

Tetraalkoxyphenanthrene: A New Precursor for Luminescent Conjugated Polymers

*Britta N. Boden, Katherine J. Jardine, Alfred C. W. Leung, Mark J. MacLachlan**

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC. V6T 1Z1

mmaclach@chem.ubc.ca

Supplementary Material

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Experimental Section

Materials and Equipment. Tetrahydrofuran (THF) was distilled over Na and benzophenone under N_2 . Diisopropylamine was distilled from NaOH under N_2 . 3,6-Dibromo-9,10-phenanthrenequinone **2**,¹ 1,4-diethynyl-2,5-dihexadecyloxybenzene **9**² and 1,4-divinyl-2,5-dihexadecyloxybenzene **12**³ were prepared according to literature procedures. Bis(triphenylphosphine)palladium(II) dichloride and tetrakis(triphenylphosphine)palladium(0) were obtained from Strem Chemicals, Inc. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. All other chemicals were purchased from Aldrich or Fisher and used as received. All reactions were carried out under nitrogen unless otherwise noted. ^1H NMR (300 or 400 MHz) and ^{13}C NMR (75.5 or 100.6 MHz) spectra were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers and were referenced internally to residual protonated solvent. Infrared spectra were obtained as KBr discs or on NaCl plates with a Bomem MB-100 spectrometer. UV-Vis spectra were obtained in HPLC grade CH_2Cl_2 on a Varian Cary 5000 UV-Vis/near IR spectrometer using a 1 cm cuvette or a microscope slide. Fluorescence spectra were obtained in CH_2Cl_2 on a PTI QuantaMaster fluorimeter using a

1 cm quartz cuvette or a microscope slide. Quantum yields were referenced to a solution of anthracene in EtOH ($\Phi = 0.30$).⁴ Electron ionization (EI) and electrospray ionization (ESI) mass spectra were obtained in the UBC Mass Spectrometry facility. Elemental analyses were obtained at the UBC Microanalytical facility. Melting points were obtained on a Fisher John's melting point apparatus. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel® columns (4.6% 300 mm) HR2, HR4 and HR5E and a Waters 2410 differential refractometer (refractive index detector). A flow rate of 0.3 mL/min was used and samples were dissolved in THF (ca. 1 mg/mL) and filtered before injection. Narrow molecular weight polystyrene standards were used for calibration purposes. It is well-known that GPC analysis of rigid-rod polymers can overestimate the molecular weights of polymers by as much as 50% when polystyrene standards are employed.

Synthesis of 3,6-dibromo-9,10-dimethoxyphenanthrene (3). Compound **3** was prepared using a published procedure for related compounds.⁵ Compound **2** (11.12 g, 30.3 mmol), Bu₄NBr (2.85 g, 8.82 mmol), Na₂S₂O₄ (16.018 g, 91.9 mmol), THF (100 mL) and H₂O (100 mL) were combined in a separatory funnel and shaken for 5 min, after which dimethyl sulfate (15 mL, 159 mmol) was added, followed by aqueous sodium hydroxide (30 mL, 14.1 M). The mixture was shaken for 3 min, during which, 100 g of ice was added, then the mixture was shaken for 12 additional minutes. The aqueous layer was separated and extracted with ethyl acetate (EtOAc) (3 x 150 mL). The combined organic layers were washed with water (3 x 100 mL), NH₄OH solution (2 x 100 mL) and brine (1 x 100 mL). The organic layer was dried with MgSO₄, filtered and the solvents were removed under vacuum, resulting in a fluffy yellow solid. Washing the product with methanol (MeOH) gave a white solid. Additional impurities were removed by flashing the product through silica with a 1:1 mixture of hexanes and methylene chloride (DCM). Yield: 10.86 g, 27.4 mmol, 90%

Data for 3. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, 2H, $J = 1.8$ Hz, aromatic CH), 8.07 (d, 2H, $J = 8.8$ Hz, aromatic CH), 7.70 (dd, 2H, $J_1 = 8.8$ Hz, $J_2 = 1.8$ Hz, aromatic CH), 4.05 (s, 6H, OCH₃); ¹³C NMR (75.5 MHz, CDCl₃) δ 144.0, 130.8, 129.1, 128.4, 125.6, 124.2, 120.7, 61.2; ESI-MS: $m/z = 419$ ([M+Na]⁺); IR (KBr): $\nu = 2964, 2934, 1619, 1589, 1483, 1424, 1347, 1313, 1121, 1094, 1066, 981, 868, 813$ cm⁻¹; UV-Vis (CH₂Cl₂) λ_{max} (ϵ) = 253 (4.9×10^4), 260 (5.4×10^4), 282 (1.8×10^4), 302 (1.3×10^4), 315 (1.4×10^4) nm (L mol⁻¹ cm⁻¹); Mp. = 162-163 °C ; Anal. Calc'd for C₁₆H₁₂O₂Br₂: C, 48.52, H, 3.05. Found C, 48.39, H, 3.21.

Synthesis of 3,6,9,10-tetramethoxyphenanthrene (4). EtOAc (1 mL) and toluene (1 mL) were added to **3** (2.26 g, 5.71 mmol), under N₂. To this mixture was added NaOMe/MeOH (25 wt%, 50 mL) and CuBr (0.081 g, 0.571 mmol). The mixture was heated to 80 °C for 16 h. After cooling to room temperature, the solution was poured into 150 mL water and extracted with DCM (3 x 150 mL), dried over MgSO₄, and filtered. Rotary evaporation of the solution gave a brown oil which was passed through silica in 1:1 hexanes to DCM. Recrystallization of the product from ethanol (EtOH) afforded 1.66 g (5.58 mmol, 98%) of a white solid.

Data for 4. ^1H NMR (300 MHz, CDCl_3) δ 8.11 (d, 2H, $J = 9.0$ Hz, aromatic), 7.89 (d, 2H, $J = 2.5$ Hz aromatic), 7.25 (dd, 2H, $J_1 = 9.0$ Hz, $J_2 = 2.5$ Hz, aromatic), 4.04 (s, 6H, OCH_3), 3.99 (s, 6H, OCH_3); ^{13}C NMR (75.5 MHz, CDCl_3) δ 157.9, 142.5, 129.5, 124.2, 124.0, 116.7, 104.9, 61.2, 55.8; ESI-MS: $m/z = 321$ ($[\text{M} + \text{Na}]^+$); IR (KBr): $\nu = 2996$, 2960, 2936, 2835, 1603, 1508, 1450, 1430, 1354, 1319, 1260, 1233, 1172, 1122, 1068, 1029, 986, 849, 832 cm^{-1} ; UV-Vis (CH_2Cl_2) λ_{max} (ϵ) = 252 (4.1×10^4), 291 (1.7×10^4), 313 (1.1×10^4) nm ($\text{L mol}^{-1} \text{cm}^{-1}$); Mp. = 74-76 $^\circ\text{C}$; Anal. Calc'd for $\text{C}_{18}\text{H}_{18}\text{O}_4$: C, 72.47; H, 6.08. Found: C, 72.18; H, 6.12.

Synthesis of 3,6-dimethoxyphenanthrene-9,10-quinone (5). Compound **4** (1.017 g, 3.4 mmol) was dissolved in acetonitrile (20 mL). A solution of ammonium cerium(IV) nitrate (3.73 g, 6.8 mmol) in acetonitrile (50 mL) was added, followed by 150 mL water. The solution was filtered and washed with water. Recrystallization from EtOH afforded 0.819 g (3.05 mmol, 90%) of a yellow solid.

Data for 5. ^1H NMR (300 MHz, CDCl_3) δ 8.18 (d, 2H, $J = 8.8$ Hz, aromatic), 7.37 (d, 2H, $J = 2.4$ Hz, aromatic), 6.94 (dd, 2H, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, aromatic), 3.95 (s, 6H, OCH_3); ^{13}C NMR (75.5 MHz, CDCl_3) δ 179.3, 166.0, 137.9, 133.6, 125.5, 114.6, 110.1, 56.1; ESI-MS: $m/z = 291$ ($[\text{M} + \text{Na}]^+$); IR (KBr): $\nu = 3083$, 2976, 2938, 2843, 1660, 1594, 1559, 1499, 1342, 1310, 1248, 1230, 1014, 864 cm^{-1} ; UV-Vis (CH_2Cl_2) λ_{max} (ϵ) = 238 (2.3×10^4), 284 (3.0×10^4), 347 (1.4×10^4) nm ($\text{L mol}^{-1} \text{cm}^{-1}$); Mp. = 226-230 $^\circ\text{C}$; Anal. Calc'd for $\text{C}_{16}\text{H}_{12}\text{O}_4$: C, 71.64; H, 4.51. Found: C, 71.90, H, 4.77.

Synthesis of 2,7-diiodo-3,6-dimethoxy-9,10-phenanthrenequinone (6). In a flask, **5** (3.99 g, 14.8 mmol), I_2 (4.16 g, 16.3 mmol), KIO_3 (1.27 g, 5.92 mmol), H_2O (15.6 mL), H_2SO_4 (1.56 mL), and HOAc (156 mL) were combined and heated to reflux. After 5 h, the solution was cooled, filtered and washed with copious amounts of H_2O . The solid was stirred in an aqueous NaSO_3 solution, filtered and washed with EtOH. Recrystallization from ethanol gave a brown solid, and from acetone gave an orange solid. Yield: 6.68 g, 12.8 mmol, 86%

Data for 6. ^1H NMR (300 MHz, CDCl_3) δ 8.58 (s, 2H, aromatic CH), 7.17 (s, 2H, aromatic CH), 4.10 (s, 6H, OCH_3); ^{13}C NMR (75.5 MHz, CDCl_3) δ 177.5, 164.1, 142.5, 137.5, 126.4, 104.5, 88.7, 57.1; ESI-MS: $m/z = 543$ ($[\text{M} + \text{Na}]^+$); IR (KBr): $\nu = 3027$, 2926, 1670, 1573, 1492, 1453, 1330, 1310, 1268, 1206, 1058, 1041, 846, 756 cm^{-1} ; UV-Vis (CH_2Cl_2) λ_{max} (ϵ) = 241 (1.5×10^4), 306 (6.3×10^4), 345 (1.3×10^4) nm ($\text{L mol}^{-1} \text{cm}^{-1}$); Mp. > 300 $^\circ\text{C}$; Anal. Calc'd for $\text{C}_{16}\text{H}_{10}\text{O}_4\text{I}_2$: C, 36.95, H, 1.94. Found C, 37.35, H 2.14.

Synthesis of 9,10-dihexyloxy-2,7-diiodo-3,6-dimethoxyphenanthrene (7a). Compound **6** (1.015 g, 2.125 mmol) was dissolved in 50 mL DMF and degassed with N_2 for 5 min. $\text{Na}_2\text{S}_2\text{O}_4$ (1.995 g, 11.46 mmol) was added to the solution and stirred for 15 min, after which K_2CO_3 (1.175 g, 8.50 mmol), Bu_4NBr (0.050g, 0.154 mmol), and 1-bromohexane (0.90 mL, 4.64 mmol) were added. The solution was heated for 16 h at 80 $^\circ\text{C}$. After

cooling, the yellow solution was poured into H₂O and extracted with EtOAc (3 x 125 mL). The organic layer was dried with MgSO₄, filtered and dried under vacuum. Chromatography on silica with 1:3 DCM/hexanes afforded a colourless oil which was recrystallized from EtOH and DCM to give white crystals. Yield: 0.398 g, 0.576 mmol, 27%

Data for 7a. ¹H NMR (300 MHz, CDCl₃) δ 8.62 (s, 2H, aromatic CH), 7.69 (s, 2H, aromatic CH), 4.12 (t, 4H, OCH₂), 4.06 (s, 6H, OCH₃), 1.85 (m, 4H, hexyloxy chain), 1.55 (m, 4H, hexyloxy chain), 1.37 (m, 8H, hexyloxy chain), 0.89 (t, 6H, hexyloxy chain); ¹³C NMR (75.5 MHz, CDCl₃) δ 155.8, 141.0, 134.3, 128.8, 126.4, 102.4, 88.6, 73.9, 56.8, 31.9, 30.6, 26.1, 22.9, 14.3; R_F (1:3 DCM/hexanes): 0.11; ESI-MS: *m/z* = 713 ([M+Na]⁺); IR (KBr): ν = 2999, 2952, 2925, 2856, 1589, 1480, 1453, 1438, 1409, 1355, 1240, 1152, 1080, 1045, 891, 833, 658 cm⁻¹; UV-Vis (CH₂Cl₂) λ_{max} (ε) = 232 (3.7 x 10⁴), 269 (5.9 x 10⁴), 299 (5.3 x 10⁴), 313 (4.3 x 10⁴) nm (L mol⁻¹ cm⁻¹); Mp. = 78-81 °C; Anal. Calc'd for C₂₈H₃₆O₄I₂: C, 48.71, H, 5.26. Found C, 48.91, H, 5.43.

Synthesis of 9,10-di-2-ethylhexyloxy-2,7-diiodo-3,6-dimethoxyphenanthrene (7b).

Compound **6** (1.199 g, 2.31 mmol) was dissolved in 50 mL DMF and degassed with N₂ for 5 min. Na₂S₂O₄ (1.204 g, 6.92 mmol) was added to the solution and stirred for 15 min, after which K₂CO₃ (1.274 g, 9.21 mmol), Bu₄NBr (0.050 g, 0.154 mmol), and 2-ethylhexylbromide (1.23 mL, 6.92 mmol) were added. The solution was heated for 16 h at 80 °C. After cooling, the yellow solution was poured into H₂O and extracted with EtOAc (3 x 125 mL). The organic layer was dried with MgSO₄, filtered and dried under vacuum. Chromatography on silica with 1:3 DCM/hexanes afforded a colourless oil which was recrystallized from EtOH and DCM to give white crystals. Yield: 0.750 g, 1.00 mmol, 44%

Data for 7b. ¹H NMR (300 MHz, CDCl₃) δ 8.64 (s, 2H, aromatic CH), 7.71 (s, 2H, aromatic CH), 4.07 (s, 6H, OCH₃) 4.00 (d, 4H, OCH₂), 1.83 (m, 2H, CH), 1.57 (m, 4H, ethex chain), 1.36 (m, 12H, ethex chain), 0.96 (m, 12H, ethex CH₃); ¹³C NMR (100.6 MHz, CDCl₃) δ 155.8, 141.3, 134.3, 128.9, 126.3, 102.5, 88.4, 76.7, 56.8, 40.8, 30.8, 29.4, 24.0, 23.4, 14.4, 11.4; R_F (1:3 DCM/hexanes): 0.14; ESI-MS: *m/z* = 769 ([M+Na]⁺); IR (KBr): ν = 3001, 2959, 2926, 2871, 1589, 1464, 1439, 1355, 1241, 1144, 1043, 886, 832, 656 cm⁻¹; UV-Vis (CH₂Cl₂) λ_{max} (ε) = 232 (2.9 x 10⁴), 269 (4.8 x 10⁴), 299 (4.5 x 10⁴), 313 (3.7 x 10⁴) nm (L mol⁻¹ cm⁻¹); Mp. = 110-112 °C; Anal. Calc'd for C₃₂H₄₄O₄I₂: C, 51.49, H, 5.94. Found C, 51.69, H 6.18.

Synthesis of 9,10-dibenzoyloxy-2,7-diiodo-3,6-dimethoxyphenanthrene (7c).

Compound **6** (0.157 g, 0.302 mmol) was dissolved in 20 mL DMF and degassed with N₂ for 5 min. Na₂S₂O₄ (0.158 g, 0.907 mmol) was added to the solution and stirred for 15 min, after which K₂CO₃ (0.405 g, 2.93 mmol), Bu₄NBr (0.050g, 0.154 mmol), and benzyl chloride (0.5 mL, 4.34 mmol) were added. The solution was heated for 16 h at 80 °C. After cooling, the yellow solution was poured into H₂O and extracted with EtOAc (3 x 75 mL). The organic layer was dried with MgSO₄, filtered and dried under vacuum.

Chromatography on silica with 1:3 DCM/hexanes afforded white crystals. Yield: 0.073 g, 0.104 mmol, 34%

Data for 7c. ^1H NMR (400 MHz, CDCl_3) δ 8.62 (s, 2H, aromatic CH), 7.70 (s, 2H, aromatic CH), 7.47 (d, 4H, aromatic CH), 7.36 (m, 6H, aromatic CH), 5.21 (s, 4H, OCH_2), 4.07 (s, 6H, OCH_3); ^{13}C NMR (100.6 MHz, CDCl_3) δ 156.1, 141.2, , 137. 3, 134.5, 129.1, 128.8, 128.7, 128.5, 126.1, 102.4, 88.7, 75.9, 56.8; EI-MS: m/z = 702 (M^+); IR (KBr): ν = 2999, 2932, 2875, 2855, 1586, 1455, 1436, 1350, 1275, 1132, 1044, 955, 896, 841, 758, 696 cm^{-1} ; UV-Vis (CH_2Cl_2) λ_{max} (ϵ) = 233 (3.2×10^4), 270 (5.0×10^4), 299 (4.7×10^4), 312 (3.7×10^4) nm ($\text{L mol}^{-1} \text{cm}^{-1}$); Mp. 213-215 $^\circ\text{C}$.

Synthesis of Model Compound 8. Compound **7a** (0.153 g, 0.222 mmol), phenylacetylene (0.2 mL, 1.82 mmol) and CuI (30 mg, 0.16 mmol) were dissolved in 10 mL toluene and 4 mL diisopropylamine. After the solution was degassed, $\text{Pd}(\text{PPh}_3)_4$ (50 mg, 0.043 mmol) was added. The reaction was heated for 1 h at 50 $^\circ\text{C}$. Upon cooling, the solution was poured into water and extracted with DCM. The organic layer was dried with MgSO_4 , filtered and dried under vacuum to obtain a brown oil. The product was chromatographed with 3:1 hexanes/DCM to obtain a yellow oil. Recrystallization from EtOH and DCM gave yellow needles. Yield: 0.114 g, 0.178 mmol, 80%

Data for 8. ^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 2H, aromatic CH), 7.79 (s, 2H, aromatic CH), 7.61 (m, 4H, aromatic CH), 7.35 (m, 6H, aromatic CH), 4.17 (t, 4H, OCH_2), 4.12 (s, 6H, OCH_3), 1.89 (m, 4H, hexyloxy chain), 1.51 (m, 4H, hexyloxy chain), 1.38 (m, 8H, hexyloxy chain), 0.91 (t, 6H, hexyloxy chain); ^{13}C NMR (75.5 MHz, CDCl_3) δ 157.6, 141.7, 132.0, 128.7, 128.5, 124.9, 123.6, 114.3, 102.9, 94.4, 86.3, 73.9, 56.4, 31.9, 30.6, 26.2, 23.0, 14.3; ESI-MS: m/z = 662 ($[\text{M}+\text{Na}]^+$); IR (KBr): ν = 2953, 2930, 2854, 1591, 1499, 1443, 1365, 1235, 1118, 1009, 832, 756, 694 cm^{-1} ; UV-Vis (CH_2Cl_2) λ_{max} (ϵ) = 295 (4.0×10^4), 353 (4.4×10^4) nm ($\text{L mol}^{-1} \text{cm}^{-1}$); Mp. = 70-72 $^\circ\text{C}$; Anal. Calc'd for $\text{C}_{44}\text{H}_{46}\text{O}_4$: C, 82.72 , H, 7.26. Found C, 82.40, H, 7.29. Fluorescence (CH_2Cl_2): λ_{em} = 456 nm (λ_{exc} = 354 nm).

Synthesis of Polymer 10. Compound **7b** (0.2035 g, 0.2726 mmol) and 1,4-diethynyl-2,5-dihexadecyloxybenzene **9** (0.1688 g, 0.2781 mmol) were dissolved in 28 mL of a 5:2 THF/diisopropylamine solution and degassed by three freeze/pump/thaw cycles. CuI (30 mg, 0.16 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (50 mg, 0.043 mmol) were added to the solution in a nitrogen filled glovebox and the mixture underwent 2 additional freeze/pump/thaw cycles. The solution was heated to reflux under vacuum for 16 h to obtain a brown solution. The solution was filtered and the solvent was removed by vacuum. After redissolution in DCM, the solution was washed with aqueous KCN, then water. The solvent was evaporated until the polymer solution was viscous, and the solution was then precipitated in MeOH and filtered to obtain a yellow solid. This was repeated twice to remove impurities. Yield: 0.256 g, 86%. The ^1H NMR spectrum was broad and only alkyl resonances could be observed in the ^{13}C spectrum.

Data for 10. ^1H NMR (300 MHz, CDCl_3) δ 8.35 (s, aromatic CH), 7.10 (s, aromatic CH), 4.14, 4.09 (m, alkoxy), 2.0-0.8 (br m, alkoxy); ^{13}C NMR (75.5 MHz, CDCl_3) δ 40.9, 32.2, 30.8, 29.9, 29.7, 29.6, 29.4, 26.2, 24.1, 23.5, 22.9, 14.4, 14.3, 11.5, resonances from the aromatic region of the spectrum were not observed; IR (KBr): ν = 3028, 2924, 2851, 1736, 1603, 1494, 1453, 1211, 1025, 756, 697, 536 cm^{-1} ; UV-Vis (CH_2Cl_2) λ_{max} = 304, 437 nm; UV-Vis (film) λ_{max} = 449 nm; decomposition begins at 150 $^{\circ}\text{C}$; Anal. Calc'd for $\text{C}_{74}\text{H}_{112}\text{O}_6$: C, 80.97, H, 10.28. Found: C, 80.89, H, 10.00. GPC: M_n = 146 142, M_w = 1 368 420, PDI = 9.36. Fluorescence (CH_2Cl_2): λ_{em} = 455 nm (λ_{exc} = 438 nm), Φ = 70%. Fluorescence (film): λ_{em} = 470 nm (λ_{exc} = 449 nm).

Synthesis of Model Compound 11. To a mixture of **7b** (0.205 g, 0.274 mmol), $\text{Pd}(\text{OAc})_2$ (0.005 g, 0.022 mmol) and tri(o-tolyl)phosphine (0.013 g, 0.043 mmol) were added anhydrous DMF (5 mL), triethylamine (3 mL) and styrene (0.3 mL, 2.6 mmol). The solution was heated at 130 $^{\circ}\text{C}$ for 20 h, after which it was diluted with CHCl_3 and washed with water. After drying with MgSO_4 and removing the solvent by evaporation, the residue was chromatographed using 3:1 hexanes/DCM to afford a yellow oil. Yield: 0.101 g, 0.145 mmol, 53%.

Data for 11. ^1H NMR (400 MHz, CDCl_3) δ 8.46 (s, 2H, aromatic CH), 7.79 (s, 2H, aromatic CH), 7.66-7.58 (m, 6H, aromatic CH), 7.40-7.20 (m, 8H, aromatic CH), 4.11 (d, 4H, OCH_2), 4.10 (s, 6H, OCH_3), 1.91 (m, 2H, CH), 1.81-1.34 (m, 18H, ethex chain), 1.05 (t, 6H, ethex chain), 0.91 (m, 6H, ethex CH_3); ^{13}C NMR (75.5 MHz, CDCl_3) δ 155.7, 142.2, 138.2, 130.3, 128.9, 128.6, 127.8, 127.7, 126.9, 124.6, 123.7, 120.5, 102.8, 76.7, 56.0, 41.0, 31.0, 29.6, 24.2, 23.5, 14.4, 11.5; EI-MS: m/z = 698 (M^+); IR (NaCl): ν = 2956, 2928, 2873, 2855, 1598, 1498, 1447, 1370, 1240, 1220, 1143, 1014, 965, 829, 752, 693 cm^{-1} ; UV-Vis (CH_2Cl_2) λ_{max} (ϵ) 235 (3.1×10^4), 301 (4.6×10^4), 362 (4.6×10^4) nm ($\text{L mol}^{-1} \text{cm}^{-1}$); High Res MS Calc'd for $\text{C}_{48}\text{H}_{58}\text{O}_4$: 698.43351. Found: 698.43323. Fluorescence (CH_2Cl_2): λ_{em} = 475 nm (λ_{exc} = 368 nm).

Synthesis of Polymer 13. Monomers **7b** (0.0642 g, 0.086 mmol) and **12** (0.0526 g, 0.086 mmol) were combined in a 100 mL Schlenk tube. To these solids were added 5 mL of dry DMF and 1 mL of distilled Bu_3N via syringe. The reaction mixture was then degassed by three freeze/pump/thaw cycles. In a nitrogen filled glovebox, $\text{Pd}(\text{OAc})_2$ (50 mg, 0.043 mmol) and (o-tol) $_3\text{P}$ (0.013 g, 0.043 mmol) were added. The reaction mixture was subsequently freeze/pump/ thawed one more time. A fluorescent green solution was obtained after heating the reaction mixture at 85 $^{\circ}\text{C}$ for 40 h. After cooling to room temperature, the solution was filtered and precipitated into 200 mL of MeOH to yield a yellow precipitate. The polymer was further purified by precipitating the polymer from DCM into MeOH. The above procedure gave 0.095 g of polymer **13** in 45% yield. The ^1H NMR spectrum was broad and only alkyl resonances could be observed in the ^{13}C spectrum.

Data for 13. ^1H NMR (300 MHz, CDCl_3) δ 8.46 (br), 7.80 (br), 7.69 (br), 7.21 (br), 6.8-6.6 (br), 4.2-3.7 (br), 2.0-0.8 (br); ^{13}C NMR (100.6 MHz, CDCl_3) δ 56.0, 40.9, 32.1, 29.9, 29.5, 26.4, 23.4, 22.9, 14.3, 11.4, resonances from the aromatic region of the spectrum were not observed; IR (NaCl): ν = 2955, 2923, 2852, 1728, 1677, 1598, 1502, 1467, 1422,

1364, 1239, 1204, 1146, 1016 cm^{-1} ; UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 431 \text{ nm}$; GPC: $M_n = 4439$, $M_w = 8702$, PDI = 1.96. Fluorescence (CH_2Cl_2): $\lambda_{\text{em}} = 499 \text{ nm}$ ($\lambda_{\text{exc}} = 441 \text{ nm}$), $\Phi = 59\%$.

Synthesis of 9,10-diethylhexyloxy-3,6-dimethoxy-2,7-divinylphenanthrene (14). A solution of tributyl(vinyl)tin (0.84 mL, 2.6 mmol) in DMF (40 mL) was added to a mixture of **7b** (0.714 g, 0.957 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.067 g, 0.095 mmol). The resulting solution was heated to 80 $^\circ\text{C}$ for 3 h and cooled. Ether (100 mL) was added to the reaction and the solution was washed (3 x 100 mL) with aqueous NH_4Cl . The organic layer was flashed through silica and the solvent was removed under vacuum. Chromatography with 7:1 hexanes/DCM afforded a pale yellow oil. Yield: 0.237 g, 0.433 mmol, 45%.

Data for 14. ^1H NMR (300 MHz, CDCl_3) δ 8.35 (s, 2H, aromatic CH), 7.76 (s, 2H, aromatic CH), 7.22 (dd, 2H, $J_{\text{trans}} = 17.7 \text{ Hz}$, $J_{\text{cis}} = 11.1 \text{ Hz}$, $\text{H}_2\text{C}=\text{CH}$), 5.96 (dd, 2H, $J_{\text{trans}} = 17.7 \text{ Hz}$, $J_{\text{gem}} = 1.5 \text{ Hz}$, $\text{C}=\text{CH}_{\text{trans}}$), 5.40 (dd, 2H, $J_{\text{cis}} = 11.1 \text{ Hz}$, $J_{\text{gem}} = 1.5 \text{ Hz}$, $\text{C}=\text{CH}_{\text{cis}}$), 4.08 (d, 4H, OCH_2), 4.05 (s, 6H, OCH_3), 1.89 (m, 2H, ethex chain), 1.63 (m, 8H, ethex chain), 1.40 (m, 8H, ethex chain), 1.02 (t, 6H, ethex chain), 0.94 (t, 6H, ethex chain); ^{13}C NMR (75.5 MHz, CDCl_3) δ 155.5, 142.2, 132.1, 130.4, 128.7, 128.8, 124.5, 120.8, 115.6, 102.6, 76.6, 55.9, 41.0, 30.9, 29.5, 24.1, 23.4, 14.3, 11.4; ESI-MS: $m/z = 569$ ($[\text{M}+\text{Na}]^+$); IR (NaCl) $\nu = 2959, 2923, 2873, 2855, 1601, 1484, 1456, 1446, 1368, 1236, 1142, 1047, 997, 901, 834 \text{ cm}^{-1}$; UV-Vis (CH_2Cl_2) λ_{max} (ϵ) = 284 (6.2×10^4), 318 (3.3×10^4) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$); High Res MS Calc'd for $\text{C}_{36}\text{H}_{50}\text{O}_4$: 546.37091. Found: 546.37118. Fluorescence (CH_2Cl_2): $\lambda_{\text{em}} = 449 \text{ nm}$ ($\lambda_{\text{exc}} = 318 \text{ nm}$).

Attempted polymerization of 14. To a mixture of **7b** (0.073 g, 0.098 mmol), **14** (0.059 g, 0.11 mmol), $\text{Pd}(\text{OAc})_2$ (0.001 g, 0.0045 mmol) and PPh_3 (0.010 g, 0.038 mmol) were added anhydrous DMF (4 mL) and triethylamine (2 mL). The resulting yellow solution was heated to reflux for 48 h, after which it was filtered and precipitated into MeOH to obtain a yellow solid. A second attempt at precipitation was unsuccessful and the product was recovered through evaporation of the solvent.

Data for 15. ^1H NMR (300 MHz, CDCl_3) δ 7.7 (br), 7.5 (br), 7.2 (br), 4.2 (br), 4.1 (br), 2.3-0.5 (br). IR (NaCl) $\nu = 2954, 2929, 2873, 2860, 1725, 1594, 1461, 1368, 1265, 1239, 1131, 1017 \text{ cm}^{-1}$; GPC: $M_n = 2238$, $M_w = 3313$.

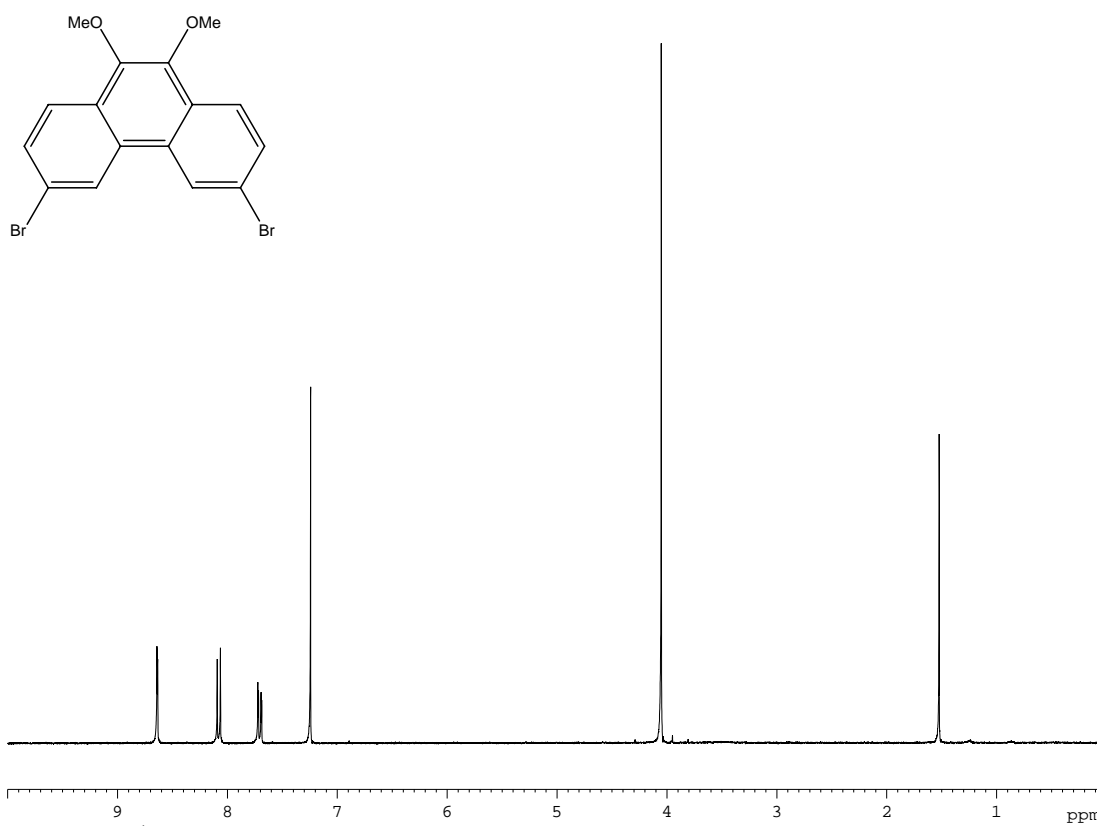


Figure 1. ^1H NMR spectrum of **3**.

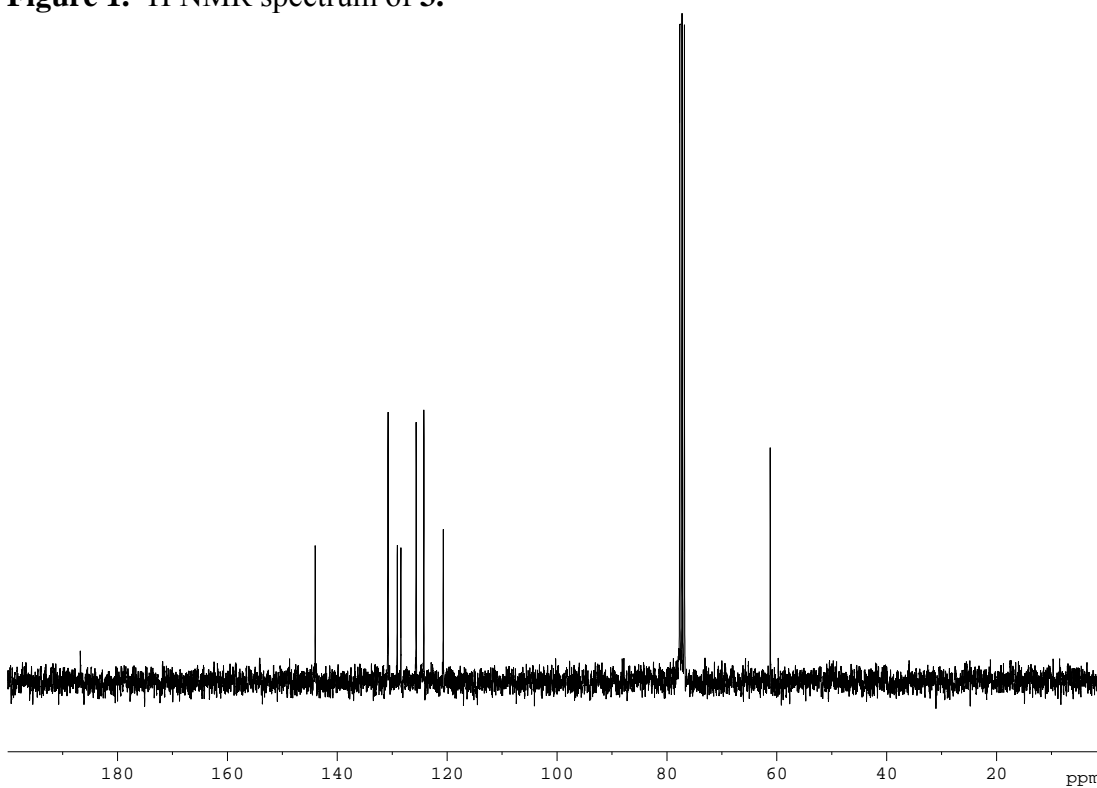


Figure 2. ^{13}C NMR spectrum of **3**.

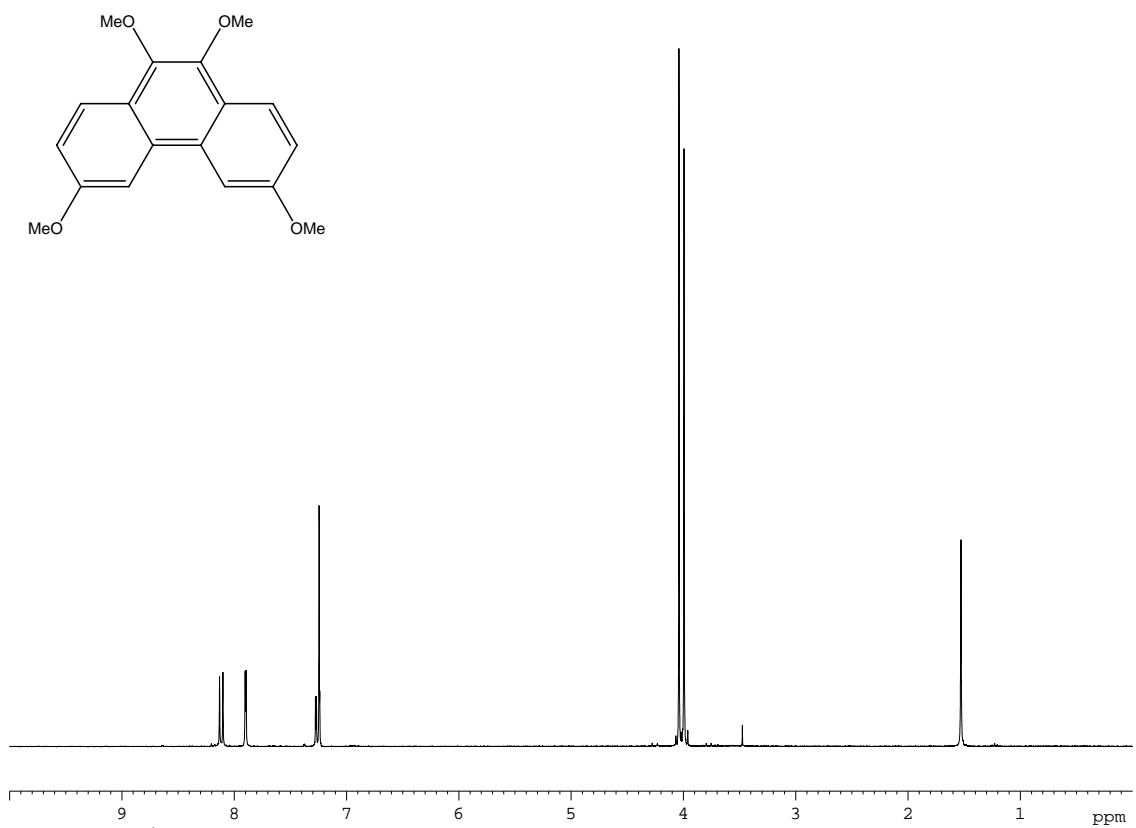


Figure 3. ^1H NMR spectrum of **4**.

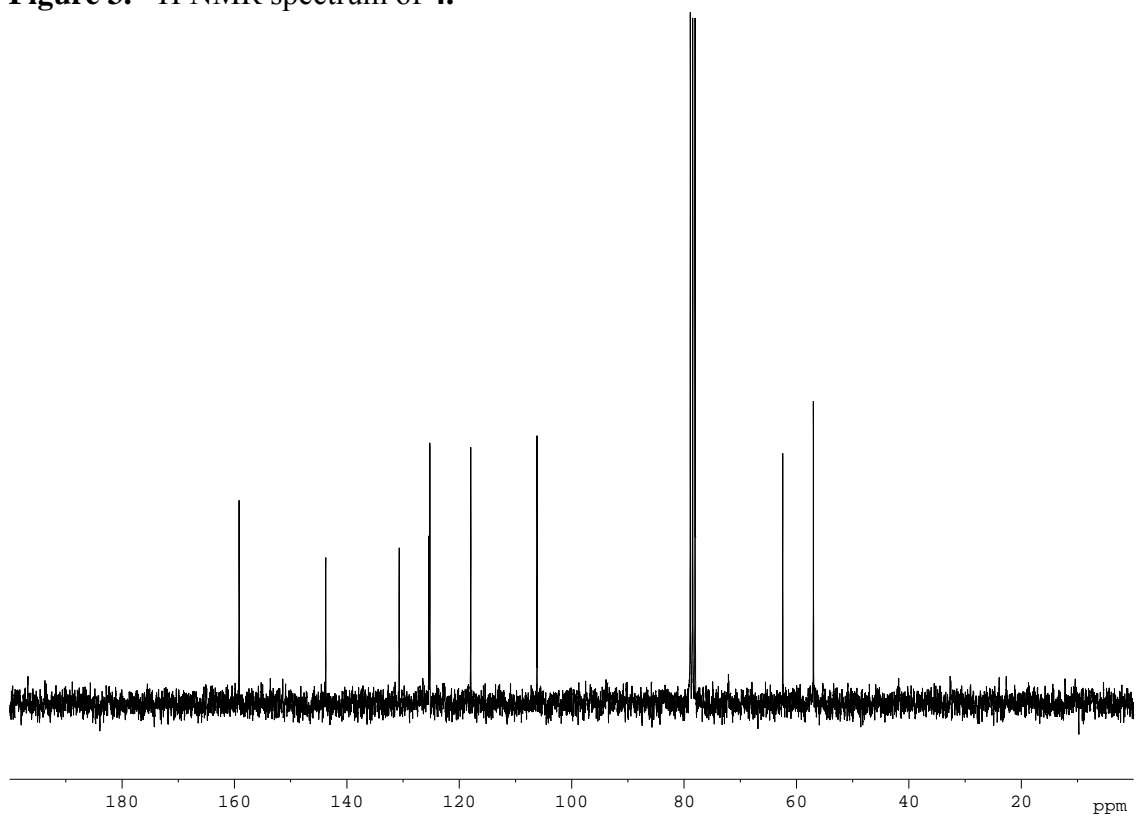


Figure 4. ^{13}C NMR spectrum of **4**.

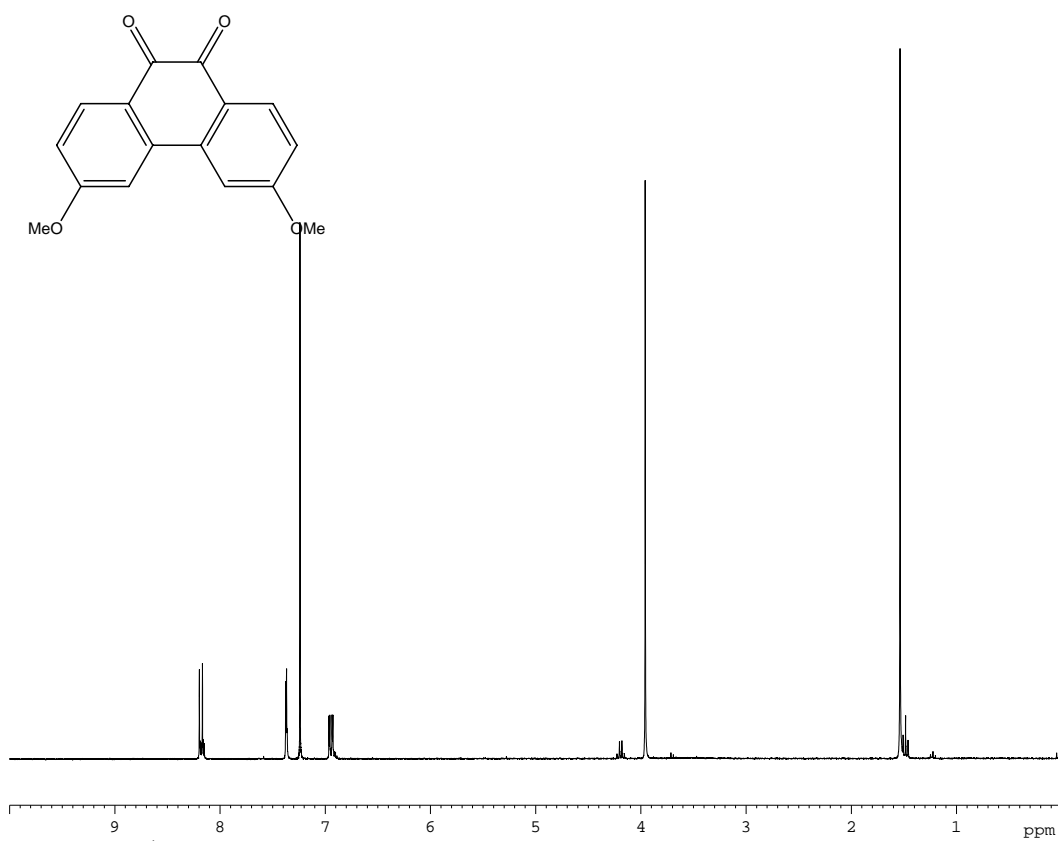


Figure 5. ^1H NMR spectrum of **5**.

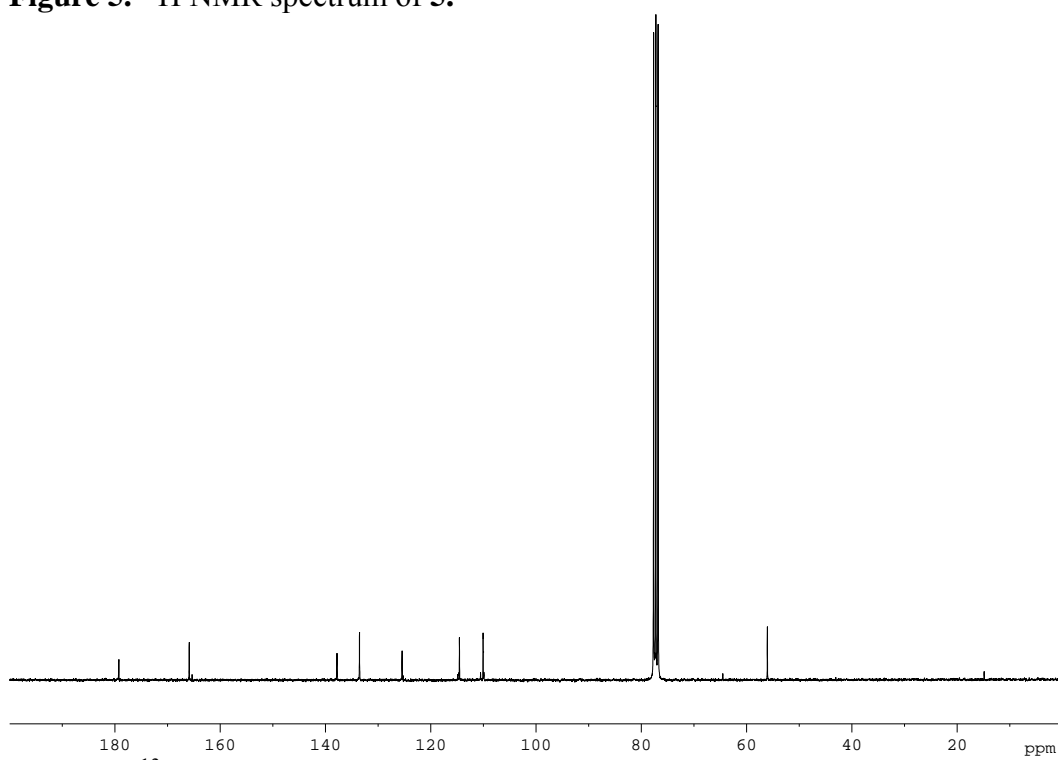


Figure 6. ^{13}C NMR spectrum of **5**.

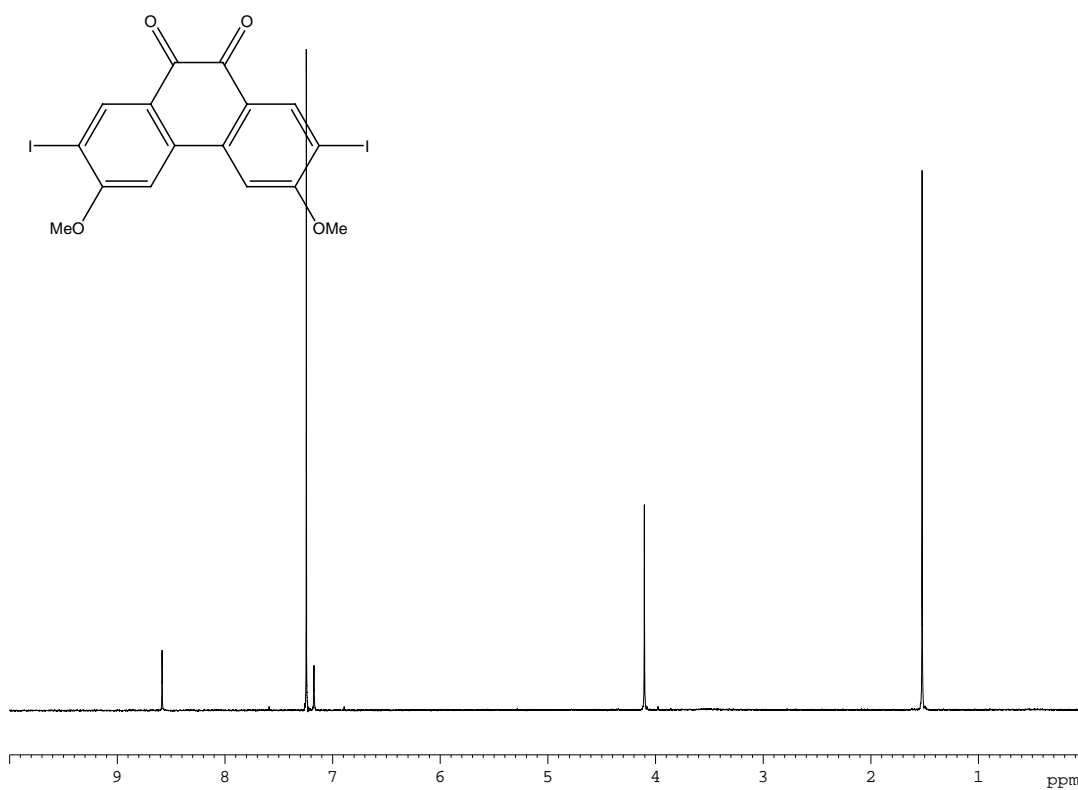


Figure 7. ^1H NMR spectrum of **6**.

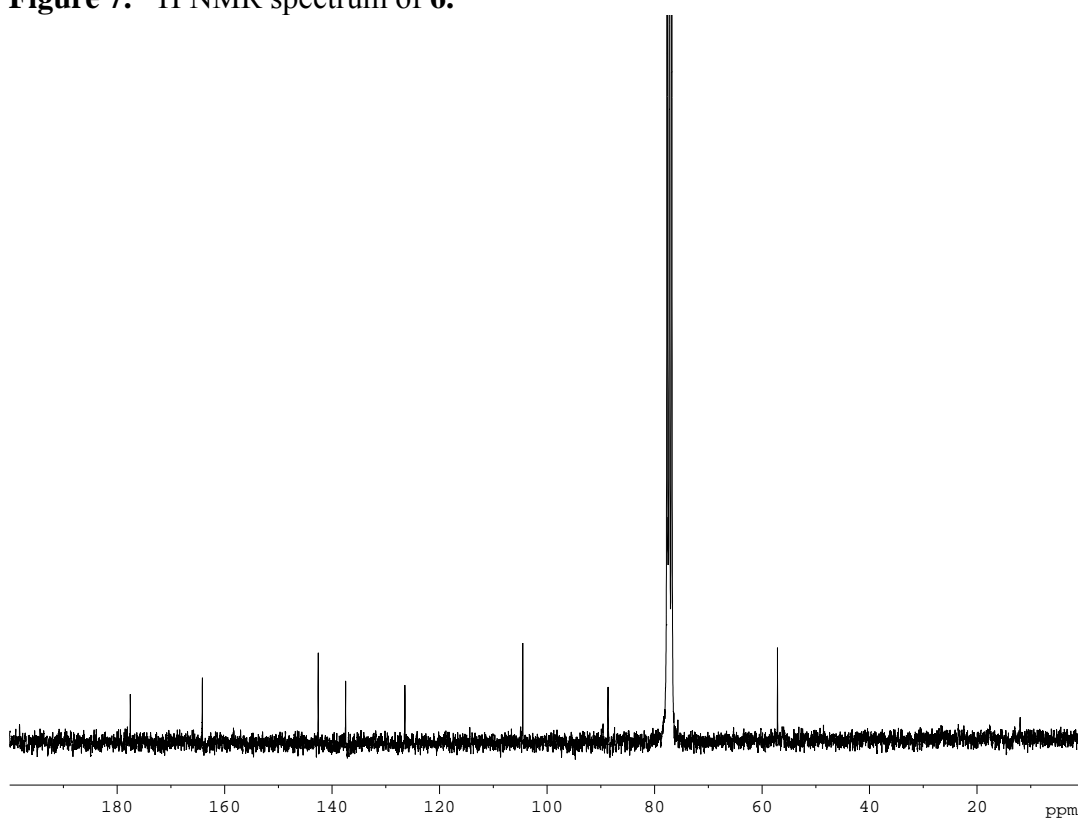


Figure 8. ^{13}C NMR spectrum of **6**.

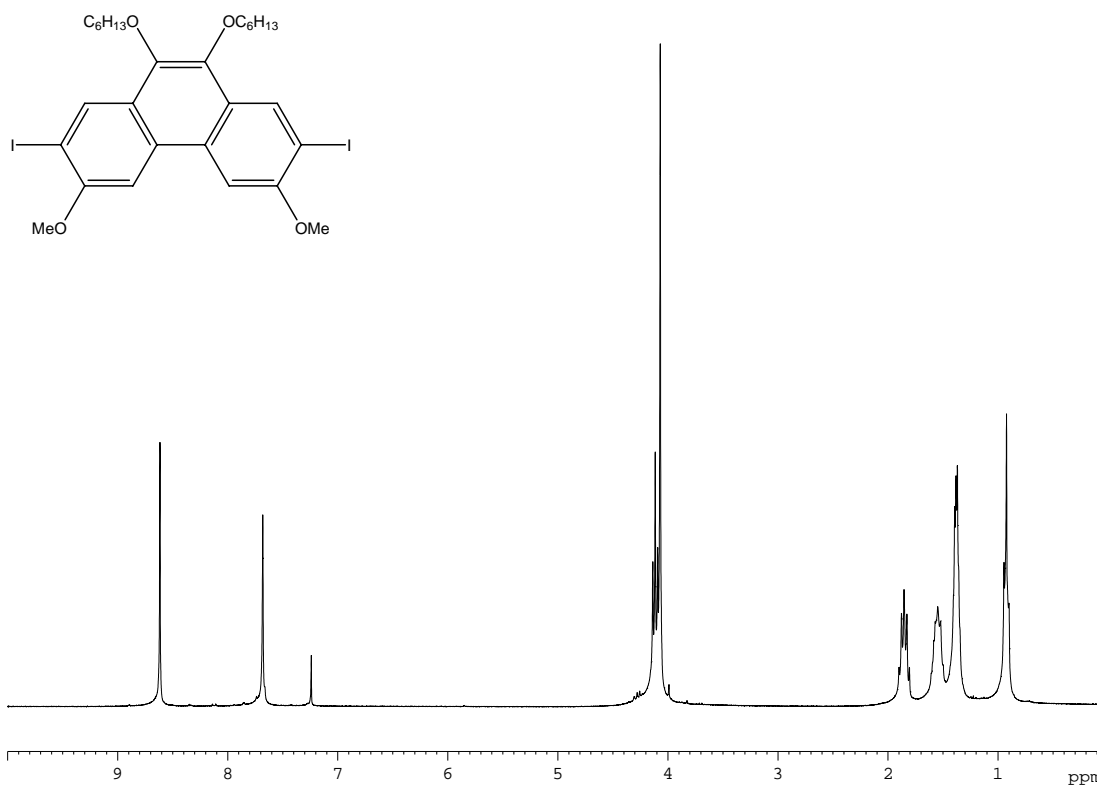


Figure 9. ^1H NMR spectrum of **7a**.

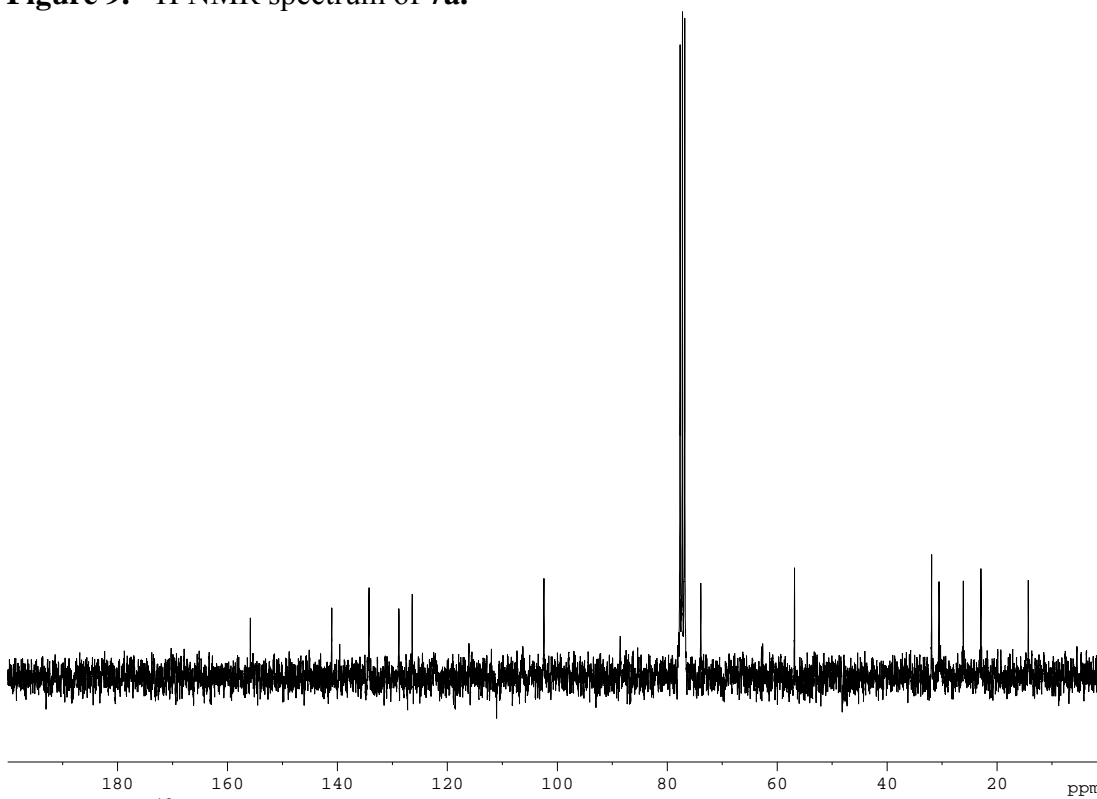


Figure 10. ^{13}C NMR spectrum of **7a**.

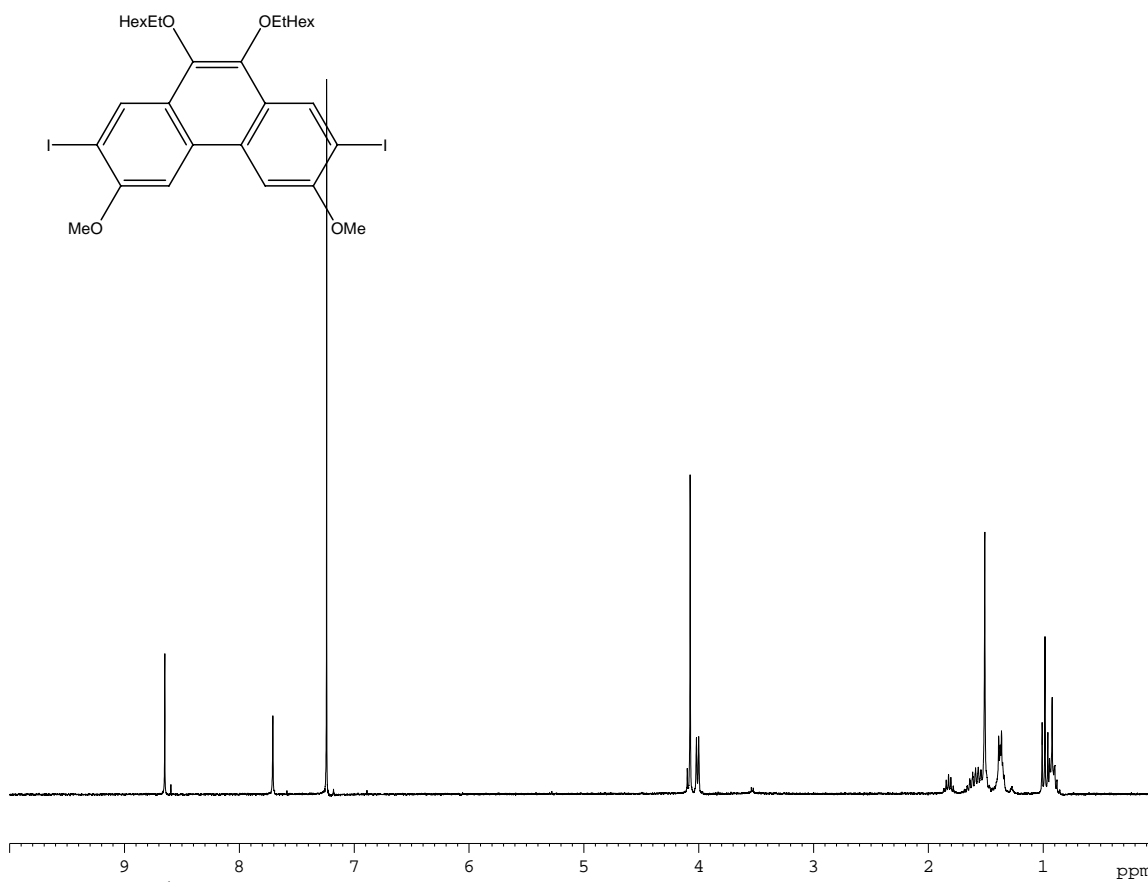


Figure 11. ^1H NMR spectrum of **7b**.

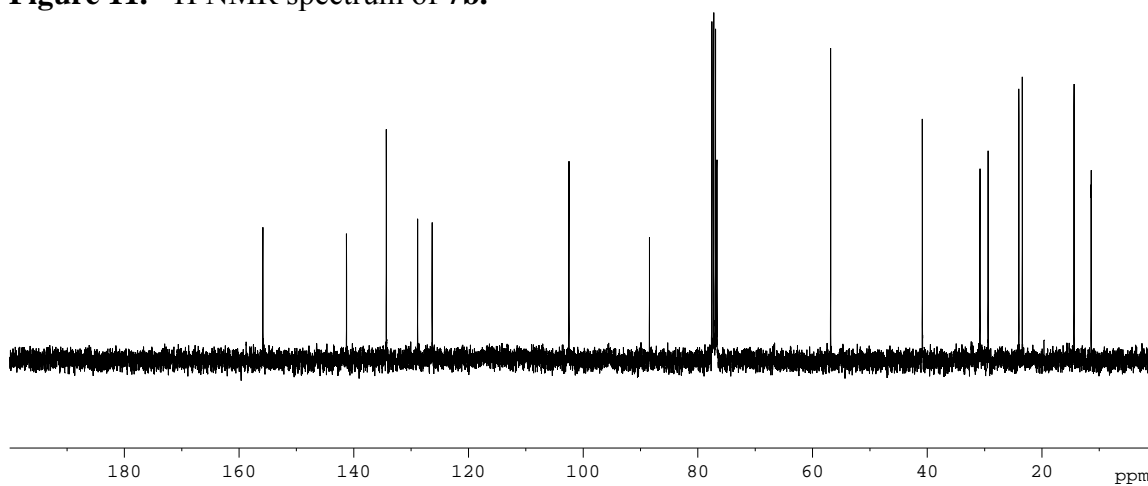


Figure 12. ^{13}C NMR spectrum of **7b**.

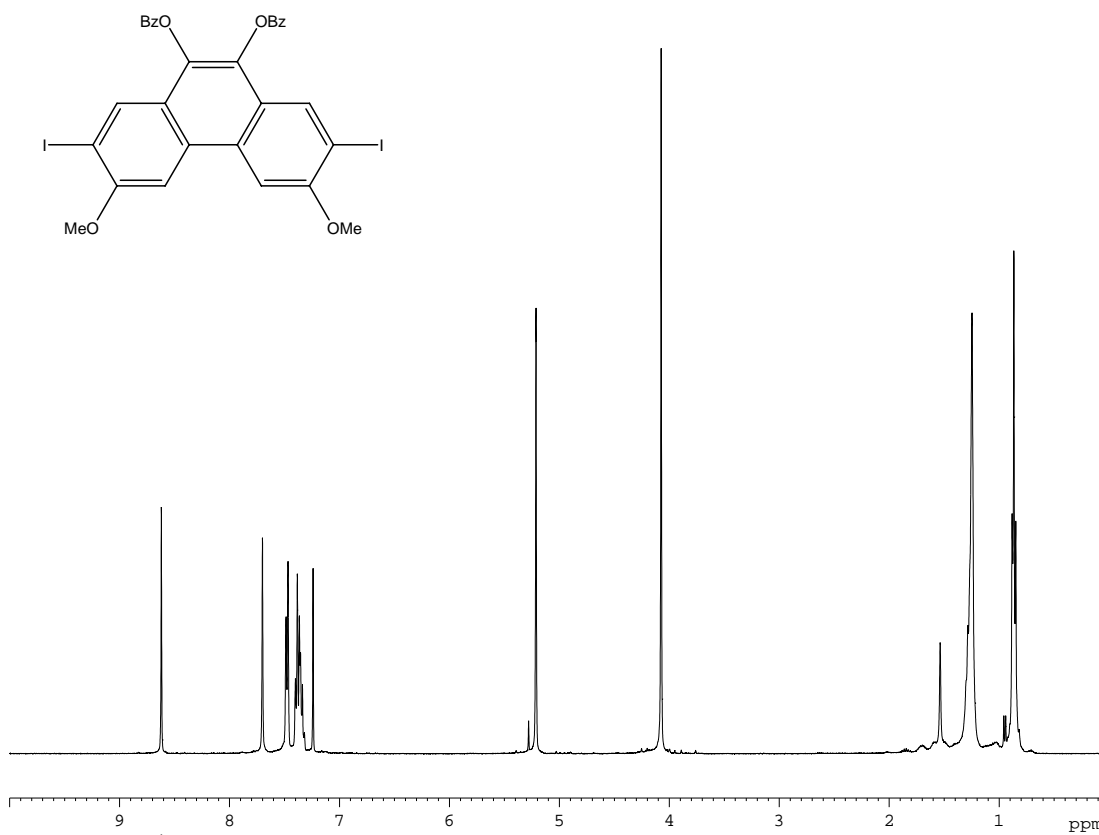


Figure 13. ^1H NMR spectrum of **7c**.

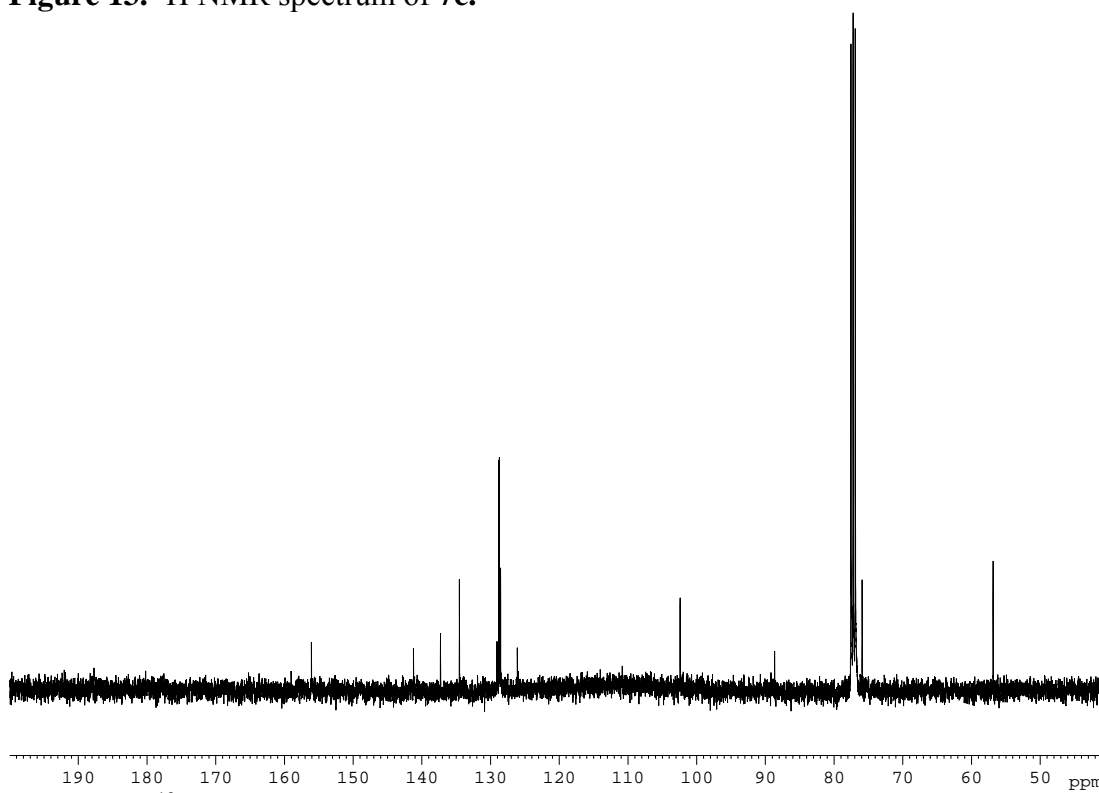


Figure 14. ^{13}C NMR spectrum of **7c**.

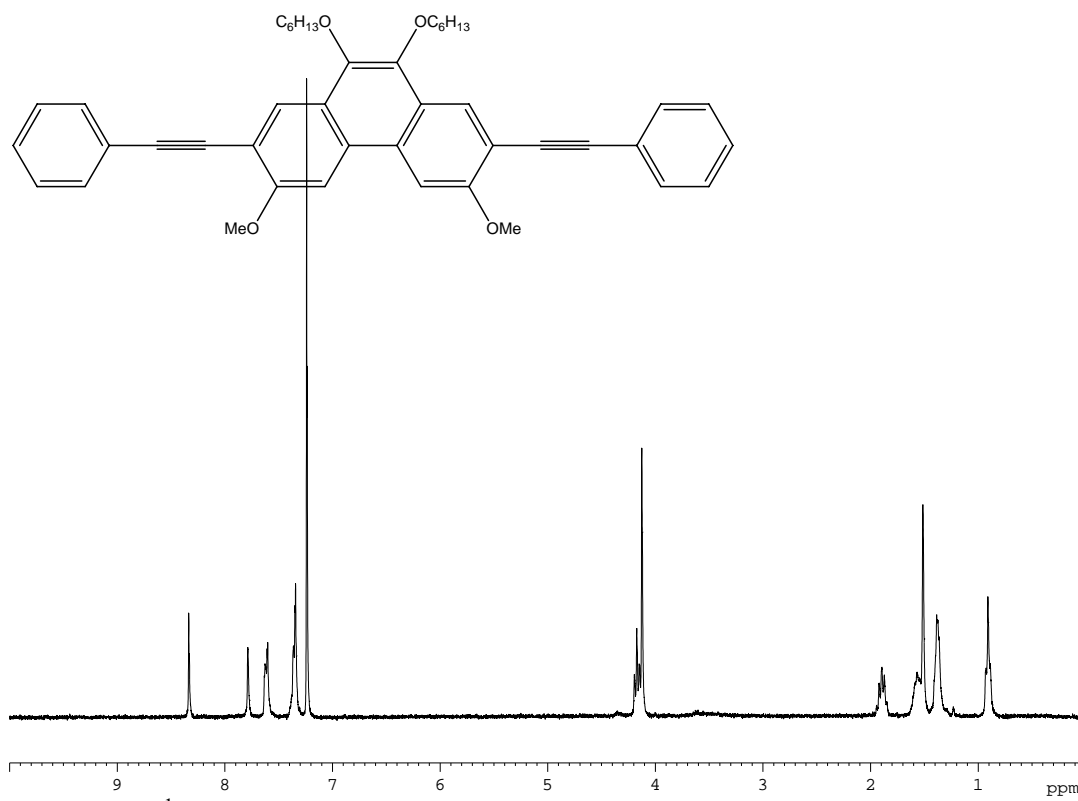


Figure 15. ^1H NMR spectrum of **8**

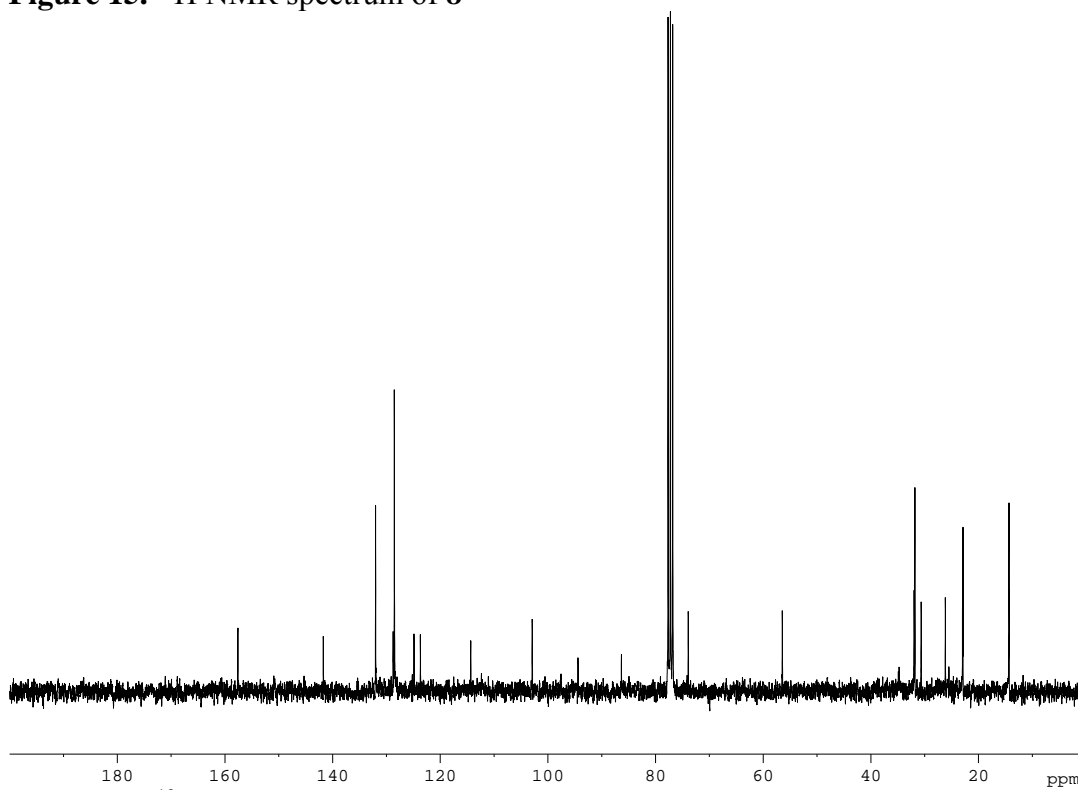


Figure 16. ^{13}C NMR spectrum of **8**.

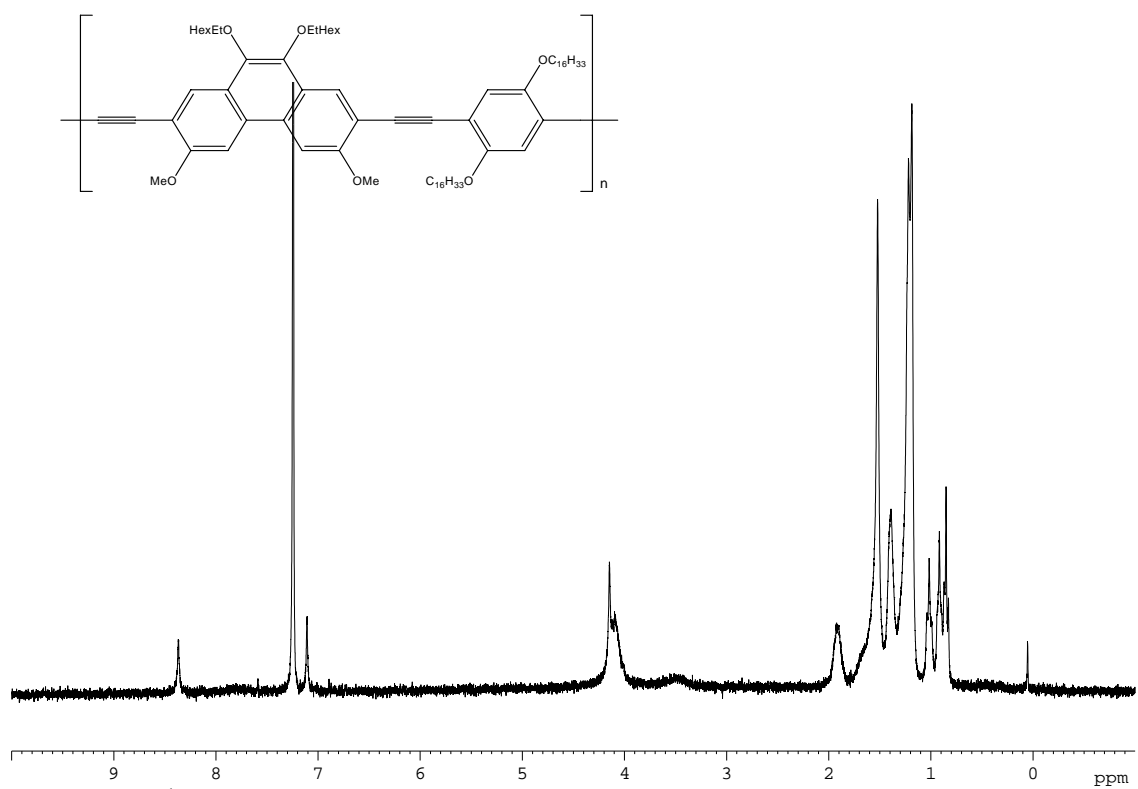


Figure 17. ^1H NMR spectrum of **10**.

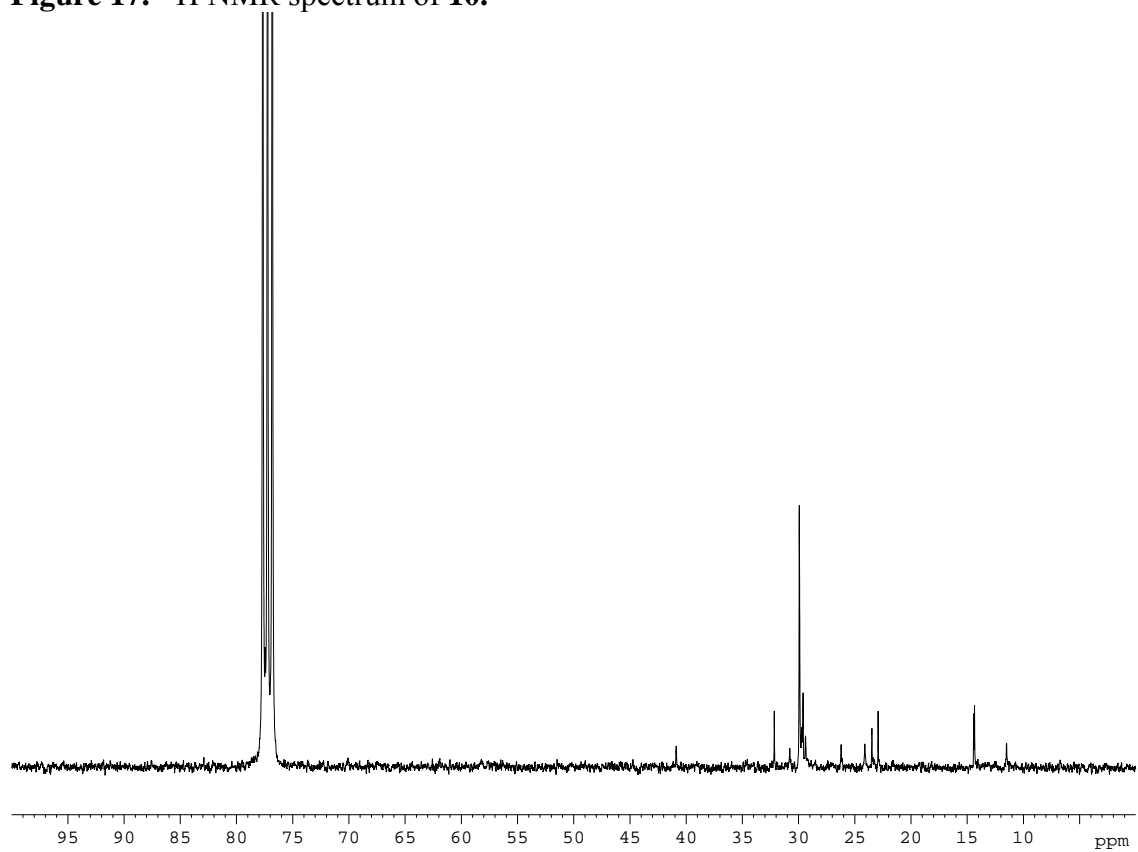


Figure 18. ^{13}C NMR spectrum of **10**.

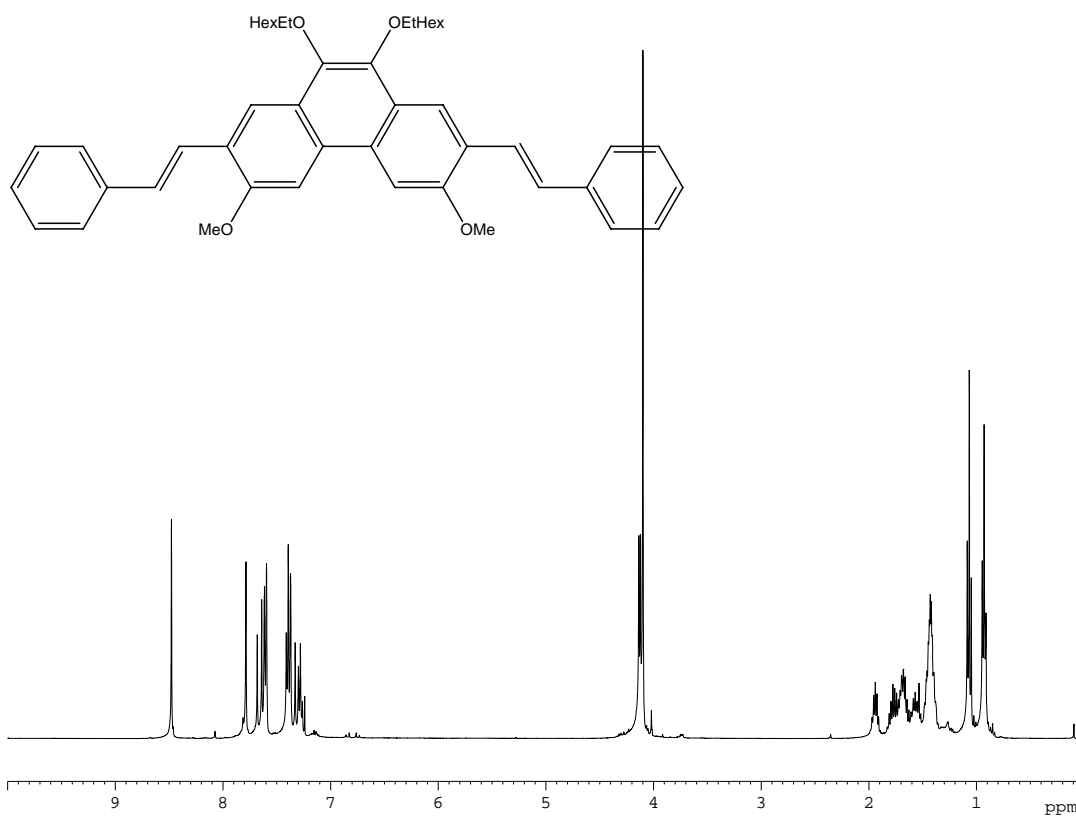


Figure 19. ^1H NMR spectrum of **11**.

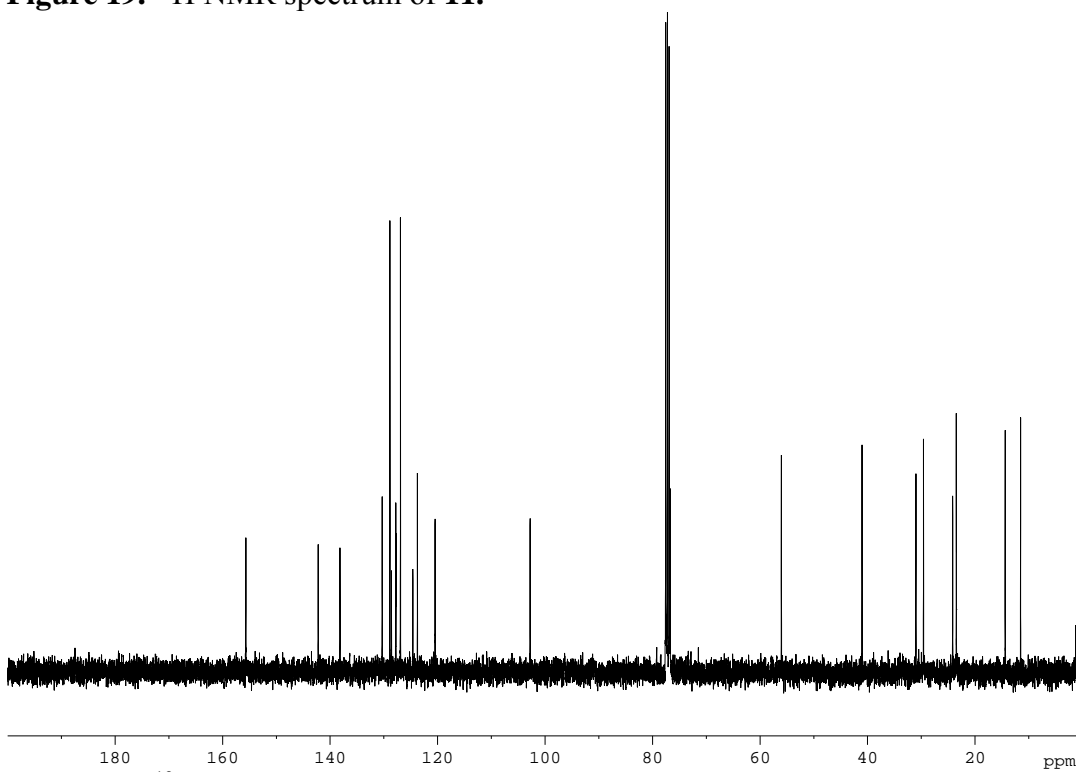


Figure 20. ^{13}C NMR spectrum of **11**.

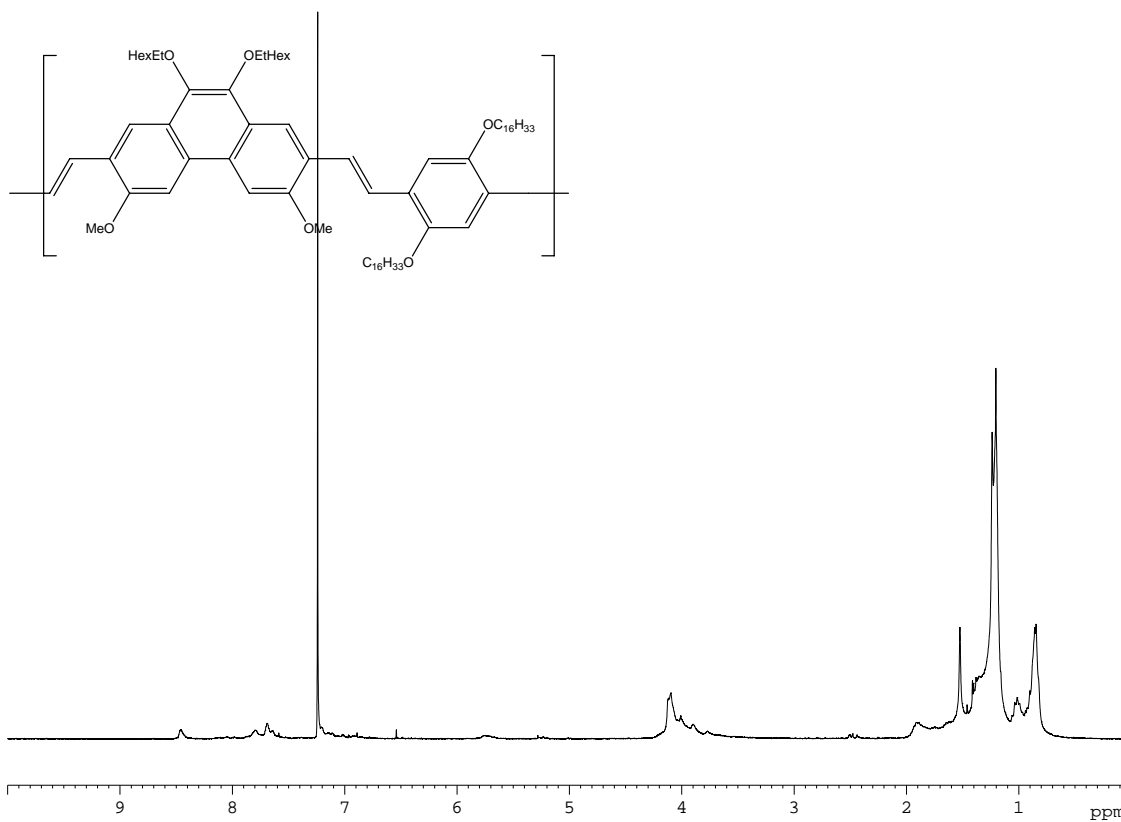


Figure 21. ^1H NMR spectrum of **13**.

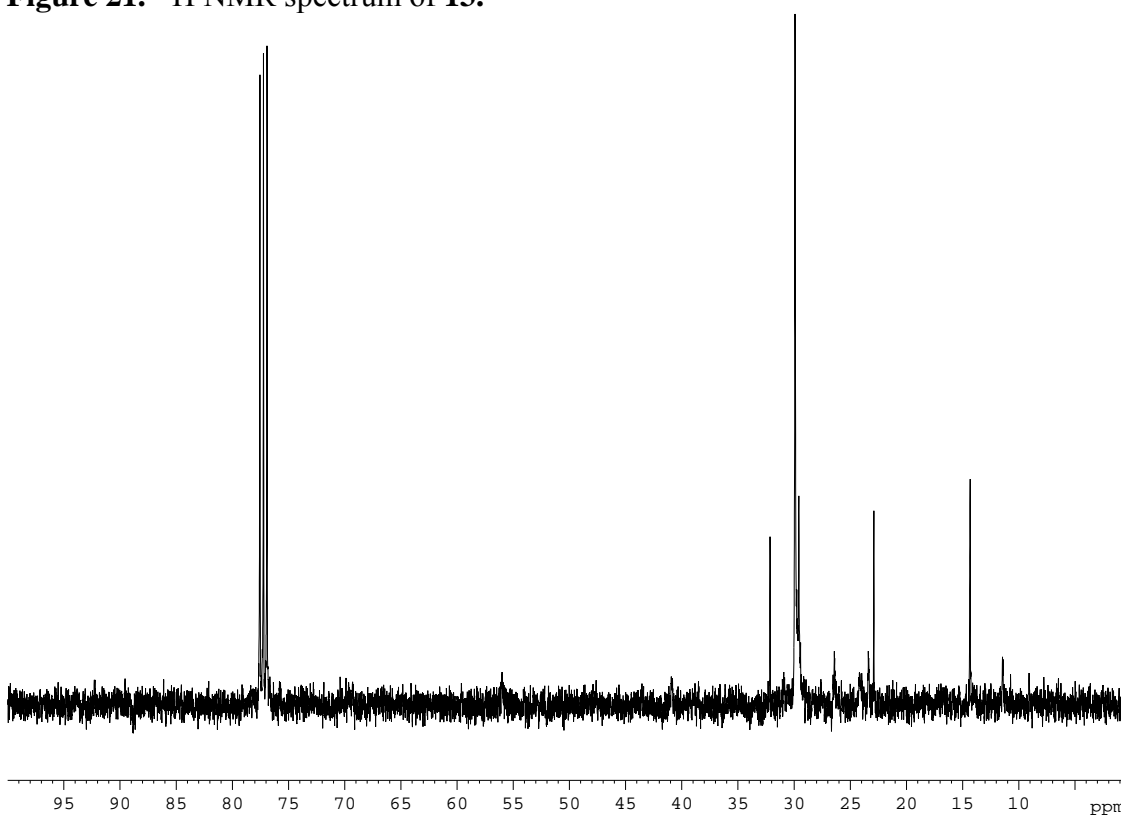


Figure 22. ^{13}C NMR spectrum of **13**.

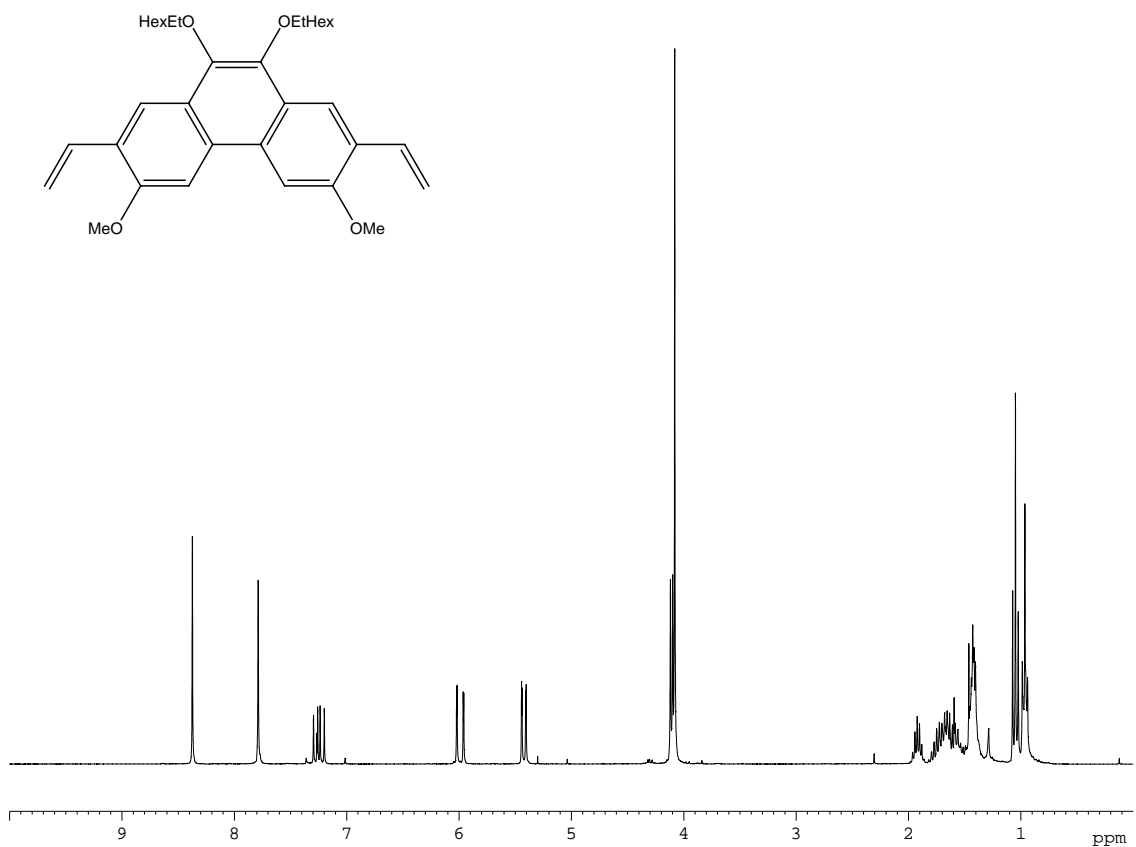


Figure 23. ^1H NMR spectrum of **14**.

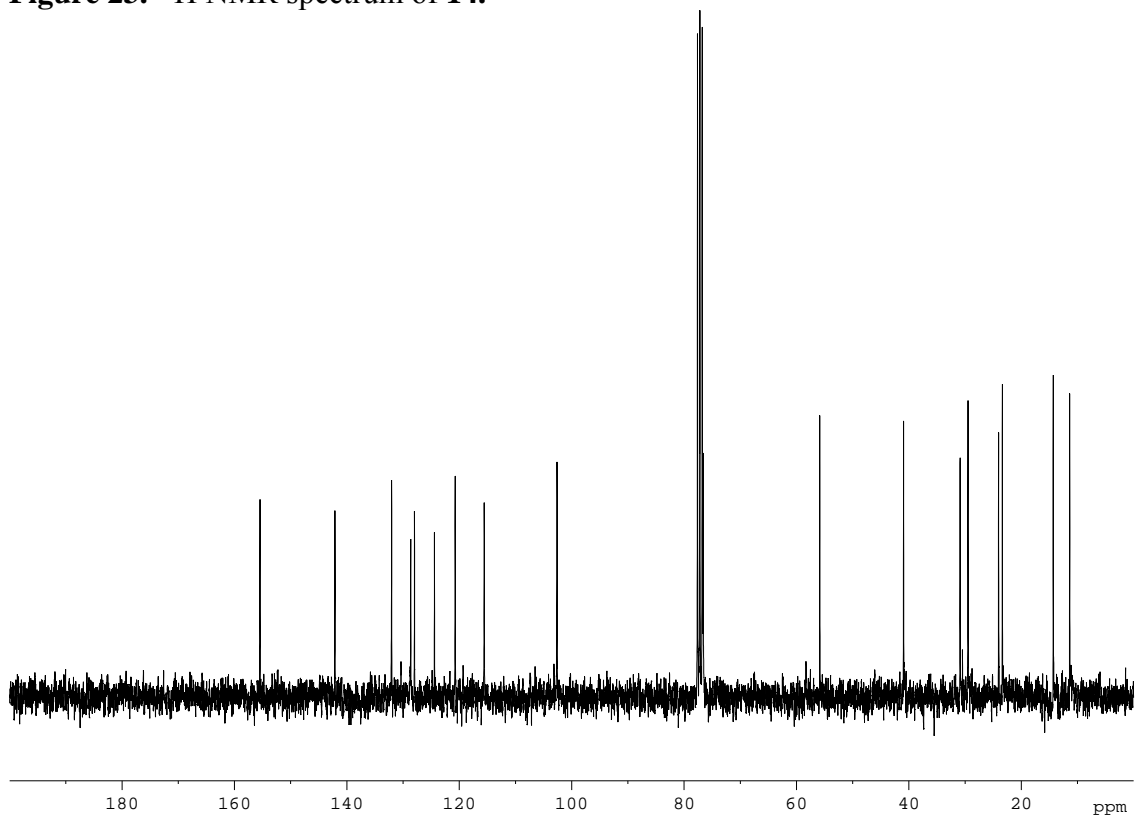


Figure 24. ^{13}C NMR spectrum of **14**.

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