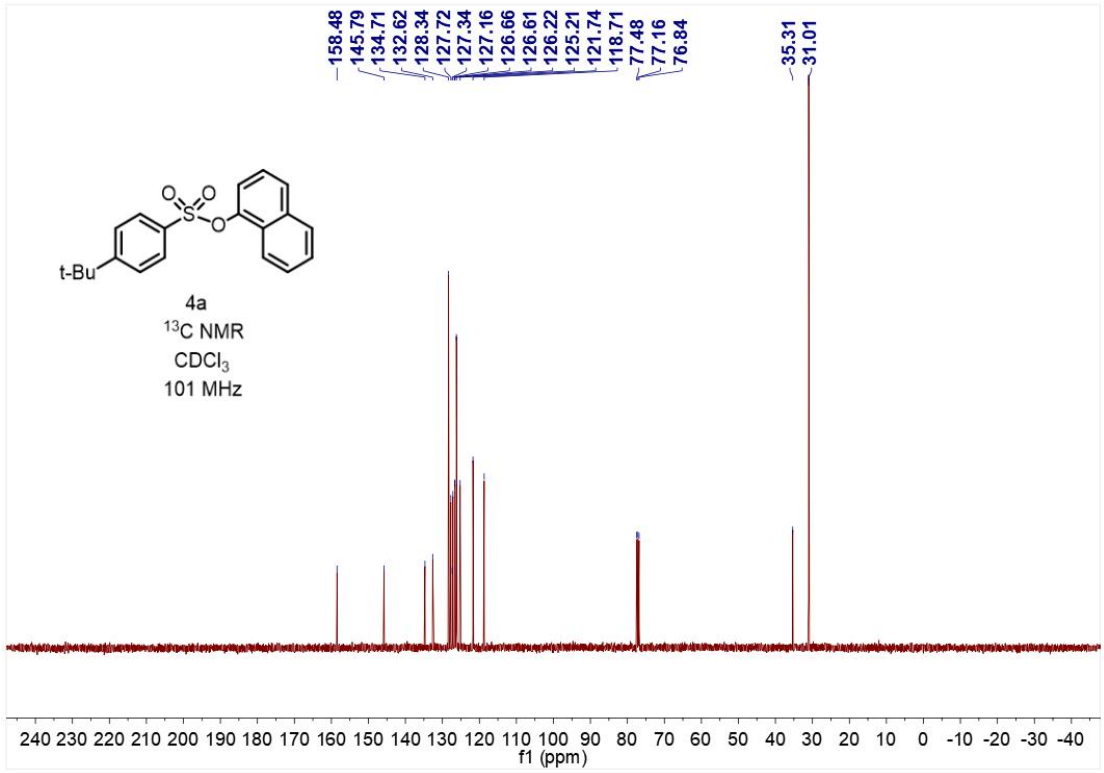

$^{13}$C NMR spectrum of **2v**



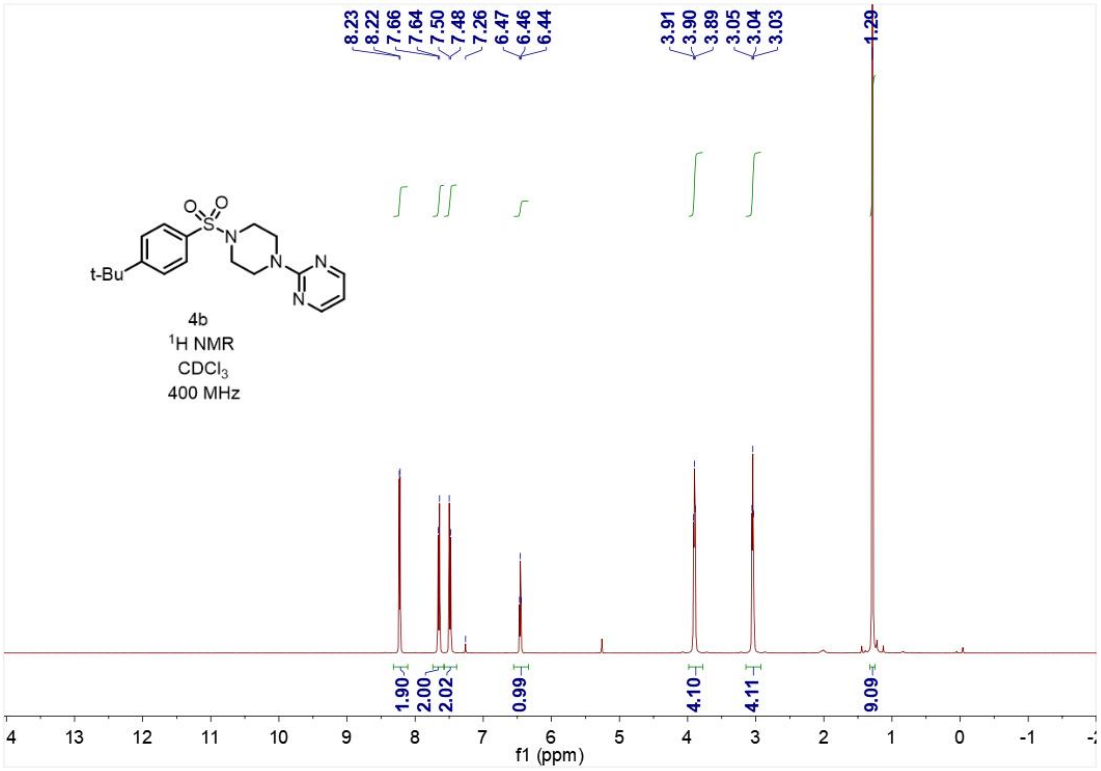
[1] H NMR spectrum of **4a**



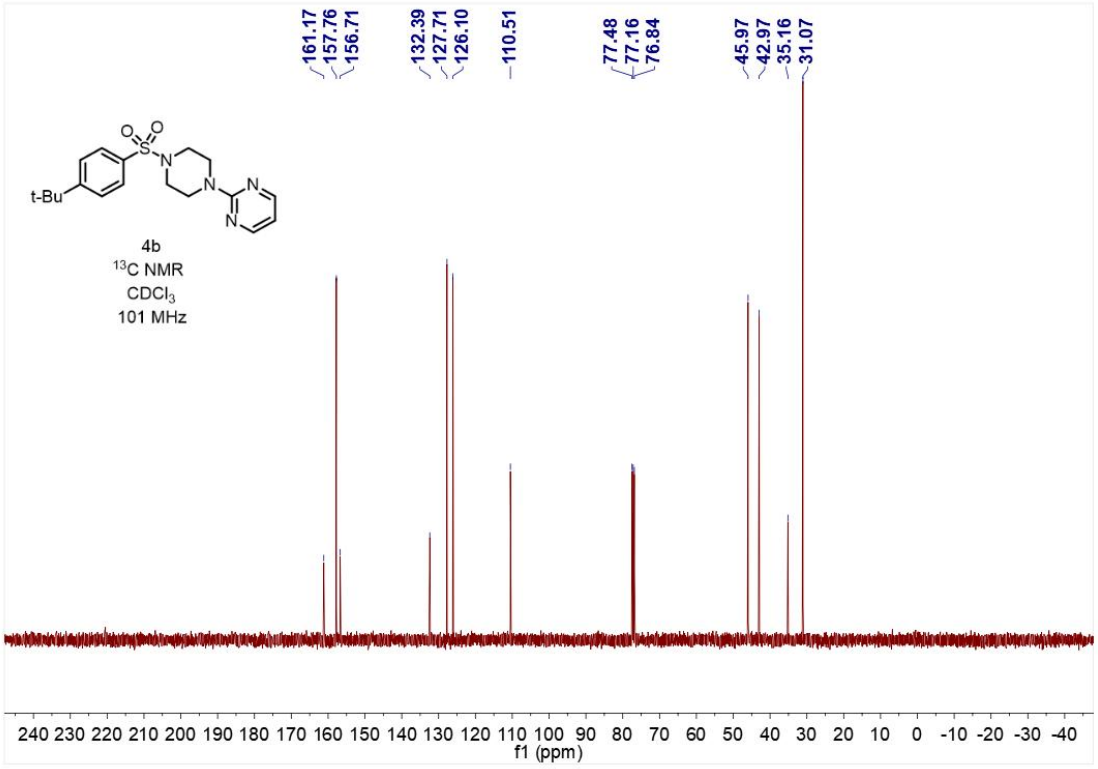

[13] C NMR spectrum of **4a**



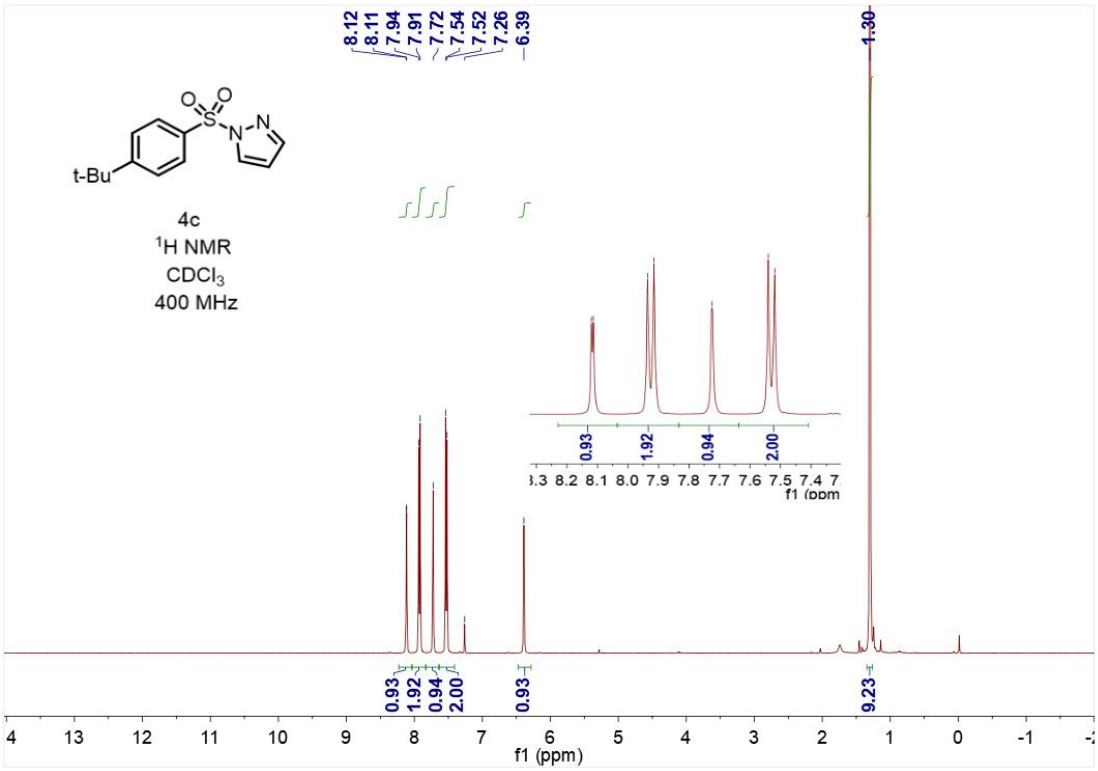
[1] H NMR spectrum of **4b**



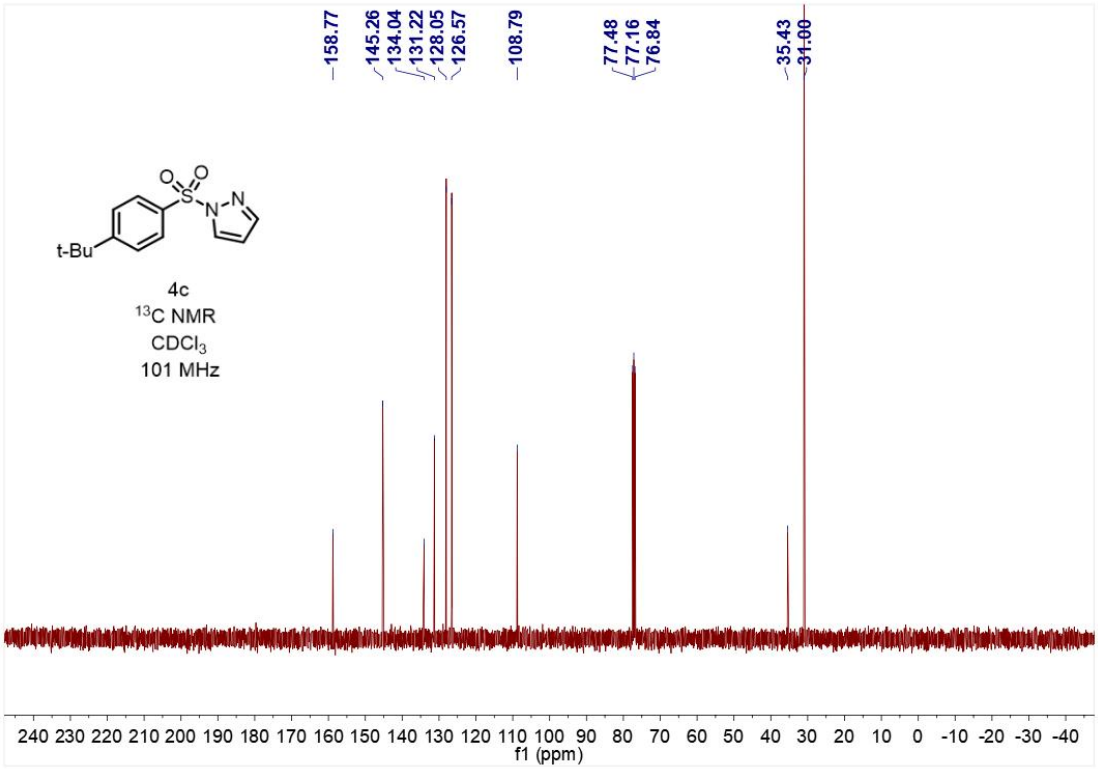

[13] C NMR spectrum of **4b**



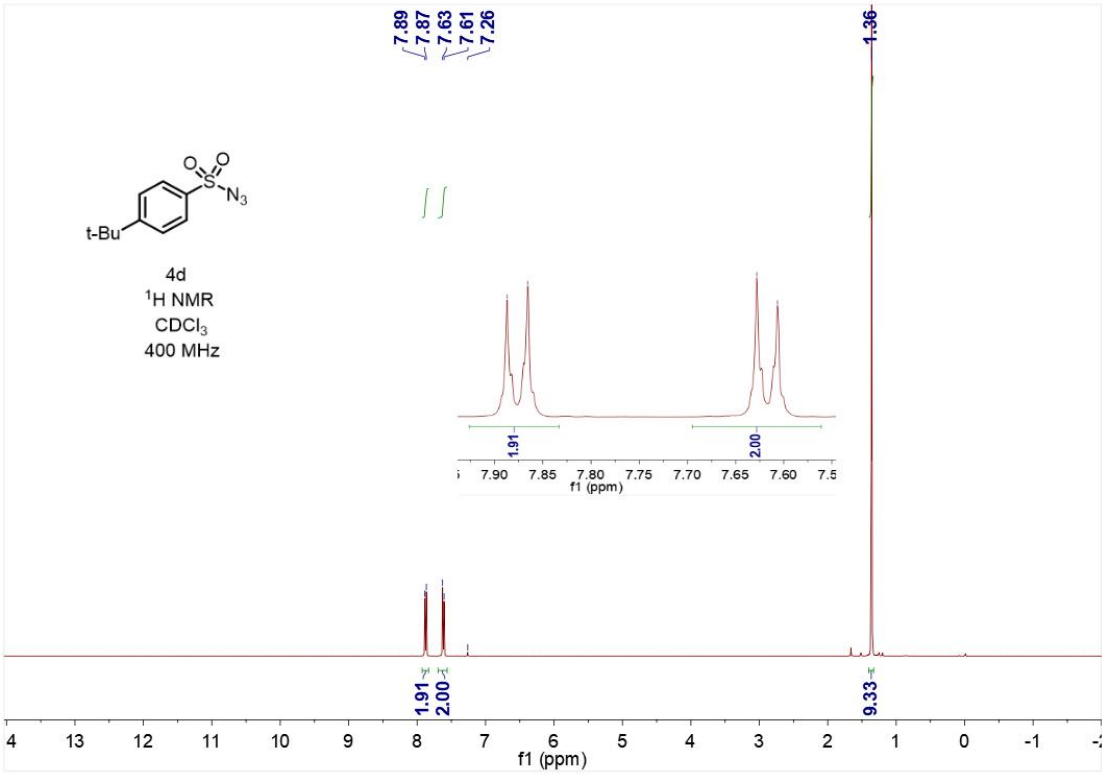
[1] H NMR spectrum of **4c**




[13] C NMR spectrum of **4c**



[1] H NMR spectrum of **4d**




[13] C NMR spectrum of **4d**