Synthesis of Unsymmetrical Sulfamides and Polysulfamides Via SuFEx Click Chemistry

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Supporting Information

Experimental Procedures

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 (^{1}H 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.

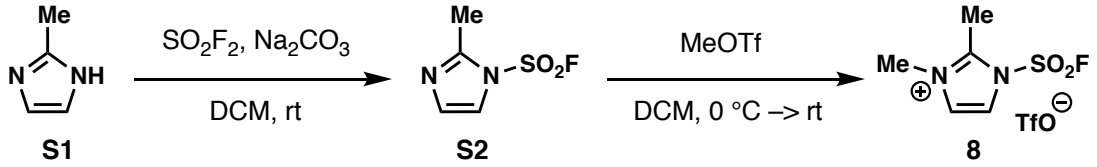
General Analytical Information

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 (*Đ)* were calculated from refractive index chromatograms against poly(methyl methacrylate) standards. ^{1}H 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 ^{1}H and ^{13}C spectra were calibrated using residual deuterated solvent as an internal reference ($CDCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; d_3-MeCN @ 1.94 ppm ^{1}H NMR, 1.32 and 118.26 ppm ^{13}C NMR; d_6-DMSO @ 2.50 ppm ^{1}H 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 ºC below decomposition temperature at 10 °C/min, cooling to −50 °C at 10 °C/min, and heating again from −50 °C to 5 ºC 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: sulfuryl fluoride is a highly toxic gas. As such, all reactions using sulfuryl 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 sulfuryl 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 sulfuryl 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 °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 °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 ºC, the desired solid precipitates.

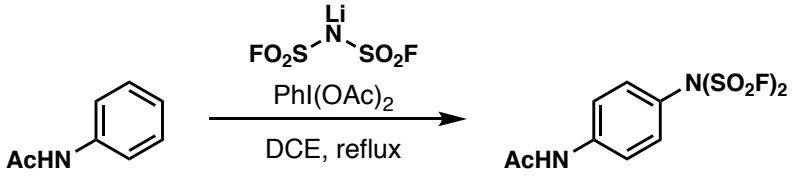
The spectroscopic data for this compound were identical to those reported in the literature (*Angew. Chem. Int. Ed.* 2018, **57**, 2605).

^{1}H 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]imidodisulfuryl difluoride (AISF, 9):



S3 **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).

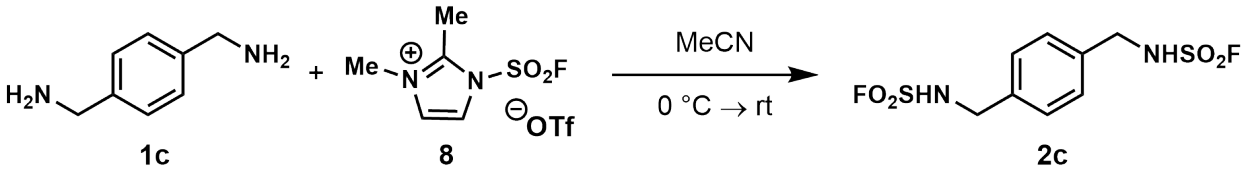
^{1}H NMR: (d_6-DMSO, 400 MHz) δ : 10.37 (s, 1 H), 7.90–7.63 (m, 4 H), 2.09 (s, 3 H) ppm.

^{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.

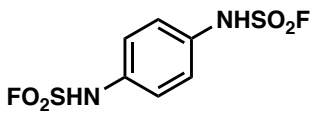
See preparation of sulfamoyl fluoride **5a** (*vide infra*) for a sulfamoylation procedure using **9**.

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



1c **8** **2c**

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 $MgSO_4$ and concentrated *in vacuo* to yield the crude product. When required, the product was then purified through column chromatography.



2b

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%).

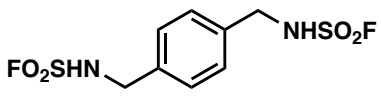
^{1}H NMR (CD_3CN, 400 MHz) δ: 8.88 (br, 2 H), 7.37 (s, 4 H) ppm.

^{13}C NMR (CD_3CN, 126 MHz) δ: 134.3, 125.1 ppm.

^{19}F NMR (CD_3CN, 470 MHz) δ: 49.5 ppm.

HRMS-ESI: calc'd. for $C_6H_5N_2O_4S_2F_2$ $[M–H]^-$ 270.9664, found 270.9662.

mp: Decomposed before melting.



2c

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 (SiO_2, 5:95 to 10:90 EtOAc:hexanes) provided **2c** as a white solid (824 mg, 75%).

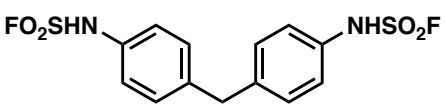
^{1}H NMR (CD_3CN, 500 MHz) δ: 7.39 (s, 4 H), 7.06 (br, 2 H), 4.41 (d, 4 H) ppm.

^{13}C NMR (CD_3CN, 126 MHz) δ: 137.1, 129.4, 48.2 ppm.

^{19}F NMR (CD_3CN, 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.



2d

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%).

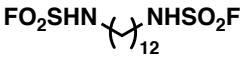
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.22 (m, 8 H), 6.78 (br, 2 H, NH), 3.99 (s, 2 H) ppm.

^{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 ºC



2e

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%).

^{1}H 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.

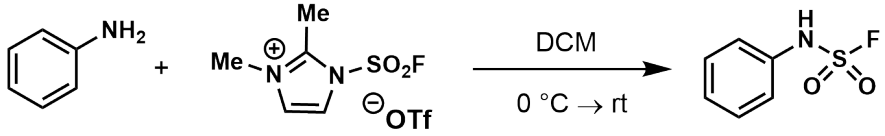
^{13}C NMR ($CDCl_3$, 126 MHz) δ: 44.9, 29.5, 29.4, 29.4, 29.0, 26.3 ppm.

^{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 ºC.

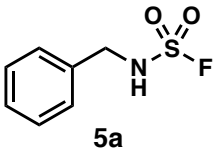
General Procedure for the Synthesis of Sulfamoyl Fluorides 5 (Using 5b as an Example)



4b **8** **5b**

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 $MgSO_4$ and concentrated *in vacuo* to afford the product as an orange oil (1.42 g, 84%) without further purification.



5a

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%).

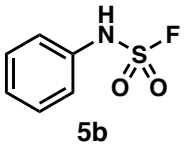
Alternatively, **5a** can be prepared using AISF **9** as the fluorosulfonation reagent. To a solution of benzylamine (**4a**) (107 mg, 1.0 mmol, 1.0 equiv) and AISF **9** (377 mg, 1.2 mmol, 1.2 equiv) in acetonitrile (3.5 mL), DBU (335 mg, 0.33 mL, 2.2 mmol, 2.2 equiv) was added dropwise at room temperature. The mixture was stirred and monitored by TLC until benzylamine (**4a**) was fully a 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 $MgSO_4$, and concentrated *in vacuo*. Column chromatography (SiO_2, 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).

^{1}H NMR ($CDCl_3$, 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.

^{13}C NMR ($CDCl_3$, 126 MHz) δ: 134.8, 129.2, 128.8, 128.1, 48.5 ppm.

^{19}F NMR ($CDCl_3$, 470 MHz) δ: 50.4 ppm.



5b

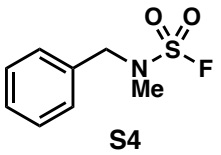
Sulfamoyl fluoride 5b was prepared following the general procedure. Starting with aniline (**4b)** (900 mg, 9.66 mmol) to afford the product as an orange oil (1.42 g, 84%).

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

^{1}H NMR (CD_3CN, 400 MHz) δ: 8.85 (br, 1 H), 7.44 (m, 2 H), 7.33 (m, 3 H) ppm.

^{13}C NMR (CD_3CN, 126 MHz) δ: 135.6, 130.7, 128.1, 123.9 ppm.

^{19}F NMR (CD_3CN, 470 MHz) δ: 50.1 ppm.



S4

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%).

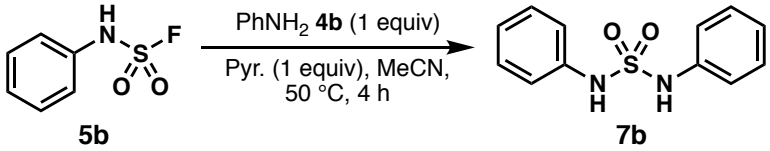
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.43–7.32 (m, 5 H), 4.48 (s, 2 H), 2.90 (d, 3 H, J = 2.2 Hz) ppm.

^{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.

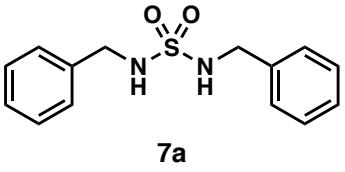
HRMS-ESI: calc'd. for $C_8H_{10}NO_2SNa$ $[M+Na]^+$ 226.0308, found 226.0302.

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



5b **7b**

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 ºC 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%).



7a

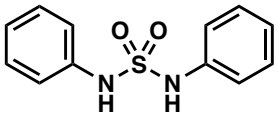
Sulfamide 7a was prepared by starting with sulfamoyl fluoride **5a** (102.7 mg, 0.543 mmol), coupling with benzylamine (**4a)** and following the general procedure to afford a white solid (144.3 mg, 96%), without further purification.

^{1}H 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 cm^{-1}.

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



7b

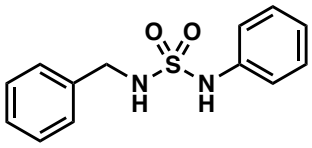
Sulfamide 7b was prepared by starting with sulfamoyl fluoride **5b** (100 mg, 0.570 mmol), coupling with aniline (**4b)** and following the general procedure to afford the product as white crystals (128 mg, 91%).

^{1}H 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).



7c

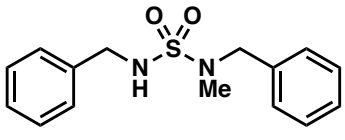
Sulfamide 7c was prepared by starting with sulfamoyl fluoride **5a** (99.6 mg, 0.526 mmol), coupling with aniline (**4b**) and following the general procedure. Crude mixture was purified column chromatography (20 % EtOAc in hexanes) to afford a white solid (114.0 mg, 83%).

Alteratively, 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%).

^{1}H 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).



7d

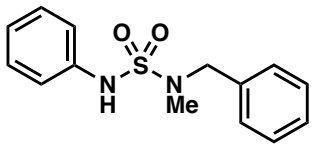
Sulfamide 7d was preparped by starting with sulfamoyl fluoride **5a** (100.1 mg, 0.529 mmol), coupling with *N*-benzylmethylamine (**4c)** and following the general procedure to afford white to yellow solid (151 mg, 98%)

^{1}H 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 $C_{15}H_{19}N_2O_2S$ $[M+H]^+$ 291.1162, found 291.1156.

mp: 72–74 ºC.



7e

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%).

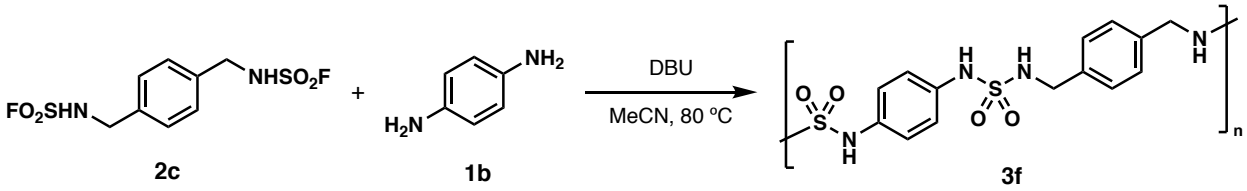
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.35–7.27 (m, 5 H), 7.22–7.09 (m, 5 H), 7.01 (br, 1 H) 4.32 (s, 2 H), 2.71 (s, 3 H) ppm.

^{13}C NMR ($CDCl_3$, 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 $C_{14}H_{17}N_2O_2S$ $[M+H]^+$ 277.1005, found 277.0998.

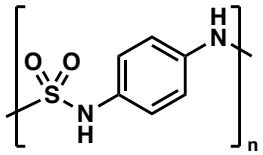
mp: 64–66 °C.

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



2c **1b** **3f**

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 ºC for 90 min. The resulting mixture was dissolved in DMF (1 mL), then precipitated in a centrifuge tube through the addition of Et_2O, 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 NH_4Cl (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 ºC 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.



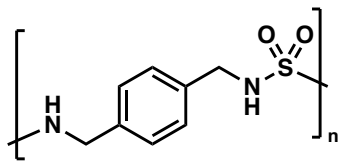
3b

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.

^{1}H NMR (*d*$_6$-DMSO, 500 MHz) δ = 9.87 (2 H), 7.01 (4 H) ppm.

13C NMR (*d*$_6$-DMSO, 126 MHz) δ = 133.6, 120.1 ppm.

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



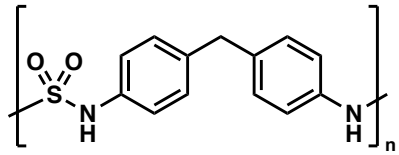
3c

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.

^{1}H 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): $\tilde{\upsilon}$ = 1143, 1311, 3263, 2932, 1614, 1067 cm^{-1}.



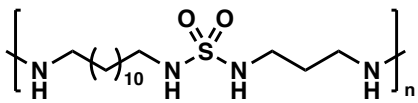
3d

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)**.

^{1}H 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): $\tilde{\upsilon}$ = 1151, 1139, 1334, 1509, 3301 cm^{-1}.



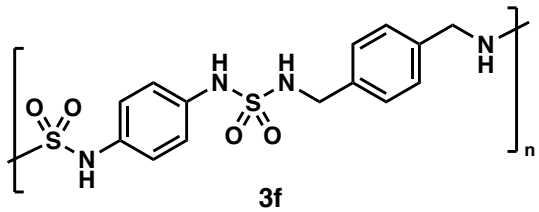
3e

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)**.

^{1}H 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): $\tilde{\upsilon}$ = 3281, 2920, 2850, 1441, 1308, 1143, 1065 cm^{-1}.



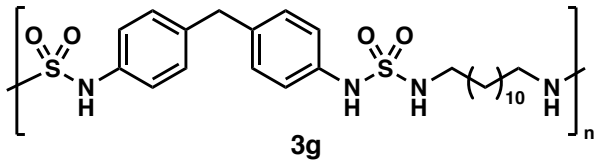
3f

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)**.

^{1}H 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): $\tilde{\upsilon}$ = 3275, 2938, 1614, 1513, 1318, 1143, 1064, 919 cm^{-1}.



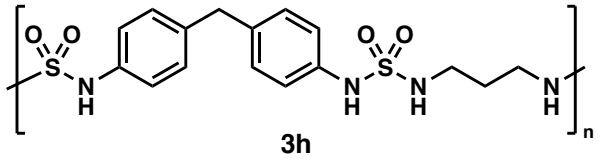
3g

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.

^{1}H 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): $\tilde{\upsilon}$ = 3281, 2921, 2849, 1509, 1326, 1143, 927 cm^{-1}.



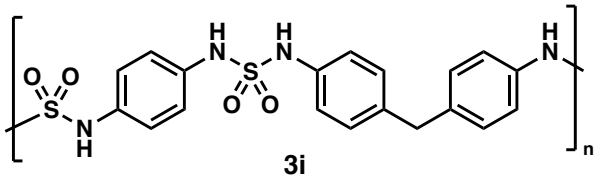
3h

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**).

^{1}H 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): $\tilde{\upsilon}$ = 3275, 1508, 1323, 1143, 933 cm^{-1}.



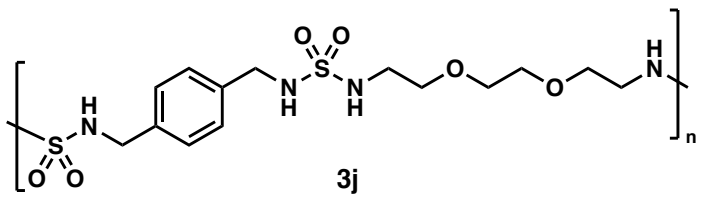
3i

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.

^{1}H 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): $\tilde{\upsilon}$ = 3270, 1610, 1508, 1315, 1147, 938 cm^{-1}.

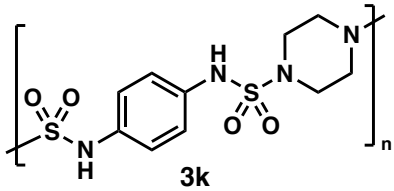


Polysulfamide 3j was obtained as a tan solid through the general procedure using compound **2c** (150 mg, 0.500 mmol) and 2,2'-(ethylenedioxy)-diethylamine (**1g)**.

^{1}H 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): $\tilde{\upsilon}$ = 3276, 2865, 1614, 1430, 1312, 1142, 1067 cm^{-1}.

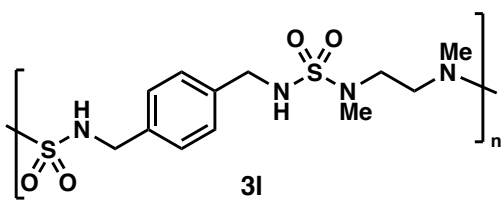


Polysulfamide 3k was obtained as a pink solid through general procedure using compound **2b** (200 mg, 0.733 mmol), piperazine (**1h)**, and pyridine as a base.

^{1}H 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): $\tilde{\upsilon}$ = 3237, 2926, 2866, 1510, 1324, 1147, 1119, 943 cm^{-1}.

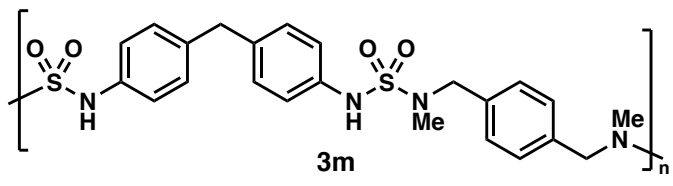


Polysulfamide 3l was obtained as a white solid through the general procedure using compound **2c** (150 mg, 0.500 mmol) and *N,N'*-dimethylethylenediamine (**1i)**.

^{1}H 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): $\tilde{\upsilon}$ = 3261, 2938, 2863, 1612, 1426, 1308, 1145, 1056, 967 cm^{-1}.

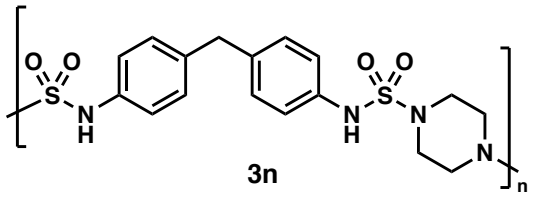


Polysulfamide 3m was obtained as an off-white solid through the general procedure using compound **2d** (100 mg, 0.276 mmol) and *N,N'*-dimethyl-*p*-xylylenediamine (**1j)**. Bis(amine) **1j** was prepared following the previous reported procedure (*Dalton Trans.*, **2011**, *40*, 12235).

^{1}H 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): $\tilde{\upsilon}$ = 3471, 3016, 2948, 1508, 1449, 1366, 1216, 1150, 909 cm^{-1}.



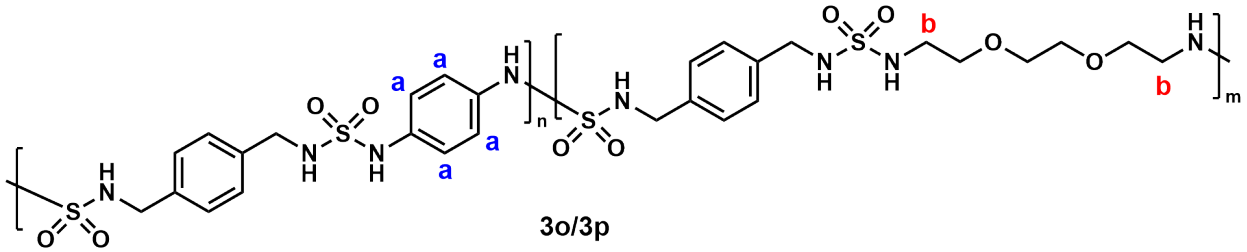
3n

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

^{1}H 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): $\tilde{\upsilon}$ = 3454, 3018, 2966, 1509, 1448, 1367, 1217, 1149, 912 cm^{-1}.



3o/3p

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)

^{1}H 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.

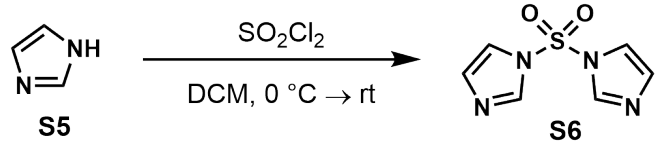
Polysulfamide 3p was obtained as an orange solid through the general procedure using compound **2c** (50 mg, 167 μmol, 3.0 equiv), 1,4-phenylenediamine (**1b**) (12 mg, 0.112 mmol, 2.0 equiv), and 2,2'-(ethylenedioxy)-diethylamine (**1g)** (8 mg, 0.056 mmol, 1.0 equiv).

^{1}H 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 ^{1}H 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 ≈ 1:4, and for **3p** n:m ≈ 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)



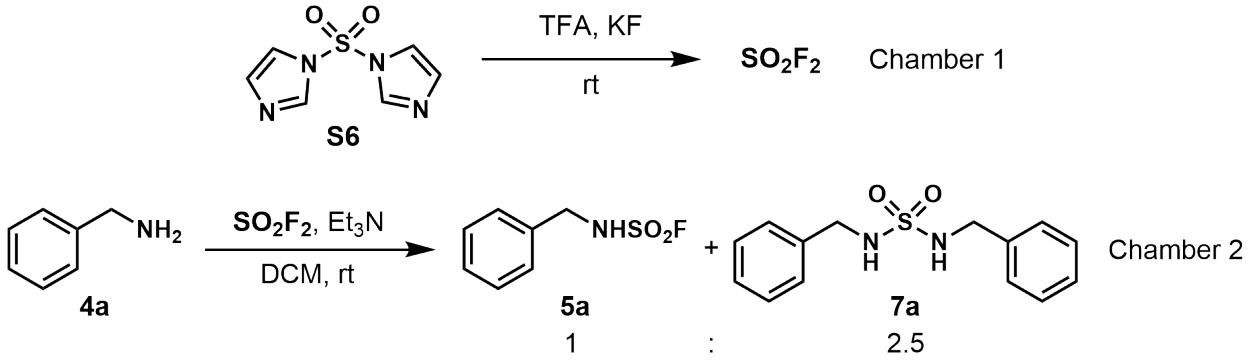
S6 was prepared according to a literature procedure (*Org. Lett.* 2017, **19**, 5244). In a flame-dried flask under nitrogen, imidazole (**S5**) (5.00 g, 73 mmol, 4.6 equiv) was suspended in anhydrous DCM (30 mL) and cooled to 0 °C. A solution of sulfuryl chloride (2.15 g, 16 mmol, 1.0 equiv) in DCM (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.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.03 (s, 1 H), 7.30 (s, 1 H), 7.14 (s, 1 H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 136.7, 132.5, 117.5 ppm.

Reaction of a Primary Amine with ex situ-generated SO_2F_2



SO_2F_2 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 $MgSO_4$ 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).

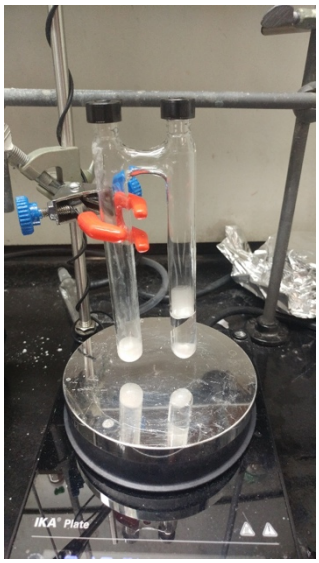


Figure S1. Two-chamber reactor for *ex situ* generation of SO_2F_2.

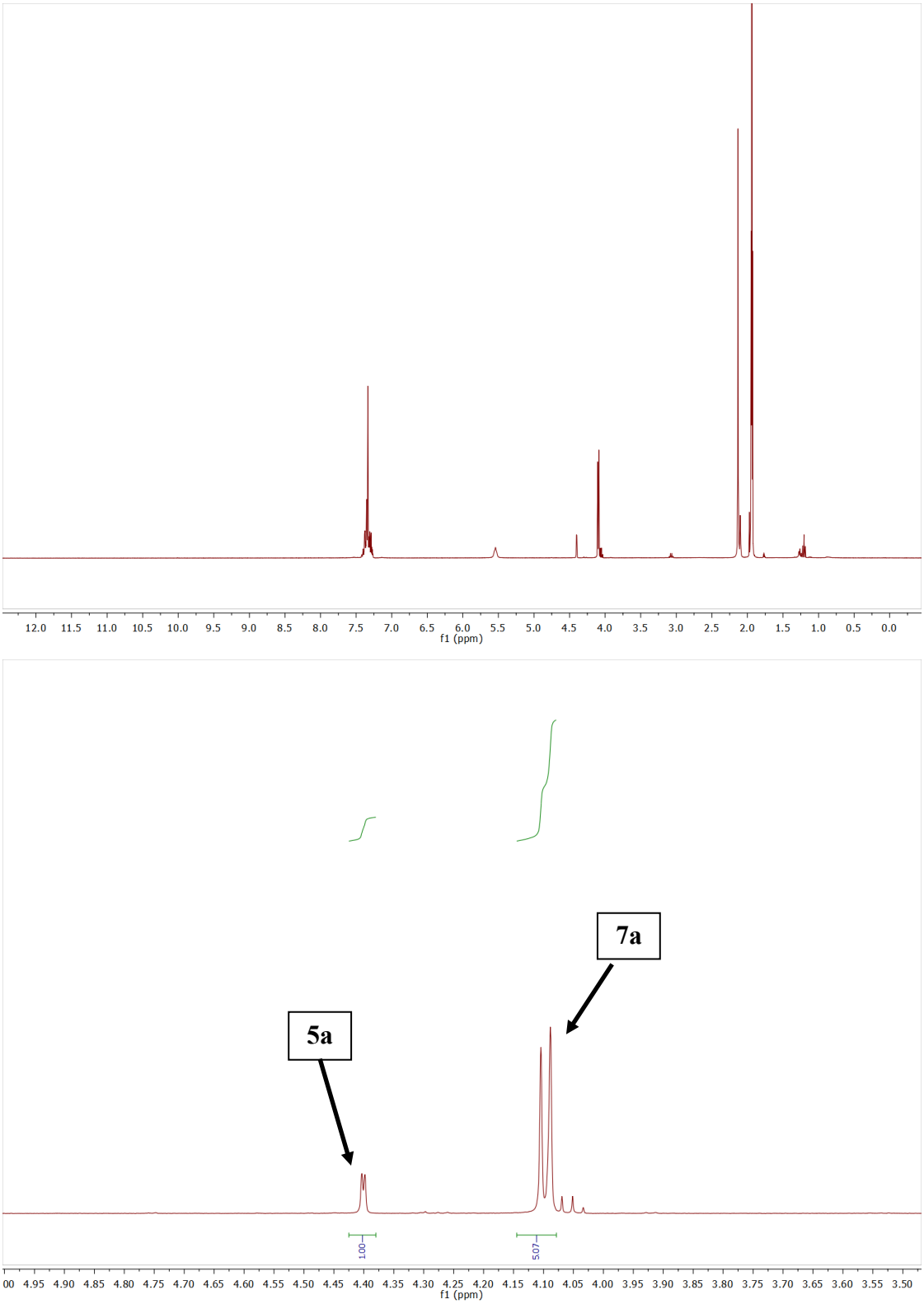
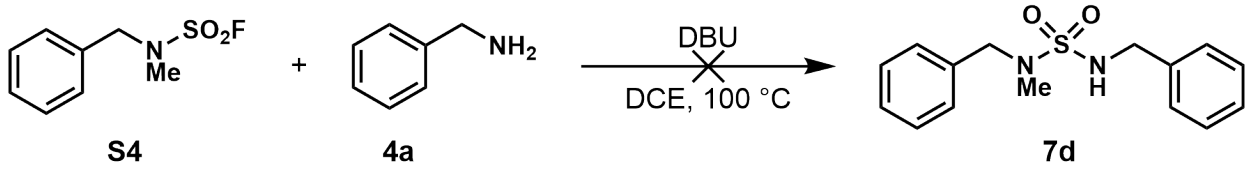


Figure S2. ^{1}H NMR (CD_3CN, 400 MHz) of the crude product obtained after workup, and inset (bottom) showing the respective benzylic signals of **5a** and **7a**

Attempt to Couple a Secondary Sulfamoyl Fluoride with a Primary Amine



S4 **4a** **7d**

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*. ^{1}H NMR analysis of the crude product showed no trace of **7d**, but only unreacted **S4**.

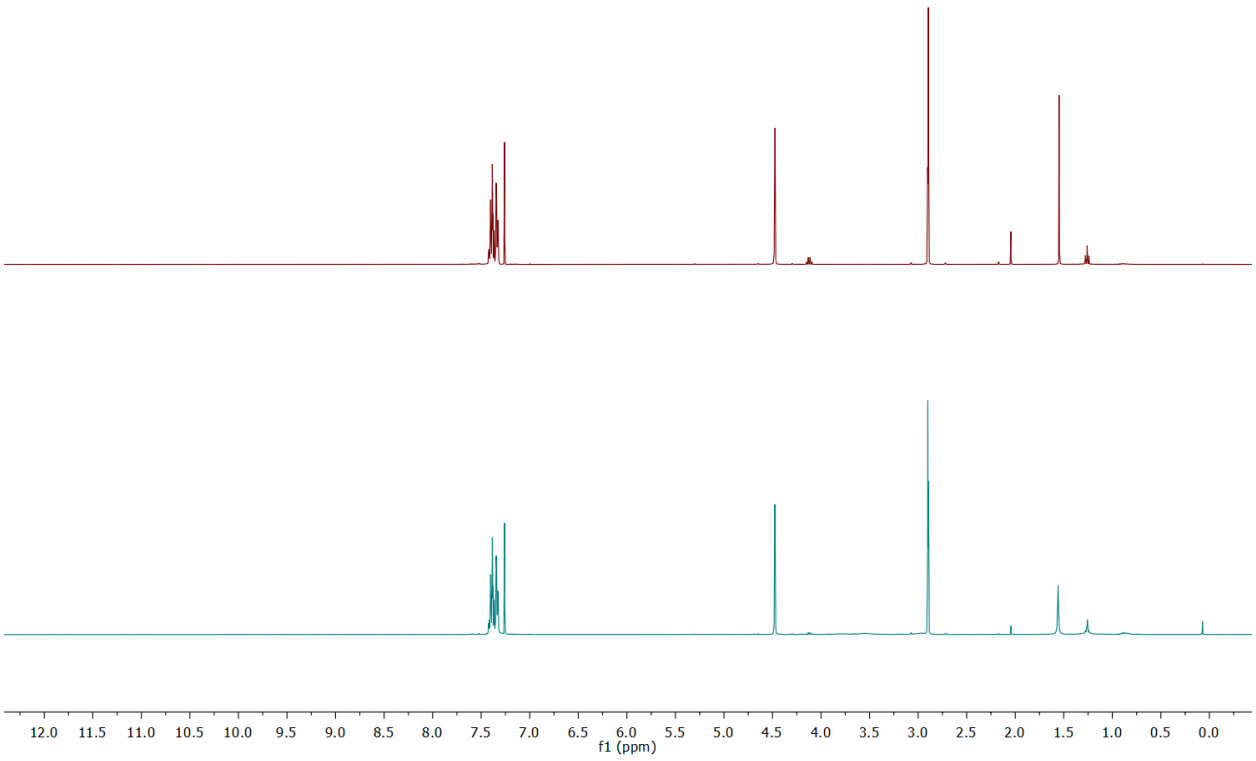
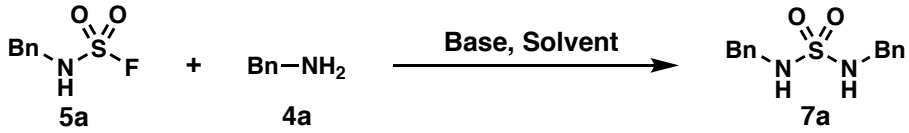


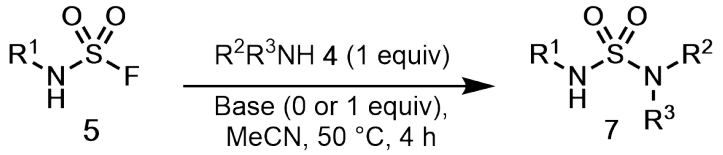
Figure S3. Top: ^{1}H NMR of compound **S4** ($CDCl_3$, 400 MHz), Bottom: ^{1}H NMR ($CDCl_3$, 400 MHz) of material obtained after attempting to react compound **S4** with benzylamine.

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



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_2CO_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



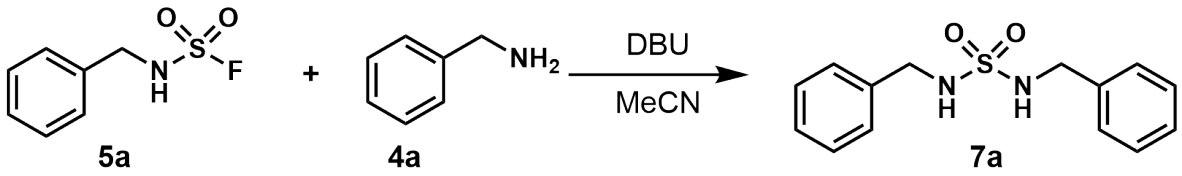
Sulfamoyl Fluoride	Amine	Yield (Using 1 equiv base)*	Yield (No base added)
5a	**4a**	**96%**	**70%**
5a	**4b**	**83%**	**74%**
5a	**4c**	**98%**	**79%**
5b	**4a**	**89%**	**63%**
5b	**4b**	**91%**	**79%**
5b	**4c**	**93%**	**52%**

(*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 $MgSO_4$, and concentrated *in vacuo*. The progress of the reaction was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene (4.2 mg, 25 μmol, 0.125 equiv) as an internal standard.

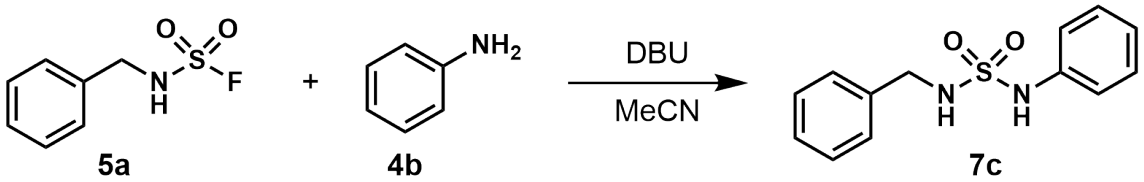
Table S3. Synthesis of sulfamide **7a**



5a 4a 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**



5a 4b 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, CD_3CN dried with activated 4 Å molecular sieves and anhydrous Et_3N were used. Anhydrous Et_3N (1.0 equiv) was added to a solution of sulfmaoyl fluoride **5a** in anhydrous CD_3CN. The resulting mixture was quickly transferred to a J. Young NMR tube under a stream of nitrogen. After heating at 80 ºC for 30 min, a ^{19}F NMR spectrum was collected, which revealed the full consumption of sulfamoyl fluoride **5a**. The new peak in the ^{19}F NMR spectrum is consistent with the formation of Et_3N•HF according to literature precedent (*J. Am. Chem. Soc.* 2016, **138**, 11360)

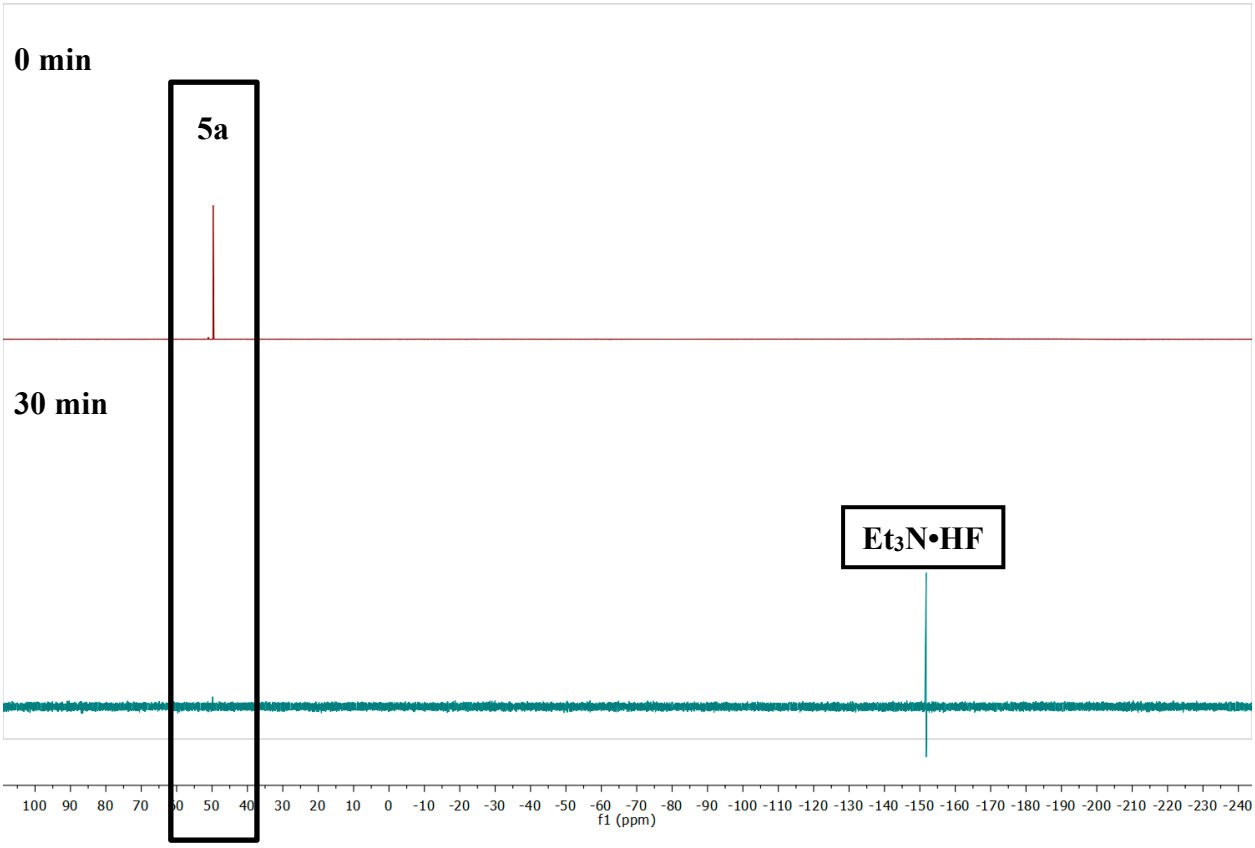
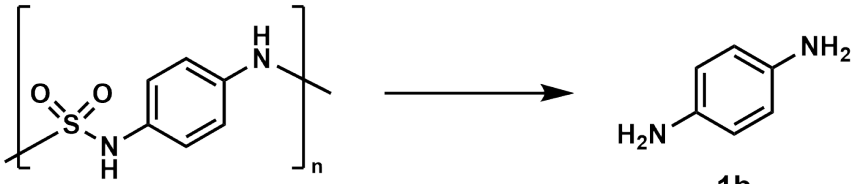


Figure S4. ^{19}F NMR (CD_3CN, 470 MHz) analysis revealed the disappearance of sulfamoyl fluoride **5a** and suggested the formation of Et_3N•HF and therefore azasulfene **6a**
Top: Sulfamoyl fluoride **5a**. Bottom: **5a** stirred with Et_3N at 80 ºC for 30 min

Hydrolysis Study of Polysulfamides

To a vial containing polymer **3b** (15 mg, 88 μmol, based on monomer unit $C_6H_6N_2O_2S$), 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)



3b **1b**

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%

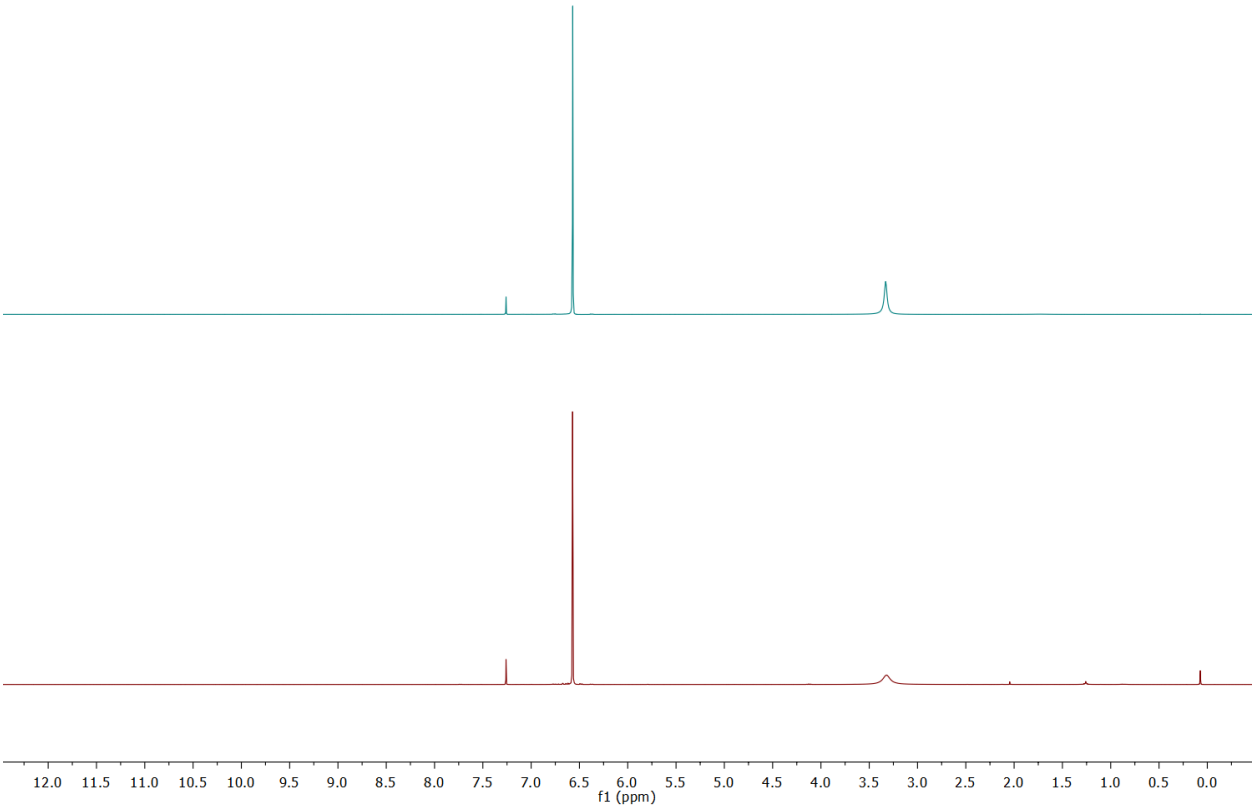
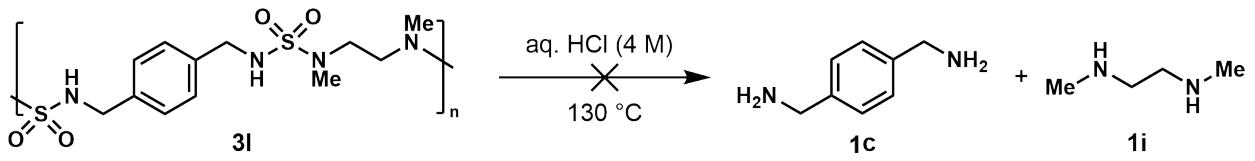


Figure S5. Top: ^{1}H NMR of purchased 1,4-phenylenediamine ($CDCl_3$, 400 MHz), Bottom: ^{1}H NMR of solid obtained after treatment of polymer **3b** with aq. HCl (4 M) at 130 °C ($CDCl_3$, 400 MHz).



When polymer **3l** 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 Interatction within Polysulfamides:

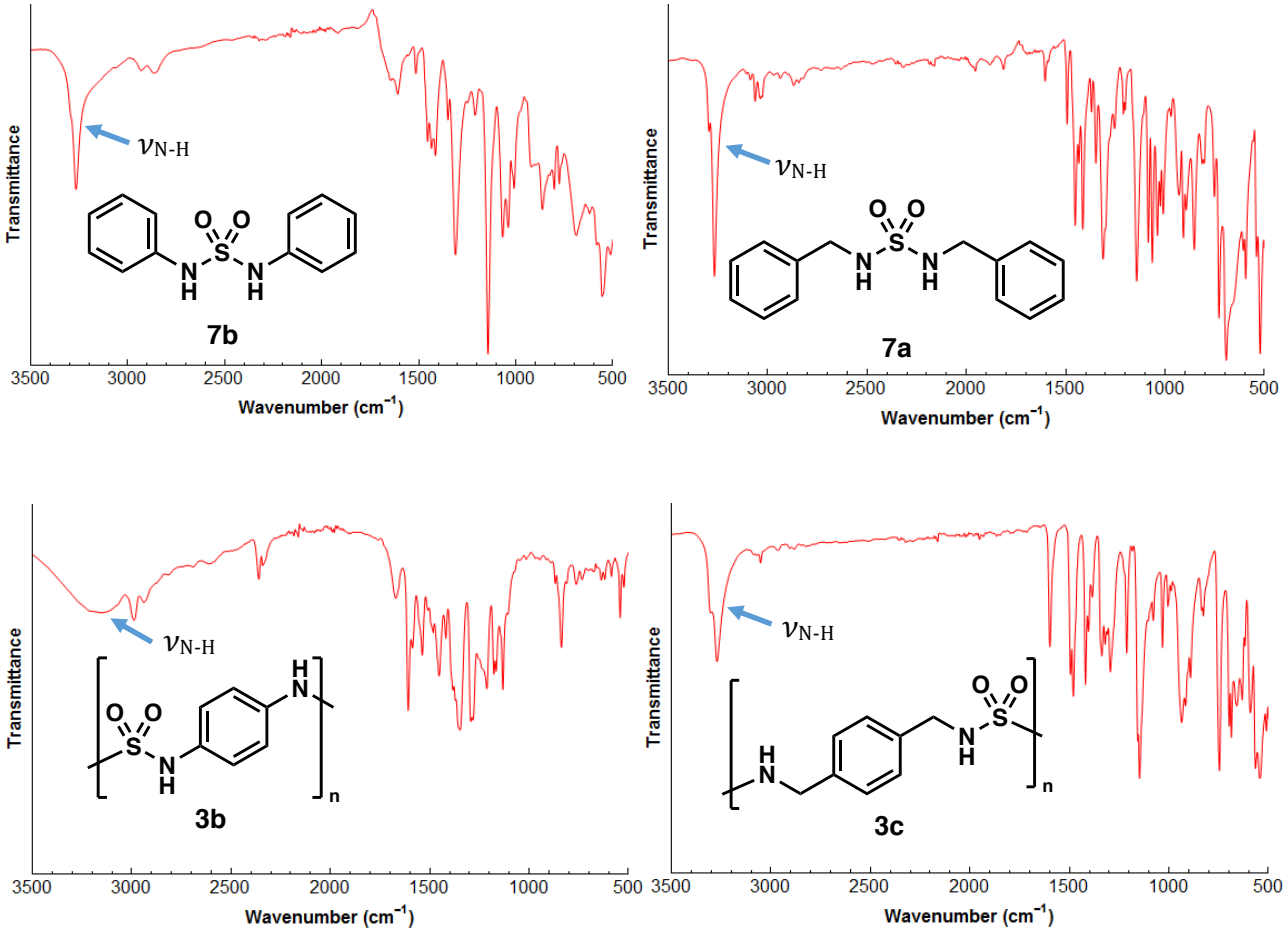


Figure S6. Comparison of FT-IR spectra of *N,N'*-diphenylsulfamide (**7a)** and *N,N'*-dibenzylsulfamide (**7b**) with that of polymers **3b** and **3c**.

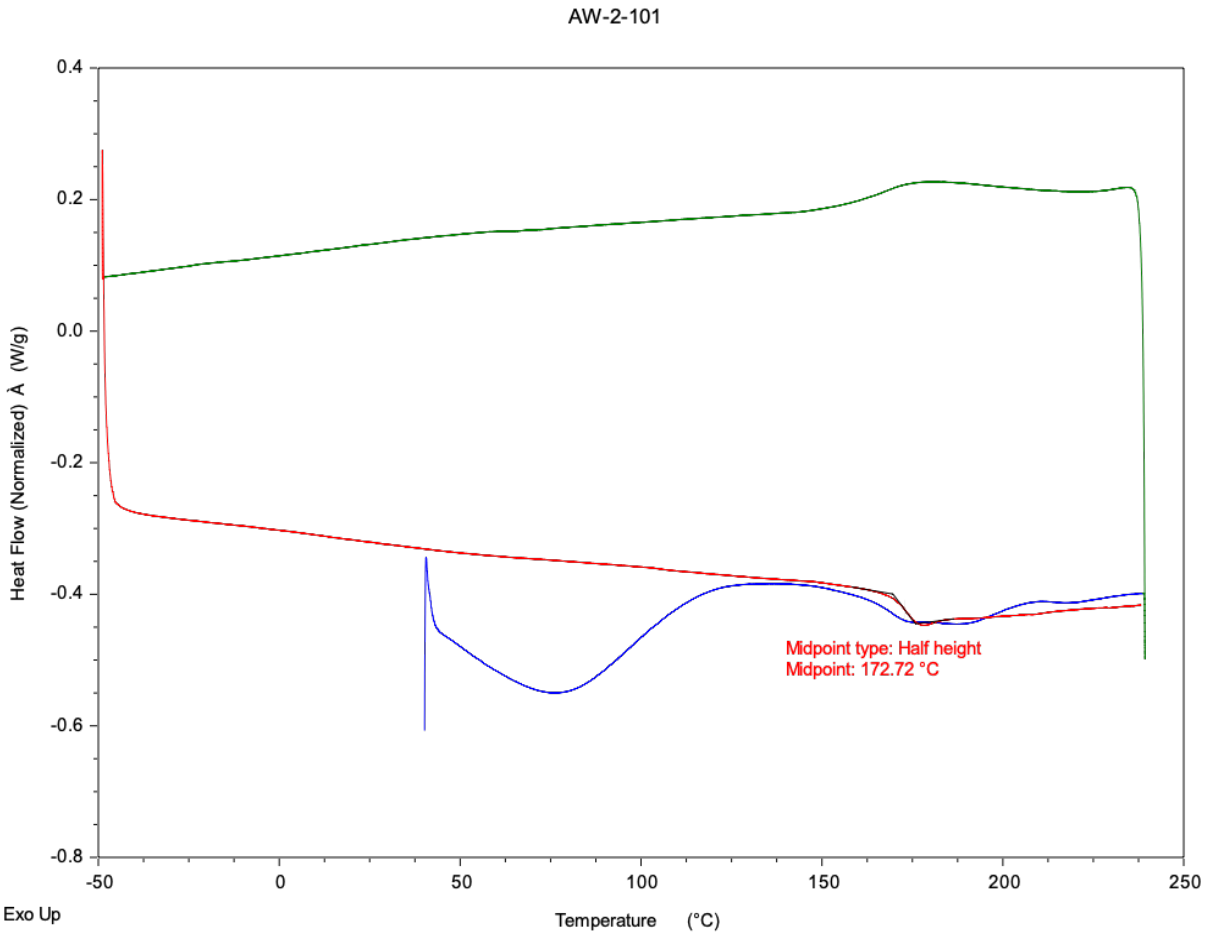
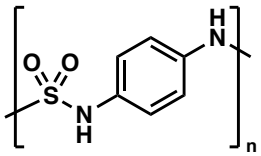


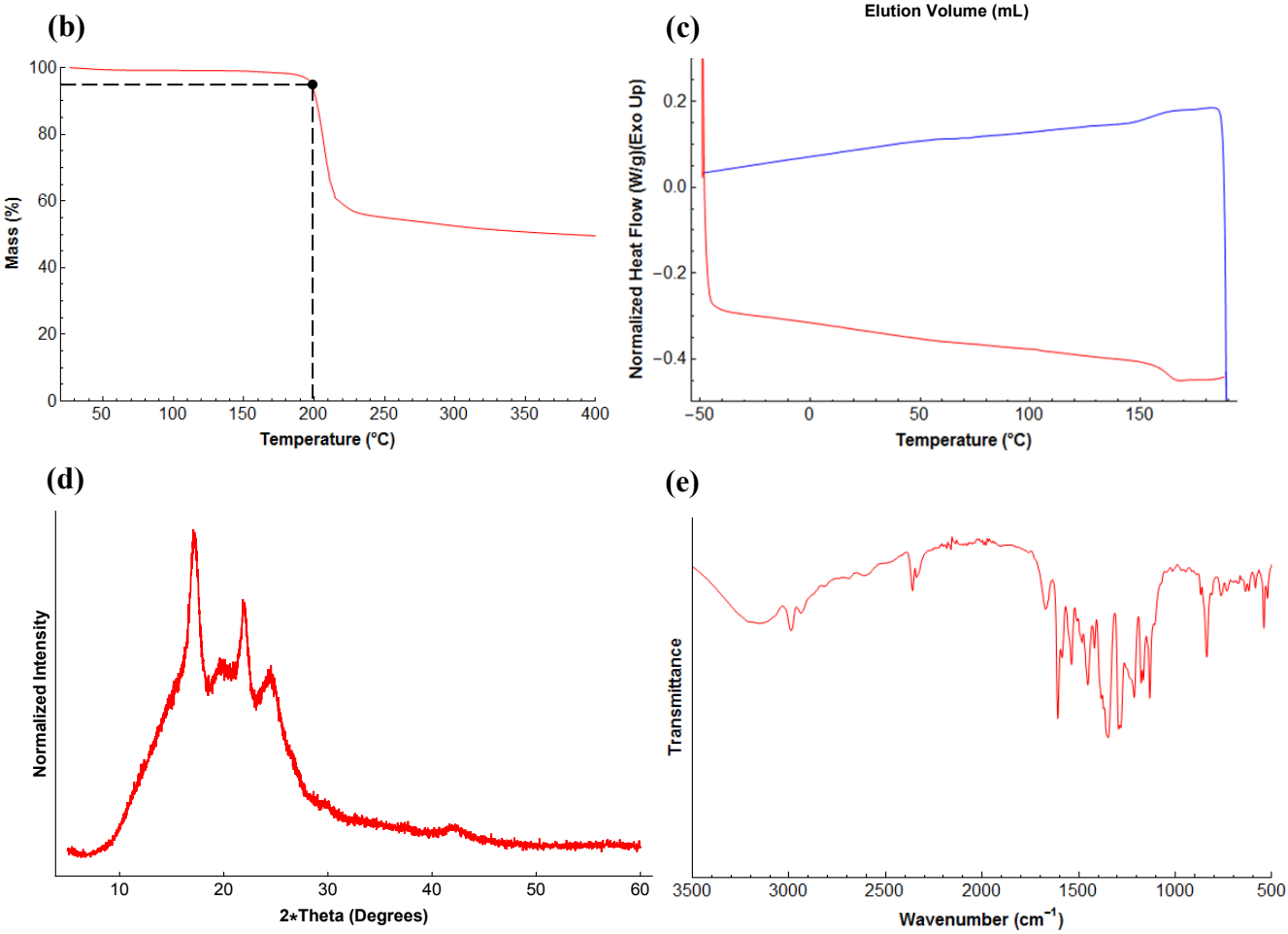
Figure S7. Example of in-software calculation of T_g for polymer **3n** (Performed using TRIOS Software, Developed by TA Instruments) (Blue: First Heating Cycle, Green: First Cooling Cycle, Red: Second Heating Cycle) For all plots shown in Figure S8 to S22, Blue: First Cooling Cycle, Red: Second Heating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

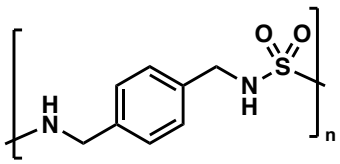
Characterization of Polysulfamides:



3b

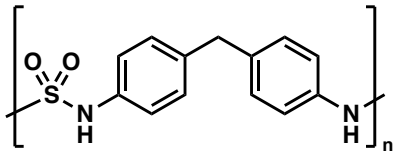
Figure S8.
Characterization of Polysulfamide 3b
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) spectrum.





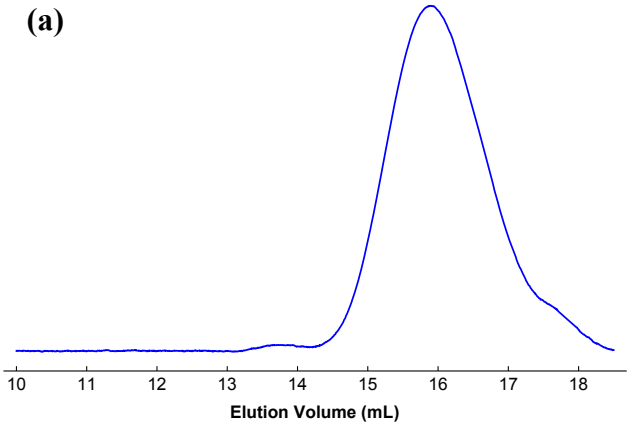
3c

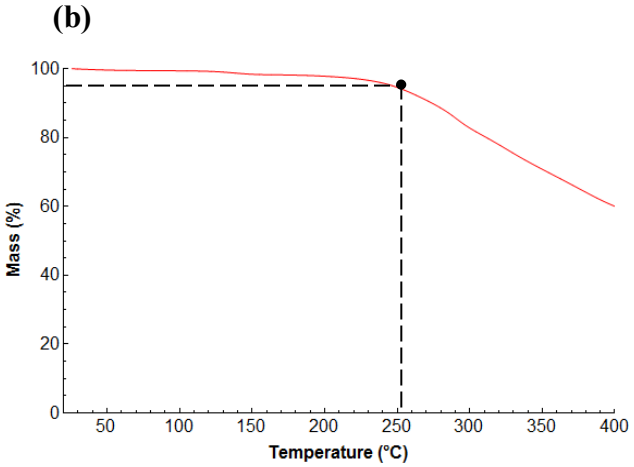
Figure S9.
Characterization of Polysulfamide 3c
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.

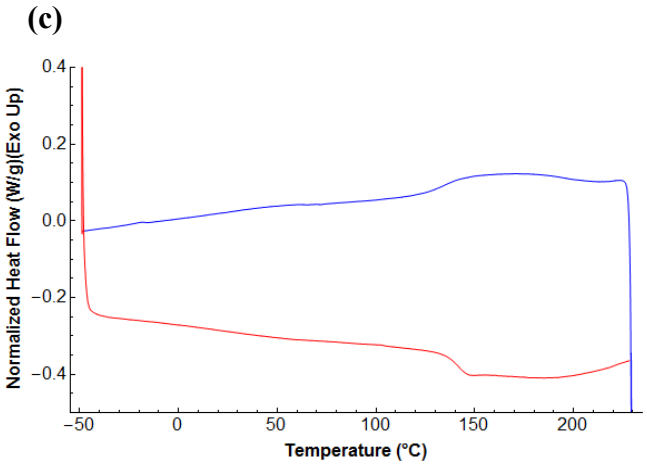


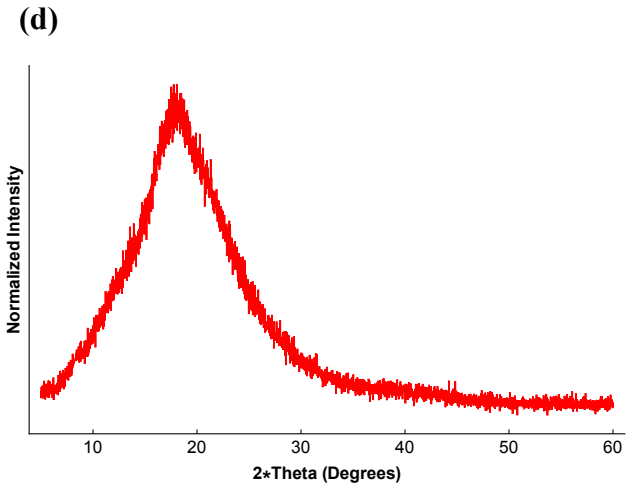
3d

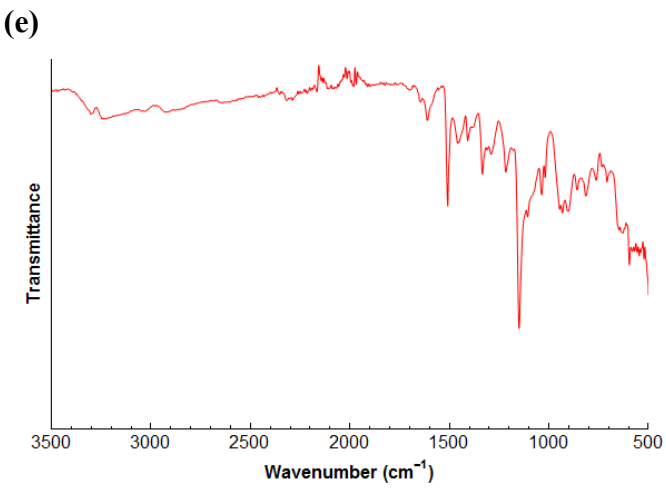
Figure S10.
Characterization of Polysulfamide 3d
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) spectrum.

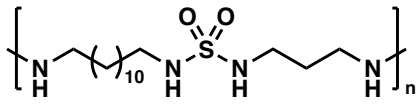






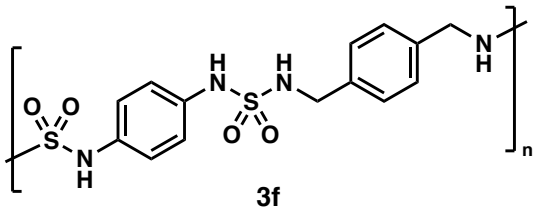






3e

Figure S11.
Characterization of Polysulfamide 3e
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD; (e) FT-IR (ATR) spectrum.



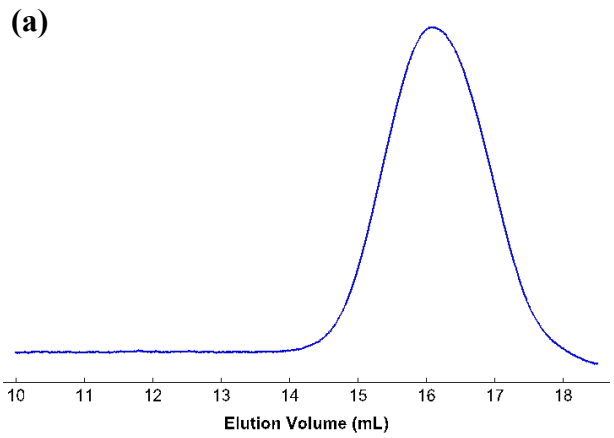
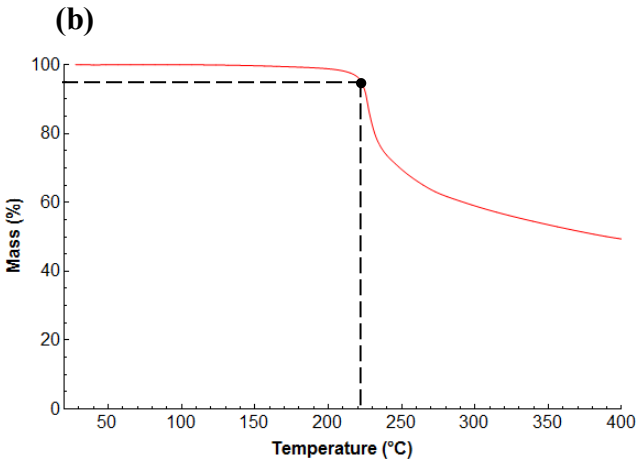
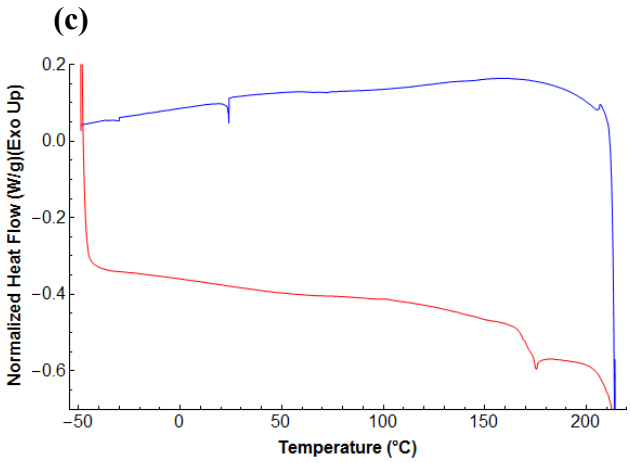
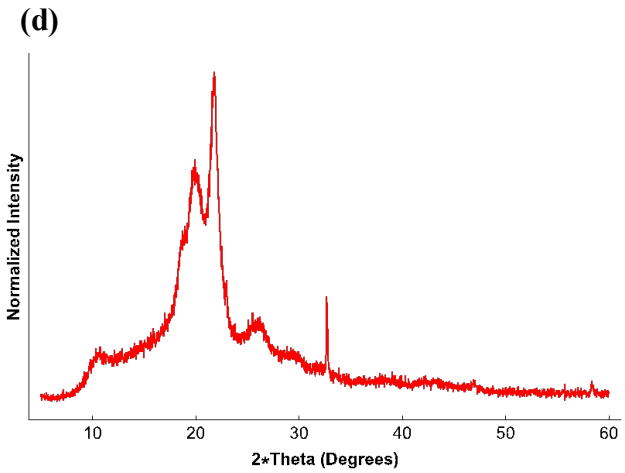
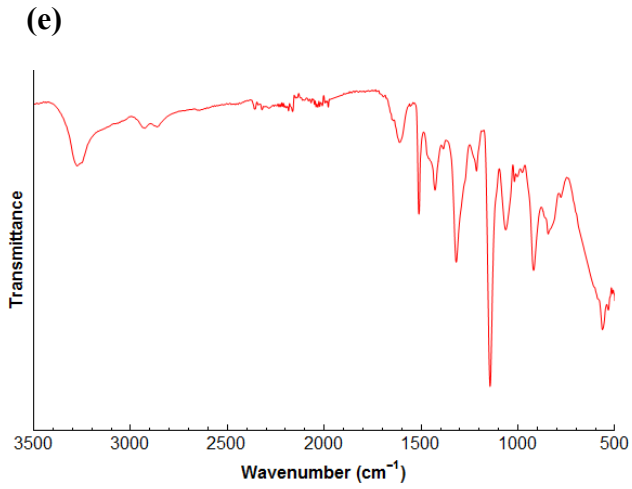


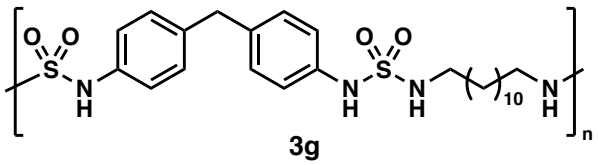
Figure S12.
Characterization of Polysulfamide 3f
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.











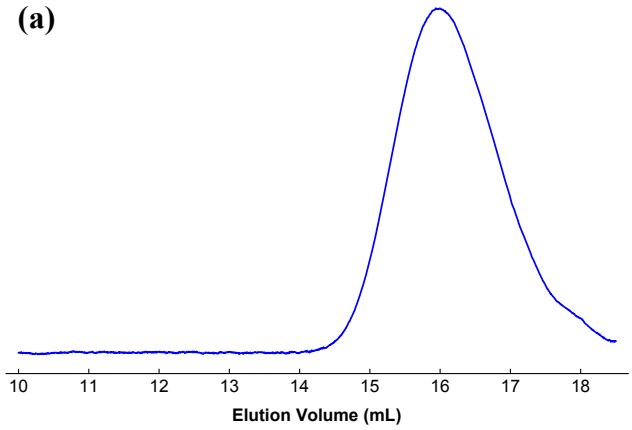
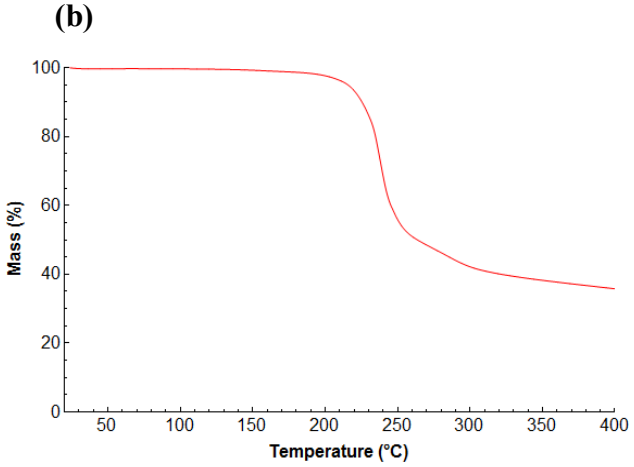
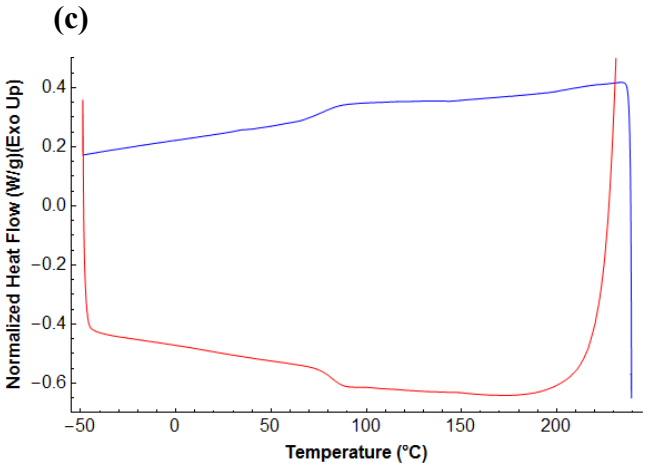
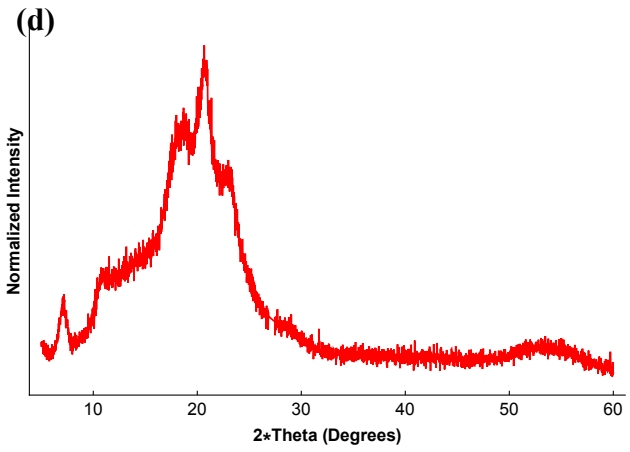
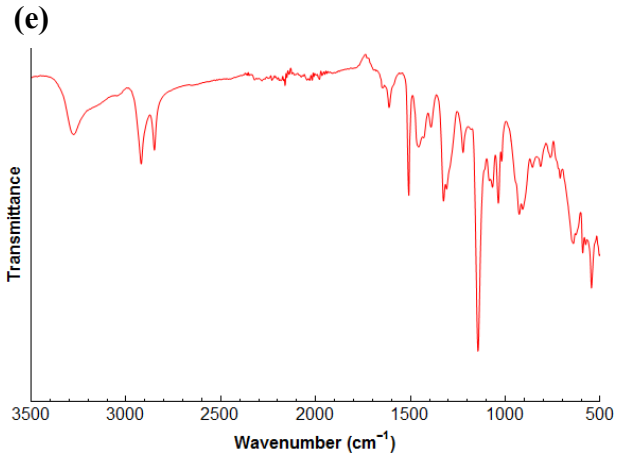


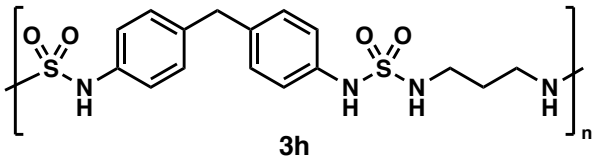
Figure S13.
Characterization of Polysulfamide 3g
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) spectrum.





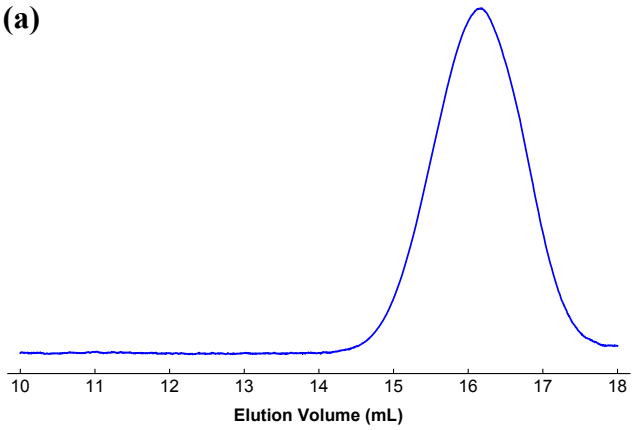


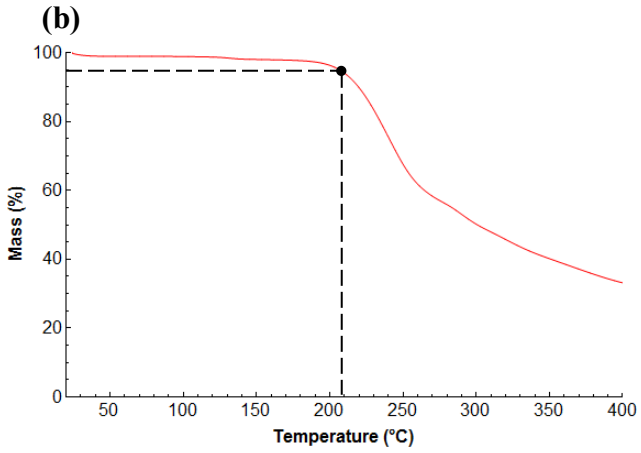


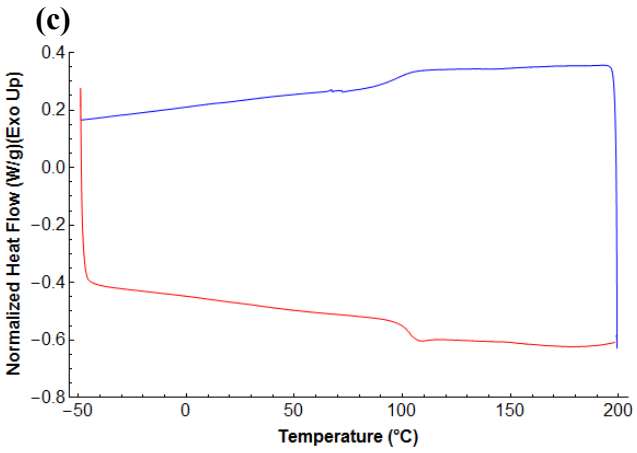


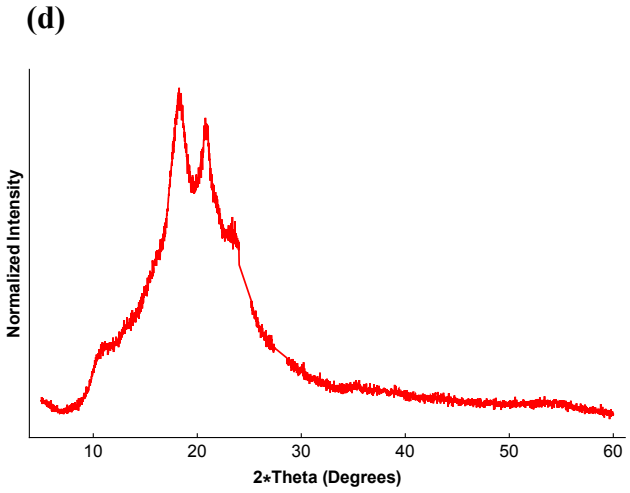
3h

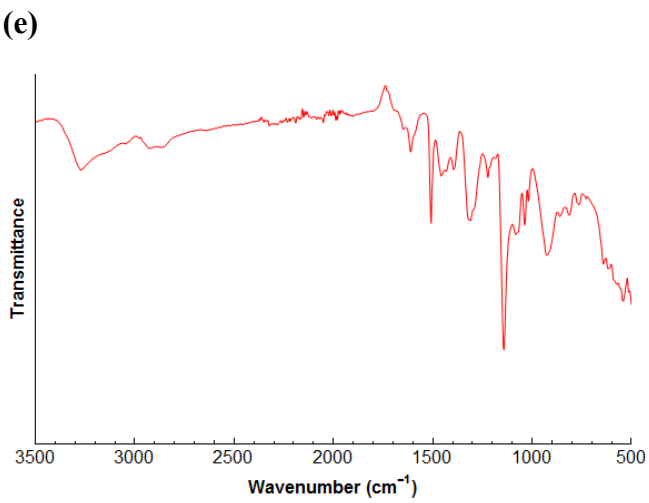
Figure S14.
Characterization of Polysulfamide 3h
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns patterns; (e) FT-IR (ATR) spectrum.

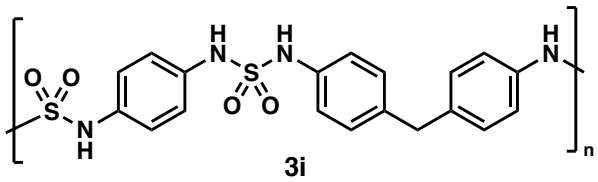












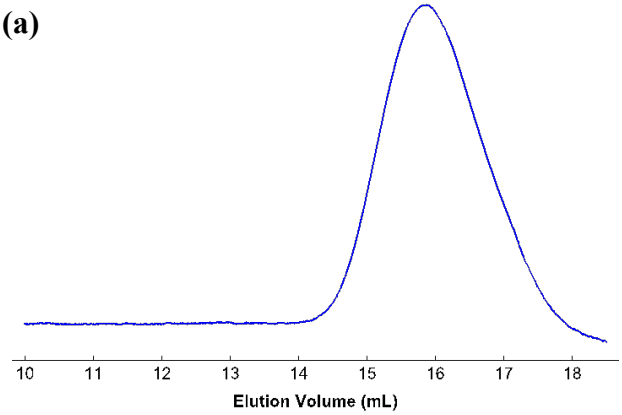
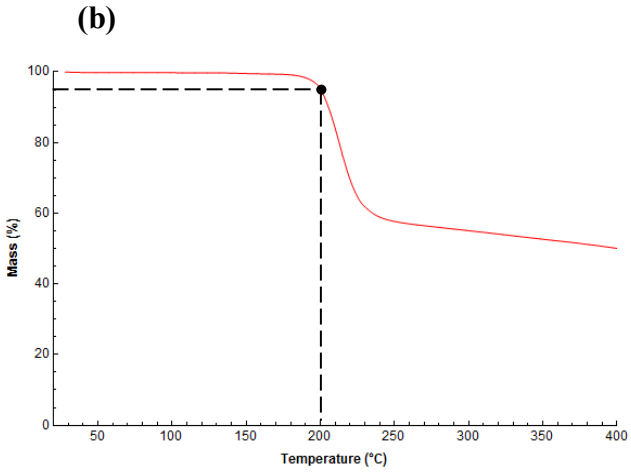
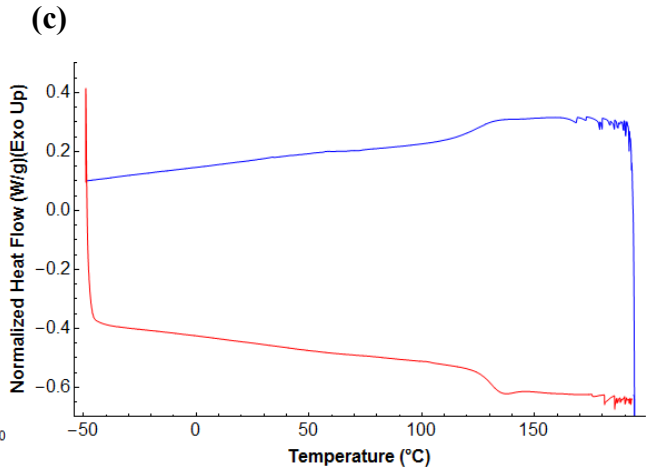
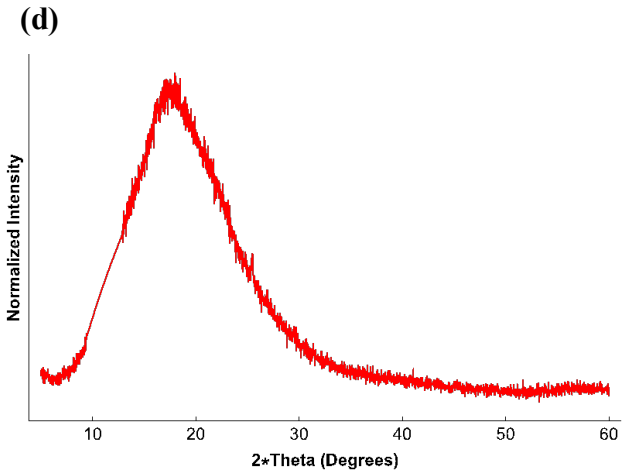
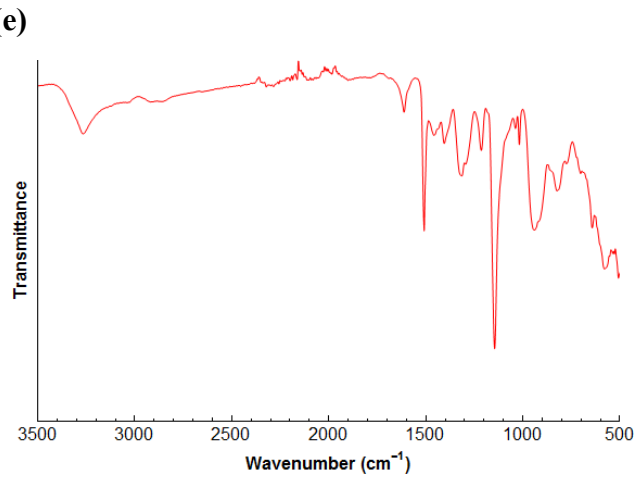


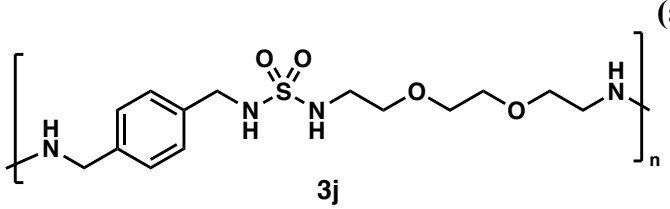
Figure S15.
Characterization of Polysulfamide 3i
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD, (e) FT-IR (ATR) spectrum.











3j

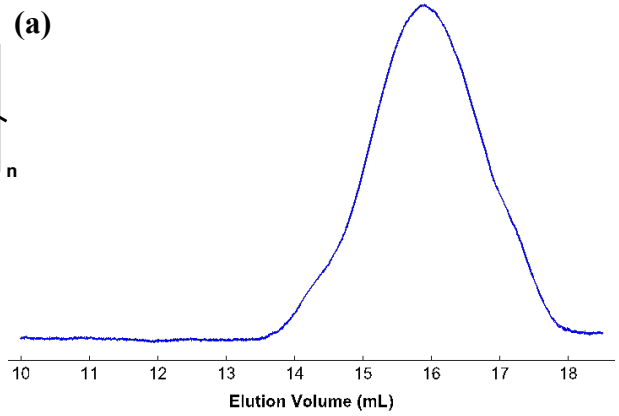
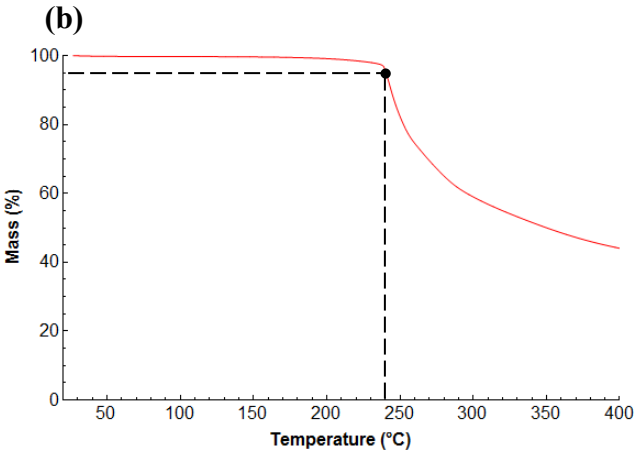
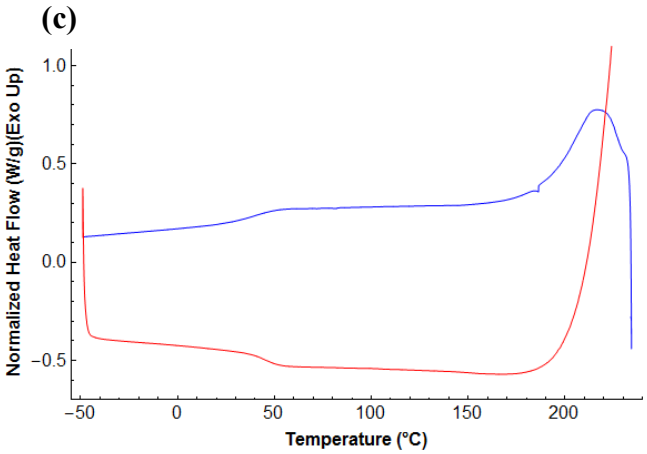
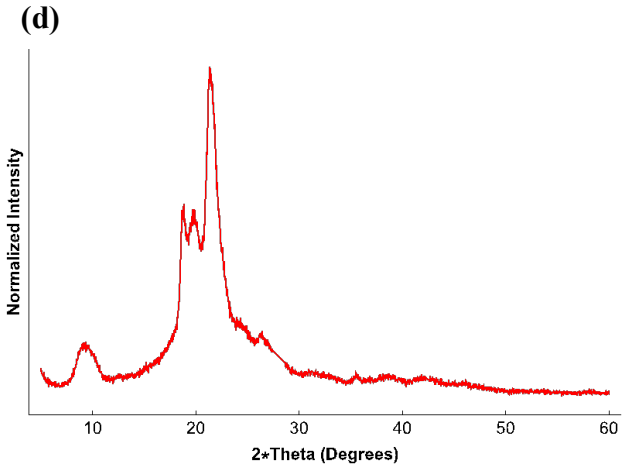
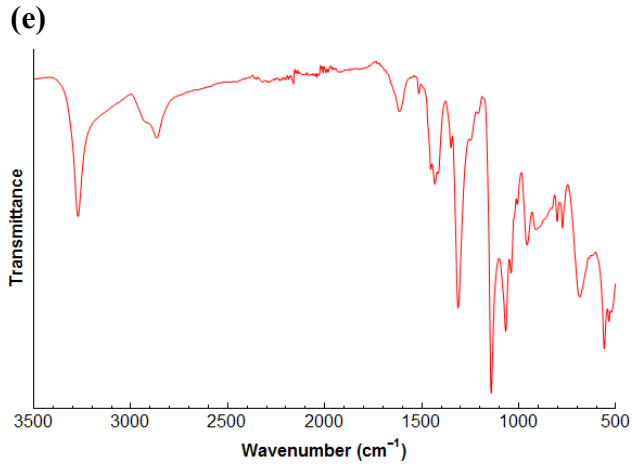


Figure S16.
Characterization of Polysulfamide 3j
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) spectrum.









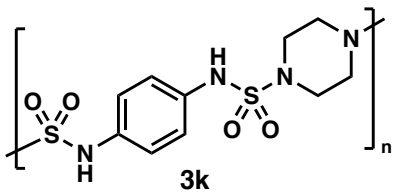
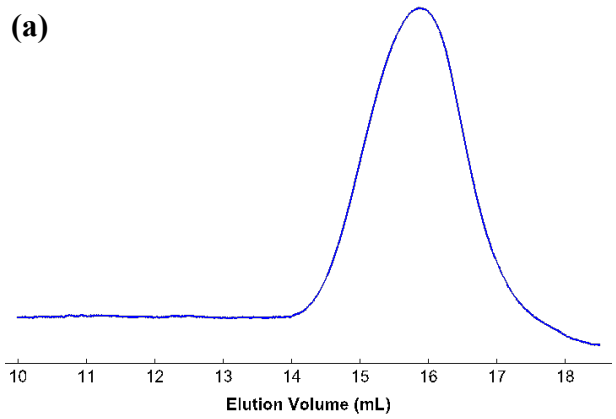
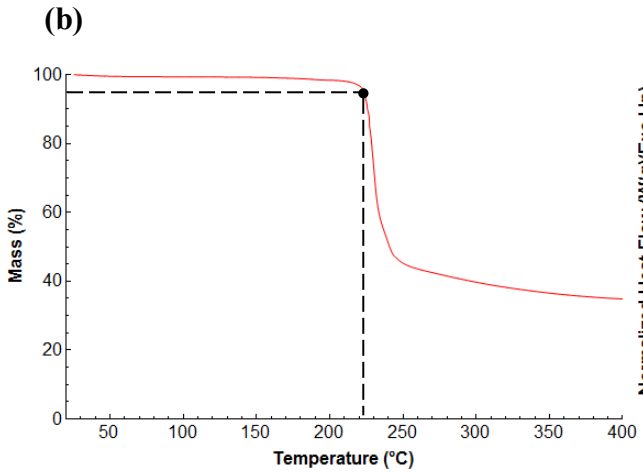
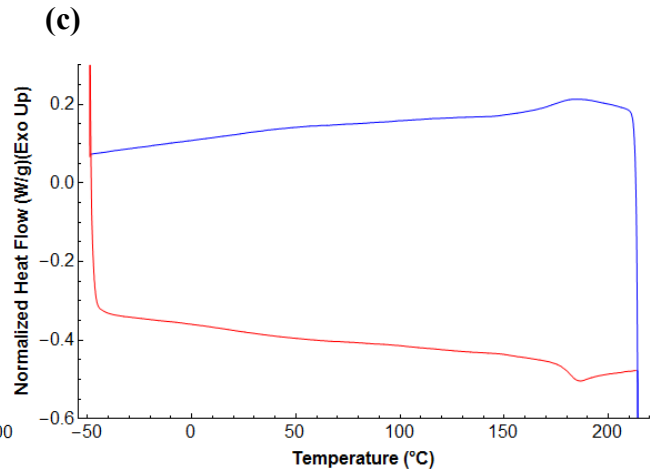
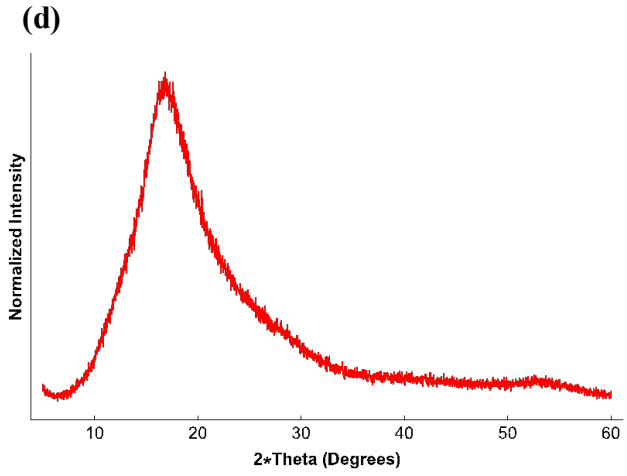


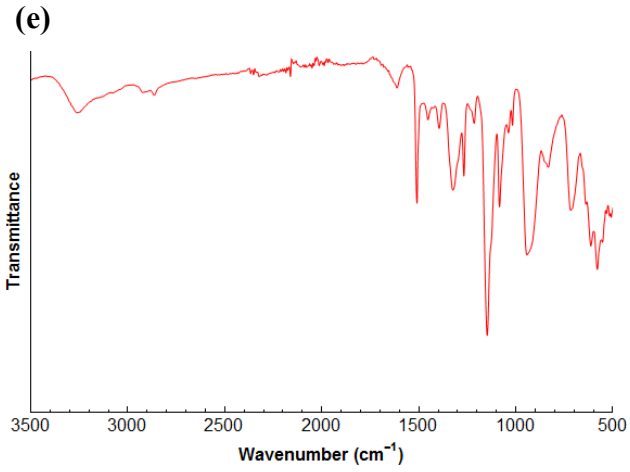
Figure S17.
Characterization of Polysulfamide 3k
(a) SEC trace; (b) TGA curve; (c) DSC curve curve; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.

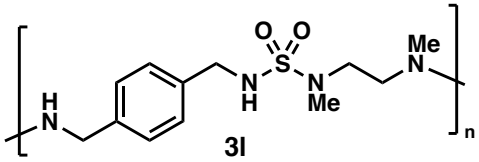






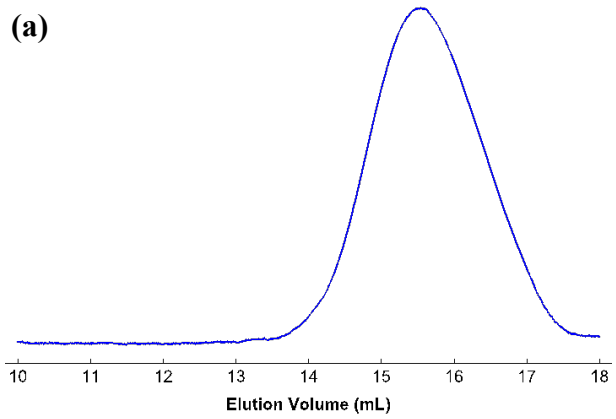


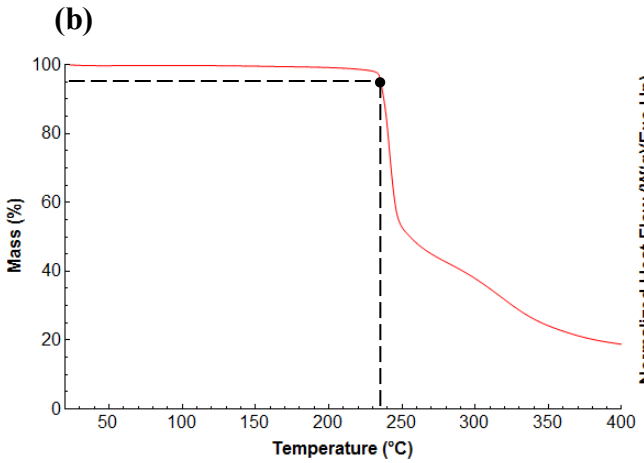


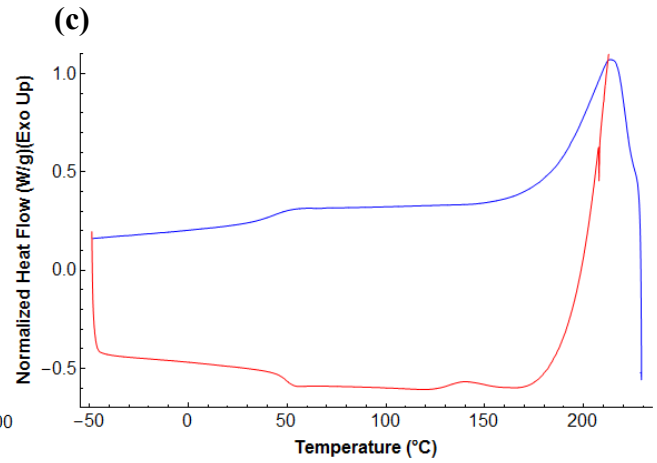


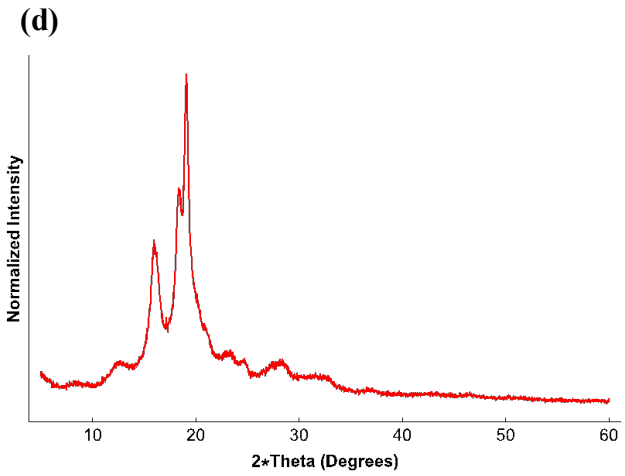
3l

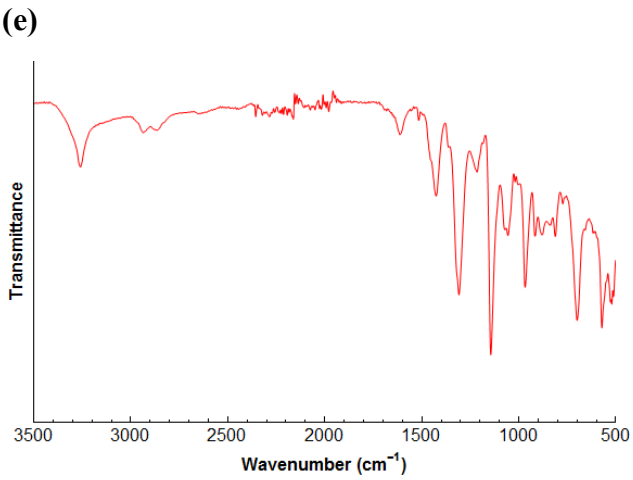
Figure S18.
Characterization of Polysulfamide 3l
(a) SEC trace; (b) TGA curve; (c) DSC; (d) Powder XRD patterns, (e) FT-IR (ATR) spectrum.

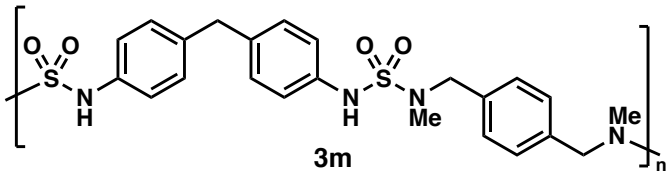






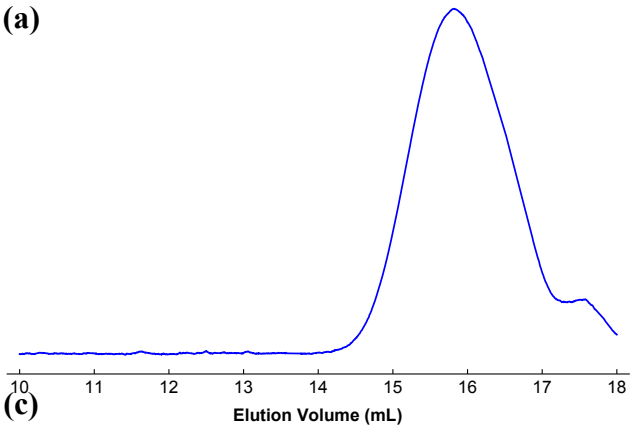


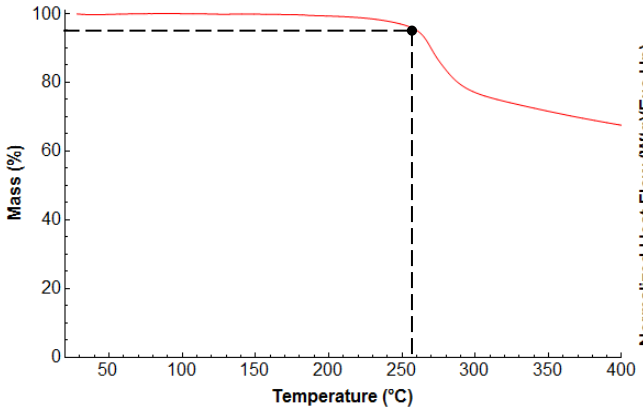


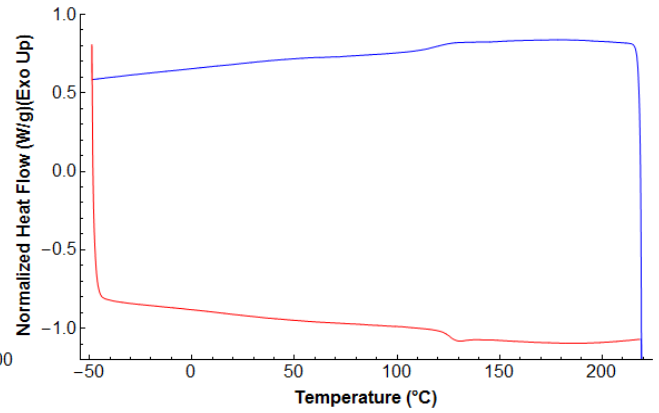


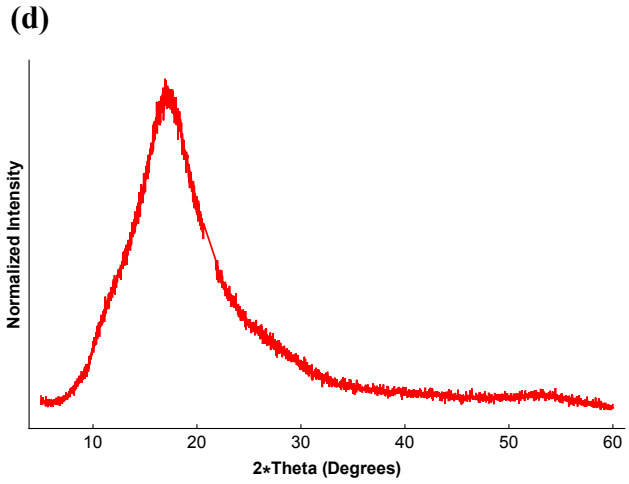
3m

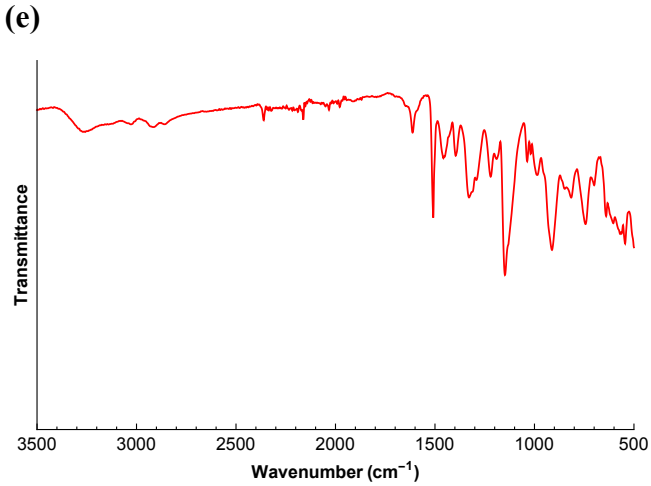
Figure S19.
Characterization of Polysulfamide 3m
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR (ATR) n.











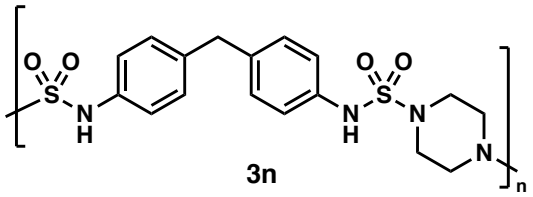


Figure S20.
Characterization of Polysulfamide 3n
(a) SEC trace; (b) TGA curve; (c) DSC curve; (d) Powder XRD patterns; (e) FT-IR.

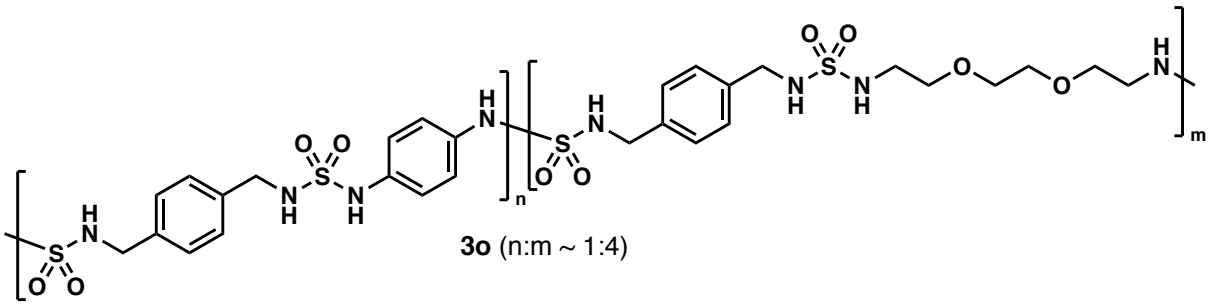
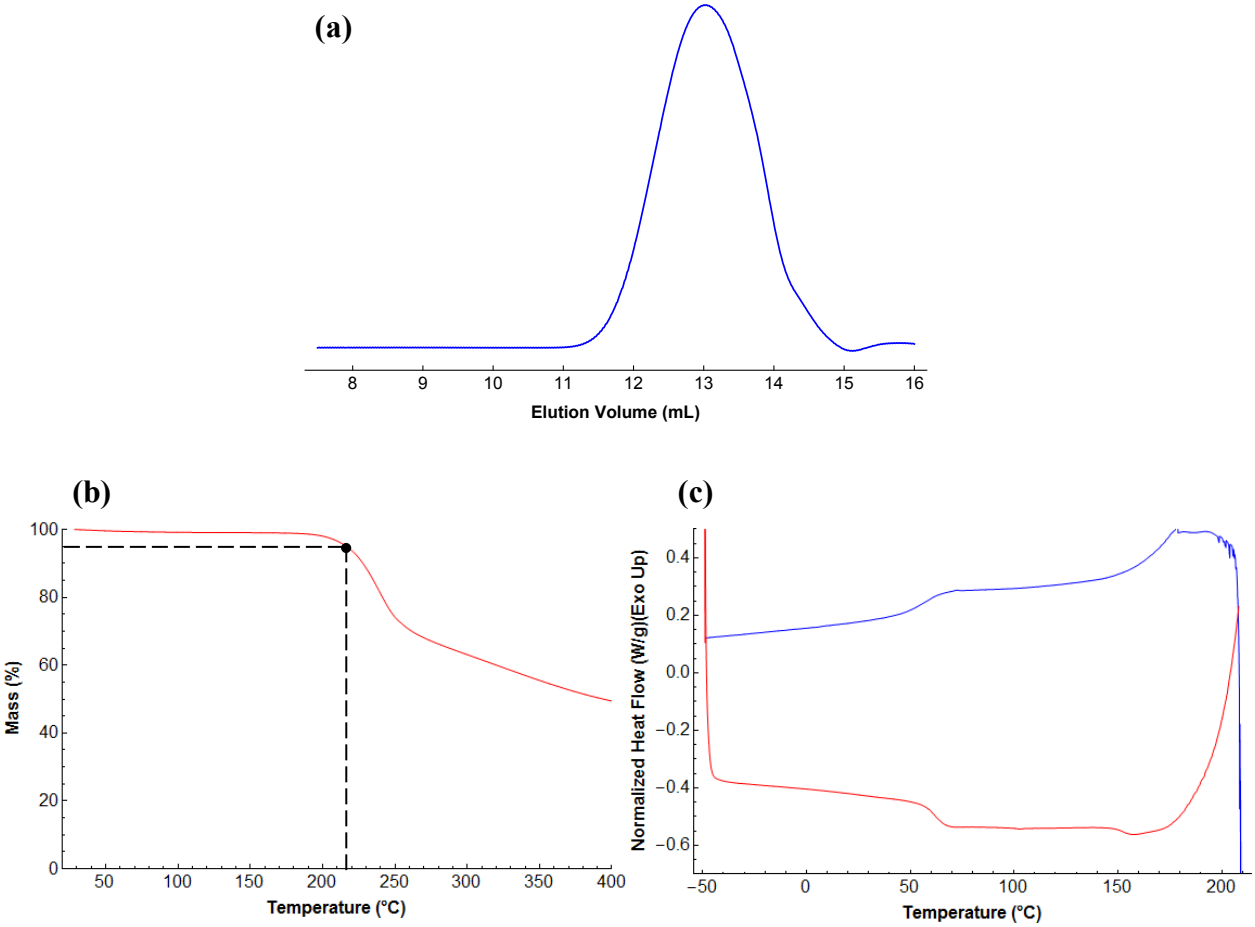


Figure S21.
Characterization of Polysulfamide 3o
(a) SEC trace; (b) TGA curve; (c) DSC curve.



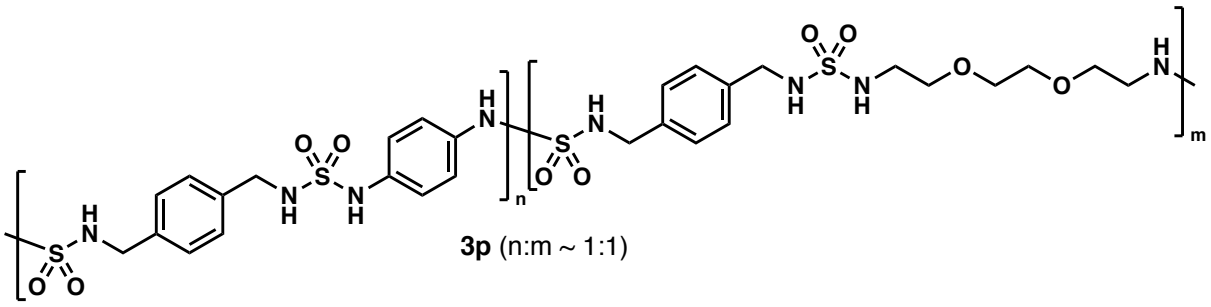
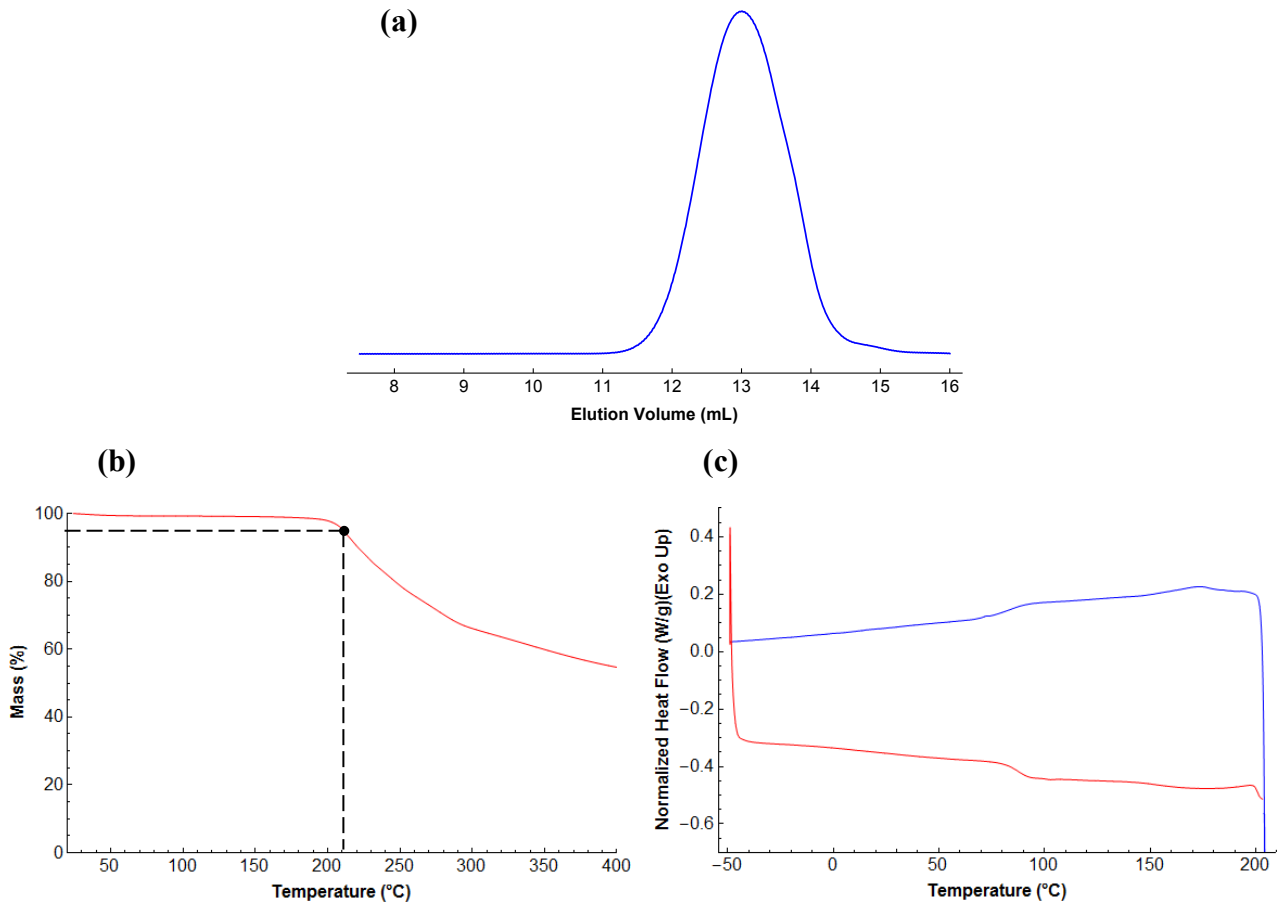


Figure S22.
Characterization of Polysulfamide 3p
(a) SEC trace; (b) TGA curve; (c) DSC curve.



Predicted T_g values of copolymers **3o** and **3p** using the Fox equation:

$$\frac{1}{T_{g,mix}} = \sum \frac{\omega_i}{T_{g,i}}$$

where $T_{g,\,mix}$ and $T_{g,\,i}$ are the glass transition temperatures of the copolymer and of the components, respectively, and ω_i is the mass fraction of component *i*, the theoretical glass transition temperatures of copolymers **3o** and **3p** were calculated using the glass transition temperatures of polymers **3f** (170 °C) and **3j** (46 °C).

Table S6. Predicted vs experimental T_g values for copolymers **3o** and **3p**

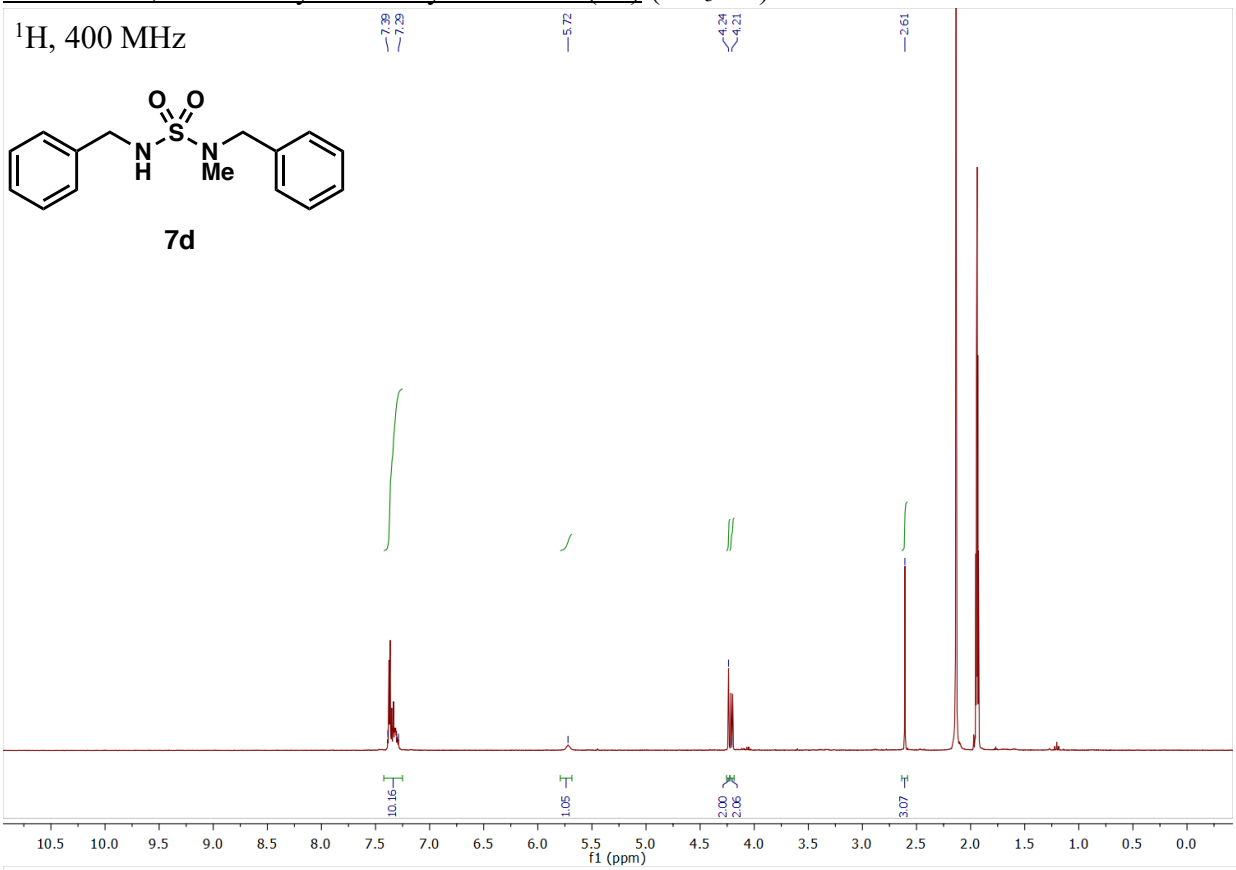
Polymer	*m:n*	Mass Fraction (ω_m)	Mass Fraction (ω_n)	Predicted T_g (°C)	Experimental T_g (°C)
3o	0.2:0.8	0.18	0.82	53	62
3p	0.5:0.5	0.47	0.53	70	88

The theoretical T_g of each polymer was significantly lower than the experimental T_g determined through DSC analysis. These discrepancies are likely the result of intermolecular interactions such as hydrogen bonding between polymers.

NMR Spectra of Synthesized Sulfamoyl Fluorides, Sulfamides, and Polysulfamides

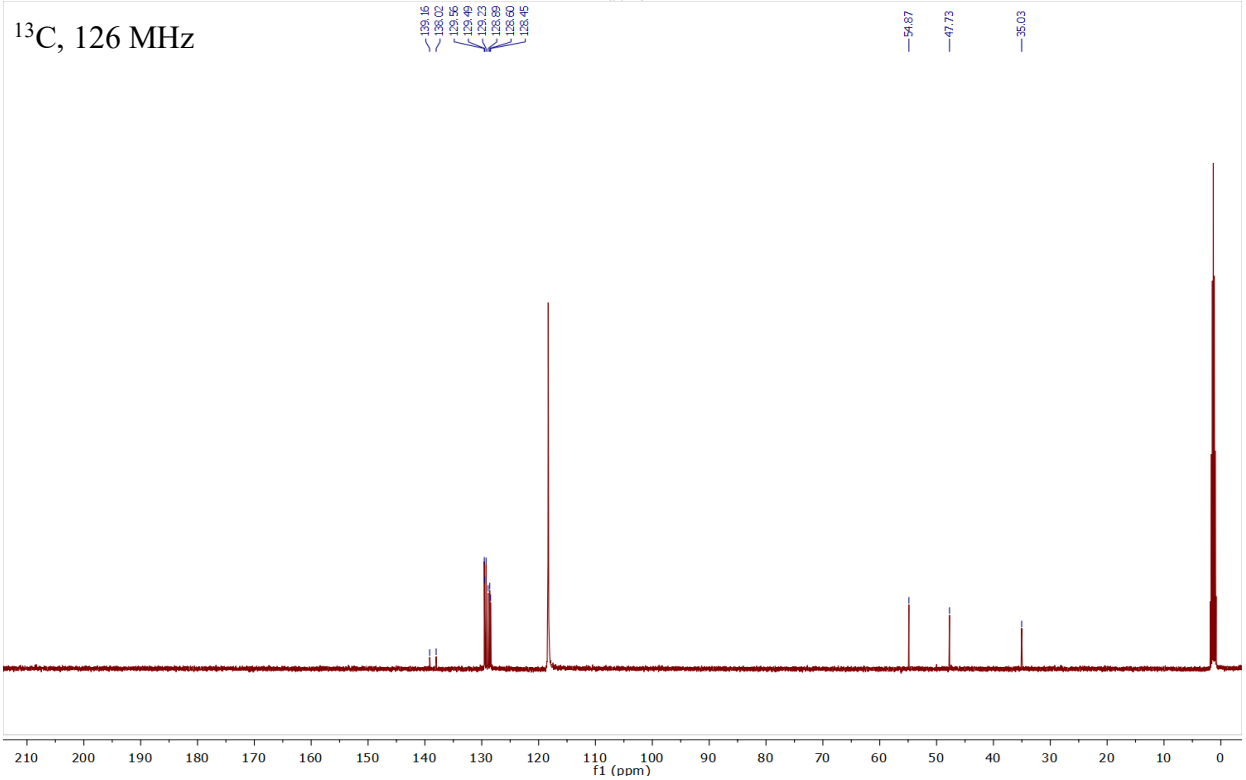
NMRs of *N,N'*-Dibenzyl-*N*-methylsulfamide (**7d**) (CD_3CN)

^1H, 400 MHz



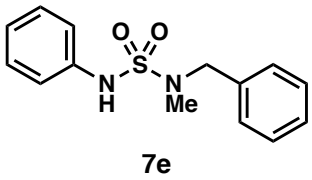
7d

^{13}C, 126 MHz



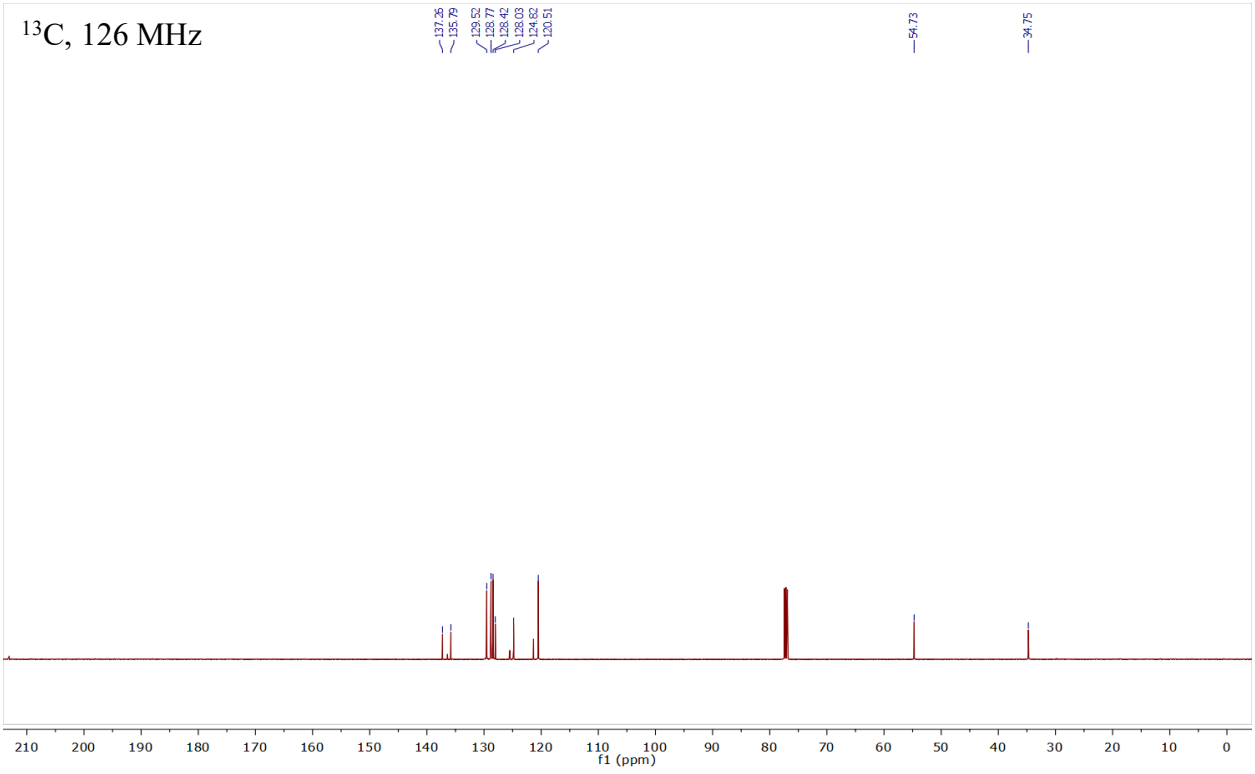
NMRs of *N*-Benzyl-*N*-methyl-*N'*-phenylsulfamide (**7e**) ($CDCl_3$)

^1H, 400 MHz



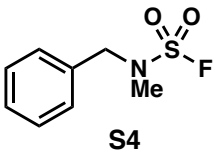
7e

^{13}C, 126 MHz



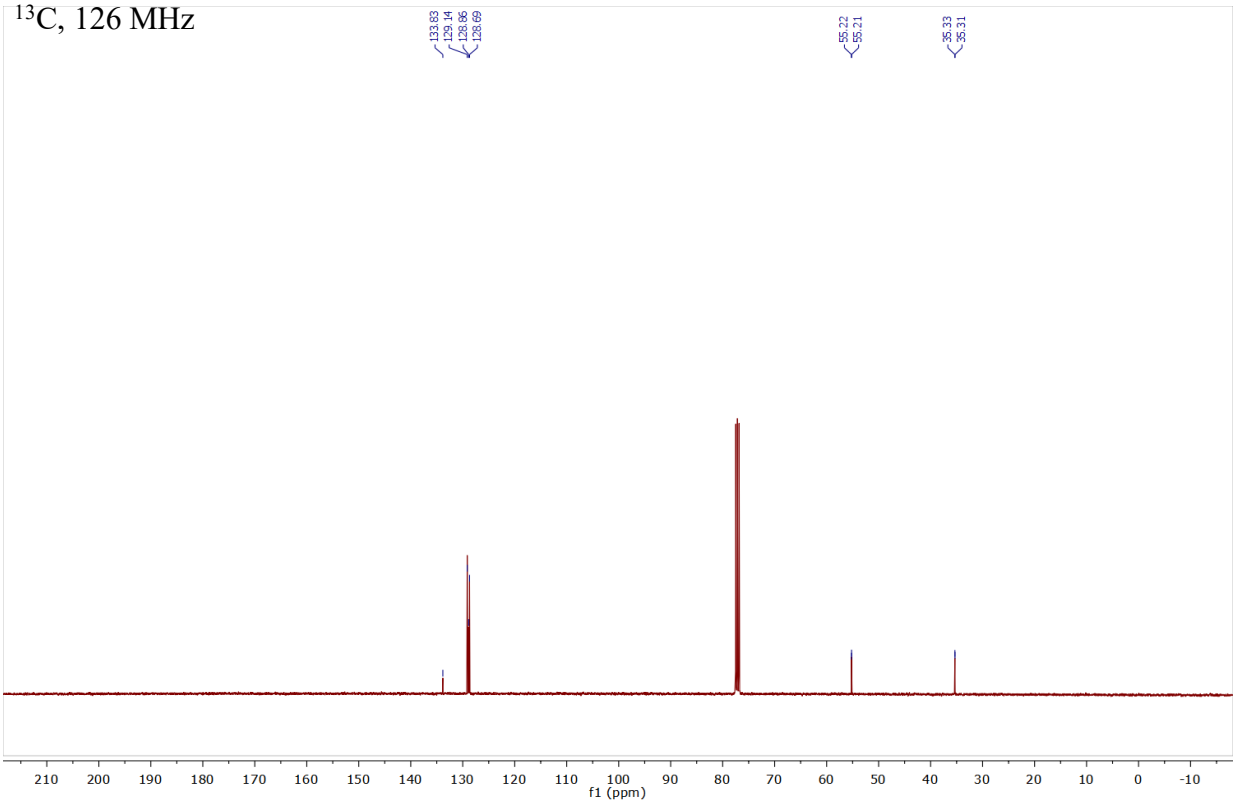
NMRs of *N*-Methylbenzylsulfamoyl Fluoride (**S4**) ($CDCl_3$)

^{1}H, 400 MHz

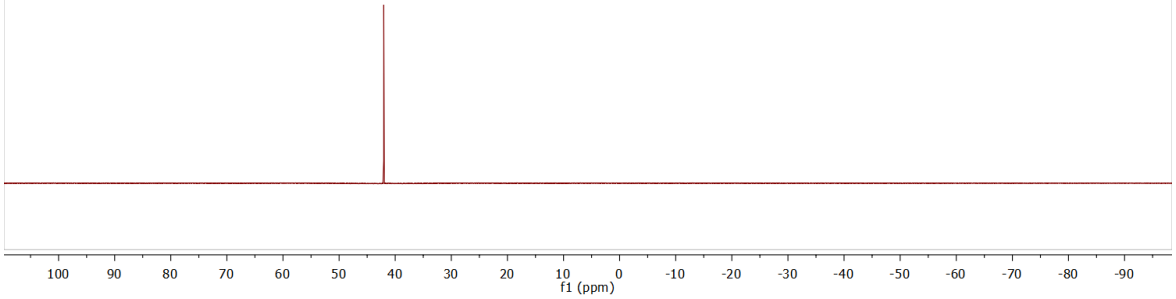


S4

^{13}C, 126 MHz

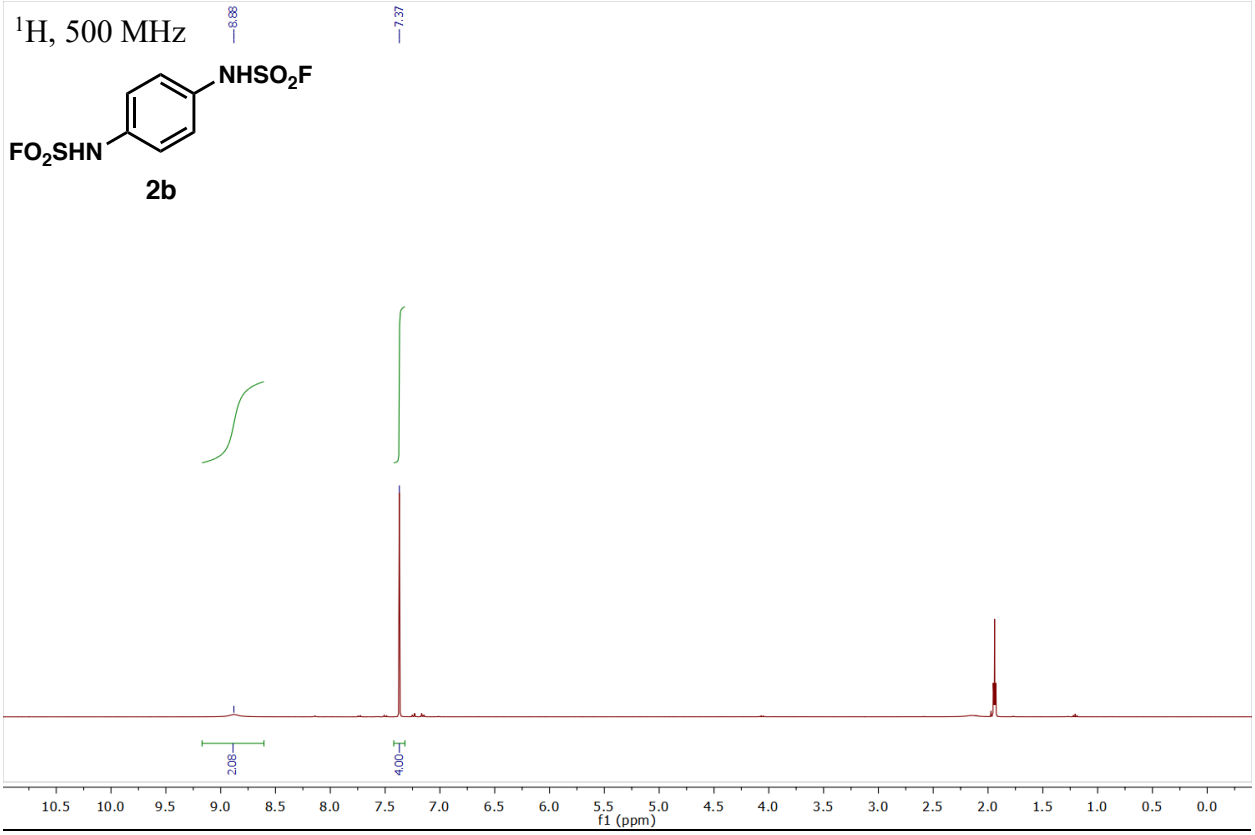


^{19}F, 470 MHz

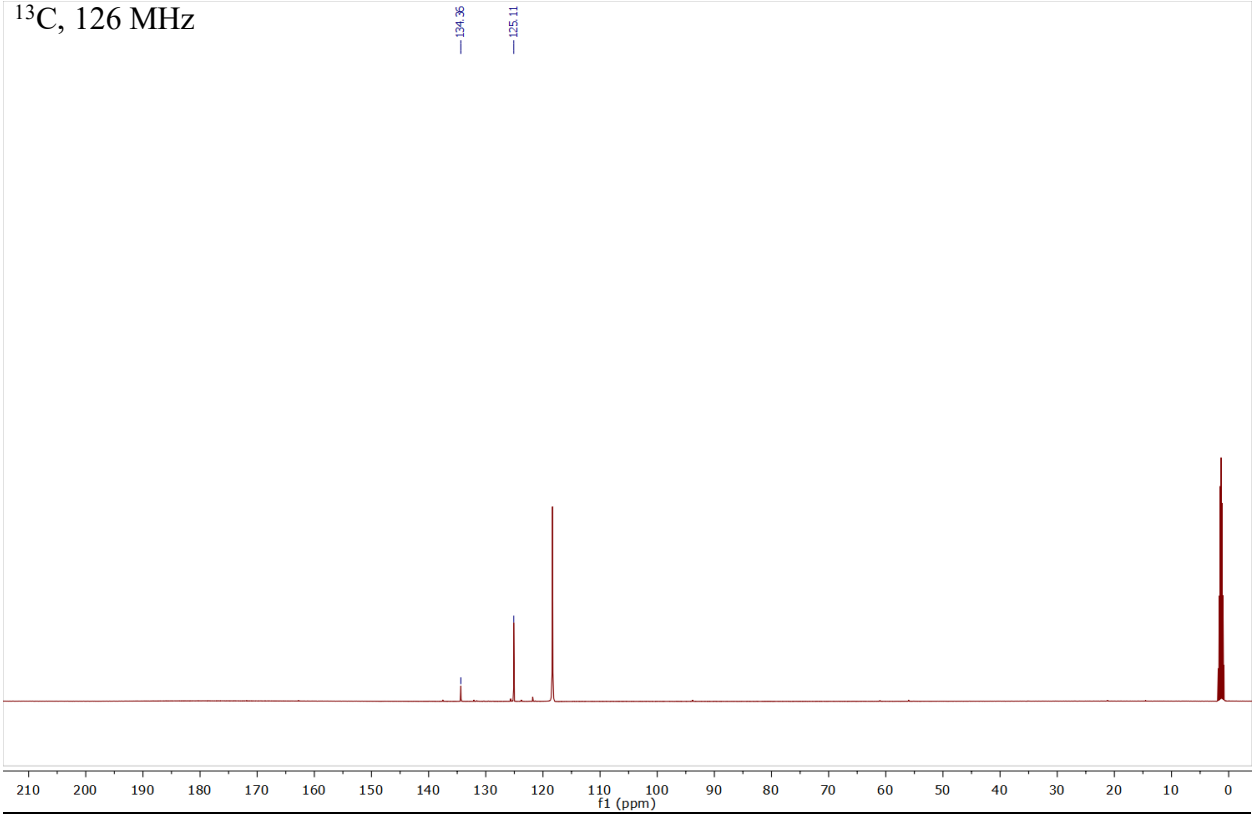


NMRs of 1,4-Phenylenebis(sulfamoyl fluoride) (**2b**) (CD_3CN)

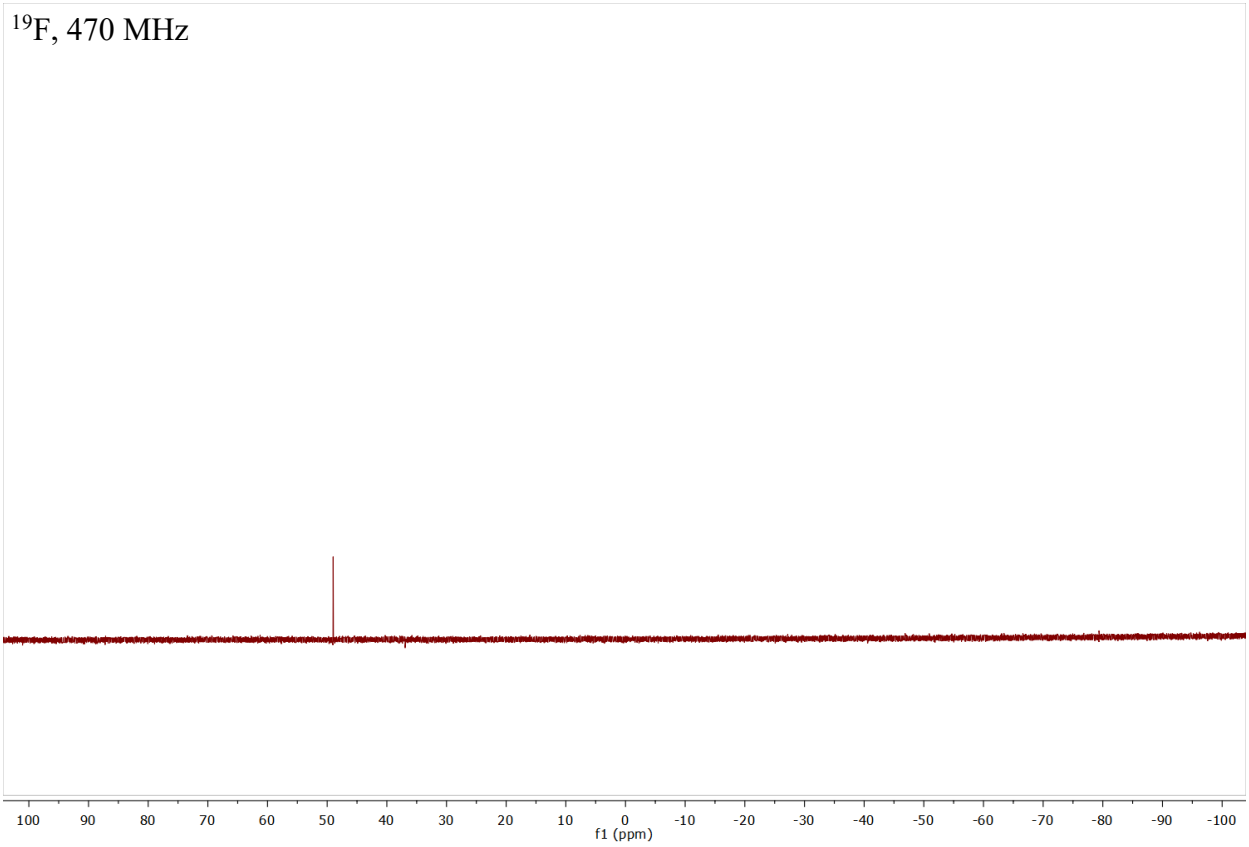
^{1}H, 500 MHz



^{13}C, 126 MHz

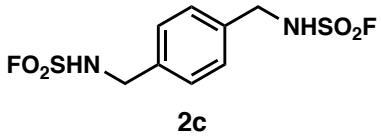


^{19}F, 470 MHz



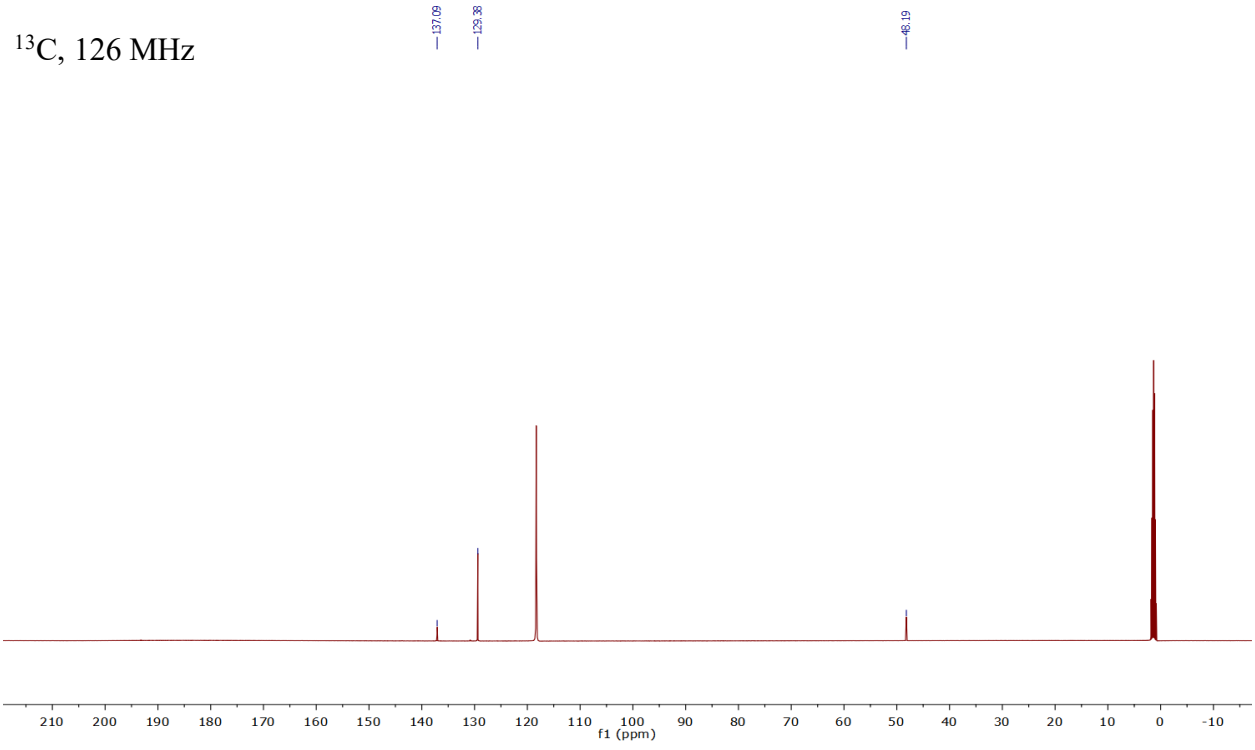
NMRs of (1,4-phenylenebis(methylene))bis(sulfamoyl fluoride) (**2c**) (CD_3CN)

^1H, 500 MHz

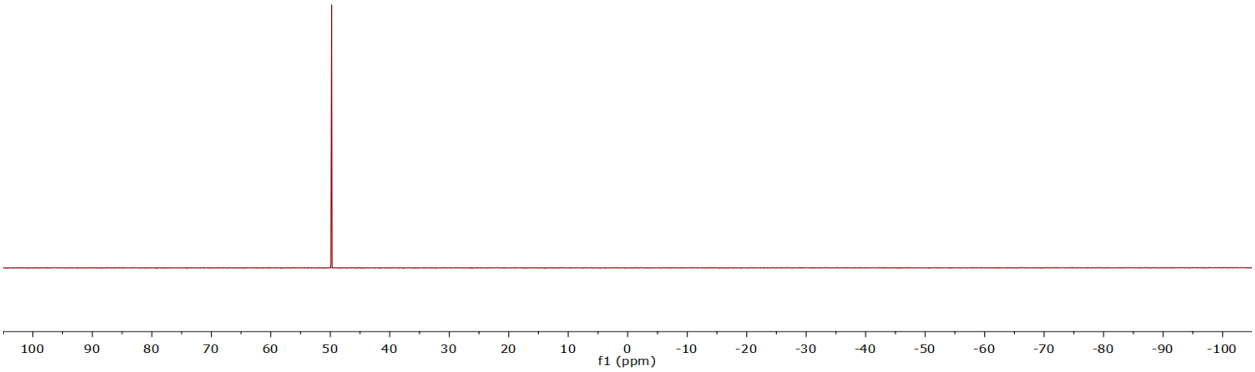


2c

^{13}C, 126 MHz

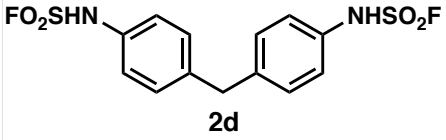


^{19}F, 470 MHz



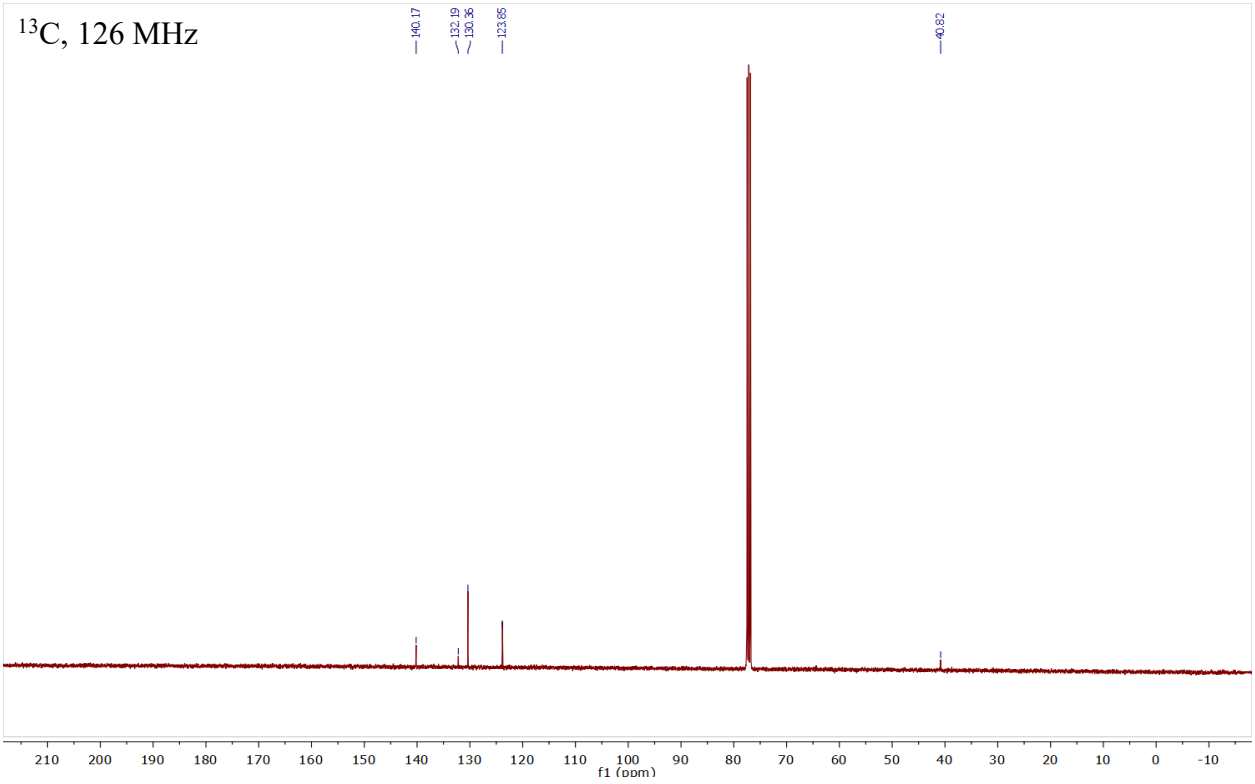
NMRs of (Methylenebis(1,4-phenylene))bis(sulfamoyl fluoride) (**2d**) ($CDCl_3$)

^{1}H, 400 MHz

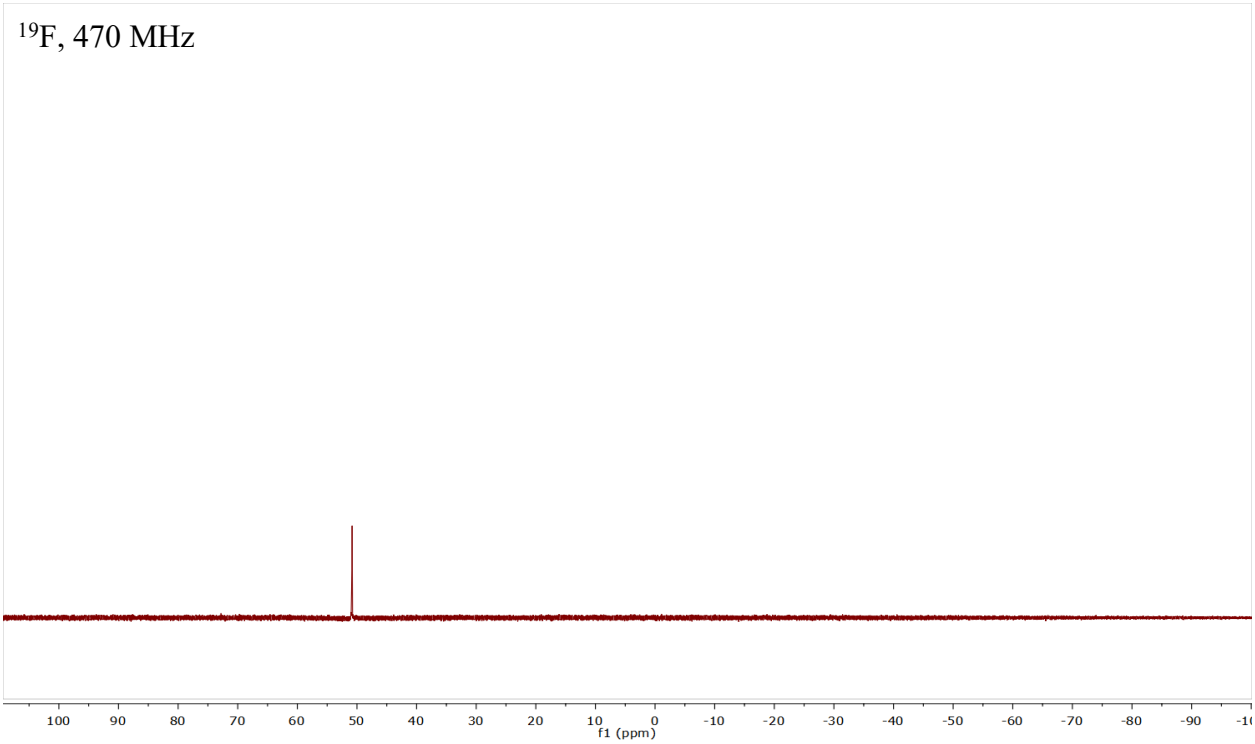


2d

^{13}C, 126 MHz



^{19}F, 470 MHz

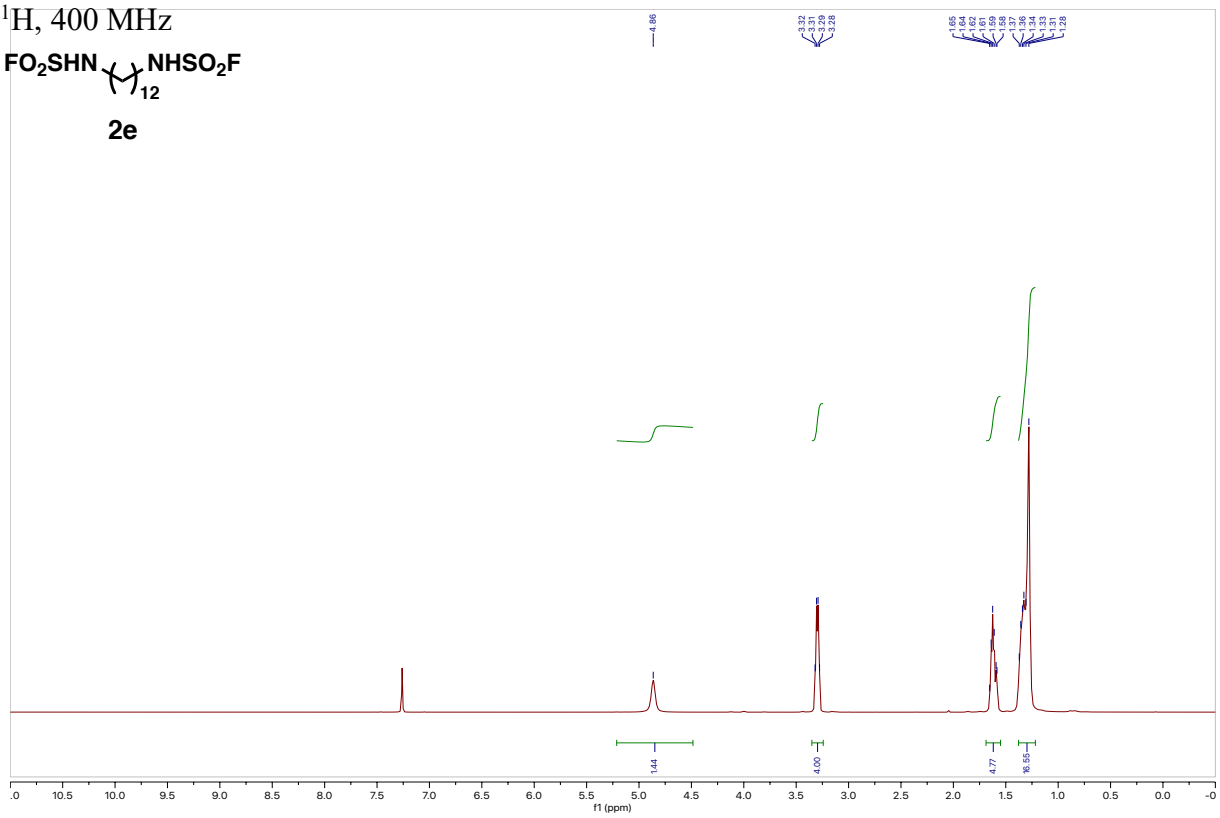


NMR of Dodecane-1,12-bis(sulfamoyl fluoride) (**2e**) ($CDCl_3$)

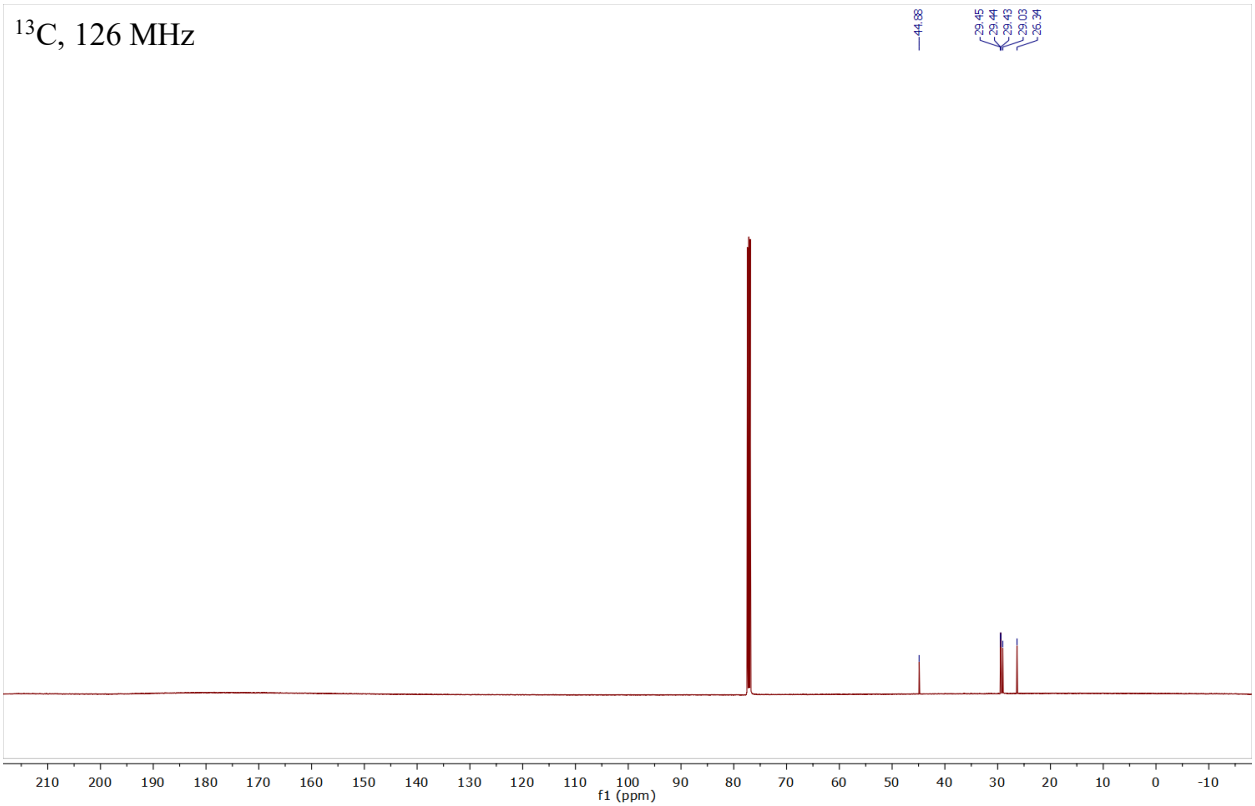
^1H, 400 MHz

$FO_2SHN-(CH_2)_{12}-NHSO_2F$

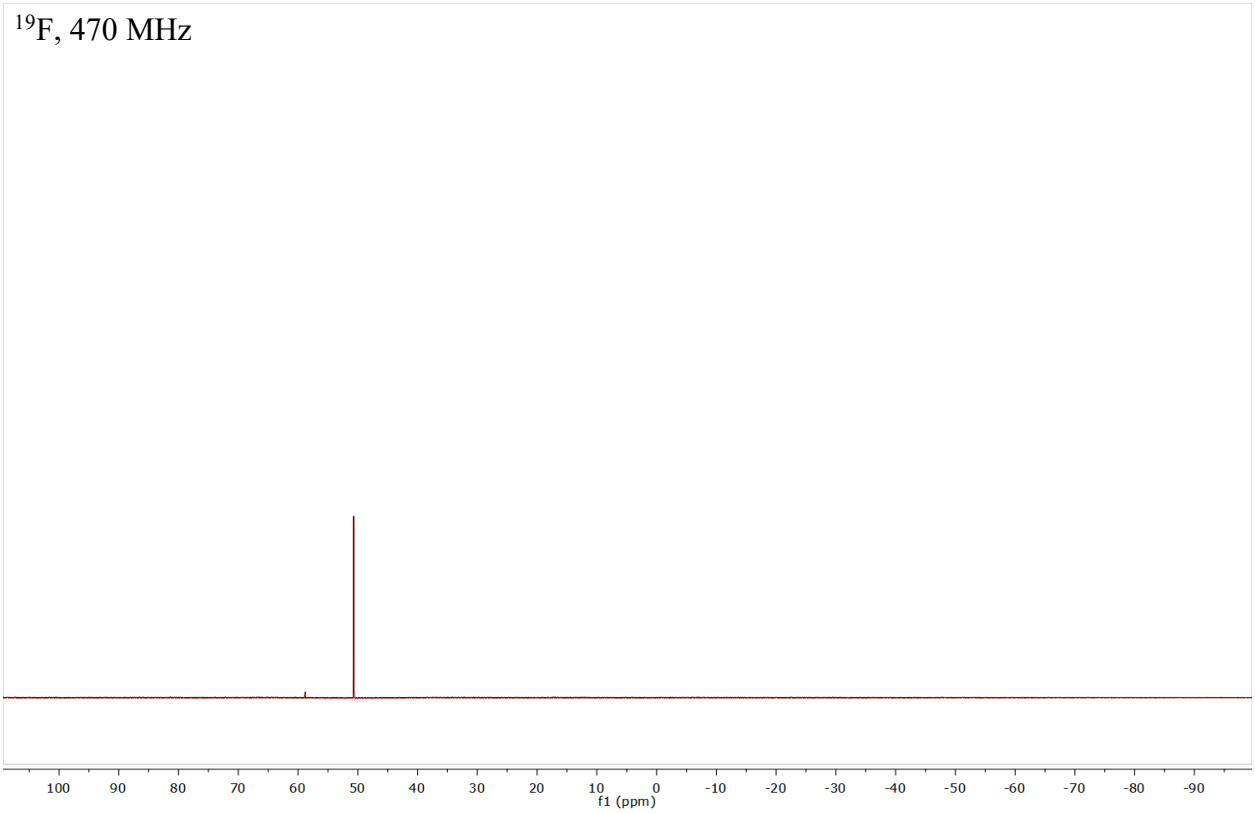
2e



^{13}C, 126 MHz

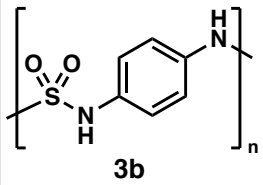


^{19}F, 470 MHz



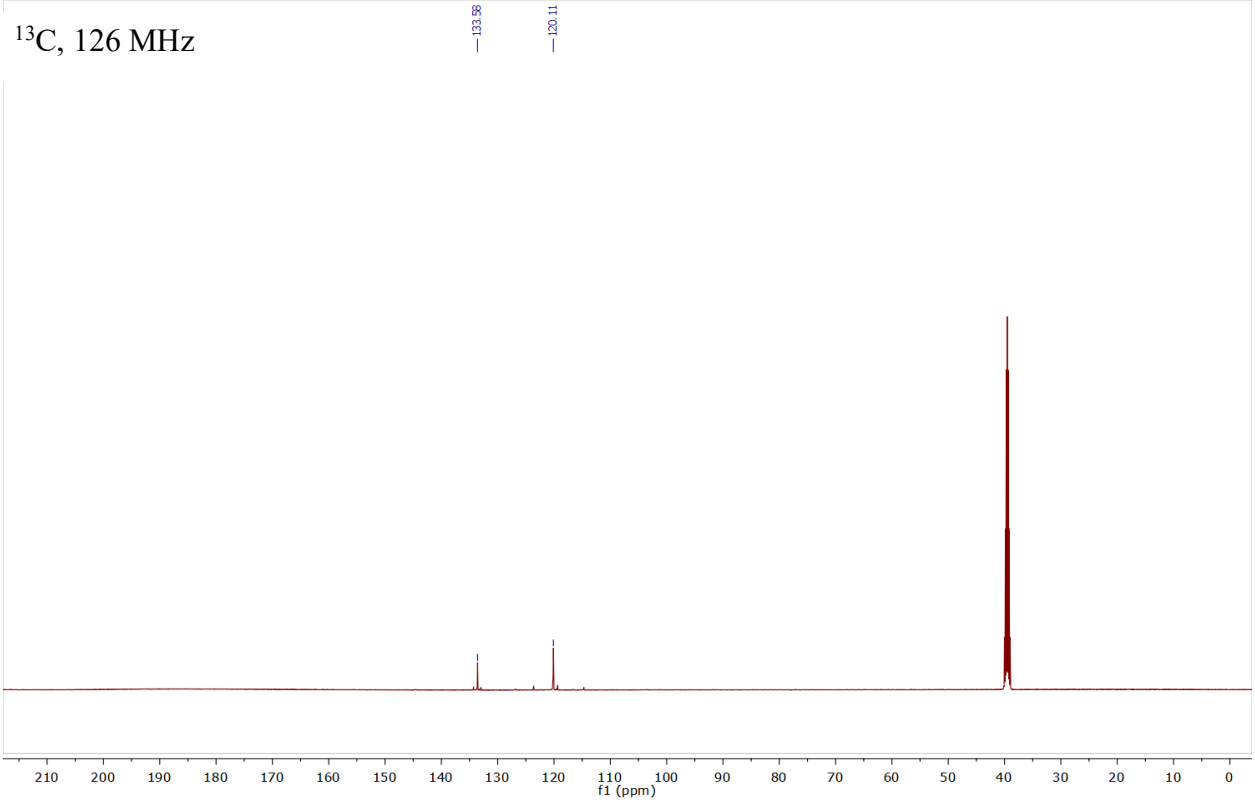
NMRs of polysulfamide **3b** (d_6-DMSO)

^{1}H, 500 MHz



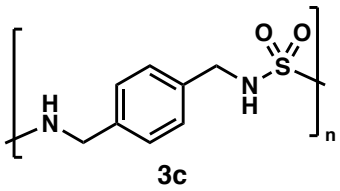
3b

^{13}C, 126 MHz



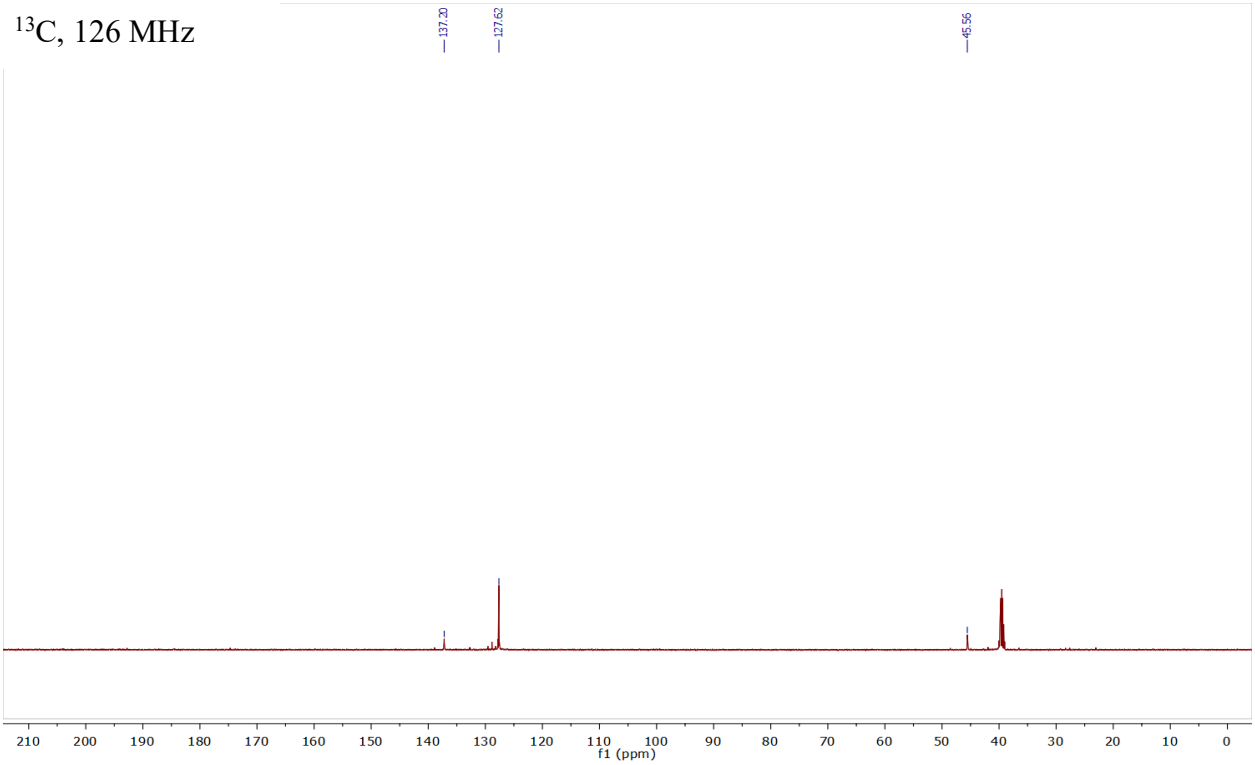
NMRs of polysulfamide **3c** (d_6-DMSO)

^{1}H, 500 MHz



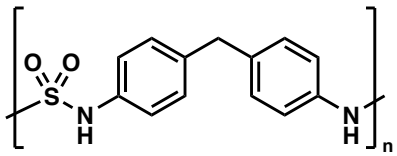
3c

^{13}C, 126 MHz



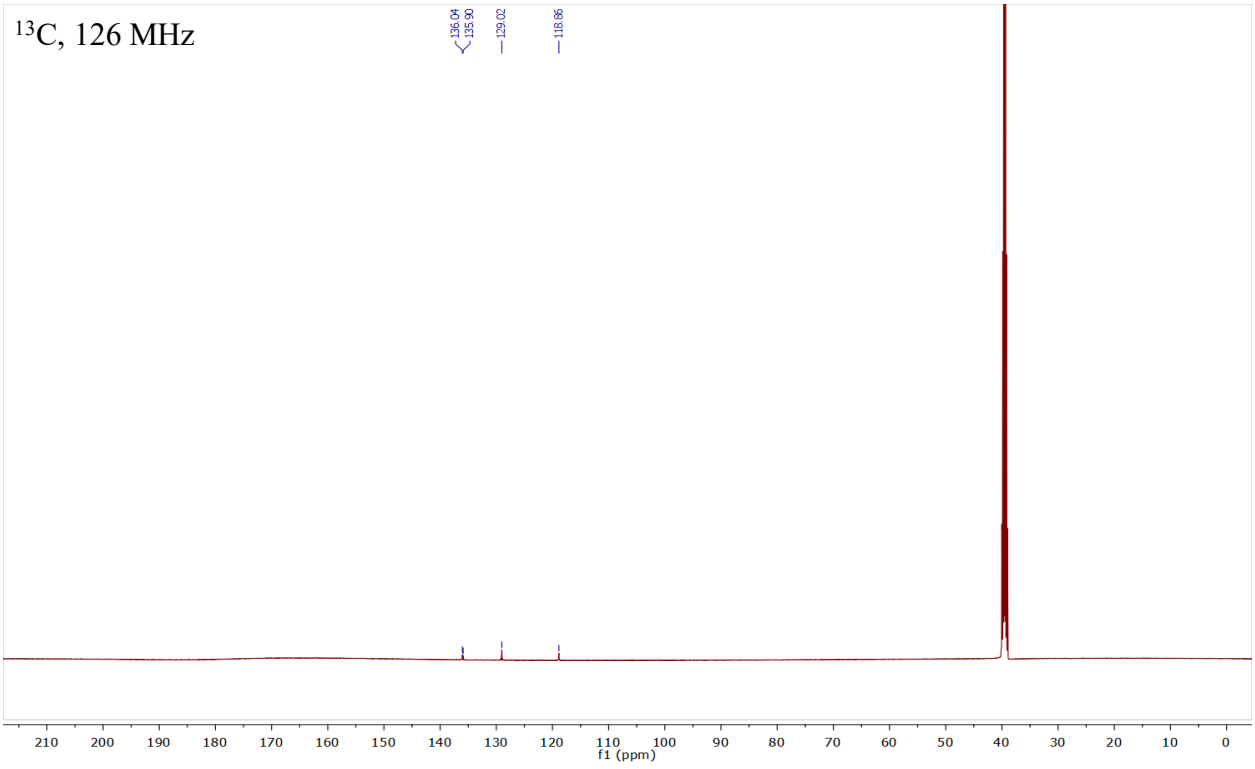
NMRs of polysulfamide **3d** (d_6-DMSO)

^{1}H, 500 MHz

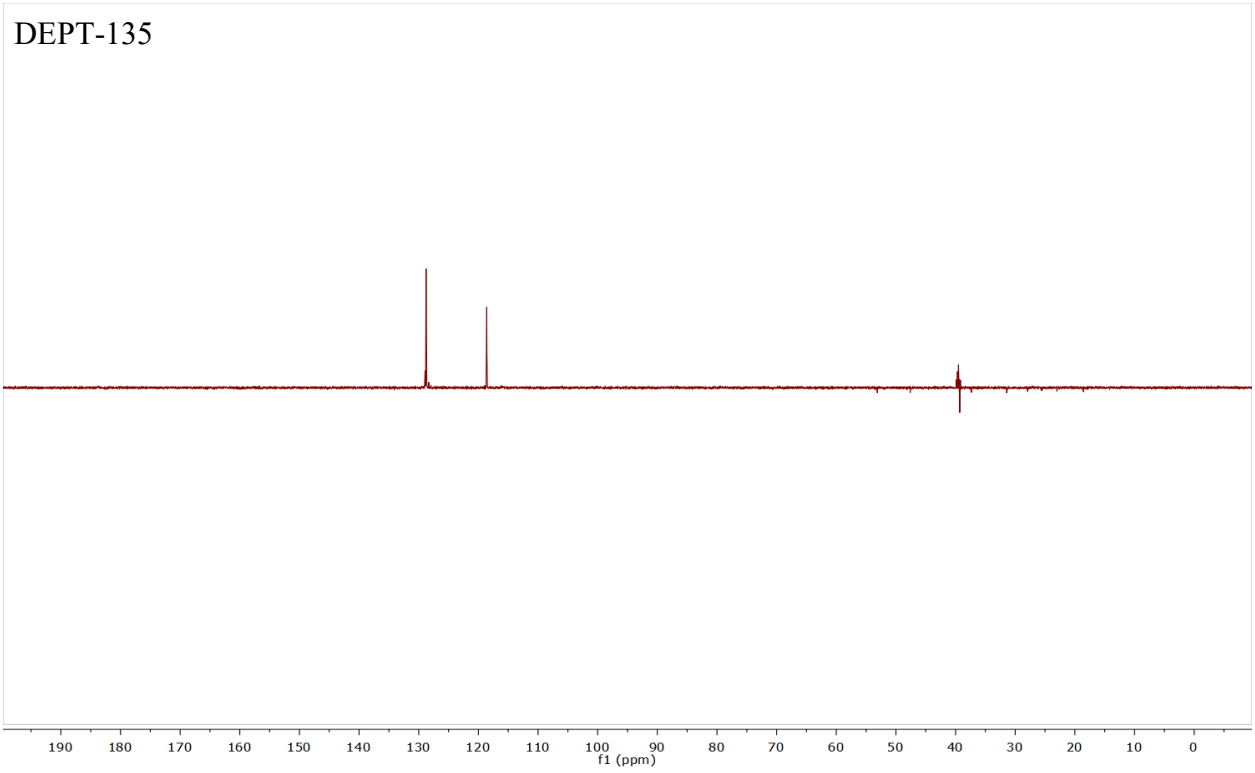


3d

^{13}C, 126 MHz



DEPT-135


190
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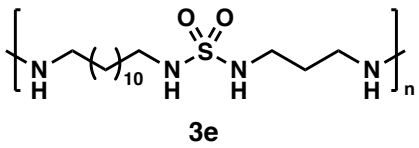
f1 (ppm)

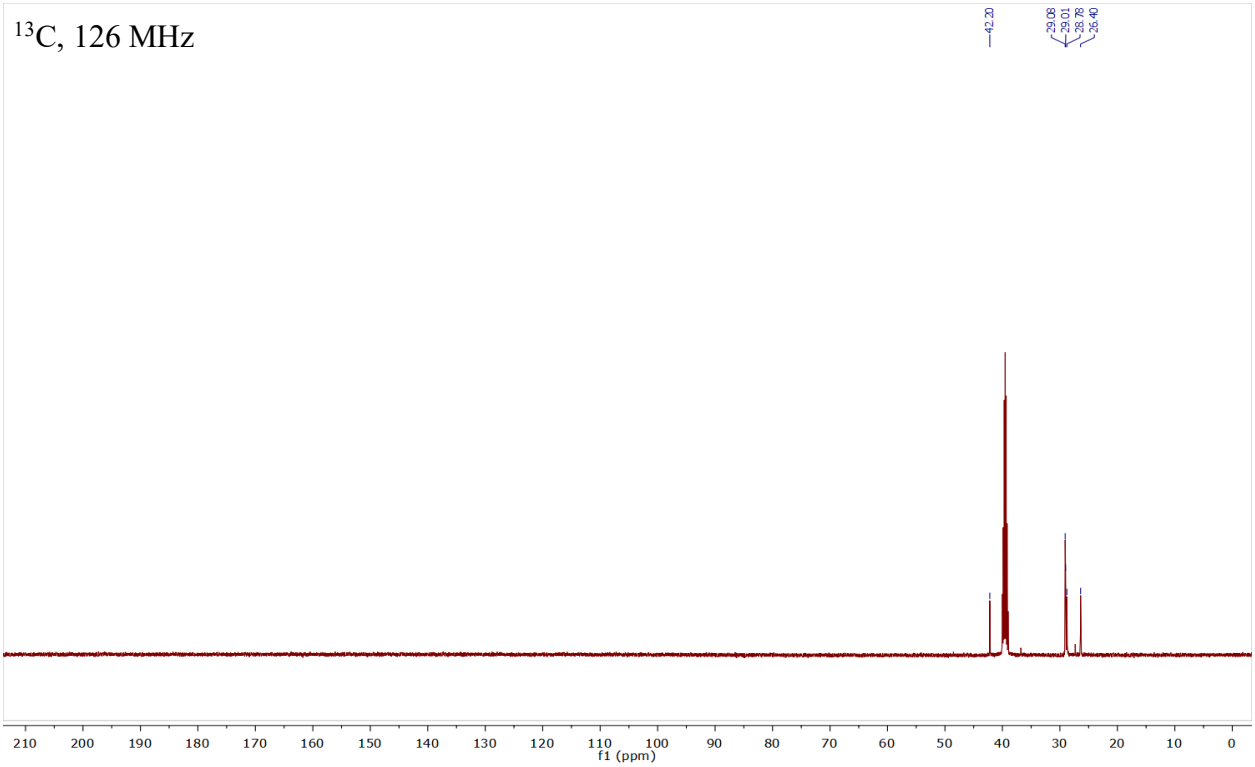
NMRs of polysulfamide **3e** (d_6-DMSO)

^{1}H, 500 MHz

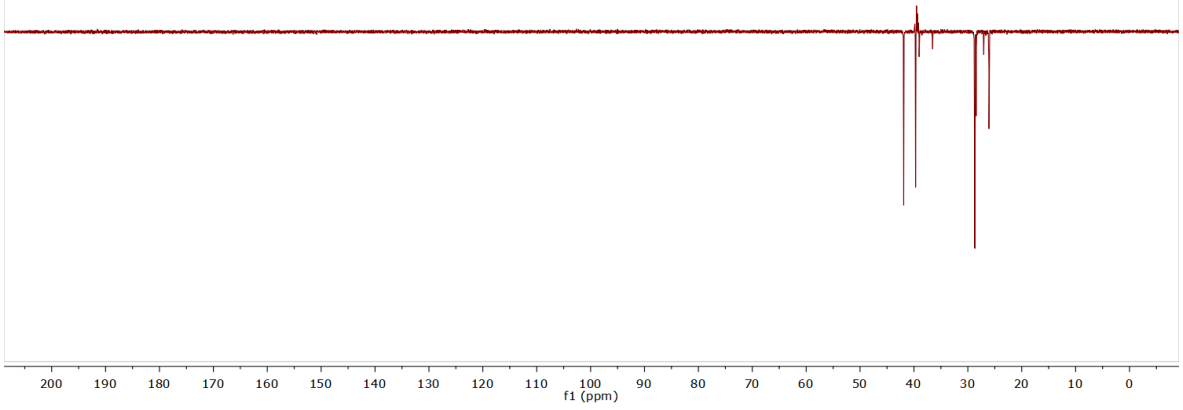


3e

^{13}C, 126 MHz



DEPT-135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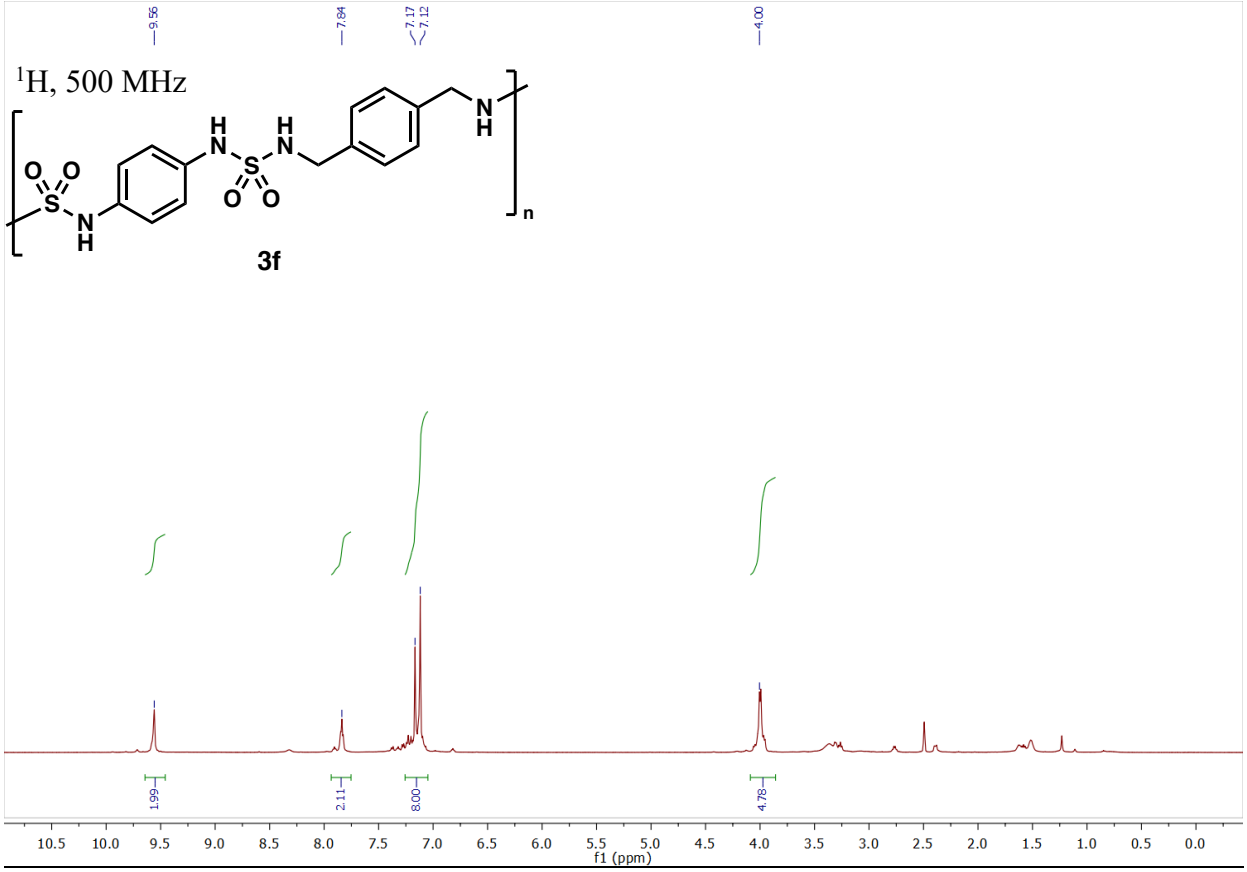
f1 (ppm)

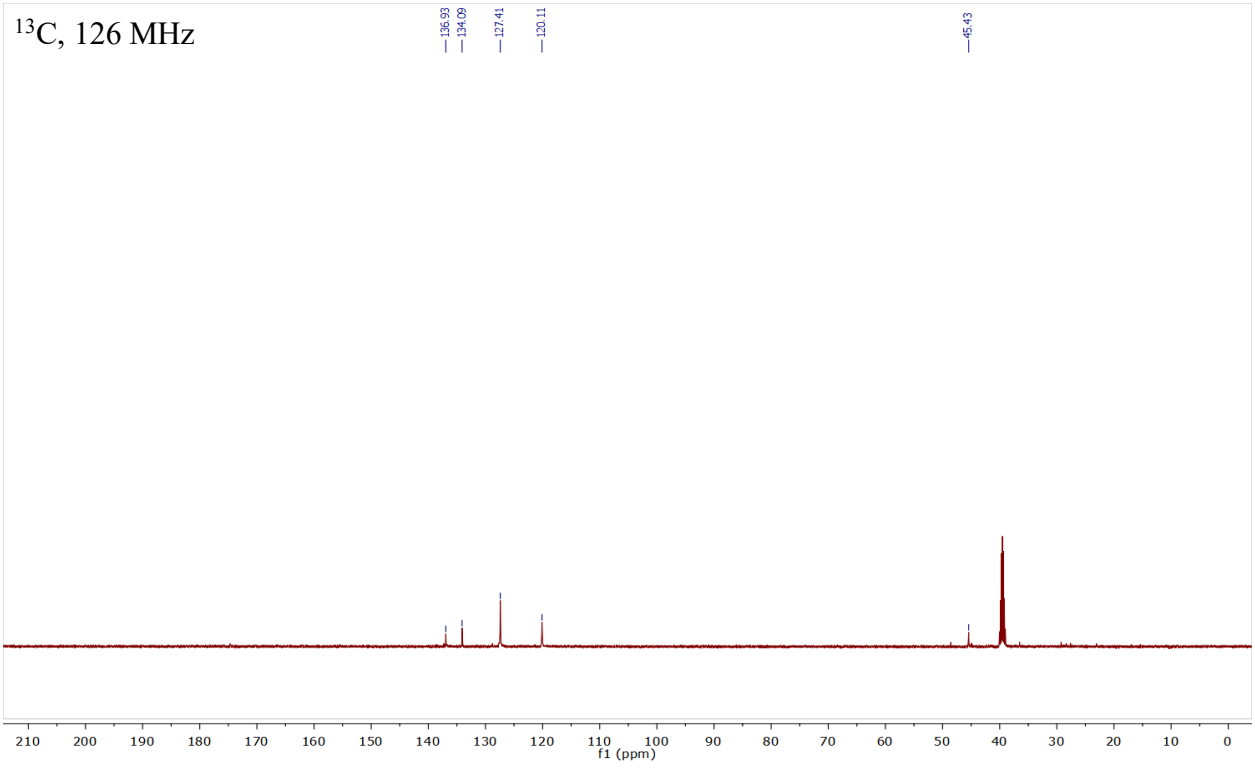
NMRs of polysulfamide **3f** (d_6-DMSO)

^{1}H, 500 MHz



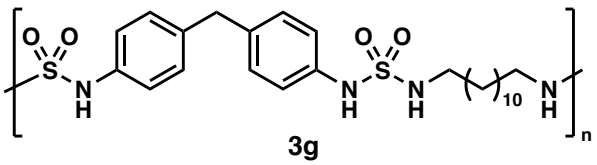
3f

^{13}C, 126 MHz

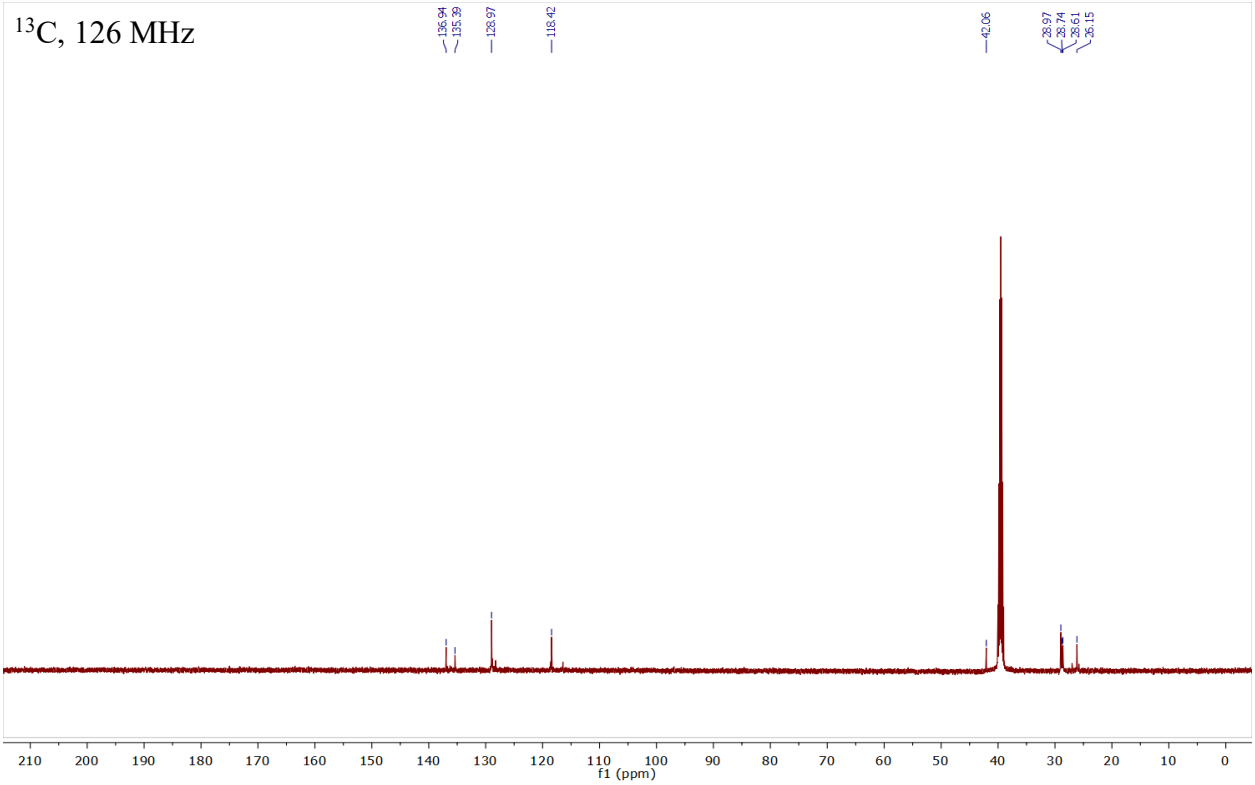


NMRs of polysulfamide **3g** (d_6-DMSO)

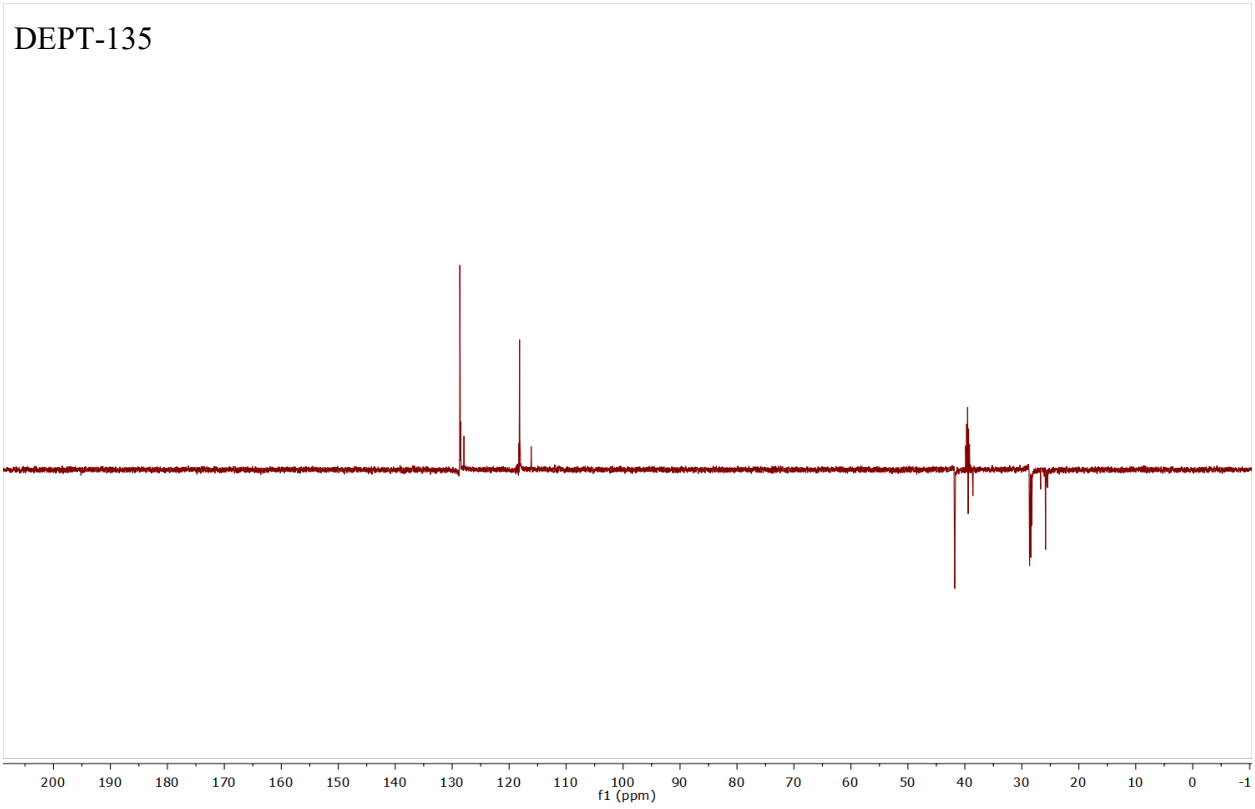
^{1}H, 500 MHz



^{13}C, 126 MHz



DEPT-135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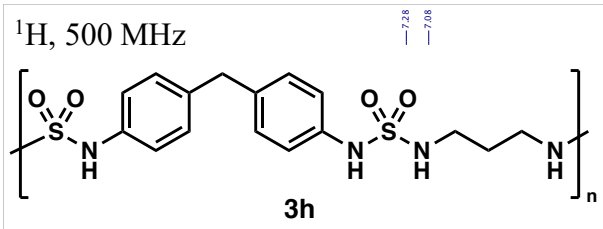
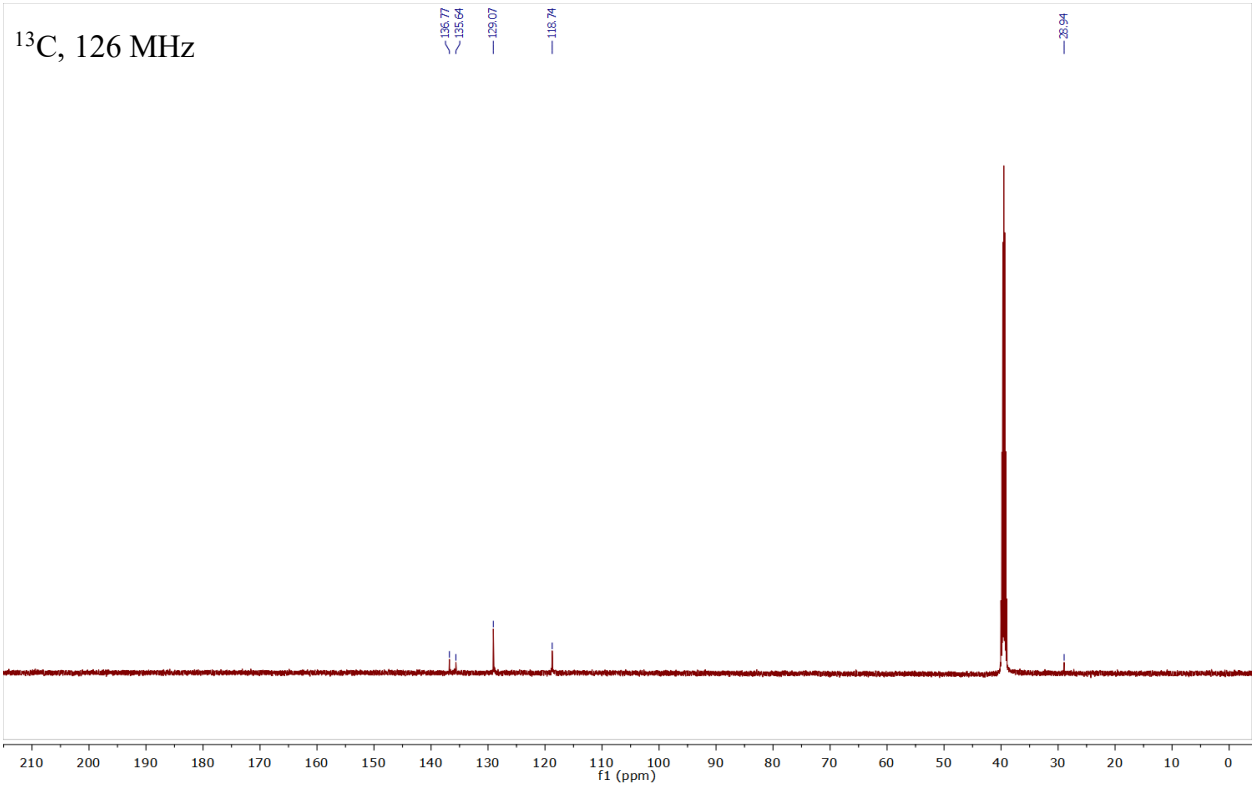
-1
f1 (ppm)

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

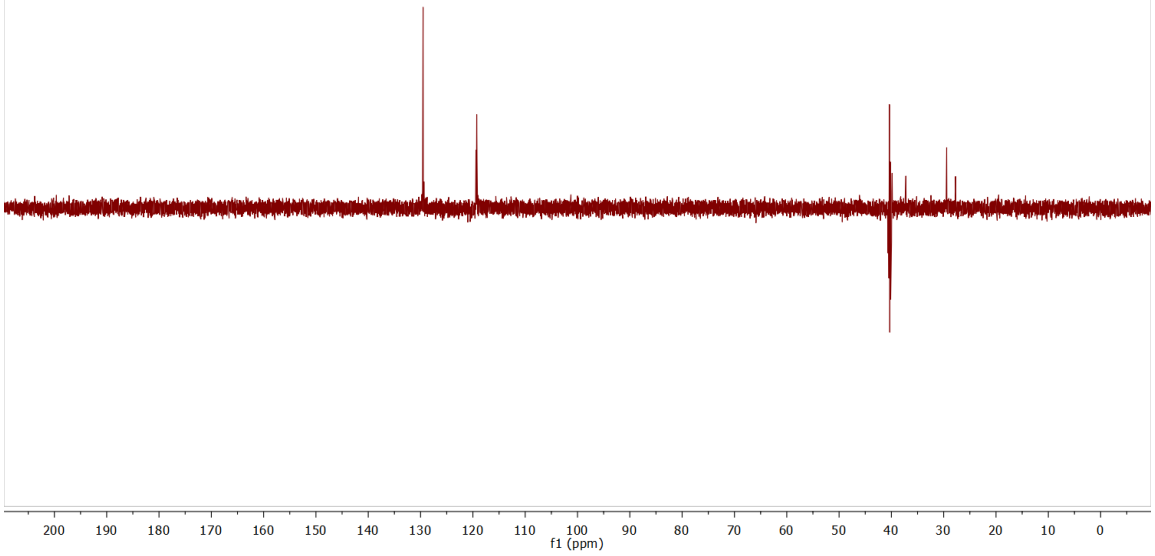
^{1}H, 500 MHz



^{13}C, 126 MHz



DEPT-135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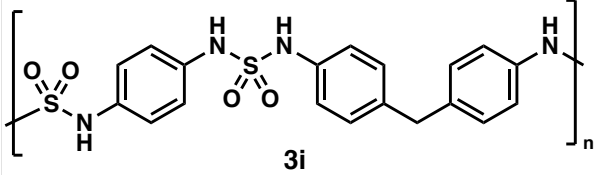
0
f1 (ppm)

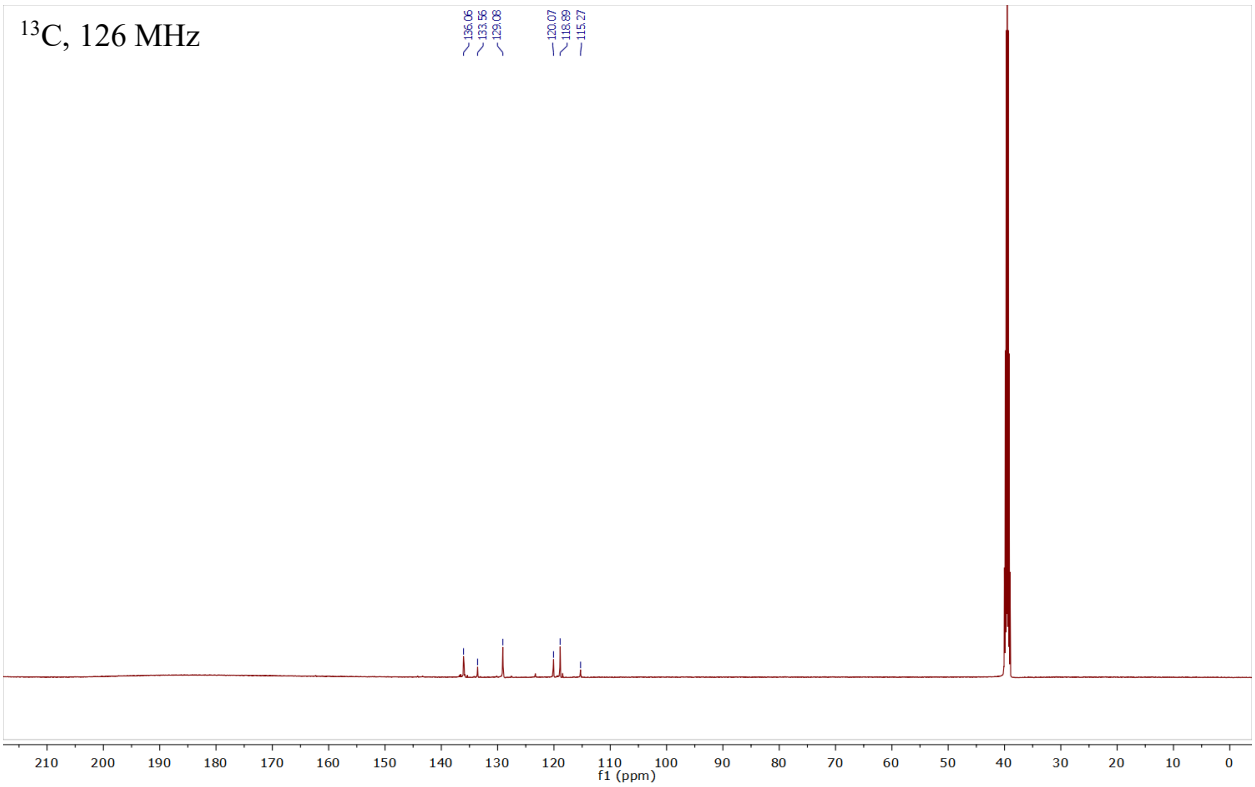
NMRs of polysulfamide **3i** (d_6-DMSO)

^{1}H, 500MHz

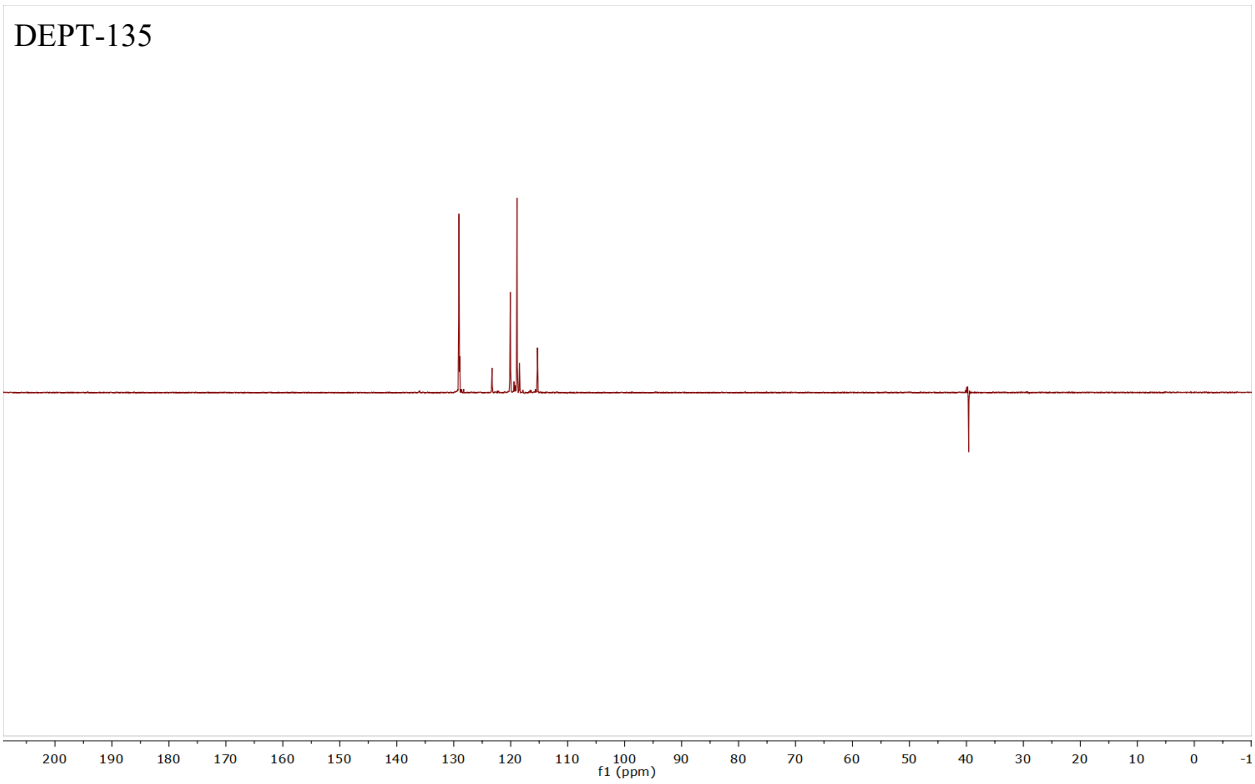


3i

^{13}C, 126 MHz



DEPT-135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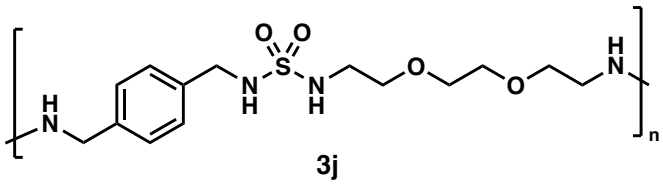
-1
f1 (ppm)

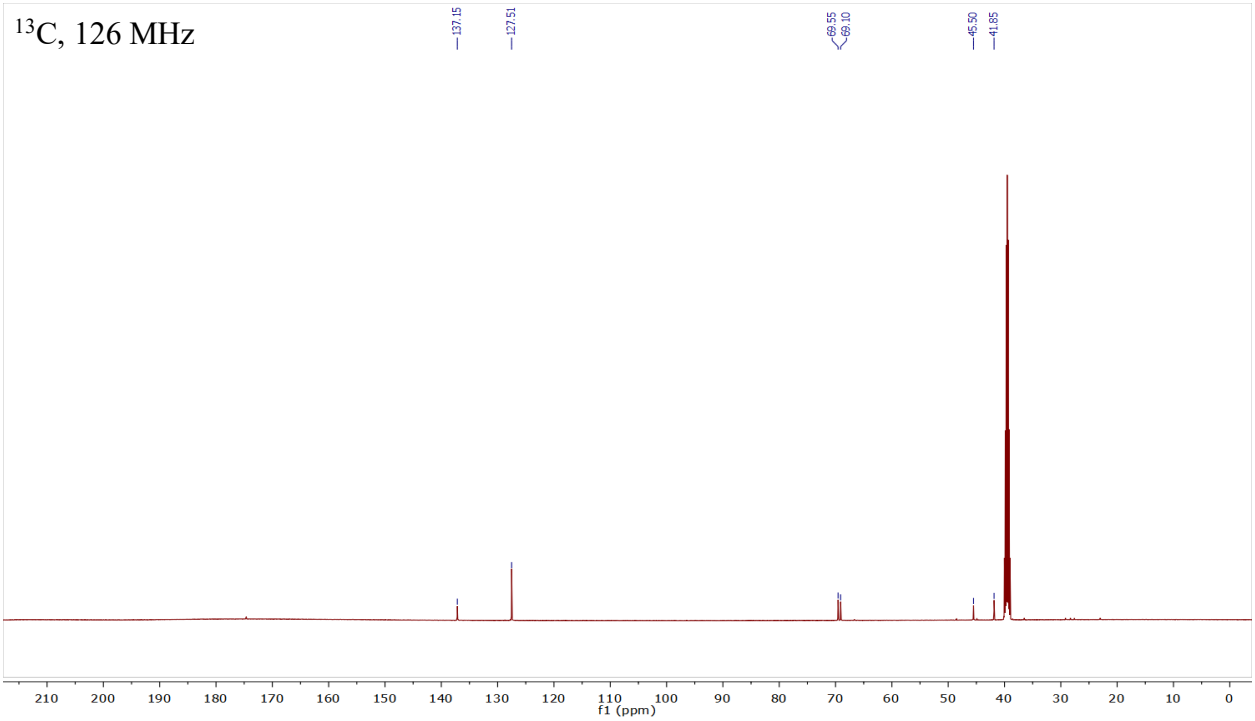
NMRs of polysulfamide **3j** (d_6-DMSO)

^{1}H, 500 MHz



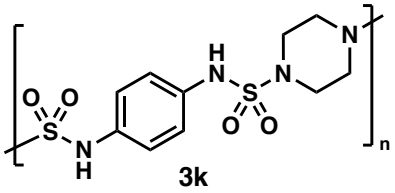
3j

^{13}C, 126 MHz



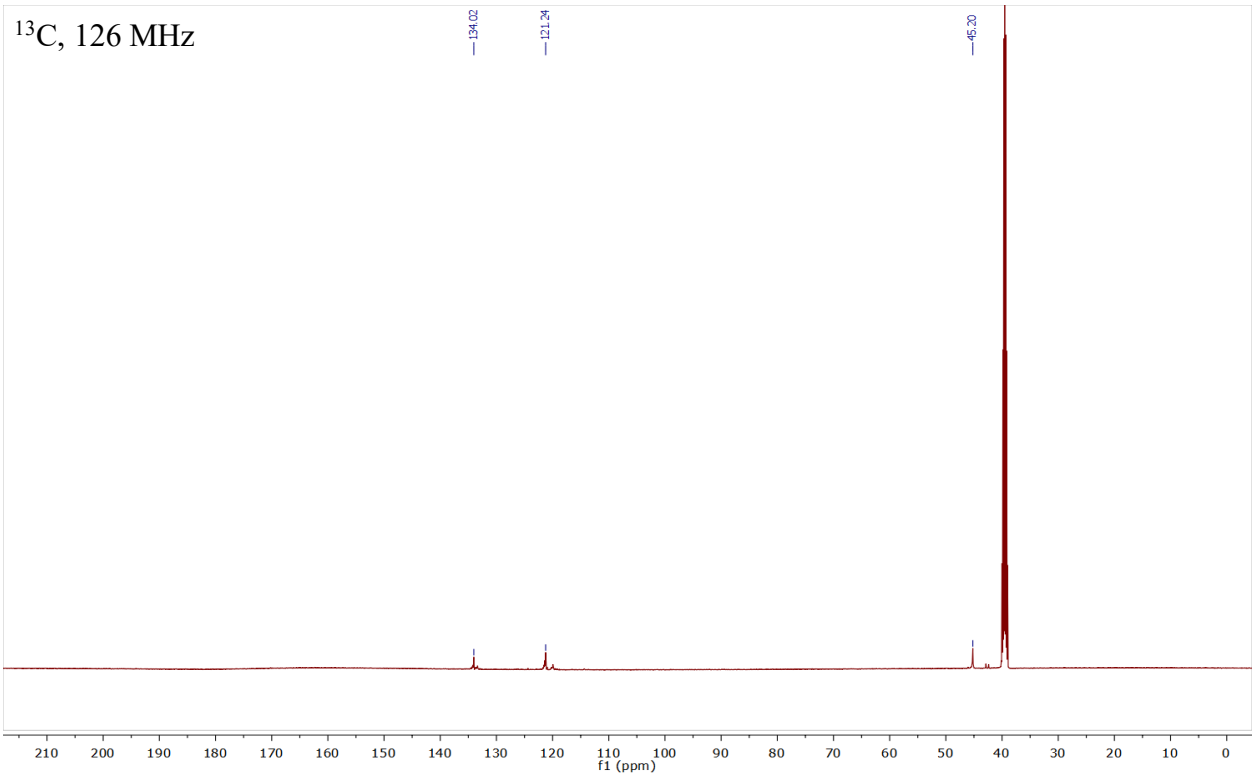
NMRs of polysulfamide **3k** (d_6-DMSO)

^{1}H, 500 MHz



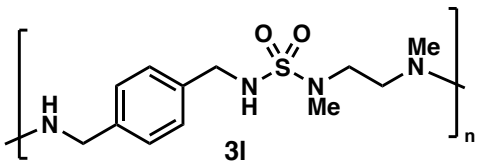
3k

^{13}C, 126 MHz



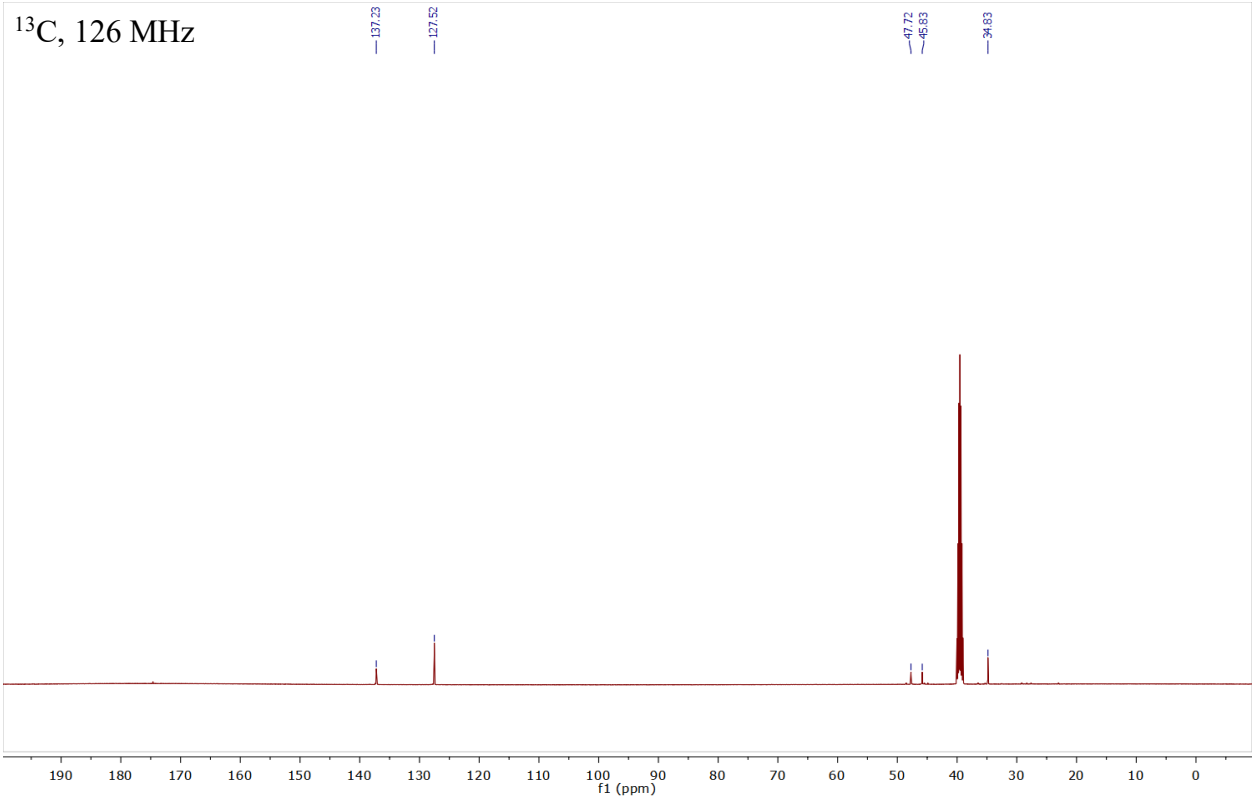
NMRs of polysulfamide **3l** (d_6-DMSO)

^{1}H, 500 MHz



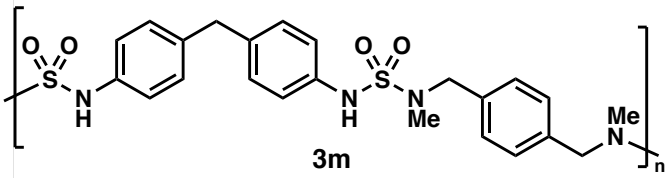
3l

^{13}C, 126 MHz

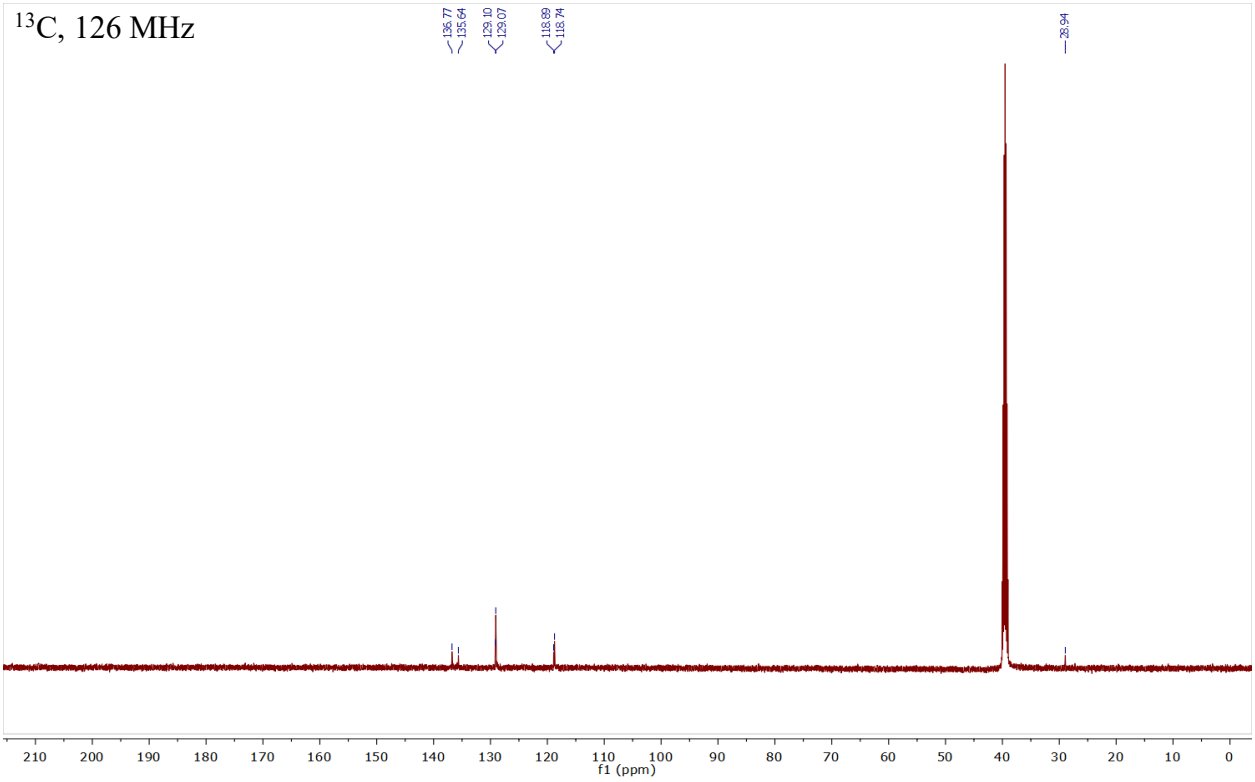


NMRs of Polysulfamide **3m** (d_6-DMSO)

^{1}H, 500 MHz



^{13}C, 126 MHz



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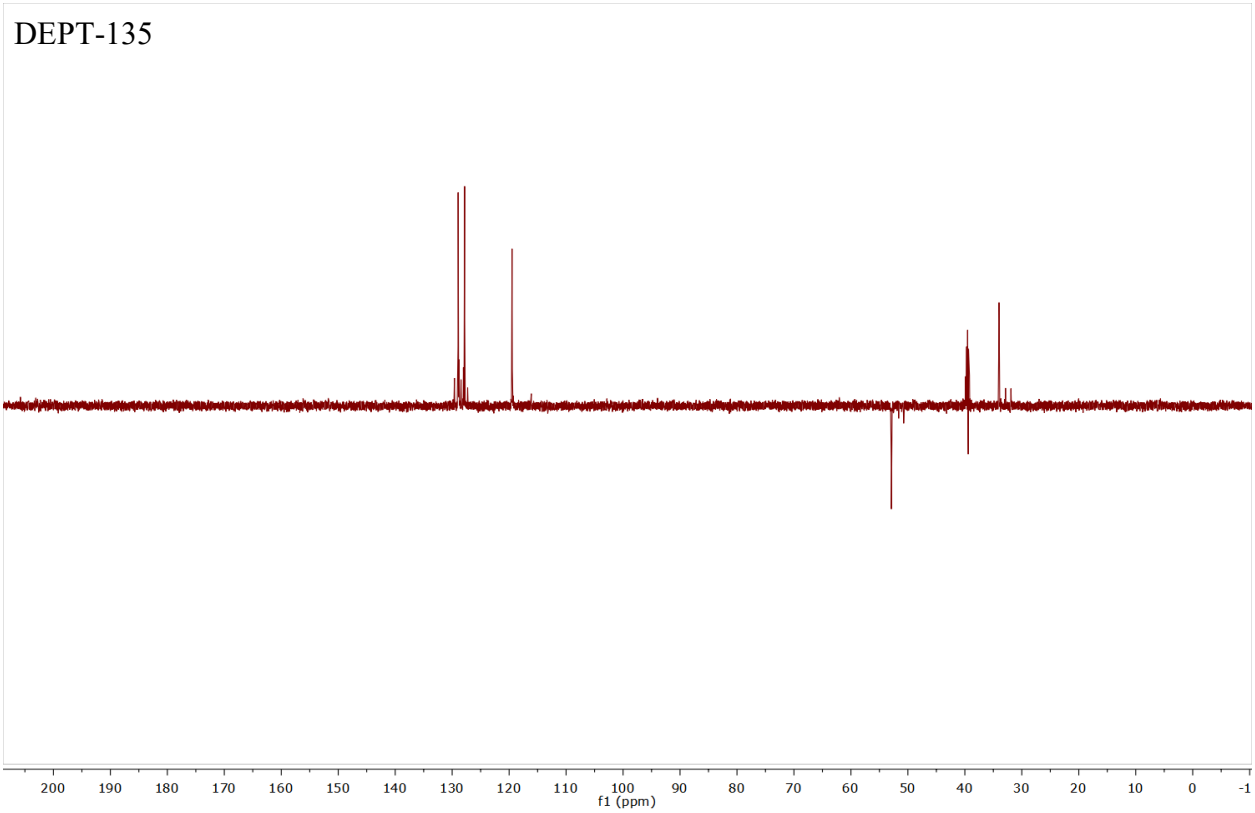
200
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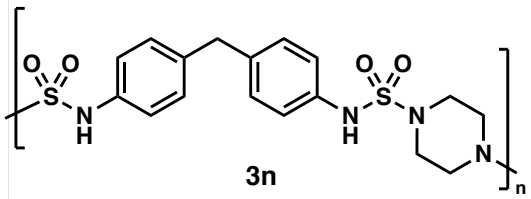
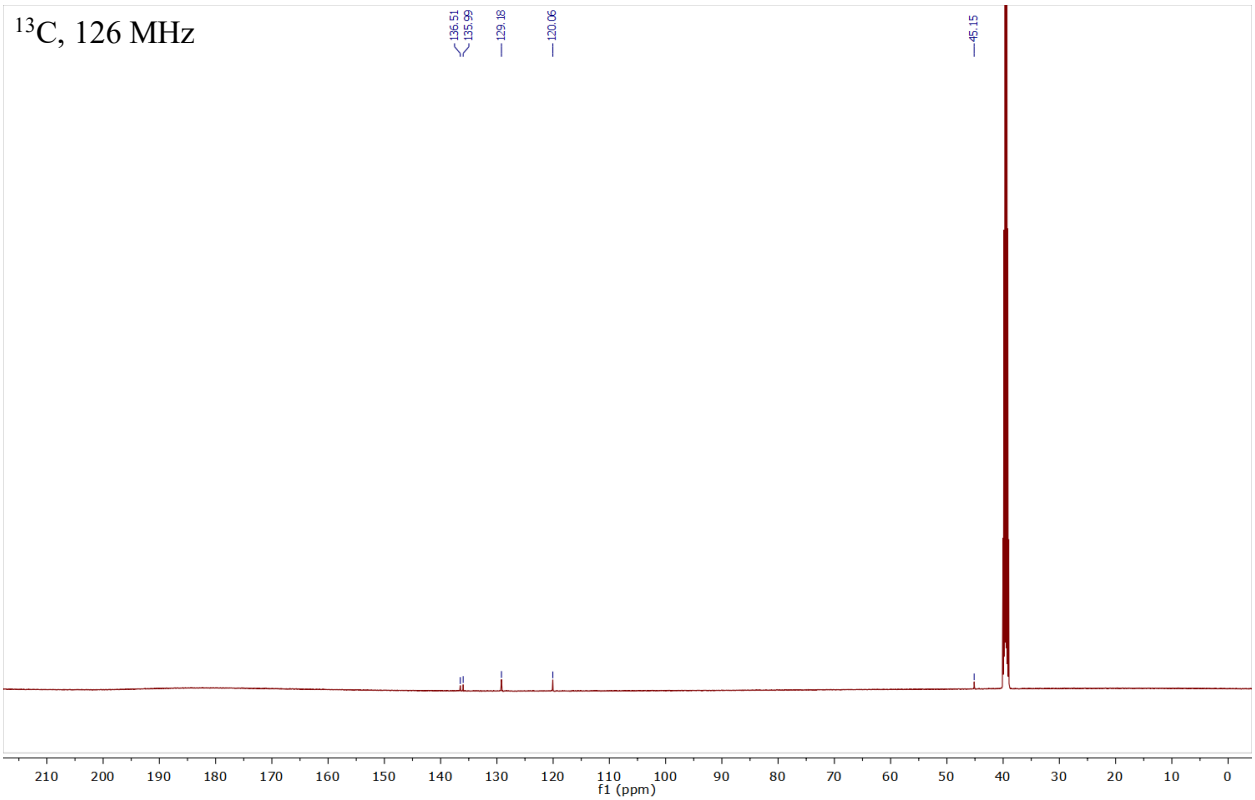
0
-1
f1 (ppm)

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

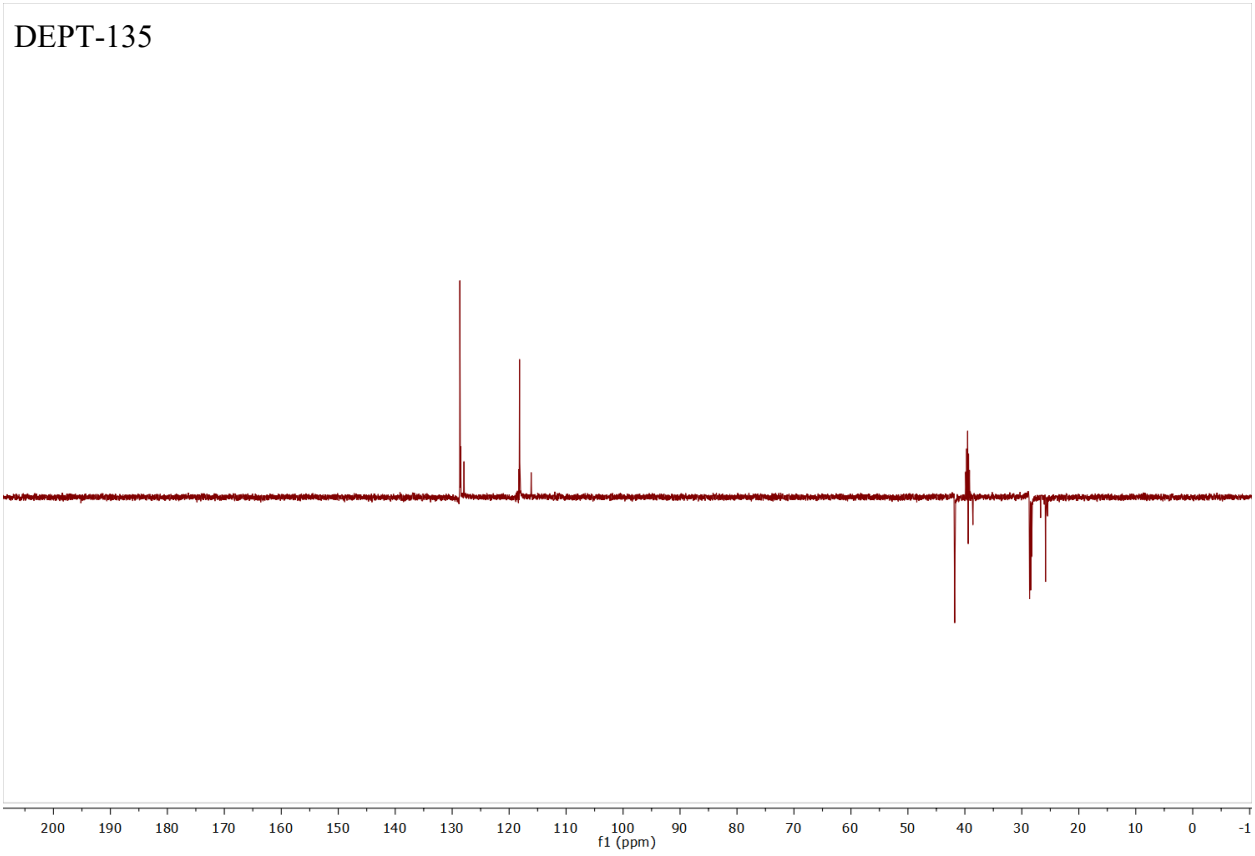
^{1}H, 500 MHz



^{13}C, 126 MHz



DEPT-135


200
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10
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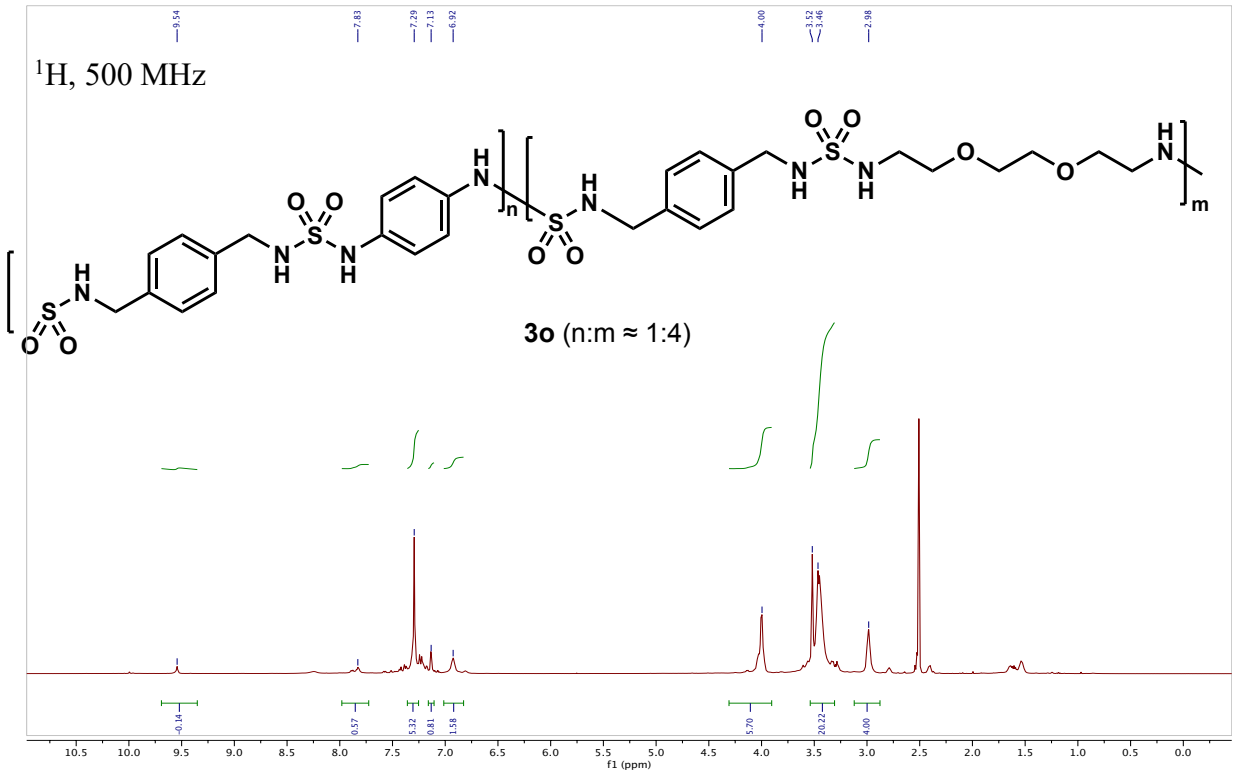
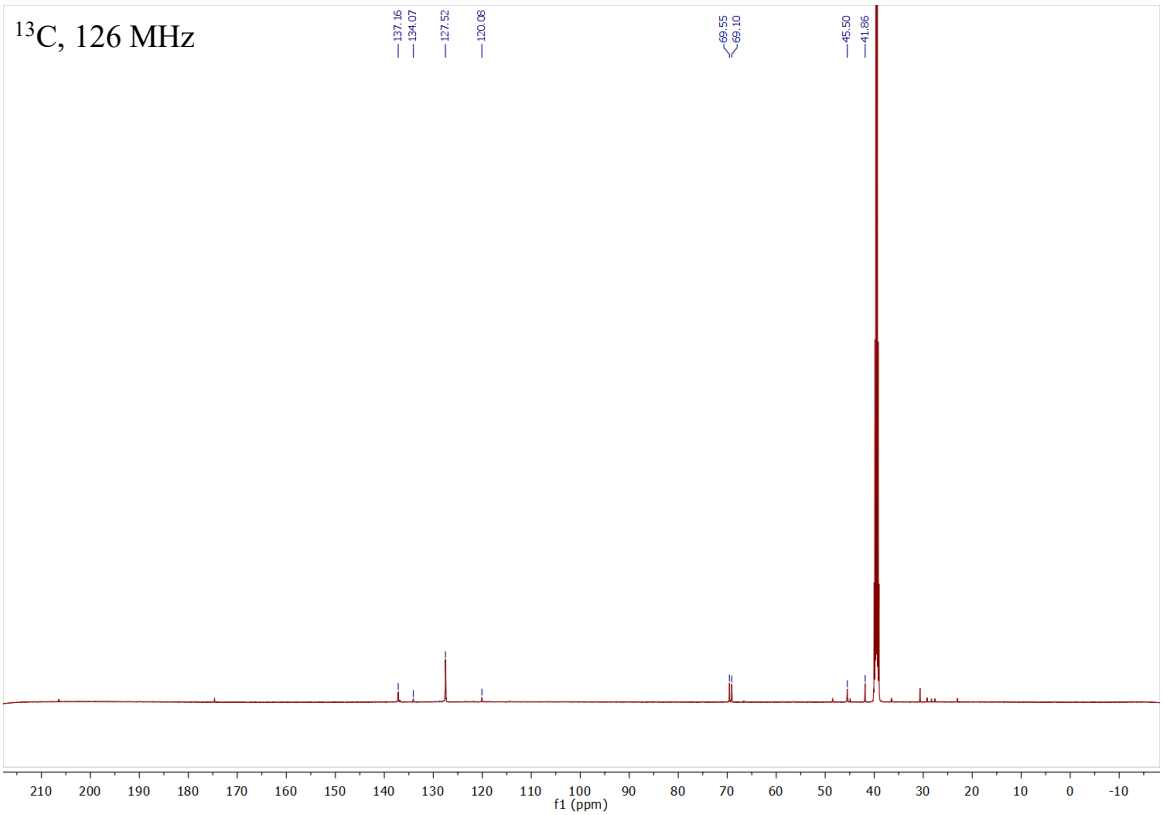
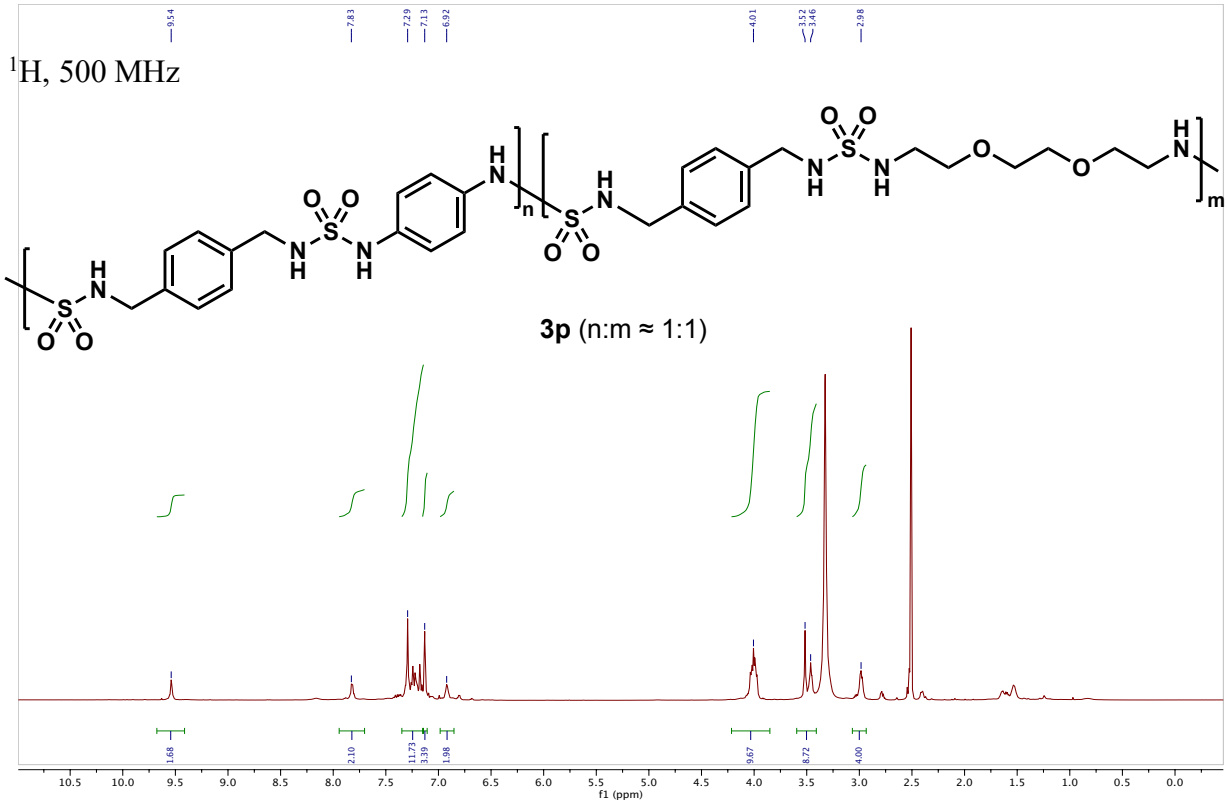
-1
f1 (ppm)

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

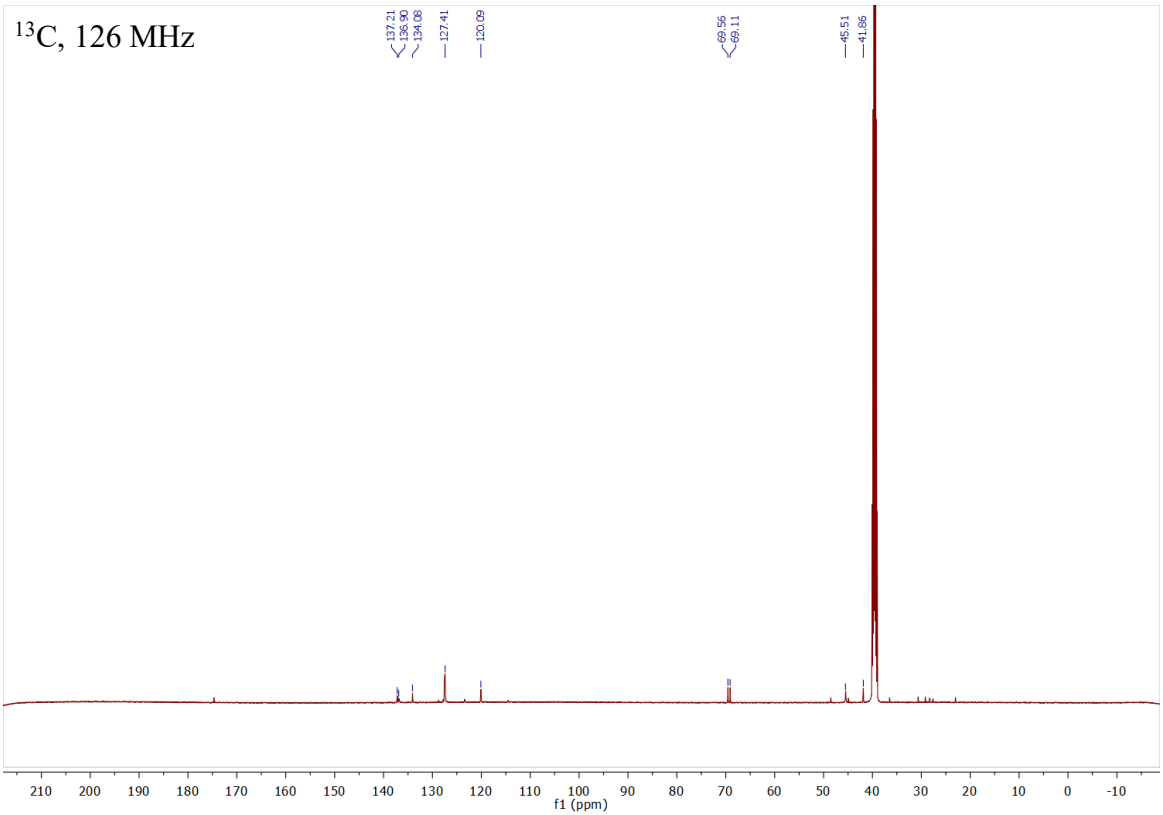




NMRs of Polysulfamide **3p** (d_6-DMSO)



^{13}C, 126 MHz


137.21
136.90
134.08
127.41
120.09
69.56
69.11
45.51
41.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)