Supporting Information

Direct Synthesis of Organothianthrenium Salts under Ball Milling Conditions

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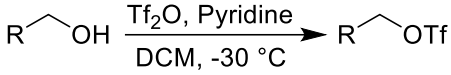
1.General Information

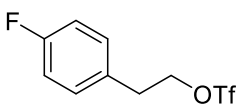
Unless otherwise noted, materials obtained from commercial suppliers were used without require further purification. All mechanochemical reactions were achieved using grinding vessels in a Retsch MM 400. The ball grinding jar (5 mL) and two balls (8.0-mm-diameter), which are made of stainless steel (SUC400B and SUS420J2, respectively), are used for standard ball milling reactions. Other types of ball grinding jars are also carried out under standard conditions, for example, 10 mL stainless-steel milling jar with two stainless-steel balls (8.0 mm) and 10 mL zirconium oxide milling jar with two zirconium oxide balls (8.0 mm). ^{1}H and ^{13}C NMR spectra were recorded on an Agilent DD2 400 MHz spectrometer. The chemical shifts in ^{1}H NMR spectra were recorded relative to $CDCl_3$ (δ 7.26 ppm) / CD_3CN (δ 1.94 ppm). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.0 ppm) / (δ 1.32 ppm). The high-resolution mass spectral (HRMS) data were obtained on Bruker Dalton maXis Q-TOF (ESI). Gas analyses were conducted with a Shimadzu GC-2014 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and an FID detector. Multiplicity was recorded as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, and m = multiplet.

2. Substrates Preparation

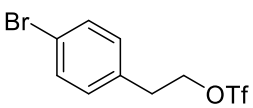


A flame-dried 100 mL flask was placed under an atmosphere of nitrogen and charged with a stir bar and alcohol (5.0 mmol, 1.0 equiv). The alcohol was dissolved in CH_2Cl_2 (20.0 mL) and cooled to -30 °C before adding pyridine (483 µL, 6.0 mmol, 1.2 equiv). While stirring, triflic anhydride (1.0 mL, 29.3 mmol, 1.20 equiv) was added dropwise, and then the reaction mixture stirred for 3 h while remaining at -5 °C. While the flask was still in a -5 °C bath, 0.5 M H_2SO_4 (30 mL) was added. The flask was removed from the cold bath, and the mixture was transferred to a separatory funnel and extracted with 3×20 mL of CH_2Cl_2. The organic layers were combined and washed 1× 50 mL of distilled water. The collected organic layers were then dried over $MgSO_4$, then filtered and concentrated to a 10 mL liquid under vacuum (without heating), which was used directly in the next step.

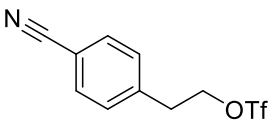
Alkyl Thianthrenium Salts



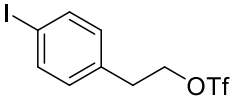
1a



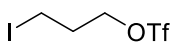
1b



1c



1d



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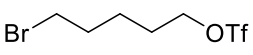
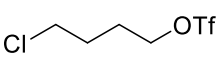


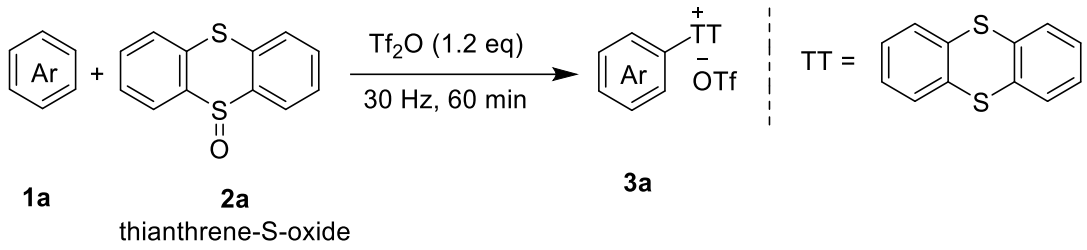
1g



1f

3. Experimental Procedures and Characterization of Products

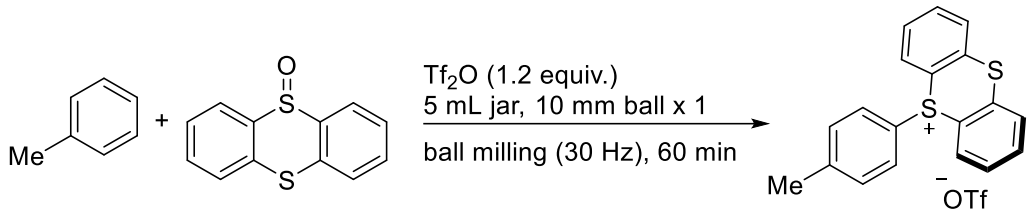
Synthesis of arylthianthrene salts



1a **2a** thianthrene-S-oxide **3a**

To a 5.0 mL Retsch stainless steel milling jar was added aryl **1a** (1.5 equiv., 0.75 mmol), thianthrene S-oxide **2a** (1.0 equiv., 0.5 mmol), and Trifluoromethanesulfonic anhydride (1.2 equiv., 0.6 mmol) under air atmosphere. A stainless-steel ball of mass 2.8 g was added and the mixture was milled at 30 Hz for 1 hours. After the reaction, the saturated sodium chloride aqueous solution was used for neutralization, the extraction was carried out with methylene chloride, the organic phase was combined with anhydrous sodium sulfate for drying, and after the solvent was removed by spin evaporation on the rotary evaporator, the crude product was purified and crystallized by methylene chloride. If the product could not be precipitated in the system, the product was purified by flash silica gel column chromatography using methylene chloride/methanol system.

Gram-scale reaction:



1aa
7.5 mmol

2aa
thianthrene-S-oxide
5.0 mmol.

3aa

Operation steps

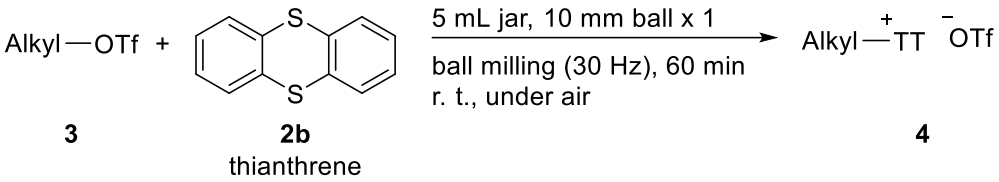
Step 1: All chemicals were added in air

Step 2: Ball milling for 60 min (30 Hz)

Step 3: Isolation of the product

To a 10.0 mL Retsch stainless steel milling jar was added aryl **1aa** (1.5 equiv., 7.5 mmol), thianthrene S-oxide **2aa** (1.0 equiv., 5.0 mmol), and Trifluoromethanesulfonic anhydride (1.2 equiv., 6.0 mmol) under air atmosphere. A stainless-steel ball of mass 2.8 g was added and the mixture was milled at 30 Hz for 1 hours. After the reaction, the saturated sodium chloride aqueous solution was used for neutralization, the extraction was carried out with methylene chloride, the organic phase was combined with anhydrous sodium sulfate for drying, and after the solvent was removed by spin evaporation on the rotary evaporator, the product was purified and crystallized by methylene chloride, afford **3aa** (1940 mg, 86%) as a faint white solid.

Optimization of thianthrenium S-(alkyl) salts[a]



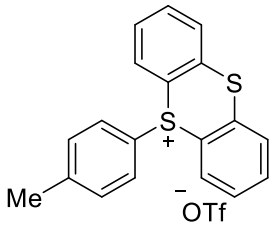
3 **2b** thianthrene **4**

entry	temperature (℃)	ratio (3:2b)	time (h)	isolated yield (%)
1	100	1:1	1	47
2	100	1:1	2	56
3	150	1:1	2	55
4	100	2:1	1	85
5	100	1:2	1	N.D.

[a]Conditions: 3 (1.0 mmol) and thianthrene 2b (0.5 mmol) in a stainless-steel ball-milling jar (5 mL) with one stainless-steel ball (diameter: 10 mm).

5-(p-Tolyl)-*5H*-thianthren-5-ium trifluoromethanesulfonate (3a)

The reaction was performed according to the general procedure. The reaction was conducted with **1a** (80 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3a** (195.3 mg, 86%) as a brown solid.

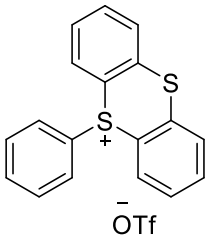


3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.8 Hz, 2H), 7.85 – 7.65 (m, 6H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 2.27 (s, 3H) ppm.**^{13}C NMR (101 MHz, $CDCl_3$)** 144.4, 136.5, 135.2, 134.9, 131.5, 130.3, 130.2, 128.0, 120.3, 118.9, 21.4 ppm. **HRMS m/z (ESI):** calcd for $C_{20}H_{15}F_3O_3S_3$ $(M–OTf)^+$ 308.0682, found 308.0656.

5-phenyl-5H-thianthren-5-ium trifluoromethanesulfonate (3b)

The reaction was performed according to the general procedure. The reaction was conducted with **1b** (68 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3b** (148.0 mg, 67%) as a white solid.

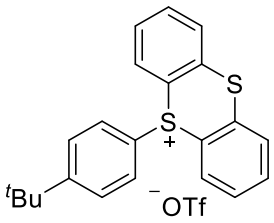


3b

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.71 – 8.65 (m, 2H), 7.89 – 7.78 (m, 6H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.21 – 7.17 (m, 2H) ppm.**^{13}C NMR (151**

MHz, Chloroform-*d*) δ 136.8 , 135.7 , 135.0 , 133.0 , 130.7 , 130.3 , 130.3 , 128.0 , 118.9 ppm.

5-(4-(*tert*-Butyl)phenyl)-5H-thianthren-5-ium trifluoromethanesul (3c)

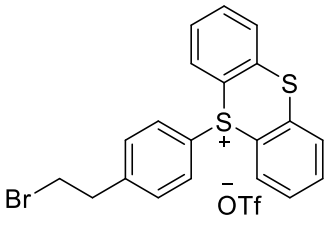


3c

The reaction was performed according to the general procedure. The reaction was conducted with **1c** (120 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3c** (200.0 mg, 80%) as a brown solid.

^{1}H NMR (400 MHz,Chloroform-d) δ 8.65 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.79 (m, 6H), 7.50 – 7.41 (m, 2H), 7.19 – 7.10 (m, 2H), 1.25 (s, 9H) ppm.**^{13}C NMR (101 MHz, Chloroform-d)** δ 157.3, 136.5, 135.6, 134.9, 130.3, 128.1, 128.0, 120.3, 118.9, 35.2, 30.9. ppm. **HRMS m/z (ESI):** calcd for $C_{23}H_{21}F_3O_3S_3$ $(M\text{-}OTf)^+$350.1152, found 350.1150.

5-(4-(2-Bromoethyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (3d)

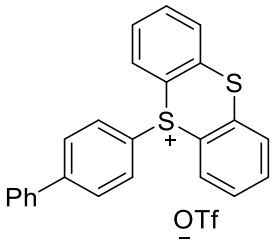


3d

The reaction was performed according to the general procedure. The reaction was conducted with **1d** (100 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3d** (250.2 mg, 91%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.53 (d, *J* = 7.2 Hz, 2H), 7.90 - 7.68 (m, 6H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 3.48 (t, *J* = 6.9 Hz, 2H), 3.12 (t, *J* = 6.9 Hz, 2H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 144.8, 136.6, 135.3, 135.1, 131.2, 130.5, 130.3, 128.2, 122.0, 118.6, 38.3, 31.8 ppm. **HRMS m/z (ESI):** calcd for $C_{26}H_{16}F_3NO_4S_3$ $(M\text{-}OTf)^+$421.9764, found 421.9766.

5-([1,1'-Biphenyl]-4-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (3e)

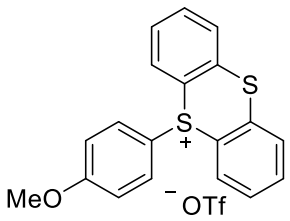


3e

The reaction was performed according to the general procedure. The reaction was conducted with **1e** (116.6 mg, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3e** (249.3 mg, 96%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.69 (d, *J* = 7.3 Hz, 2H), 7.88 – 7.72 (m, 6H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.34 (m, 5H), 7.27 (d, *J* = 6.2 Hz, 2H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 146.1, 138.2, 136.6, 135.6, 134.9, 130.3, 130.3, 129.2, 129.1, 129.0, 128.6, 127.2, 122.2, 118.9 ppm. **HRMS m/z (ESI):** calcd for $C_{25}H_{17}F_3O_3S_3$ $(M+H)^+$519.0365, found 519.0321.

5-(4-Methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (3f)



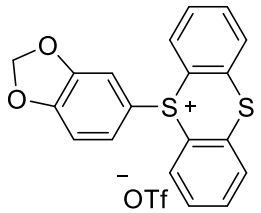
3f

The reaction was performed according to the general procedure. The reaction was conducted with **1f** (82 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The

product was purified and crystallized by diethyl ether, afford **3f** (230.4 mg, 97%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, J = 7.7 Hz, 2H), 7.85 – 7.69 (m, 6H), 7.28 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 9.1 Hz, 2H), 3.78 (s, 3H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 163.7, 136.2, 134.9, 134.7, 130.7, 130.3, 130.2, 120.0, 116.6, 113.5, 56.0 ppm. **HRMS m/z (ESI):** calcd for $C_{20}H_{15}F_3O_4S_3$ $(M–OTf)^+$324.0632, found 324.0610.

5-(benzo[d][1,3]dioxol-5-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (3g)

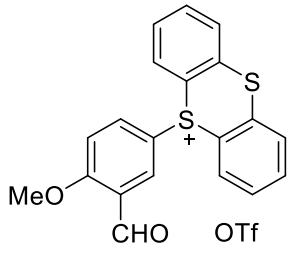


3g

The reaction was performed according to the general procedure. The reaction was conducted with **1g** (82 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3g** (132.3 mg, 54%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.42 (d, *J* = 7.8 Hz, 2H), 7.86 – 7.75 (m, 4H), 7.69 (t, *J* = 6.8 Hz, 2H), 6.87 – 6.72 (m, 2H), 6.60 (s, 1H), 5.99 (s, 2H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 152.5, 149.8, 136.1, 134.9, 134.8, 130.3, 130.2, 124.6, 119.0, 115.4, 110.0, 107.8, 103.1 ppm. **HRMS m/z (ESI):**calcd for $C_{20}H_{13}F_3O_5S_3$ $(M-OTf)^+$337.0351, found 337.0357.

5-(3-Formyl-4-methoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (3h)

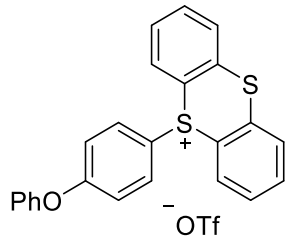


3h

The reaction was performed according to the general procedure. The reaction was conducted with **1h** (102.1 mg, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3h** (250.3 mg, 62%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 10.27 (s, 1H), 8.58 (d, *J* = 7.5 Hz, 2H), 7.94 – 7.69 (m, 7H), 7.39 (s, 1H), 7.21 (d, *J* = 9.0 Hz, 1H), 3.95 (s, 3H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 187.1, 164.7, 136.7, 136.3, 135.3, 135.0, 130.43, 130.36, 127.8, 125.5, 118.9, 115.4, 115.1, 56.7 ppm. **HRMS m/z (ESI):** calcd for $C_{21}H_{15}F_3O_5S_3$ $(M\text{-}OTf)^+$351.0508, found 351.0509.

5-(4-Phenoxyphenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (3i)



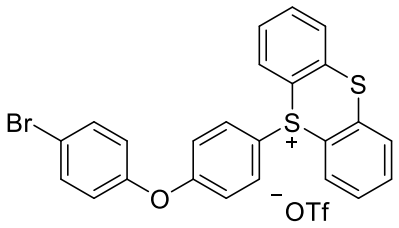
3i

The reaction was performed according to the general procedure. The reaction was conducted with **1i** (120 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3i** (203.9 mg, 76%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d)δ 8.57 (d, J = 7.7 Hz, 2H), 7.86 - 7.68 (m, 6H), 7.35 (t, J = 8.0 Hz, 2H), 7.24 - 7.15 (m, 3H), 7.01 - 6.90 (m, 4H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 162.4, 154.2, 136.3, 135.1, 134.8, 130.5, 130.32, 130.25, 125.5,

120.5, 119.1, 119.0, 115.6 ppm. **HRMS m/z (ESI):** calcd for $C_{25}H_{17}F_3O_4S_3$ (M-OTf)$^+$385.0715, found 385.0719.

5-(4-(4-Bromophenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (3j)

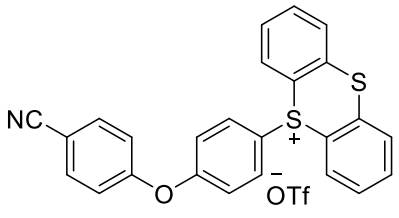


3j

The reaction was performed according to the general procedure. The reaction was conducted with **1j** (130 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3j** (289.8 mg, 95%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.59 (d, *J* = 7.4 Hz, 2H), 7.88 – 7.67 (m, 6H), 7.46 (dd, *J* = 8.9, 3.1 Hz, 2H), 7.29 – 7.16 (m, 2H), 6.91 (dd, J = 31.2, 6.0 Hz, 4H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ160.8, 154.3, 135.7, 135.6, 135.2, 133.7, 131.2, 130.7, 130.1, 122.7, 121.2 (q, *J* = 342.6 Hz), 120.1, 119.7, 118.2, 117.6 ppm. **HRMS m/z (ESI):** calcd for $C_{25}H_{16}BrF_3O_4S_3$ (M+H)$^+$612.9419, found 612.9422.

5-(4-(4-Cyanophenoxy)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (3k)



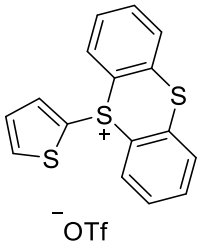
3k

The reaction was performed according to the general procedure. The reaction was conducted with **1k** (146.4 mg, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3k** (172.5 mg, 62%)

as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.59 (d, *J* = 7.7 Hz, 2H), 7.93 – 7.70 (m, 6H), 7.63 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.27 (dd, *J* = 9.1, 2.5 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 4H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 159.8, 158.7, 136.4, 135.5, 134.9, 134.5, 130.8, 130.4, 130.3, 120.7, 120.0, 119.0, 118.2, 108.3 ppm. **HRMS m/z (ESI):** calcd for $C_{26}H_{16}F_3NO_4S_3$ $(M+Na)^+$582.0086, found 582.0081.

5-(thiophen-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (3l)

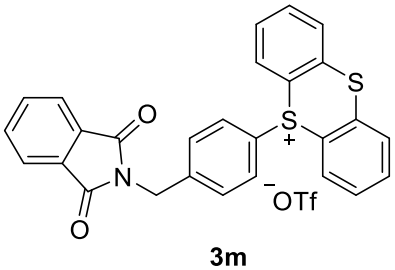


3l

The reaction was performed according to the general procedure. The reaction was conducted with **1l** (60 μL, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3l** (165.8 mg, 74%) as a brown solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.57 – 8.53 (m, 2H), 8.19 (dd, *J* = 4.0, 1.3 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.79 (td, *J* = 7.9, 1.2 Hz, 2H), 7.73 – 7.67 (m, 3H), 7.15 (dd, *J* = 5.1, 4.0 Hz, 1H) ppm. **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 140.0 , 136.9 , 135.8 , 134.8 , 134.3 , 130.3 , 130.0 , 128.7 , 122.1 , 120.8 .

5-(4-((1,3-Dioxoisoindolin-2-yl)methyl)phenyl)-5H-thianthren-5-ium trifluoromethanesulfonate (3m)



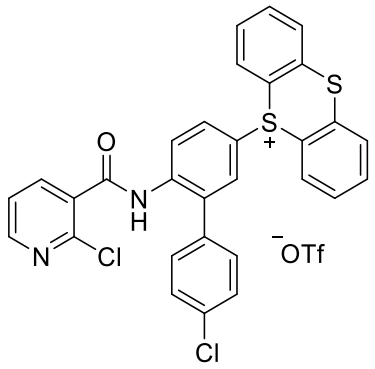
3m

The reaction was performed according to the general procedure. The reaction was conducted with **1m** (177.9 mg, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5

mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3m** (127.1 mg, 42%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.64 (d, *J* = 7.8 Hz, 2H), 7.88 – 7.67 (m, 10H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 4.79 (s, 2H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 167.7, 141.78, 136.5, 135.8, 134.8, 134.4, 131.8, 130.6, 130.3, 130.1, 128.5, 123.5, 118.8, 40.6 ppm. **HRMS m/z (ESI):** calcd for $C_{28}H_{18}F_3NO_5S_3$ $(M+Na)^+$624.0191, found 624.0197.

5-(4'-Chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate (3n)

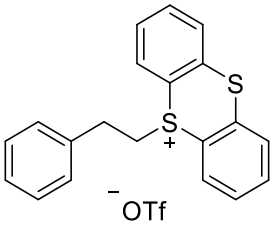


3n

The reaction was performed according to the general procedure. The reaction was conducted with **1n** (257.4 mg, 0.75 mmol, 1.5 equiv) , thianthrenuim S-oxide **2a** (116.5 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (100 μL, 0.6 mmol, 1.2 equiv) ball milling for 1h. The product was purified and crystallized by diethyl ether, afford **3n** (132.3 mg, 54%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.63 (d, *J* = 7.6 Hz, 2H), 8.55 (d, *J* = 8.9 Hz, 1H), 8.48 (s, 1H), 8.42 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.07 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.87 – 7.70 (m, 6H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.34 (dd, *J* = 7.7, 4.7 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.14 (d, *J* = 9.0 Hz, 1H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 162.8, 151.7, 146.4, 140.4, 139.2, 136.5, 135.7, 135.5, 134.9, 134.3, 133.4, 130.6, 130.4, 130.3, 130.2, 130.1, 129.8, 128.4, 123.2, 123.1, 118.9, 118.6 ppm. **HRMS m/z (ESI):**calcd for $C_{30}H_{19}Cl_2N_2OS_2$ $(M)^+$557.0310, found 557.0316.

5-Phenethyl-5H-thianthren-5-ium trifluoromethanesulfonate (5a)

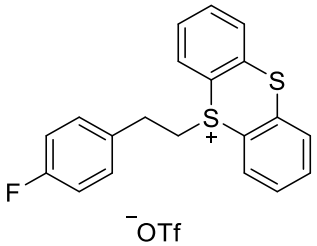


5a

The reaction was performed according to general procedure.The reaction was conducted with **4a** (254.4 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** 216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5a** (200.0 mg, 85%) as a white solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.10 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.4 Hz, 2H), 7.73 (t, J = 7.5 Hz, 2H), 7.58 (t, J = 7.4 Hz, 2H), 7.16 (d, J = 6.7 Hz, 3H), 7.09 (d, J = 6.5 Hz, 2H), 4.01 (t, J = 7.4 Hz, 2H), 2.97 (t, J = 7.3 Hz, 2H) ppm. **^{13}C NMR (151 MHz, Chloroform-d)** δ 135.7, 135.0, 134.5, 134.3, 130.2, 129.8, 128.9, 128.6, 117.2, 41.7, 30.5 ppm.

5-(4-Fluorophenethyl)-5H-thianthren-5-ium trifluoromethanesulfonate (5b)



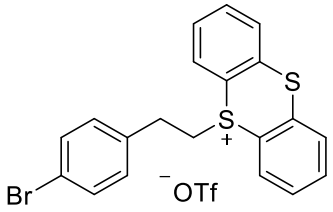
5b

The reaction was performed according to general procedure. The reaction was conducted with **4b** (272.3 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5b** (134.1 mg, 55%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.14 (d, J = 6.5 Hz, 2H), 7.80 (d, J = 6.5 Hz, 2H), 7.72 (t, J = 10.2 Hz, 2H), 7.59 (t, J = 10.1 Hz, 2H), 7.17 – 7.03 (m, 2H), 6.84 (t, J = 11.6 Hz, 2H), 4.08 – 3.93 (m, 2H), 3.03 – 2.87 (m, 2H) ppm. **^{13}C NMR (101 MHz, Chloroform-d)** δ 162.3 (d, J = 246.9 Hz), 135.8, 135.0, 134.5, 131.1 (d, J = 3.3 Hz),

131.1, 130.6 (d, J = 8.2 Hz), 130.6, 130.2, 130.1, 117.7, 116.0 (d, J = 21.5 Hz), 41.67, 30.00 ppm.

5-(4-Bromophenethyl)-5H-thianthren-5-ium trifluoromethanesulfonate (5c)

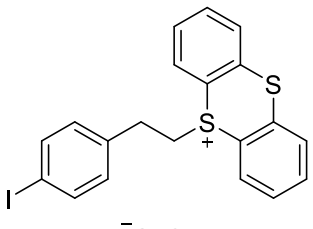


5c

The reaction was performed according to general procedure. The reaction was conducted with **4c** (333.2 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5c** (178.2 mg, 65%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.70 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 3.98 (t, *J* = 7.7 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 135.7, 134.8, 134.4, 134.3, 132.0, 130.5, 130.1, 130.0, 121.6, 117.6, 41.3, 30.1 ppm.

5-(4-Iodophenethyl)-5H-thianthren-5-ium trifluoromethanesulfonate (5d)



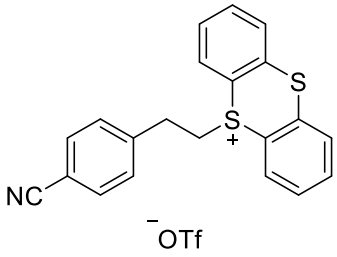
5d

The reaction was performed according to general procedure. The reaction was conducted with **4d** (380.4 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5d** (193.2 mg, 65%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.19 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.72 (t, J = 7.6 Hz, 2H), 7.61 (t, J = 7.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 4.09 – 3.96 (m, 2H), 2.98 (t, J = 7.6 Hz, 2H). **^{13}C NMR (101 MHz,**

Chloroform-d) δ 138.0, 135.7, 135.0, 134.8, 134.4, 130.8, 130.1, 130.0, 117.5, 93.2, 41.3, 30.2 ppm.

5-(4-Cyanophenethyl)-5H-thianthren-5-ium trifluoromethanesulfonate (5e)

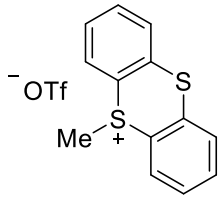


5e

The reaction was performed according to general procedure. The reaction was conducted with **4e** (279.5 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5e** (160.8 mg, 65%) as a white solid.

^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 8.03 – 7.96 (m, 2H), 7.94 – 7.88 (m, 2H), 7.79 (t, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 3.97 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H) ppm. **^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$)** δ 142.4, 137.1, 135.7, 135.2, 133.6, 131.3, 130.6, 130.6, 119.4, 117.8, 112.0, 41.4, 31.1, 1.7 ppm.

5-Methyl-5H-thianthren-5-ium trifluoromethanesulfonate (5f)



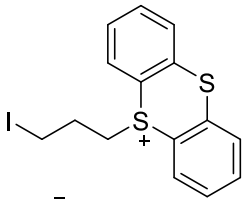
5f

The reaction was performed according to general procedure. The reaction was conducted with **4f** (164.5 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5f** (171.0 mg, 90%) as a white solid.

^{1}H NMR (600 MHz, Acetonitrile-*d*$_3$) δ 8.11 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.94 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.80 (td, *J* = 7.8, 1.3 Hz, 2H), 7.69 (td, *J* = 7.9, 1.2 Hz, 2H), 3.16 (s, 3H). **^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$)** δ 136.8, 135.4, 134.5, 131.2, 130.6, 118.3,

25.6 ppm.

5-(3-Iodopropyl)-5H-thianthren-5-ium trifluoromethanesulfonate (5g)

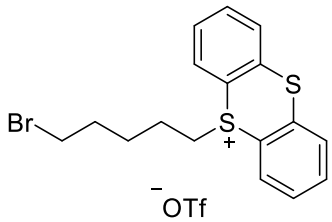


5g

The reaction was performed according to general procedure. The reaction was conducted with **4g** (318.2 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5g** (162.8 mg, 61%) as a gray solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 2H), 3.89 – 3.66 (m, 2H), 3.09 (t, *J* = 6.6 Hz, 2H), 2.14 – 1.94 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 135.7, 134.7, 134.2, 130.2, 129.8, 116.4, 40.9, 27.6, 1.3 ppm.

5-(5-Bromopentyl)-5H-thianthren-5-ium trifluoromethanesulfonate (5h)

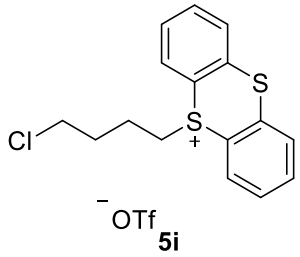


5h

The reaction was performed according to general procedure. The reaction was conducted with **4h** (299.6 mg, 1.0 mmol, 2.0 equiv.) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5h** (167.5 mg, 65%) as a gray solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 2H), 3.79 – 3.72 (m, 2H), 3.29 (t, *J* = 6.5 Hz, 2H), 1.77 (p, *J* = 6.6 Hz, 2H), 1.59 – 1.50 (m, 4H) ppm.**^{13}C NMR (151 MHz, Chloroform-*d*)** δ 135.7, 134.7, 134.6, 130.2, 130.0, 117.0, 40.2, 33.2, 31.5, 26.3, 23.6 ppm.

5-(6-Chlorohexyl)-5H-thianthren-5-ium trifluoromethanesulfonate (5i)



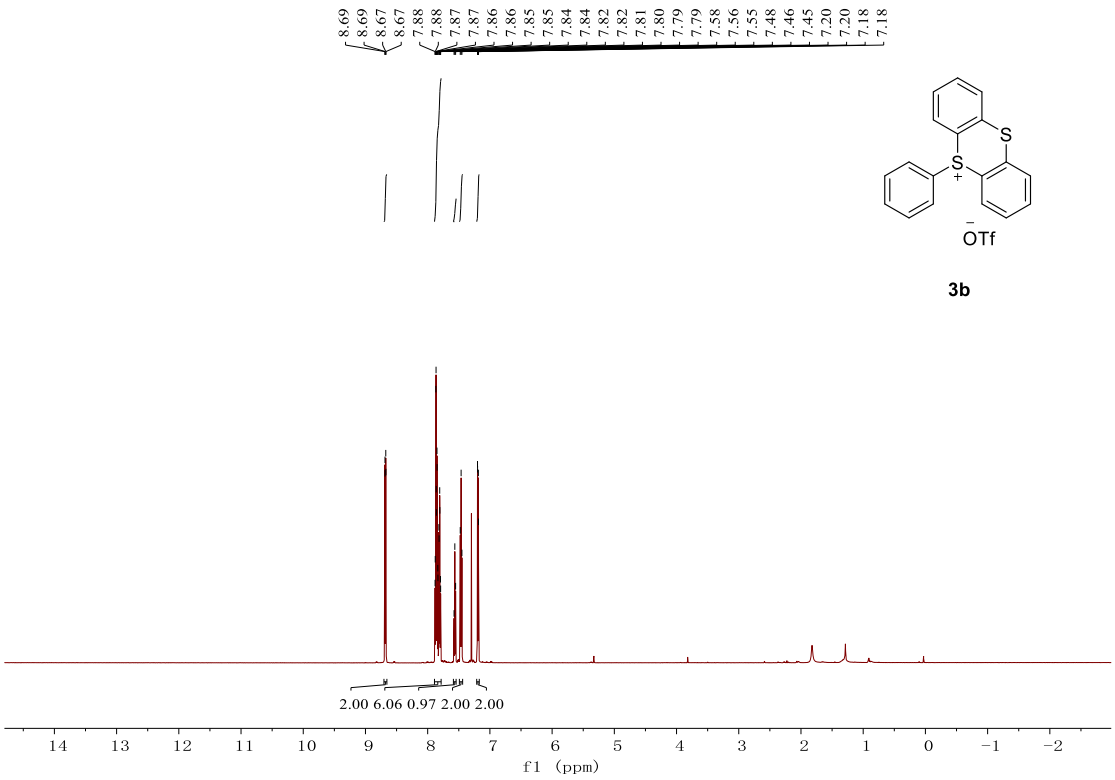
5i

The reaction was performed according to general procedure. The reaction was conducted with **4i** (240.9 mg, 0.75 mmol) and thianthrene **2b** (216.5 mg, 0.5 mmol, 1.0 equiv.) ball milling for 1h. The product was isolated by column chromatography on silica, afford **5i** (157.3 mg, 69%) as a faint yellow oil.

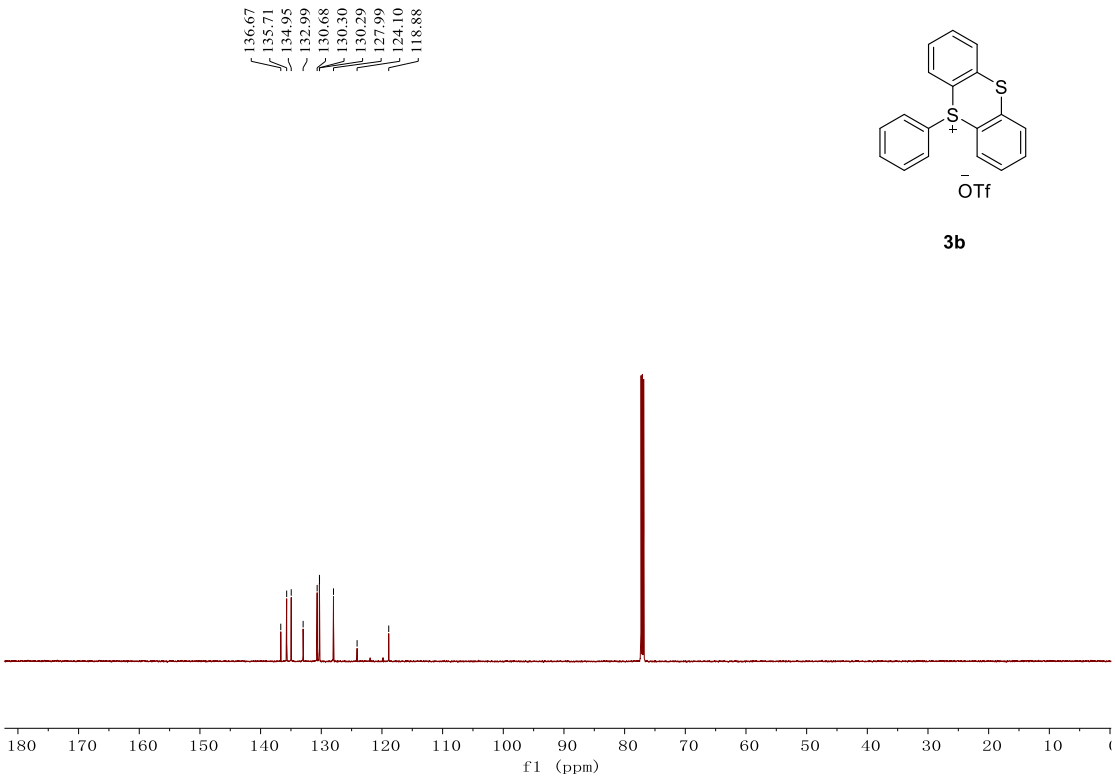
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 2H), 3.84 – 3.75 (m, 2H), 3.46 (t, *J* = 6.0 Hz, 2H), 1.88 (d, *J* = 6.8 Hz, 2H), 1.69 (p, *J* = 7.7 Hz, 2H) ppm. **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 135.8, 134.7, 134.7, 130.2, 130.0, 116.8, 43.7, 39.6, 30.1, 21.9 ppm.

4. Copies of NMR Spectra

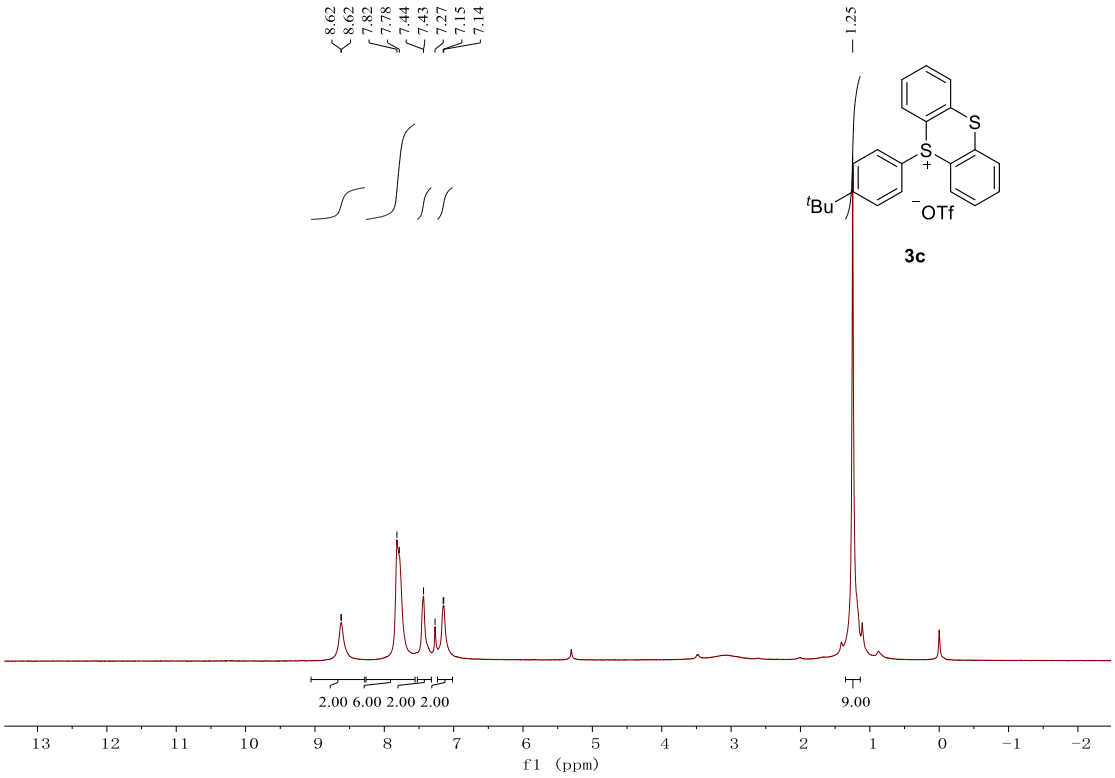
^{1}H NMR (600 MHz, Chloroform-d)



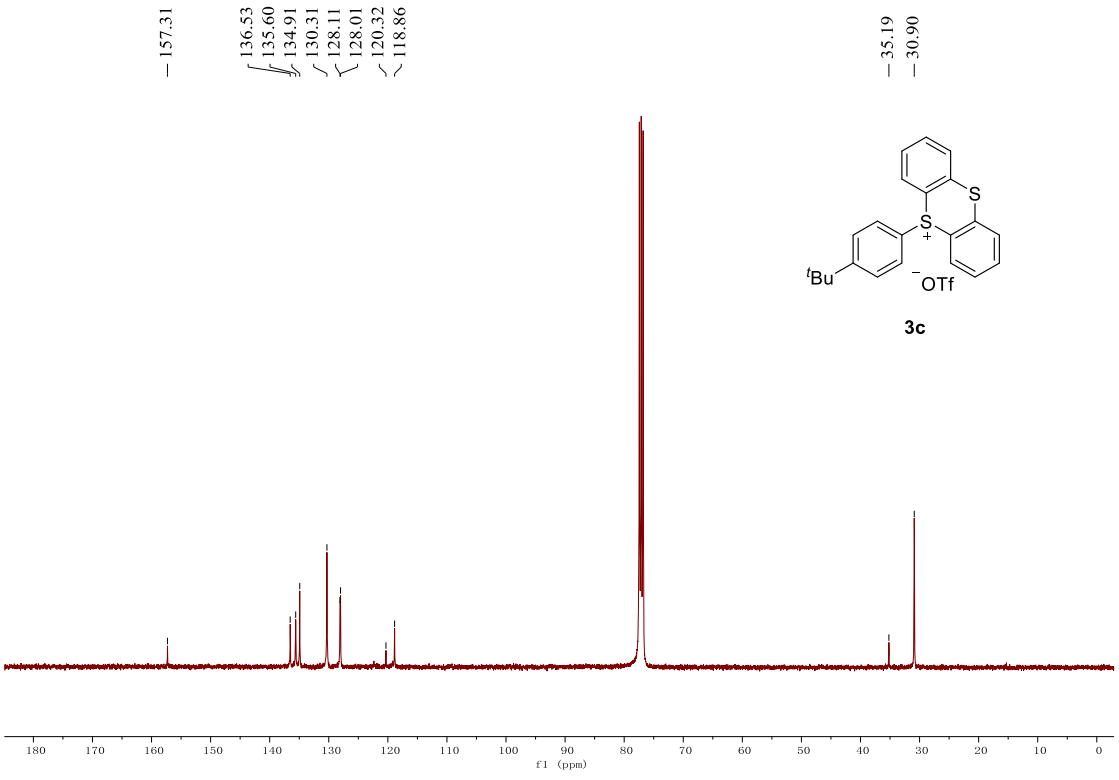
^{13}C NMR (151 MHz, Chloroform-d)



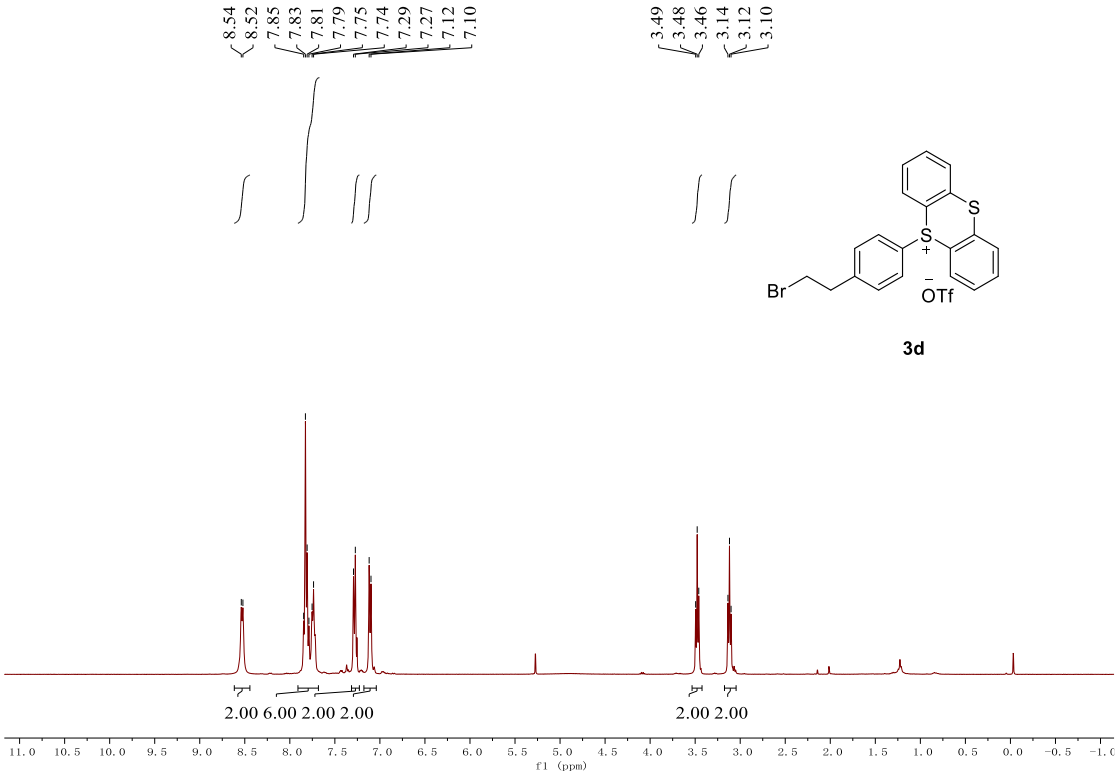
^{1}H NMR (400 MHz,Chloroform-d)



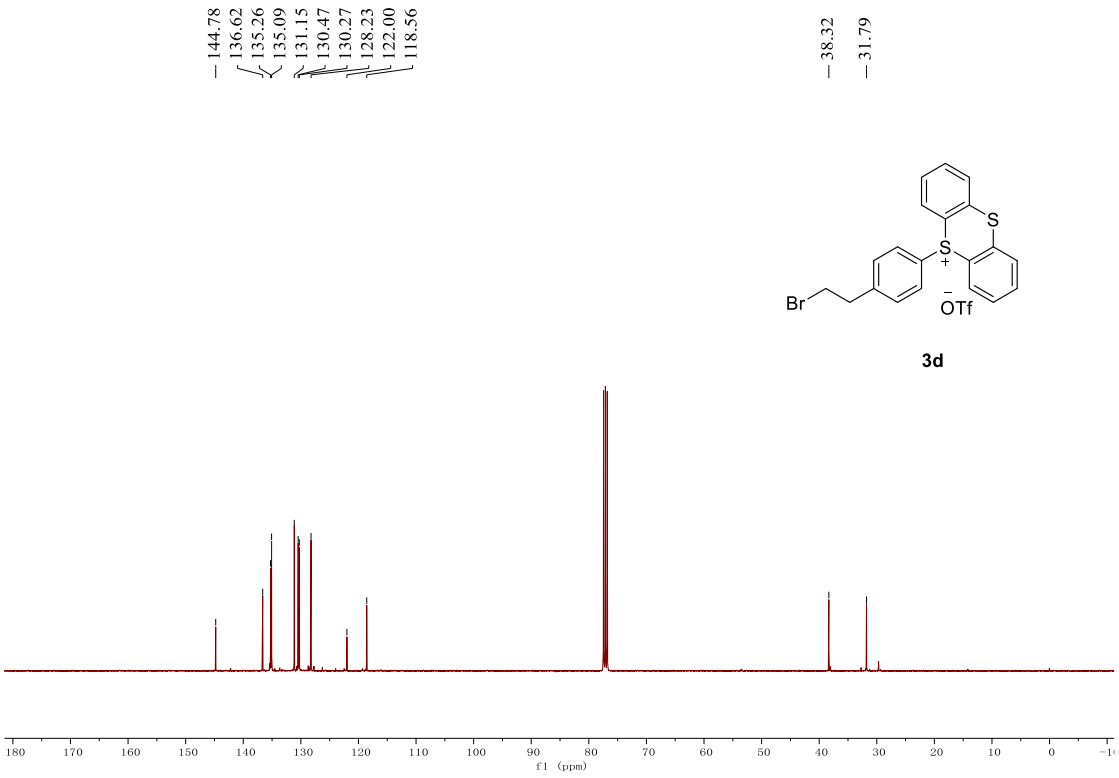
^{13}C NMR (101 MHz, Chloroform-d)



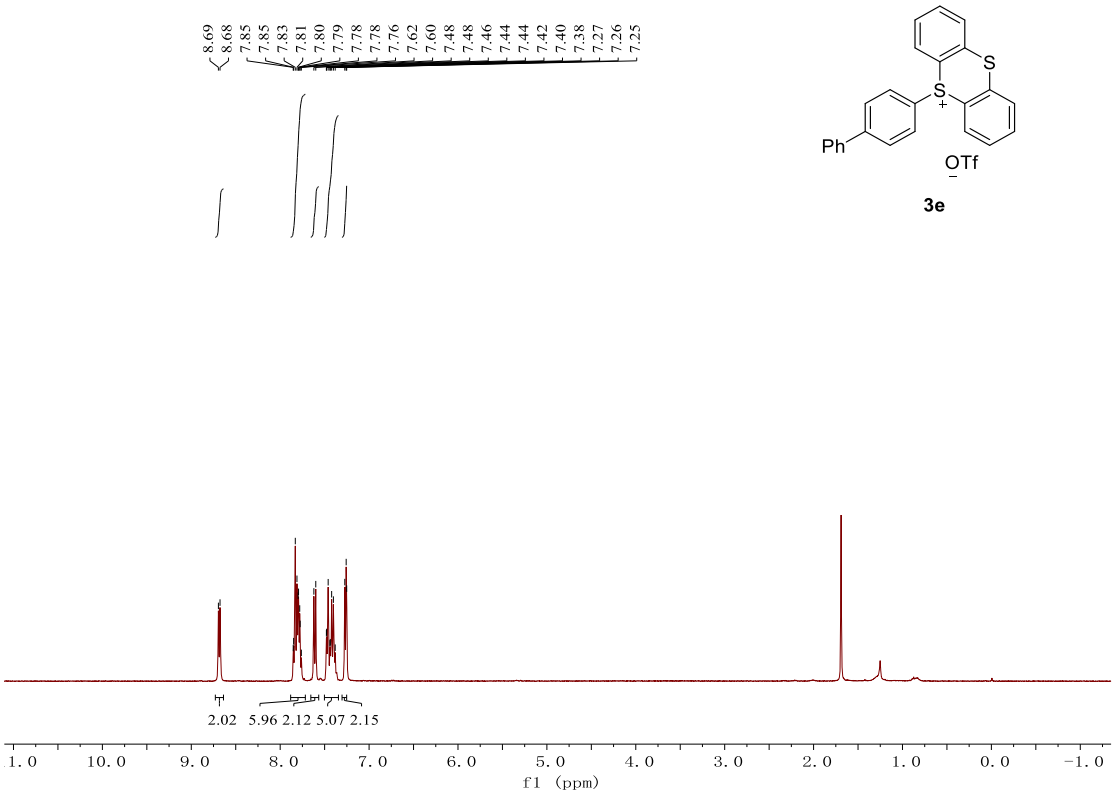
^{1}H NMR (400 MHz, Chloroform-d)



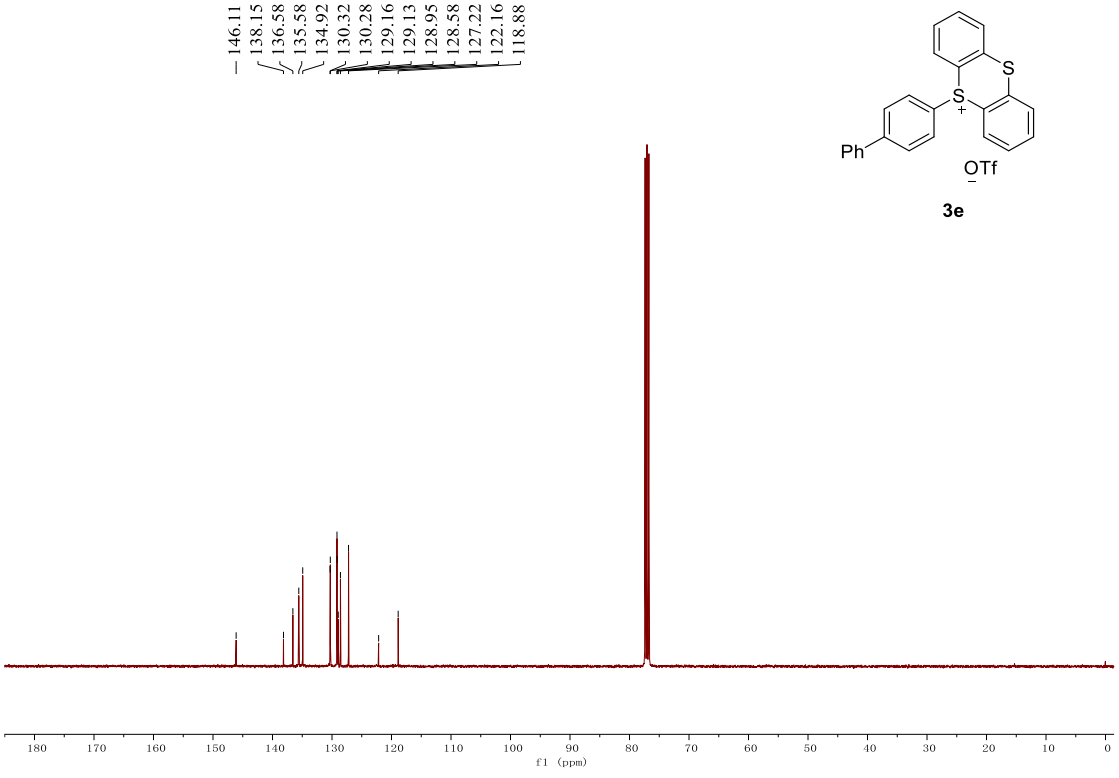
^{13}C NMR (101 MHz, Chloroform-d)



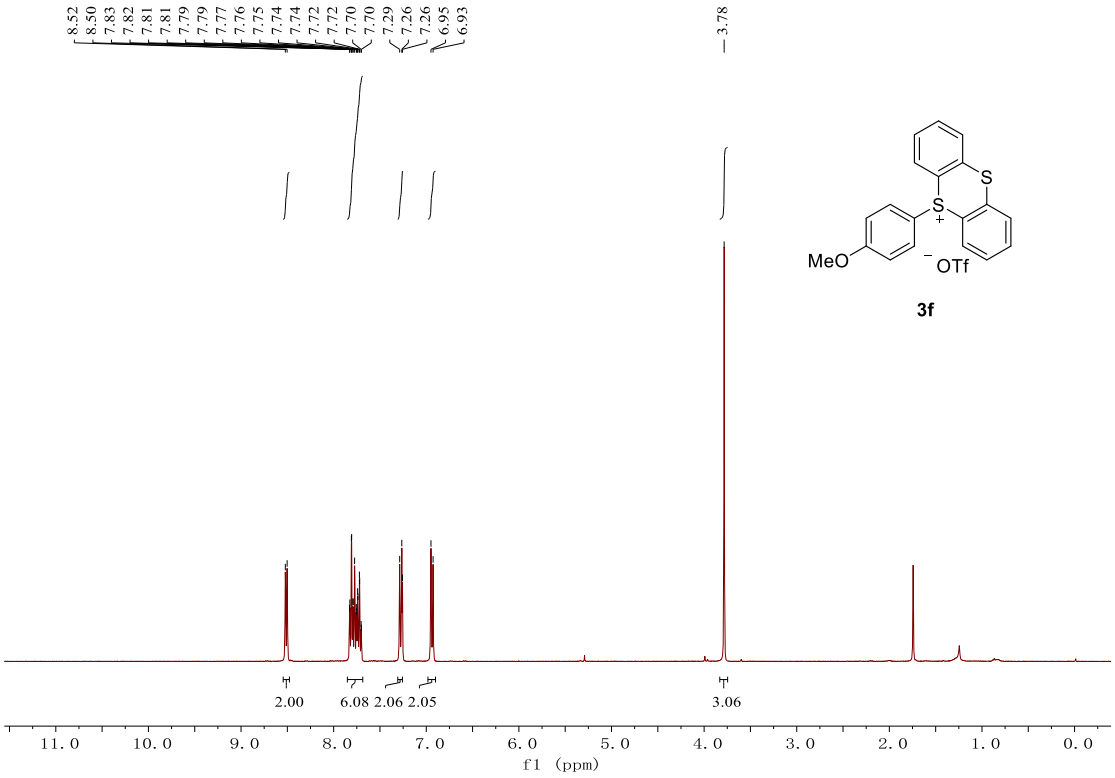
^{1}H NMR (400 MHz,Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)

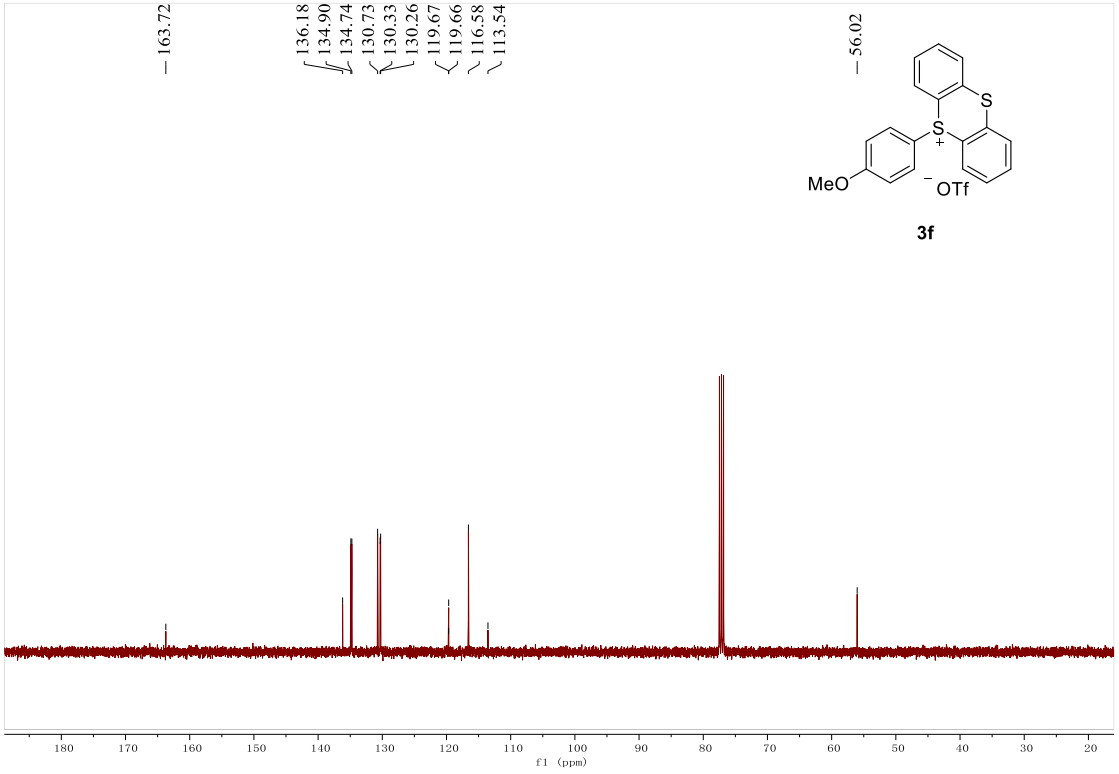


^{1}H NMR (400 MHz, Chloroform-d)



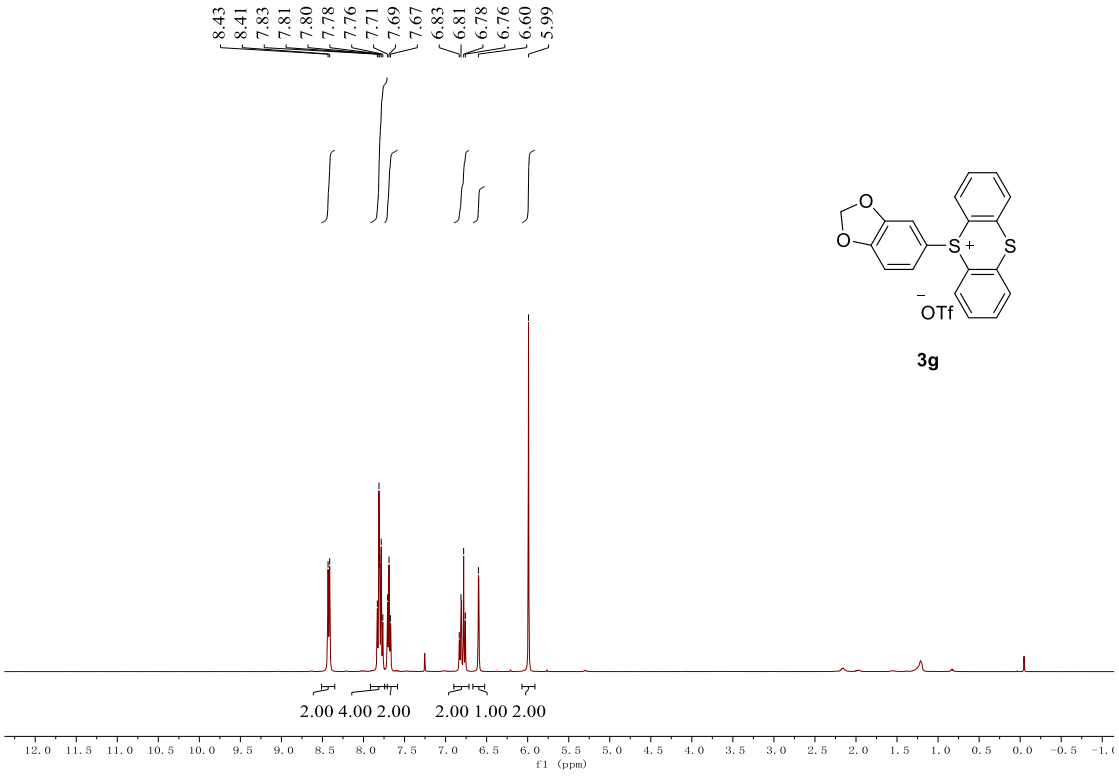
3f

^{13}C NMR (101 MHz, Chloroform-d)



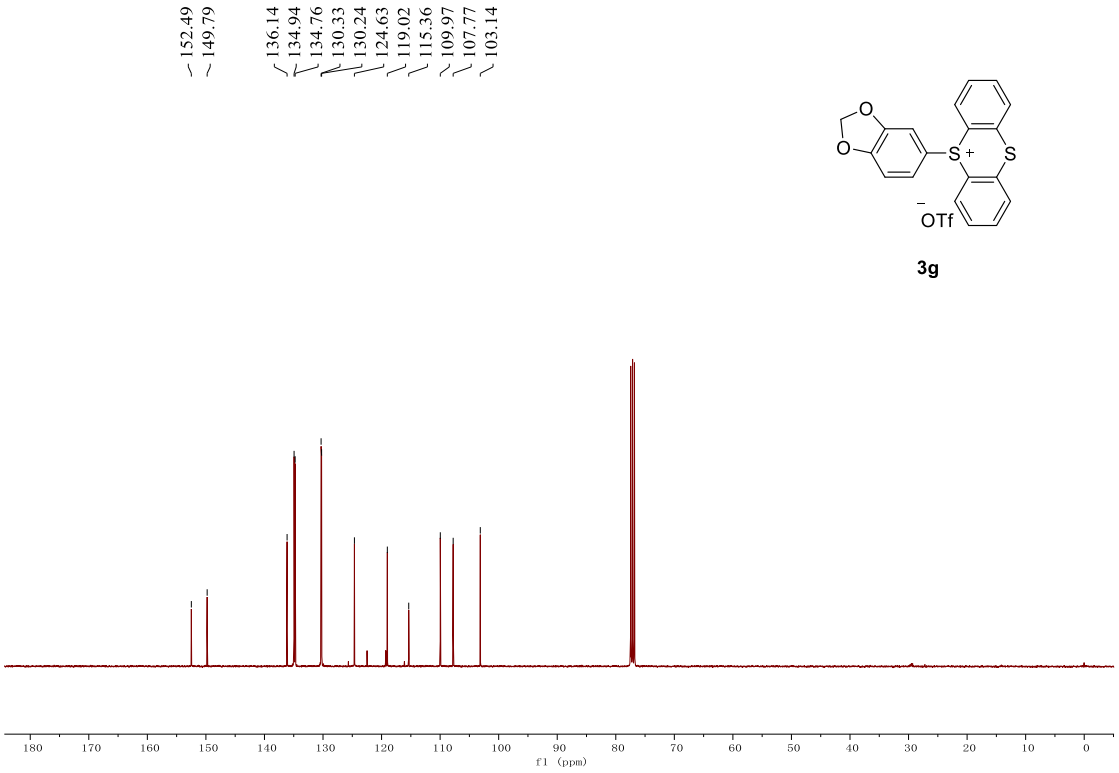
3f

^{1}H NMR (400 MHz, Chloroform-d)



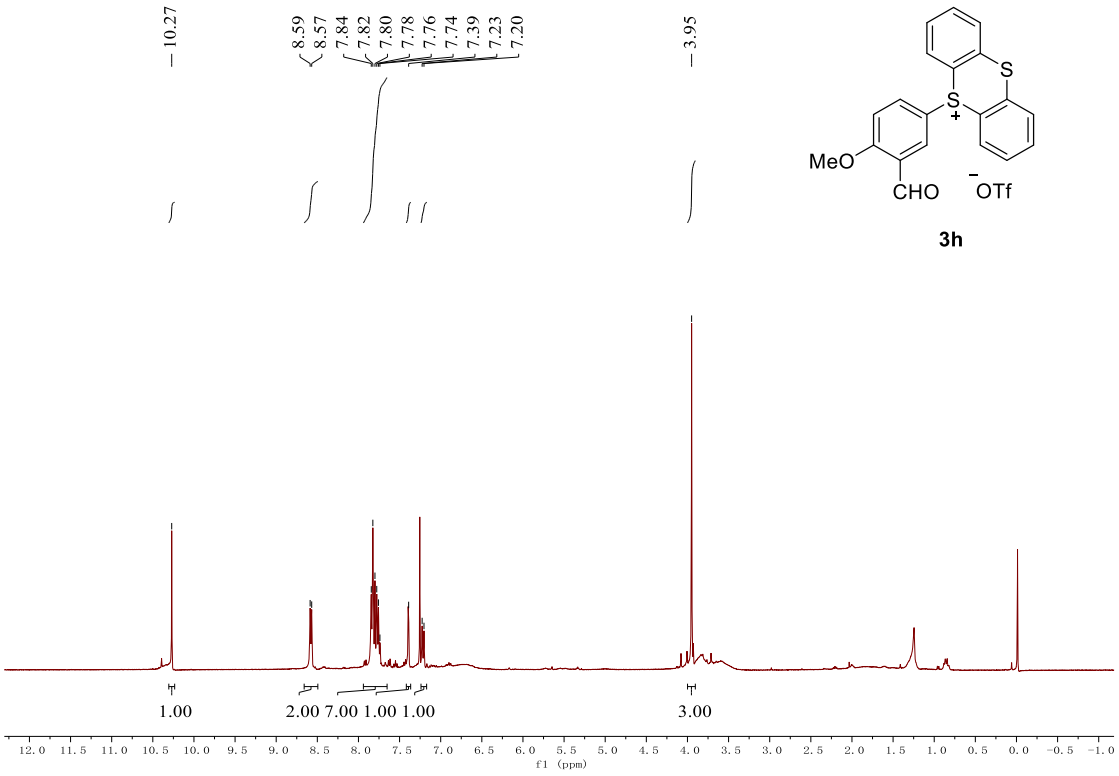
3g

^{13}C NMR (101 MHz, Chloroform-d)

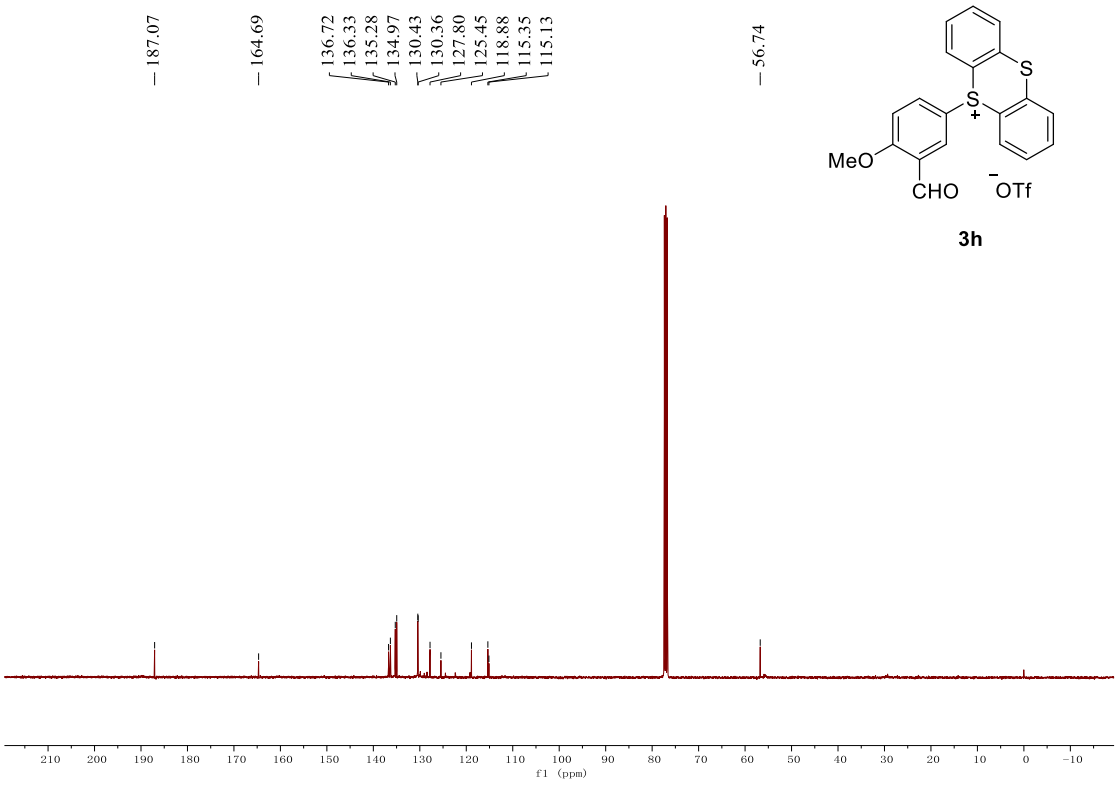


3g

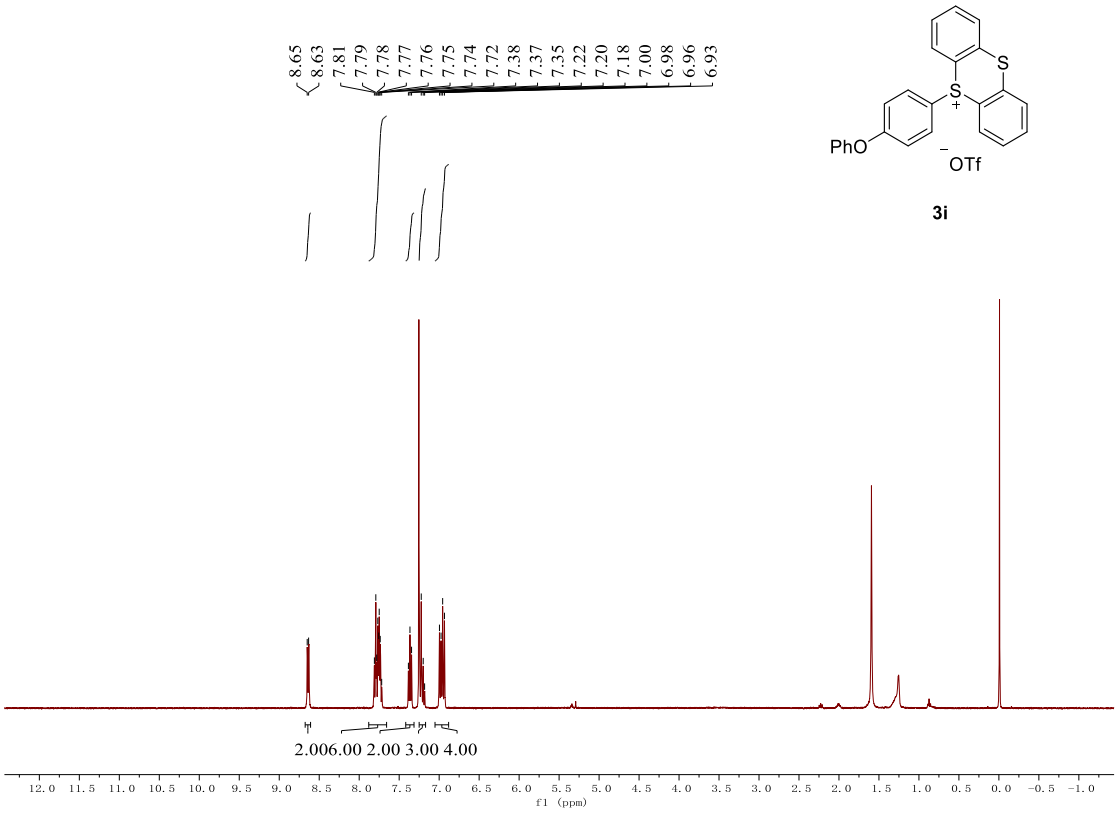
^{1}H NMR (400 MHz, Chloroform-d)



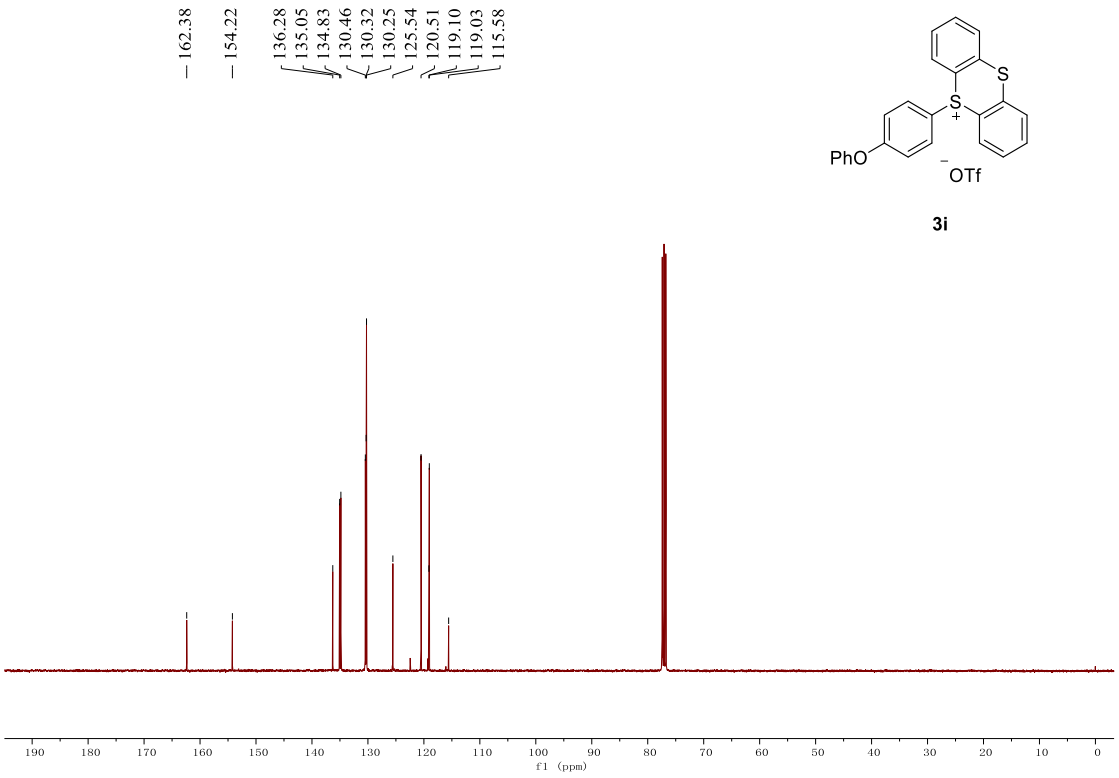
^{13}C NMR (101 MHz, Chloroform-d)



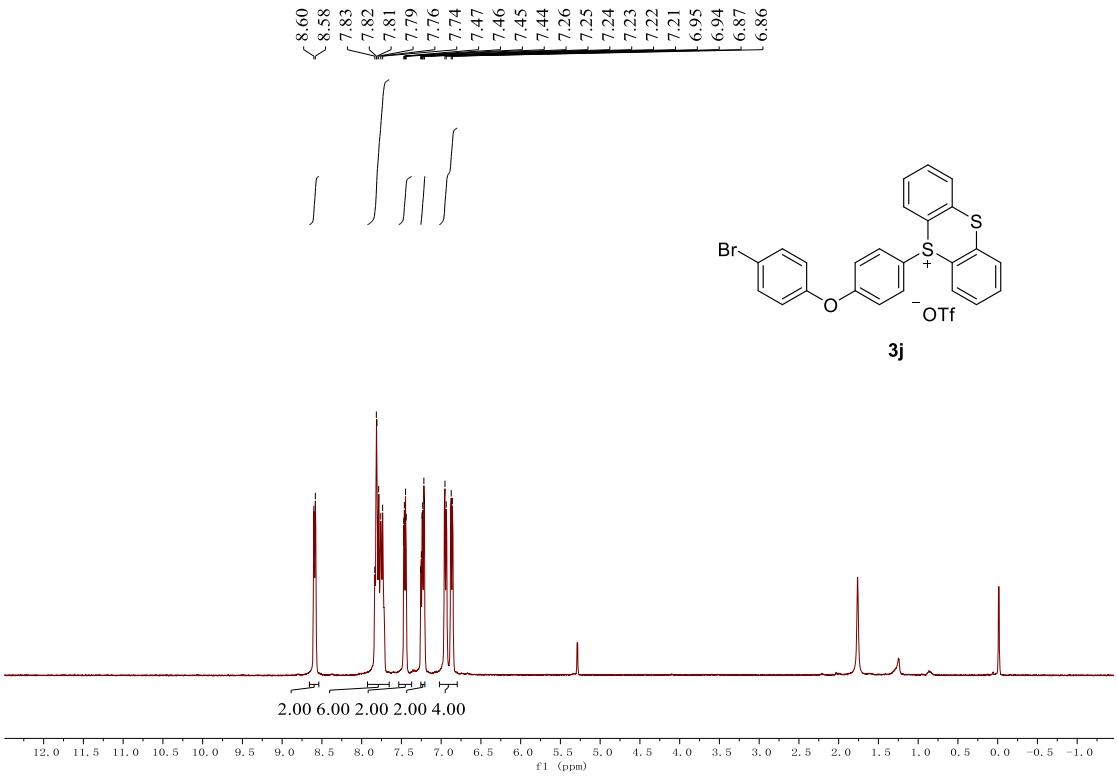
^{1}H NMR (400 MHz, Chloroform-d)



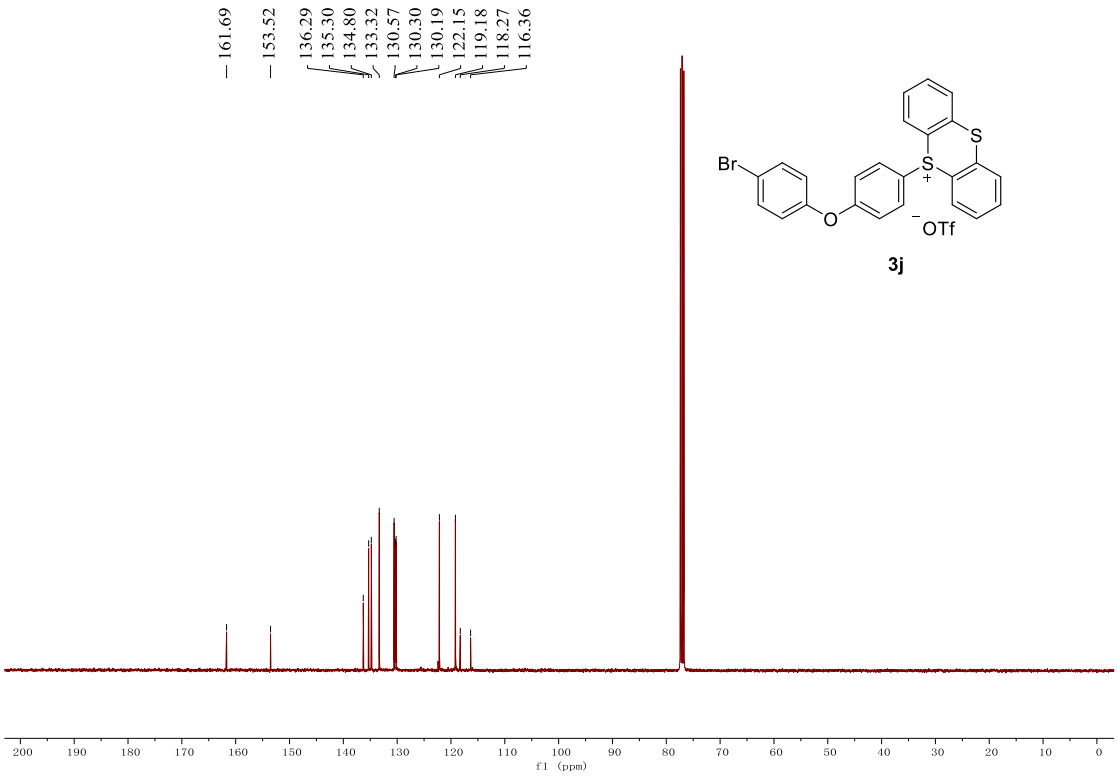
^{13}C NMR (101 MHz, Chloroform-d)



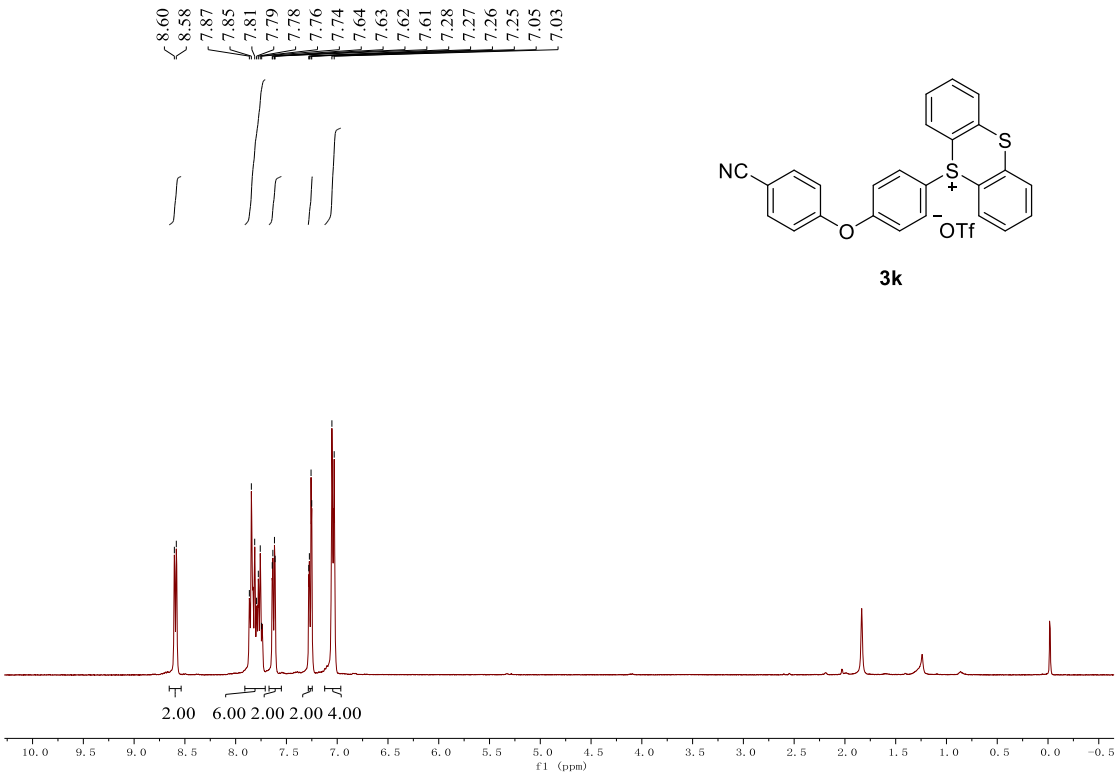
^{1}H NMR (400 MHz, Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)

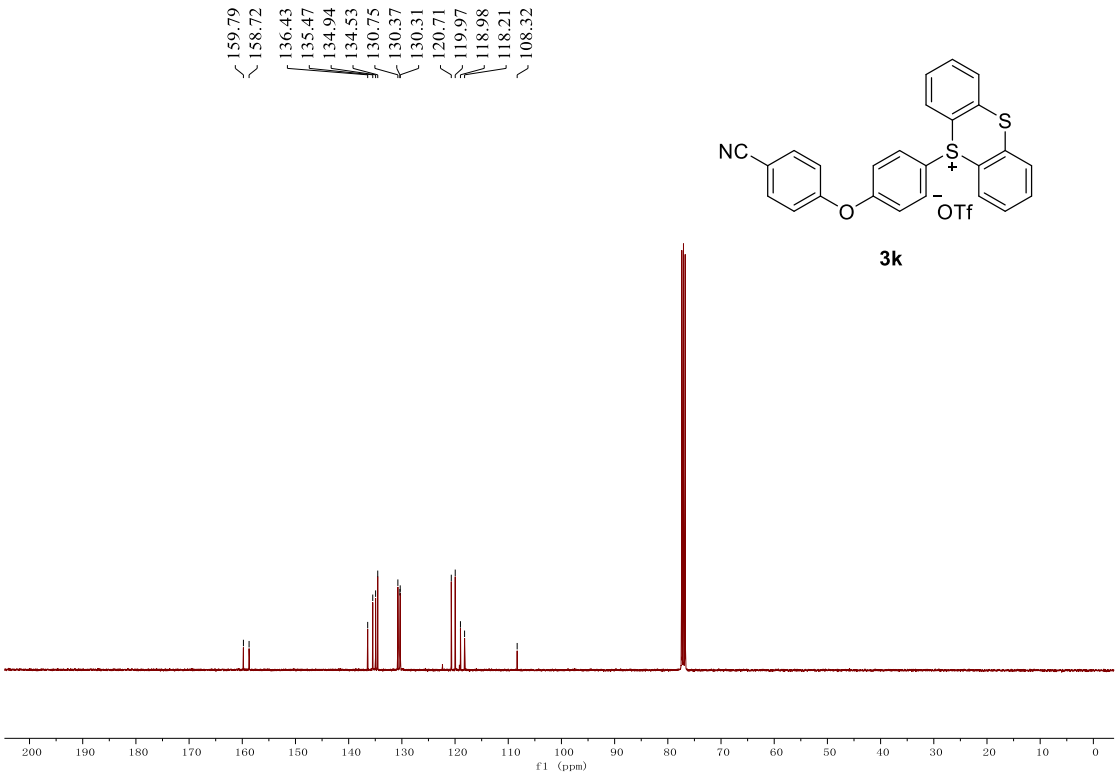


^{1}H NMR (400 MHz, Chloroform-d)



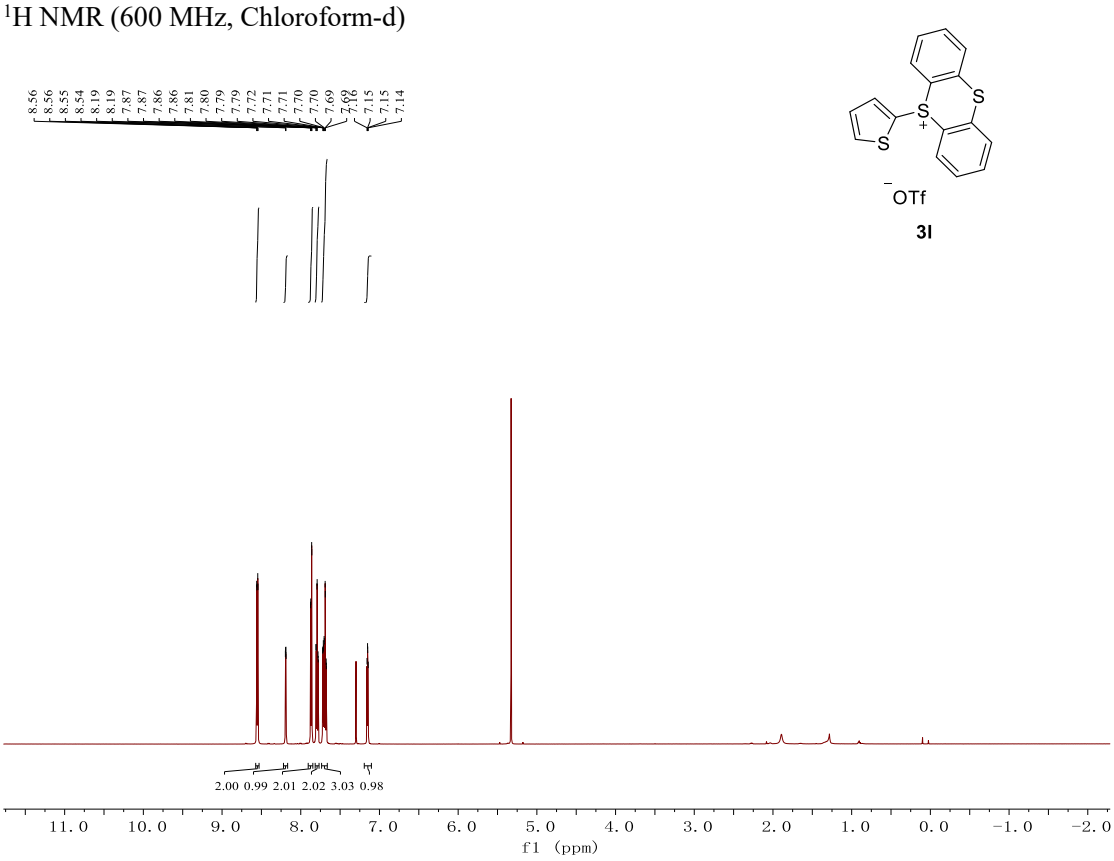
3k

^{13}C NMR (101 MHz, Chloroform-d)



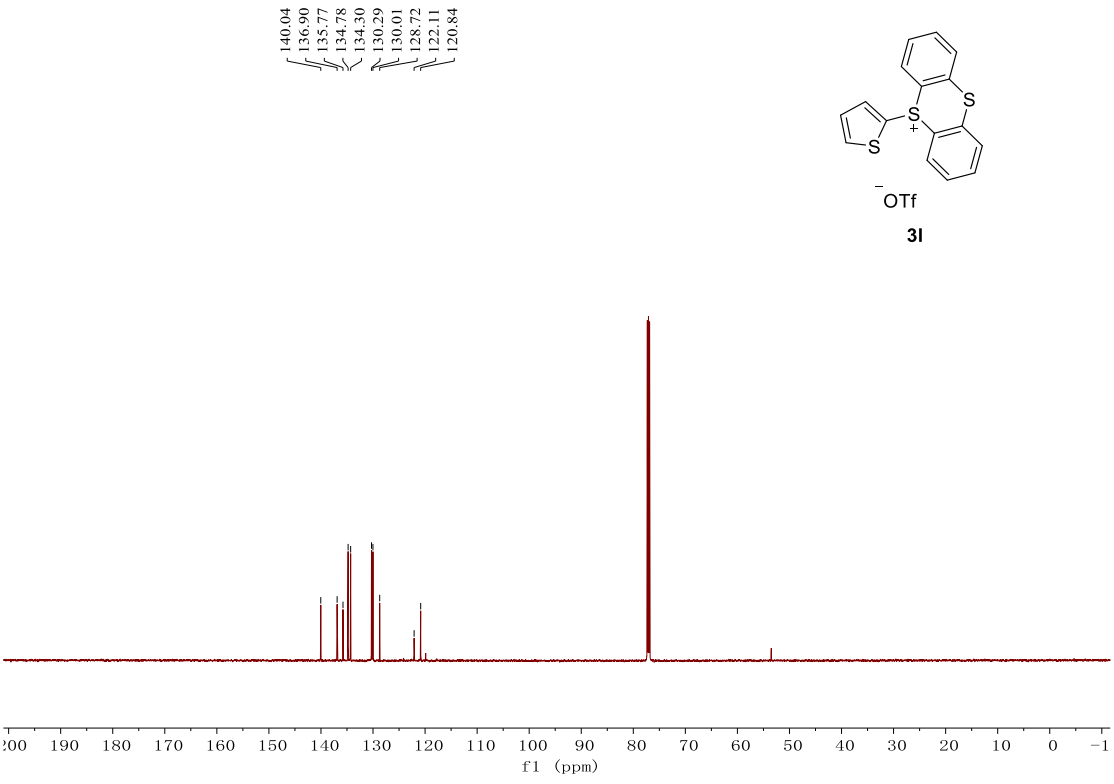
3k

^{1}H NMR (600 MHz, Chloroform-d)



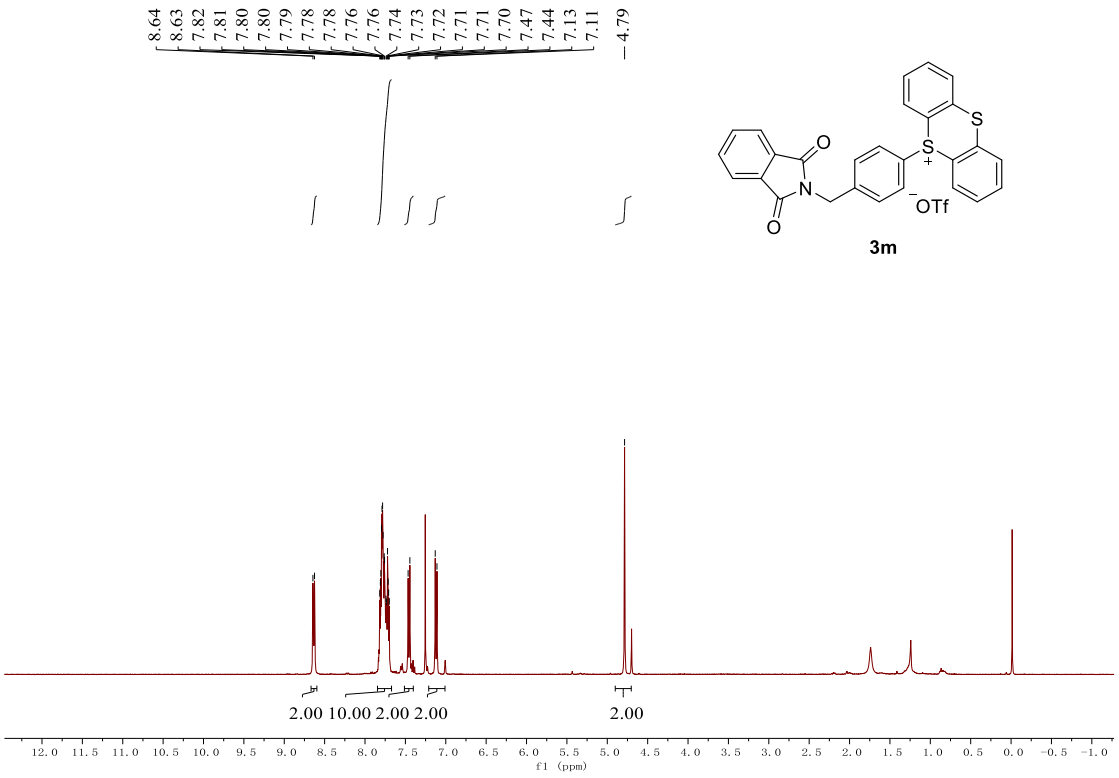
3l

^{13}C NMR (151 MHz, Chloroform-d)



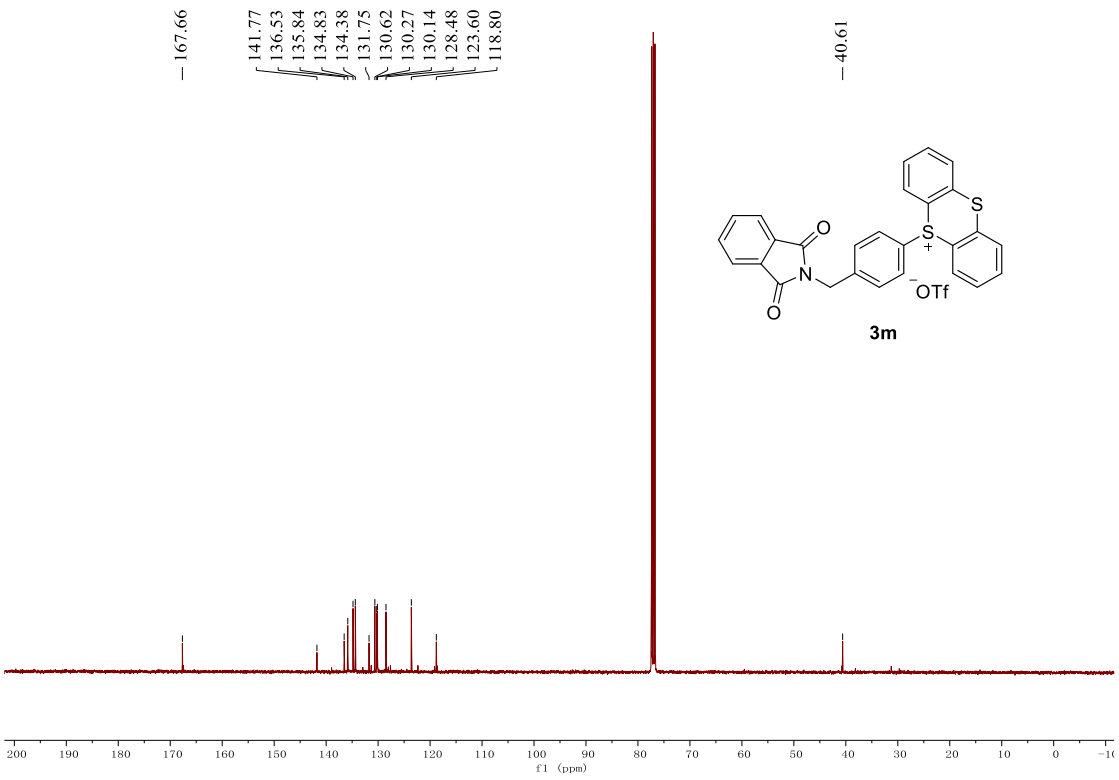
3l

^{1}H NMR (400 MHz, Chloroform-d)



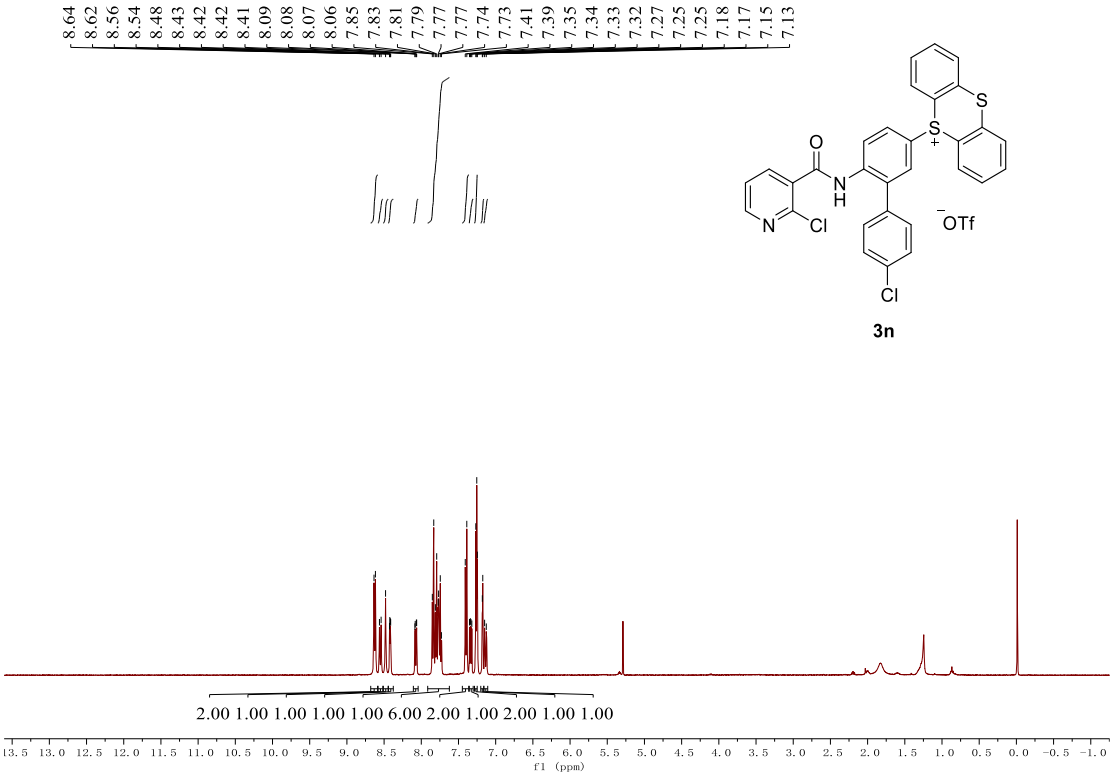
3m

^{13}C NMR (101 MHz, Chloroform-d)

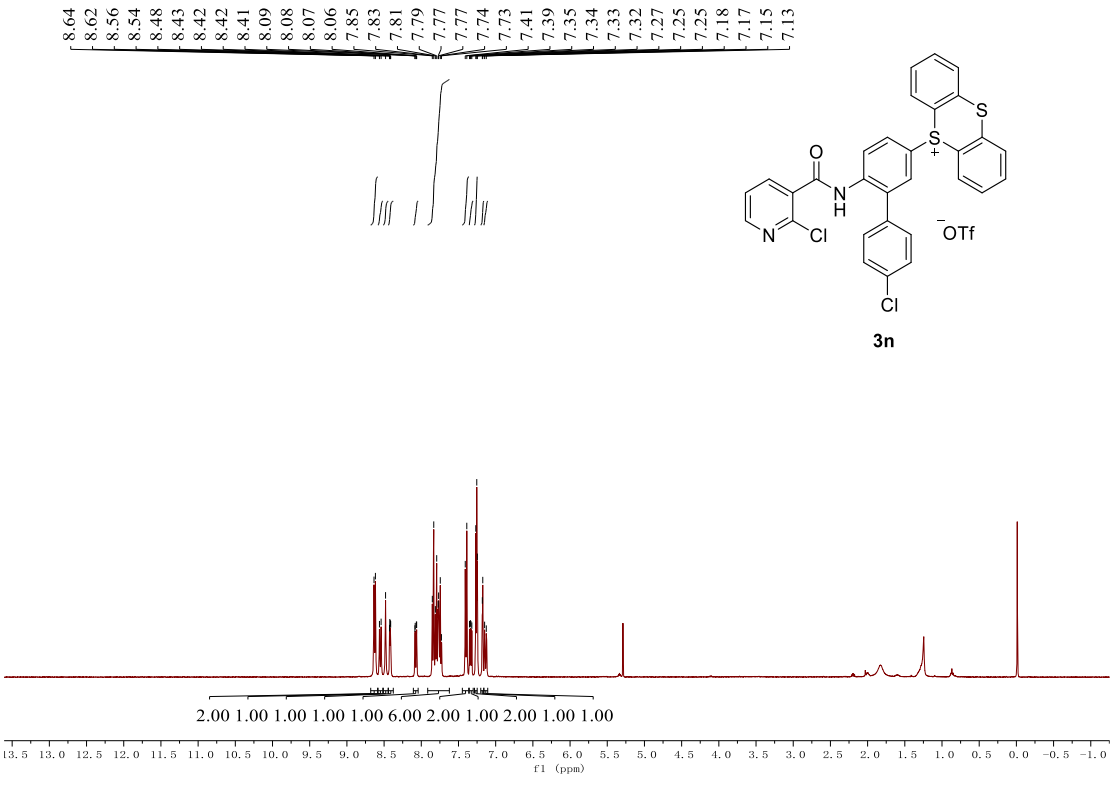


3m

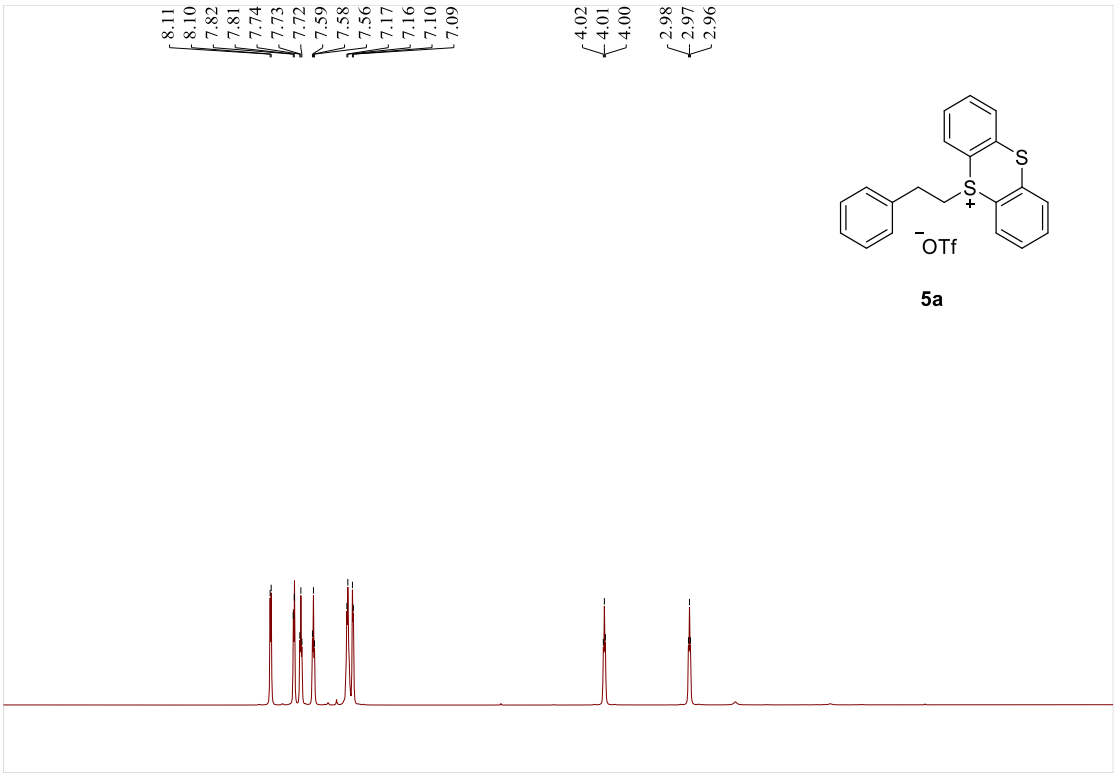
^{1}H NMR (400 MHz, Chloroform-d)



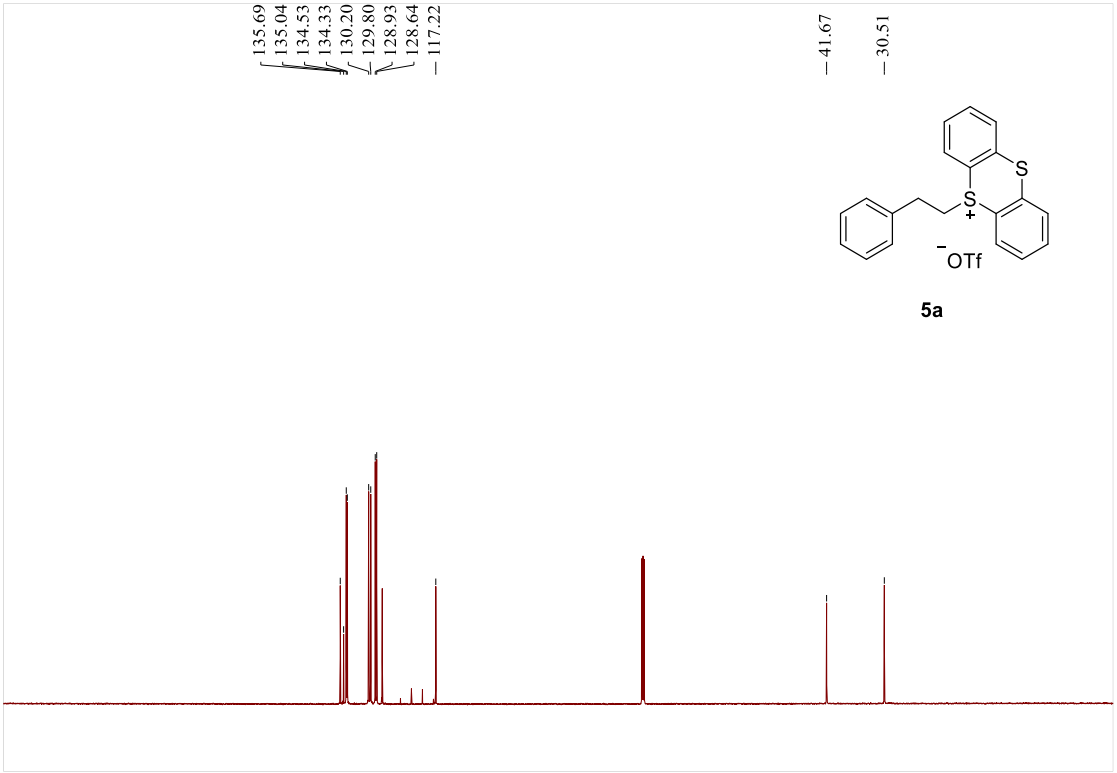
^{13}C NMR (101 MHz, Chloroform-d)



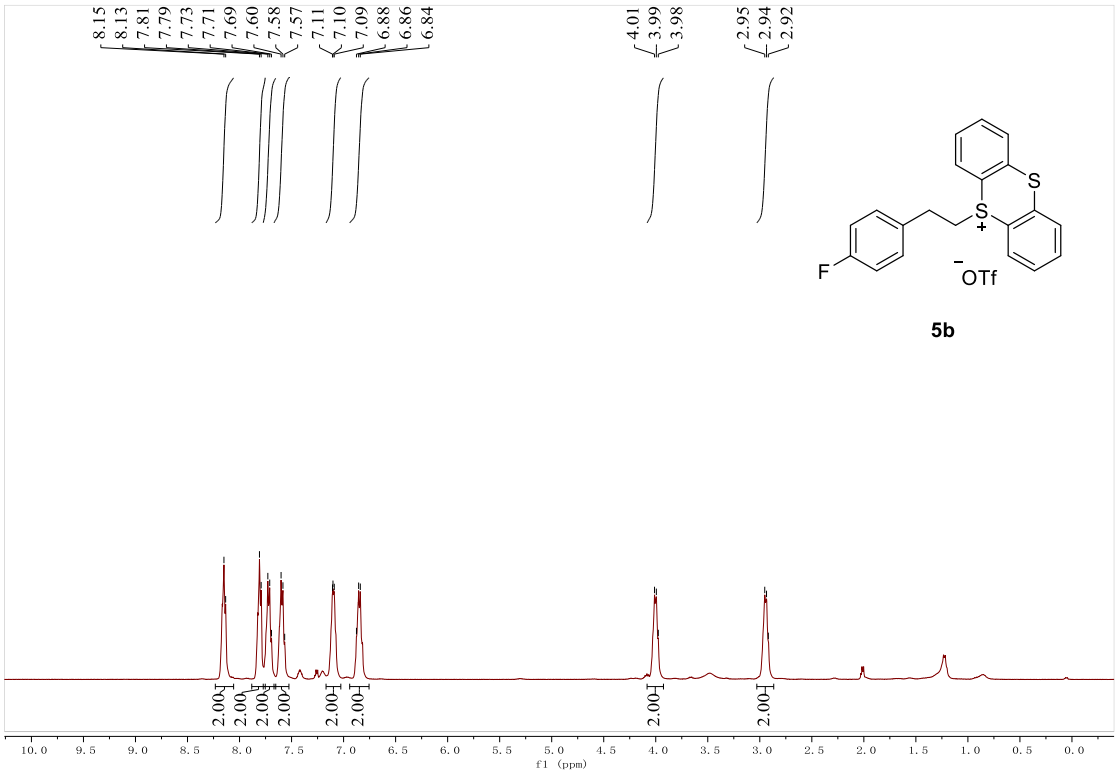
^{1}H NMR (600 MHz, Chloroform-d)



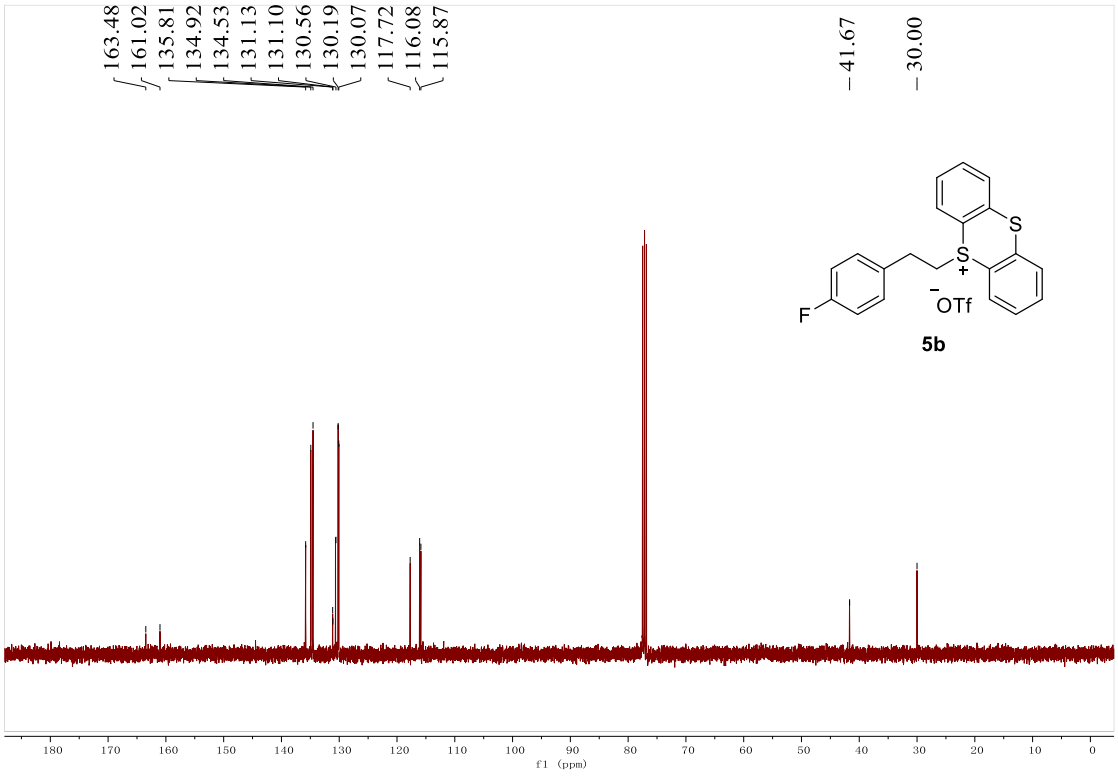
^{13}C NMR (101 MHz, Chloroform-d)



^{1}H NMR (400 MHz, Chloroform-d)

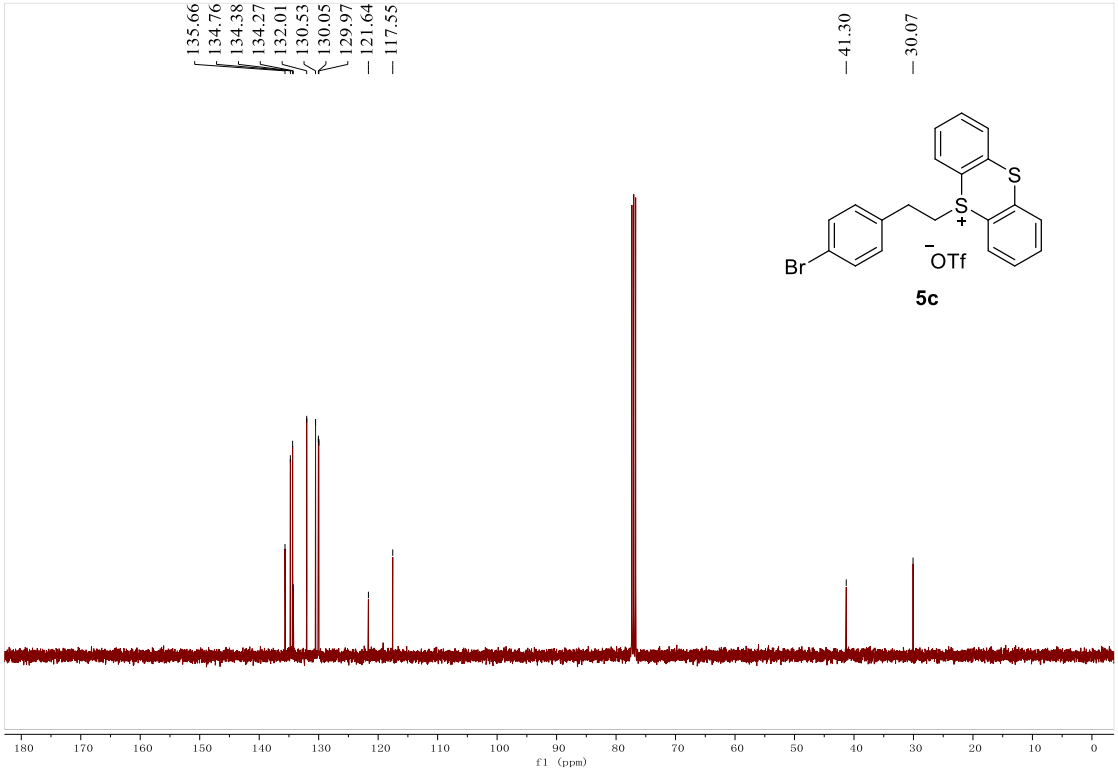


^{13}C NMR (101 MHz, Chloroform-d)

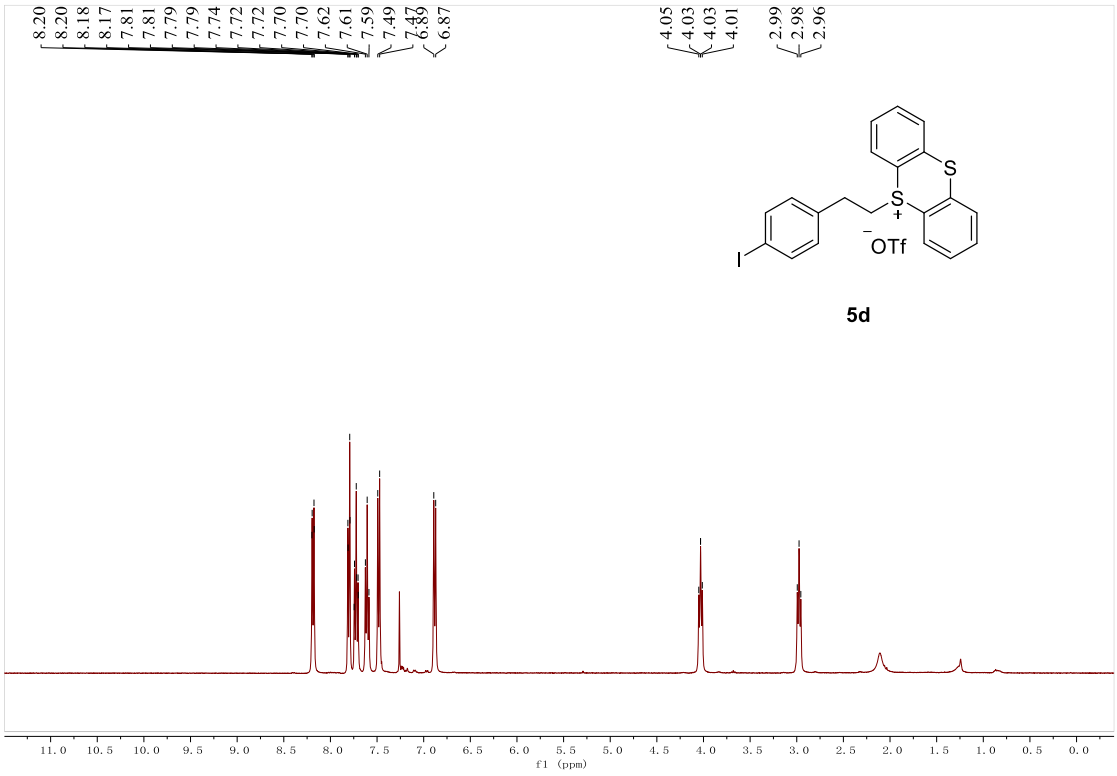


^{1}H NMR (400 MHz, Chloroform-*d*)

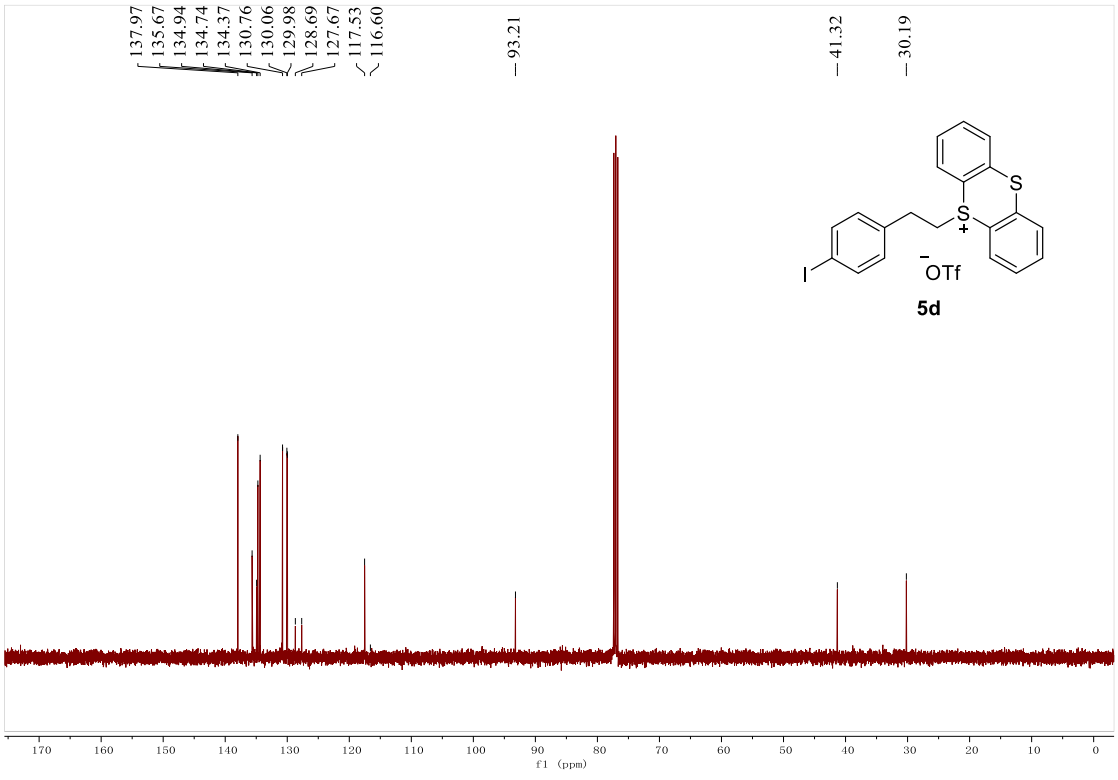
^{13}C NMR (101 MHz, Chloroform-*d*)



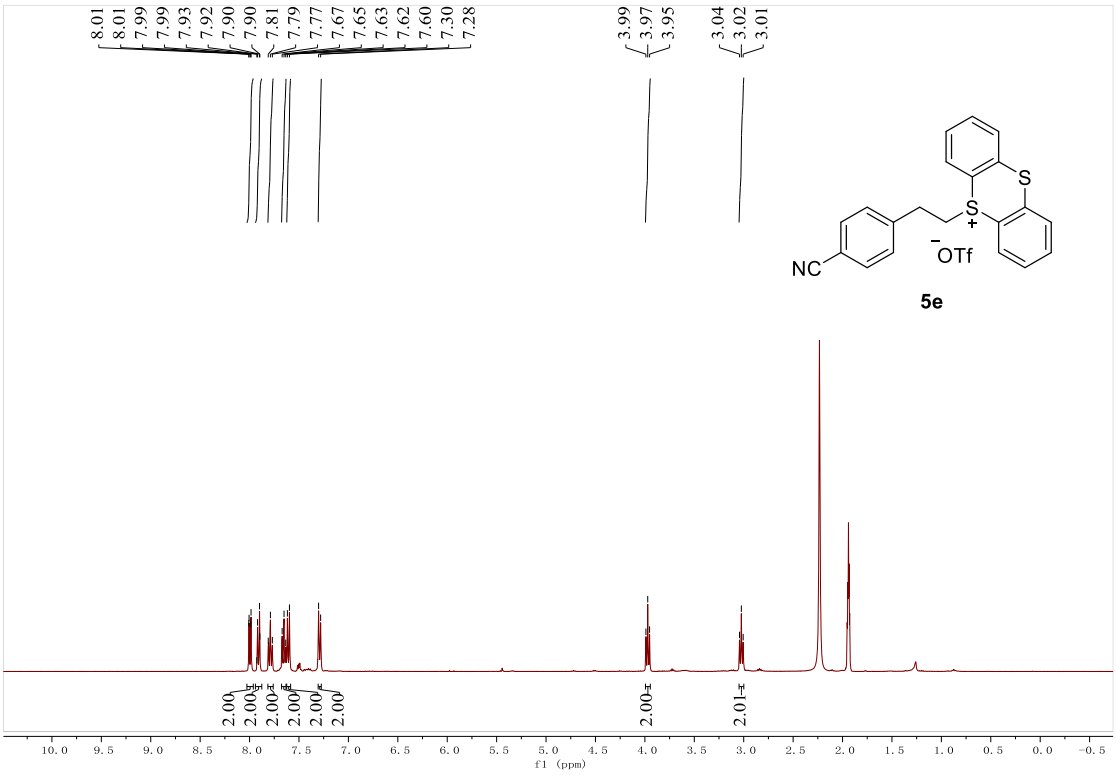
^{1}H NMR (400 MHz, Chloroform-*d*)



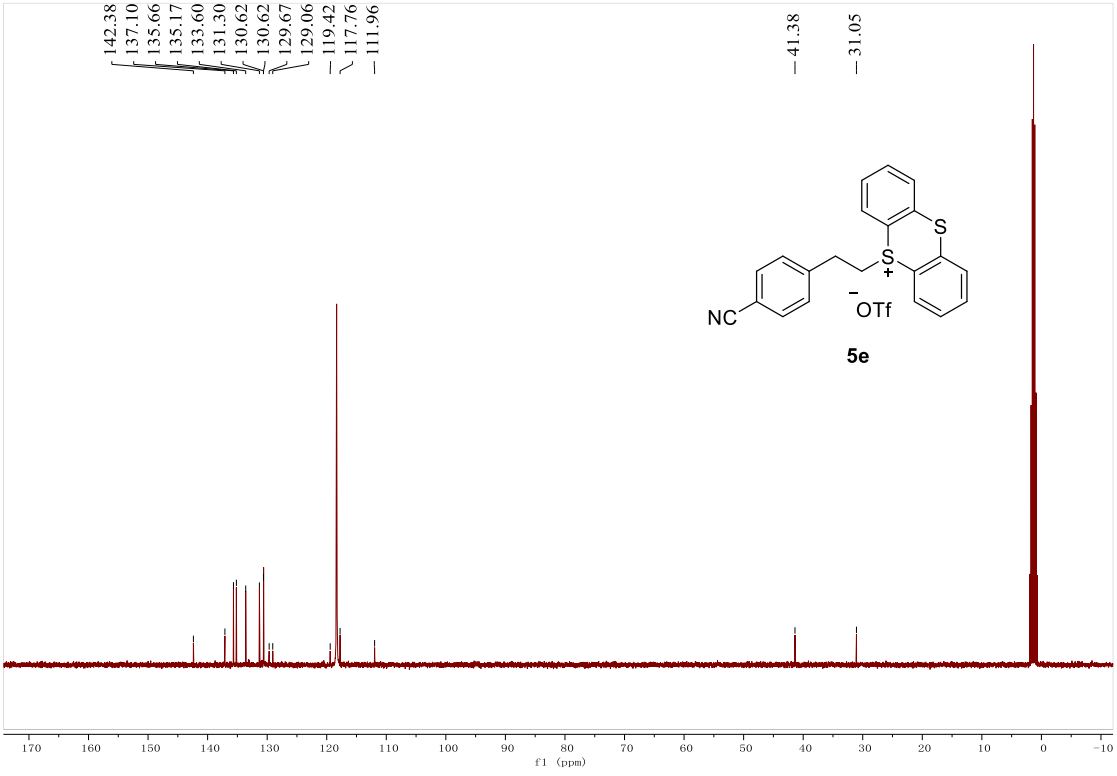
^{13}C NMR (101 MHz, Chloroform-*d*)



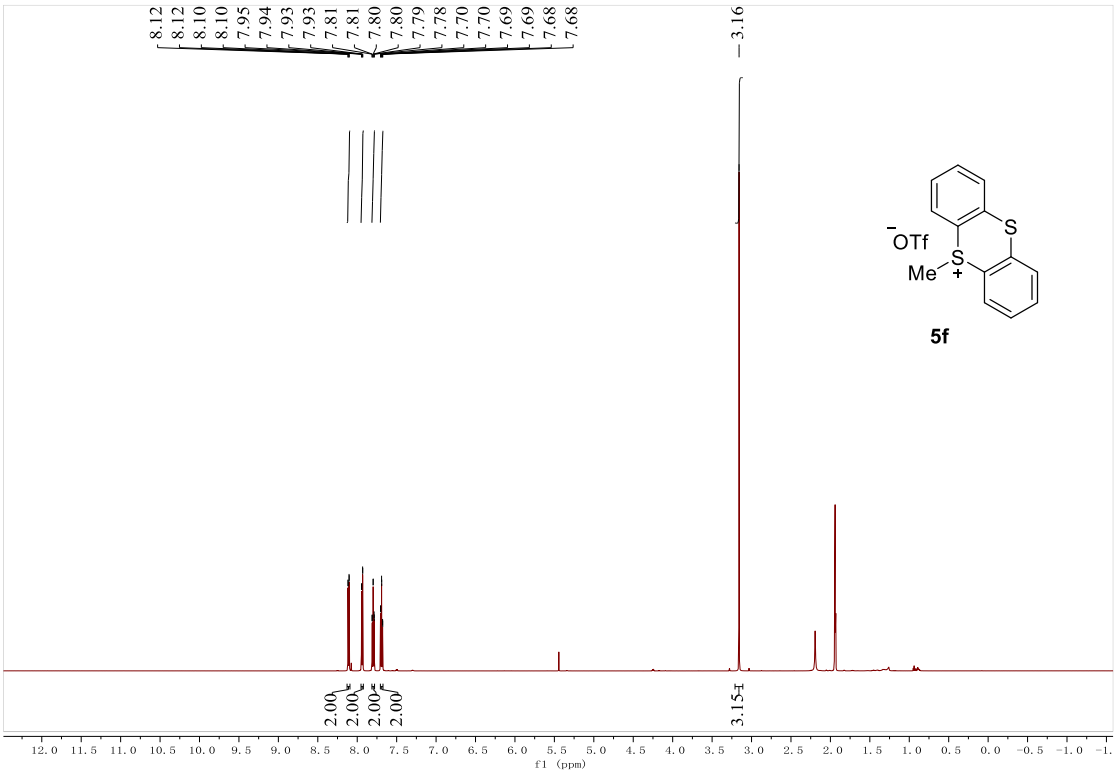
^{1}H NMR (400 MHz, Acetonitrile-d_3)



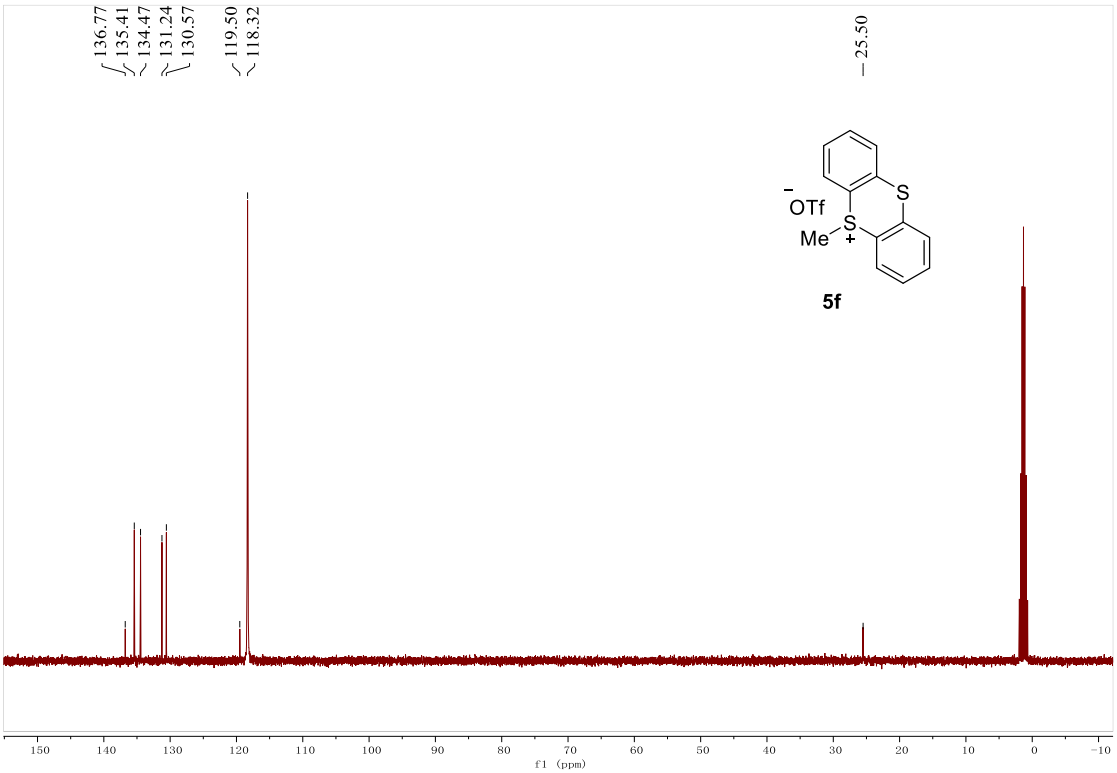
^{13}C NMR (101 MHz, Acetonitrile-d_3)



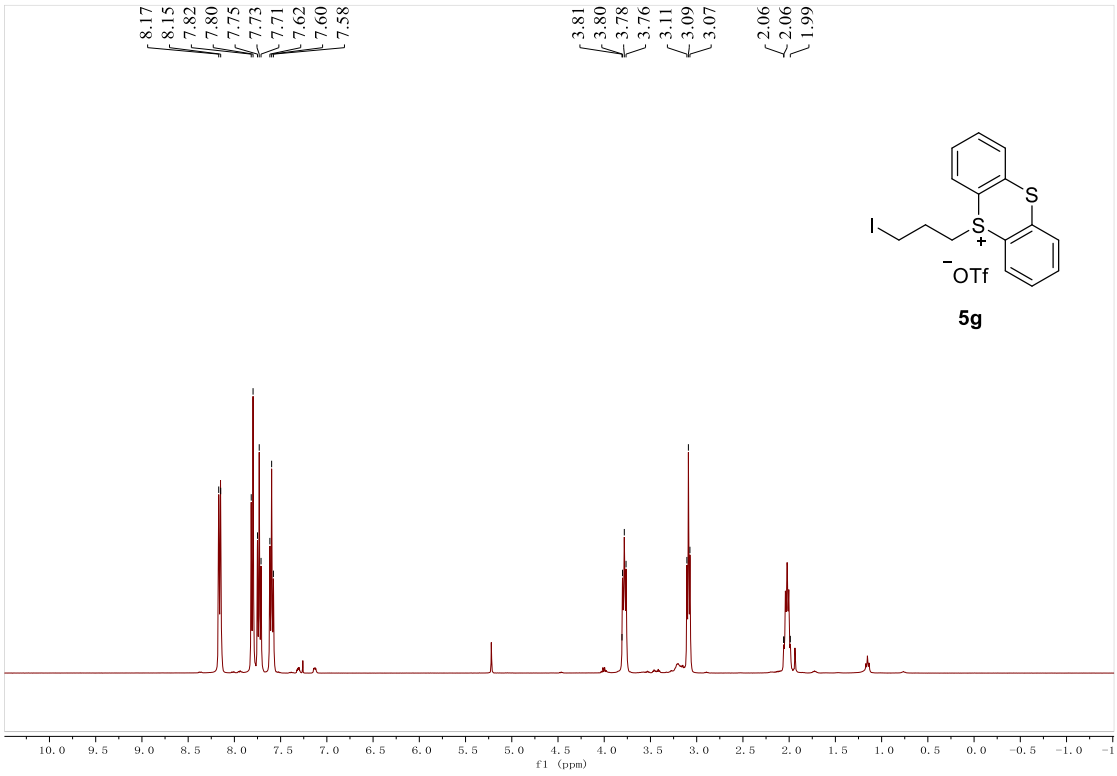
^{1}H NMR (600 MHz, Acetonitrile-d_3)



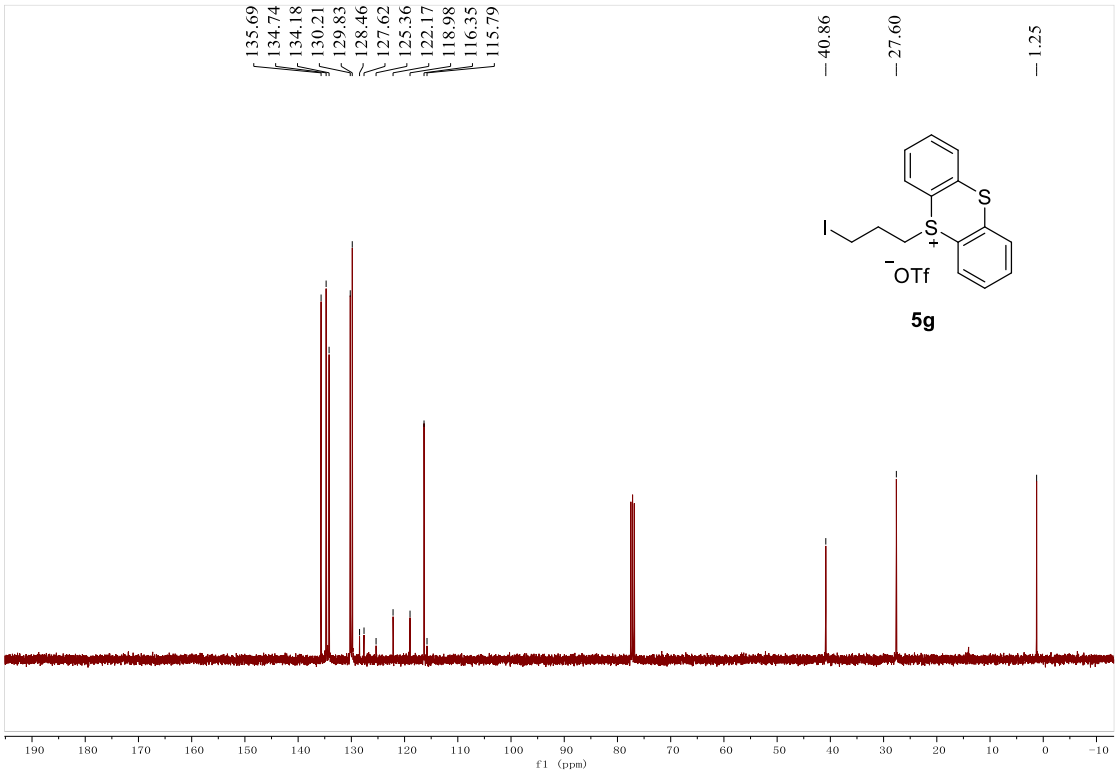
^{13}C NMR (151 MHz, Chloroform-*d*)



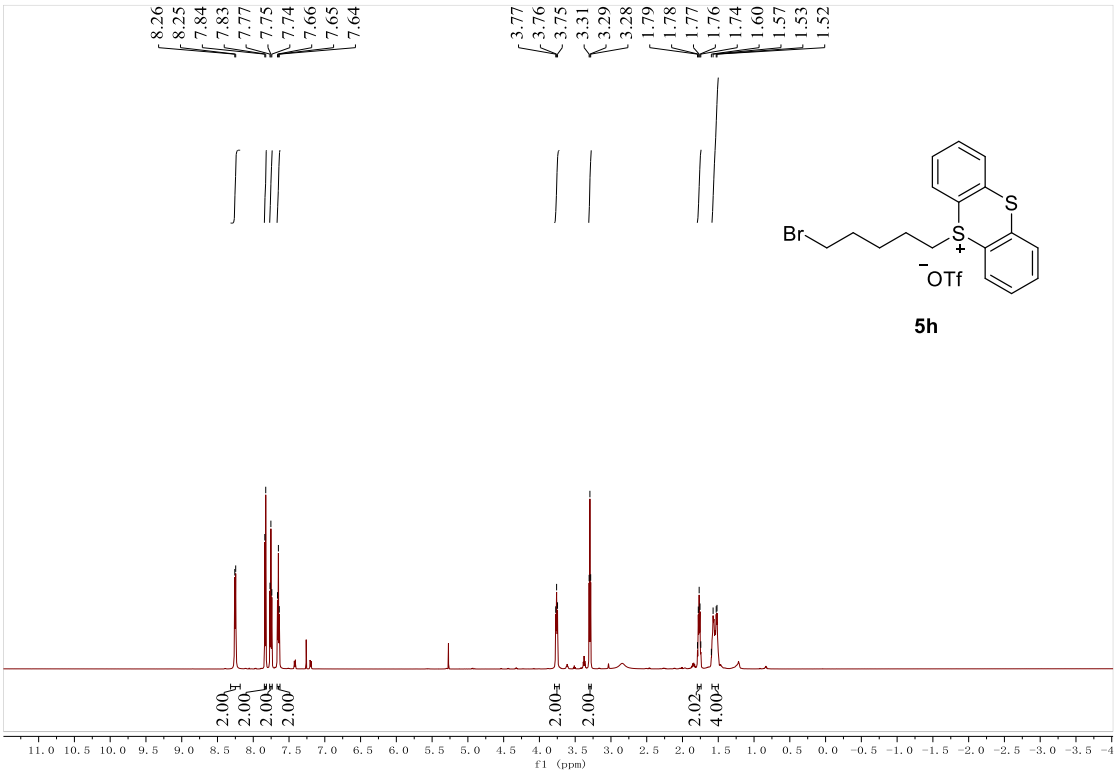
^{1}H NMR (400 MHz, Chloroform-*d*)



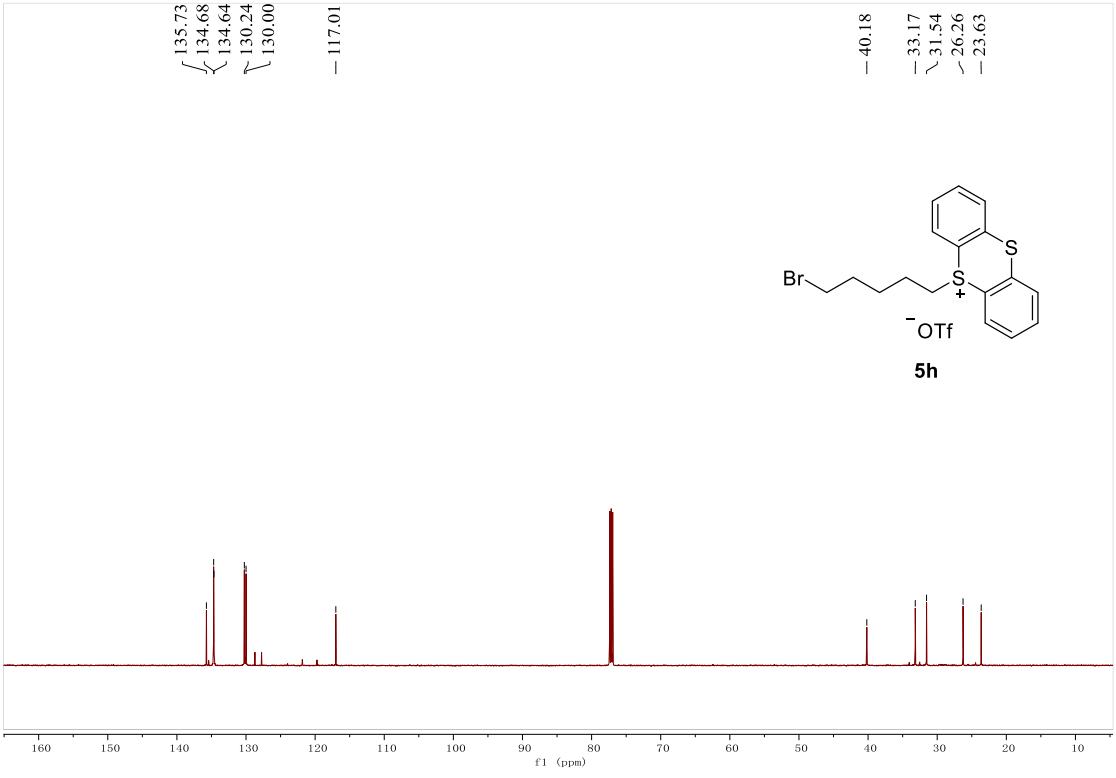
^{13}C NMR (101 MHz, Chloroform-*d*)



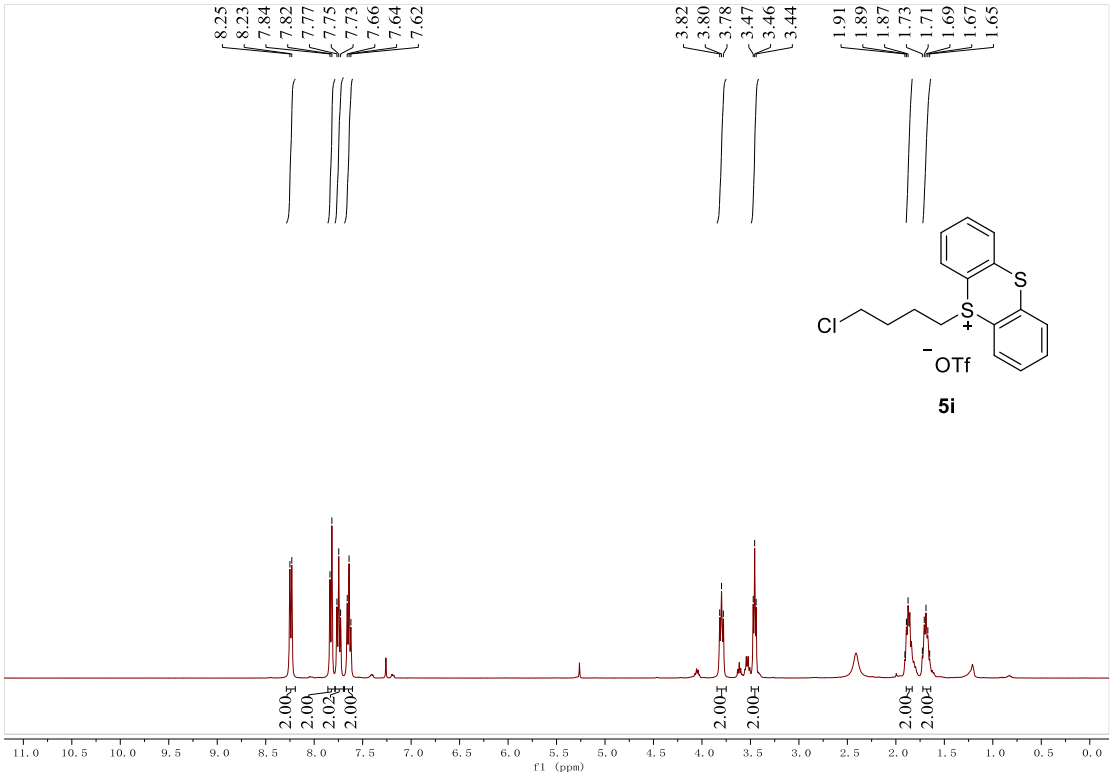
^{1}H NMR (600 MHz, Chloroform-*d*)



^{13}C NMR (151 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)