

Synthesis of Unsymmetrical Sulfamides and Polysulfamides Via SuFEx Click Chemistry

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In this manuscript, we report practical, robust, and efficient conditions to synthesize a variety of unsymmetrical sulfamides via Sulfur(VI) Fluoride Exchange (SuFEx) click chemistry. This SuFEx strategy was subsequently harnessed to prepare a broad array of polysulfamides through polycondensation. The generality of the conditions allowed the synthesis of polymers with diverse architectures.

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Synthesis of Unsymmetrical Sulfamides and Polysulfamides Via SuFEx Click Chemistry

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ABSTRACT: As hydrogen-bond donors and acceptors, *N,N'*-disubstituted sulfamides have been used in a range of applications from medicinal chemistry to anion-binding catalysis. However, compared to ureas or thioureas, the utilization of this unique moiety remains marginal, in part because of a lack of general synthetic methods to access unsymmetrical sulfamides. Specifically, polysulfamides are a virtually unknown type of polymers despite their potential utility in non-covalent dynamic networks, an intense area of research in materials science. We report herein a practical and efficient process to prepare unsymmetrical sulfamides via Sulfur(VI)-Fluoride Exchange (SuFEx) click chemistry. This process was then applied to synthesize polysulfamides. Thermal analysis showed that this family of polymers possess high thermal stability and tunable glass transition temperatures. Finally, hydrolysis studies indicated that aromatic polysulfamides could be recycled back to their constituting monomers at the end of their life cycle.

Condensation polymerization is at the core of many industrial processes producing high-commodity polymers, such as polyesters, polyamides, polycarbonates, and polyurethanes. The syntheses of these polymers largely rely on robust and high-yielding condensation reactions at activated carbonyl groups and have been optimized over decades of chemical research. The recent development of the Sulfur(VI)-Fluoride Exchange (SuFEx) click chemistry^{1–3} has enabled the synthesis of unique classes of polymers wherein the conventional carbonyl group is replaced by the more esoteric –SO₂– linker. For example, polysulfates^{4–7} and polysulfonates^{8–9} have been accessed and their properties compared to the analogous polycarbonates and polyesters. Among the family of hexavalent sulfur moieties, sulfamides are especially intriguing. As an SO₂ analog of ureas, sulfamides can engage in hydrogen bonding as hydrogen-bond donors and acceptors,^{10,11} a powerful feature for materials science and organic chemistry alike. For example, aliphatic *N,N'*-disubstituted sulfamides have been used as gelators to trigger the assembly of 3D networks and vesicles.^{12–14} In a medicinal chemistry setting, sulfamides can be used as bioisosteres for amides, ureas, and carbamates, and have become more common in the medicinal chemist's arsenal.¹⁵ For example, the broad-spectrum antibiotic doripenem contains a monosubstituted sulfamide pharmacophore.¹⁶ Hydrogen-bonding organocatalysis could become a natural avenue of research for these compounds, but only a handful of useful transformations have been reported with sulfamides thus far.^{17–21} A lack of attention towards this family of molecules stems from the challenging preparation of *unsymmetrical sulfamides*. Similarly, while polyureas are used as a commodity polymer (e.g., spandex), only a few syntheses of polysulfamides have been reported, rendering their properties underexplored.²² Early work in the 1960s demonstrated that condensation between aliphatic bis(amine) **1a** and sulfamide (**2a**) at high temperatures produced insoluble macromolecules that were not fully characterized (Figure 1a).^{23–25} More recently, Rudkevich and coworkers synthesized oligomer **3b** (*M_n* = 1.7 kg/mol) using 1,4-phenylenediamine (**1b**) in combination with SO₂, I₂, and pyridine or triethylamine (Figure 1a).²² The authors postulated the generation of a variety of hexavalent species including SO₂I₂.²⁶ Considering the Carothers equation,²⁷ we hypothesized that in order to obtain polysulfamides with higher degrees of polymerization (DP), we should identify conditions that 1) afford control over the stoichiometry of AA/BB type monomers, and 2) avoid potential deleterious oxidative side-reactions that diminish the overall yield. We report herein the development of conditions based on SuFEx click chemistry for the high-yielding preparation of isolable sulfamoyl fluorides, unsymmetrical sulfamides, and polysulfamides (Figure 1b).

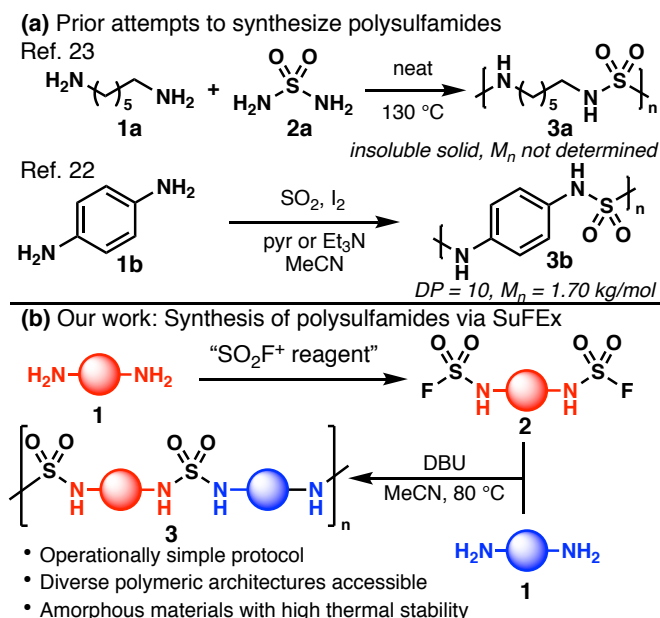


Figure 1. a) Early efforts toward polysulfamides led to oligomers or insoluble solids. b) Synthesis of fully characterizable polysulfamides via SuFEx click chemistry.

While several methods producing sulfamides have been reported, they generally suffer from narrow substrate scope and variable yields.^{28–37} Moreover, the iterative addition of two different amines to an electrophilic sulfur(VI) reagent is often complicated by either the high instability of the intermediate or, on the contrary, insufficient reactivity of this species. SuFEx is attractive due to its mildness, efficiency, atom-economy, and stability of the fluoride-containing intermediate. For example, Sharpless disclosed an efficient synthesis of an unsymmetrical tetraalkylated sulfamide using SO_2F_2 and two secondary amines. Importantly, the sulfamoyl fluoride intermediate could be isolated and purified.³⁸ However, these conditions are known to be unsuitable for primary amines.^{1,39} Indeed, treating benzylamine (**4a**) with SO_2F_2 (commercial or ex-situ generated)⁴⁰ led to the formation of undesired symmetrical sulfamide **7a** as the major product, likely through the generation of azasulfene **6a** (Figures 2a and S1,2).⁴¹ We instead turned our attention to SO_2F_2 alternatives. Sulfamides have been synthesized using thionyl tetrafluoride (SOF_4), but this gas is not commercially available and its preparation is hazardous.⁴² Dong and Sharpless demonstrated that imidazolium derivative **8**, a shelf-stable crystalline solid analog of SO_2F_2 , allows for the preparation of monosubstituted sulfamoyl fluoride in high yield (Figure 2b).⁴³ We were pleased to find that this reagent afforded a variety of bis(sulfamoyl fluoride) monomers (**2b–e**) when used in combination with simple primary bis(amine)s in DCM (Figure 2c). Notably, no precautions were taken to remove water and oxygen from the reaction, and both alkyl and aryl monomers can be synthesized in good yields. These monomers are shelf-stable for several days, but should be stored at 0 °C for extended periods of time to prevent slow decomposition. While decomposition is rapid in basic media, these monomers, apart from **2b**, exhibit high tolerance to acidic conditions and can be purified through column chromatography. Yet, most impurities can be removed through aqueous workup, which is a testament to the practicality of the sulfamoylation protocol. Finally, it was found that [4-(acetilamino)phenyl]imidodisulfuryl difluoride (AISF, **9**),⁴⁴ another crystalline solid analog of SO_2F_2 , can also be used to functionalize primary alkyl amines (Figure 2b). Yields were found to be lower and these conditions are not applicable to aromatic amines, but SO_2F_2 is not required for the preparation of AISF—by contrast to that of **8**—which can be advantageous for laboratories not equipped with this reagent.

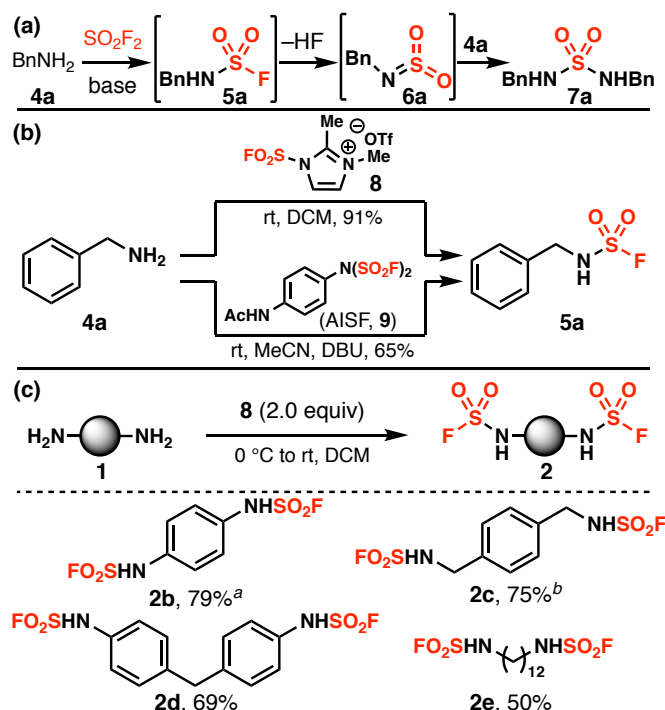


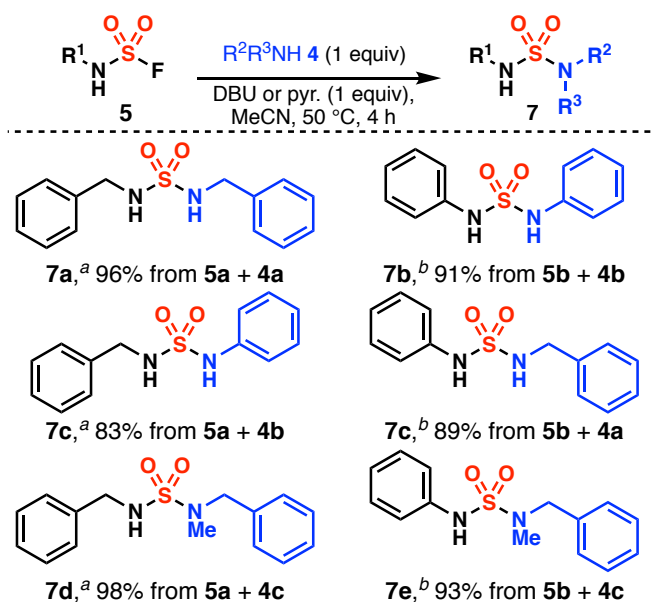
Figure 2. a) Undesired formation of symmetrical sulfamide **7a** from **4a** using SO_2F_2 . b) Sulfamoylation of primary amines with reagents **8** or **9**. c) Synthesis of bis(sulfamoyl fluoride) **2** monomers from primary bis(amines) **1**. Deviations from standard conditions: ^a1.8 equiv of **8**; ^bMeCN as solvent.

With sulfamoyl fluoride monomers in hand, we focused on the optimization of the second step of the SuFEx coupling. Treatment of **5a** with benzylamine (**4a**) in MeCN afforded dibenzylsulfamide (**7a**) in 70% yield after 2 h at 80 °C (Table 1, entry 1). Addition of a catalytic amount of DBU increased the yield to 78%, while with a stoichiometric amount of DBU, the yield improved to 97% (entries 2–3). Using a less basic aromatic amine as the coupling partner resulted in lower yield in the absence of additional base (Tables S1,2). With our goal of developing a robust and universal protocol independent of the innate basicity of the amine partner, the amount of added base was kept to at least one equivalent, which also allows for trapping the resulting fluoride as a base- H^+ - F^- salt. Triethylamine and potassium carbonate were found to afford similar yields to DBU (entries 4 and 5). Pyridine (entry 6) did not provide a noticeable improvement as compared to entry 1 but was found to perform best for aryl sulfamoyl fluorides (Figure 3). A variety of solvents were screened as well (Table S1). Interestingly, a nonpolar aromatic solvent such as PhMe delivered **7a** in a similar yield as with MeCN, while DMF showed a decrease in yield (entries 7–8). Finally, quantitative yield could be achieved by running the reaction in MeCN at 50 °C for 4 h (entry 9).⁴⁵ Again, all reactions were performed without removal of water or oxygen, which renders the overall SuFEx process operationally very simple. The optimized conditions were then used to synthesize a variety of sulfamides (Figure 3). Monosubstituted alkyl sulfamoyl fluoride **5a** was coupled with benzylamine (**4a**) and aniline (**4b**) in high yields (products **7a,c**) using DBU. Monosubstituted aryl sulfamoyl fluoride **5b** afforded similar yields with the same coupling partners (products **7b,c**) using pyridine instead. Secondary amines such as *N*-benzylmethylamine (**4c**) can also be used in the second step to deliver trisubstituted sulfamides **7d** and **7e**. The lack of reactivity of dialkylated sulfamoyl fluoride such as **S4** (Figure S3), as well as ^{19}F NMR analysis of a solution of **5a** and base (Figure S4), strongly suggest the generation of azasulfene intermediates in this process.⁴¹

Table 1. Optimization of the Sulfamide Synthesis

Entry ^a	Solvent	Temp. (°C)	Base (equiv)	Time (h)	Yield (%) ^b
1	MeCN	80	—	2	70
2	MeCN	80	DBU (0.1)	2	78
3	MeCN	80	DBU (1.0)	2	97
4	MeCN	80	Et ₃ N (1.0)	2	95
5	MeCN	80	K ₂ CO ₃ (1.0)	2	94
6	MeCN	80	Pyr. (1.0)	2	71
7	PhMe	80	DBU (1.0)	2	89
8	DMF	80	DBU (1.0)	2	77
9	MeCN	50	DBU (1.0)	4	99

^aReactions were run on 0.1 mmol scale; ^bNMR yields using an internal standard.

**Figure 3.** Synthesis of a variety of sulfamides via SuFEx with isolated yields (0.5–0.6 mmol scale). ^aDBU; ^bpyridine

These reaction conditions were then applied to the synthesis of polysulfamides using bis(sulfamoyl fluoride) monomers **2** and commercially available bis(amines) **1** (Figure 4). Although premature precipitation of the growing polymers in MeCN was observed initially, this was overcome by increasing the temperature of the reaction to 80 °C and adding an excess of DBU (5 equiv). A

broad array of polymers was obtained with diverse architectures and M_n 's between 3 and 9 kg/mol. Notably, polymer **3b** showed a DP of 39 ($M_n = 6.69$ kg/mol) using this protocol, which compares favorably to the prior synthesis of **3b** (DP = 10, $M_n = 1.70$ kg/mol, Figure 1a).²² Attempts to directly polymerize bis(amine) monomer **1b** with SO_2F_2 failed. Additionally, aryl and alkyl sulfamides can be incorporated in the polymer backbone with similar ease. All synthesized polymers were soluble in DMSO and most in DMAc or DMF, which allowed for full characterization using NMR and size-exclusion chromatography (SEC) (Supporting Information). Thermal properties of this family of polymers were explored via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All polymers exhibited high thermal stability with decomposition temperatures ranging from 198 °C for **3b** to 265 °C for **3n**. Although polymers **3b–n** all contain hydrogen-bond donors and acceptors in their repeating units, an impressive range of glass-transition temperatures were measured. T_g 's as low as 46 °C and 49 °C were determined for **3j** and **3l** with aliphatic segments in the backbone, while T_g 's above 170 °C were observed for **3f**, **3k**, and **3n**, all three polymers characterized by stiffer aromatic and cyclic repeating motifs. Copolymers **3o** and **3p** were synthesized using bis(sulfamoyl fluoride) **2c** and bis(amine)s **1b** and **1g** in different ratios. The T_g 's of **3o** and **3p**, 62 °C and 88 °C respectively, are in between that of homopolymers **3j** (46 °C) and **3f** (170 °C). Overall, T_g increases with an increasing amount of monomer **1b**, which highlights the facile tunability of T_g as a function of the molecular structure of the monomers. Strikingly, DSC analysis revealed an absence of crystallization and melting temperatures for all these materials. This thermal response contrasts with the melting temperatures measured in low-molecular-weight sulfamide films¹³ and the high-crystallinity observed with these small molecules.^{10–14} Powder X-ray diffraction performed on polysulfamides **3b–3n** provided a more precise depiction of their structural order (Supporting Information). Polysulfamides exhibited varying degrees of crystallinity, from amorphous for **3i**, **3k**, **3m**, and **3n** to semicrystalline for **3c**, **3e**, **3f**, **3j**, and **3l**. This behavior is reminiscent of work by Aida and coworkers,⁴⁶ which demonstrated that low M_n polythioureas may be amorphous due to a zig-zag arrangement of the hydrogen-bond network. As a result, these polythioureas can be processed into materials mechanically robust and self-healable. Polyureas, on the other hand, are generally characterized by a linear array of hydrogen-bond networks,^{47,48} rendering them semicrystalline and brittle. IR spectroscopy was used to probe the hydrogen-bond interactions in **3b–3n** in the solid state. Strong $\tilde{\nu}_{\text{NH}}$ peaks at approximately 3290 cm^{-1} were found in both **3c** and *N,N'*-dibenzylsulfamide (**7a**) (Figure S6) and are consistent with N–H bonds engaged in hydrogen-bonding based on prior studies.^{12–14} By contrast, the IR spectrum of **3b** displayed much broader $\tilde{\nu}_{\text{NH}}$ peaks, suggesting that the structure of the backbone strongly affects the hydrogen bonding ability of the repeating sulfamide groups. In-depth characterization of the hydrogen-bonding architecture in various polysulfamides will therefore be necessary to shed light on their specific thermal and mechanical properties.

The synthesized polysulfamides showcased high thermal stability, a desirable feature for many applications. However, the global accumulation of plastic waste has created a dire environmental crisis that must be addressed by the development of recyclable polymers. Knowing the hydrolytic stability of polyureas,⁴⁹ the depolymerization of the synthesized polysulfamides was investigated. While alkyl polysulfamide **3l** displayed remarkable stability in acidic or basic media at elevated temperatures (Supporting Information), aryl polysulfamide **3b** could be hydrolyzed in a variety of aqueous conditions.^{50,51} **3b** was typically suspended in an aqueous solution and heated for 40 h. The resulting aqueous solution was then extracted at pH~14 with EtOAc and the amount of bis(amine) monomer **1b** was quantified (Table 2). After treatment with a basic solution containing NaOH or NH_4OH for 40 h at 80 °C or 125 °C, up to 53% of pure **1b** was isolated, while in HCl at 125 °C for the same amount of time, the recovery was improved to 74%. This initial study will serve as a blueprint to investigate the recyclability potential of aromatic polysulfamides.

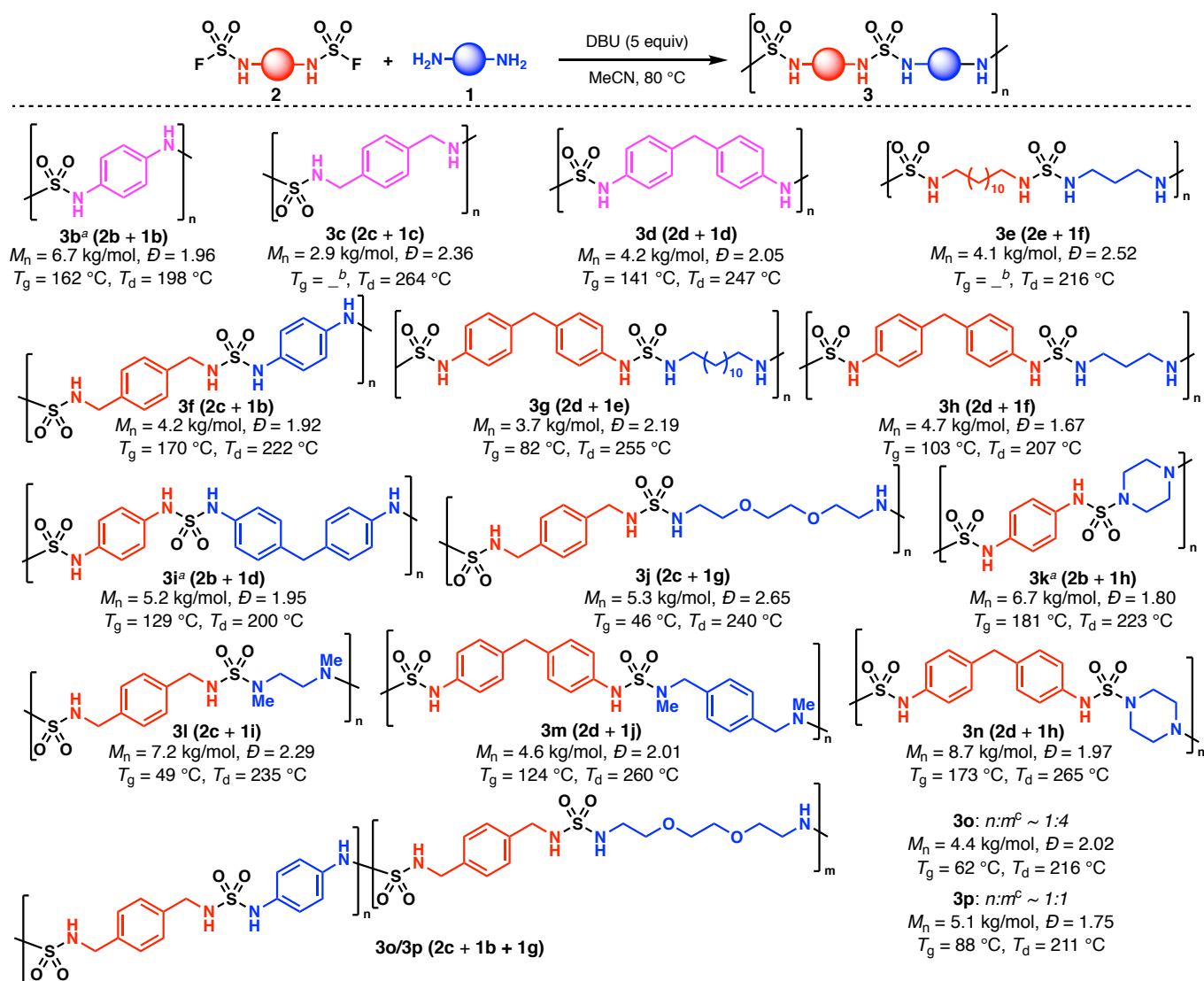


Figure 4. Synthesized polysulfamides via SuFEx chemistry. M_n 's and \bar{D} 's were determined by SEC (DMAc + 5% LiCl) using poly(methyl methacrylate) standards. T_d = 5% weight loss temperature. ^aPyridine was used instead of DBU. ^b No clear T_g was observed by DSC. ^c Determined by ^1H NMR.

Table 2. Hydrolysis of Aryl Polysulfamides

$ \left[\text{SO}_2\text{NH-Ar-NH-SO}_2\text{NH} \right]_n \xrightarrow[\text{monomer recycling}]{\text{aq. base or acid, no organic solvent, heat}} \text{H}_2\text{N-Ar-NH}_2 $			
Entry ^a	Aq. Base/Acid	Temp. (°C)	Monomer Recovery (%) ^b
1	NaOH (4 M)	80	32
2	NaOH (4 M)	125	42
3	NH ₄ OH (18 M)	80	53
4	HCl (4 M)	80	63 ^c
5	HCl (4 M)	125	74

^aHydrolysis reactions were conducted for 40 h. ^bBased on isolated **1b**. ^cSome polymer remained in suspension.

In summary, we have developed an efficient, practical, and general synthesis of sulfamides and polysulfamides based on SuFEx click chemistry. We anticipate that this robust and mild method will impact the fields of medicinal chemistry and hydrogen-bond catalysis, areas in which sulfamides have demonstrated exciting promise. This process was adapted to produce and evaluate polysulfamides, a virtually unknown class of polymers. Characterization of these polymers revealed a high thermal stability as well as modular T_g 's depending on the monomer structure. IR spectroscopy and power X-ray diffraction revealed that hydrogen-bonding interactions and the degree of crystallinity are strongly influenced by the structure of the polymer backbone. Finally, aromatic polysulfamide **3b** was depolymerized upon heating in basic or acidic aqueous solution, which suggests that these materials could be efficiently recycled after use.

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General Reagent Information

All reactions were carried out under ambient atmosphere unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) was purified by vacuum distillation with Potassium hydroxide (KOH) and stored over activated 4 Å molecular sieves under nitrogen atmosphere. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 250 μm SiliCycle SiliaPlate™ silica plates (F254), using UV light as the visualizing agent and an acidic solution of *p*-anisaldehyde and heat, ceric ammonium molybdate and heat, or KMnO_4 and heat, or ninhydrin and heat as developing agents. Flash silica gel chromatography was performed using SiliCycle SiliaFlash® Irregular Silica Gel (60 Å, particle size 40–063 μm). Polymers were isolated after precipitation using an Eppendorf Model 5804 centrifuge, and dried using a VWR Model 1410 vacuum oven.

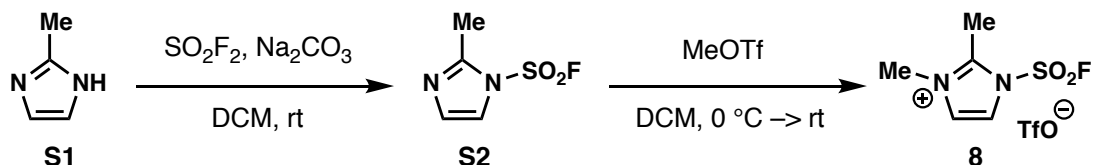
General Analytical Information

SEC of polymer samples was performed using two systems: Viscotek TDA302 and GPCmax with RI, dual-angle LS with two columns, I-MBHMW and I-MBLMW, in series at a flow rate of 0.5 mL/min and a EcoSEC Elite® HLC-8420GPC with RI and column TSKgel® SuperAWM-H at a flow rate of 0.2 mL/min. *N,N*-Dimethylacetamide (DMAc) with 0.5% LiCl was used as the eluent in both SEC systems. Number-average molecular weight (M_n), weight-average molecular weights (M_w) and dispersities (\bar{D}) were calculated from refractive index chromatograms against poly(methyl methacrylate) standards. ^1H Nuclear magnetic resonance (NMR) spectra were recorded on two Bruker Avance NEO 400 MHz and a Bruker Avance 500 MHz; ^{13}C spectra were recorded on a Bruker Avance 500 MHz and a VNMRs 500MHz; ^{19}F spectra were recorded using a Varian Inova 500 MHz instrument and calibrated by a solution of CFCl_3 in CDCl_3 (@ 0.65 ppm ^{19}F NMR). All ^1H and ^{13}C spectra were calibrated using residual deuterated solvent as an internal reference (CDCl_3 @ 7.26 ppm ^1H NMR, 77.16 ppm ^{13}C NMR; d_3 -MeCN @ 1.94 ppm ^1H NMR, 1.32 and 118.26 ppm ^{13}C NMR; d_6 -DMSO @ 2.50 ppm ^1H NMR, 39.52 ppm ^{13}C NMR). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time-of-flight

(ESI-TOF) reflection experiments. Melting points were recorded on a Fisher-Johns 13-144 melting point apparatus and are uncorrected. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 5500 Thermogravimetric Analyzer or an Instruments Q500 Analyzer. Typically, samples were heated at 10 °C/min to 600 °C under nitrogen. Data were processed using Universal Analysis 2000 for windows software. Differential scanning calorimetry (DSC) was performed using a TA instrument DSC 2500. Samples were prepared in aluminum pans and were analyzed using the following heating program: -50 °C to 5 °C below decomposition temperature at 10 °C/min, cooling to -50 °C at 10 °C/min, and heating again from -50 °C to 5 °C below decomposition temperature at 10 °C/min. The data were processed using TA Instruments TRIOS for Windows software. All reported T_g 's were taken from the second heating cycle. FT-IR spectra were acquired using an Agilent Cary 630 FT-IR in the ATR mode. All plots and spectra (SEC, DSC, TGA, XRD, and FT-IR) were produced using raw instrumental data and Wolfram Mathematica version 12.1, unless otherwise noted.

Experimental procedure

Synthesis of 1-(fluorosulfonyl)-2,3-dimethyl-1H-imidazol-3-ium triflate (**8**)



Caution: sulfuric fluoride is a highly toxic gas. As such, all reactions using sulfuric fluoride should be carried out in a well-ventilated fume hood to avoid exposure and inhalation.

Compound 8 was prepared following a previously reported procedure (*Angew. Chem. Int. Ed.* 2018, **57**, 2605) with some slight modifications. In a flame-dried flask containing a suspension of 2-methylimidazole (**S1**) (4.93 g, 60.0 mmol, 1.0 equiv) and sodium carbonate (15.9 g, 150 mmol, 2.5 equiv) in anhydrous DCM (60 mL) the pressure was reduced using a Schlenck line until the DCM began boiling, and a balloon containing sulfuric fluoride gas (approx. 1.5 L) was introduced. The mixture was stirred until full conversion of the imidazole was confirmed by NMR. If full conversion was not reached after 18 hours, a second balloon of sulfuric fluoride was added. Solid residues were removed by filtration over a silica plug eluted with DCM . The filtrate was washed with distilled water (3 x 50 mL). The aqueous fractions were then combined and extracted with DCM (50 mL). The organic fractions were combined and washed with brine (50 mL) before drying over MgSO_4 . The solvent was evaporated *in vacuo* using a $20\text{ }^\circ\text{C}$ bath and a pressure of 200 mbar to avoid distilling away volatile sulfamoyl fluoride **S2**. When a volume of roughly 60 mL of solution was reached, the solution was cooled to $0\text{ }^\circ\text{C}$. Methyl trifluoromethanesulfonate (9.85 g, 60 mmol, 1.0 equiv) was then added to the mixture over 15 min using a syringe pump with vigorous stirring. The mixture was then warmed to room temperature and allowed to stir for 2 h, during which time the product precipitated from the solution. **8** was collected by vacuum filtration as a white solid (15.7 g, 79% over 2 steps) and washed thoroughly with methyl *tert*-butyl ether (MTBE). Note: Likely due to the presence of residual methyl trifluoromethylsulfonate, the product sometimes collects as a dense brown oil rather than a white solid. Here, the DCM can be removed first *in vacuo*, then upon addition of MTBE (50 mL) and stirring the mixture vigorously at $0\text{ }^\circ\text{C}$, the desired solid precipitates.

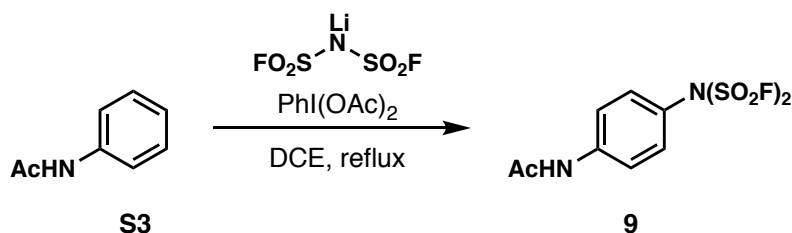
The spectroscopic data for this compound were identical to those reported in the literature (*Angew. Chem. Int. Ed.* 2018, **57**, 2605).

^1H NMR (CD_3CN , 400 MHz) δ : 7.87 (d, 1 H, $J = 2.5$ Hz), 7.54 (d, 1 H, $J = 2.5$ Hz), 3.85 (s, 3 H), 2.86 (s, 3 H) ppm.

^{13}C NMR (CD_3CN , 126 MHz) δ : 151.4, 125.5, 122.1, 122.0 (q, $J = 318$ Hz), 37.5, 12.9 ppm.

^{19}F NMR δ : (CD_3CN , 470 MHz) δ : 61.4 (s, 1 F), -78.1 (s, 3 F) ppm.

Synthesis of [4-(acetylamino)phenyl]imidodisulfonyl difluoride (AISF, **9):**



AISF (**9**) was prepared following a previously reported procedure (*Org. Lett.* 2018, **20**, 812) with slight modifications. A solution of (diacetoxyiodo)benzene (8.24 g, 25.6 mmol, 1.5 equiv) and lithium bis(fluorosulfonyl)imide (6.38 g, 34.1 mmol, 2.0 equiv) in DCE (30 mL) was stirred at 100 °C in a flame-dried 3-necked round bottom flask adapted with a condenser. A solution of acetanilide (**S3**) (2.31 g, 17.1 mmol, 1.0 equiv) in DCE (35 mL) was slowly added to the refluxing mixture over 25 min. After stirring for an additional 15 min, the mixture was cooled to room temperature and activated carbon (4 g) was added. The mixture was stirred for 18 h at room temperature, then filtered through a short silica plug and washed with EtOAc. The filtrate was concentrated *in vacuo*. Column chromatography (SiO_2 , 10:90 to 30:70 EtOAc:hexanes) allowed to remove most of the impurities. Recrystallization of the resulting brown solid with the minimum of EtOAc and slow addition of hexanes afforded **9** as crystalline white needles (3.42 g, 65%).

The spectroscopic data for this compound were identical to those reported in the literature (*Org. Lett.* 2018, **20**, 812).

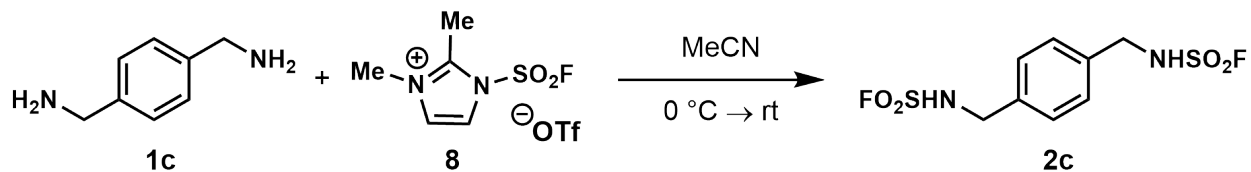
^1H NMR: (d_6 -DMSO, 400 MHz) δ : 10.37 (s, 1 H), 7.90–7.63 (m, 4 H), 2.09 (s, 3 H) ppm.

^{13}C NMR: (d_6 -DMSO, 126 MHz) δ : 169.1, 142.9, 130.3, 126.1, 120.3, 24.1 ppm.

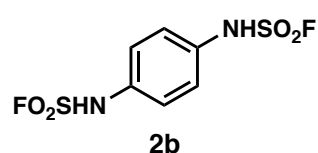
^{19}F NMR: (d_6 -DMSO, 470 MHz) δ : 56.8 (s, 2 F) ppm.

See preparation of sulfamoyl fluoride **5a** (*vide infra*) for a sulfamoylation procedure using **9**.

General Procedure for the Synthesis of Bis(sulfamoyl fluoride) Monomers **2 (Using **2c** as an Example)**



Reagent **8** (2.41 g, 7.33 mmol, 2.0 equiv) was added to a mixture of bis(amine) **1c** (500 mg, 3.67 mmol, 1.0 equiv) in MeCN (15 mL) at 0 °C. The mixture was brought to room temperature and stirred for 2 h, subsequently diluted with ethyl acetate (10 mL), and washed with HCl (0.1 M, 2 x 10 mL) and brine (10 mL). The organic phase was dried over MgSO₄ and concentrated *in vacuo* to yield the crude product. When required, the product was then purified through column chromatography.



Bis(sulfamoyl fluoride) **2b** was obtained as a brown solid using 1,4-phenylenediamine (**1b**) (100 mg, 0.925 mmol), **8** (546 mg, 1.67 mmol, 1.8 equiv), and DCM as the solvent. The product was noted to decompose during column chromatography using silica gel (deactivated or not). Using only 1.8 equiv of **8** prevented the formation of undesired side products and delivered pure **2b** as a brown solid without further purification (180 mg, 79%).

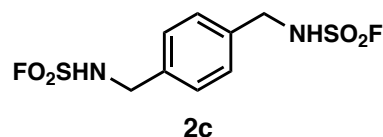
¹H NMR (CD₃CN, 400 MHz) δ: 8.88 (br, 2 H), 7.37 (s, 4 H) ppm.

¹³C NMR (CD₃CN, 126 MHz) δ: 134.3, 125.1 ppm.

¹⁹F NMR (CD₃CN, 470 MHz) δ: 49.5 ppm.

HRMS-ESI: calc'd. for C₆H₅N₂O₄S₂F₂ [M-H]⁻ 270.9664, found 270.9662.

mp: Decomposed before melting.



Bis(sulfamoyl fluoride) **2c** was obtained as a white solid using *p*-xylylenediamine (**1c**) (500 mg, 3.67 mmol) and MeCN as the solvent. Column chromatography (SiO₂, 5:95 to 10:90 EtOAc:hexanes) provided **2c** as a white solid (824 mg, 75%).

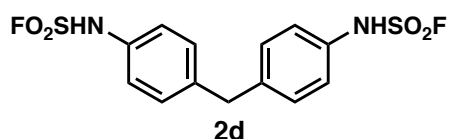
¹H NMR (CD₃CN, 500 MHz) δ: 7.39 (s, 4 H), 7.06 (br, 2 H), 4.41 (d, 4 H) ppm.

¹³C NMR (CD₃CN, 126 MHz) δ: 137.1, 129.4, 48.2 ppm.

¹⁹F NMR (CD₃CN, 470 MHz) δ: 50.3 ppm.

HRMS-ESI: calc'd. for $C_6H_9N_2O_4S_2F_2$ $[M-H]$ 298.9977, found 298.9973.

mp: 145–146 °C.



Bis(sulfamoyl fluoride) 2d was obtained using 4,4'-diaminodiphenylmethane (**1d**) (793 mg, 4.0 mmol) and DCM as the solvent. Column chromatography (SiO_2 , 10:90 to 20:80 EtOAc:hexanes) provided **2d** as a yellowish solid (1.00 g, 2.76 mmol, 69%).

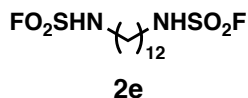
1H NMR ($CDCl_3$, 400 MHz) δ : 7.22 (m, 8 H), 6.78 (br, 2 H, NH), 3.99 (s, 2 H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz) δ : 140.2, 132.2, 130.4, 123.8, 40.8 ppm.

^{19}F NMR ($CDCl_3$, 470 MHz) δ : 50.8 ppm.

HRMS-ESI: calc'd. for $C_{13}H_{11}N_2O_4S_2F_2$ $[M-H]^-$ 361.0123, found 361.0132.

mp: 96–99 °C



Bis(sulfamoyl fluoride) 2e was obtained using 1,12-diaminododecane (**1e**) (200 mg, 1.0 mmol) as the starting bis(amine) and DCM as the solvent. Column chromatography (SiO_2 , 5:95 to 10:90 EtOAc:hexanes) provided **2e** as a white solid (183 mg, 0.502 mmol, 50%).

1H NMR ($CDCl_3$, 400 MHz) δ : 4.86 (br, 2 H, NH), 3.32–3.28 (ddd, $J = 5.2, 5.2, 1.9$ Hz, 4 H), 1.65–1.58 (m, 4 H), 1.37–1.28 (m, 16 H) ppm.

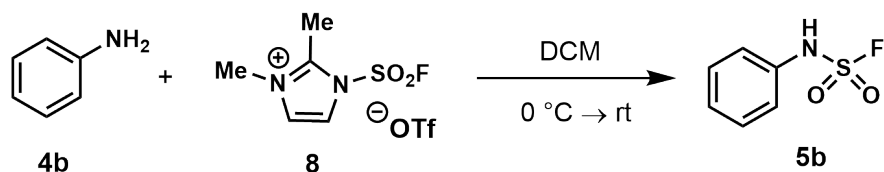
^{13}C NMR ($CDCl_3$, 126 MHz) δ : 44.9, 29.5, 29.4, 29.4, 29.0, 26.3 ppm.

^{19}F NMR ($CDCl_3$, 470 MHz) δ : 50.7 ppm.

HRMS-ESI: calc'd. for $C_{12}H_{25}N_2O_4S_2F_2$ $[M-H]^-$ 363.1218, found 363.1228.

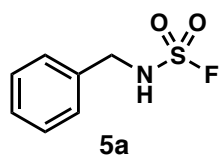
mp: 64–66 °C.

General Procedure for the Synthesis of Sulfamoyl Fluorides 5 (Using 5b as an Example)



To aniline (**4b**) (900 mg, 9.66 mmol, 1.0 equiv) in dry DCM (30 mL) stirring in an ice-bath Compound **8** (3.18 g, 9.66 mmol, 1.0 equiv) was added. The reaction was brought to room temperature and stirred for 2–4 h, until the starting amine was seen to be fully consumed by TLC.

After completion, the resulting mixture was diluted with DCM (10 mL) and washed with 0.1M HCl (3 x 15 mL) and brine (20 mL). The organic layer was dried over MgSO₄ and concentrated *in vacuo* to afford the product as an orange oil (1.42 g, 84%) without further purification.



Sulfamoyl Fluoride 5a was prepared following the general procedure. Starting with benzylamine (**4a**) (0.11 mL, 0.107 g, 1.0 mmol) to afford the product as a yellow oil (0.173 g, 91%).

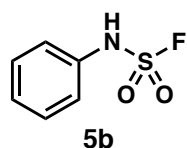
Alternatively, **5a** can be prepared using AISF **9** as the fluorosulfonation reagent. To a solution of benzylamine (**4a**) (107 mg, 1.0 mmol, 1.0 equiv) and AISF **9** (377 mg, 1.2 mmol, 1.2 equiv) in acetonitrile (3.5 mL), DBU (335 mg, 0.33 mL, 2.2 mmol, 2.2 equiv) was added dropwise at room temperature. The mixture was stirred and monitored by TLC until benzylamine (**4a**) was fully consumed (about 3 h). The mixture was diluted with EtOAc (5 mL) and washed with HCl (0.5 M, 10 mL x 2) and brine (10 mL), dried over MgSO₄, and concentrated *in vacuo*. Column chromatography (SiO₂, 10:90 EtOAc:hexanes) afforded **5a** as a yellow oil (123 mg, 65%).

The spectroscopic data for this compound were identical to those reported in the literature (*Angew. Chem. Int. Ed.* **2018**, *57*, 2605).

¹H NMR (CDCl₃, 400 MHz) δ: 7.42 - 7.33 (m, 5 H), 5.15 (br, 1 H), 4.45 (d, *J* = 5.6 Hz, 2 H) ppm.

¹³C NMR (CDCl₃, 126 MHz) δ: 134.8, 129.2, 128.8, 128.1, 48.5 ppm.

¹⁹F NMR (CDCl₃, 470 MHz) δ: 50.4 ppm.



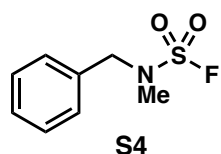
Sulfamoyl fluoride 5b was prepared following the general procedure. Starting with aniline (**4b**) (900 mg, 9.66 mmol) to afford the product as an orange oil (1.42 g, 84%).

The spectroscopic data for this compound were identical to those reported in the literature (*Angew. Chem. Int. Ed.* **2018**, *57*, 2605).

¹H NMR (CD₃CN, 400 MHz) δ: 8.85 (br, 1 H), 7.44 (m, 2 H), 7.33 (m, 3 H) ppm.

¹³C NMR (CD₃CN, 126 MHz) δ: 135.6, 130.7, 128.1, 123.9 ppm.

¹⁹F NMR (CD₃CN, 470 MHz) δ: 50.1 ppm.



Sulfamoyl Fluoride S4 was prepared following the general procedure. Starting with N-benzylmethylamine (**4c**) (0.13 mL, 1.0 mmol), using MeCN as solvent to afford the product as colorless oil (171.2 mg, 0.84 mmol, 84%).

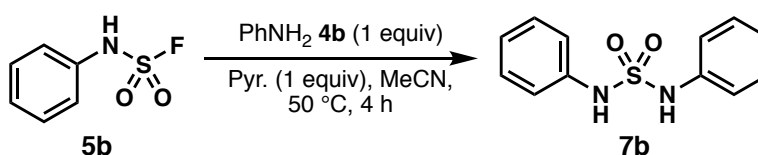
^1H NMR (CDCl_3 , 400 MHz) δ : 7.43–7.32 (m, 5 H), 4.48 (s, 2 H), 2.90 (d, 3 H, $J = 2.2$ Hz) ppm.

^{13}C NMR (CDCl_3 , 126 MHz) δ : 133.8, 129.1, 128.8, 128.7, 55.2, 35.3 ppm.

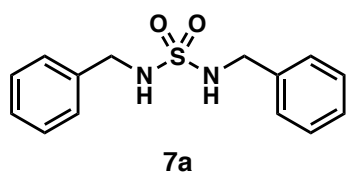
^{19}F NMR (CDCl_3 , 470 MHz) δ : 42.0 ppm.

HRMS-ESI: calc'd. for $\text{C}_8\text{H}_{10}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 226.0308, found 226.0302.

General Procedure for the Synthesis of Sulfamides 7 (Using 7b as an Example)



To the sulfamoyl fluoride **5b** (100 mg, 570 μmol , 1.0 equiv) in acetonitrile (5 mL) the amine **4b** (62 mg, 570 μmol , 1.0 equiv) and pyridine (45 mg, 570 μmol , 1.0 equiv; DBU for compound **5a**, pyridine for compound **5b**) were added. The reaction mixture was heated to 50 $^\circ\text{C}$ and stirred for 4–5 h, until none of the sulfamoyl fluoride could be observed by TLC. After all the sulfamoyl fluoride was consumed, 1M HCl (10 mL) was added into residue to stop the reaction. The mixture was extracted with ethyl acetate (3 x 5 mL). The organic fractions were combined, dried over MgSO_4 and concentrated *in vacuo* to yield product **7b** as a white crystalline solid (128 mg, 91%).



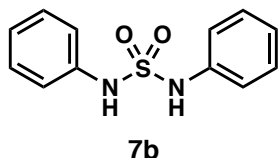
Sulfamide 7a was prepared by starting with sulfamoyl fluoride **5a** (102.7 mg, 0.543 mmol), coupling with benzylamine (**4a**) and following the general procedure to afford a white solid (144.3 mg, 96%), without further purification.

^1H NMR (d_6 -DMSO, 400 MHz) δ : 7.45 (t, 2 H, $J = 6.2$ Hz), 7.32 (m, 8 H), 7.26 (m, 2 H), 4.01 (d, 2 H, $J = 6.3$ Hz) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ : 138.4, 128.2, 127.7, 127.0, 45.8 ppm.

IR (neat): $\tilde{\nu} = 3269, 3062, 1453, 1414, 1313, 1142, 908 \text{ cm}^{-1}$.

The spectroscopic data for this compound were identical to those reported in the literature (*Org. Lett.* **2016**, *15*, 3726-3729).



Sulfamide 7b was prepared by starting with sulfamoyl fluoride **5b** (100 mg, 0.570 mmol), coupling with aniline (**4b**) and following the general procedure to afford the product as white crystals (128 mg, 91%).

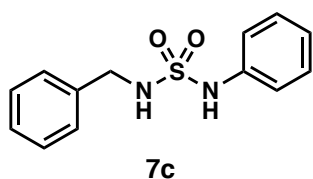
^1H NMR (CDCl_3 , 400 MHz) δ = 7.26 (t, J = 7.5 Hz, 4 H), 7.13 (t, J = 7.5 Hz, 2 H),

7.07 (d, J = 7.5 Hz, 4 H), 6.83 (br, 1 H) ppm.

^{13}C NMR (CDCl_3 , 126 MHz) δ = 136.5, 129.6, 125.6, 121.4 ppm.

IR (neat): $\tilde{\nu}$ = 3217, 3051, 1598, 1481, 1419, 1337, 1294, 1147, 1032, 938 cm^{-1} .

The spectroscopic data for this compound were identical to those reported in the literature (*Org. Lett.* **2016**, *15*, 3726).



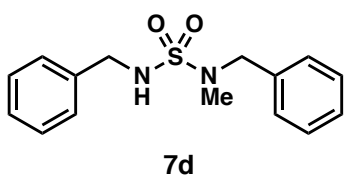
Sulfamide 7c was prepared by starting with sulfamoyl fluoride **5a** (99.6 mg, 0.526 mmol), coupling with aniline (**4b**) and following the general procedure. Crude mixture was purified column chromatography (20 % EtOAc in hexanes) to afford a white solid (114.0 mg, 83%).

Alternatively, starting with sulfamoyl fluoride **5b** (100 mg, 0.570 mmol), coupling with benzylamine (**4a**) to yield the same product without further purification (133 mg, 89%).

^1H NMR (CDCl_3 , 400 MHz) δ = 7.29 (t, J = 7.5 Hz, 2 H), 7.27–7.23 (m, 3 H), 7.17–7.10 (m, 5 H), 6.93 (br, 1 H), 4.95 (t, J = 6.0, 1 H), 4.18 (d, J = 6.0 Hz, 2 H) ppm.

^{13}C NMR (CDCl_3 , 126 MHz) δ = 137.1, 136.2, 129.6, 129.0, 128.3, 128.2, 124.8, 120.1, 47.6 ppm.

The spectroscopic data for this compound were identical to those reported in the literature (*Org. Lett.* **2016**, *15*, 3726).



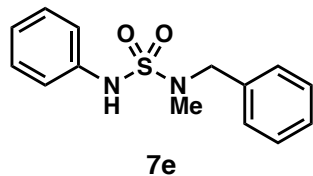
Sulfamide 7d was prepared by starting with sulfamoyl fluoride **5a** (100.1 mg, 0.529 mmol), coupling with *N*-benzylmethylamine (**4c**) and following the general procedure to afford white to yellow solid (151 mg, 98%)

^1H NMR (CD_3CN , 400 MHz) δ = 7.39–7.29 (m, 10 H), 5.72 (br, 1 H, NH), 4.24 (s, 2 H), 4.21–4.20 (d, 2 H, J = 6.4 Hz), 2.61 (s, 3 H) ppm.

^{13}C NMR (CD_3CN , 126 MHz) δ = 139.2, 138.1, 129.6, 129.5, 129.2, 128.9, 128.6, 128.5, 54.9, 47.8, 35.1 ppm.

HRMS-ESI: calc'd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 291.1162, found 291.1156.

mp: 72–74 °C.



Sulfamide 7e was prepared by starting with sulfamoyl fluoride **5b** (100 mg, 0.570 mmol), coupling with *N*-benzylmethylamine (**4c**) and following the general procedure to afford the product as an off-white solid (146 mg, 93%).

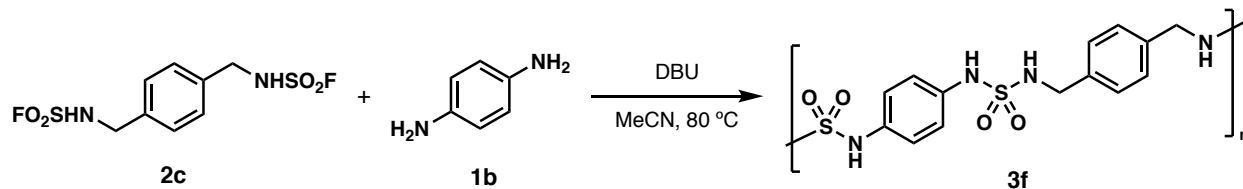
¹H NMR (CDCl₃, 500 MHz) δ = 7.35–7.27 (m, 5 H), 7.22–7.09 (m, 5 H), 7.01 (br, 1 H) 4.32 (s, 2 H), 2.71 (s, 3 H) ppm.

¹³C NMR (CDCl₃, 126 MHz) δ = 137.3, 135.8, 129.6, 129.5, 128.8, 128.4, 128.0, 124.8, 120.5 ppm.

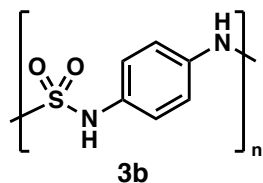
HRMS-ESI: calc'd. for C₁₄H₁₇N₂O₂S [M+H]⁺ 277.1005, found 277.0998.

mp: 64–66 °C.

General Procedure for the Synthesis of Polysulfamides 3 (Using 3f as an Example)



To a 0.5M solution of bis(sulfamoyl fluoride) **2c** (150 mg, 0.500 mmol, 1.0 equiv) in MeCN (1.0 mL), DBU (380 mg, 2.50 mmol, 5.0 equiv) and bis(amine) **1b** (54 mg, 0.500 mmol, 1.0 equiv) were added. The mixture was stirred at 80 °C for 90 min. The resulting mixture was dissolved in DMF (1 mL), then precipitated in a centrifuge tube through the addition of Et₂O, until a volume of 50 mL was reached. After centrifuging and removing the supernatant liquid, the resulting dark orange solid was re-dissolved in DMF (1 mL) and re-precipitated through the addition of saturated NH₄Cl (aq) until a volume of 50 mL was reached. The solid was then washed with distilled water (2 x 50 mL) and once with isopropanol (50 mL). The polymer was dried *in vacuo* (< 1 mmHg) at 100 °C for 18 hours to obtain the final polymer as a dark orange solid (150 mg). Molecular weight and polymer distribution were determined through SEC. The bis(amine)s (**1**) were commercially available, unless otherwise noted.

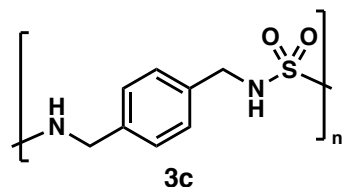


Polysulfamide 3b was obtained as a purple solid through the general procedure using compound **2b** (200 mg, 0.733 mmol), 1,4-phenylenediamine (**1b**), and pyridine as a base.

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.87 (2 H), 7.01 (4 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 133.6, 120.1 ppm.

IR (neat): $\tilde{\nu}$ = 3187, 2992, 2938, 2360, 1609, 1538, 1454, 1351, 1294, 1177, 1132, 837 cm^{-1} .

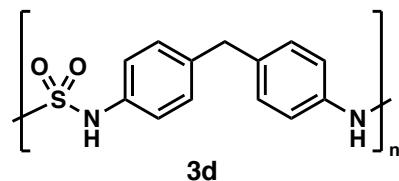


Polysulfamide 3c was obtained as an off-white solid by the general procedure using compound **2c** (150 mg, 0.500 mmol) and *p*-xylylenediamine (**1c**). *N,N'*-Dimethylacetamide was used as the solvent for reprecipitation due to poor solubility in DMF.

^1H NMR (d_6 -DMSO, 500 MHz) δ = 7.44 (4 H), 7.29 (4 H), 4.01 (4 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 137.7, 128.1, 46.0 ppm.

IR (neat): $\tilde{\nu}$ = 1143, 1311, 3263, 2932, 1614, 1067 cm^{-1} .



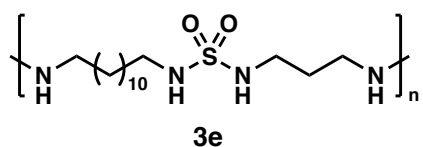
Polysulfamide 3d was obtained as an off-white solid through the general procedure using compound **2d** (100 mg, 0.276 mmol) and 4,4'-diaminomethylenedianiline (**1d**).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.98 (2 H), 7.04 (d, J = 8.5

Hz, 2 H), 6.99 (d, J = 8.5 Hz, 2 H), 3.73 (2 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 136.0, 135.9, 129.0, 120.8, 39.3 ppm.

IR (neat): $\tilde{\nu}$ = 1151, 1139, 1334, 1509, 3301 cm^{-1} .

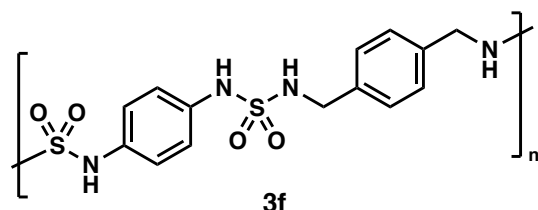


Polysulfamide 3e was obtained as an off-white solid by the general procedure using compound **2e** (100 mg, .274 mmol) and 1,3-propanediamine (**1f**).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 6.73 (br, 4 H, NH), 2.74-2.84 (m, 8 H), 1.63 (m, 2 H), 1.42 (m, 4 H), 1.24 (br, 16 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 42.1, 39.7, 39.0, 36.5, 29.0, 28.9, 28.7, 26.3 ppm.

IR (neat): $\tilde{\nu}$ = 3281, 2920, 2850, 1441, 1308, 1143, 1065 cm^{-1} .

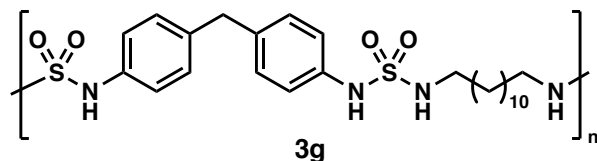


Polysulfamide 3f obtained as a dark orange solid through the general procedure using compound **2c** (150 mg, 0.500 mmol, 1.0 equiv) and 1,4-phenylenediamine (**1c**).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.56 (2 H), 7.84 (2 H), 7.17 (4 H), 7.12 (4 H), 4.00 (4 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 142.1, 139.3, 132.6, 125.3, 50.6 ppm.

IR (neat): $\tilde{\nu}$ = 3275, 2938, 1614, 1513, 1318, 1143, 1064, 919 cm^{-1} .



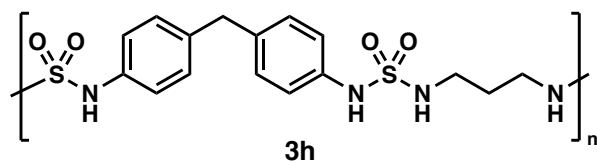
Polysulfamide 3g was obtained as an off-white solid through the general procedure using compound **2d** (100 mg, 0.276 mmol) and 1,12-diaminododecane (**1e**). Starting with 100 mg

bis(sulfamoyl fluoride) monomer.

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.46 (br, 2 H), 7.28 (br, 2H), 7.07 (s, 8 H), 3.78 (s, 2 H), 2.78 (m, 4 H), 1.33-1.14 (m, 20 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 137.4, 135.9, 129.4, 118.4, 42.0, 41.8, 28.9, 28.7, 28.5, 26.1 ppm.

IR (neat): $\tilde{\nu}$ = 3281, 2921, 2849, 1509, 1326, 1143, 927 cm^{-1} .

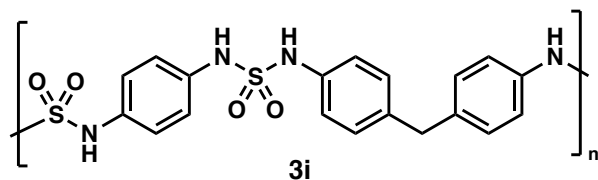


Polysulfamide 3h was obtained as an off-white solid through the general procedure using compound **2d** (100 mg, 0.276 mmol) and 1,3-propanediamine (**1f**).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 7.28 (br, 2H), 7.07 (q, 8 H, J = 8.5Hz), 3.77 (s, 2 H), 2.78 (t, 4 H, J = 6.8 Hz), 1.53 (tt, 2 H, J = 6.8 Hz) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 136.8, 135.6, 129.1, 118.7, 39.9, 36.8, 29.0, 27.3 ppm.

IR (neat): $\tilde{\nu}$ = 3275, 1508, 1323, 1143, 933 cm^{-1} .



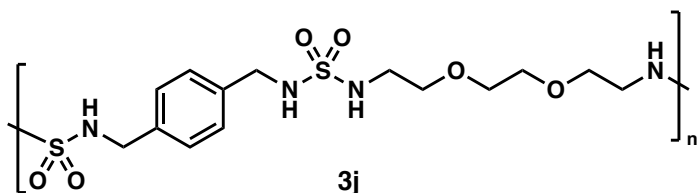
Polysulfamide 3i was obtained as a light purple solid through the general procedure using compound **2b** (200 mg, 0.733 mmol), 4,4'-diaminomethylenedianiline (**1d**), and pyridine as

a base.

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.92 (4 H), 7.02 (12 H), 3.75 (2 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 136.1, 135.9, 133.6, 129.1, 120.1, 118.9, 39.6 ppm.

IR (neat): $\tilde{\nu}$ = 3270, 1610, 1508, 1315, 1147, 938 cm^{-1} .

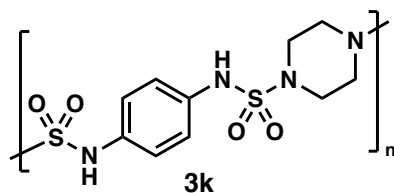


Polysulfamide 3j was obtained as a tan solid through the general procedure using compound **2c** (150 mg, 0.500 mmol) and 2,2'-(ethylenedioxy)-diethylamine (**1g**).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 7.29 (4 H), 6.92 (2 H), 4.00 (4 H), 3.51 (4 H), 3.46 (4 H), 2.98 (4 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 137.1, 127.5, 69.5, 69.1, 45.5, 41.8 ppm.

IR (neat): $\tilde{\nu}$ = 3276, 2865, 1614, 1430, 1312, 1142, 1067 cm^{-1} .

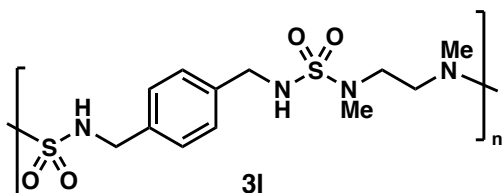


Polysulfamide 3k was obtained as a pink solid through general procedure using compound **2b** (200 mg, 0.733 mmol), piperazine (**1h**), and pyridine as a base.

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.85 (2 H), 7.11 (4 H), 3.09 (8 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 134.0, 121.2, 45.2 ppm.

IR (neat): $\tilde{\nu}$ = 3237, 2926, 2866, 1510, 1324, 1147, 1119, 943 cm^{-1} .

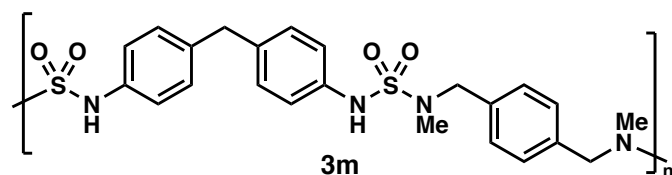


Polysulfamide 3l was obtained as a white solid through the general procedure using compound **2c** (150 mg, 0.500 mmol) and *N,N'*-dimethylethylenediamine (**1i**).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 7.67 (2 H), 7.30 (4 H), 4.06 (4 H), 3.18 (4 H), 2.70 (6 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 137.2, 127.5, 47.7, 45.8, 34.8 ppm.

IR (neat): $\tilde{\nu}$ = 3261, 2938, 2863, 1612, 1426, 1308, 1145, 1056, 967 cm^{-1} .



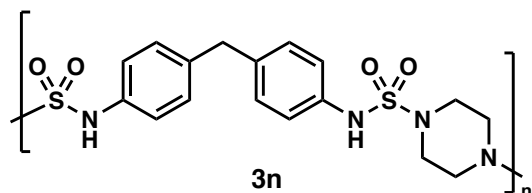
Polysulfamide 3m was obtained as an off-white solid through the general procedure using compound **2d** (100 mg, 0.276 mmol) and *N,N'*-dimethyl-*p*-xylylenediamine (**1j**).

Bis(amine) **1j** was prepared following the previous reported procedure (*Dalton Trans.*, **2011**, 40, 12235).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.90 (2 H), 7.13 (8 H), 7.06 (4 H), 4.16 (4 H), 3.84 (2 H), 2.52 (6 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 136.8, 135.6, 129.1, 118.9, 118.7, 52.9, 39.4, 28.9 ppm.

IR (neat): $\tilde{\nu}$ = 3471, 3016, 2948, 1508, 1449, 1366, 1216, 1150, 909 cm^{-1} .



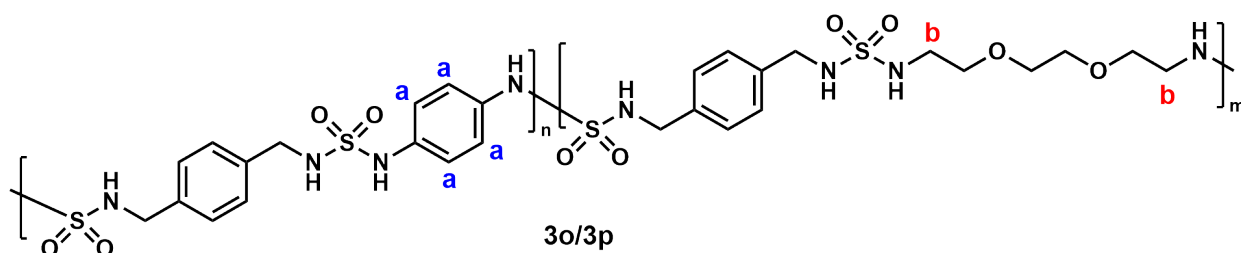
Polysulfamide 3n was obtained as an off-white solid through the general procedure using compound **2d** (100 mg, 0.276 mmol) and piperazine (**1h**).

^1H NMR (d_6 -DMSO, 400 MHz) δ = 9.87 (br, 2 H),

7.07 (s, 8 H), 3.80 (s, 2 H), 3.05 (s, 8 H) ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 136.5, 136.0, 129.2, 120.1, 41.8, 40.0, 39.3 ppm.

IR (neat): $\tilde{\nu}$ = 3454, 3018, 2966, 1509, 1448, 1367, 1217, 1149, 912 cm^{-1} .



Polysulfamide 3o was obtained as an orange solid through the general procedure using compound **2c** (50 mg, 167 μmol , 3.0 equiv), 1,4-phenylenediamine (**1b**) (6 mg, 0.056 mmol, 1.0 equiv), and 2,2'-(ethylenedioxy)-diethylamine (**1g**) (16 mg, 0.112 mmol, 2.0 equiv)

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.54, 7.83, 7.29, 7.13, 6.92, 4.00, 3.52, 3.46, 2.98 ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 137.2, 134.1, 128.2, 120.6, 69.6, 69.1, 45.5, 41.9 ppm.

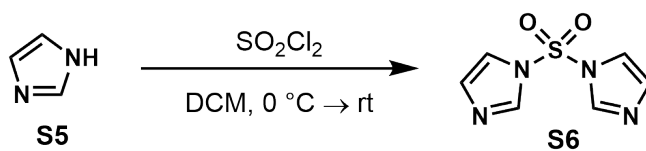
Polysulfamide 3p was obtained as an orange solid through the general procedure using compound **2c** (50 mg, 167 μmol , 3.0 equiv), 1,4-phenylenediamine (**1b**) (12 mg, 0.112 mmol, 2.0 equiv), and 2,2'-(ethylenedioxy)-diethylamine (**1g**) (8 mg, 0.056 mmol, 1.0 equiv).

^1H NMR (d_6 -DMSO, 500 MHz) δ = 9.54, 7.83, 7.29, 7.13, 4.01, 3.52, 3.46, 2.98 ppm.

^{13}C NMR (d_6 -DMSO, 126 MHz) δ = 137.2, 134.1, 127.4, 120.6, 69.6, 69.1, 45.5, 41.8 ppm.

Based on the integration of the ^1H NMR peaks located at 7.13 and 2.98 ppm, corresponding to the protons marked at positions “a” and “b” respectively, it was found that for **3o** n:m \approx 1:4, and for **3p** n:m \approx 1:1. The observed discrepancies between the initial ratios of monomer and the ratios of incorporated repeating units are likely due to the higher nucleophilicity of aliphatic amines compared to that of aryl amines.

Preparation of 1,1'-Sulfonyldiimidazole (S6)



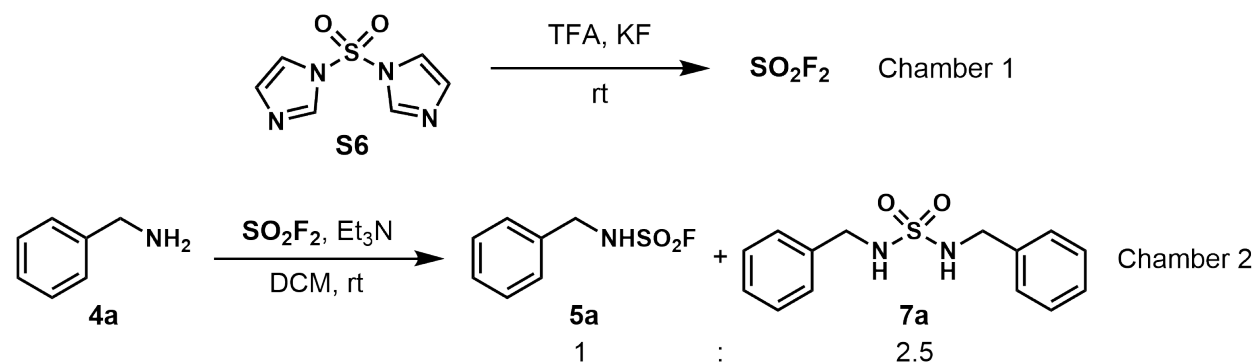
S6 was prepared according to a literature procedure (*Org. Lett.* 2017, **19**, 5244). In a flame-dried flask under nitrogen, imidazole (S5) (5.00 g, 73 mmol, 4.6 equiv) was suspended in anhydrous DCM (30 mL) and cooled to 0 °C. A solution of sulfonyl chloride (2.15 g, 16 mmol, 1.0 equiv) in DCM (6 mL) was added dropwise over 15 min. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The resulting heterogenous mixture was filtered using a fritted funnel, and the remaining solid was washed several times with DCM. The filtrate was concentrated *in vacuo* to yield a bright yellow solid. The solid was recrystallized in boiling isopropanol, isolated via vacuum filtration, and washed with cold isopropanol to obtain the title compound as a white crystalline solid (2.25 g, 71%).

The spectroscopic data for this compound were identical to those reported in the literature.

¹H NMR (CDCl₃, 400 MHz) δ: 8.03 (s, 1 H), 7.30 (s, 1 H), 7.14 (s, 1 H) ppm.

¹³C NMR (CDCl₃, 101 MHz) δ: 136.7, 132.5, 117.5 ppm.

Reaction of a Primary Amine with *ex situ*-generated SO₂F₂



SO₂F₂ was generated *ex situ* according to a literature procedure (*Org. Lett.* 2017, **19**, 5244). To one chamber of a small two-chamber reactor (Figure S1) benzylamine (4a) (107 mg, 1.0 mmol, 1.0 equiv) and triethylamine (204 mg, 2.0 mmol, 2.0 equiv) were dissolved in DCM (4 mL). In the second chamber, S6 (279 mg, 1.5 mmol, 1.5 equiv) and potassium fluoride (232 mg, 4.0 mmol, 4.0 equiv) were combined. A stir bar was added to each chamber, and the reactor was sealed with

phenolic caps fitted with PTFE septa. To the second chamber, trifluoroacetic acid (1 mL, excess) was added via syringe. The contents of each chamber were stirred at room temperature for 18 h. The contents of the first chamber were transferred to a separatory funnel and diluted with EtOAc (4 mL). The organic layer was washed with HCl (0.1 M, 2 x 5 mL) and brine (5 mL), then dried over MgSO₄ and concentrated *in vacuo*. ¹H NMR analysis of the crude product revealed a 2.5:1 ratio in favor to **7a** compared to the desired **5a** (Figure S2).

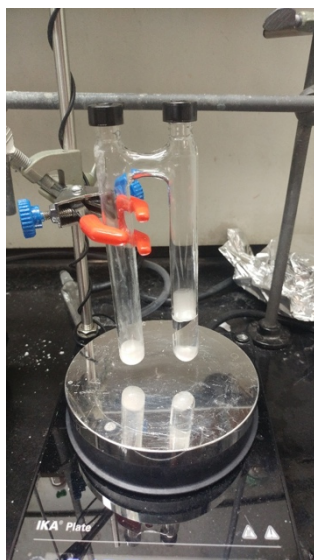


Figure S1. Two-chamber reactor for *ex situ* generation of SO₂F₂.

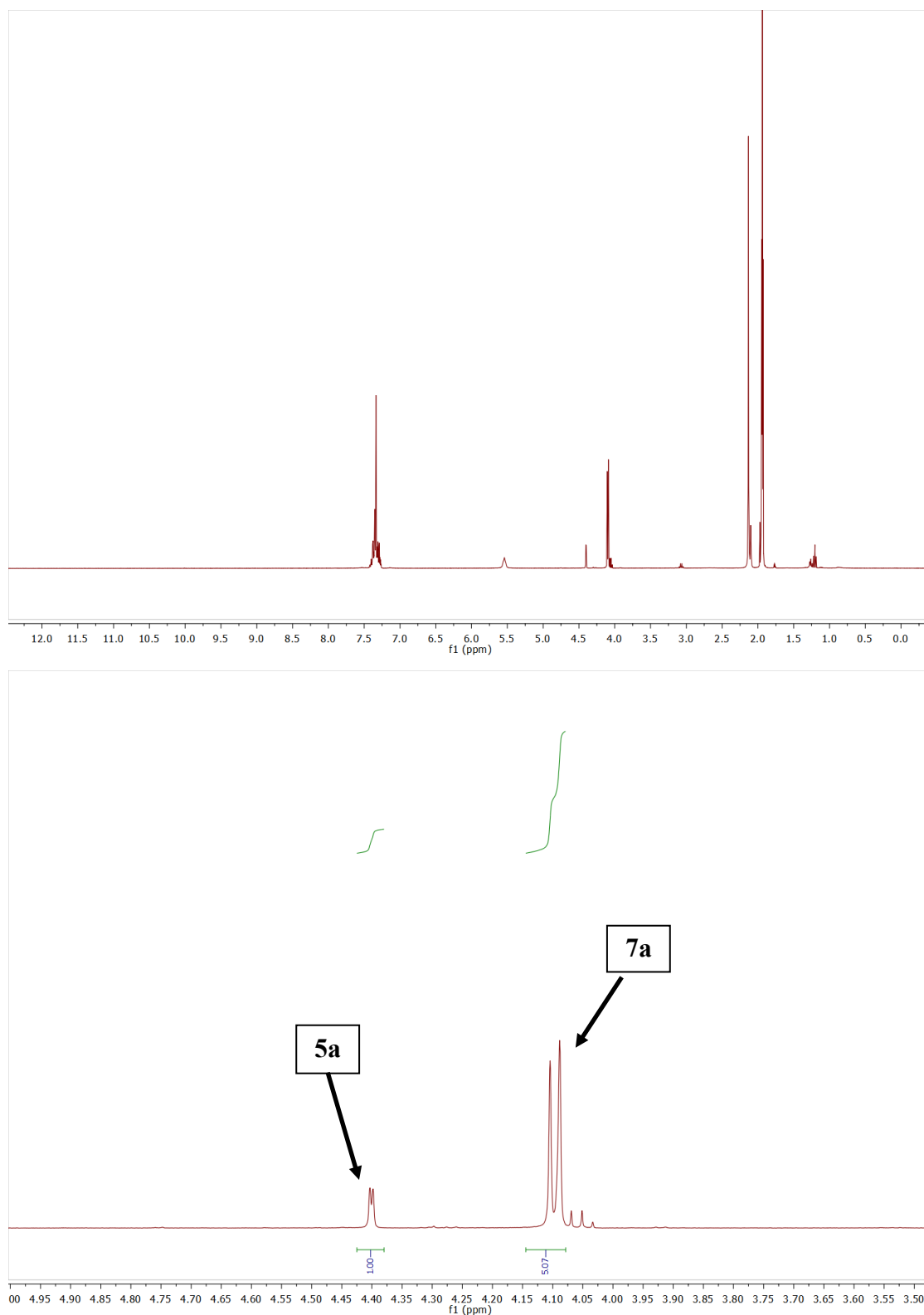
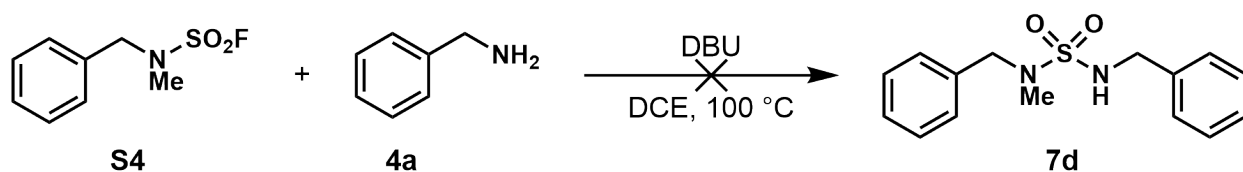


Figure S2. ^1H NMR (CD_3CN , 400 MHz) of the crude product obtained after workup, and inset (bottom) showing the respective benzylic signals of **5a** and **7a**

Attempt to Couple a Secondary Sulfamoyl Fluoride with a Primary Amine



To a solution of compound **S4** (7.0 mg, 34 μmol , 1.0 equiv) in 1,2-dichloroethane (0.4 mL), DBU (8 mg, 52 μmol , 1.5 equiv) and benzylamine (**4a**) (5.5 mg, 52 μmol , 1.5 equiv) were added. The mixture was stirred at 100 °C for 18 h. The mixture was diluted with 1 mL EtOAc and washed with HCl (0.1 M, 1 mL) followed by brine (1 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. ^1H NMR analysis of the crude product showed no trace of **7d**, but only unreacted **S4**.

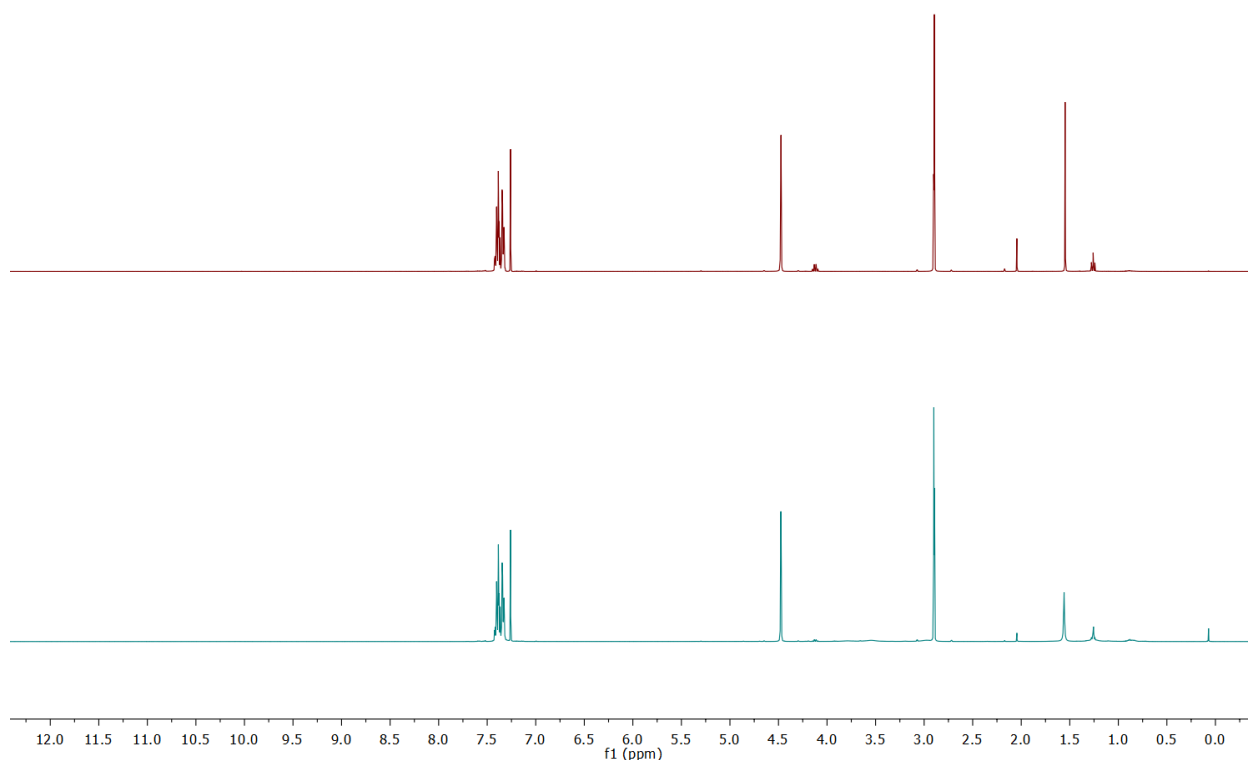
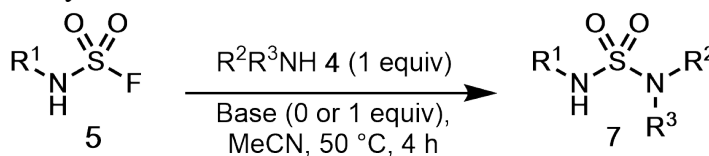


Figure S3. Top: ^1H NMR of compound **S4** (CDCl_3 , 400 MHz), Bottom: ^1H NMR (CDCl_3 , 400 MHz) of material obtained after attempting to react compound **S4** with benzylamine.

Table S1. Representative conditions screened for the synthesis of sulfamide **7a**

<div style="display: flex; align-items: center; justify-content: center; gap: 20px;"> <div style="text-align: center;"> $\text{Bn}-\text{N}(\text{H})-\text{SO}_2\text{F}$ 5a </div> <div>+</div> <div style="text-align: center;"> $\text{Bn}-\text{NH}_2$ 4a </div> <div> $\xrightarrow{\text{Base, Solvent}}$ </div> <div style="text-align: center;"> $\text{Bn}-\text{N}(\text{H})-\text{SO}_2-\text{N}(\text{H})-\text{Bn}$ 7a </div> </div>						
Entry	Eq. of amine	Base	Solvent	Temp.	Time	Yields (%)
1	1.5	TEA (1.5 eq.)	MeCN	80 °C	2 h	91
2	1.5	TEA (1.5 eq.)	DMF	80 °C	2 h	68
3	1.5	TEA (1.5 eq.)	DCE	80 °C	2 h	79
4	1.5	TEA (1.5 eq.)	THF	80 °C	2 h	74
5	1.5	TEA (1.5 eq.)	DME	80 °C	2 h	trace
6	1.5	TEA (1.5 eq.)	Toluene	80 °C	2 h	95
7	1.5	TEA (1.5 eq.)	Benzene	80 °C	2 h	89
8	1.5	TEA (1.5 eq.)	NMP	80 °C	2 h	73
9	1.5	DBU (1.5 eq.)	MeCN	80 °C	2 h	96
10	1.5	Cs ₂ CO ₃ (1.5 eq.)	MeCN	80 °C	2 h	97
11	1.5	DBU (1.5 eq.)	MeCN	80 °C	2 h	68
12	1	DBU (1 eq.)	MeCN	80 °C	2 h	97
13	1	DBU (0.1 eq)	MeCN	80 °C	2 h	78
14	1	DBU (2.5 eq.)	MeCN	80 °C	2 h	88
15	1	DBU (2.5 eq.)	MeCN	80 °C	0.5 h	86
16	1	DBU (2.5 eq.)	MeCN	80 °C	1 h	91
17	1	DBU (2.5 eq.)	MeCN	80 °C	4 h	99
18	1	DBU (2.5 eq.)	MeCN	50 °C	2 h	76
19	1	DBU (2.5 eq.)	MeCN	50 °C	8 h	92
20	1	DBU (2.5 eq.)	MeCN	rt	24 h	76
21	1	DBU (1 eq.)	MeCN	80 °C	2 h	96

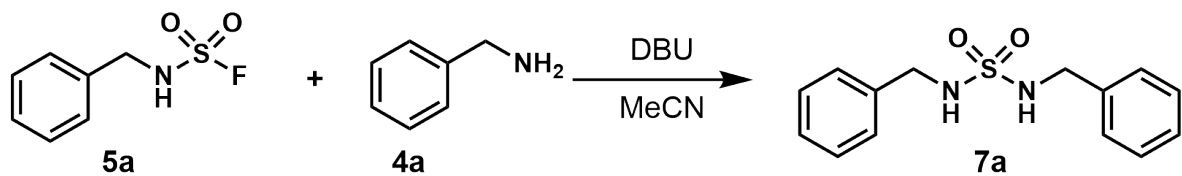
Table S2. Synthesis of sulfamides **7a-e** with and without added base

Sulfamoyl Fluoride	Amine	Yield (Using 1 equiv base)*	Yield (No base added)
5a	4a	96%	70%
5a	4b	83%	74%
5a	4c	98%	79%
5b	4a	89%	63%
5b	4b	91%	79%
5b	4c	93%	52%

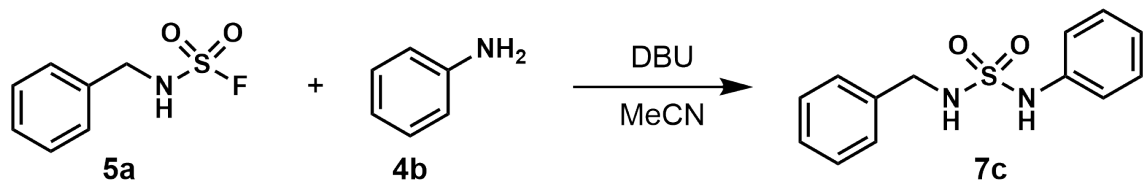
(*DBU was used as base with compound **5a**, pyridine with compound **5b**)

Monitoring the Sulfamide Synthesis

To a flame-dried vial under a nitrogen atmosphere, sulfamoyl fluoride **5a** (38 mg, 0.20 mmol, 1.0 equiv) was dissolved in anhydrous MeCN (2 mL). Amine **4** (0.20 mmol, 1.0 equiv) and DBU (30 mg, 0.20 mmol, 1.0 equiv) were added. The mixture was stirred at the indicated temperature for 24 h. For each time point, an aliquot of the reaction mixture (0.25 mL) was collected with a syringe. Each aliquot was immediately quenched with HCl (1 M, 1 mL). The aqueous mixture was then extracted with EtOAc (2 x 1 mL). The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo*. The progress of the reaction was determined by ¹H NMR using 1,3,5-trimethoxybenzene (4.2 mg, 25 μmol, 0.125 equiv) as an internal standard.

Table S3. Synthesis of sulfamide 7a

Time	0 °C Yield (%)	20 °C Yield (%)	50 °C Yield (%)	80 °C Yield (%)
30 min	7	10	60	86
1 h	9	17	65	94
2 h	12	25	76	91
4 h	15	25	79	99
8 h	20	51	92	-
24 h	37	76	99	-

Table S4. Synthesis of sulfamide 7c

Time	20 °C Yield (%)	50 °C Yield (%)	80 °C Yield (%)
30 min	6	28	60
1 h	13	34	76
2 h	26	53	74
4 h	25	90	77
8 h	14	90	83
24 h	55	97	-

Investigation of the Generation of Azasulfene Intermediate **6a**:

In order to avoid any potential reaction between azasulfene **6a** and trace of water, CD₃CN dried with activated 4 Å molecular sieves and anhydrous Et₃N were used. Anhydrous Et₃N (1.0 equiv) was added to a solution of sulfamoyl fluoride **5a** in anhydrous CD₃CN. The resulting mixture was quickly transferred to a J. Young NMR tube under a stream of nitrogen. After heating at 80 °C for 30 min, a ¹⁹F NMR spectrum was collected, which revealed the full consumption of sulfamoyl fluoride **5a**. The new peak in the ¹⁹F NMR spectrum is consistent with the formation of Et₃N•HF according to literature precedent (*J. Am. Chem. Soc.* 2016, **138**, 11360)

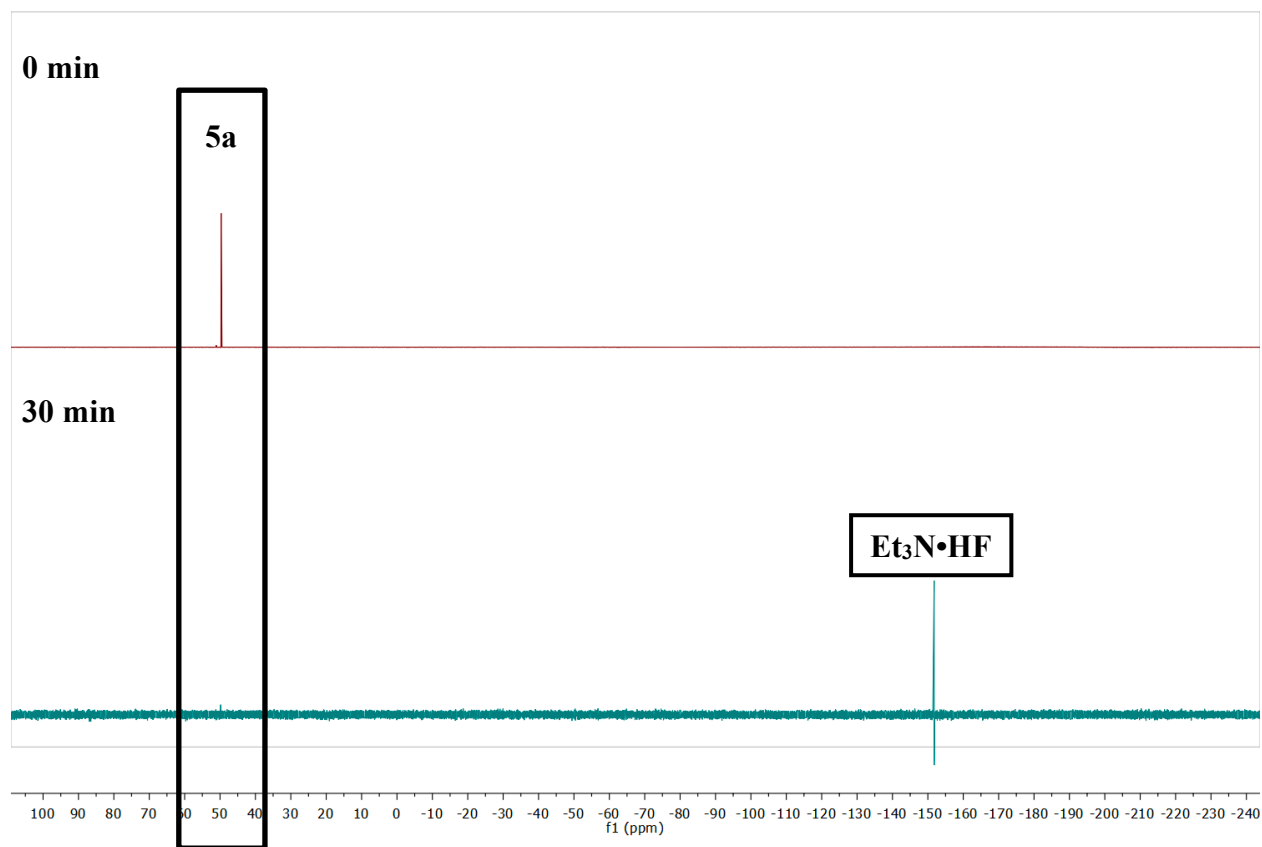
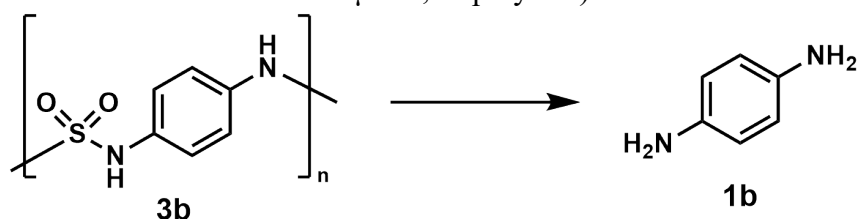


Figure S4. ¹⁹F NMR (CD₃CN, 470 MHz) analysis revealed the disappearance of sulfamoyl fluoride **5a** and suggested the formation of Et₃N•HF and therefore azasulfene **6a**
Top: Sulfamoyl fluoride **5a**. Bottom: **5a** stirred with Et₃N at 80 °C for 30 min

Hydrolysis Study of Polysulfamides

To a vial containing polymer **3b** (15 mg, 88 μmol , based on monomer unit $\text{C}_6\text{H}_6\text{N}_2\text{O}_2\text{S}$), 2 mL (excess in all cases) of the respective aqueous base or acid solution was added. The mixture was stirred at the indicated temperature for 40 h. If the aqueous solution was acidic, the solution was placed in an ice bath and solid sodium hydroxide was added to the mixture until a pH of 14 was reached. The aqueous mixture was extracted with EtOAc (3 x 1 mL). The organic fractions were combined, dried over MgSO_4 , and concentrated *in vacuo*. Yields were determined based on the mass of product obtained.

Table S5. Degradation reactions performed on polymer **3b** (*Experiment performed with 30 mg, 176 μmol , of polymer)



Degradation Medium	Temperature (°C)	Mass 1b Obtained	Yield
NH_4OH (conc.)*	80	10 mg	53%
NaOH (4 M)	130	4 mg	42%
NaOH (4 M)	80	3 mg	32%
HBr (4 M)*	130	13 mg	70%
HCl (4 M)	130	7 mg	74%
HCl (4 M)	80	6 mg	63%
HCl (4 M)	20	0 mg	0%
HCl (conc.)	20	0 mg	0%
H_2SO_4 (2 M)	20	0 mg	0%
H_2SO_4 (conc.)	20	<1 mg	<10%

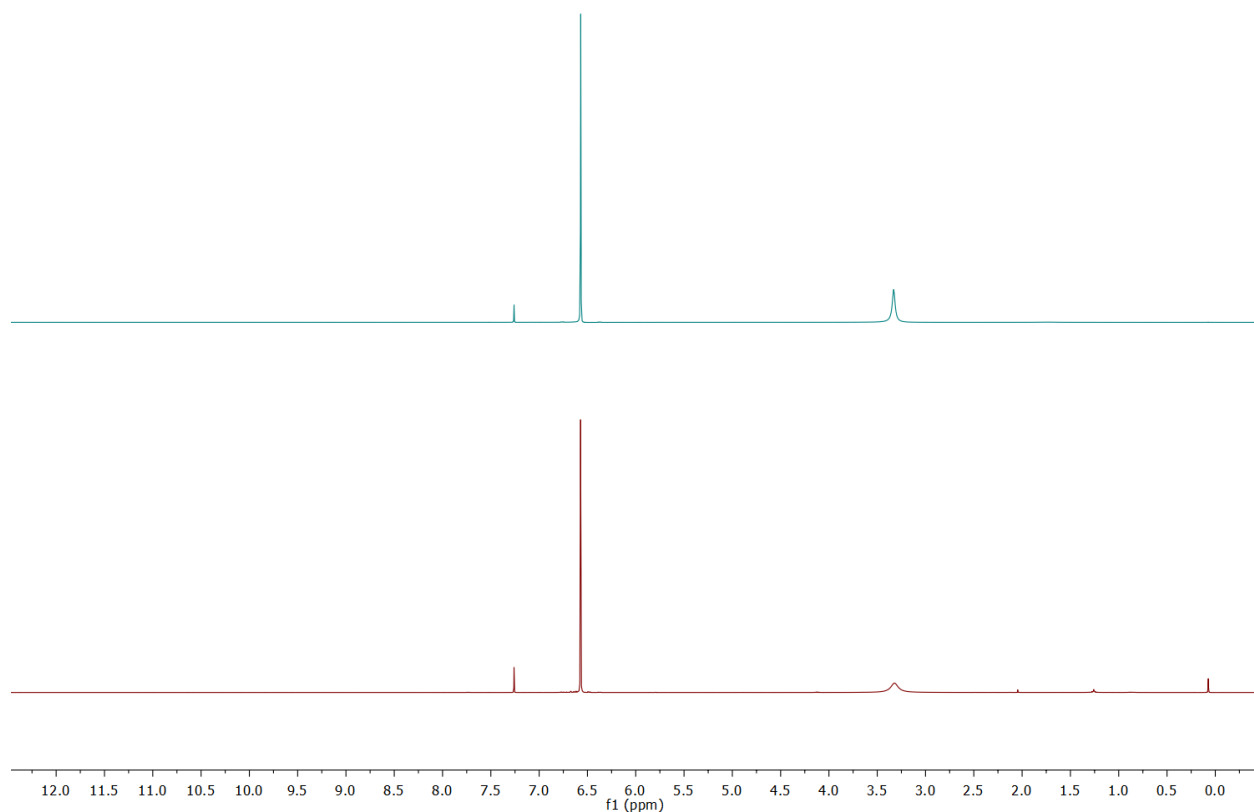
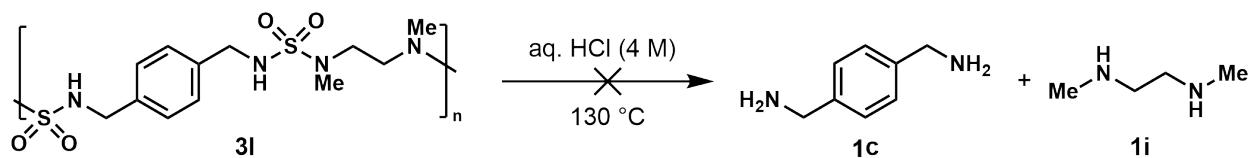


Figure S5. Top: ^1H NMR of purchased 1,4-phenylenediamine (CDCl_3 , 400 MHz), Bottom: ^1H NMR of solid obtained after treatment of polymer **3b** with aq. HCl (4 M) at 130 °C (CDCl_3 , 400 MHz).



When polymer **3I** was mixed with HCl (4 M) at 130 °C following the above procedure, the mixture remained a suspension of the polymer after 40 h. The solution was made alkaline and extracted with EtOAc, but no detectable amount of monomers **1c** or **1i** was isolated.

IR Analysis of Hydrogen-bonding Interaction within Polysulfamides:

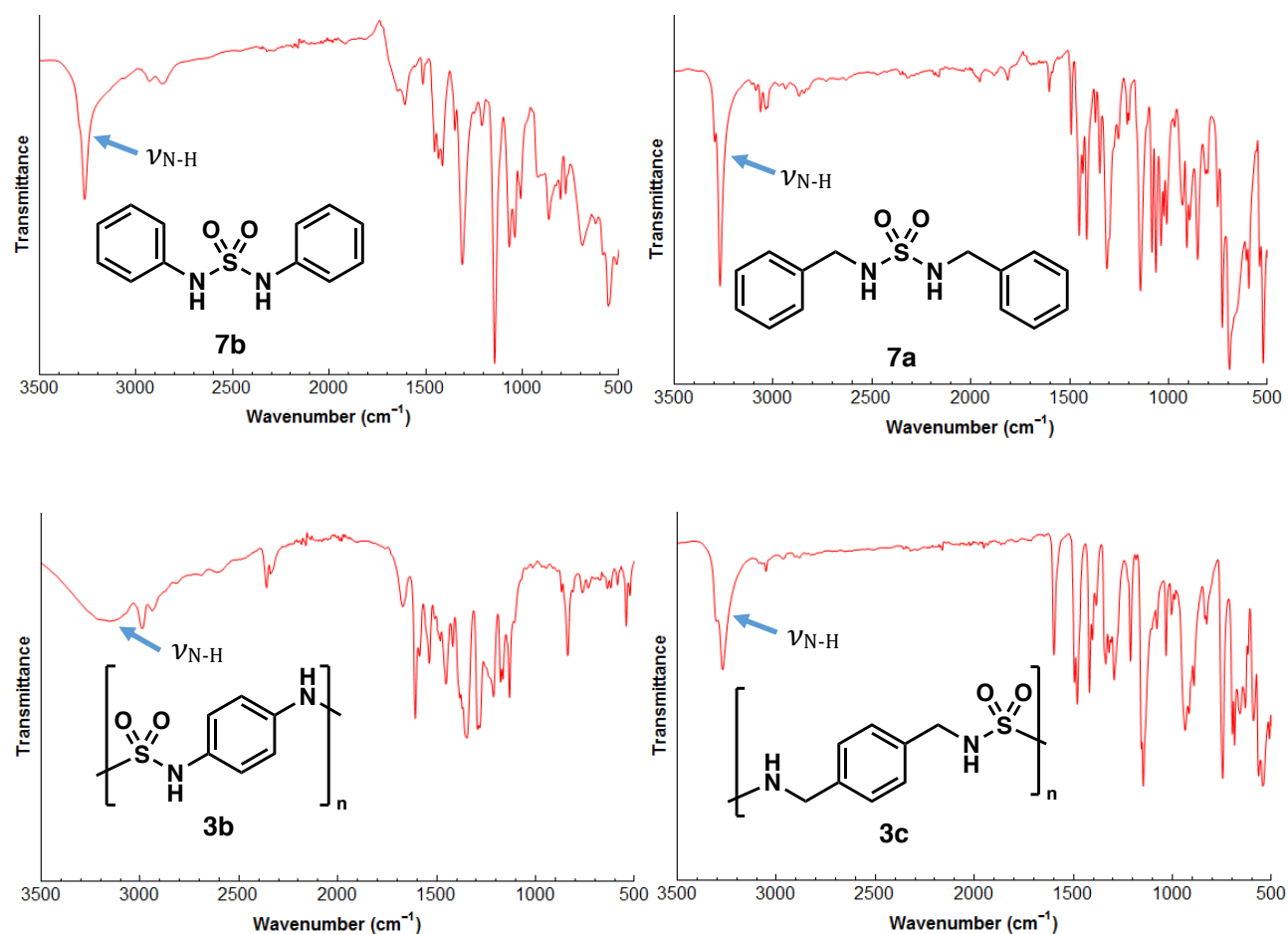


Figure S6. Comparison of FT-IR spectra of *N,N'*-diphenylsulfamide (**7a**) and *N,N'*-dibenzylsulfamide (**7b**) with that of polymers **3b** and **3c**.

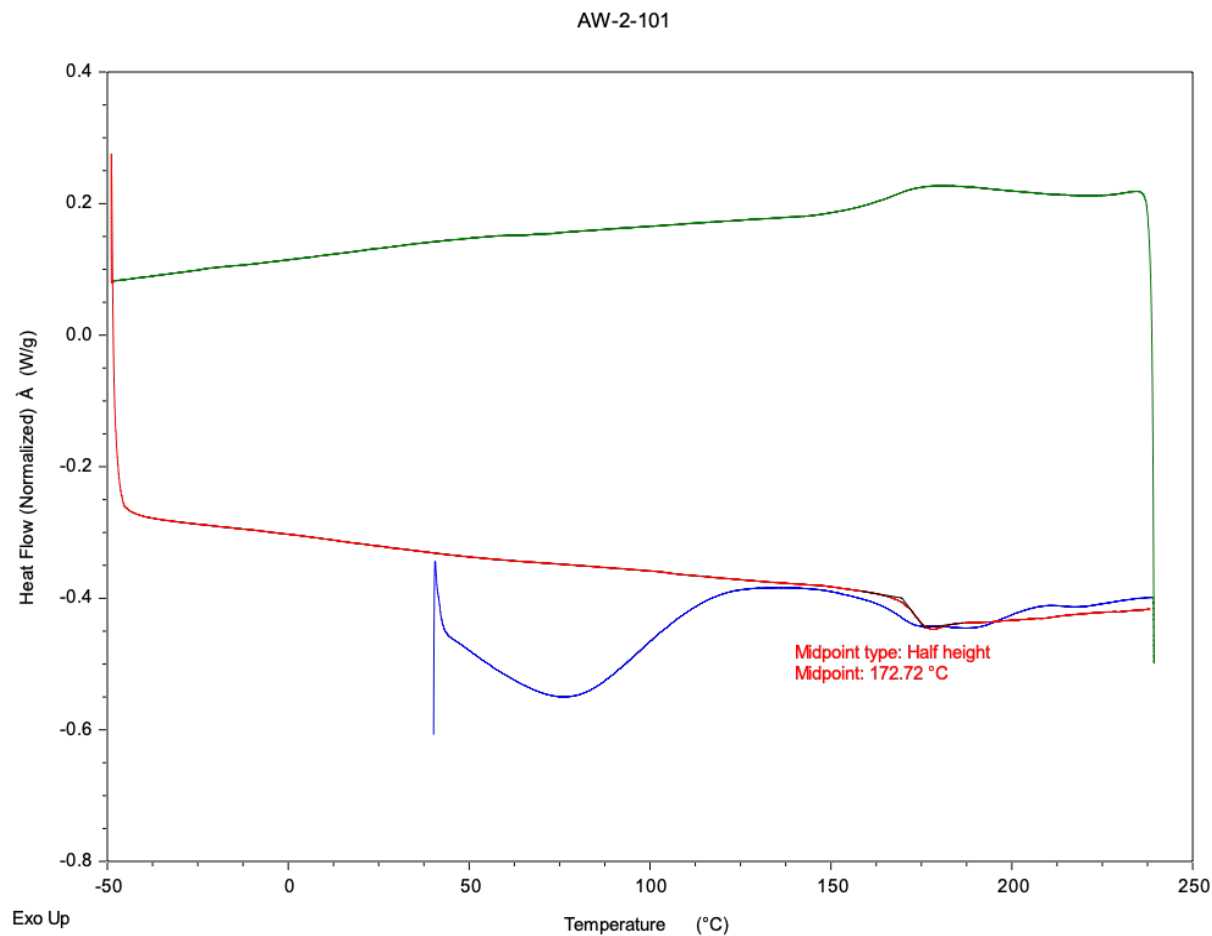


Figure S7. Example of in-software calculation of T_g for polymer **3n** (Performed using TRIOS Software, Developed by TA Instruments) (Blue: First Heating Cycle, Green: First Cooling Cycle, Red: Second Heating Cycle) For all plots shown in Figure S8 to S22, Blue: First Cooling Cycle, Red: Second Heating Cycle.

Characterization of Polysulfamides:

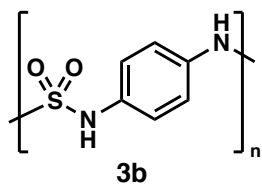
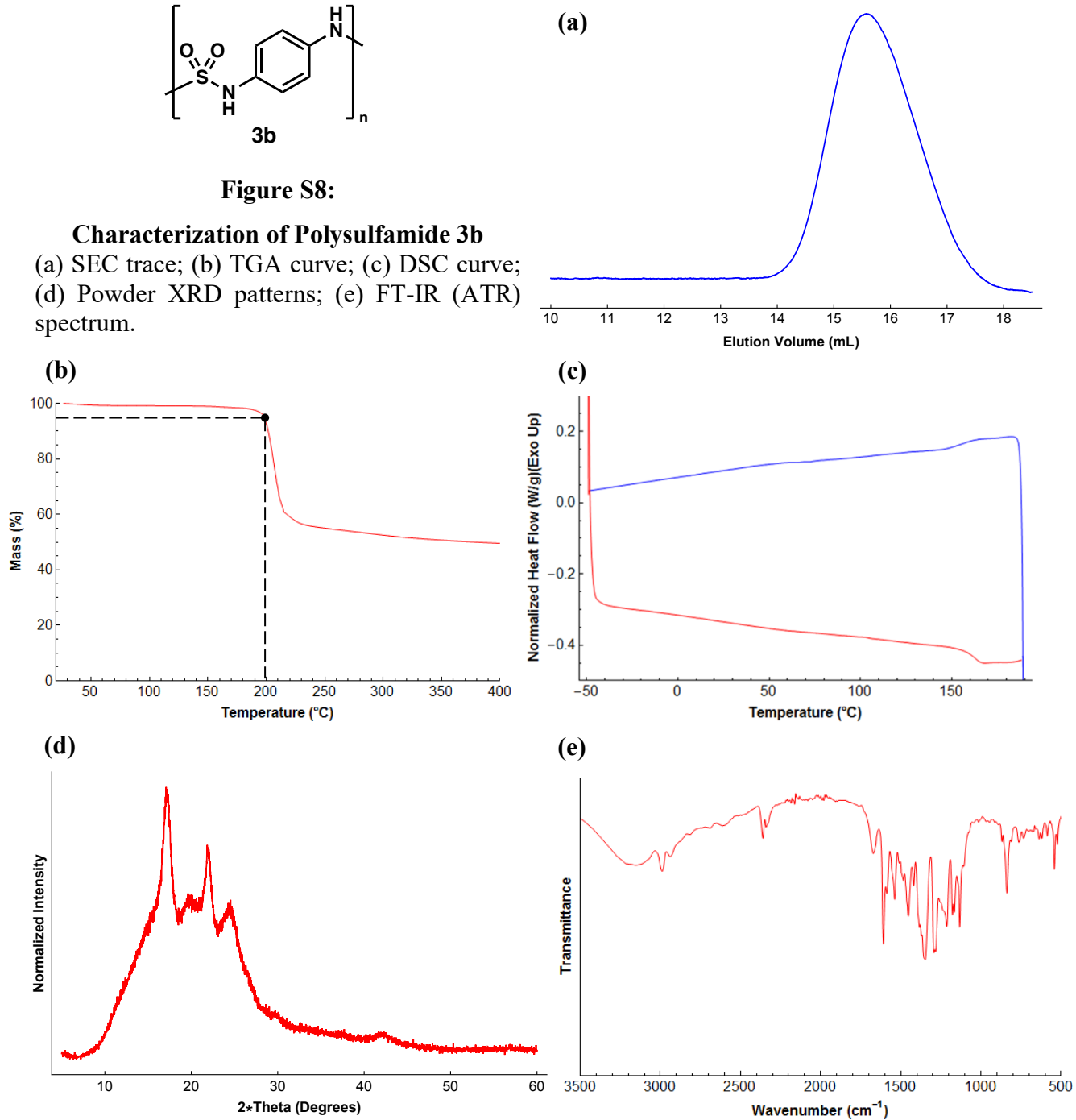


Figure S8:

Characterization of Polysulfamide 3b

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) spectrum.



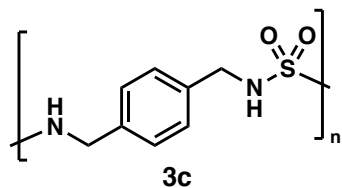
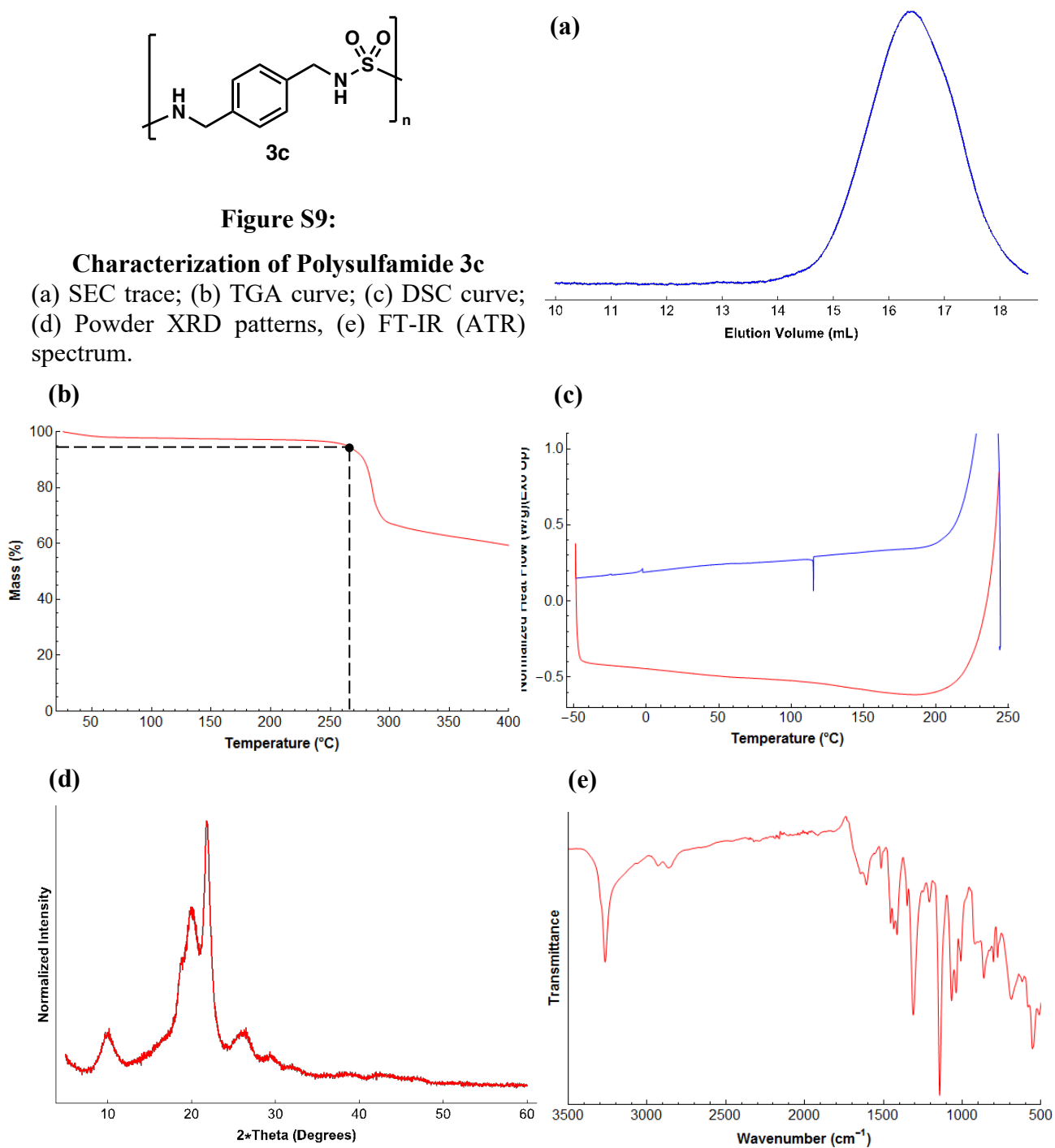


Figure S9:

Characterization of Polysulfamide 3c

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.



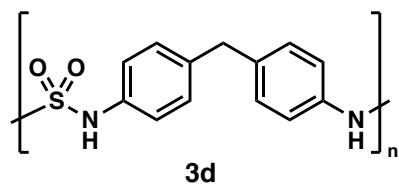
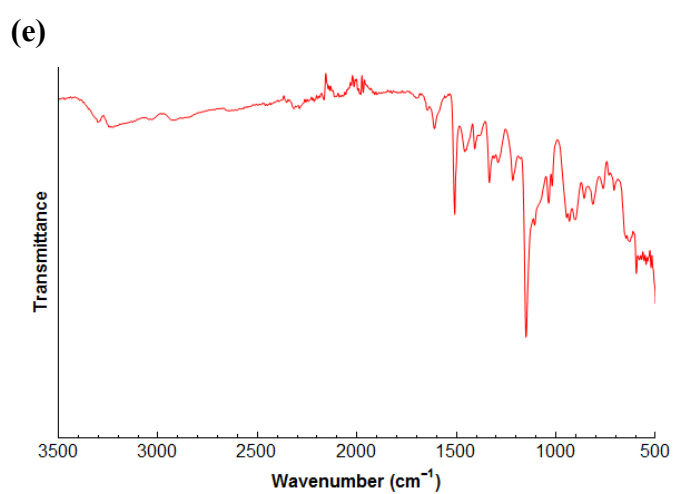
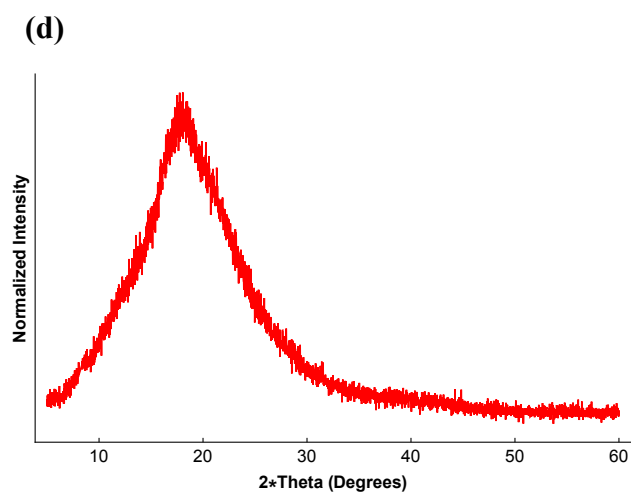
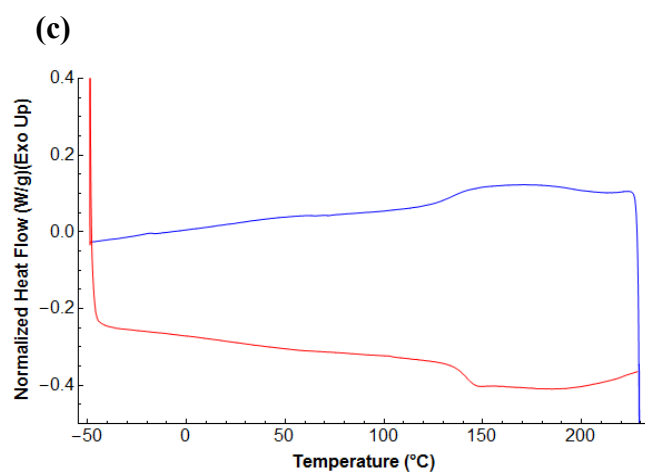
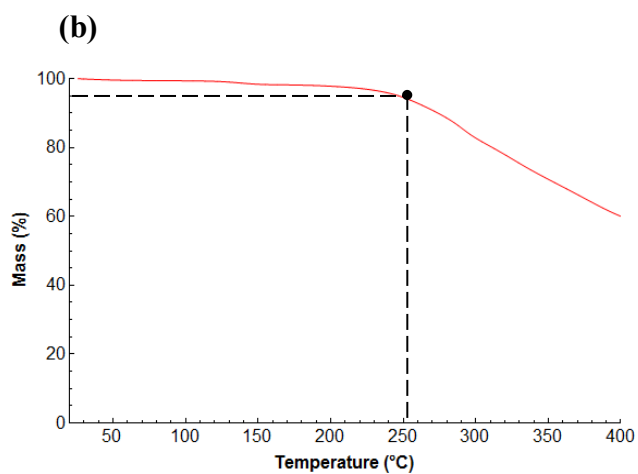
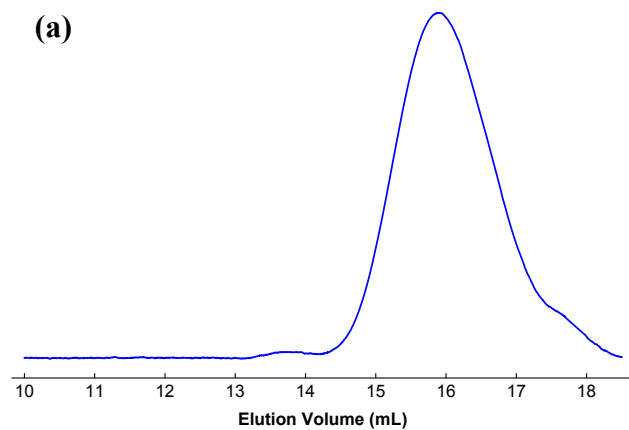


Figure S10:

Characterization of Polysulfamide 3d

(a) SEC trace; (b) TGA curve; (c) DSC curve;
(d) Powder XRD patterns; (e) FT-IR (ATR)
spectrum.



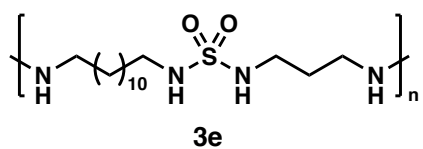
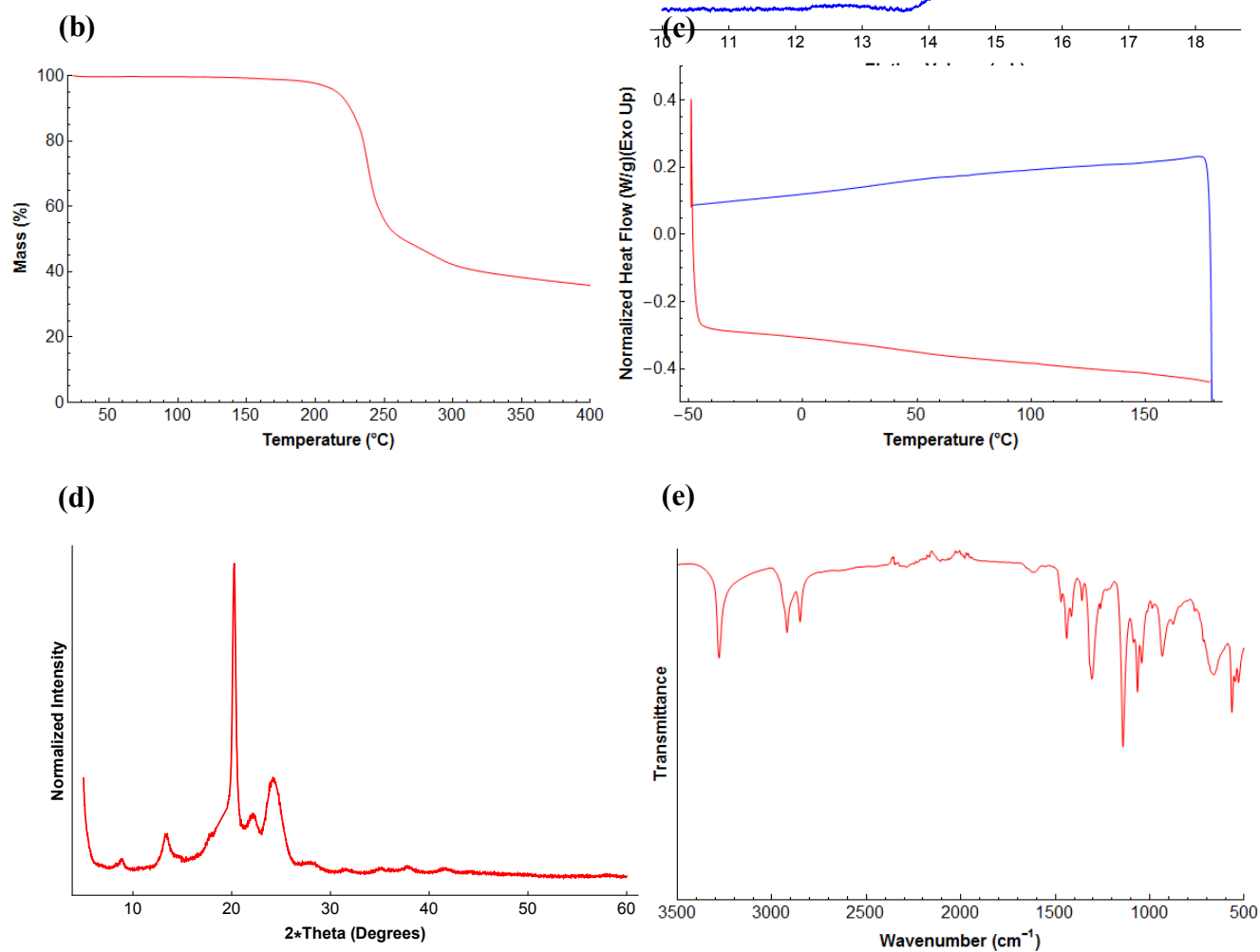


Figure S11:

Characterization of Polysulfamide 3e

(a) SEC trace; (b) TGA curve; (c) DSC curve;
(d) Powder XRD; (e) FT-IR (ATR) spectrum.



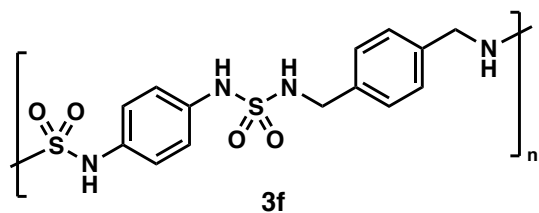
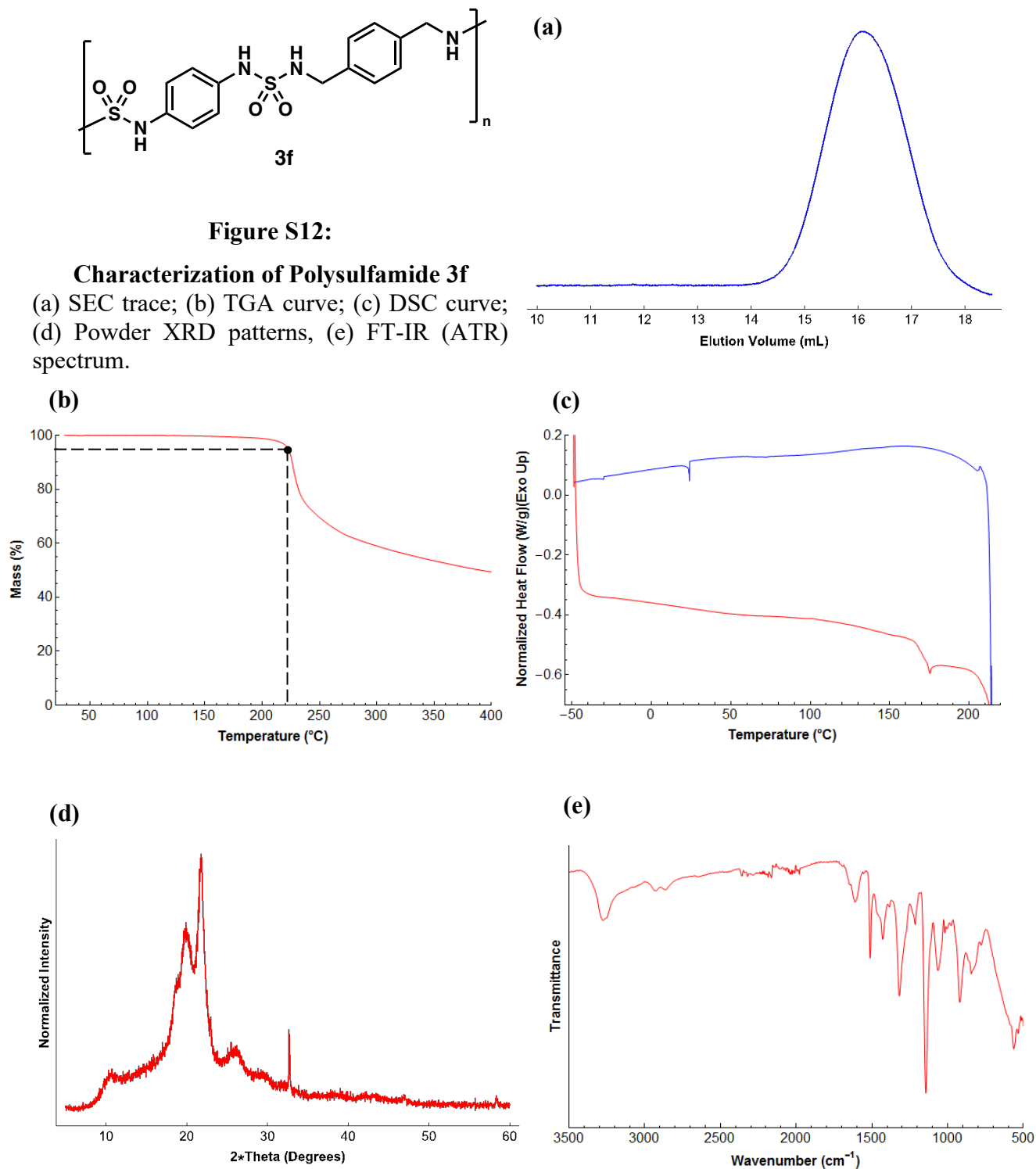


Figure S12:

Characterization of Polysulfamide 3f

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.



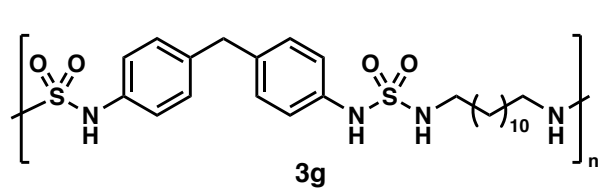
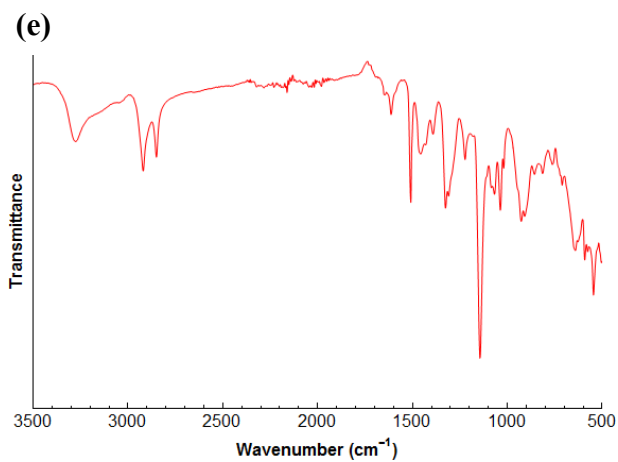
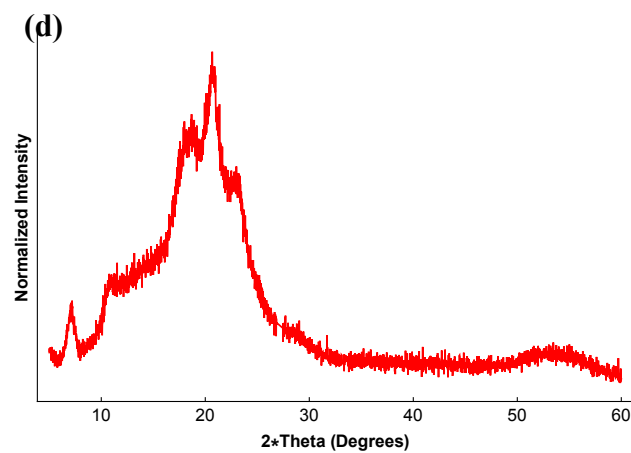
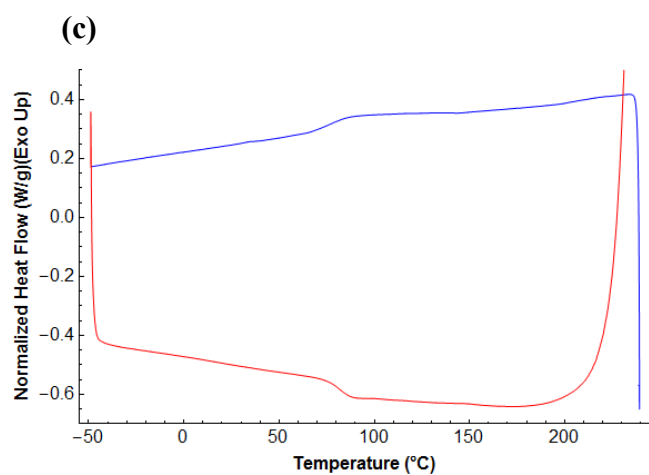
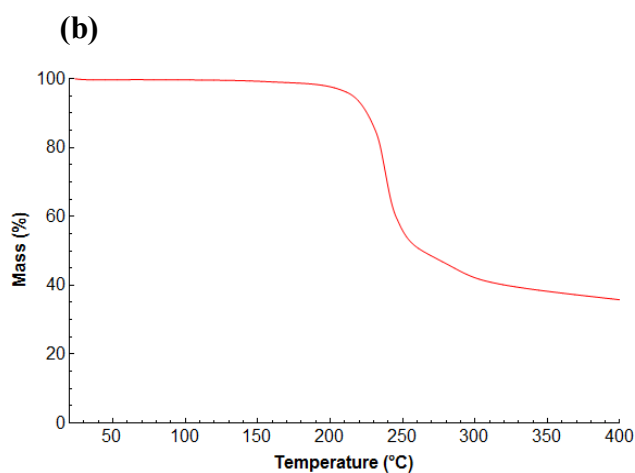
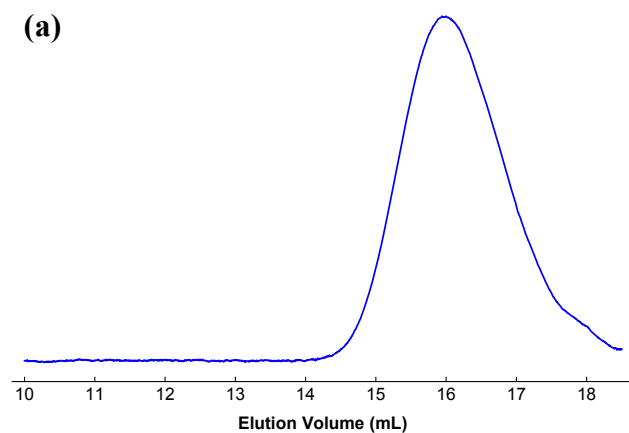


Figure S13:

Characterization of Polysulfamide 3g

(a) SEC trace; (b) TGA curve; (c) DSC curve;
(d) Powder XRD patterns; (e) FT-IR (ATR)
spectrum.



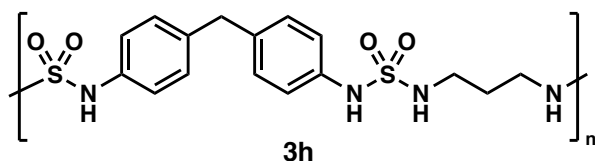
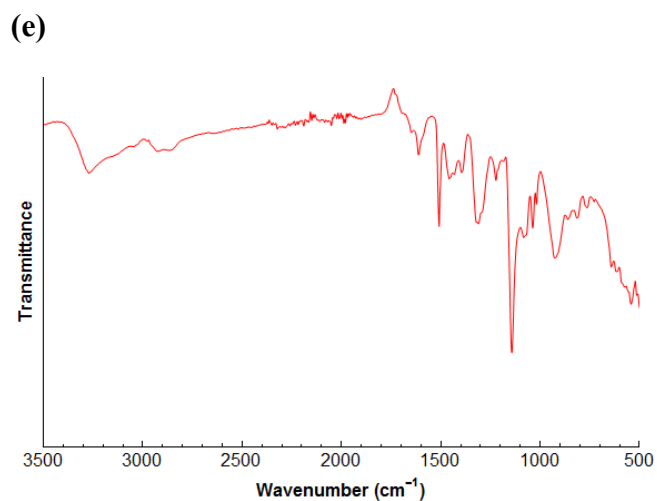
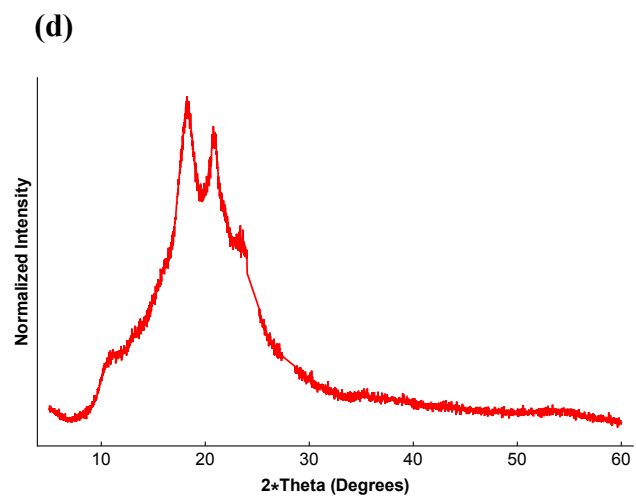
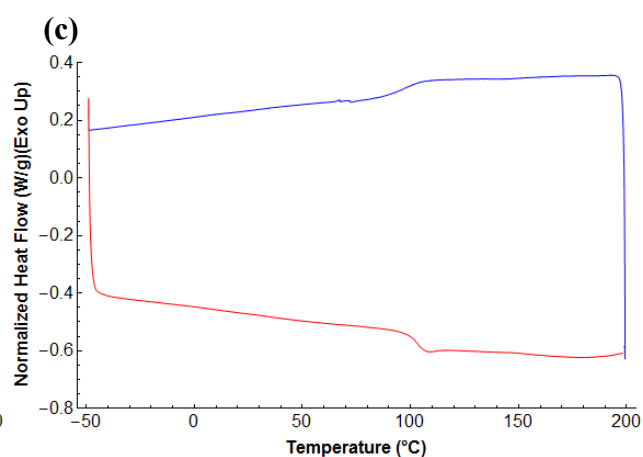
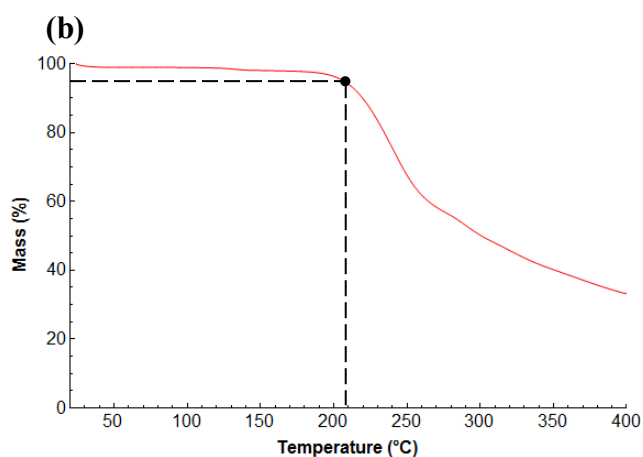
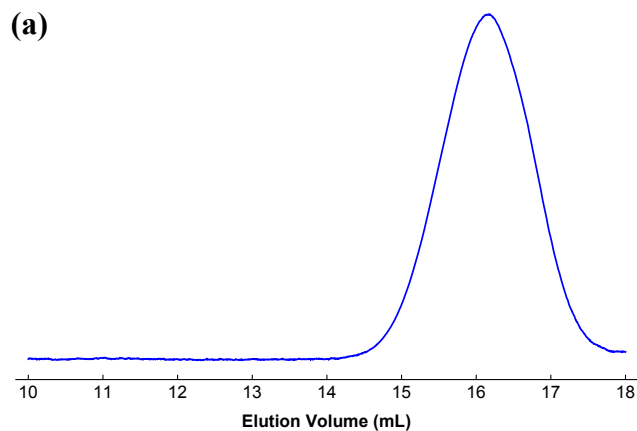


Figure S14:

Characterization of Polysulfamide 3h

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) spectrum.



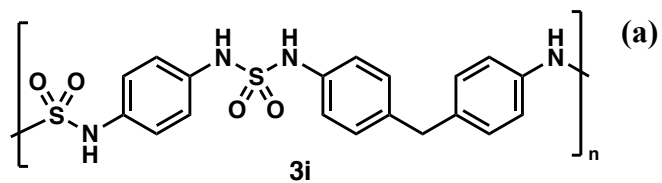
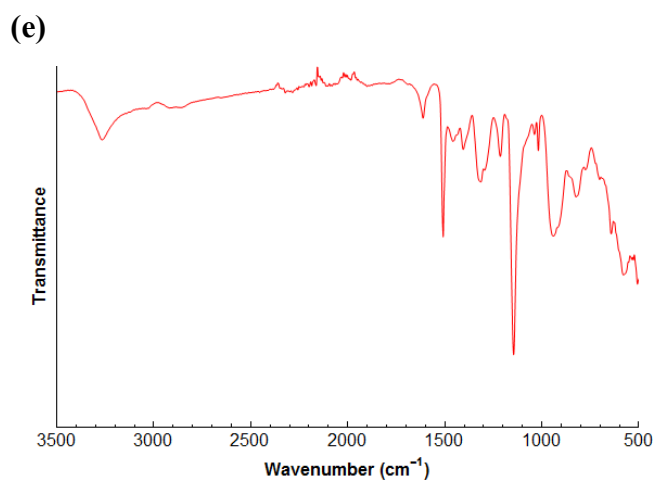
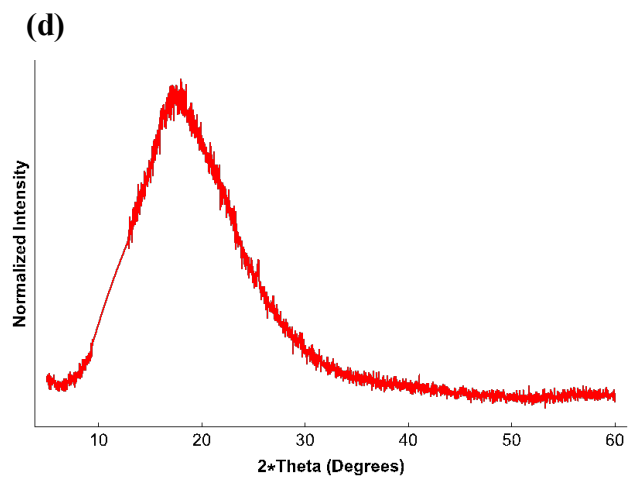
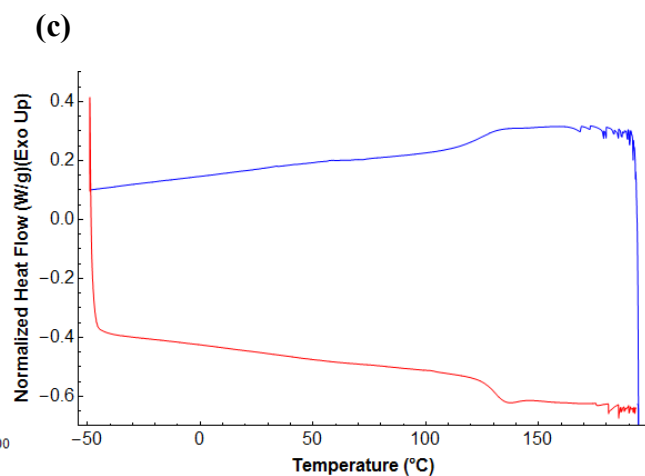
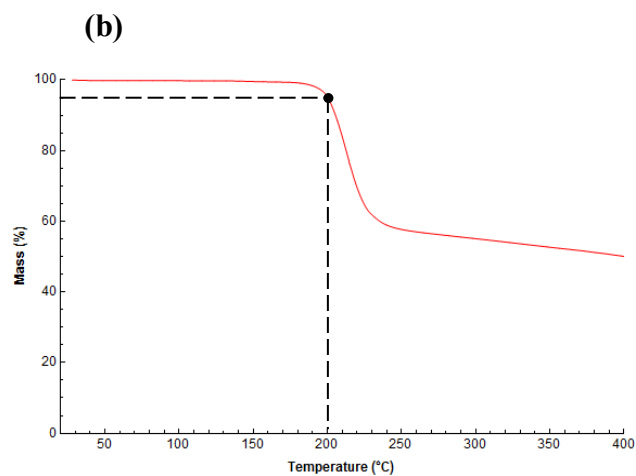
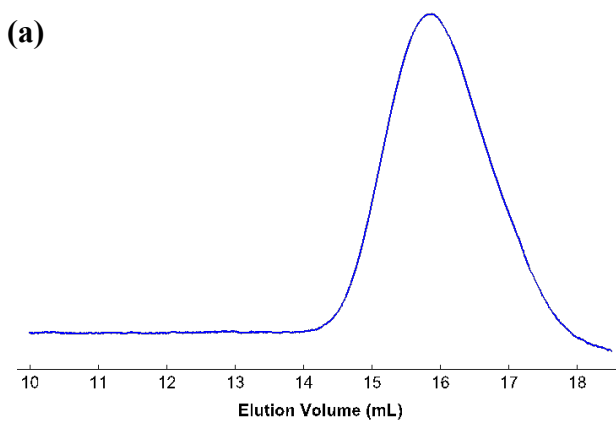


Figure S15:

Characterization of Polysulfamide 3i

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD, (e) FT-IR (ATR) spectrum.



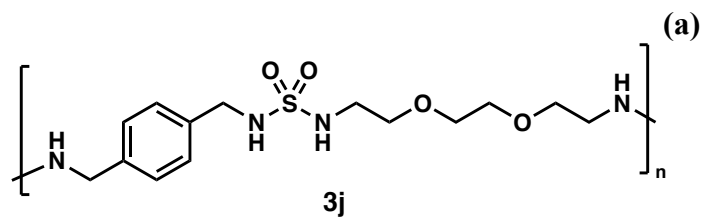
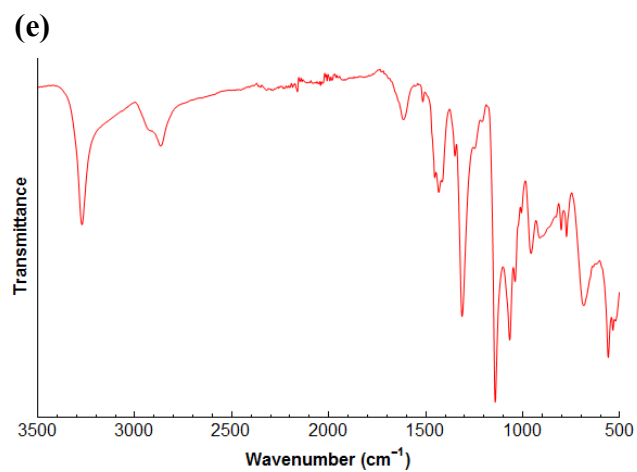
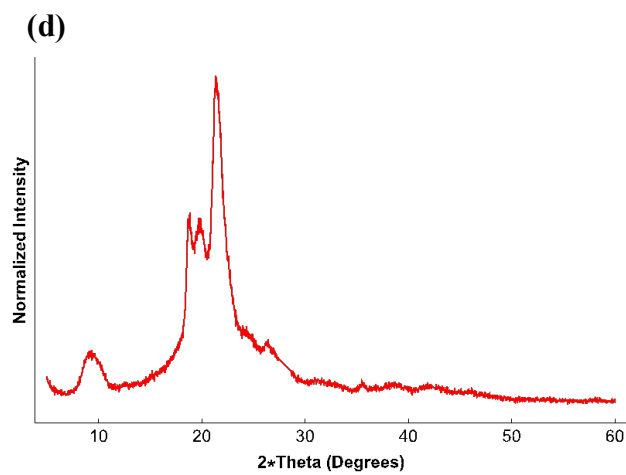
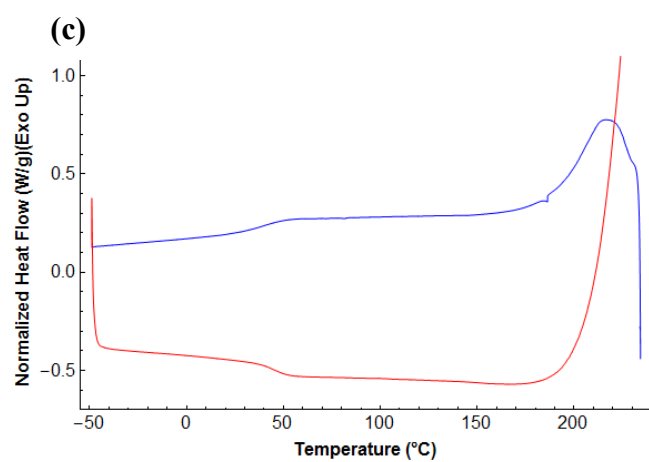
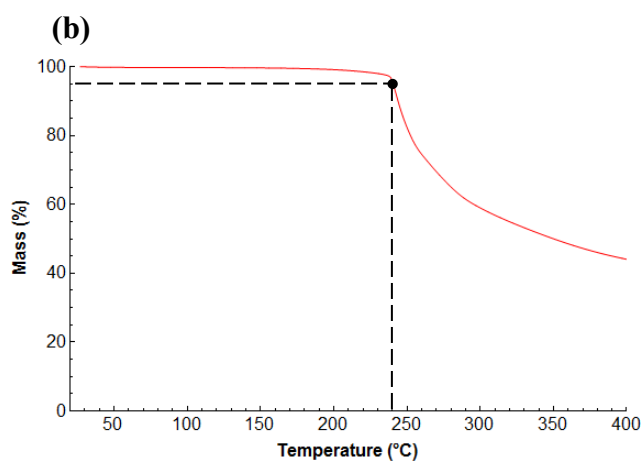
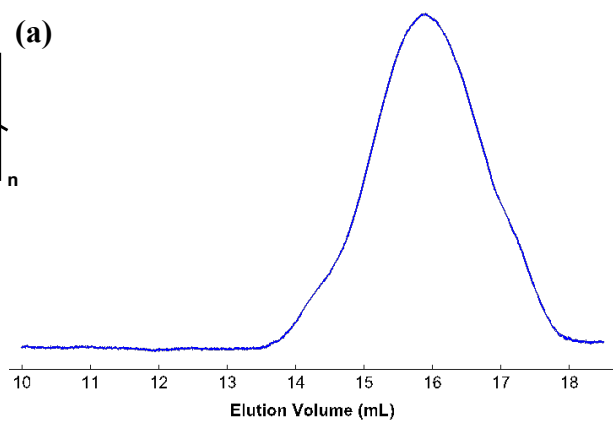


Figure S16:

Characterization of Polysulfamide 3j

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) spectrum.



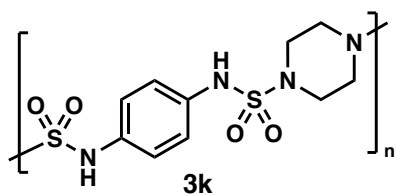
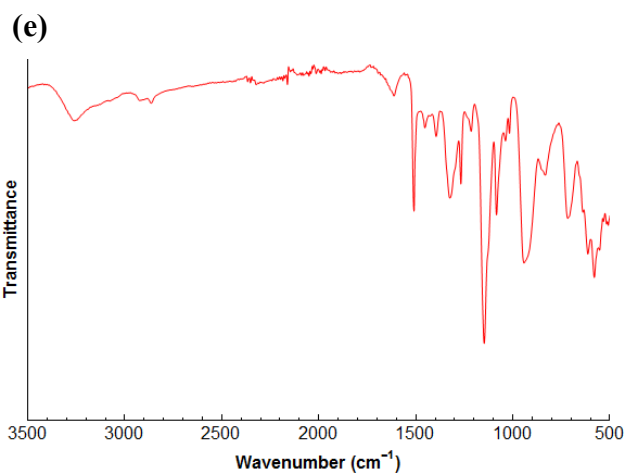
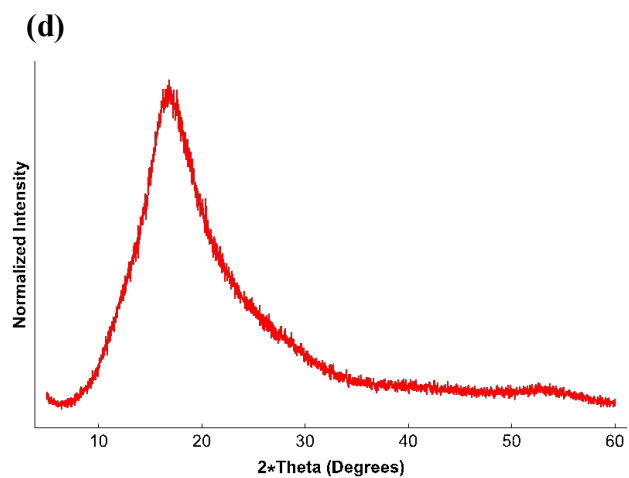
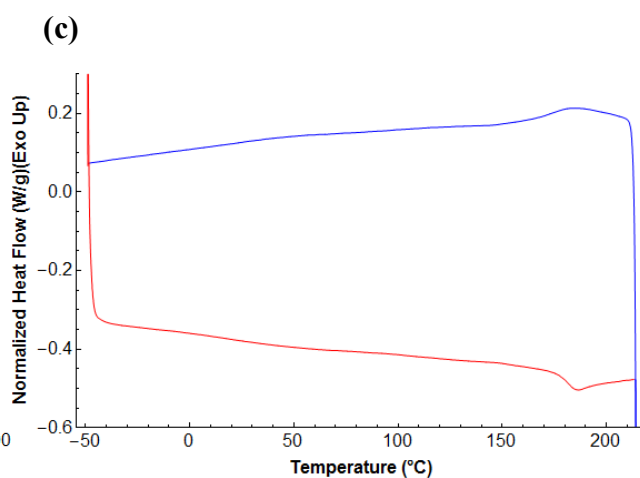
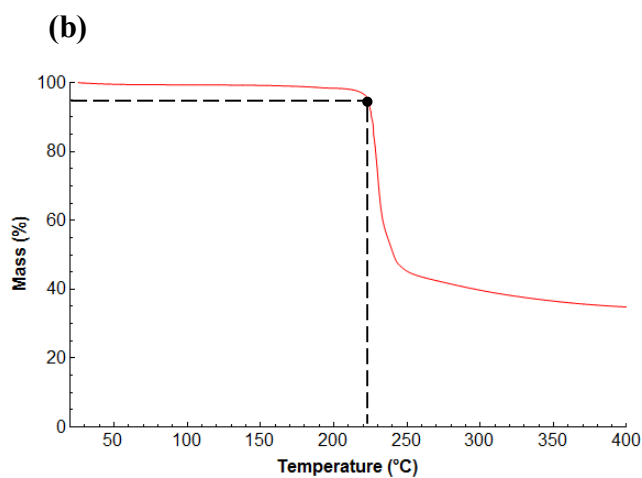
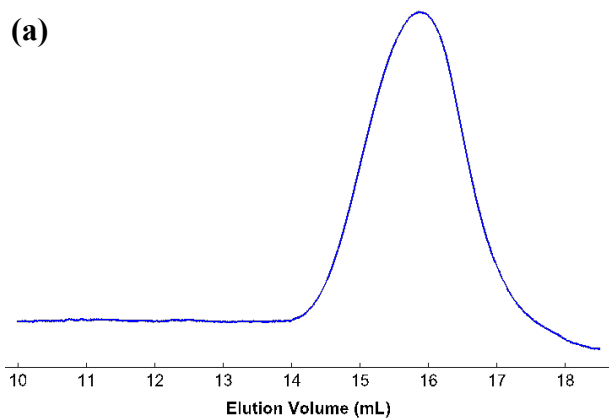


Figure S17:

Characterization of Polysulfamide 3k

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.



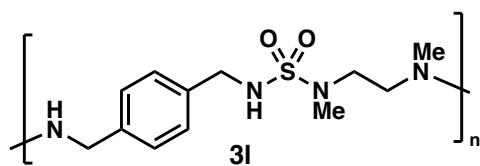
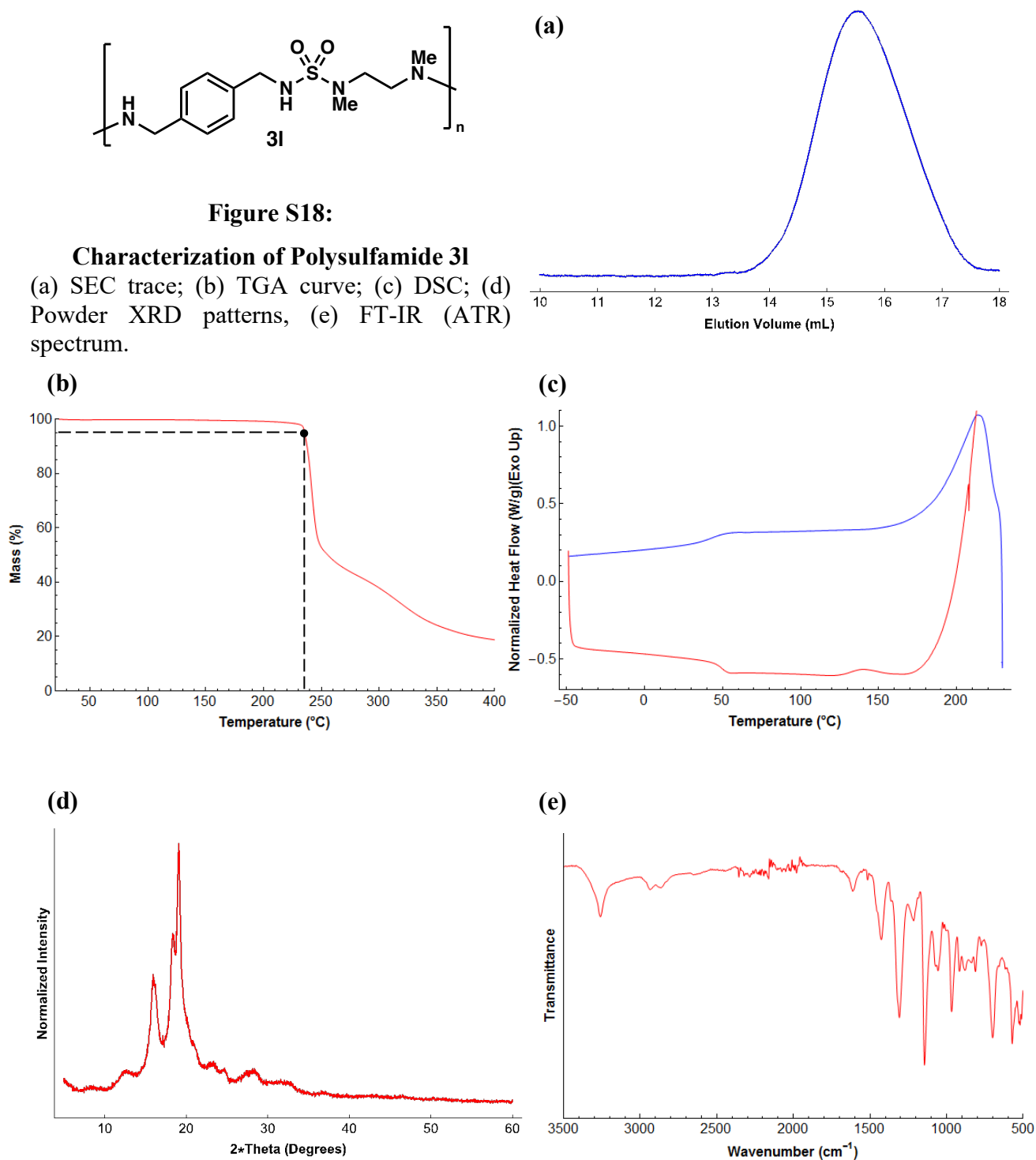


Figure S18:

Characterization of Polysulfamide 3I

(a) SEC trace; (b) TGA curve; (c) DSC; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.



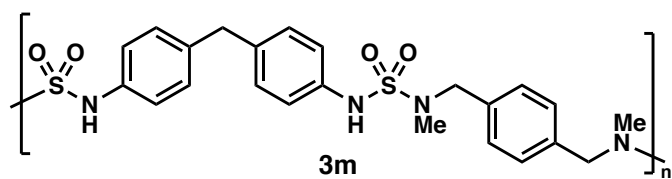


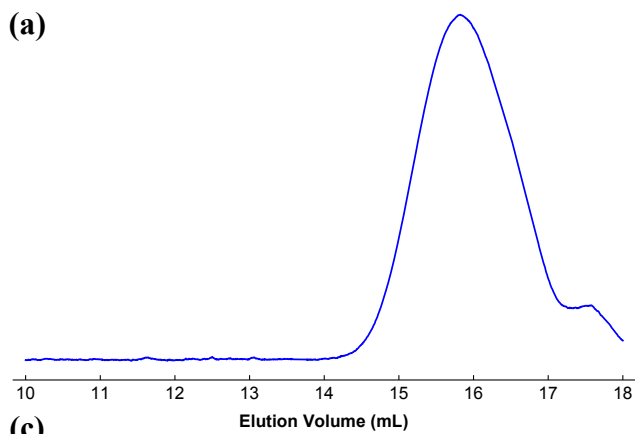
Figure S19:

Characterization of Polysulfamide 3m

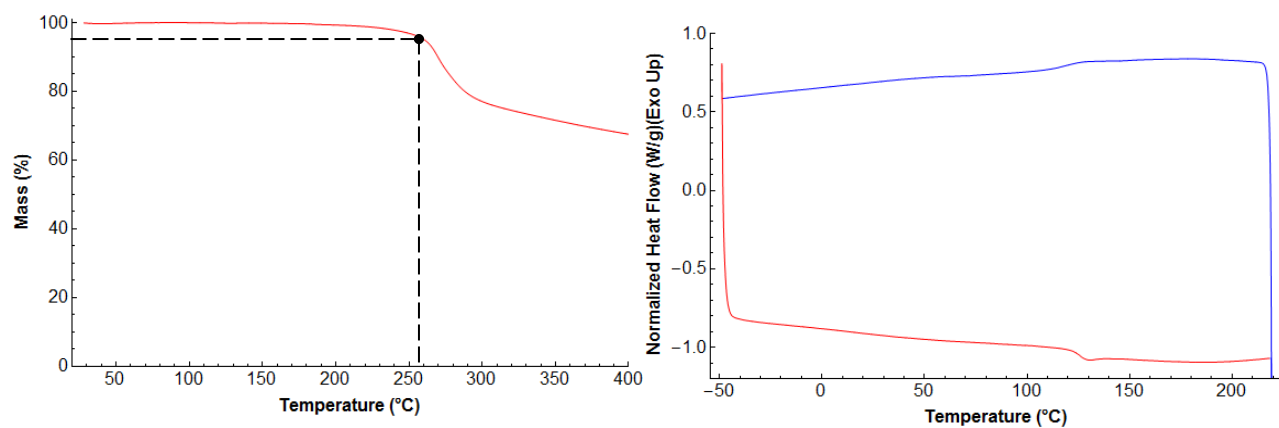
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR)

(b) n.

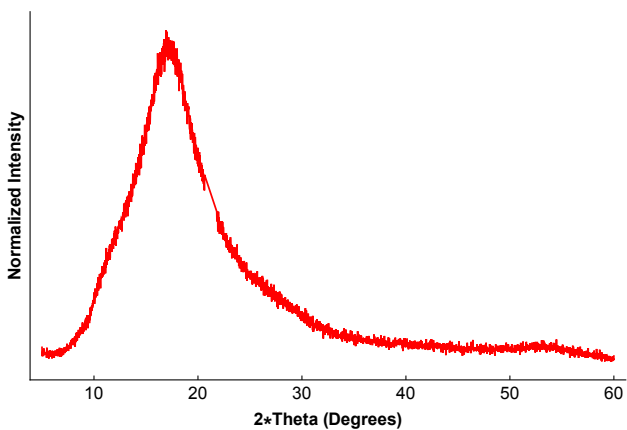
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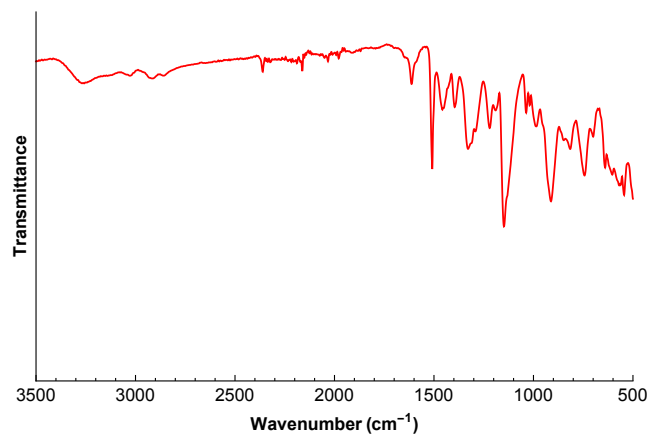
(c)



(d)



(e)



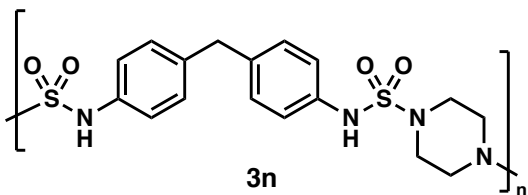
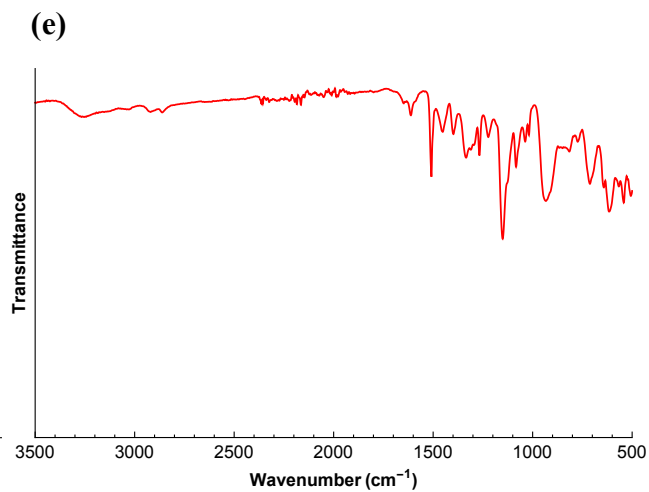
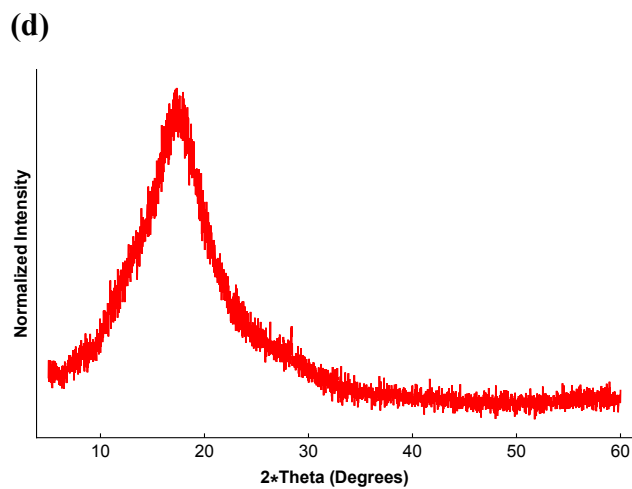
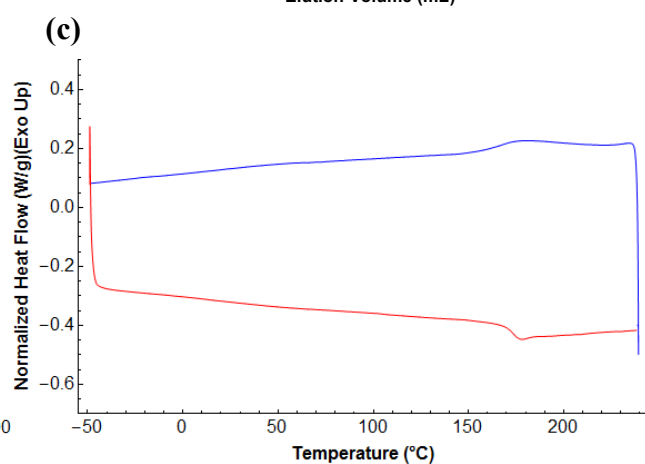
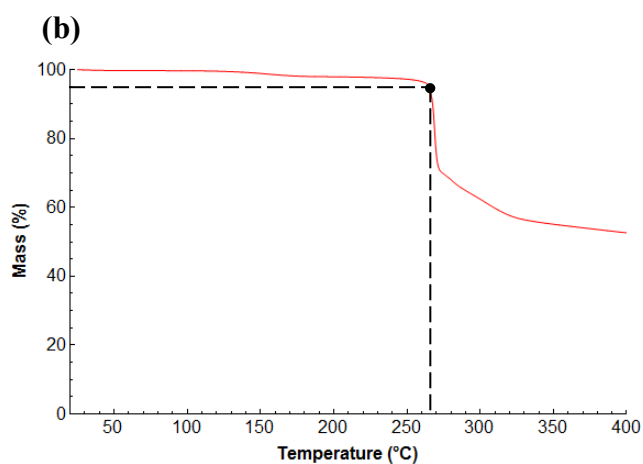
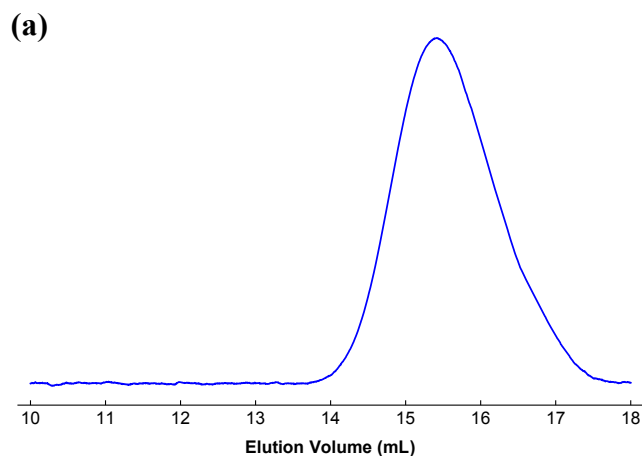


Figure S20:

Characterization of Polysulfamide 3n

(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR.



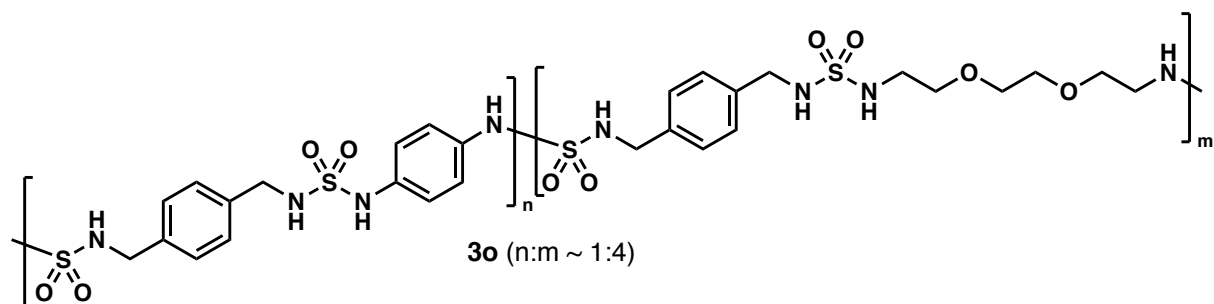
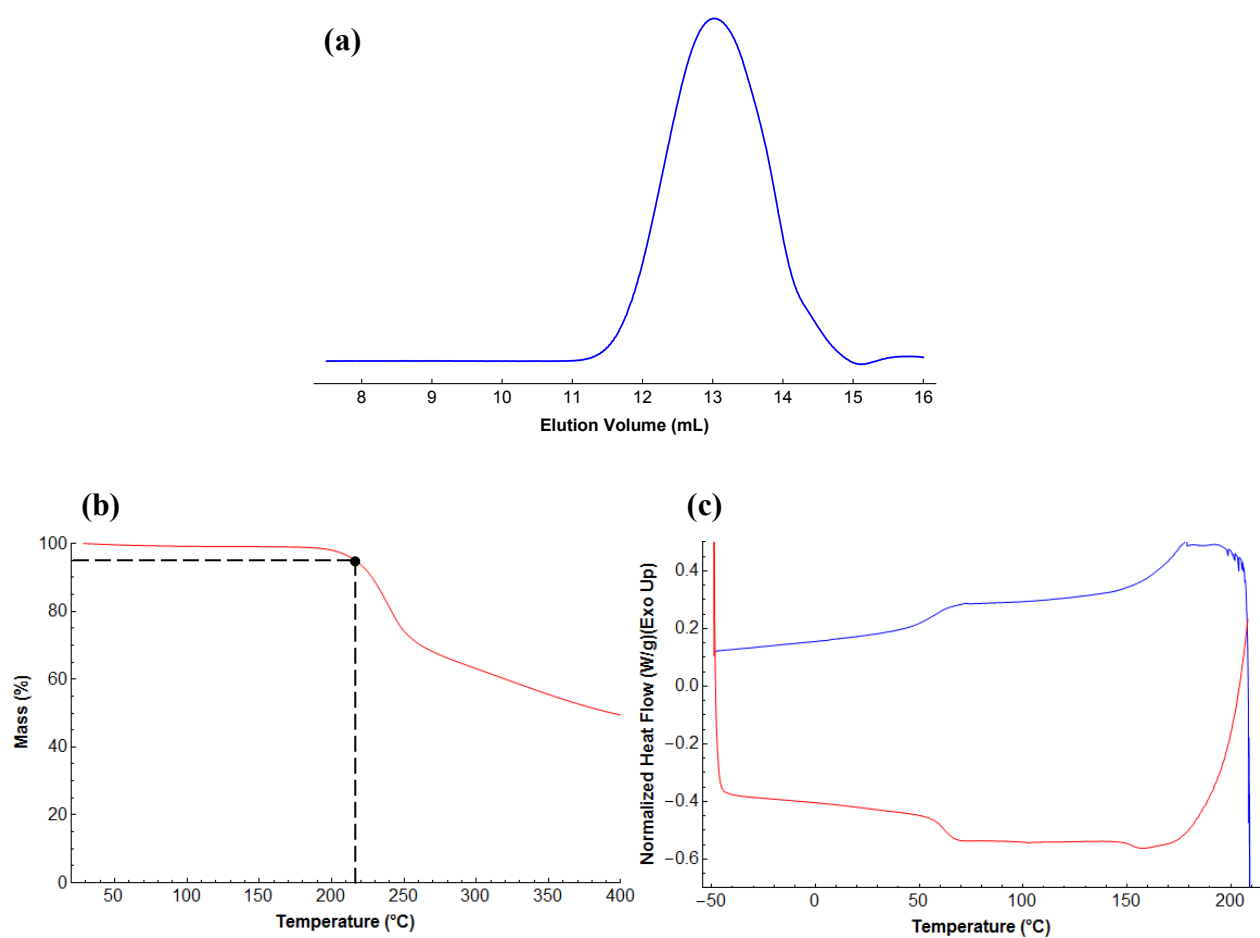


Figure S21:

Characterization of Polysulfamide 3o

(a) SEC trace; (b) TGA curve; (c) DSC curve.



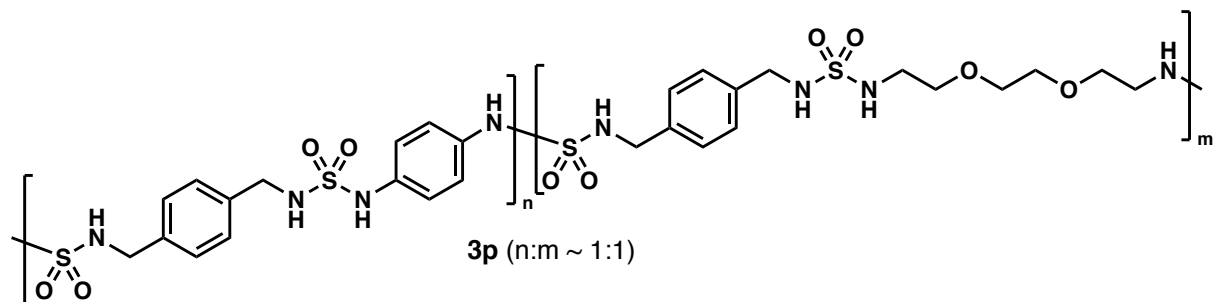
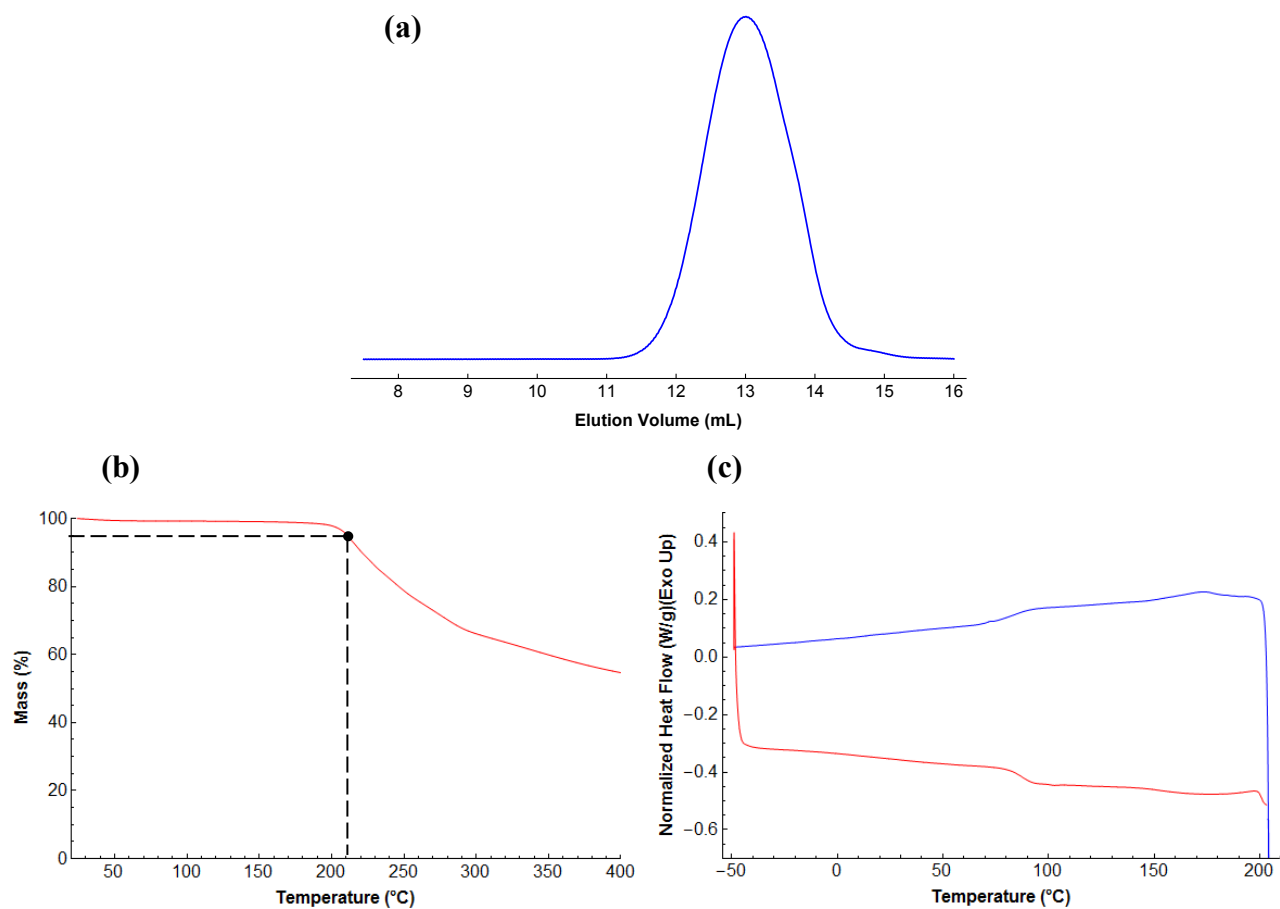
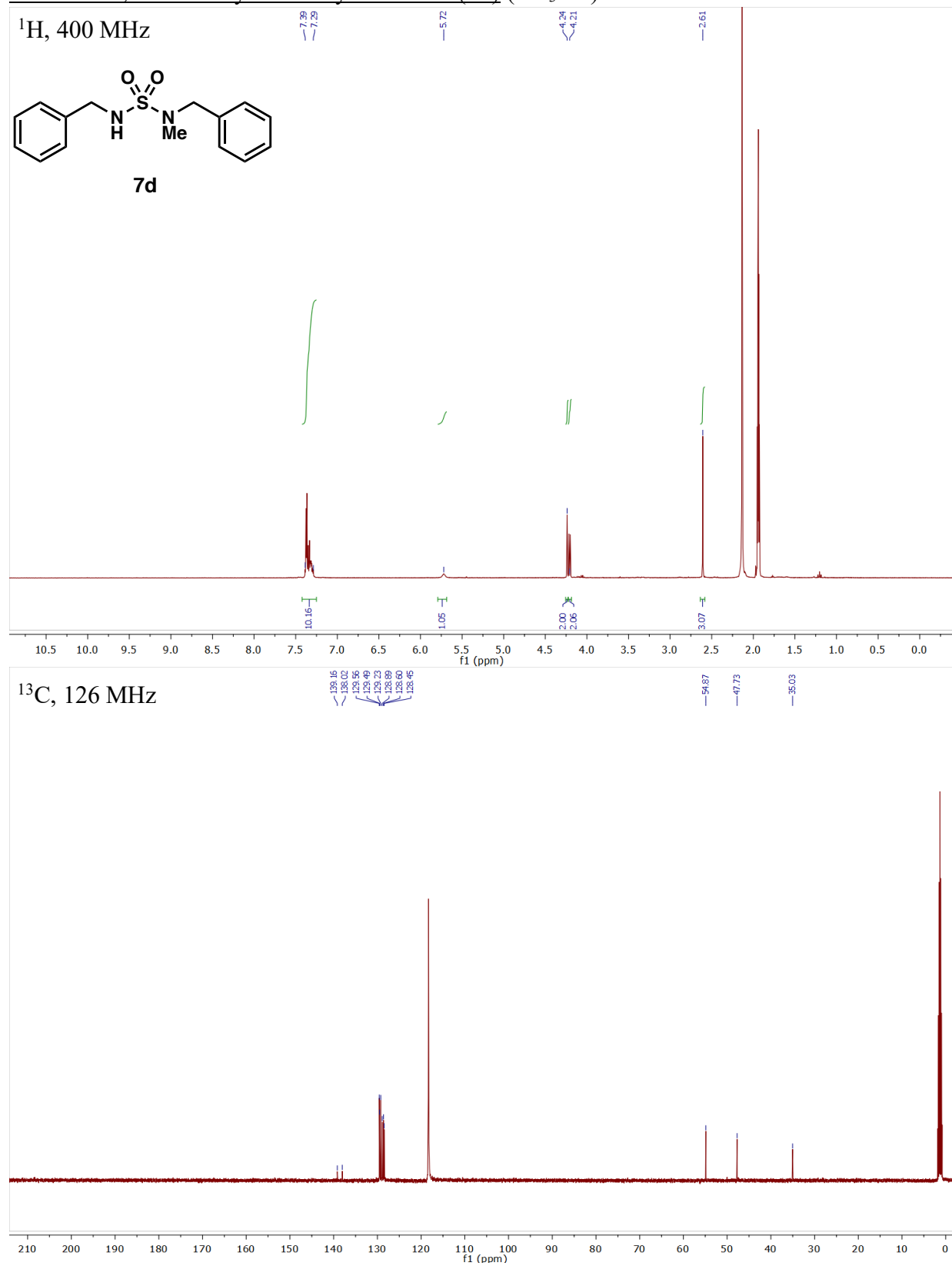


Figure S22:
Characterization of Polysulfamide 3p
 (a) SEC trace; (b) TGA curve; (c) DSC curve.

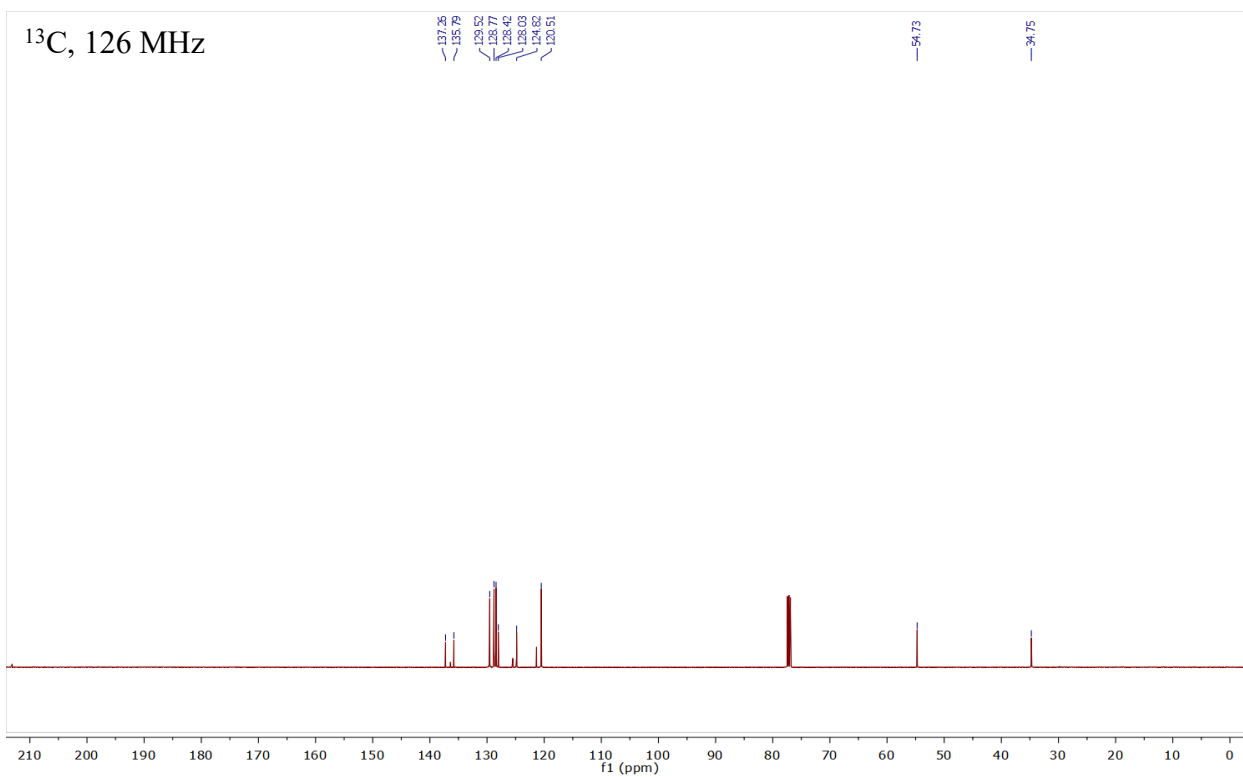
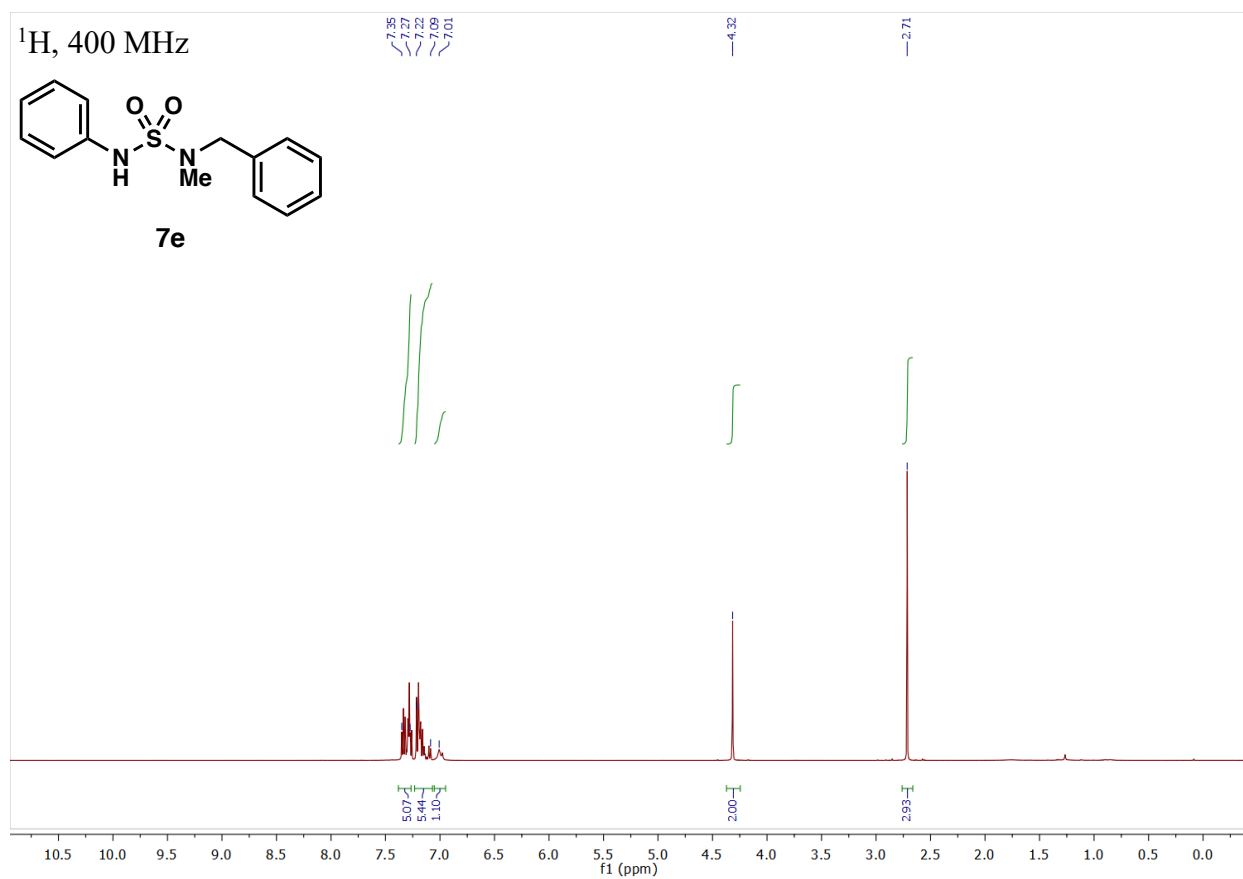


NMR Spectra of Synthesized Sulfamoyl Fluorides, Sulfamides, and Polysulfamides

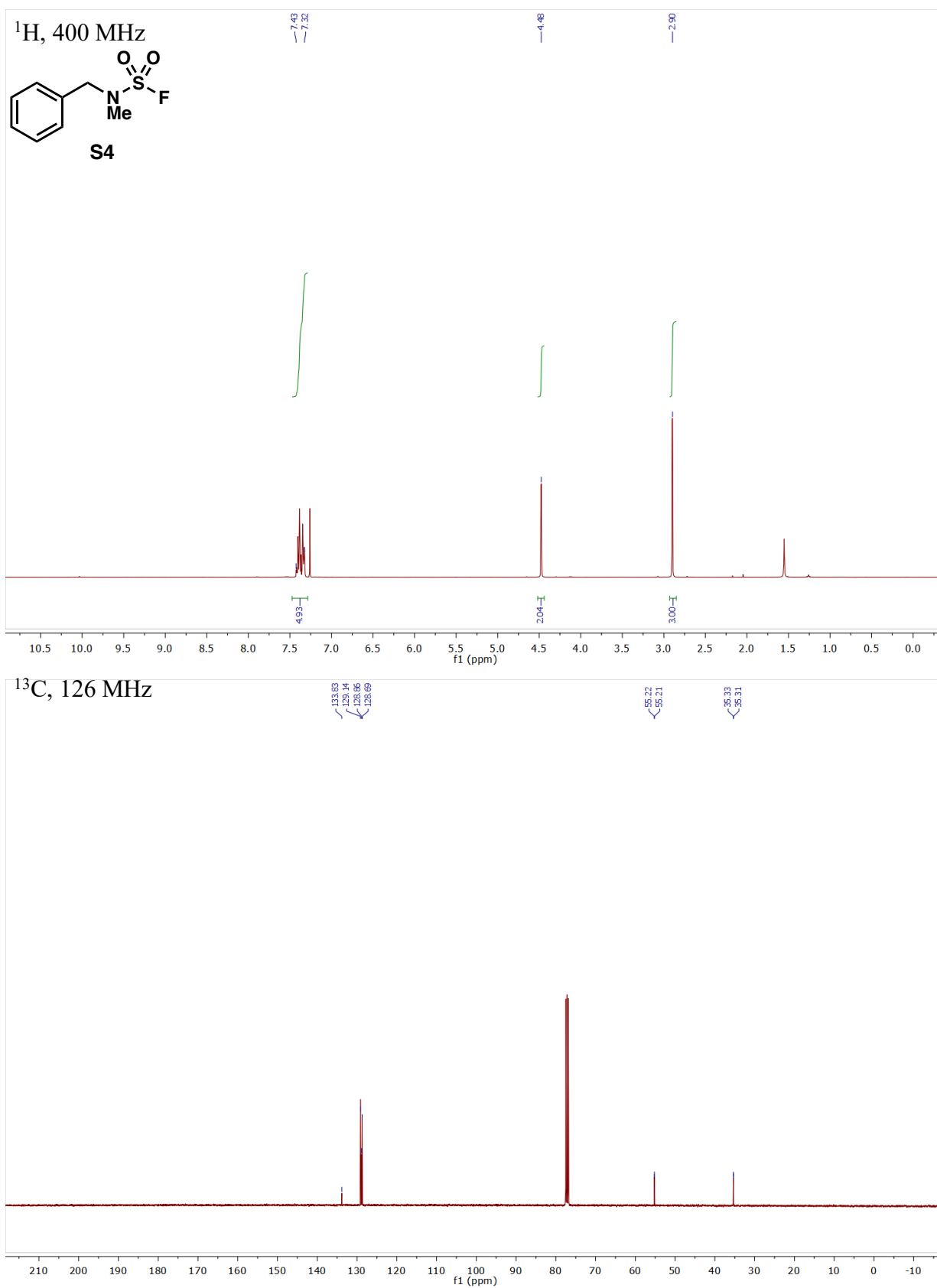
NMRs of *N,N'*-Dibenzyl-*N*-methylsulfamide (**7d**) (CD₃CN)



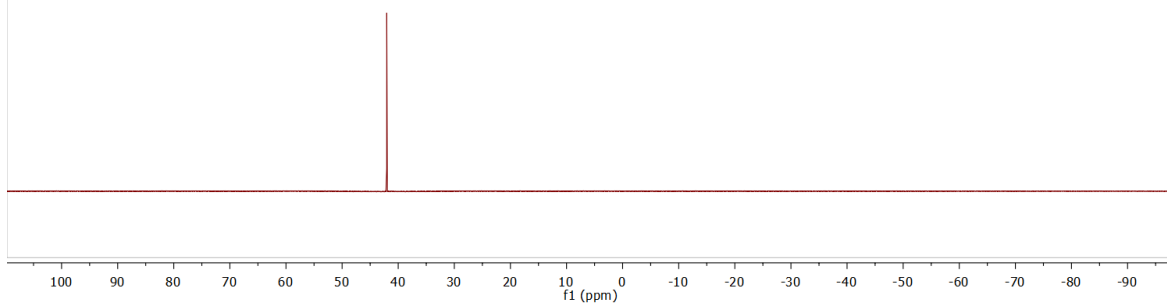
NMRs of *N*-Benzyl-*N*-methyl-*N'*-phenylsulfamide (**7e**) (CDCl₃)



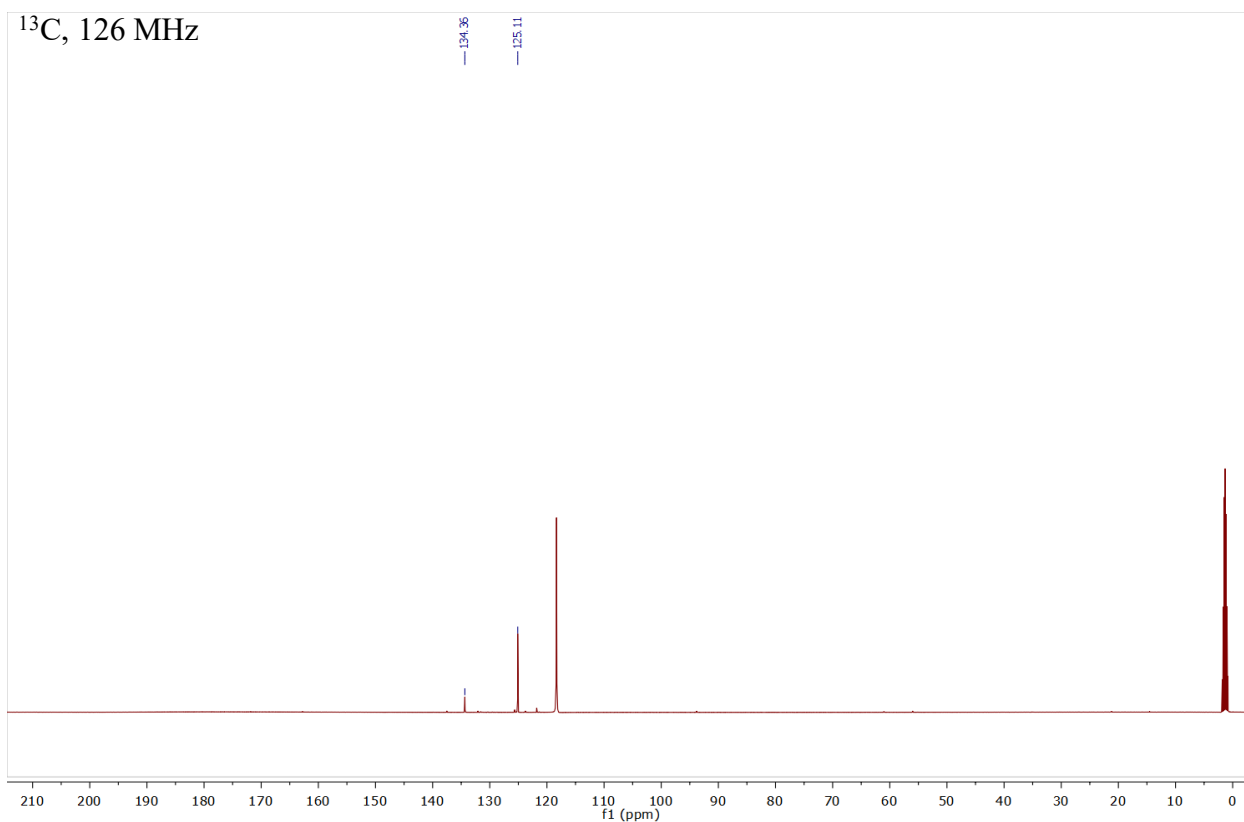
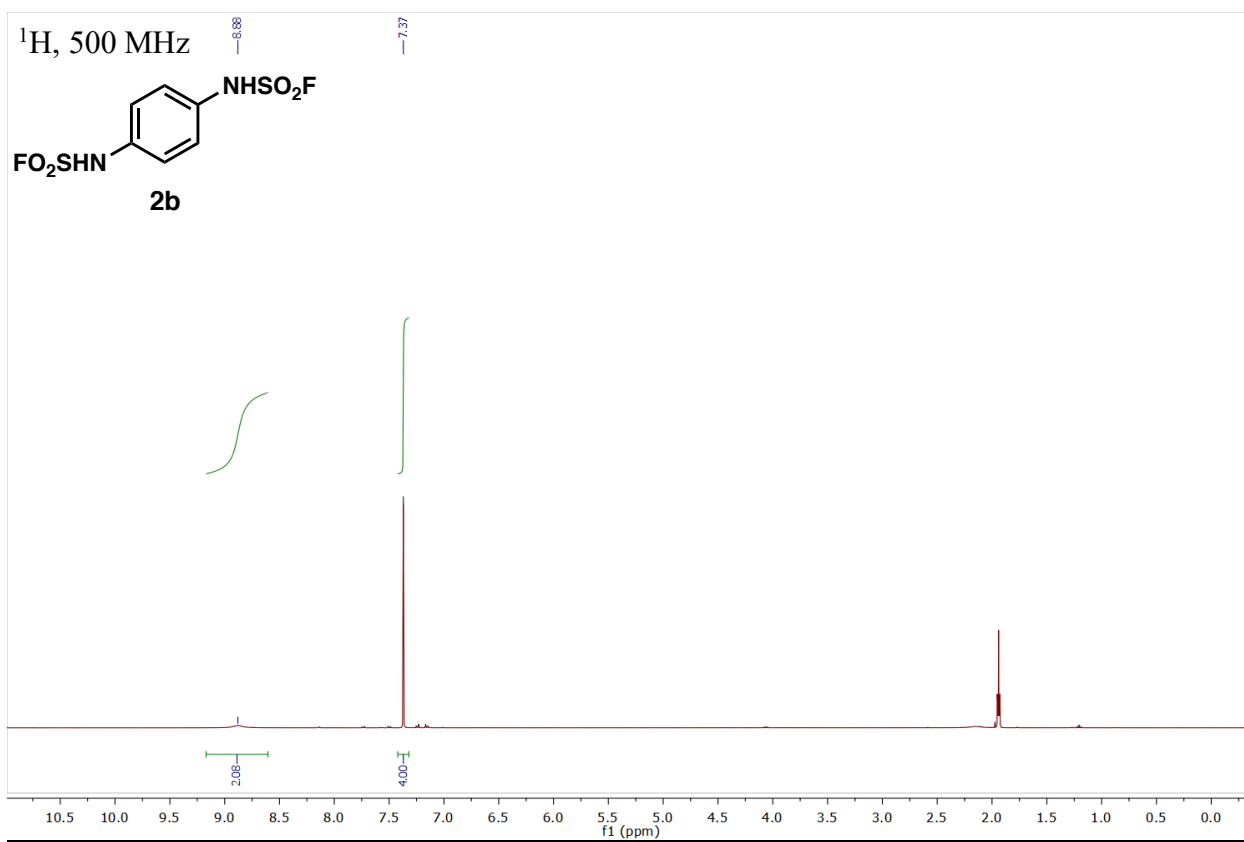
NMRs of *N*-Methylbenzylsulfamoyl Fluoride (**S4**) (CDCl₃)

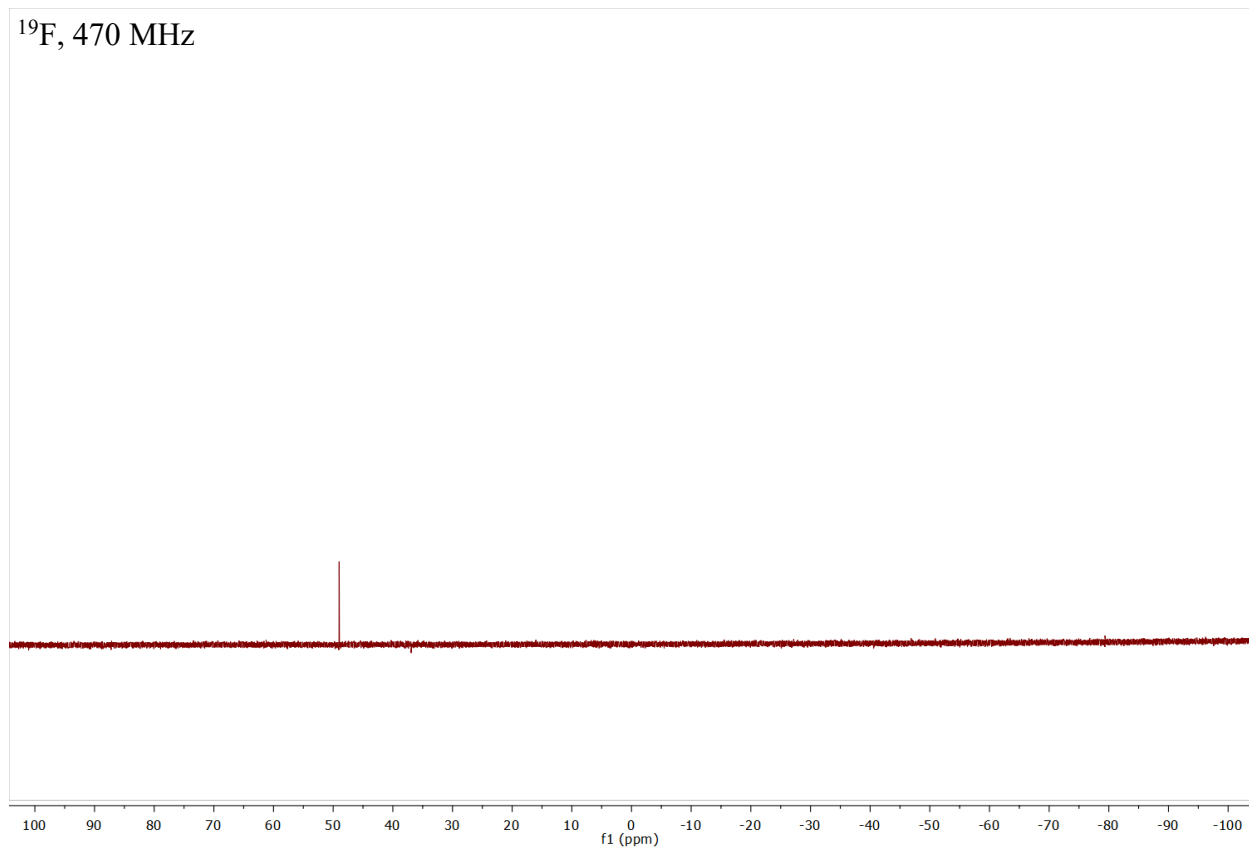


^{19}F , 470 MHz



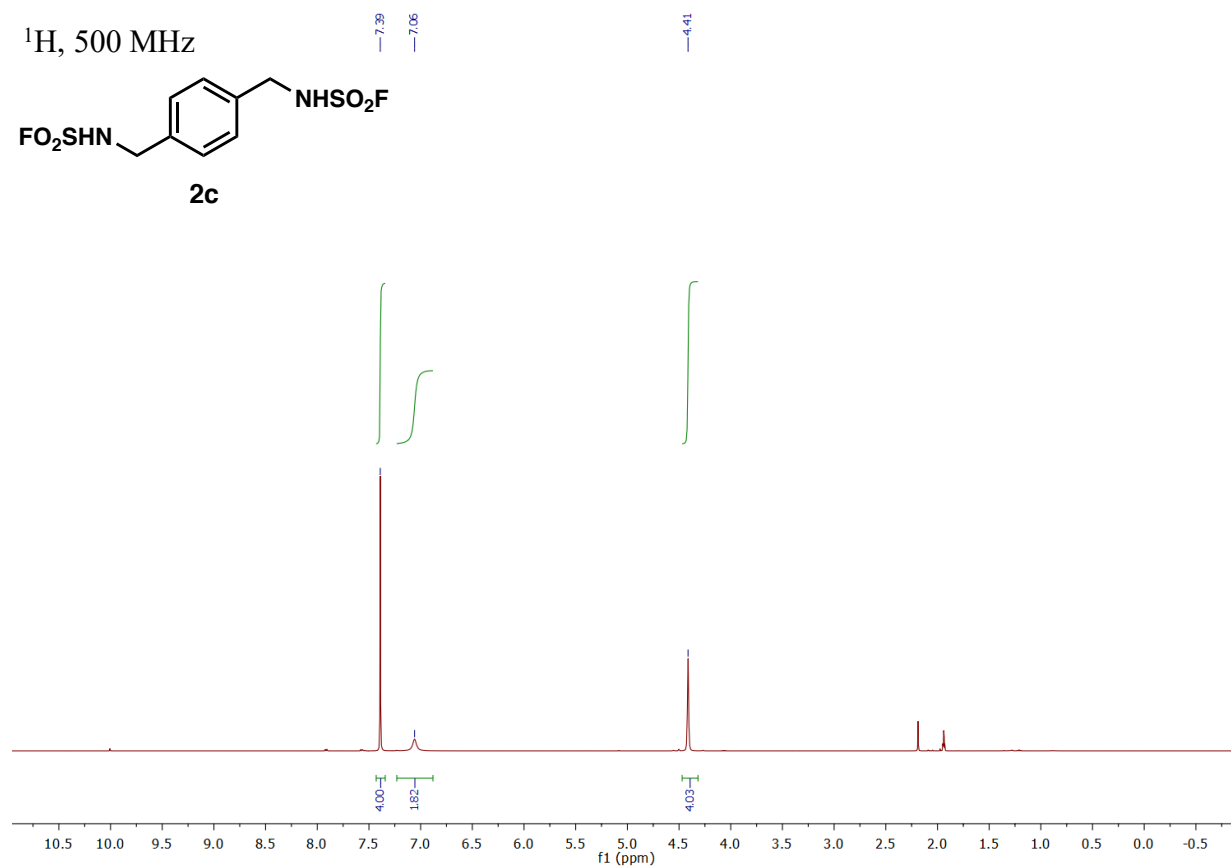
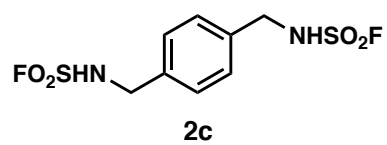
NMRs of 1,4-Phenylenebis(sulfamoyl fluoride) (**2b**) (CD₃CN)



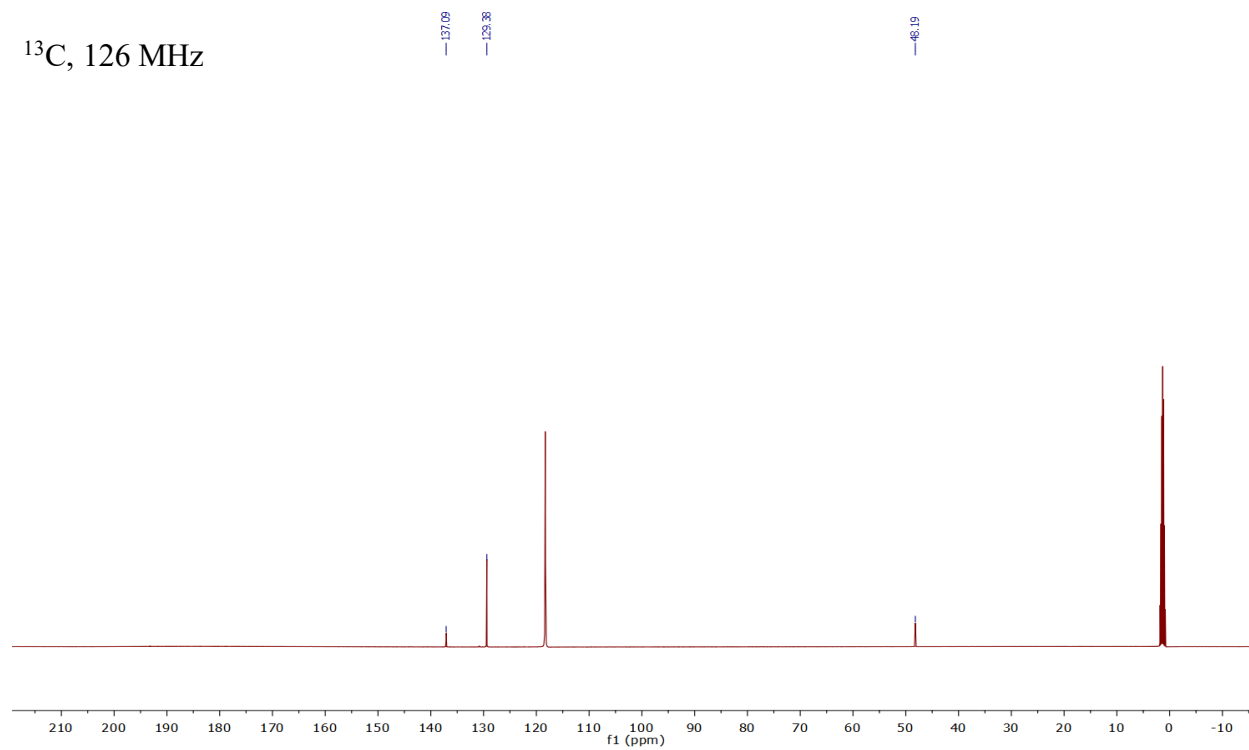


NMRs of (1,4-phenylenebis(methylene))bis(sulfamoyl fluoride) (**2c**) (CD₃CN)

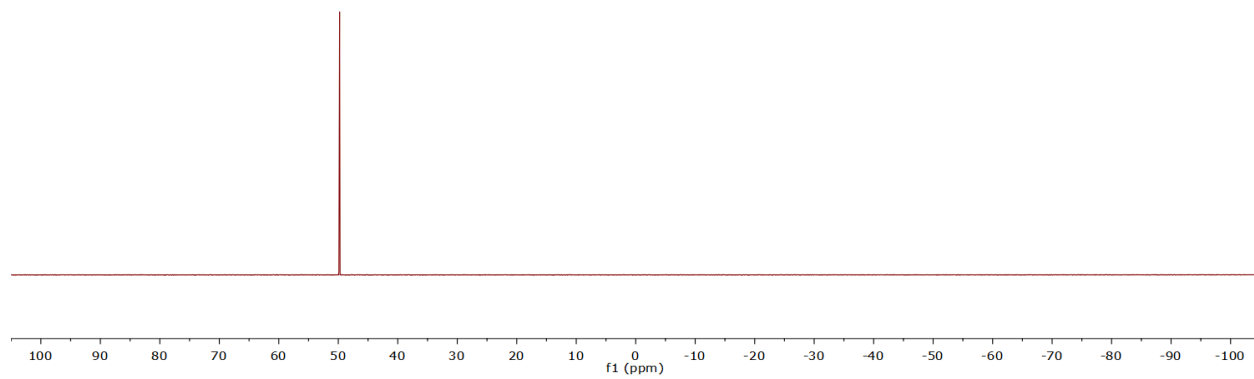
¹H, 500 MHz



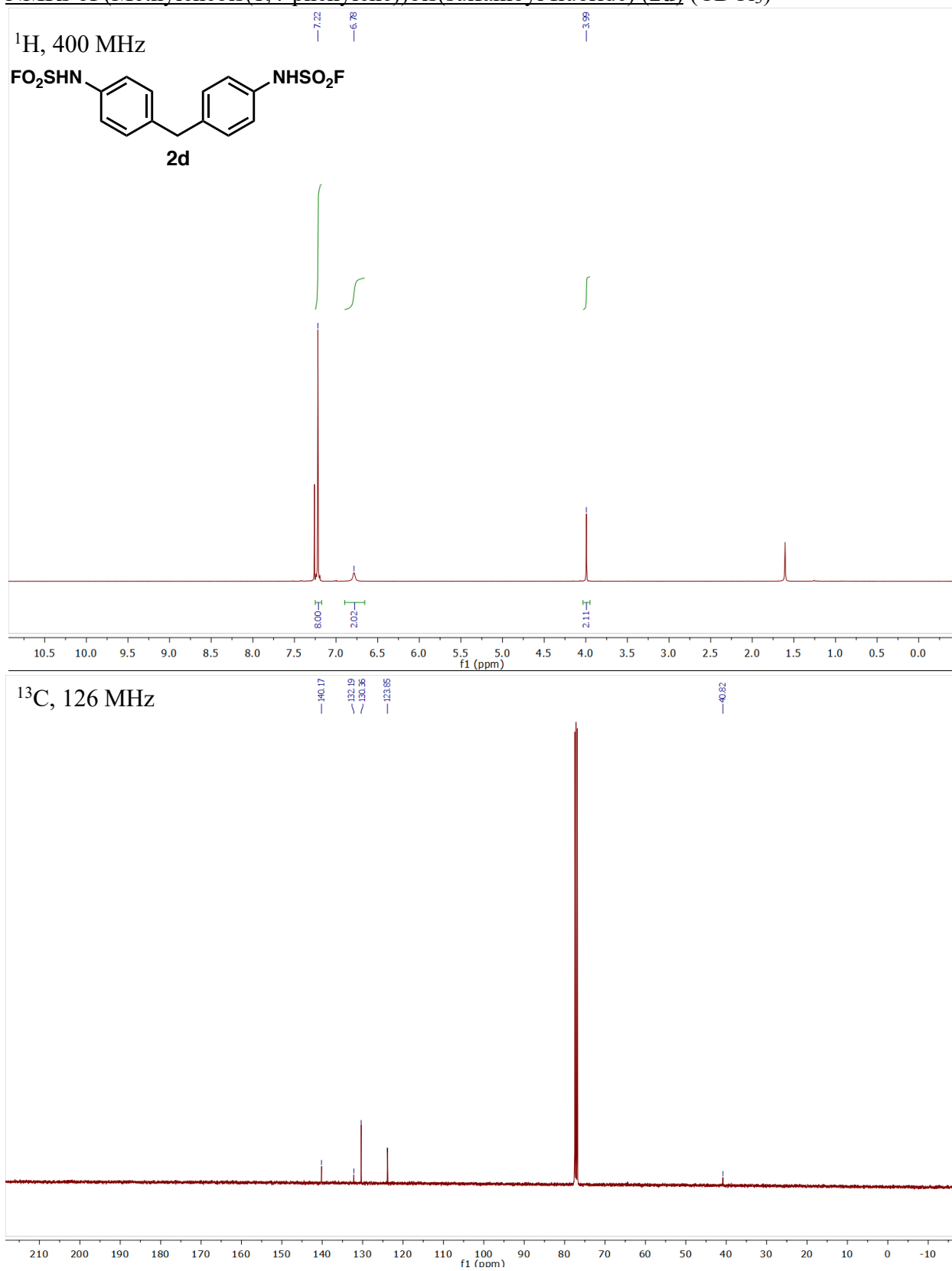
¹³C, 126 MHz



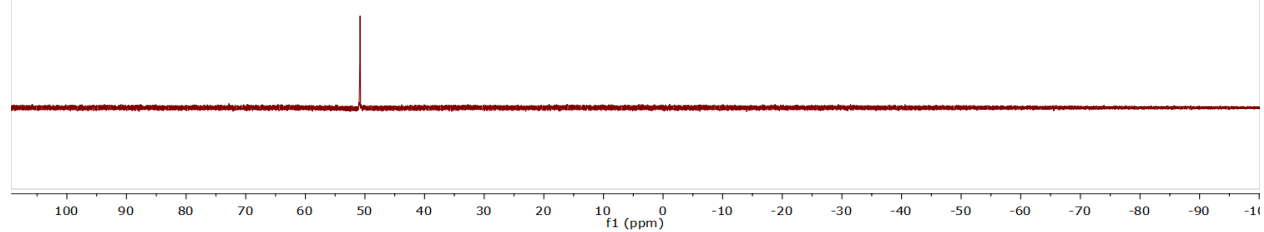
^{19}F , 470 MHz



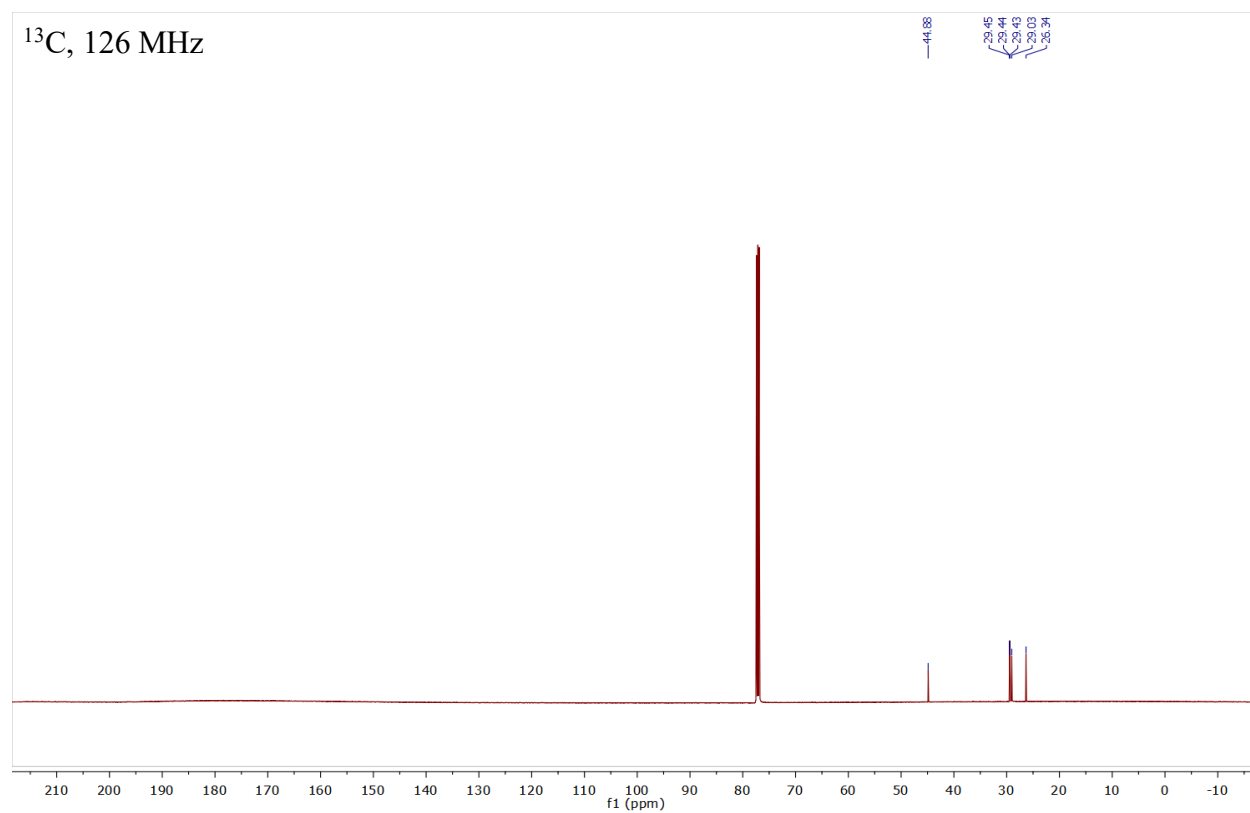
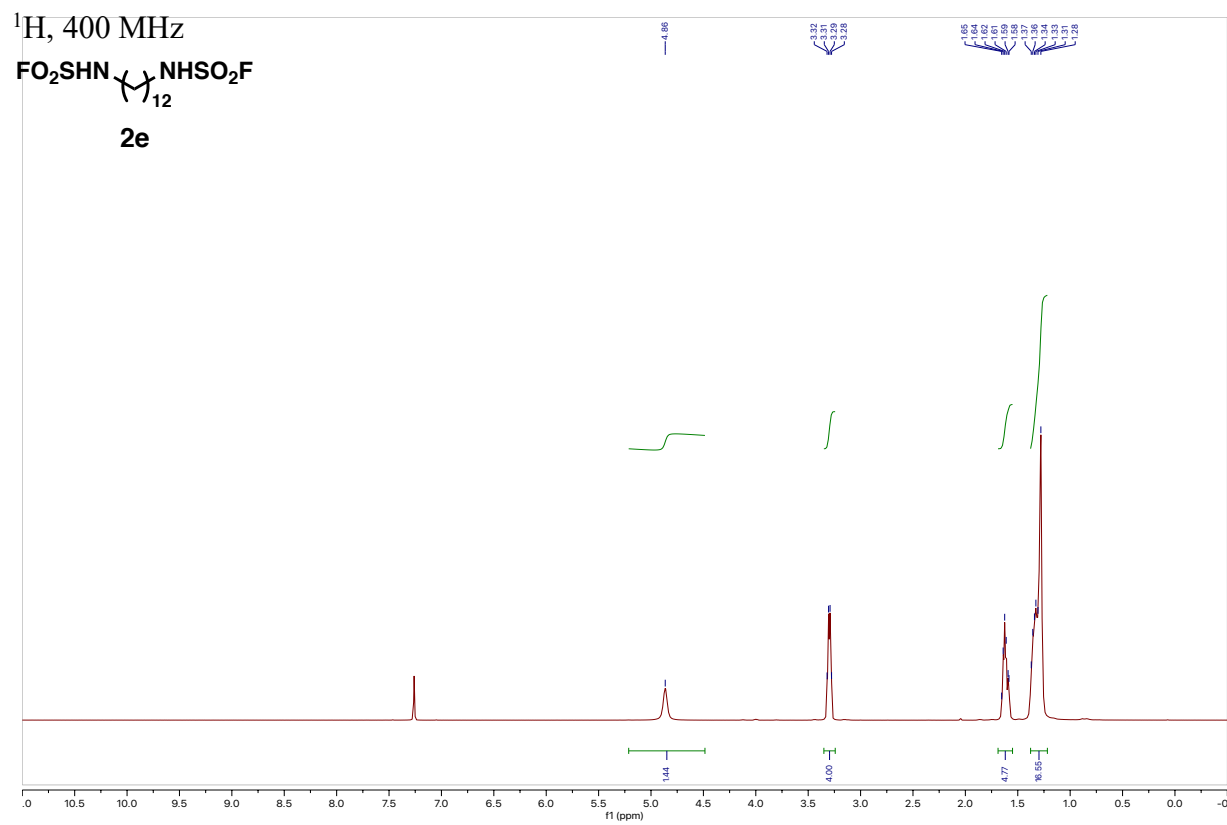
NMRs of (Methylenebis(1,4-phenylene))bis(sulfamoyl fluoride) (**2d**) (CDCl₃)

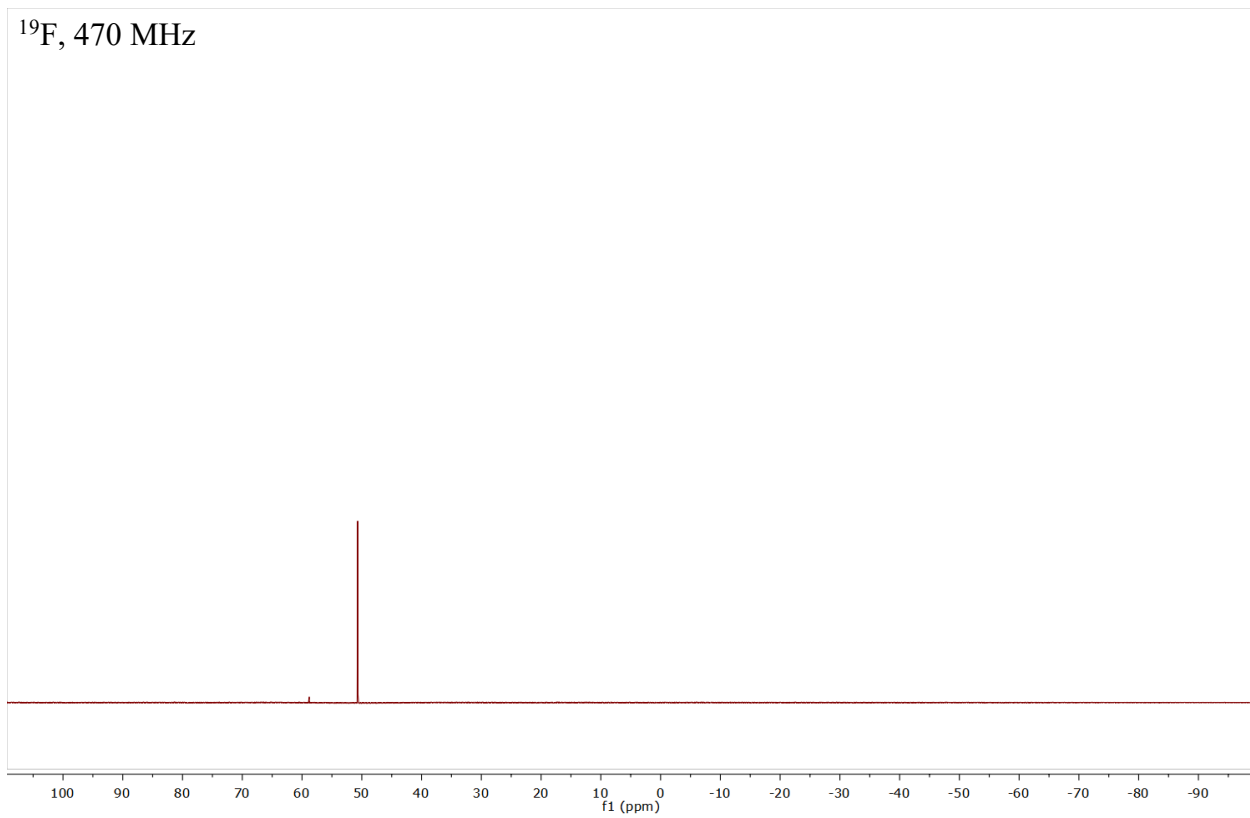


^{19}F , 470 MHz

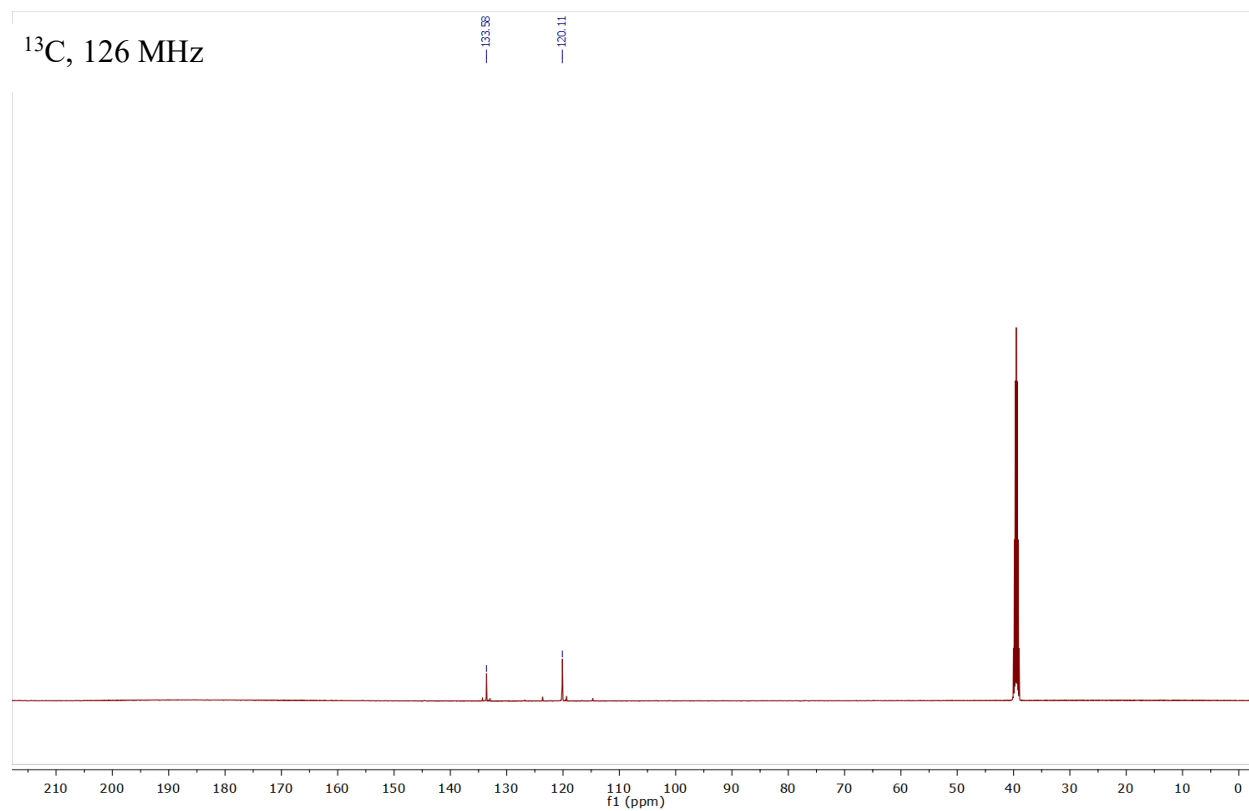
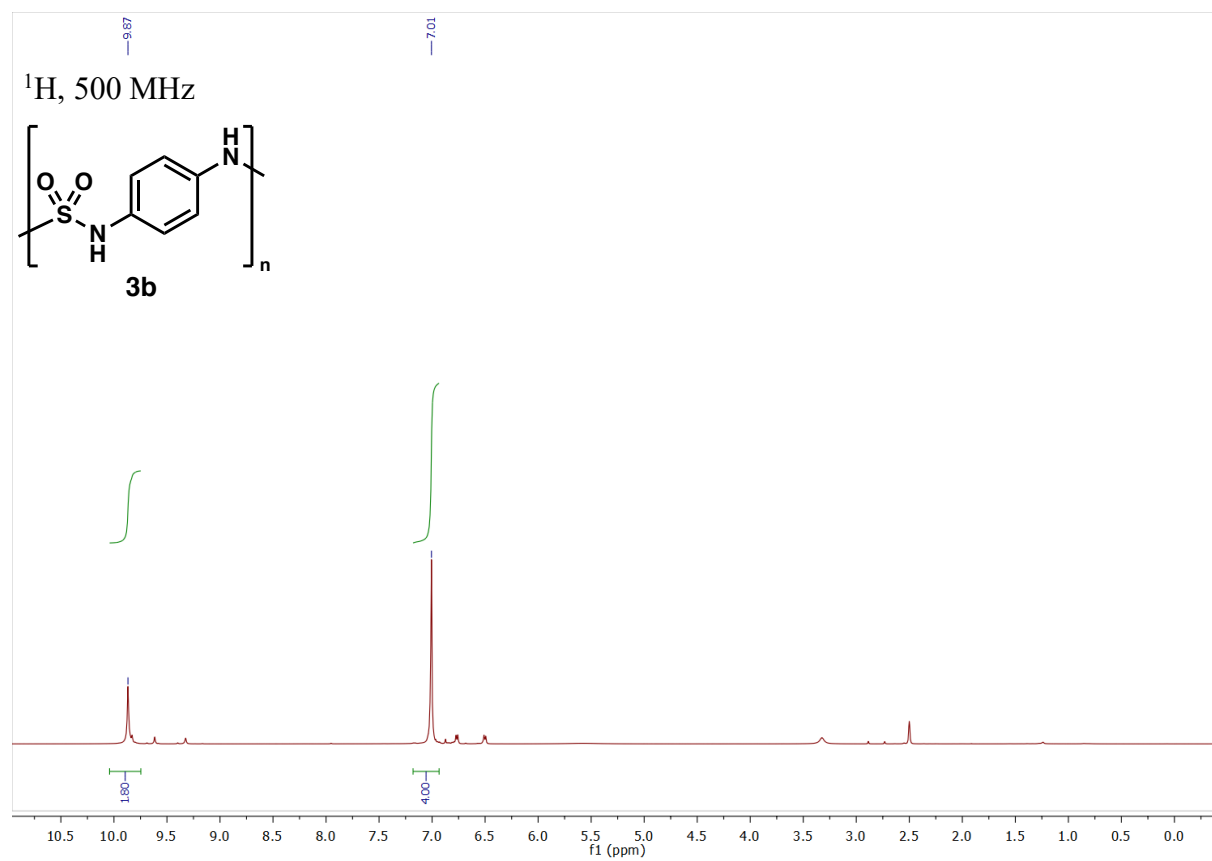


NMR of Dodecane-1,12-bis(sulfamoyl fluoride) (**2e**) (CDCl₃)

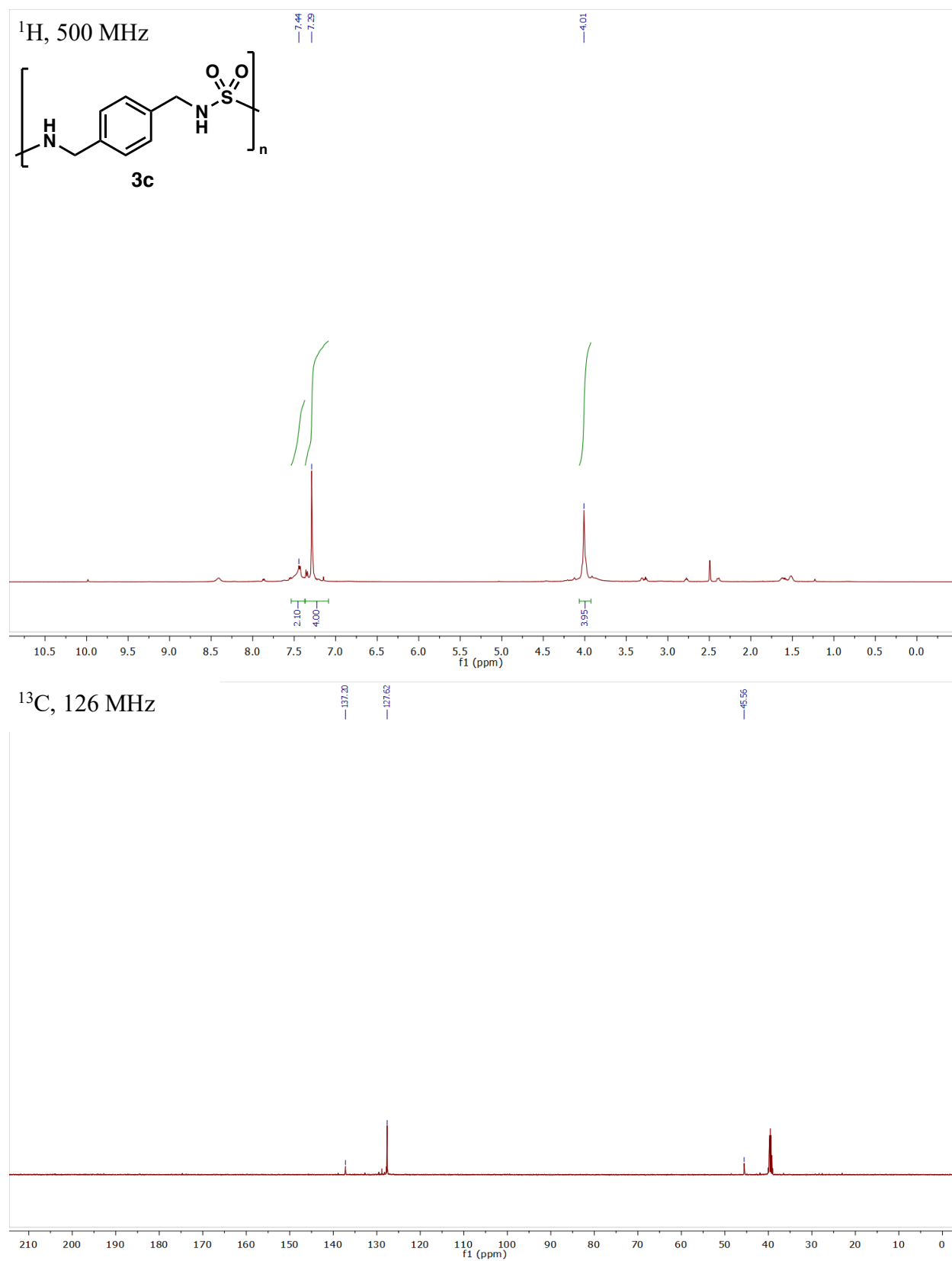




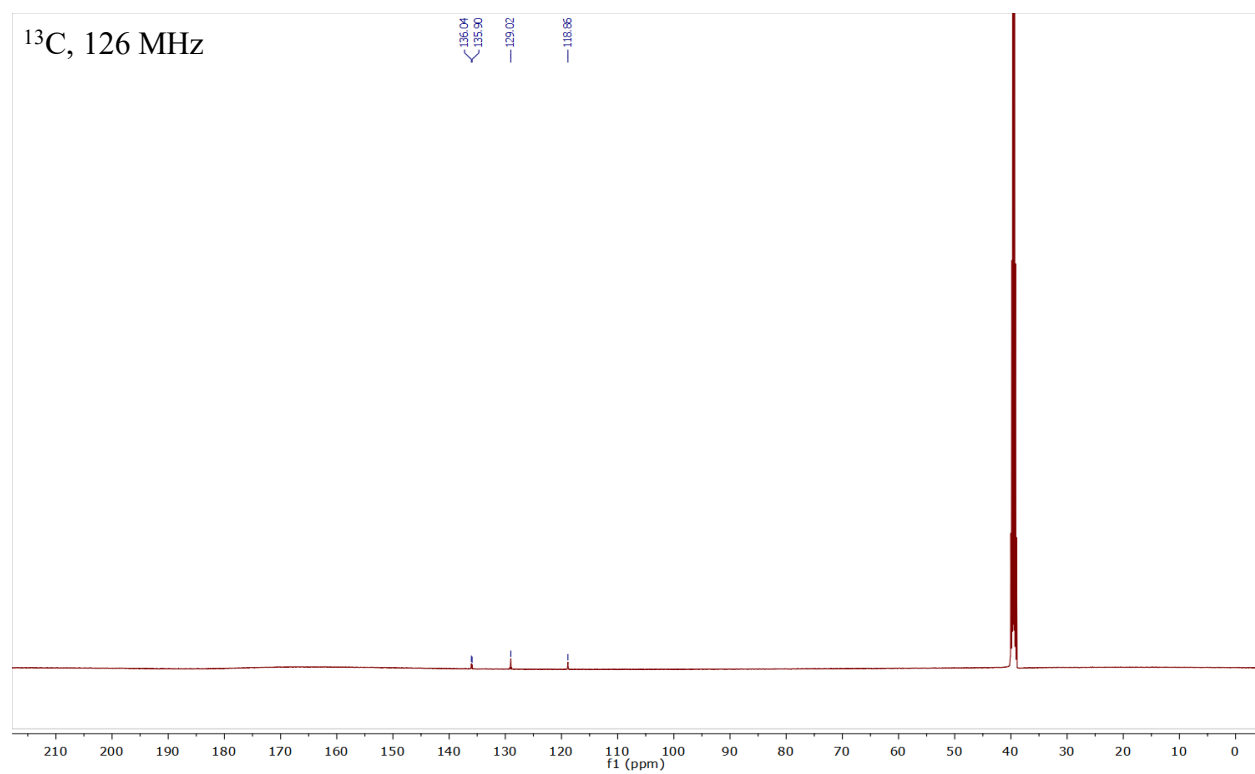
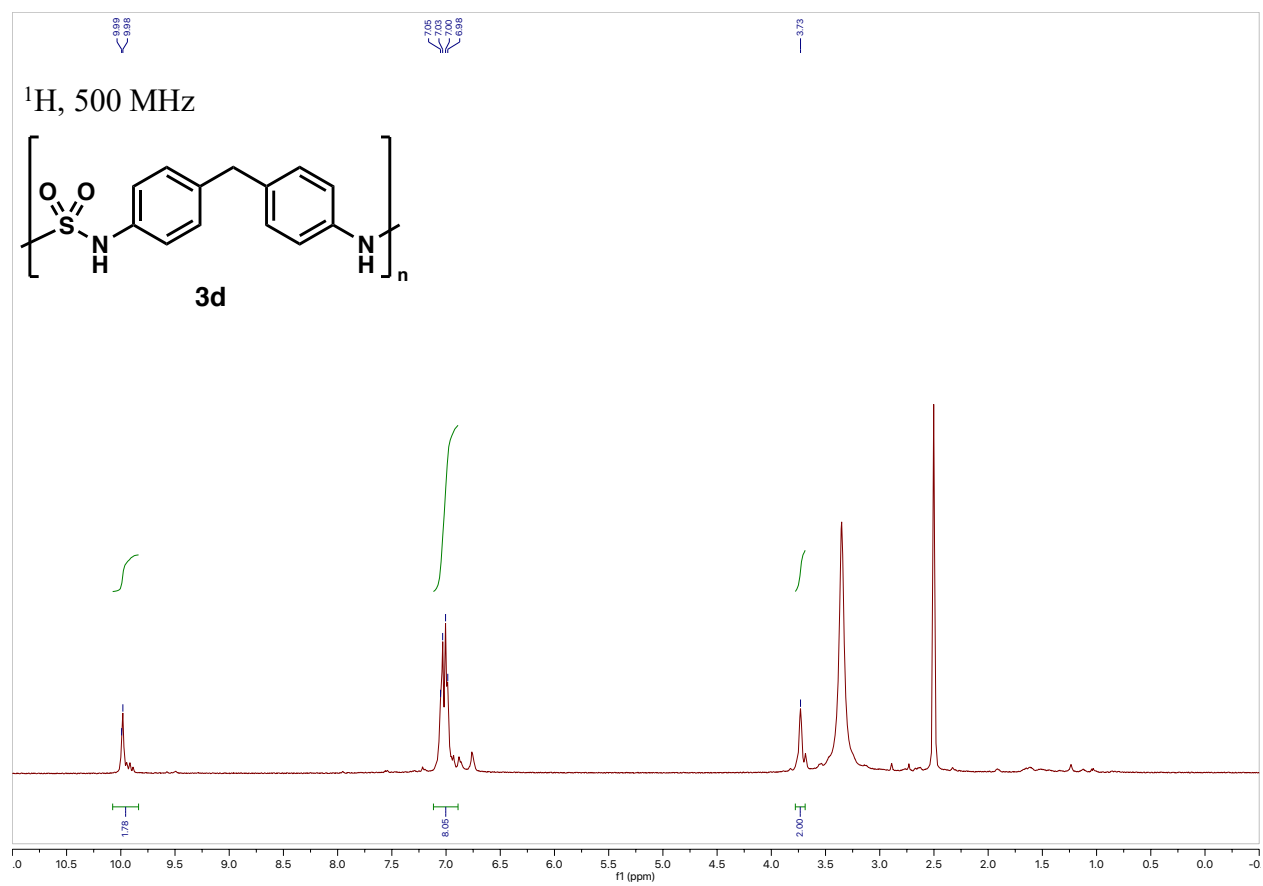
NMRs of polysulfamide **3b** (d_6 -DMSO)



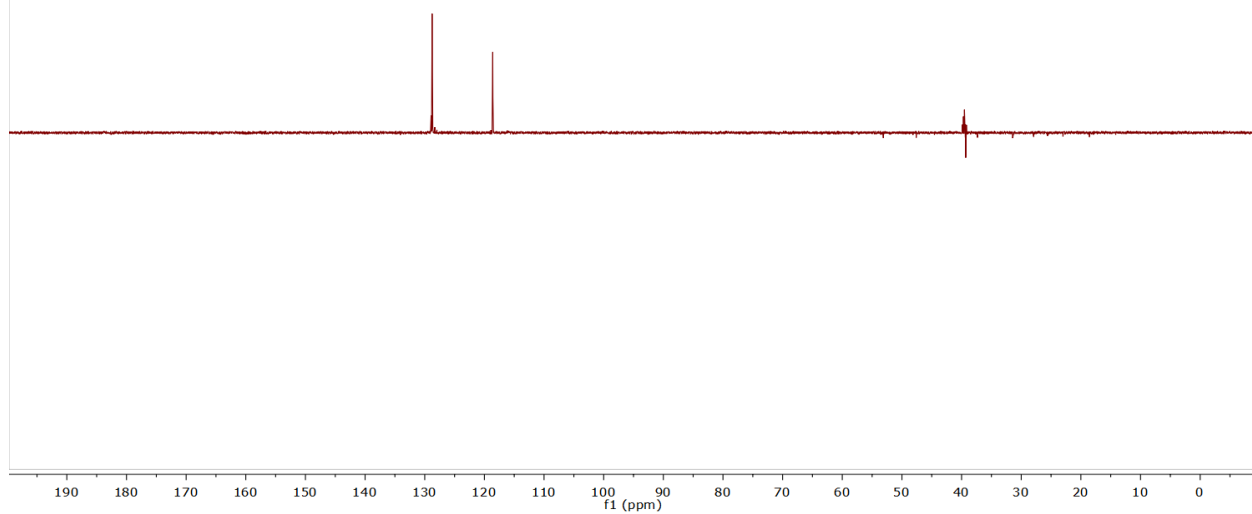
NMRs of polysulfamide **3c** (*d*₆-DMSO)



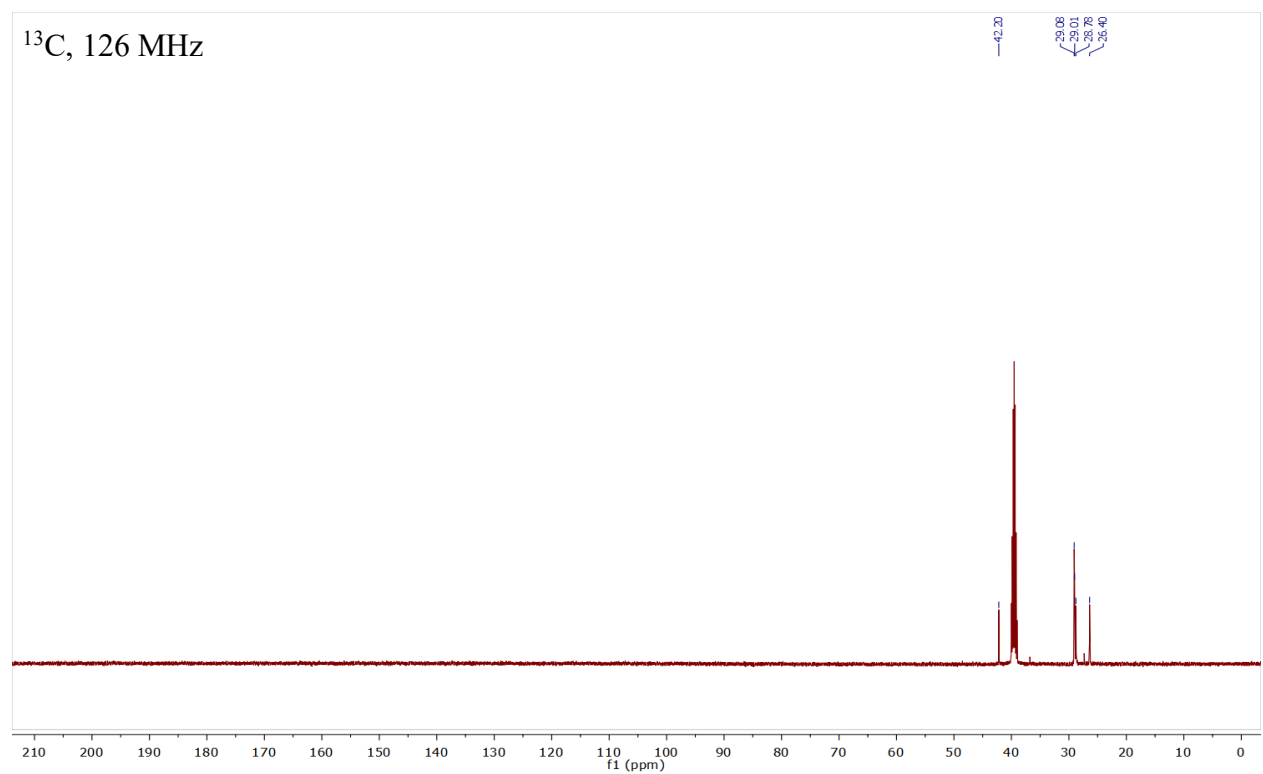
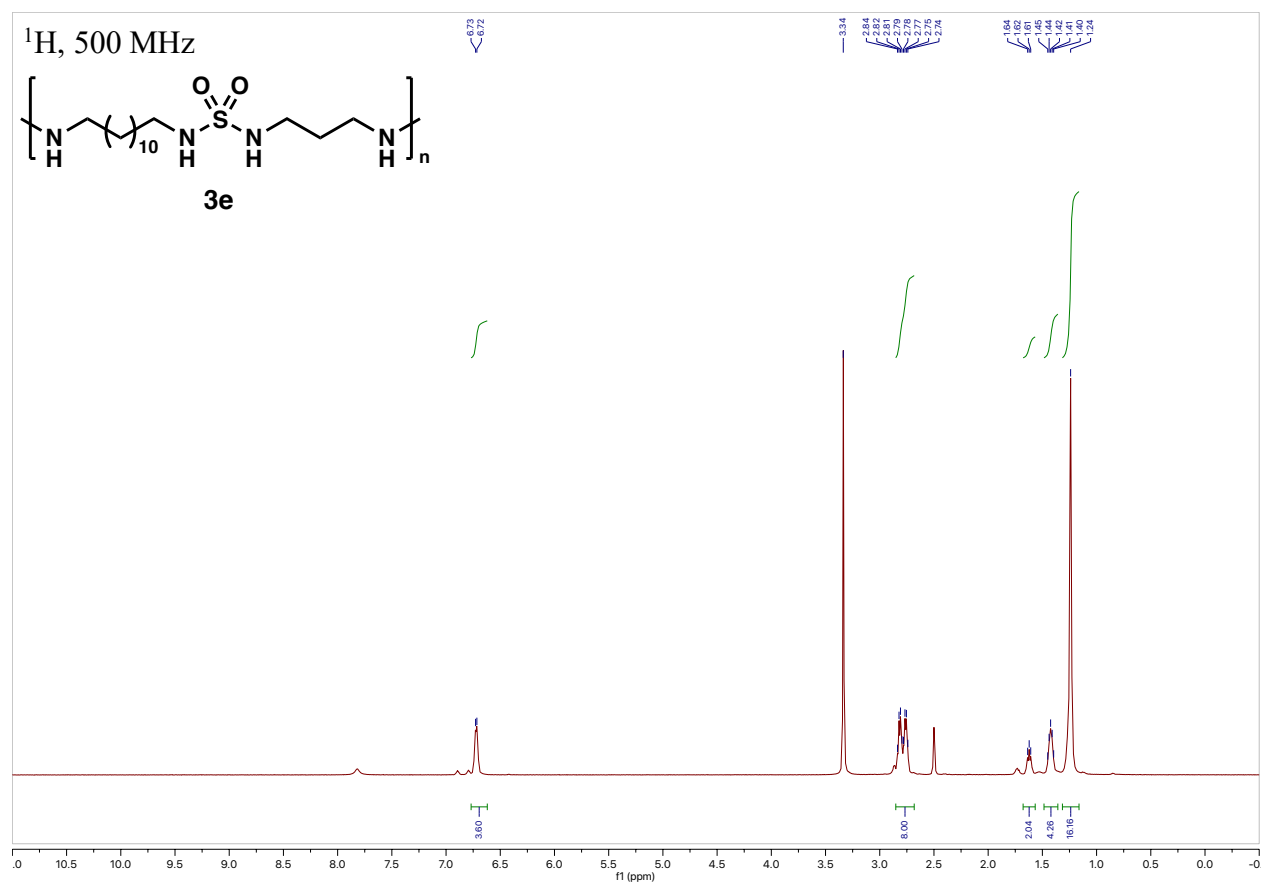
NMRs of polysulfamide **3d** (d_6 -DMSO)



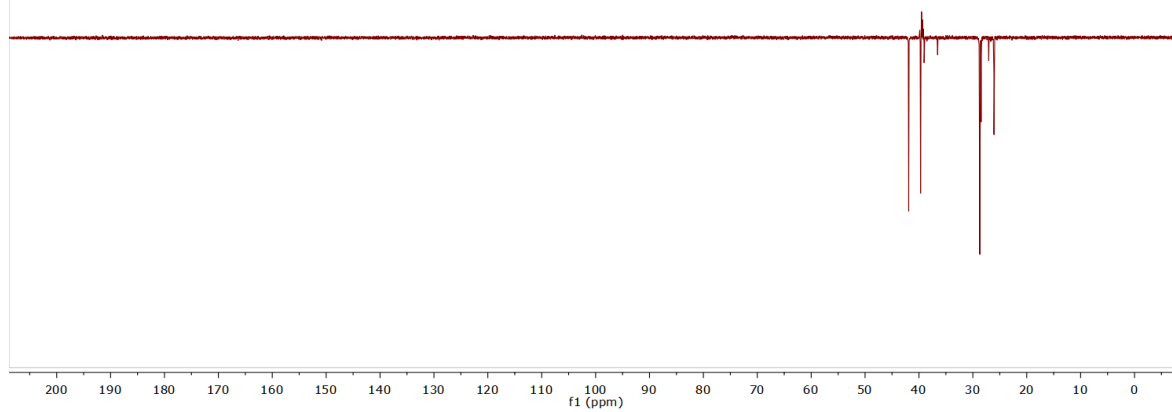
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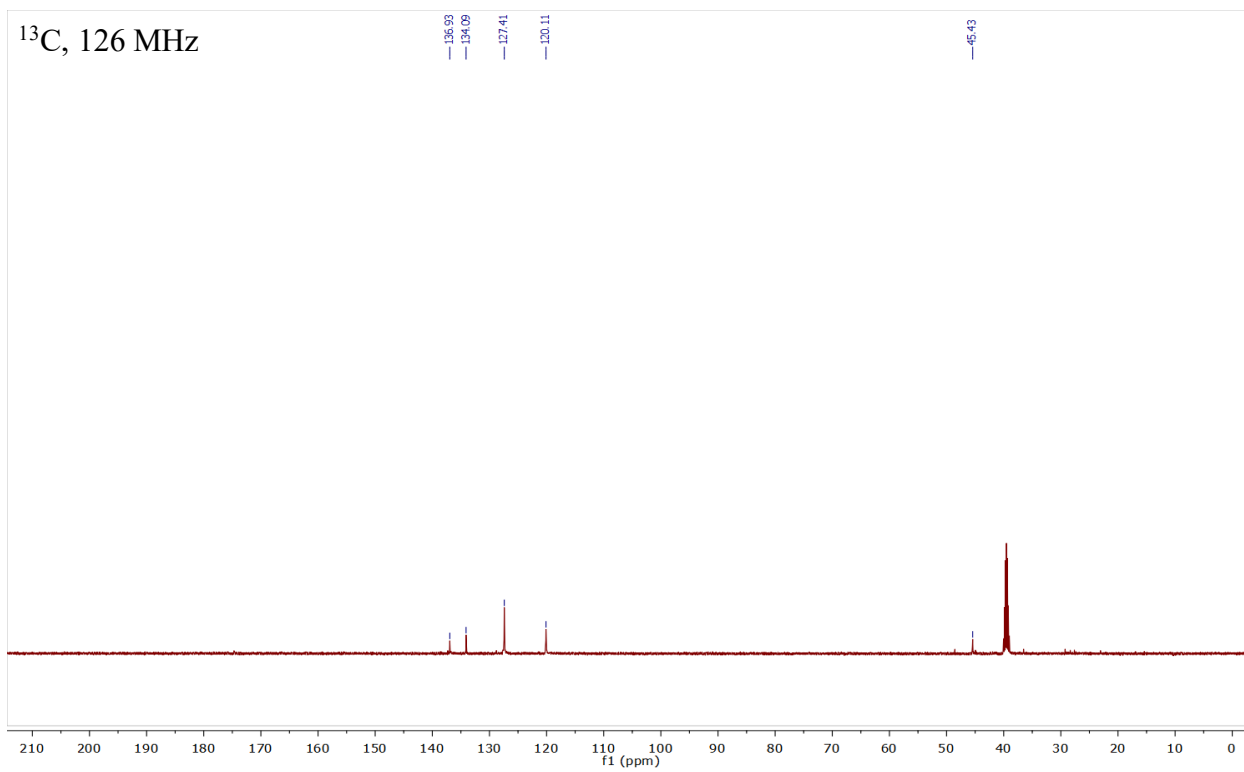
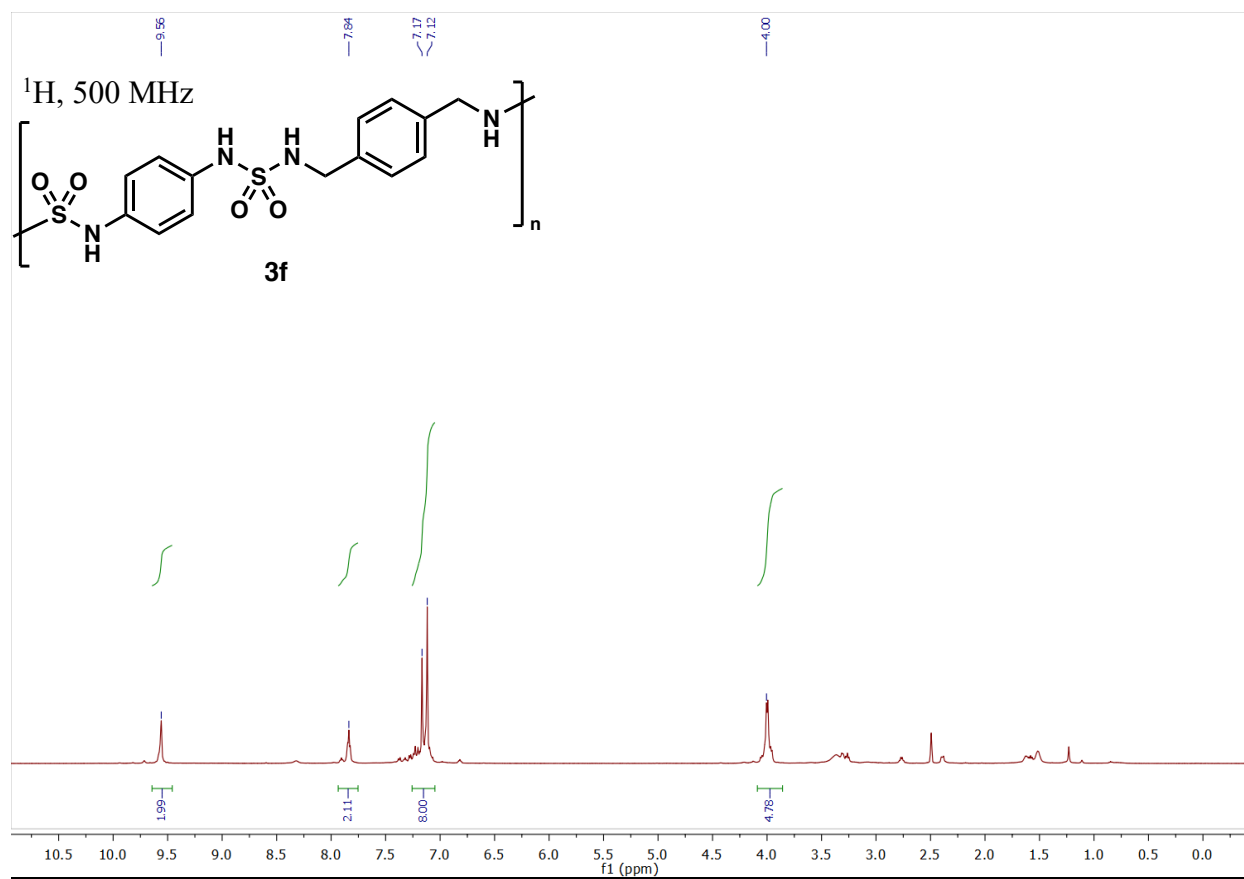
NMRs of polysulfamide **3e** (*d*₆-DMSO)



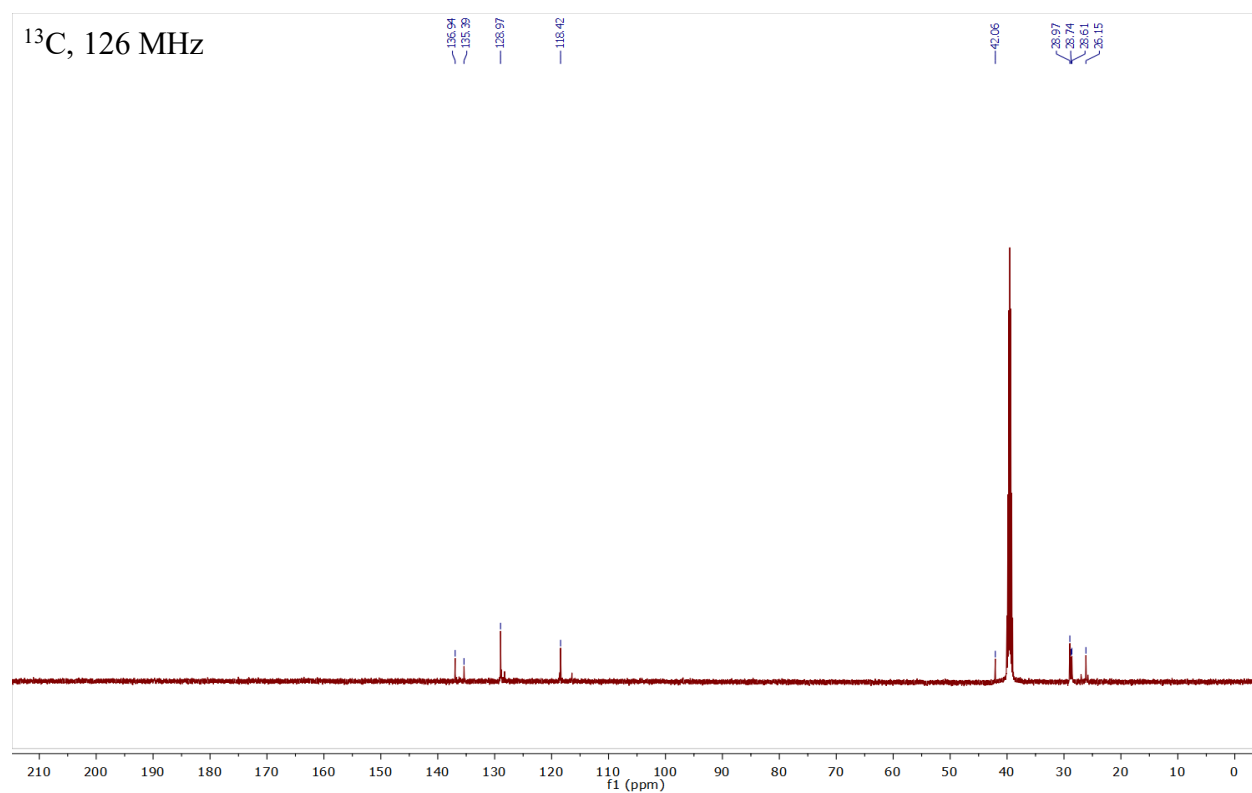
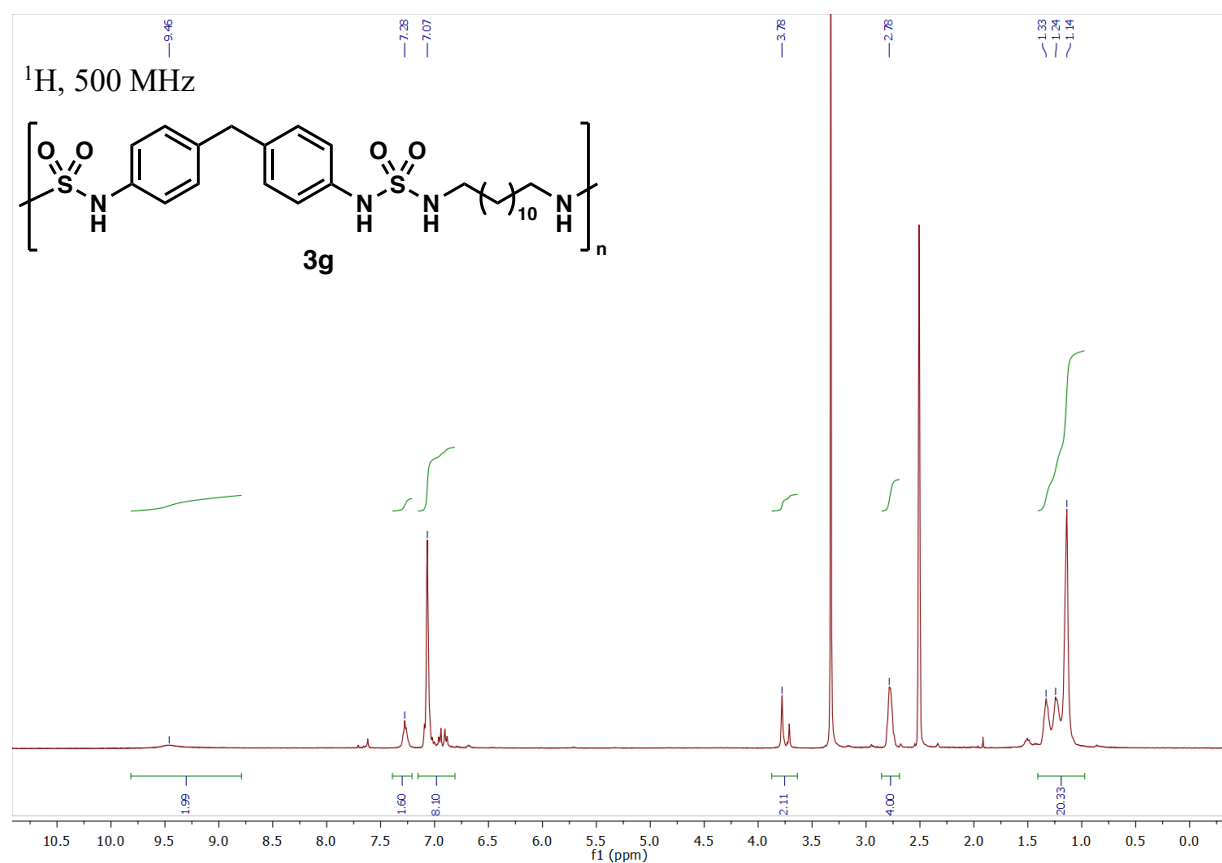
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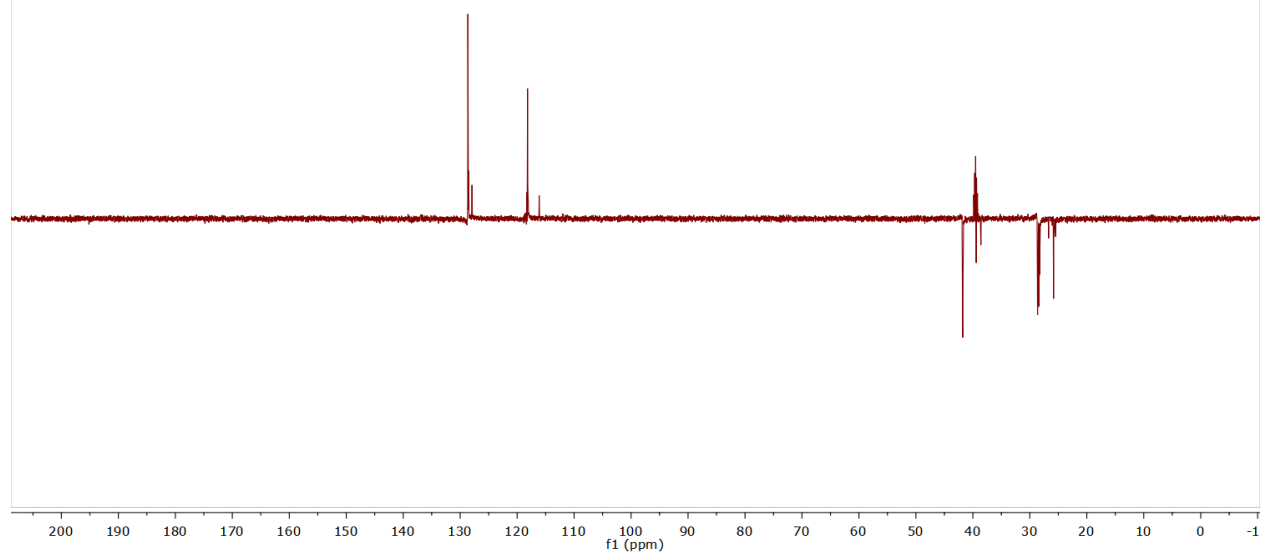
NMRs of polysulfamide **3f** (d_6 -DMSO)



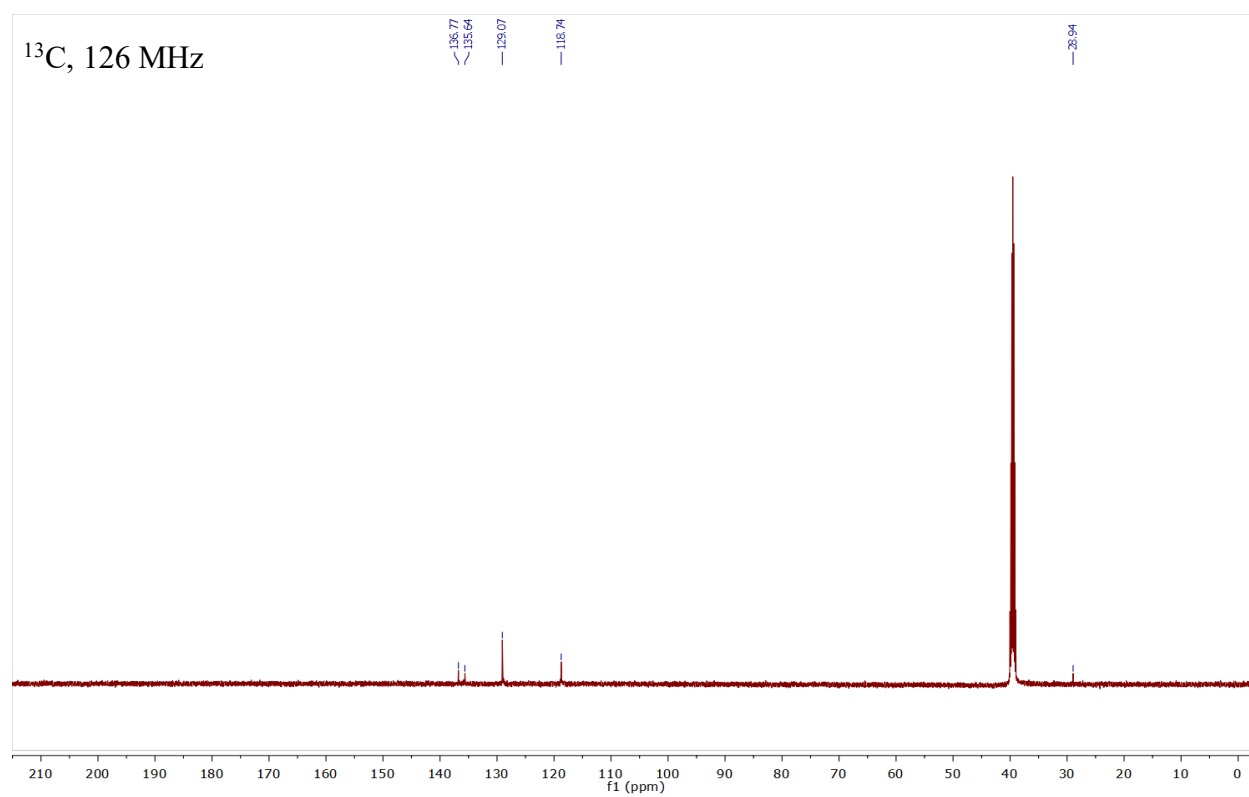
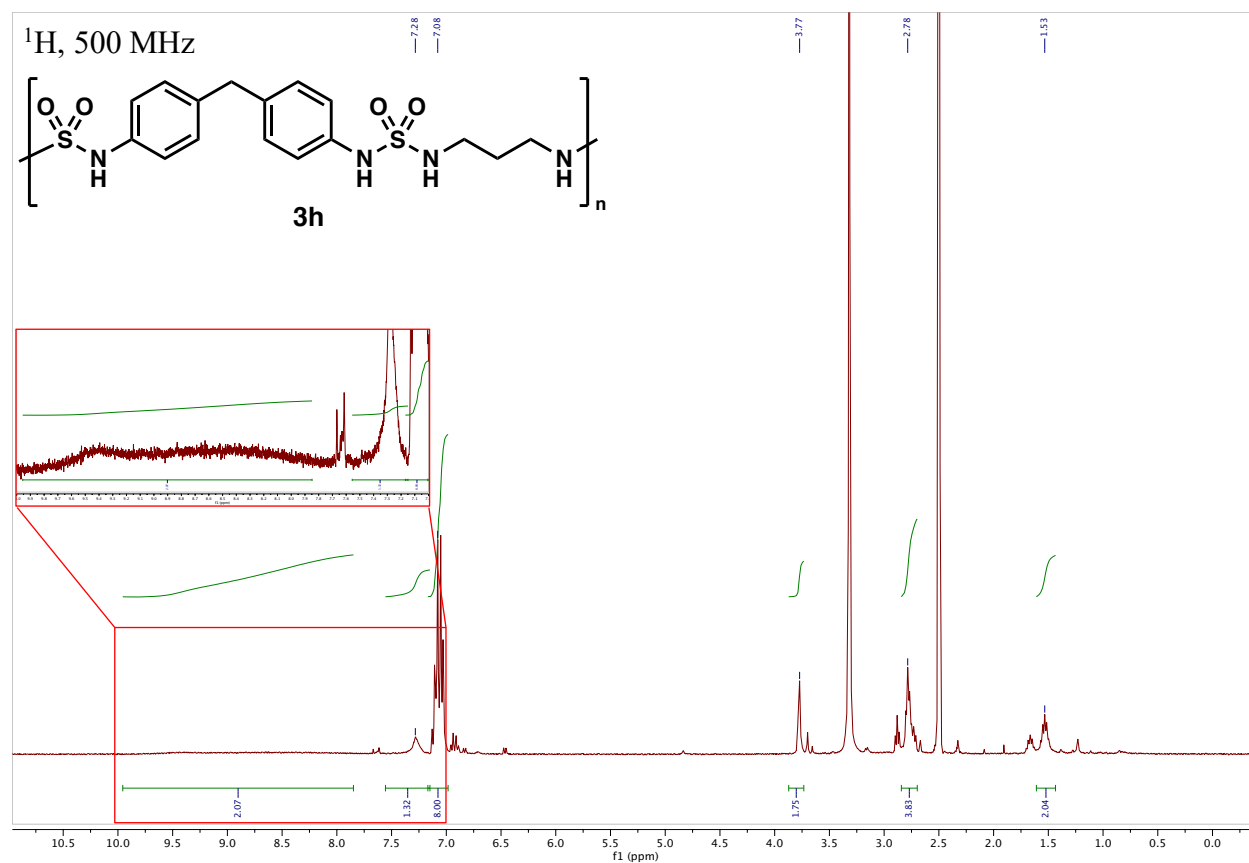
NMRs of polysulfamide **3g** (d_6 -DMSO)



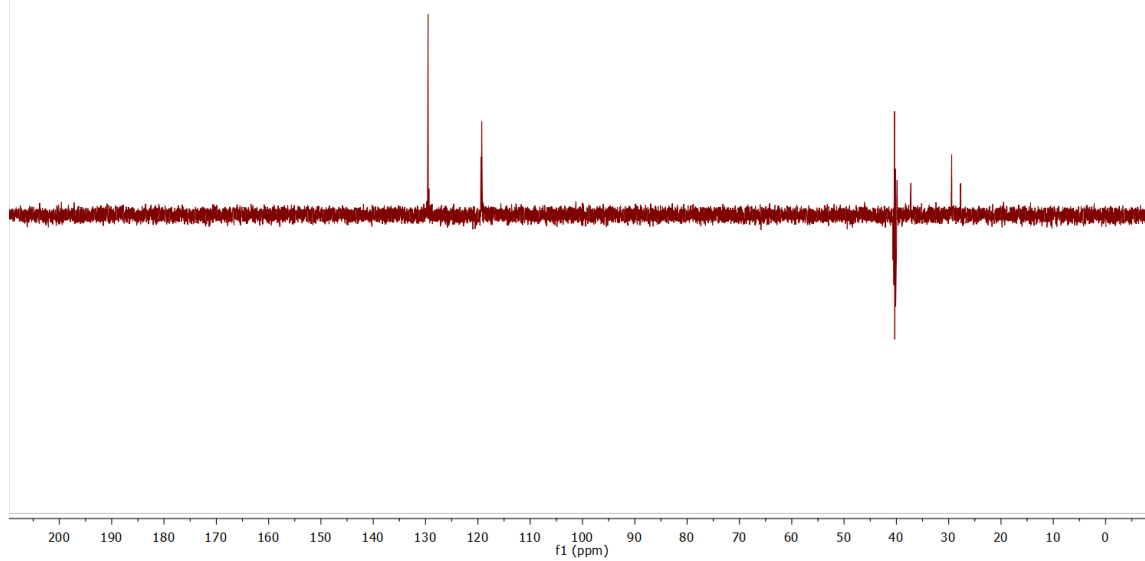
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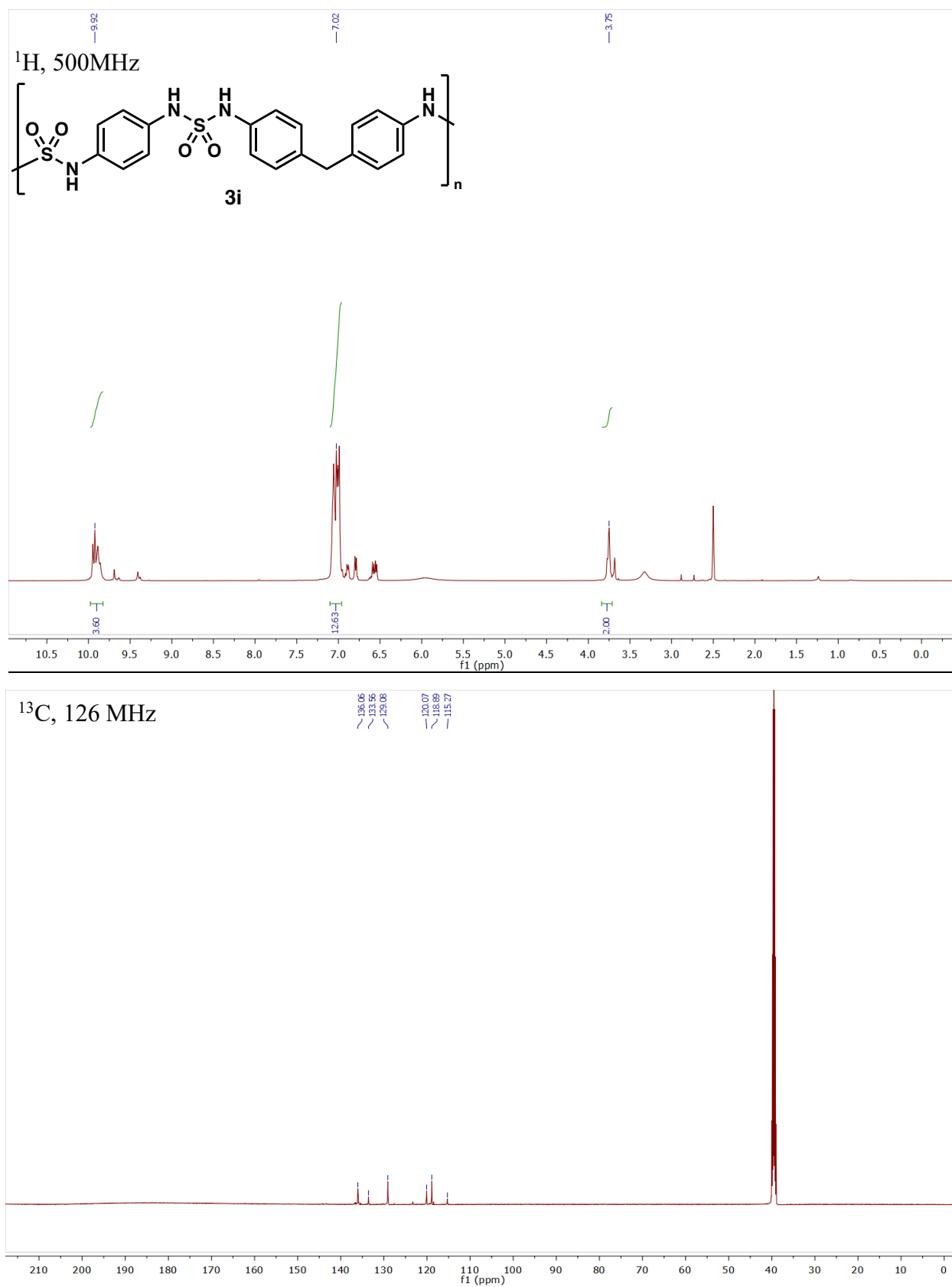
NMRs of polysulfamide **3h** (d_6 -DMSO)



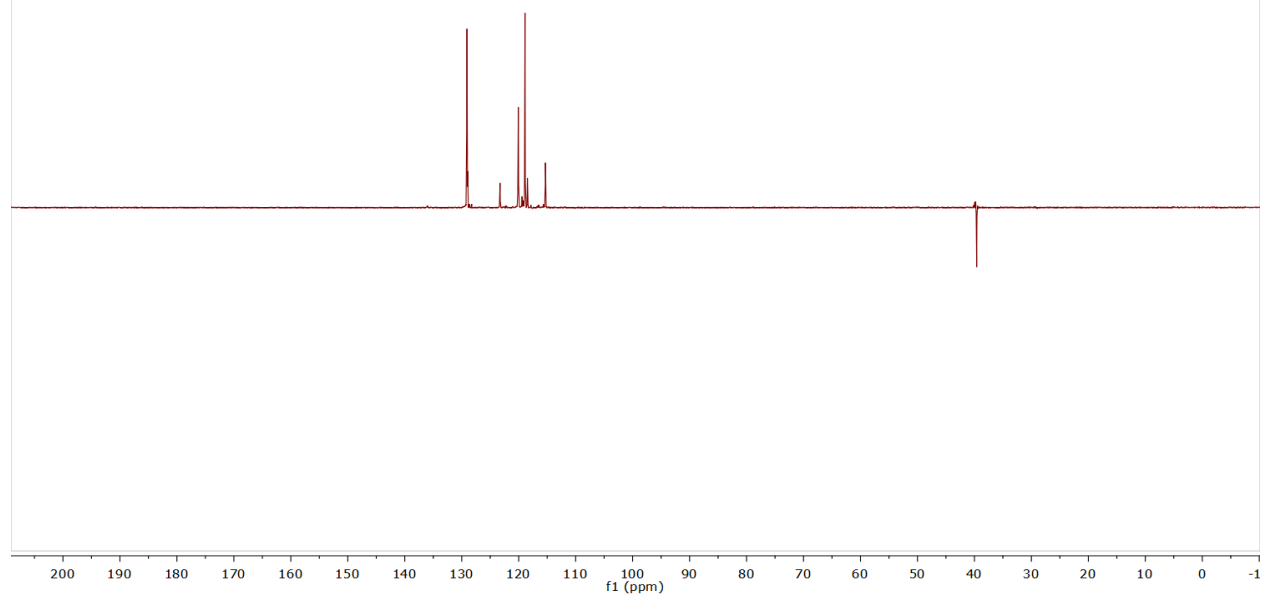
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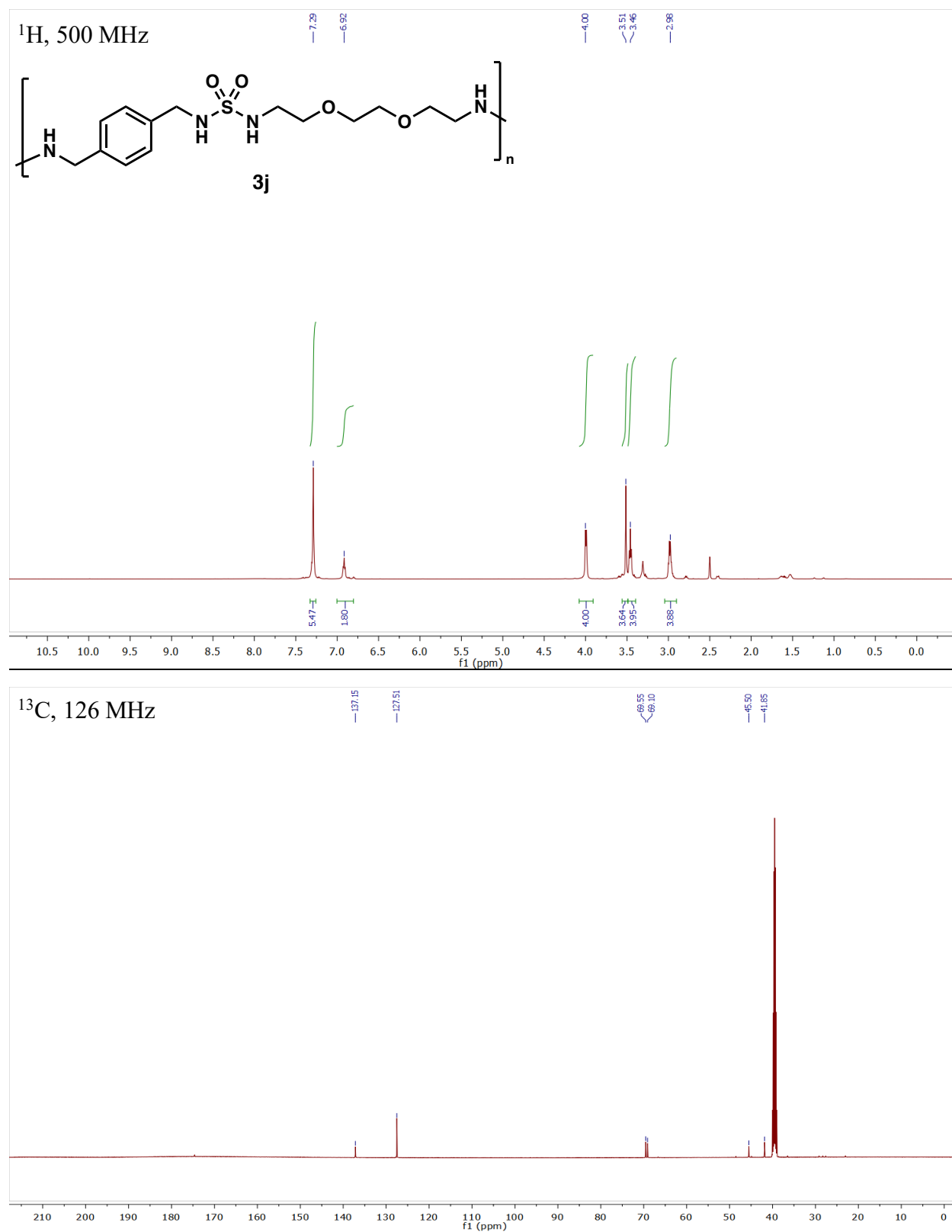
NMRs of polysulfamide **3i** (d_6 -DMSO)



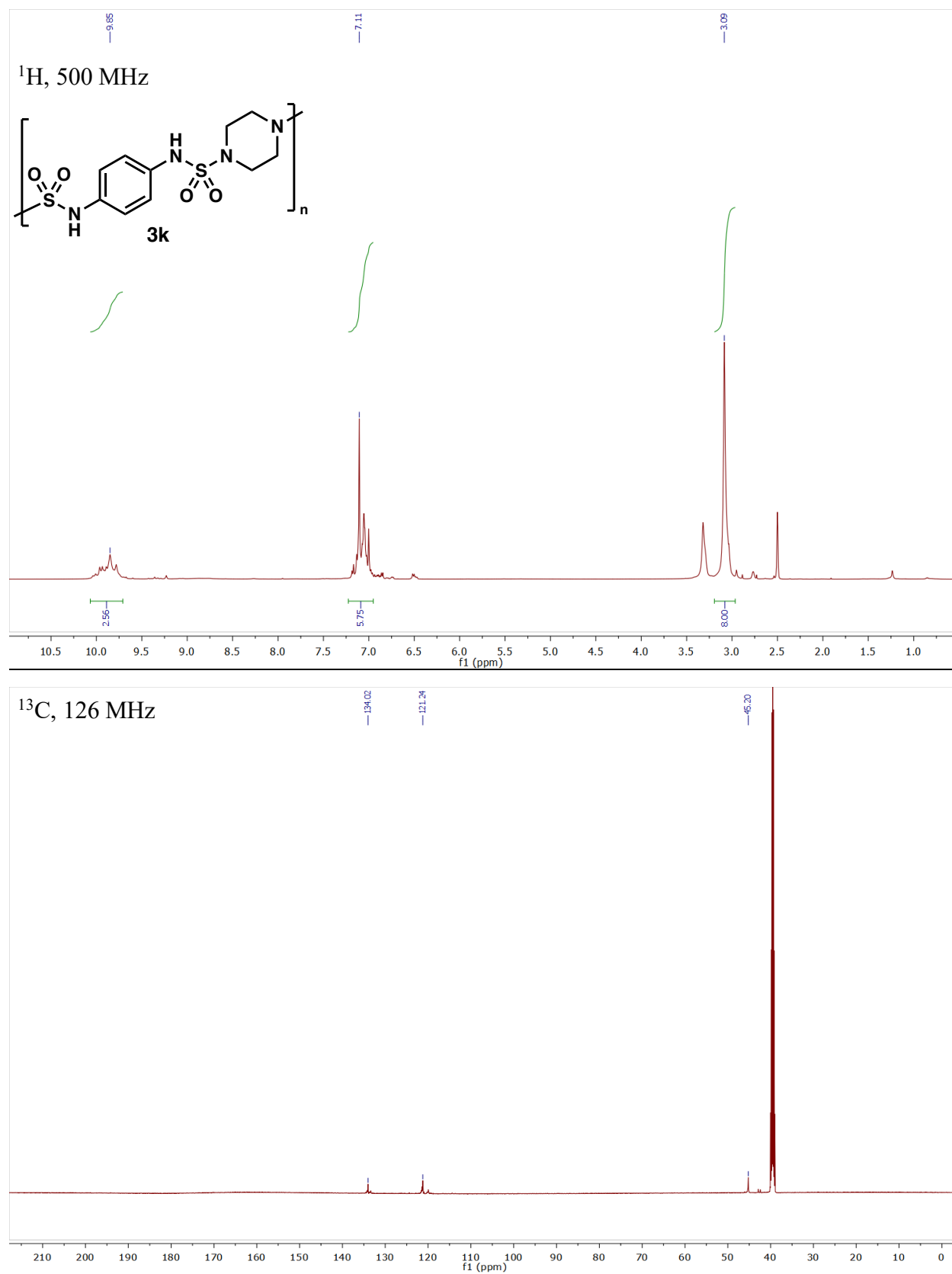
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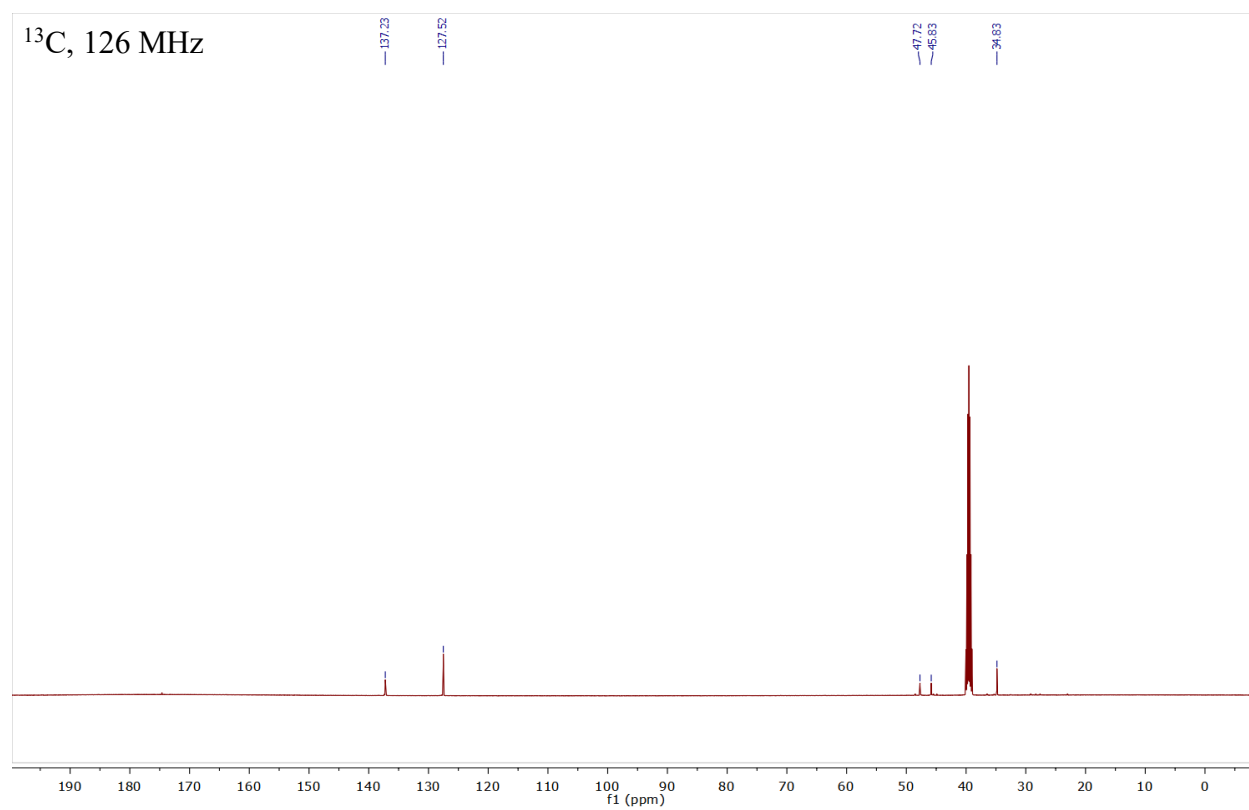
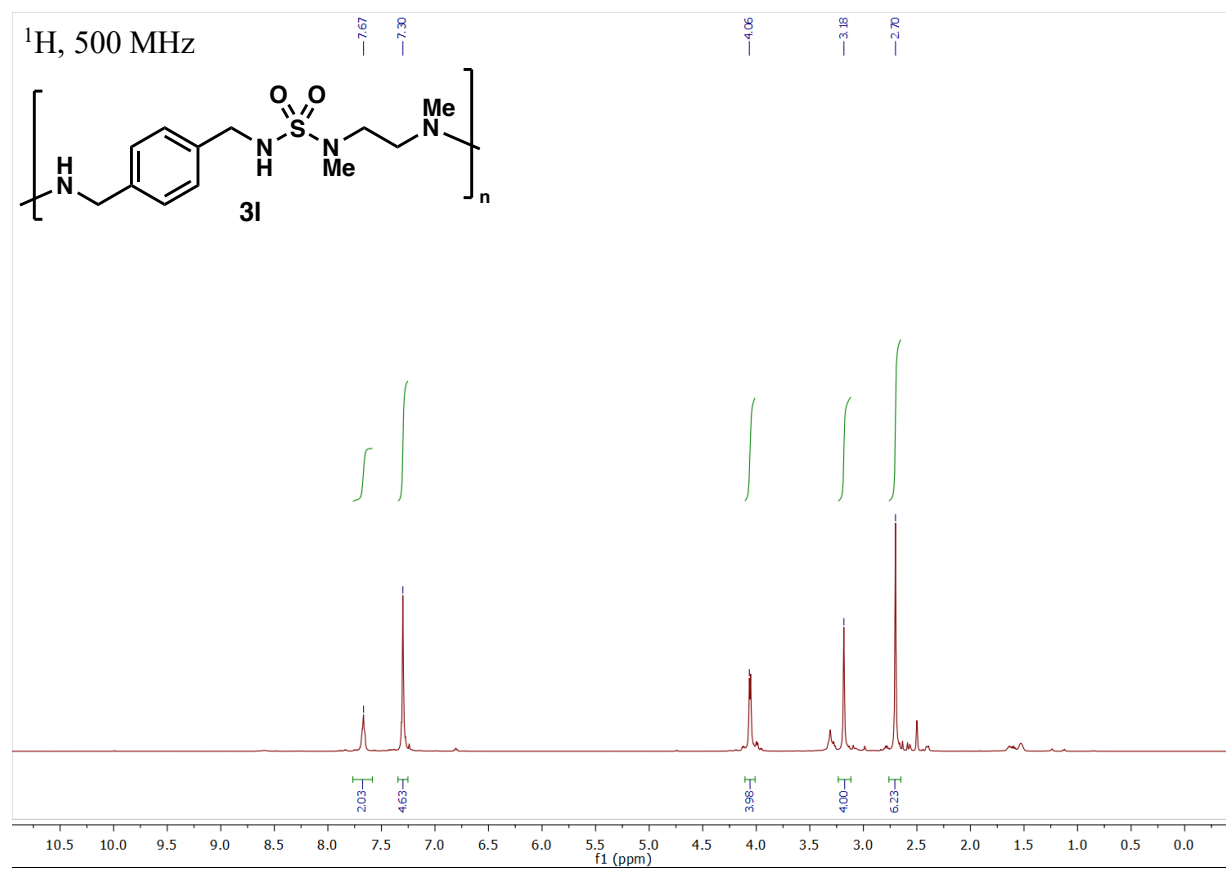
NMRs of polysulfamide **3j** (*d*₆-DMSO)



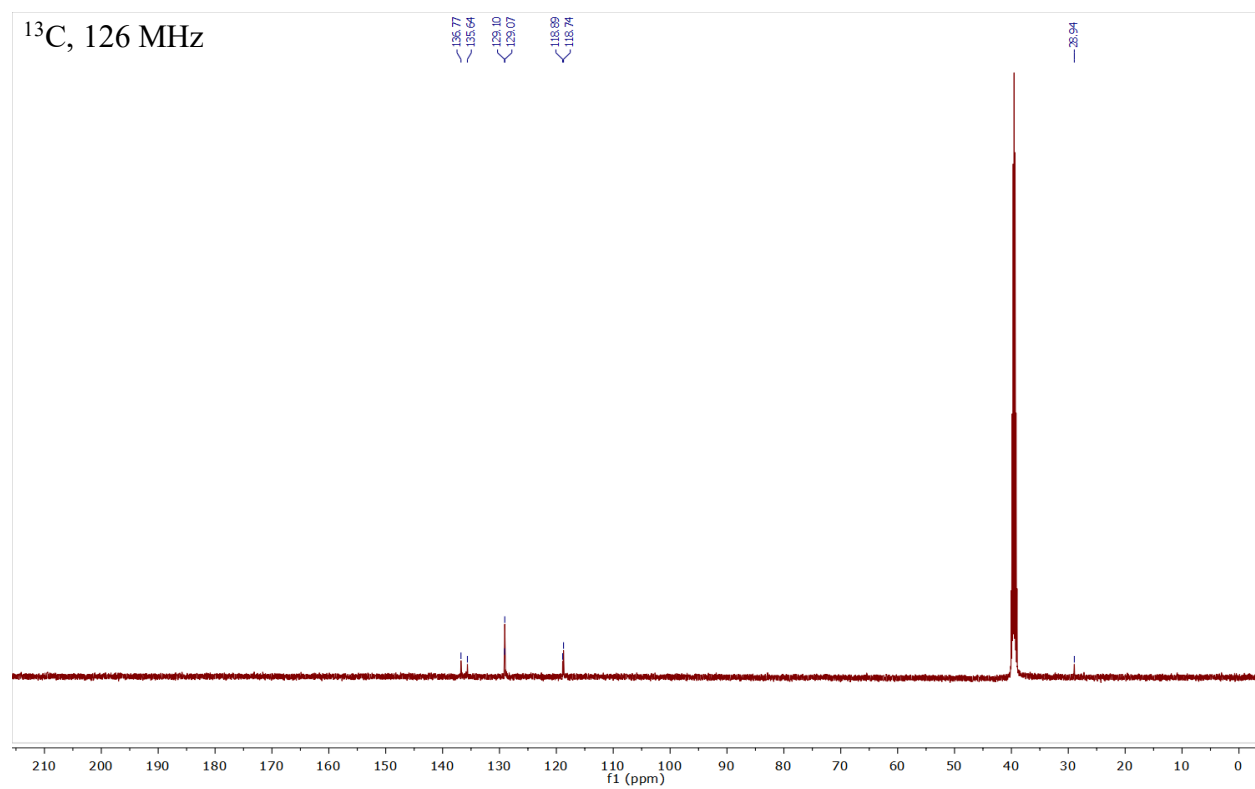
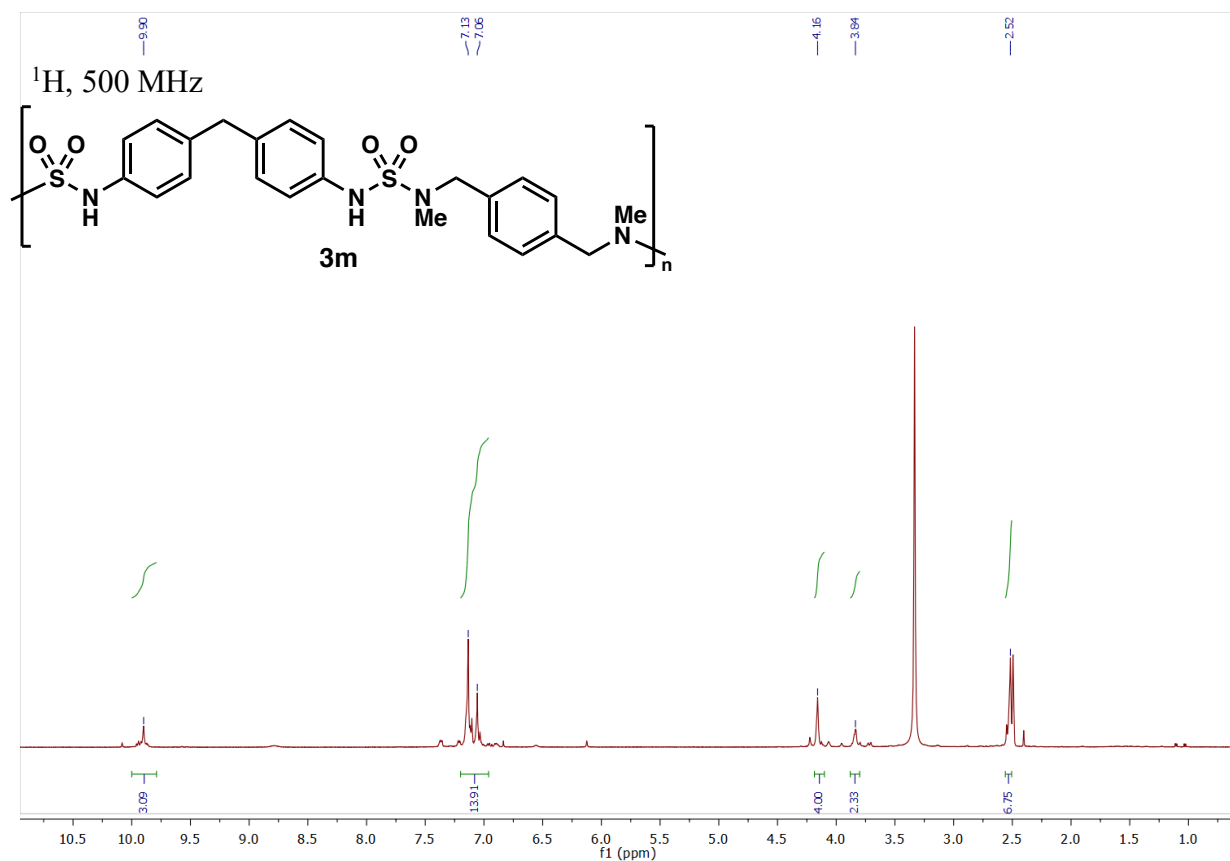
NMRs of polysulfamide **3k** (d_6 -DMSO)



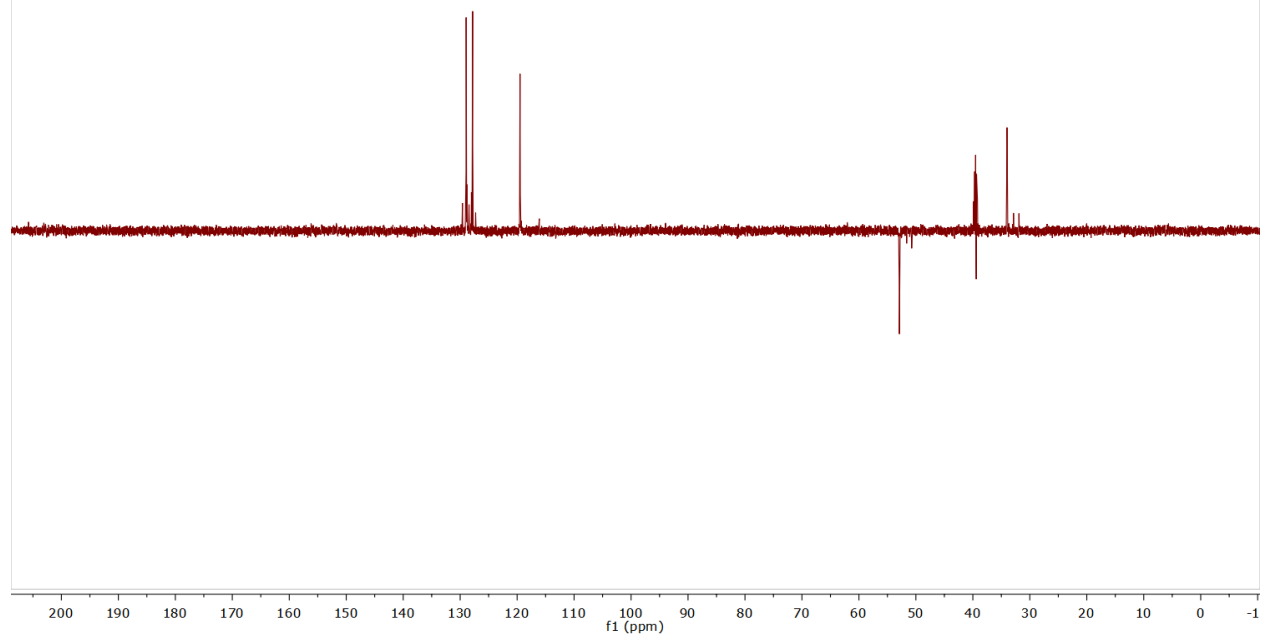
NMRs of polysulfamide **3I** (d_6 -DMSO)



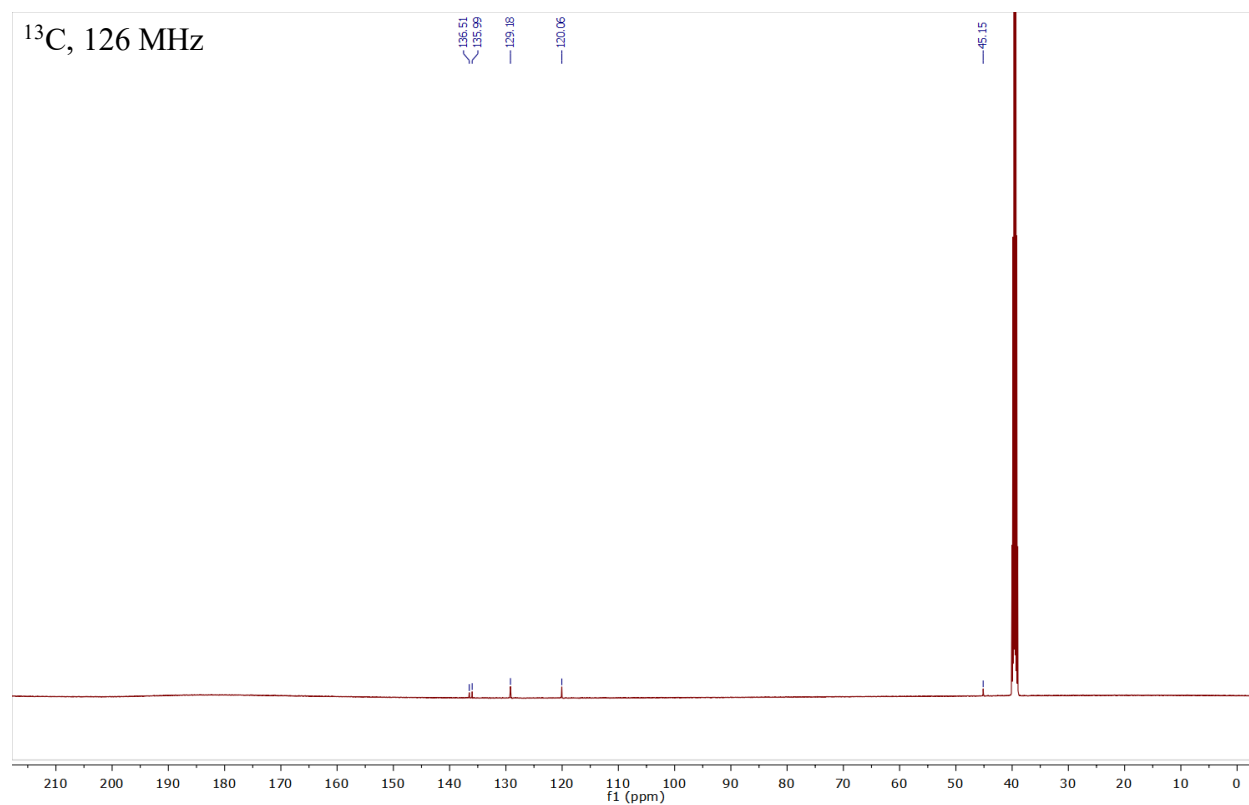
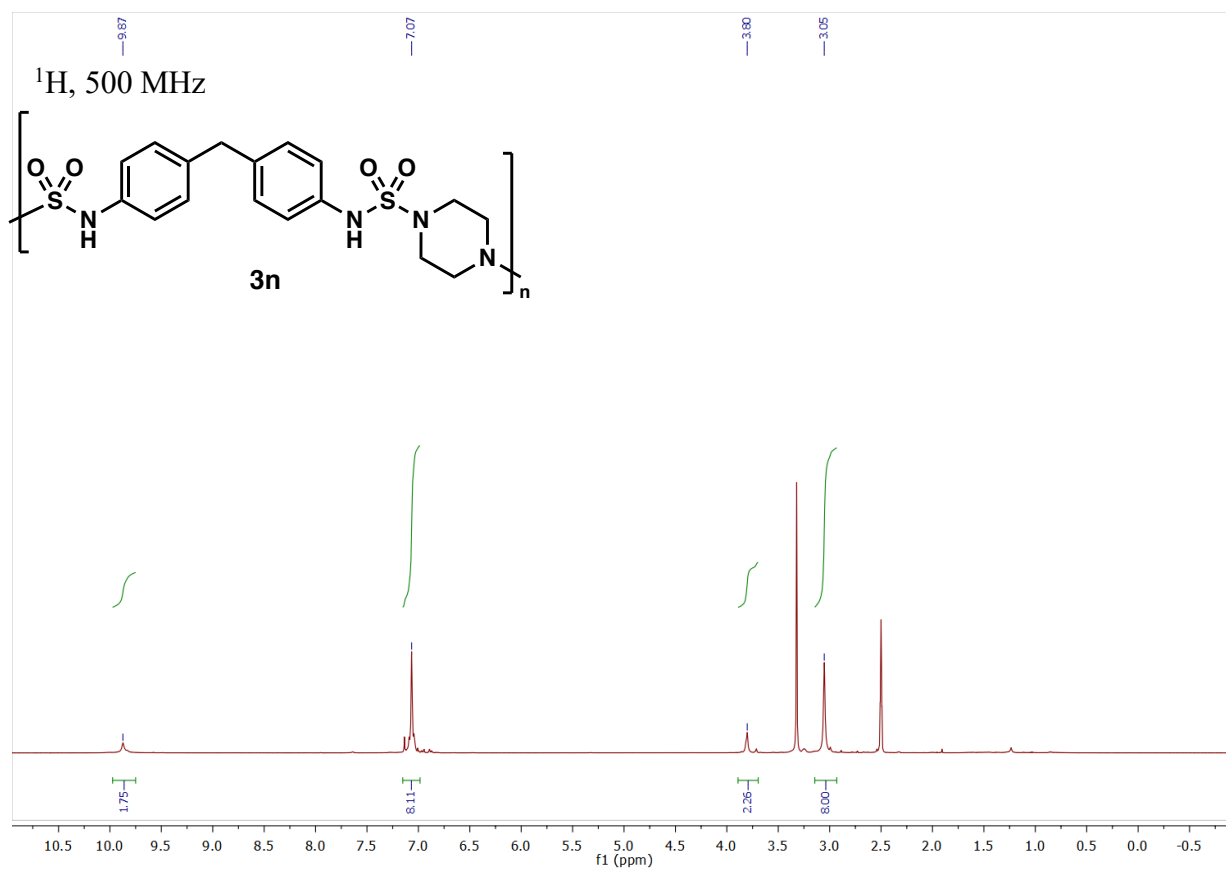
NMRs of Polysulfamide **3m** (*d*₆-DMSO)



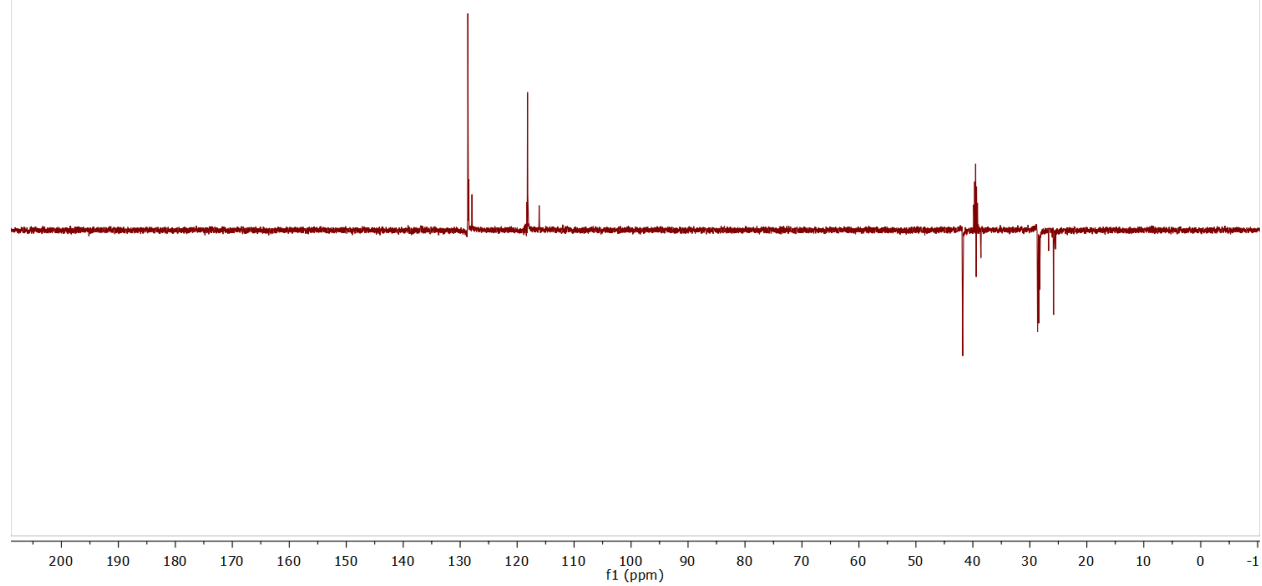
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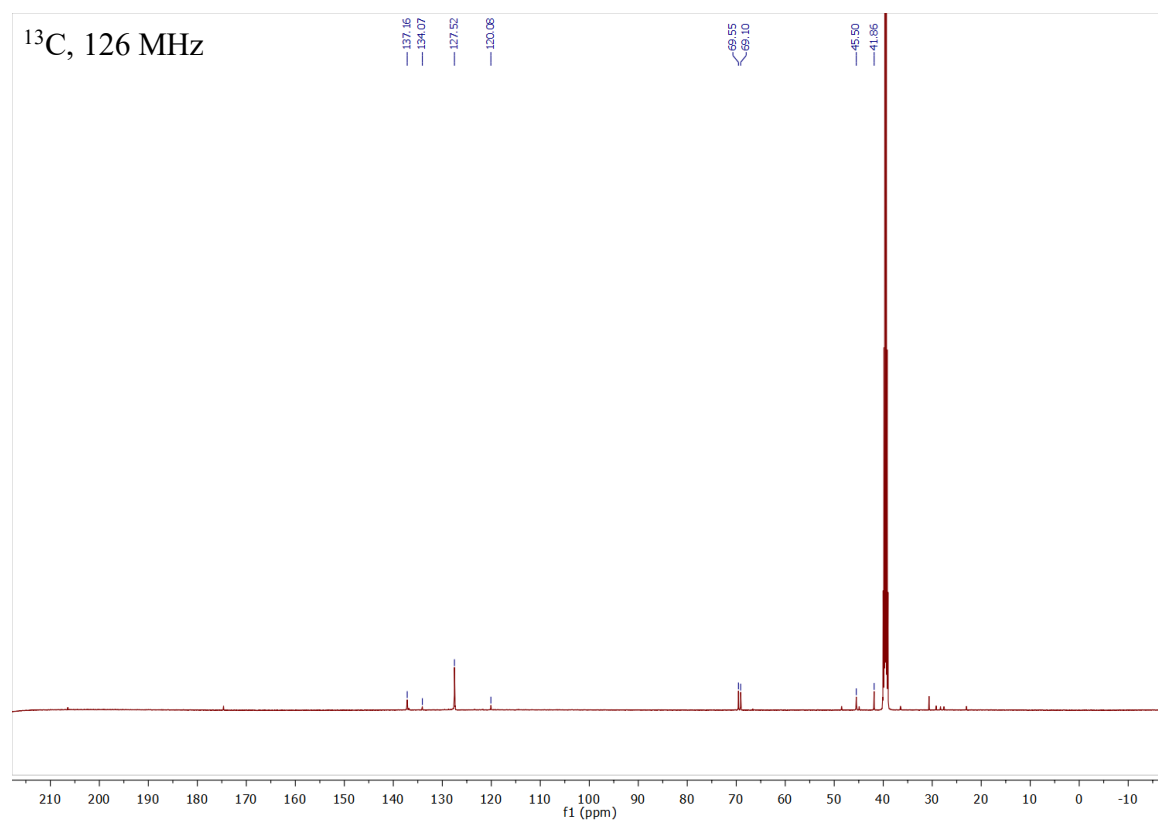
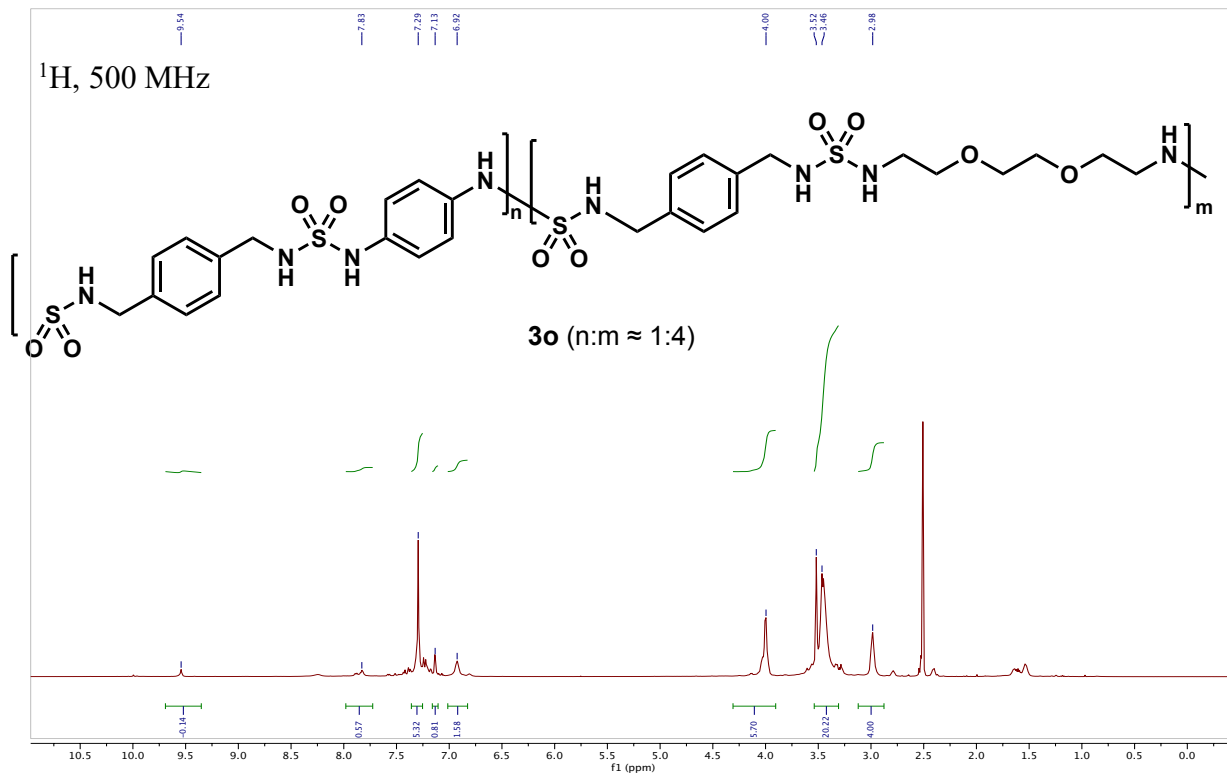
NMRs of Polysulfamide **3n** (*d*₆-DMSO)



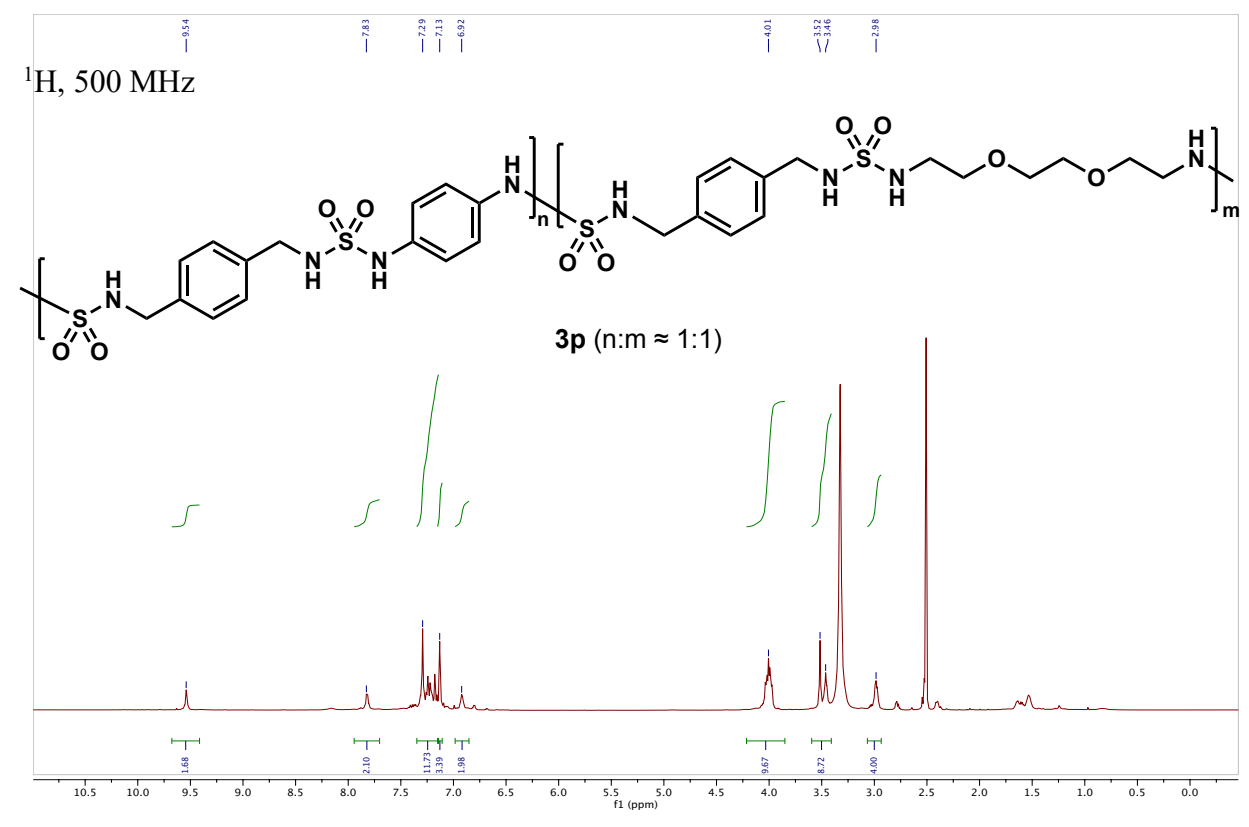
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NMRs of Polysulfamide **3o** (d_6 -DMSO)



NMRs of Polysulfamide **3p** (d_6 -DMSO)





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