Supramolecular Bottlebrush Copolymers from Crown-Ether Functionalized Poly(*p*-phenylenevinylene)s

Anahita Keer, Arielle Mann, Chengyuan Wang, and Marcus Weck*

Molecular Design Institute and Department of Chemistry, New York University, New York, NY 10003.

Table of Contents

Materials and Methods

All chemicals were purchased from Ambeed, Thermo Fisher, Oakwood Chemicals, TCI Chemicals, or Sigma Aldrich and used as received unless otherwise indicated. All reactions were carried out under ambient conditions unless otherwise noted. Flash column chromatography was performed using silica gel 60 Å (230-400 mesh) from Sorbent Technologies.

NMR spectroscopy characterizations were conducted at 25 ˚C, unless otherwise noted, on Bruker Avance 400 MHz, 500 MHz, 600 MHz, or 800 MHz spectrometers. Chemical shifts are reported in ppm and referenced to solvent residual peaks. Splitting patterns are reported as singlets (s), doublets (d), doublet of doublets (dd), triplets (t), quartets (q) or multiplets (m).

Mass spectra of samples in filtered methanol or acetonitrile were acquired with an Agilent 6224 Accurate-Mass TOF/LC/MS Spectrometer using an ESI ion-source. The samples were separated and analyzed by an Agilent 1260 Infinity HPLC equipped with CHIRALPAK IA-3 column.

Gel-permeation chromatography (GPC) characterizations were obtained from a Shimadzu pump coupled to a Shimadzu UV and RI detectors with tetrahydrofuran (THF) as the mobile phase. The injection volume was 50 µL and the flow rate was 1 mL/min on a Shimadzu column set (100, 1000, 100,000 Å, linear mixed bed). The GPC instruments were calibrated using poly(styrene) standards (EasiCal, Agilent Technologies, Santa Clara, CA) and characterizations were carried out at 25 °C. *M*n and Đ represent number average molecular weight and dispersity, respectively.

Absorption spectra were obtained using a Cary 100 UV-VIS Spectrophotometer by Agilent Technologies. Fluorescence spectra were collected on a QuantaMaster 40 Photon Technology International spectrofluorometer equipped with Xenon lamp source, emission and excitation monochromators, excitation correction unit, and PMT detector. All measurements were conducted at 25.0 ± 0.1 °C maintained by a Quantum Northwest cuvette temperature controller. Emission and excitation spectra were corrected for the wavelength-dependent response and wavelength dependent lamp intensity.

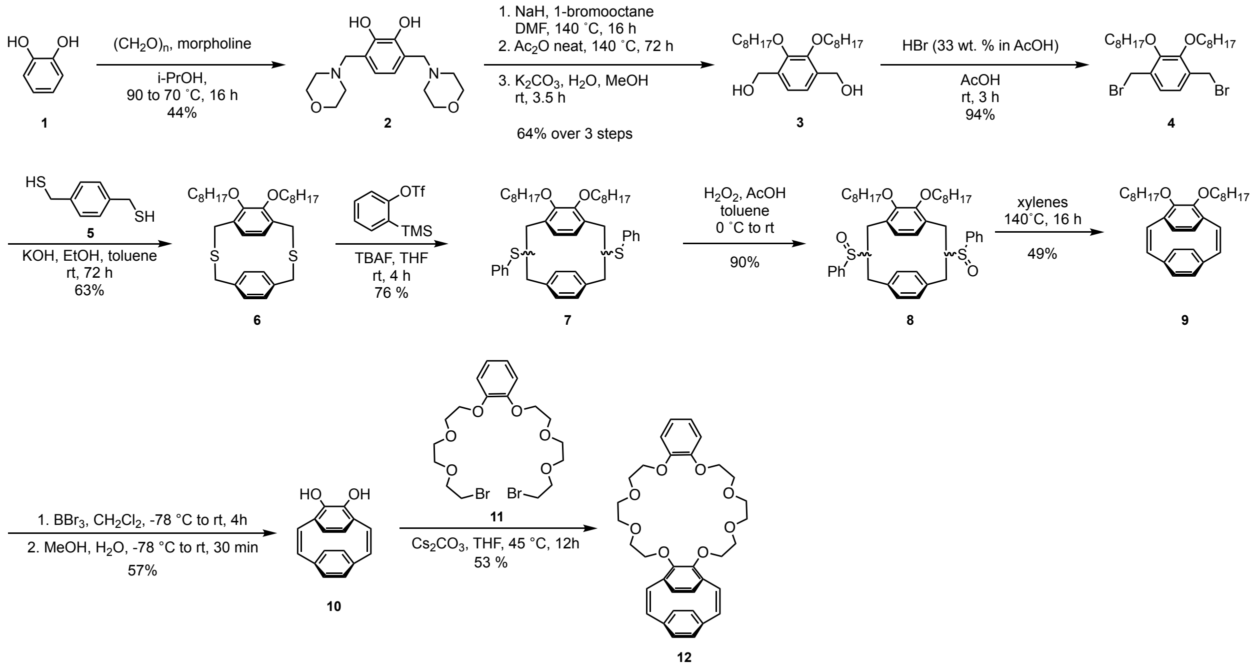
A 365 nm UV lamp (15W UVP Black Ray UV Bench LampXX-15L) was used for photoisomerization.

Hydrodynamic diameters of the homopolymer and assembled bottlebrush were determined at 25 °C in 1:1 chloroform: acetonitrile by dynamic light scattering (DLS) using Malvern Zetasizer nano series with a 663 nm module.

Isothermal titration calorimetry (ITC) measurements were performed on a TA Nano ITC isothermal titration calorimeter at 25.00 °C using HPLC grade $CHCl_3$ (passed through a plug with basic alumina prior to use) and HPLC grade CH_3CN (distilled prior to use). A total of 50 µL of the titrant was titrated into 150 µL of the analyte in 20 additions with 150 s intervals. Data simulation and modelling was applied to each measurement with the single-site binding model. The association constant from ITC was obtained from the average of three measurements.

X-ray diffraction data was collected on a Bruker D8 DISCOVER GADDS microdiffractometer equipped with a VÅNTEC-2000 area detector. X-rays were generated with a sealed Cu tube, monochromated by a graphite crystal, and collimated by a 0.5 mm MONOCAP (λ = 1.54178 Å). Polymer samples were dried under high vacuum and the powder was scraped into Kapton tubes. Measurements were collected at room temperature.

Crown-Ether Substituted [2.2]Para-cyclophane-1,9-diene Synthesis, Monomer 12



Scheme S1: Synthetic route to monomer **12**.

Compounds **2**, **3**, **4**, **5**, **11**, and (trimethylsilyl)phenyl trifluoromethanesulfonate were synthesized according to reported procedures.[1, 2]

Compound 6

To a three-neck 2 L round bottom flask equipped with a stir bar, pressure equilibrating addition funnel, septa, and stop cock, potassium hydroxide (3.38 g, 0.0601 mol) was added and dissolved in ethanol (700 mL). To the addition funnel, a solution of compound **4** (6.41 g, 0.0123 mol) and compound **5** (2.10 g, 0.0123 mol) dissolved in toluene (500 mL) was added. Both solutions were degassed for 30 minutes with argon. The toluene solution in the funnel was allowed to drip into the round bottom flask over a period of 72 h at room temperature, and then allowed to stir for an additional 24 h. The resulting solution was condensed under reduced pressure. The red oil was run through a plug of silica, which was washed with copious amounts of dichloromethane. After rotary evaporation, the translucent red oil was adhered to silica and purified by flash chromatography on silica wherein a gradient eluent system of 3:1 to 2:1 hexanes:dichloromethane was used. Condensation yielded compound **6** as a yellow oil (4.13 g, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 2.5 Hz, 2H), 6.89 (s, 2H), 6.52 – 6.44 (m, 2H), 4.14 – 3.93 (m, 6H), 3.81 (qd, J = 14.9, 2.0 Hz, 4H), 3.55 (dd, J = 14.8, 2.0 Hz, 2H), 1.88 – 1.73 (m, 4H), 1.59 – 1.43 (m, 5H), 1.43 – 1.25 (m, 17H), 0.90 (qt, J = 3.1, 1.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 136.0, 129.9, 129.2, 129.0, 126.4, 73.1, 38.4, 33.0, 32.0, 30.6, 29.7, 29.4, 26.3, 22.8, 14.3.

HRMS (ESI) *m/z* calculated for $C_{32}H_{48}O_2S_2$ $(M+Na)^+$ 551.2988, found 551.3013.

Compound 7

Compound **6** (7.81 g, 0.0148 mol) was dried in a Schlenk flask equipped with a stir bar and an addition funnel. 2-(trimethylsilyl)phenyl trifluoromethanesulfonate was sealed under argon (11.05 g, 0.0370 mol), dissolved in dry tetrahydrofuran (THF) (147 mL) and added to the flask. Tetra-n-butylammonium fluoride hydrate (TBAF•$3H_2O$) (16.31 g, 0.0624 mol) was dried and dissolved in dry THF (345 mL). It was transferred into the addition funnel and dispensed into the flask over 5 h. The solution was stirred for an additional hour, condensed, and purified via flash chromatography in 3:1 hexanes:dichloromethane to yield a thick yellow oil (mixture of diastereomers, 7.64 g, 76%).

HRMS (ESI) *m/z* calculated for $C_{44}H_{56}O_2S_2$ $(M+Na)^+$ 703.3614, found 703.3618.

Compound 8

Compound **7** (8.59 g, 0.013 mol) was dissolved in toluene (160 mL) in a 500 mL round-bottom flask equipped with a stir bar. After cooling to 0 °C, glacial acetic acid (80 mL) was added to the flask. Using a syringe pump, hydrogen peroxide (3.2 mL, 32 wt. %) was added over 40 min and then warmed to room temperature. After stirring for 16 h, the reaction mixture was diluted with dichloromethane (150 mL), deionized water (100 mL), and brine (50 mL), and the organic layer was separated and washed with brine (150 mL). The aqueous layer was extracted with dichloromethane (100 mL, x3) and the combined organic layers were washed with saturated sodium bicarbonate (100mL, x3), dried with magnesium sulfate, filtered, and condensed to afford a bright light green oil (mixture of diastereomers, 8.13 g, 90%).

HRMS (ESI) *m/z* calculated for $C_{44}H_{56}O_4S_2$ $(M+Na)^+$ 736.3545, found 736.3504.

Compound 9

Compound **8** (8.36 g, 0.012 mol) was dissolved in degassed, anhydrous xylenes (260 mL) and refluxed under argon for 16 h. The reaction was cooled to room temperature and condensed to afford a red oil, which was purified by flash chromatography with a gradient eluent system of 6:1 to 1:1 hexanes:dichloromethane. Compound **9** was a bright yellow oil (2.64 g, 49%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 10.1 Hz, 2H), 6.91 – 6.80 (m, 4H), 6.58 (d, *J* = 1.6 Hz, 2H), 6.05 (s, 2H), 4.06 (dt, *J* = 9.7, 6.8 Hz, 2H), 3.77 (dt, *J* = 9.7, 6.8 Hz, 2H), 1.79 – 1.62 (m, 4H), 1.47 – 1.21 (m, 22H), 0.95 – 0.81 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 138.5, 136.3, 133.9, 130.6, 130.4, 128.7, 127.2, 32.3, 30.6, 29.9, 29.8, 26.5, 23.1, 14.6.

HRMS (ESI) *m/z* calculated for $C_{32}H_{44}O_2$ $(M+Na)^+$ 461.3414, found 461.3423.

Compound 10

Compound **9** (0.55 g, 0.00119 mol) was placed in a stir-bar equipped Schlenk flask and dissolved in anhydrous dichloromethane (17 mL) under argon and cooled to -78 °C in an acetone-dry ice bath. Boron tribromide (10 mL, 1 M in CH_2Cl_2) was added over 34 min, warmed to room temperature, and stirred for 4 h. The reaction changed from bright yellow, to orange, and then to deep brown. Two drops of methanol and a copious amount of water was added slowly to quench the reaction at -78 °C. The compound was extracted with dichloromethane, condensed, and purified via flash chromatography in 3.5:1 hexanes:ethyl acetate, followed by recrystallization in toluene. Compound **10** was a white, fluffy, crystalline solid (0.162 g, 57%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 10.0 Hz, 2H), 6.89 (d, *J* = 1.8 Hz, 2H), 6.82 (d, *J* = 10.0 Hz, 2H), 6.56 (d, *J* = 1.6 Hz, 2H), 6.11 (s, 2H), 4.87 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.8, 137.9, 132.1, 131.2, 125.6, 124.7, 124.2.

HRMS (ESI) *m/z* calculated for $C_{16}H_{12}O_2$ $(M+K)^+[-H_2O]$ 257.036, found 257.039.

Compound 12

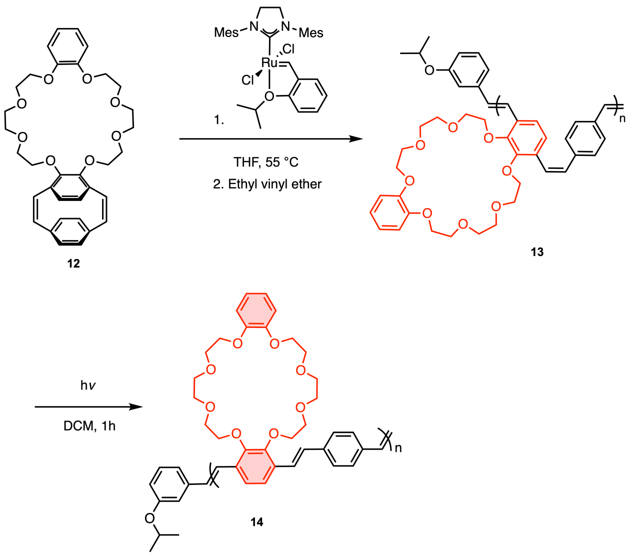
In a Schlenk flask equipped with a stir bar, cesium carbonate and tetrahydrofuran (THF) (10 mL) were added, sealed under argon, and heated to 45 °C. Compound **10** (0.44 g, mol) was placed in round bottom flask and dissolved in tetrahydrofuran (20 mL). The round-bottom was further rinsed out with THF (10 mL), which was added to the Schlenk flask and left stirring for 30 min. Compound **11** (1.2 g, mol) was dissolved in THF (49 mL) and added into the reaction mixture over 16 hours. Upon completion, the reaction was further stirred for 9 hours, cooled to room temperature, condensed into a black oil, diluted in dichloromethane (200 mL), washed with deionized water (100 mL, x5), extracted with dichloromethane (100 mL, x5), washed with brine (100 mL, x3), dried with magnesium sulfate, and condensed into a deep orange oil. Further purification was done by adhering the oil to silica and using flash chromatography in 1:3 hexanes:ethyl acetate to give compound **12** as a thick, orange oil (0.568 g, 53%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 10.1 Hz, 2H), 6.88 (d, *J* = 3.0 Hz, 4H), 6.85 (s, 2H), 6.83 (d, *J* = 1.9 Hz, 3H), 6.58 (d, *J* = 1.5 Hz, 2H), 6.04 (s, 2H), 4.32 – 4.23 (m, 2H), 4.12 (dd, *J* = 4.9, 3.9 Hz, 4H), 3.99 (ddd, *J* = 11.0, 6.8, 4.2 Hz, 2H), 3.87 (td, *J* = 4.0, 1.4 Hz, 4H), 3.84 – 3.64 (m, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 149.0, 138.0, 136.2, 133.3, 129.9, 129.8, 128.2, 126.9, 121.5, 114.3, 72.6, 71.1, 70.8, 70.4, 69.9, 69.4.

HRMS (ESI) *m/z* calculated for $C_{34}H_{38}O_8$ $(M+Na)^+$ 597.246, found 597.247.

Ring Opening Metathesis Polymerization (ROMP)



Scheme S2: ROMP of monomer **12.**

In-situ ^{1}H NMR experiment

Monomer **12** (20 mg, 3.48 x 10^{-5} mol) and Hoveyda-Grubbs 2nd generation initiator (HGII) (2.18 mg, 3.48 x 10^{-6} mol) were individually weighted out into 1-dram vials and brought into a nitrogen filled glovebox. Monomer **12** and HGII were separately dissolved in THF-d_8 totaling 0.70 mL ([12] = 0.05 M) and transferred into a *J* Young tube that was sealed. The sample was removed from the glovebox, wrapped in aluminum foil, and placed in an ice bath. The sample was then inserted into a 600 MHz NMR spectrometer set to 25 ˚C from t=0. The spectrometer was then heated to 48 ˚C and ^{1}H NMR spectra were recorded every 20 minutes until the ROMP was complete.

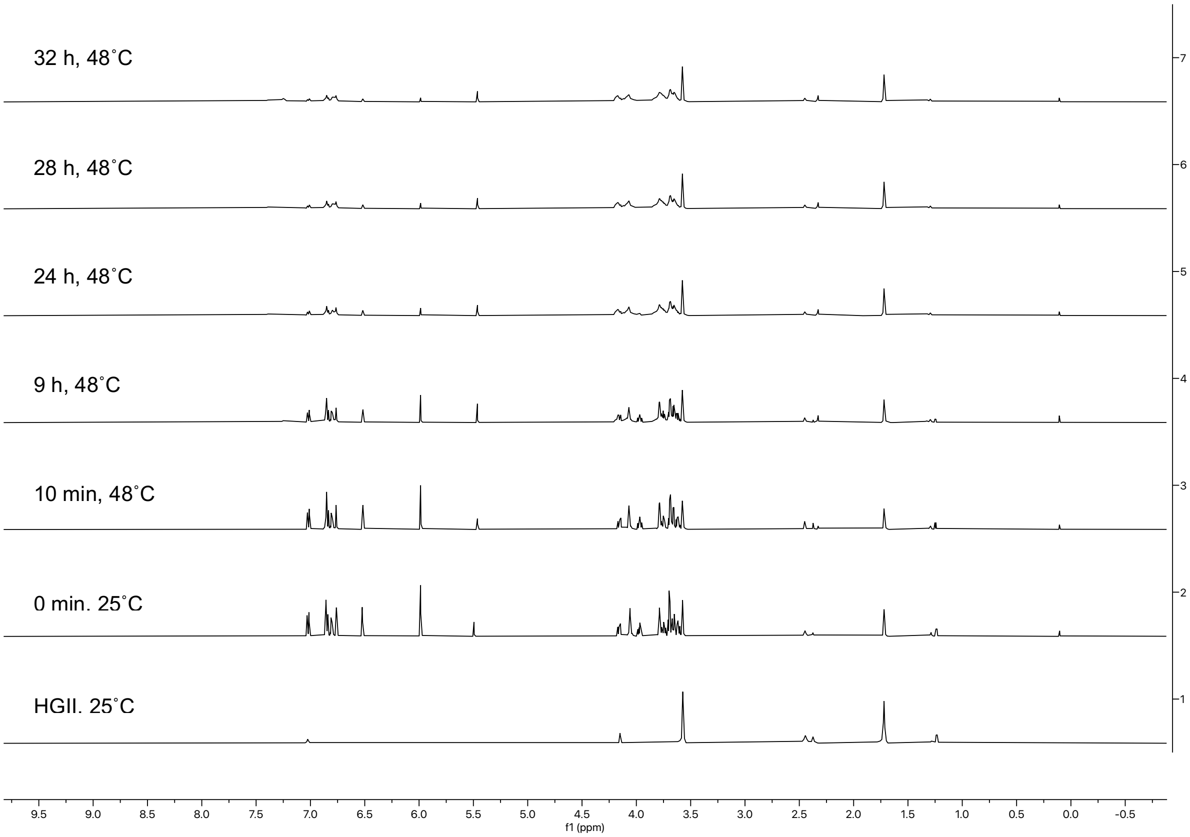


Figure S1: *in-situ* ^{1}H NMR experiment of the ROMP of monomer **12**.

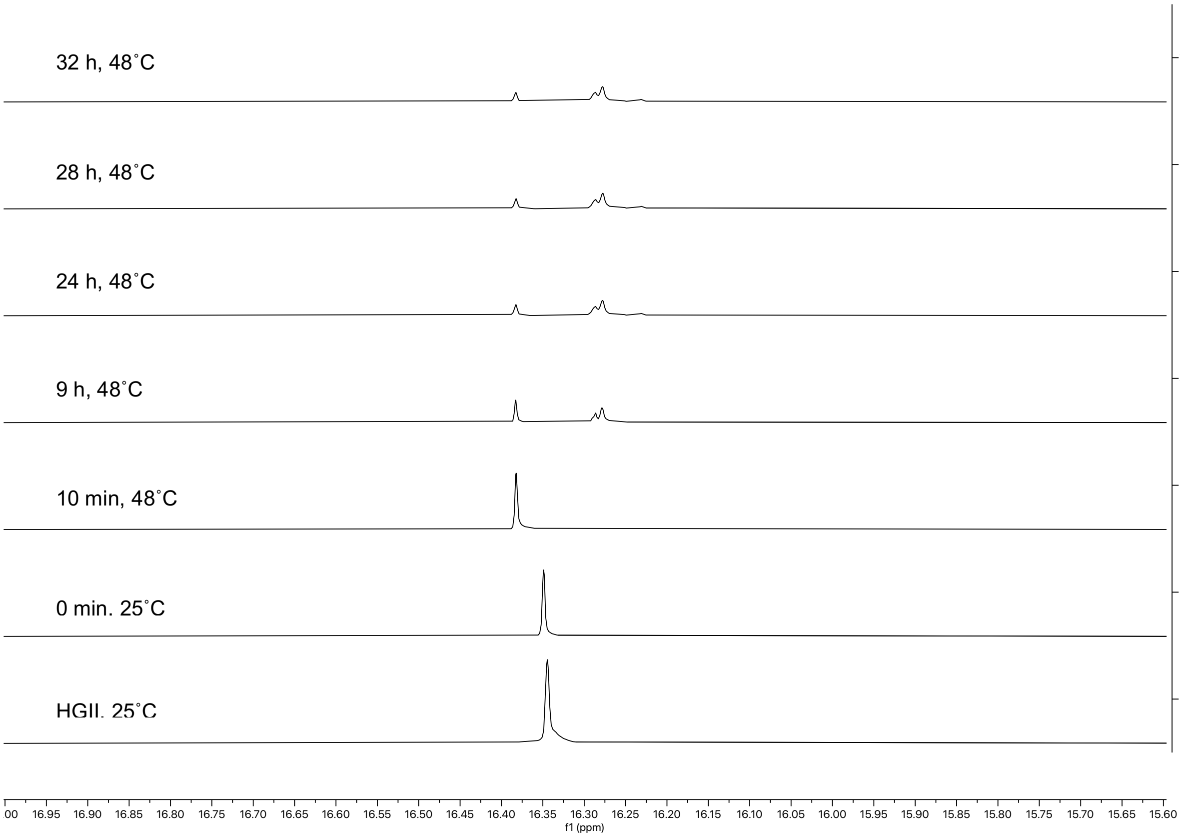


Figure S2: *in-situ* ^{1}H NMR experiment (carbene region) of the ROMP of monomer **12**.

ROMP of 12 with HGII, Polymers 13a-d

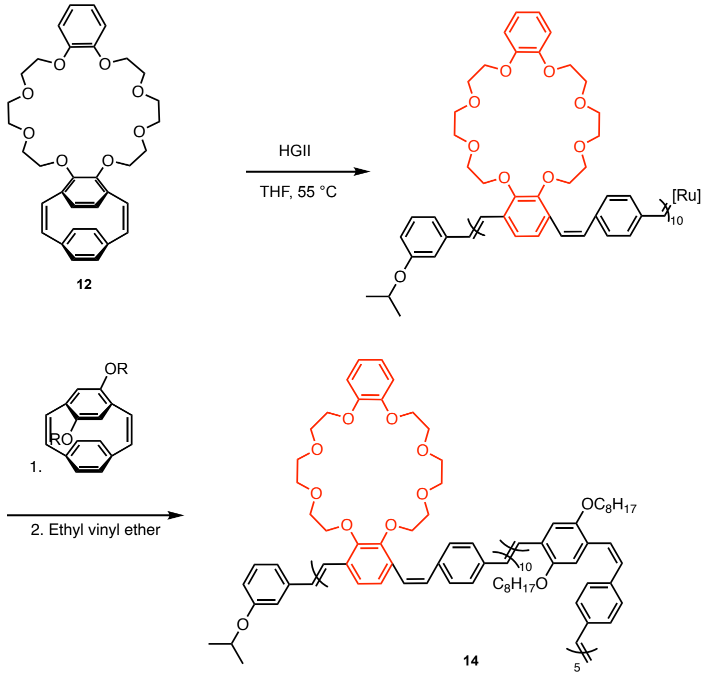
General polymerization procedure: In a nitrogen filled glovebox a stock solution of HGII initiator (10 mol. %) was prepared in anhydrous, degassed THF. Monomer **12** (20 mg, 3.48 x 10^{-5} mol) was weighted out into a 1-dram vial and brought into the glovebox, dissolved in anhydrous, degassed THF and transferred to an oven dried Schlenk tube equipped with a stir bar. An appropriate amount of the catalyst solution for **6** (0.05 M) and the desired equivalence of monomer-to-catalyst (5, 10, 15, 30, or 50). The Schlenk tube was sealed and removed from the glove box where it was subsequently wrapped in aluminum foil and placed in an oil bath at 55 ˚C and stirred until complete monomer conversion (3.5 hours/ monomer based of the *in-situ* NMR experiment). The reaction was cooled to room temperature and a large excess of deoxygenated ethyl vinyl ether (0.1 mL) was added and allowed to stir at room temperature for 4 hours. The reaction was opened to air and precipitated into cold methanol. It was centrifuged for 20 minutes at 3000 rpm, decanted, reprecipitated, and centrifuged and decanted again. A short methanol/Celite column was run washing with methanol followed by extraction of the polymer with dichloromethane. The dichloromethane layer was evaporated under reduced pressure in the dark to give the crown ether-substituted poly(*p*-phenylene vinylene)s (CE-PPV) as yellow-green films.

Photoisomerization, Polymer 14

The polymers were dissolved in dichloromethane (10 mg/ mL), covered with a cardboard box, exposed to UV light at 365 nm for 2 hours, and evaporated under reduced pressure to give the all-*trans* isomer with a quantitative yield. After photo-isomerization, polymer **14** was visibly darker as an ocher-yellow film.

Diblock Extension, Polymer 15

In a nitrogen filled glovebox a stock solution of HGII initiator (10 mol. %) was prepared in anhydrous, degassed THF. Monomer **12** (20 mg, 3.48 x 10^{-5} mol) was weighted out into a 1-dram vial and brought into the glovebox, dissolved in anhydrous, degassed THF and transferred to an oven dried Schlenk tube equipped with a stir bar. An appropriate amount of the catalyst solution for **12** (0.05 M) and the desired equivalence of monomer-to-catalyst (10:1). The Schlenk tube was sealed and removed from the glove box where it was subsequently wrapped in aluminum foil and placed in an oil bath at 55 ˚C and stirred until complete monomer conversion (3.5 hours/ monomer based of the *in-situ* NMR experiment). The reaction was cooled to room temperature and brought back into the glove box, where *para*-dioctyloxy-[2.2]paracyclophane-1,9-diene (5 equivalents) in degassed THF was added to the Schlenk tube and sealed.[3] The tube was removed from the glove box and placed back in the oil bath at 55 ˚C while wrapped in aluminum foil. Upon stirring for 24 hours, a large excess of deoxygenated ethyl vinyl ether (0.1 mL) was added and allowed to stir at room temperature for 4 hours. The reaction was opened to air and precipitated into cold methanol. It was centrifuged for 20 minutes at 3000 rpm, decanted, reprecipitated, and centrifuged and decanted again. A short methanol/Celite column was run washing with methanol followed by extraction of the polymer with dichloromethane. The dichloromethane layer was evaporated under reduced pressure in the dark to give the diblock PPV **15** as an orange film.



Scheme S3: Dibolock extension to form copolymer **14**.

MALDI-ToF-MS

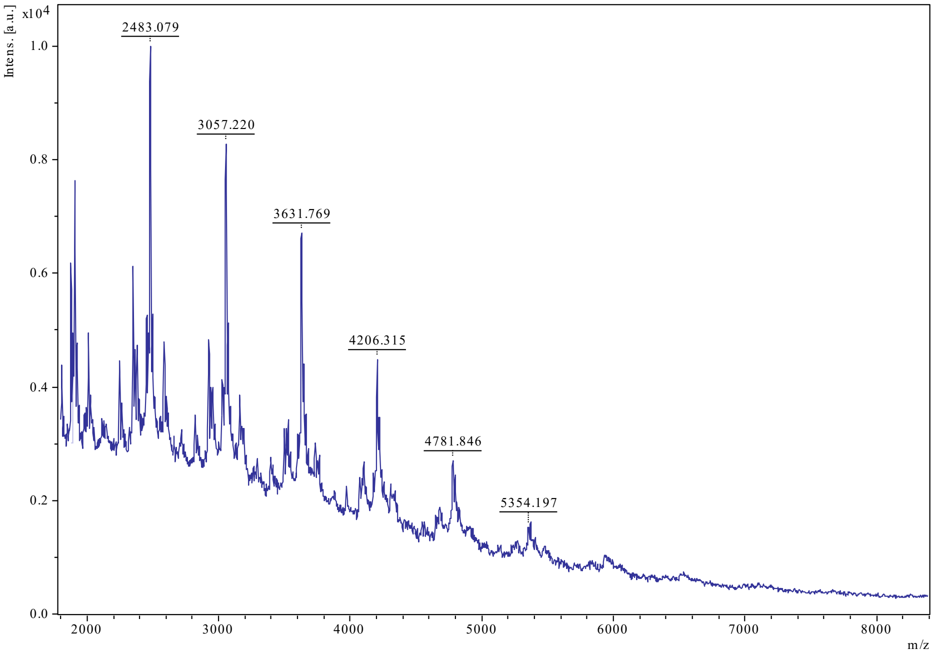


Figure S3: MALDI-TOF mass spectrum of **13b** in dithranol.

The MALDI-ToF-MS sample of **13b** was prepared in dithranol. The major peaks are separated by an interval of 575 Da, which corresponds to the molecular weight of monomer **12**, CE-*p*Cpd. This series of peaks suggests that the polymers are terminated with vinyl and isopropoxy-phenyl end-groups as expected.

Optical Data

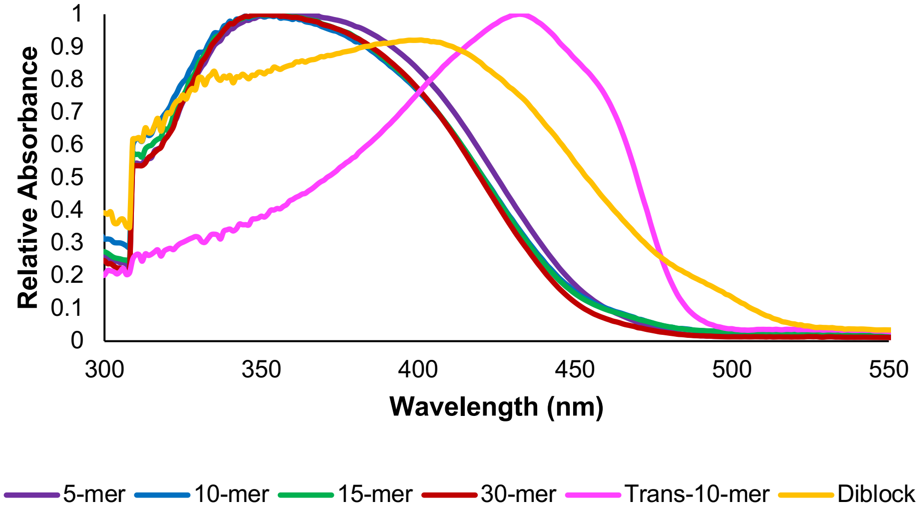


Figure S4: Absorbance of CE-PPV. Polymers **13a-d** (purple, blue, green, maroon), **14** (pink), and **15** (yellow).

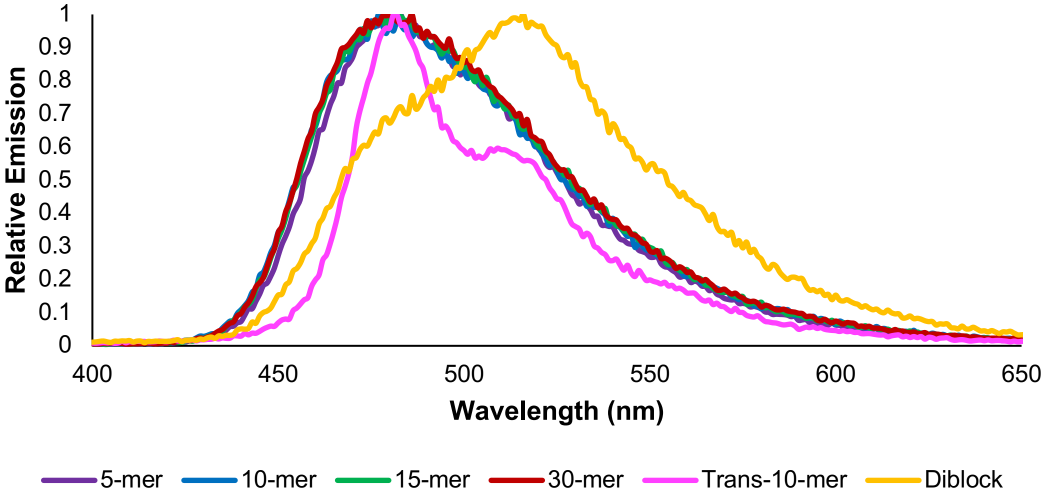
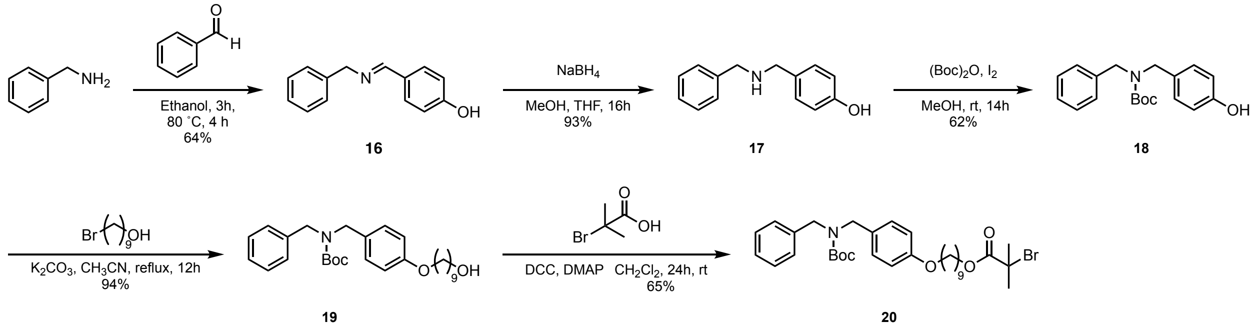


Figure S5: Emission of CE-PPV. Polymers **13a-d** (purple, blue, green, maroon), **14** (pink), and **15** (yellow).

Dibenzylamine Functionalized Initiator Synthesis



Scheme S4: Synthesis of functionalized atom-transfer radical polymerization initiator **20**.

Compounds **16**, **17**, and **18** were synthesized according to published procedures.[4, 5]

Compound 19

Compound **18** (1.46 g, 0.0047 mol) and 9-bromo-nonan-1-ol (1.16 g, 0.0053 mol) were dissolved in acetonitrile (60 mL) in a round-bottom flask equipped with a stir bar. Potassium carbonate (1.31 g, 0.0096 mol) was added, and the reaction was refluxed at 82 °C for 12 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure. Water (50 mL) was added, and the product was extracted with dichloromethane (30mL, x3). The organic layer was washed with water (30 mL, x1), followed by brine (30 mL, x1), dried with magnesium sulfate, filtered, and condensed. Without further purification, compound **19** was a light brown oil (2.00 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 3H), 7.25 – 7.10 (m, 4H), 6.86 – 6.82 (m, 1H), 4.42 – 4.21 (m, 4H), 3.95 (t, *J* = 6.5 Hz, 1H), 3.65 (t, *J* = 6.6 Hz, 2H), 3.41 (td, *J* = 6.9, 0.9 Hz, 1H), 1.82 (dp, *J* = 31.2, 6.8 Hz, 2H), 1.64 – 1.42 (m, 17H), 1.40 – 1.18 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 155.8, 128.3, 126.9, 115.1, 114.3, 79.8, 67.8, 62.9, 62.9, 33.9, 32.6, 32.7, 32.6, 29.3, 29.2, 28.3, 25.9, 25.6, 25.5.

HRMS (ESI) *m/z* calculated for $C_{19}H_{23}NO_3$ $(M+Na)^+$ 478.295, found 478.293.

Compound 20

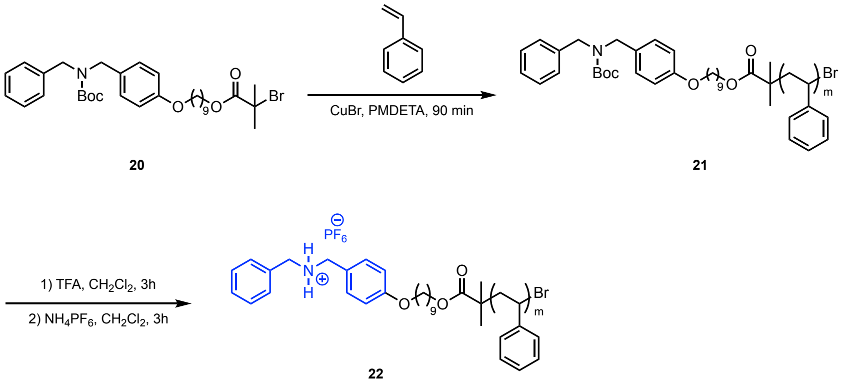
In a round-bottomed flask equipped with a stir bar, compound **19** (2.00 g, 0.0044 mol) was dissolved in dichloromethane (10 mL) and cooled to 0 °C. 2-bromo-2-methylpropanoic acid (1.56 g, 0.0093 mol) was added to the flask. Dicyclohexylcarbo-diimide (DCC) (1.87 g, 0.0090 mol) was dissolved in dichloromethane (40 mL) and added slowly. 4-dimethylaminopyridine (DMAP) (0.25 g, 0.0021 mol) was dissolved in dichloromethane (3 mL) and added at a rate of 1 mL/ min. The reaction was stirred for 1 hour, warmed to room temperature, and continued to stir for 36 hours. It was then filtered through cotton with dichloromethane twice. The filtrate was washed with a 5% solution of sodium bicarbonate (10 mL, x4) and dried with magnesium sulfate, filtered, and condensed. The crude compound was purified with flash chromatography in 9:1 hexanes:ethyl acetate to give compound **10** as a colorless oil (1.73 g, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.25 – 7.17 (m, 3H), 7.12 – 7.05 (m, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 4.36 (d, *J* = 24.7 Hz, 4H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 1H), 2.07 (s, 2H), 1.93 (s, 4H), 1.82 – 1.65 (m, 3H), 1.49 (s, 13H), 1.35 (s, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 156.0, 129.9, 128.6, 128.5, 127.2, 121.1, 114.5, 80.3, 80.0, 68.1, 66.2, 56.1, 55.4, 30.9, 30.7, 29.5, 29.3, 29.2, 28.5, 28.5, 28.4, 27.8, 26.1, 25.8.

HRMS (ESI) *m/z* calculated for $C_{19}H_{23}NO_3$ $(M+Na)^+$ 628.244, found 628.241.

Atom-Transfer Radical Polymerization (ATRP)



Scheme S5: Synthesis of PS-DBA$^+$, **22**.

Polymer 21

Inhibitors were removed from styrene by running it through an alumina plug. Compound **20** (0.21g, 3.4 x 10^{-4} mol) was added to an argon purged Schlenk flask. Under argon, styrene (7.70 mL, 0.0664 mol) and pentamethyldiethylenetriamine (PMDETA) were added to the flask and freeze-pump-thawed three times. Copper bromide (0.05g, 3.4 x 10^{-4} mol) was added and an aliquot of the reaction mixture was taken out for GPC and NMR spectroscopy measurements at 0 min. Another round of freeze-pump-thawing later, the reaction was placed into a pre-heated oil bath at 90 ˚C. Aliquots were taken every 30 min to monitor the livingness of the polymerization. The polymerization was quenched by opening to air at 4 hours and 10 minutes, reaching <50% conversion. The crude mixture was diluted with THF and passed through a short alumina column. The mixture was condensed under reduced pressure and precipitated out in cold methanol. The product was filtered and dried under vacuum to afford a white powder of polymer **21** (68%, M_n = 4520 Da, Đ = 1.03).

Polymer 22

Compound **21** (0.49 g, 1.11 x 10^{-4} mol) was dissolved in dichloromethane (4 mL, 0.3 M). Trifluoracetic acid (1 mL) was added slowly at 0 ˚C and warmed to room temperature. The reaction was stirred for 3 hours. Ammonium hexafluorophosphate (0.30 g, 0.002 mol) was dissolved in dichloromethane (10 mL, 0.2 M), added to the reaction, and stirred for 3 hours. The crude product was further diluted in dichloromethane (50 mL), washed with water (25 mL, x3), dried with magnesium sulfate, and condensed to give polymer **22** as a fine white solid (0.42 g, 85%).

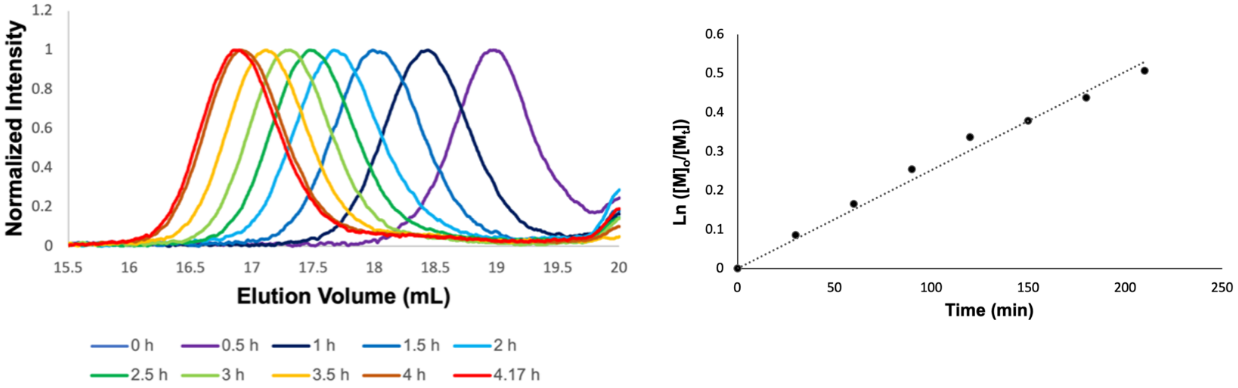


Figure S6: Increasing molecular weight of PS as ATRP progresses (GPC in THF) (left) and semi-logarithmic kinetic plot of ATRP (right). The increase in molecular weight is determined through GPC against poly(styrene) standards in THF under a UV-Vis detector. The M_n from GPC is correlated with conversion from NMR spectroscopy. The initial concentration of styrene is 8.64 M as a neat solution. The changes in concentration were determined through NMR spectroscopy. The percent conversion of monomer with respect to time was determined through NMR spectroscopy.

Assembly Studies

DB24C8 + PS-DBA$^+$

Stock solutions of polymer **22** and commercial dibenzo-24-crown-8 (DB24C8) were prepared in deuterated chloroform and mixed in a 1:1 molar equivalent solution to form host-guest complex DB24C8-PS-DBA$^+$.

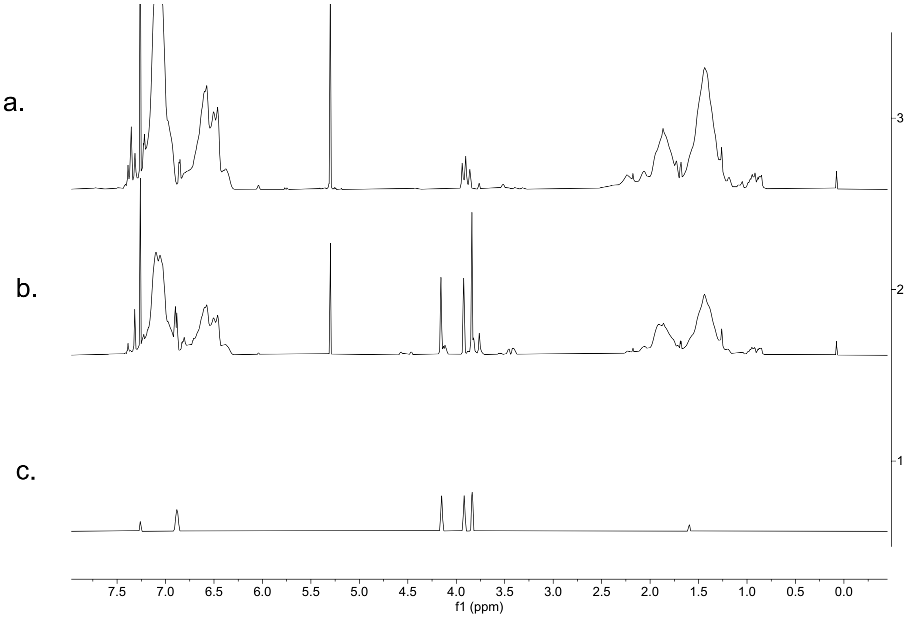


Figure S7: Host-guest complex DB24C8-PS-DBA$^+$. S7a is PS-DBA$^+$, S7b is DB24C8-PS-DBA$^+$, and S7c is DB24C8.

CE-*p*Cpd with DBA$^+$

Commercially available dibenzyl amine was acidified and stabilized with a counterion. Stock solutions of monomer **12** and DBA$^+$ were prepared in deuterated chloroform and mixed in a 1:1 molar equivalent solution to form host-guest complex CE-*p*Cpd with DBA$^+$.

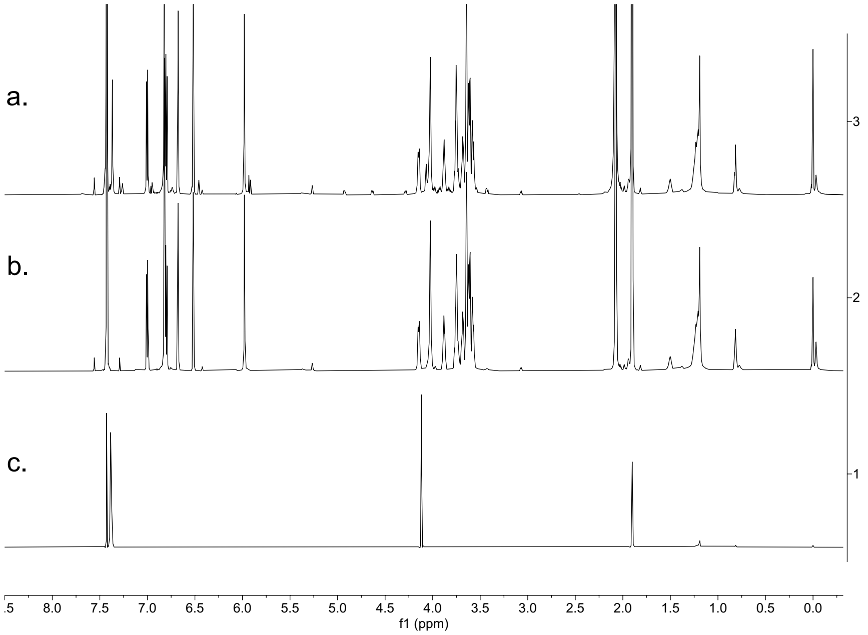


Figure S8: a) Host-Guest complex CE-*p*Cpd-DBA$^+$, b) CE-*p*Cpd, and c) DBA$^+$ spectral overlay.

Dethreading the Pseudorotaxane

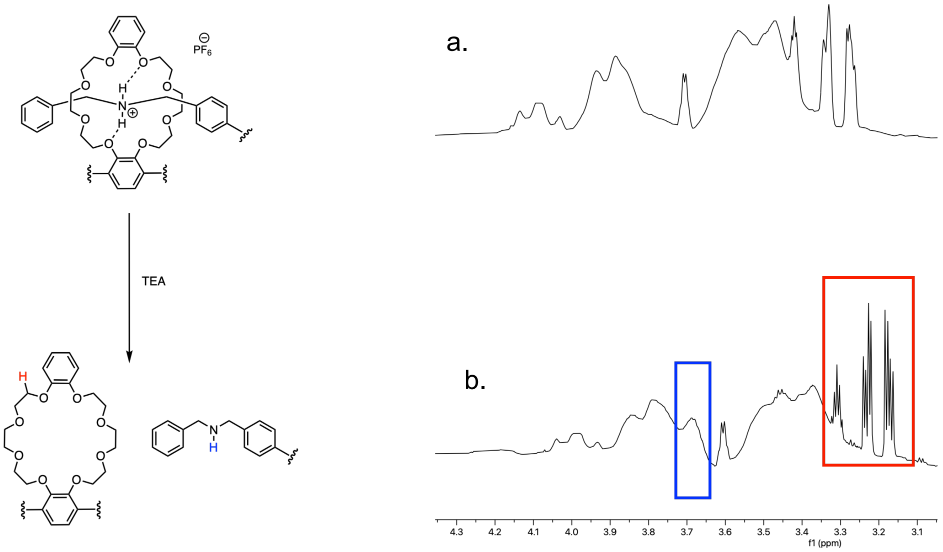


Figure S9: a) Self-assembled CE-PPV-PS-DBA$^+$ bottlebrush. b) Dethreaded rotaxane when treated with triethylamine (TEA).

Isothermal Calorimetry (ITC)

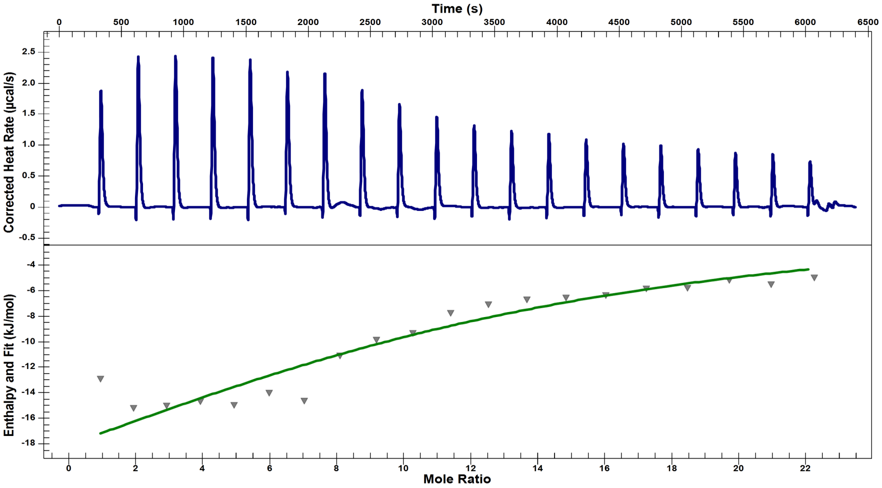
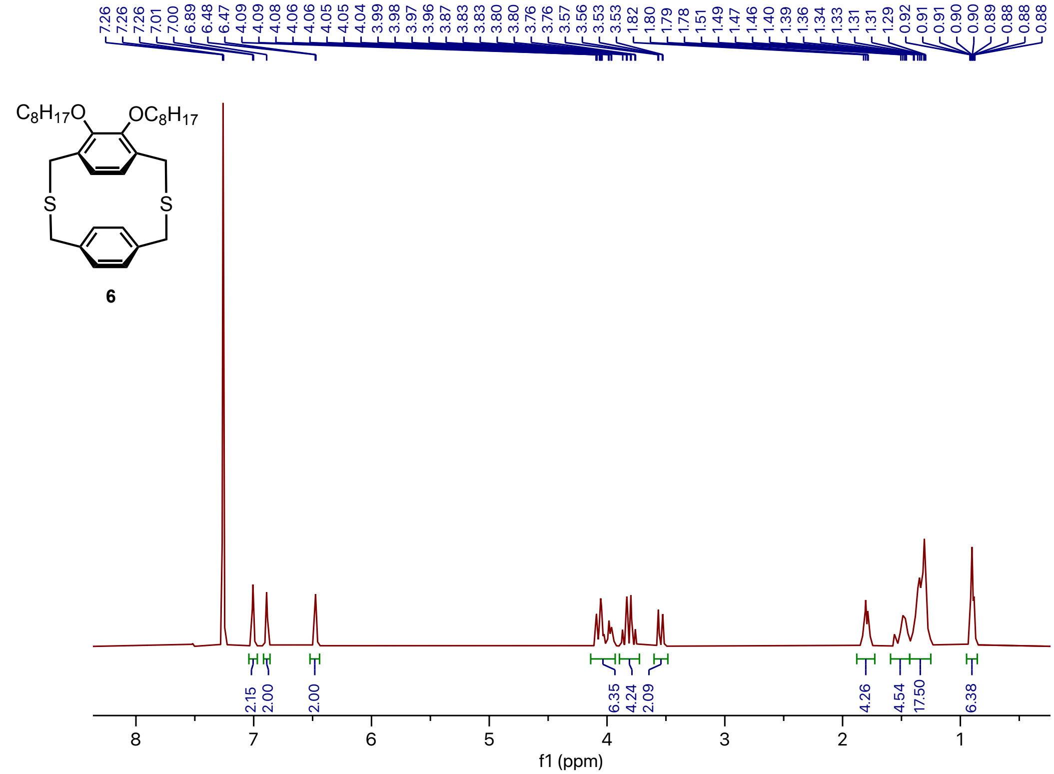
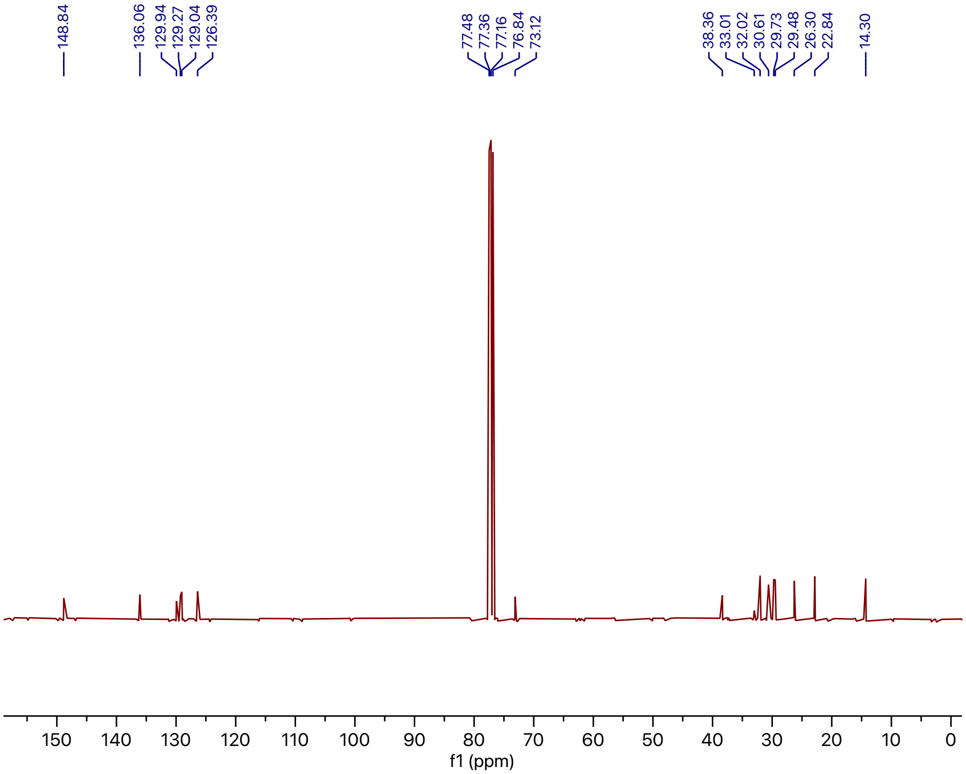


Figure S10: Representative ITC binding isotherm and plot of the normalized fit for the titration of PS-DBA$^+$ with CE-PPV to form bottlebrush copolymers.

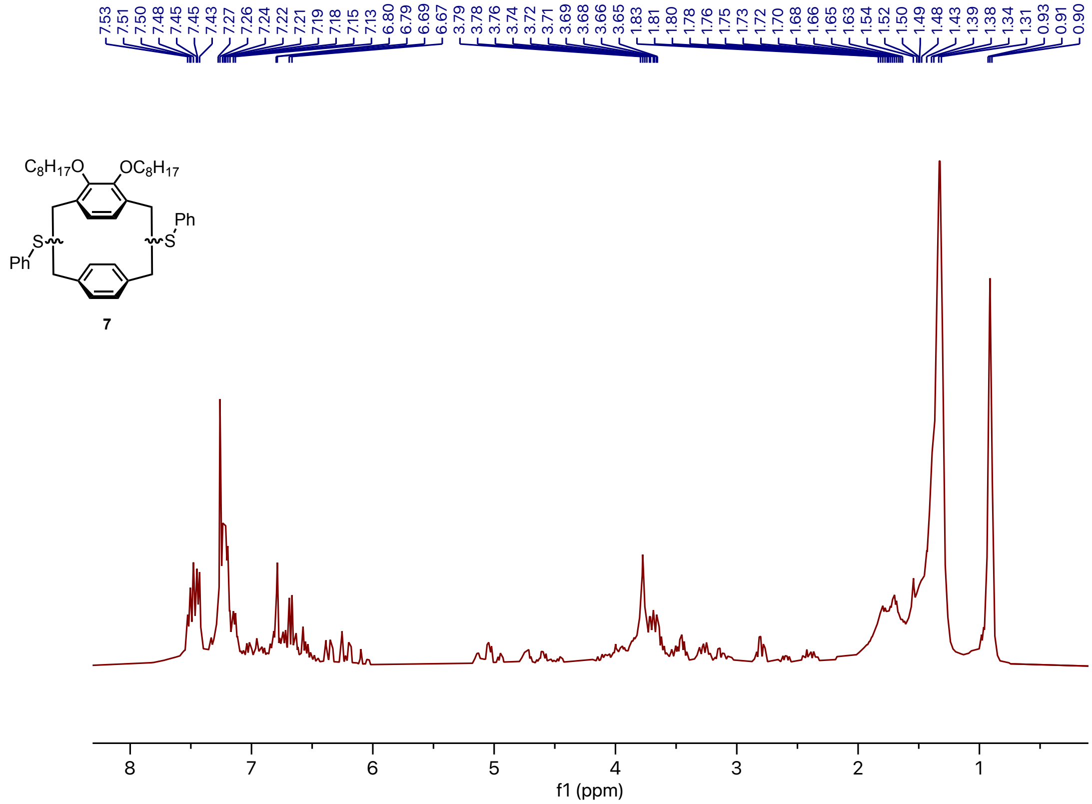
NMR Spectra

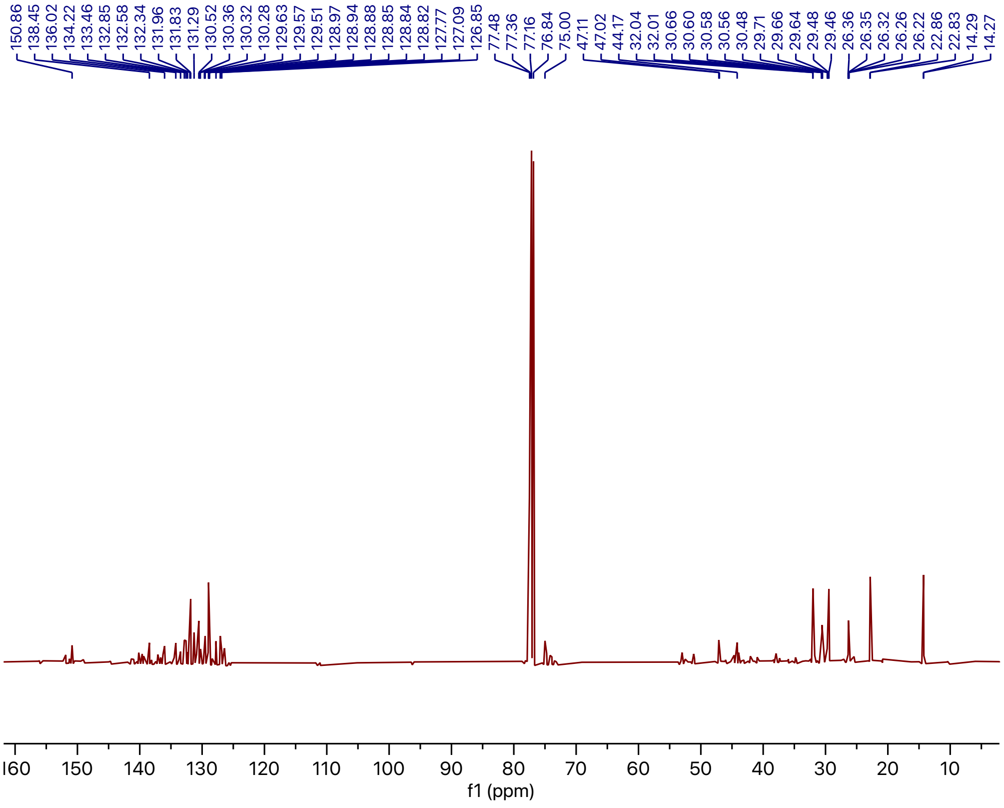
Compound 6: ^{1}H NMR and ^{13}C NMR spectra.



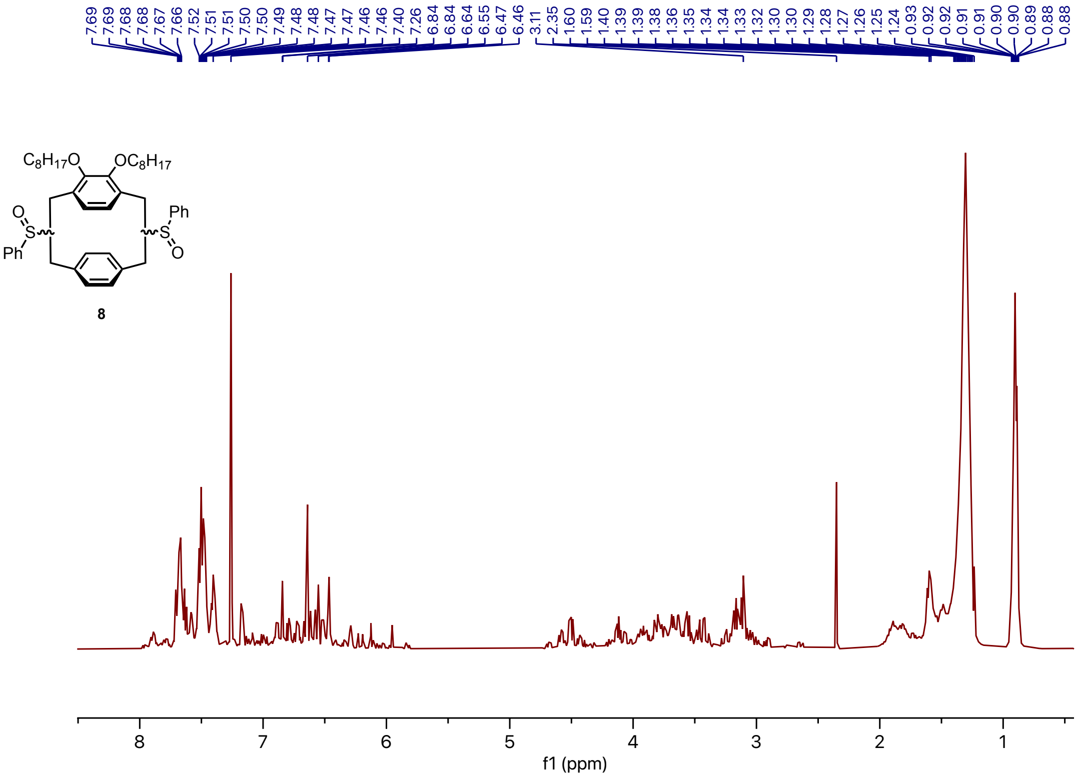


Compound 7: ^{1}H NMR and ^{13}C NMR spectra.

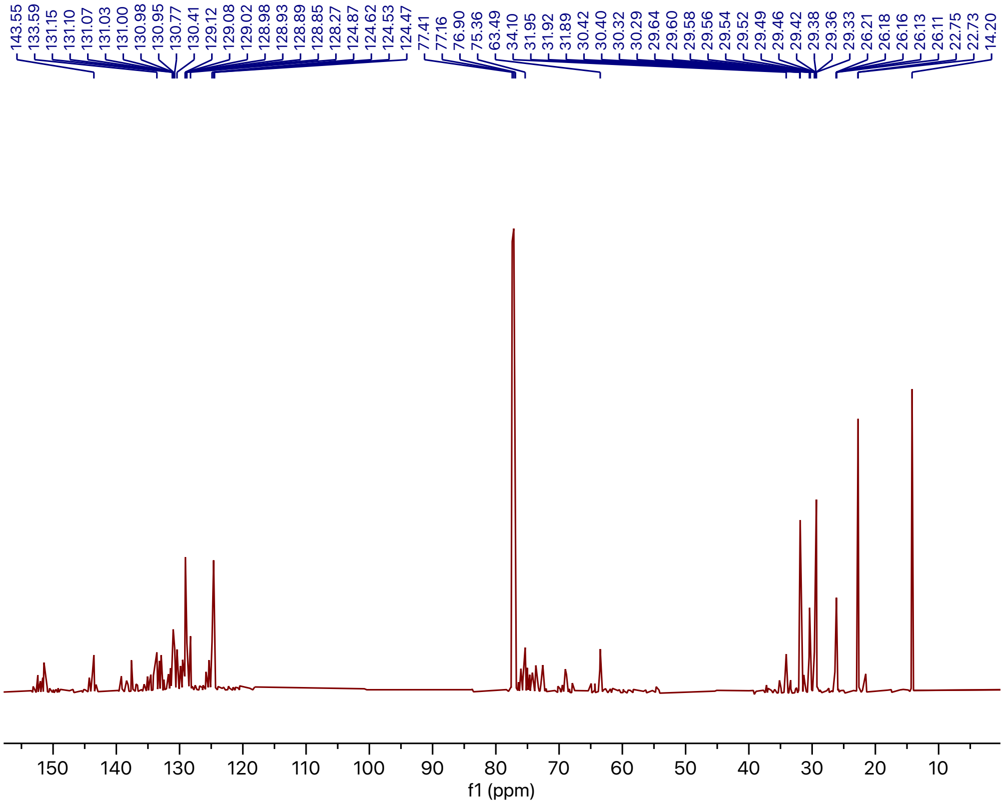




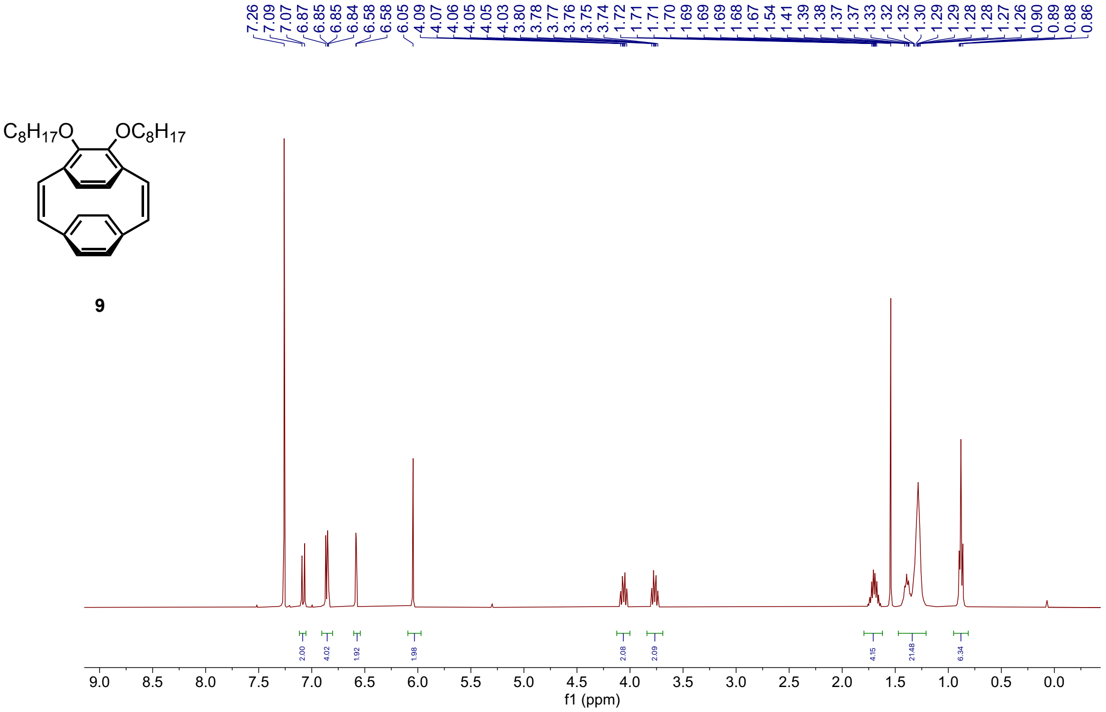
Compound 8: ^{1}H NMR and ^{13}C NMR spectra.



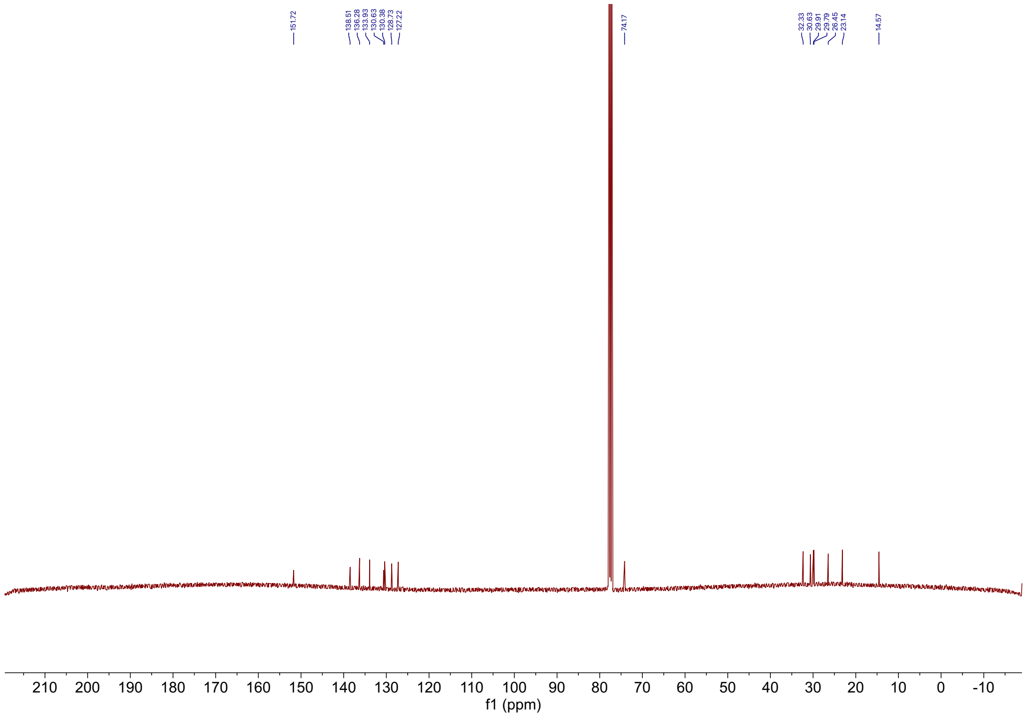
8



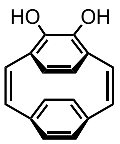
Compound 9: ^{1}H NMR and ^{13}C NMR spectra.



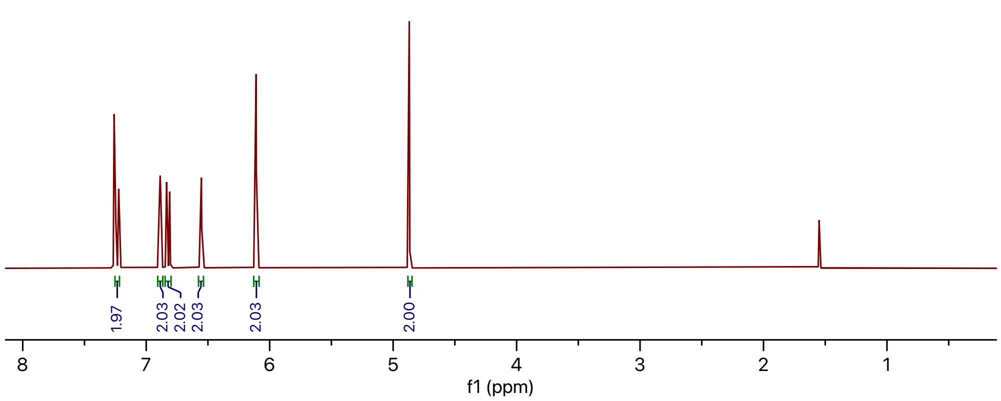
9

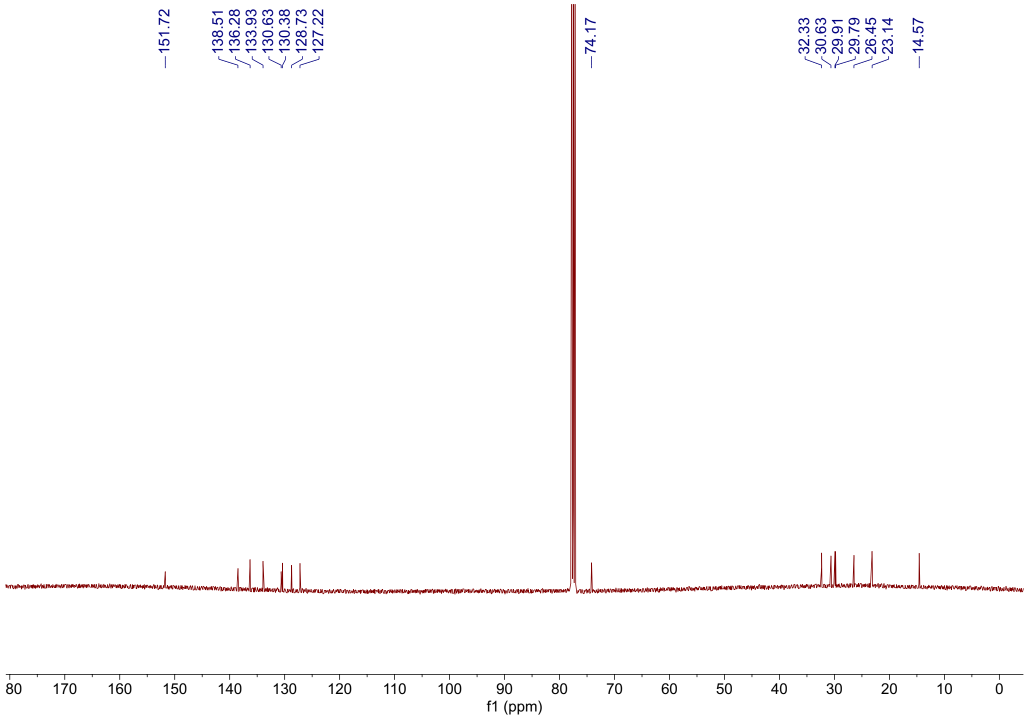


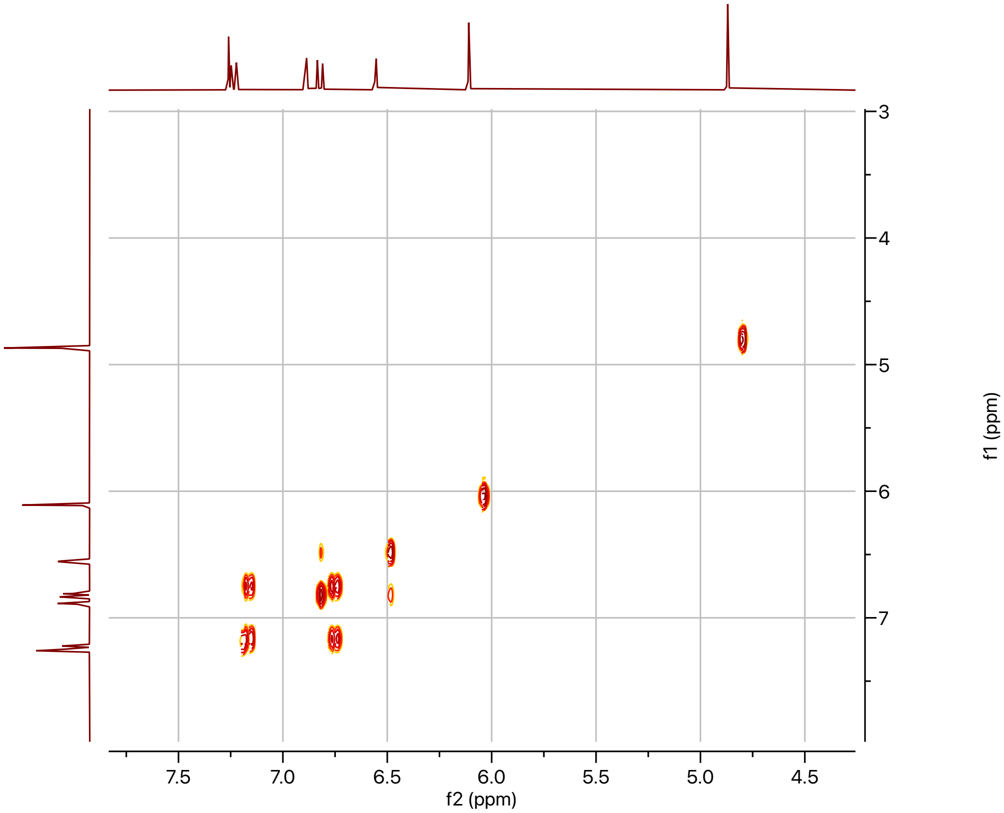
Compound 10: ^{1}H, ^{13}C, COSY, HSQC, and HMBC spectra.



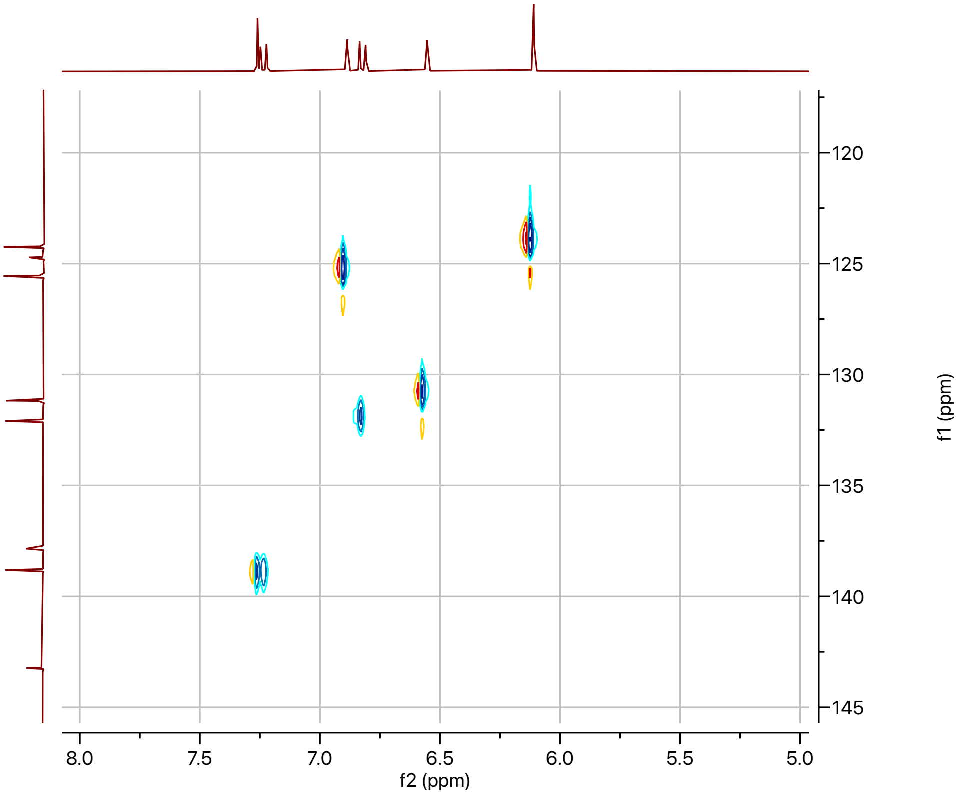
10



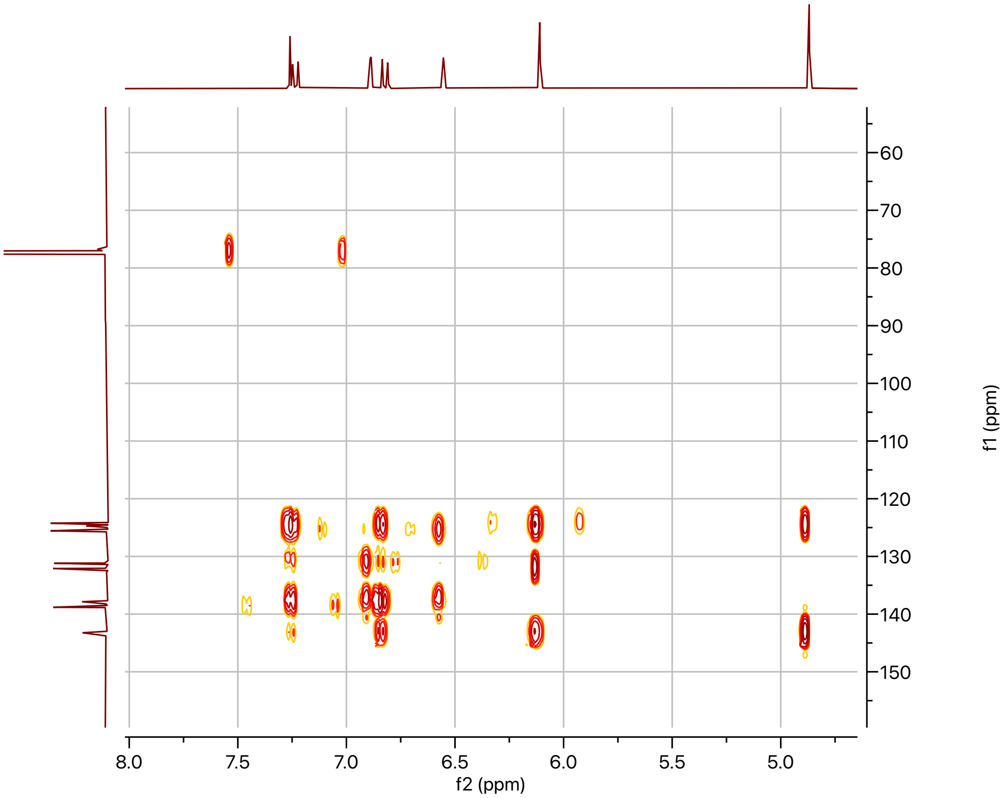




3
4
5
6
7
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f2 (ppm)

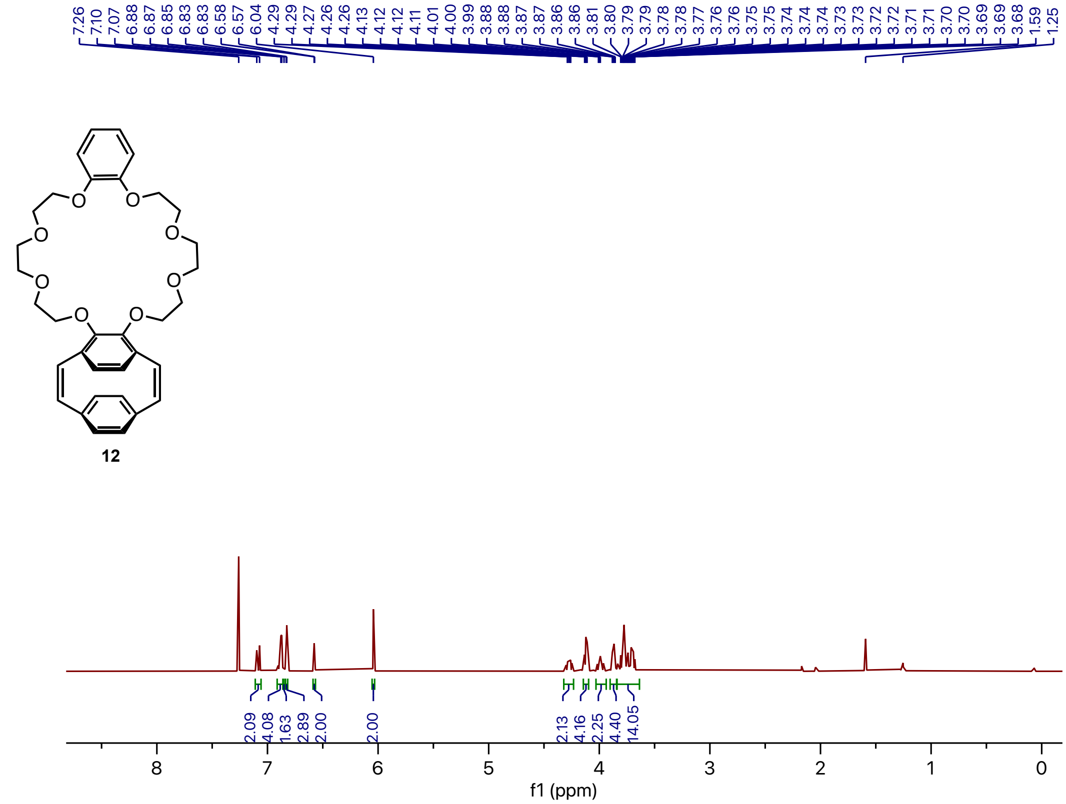


120
125
130
135
140
145
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f2 (ppm)

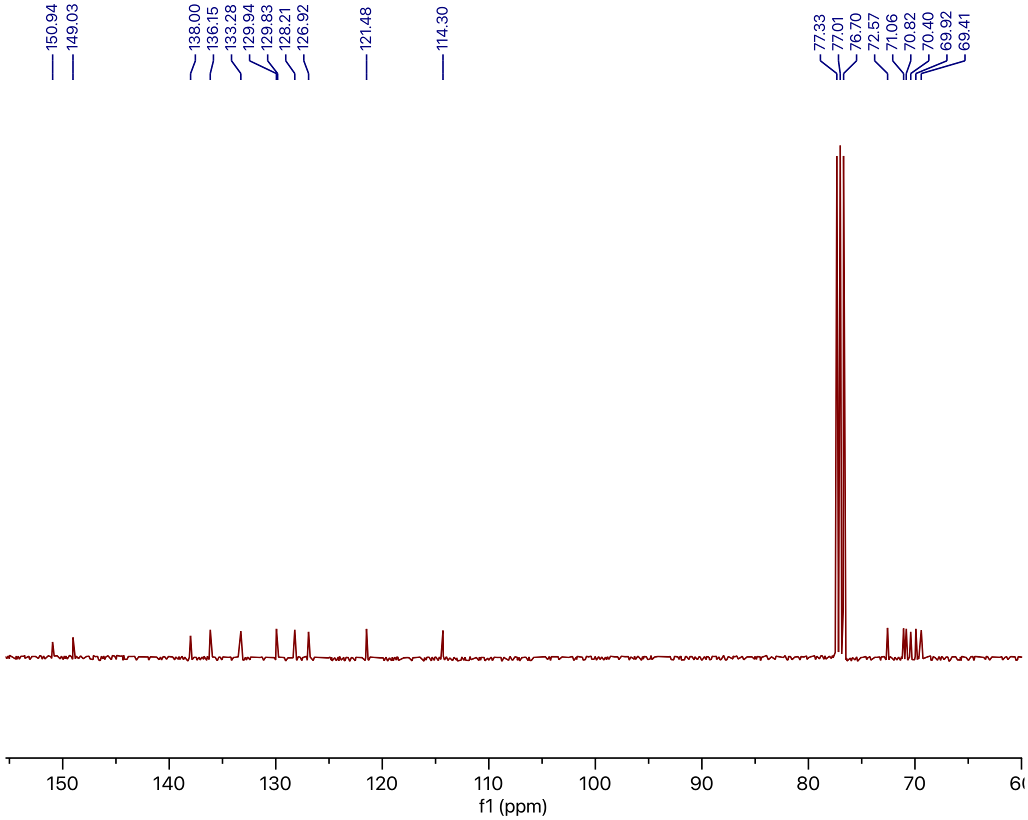


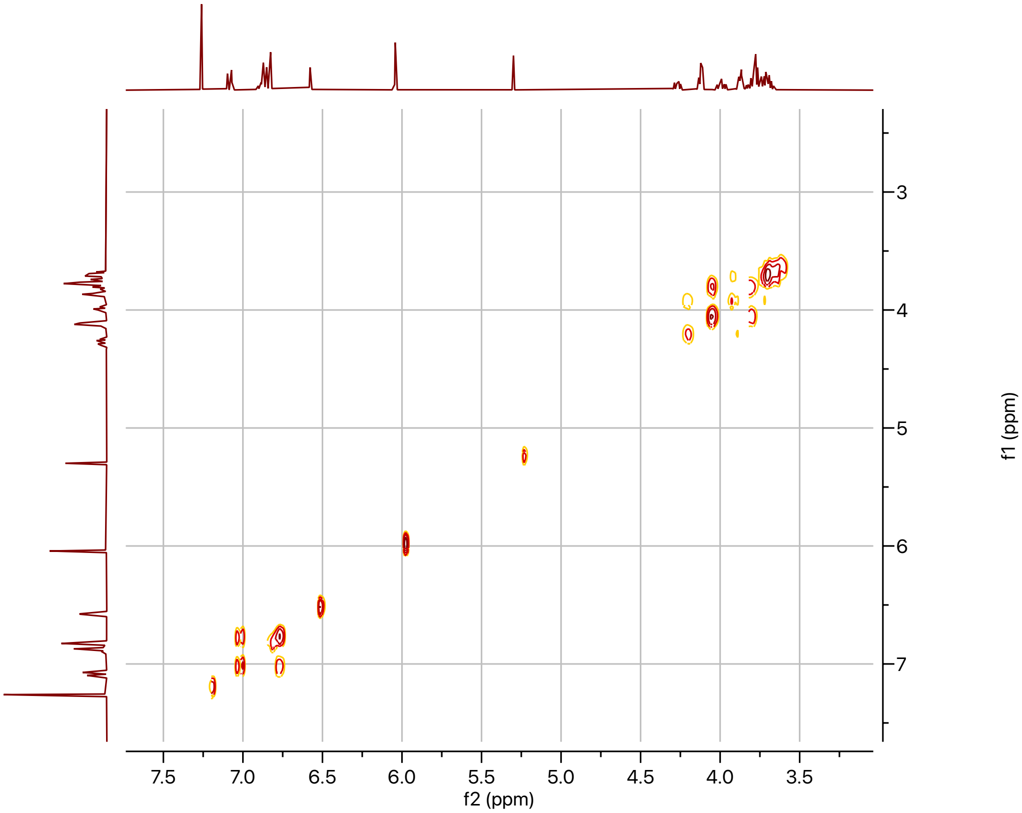
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f2 (ppm)

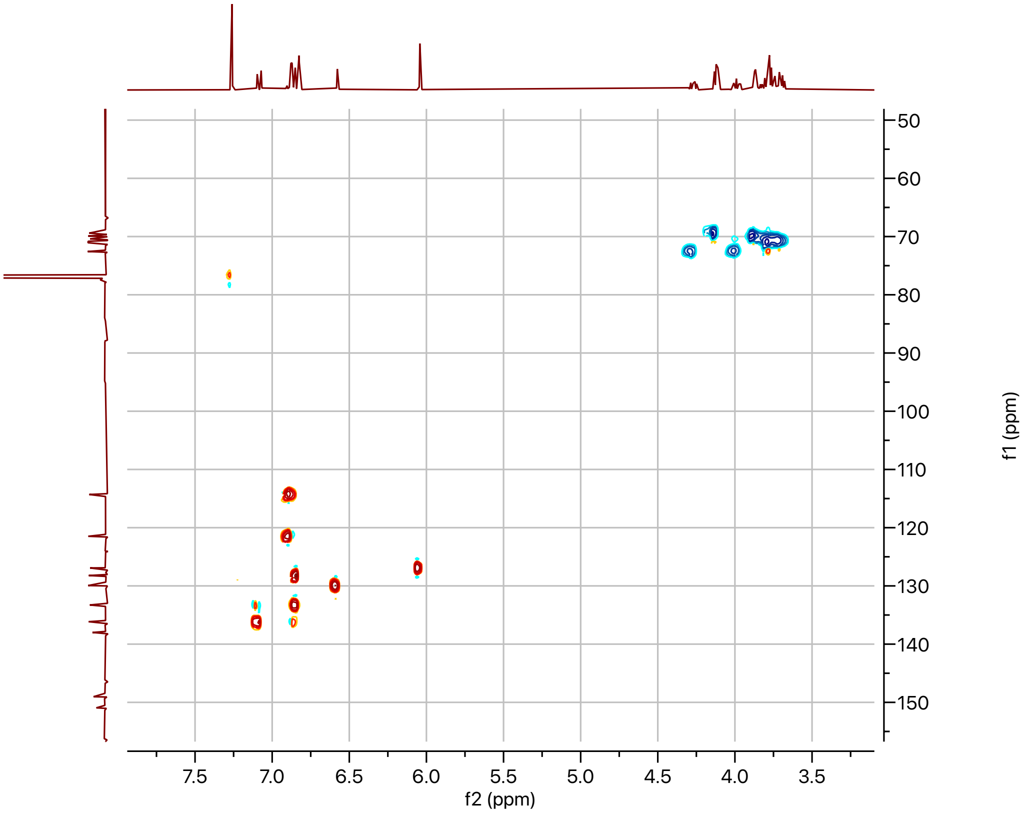
Compound 12: ^{1}H, ^{13}C, COSY, HSQC, and HMBC spectra.

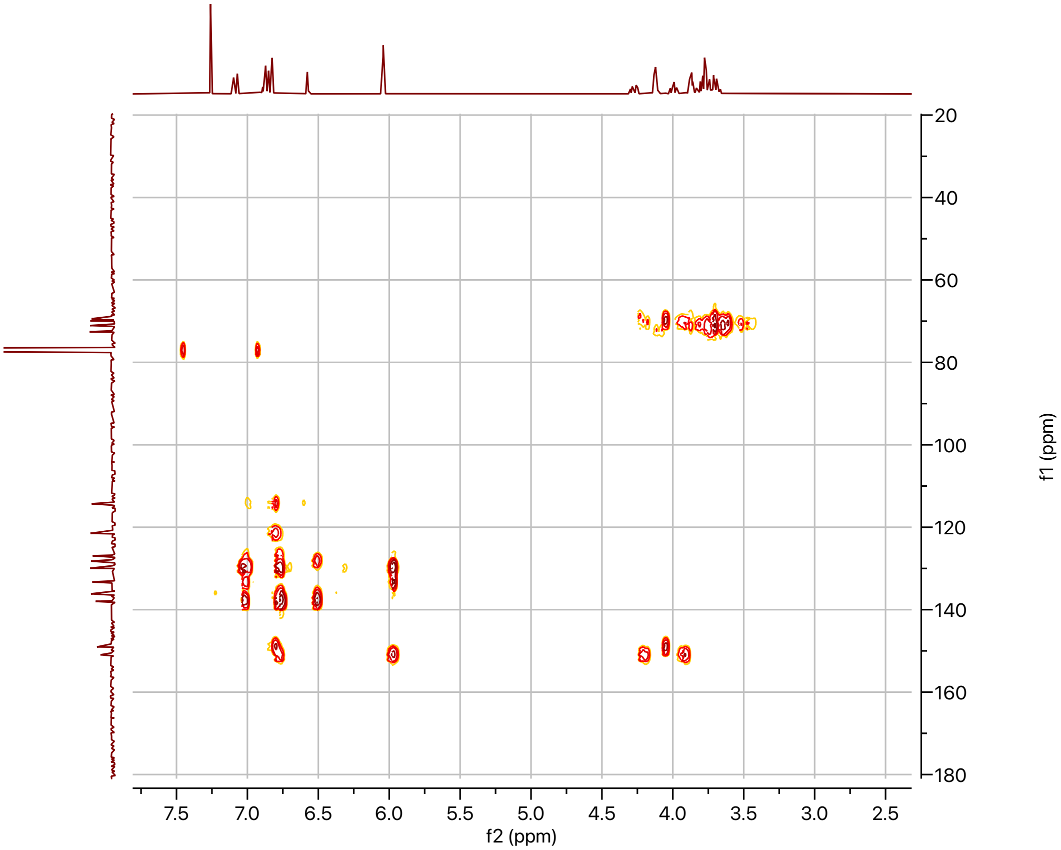


12

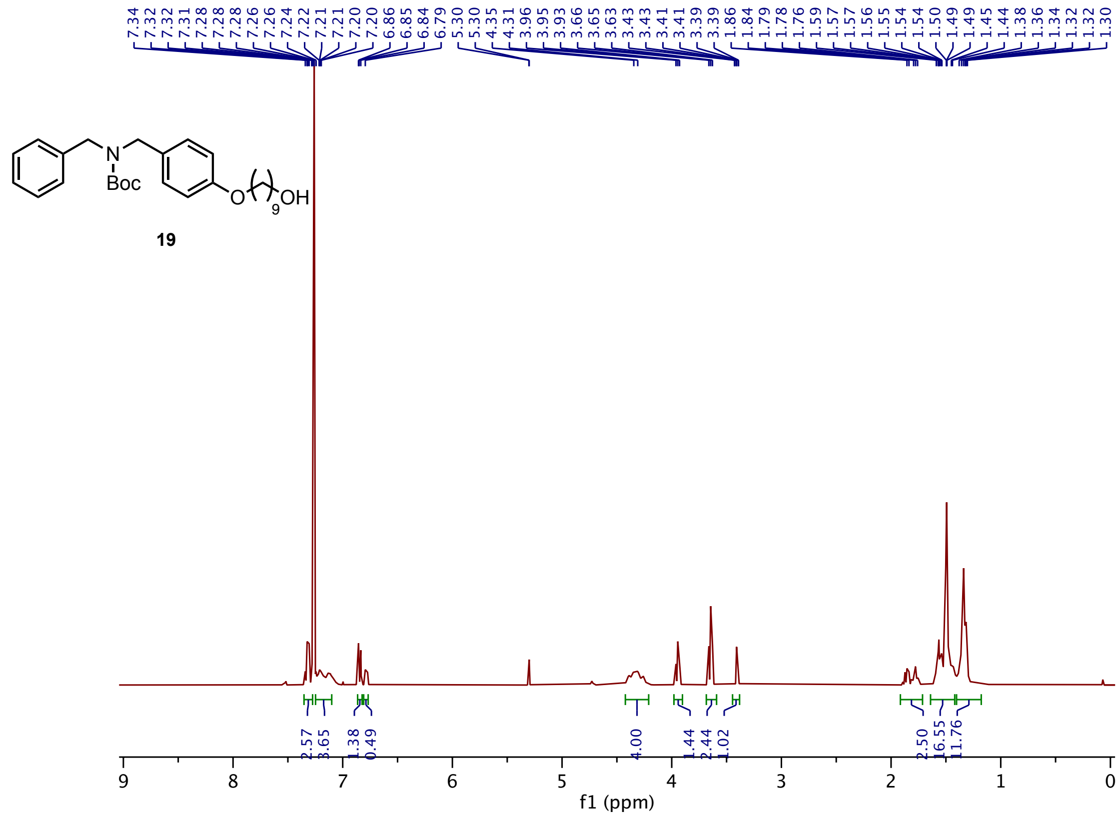



3
4
5
6
7
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)

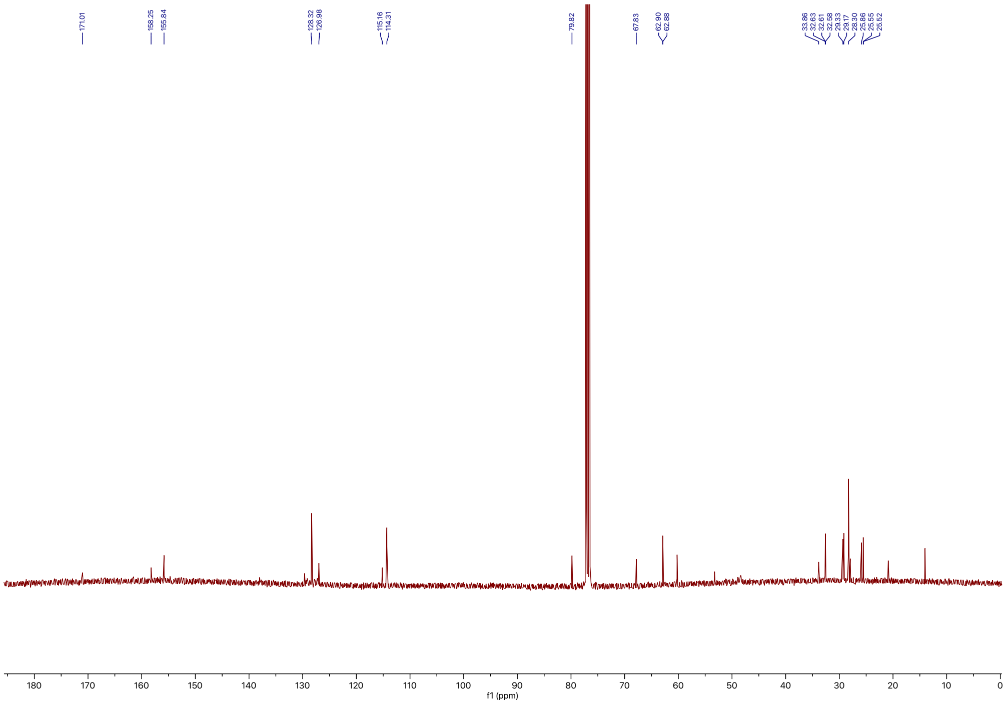

50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)


20
40
60
80
100
120
140
160
180
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)

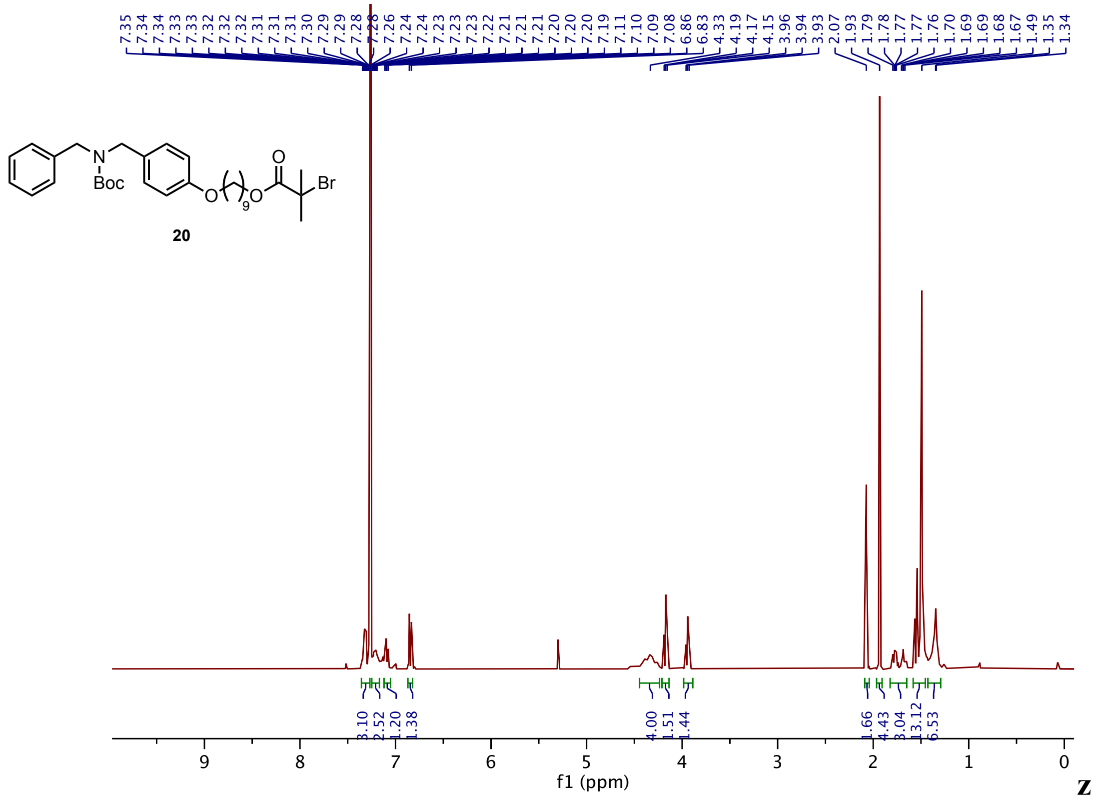
Compound 19: ^{1}H and ^{13}C NMR spectra.

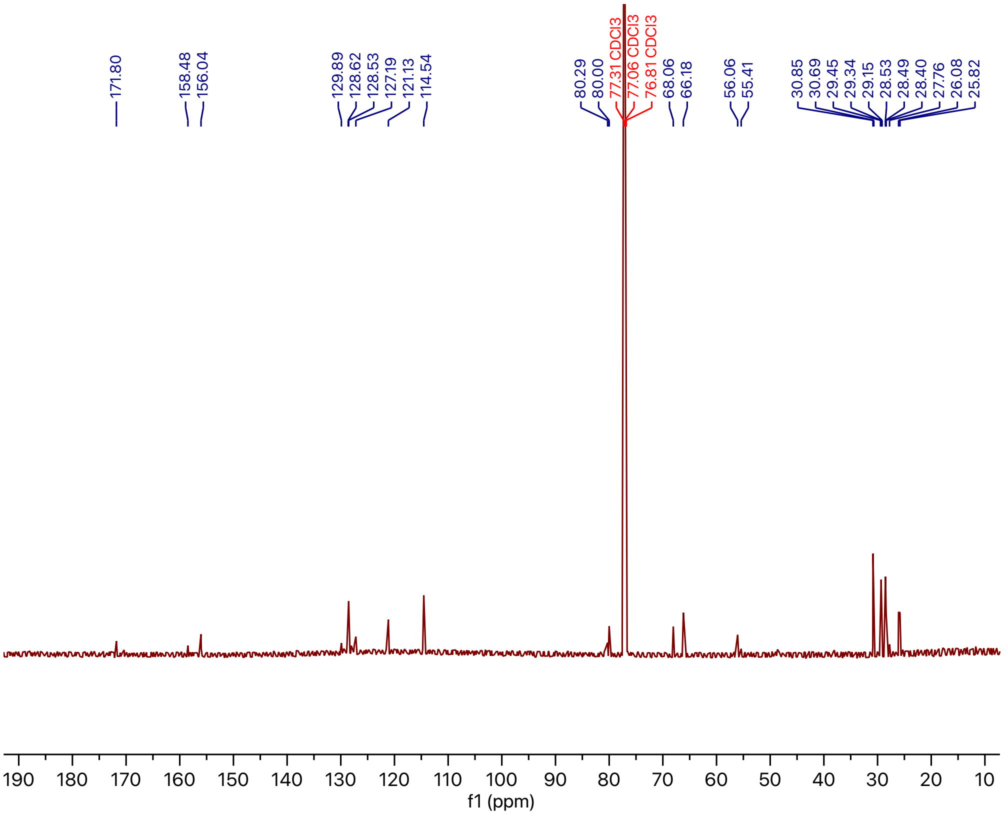


19

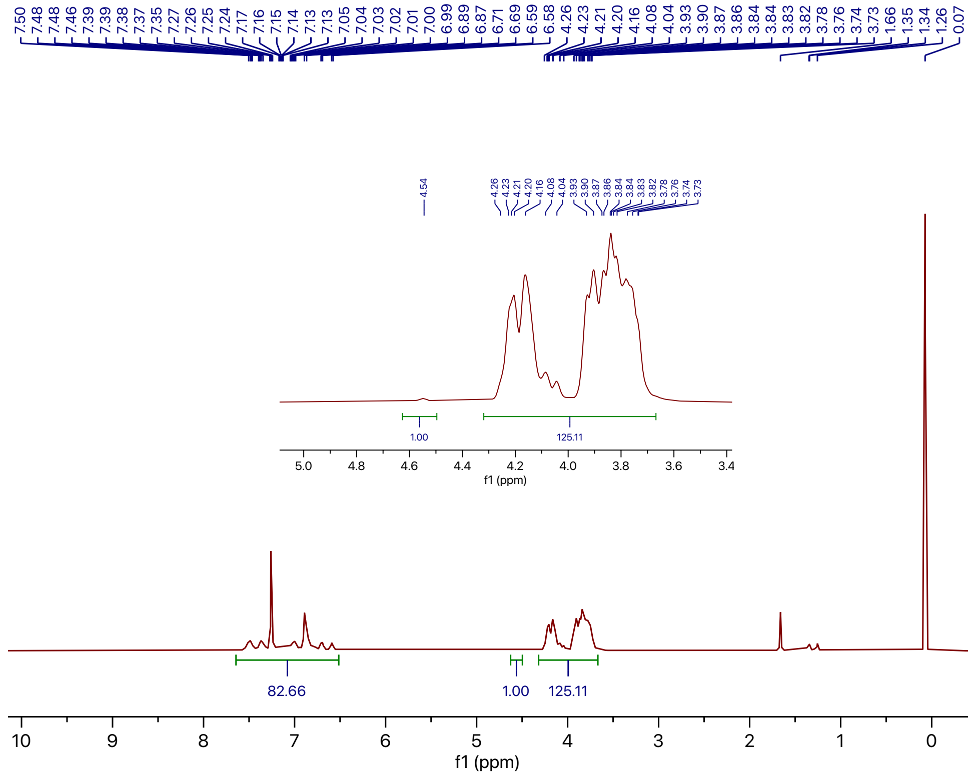


Compound 20: ^{1}H and ^{13}C NMR spectra.

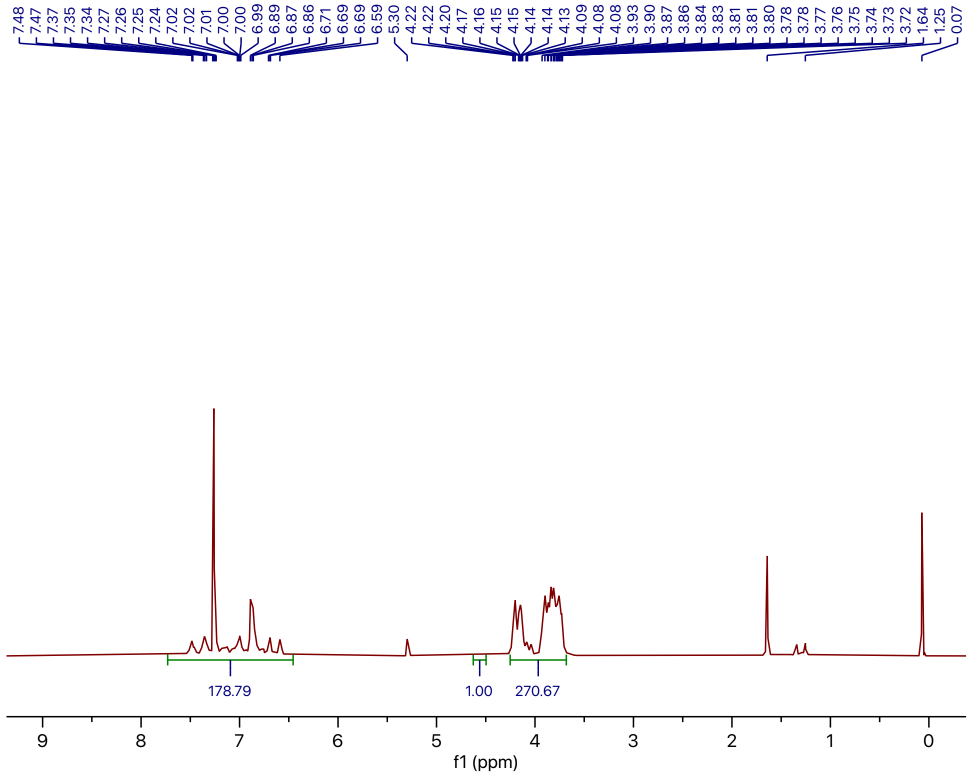




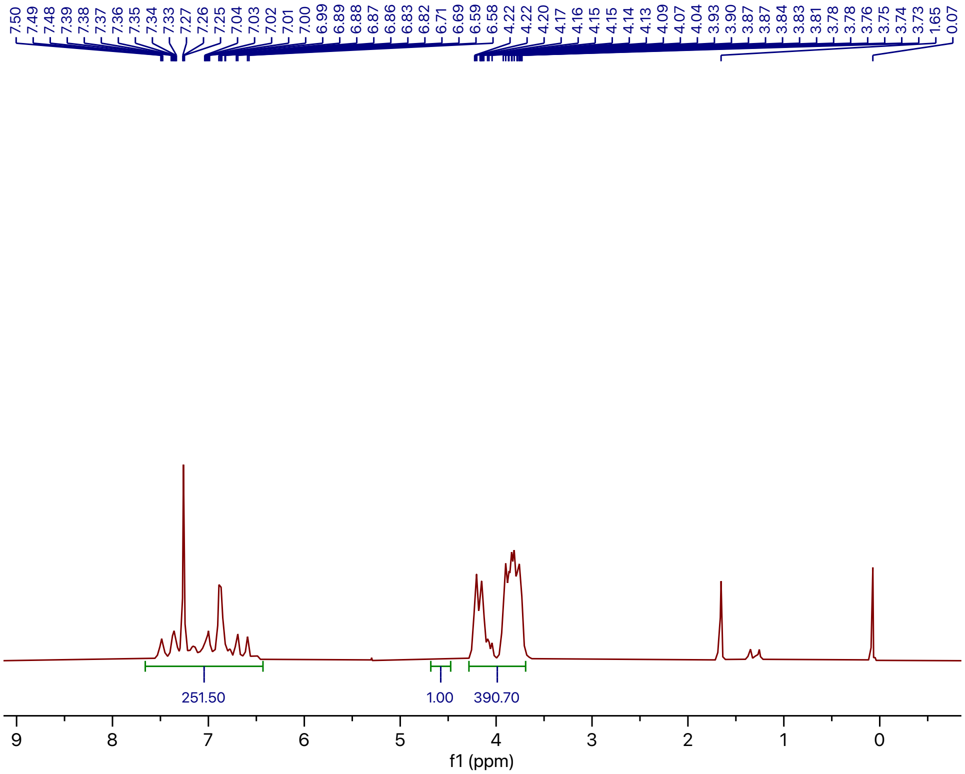
Polymer 13a: ^{1}H NMR spectrum.



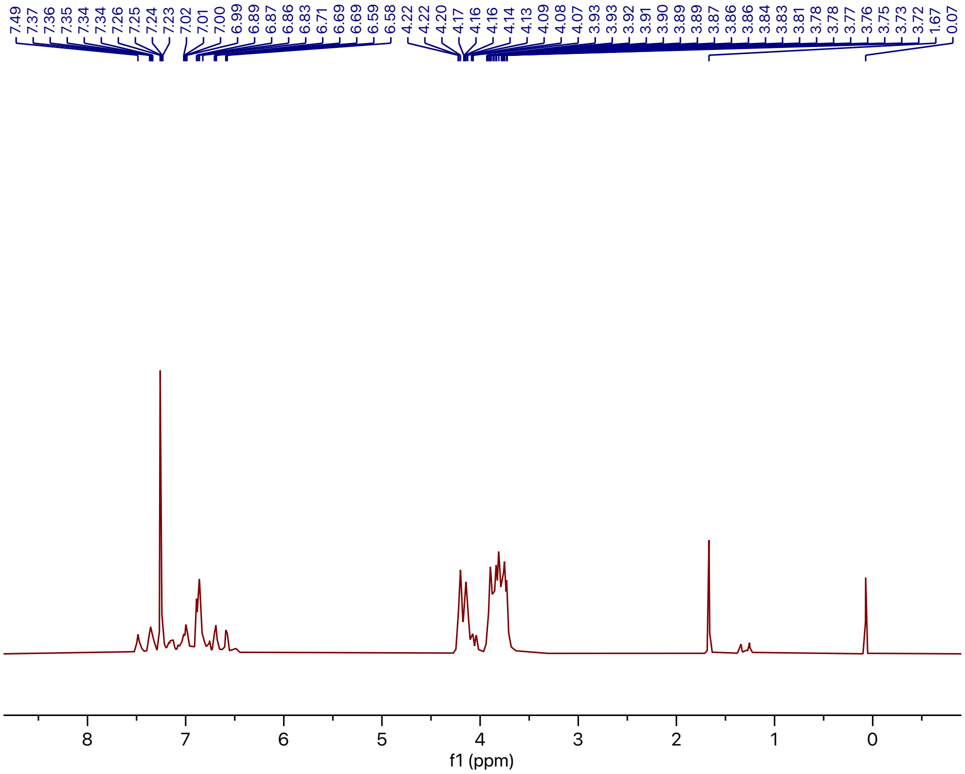
Polymer 13b: ^{1}H NMR spectrum.



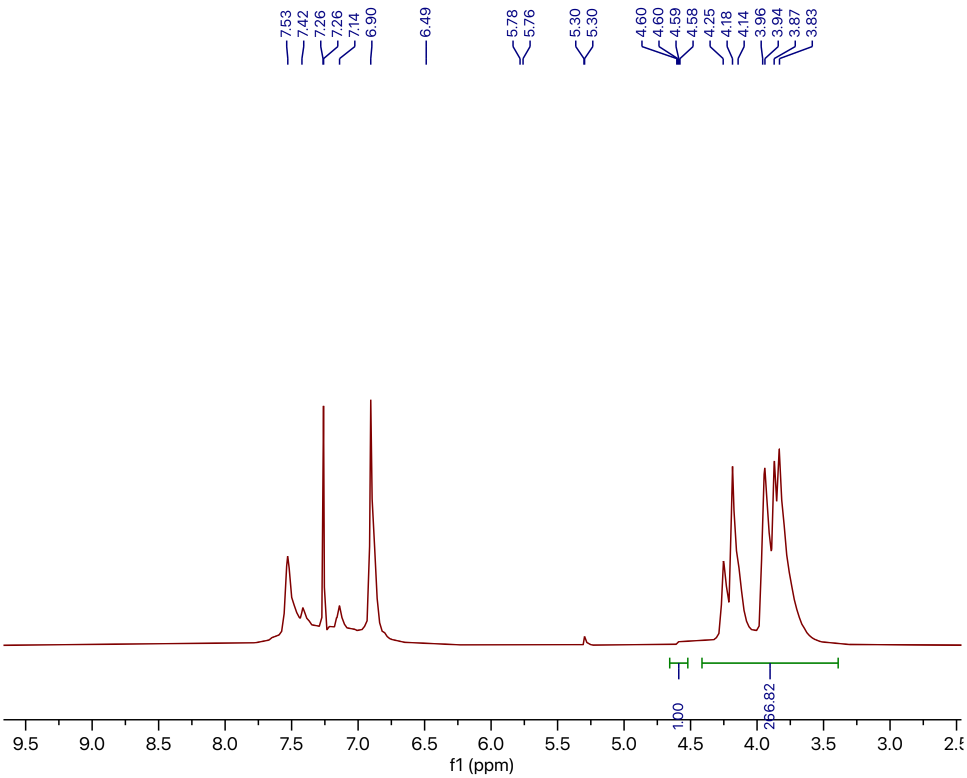
Polymer 13c: ^{1}H NMR spectrum.



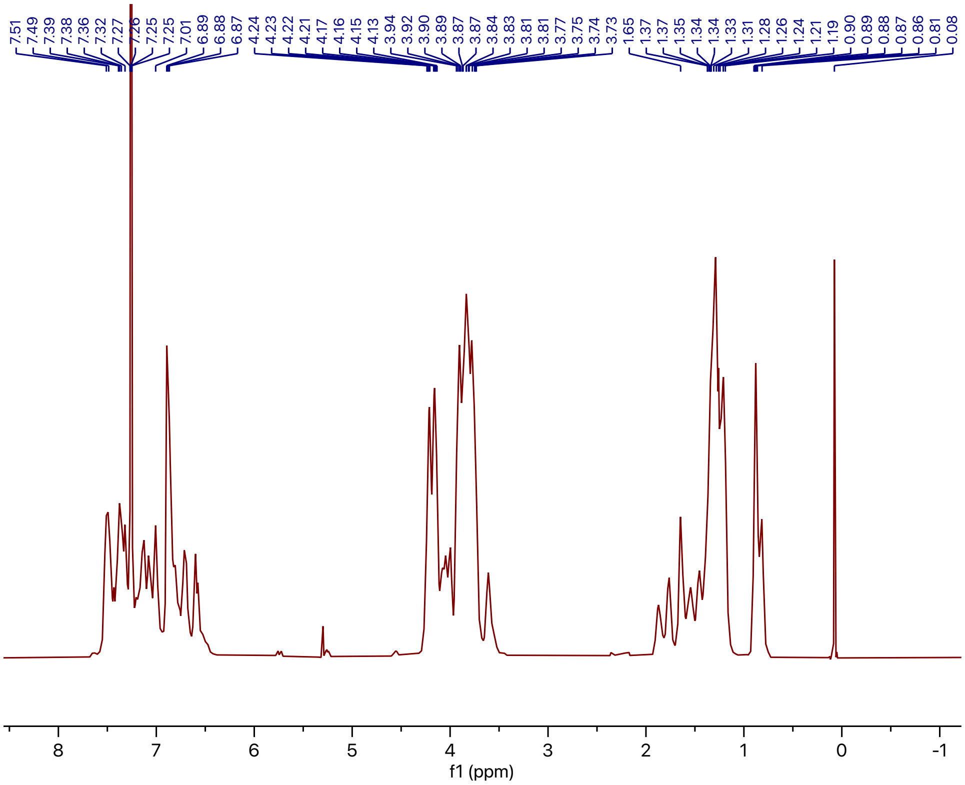
Polymer 13d: ^{1}H NMR spectrum.



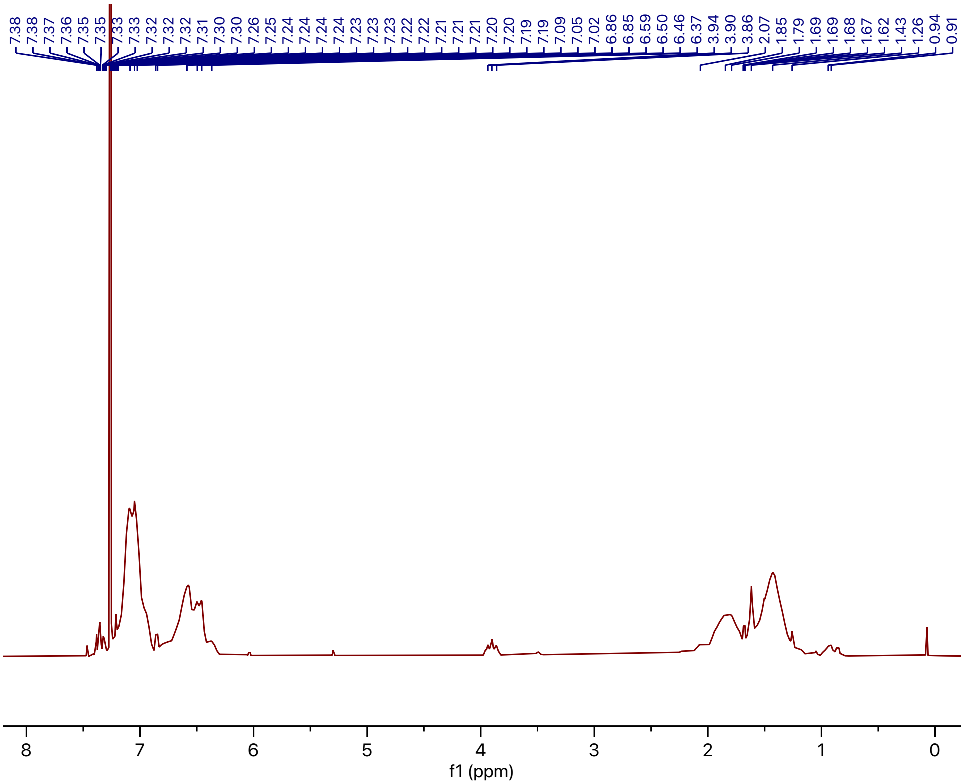
Polymer 14: ^{1}H NMR spectrum.



Polymer 15: ^{1}H NMR spectrum.



Polymer 22: ^{1}H NMR spectrum.



References

1. A. Mann and M. Weck, *ACS Macro Lett.*, 2022, **11**, 1055-1059.
2. H. Liu, Z. Hu and X. Ji, *Chem. Eur. J.*, 2024, **30**, e202400099.
3. C. Y. Yu and M. L. Turner, *Angew. Chem. Int. Ed.*, 2006, **45**, 7797-7800.
4. Z.-T. Shi, J.-J. Yu, Q. Zhang, M.-M. Li, W.-J. Liang, C.-X. Zhao and D.-H. Qu, *Chem. Commun.*, 2019, **55**, 10292-10295.
5. M. Curcio, F. Nicoli, E. Paltrinieri, E. Fois, G. Tabacchi, L. Cavallo, S. Silvi, M. Baroncini and A. Credi, *J. Am. Chem. Soc.*, 2021, **143**, 8046-8055.