Supporting Information

Efficient Synthesis of Rigid Ladder Polymers via Palladium Catalyzed Annulation

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Experimental Section

Materials. All reagents were obtained from commercial venders and used as received unless otherwise noted. Dry toluene and THF were collected from dry solvent columns.

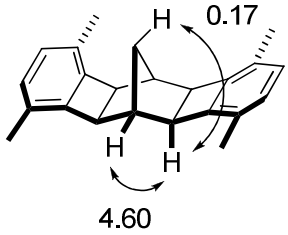
Characterizations. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Varian Mercury 400 or Varian Inova 300 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.26). High-resolution mass spectra were run on a GCT premier from Waters Technology with an Agilent 7890A GC and a DB-5MS column from Agilent. Gel permeation chromatography (GPC) was carried out in THF on two PolyPore columns (Agilent) connected in series with a DAWN multiangle laser light scattering (MALLS) detector and an Optilab T-rEX differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/d*c* values were obtained for each injection by assuming 100% mass elution from the columns. The TGA was measured under Ar atmosphere using Netzsch STA 449 with a heating rate of 2.5 °C/min to 800 °C. The BET (Brunauer–Emmett–Teller) were measured on a Surface Area and Porosity Analyzer (Micromeritics ASAP 2020).

I. Typical procedure for palladium catalyzed annulation of 2-bromo-1,4-dimethylbenzene and norbornadiene (NBD).

To a 15 mL glass tube was added palladium acetate (2.2 mg, 0.01 mmol) and triphenylphosphine (5.2 mg, 0.02 mmol). The tube was transferred into a glove-box, and

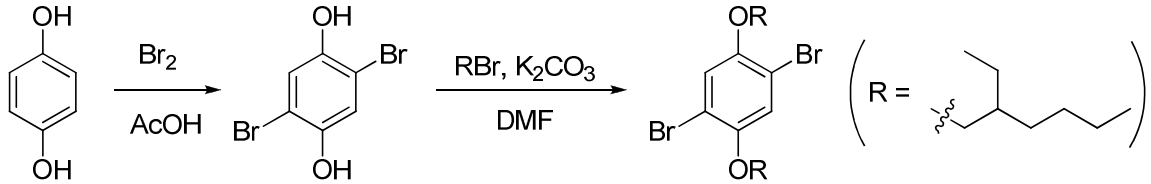
cesium carbonate (326 mg, 1 mmol), 5 mL toluene, 2-bromo-1,4-dimethylbenzene (185 mg, 1 mmol) and NBD (51 μL, 0.5 mmol) were added. The tube was then sealed with a Teflon valve and taken out of glove-box. The mixture was stirred at room temperature for 5 min, and then heated to 115 °C for 5 h. After that time, the mixture was cooled to room temperature and passed through a thin layer of Celite to remove inorganic salt. Filtered solution was rotovaped and ^{1}H NMR was taken on the crude mixture to determine conversion. Pure product 3 was purified by silica gel chromatography (eluted with Hexane) as a white crystal (> 95% yield under optimized conditions). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 4H), 3.33 (s, 4H), 2.49 (s, 2H), 2.28 (s, 12H), 0.87 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2, 129.1, 128.4, 47.8, 35.4, 26.4, 16.2. HRMS (Ammnia CI) *m/z* calcd for $C_{23}H_{28}N$ $[M+NH_4]^+$ = 318.2222, found 318.2234.

NOE (Figure S6) showed *exo*-isomer only:



II. Monomer Synthesis

(A) 1,4-dibromo-2,5-bis(2-ethylhexyloxy)benzene (4b) [CAS# 191867-85-3]



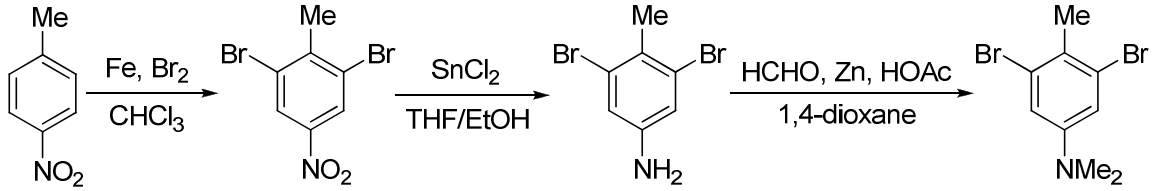
4b

2,5-dibromohydroquinone was synthesized according to a literature procedure.[1] In a 100 mL two-neck flask, hydroquinone (10 g, 0.09 mol) was dissolved in 90 mL glacial acetic acid. Bromine (9.2 mL, 0.18 mol) in 20 mL glacial acetic acid was then added

dropwise at 0 °C. After stirring for 4 h at 35 °C, most of acetic acid was removed under reduced pressure. The suspension was filtered, and the solid was washed with cold glacial acetic acid. Recrystallization from glacial acetic acid gave 2,5-dibromohydroquinone as a white solid (15.6 g, 65% yield).

1,4-dibromo-2,5-bis(2-ethylhexyloxy)benzene (4b) was synthesized according to a literature procedure.[2] A mixture of DMF (80 mL), anhydrous potassium carbonate (13.83 g, 0.1 mol), 2-ethylhexyl bromide (25 mL) and 2,5-dibromohydroquinone (13.4 g, 0.05 mol) was stirred and heated at 100 °C under a nitrogen atmosphere for 24 h. The mixture was cooled to 20 °C then filtered to remove the inorganic solid. The filtrate was rotovaped to remove DMF. The residue was purified by silica gel chromatography (eluted with Hexane) and concentrated to obtain **4b** as colorless oil (18 g, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 (s, 2H), 3.83 (d, J = 6.0 Hz, 4H), 1.79–1.71 (m, 2H), 1.54–1.32 (m, 16H), 0.93 (t, J = 7.5 Hz, 12H).

(B) 3,5-dibromo-*N*,*N*,4-trimethylaniline (4c) [CAS# 64230-12-2]



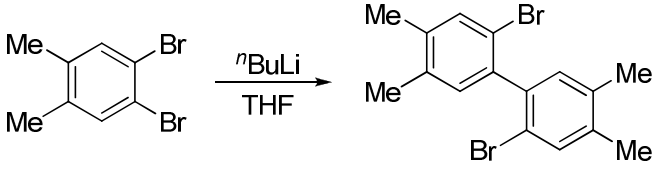
4c

1,3-dibromo-2-methyl-5-nitrobenzene was synthesized according to a literature procedure.[3] Bromine (42.0 g, 260 mmol) was added dropwise to a solution of *p*-nitrotoluene (10.0 g, 36.0 mmol) and iron powder (0.80 g, 14.1 mmol) in chloroform (20 ml) at 0 °C. The mixture was refluxed at 50 °C for 48 h. The reaction mixture was cooled to 0 °C and neutralized with a saturated aqueous sodium sulfite solution. After extraction with chloroform, the organic phase was washed with aqueous sodium carbonate solution (50 mL) and water (2×50 mL), dried over anhydrous sodium sulfate and concentrated. Distillation (100 °C/1 mmHg) under reduced pressure gave crude product, which was recrystallized from Hexane to give the pure 1,3-dibromo-2-methyl-5-nitrobenzene as a yellow crystal (13.1 g, 60% yield).

3,5-dibromo-4-methylaniline. 1,3-Dibromo-2-methyl-5-nitrobenzene (2.83 g, 9.6 mmol) was dissolved in THF/EtOH (25 mL/25 mL), and then $SnCl_2 \cdot 2H_2O$ (10.8 g, 47.9 mmol) was added. The mixture was stirred at room temperature for 3 h. After the solvent was removed, NaOH solution (6 g/50 mL) was added, and the mixture was stirred for 1.5 h. The solution was extracted with EtOAc (2×50 mL) and dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was obtained as a yellow solid, and was used without further purification in the next step.

3,5-dibromo-*N*,*N*,4-trimethylaniline (4c). A mixture of 3,5-dibromo-4-methylaniline, acetic acid (4.1 mL, 72 mmol), 37% aqueous formaldehyde (2.8 mL, 27 mmol), zinc dust (2.34g, 36 mmol) and 9 mL 1,4-dioxane was stirred at room temperature in a water bath. After completion of the reaction, a saturated aqueous NaOH solution (25 mL) was added. The mixture was extracted with ether (3×25 mL), and dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by silica gel chromatography (eluted with Hexane) and concentrated to obtain **4c** as a white solid (1.6 g, two steps, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 2H), 2.90 (s, 6H), 2.45 (s, 3H).

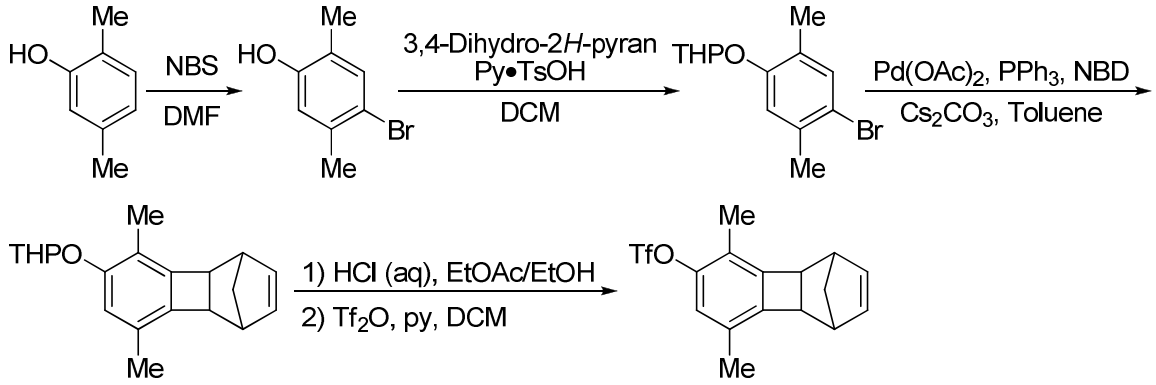
(C) 2,2'-dibromo-4,4',5,5'-tetramethylbiphenyl (4d) [CAS# 211434-29-6]



4d

2,2'-dibromo-4,4',5,5'-tetramethylbiphenyl (4d) was synthesized according to a literature procedure.[4] To a stirred solution of 1,2-dibromo-4,5-dimethylbenzene (5.28 g, 20 mmol) in dry THF (80 mL) was added n-butyllithium (6.25 mL, 1.6 M in Hexane, 10 mmol) at −78 °C. After the addition of n-butyllithium, the reaction mixture was stirred for 1 h at −78 °C. The reaction was allowed to warm to room temperature and stirred for another 1 h, and then was treated with aq. 5% HCl (50 mL). The organic layer was separated and the aqueous layer was extracted with ether (3×50 mL). The extracts were combined and dried over anhydrous Na_2SO_4. Recrystallization from absolute ethanol gave **4d** (4.9 g, 67% yield) as a white crystal. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (s, 2H), 7.02 (s, 2H), 2.31 (s, 6H), 2.26 (s, 6H).

(D) 5,8-dimethyl-6-trifluoromethanesulfonyloxy-1,4,4a,8b-tetrahydro-1,4-methano-biphenylene (4e)



4e

4-bromo-2,5-dimethylphenol was synthesized according to a literature procedure.[5] A solution of NBS (14.2 g, 80 mmol) in 50 mL of DMF was added dropwise to 2,5-dimethylphenol (10.0 g, 81.9 mmol) dissolved in 125 mL of DMF. The solution was stirred at room temperature overnight. Water (200 mL) was added to quench the reaction. Diethyl ether and 2 M HCl were added. The aqueous phase was extracted twice with diethyl ether. The combined organic phase was washed with 2 M HCl and then water. The organic extracts were dried over Na_2SO_4 and evaporated to yield an oil that solidified upon standing. The crude product was recrystallized from Hexane to yield 12 g (73%) of 4-bromo-2,5-dimethylphenol as needles.

2-(4-bromo-2,5-dimethylphenoxy)tetrahydro-2*H*-pyran was synthesized according to a literature procedure with minor modifications.[6] To 4-bromo-2,5-dimethylphenol (4.0 g, 20 mmol) in dichloromethane (120 mL), pyridinium *p*-toluenesulfonate (0.5 g, 2 mmol) and 3,4-dihydro-2*H*-pyran (5.5 mL, 60 mmol) were added, and the mixture was stirred at room temperature under nitrogen overnight. After removing the solvent, the residue was chromatographed through silica column (eluted with Hexane/EtOAc=100:1) and concentrated to obtain 2-(4-bromo-2,5-dimethylphenoxy)tetrahydro-2*H*-pyran as colorless oil (5.4 g, 95% yield).

5,8-dimethyl-6-(tetrahydro-2*H*-pyran-2-yloxy)-1,4,4a,8b-tetrahydro-1,4-methano-biphenylene. To a 50 mL glass tube was added palladium acetate (45 mg, 0.2 mmol), triphenylphosphine (106 mg, 0.4 mmol) and 2-(4-bromo-2,5-dimethylphenoxy)

tetrahydro-2*H*-pyran (1.43 g, 5 mmol). The tube was transferred into a glove-box, and cesium carbonate (1.63 g, 5 mmol), 25 mL toluene and NBD (1.38 g, 15 mmol) were added. The mixture was stirred at room temperature for 5 min, and then heated to 130 °C overnight. After the reaction was completed, the mixture was cooled to room temperature, and then passed through a thin layer of Celite to remove inorganic salt. Hexane (2×25 mL) was used to wash the residue. Combined organic solution was concentrated and purified by silica gel chromatography (eluted with hexane) to give 5,8-dimethyl-6-(tetrahydro-2*H*-pyran-2-yloxy)-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene as colorless oil (1.3 g, 90% yield).

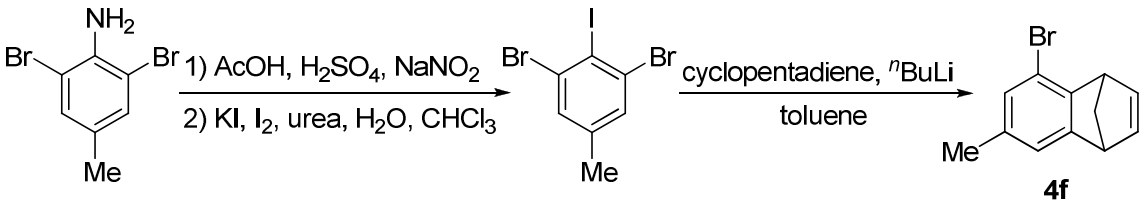
5,8-dimethyl-6-hydroxy-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene .

5,8-dimethyl-6-(tetrahydro-2*H*-pyran-2-yloxy)-1,4,4a,8b-tetrahydro-1,4-methano-biphenylene (870 mg, 2.9 mmol) was dissolved in a mixture of EtOAc (20 mL) and EtOH (5 mL) and then conc. HCl (0.5 mL) was added. The mixture was stirred at room temperature under nitrogen overnight. After removing the solvent, the residue was chromatographed through silica column (eluted with Hexane/EtOAc=20:1) and concentrated to obtain 5,8-dimethyl-6-hydroxy-1,4,4a,8b-tetrahydro-1,4-methano-biphenylene as a white solid (556 mg, 90% yield).

5,8-dimethyl-6-trifluoromethanesulfonyloxy-1,4,4a,8b-tetrahydro-1,4-methano-biphenylene (4e). 5,8-dimethyl-6-hydoxy-1,4,4a,8b-tetrahydro-1,4-methano-biphenylene (465 mg, 2.2 mmol) was dissolved in CH_2Cl_2 (10 mL), and pyridine (0.23 mL) was added. The mixture was kept at 0°C under nitrogen. After dropwise addition of triflic anhydride (0.45 mL, 2.6 mmol), the reaction mixture was stirred at room temperature overnight. Water (10 mL) was added to quench the reaction. Organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. After removing the solvent, the yellow oil was chromatographed through silica column (eluted with Hexane) and concentrated to obtain **4e** as colorless oil (580 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.25 (d, *J* = 1.5 Hz, 2H), 3.06 (dd, *J* = 4.0, 8.0 Hz, 2H), 2.81 (d, *J* = 1.5 Hz, 2H), 2.21 (s, 6H), 1.33 (d, *J* = 9.0 Hz, 1H), 0.83 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.8, 146.3, 144.0, 136.6, 136.4, 131.7, 122.6, 121.2, 45.5, 45.1, 41.4, 40.4,

40.4, 16.4, 11.3. HRMS (Ammnia CI) *m/z* calcd for $C_{16}H_{19}F_3NO_3S$ $[M+NH_4]^+$ = 362.1038, found 362.1032.

(E) 1,4-dihydro-5-bromo-7-methyl-1,4-methanonaphthalene (4f)



1,3-dibromo-2-iodo-5-methylbenzene was synthesized according to a literature procedure.[7] A solution of 4-Methyl-2,6-dibromoaniline (10 g, 38 mmol), glacial acetic acid (200 mL) and concentrated H_2SO_4 (40 mL) was slowly added to a mixture of $NaNO_2$ (6.9 g, 100 mmol), concentrated H_2SO_4 (50 mL), and glacial acetic acid (100 mL) at 0 °C. After addition, the mixture was stirred for another hours at 0 °C. The resulting mixture was then added to a freshly prepared solution of KI (34.7 g, 209 mmol), I_2 (48 g, 189 mmol), urea (4.6 g, 76 mmol), H_2O (400 mL), and $CHCl_3$ (100 mL), and was stirred at room temperature for overnight. Na_2SO_3 (46 g, 365 mmol) was added to quench the reaction. Organic phase was separated, and the aqueous phase was extracted with $CHCl_3$ (2×300 mL). The combined organic phases were washed with saturated Na_2CO_3 (300 mL), brine and dried over Na_2SO_4. Purification of the crude product by silica gel column chromatography (eluted with Hexane) afforded the pure product as a white solid (7.5 g, 84% yield).

1,4-dihydro-5-bromo-7-methyl-1,4-methanonaphthalene (4f) was synthesized according to a literature procedure with minor modifications.[8] 1,3-dibromo-2-iodo-5-methylbenzene (5.2 g, 13.8 mmol) and cyclopentadiene (4.5 g, 69.1 mmol) were stirred in toluene (60 mL) at 0 °C under nitrogen. To this solution was added *n*-BuLi (9.0 mL, 1.6 M in hexane, 14.5 mmol) dropwise over 12 min. After another 10 min at 0 °C, the mixture was allowed to warm to room temperature, and was treated with saturated aq. NH_4Cl solution (50 mL) and extracted with EtOAc (2×50 mL). The organic layer was dried over Na_2SO_4. Purification of the concentrated crude product by silica gel column

chromatography (eluted with Hexane) afforded **4f** as colorless oil (1.6 g, 49%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.89 (s, 1H), 6.86–6.78 (m, 2H), 4.00 (d, J = 39.0 Hz, 1H), 2.26 (s, 3H), 2.32–2.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 148.8, 143.1, 142.6, 136.2, 127.5, 121.7, 115.9, 69.1, 51.3, 50.5, 20.9. HRMS (Ammnia CI) *m/z* calcd for $C_{12}H_{11}Br$ $[M]^+$ = 234.0044, found 234.0040.

III. Palladium catalyzed ladder polymerization

Typical procedure. To a 15 mL glass tube was added palladium acetate (2.2 mg, 0.01 mmol) and triphenylphosphine (5.2 mg, 0.02 mmol). The tube was transferred into a glove-box, and cesium carbonate (326 mg, 1 mmol), 1 mL toluene, and monomer(s) (0.5 mmol) containing a trace amount of BHT were added. The tube was then sealed with a Teflon valve and taken out of glove-box. The mixture was stirred at room temperature for 5 min, and then heated to 115 °C for the desired time. After the polymerization was completed, the mixture was cooled to room temperature and passed through a thin layer of Celite to remove inorganic salt. THF (2×5 mL) was used to wash the residue. Filtered solution was rotovaped and ^{1}H NMR was taken on the crude mixture to determine conversion. The residual was then dissolved in THF, and EtOAc was added dropwise to the stirring solution to cause polymer precipitation. The precipitated polymer was collected and dried under vacuum, except for **poly(4b)**, which was difficult to precipitate. Model compounds **3d** and **3f** were synthesized in a similar fashion.

Poly(4a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (br, 4H), 2.25 (br, 2H), 2.02 (br, 6H), 0.67 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 124.0, 47.2, 35.8, 26.2, 12.0; GPC: M_n = 29,000 Da, PDI = 1.38.

Model compound **3a-Br$_2$** (isomers) were synthesized according to standard procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (s, 2H), 3.18 (dd, J = 3.6, 23.7 Hz, 4H), 2.35 (s, 2H), 2.18 (s, 6H), 2.14 (s, 6H), 0.75 (s, 2H).

Poly(4b). was purified by passing through a silica plug (eluted with Hexane/EtOAc first 20:1 and then 6:1) and isolated as a thick solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95 (br, 4H), 3.18 (br, 4H), 2.37 (br, 2H), 1.65 (br, 2H), 1.33 (br, 16H), 0.92 (br, 14H); ^{13}C NMR

(75 MHz, $CDCl_3$): δ 142.4, 130.6, 72.3, 49.1, 47.8, 39.7, 38.5, 30.4, 29.1, 23.7, 23.0, 14.1, 11.1; GPC: M_n = 13,000 Da, PDI = 1.34.

Poly(4a/b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.99 (br, 0.4H), 3.12 (br, 4H), 2.29 (br, 2H), 2.06 (br, 5.4H), 1.73 (br, 0.2H), 1.38 (br, 1.6H), 0.96 (br, 3.2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.2, 130.6, 123.9, 72.4, 48.8, 47.2, 39.5, 38.8, 35.8, 30.4, 29.1, 26.2, 23.7, 23.1, 14.2, 12.0, 11.1; GPC: M_n = 16000 Da, PDI = 1.58.

Poly(4c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (br, 4H), 2.94 (br, 6H), 2.28 (br, 2H), 1.96 (br, 3H), 0.88 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.0, 139.2, 127.4, 116.0, 49.7, 47.0, 41.5, 38.3, 25.4, 11.2; GPC: M_n = 36,000 Da, PDI = 1.36.

Poly(4d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (br, 2H), 3.63 (br, 2H), 3.45 (br, 2H), 2.57 (br, 2H), 2.43 (br, 6H), 2.24 (br, 6H), 0.95 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.5, 139.6, 136.0, 130.3, 129.4, 127.5, 49.1, 47.7, 35.9, 26.4, 20.1, 13.8; GPC: M_n = 13,000 Da, PDI = 1.66.

Model compound **3d** (isomers) were synthesized according to standard procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 2H), 3.24 (dd, J = 3.3, 55.8 Hz, 4H), 2.46 (s, 2H), 2.29 (s, 2H), 2.28 (s, 6H), 2.10 (s, 6H), 1.65–1.62 (m, 4H), 1.25–1.23 (m, 4H), 0.96 (s, 4H).

Poly(4e). ^{1}H NMR and ^{13}C NMR are the same as **poly(4a)**; GPC: M_n = 12,000 Da, PDI = 1.28.

Poly(4f). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (br, 1H), 3.35 (br, 4H), 2.33 (br, 3H), 1.71 (br, 1H), 1.37 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.8, 140.8, 138.4, 137.0, 128.3, 121.6, 48.3, 43.1, 40.1, 16.8; GPC: M_n = 14,000 Da, PDI = 1.28.

Model compound **3f** (isomers) were synthesized according to standard procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (s, 1H), 7.00 (s, 1H), 6.96 (s, 1H), 6.77 (br, 2H), 3.95–3.81 (m, 2H), 3.51–3.22 (m, 4H), 2.31–2.17 (m, 7H), 1.69–1.56 (m, 1H), 1.37–1.23 (m, 2H).

IV. Figures and Spectra

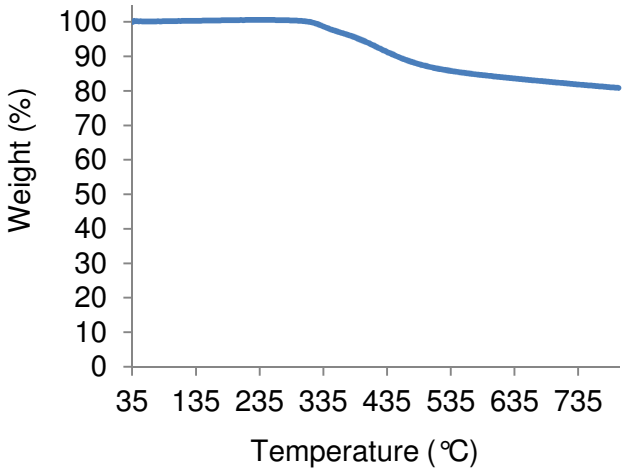


Figure S1. TGA trace of **poly(4a)** measured under Ar atmosphere with a heating rate of 2.5 °C/min to 800 °C. Thermal degradation starts at 315°C with 14% mass loss between 315 and 496 °C, and 5% mass loss between 496 and 800 °C.

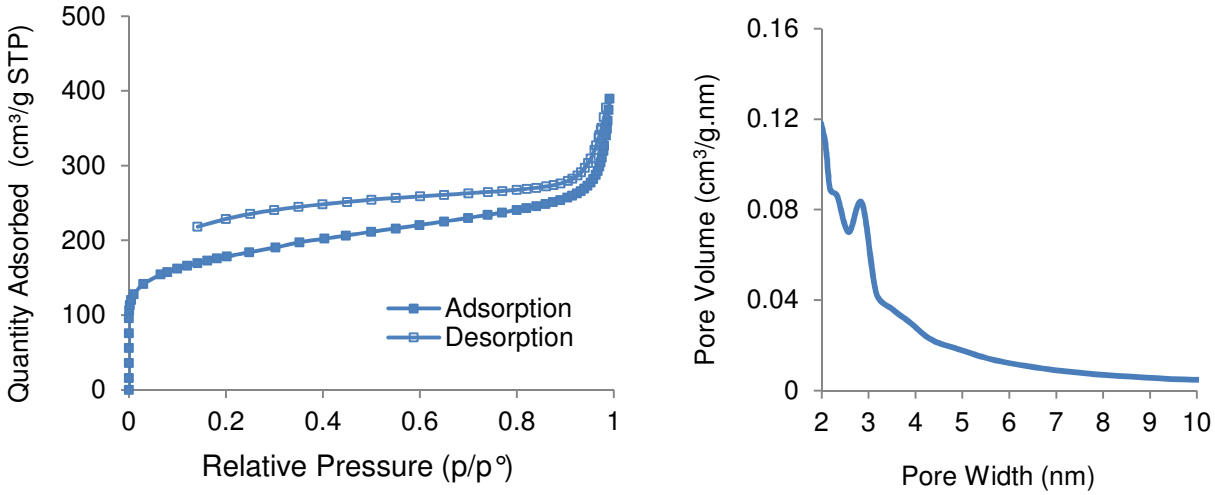


Figure S2. N_2 adsorption and desorption isotherms for **poly(4a)** at 77 K. The BET analysis of the surface area gives 620 m^2 g^{-1} and total pore volume of 0.56 cm^3 g^{-1}. t-Plot Micropore Area 270 m²/g and t-Plot External Surface Area 350 m²/g.

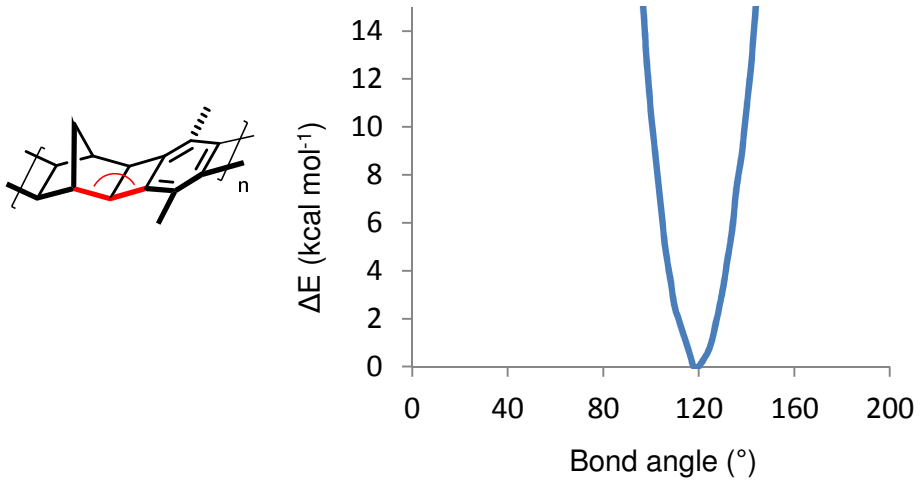


Figure S3. DFT calculation (B3LYP/6-31G*) of the energy barrier for bending of the highlighted bond in BCB ladder polymer linkage. Calculation was performed by fixing other bond angles in the optimized structure and only varying the highlighted bond angle from 92 to 146° at 2° increments.

^{1}H NMR and ^{13}C NMR spectra of small molecules and polymers

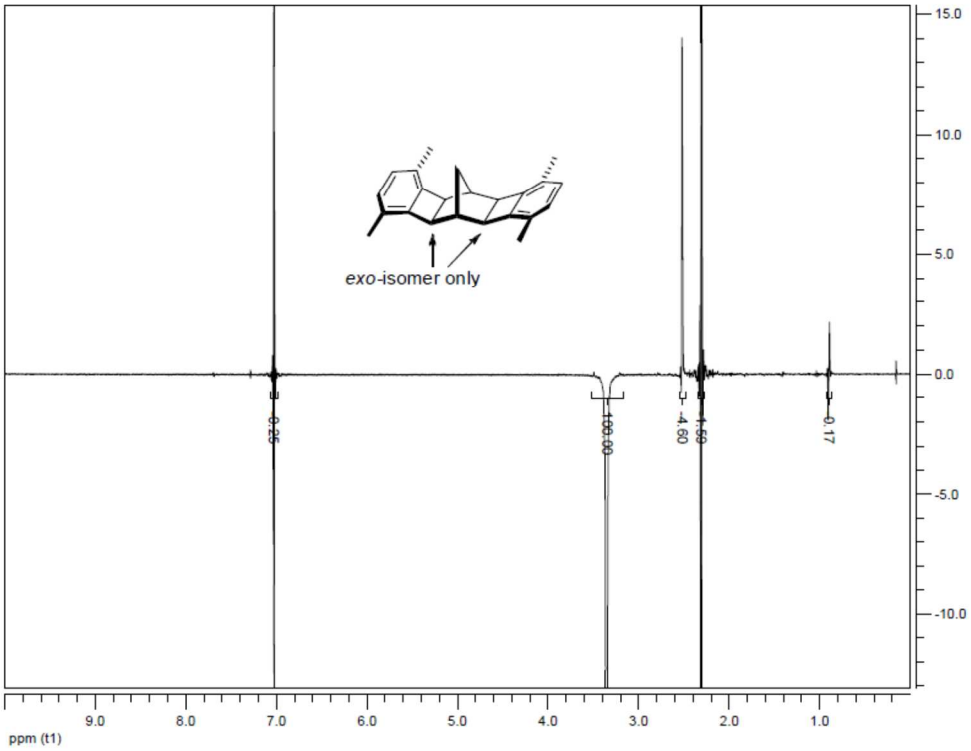


Figure S4. NOE spectrum of **3**

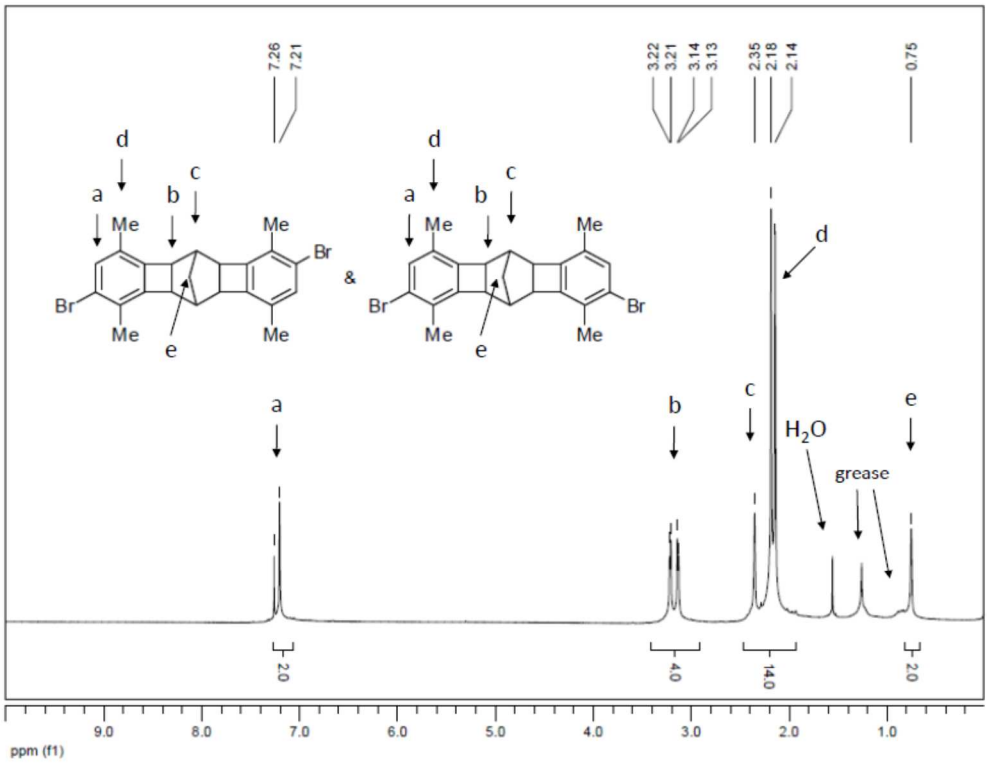


Figure S5. ^{1}H NMR spectrum of model compound **3-Br$_2$** (exist in regioisomers)

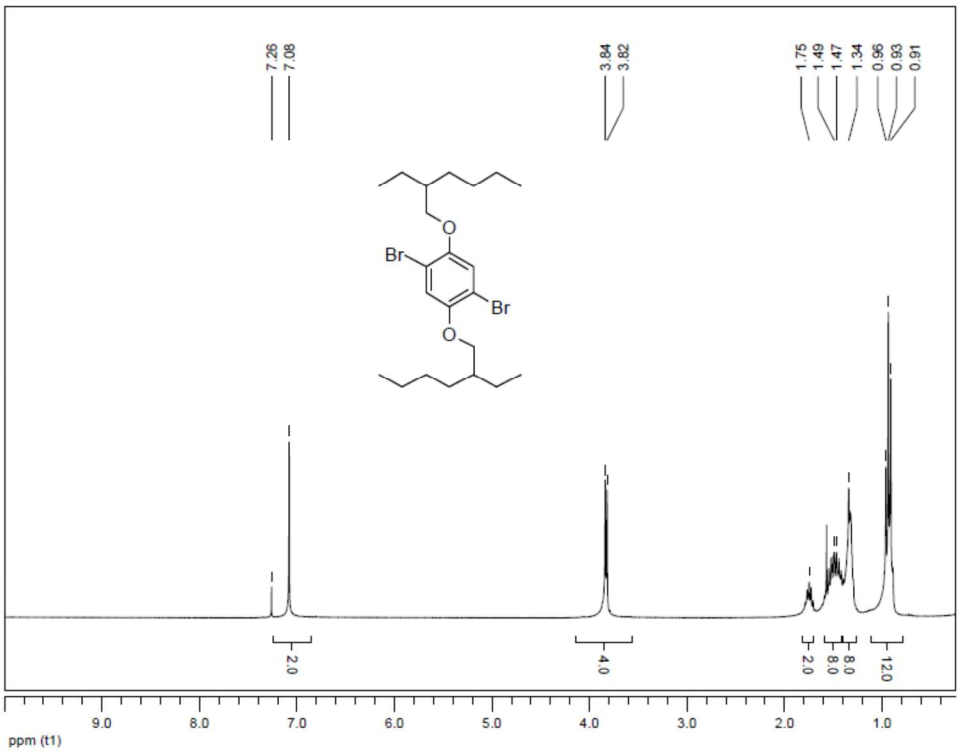


Figure S6. ^{1}H NMR spectrum of **4b**

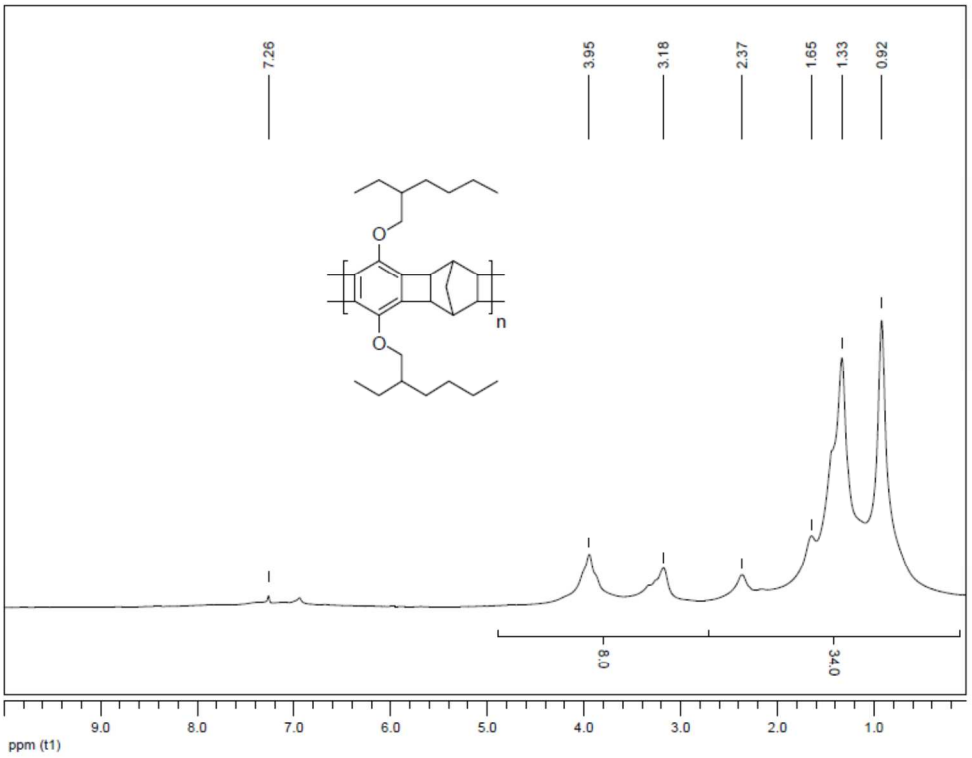


Figure S7. ^{1}H NMR spectrum of **poly(4b)**

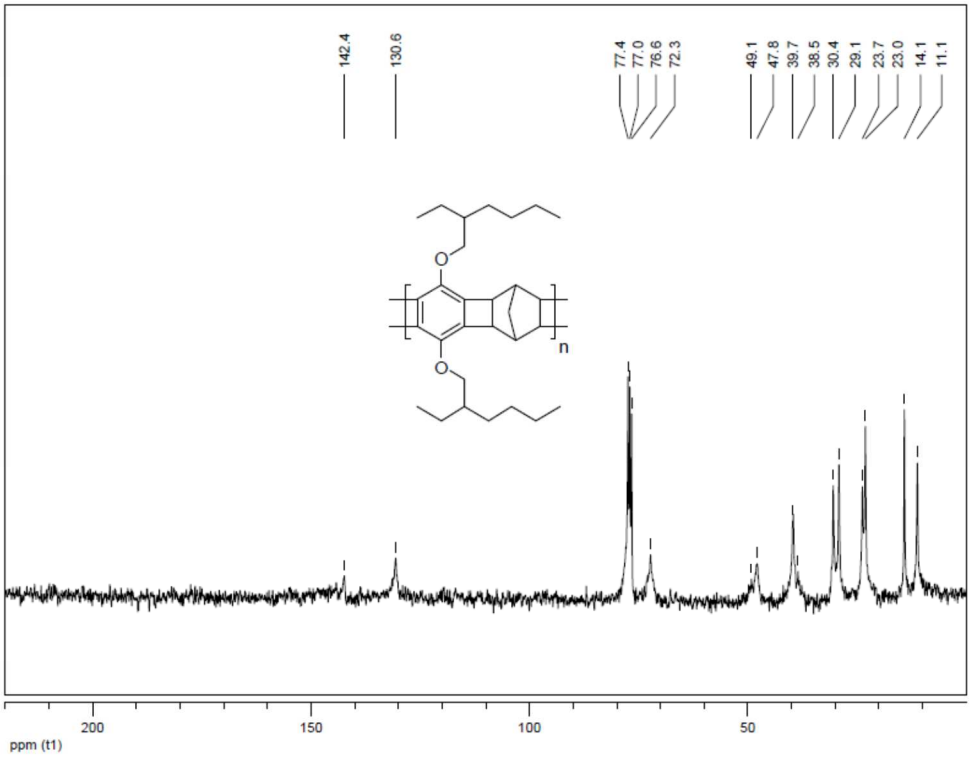


Figure S8. ^{13}C NMR spectrum of **poly(4b)**

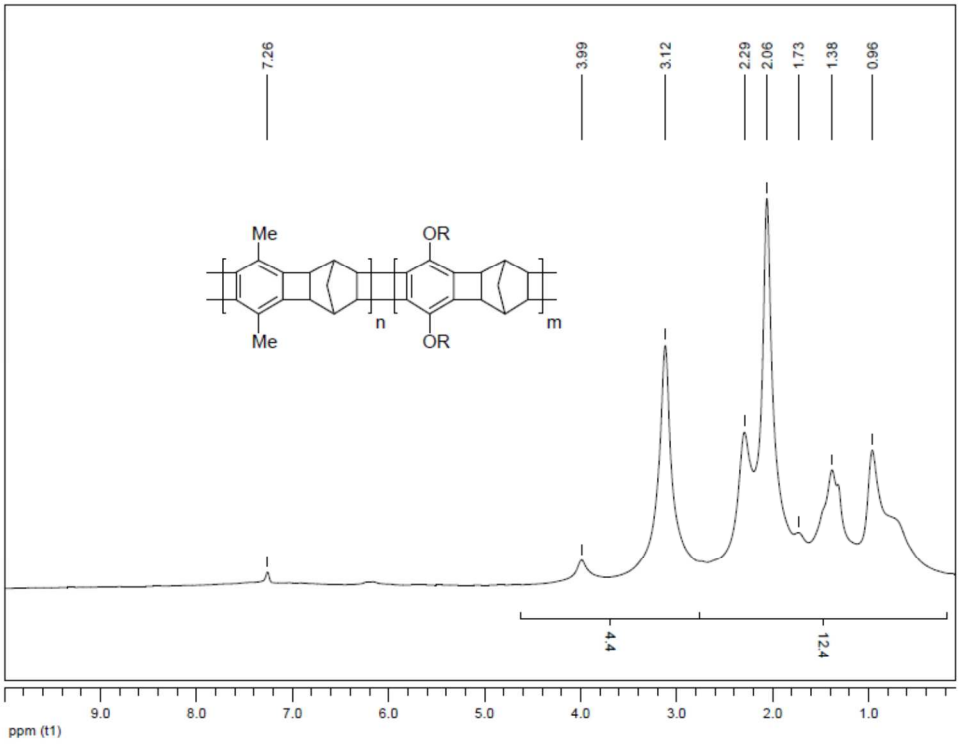


Figure S9. ^{1}H NMR spectrum of **poly(4a/b)**

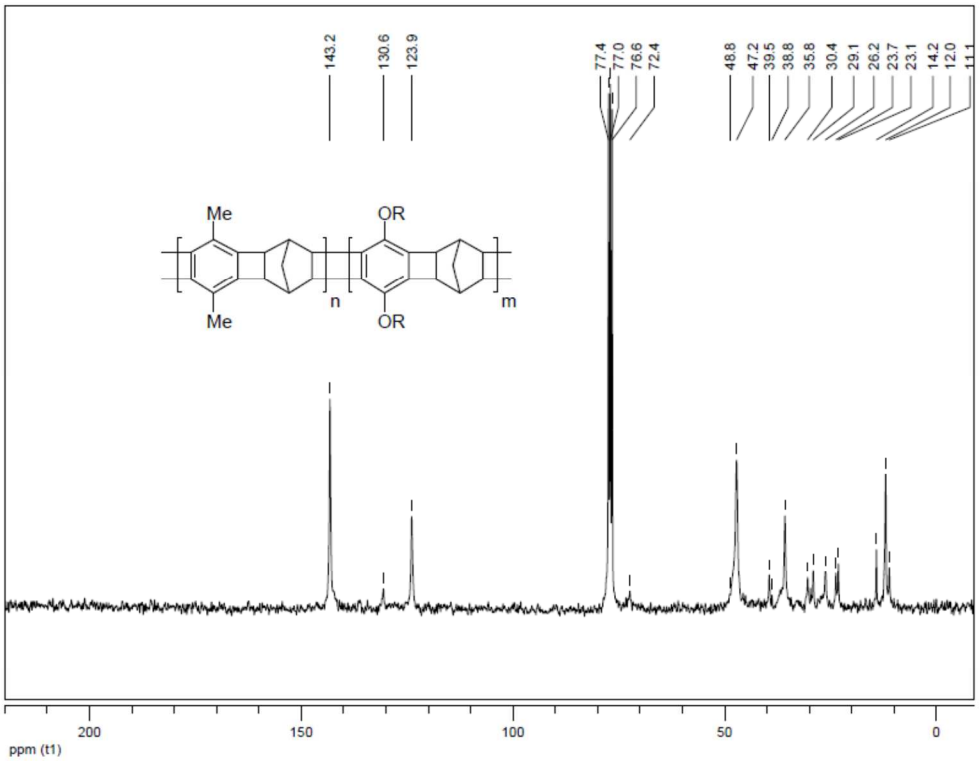


Figure S10. ^{13}C NMR spectrum of **poly(4a/b)**

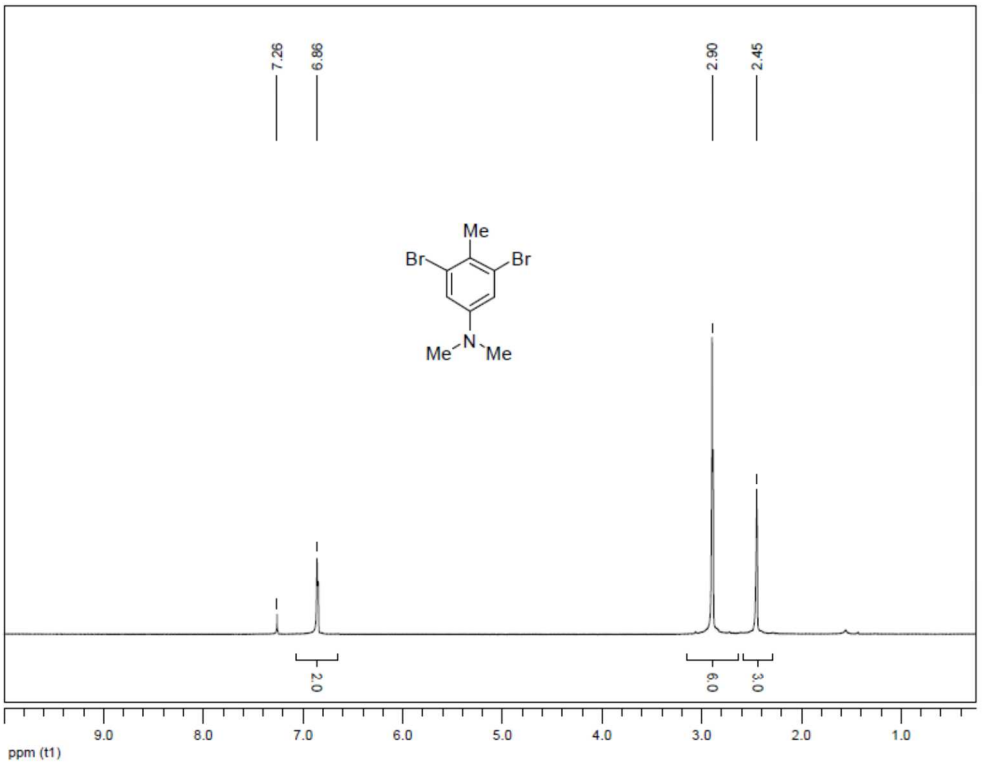


Figure S11. ^{1}H NMR spectrum of **4c**

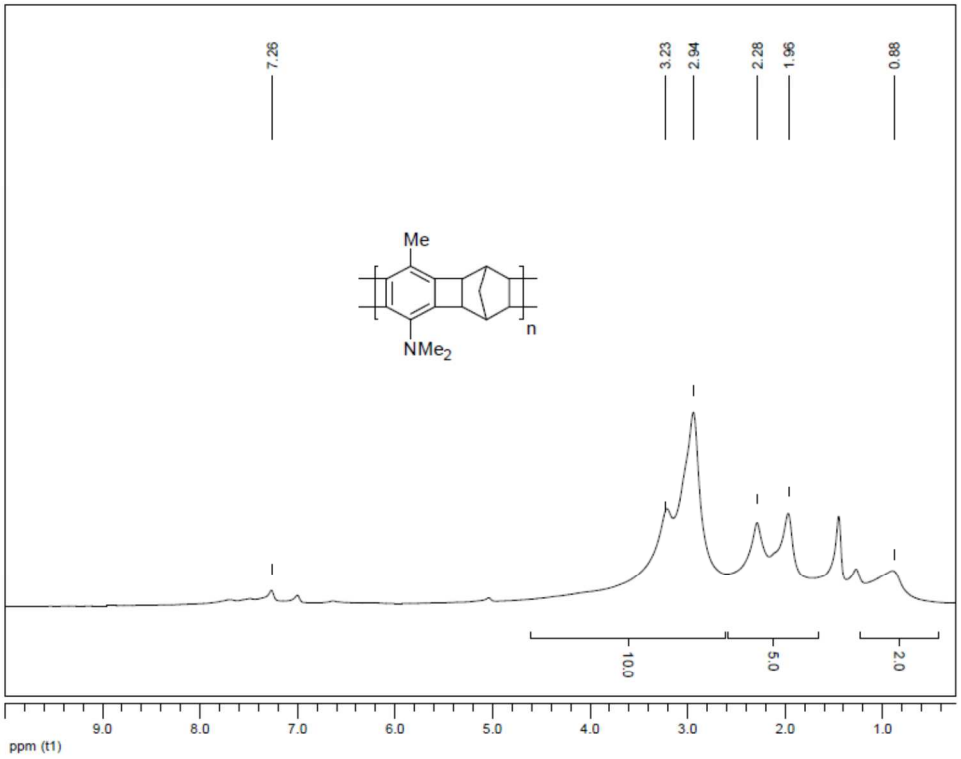


Figure S12. ^{1}H NMR spectrum of **poly(4c)**

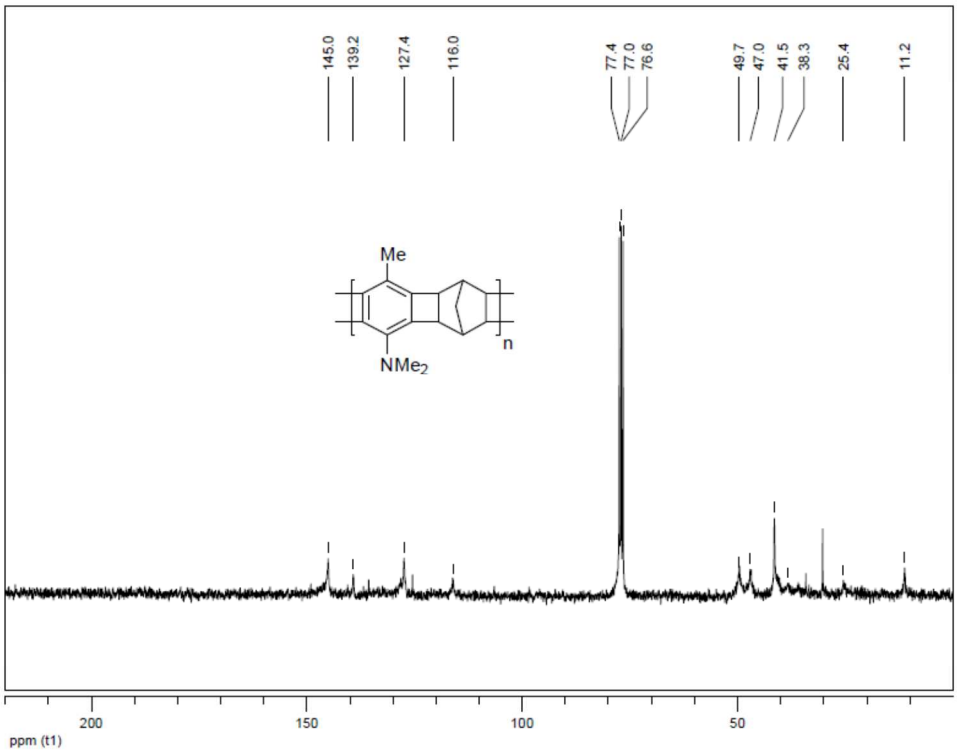


Figure S13. ^{13}C NMR spectrum of **poly(4c)**

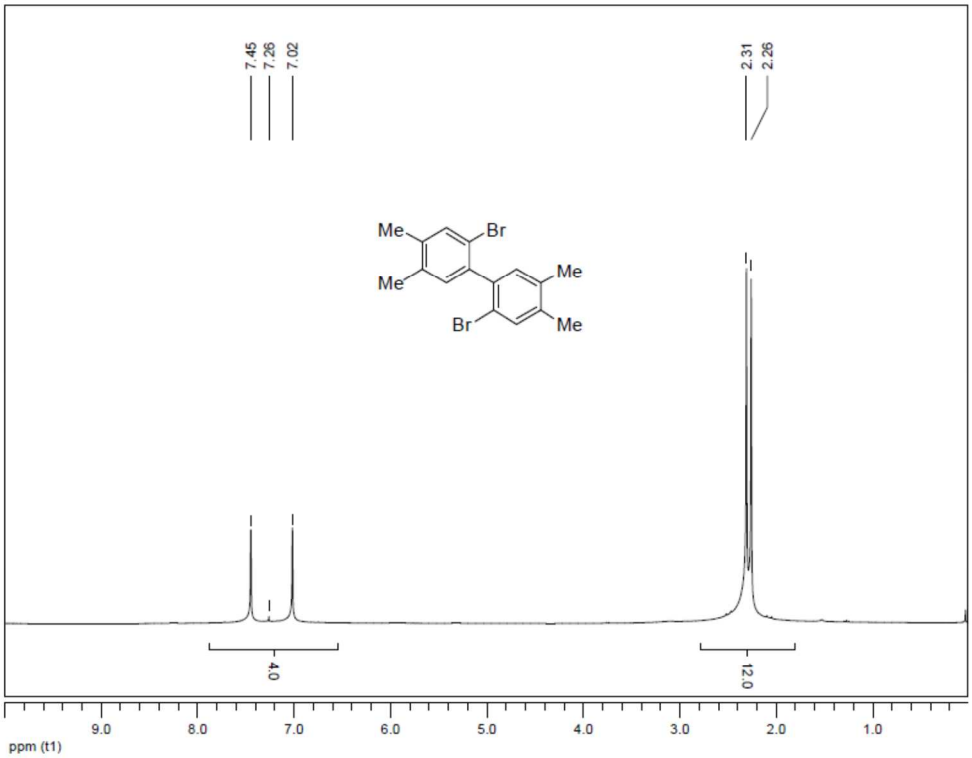


Figure S14. ^{1}H NMR spectrum of **4d**

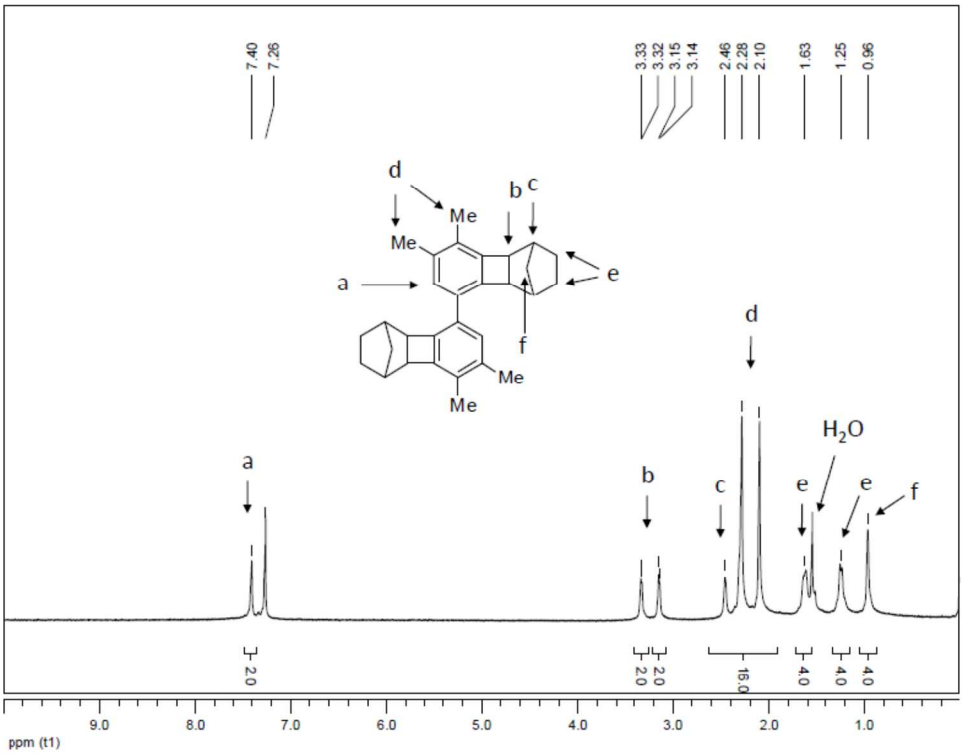


Figure S15. [1]H NMR spectrum of model compound **3d**

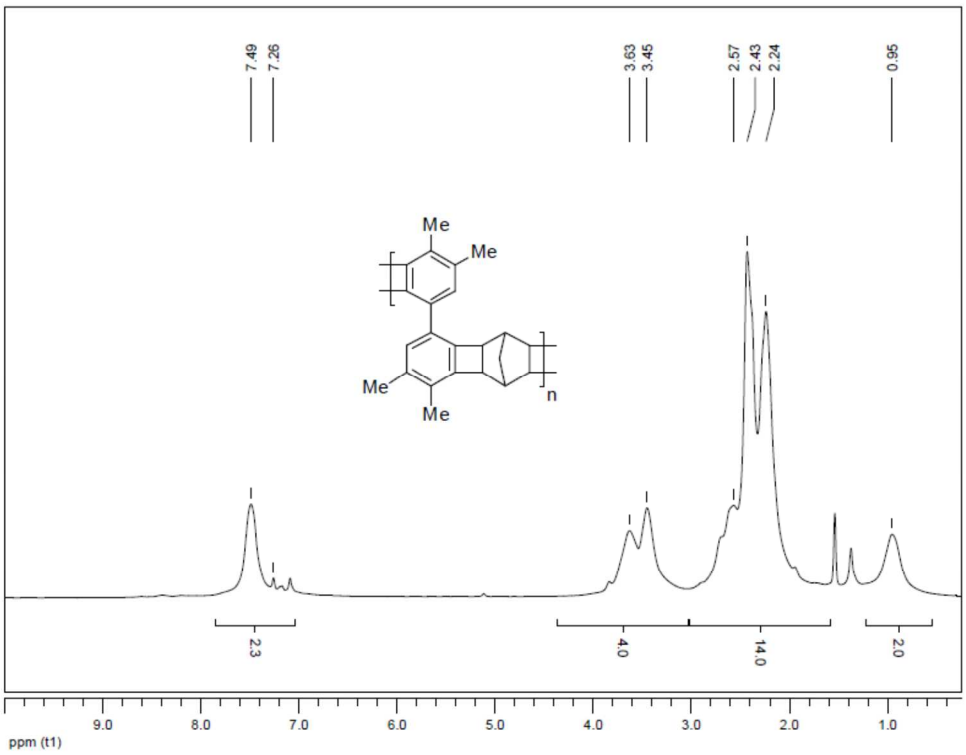


Figure S16. [1]H NMR spectrum of **poly(4d)**

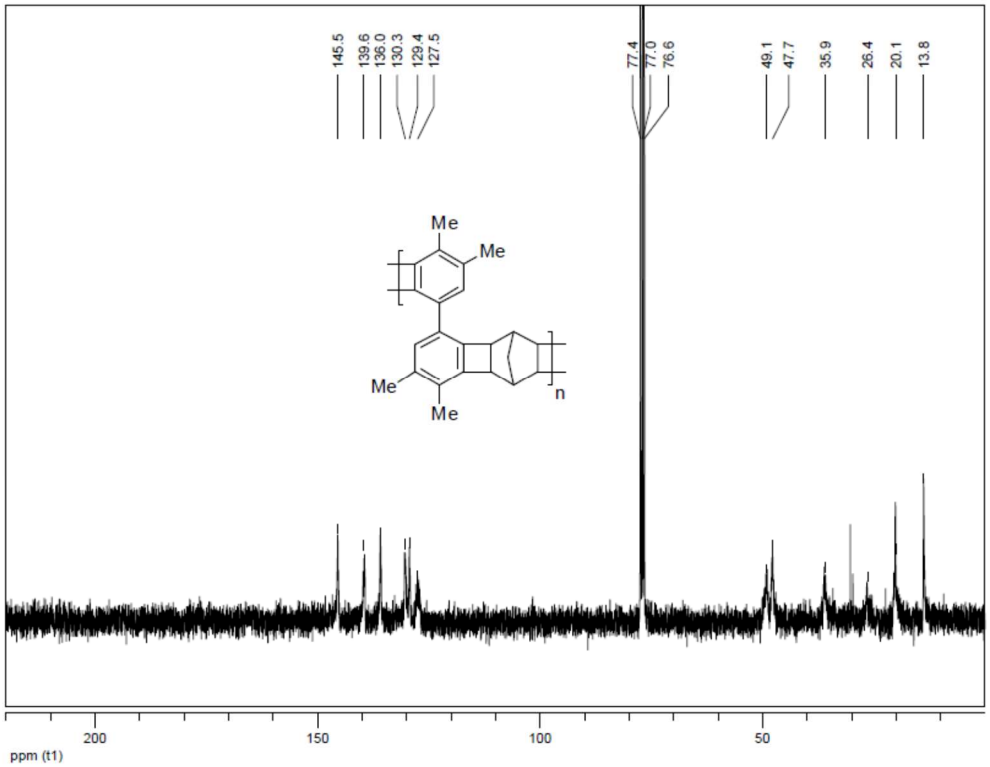


Figure S17. ^{13}C NMR spectrum of **poly(4d)**

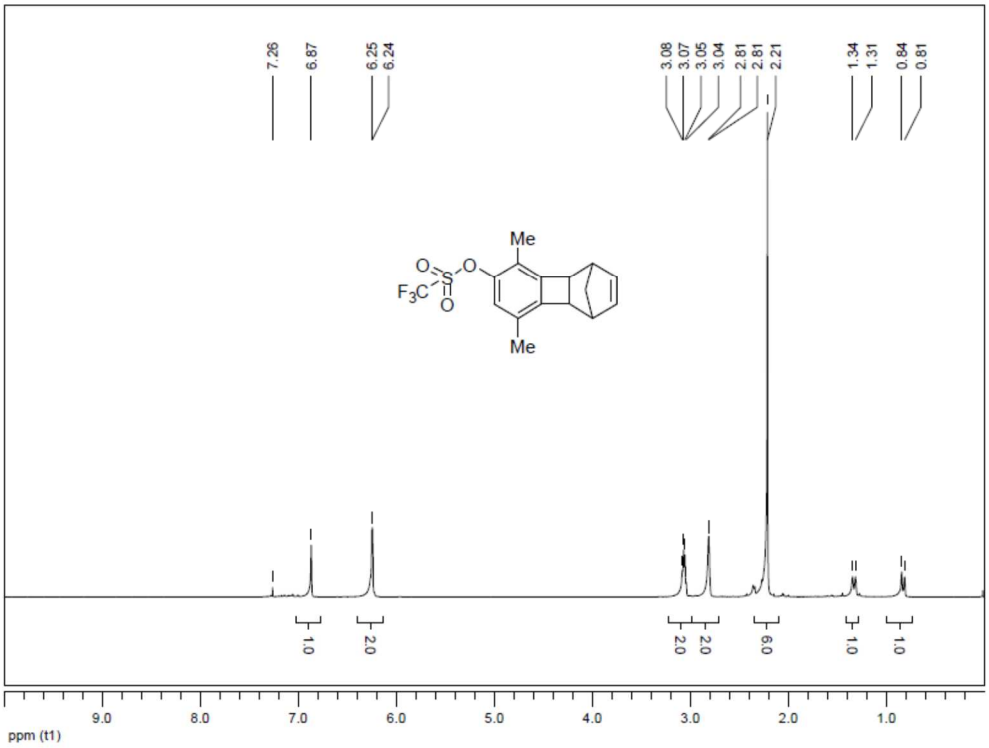


Figure S18. ^{1}H NMR spectrum of **4e**

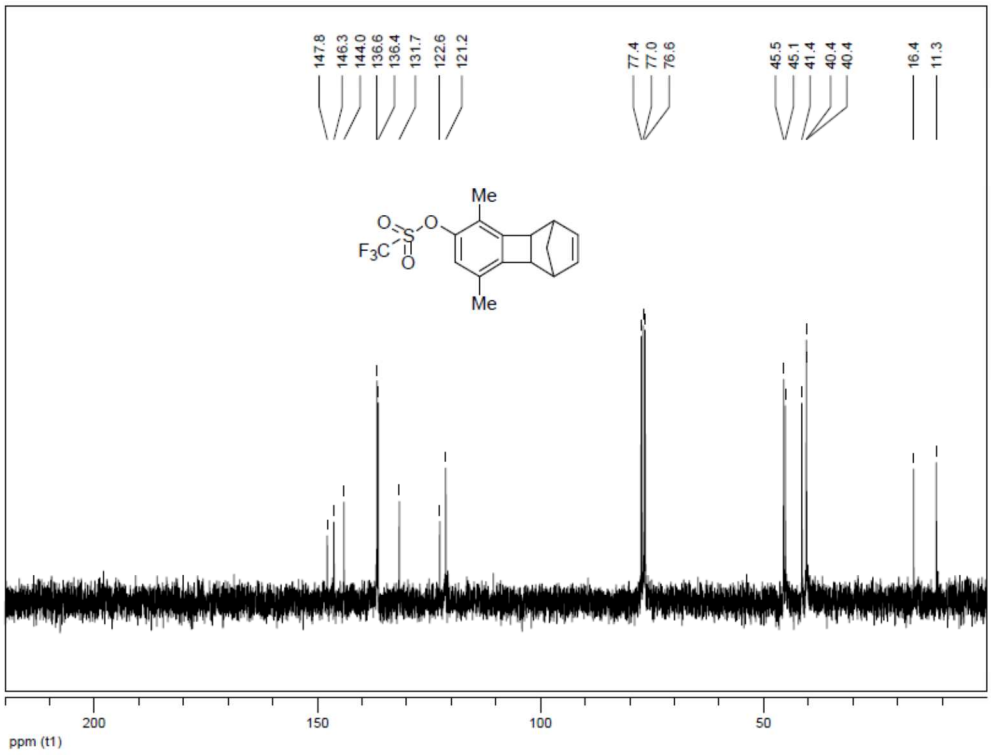


Figure S19. ^{13}C NMR spectrum of **4e**

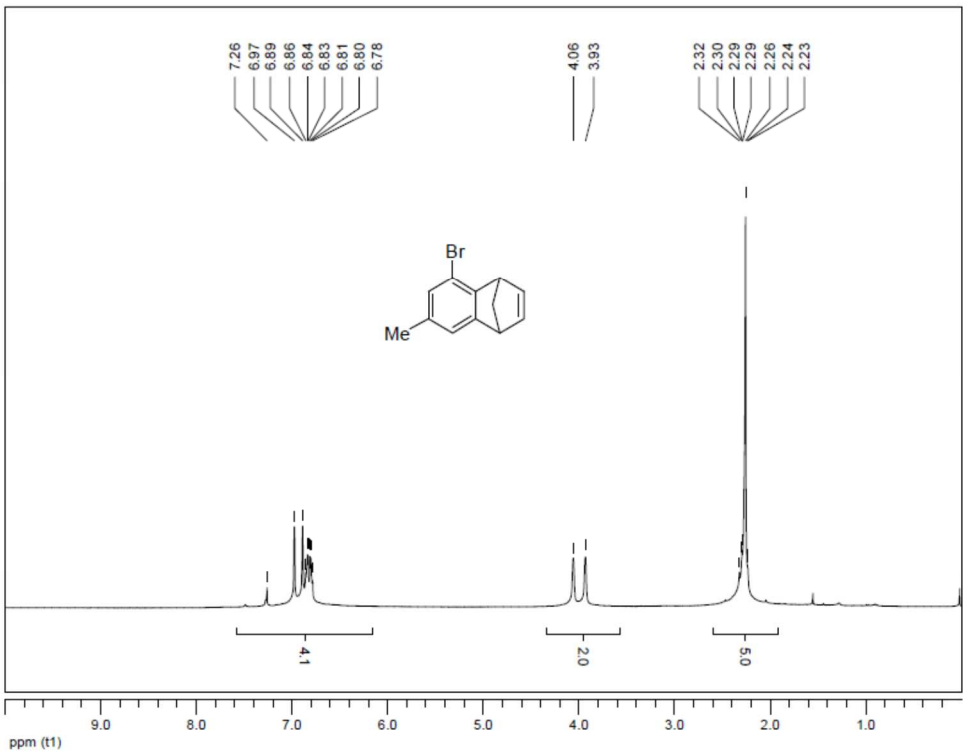


Figure S20. ^{1}H NMR spectrum of **4f**

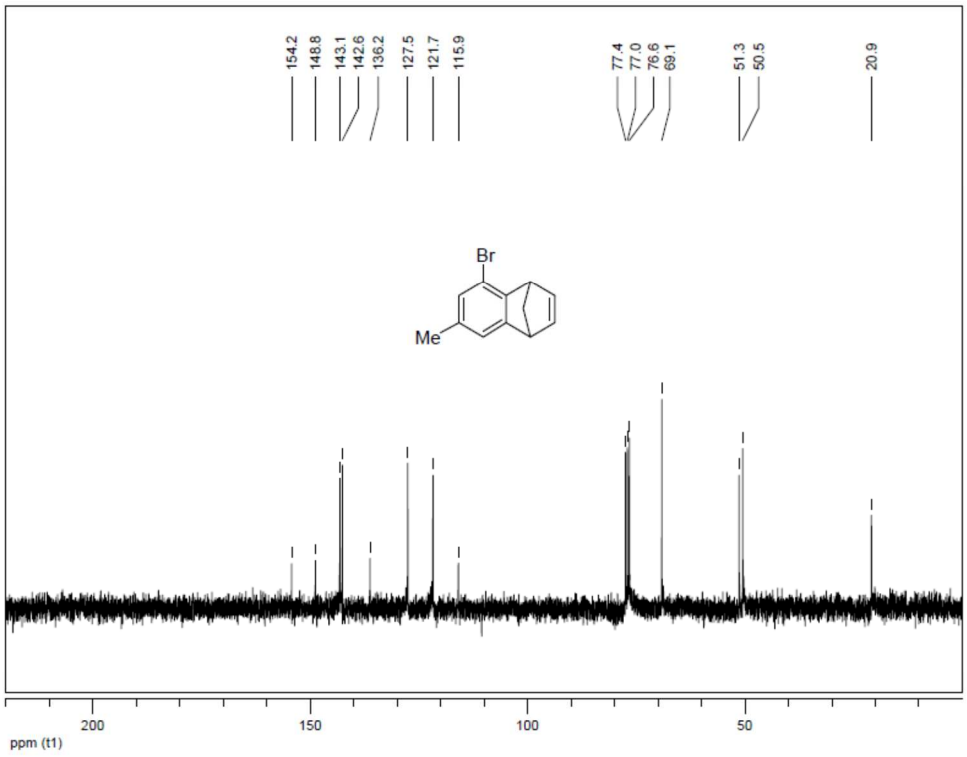


Figure S21. ^{13}C NMR spectrum of **4f**

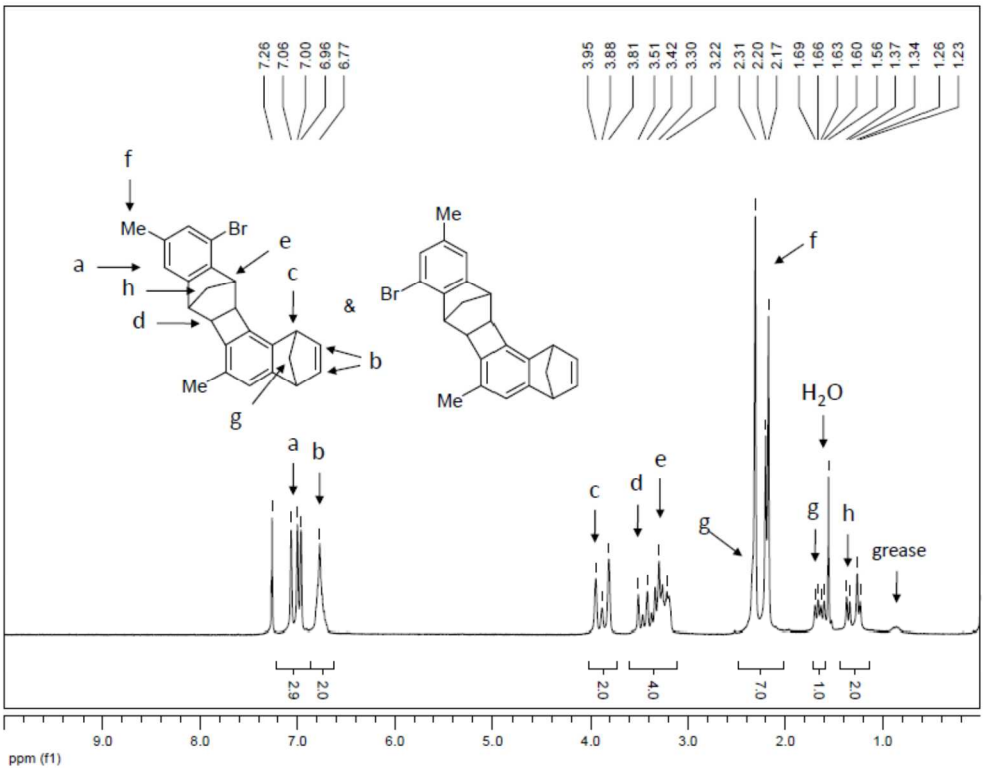


Figure S22. ^{1}H NMR spectrum of model compound **3f** (exist in regioisomers)

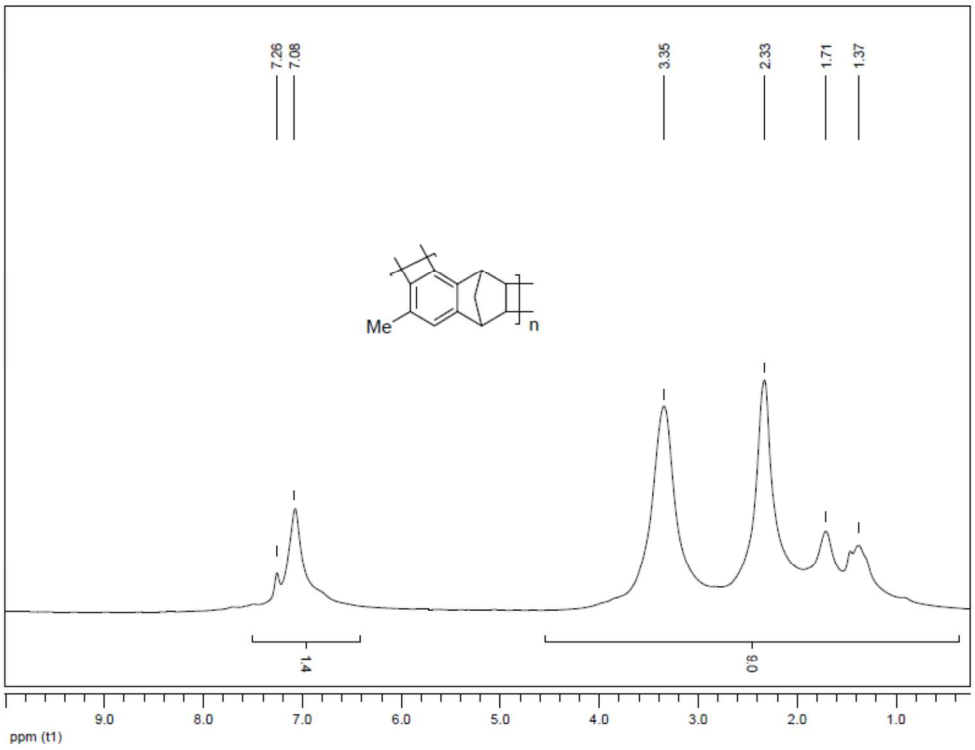


Figure S23. ^{1}H NMR spectrum of **poly(4f)**

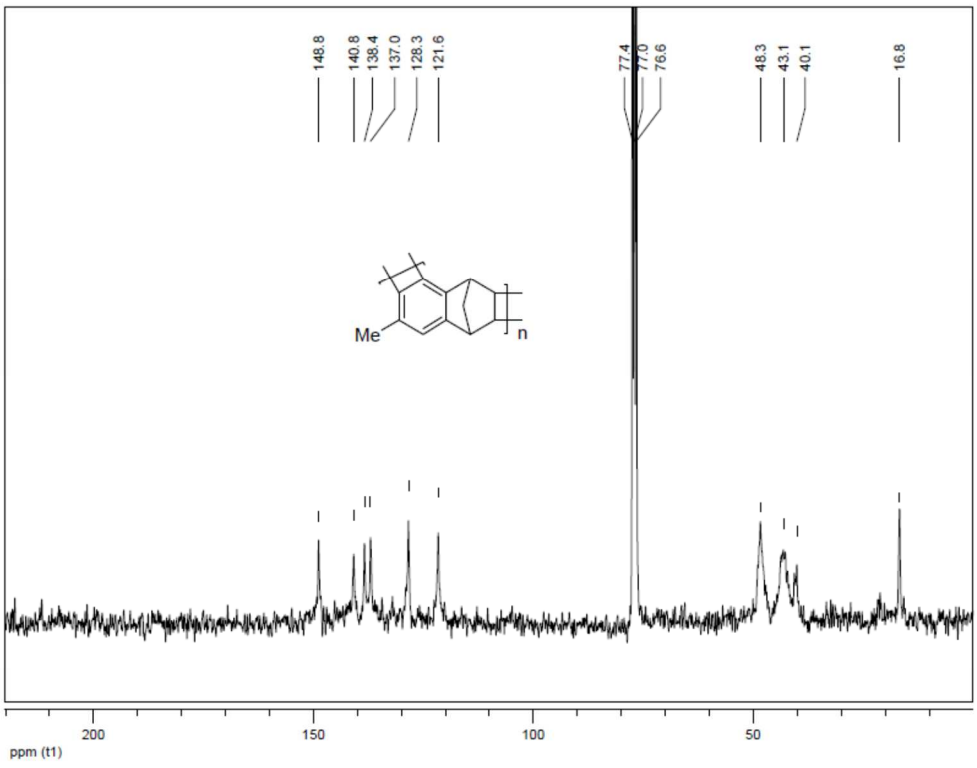


Figure S24. ^{13}C NMR spectrum of **poly(4f)**

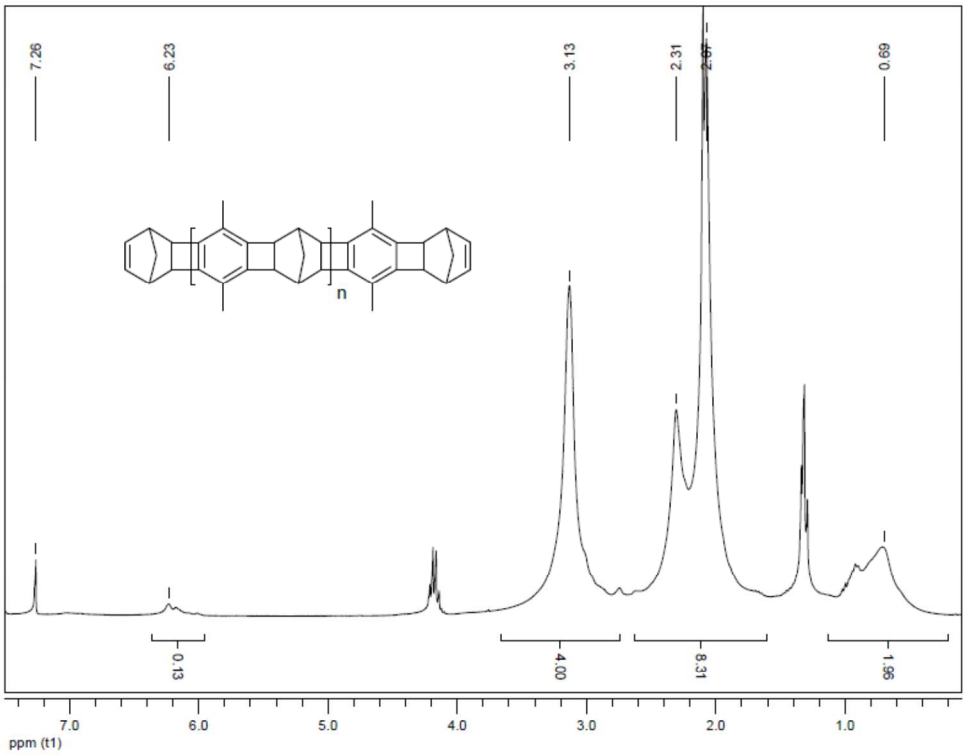


Figure S25. ^{1}H NMR spectrum of norbornene-terminated **poly(4a)**

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