

Resorcinarene Cavitand Polymers for the Remediation of Halomethanes and 1,4-Dioxane

Luke P. Skala, Anna Yang, Max J. Klemes, Leilei Xiao and William R. Dichtel*

*Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208, United States*

Supplementary Information

Correspondence Address
Professor William R. Dichtel Department of Chemistry Northwestern University 2145 Sheridan Road Evanston, IL 60208 (USA) wdichtel@northwestern.edu

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A. Materials and Instrumentation.

Materials: Reagents were purchased from Millipore-Sigma and used as received unless noted otherwise. Anhydrous DMSO was purchased through Millipore-Sigma (276855-1L) and dried over sieves. Fisher Chemical granular anhydrous potassium carbonate (173511) was used for all synthetic procedures. Activated carbon (Filtrisorb 600) was sourced from Calgon Carbon and received in granular form. The adsorbent was ground with a mortar and pestle and sieved to a particle size between 90–45 μm to match the particle size of the resorcinarene polymers. Ambersorb 560 was sourced from Dow Chemical Company. The resin was used as received. 20 and 40 mL glass vials with open-cap PTFE septa were purchased from Chemglass Life Sciences (CG490401). 4 mL glass vials were purchased through Fisher Scientific (03-339-22B). These vials were used with screw caps with PTFE/Silicone septums purchased from Millipore-Sigma (SU860078). 20 mL headspace vials (27199) and PTFE/silicone crimp seals (27362) were purchased from Millipore-Sigma. 0.2 μm CHROMAFIL Xtra H-PTFE-20/13 (Hydrophilic PTFE) filters were purchased from Macherey-Nagel.

Critical Point Dryer: Supercritical CO_2 activation was performed on a Leica EM CPD 300. Samples were stored in tea bags for both Soxhlet extraction and critical point drying. Immediately following Soxhlet extraction with methanol, the samples were transferred to the drying chamber without fully removing residual methanol. The drying chamber was cooled to 15 $^{\circ}\text{C}$ and filled with CO_2 at the “fast” setting rate. A delay of 120 seconds was used with an exchange speed of “5” and 45 cycles of CO_2 exchange. The samples were then cooled to 40 $^{\circ}\text{C}$ on the “slow” setting and the pressure was also relieved on the “slow 20%” setting.

Solid-State ^{19}F MAS NMR Spectroscopy: Solid-state ^{19}F NMR spectroscopy was performed on a Bruker Avance 600 MHz NMR spectrometer using a Bruker HX 1.3 mm MAS probe, in which the ^1H channel was tuned to ^{19}F . The sample spinning rate was controlled by a Bruker pneumatic MAS unit at 48 kHz. The ^{19}F 90° pulse length was used and in all ^{19}F experiments, 2048 scans were collected for each sample. Flufenamic acid was used as an external standard, and its ^{19}F resonance was set to -61.5 ppm.¹

Solution ^{19}F NMR Spectroscopy: 3-(trifluoromethyl)benzonitrile (-61.75 ppm) was used to reference the fluorine peak shifts for **S1** and **S2**, as well as for analyzing model reactions involving these compounds. The peak shift of 3-(trifluoromethyl)benzonitrile was determined via comparison to Flufenamic acid.

Solution Nuclear Magnetic Resonance Spectroscopy: Both ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance III 500 MHz equipped with a DHC CryoProbe. ^{19}F NMR spectra were obtained on an Agilent 500 MHz DD2 spectrometer.

Solid State ^{13}C Cross Polarization Magic Angle Spinning (CP-MAS) NMR Spectroscopy: Spectra were taken on a Varian 400 MHz with a spinning rate of 15 KHz. The spectra were referenced using adamantane as an external standard.

Surface Area Analysis was performed on a Micromeritics ASAP 2420 Accelerated Surface Area and Porosity Analyzer. At least 25 mg of polymer was used for each analysis. The sample was degassed at 40°C until the offgas rate was less than $1.0\ \mu\text{mHg}/\text{min}$. Isotherms were performed using ultrahigh purity N_2 at 77K. Brunauer-Emmett-Teller surface areas (S_{BET}) were calculated using the linear region (P/P_0 of 0.05-0.1) of the isotherm.

Infrared Spectroscopy was performed on a Nicolet iS10 FT-IR with a Diamond ATR.

Thermogravimetric Analysis: Thermal stability was assessed on a Netzsch's Simultaneous Thermal Analysis coupled to a GC-MS under a He atmosphere. Approximately 5 mg of polymer was used for each analysis. A temperature range of 20–800 °C and 10 °C/min ramp rate were used.

Scanning Electron Microscopy: Polymer powders were attached to aluminum sample holders with double sided carbon tape. Samples were coated with 6nm of Osmium and imaged with a FEI Quanta 650 ESEM. Images were collected using a large field detector in low vacuum mode at an accelerating voltage of 25 kV.

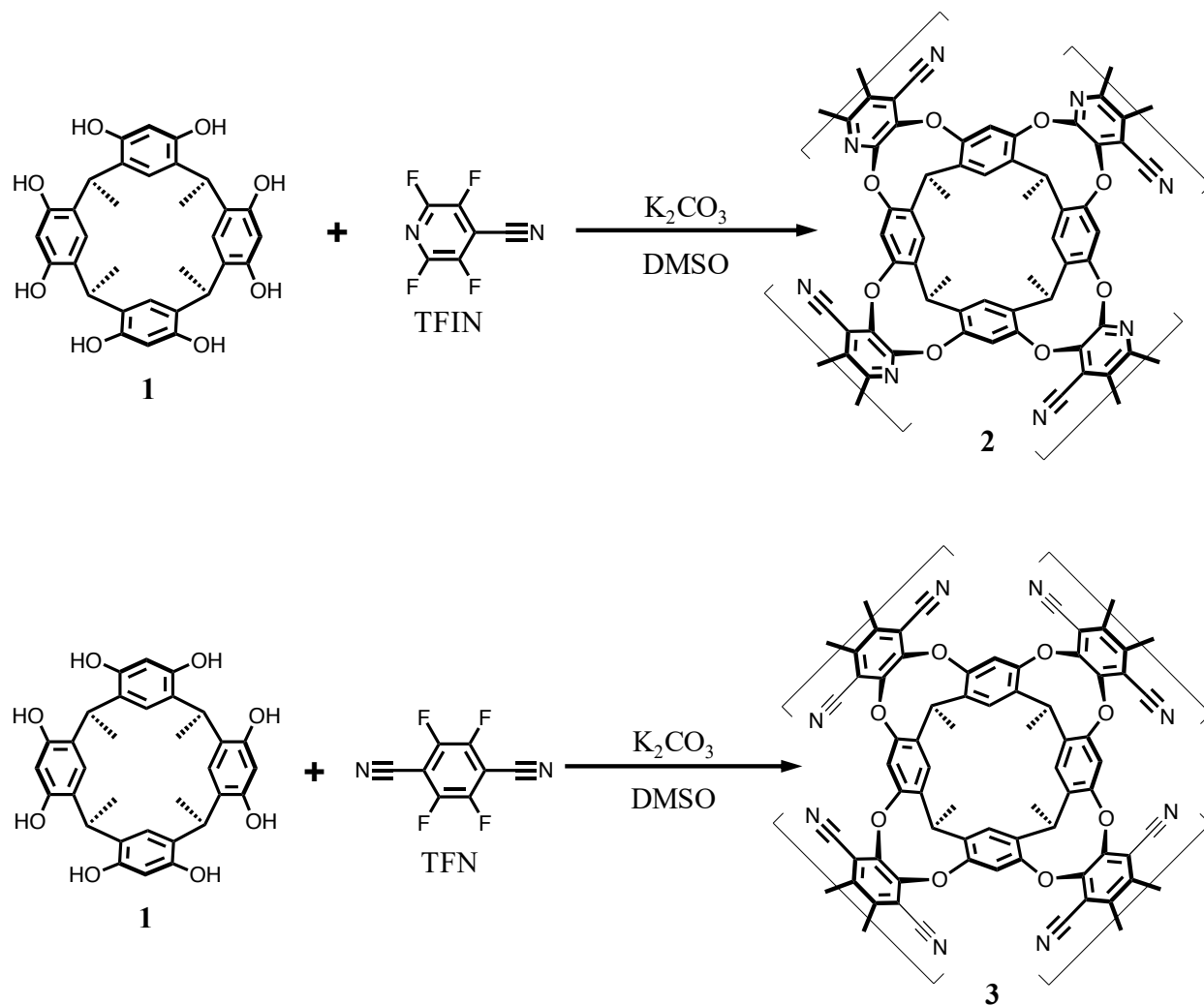
Gas Chromatography Mass Spectroscopy (GC-MS) was performed on an Agilent 6890N GC system with an Agilent 5973 mass selective detector. Samples were injected using an Agilent 7697A headspace sampler. For each measurement, 2 mL of a liquid sample was loaded into a 20 mL vial, which was crimp sealed with a silicone cap. The sample was incubated in a headspace sampler for 7 minutes at 80 °C. While being incubated the samples were shaken (71 min^{-1}). The vapor phase (0.2 mL) was injected into the GC-MS with a split ratio of 20:1. The headspace loop and transfer line were set to 90 °C and 100 °C respectively. The oven temperature was held at 45 °C for 3 min and heated to 200 °C (40 °C/min) and held for 1 minute. An ion extraction was performed on the chromatogram using the most abundant ion of the analyte of interest (see table below). The relevant peak was integrated to obtain a value for the residual analyte concentration. Standard curves were constructed with each analyte to determine the linear concentration regime and detection limit (see standard curves below).

Halomethane	Retention Time (minutes)	Ion Used (Da)
CH ₂ Cl ₂	2.271	84
CHCl ₃	3.223	83
CCl ₄	1.930	117
CHBrCl ₂	4.588	83
CHBr ₂ Cl	5.65	129
CHBr ₃	6.465	173

Table S1. Retention time of halomethane pollutants and ions used for their quantification.

Electrospray Ionization - Mass Spectroscopy (ESI-MS): Detection of phenoxy-substituted products **S3** and **S4** were conducted using Bruker ESI-ion trap mass spectrometer (Amazon SL). The mobile phase consisted of CH₃OH and CH₂Cl₂. Samples were injected at 1 µL volumes directly to the mass spectrometer with a loading pump delivering 200 µL min⁻¹ of a mobile phase consisting of 50% CH₂Cl₂. The mass spectrometer was operated with electrospray ionization in alternating polarity mode. The mass range sampled was from 50 to 2200 *m/z*.

B. Synthetic Procedures

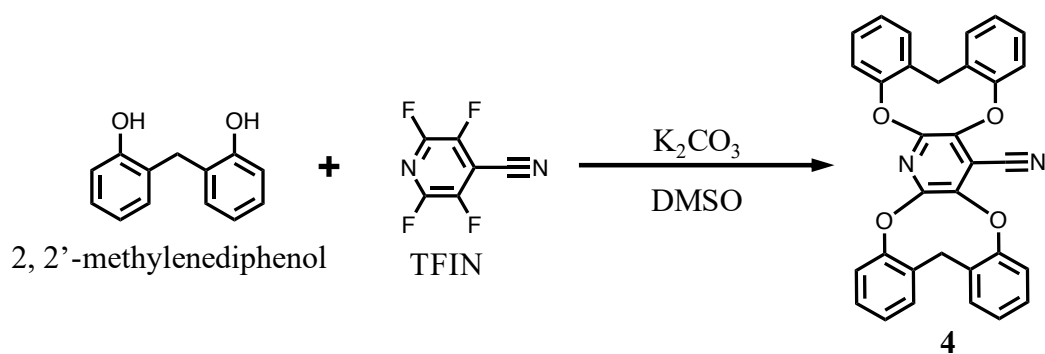


General Polymerization Procedure: Resorcinarene (**1**, 125 mg, 0.230 mmol) and TFIN (81 mg, 0.46 mmol) or TFN (91 mg, 0.46 mmol) were added to a 20 mL reaction vial. Anhydrous DMSO (4 mL) was added using a syringe. The vial was heated to dissolve the monomers. After the monomers were fully dissolved, K_2CO_3 (636 mg, 4.60 mmol) was added and the reaction was immediately placed on a heating block preheated to 150 °C. The reaction mixture was heated at 150 °C for 3 hours and gelled within 5 minutes. The surface temperature of the heating block was measured with an IR thermometer to be ~162 °C. Following 3 hours of heating the reaction was

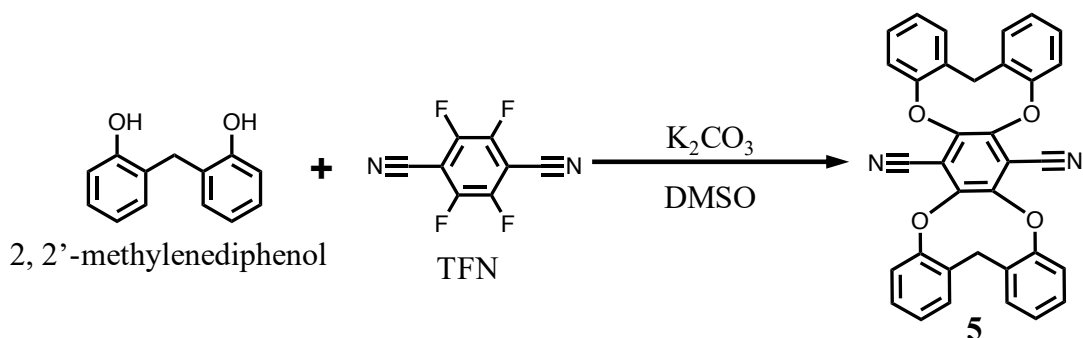
cooled to RT. Nanopure H₂O was added to the sample, and the gel was pulverized with a spatula. The pulverized gel was then filtered and placed into 50 mL of nanopure H₂O. A solution of HCl (1 M) was slowly added until a pH of 1-3 was reached. The solution was then stirred for an additional 10 minutes. The polymer was stirred in acetone (100 mL) for 45 minutes. The polymer was continuously washed with hot MeOH in a Soxhlet extractor, after which it was activated using supercritical CO₂. The isolated polymers were grinded into a powder using a mortar and pestle and sieved to a particle size of 90-45 μ m to match that of the activated carbon benchmarks. The resulting polymers were isolated in 93% and 97% yield for **2** and **3**, respectively. Theoretical yields were based on the initial masses of the monomers and corrected based on their combustion analysis to account for the residual fluorine content.

	Reaction Conditions				Elemental analysis			Removal Study		
Polymer	[Resorcinarene] (mmol)	[TFIN or TFN] (mmol)	Reaction Temp (°C)	[K ₂ CO ₃] (M)	F%	N%	Flourine Per Linker	[CHCl ₃] (μg/L)	[Absorbant] (mg/L)	CHCl ₃ removal (%)
2	57.5	115	75	1.15	N/A	N/A	N/A	100	30	74.3
2	57.5	115	75	0.46	N/A	N/A	N/A	100	30	67.6
2	57.5	115	75	0.23	N/A	N/A	N/A	100	30	68.9
2	57.5	115	75	1.15	4.09	7.02	0.9	100	50	80.3
2	57.5	115	150	1.15	3.45	6.95	0.7	100	50	87.2
2	38.3	77	150	0.77	No Polymer Isolated					
2	57.5	115	150	1.15	3.45	6.95	0.7	100	30	85.2
2	115	230	150	2.3	N/A	N/A	N/A	100	30	64.8
3	57.5	115	75	1.15	5.26	6.34	1.2	100	300	55
3	57.5	115	120	1.15	3.94	6.33	0.9	100	300	78.7
3	57.5	115	150	1.15	3.19	6.43	0.7	100	300	86.2

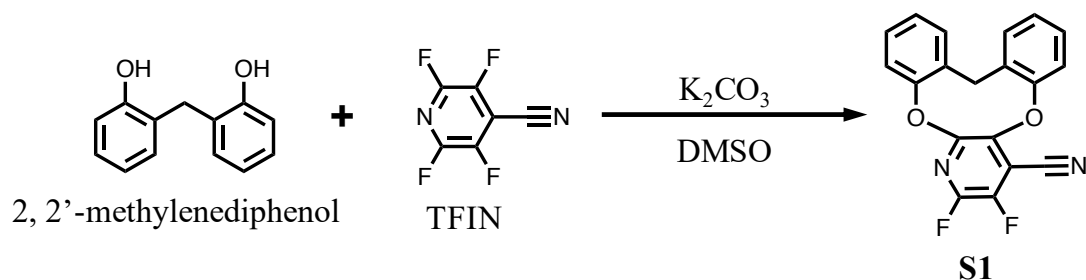
Table S2. Optimization of the polymerization procedure based on minimizing residual fluorine content and maximizing CHCl₃ adsorption.



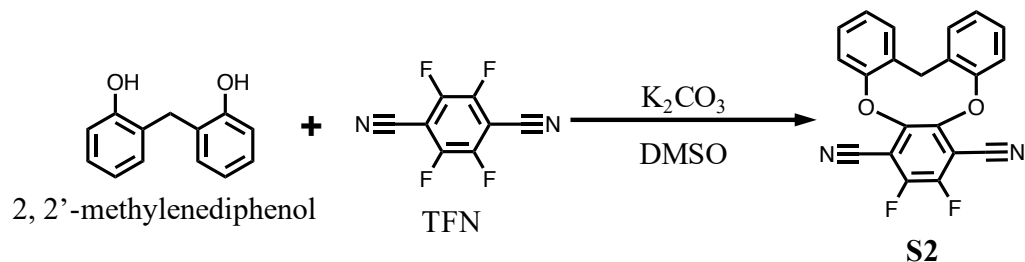
Synthesis of Model Compound 4: 2,2'-methylenediphenol (184 mg, 0.92 mmol) and **TFIN** (81 mg, 0.46 mmol) were added to a 20 mL reaction vial. Anhydrous DMSO (4 mL) was added using a syringe. The vial was heated to dissolve the 2,2'-methylenediphenol. When the monomers were fully dissolved, K_2CO_3 (127 mg, 0.92 mmol) was added. The solution was then heated at 150 °C for 25 minutes and monitored via TLC (SiO_2 , 40:60 hexanes:DCM). The reaction solution was cooled to room temperature and then added to an excess of brine, and the resulting precipitate was recovered by filtration. The recovered solids were dissolved in DCM and purified using column chromatography (silica, 40:60 hexanes:DCM). The product was then dried under vacuum at 100 °C to provide **4** (77 mg, 34% yield). **4**: ^1H NMR (500 MHz, CD_2Cl_2): δ 7.31-7.25 (m, 6H), 7.23-7.21 (m, 4H), 7.19-7.14 (m, 6H), 3.97 (s, 4H) ^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.81, 154.36, 144.34, 143.92, 133.97, 131.67, 131.37, 130.65, 128.67, 128.50, 126.45, 124.03, 120.97, 111.92, 107.39, 33.16 ppm. HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{20}\text{N}_2\text{O}_4$ $[\text{M}^*]^+$ 496.1423, found 496.1425.



Synthesis of Model Compound 5: 2,2'-methylenediphenol (184 mg, 0.92 mmol) and TFN (91 mg, 0.46 mmol) was added to a 20 mL reaction vial. 4 mL of anhydrous DMSO was added using a syringe. The vial was heated to dissolve the 2,2'-methylenediphenol. When the monomers were fully dissolved, K_2CO_3 (127 mg, 0.92 mmol) was added. The solution was then heated at 150 °C for 25 minutes and monitored via TLC (SiO_2 , 20:80 hexanes:DCM). The reaction solution was cooled to room temperature and then added to an excess of brine, and the resulting precipitate was recovered by filtration. The recovered solids were dissolved in DCM and purified using column chromatography (SiO_2 , 20:80 hexanes:DCM). The product was then dried under vacuum at 100 °C to provide **5** (55 mg, 23% yield). **5**: ^1H NMR (500 MHz, CD_2Cl_2): δ 7.28 (ddd, $J=9.05$, 7.28, 1.72 Hz, 6H), 7.24 (dd, $J=6.98$, 1.68 Hz, 6H), 7.17 (ddd, $J=8.23$, 6.98, 1.29 Hz 4H), 4.09 (s, 4H) ^{13}C NMR (126 MHz, CDCl_3) δ 154.44, 147.62, 130.91, 130.69, 128.25, 126.11, 122.23, 112.12, 107.27, 33.78 ppm. Elemental Analysis: calcd for $\text{C}_{34}\text{H}_{20}\text{N}_2\text{O}_4$ C, 78.45; H, 3.87; N, 5.38 found C, 78.39; H, 3.60; N, 5.32.



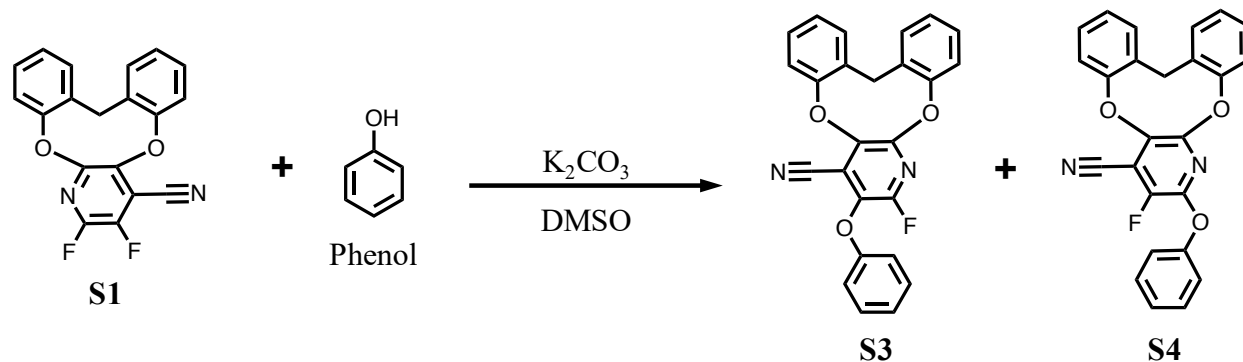
Synthesis of S1: 2,2'-methylenediphenol (184 mg, 0.92 mmol) and **TFIN** (162 mg, 0.92 mmol) was added to a 20 mL reaction vial. Anhydrous DMSO (8 mL) was added using a syringe. The vial was heated to dissolve the 2,2'-methylenediphenol. When the monomers were fully dissolved, K_2CO_3 (127 mg, 0.92 mmol) was added. The solution was then heated at 150 °C for 5 minutes, and reaction times longer than 10 minutes provided diminished yields. The reaction was monitored via TLC (SiO_2 , 50:50 hexanes:DCM). The reaction solution was cooled to room temperature and then added to an excess of brine, and the resulting precipitate was recovered by filtration. The recovered solids were dissolved in DCM and purified using column chromatography (SiO_2 , 50:50 hexanes:DCM). The product was then dried under vacuum at 100 °C to provide **S1** (50 mg, 16% yield). **S1:** ^1H NMR (500 MHz, DMSO): δ 7.47 (dd, $J = 7.54$, 1H), 7.33-7.29 (m, 3H), 7.26-7.21 (m, 2H), 7.21-7.16 (m, 2H), 3.96 (s, 2H) ^{13}C NMR (126 MHz, DMSO) δ 153.58, 152.78, 143.03 (dd, $J = 265.82$, 31.56 Hz), 142.91 (d, $J = 6.14$ Hz), 142.29 (dd, $J = 3.48$, 11.11 Hz), 142.27 (dd, $J = 14.32$, 236.69 Hz), 133.69, 131.60, 130.71, 130.10, 128.52, 128.25, 126.46, 126.13, 123.00, 119.99, 109.40 (d, $J = 4.02$ Hz), 106.11 (dd, $J = 13.89$, 4.19 Hz), 31.43 ^{19}F NMR (376 MHz, DMSO) δ -91.91 (d, $J = 24.97$ Hz), -136.39 (d, $J = 24.93$ Hz) ppm. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{11}\text{F}_2\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 337.0788, found 337.0774.



Synthesis of S2: 2,2'-methylenediphenol (92 mg, 0.46 mmol) and **TFN** (91 mg, 0.46 mmol) was added to a 20 mL reaction vial. Anhydrous DMSO (4 mL) was then added to the reaction vial using a syringe. The vial was heated to dissolve the 2,2'-methylenediphenol. When the monomers were fully dissolved, K_2CO_3 (64 mg, 0.46 mmol) was added. The solution was then heated at 150 °C for 5 minutes. Running the reaction longer than 10 minutes resulted in diminished yields. This reaction was monitored via TLC (SiO_2 , 80:20 hexanes:ethyl acetate). The reaction solution was cooled to room temperature and then added to an excess of brine, and the resulting precipitate was recovered by filtration. The recovered solids were dissolved in DCM and purified using column chromatography (SiO_2 , 80:20 hexanes:ethyl acetate). The product was then dried under vacuum at 100 °C to provide **S1** (34 mg, 20% yield). **S1:** ^1H NMR (500 MHz, DMSO): δ 7.35-7.32 (m, 2H), 7.31-7.27 (m, 4H), 7.23-7.20 (m, 2H), 4.09 (s, 2H) ^{13}C NMR (126 MHz, DMSO) δ 153.54, 147.26 (dd, $J = 259.73, 15.73$ Hz), 146.16 (d, $J = 2.81$ Hz), 131.63, 130.59, 128.33, 126.38, 121.65, 109.64, 102.51 (dd, $J = 10.54, 7.06$ Hz), 32.16 ^{19}F NMR (470 MHz, DMSO) δ -132.72 ppm.

C. ^{19}F MAS NMR Spectroscopy Studies

Model Reaction for ^{19}F MAS Solid State Spectroscopy:



A 1:1 ratio of **S1** (17 mg, 0.05 mmol) and phenol (4.7 mg, 0.05 mmol) was added to a 4 mL reaction vial. Anhydrous DMSO (1 mL) was then added using a syringe. 3-(trifluoromethyl)benzonitrile (2 μL) was added to the reaction and used as an internal standard. The vial was heated to dissolve **S1** and phenol. When the monomers were fully dissolved, 6.9 mg of K_2CO_3 (6.9 mg, 0.05 mmol) was added to the reaction vial. The reaction was then heated at 150 $^\circ\text{C}$ for 25 minutes. Aliquots of 100 μL of the reaction were taken prior to adding K_2CO_3 , as well as 5, 15, and 25 minutes after base addition. These aliquots were centrifuged, added to 0.5 mL of DMSO, and analyzed by solution ^{19}F NMR spectroscopy. The spectra exhibited two new singlets: one at -84.67 ppm, corresponding to substitution adjacent to the nitrile (**S3**), and the other at -133.25 ppm, corresponding to substitution adjacent to pyridine (**S4**). This model reaction exhibited a 7:1 preference for **S3** relative to **S4**. This finding suggests that the position adjacent to the nitrile is more electrophilic, presumably due to electron withdrawing of the nitrile substituent. The formation of **S3** and **S4** was also confirmed by ESI-MS.

^{19}F NMR of Crude Model Reaction:

Reaction time: 15 minutes



Reaction time: 0 minutes

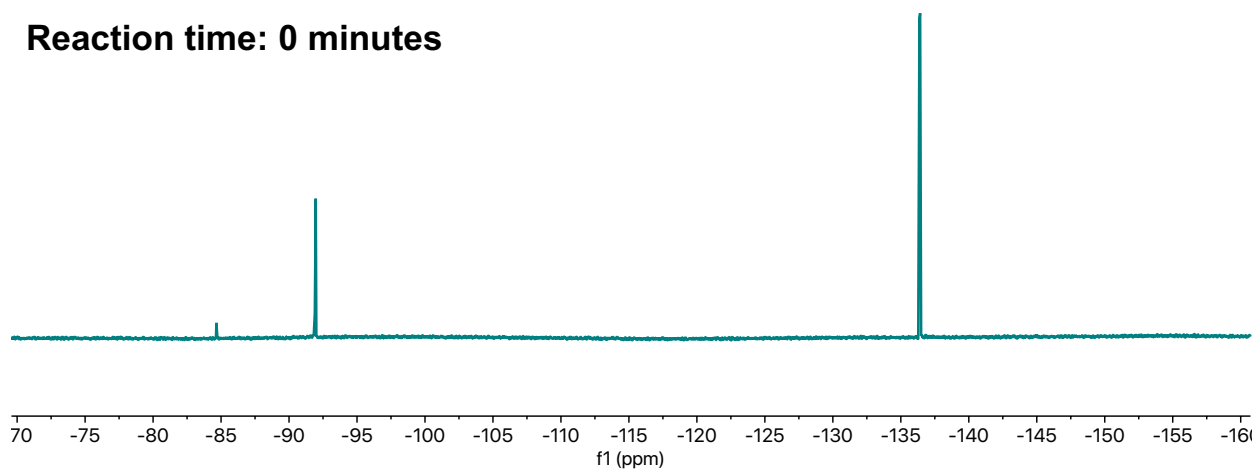


Figure S1. Partial ^{19}F NMR spectra of **S1** (bottom) and after reacting with phenol for 15 minutes (top).

Electrospray Ionization Mass Spectroscopy (ESI-MS) for Confirmation of S3 and S4 in the Model Reaction:

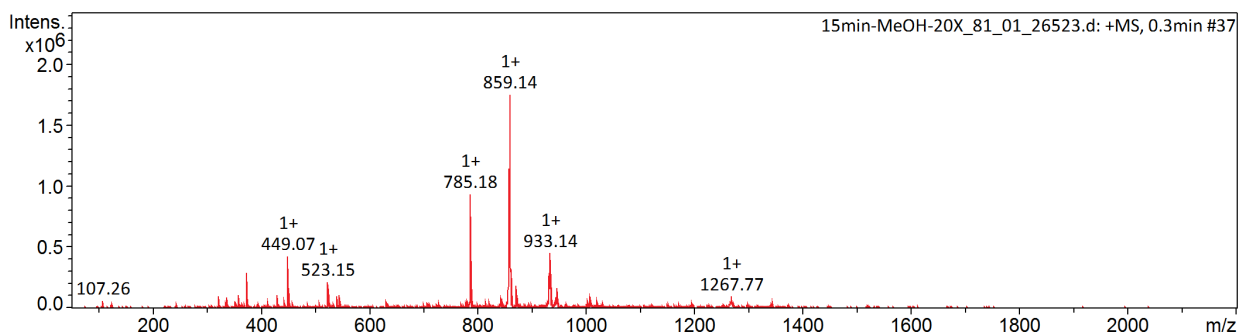


Figure S2. ESI-MS of crude reaction mixture of **S1** and phenol after 15 minutes of reaction time. Most abundant adducts are 859.14, corresponding to $[2\mathbf{S3/4}+\mathbf{K}^+]$ (Calcd 859.18) as well as 785.18 corresponding to $[\mathbf{S1}+\mathbf{S3/4}+\mathbf{K}^+]$ (Calcd 785.14). The spectra were obtained in positive mode.

¹⁹F MAS NMR Spectrum of **2**:

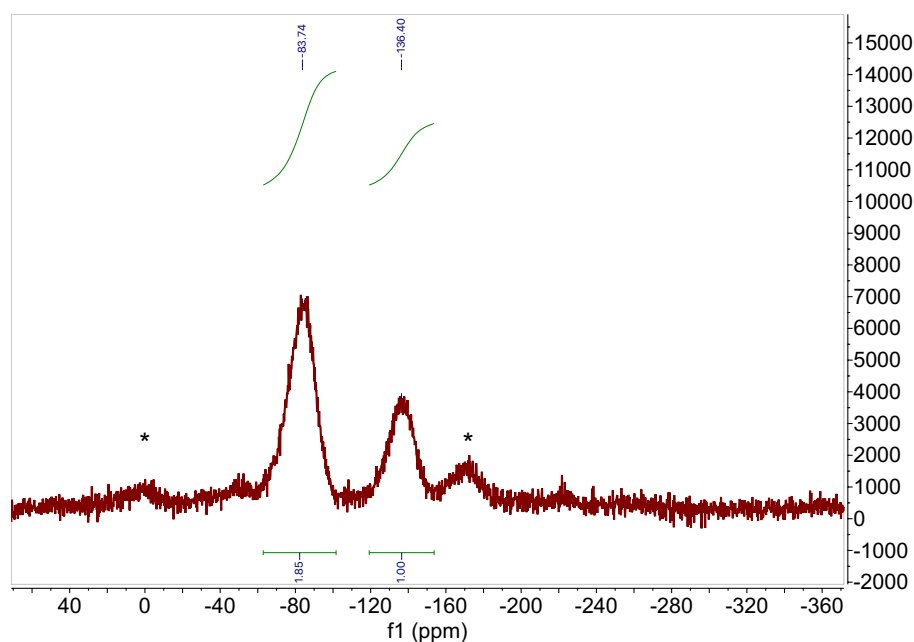


Figure S3. ¹⁹F MAS NMR Spectrum of **2**. Starred peaks are spinning side bands correlated to peaks at -83.74 ppm.

^{19}F MAS NMR Spectrum of **2 and ^{19}F Solution NMR of **S1**:**

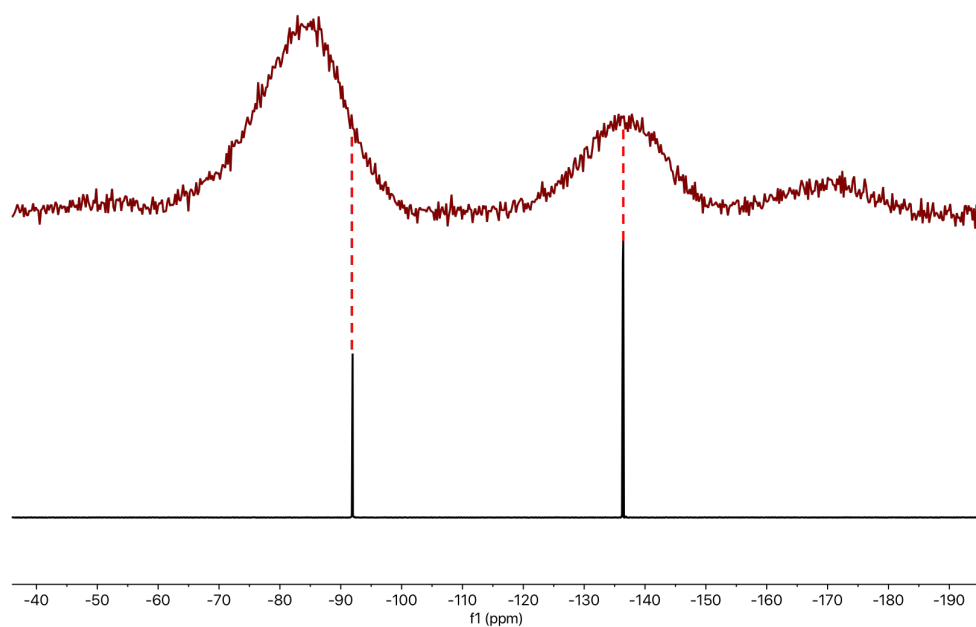


Figure S4. The bottom spectrum represents the ^{19}F solution NMR of **S1**. The top spectrum is the ^{19}F MAS NMR spectrum of **2**. Red dotted lines were added for clarity.

^{19}F MAS NMR Spectrum of **2 and ^{19}F Solution NMR Spectrum of the Model Reaction:**

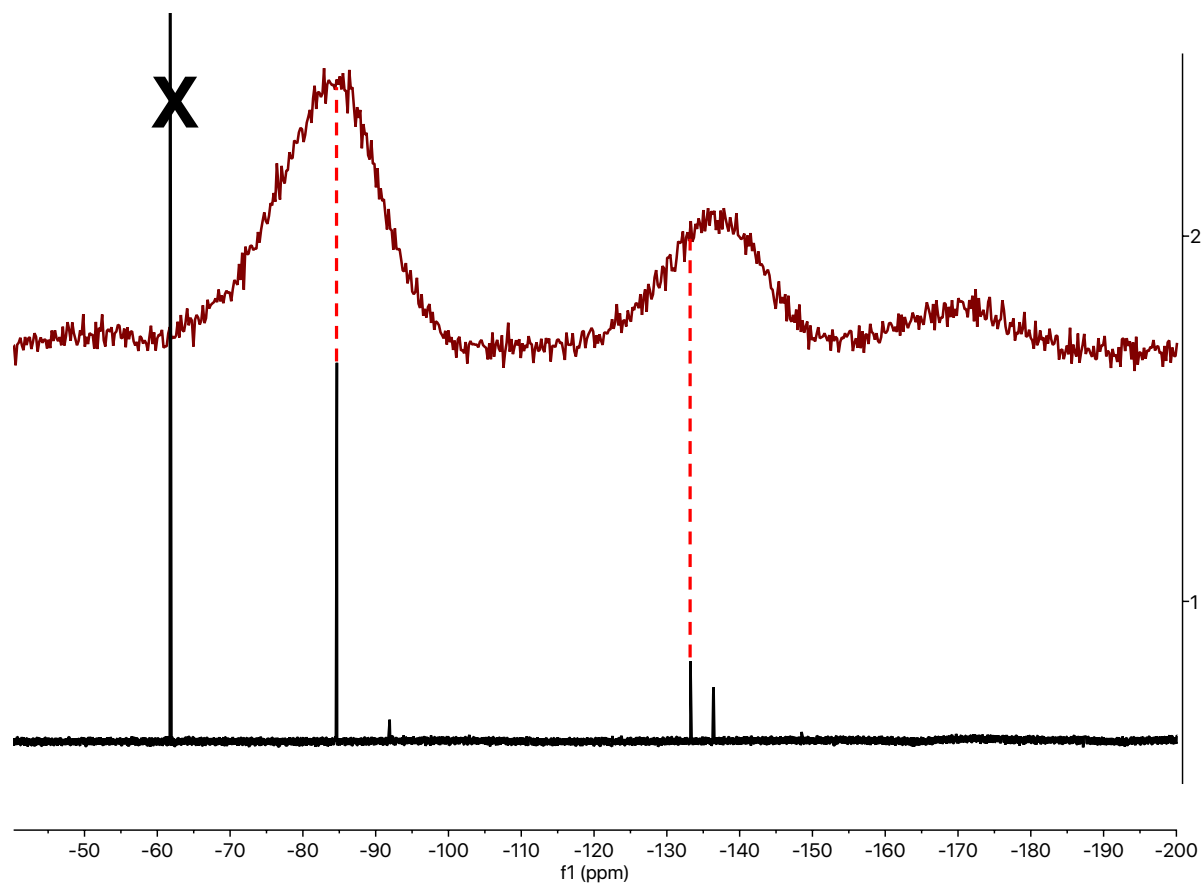


Figure S5. Bottom spectrum: solution-phase ^{19}F NMR spectrum of the crude reaction mixture of **S1** and phenol after 15 minutes of reaction time. This spectrum is overlaid with the ^{19}F MAS NMR spectrum of **2**. The X designates the internal standard peak at -61.75 ppm. For further clarity, red dotted lines were added over peaks corresponding to fluorine signals for **S3** and **S4**.

^{19}F MAS NMR Spectrum of **3:**

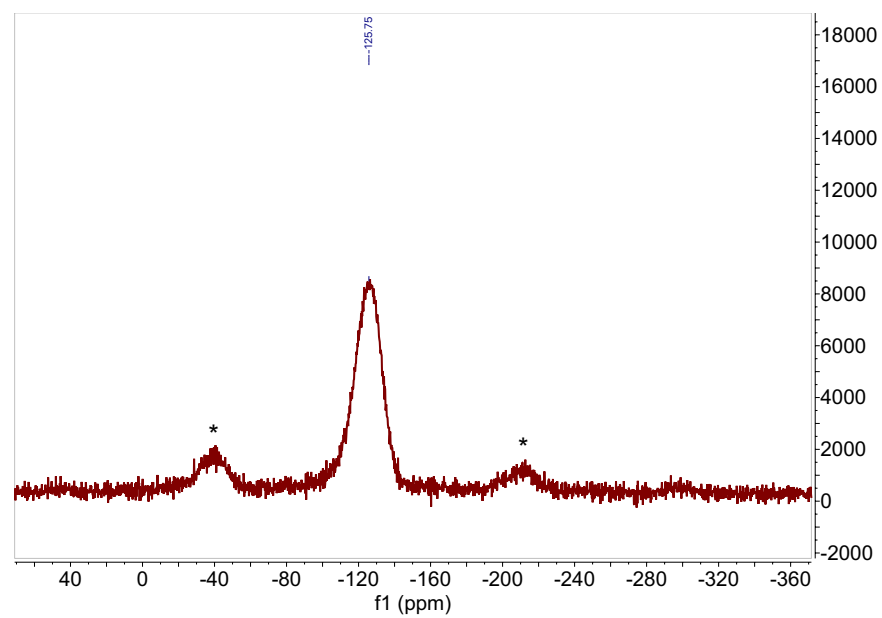


Figure S6. ^{19}F MAS NMR spectrum of **3**. Starred peaks are spinning side bands correlated to peaks at -125.75 ppm.

^{19}F MAS NMR Spectrum of **3 and ^{19}F Solution NMR of **S2**:**

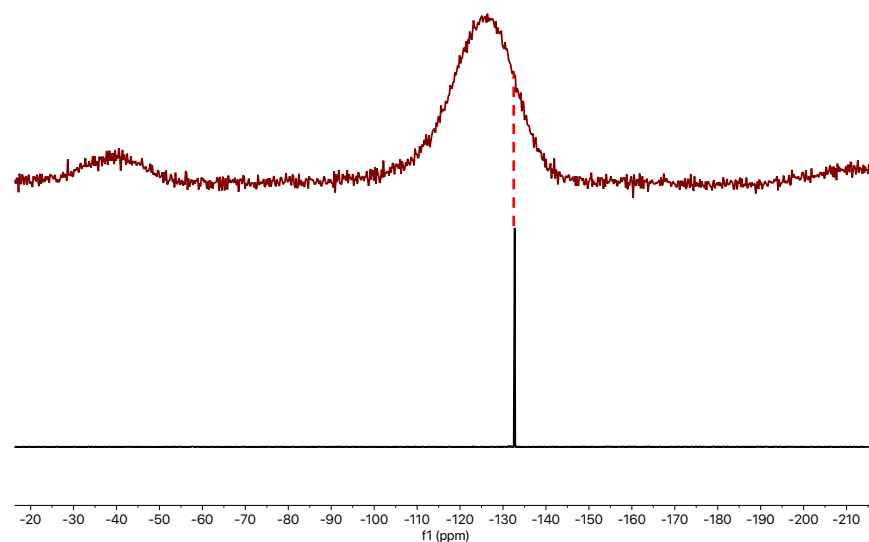


Figure S7. Bottom spectrum: Solution-phase ^{19}F NMR spectrum of the crude reaction mixture of **S2**. This spectrum is overlaid with the solid-state ^{19}F MAS NMR spectrum of **3**.

^{19}F MAS NMR Spectroscopy Discussion:

These experiments were performed to gain insight into the termination and defects in the polymers by comparing their ^{19}F MAS NMR spectra to those of model compounds. The spectrum of **2** features two resonances centered at -83.7 and -136.4 ppm with an integration ratio of 2:1. To determine if these resonances correspond to the presence of orthogonal fluorines, this spectrum was compared to the ^{19}F solution NMR of **S1**. The doublet of **S1** at -136.39 ppm matches the resonance at -136.4 ppm of **2**. This peak at -136.39 ppm corresponds to the fluorine that is orthogonal to the nitrile. The other doublet of **S1** (-91.92 ppm) corresponds to the fluorine orthogonal to the pyridine. This peak does not match the peak at -83.7 ppm for **2**. We hypothesized

that this mismatch may be due to overlapping signals from trisubstituted linkers that have unreacted fluorine adjacent to the pyridine. Therefore, we performed a model reaction of **S1** with phenol to obtain **S3** and **S4** (see above). The spectrum of **S3** shows the appearance of a singlet at -84.7 ppm, which is in good agreement with the peak of **2** at -83.7 ppm. Additionally, the model reaction also produced **S4** with a singlet at -133.25 ppm. This peak is not in good agreement with the spectra of **2**, suggesting a low abundance of trisubstituted linkers with residual fluorine adjacent to the nitrile. It is possible that this signal at -133.25 is obscured by the signal at -136.39 ppm. However, model reactions suggest that substitution should be most favorable adjacent to the nitrile (see above). Therefore, we believe it is probable that relatively few linkages with substitution patterns similar to **S4** are present in the polymer network. These results suggest that residual fluorines are most likely present as either 1,2-disubstituted linkages and as trisubstituted linkages with the residual fluorine adjacent to the pyridine.

In the case of polymer **3**, the ^{19}F MAS NMR spectra showcases a distinct peak at -125.75 ppm. This peak does not correspond to model compound **S2**, which has orthogonal fluorines. This is most likely due to an abundance of trisubstituted linkages being present in the polymer.

The proper chemical shifts of **S3** and **S4** were determined from ^{19}F NMR spectra that contained an internal standard (3-(trifluoromethyl)benzonitrile -61.75 ppm).

D. Elemental Analysis

C, H, and N analysis was performed using a combustion method (Robinson Microlit). Fluorine analysis was conducted using an ion-selective electrode method. Measurements were conducted in duplicate. The ratio of either **TFIN** or **TFN** to **1** in each polymer sample was determined by

comparing the carbon to nitrogen ratio. The number of residual fluorines per **TFIN**/TFN was calculated based upon the fluorine to nitrogen ratio.

Polymer	C %	H %	N %	F %
2	65.88 +/- 0.08	3.65 +/- 0.10	6.95 +/- 0.01	3.45 +/- 0.05
3	66.66 +/- 0.04	3.21 +/- 0.06	6.43 +/- 0.01	3.19 +/- 0.06

Table S3. Elemental composition of **2** and **3**.

E. Thermogravimetric Analysis

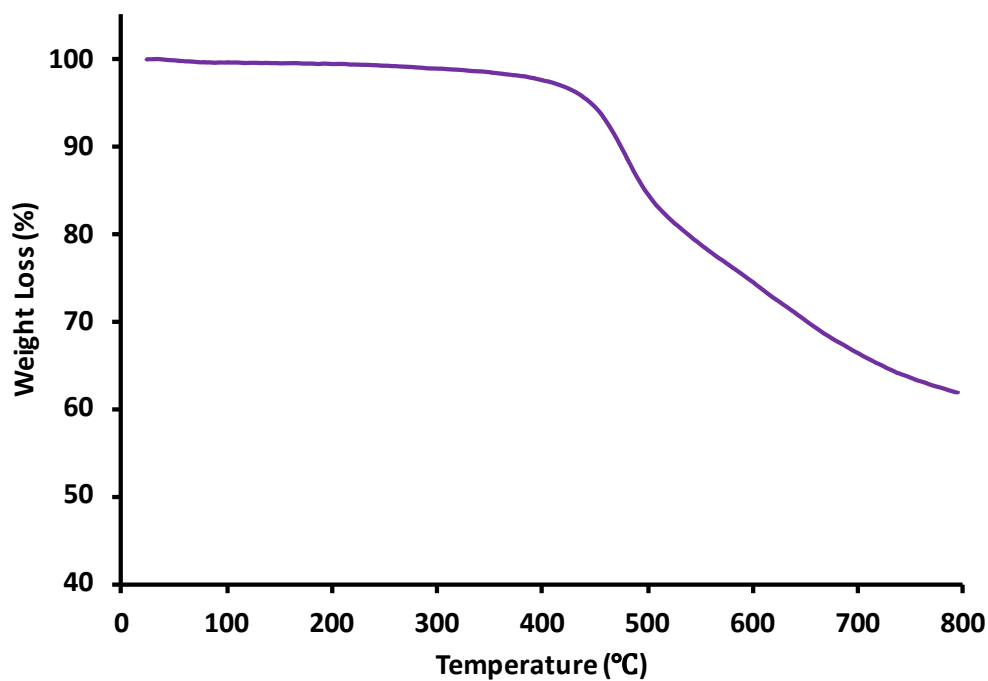


Figure S8. Thermogravimetric analysis of **2**.

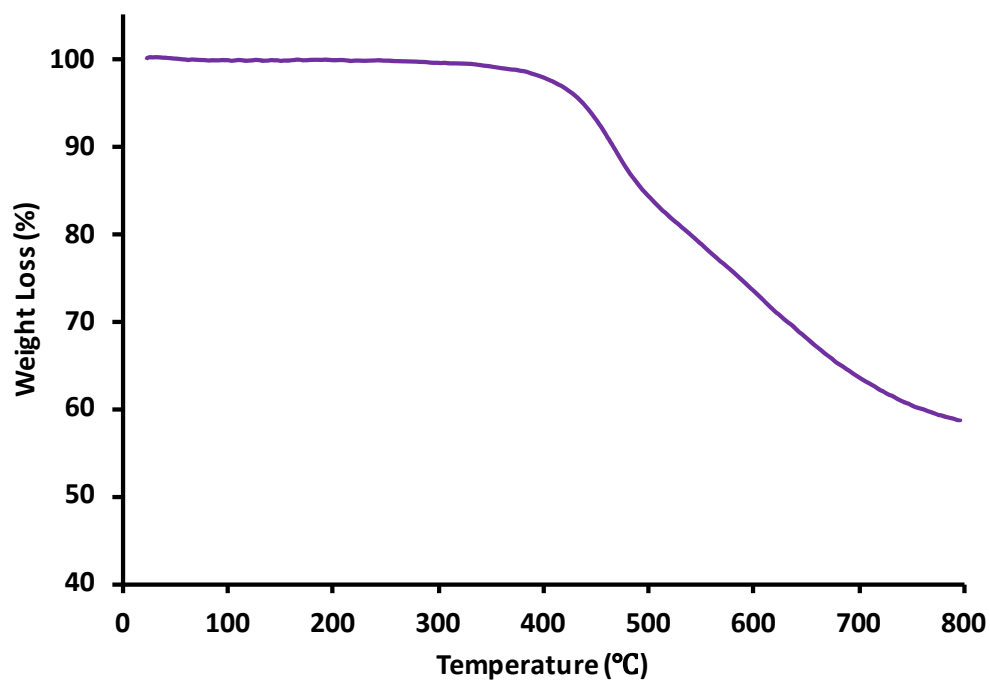


Figure S9. Thermogravimetric analysis of **3**.

F. Scanning Electron Microscopy

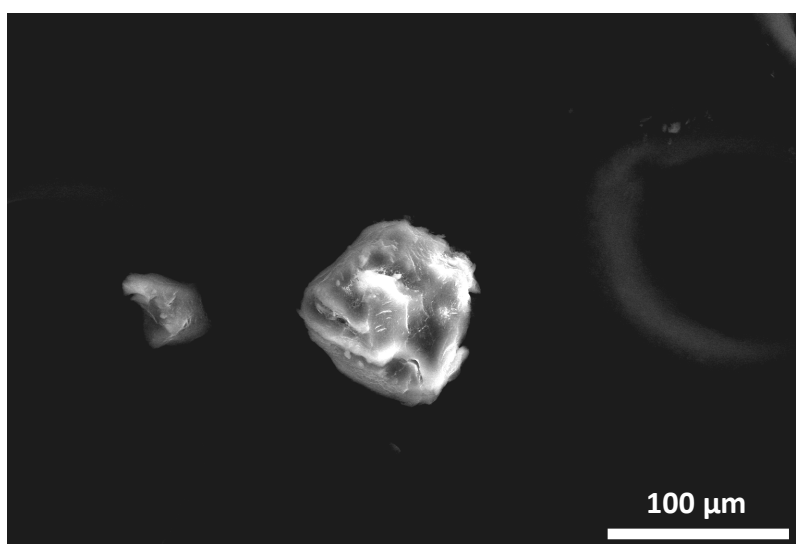


Figure S10. Scanning electron microscopy of **2** polymer particles following sieving.

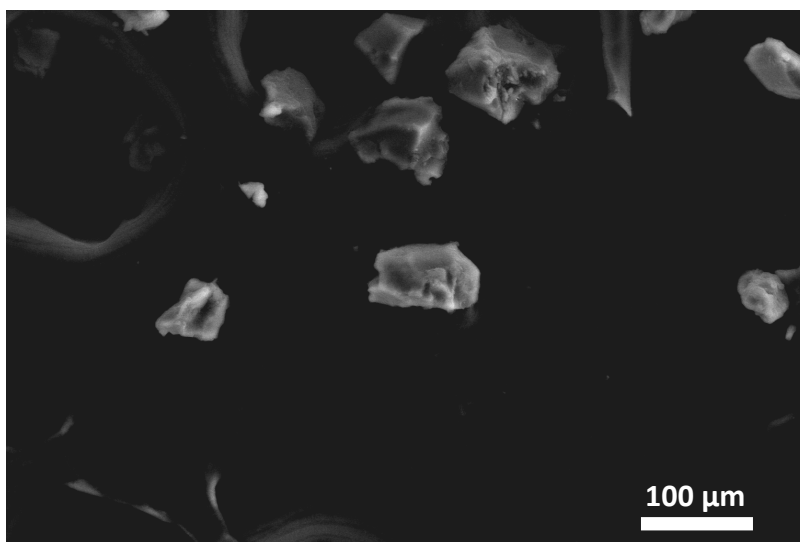


Figure S11. Scanning electron microscopy of **3** polymer particles following sieving.

G. CHCl_3 Removal Studies

General CHCl_3 Removal Experiments:

To prepare a sample for CHCl_3 removal, a stock solution (10 mL, 200 $\mu\text{g/L}$ CHCl_3 in nanopure H_2O) was transferred into a 20 mL glass reaction vial. A suspension of adsorbent in nanopure water (10 mL, 60 mg/L adsorbent) was added. A Teflon stir bar was added to the solution and the sample was closed and wrapped in parafilm. These samples were made in triplicate and were stirred at 400 rpm for 24 hours. In parallel, two control samples were prepared using nanopure H_2O (10 mL) in place of the adsorbent suspension. One of the control samples was stirred at 400 rpm in tandem with the 3 other experimental samples. The other control was stored at 4 °C. After 24 hours, the four stirred vials were transferred to a glass syringe and filtered with a 0.2 μm HPTFE filter directly into a headspace vial (2 mL liquid per headspace vial). The sample stored at 4 °C was added directly to a headspace vial. The headspace vials were crimped with silicone lids, and the samples were stored at 4 °C until analysis by headspace-GCMS (see above). During this

experimental procedure, we advise that the solution should come into minimal contact with plastic. Minimizing vial headspace was also crucial in inhibiting loss of CHCl₃ due to evaporation as we were developing and evaluating the reliability of the above procedure.

Removal Calculations:

Integration values of analyte peaks were used to calculate percent removal. To confirm no analyte was lost due to evaporation or experimental error, control samples stored at 4 °C were compared to the control samples stirred overnight. If no significant difference in CHCl₃ concentration (<10%) was observed between the stored control and the stirred control sample, then the experimental samples were assumed to be unaffected by the experimental procedure. The control sample that was stirred in tandem with the other experimental samples was used as the reference when determining percent removal using the following equation:

$$\left(1 - \frac{\text{Experimental sample integration value}}{\text{Stirred control integration value}}\right) \times 100 = \text{Percent Removal}$$

All removal experiments were calculated this way unless otherwise noted.

Kinetics of CHCl_3 Removal:

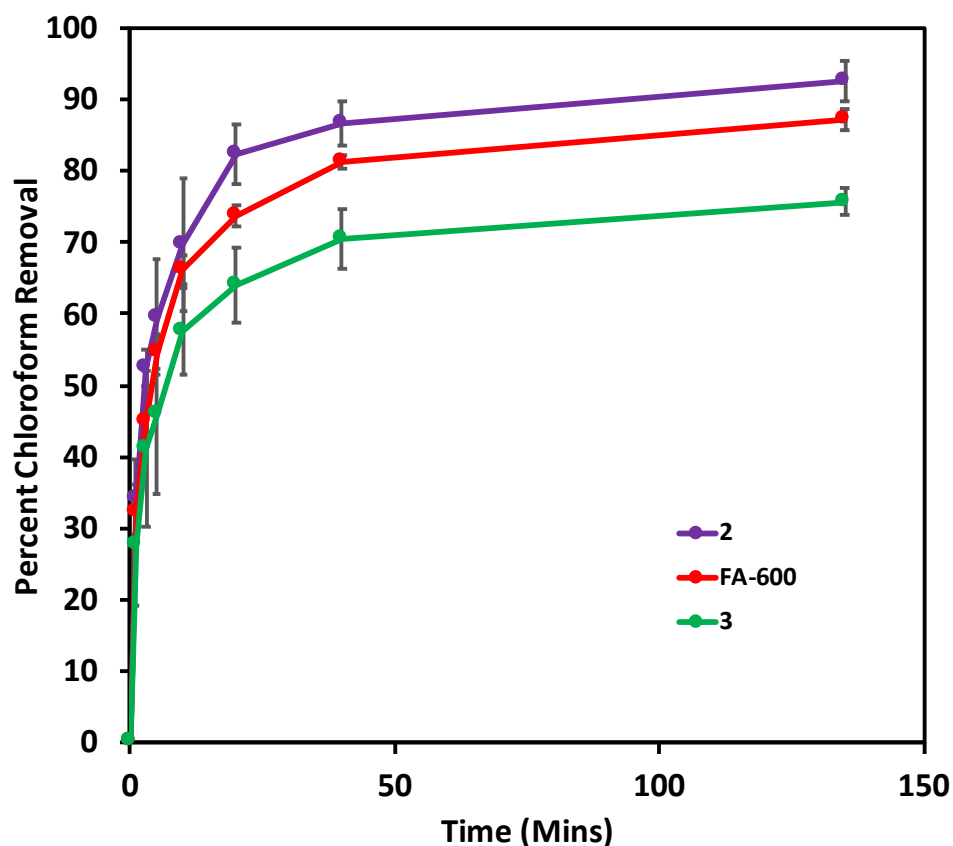


Figure S12. Kinetic removal trace of CHCl_3 (100 $\mu\text{g/L}$ initial concentration) with **2**, **3**, and **FA600** (100 mg/L).

A CHCl_3 stock solution (30 mL, 133 $\mu\text{g/L}$ CHCl_3 in nanopure water) was transferred into a 40 mL glass reaction vial. A Teflon stir bar was added to the solution. A suspension of adsorbent (10 mL, 400 mg/L in nanopure water) was added to the CHCl_3 stock solution and stirred at 400 rpm. The timer was started as soon as the 10 mL suspension was added. Aliquots (3 mL) were transferred to glass syringes and filtered with HPTFE filters directly into glass headspace vials (2 mL of sample per headspace vial). All headspace vials were crimped with a silicone lid. These aliquots were taken at time points of 1, 3, 5, 10, 20, 40, and 135 minutes. In-between each aliquot the vial

was sealed closed. The zero-time point of this experiment was taken from a mixture of the CHCl_3 stock solution (30 mL) and nanopure water (10 mL) without adsorbent. This sample was also filtered with a HPTFE filter directly into a headspace vial (2 mL). This process was repeated in triplicate. The samples were stored at 4 °C until analysis by headspace-GCMS (see above). Percent removal was calculated using the equation below.

$$\left(1 - \frac{\text{Peak Area of Time Point } X}{\text{Peak Area of Time Point Zero}}\right) \times 100 = \text{Percent Removal}$$

CHCl_3 Isotherms:

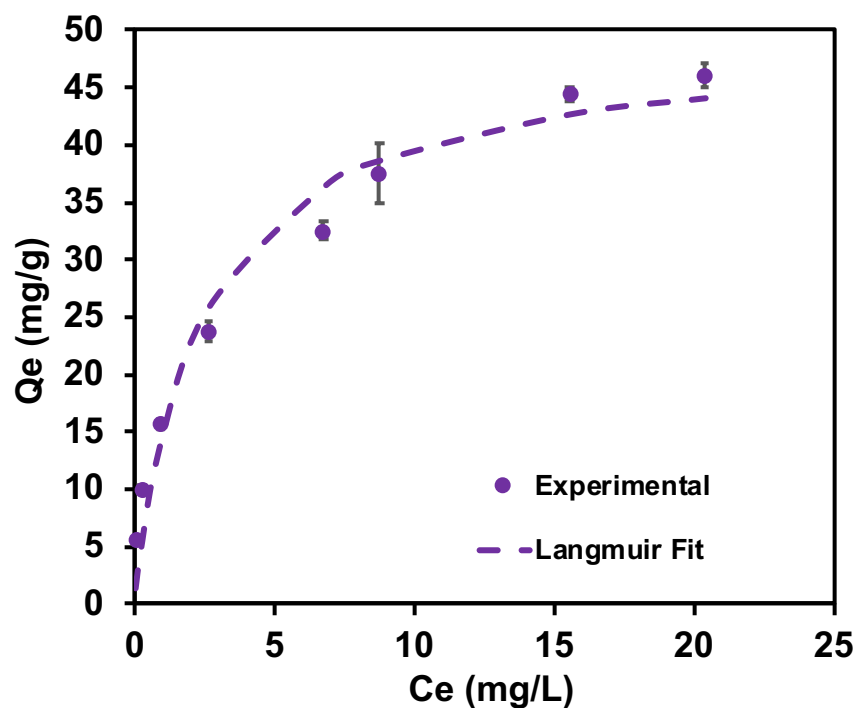


Figure S13. Isotherm of **2** (100 mg/L) at high CHCl_3 content. The Langmuir fit provided a R^2 of 0.987, a K_L of $4.91 \cdot 10^4 \text{ M}^{-1}$, and a Q_{max} of 49 mg/g.

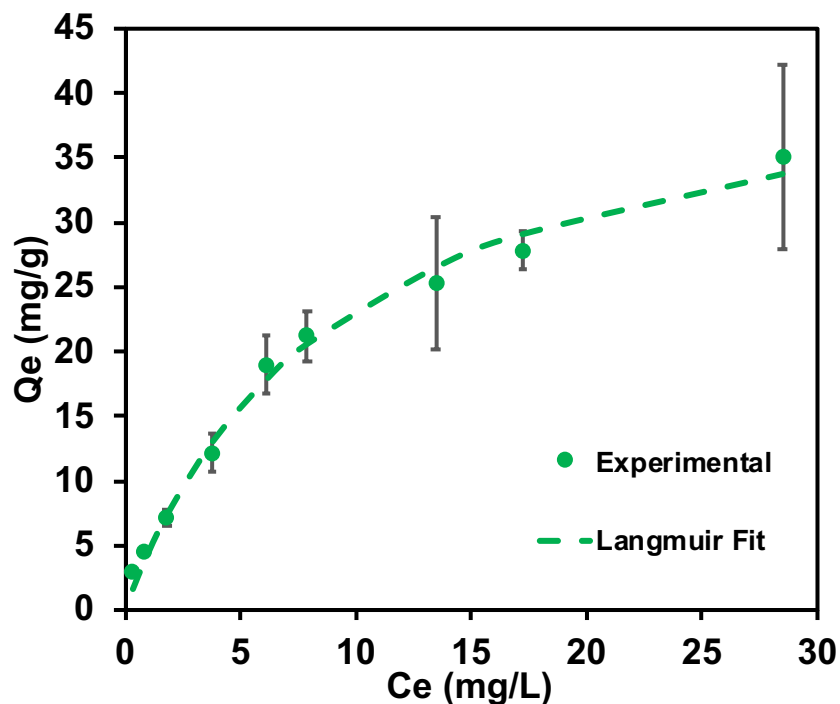


Figure S14. Isotherm of **3** (100 mg/L) at high CHCl_3 content. The Langmuir fit provided a R^2 of 0.996, a K_L of $1.29 \cdot 10^4 \text{ M}^{-1}$, and a Q_{max} of 45 mg/g.

High CHCl_3 Content Isotherm: CHCl_3 stock solutions were made at concentrations of 26.32, 21.05, 13.16, 10.53, 10.53, 5.26, 2.63, 1.32, 0.658 mg/L for **2** and concentrations of 33.7, 21.05, 16.85, 10.53, 8.43, 5.26, 2.63, 1.32, 0.658 mg/L for **3**. Stock solutions (19 mL) were pipetted into their respective 20 mL glass vial. A suspension of adsorbent (1 mL, 2 g/L) was added to each vial. A Teflon stir bar was added to the solution and the sample was closed and wrapped in parafilm. Each sample concentration was made in triplicate. Samples were stirred at 400 rpm for 24 hours. Two control samples were made with each CHCl_3 stock solution (19 mL) and nanopure water (1 mL). One of the control samples for each concentration was stirred at 400 rpm in tandem with the 3 other experimental samples.

The other control was stored at 4 °C. After 24 hours the stirring vials were transferred to a glass syringe and filtered with a 0.2 µm HPTFE filter directly into a headspace vial (2 mL per headspace vial). The sample stored at 4 °C was added directly to a headspace vial without filtering (2 mL). All headspace vials were crimped with a silicone lid. The headspace samples were now stored at 4 °C until analysis by headspace-GCMS (see above).

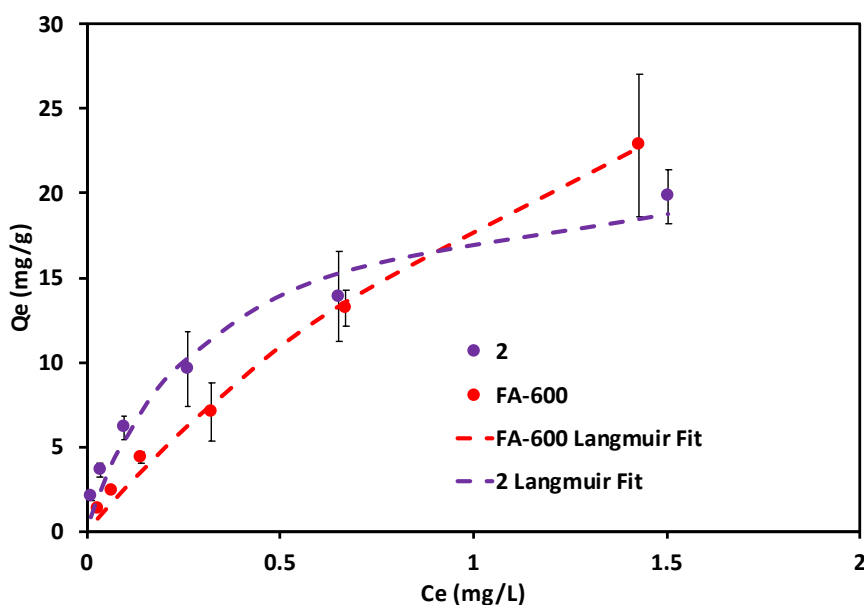


Figure S15. Isotherm of **2** and **FA600** (25mg/L) at environmentally relevant CHCl_3 content. The Langmuir fit provided a R^2 of 0.989 and 0.998 for **2** and **FA600** respectively. The K_L of **2** and **FA600** was calculated to be 3.70×10^5 and $3.49 \times 10^4 \text{ M}^{-1}$ respectively.

Isotherm at Environmentally Relevant Concentrations: CHCl_3 stock solutions were made at concentrations of 2666, 1333, 666, 332, 166, and 83 µg/L. Each stock (3 mL) was pipetted into their respective vials. A suspension of adsorbent (1 mL, 100 mg/L) was added

to each vial. A Teflon stir bar was added to the solution and the sample was closed with a PTFE septum and wrapped in parafilm. These samples were made in triplicate and were stirred at 700 rpm for 24 hours. Two control samples for each CHCl₃ concentration were made with the CHCl₃ stock solutions (3 mL) and nanopure water (1 mL). One of the control samples for each concentration was stirred at 700 rpm in tandem with the 3 other experimental samples. The other control was stored at 4 °C. After 24 hours the stirring vials were transferred to a glass syringe and filtered with a 0.2 µm HPTFE filter directly into a headspace vial (2 mL per headspace vial). The sample stored at 4 °C was added directly to a headspace vial without filtering (2 mL). All headspace vials were crimped with a silicone lid. The samples were stored at 4 °C until analysis by headspace-GCMS (see above). A suitable isotherm of **3** was not able to be obtained due to lack of significant CHCl₃ removal at these conditions.

Isotherm Calculations:

All isotherms were fit to a Langmuir absorption model with a non-linear least square regression of the equation below.

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{C_e \times Q_m \times K_L}$$

C_e : Residual CHCl₃ content (mg/L)

Q_m : Maximum absorption capacity (mg/g)

q_e : Amount of CHCl₃ removed at equilibrium (mg/g)

K_L : Langmuir equilibrium constant which represents the ratio absorption and desorption rates (L/mg)

Langmuir fits were able to provide Q_m and K_L for the adsorbents tested.

TGA experiment for reactivation:

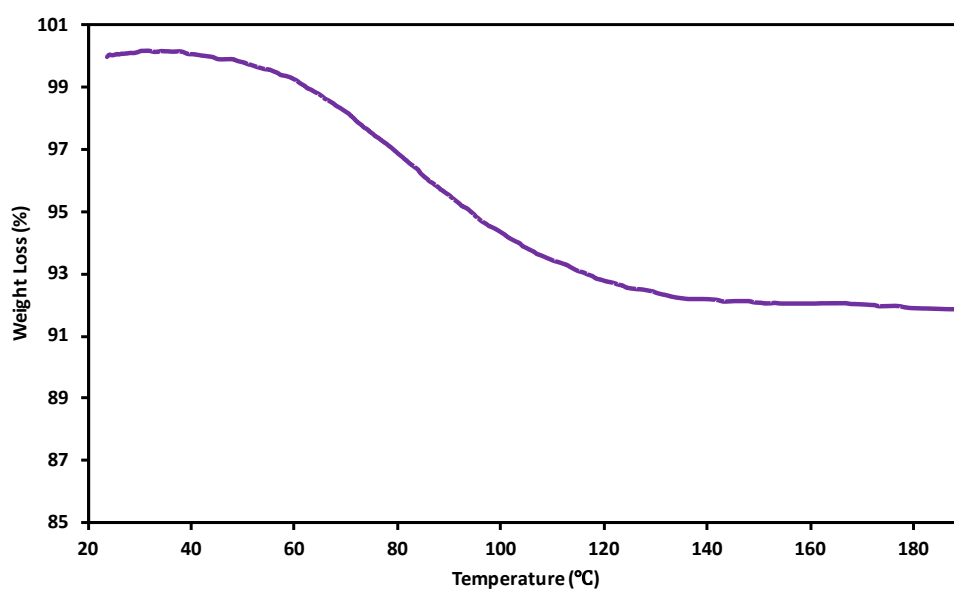


Figure S16. TGA of **2** after exposure to CHCl_3 vapor. Mass loss from 60-120 °C is due to the off gassing of CHCl_3 .

A suitable regeneration temperature for **2** was determined by thermogravimetric analysis (TGA). Adsorbent (14 mg) was placed in a 4 mL vial. The 4 mL vial with adsorbent was placed in a 20 mL glass vial containing CHCl_3 (2 mL) for 24 hours. This process led to CHCl_3 uptake from the vapor phase by the polymer. After 24 hours the 4 mL vial with adsorbent was removed and left

open to air to allow for any excess CHCl_3 to leave the vial. TGA was then performed on the polymer using the same procedure as described previously. A transition from 60-120 °C was observed resulting in a loss of 8% weight. Tandem GC/MS was able to identify CHCl_3 as the species responsible for the loss in weight. The results from these experiments suggested that 120 °C should be sufficient for reactivation of the polymer.

Recycling experiment:

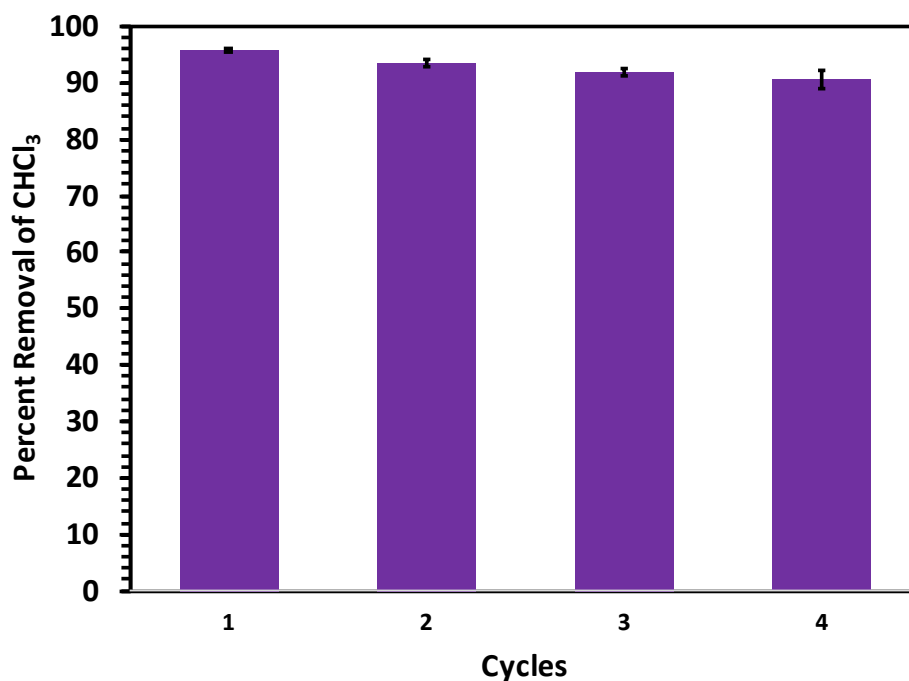


Figure S17. Removal of CHCl_3 (7 mg/L) with **2** (1000 mg/L) over four thermal regeneration cycles. The polymer was regenerated under vacuum at 125 °C.

Conditions were chosen to make polymer recovery feasible and to challenge the polymer at high enough CHCl_3 concentration to evaluate reactivation and performance loss. Removal studies were performed in 20 mL vials with 20 mg of **2** (1000 mg/L) in each vial. A stock solution of CHCl_3 (7 mg/L) was added to the vial along with a Teflon stir bar. The sample was then stirred at 400 rpm for 30 minutes. The vial was removed from stirring for 15 minutes to allow the polymer to settle to the bottom of the vial. 3 mL of sample was taken from the top of the vial, taking care to not disturb the settled polymer. The aliquot (3 mL) was added to a glass syringe and filtered through a 0.2 μm HPTFE filter into a headspace GC-MS vial (2 mL). The samples were stored at 4 °C until analysis by headspace-GCMS. The remaining samples were then filtered to retrieve the polymer. The polymer was returned to the vial and heated to 125 °C under vacuum (~40 mmHg) for 30 minutes. The polymer was then re-subjected to CHCl_3 (7 mg/L). This process occurs for 4 total cycles. As a control CHCl_3 stock solutions (7 mg/L) was stirred for 30 min and filtered with a glass syringe and HPTFE filter. Headspace GC-MS was conducted to evaluate residual CHCl_3 content (see method above). The control was used as a reference for the percent removal of CHCl_3 for each cycle. All measurements were conducted in triplicate. The polymer removed 96% of the CHCl_3 for the first cycle and 91% for the 4th cycle. This small drop in performance may be due to polymer loss over consecutive filtration operations. Overall, these results suggest that the polymer can be recycled and reused while maintaining a high level of performance.

H. 1,4-Dioxane Removal

To determine accurate and precise 1,4-dioxane concentrations at $\mu\text{g/L}$ concentrations, special sample preparation and use of Selected Ion Monitoring (SIM) GC/MS are required according to the EPA method 522.

A 1,4-dioxane stock solution (1.00 g/L in nanopure water) was prepared and diluted sequentially to a final concentration of 100 µg/L. 1,4-dioxane samples (100 mL, 100 µg/L in nanopure water) in triplicate were prepared in a plastic bottle charged with a stir bar, then 50 mg or 10 mg of polymer adsorbent (**2**, **3**, **FA600** or **Ambersorb 560**) was added to each sample. As a control, 1,4-dioxane samples (100 mL, 100 µg/L in nanopure water) with no adsorbent were prepared in triplicate. The samples were stirred overnight at 500 rpm. Stirring was stopped, and each adsorbent was allowed to settle for 20 min, after which approximately 80 mL of the solution was transferred to a 100 mL brown glass bottle. These samples were packed in a chiller box with an ice bag and shipped to Pace Analytical company for analysis.

1,4-Dioxane Removal in Tap Water:

Tap water was sourced from water at the Northwestern Technological Institute. The tap water was spiked with 100 µg/L of 1,4-dioxane following the procedure from above. Tap water removal was performed with **2**, **FA600**, and **Ambersorb 560** (500 mg/L). Removal experiments were performed in triplicate. However, one sample of **2** in tap water was damaged during shipping, such that this measurement was performed in duplicate.

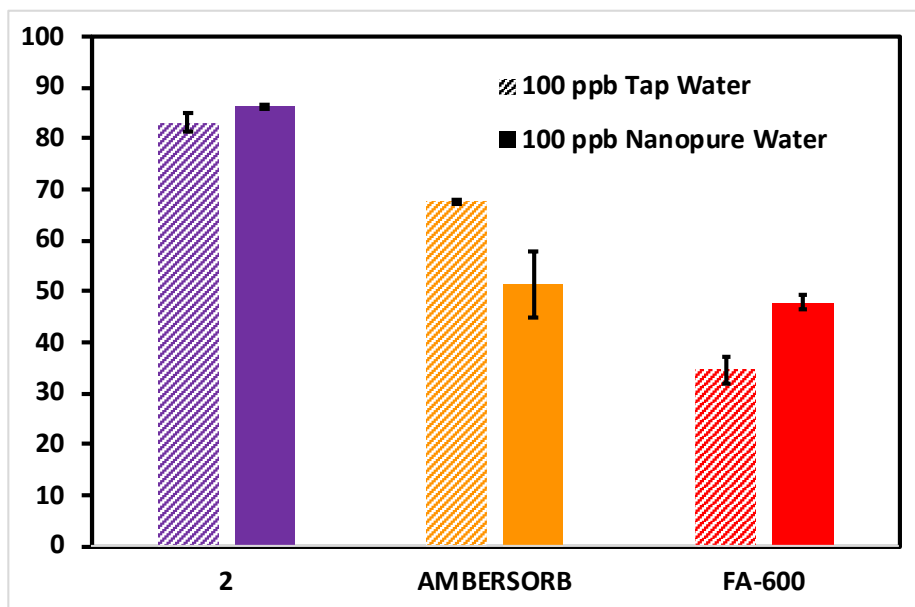


Figure S18. Removal of 1,4-Dioxane (100 µg/L) with 2, Ambersorb 560, and FA600 (500 mg/L) in both tap water and nanopure water.

I. Standard Curves

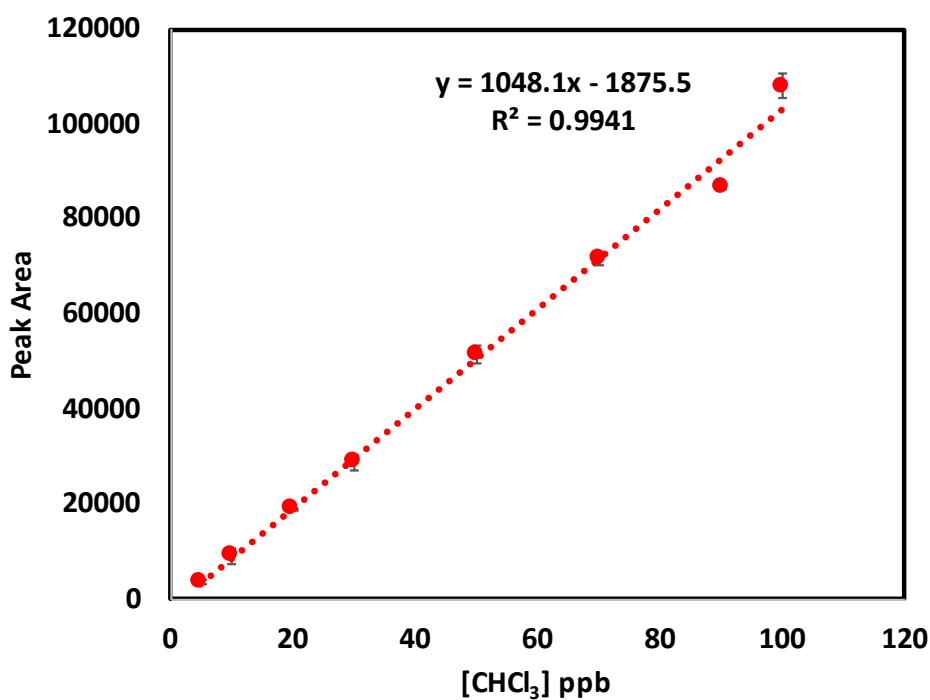


Figure S19. GC-MS CHCl₃ standard curve from 5–100 µg/L.

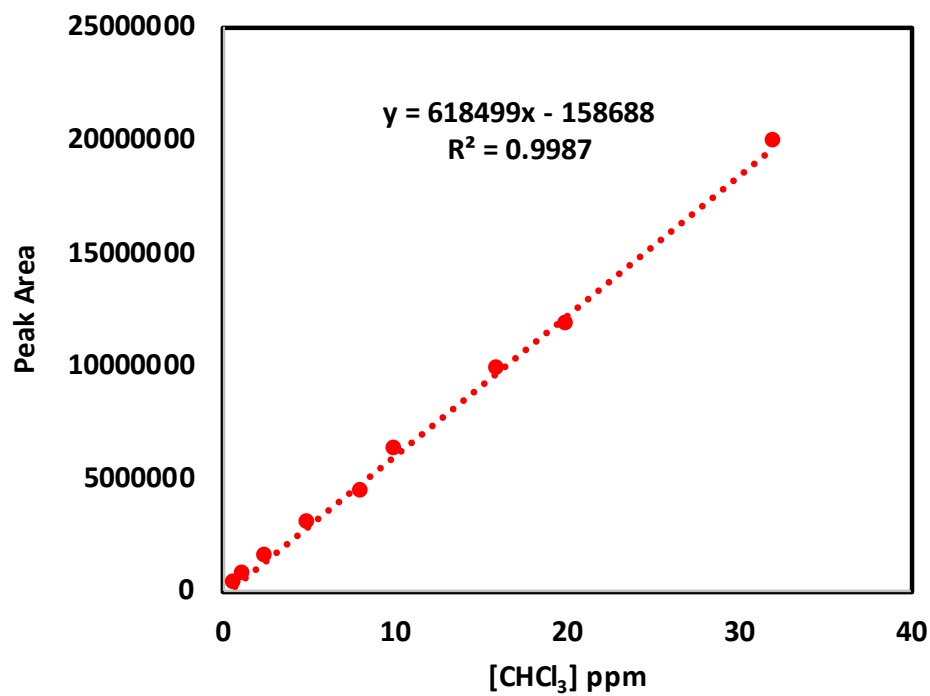


Figure S20. GC-MS CHCl_3 standard curve from 0.625–30 mg/L.

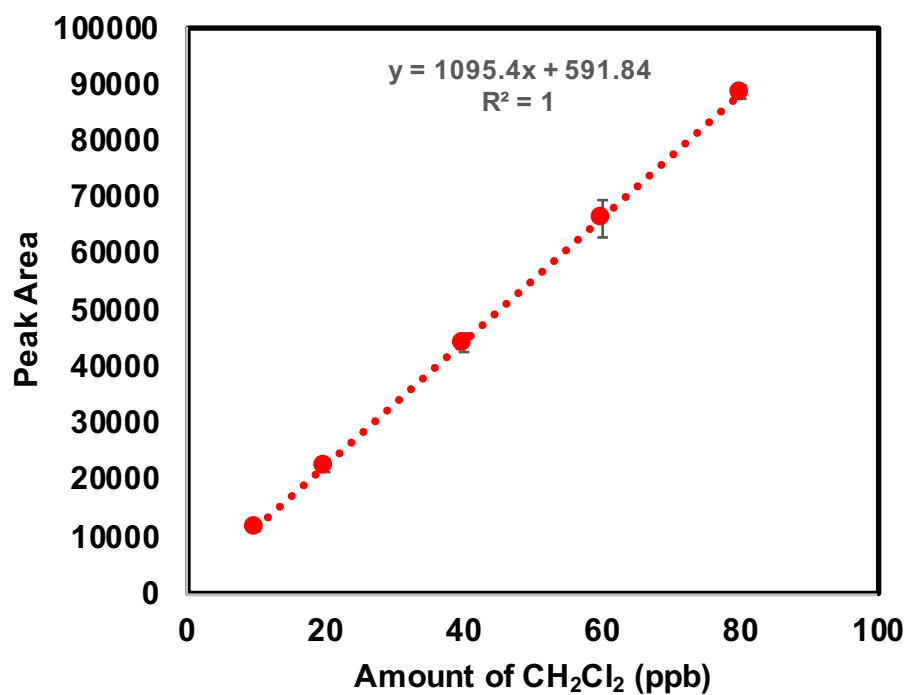


Figure S21. GC-MS CH_2Cl_2 standard curve from 10–80 $\mu\text{g/L}$.

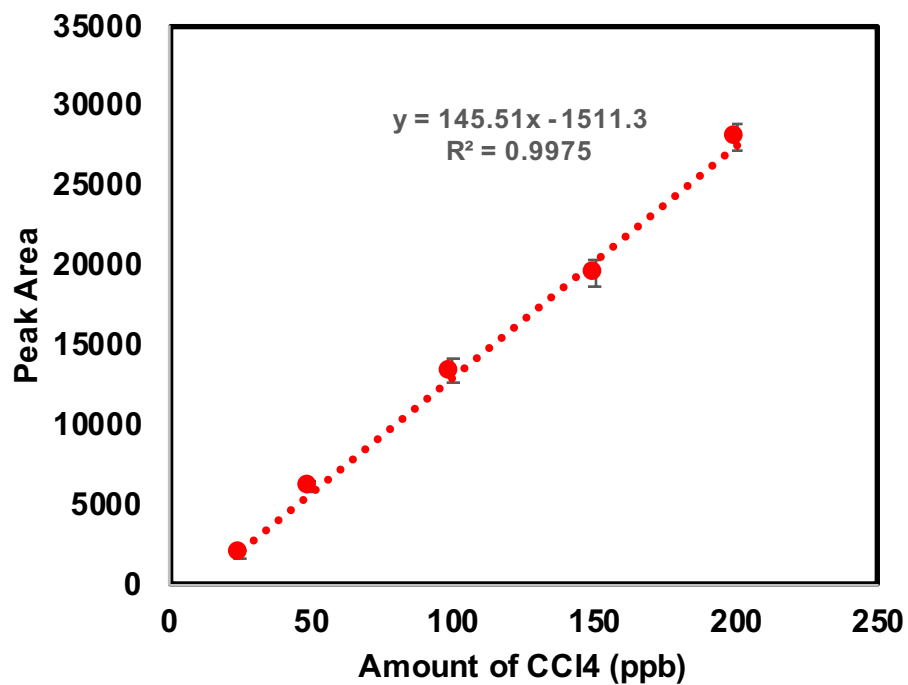


Figure S22. GC-MS CCl₄ standard curve from 10–80 µg/L.

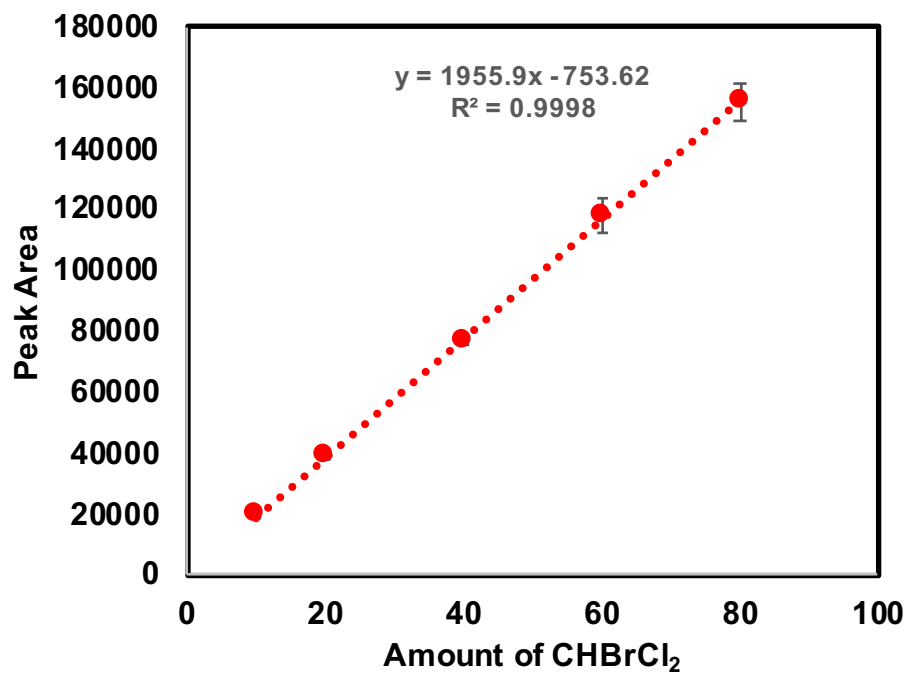


Figure S23. GC-MS CHBrCl₂ standard curve from 10–80 µg/L.

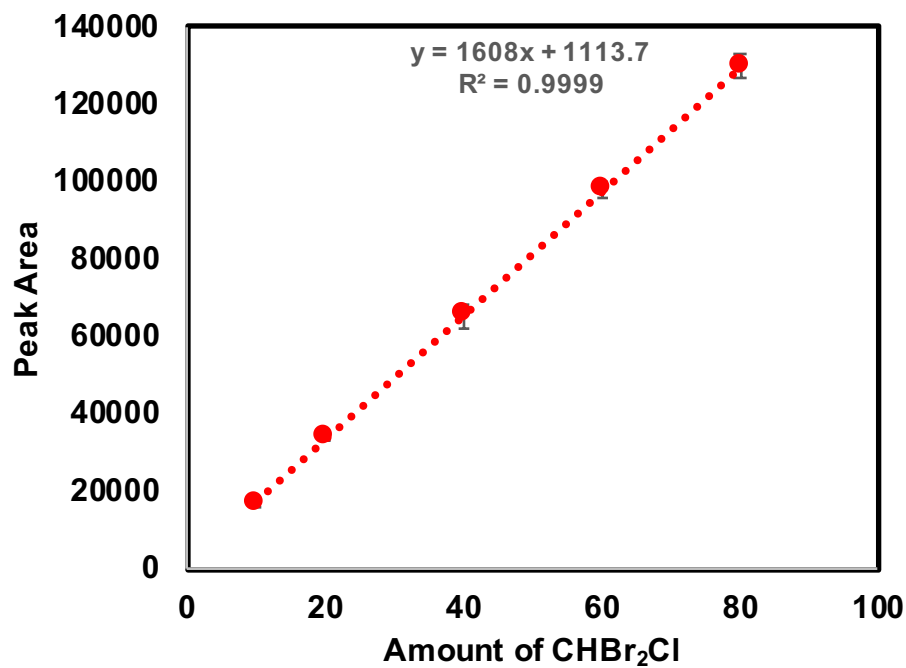


Figure S24. GC-MS CHBr₂Cl standard curve from 10–80 µg/L.

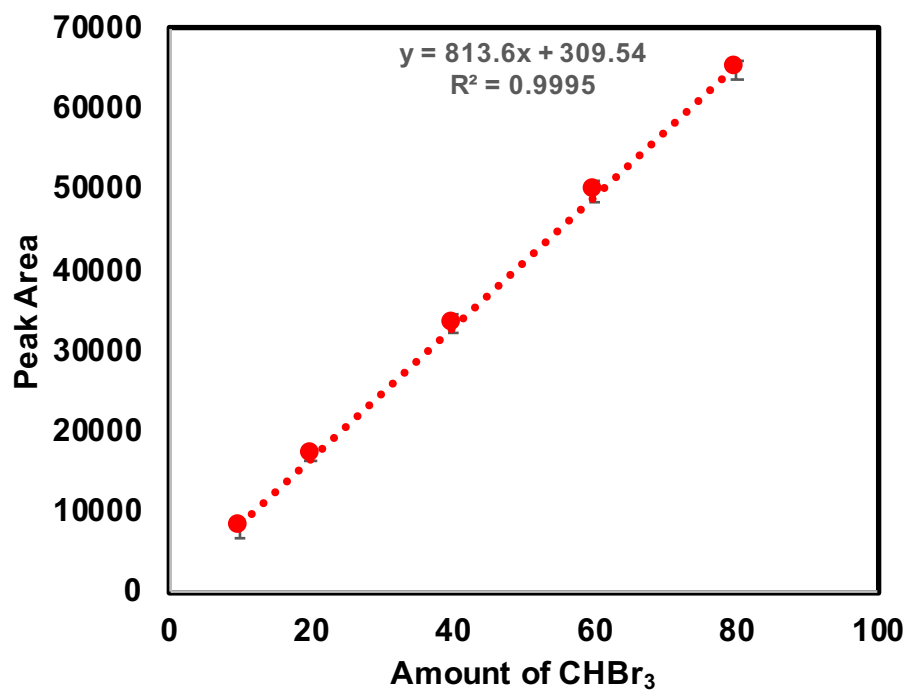


Figure S25. GC-MS CHBr₃ standard curve from 10–80 µg/L.

J. ^1H , ^{13}C , and ^{19}F NMR Spectra of Synthesized Compounds

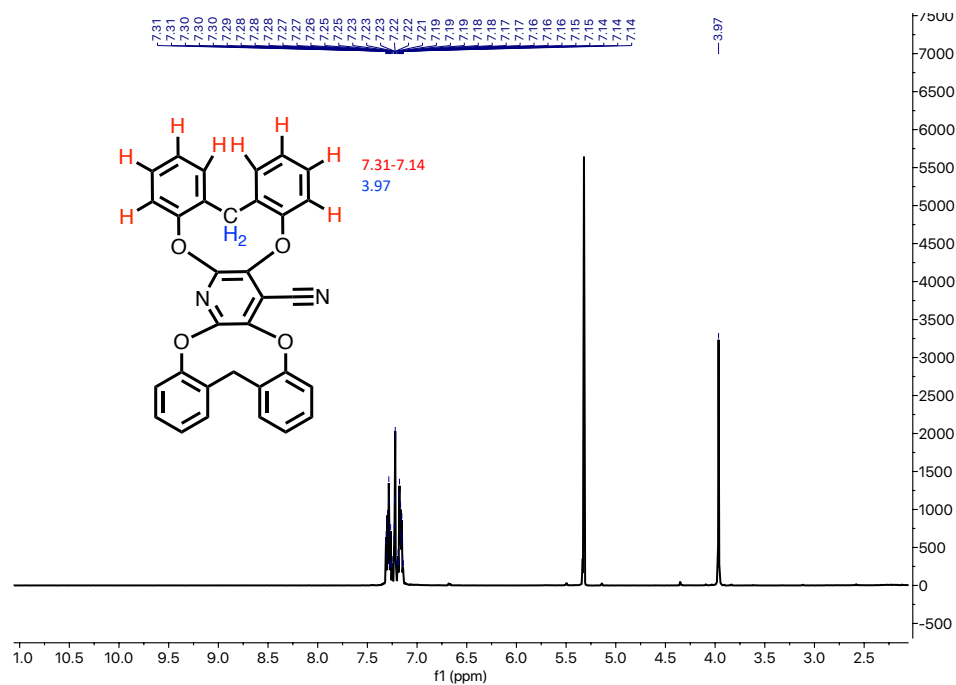


Figure S26. ^1H NMR spectrum (500 MHz, 298K, CD_2Cl_2) of 4

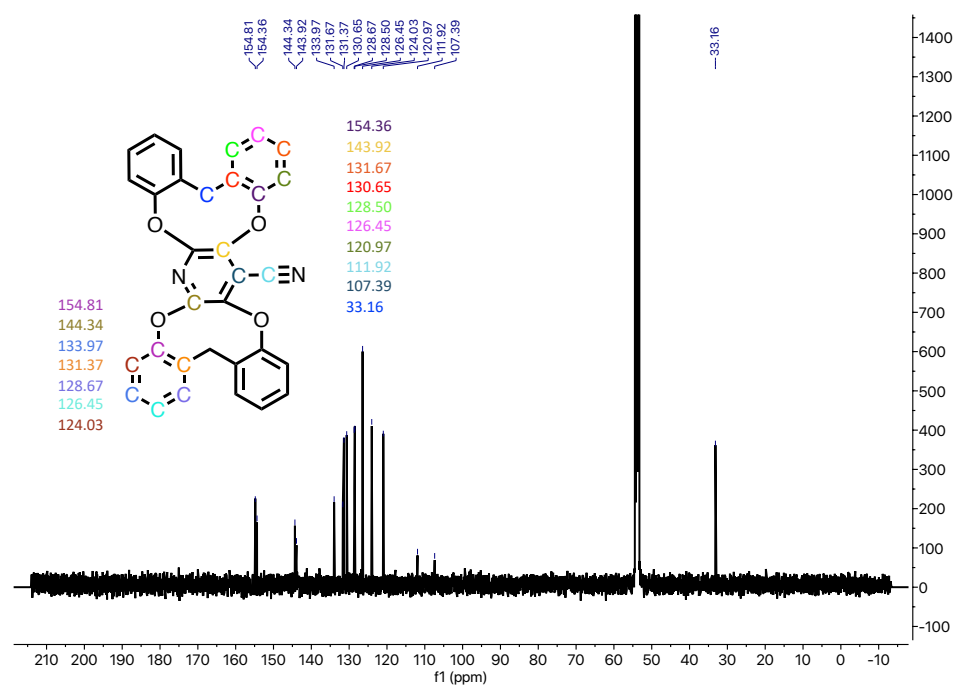


Figure S27. ^{13}C NMR spectrum (126 MHz, 298K, CD_2Cl_2) of 4

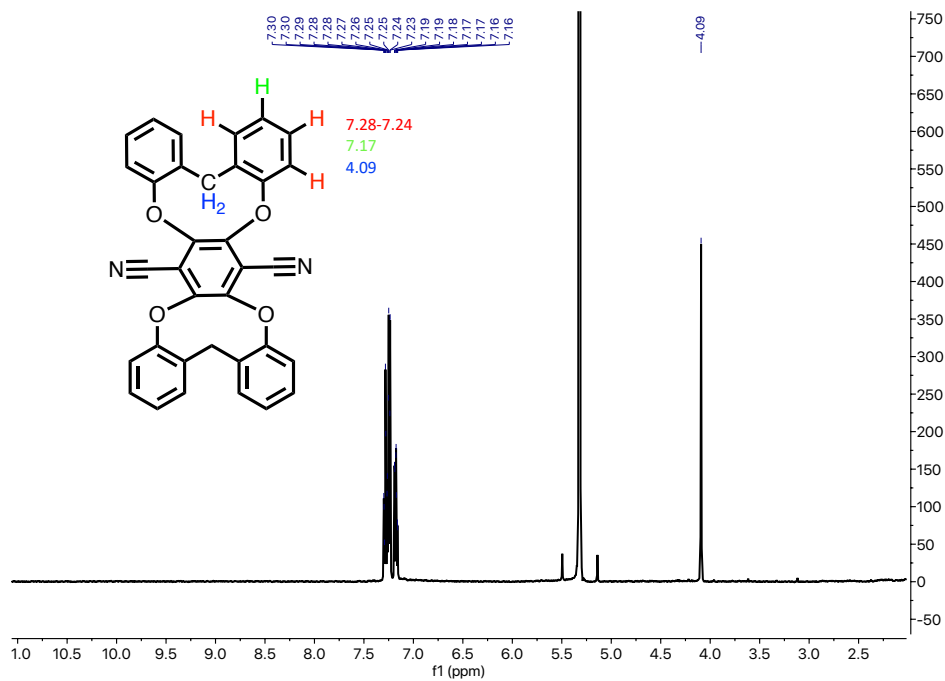


Figure S28. ^1H NMR spectrum (500 MHz, 298K, CD_2Cl_2) of **5**

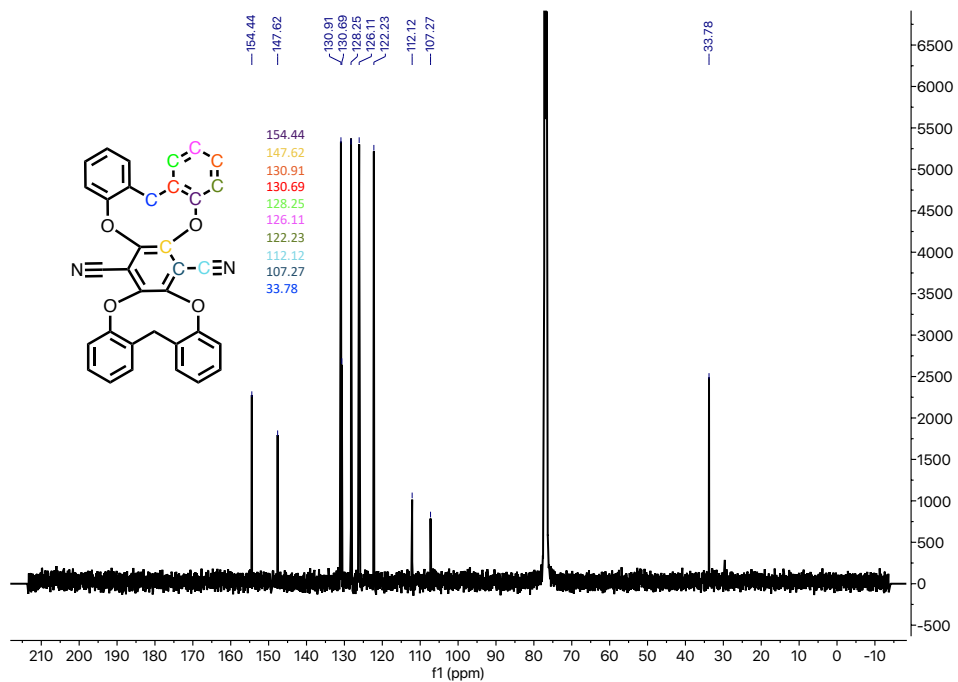


Figure S29. ^{13}C NMR spectrum (126 MHz, 298K, CDCl_3) of **5**

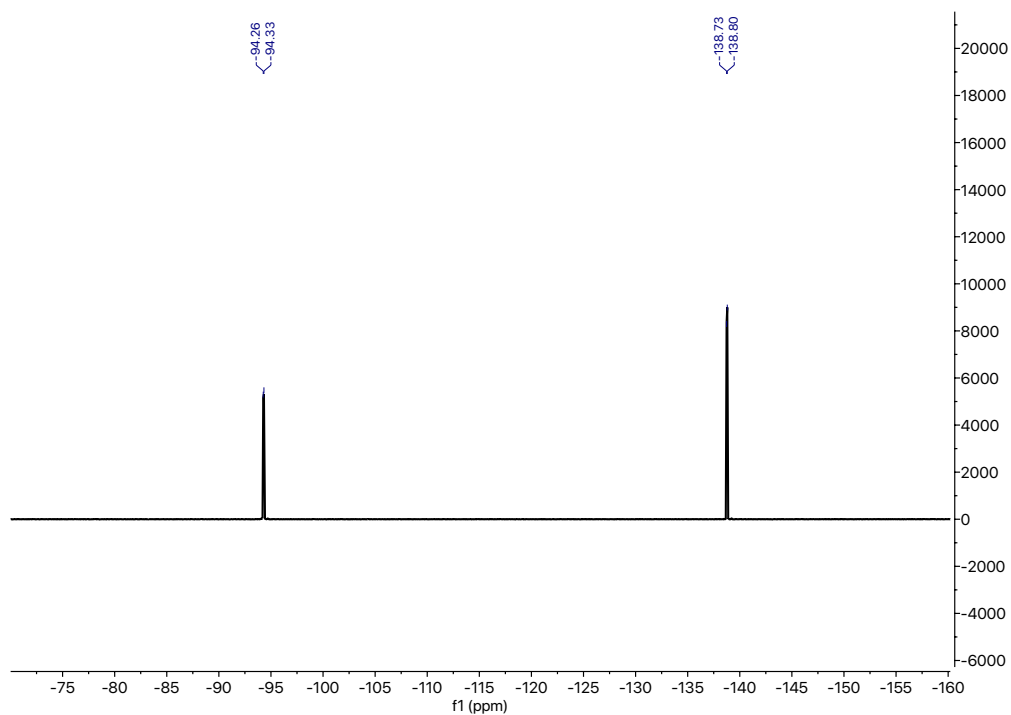


Figure S32. ¹⁹F NMR spectrum (376 MHz, 298K, DMSO) of S1

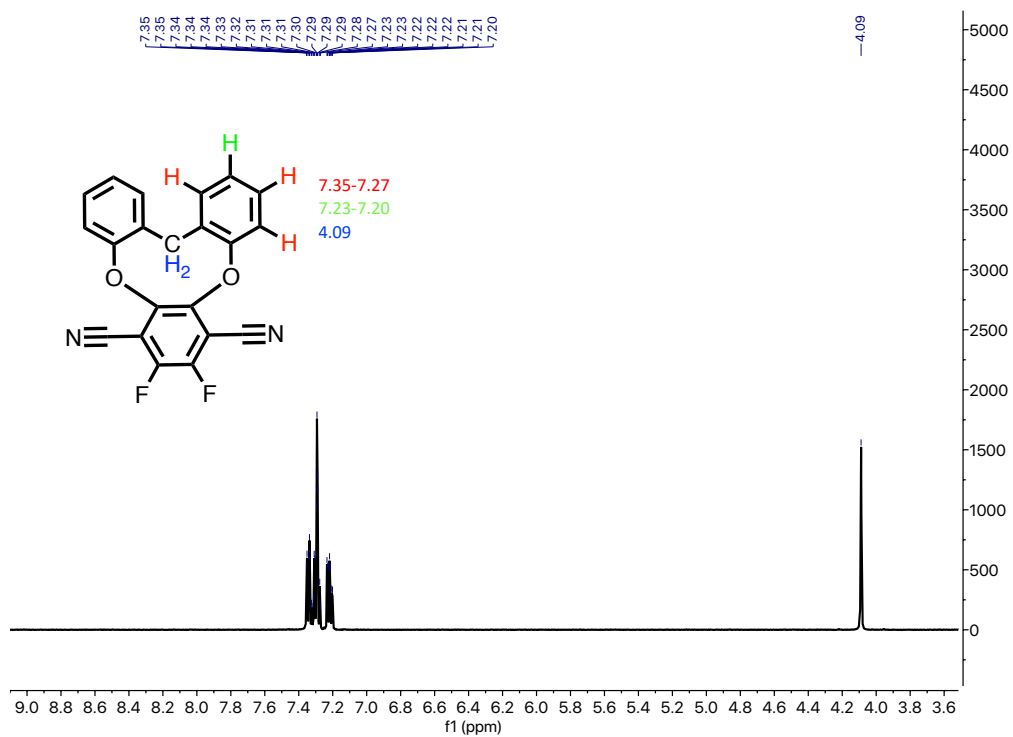


Figure S33. ¹H NMR spectrum (500 MHz, 298K, DMSO) of S2

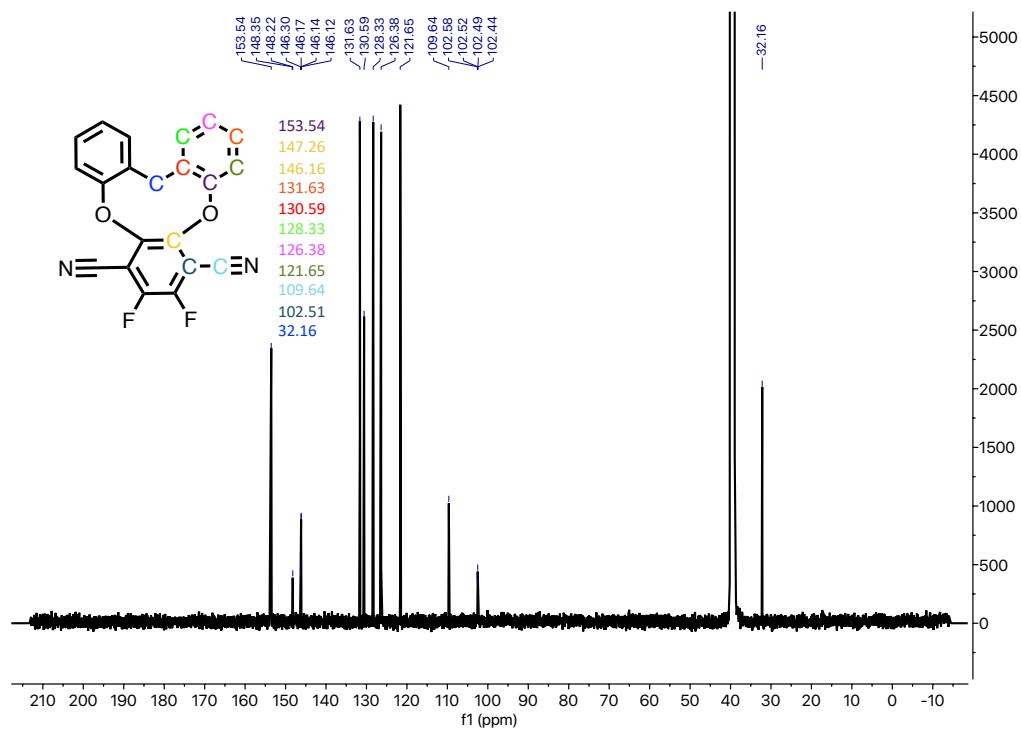


Figure S34. ¹³C NMR spectrum (126 MHz, 298K, DMSO) of **S2**

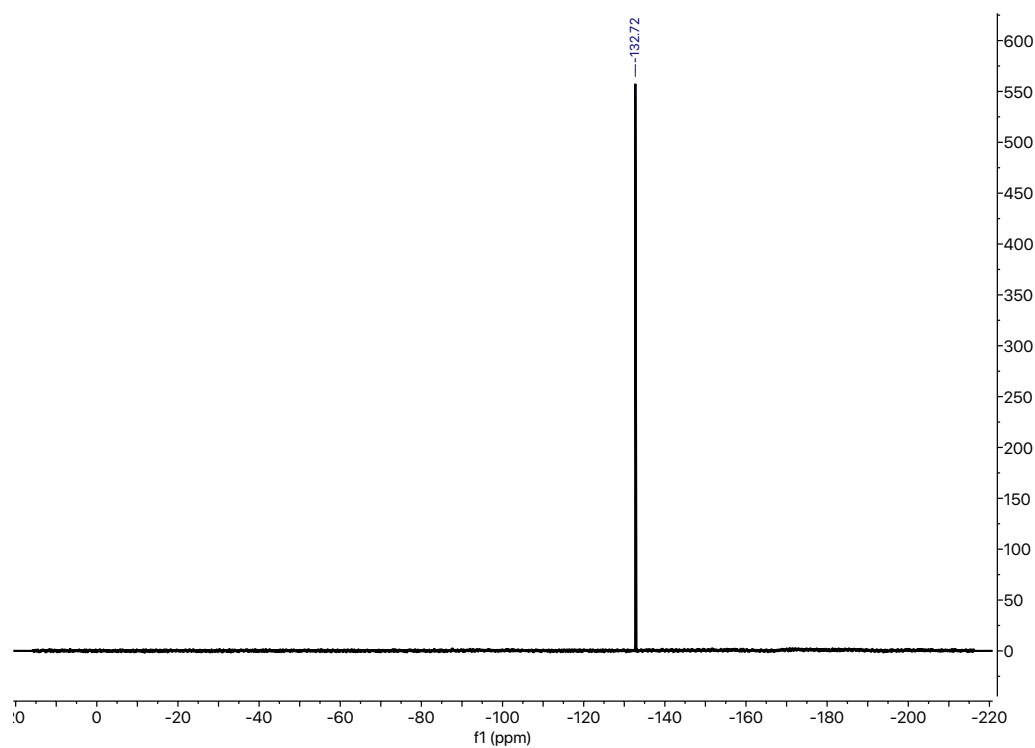


Figure S35. ¹⁹F NMR spectrum (470 MHz, 298K, DMSO) of **S2**

K. Infrared Spectra

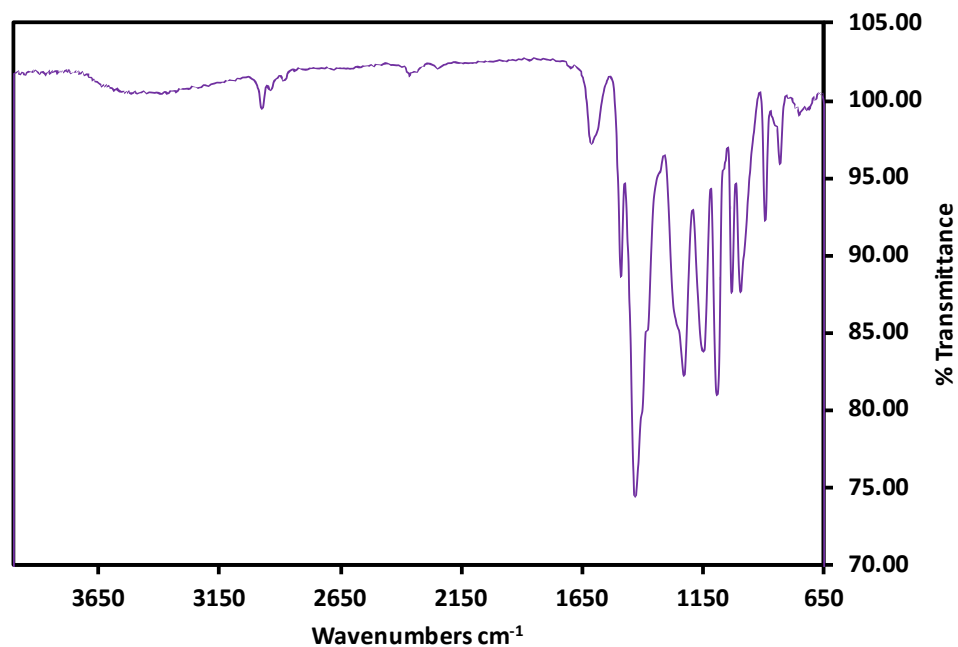


Figure S36. Infrared spectrum of **2**

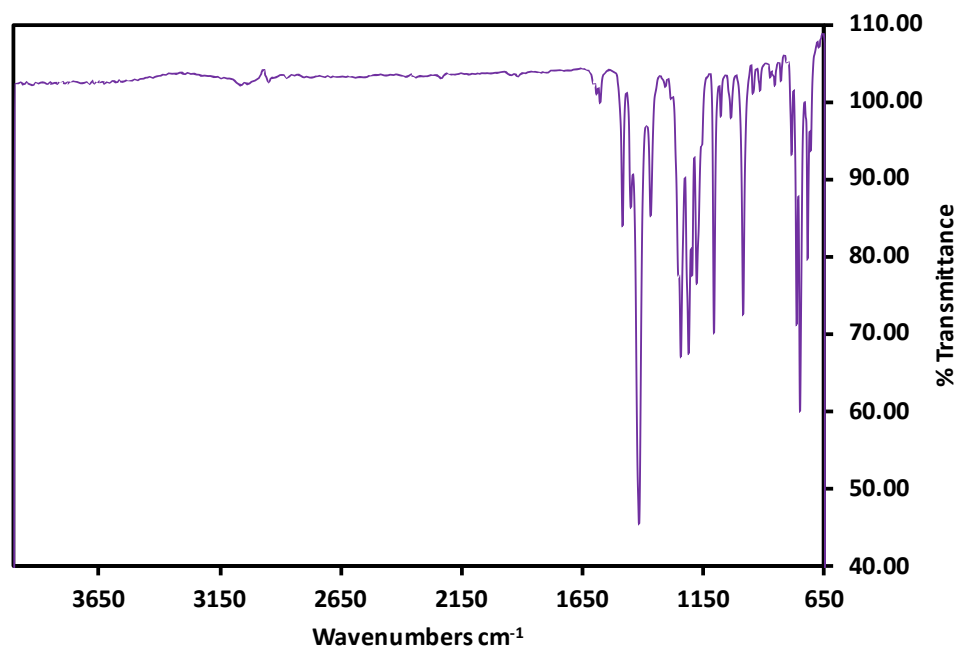


Figure S37. Infrared spectrum of **4**

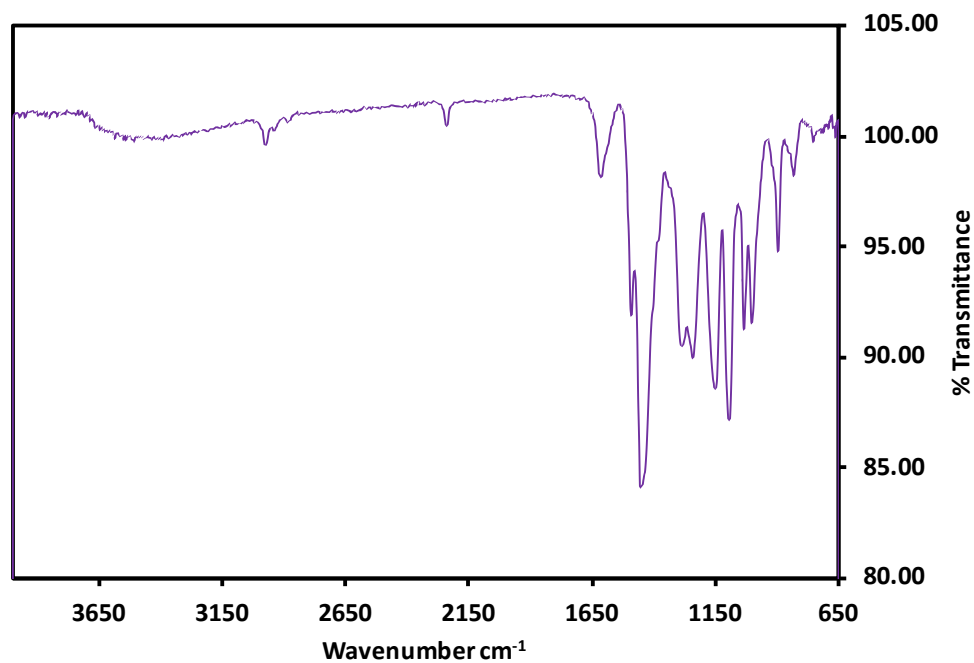


Figure S38. Infrared spectrum of **3**

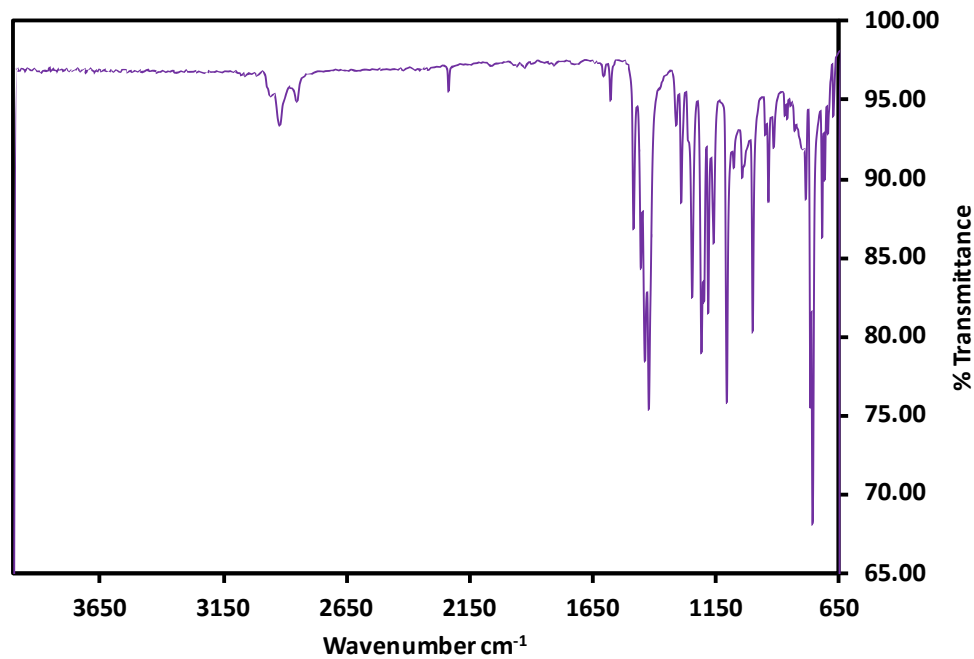


Figure S39. Infrared spectrum of **5**

L. References

- (1) Fu, R.; Hernández-Maldonado, A. J. Boosting Sensitivity and Suppressing Artifacts via Multi-Acquisition in Direct Polarization NMR Experiments with Small Flip-Angle Pulses. *J. Magn. Reson.* **2018**, *293*, 34–40. <https://doi.org/10.1016/j.jmr.2018.05.015>.