Supplementary Information of

Framework vs. Side-chain Amphidynamic Behaviour in Oligo-(Ethylene Oxide) Functionalized Covalent Organic Frameworks

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Section S1. **Materials and Methods.**

All starting materials and solvents, unless otherwise specified, were obtained from commercial sources (Aldrich, Fisher) and used without further purification. All reactions were performed at ambient laboratory conditions, and no precautions were taken to exclude oxygen or atmospheric moisture unless otherwise specified. Anhydrous *N,N*-dimethylformamide (DMF), Dichloromethane (DCM), tetrahydrofuran (THF) were purified using a custom-built alumina-column based solvent purification system (Innovative Technology). Anhydrous Dioxane, 1,2-dichloroethane (DCE), 1,2-dichlorobenzene (DCB), and dry acetone were obtained from Aldrich (Sureseal). Triethylamine (TEA) was distilled and stored under $N_2(g)$ from CaH_2 into molecular sieves. Deuterated solvents ($CDCl_3$ and DMSO) were obtained from Cambridge Isotope Lab. Triformylphloroglucinol (Tp) was prepared according to published procedures. [S1-S4]

High-resolution ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected using a Bruker AVANCE-III 400 MHz spectrometer. The chemical shifts were reported relative to the solvent residual signal. NMR data was processed using MestReNova package (v. 10.0.2). Liquid chromatography-mass spectra (LC-MS) were recorded using an agilent 6230 TOF coupled with an Agilent Zorbax SB-C18 analytical column. Fourier-transform infrared spectra were recorded using a Perkin Elmer Spectrum ONE universal FT-IR ATR. 32 scans were collected for each sample at a resolution of 120 000 cm^{-1} from 4000-650 cm^{-1}.

Powder X-ray diffraction measurements were performed using a Rigaku Miniflex 600 diffractometer, with 2θ Bragg-Brentano geometry, with a 300 mm goniometer diameter, and a 600 W (40 kV, 15 mA) X-ray tube source using Ni-filtered CuK_α (λ = 1.5418 Å) radiation, equipped with a high-resolution D/tex 250 detector, 5.0° incident and receiving Soller slits, a 0.625° divergent slit, a 1.25° scattering slit, and a 0.3 mm receiving slit and a Ni-CuK_β filter and a antiscattering blade. Samples were measured from 2 to 30 degrees with a step size of 0.02 degrees and a scan rate of 0.5 min per step. Powder samples were prepared by dropping the powder sample on glass silicon zero-background sample holder and gently pressing the powder with a glass slide.

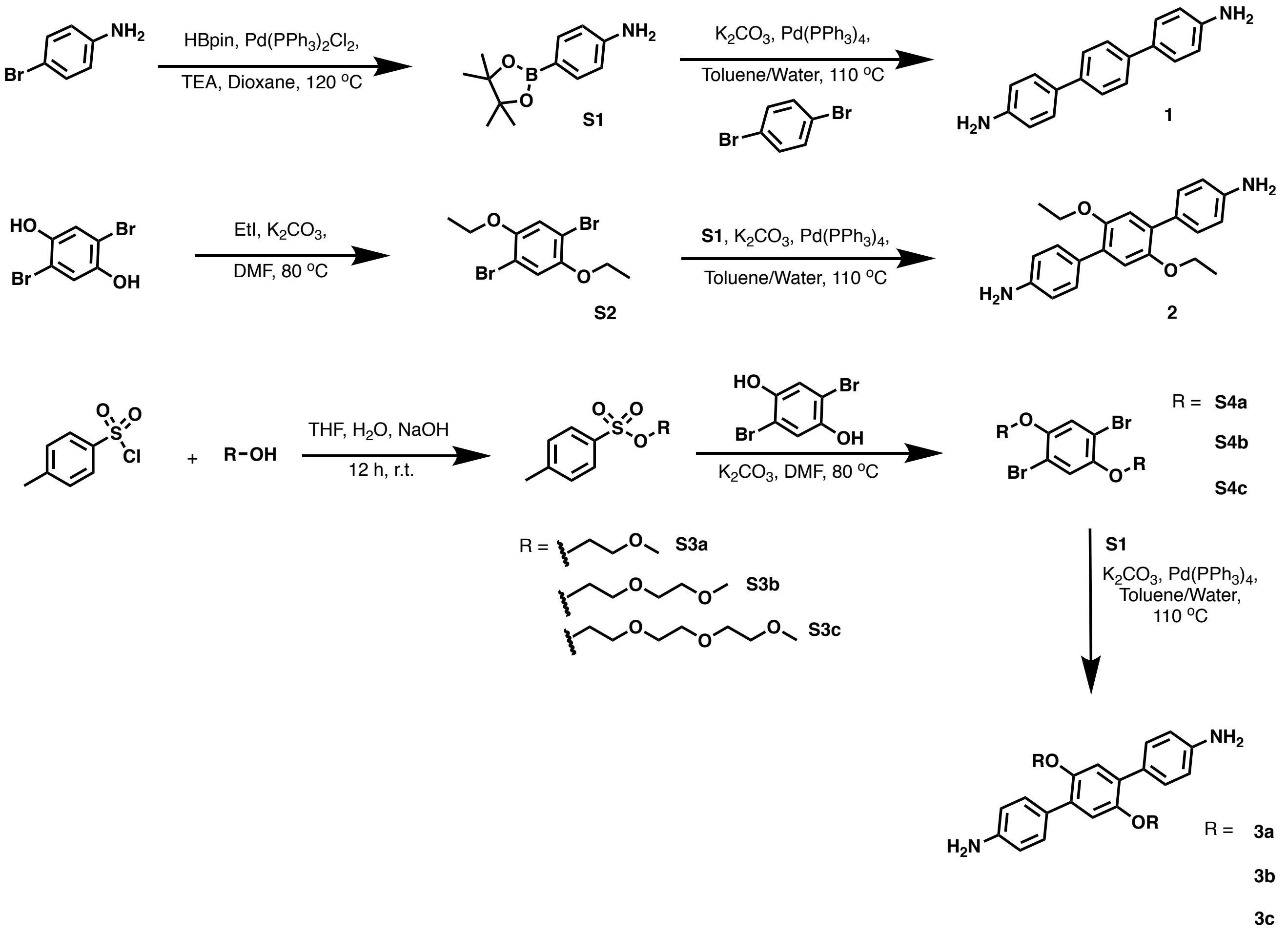
Microwave synthesis were performed using a CEM Discover LabMate Microwave reactor, using a IntelliVent Attenuator Assembly as the pressure device for the experiments. The vessels used for the crystallizations were the 10-mL thick walled pyrex reaction vessels. The sample vessels were placed in the open vessel attenuator with the spacer and capped with the IntelliVent attenuator for each of the runs. The microwave was set to 250 w, 175 °C, pressure set to 50 psi, and with varying times according to each COF.

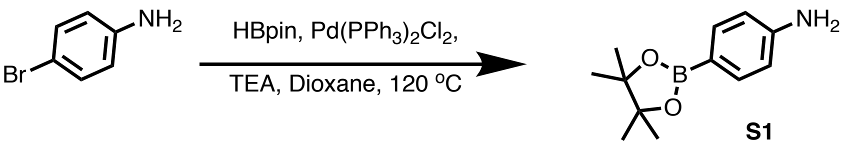
Simulated PXRD patterns were calculated using the Reflex module in Materials Studio (v8.0, Biovia) from the CIF file of the respective COF retrieved from their respective publications. [S5]

Solid-state ^{13}C nuclear magnetic resonance was measured on an Agilent DD2 500 MHz narrow-bore spectrometer with a frequency 125.6816571 MHz with an Agilent 1.6 mm T3 probe. A spectral width of 29.7 kHz was employed, and 500 complex points were collected. All spectra employed ^{1}H decoupling at a frequency of 499.77755 MHz using SPINAL decoupling with a 3.0 μs decoupling pulse. Samples were packed in a 1.6 mm zirconia oxide rotor. T_1 value of ^{13}C was measured using a saturation recovery pulse sequence with 300 saturation pulses and recovery times varying from 0.10 to 40.0 s. The spectra were acquired at a spinning speed of 15.0 kHz.

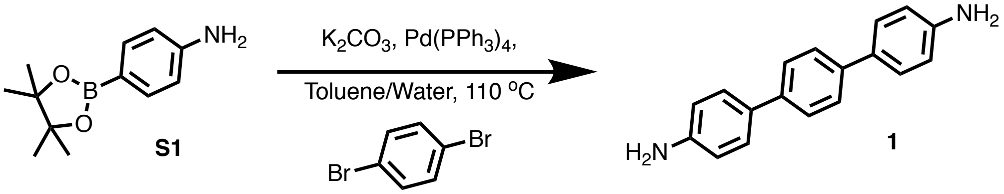
Section S2. **Synthetic Procedures.**

General Synthetic Scheme for monomers:



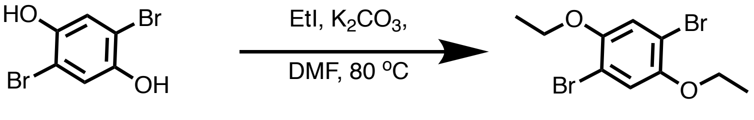


Compound S1. 4-bromoaniline (2.00 g, 12.0 mmol), Pd $(PPh_3)_2Cl_2$ (0.300 g, 1.20 mmol), triethylamine (6.5 mL, 46.5 mmol), and 1,4-dioxane (45 mL) were loaded in a 250 mL Schlenk flask loaded with a magnetic stirrer. The mixture was bubbled with N_2(*g*) for 20 min, after which 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.1 mL, 34.9 mmol) was added dropwise under N_2(*g*) over the course of 10 min observing mild gas evolution. Under N_2(*g*) flow, a water cooled condenser was attached to the top of the flask and a rubber septum and a bubbler and N_2(*g*) inlet at the top. The reaction mixture was heated to 120 ºC for 12 h followed by TLC. The reaction mixture was cooled to room temperature, quenched with water (80 mL), extracted with EtOAc (3 × 50 mL) and the combined organic extracts were rinsed with water (3 × 50 mL), brine (3 × 50 mL), dried over anhydrous Na_2SO_4(*s*) and filtered over celite. Activated charcoal (*ca*. 2 g) was added to the organic extract, heated to 45 ºC, stirred for 15 min, and hot filtered over a plug of silica gel. Removal of the solvent at 40 ºC under reduced pressure in a rotary evaporator afforded a yellow solid. Yield: 2.4 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ 7.65 – 7.58 (d, 1H), 6.69 – 6.63 (d, 1H), 3.83 (s, 1H), 1.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.61, 136.76, 114.42, 83.63, 77.04, 25.20.



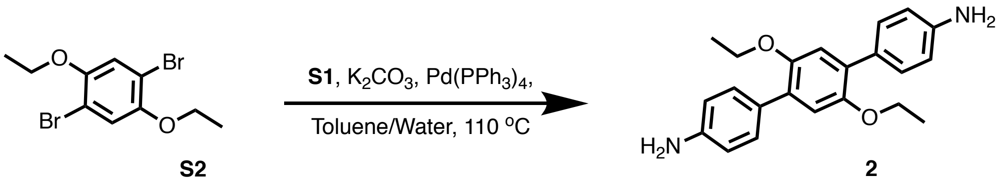
Monomer 1. 1,4-dibromobenzene (0.980 g, 4.15 mmol), **S1** (2.0 g, 9.13 mmol), $Pd(PPh_3)_4$ (0.3 g, 0.415 mmol), K_2CO_3 (8.6 g, 62.3 mmol), water (10 mL), toluene (10 mL) were loaded in a 50 mL Schlenk flask loaded with a magnetic stirrer. The mixture was flash frozen in liquid N_2, evacuated to an internal pressure of 50 mtorr, and allowed to thaw under static vacuum. The freeze/pump/thaw procedure was repeated three more times, after which the flask was backfilled with N_2(*g*) and under N_2 flow a water cooled condenser was attached with a red septum, bubbler and a positive N_2(*g*) flow at the top. The reaction mixture was heated to 120 ºC for 24 h under $N_{2(g)}$, tracked by TLC. The reaction mixture was cooled to room temperature, quenched with water (5 mL), extracted with EtOAc (3 × 10 mL) and the combined organic extracts were rinsed with water (3 × 10 mL), brine (3 × 10 mL), dried over anhydrous Na_2SO_4(*s*) and filtered through celite. Removal of the

solvent at 40 ºC under reduced pressure in a rotary evaporator followed by column chromatography (SiO_2, 45% EtOAc in hexanes) afforded a white solid. Yield: 0.560 g (52%). ^1H NMR (400 MHz, DMSO-d_6) δ 7.53 (s, 1H), 7.39 – 7.35 (d, 1H), 6.66 – 6.62 (d, 1H), 5.20 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 148.18, 137.93, 127.11, 126.82, 125.55, 114.22, 99.51, 39.52. HRMS (ESI-TOF) m/z calculated for $C_{18}H_{16}N_2$ $[M+H]^+$: 261.1393, found 261.1355.



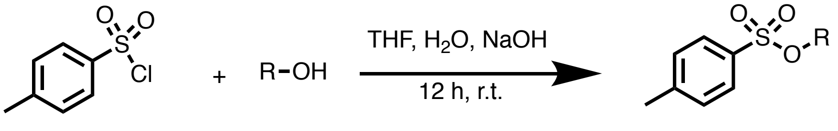
S2

Compound S2. 2,5-dibromo-hydroquinone (9.0 g, 33.59 mmol), and K_2CO_3 (27.8 g, 201.5 mmol) were loaded in a 250 mL flame dried Schlenk flask loaded with a magnetic stirrer. The flask was evacuated to a pressure of 150 mtorr and backfilled with N_2(*g*), purge procedure three times. Anhydrous DMF (135 mL) and iodoethane (5.95 mL, 11.56 g, 73.4 mmol) were added to the flask dropwise under N_2(*g*). The solution was stirred at room temperature for 4 h at room temperature and then heated to 80 ºC with stirring for 40 h followed by TLC. The reaction was cooled to room temperature and quenched with aqueous 1 M HCl (100 mL) and stored at 4 ºC for 12 h. A crystalline white solid was formed and purified by filtration using a medium porosity glass frit funnel, rinsed with cold water and dried under vacuum at room temperature. Yield 10.10 g (93%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 4.05 (q, J = 7.0 Hz, 2H), 1.34 – 1.28 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.16, 118.82, 111.35, 77.16, 66.11, 14.90.

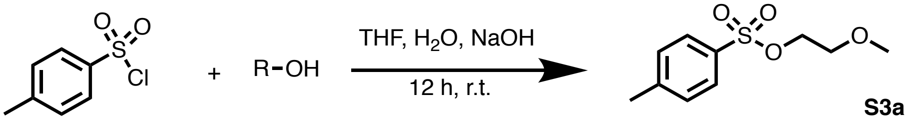


S2 **2**

Monomer 2. **S2** (0.309 mmol), **S1** (0.772 mmol), Pd(PPh3)4 (0.031 mmol), K2CO3 (4.64 mmol), water (1 mL), toluene (1 mL) were loaded in a 50 mL Schlenk flask loaded with a magnetic stirrer. The mixture was flash frozen in liquid N_2, evacuated to an internal pressure of 50 mtorr, and allowed to thaw under static vacuum. The freeze/pump/thaw procedure was repeated three more times, after which the flask was backfilled with N_2(*g*) and under N_2 flow a water-cooled condenser was attached with a red septum, bubbler and a positive N_2(*g*) flow at the top. The reaction mixture was heated to 120 ºC for 24 h under N_2(*g*), tracked by TLC. The reaction mixture was cooled to room temperature, quenched with water (5 mL), extracted with EtOAc (3 × 10 mL) and the combined organic extracts were rinsed with water (3 × 10 mL), brine (3 × 10 mL), dried over anhydrous Na_2SO_4(*s*) and filtered through celite. Removal of the solvent at 40 ºC under vacuum in a rotary evaporator followed by column chromatography (SiO_2, 45% EtOAc in hexanes) afforded an off pale/white solid. Yield: 0.040 g (37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (d, 2H), 6.94 (s, 1H), 6.78 – 6.69 (d, 2H), 3.97 (q, J = 7.0 Hz, 2H), 3.71 (s, 2H), 1.31 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 149.50, 147.54, 129.67, 129.18, 125.40, 115.39, 113.39, 99.51, 73.50, 64.33, 39.52. HRMS (ESI-TOF) m/z calculated for $C_{22}H_{25}N_2O_2$ [M+H]$^+$: 349.1916, found 349.1893.

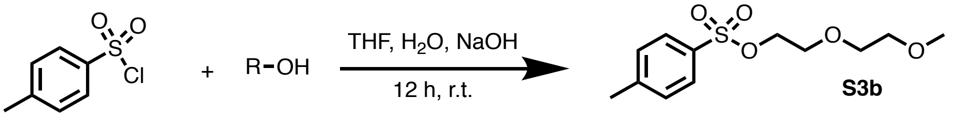


General Procedure for S3a-c. Three seprate flasks were prepared; flask 1 was composed of p-toluenesulfonylchloride (TsCl) (237.0 mmol) dissolved in THF (74 mL), flask 2 had NaOH (367.0 mmol) dissolved in H_2O (74 mL), flask 3 was composed of the alcohol (131.0 mmol) dissolved in THF (74 mL). Flask 2 and 3 were combined and then to an addition funnel flask 3 was added to it and placed over the flask 2 and 3 mixture to be added dropwise for 12h at room temperature, tracked by TLC. The reaction was quenched with water (100 mL) and extracted with DCM (2 × 60 mL) dried over anhydrous Na_2SO_4(*s*) and filtered through celite. The organic layer was reduced under pressure to afford a clear oil.



S3a

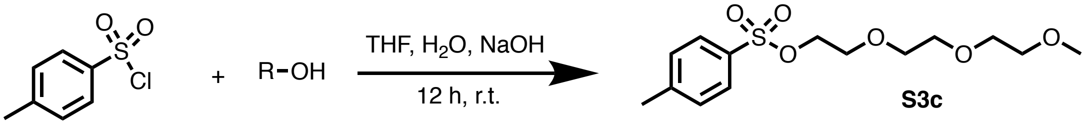
Compound S3a. Yield 20.08 g (87.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (d, 1H), 7.36 – 7.31 (d, 1H), 4.17 – 4.12 (m, 1H), 3.60 – 3.53 (m, 1H), 2.44 (s, J = 0.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.18, 133.32, 130.17, 128.31, 70.27, 69.42, 59.36, 22.00. HRMS (ESI-TOF) m/z calculated for $C_{10}H_{15}O_4S$ [M+H]$^+$: 231.0691, found 231.0663.



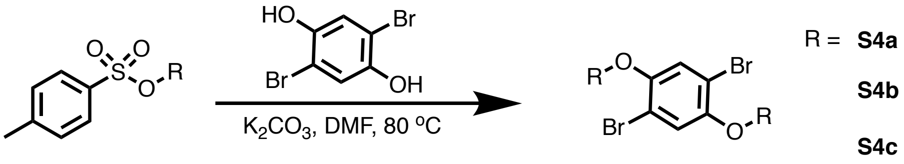
S3b

Compound S3b. Yield 19.08 g (84.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (d, 1H), 7.36 – 7.31 (d, 1H), 4.19 – 4.14 (m, 1H), 3.70 – 3.65 (m, 1H), 3.59 – 3.55 (m, 1H), 3.49 –

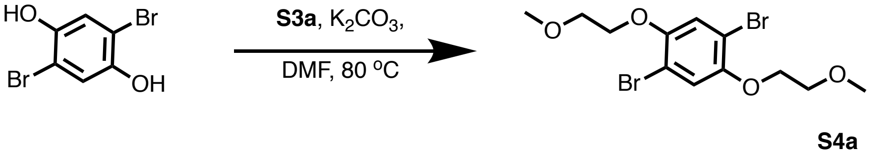
3.44 (m, 1H), 2.44 (s, J = 0.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.15, 133.32, 130.15, 128.34, 72.15, 71.03, 69.57, 69.06, 59.40, 21.99. HRMS (ESI-TOF) m/z calculated for $C_{12}H_{19}O_5S$ $[M+H]^+$: 275.0953, found 275.0959.



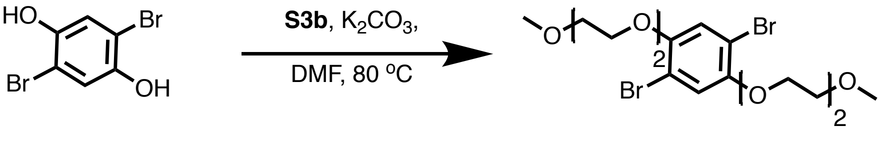
Compound S3c. Yield 6.50 g (33.0%). 1H NMR (400 MHz, $CDCl_3$-*d*) δ 7.85 (d, J = 8.3 Hz, 1H), 7.39 (d, J = 7.9 Hz, 1H), 4.23 – 4.19 (m, 1H), 3.80 (t, J = 6.7 Hz, 1H), 3.76 – 3.72 (m, 1H), 3.68 – 3.63 (m, 3H), 3.60 – 3.56 (m, 1H), 3.42 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.90, 133.15, 129.93, 128.10, 77.16, 72.03, 70.87, 70.69, 70.67, 69.35, 68.80, 68.10, 59.15, 25.74, 21.76. HRMS (ESI-TOF) m/z calculated for $C_{14}H_{23}O_6S$ $[M+H]^+$: 319.1215, found 319.1220.



General procedure for S4a-c. 2,5-dibromo-hydroquinone (0.747 mmol), **S3a-c** (1.87 mmol), and K_2CO_3 (4.48 mmol) were loaded in a 50 mL flame dried Schlenk flask loaded with a magnetic stirrer. The flask was evacuated to a pressure of 150 mtorr and backfilled with N_2(*g*), repeating this purge procedure 3 times. Anhydrous DMF (4 mL) was added to the flask under N_2(*g*). The solution was stirred and heated to 80 ºC with stirring for 12 h and tracked by TLC. The reaction was cooled to room temperature and quenched with water (20 mL) and a precipitant was formed. A crystalline white solid was obtained and purified by filtration using a medium porosity glass frit funnel, rinsed with water and dried under vacuum.

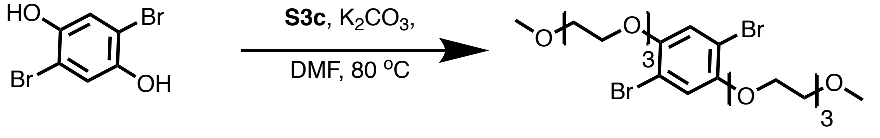


Compound S4a. Using **S3a**. Yield 0.280 g (89.0 %). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.26 (s, 1H), 4.13 – 4.08 (m, 2H), 3.72 – 3.66 (m, 2H), 3.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.54, 119.43, 111.66, 77.16, 71.01, 70.27, 59.58.



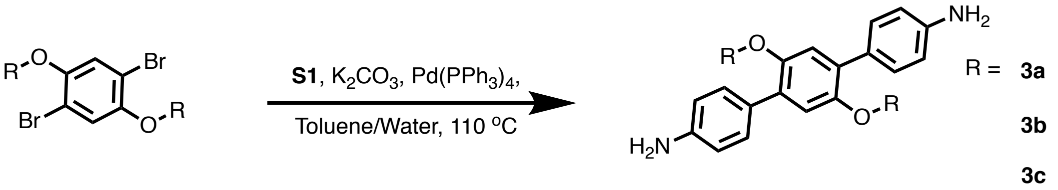
S4b

Compound S4b. Using **S3b**. Yield 0.240 g (60.0 %). ^{1}H NMR (500 MHz, CD_3CN) δ 7.30 – 7.27 (s, 1H), 4.11 (td, J = 4.5, 2.0 Hz, 3H), 3.78 (dtd, J = 5.8, 2.8, 1.2 Hz, 2H), 3.64 (ddd, J = 6.1, 3.1, 1.1 Hz, 2H), 3.51 – 3.46 (m, 2H), 3.32 – 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.46, 119.52, 119.32, 111.52, 77.16, 72.16, 71.14, 70.41, 70.38, 69.73, 59.24. HRMS (ESI-TOF) m/z calculated for $C_{16}H_{25}Br_2O_6$ $[M+H]^+$: 472.9997, found 472.9995.

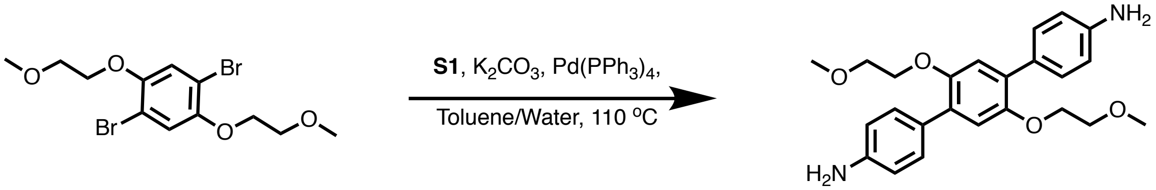


S4c

Compound S4c. Using **S3c**. Yield 4.9 g (70.0 %). ^{1}H NMR (400 MHz, CD_3CN) δ 7.09 (s, 1H), 4.10 – 4.04 (m, 2H), 3.83 – 3.78 (m, 2H), 3.73 – 3.68 (m, 2H), 3.64 – 3.58 (m, 4H), 3.52 – 3.46 (m, 2H), 3.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.59, 150.39, 119.23, 111.44, 77.16, 72.03, 71.17, 70.81, 70.67, 70.28, 69.66, 59.12, 36.56, 31.50, 14.28. HRMS (ESI-TOF) m/z calculated for $C_{20}H_{33}Br_2O_8$ $[M+H]^+$: 561.0522, found 561.0519.

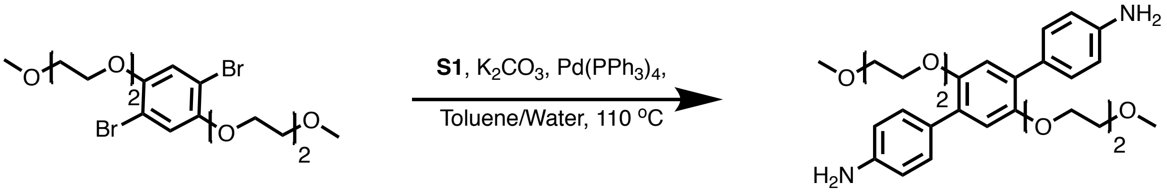


General Procedure for 3a-c. **S3a-c** (0.309 mmol), **S1** (0.772 mmol), Pd(PPh3)4 (0.031 mmol), K_2CO_3 (4.64 mmol), water (1 mL), toluene (1 mL) were loaded in a 50 mL Schlenk flask loaded with a magnetic stirrer. The mixture was flash frozen in liquid N_2, evacuated to an internal pressure of 50 mtorr, and allowed to thaw under static vacuum. The freeze/pump/thaw procedure was repeated three more times, after which the flask was backfilled with N_2(*g*) and under N_2 flow a water cooled condenser was attached with a red septum, bubbler and a positive N_2(*g*) flow at the top. The reaction mixture was heated to 120 ºC for 24 h under N_2(*g*), tracked by TLC. The reaction mixture was cooled to room temperature, quenched with water (5 mL), extracted with EtOAc (3 × 10 mL) and the combined organic extracts were rinsed with water (3 × 10 mL), brine (3 × 10 mL), dried over anhydrous Na_2SO_4(*s*) and filtered through celite. Removal of the solvent at 40 ºC under reduced pressure in a rotary evaporator followed by column chromatography (SiO_2, 45% EtOAc in hexanes) afforded a tan solid.



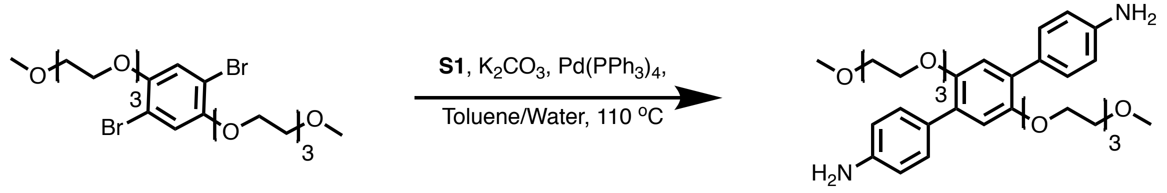
3a

Monomer 3a. With **S4a** removal of the solvent at 40 ºC under vacuum in a rotary evaporator followed by column chromatography (SiO_2, 75% EtOAc in hexanes) afforded an off tan solid. Yield: 0.360 g (36%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.33 – 7.28 (m, 2H), 6.88 (s, 1H), 6.61 – 6.55 (m, 2H), 5.11 (s, 2H), 4.06 – 4.00 (m, 2H), 3.59 (dd, J = 3.8, 2.2 Hz, 2H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 149.62, 147.60, 129.76, 129.11, 128.89, 128.19, 125.20, 115.33, 113.36, 70.68, 68.26, 58.21, 39.52. HRMS (ESI-TOF) m/z calculated for $C_{24}H_{29}N_2O_4$ [M+H]$^+$: 409.2127, found 409.2120.



3b

Monomer 3b. With **S4b** removal of the solvent at 40 ºC under vacuum in a rotary evaporator followed by column chromatography (SiO_2, neat EtOAc) afforded an off tan/yellow solid. Yield: 0.850 g (42%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.35 – 7.29 (m, 2H), 6.89 (s, 1H), 6.60 – 6.55 (m, 2H), 5.12 (s, 2H), 4.03 (dd, J = 5.6, 3.8 Hz, 2H), 3.69 – 3.64 (m, 2H), 3.56 – 3.52 (m, 2H), 3.45 – 3.41 (m, 2H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 149.59, 147.59, 129.78, 129.07, 125.19, 115.28, 113.34, 71.32, 71.25, 69.92, 69.83, 69.70, 69.60, 69.16, 68.42, 58.09, 58.02, 40.15, 39.94, 39.73, 39.52, 39.52, 39.31, 39.10, 38.90.



3c

Monomer 3c. With **S4c** removal of the solvent at 40 ºC under vacuum in a rotary evaporator followed by column chromatography (SiO_2, 15% MeCN/EtOAc) afforded an off tan/brown solid. Yield: 0.600 g (18%). ^{1}H NMR (500 MHz, DMSO-d6) δ = 7.35 – 7.29

(d, 2H), 6.88 (s, 1H), 6.61 – 6.55 (d, 2H), 5.11 (s, 2H), 4.06 – 4.00 (m, 2H), 3.69 – 3.63 (m, 2H), 3.55 – 3.47 (m, 6H), 3.42 – 3.38 (m, 2H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 149.58, 147.59, 129.78, 129.07, 125.20, 115.28, 113.34, 71.25, 69.92, 69.84, 69.60, 69.16, 68.43, 58.02, 40.15, 39.94, 39.73, 39.52, 39.31, 39.10, 38.90.

Synthesis of COFs:

TfpTP-H COF. Monomer 1 (0.020 g, 0.0714 mol) and Tfp (0.010 g, 0.0476 mol) were loaded in the microwave pyrex reaction vessel. DCE (1.5 mL) dioxane (1.5 mL), and 8 M aqueous acetic acid (100 μL) (17:17:1 *v*/*v*/*v*) were added and the mixture was mixed in an ultrasonic bath for 5 min. The tube was transferred to the microwave reactor and it was operated at 250 w and 175 ^{o}C, for 10 min. An off yellow solid was obtained, filtered and rinsed with 10-15 mL of dry acetone. The filtered solid was transferred to a glass vial and immersed in dry acetone (3 mL) for 3 d, replacing the acetone each a total of nine times during this period, while storing the vial in a desiccator. The solid was filtered and activated by heating to 120 ^{o}C under high vacuum (<10 mtorr) for 12 h obtaining a yellow solid. Yield: 0.025 g (83%). Product was characterized via Powder X-Ray diffraction.

TfpTP-OEt COF. Monomer 2 (0.025 g, 0.0714 mol) and Tfp (0.010 g, 0.0476 mol) were loaded in the microwave pyrex reaction vessel. DCE (1.5 mL) dioxane (1.5 mL), and 8 M aqueous acetic acid (100 μL) (17:17:1 *v*/*v*/*v*) were added and the mixture was mixed in an ultrasonic bath for 15 min. The tube was transferred to the microwave reactor and it was operated at 250 w and 175 ^{o}C, for 15 min. An orange solid was obtained, filtered and rinsed with 10-15 mL of dry acetone. The filtered solid was transferred to a glass vial and immersed in dry acetone (3 mL) for 3 d, replacing the acetone each a total of nine times during this period, while storing the vial in a desiccator. The solid was filtered and activated by heating to 120 ^{o}C under high vacuum (<10 mtorr) for 12 h obtaining a orange solid. Yield: 0.030 g (85%). Product was characterized via Powder X-ray diffraction.

TfpTP-OMEG COF. Monomer 3a (0.030 g, 0.0714 mol) and Tfp (0.010 g, 0.0476 mol) were loaded in the microwave pyrex reaction vessel. DCB (1.5 mL) n-propanol (1.5 mL), and 8 M aqueous acetic acid (100 μL) (17:17:1 *v*/*v*/*v*) were added and the mixture was mixed in an ultrasonic bath for 5 min. The tube was transferred to the microwave reactor and it was operated at 250 w and 175 ^{o}C, for 20 min. An off yellow solid was obtained, filtered and rinsed with 10-15 mL of dry acetone. The filtered solid was transferred to a glass vial and immersed in dry acetone (3 mL) for 3 d, replacing the acetone each a total of nine times during this period, while storing the vial in a desiccator. The solid was filtered and activated by heating to 120 ^{o}C under high vacuum (<10 mtorr) for 12 h obtaining a yellow solid. Yield: 0.030 g (75%). Product was characterized via Powder X-ray diffraction.

TfpTP-ODEG COF. Monomer 3b (0.040 g, 0.0714 mol) and Tfp (0.010 g, 0.0476 mol) were loaded in the microwave pyrex reaction vessel. DCB (1.5 mL) n-propanol (1.5 mL), and 8 M aqueous acetic acid (100 μL) (17:17:1 *v*/*v*/*v*) were added and the mixture was mixed in an ultrasonic bath for 5 min. The tube was transferred to the microwave reactor and it was operated at 250 w and 175 ^{o}C, for 20 min. An brown solid was obtained, filtered and rinsed with 10-15 mL of dry acetone. The filtered solid was transferred to a glass vial and immersed in dry acetone (3 mL) for 3 d, replacing the acetone each a total of nine times during this period, while storing the vial in a desiccator. The solid was filtered and activated by heating to 120 ^{o}C under high vacuum (<10 mtorr) for 12 h obtaining a brown solid. Yield: 0.030 g (60%). Product was characterized via Powder X-ray diffraction.

TfpTP-OTEG COF. Monomer 3c (0.045 g, 0.0714 mol) and Tfp (0.010 g, 0.0476 mol) were loaded in the microwave pyrex reaction vessel. DCB (1.5 mL) n-propanol (1.5 mL), and 8 M aqueous acetic acid (100 μL) (17:17:1 *v*/*v*/*v*) were added and the mixture was mixed in an ultrasonic bath for 5 min. The tube was transferred to the microwave reactor and it was operated at 250 w and 175 °C, for 20 min. A brown solid was obtained, filtered and rinsed with 10-15 mL of dry acetone. The filtered solid was transferred to a glass vial and immersed in dry acetone (3 mL) for 3 d, replacing the acetone each a total of nine times during this period, while storing the vial in a desiccator. The solid was filtered and activated by heating to 120 °C under high vacuum (<10 mtorr) for 12 h obtaining a brown solid. Yield: 0.023 g (41%). Product was characterized via Powder X-ray diffraction.

Section S3. **PXRD models**

Table S1. Space group and unit cell parameters

COF	**Space group**	***a* (Å)**	***c* (Å)**
TfpTP-H	*P*6/*m*	38.3739	3.4752
TfpTP-OEt	*P*6/*m*	38.6460	3.9846
TfpTP-OMEG	*P*6/*m*	38.6424	3.9980
TfpTP-ODEG	*P*6/*m*	38.6385	4.0044
TfpTP-OTEG	*P*6/*m*	38.6321	3.9951

Table S2. Atom positions of **TfpTP-H.**

TfpTP-H			
Atom	***x/a***	***y/b***	***z/c***
O1	0.29617	0.58578	0.50000
N2	0.37054	0.58780	0.50000
C3	0.31333	0.62237	0.50000
C4	0.35819	0.64625	0.50000
C5	0.38298	0.63015	0.50000
C6	0.47462	0.51776	0.50000
C7	0.45841	0.47566	0.50000
C8	0.51698	0.54156	0.50000
H9	0.42655	0.45489	0.50000
H10	0.41487	0.65120	0.50000
H11	0.53232	0.57389	0.50000
H12	0.34019	0.56620	0.50000
C13	0.44786	0.53646	0.50000
C14	0.39741	0.57165	0.50000
C15	0.38090	0.52986	0.50000
C16	0.40539	0.51252	0.50000
C17	0.46416	0.57870	0.50000
C18	0.43949	0.59591	0.50000
H19	0.45418	0.62823	0.50000
H20	0.49601	0.59951	0.50000
H21	0.38994	0.48019	0.50000
H22	0.34857	0.51037	0.50000

Table S3. Atom positions of **TfpTP-OEt**

TfpTP-OEt			
Atom	***x/a***	***y/b***	***z/c***
H1	0.58191	0.65850	0.72311
H2	0.59467	0.60133	0.72577
O3	0.29730	0.58639	0.50000

N4	0.37163	0.58939	0.50000
C5	0.31395	0.62271	0.50000
C6	0.35848	0.64688	0.50000
C7	0.38348	0.63133	0.50000
C8	0.47679	0.52031	0.50000
C9	0.45891	0.47818	0.50000
C10	0.51937	0.54232	0.50000
H11	0.42731	0.46020	0.50000
H12	0.41507	0.65254	0.50000
O13	0.53952	0.58443	0.50000
H14	0.34158	0.56765	0.50000
C15	0.45007	0.53957	0.50000
C16	0.39870	0.57382	0.50000
C17	0.38290	0.53252	0.50000
C18	0.40761	0.51575	0.50000
C19	0.46527	0.58156	0.50000
C20	0.44032	0.59817	0.50000
C21	0.58214	0.60770	0.50000
C22	0.59431	0.65158	0.50000
H23	0.45452	0.63026	0.50000
H24	0.49629	0.60342	0.50000
H25	0.62736	0.67044	0.50000
H26	0.39158	0.48372	0.50000
H27	0.35082	0.51285	0.50000

Table S4. Atom positions of **TfpTP-OMEG**

TfpTP-OMEG			
Atom	***x/a***	***y/b***	***z/c***
H1	0.59499	0.60132	0.72484
H2	0.41765	0.34199	0.27568
O3	0.29720	0.58637	0.50000
N4	0.37148	0.58927	0.50000
C5	0.31389	0.62270	0.50000
C6	0.35843	0.64682	0.50000
C7	0.38338	0.63122	0.50000
C8	0.47676	0.52029	0.50000
C9	0.45891	0.47817	0.50000
C10	0.51937	0.54234	0.50000
H11	0.42732	0.46021	0.50000
H12	0.41498	0.65240	0.50000
O13	0.53959	0.58451	0.50000
H14	0.34144	0.56754	0.50000
C15	0.44997	0.53948	0.50000
C16	0.39856	0.57369	0.50000

C17	0.38277	0.53239	0.50000
C18	0.40750	0.51563	0.50000
C19	0.46513	0.58144	0.50000
C20	0.44018	0.59804	0.50000
C21	0.58241	0.60770	0.50000
C22	0.59529	0.65185	0.50000
H23	0.45440	0.63012	0.50000
H24	0.49612	0.60325	0.50000
H25	0.39149	0.48359	0.50000
H26	0.35069	0.51271	0.50000
O27	0.36264	0.32524	0.50000
C28	0.35214	0.28489	0.50000

Table S5. Atom positions of **TfpTP-ODEG**

TfpTP-ODEG			
Atom	***x/a***	***y/b***	***z/c***
H1	0.59532	0.60148	0.72450
H2	0.41762	0.34213	0.27601
O3	0.29725	0.58637	0.50000
N4	0.37159	0.58935	0.50000
C5	0.31393	0.62270	0.50000
C6	0.35846	0.64686	0.50000
C7	0.38346	0.63130	0.50000
C8	0.47682	0.52034	0.50000
C9	0.45892	0.47820	0.50000
C10	0.51944	0.54235	0.50000
H11	0.42738	0.46022	0.50000
H12	0.41506	0.65251	0.50000
O13	0.53981	0.58453	0.50000
H14	0.34153	0.56763	0.50000
C15	0.45004	0.53954	0.50000
C16	0.39868	0.57379	0.50000
C17	0.38286	0.53249	0.50000
C18	0.40757	0.51570	0.50000
C19	0.46524	0.58150	0.50000
C20	0.44031	0.59813	0.50000
C21	0.58260	0.60770	0.50000
C22	0.59536	0.65170	0.50000
H23	0.45453	0.63022	0.50000
H24	0.49625	0.60326	0.50000
H25	0.39155	0.48367	0.50000
H26	0.35076	0.51288	0.50000
O27	0.36257	0.32573	0.50000
C28	0.35152	0.28500	0.50000

C29	0.69387	0.74127	0.50000
O30	0.70489	0.78174	0.50000
C31	0.74654	0.80211	0.50000

Table S6. Atom positions of **TfpTP-OTEG**

TfpTP-OTEG			
Atom	***x/a***	***y/b***	***z/c***
H1	0.59560	0.60083	0.72481
H2	0.41548	0.34156	0.27557
O3	0.29747	0.58637	0.50000
N4	0.37195	0.58967	0.50000
C5	0.31406	0.62270	0.50000
C6	0.35860	0.64701	0.50000
C7	0.38372	0.63159	0.50000
C8	0.47701	0.52054	0.50000
C9	0.45896	0.47838	0.50000
C10	0.51963	0.54242	0.50000
H11	0.42743	0.46057	0.50000
H12	0.41532	0.65285	0.50000
O13	0.54026	0.58466	0.50000
H14	0.34191	0.56791	0.50000
C15	0.45033	0.53983	0.50000
C16	0.39906	0.57416	0.50000
C17	0.38319	0.53287	0.50000
C18	0.40784	0.51604	0.50000
C19	0.46562	0.58181	0.50000
C20	0.44071	0.59849	0.50000
C21	0.58311	0.60736	0.50000
C22	0.59697	0.65164	0.50000
H23	0.45493	0.63059	0.50000
H24	0.49667	0.60349	0.50000
H25	0.39171	0.48401	0.50000
H26	0.35109	0.51328	0.50000
O27	0.36093	0.32702	0.50000
C28	0.34828	0.28595	0.50000
C29	0.69724	0.73828	0.50000
O30	0.71074	0.77933	0.50000
C31	0.75251	0.79714	0.50000
C32	0.22754	0.15733	0.50000
O33	0.18590	0.14015	0.50000
C34	0.17131	0.09901	0.50000

Section S4. **Saturation recovery analysis of each COF**

Figure S1. TfpTP-H COF ^{13}C saturation recovery analysis

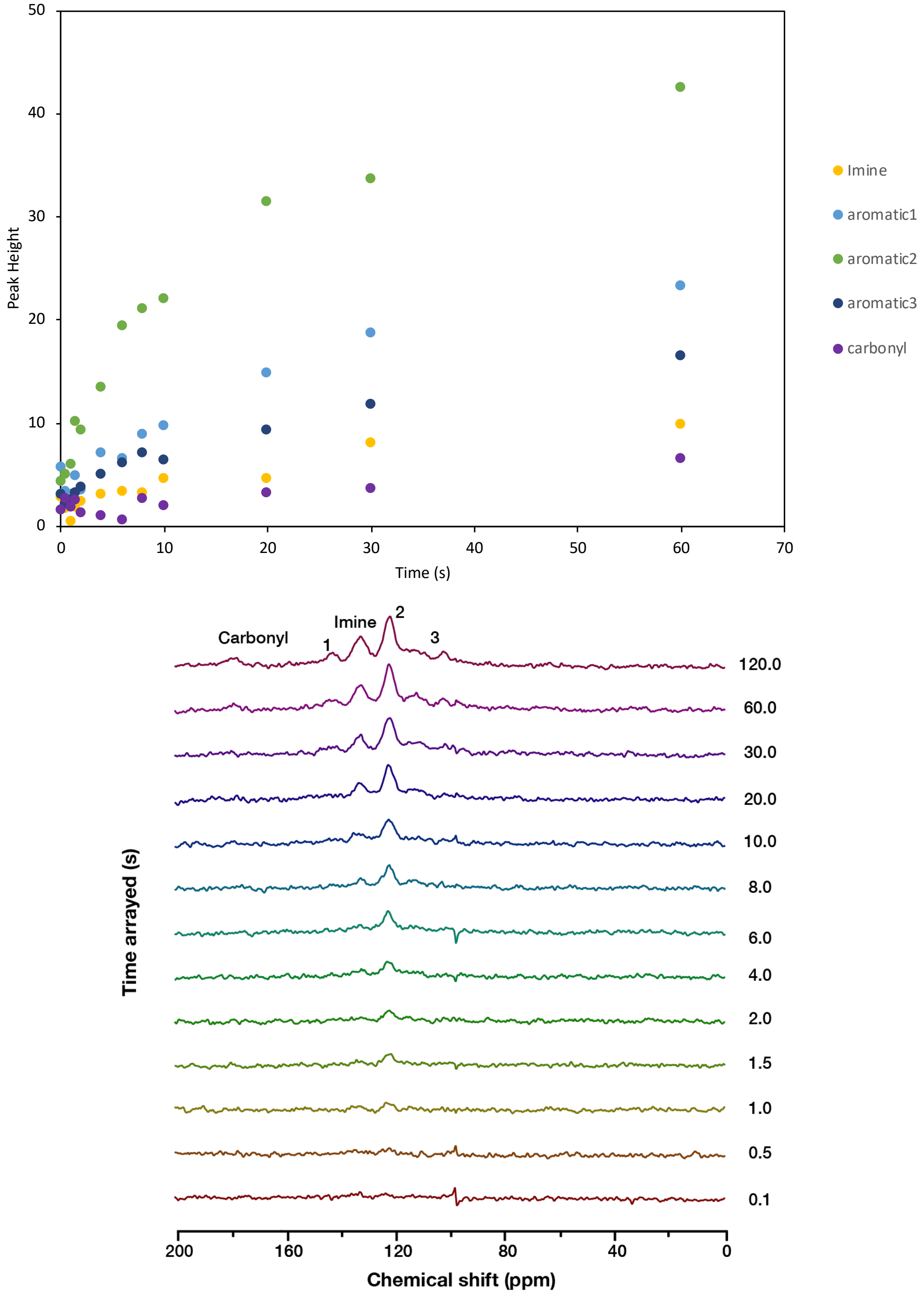


Figure S2. TfpTP-OEt COF ^{13}C saturation recovery analysis

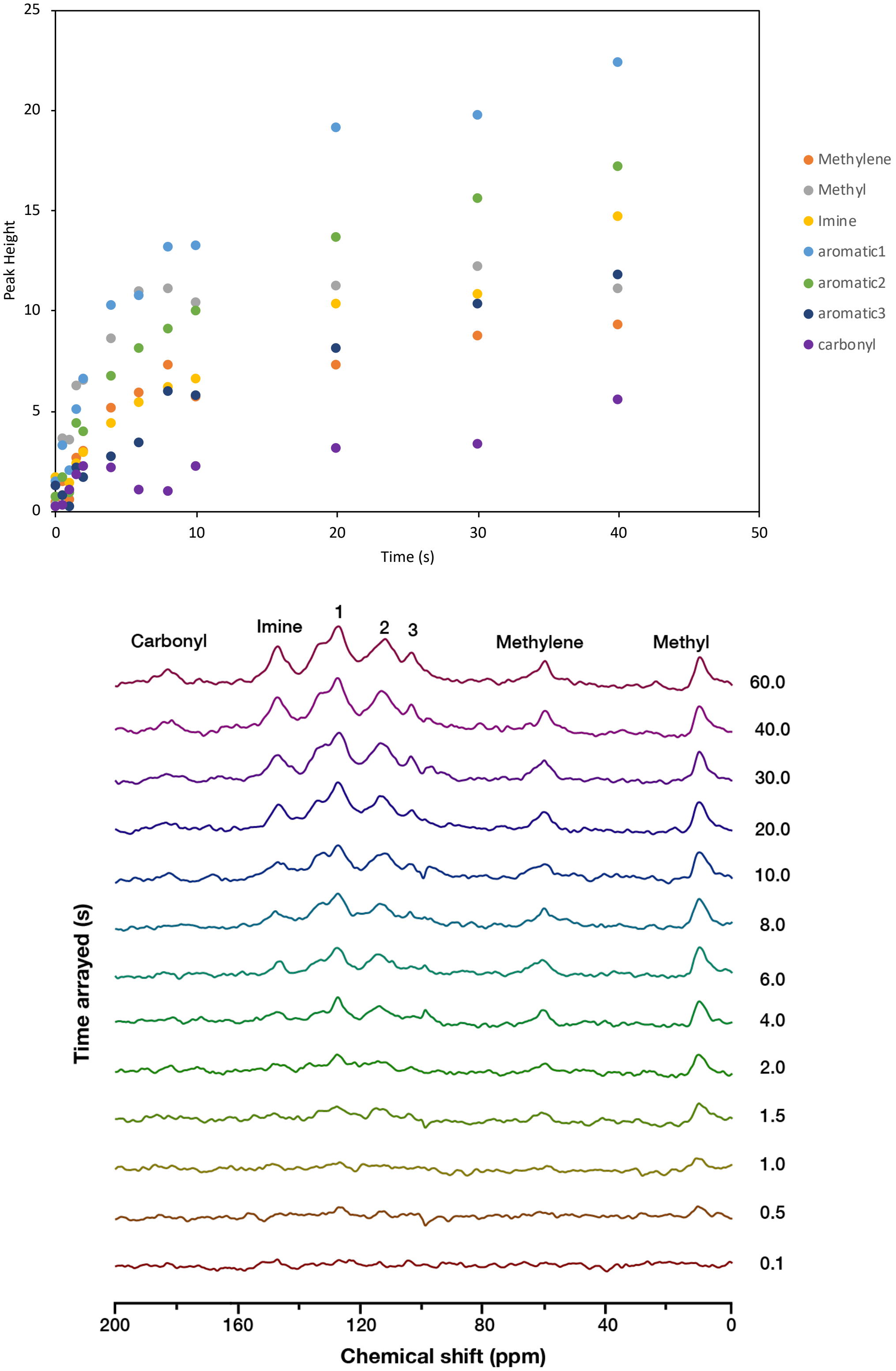


Figure S3. TfpTP-OMEG COF ^{13}C saturation recovery analysis

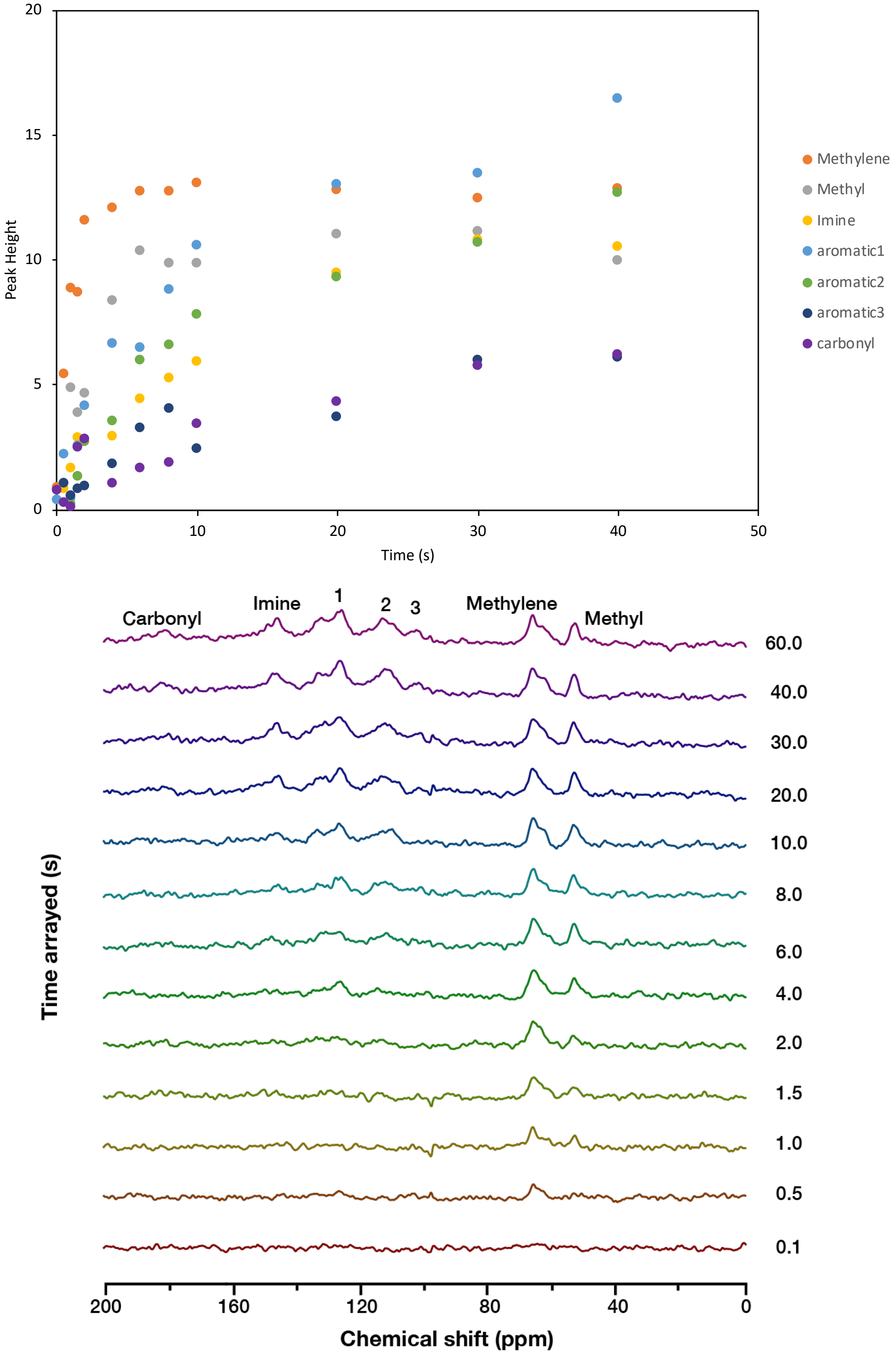
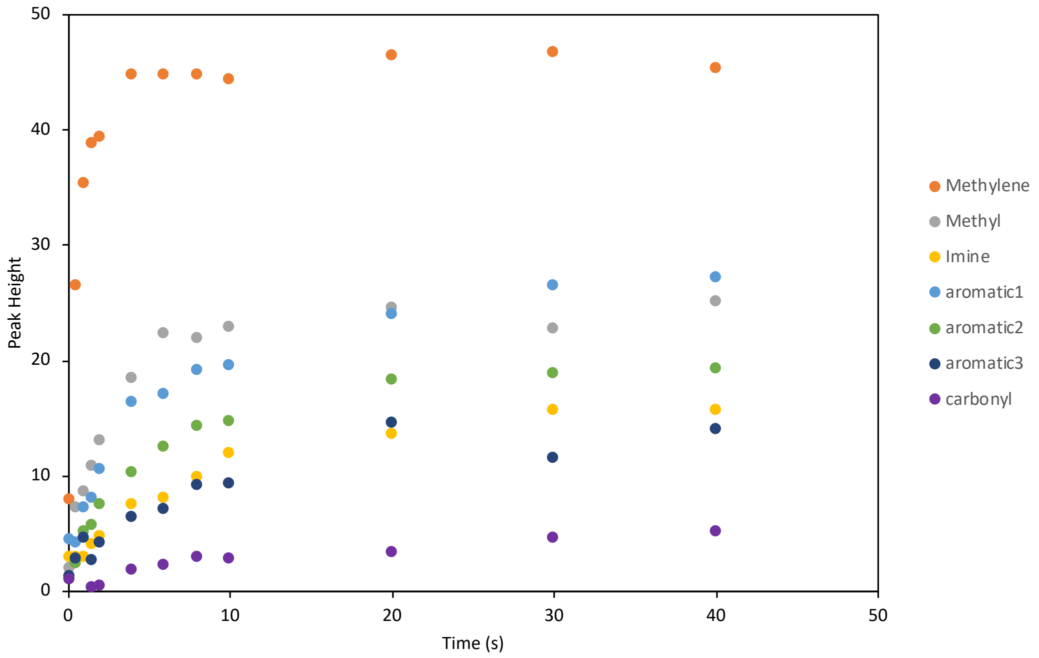


Figure S4. TfpTP-ODEG COF ^{13}C saturation recovery analysis



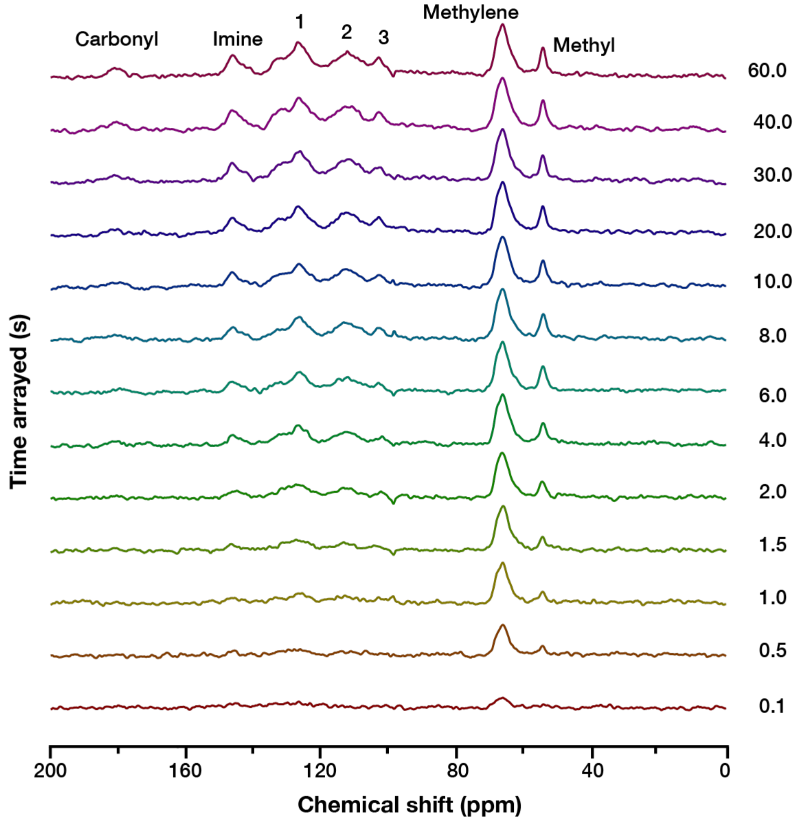
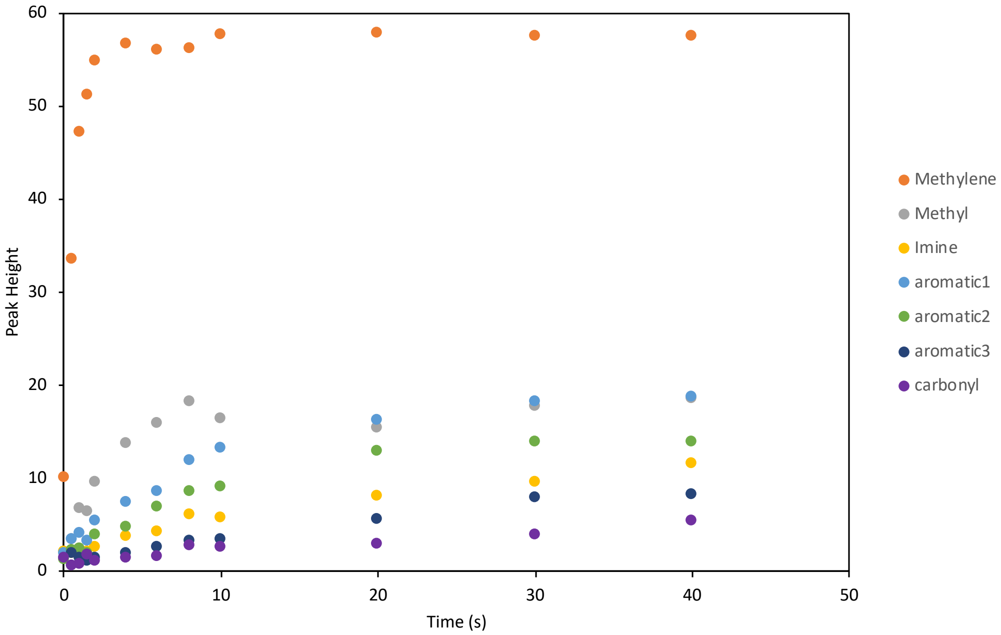
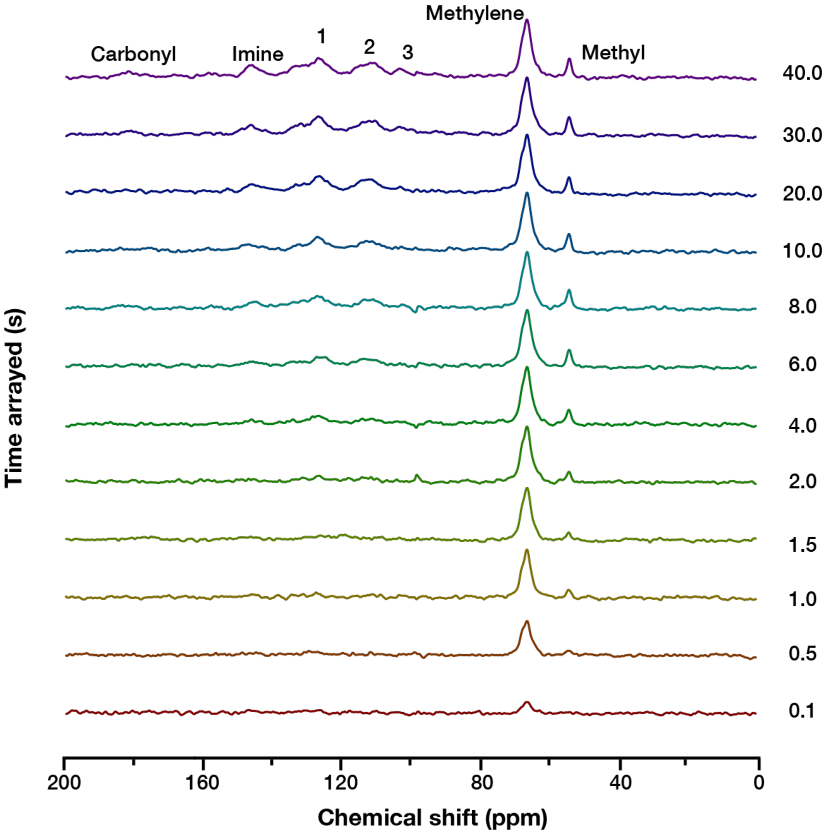


Figure S5. TfpTP-OTEG COF ^{13}C saturation recovery analysis



60
50
40
30
20
10
0
Peak Height
0
10
20
30
40
50
Time (s)
● Methylene
● Methyl
● Imine
● aromatic1
● aromatic2
● aromatic3
● carbonyl



Carbonyl
Imine
1
2
3
Methylene
Methyl
40.0
30.0
20.0
10.0
8.0
6.0
4.0
2.0
1.5
1.0
0.5
0.1
Time arrayed (s)
200
160
120
80
40
0
Chemical shift (ppm)

Table S7. T1 calculated constants

COF	Peak	T1	Std. dev.
TfpTP–H			
	Carbonyl	33.51554019	1.22853479
	Imine	29.07007499	1.29449611
	Aromatic 1	23.37267896	2.36505477
	Aromatic 2	14.27862036	3.59814115
	Aromatic 3	15.54038319	1.62870461
	Aromatic 4	23.58139027	0.54758113
TfpTP-OEt			
	Carbonyl	27.25114224	0.90694629
	Imine	17.56359706	1.01877924
	Aromatic 1	10.17916103	1.68357824
	Aromatic 2	12.27625202	1.14322238
	Aromatic 3	18.09525302	0.68171869
	Methylene	7.665132614	1.00879912
	Methyl	2.306548604	0.6608706
TfpTP-OMEG			
	Carbonyl	19.11118614	0.89171777
	Imine	15.75019576	0.90907115
	Aromatic 1	11.23203517	1.10870297
	Aromatic 2	12.28876969	1.14693784
	Aromatic 3	18.2546477	0.89347743
	Methylene	1.348947271	1.45081684
	Methyl	2.765489124	0.79762573
TfpTP-ODEG			
	Carbonyl	19.86286339	1.06050189
	Imine	9.586386044	1.56307023
	Aromatic 1	6.793677455	2.83913723

	Aromatic 2	7.036298776	1.67704621
	Aromatic 3	9.765533016	1.7043793
	Methylene	0.705406526	1.99451193
	Methyl	2.71352315	1.37003292
TfpTP-OTEG			
	Carbonyl	16.27824313	0.69859408
	Imine	12.84786604	1.01106438
	Aromatic 1	8.084473521	1.14372623
	Aromatic 2	8.506226626	0.68053202
	Aromatic 3	14.77968018	0.69513392
	Methylene	0.588876041	0.93036114
	Methyl	2.961691151	1.26893222

Section S5. **TGA analysis**

Figure S6. TfpTP-OEt COF

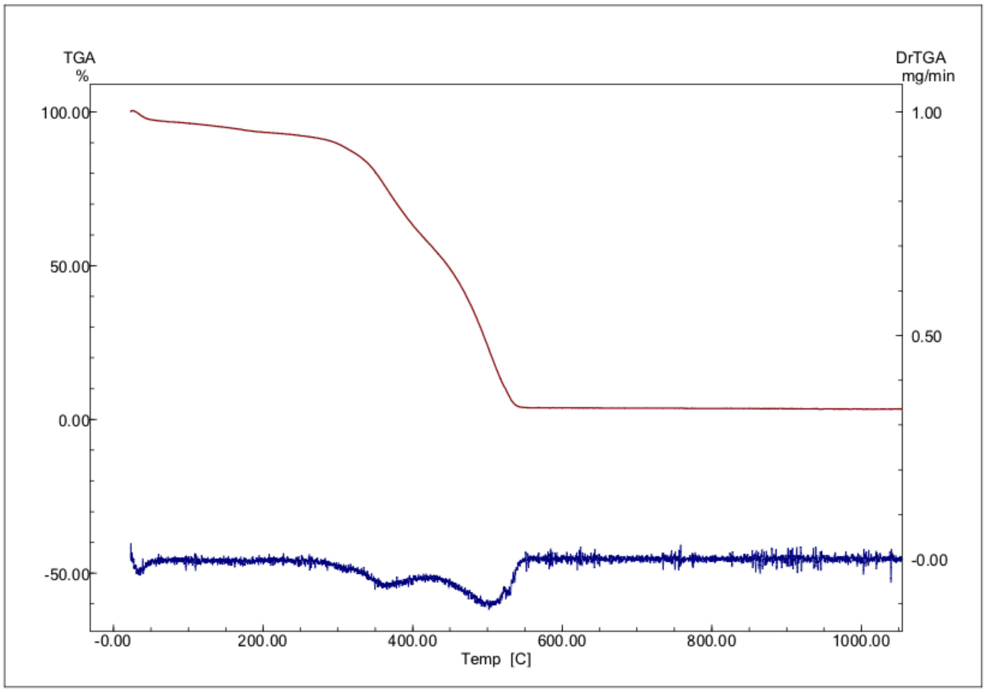


Figure S7. TfpTP-OMEG

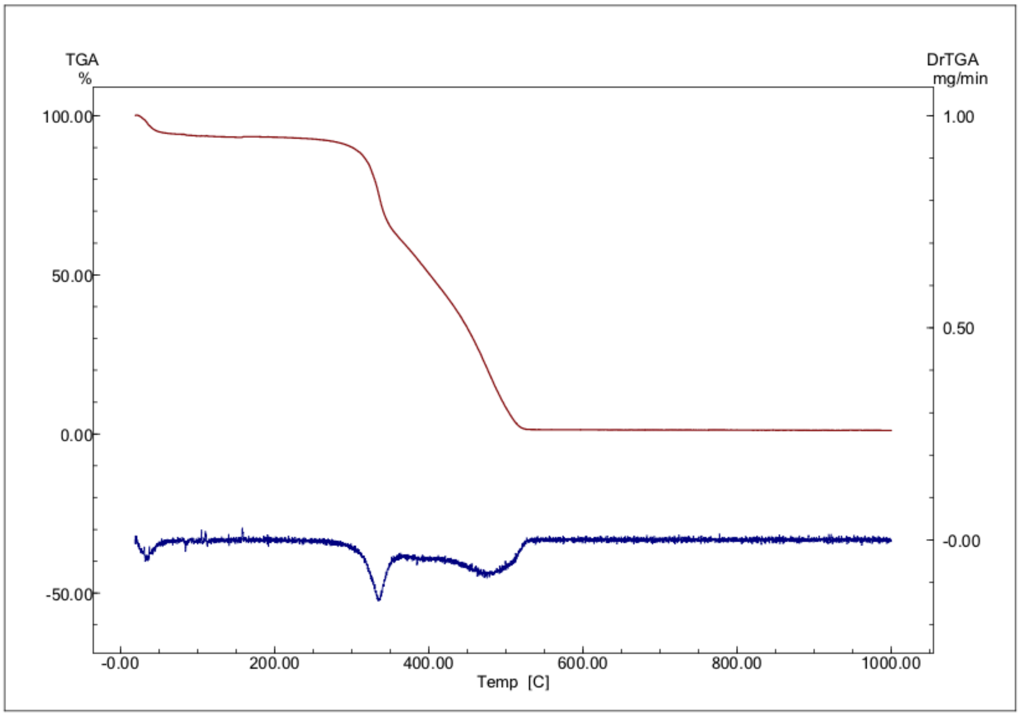


Figure S8. TfpTP-ODEG

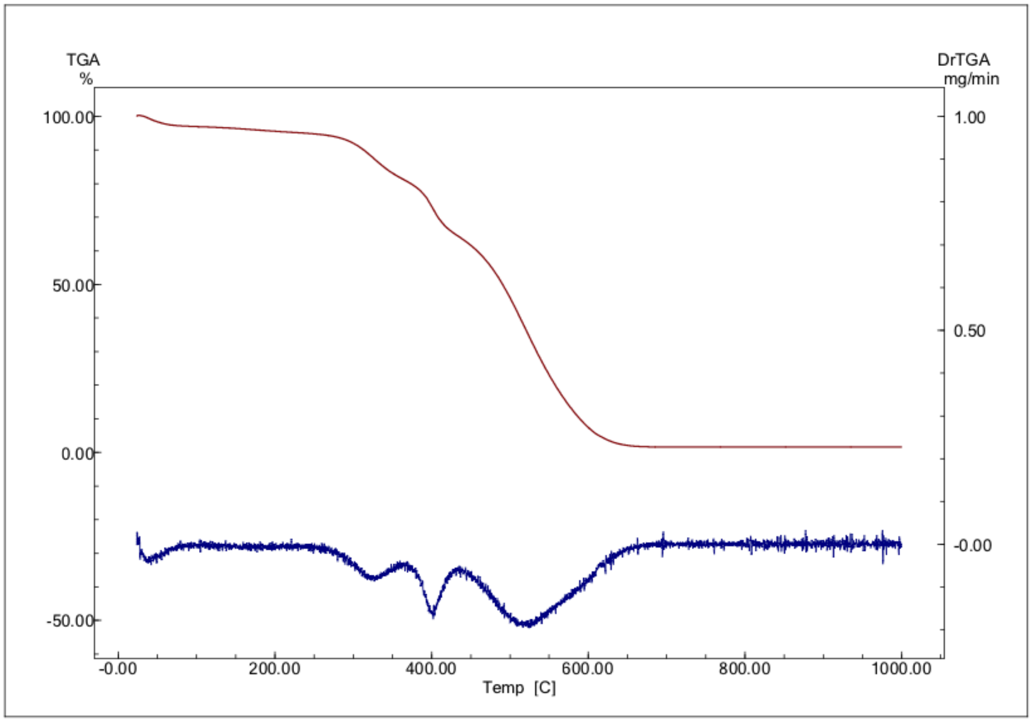
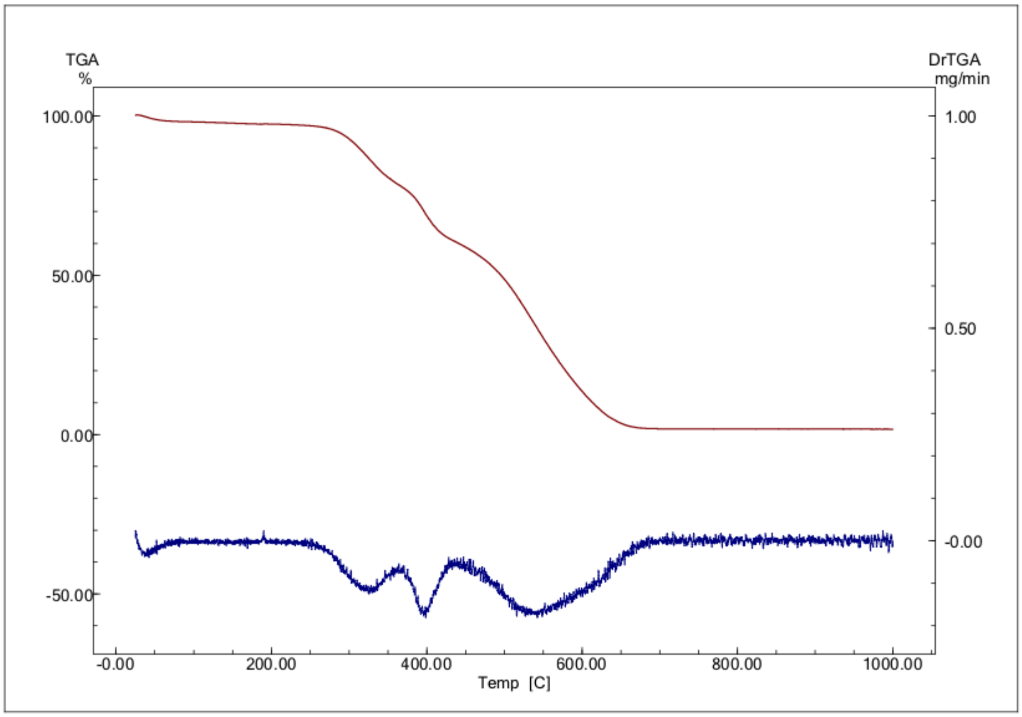


Figure S9. TfpTP-OTEG



Section S6. **FT-IR**

Figure S10. FT-IR of TfpTP-H

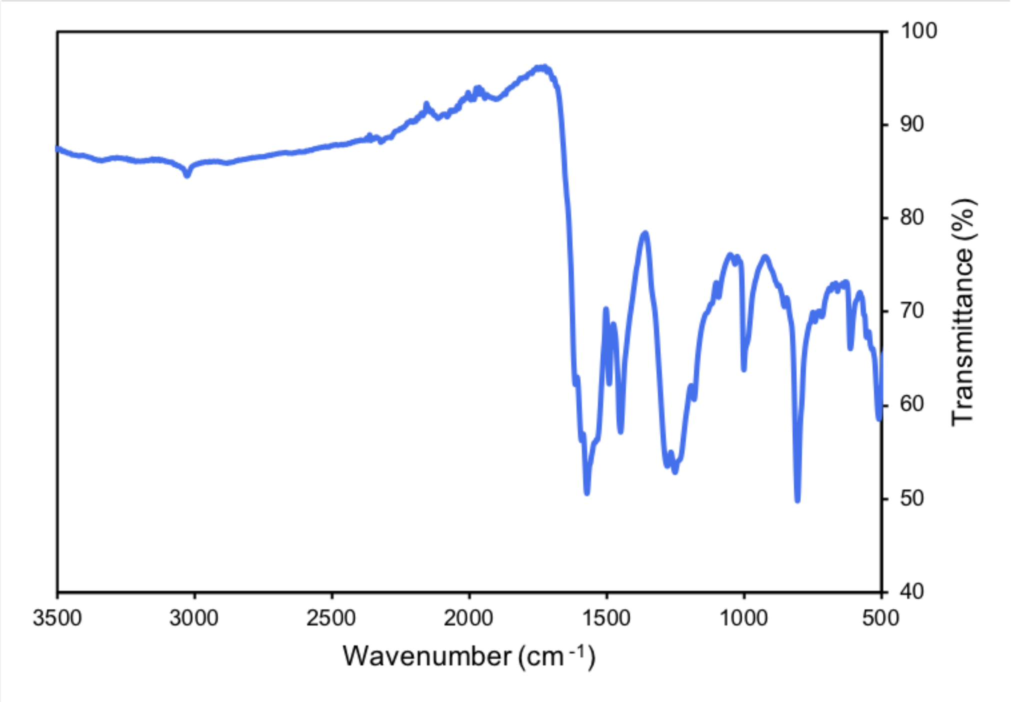


Figure S11. FT-IR of TfpTP-OEt

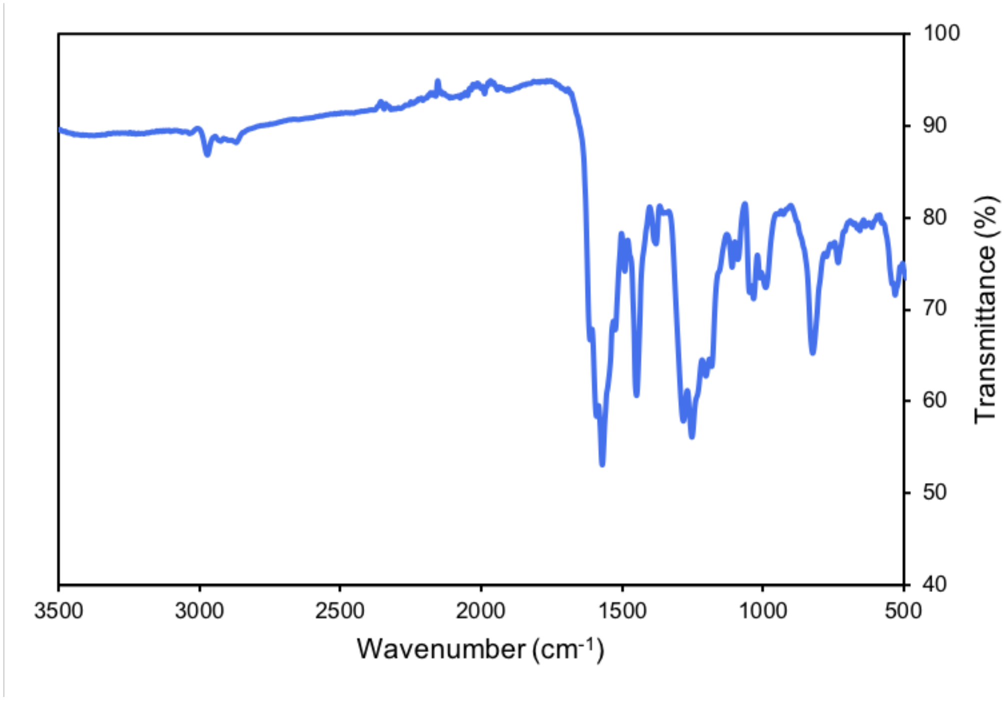


Figure S12. FT-IR of TfpTP-OMEG

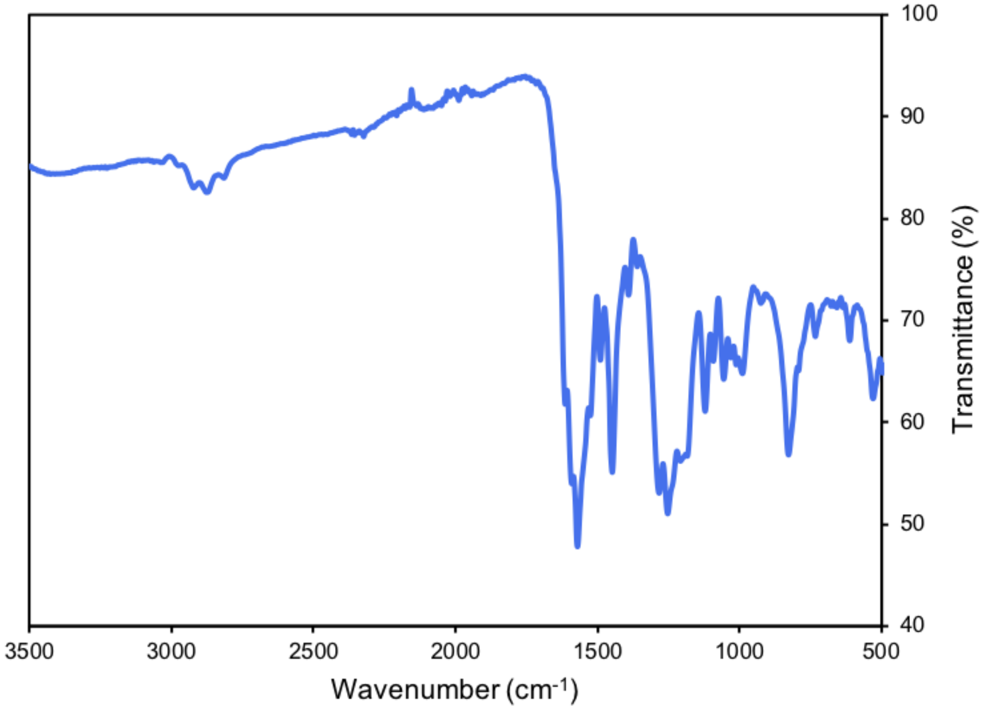


Figure S13. FT-IR of TfpTP-ODEG

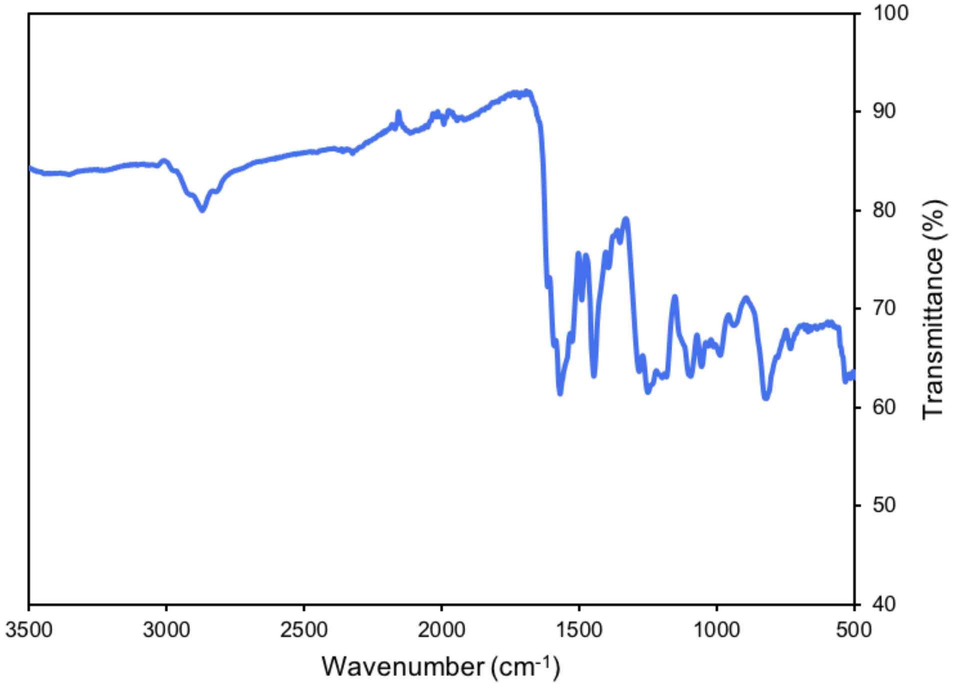
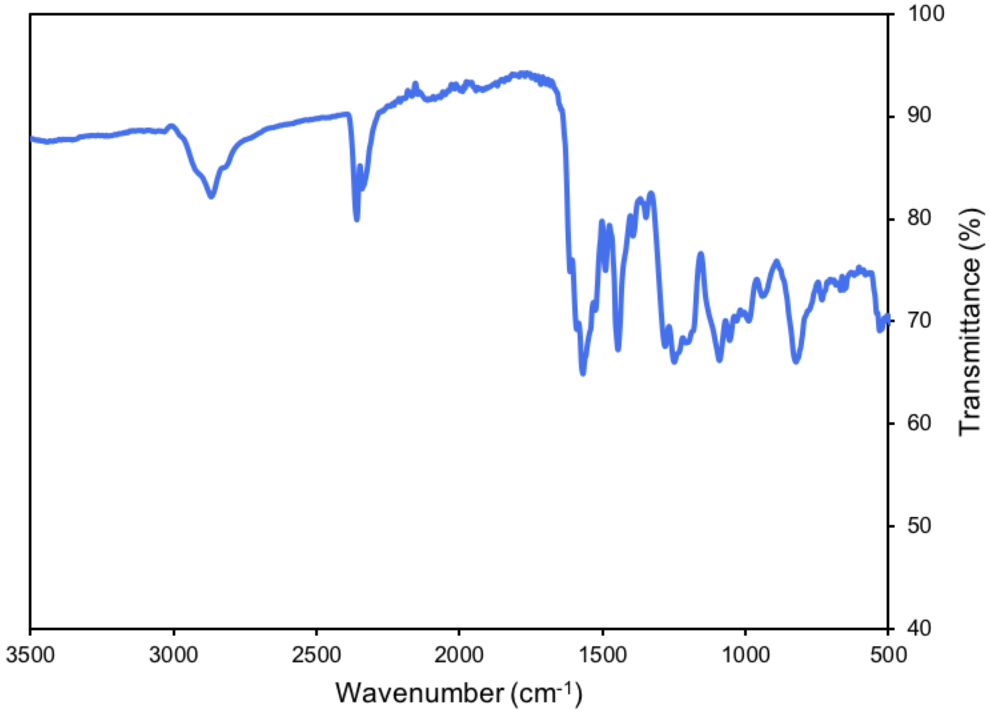


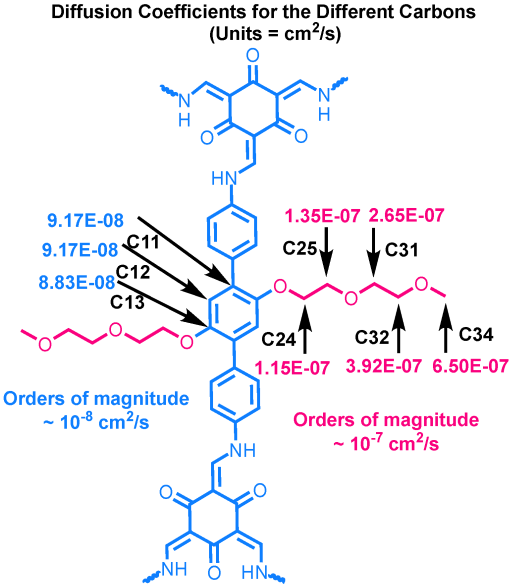
Figure S14. FT-IR of TfpTP-OTEG



Section S7. **Molecular Dynamics (MD)**

Molecular Dynamics (MD) simulations were performed using the LAMMPS simulation engine with a 1 femtosecond (fs) time step.[S6] We used the Dreiding force field to treat the interactions. Similar results were found with the UFF force field. The long-range electrostatics effects were treated using the Particle-Particle Particle-Mesh Ewald[S7] technique, with a real space cutoff of 10 Å and an accuracy tolerance of 10^{-5}. For each MD simulation we started with the equilibrium geometry from 500 steps of Conjugated Gradient (CG) minimization (cell coordinates and atom positions) followed by 10 picoseconds (ps) of NVT dynamics to heat the system from 10 K to 298 K. Finally, we ran NPT dynamics at 1 atm and 298 K for 10 nanoseconds (ns) from which we collect all relevant data. The temperature damping constant was 0.1 ps while the pressure damping constant was 2.0 ps. The equations of motion used are those of Shinoda *et al.*[S8], which combine the hydrostatic equations of Martyna *et al.*[S9] with the strain energy proposed by Parrinello and Rahman.[S10] The time integration schemes closely follow the time-reversible measure-preserving Verlet integrators derived by Tuckerman *et al.*[S11]

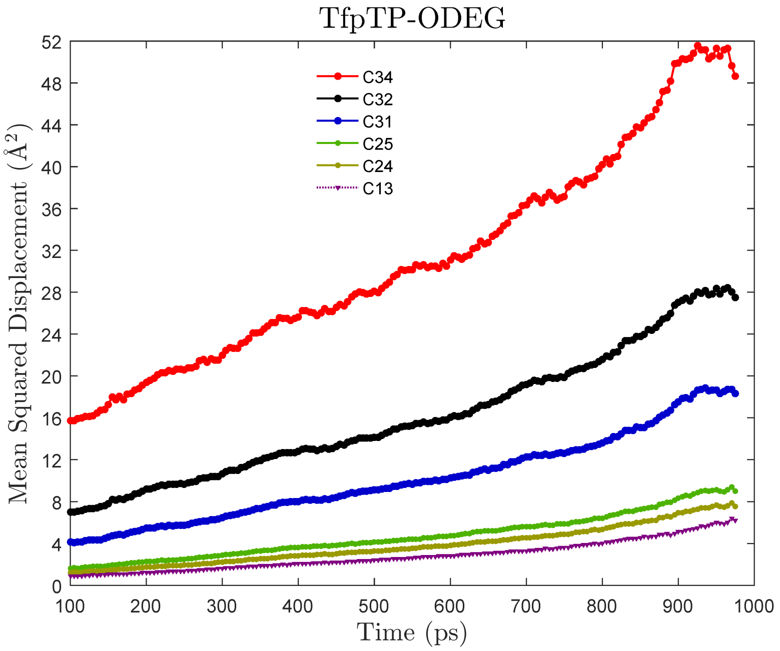
The different diffusion coefficients were calculated by calculating the mean squared deviation (MSD) and plot it with respect to the time. The backbone atoms (*e.g.*, C11, C12, C13) have around the same diffusion coefficient in the range of 10^{-8} cm^2 s^{-1}. On the other hand, the carbons that belong to the side chain (*e.g.*, C24, C25, C31, C32, C34) have a larger of magnitude for the diffusion coefficient of around 10^{-7} cm^2 s^{-1}.

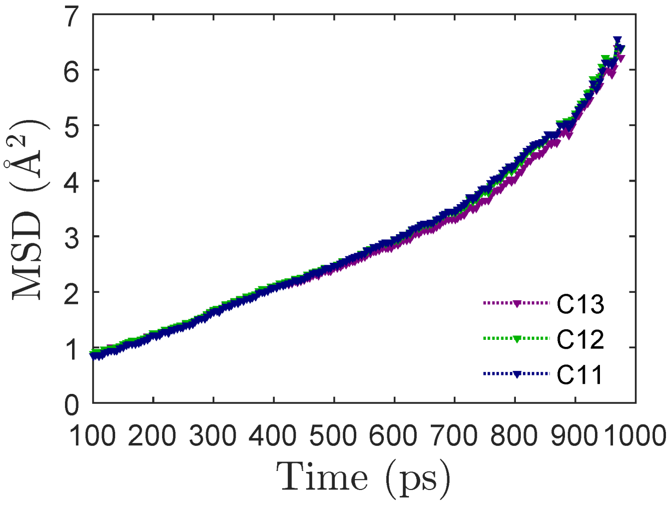


TfpTPODEG

The fitting equation along with the R^2 valued are as follows (Units: x = ps, y = $Å^2$):

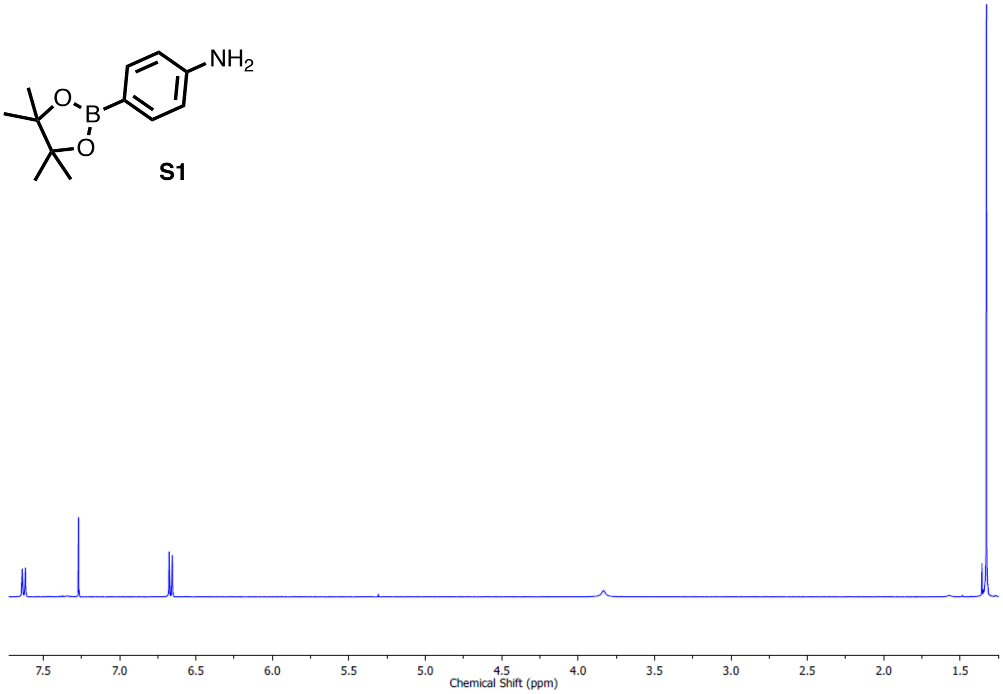
C34: $y = 0.0390x + 10.121$, $R^2 = 0.9642$
C32: $y = 0.0235x + 3.4685$, $R^2 = 0.9659$
C31: $y = 0.0159x + 1.6436$, $R^2 = 0.9635$
C25: $y = 0.0081x + 0.3808$, $R^2 = 0.9597$
C24: $y = 0.0069x + 0.0877$, $R^2 = 0.9595$
C13: $y = 0.0053x - 0.0487$, $R^2 = 0.9459$
C12: $y = 0.0055x - 0.0989$, $R^2 = 0.9516$
C11: $y = 0.0055x - 0.0981$, $R^2 = 0.9581$





Section S8. **Solution NMR spectra**

Figure S15. 4-amino-phenyl-boronic pinacol ester:



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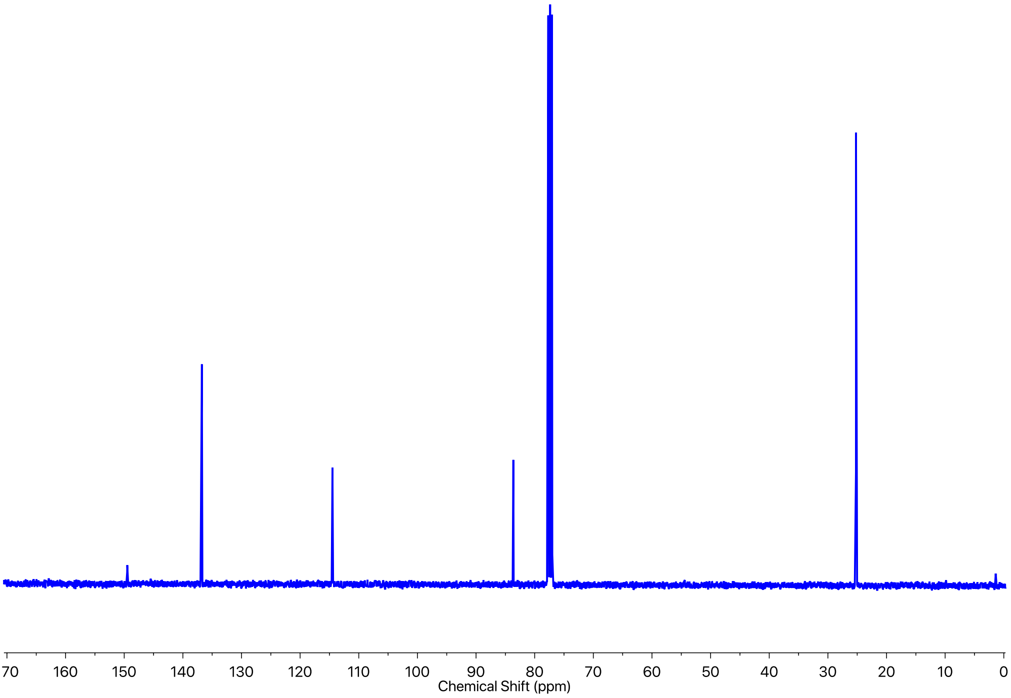
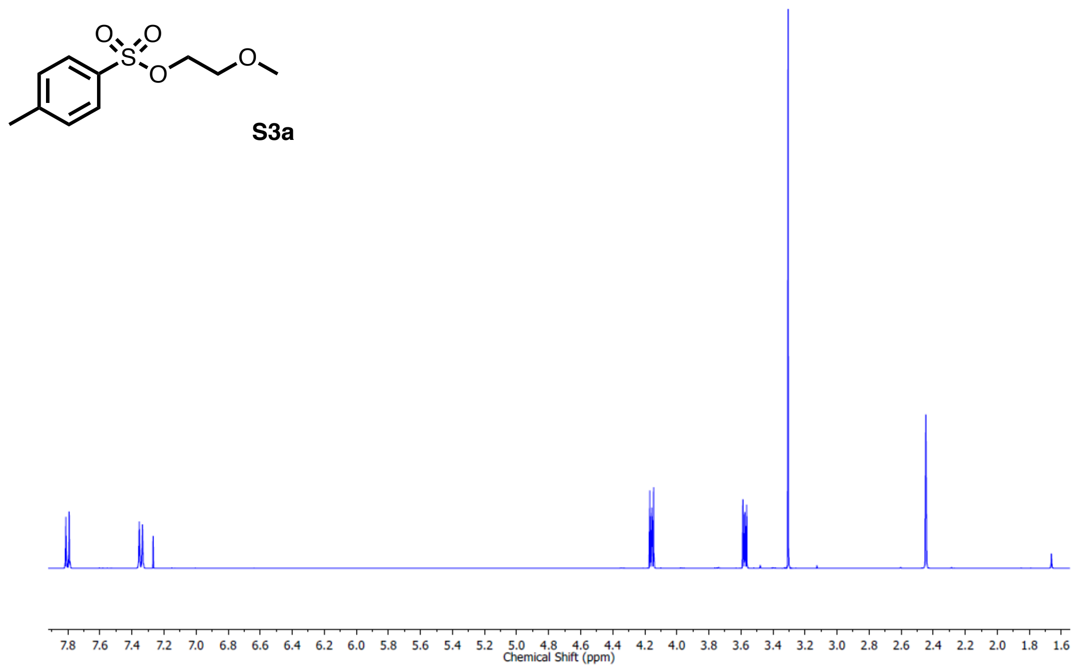


Figure S16. 2-methoxyethyl p-toluenesulfonate:



S3a

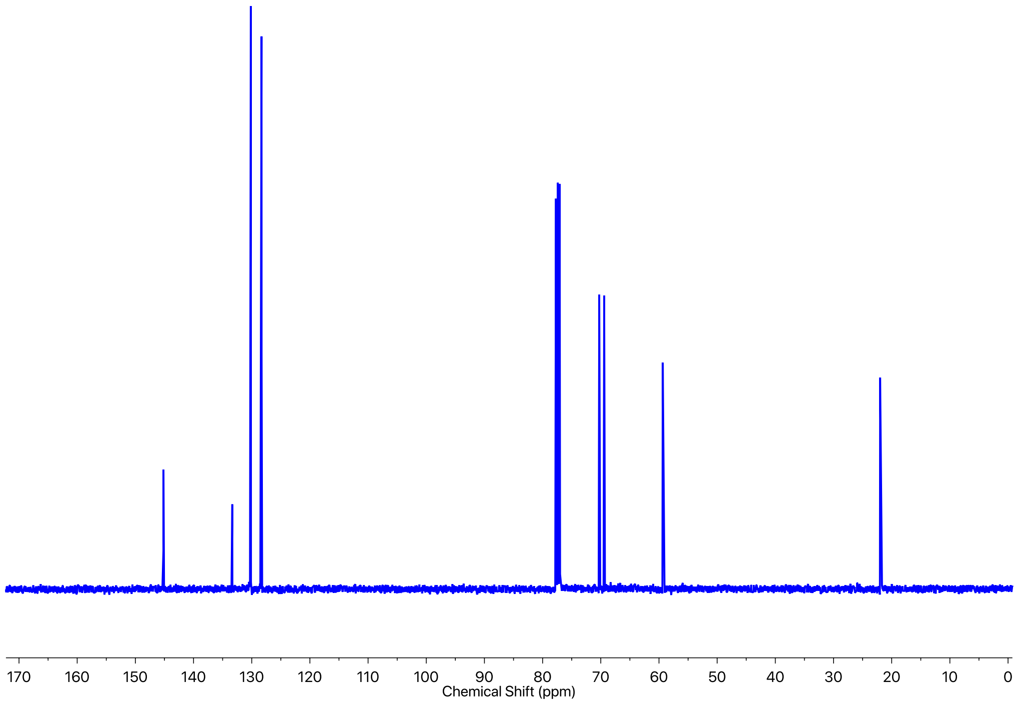
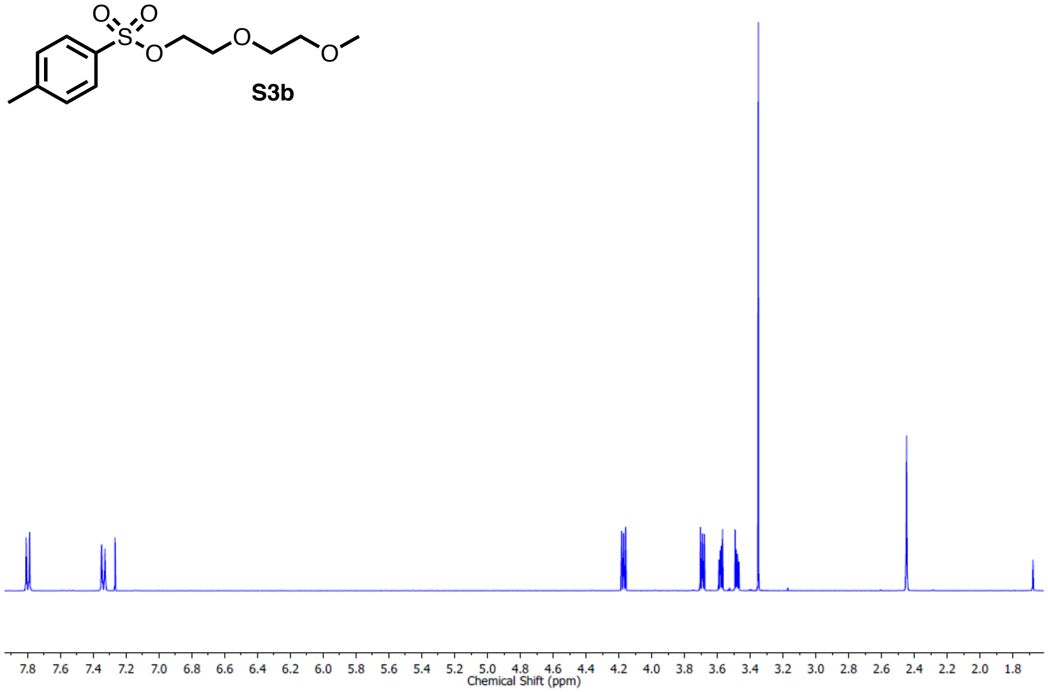


Figure S17. 2-(2-Methoxyethoxy) ethyl p-toluenesulfonate:


S3b

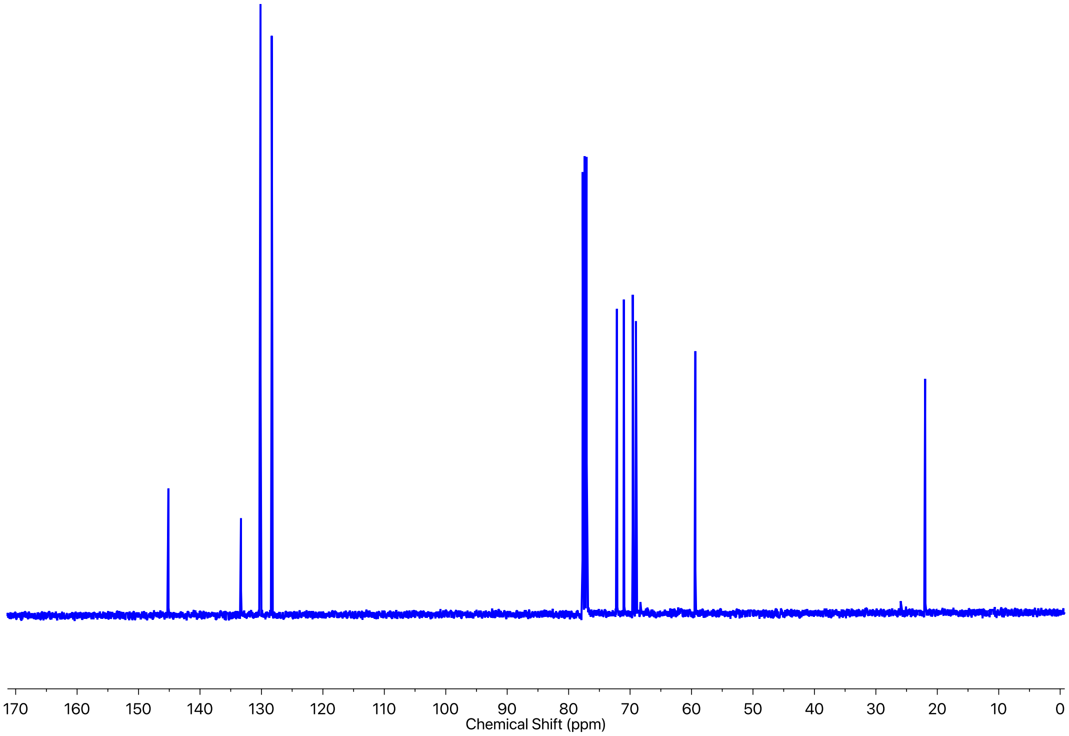
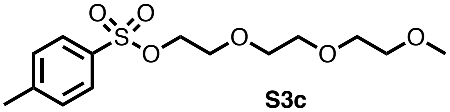
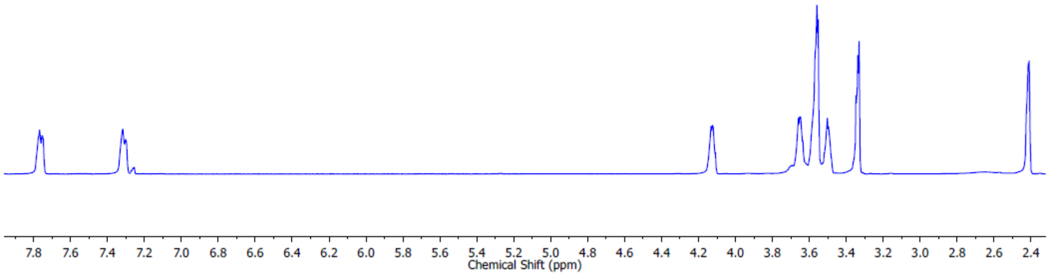


Figure S18. 3-(2-Methoxyethoxy) ethyl p-toluenesulfonate:



S3c



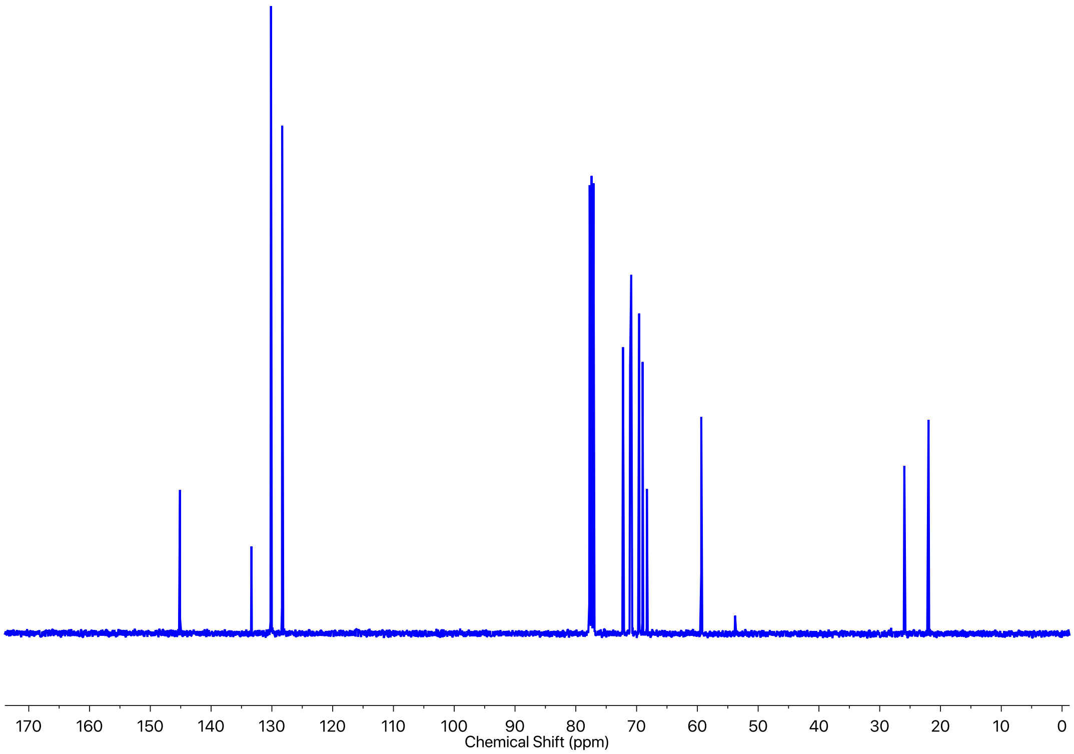
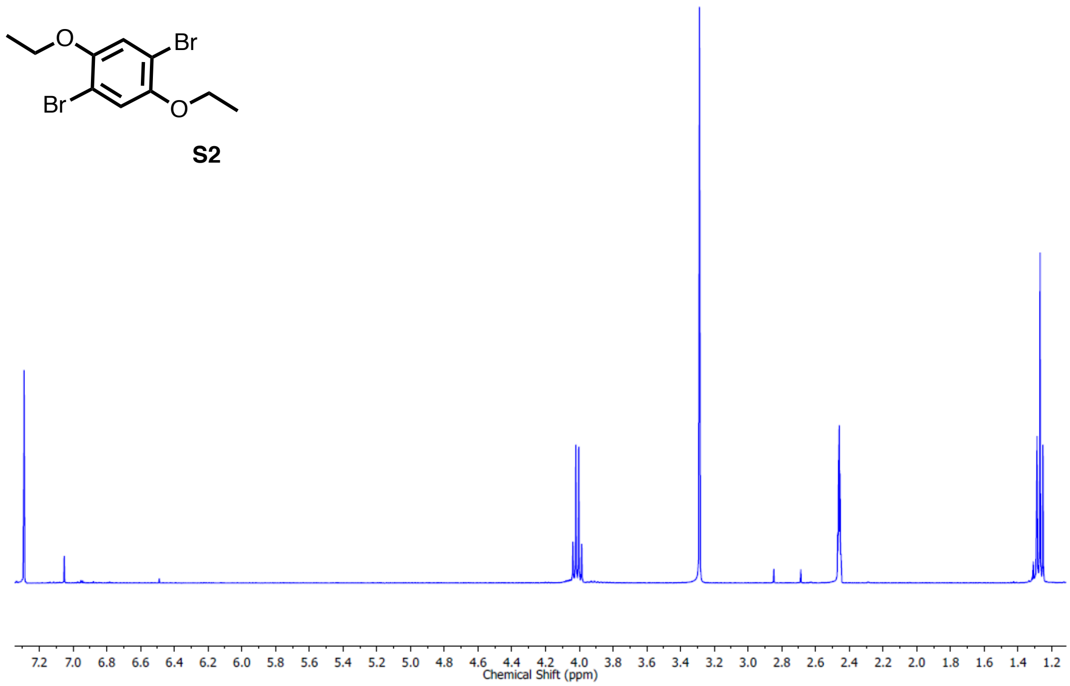


Figure S19. 1,4-dibromo-2,5-diethoxybenzene:



S2

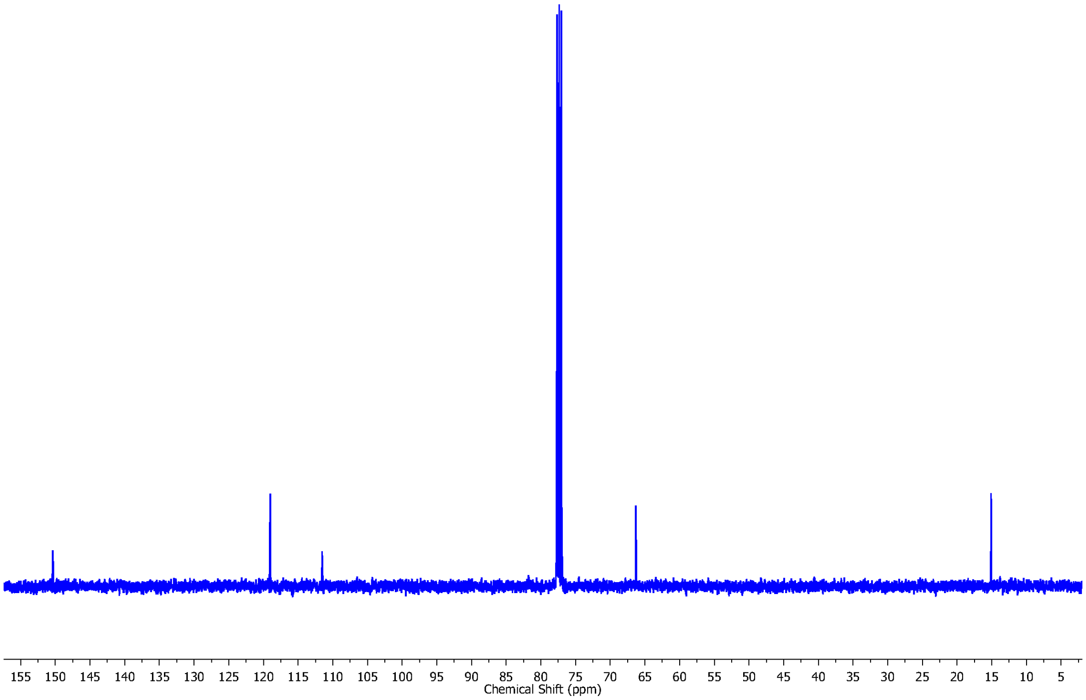
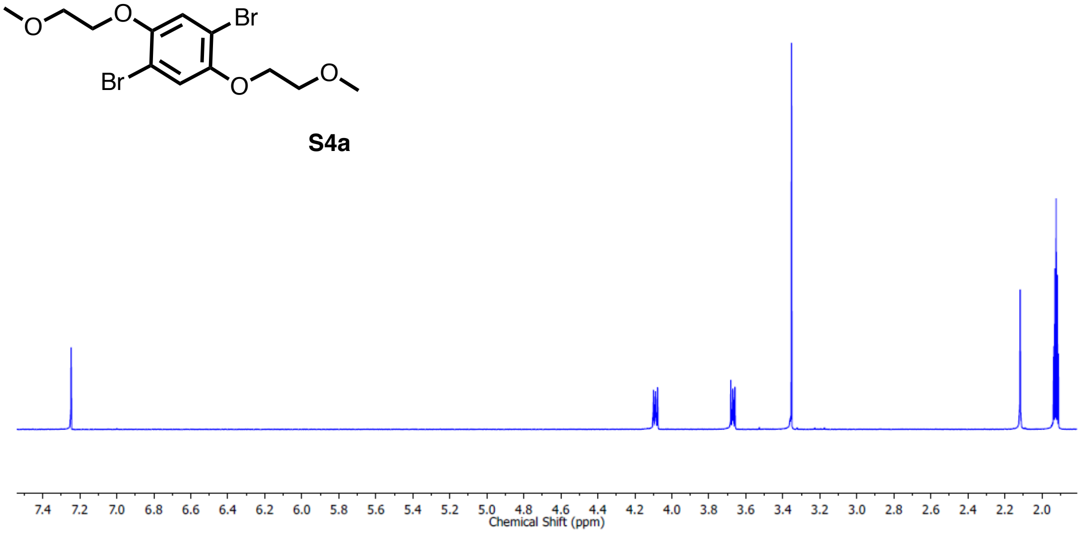


Figure S20. 1,4-dibromo-2,5-di(2-methoxyethoxy) ethylbenzene:

S4a



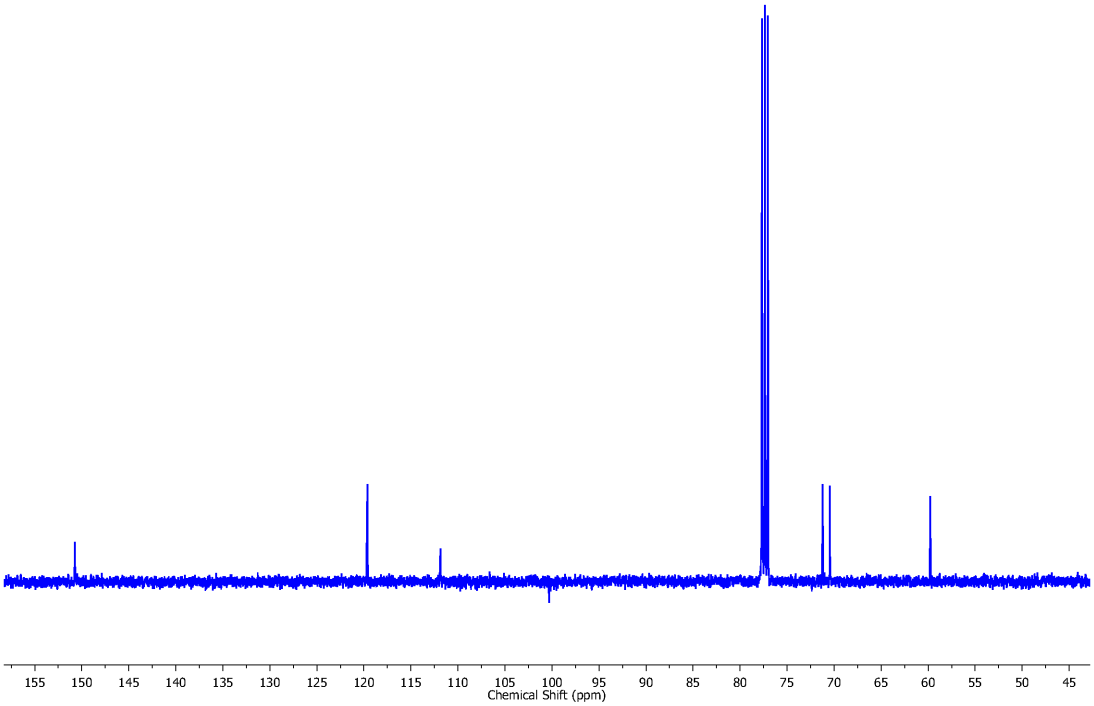
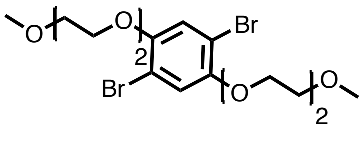
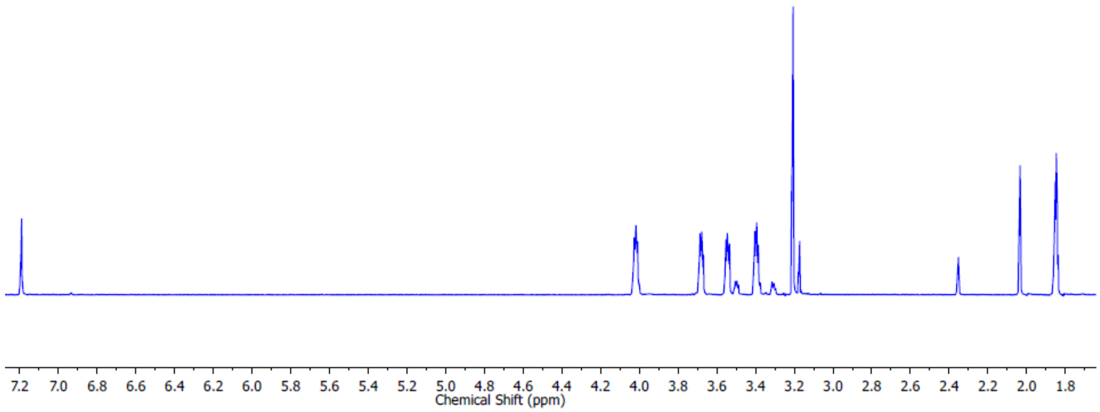


Figure S21. 1,4-dibromo-2,5-di(2-(2-methoxyethoxy)) ethylbenzene:



S4b



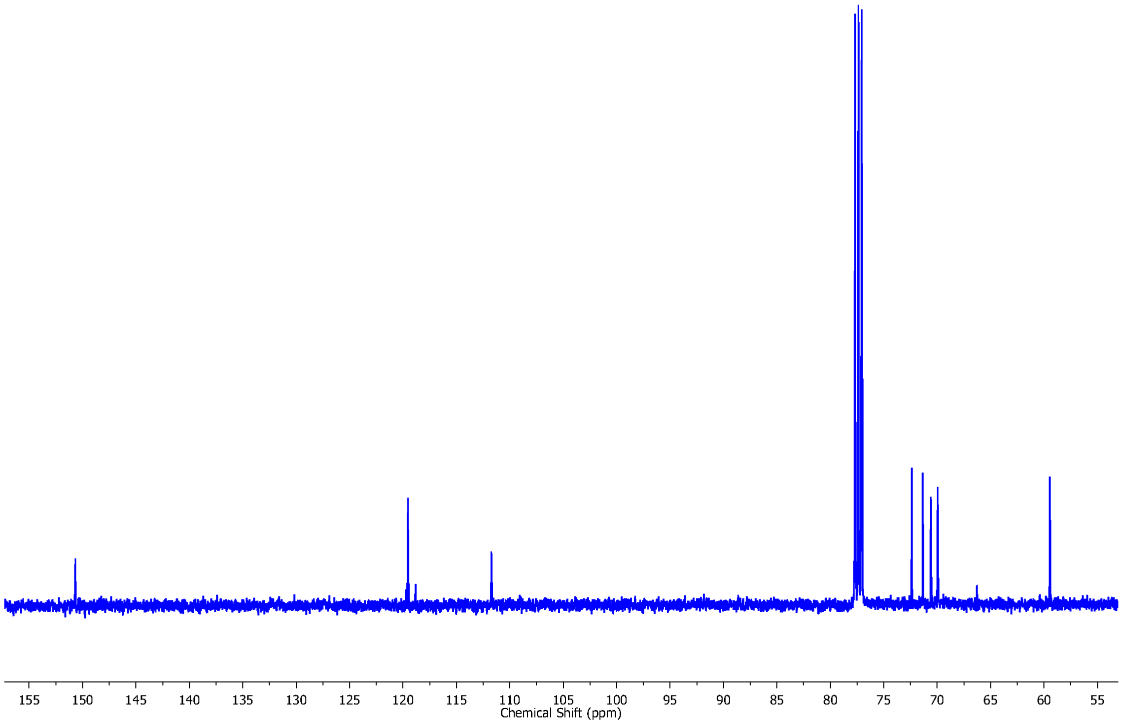


Figure S22. 1,4-dibromo-2,5-di(3-(2-methoxyethoxy)) ethylbenzene:

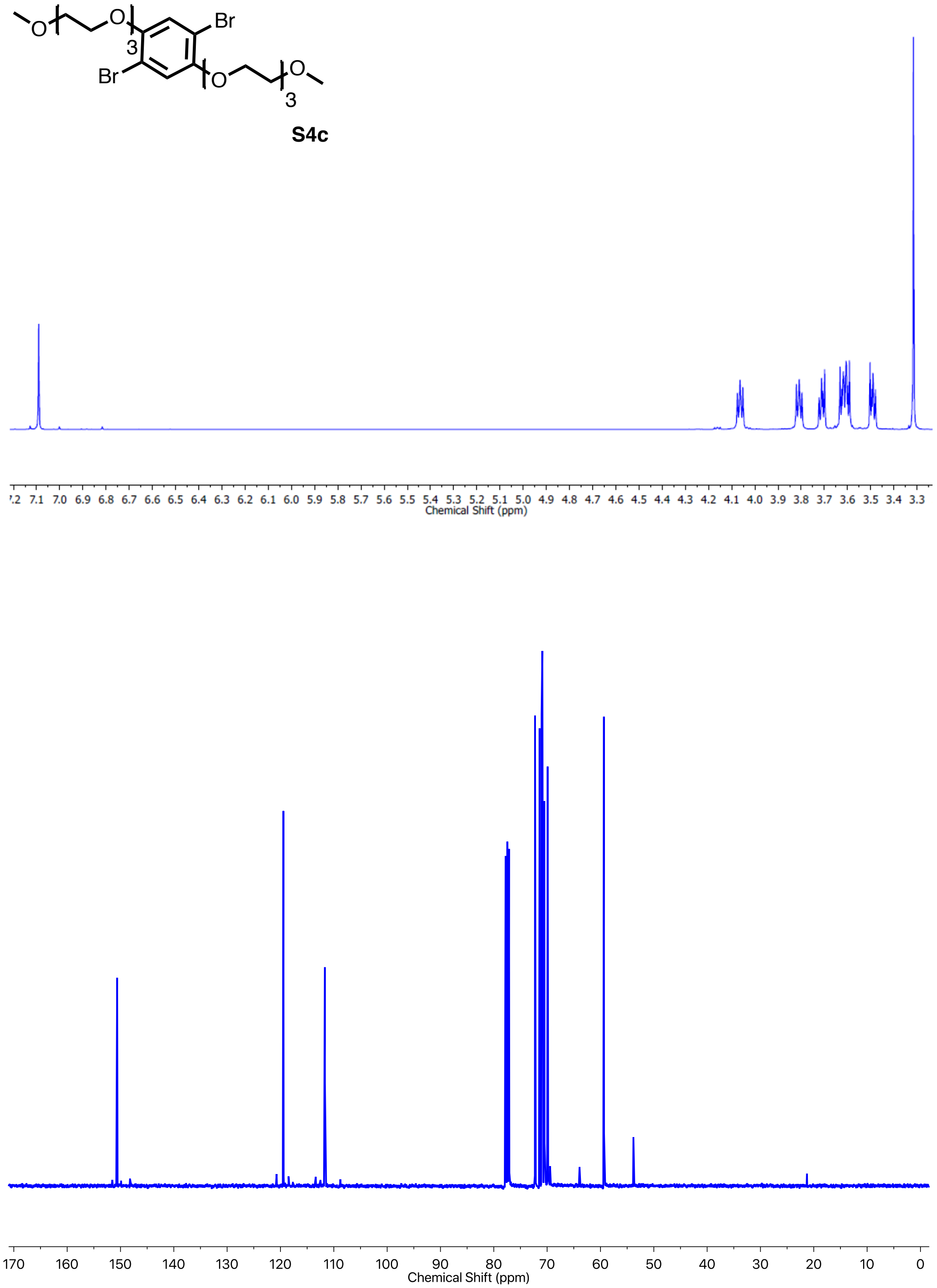
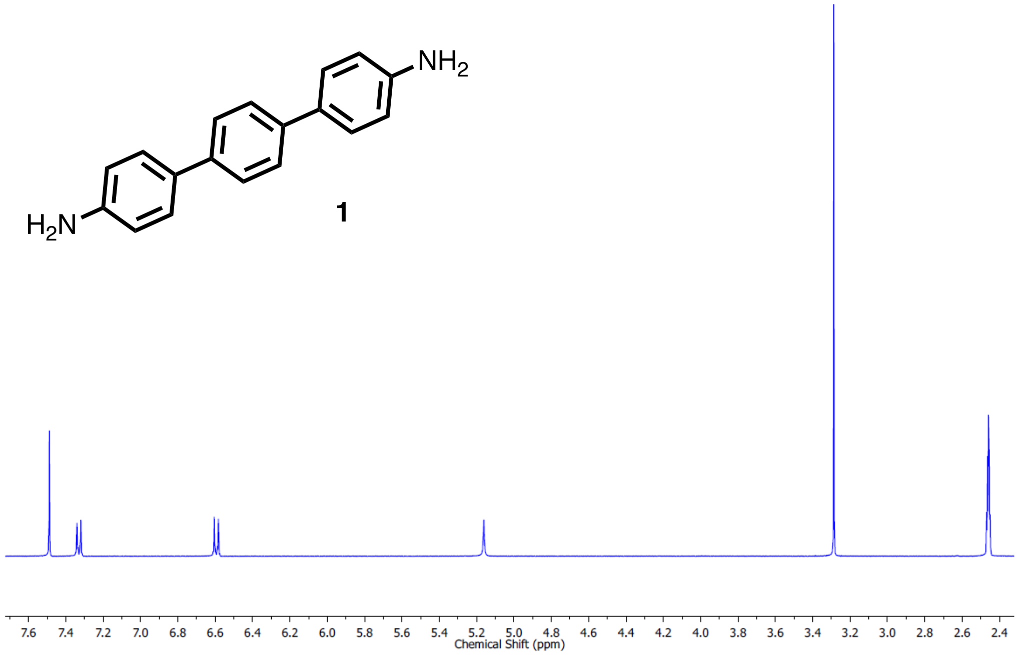

S4c

Figure S23. 4,4’-diamino-p-terphenyl:



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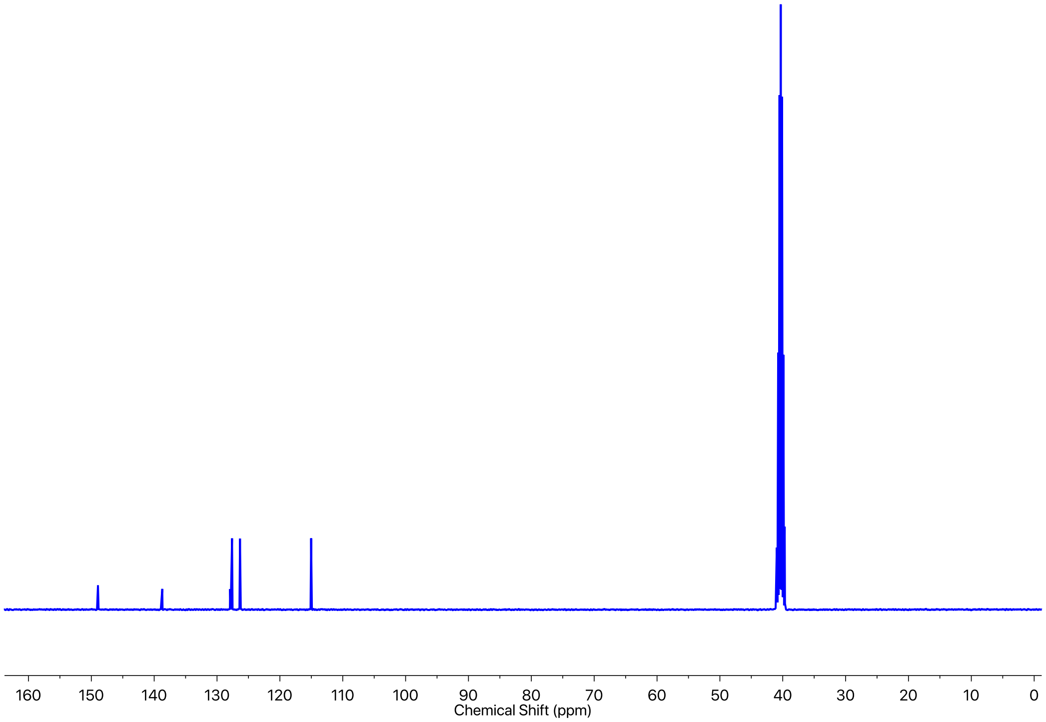
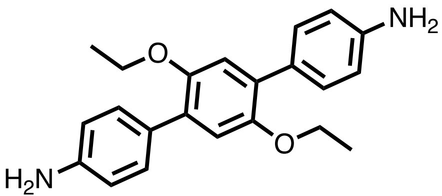


Figure S24. 1,4-diethoxy-2,5-di(p-aminophenyl)benzene:



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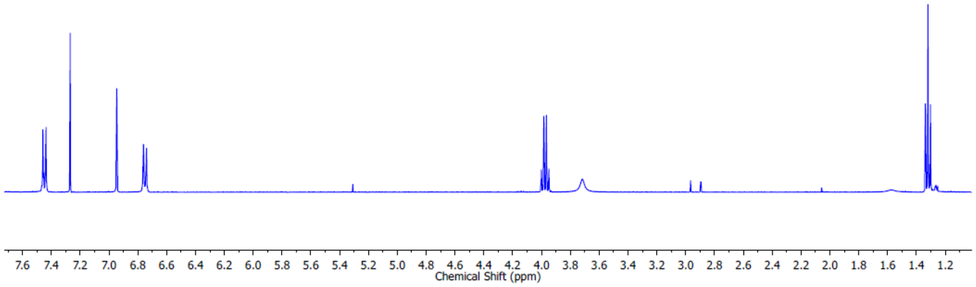


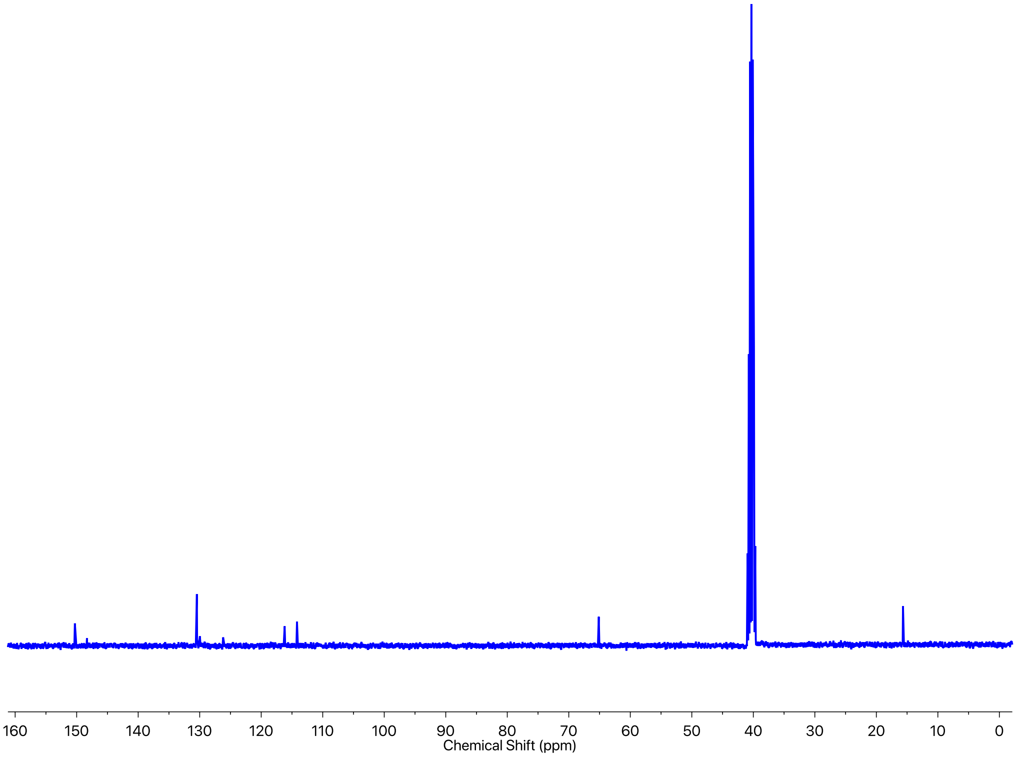
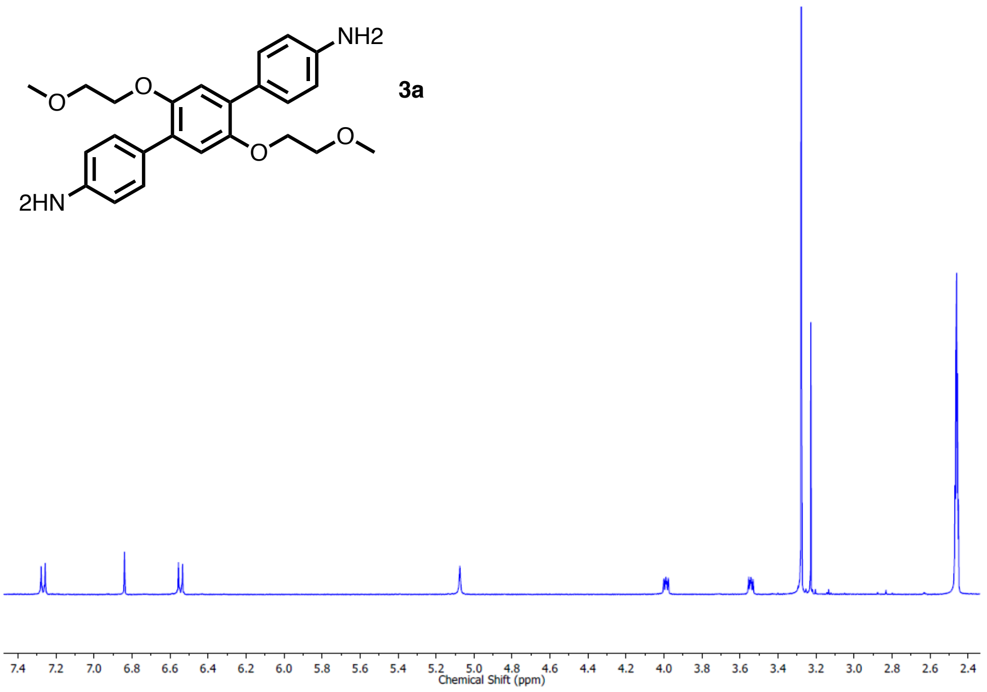


Figure S25. 1,4-di((2-methoxyethoxy)ethyl)-2,5-di(p-aminophenyl)benzene:



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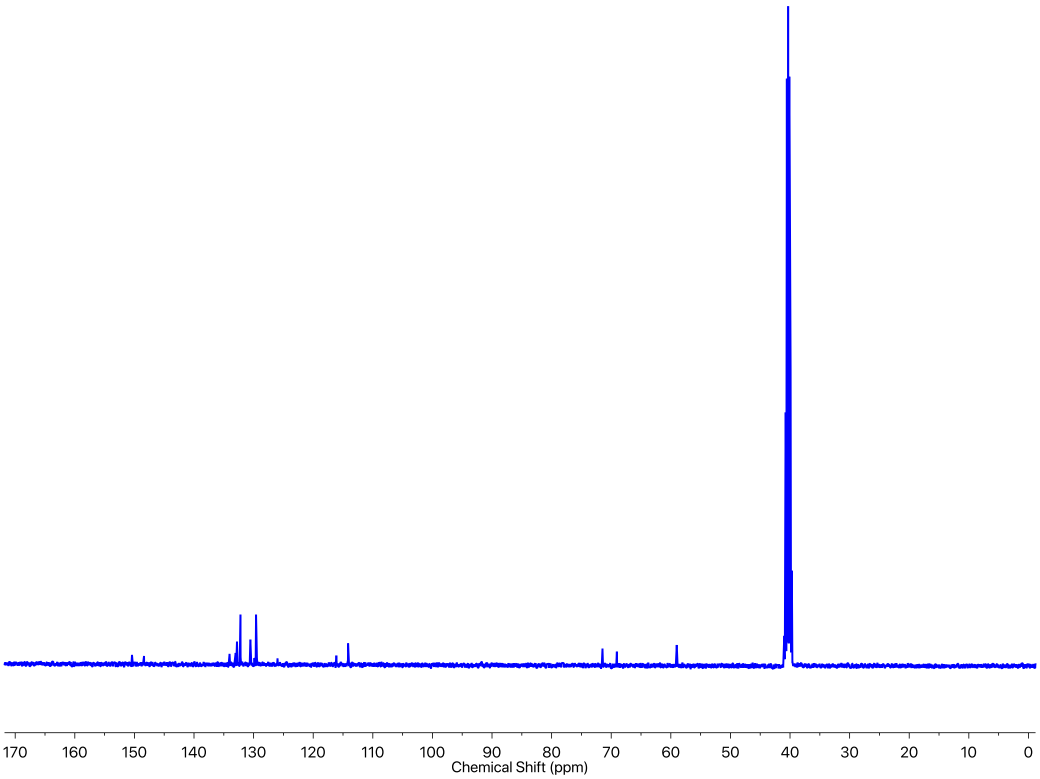
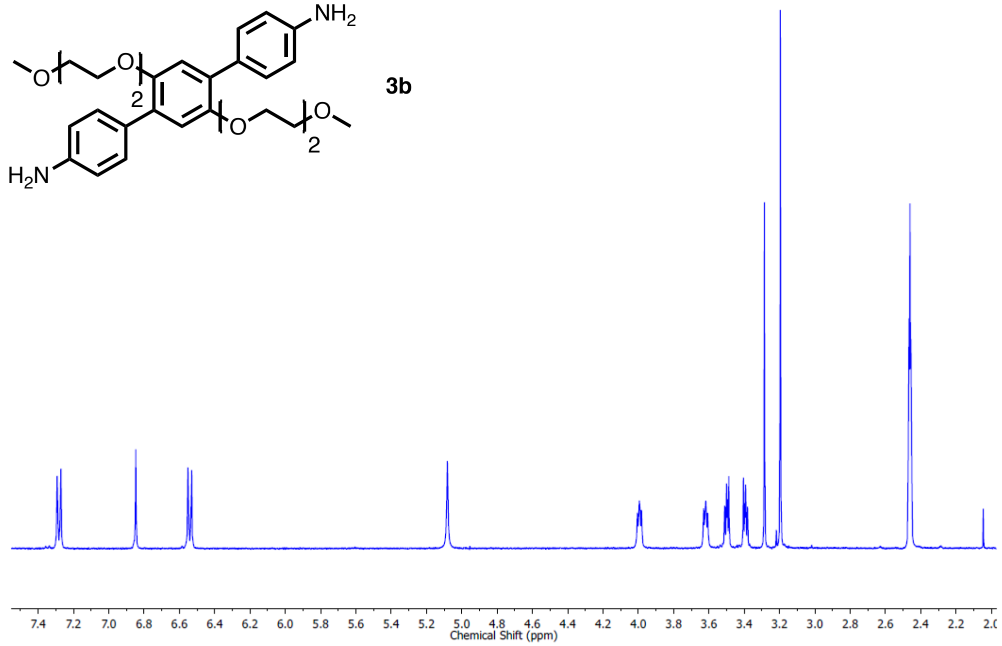


Figure S26. 1,4-di(2-(2-methoxyethoxy)ethyl)-2,5-di(p-aminophenyl)benzene:



3b

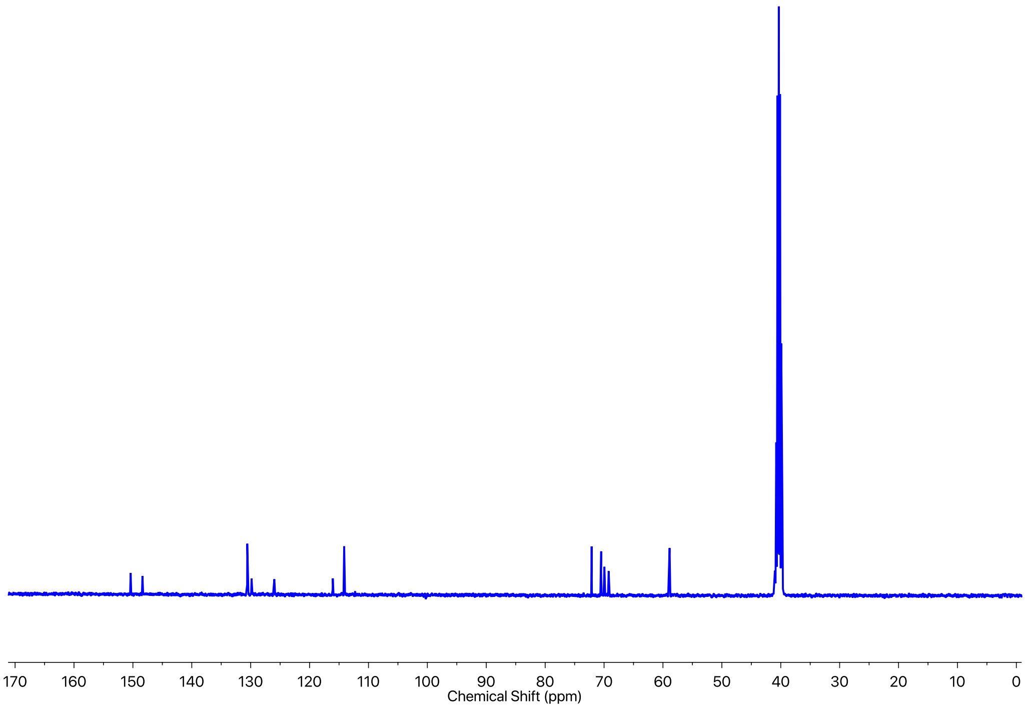
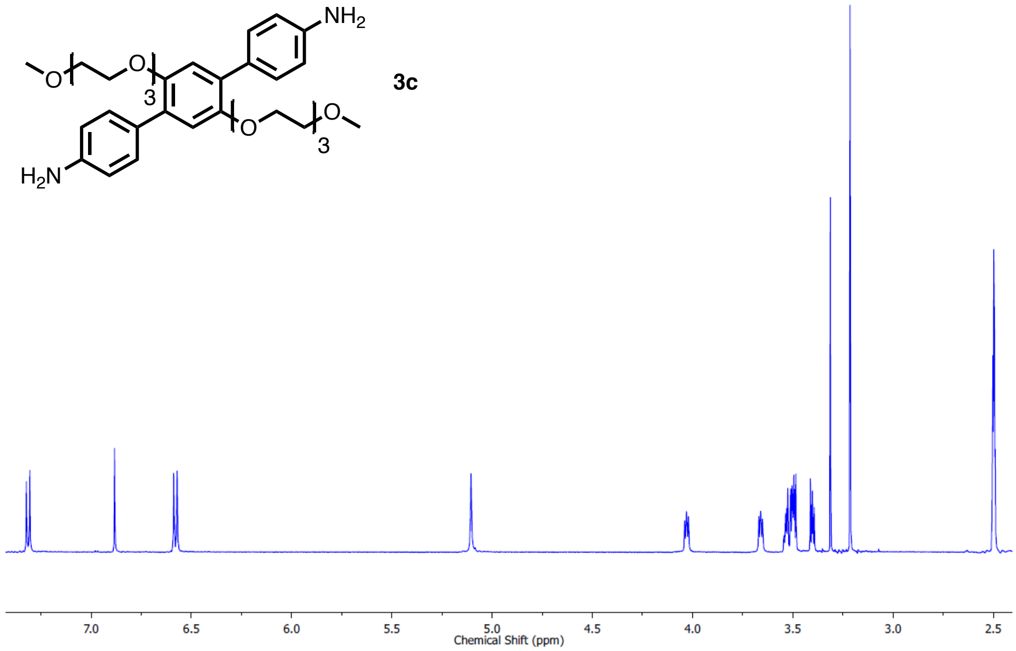
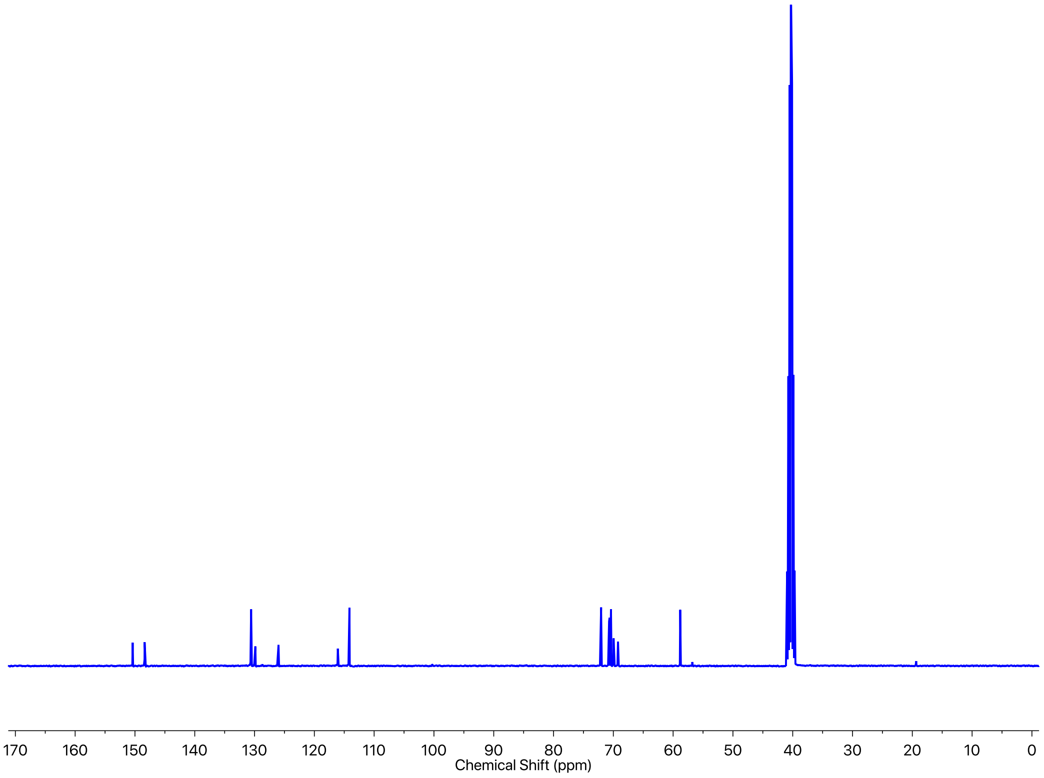


Figure S27. 1,4-di(3-(2-methoxyethoxy)ethyl)-2,5-di(*p*-aminophenyl)benzene:





Section S9. **References**

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