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The first SuFEx click chemistry synthesis of SOF₄-derived copolymers based upon the polymerization of bis(iminosulfur oxydifluorides) and bis(aryl silyl ethers) is described. This novel class of SuFEx polymer presents two key characteristics: First, the newly created [-N=S(=O)F-O-] polymer backbone linkages are themselves SuFExable and primed to undergo further high-yielding and precise SuFEx-based post-modification with phenols or amines to yield branched functional polymers. Second, studies of individual polymer chains of several of these new materials indicate the presence of helical polymer structures, which itself suggests a preferential approach of new monomers onto the growing polymer chain upon the formation of the stereogenic linking moiety.

Click chemistry was inspired by considering the biogenesis of Nature's primary bio-polymers: proteins, DNA/RNA and polysaccharides, all of which are created through the union of reactive modules through heteroatom linkages.^{1,2} Since describing the underpinning philosophy of click chemistry, Sharpless and co-workers have developed two key click reactions that enable the formation of stable connections with unparalleled efficiency — namely the Cu(I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC) in 2002,^{3,4} and more recently, the Sulfur Fluoride Exchange (SuFEx) reaction in 2014.⁵ While CuAAC has had a perspective-changing impact in many areas, including drug discovery,⁶⁻⁹ bioconjugation,^{10,11} and material science,¹²⁻¹⁵ for polymer construction, it is mainly utilized for polymer functionalization rather than backbone formation.^{16,17} The new generation of metal-free SuFEx connective technology¹⁸⁻²² is characterized by the exchange of aryl silyl ethers or amines, often through discrete SuFExable hubs such as sulfuryl fluoride (SO₂F₂),⁵ thionyl tetrafluoride (SOF₄),^{23,24} ethenesulfonyl fluoride (ESF)^{5,18,25} and 1-bromoethene-sulfonyl fluoride (BESF)²⁶⁻²⁸ (Figure 1). The powerful combination of reaction efficiency and linkage stability renders SuFEx perfect for polymer synthesis, and this was first demonstrated by Dong and Gao *et al.* through the synthesis of a number of SO₂F₂-derived polysulfate-SuFEx copolymers of bis(aryl silyl ethers) with bis(aryl fluorosulfates) in the presence of DBU or highly efficient catalyst (Me₂N)₃S⁺[FHF]⁻ (Figure 1B).^{29,30} Wu and co-workers later reported the bifluoride ion-catalyzed polycondensation of a selection of ESF-derived bis(alkylsulfonyl fluorides) with bis(aryl silyl ethers), to give the corresponding polysulfonate SuFEx polymers in excellent yield (Figure 1B).³¹ These SuFEx polymerization reactions occurred under mild conditions and without significant increase in temperature during the course of the reaction,^{29,30} giving rise to novel materials with interesting properties, including hydrolytic stability, thermal stability and tensile modulus.

Encouraged by the successful applications of SO₂F₂ and ESF as SuFEx connectors in polymer chemistry, we explored thionyl tetrafluoride (SOF₄) as a new connective hub²³ for SuFEx polymer

synthesis. Unlike the related achiral SO_2F_2 and ESF connectors, SOF_4 is the first multidimensional SuFExable hub that can reliably form four discrete ligand connections through the stereogenic tetrahedral sulfur(VI) center [e.g. $\text{R}-\text{N}=\text{S}(=\text{O})(\text{F})-\text{OR}'$]. This unique feature of SOF_4 derivatives creates untold opportunities for click chemistry,²³ and in the context of polymer science, an opportunity for the incredibly challenging goal of post-polymerization modification of the polymer spine (Figure 1C).

Herein, we report the synthesis of a new family of SuFExable polymers derived from SOF_4 . The unprecedented three-dimensional functional materials are helical in structure, and combine the powerful combination of high efficiency of SuFEx- polymerization and robust SuFEx-enabled post-polymerization modifications, giving access to materials with rational control of composition, conformation and functionality.

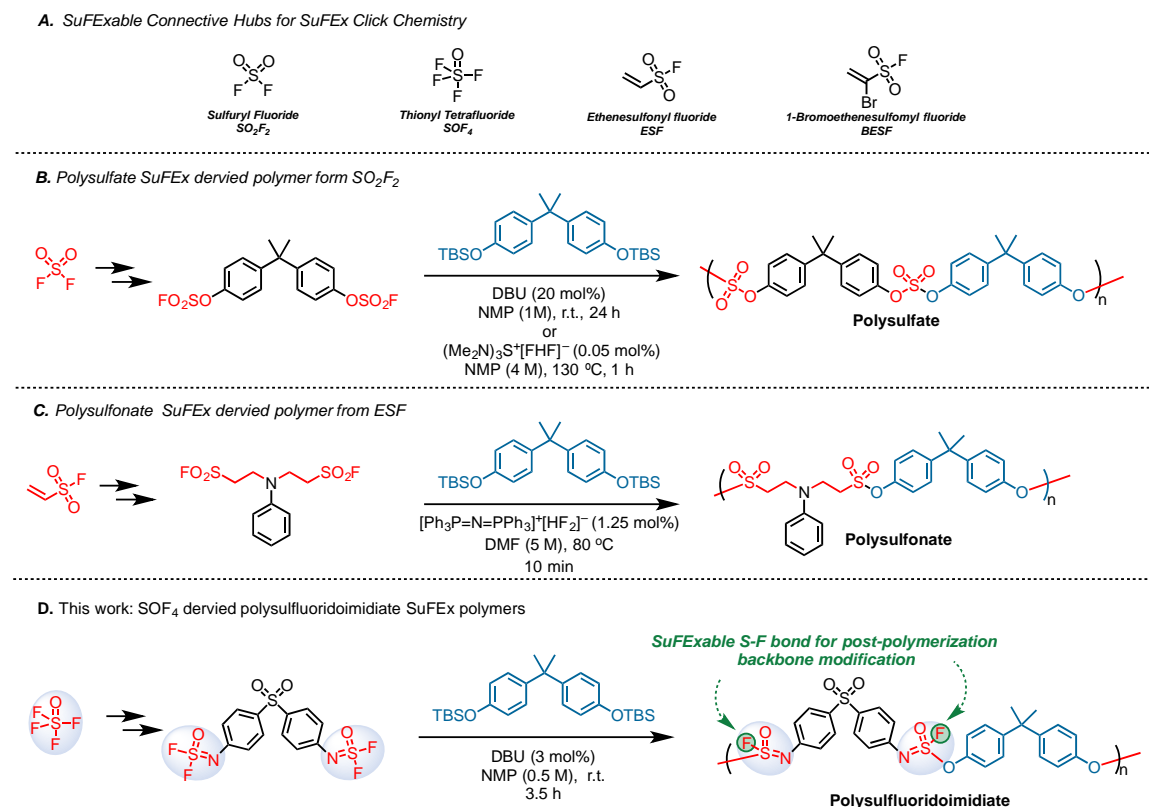


Figure 1: A. Connective SuFEx hubs for creating S-centered linkages; B. Polysulfate materials derived from SO_2F_2 ; C. Polysulfonate materials derived from ESF. D. New polysulfurido-imide materials derived from the multidimensional SuFEx connector SOF_4 .

Results and Discussion

Polymer synthesis. The bis(iminosulfur oxydifluoride) (**1-1**) (prepared as previously described from SOF_4 ²³ and 4,4'-diaminodiphenyl sulfone), and the bisphenol A bis(*t*-butyldimethylsilyl ether)^{29,30} (**2-1**)

were chosen as model substrates. Informed by our earlier studies with SOF_4 , DBU was chosen as the preferred SuFEx polymerization catalyst due to its moderate reactivity. We anticipated that under such conditions, the polymerization process would proceed through just one of the two available S–F bonds of the iminosulfur oxydifluoride, thereby avoiding cross-linking and branching reactions.²³ When a 1:1 mixture of the difluoride and silyl ether (30 mmol scale) was dissolved in NMP followed by the addition of 2 mol% DBU,^{5,29} a reaction was observed to occur almost immediately at room temperature. Stirring the reaction mixture for a further 5 min resulted in the formation of a viscous solution—accompanied by a slight increase in the reaction temperature (to 40 ~ 50 °C). After 3.5 h, the starting materials had been fully consumed and the colorless $[\text{Ar}-\text{N}=\text{S}(=\text{O})(\text{F})-\text{OAr}]$ -linked polymer **3-1** was isolated in 99% yield with a Mw of 197 kDa, i.e., containing ca. 326 monomers, and a polydispersity index (PDI) of 1.8 (Figure 1D).³²

With the demonstration that SOF_4 could be successfully incorporated as a key unit in a polymer spine, we next explored the substrate scope of this reaction with a view to making a family of structurally diverse polymers. The polymerization reaction of **1-1** was examined with a selection of aryl silyl ethers comprising different functional groups (**2-1** ~ **2-12**) — each giving rise to polymers **3-1** ~ **3-12** in excellent yields (82 to 99%, Figure 2A), with distribution of molecular weights ranging from 36 to 295 kDa and typical PDIs of ~1.7 (values ranging from 1.4 to 2.3). Similarly, the polymerization reaction worked equally well with a selection of bis(iminosulfur oxydifluorides) (themselves prepared from SOF_4 and the corresponding bis-arylamines), and a number of bis(aryl silyl ethers) to give a diverse array of new polymers (**3-13** to **3-31**) with excellent yields. Due to the lower reactivity of benzylic substrates, both the *meta* and *para*-bis(benzylic iminosulfur oxydifluorides) required longer reactions times (24 h) and an increased catalyst loading of 10 mol% DBU (**3-32**, **3-33**).

Examination of the collective ^1H NMR, ^{13}C NMR and ^{19}F NMR data of the polymers revealed surprisingly uncomplicated spectra, as if belonging to a small molecule [See SI]. Figure 2B shows representative NMR spectra for the bisphenol A derived polymer **3-1**. Considering that the connective sulfur center is stereogenic and could result in numerous diastereoisomers in an uncontrolled polymerization event—the spectra are unusually simple.

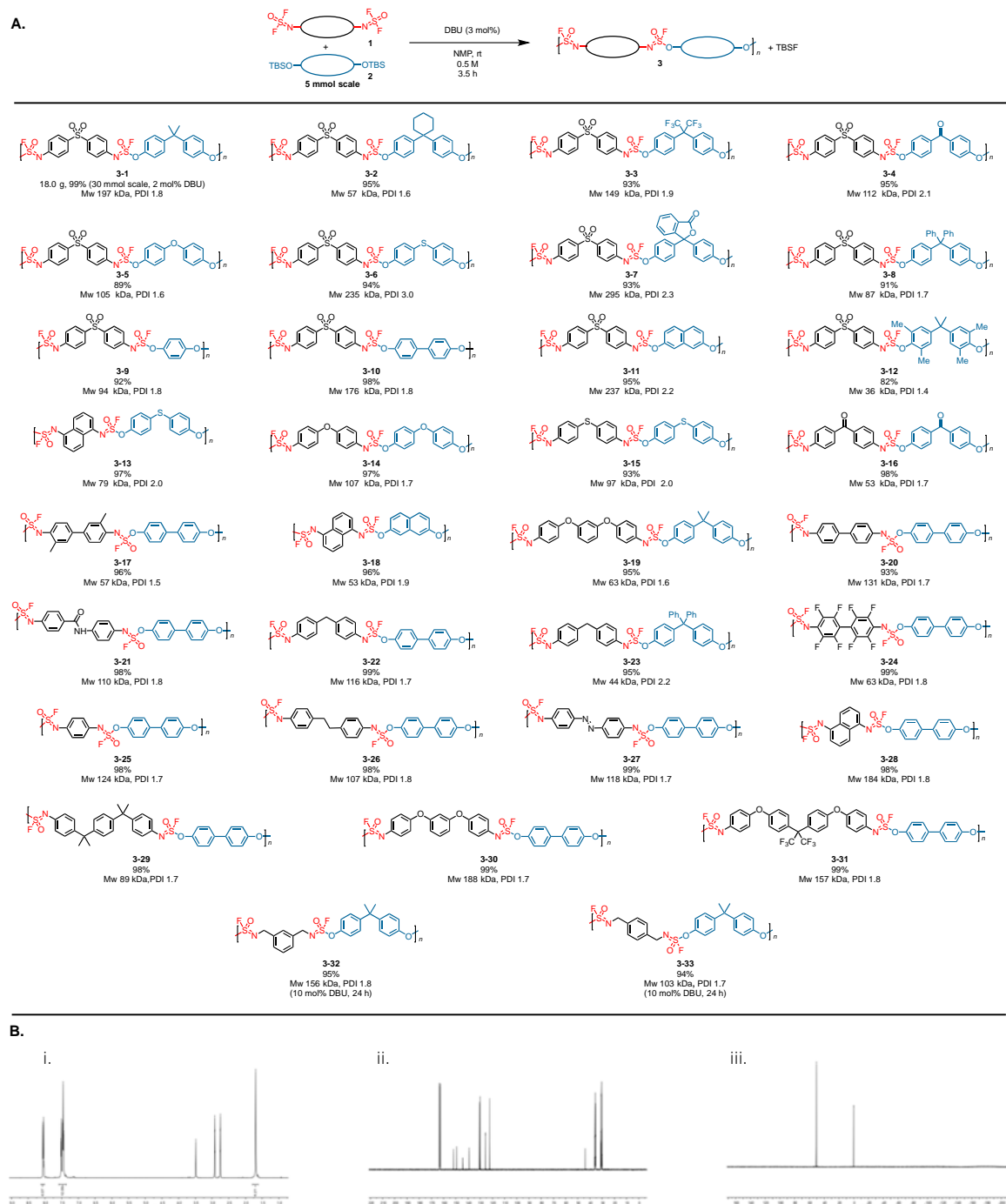


Figure 2. A. Synthesis of SOF₄-derived copolymers from the polymerization of SuFExable bis(iminosulfur oxydifluoride) and bis(silyl ether) monomers. Reaction conditions: For **3-1**: bis(iminosulfur oxydifluoride) (12.49 g, 30 mmol), BPA-TBS (13.70 g, 30 mmol) and DBU (91.3 mg, 0.6 mmol) were reacted in 40 mL NMP (3.5 h; r.t.). For **3-32**, **3-33**: bis(iminosulfur oxydifluoride) (5 mmol) and bis(silyl ether) (5 mmol) and DBU (0.50 mmol) were reacted in 10 mL NMP (24 h; r.t.). For others: bis(iminosulfur oxydifluoride) (5 mmol) and bis(silyl ether) (5 mmol) and DBU (0.15 mmol) were reacted in 10 mL NMP (3.5 h; r.t.); B. Representative example NMR spectra of **3-1** in DMF-*d*₇ as solvent. i) ¹H NMR; ii) ¹³C NMR; iii) ¹⁹F NMR (CFCl₃ internal standard peak appears at 0 ppm).

Polymer functionalization. Post-polymerization modification (PPM) is an important technique that allows the tuning and manipulation of polymer properties by imparting new function.³³⁻³⁷ Hence, SuFEx modification of the remaining S(VI)–F bond of the polymeric materials would be a major advantage. From our earlier studies on SOF₄ derivatives, we found that 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) is an efficient SuFEx catalyst⁵ for activating the exchange of remaining S(VI)–F bond of sulfurofluoridoimides with aryl silyl ethers, to form the corresponding sulfurimide products.²³ This fidelity was also achieved with the SOF₄-derived polymers: BEMP-catalyzed SuFEx branching of the polymer **3-1** occurred flawlessly with the *tert*-butyldimethyl(4-(1,2,2-triphenylvinyl)phenoxy)silane (**4**) to give the polymer **5** in 95% yield (Figure 3A). The polymer **5** was shown to display a strong aggregation-induced emission (AIE) effect,³⁸ exhibiting dramatically enhanced photoluminescence efficiency as water content increased from 0% to 99%. AIE fluorophores have wide application in the fields of energy, optoelectronics, life science, and the environment, presenting significant opportunities for SOF₄-SuFEx polymers (Figure 3B) [For experimental details and fluorescence spectra of polymer **3-1** and 4-(1,2,2-triphenylvinyl)phenol, see Supporting Information.]

The SuFEx derivatization of the polymer **3-1** also occurred readily with the *tert*-butyl(3-ethynylphenoxy) dimethylsilane (**6**), to give the alkyne-functionalized polymer **7** in excellent yield (Figure 3C). The remarkable efficiency of the reaction is confirmed by a degree of substitution of at least 93% based on the ratio of methyl vs. terminal alkynyl protons in the ¹H NMR [see Supporting Information].³⁹ The surgical installation of the alkyne unit enables further click chemistry functionalization through CuAAC, thereby offering a truly modular platform for creating new and unprecedented functional polymers. This was demonstrated by the reaction of polymer **7** with an azide-bearing AZT derivative **8** under ligand-accelerated CuAAC conditions^{40,41} to give the triazole-linked nucleoside polymer **9** in 96% yield. Analysis of the ¹H NMR spectrum revealed that – as far as observable from the absence of any remaining terminal alkyne protons – all pendant alkyne groups of the parent polymer had been consumed [see Supporting Information].

The reaction of the remaining S–F bonds of the SuFEx polymer **3-1** was also feasible with the secondary amines such as pyrrolidine (**10**) and 4-ethynylpiperidine (**11**), yielding the branched polymers **12** and **13** conveniently (Figure 3D). In a final demonstration of the power of combined sequential click chemistry, the SuFEx polymer **3-1** and the PEG-linked azido-vancomycin derivative **14** were reacted under CuAAC conditions to yield the complex vancomycin-derived polymer **15** in 50% isolated yield (Figure 3E) [see Supporting Information].

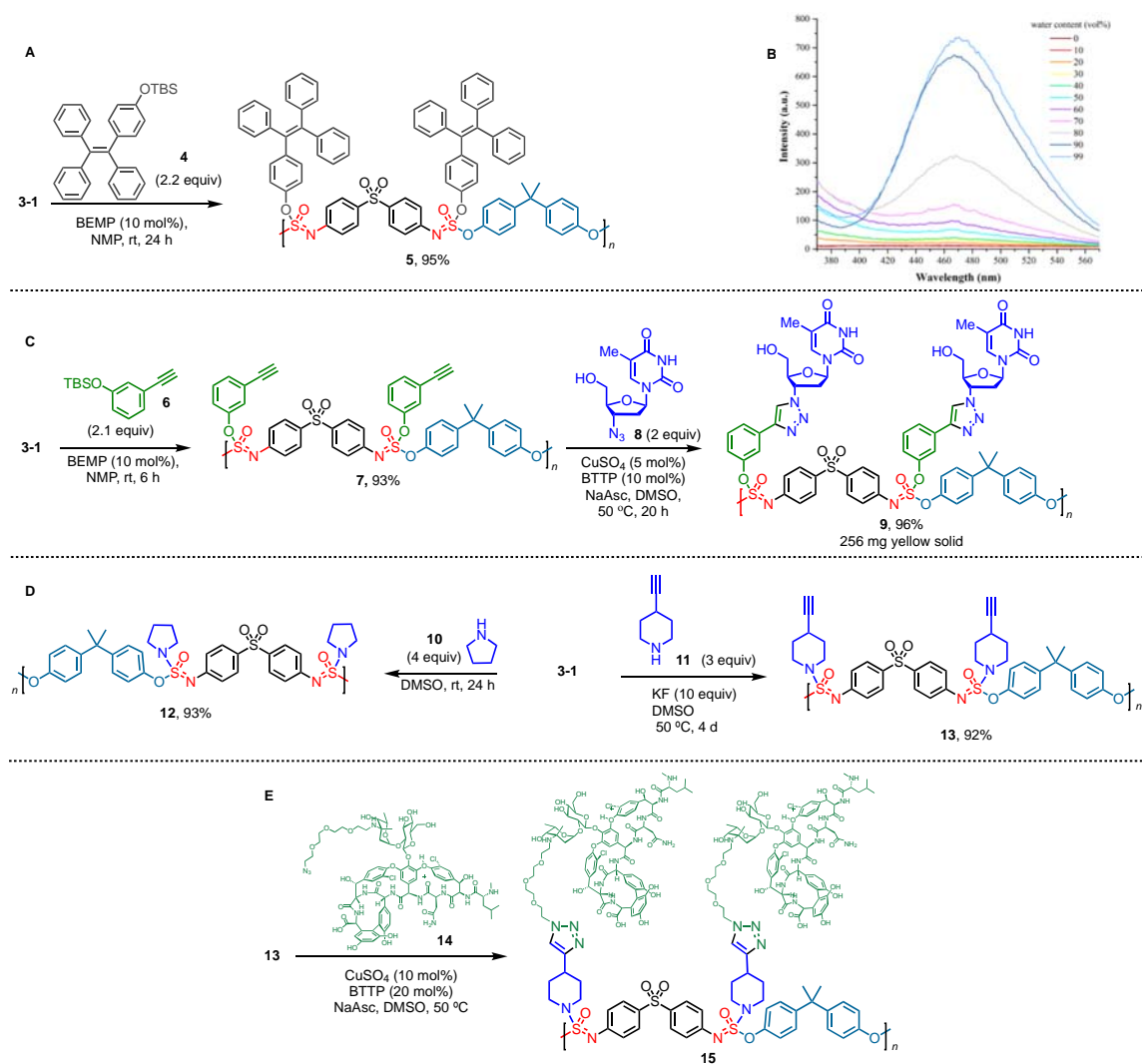


Figure 3. Post-polymerization modification of polymer **3-1** using sequential SuFEx and CuAAC click chemistry: A. SuFEx Synthesis of triphenylvinyl phenoxy-branched polymer **5**; B. Fluorescence spectra of **5** (5 μ M of the repeat unit) in THF/H₂O (v/v = 100:0 ~ 1:99); C. Stepwise synthesis of alkyne-functionalized polymer **7** by SuFEx, and subsequent CuAAC synthesis of polymer **9** with an azide-bearing AZT derivative; D. Post-polymerization SuFEx modification of **3-1** with secondary amines; E. CuAAC post-polymerization modification of polymer **13** with an azido-derivative of vancomycin to give the functionalized polymer **15**.

Polymer structure. The uncomplicated ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra of all the new SuFEx polymers inspired us to further explore the 3D structure of these interesting materials. In view of the tetrahedral sulfur core of the ~N=S(=O)F-O~ linkage, we anticipated that the SOF₄-based polymers might also display three-dimensional features beyond random coiling—as observed for a variety of helical polymers.^{42,43} We therefore assessed three representative SuFEx polymers: first **3-23**, and subsequently **3-9** and **5** – by atomic force microscopy (AFM, tapping mode); molecular mechanics

studies; scanning Auger microscopy, and high-resolution SEM and TEM measurements. [Details regarding the synthesis and NMR characterization are presented in the Supporting Information.]

First, an atomistic model of the polymer **3-23** was built as a 32-mer, and the structure thereof optimized with a generically applicable force field for organic materials (PCFF force field)⁴⁴ without any constraints. This yielded a helical structure with a diameter of 4.9 ± 0.4 nm (Figure 4a-b). Experimental studies of individual surface-deposited polymer chains followed. Polymer **3-23** was dissolved in dichloromethane and a few droplets of that solution were dropped onto an atomically flat, hexadecyne-coated Si(111) surface,⁴⁵ after which the solvent was allowed to evaporate at room temperature. Next, AFM topography images of **3-23** were obtained as deposited on these Si(111) surfaces, which clearly displayed many individual polymer wires (Figure 4c-e). These individual polymer chains revealed a near-constant height of 4.1 ± 0.7 nm (measured at 46 points on multiple polymer chains on the surface; Figure 4d). This height clearly surpasses the size of any moiety present in the polymer chain of **3-23**, but correlates very well to the theoretical prediction of the diameter of the helix formed by individual polymer chains. To corroborate the height as obtained by AFM, high-resolution SEM analysis was performed to obtain the width of individual polymer chains. This yielded a width of 4.8 ± 0.5 nm (measured at 50 points on multiple polymer chains on the surface; Figure 4f). The height and width agree very well with the hypothesized helical character of polymer wires (**3-23**). To confirm that the observed wires indeed correspond to the SuFEx polymer, scanning Auger microscopy was employed. As can be seen in Figure 4g-l, the wire-like structures comprise the elements expected to be present in the polymer, namely O, C, S, N, and F, thus corroborating that indeed the SuFEx polymer wires with functional $\sim\text{N}=\text{S}(=\text{O})\text{F}-\text{O}\sim$ moiety were being observed. Finally, high-resolution TEM measurements were used to zoom in on the structure. First, the TEM measurements (Figure 4n) at 30 points revealed a width of 4.5 ± 0.6 nm for individual polymer chains, in agreement with both our modelling and SEM data, and strongly indicating a helical structure. Second, the zoomed-in TEM data in Figure 4m and 4o also clearly indicate a repeating structure: the red triangles in these figures are placed at points of increased intensity, which occur at highly regular intervals, as to be expected for a single helical polymer. This is observable for individual polymer chains (Figure 4m), but also for chains that are adjacent to each other (Figure 4o). Analogous to the polymer-structure optimized *in vacuo* that yields a pitch of 5.0 nm, the high-resolution TEM image yields a polymer pitch of ca. 3.1 nm. We tentatively attribute this difference to the attractive polymer-surface interactions, which may slightly compress the polymer, without affecting the helix diameter.

The helical structure of the simulated polymer can be best understood by considering the stereogenic nature of the $\sim\text{N}=\text{S}(=\text{O})\text{F}-\text{O}\sim$ linker. The 32-mer was constructed by taking an enantiomerically pure monomer (in this case the (*R*)-configuration at the stereogenic sulfur center), copying that to make the dimer, and repeating this doubling four more times to get the 32-mer. Hence in this simple model, by

fixing the (*R*)-configuration at the tetrahedral S(VI) centers, the predicted helical structure correlates well with experimental observations. Two additional remarks are in order here. First, in the absence of chiral induction, we infer equal amounts of both homochiral helical polymers. Second, these observed stereoselectivity results suggest that somehow in the growing polymer chain, the formation of each new sulfur connection is guided by the configuration of the chain and its existing sulfur stereocenters. This likely requires some reversibility at the individual backbone linkage sites, just to sort out the absolute configurations of individual chains. Boundary conditions for such a mechanism are set by the survival of (at least the large majority of) S-F bonds on all the linkage sites and especially by the apparent identity of the magnetic environment around each of the >600 S-F units at the linker sites and by the absence of cross-linking products in the follow-up SuFEx reaction to create the side-chains.

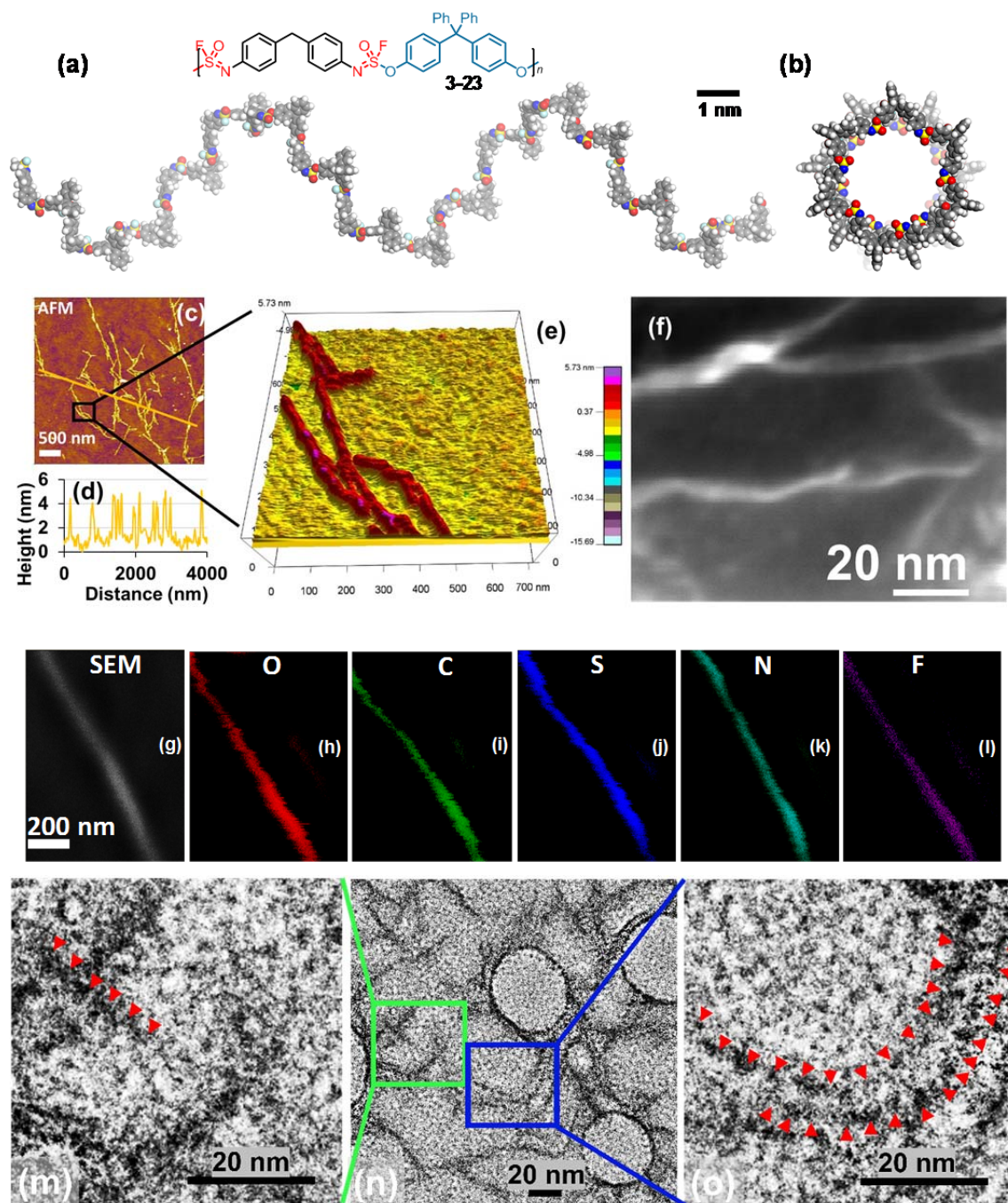


Figure 4. (a-b) PCFF-optimized structure of **3-23** (side view and top view) Color code: C, grey; O, red; N, blue; F, cyan; S, yellow. (c-e) AFM height image ($5 \times 5 \mu\text{m}^2$ and $0.8 \times 0.8 \mu\text{m}^2$), and 3D image of **3-23** as deposited on hexadecyne-modified Si(111) with the height profile along the line. (f) High-resolution SEM image of **3-23** deposited on a TEM grid. (g-l) SEM/AES image of polymer **3-23** coated on hexadecanethiol-modified gold surfaces, and AES images on the same surface for the elements O, C, S, N and F. High-resolution TEM (m-o) images of polymer **3-23**.

Furthermore, molecular modelling studies on 20 of the polymers from Figure 2 predict that all form helical structures, although for most polymers the helical structure only display a diameter less than 1.5

nm, which would be hard to detect by AFM [refer to Supporting Information]. We surmise that the size of the groups would strongly affect the diameter of the polymer chain. To this end we also investigated the structure of **5** (as a polymer with a bulky substituent) and **3-9** (as a representative polymer with relatively small groups) in detail. Both displayed helical structures in molecular modelling, with diameters of 5.7 ± 0.4 nm and 2 ± 1 nm, respectively. These values correlate very well with AFM-measured heights of 6.9 ± 1.1 nm and 2.1 ± 0.2 nm, respectively, as well as the TEM-observed widths of 5.5 ± 0.3 nm and 2.3 ± 0.4 nm, respectively [see Figure S13 and S10 in the Supporting Information]. The latter is in the same range observed for double-stranded DNA helices (2.3 ± 0.2 nm).⁴⁶ Finally, inverting the configuration at all sulfur atoms in the atomistic polymer models, resulted in a helix that rotated the other way around, while random variation of the configuration of the sulfur(VI) atom yielded chaotic, non-helical polymers in the simulation. Such random configuration would also lead to broad NMR peaks, in contrast with observation.

Conclusions:

In summary, we have described a new class of modular SuFEx copolymers linked through SOF_4 derived $[-\text{N}=\text{S}(=\text{O})(\text{F})-\text{O}-]$ hubs and bisphenol monomers. These polymers were prepared with high efficiency from the corresponding bis(iminosulfur oxydifluorides) and bis(arylsilyl ethers) under DBU catalyzed SuFEx conditions. The multidimensional connectivity of the S(VI) hub derived from SOF_4 , presents a unique opportunity for post-polymerization modification, that was demonstrated here through the controlled and near quantitative installation of aryl silyl ethers and amines to the spine of the polymer. Further derivatization of the alkyne-decorated SuFEx-polymers **7** and **13** were demonstrated using CuAAC click chemistry, delivering the two new functional polymers **9** and **15** with potential application in polymer-drug conjugates. The triphenylvinyl phenoxy-branched polymer **5** showed an aggregation-induced emission (AIE) effect, while the vancomycin-decorated polymer **15** offers potentially useful antibacterial properties. Collectively, these examples showcase the potential of the novel SOF_4 -derived materials in diverse applications. An in-depth structure study combining AFM, high-resolution SEM, high-resolution TEM and molecular modelling reveals that the conformations of the novel polymers are helical, which correlates well with the simple NMR spectra of these polymers. While the mechanism of the polymer formation is far from understood, the helical structures of the polymers suggest an unprecedented degree of self-referential control, stereochemical and otherwise, over the constitution of the evolving polymer chains.

Methods

Full details of the methods are provided in the Supplementary Information.

Procedure for the synthesis of the polymer 3-1 (30 mmol scale) To a round-bottomed flask (250 mL) with a magnetic stir bar was added the bis(iminosulfur oxydifluoride) (12.49 g, 30 mmol), BPA-TBS (13.70 g, 30 mmol) and 40 mL of anhydrous NMP. The flask was sealed with a Suba-Seal® Septa, vacuumized with a needle linked with a pump until there were no bubbles formed in the solution (5-10 minutes). Then DBU (91.3 mg, 90 μ L, 0.6 mmol, $d = 1.018$ g/mL) was added into the flask via a needle. After stirring at room temperature for 15 minutes, the solution became a jam and the stir bar stopped moving. After staying at room temperature for 3.5 hours, 50 mL of DMF was added. The flask was shaken to promote the dissolution and the resulting solution was poured slowly into 600 mL of MeOH with mechanical stirring. The solution was stirred in MeOH for 20 minutes and filtrated. The white solid was washed with MeOH three times (150 mL X 3) and then dried in the vacuum oven (60 $^{\circ}$ C) for 24 hours to give 18.0 g of the polymer **3-1** (99%). $M_w^{ps} = 197$ kDa. PDI = 1.8. T_g (DSC) = 150.8 $^{\circ}$ C. T_d (5% weight loss, TGA) = 261.2 $^{\circ}$ C. ^1H NMR (600 MHz, DMF- d_7) δ 8.05 (d, $J = 8.4$ Hz, 4H), 7.58 – 7.36 (m, 12H), 1.70 (s, 6H). ^{13}C NMR (151 MHz, DMF) δ 151.90, 149.29, 144.39 (d, $J = 2.7$ Hz), 139.14, 130.56, 130.11, 125.68 (d, $J = 2.8$ Hz), 122.26, 43.87, 31.09. ^{19}F NMR (376 MHz, DMF- d_7) δ 50.69.

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Author contributions

H. Z., K. B. S. and J. E. M. supervised the work. S. L., K. B. S., P. W., J. L. and J. E. M. conceived and designed the syntheses of the SOF₄-derived polymers. S. L., G. L., B. G., S.P. P., X. C. and H. K. performed the synthesis and characterization of the polymers. F. Z., L. M. K., Y. L. and J. Lu collected and analyzed the DSC and TGA data of all polymers. S. P. P. performed molecular modeling, AFM and scanning Auger experiments. H. D. performed the SEM and TEM experiments. R. E. I. and T. P. S. C. performed the antibacterial assays. S. L., H. Z., K. B. S and J. E. M. contributed to the preparation of the

manuscript. All authors discussed the results and commented on the manuscript.

Additional information

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Competing financial interests

The authors declare the following competing financial interest(s): Sharpless, K. B., Wu, P.; Li, S.; Liu, Z.; Gao, B., Thionyl tetrafluoride modified compounds and uses; provisional patent application Serial Number US62/427,489, filed on Nov/29/2016. International patent application no. PCT/US2017/063746.

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SuFExable Polymers with Helical Structures Derived from Thionyl Tetrafluoride (SOF₄)

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1. General Information:

Abbreviations:

BEMP = 2-*tert*-butylimino-2-diethylamino-1,3-dimethyl perhydro-1,3,2-diazaphosphorine; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; TMS = trimethylsilyl; TBS = *tert*-butyldimethylsilyl

^1H spectra were recorded on Bruker AV-600, Bruker AV-400 instruments; ^{13}C NMR were recorded on Bruker AV-600. ^{19}F NMR were recorded on Bruker AV-400. The chemical shifts (δ) are expressed in parts per million relative to TMS or residual deuterated acetonitrile, DMF and DMSO as internal standards. Proton magnetic resonance (^1H NMR) spectra were recorded at 600, or 400 MHz. Carbon magnetic resonance (^{13}C NMR) spectra were recorded at 151 MHz or 101 MHz. Fluorine magnetic resonance (^{19}F NMR) spectra were recorded at 376 MHz. NMR acquisitions were performed at 295 K unless otherwise noted. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; br s, broad singlet. Infrared spectra were recorded as pure undiluted samples using ThermoNicolet Avatar 370 Fourier transform infrared spectrometer with a Smart MIRacleTM HATR attachment. Melting points (mp) were determined using a Thomas-Hoover melting point apparatus and are uncorrected. GC-MS data were recorded on an Agilent 7890A GC system with an Agilent 5975C Inert MSD system or SHIMADZU GCMS-QP2010 SE operating in the electron impact (EI+) mode. LC-MS was performed on an Agilent 1260 LC/MSD with an Agilent 6120 quadrupole mass spectrometer (electrospray ionization, ES) eluting with 0.1% trifluoroacetic acid in H_2O and 0.05% trifluoroacetic acid in CH_3CN . High resolution mass spectrometry was performed on an Agilent ES-TOF instrument. Percoated Merck F-254 silica gel plates were used for thin layer analytical chromatography (TLC) and visualized with short wave UV light or by potassium permanganate stain. Column chromatography was performed using EMD (Merck) Silica Gel 60 (40-63 μm). Extra dry solvents over molecular sieves were purchased from Aldrich or Acros Organics including acetonitrile (CH_3CN), tetrahydrofuran (THF), dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP). All of the bis(amines) used in this study are commercially available.

The polymer molecular weight (weight-average, M_w^{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 °C). All samples/standards were tested at 100 μL loadings (1.0 mg/mL).

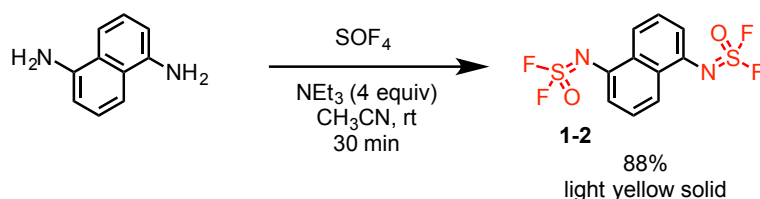
The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were carried out at *Lawrence Berkeley National Laboratory* and *Soochow university*. TGA were carried out on TGA- MS Q5000 under nitrogen using aluminum pans (20 °C/min started from 25 °C and ended at 600 °C). The DSC were carried out on TA Q200 with a heat rate of 5 °C/min.

2. Preparation of the monomer iminosulfur oxydifluorides

The reaction of amines with SOF₄ to prepare the iminosulfur oxydifluoride monomer

(sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (**1-1**) and 1,4-phenylenedisulfurimidoyl difluoride (**1-12**) were prepared from the bis(amines) and SOF₄ according to previous procedure: S. Li, P. Wu, J. E. Moses, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2017**, *56*, 2903.

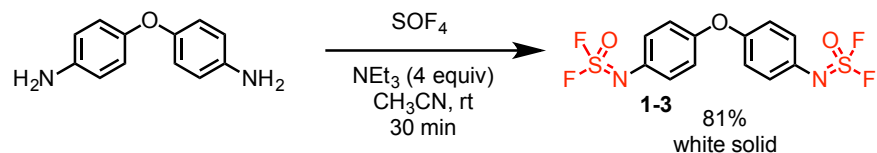
General procedure I was described for the specific example of naphthalene-1,5-diamine to naphthalene-1,5-diyldisulfurimidoyl difluoride (**1-2**)



A 250 mL round-bottomed flask was charged with a magnetic stir bar, naphthalene-1,5-diamine (1.90 g, 12 mmol), acetonitrile (30 mL) and triethylamine Et₃N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol). The flask was then sealed with a Suba-Seal® Septa and an empty balloon attached to a needle fixed syringe was inserted into the flask. A needle linked to a vacuum pump was then inserted into the flask and the atmosphere evacuated under reduced pressure until bubbles formed and the balloon became tense. The needle connected to the vacuum pump was then removed. Next, SOF₄ was introduced into the flask via a needle in small batches and monitored by TLC until the diamine was fully converted to the bis-iminosulfur oxydifluoride. 2 ~ 3 batches of SOF₄ gas was introduced and the whole process took about 30 minutes (more batches SOF₄ was applied in larger scale reaction). After the completion of the reaction, the HF (amine salt) in the reaction mixture was quenched with 20 g silica gel slowly under 0 °C. After stirring at 0 °C for 5 minutes, CH₃CN was removed with rotary evaporator under reduced pressure. The product was purified by flash column chromatography over silica gel (hexanes/Ethyl acetate = 10/1) to afford **1-2** (3.460 g, 88%) as light-yellow solid.

^1H NMR (600 MHz, CDCl_3) δ 8.09 (d, J = 8.5 Hz, 2H), 7.52 (dd, J = 8.5, 7.4 Hz, 2H), 7.33 (d, J = 7.4 Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 132.79 (t, J = 3.4 Hz), 129.84 (t, J = 3.0 Hz), 126.37, 121.59, 119.93 (t, J = 2.8 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 46.63. EI (m/z): 326 $[\text{M}]^+$.

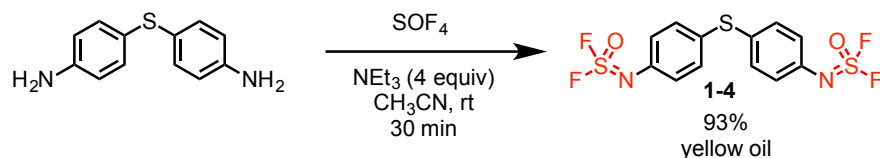
(oxybis(4,1-phenylene))disulfurimidoyl difluoride (1-3)



Following the **general procedure I**: The reaction of 4,4'-oxydianiline (2.4 g, 12 mmol), Et_3N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF_4 in 30 mL of CH_3CN afforded **1-3** (3.593 g, 81%) as white solid.

^1H NMR (600 MHz, CDCl_3) δ 7.13 – 7.07 (m, 4H), 7.04 – 6.94 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 154.97, 131.55 (t, J = 3.0 Hz), 124.88 (t, J = 3.0 Hz), 119.89. ^{19}F NMR (376 MHz, CDCl_3) δ 45.88. EI (m/z): 368 $[\text{M}]^+$.

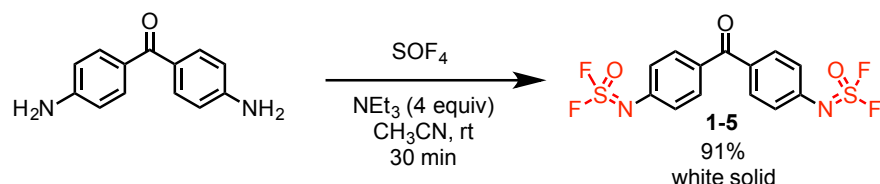
(thiobis(4,1-phenylene))disulfurimidoyl difluoride (1-4)



Following the **general procedure I**: The reaction of 4,4'-thiodianiline (2.59 g, 12 mmol), Et_3N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF_4 in 30 mL of CH_3CN afforded **1-4** (4.300 g, 93%) as yellow oil.

^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.33 (m, 4H), 7.14 – 7.06 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 135.34 (t, J = 3.0 Hz), 133.31, 132.37, 124.40 (t, J = 3.0 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 46.41. EI (m/z): 384 $[\text{M}]^+$.

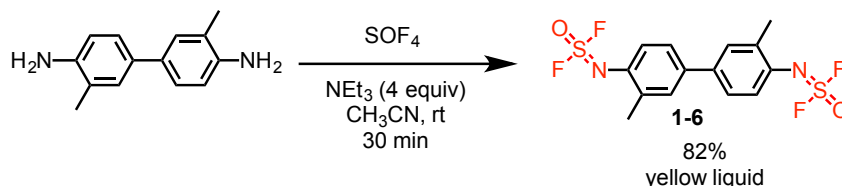
(carbonylbis(4,1-phenylene))disulfurimidoyl difluoride (1-5)



Following the **general procedure I**: The reaction of 4,4'-oxydianiline (2.55 g, 12 mmol), Et_3N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF_4 in 30 mL of CH_3CN afforded **1-5** (4.169 g, 93%) as white solid.

^1H NMR (600 MHz, CDCl_3) δ 7.85 – 7.78 (m, 4H), 7.26 – 7.23 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 193.89, 139.96 (t, $J = 2.6$ Hz), 134.96, 131.66, 123.51 (t, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 46.77. ESI (m/z): 381[M+H] $^+$.

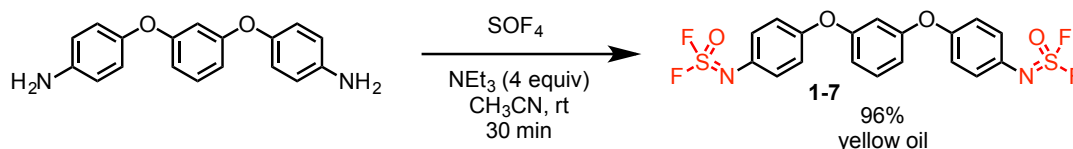
(3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)disulfurimidoyl difluoride (1-6)



Following the **general procedure I**: The reaction of 3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2.54 g, 12 mmol), Et_3N (6.7 mL, $d = 0.725$ g/mL, 4.86 g, 48 mmol), and SOF_4 in 30 mL of CH_3CN afforded **1-6** (3.727 g, 82%) as yellow liquid.

^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 2.2$ Hz, 2H), 7.35 (dd, $J = 8.2, 2.2$ Hz, 2H), 7.14 (d, $J = 8.2$ Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 138.16, 134.34 (t, $J = 3.2$ Hz), 133.43 – 132.88 (m), 129.64, 125.46, 123.27 (d, $J = 2.5$ Hz), 18.21. ^{19}F NMR (376 MHz, CDCl_3) δ 47.29. EI (m/z): 380 [M] $^+$.

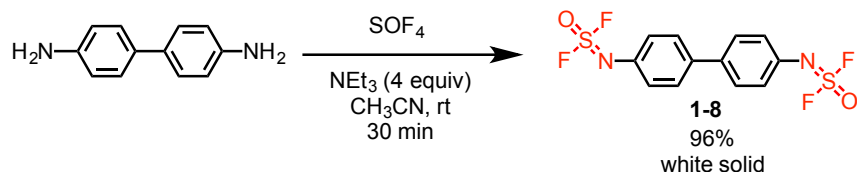
((1,3-phenylenebis(oxy))bis(4,1-phenylene))disulfurimidoyl difluoride (1-7)



Following the **general procedure I**: The reaction of 4,4'-(1,3-phenylenebis(oxy))dianiline (3.50 g, 12 mmol), Et_3N (6.7 mL, $d = 0.725$ g/mL, 4.86 g, 48 mmol), and SOF_4 in 30 mL of CH_3CN afforded **1-7** (5.299 g, 96%) as yellow liquid.

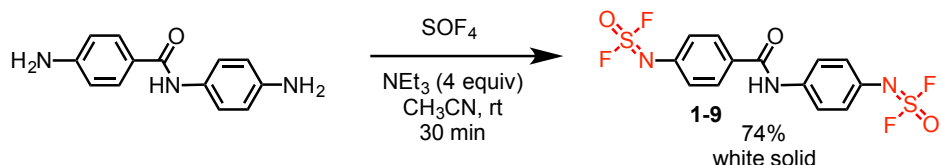
^1H NMR (600 MHz, CDCl_3) δ 7.31 (t, $J = 8.2$ Hz, 1H), 7.17 – 7.10 (m, 4H), 7.08 – 7.00 (m, 4H), 6.76 (dd, $J = 8.2, 2.3$ Hz, 2H), 6.69 (t, $J = 2.3$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.40, 154.65, 131.61 (t, $J = 2.9$ Hz), 130.63, 124.84 (t, $J = 3.0$ Hz), 120.18, 113.45, 109.32. ^{19}F NMR (376 MHz, CDCl_3) δ 45.88. EI (m/z): 460 [M] $^+$.

[1,1'-biphenyl]-4,4'-diyldisulfurimidoyl difluoride (1-8)



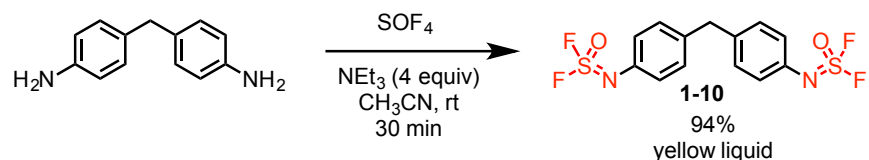
Following the **general procedure I**: The reaction of benzidine (2.21 g, 12 mmol), Et₃N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF₄ in 30 mL of CH₃CN afforded **1-8** (4.028 g, 96%) as white solid. ¹H NMR (600 MHz, CDCl₃) δ 7.57 – 7.51 (m, 4H), 7.24 – 7.18 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 137.97, 135.60 (t, *J* = 2.8 Hz), 128.20, 123.97 (t, *J* = 2.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ 46.35. EI (m/z): 352 [M]⁺.

(4-((4-((difluoro(oxo)-λ⁶-sulfaneylidene)amino)phenyl)carbamoyl)phenyl)sulfurimidoyl difluoride (1-9)



Following the **general procedure I**: The reaction of 4-amino-N-(4-aminophenyl)benzamide (2.73 g, 12 mmol), Et₃N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF₄ in 30 mL of CH₃CN afforded **1-9** (3.523 g, 74%) as white solid. ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.42 (s, 1H), 8.12 – 7.92 (m, 2H), 7.91 – 7.80 (m, 2H), 7.48 – 7.34 (m, 2H), 7.34 – 7.23 (m, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 164.53, 138.05 (d, *J* = 2.8 Hz), 137.48, 132.78, 130.53 (t, *J* = 2.6 Hz), 129.64, 123.66 (d, *J* = 2.9 Hz), 123.49 (d, *J* = 2.8 Hz), 121.59. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ 47.83, 47.46. ESI (m/z): 396 [M+H]⁺.

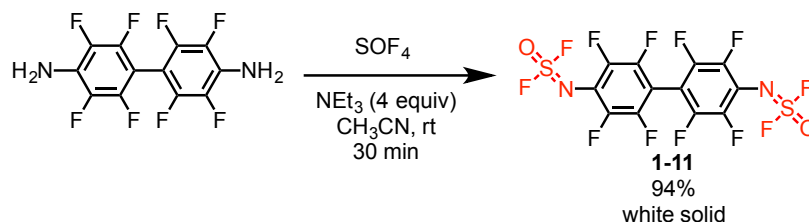
(methylenebis(4,1-phenylene))disulfurimidoyl difluoride (1-10)



Following the **general procedure I**: The reaction of 4,4'-methylenedianiline (2.38 g, 12 mmol), Et₃N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF₄ in 30 mL of CH₃CN afforded **1-10** (4.125 g, 94%) as yellow liquid.

^1H NMR (600 MHz, CDCl_3) δ 7.17 – 7.12 (m, 4H), 7.09 – 7.03 (m, 4H), 3.94 (s, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 138.61, 134.35 (t, $J = 2.9$ Hz), 130.07, 123.63 (t, $J = 3.0$ Hz), 40.60. ^{19}F NMR (376 MHz, CDCl_3) δ 46.15. EI (m/z): 366 $[\text{M}]^+$.

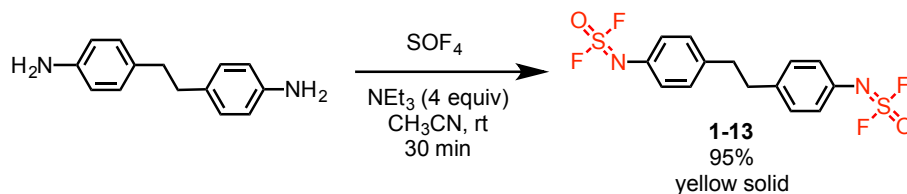
(perfluoro-[1,1'-biphenyl]-4,4'-diyl)disulfurimidoyl difluoride (1-11)



Following the **general procedure I**: The reaction of octafluoro-[1,1'-biphenyl]-4,4'-diamine (3.93 g, 12 mmol), Et_3N (6.7 mL, $d = 0.725$ g/mL, 4.86 g, 48 mmol), and SOF_4 in 30 mL of CH_3CN afforded **1-11** (5.573 g, 94%) as white solid.

^{13}C NMR (151 MHz, CDCl_3) δ 145.49 – 143.40 (m), 142.82 – 140.70 (m), 118.00 (t, $J = 15.0$ Hz), 103.86 (t, $J = 16.7$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 49.31 – 49.15 (m), -137.70 – -137.90 (m), -147.90 – -148.10 (m). EI (m/z): 496 $[\text{M}]^+$.

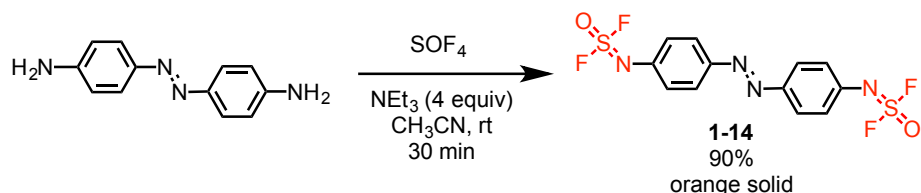
(ethane-1,2-diylbis(4,1-phenylene))disulfurimidoyl difluoride (1-13)



Following the **general procedure I**: The reaction of 4,4'-(ethane-1,2-diyl)dianiline (2.55 g, 12 mmol), Et_3N (6.7 mL, $d = 0.725$ g/mL, 4.86 g, 48 mmol), and SOF_4 in 30 mL of CH_3CN afforded **1-13** (4.337 g, 95%) as white solid.

^1H NMR (600 MHz, CDCl_3) δ 7.14 – 7.10 (m, 4H), 7.05 – 7.01 (m, 4H), 2.89 (s, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 139.30, 134.09 (t, $J = 3.0$ Hz), 129.67, 123.40 (t, $J = 2.9$ Hz), 37.05. ^{19}F NMR (376 MHz, CDCl_3) δ 46.10. EI (m/z): 380 $[\text{M}]^+$.

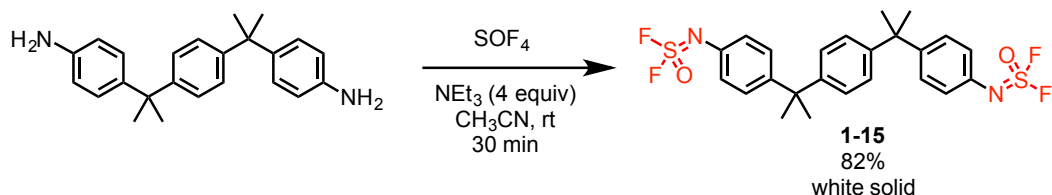
(*E*)-4-((4-((difluoro(oxo)- λ^6 -sulfaneylidene)amino)phenyl)diazenyl)phenyl)sulfurimidoyl difluoride (1-14)



Following the **general procedure I**: The reaction of (*E*)-4,4'-(diazene-1,2-diyl)dianiline (2.55 g, 12 mmol), Et₃N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF₄ in 30 mL of CH₃CN afforded **1-14** (4.101 g, 90%) as orange solid.

¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.90 (m, 4H), 7.31 – 7.23 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 150.27, 138.48 (t, *J* = 2.7 Hz), 124.38, 124.22 (t, *J* = 2.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ 46.59. EI (m/z): 380 [M]⁺.

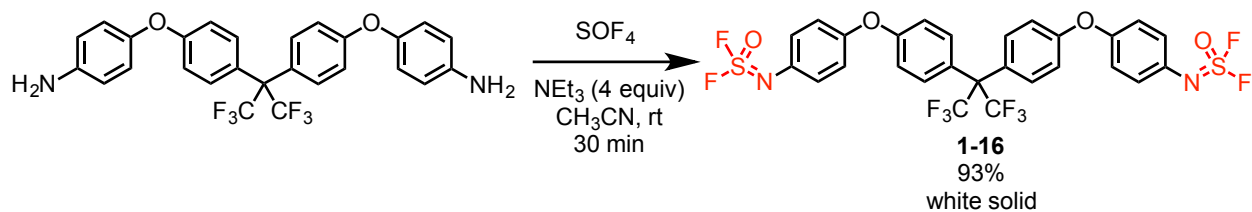
((1,4-phenylenebis(propane-2,2-diyl))bis(4,1-phenylene))disulfurimidoyl difluoride (1-15)



Following the **general procedure I**: The reaction of 4,4'-(1,4-phenylenebis(propane-2,2-diyl))dianiline (4.13 g, 12 mmol), Et₃N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF₄ in 30 mL of CH₃CN afforded **1-15** (5.019 g, 82%) as white solid.

¹H NMR (600 MHz, CDCl₃) δ 7.23 – 7.18 (m, 4H), 7.10 (s, 4H), 7.05 – 6.98 (m, 4H), 1.65 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 148.76, 147.40, 133.58, 128.07, 126.35, 122.95 (d, *J* = 3.1 Hz), 42.29, 30.69. ¹⁹F NMR (376 MHz, CDCl₃) δ 46.36. EI (m/z): 512 [M]⁺.

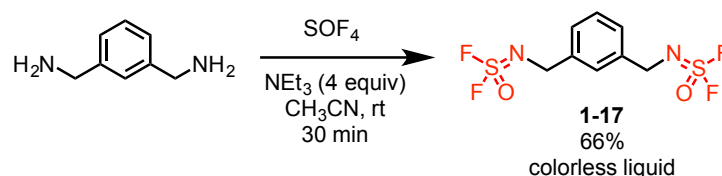
(((((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))disulfurimidoyl difluoride (1-16)



Following the **general procedure I**: The reaction of 4,4'-(((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))dianiline (6.22 g, 12 mmol), Et₃N (6.7 mL, d = 0.725 g/mL, 4.86 g, 48 mmol), and SOF₄ in 30 mL of CH₃CN afforded **1-16** (7.658 g, 93%) as white solid.

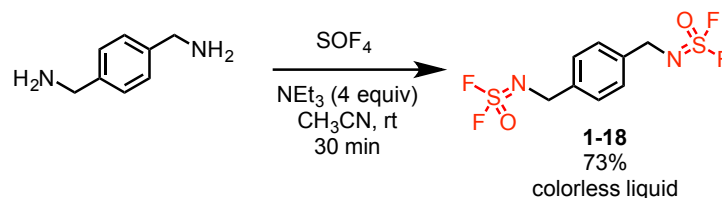
¹H NMR (600 MHz, CDCl₃) δ 7.36 (d, *J* = 8.6 Hz, 4H), 7.16 – 7.10 (m, 4H), 7.10 – 7.03 (m, 4H), 7.00 – 6.91 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 157.84, 153.96, 132.11 (t, *J* = 3.0 Hz), 131.79, 124.98 (t, *J* = 2.8 Hz), 120.90, 117.49. ¹⁹F NMR (376 MHz, CDCl₃) δ 45.90, -64.55. EI (m/z): 686 [M]⁺.

(1,3-phenylenebis(methylene))disulfurimidoyl difluoride (**1-17**)



Following the **general procedure I**: The reaction of 1,3-phenylenedimethanamine (1.36 g, 10 mmol), Et₃N (5.58 mL, d = 0.725 g/mL, 4.05 g, 40 mmol), and SOF₄ in 25 mL of CH₃CN afforded **1-17** (2.000 g, 66%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.34 (m, 1H), 7.33 – 7.27 (m, 3H), 4.54 (t, *J* = 4.0 Hz, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 137.03, 129.19, 126.78, 125.93, 48.97. ¹⁹F NMR (376 MHz, CDCl₃) δ 46.85. EI (m/z): 304 [M]⁺.

(1,4-phenylenebis(methylene))disulfurimidoyl difluoride (**1-18**)

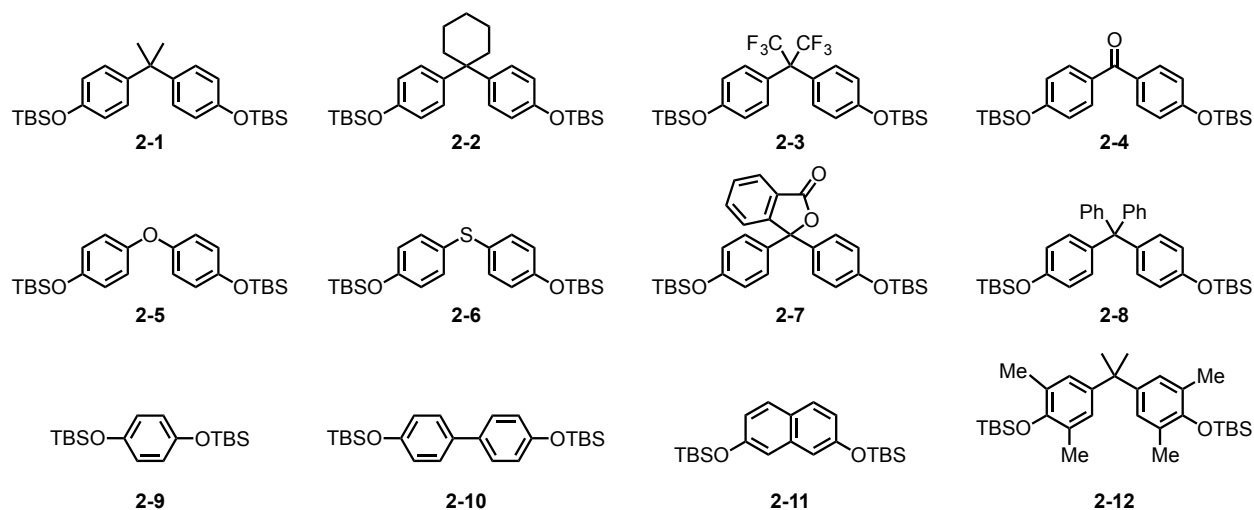


Following the **general procedure I**: The reaction of 1,4-phenylenedimethanamine (1.36 g, 10 mmol), Et₃N (5.58 mL, d = 0.725 g/mL, 4.05 g, 40 mmol), and SOF₄ in 25 mL of CH₃CN afforded **1-18** (2.223 g, 73%) as colorless liquid.

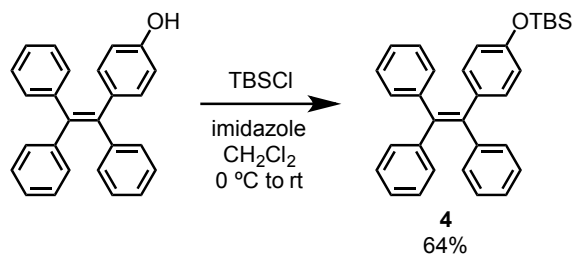
¹H NMR (400 MHz, CDCl₃) δ 7.34 (s, 4H), 4.60 – 4.45 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 136.22, 127.60, 48.85. ¹⁹F NMR (376 MHz, CDCl₃) δ 46.93. EI (m/z): 304 [M]⁺.

3. Preparation of the monomer silyl ethers

The TBS ethers used in this paper (listed below) were prepared from TBSCl and the corresponding phenols according to references: J. Dong, L. Krasnova, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2014**, 53, 9430; B. Gao, L. Zhang, Q. Zheng, F. Zhou, L. M. Klivansky, J. Lu, Y. Liu, J. Dong, P. Wu, K. B. Sharpless, *Nature Chem.* **2017**, 9, 1083.



Preparation of *tert*-butyldimethyl(4-(1,2,2-triphenylvinyl)phenoxy)silane (**4**)



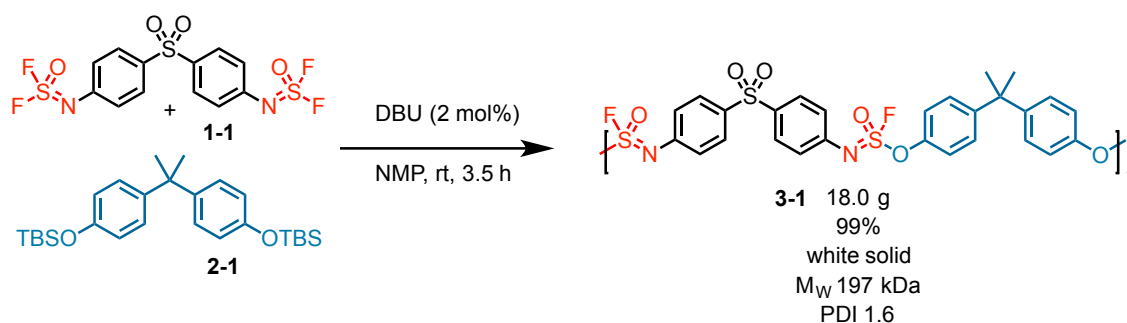
A 100 mL round-bottomed flask was charged with a magnetic stir bar, 4-(1,2,2-triphenylvinyl)phenol (1.750 g, 5 mmol), imidazole (0.845 g, 12.4 mmol) and 15 mL of chloromethane (CH₂Cl₂). The solution was stirred at room temperature for 10 mins, then TBSCl (0.980 g, 6.5 mmol) was added at 0 °C (ice bath). The resulting mixture was stirred at room temperature until the full conversion of starting compound to the silyl ether, monitored by TLC. Precipitates were removed by filtration. The filtrate was concentrated under reduced pressure on a rotary evaporator. The resulting crude product was dissolved in 30 mL of ethyl acetate (EtOAc), which was subsequently washed with water (20 mL X 3) and saturated aqueous solution of NaCl. The organic phase was dried over anhydrous MgSO₄. After filtration, the filtrate was subjected to evaporation to remove EtOAc. The product was purified by flash column chromatography

over silica gel (hexanes/CH₂Cl₂ = 4/1) afforded *tert*-butyldimethyl(4-(1,2,2-triphenylvinyl)phenoxy)silane **4** (1.487 g, 64%) as white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.13 – 6.96 (m, 15H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 8.6 Hz, 2H), 0.94 (s, 9H), 0.14 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 154.22, 144.00, 143.93, 143.85, 140.69, 140.14, 136.78, 132.44, 131.36, 131.33, 127.59, 127.55, 126.31, 126.22, 126.18, 119.31, 25.69, 18.23, -4.44. IR (KBr, cm⁻¹) 3727, 3421, 2957, 2928, 2855, 1602, 1503, 1442, 1264, 1168, 1075, 1029.

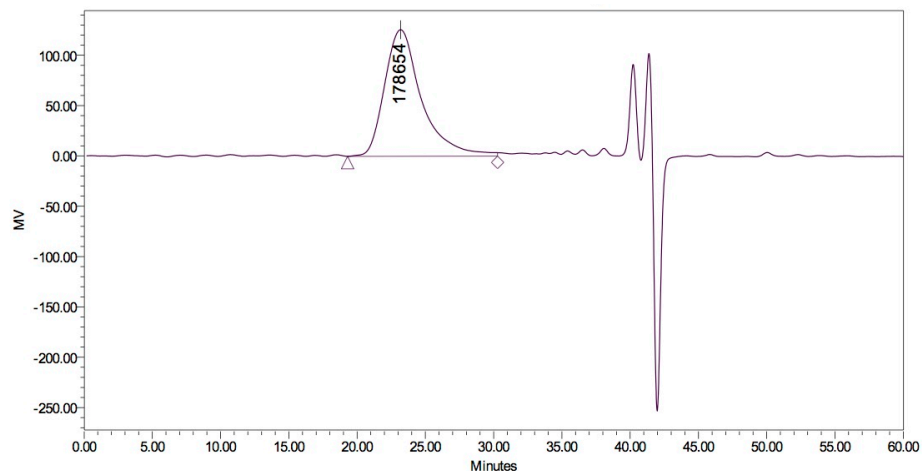
4. Synthesis of the polymer from iminosulfur oxydifluorides and silyl ethers

Procedure for the synthesis of the polymer **3-1** (30 mmol scale)



To a round-bottomed flask (250 mL) with a magnetic stir bar was added the bis(iminosulfur oxydifluoride) (12.49 g, 30 mmol), BPA-TBS (13.70 g, 30 mmol) and 40 mL of anhydrous NMP. The flask was sealed with a Suba-Seal® Septa, vacuumized with a needle linked with a pump until there were no bubbles formed in the solution (5-10 minutes). Then DBU (91.3 mg, 90 μL, 0.6 mmol, *d* = 1.018 g/mL) was added into the flask via a needle. After stirring at room temperature for 15 minutes, the solution became a jam and the stir bar stopped moving. After staying at room temperature for 3.5 hours, 50 mL of DMF was added. The flask was shaken to promote the dissolution and the resulting solution was poured slowly into 600 mL of MeOH with mechanical stirring. The solution was stirred in MeOH for 20 minutes and then filtrated. The white solid was washed with MeOH three times (150 mL X 3) and then dried in the vacuum oven (60 °C) for 24 hours to give 18.0 g of the polymer **3-1** (99%).

¹H NMR (600 MHz, DMF-*d*₇) δ 8.05 (d, *J* = 8.4 Hz, 4H), 7.58 – 7.36 (m, 12H), 1.70 (s, 6H). ¹³C NMR (151 MHz, DMF-*d*₇) δ 151.90, 149.29, 144.39 (d, *J* = 2.7 Hz), 139.14, 130.56, 130.11, 125.68 (d, *J* = 2.8 Hz), 122.26, 43.87, 31.09. ¹⁹F NMR (376 MHz, DMF-*d*₇) δ 50.69; M_w^{ps} = 197 kDa. PDI = 1.8. *T_g* (DSC) = 150.8 °C. *T_d* (5% weight loss, TGA) = 261.2 °C.



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	109182	197400	178654	336371	588214	1.807988	1.704003	2.979801

Figure S1. GPC trace of the 3-1

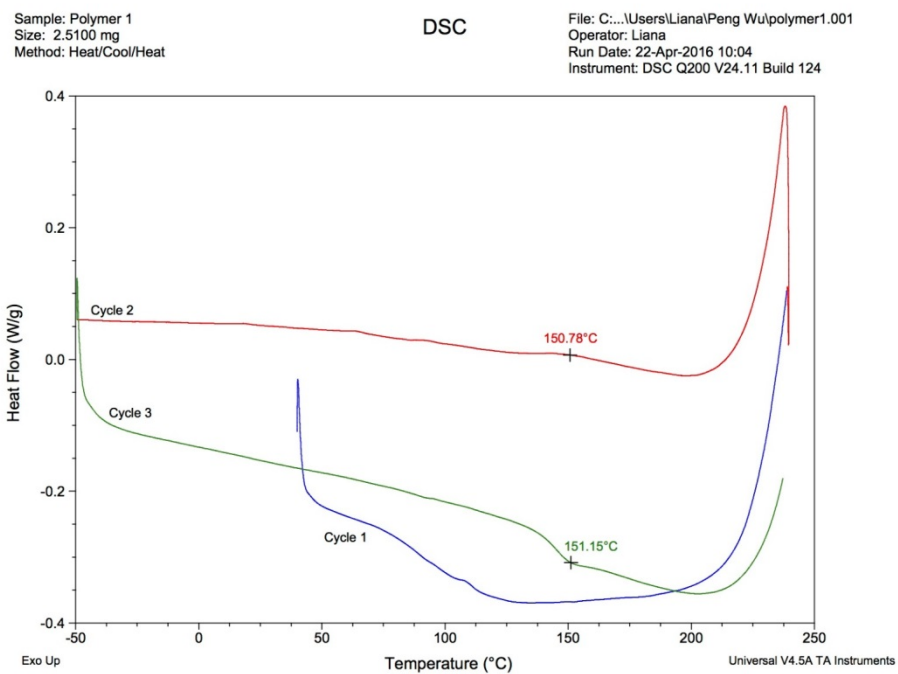


Figure S2. Differential scanning calorimetry (DSC) analysis of 3-1.

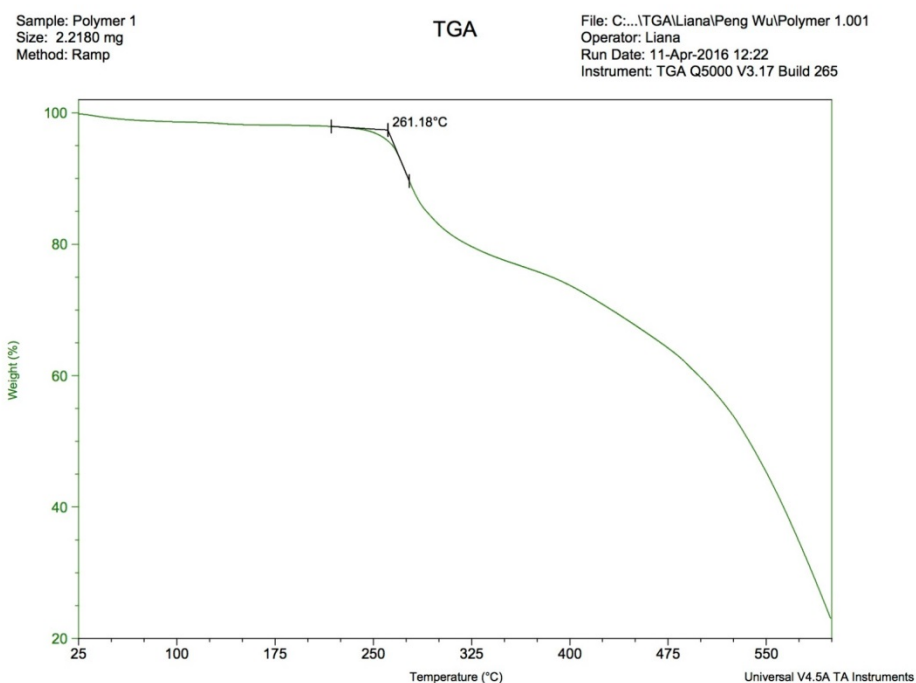
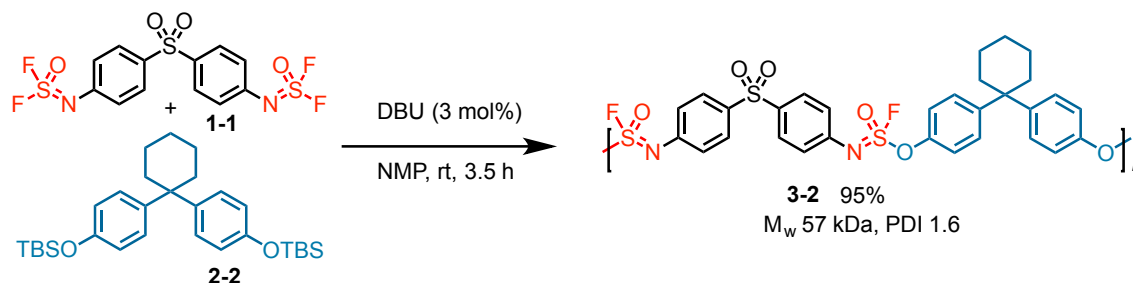


Figure S3. Thermal gravimetric analysis (TGA) of 3-1 (5 % weight loss at 261.2 °C).

General procedure II for making the polymer (5 mmol scale):

To a vial (60 mL) with a magnetic stir bar was added the bis(iminosulfur oxydifluoride) (5 mmol), bisphenol-TBS (5 mmol) and 10 mL of anhydrous NMP. The vial was sealed with a rubber Septa, vacuumized with a needle linked with a pump until there were no bubbles formed in the solution (5-10 minutes). Then DBU (0.15 mmol, $d = 1.018 \text{ g/mL}$) was added into the vial via a needle. After stirring at room temperature for 15 minutes, the solution became a jam and the stir bar stopped moving. After staying at room temperature for 3.5 hours, 10 mL of DMF was added. The flask was shaken to promote the dissolution and the resulting solution was poured slowly into 150 mL of MeOH with stirring. The solution was stirred in MeOH for 20 minutes and then filtrated. The white solid was purified using ultrasonic cleaning by immersing in 50 mL MeOH for 10 min (3 times) and then dried in the vacuum oven (60 °C) for 24 hours to give the polymer.

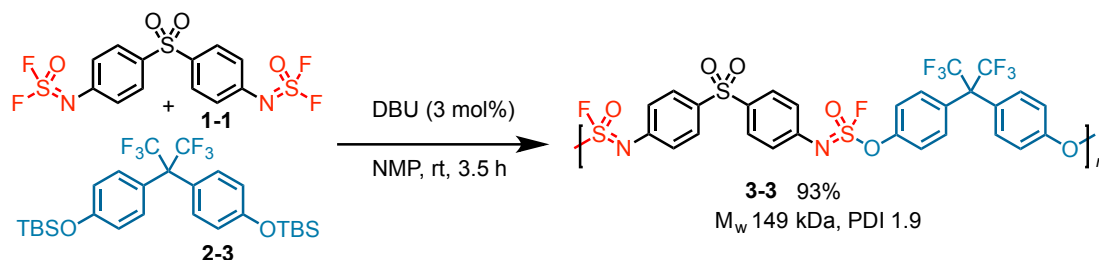
Synthesis of the polymer 3-2



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), ((cyclohexane-1,1-diylbis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (2.484 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-2** (3.060 g, 95%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.04 (d, $J = 8.7 \text{ Hz}$, 4H), 7.56 (d, $J = 9.1 \text{ Hz}$, 4H), 7.50 (d, $J = 9.0 \text{ Hz}$, 4H), 7.45 (d, $J = 8.7 \text{ Hz}$, 4H), 2.37 – 2.29 (s, 4H), 1.56 – 1.39 (m, 6H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 149.93, 149.06, 144.37 (d, $J = 2.6 \text{ Hz}$), 139.14, 130.55, 130.46, 125.66 (d, $J = 2.6 \text{ Hz}$), 122.44, 46.98, 37.49, 26.81, 23.71. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 50.58. $M_w^{ps} = 57 \text{ kDa}$. PDI = 1.6. T_g (DSC) = 126.6 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 241.3 $^\circ\text{C}$.

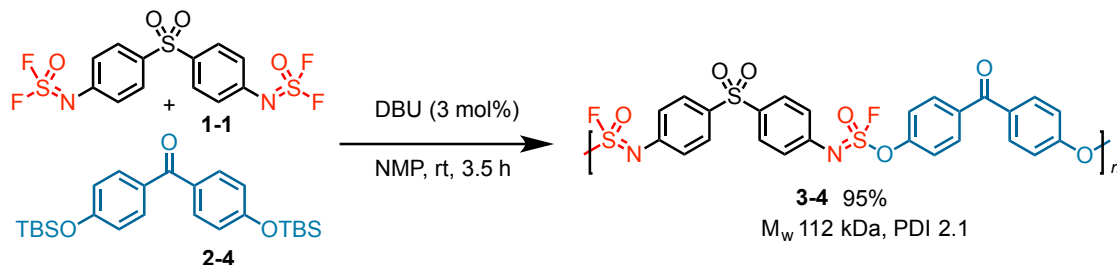
Synthesis of the polymer 3-3



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), (((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (2.824 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-3** (3.318 g, 93%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.09 (d, $J = 8.2 \text{ Hz}$, 4H), 7.82 (d, $J = 8.6 \text{ Hz}$, 4H), 7.67 (d, $J = 8.6 \text{ Hz}$, 4H), 7.51 (d, $J = 8.3 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.71, 144.05 (d, $J = 2.5 \text{ Hz}$), 139.35, 133.99, 133.75, 130.62, 125.77 (d, $J = 2.3 \text{ Hz}$), 125.02 (q, $J = 286.9 \text{ Hz}$), 123.28, 65.14 (p, $J = 26.3$, 25.2 Hz). ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.85, -63.10. $M_w^{ps} = 149 \text{ kDa}$. PDI = 1.9. T_g (DSC) = 124.2 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 261.1 $^\circ\text{C}$.

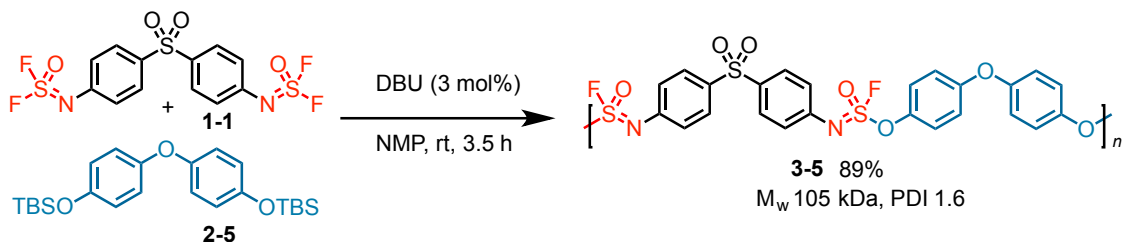
Synthesis of the polymer 3-4



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)methanone (2.214 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-4** (2.806 g, 95%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.09 (d, $J = 8.7 \text{ Hz}$, 4H), 8.03 (d, $J = 8.8 \text{ Hz}$, 4H), 7.83 (d, $J = 8.7 \text{ Hz}$, 4H), 7.53 (d, $J = 8.7 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 194.18, 153.81, 144.07 (d, $J = 2.7 \text{ Hz}$, 4H), 139.33, 138.23, 133.57, 130.63, 125.79 (d, $J = 2.7 \text{ Hz}$), 123.00. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 52.30. $M_w^{ps} = 112 \text{ kDa}$. PDI = 2.1. T_g (DSC) = 121.3 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 260.2 $^\circ\text{C}$.

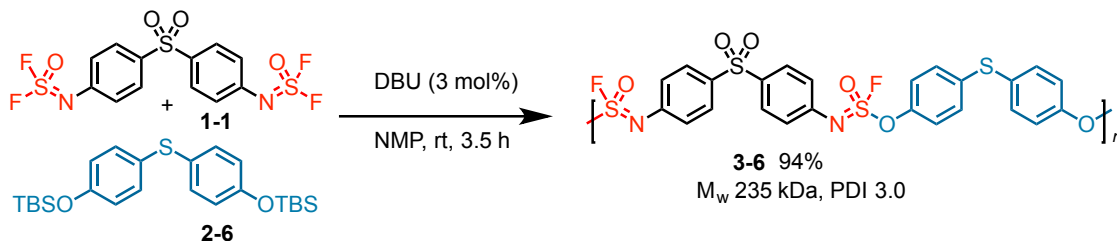
Synthesis of the polymer 3-5



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), ((oxybis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (2.154 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-5** (2.587 g, 89%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.08 (d, $J = 8.7 \text{ Hz}$, 4H), 7.68 (d, $J = 9.1 \text{ Hz}$, 4H), 7.50 (d, $J = 8.7 \text{ Hz}$, 4H), 7.28 (d, $J = 9.1 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 157.53, 146.86, 144.33 (d, $J = 2.8 \text{ Hz}$), 139.18, 130.58, 125.71 (d, $J = 2.7 \text{ Hz}$), 124.66, 121.79. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 50.56. $M_w^{ps} = 105 \text{ kDa}$. PDI = 1.6. T_g (DSC) = 114.2 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 209.3 $^\circ\text{C}$.

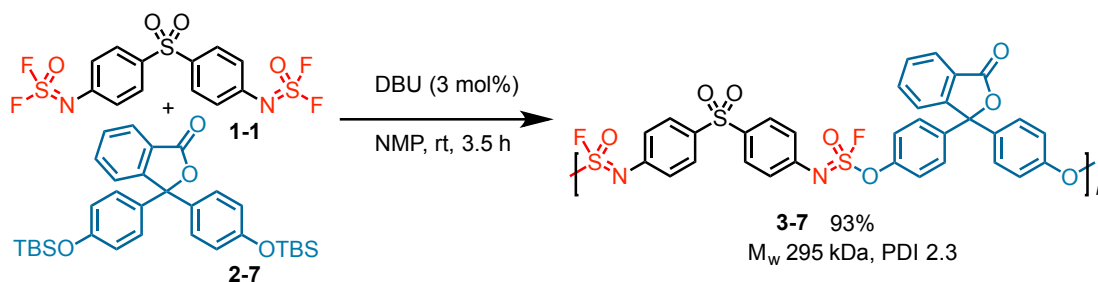
Synthesis of the polymer 3-6



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)sulfane (2.234 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-6** (2.793 g, 94%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.06 (d, $J = 8.4 \text{ Hz}$, 4H), 7.66 (d, $J = 8.6 \text{ Hz}$, 4H), 7.58 (d, $J = 8.6 \text{ Hz}$, 4H), 7.49 (d, $J = 8.4 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 150.50, 144.19, 139.23, 136.87, 134.13, 130.59, 125.73, 124.03. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.37. $M_w^{ps} = 235 \text{ kDa}$. PDI = 3.0. T_g (DSC) = 115.5 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 211.7 $^\circ\text{C}$.

Synthesis of the polymer 3-7

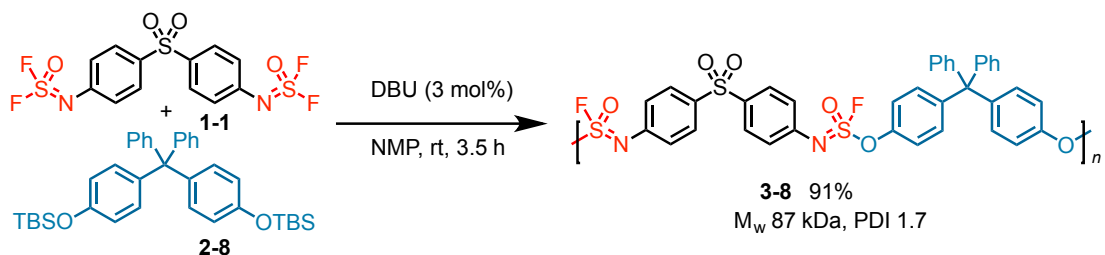


Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), 3,3-bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)isobenzofuran-1(3*H*)-one (2.734 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-7** (3.214 g, 93%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.07 (d, $J = 7.8 \text{ Hz}$, 1H), 8.06 – 8.01 (m, 5H), 7.95 (t, $J = 7.6 \text{ Hz}$, 1H), 7.78 (t, $J = 7.5 \text{ Hz}$, 1H), 7.69 (d, $J = 8.7 \text{ Hz}$, 4H), 7.65 (d, $J = 8.8 \text{ Hz}$, 4H), 7.50 – 7.42 (m, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 169.45, 151.79, 151.20, 144.15, 142.51, 139.22, 136.57, 131.68, 130.58, 130.52,

127.14, 125.84, 125.80, 125.72, 123.19, 90.71. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.34, 51.31. M_w^{ps} = 295 kDa. PDI = 2.3. T_g (DSC) = 165.2 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 266.3 $^\circ\text{C}$.

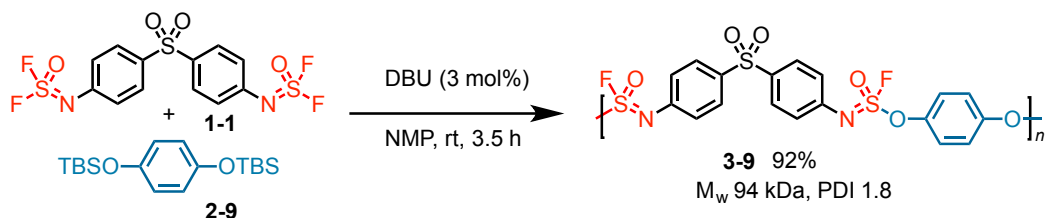
Synthesis of the polymer 3-8



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylmethane (2.905 g, 5.0 mmol) and DBU (23 μL , d = 1.018 g/mL, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-8** (3.311 g, 91%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.06 (d, J = 8.3 Hz, 4H), 7.57 (d, J = 8.5 Hz, 4H), 7.52 – 7.43 (m, 8H), 7.37 (t, J = 7.6 Hz, 4H), 7.30 – 7.20 (m, 6H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 149.29, 148.31, 146.85, 144.30 (d, J = 2.6 Hz), 139.20, 133.96, 131.61, 130.57, 129.32, 127.67, 125.72 (d, J = 2.3 Hz), 122.04, 65.58. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.01. M_w^{ps} = 87 kDa. PDI = 1.7. T_g (DSC) = 148.4 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 251.9 $^\circ\text{C}$.

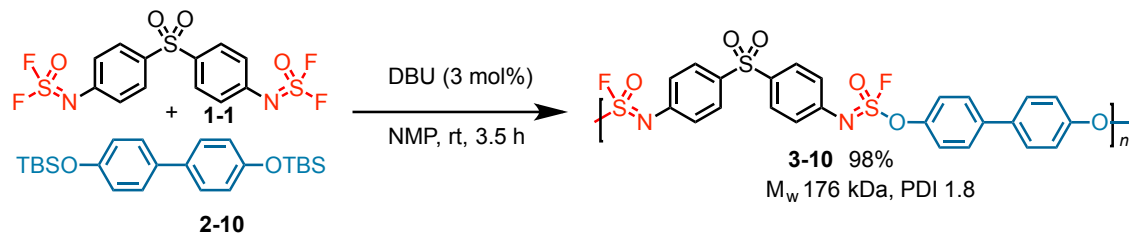
Synthesis of the polymer 3-9



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), 1,4-bis((*tert*-butyldimethylsilyl)oxy)benzene (1.693 g, 5.0 mmol) and DBU (23 μL , d = 1.018 g/mL, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-9** (2.241 g, 92%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.08 (d, J = 8.6 Hz, 4H), 7.89 (s, 4H), 7.51 (d, J = 8.7 Hz, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 150.36, 143.97 (d, J = 2.8 Hz), 139.33, 130.62, 125.76 (d, J = 2.7 Hz), 125.38. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.44. M_w^{ps} = 94 kDa. PDI = 1.8. T_g (DSC) = 109.0 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 248.8 $^\circ\text{C}$.

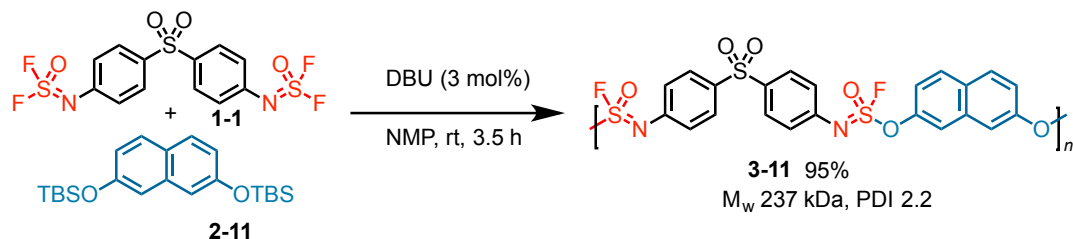
Synthesis of the polymer 3-10



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-10** (2.766 g, 98%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.08 (d, $J = 8.7 \text{ Hz}$, 4H), 7.94 (d, $J = 8.7 \text{ Hz}$, 4H), 7.72 (d, $J = 8.7 \text{ Hz}$, 4H), 7.52 (d, $J = 8.7 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.11, 144.30 (d, $J = 2.7 \text{ Hz}$), 140.68, 139.23, 130.61, 130.53, 125.74 (d, $J = 2.7 \text{ Hz}$), 123.23. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.15. $M_w^{ps} = 176 \text{ kDa}$. PDI = 1.8. T_g (DSC) = 142.0°C . T_d (5% weight loss, TGA) = 224.2°C .

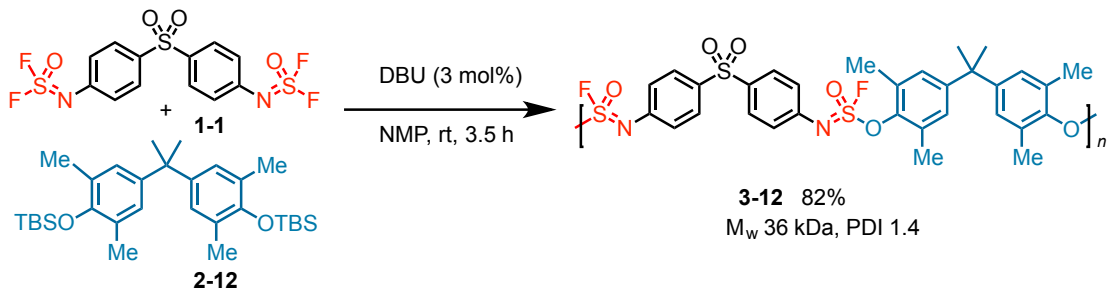
Synthesis of the polymer 3-11



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), 2,7-bis((*tert*-butyldimethylsilyl)oxy)naphthalene (1.944 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-11** (2.559 g, 95%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.42 (d, $J = 2.6 \text{ Hz}$, 2H), 8.32 (d, $J = 9.1 \text{ Hz}$, 2H), 8.08 (d, $J = 8.7 \text{ Hz}$, 4H), 7.84 (dd, $J = 9.0, 2.5 \text{ Hz}$, 2H), 7.53 (d, $J = 8.7 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 149.91, 144.20 (d, $J = 2.6 \text{ Hz}$), 139.28, 134.99, 132.83, 132.51, 130.62, 125.76 (d, $J = 2.4 \text{ Hz}$), 122.37, 120.98. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.74. $M_w^{ps} = 237 \text{ kDa}$. PDI = 2.2. T_g (DSC) = 127.8°C . T_d (5% weight loss, TGA) = 237.3°C .

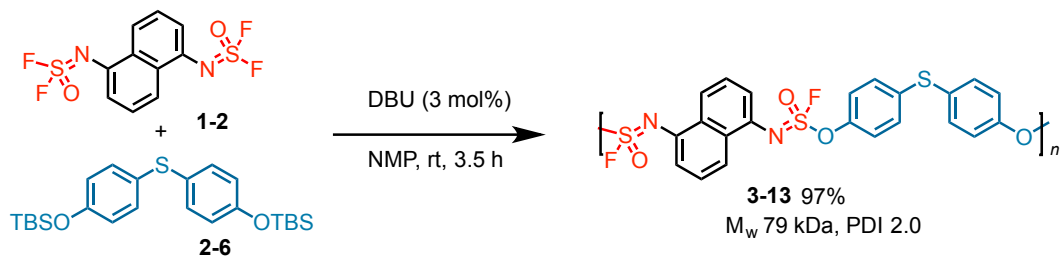
Synthesis of the polymer 3-12



Following the **general procedure II**: The reaction of (sulfonylbis(4,1-phenylene))disulfurimidoyl difluoride (2.082 g, 5.0 mmol), ((propane-2,2-diylbis(2,6-dimethyl-4,1-phenylene))bis(oxy)) bis(*tert*-butyltrimethylsilyl ether) (2.565 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-12** (2.706 g, 82%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.99 (d, $J = 8.7 \text{ Hz}$, 4H), 7.37 (d, $J = 8.8 \text{ Hz}$, 4H), 7.15 (s, 4H), 2.28 (s, 12H), 1.64 (s, 6H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.30, 147.83, 144.30, 144.29 (d, $J = 2.6 \text{ Hz}$), 139.16, 131.64, 130.45, 129.45, 125.68, 43.29, 31.01, 17.23. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 58.35. $M_w^{ps} = 36 \text{ kDa}$. PDI = 1.4. T_g (DSC) = 116.4 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 190.6 $^\circ\text{C}$.

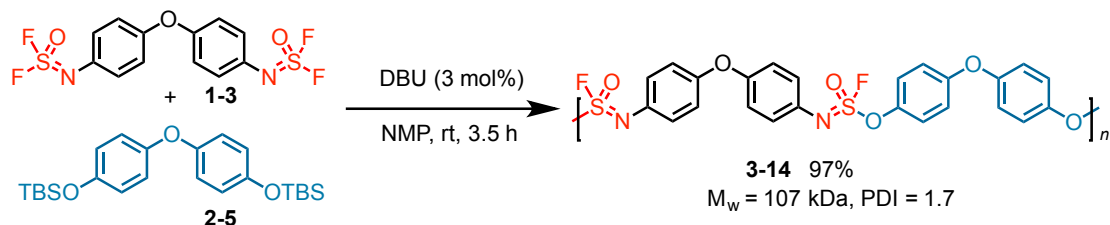
Synthesis of the polymer 3-13



Following the **general procedure II**: The reaction of naphthalene-1,5-diylbisulfurimidoyl difluoride (1.631 g, 5.0 mmol), bis(4-((*tert*-butyltrimethylsilyl)oxy)phenyl)sulfane (2.234 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-13** (2.446 g, 97%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.04 (d, $J = 8.3 \text{ Hz}$, 2H), 7.73 – 7.39 (m, 12H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 150.69, 136.71, 135.86 (d, $J = 3.3 \text{ Hz}$), 134.11, 131.11 (d, $J = 3.0 \text{ Hz}$), 127.62, 124.07, 121.67, 120.72. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 52.14. $M_w^{ps} = 79 \text{ kDa}$. PDI = 2.2. T_g (DSC) = 81.6 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 194.8 $^\circ\text{C}$.

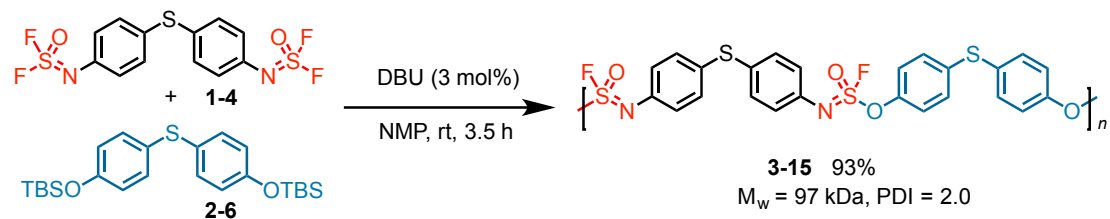
Synthesis of the polymer 3-14



Following the **general procedure II**: The reaction of (oxybis(4,1-phenylene))disulfurimidoyl difluoride (1.842 g, 5.0 mmol), ((oxybis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (2.154 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-14** (2.568 g, 97%) as gray solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.67 – 7.60 (m, 4H), 7.33 – 7.25 (m, 8H), 7.14 – 7.07 (m, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 157.41, 155.51, 147.01, 134.94 (d, $J = 3.3 \text{ Hz}$), 126.14 (d, $J = 3.0 \text{ Hz}$), 124.62, 121.73, 120.94. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 49.93. $M_w^{ps} = 107 \text{ kDa}$. PDI = 1.7. T_g (DSC) = 62.2 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 189.9 $^\circ\text{C}$.

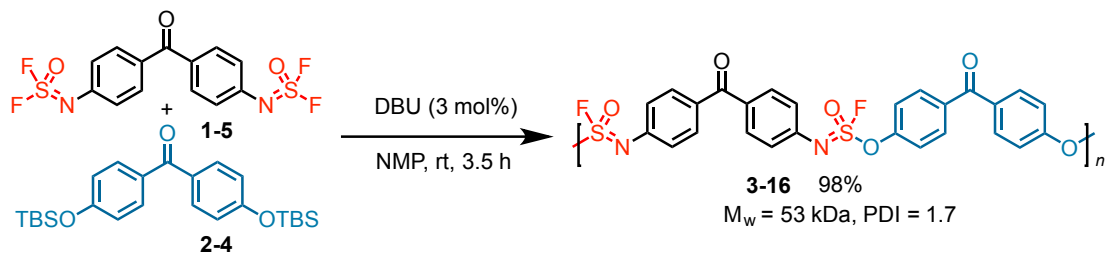
Synthesis of the polymer 3-15



Following the **general procedure II**: The reaction of (thiobis(4,1-phenylene))disulfurimidoyl difluoride (1.922 g, 5.0 mmol), bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)sulfane (2.234 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-15** (2.619 g, 93%) as gray solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.66 – 7.56 (m, 8H), 7.45 – 7.38 (m, 4H), 7.31 – 7.23 (m, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 150.60, 138.79 (d, $J = 3.1 \text{ Hz}$), 136.67, 134.12, 133.49, 132.95, 125.76 (d, $J = 3.0 \text{ Hz}$), 124.00. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.22. $M_w^{ps} = 97 \text{ kDa}$. PDI = 2.0. T_g (DSC) = 60.7 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 192.0 $^\circ\text{C}$.

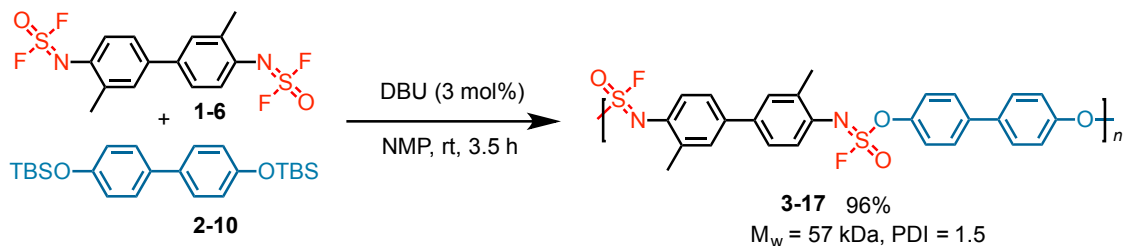
Synthesis of the polymer 3-16



Following the **general procedure II**: The reaction of (carbonylbis(4,1-phenylene))disulfurimidoyl difluoride (1.902 g, 5.0 mmol), bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)methanone (2.214 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-16** (2.716 g, 98%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.06 (d, $J = 8.8 \text{ Hz}$, 4H), 7.88 (d, $J = 8.8 \text{ Hz}$, 4H), 7.86 (d, $J = 8.7 \text{ Hz}$, 4H), 7.47 (d, $J = 8.7 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 194.79, 194.23, 153.89, 143.16 (d, $J = 2.8 \text{ Hz}$), 138.20, 135.34, 133.59, 132.73, 124.66 (d, $J = 2.6 \text{ Hz}$), 123.02. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 52.42. $M_w^{ps} = 53 \text{ kDa}$. PDI = 1.7. T_g (DSC) = 98.5 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 255.8 $^\circ\text{C}$.

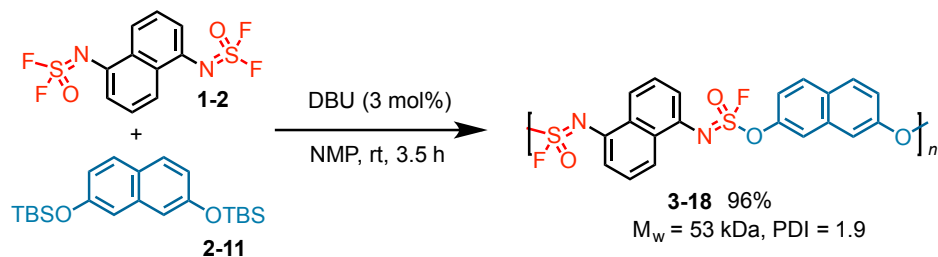
Synthesis of the polymer 3-17



Following the **general procedure II**: The reaction of (3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)disulfurimidoyl difluoride (1.902 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-17** (2.520 g, 96%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.97 (d, $J = 7.6 \text{ Hz}$, 4H), 7.70 (d, $J = 7.7 \text{ Hz}$, 4H), 7.66 (d, $J = 2.5 \text{ Hz}$, 2H), 7.59 (d, $J = 8.3 \text{ Hz}$, 2H), 7.37 (d, $J = 8.2 \text{ Hz}$, 2H), 2.33 (s, 6H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.29, 140.53, 138.03, 137.46 (d, $J = 3.1 \text{ Hz}$), 134.13 (d, $J = 3.2 \text{ Hz}$), 130.41, 130.26, 126.34, 124.35, 123.28, 18.70. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 53.22. $M_w^{ps} = 57 \text{ kDa}$. PDI = 1.5. T_g (DSC) = 103.3 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 199.1 $^\circ\text{C}$.

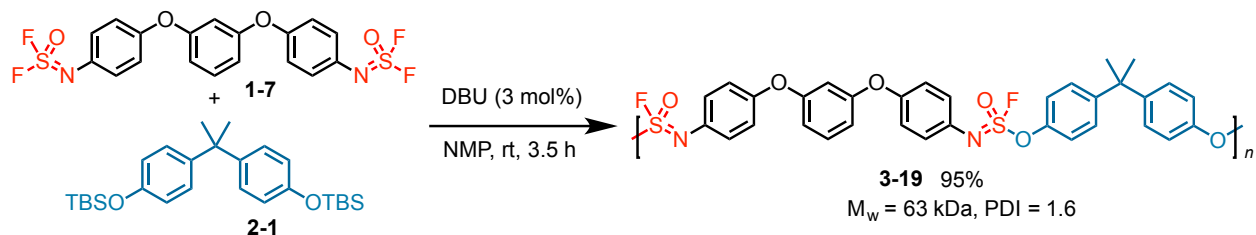
Synthesis of the polymer 3-18



Following the **general procedure II**: The reaction of naphthalene-1,5-diyldisulfurimidoyl difluoride (1.631 g, 5.0 mmol), 2,7-bis((*tert*-butyldimethylsilyl)oxy)naphthalene (1.944 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-18** (2.144 g, 96%) as gray solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.40 (s, 2H), 8.29 (d, $J = 9.2 \text{ Hz}$, 2H), 8.04 (t, $J = 4.8 \text{ Hz}$, 2H), 7.83 (d, $J = 9.1 \text{ Hz}$, 2H), 7.56 (d, $J = 5.0 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 150.03, 135.85 (d, $J = 3.1 \text{ Hz}$), 135.05, 132.70, 132.38, 131.10 (d, $J = 2.7 \text{ Hz}$), 127.57, 122.40, 121.68, 121.00, 120.72. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 52.46. $M_w^{PS} = 53 \text{ kDa}$. PDI = 1.9. T_g (DSC) = 107.3 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 206.2 $^\circ\text{C}$.

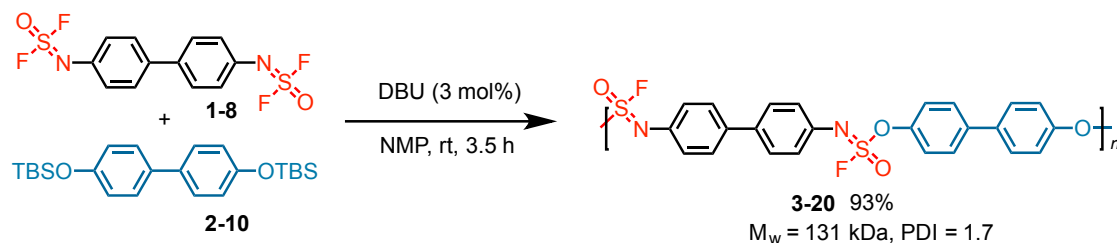
Synthesis of the polymer 3-19



Following the **general procedure II**: The reaction of ((1,3-phenylenebis(oxy))bis(4,1-phenylene))disulfurimidoyl difluoride (2.302 g, 5.0 mmol), ((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (2.284 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-19** (3.079 g, 95%) as gray solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.52 – 7.43 (m, 8H), 7.41 (t, $J = 8.2 \text{ Hz}$, 1H), 7.29 – 7.22 (m, 4H), 7.16 – 7.08 (m, 4H), 6.78 (dd, $J = 8.2, 2.4 \text{ Hz}$, 2H), 6.70 (t, $J = 2.4 \text{ Hz}$, 1H), 1.71 (s, 6H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 159.86, 154.79, 151.67, 149.41, 135.34 (d, $J = 3.2 \text{ Hz}$), 132.22, 130.03, 126.13 (d, $J = 2.8 \text{ Hz}$), 122.22, 121.46, 114.11, 109.69, 43.83, 31.13. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 50.16. $M_w^{PS} = 63 \text{ kDa}$. PDI = 1.6.

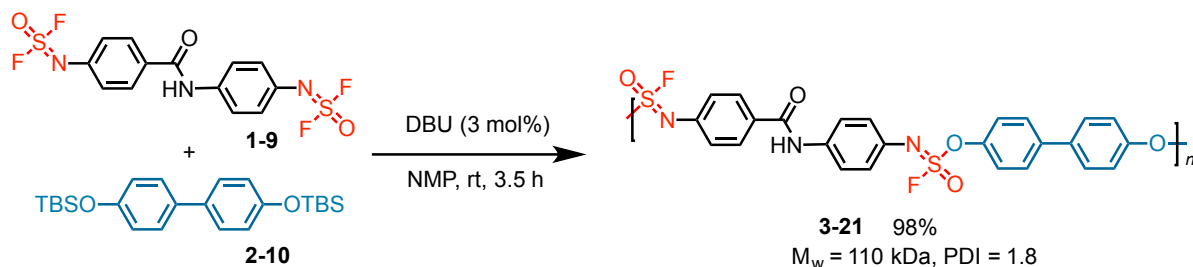
Synthesis of the polymer **3-20**



Following the **general procedure II**: The reaction of [1,1'-biphenyl]-4,4'-diylsulfurimidoyl difluoride (1.762 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-20** (2.322 g, 93%) as white solid. This polymer is hard to dissolve in regular deuterated solvent.

$M_w^{ps} = 131 \text{ kDa}$. $\text{PDI} = 1.7$. T_g (DSC) = 92.4 $^{\circ}\text{C}$. T_d (5% weight loss, TGA) = 201.2 $^{\circ}\text{C}$.

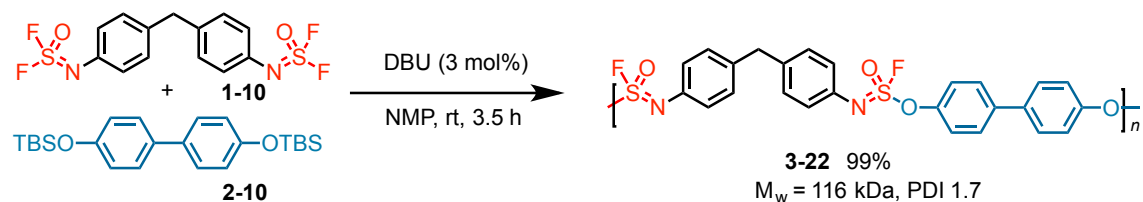
Synthesis of the polymer **3-21**



Following the **general procedure II**: The reaction of (4-((4-((difluoro(oxo)- λ^6 -sulfaneylidene)amino)phenyl)carbamoyl)phenyl)sulfurimidoyl difluoride (1.977 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-21** (2.649 g, 98%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 10.41 (s, 1H), 8.15 (d, $J = 8.3 \text{ Hz}$, 2H), 7.99 (dd, $J = 10.1, 7.6 \text{ Hz}$, 6H), 7.81 – 7.65 (m, 4H), 7.43 (d, $J = 8.2 \text{ Hz}$, 2H), 7.30 (d, $J = 8.6 \text{ Hz}$, 2H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 165.96, 151.25 (d, $J = 4.4 \text{ Hz}$), 151.17 (d, $J = 4.1 \text{ Hz}$), 142.44, 140.64 (d, $J = 8.8 \text{ Hz}$), 140.46 (d, $J = 8.8 \text{ Hz}$), 138.14, 134.83, 133.00, 130.52, 130.50, 130.48, 130.44, 130.42, 124.78 (d, $J = 2.5 \text{ Hz}$), 124.50 (d, $J = 2.6 \text{ Hz}$), 123.25, 123.23, 123.21, 122.56. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.11, 50.64. $M_w^{ps} = 110 \text{ kDa}$. $\text{PDI} = 1.8$. T_g (DSC) = 66.8 $^{\circ}\text{C}$. T_d (5% weight loss, TGA) = 196.7 $^{\circ}\text{C}$.

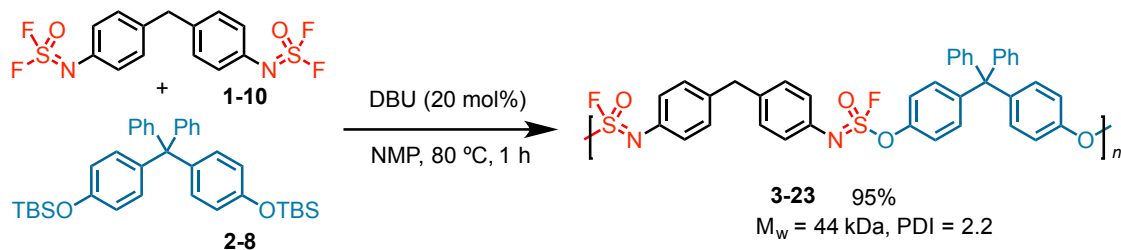
Synthesis of the polymer 3-22



Following the **general procedure II**: The reaction of (methylenebis(4,1-phenylene))disulfurimidoyl difluoride (1.832 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μ L, $d = 1.018$ g/mL, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-22** (2.548 g, 99%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.97 – 7.88 (m, 4H), 7.70 – 7.62 (m, 4H), 7.36 – 7.29 (m, 4H), 7.24 – 7.18 (m, 4H), 4.00 (s, 2H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.21, 140.46, 139.63, 137.47 (d, $J = 3.2$ Hz), 131.17, 130.39, 124.67 (d, $J = 2.8$ Hz), 123.18, 41.12. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.00. $M_w^{ps} = 116$ kDa. PDI = 1.7. T_g (DSC) = 86.4 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 207.6 $^\circ\text{C}$.

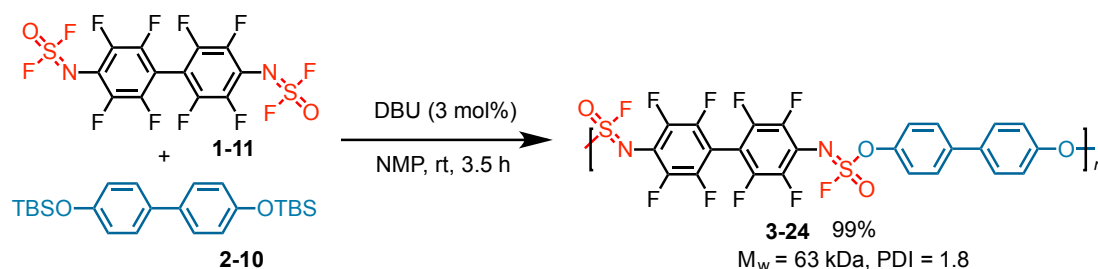
Synthesis of the polymer 3-23 (For AFM, TEM and SEM study)



(Methylenebis(4,1-phenylene))disulfurimidoyl difluoride (0.13 mmol) and bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylmethane (0.13 mmol) were combined in a 10 mL oven-dried round bottom glass equipped with a Teflon-coated magnetic stir bar. The glass was capped with a Teflon-coated rubber septum, purged with argon. Dry NMP (1.0 mL) was added and the vial was placed into a pre-heated 80 $^\circ\text{C}$ oil bath. Base catalyst 1,8-diazabicyclo(5.4.0)undec-7-ene (20 mol%, 4 μ L) was added via a micro-syringe under stirring. The reaction was run for 1 h. During the course of the reaction, the mixture turned highly viscous and yellow-brown. 0.5 mL NMP was added at the end of the reaction to dissolve the crude polymer. The warm NMP solution was slowly poured into 20 mL of cold methanol under vigorous stirring. The polymers precipitated as white fiber or powder once the NMP solution touched the methanol. Polymer **3-23** was collected via filtration and was dried at 70 $^\circ\text{C}$ for 3 h *in vacuo* (10.0 mbar) to afford **3-23** (0.088 g, 95%) as white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.33-7.01 (m, 26H), 3.96-3.94 (d, J = 8 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 148.4, 146.4, 145.4, 137.6, 132.6, 130.9, 130.8, 130.1, 129.8, 129.7, 127.9, 127.7, 126.6, 123.8, 123.76, 123.73, 123.70, 123.66, 123.57, 120.46, 64.3, 40.66. ^{19}F NMR (376 MHz, CDCl_3) δ 50.3. M_w^{ps} = 44 kDa. PDI = 2.2. T_g (DSC) = 84.9 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 236.1 $^\circ\text{C}$.

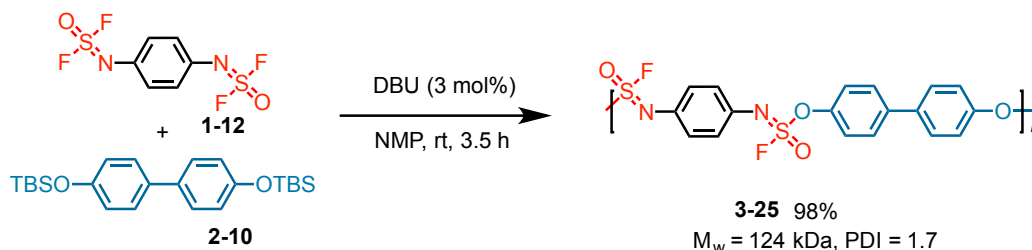
Synthesis of the polymer 3-24



Following the **general procedure II**: The reaction of (perfluoro-[1,1'-biphenyl]-4,4'-diyl)disulfurimidoyl difluoride (2.481 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , d = 1.018 g/mL, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-24** (3.200 g, 99%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.07 – 7.97 (m, 4H), 7.87 – 7.73 (m, 4H); ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.13, 145.48 (dd, J = 252.9, 13.5 Hz), 143.18 (dd, J = 250.2, 13.0 Hz), 140.97, 130.69, 123.25, 121.38 (t, J = 14.8 Hz), 103.60 (t, J = 14.4 Hz). ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 55.49, -139.00 (d, J = 25.1 Hz), -148.49 (d, J = 27.1 Hz). M_w^{ps} = 63 kDa. PDI = 1.8. T_g (DSC) = 108.8 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 249.5 $^\circ\text{C}$.

Synthesis of the polymer 3-25

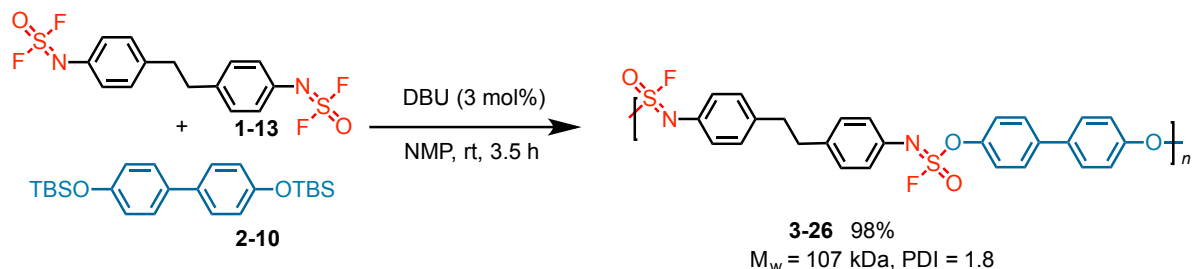


Following the **general procedure II**: The reaction of 1,4-phenylenedisulfurimidoyl difluoride (1.381 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , d = 1.018 g/mL, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-25** (2.077 g, 98%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.97 (d, J = 8.5 Hz, 4H), 7.70 (d, J = 8.4 Hz, 4H), 7.33 (s, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.21, 140.54, 136.56 (d, J = 3.0 Hz), 130.45, 125.88 (d, J = 2.7 Hz), 123.21. ^{19}F

NMR (376 MHz, DMF- d_7) δ 50.66. M_w^{ps} = 124 kDa. PDI = 1.7. T_g (DSC) = 83.9 °C. T_d (5% weight loss, TGA) = 212.7 °C.

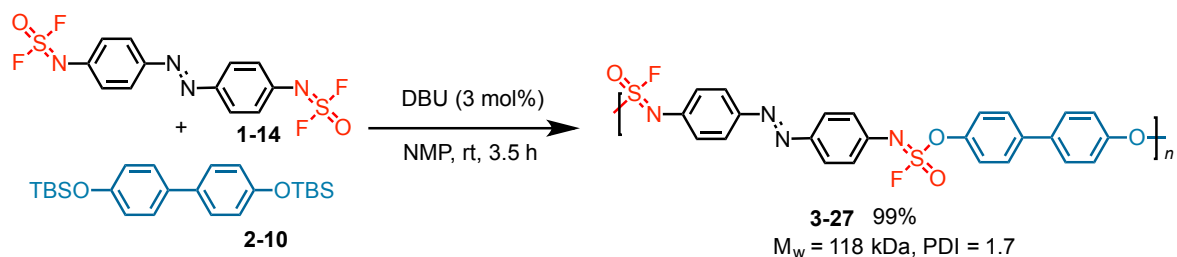
Synthesis of the polymer 3-26



Following the **general procedure II**: The reaction of (ethane-1,2-diylbis(4,1-phenylene))disulfur imidoyle difluoride (1.902 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μ L, d = 1.018 g/mL, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-26** (2.590 g, 98%) as white solid.

^1H NMR (600 MHz, DMF- d_7) δ 7.94 (d, J = 8.9 Hz, 4H), 7.66 (d, J = 8.7 Hz, 4H), 7.32 (d, J = 8.4 Hz, 4H), 7.18 (d, J = 8.2 Hz, 4H), 2.93 (s, 4H). ^{13}C NMR (151 MHz, DMF- d_7) δ 151.20, 140.45, 139.93, 137.25 (d, J = 3.2 Hz), 130.86, 130.39, 124.44 (d, J = 2.6 Hz), 123.18, 37.82. ^{19}F NMR (376 MHz, DMF- d_7) δ 51.03. M_w^{ps} = 107 kDa. PDI = 1.8. T_g (DSC) = 88.8 °C. T_d (5% weight loss, TGA) = 209.5 °C.

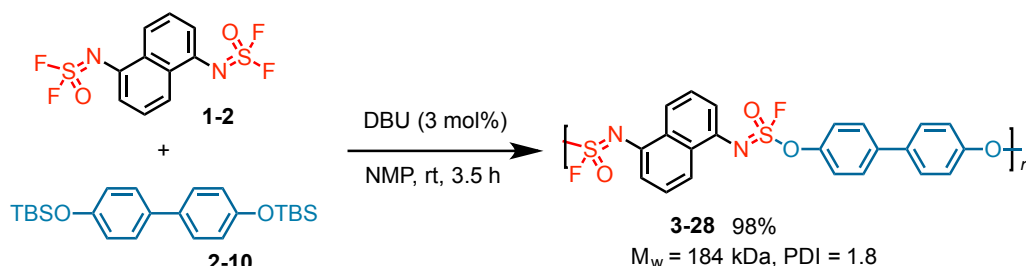
Synthesis of the polymer 3-27



Following the **general procedure II**: The reaction of (*E*)-4-((4-((difluoro(oxo)- λ^6 -sulfaneylidene)amino)phenyl)diazenyl)phenyl)sulfurimidoyl difluoride (1.902 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μ L, d = 1.018 g/mL, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-27** (2.605 g, 99%) as orange solid.

^1H NMR (600 MHz, DMF- d_7) δ 8.04 – 7.94 (m, 8H), 7.75 (d, J = 9.0 Hz, 4H), 7.50 (d, J = 8.7 Hz, 4H). ^{13}C NMR (151 MHz, DMF- d_7) δ 151.19, 150.67, 142.28, 140.64, 130.52, 125.56 (d, J = 2.8 Hz), 125.37, 123.26. ^{19}F NMR (376 MHz, DMF- d_7) δ 51.11. M_w^{ps} = 118 kDa. PDI = 1.7. T_g (DSC) = 118.9 °C. T_d (5% weight loss, TGA) = 210.8 °C.

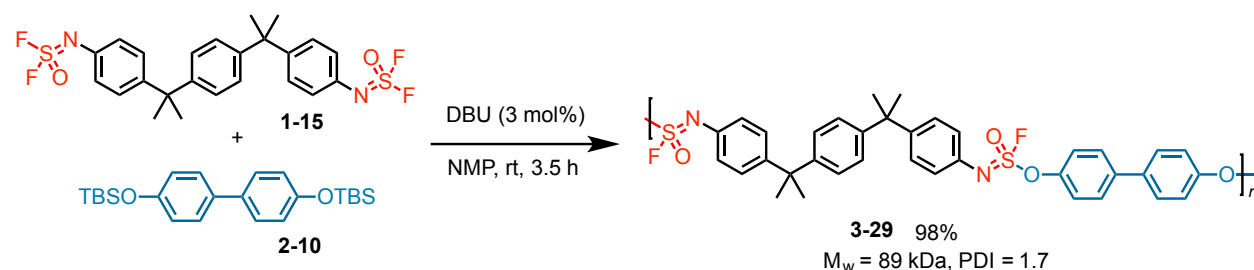
Synthesis of the polymer 3-28



Following the **general procedure II**: The reaction of naphthalene-1,5-diyldisulfurimidoyl difluoride (1.631 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-28** (2.326 g, 98%) as orange solid. This polymer is hard to dissolve in regular deuterated solvent.

$M_w^{ps} = 184 \text{ kDa}$. PDI = 1.8. T_d (5% weight loss, TGA) = 200.3 $^{\circ}\text{C}$.

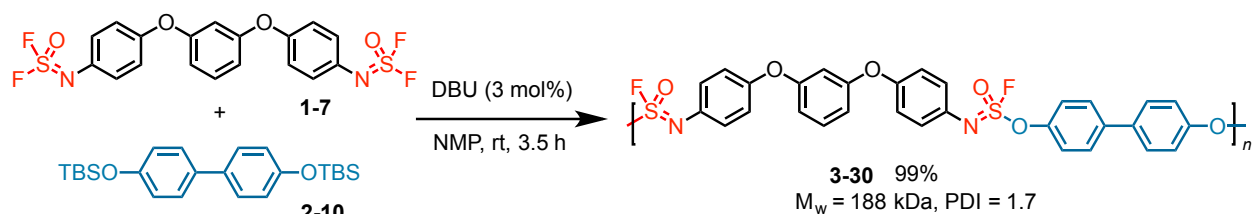
Synthesis of the polymer 3-29



Following the **general procedure II**: The reaction of ((1,4-phenylenebis(propane-2,2-diyl))bis(4,1-phenylene))disulfurimidoyl difluoride (2.563 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-29** (3.226 g, 98%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.91 (d, $J = 8.5 \text{ Hz}$, 4H), 7.65 (d, $J = 8.3 \text{ Hz}$, 4H), 7.29 (d, $J = 8.6 \text{ Hz}$, 4H), 7.23 – 7.11 (m, 8H), 1.64 (s, 13H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 151.20, 148.71, 140.45, 136.92 (d, $J = 3.3 \text{ Hz}$), 130.38, 129.05, 127.42, 124.10 (d, $J = 2.7 \text{ Hz}$), 123.19, 43.07, 31.26. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 51.45. $M_w^{ps} = 89 \text{ kDa}$. PDI = 1.7. T_g (DSC) = 112.9 $^{\circ}\text{C}$. T_d (5% weight loss, TGA) = 206.3 $^{\circ}\text{C}$.

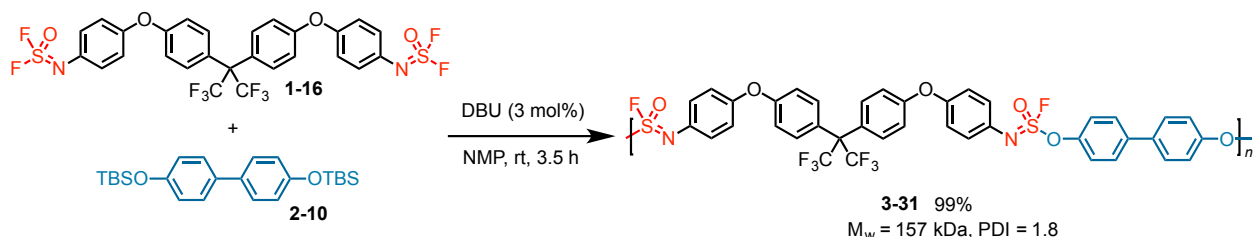
Synthesis of the polymer 3-30



Following the **general procedure II**: The reaction of ((1,3-phenylenebis(oxy))bis(4,1-phenylene))disulfurimidoyl difluoride (2.302 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-30** (3.001 g, 99%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.95 (d, $J = 8.8 \text{ Hz}$, 4H), 7.68 (d, $J = 8.7 \text{ Hz}$, 4H), 7.42 (t, $J = 8.2 \text{ Hz}$, 1H), 7.34 – 7.28 (m, 4H), 7.19 – 7.13 (m, 4H), 6.80 (dd, $J = 8.2, 2.4 \text{ Hz}$, 2H), 6.73 (t, $J = 2.4 \text{ Hz}$, 1H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 159.87, 154.89, 151.21, 140.51, 135.25 (d, $J = 3.2 \text{ Hz}$), 132.24, 130.43, 126.18 (d, $J = 2.8 \text{ Hz}$), 123.21, 121.50, 114.16, 109.77. ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 50.62. $M_w^{ps} = 188 \text{ kDa}$. PDI = 1.7. T_g (DSC) = 75.8 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 202.1 $^\circ\text{C}$.

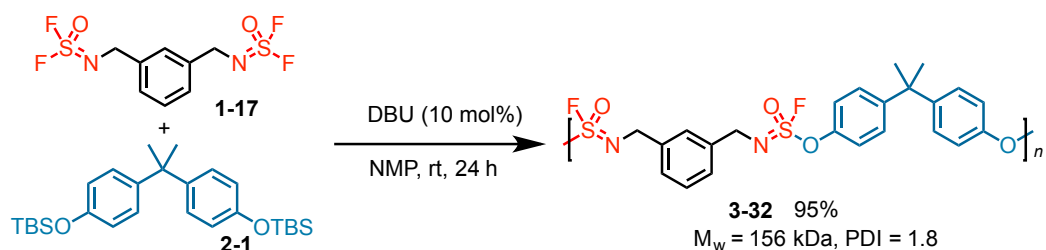
Synthesis of the polymer 3-31



Following the **general procedure II**: The reaction of (((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))disulfurimidoyl difluoride (3.433 g, 5.0 mmol), 4,4'-bis((*tert*-butyldimethylsilyl)oxy)-1,1'-biphenyl (2.074 g, 5.0 mmol) and DBU (23 μL , $d = 1.018 \text{ g/mL}$, 23.4 mg) in 10 mL of anhydrous NMP afforded **3-31** (4.224 g, 99%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.97 (d, $J = 8.7 \text{ Hz}$, 4H), 7.70 (d, $J = 8.4 \text{ Hz}$, 4H), 7.46 (d, $J = 8.5 \text{ Hz}$, 4H), 7.35 (d, $J = 8.8 \text{ Hz}$, 4H), 7.21 (d, $J = 8.8 \text{ Hz}$, 4H), 7.17 (d, $J = 9.0 \text{ Hz}$, 4H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 159.48, 154.14, 151.22, 140.53, 135.76 (d, $J = 3.1 \text{ Hz}$), 132.95, 130.44, 128.21, 126.33 (d, $J = 2.8 \text{ Hz}$), 123.23, 122.15, 118.80, 64.72 (q, $J = 25.1 \text{ Hz}$). ^{19}F NMR (376 MHz, $\text{DMF-}d_7$) δ 50.62, -63.20. $M_w^{ps} = 157 \text{ kDa}$. PDI = 1.8. T_g (DSC) = 117.6 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 205.6 $^\circ\text{C}$.

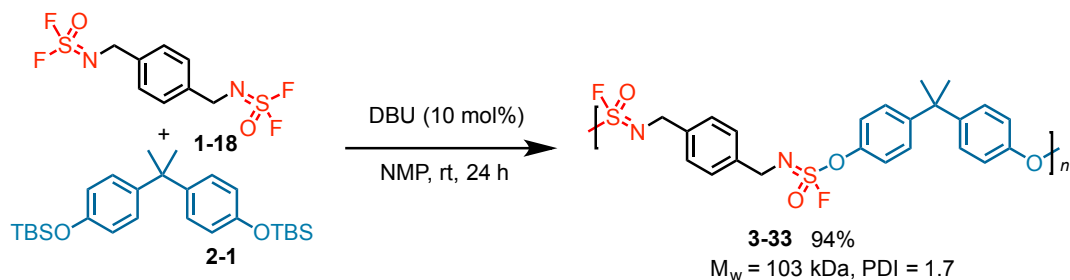
Synthesis of the polymer 3-32



Following the **general procedure II**: The reaction of (1,3-phenylenebis(methylene))disulfurimidoyl difluoride (1.521 g, 5.0 mmol), ((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (2.284 g, 5.0 mmol) and DBU (69 μL , $d = 1.018 \text{ g/mL}$, 76.5 mg) in 5 mL of anhydrous NMP afforded **3-32** (2.340 g, 95%) as white solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.57 – 7.03 (m, 12H), 4.54 (d, $J = 4.2 \text{ Hz}$, 4H), 1.60 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 149.74, 147.70, 138.18, 138.16, 128.51, 126.17, 125.96, 120.92, 48.33, 42.33, 30.13. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ 49.73. $M_w^{ps} = 156 \text{ kDa}$. T_g (DSC) = 45.9 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 190.5 $^\circ\text{C}$.

Synthesis of the polymer 3-33

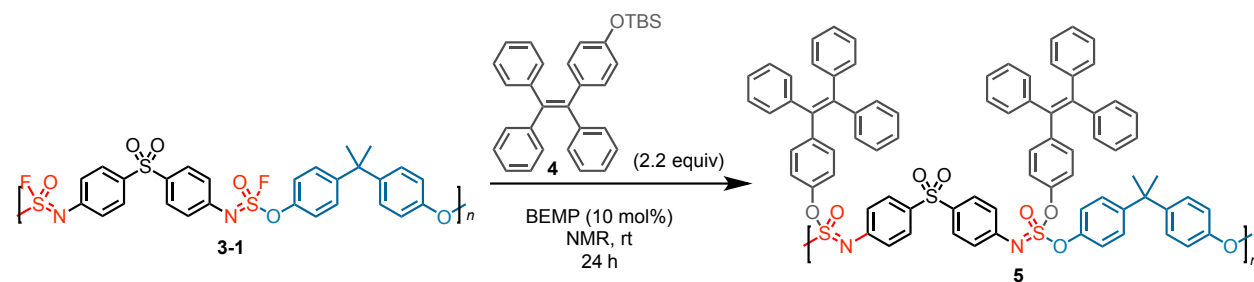


Following the **general procedure II**: The reaction of (1,4-phenylenebis(methylene))disulfurimidoyl difluoride (1.521 g, 5.0 mmol), ((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(*tert*-butyldimethylsilane) (2.284 g, 5.0 mmol) and DBU (69 μL , $d = 1.018 \text{ g/mL}$, 76.5 mg) in 5 mL of anhydrous NMP afforded **3-33** (2.315 g, 94%) as white solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.42 – 7.20 (m, 12H), 4.52 (d, $J = 4.2 \text{ Hz}$, 4H), 1.62 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 149.77, 147.72, 137.05, 128.53, 127.29, 120.94, 48.17, 42.35, 30.15. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ 49.82. $M_w^{ps} = 103 \text{ kDa}$. T_g (DSC) = 54.9 $^\circ\text{C}$. T_d (5% weight loss, TGA) = 232.8 $^\circ\text{C}$.

5. Post-polymerization modification of the polymers

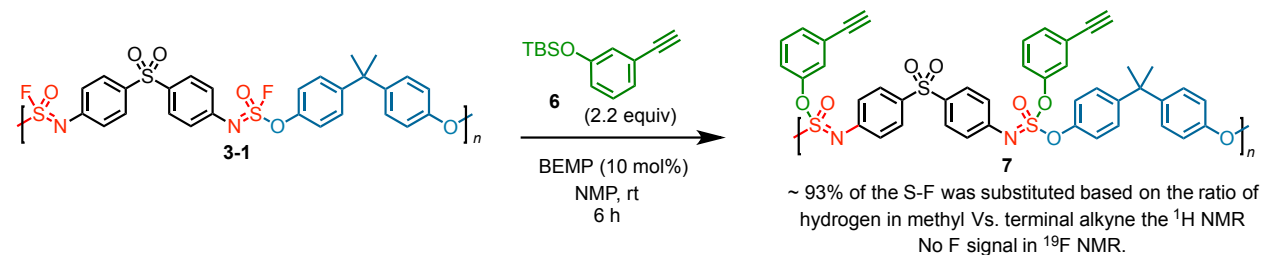
Synthesis of the polymer 5



To a vial (50 mL) with a magnetic stir bar was added the polymer **3-1** (604 mg, 1 mmol), ArOTBS **4** (1.26 g, 2.7 mmol) and 10 mL of anhydrous NMP. The flask was sealed with a Suba-Seal® Septa, vacuumized with a needle linked with a pump until there were no bubbles formed in the solution (5-10 min). Then BEMP (0.1 mL, 1 M) was added into the vial via a needle. After stirring at room temperature for 24 h, the resulting solution was poured into 150 mL of hexanes slowly with stirring. The polymer was filtrated. The white solid was re-dissolved in 15 mL of CH₂Cl₂, and slowly poured into 200 mL of hexanes then filtrated. The white solid was immersed in 200 mL MeOH for 7 h then further purified by ultrasonic cleaning for 10 min. After drying in the vacuum, 1.277 g of polymer **5** (95%) was obtained as white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.3 Hz, 4H), 7.25 – 6.73 (m, 50H), 1.63 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 149.51, 148.30, 148.14, 145.90, 143.46, 143.14, 143.09, 142.95, 142.12, 139.20, 136.21, 132.77, 131.20, 131.16, 131.14, 128.86, 128.27, 127.82, 127.68, 126.74, 126.72, 126.69, 123.78, 121.22, 120.86, 42.72, 30.78. IR (KBr, cm⁻¹) 3054, 2970, 1623, 1616, 1589, 1493, 1457, 1444, 1354, 1279, 1149, 1108, 1074, 1016.

Synthesis of the polymer 7

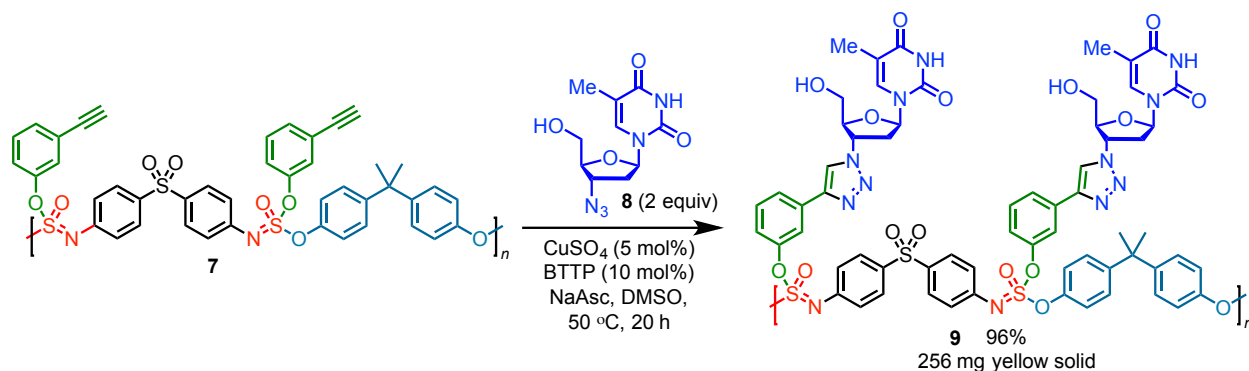


To a vial (50 mL) with a magnetic stir bar was added the polymer **3-1** (604 mg, 1 mmol), ArOTBS **6** (511 mg, 2.2 mmol) and 10 mL of anhydrous NMP. The flask was sealed with a Suba-Seal® Septa, vacuumized with a needle linked with a pump until there were no bubbles formed in the solution (5-10 min). Then BEMP (0.1 mL, 1 M) was added into the vial via a needle. After stirring at room temperature for 9 h, the resulting solution was poured into 150 mL of MeOH slowly with stirring. The polymer was

filtrated. The white solid was washed with MeOH three times (3×10 mL) and dried in the vacuum oven ($60\text{ }^{\circ}\text{C}$) for 24 h to give 742 mg of polymer **7** (93%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 8.19 – 8.13 (m, 4H), 7.79 – 7.68 (m, 8H), 7.63 – 7.51 (m, 12H), 4.49 (s, 2H), 1.85 (s, 6H); ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 149.81, 131.24, 130.62, 128.94, 128.45, 124.58, 123.96, 123.78, 122.27, 121.06, 81.50, 81.37, 42.38, 29.82.

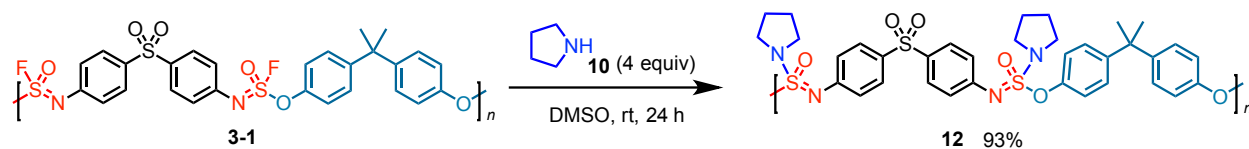
Synthesis of the polymer **9**



To a vial (20 mL) with magnetic stir was added the polymer **7** (160 mg), AZT **8** (107 mg, 0.4 mmol) and 4 mL of DMSO. The mixture was stirred at room temperature until the solid was dissolved. To a 1 mL microcentrifuge tube was added CuSO_4 (0.01 mmol, 0.1 mL, 0.1 mol/L in H_2O), BTTP (9.0 mg, 0.02 mmol) and DMSO (0.1 mL). The mixture was shaken until all the BTTP was dissolved and then 25 mg of sodium ascorbate was added to this blue solution and the color was changed to light yellow immediately. This mixture was transferred to the 20 mL vial and the mixture was heated to $50\text{ }^{\circ}\text{C}$ (oil bath) for 20 h. The resulting solution was poured into 100 mL of MeOH slowly with stirring. The polymer was filtrated. The white solid was washed with MeOH three times (3×3 mL) and dried in the vacuum oven ($60\text{ }^{\circ}\text{C}$) for 24 h to give 256 mg of polymer **9** (96%) as gray solid.

^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.35 (s, 2H), 8.87 (s, 2H), 7.97 – 7.74 (m, 10H), 7.54 (t, $J = 7.9$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 14H), 6.44 (t, $J = 6.6$ Hz, 2H), 5.54 – 5.10 (m, 4H), 4.27 (q, $J = 4.1$ Hz, 2H), 3.70 – 3.65 (m, 4H), 2.80 – 2.70 (m, 4H), 1.80 (s, 6H), 1.57 (s, 6H); ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 163.72, 150.43, 150.19, 149.57, 147.50, 145.29, 145.01, 136.21, 135.95, 132.85, 131.08, 129.00, 128.51, 124.55, 123.80, 121.94, 121.10, 120.74, 117.78, 109.65, 84.40, 83.90, 60.71, 59.51, 42.33, 40.06, 37.14, 30.16, 12.26.

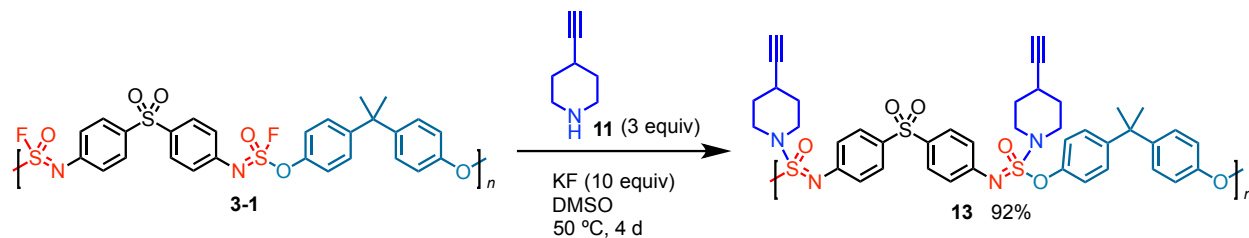
Synthesis of the polymer 12



Polymer **3-1** (604 mg, 1 mmol repeat unit) and a pyrrolidine **10** (0.33 mL, $d = 0.866$ g/mL, 285 mg) were dissolved in 5 mL of DMSO and 3 mL of DMF. The reaction was stirred at room temperature for 24 h until the complete substitution of all fluorides in the starting polymer (checked with ^{19}F NMR). The resulting solution was poured into 100 mL of MeOH slowly with stirring. The solution was stirred in MeOH for 20 min and filtrated. The white solid was purified using ultrasonic cleaning by immersing in 50 mL MeOH for 10 min (3 times) and then dried in the vacuum oven (60 °C) for 24 h to give the polymer **12** (660 mg, 93%) as white solid.

^1H NMR (600 MHz, $\text{DMF-}d_7$) δ 7.91 – 7.81 (m, 4H), 7.30 (s, 8H), 7.27 – 7.19 (m, 4H), 3.49 – 3.36 (m, 8H), 2.05 – 1.81 (m, 8H), 1.65 (s, 6H). ^{13}C NMR (151 MHz, $\text{DMF-}d_7$) δ 150.22, 149.81, 149.52, 136.16, 129.89, 129.22, 124.11, 123.04, 50.65, 43.52, 31.29, 26.55.

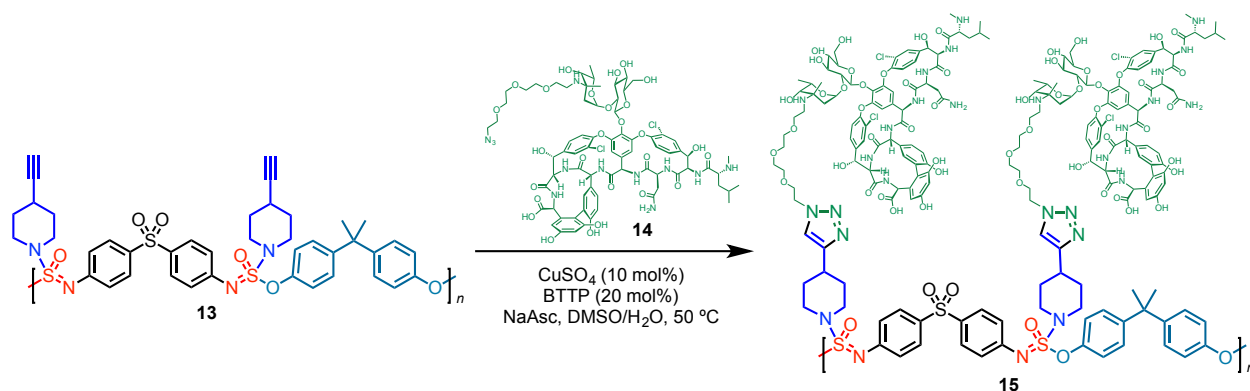
Synthesis of the polymer 13



Polymer **3-1** (303 mg, 0.5 mmol repeat unit), 4-ethynylpiperidine **11** (164 mg, 1.5 mmol) and KF (291 mg, 5 mmol) were dissolved in 5 mL of DMSO. The reaction was stirred at room temperature for 4 days until the complete substitution of all fluorides in the starting polymer (checked with ^1H NMR). The resulting solution was poured into 50 mL of MeOH/ H_2O (9:1) slowly with stirring. The solution was stirred for 20 min and filtrated. The white solid was purified using ultrasonic cleaning by immersing in 25 mL MeOH for 10 min (3 times) and then dried in the vacuum oven (60 °C) for 24 h to give the polymer **13** (362 mg, 92%) as white solid.

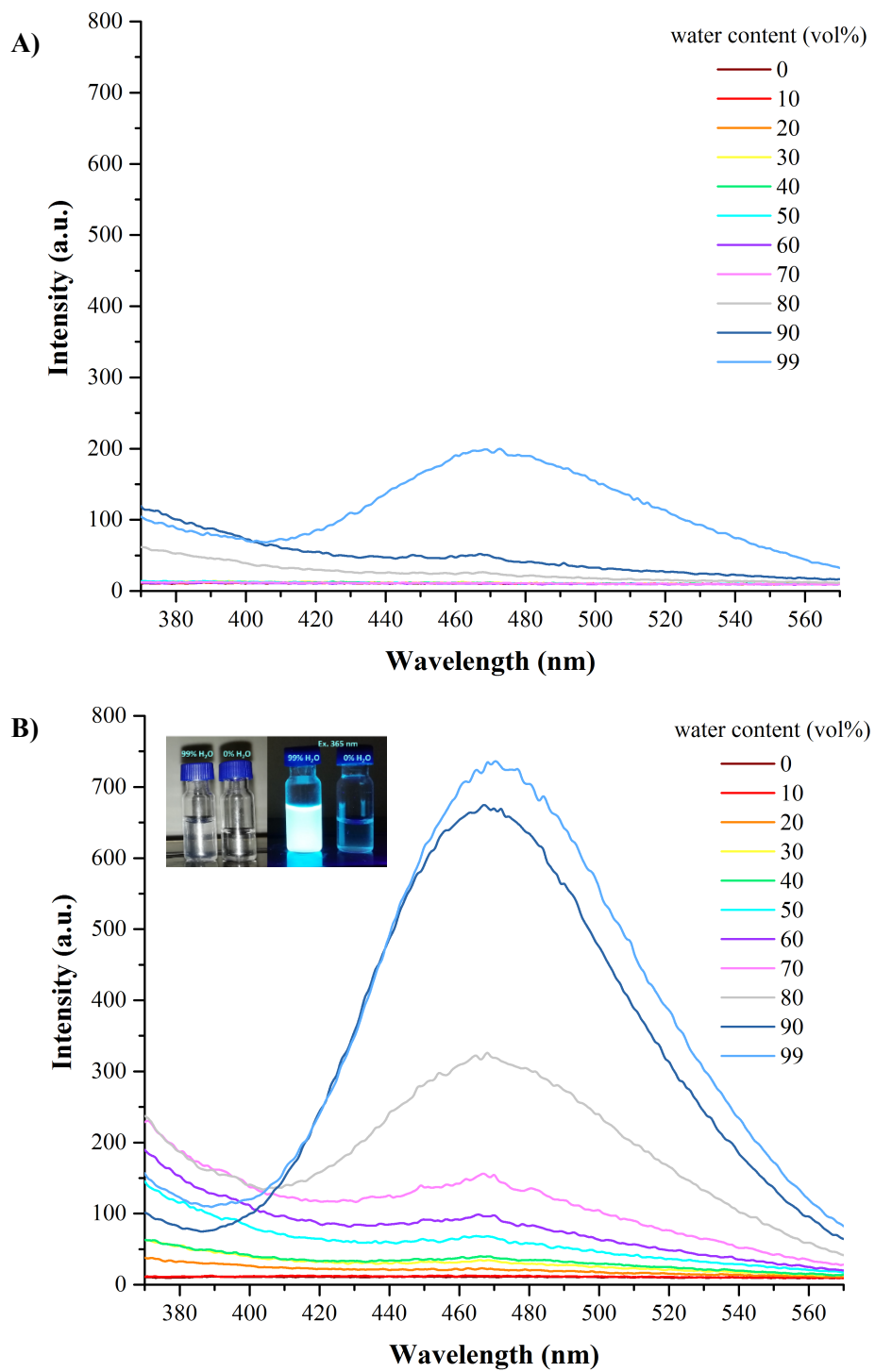
^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 4H), 7.20 – 7.12 (m, 8H), 3.73 – 3.60 (m, 4H), 3.46 – 3.34 (m, 4H), 2.72 – 2.56 (m, 2H), 2.14 (d, $J = 2.4$ Hz, 2H), 1.98 – 1.83 (m, 4H), 1.80 – 1.68 (m, 4H), 1.62 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.89, 148.15, 148.00, 134.96, 128.70, 128.01, 123.08, 121.50, 85.05, 70.66, 45.37, 45.30, 42.58, 30.79, 30.34, 25.65.

Synthesis of the vancomycin polymer **15**



To a vial (20 mL) with a magnetic stir bar was added the polymer **13** (39 mg, 0.05 mmol), Vancomycin-azide **14** (165 mg, 0.1 mmol) and 5 mL of DMSO and 0.5 mL of H_2O . The mixture was stirred at room temperature. To a 1 mL microcentrifuge tube was added CuSO_4 (0.01 mmol, 50 μL , 0.1 mol/L in H_2O), BTTP (5 mg, 0.01 mmol) and DMSO (0.1 mL). The mixture was shaken until all the BTTP was dissolved and then 13 mg of sodium ascorbate was added to this blue solution. The color changed to light yellow immediately. This mixture was transferred to the 20 mL vial and the mixture was heated to 50 °C (oil bath) for 20 h. The resulting solution was poured into 20 mL of MeOH slowly with stirring. The polymer was filtrated. The white solid was washed with MeOH three times (3×3 mL) and then dried in the vacuum oven (60 °C) for 24 h to give 100 mg of polymer **15** as gray solid.

6. AIE effect of the TPE-modified polymer



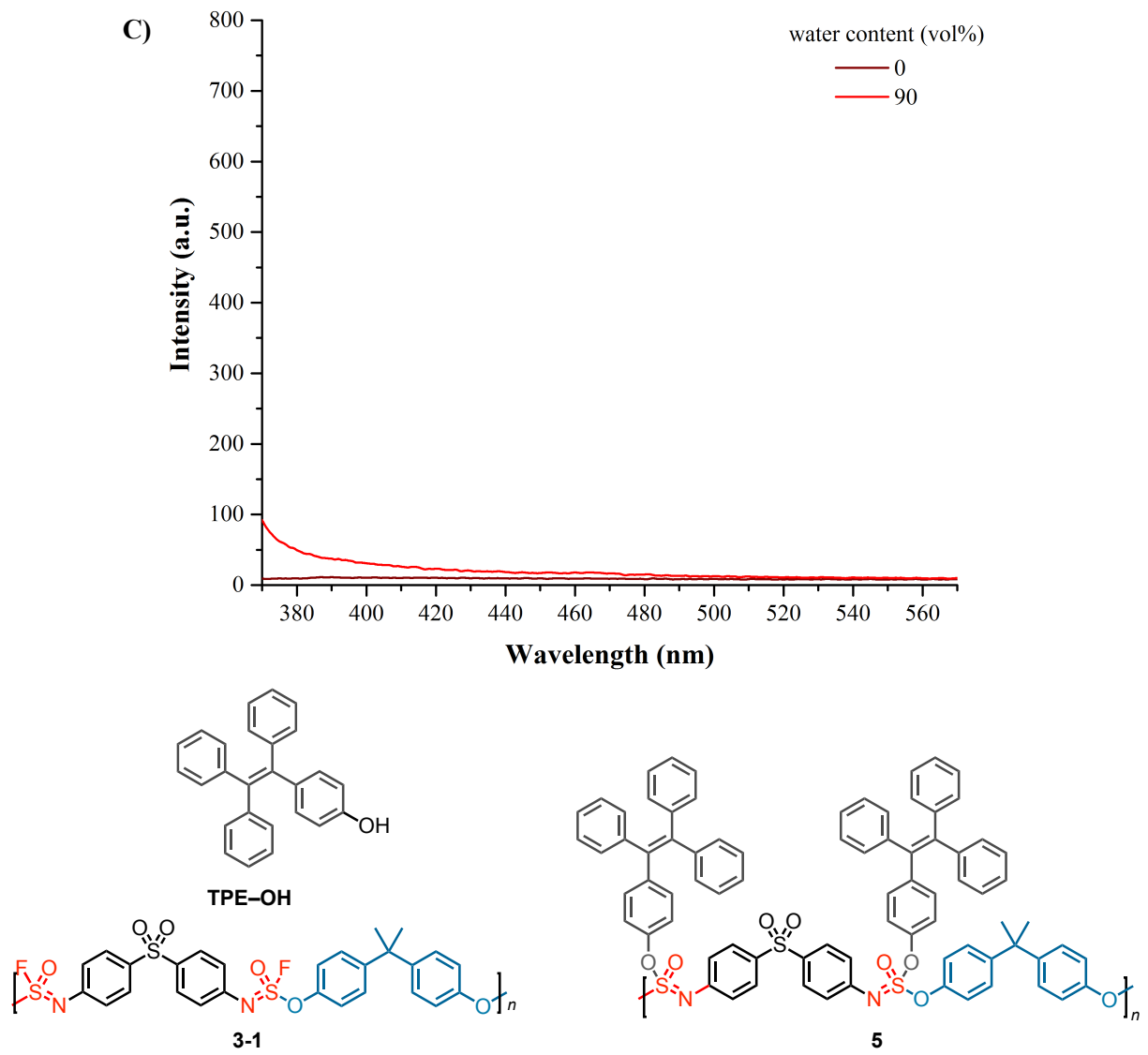


Figure S4. Fluorescence spectra of A) TPE-OH (10 μ M). B) **5** (5 μ M of the repeat unit) in THF/H₂O (v/v = 100:0 ~ 1:99). Insert: photographs showing visible light fluorescence upon ultraviolet illumination. and C) **3-1** (5 μ M of the repeated unit) in THF/H₂O excited at 350 nm. (Slit width: ex 3 nm, em 5 nm).

7. Fluorescence spectra of TPE-OH, **3-1** and **5**

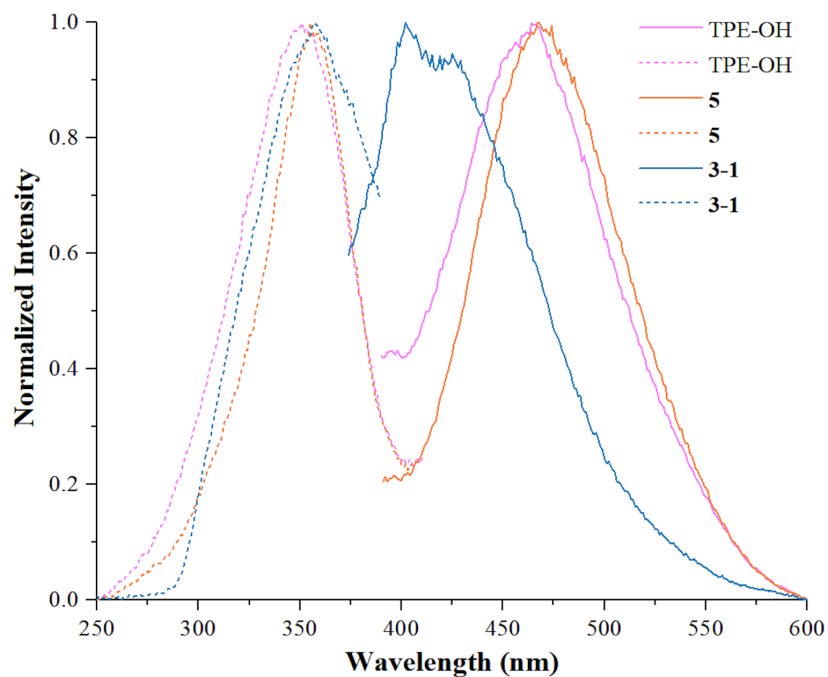


Figure S5. Fluorescence spectra of TPE-OH, **3-1** and **5** (short dash for excitation and line for emission). Measurement: TPE-OH (10 μ M) in THF/H₂O (V:V= 1:99), **5** (5 μ M of the repeat unit) in THF/H₂O (V:V= 1:99), the excitation spectra were recorded with the emission wavelength set at 450 nm, and the emission spectra were recorded with the excitation wavelength set at 350 nm. **3-1** (5 mM) in THF, the excitation spectra were recorded with the emission wavelength set at 416 nm, and the emission spectra were recorded with the excitation wavelength set at 350 nm.

8. Structure study

Atomic force microscope (AFM): The topography of the plasma-activated CrN surfaces was studied with an Asylum MFP-3D atomic force microscope (AFM) in tapping mode. The imaging was performed in tapping mode in air using OMCL-AC240 silicon cantilevers (Olympus Corporation, Japan) with a stiffness of 1.54 N/m. Images were flattened with a third-order flattening procedure using the MFP3D software.

Scanning electron microscopy/Auger electron spectroscopy (SEM/AES): AES measurements were performed at room temperature with a scanning Auger electron spectroscopy (JEOL Ltd. JAMP-9500F field emission scanning Auger microprobe) system. Samples were prepared by spreading powder particles over a gold-coated surface. AES spectra were acquired with a primary beam of 2 keV. For Auger elemental analysis an 8 nm probe diameter was used. Elemental mapping was analyzed by AES. Elemental images were acquired with a primary beam of 2 keV. The take-off angle of the instrument was 0°. The colored images are elemental distribution maps over the area shown in the upper right image.

Transmission electron microscopy (TEM/SEM): Polymer solutions (0.2 mg/mL in THF): ultrathin carbon Grid (~4 nm thickness, Tedpella ultrathin carbon film on lacey carbon support film, 400 mesh, copper) was pre-treated by plasma cleaner for 10 s, then a drop of diluted sample in THF was deposited on the grid surface for a few seconds and the excess of solution was removed by fiber free paper. After that this grid was deepened in uranyl acetate solution then the excess of uranyl solution was removed by fiber free paper. Here in this study Uranyl acetate was used as a negative stain for imaging. TEM grid was mounted in a single tilt sample holder and then introduced in the microscope for imaging. Microscope: TEM analyses were performed using a Titan FEG-300KV. 4 K Ceta camera, and GMS software for data acquisition. *SEM (Scanning Electron Microscope):* Same TEM grid was mounted in SEM: field emission scanning electron microscopy (FE-SEM, Quanta FEG450, FEI) using a solid-state back scattering electron detector (VCD).

Molecular Mechanics Studies: Geometry optimization of the polymers was performed using molecular mechanics calculations using the Polymer Consistent Force Field (PCFF) as implemented in the Dassault

Systèmes BIOVIA, Materials Studio 6.0, San Diego molecular modeling package. To this aim, first the polymer structure was drawn in ChemDraw with 32 repeating units. This structure was transferred in Chem3D, optimized using the MMFF94 force field as implemented in that, and the resulting structure saved and converted to the *.mol format, which can be read by Materials Studio. This structure was then imported in Materials Studio and further optimized using the Forcite minimizer and the PCFF force field, with “high-convergence” criteria and the “smart optimizer” algorithm. No further restrictions were applied.

Quantum-chemical calculations: The quantum chemical calculations were run using the Gaussian 16 suite of programs with the functionals, basis sets and solvent models as implemented in there. For our calculations we used the xB97XD functional, the SMD solvation model and standard 6-311+G(d,p) basis sets. The keywords used to run these calculations and the obtained zero-point energy-corrected energies are given below in Hartree. This yields the reaction energies given in the most right column (in kcal/mol).

Table S1: Quantum-chemical calculations using the wB97xd functional in vacuo, and with the SMD solvation model to represent DMF or DMSO (first line represents the keywords used in Gaussian 16 to run the calculations):

#p opt wB97xd/6-311+g(d,p) pop=nboread freq=noraman					
	SuFEx molecule (Hartree)	TBDS (Hartree)	Product (Hartree)	F-TBDS (by-product) (Hartree)	ΔE (kcal mol ⁻¹)
~CH ₂ SO ₂ F	-727.574993	-833.802751	-934.473237	-626.919129	-9.18
~OSO ₂ F	-955.143103	-833.802751	-1162.045738	-626.919129	-11.93
~N=S(=O)F ₂	-959.260898	-833.802751	-1166.167749	-626.919129	-14.58

#p opt wB97xd/6-311+g(d,p) freq=noraman SCRF=(Solvent=n,n-DiMethylFormamide)					
	SuFEx molecule (Hartree)	TBDS (Hartree)	Product (Hartree)	F-TBDS (by-product) (Hartree)	ΔE (kcal mol ⁻¹)
~CH ₂ SO ₂ F	-727.664563	-834.100548	-934.659082	-627.122489	-10.33
~OSO ₂ F	-955.258936	-834.100548	-1162.25856	-627.122489	-13.53
~N=S(=O)F ₂	-959.373862	-834.100548	-1166.378053	-627.122489	-16.40

#p opt wB97xd/6-311+g(d,p) freq=noraman SCRF=(Solvent=DiMethylSulfoxide)					
	SuFEx molecule (Hartree)	TBDS (Hartree)	Product (Hartree)	F-TBDS (by-product) (Hartree)	ΔE (kcal mol ⁻¹)

$\sim\text{CH}_2\text{SO}_2\text{F}$	-727.664657	-834.100606	-934.659214	-627.122531	-10.34
$\sim\text{OSO}_2\text{F}$	-955.259008	-834.100606	-1162.258680	-627.122531	-13.55
$\sim\text{N}=\text{S}(=\text{O})\text{F}_2$	-959.374194	-834.100606	-1166.378151	-627.122531	-16.24

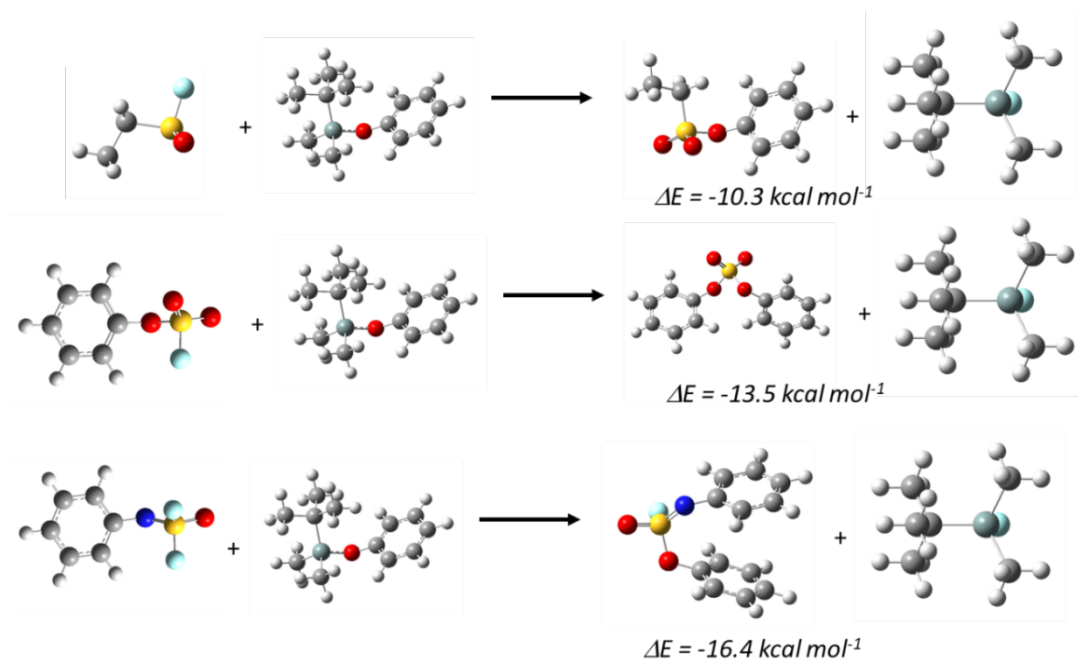


Figure S6. Quantum-chemical wB97XD/6-311+G(d,p) density functional calculations of selected SuFEx model reactions with an SMD continuum model to mimic DMF ($\epsilon = 37.2$) or DMSO ($\epsilon = 46.8$) as solvents.

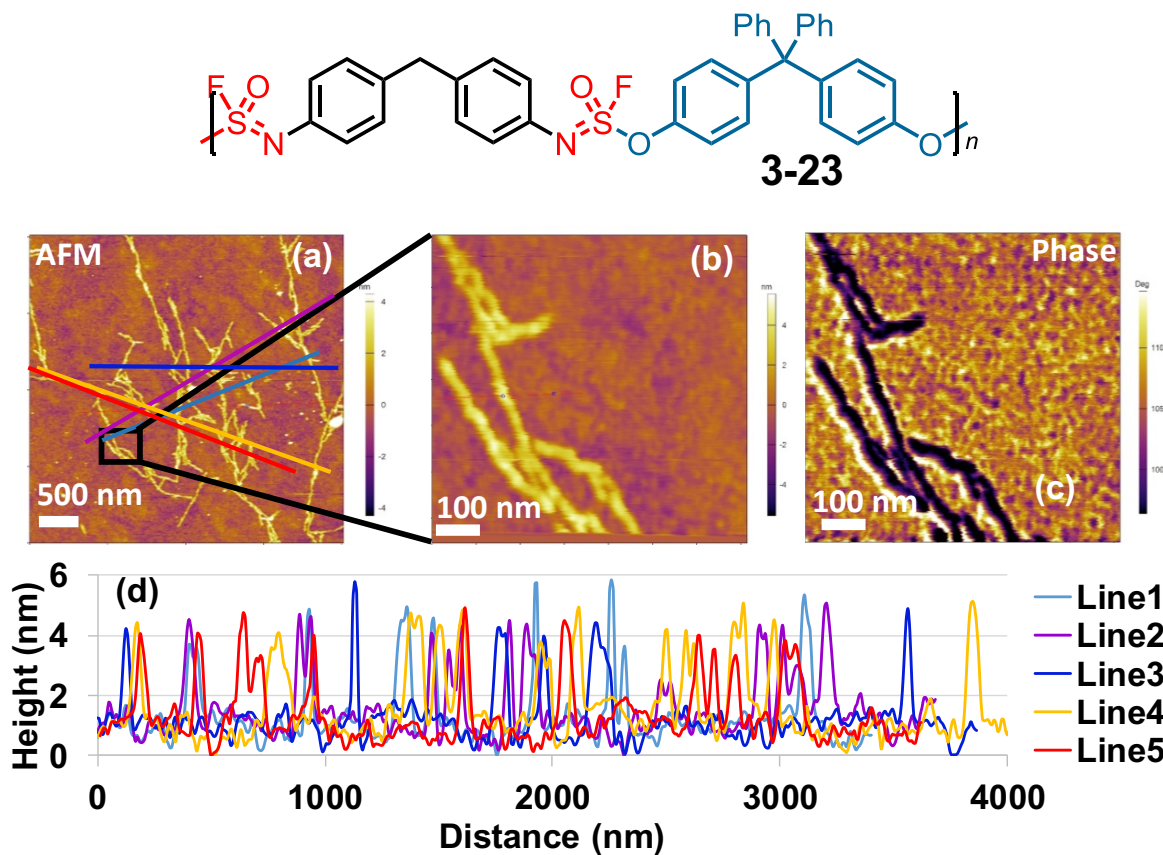


Figure S7: (a-d) Characteristic AFM height images of polymer **3-23** (concentration of 1 μM of repeated unit) as deposited on hexadecyne-modified Si(111).

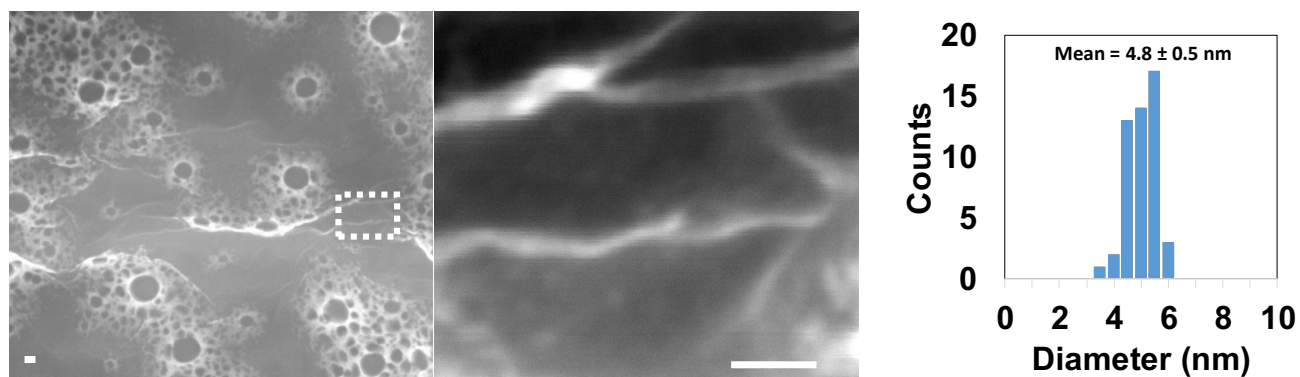


Figure S8: SEM image of polymer **3-23** as deposited onto a TEM grid.

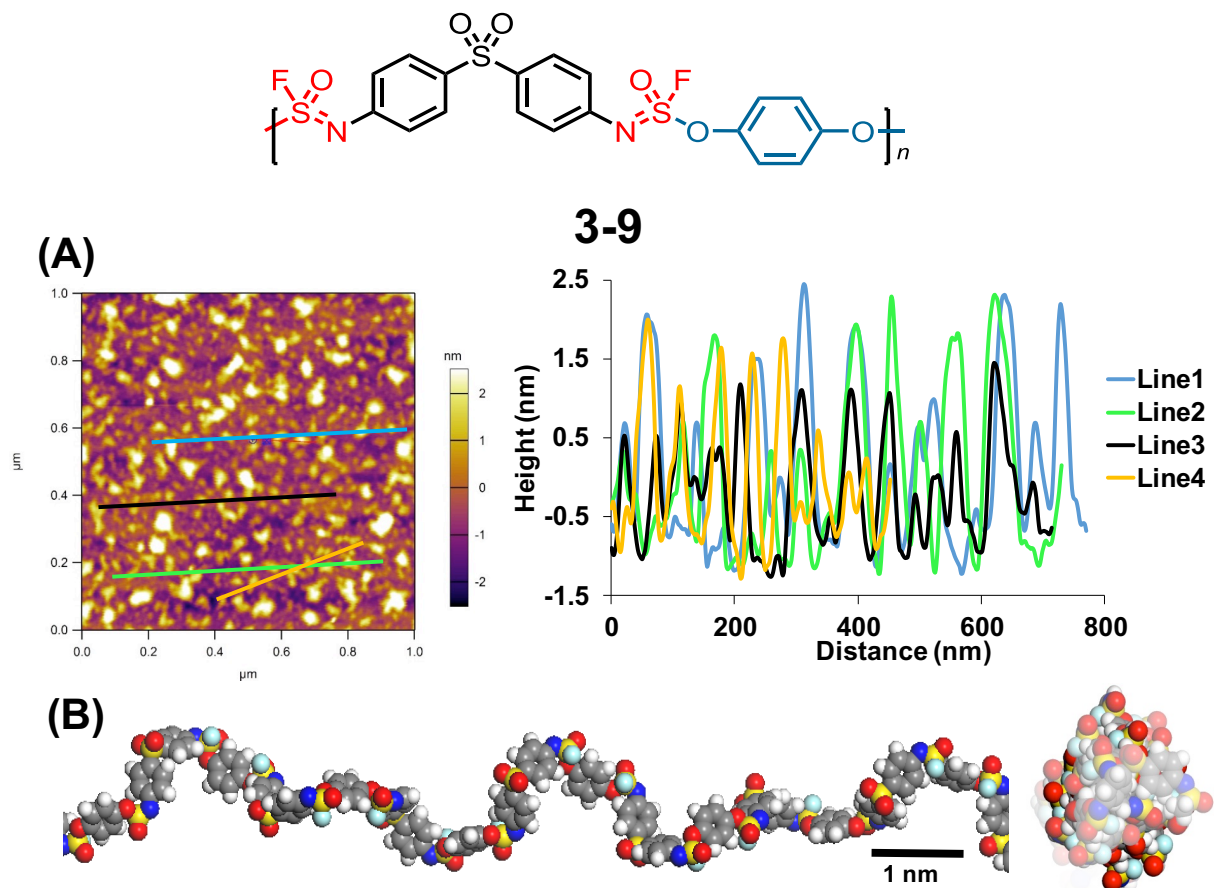


Figure S9: (A) AFM height image ($1 \times 1 \mu\text{m}^2$ and $0.5 \times 0.5 \mu\text{m}^2$) of polymer **3-9** (concentration of $1 \mu\text{M}$ of the repeated unit) as deposited on hexadecyne-modified Si(111) with the height profile along the line. (B) PCFF-optimized structure of **3-9** (side view and top view).

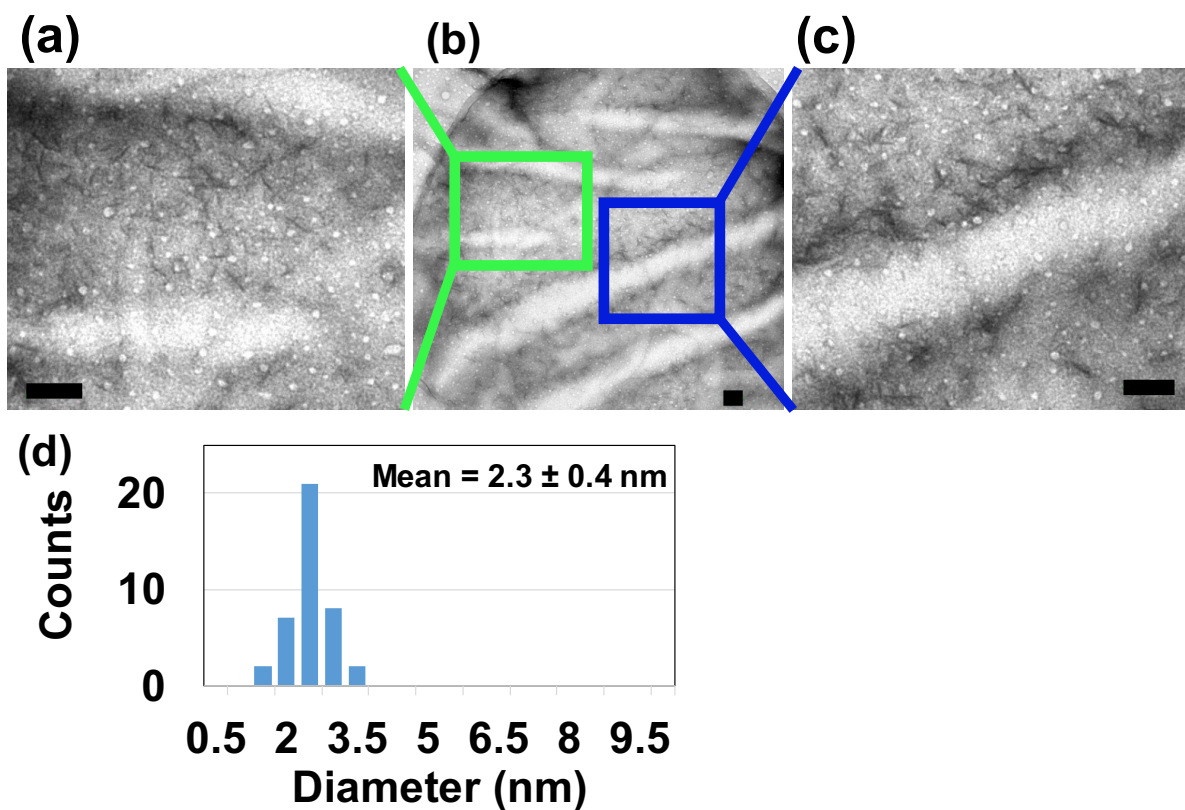


Figure S10: High-resolution TEM (a-c) images of polymer **3-9** in CHCl₃ [black wires in the TEM images] and (d) histogram generated for the width of polymer **3-9** wires (40 measurements). Resulting diameter 2.3 ± 0.4 nm. Scale bar: 50 nm in all figures.

Similar data were obtained for polymer **5**:

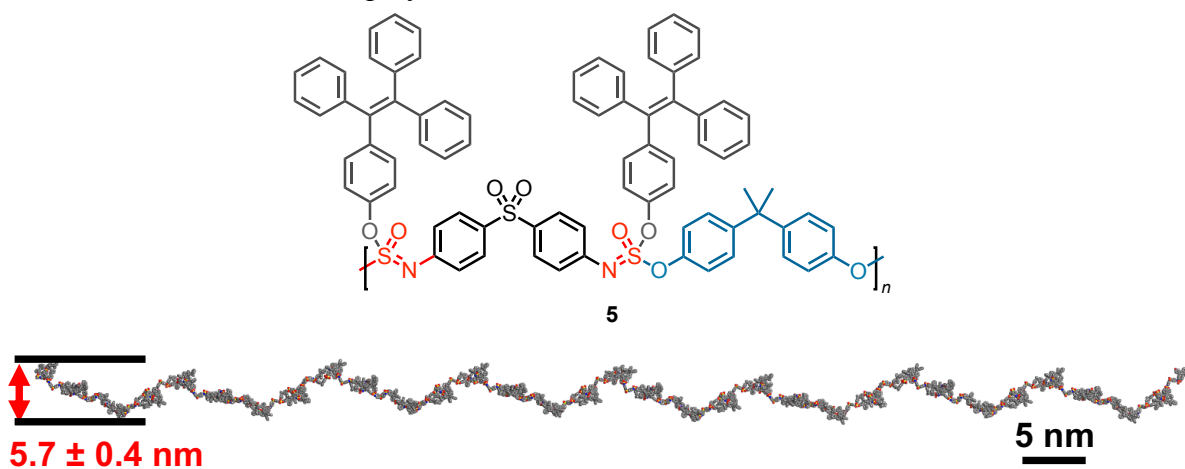


Figure S11: PCFF-optimized structure of **5** (side view and top view).

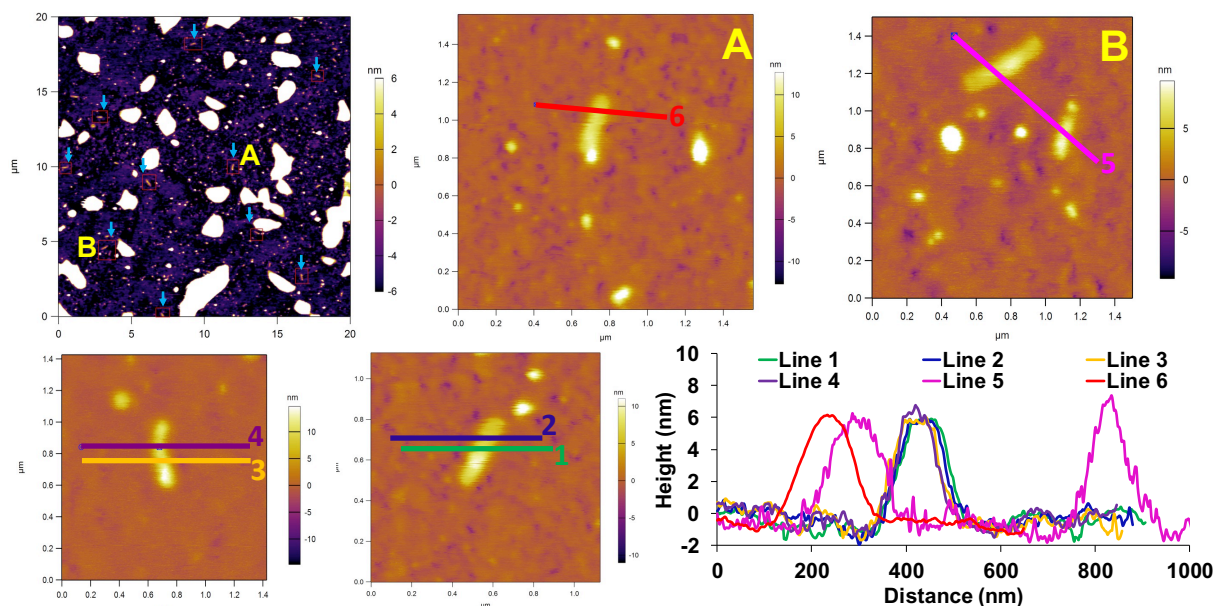


Figure S12: (Top left): AFM height image of polymer **5** as deposited (from a solution in THF, concentration of 1 μM of repeated unit) on hexadecyne-modified Si(111), with the areas A and B, zoomed-in images of which are presented *top middle* and *top right*. *Bottom left* and *bottom middle* are two more representative AFM topography images. The height profiles along the lines 1-6 shown in the zoomed-in AFM images are presented in the image *bottom right*, pointing to a height of the polymer wire of 6.9 ± 1.1 nm.

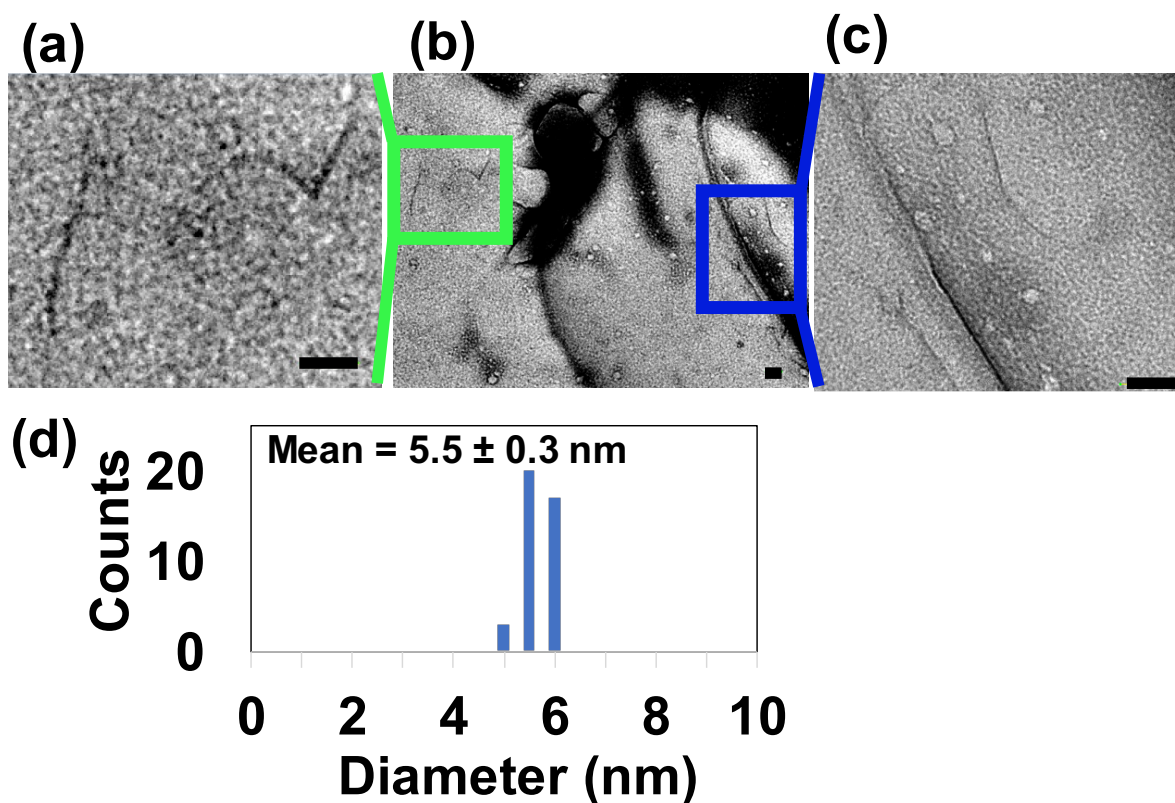


Figure S13: High-resolution TEM (a-c) images of polymer **5** in CHCl_3 [black wires in the TEM images] and (d) histogram generated for the width of polymer **5** wires (40 measurements). Resulting diameter 5.5 ± 0.3 nm. Scale bar: 50 nm in all figures.

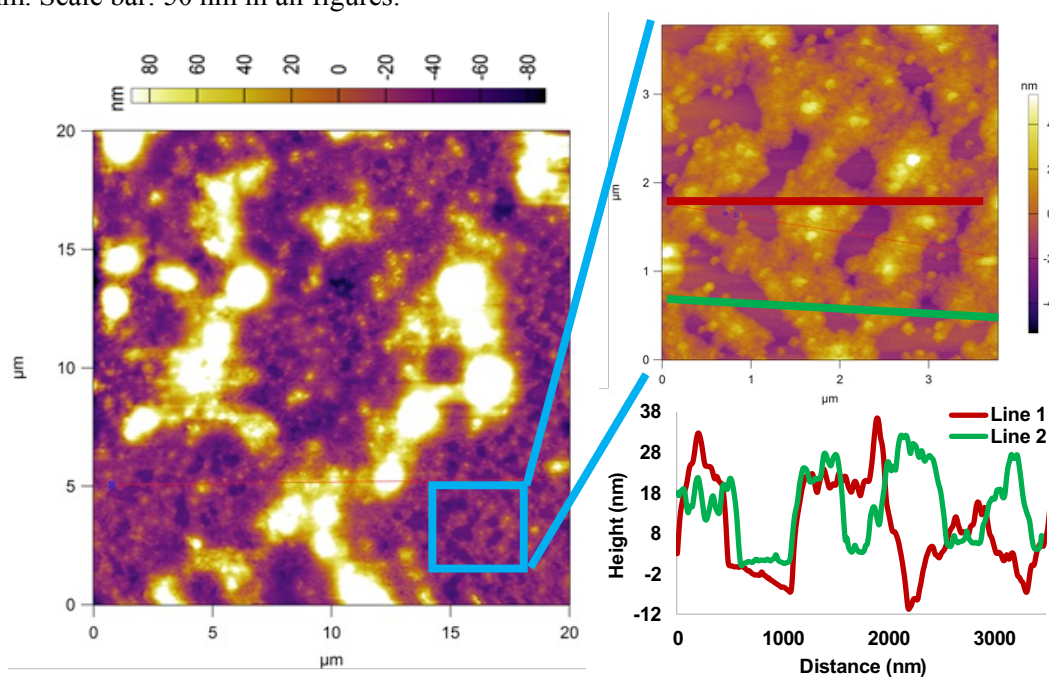


Figure S14: AFM height image of polymer **5** as deposited from a THF:H₂O mixture (1:99, concentration of 0.8 μM of the repeated unit) on hexadecyne-modified Si(111) with the height profile along the line.

Antibacterial Assays: The minimum inhibitory concentration (MIC) was determined using a broth microdilution method according to guidelines defined by the Clinical Laboratory Standards Institute.

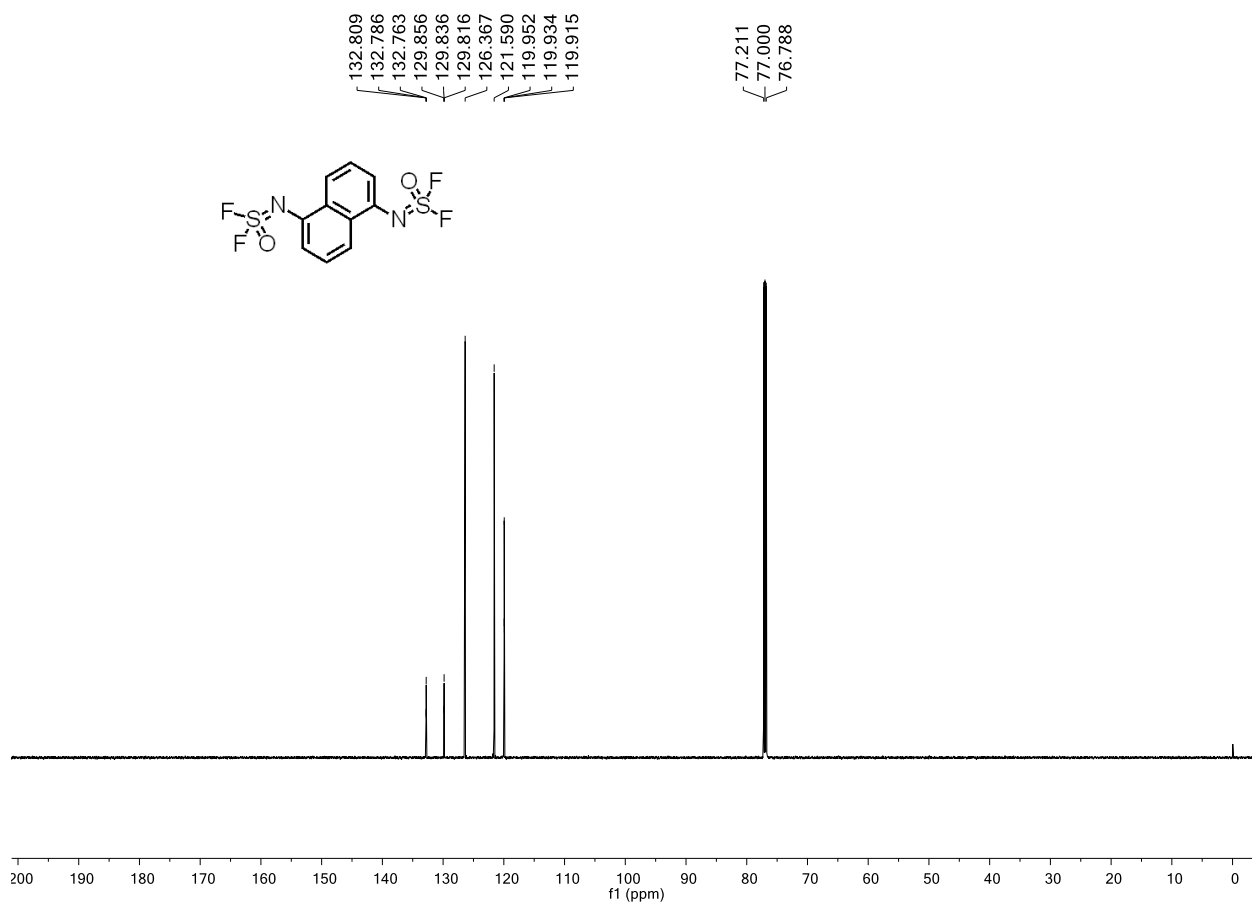
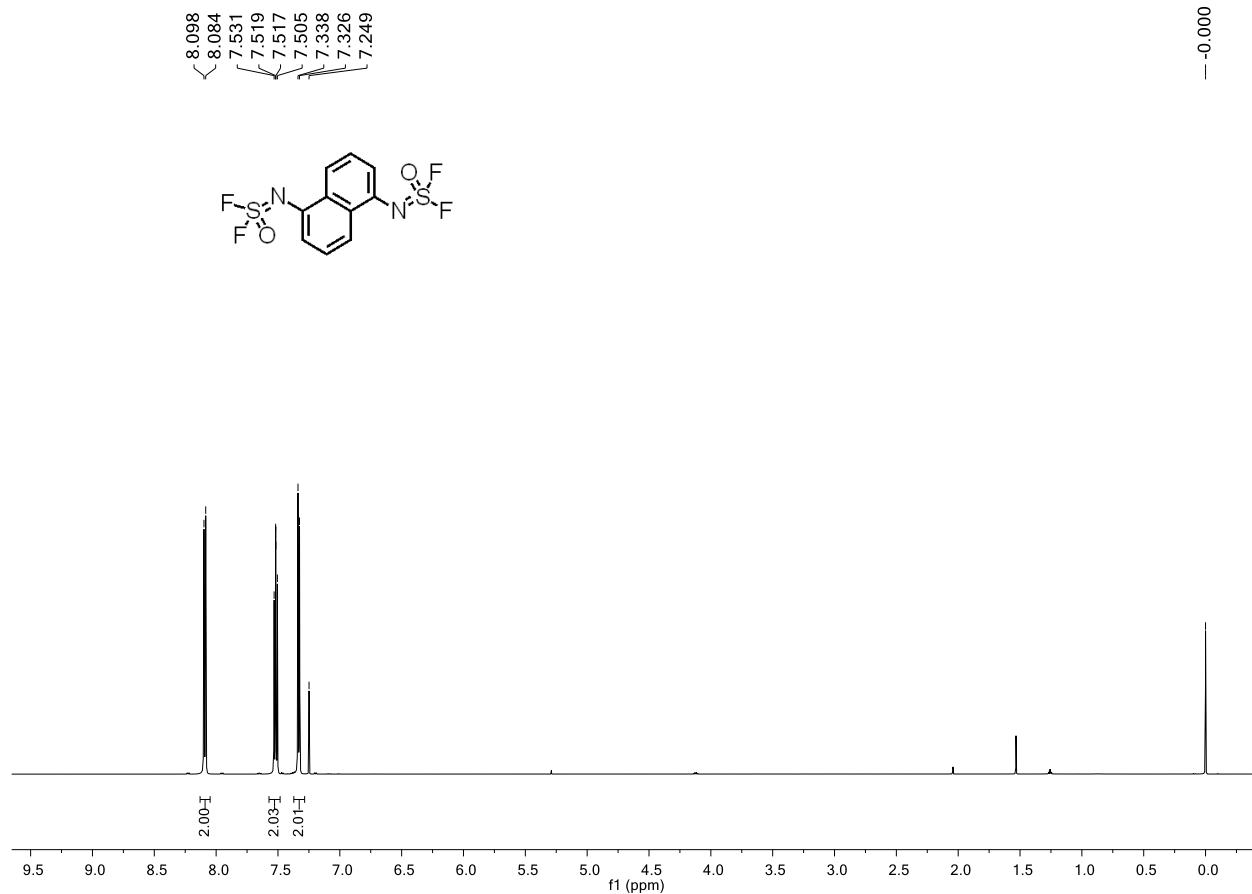
[**National Committee for Clinical Laboratory Standards.** 2003. *Methods for dilution antimicrobial susceptibility tests for bacteria that grow aerobically, 6th ed. Approved standard. NCCLS publication no. M7-A6.* National Committee for Clinical Laboratory Standards, Wayne, Pa.; **National Committee for Clinical Laboratory Standards.** 2004. *Standards for antimicrobial susceptibility testing, 13th informational supplement. NCCLS publication no. M100-S14.* National Committee for Clinical Laboratory Standards, Wayne, Pa.]. An inoculum of 1×10^5 colony forming units per mL was used and the testing conducted using tryptic soy broth in 96 well plates. Plates were incubated at 37° C for 20 hours and growth assessed by measuring the absorbance at 600 nm. The MIC value is defined as the lowest concentration of inhibitor where no bacterial growth is observed. Experiments were repeated with 3 biological replicates (Table S2).

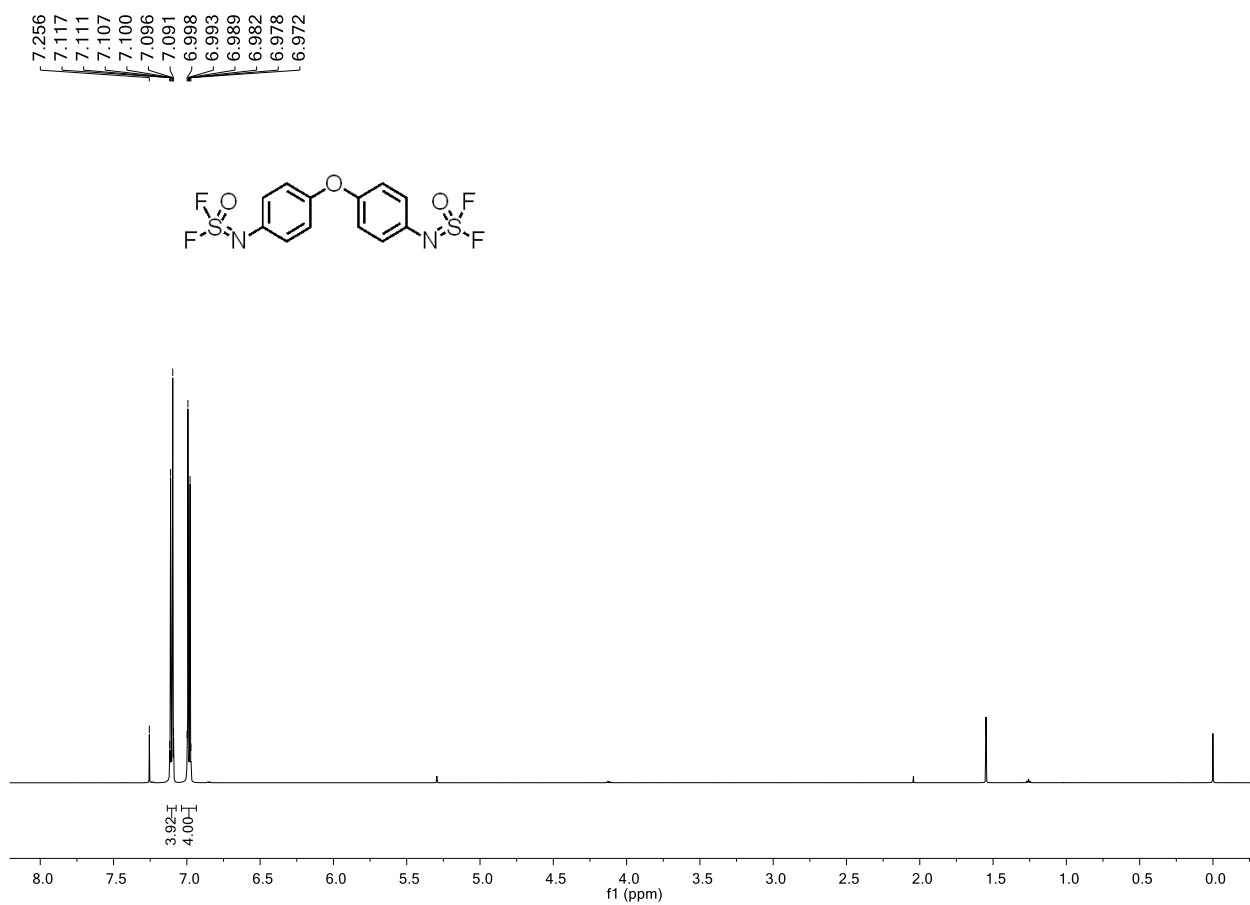
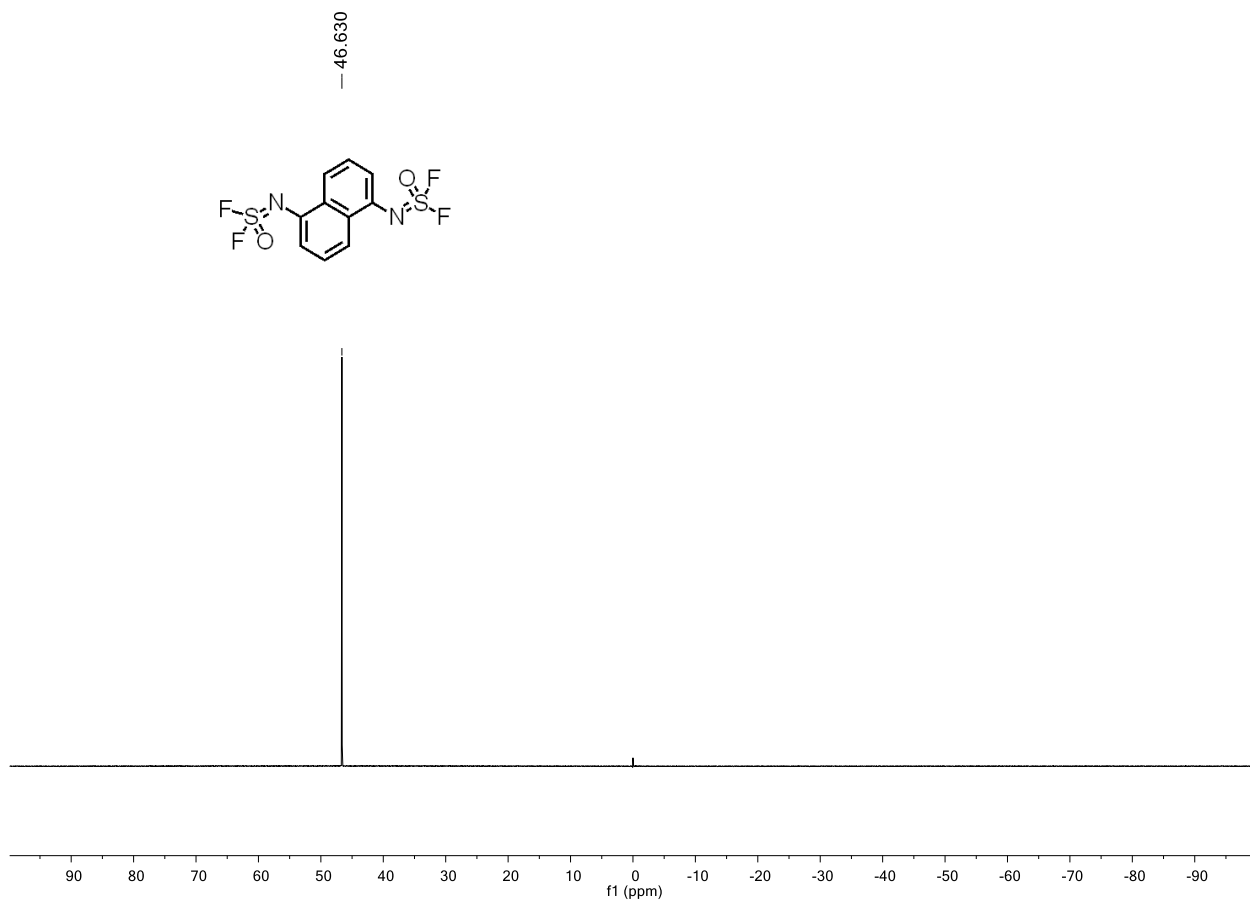
Table S2: Antibacterial assays performed in triplicate to yield minimum inhibitory concentration values for polymer **15** and vancomycin against methicillin-sensitive *Staphylococcus aureus* (MSSA) ATCC 9144, methicillin-resistant *S. aureus* (MRSA) ATCC BAA-1717, vancomycin-susceptible enterococcus (VSE) ATCC BAA-2127, and vancomycin-resistant enterococci (VRE).

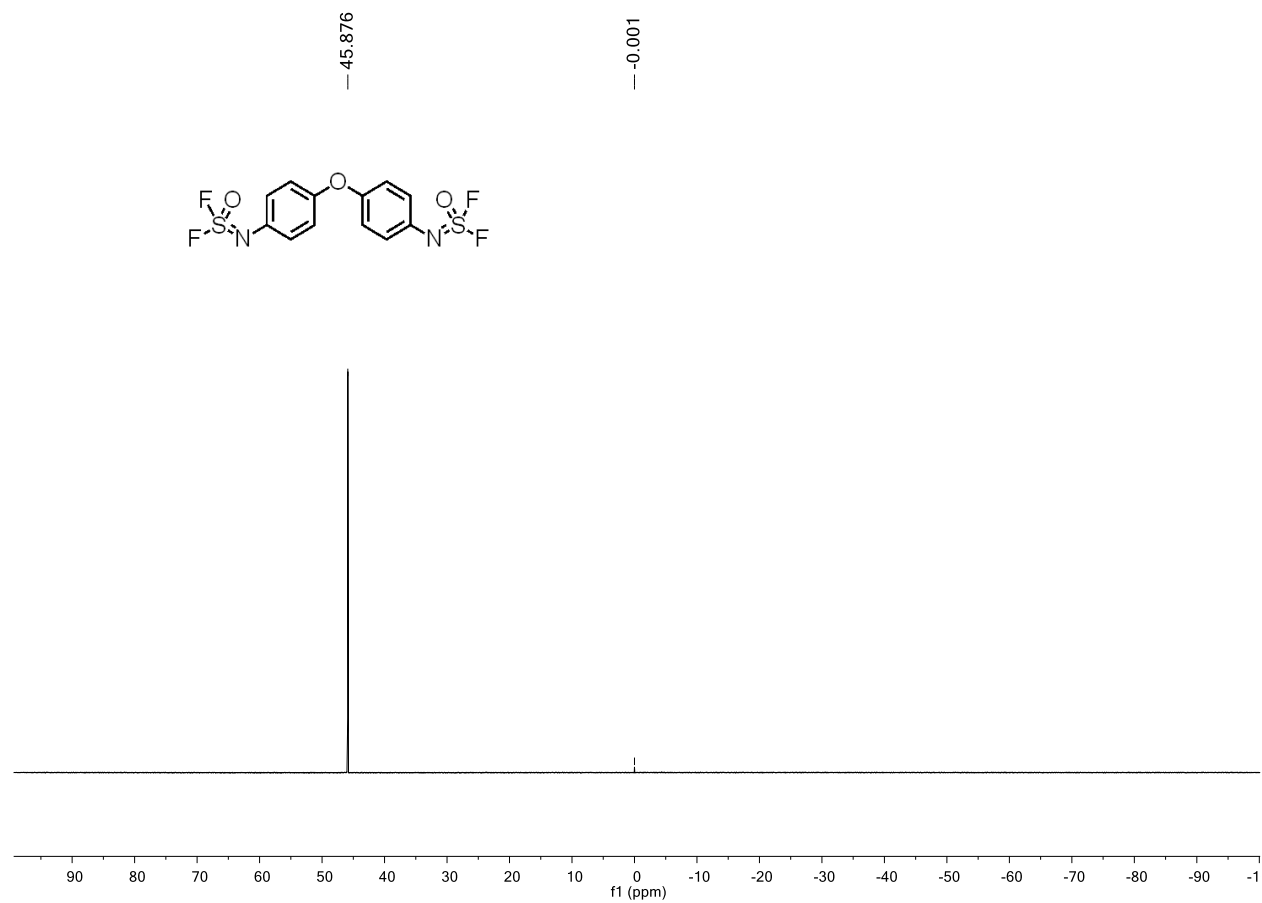
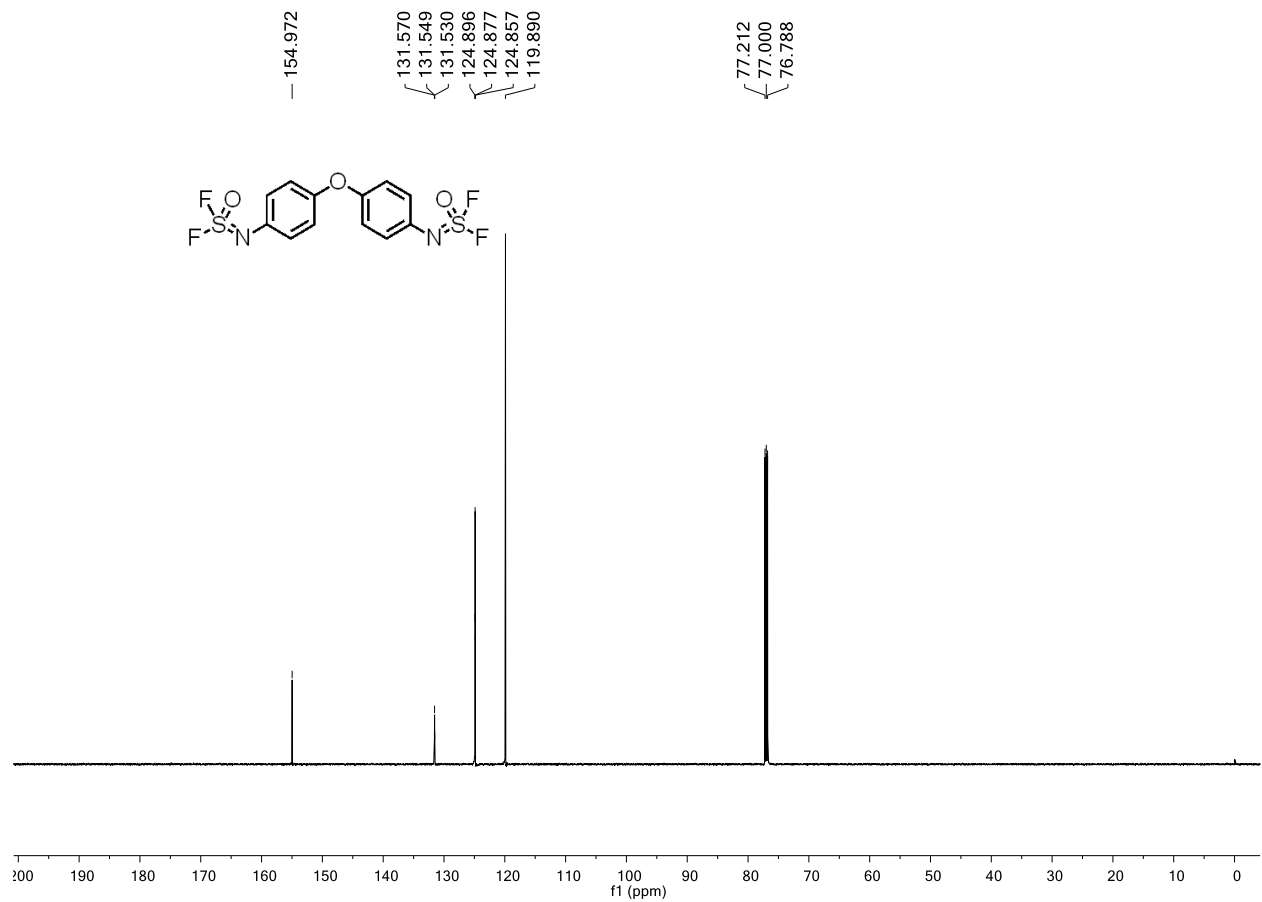
	MIC (µg/mL)			
	VSE 2127	VRE 49609	MSSA 9144	MRSA 1717
Vancomycin	1-2	16	1	1-2
Polymer 15	16	16	32-64	32

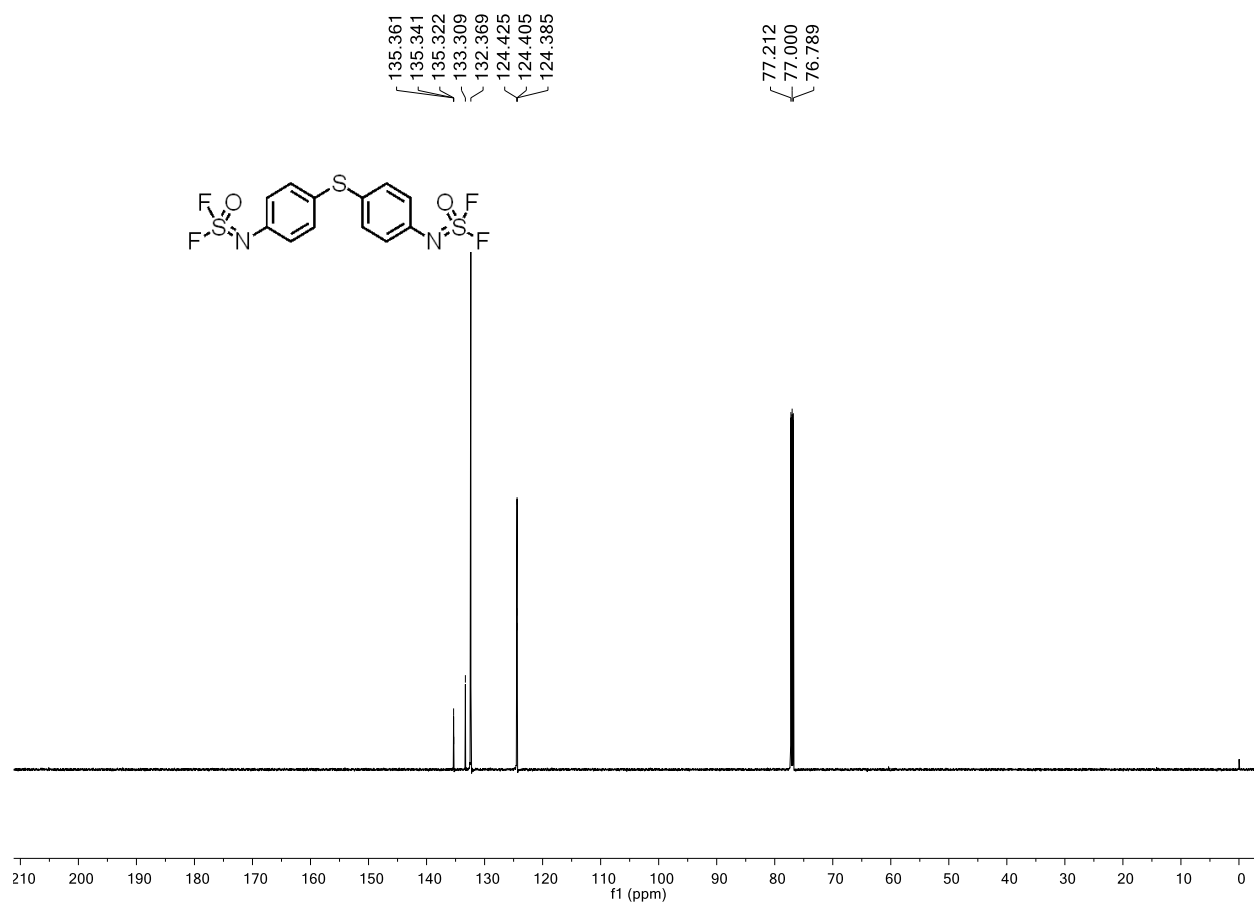
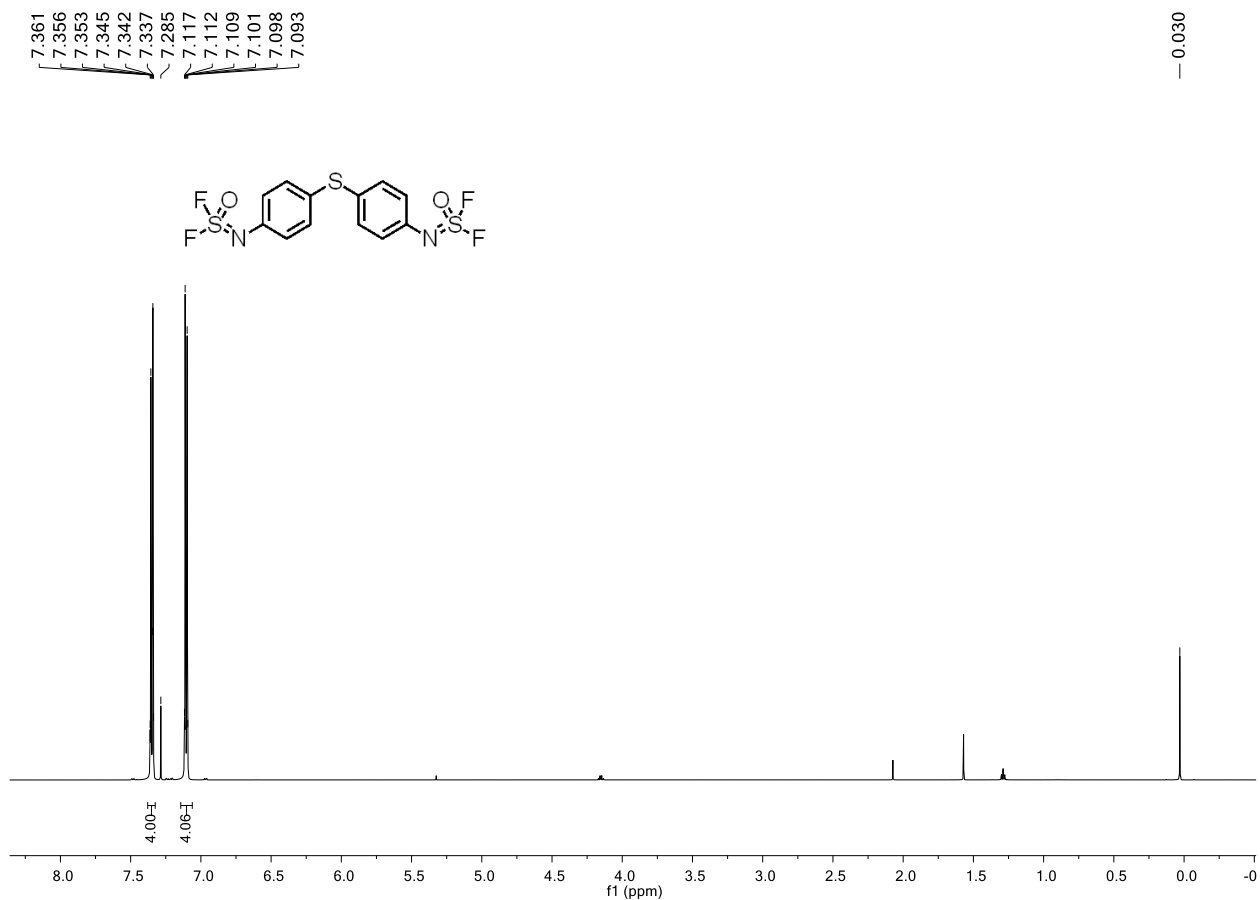
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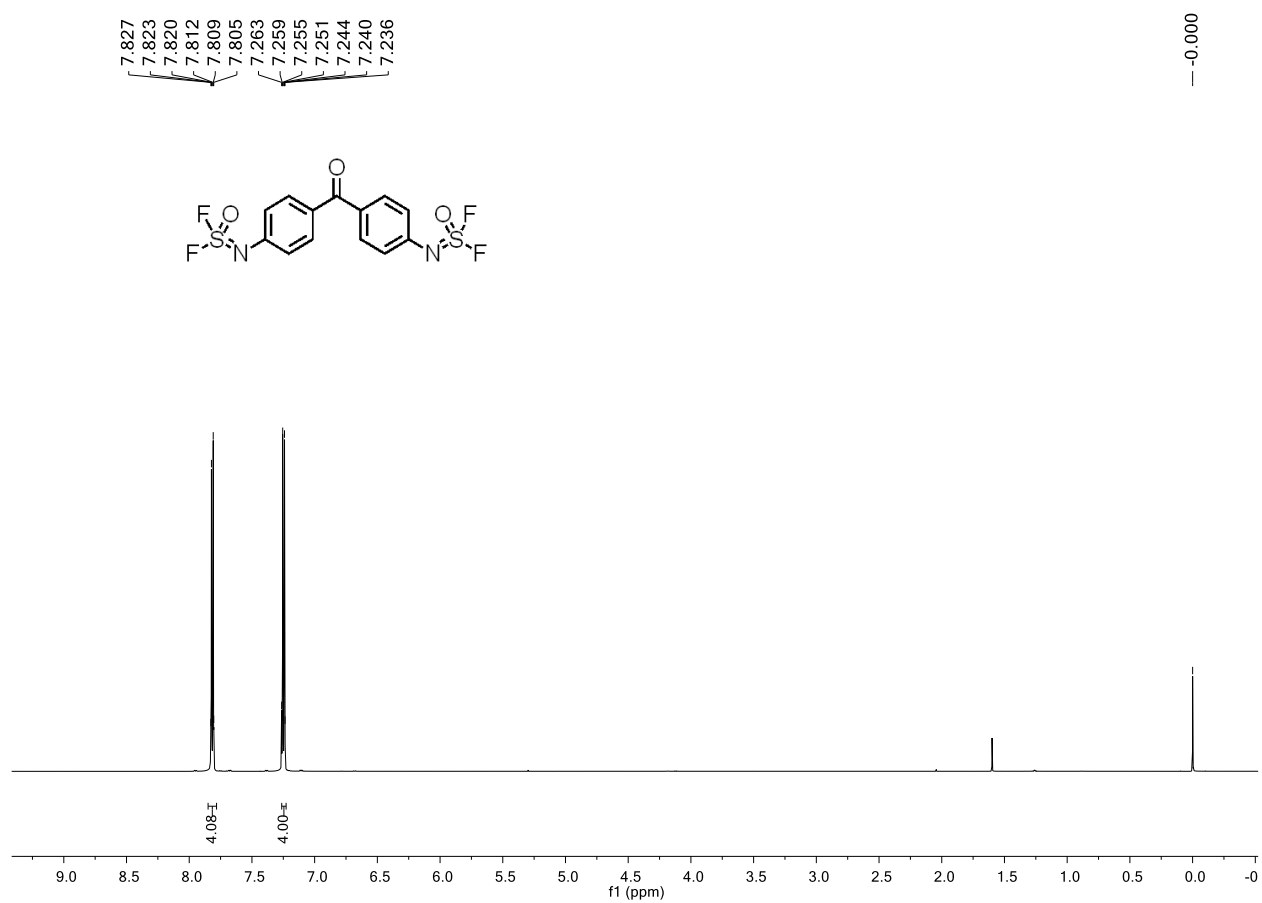
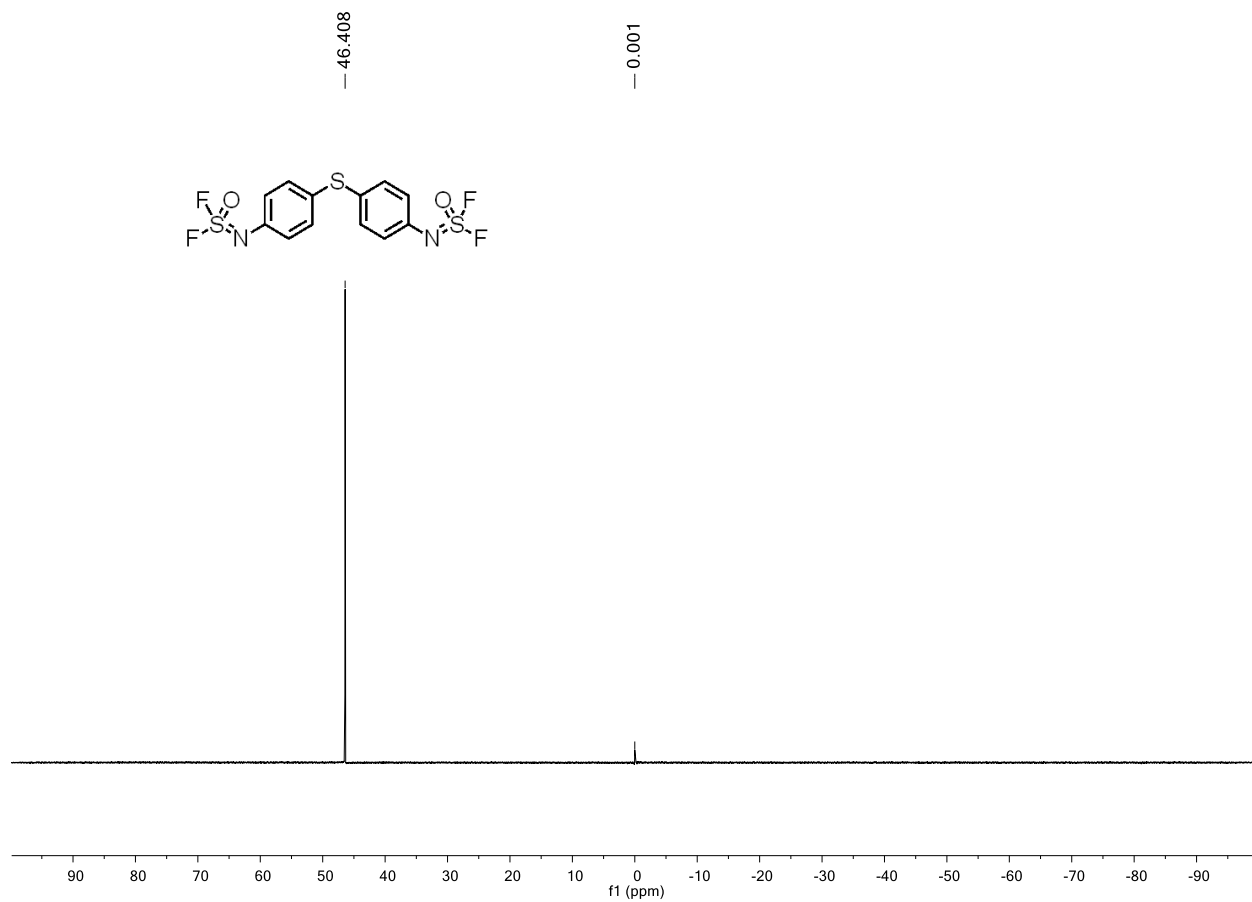
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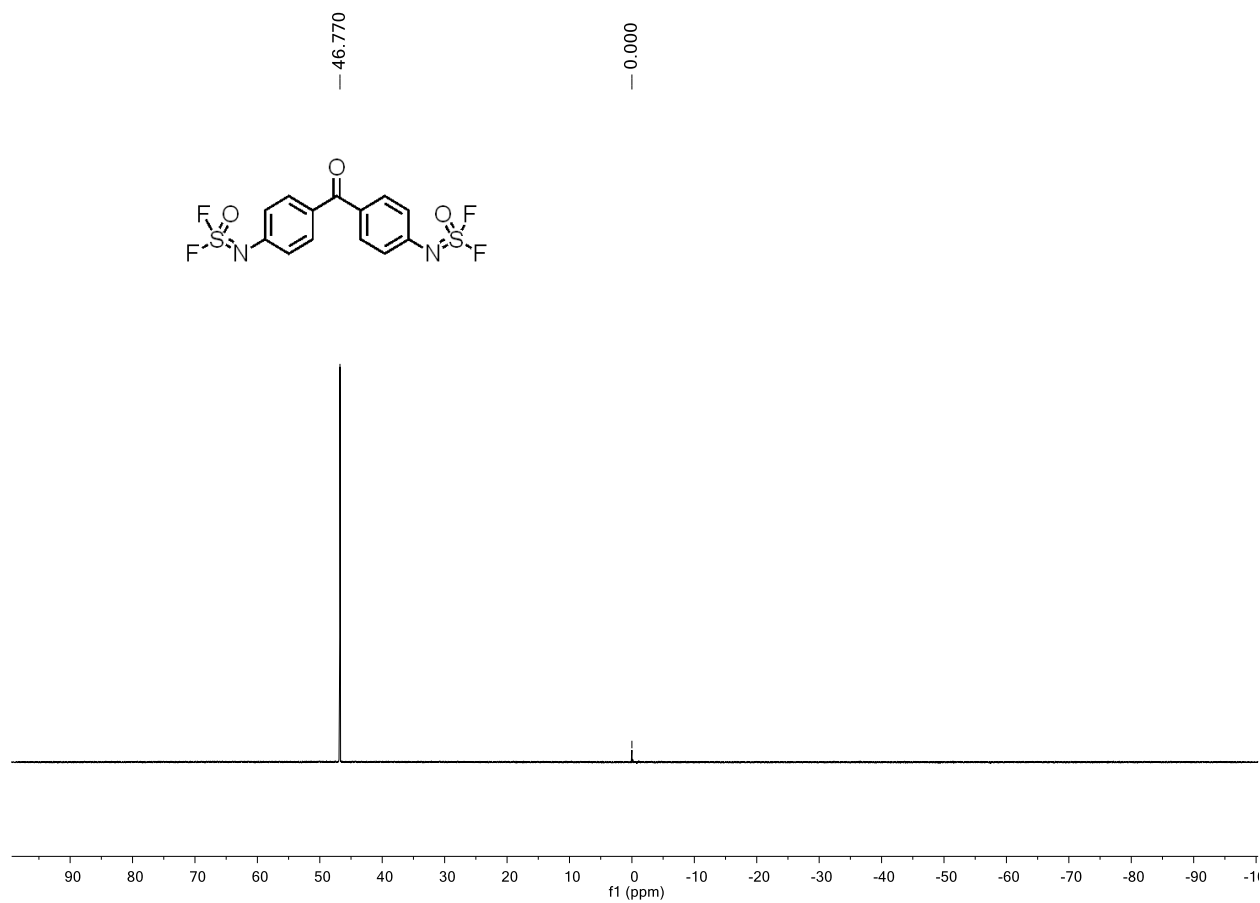
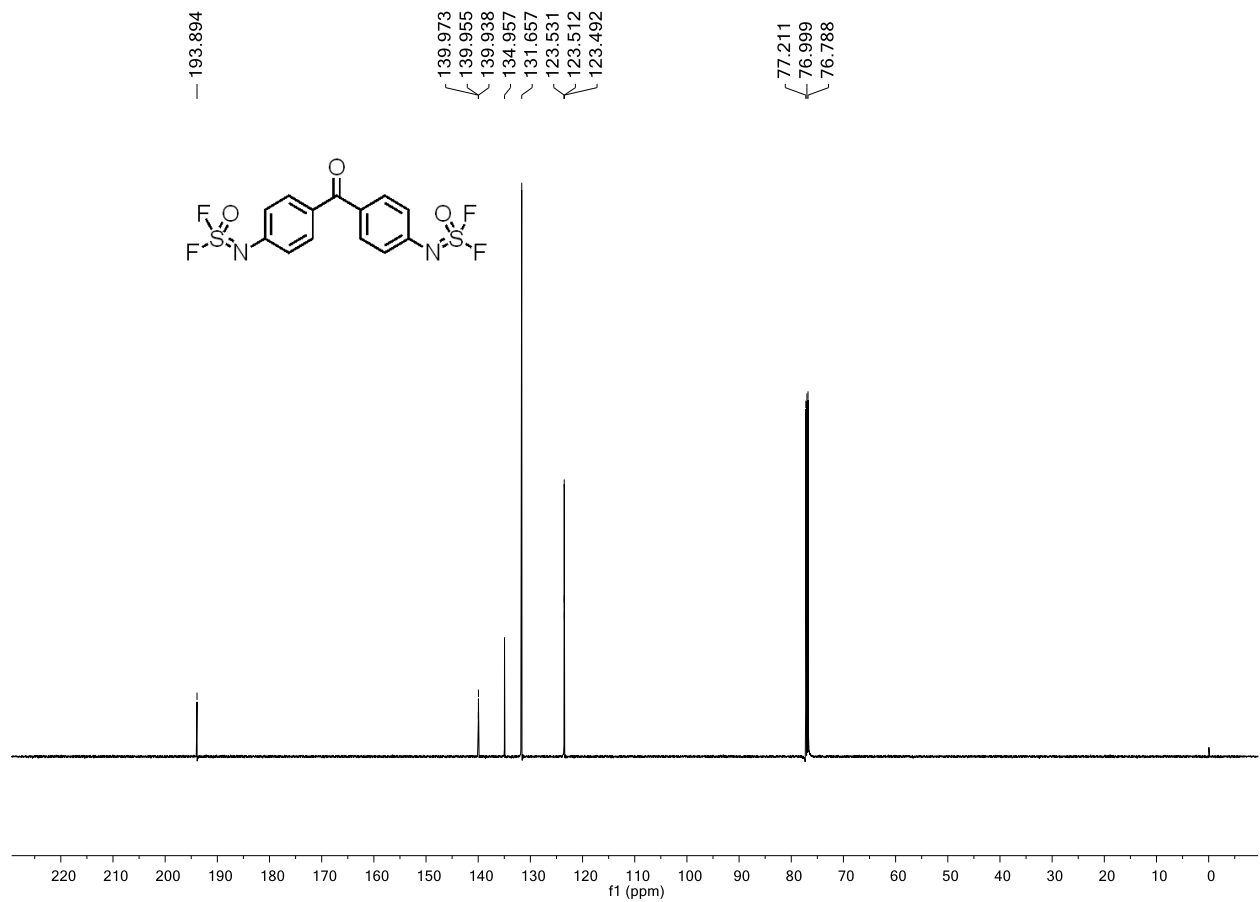


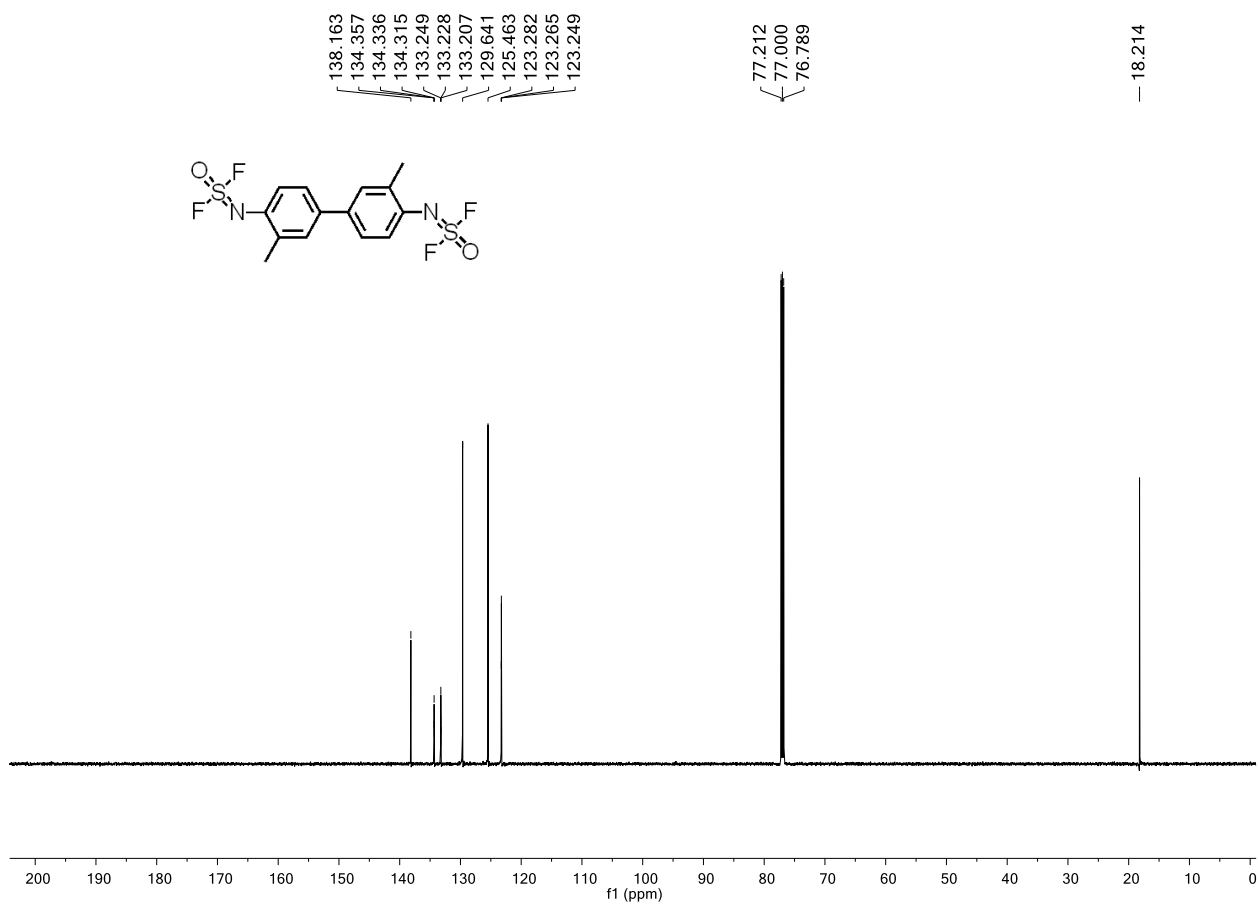
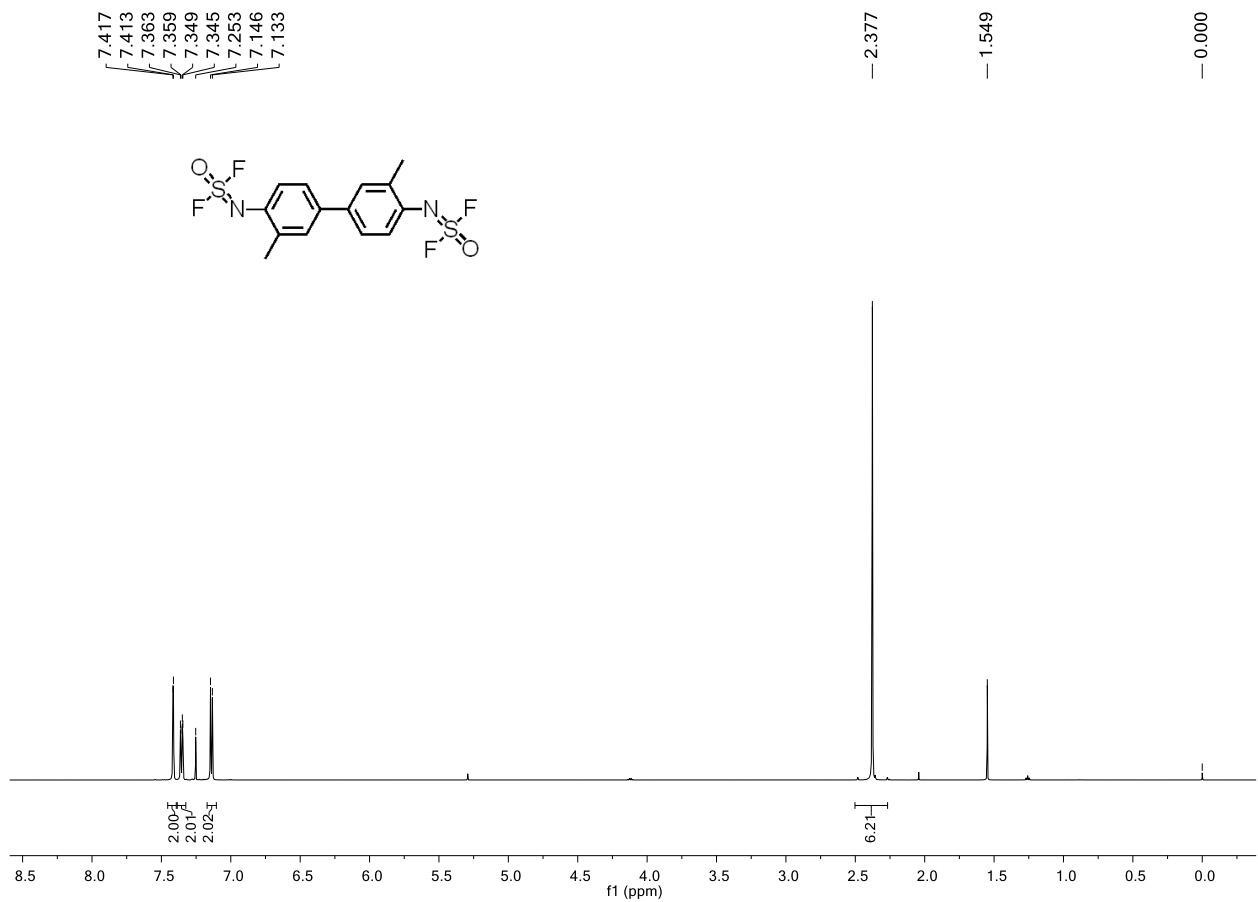


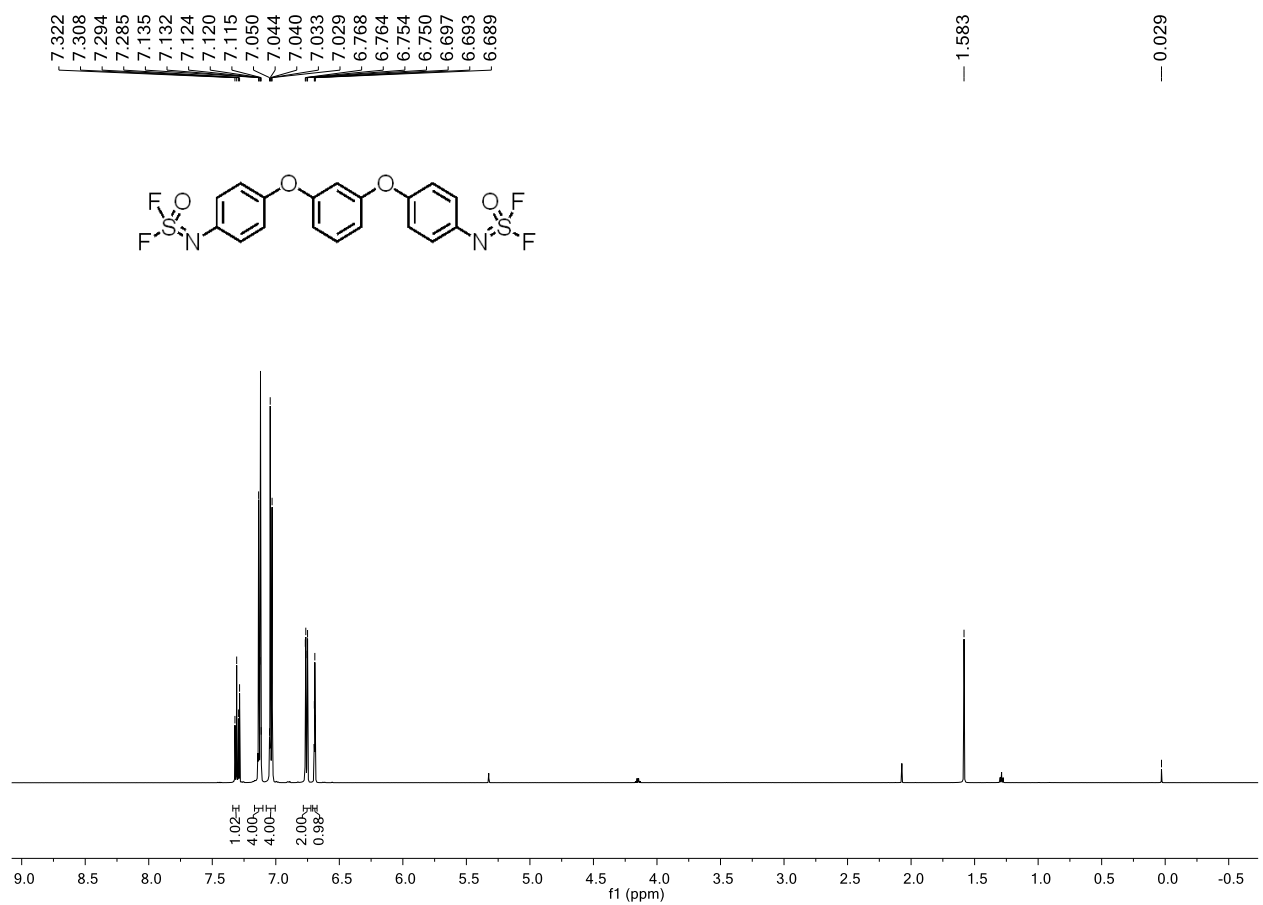
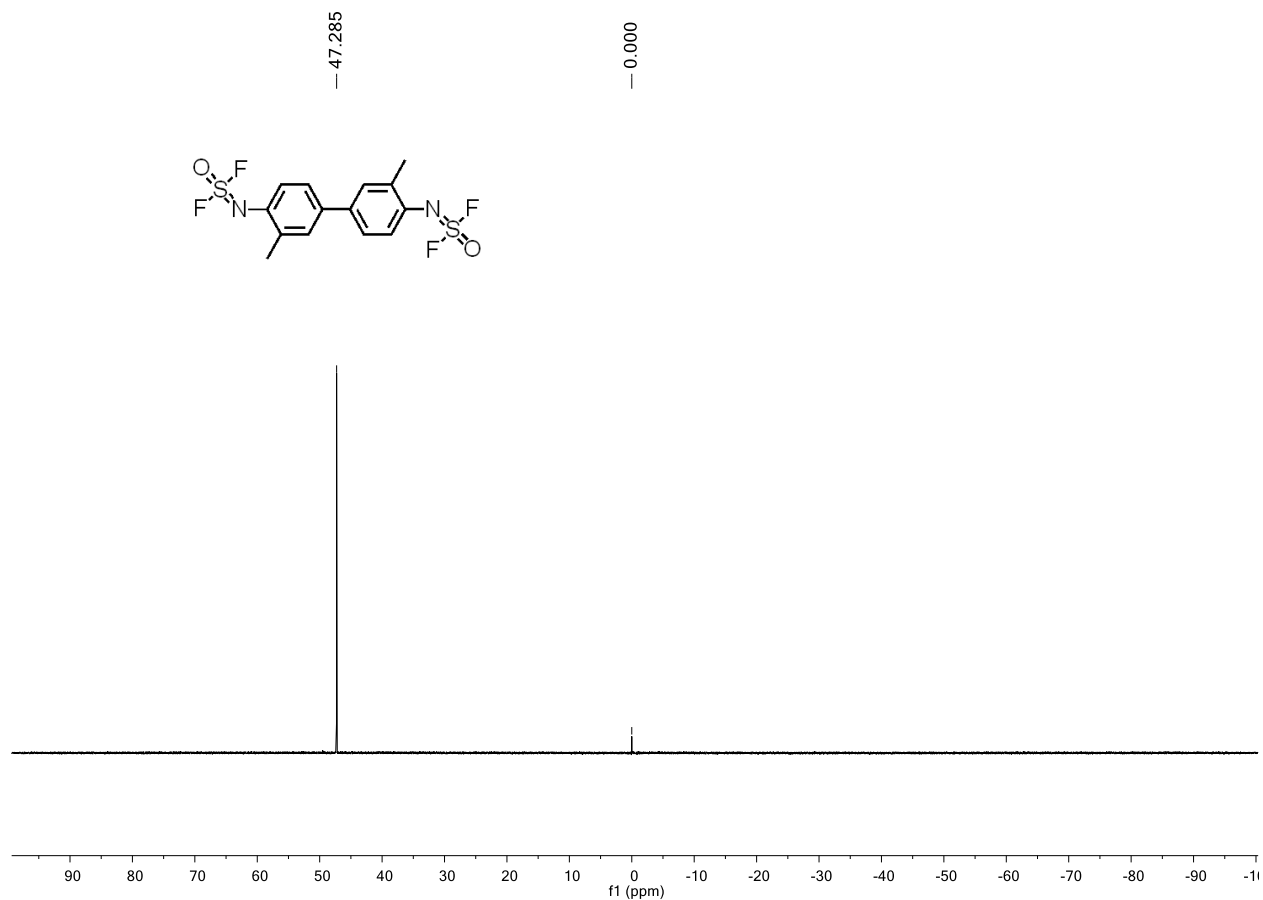


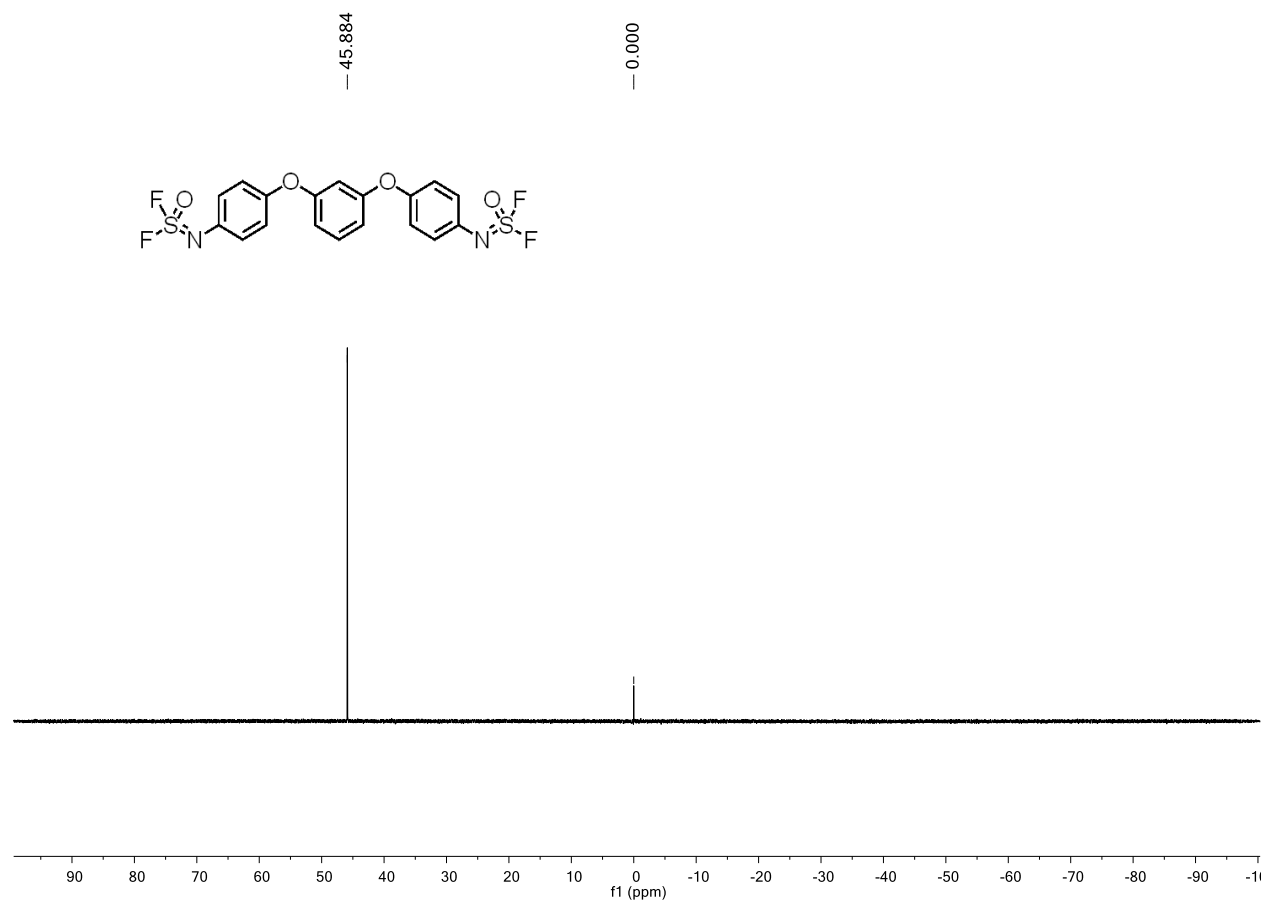
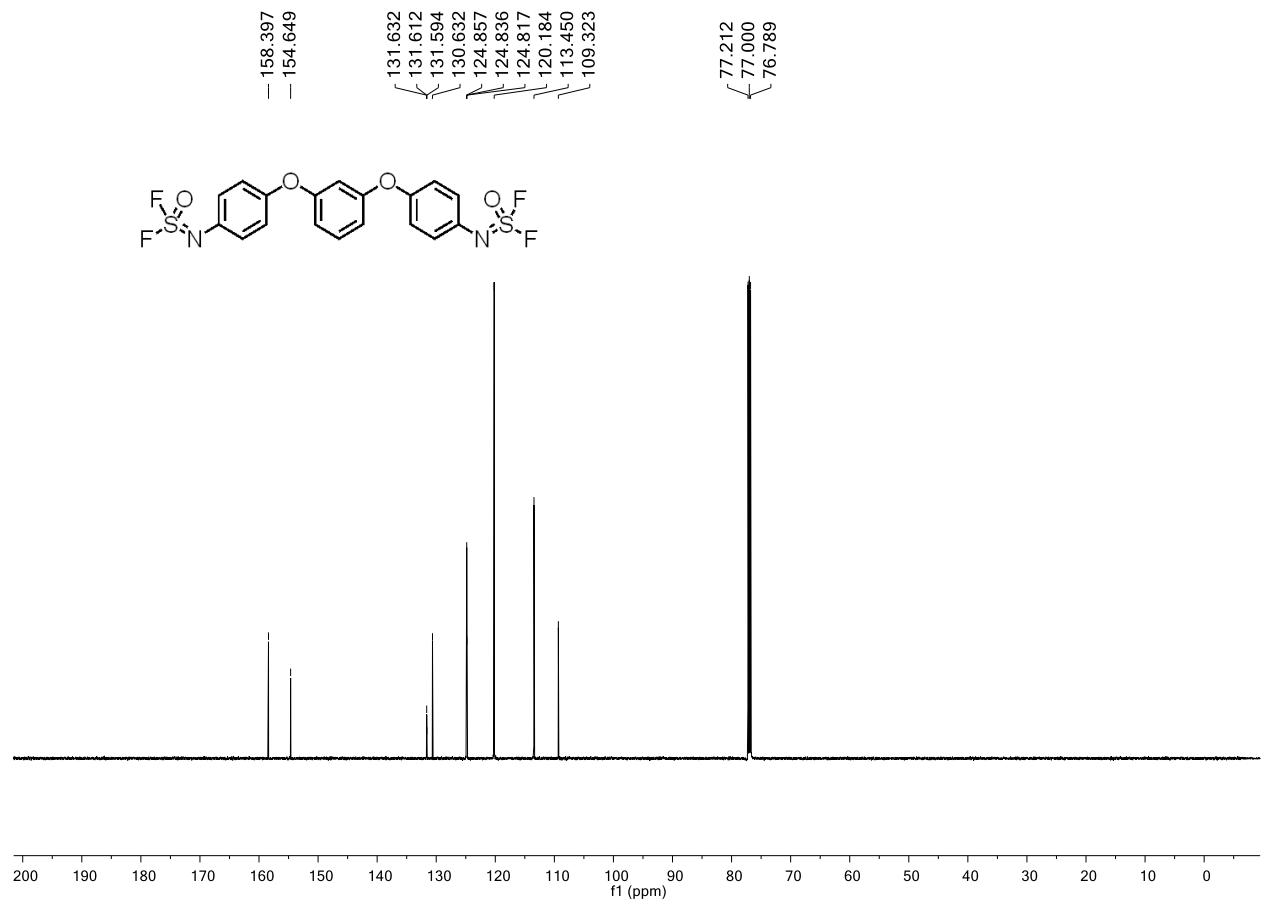


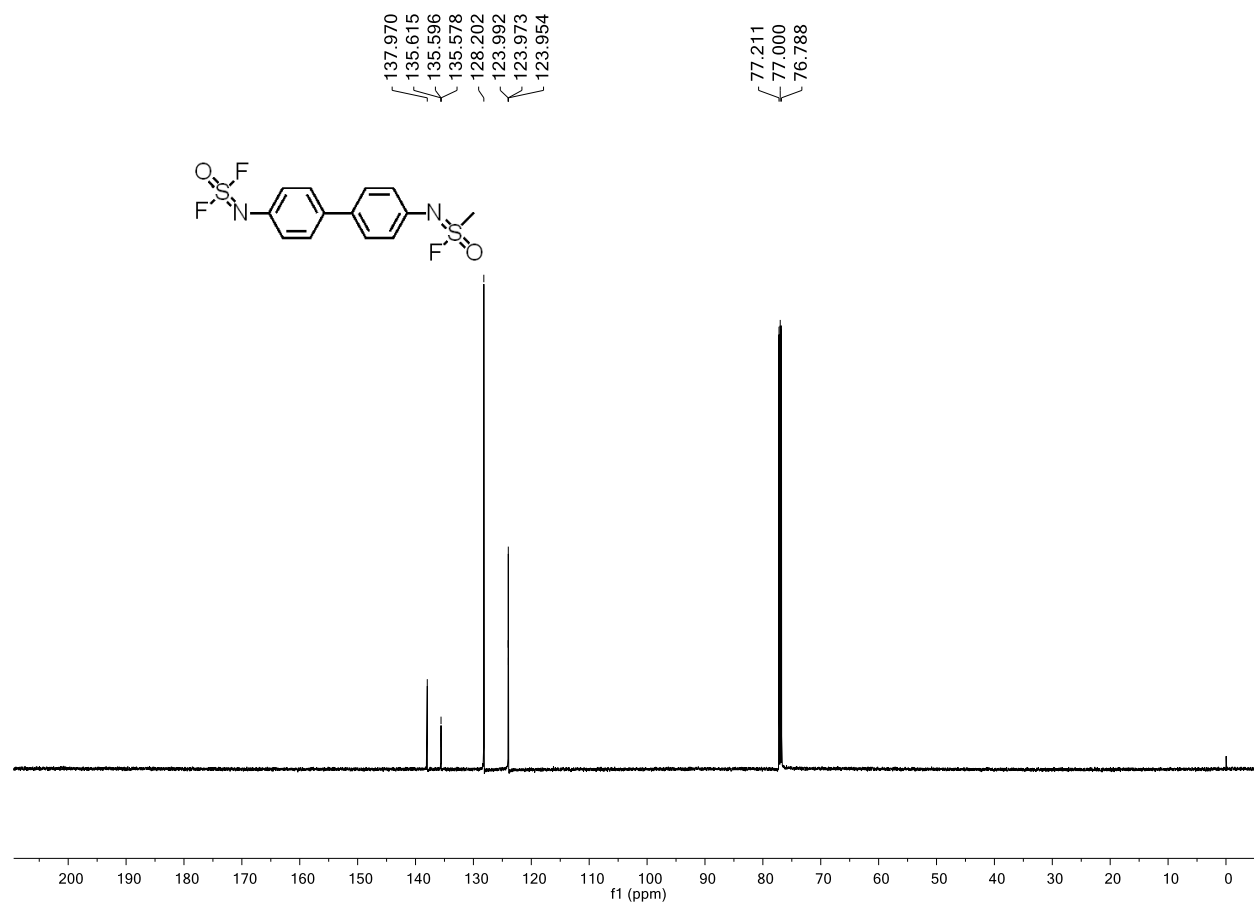
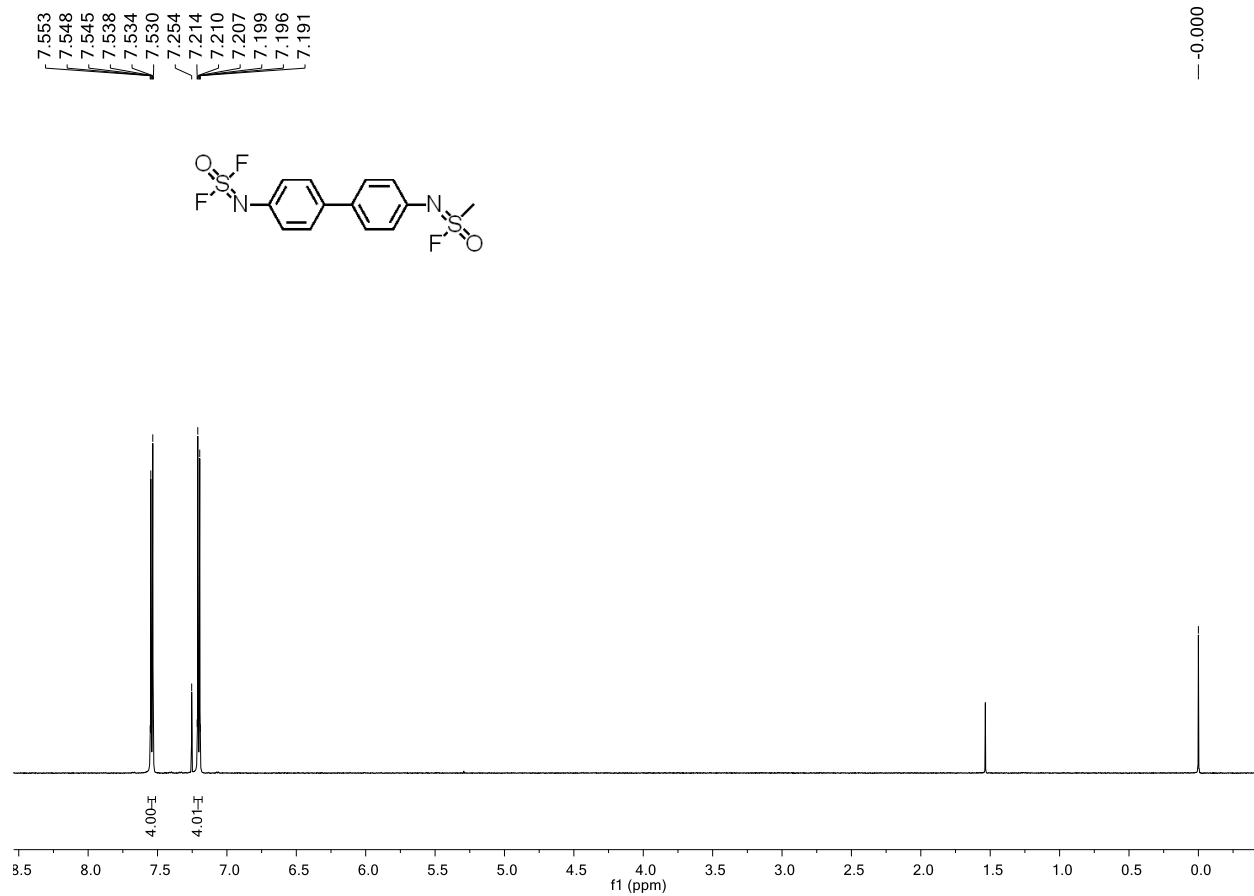


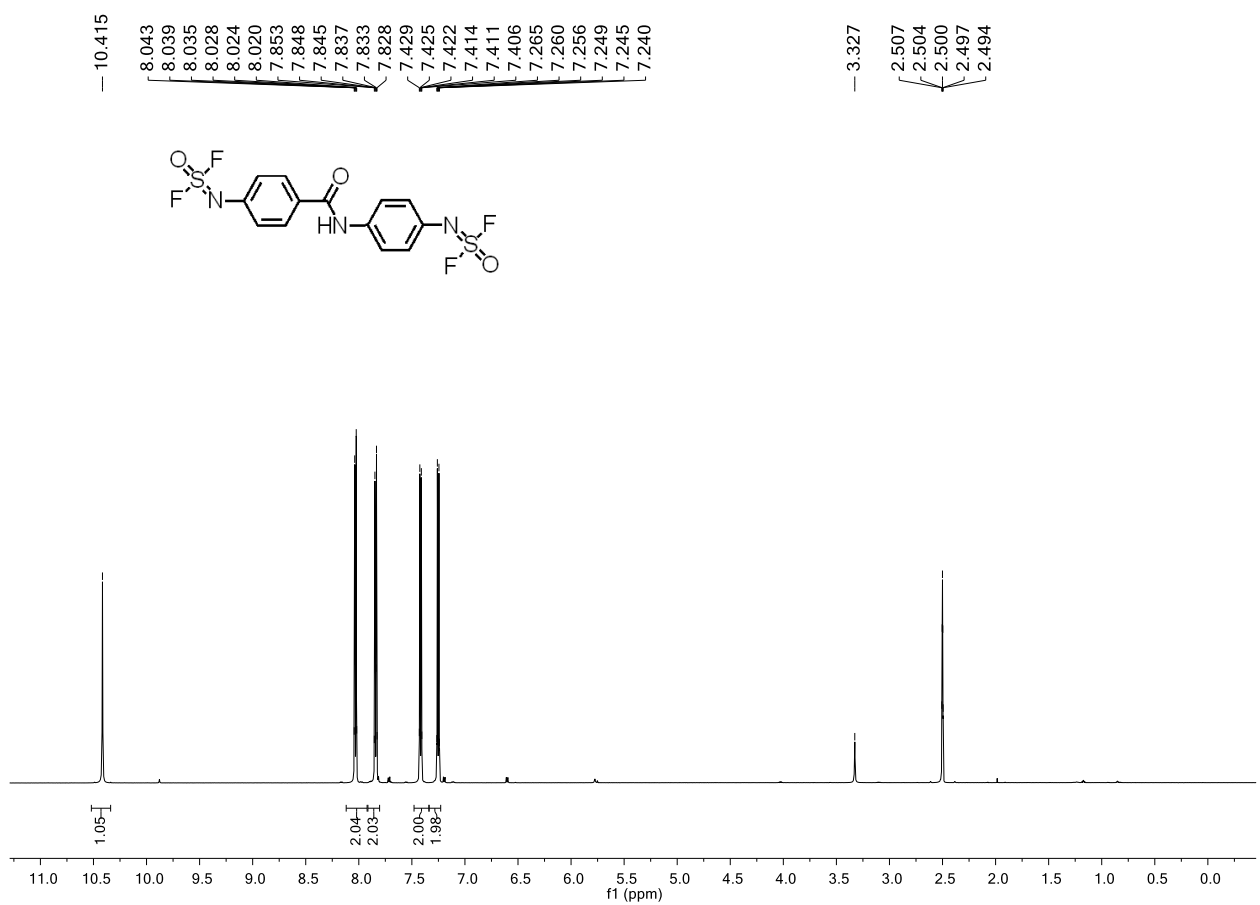
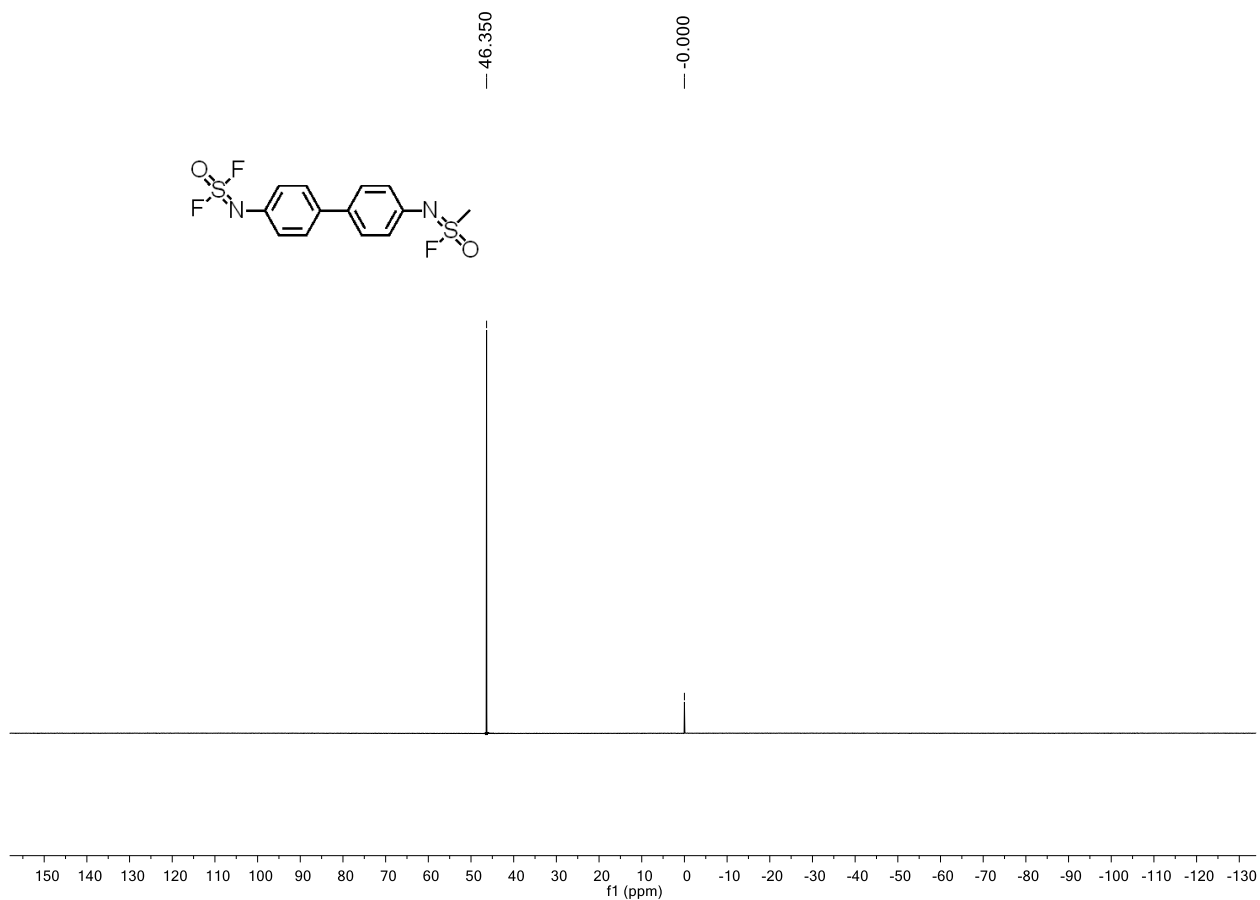


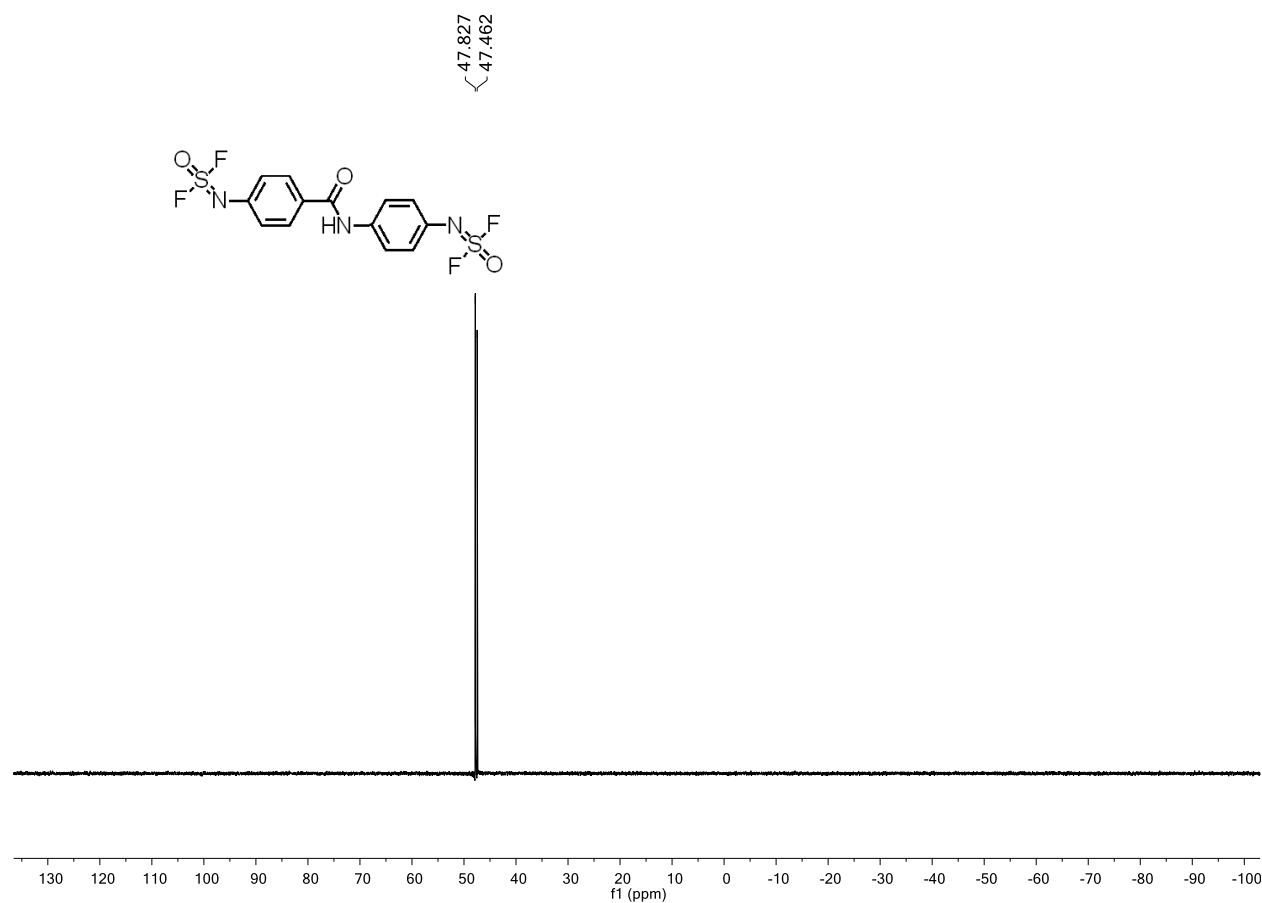
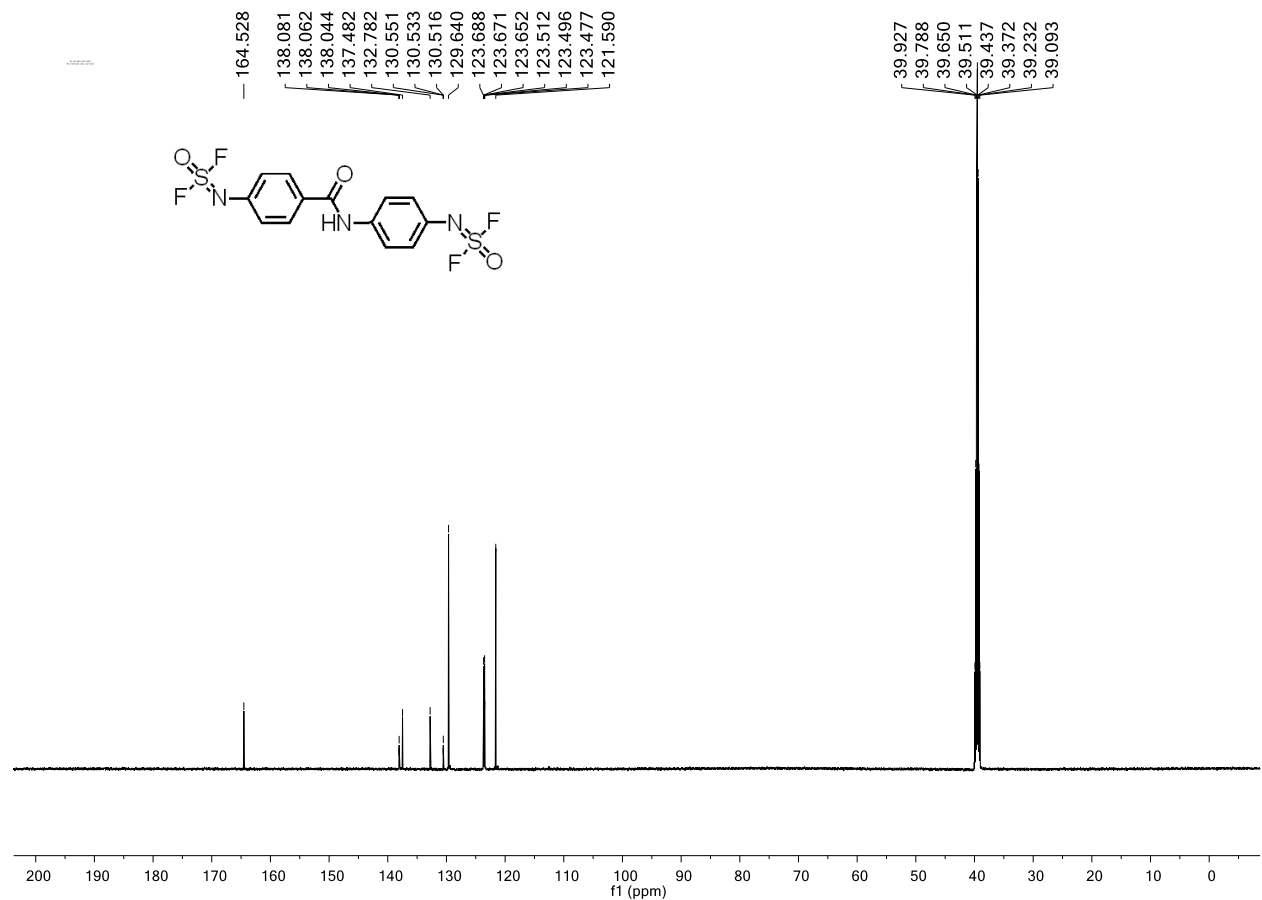


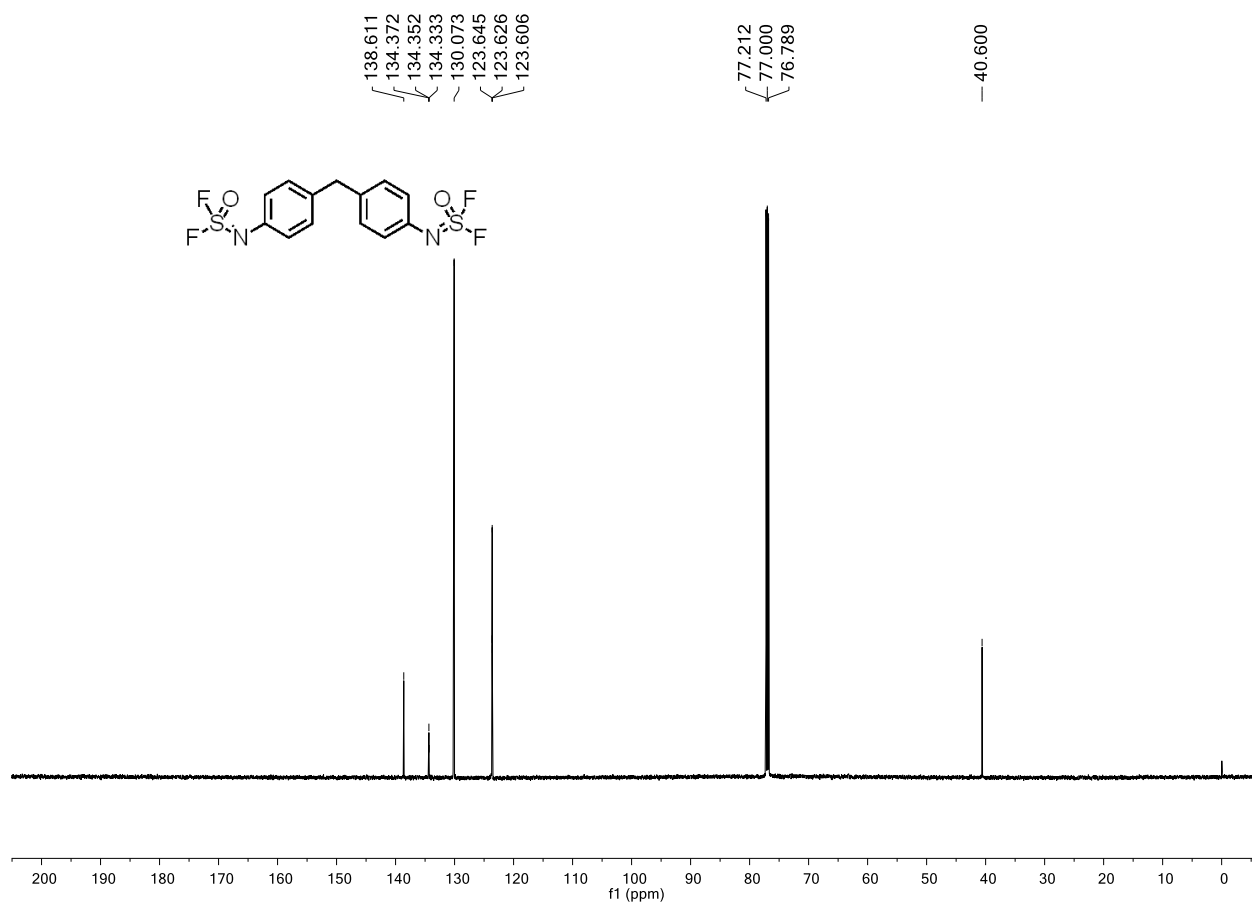
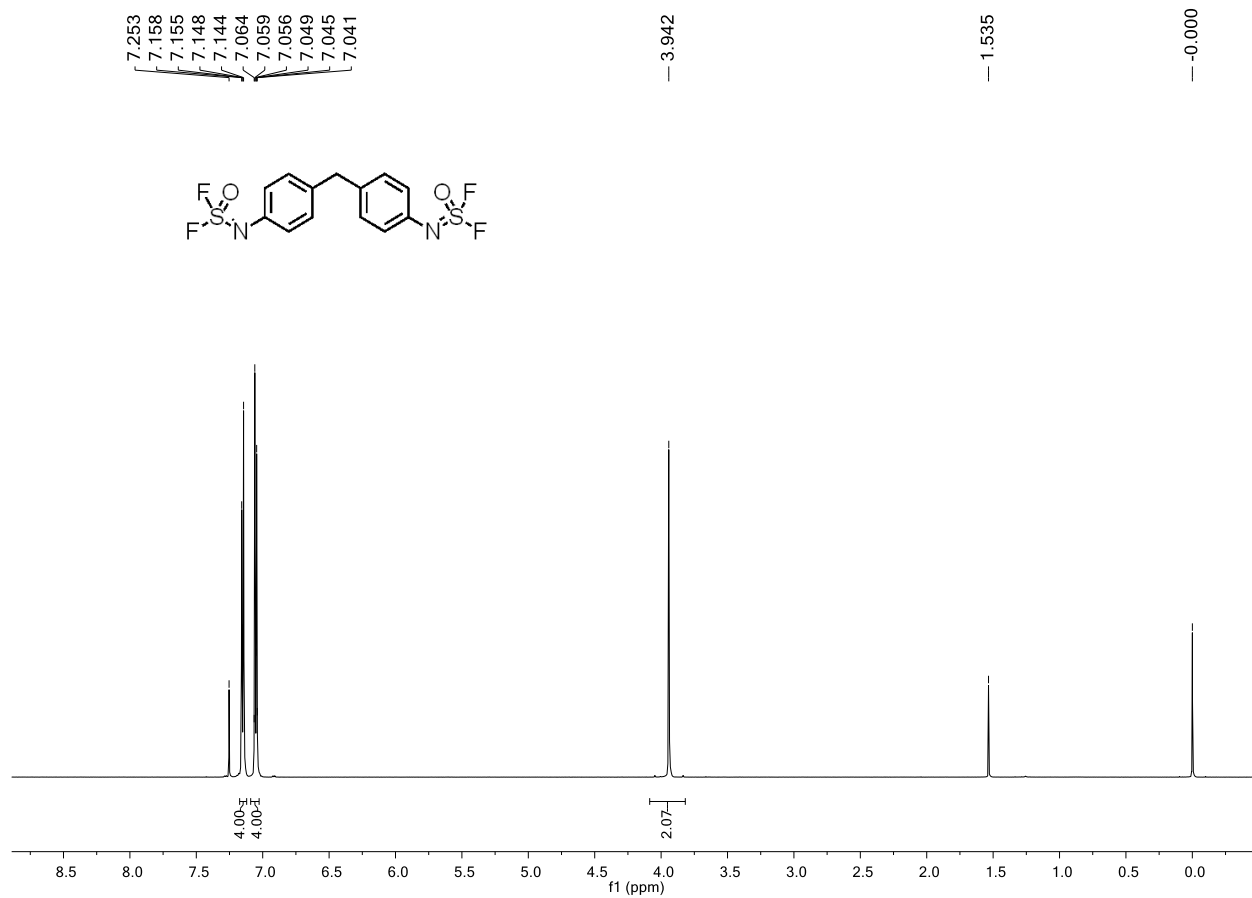


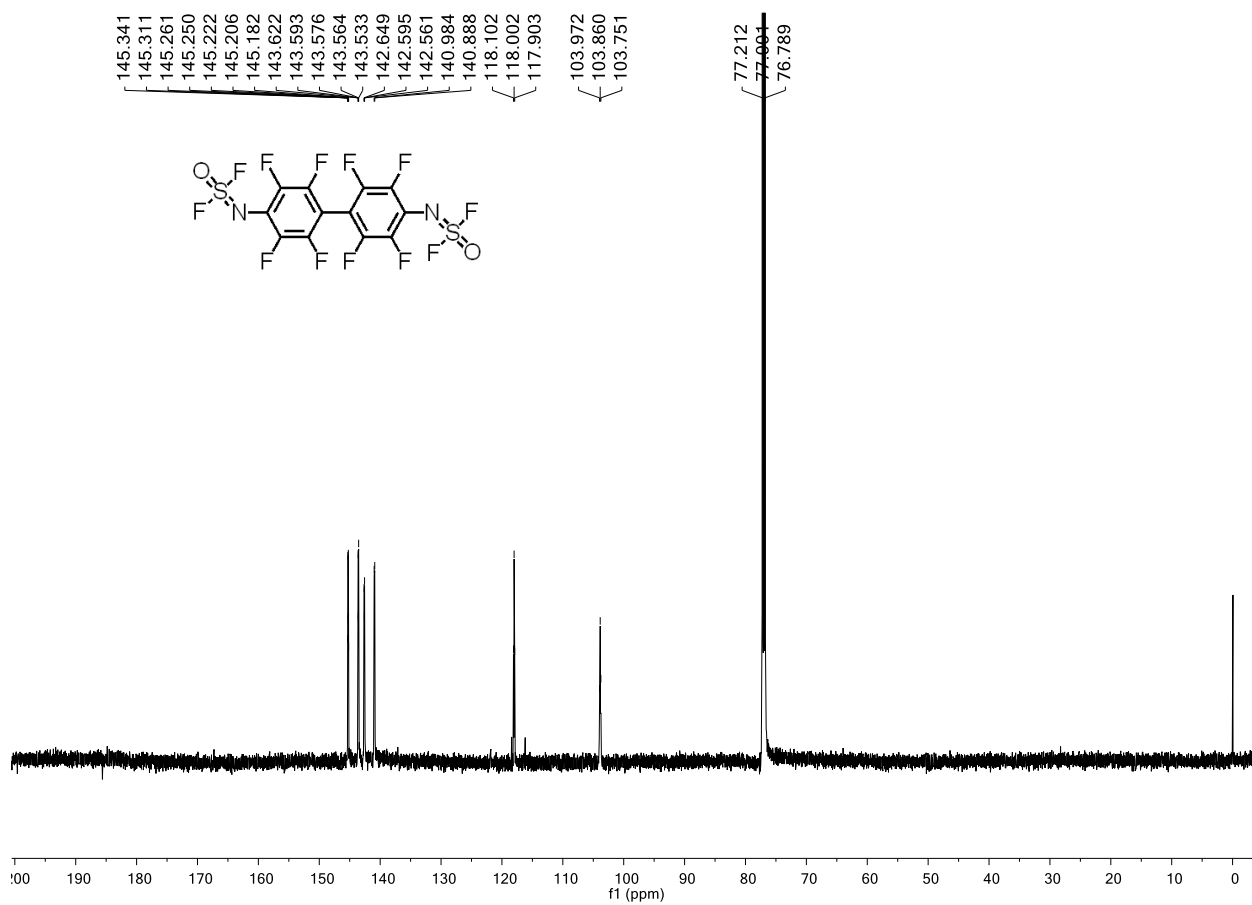
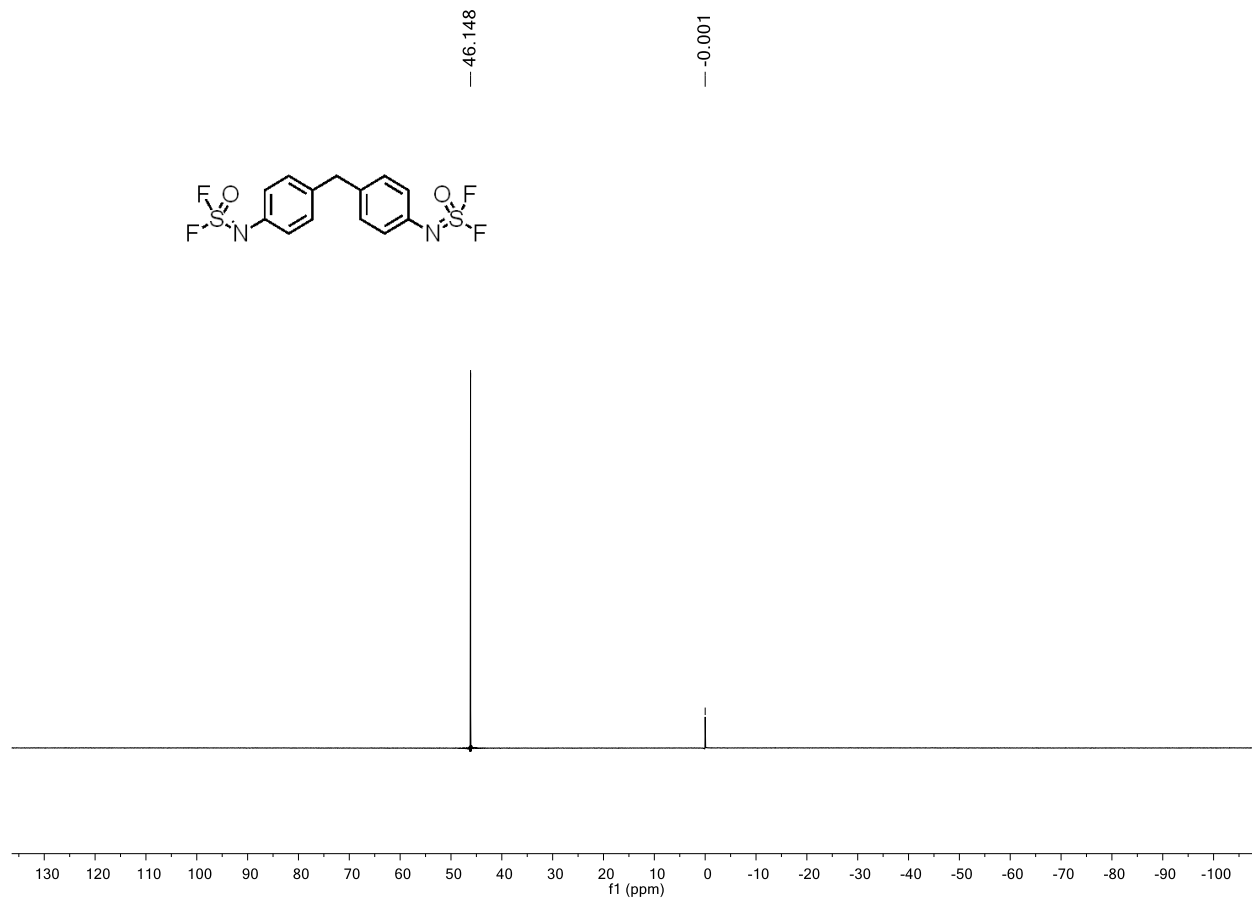


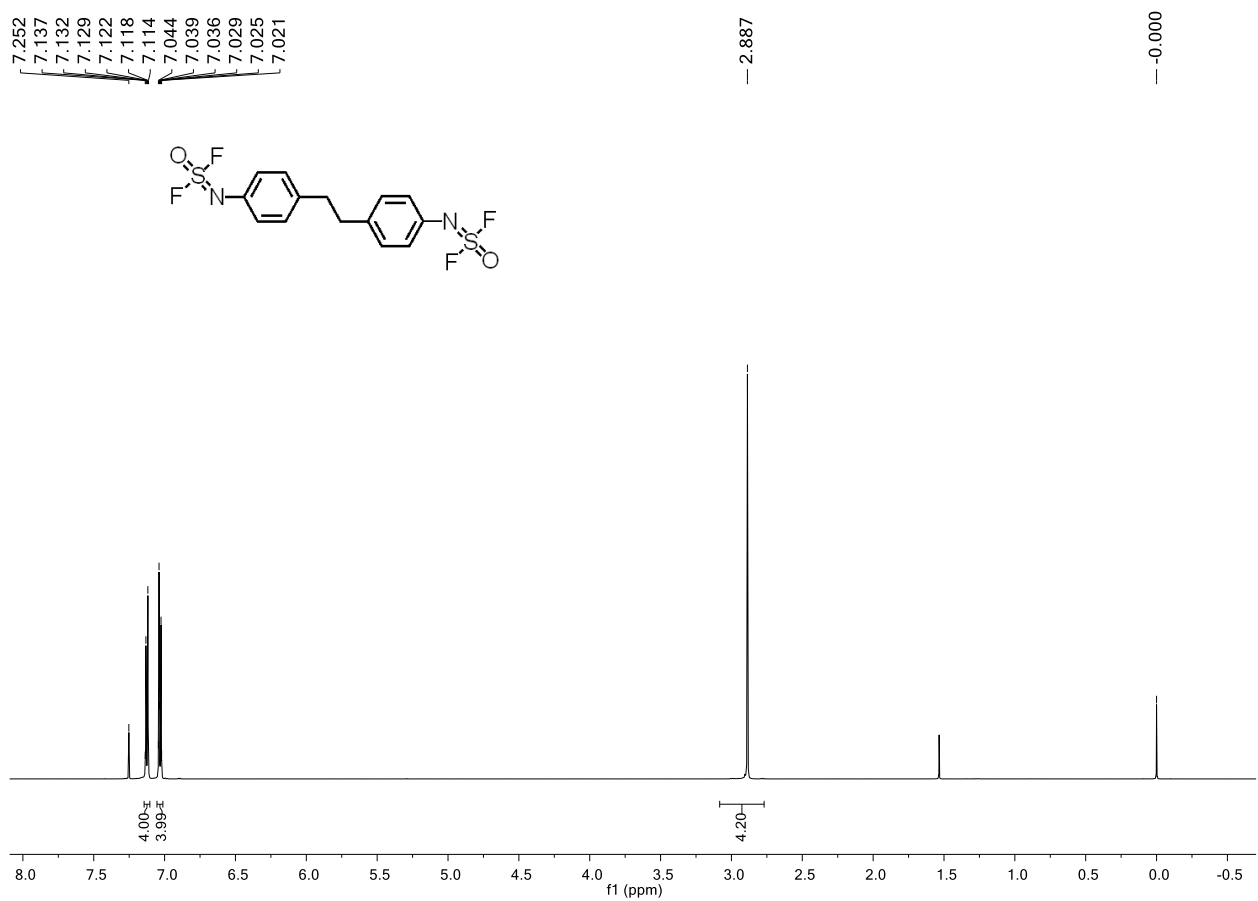
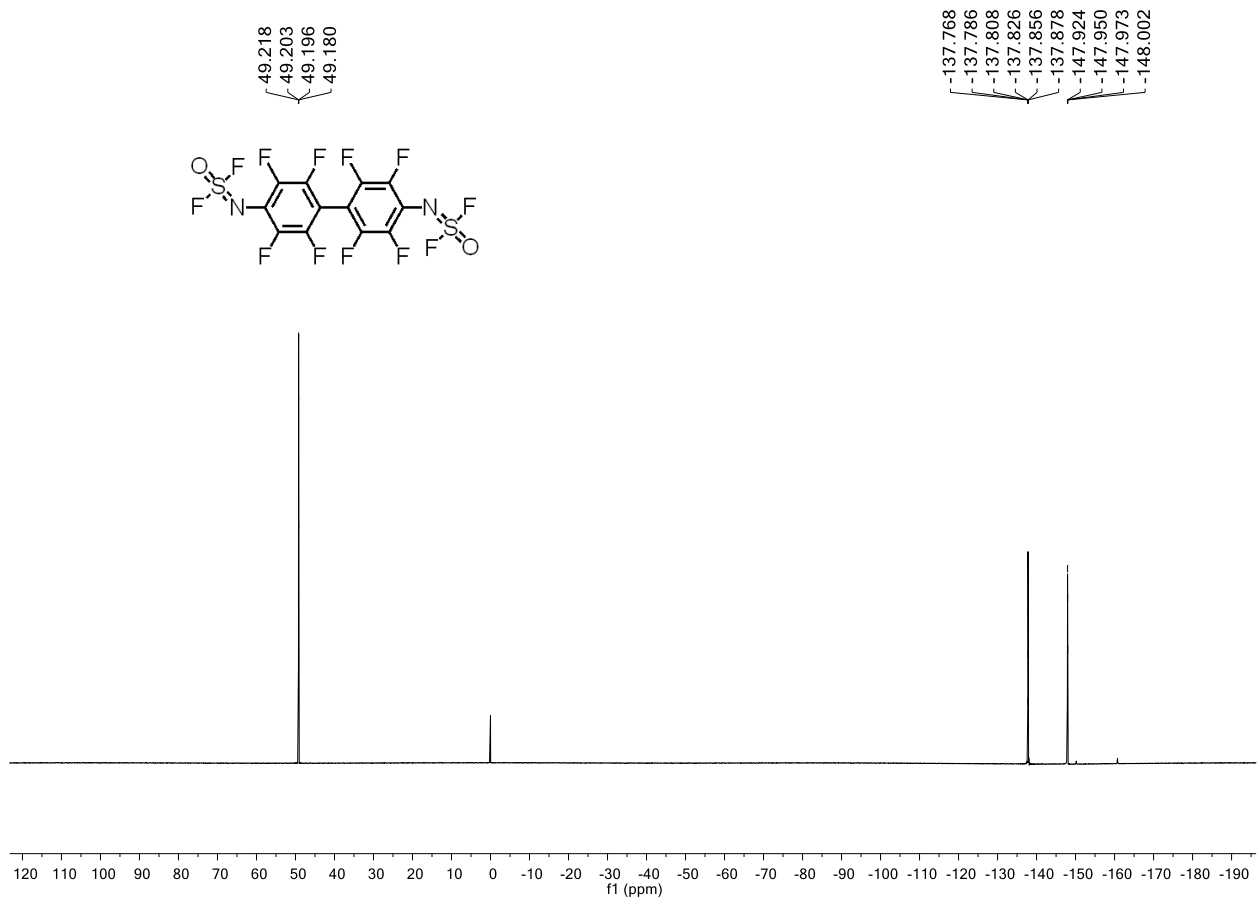


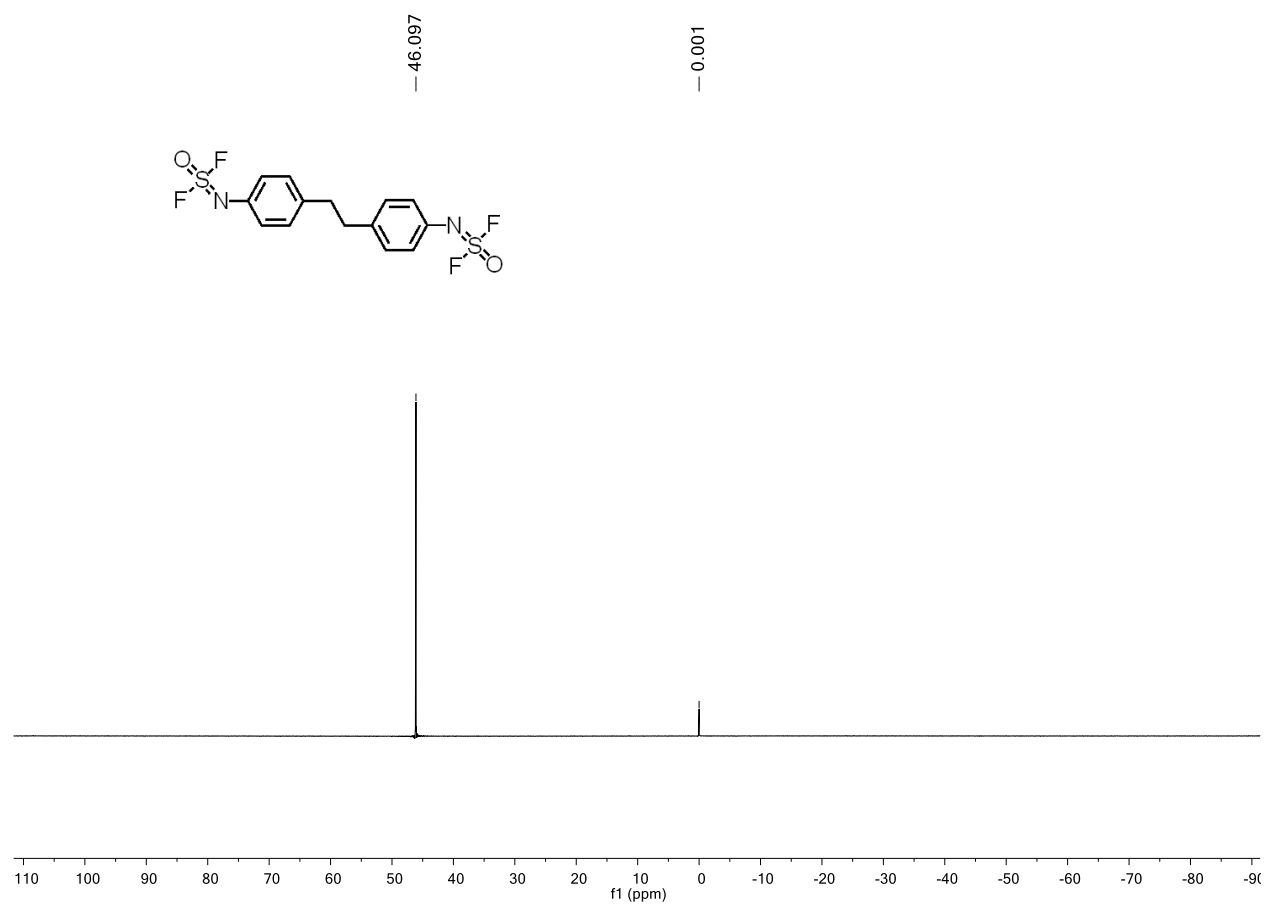
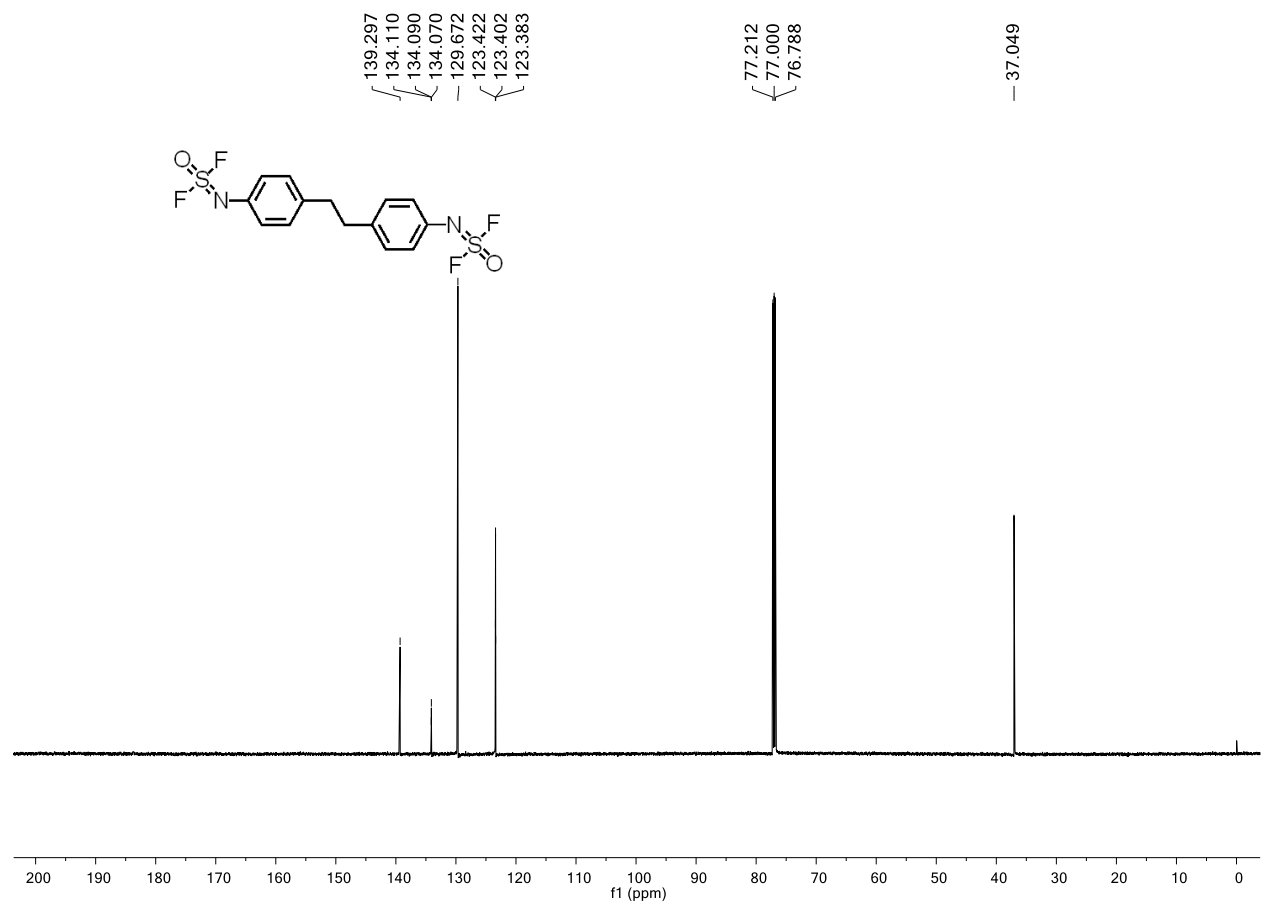


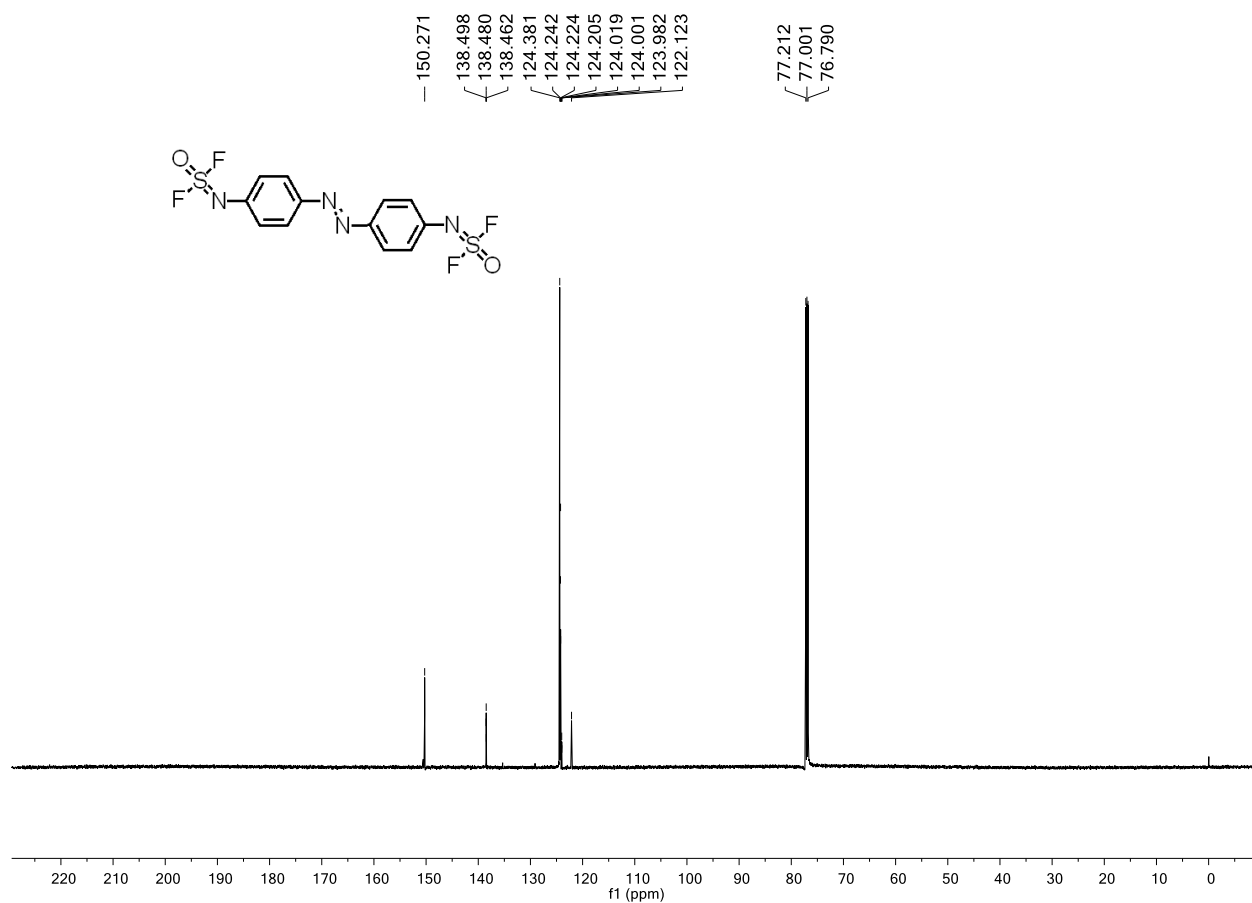
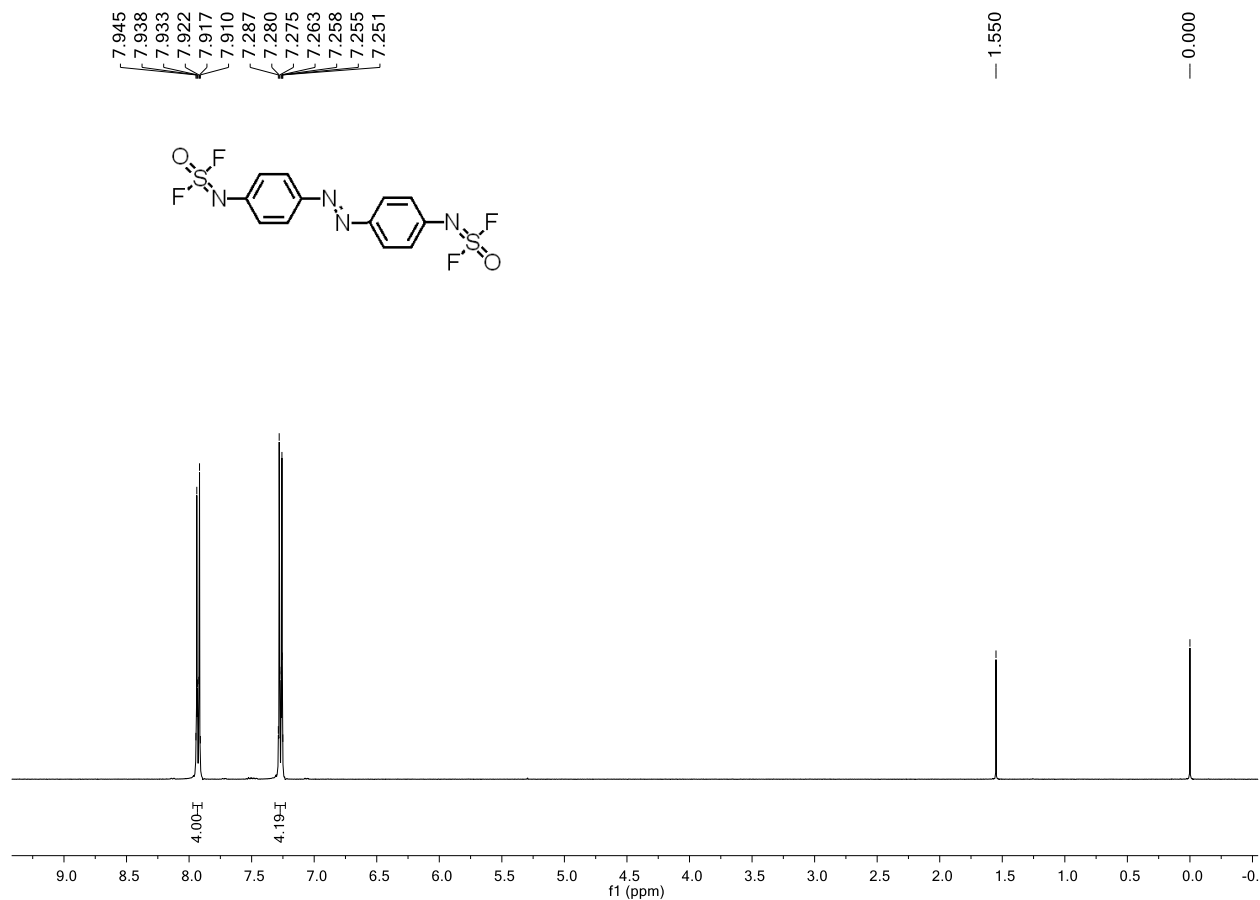


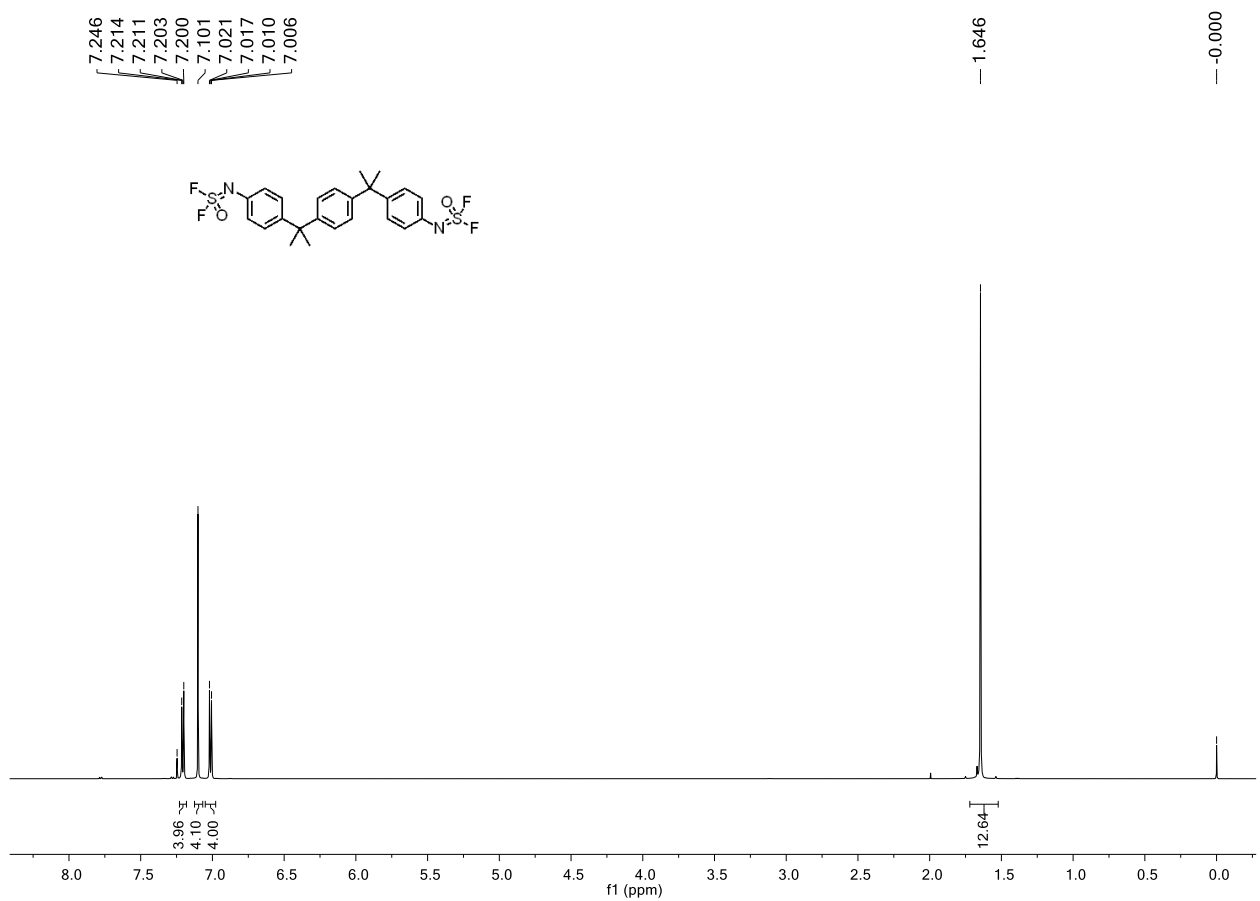
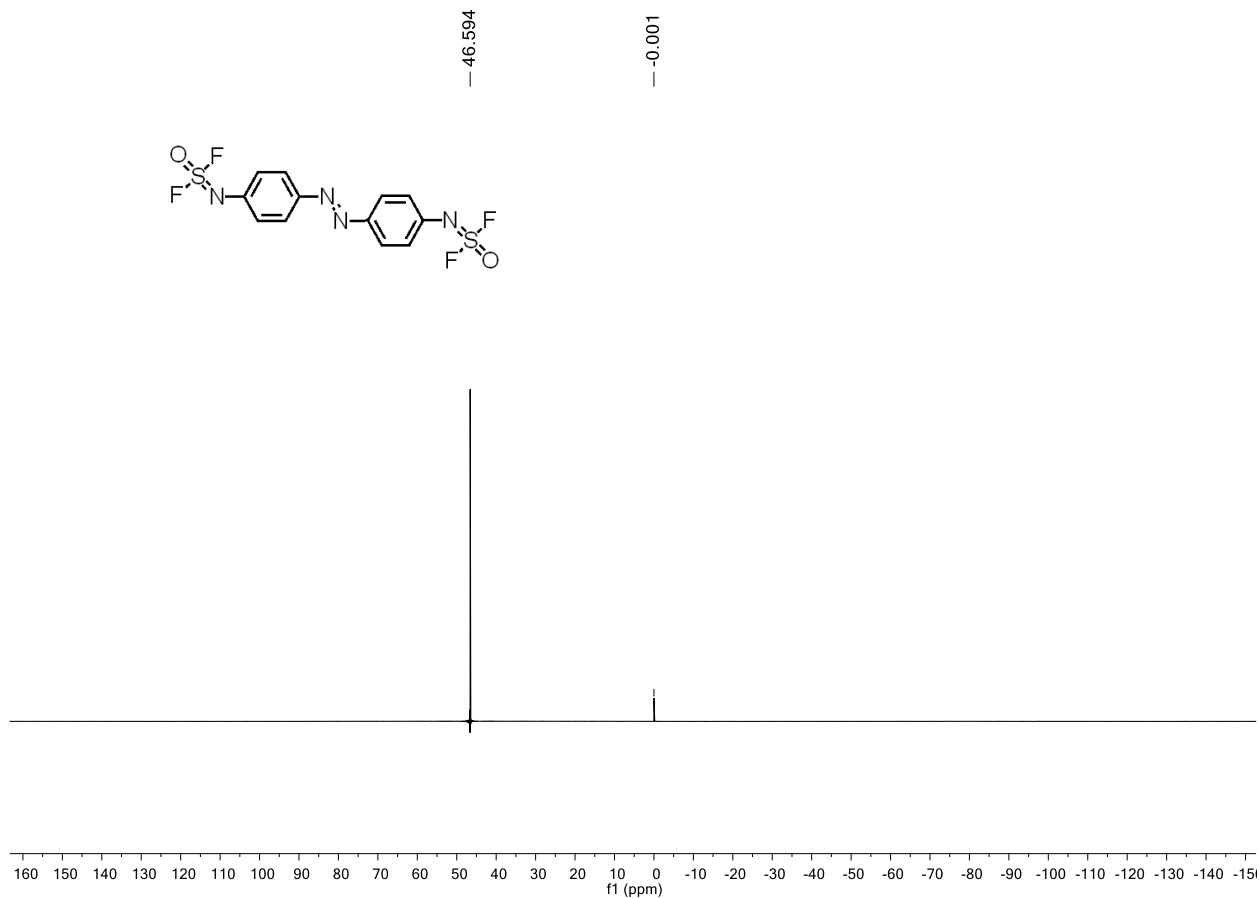


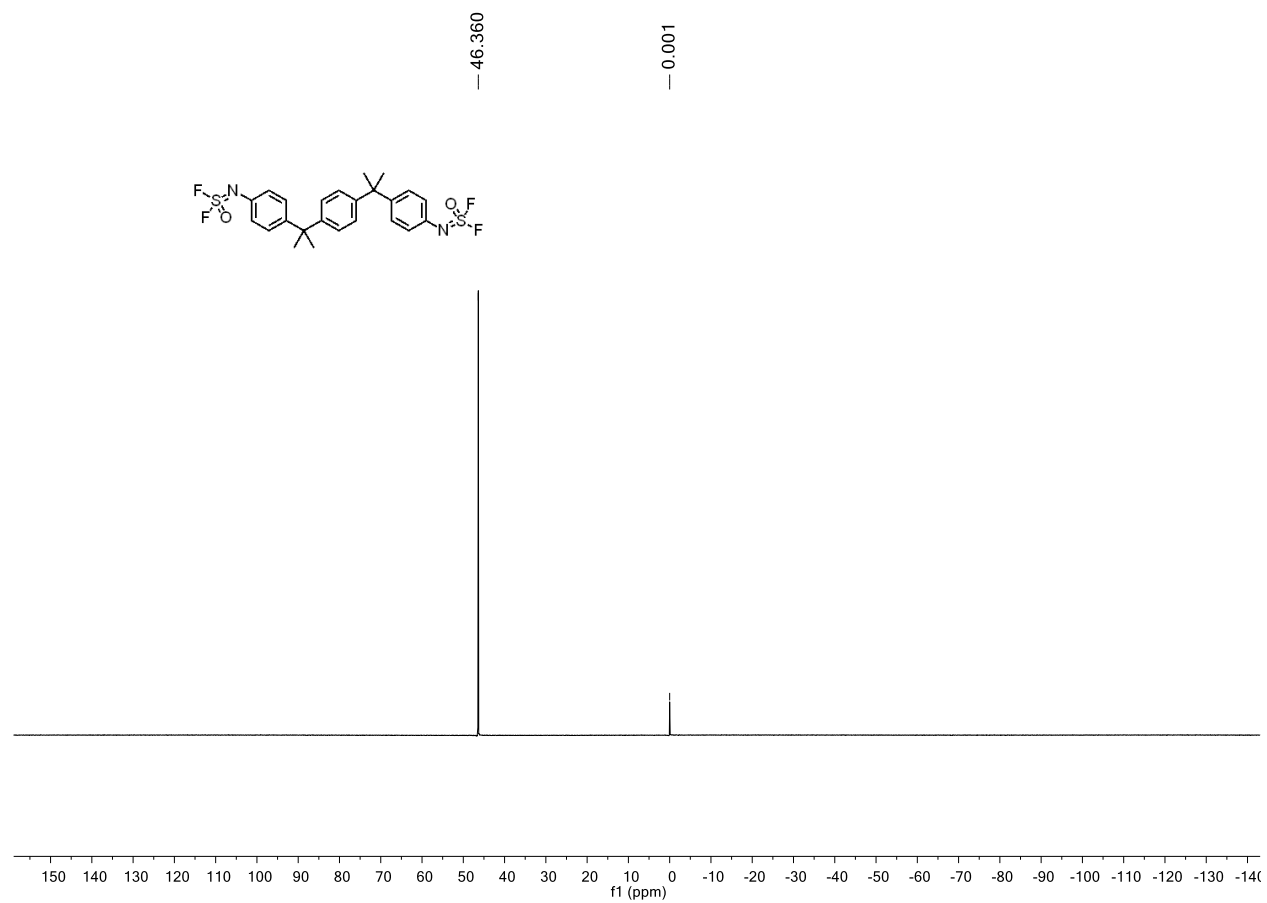
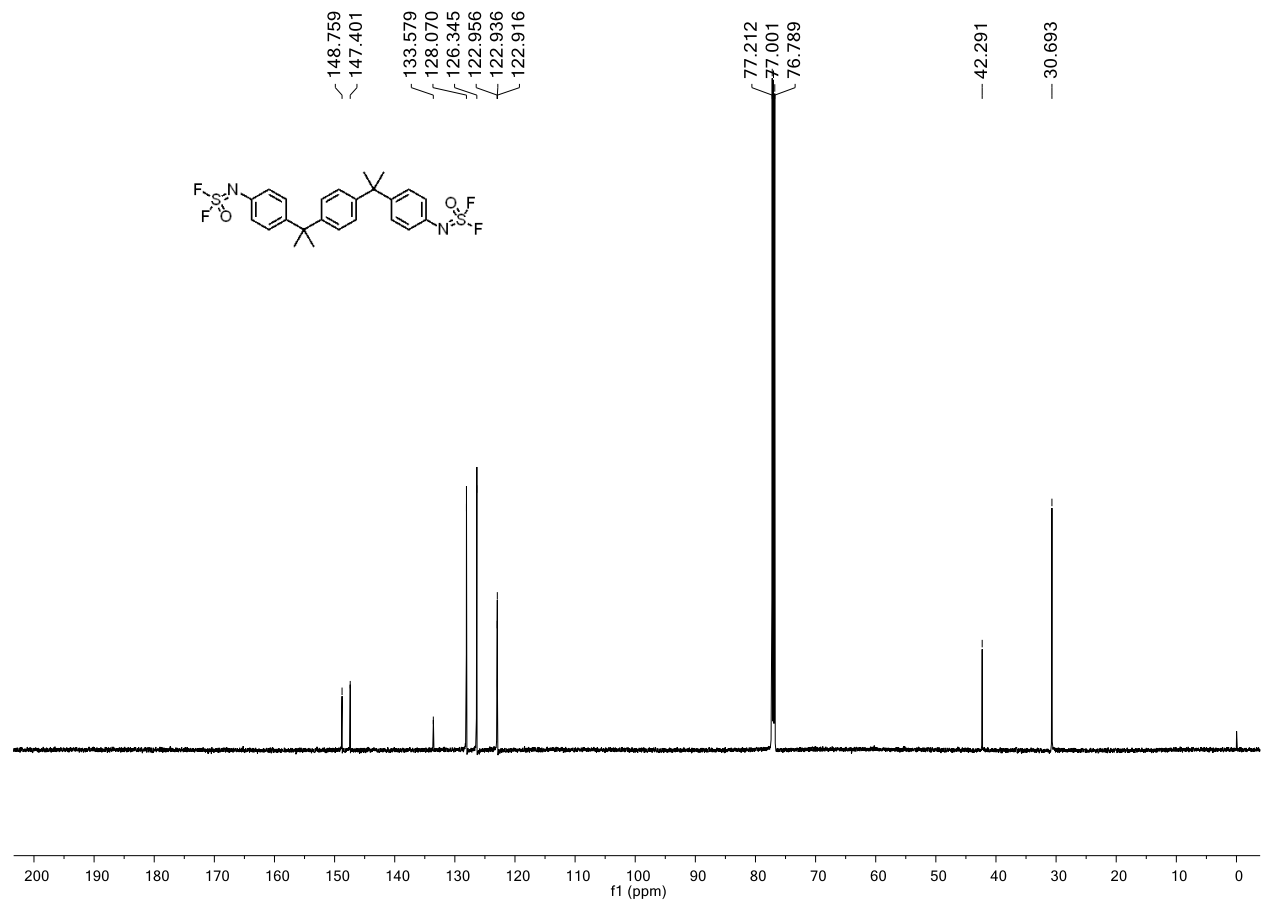


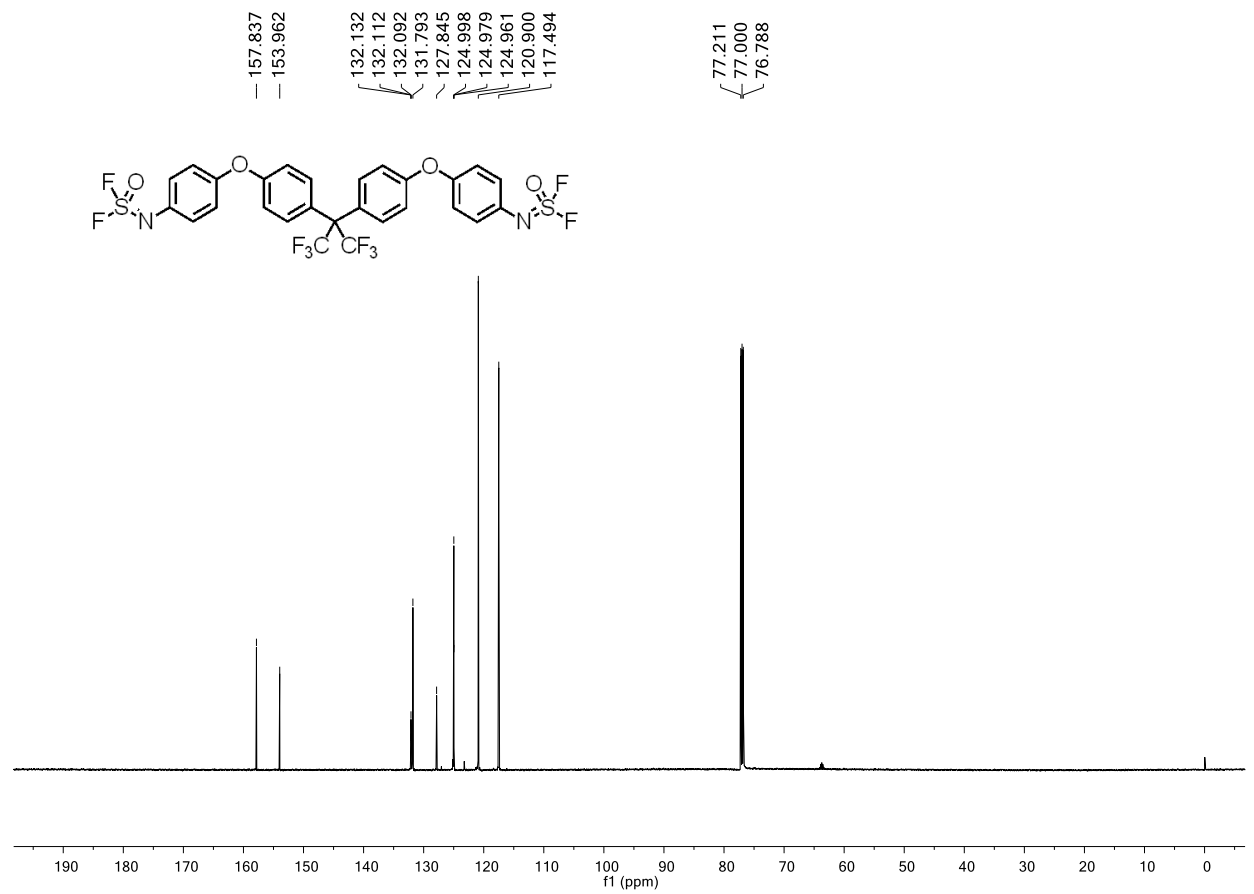
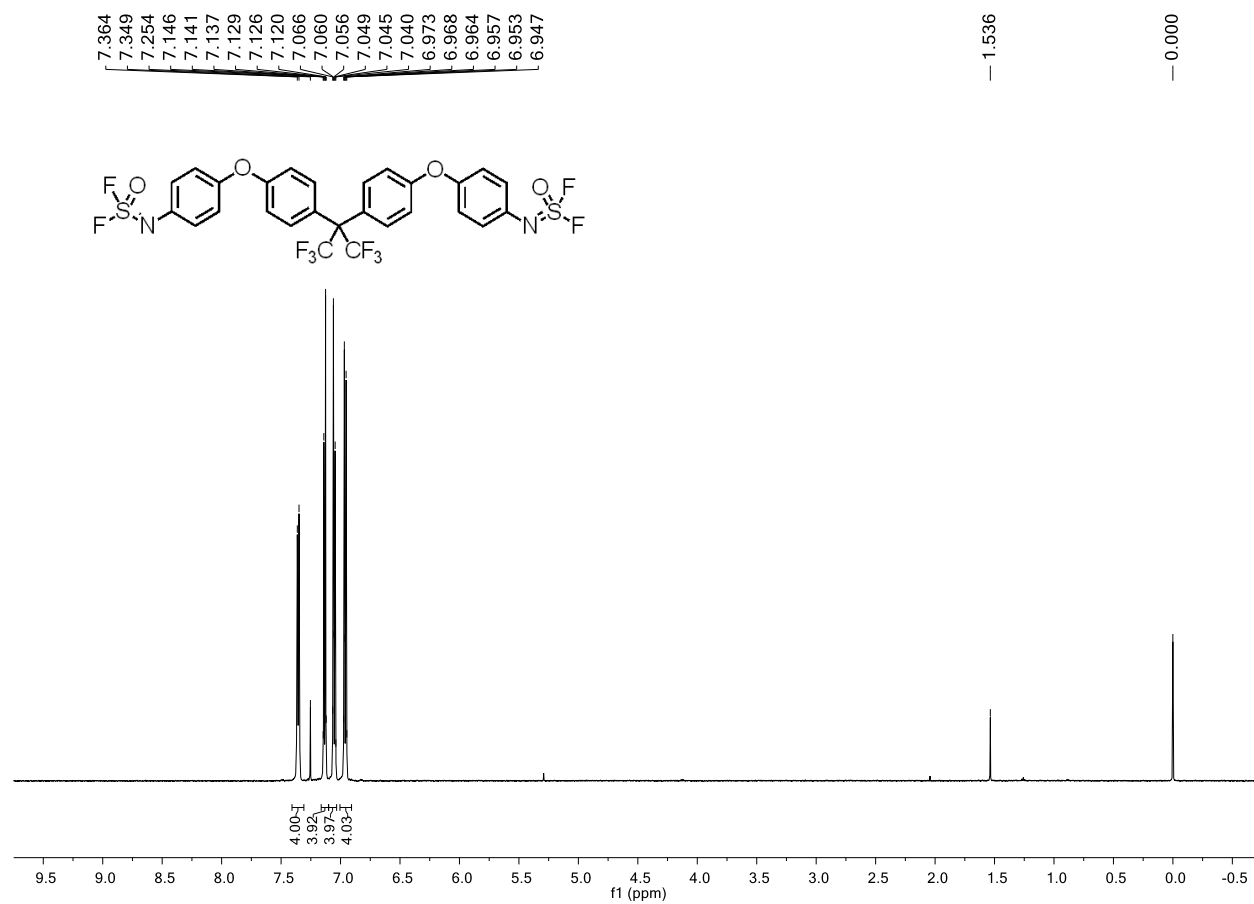


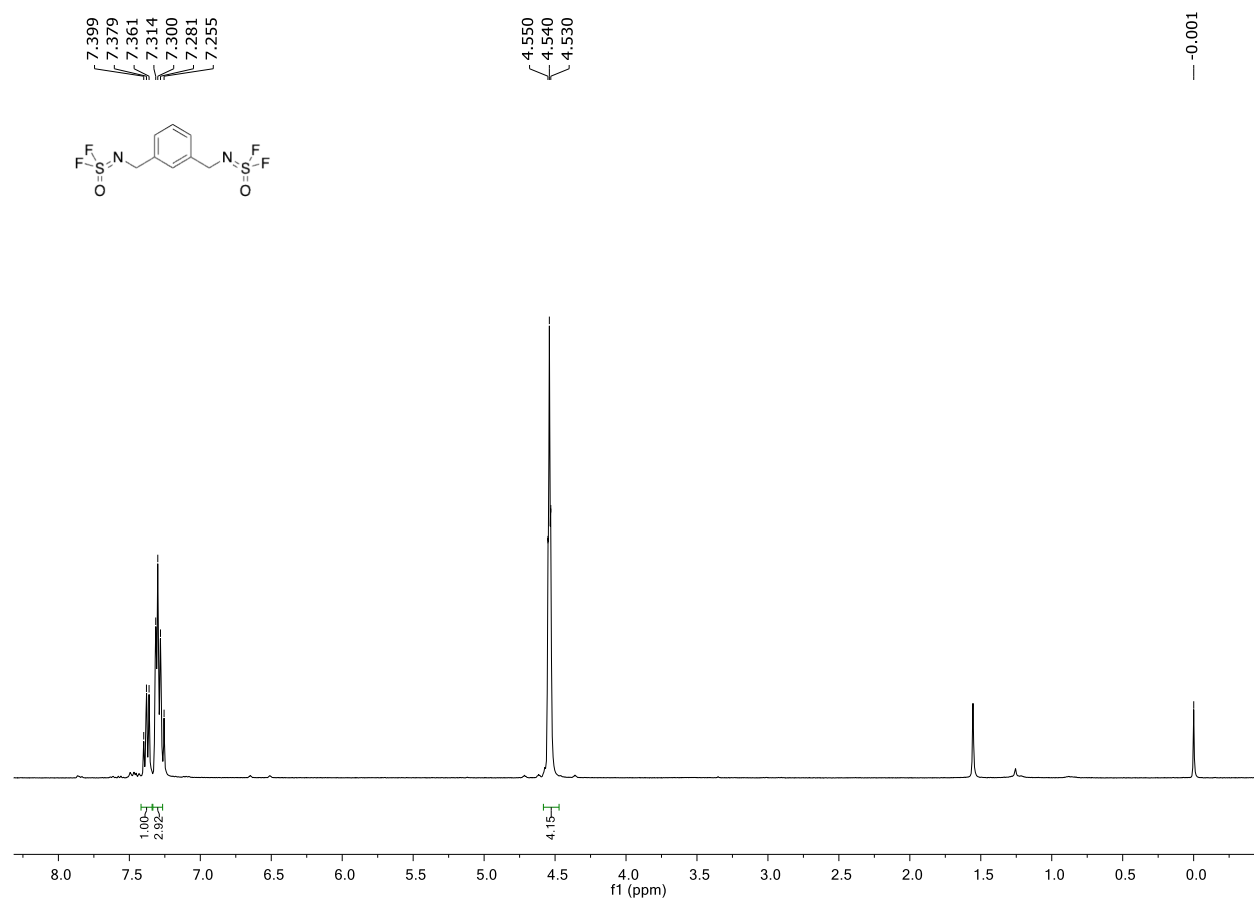
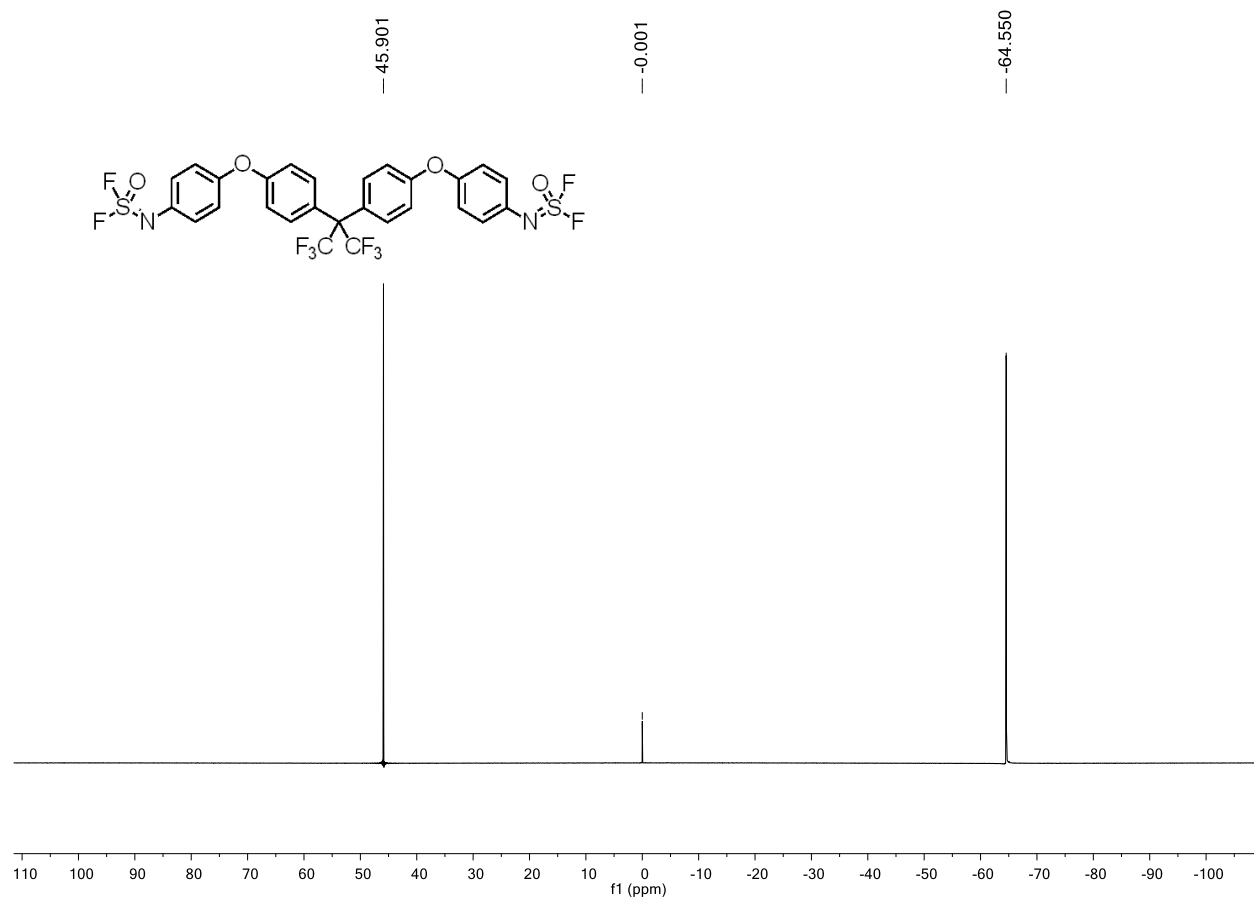


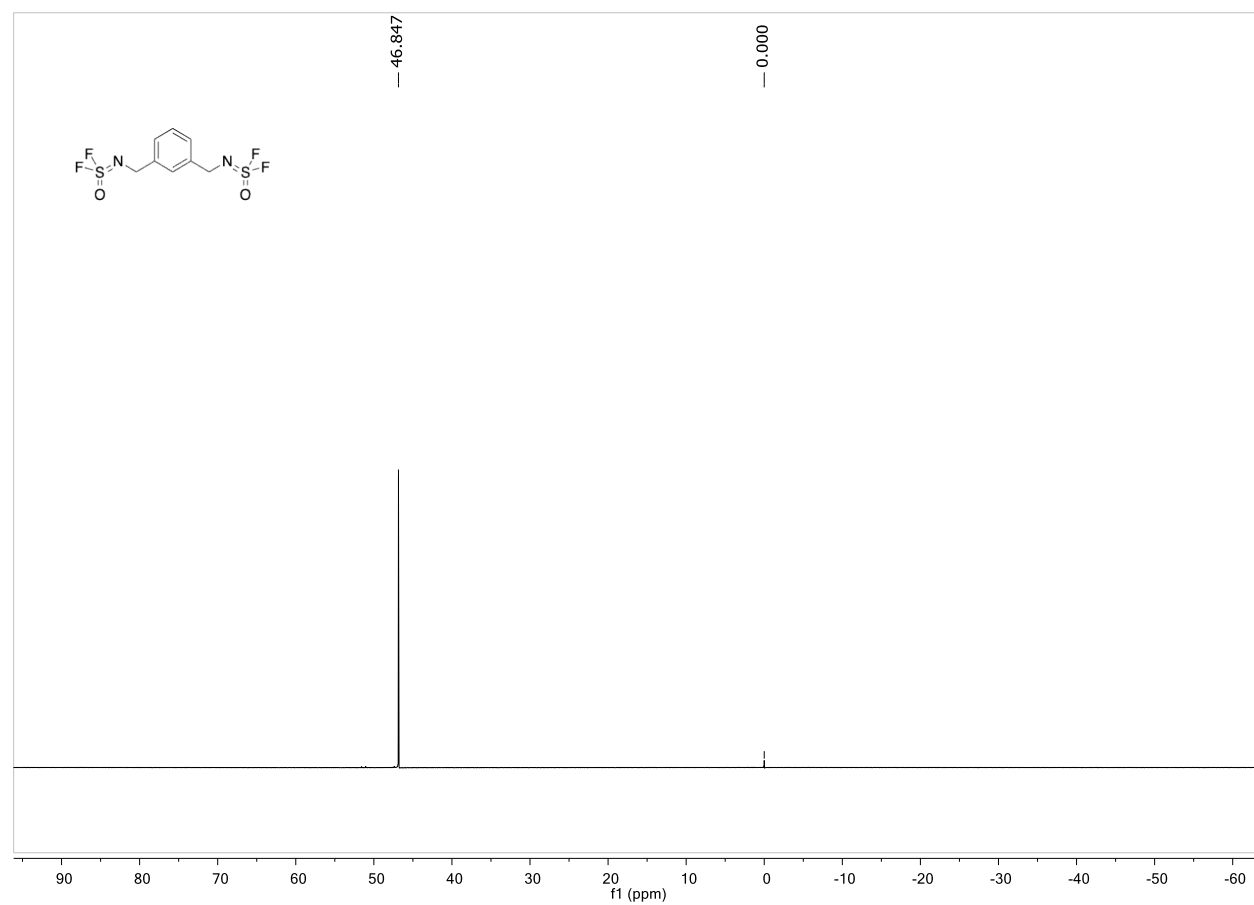
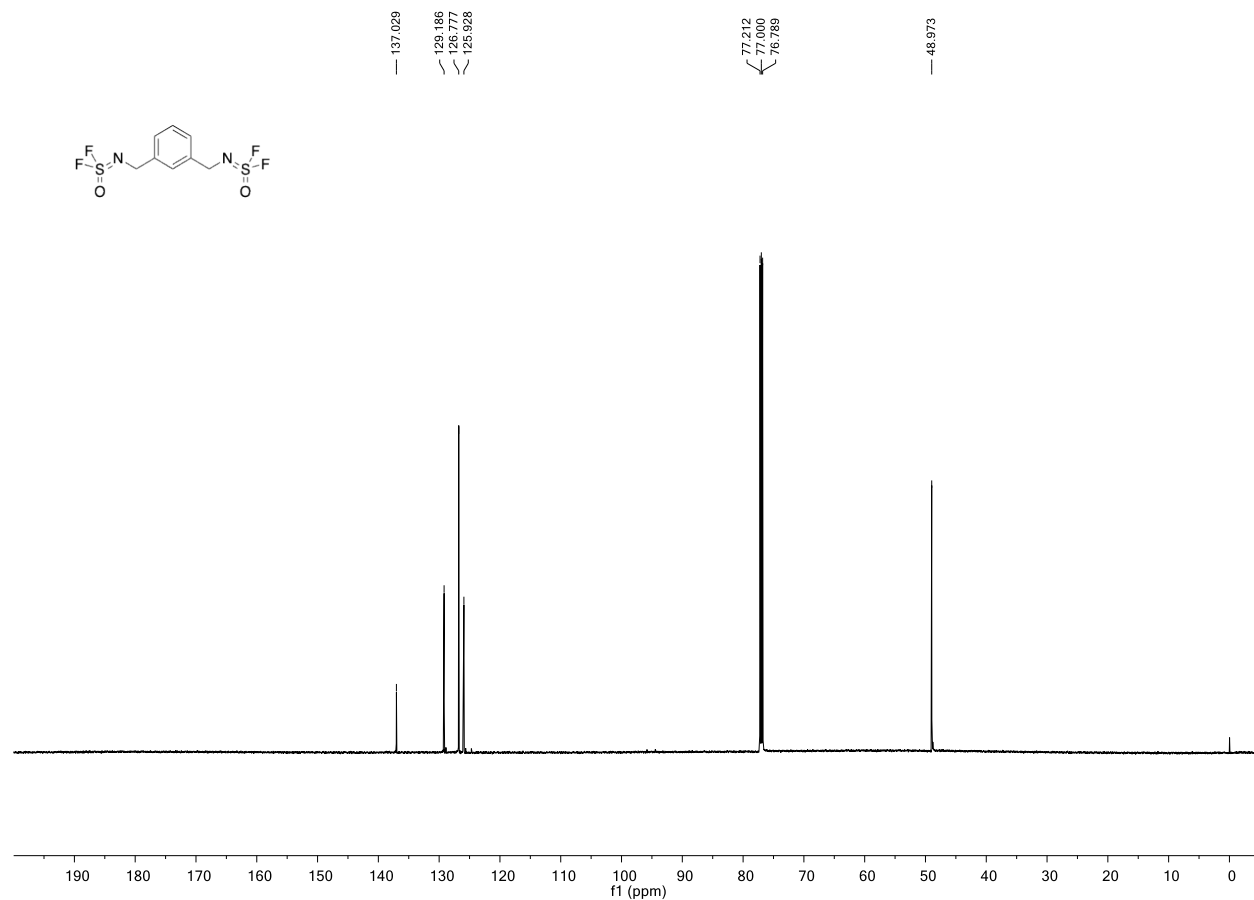


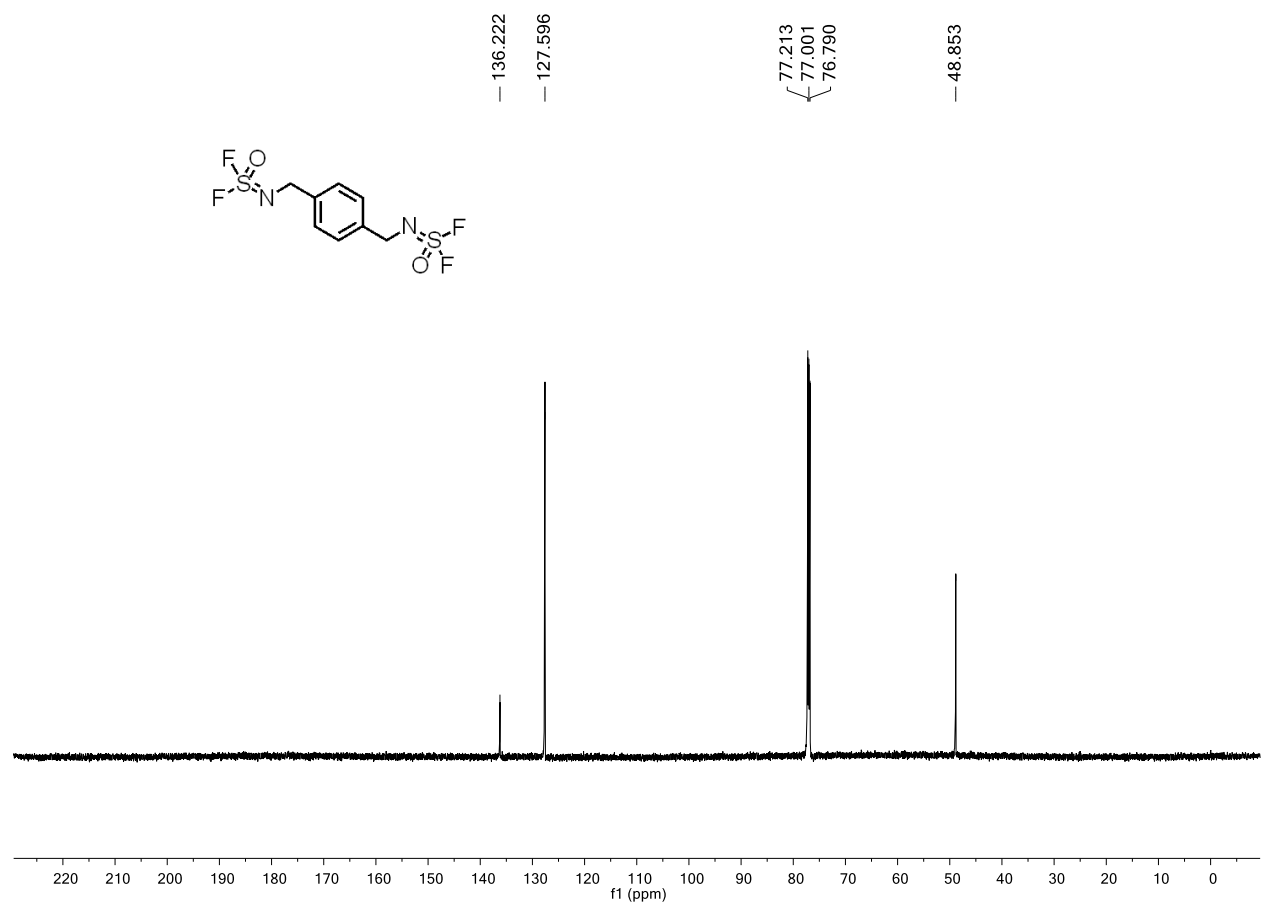
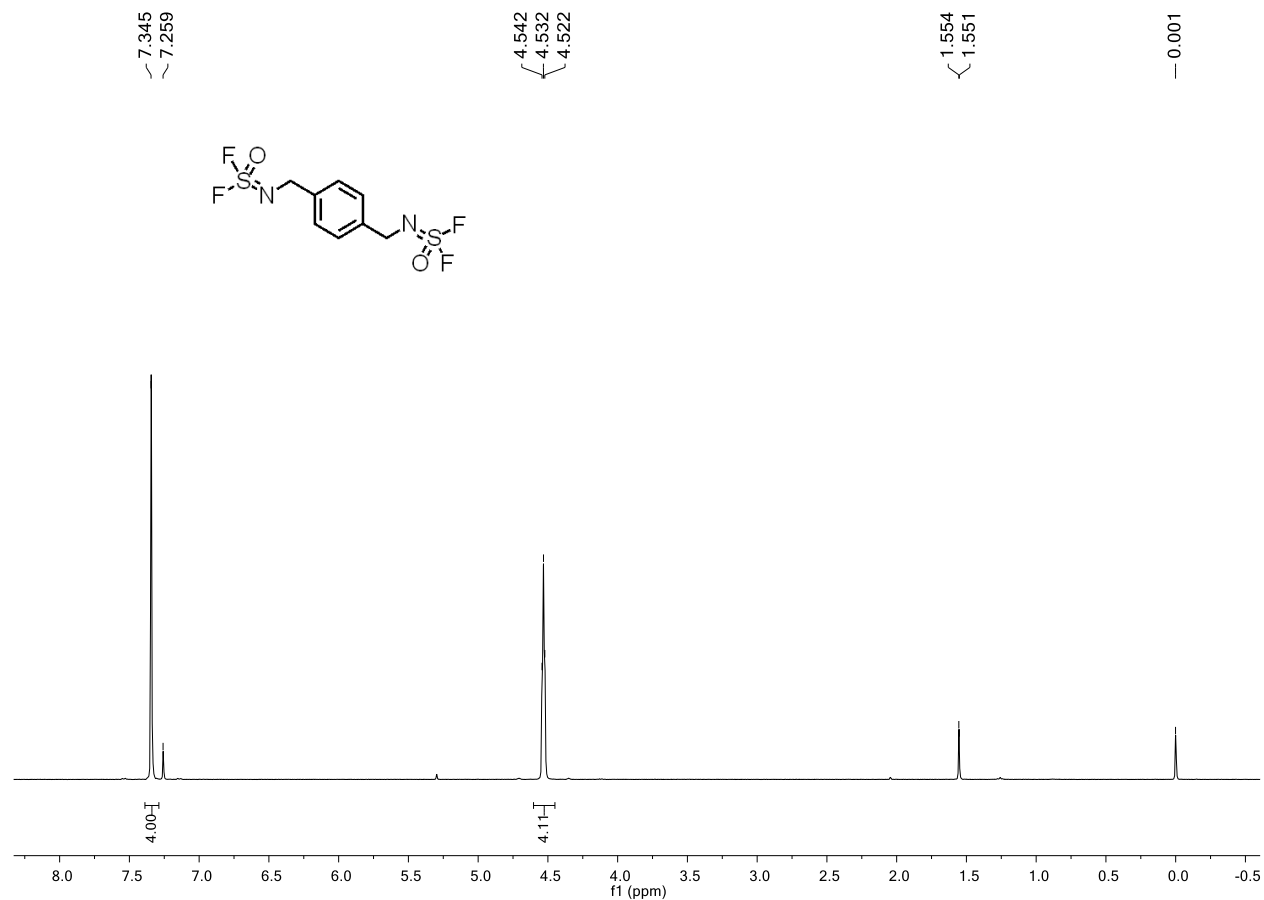


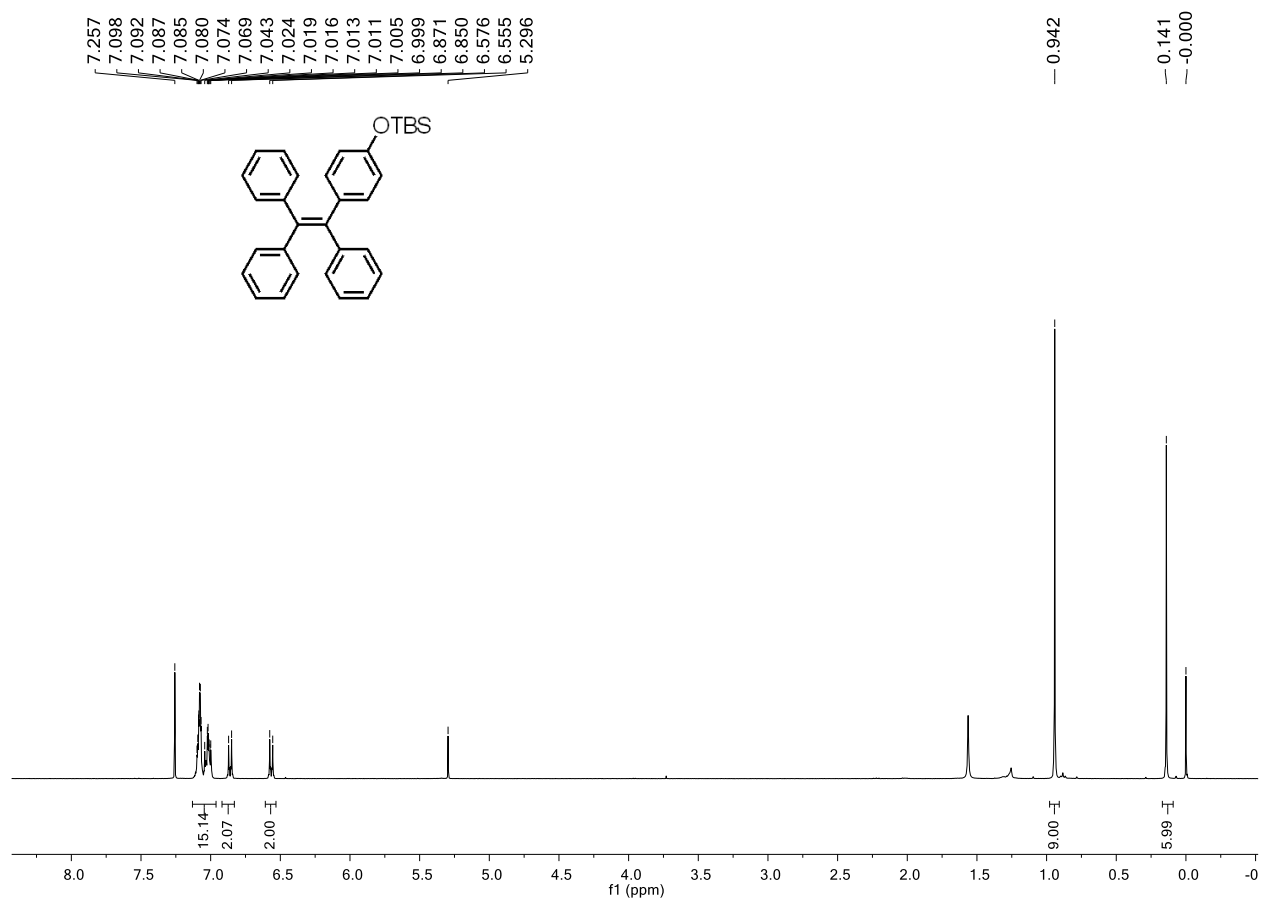
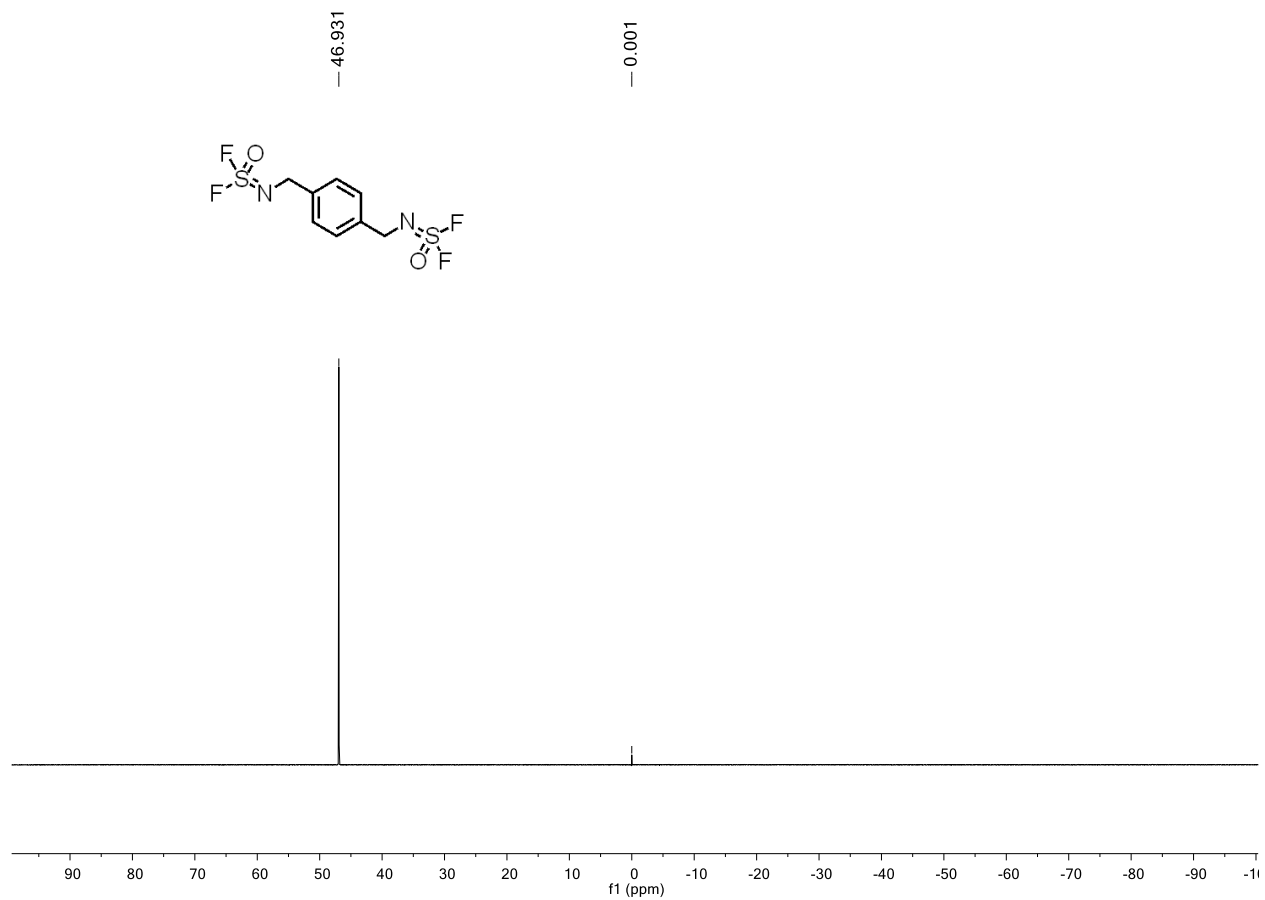


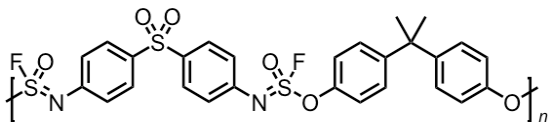
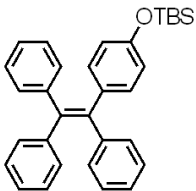


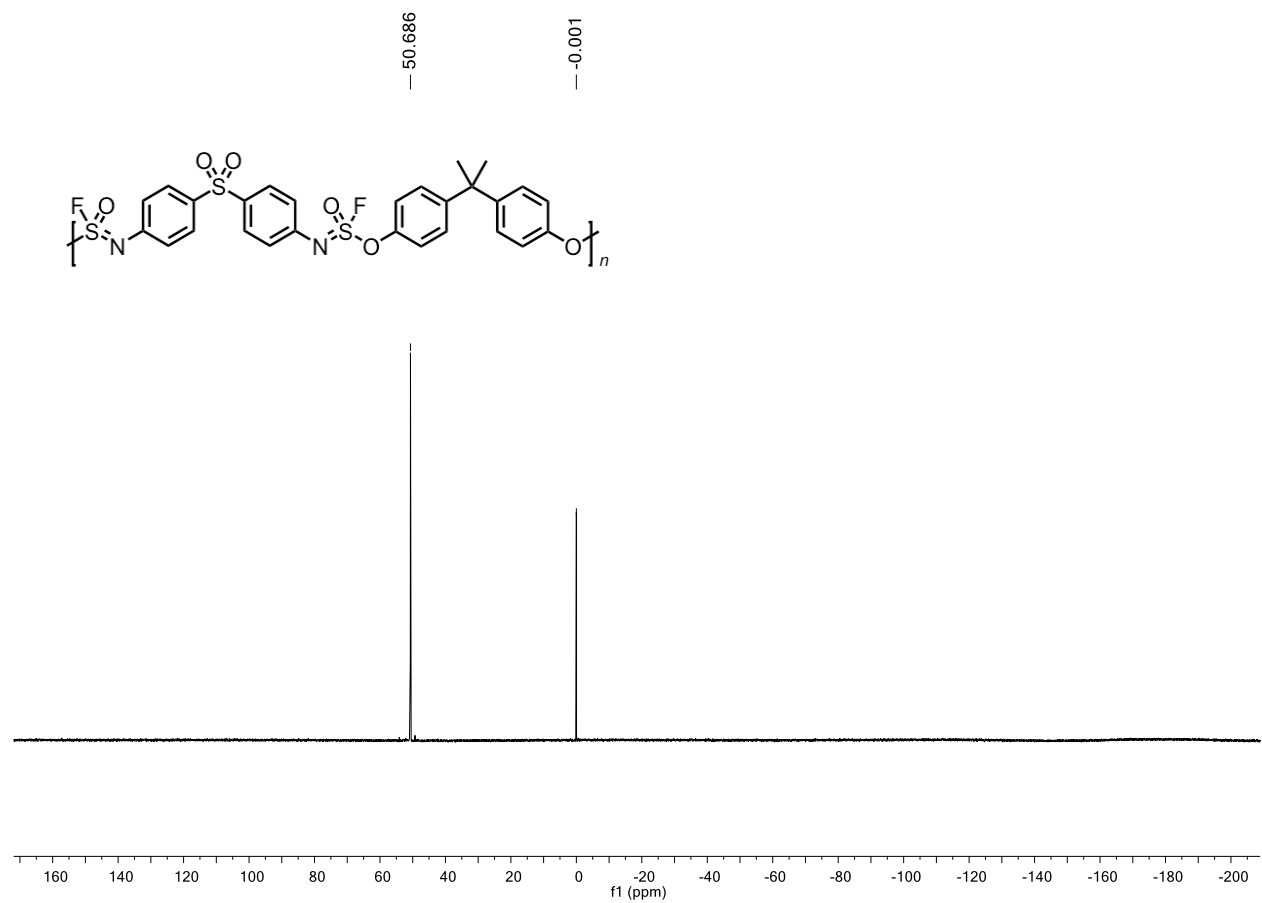
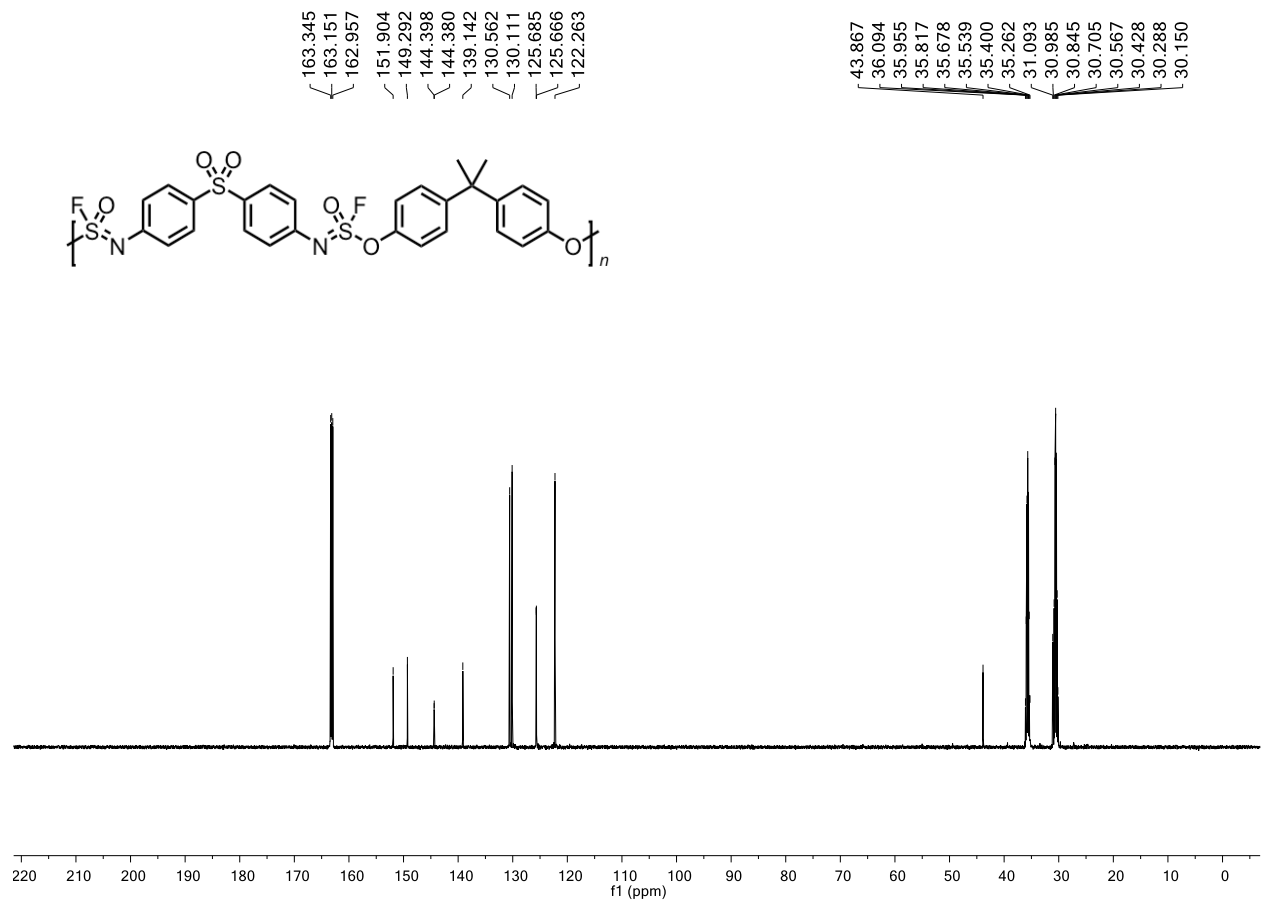


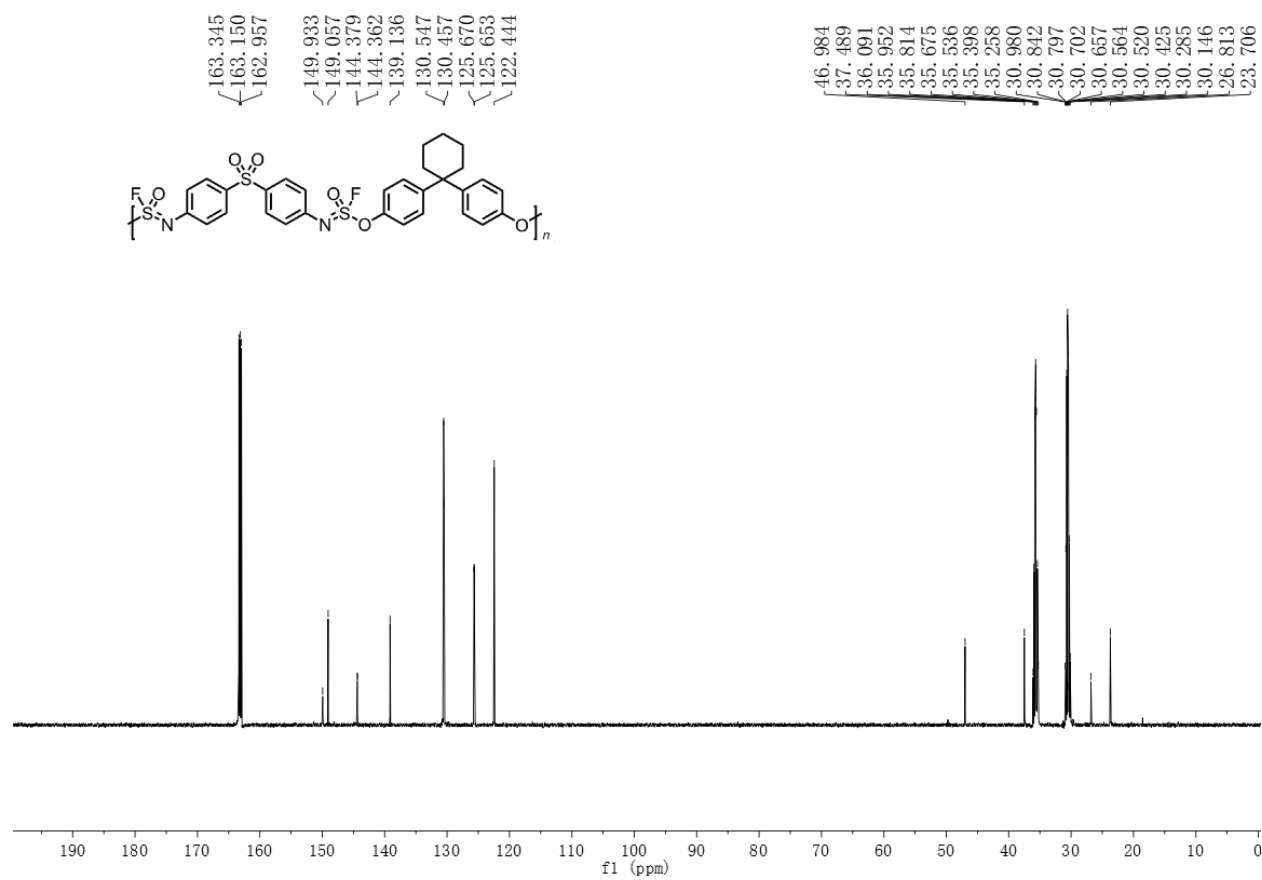
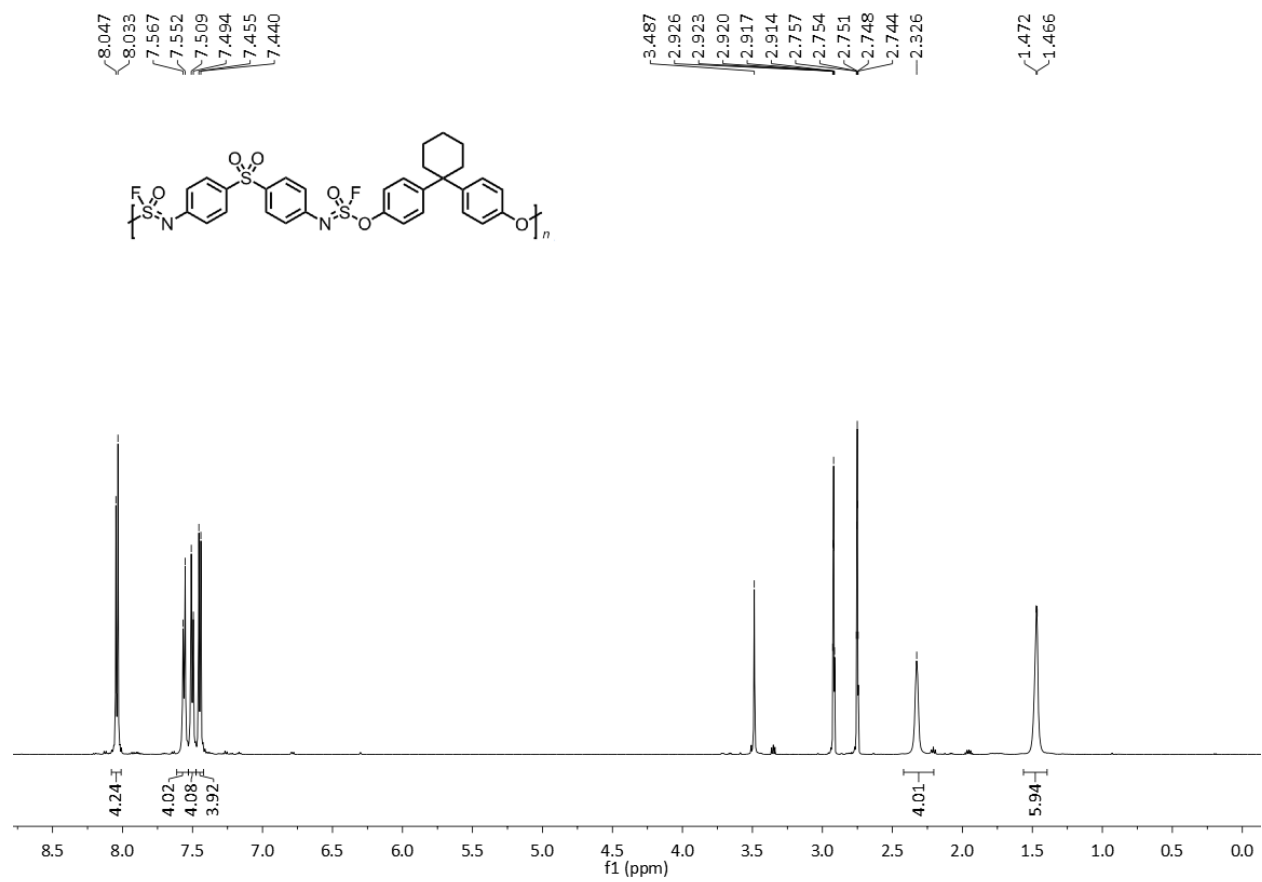


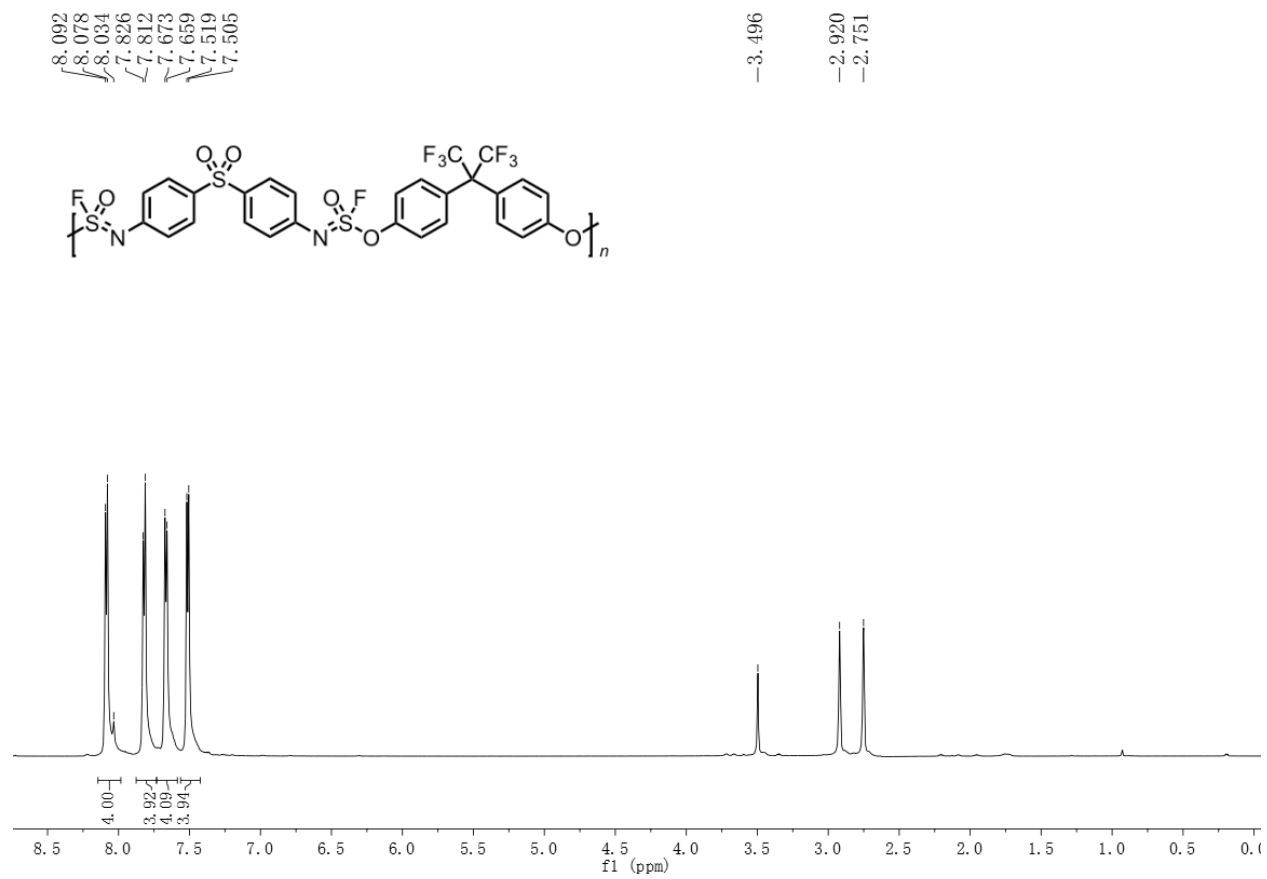
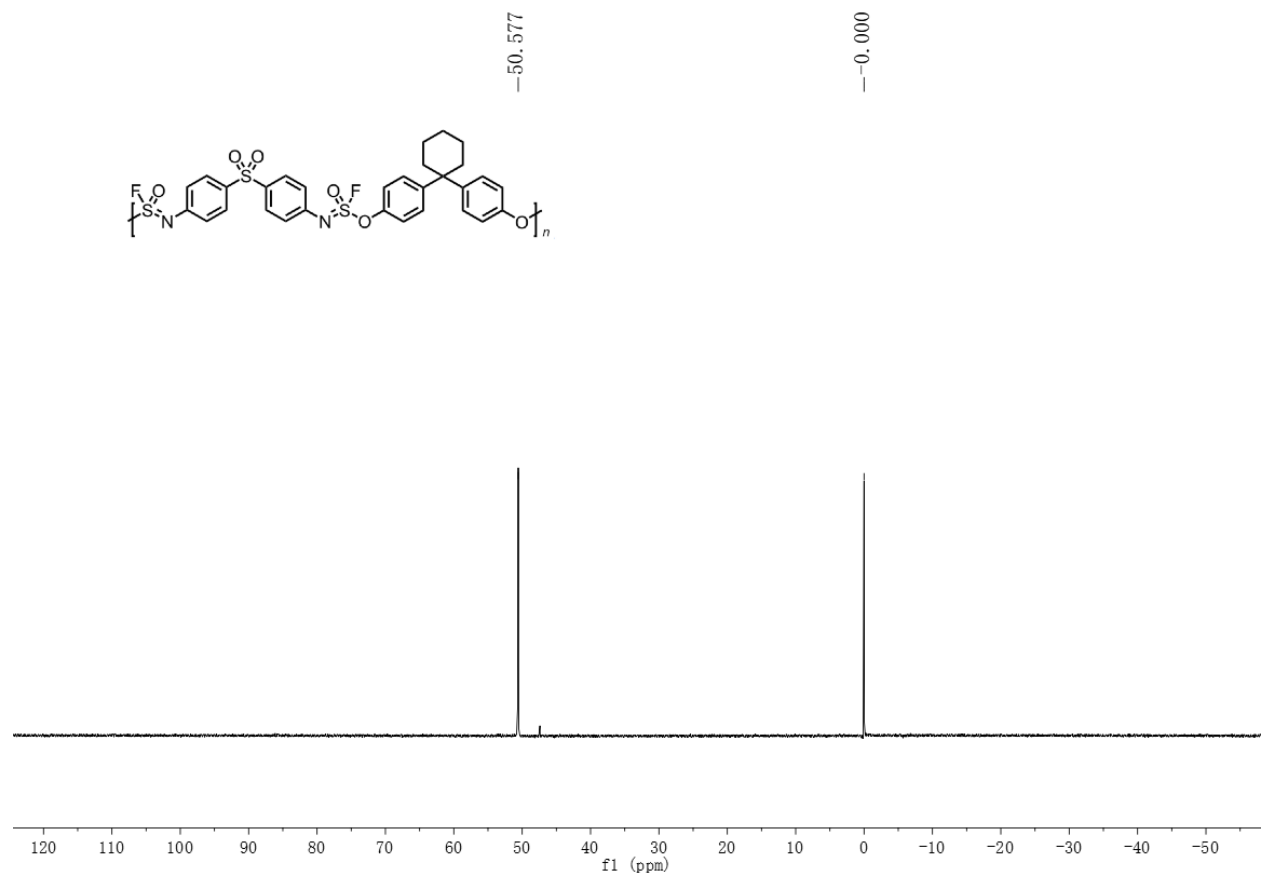


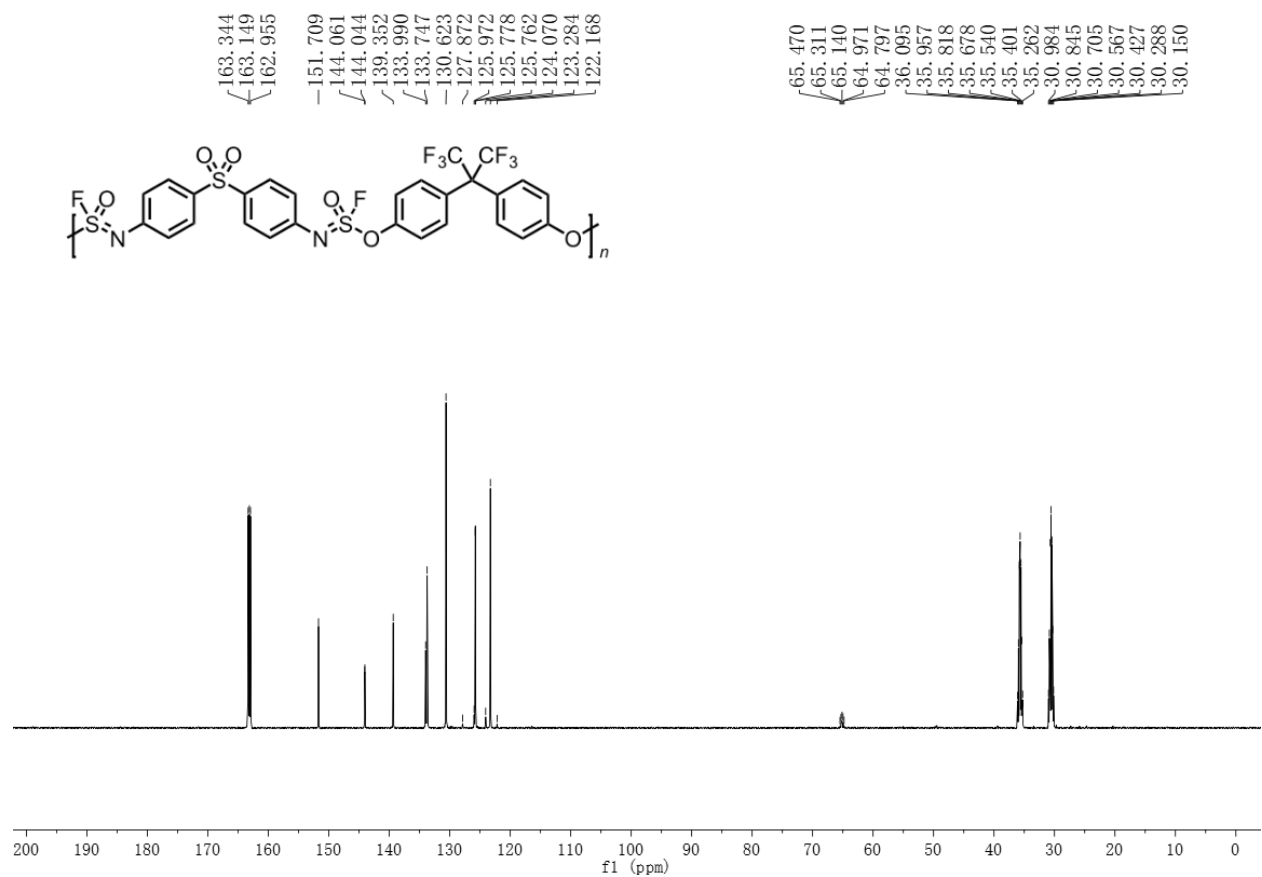


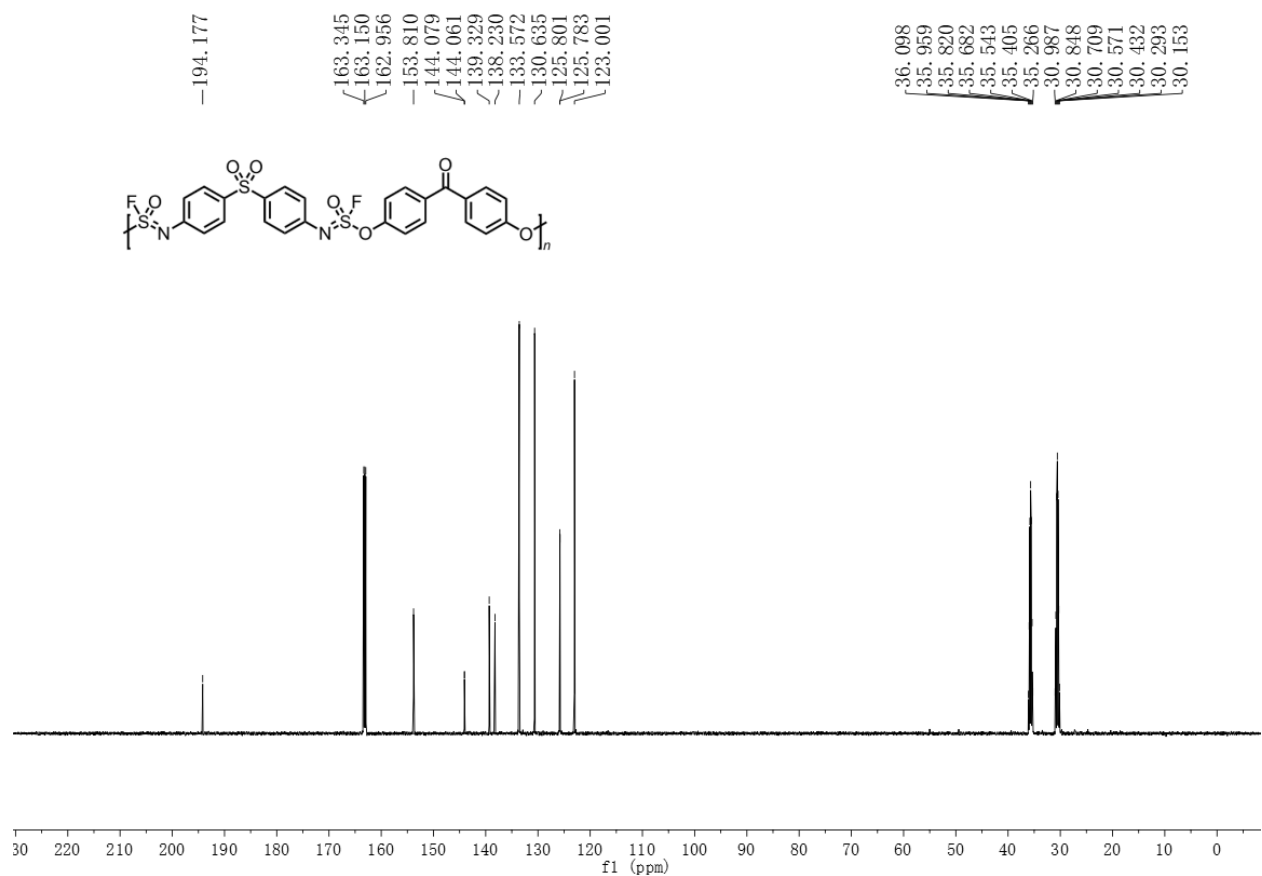
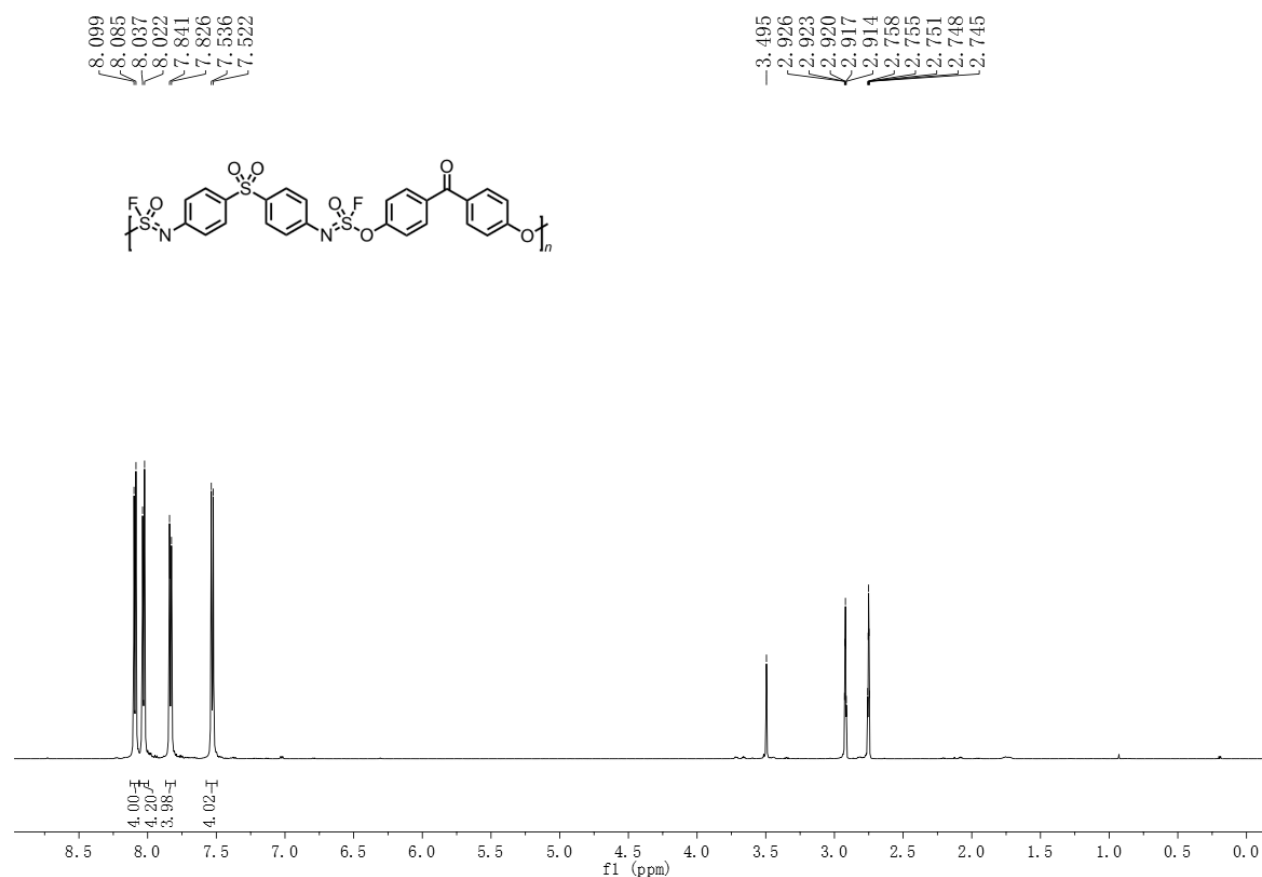


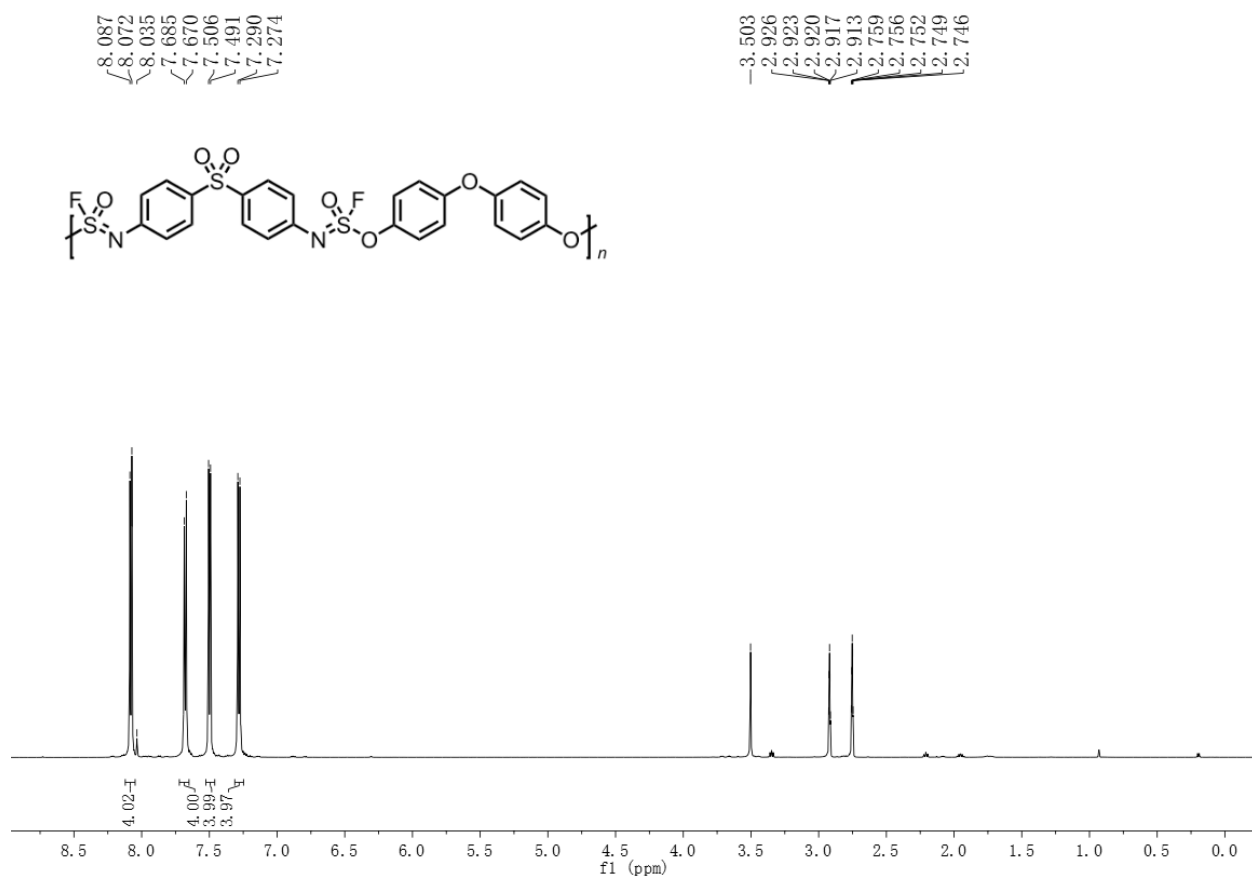


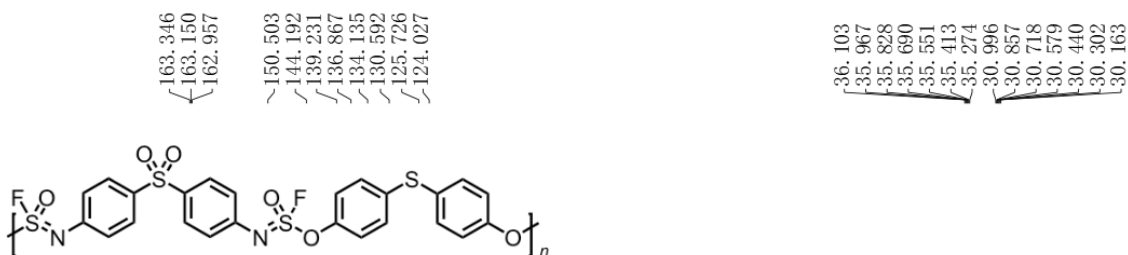
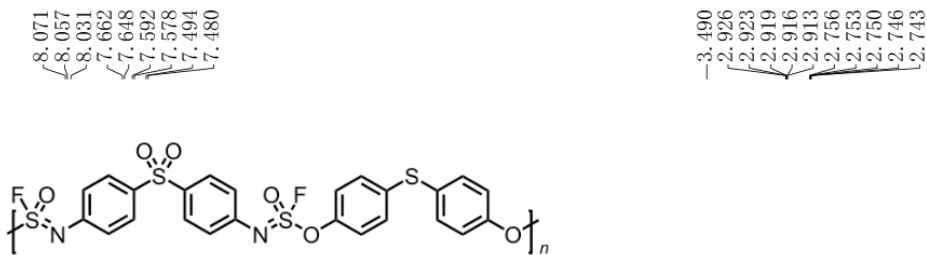


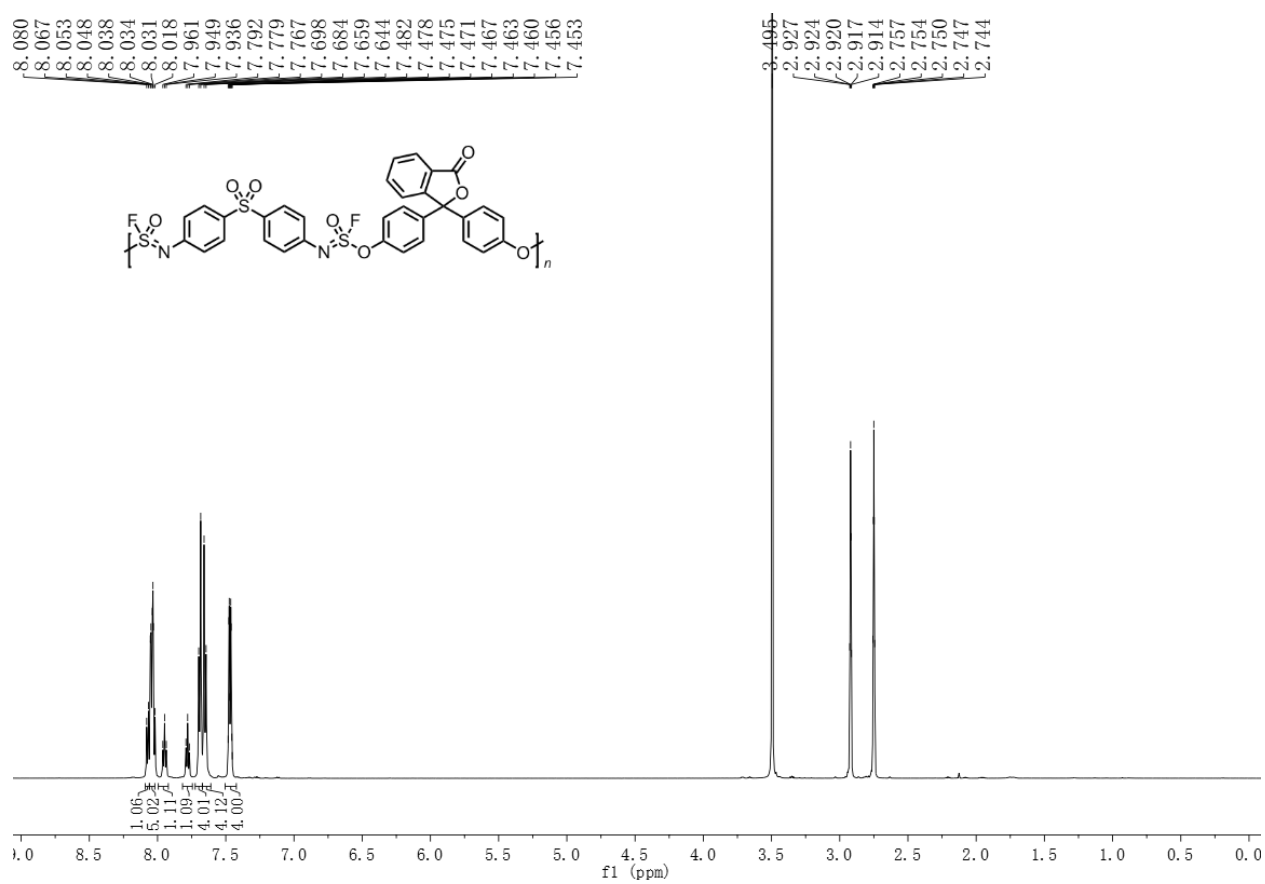


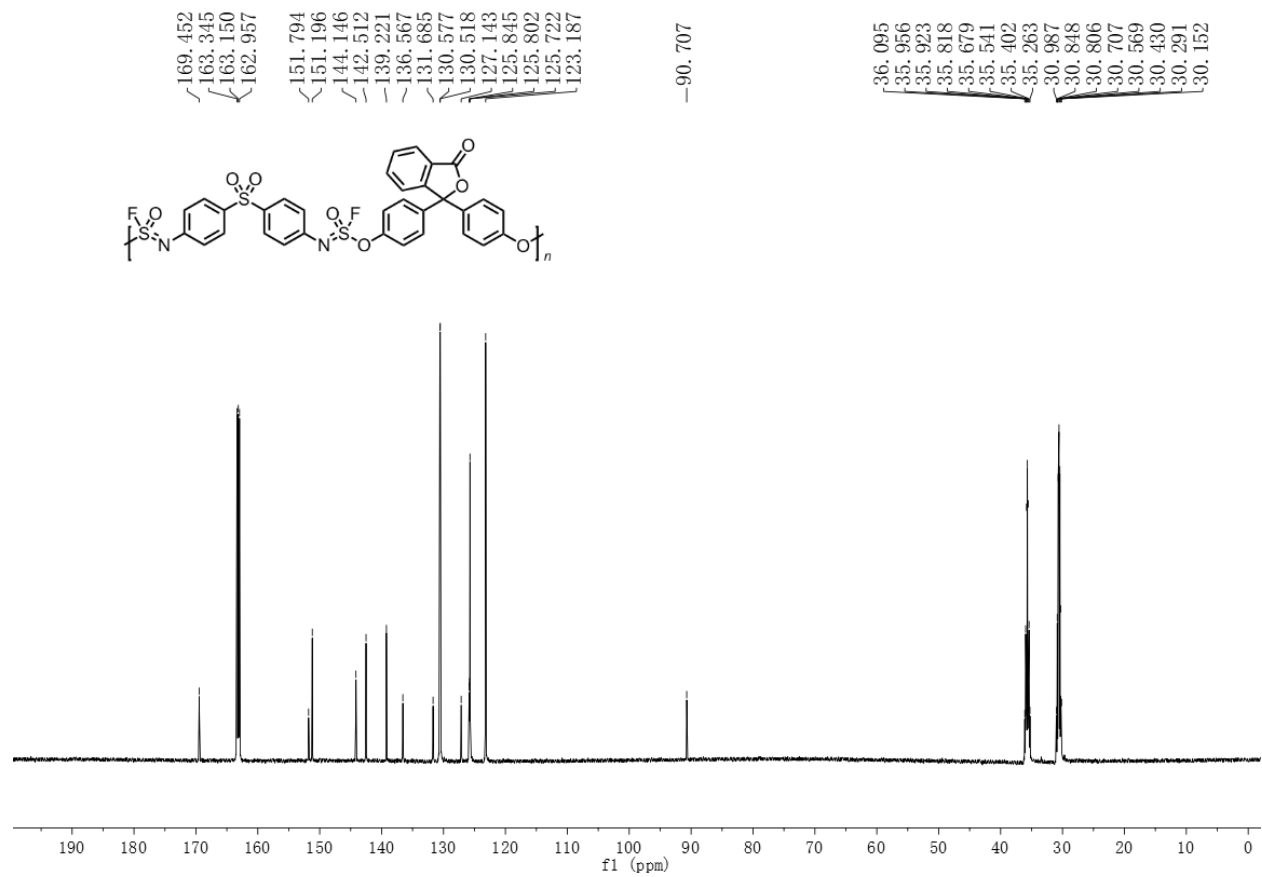


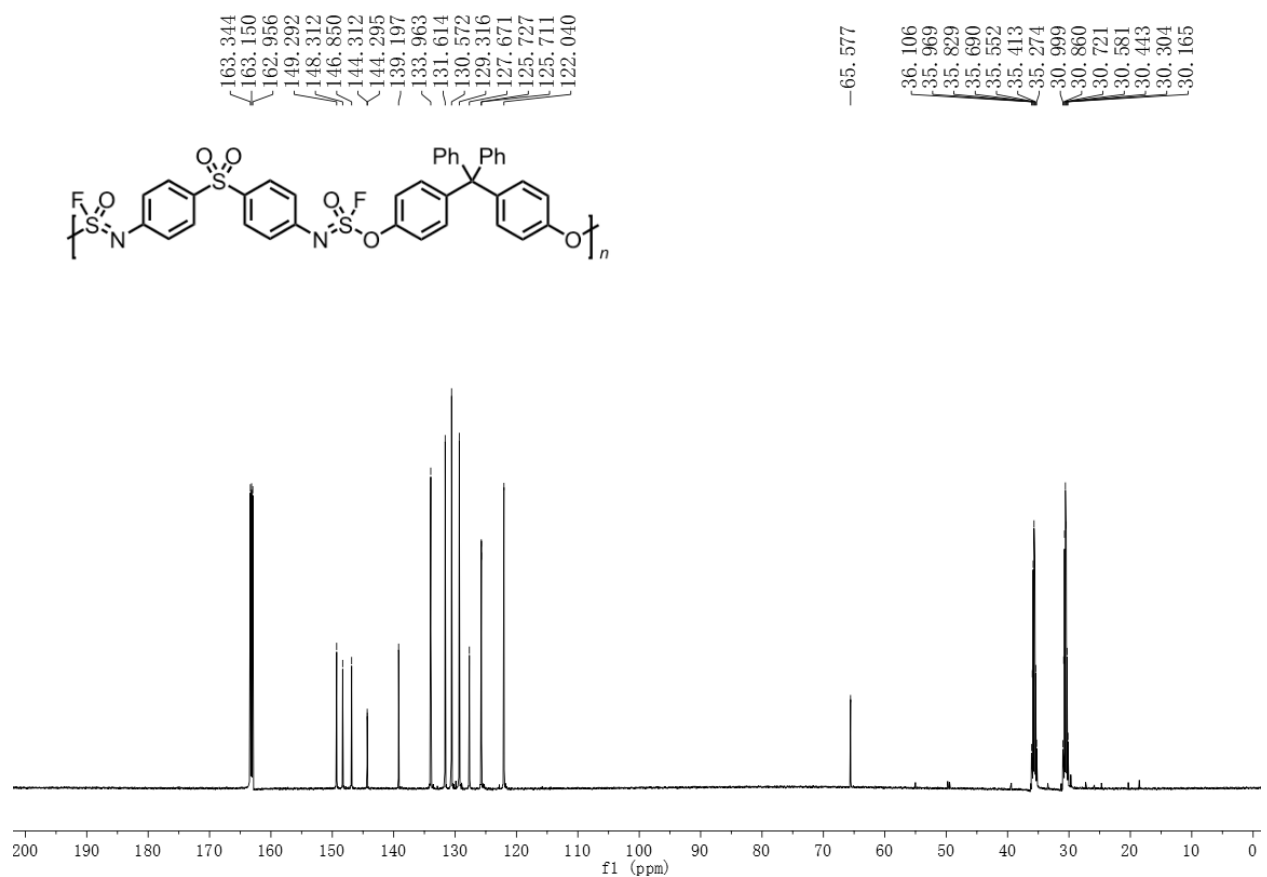
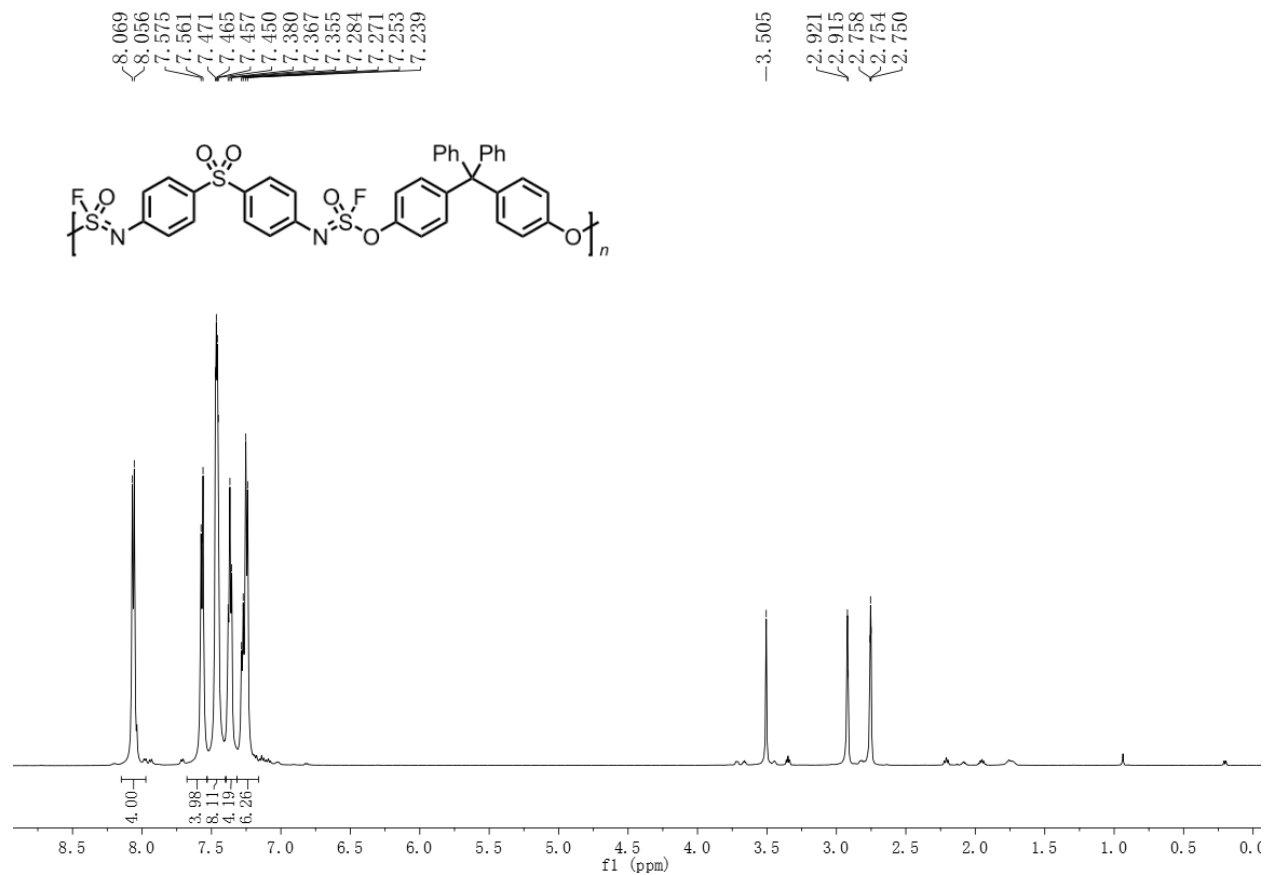


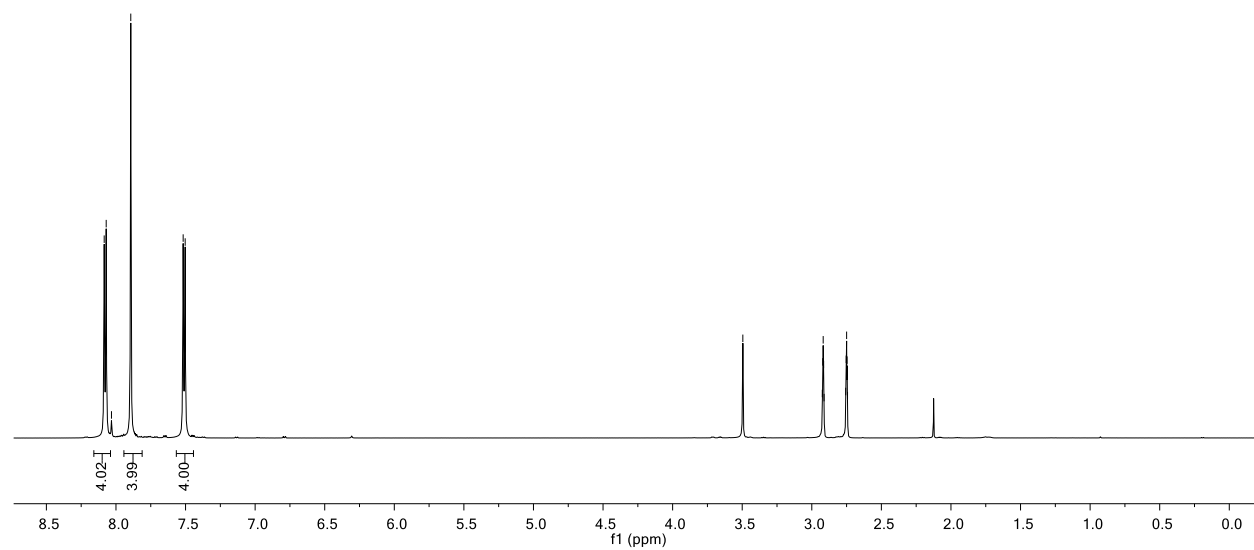
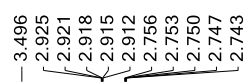
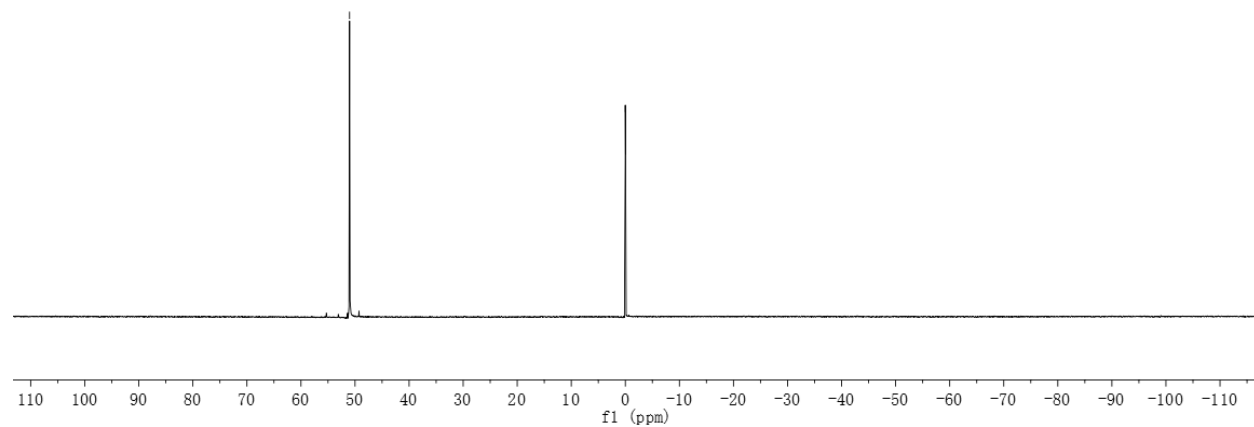


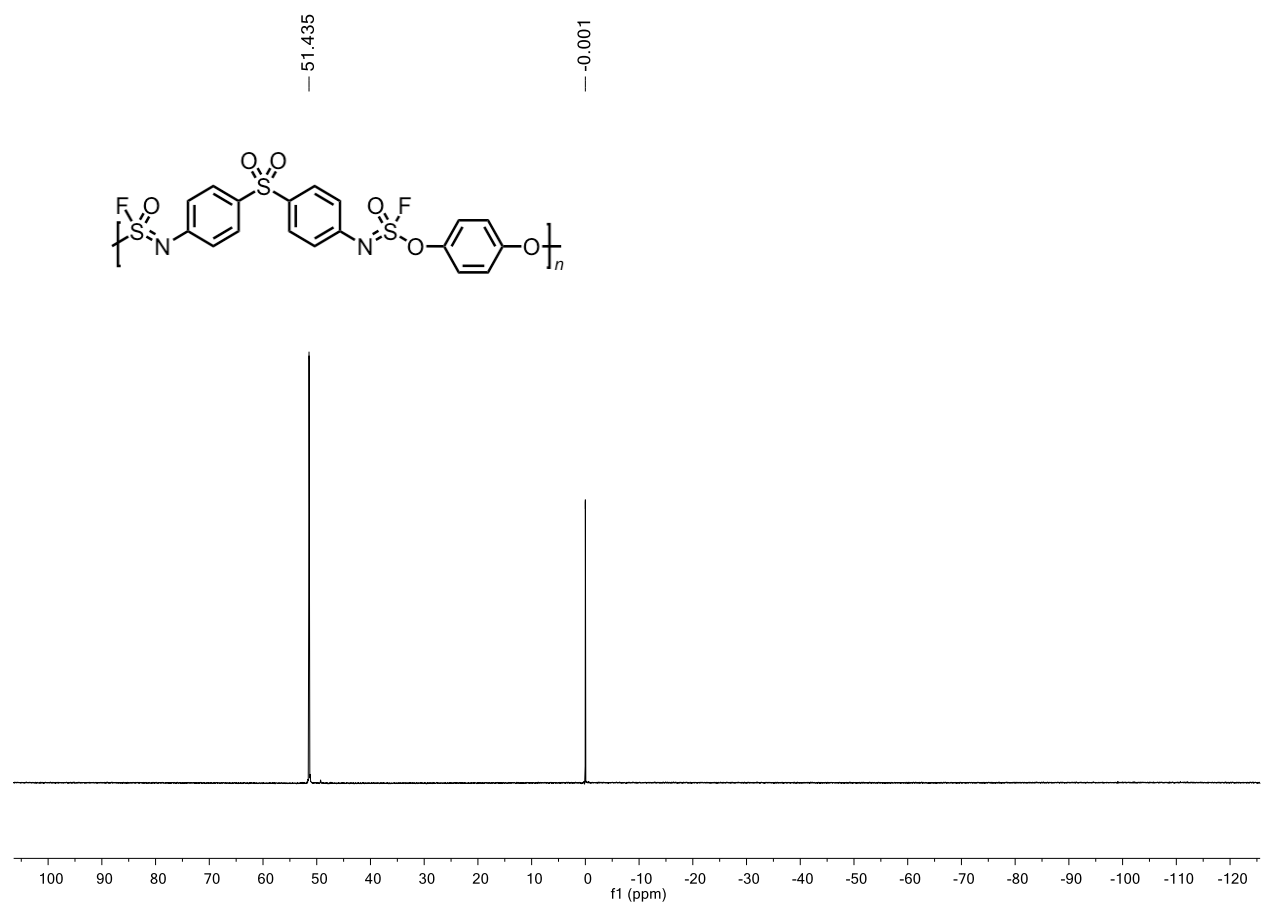
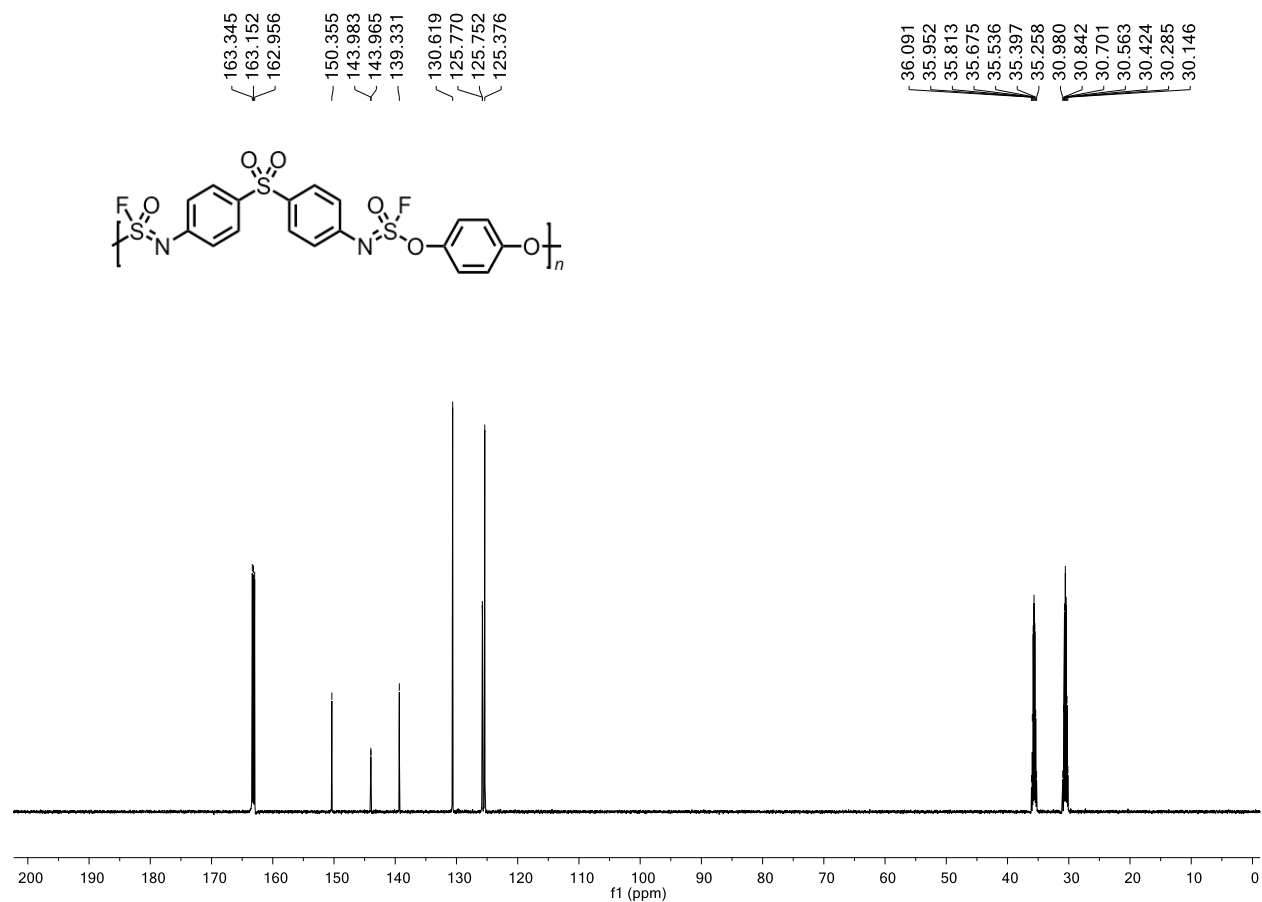


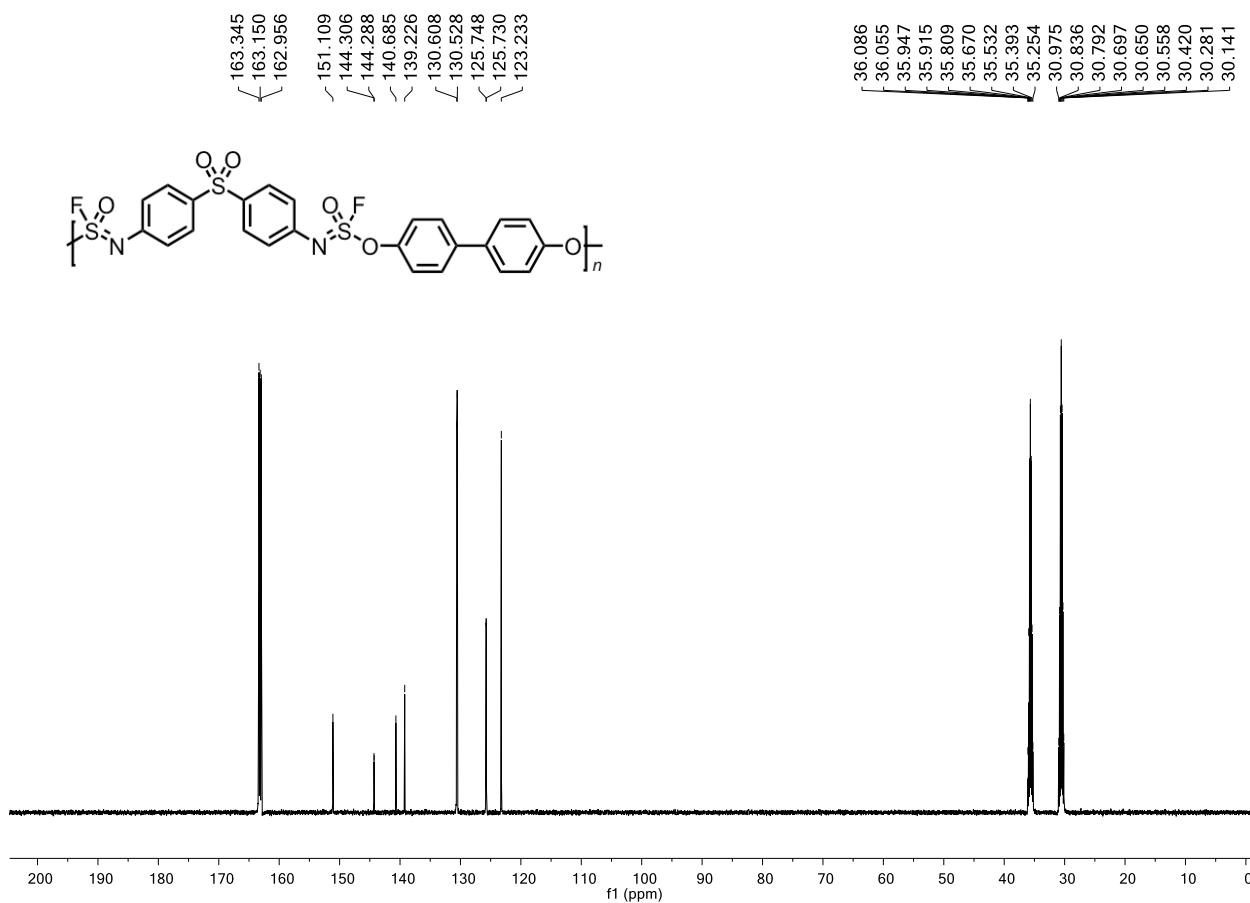
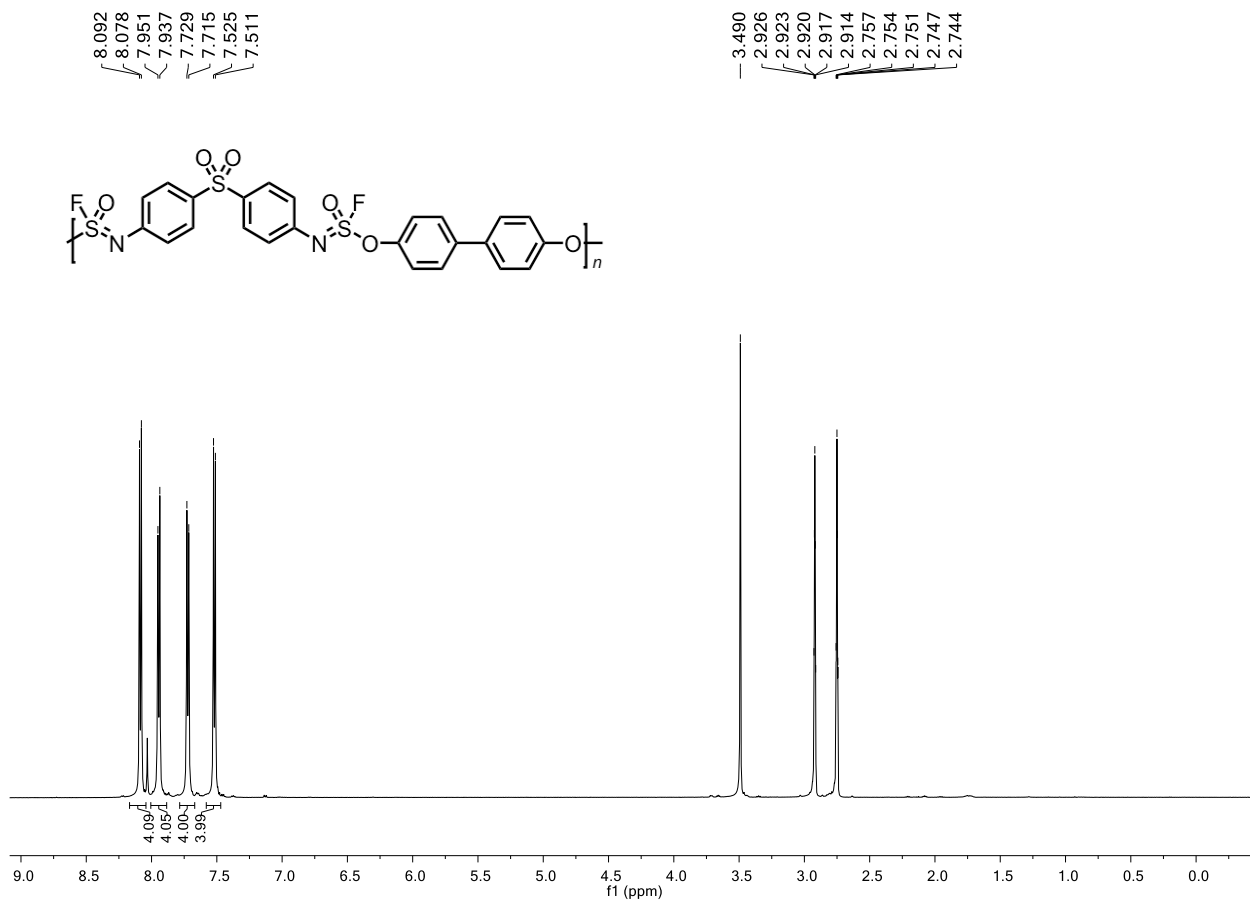


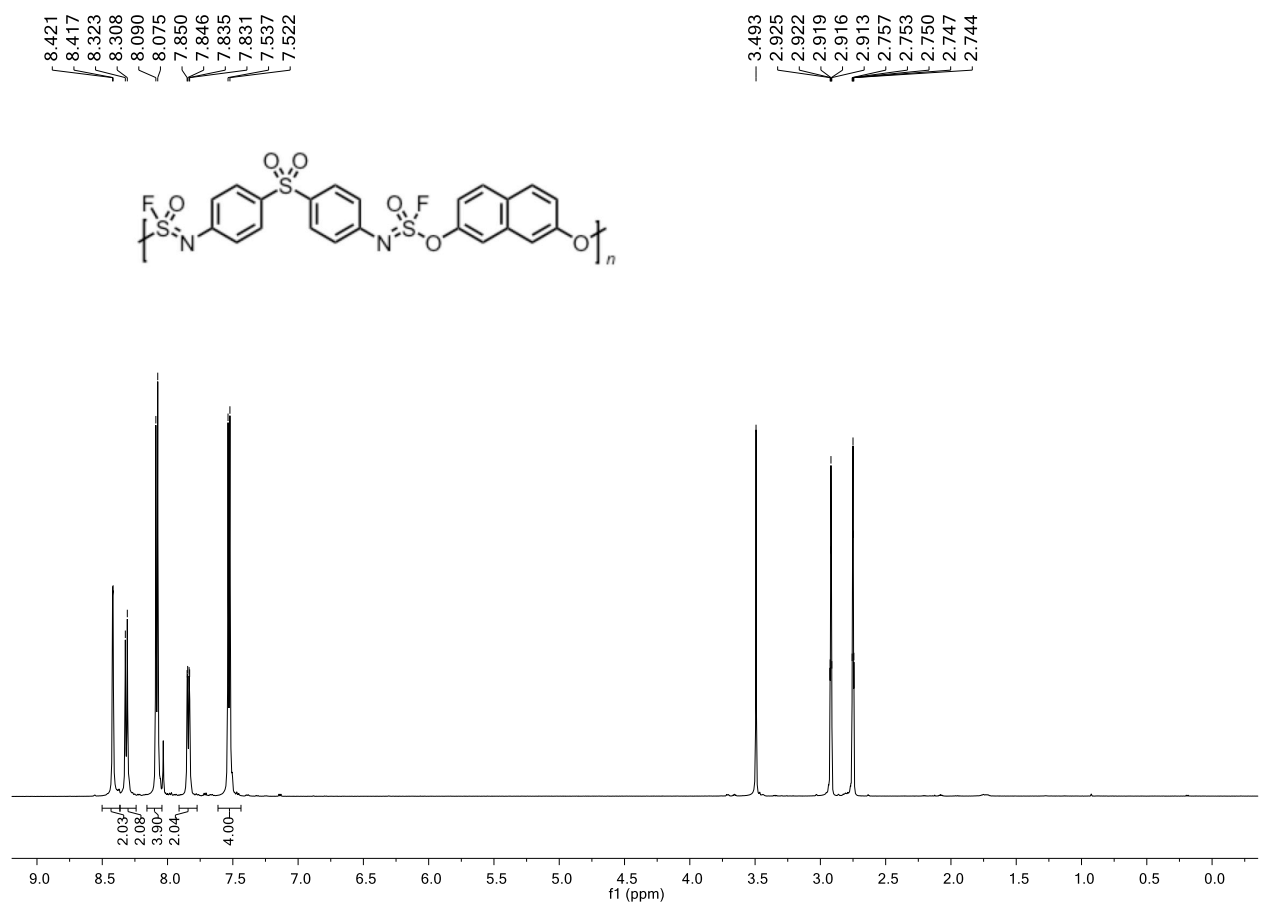
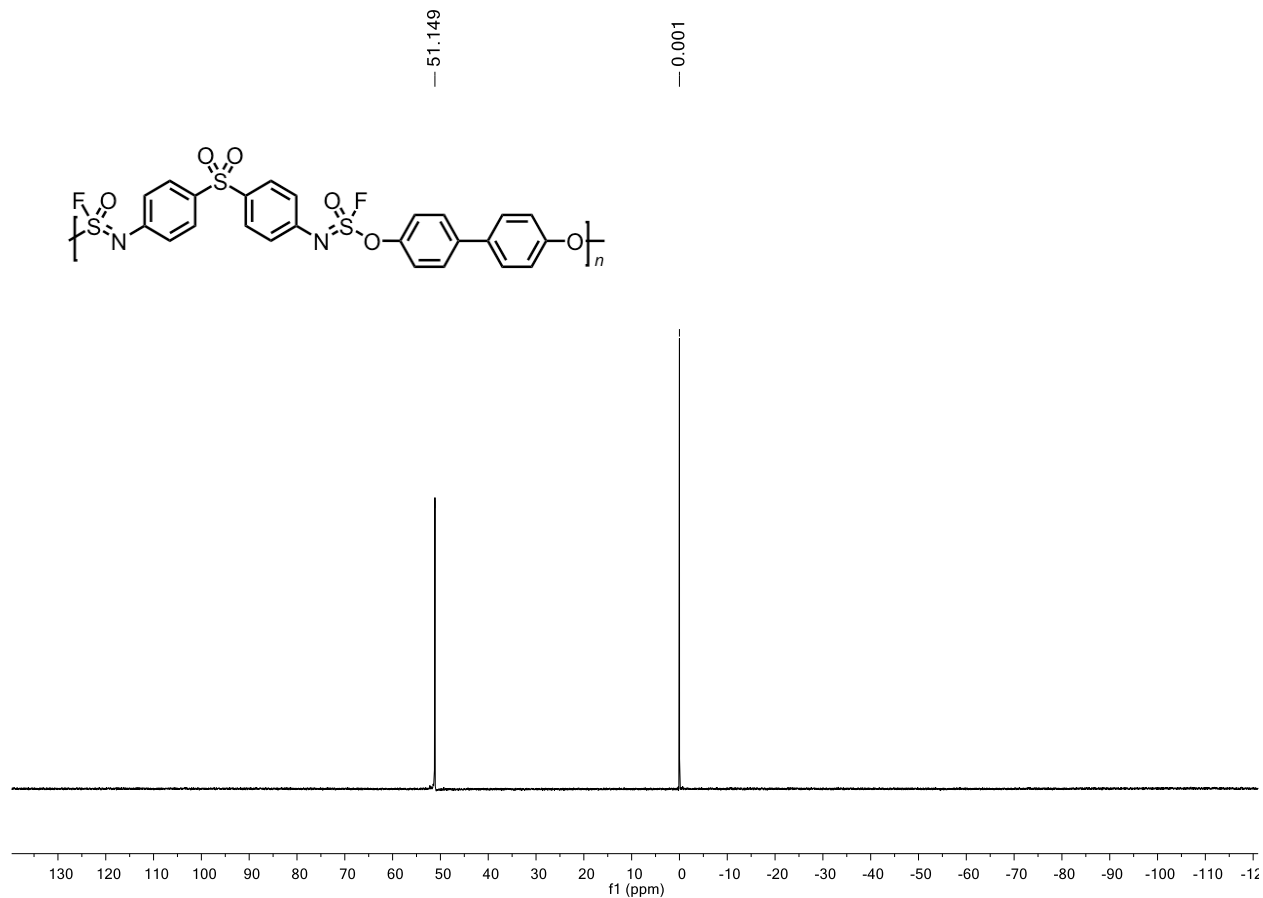


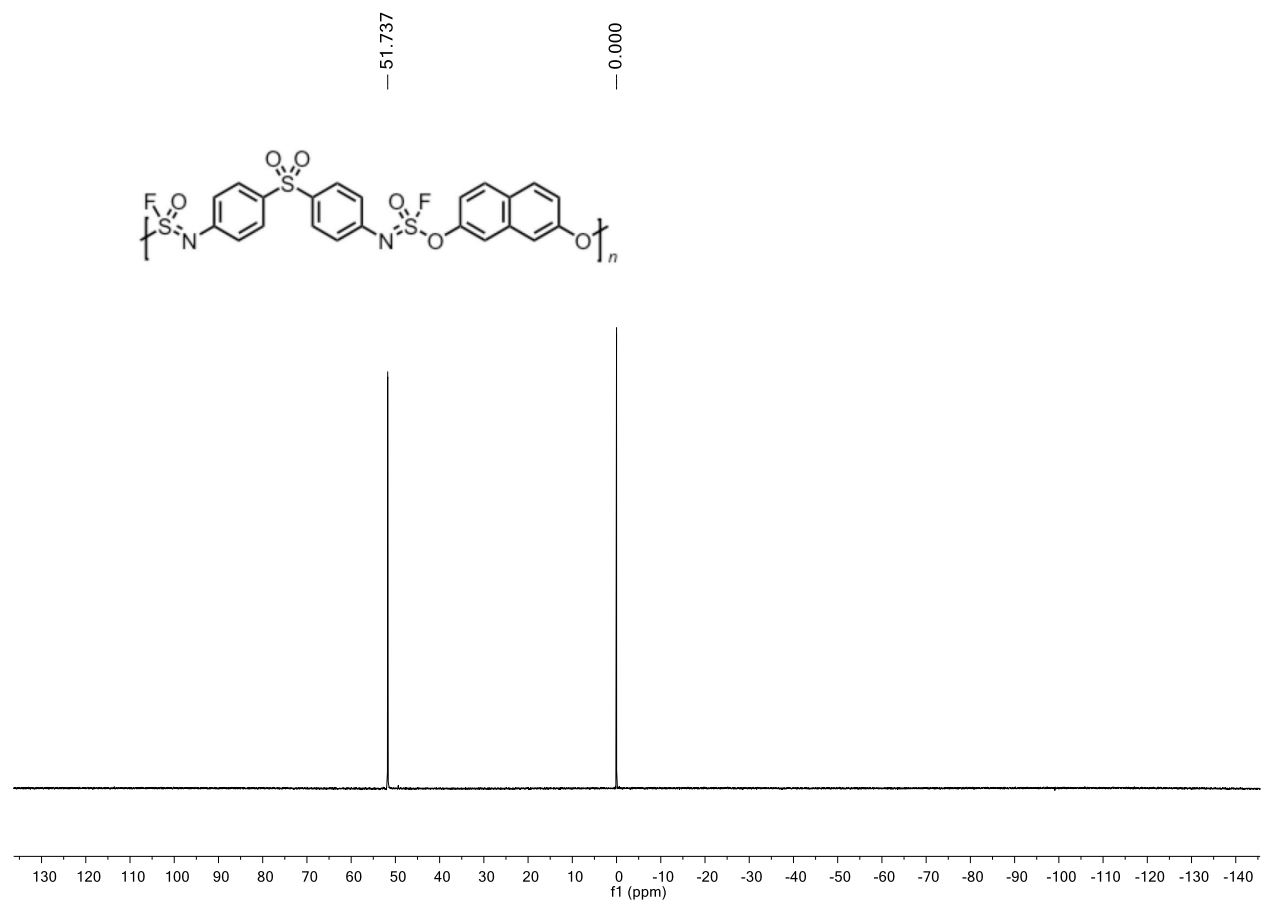
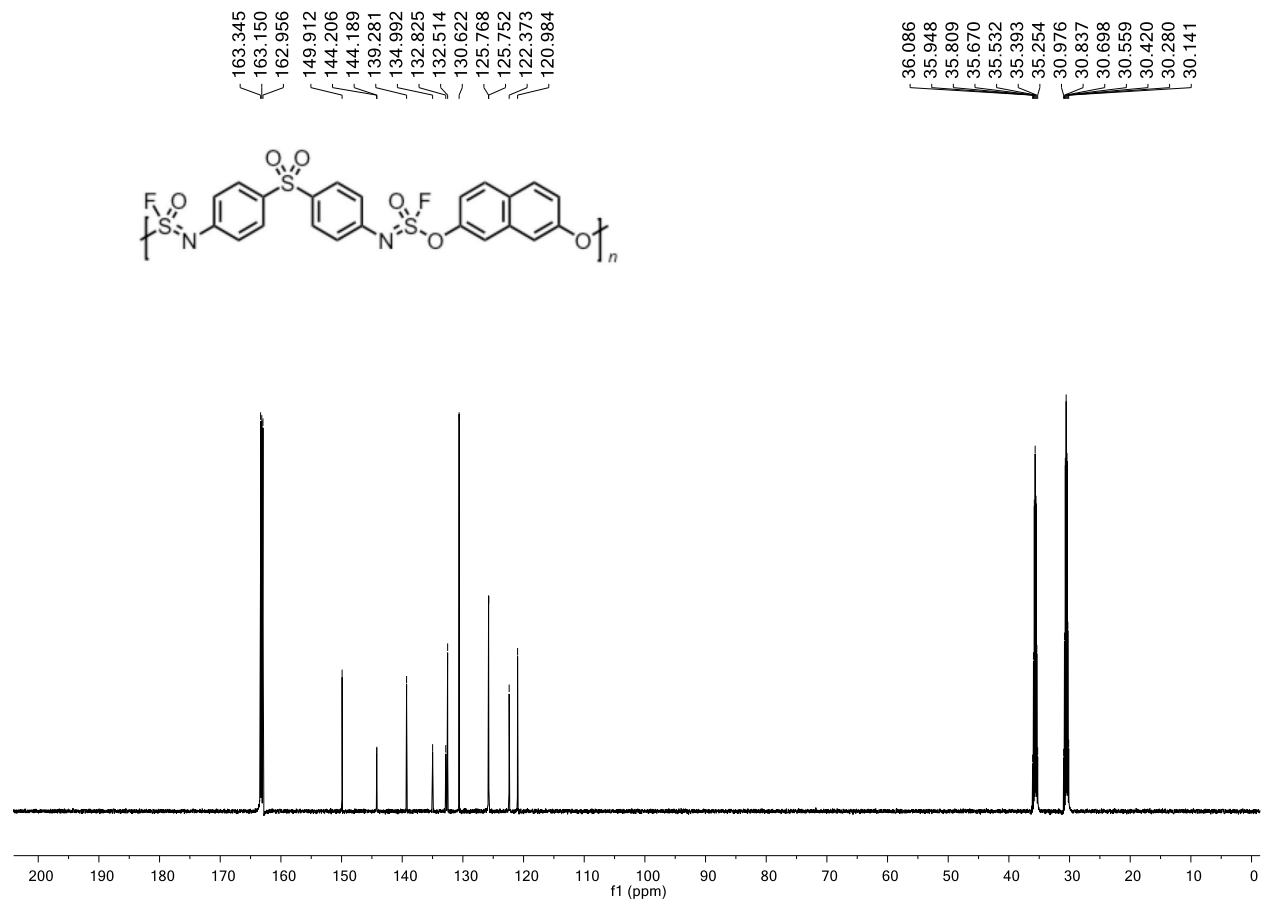


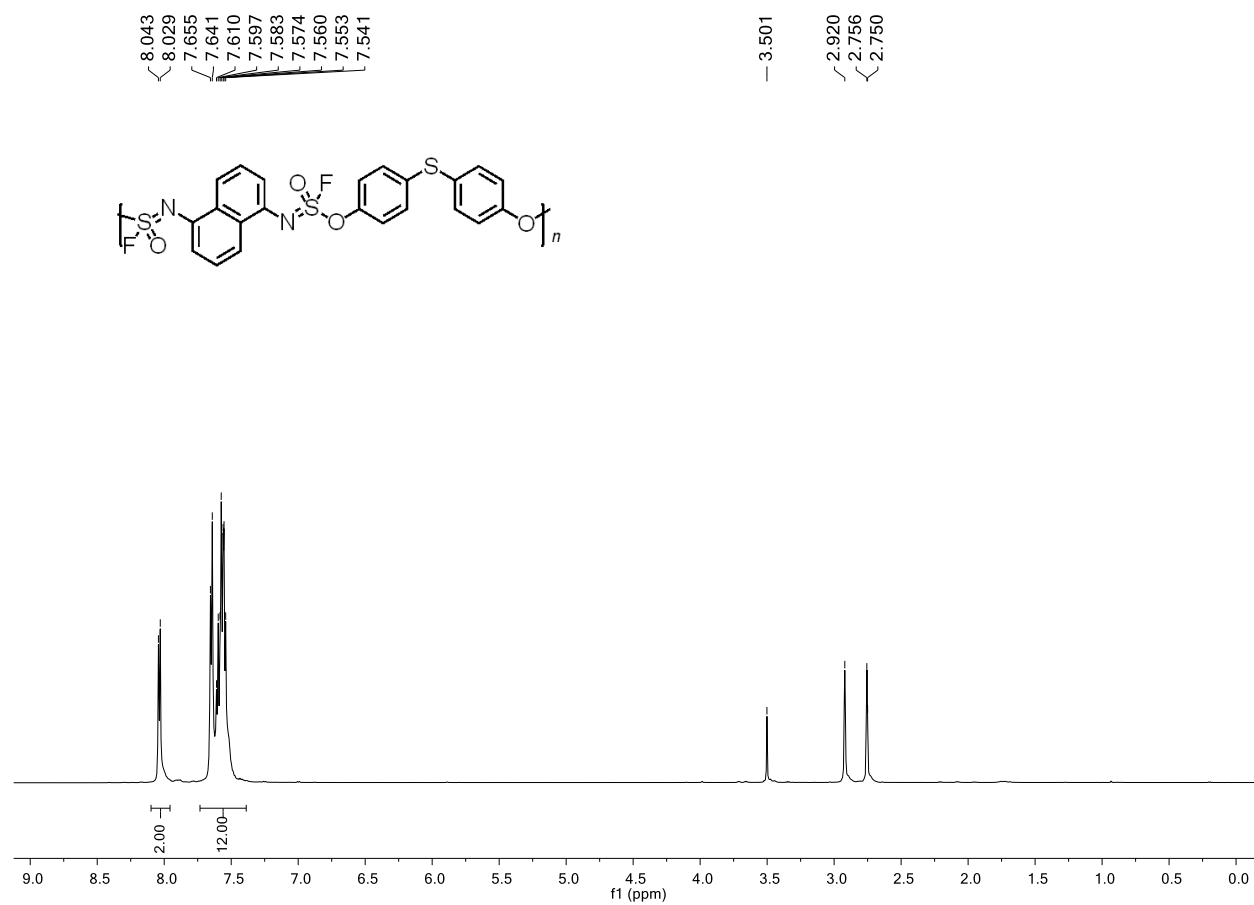
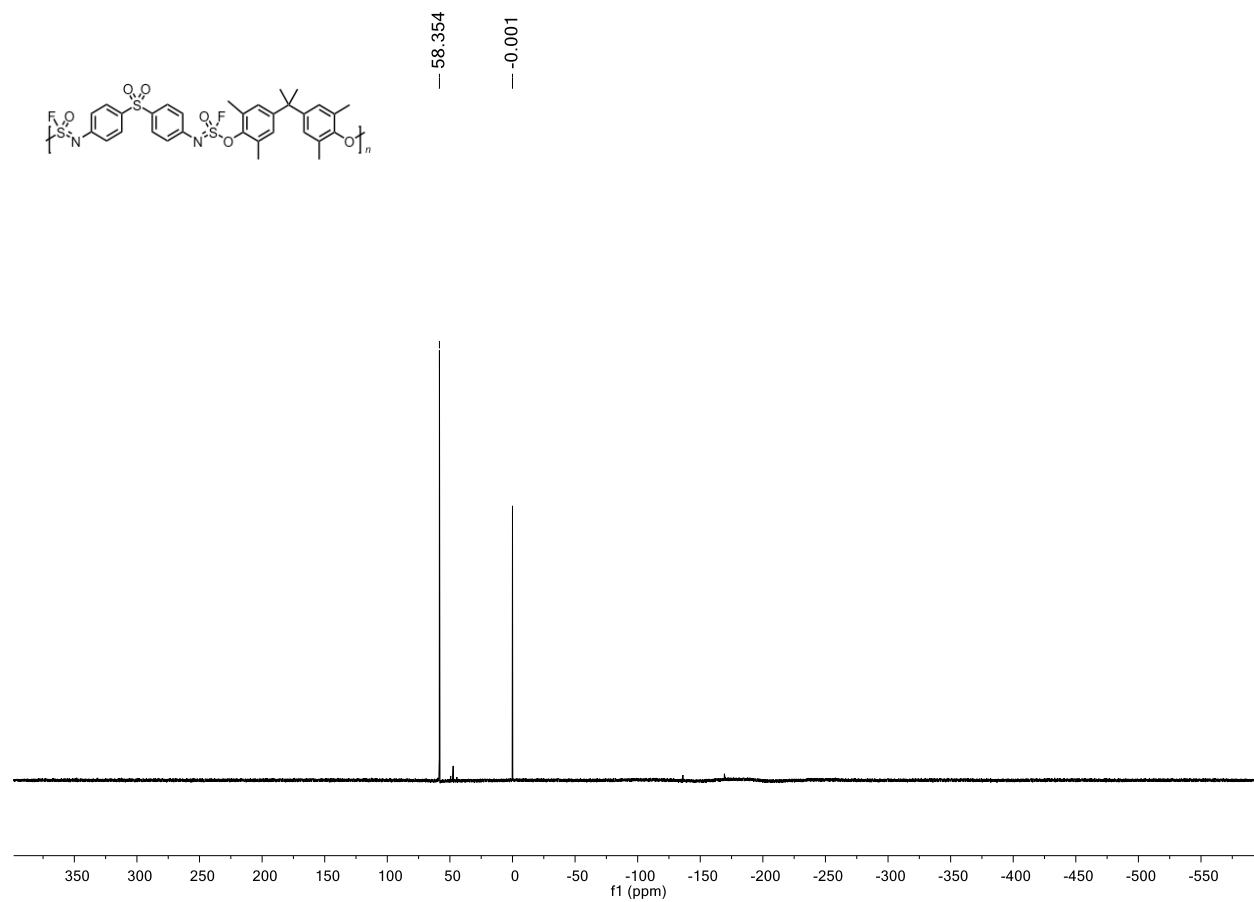


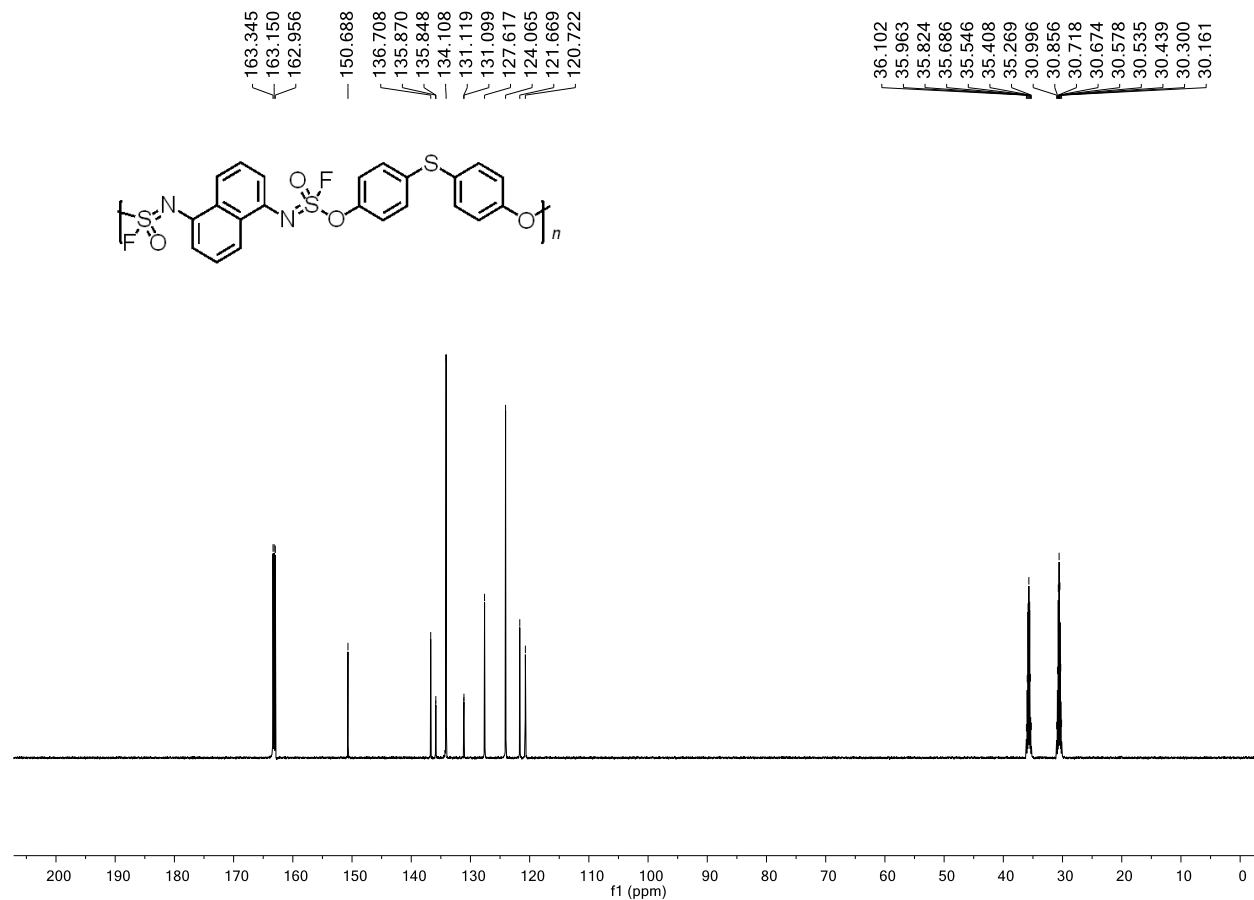


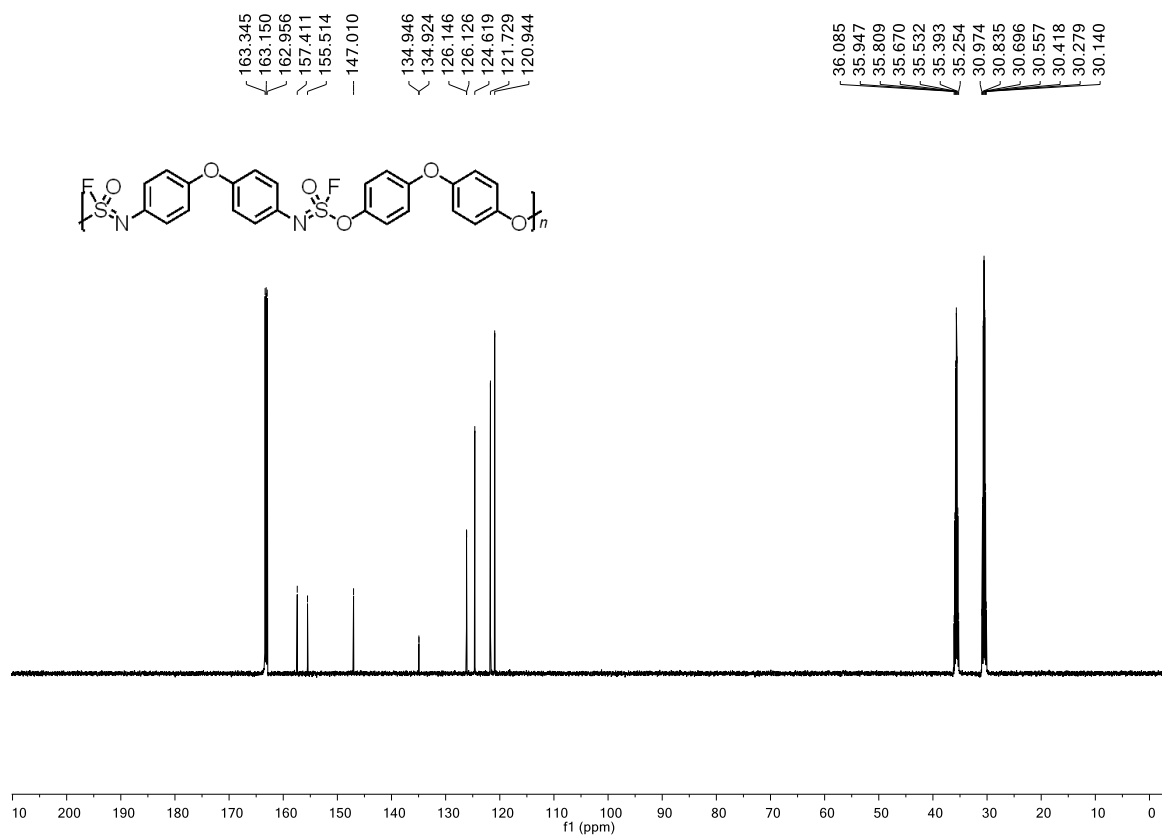
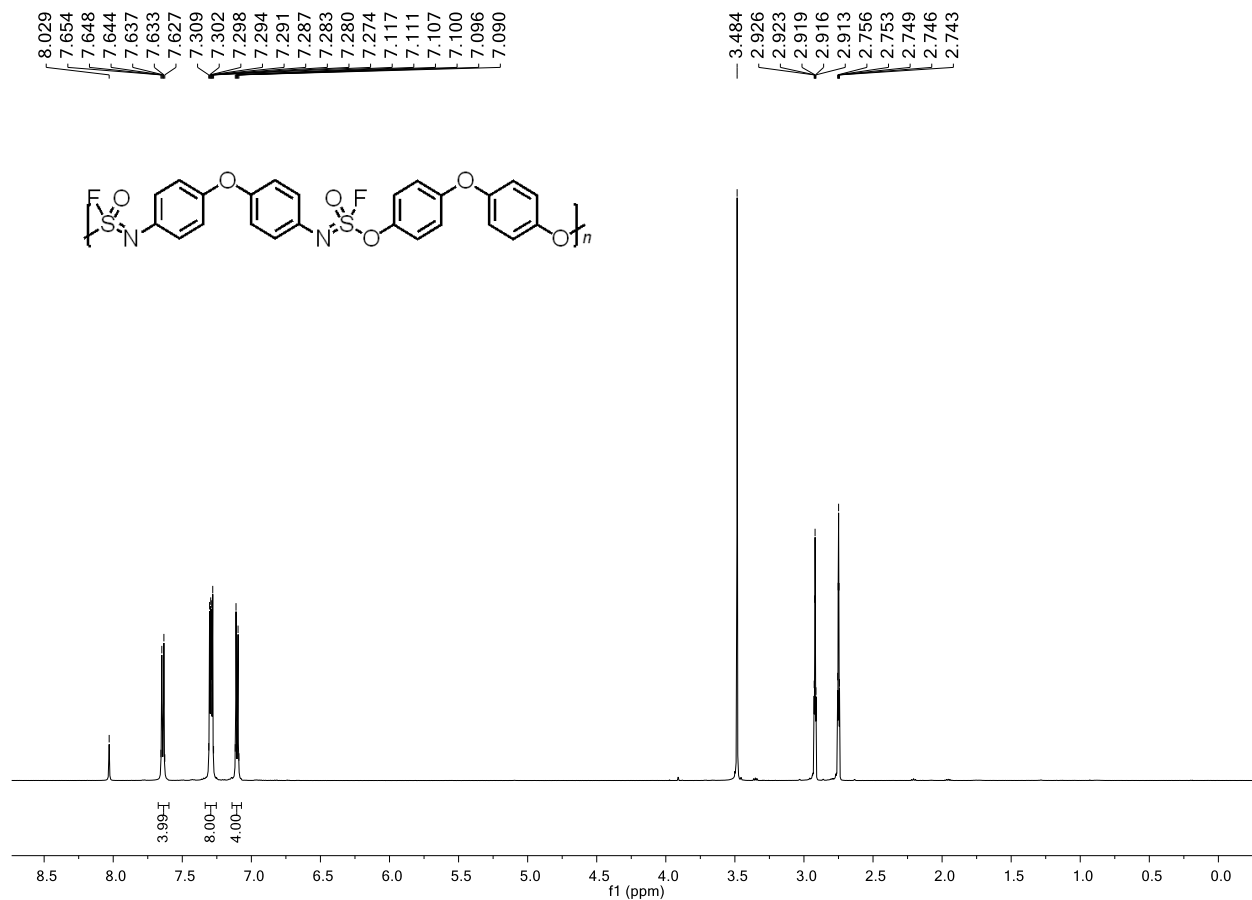


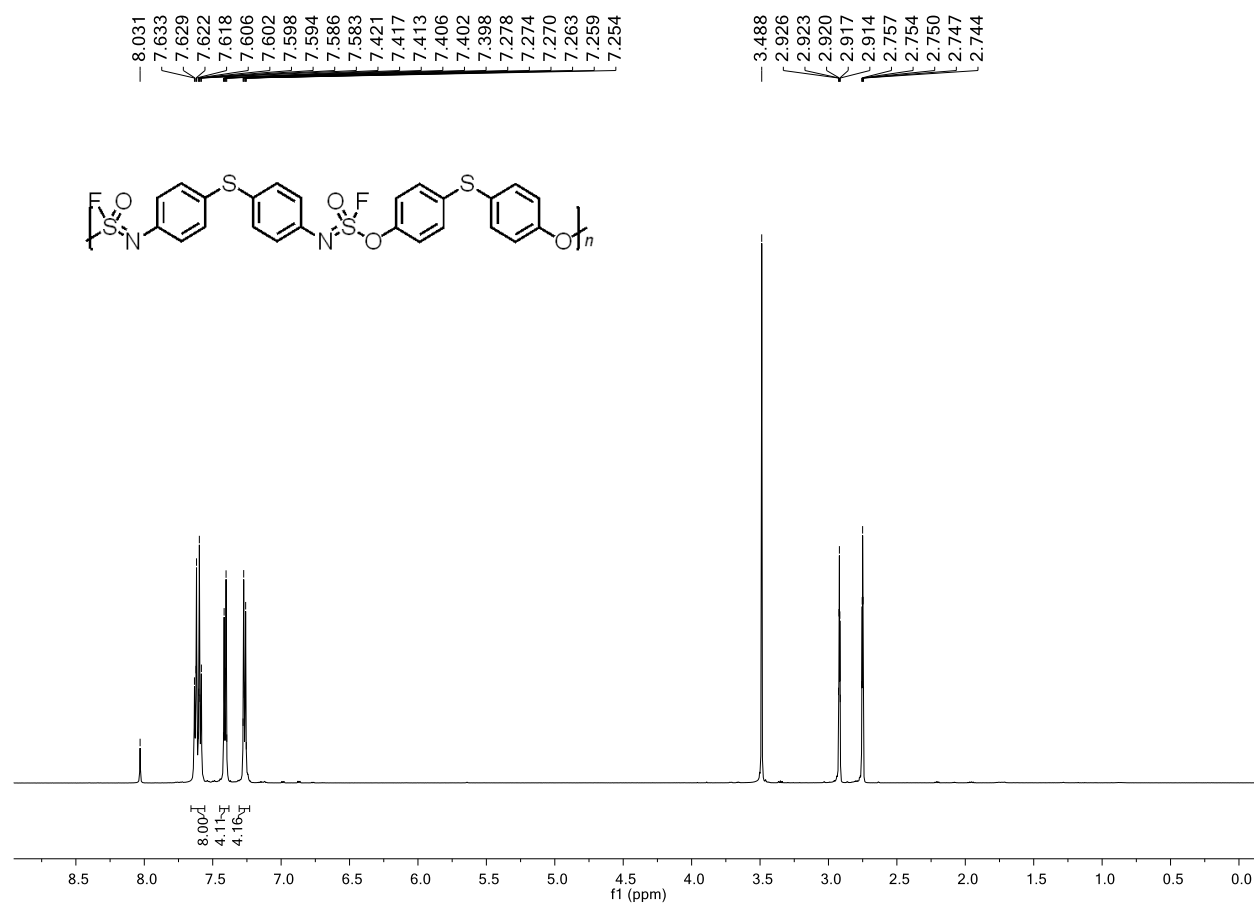
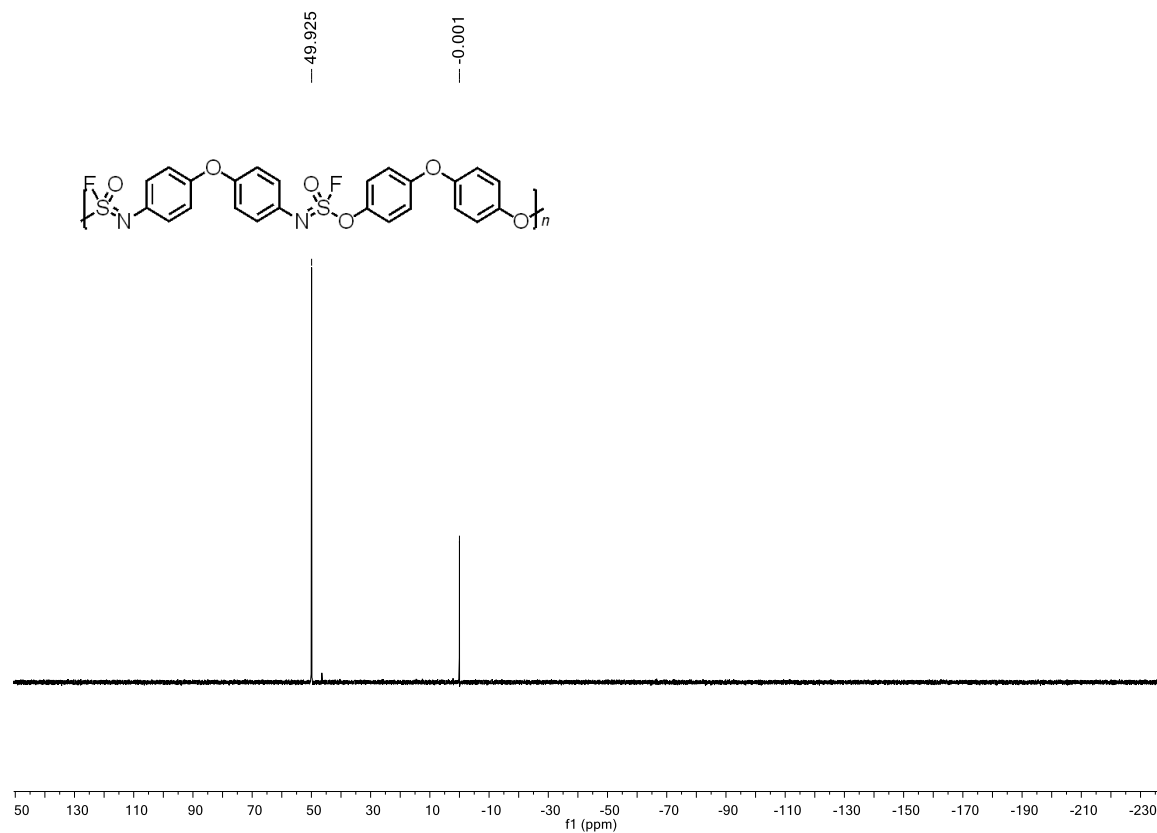


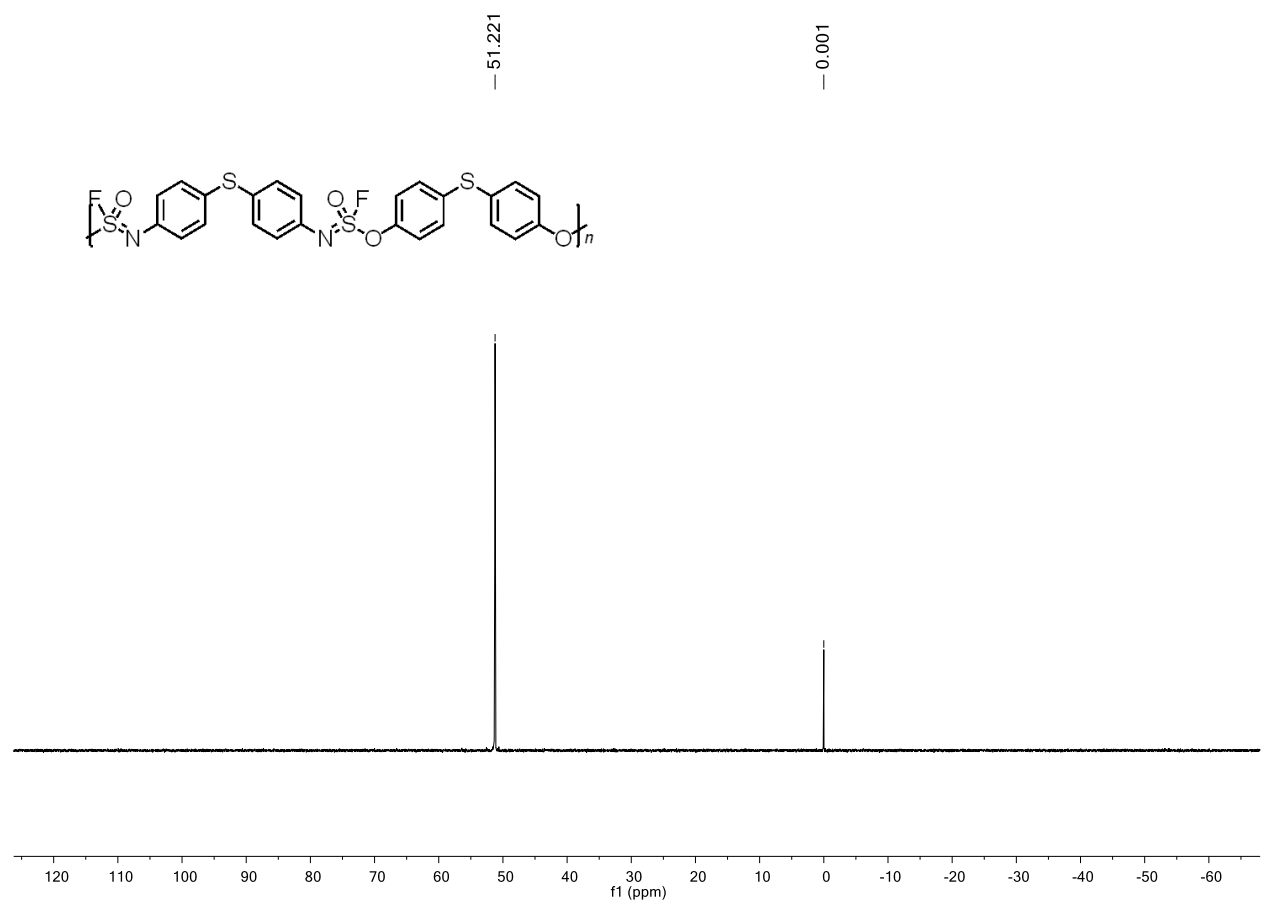
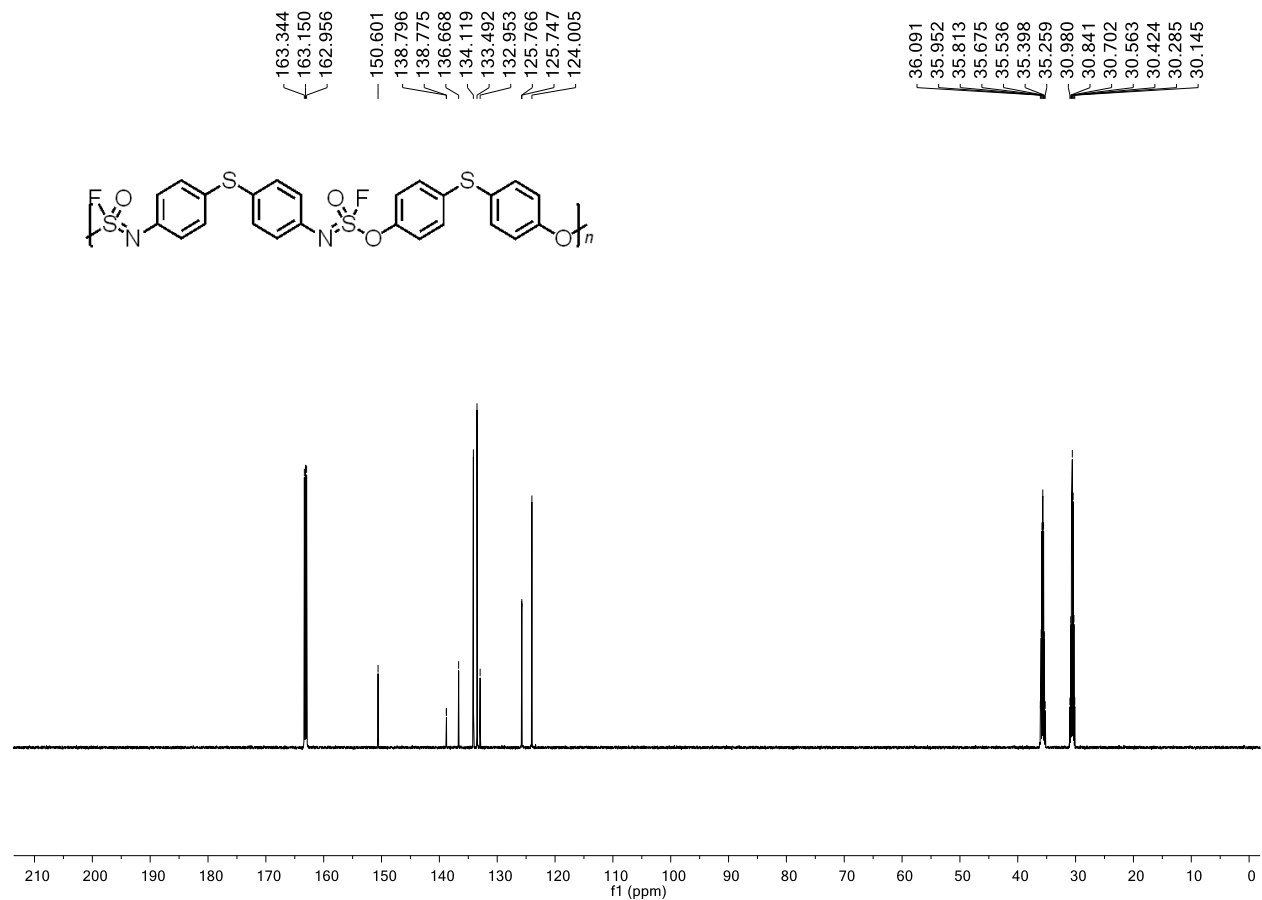


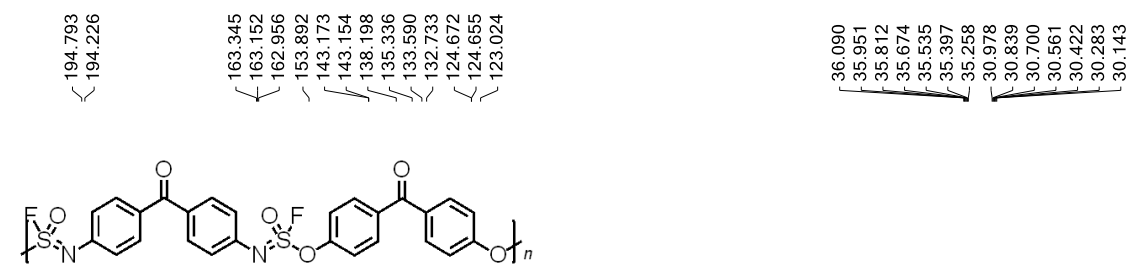
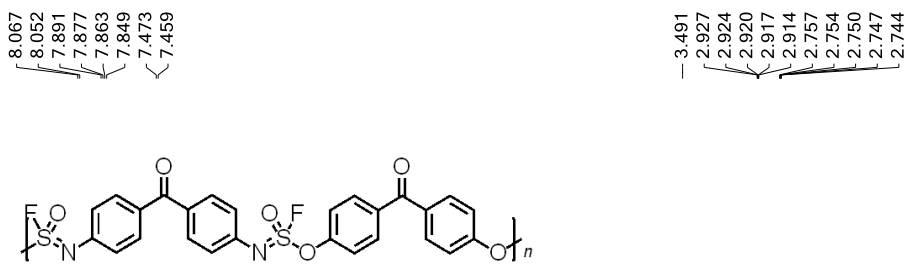


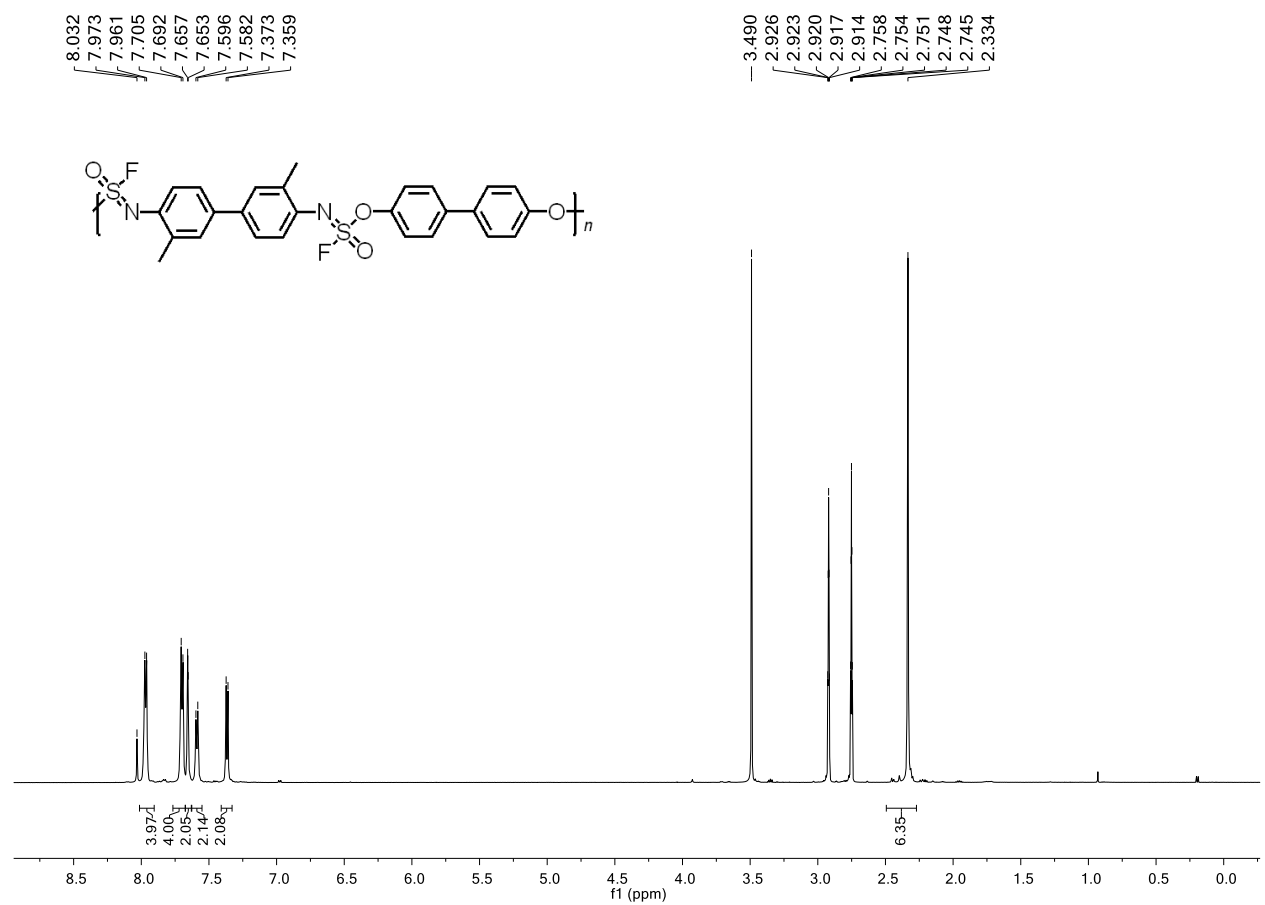
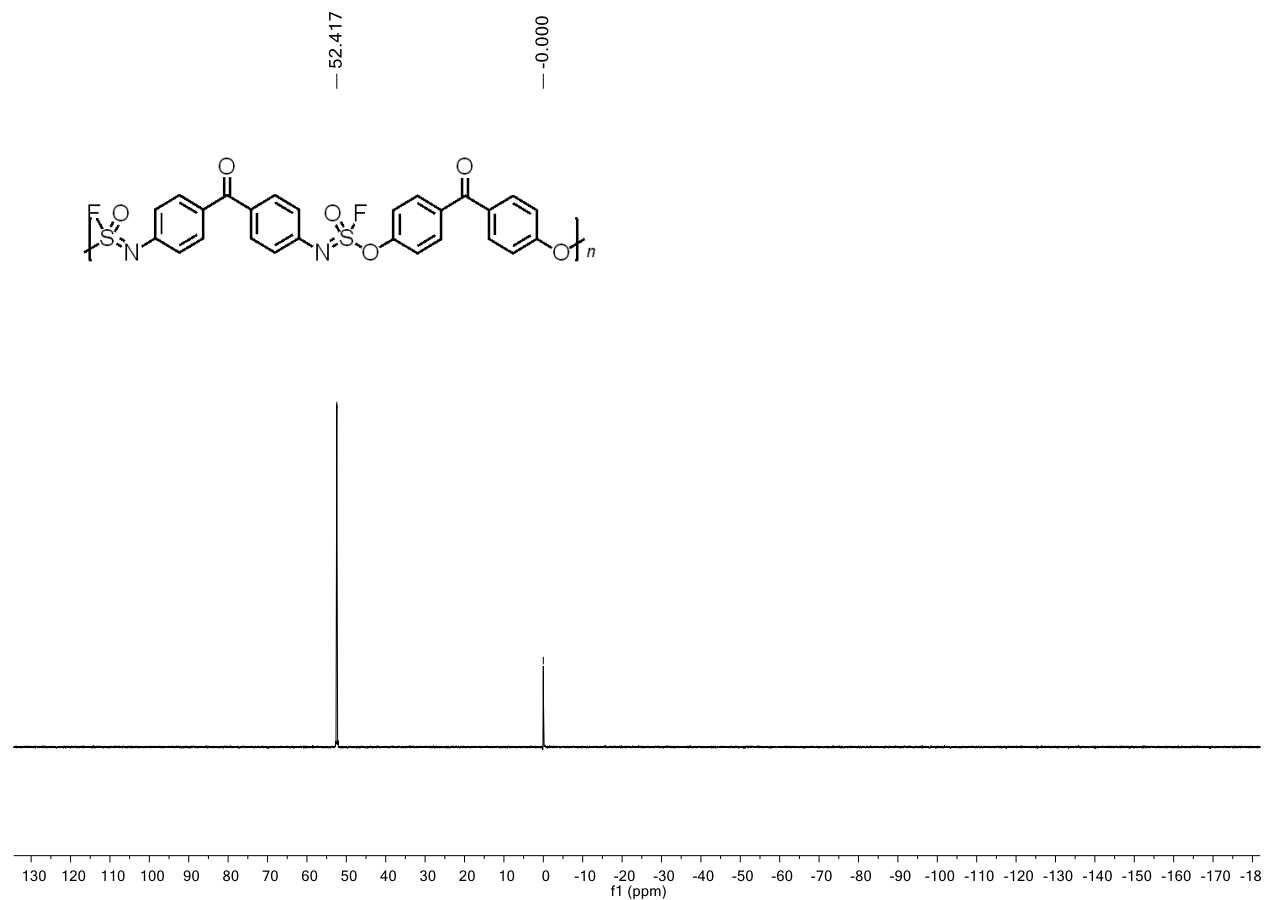


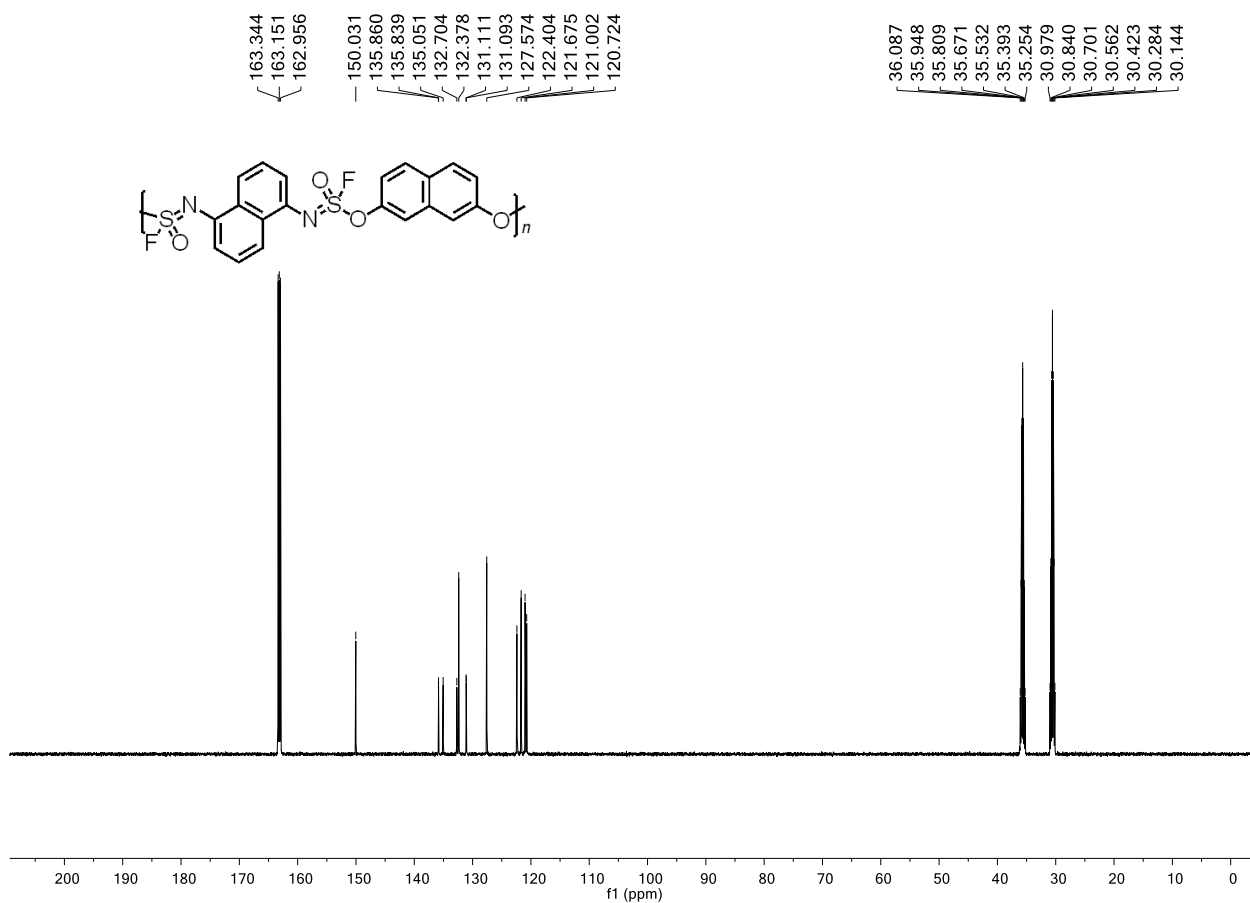
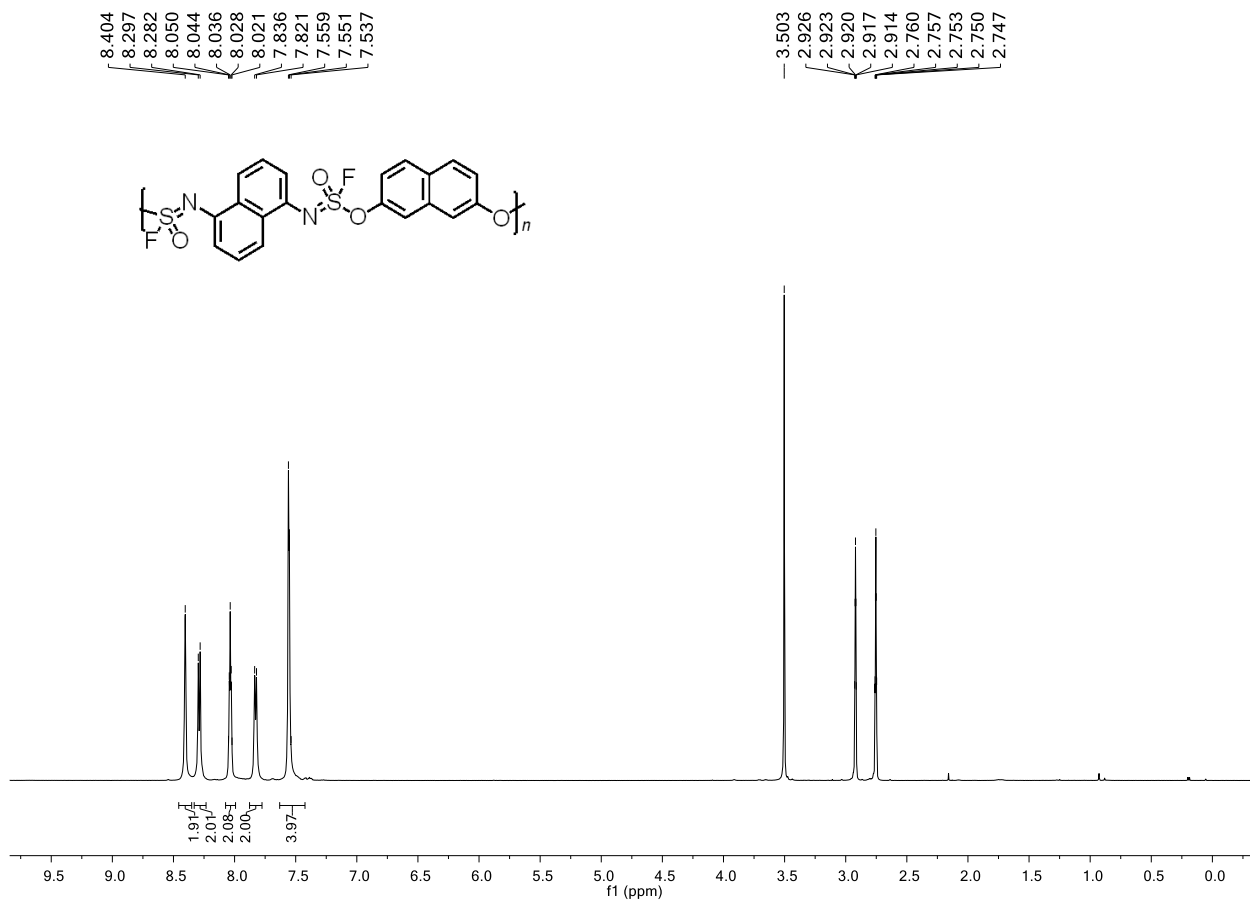


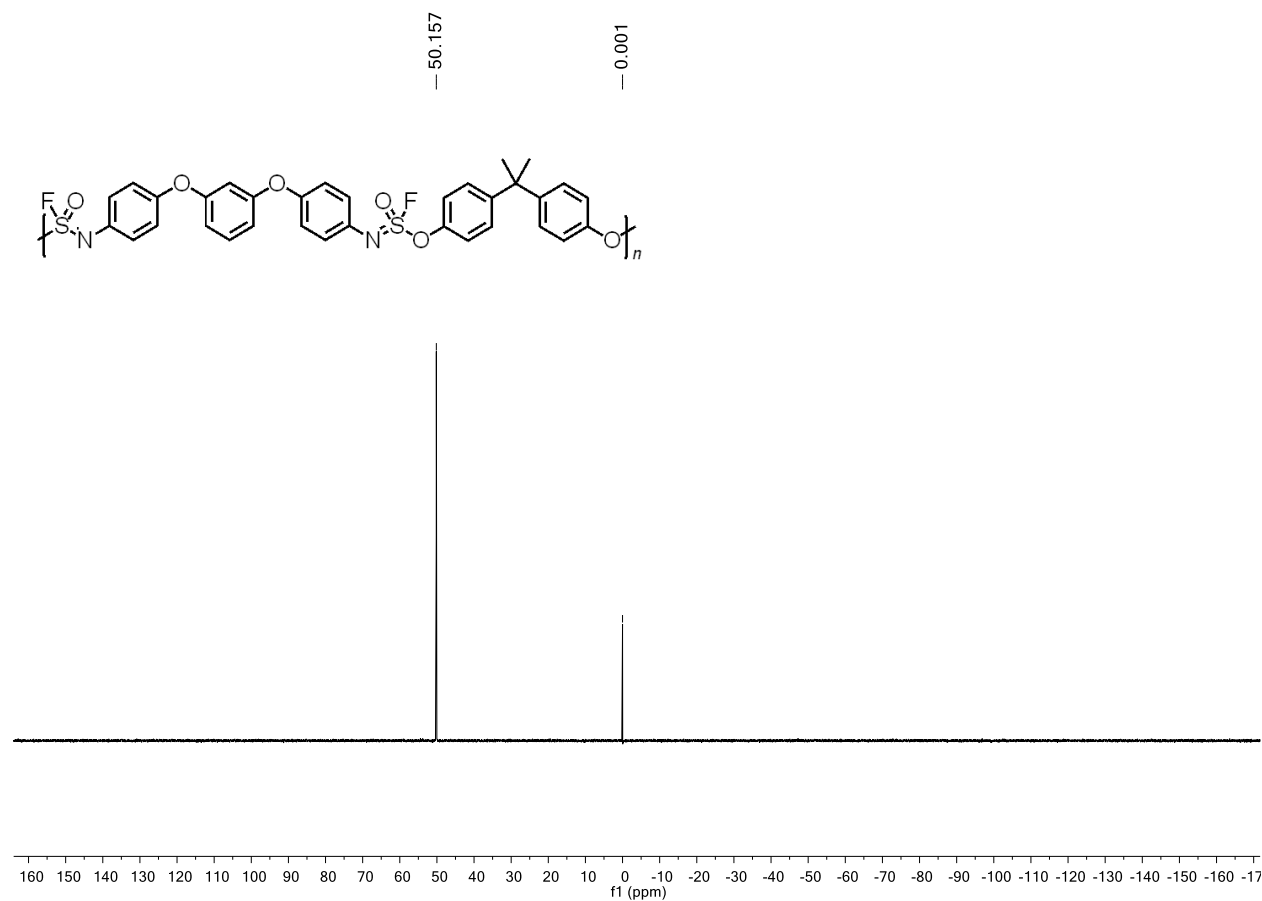
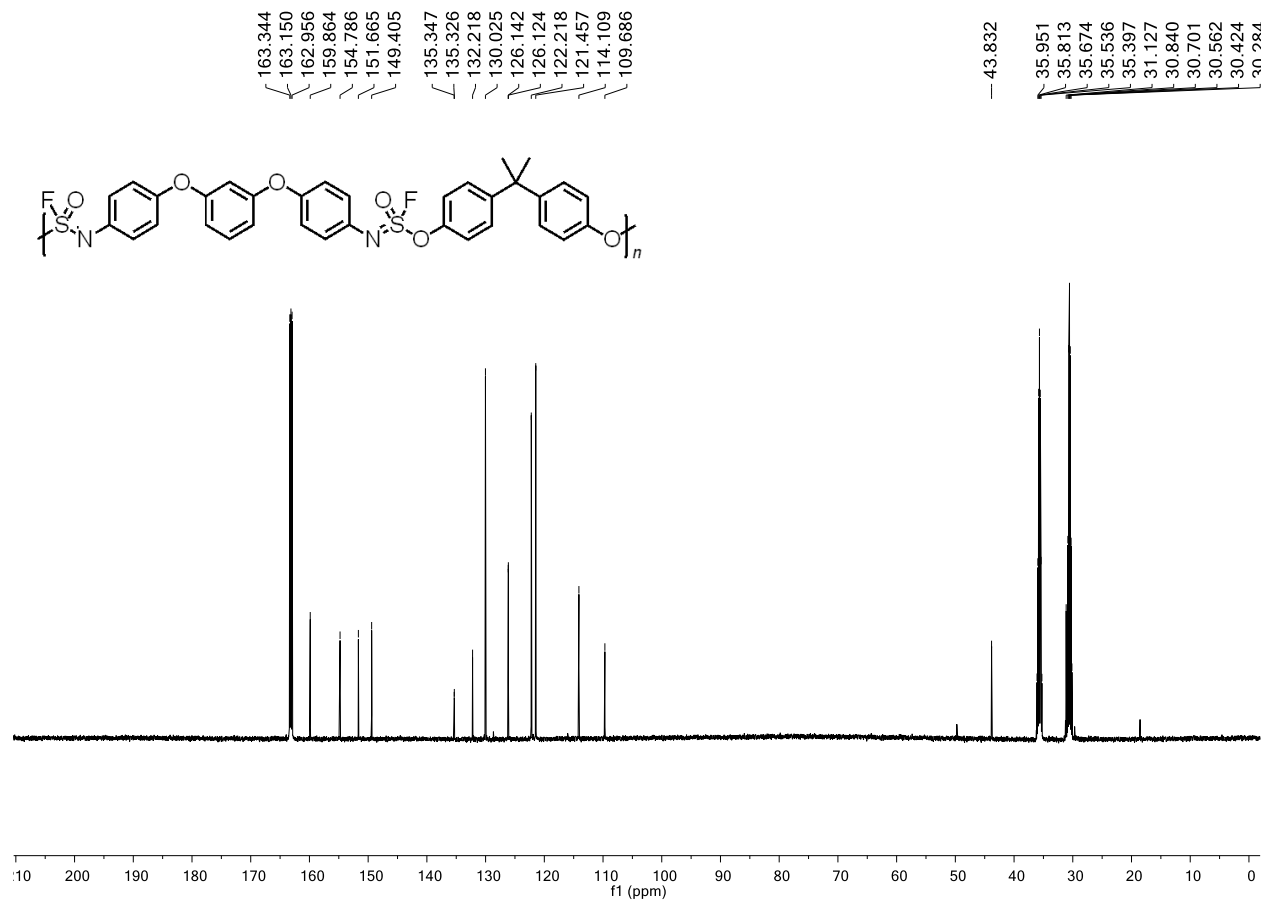


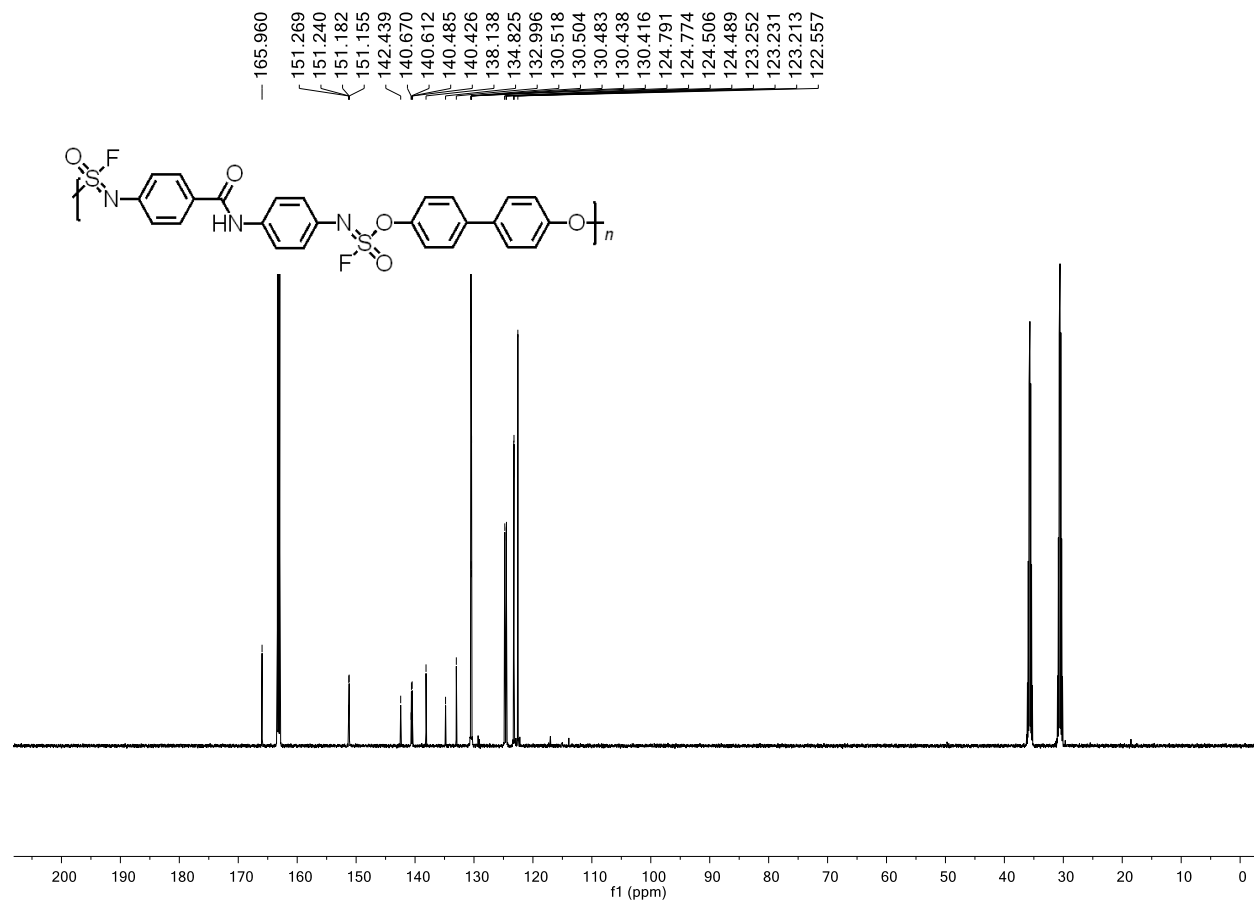
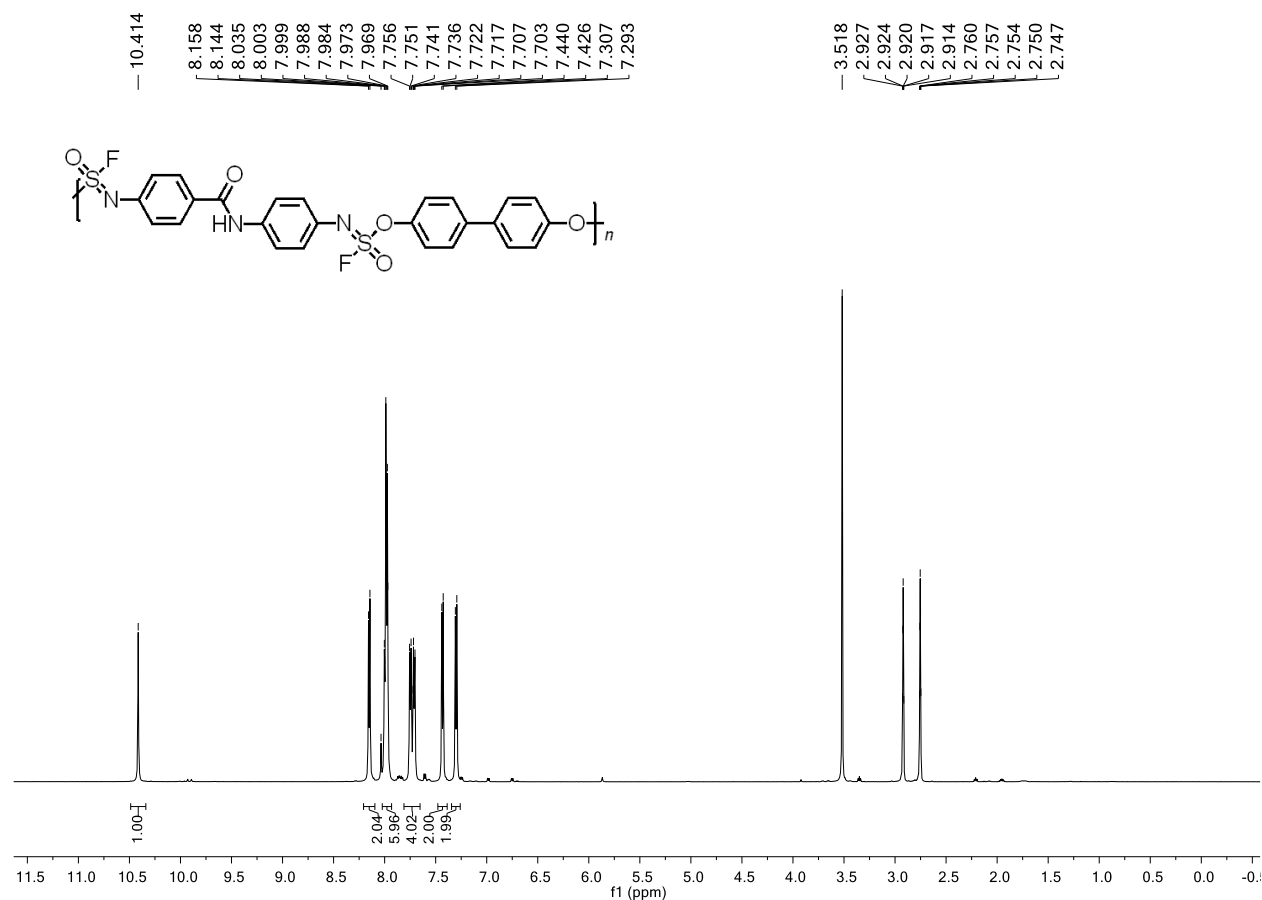


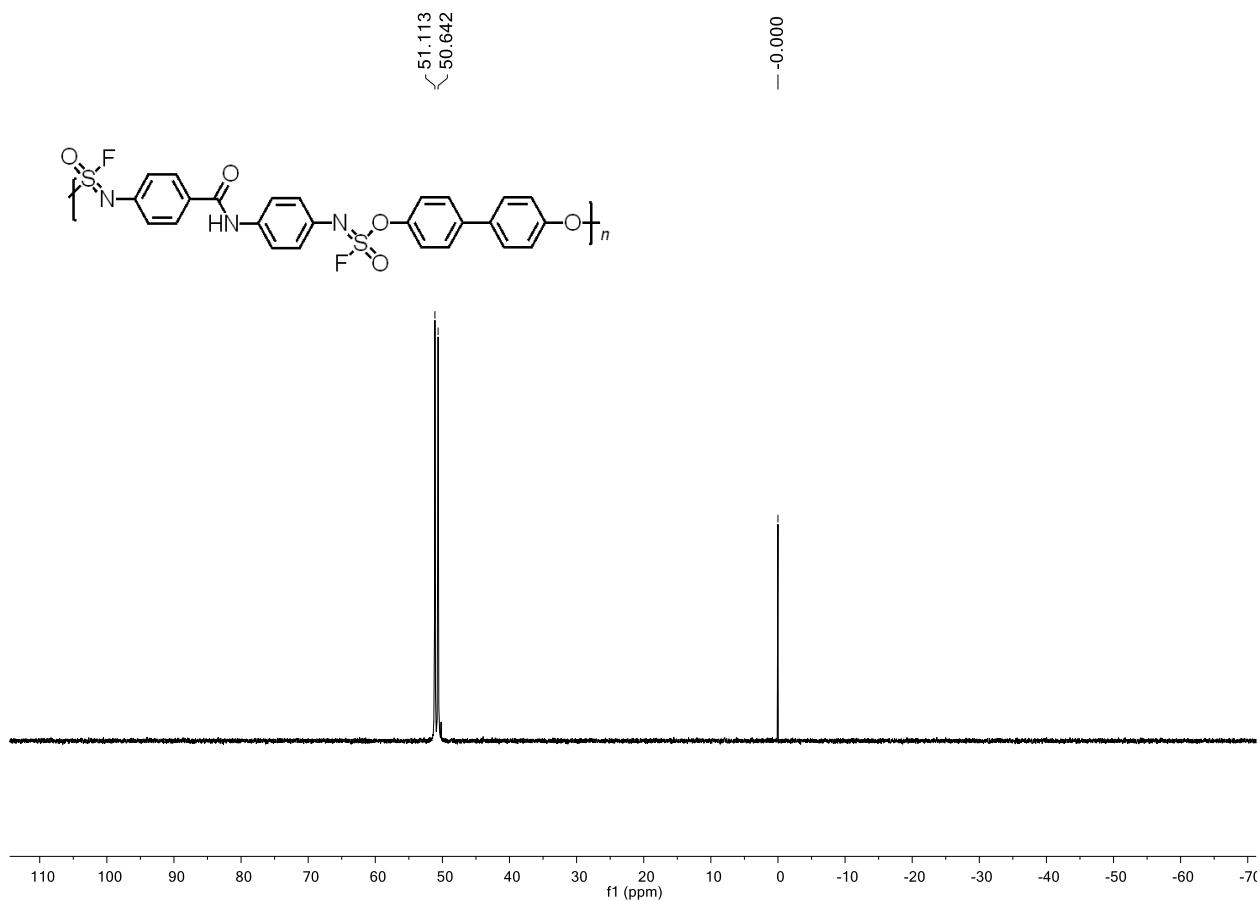
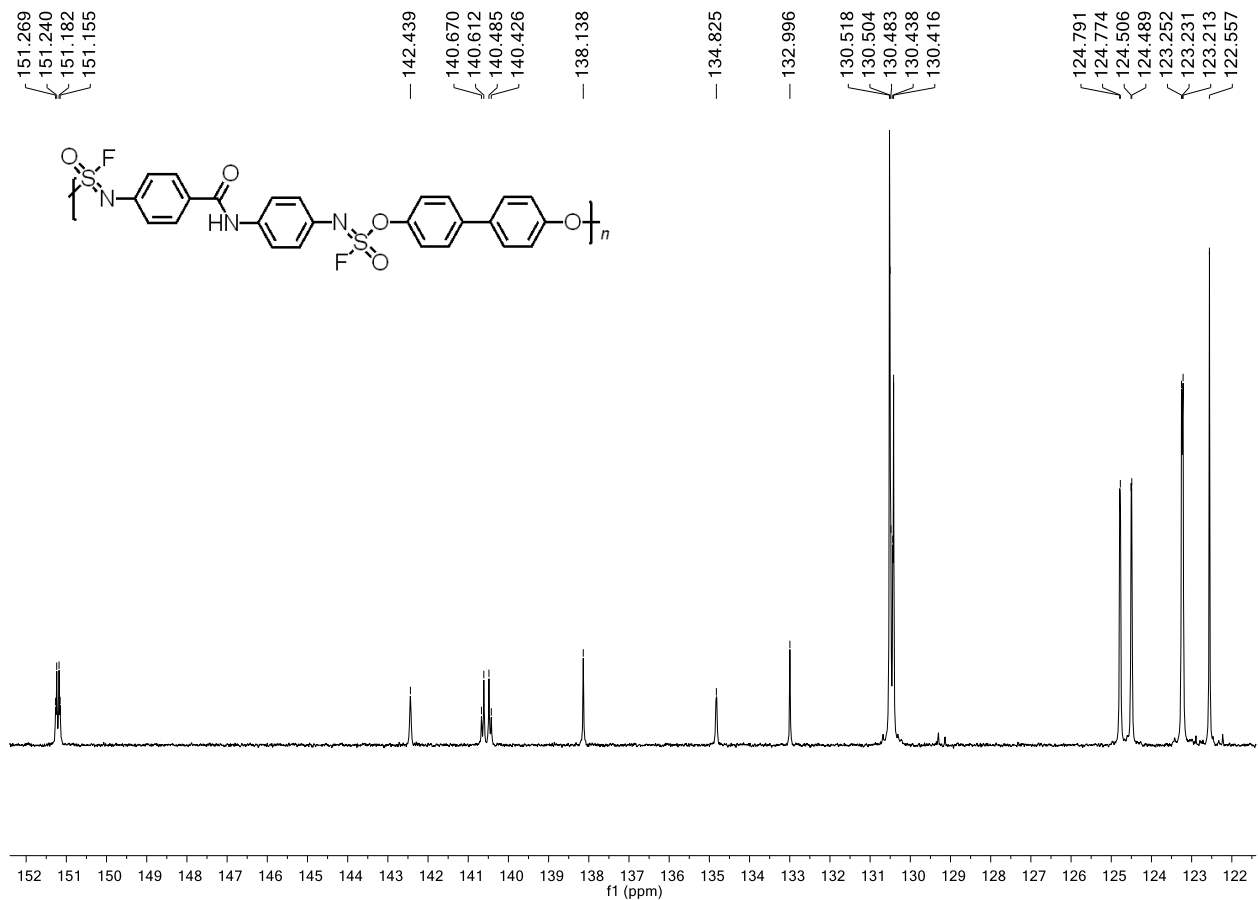


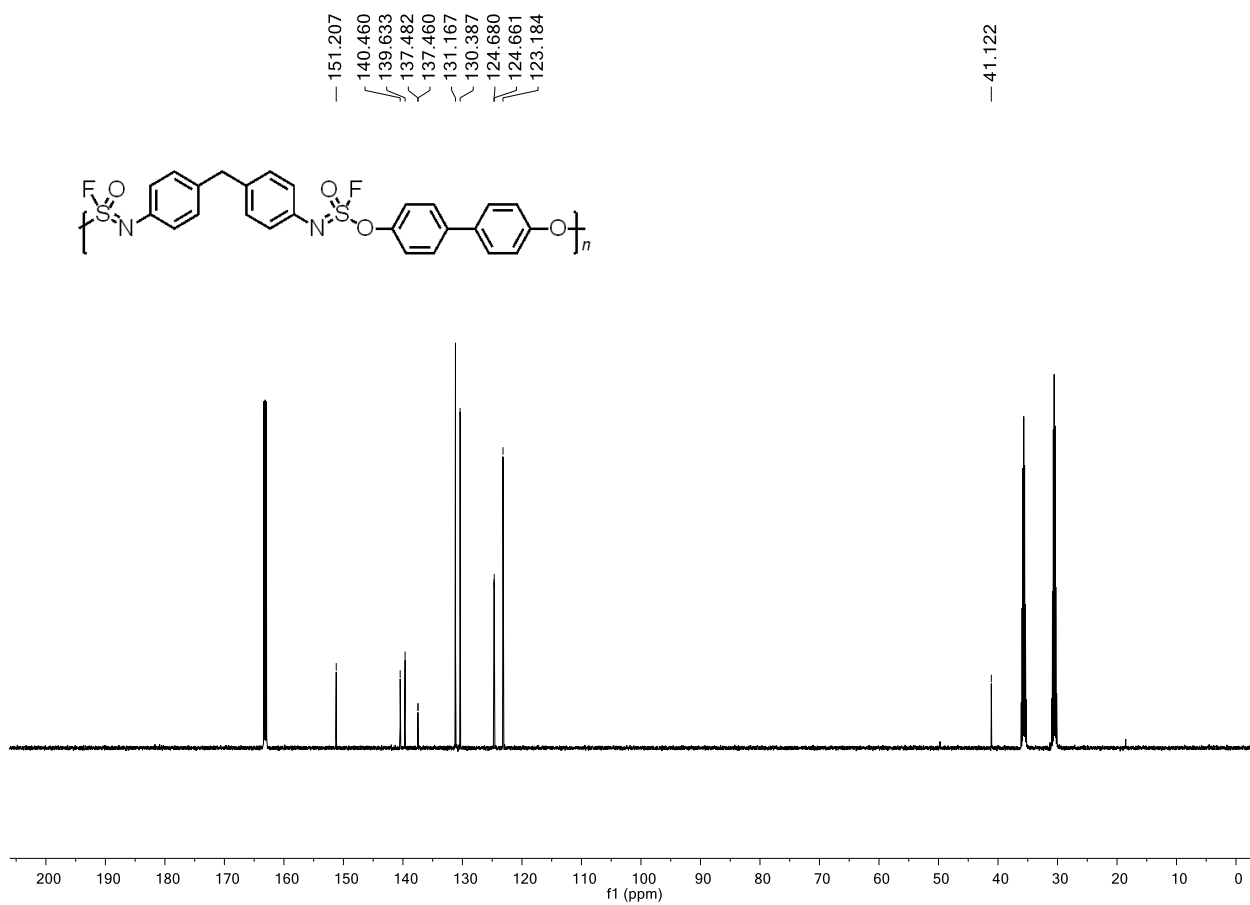
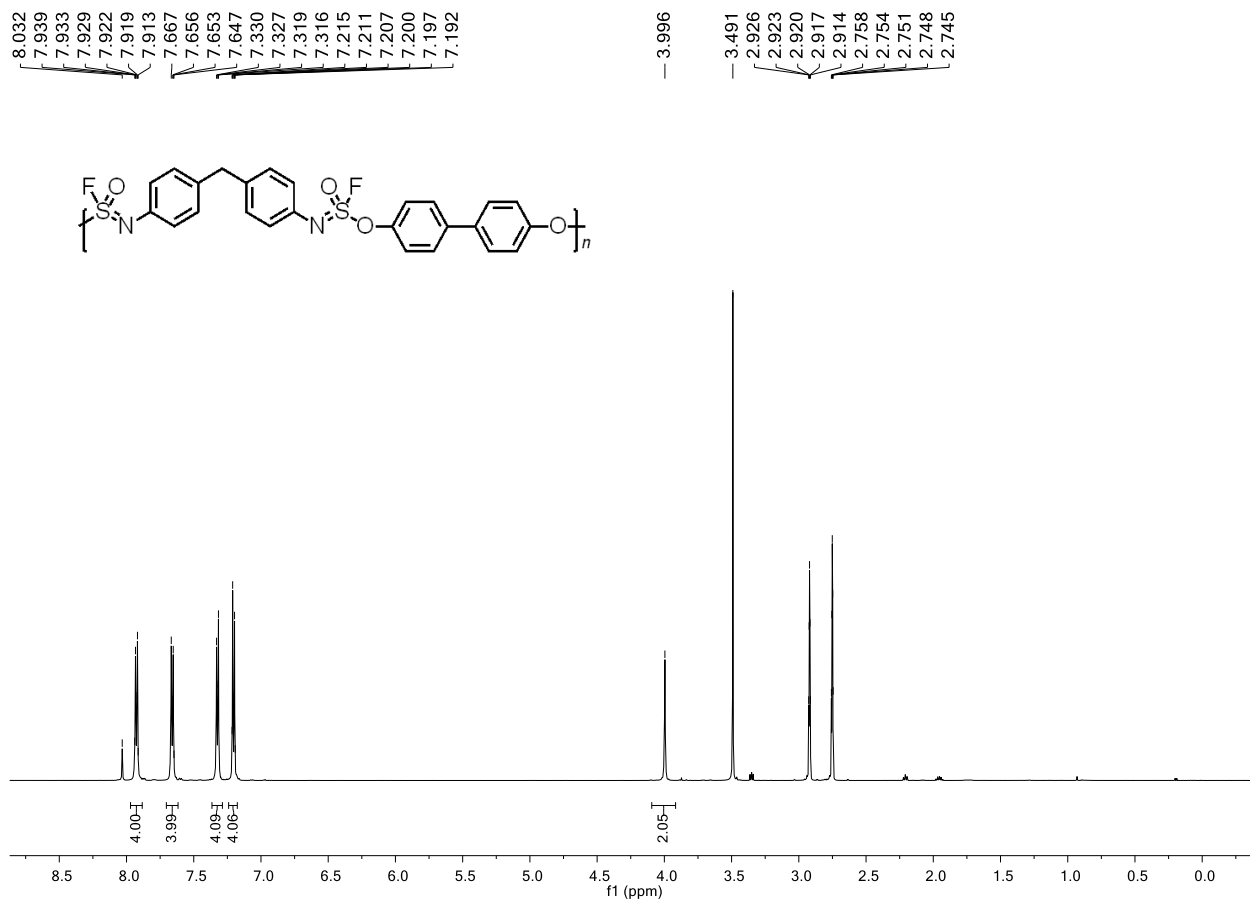


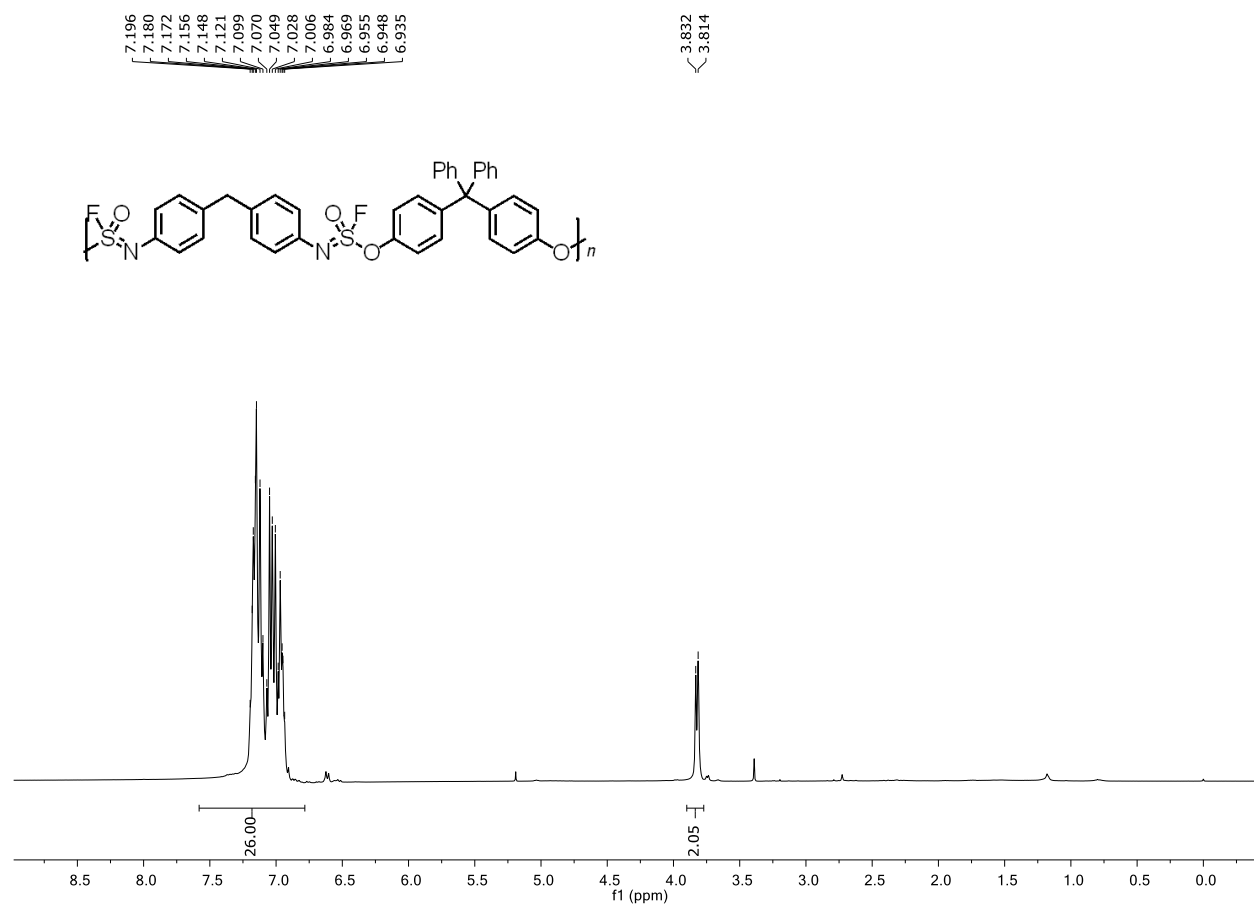
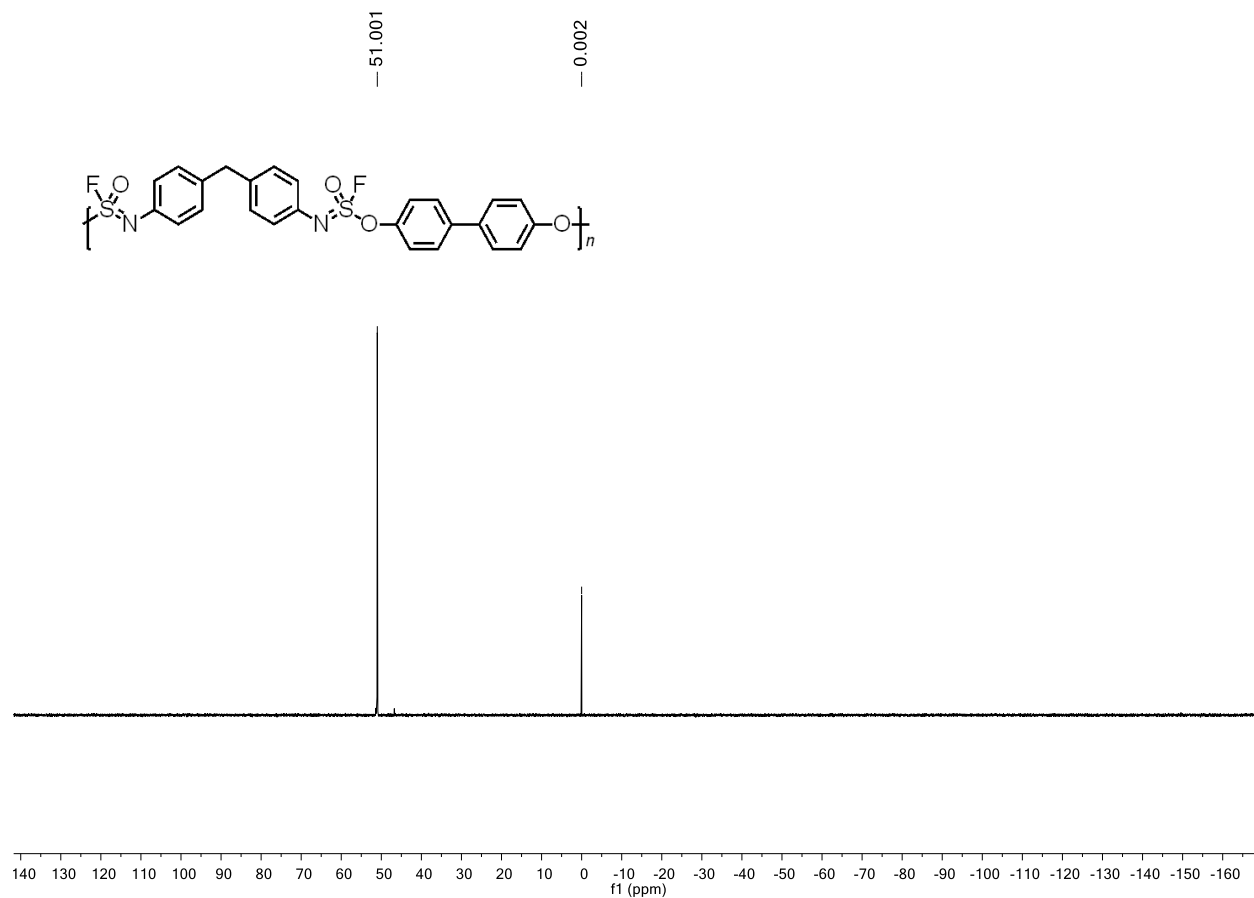


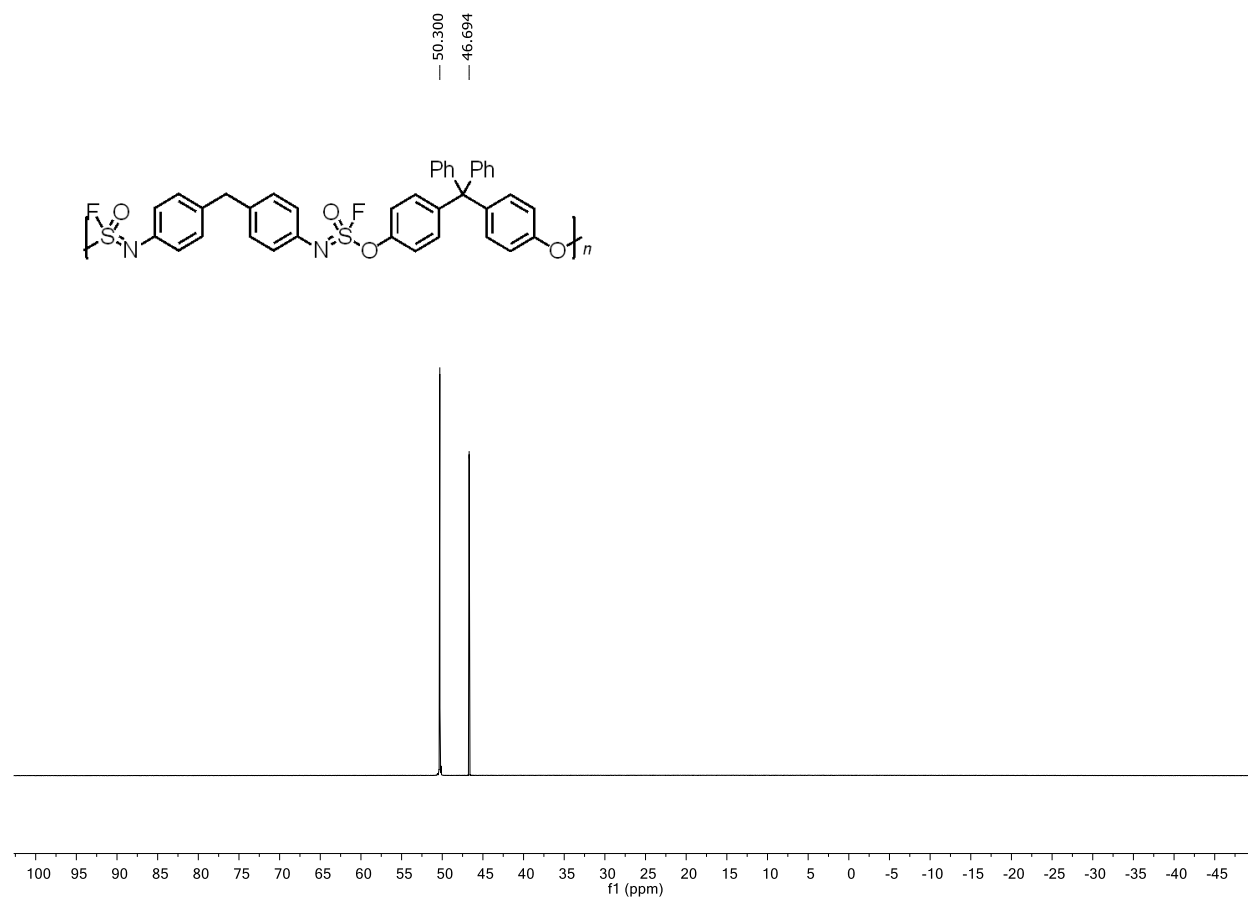
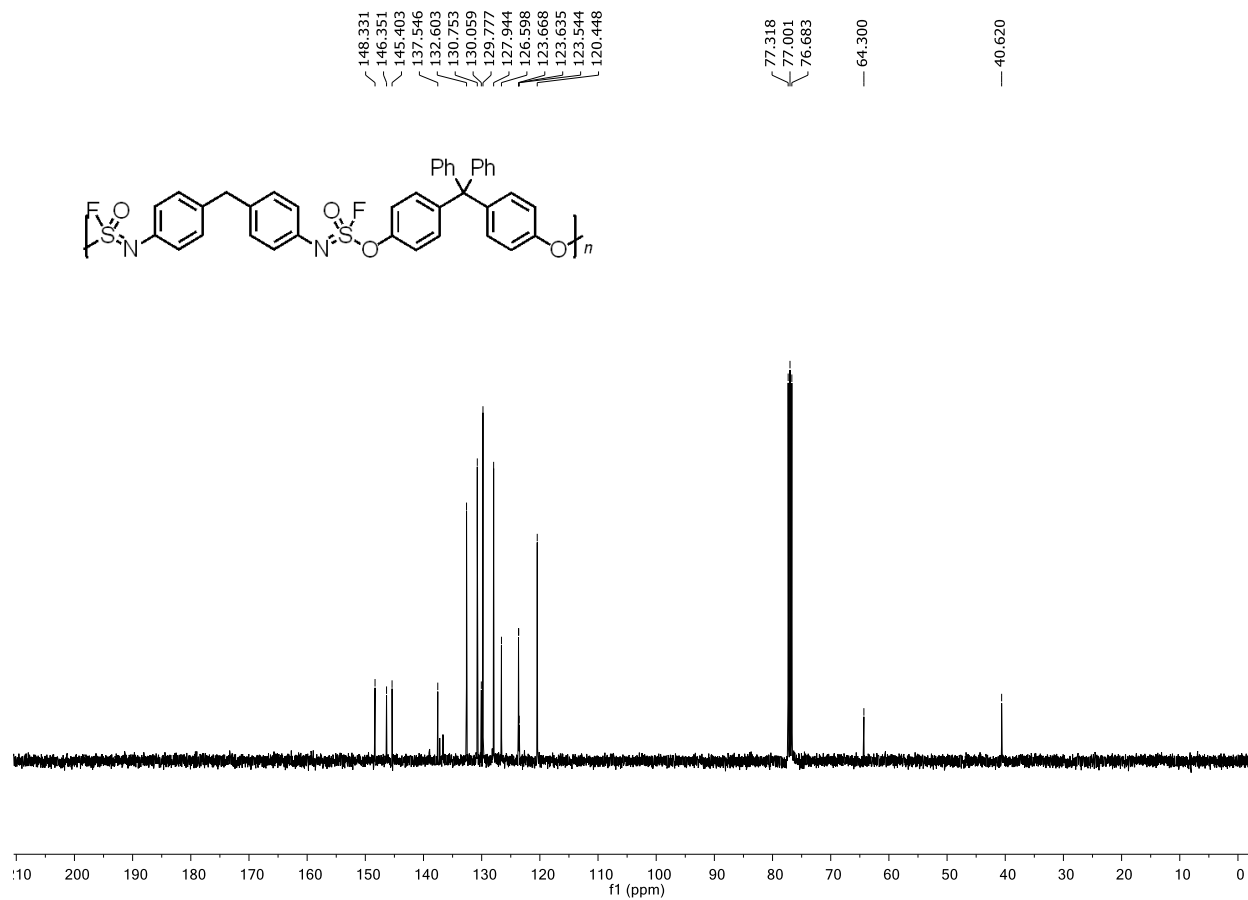


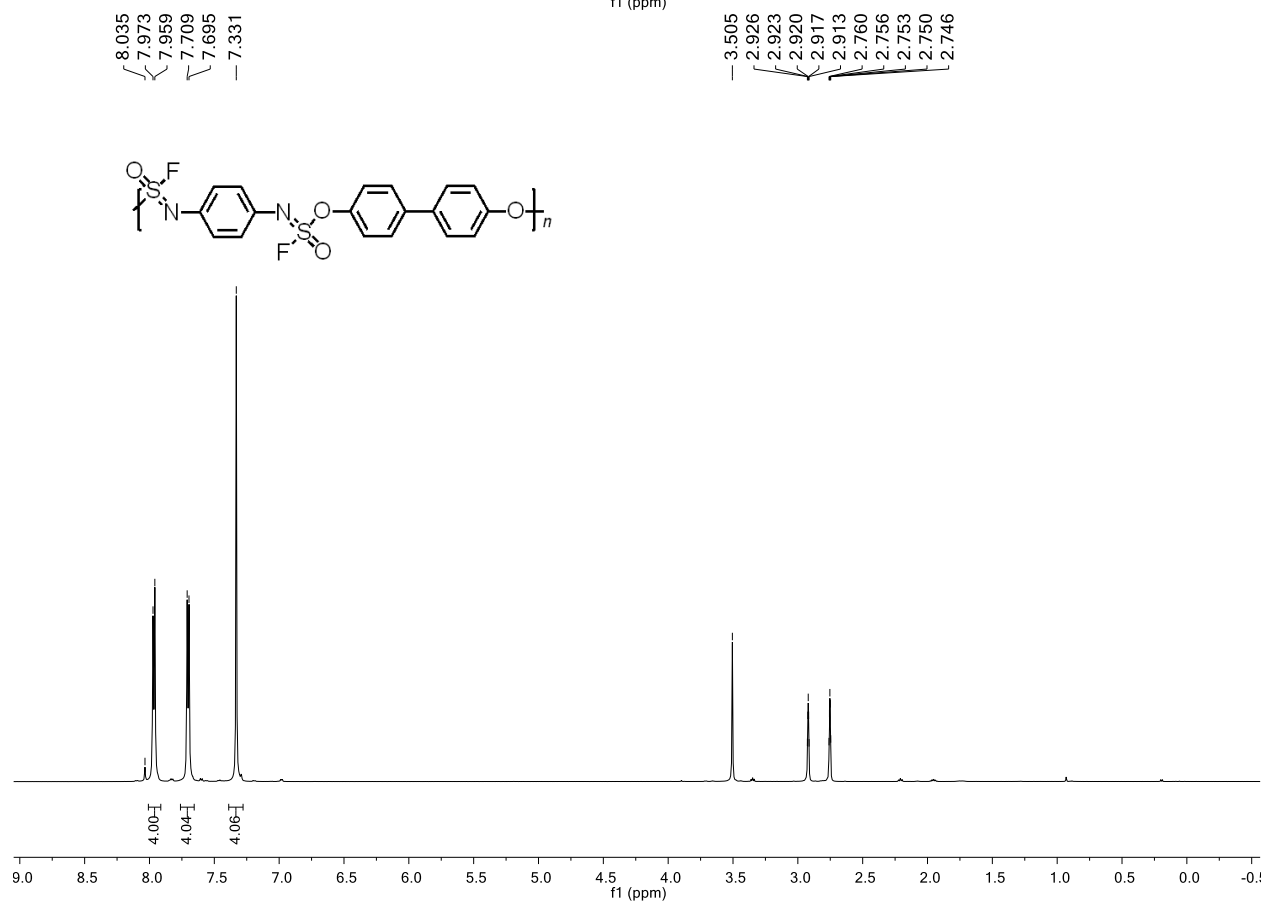
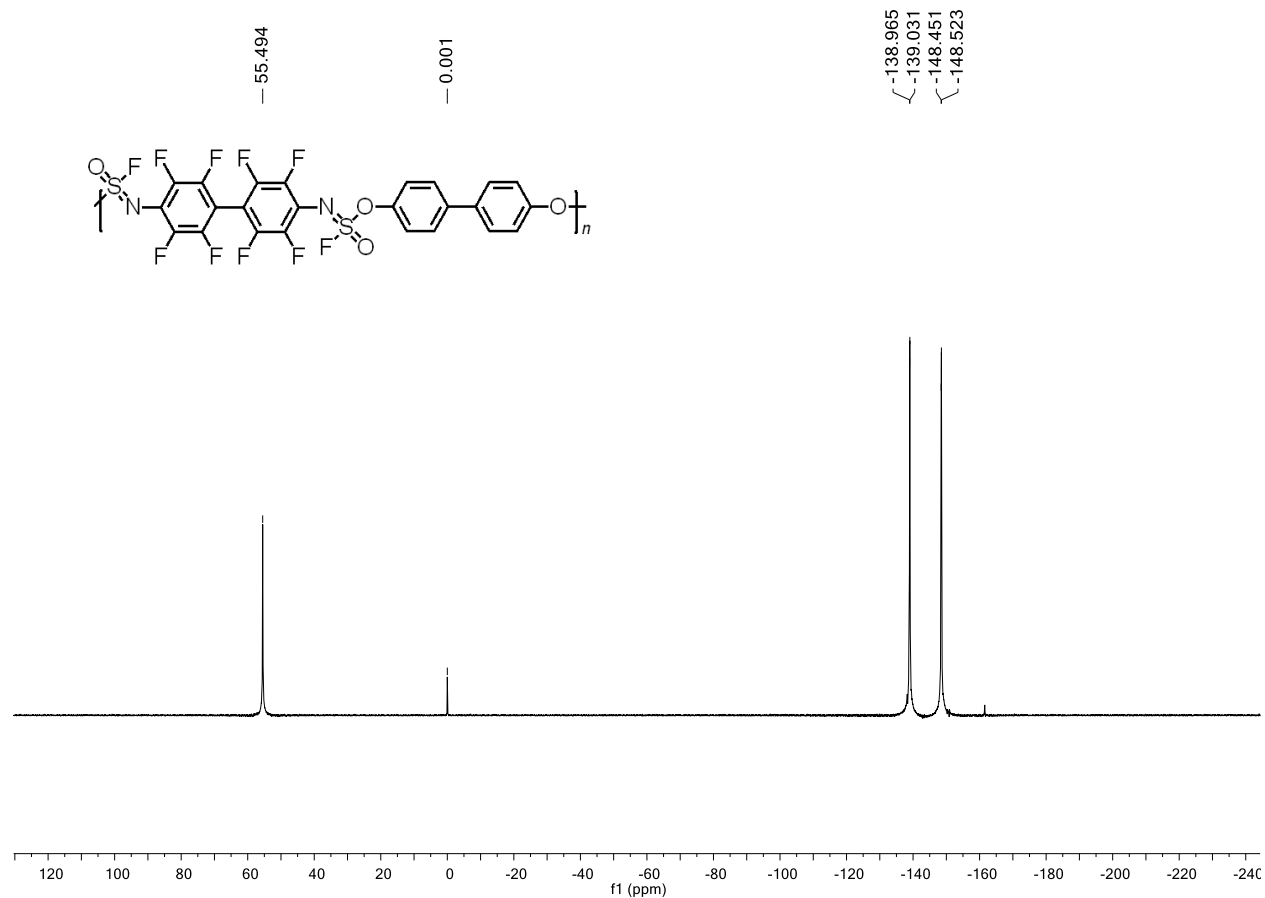


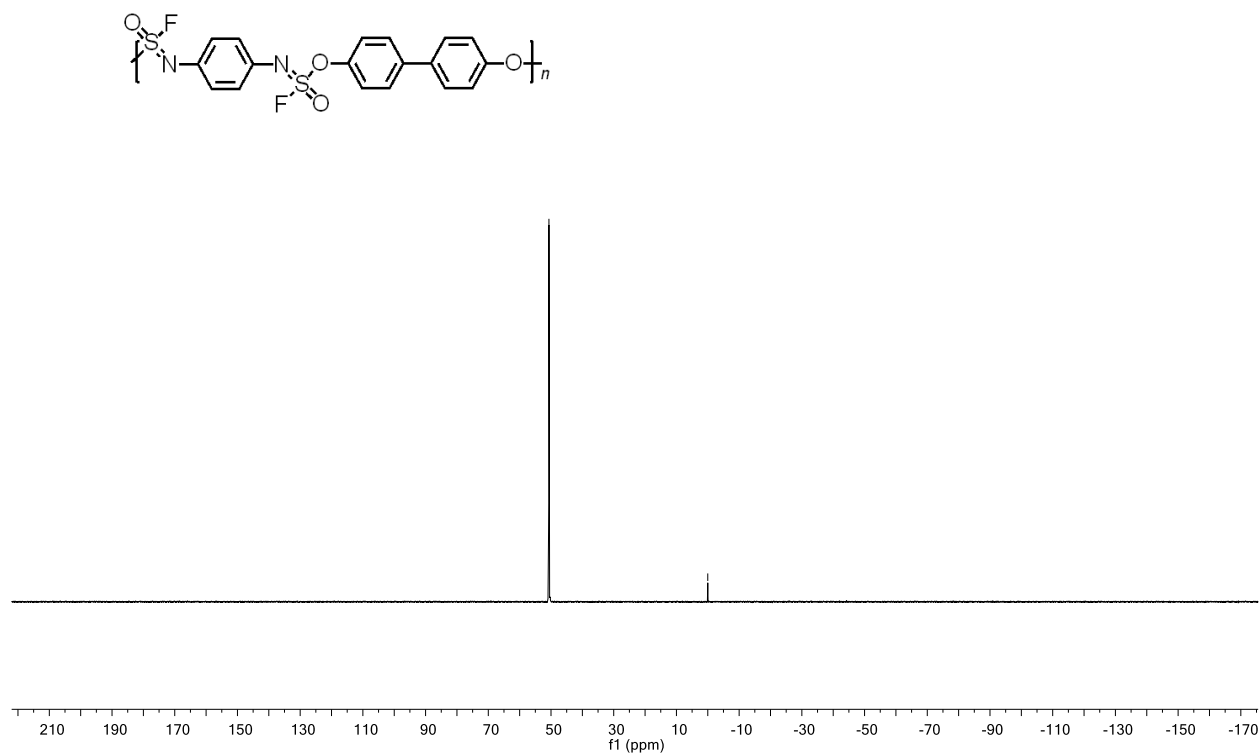
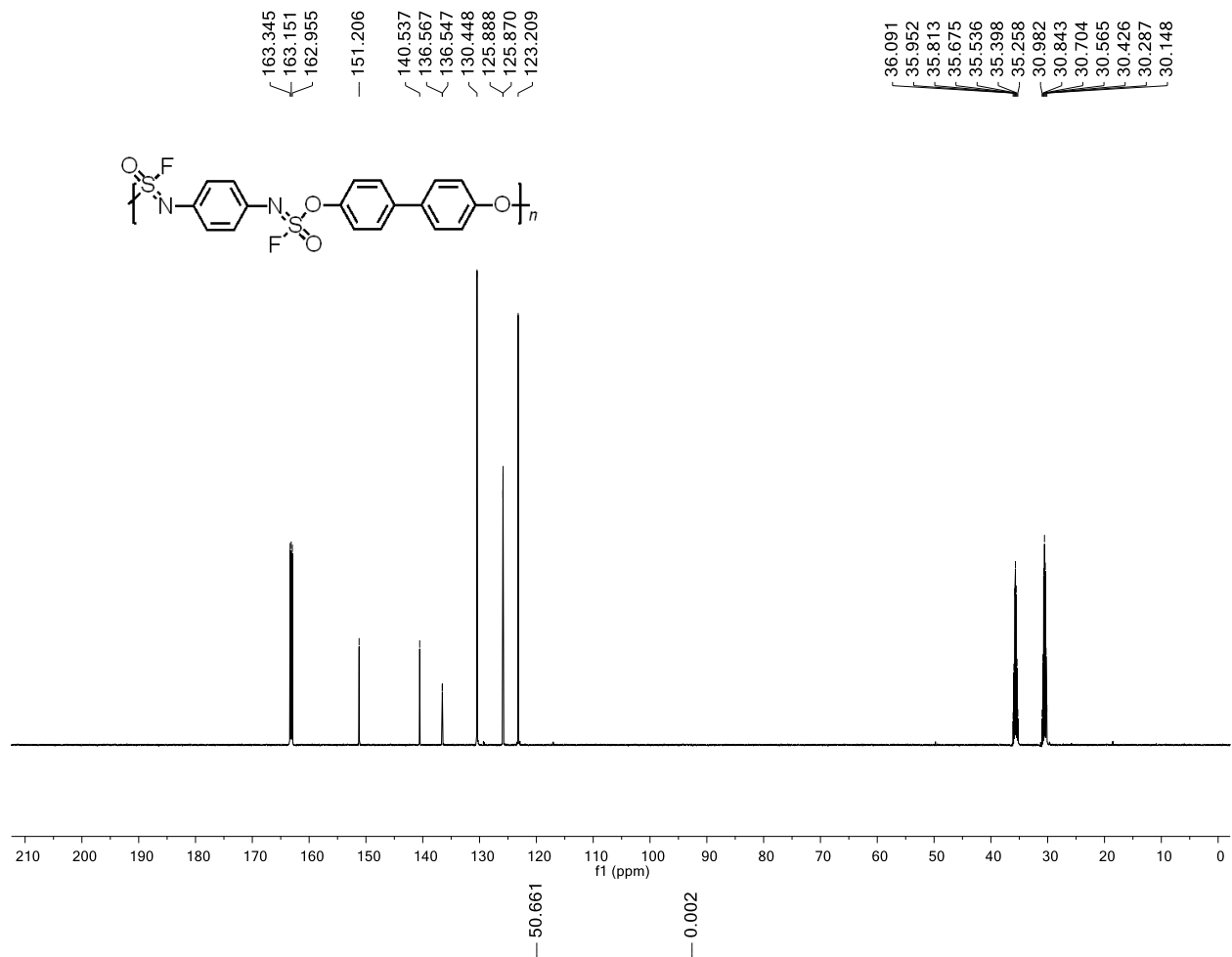


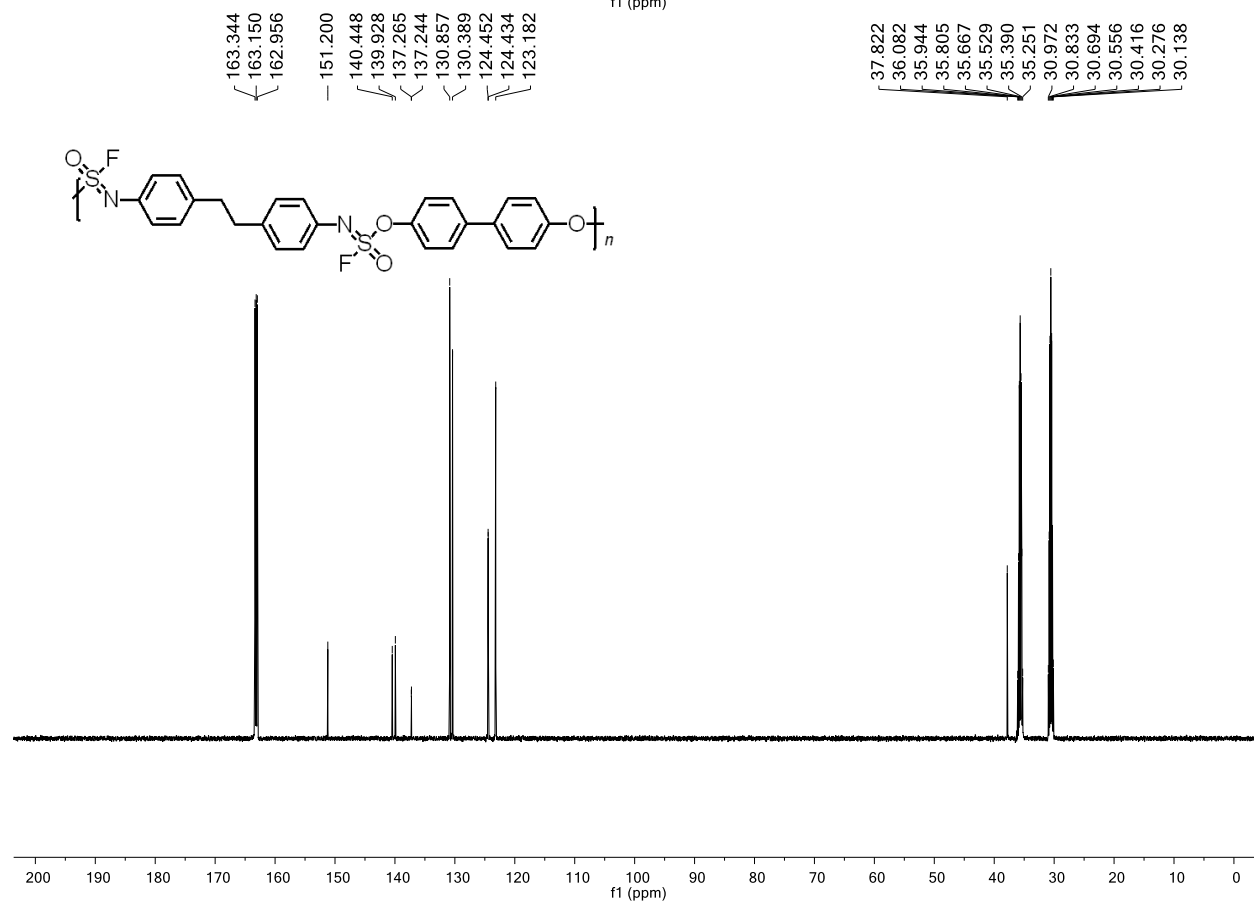
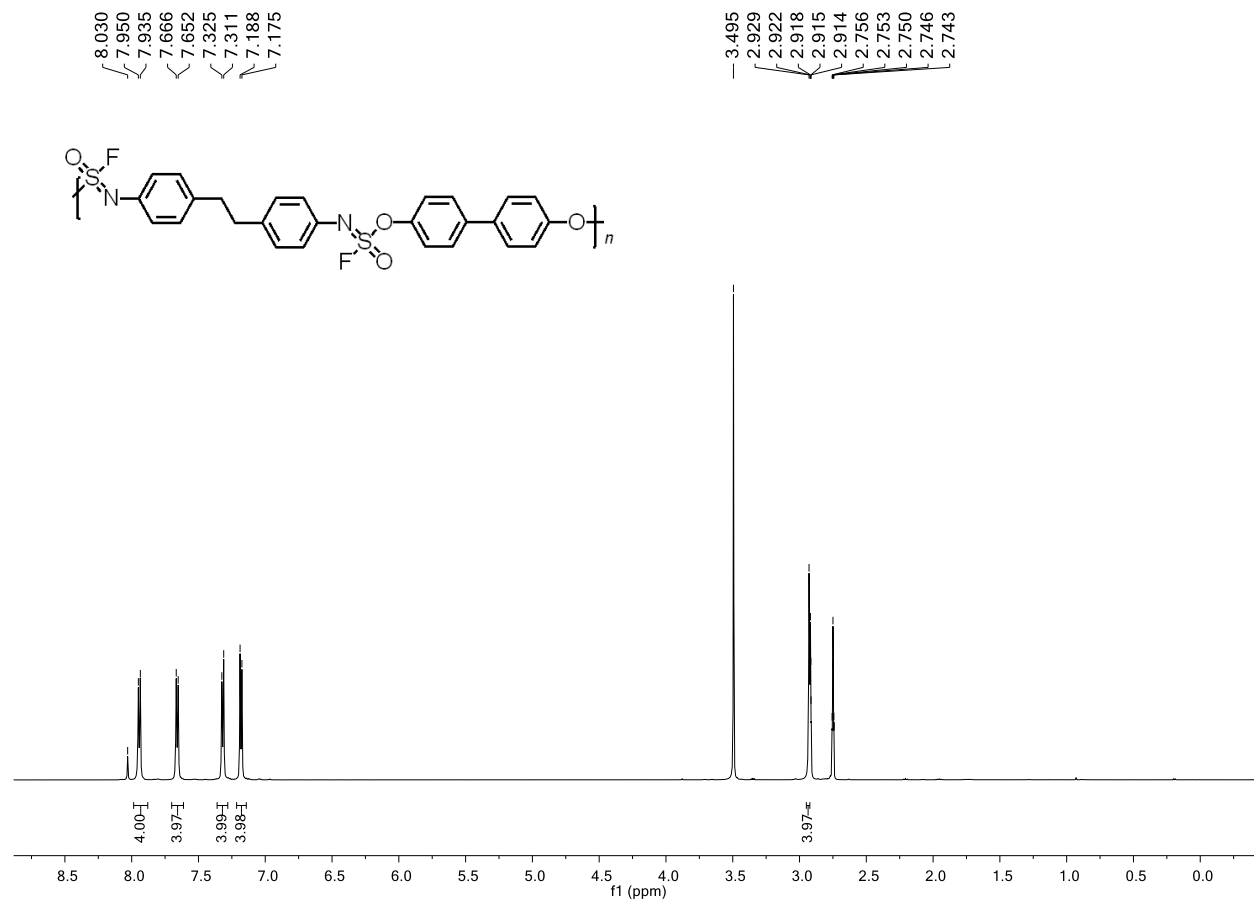


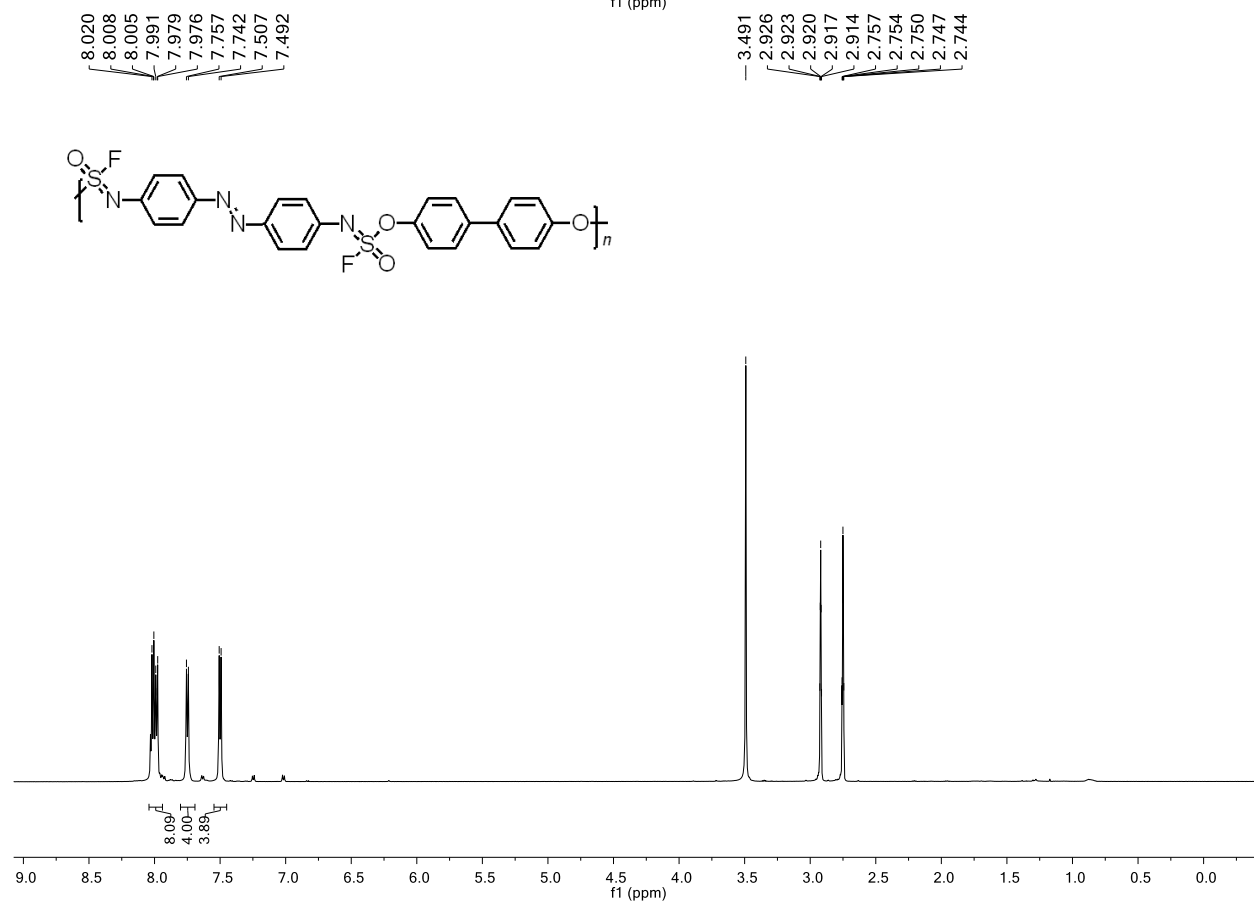
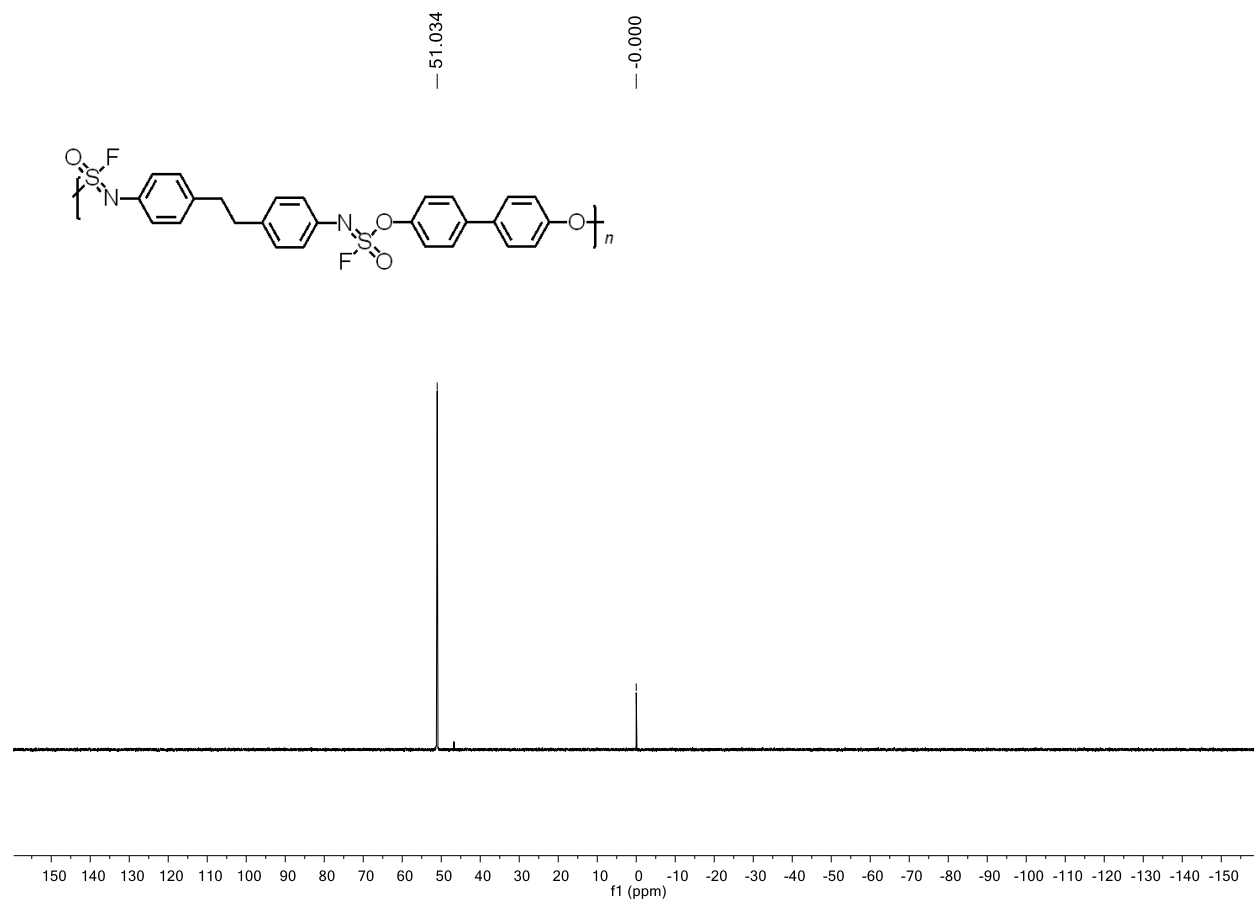


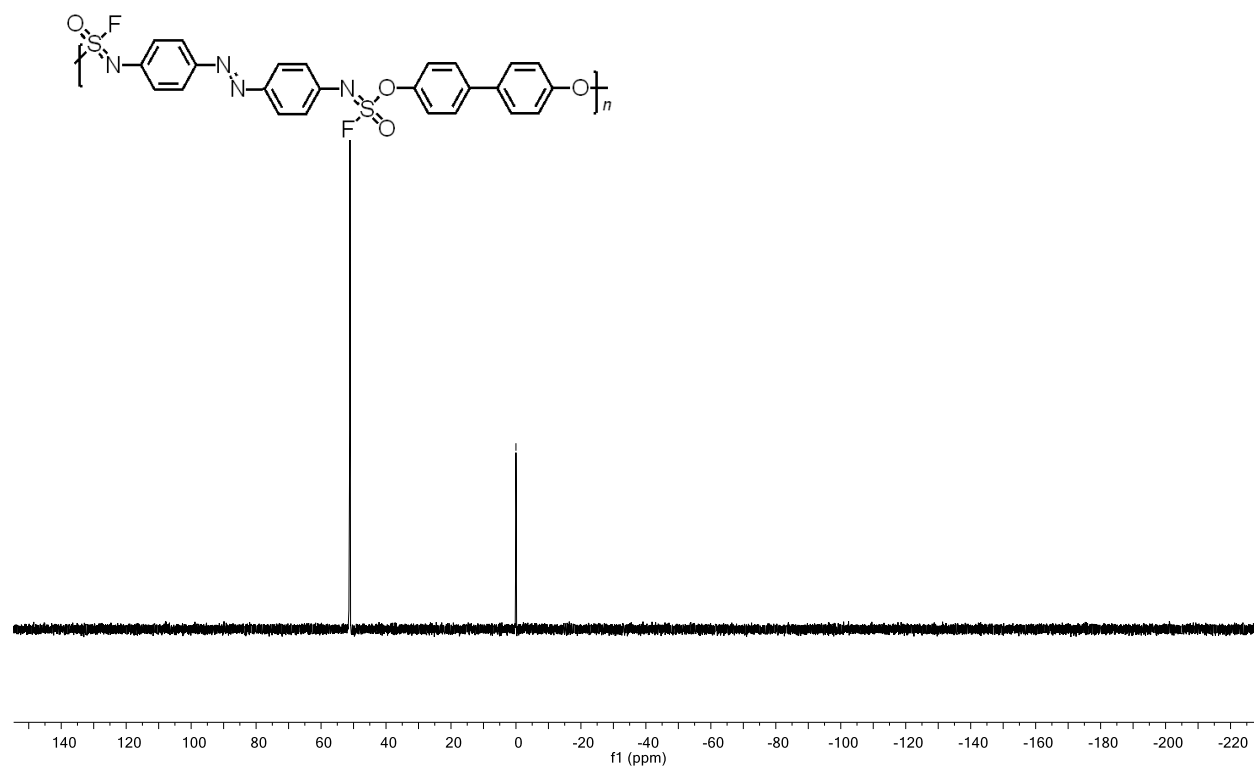
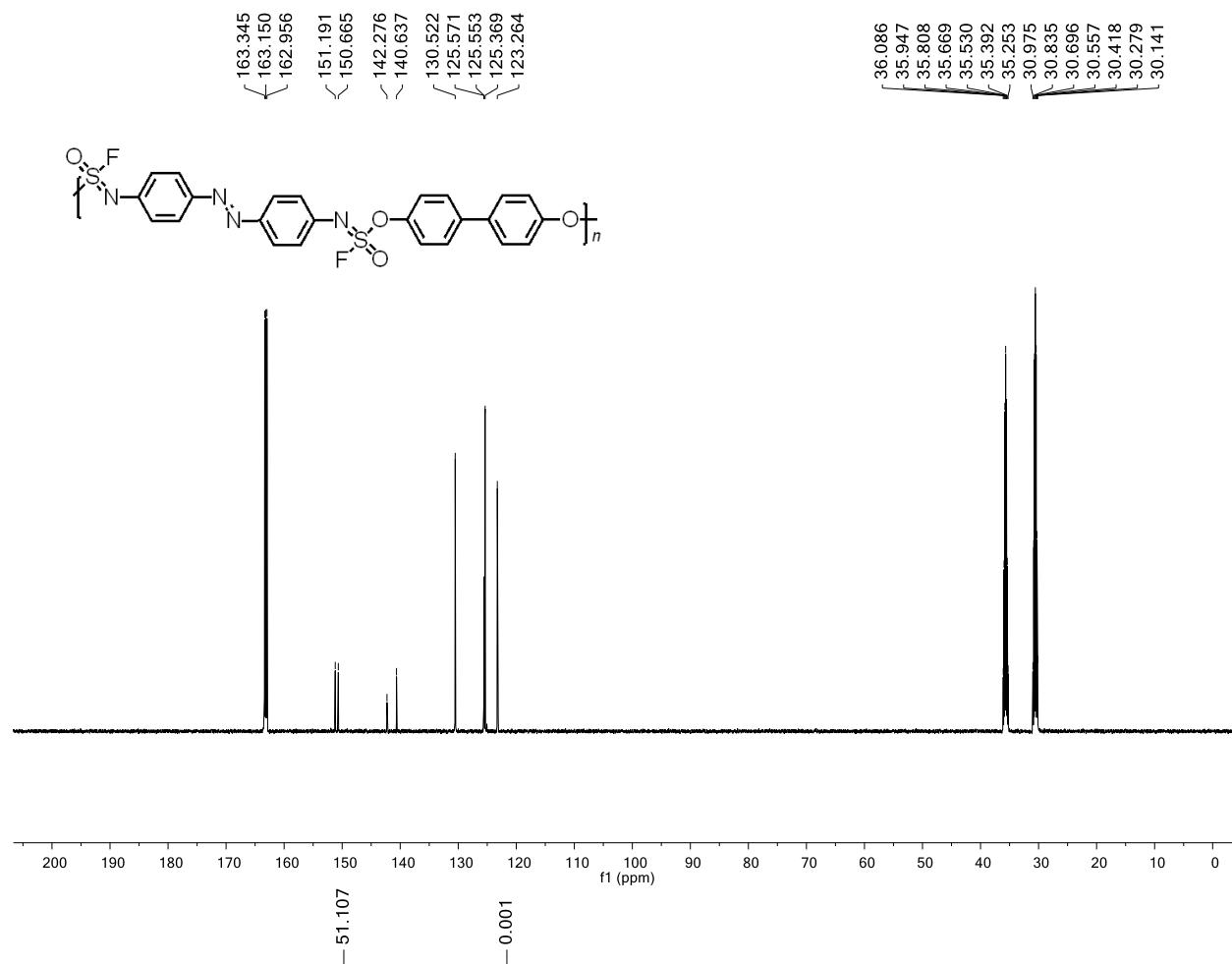


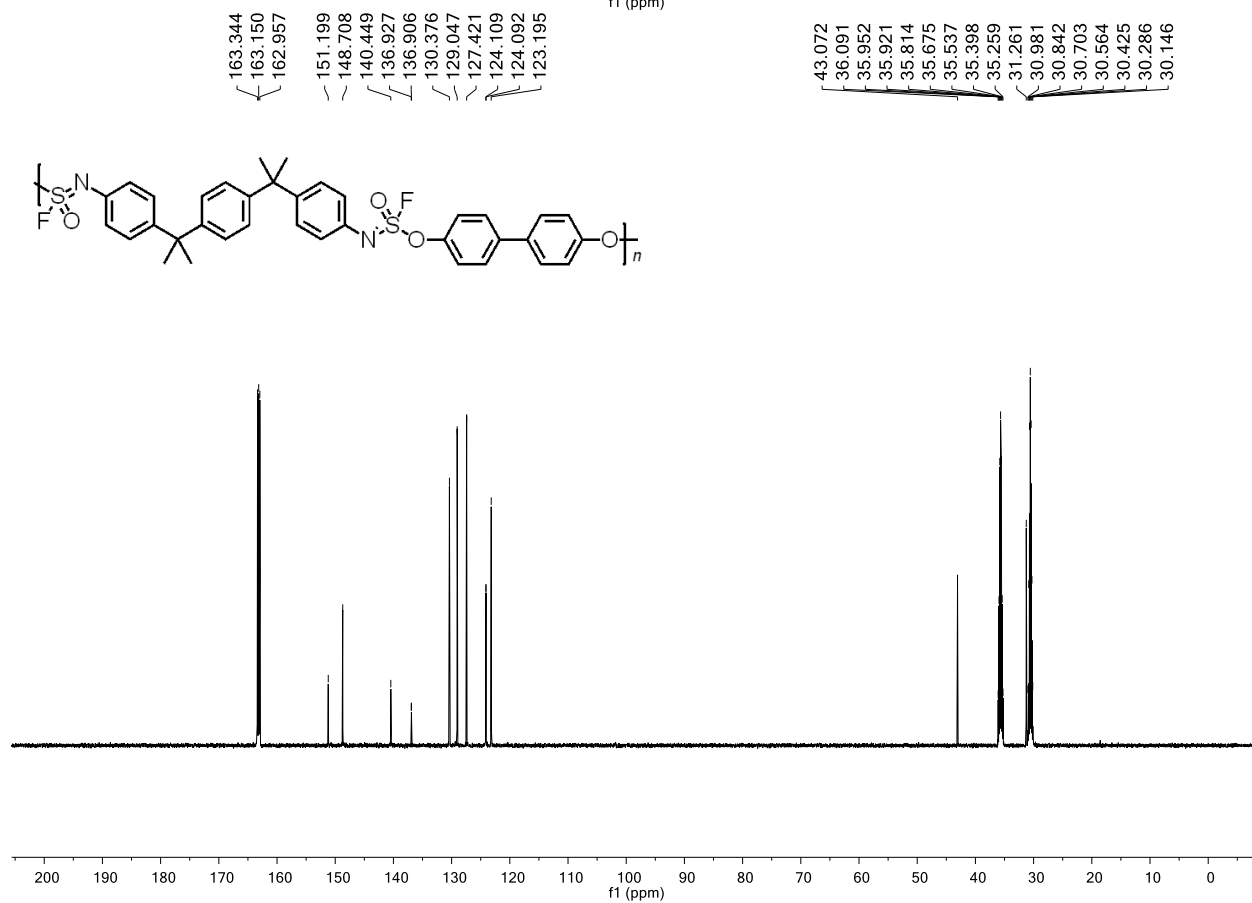
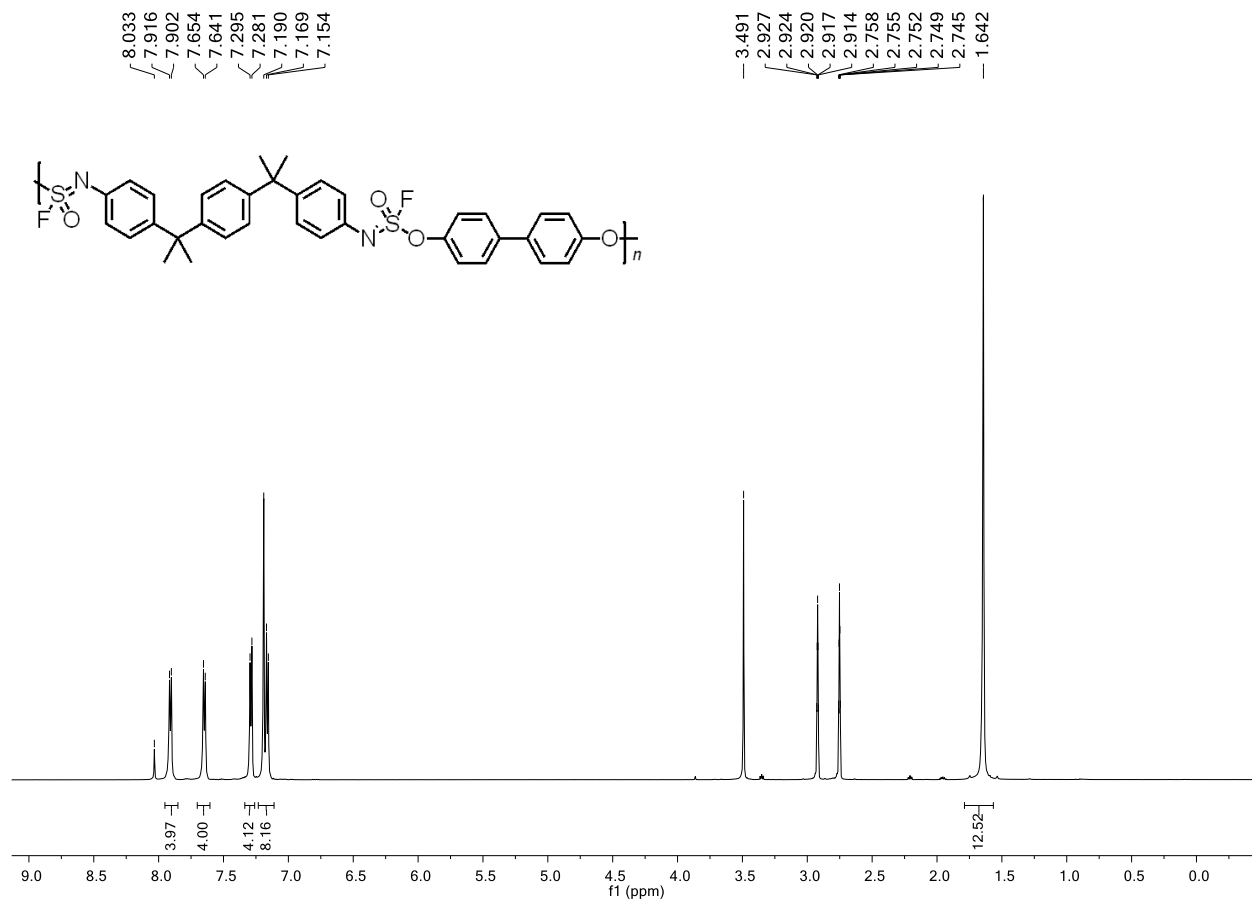


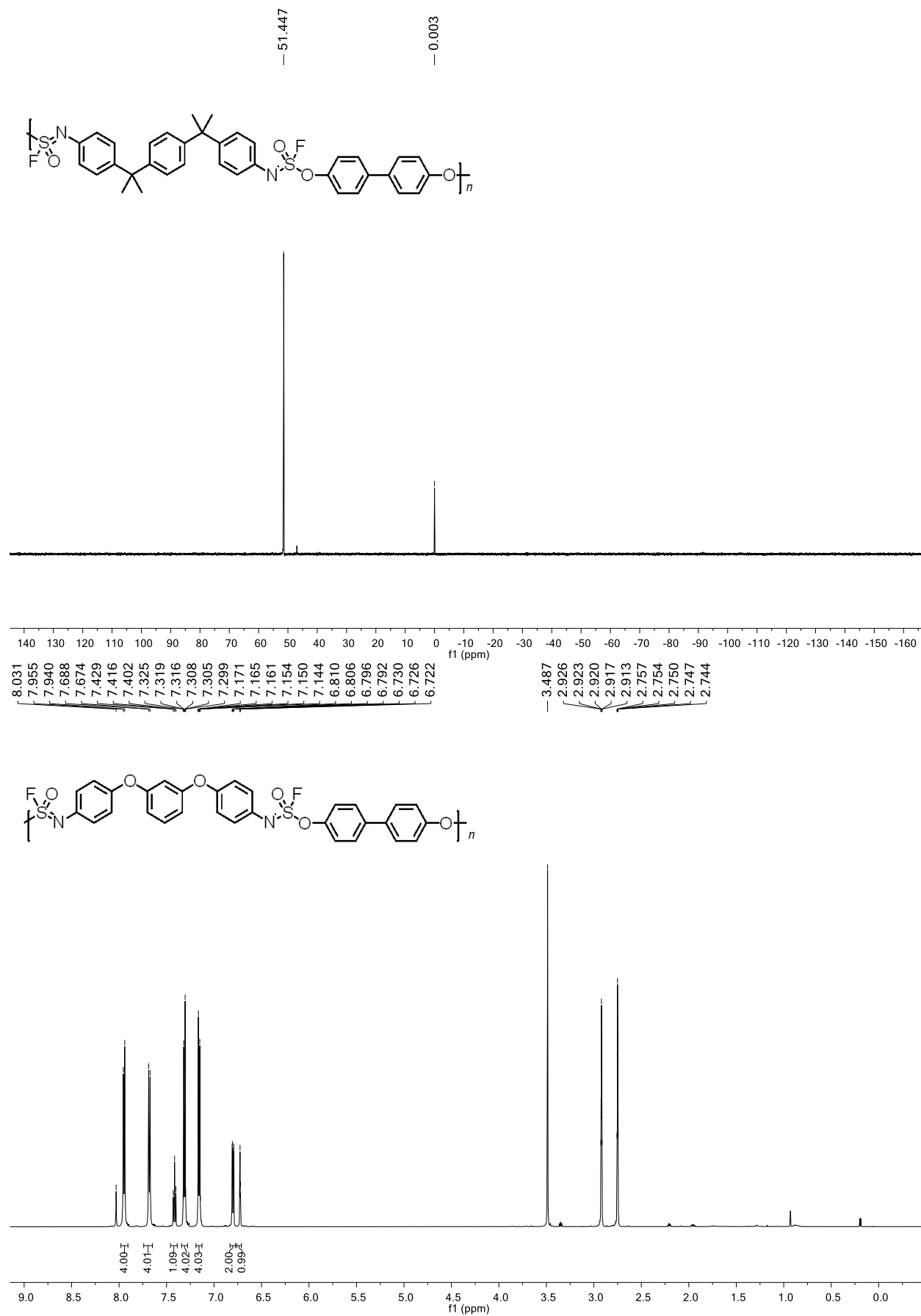


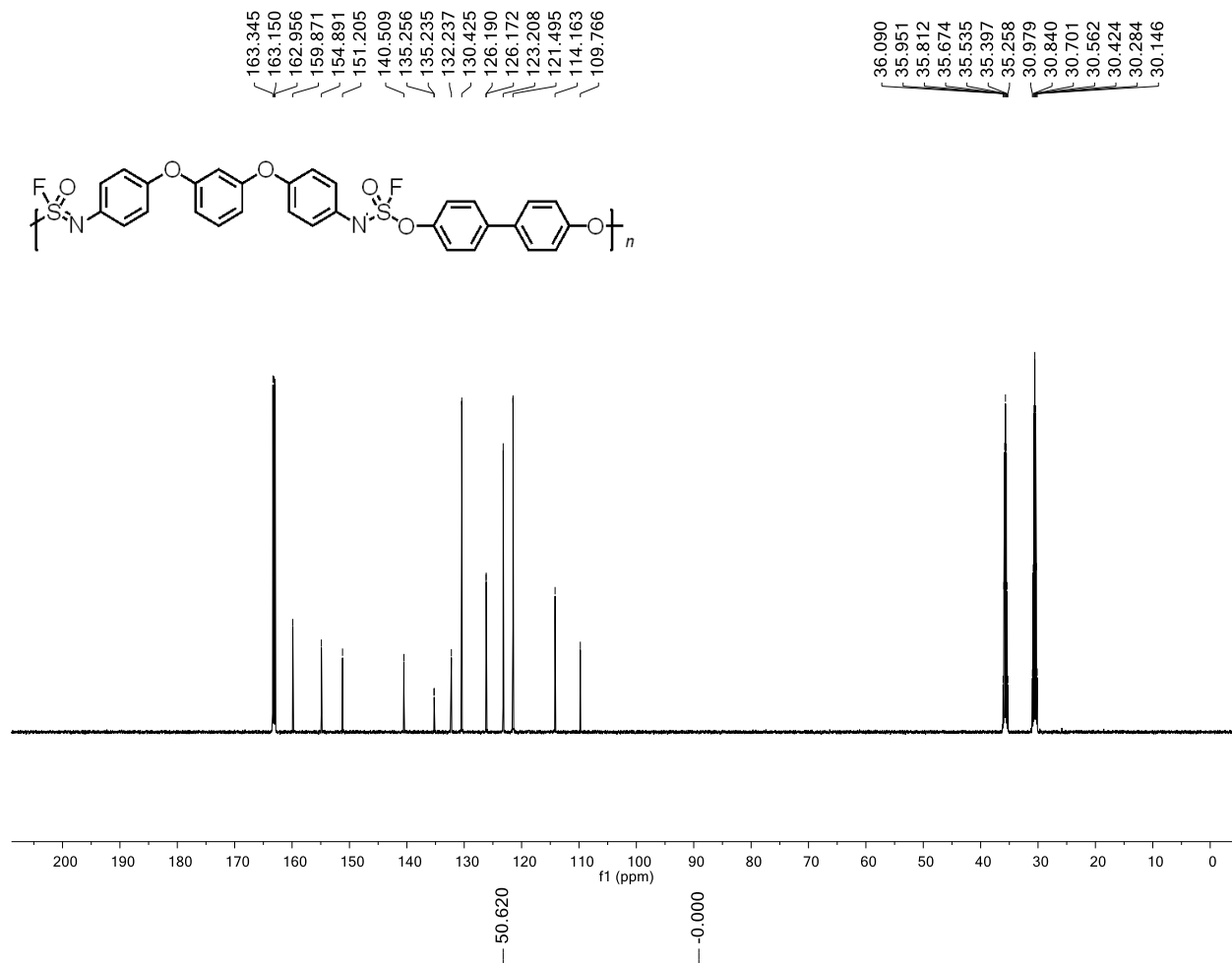


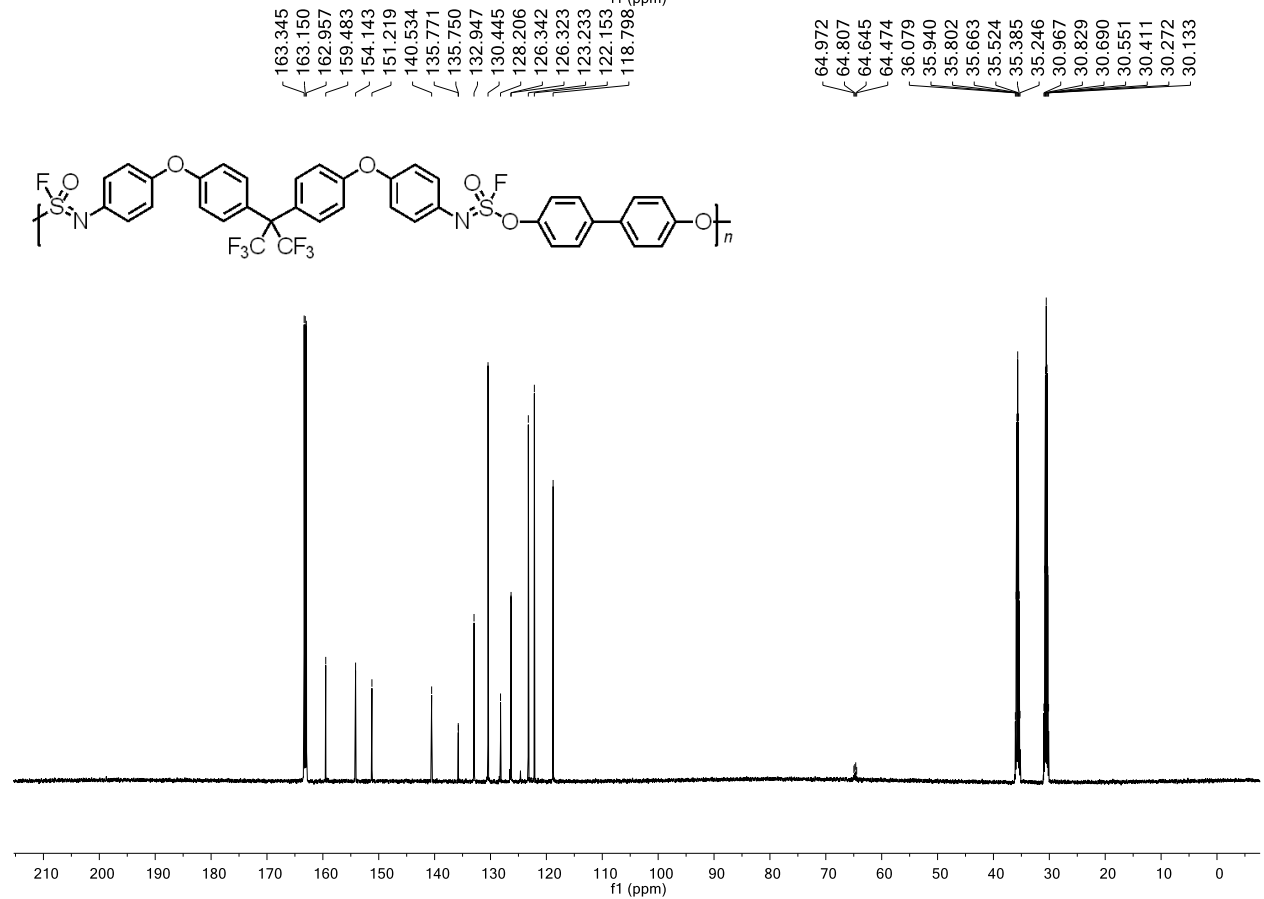
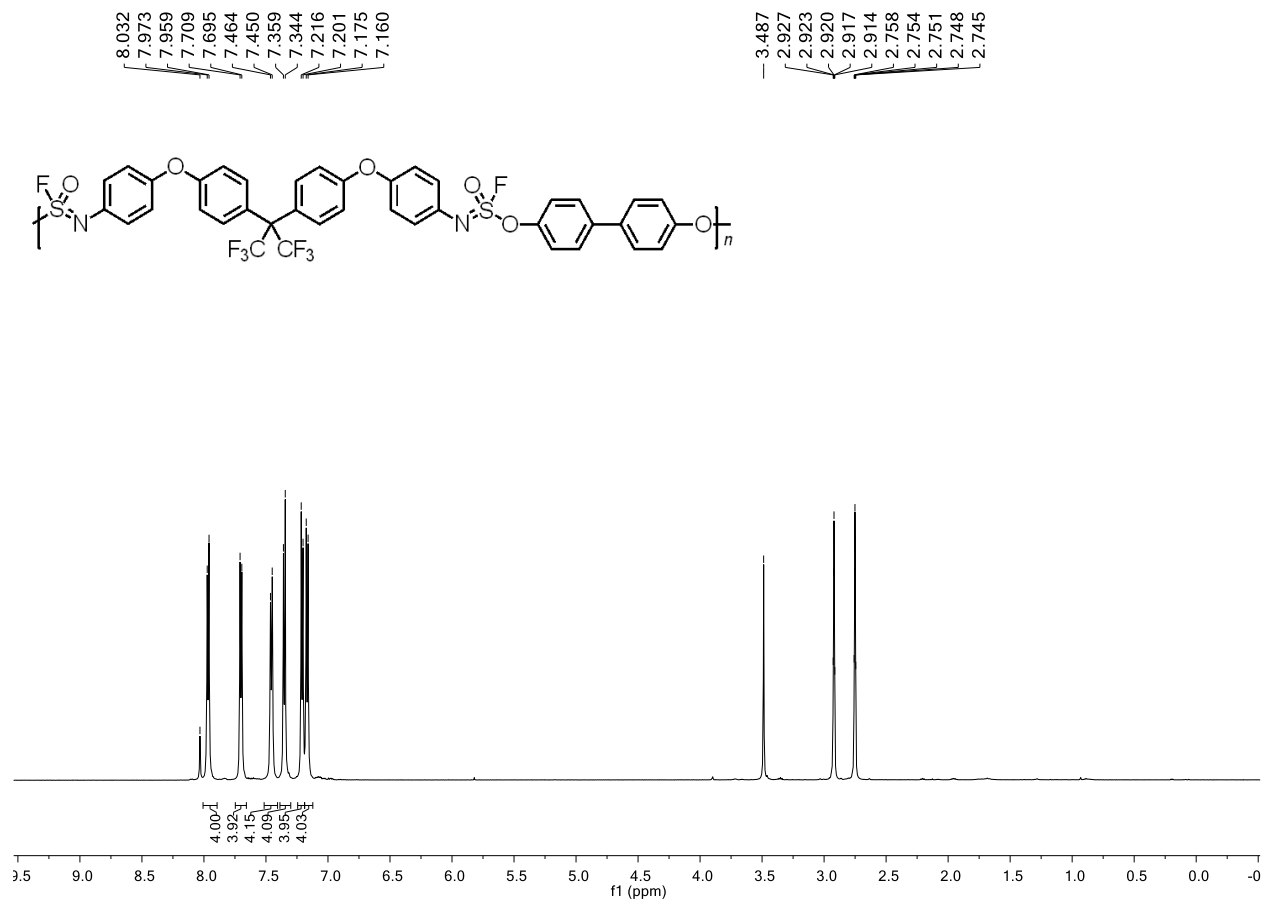


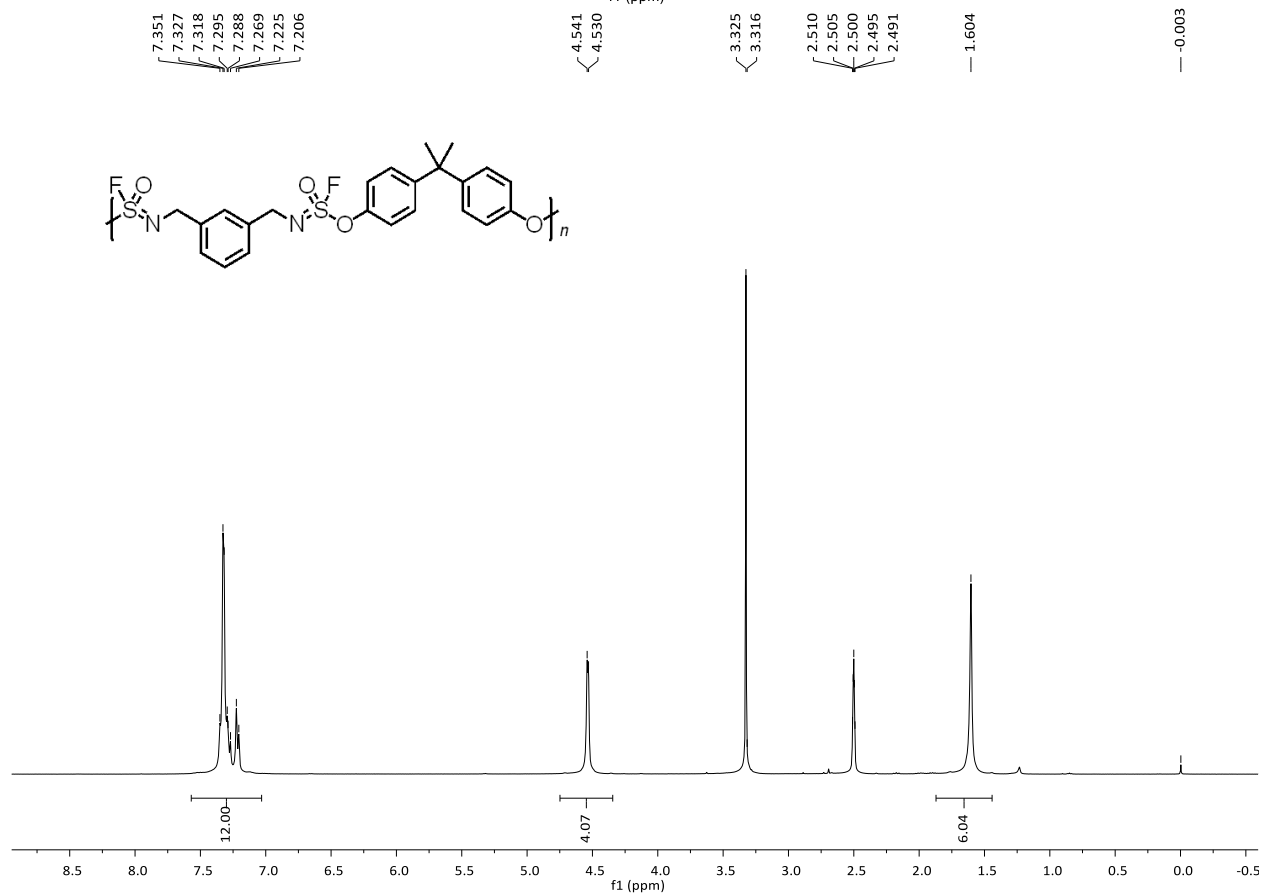
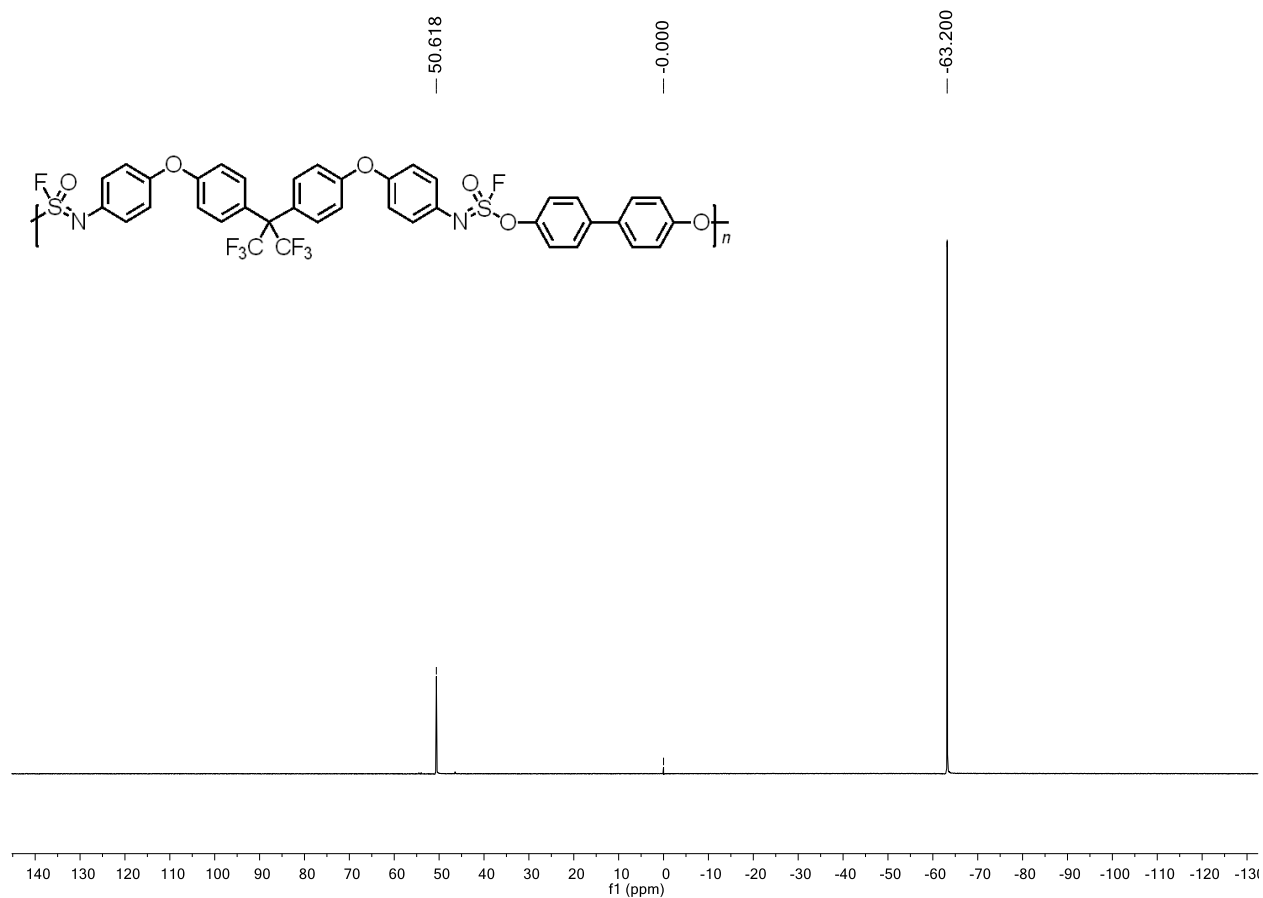


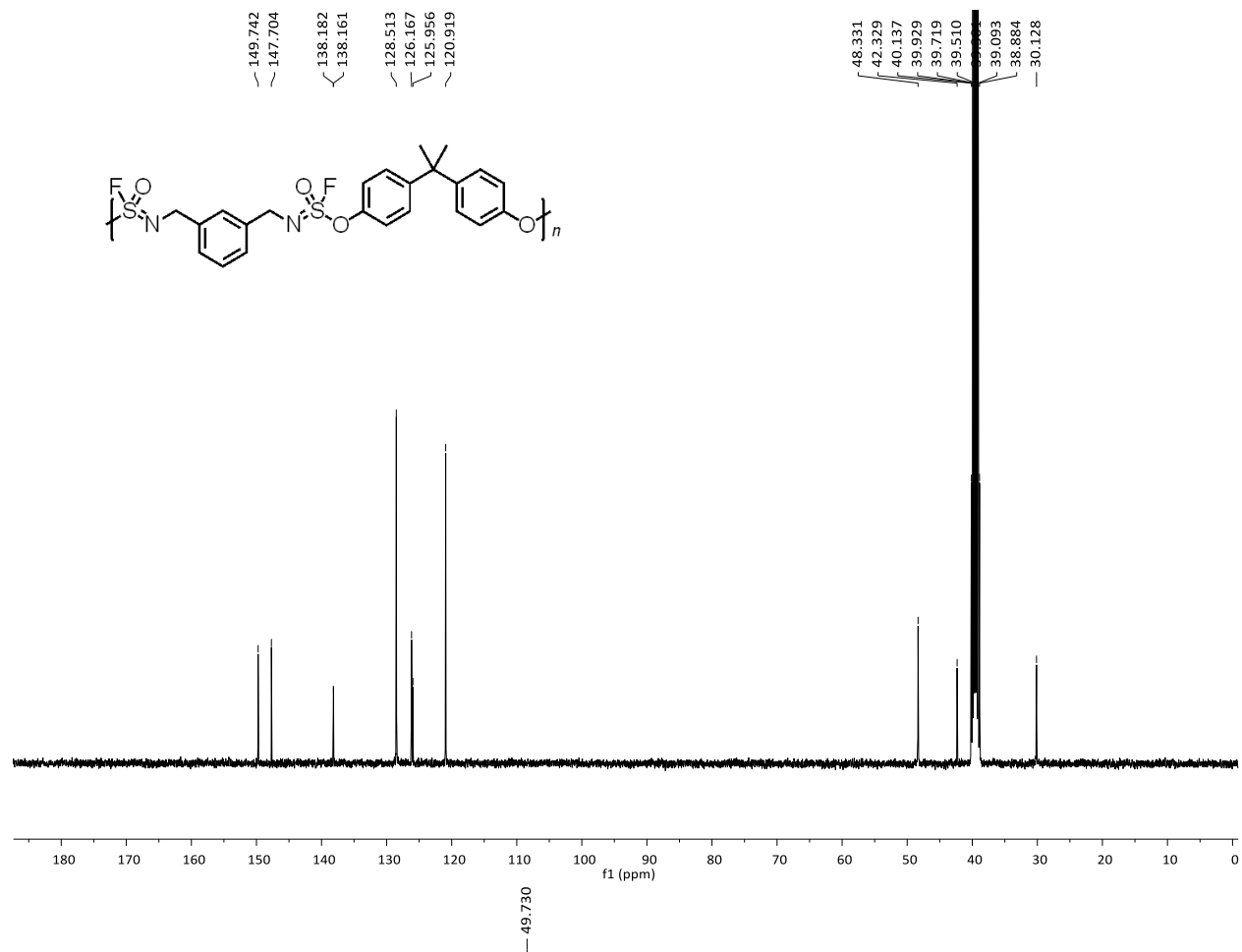


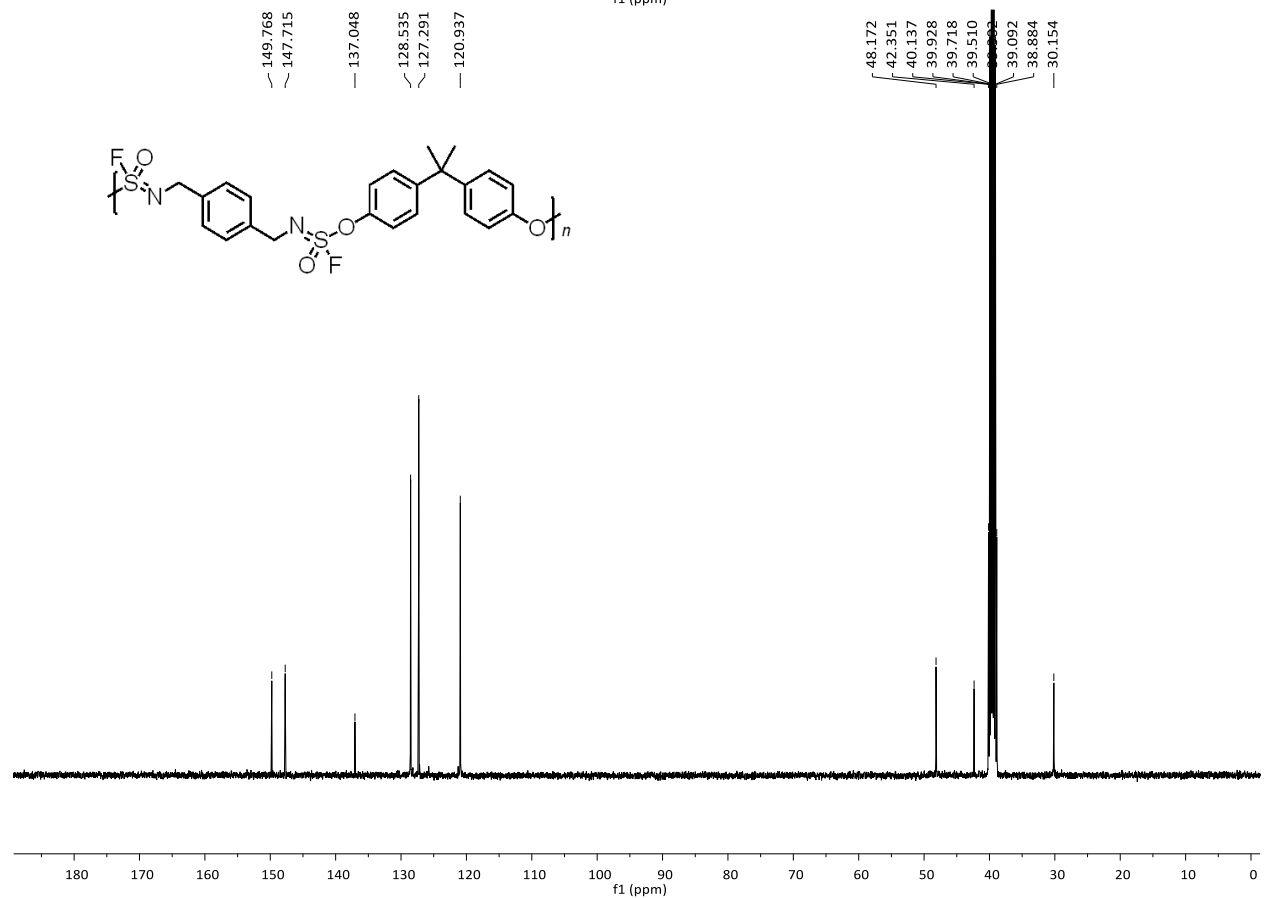
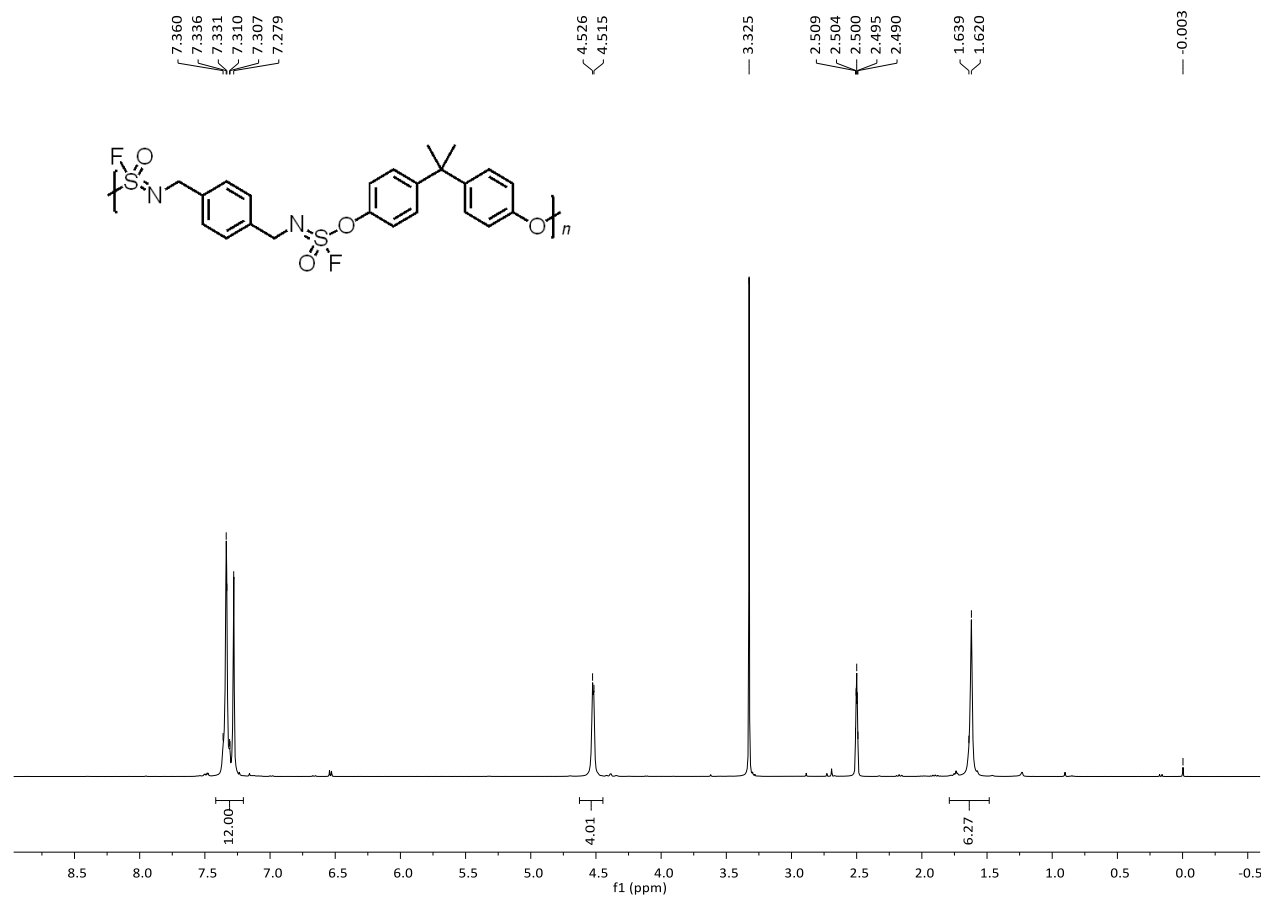


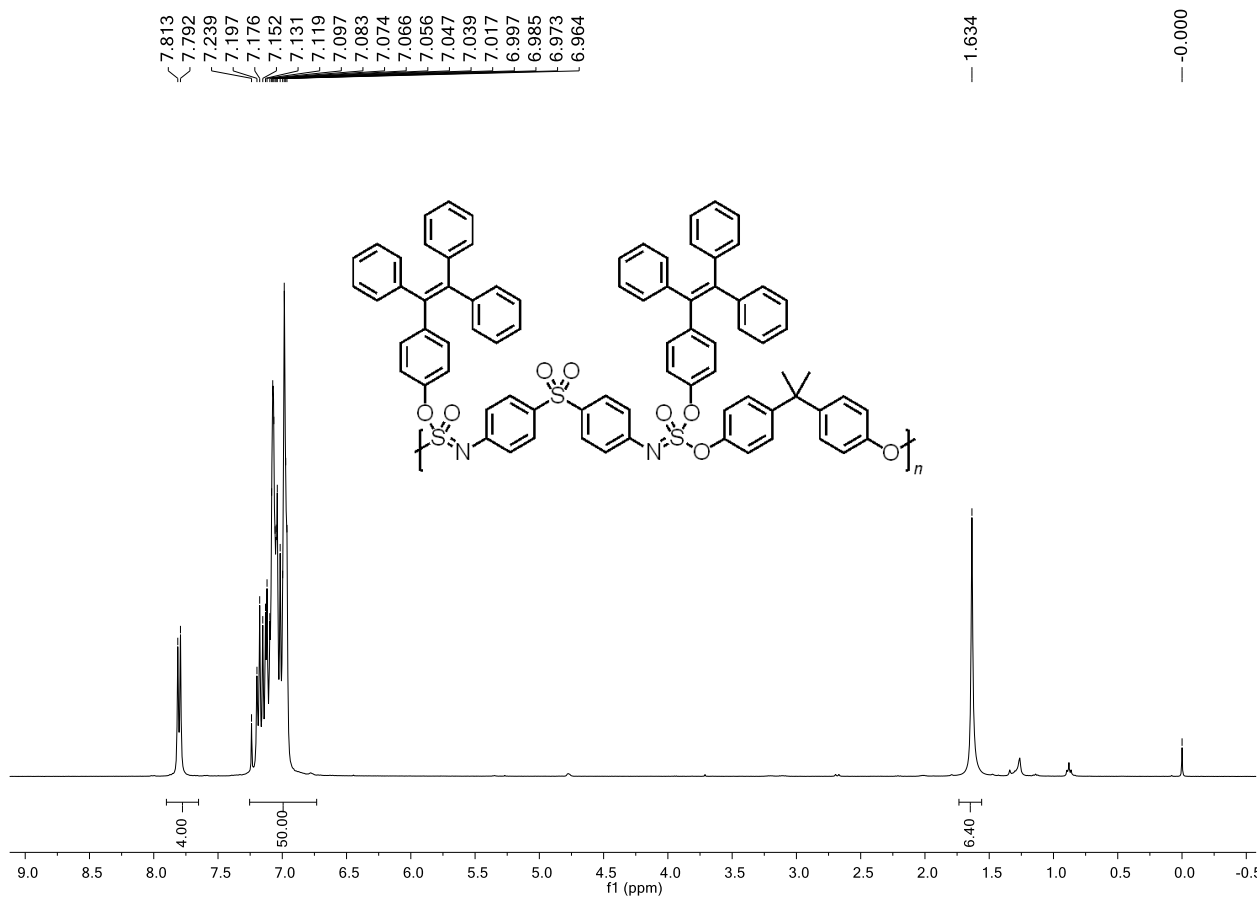
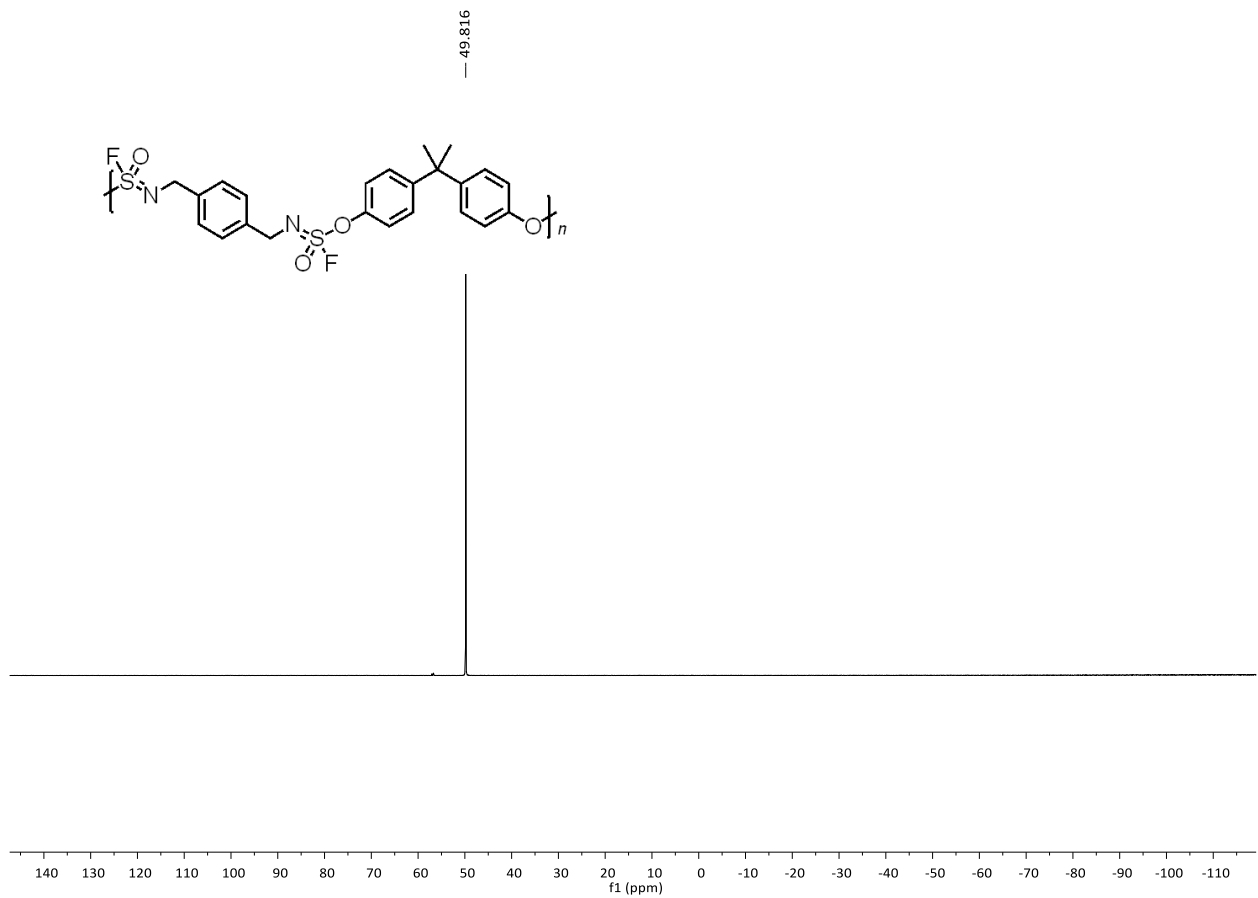


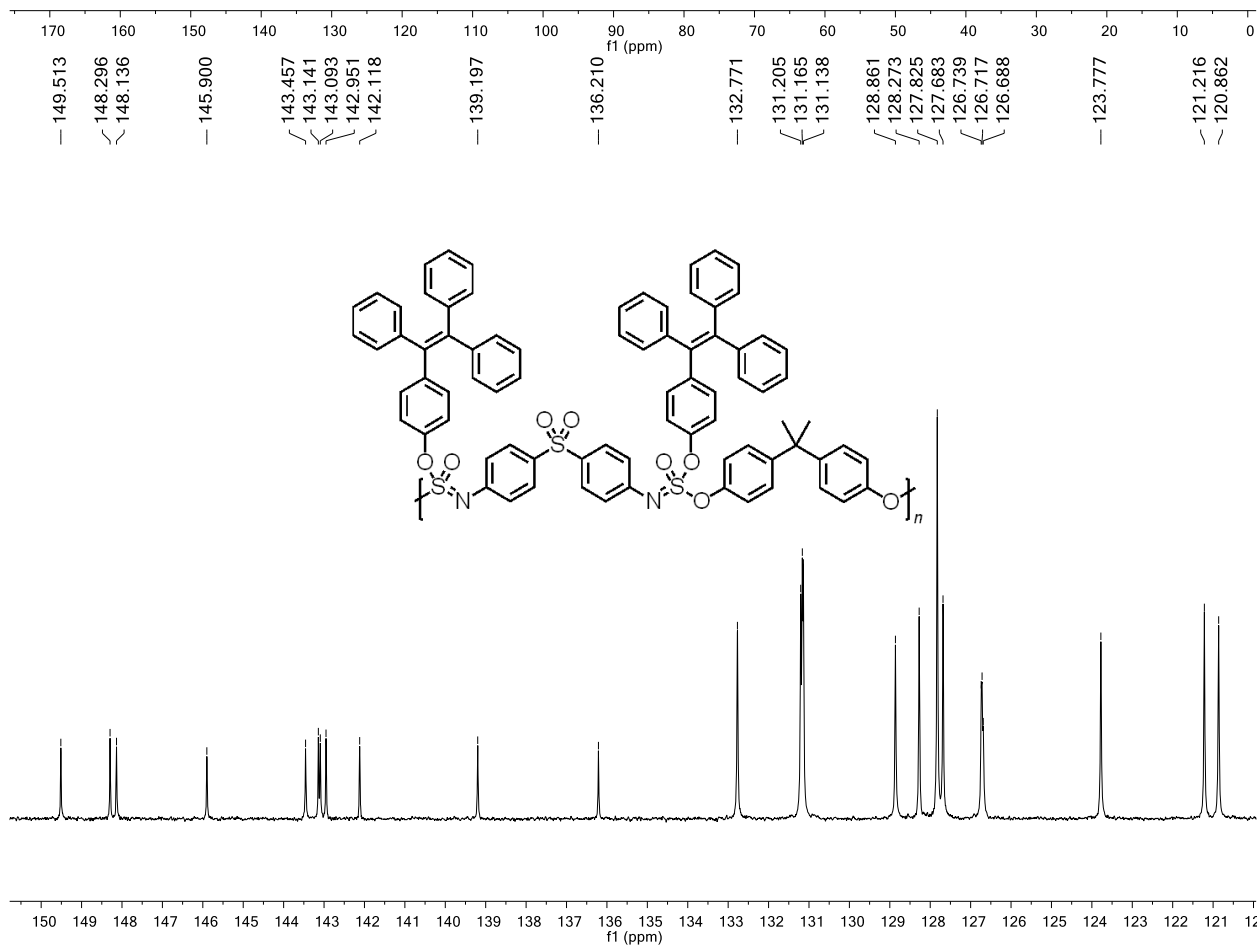
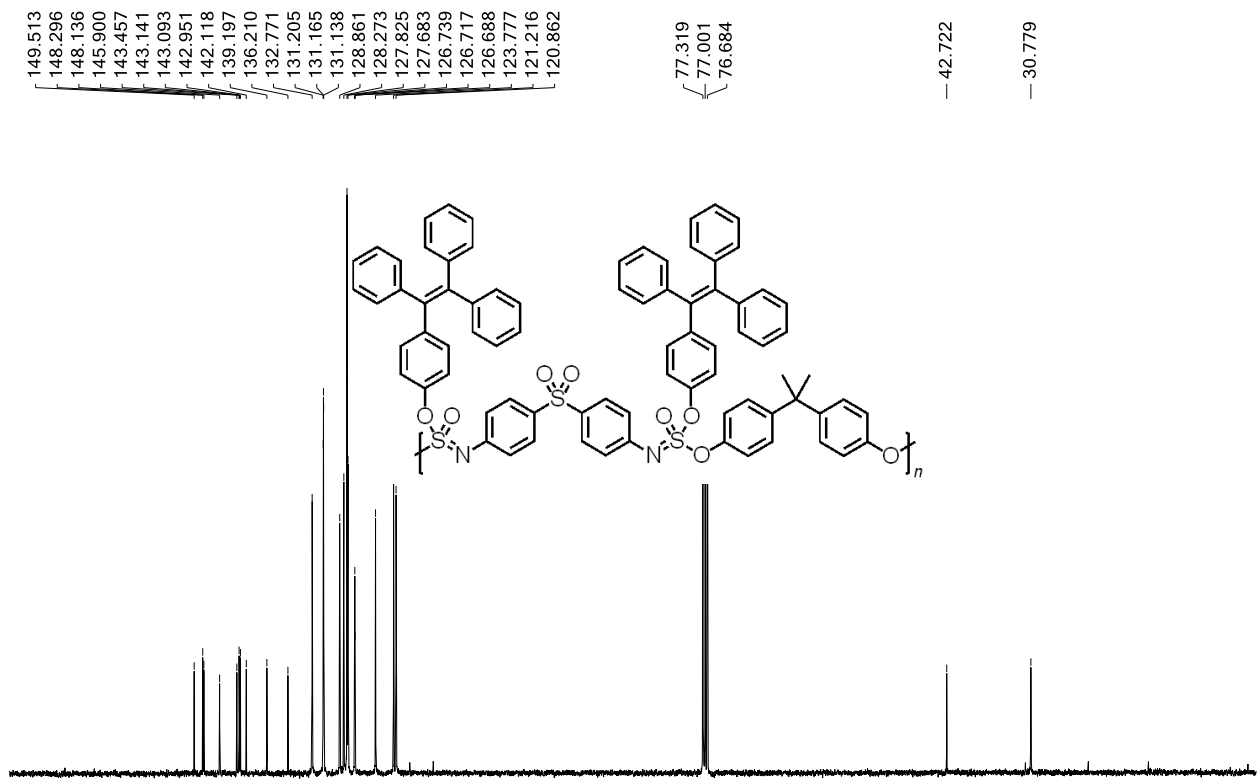


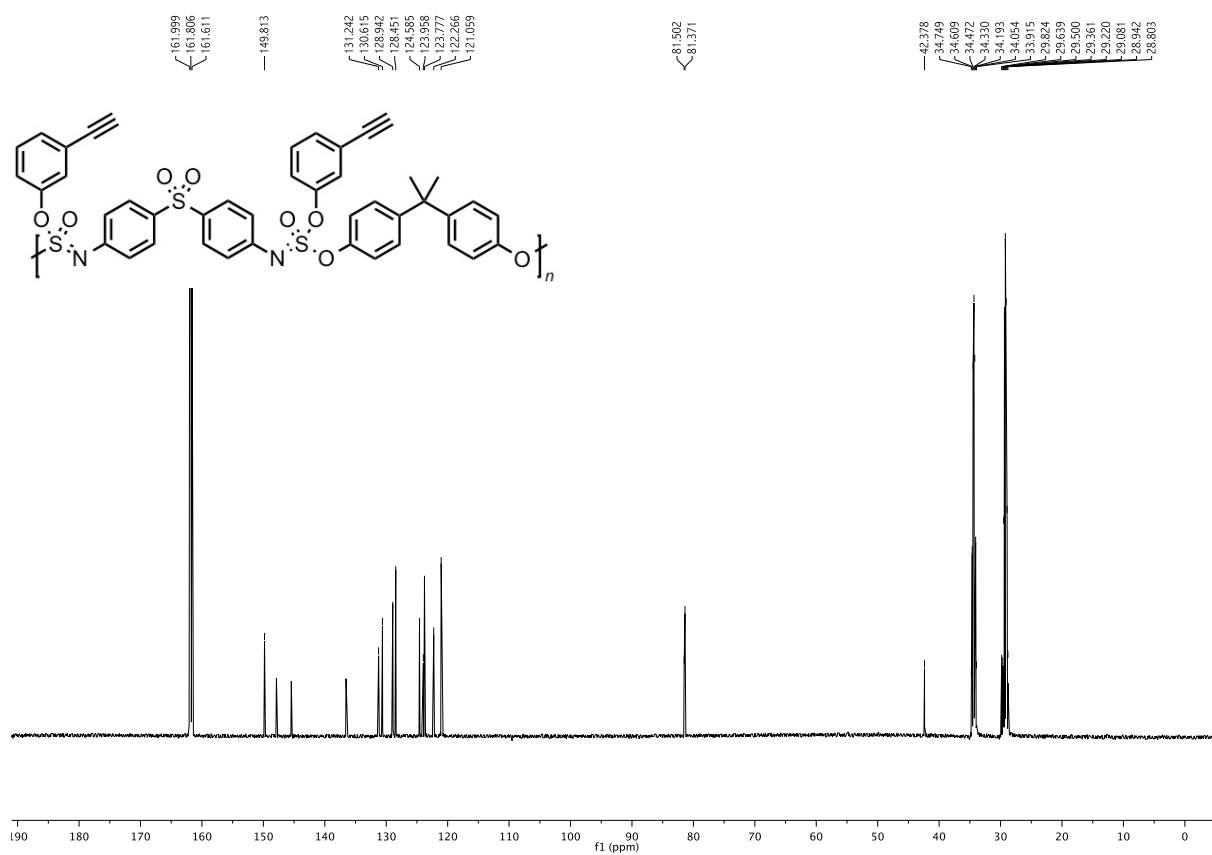


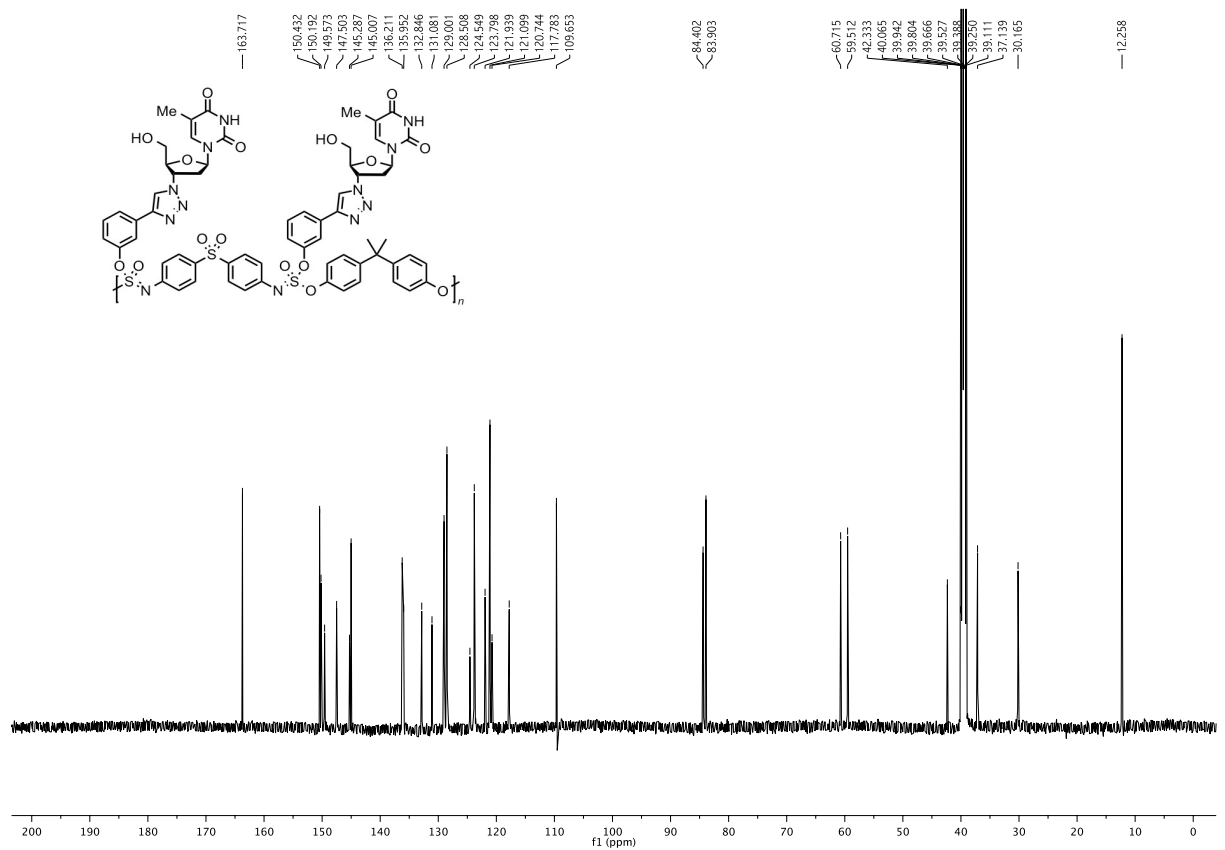
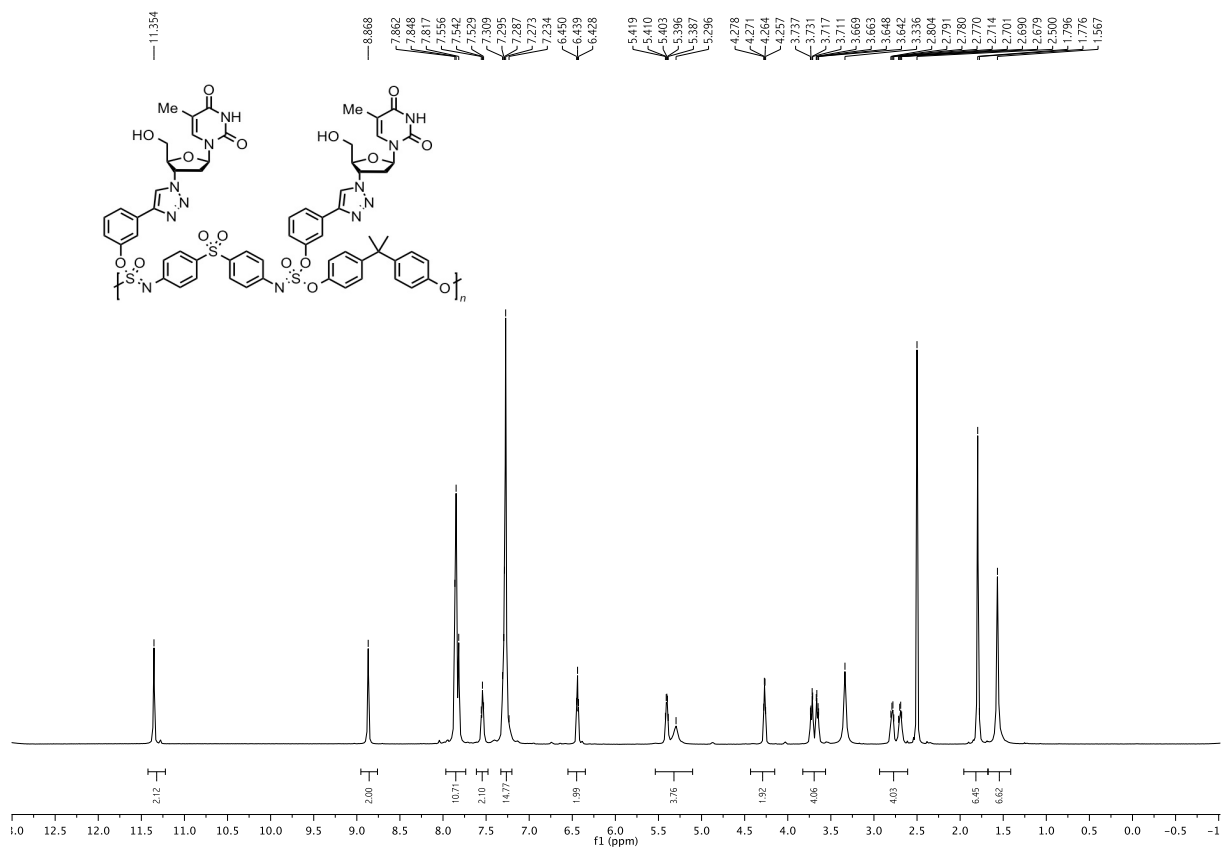


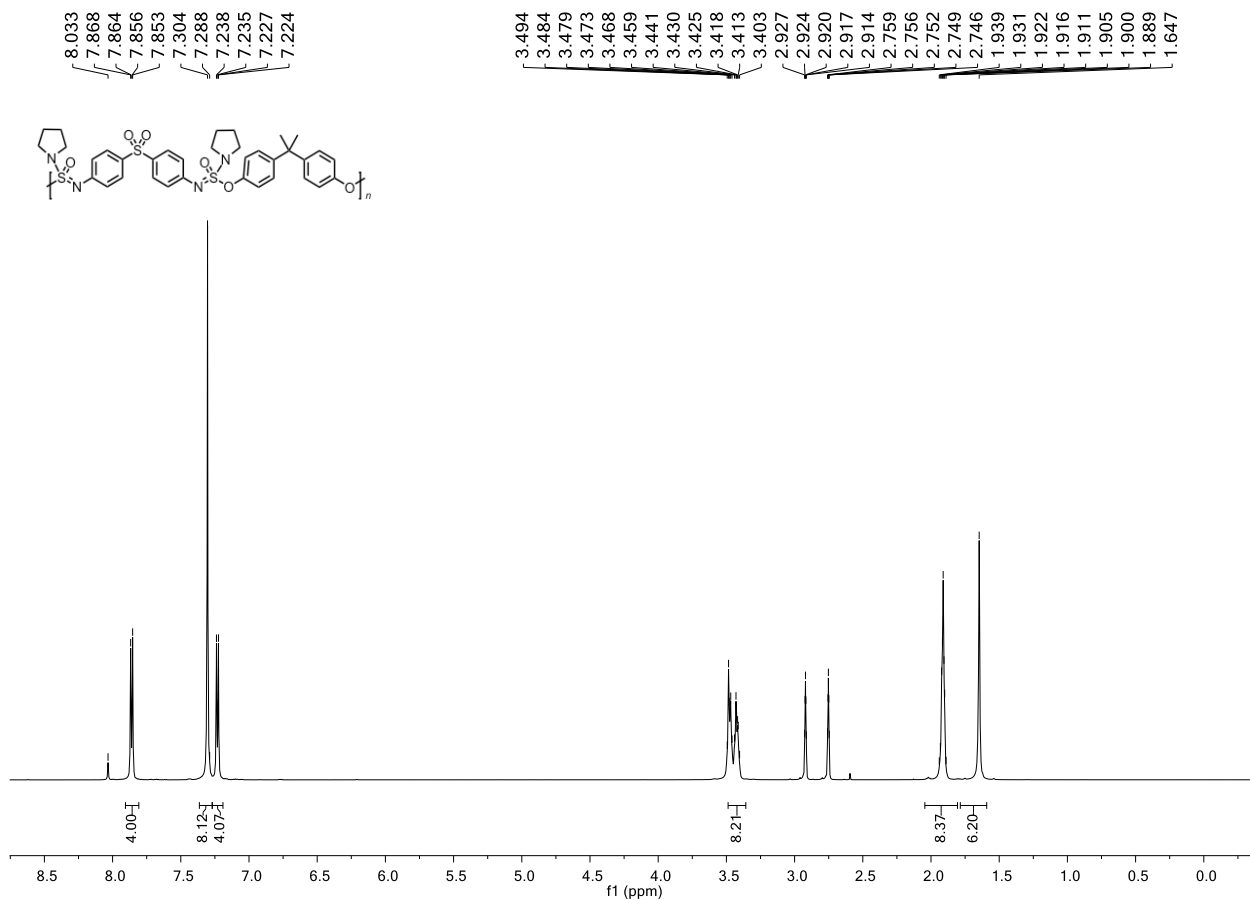


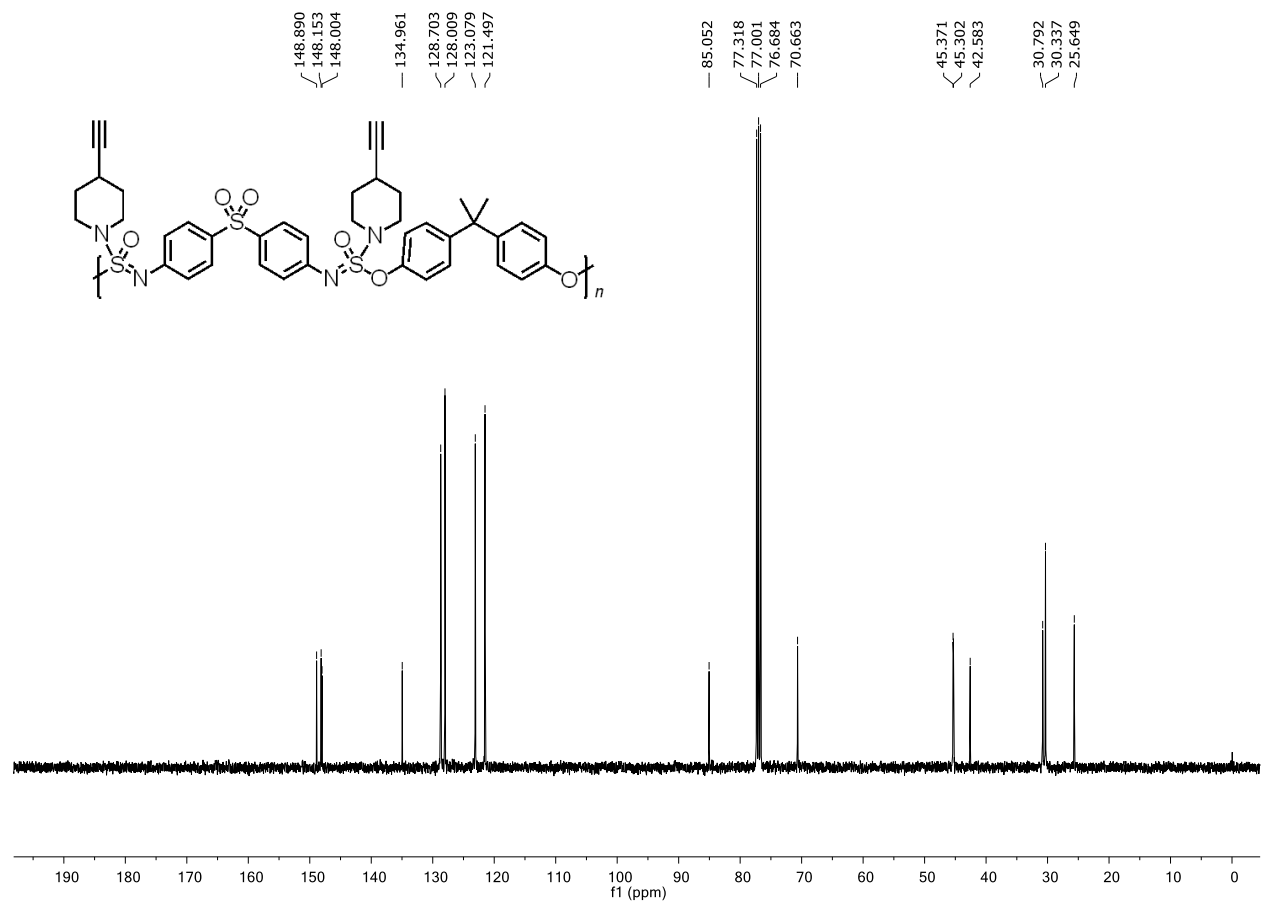
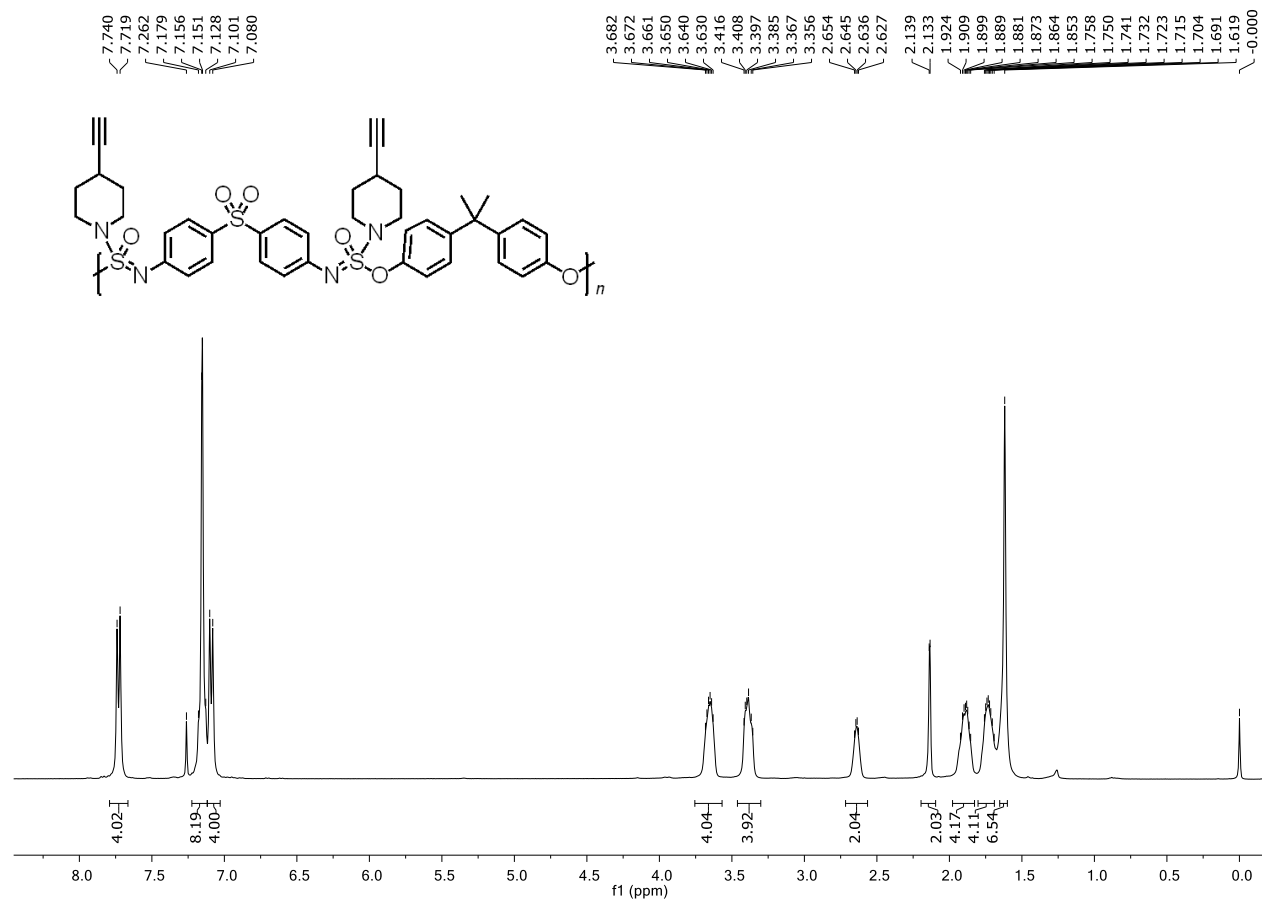












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