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Bifluoride-catalysed sulfur(vi) fluoride exchange reaction for the synthesis of polysulfates and polysulfonates

Bing Gao[1], Linda Zhang[2], Qinheng Zheng[1], Feng Zhou[3], Liana M. Klivansky[4], Jianmei Lu[3], Yi Liu[4], JiaJia Dong[5*], Peng Wu[2*] and K. Barry Sharpless[1,5*]

[1]Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA.

[2]Department of Molecular Medicine, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA.

[3]College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou, Nano Science and Technology, Soochow University, Suzhou 215123, China.

[4]The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

[5]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Ling-Ling Road, Shanghai 200032, China.

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1, Materials and Instrumentation

All commercial chemicals were used as received unless otherwise noted. Extra dry solvents over molecular sieves were purchased from Acros Organics, including acetonitrile (CH_3CN), tetrahydrofuran (THF), dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP). Merck F-254 silica gel plates were used for thin layer analytical chromatography (TLC). Column chromatography purification was carried out using EMD (Merck) Silica Gel 60 (40-63 am).

^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker DRX-500, AMX-400, or Varian Inova-400 at 295 K. Chemical shifts (δ) were quoted in parts per million (ppm), and referenced to the appropriate NMR solvent residual peaks. Melting points were recorded on a Barnstead Electrothermal 9300 digital capillary melting point apparatus. GC-MS data were recorded on an Agilent 7890A GC system with an Agilent 5975C Inert MSD system operating in electron impact ionization (EI) mode. The single crystal X-ray diffraction results were obtained at the *UCSD Crystallography Lab* on a Bruker Kappa APEX-II Ultra CCD diffractometer equipped with Mo K_α radiation ($\lambda = 0.71073$). Elemental analysis data were collected at *Shanghai Institute of Organic Chemistry*, *Chinese Academy of China, Shanghai, China*.

The polymer molecular weight (number-average, M_n^{ps}) and polydispersity (PDI) relative to polystyrene were measured by Waters 1515 Gel Permeation Chromatography (GPC) system. It was equipped with a diode-array, a refractive index detector 2414, and a series of MZ-Gel *SDplus* 500 Å, 10E3 Å, 10E4 Å columns. The system was calibrated with *EasyVial PS-M* polystyrene standards (*Agilent Technologies,* $M_p = 364000, 217900, 113300, 47190, 30230, 13270, 6940, 2780, 1220, 935, 370, 162$ g/mol). HPLC grade DMF was used as mobile phase with 0.05 mol/L of LiBr as additives (*Acros Organics*, 99.999% grade). The elution rate was 0.8 mL/min (column temperature, 40 ^{o}C). All samples/standards were tested at 100 μL loadings (1.0 g/mL).

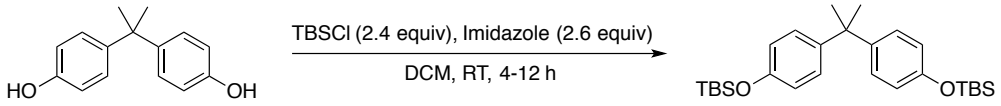
The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were carried out at *Lawrence Berkeley National Laboratory* with the assistance of Liana M. Klivansky and Dr. Yi Liu, and at *Soochow university* with the assistance of Feng Zhou, Bin Xu, Dr. Qing-Feng Xu and Jian-Mei Lu. TGA were carried out on TGA-MS Q5000 under nitrogen using aluminum pans (20 ^{o}C/min started from 25 ^{o}C and ended at 600 ^{o}C). The DSC were carried out on TA Q200 with a heat rate of 5 ^{o}C/min.

The ion-exchange experiment with anhydrous HF was carried out at Dr. Philip Dawson's Lab*, The Scripps Research Institute, La Jolla Campus, CA, USA*.

2, Experimental Section

2-1, General procedure for the preparation of monomers

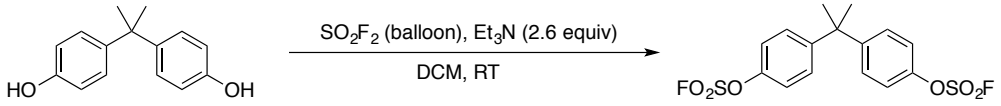
2-1-1, The preparation of monomer A from bisphenols.[1] (take **A-1** as an example).



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_2Cl_2 solution of TBSCl (48 mmol) 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 resulting crude product was heated to 70 ^oC *in vacuo* (2.0 torr) until TBS-O-TBS was completely removed, giving pure product as white solid at room temperature.

(Note: The silylation reaction is near quantitative. No further purifications are required for most products. In case flash column chromatography purification was needed, the column packed with silica gel should be pre-washed with 10% (v/v) of Et_3N in Hexane. Because some TBS ethers of phenol might be sensitive to the weak acidity nature of the silica gel, which causes the decomposition of TBS–OAr back to phenol. Hexane and ethyl acetate are used as eluent.)

2-1-2, The preparation of monomer B from bisphenols.[1] (take **B-1** as an example)

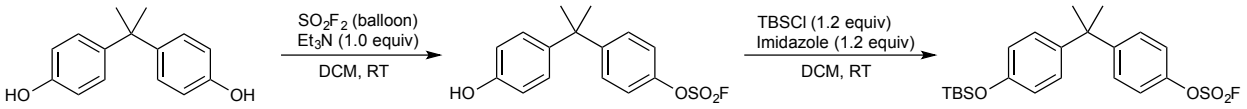


In a 500 mL round-bottom flask equipped with a stir bar, bisphenol-A (20 mmol) was dissolved in 100 mL dichloromethane (CH_2Cl_2). Triethylamine (52 mmol) was added and the resulting solution was stirred at room temperature for 10 mins. The flask was charged with gentle vacuum, then quickly filled with SO_2F_2 gas via a syringe attached balloon. The reaction was allowed stirring at room temperature until the full conversion of starting compound to target bisfluorosulfate, monitored by TLC and LC-MS. CH_2Cl_2 was then evaporated away on rotary evaporator, the resulting crude product was dissolved in 100 mL ethyl acetate (EtOAc). It was subsequently washed with 50 mL aqueous HCl (1.0 M, 3 times), 50 mL saturated aqueous solution of $NaHCO_3$, then 50 mL saturated brine. The organic phase was dried over anhydrous Na_2SO_4. After filtration,

the removal of EtOAc gave bisfluorosulfate as white solid, which was further crystallized from Hexane/EtOAc, giving colorless crystalline.

(Note: For more demanding substrates, acetonitrile was used as solvent and 2.6 equivalent of N,N-diisopropylethylamine was used as base.)

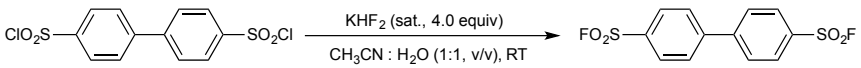
2-1-3, The preparation of AB type monomers from bisphenols. (take **AB-1** as an example)



Step 1, In a 1.0 L round-bottom flask equipped with a stir bar, bisphenol-A (45.6 g, 0.2 mol) was dissolved in 400 mL CH_2Cl_2. Triethylamine (0.21 g, 0.2 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 (1.0 M, 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). The bisfluorosulfate product **B-1** was eluted out first (37g, 24% yield), followed by the mono-functionalized adduct (14 g, 23% yield). The unconverted starting compounds was recovered at last (23 g, 51% recovery).

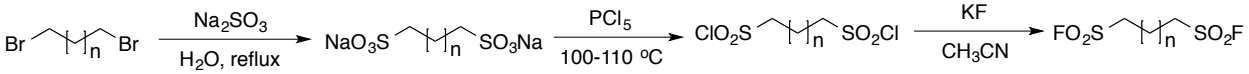
Step 2, In a 500 mL round-bottom flask equipped with a stir bar, mono-functionalized intermediate (13 g, 42 mmol) and TBSCl (7.6 g, 50.4 mmol) were combined and dissolved in 100 mL CH_2Cl_2. Imidazole (3.4 g, 50.4 mmol) was slowly added under vigorous stirring. The resulting mixture was further stirred at room temperature for another 2 hours. The precipitates were removed by filtration; the filtrate was then concentrated. The resulting crude product was dissolved in 100 mL EtOAc, which was washed with 50 mL saturated aqueous solution of $NaHCO_3$ (3 times) and 50 mL saturated brine. The organic solution was concentrated, then subjected to flash column chromatography purification (silica gel pre-washed with 10% (v/v) of Et_3N in Hexane; Hexane/EtOAc = 10:1 as eluent). **AB-1** was obtained as colorless oil, 15.2 g (86% yield).

2-1-4, The preparation of aromatic bis(sulfonyl fluoride).[1]



Aromatic bis(sulfonyl fluoride) was prepared from aromatic bis(sulfonyl chloride) according to the protocol reported in reference [1].

2-1-5, The preparation of aliphatic bis(sulfonyl fluoride).[2,3]

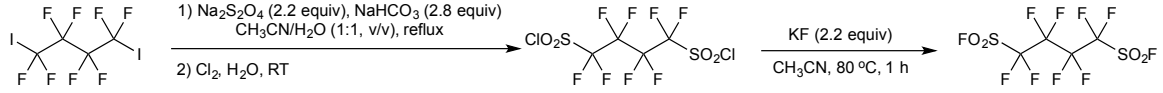


Step 1, To the aqueous solution of sodium sulfite (Na_2SO_3, 126 g, 1.0 mol, in 300 mL distilled water), bis(alkyl bromide) (0.5 mol) was added. The reaction was refluxed until the organic phase was completely consumed. The resulting mixture was cooled to room temperature, white precipitates crashed out gradually. The precipitates were collected by filtration and dried at 120 ^oC for 4 hours to give dry bis(sodium alkyl sulfonate).

Step 2, In a 500 mL three-neck round-bottom flask equipped with a stir bar and a reflux condenser, 0.2 mol of dry bis(sodium alkyl sulfonate) and 0.44 mol of phosphorus pentachloride were combined under N_2 atmosphere. The flask was heated to 110 ^oC for 2 hours, during which course the solid mixture gradually turn to suspension. It was allowed to react for another 2 hours, then cooled to room temperature. The mixture was slowly poured into ice water under vigorous stirring. Pale white solid crashed out which was collected via filtration, washed with distilled water, then dried *in vacuo* (2.0 torr). The crude product was used directly for the next step reaction without further purification.

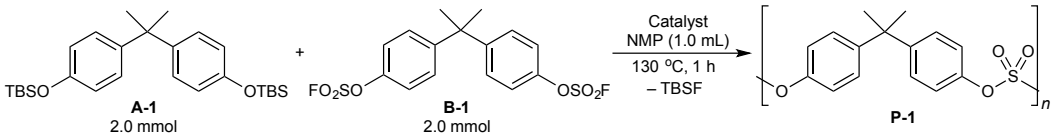
Step 3, In a 250 mL round-bottom flask equipped with a stir bar and a reflux condenser, 50.0 mmol of aliphatic bis(sulfonyl chloride) and 110 mmol of potassium fluoride were combined in 30 mL CH_3CN. The mixture was refluxed at 80 ^oC until ^1H NMR test indicated the reaction has achieved full conversion. CH_3CN was evaporated away. The resulting solid was partly soluble in 30 mL EtOAc (the insoluble slat was removed by filtration). The solution was concentrated for crystallization (Hexane/EtOAc). Pure aliphatic bis(sulfonyl fluoride) were obtained as white solid.

2-1-6, The perfluoroaliphatic bis(sulfonyl fluoride) was prepared following the reported procedure[4]



2-2, General procedure for the synthesis of polysulfates and polysulfonates

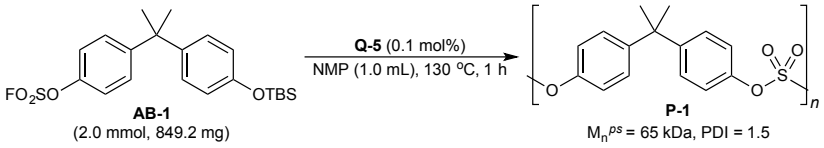
2-2-1, The polycondensation of monomers A and B (take **P-1** as an example)



Monomers **A-1** (2.0 mmol) and **B-1** (2.0 mmol) were combined in a 10 mL oven-dried glass vial equipped with a Teflon-coated magnetic stir bar. The vial was screw-capped with a Teflon-coated rubber septum, purged with nitrogen (A N_2 balloon was attached to the vial through a syringe). Dry NMP (1.0 mL) was added, and the vial was placed into a pre-heated 130 ^oC oil bath. Catalyst tris(dimethylamino)sulfonium bifluoride (**Q-5**, 0.1 M in dry CH_3CN , 40 μL) was added via micro-syringe under stirring. The reaction was run for 1 hour, during which course the reaction mixture turned highly viscous. 4 mL DMF was added at the end of the reaction to dissolve the crude polymer. The warm DMF solution was slowly poured into 100 mL of cold methanol under vigorous stirring. Polymers precipitated as white fiber or powder once the DMF solution touched the methanol. The polymer **P-1** was collected via filtration and were dried at 70 ^oC for 3 hours *in vacuo* (2.0 torr). Molecular weight and polymer distribution was determined on GPC.

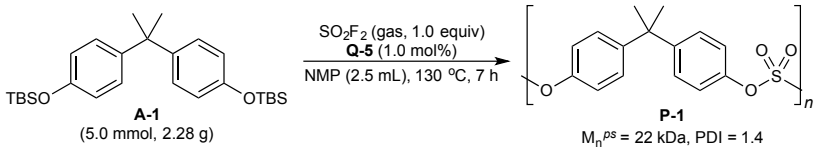
*(Note: when inorganic slats were used as catalyst, such as $K^+[FHF]^-$, they were combined with the **A**, **B** monomers before the reaction vial was heated to 130 ^oC.)*

2-2-2, The polycondensation of AB type monomer (take the polycondensation of monomer **AB-1** as an example).

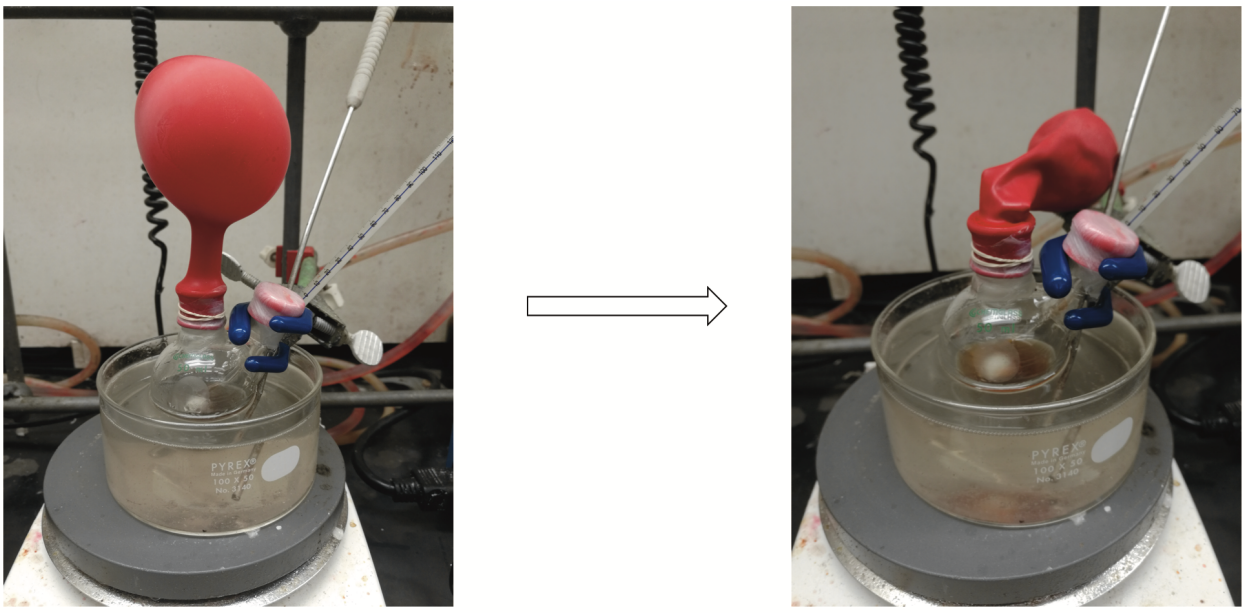


Monomers **AB-1** (849.2 mg, 2.0 mmol) were added to a 10 mL oven-dried glass vial equipped with a Teflon-coated magnetic stir bar. The vial was screw-capped with a Teflon-coated rubber septum, purged with nitrogen through a N_2 balloon attached via a syringe. Dry NMP (0.5 mL) was injected into the vial, then it was placed into a pre-heated 130 ^oC oil bath. With stirring, catalyst **Q-5** (0.1 M in CH_3CN, 20 μL) was added via a micro-syringe. The reaction was maintained stirring for 1 hour. Thereafter, 2 mL DMF was added to dissolve the polymers at 130 ^oC. The resulting DMF solution was slowly poured into 50 mL methanol under vigorous stirring. Polymeric fiber precipitated once the warm DMF solution touch the cold methanol. The polymers were collected via filtration and dried at 70 ^oC for 3 hours *in vacuo* (2.0 torr). Molecular weight and distribution of resulting polymer **P-1** was determined on GPC.

2-2-3, The polycondensation of bis(aryl silyl ether) with sulfuryl fluoride gas (SO_2F_2) (take the reaction between **A-1** and SO_2F_2 as an example).



To a dry two-neck round-bottom flask (50 mL) equipped with a stir bar, was added monomer **A-1** (2.28 g, 5.0 mmol). One of the neck was attached to a balloon, the other was sealed with a rubber septum (Fig. 1a). Air in the flask was removed under vacuum and refilled with N_2 (make sure no/little N_2 reserve in the attached balloon). The flask was weighed on the balance before SO_2F_2 gas was introduced, and was monitored until the net weight of SO_2F_2 introduced from a cylinder reached 520 mg (± 3 mg, 1.0 equiv). Dry NMP (2.5 mL) was subsequently injected into the flask via a syringe. The flask was carefully sealed to avoid leaking, and was placed into a pre-heated 130 °C oil bath with stirring. Catalyst **Q-5** (0.5 M in CH_3CN, 100 μL) was added via a micro-syringe. The reaction was allowed running for 7 hours. Thereafter, another 2.5 mL of DMF was added to dissolve the polymer at 130 °C. The resulting DMF solution was slowly poured into 50 mL of methanol under vigorous stirring. Polymers crashed out as white powder in methanol. They were collected via filtration and dried at 70 °C for 3 hours *in vacuo* (2.0 torr). Molecular weight and polydispersity were determined on GPC (M_n^{ps} = 22 kDa, PDI = 1.4).



***1*#**, at the beginning of the reaction

***2*#**, at the end of the reaction

Figure 1 | Images of the polycondensation reaction of bis(aryl silyl ether) A-1 with sulfuryl fluoride (SO_2F_2). Left ($1^{\#}$): Image at the beginning of the reaction. Right ($2^{\#}$): Image at the end of the reaction.

2-3, The preparation of bifluoride and poly(hydrogen fluoride) catalysts

2-3-1, The preparation of onium bifluoride ($Q^+[FHF]^-$) through ion-exchange of onium halide (Q^+X^-) with silver bifluoride ($Ag^+[FHF]^-$)

In the glovebox, a 20 mL polypropylene plastic vial equipped with a Teflon-coated stir bar was charged with 80.8 mg silver bifluoride (0.5 mmol). The vail was well-sealed by rubber septum before taken out of the glovebox. Dry acetonitrile (2 mL) was added to give a suspension, which was stirred under N_2 atmosphere. To another vial in the glovebox, Q^+X^- (X = Cl or Br, 0.5 mmol) was weighed. It was later dissolved in 2 mL dry acetonitrile. The solution was transferred dropwise to the stirring $Ag^+[FHF]^-$ suspension in acetonitrile via a syringe. Another 1 mL acetonitrile was used to wash the onium halide vial and the syringe, which was subsequently added to the reaction mixture. The suspension was vigorously stirred for another 1 hour (5 mL in total). After deposition, the solution was extracted into a 10 mL syringe, then filtered over a micro-filter (4 μm) during the transfer to another N_2 purged dry polypropylene vial (20 mL). The resulting 0.1 M acetonitrile stock solution was used directly (sealed and stored in dry box).

(Note: To obtain the crystal of $Q^+[FHF]^-$, the acetonitrile solution was concentrated to approximately 1 mL. Anhydrous Et_2O was slowly added until the formation of precipitate. A few drops of dry acetonitrile were added to make the solution slightly unsaturated. The solution was filtrated while being transferred to another plastic vial via syringe, which was later sealed and set in fridge. Colorless crystals were obtained at the bottom of the plastic vial within one or two days.)

2-3-2, The preparation of tris(dimethylamimo)sulfonium bifluoride Q-5[5]

In the glovebox, to a 20 mL polypropylene plastic vial equipped with a Teflon-coated stir bar was charged with 1.122 g (4.07 mmol) tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF). The vial was taken out of the glovebox and protected under N_2 atmosphere. Dry acetonitrile (1.0 mL) was added to dissolve TASF. Subsequently with stirring, distilled water (60 μL, 3.3 mmol) was added via a micro-syringe. The rapid formation of an oily phase was observed on the top layer. The reaction was maintained stirring for another 30 mins. Acetonitrile was evaporated away to give pale-yellow solid as crude product. Dry tetrahydrofuran (10 mL) was added to wash the crude product for 10 min then removed via syringe thereafter. The resulting crude product was further washed twice with 10 mL of THF. After that, it was dried *in vacuo* (2.0 torr) at ambient temperature for 3 days. **Q-5** was obtained as white solid (791 mg, 95% yield).

2-3-3, The preparation of onium dihydrogentrifluoride ($Q^+[H_2F_3]^-$) via ion-exchange of onium halide (Q^+X^-) with excess potassium bifluoride[6]

In a 100 mL polypropylene bottle, Q^+X^- (5.0 mmol) was dissolved in 20 mL CH_2Cl_2 (or CH_3CN), which was subsequently equilibrated with 50 mL aqueous solution of potassium bifluoride (19 g,

250.0 mmol) at room temperature for 30 min under vigorous stirring. The aqueous phase was removed by funnel separation (**Caution: use a plastic funnel, do not allow the organic solution touch any glass containers**). The organic solution was treated with another 50 mL aqueous solution of potassium bifluoride (19 g) for another 30 min, and this process was repeated for a third round. Finally, the resulting organic solution was concentrated to give crude product. $Q^+[H_2F_3]^-$ of higher purity was obtained via crystallization of the crude product in MeOH/Et_2O (or DCM/Et_2O).

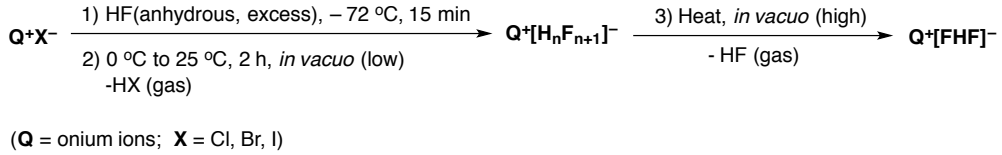
2-3-4, The preparation of onium hydrogen fluoride ($Q^+[H_nF_{n+1}]^-$) from onium hydroxide (Q^+OH^-)

To a 20 mL polypropylene plastic vial equipped with a Teflon-coated stir bar was added 5.0 mmol Q^+OH^-. The vial was incubated in an ice-water bath for 10 mins under the protection of N_2 atmosphere. A 5(n+1) mmol hydrofluoric acid (48 wt.% in H_2O) was added dropwise with stirring (n= 1, 2, 3, 4, 5, …). The mixture was stirred for 10 mins at 0 ^oC and another 20 mins at room temperature. The resulting $Q^+[H_nF_{n+1}]^-$ was used as 0.1 M stock solution in CH_3CN (water introduced by the hydrofluoric acid was not removed).

2-3-5, The preparation of onium hydrogen fluoride ($Q^+[H_nF_{n+1}]^-$) from onium fluoride (Q^+F^-), onium bifluoride ($Q^+[FHF]^-$), or onium dihydrogentrifluoride ($Q^+[H_2F_3]^-$)

To a 20 mL polypropylene plastic vial equipped with a Teflon-coated stir bar was added 0.4 mL CH_3CN solution of Q^+F^-, ($Q^+[FHF]^-$ or $Q^+[H_2F_3]^-$, 0.2 mmol, 0.5 M in CH_3CN). The vial was incubated in an ice-water bath for 10 mins under N_2 atmosphere, then with stirring was added 0.2x mmol of HF (0.5 M in CH_3CN, prepared from 48 wt.% of hydrofluoric acid and dry CH_3CN, x = 1, 2, 3, 4, 5, …). A certain amount of dry CH_3CN was added to make the concentration of resulting mixture as 0.1 M. The mixture was stirred for 10 mins at 0 ^oC and another 20 mins at room temperature. The resulting $Q^+[H_nF_{n+1}]^-$ stock solution was used directly (without the removal of water introduced from hydrofluoric acid).

2-3-6, The preparation of onium hydrogen fluoride ($Q^+[H_nF_{n+1}]^-$) via ion-exchange of onium chloride "Q^+Cl^-" with anhydrous HF[7]



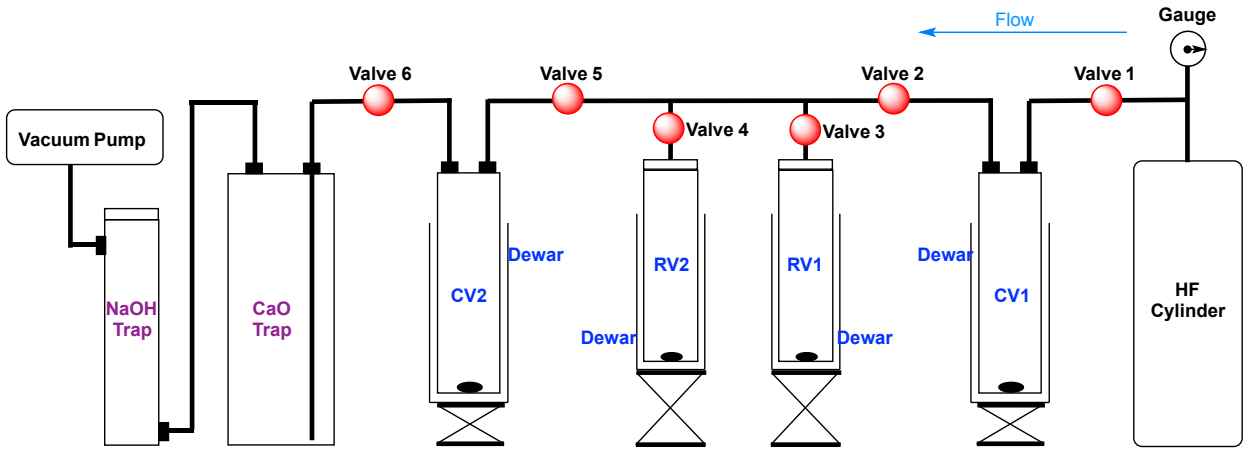


Figure 2 | Schematic diagram of the ion-exchange apparatus.

(***Note: Anhydrous hydrogen fluoride is dangerous for its strong corrosiveness and toxicity. It must be manipulated in specific apparatus under the guidance of HF experts***. *This experiment was conducted at Dr. Philip Dawson's lab, The Scripps Research Institute, La Jolla campus. The diagram above is a schematic depiction of the Teflon-made apparatus. For more information, please read the reference [7].*)

(Abbreviation: CV1= collection vessel No. 1, RV1 = reaction vessel No. 1, RV2 = reaction vessel No. 2, CV2 = collection vessel No. 2)

- *Step 1*, check each part of the apparatus and the vacuum conditions of the whole system, make sure they all function well;
- *Step 2*, close valve 1, 3, and 4 (RV1 and RV2 unloaded), open valve 2, 5, and 6, and the vacuum pump;
- *Step 3*, close valve 2, 3, and 4, open valve 1, 5, and 6, and then the HF cylinder; CV1 was place in a dry ice-ethanol Dewar, HF was therefore transferred to CV1. CV2 was kept in a dry ice-ethanol Dewar until otherwise noted;
- *Step 4*, close HF cylinder, keep CV1 in ice-ethanol Dewar unless otherwise noted. RV1 containing sample 1 and RV2 containing sample 2 were loaded; The Teflon-coated bars inside each vessel were kept stirring;

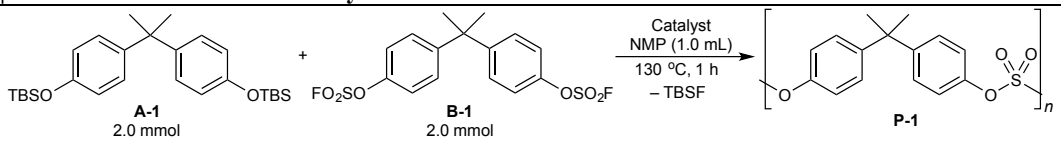
- *Step 5*, close valve 4, and 5, open valve1, 2, 3, and 6. RV1 was placed in a dry ice-ethanol Dewar unless otherwise noted; CV1 was heated with warm water (50 ^{o}C), A desired amount of HF was transferred from CV1 to RV1;
- *Step 6*, close valve 3 and 5, open valve 1, 2, 4, and 6. RV2 was placed in a dry ice-ethanol Dewar, CV1 was heated with warm water (50 ^{o}C), A desired amount of HF was transferred from CV1 to RV2;
- *Step 7*, close valve 3, 4, and 6, open valve 1, 2, and 5; Keep heating CV1 with 50 ^{o}C water bath, and cooling RV1, RV2, and CV2 with dry ice-ethanol bath. The residual HF in CV1 was transfer to CV2;
- *Step 8*, open valve 1-5, partly open valve 6; Keep the system under gentle vacuum condition; Replace the dry ice-ethanol bath of RV1 and RV2 with ice water bath; The reactions were maintained at 0 ^{o}C for 30 mins; Bubbles of HCl slowly formed from the liquid reaction mixtures and were removed due to the gentle vacuum condition;
- *Step 9*, replace the ice water bath with ambient water bath (25 ^{o}C), keep the reaction running for another 1 hour. Bubbles were constantly removed from the liquid reaction mixtures;
- *Step 10*, rise the temperature of water bath to 70 ^{o}C and keep the reaction mixture stirring until all the HCl and HF residue were completely removed from RV1 and RV2.
- *Step 11*, fully open valve 1-6, warm CV2 to room temperature with water bath. HF in CV2 was removed and absorbed in CaO trap.
- *Step 12*, close valve 3, and 4, unload RV1 and RV2 and quickly transfer them to glove box; Samples were subsequently transfer from RV1 and RV2 to small polypropylene plastic vials which were store in glove box.
- *Step 13*, work-up (clean RV1 and RV2).

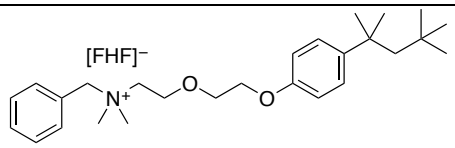
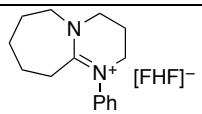
(Note: The crude product obtained after "Step 12" is normally poly(hydrogen fluoride) $Q^{+}[H_nF_{n+1}]^{-}$ *(n > 1). It can be converted to bifluoride adduct* $Q^{+}[FHF]^{-}$ *by further removing HF at higher temperature in vacuo (in PTFE vial). The reaction time and temperature varies depending on specific cations* Q^{+}*, as well as the vacuum conditions involved. For the preparation of* $EMI^{+}[FHF]^{-}$, we obtained $EMI^{+}[H_3F_4]^{-}$ *after "Step 12" as colorless liquid. It was further heated at 90 ^{o}C for 14 hours in vacuo (oil pump, 2.0 torr), giving* $EMI^{+}[FHF]^{-}$ *as waxy solid.)*

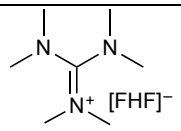
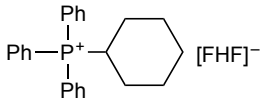
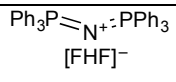
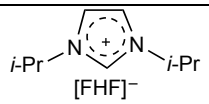
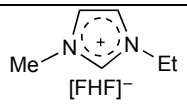
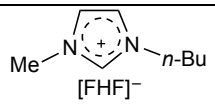
2-4, Catalyst evaluation

The synthesis of **P-1** from the polycondensation of **A-1** (2.0 mmol) and **B-1** (2.0 mmol) was employed as model reaction for the catalyst evaluation. Experiments were conducted following the general procedure described in *Supplementary Section 2-2-1* unless otherwise noted. Number-average molecular weight (M_n^{ps}) and polydispersity (PDI) were recorded on GPC. In most cases, catalyst-loadings listed in Table 1 and Table 2 are the minimum molar ratio required to give polysulfates with M_n^{ps} higher than 20 kDa. Therefore, the catalyst-loadings may vary based on specific catalyst employed. All catalyst-loading is the mole ratio to the total amount of both monomers, not to one monomer. Because each (**A** or **B**) monomer has two reactive sites.

Table 1 | Evaluation of bifluoride catalysts with DBU and BEMP as controls.



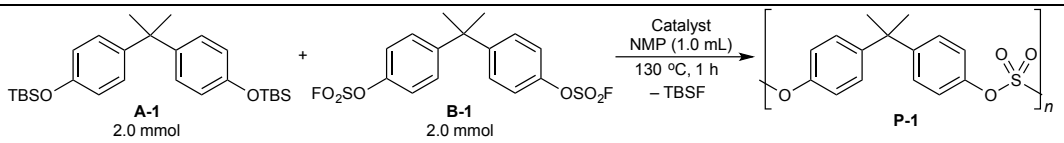
Entry	Catalysts	Loading (mole ratio)	M_n^{ps} (kDa)	PDI
1	DBU	10%	30	1.4
2	BEMP	1%	88	1.6
3[a]	KF	2.0%	oligomers	
4[a]	$K^+[FHF]^-$	2.0%	28	1.4
5[a]	$K^+[FHF]^-$	1.0%	oligomers	
6[a]	$K^+[FHF]^-$ (+ Bu_4NCl)	2.0% (+ 1.0%)	91	1.5
7[a]	$K^+[FHF]^-$ (+ 18-crown-6 ether)	2.0% (+ 1.0%)	103	1.5
8[a]	$NH_4^+[FHF]^-$	2.0%	no reaction	
9	$Me_4N^+[FHF]^-$ (**Q-1**)	0.1%	34	1.4
10	$Et_4N^+[FHF]^-$	0.2%	82	1.6
11	*n*-$Bu_4N^+[FHF]^-$ (**Q-2**)	0.1%	46	1.5
12	$[PhCH_2N(CH_2CH_3)_3]^+[FHF]^-$	0.1%	34	1.5
13		0.25%	56	1.8
14		0.1%	12	1.3

15	 (**Q-6**)	0.08%	101	2.0
16	 (**Q-7**)	0.25%	78	1.6
17	$Me_4P^+[FHF]^-$	0.1%	38	1.6
18	n-$Bu_4P^+[FHF]^-$	0.5%	76	2.4
19	$[n\text{-}Bu_3P(CH_2)_{15}CH_3]^+[FHF]^-$ (**Q-9**)	0.1%	82	1.6
20	$[Ph_3PMe]^+[FHF]^-$	0.5%	89	1.6
21	$[Ph_3P(CH_2CH_2CH_3)]^+[FHF]^-$	0.2%	88	1.7
22	$[Ph_3P(CH_2OCH_3)]^+[FHF]^-$	0.5%	53	1.6
23		0.15%	51	1.6
24	 (PNP$^+$[FHF]$^-$, **Q-10**)	0.1%	77	1.6
25	$Ph_4As^+[FHF]^-$ (**Q-8**)	0.25%	86	1.6
26	 (**Q-3**)	0.1%	83	1.7
27		0.5%	72	1.6
28	 (**Q-4**)	0.1%	47	1.7
29	$(Me_2N)_3S^+[Me_3SiF_2]^-$ (TASF)	0.25%	116	1.8
30	$(Me_2N)_3S^+[FHF]^-$ (**Q-5**)	0.05%	92	1.7
31	**Q-5**	0.10%	120	1.6
32	**Q-5**	0.5%	98	1.7
33	**Q-5**	1.0%	122	2.0
34[b]	**Q-5**	0.1%	28	1.6

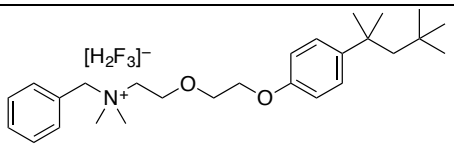
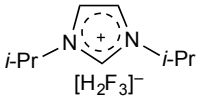
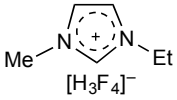
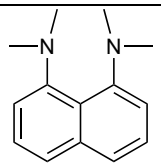
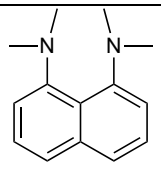
35[c]	**Q-5**	0.1%	19	1.3

All bifluoride salts with organic cations were used as 0.1 M stock solution in CH_3CN. [a] The reaction was allowed to run for 17 hours. [b] Trimethyl silyl ether (TMS) of bisphenol-A was used. [c] Triethyl silyl ether (TES) of bisphenol-A was used.

Table 2 | Evaluation of poly(hydrogen fluoride) salts as catalyst.



Entry	Catalyst	Loading (mole ratio)	M_n^{ps} (kDa)	PDI
1	$PNP^+[H_2F_3]^-$ (**Q-11**)	0.25%	128	1.8
2	$PNP^+[H_2F_3]^-$ + HF (aq. 48 wt.%) (1:1 mole ratio) (**Q-12**)	0.5%	81	1.6
3	$PNP^+[H_2F_3]^-$ + HF (aq. 48 wt.%) (1:2 mole ratio) (**Q-13**)	0.5%	58	1.5
4	$PNP^+[H_2F_3]^-$ + HF (aq. 48 wt.%) (1:7 mole ratio) (**Q-14**)	0.5%	20	1.3
5	*n*-$Bu_4N^+F^-(H_2O)_3$ + HF (aq. 48 wt.%) (1:2 mole ratio)	0.5%	58	1.6
6	*n*-$Bu_4N^+F^-(H_2O)_3$ + HF (aq. 48 wt.%) (1:3 mole ratio)	0.5%	68	1.5
7	*n*-$Bu_4N^+F^-(H_2O)_3$ + HF (aq. 48 wt.%) (1:9 mole ratio)	0.5%	20	1.3
8	*n*-$Bu_4N^+F^-(H_2O)_3$ + $Py\cdot(HF)_x$ (1:1 mole ratio)	0.4%	24	1.4
9	*n*-$Bu_4N^+F^-(H_2O)_3$ + $Et_3N\cdot3HF$ (1:1 mole ratio)	0.4%	41	1.5
10	*n*-$Bu_4N^+Cl^-$ + $Py\cdot(HF)_x$ (1:1 mole ratio)	0.1~10%	no reaction	

11	*n*-$Bu_4N^+Cl^-$ + $Et_3N{\cdot}3HF$ (1:1 mole ratio)	0.1~10%	no reaction	
12	*n*-$Bu_4P^+[H_2F_3]^-$	0.25%	54	1.7
13	$[PhCH_2PPh_3]^+[H_2F_3]^-$	0.5%	66	2.2
14		0.25%	71	1.6
15		0.25%	31	1.5
16		0.5%	35	1.5
17	HF (aq. 48 wt.%)	0.5~10%	oligomers	
18	$Et_3N{\cdot}(HF)_3$	0.5~10%	oligomers	
19	$Py{\cdot}(HF)_x$ (Olah's reagent, 70 wt.% HF)	0.5~10%	oligomers	
20	DBU + HF (aq. 48 wt.%) (1:2, mole ratio)	10%	15	1.3
21	BEMP + HF (aq. 48 wt.%) (1:2, mole ratio)	5%	32	1.5
22	 (proton sponge) + HF (aq. 48 wt.%) (1:1, mole ratio)	0.5~1.0%	oligomers	
23	 (proton sponge) + HF (aq. 48 wt.%) (1:2, mole ratio)	0.5~1.0%	oligomers	

2-5, The effect of reaction temperature on the polycondensation of A-1 and B-1

2-5-1, General procedure monitoring the polymerization process (80 ^{o}C)

A-1 (1.570 g, 4.0 mmol) and **B-1** (1.827 g, 4.0 mmol) were combined in a two-neck 25 mL round-bottom flask, equipped with a Teflon-coated magnetic stir bar and a reflux condenser. The flask was purged with nitrogen gas. Dry NMP (4.0 mL) was added, and the flask was placed into a pre-heated 80 ^{o}C oil bath with stirring. Thermal equilibrium was established between the solution in the flask and the oil bath within 5 mins. Catalyst **Q-5** (0.5 mol%, 0.1 M in dry CH_3CN) was added via micro-syringe. The reaction was triggered instantly upon the addition of catalyst. 2 min later after the addition of catalyst, the first batch of sample (0.1 mL) was extracted from the reaction mixture via a syringe. About 0.02 mL of the sample was dissolved in 0.7 mL of d^2-DCM and was subjected to ^{19}F NMR and ^{1}H NMR analysis (Fig. 4, 5). The other 0.08 mL was quenched in excess MeOH to give white powder precipitate. After filtration, the white powder was dried in a 70 ^{o}C oven for 2 hours, then subjected to GPC analysis. As the polymerization proceeded, the reaction mixture was constantly monitored by GPC following the procedure above, over a course of 5 hours (Table 3 & Fig. 3).

2-5-2, Summary of experimental data.

Table 3, Summary of molecular weight and polydispersity at 80 ^{o}C, 100 ^{o}C, and 120 ^{o}C.

	80 ^{o}C		100 ^{o}C		120 ^{o}C	
Checkpoint (min)	M_n^{ps} (kDa)	PDI	M_n^{ps} (kDa)	PDI	M_n^{ps} (kDa)	PDI
2	27	1.5	35	1.5	43	1.5
5	27	1.4	36	1.5	47	1.5
10	29	1.5	38	1.6	52	1.5
20	30	1.5	41	1.6	57	1.6
30	32	1.5	42	1.6	63	1.5
40	32	1.5	45	1.5	69	1.5
50	33	1.5	50	1.5	71	1.5
60	32	1.5	51	1.5	71	1.6
90	34	1.5	54	1.6	71	1.6
120	34	1.5	55	1.6	74	1.6
150	39	1.4	61	1.6	73	1.6

180	36	1.5	60	1.6	76	1.5
210	38	1.5	63	1.6	74	1.6
240	39	1.4	66	1.6	75	1.6
270	39	1.5	67	1.6	76	1.6
300	41	1.5	67	1.6	74	1.6

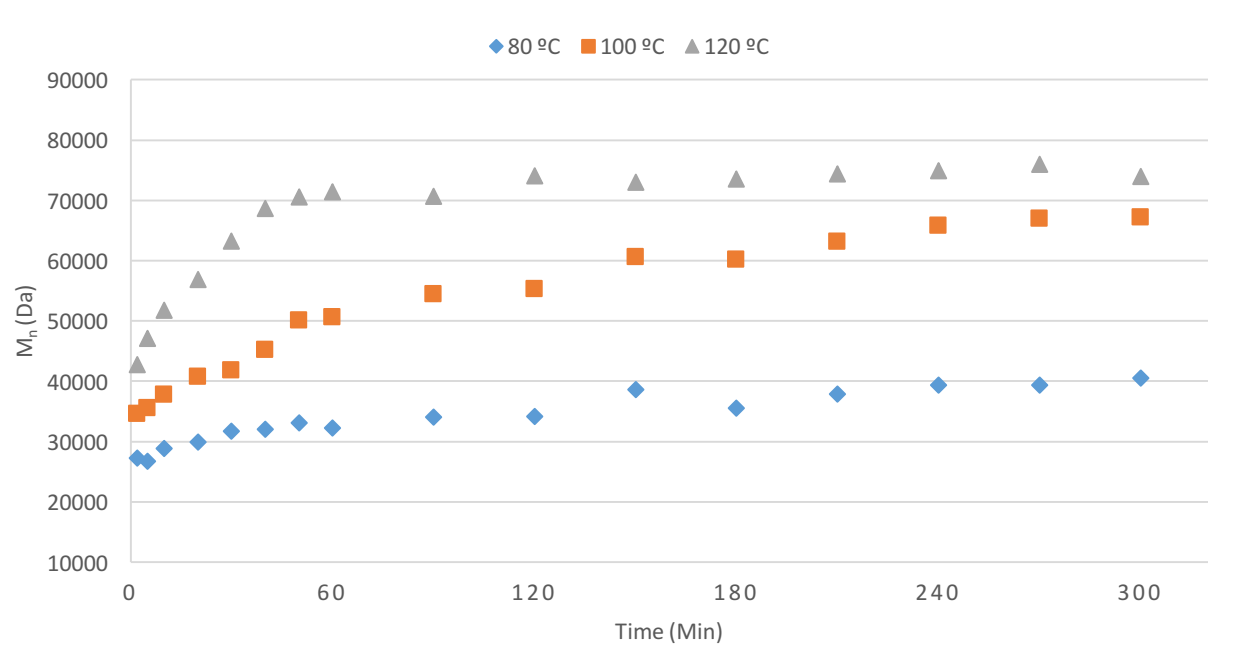


Figure 3 | Plot of the molecular weight (M_n^{ps}) *vs* reaction time at different reaction temperatures.

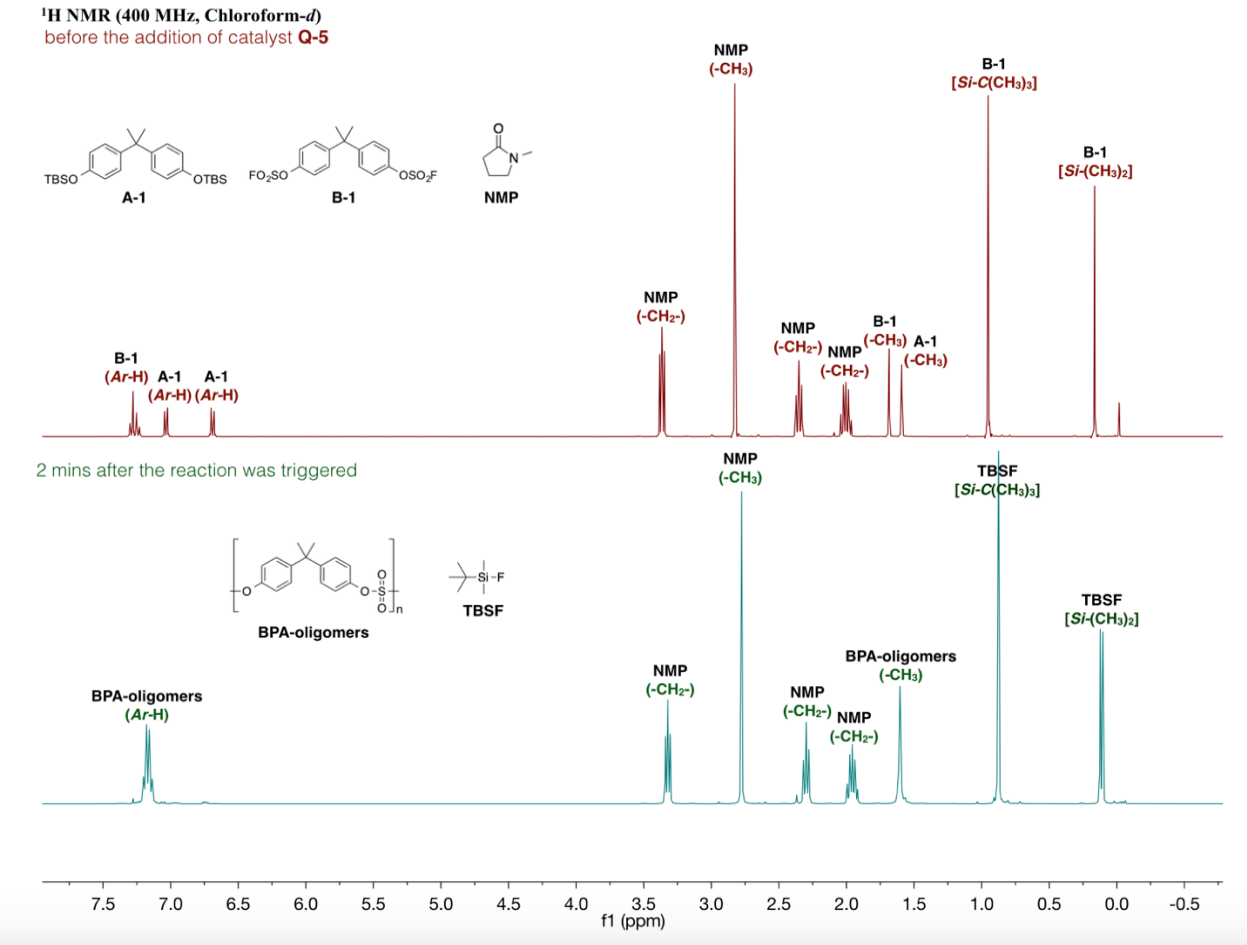


Figure 4 | ^{1}H NMR spectra of the polymerization (before, and 2 mins after the addition of the catalyst).

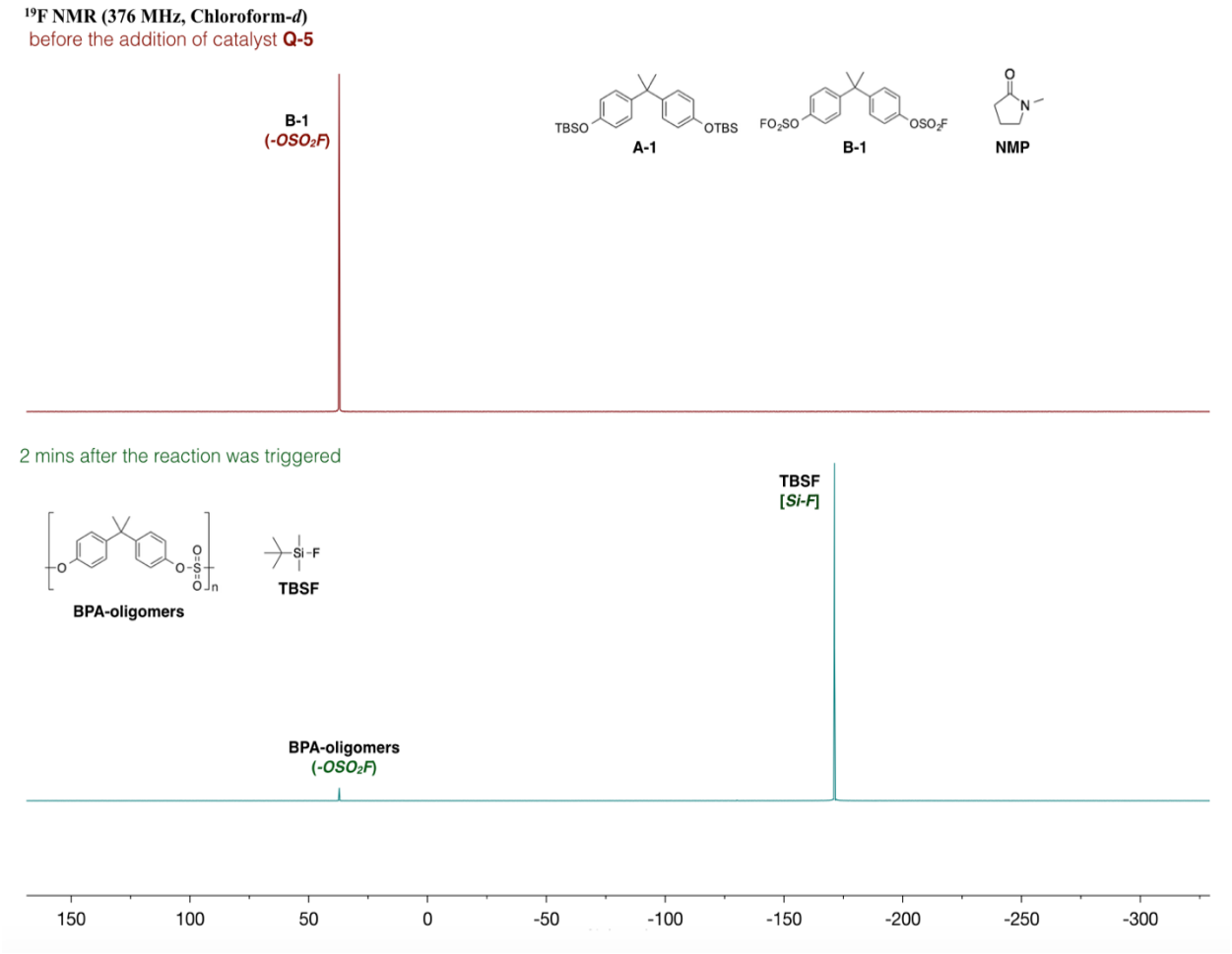
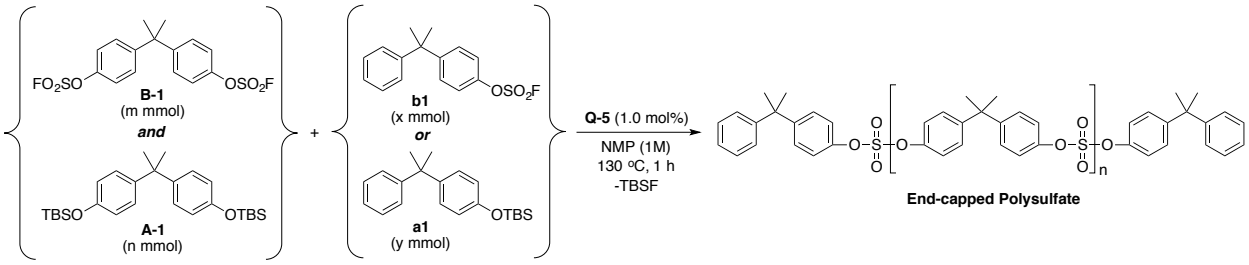


Figure 5 | ^{19}F NMR spectra of the polymerization (before, and 2 mins after the addition of the catalyst).

2-6, The effect of mono-functional chain terminators on the molecular weight of polysulfate



*Two sets of experiments were carried out. In the first set, difunctional monomer **B-1** (1.0 mmol) was in excess over **A-1** (n mmol). Monofunctional nomomer **a1** (y mmol, y = 2 – 2n) was employed to make the total amounts of both functionalities (–OSO_2F and –OTBS) in equal equivalent. In the other set, difunctional monomer **A-1** (1.0 mmol) was in excess over **B-1** (m mmol), and monofunctional monomer **b1** (x mmol, x = 2 – 2m) was employed to make the total amounts of both functionalities (–OSO_2F and –OTBS) in equal equivalent. All experiments were conducted at 130 °C in NMP (1.0 M) for one hour, with a 1.0 mol% of **Q-5** as catalysts. One example is given as below.*

Monomers **B-1** (392.4 mg, 1.0 mmol), **A-1** (434.0 mg, 0.95 mmol), and **a1** (32.7 mg, 0.1 mmol) were combined in a 10 mL oven-dried glass vial. The vial was equipped with a Teflon-coated magnetic stir bar and screw-capped with a Teflon-coated rubber septum. Degassed and then refilled with nitrogen, the vial was subsequently connected to a N_2 balloon via a syringe. Dry NMP (1.0 mL) was injected in, then it was placed into a pre-heated 130 °C oil bath with stirring. Catalyst **Q-5** (0.2 M in dry CH_3CN, 100 μl) was added via a micro-syringe. The reaction was allowed running for 1 hour, then 4 mL DMF was added to dissolve the resulting polymer. The warm DMF solution was poured into 50 mL of cold methanol under vigorous stirring. Polysulfate precipitated in the form of fiber or powder once the warm DMF solution touched the cold methanol. The precipitate was collected via filtration and dried at 70 °C for 2 hours under vacuum condition (2.0 torr). Molecular weight and polymer distribution was determined on GPC (Table 4).

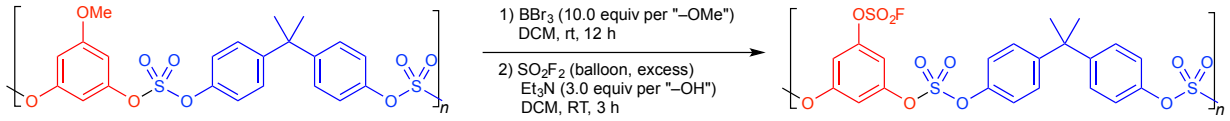
Table 4. The effect of mono-functional chain terminators as additives on the molecular weight and polydispersity of resulting polysulfates.

Entry	**B-1** (equiv.)	**A-1** (equiv.)	**a1**/**b1** (equiv.)	Yield	M_n^{ps} (kDa)	PDI
1	1.0	1.0		>99%	72	1.6
2	1.0	0.9975	**a1** (0.005)	99%	55	1.6
3	1.0	0.995	**a1** (0.01)	97%	48	1.5
4	1.0	0.99	**a1** (0.02)	96%	30	1.5
5	1.0	0.98	**a1** (0.04)	96%	30	1.5

6	1.0	0.97	**a1** (0.06)	93%	29	1.4
7	1.0	0.96	**a1** (0.08)	89%	25	1.3
8	1.0	0.95	**a1** (0.10)	66%	21	1.3
9	0.9975	1.0	**b1** (0.005)	>99%	60	1.4
10	0.995	1.0	**b1** (0.01)	>99%	49	1.6
11	0.99	1.0	**b1** (0.02)	99%	36	1.5
12	0.98	1.0	**b1** (0.04)	89%	30	1.5
13	0.97	1.0	**b1** (0.06)	93%	25	1.4
14	0.96	1.0	**b1** (0.08)	>99%	23	1.4
15	0.95	1.0	**b1** (0.10)	96%	22	1.4

2-7, Post-polymerization modification of polysulfates

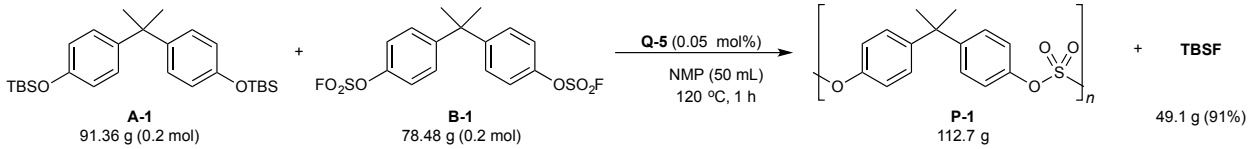
(Converting methoxy group (–OMe) of polysulfate **P-11a** to fluorosulfate (–OSO_2F))



Step 1, To an oven-dried two-neck flask (50 mL) equipped with a stir bar, was added 492 mg of polysulfate **P-11a** (approximately 1.0 mmol of methoxy groups, calculated based on the molecular weight of smallest repeat unit). The flask was sealed by rubber septum and protected under nitrogen atmosphere. The polymer was dissolved in 10 mL anhydrous CH_2Cl_2 under stirring. BBr_3 (10.0 mol) was added dropwise to the stirring solution at room temperature. The reaction was maintained stirring overnight (12 hours). As monitored by ^{1}H NMR, the methoxy group was completely consumed. The mixture was concentrated to 1~2 ml, then dropped to cold water under vigorous stirring. White fiber crashed out on the surface of water. The polymer fiber was later collected via filtration, washed three times with distilled water, then dried *in vacuo* (2.0 torr) at 50 ^{o}C for 2 hours.

Step 2, The crude product obtained in *step 1* was dissolved in DCM (10 mL) in a 50 mL single-neck flask. Et_3N (1.0 mL, 7.26 mmol) was added to the stirring solution. The flask was sealed by rubber septum and left stirring for 15 mins at room temperature. The flask was charged with gentle vacuum condition, then filled with excess SO_2F_2 gas (supplied via a syringe connected balloon). The reaction was kept running at room temperature, monitored by ^{1}H NMR and ^{19}F NMR until it went complete. The resulting solution was concentrated to 1~2 mL, dropped to the co-solvent of MeOH and H_2O (1:2, v/v). White polymer powder crashed out. The powder was collected via filtration and washed with distilled water three times. It was later dried *in vacuo* (2.0 torr) at 50 ^{o}C for 5 hours (311 mg, 55% yield for two steps), then subjected to GPC analysis.

2-8, 100-gram scale synthesis of polysulfate P-1 catalyzed by Q-5



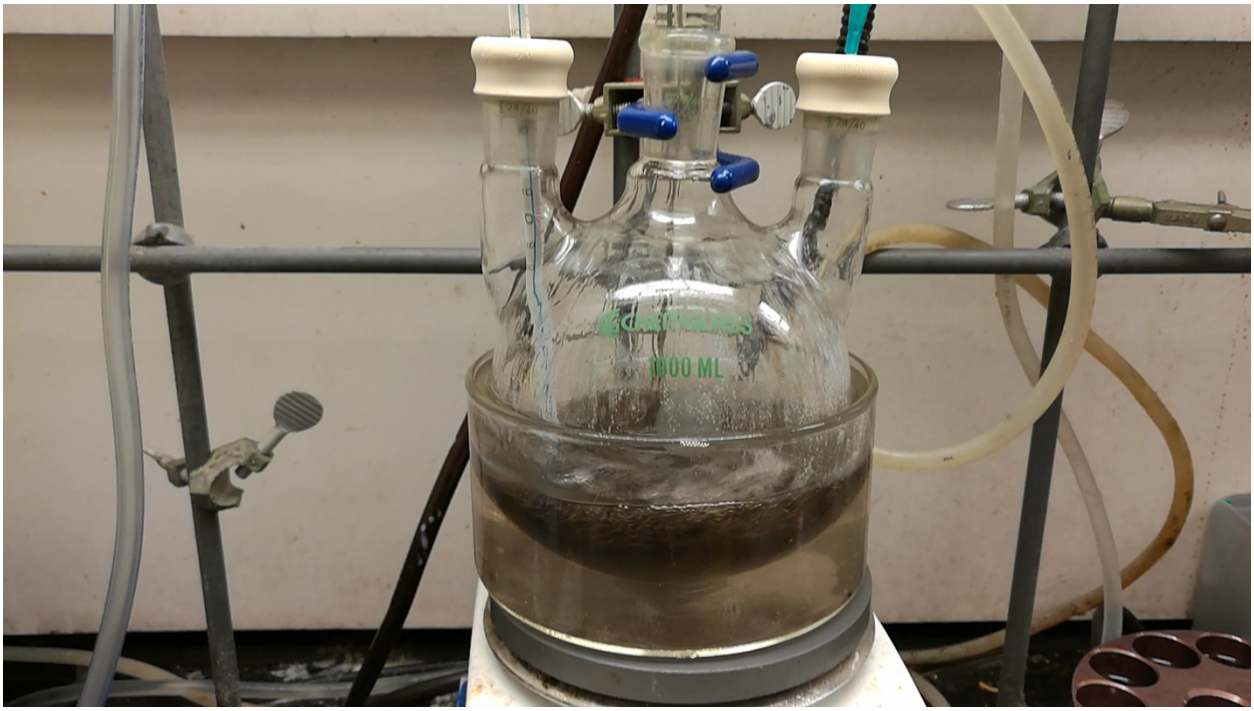
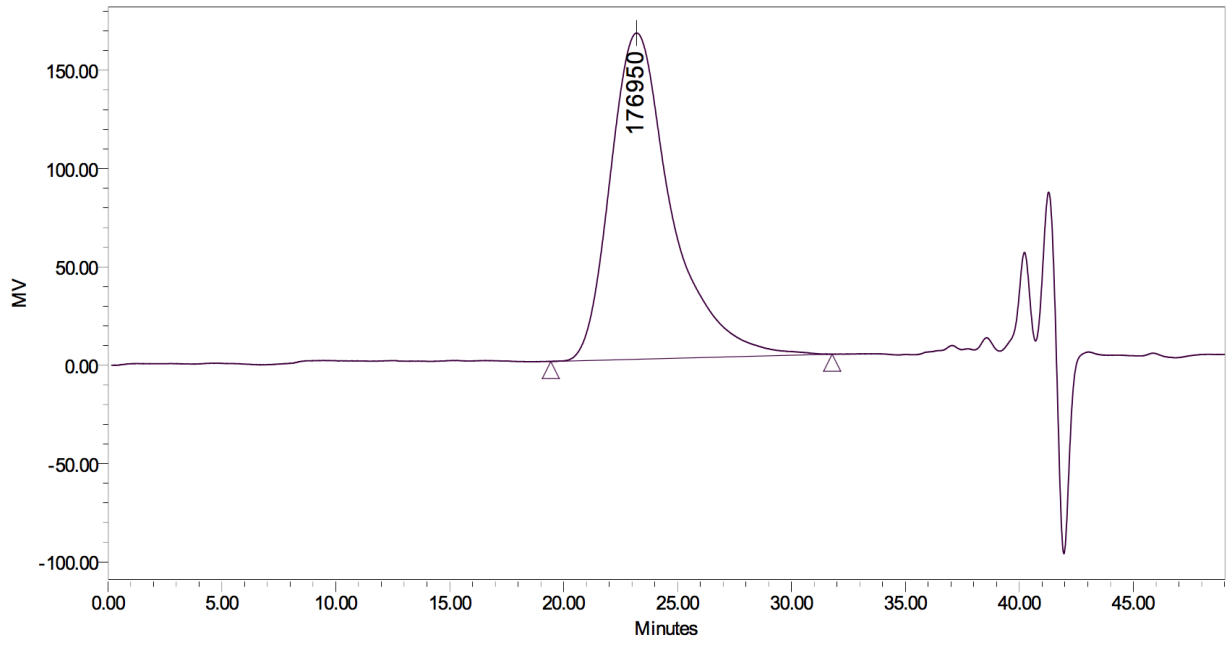


Figure 6 | Image of the large scale synthesis of P-1 catalyzed by Q-5.

Monomers **A-1** (91.36 g, 0.2 mol) and **B-1** (78.48 g, 0.2 mol) were combined in a dry 1 L three-neck round-bottom flask equipped with a Teflon™-coated magnetic stir bar, a thermometer, and a reflux condenser. The flask was purged with nitrogen gas, to which dry NMP (50 mL) was added. The flask was put into a pre-heated oil bath (130 °C, oil temperature). Monomers were gradually dissolved in NMP, and the internal temperature stabilized at 123 °C. Under vigorous stirring, catalyst **Q-5** (0.1 M in dry CH_3CN, 2.0 mL, 0.0002 mol) was added. The reaction initiated instantaneously. The internal temperature first rose to 135 °C, then quickly dropped to 100 °C ~ 110 °C because of the refluxing of TBSF. The polymerization reaction was allowed to run for 1 h, during which course the reaction mixture turned highly viscous and the internal temperature stabilized at around 120 °C. The flask was subsequently cooled to room temperature. TBSF was then distilled out from the reaction mixture as colorless oil at 80 °C under gentle vacuum conditions (49.1 g, 91% yield, Fig. 7). After the distillation, 250 mL of DMF was added to the reaction flask to dissolve the polymer at 120 °C. The warm DMF solution was then slowly dropped into 2 L methanol with vigorous mechanical stirring at room temperature. White **P-1** fibers precipitated in methanol, which was collected via filtration, then dried at 70 °C for 12 h to give 112.7 g dry

polymer (M_n^{ps} = 110 kDa, PDI = 1.7, Fig. 7 & 8), DSC (T_g = 89.6 ^oC, Fig. 9) and TGA (5% decomposition at 370.3 ^oC, Fig. 10) analysis. The cyclic oligomer in **P-1** is between 3 wt.%- 4 wt.% based on ^1H NMR analysis.

Figure 7 | Dry P-1 as fibrous solid (left) and TBSF in a plastic bottle (right).



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		110926	191634	176950	304964	459222	1.727585	1.591389	2.396351

Figure 8 | GPC trace of the P-1.

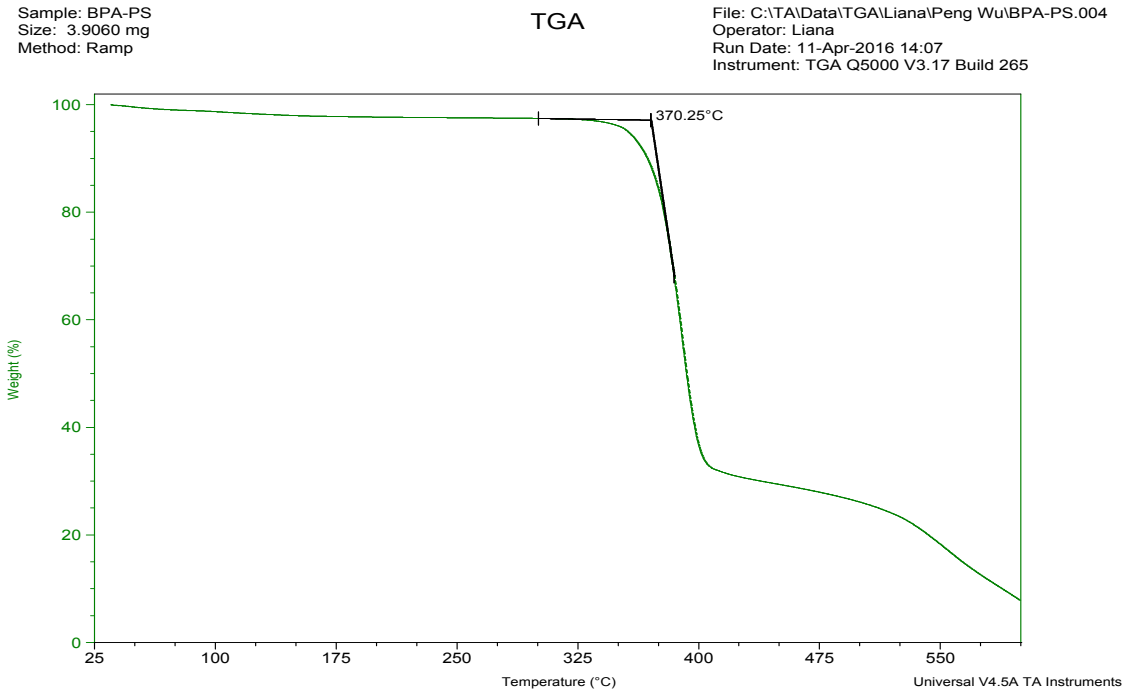


Figure 9 | Thermal gravimetric analysis (TGA) of P-1 (5 % weight loss at 370.3 ^{o}C).

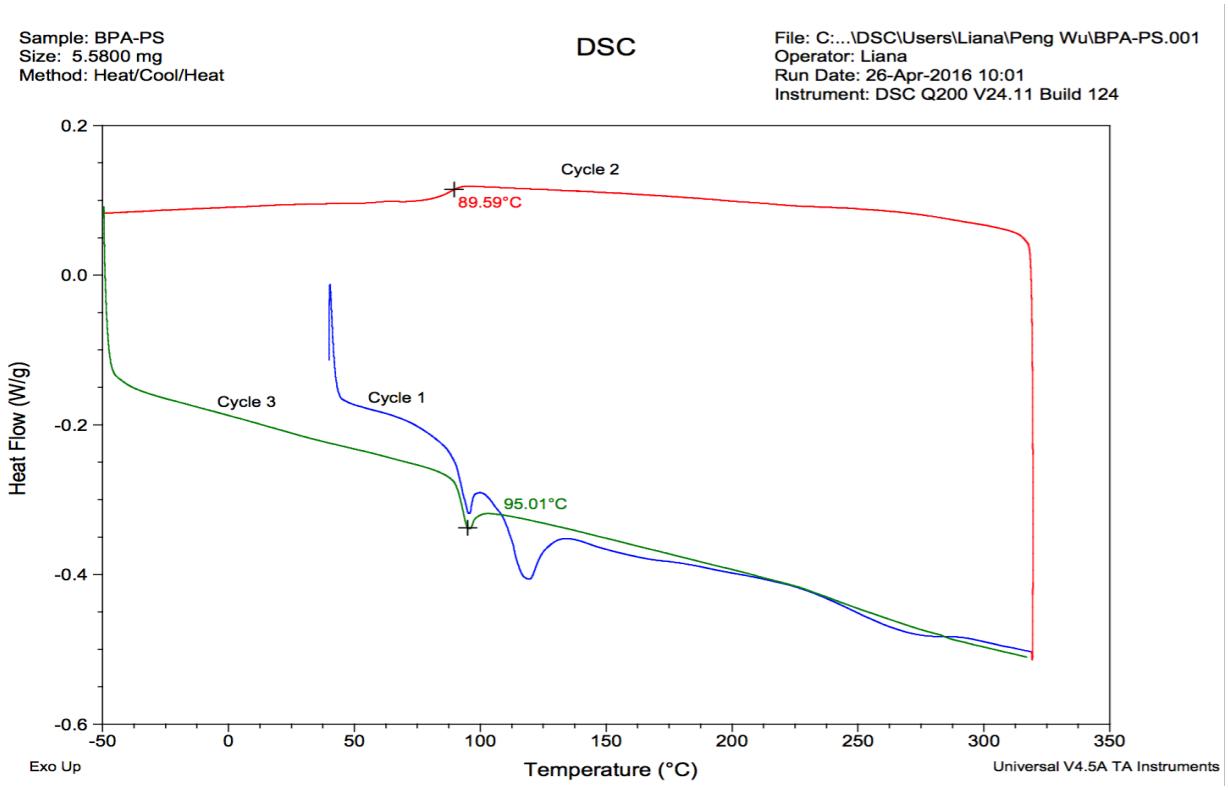
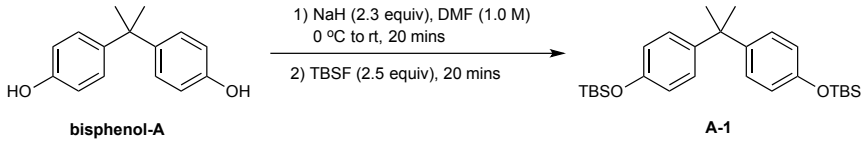


Figure 10 | Differential scanning calorimetry (DSC) analysis of P-1.

2-9, The preparation of monomer A-1 from bisphenol-A and TBSF



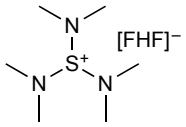
bisphenol-A **A-1**

A 50 mL three-neck flask, equipped with a stir bar, was purged with nitrogen gas. Bisphenol-A (1.14 g, 5 mmol) was dissolved in 5 mL dry DMF in the flask. The flask was placed into an ice-water bath, then 460 mg sodium hydride (NaH, 60% in mineral oil, 11.5 mmol) was added to the stirring solution. The reaction was allowed running for 5 min in ice-water bath, then 15 mins at room temperature. TBSF (1.68 g, 12.5 mmol) was then injected into the reaction mixture at room temperature. The reaction was initiated instantly and was slightly exothermic. After 20 mins at room temperature, the resulting mixture was poured into ice-water. White solid crashed out immediately, which was collected via filtration (washed with distilled water). The solid crude product was dissolved in 30 mL ethyl acetate and dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated on evaporator. 2.3 g white solid was obtained. It was further dried *in vacuo* (2.0 torr) at 75 ^{o}C for 2 hours to give 2.19 g pure **A-1** (96% yield).

3, Analytical Section

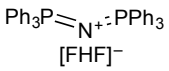
3-1, Spectroscopic data of catalysts

(*Note: all NMR spectra of the bifluoride and poly(hydrogen fluoride) catalysts were recorded in PTFE tube at room temperature.*)



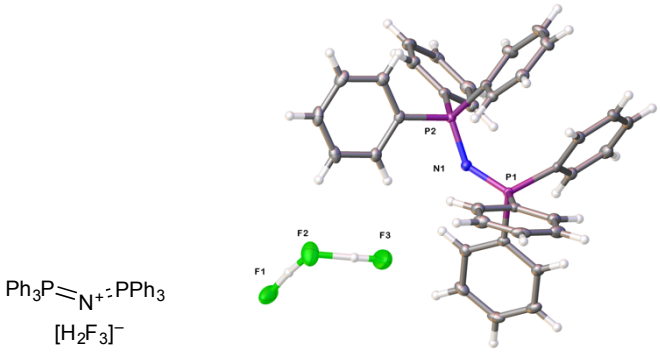
Tris(dimethylamimo)sulfonium bifluoride (Q-5)[5,8]

Q-5 was prepared following procedure **2-3-2**. White solid. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ-149.81 (m). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 2.88. Anal. Calcd. for $C_6H_{19}F_2N_3S$: C, 35.45; H, 9.42; N, 20.67; F, 18.69; Found: C, 35.16; H, 9.66; N, 20.91; F, 18.64.



Bis(triphenyl-λ5-phosphanylidene)ammonium hydrogendifluoride (Q-10, PNP$^+$[FHF]$^-$)[9]

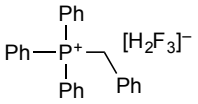
Q-10 was prepared following procedure **2-3-1**. Colorless crystalline. ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 14.44 (br, 1H), 7.75 (t, J = 7.7 Hz, 6H), 7.67 (dd, J = 13.1, 7.7 Hz, 12H), 7.59 – 7.55 (m, 12H). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -163.81 (br). ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 134.02, 132.74 – 132.58 (m), 129.89 – 129.69 (m), 127.64 (dd, J = 107.7, 2.6 Hz). ^{31}P NMR (162 MHz, Acetonitrile-d_3) δ 21.72. Anal. Calcd. for $C_{36}H_{35}F_2NO_2P_2$ (PNP$^+$[FHF]$^-$ •2H_2O): C, 70.47; H, 5.75; N, 2.28; F, 6.19; Found: C, 70.21; H, 5.76; N, 2.41; F, 7.71.



Bis(triphenyl-λ5-phosphanylidene)ammonium dihydrogentrifluoride (PNP$^+$[H_2F_3]$^-$)

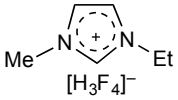
PNP$^+$[H_2F_3]$^-$ was prepared following procedure **2-3-3**. Colorless crystalline (from CH_2Cl_2/Et_2O). ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 13.69 (br), 7.75 (t, J = 7.3 Hz, 6H), 7.67 (dd, J = 12.6, 7.8 Hz, 12H), 7.58 – 7.56 (m, 12H). ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 134.02, 132.74 – 132.58

(m), 129.95 – 129.62 (m), 127.64 (dd, J = 107.7, 2.6 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -166.69 (br). ^{31}P NMR (162 MHz, Acetonitrile-d_3) δ 21.97.



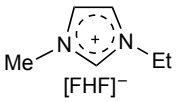
Benzyltriphenylphosphonium hydrogendifluoride ($[PhCH_2PPh_3]^+[H_2F_3]^-$)[10]

$[PhCH_2PPh_3]^+[H_2F_3]^-$ was prepared following procedure **2-3-3**. Colorless crystalline (from MeOH/Et_2O). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.76 (m, 3H), 7.67 – 7.56 (m, 12H), 7.26 – 7.21 (m, 1H), 7.13 (t, J = 7.5 Hz, 2H), 6.95 (dd, J = 7.9, 2.4 Hz, 2H), 4.89 (d, J = 14.4 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-d) δ -167.97 (br, 3F). Anal. Calcd. for $C_{25}H_{24}F_3P$: C, 72.81; H, 5.87. Found: C, 72.78; H, 6.25.



1-Ethyl-3-methylimidazolium trihydrogentetrafluoride ($EMI^+[H_3F_4]^-$)

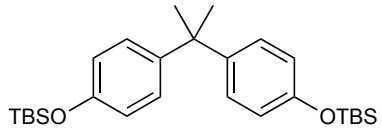
$EMI^+[H_3F_4]^-$ was prepared following procedure **2-3-6**. Colorless liquid. ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 11.76 (s, 3H), 8.53 (s, 1H), 7.42 (s, 1H), 7.36 (s, 1H), 4.17 (q, J = 7.3 Hz, 2H), 3.83 (s, 3H), 1.45 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 137.03, 124.85, 123.18, 46.03, 36.90, 15.68. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -173.52. Anal. Calcd. for $C_6H_{15}F_4N_2$: C, 37.89; H, 7.42; N, 14.73; F, 39.96. Found: C, 37.88; H, 7.43, N, 15.09, F, 36.24, Cl (residual) < 0.1 mol%.



1-Ethyl-3-methylimidazolium hydrogendifluoride ($EMI^+[FHF]^-$)

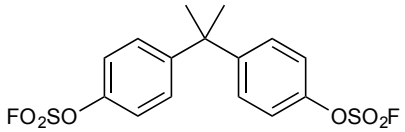
$EMI^+[FHF]^-$ was prepared following procedure **2-3-6**. Waxy solid. ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 14.62 (s, 1H), 9.32 (s, 1H), 7.48 (s, 1H), 7.43 (s, 1H), 4.19 (q, J = 7.3 Hz, 2H), 3.85 (s, 3H), 1.43 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 138.42, 124.60, 122.95, 45.71, 36.67, 15.75. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -123.81. Anal. Calcd. for $C_6H_{13}F_2N_2$: C, 47.99; H, 8.05; N, 18.65; F, 25.30. Found: C, 44.06; H, 7.76, N, 17.52, F, 28.33.

3-2, Spectroscopic data of monomers.



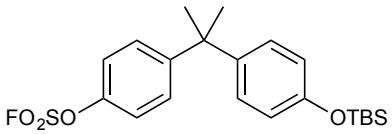
4,4'-(Propane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(tert-butyldimethylsilane) (A-1).[1]

A-1 was prepared following procedure **2-1-1**. White solid (99% yield). m.p. 82-84 ^{o}C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.09 – 7.02 (m, 4H), 6.74 – 6.67 (m, 4H), 1.61 (s, 6H), 0.97 (s, 18H), 0.18 (s, 12H). GC-MS (EI), $[M]^{+}$, m/z = 456.4.



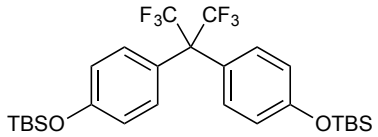
4,4'-(Propane-2,2-diyl)bis(4,1-phenylene) disulfofluoridate (B-1).[1]

B-1 was prepared following procedure **2-1-2**. Colorless crystalline (crystallized from Hexane, 96% yield). m.p. 51-53 ^{o}C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 8H), 1.70 (s, 6H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 37.27 (s, 2F). GC-MS (EI), $[M]^{+}$, m/z = 392.1.



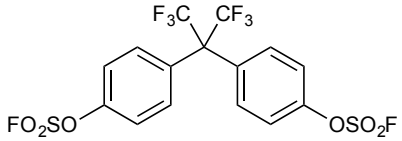
4-(2-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)propan-2-yl)benzenesulfonic hypofluorous anhydride (AB-1)

AB-1 was prepared following procedure **2-1-3**. Colorless liquid, 15.2 g (86% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 2H), 7.27 – 7.19 (m, 2H), 7.12 – 7.03 (m, 2H), 6.82 – 6.73 (m, 2H), 1.68 (s, 6H), 1.00 (s, 9H), 0.22 (s, 6H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ 37.06 (s, 1F); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.73, 152.01, 147.92, 142.11, 128.72, 127.64, 120.14, 119.52, 42.34, 30.90, 25.67, 18.17, -4.39. GC-MS (EI), m/z = 424.2 ($[M]^{+}$), 409.2, 303.2, 275.2, 195.1, 73.1.



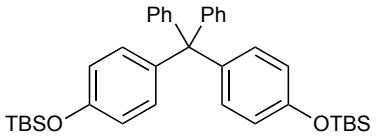
(((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (A-2)[1]

A-2 was prepared following procedure **2-1-1**. White solid (84% yield). m.p. 164-166 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.6 Hz, 4H), 6.83 (d, *J* = 8.6 Hz, 4H), 1.01 (s, 18H), 0.25 (s, 12H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.39 (s, 6F). GC-MS (EI), $[M]^+$, m/z = 564.3.



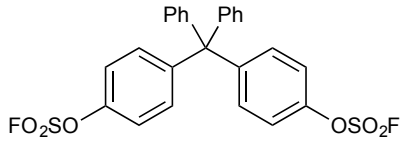
(perfluoropropane-2,2-diyl)bis(4,1-phenylene) bis(sulfurofluoridate) (B-2)[1]

B-2 was prepared following procedure **2-1-2**. Colorless crystalline (crystallized from Hexane, 92% yield). m.p. 127-129 ^{o}C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.7 Hz, 4H), 7.44 – 7.39 (m, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 38.44 (s, 2F), -64.05 (s, 6F). GC-MS (EI), $[M]^+$, m/z = 500.0.



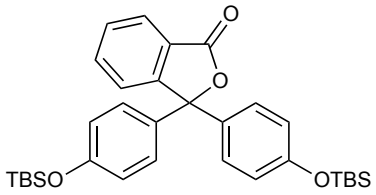
bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylmethane (A-3)

A-3 was prepared following procedure **2-1-1**. White solid (94% yield). m.p. 172-174 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.17 (m, 4H), 7.14 – 7.11 (m, 6H), 6.97 (d, *J* = 8.7 Hz, 4H), 6.66 (d, *J* = 8.7 Hz, 4H), 0.93 (s, 18H), 0.15 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.93, 147.77, 140.20, 132.61, 131.57, 127.71, 126.20, 119.09, 64.17, 26.12, 18.62, -3.92. GC-MS (EI), m/z = 580.5 ($[M]^+$), 503.4, 373.3, 158.2, 73.1.



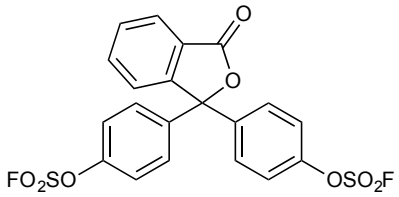
(diphenylmethylene)bis(4,1-phenylene) bis(sulfurofluoridate) (B-3)

B-3 was prepared following procedure **2-1-2**. White solid (98% yield). m.p. 169-171 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 8H), 7.26 – 7.23 (m, 6H), 7.16 – 7.13 (m, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 37.67 (s, 2F). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.66, 147.34, 145.60, 133.28, 131.17, 128.50, 127.18, 120.47, 64.79. GC-MS (EI), m/z = 516.1 ([M]$^{+}$), 439.1, 341.1.



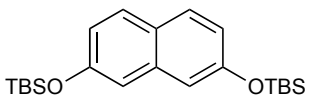
3,3-bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)isobenzofuran-1(3*H*)-one (A-4)

A-4 was prepared following procedure **2-1-1**. White solid (96% yield). m.p. 123-125 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 4H), 6.77 (d, *J* = 8.7 Hz, 4H), 0.97 (s, 18H), 0.19 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.28, 156.26, 153.10, 134.42, 134.07, 129.53, 128.95, 126.26, 126.04, 124.51, 120.18, 92.12, 26.05, 18.57, -3.98. GC-MS (EI), m/z = 546.4 ([M]$^{+}$), 502.4, 297.2, 73.1.



(3-oxo-1,3-dihydroisobenzofuran-1,1-diyl)bis(4,1-phenylene) bis(sulfurofluoridate) (B-4)[1]

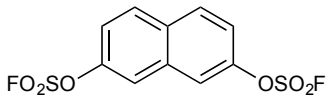
B-4 was prepared following procedure **2-1-2**. White solid (97% yield). m.p. 95-97 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.80 (td, *J* = 7.6, 1.2 Hz, 1H), 7.66 (td, *J* = 7.5, 1.0 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 4H), 7.39 – 7.35 (m, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 37.99 (s, 2F). GC-MS (EI), m/z = 482.1 ([M]$^{+}$), 339.1, 307.1, 104.1.



2,7-bis((*tert*-butyldimethylsilyl)oxy)naphthalene (A-5)

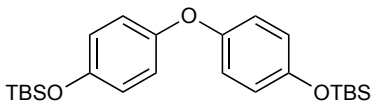
A-5 was prepared following procedure **2-1-1**. White solid (92% yield). m.p. 56-58 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 2.3 Hz, 2H), 6.96 (dd, *J* = 8.8,

2.3 Hz, 2H), 1.06 (d, *J* = 0.9 Hz, 18H), 0.28 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.31, 136.49, 129.45, 125.55, 120.26, 114.32, 26.19, 18.70, -3.86. GC-MS (EI), m/z = 388.3 ([M]$^+$).



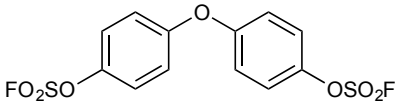
Naphthalene-2,7-diyl bis(sulfurofluoridate) (B-5)[1]

B-5 was prepared following procedure **2-1-2**. White solid (93% yield). m.p. 121-123 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.9 Hz, 2H), 7.91 (d, *J* = 2.1 Hz, 2H), 7.57 (dd, *J* = 8.9, 2.1 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 38.19 (s, 2F). GC-MS (EI), m/z = 324.0 ([M]$^+$), 213.1, 130.2, 102.1.



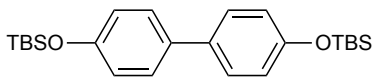
((oxybis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (A-6)[1]

A-6 was prepared following procedure **2-1-1**. Colorless liquid (98% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.88 – 6.80 (m, 4H), 6.80 – 6.73 (m, 4H), 0.98 (s, 18H), 0.18 (s, 12H). GC-MS (EI), m/z = 430.3 ([M]$^+$), 181.1, 73.1.



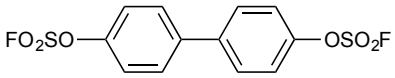
oxybis(4,1-phenylene) bis(sulfurofluoridate) (B-6)[1]

B-6 was prepared following procedure **2-1-2**. White solid (91% yield). m.p. 53-55 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.1 Hz, 4H), 7.10 (d, *J* = 8.1 Hz, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 36.93 (s, 2F). GC-MS (EI), m/z = 366.0 ([M]$^+$), 283.1, 200.1, 64.1.



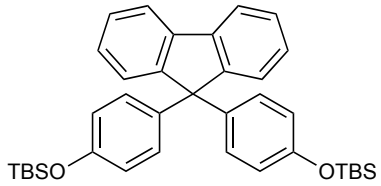
4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (A-7)

A-7 was prepared following procedure **2-1-1**. White solid (95% yield). m.p. 64-66 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.3 Hz, 4H), 6.91 (d, *J* = 8.3 Hz, 4H), 1.04 (s, 18H), 0.26 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.23, 134.54, 128.11, 120.74, 26.22, 18.72, -3.89. GC-MS (EI), m/z = 414.3 ([M]$^+$), 357.2, 150.2, 73.1.



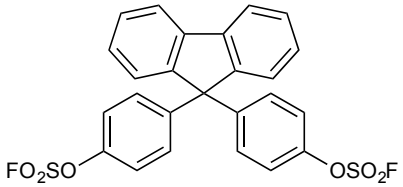
[1,1'-biphenyl]-4,4'-diyl bis(sulfurofluoridate) (B-7)

B-7 was prepared following procedure **2-1-2**. White solid (98% yield). m.p. 97-99 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.6 Hz, 4H), 7.48 (d, *J* = 8.6 Hz, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 37.68. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.30, 140.39, 129.62, 121.92. GC-MS (EI), m/z = 350.0 ([M]$^{+}$), 267.1, 156.1, 128.2.



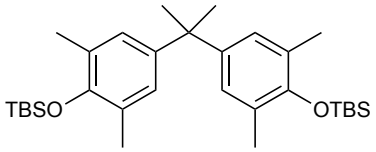
(((9*H*-fluorene-9,9-diyl)bis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (A-8)

A-8 was prepared following procedure **2-1-1**. White solid (89% yield), m.p. 209-211 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.1 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 4H), 6.70 (d, *J* = 8.5 Hz, 4H), 0.98 (s, 18H), 0.19 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.67, 152.36, 140.38, 139.05, 129.57, 127.98, 127.64, 126.59, 120.46, 119.82, 64.71, 26.08, 18.55, -3.96. GC-MS (EI), m/z = 578.4 ([M]$^{+}$), 371.3, 329.2, 157.2, 73.1.



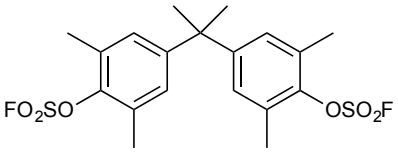
(9*H*-fluorene-9,9-diyl)bis(4,1-phenylene) bis(sulfurofluoridate) (B-8)

B-8 was prepared following procedure **2-1-2**. White solid (96% yield). m.p. 246-248 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.42 (td, *J* = 7.6, 7.0, 2.2 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.27 – 7.26 (m, 4H), 7.21 (d, *J* = 8.8 Hz, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 37.47 (s, 2F). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.95, 149.34, 146.49, 140.46, 130.36, 128.78, 128.68, 126.26, 121.27, 121.07, 64.89. GC-MS (EI), m/z = 514.1 ([M]$^{+}$), 431.2, 151.1.



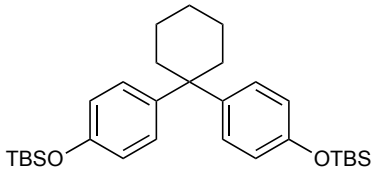
((propane-2,2-diylbis(2,6-dimethyl-4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (A-9)

A-9 was prepared following procedure **2-1-1**, purified by flash column chromatography (Hexane/EtOAc = 10:1). White solid (81% yield). m.p. 93-95 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 (s, 4H), 2.20 (s, 12H), 1.62 (s, 6H), 1.06 (s, 18H), 0.22 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.08, 144.01, 127.84, 127.60, 41.77, 31.56, 26.61, 19.22, 18.53, -2.42. GC-MS (EI), m/z = 512.4 ([M]$^{+}$), 497.4, 235.2, 73.1.



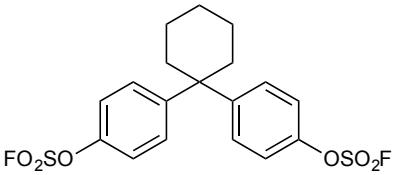
Propane-2,2-diylbis(2,6-dimethyl-4,1-phenylene) bis(sulfurofluoridate) (B-9)

B-9 was prepared following procedure **2-1-2**, purified by flash column chromatography (Hexane/EtOAc = 10:1). White solid (82% yield). m.p. 92-94 ^{o}C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.92 (s, 2H), 2.34 (s, 12H), 1.62 (s, 6H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 42.94 (s, 2F). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.26, 147.34, 130.80, 128.56, 42.76, 31.11, 17.16 (d, *J* = 2.8 Hz). GC-MS (EI), m/z = 448.1 ([M]$^{+}$), 433.1, 229.0.



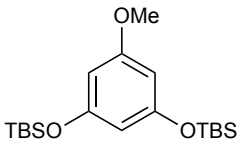
((cyclohexane-1,1-diylbis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (A-10)

A-10 was prepared following procedure **2-1-1**. White solid (94% yield), m.p. 72-74 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.6 Hz, 4H), 6.76 (d, *J* = 8.6 Hz, 4H), 2.23 – 2.20 (m, 4H), 1.60 – 1.49 (m, 6H), 1.01 (s, 18H), 0.22 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.43, 142.03, 128.51, 119.81, 45.62, 37.95, 26.94, 26.13, 23.40, 18.59, -3.94. GC-MS (EI), m/z = 496.4 ([M]$^{+}$), 453.3, 73.1.



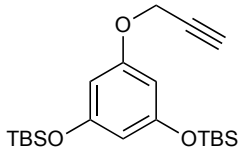
Cyclohexane-1,1-diylbis(4,1-phenylene) bis(sulfurofluoridate) (B-10)

B-10 was prepared following procedure **2-1-2**. White solid (97% yield). m.p. 91-93 ^{o}C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.33 (m, 4H), 7.26 – 7.24 (m, 4H), 2.29 – 2.26 (m, 4H), 1.56 – 1.52 (m, 6H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 37.29 (s, 2F). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.89, 148.40, 129.52, 121.13, 46.49, 37.56, 26.39, 23.03. GC-MS (EI), m/z = 432.1 ([M]$^{+}$), 376.0, 189.0.



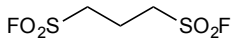
((5-methoxy-1,3-phenylene)bis(oxy))bis(*tert*-butyldimethylsilane) (A-11)

A-11 was prepared following procedure **2-1-1**, purified by flash column chromatography (Hexane/EtOAc = 5:1). White solid (61% yield). m.p. 36-37 ^{o}C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.05 (d, *J* = 1.9 Hz, 2H), 5.97 (t, *J* = 1.9 Hz, 1H), 3.73 (s, 3H), 0.97 (s, 18H), 0.19 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.49, 157.55, 105.39, 100.22, 55.59, 26.10, 18.63, -3.99. GC-MS (EI), m/z = 368.2 ([M]$^{+}$), 311.2, 269.0, 73.1.



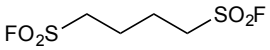
((5-(prop-2-yn-1-yloxy)-1,3-phenylene)bis(oxy))bis(*tert*-butyldimethylsilane) (A-12)

A-12 was prepared following procedure **2-1-1**, purified by flash column chromatography (Hexane/EtOAc = 10:1). Colorless oil (94% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.12 (d, *J* = 2.1 Hz, 2H), 6.00 (t, *J* = 2.1 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 2H), 2.52 (t, *J* = 2.4 Hz, 1H), 0.97 (s, 18H), 0.19 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.41, 157.54, 106.29, 101.14, 79.02, 75.86, 56.24, 26.10, 18.63, -4.00. GC-MS (EI), m/z = 392.2 ([M]$^{+}$), 335.2, 73.1.



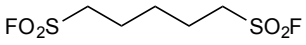
Propane-1,3-disulfonyl difluoride (B-13)

B-13 was prepared following procedure **2-1-5**. Crystalline solid from Hexane/EtOAc (73% yield for the fluorination step). m.p. 33-34 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.66 (q, *J* = 6.7 Hz, 4H), 2.61 (p, *J* = 6.7 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 54.52 (s, 2F). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 48.46 (d, *J* = 19.1 Hz), 18.63.



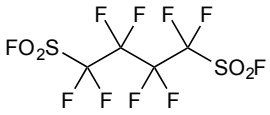
butane-1,4-disulfonyl difluoride (B-14)

B-14 was prepared following procedure **2-1-5**. Crystalline solid from Hexane/EtOAc (80% yield for the fluorination step). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.62 – 3.10 (m, 4H), 2.19 (m, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 54.56 (s, 2F). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 50.23 (d, *J* = 17.8 Hz), 22.27.



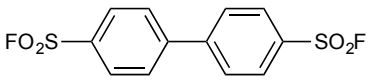
Pentane-1,5-disulfonyl difluoride (B-15)

B-15 was prepared following procedure **2-1-5**. Crystalline solid from Hexane/EtOAc (92% yield for the fluorination step). m.p. 29-31 ^{o}C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.41 (td, *J* = 7.5, 4.1 Hz, 4H), 2.03 (dd, *J* = 7.5, 8.0 Hz, 4H), 1.73 (p, *J* = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.94 (s, 2F). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 50.58 (d, *J* = 17.1 Hz), 26.27, 23.20.



1,1,2,2,3,3,4,4-octafluorobutane-1,4-disulfonyl difluoride (B-16)[4]

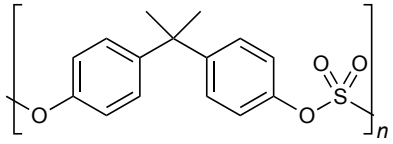
B-16 was prepared following procedure **2-1-6**. Colorless oil (27% yield at the fluorination step, challenging to isolate due to its low boil point). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 47.08 (2F), -108.03 (4F), -119.98 (4F).



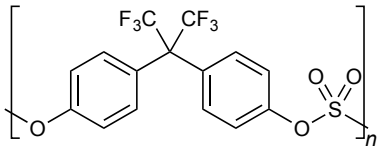
[1,1'-biphenyl]-4,4'-disulfonyl difluoride (B-17)[4]

B-17 was prepared following procedure **2-1-4**. White solid (79% yield). m.p. 193-195 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.0 Hz, 4H), 7.91 (d, *J* = 8.0 Hz, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 66.09 (s, 2F). GC-MS (EI), m/z = 318.0 ([M]$^{+}$), 251.1, 223.1, 152.2, 51.1.

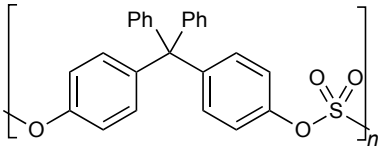
3-3, Spectroscopic data of polymers



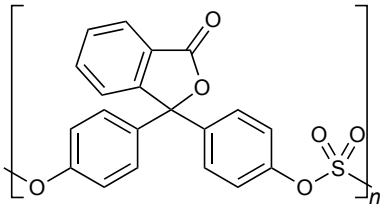
Polysulfate **P-1**,[1] prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.04 g). White fiber. ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.28 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 1.68 (s, 2H). M_n^{ps} = 92 kDa. PDI = 1.7. T_g (DSC) = 97.2 °C. T_d (5% weight loss, TGA) = 370.3 °C.



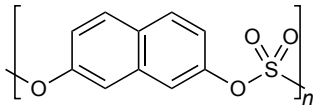
Polysulfate **P-2**,[1] prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.51 g). ^{1}H NMR (500 MHz, DMF-d_7) δ 7.85 – 7.80 (m, 4H), 7.76 – 7.72 (m, 4H); ^{19}F NMR (376 MHz, DMF-d_7) δ -63.85; ^{13}C NMR (126 MHz, DMF-d_7) δ 151.31, 132.93, 132.64, 124.47 (q, *J* = 285.4 Hz), 122.16. M_n^{ps} = 84 kDa. PDI = 1.6. T_g (DSC) = 106.8 °C. T_d (5% weight loss, TGA) = 397.7 °C.



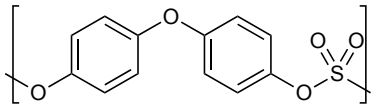
Polysulfate **P-3**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.70 g). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.38 – 7.31 (m, 8H), 7.29 – 7.25 (d, *J* = 8.8 Hz, 10H). ^{13}C NMR (126 MHz, DMF-d_7) δ 148.90, 146.84, 146.41, 133.11, 131.01, 128.60, 126.97, 121.07, 64.86. M_n^{ps} = 37 kDa. PDI = 1.5. T_g (DSC) = 158.2 °C. T_d (5% weight loss, TGA) = 340.7 °C.



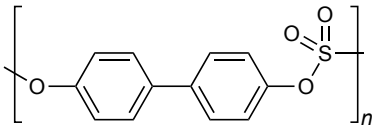
Polysulfate **P-4**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.56 g, the stereochemistry was not determined). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 8.03 (d, J = 7.6 Hz, 1H), 7.84 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.7 Hz, 4H), 7.39 (d, J = 8.6 Hz, 4H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 168.99, 150.96, 150.72, 140.57, 135.14, 130.47, 129.38, 126.63, 125.62, 124.40, 121.62, 90.15. M_n^{ps} = 37 kDa. PDI = 1.6. T_g (DSC) = 199.5 °C. T_d (5% weight loss, TGA) = 395.5 °C.



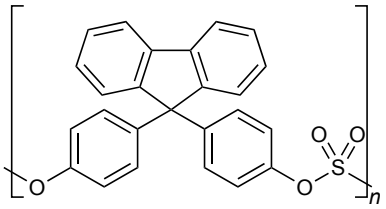
Polysulfate **P-5**,[1] prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 892 mg). ^{1}H NMR (500 MHz, DMF-d_7) δ 8.53 (d, J = 2.1 Hz, 2H), 8.38 (d, J = 9.1 Hz, 2H), 7.88 (dd, J = 9.1, 2.1 Hz, 2H). ^{13}C NMR (126 MHz, DMF-d_7) δ 149.50, 134.61, 131.60, 131.51, 121.56, 119.73. M_n^{ps} = 64 kDa. PDI = 1.7. T_g (DSC) = 100.4 °C. T_d (5% weight loss, TGA) = 356.6 °C.



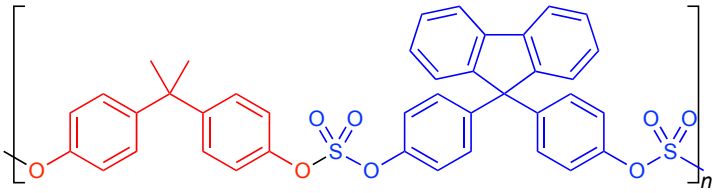
Polysulfate **P-6**,[1] prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.03 g). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.50 (d, J = 9.0 Hz, 4H), 7.20 (d, J = 9.0 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.37, 145.47, 122.99, 120.35. M_n^{ps} = 48 kDa. PDI = 2.1. T_d (5% weight loss, TGA) = 343.1 °C.



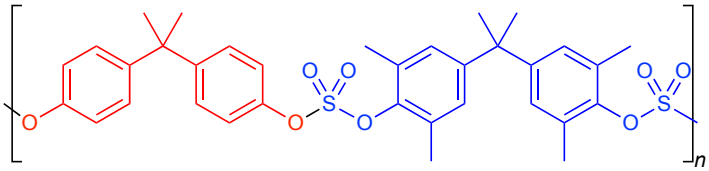
Polysulfate **P-7**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 987 mg). ^{1}H NMR (500 MHz, DMF-d_7) δ 8.05 (d, J = 8.7 Hz, 4H), 7.76 (d, J = 8.7 Hz, 4H). ^{13}C NMR (126 MHz, DMF-d_7) δ 150.69, 139.47, 129.64, 122.25. M_n^{ps} = 79 kDa. PDI = 1.7. T_g (DSC) = 120.4 °C. T_d (5% weight loss, TGA) = 350.9 °C.



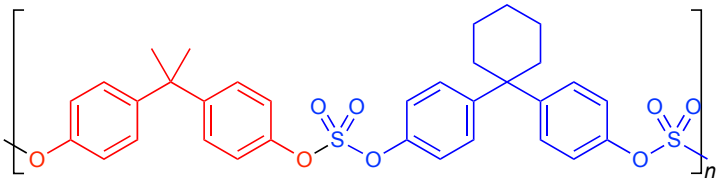
Polysulfate **P-8a**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.80 g). ^{1}H NMR (500 MHz, DMF-d_7) δ 8.07 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.43 – 7.36 (m, 5H). ^{13}C NMR (126 MHz, DMF-d_7) δ 150.48, 149.69, 146.01, 140.42, 130.28, 128.76, 128.72, 126.54, 121.74, 121.27, 65.00. M_n^{ps} = 52 kDa. PDI = 1.4. T_d (5% weight loss, TGA) = 353.5 °C.



Polysulfate **P-8b**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.63 g). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.82 (d, J = 7.3 Hz, 2H), 7.43 – 7.12 (m, 22H), 1.68 – 1.66 (m, 6H). ^{13}C NMR (126 MHz, DMF-d_7) δ 150.50, 150.42, 149.75, 148.88, 146.03, 140.46, 130.34, 130.29, 129.18, 128.78, 126.59, 121.74, 121.31, 121.23, 65.04, 43.04, 30.52. M_n^{ps} = 74 kDa. PDI = 1.6. T_d (5% weight loss, TGA) = 374.6 °C.

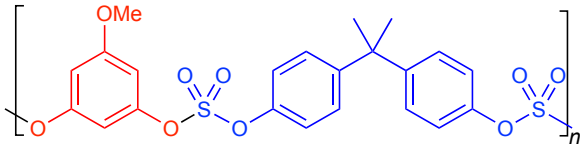


Polysulfate **P-9**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.28 g). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.41 – 7.35 (m, 8H), 7.11 – 7.08 (m, 4H), 2.45 – 2.40 (m, 12H), 1.81 (s, 6H), 1.74 (s, 6H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 150.15, 149.71, 148.95, 146.99, 131.45, 128.76, 128.30, 121.33, 43.13, 42.56, 30.90, 30.87, 17.35. M_n^{ps} = 57 kDa. PDI = 1.7. T_g (DSC) = 116.1 °C. T_d (5% weight loss, TGA) = 319.8 °C.

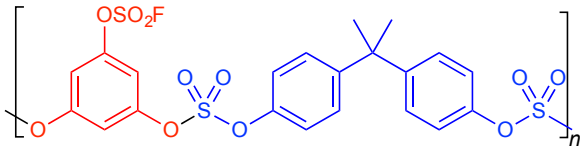


Polysulfate **P-10**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 1.18 g). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.43 – 7.41 (m, 4H), 7.39 – 7.28 (m, 12H),

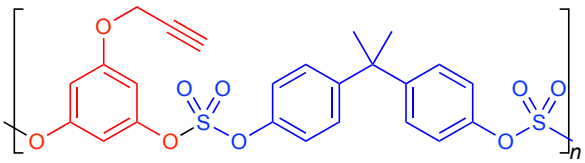
2.37 (br, 4H), 1.77 (s, 6H), 1.66 – 1.57 (m, 6H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 150.08, 148.87, 148.62, 148.13, 129.18, 128.82, 121.17, 120.97, 46.28, 43.09, 37.42, 30.87, 26.44, 23.11. M_n^{ps} = 94 kDa. PDI = 1.7. T_g (DSC) = 108.4 °C; T_d (5% weight loss, TGA) = 365.66 °C.



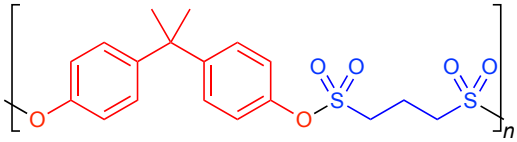
Polysulfate **P-11a**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 0.5 mol% **Q-5** was used as catalyst, 772 mg). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.38 (d, J = 8.8 Hz, 4H), 7.32 (d, J = 8.8 Hz, 4H), 7.05 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 2.0 Hz, 2H), 3.88 (s, 3H), 1.76 (s, 6H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 161.88, 151.48, 150.32, 148.72, 128.95, 120.97, 107.02, 106.85, 56.58, 43.14, 30.86. M_n^{ps} = 33 kDa. PDI = 1.5. T_g (DSC) = 72.6 °C. T_d (5% weight loss, TGA) = 213.2 °C.



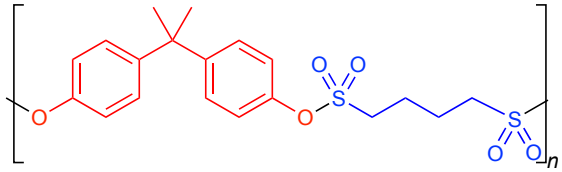
Polysulfate **P-11b**, prepared following the procedure described in Section **2-7** (1.0 mmol scale, 311 mg, 55% yield). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.56 – 7.19 (m, 11H), 1.71 (s, 6H). ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ 38.76 (s, 1F). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 151.34, 150.59, 150.23, 148.59, 129.11, 120.87, 115.72, 114.47, 43.20, 30.82. M_n^{ps} = 38 kDa. PDI = 1.9. T_d (5% weight loss, TGA) = 282.4 °C.



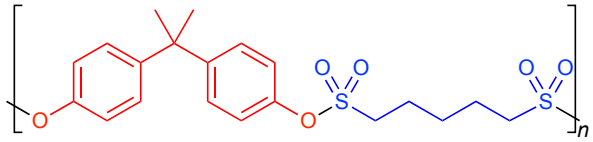
Polysulfate **P-12**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 5.0 mol% of **Q-5** was used as catalyst, 578 mg). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.37 – 7.33 (m, 8H), 7.14 – 7.04 (m, 3H), 4.80 (s, 2H), 2.70 (m, 1H), 1.77 (s, 6H). M_n^{ps} = 16 kDa. PDI = 1.3.



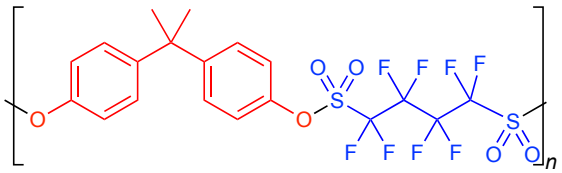
Polysulfonate **P-13**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 5.0 mol% of **Q-5** was used as catalyst, 615 mg). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.36 (d, J = 8.7 Hz, 4H), 7.26 (d, J = 8.7 Hz, 4H), 3.60 (t, J = 7.1 Hz, 4H), 2.68 (p, J = 7.3 Hz, 2H), 1.76 (s, 6H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 149.95, 147.31, 128.86, 121.93, 48.51, 43.05, 30.89, 19.00. M_n^{ps} = 23 kDa. PDI = 1.3. T_g (DSC) = 85.9 °C. T_d (5% weight loss, TGA) = 298.2 °C.



Polysulfonate **P-14**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 5.0 mol% of **Q-5** was used as catalyst, 583 mg). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.37 (d, J = 8.5 Hz, 4H), 7.26 (d, J = 8.5 Hz, 4H), 3.41 (m, 4H), 2.24 (m, 4H), 1.77 (s, 6H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 149.81, 147.40, 128.79, 121.93, 49.93, 43.02, 30.89, 22.63. M_n^{ps} = 13 kDa. PDI = 1.2. T_g (DSC) = 85.9 °C. T_d (5% weight loss, TGA) = 303.8 °C.

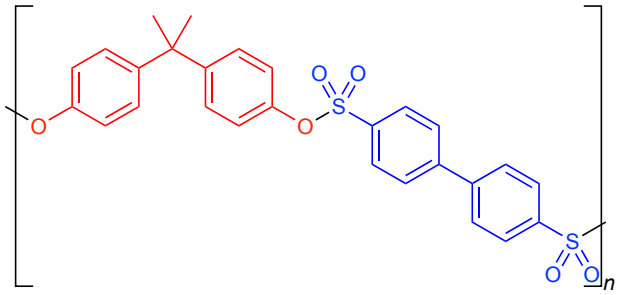


Polysulfonate **P-15**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 5.0 mol% **Q-5** was used as catalyst, 709 mg). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.38 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 8.5 Hz, 4H), 3.38 (t, J = 7.5 Hz, 4H), 2.10 (tt, J = 7.5, 7.6 Hz, 4H), 1.78 (m, 8H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 149.74, 147.49, 128.76, 121.96, 50.32, 43.02, 30.91, 26.95, 23.53. M_n^{ps} = 23 Da. PDI = 1.4. T_d (5% weight loss, TGA) = 204.7 °C. T_d (21% weight loss, TGA) = 352.7 °C.



Polysulfonate **P-16**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 5.0 mol% **Q-5** was used as catalyst, 811 mg). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.40 (d, J = 8.4 Hz, 4H), 7.31 (d, J = 8.4 Hz, 4H), 1.79 (s, 6H). ^{19}F NMR (376 MHz, Methylene

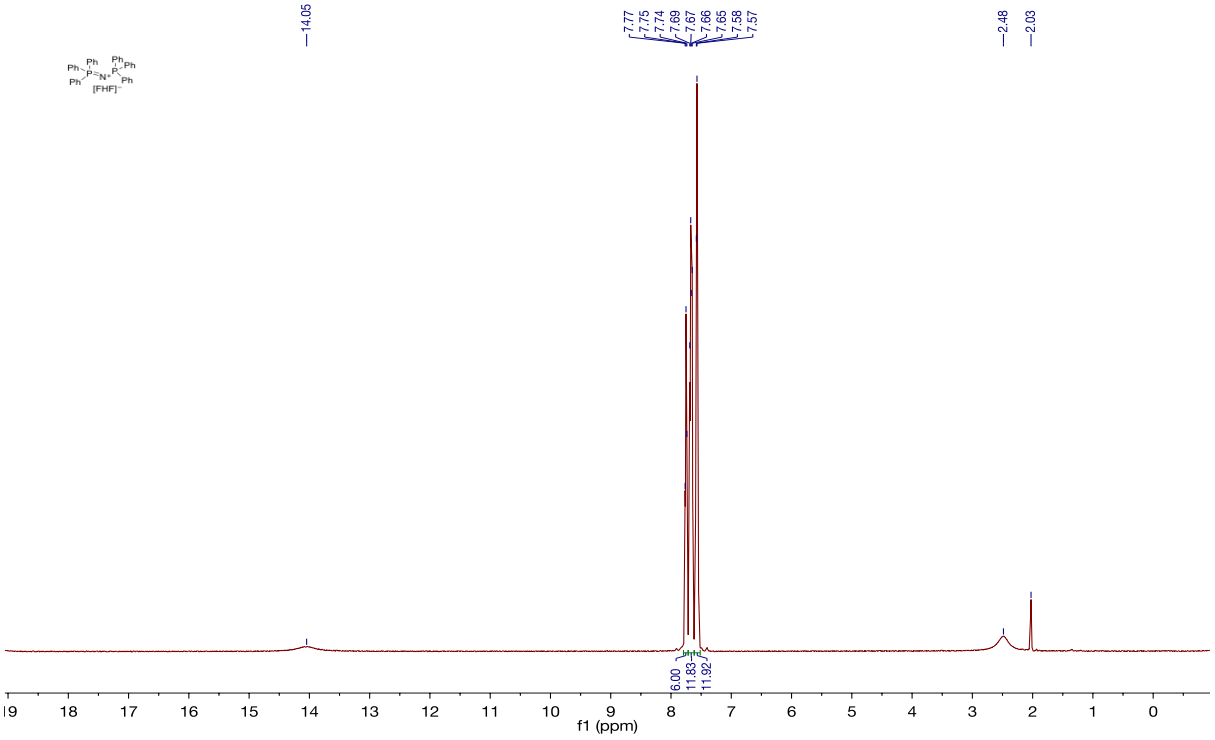
Chloride-d_2) δ -109.24 (s, 4F), -120.10 (s, 4F). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 150.75, 148.38, 129.05, 121.34, 115.20 (d, J = 304.8 Hz), 110.9 (d, J = 273.1 Hz), 43.23, 30.81. M_n^{ps} = 23 kDa. PDI = 1.3. T_d (5% weight loss, TGA) = 306.8 °C.



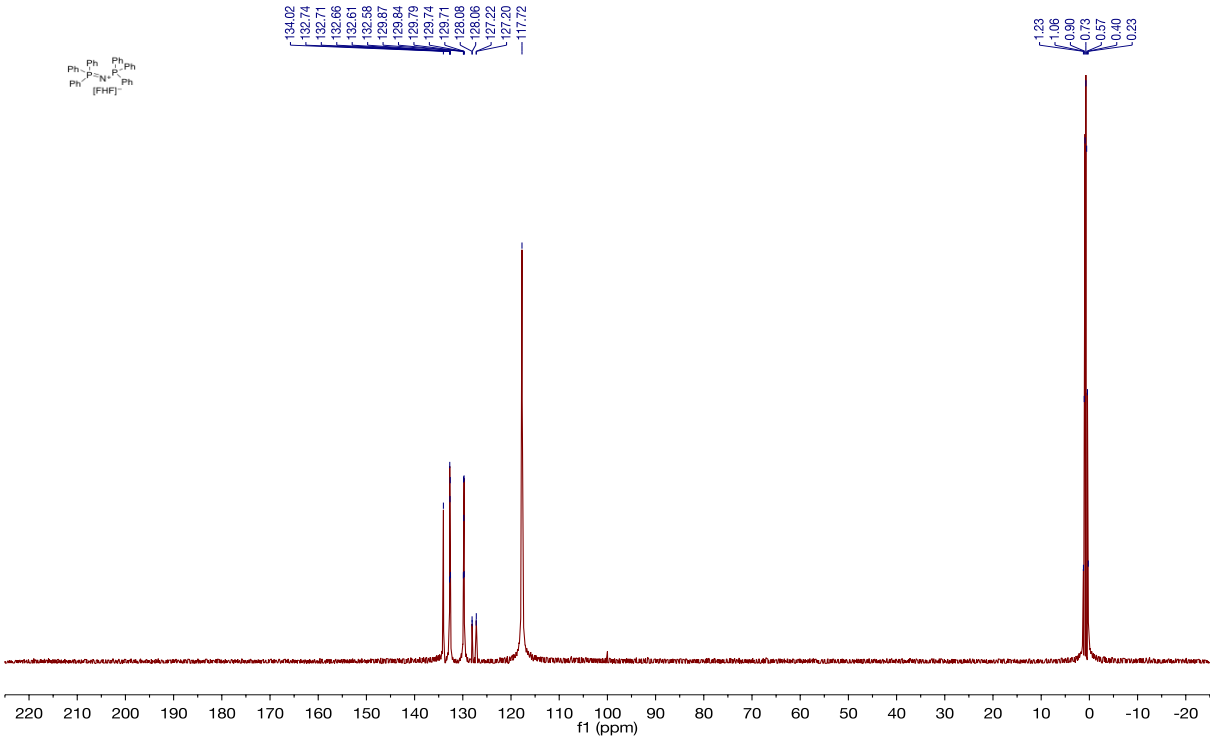
Polysulfonate **P-17**, prepared following the procedure described in Section **2-2-1** (2.0 mmol scale, 0.5 mol% **Q-5** was used as catalyst, 974 mg). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 8.02 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 149.77, 147.86, 145.05, 135.97, 129.50, 128.60, 128.50, 122.13, 42.95, 30.80. M_n^{ps} = 64578 Da. PDI = 1.5. T_g (DSC) = 176.2 °C; T_d (5% weight loss, TGA) = 392.8 °C.

3-4, Copies of the NMR spectra of new compounds

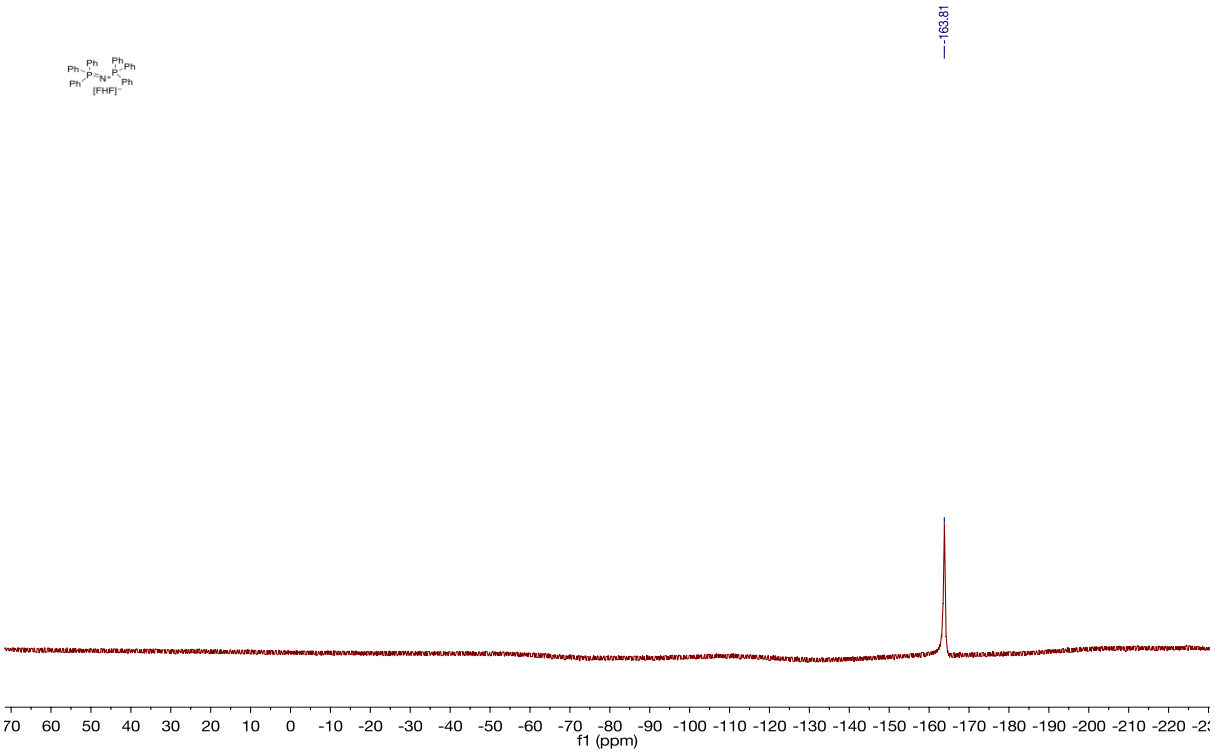
^{1}H NMR **($PNP^{+}[FHF]^{-}$)**



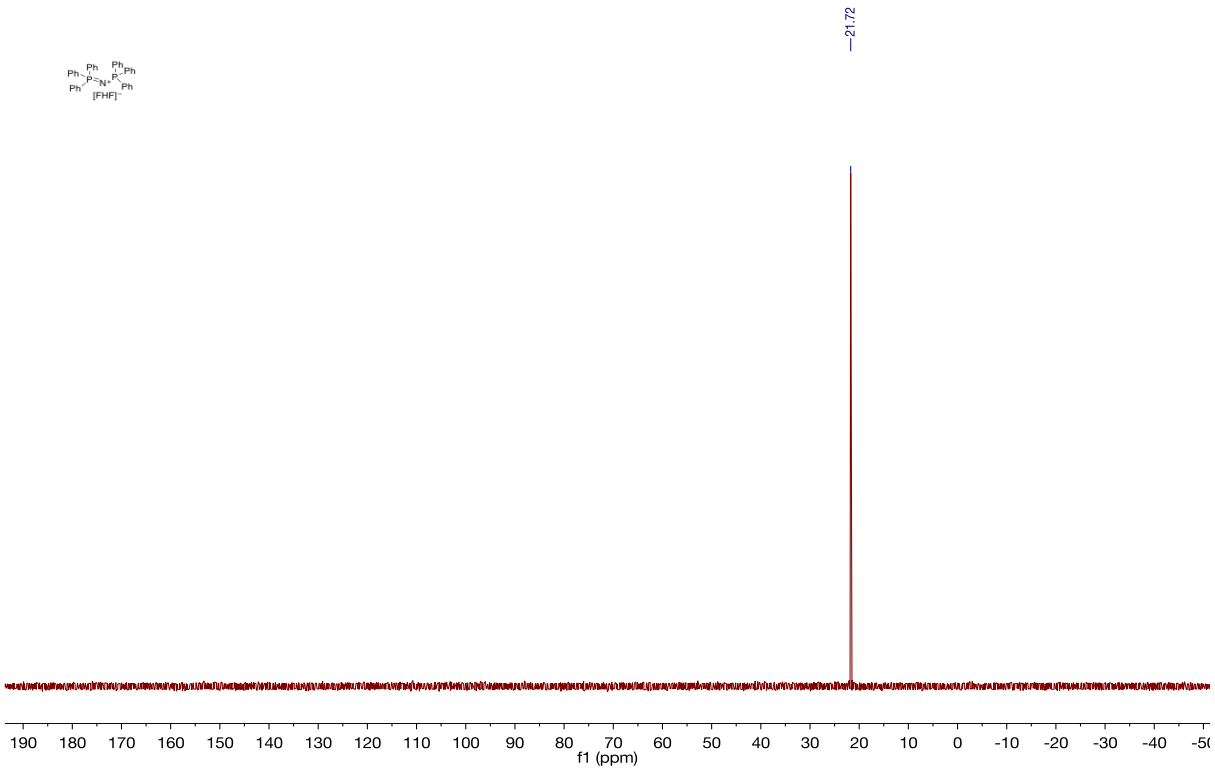
^{13}C NMR* **($PNP^{+}[FHF]^{-}$)**



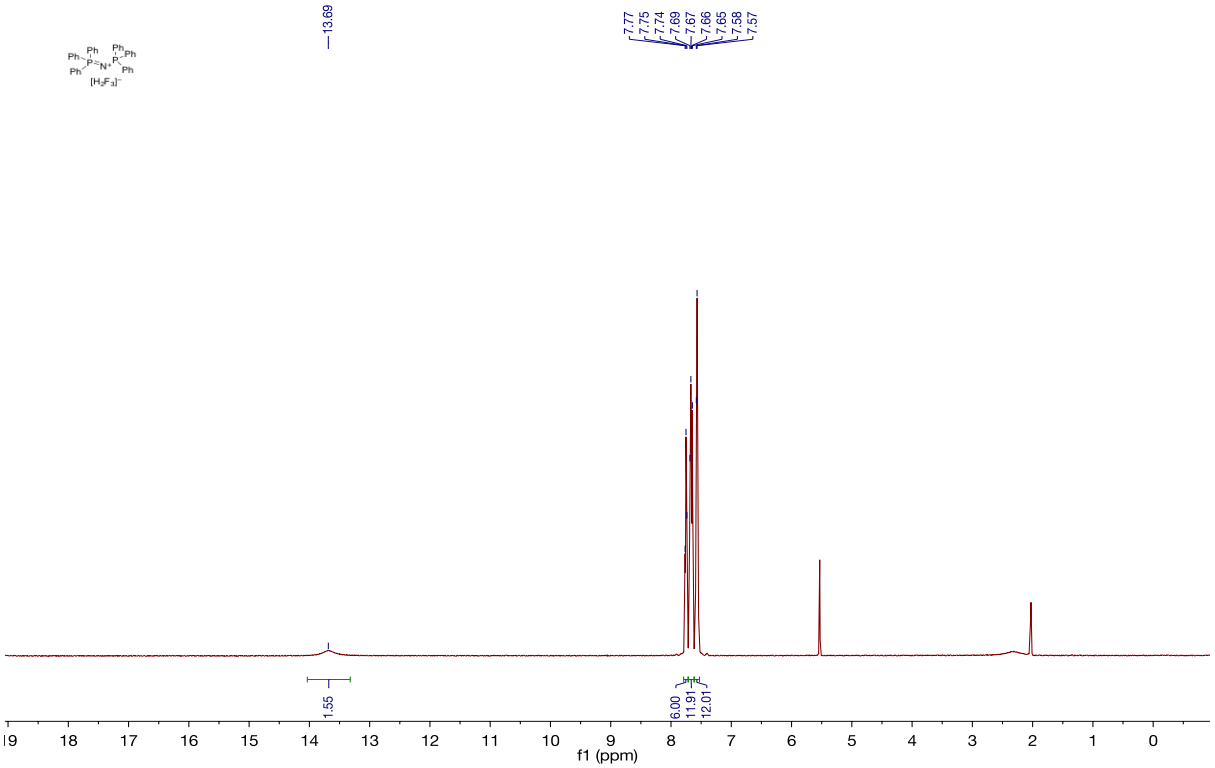
^{19}F NMR **(PNP^{+}[FHF]$^{-}$)**



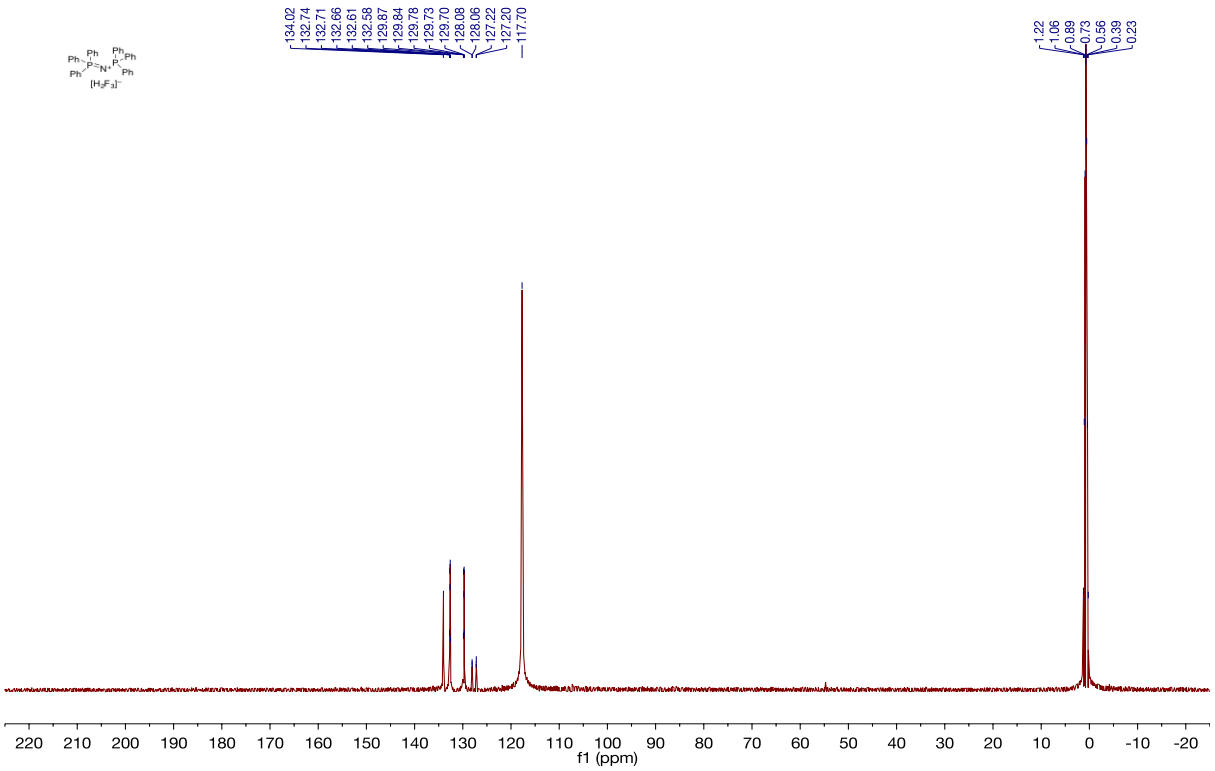
^{31}P NMR **(PNP^{+}[FHF]$^{-}$)**



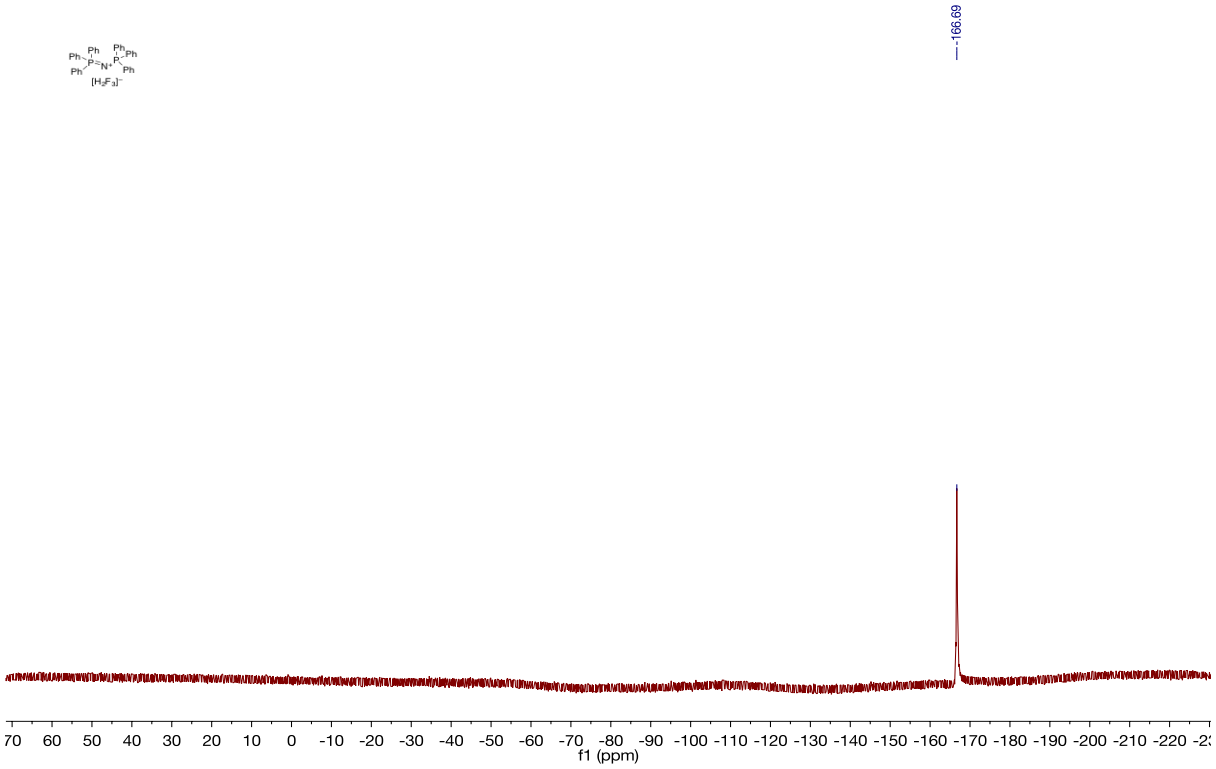
^{1}H NMR **($PNP^{+}[H_2F_3]^{-}$)**



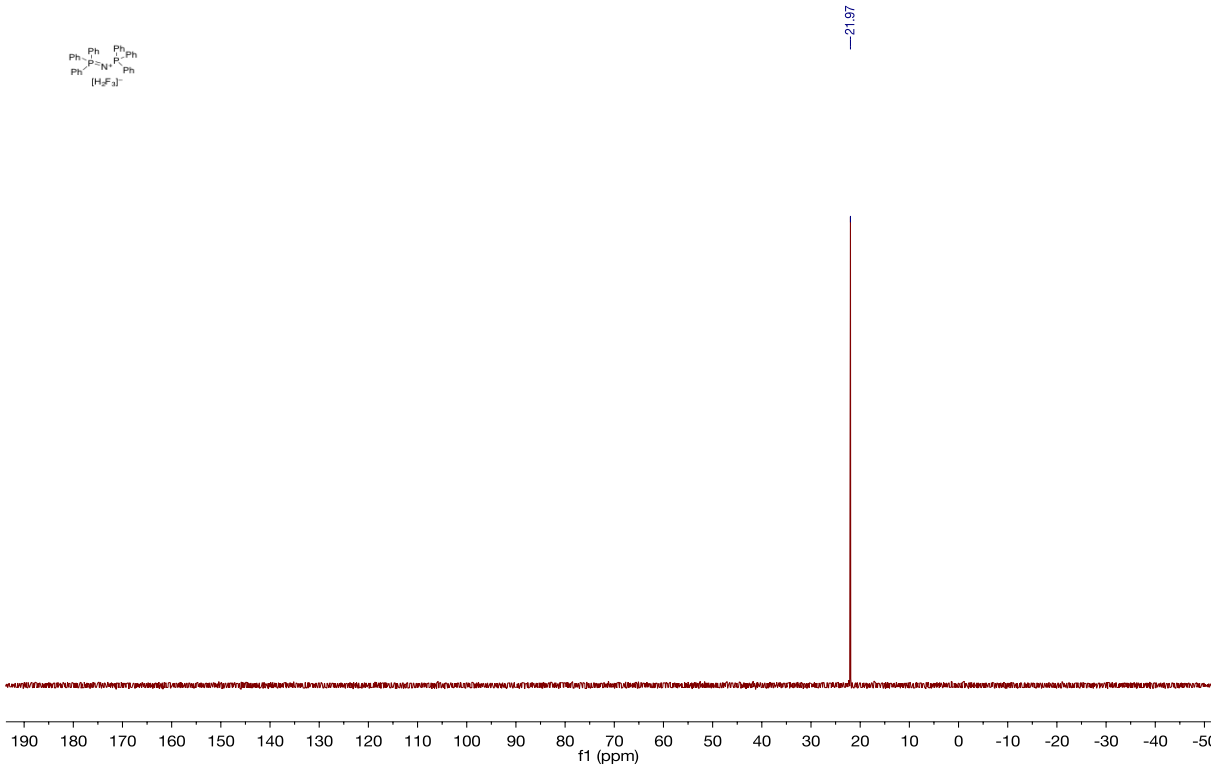
^{13}C NMR **($PNP^{+}[H_2F_3]^{-}$)**



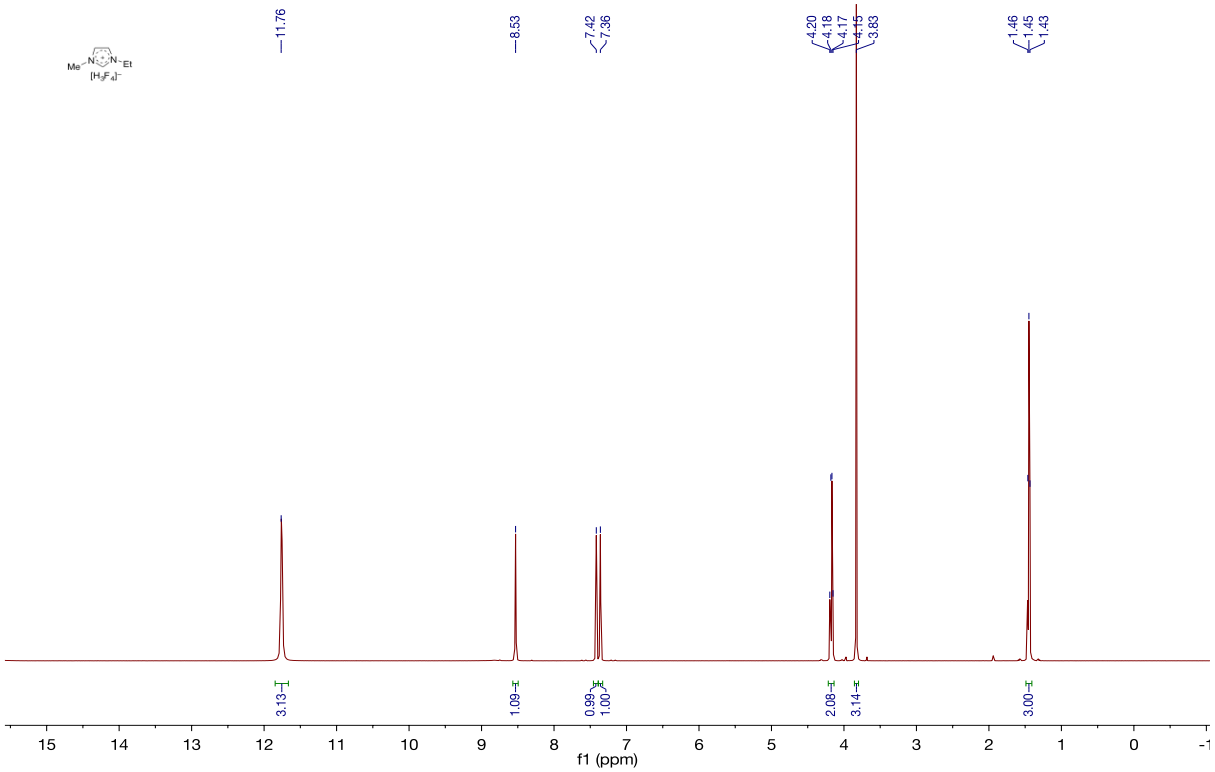
^{19}F NMR **($PNP^{+}[H_2F_3]^{-}$)**



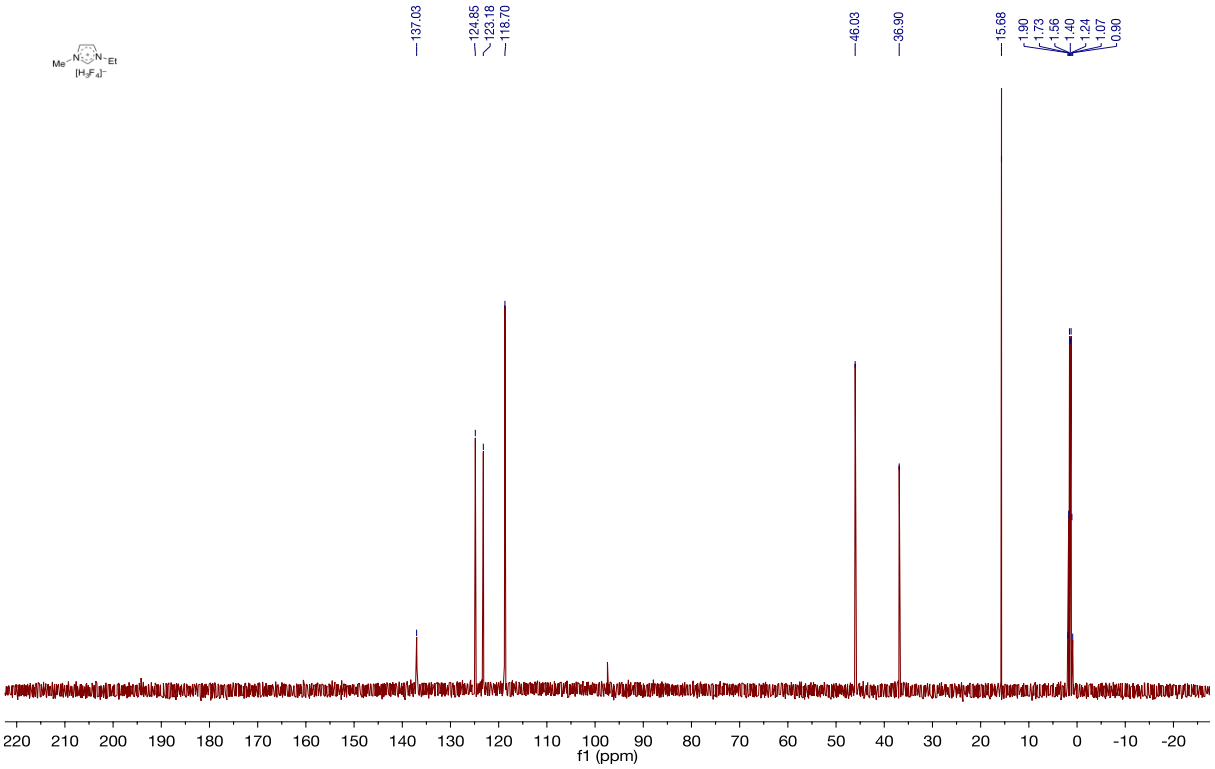
^{31}P NMR **($PNP^{+}[H_2F_3]^{-}$)**



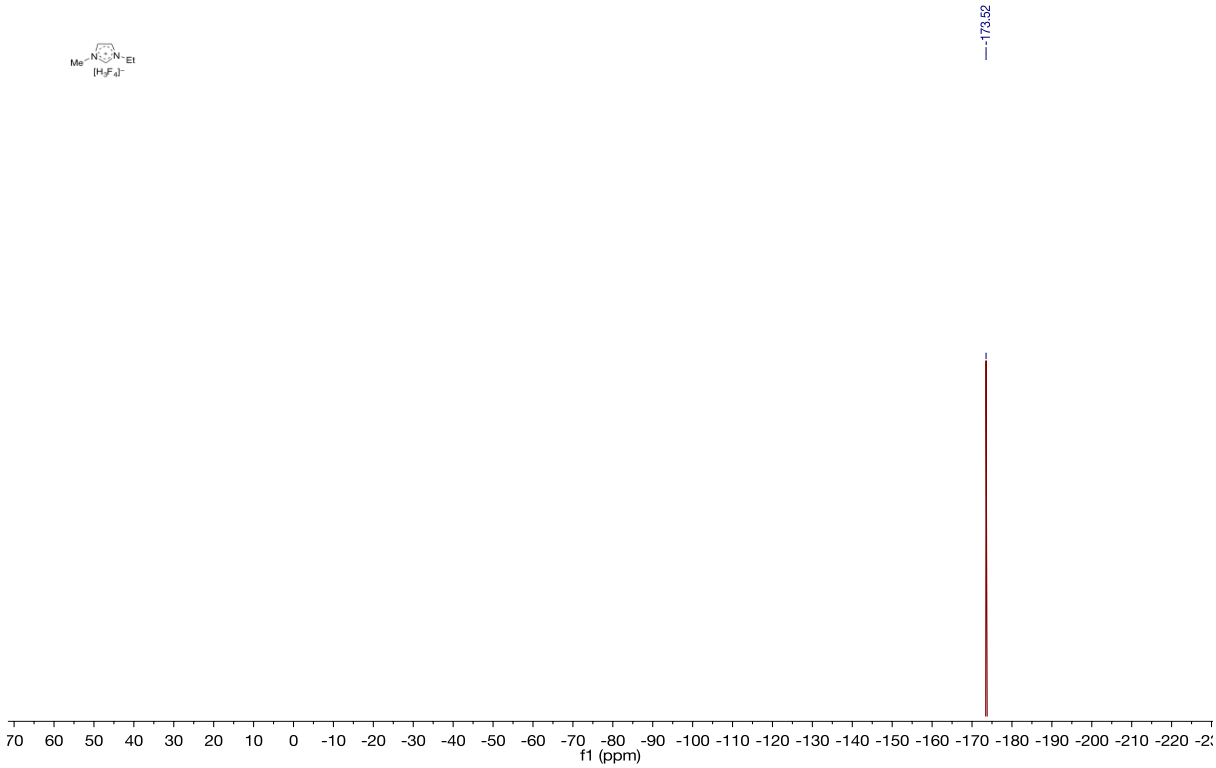
^{1}H NMR **($EMI^{+}[H_3F_4]^{-}$)**



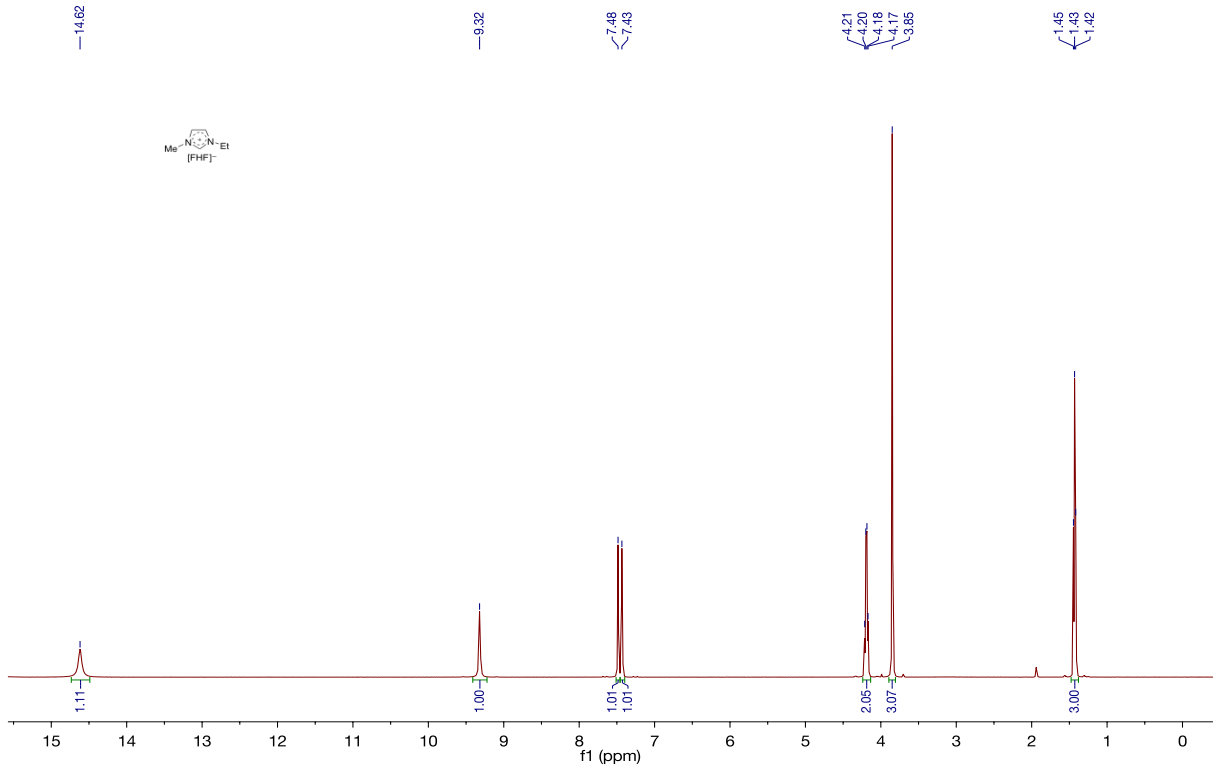
^{13}C NMR **($EMI^{+}[H_3F_4]^{-}$)**



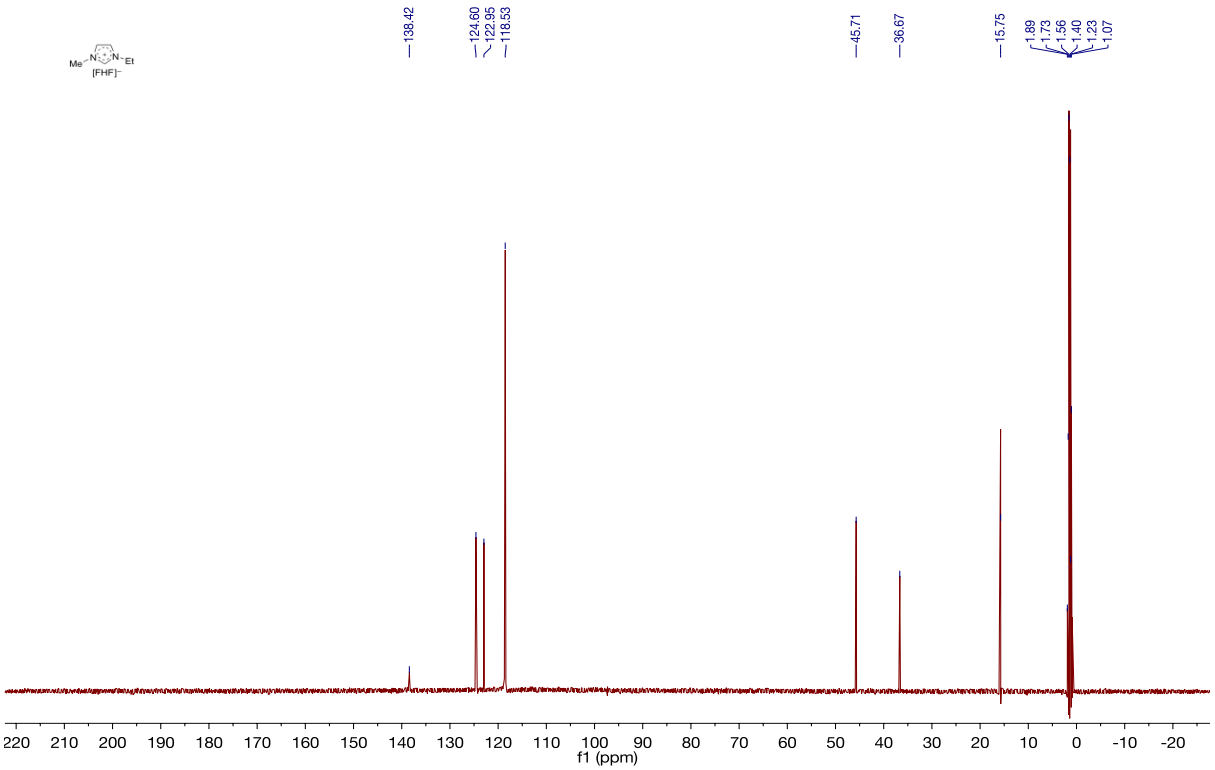
^{19}F NMR **($EMI^+[H_3F_4]^-$)**



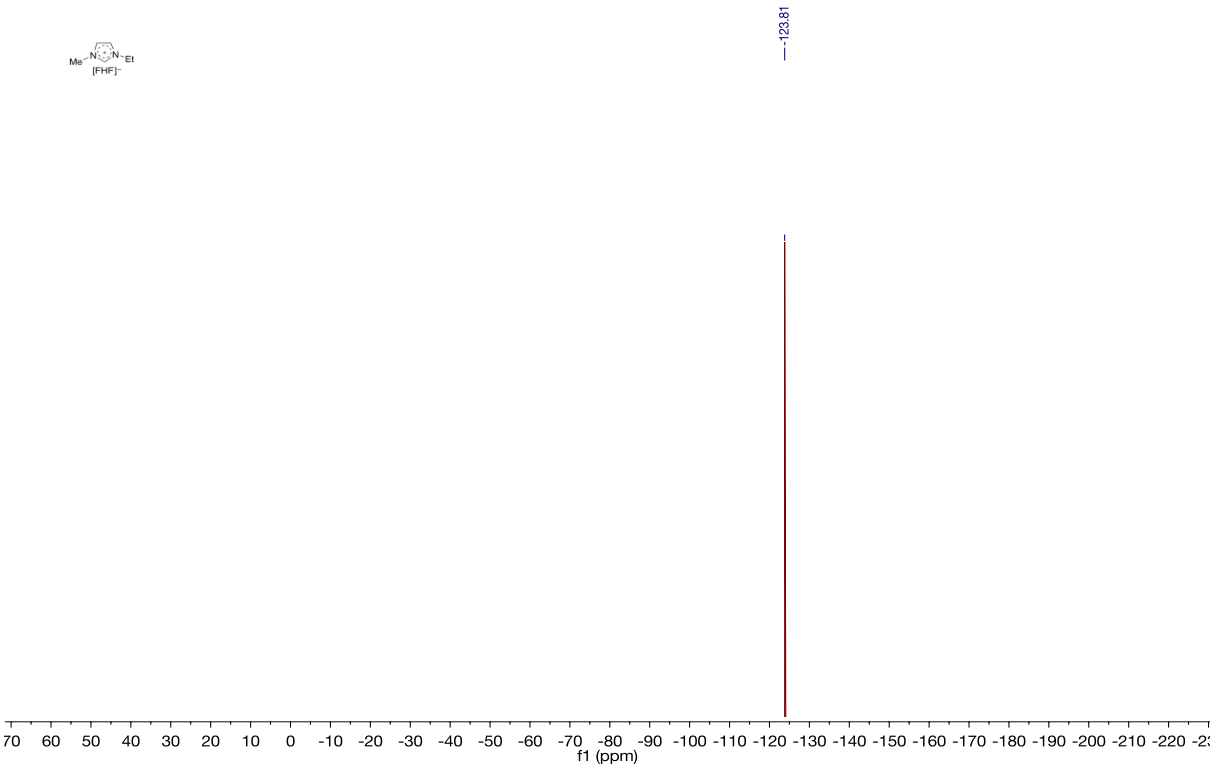
^{1}H NMR **($EMI^+[FHF]^-$)**



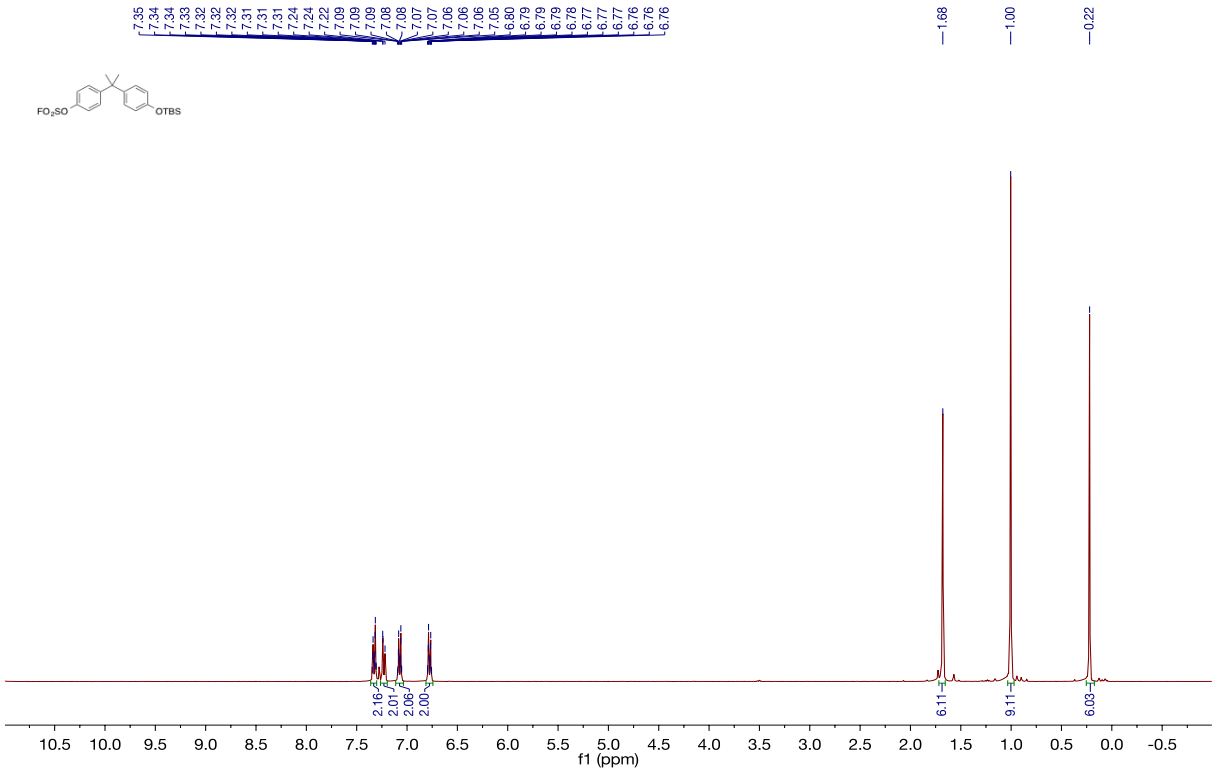
^{13}C NMR **($EMI^+[FHF]^-$)**



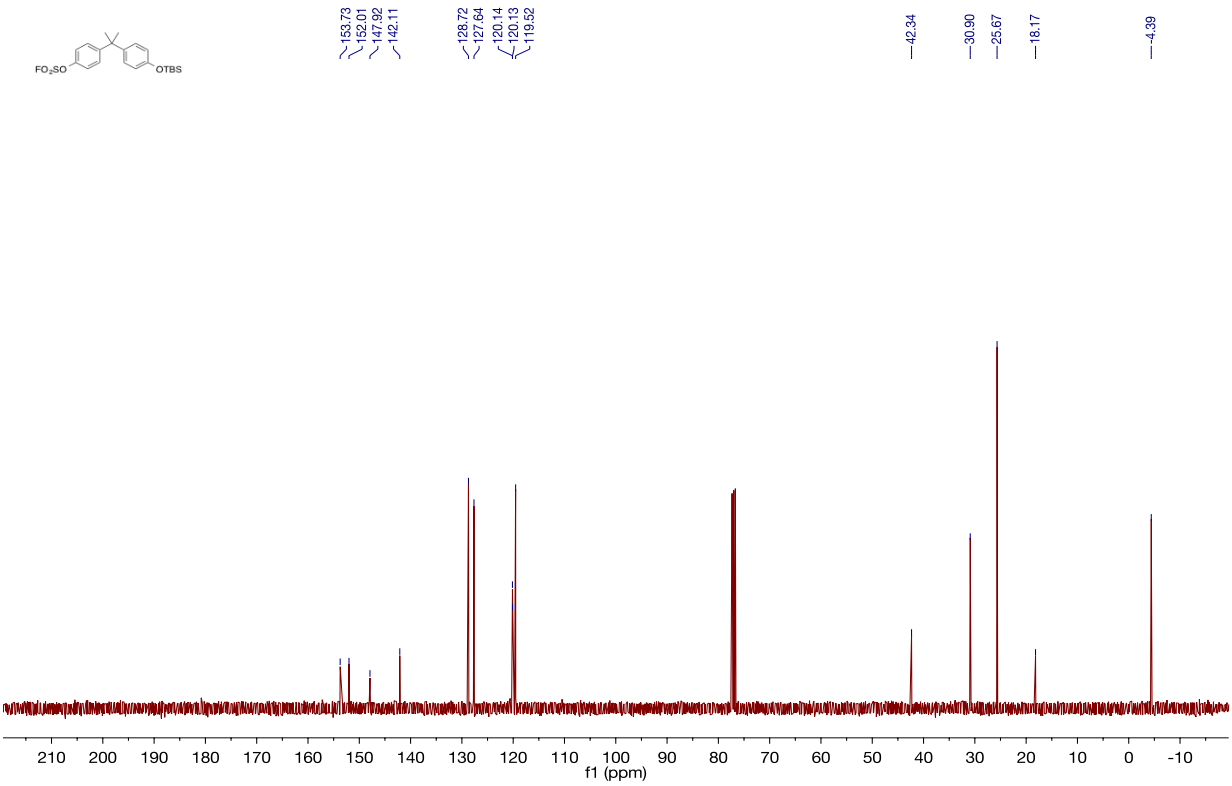
^{19}F NMR **($EMI^+[FHF]^-$)**



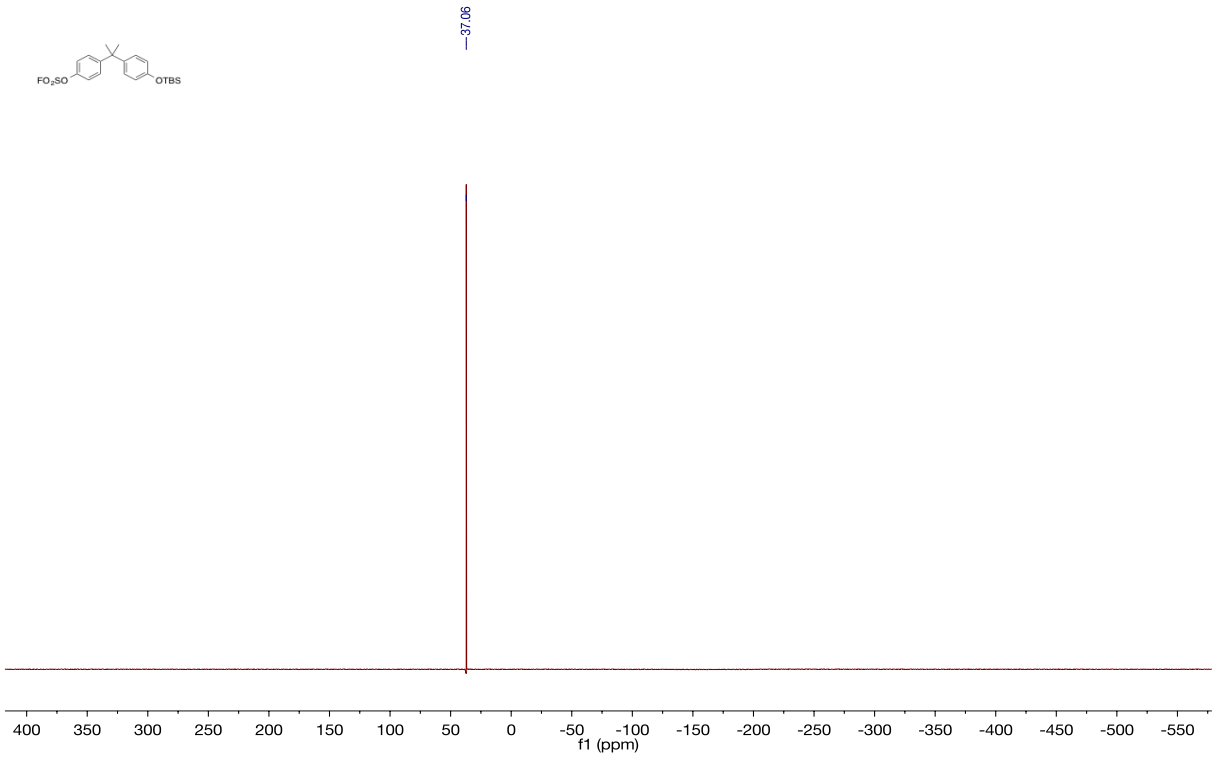
***^{1}H NMR* (AB-1)**



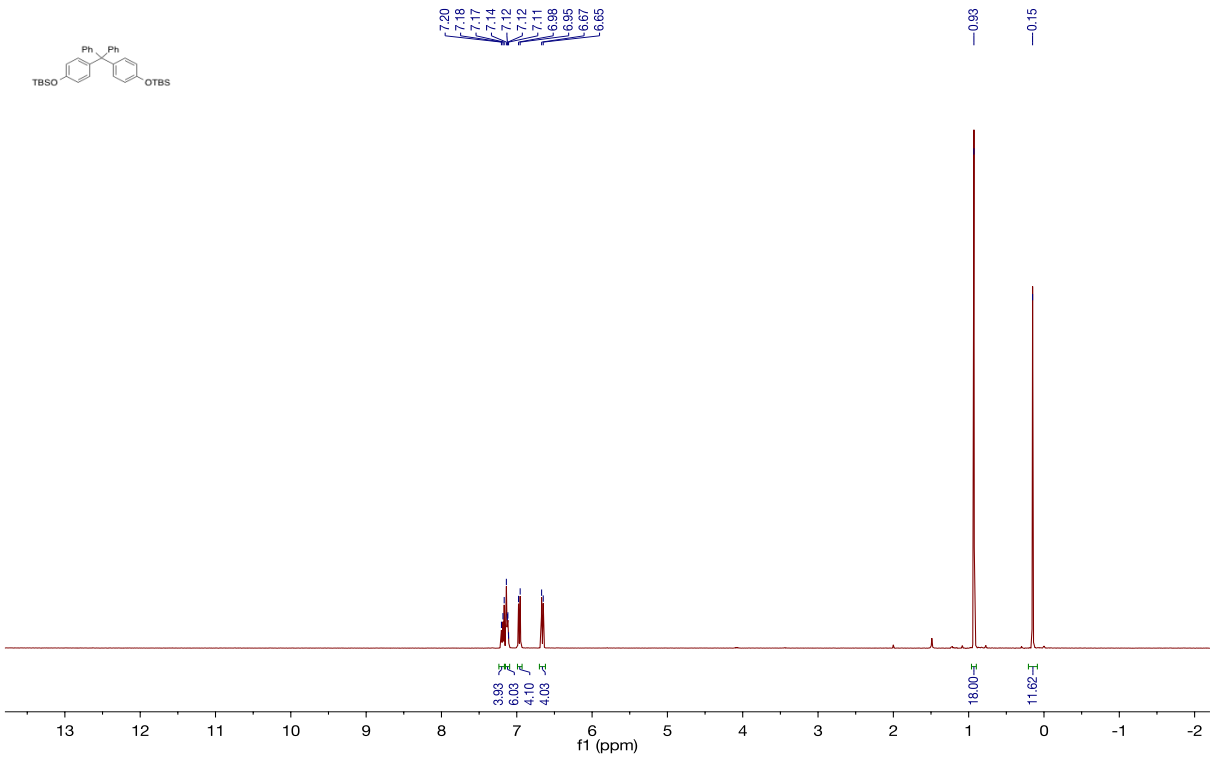
***^{13}C NMR* (AB-1)**



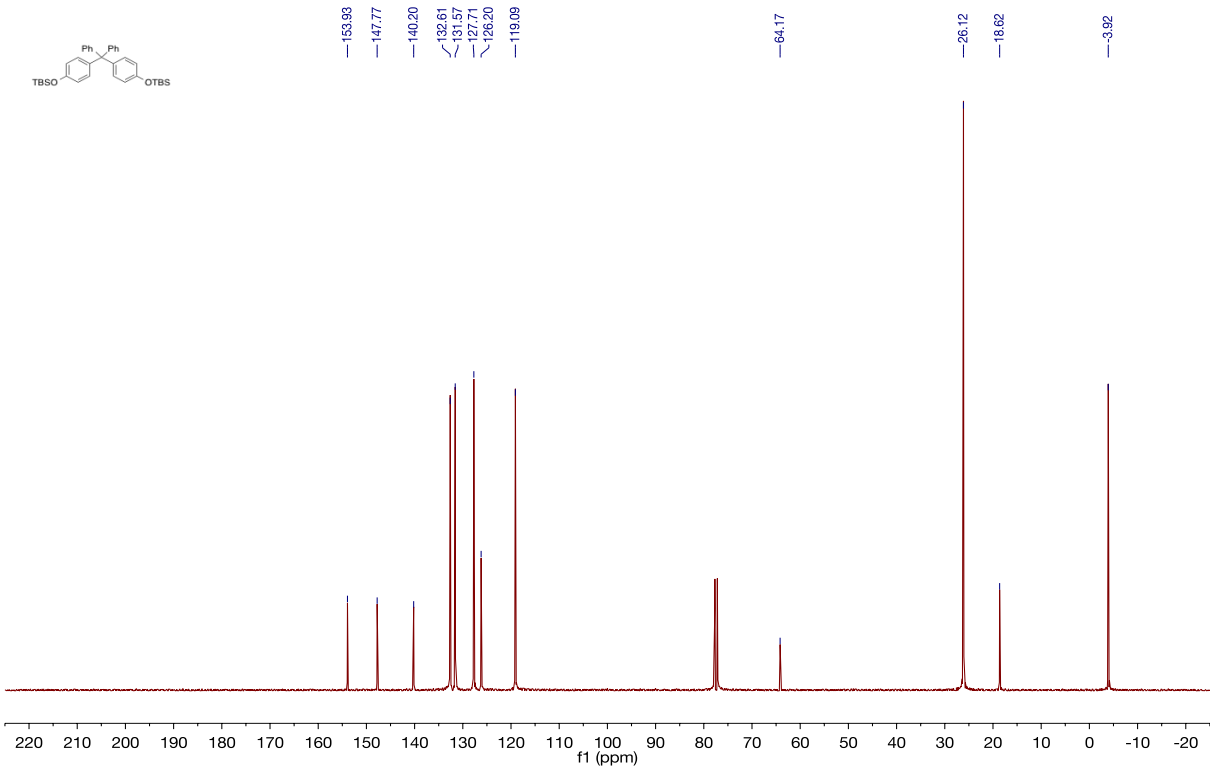
***^{19}F NMR* (AB-1)**



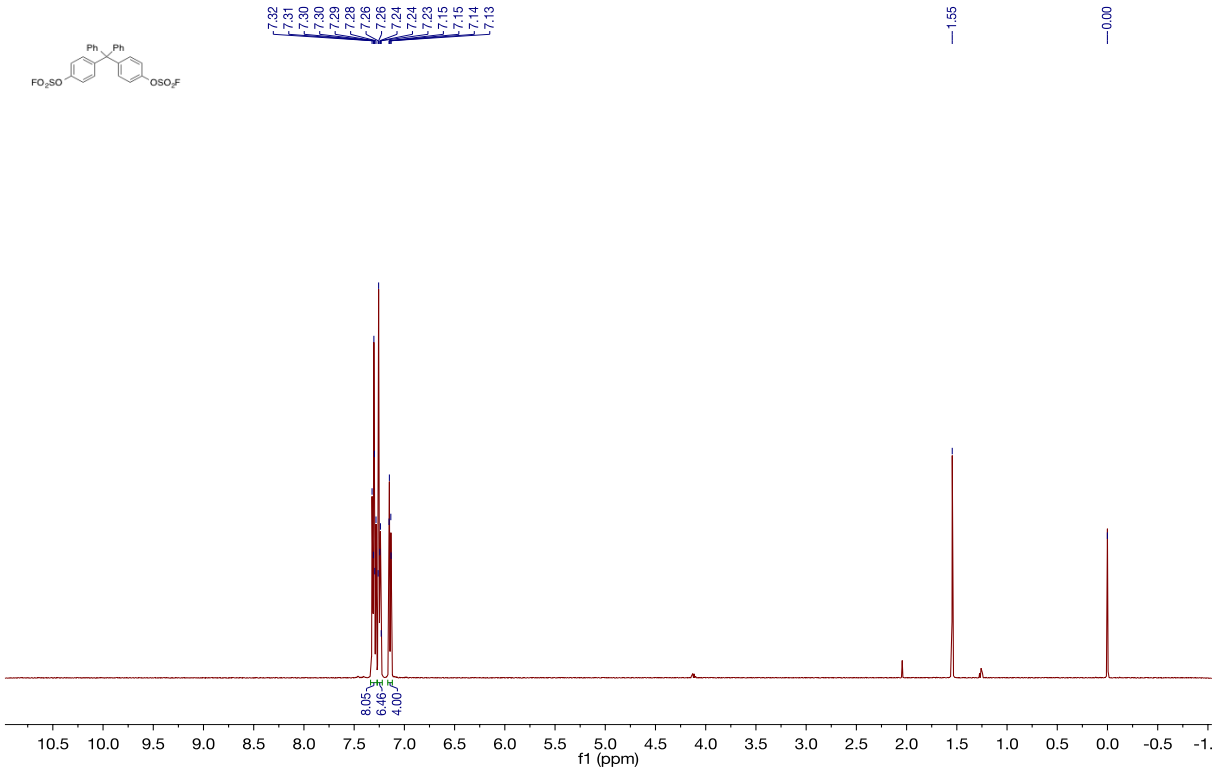
***^{1}H NMR* (A-3)**



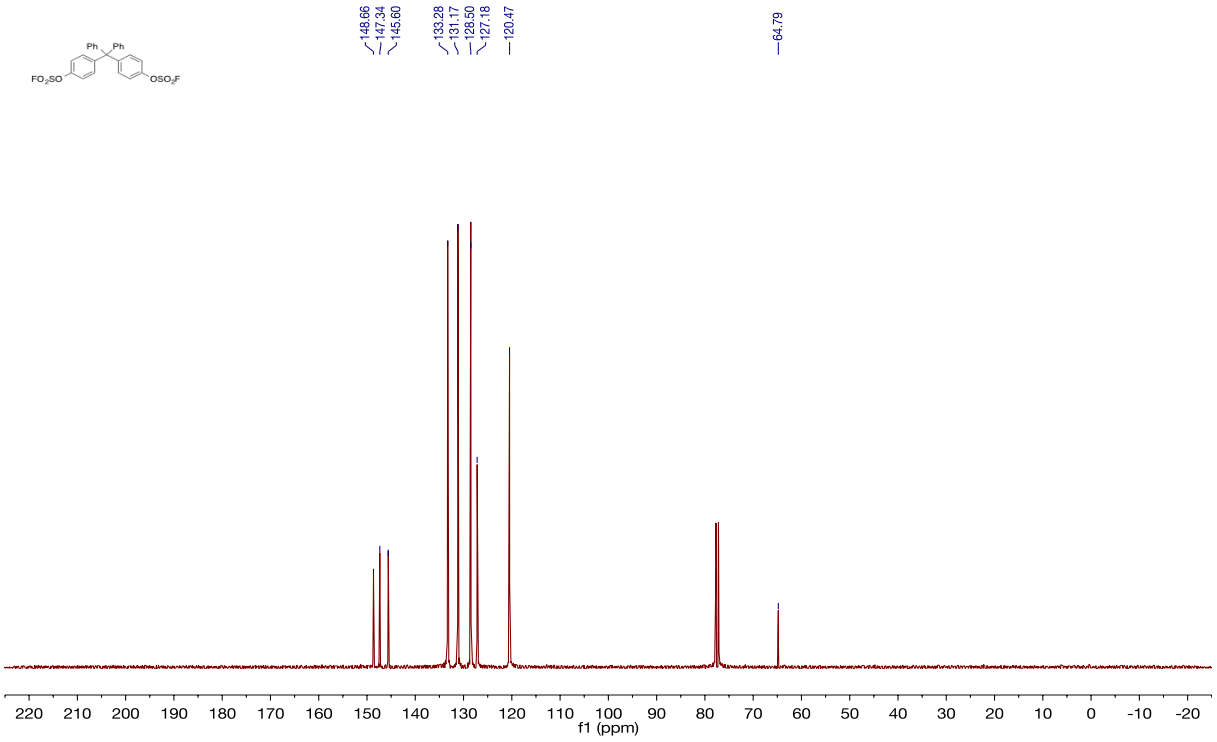
***^{13}C NMR* (A-3)**



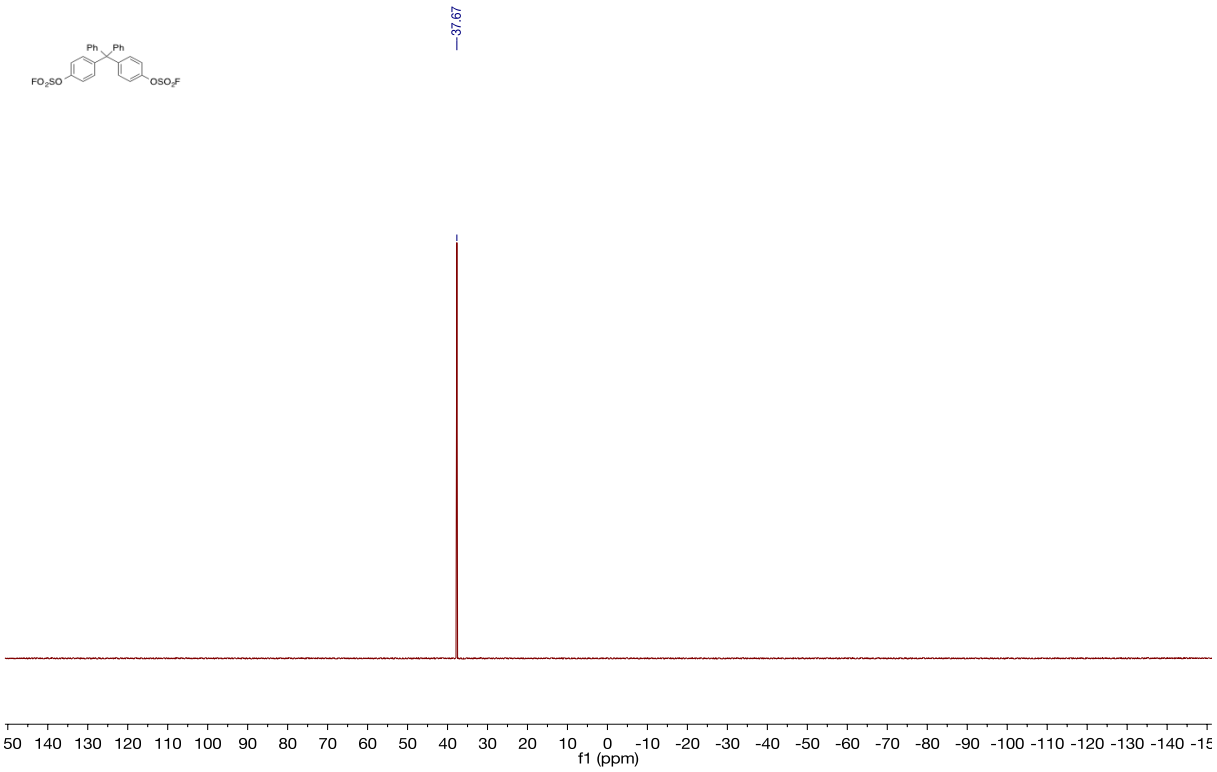
***^{1}H NMR* (B-3)**



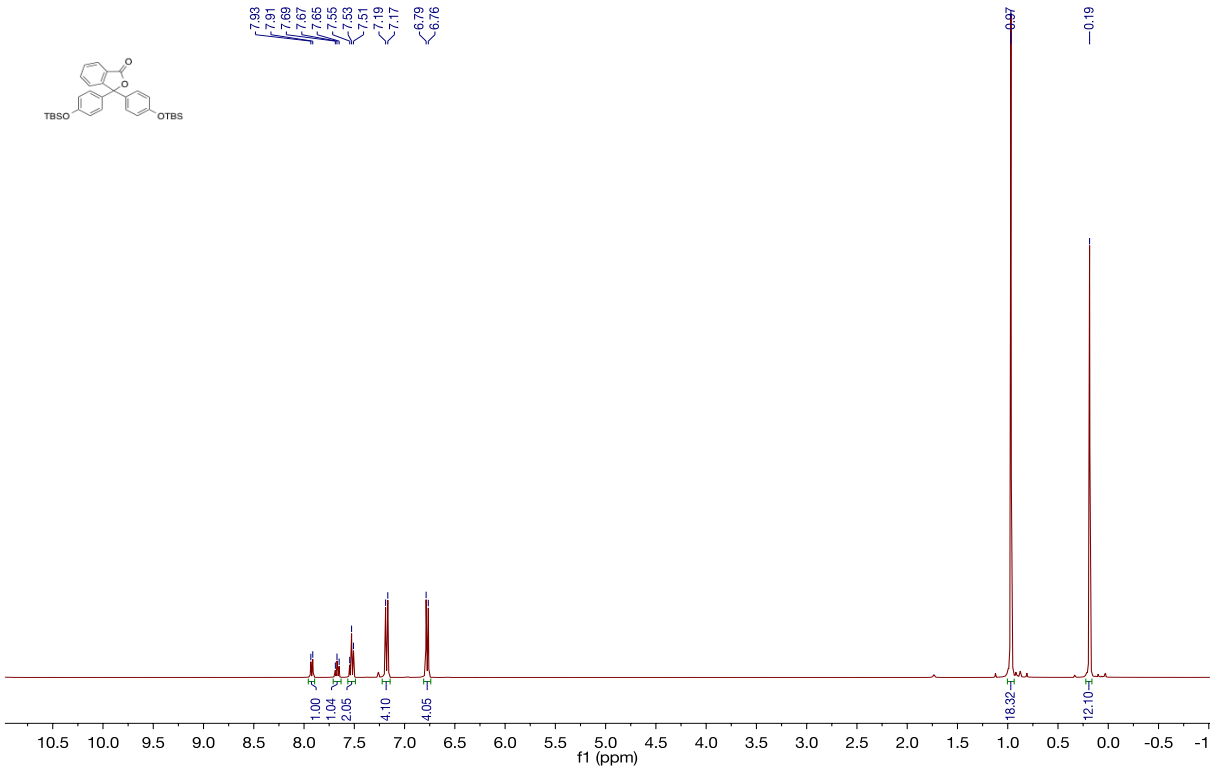
***^{13}C NMR* (B-3)**



***^{19}F NMR* (B-3)**



***^{1}H NMR* (A-4)**



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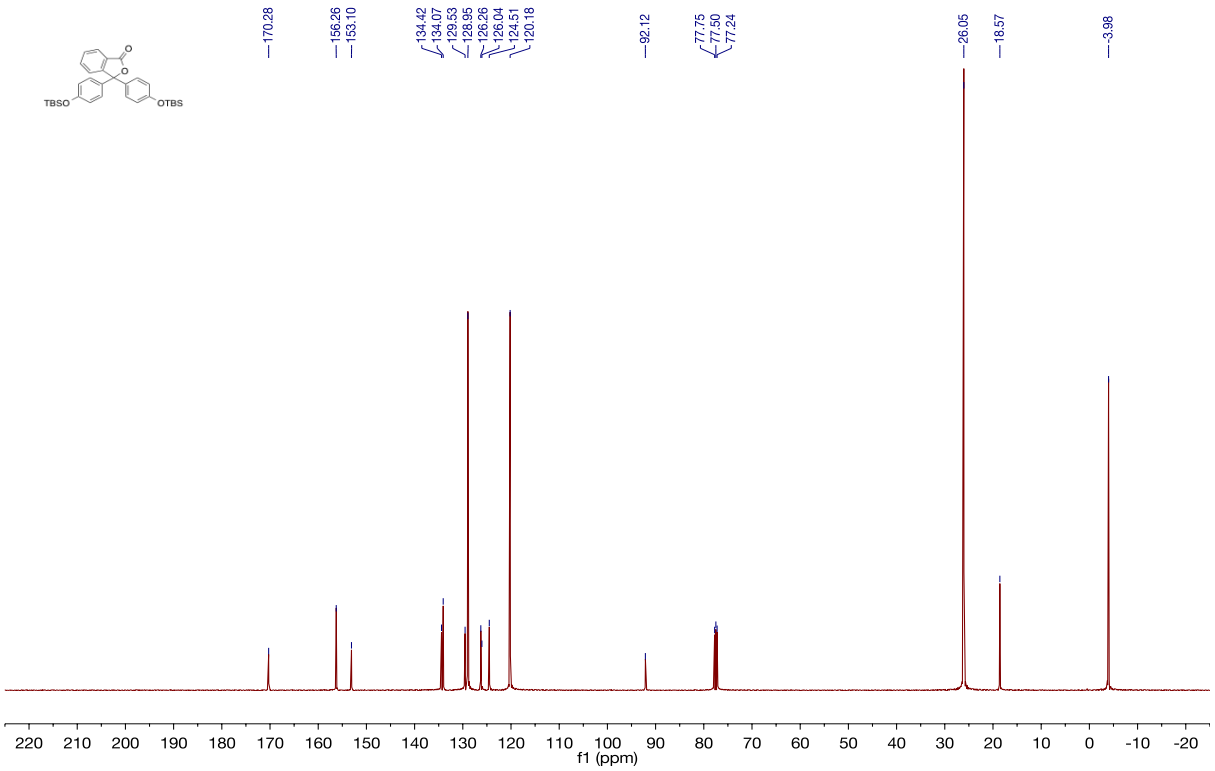
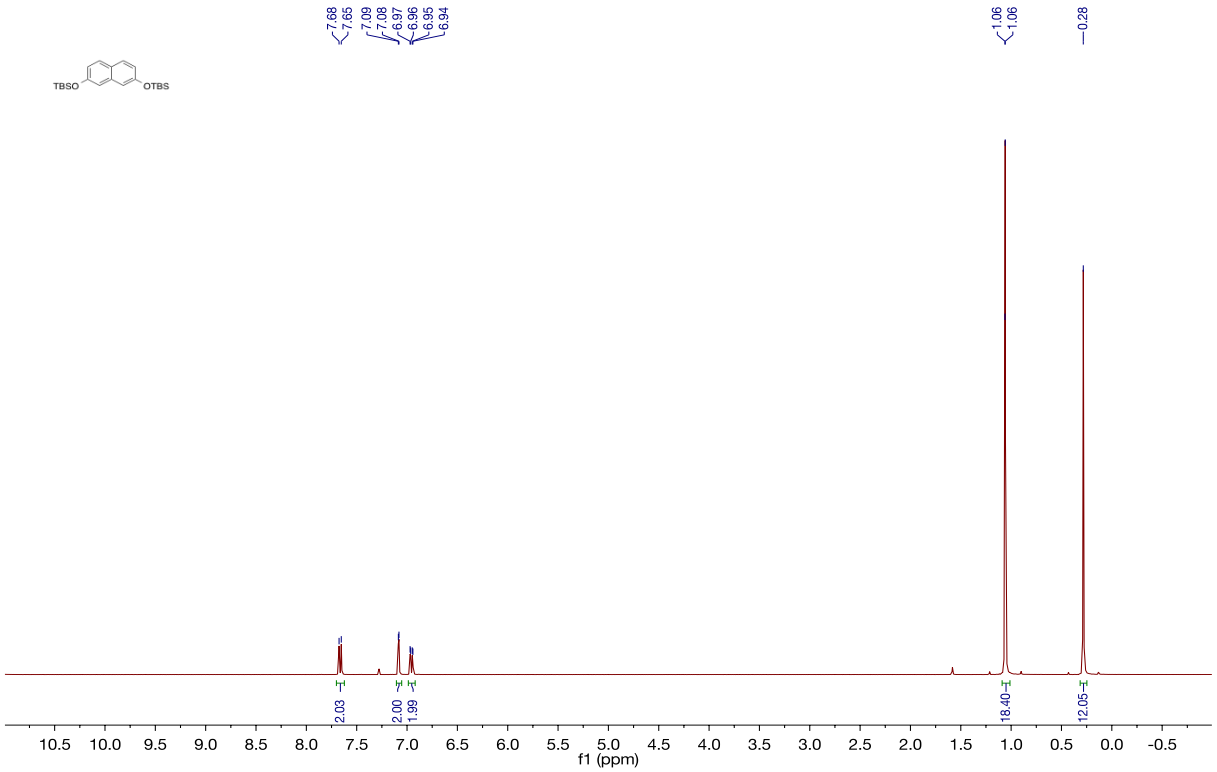
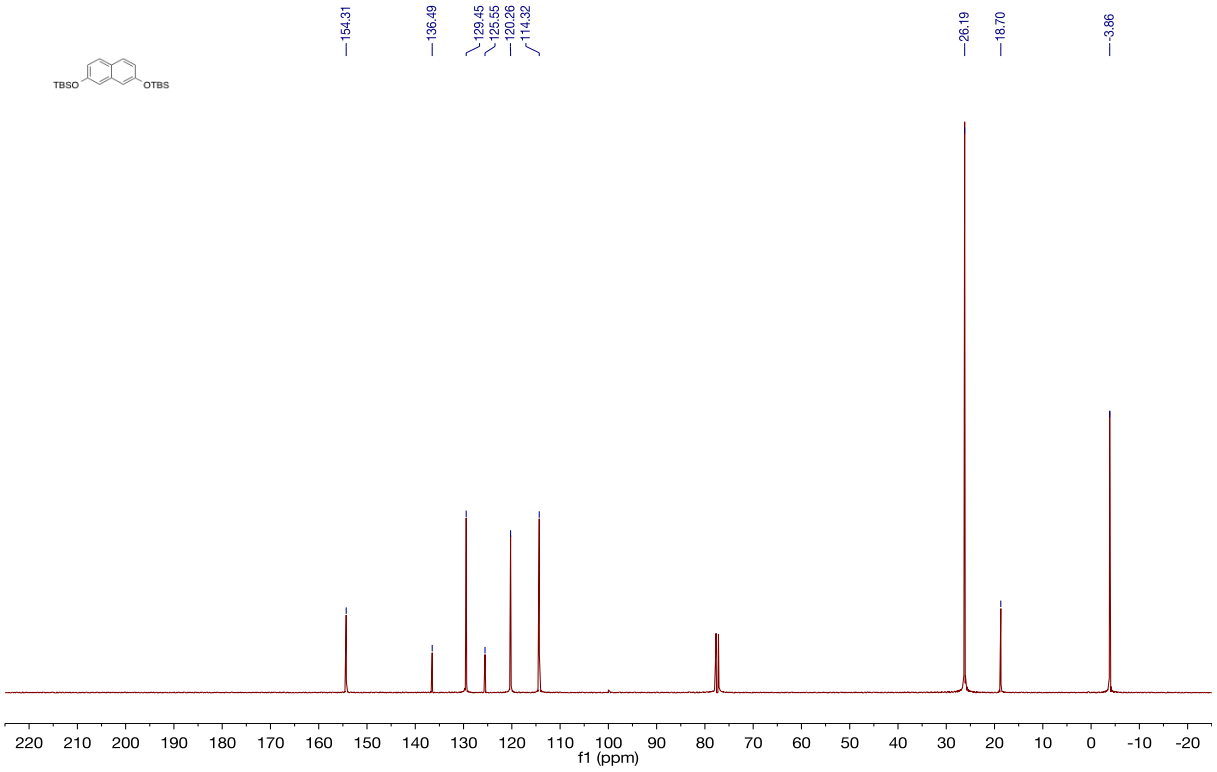


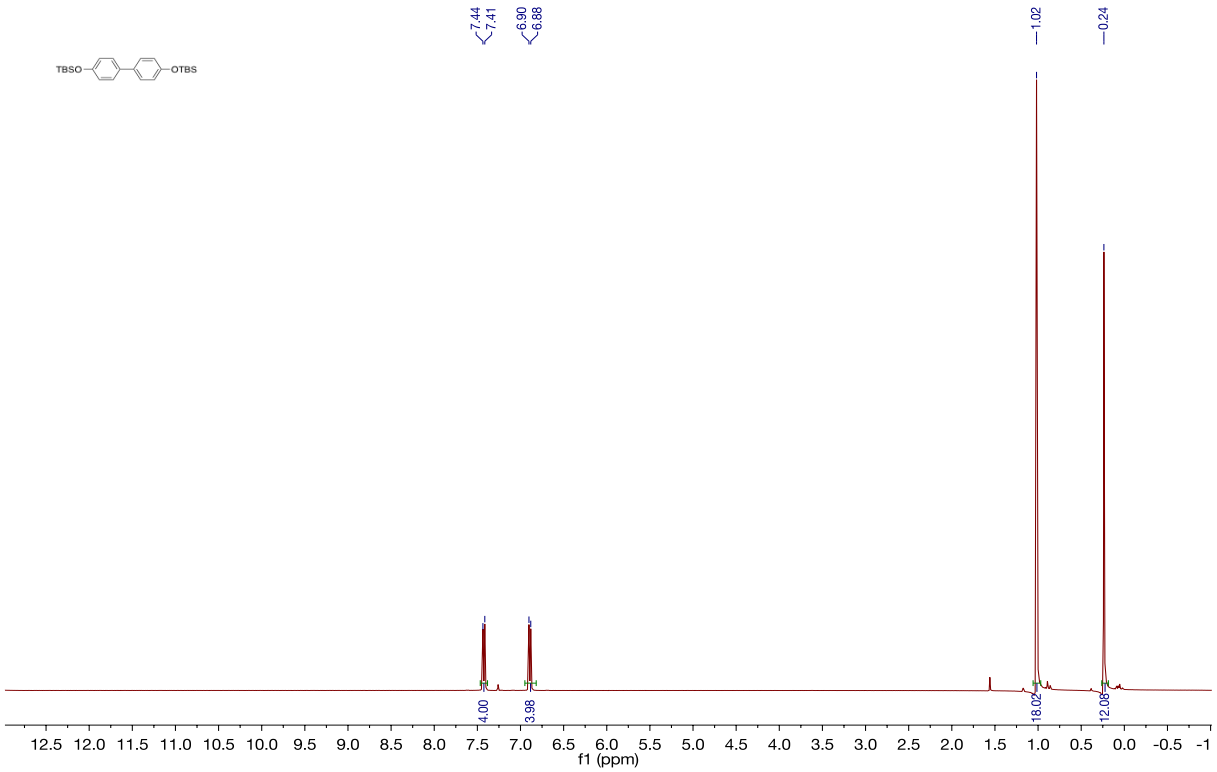
***^{1}H NMR* (A-5)**



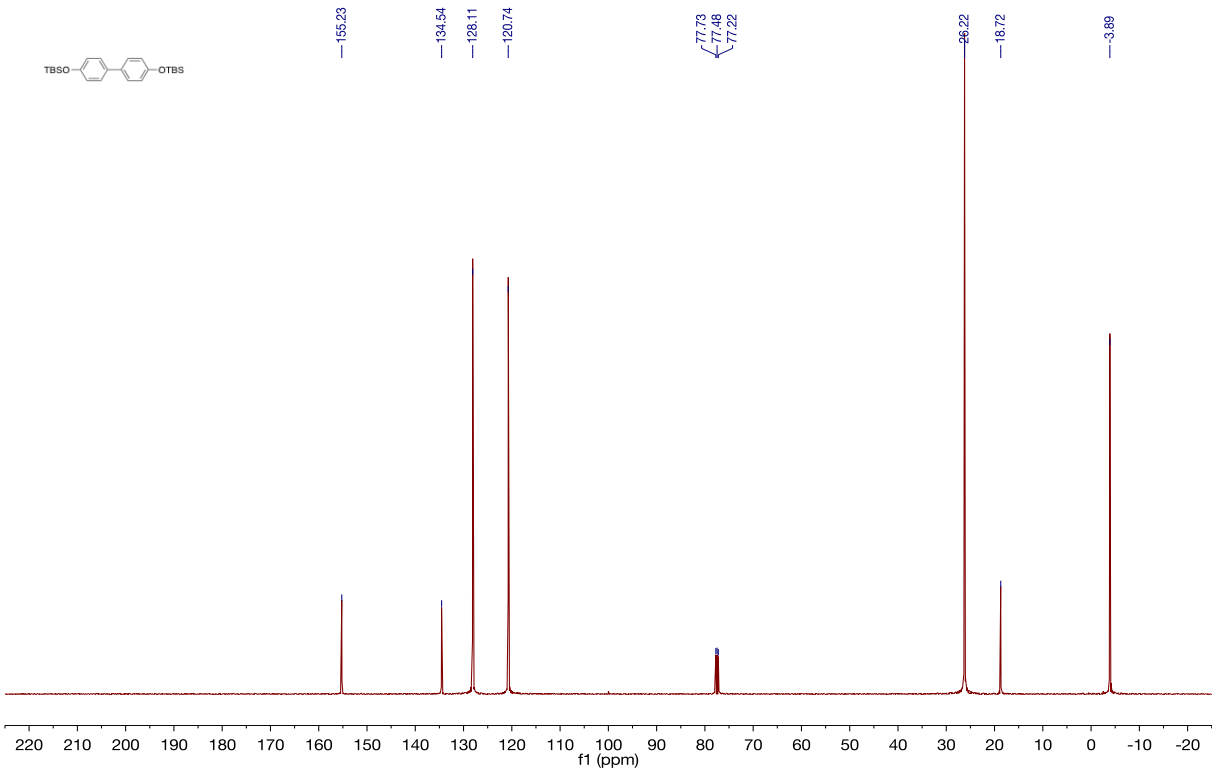
***^{13}C NMR* (A-5)**



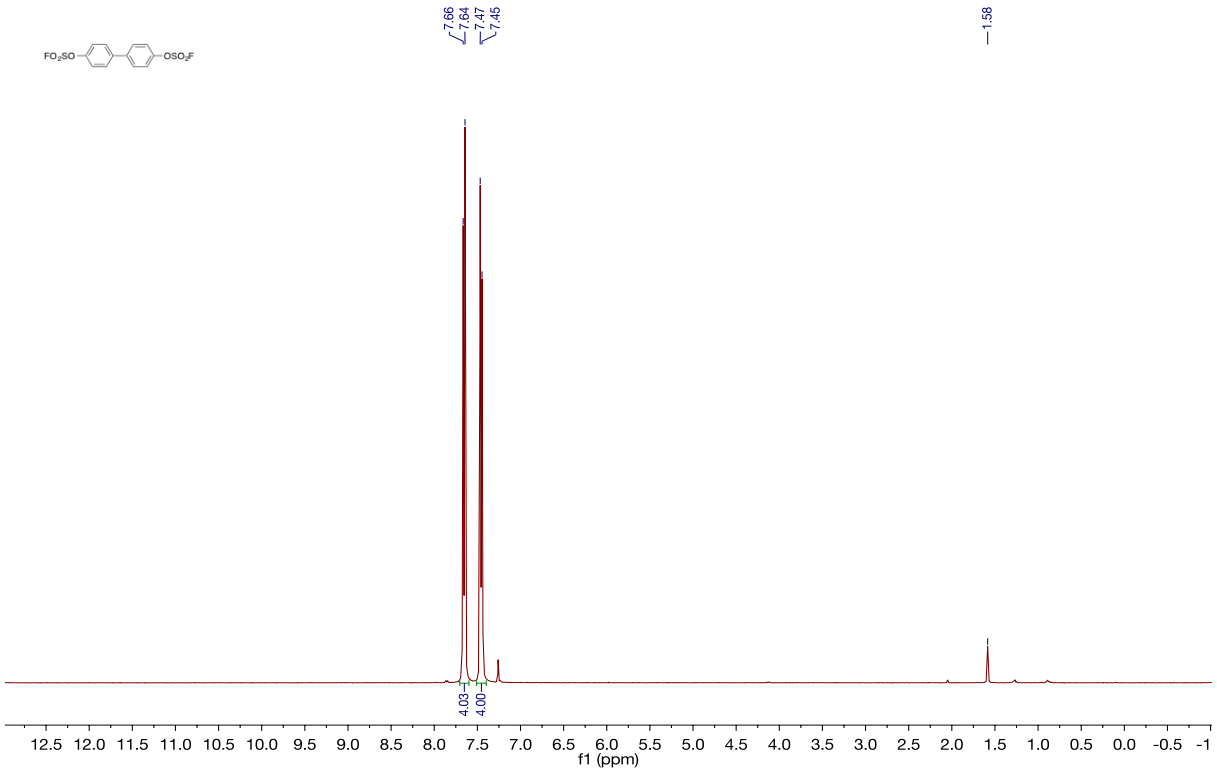
***^{1}H NMR* (A-7)**



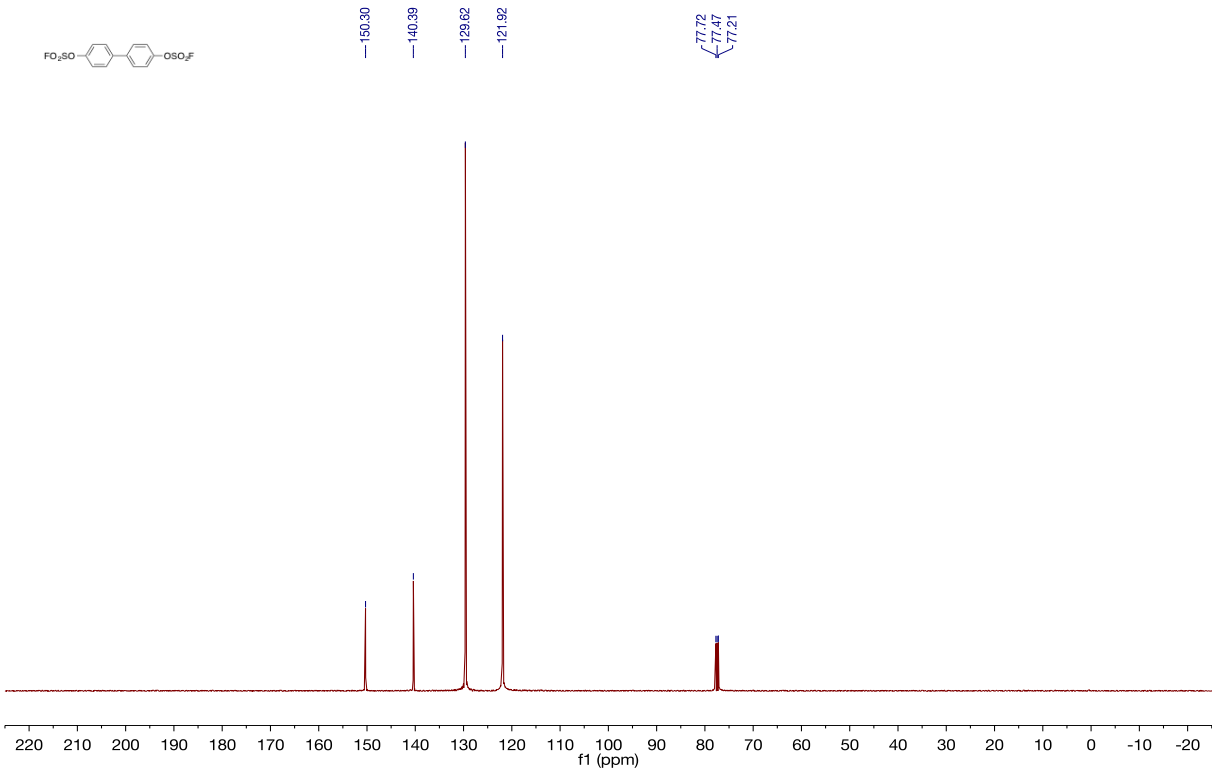
***^{13}C NMR* (A-7)**



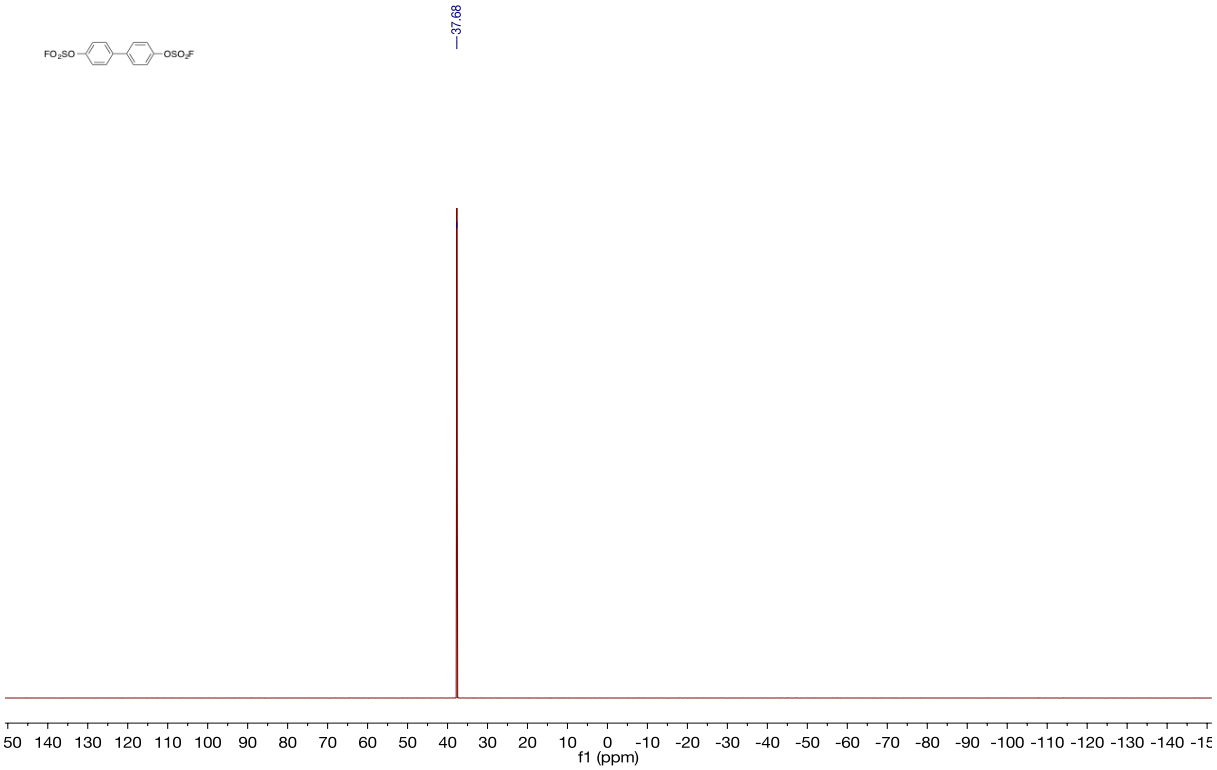
[1]H NMR **(B-7)**



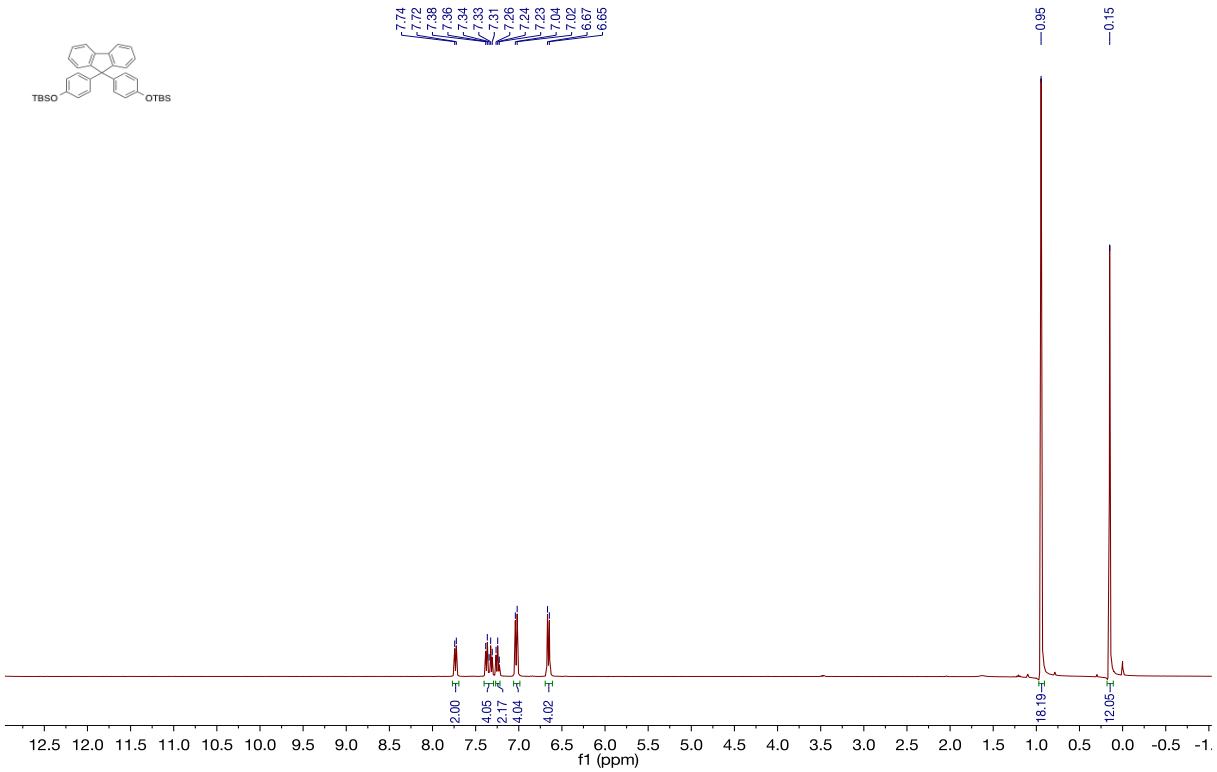
[13]C NMR **(B-7)**



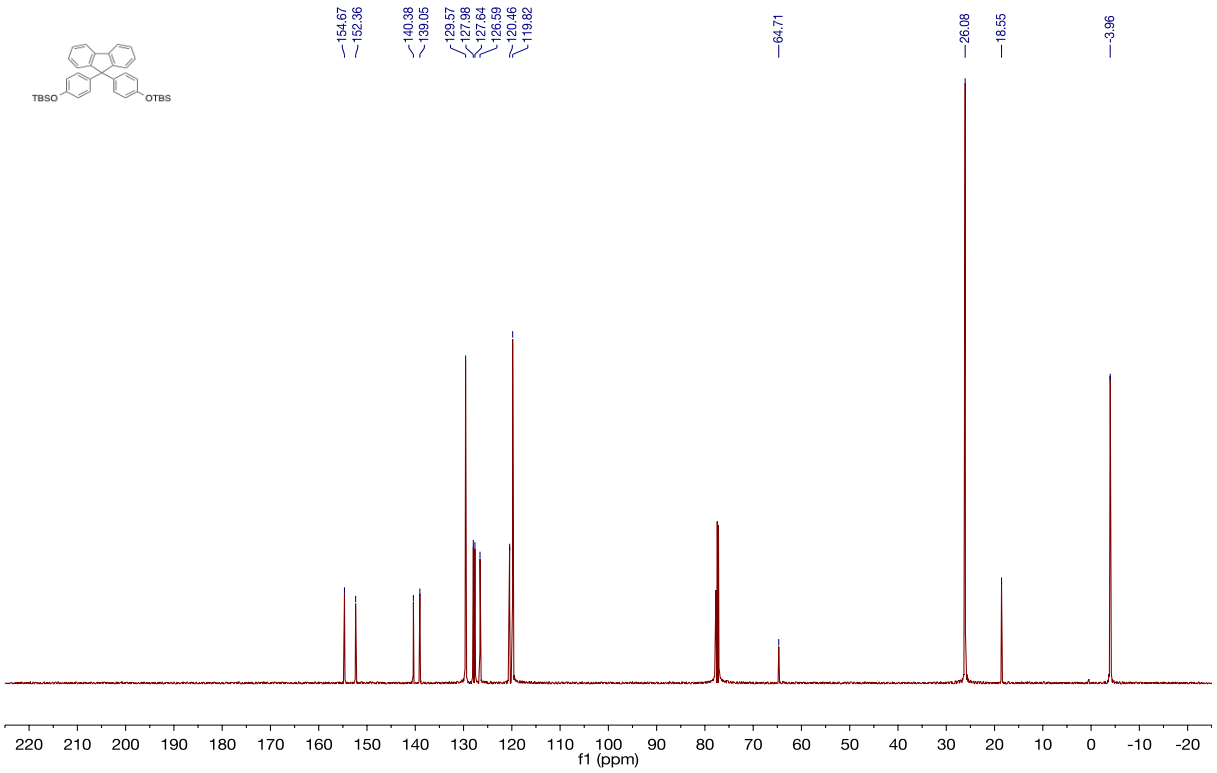
***^{19}F NMR* (B-7)**



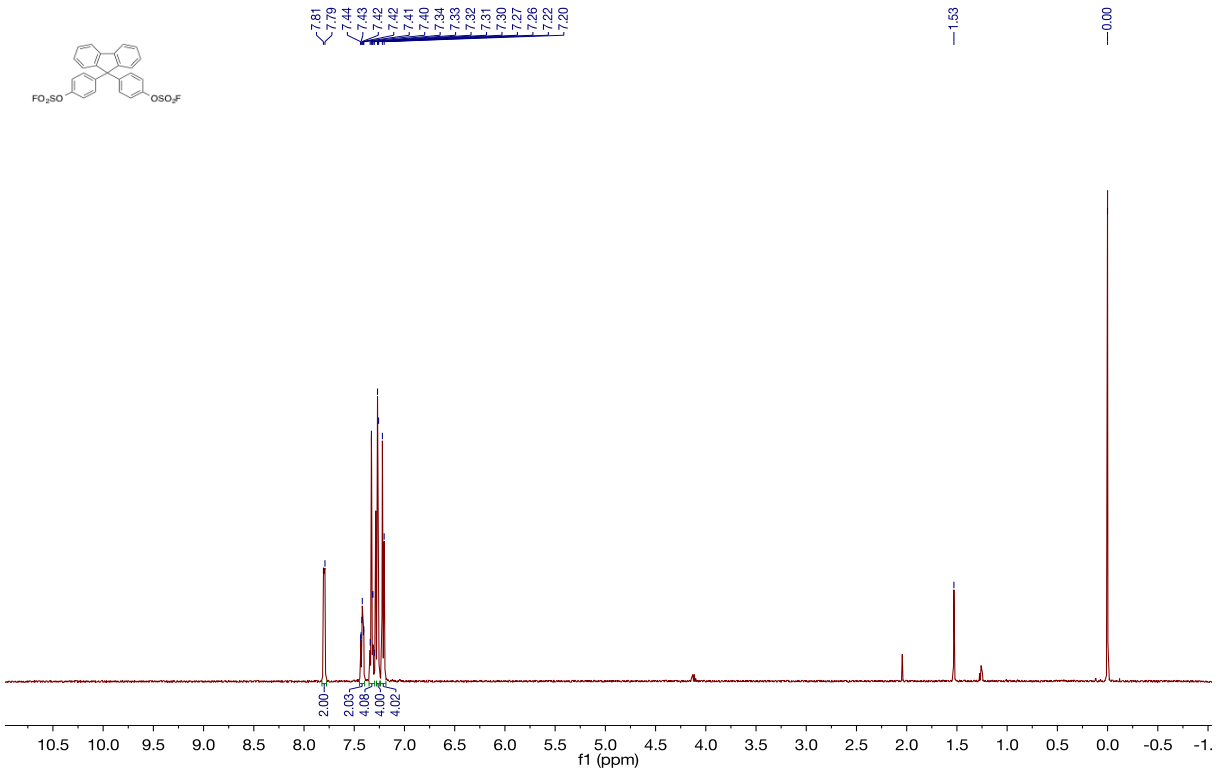
***^{1}H NMR* (A-8)**



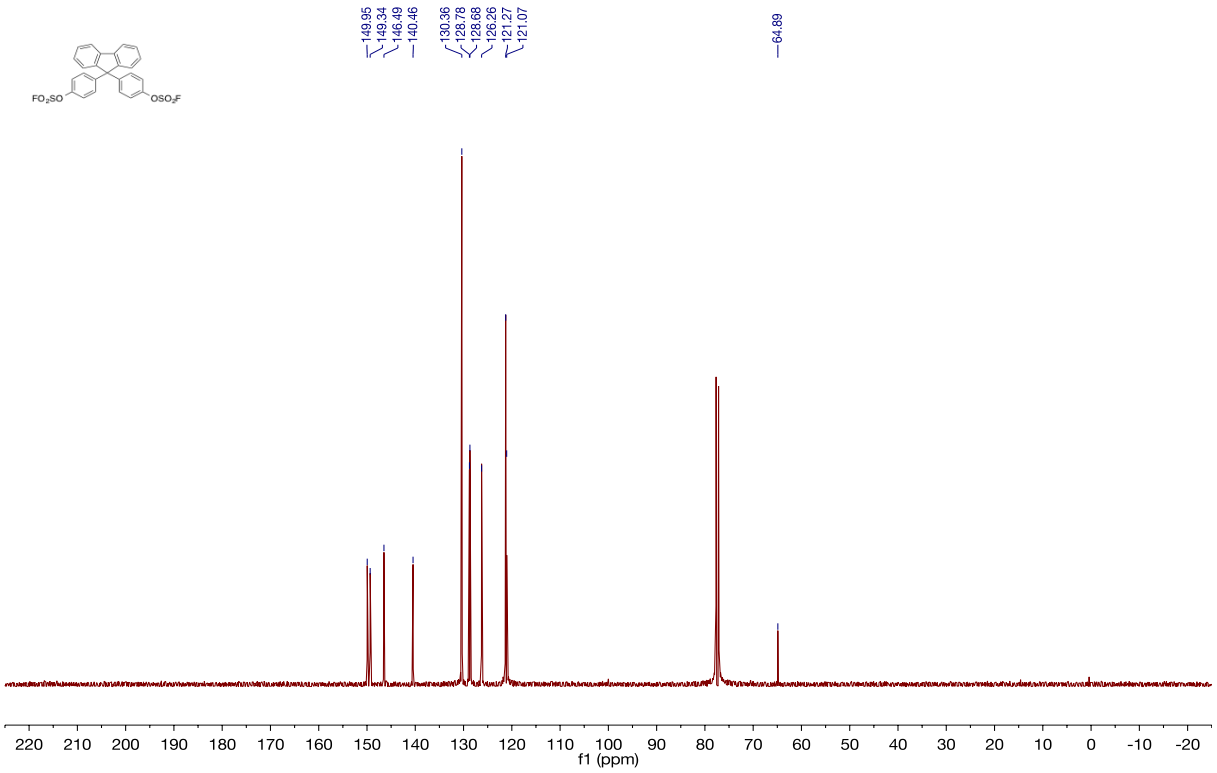
***^{13}C NMR* (A-8)**



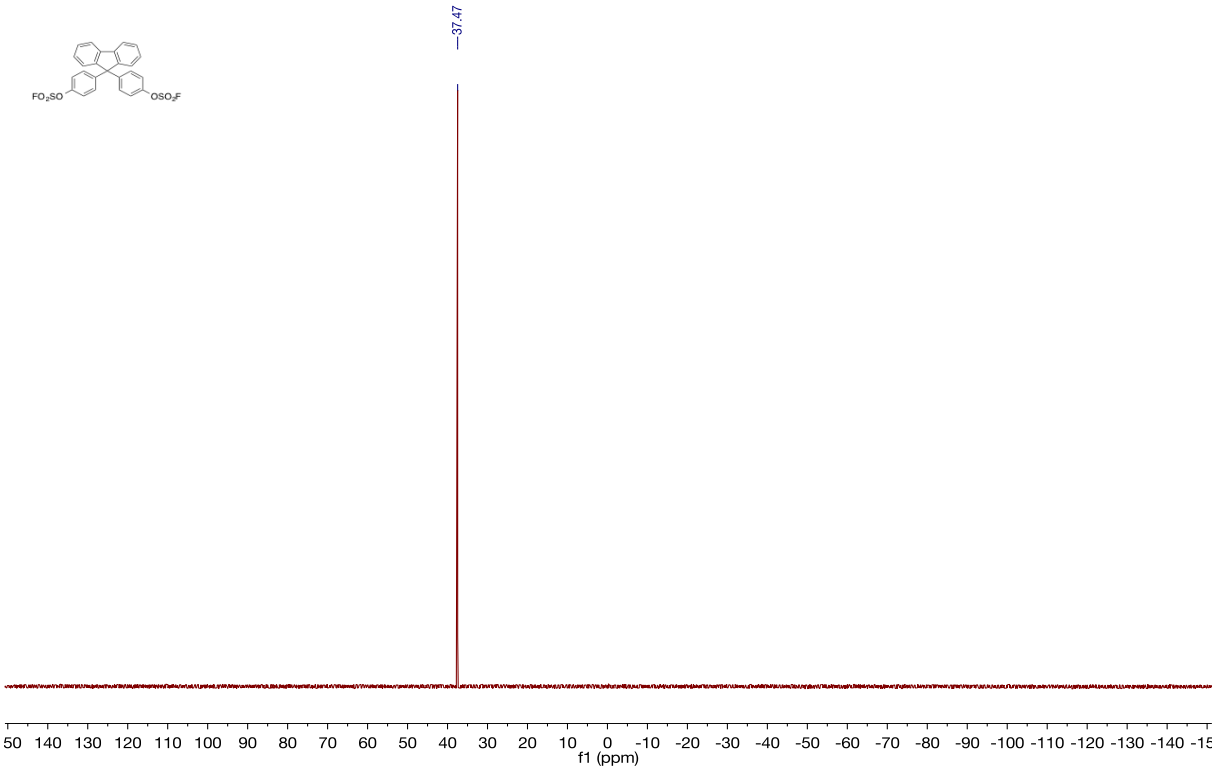
***^{1}H NMR* (B-8)**



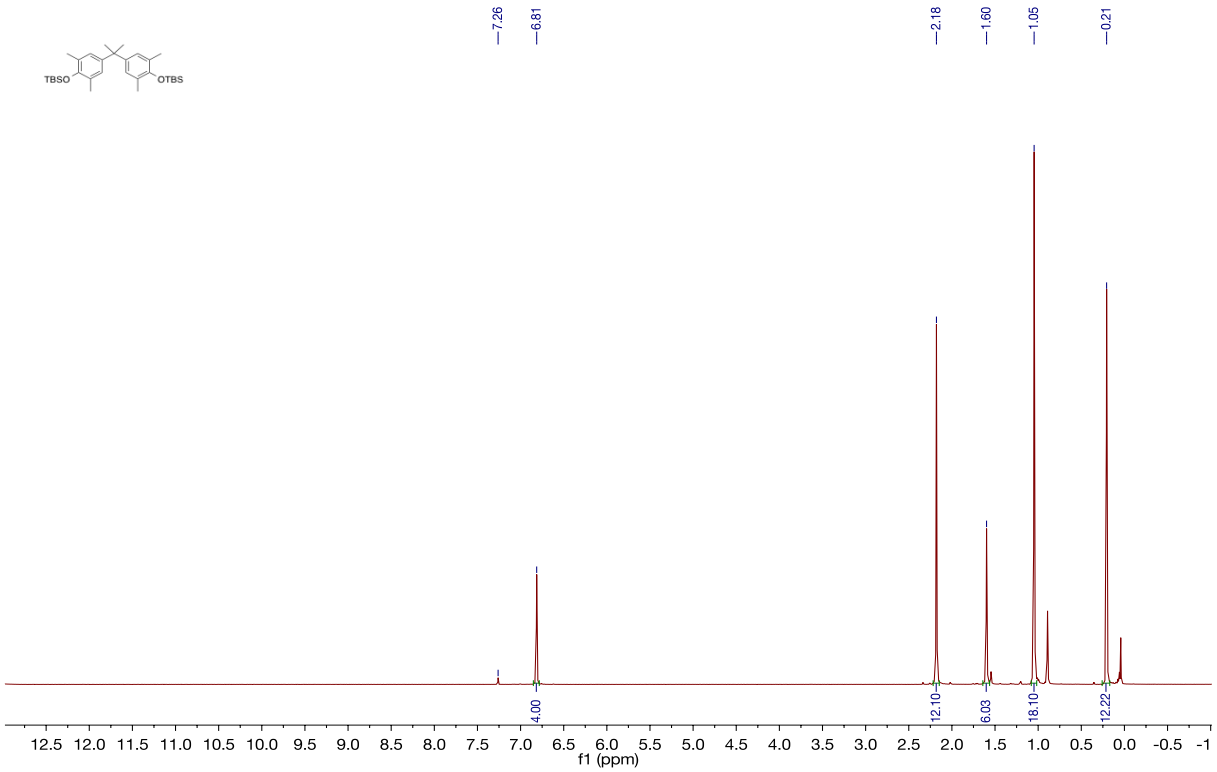
^{13}C NMR **(B-8)**



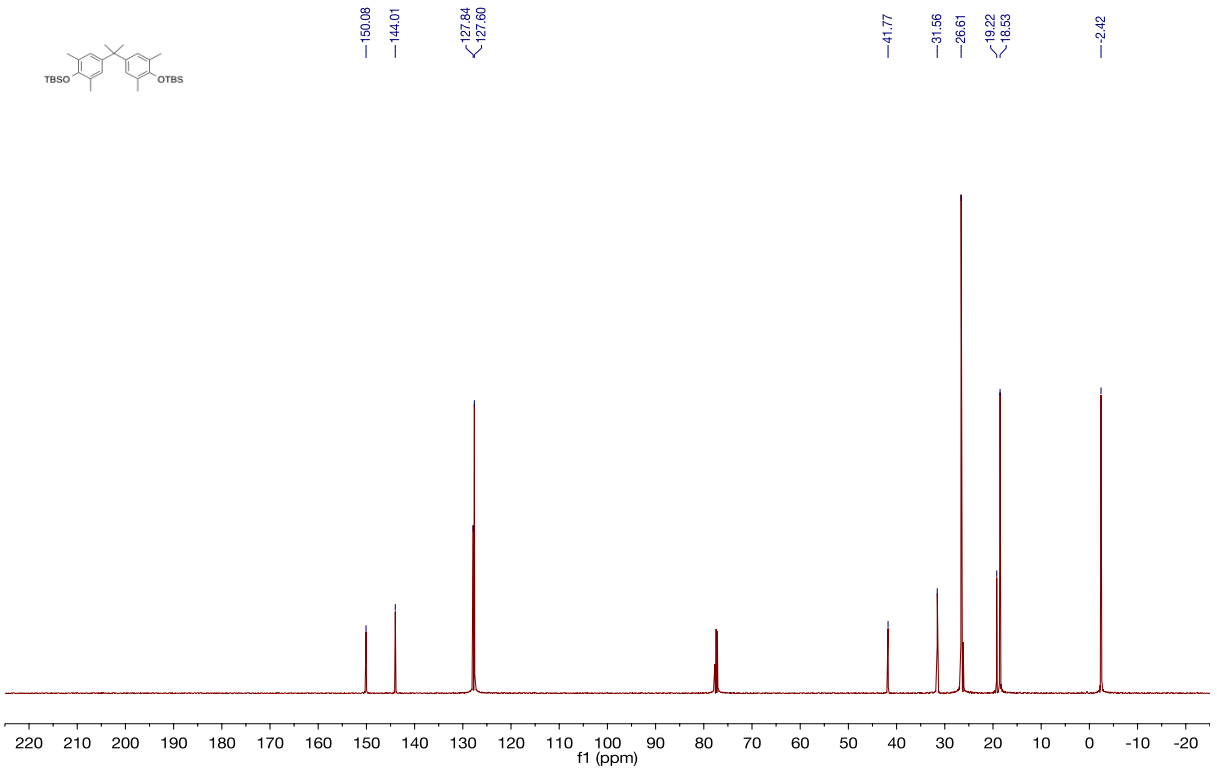
^{19}F NMR **(B-8)**



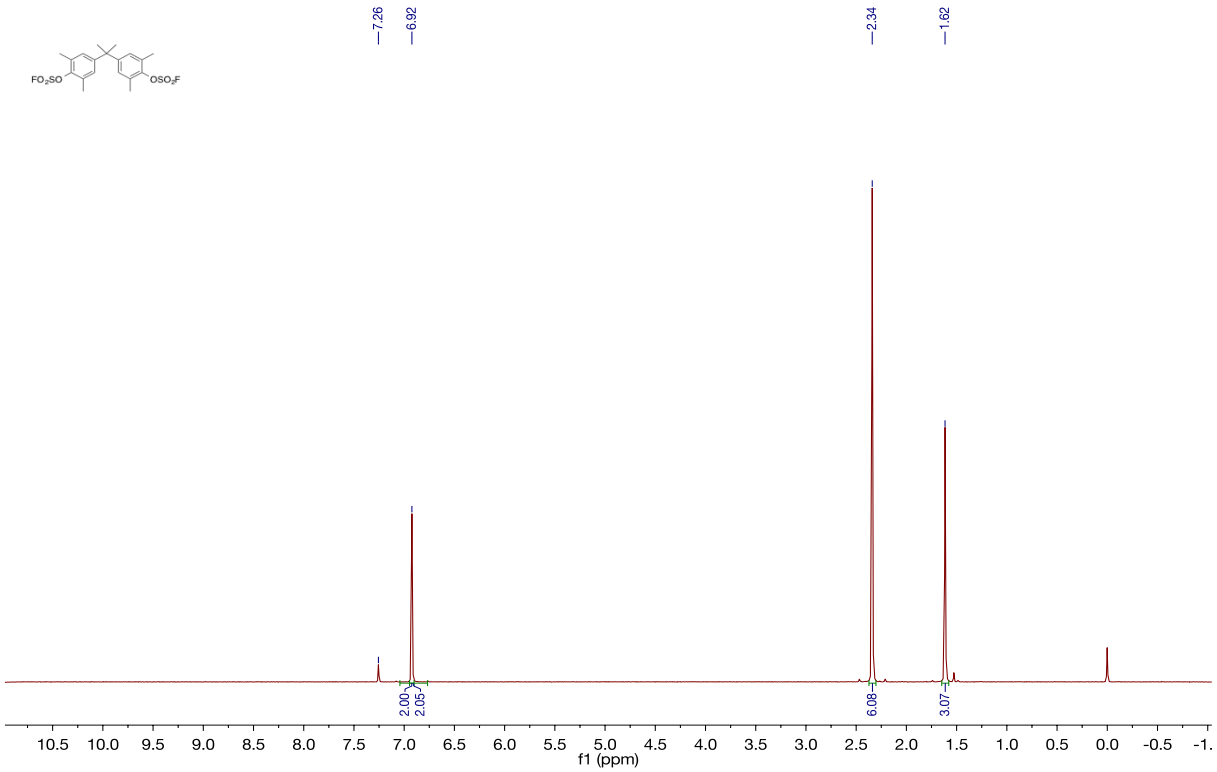
***[1]H NMR* (A-9)**



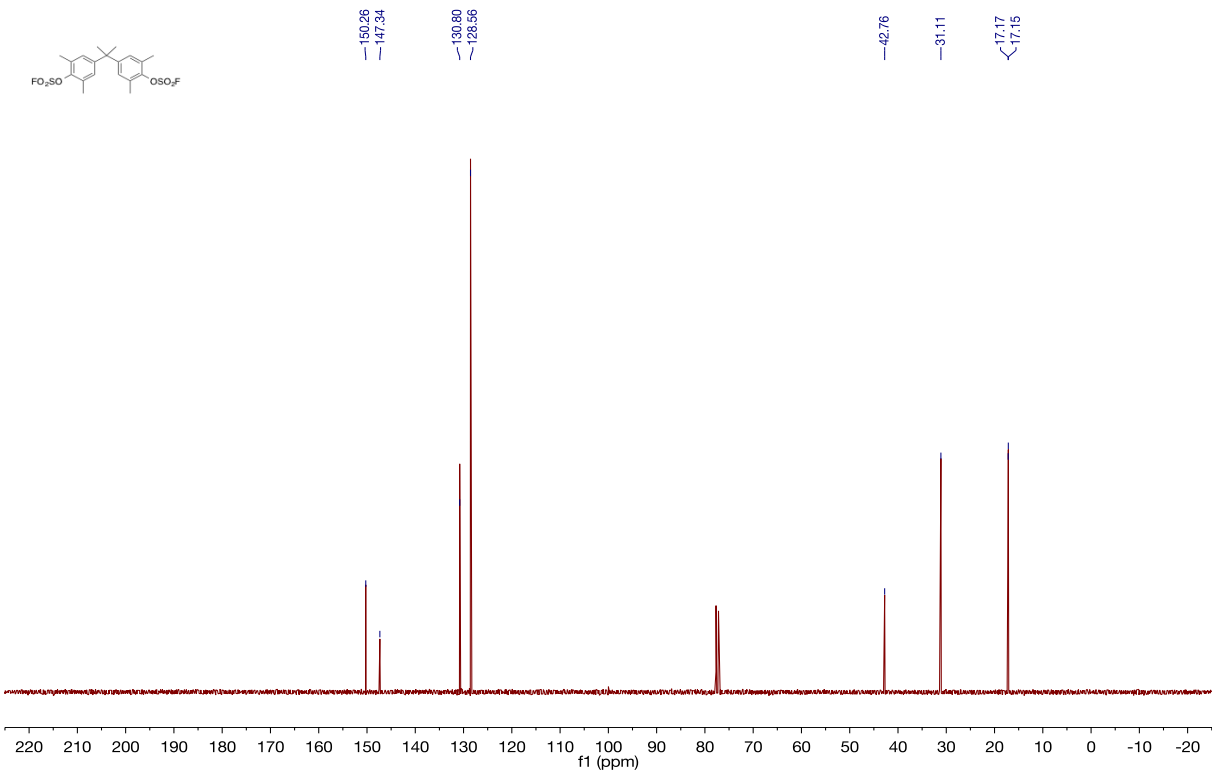
***[13]C NMR* (A-9)**



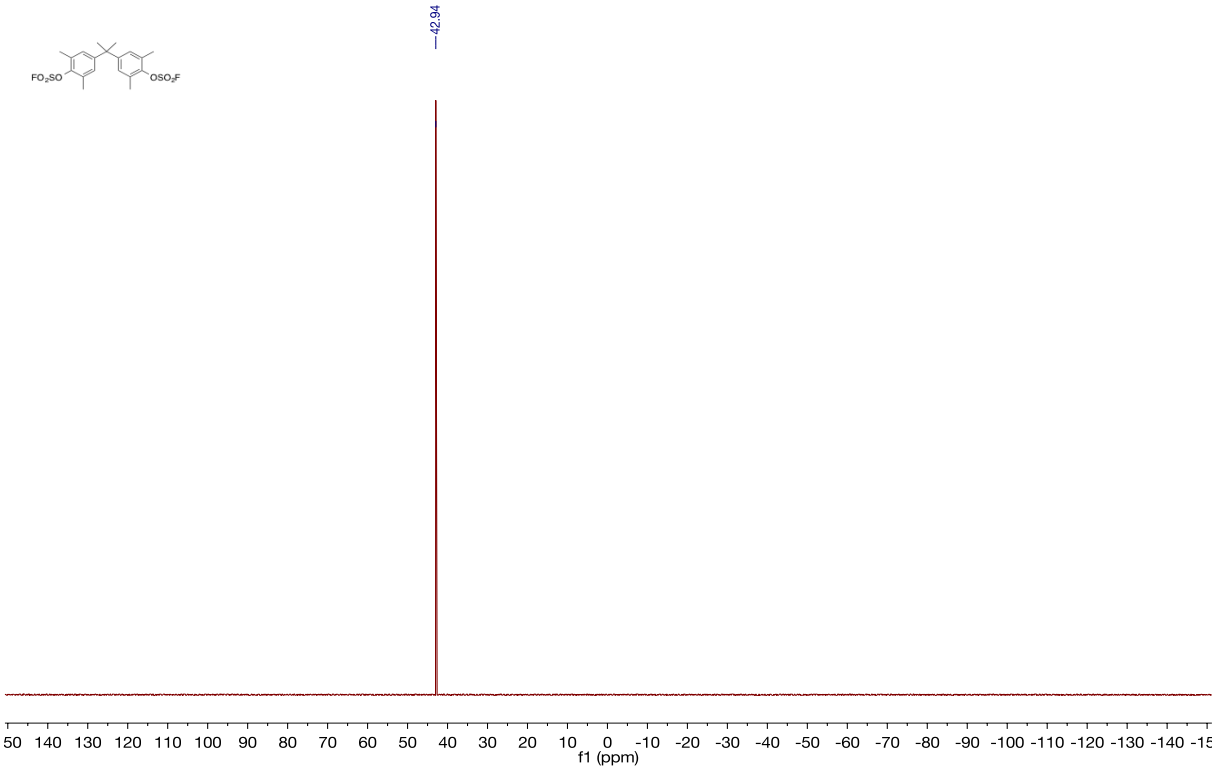
***[1]H NMR* (B-9)**



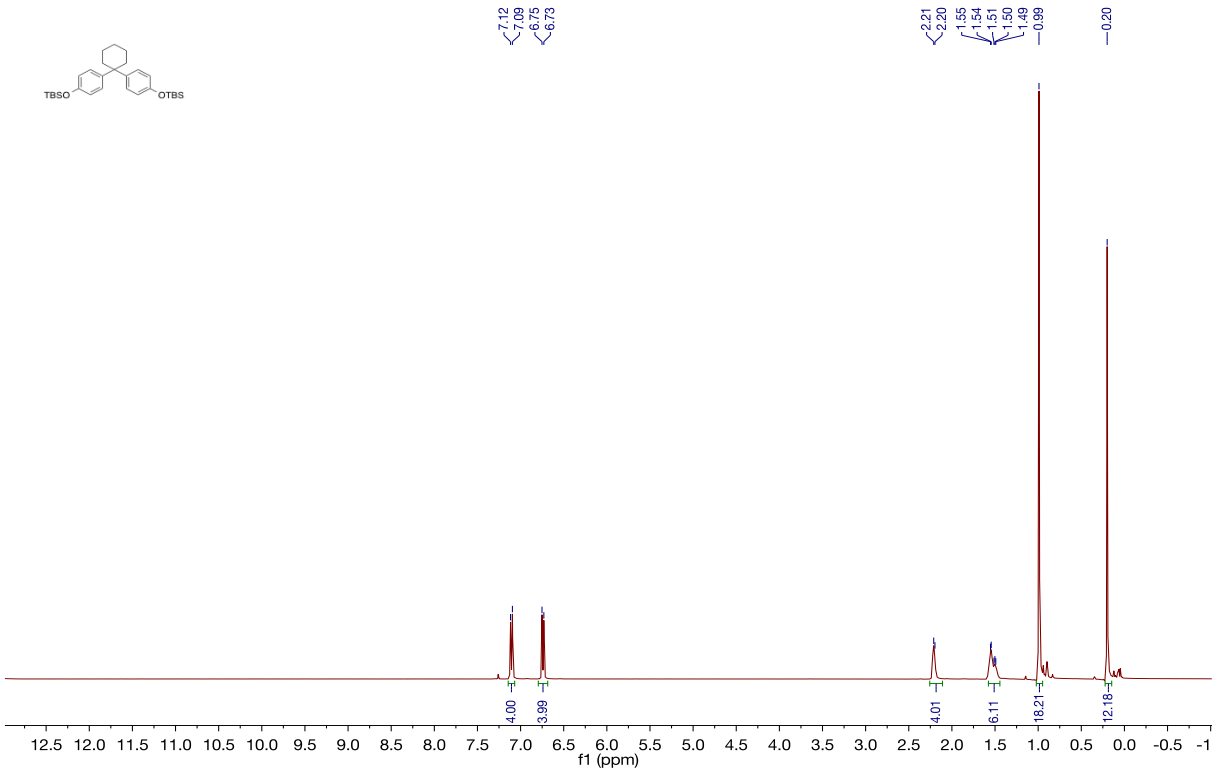
***[13]C NMR* (B-9)**



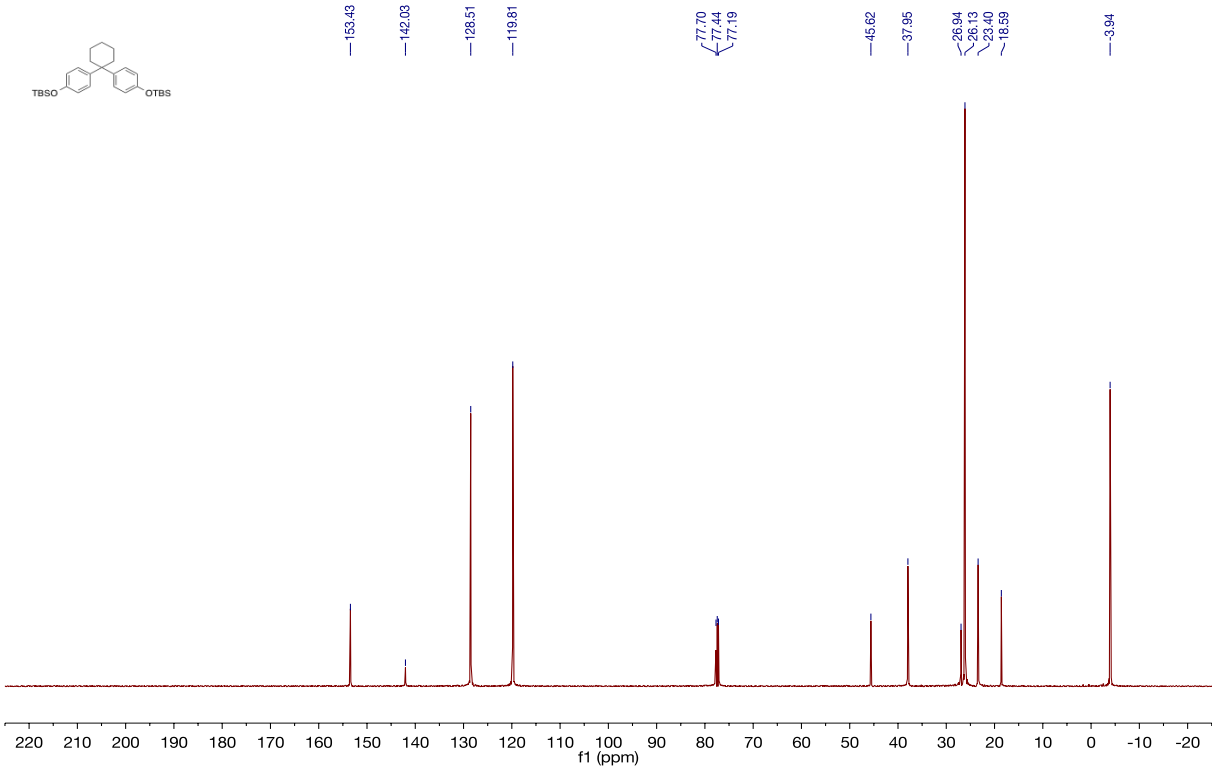
***^{19}F NMR* (B-9)**



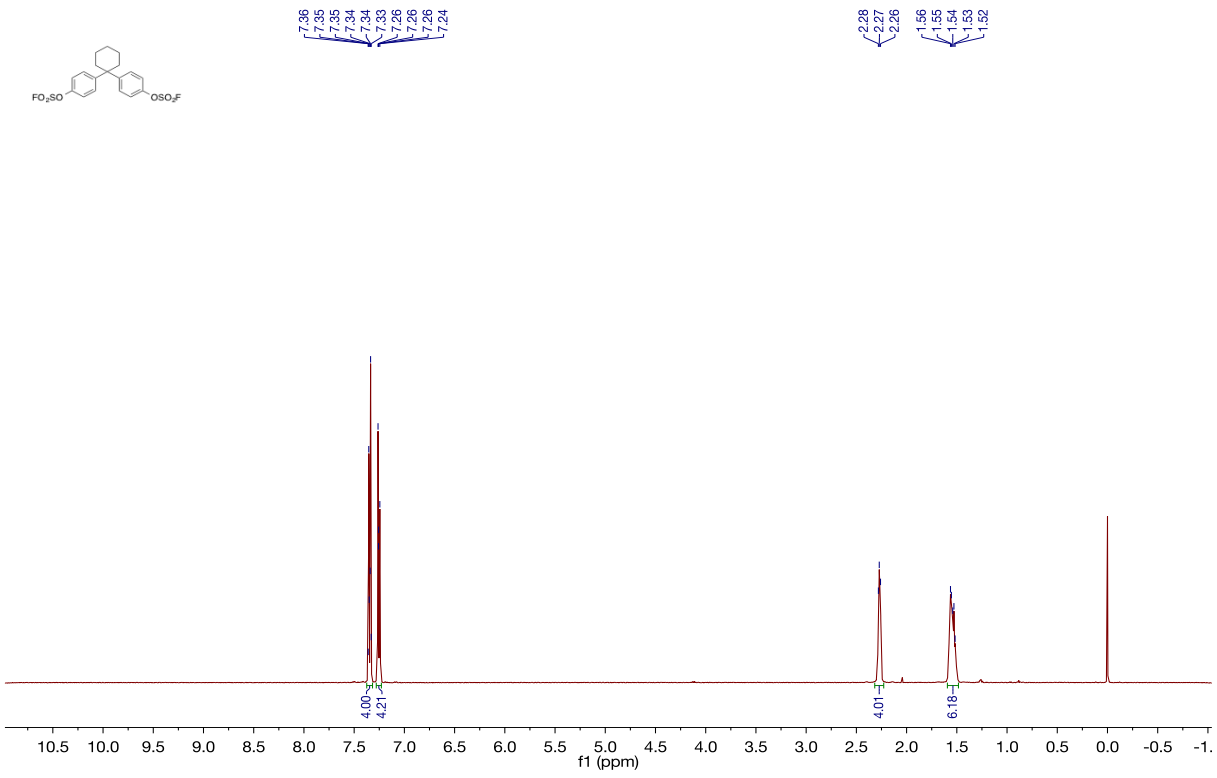
***^{1}H NMR* (A-10)**



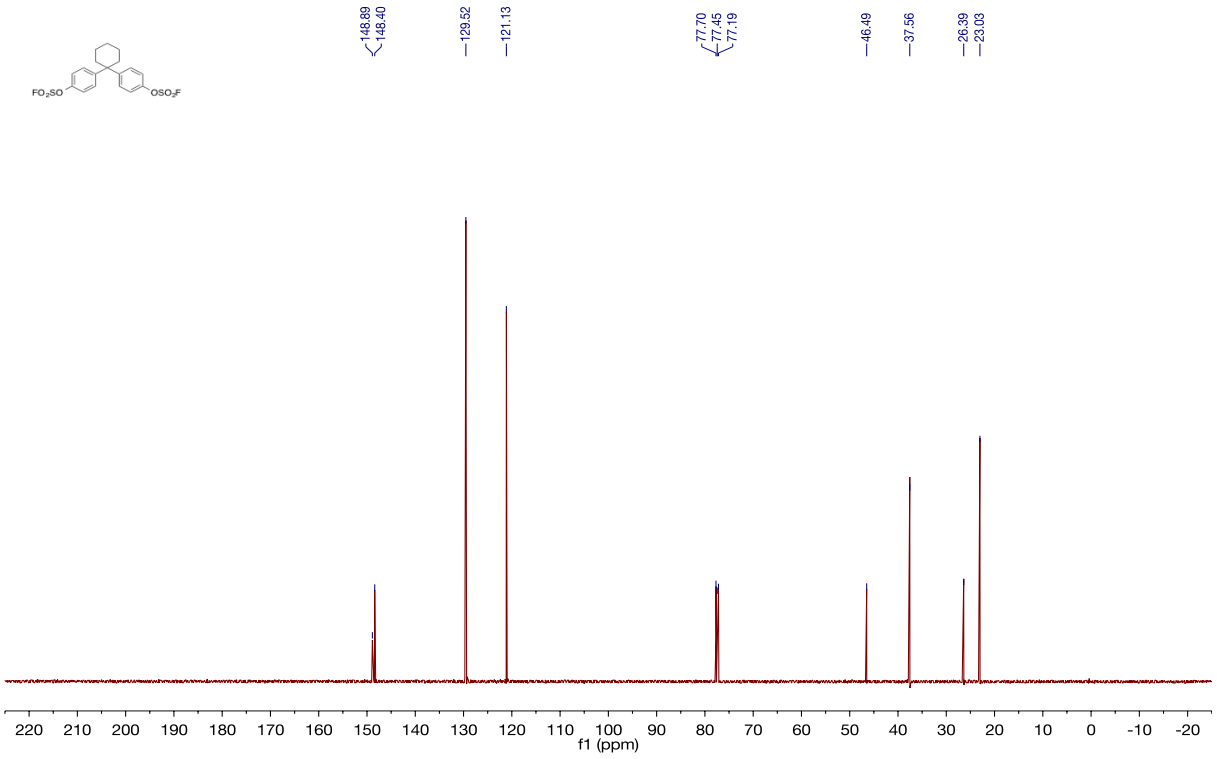
***^{13}C NMR* (A-10)**



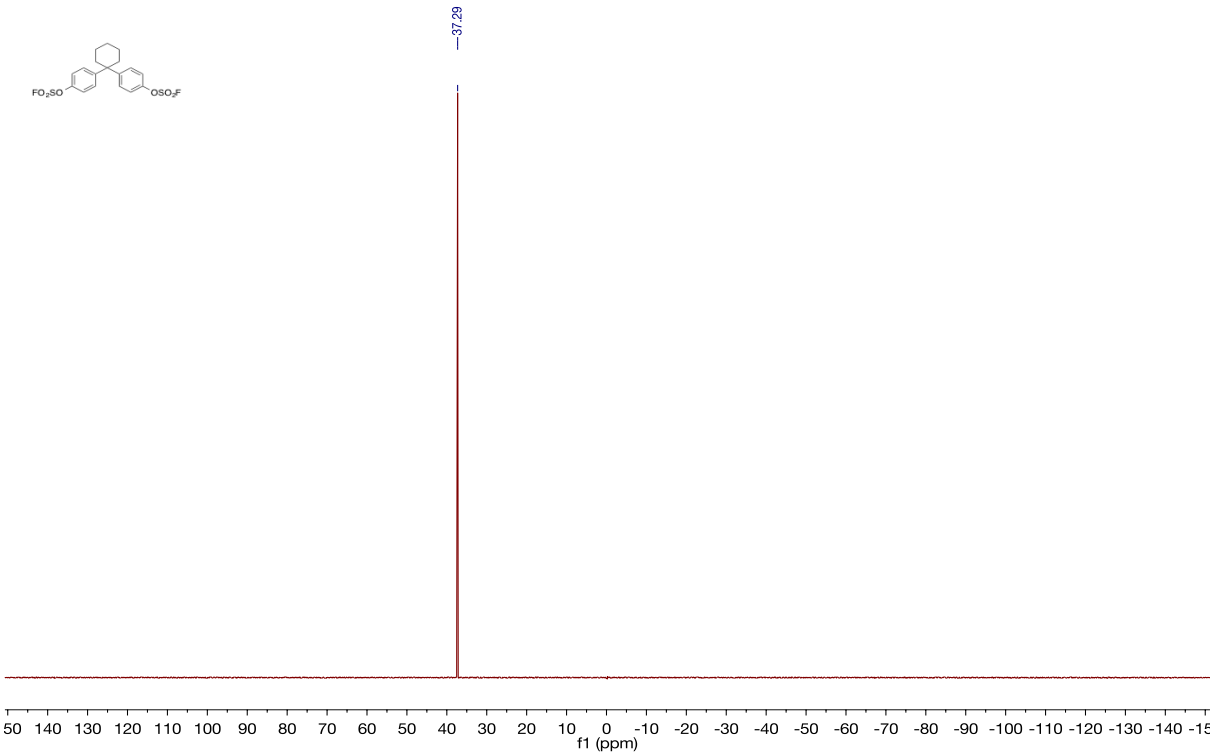
***^{1}H NMR* (B-10)**



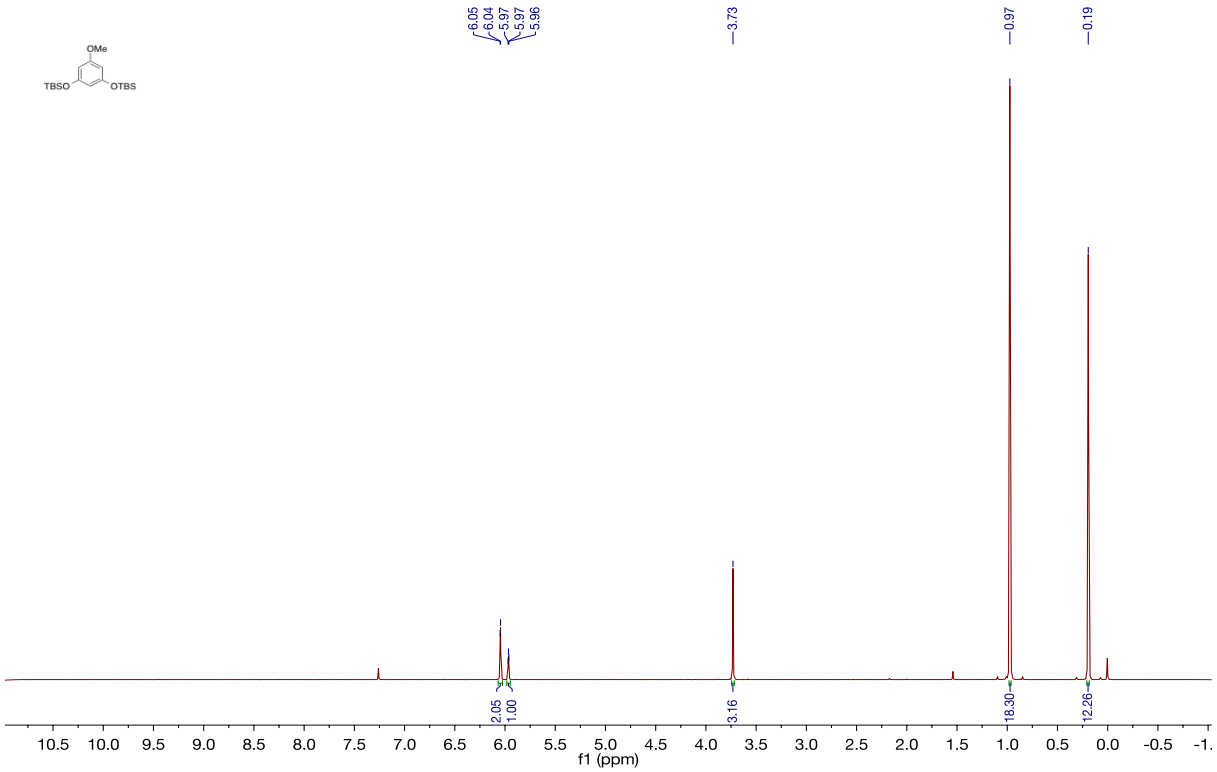
^{13}C NMR **(B-10)**



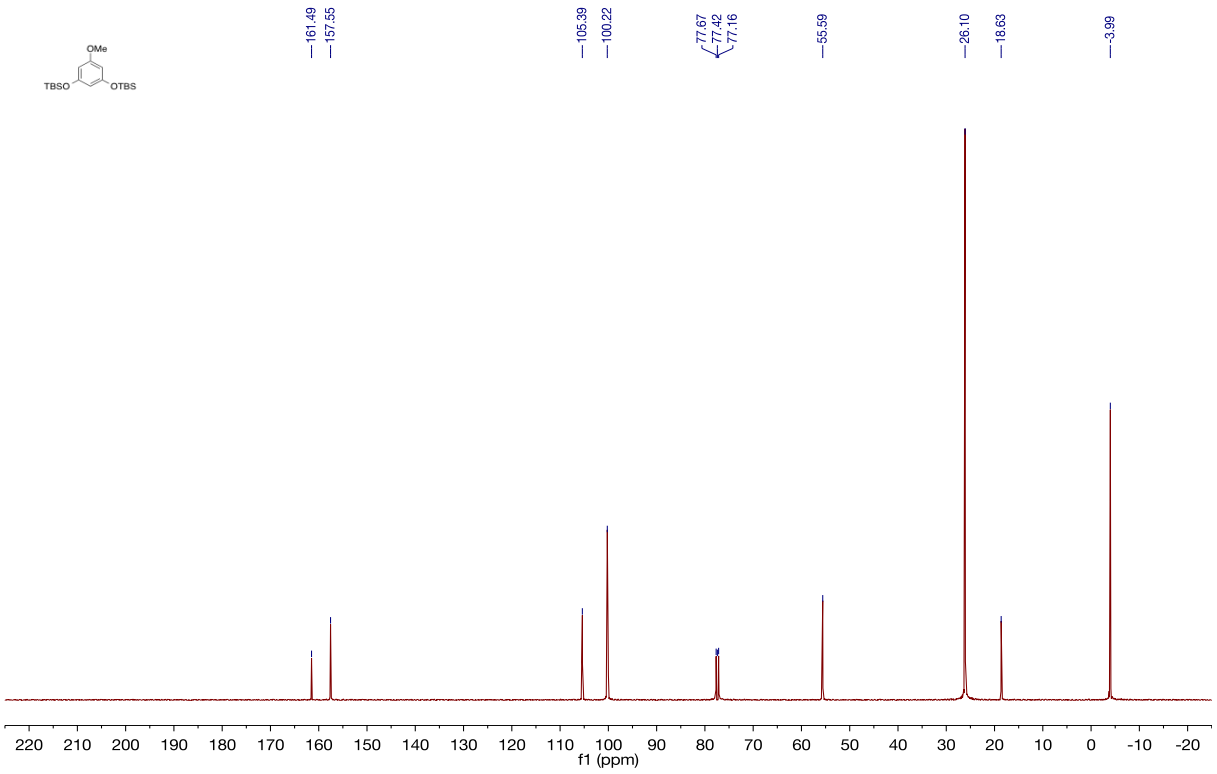
^{19}F NMR **(B-10)**



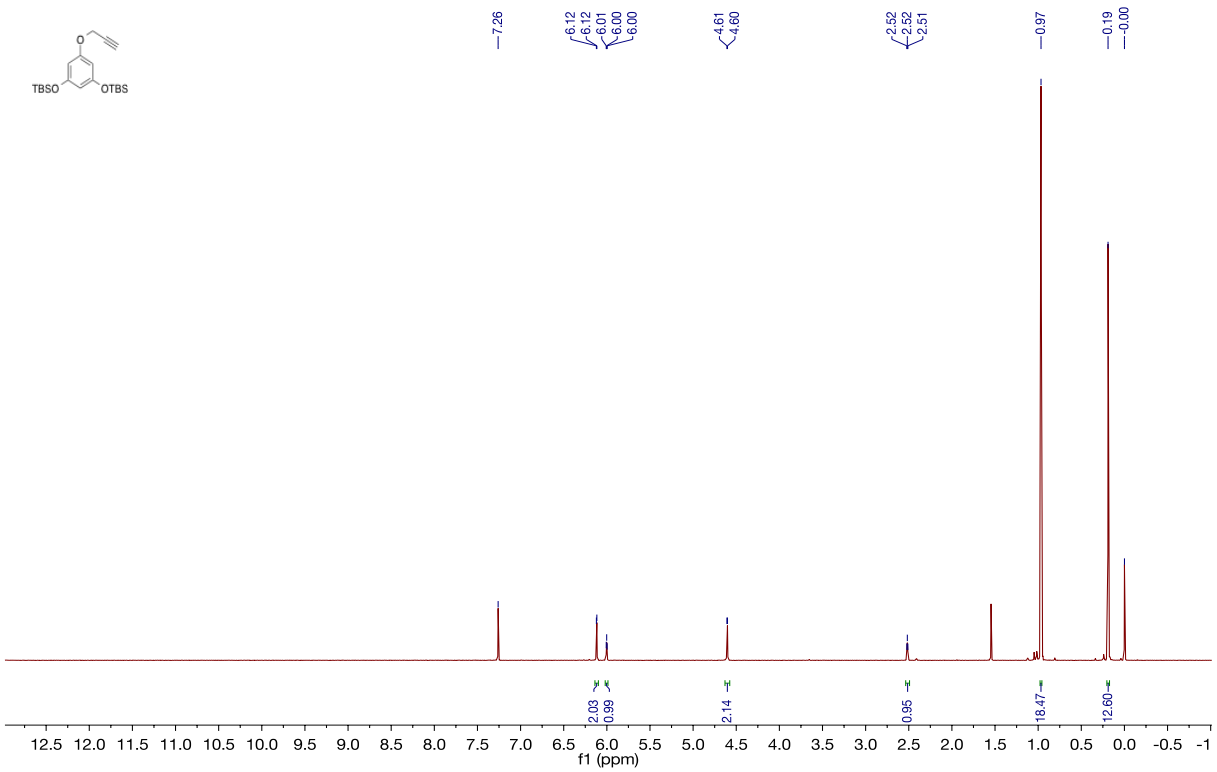
***^{1}H NMR* (A-11)**



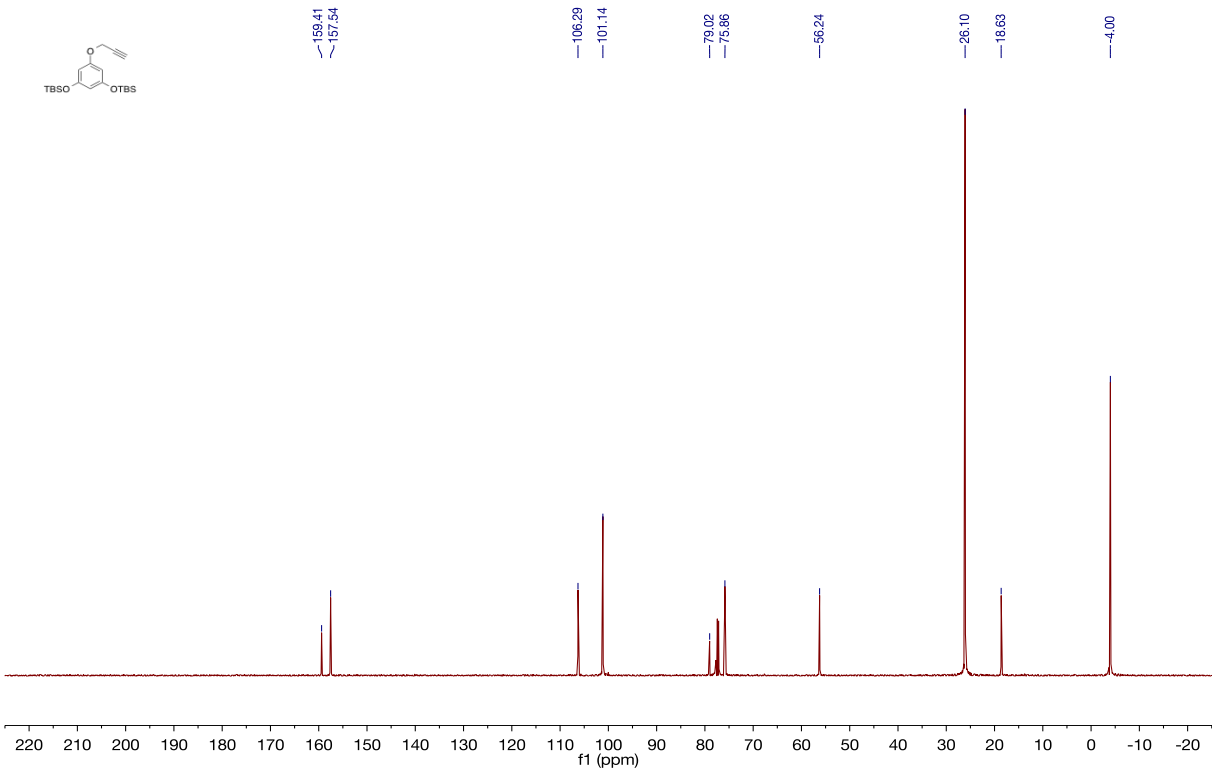
***^{13}C NMR* (A-11)**



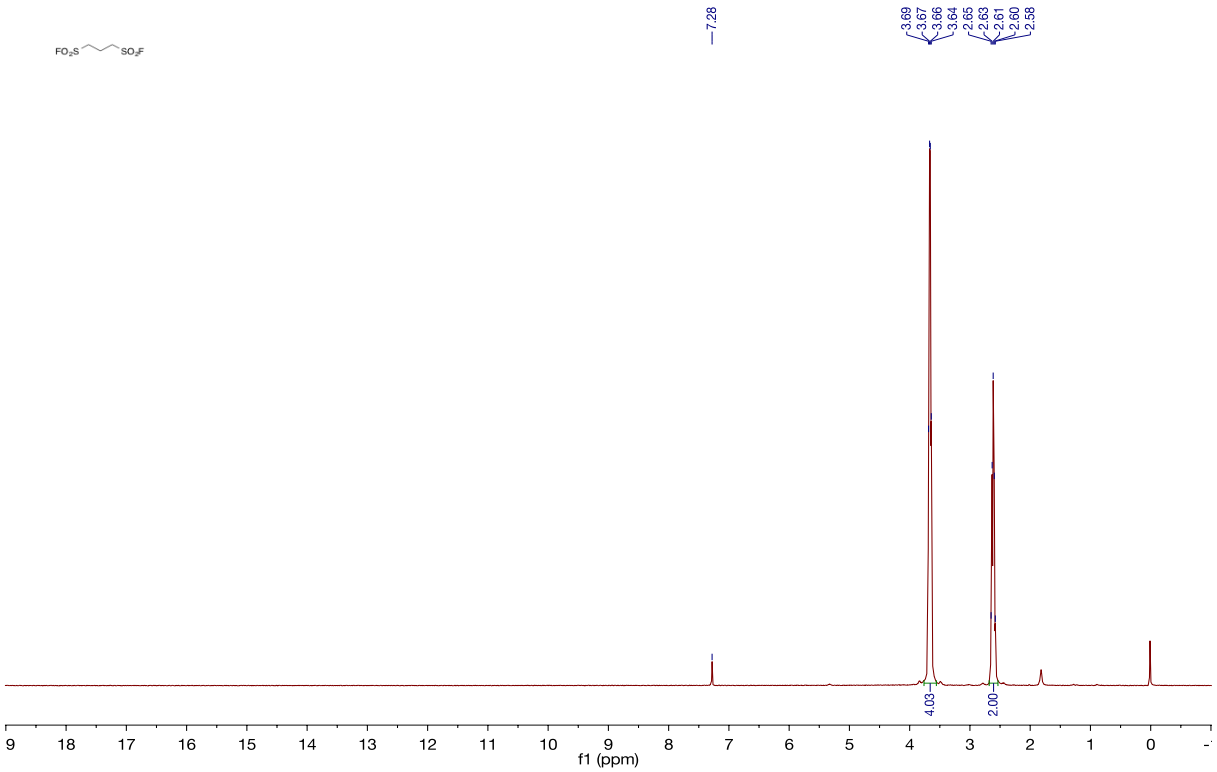
***[1]H NMR* (A-12)**



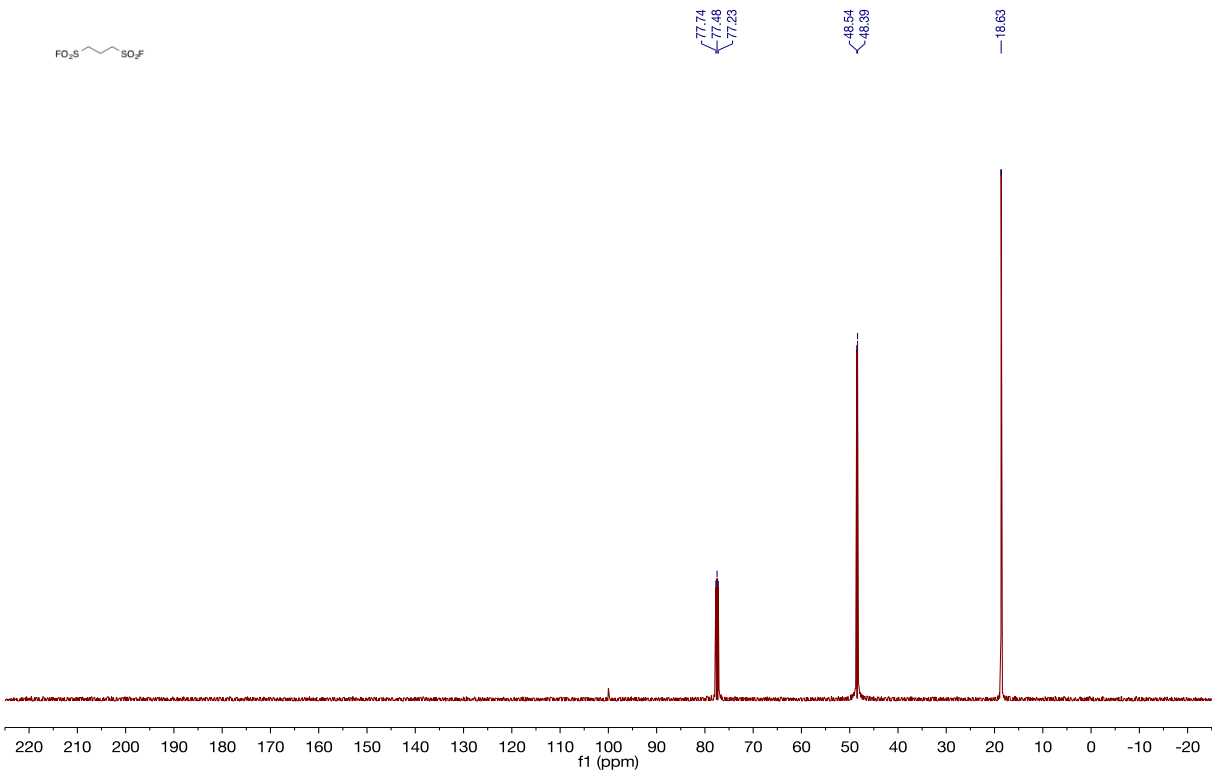
***[13]C NMR* (A-12)**



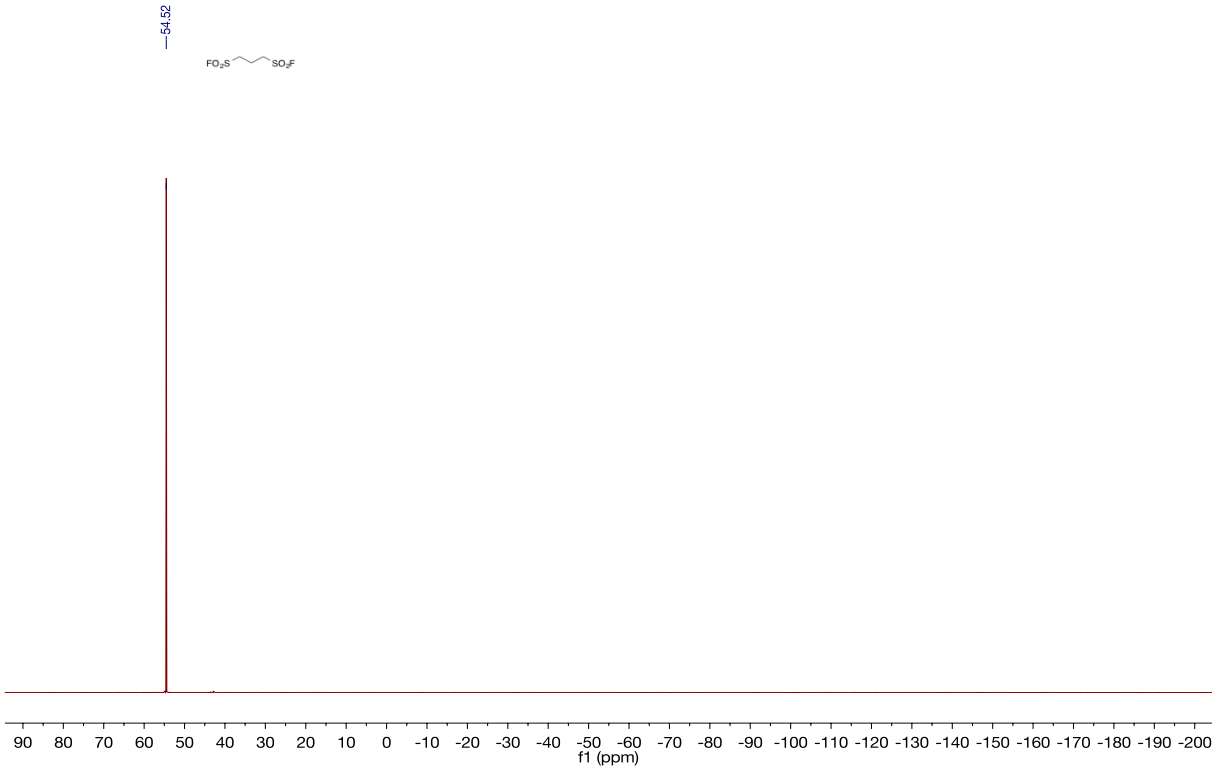
^{1}H NMR **(B-13)**



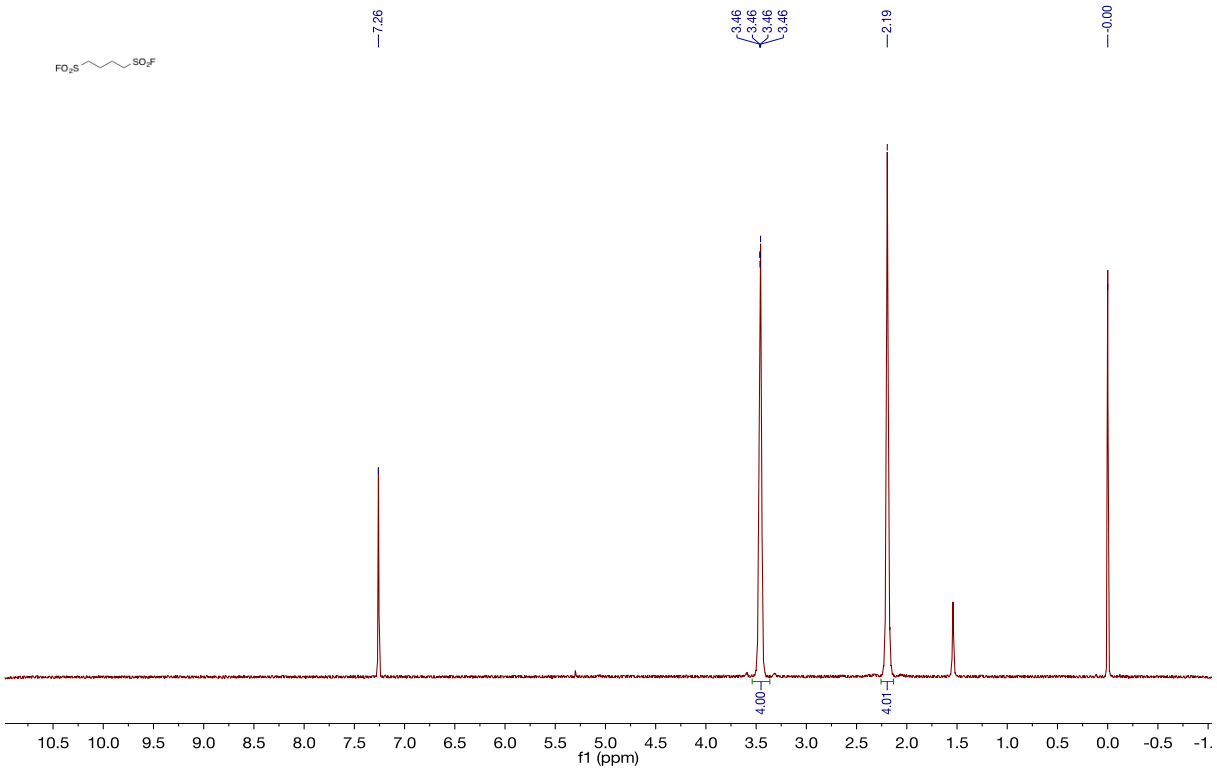
^{13}C NMR **(B-13)**



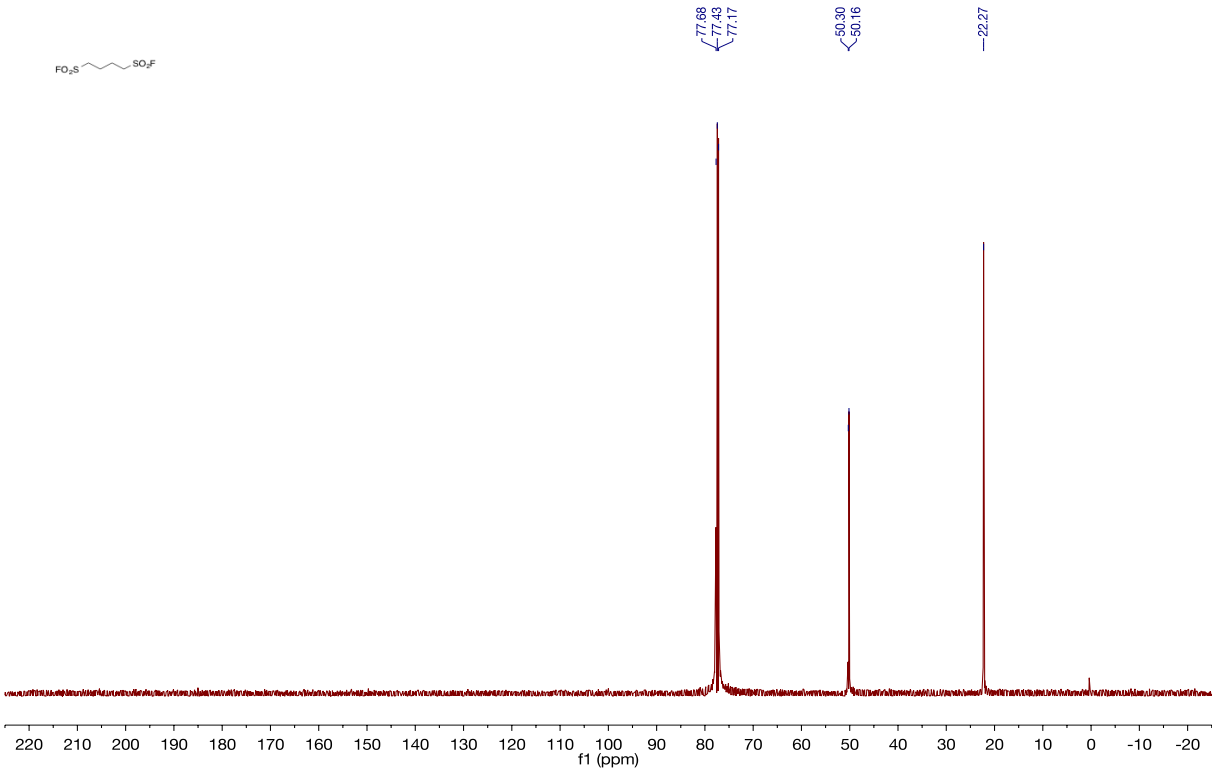
^{19}F NMR **(B-13)**



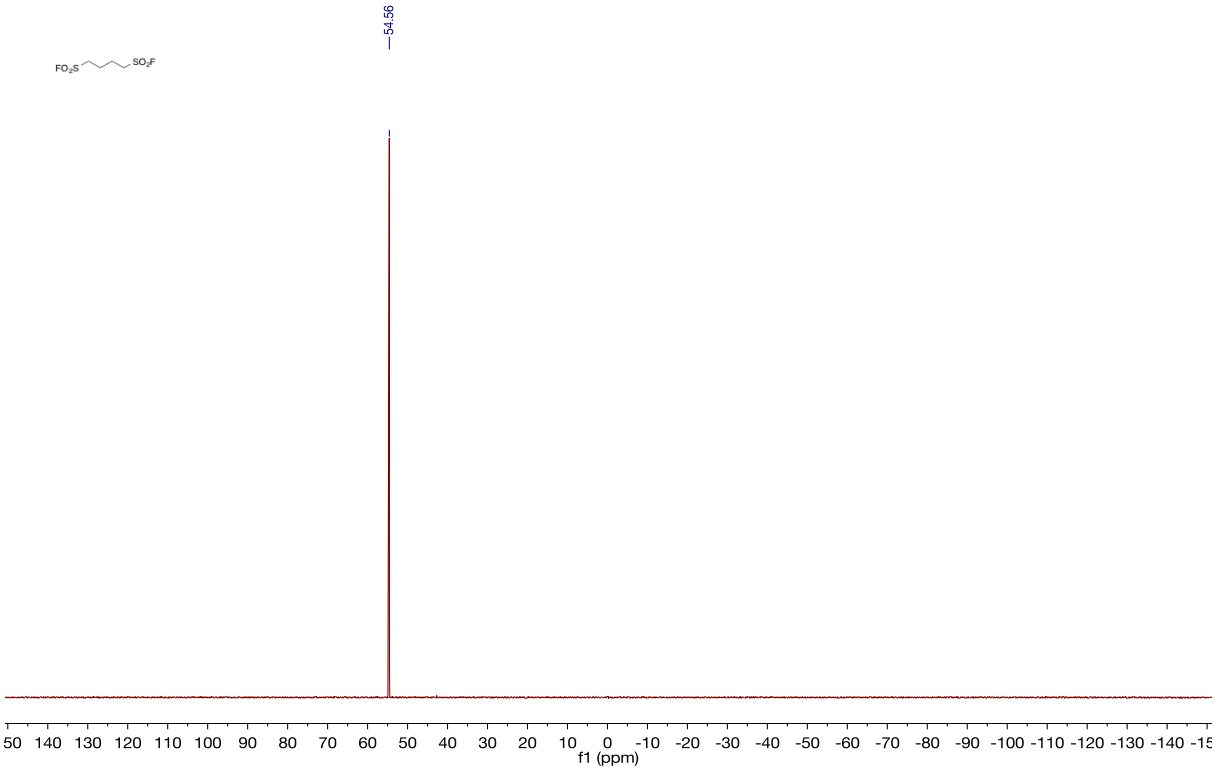
^{1}H NMR **(B-14)**



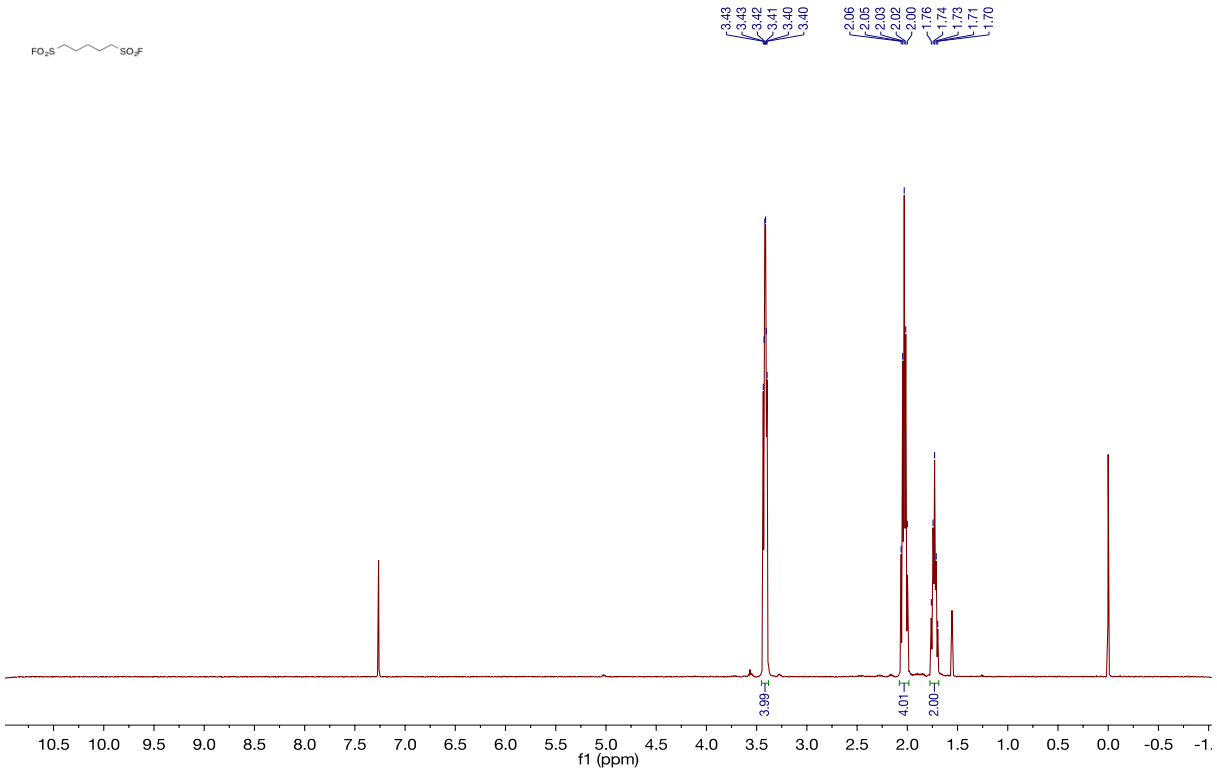
^{13}C NMR **(B-14)**



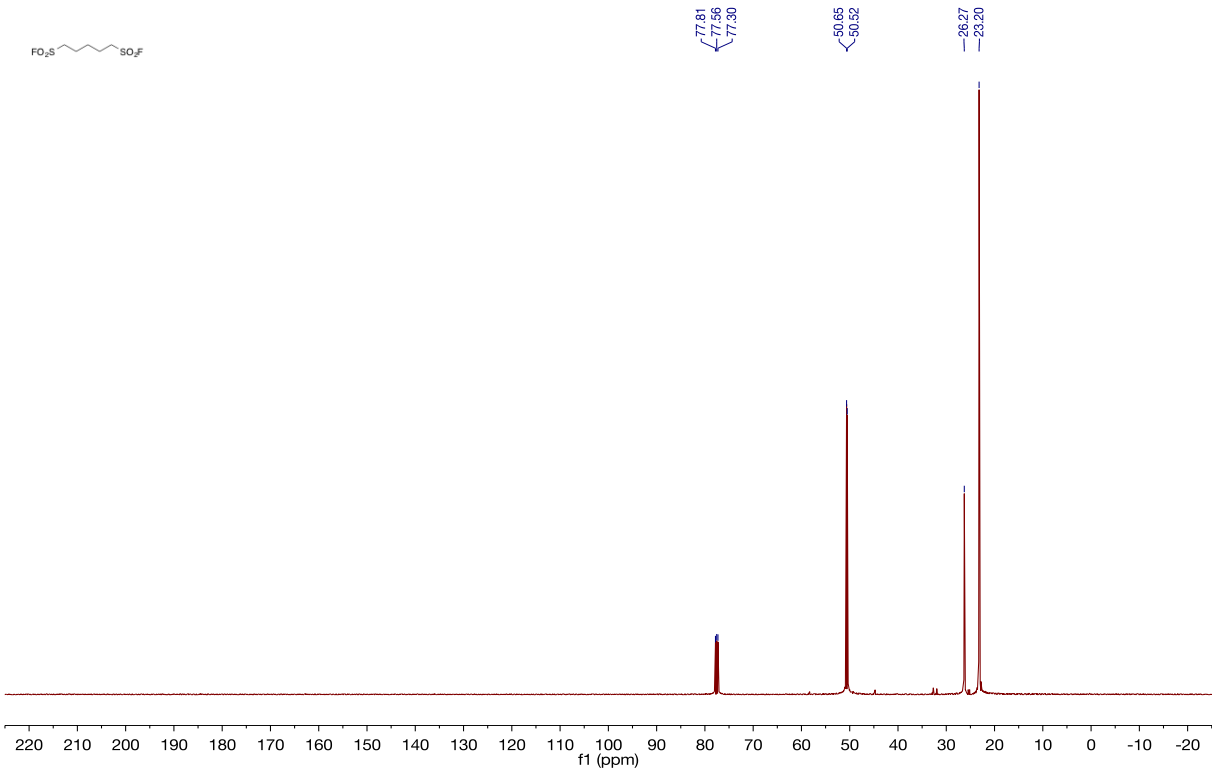
^{19}F NMR **(B-14)**



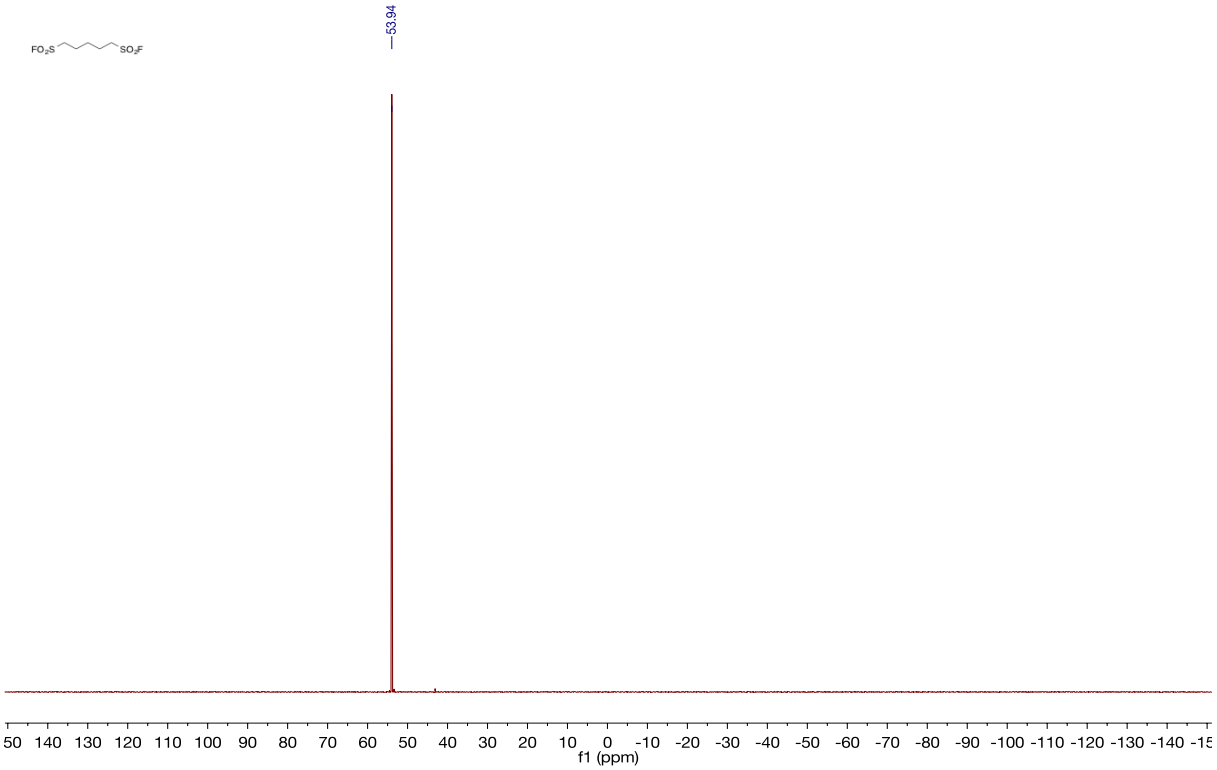
***[1]H NMR* (B-15)**



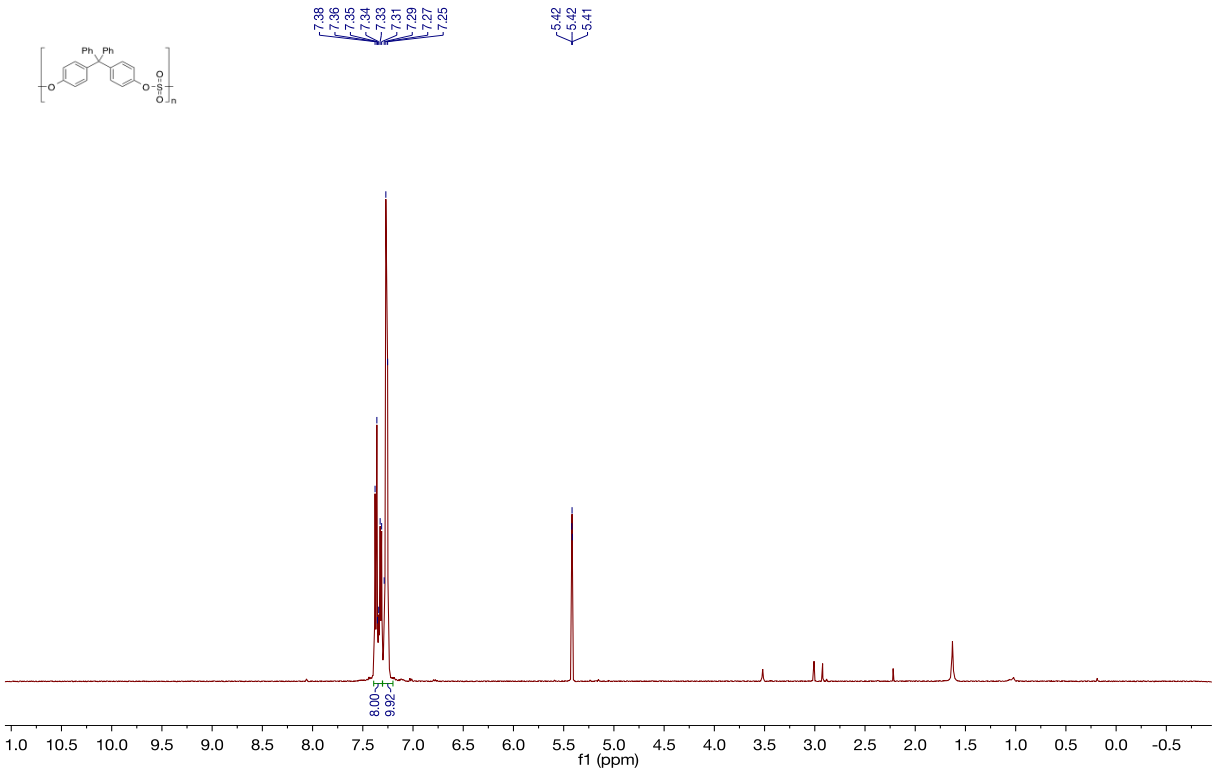
***[13]C NMR* (B-15)**



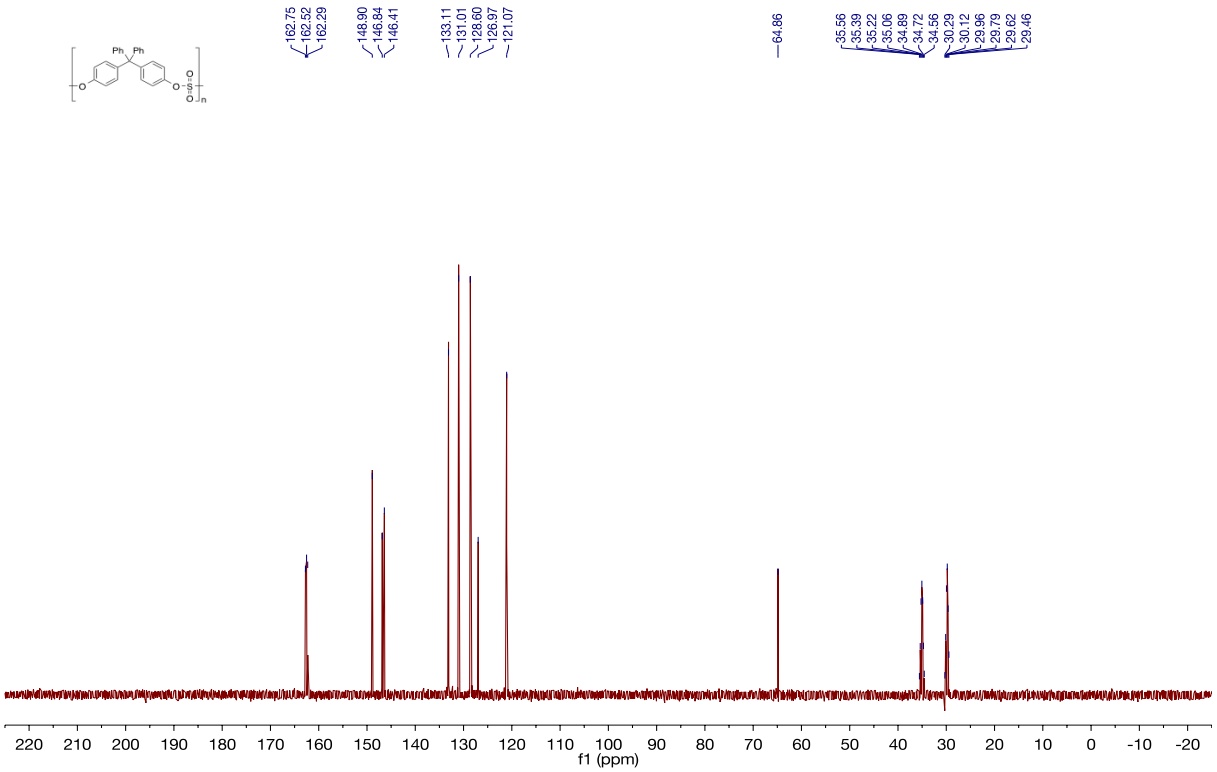
***^{19}F NMR* (B-15)**



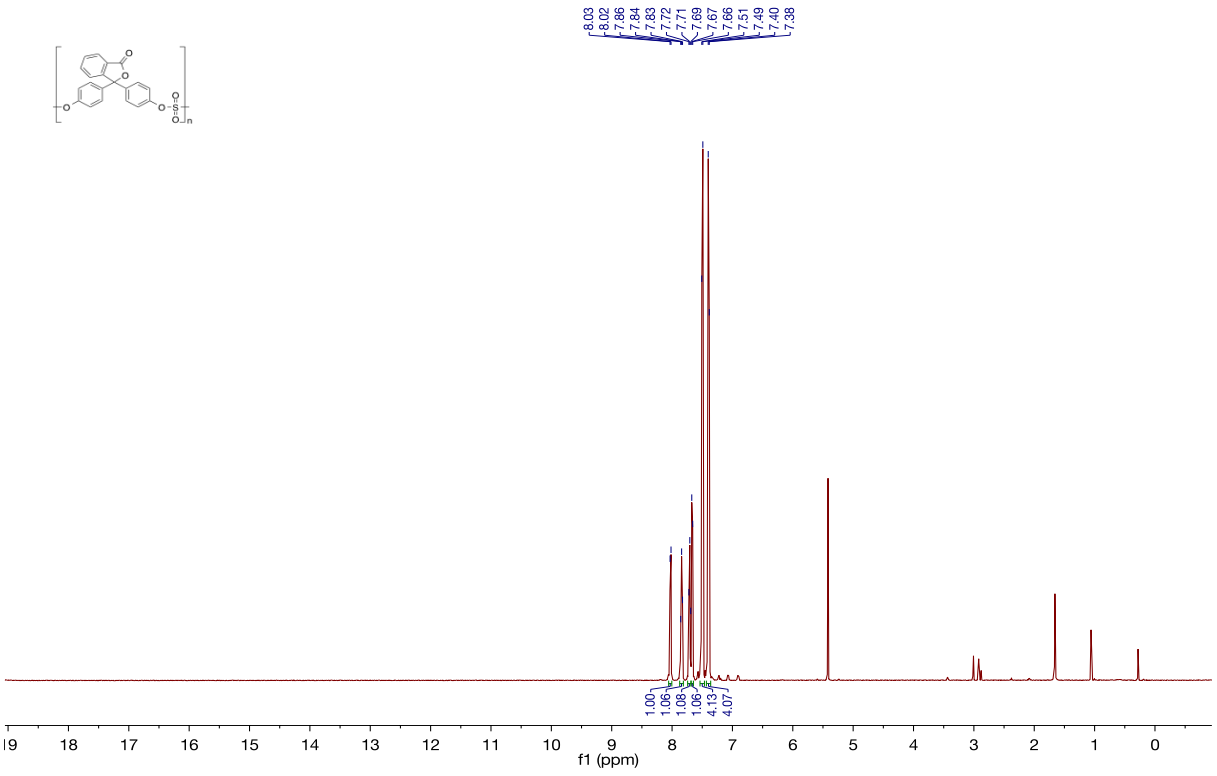
***^{1}H NMR* (P-3)**



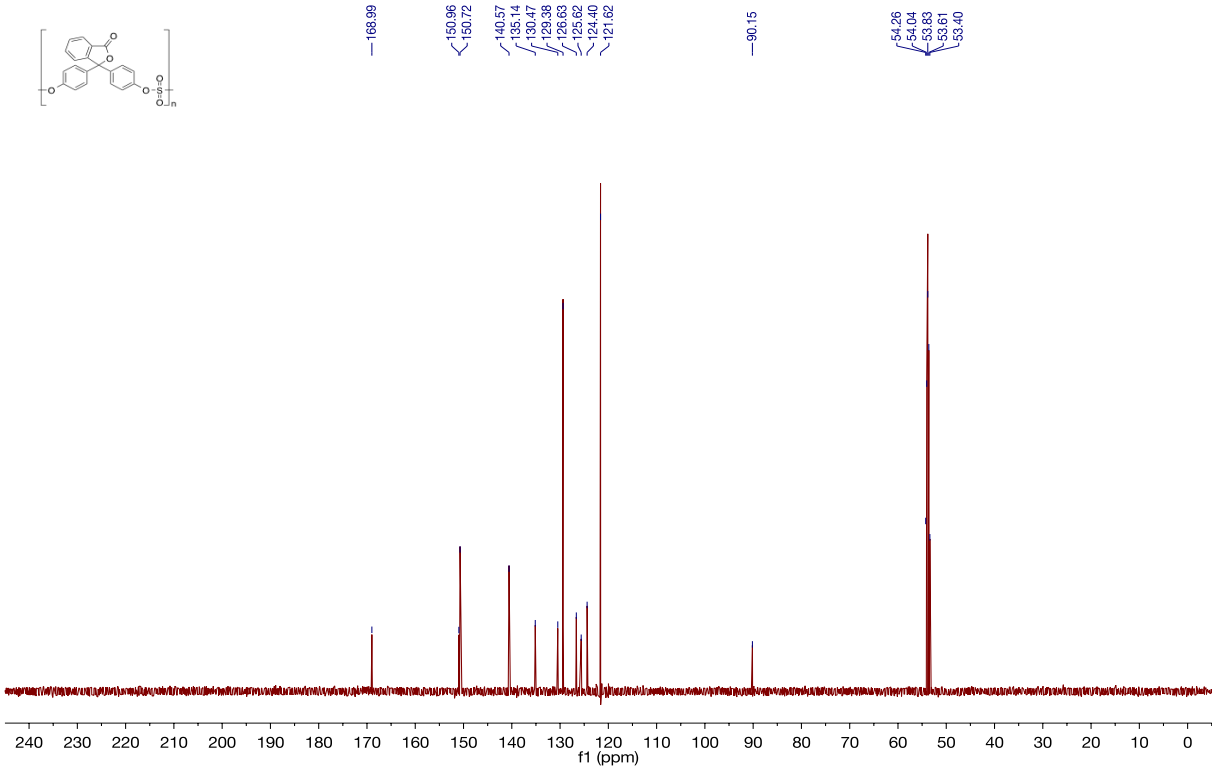
^{13}C NMR **(P-3)**



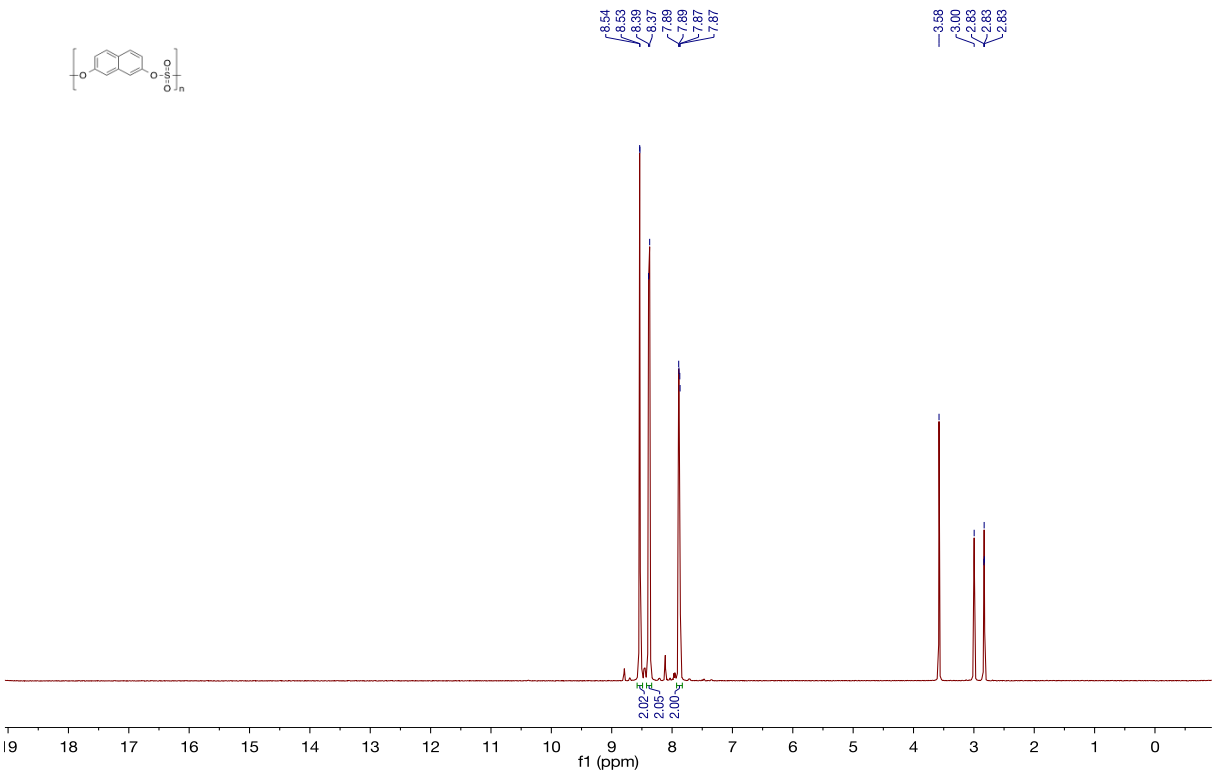
^{1}H NMR **(P-4)**



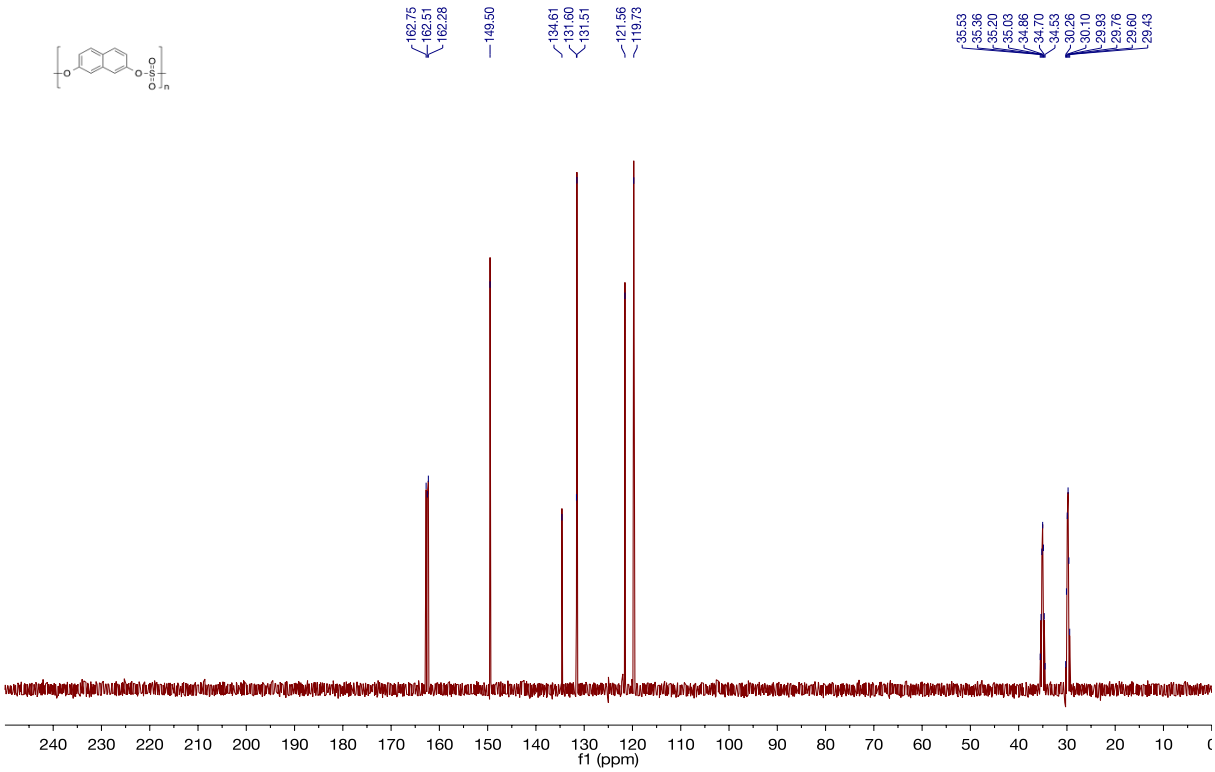
***^{13}C NMR* (P-4)**



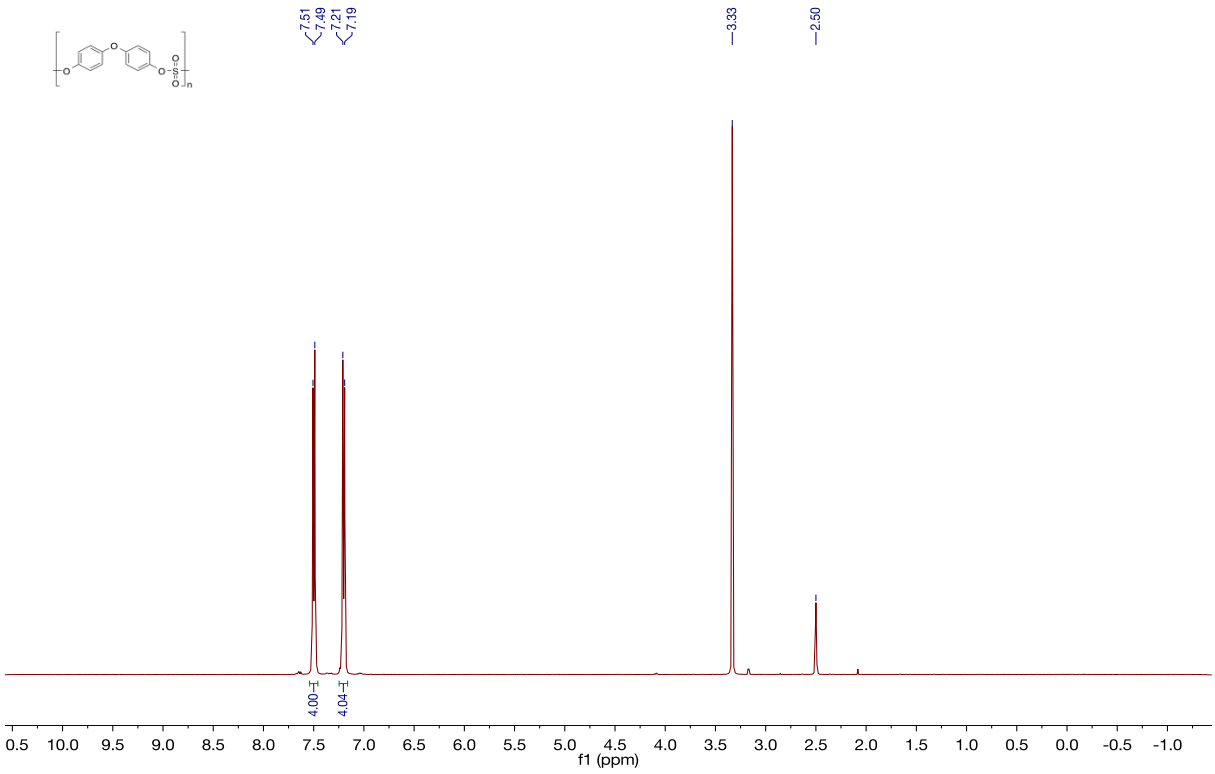
***^{1}H NMR* (P-5)**



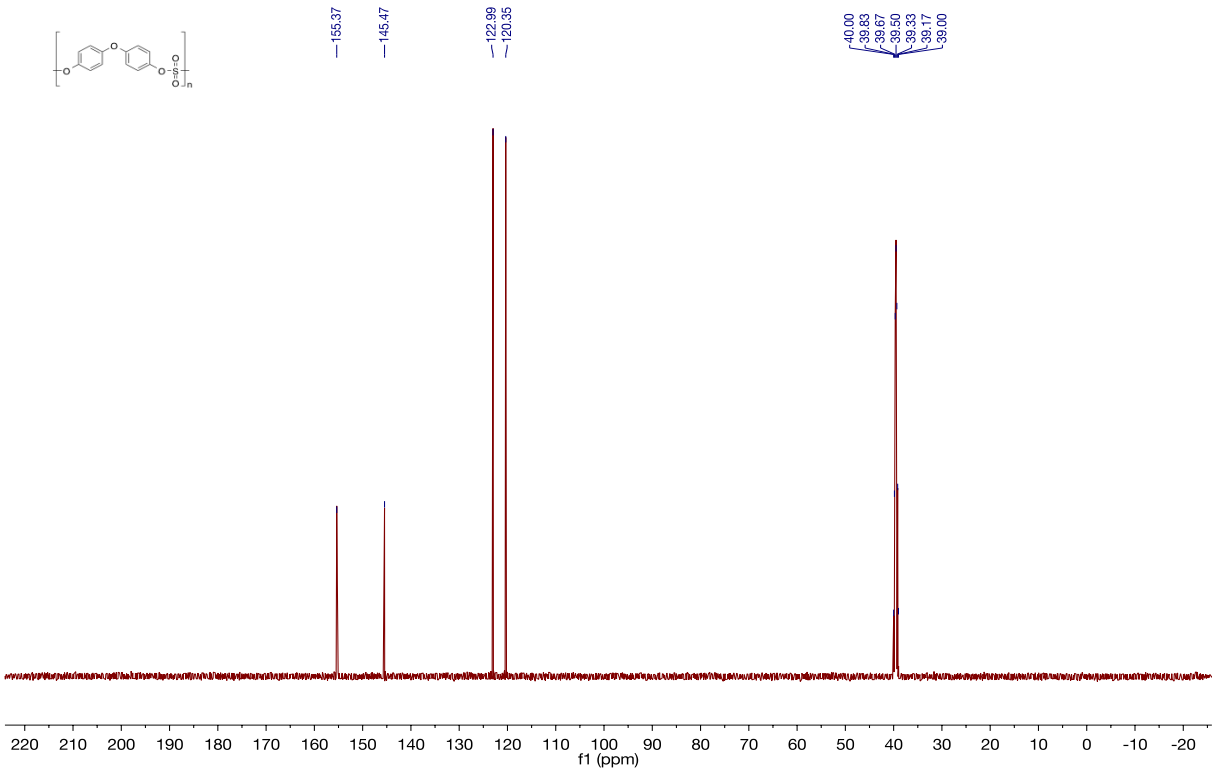
***^{13}C NMR* (P-5)**



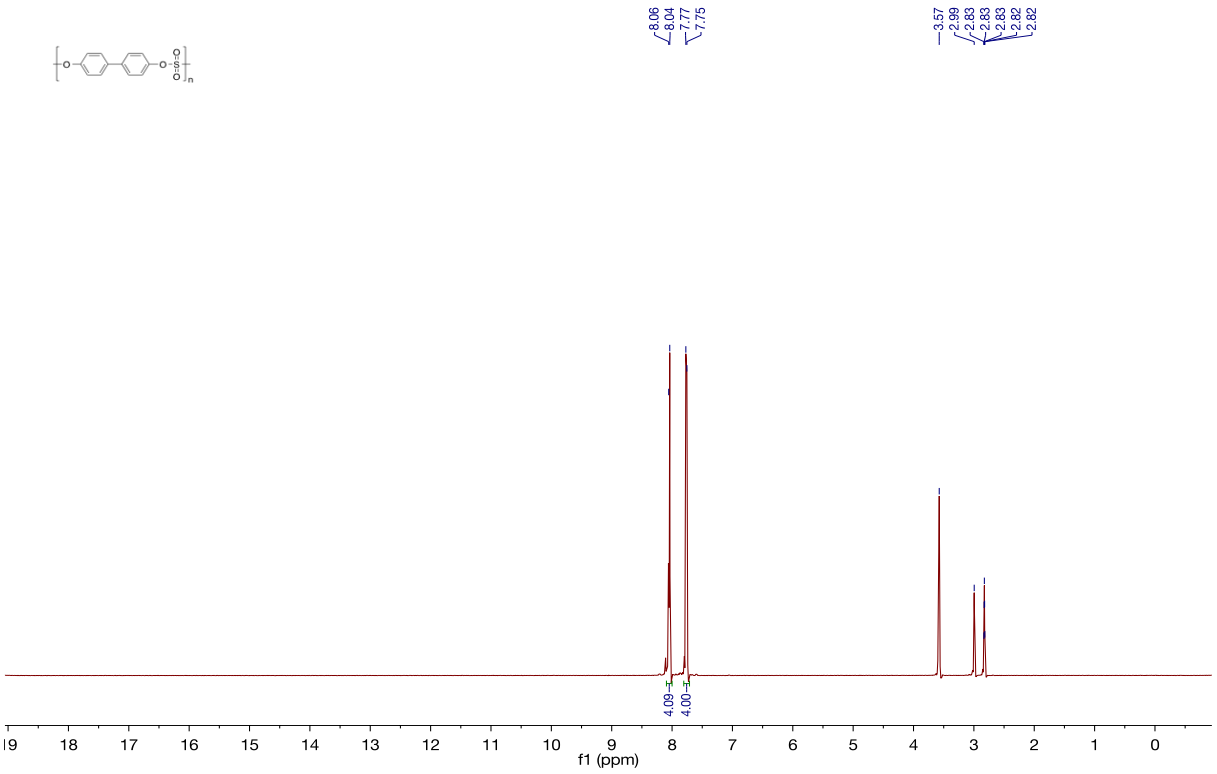
***^{1}H NMR* (P-6)**



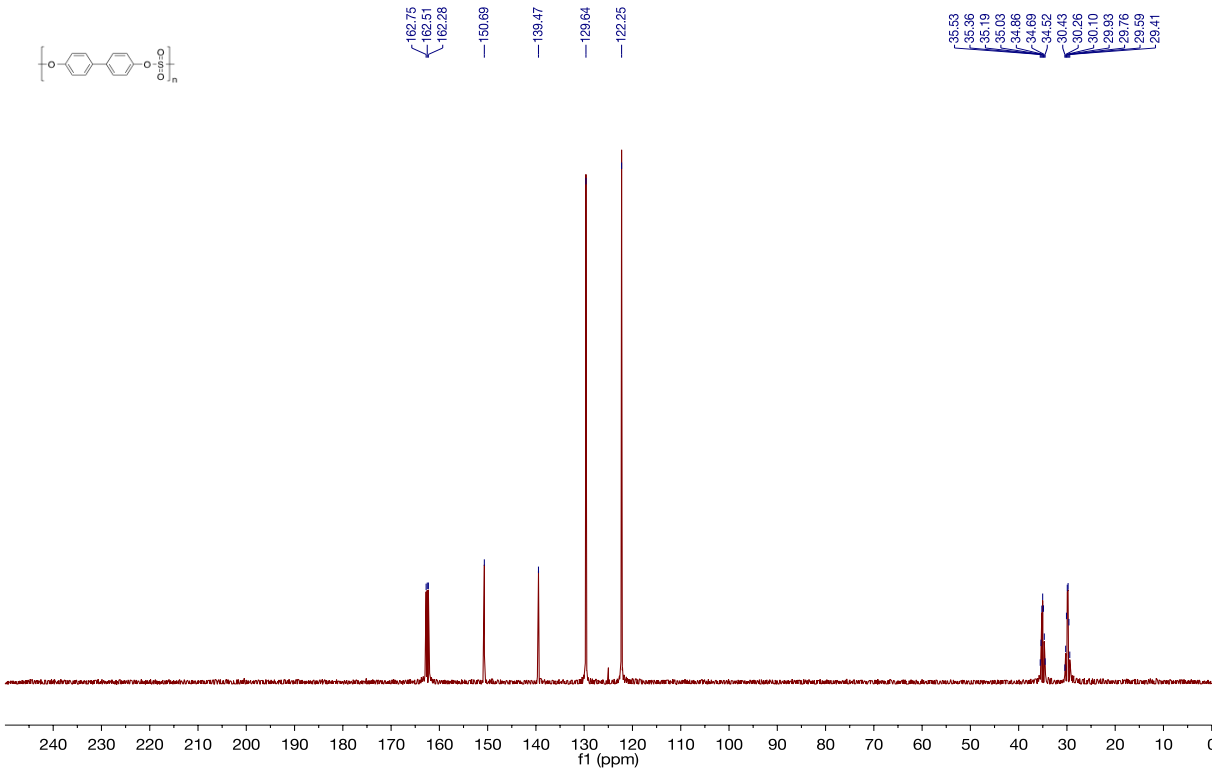
***^{13}C NMR* (P-6)**



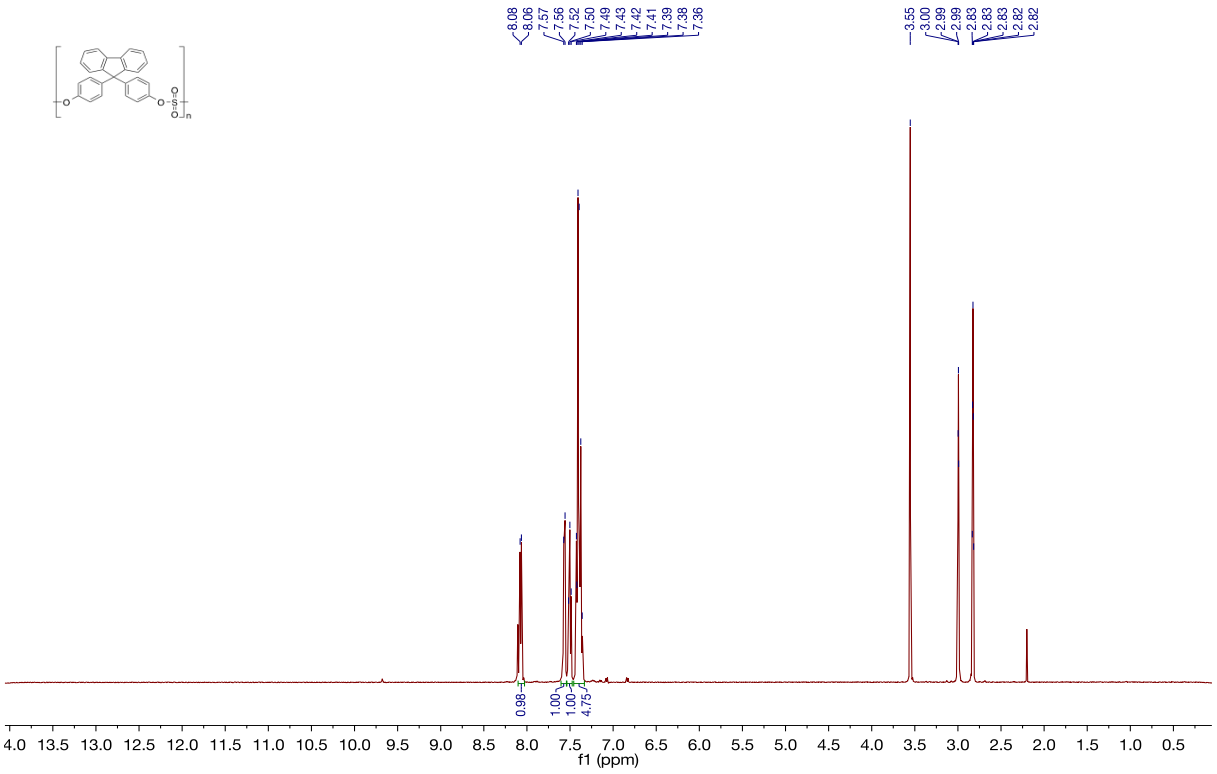
***^{1}H NMR* (P-7)**



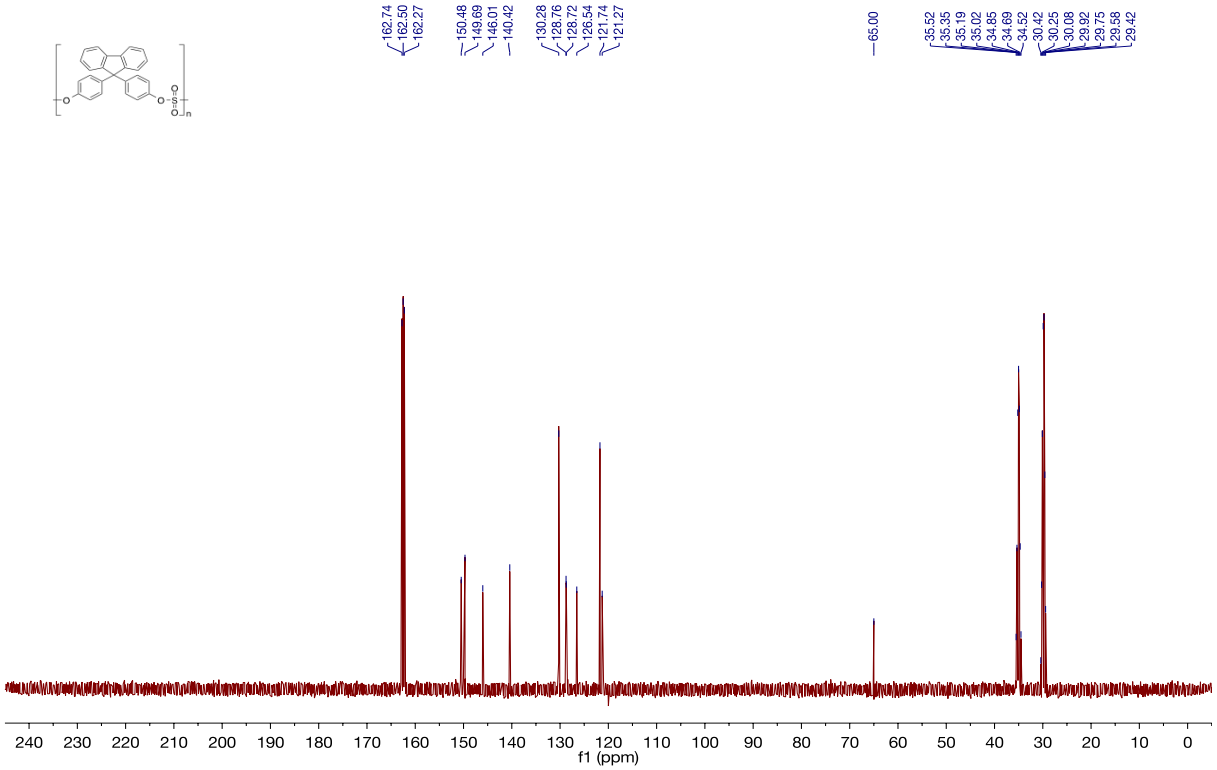
***^{13}C NMR* (P-7)**



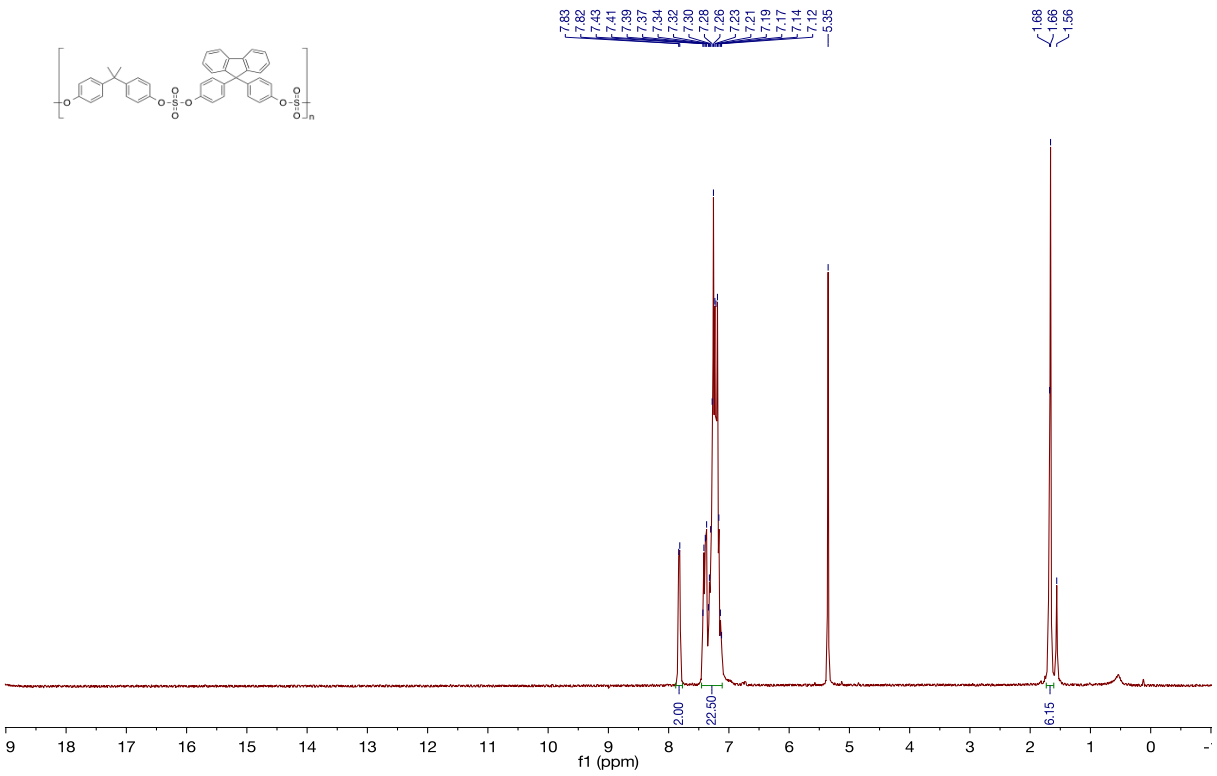
***^{1}H NMR* (P-8a)**



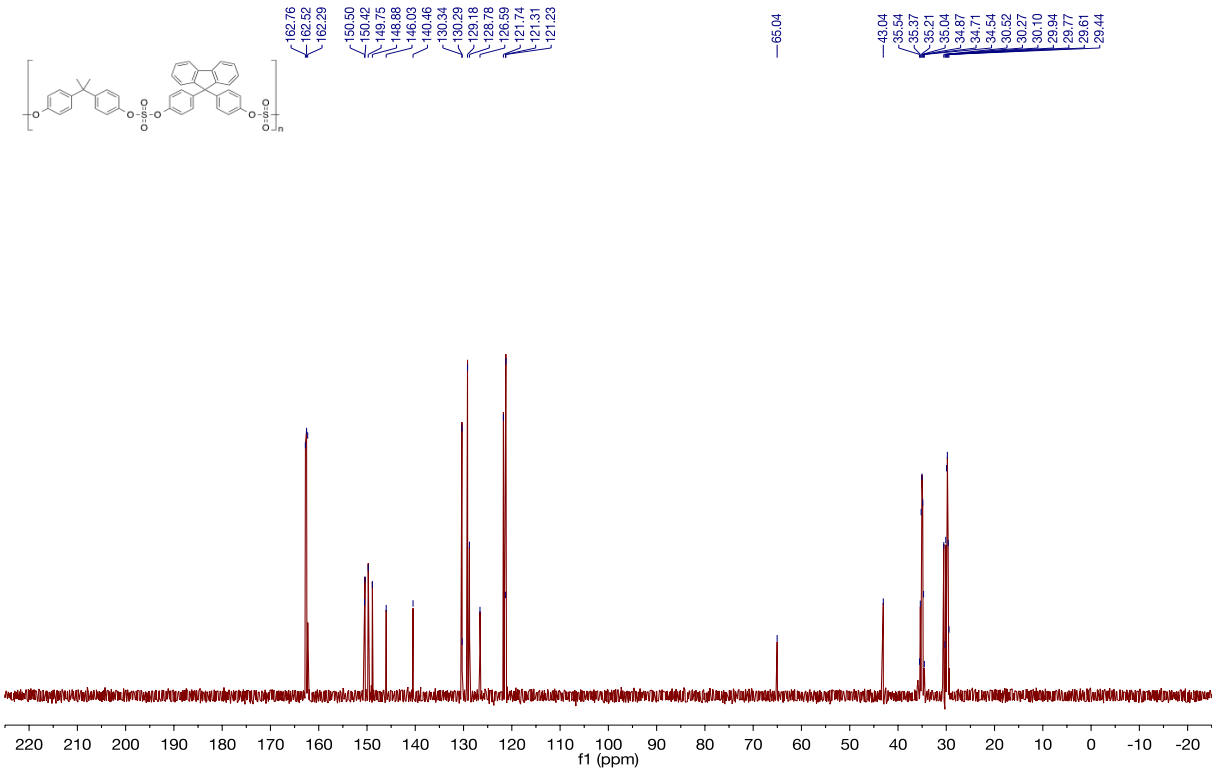
***^{13}C NMR* (P-8a)**



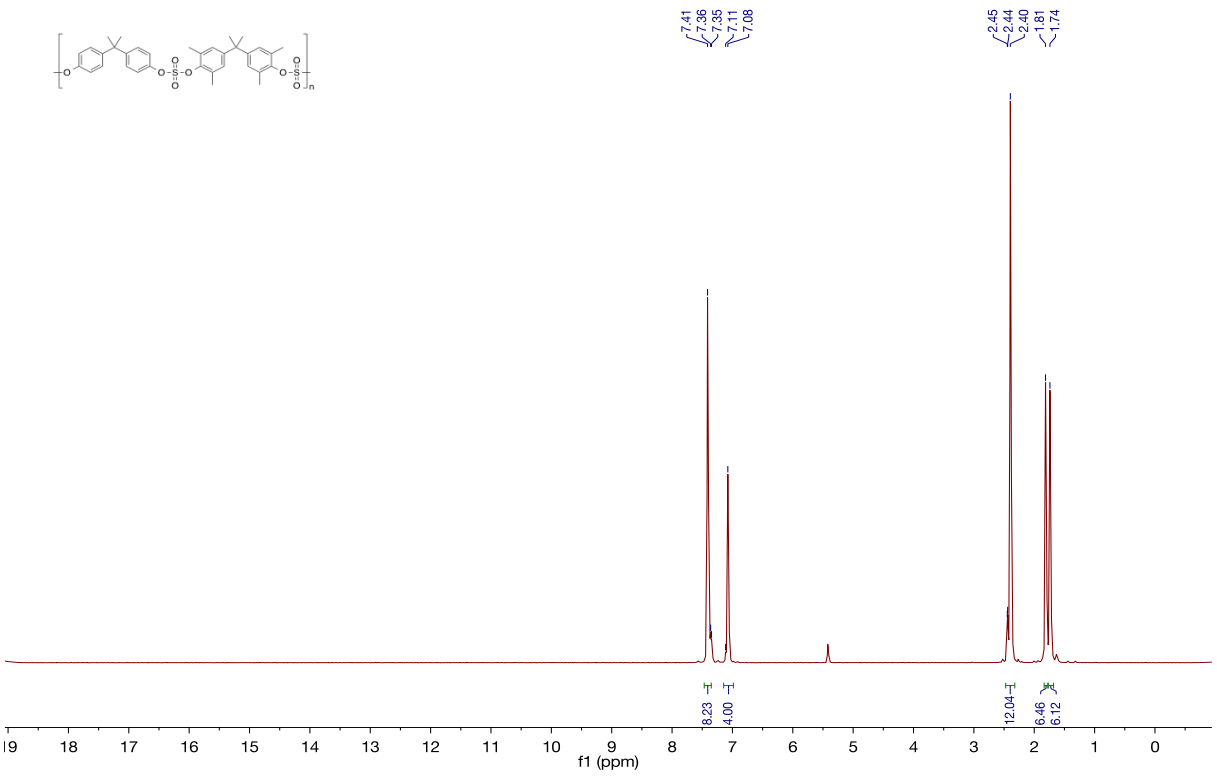
***^{1}H NMR* (P-8b)**



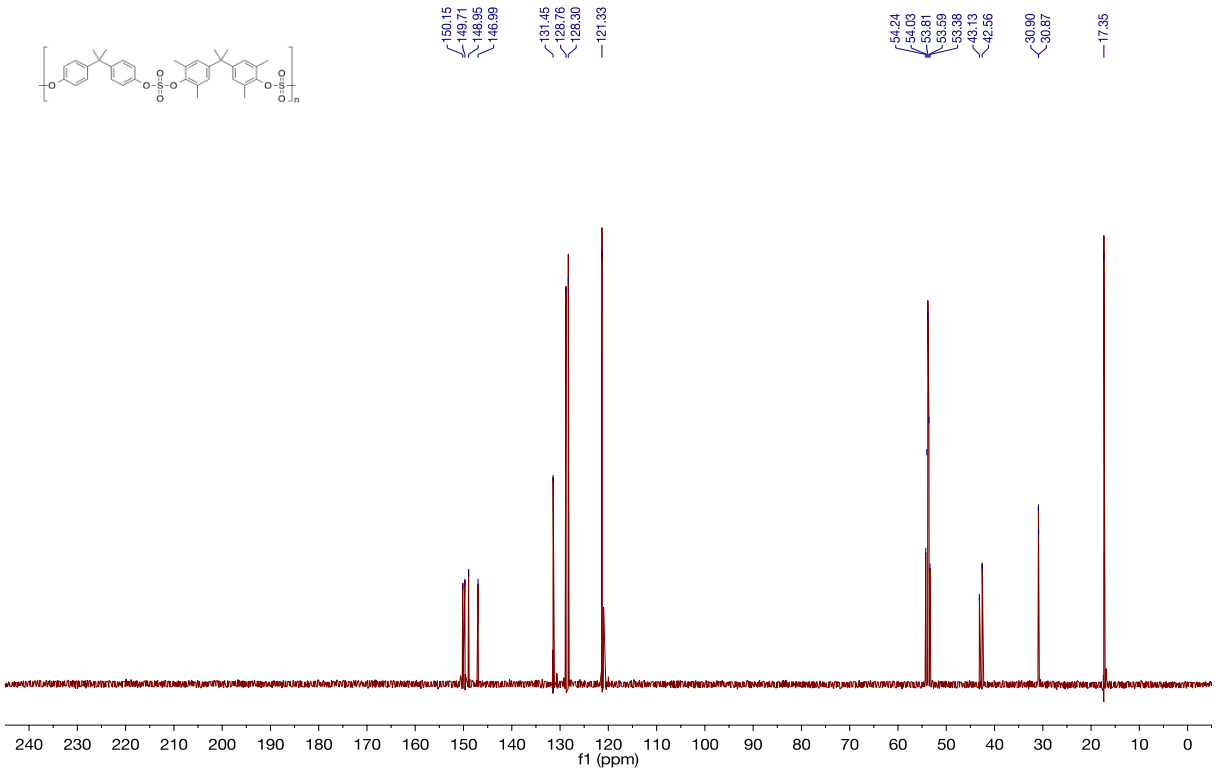
***^{13}C NMR* (P-8b)**



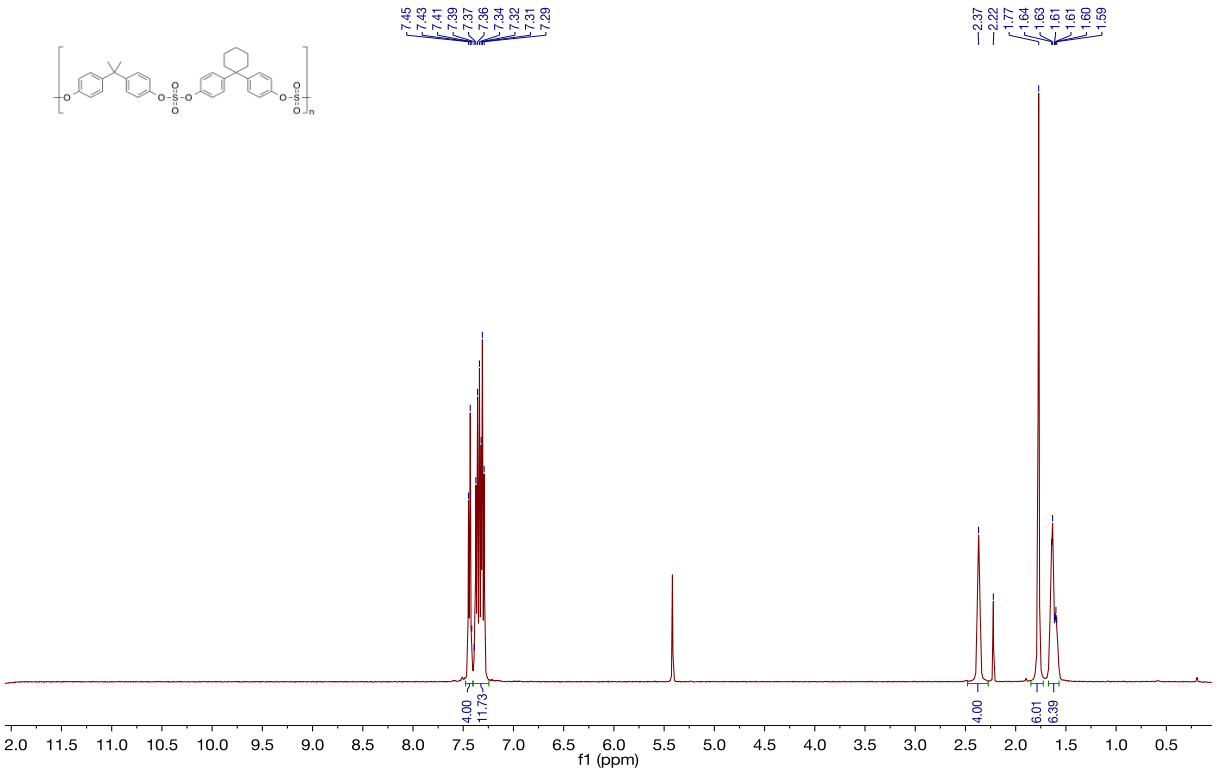
***^{1}H NMR* (P-9)**



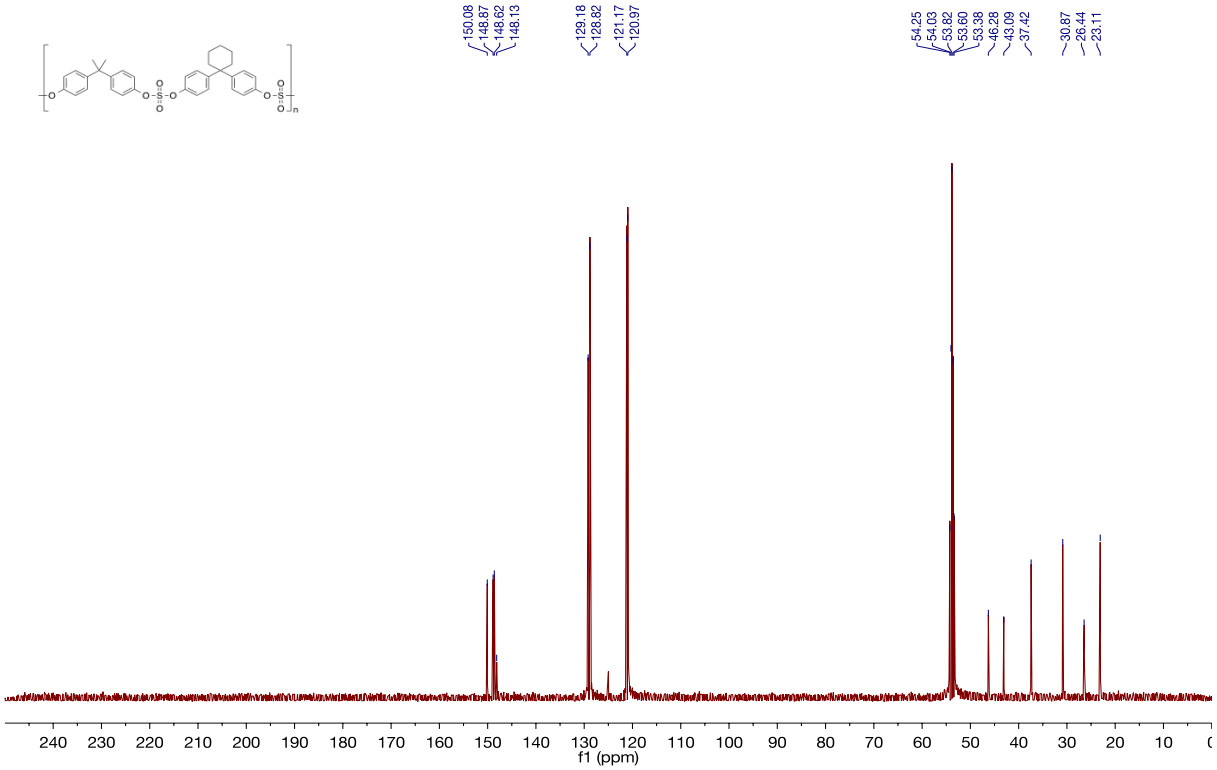
***^{13}C NMR* (P-9)**



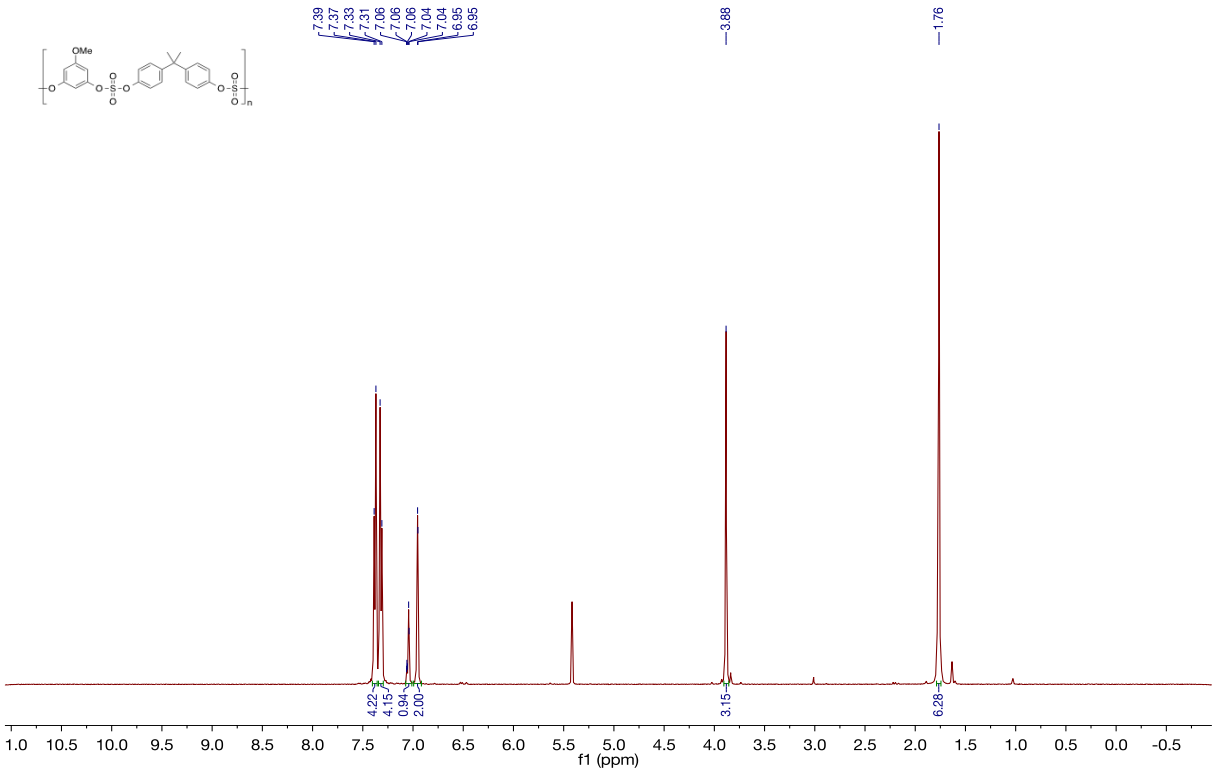
***^{1}H NMR* (P-10)**



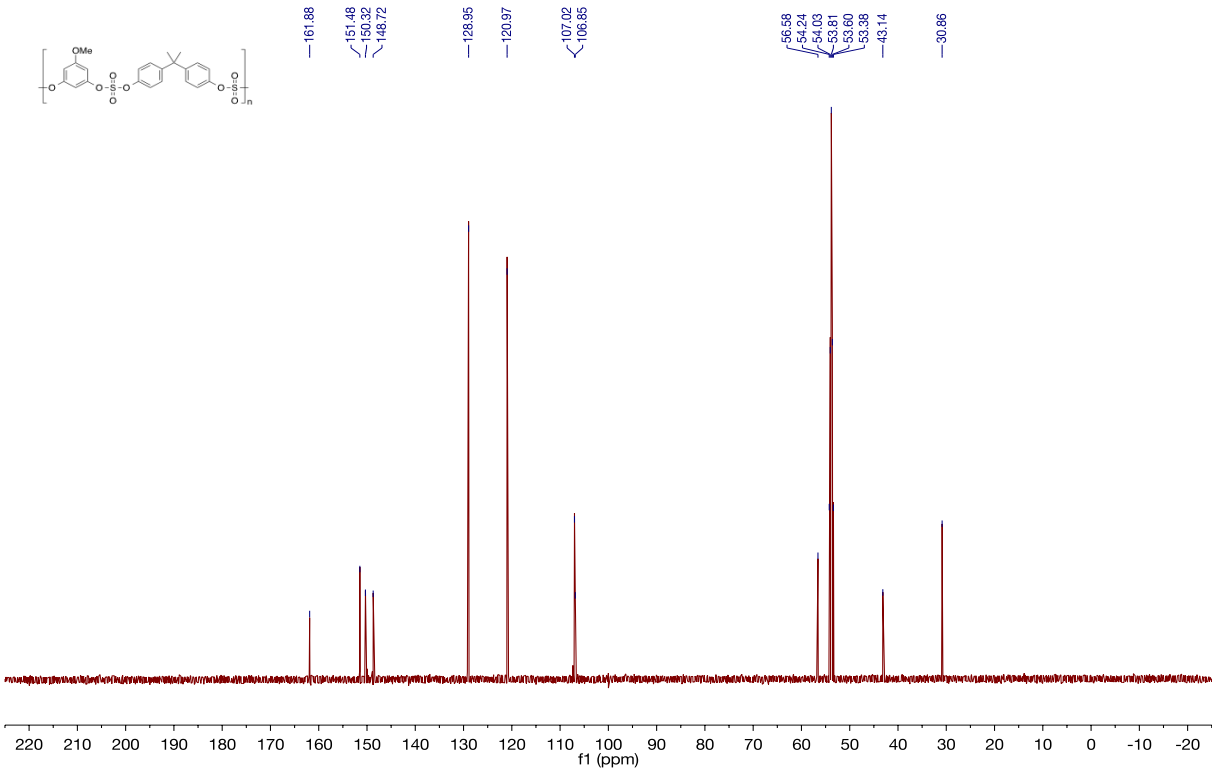
***^{13}C NMR* (P-10)**



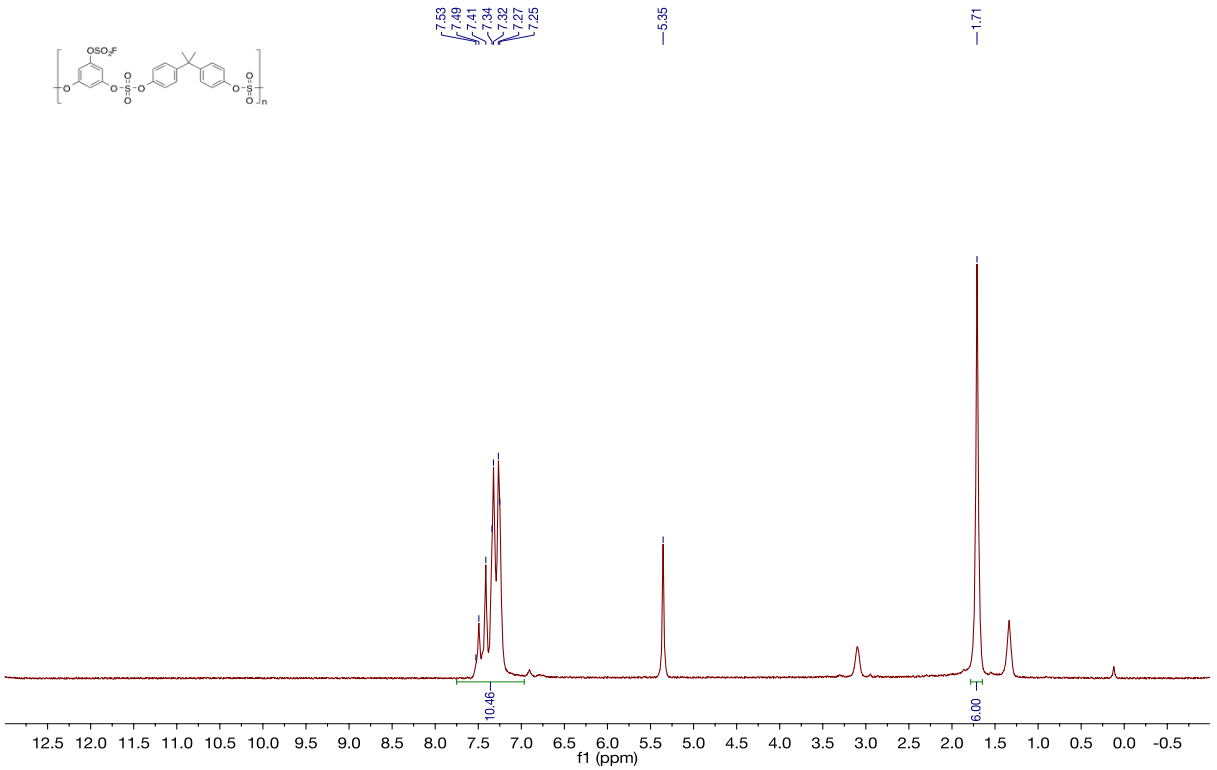
***^{1}H NMR* (P-11a)**



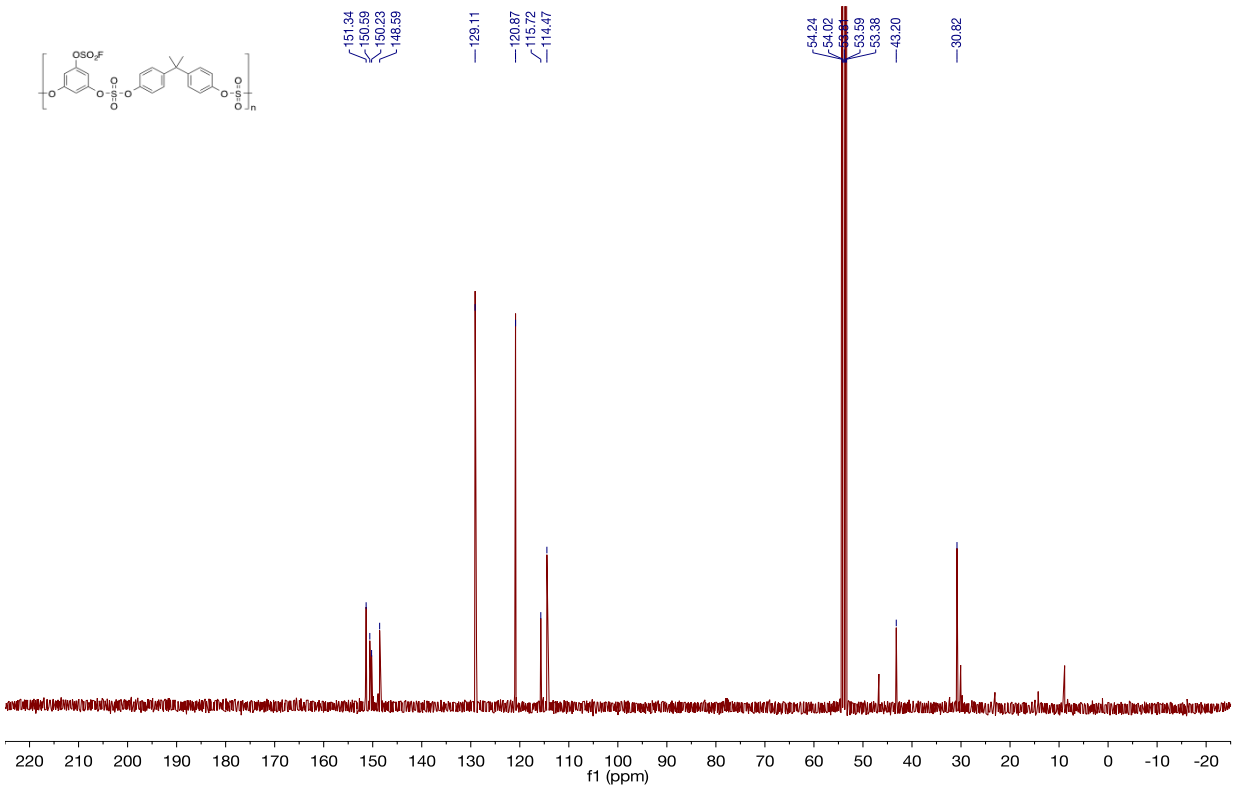
***^{13}C NMR* (P-11a)**



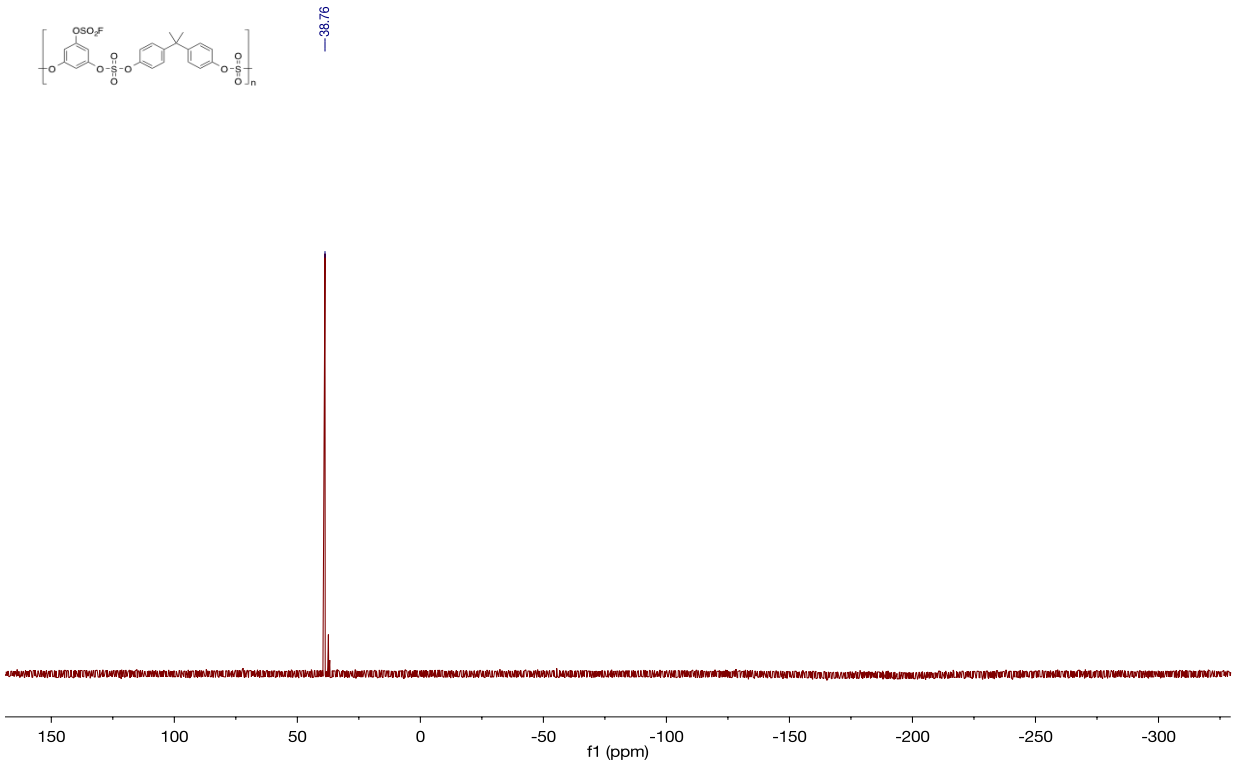
***^{1}H NMR* (P-11b)**



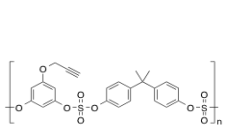
***^{13}C NMR* (P-11b)**



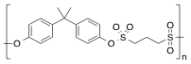
***^{19}F NMR* (P-11b)**



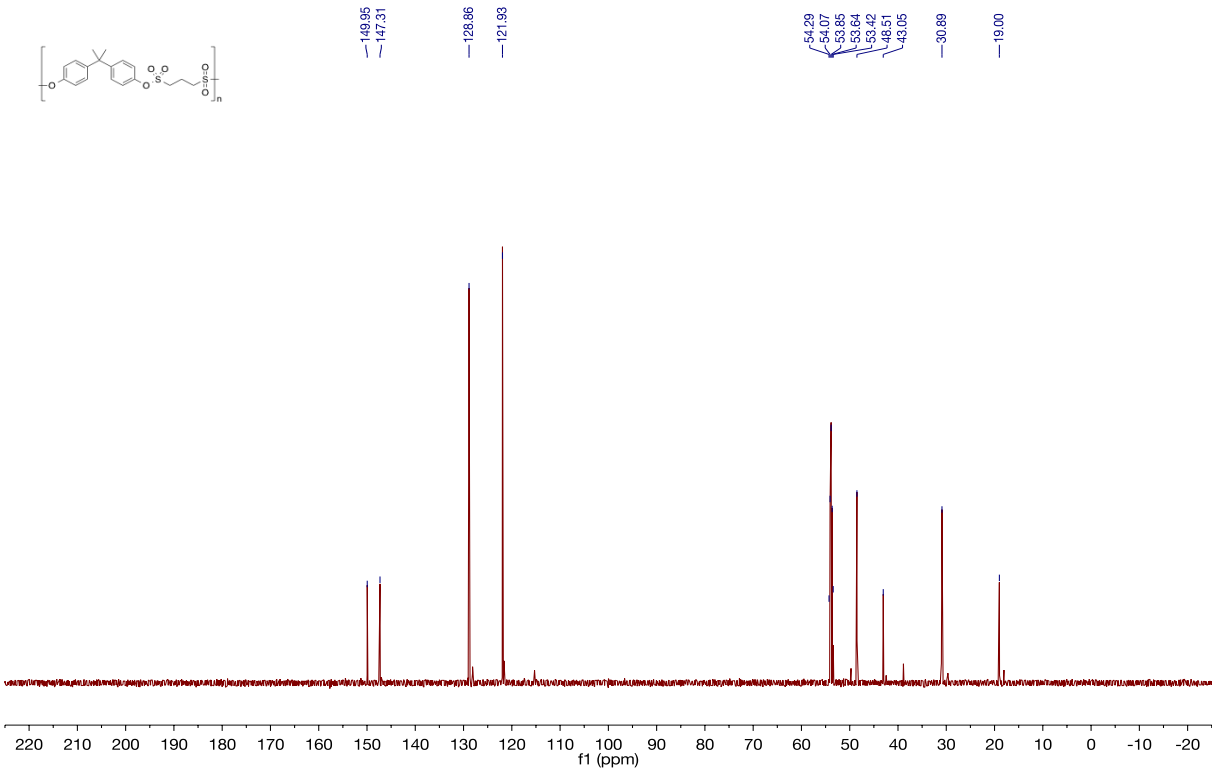
***^{1}H NMR* (P-12)**



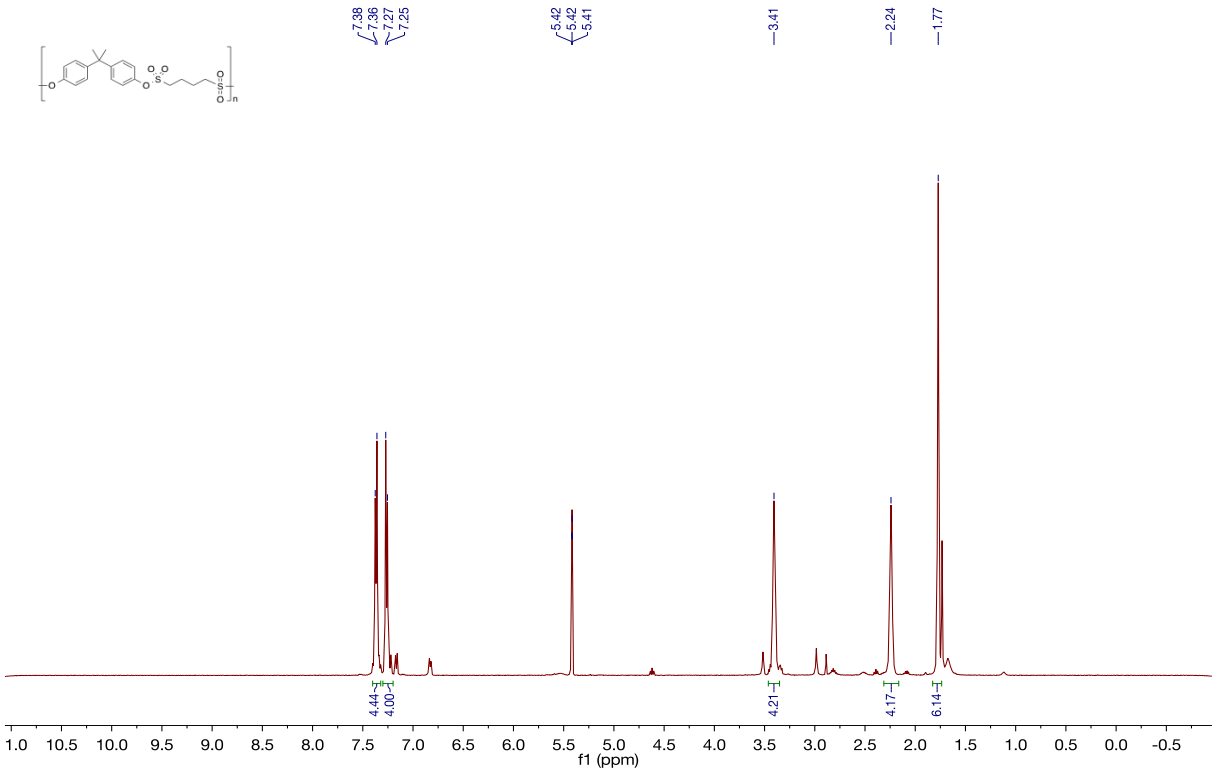
***^{1}H NMR* (P-13)**



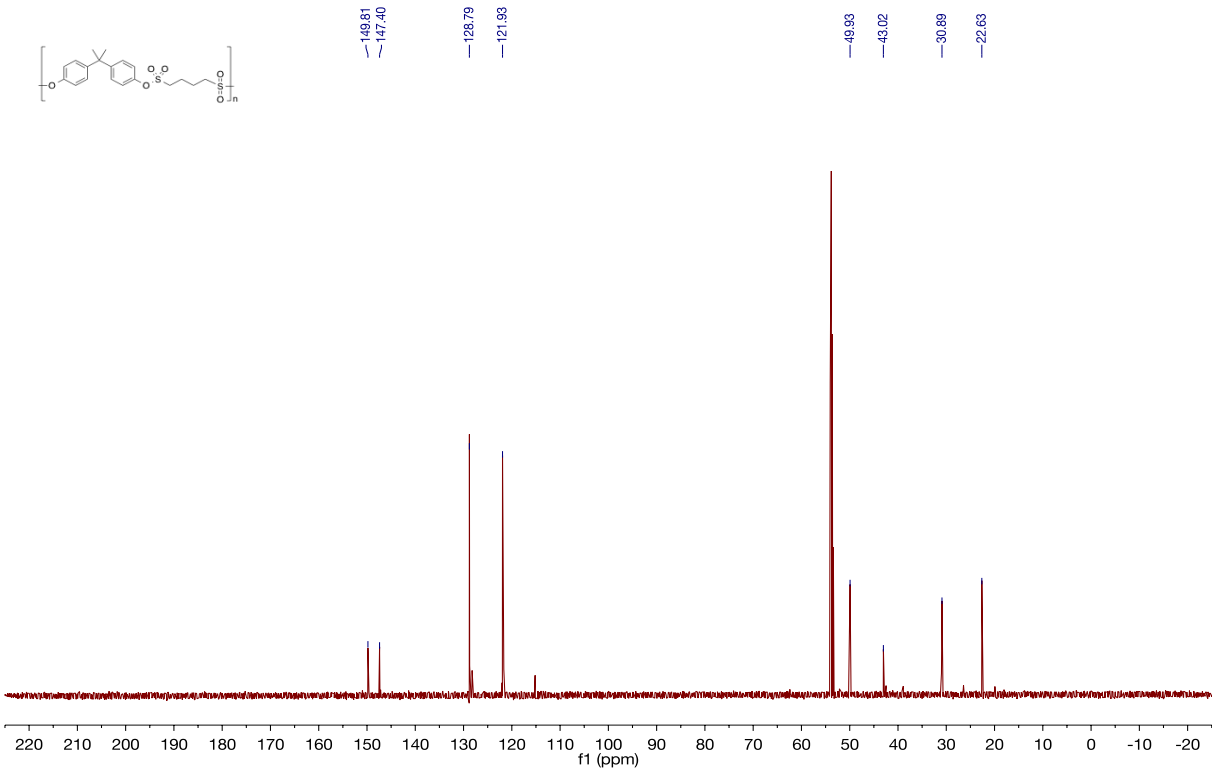
***^{13}C NMR* (P-13)**



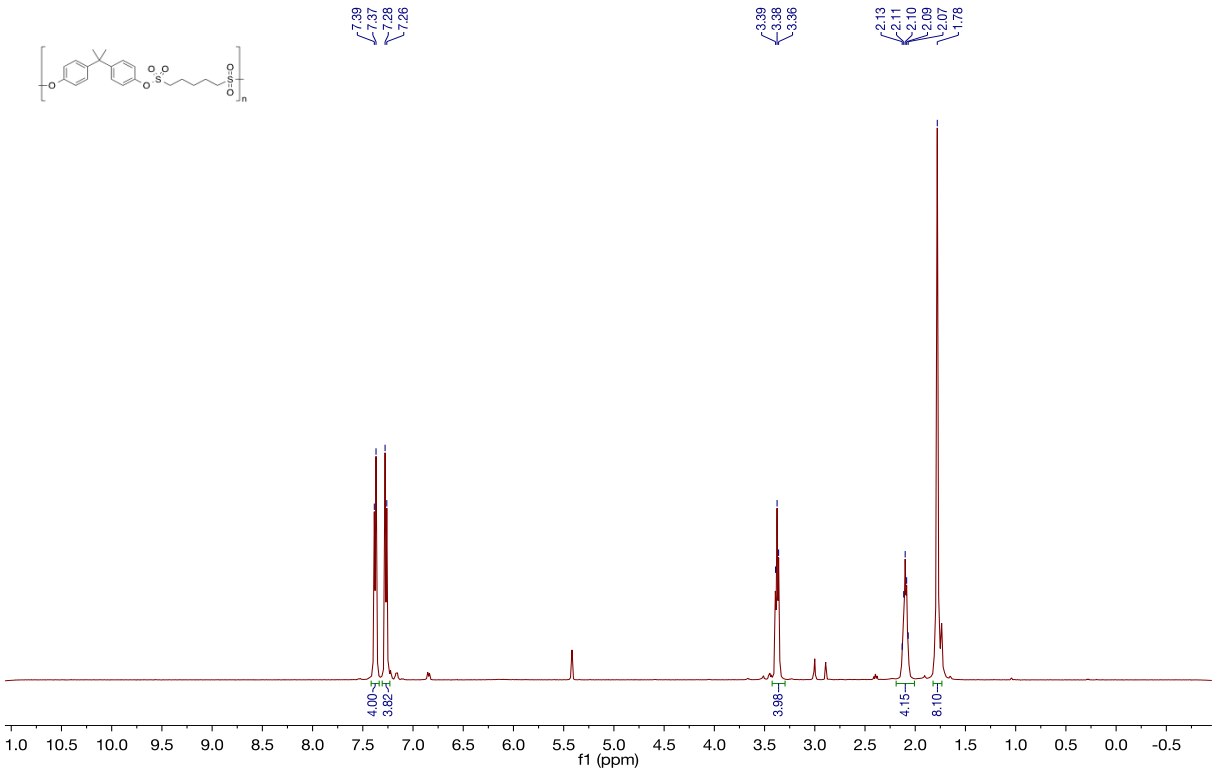
***^{1}H NMR* (P-14)**



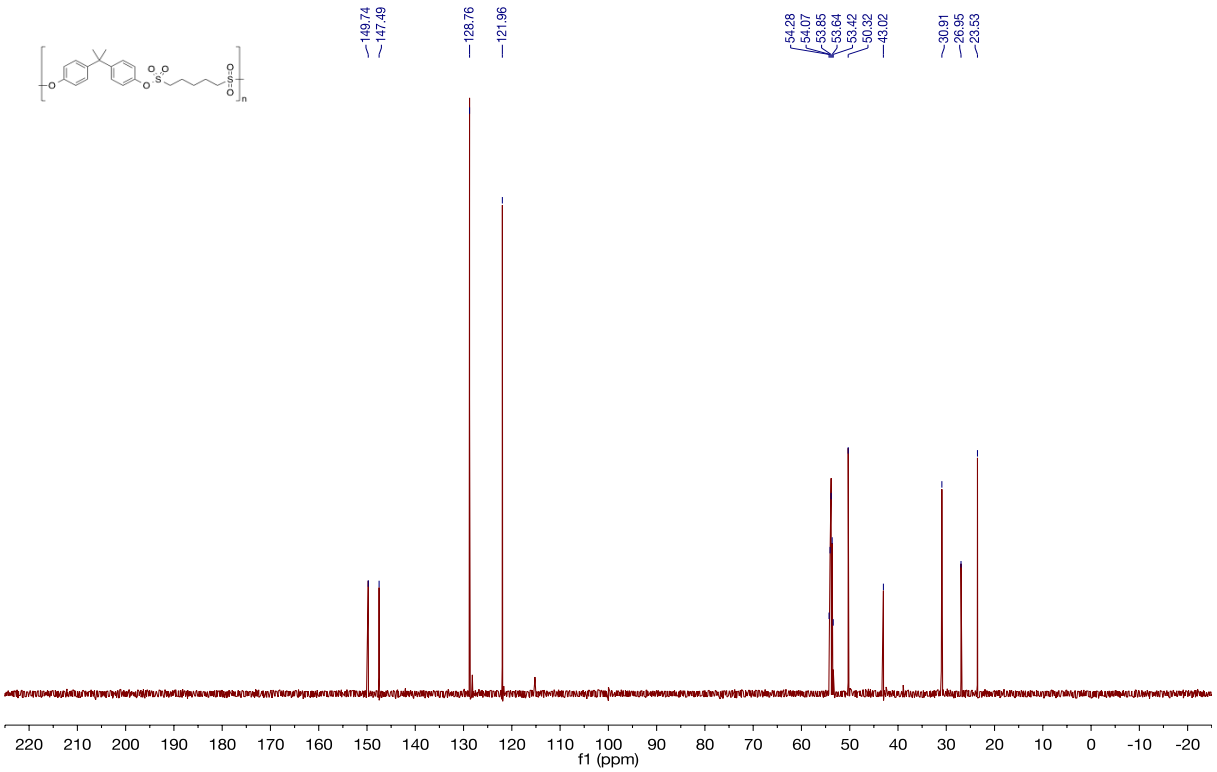
^{13}C NMR **(P-14)**



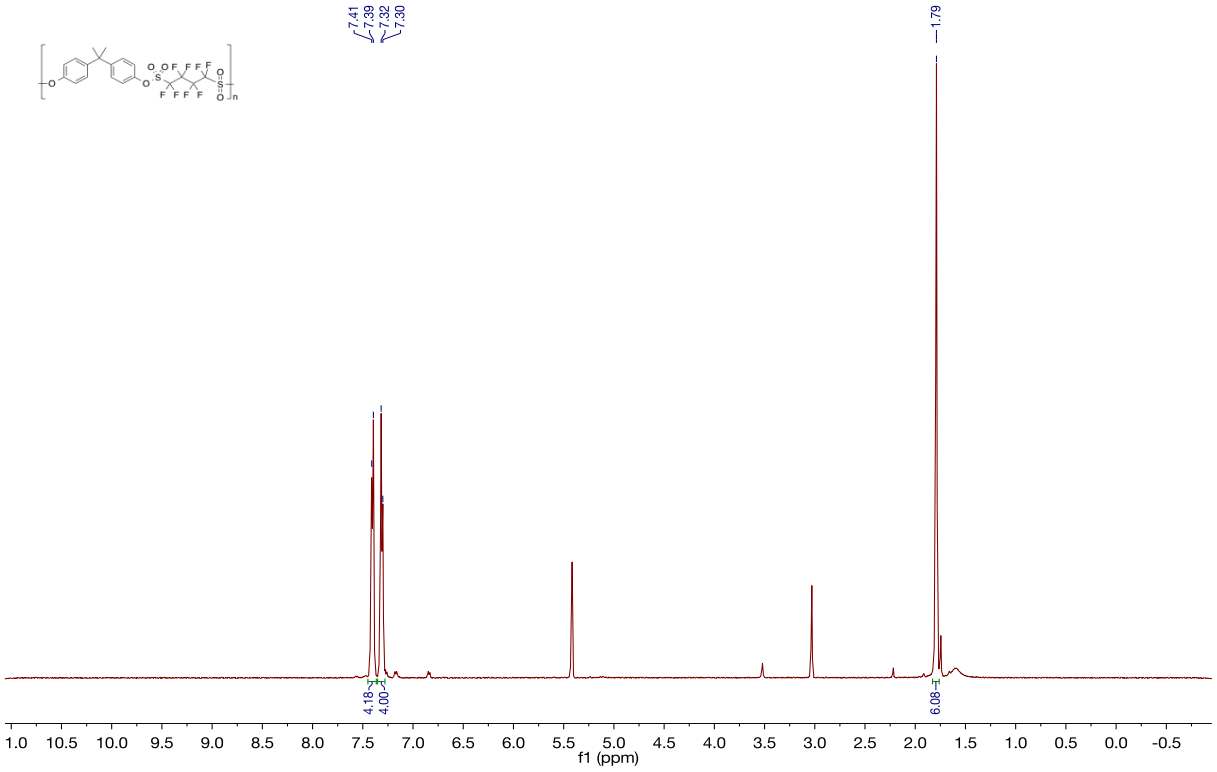
^{1}H NMR **(P-15)**



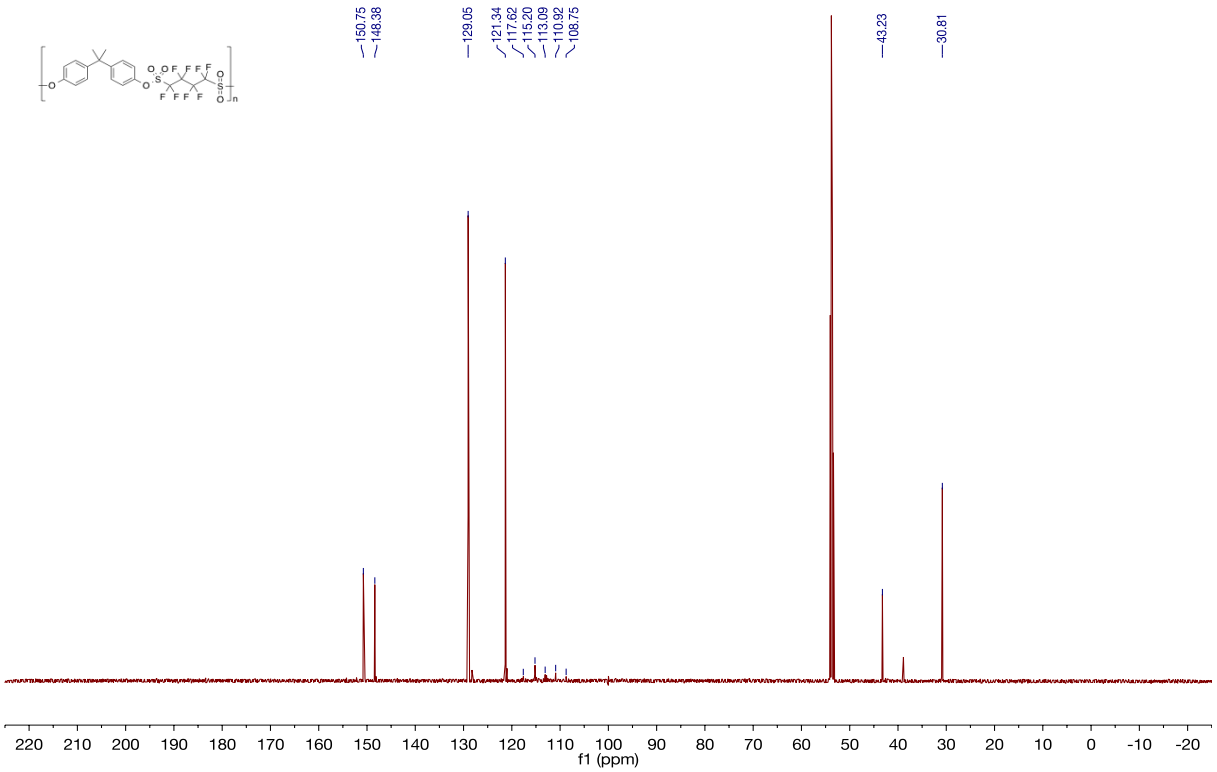
***^{13}C NMR* (P-15)**



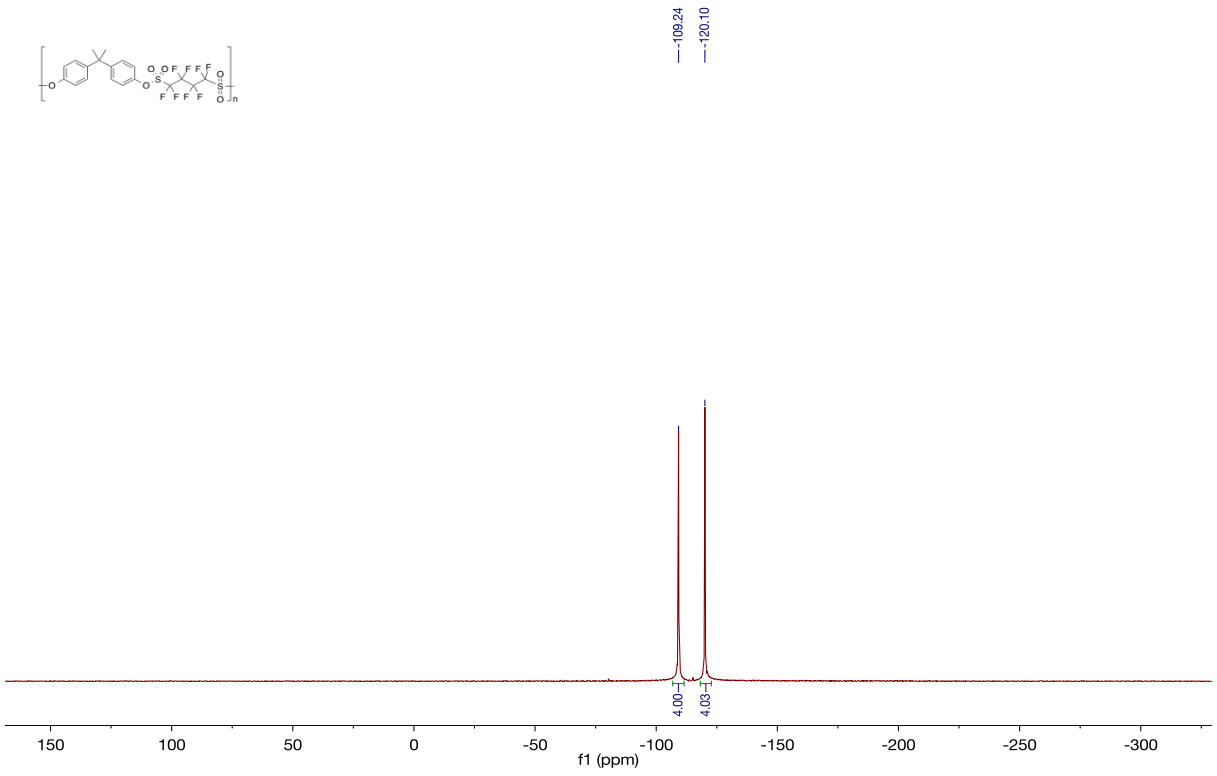
***^{1}H NMR* (P-16)**



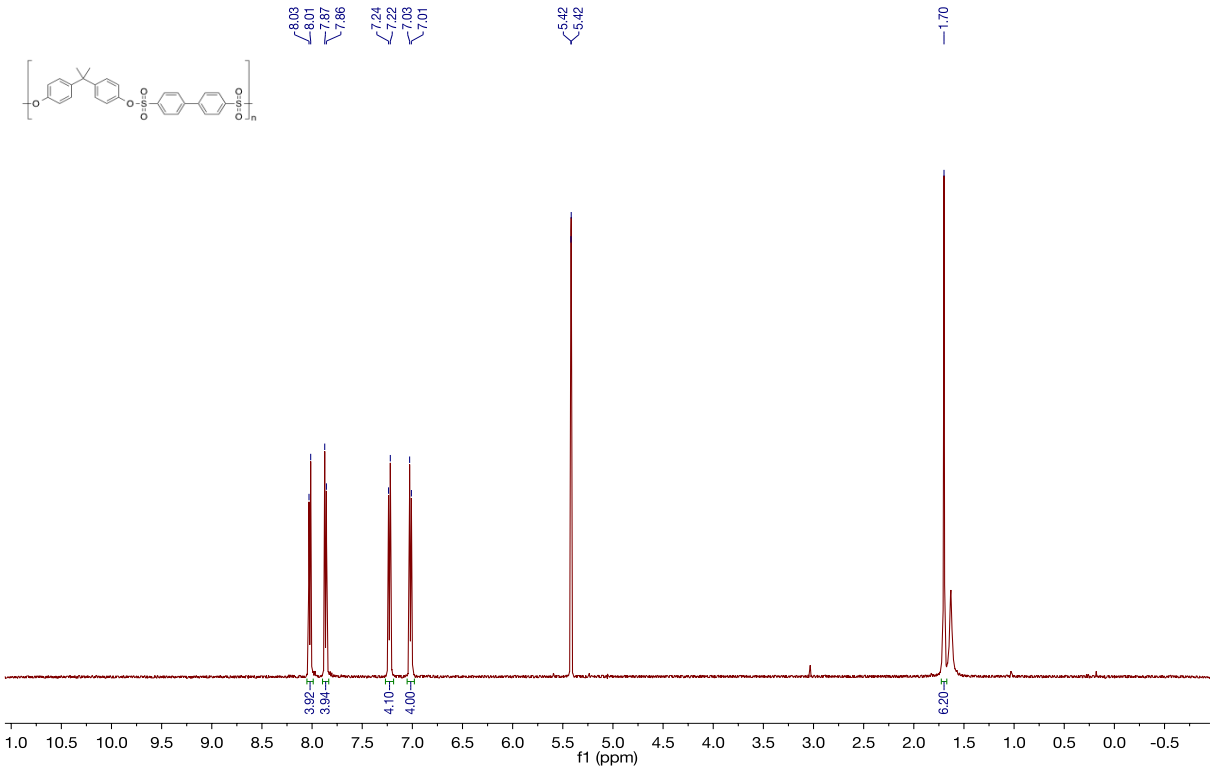
^{13}C NMR **(P-16)**



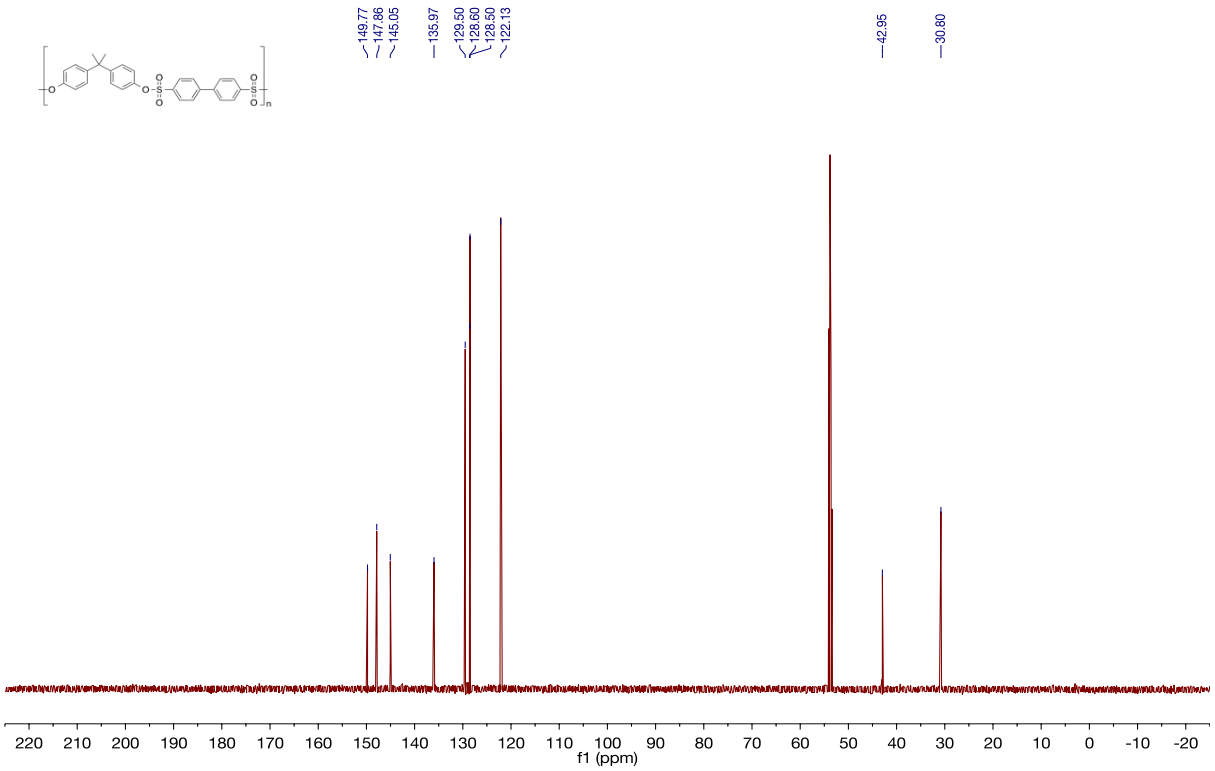
^{19}F NMR **(P-16)**



***^{1}H NMR* (P-17)**



***^{13}C NMR* (P-17)**



3-5, Copies of X-ray Crystallographic Analysis

$Ph_3P{=}N^{+}{:}PPh_3$
$[H_2F_3]^-$

($PNP^+[H_2F_3]^-$)

(CCDC number: 1522316)

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II Ultra CCD diffractometer equipped with Mo K_α radiation (λ = 0.71073). Crystals of the subject compound were used as received (grown from DCM/Ether). A 0.14x 0.10 x 0.10 mm colorless block was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using exposure time 10s with a scan width of 0.5°. Data collection was 100.0% complete to 25.242° in θ. A total of 111676 reflections were collected covering the indices, -11<=h<=11, -21<=k<=21, -26<=l<=26. 4024 reflections were found to be symmetry independent, with a R_{int} of 0.0520. Indexing and unit cell refinement indicated a primitive, **Triclinic** lattice. The space group was found to be ***P*-1**. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table 1.

Notes:
Two molecules in asymmetric unit. Position of hydrogen atoms in the $H_2F_3^-$ was found a they isotropic thermal parameter freely refined, Hydrogen bonds summarized in Table 6. DCM solvate fully ordered

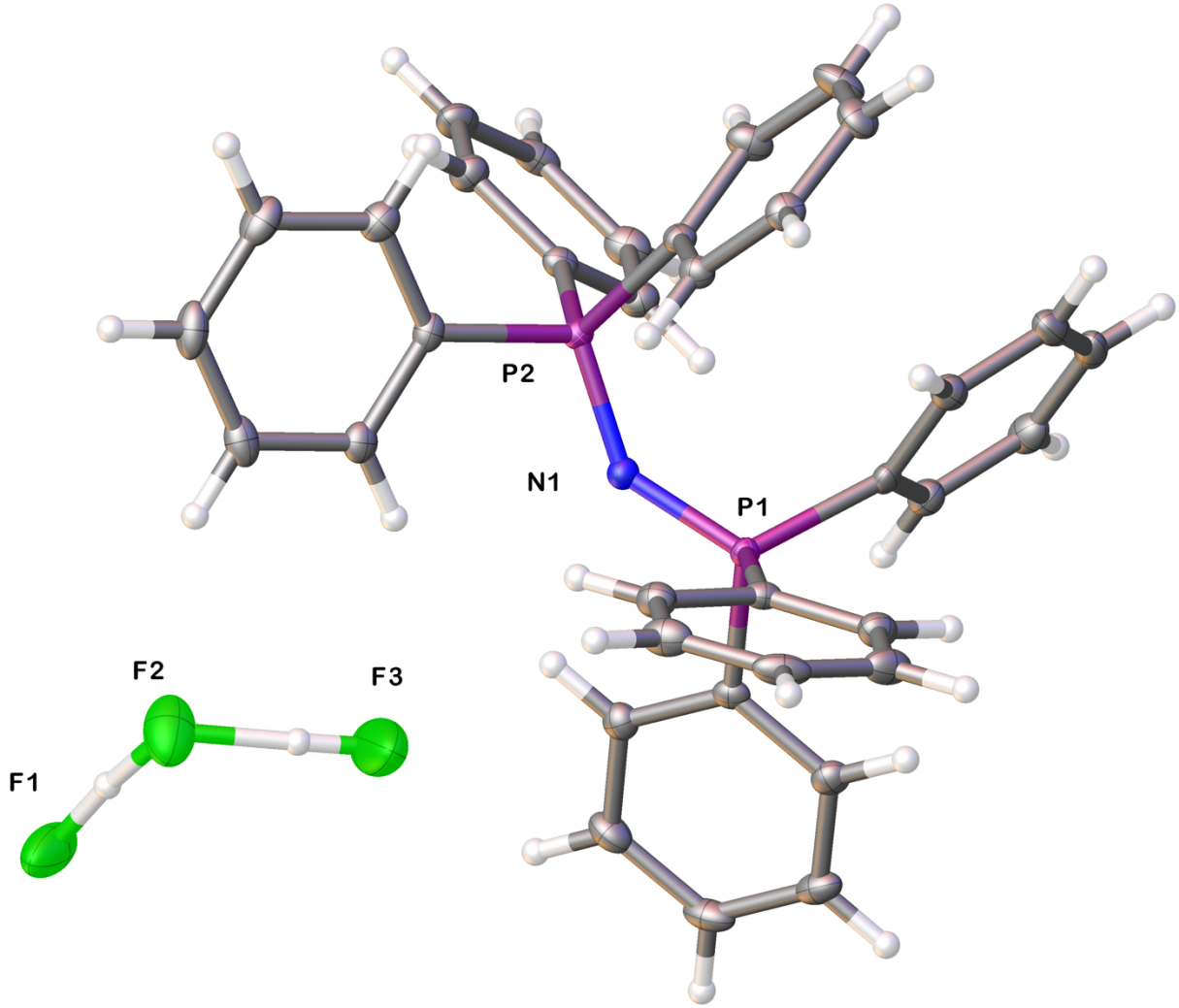

P2
N1
P1
F2
F3
F1

Table 1. Crystal data and structure refinement.

Report date	2016-07-03	
Identification code	GA28003	
Empirical formula	C37 H34 Cl2 F3 N P2	
Molecular formula	C36 H30 N P2, F3 H2, C H2 Cl2	
Formula weight	682.49	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.4494(4) Å	α= 89.671(2)°.
	b = 16.8459(12) Å	β= 83.274(2)°.
	c = 20.9986(11) Å	γ = 86.339(2)°.
Volume	3312.8(3) $Å^3$	
Z	4	
Density (calculated)	1.368 Mg/m^3	
Absorption coefficient	0.338 mm^{-1}	
F(000)	1416	
Crystal size	0.14 x 0.1 x 0.1 mm^3	
Crystal color, habit	colorless block	
Theta range for data collection	1.555 to 26.395°.	
Index ranges	-11<=h<=11, -21<=k<=21, -26<=l<=26	
Reflections collected	111676	
Independent reflections	13563 [R(int) = 0.0520]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5595 and 0.5376	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13563 / 0 / 827	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0879	
R indices (all data)	R1 = 0.0429, wR2 = 0.0943	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.770 and -0.751 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	8006(1)	2628(1)	8274(1)	11(1)
P(2)	10277(1)	2761(1)	7190(1)	11(1)
N(1)	8781(1)	2575(1)	7563(1)	14(1)
C(1)	6516(2)	2010(1)	8321(1)	14(1)
C(2)	5696(2)	1904(1)	8911(1)	17(1)
C(3)	4538(2)	1434(1)	8943(1)	21(1)
C(4)	4186(2)	1079(1)	8394(1)	23(1)
C(5)	4989(2)	1190(1)	7808(1)	22(1)
C(6)	6161(2)	1656(1)	7767(1)	17(1)
C(7)	9101(2)	2268(1)	8875(1)	14(1)
C(8)	10039(2)	2753(1)	9130(1)	17(1)
C(9)	10967(2)	2439(1)	9549(1)	21(1)
C(10)	10953(2)	1641(1)	9717(1)	22(1)
C(11)	10042(2)	1152(1)	9461(1)	22(1)
C(12)	9118(2)	1458(1)	9040(1)	18(1)
C(13)	7297(2)	3624(1)	8483(1)	14(1)
C(14)	6974(2)	3862(1)	9122(1)	18(1)
C(15)	6388(2)	4626(1)	9266(1)	23(1)
C(16)	6105(2)	5150(1)	8778(1)	24(1)
C(17)	6402(2)	4911(1)	8142(1)	23(1)
C(18)	6997(2)	4151(1)	7991(1)	18(1)
C(19)	9992(2)	3305(1)	6473(1)	14(1)
C(20)	8654(2)	3323(1)	6253(1)	17(1)
C(21)	8442(2)	3712(1)	5682(1)	21(1)
C(22)	9567(2)	4071(1)	5330(1)	24(1)
C(23)	10895(2)	4059(1)	5552(1)	23(1)
C(24)	11115(2)	3684(1)	6126(1)	18(1)
C(25)	11342(2)	3349(1)	7637(1)	13(1)
C(26)	12596(2)	3038(1)	7858(1)	20(1)
C(27)	13274(2)	3485(1)	8272(1)	24(1)
C(28)	12713(2)	4236(1)	8464(1)	21(1)
C(29)	11486(2)	4558(1)	8229(1)	17(1)

C(30)	10800(2)	4117(1)	7818(1)	15(1)
C(31)	11289(2)	1846(1)	6952(1)	14(1)
C(32)	11118(2)	1178(1)	7344(1)	17(1)
C(33)	11878(2)	464(1)	7171(1)	21(1)
C(34)	12802(2)	413(1)	6606(1)	20(1)
C(35)	12969(2)	1073(1)	6213(1)	21(1)
C(36)	12219(2)	1790(1)	6385(1)	18(1)
F(1)	3854(2)	2413(1)	5080(1)	57(1)
F(2)	5156(2)	3244(1)	5614(1)	50(1)
F(3)	5292(2)	2894(2)	6667(1)	98(1)
Cl(1)	6557(1)	545(1)	5272(1)	30(1)
Cl(2)	8370(1)	1106(1)	6192(1)	37(1)
C(37)	7163(2)	1384(1)	5637(1)	34(1)
P(1')	7897(1)	2451(1)	3264(1)	11(1)
P(2')	10188(1)	2664(1)	2196(1)	11(1)
N(1')	8710(1)	2436(1)	2562(1)	14(1)
C(1')	6417(2)	1832(1)	3258(1)	14(1)
C(2')	5528(2)	1710(1)	3824(1)	19(1)
C(3')	4360(2)	1252(1)	3816(1)	23(1)
C(4')	4076(2)	920(1)	3246(1)	25(1)
C(5')	4947(2)	1047(1)	2682(1)	24(1)
C(6')	6118(2)	1507(1)	2683(1)	18(1)
C(7')	8969(2)	2066(1)	3865(1)	14(1)
C(8')	9822(2)	2555(1)	4172(1)	18(1)
C(9')	10741(2)	2228(1)	4587(1)	22(1)
C(10')	10820(2)	1414(1)	4698(1)	21(1)
C(11')	9997(2)	922(1)	4388(1)	21(1)
C(12')	9070(2)	1244(1)	3974(1)	17(1)
C(13')	7155(2)	3430(1)	3514(1)	14(1)
C(14')	6732(2)	3602(1)	4159(1)	18(1)
C(15')	6111(2)	4348(1)	4338(1)	22(1)
C(16')	5917(2)	4927(1)	3877(1)	21(1)
C(17')	6312(2)	4754(1)	3232(1)	20(1)
C(18')	6924(2)	4005(1)	3048(1)	17(1)
C(19')	9827(2)	3237(1)	1503(1)	14(1)

C(20')	8470(2)	3242(1)	1299(1)	15(1)
C(21')	8188(2)	3667(1)	753(1)	19(1)
C(22')	9262(2)	4073(1)	407(1)	21(1)
C(23')	10612(2)	4067(1)	607(1)	21(1)
C(24')	10896(2)	3656(1)	1157(1)	17(1)
C(25')	11214(2)	3248(1)	2667(1)	14(1)
C(26')	12457(2)	2939(1)	2897(1)	23(1)
C(27')	13096(2)	3380(1)	3331(1)	28(1)
C(28')	12505(2)	4120(1)	3533(1)	23(1)
C(29')	11284(2)	4440(1)	3294(1)	18(1)
C(30')	10638(2)	4007(1)	2862(1)	15(1)
C(31')	11244(2)	1772(1)	1925(1)	13(1)
C(32')	10987(2)	1059(1)	2246(1)	18(1)
C(33')	11742(2)	358(1)	2030(1)	22(1)
C(34')	12745(2)	366(1)	1492(1)	21(1)
C(35')	13012(2)	1072(1)	1175(1)	21(1)
C(36')	12271(2)	1779(1)	1389(1)	18(1)
Cl(1')	6634(1)	449(1)	250(1)	27(1)
Cl(2')	8550(1)	916(1)	1159(1)	30(1)
C(37')	7186(2)	1242(1)	691(1)	26(1)
F(1')	3699(1)	3609(1)	-83(1)	45(1)
F(2')	5159(2)	2658(1)	376(1)	71(1)
F(3')	5138(1)	2795(1)	1467(1)	49(1)

Table 3. Bond lengths [Å] and angles [°] for GA28003 ($PNP^{+}H_2F_3^{-}$).

P(1)-N(1)	1.5842(13)	P(1')-N(1')	1.5796(13)
P(1)-C(1)	1.7967(15)	P(1')-C(1')	1.7975(15)
P(1)-C(7)	1.8032(15)	P(1')-C(7')	1.8026(15)
P(1)-C(13)	1.8043(15)	P(1')-C(13')	1.8063(15)
P(2)-N(1)	1.5826(13)	P(2')-N(1')	1.5824(13)
P(2)-C(19)	1.7969(15)	P(2')-C(19')	1.7955(15)
P(2)-C(25)	1.7987(15)	P(2')-C(25')	1.8009(15)
P(2)-C(31)	1.8035(15)	P(2')-C(31')	1.8072(15)
C(1)-C(2)	1.399(2)	C(1')-C(2')	1.396(2)
C(1)-C(6)	1.394(2)	C(1')-C(6')	1.394(2)
C(2)-H(2)	0.9500	C(2')-H(2')	0.9500
C(2)-C(3)	1.386(2)	C(2')-C(3')	1.388(2)
C(3)-H(3)	0.9500	C(3')-H(3')	0.9500
C(3)-C(4)	1.386(2)	C(3')-C(4')	1.386(3)
C(4)-H(4)	0.9500	C(4')-H(4')	0.9500
C(4)-C(5)	1.385(2)	C(4')-C(5')	1.385(3)
C(5)-H(5)	0.9500	C(5')-H(5')	0.9500
C(5)-C(6)	1.393(2)	C(5')-C(6')	1.392(2)
C(6)-H(6)	0.9500	C(6')-H(6')	0.9500
C(7)-C(8)	1.396(2)	C(7')-C(8')	1.398(2)
C(7)-C(12)	1.405(2)	C(7')-C(12')	1.401(2)
C(8)-H(8)	0.9500	C(8')-H(8')	0.9500
C(8)-C(9)	1.393(2)	C(8')-C(9')	1.389(2)
C(9)-H(9)	0.9500	C(9')-H(9')	0.9500
C(9)-C(10)	1.388(2)	C(9')-C(10')	1.389(2)
C(10)-H(10)	0.9500	C(10')-H(10')	0.9500
C(10)-C(11)	1.383(2)	C(10')-C(11')	1.386(2)
C(11)-H(11)	0.9500	C(11')-H(11')	0.9500
C(11)-C(12)	1.388(2)	C(11')-C(12')	1.389(2)
C(12)-H(12)	0.9500	C(12')-H(12')	0.9500
C(13)-C(14)	1.394(2)	C(13')-C(14')	1.394(2)
C(13)-C(18)	1.401(2)	C(13')-C(18')	1.399(2)
C(14)-H(14)	0.9500	C(14')-H(14')	0.9500
C(14)-C(15)	1.388(2)	C(14')-C(15')	1.388(2)

C(15)-H(15)	0.9500	C(15')-H(15')	0.9500
C(15)-C(16)	1.388(3)	C(15')-C(16')	1.390(2)
C(16)-H(16)	0.9500	C(16')-H(16')	0.9500
C(16)-C(17)	1.386(3)	C(16')-C(17')	1.388(2)
C(17)-H(17)	0.9500	C(17')-H(17')	0.9500
C(17)-C(18)	1.389(2)	C(17')-C(18')	1.391(2)
C(18)-H(18)	0.9500	C(18')-H(18')	0.9500
C(19)-C(20)	1.394(2)	C(19')-C(20')	1.398(2)
C(19)-C(24)	1.401(2)	C(19')-C(24')	1.400(2)
C(20)-H(20)	0.9500	C(20')-H(20')	0.9500
C(20)-C(21)	1.394(2)	C(20')-C(21')	1.391(2)
C(21)-H(21)	0.9500	C(21')-H(21')	0.9500
C(21)-C(22)	1.390(3)	C(21')-C(22')	1.392(2)
C(22)-H(22)	0.9500	C(22')-H(22')	0.9500
C(22)-C(23)	1.388(3)	C(22')-C(23')	1.389(2)
C(23)-H(23)	0.9500	C(23')-H(23')	0.9500
C(23)-C(24)	1.389(2)	C(23')-C(24')	1.387(2)
C(24)-H(24)	0.9500	C(24')-H(24')	0.9500
C(25)-C(26)	1.392(2)	C(25')-C(26')	1.391(2)
C(25)-C(30)	1.398(2)	C(25')-C(30')	1.401(2)
C(26)-H(26)	0.9500	C(26')-H(26')	0.9500
C(26)-C(27)	1.391(2)	C(26')-C(27')	1.393(2)
C(27)-H(27)	0.9500	C(27')-H(27')	0.9500
C(27)-C(28)	1.384(2)	C(27')-C(28')	1.382(2)
C(28)-H(28)	0.9500	C(28')-H(28')	0.9500
C(28)-C(29)	1.390(2)	C(28')-C(29')	1.386(2)
C(29)-H(29)	0.9500	C(29')-H(29')	0.9500
C(29)-C(30)	1.384(2)	C(29')-C(30')	1.387(2)
C(30)-H(30)	0.9500	C(30')-H(30')	0.9500
C(31)-C(32)	1.398(2)	C(31')-C(32')	1.396(2)
C(31)-C(36)	1.395(2)	C(31')-C(36')	1.398(2)
C(32)-H(32)	0.9500	C(32')-H(32')	0.9500
C(32)-C(33)	1.387(2)	C(32')-C(33')	1.390(2)
C(33)-H(33)	0.9500	C(33')-H(33')	0.9500
C(33)-C(34)	1.387(2)	C(33')-C(34')	1.387(2)

C(34)-H(34)	0.9500	C(34')-H(34')	0.9500
C(34)-C(35)	1.387(2)	C(34')-C(35')	1.384(2)
C(35)-H(35)	0.9500	C(35')-H(35')	0.9500
C(35)-C(36)	1.388(2)	C(35')-C(36')	1.391(2)
C(36)-H(36)	0.9500	C(36')-H(36')	0.9500
F(1)-H(1)	1.15(4)	Cl(1')-C(37')	1.7702(18)
F(2)-H(1)	1.15(4)	Cl(2')-C(37')	1.7691(18)
F(2)-H(2A)	1.40(4)	C(37')-H(37C)	0.9900
F(3)-H(2A)	0.90(4)	C(37')-H(37D)	0.9900
Cl(1)-C(37)	1.769(2)	F(1')-H(1')	1.08(5)
Cl(2)-C(37)	1.765(2)	F(2')-H(1')	1.26(5)
C(37)-H(37A)	0.9900	F(2')-H(2'A)	1.28(4)
C(37)-H(37B)	0.9900	F(3')-H(2'A)	1.02(4)

N(1)-P(1)-C(1)	107.64(7)	N(1')-P(1')-C(1')	106.96(7)
N(1)-P(1)-C(7)	114.30(7)	N(1')-P(1')-C(7')	113.92(7)
N(1)-P(1)-C(13)	112.13(7)	N(1')-P(1')-C(13')	113.06(7)
C(1)-P(1)-C(7)	106.49(7)	C(1')-P(1')-C(7')	107.68(7)
C(1)-P(1)-C(13)	107.00(7)	C(1')-P(1')-C(13')	106.70(7)
C(7)-P(1)-C(13)	108.87(7)	C(7')-P(1')-C(13')	108.15(7)
N(1)-P(2)-C(19)	109.14(7)	N(1')-P(2')-C(19')	108.02(7)
N(1)-P(2)-C(25)	114.27(7)	N(1')-P(2')-C(25')	113.90(7)
N(1)-P(2)-C(31)	109.93(7)	N(1')-P(2')-C(31')	109.72(7)
C(19)-P(2)-C(25)	107.05(7)	C(19')-P(2')-C(25')	107.89(7)
C(19)-P(2)-C(31)	107.51(7)	C(19')-P(2')-C(31')	108.09(7)
C(25)-P(2)-C(31)	108.70(7)	C(25')-P(2')-C(31')	109.06(7)
P(2)-N(1)-P(1)	138.07(9)	P(1')-N(1')-P(2')	139.51(9)
C(2)-C(1)-P(1)	119.76(12)	C(2')-C(1')-P(1')	119.82(12)
C(6)-C(1)-P(1)	119.88(12)	C(6')-C(1')-P(1')	120.05(12)
C(6)-C(1)-C(2)	120.35(14)	C(6')-C(1')-C(2')	120.06(14)
C(1)-C(2)-H(2)	120.3	C(1')-C(2')-H(2')	120.1
C(3)-C(2)-C(1)	119.50(15)	C(3')-C(2')-C(1')	119.88(16)
C(3)-C(2)-H(2)	120.3	C(3')-C(2')-H(2')	120.1
C(2)-C(3)-H(3)	119.9	C(2')-C(3')-H(3')	120.0

C(4)-C(3)-C(2)	120.28(15)	C(4')-C(3')-C(2')	119.99(16)
C(4)-C(3)-H(3)	119.9	C(4')-C(3')-H(3')	120.0
C(3)-C(4)-H(4)	119.9	C(3')-C(4')-H(4')	119.9
C(5)-C(4)-C(3)	120.30(15)	C(5')-C(4')-C(3')	120.30(15)
C(5)-C(4)-H(4)	119.9	C(5')-C(4')-H(4')	119.9
C(4)-C(5)-H(5)	119.9	C(4')-C(5')-H(5')	119.9
C(4)-C(5)-C(6)	120.26(16)	C(4')-C(5')-C(6')	120.28(16)
C(6)-C(5)-H(5)	119.9	C(6')-C(5')-H(5')	119.9
C(1)-C(6)-H(6)	120.3	C(1')-C(6')-H(6')	120.3
C(5)-C(6)-C(1)	119.31(15)	C(5')-C(6')-C(1')	119.47(15)
C(5)-C(6)-H(6)	120.3	C(5')-C(6')-H(6')	120.3
C(8)-C(7)-P(1)	121.56(12)	C(8')-C(7')-P(1')	121.39(12)
C(8)-C(7)-C(12)	119.22(14)	C(8')-C(7')-C(12')	119.34(14)
C(12)-C(7)-P(1)	118.88(12)	C(12')-C(7')-P(1')	118.87(12)
C(7)-C(8)-H(8)	119.9	C(7')-C(8')-H(8')	119.9
C(9)-C(8)-C(7)	120.23(15)	C(9')-C(8')-C(7')	120.10(15)
C(9)-C(8)-H(8)	119.9	C(9')-C(8')-H(8')	119.9
C(8)-C(9)-H(9)	120.1	C(8')-C(9')-H(9')	119.9
C(10)-C(9)-C(8)	119.89(16)	C(10')-C(9')-C(8')	120.11(15)
C(10)-C(9)-H(9)	120.1	C(10')-C(9')-H(9')	119.9
C(9)-C(10)-H(10)	119.8	C(9')-C(10')-H(10')	119.9
C(11)-C(10)-C(9)	120.38(15)	C(11')-C(10')-C(9')	120.24(15)
C(11)-C(10)-H(10)	119.8	C(11')-C(10')-H(10')	119.9
C(10)-C(11)-H(11)	119.9	C(10')-C(11')-H(11')	120.0
C(10)-C(11)-C(12)	120.20(16)	C(10')-C(11')-C(12')	120.07(15)
C(12)-C(11)-H(11)	119.9	C(12')-C(11')-H(11')	120.0
C(7)-C(12)-H(12)	120.0	C(7')-C(12')-H(12')	119.9
C(11)-C(12)-C(7)	120.06(15)	C(11')-C(12')-C(7')	120.12(15)
C(11)-C(12)-H(12)	120.0	C(11')-C(12')-H(12')	119.9
C(14)-C(13)-P(1)	121.42(12)	C(14')-C(13')-P(1')	120.86(12)
C(14)-C(13)-C(18)	119.77(14)	C(14')-C(13')-C(18')	119.81(14)
C(18)-C(13)-P(1)	118.71(12)	C(18')-C(13')-P(1')	119.22(11)
C(13)-C(14)-H(14)	120.0	C(13')-C(14')-H(14')	120.0
C(15)-C(14)-C(13)	119.93(15)	C(15')-C(14')-C(13')	119.90(15)
C(15)-C(14)-H(14)	120.0	C(15')-C(14')-H(14')	120.0

C(14)-C(15)-H(15)	119.9	C(14')-C(15')-H(15')	119.9
C(14)-C(15)-C(16)	120.20(16)	C(14')-C(15')-C(16')	120.28(15)
C(16)-C(15)-H(15)	119.9	C(16')-C(15')-H(15')	119.9
C(15)-C(16)-H(16)	119.9	C(15')-C(16')-H(16')	120.0
C(17)-C(16)-C(15)	120.10(15)	C(17')-C(16')-C(15')	120.01(15)
C(17)-C(16)-H(16)	119.9	C(17')-C(16')-H(16')	120.0
C(16)-C(17)-H(17)	119.9	C(16')-C(17')-H(17')	119.9
C(16)-C(17)-C(18)	120.28(16)	C(16')-C(17')-C(18')	120.12(15)
C(18)-C(17)-H(17)	119.9	C(18')-C(17')-H(17')	119.9
C(13)-C(18)-H(18)	120.2	C(13')-C(18')-H(18')	120.1
C(17)-C(18)-C(13)	119.70(15)	C(17')-C(18')-C(13')	119.84(14)
C(17)-C(18)-H(18)	120.2	C(17')-C(18')-H(18')	120.1
C(20)-C(19)-P(2)	119.20(12)	C(20')-C(19')-P(2')	119.15(11)
C(20)-C(19)-C(24)	120.40(14)	C(20')-C(19')-C(24')	120.06(14)
C(24)-C(19)-P(2)	120.36(12)	C(24')-C(19')-P(2')	120.77(12)
C(19)-C(20)-H(20)	120.2	C(19')-C(20')-H(20')	120.2
C(21)-C(20)-C(19)	119.55(15)	C(21')-C(20')-C(19')	119.67(14)
C(21)-C(20)-H(20)	120.2	C(21')-C(20')-H(20')	120.2
C(20)-C(21)-H(21)	120.0	C(20')-C(21')-H(21')	120.0
C(22)-C(21)-C(20)	119.97(16)	C(20')-C(21')-C(22')	119.97(15)
C(22)-C(21)-H(21)	120.0	C(22')-C(21')-H(21')	120.0
C(21)-C(22)-H(22)	119.8	C(21')-C(22')-H(22')	119.8
C(23)-C(22)-C(21)	120.39(15)	C(23')-C(22')-C(21')	120.43(15)
C(23)-C(22)-H(22)	119.8	C(23')-C(22')-H(22')	119.8
C(22)-C(23)-H(23)	119.9	C(22')-C(23')-H(23')	120.0
C(22)-C(23)-C(24)	120.26(16)	C(24')-C(23')-C(22')	120.01(15)
C(24)-C(23)-H(23)	119.9	C(24')-C(23')-H(23')	120.0
C(19)-C(24)-H(24)	120.3	C(19')-C(24')-H(24')	120.1
C(23)-C(24)-C(19)	119.40(16)	C(23')-C(24')-C(19')	119.85(15)
C(23)-C(24)-H(24)	120.3	C(23')-C(24')-H(24')	120.1
C(26)-C(25)-P(2)	122.16(12)	C(26')-C(25')-P(2')	122.29(12)
C(26)-C(25)-C(30)	119.81(14)	C(26')-C(25')-C(30')	119.66(14)
C(30)-C(25)-P(2)	117.71(11)	C(30')-C(25')-P(2')	117.66(11)
C(25)-C(26)-H(26)	120.2	C(25')-C(26')-H(26')	120.2
C(27)-C(26)-C(25)	119.64(15)	C(25')-C(26')-C(27')	119.62(15)

C(27)-C(26)-H(26)	120.2	C(27')-C(26')-H(26')	120.2
C(26)-C(27)-H(27)	119.8	C(26')-C(27')-H(27')	119.8
C(28)-C(27)-C(26)	120.36(15)	C(28')-C(27')-C(26')	120.42(16)
C(28)-C(27)-H(27)	119.8	C(28')-C(27')-H(27')	119.8
C(27)-C(28)-H(28)	119.9	C(27')-C(28')-H(28')	119.9
C(27)-C(28)-C(29)	120.11(15)	C(27')-C(28')-C(29')	120.27(15)
C(29)-C(28)-H(28)	119.9	C(29')-C(28')-H(28')	119.9
C(28)-C(29)-H(29)	120.0	C(28')-C(29')-H(29')	120.1
C(30)-C(29)-C(28)	119.91(14)	C(28')-C(29')-C(30')	119.83(15)
C(30)-C(29)-H(29)	120.0	C(30')-C(29')-H(29')	120.1
C(25)-C(30)-H(30)	119.9	C(25')-C(30')-H(30')	119.9
C(29)-C(30)-C(25)	120.12(14)	C(29')-C(30')-C(25')	120.15(14)
C(29)-C(30)-H(30)	119.9	C(29')-C(30')-H(30')	119.9
C(32)-C(31)-P(2)	118.78(12)	C(32')-C(31')-P(2')	118.95(12)
C(36)-C(31)-P(2)	121.51(12)	C(32')-C(31')-C(36')	119.72(14)
C(36)-C(31)-C(32)	119.70(14)	C(36')-C(31')-P(2')	121.29(12)
C(31)-C(32)-H(32)	120.0	C(31')-C(32')-H(32')	120.0
C(33)-C(32)-C(31)	120.00(15)	C(33')-C(32')-C(31')	119.99(15)
C(33)-C(32)-H(32)	120.0	C(33')-C(32')-H(32')	120.0
C(32)-C(33)-H(33)	120.0	C(32')-C(33')-H(33')	120.0
C(34)-C(33)-C(32)	120.01(15)	C(34')-C(33')-C(32')	120.08(15)
C(34)-C(33)-H(33)	120.0	C(34')-C(33')-H(33')	120.0
C(33)-C(34)-H(34)	119.9	C(33')-C(34')-H(34')	119.9
C(35)-C(34)-C(33)	120.22(15)	C(35')-C(34')-C(33')	120.14(15)
C(35)-C(34)-H(34)	119.9	C(35')-C(34')-H(34')	119.9
C(34)-C(35)-H(35)	119.9	C(34')-C(35')-H(35')	119.8
C(34)-C(35)-C(36)	120.18(15)	C(34')-C(35')-C(36')	120.36(15)
C(36)-C(35)-H(35)	119.9	C(36')-C(35')-H(35')	119.8
C(31)-C(36)-H(36)	120.1	C(31')-C(36')-H(36')	120.1
C(35)-C(36)-C(31)	119.88(15)	C(35')-C(36')-C(31')	119.70(15)
C(35)-C(36)-H(36)	120.1	C(35')-C(36')-H(36')	120.1
H(1)-F(2)-H(2A)	116(2)	Cl(1')-C(37')-H(37C)	109.3
Cl(1)-C(37)-H(37A)	109.3	Cl(1')-C(37')-H(37D)	109.3
Cl(1)-C(37)-H(37B)	109.3	Cl(2')-C(37')-Cl(1')	111.46(10)
Cl(2)-C(37)-Cl(1)	111.79(10)	Cl(2')-C(37')-H(37C)	109.3

Cl(2)-C(37)-H(37A)	109.3	Cl(2')-C(37')-H(37D)	109.3
Cl(2)-C(37)-H(37B)	109.3	H(37C)-C(37')-H(37D)	108.0
H(37A)-C(37)-H(37B)	107.9	H(1')-F(2')-H(2'A)	108(2)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$).

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	11(1)	11(1)	11(1)	-1(1)	-1(1)	0(1)
P(2)	12(1)	10(1)	12(1)	0(1)	0(1)	0(1)
N(1)	14(1)	16(1)	13(1)	-1(1)	-1(1)	-2(1)
C(1)	11(1)	11(1)	18(1)	1(1)	-2(1)	1(1)
C(2)	15(1)	16(1)	19(1)	0(1)	0(1)	2(1)
C(3)	14(1)	21(1)	26(1)	7(1)	2(1)	1(1)
C(4)	14(1)	19(1)	37(1)	7(1)	-6(1)	-4(1)
C(5)	21(1)	18(1)	28(1)	0(1)	-10(1)	-4(1)
C(6)	18(1)	16(1)	18(1)	1(1)	-3(1)	1(1)
C(7)	13(1)	18(1)	10(1)	-1(1)	1(1)	1(1)
C(8)	16(1)	18(1)	17(1)	-2(1)	-2(1)	0(1)
C(9)	16(1)	30(1)	19(1)	-6(1)	-4(1)	1(1)
C(10)	16(1)	35(1)	15(1)	2(1)	-1(1)	7(1)
C(11)	21(1)	21(1)	21(1)	6(1)	1(1)	3(1)
C(12)	18(1)	18(1)	17(1)	1(1)	-1(1)	-1(1)
C(13)	10(1)	13(1)	19(1)	-2(1)	-1(1)	-1(1)
C(14)	16(1)	20(1)	19(1)	-4(1)	-1(1)	0(1)
C(15)	17(1)	24(1)	28(1)	-11(1)	1(1)	-1(1)
C(16)	13(1)	14(1)	43(1)	-7(1)	0(1)	0(1)
C(17)	18(1)	17(1)	35(1)	5(1)	-3(1)	1(1)
C(18)	16(1)	18(1)	21(1)	2(1)	-2(1)	0(1)
C(19)	20(1)	10(1)	12(1)	-1(1)	-1(1)	0(1)
C(20)	22(1)	13(1)	15(1)	-2(1)	-2(1)	0(1)
C(21)	32(1)	14(1)	18(1)	-2(1)	-10(1)	1(1)
C(22)	43(1)	14(1)	15(1)	2(1)	-6(1)	1(1)
C(23)	34(1)	14(1)	20(1)	2(1)	4(1)	-4(1)
C(24)	22(1)	13(1)	19(1)	0(1)	0(1)	-1(1)
C(25)	13(1)	13(1)	14(1)	0(1)	-1(1)	-2(1)

C(26)	16(1)	16(1)	29(1)	-2(1)	-4(1)	2(1)
C(27)	16(1)	22(1)	37(1)	0(1)	-12(1)	1(1)
C(28)	21(1)	21(1)	24(1)	-1(1)	-8(1)	-6(1)
C(29)	20(1)	12(1)	20(1)	-2(1)	-2(1)	-2(1)
C(30)	14(1)	14(1)	17(1)	2(1)	-2(1)	0(1)
C(31)	13(1)	12(1)	16(1)	-3(1)	-2(1)	-1(1)
C(32)	17(1)	16(1)	19(1)	0(1)	0(1)	-2(1)
C(33)	21(1)	13(1)	29(1)	1(1)	-5(1)	-1(1)
C(34)	16(1)	14(1)	31(1)	-8(1)	-8(1)	3(1)
C(35)	16(1)	24(1)	22(1)	-6(1)	0(1)	3(1)
C(36)	18(1)	17(1)	19(1)	-1(1)	0(1)	1(1)
F(1)	48(1)	93(1)	31(1)	-19(1)	7(1)	-34(1)
F(2)	71(1)	47(1)	36(1)	4(1)	-13(1)	-28(1)
F(3)	48(1)	200(2)	49(1)	53(1)	-11(1)	-32(1)
Cl(1)	28(1)	28(1)	34(1)	0(1)	2(1)	-3(1)
Cl(2)	45(1)	38(1)	26(1)	-8(1)	-2(1)	2(1)
C(37)	40(1)	22(1)	38(1)	-3(1)	-2(1)	2(1)
P(1')	11(1)	11(1)	11(1)	0(1)	-1(1)	0(1)
P(2')	11(1)	10(1)	12(1)	-1(1)	-1(1)	-1(1)
N(1')	14(1)	16(1)	13(1)	-1(1)	-1(1)	-2(1)
C(1')	12(1)	12(1)	18(1)	1(1)	-2(1)	1(1)
C(2')	17(1)	16(1)	21(1)	1(1)	2(1)	0(1)
C(3')	14(1)	20(1)	33(1)	8(1)	4(1)	1(1)
C(4')	14(1)	19(1)	45(1)	9(1)	-10(1)	-4(1)
C(5')	25(1)	20(1)	28(1)	3(1)	-14(1)	-4(1)
C(6')	18(1)	16(1)	19(1)	2(1)	-5(1)	-2(1)
C(7')	13(1)	16(1)	11(1)	0(1)	0(1)	1(1)
C(8')	18(1)	16(1)	19(1)	-2(1)	-4(1)	0(1)
C(9')	21(1)	27(1)	19(1)	-3(1)	-6(1)	0(1)
C(10')	17(1)	30(1)	15(1)	2(1)	-2(1)	6(1)
C(11')	23(1)	18(1)	20(1)	5(1)	0(1)	3(1)
C(12')	19(1)	16(1)	16(1)	0(1)	-2(1)	-1(1)
C(13')	12(1)	12(1)	17(1)	-2(1)	-1(1)	0(1)
C(14')	21(1)	18(1)	16(1)	0(1)	-3(1)	2(1)
C(15')	26(1)	22(1)	18(1)	-5(1)	-1(1)	5(1)

C(16')	18(1)	15(1)	30(1)	-4(1)	-2(1)	3(1)
C(17')	18(1)	16(1)	25(1)	5(1)	-2(1)	1(1)
C(18')	16(1)	18(1)	16(1)	2(1)	0(1)	-1(1)
C(19')	17(1)	11(1)	12(1)	-2(1)	0(1)	1(1)
C(20')	18(1)	13(1)	14(1)	-2(1)	0(1)	-2(1)
C(21')	22(1)	17(1)	19(1)	-2(1)	-6(1)	0(1)
C(22')	32(1)	15(1)	14(1)	1(1)	-3(1)	0(1)
C(23')	26(1)	14(1)	20(1)	2(1)	3(1)	-4(1)
C(24')	17(1)	14(1)	21(1)	-1(1)	2(1)	-1(1)
C(25')	13(1)	14(1)	15(1)	-1(1)	-1(1)	-2(1)
C(26')	18(1)	15(1)	35(1)	-6(1)	-9(1)	3(1)
C(27')	21(1)	24(1)	43(1)	-5(1)	-18(1)	3(1)
C(28')	24(1)	21(1)	27(1)	-4(1)	-10(1)	-5(1)
C(29')	20(1)	13(1)	22(1)	-3(1)	-2(1)	-1(1)
C(30')	14(1)	15(1)	18(1)	1(1)	-3(1)	-1(1)
C(31')	12(1)	13(1)	16(1)	-3(1)	-4(1)	0(1)
C(32')	17(1)	16(1)	20(1)	-1(1)	-3(1)	-1(1)
C(33')	21(1)	14(1)	31(1)	-1(1)	-6(1)	0(1)
C(34')	17(1)	18(1)	30(1)	-10(1)	-10(1)	5(1)
C(35')	14(1)	28(1)	20(1)	-7(1)	-2(1)	4(1)
C(36')	16(1)	19(1)	19(1)	-2(1)	-2(1)	1(1)
Cl(1')	28(1)	29(1)	26(1)	-2(1)	-5(1)	-6(1)
Cl(2')	28(1)	40(1)	22(1)	-4(1)	-7(1)	2(1)
C(37')	28(1)	24(1)	28(1)	-6(1)	-8(1)	3(1)
F(1')	34(1)	52(1)	48(1)	-7(1)	-6(1)	4(1)
F(2')	100(1)	70(1)	38(1)	-7(1)	-12(1)	45(1)
F(3')	38(1)	64(1)	45(1)	4(1)	-5(1)	-14(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3).

	x	y	z	U(eq)
H(2)	5932	2151	9286	20
H(3)	3982	1356	9342	25
H(4)	3391	758	8419	27
H(5)	4740	946	7434	26
H(6)	6713	1732	7366	20

H(8)	10044	3300	9018	21
H(9)	11609	2769	9719	26
H(10)	11573	1429	10009	27
H(11)	10048	605	9573	26
H(12)	8497	1120	8864	21
H(14)	7156	3503	9457	22
H(15)	6178	4790	9701	28
H(16)	5708	5672	8878	28
H(17)	6197	5270	7810	28
H(18)	7200	3989	7556	22
H(20)	7891	3071	6492	20
H(21)	7530	3733	5532	25
H(22)	9426	4326	4936	29
H(23)	11657	4308	5310	28
H(24)	12019	3684	6282	22
H(26)	12986	2524	7725	24
H(27)	14127	3273	8425	29
H(28)	13167	4533	8756	26
H(29)	11118	5081	8350	21
H(30)	9959	4336	7659	18
H(32)	10482	1212	7730	21
H(33)	11765	11	7439	25
H(34)	13322	-76	6489	24
H(35)	13598	1034	5826	25
H(36)	12340	2242	6116	22
H(1)	4560(40)	2810(20)	5331(18)	116(13)
H(2A)	5220(40)	3060(20)	6262(18)	95(11)
H(37A)	7639	1724	5302	40
H(37B)	6334	1699	5860	40
H(2')	5721	1940	4214	22
H(3')	3755	1167	4201	27
H(4')	3280	603	3242	30
H(5')	4744	819	2292	28
H(6')	6710	1599	2295	21
H(8')	9772	3112	4096	21

H(9')	11316	2562	4796	26
H(10')	11440	1193	4986	25
H(11')	10066	364	4460	25
H(12')	8504	906	3763	20
H(14')	6869	3209	4476	22
H(15')	5817	4464	4778	27
H(16')	5515	5442	4002	25
H(17')	6165	5147	2917	24
H(18')	7185	3885	2607	20
H(20')	7744	2957	1532	18
H(21')	7263	3680	617	23
H(22')	9071	4357	31	25
H(23')	11341	4344	368	25
H(24')	11815	3658	1299	21
H(26')	12868	2431	2759	27
H(27')	13945	3170	3489	34
H(28')	12936	4412	3836	28
H(29')	10892	4954	3427	22
H(30')	9802	4225	2699	18
H(32')	10296	1052	2613	21
H(33')	11572	-127	2250	26
H(34')	13250	-115	1341	26
H(35')	13705	1075	809	25
H(36')	12462	2264	1172	22
H(37C)	7539	1660	391	31
H(37D)	6357	1478	975	31
H(1')	4270(50)	3160(30)	170(20)	135(15)
H(2'A)	5120(30)	2753(19)	982(17)	87(10)

Table 6. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
F(2)-H(1)...F(1)	1.15(4)	1.15(4)	2.3018(17)	174(4)
F(3)-H(2A)...F(2)	0.90(4)	1.40(4)	2.301(2)	175(4)
F(1')-H(1')...F(2')	1.08(5)	1.26(5)	2.3252(19)	167(4)
F(3')-H(2'A)...F(2')	1.02(4)	1.28(4)	2.3025(19)	176(3)

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