Supporting Information

β-Strand Inspired Bifacial π-Conjugated Polymers

Saikat Chaudhuri, Manikandan Mohanan[†], Andreas V. Willems[†], Jeffery A. Bertke, Nagarjuna Gavvalapalli*

Department of Chemistry, and Institute for Soft Matter Synthesis and Metrology,

Georgetown University, Washington D.C. 20057

1.0 General Information

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Reagents used for polymer synthesis were purchased from Fisher, Acros, Alfa Aesar and Sigma Aldrich. All air or moisture-sensitive reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Thin layer chromatography was performed using Silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, $KMnO_4$ stain and other stains. Silica gel of particle size 230-400 mesh was used for flash chromatography. Unless otherwise stated, all starting materials and reagents were used without further purification.

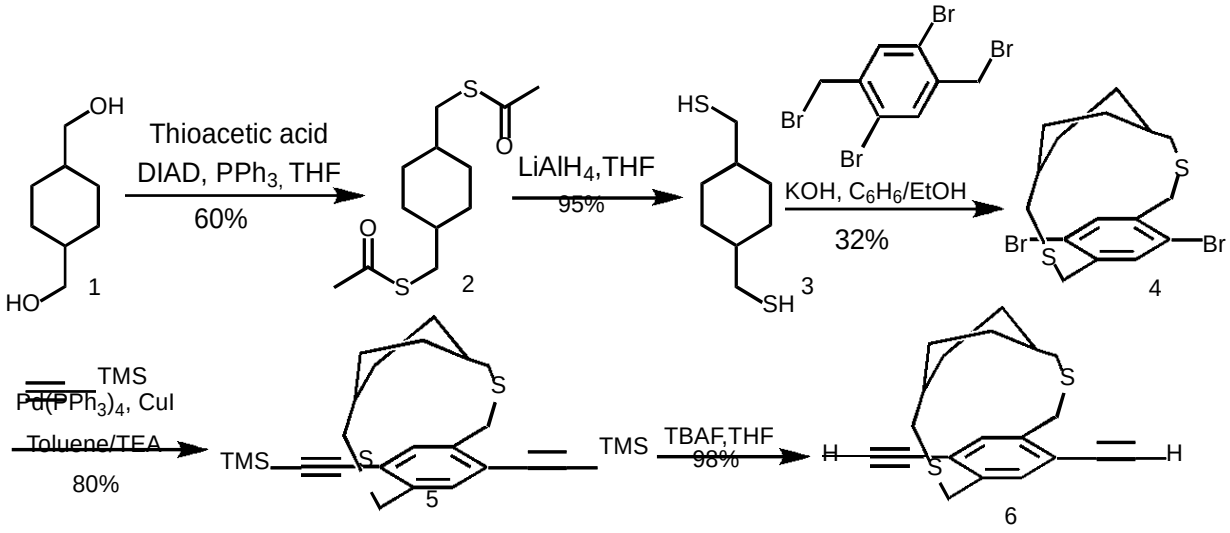
^{1}H and ^{13}C NMR spectra were recorded on Varian 400-MR NMR. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak $CDCl_3$: 7.26 for ^{1}H; and $CDCl_3$: 77.36 for ^{13}C; Coupling constants (*J*) are expressed in Hertz (Hz). Splitting patterns are designated as s(singlet), br(broad signal), d(doublet), t(triplet), dd(doublet of doublets), dt(doublet of triplets), dq(doublet of quartets), m(multiplet), and q(quartet). High resolution ESI mass spectra were recorded on a Water Synapt G2-Si (University of Illinois). UV-vis absorption spectra were recorded on Agilent Technologies Cary Series 5000 UV-vis-NIR Spectrophotometer. Fluorescence absorption spectra were recorded on Horiba Scientific Fluoromax-4 Spectrophotometer. Molecular weight measurements of polymers were performed by gel permeation chromatography (GPC) on Agilent Technologies 1260 Infinity. The column chromatography of UV active compounds was performed on Biotage Isolera one 3.0.

Polymer solubility limits are determined by dissolving polymer in chloroform at elevated temperature (55 ^{o}C) for about 20 minutes and then bringing it to room temperature. The amount of polymer dissolved in the chloroform was determined using the Beer-Lambert law. The fluorescence quenching studies of polymers were performed in the solution state by adding different concentrations of quencher (TCNQ) in v/v to the 10 μM solution of polymer solution in chloroform and UV-vis absorption spectra were recorded.

PXRD data was collected on a Rigaku R-Axis Rapid-S diffractometer equipped with a curved image plate detector and a three-circle goniometer. Data was collected using a Cu k-alpha (λ = 1.5418 Å) fine-focus sealed tube source with a graphite monochromator.

Samples were packed into a 0.3mm kapton film capillary which was mounted onto the goniometer head. The sample was rotated at 1^{o}/second for the duration of the four hour collection. The single crystals of each compound were mounted under mineral oil on a Mitegen micromount and immediately placed in a cold nitrogen stream at 100(2) K prior to data collection. Data for compounds Dibromo Cyclohexanocyclophane, and Cyclohexanocyclophane dimer were collected on a Bruker D8 Quest equipped with a Photon100 CMOS detector and a Mo ImS source. Data for compound Dibromo Adamantanocyclophane was collected on a Bruker DUO equipped with an APEXII CCD detector and Mo fine-focus sealed source.

2.0 General Reaction Scheme for the Synthesis of 6:



Synthesis of Cyclohexane-1,4-diylbis(methylene)) diethanethioate (2)

In an oven-dried round-bottom flask triphenyl phosphine (44.6 g, 170.0 mmol, 4.0 equiv.) was taken in THF. The reaction vessel was kept in an ice bath maintaining 0 ˚C. DIAD (33.3 mL, 170.0 mmol, 4.0 equiv.) was added dropwise to the solution. After the complete addition of DIAD, the whole reaction mixture turned brownish white. In another round-bottom flask cyclohexane di-methanol (**1**) (6 g, 42.5 mmol, 1equiv.) and thioacetic acid (18.8 mL, 255 mmol, 6 equiv.) was taken in THF. This mixture was added dropwise to the brownish white solution. After complete addition, stirring was continued for another 3 hours. The crude mixture was purified by flash column chromatography to afford **2** as a colorless foul-smelling liquid (6.5 g, 60% yield). R_f = 0.40 (3% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.86 (d, *J* = 7.2 Hz, 1H), 2.77 (d, *J* = 6.7 Hz, 3H), 2.31 (t, *J* = 2.0 Hz, 6H), 1.80 (t, *J* = 9.4 Hz, 3H), 1.66 – 1.31 (m, 4H), 1.02 – 0.87 (m, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 196.1, 38.1, 36.0, 32.2, 30.9, 28.1; **HRMS** (ESI) m/z 261.0907 $[M + H]^+$; calculated for $[C_{12}H_{20}O_2S_2 + H]^+$: 261.0983.

Synthesis of Cyclohexane-1,4-diyldimethanethiol (3)

The reduction of thio-ester to thiol using lithium aluminium hydride was performed using a slightly modified procedure from literature.[1] The purified product cyclohexane dimethane thioester (**2**) (6 g, 23.04 mmol, 1.0 equiv.) was taken in THF (80 mL) at 0 °C. To that mixture, $LiAlH_4$ powder (2.2 g, 57.6 mmol, 2.5 equiv) was added pinch wise over 30

minutes at 0 °C and stirring was continued for 3 hours. The mixture was quenched by careful addition of EtOAc (100 mL), H_2O (5 mL). The TLC showed complete consumption of starting material. Then the mixture was then filtered through a celite pad and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The thiol was purified by flash column chromatography by using n-Hexane/EtOAc as eluent to obtain the compound **3** as a foul-smelling liquid (3.8 g, 95% yield). R_f = 0.6 (3% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.36 (t, *J* = 7.07 Hz, 4H), 1.85 (d, *J* = 7.37 Hz, 3H), 1.52-1.22 (m, 5H), 0.95-0.85 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 41.3, 31.9, 31.7; **HRMS** (ESI) m/z 176.0495 $[M]^+$; calculated for $[C_8H_{16}S_2]^+$: 176.0693.

Synthesis of 1^2,1^5-dibromo-3,7-dithia-1(1,4)-benzena-5(1,4)-cyclohexanacyclooctaphane (4)

A benzene solution of 1,4-dibromo-2,5-bis(bromomethyl)benzene (1.24 g, 6.8 mmol, 1 equiv.) and 1,4-bis(mercaptomethyl) cyclohexane (**3**) (1.21 g, 6.86 mmol, 1 equiv.) was added drop wise over a period of 30 hours to a solution of KOH (0.6 g, 1.5 mmol) in absolute ethanol (200 ml) using the high dilution technique. The solution was refluxed for an additional 24 hours. The whole reaction mixture was concentrated *in vacuo* to give a viscous residue. The crude mixture was purified by flash column chromatography and the residue was extracted with CH_2Cl_2 (3 × 20 ml). The extract was dried over $MgSO_4$, filtered, and evaporated to give a waxy residue. The residue was separated chromatographically on silica gel with CH_2Cl_2/*n*-hexane (2/3: v/v) as an eluent to provide **4** as a white crystalline powder (956 mg, 32% yield). R_f = 0.35 (5% DCM in hexane),**^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.57-7.44 (m, 2H), 4.14-3.97 (m, 2H), 3.55 (dd, *J* = 32.3, 13.6 Hz, 2H), 2.48-2.17 (m, 4H), 1.65-1.40 (m, 4H), 1.33-1.25 (m, 3H), 0.87-0.66 (m, 2H), -0.48-(-0.54); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 141.6, 138.2, 136.9, 135.8, 124.7, 123.240.0, 37.9, 36.4, 35.6, 32.8, 32.3, 29.6, 25.8, 25.6, 24.8, 24.5; **HRMS** (ESI) m/z 434.9544 $[M + H]^+$; calculated for $[C_{16}H_{20}Br_2S_2 + H]^+$: 521.1717.

Synthesis of 1^2,1^5-bis((trimethylsilyl)ethynyl)-3,7-dithia-1(1,4)-benzena-5(1,4)-cyclohexanacyclooctaphane (5)

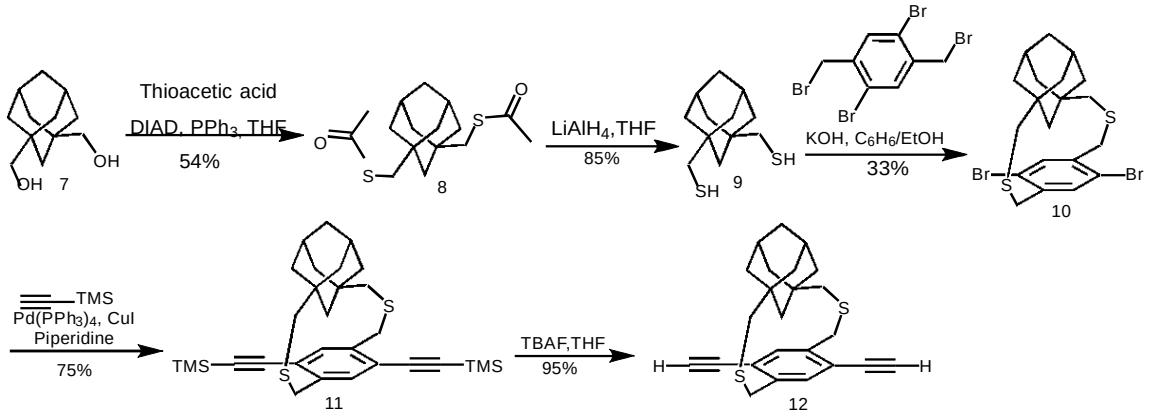
In an oven dried Schlenk flask dibromo-*p*-cyclohexanocyclophane **4** (470 mg, 1.1 mmol, 1 equiv.) was taken and brought into the glove box, tetrakis(triphenylphosphine)palladium(0) (120 mg, 0.11 mmol, 10 mol%) and copper (I) iodide (20 mg, 0.11 mmol, 10 mol%) were added along with dry and degassed triethylamine (7 mL) and toluene (7 mL). Then TMS-acetylene (900 µL, 6.5 mmol) was added and the reaction mixture was stirred at 80°C for 2 hours. The crude reaction mixture was evaporated, extracted with dichloromethane (2 x 20 mL), filtered through celite, and reevaporated. The residue was separated chromatographically on silica gel with CH_2Cl_2/*n*-hexane gradient (0%-30% DCM) as an eluent to yield **5** as a white crystalline compound (414 mg, 80% yield). R_f = 0.50 (5% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.47-7.30 (m, 2H), 4.28-4.09 (m, 2H), 3.55-3.43 (m, 4H), 2.50-2.10 (m, 4H), 1.62 (t, *J* = 6.78 Hz, 1H), 1.51-1.34 (m, 6H), 0.77-0.62 (m, 2H), -0.49-(-0.59) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.8, 140.7, 139.1, 135.1, 134.1, 125.2,123.1, 103.3,103.0, 102.2,102.0, 40.2, 36.4, 35.5, 34.8, 33.0, 32.3, 29.6, 26.0,25.3, 24.7, 24.4, 0.49, 0.46; **HRMS** (ESI) m/z 471.2045 $[M + H]^+$; calculated for $[C_{26}H_{38}S_2Si_2 + H]^+$: 471.2032.

Synthesis of 1^2,1^5-diethynyl-3,7-dithia-1(1,4)-benzena-5(1,4)- cyclohexanacyclooctaphane (6)

TMS-acetylated *p*-cyclohexanocyclophane **5** (370 mg, 0.79 mmol, 1 equiv.) was taken in THF (10 mL) and cooled to 0°C. Tetrabutylammonium fluoride (1.0 M in THF, 2.4 mL, 2.4 mmol) was added and the reaction mixture stirred for 1 hour at the same temperature, and then at room temperature for 30 min. The reaction was quenched by addition of H_2O. The organic layer was separated through a separatory funnel. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/*n*-hexane gradient (0%-8% DCM) as an eluent to yield **6** as a white crystalline compound (253 mg, 98% yield). R_f = 0.40 (5% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.54-7.37 (m, 2H), 4.26 (d, *J* = 13.5 Hz, 1H), 4.13 (d, *J* = 12.9 Hz, 1H), 3.59-3.40 (m, 4H), 2.49-2.13 (m, 4H), 1.63 (t, *J* = 5.70 Hz, 1H), 1.53-1.21 (m, 6H), 0.79-0.64 (m, 2H), !0.54-(!0.61); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.1, 139.4, 135.8, 134.8, 124.4, 122.5, 40.1, 36.3, 35.4, 34.7, 32.9, 32.2, 29.6, 25.9, 25.3,

24.6, 24.4; **HRMS** (ESI) m/z 327.1246 $[M + H]^+$; calculated for $[C_{20}H_{22}S_2 + H]^+$: 327.1241.

3.0 General reaction Scheme for the Synthesis of 12:



Procedure for the Synthesis of Adamantane-1,3-diyl)bis(methylene)) diethanethioate (8)

Compound **8** was synthesized from compound **7** following the same procedure used for compound **2**. The compound **8** was obtained as a colorless foul-smelling liquid (4.3 g, 54% yield). R_f = 0.50 (2% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.67 (s, 4H), 2.27 (s, 6H), 1.97 (s, 2H), 1.48 (s, 2H), 1.40-1.29 (m, 8H), 1.17 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 195.6, 45.3, 42.0, 40.7, 36.0, 34.2, 30.9, 28.8; **HRMS** (ESI) m/z 313.1295 $[M + H]^+$; calculated for $[C_{16}H_{24}O_2S_2 + H]^+$: 313.1296.

Procedure for the Synthesis of Adamantane-1,3-diyl)dimethanethiol (9)

Compound **9** was synthesized from compound **8** following the same procedure used for compound **3**. The compound **9** was obtained as a white solid, (2.8 g, 85% yield), R_f = 0.50 (2% EtOAc in hexane).**^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.31 (d, *J* = 8.73 Hz, 4H), 2.08 (t, *J* = 2.66 Hz, 2H), 1.56 (brs, 2H), 1.48-1.38 (m, 8H), 1.25 (s, 2H), 1.10 (t, *J* = 8.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 44.7, 40.8, 38.7, 36.6, 34.5, 29.2; **HRMS** (ESI) m/z 228.1003 $[M]^+$; calculated for $[C_{12}H_{20}S_2]^+$: 228.1000.

Procedure for the Synthesis of 5^2,5^5-dibromo-3,7-dithia-1(1,3)-adamantana-5(1,4)-benzenacyclooctaphane (10)

Compound **10** was synthesized from compound **9** following the same procedure used for compound **4**.[2] The compound **10** was obtained as a white solid (812 mg, 33% yield). R_f = 0.40 (5% DCM in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.32 (brs, 1H), 3.84-3.42 (br AB, *J* = 12.5 Hz, 4H), 2.64 (d, *J* = 13.46 Hz, 2H), 1.91-1.43 (m, 4H), 1.15-1.12 (m, 4H), 0.93 (d, J = 12.52 Hz, 2H), -0.26 (brs, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 141.1, 136.2, 124.4, 45.0, 43.4, 39.3, 37.9, 37.0, 34.4, 29.4; **HRMS** (ESI) m/z 486.9771 $[M + H]^+$; calculated for $[C_{20}H_{24}Br_2S_2 + H]^+$: 486.9764.

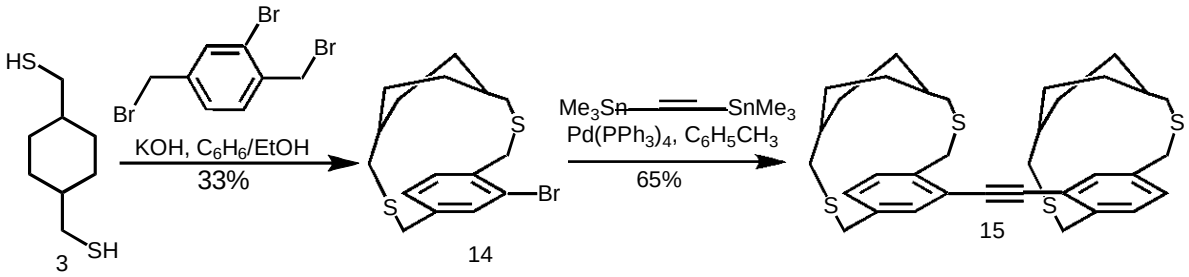
Procedure for the Synthesis of 5^2,5^5-bis((trimethylsilyl)ethynyl)-3,7-dithia-1(5,7)-adamantana-5(1,4)-benzenacyclooctaphane (11)

Compound **11** was synthesized from compound **10** following the same procedure used for compound **5** except piperidine was used instead of mixture of toluene and triethyl amine. The compound **11** was obtained as a white crystalline powder (404 mg, 75% yield). R_f = 0.35 (5% DCM in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.51 (s, 2H), 4.23 (d, *J* = 13.3 Hz, 2H), 3.42 (d, *J* = 13.3 Hz, 2H), 2.59 (d, *J* = 13.6 Hz, 2H), 2.20 (d, *J* = 13.6 Hz, 2H), 1.90 (t, *J* = 2.7 Hz, 2H), 1.56 (s, 1H), 1.49-1.44 (m, 3H), 1.24-1.14 (m, 4H), 0.94-0.92 (m, 2H), 0.27 (s, 18H), !0.10 (brs, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.9, 134.8, 124.2, 103.4, 100.7, 44.5, 42.8, 38.8, 36.6, 34.8, 33.8, 29.1, 0.0; **HRMS** (ESI) m/z 523.2365 $[M + H]^+$; calculated for $[C_{30}H_{42}S_2Si_2 + H]^+$: 523.2345.

Procedure for the Synthesis of 5^2,5^5-diethynyl-3,7-dithia-1(1,3)-adamantana-5(1,4)-benzenacyclooctaphane (12)

Compound **12** was synthesized from compound **11** following the same procedure used for compound **6**. The compound **12** was obtained as a white crystalline powder (137 mg, 95% yield). R_f = 0.45 (5% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.56 (s, 1H), 7.26 (s, 1H), 4.21 (d, *J* = 13.38 Hz, 1H), 4..1 (d, *J* = 10.8 Hz, 1H), 3.48-3.35 (m, 4H), 2.62 (d, *J* = 9.33 Hz, 2H), 2.12 (d, *J* = 12.7 Hz, 1H), 1.90-1.78 (m, 3H), 1.56-1.43 (m, 4H), 1.13-0.92 (m, 6H), -0.12 (s, 1H), -0.25 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.7, 135.9, 123.9, 85.3, 83.4, 45.2, 43.4, 39.3, 37.6, 37.0, 35.3, 34.3; **HRMS** (ESI) m/z 379.1561 $[M + H]^+$; calculated for $[C_{24}H_{26}S_2 + H]^+$: 521.1545.

4.0 General reaction Scheme for the Synthesis of 15:



Procedure for the Synthesis of 1[2]-bromo-3,7-dithia-1(1,4)-benzena-5(1,4)-cyclohexanacyclooctaphane (14)

Compound **14** was synthesized by reacting 1,4-bis(mercaptomethyl) cyclohexane (**3**) (462 mg, 2.62 mmol, 1 equiv.) and 1-bromo-2,5-bis(bromomethyl)benzene (900 mg, 2.62 mmol, 1 equiv.) under similar conditions used for compound **4**. The compound **14** was obtained as a crystalline white solid (309 mg, 33% yield). R_f = 0.35 (3% DCM in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.57-7.05 (m, 3H), 4.21-4.00 (m, 1H), 3.67-3.54 (m, 3H), 2.64-2.17 9m, 4H), 1.61-0.60 (m, 9H), -0.58 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.7, 140.3, 139.2, 139.1, 135.7, 135.2, 133.7, 133.0, 131.4, 130.0, 128.1, 125.8, 40.3, 39.6, 38.4, 38.0, 37.0, 36.4, 36.1, 35.3, 35.0, 32.8, 32.4, 31.5, 30.9, 29.3, 292, 25.5, 25.4, 25.2, 25.1, 24.6, 24.18, 24.16.

Procedure for the Synthesis of 1,2-di(3,7-dithia-1(1,4)-benzena-5(1,4)-cyclohexanacyclooctaphane-12-yl)ethyne (15)

In an oven-dried round-bottom flask monobromo cyclohexylcyclophane (**14**) (50 mg, 0.14 mmol, 1 equiv.), bis(trimethylstannyl) acetylene (25 mg, 0.07 mmol, 0.5 equiv), and $Pd(PPh_3)_4$ (4 mg, 2 mol%) were dissolved in 3 ml of dry toluene under N_2. After the reaction solution was refluxed for 10 h, the solvent was removed under vacuum. The crude mixture was purified by flash column chromatography and the residue was extracted with CH_2Cl_2 (3 × 20 ml). The extract was dried over $MgSO_4$, filtered, and evaporated to give a waxy residue. The residue was separated chromatographically on silica gel with EtOAc/*n*-hexane as an eluent to afford **15** as a white crystalline solid (26 mg, 65% yield). R_f = 0.35 (2% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.50-7.30 (m, 6H), 4.44-4.24 (m, 2H), 3.72-3.65 (m, 5H), 2.48-2.14 (m, 8H), 1.61-1.25 (m, 14H), 0.69-0.67 (m, 4H), -0.55 (s, 2H), **^{13}C NMR** (100

MHz, $CDCl_3$) δ: 143.1, 142.3, 140.9, 140.8, 136.9, 135.0, 134.3, 134.28, 133.6, 132.0, 127.0, 126.98, 94.6, 94.5, 42.5, 42.2, 41.0, 39.7, 38.7, 37.5, 37.4, 37.2, 35.4, 35.1, 34.9, 33.7, 33.1, 31.7, 31.5, 27.8, 27.3, 26.7, 26.3.

5.0 General Procedure for Glaser-Hay Polymerization

Diacetylene-cyclophane 3 (300 mg, 0.92 mmol) was taken in toluene (20 mL), copper (I) chloride (45 mg, 0.46 mmol) and N,N,N',N'-tetramethylethylenediamine (53 mg, 0.46 mmol) were added. The flask was bubbled with air for 2 min. The reaction mixture was stirred at 55 °C until precipitate started forming. The suspension was precipitated in methanol (100 mL) and filtered. The solid was washed with methanol, *n*-hexanes, and ethyl acetate. The crude polymer was purified by Soxhlet with ethyl acetate for 24 hoursand then with chloroform for another 24 hour. Other bifacial polymers as well as the PPB were synthesized following similar protocol. Polymerization details including solvent, time, and yield are shown in this table.

Polymers	Mn (kDa)	Solvent	Time	Yield (%)
BiP-1	10.9	Toluene : Acetonitrile (4 : 1)	10 Min.	43
BiP-2a	15.0	Toluene	45 Min.	48
BiP-2b	23.0	Toluene : Acetonitrile (4 : 1)	35 Min.	40
BiP-3	19.0	Toluene	35 Min.	50
PPB	16.1	Toluene	12 hours	50

BiP-1: (52 mg, 43% yield), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.63-7.47 (m, 2H), 4.25-4.10 (m, 2H), 3.68-3.55 (m, 2H), 2.48-2.21 (m, 4H), 1.67-0.74 (m, 9H), -0.50 (brs, 1H).

BiP-2a/2b: (46 mg, 40% yield), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.68 (brs, 1H), 7.36 (brs, 1H), 4.22-4.08 (m, 2H), 3.50 (d, *J* = 38.5 Hz, 2H), 2.73 (brs, 2H), 2.02-1.82 (m, 3H), 1.54-1.47 (m. 5H), 1.26-1.21 (m, 5H), 0.95-0.84 (m, 3H), !0.03 (brs, 1H), !0.15 (brs, 1H).

BiP-3: (45 mg, 50% yield), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.67-7.36 (m, 4H), 4.20-4.07 (m, 4H), 3.65-3.31 (m, 4H), 2.72-1.95 (m, 8H), 1.47-0.76 (m, 22H), -0.40-(-0.16) (m, 2H), -0.49 (s, 1H).

PPB: (100 mg, 50% yield), **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36 (brs, 1H), 2.76 (brs, 4H), 1.65-1.64 (m, 4H), 1.39-1.26 (m, 12H), 0.91 (t, *J* = 6.49 Hz, 6H).

6.0 Single Crystal XRD of Compounds 4, 10 and 15

$C_{20}H_{24}Br_2S_2$ (**Dibromo Adamantanocyclophane**; CCDC 1885229)

A structural model consisting of one molecule per asymmetric unit was developed. All hydrogen atoms were included as riding idealized contributors. The H atom U's were assigned as 1.2 times the carrier U_{eq}.

$C_{16}H_{20}Br_2S_2$ (**Dibromo Cyclohexanocyclophane**; CCDC 1885230)

A structural model consisting of one molecule per asymmetric unit was developed. The $CH_2(C_6H_{10})CH_2$ moiety of the molecule is disordered over three orientations. The site occupancies of the three orientations refined to approximately 44:42:14%. The like C-C distances were restrained to be similar. Similar displacement amplitudes were imposed on disordered sites overlapping by less than the sum of van der Waals radii. All hydrogen atoms were included as riding idealized contributors. The H atom U's were assigned as 1.2 times the carrier U_{eq}.

$C_{34}H_{42}S_4$ (**Cyclohexanocyclophane dimer**; CCDC 1885228)

A structural model consisting of one half of the dimeric molecule per asymmetric unit was developed. The $SCH_2(C_6H_{10})$ moiety of the molecule is disordered over two orientations. The site occupancies of the two orientations refined to approximately 76:24%. The like S-C and C-C distances were restrained to be similar. The S1B atom was restrained to behave relatively isotropic. Similar displacement amplitudes were imposed on disordered sites overlapping by less than the sum of van der Waals radii. All hydrogen atoms were included as riding idealized contributors. The H atom U's were assigned as 1.2 times the carrier U_{eq}. The datum crystal exhibited non-merohedral twinning. The ratio of the primary to the

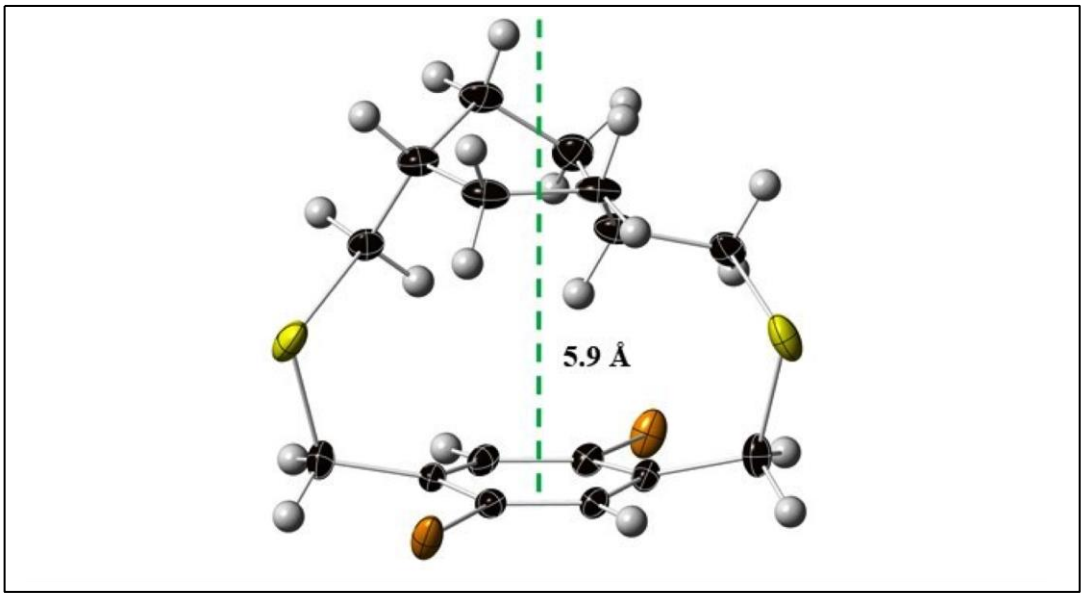
secondary domain refined to approximately 52:48%. The twin law by row that relates the two domains is as follows: (1 0 0.216), (0 -1 0), (0 0 -1).

Table 1: Crystal data and structure refinement for Dibromo Adamantanocyclophane **(10)**, Dibromo Cyclohexanocyclophane **(4)**, and Cyclohexanocyclophane dimer **(15)**.

	Adamantyl **(10)**	Cyclohexyl **(4)**	Cyclohexyl dimer **(15)**
Empirical formula	$C_{20}H_{24}Br_2S_2$	$C_{16}H_{20}Br_2S_2$	$C_{34}H_{42}S_4$
Formula weight	488.33	436.26	578.91
Wavelength/ Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pbca	Pbca	C2/c
a/Å	10.1337(10)	12.5420(6)	21.3616(17)
b/Å	12.5991(13)	9.1015(5)	9.0556(7)
c/Å	30.300(3)	28.8047(15)	15.3872(12)
α/deg	90	90	90
β/deg	90	90	94.439(3)
γ/deg	90	90	90
Volume/$Å^3$	3868.6(7)	3288.1(3)	2967.6(4)
Z	8	8	4
dcalc/g cm^{-3}	1.677	1.763	1.296
Absorption coefficient/mm^{-1}	4.407	5.173	0.343
Max./min. transmission	0.67886/0.49984	0.9795/0.3843	0.745490/0.635101
Size/mm	0.277x0.222x0.148	0.242x0.158x0.149	0.543x0.395x0.177
Reflections collected	29762	168917	122898
Independent reflections	4834	4100	6969
Parameters refined	217	329	246
R(int)	0.0285	0.0271	0.0821
Goodness-of-fit on F^2	1.049	1.062	1.055
R1, wR2 [$I > 2\sigma(I)$]	0.0199, 0.0433	0.0173, 0.0405	0.0578, 0.1568
R1, wR2 (all data)	0.0251, 0.0446	0.0184, 0.0409	0.0603, 0.1595
Largest peak, hole/ e $Å^{-3}$	0.387, -0.392	0.506, -0.557	0.797, -0.55

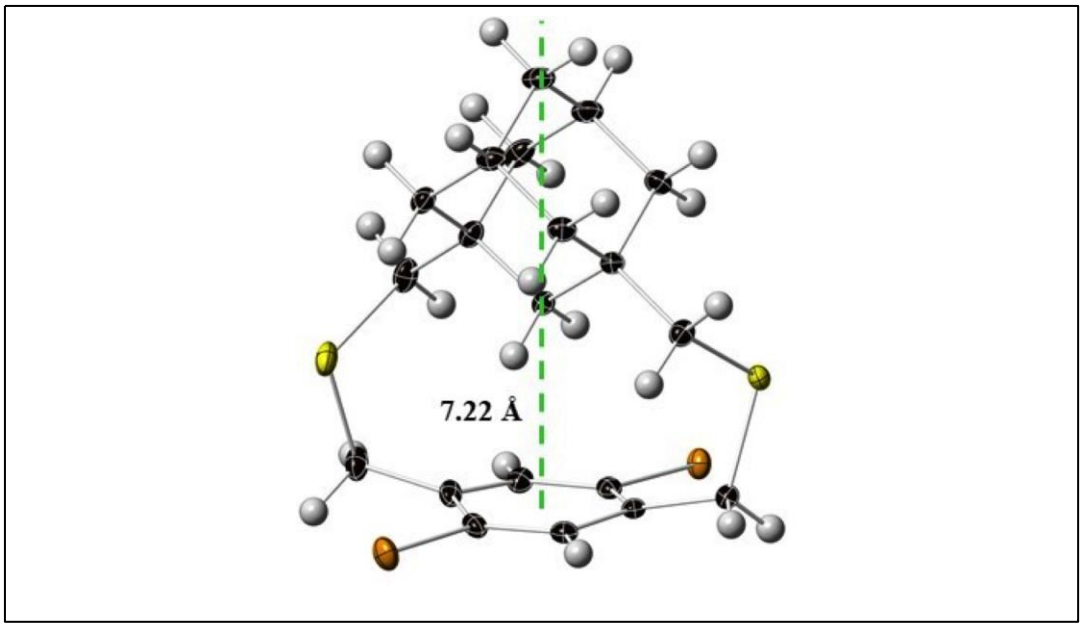
Single Crystal XRD of Compound 4:

Figure S1-a: A thermal ellipsoid plot of **Dibromo Cyclohexanocyclophane (4)**. For clarity, only the primary orientation of disordered sites is shown. Ellipsoids are shown at 50% probability. Black – C, Yellow – S, Orange – Br, White – H



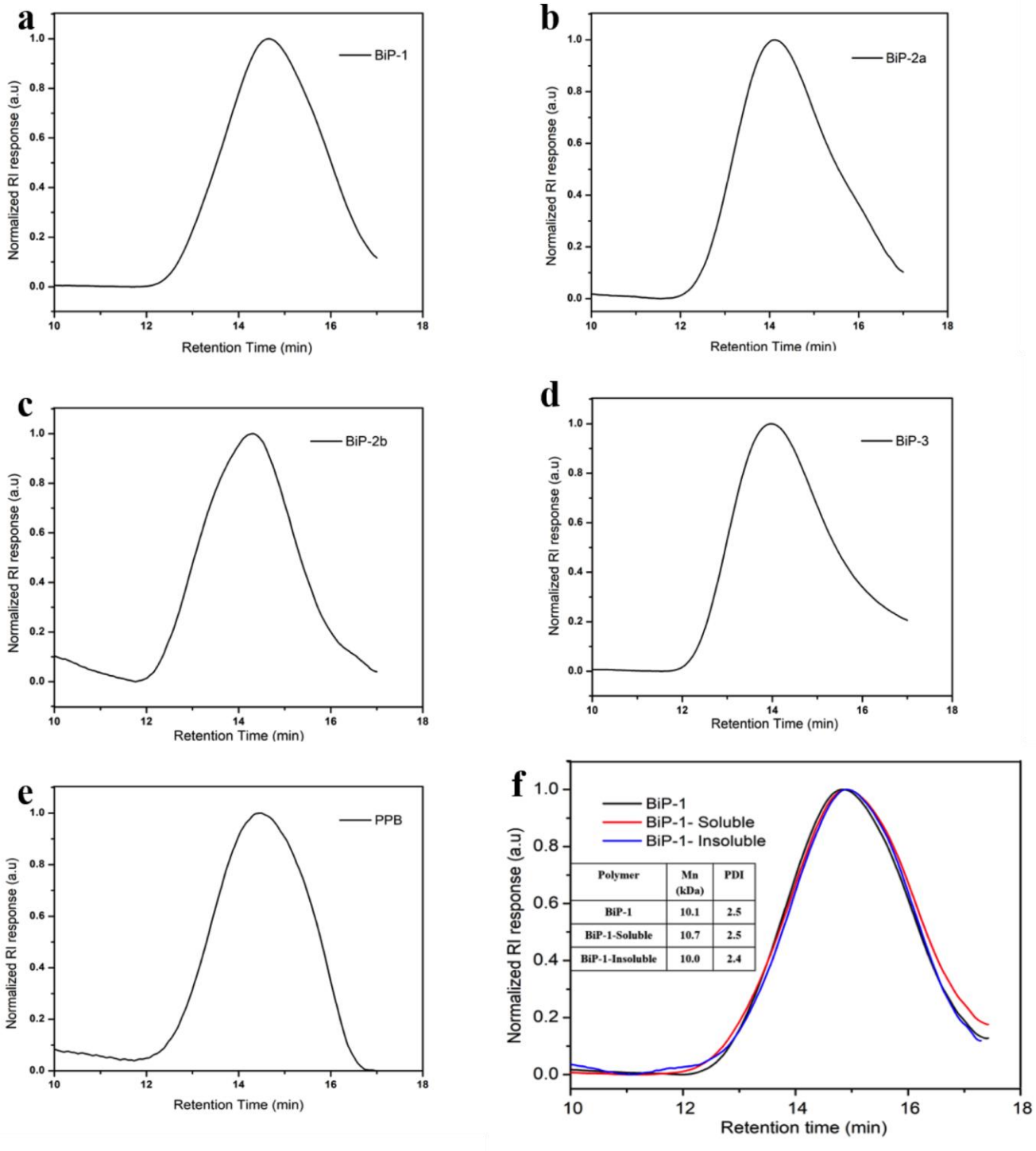
Single Crystal XRD of 10

Figure S2-a: A thermal ellipsoid plot of **Dibromo Adamantanocyclophane (10)**. Ellipsoids are shown at 50% probability. Black – C, Yellow – S, Orange – Br, White – H.



7.0 Gel Permeation Chromatography (GPC) Traces of Polymers

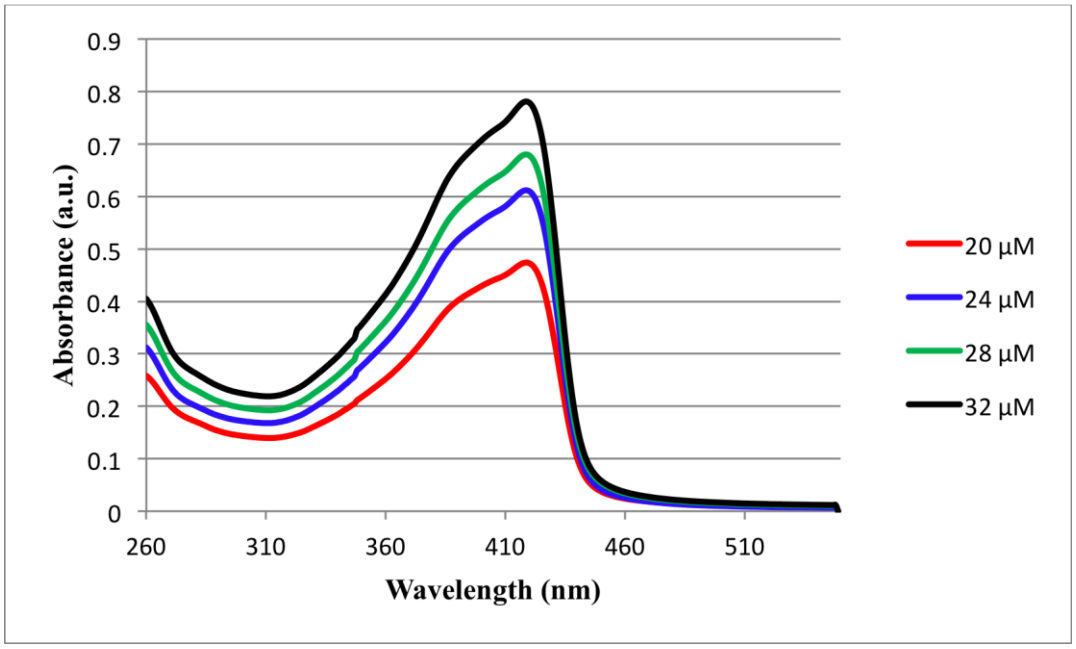
Figure S3:



Polymer	Mn (kDa)	PDI
BiP-1	10.1	2.5
BiP-1-Soluble	10.7	2.5
BiP-1-Insoluble	10.0	2.4

8.0 Molar Extinction Coefficient Determination Plots

Figure S4: BiP-1



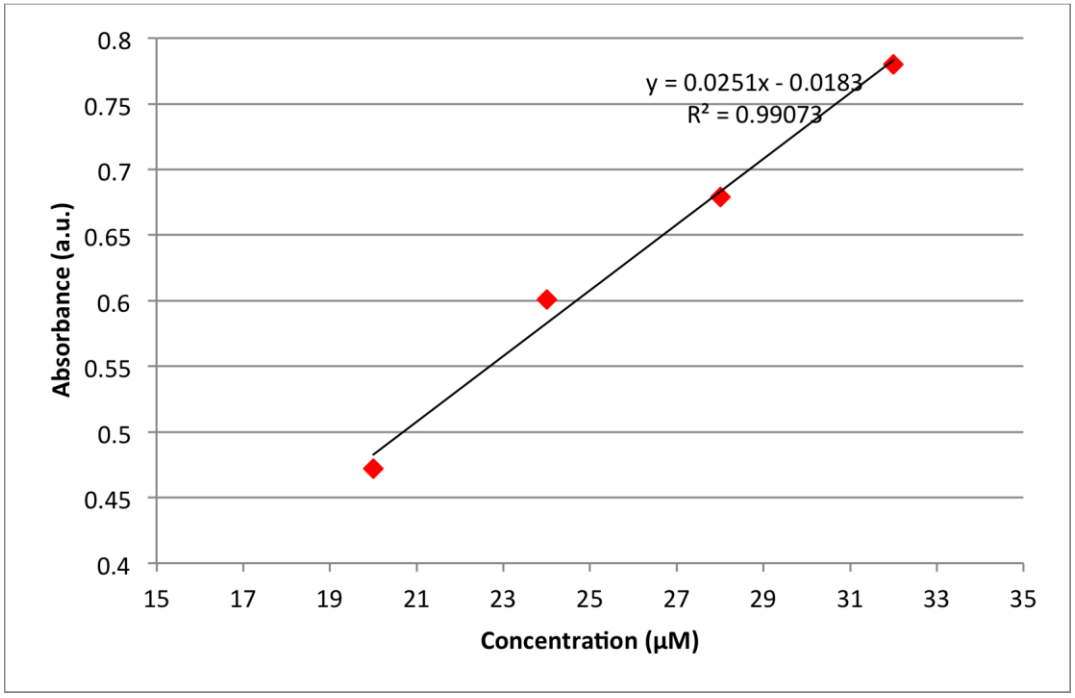
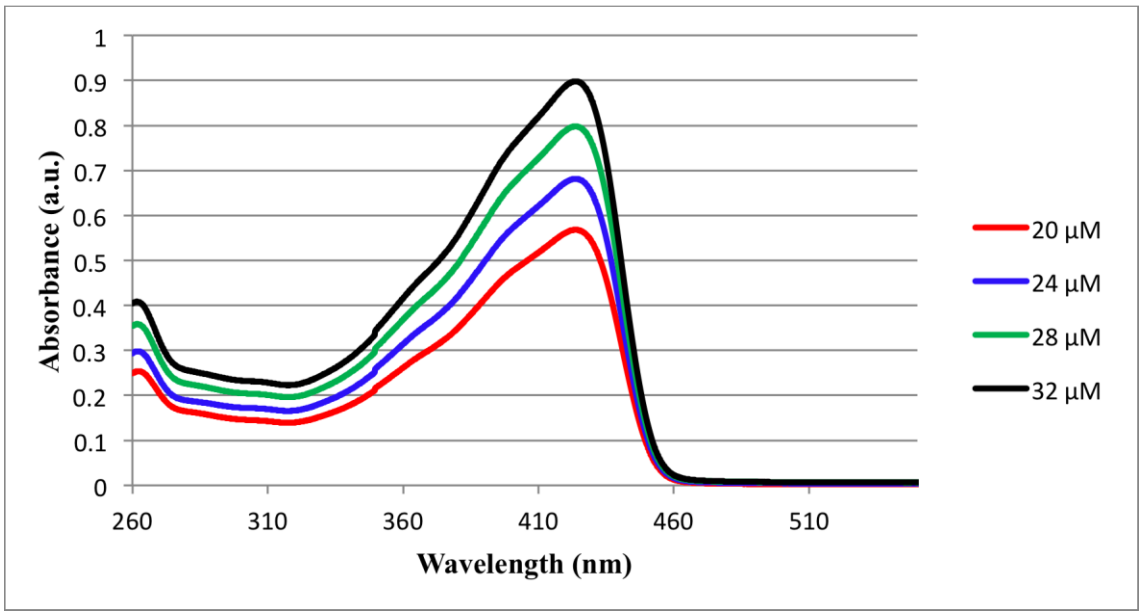


Figure S5: BiP-2a



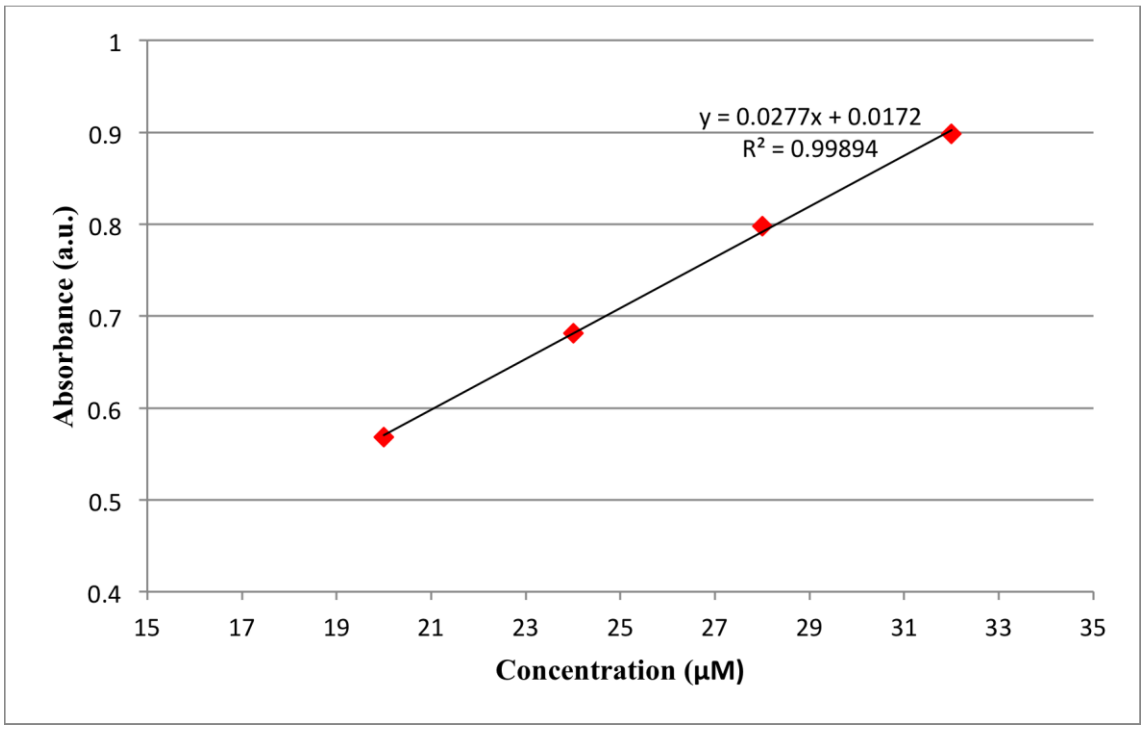
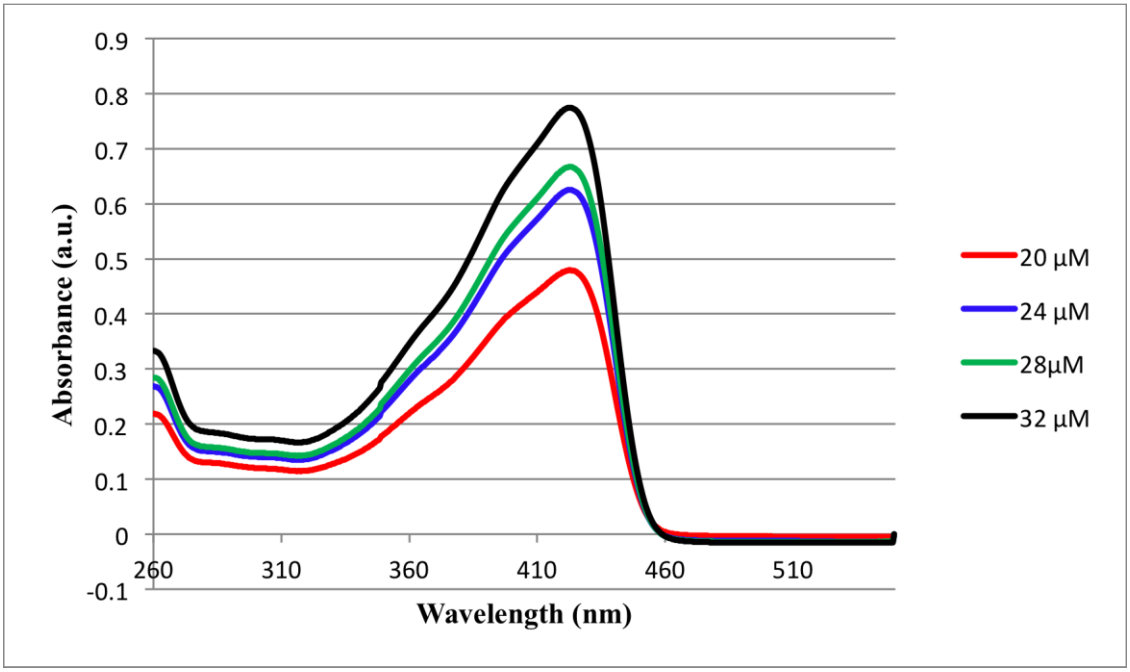


Figure S6: BiP-2b



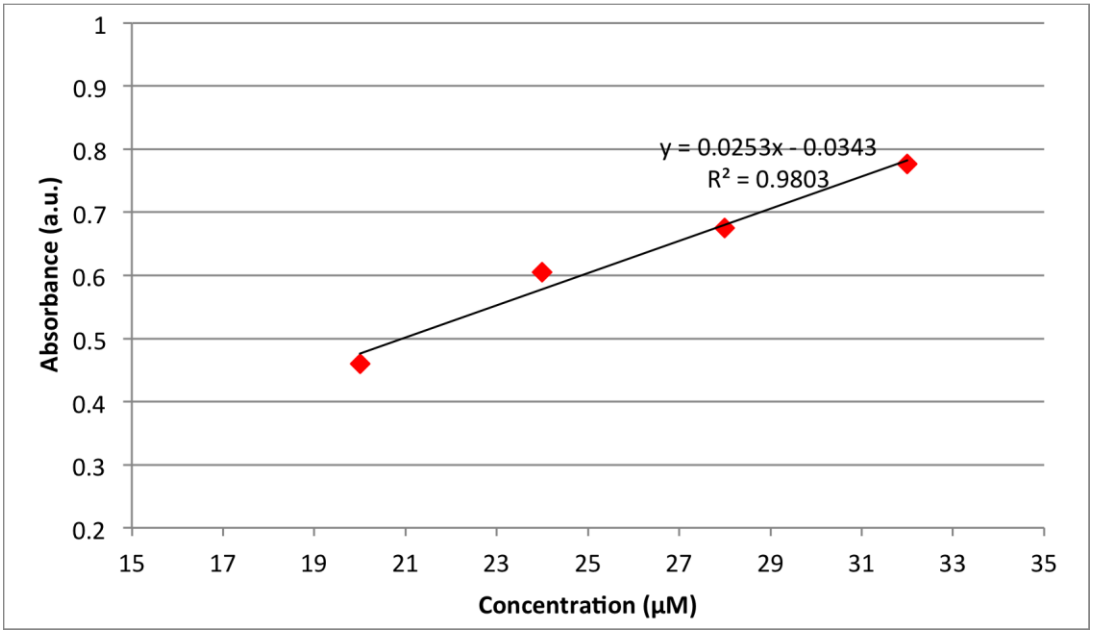
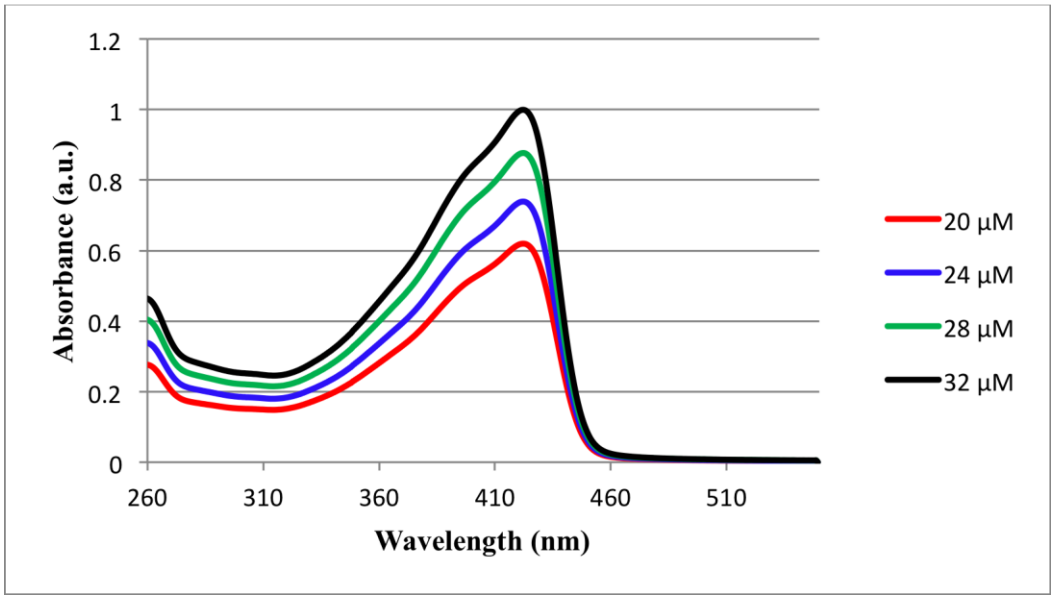


Figure S7: BiP-3



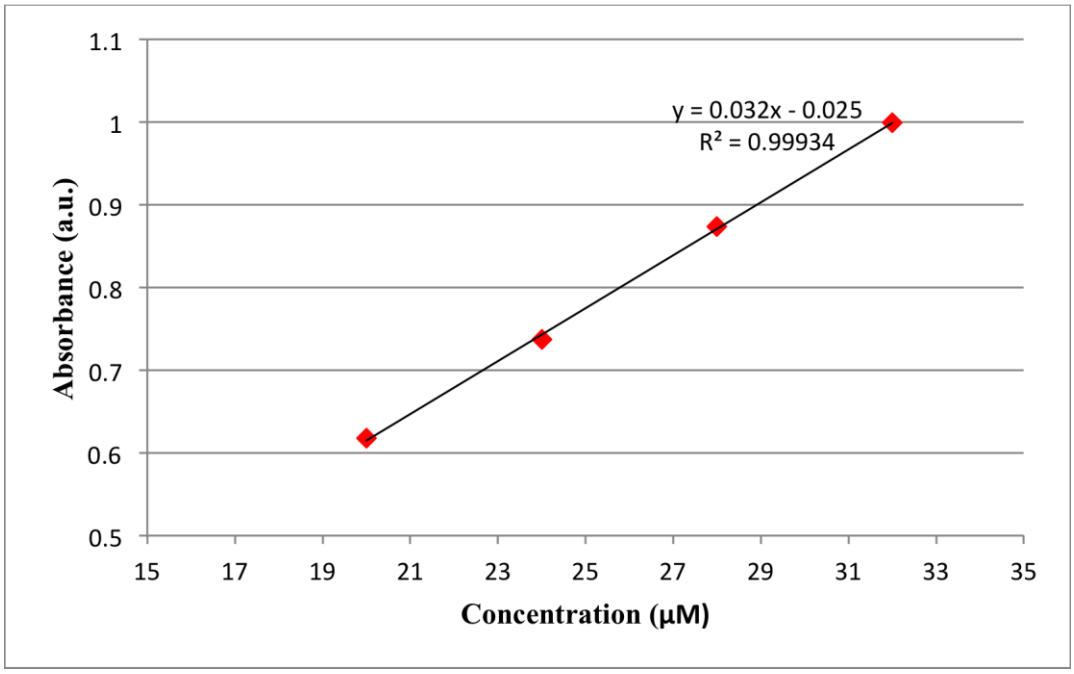
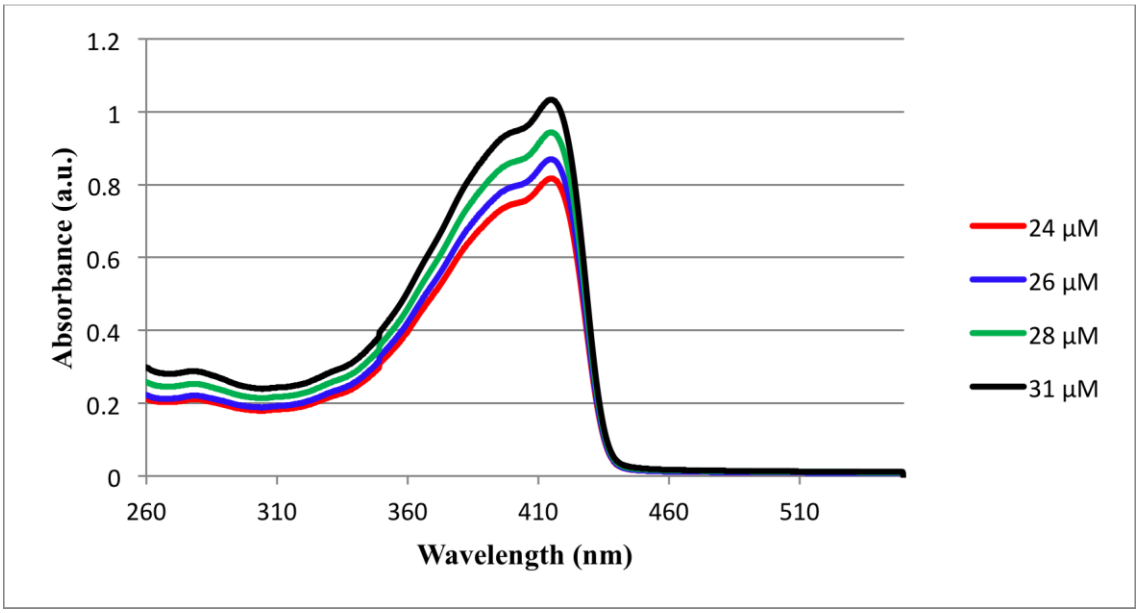
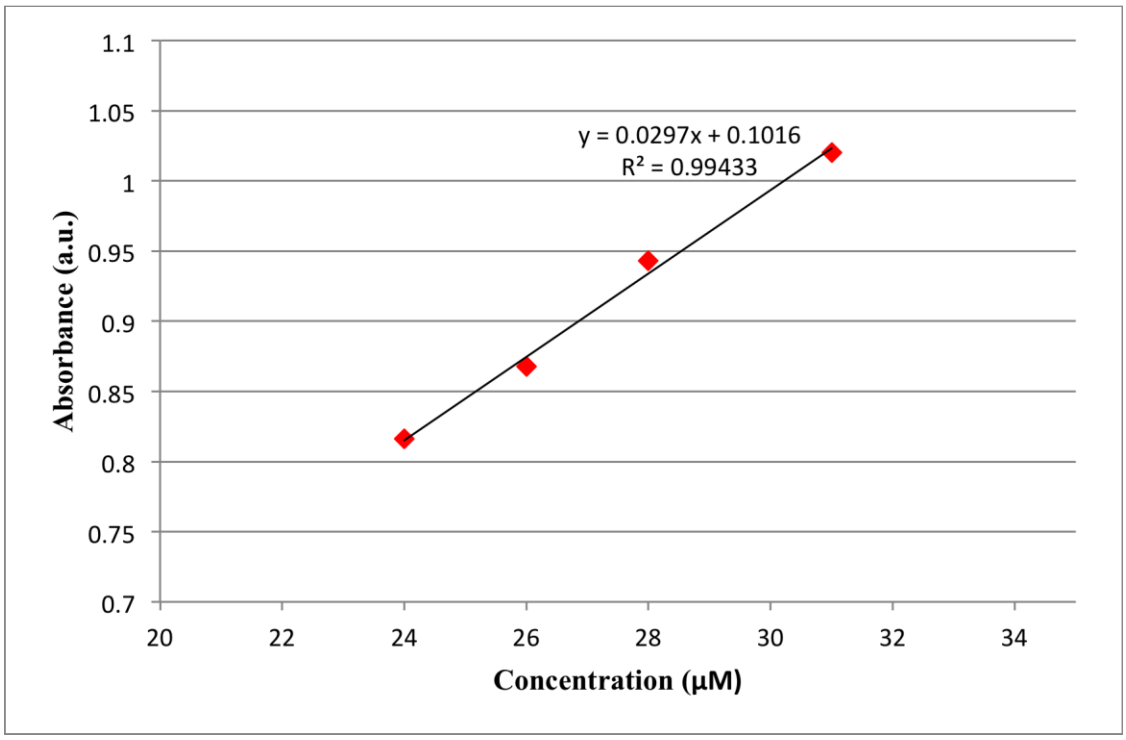


Figure S8: PPB





9.0 Polymer Fluorescence Quenching Studies

(Polymers were excited at the corresponding absorption maximum)

Figure S9: BiP-2b (TCNQ to polymer repeat unit concentration is shown in the legend)

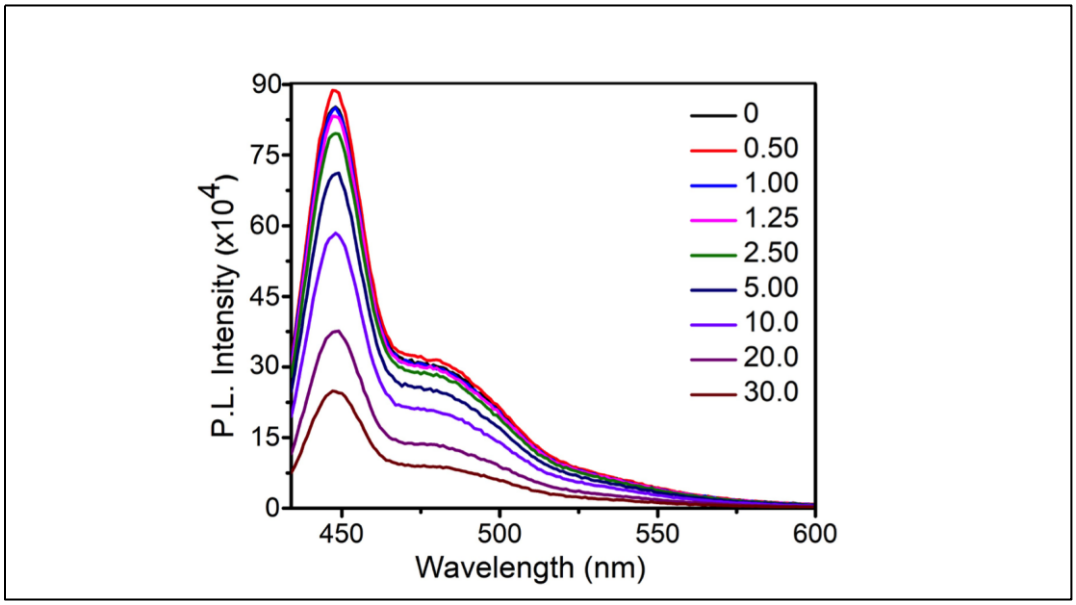


Figure S10: BiP-3 (TCNQ to polymer repeat unit concentration is shown in the legend)

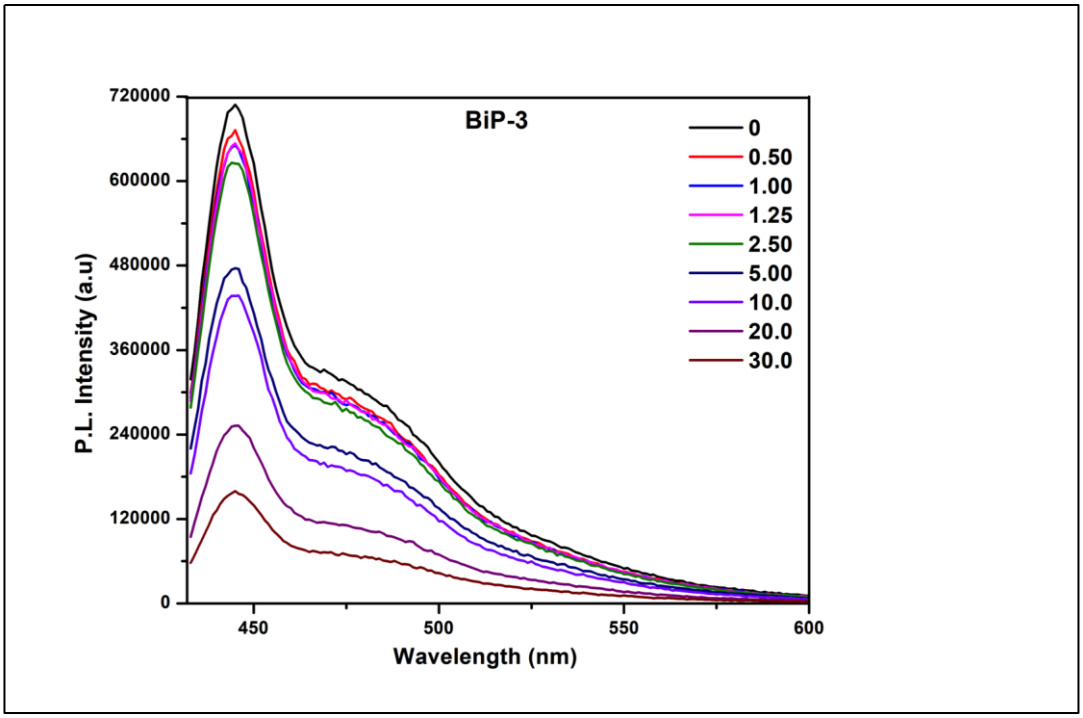


Figure S11a: PPB (TCNQ to polymer repeat unit concentration is shown in the legend)

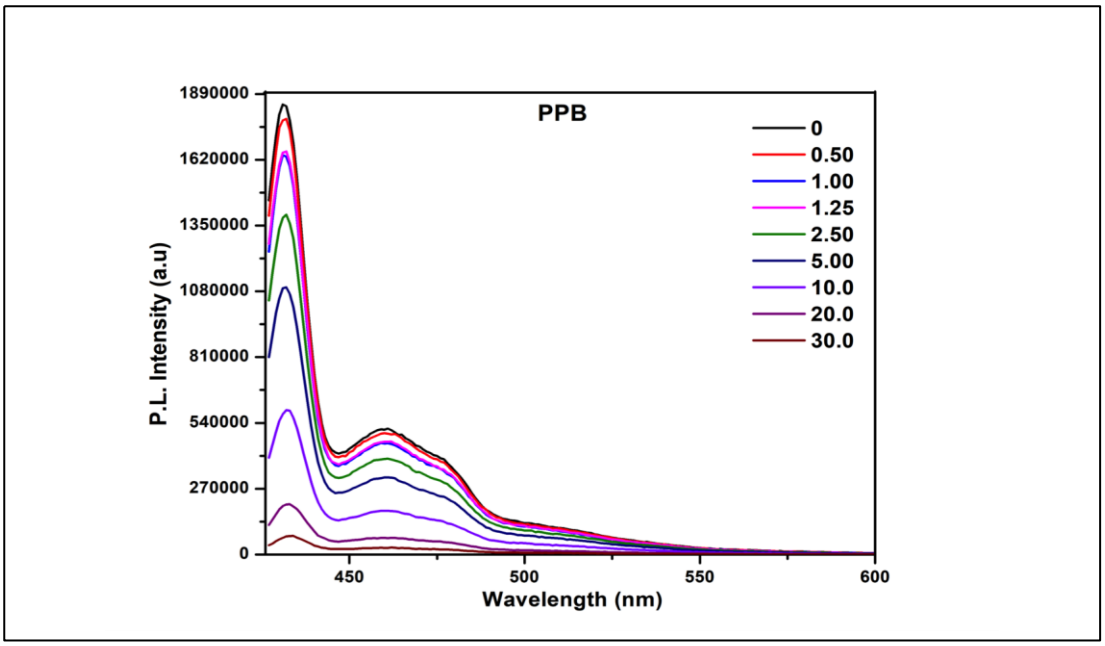
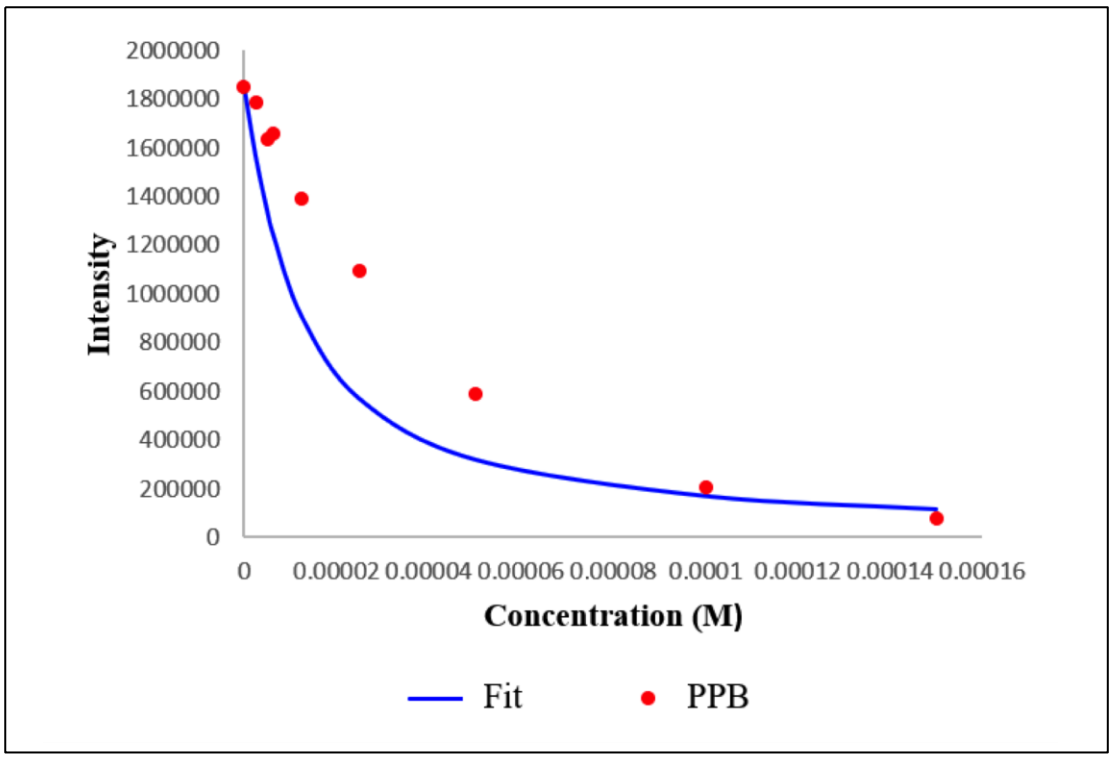
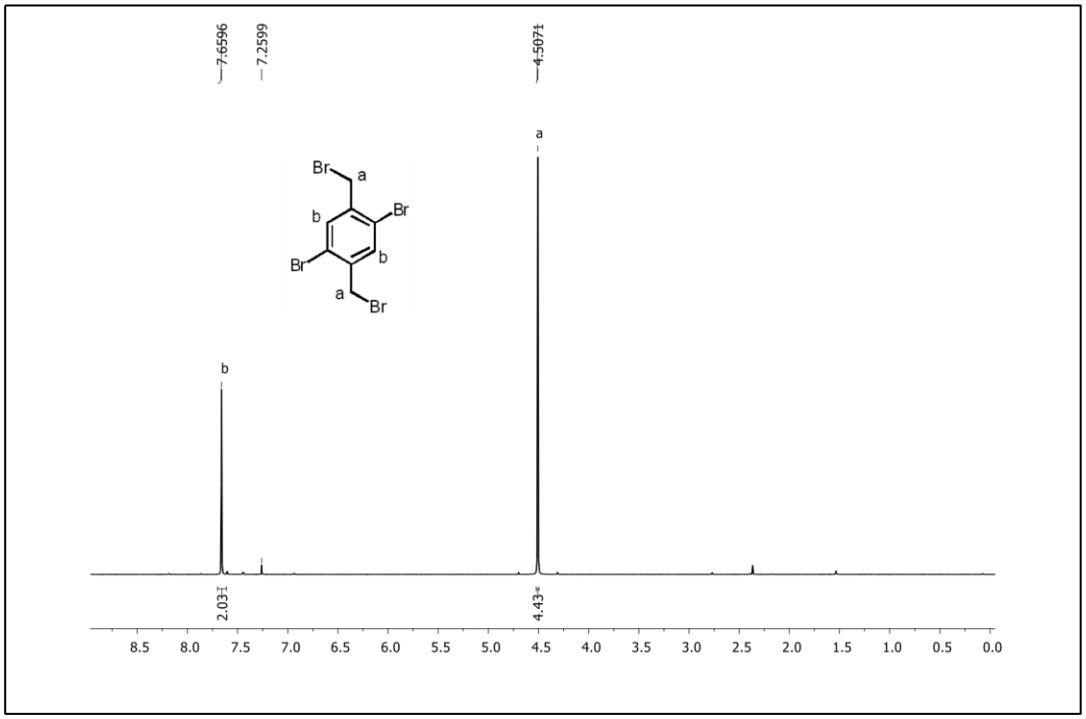


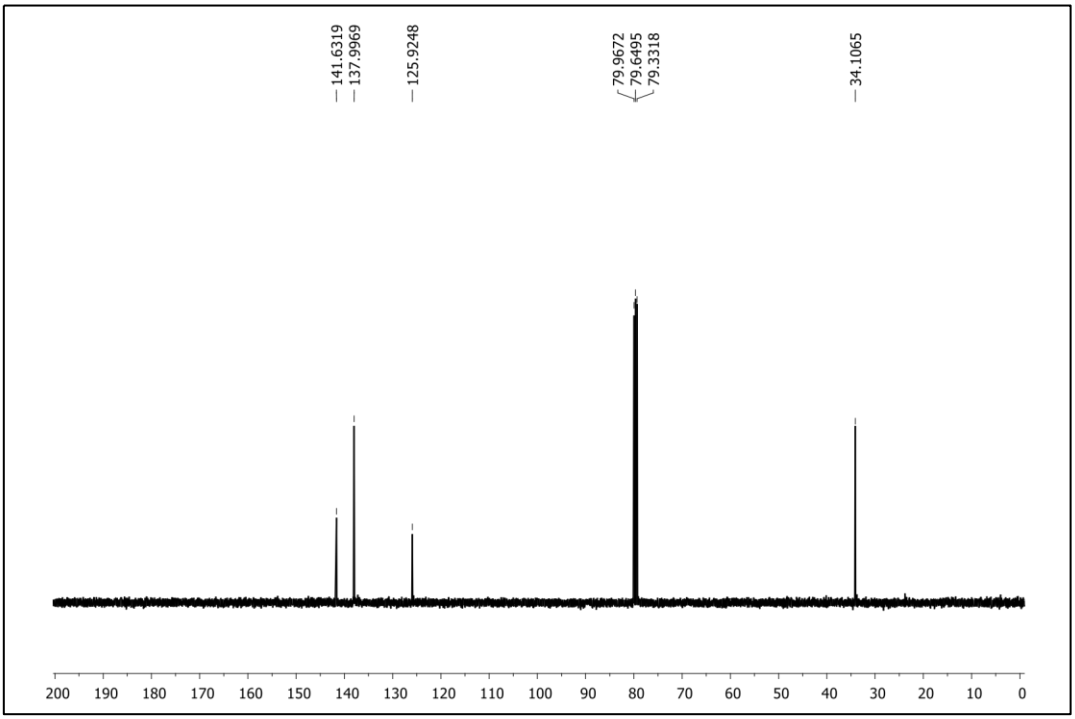
Figure S12b: Stern Volmer Plot of PPB



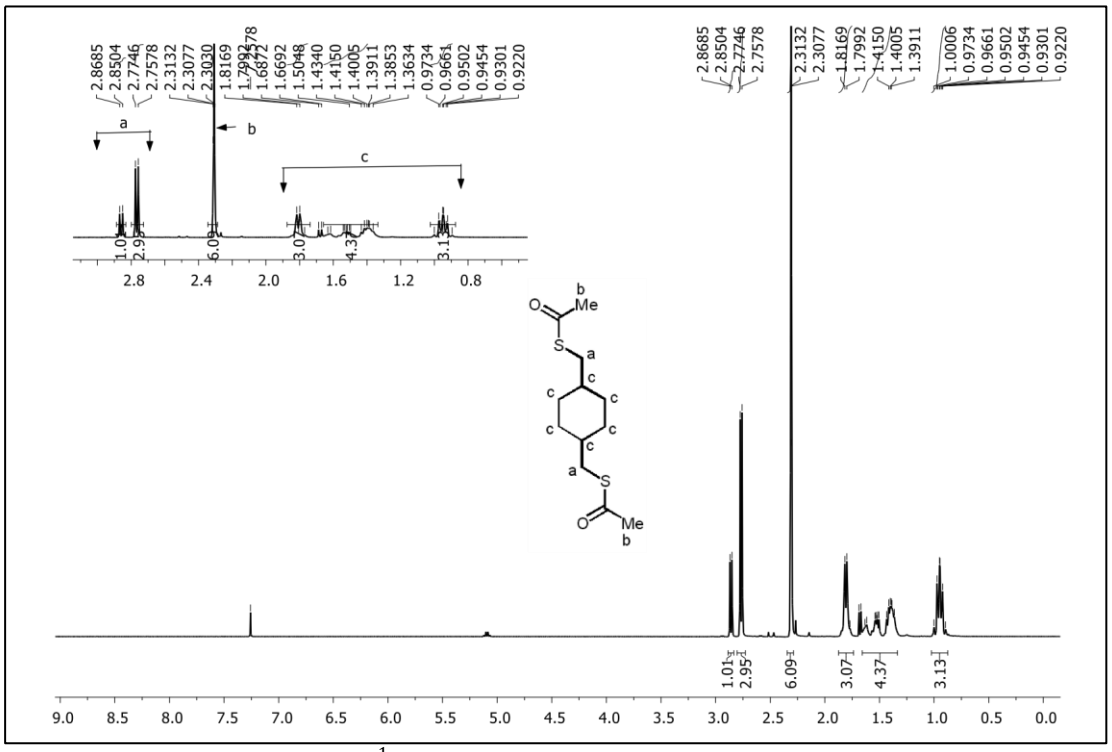
10.0 ^{1}H and ^{13}C NMR Spectra



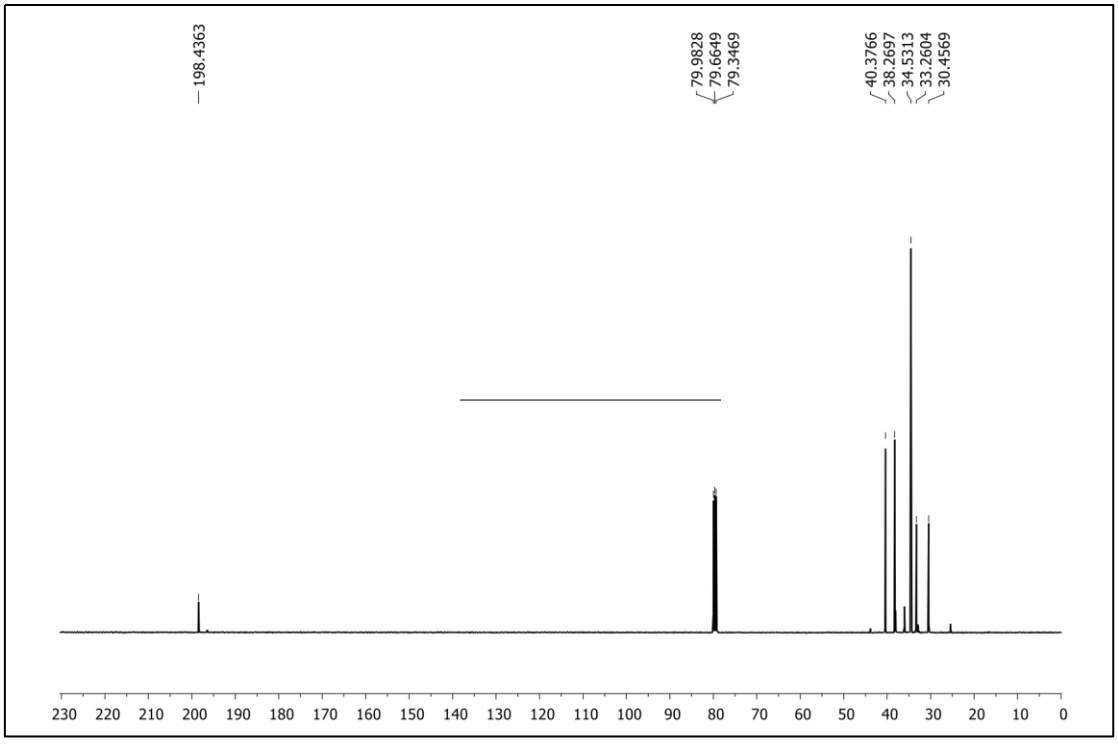
^{1}H NMR (400 MHz, $CDCl_3$) of 16



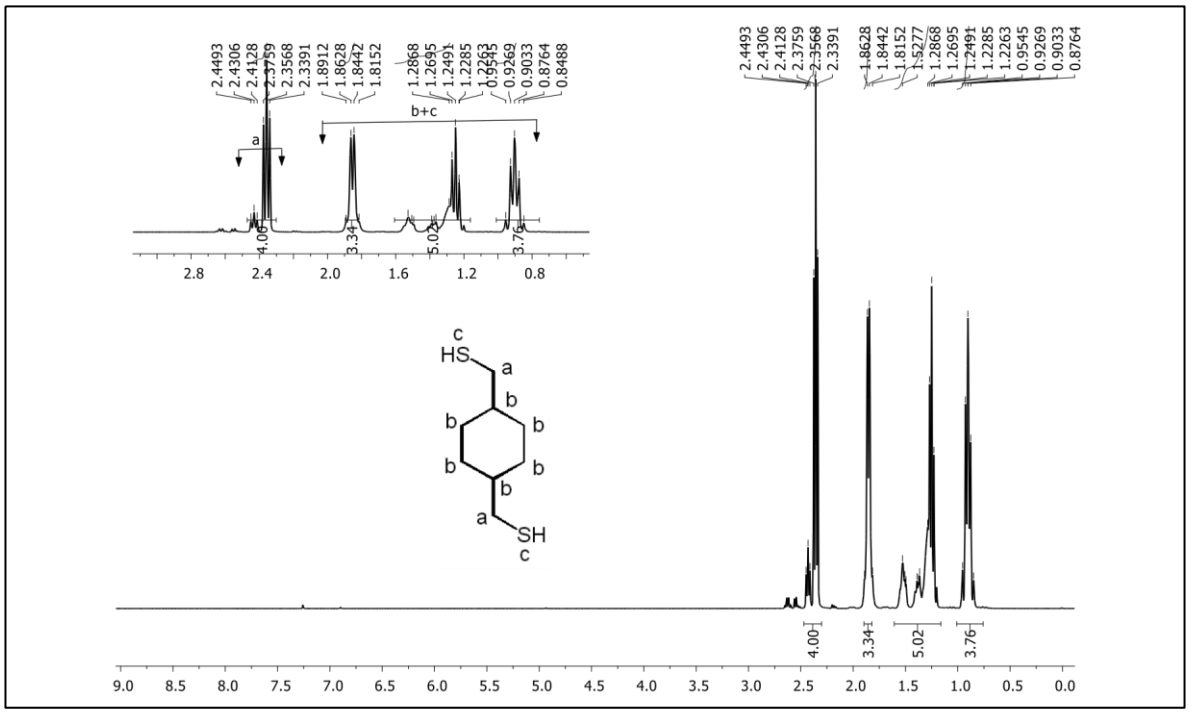
^{13}C NMR (100 MHz, $CDCl_3$) of 16



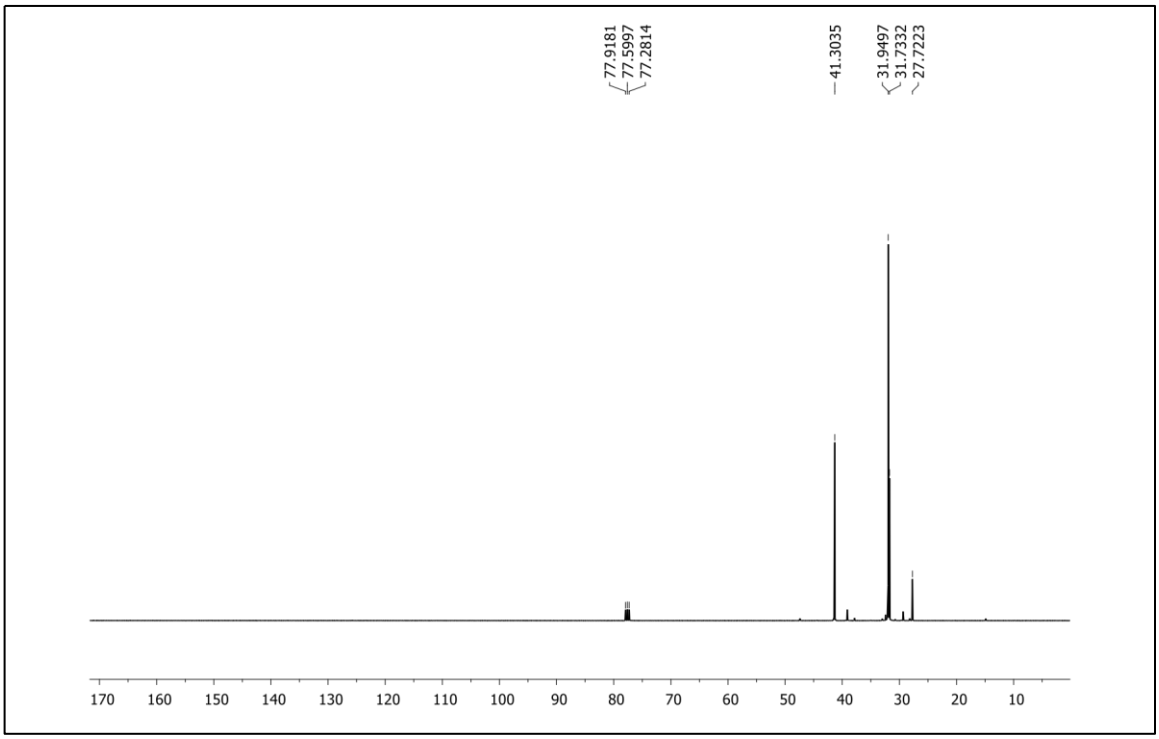
^{1}H NMR (400 MHz, $CDCl_3$) of 2



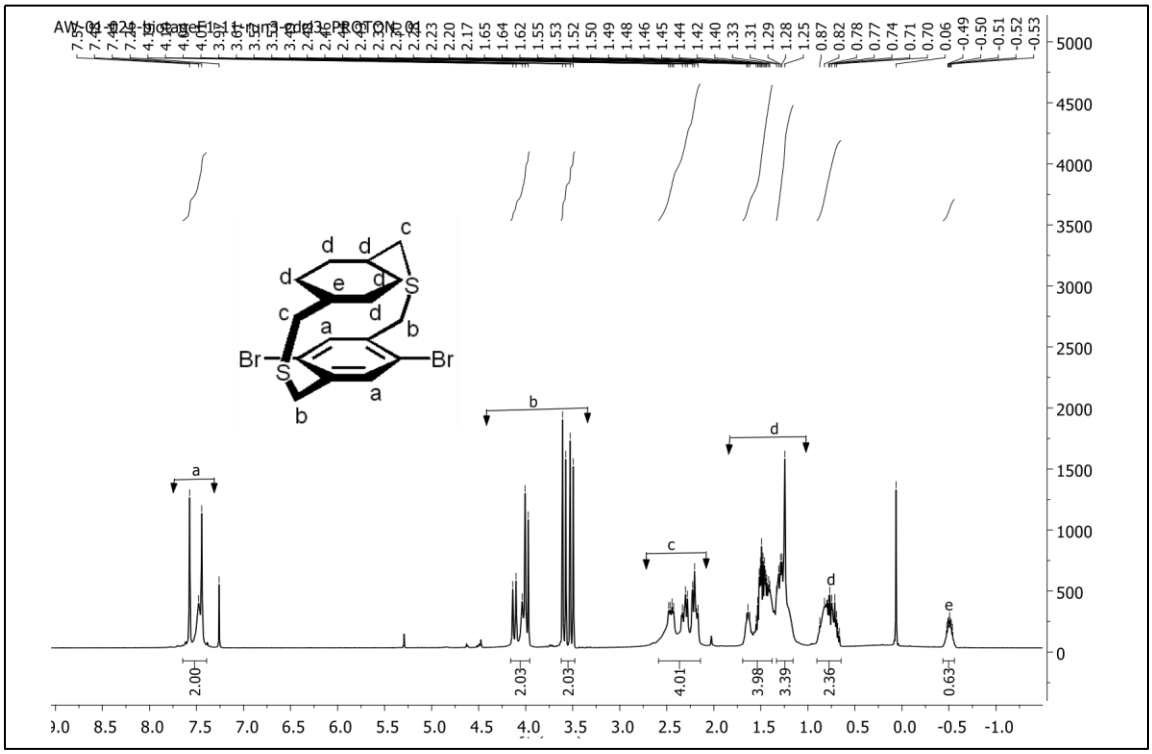
^{13}C NMR (100 MHz, $CDCl_3$) of 2



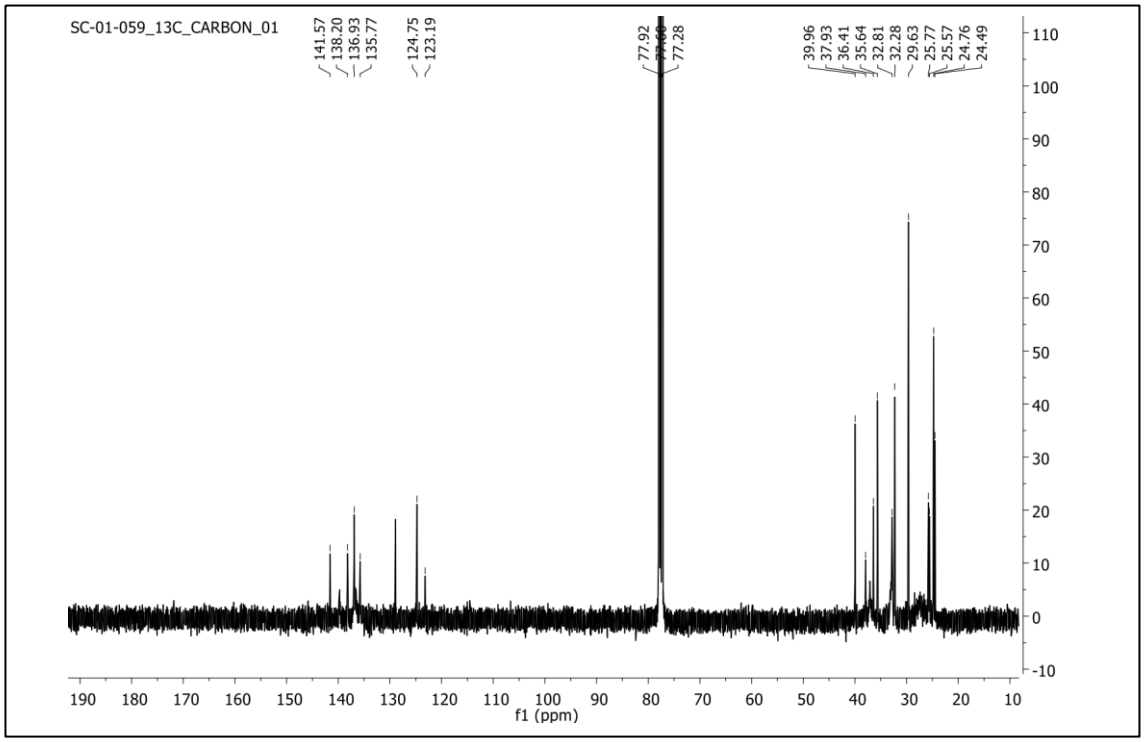
^{1}H NMR (400 MHz, $CDCl_3$) of 3



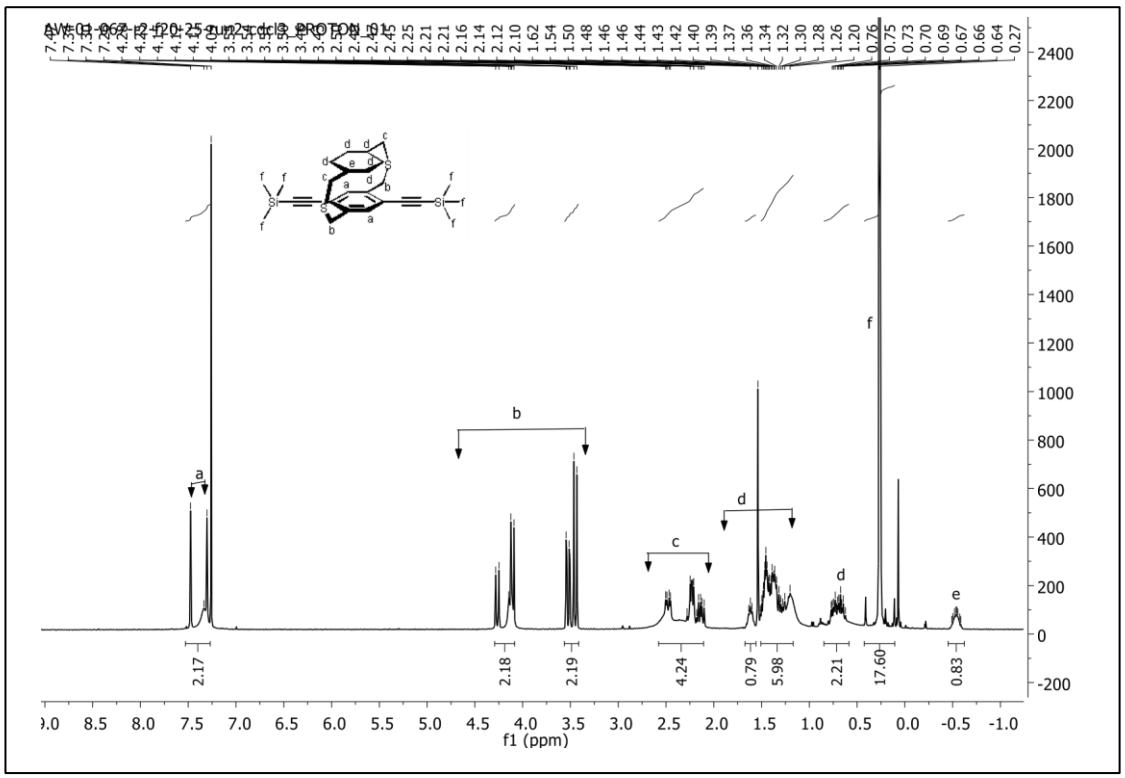
^{13}C NMR (100 MHz, $CDCl_3$) of 3



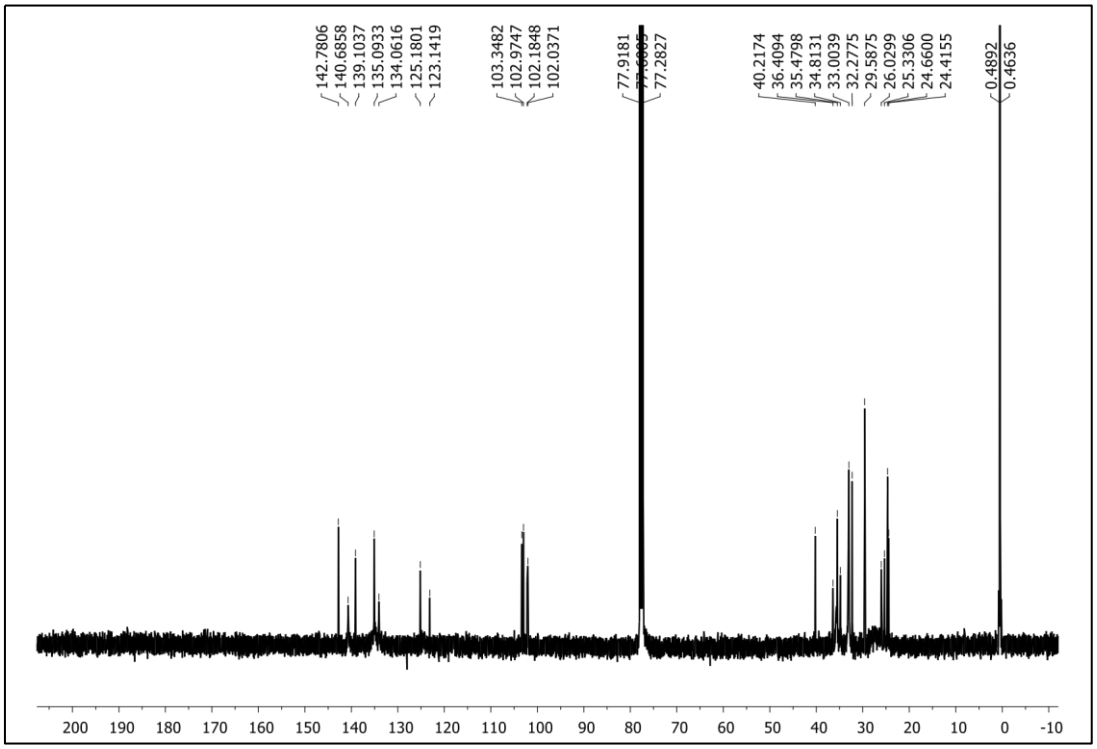
^{1}H NMR (400 MHz, $CDCl_3$) of 4



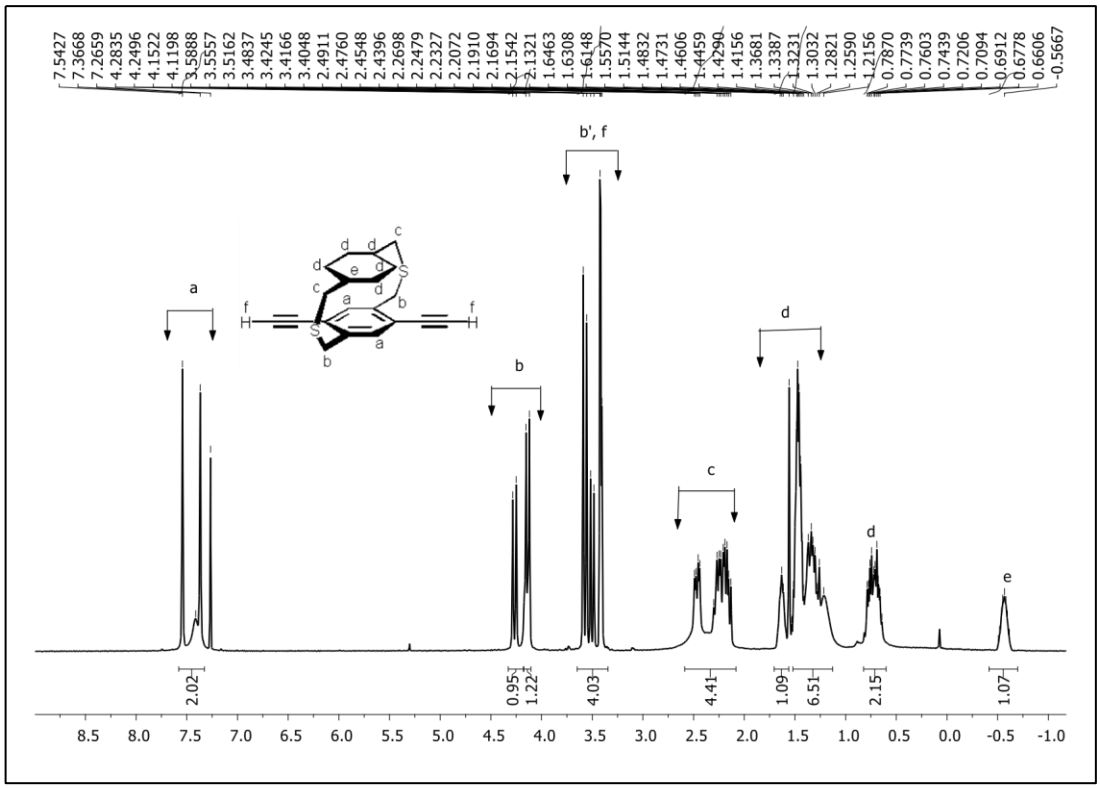
^{13}C NMR (100 MHz, $CDCl_3$) of 4



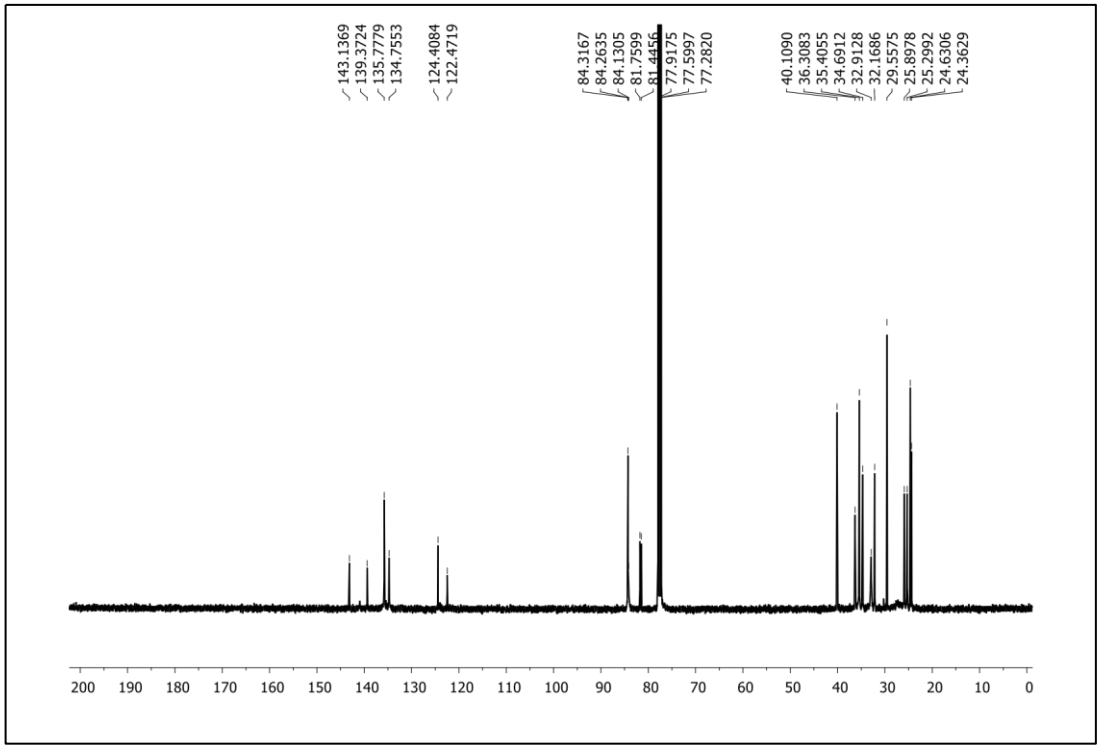
^{1}H NMR (400 MHz, $CDCl_3$) of 5



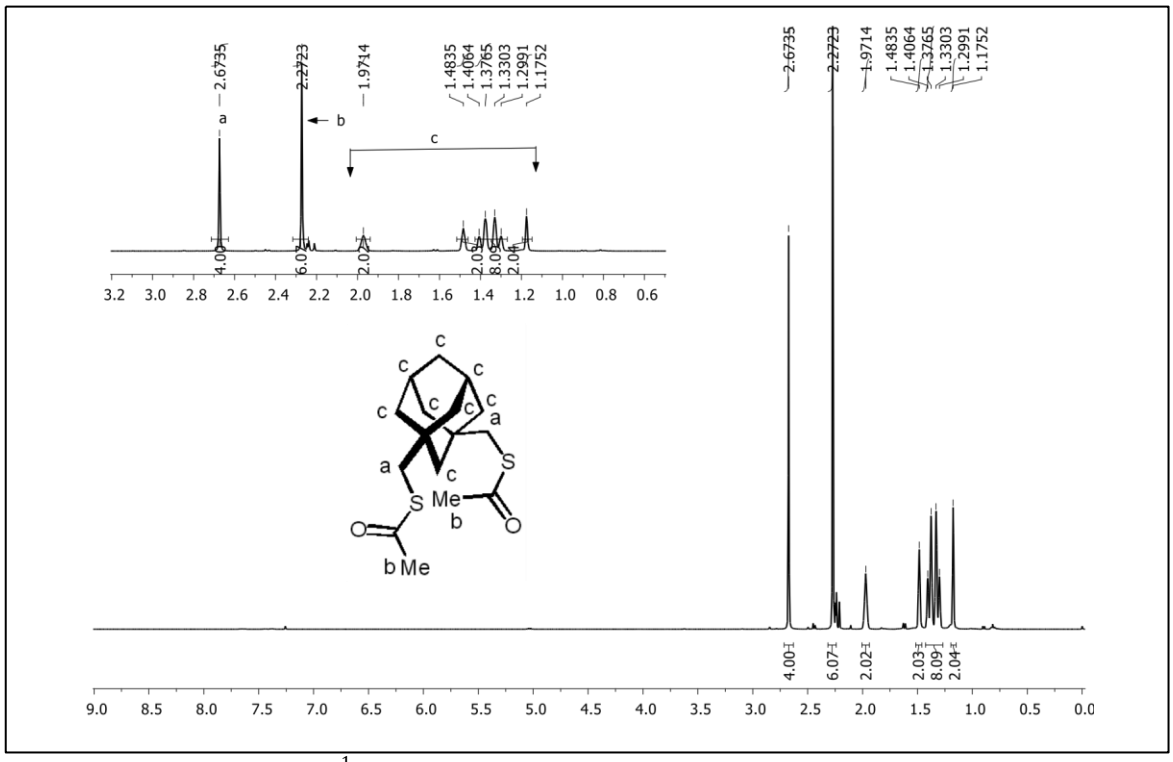
^{13}C NMR (100 MHz, $CDCl_3$) of 5



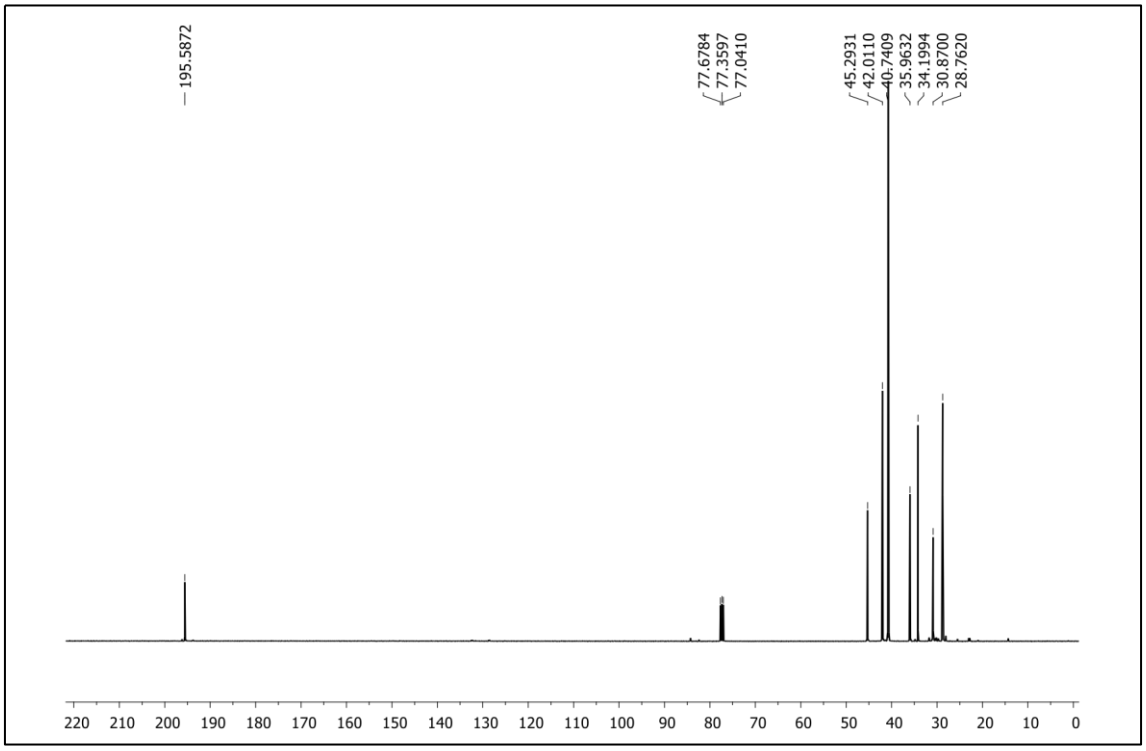
^{1}H NMR (400 MHz, $CDCl_3$) of 6



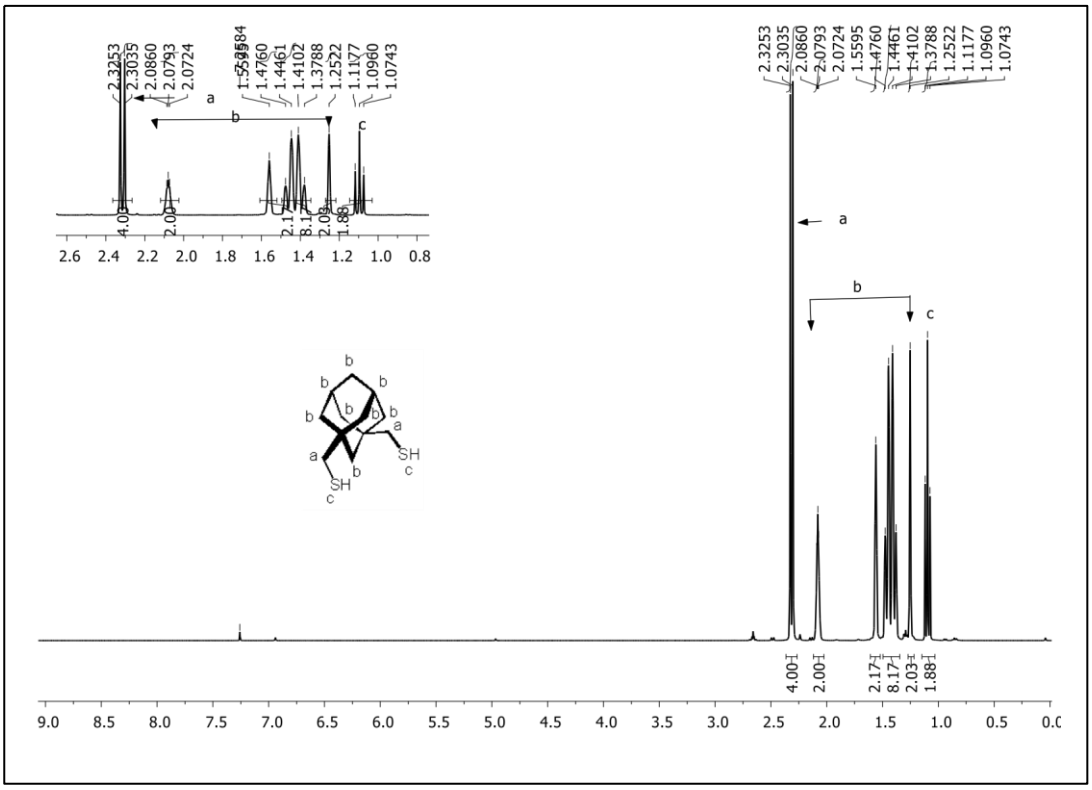
^{13}C NMR (100 MHz, $CDCl_3$) of 6



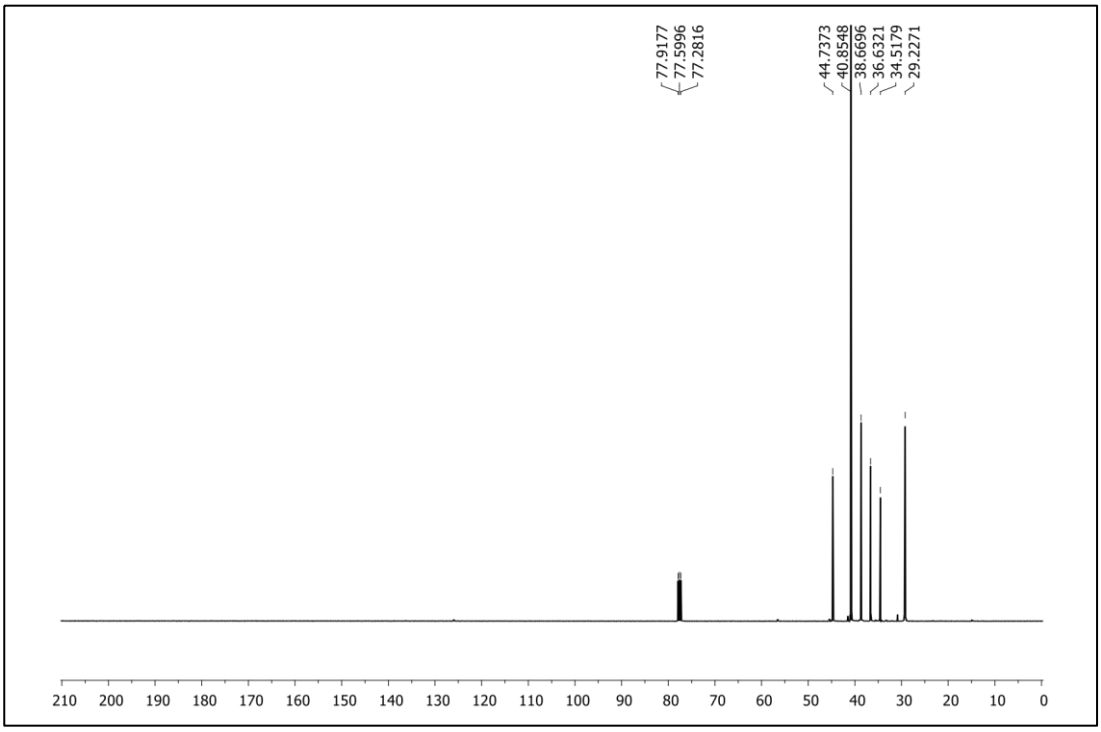
^{1}H NMR (400 MHz, $CDCl_3$) of 8



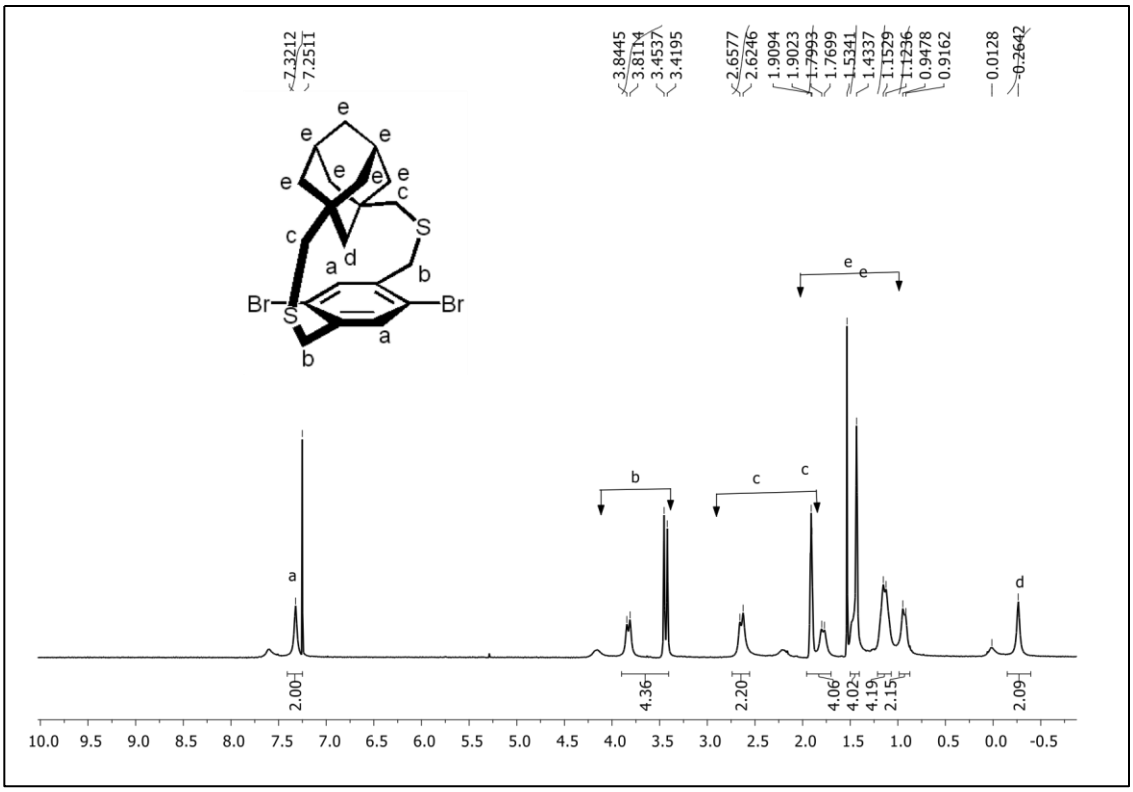
^{13}C NMR (100 MHz, $CDCl_3$) of 8



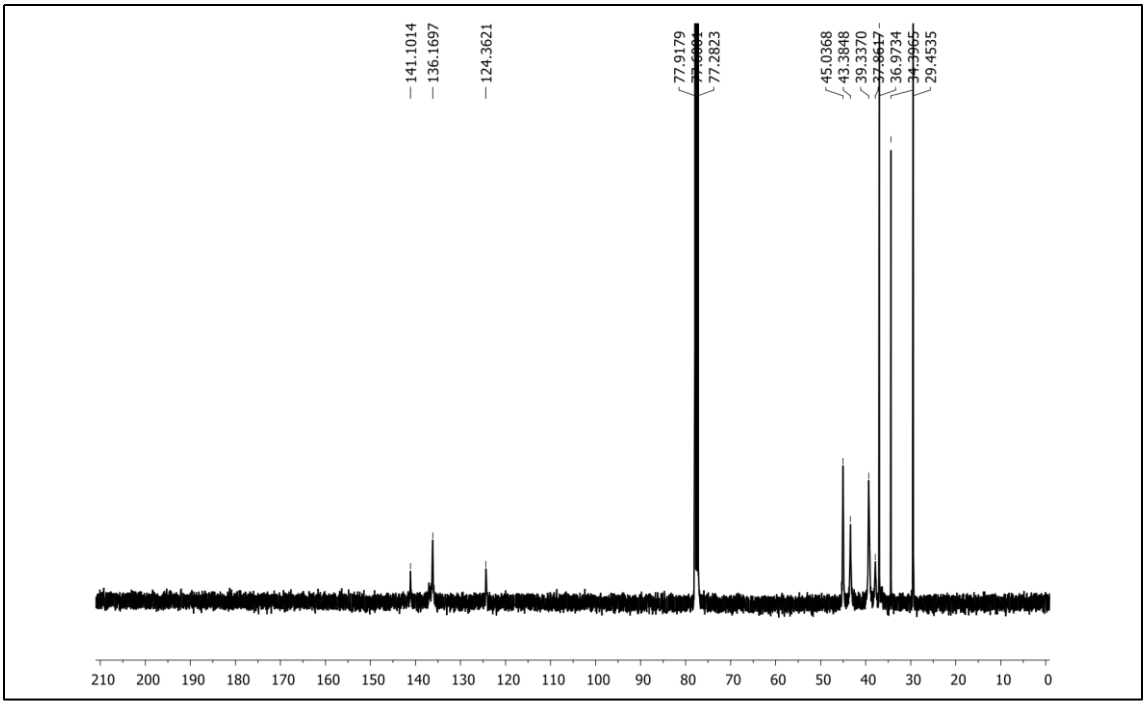
^{1}H NMR (400 MHz, $CDCl_3$) of 9



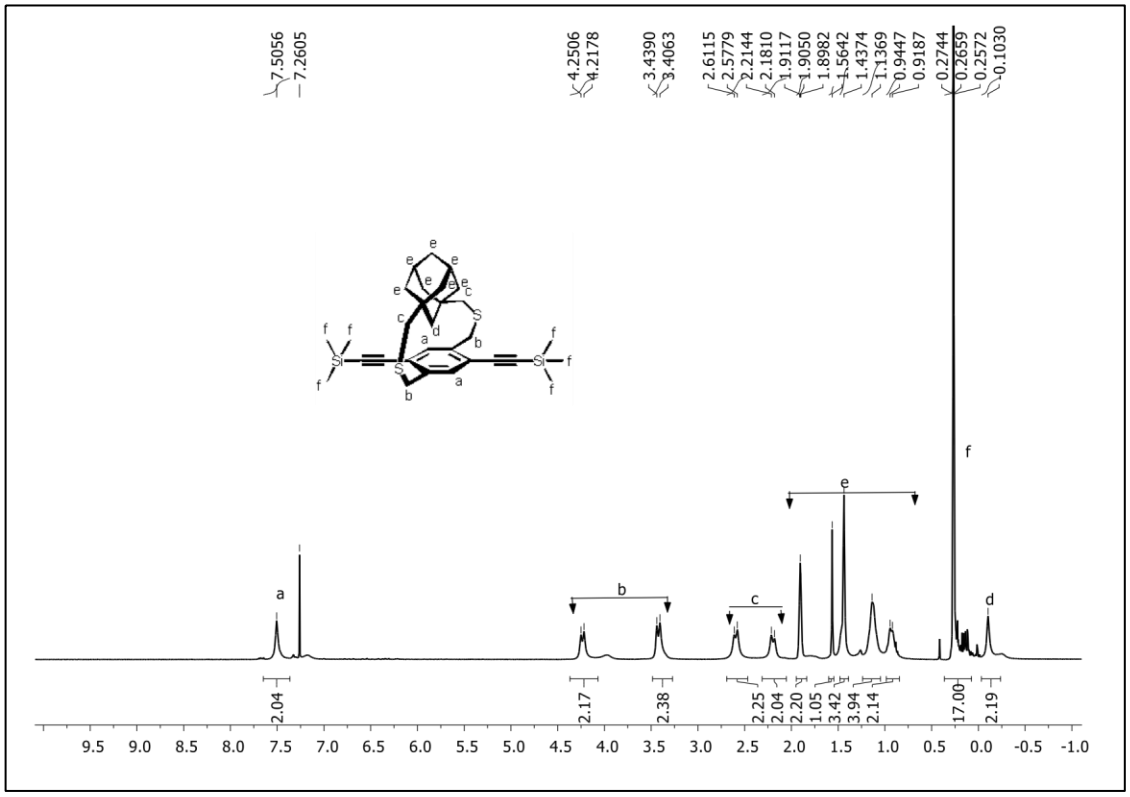
^{13}C NMR (100 MHz, $CDCl_3$) of 9



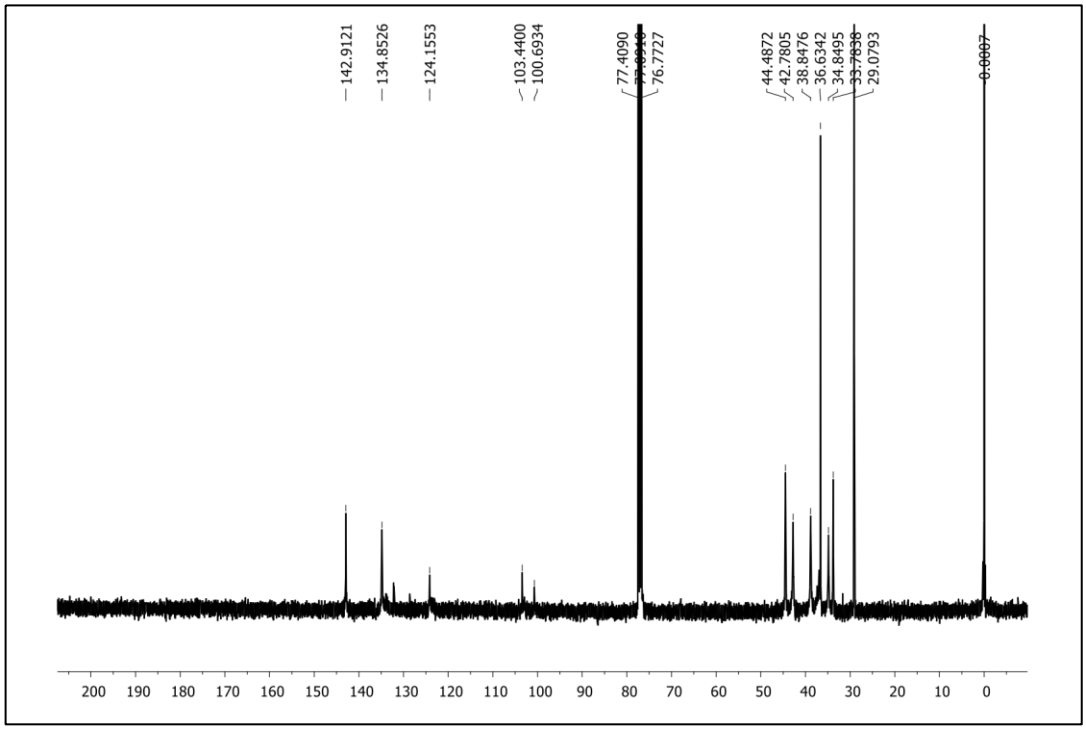
^{1}H NMR (400 MHz, $CDCl_3$) of 10



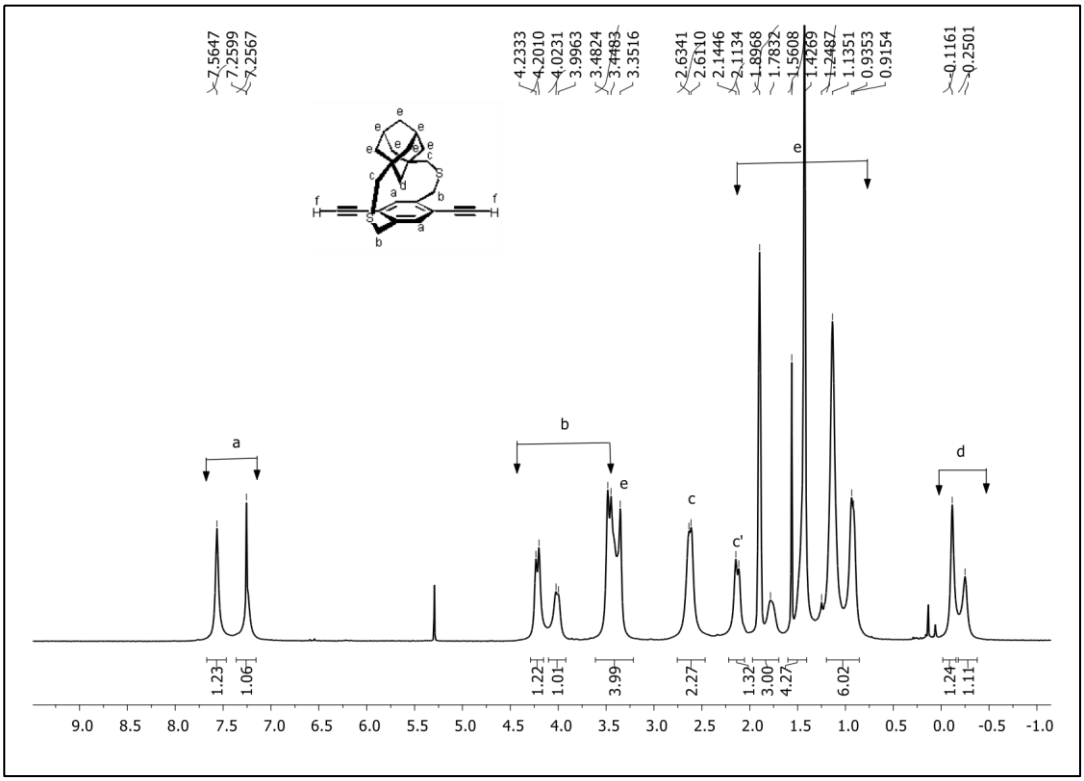
^{13}C NMR (100 MHz, $CDCl_3$) of 10



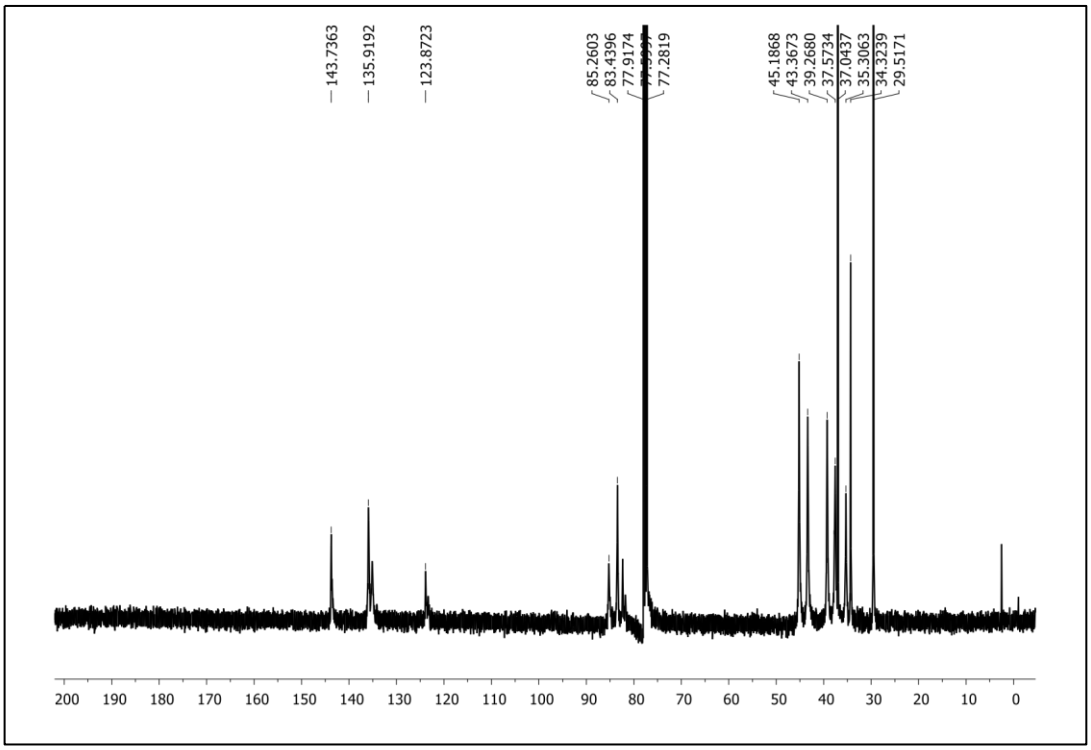
^{1}H NMR (400 MHz, $CDCl_3$) of 11



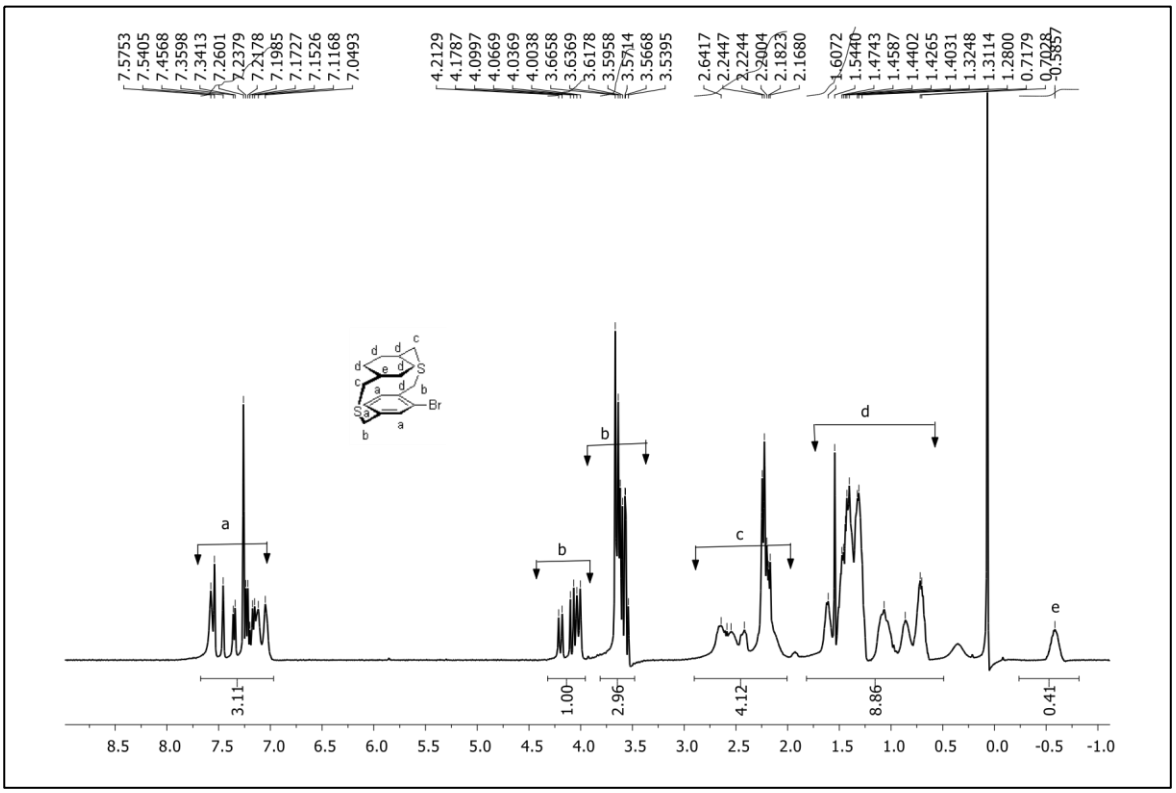
^{13}C NMR (100 MHz, $CDCl_3$) of 11



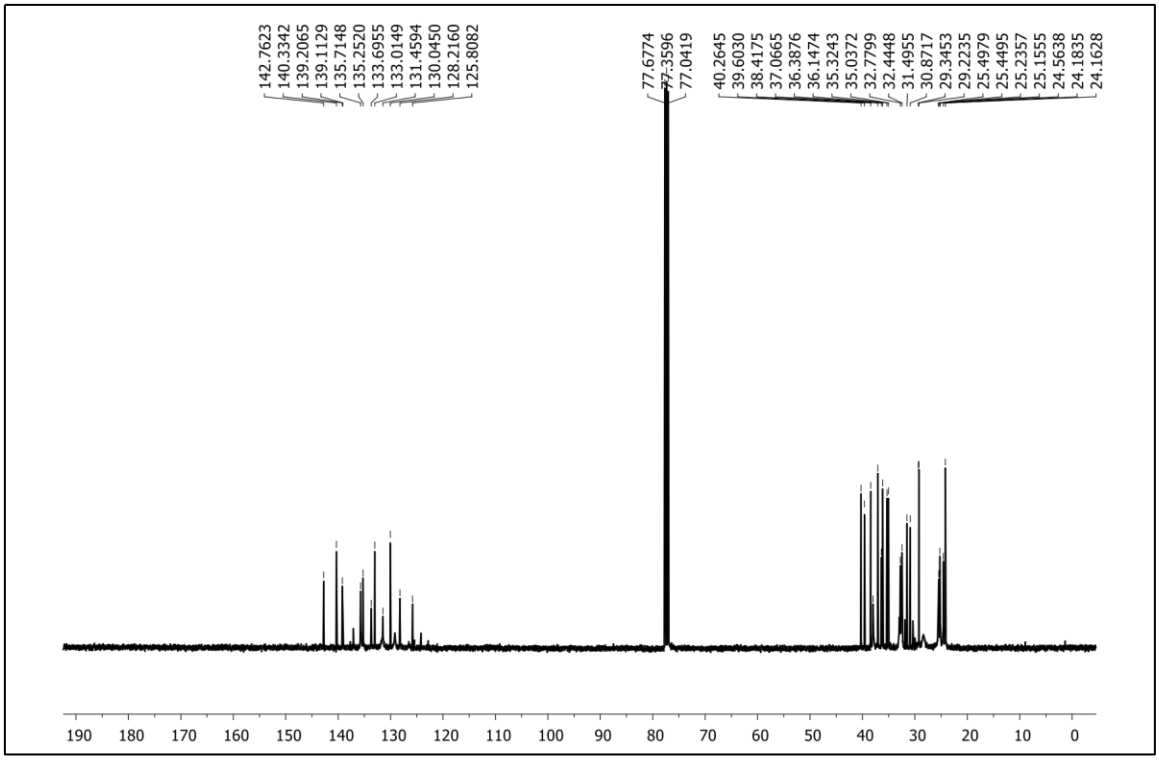
^{1}H NMR (400 MHz, $CDCl_3$) of 12



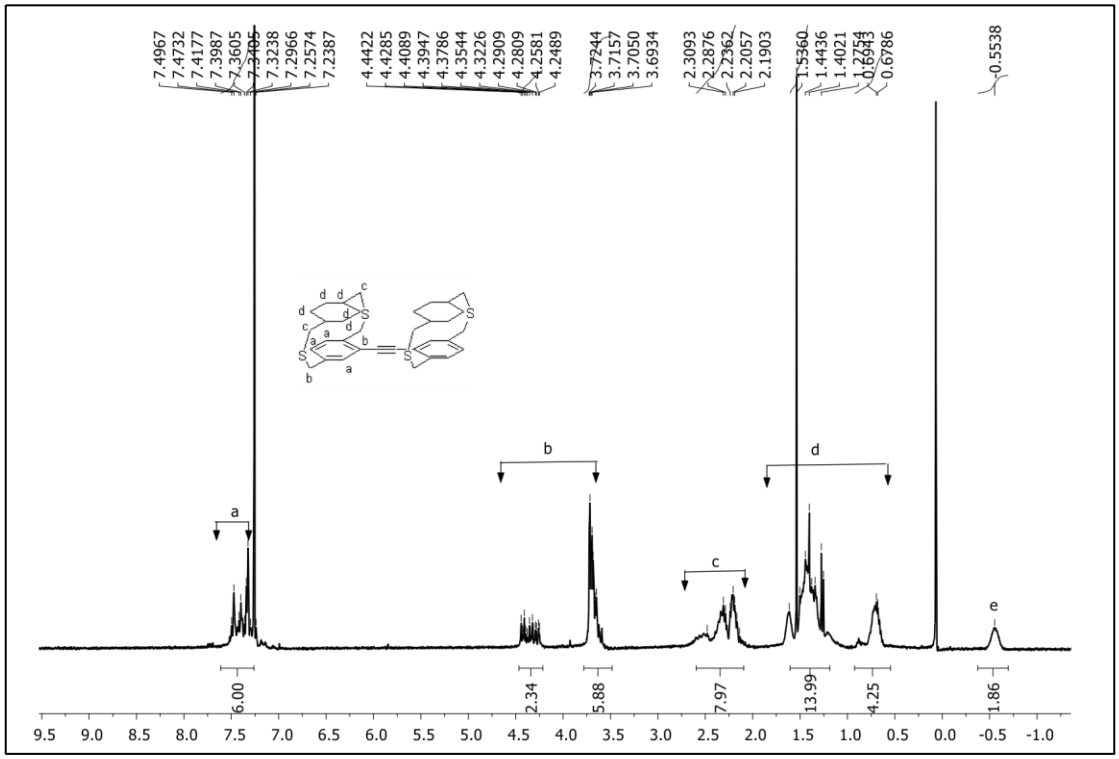
^{13}C NMR (100 MHz, $CDCl_3$) of 12



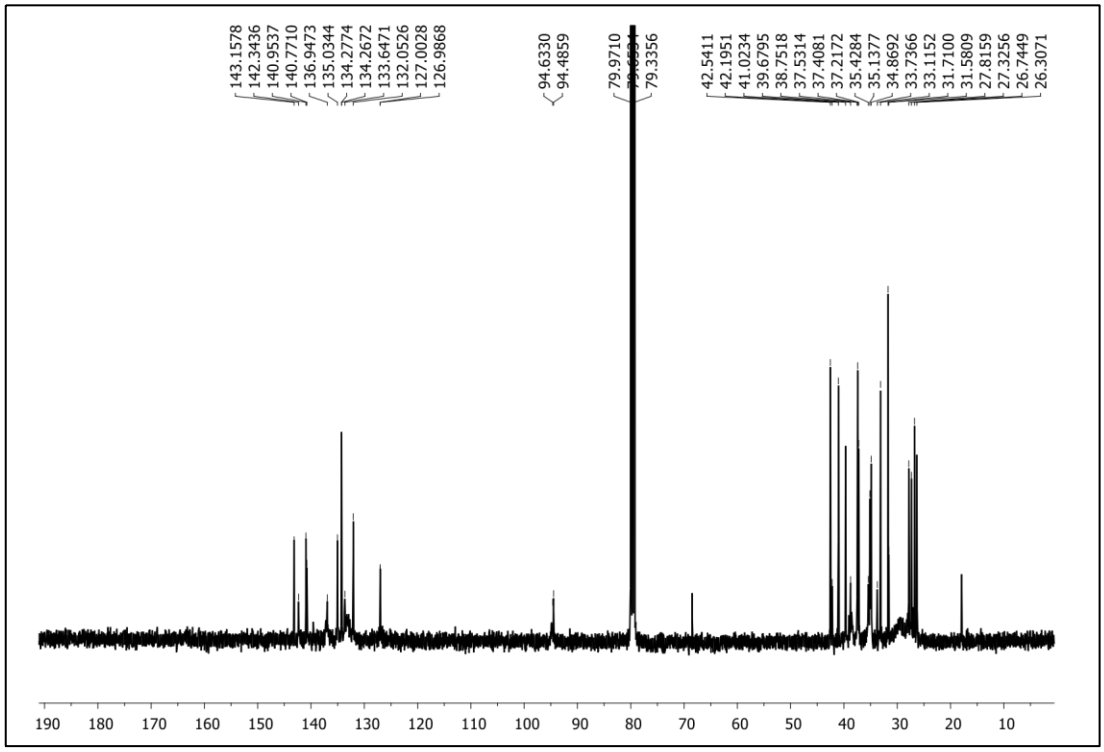
^{1}H NMR (400 MHz, $CDCl_3$) of 14



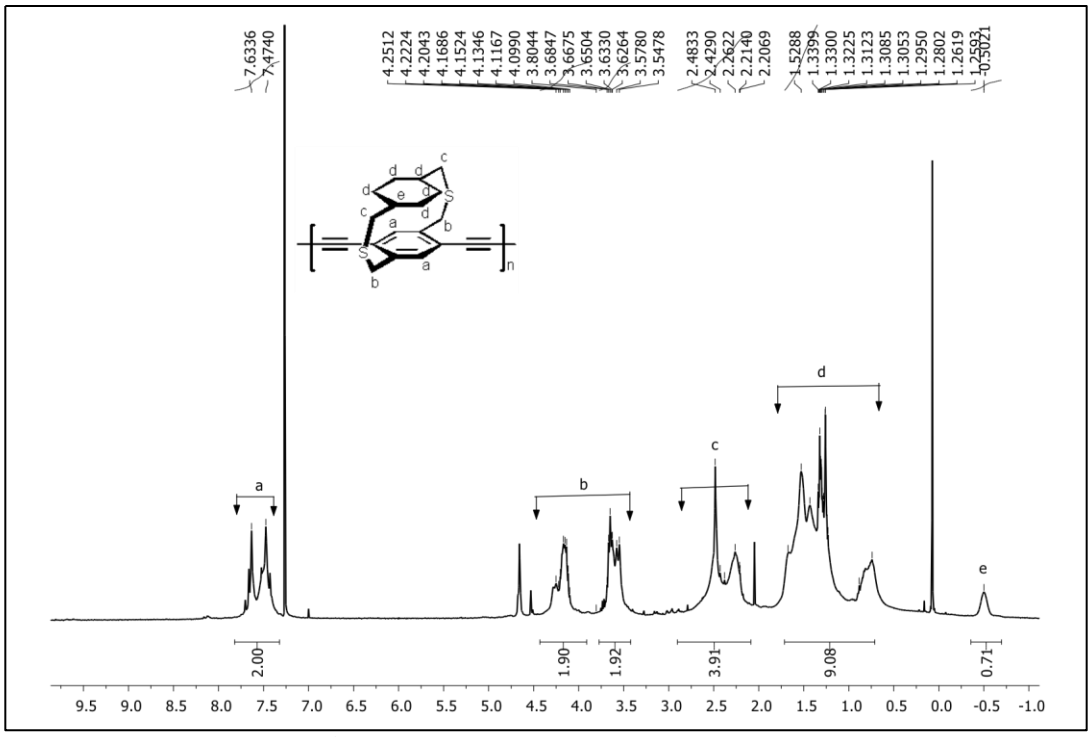
^{13}C NMR (100 MHz, $CDCl_3$) of 14



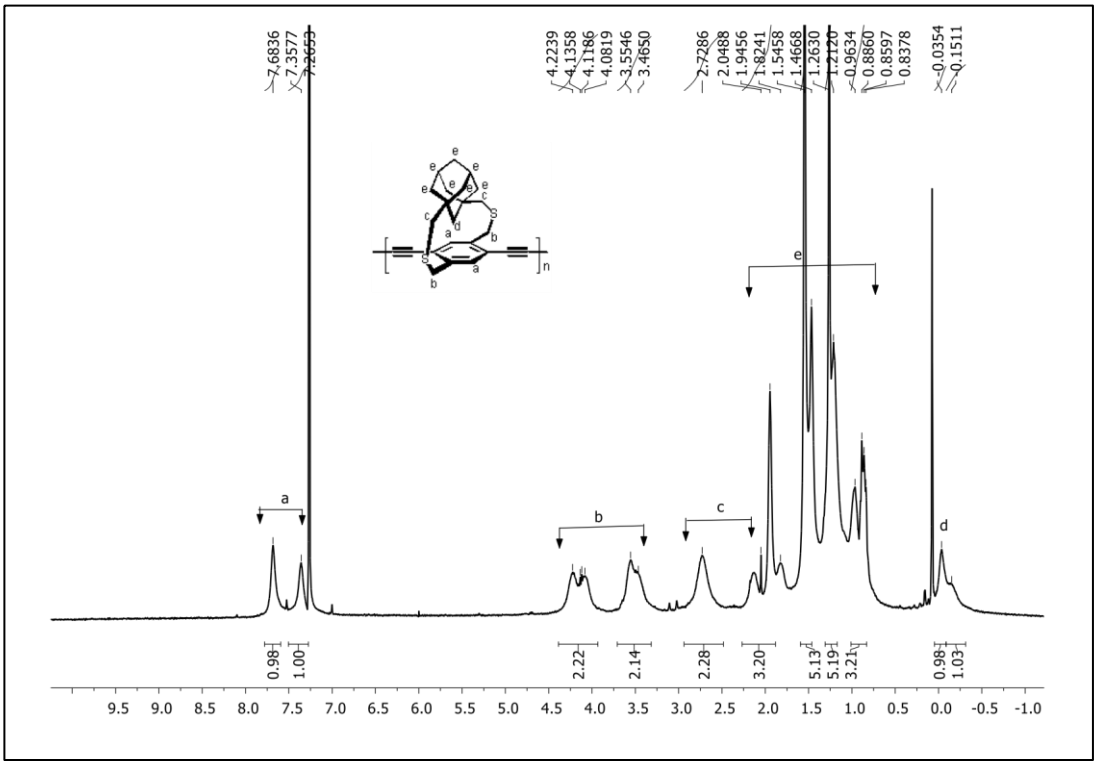
^{1}H NMR (400 MHz, $CDCl_3$) of 15



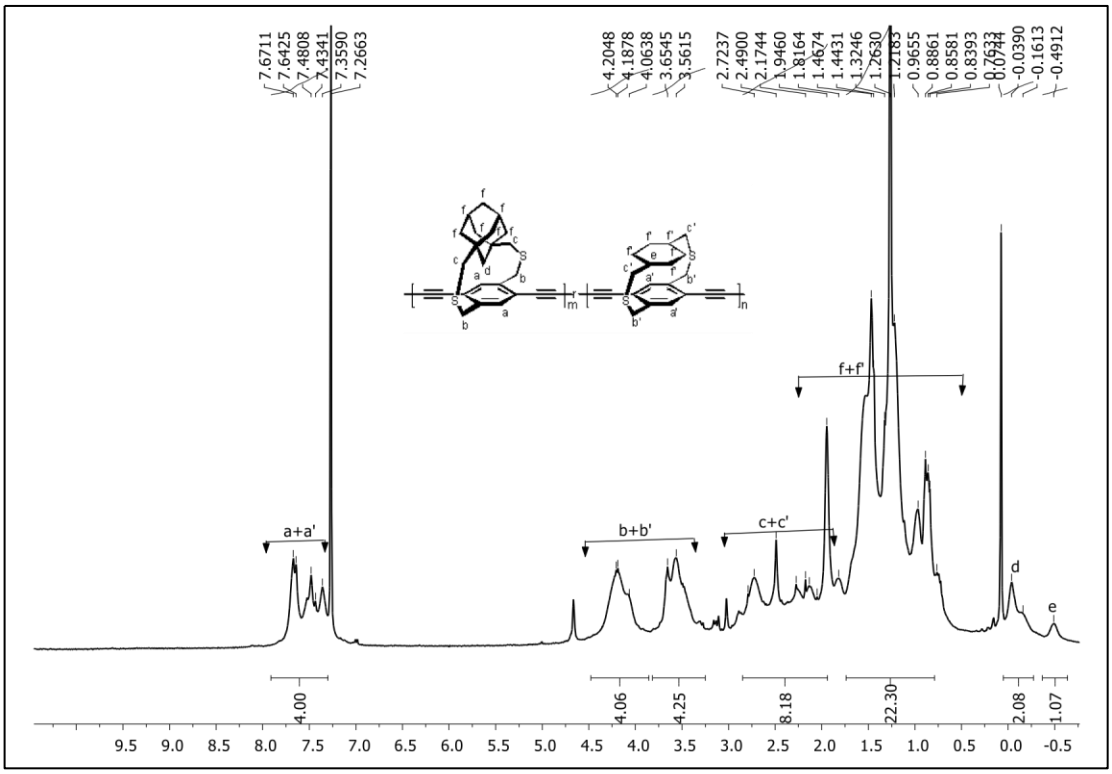
^{13}C NMR (100 MHz, $CDCl_3$) of 15



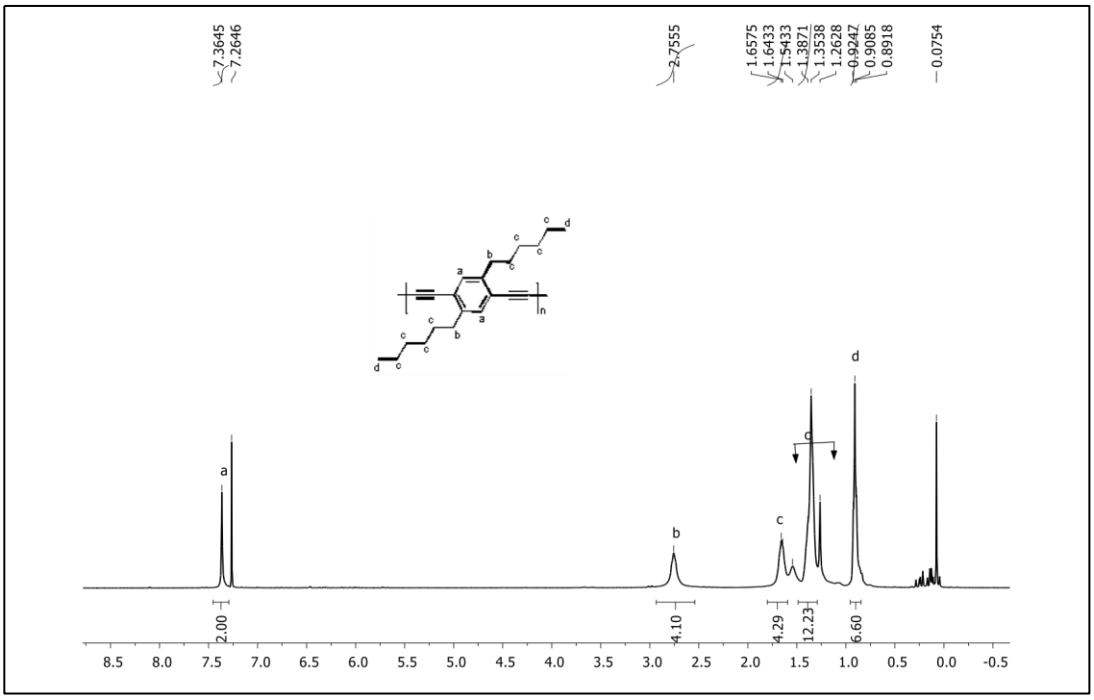
^{1}H NMR (400 MHz, $CDCl_3$) of BiP-1



^{1}H NMR (400 MHz, $CDCl_3$) of BiP-2a/2b



^{1}H NMR (400 MHz, $CDCl_3$) of BiP-3



^{1}H NMR (400 MHz, $CDCl_3$) of PPB

11.0 References and Note:

1. R. P. Volante, *Tetrahedron Lett.* 1981, **22**, 3119.
2. R. Lemmerz, M. Nieger, M, VÖgtle, *J. Chem. Soc., Chem. Commun*. 1993, 1168.