Supporting Information

Preparation of Aryl Polysulfonates via a highly efficient SuFEx click reaction, their controllable degradation and functionalized behavior

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Experimental

Materiels

All the materials General Methods. All starting materials were purchased from Aldrich, Acros, AKScientific, Fisher, Lancaster, VWR, or TCI chemical companies and used as received. Solvents were purchased from Fisher or VWR and used without extra drying, distillation or special handling practices.

Characterization

^{1}H NMR and ^{13}C NMR ^{19}F NMR spectra were recorded using INOVA 400 or 600 MHz NMR spectrometers, with $CDCl_3$ or DMSO-d_6 or DMF-d_7 as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. The molecular weights and polydispersity index (PDI), relative to PS, were measured using a Waters 1515 GPC with THF/DMF as a mobile phase at a flow rate of 1 mL min^{-1} and with a column temperature of 30 °C. UV-visible absorption spectra were recorded on a Shimadzu RF540 spectrophotometer. Room temperature emission spectra were recorded using an Edinburgh-920 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TA Instruments Dynamic TGA 2950 at a heating rate of 10 °C min^{-1} under an N_2 flow rate of 50 mL min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a Shimadzu DSC 860A 85 instrument at a heating rate of 10°C /min under N2. Percoated Merck F-254 silica gel plates were used for thin layer analytical chromography (TLC) and visualized with short wave UV light or by potassium permanganate stain. gas. Matrix-assisted laser desorptionionization−time-of-flight (MALDI-TOF) MS spectra were obtained using a ABI 4700 MALDI TOF/TOF. Spectra of sequence polymers

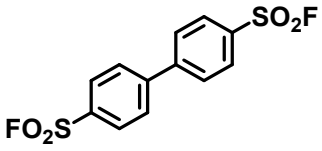
were recorded in linear mode (polarity: positive). trans-2-[3-(4-tert-Butylphenyl)-2-methylpropenylidene]-malononitrile (DCTB, 20 mg/mL in THF) was used as the matrix and CF_3COONa (1 mg/mL in THF) as the cation source for all the polymers. 20 μL of polymer solution (1 mg/mL in THF), 20 μL of DCTB solution, and 2 μL of CF_3COONa solution were mixed in an Eppendorf tube, vortexed, and centrifuged. 1 μL of solution was placed on the target plate spot, the solvent evaporated at ambient condition for the measurement.

Synthesis of Monomers

The preparation of aromatic bis(sulfonyl fluoride).

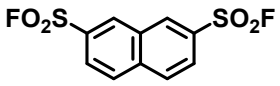
General procedure for the preparation of aromatic bis(sulfonyl fluoride).S1 was adapted as an example.

(1) Biphenyl-4,4'-disulfonyl difluoride (S1)



Biphenyl-4,4'-disulfonylchloride (5.0 g) was dissolved in 40 mL acetonitrile and 5 mL water with stirring. To this mixture was added 4 equiv. of saturated aqueous KHF_2 (4.9 g). The reaction was allowed to proceed 3 h. The mixture was extracted twice with 30 mL ethyl acetate. The organic fractions were combined, washed with water, brine, and then dried over $MgSO_4$. Solvent was removed under vacuum to provide as a yellow solid (4.1 g, 90%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.1 Hz, 4H), 7.94 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.74, 133.45, 133.29, 129.32, 128.71. ^{19}F NMR (564 MHz, Chloroform-*d*) δ 66.32.

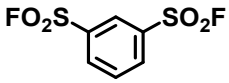
(2) naphthalene-2,7-disulfonyl difluoride(S2)



Naphthalene-2,7-disulfonate (1.0 g, 3.54 mmol) was added to phosphorus pentachloride (0.835 g, 7.08 mmol). The mixture was heated under reflux for 16 hours and then cooled to room

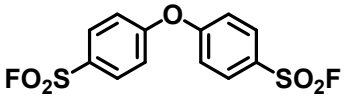
temperature. The solution was quenched with $CHCl_3$. The organic layer was dried with $MgSO_4$ and concentrated to give the desired compound. The solvent of the collected organic phase was removed under reduced pressure to give naphthalene-2,7-disulfonyldichloride.The solid residue was recrystallized from $CHCl_3$ (15 mL). Naphthalene-2,7-disulfonyl dichloride was dissolved in acetonitrile, potassium fluorohydride was dissolved in water, and the two solutions were mixed and stirred at room temperature for 24 hours. After completion of the reaction, the mixture was extracted with EtOAc. The organic fractions were combined, washed with water, brine, and then dried over MgSO4. Solvent was removed under vacuum to provide as a colourless solid. (0.73 g, 73%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (s, 2H), 8.28 (s, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.33, 132.77, 132.60, 132.11, 130.52, 126.48. ^{19}F NMR (564 MHz, Chloroform-*d*) δ 66.30.

(3) Benzene-1,3-disulfonyl fluoride（S3）



To benzene-1,3-disulfonic acid disodium salt (25.0 g, 88.6 mmol) was added PCl_5 (40.0 g, 193 mmol). The solid reaction mixture was then stirred at 90 °C for 16 h, cooled to roomtemperature before the addition of H_2O (200 mL). The crude mixture was extracted with Et_2O (500 mL), washed with H_2O (500 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent removed under reduced pressure gave the crude product benzene-1,3-disulfonyl dichloride. benzene-1,3-disulfonyl dichloride was dissolved in acetonitrile, potassium fluorohydride was dissolved in water, and the two solutions were mixed and stirred at room temperature for 24 hours. After completion of the reaction, the mixture was extracted with EtOAc. The organic fractions were combined, washed with water, brine, and then dried over MgSO4. Solvent was removed under vacuum to provide as a colourless solid (18.5 g, 76%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.43 (dd, *J* = 8.0, 1.9 Hz, 2H), 7.99 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 134.80, 131.62, 128.57. ^{19}F NMR (564 MHz, Chloroform-*d*) δ 66.70.

(4) 4,4'-oxydibenzenesulfonyl fluoride（S4）

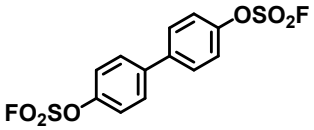


Following the general procedure above for the preparation was isolated as white powder (Yields 87%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (s, 4H), 7.54 (s, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.09, 131.34, 128.76, 128.59, 119.92.

The preparation of aryl bis(fluorosulfates).

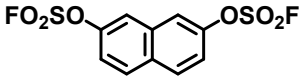
General procedure for the preparation of aryl bis(fluorosulfates) The synthesis of O1 was adapted as an example

(1) [1,1'-biphenyl]-4,4'-diyl bis(sulfurofluoridate) (O1)



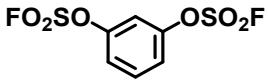
In a 1.0 L round-bottom flask equipped with a stir bar, [1,1'-biphenyl]-4,4'-diol (37.2 g, 0.2 mol) was dissolved in 400 mL CH_2Cl_2. Triethylamine (50.5 g, 0.5 mol) was added, and the solution was stirred at room temperature for 10 mins. The flask was charged with gentle vacuum, then quickly filled with SO_2F_2 gas via a syringe attached balloon. The reaction mixture was allowed stirring at room temperature for 4 hours. Then CH_2Cl_2 was evaporated away, and the crude product was dissolved in 200 mL EtOAc, which was subsequently washed with 100 mL aqueous HCl (1.0M, 3 times), 50 mL saturated aqueous solution of $NaHCO_3$, and 50 mL of saturated brine. The organic phase was concentrated and subjected to flash column chromatography purification(Hexane/EtOAc). O1 was isolated as White solid (95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (t, *J* = 5.9 Hz, 4H), 7.76 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.73, 133.37 (d, *J* = 25.4 Hz), 129.34, 128.70. ^{19}F NMR (564 MHz, Chloroform-*d*) δ 66.35.

(2) Naphthalene-2,7-diyl disulfofluoridate（O2）



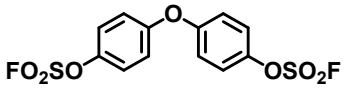
Naphthalene-2,7-diyl disulfofluoridate O2 was prepared following literature. O2 was isolated as white powder (87%)^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, *J* = 2.5 Hz, 2H), 8.35 (d, *J* = 9.1 Hz, 2H), 7.89 (dd, *J* = 9.0, 2.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.67, 133.55, 131.51, 131.05, 120.70, 119.16. ^{19}F NMR (564 MHz, Chloroform-*d*) δ 38.40.

(3) 1,3-phenylene bis(sulfurofluoridate)(O3)



O3 was prepared Following the general procedure above for the preparation .White solid(yield 90%)^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (s, 1H), 7.87 (d, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.93, 131.93, 121.46, 114.98. ^{19}F NMR (564 MHz, Chloroform-*d*) δ 38.60, 38.56 (d, J = 4.0 Hz).

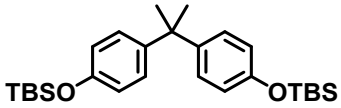
(4） oxybis(4,1-phenylene) bis(sulfurofluoridate)（O4）



4,4'-Oxybis(4,1-phenylene) disulfofluoridate O4 was prepared following the general procedure.O4 was isolated as white crystalline solid (yield 75%) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, J = 8.7 Hz, 4H), 7.27 (d, J = 8.8 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.25, 145.65, 122.69, 120.39. ^{19}F NMR (564 MHz, Chloroform-*d*) δ 37.13, 37.09.

The preparation of monomers

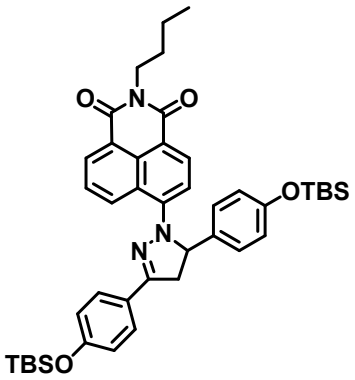
(4,4'-(Propane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(tert-butyldimethylsilane) (1a)



In a 500 mL round-bottom flask equipped with a stir bar, bisphenol-A (20 mmol) and imidazole(52 mmol) were combined and dissolved in 100 mL of chloromethane (CH_2Cl_2). The solution was stirred at room temperature for 10 mins, then was added 20 mL CH_2C_{l2} solution of TBSCl (48mmol) dropwise within 20 mins. The resulting mixture was stirred at room temperature until the full conversion of starting compound to target product, monitored by TLC and LC-MS. Precipitates were removed by filtration. The filtrate was concentrated on rotary evaporator. The resulting crude product was dissolved in 100 mL of ethyl acetate (EtOAc), which was subsequently washed with 50 mL saturated aqueous solution of $NaHCO_3$ (3 times) and 50 mL saturated aqueous solution of NaCl. The organic phase was dried over anhydrous Na_2SO_4. After filtration, the filtrate was subjected to evaporation to remove EtOAc. The crude product through flash column chromatography purification(Hexane/EtOAc) as white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (d, *J* = 8.6 Hz, 4H), 6.71 (d, *J* = 8.6 Hz, 4H), 1.62 (s, 6H), 0.97 (s, 18H), 0.19 (s, 12H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.20, 143.63, 127.62, 119.12, 41.69, 31.05, 25.65, 18.13, -4.43.

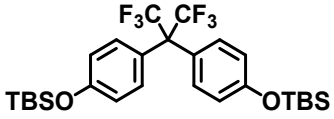
6-(3,5-bis(4-((tert-butyldimethylsilyl)oxy)phenyl)-4,5-dihydro-1H-pyrazol-1-yl)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione（1b）



6-(3,5-bis(4-hydroxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (1.012g, 2mmol)and imidazole (0.354g, 5.2mmol) were dissolved in dichloromethane (40 mL). And then the solution of tert-butyldimethylsilyl chloride (0.97 g, 4.8 mmol) in the dichloromethane (4 mL) was dropwise added into the reaction mixture. The reaction mixture was allowed to stir at room temperature for 24 hrs. After the reaction was completed, the mixture was extracted with ethyl acetate and washed successively with sodium bicarbonate solution and water. The solution was removed by rotary evaporation in vacuum. And the product was purified by silica-gel column chromatography to give a pale yellow powder with a yield of 75%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.68 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 6.9 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 3H), 7.18 (s, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 6.9 Hz, 3H), 5.59 (d, *J* = 7.7 Hz, 1H), 4.15 (s, 2H), 3.90 – 3.78 (m, 1H), 3.21 (s, 1H), 2.18 (s, 2H), 1.43 (s, 2H), 1.01 (s, 10H), 0.94 (s, 11H), 0.25 (s, 6H), 0.15 (s, 6H).

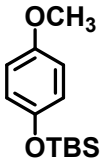
(((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))bis(tert-butyldimethylsilane) （1c）



1C was prepared following literature[1], compound was afforded as white solid in 91% yield.

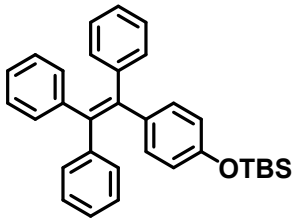
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.5 Hz, 4H), 6.85 – 6.74 (m, 4H), 0.99 (s, 18H), 0.23 (s, 12H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.97, 131.40, 126.01, 119.37, 25.57, 18.13, -4.43

The preparation of Small molecules



tert-butyl(4-methoxyphenoxy)dimethylsilane(TBMP-OTBS)was prepared following procedure above.

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.77 (q, *J* = 8.7 Hz, 4H), 3.68 (s, 3H), 0.93 (s, 9H), 0.14 (s, 6H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.06, 149.32, 120.58, 114.44, 55.59, 25.70, 18.16, -4.52.



TPE-OTBS was prepared following was prepared following procedure above.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.12 – 7.03 (m, 9H), 6.96 – 6.89 (m, 6H), 6.82 – 6.77 (m, 2H), 6.59 – 6.55 (m, 2H), 0.87 (s, 9H), 0.09 (s, 6H).

The preparation of catalyst [$(Ph_3P=N\text{-}PPh_3)^+$ HF_2^-] (0.2 M)

[$(Ph_3P=N\text{-}PPh_3)^+$ HF_2^-] was prepared following literature[1].To a well stirred solution (suspension) of $AgHF_2$ (10 mmol) in CH_3CN (45 mL) in a 100 mL plastic bottle (the bottle was covered by aluminum foil to avoid light) with a rubber septa was added a solution of [$(Ph_3P=N\text{-}PPh_3)^+$ Cl^-] (10 mmol) in CH_3CN (5 mL) in 5 min by syringe under argon atmosphere. The mixture was allowed to stir at room temperature for 30 min, and then sonicated at room temperature for another 30 min.

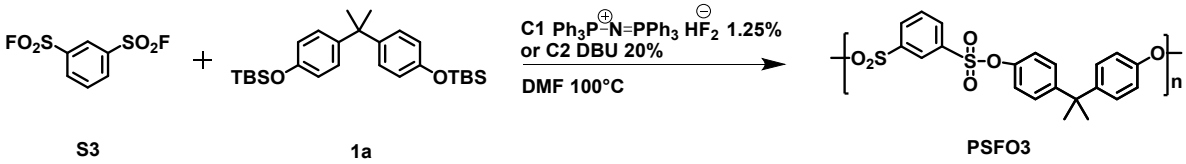
It was then centrifuged (2000 rpm), and the supernatant was transferred under argon by syringe into a plastic bottle as a 0.2 M stock catalyst solution (microwave oven activated molecular sieves was preloaded to keep the solution dry).

Synthesis of polymers

Synthesis of polysulfonates

General procedure for the preparation of polysulfonates

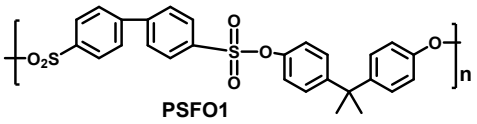
The synthesis of poly-bisphenol-A-(2,2'-(phenylazanediyl)bis(ethane-1-sulfonate) **PSFO3** was adapted as an example



S3 1a PSFO3

To an oven dried test tube with stir bar was added 2,2'-(phenylazanediyl)bis(ethane-1-sulfonyl fluoride) (0.5 mmol) and bisphenol A bis(t-butyldimethylsilyl) ether (0.5 mmol). The tube was purged three times with argon and then charged with DMF (0.1 mL) andThe mixture was heated to 80 °C with stirring for 10 minutes under argon atmosphere, and then an additional $(Ph_3P{=}N\text{-}PPh_3)^+HF_2^-$ (0.2 M in acetonitrile, 65 μL, 1.25 mol%) or 20% DBU was added to the reaction solution. The solution was added slowly by pipette into a flask containing methanol (50 mL) with vigorously stirring to precipitate the desired polysulfonate PSFO3. The precipitate was then isolated by filtration, washed with MeOH (20 mL), and dried under high vacuum pimp at 60 °C to provide 247 mg white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.33 – 8.15 (m, 2H), 7.93 (t, J = 7.9 Hz, 1H), 7.77 (s, 1H), 7.06 (d, J = 8.7 Hz, 4H), 6.84 (d, J = 8.7 Hz, 4H), 1.42 (s, 6H).

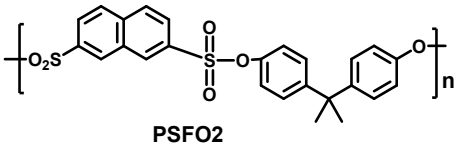
PSFO1



PSFO1

Prepared following the general procedure ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.03 – 7.84 (m, 8H), 7.13 (s, 4H), 6.94 (s, 4H), 1.51 (s, 6H).

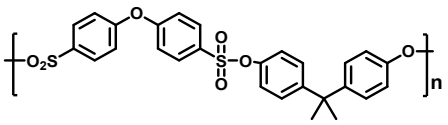
PSFO2



PSFO2

Prepared following the general procedure ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.94 – 8.80 (m, 2H), 8.40 – 8.25 (m, 2H), 8.13 – 8.01 (m, 2H), 7.11 – 6.99 (m, 4H), 7.00 – 6.82 (m, 4H), 1.44 (dt, J = 14.8, 4.6 Hz, 6H).

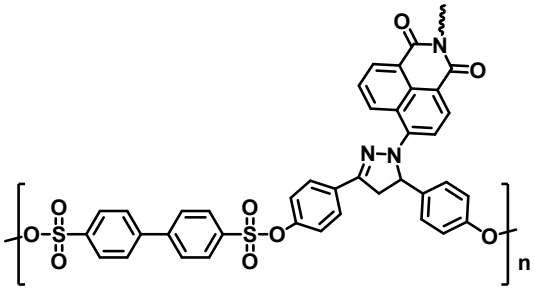
PSFO4



PSFO4 1

Prepared following the general procedure ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.86 (d, J = 8.4 Hz, 4H), 7.38 (dd, J = 113.5, 8.3 Hz, 4H), 7.12 (dd, J = 30.3, 8.6 Hz, 4H), 6.97 (dd, J = 61.6, 8.5 Hz, 4H), 1.53 (s, 6H).

PSFO1-TPP



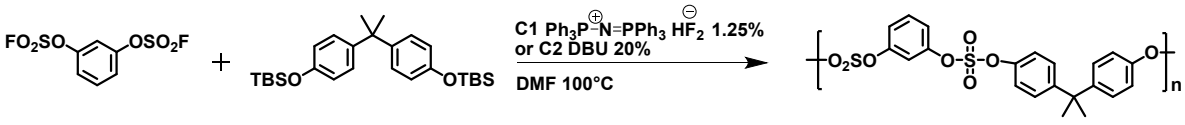
PSFO$_1$-TPP

Prepared following the general procedure ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.62 – 9.15 (m, 1H), 8.34 – 7.98 (m, 3H), 7.94 – 7.65 (m, 8H), 7.57 (t, J = 10.4 Hz, 3H), 7.46 – 7.25 (m, 2H), 7.13 (s, 2H), 6.97 (s, 2H), 5.88 (s, 1H), 3.85 (s, 3H), 3.27 – 3.03 (m, 1H), 1.43 (s, 2H), 1.20 (d, J = 19.0 Hz, 3H), 0.96 – 0.55 (m, 4H).

Synthesis of polysulfates

General procedure for the preparation of polysulfates

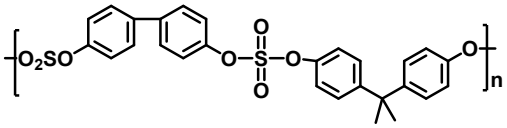
The synthesis of Poly-bisphenol-A-(2,2'-(phenylazanediyl)bis(ethane-1-sulfonate) PSFA3 was adapted as an example



O3 1a PSFA3

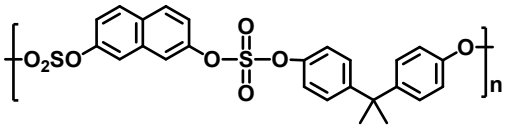
To an oven dried test tube with stir bar was added 2,2'-(phenylazanediyl)bis(ethane-1-sulfonyl fluoride) (0.5 mmol) and bisphenol A bis(t-butyldimethylsilyl) ether (0.5 mmol). The tube was purged three times with argon and then charged with DMF (0.1 mL) The mixture was heated to 80℃ with stirring for 10 minutes under argon atmosphere, and then an additional $(Ph_3P{=}N{-}PPh_3)^+HF_2^-$ (0.2 M in acetonitrile, 65 μL, 1.25 mol%) was added to the reaction solution. The solution was added slowly by pipette into a flask containing methanol (50 mL) with vigorously stirring to precipitate the desired polysulfonate PSFA3. The precipitate was then isolated by filtration, washed with MeOH (20 mL), and dried under high vacuum pimp at 60℃ to provide 247 mg white solid.

PSFA1 prepared following the procedure ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.93 – 7.72 (m, 4H), 7.48 (d, J = 7.9 Hz, 4H), 7.34 (s, 8H), 1.62 (s, 6H).



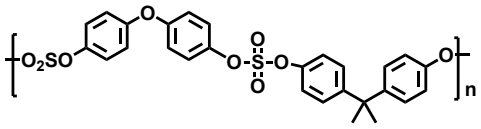
PSFA1

PSFA2 prepared following the procedure ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.18 (d, J = 38.6 Hz, 4H), 7.58 (s, 2H), 7.35 (d, J = 30.2 Hz, 8H), 1.59 (s, 6H).



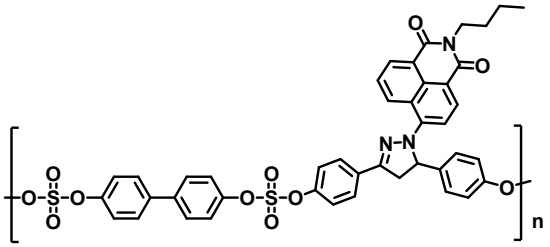
PSFA2

PSFA4 prepared following the procedure ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.43 (s, 4H), 7.32 (s, 8H), 7.13 (d, J = 8.9 Hz, 4H), 1.61 (s, 6H).



PSFA4

PSFA1-TPP prepared following the procedure



PSFA1-TPP

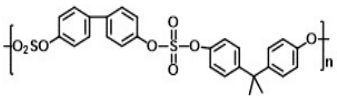
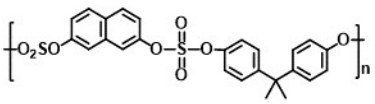
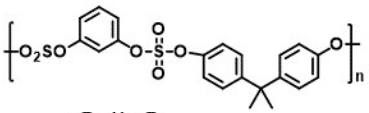
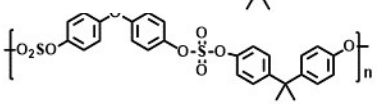
□	Polysulfates	T	C1		C2		Td
			Mn	PDI	Mn	PDI	
PSFA1		RT	23800	1.5	17600	1.5	-
		373K	38600	1.5	33700	1.5	336
PSFA2		373K	21900	1.3	25000	1.5	353
PSFA3		373K	17100	1.4	20800	1.4	353
PSFA4		373K	46300	1.5	56000	1.5	339

Table S1:The reaction conditions and GPC results of Polysulfates

Table S2:Degradation behavior of PSFO1 in different organic bases or solvent

	Base solution					Solvent（DBU）		
□	Na_2CO_3	TMA	Py	DMAP	□	THF	CH_2Cl_2	DMF
before	73600(1.5)	73900(1.5)	73900(1.5)	73900(1.5)	before	35600(1.6)	35600(1.6)	35600(1.6)
after	72000(1.6)	71100(1.7)	69800(1.7)	61400(1.8)	after	13400(1.3)	10600(1.2)	9000(1.2)

Table S3:Degradation behavior of PSFO1 in different amounts of catalyst

□	5%	10%	20%	30%
before	35600(1.6)	35600(1.6)	35600(1.6)	35600(1.6)
after	11300(1.1)	10100(1.1)	10800(1.1)	10100(1.1)

Figure S1:Plot of the molecular weight (Mn ps) of PSFA1 and PSFO1 vs reaction time at 100°C

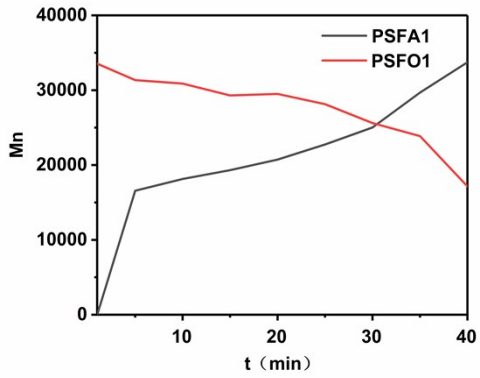


Figure S2: LC-MS analysis of the reaction

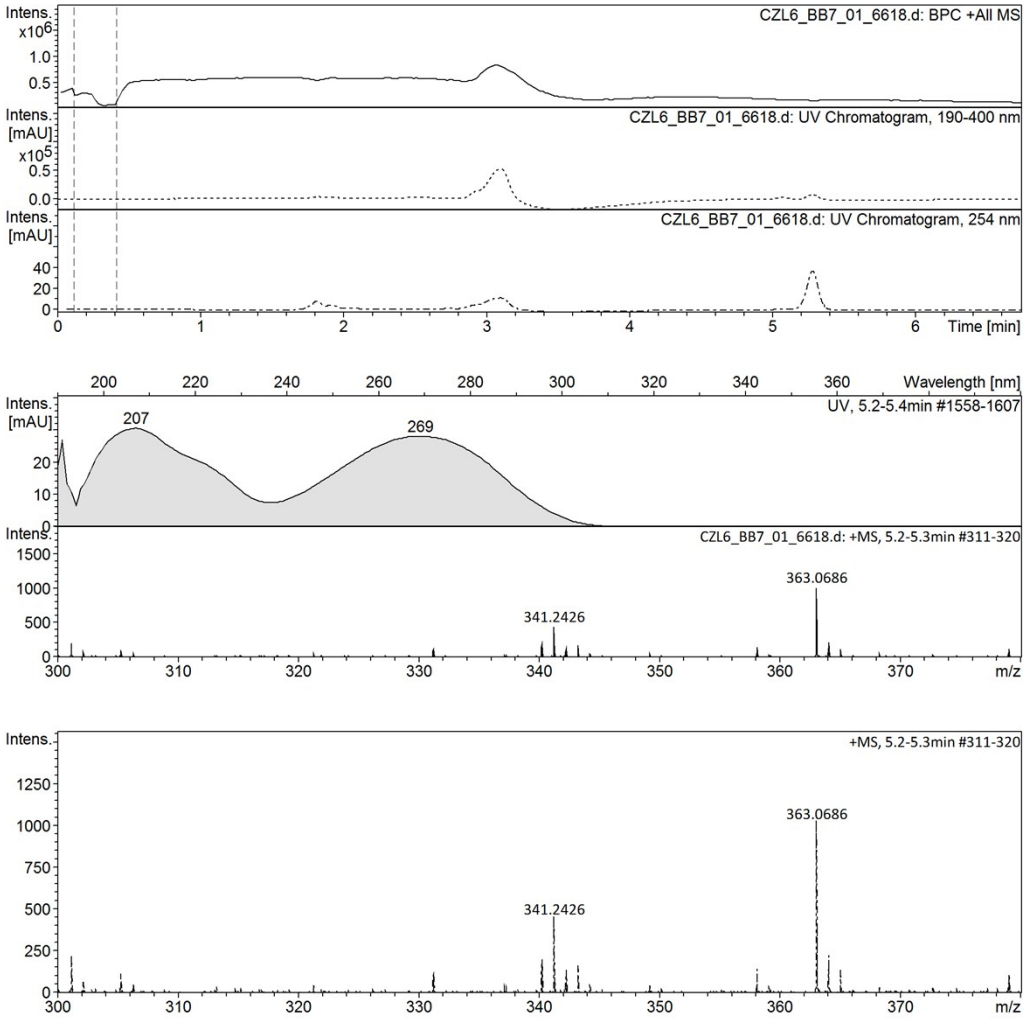


Figure S3: ^{1}HNMR spectra of PSFO2-TPE

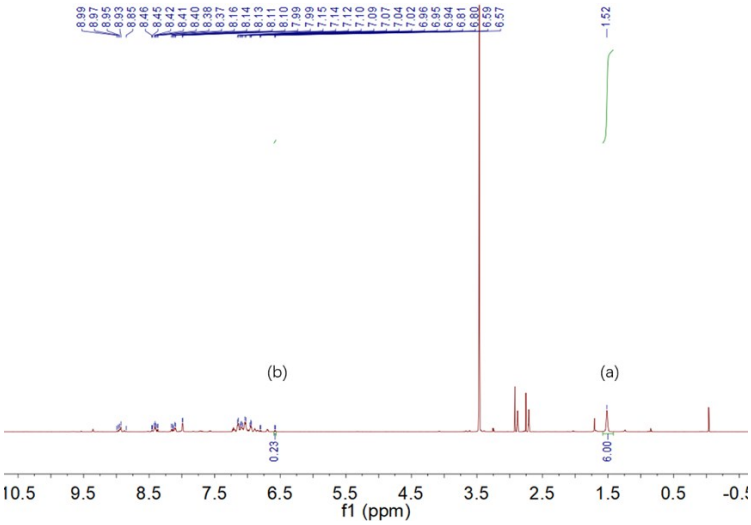
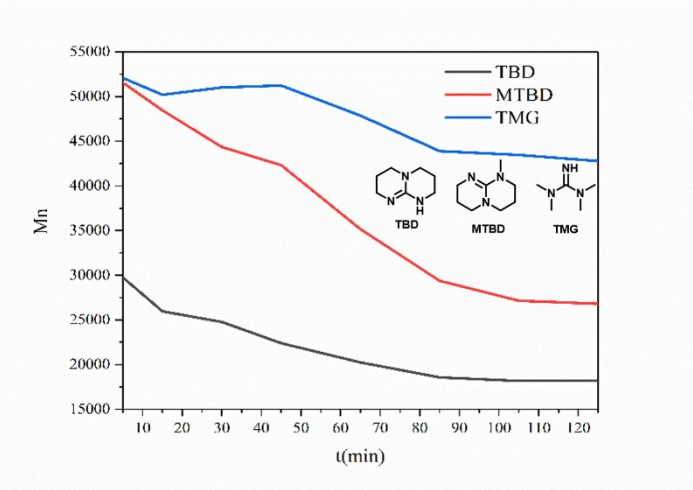


Table S3: The molecular weight (Mn ps) of PSFO1 use 3 catalysts vs reaction time at 100°C

Catalysts	TBD	MTBD	TMG
5min	29759	51559	52066
15min	25961	48451	50193
30min	24766	44350	51007
45min	22387	42315	51218
65min	20244	35154	47853
85min	18563	29375	43885
105min	18165	27140	43452
125min	18187	26805	42771

Figure S4: Plot of the molecular weight (Mn ps) of PSFO1 use 3 catalysts vs reaction time at



100°C

Figure S5. IR spectra of PSFO2 and PSFO2-OTBS; TPE-OTBS

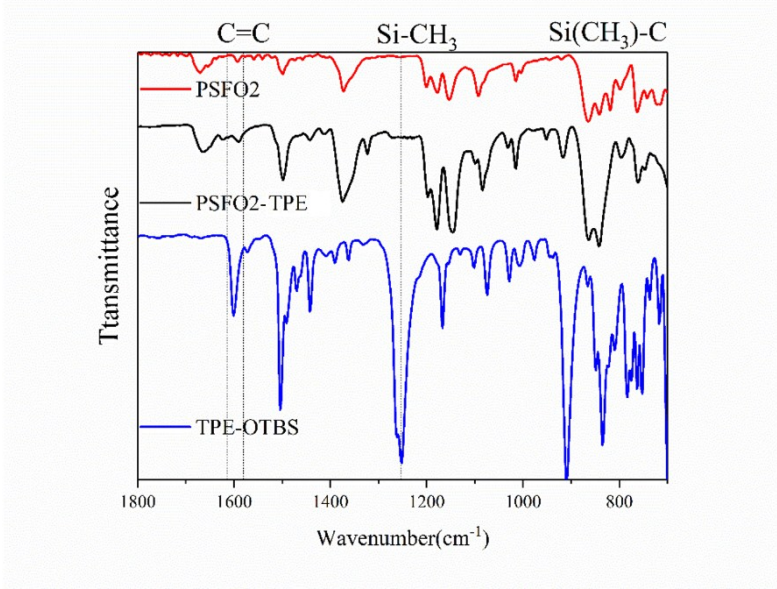
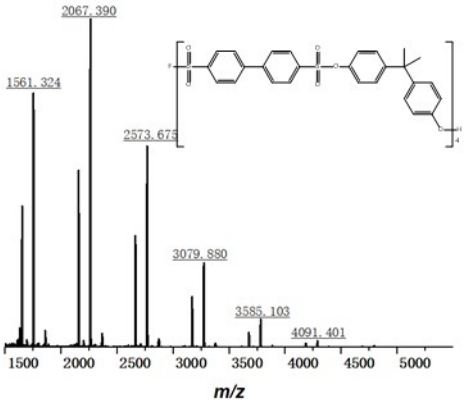
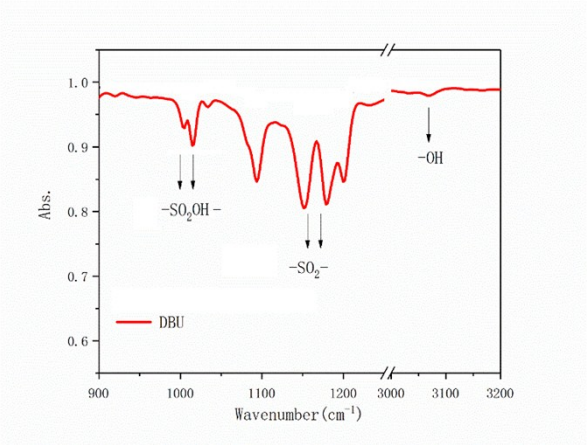


Figure S6: MALDI-TOF mass spectrum of the polymer PSFO1 treated with DBU.



End-Group Analysis by MALDI-TOF MS. We conduct the end-group analysis using formula : $P_m = E_m + C_m + nRU_m$. where E_m represents the end group mass, P_m is the chosen polymer peak mass, C_m is the cation ion mass, n is the RU number, and RU_m represents the mass of the RU. In Positive mode,-SO_3H was calculated as -SO_3Na^2, Thus, $P_m = E_m + C_m + nRU_m = 1+19+23+4X\ 506=2067$, which is composed of -$SO_3H$ and -OH end groups. The peak mass of 2067.390 Da in Figure was in good agreement with the expected molecular weight.

Figure S7: FTIR spectra of polymer PSFO1 treating by DBU.



Preparation of PSFO1-OCH_3

The prepared PSFO1 polymer(200mg) was placed in a 5 ml round bottom flask equipped with a magnetic stirrer, and DMF (1ml)was added,and heat to completely dissolve it. Then, DBU and tert-butyl(4-methoxyphenoxy)dimethylsilane(200mg) were separately added and then heated to 100 °C for 6 hours. The entire reaction is carried out in a constant stream of N_2 . After the end of the reaction, the reactor was naturally cooled to room temperature, which was precipitated into MeOH to precipitate a polymer. The obtained solution was centrifuged at 8000 rpm for 10 minutes twice to wash away impurities. The precipitate was filtered and washed three times with MeOH, suction filtered, and then dried in vacuo in an oven at 60 ° C for 6 hours. The blocked product was obtained. After the reaction is completed, it is then dialyzed in a dialysis bag to remove small molecules. The solid was obtained from the solution by freeze drying and vacuum-baked in an oven at 60 ° C for 6 hours. A white solid was obtained. (Yield: about 25%).

Preparation of PSFO2-TPE

The prepared PSFO2 polymer(200mg) was placed in a 5 ml round bottom flask equipped with a

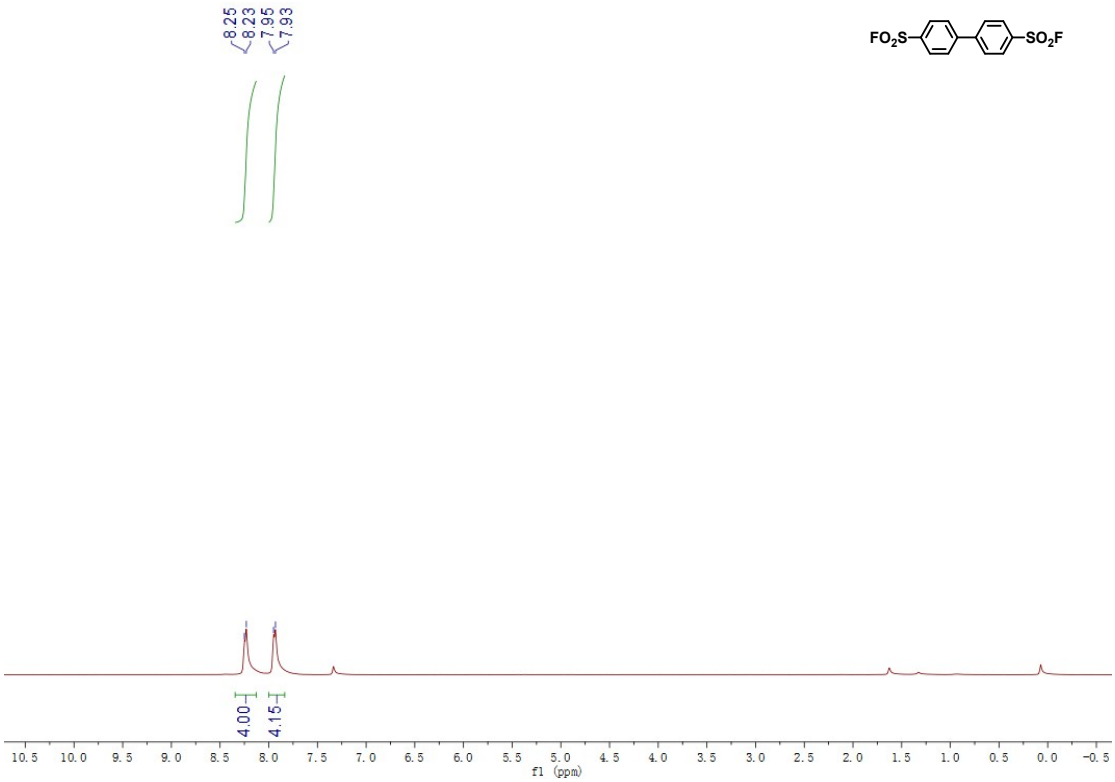
magnetic stirrer, and DMF (2ml)was added,and heat to completely dissolve it. Then, DBU(20%)and TPE-OTBS(200mg) were separately added and then heated to 100 °C for 6 hours. The entire reaction is carried out in a constant stream of N2 . After the end of the reaction, the reactor was naturally cooled to room temperature, which was precipitated into MeOH to precipitate a polymer. The obtained solution was centrifuged at 8000 rpm for 10 minutes twice to wash away impurities. The precipitate was filtered and washed three times with MeOH, suction filtered, and then dried in vacuo in an oven at 60 °C for 6 hours. The blocked product was obtained. After the reaction is completed, it is then dialyzed in a dialysis bag to remove small molecules. The solid was obtained from the solution by freeze drying and vacuum-baked in an oven at 60 °C for 6 hours. A white solid was obtained. (Yield: about 20%).

Preparation of PSFO1-TPP-CF_3

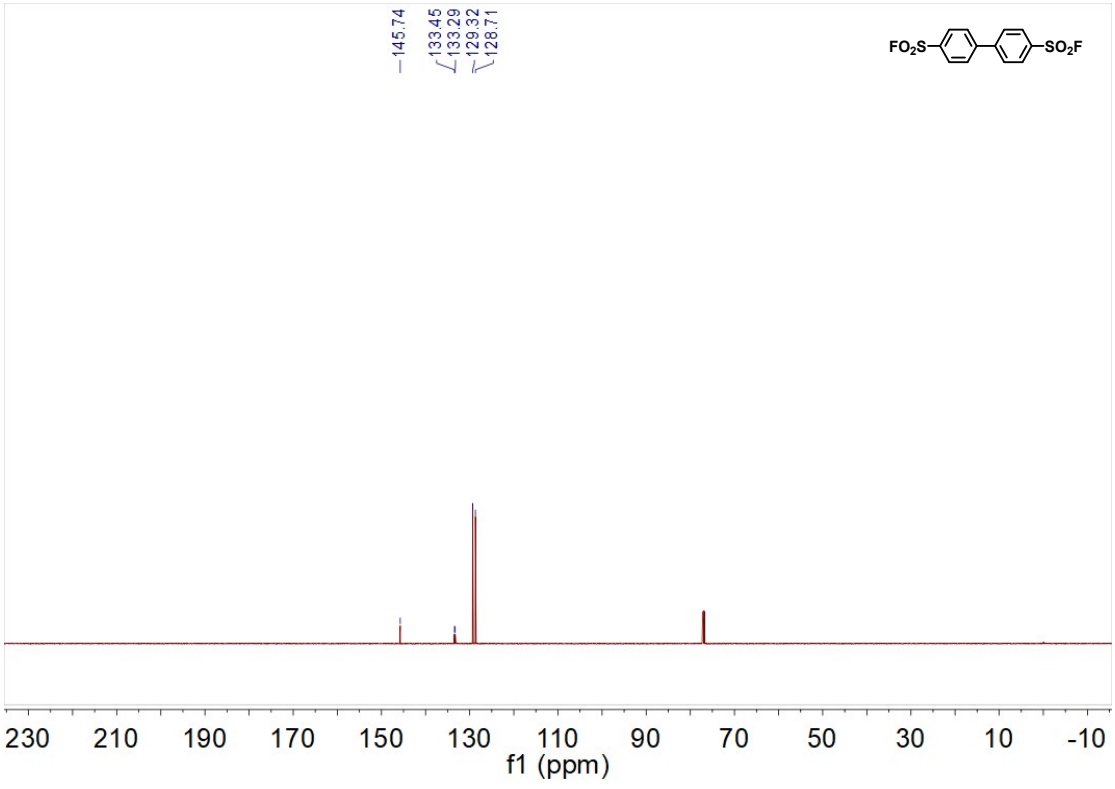
The prepared PSFO1-TPP polymer(50mg) was placed in a 5 ml round bottom flask equipped with a magnetic stirrer, and DMF (1ml)was added, and heat to completely dissolve it. Then, DBU (20%)and MTPP-OTBS(80mg) were separately added and then heated to 100 °C for 6 hours. The entire reaction is carried out in a constant stream of N_2 . After the end of the reaction, the reactor was naturally cooled to room temperature, which was precipitated into MeOH to precipitate a polymer. The obtained solution was centrifuged at 8000 rpm for 10 minutes twice to wash away impurities. The precipitate was filtered and washed three times with MeOH, suction filtered, and then dried in vacuo in an oven at 60 °C for 6 hours. The blocked product was obtained. After the reaction is completed, it is then dialyzed in a dialysis bag to remove small molecules. The solid was obtained from the solution by freeze drying and vacuum-baked in an oven at 60 ° C for 6 hours. A white solid was obtained. (Yield: about 18%).

Copies of the NMR spectra

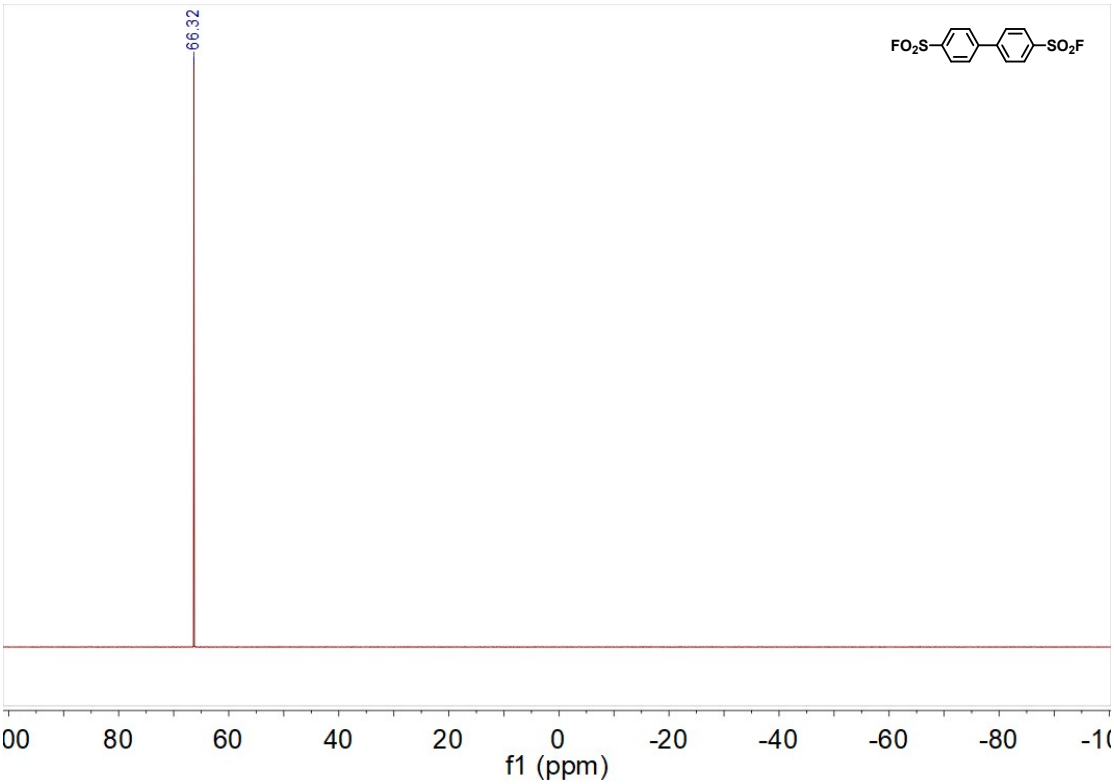
^{1}H NMR (S-1)



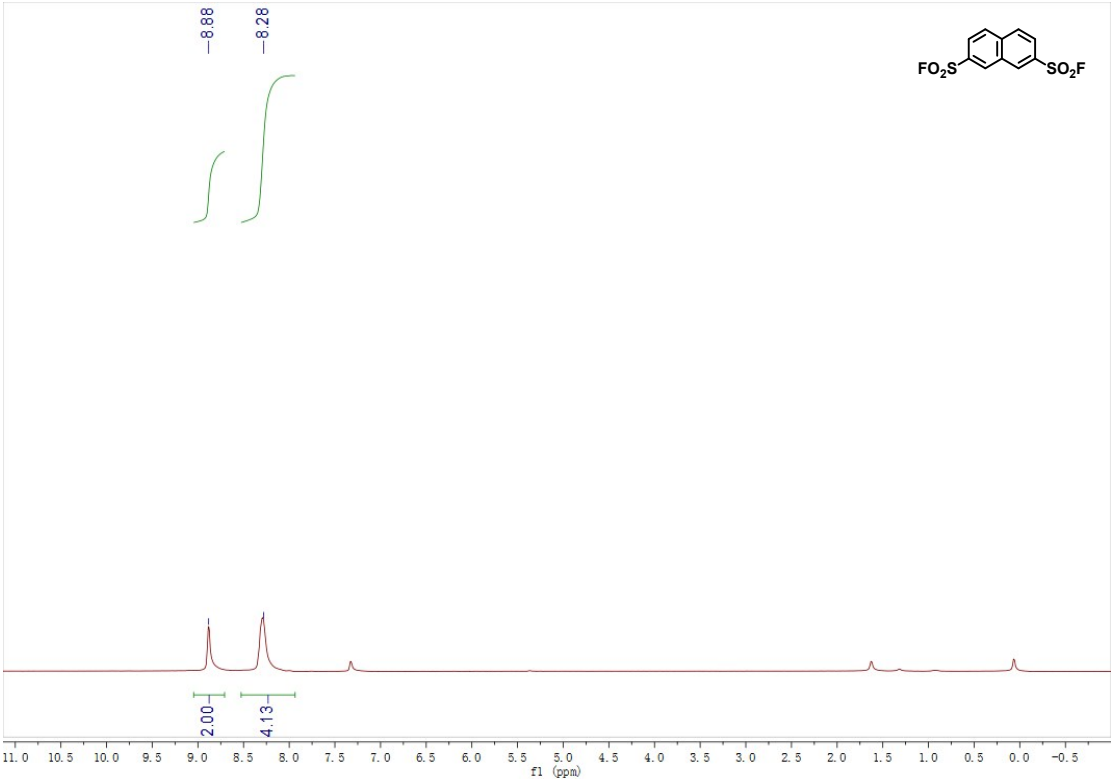
^{13}C NMR (S-1)



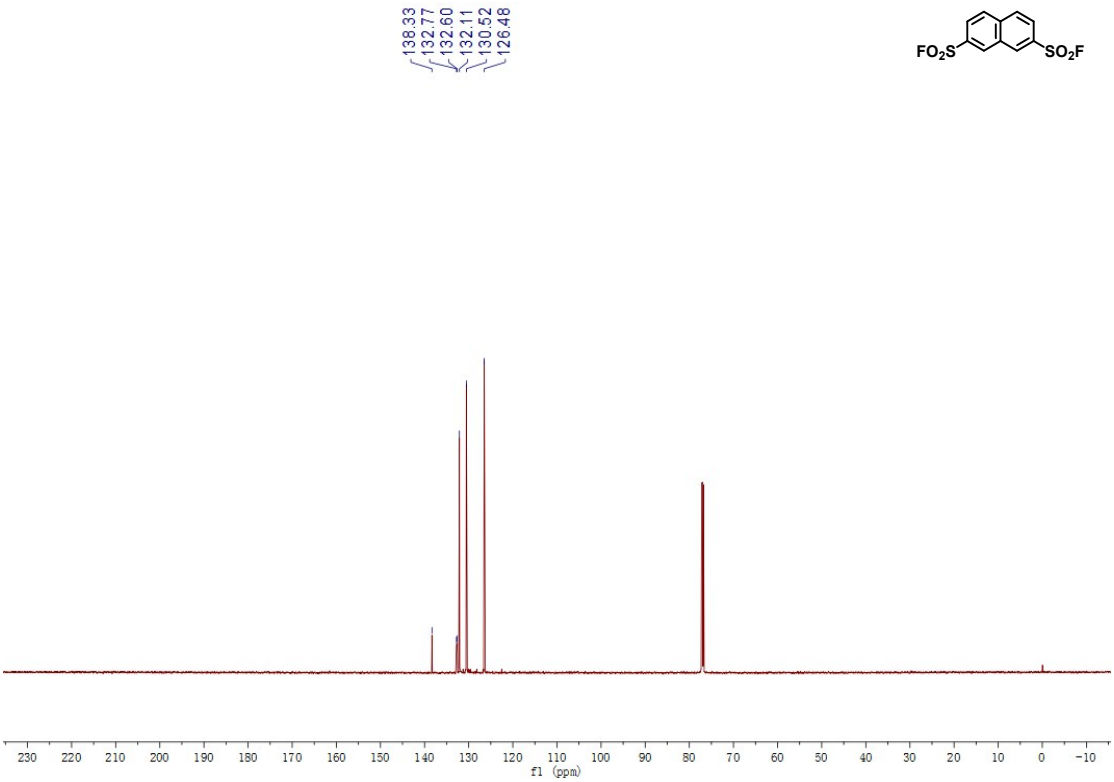
^{19}F NMR (S-1)



^{1}H NMR (S-2)



^{13}C NMR (S-2)



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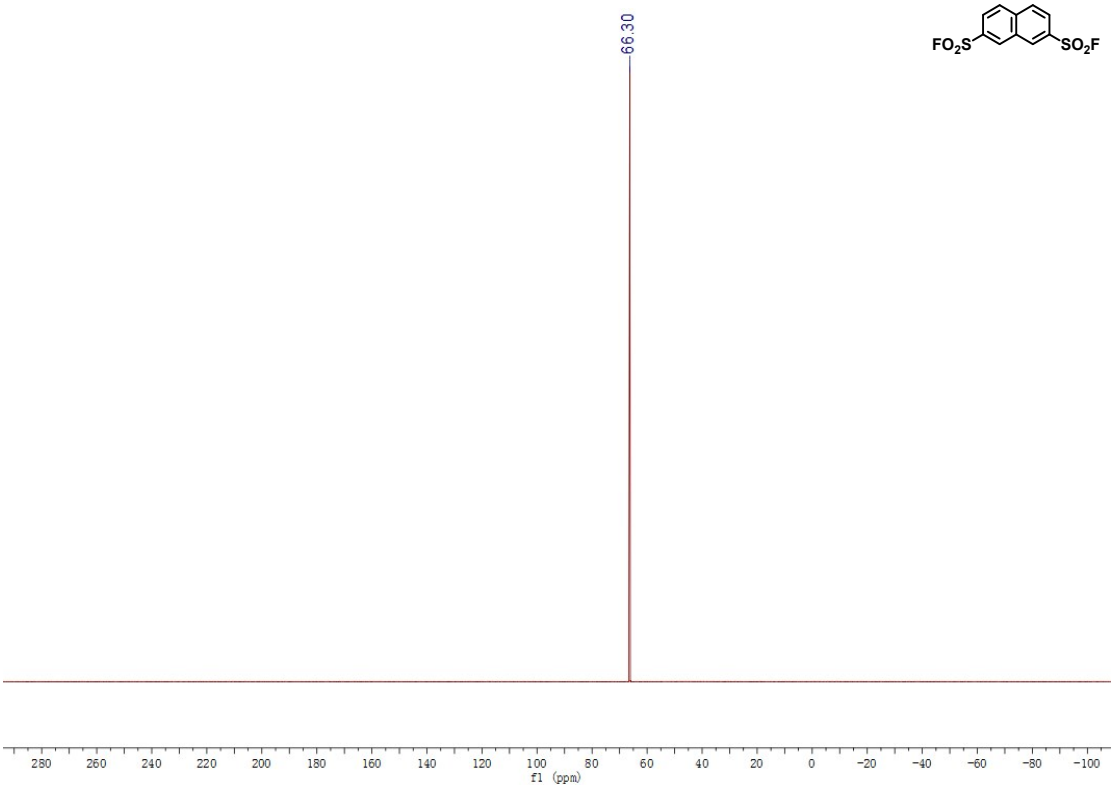
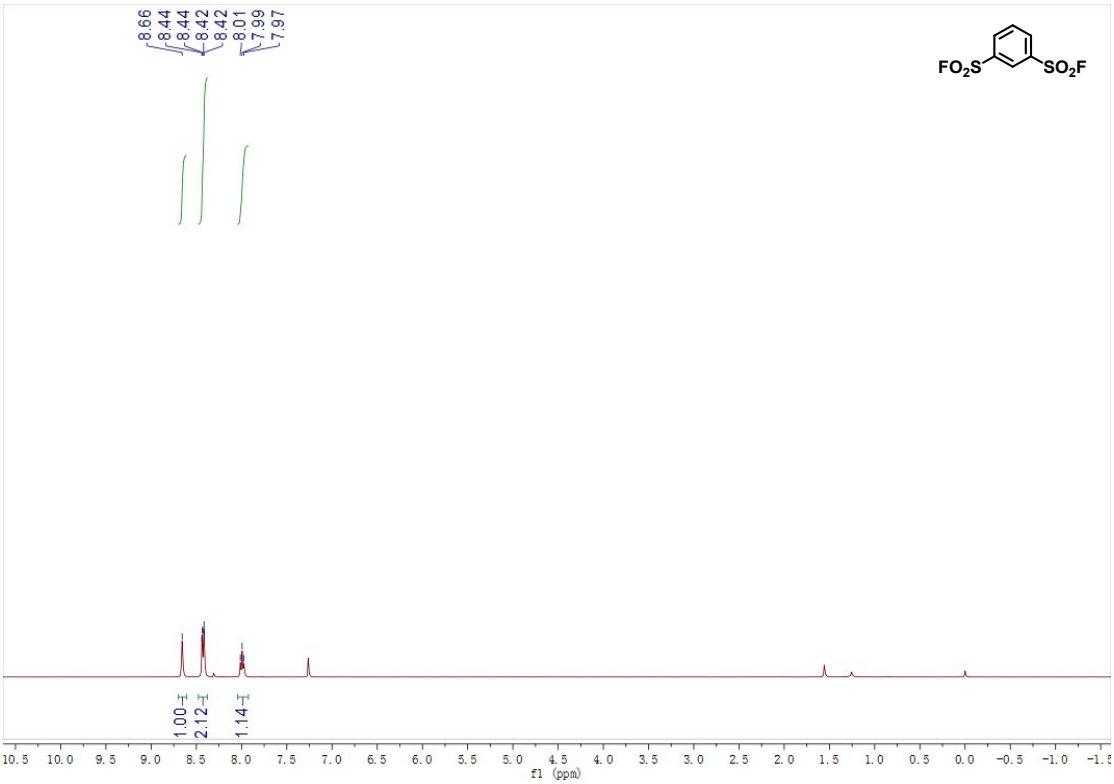


^{1}H NMR (S-3)



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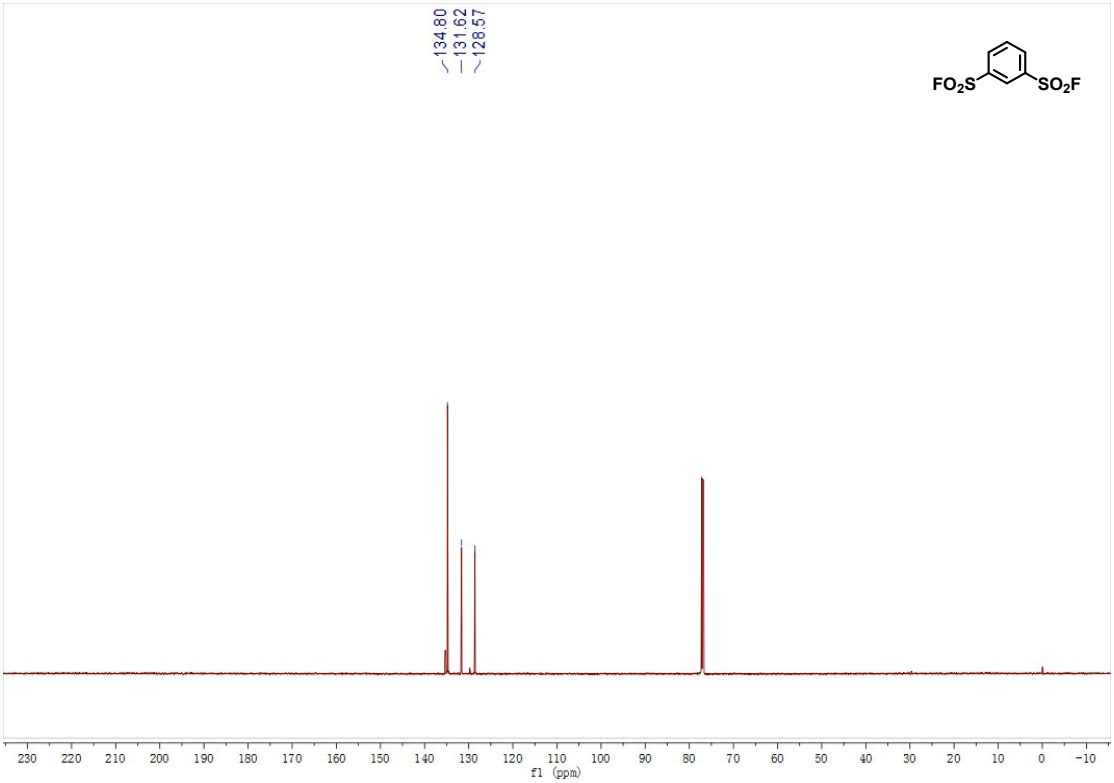
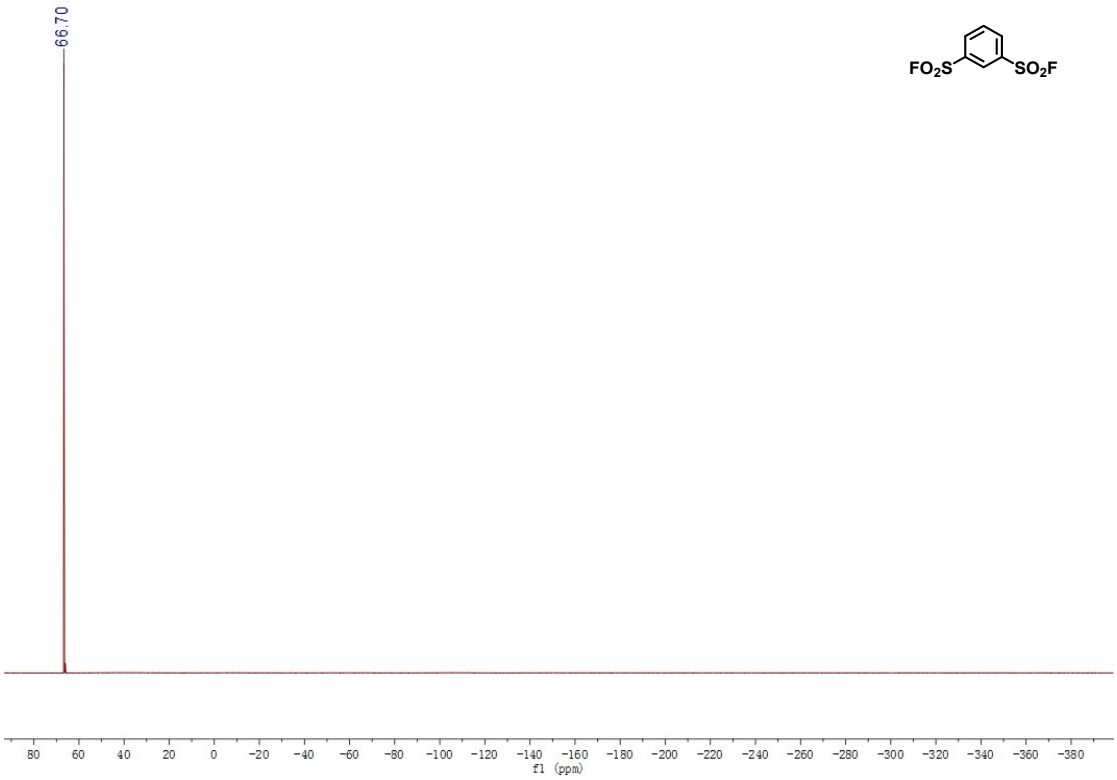
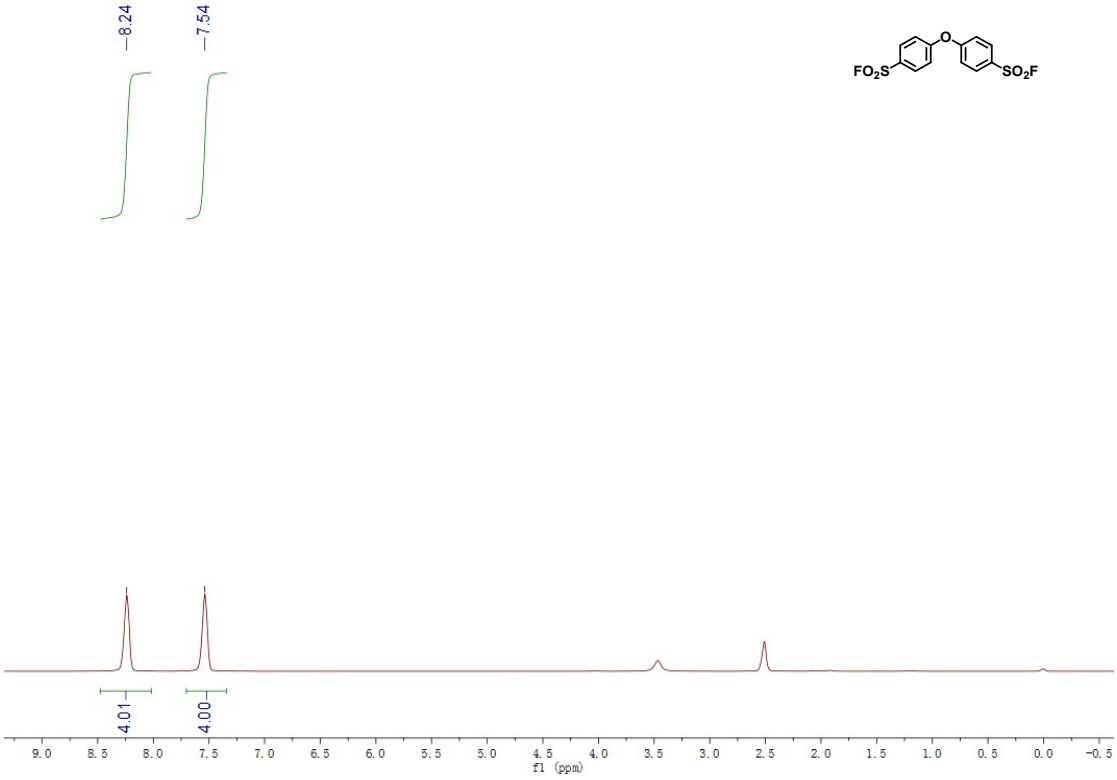


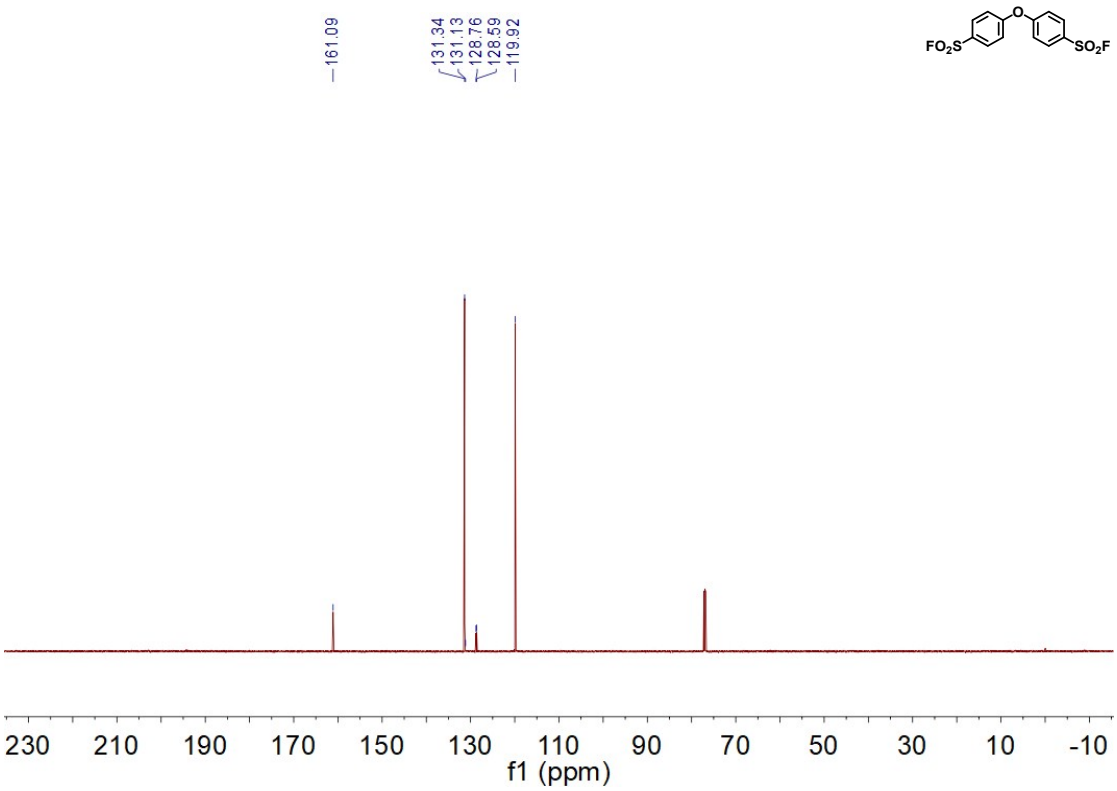
^{19}F NMR (S-3)



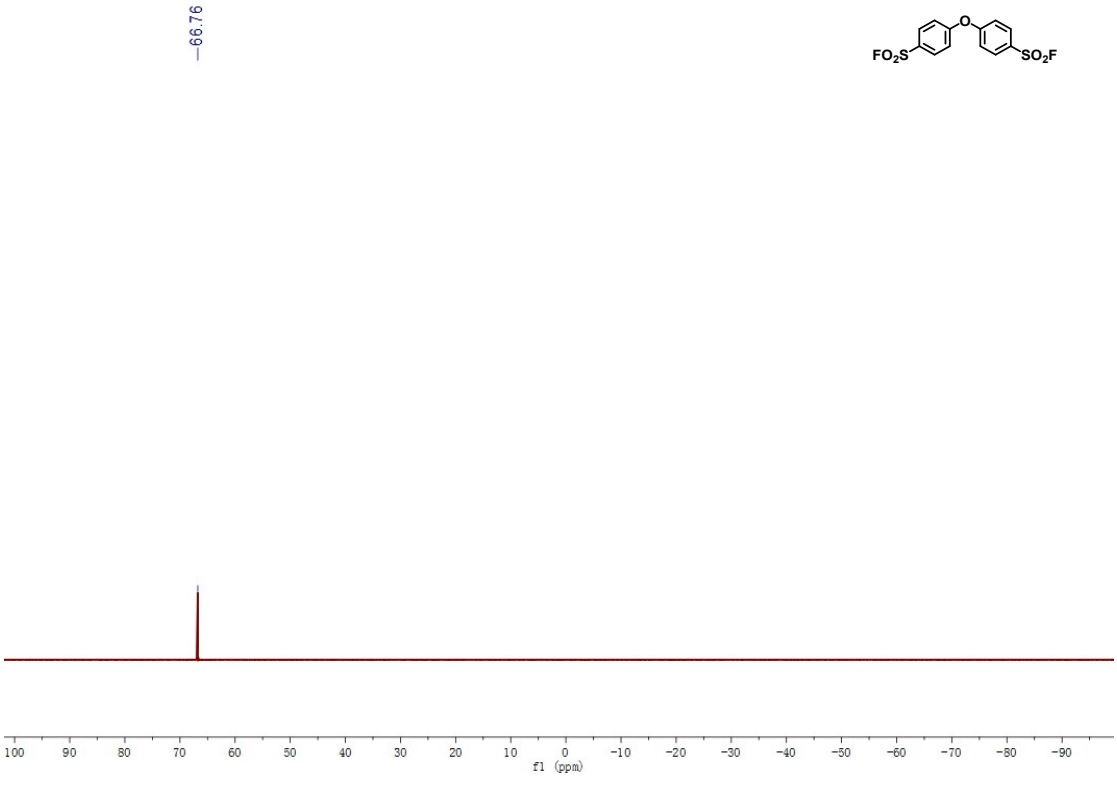
^{1}H NMR (S-4)



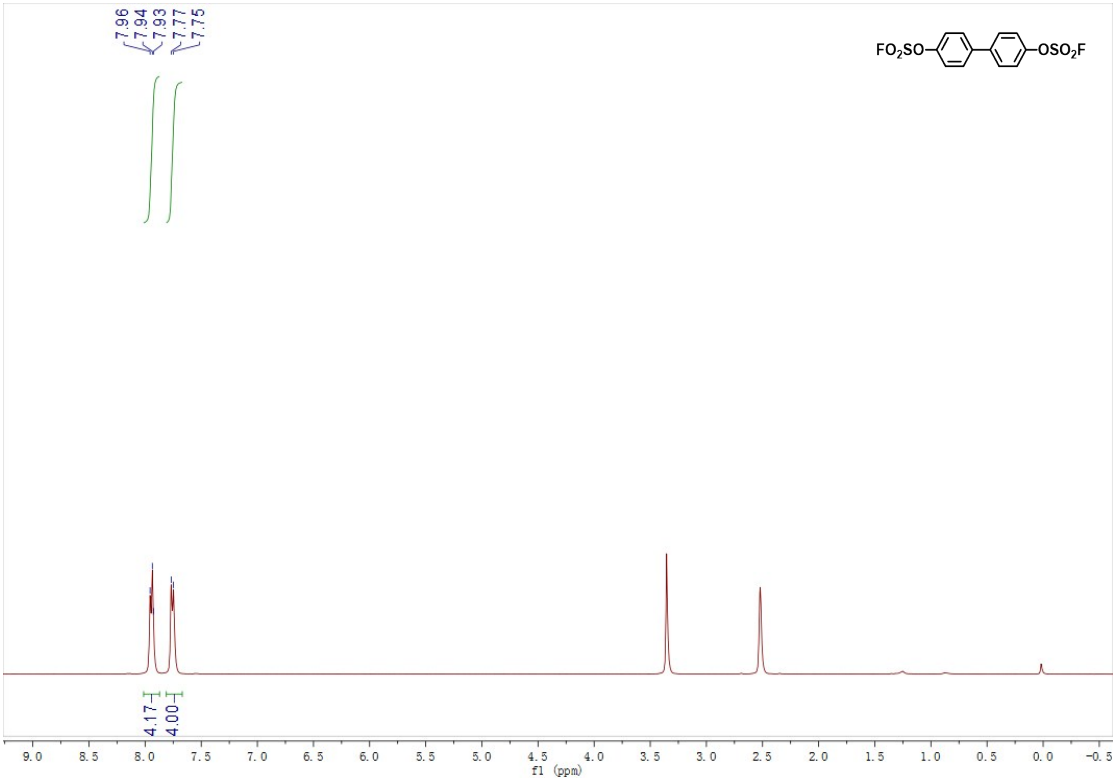
^{13}C NMR (S-4)



^{19}F NMR (S-4)



^{1}H NMR (O-1)



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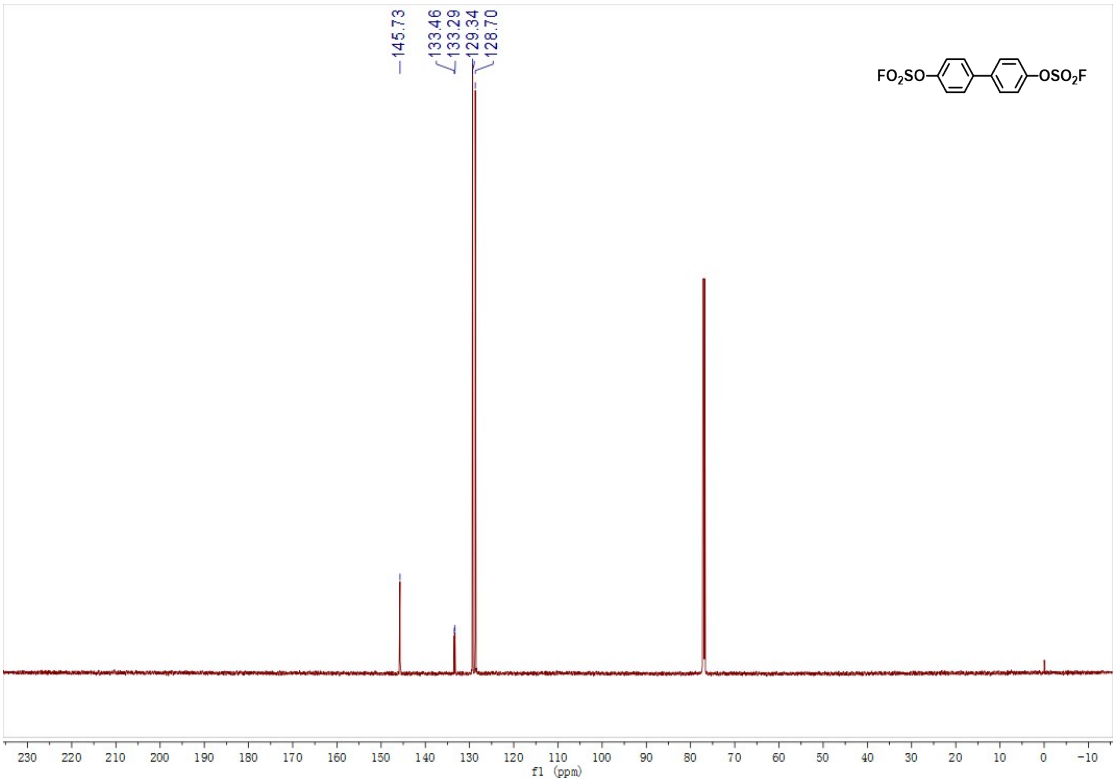

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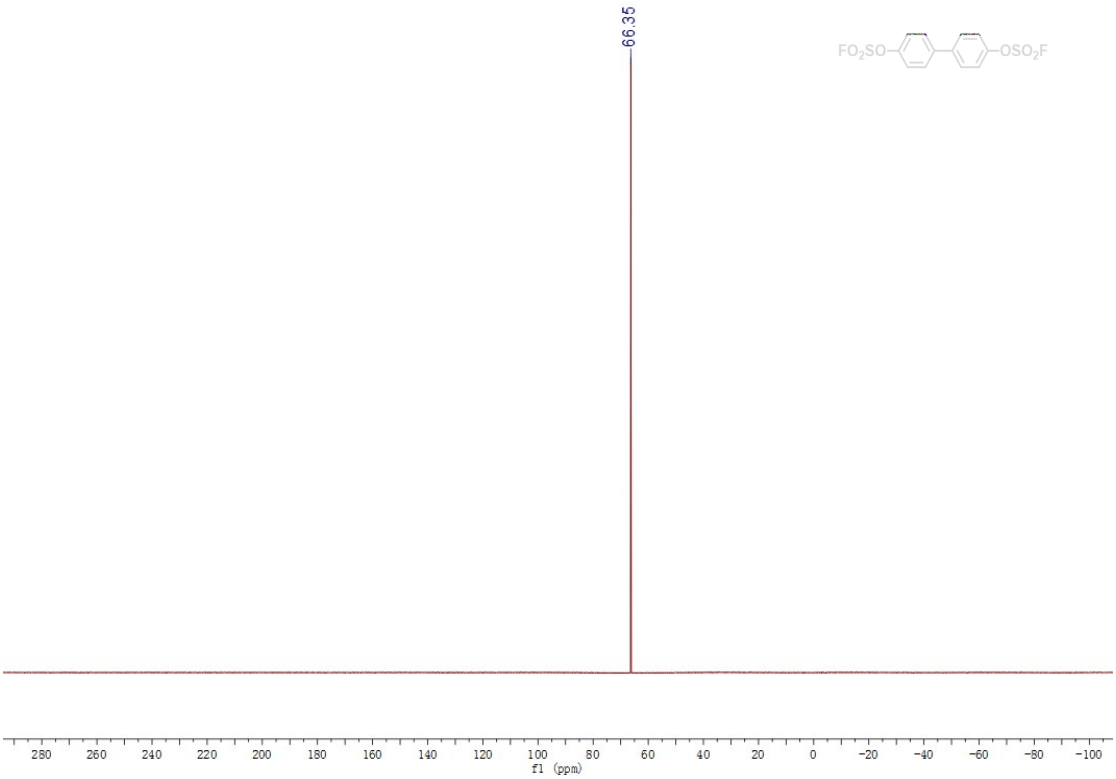

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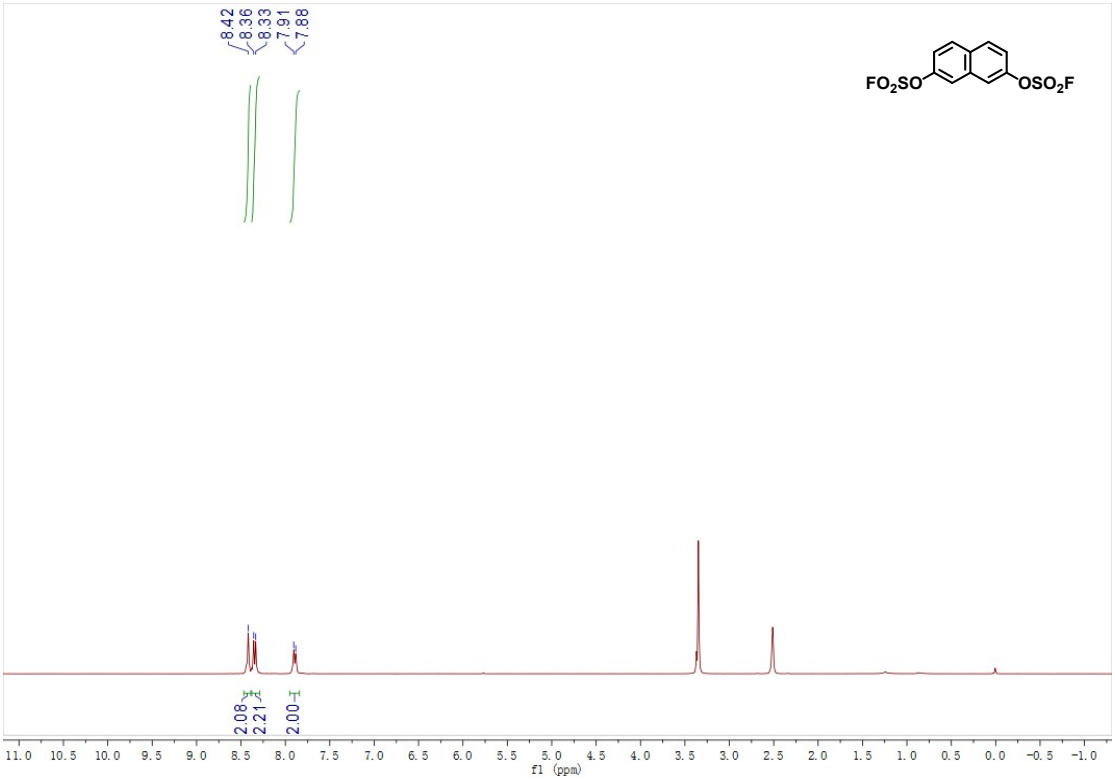

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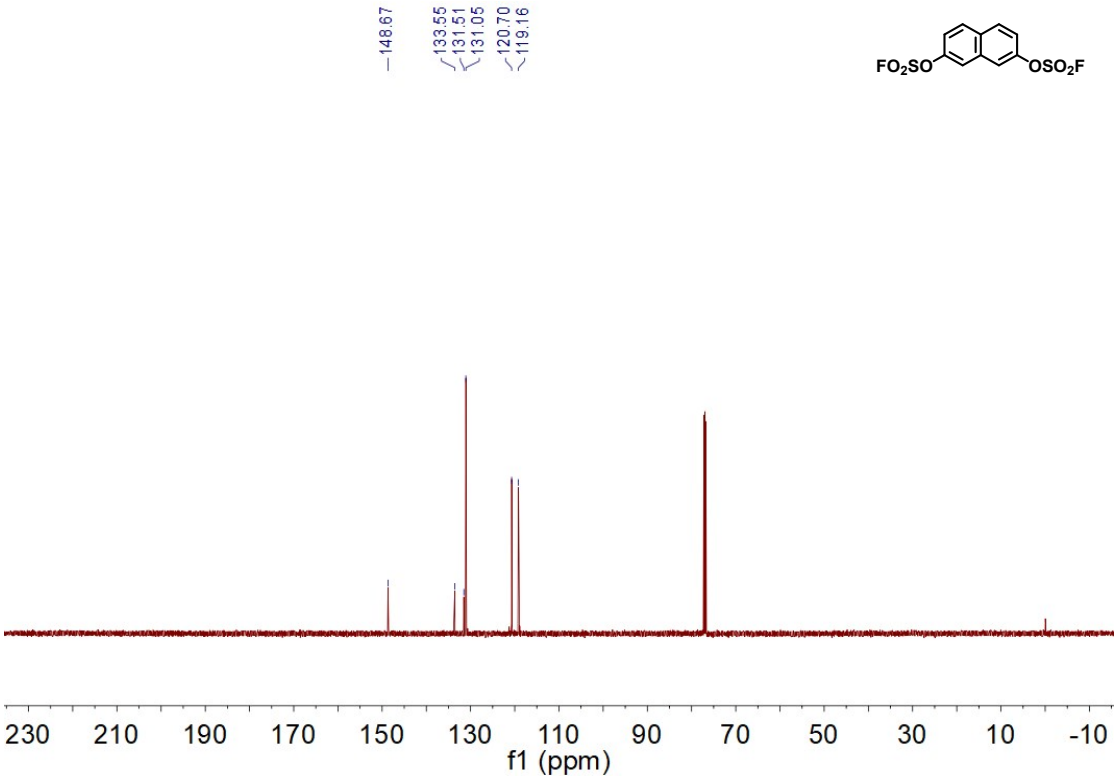
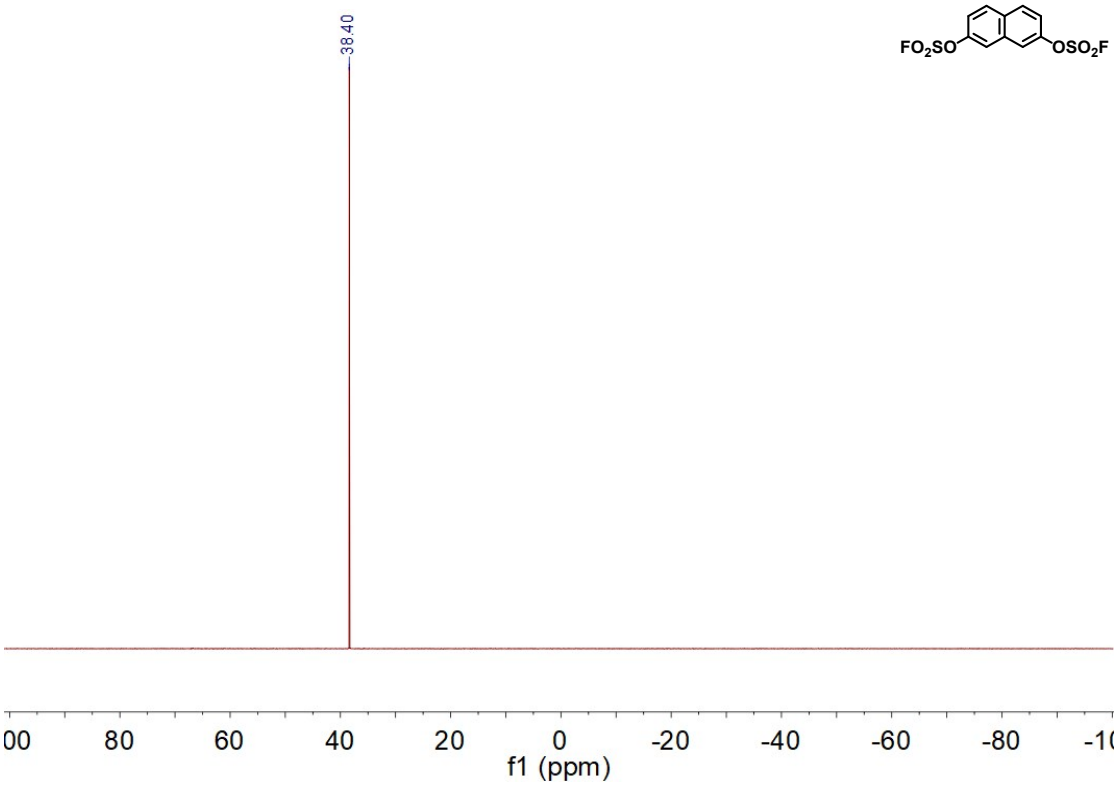
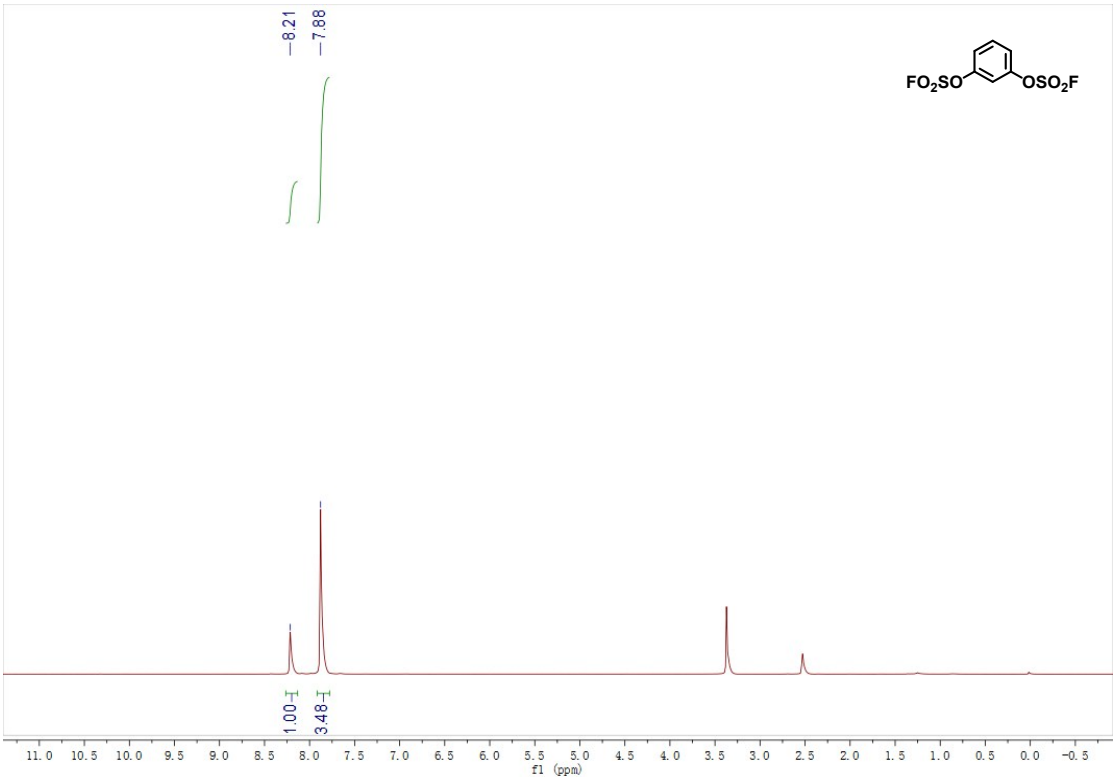


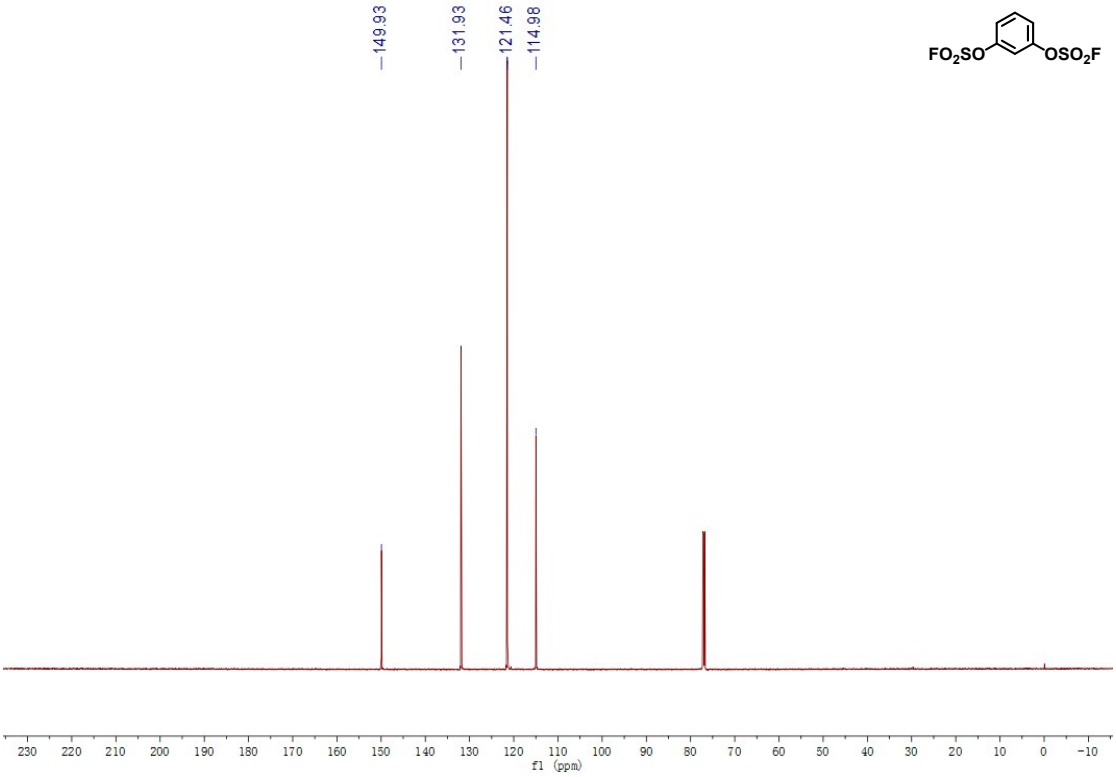
^{19}F NMR (O-2)



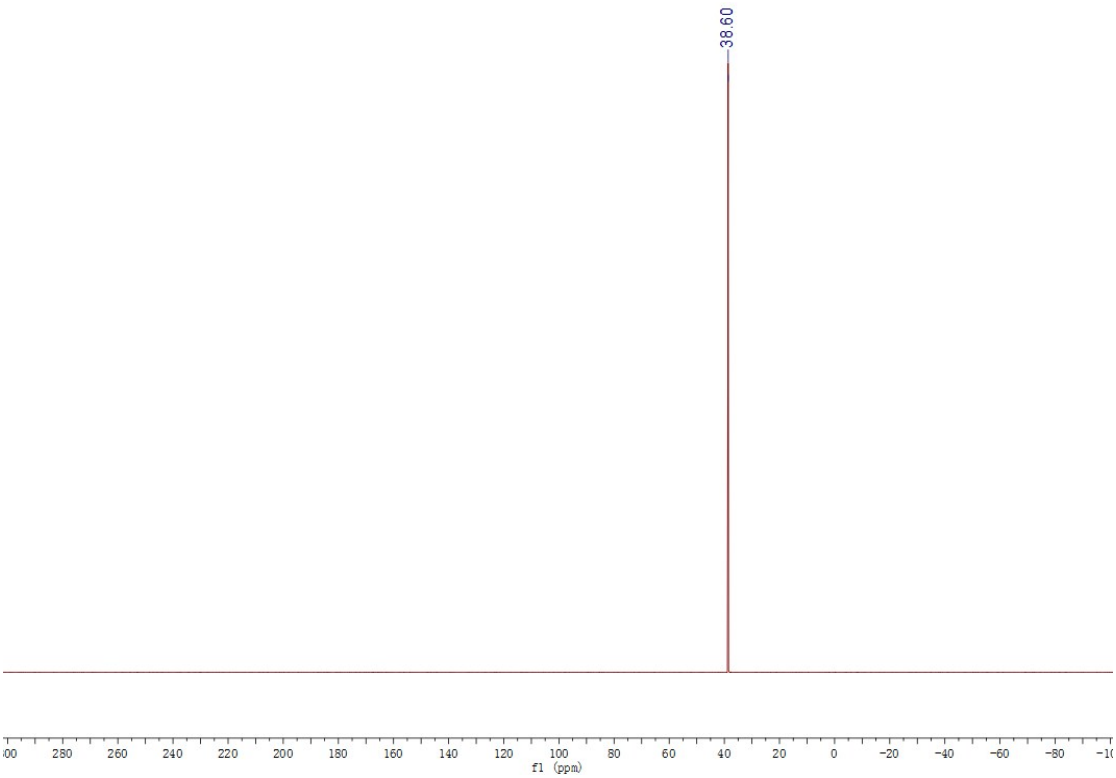
^{1}H NMR (O-3)



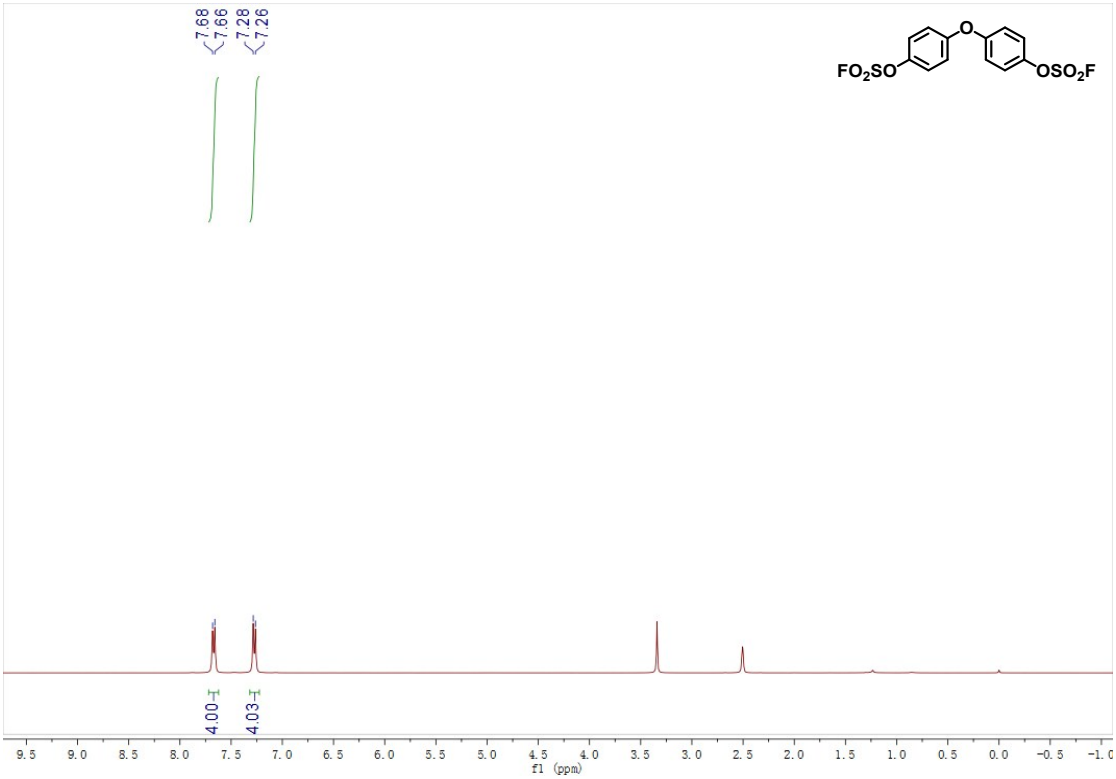
^{13}C NMR (O-3)



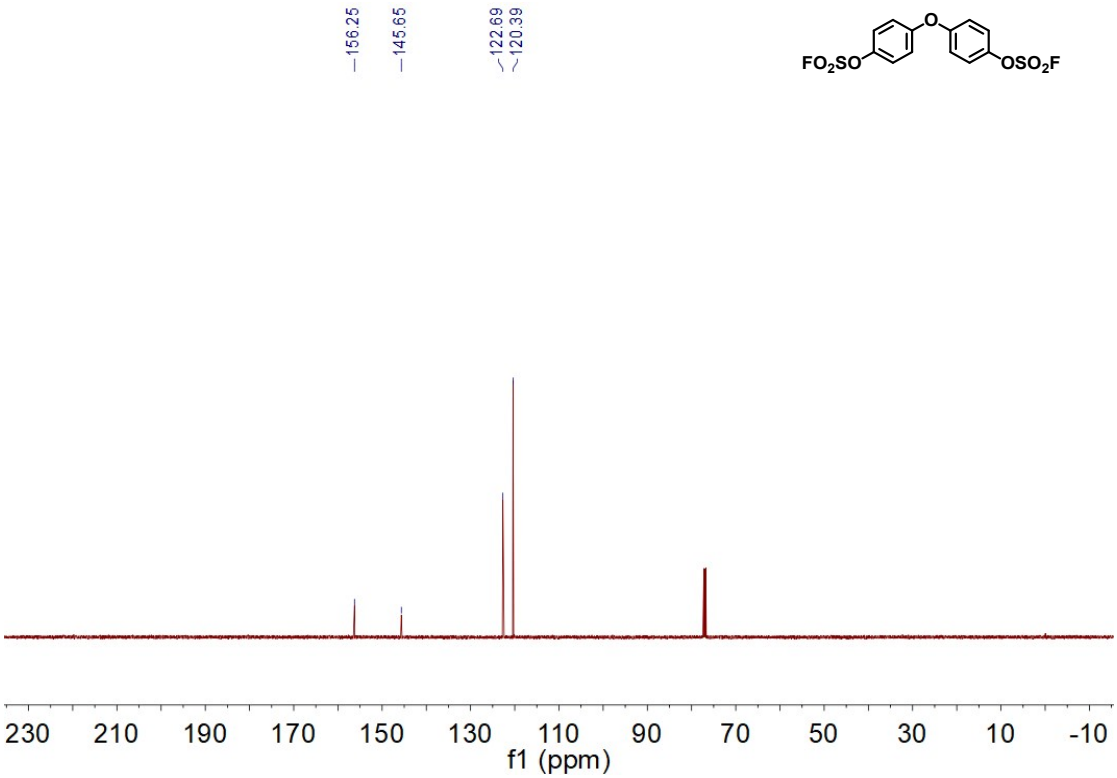
^{19}F NMR (O-3)



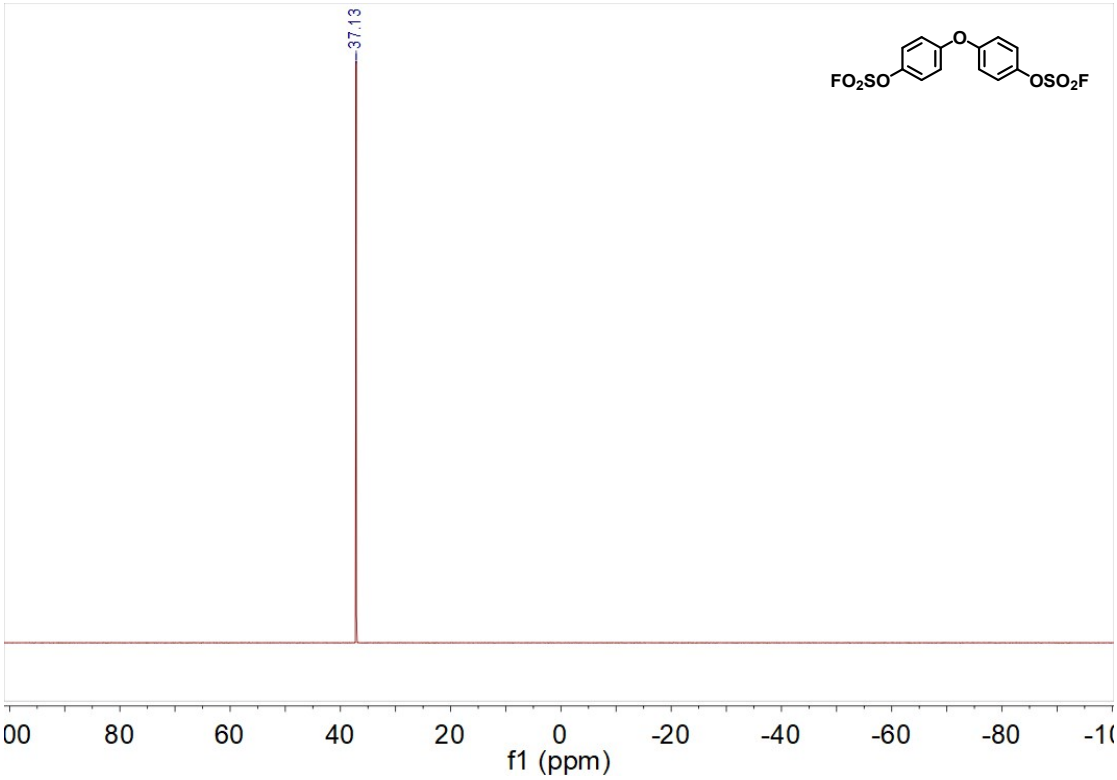
^{1}H NMR (O-4)



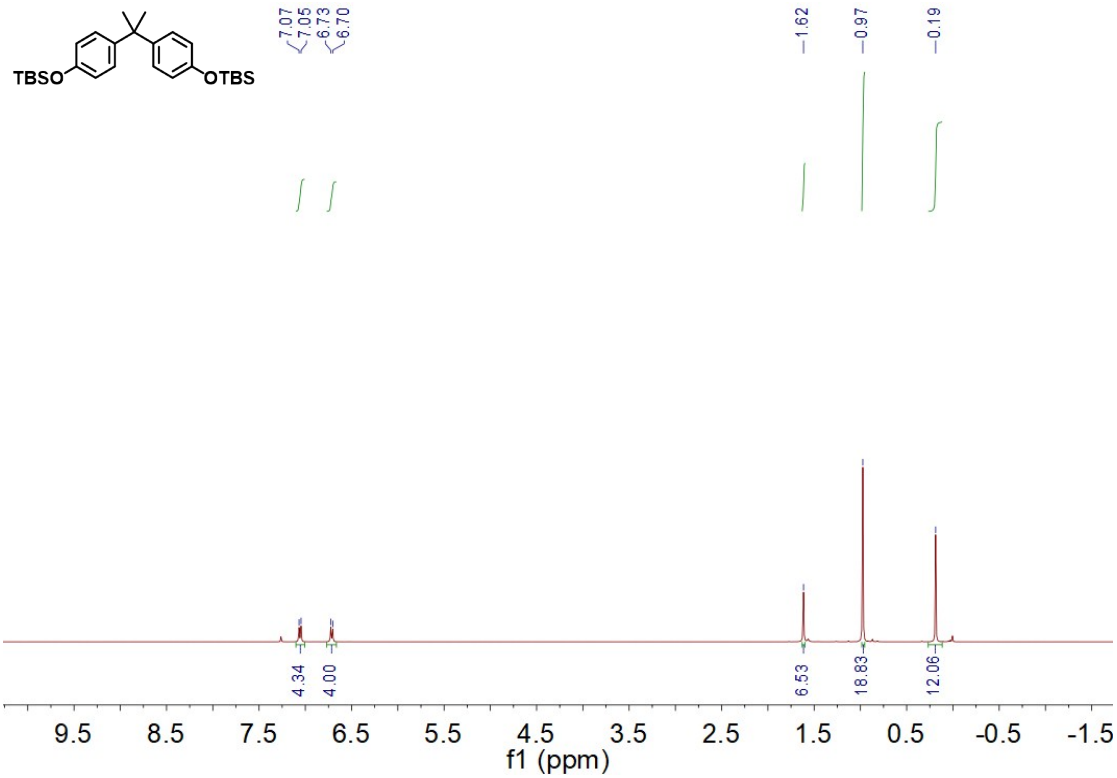
^{13}C NMR (O-4)



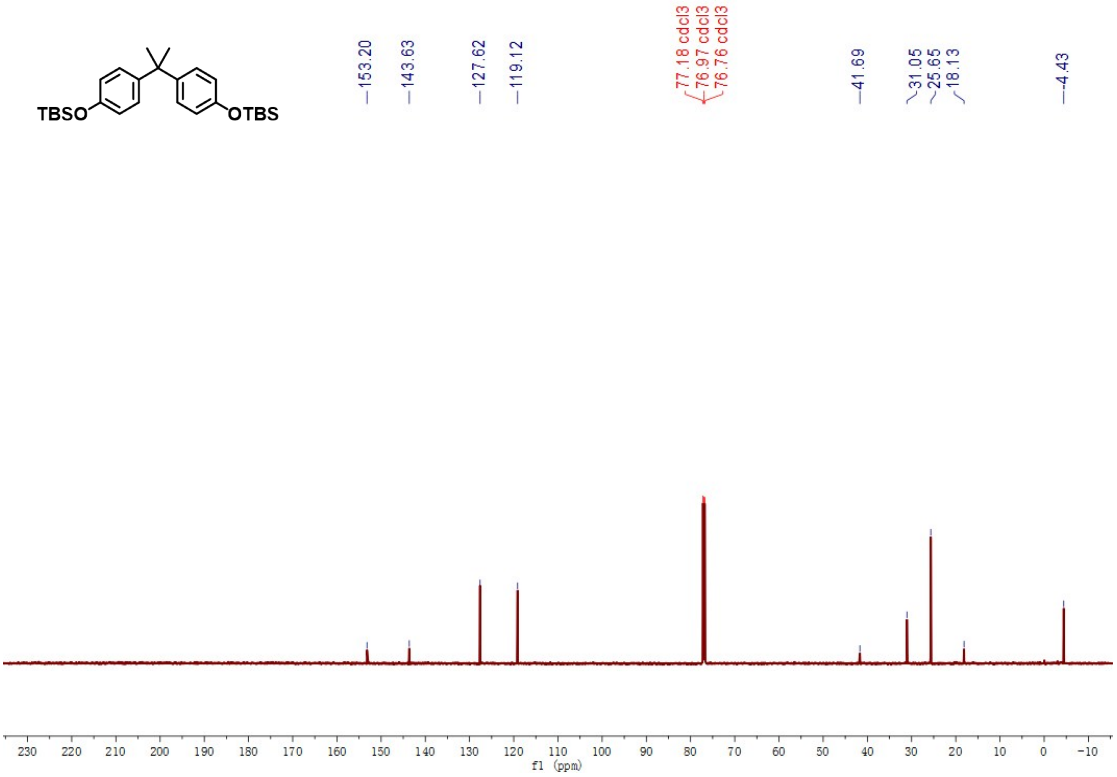
^{19}F NMR (O-4)



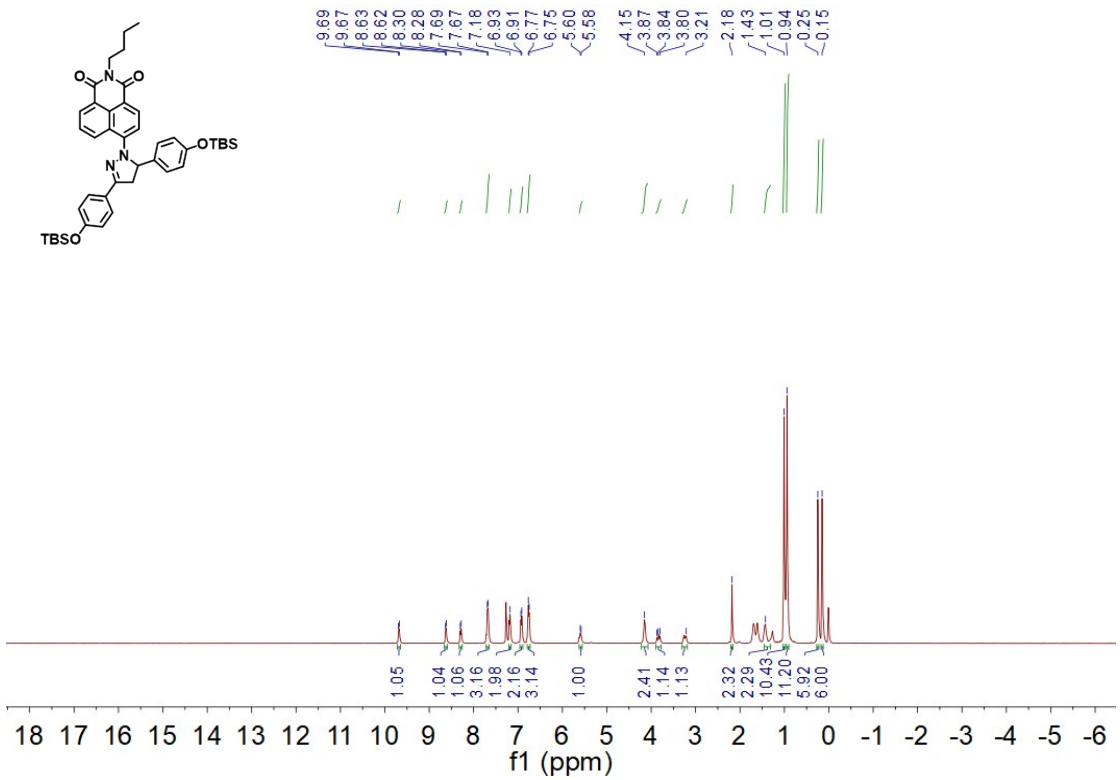
^{1}H NMR (1a)



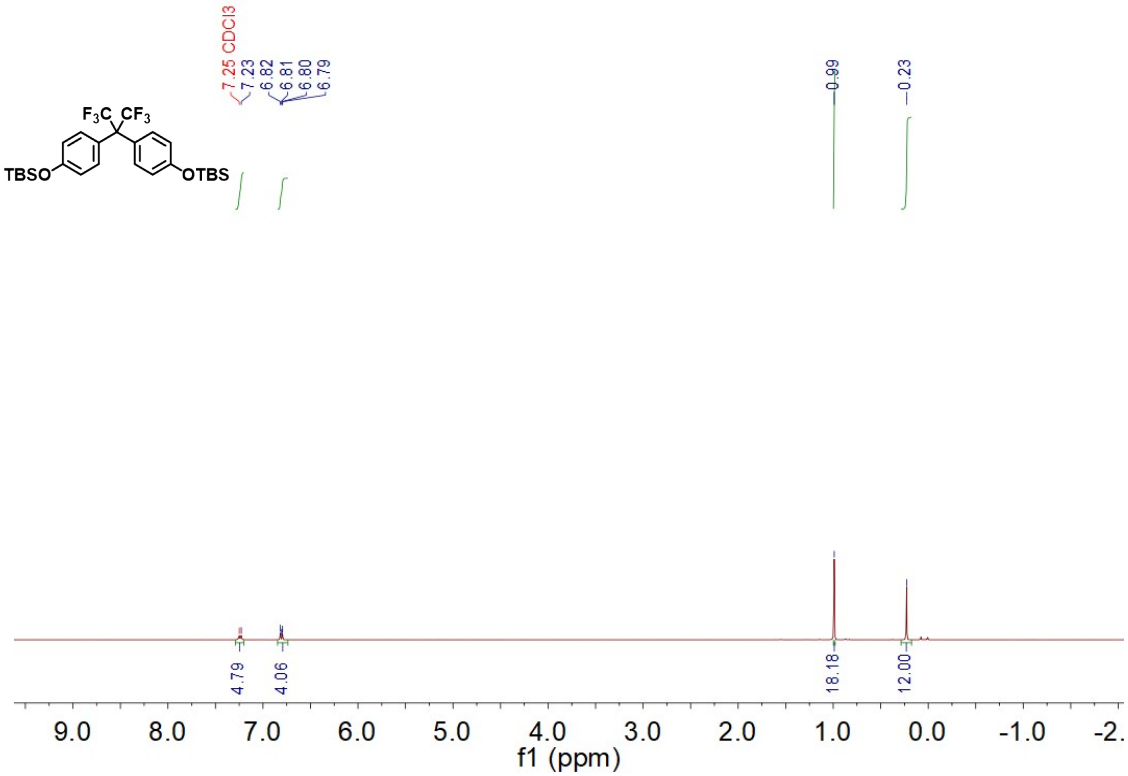
^{13}C NMR(1a)



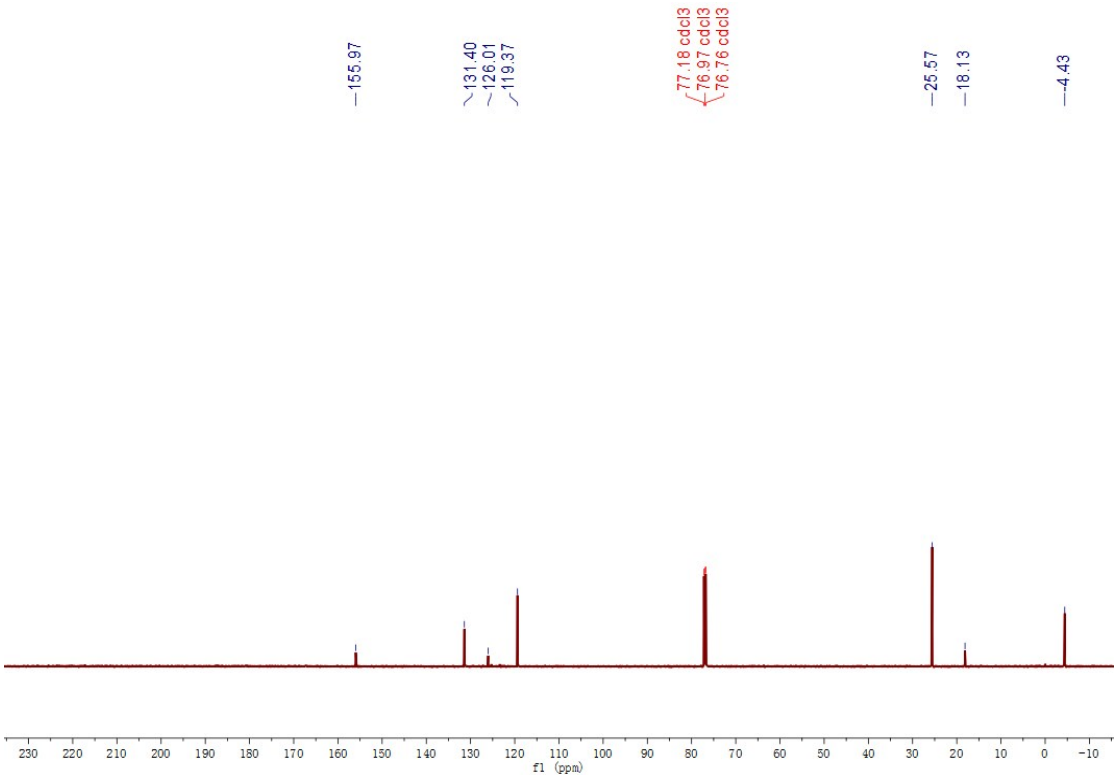
^{1}H NMR (1b)



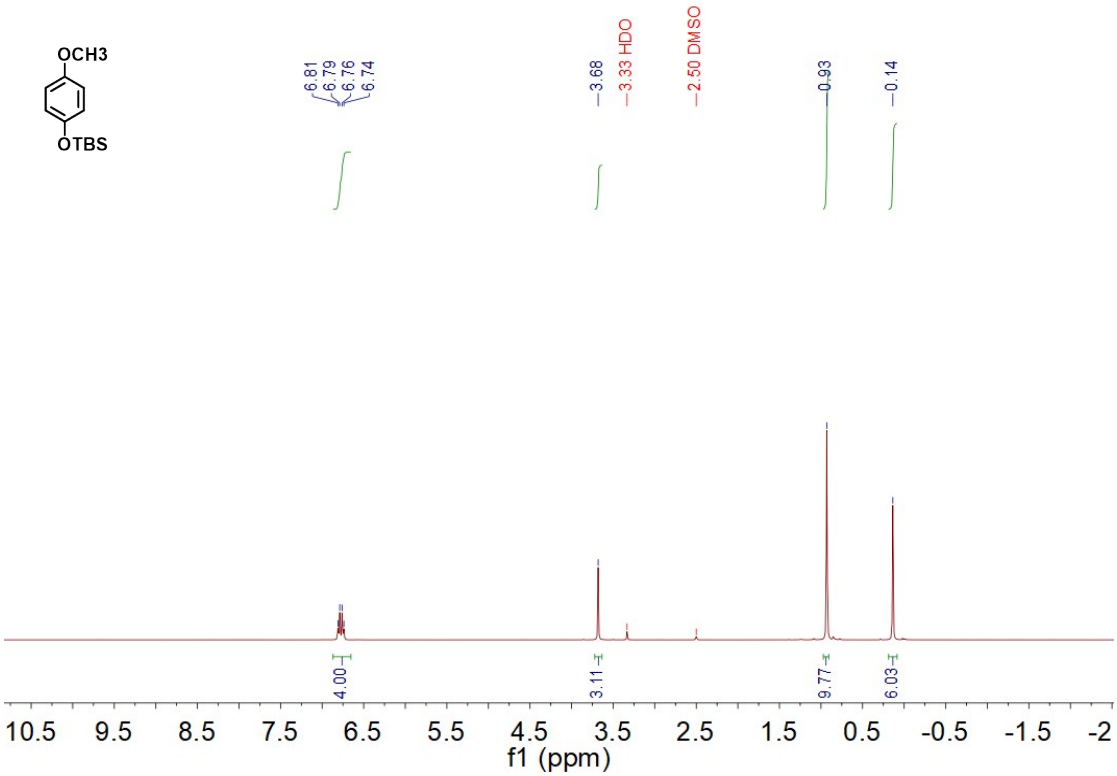
^{1}H NMR (1c)



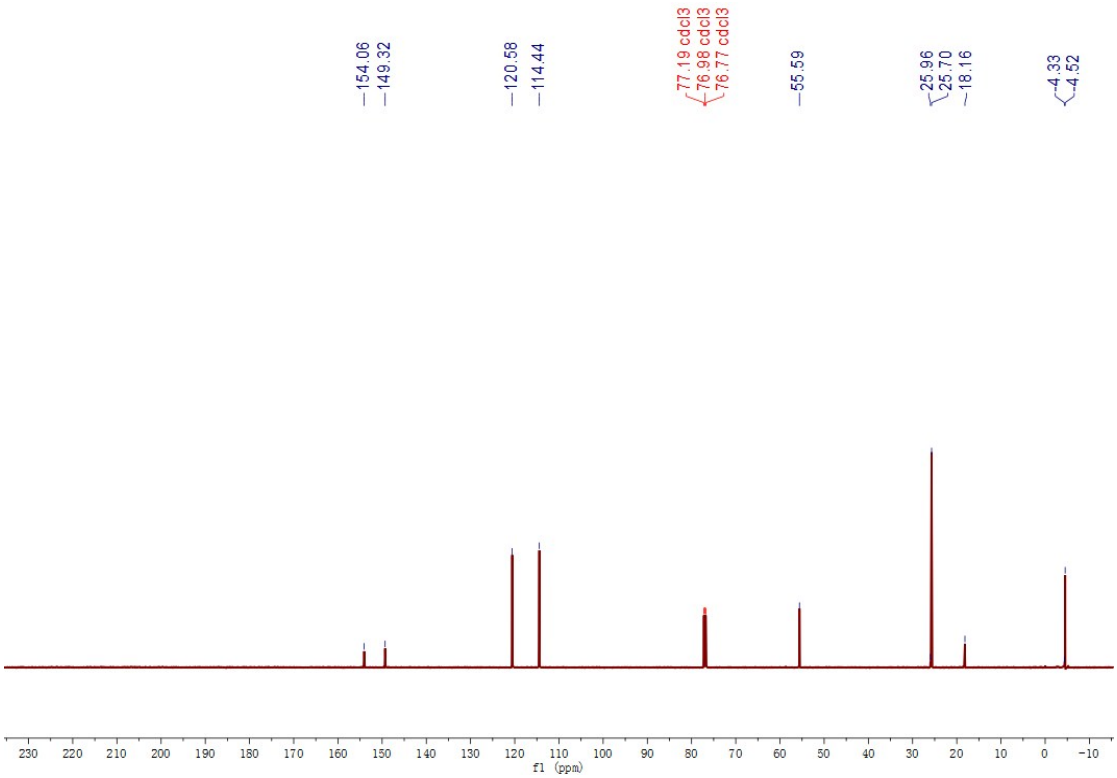
^{13}C NMR(1c)



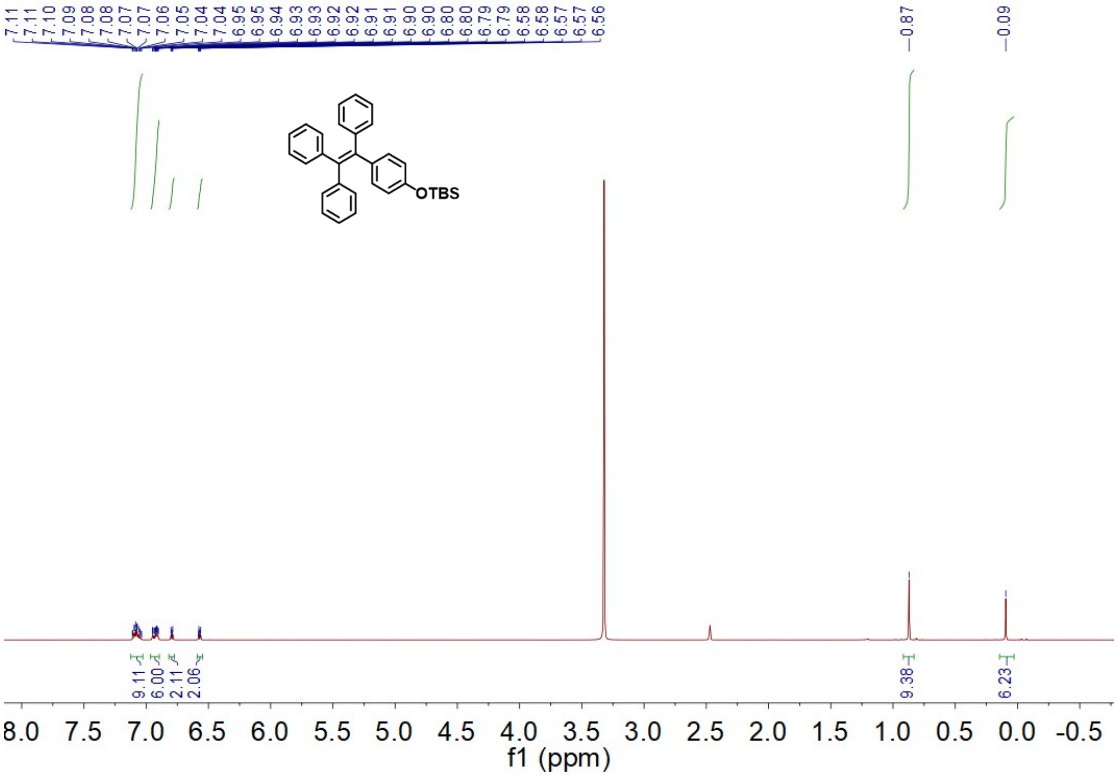
^{1}H NMR (TBMP-OTBS)



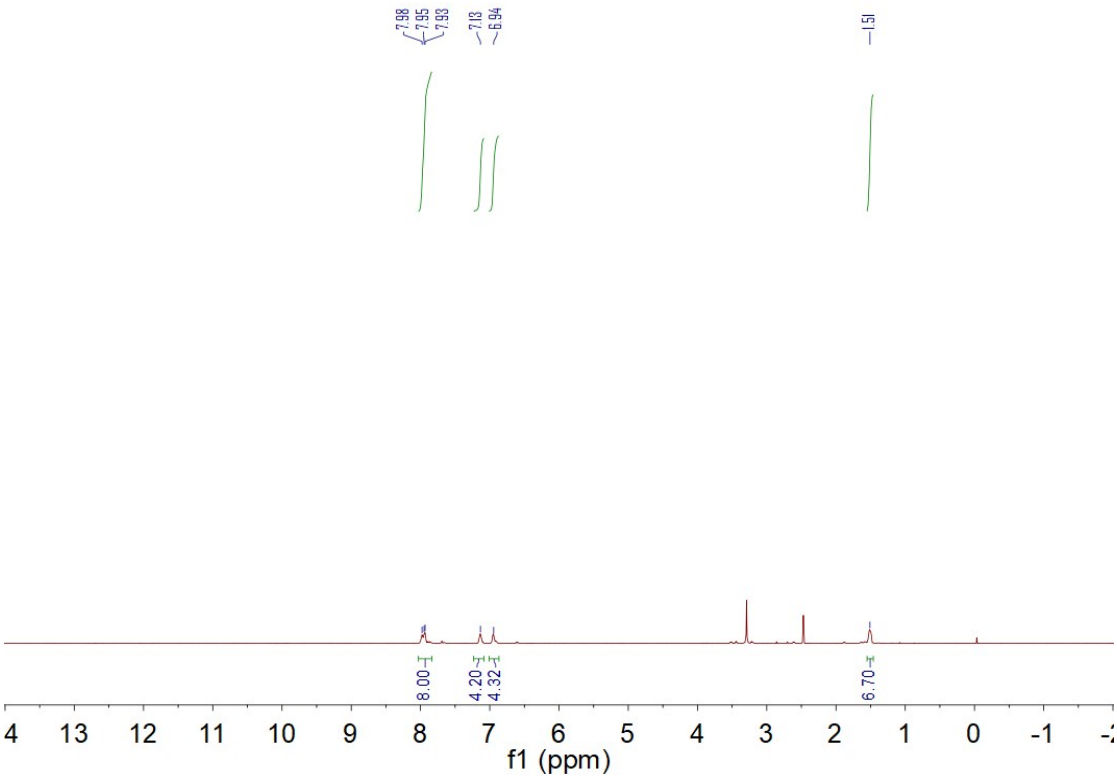
^{13}C NMR(TBMP-OTBS)



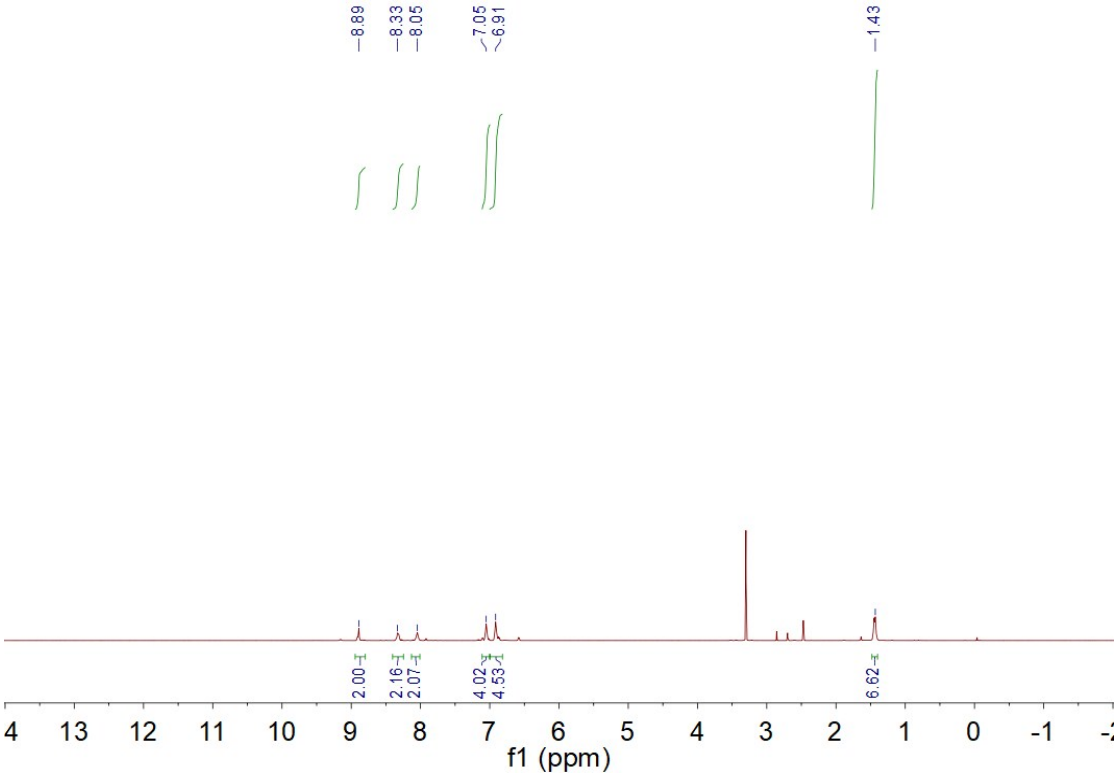
^{1}H NMR (TPE-OTBS)



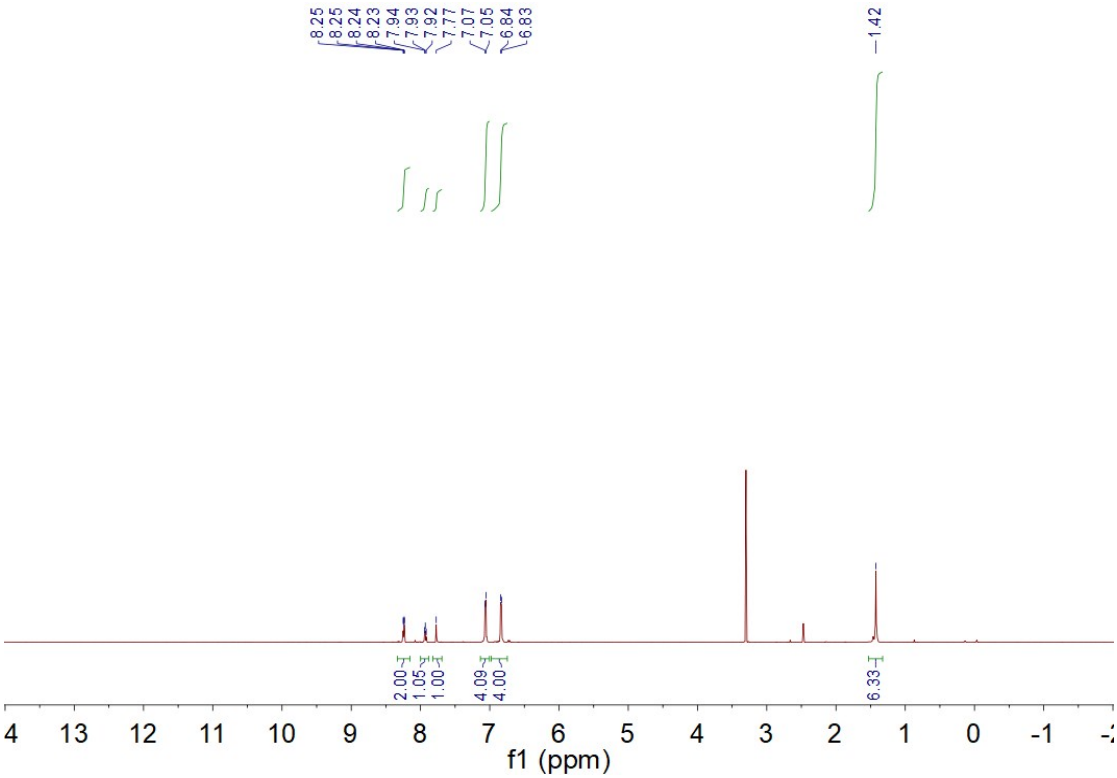
^{1}H NMR (PSFO1)



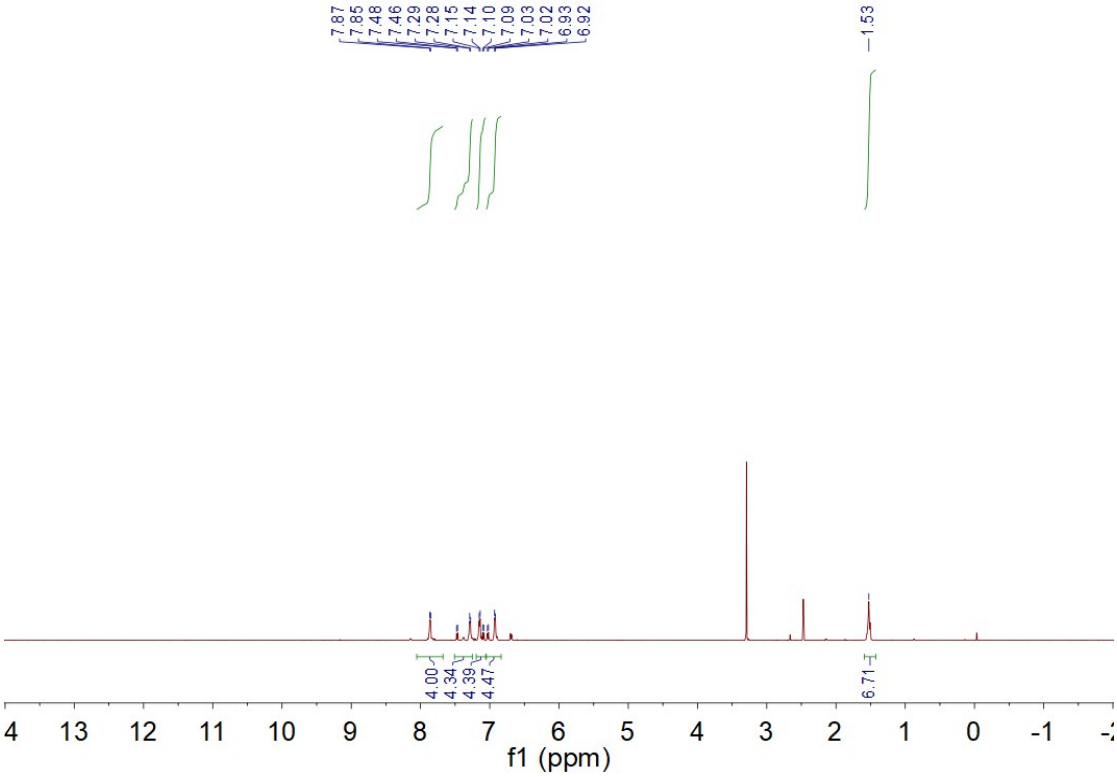
^{1}H NMR (PSFO2)



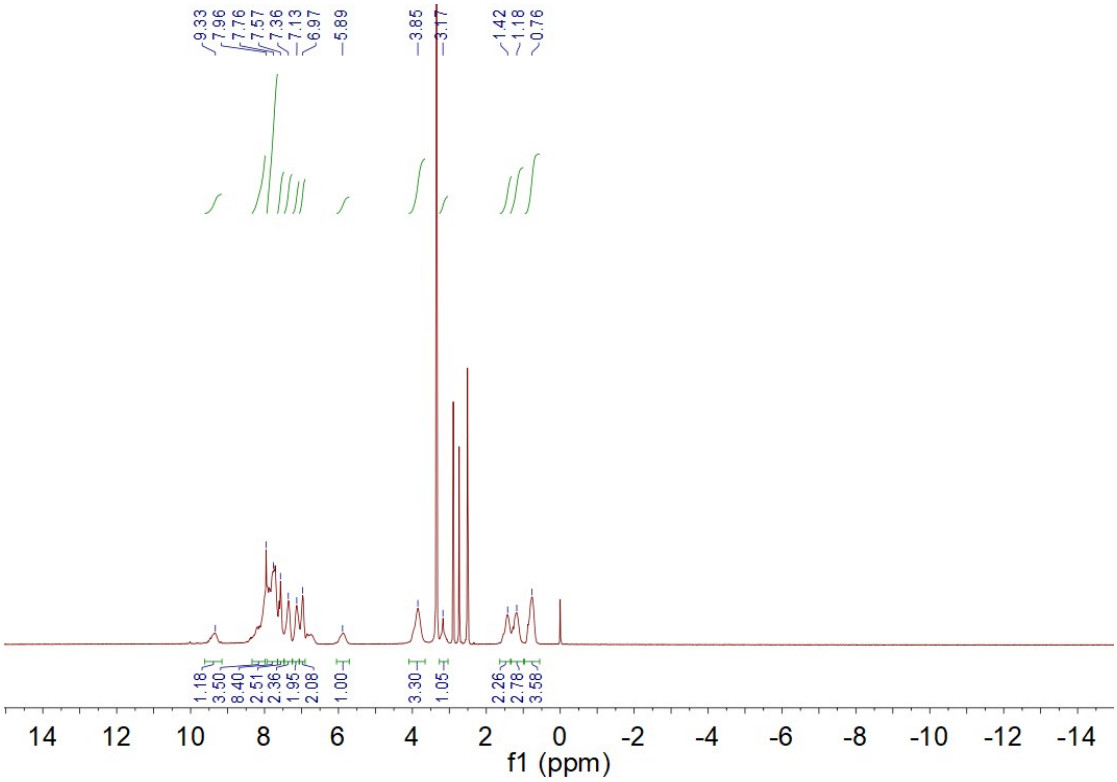
^{1}H NMR (PSFO3)


8.25
8.25
8.24
8.23
7.94
7.93
7.92
7.77
7.07
7.05
6.84
6.83
1.42
2.00
1.05
1.00
4.09
4.00
6.33
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

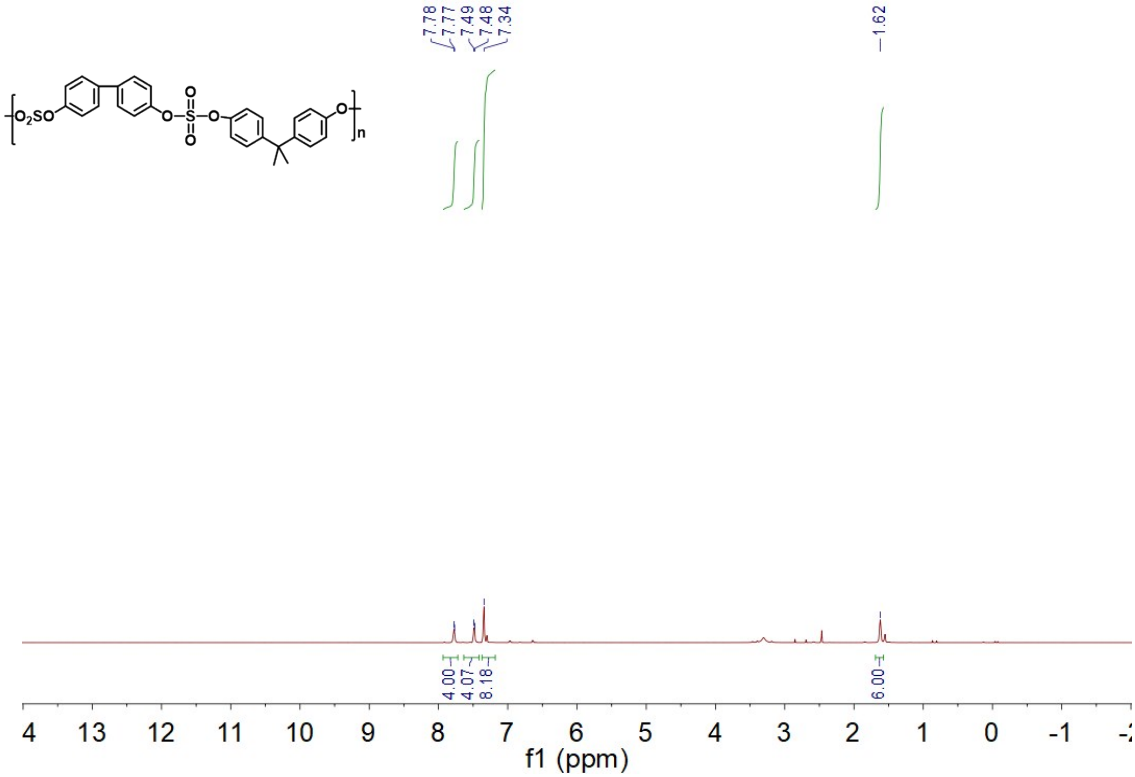
[1]H NMR (PSFO4)


7.87
7.85
7.48
7.46
7.29
7.28
7.15
7.14
7.10
7.09
7.03
7.02
6.93
6.92
1.53
4.00
4.34
4.39
4.47
6.71
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

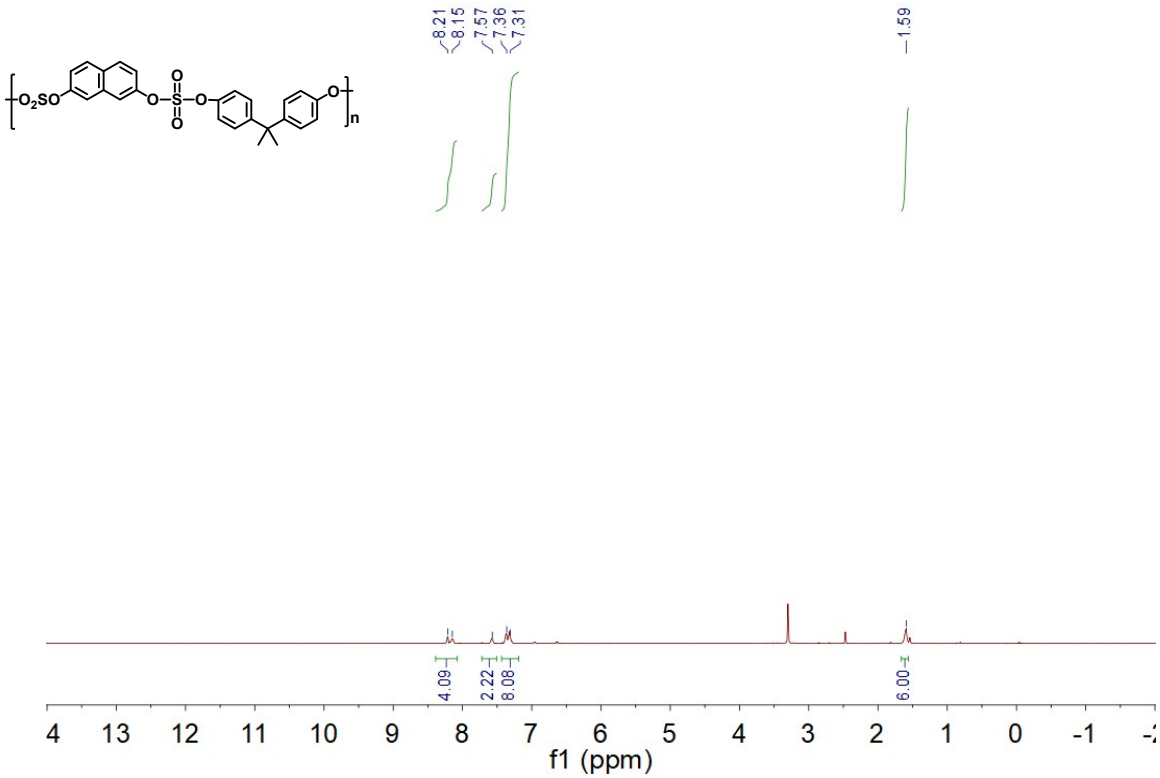
^{1}H NMR (PSFO1-TPP)



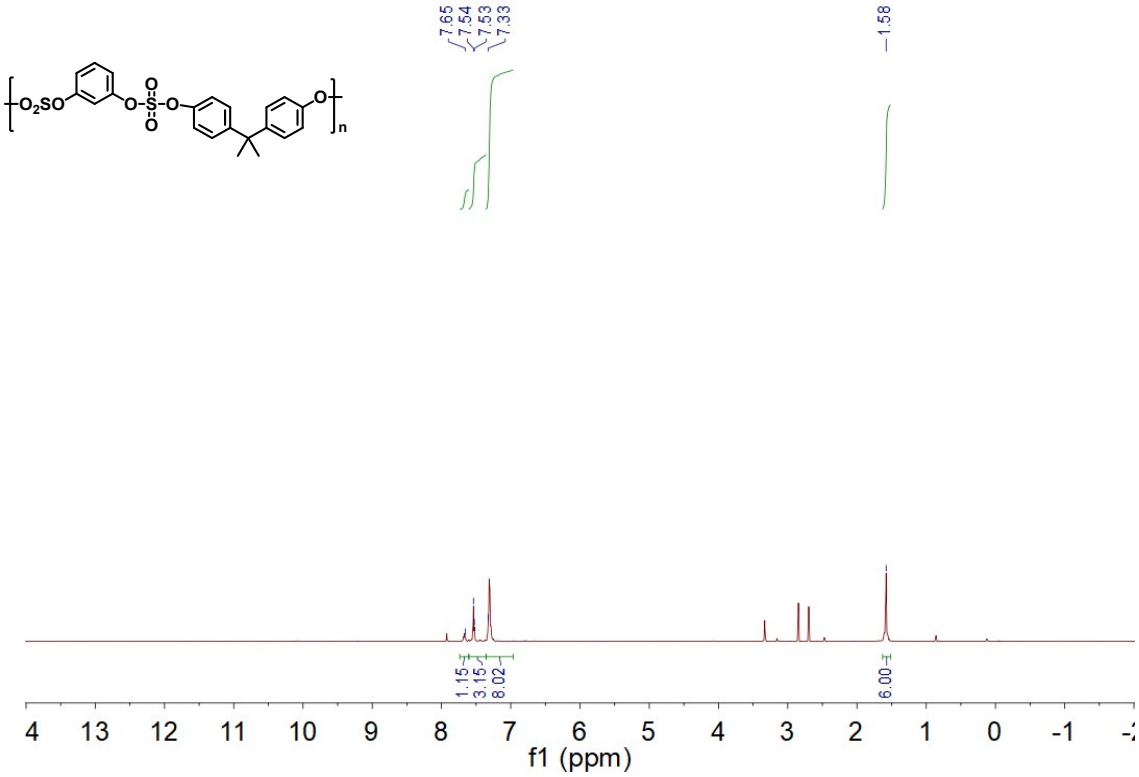
^{1}H NMR (PSFA1)



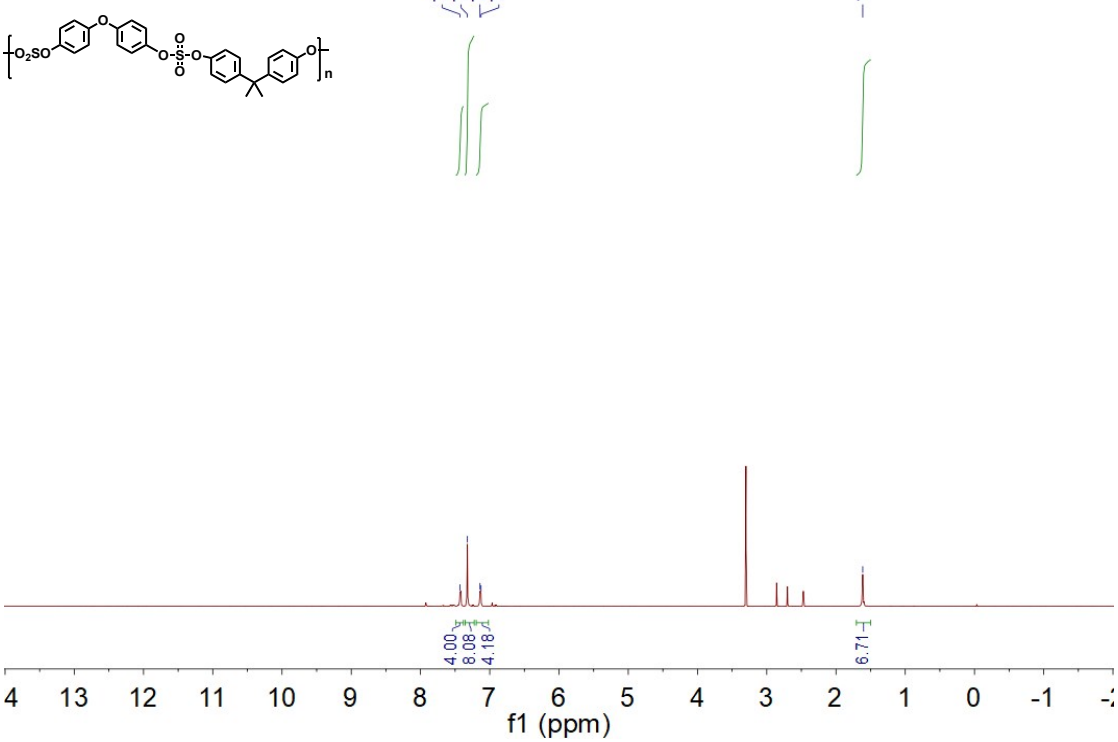
^{1}H NMR (PSFA2)



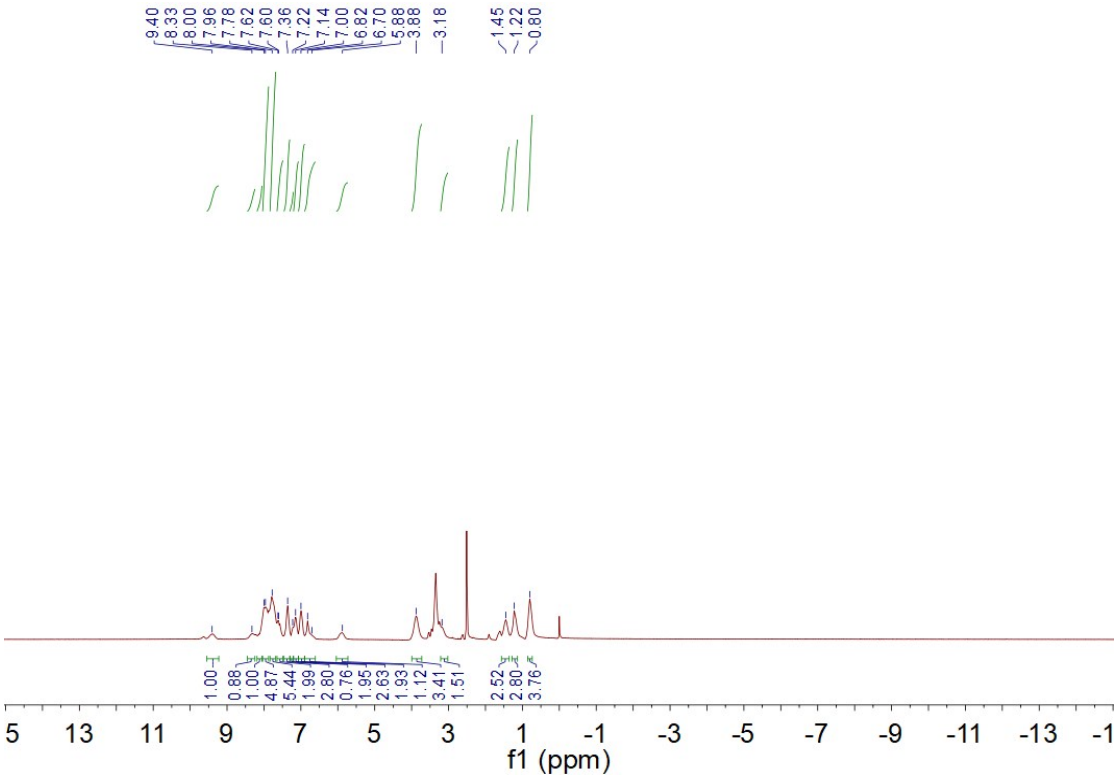
^{1}H NMR (PSFA3)



^{1}H NMR (PSFA4)

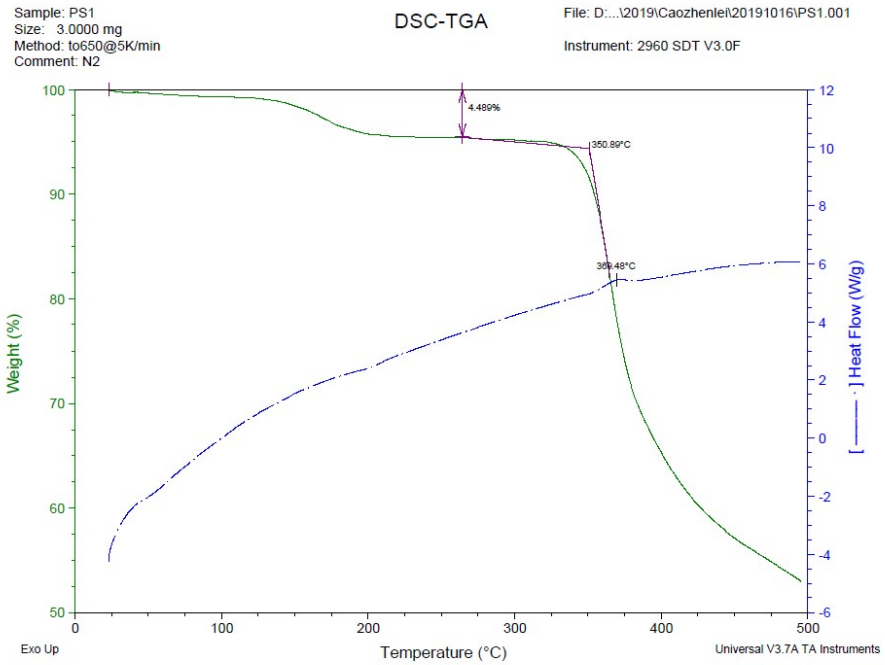


^{1}H NMR (PSFO1-TPP-CF_3)

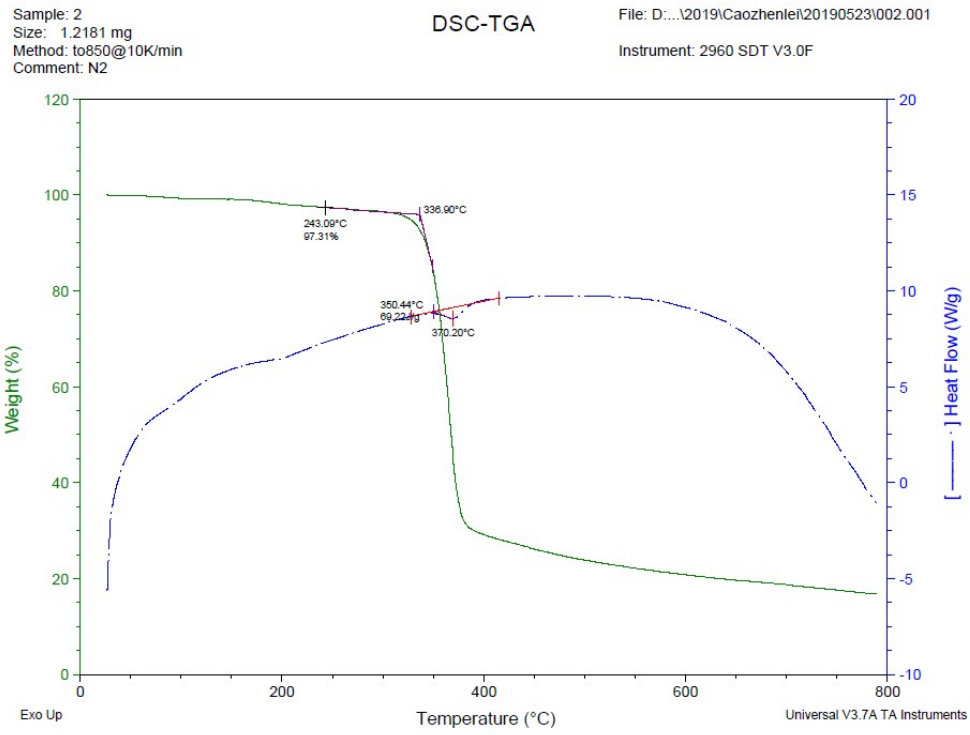


Thermal gravimetric analysis (TGA) of Polysulfonates and polysulfates

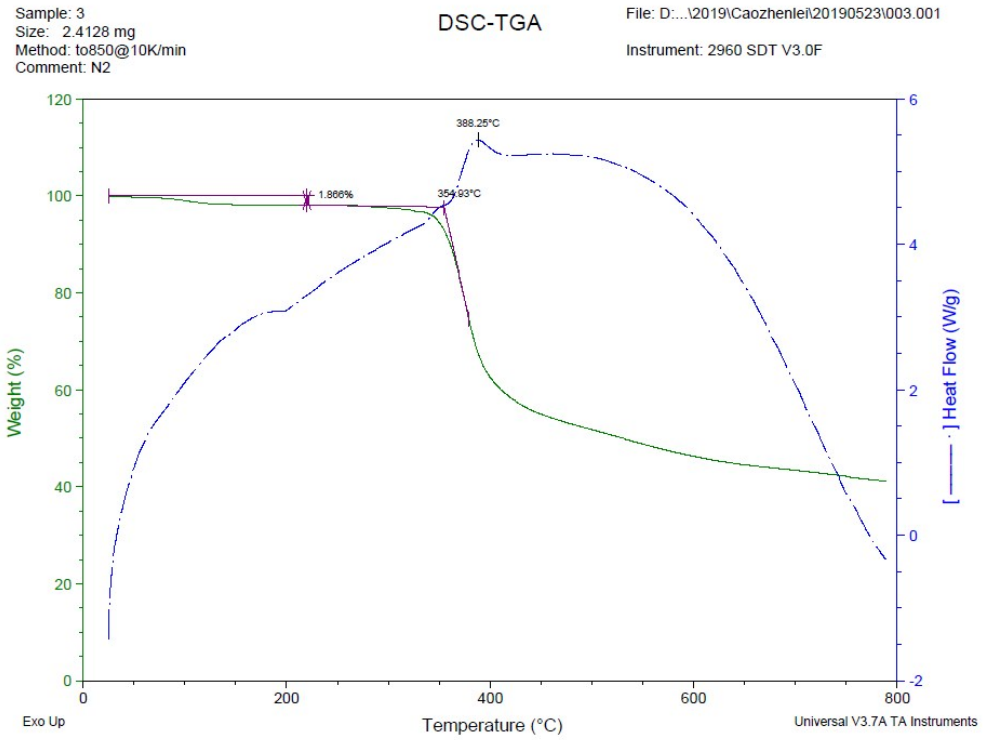
Thermal gravimetric analysis (TGA) of PSFO1



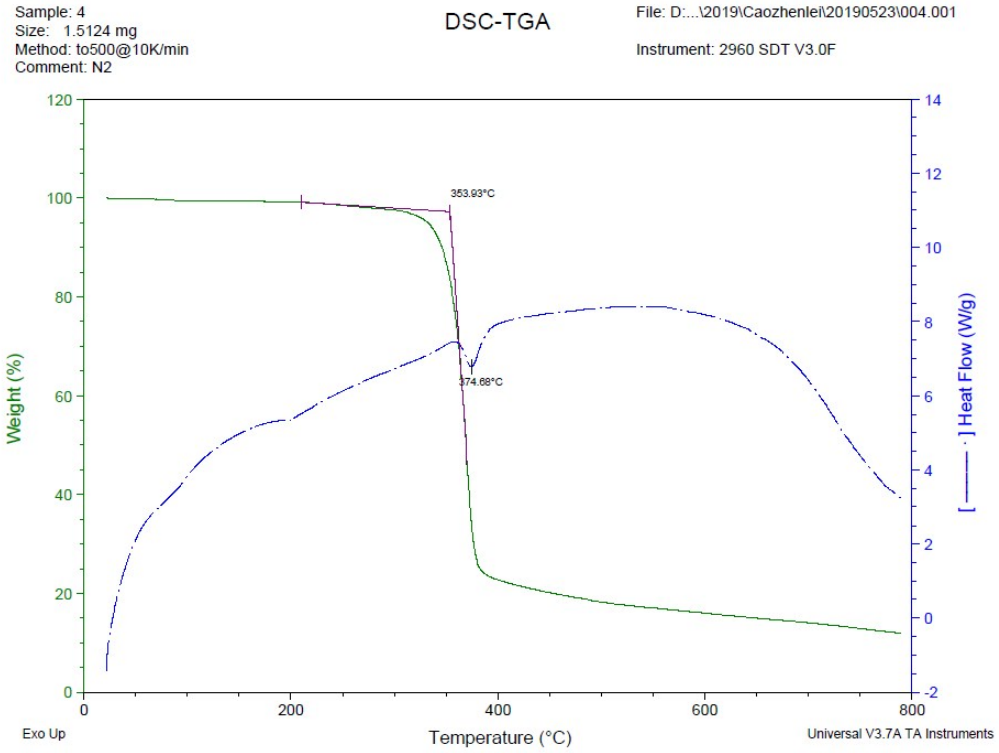
Thermal gravimetric analysis (TGA) of PSFO2



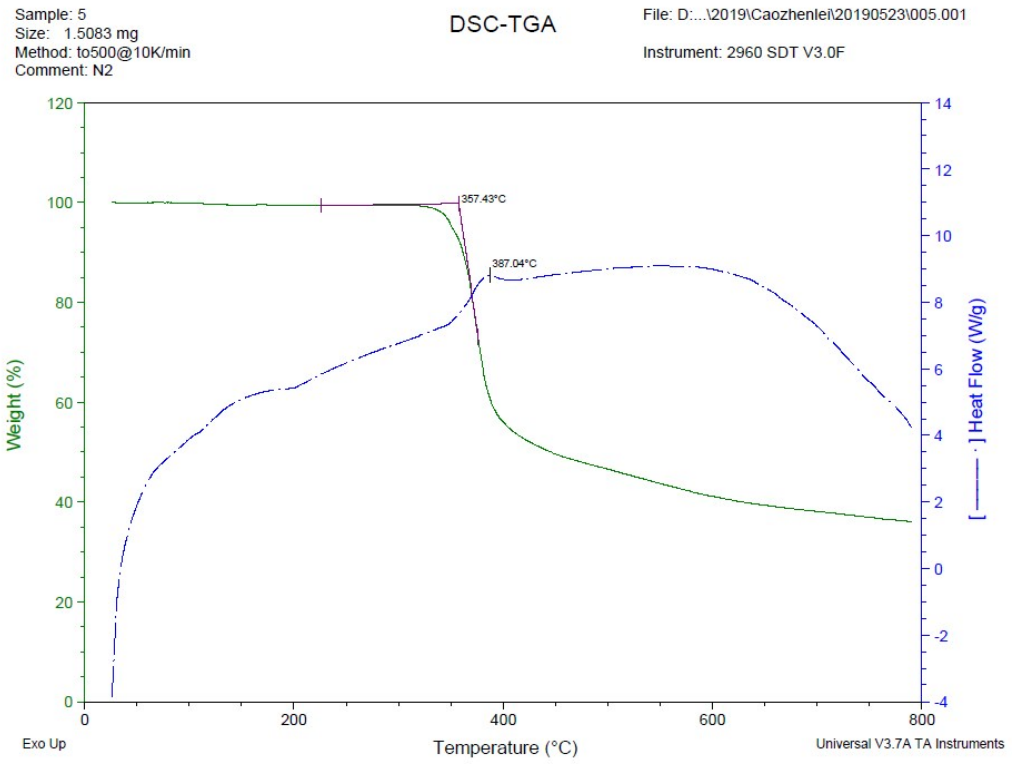
Thermal gravimetric analysis (TGA) of PSFO3



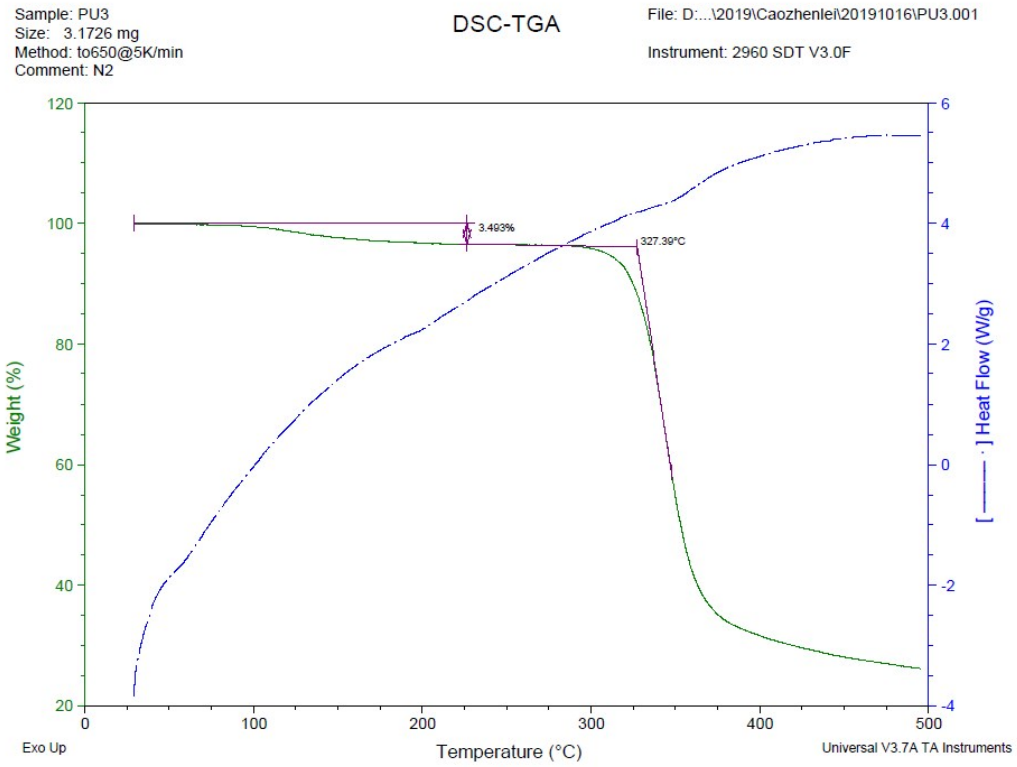
Thermal gravimetric analysis (TGA) of PSFO4



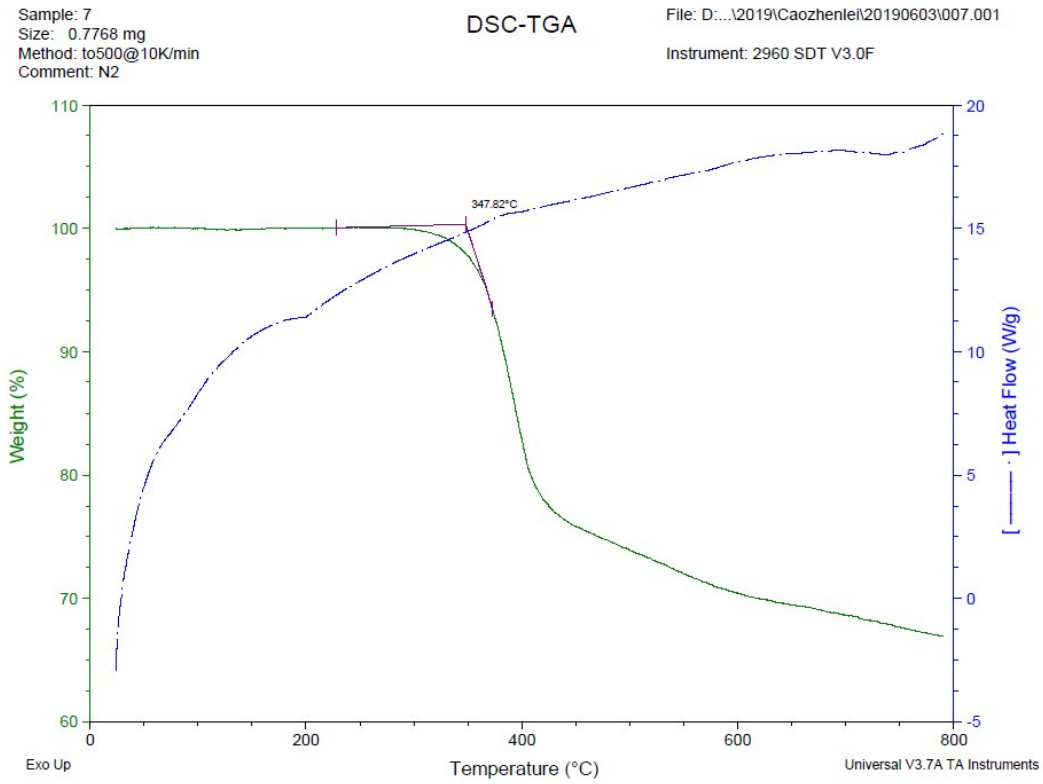
Thermal gravimetric analysis (TGA) of PSFA1



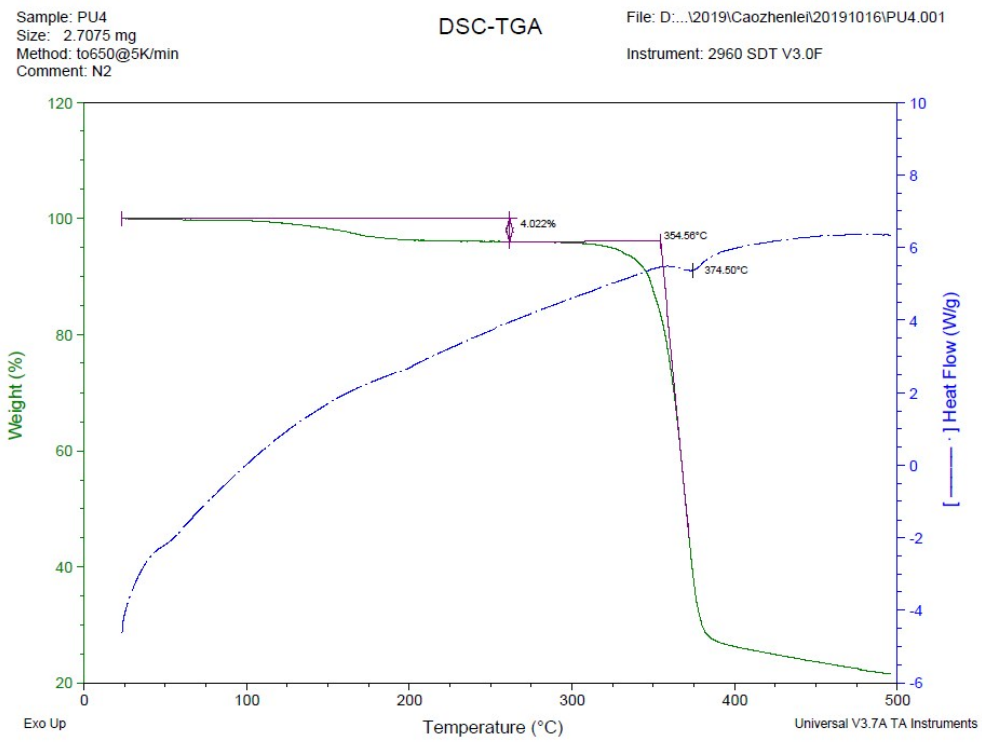
Thermal gravimetric analysis (TGA) of PSFA2



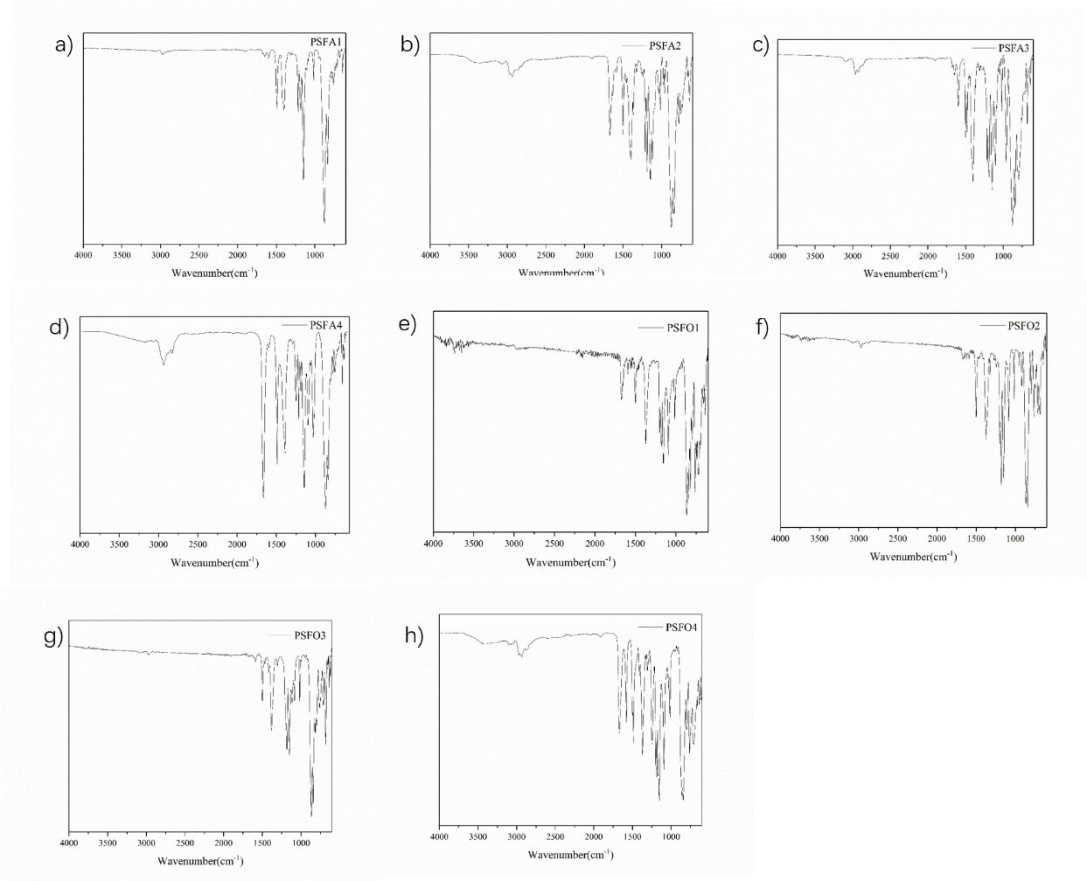
Thermal gravimetric analysis (TGA) of PSFA3



Thermal gravimetric analysis (TGA) of PSFA4



IR Spectroscopic Analysis

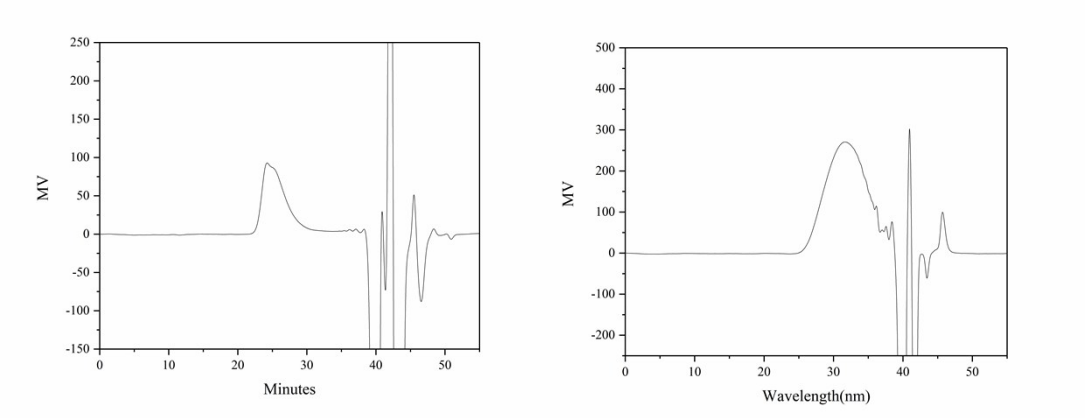


The IR spectra of (a)PSFA1, (b)PSFA2, (c)PSFA3, (d) PSFA4, (e)PSFO1, (f) PSFO2, (g)PSFO3, (h)PSFO4

GPC Results

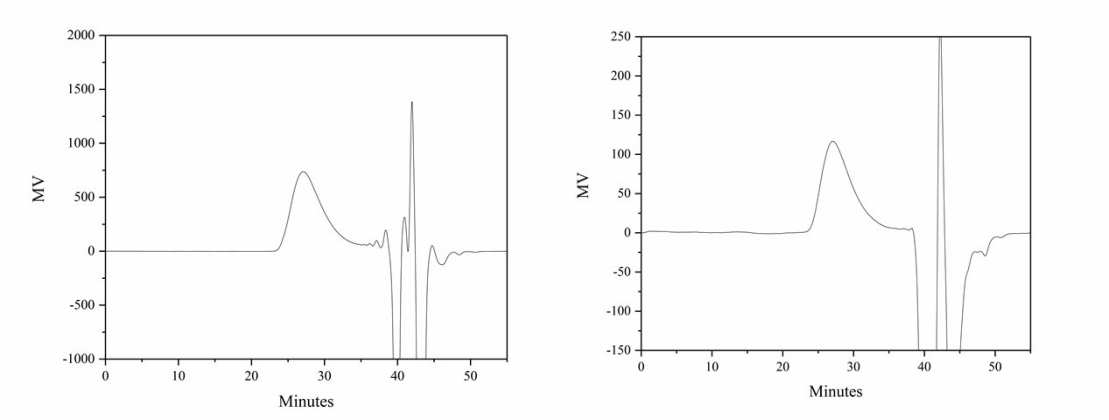
GPC trace of the PSFO1.

Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFO1**	24.250	73659	105266	141924	139951	1.429
C2	**PSFO1**	31.597	13415	17730	15970	23037	1.322



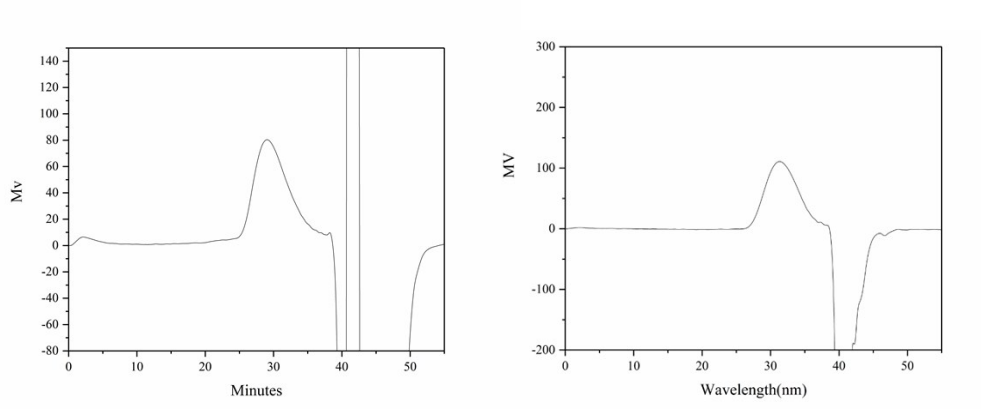
GPC trace of the PSFO2.

Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFO2**	27.081	31920	47095	49739	65284	1.475
C2	**PSFO2**	28.289	23867	36447	38932	50939	1.527



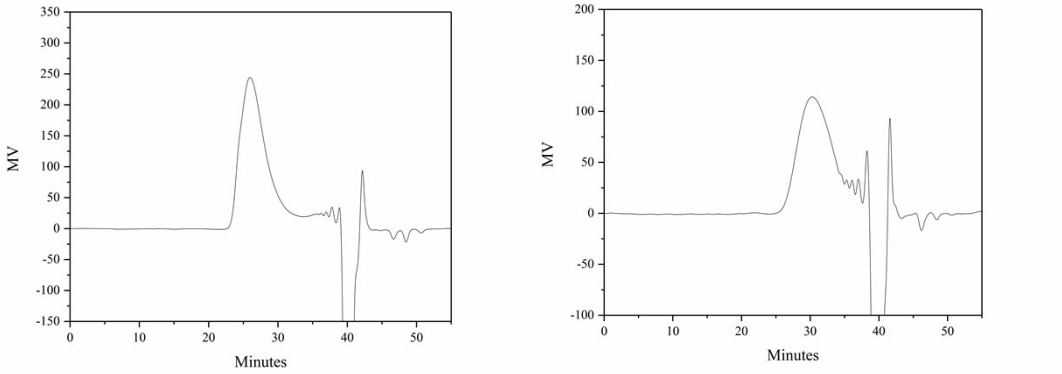
GPC trace of the PSFO3.

Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFO3**	29.025	20737	30536	30989	43374	1.472
C2	**PSFO3**	31.700	12764	16430	15433	20729	1.287



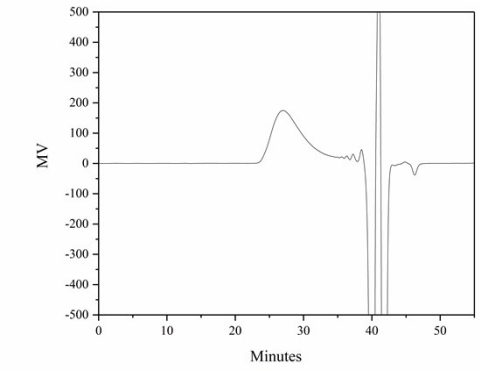
GPC trace of the PSFO4.

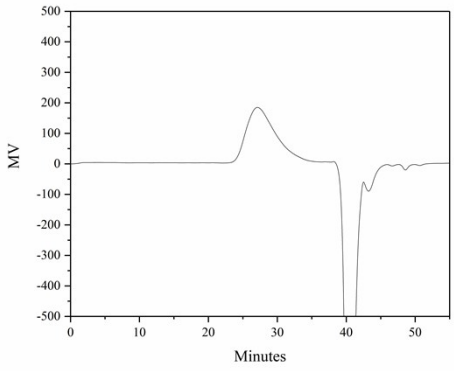
Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFO3**	25.094	49333	74861	77864	105185	1.517
C2	**PSFO3**	30.217	17070	21540	20616	27332	1.262



GPC trace of the PSFA1.

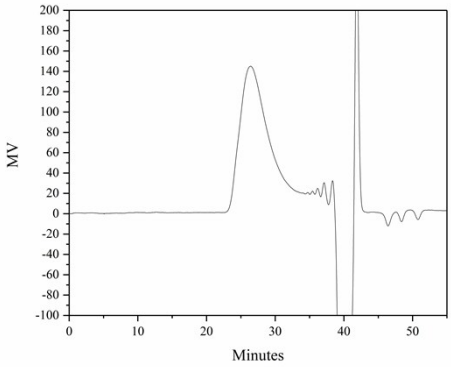
Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFA1**	26.098	38640	61583	66936	89082	1.594
C2	**PSFA1**	27.046	33738	54162	57977	78818	1.605





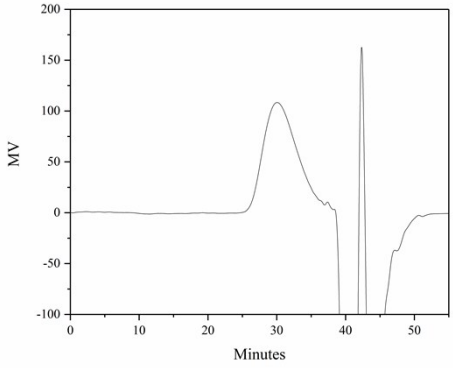
GPC trace of the PSFA2.

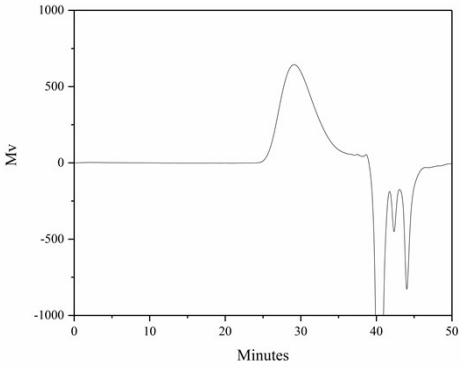
Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFA2**	28.036	21915	29542	30906	38401	1.348
C2	**PSFA2**	28.242	25021	37506	39489	52835	1.499



GPC trace of the PSFA3.

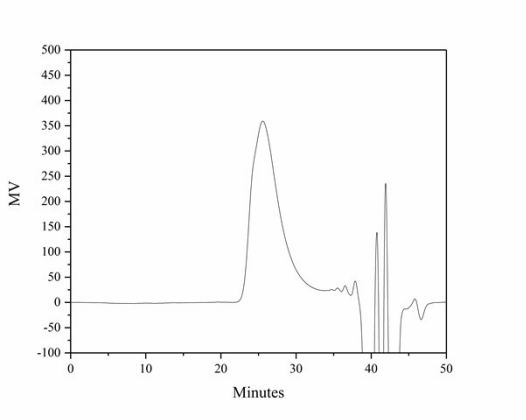
Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFA3**	30.016	17151	24044	24070	32315	1.402
C2	**PSFA3**	29.105	20859	29644	29770	39855	1.421





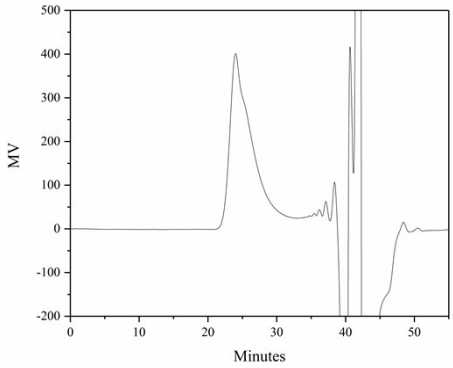
GPC trace of the PSFA4.

Catalyst	Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
C1	**PSFA3**	25.941	46290	46290	73356	94528	1.494
C2	**PSFA3**	25.569	55821	81315	82461	110280	1.457

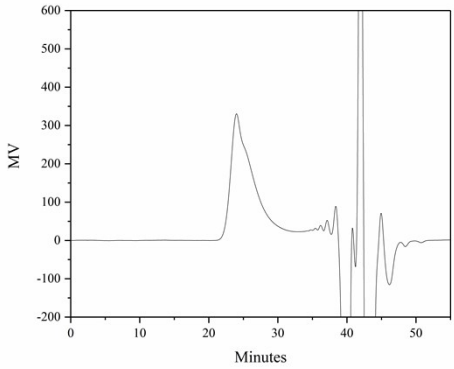


Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
	24.250	73659	105266	141924	139951	1.429

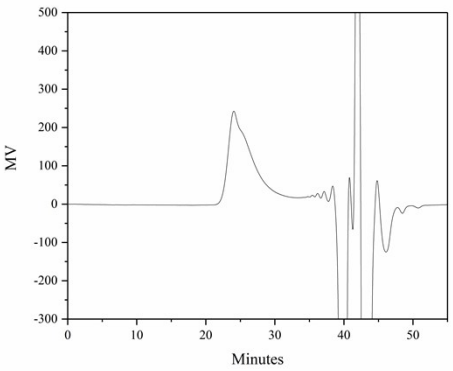
Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
	24.016	71160	121311	161817	173892	1.705



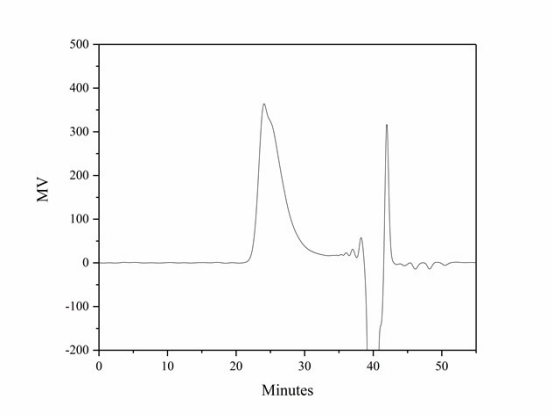
Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
	24.005	69845	121006	162591	174301	1.732



Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
	24.053	61418	111630	111630	165090	1.818

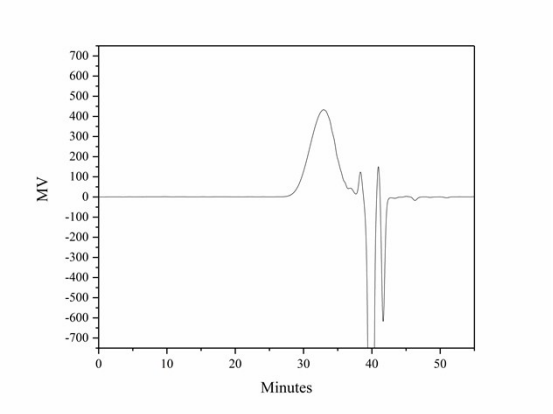


Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
	24.083	72065	112253	153025	157467	1.558

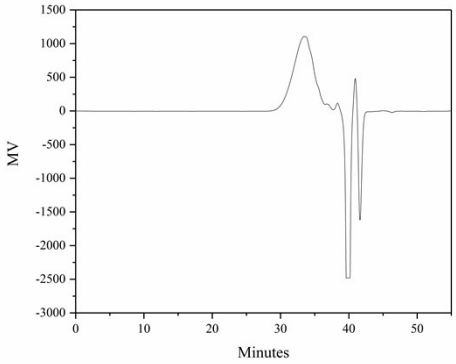


Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
PSFO1	26.248	35677	59257	64181	84908	1.661

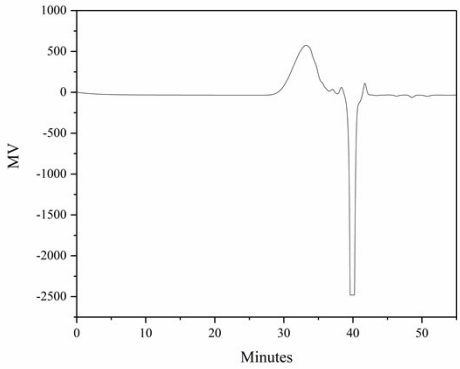
Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
5%	32.929	11326	12731	11885	14146	1.124



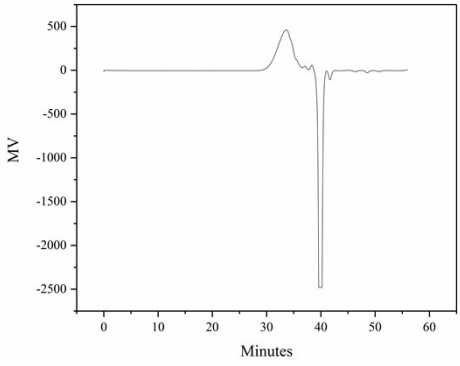
Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
10%	33.431	10184	11195	10762	12177	1.099



Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
20%	33.244	10889	12145	11173	13369	1.115



Sample Name	RT (min)	Mn	Mw	MP	Mz	Poly-dispersity
30%	33.697	10137	11115	10186	12047	1.097



References

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