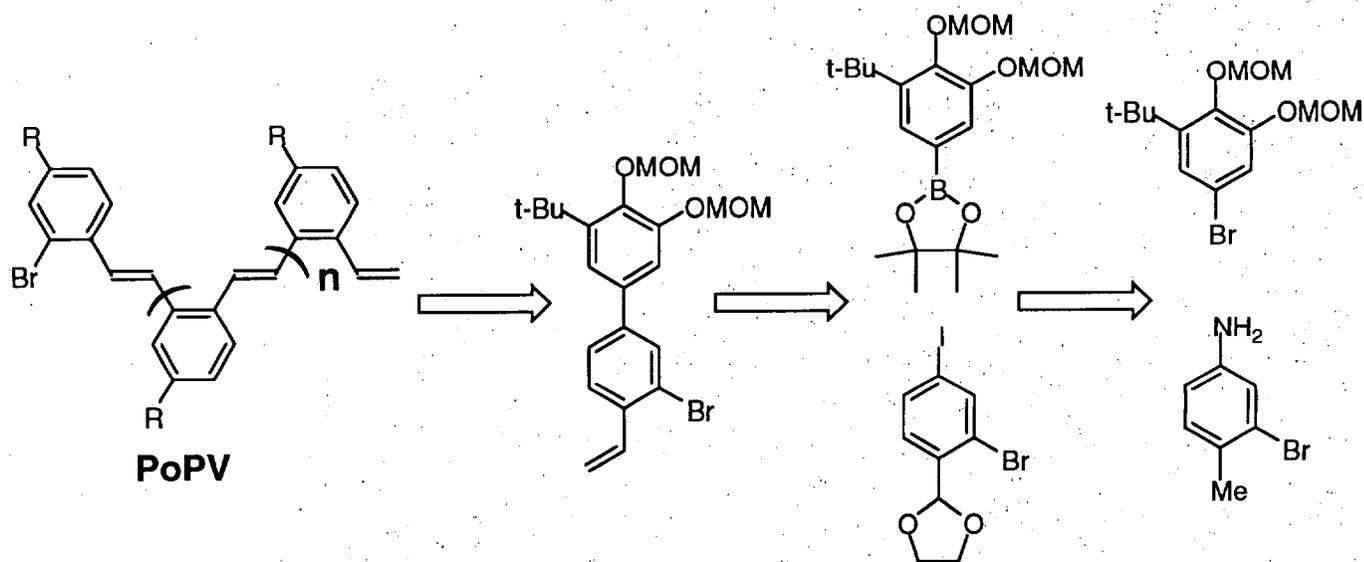
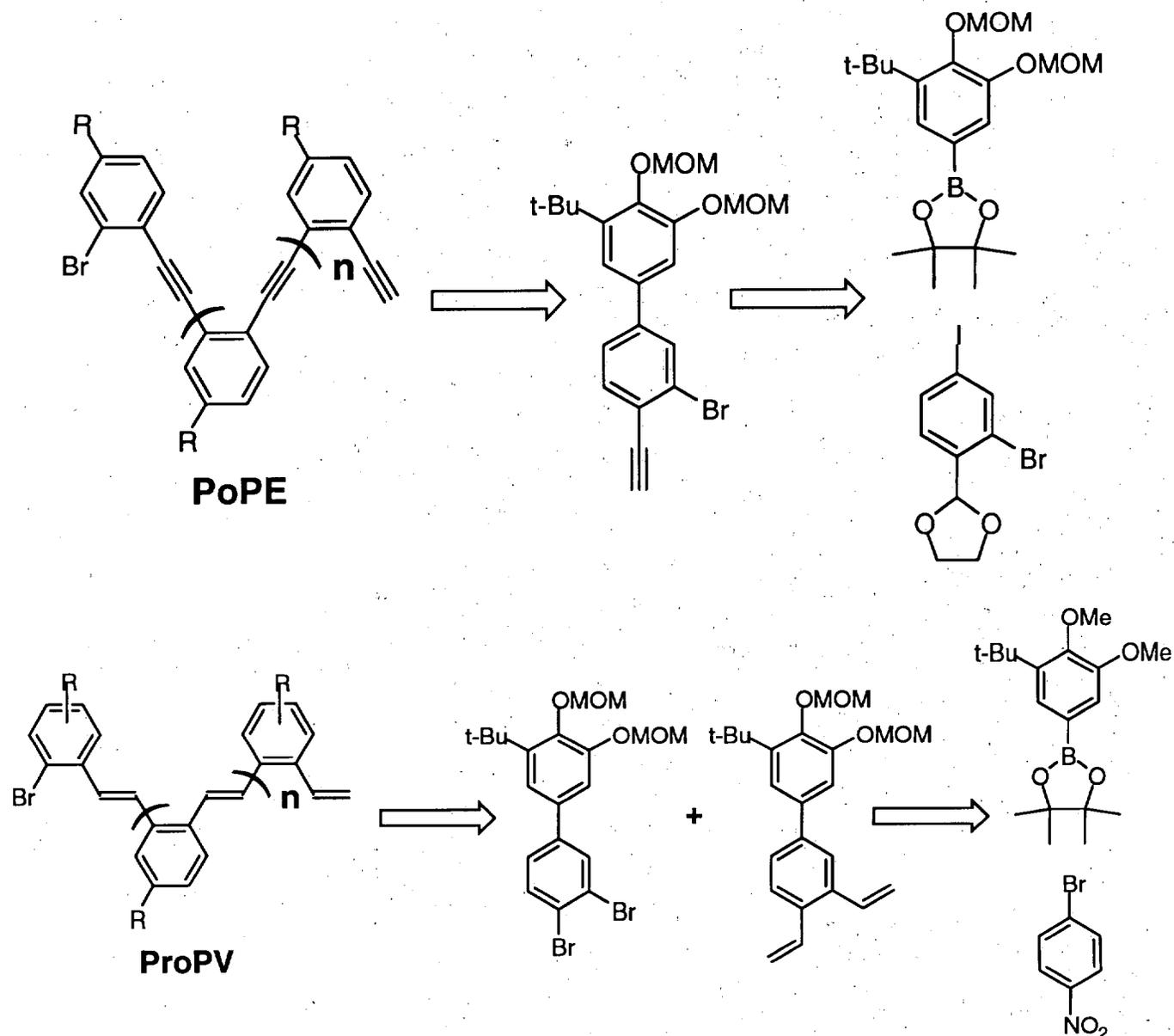


Synthetic and Experimental Design. Retrosynthetic analyses of our protected catechol polymers (PoPV[CatMOM₂], PoPV[CatMOM₂], ProPV[CatMOM₂]) are given in Scheme 3. Methoxymethyl-protection was chosen since this group can be removed under mild conditions that will not compromise the polymer main chain. The syntheses feature two different Pd-catalyzed coupling reactions. A polymer with random orientation of semiquinone groups (from ProPV[CatMOM₂]) was prepared to determine experimentally both the existence and the strength of *antiferromagnetic* interactions in the absence of a head-to-tail arrangement of radical units.

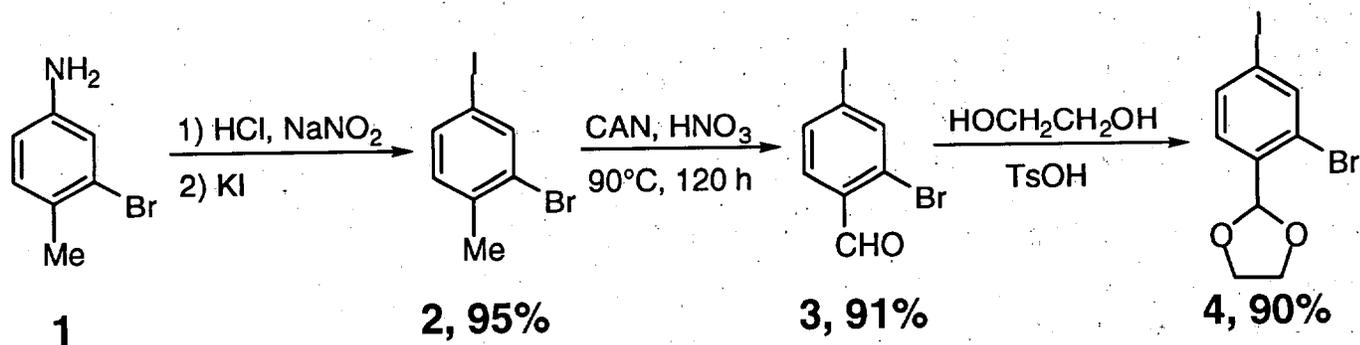




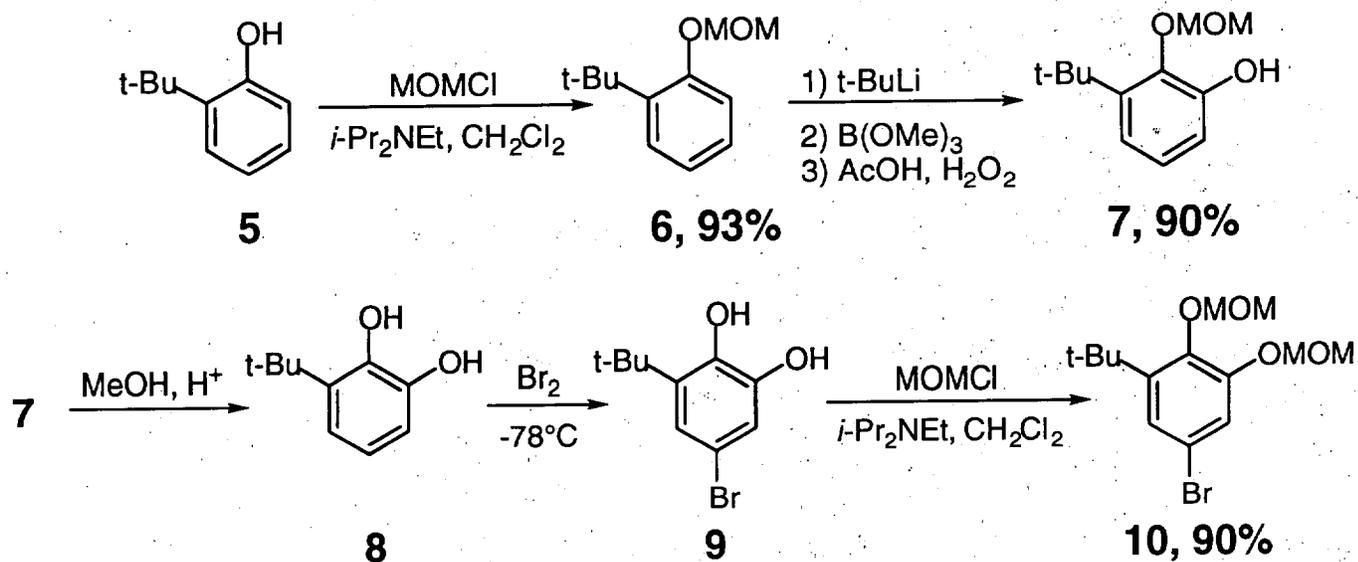
Scheme 3. Retrosynthetic Analyses of Quinone Polymers.

PoPV Monomer Synthesis. 2-Bromo-4-iodotoluene **2** was synthesized in good yield from commercially-available aniline derivative **1** by diazonium salt reactions with potassium iodide as previously described in the literature.¹ Conversion of the toluene derivative **2** to the benzaldehyde

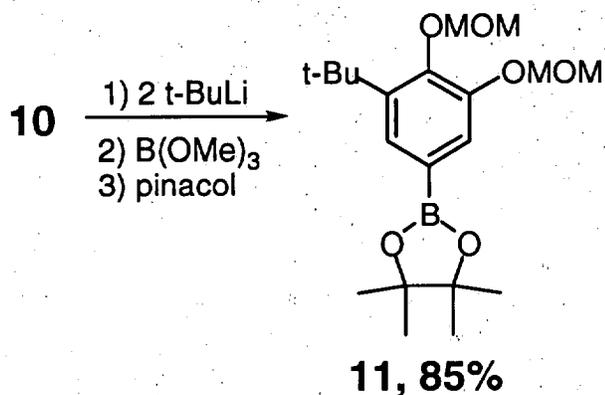
derivative **3** was affected with ceric ammonium nitrate.² Ketalization was achieved using a standard protocol giving **4**.



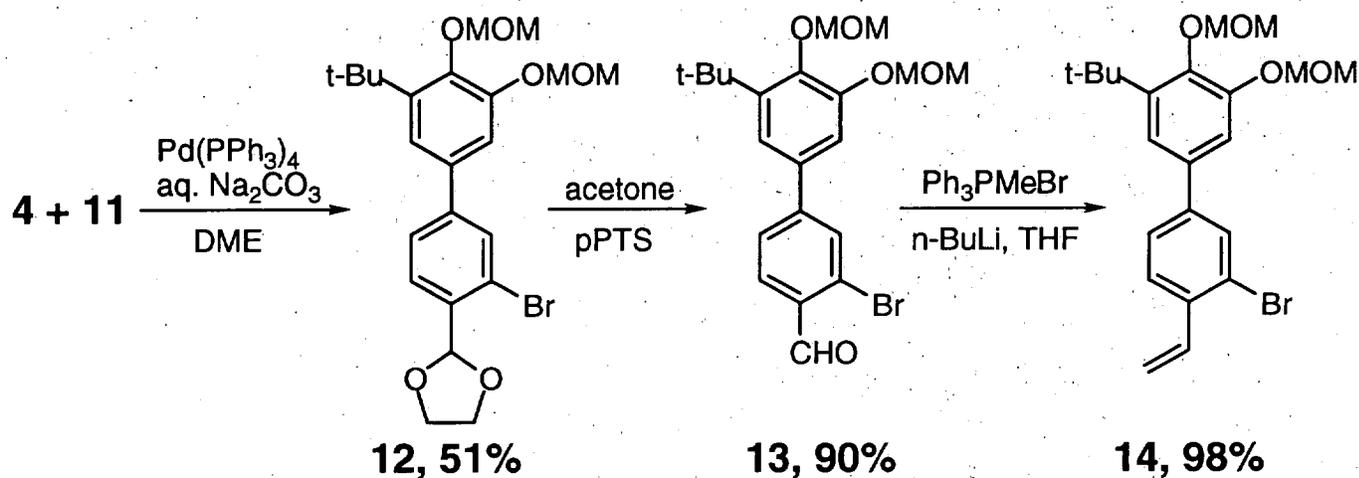
Compound **6** was prepared from 2-*t*-butylphenol and MOMCl.³ The protected phenol was treated with *t*-butyllithium in pentane followed by reaction with trimethylborate; subsequent oxidation with hydrogen peroxide gave compound **7**. Deprotection of **7** gave catechol **8** which was brominated to yield **9** and reprotected with MOMCl to produce intermediate **10** in excellent yield.



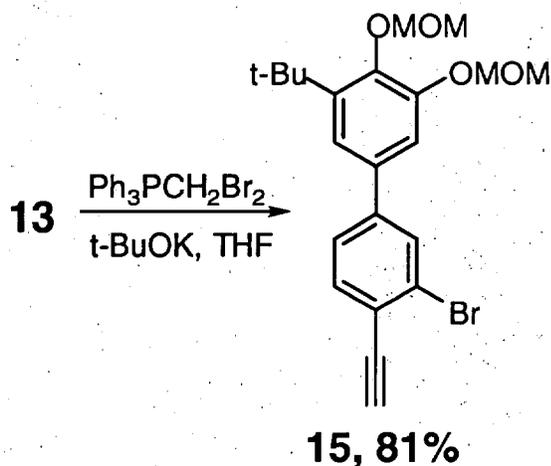
Transmetalation of bromide **10** followed by reaction with trimethylborate and ester exchange with pinacol gave the **11** in good yield.



The Suzuki cross coupling reaction^{4,5} produced the biaryl 12. The protected aldehyde 12 was unmasked to 13 and subjected to the Wittig reaction yielding monomer 14. The FTIR spectrum of 14 displays peaks at 1013 cm^{-1} associated with the vinylidene, while the FT-Raman spectrum exhibits peaks at 1625 and 1599 cm^{-1} associated with the vinylidene ($-\text{CH}=\text{CH}_2$) and the $\text{C}=\text{C}$ aromatic stretches, respectively.

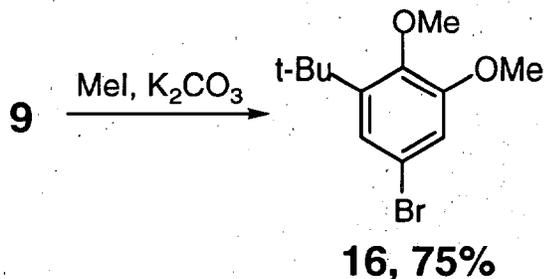


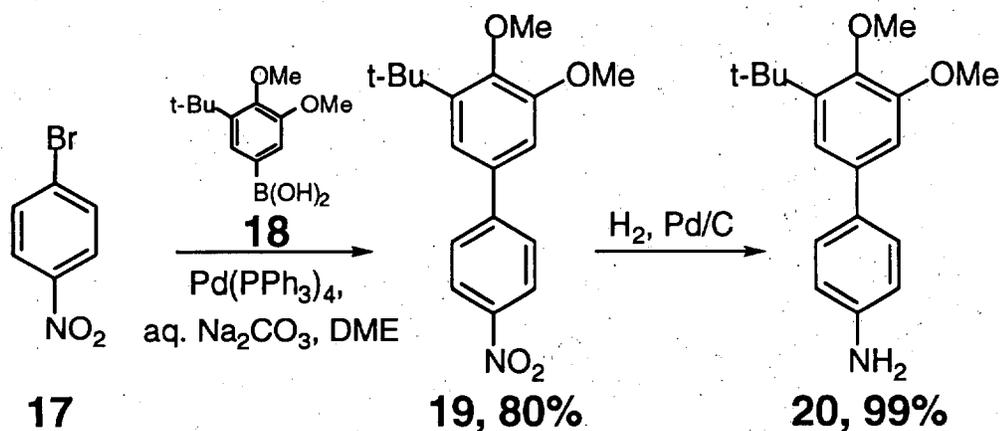
PoPE Monomer Synthesis. Synthesis of the monomer for PoPE[CatMOM₂] is readily obtained from aldehyde 13 by treatment with the ylide of bromomethyltriphenylphosphonium bromide followed by dehydrohalogenation⁶. Acetylene monomer 16 is thus produced in 81% yield.



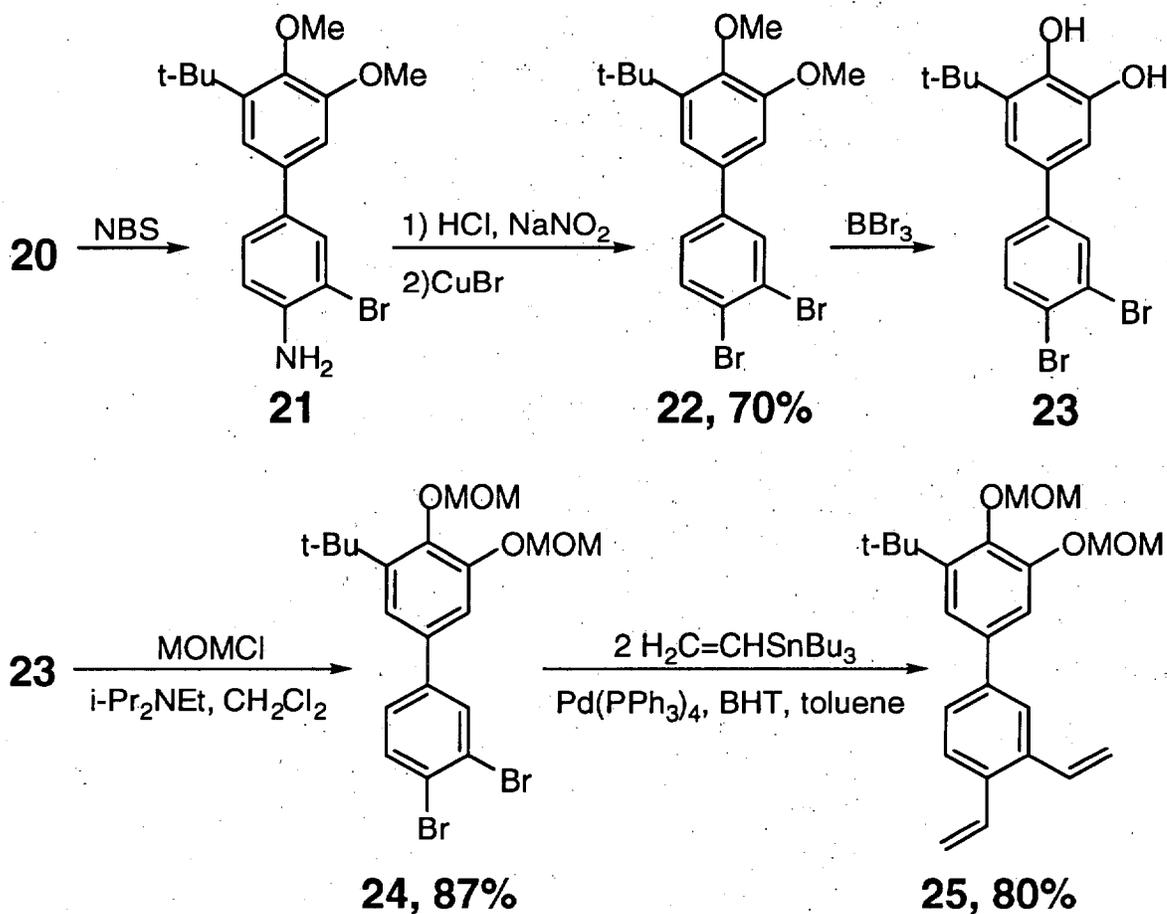
The FT-Raman spectrum of the acetylene monomer **15** shows absorptions at 2105 cm^{-1} for the terminal acetylene and a peak at 1597 cm^{-1} associated with the C=C bond stretches of the aromatic ring.

ProPV Monomer Synthesis. Synthesis of the monomers for preparation of ProPV[CatMOM₂] is shown below. Because of the functionality of the first few biaryl compounds, we chose to use the methyl protecting-group and then convert to the MOM group prior to polymerization. Catechol derivative **9** was methylated and the resulting material was purified by sublimation to produce **16** as a white solid. Transmetalation of **16** and reaction with trimethylborate followed by aqueous workup yields the boronic acid **18**. Suzuki reaction of **17** with *p*-bromonitrobenzene gave the nitrobiphenyl derivative **19**. Reduction of **19** gave the aminobiphenyl derivative, **20**.





Bromination of the aminobiphenyl **20** using NBS followed by the Sandmeyer reaction⁷ leads to the dibromide **22**. Deprotection to the dibromide **23** and reprotection with MOMCl gives monomer **24**. The divinyl monomer **25** was prepared conveniently by Stille cross-coupling reaction of **24** with tributyl(vinyl)tin.⁸⁻¹⁰



All reagents were purchased from Aldrich, unless otherwise specified. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium benzophenone-ketyl. Toluene was distilled from sodium. Methylene chloride was distilled from calcium hydride.

Synthetic procedures were performed using standard Schlenk techniques. All air sensitive reactions were performed in oven-dried glassware under an argon atmosphere and were stirred magnetically, unless otherwise specified. Solvent distillations, and electrochemistry were carried out under an inert atmosphere of nitrogen. Melting points and heats of fusion were determined by differential scanning calorimetry using Perkin-Elmer DSC-7 calibrated with an indium standard.

Flash column chromatography was done on silica gel (60, 230 - 400 mesh ASTM) purchased from American Scientific Products or Baxter Scientific. Radial preparative-layer chromatography (radial PLC) was performed on a Chromatotron (Harrison Associates, Palo Alto, CA) using glass plates coated with 1, 2, or 4 mm layers of Kieselgel 60 PF₂₅₄ containing gypsum. TLC analyses were performed on Whatman TLC plates with fluorescent 250 μm silica gel layer on aluminum backing. Visualization was accomplished with UV light, I_2 , a 5% solution of phosphomolybdic acid in ethanol or 0.5% solution of 2,4-dinitrophenylhydrazine in ethanol. Low pressure liquid chromatography (LPLC) was performed using FMI Lab pump (Fluid Metering, Inc., Oyster Bay, NY) and either Type B or C Lobar® Fertigsäule Große LiChroprep columns (E. Merck, Darmstadt, Germany). Bio-Beads® S-X1 Beads (mesh size = 200-400; M.W. exclusion limit = 14,000; M.W. operating range 600 - 14,000) and Bio-Beads® S-3X Beads: (mesh size = 200 - 400; M.W. exclusion limit = 2,000; and M.W. operating range = up to 2,000) were used for gel permeation separations of the materials prepared in this work (100% CH_2Cl_2). Gel Permeation Chromatography (high pressure) was carried out in THF, using a Waters Associates HPLC pump equipped with a Differential Refractometer R410 (Waters Associates) and four columns (Showdex KF-800 in series) in tandem. Polystyrene standards were used for calibration.

Combustion analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. High-resolution (HRMS) and Field Desorption (FDMS) mass spectral analyses were carried out at North Carolina State University. GC/MS analyses were carried out on a Hewlett Packard 5895B GC/MS system. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FTIR spectrophotometer. Raman spectra were carried out at GlaxoWellcome on a Nicolet FT-Raman 950 spectrometer equipped with an excitation laser of a Neodymium YVO₄ at a wavelength of 1064 nm and a HeNe laser at wavelength of 632.8 nm.

Fluorescence and Excitation Spectra were measured with a SPEX Fluoromax™ Spectrofluorometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are in δ units (ppm) using CDCl_3 (7.26 ppm) was used as an internal reference for ^1H NMR and the CDCl_3 absorption (77.0 ppm) for ^{13}C NMR spectra. Coupling constants (J) are reported in Hertz. NMR splitting patterns are designated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; and b, broad.

Electrochemical and EPR experiments were performed as described previously.¹¹

2-Bromo-4-iodotoluene (2). A solution of the amine hydrochloride was prepared by adding with vigorous stirring 6.5 mL of deionized water to 3-bromo-4-methylaniline (4.78 g, 25.7 mmol) followed 6.5 mL of concentrated HCl. The solution was heated to 60 °C and stirred for 30 min to improve the solubility and reduce the particle size. The solution was cooled to 0 °C. A solution of NaNO_2 (1.9 g, 27.4 mmol) in 4.1 mL H_2O was added dropwise to the amine hydrochloride solution maintaining the temperature at 0 – 5 °C. Then a solution of KI (4.52 g, 27.2 mmol) in 4.5 g H_2O was added dropwise with vigorous stirring maintaining the temperature at 0 – 5 °C. After most of the N_2 evolved, the reaction mixture was heating to 60 °C, cooled to room temperature, diluted with Et_2O . The organic layer was washed with $\text{Na}_2\text{S}_2\text{O}_3$ (3 x 50 mL); brine (3 X 50 mL); dried over Na_2SO_4 ; filtered; and solvent concentrated *in vacuo* to give the crude product. Purification by flash chromatography (100% pet ether) gave 7.2 g (95%) of 2. TLC: R_f 0.2 (silica gel, 10% pet ether); ^1H NMR (300 MHz, CDCl_3) δ 7.86 (s, 1 H), 7.50 (d, $J = 7.6$ Hz, 1 H) 6.93 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.2, 137.6, 136.4, 132.3, 125.9, 90.8, 22.77; FTIR (KBr): 3048, 2953, 1574, 1548, 1464, 1364, 1036, 803, 674 cm^{-1} .

2-Bromo-4-iodo-benzaldehyde (3). A stirred solution of 2-bromo-4-iodo-toluene (5.75 g, 19.4 mmol) in 8M HNO_3 (97 mL) was heated at 90 °C. Ceric ammonium nitrate (Acros) (42.5 g, 77.5 mmol) was added portionwise over a period of 2 d at such a rate that the reaction mixture remained pale yellow. After the addition of the ceric ammonium nitrate, the solution was heated and stirred for an additional 3 d at 90 °C. Upon completion of the reaction, the solution was yellow to colorless. The mixture was extracted with CH_2Cl_2 , and the organic extracts were washed with water (3 x 50 mL), saturated aqueous NaHCO_3 (3 x 50 mL), and brine (3 x 50 mL). The organic phase was dried over Na_2SO_4 , filtered and concentrated *in vacuo* to give the crude product. Purification by flash chromatography (deactivated silica gel, 10% CH_2Cl_2 /pet ether) gave 5.50 g (91%) of 3 as a white solid, mp 79-80 °C. TLC: R_f 0.2

(silica gel, 10% EtOAc/pet ether); ^1H NMR (300 MHz, CDCl_3) δ 10.27 (s, 1 H), 8.04 (s, 1 H), 7.78 (d, $J = 8.2$ Hz, 1 H) 7.57 (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 190.5, 141.8, 137.2, 132.8, 130.5, 127.0, 102.3; FTIR (KBr): 3049, 2922, 1740, 1639, 1464, 1278, 1038, 908, 804, 737 cm^{-1} ; Anal. Calcd for $\text{C}_4\text{H}_7\text{BrIO}$: C, 27.04; H, 1.30. Found: C, 27.06; H, 1.30.

2-(4-iodo-2-bromophenyl)-1,3-dioxolane (4). A solution of **3** (7.68 g, 24.70 mmol) ethylene glycol (Fisher) (3.4 g, 54.34 mmol), and a catalytic amount of *p*-toluenesulfonic acid (Fisher) (0.47 g, 2.47 mmol) in toluene (250 mL) was refluxed for 15 h using a Dean-Stark trap to remove water. Solid NaHCO_3 was added and the toluene was evaporated off to form a concentrated solution, and diluted with Et_2O . The solution was washed with saturated aqueous NaHCO_3 (3 x 50 mL) and brine (3 x 50 mL). After drying over anhydrous Na_2SO_4 , the solvent was removed *in vacuo* to give the crude product which was purified by flash chromatography (deactivated silica gel, 10% CH_2Cl_2 /pet ether) to afford 7.89 g (90%) of **4** as a white solid. TLC: R_f 0.35 (deactivated silica gel, 10% EtOAc/pet ether); ^1H NMR (300 MHz, CDCl_3) δ 7.92 (s, 1 H) 7.66 (d, $J = 8.1$ Hz, 1 H), 7.31 (d, $J = 8.1$ Hz, 1 H), 6.01 (s, 1 H), 4.09 (dd, $J = 3.5, 15.7$ Hz, 4 H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.9, 136.6, 136.5, 129.2, 123.6, 102.2, 95.1, 65.5; FTIR (neat): 3049, 2922, 1639, 1464, 1278, 1038, 908, 804, 737 cm^{-1} ; Anal. Calcd for $\text{C}_9\text{H}_8\text{BrIO}_2$: C, 30.45; H, 2.27. Found: C, 30.57; H, 2.27.

1-tert-Butyl-2-methoxymethoxybenzene (6). To a 0 °C solution of **5** (150 g, 1 mol) in 1.25 L of CH_2Cl_2 was added *N,N*-diisopropylethylamine (388 g, 1.0 L, 6 mol) followed by a catalytic amount of DMAP (12 g, 0.1 mol) and methoxymethyl chloride (MOMCl) (200g, 5 mol). The temperature was maintained at 0 °C for 1 h and then the mixture was heated to reflux until the TLC (deactivated silica gel, 1:3 Et_2O /pet ether) showed no starting material (**1d**). The red solution was diluted with diethyl ether and washed with cold 0.5 M HCl (3 x 150 mL) and saturated aqueous NaHCO_3 (2 x 150 mL). The combined aqueous extracts were extracted once with diethyl ether (30 mL). The organic layers were combined, dried over Na_2SO_4 , filtered and concentrated *in vacuo* to give the crude product. Purification by vacuum distillation (~0.7 torr, 78 - 84 °C) to give 180 g (0.9 mol, 93%) of **6** as a light yellow oil. TLC: R_f 0.2 (silica gel, 10% EtOAc/pet ether); ^1H NMR (300 MHz, CDCl_3) δ 7.35 (dd, $J = 1.6, 7.9$ Hz, 1 H), 7.02 (m, 2 H), 6.98 (td, $J = 1.8, 6.1$ Hz, 1 H), 5.28 (s, 2 H), 3.54 (s, 3 H), 1.46 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 156.0, 137.9, 126.9, 126.6, 121.2, 114.2, 93.8, 55.4, 34.6, 27.7; FTIR (neat): 3059, 2998, 2955, 2910, 2824, 2785, 1598, 1580, 1489, 1445, 1404, 1360, 1228, 1193, 1155, 1133, 1076, 1005, 923, 753 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$: C, 74.19; H, 9.34. Found: C, 74.33; H, 9.46.

3-tert-Butyl-2-methoxymethoxyphenol (7). To a 0 °C solution of 6 (48.6 g, 0.25 mol) in pentane (625 mL) mechanically stirred with a Teflon stirrer blade, *t*-BuLi (167 mL, 0.25 mol, 1.7 M in pentane) was added dropwise. The solution was stirred for 15 min. at 0 °C and was allowed to warm to room temperature and then the pentane was removed under an argon stream. The resulting yellow dough was dissolved in THF (950 mL) to give 0.25 M reddish-orange solution which was cooled to -78 °C and then trimethylborate (34.1 mL, 31.2 g, 0.3 mol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 2 h. After cooling the reaction mixture to 0 °C, glacial acetic acid (21.5 mL, 0.38 mol) and hydrogen peroxide (31.2 mL of 30% aq. solution, 9.4 g, 0.275 mol) were added dropwise via pipette. The turbid solution was stirred overnight at room temperature. The reaction mixture was diluted with 500 mL pet ether and washed with saturated Fe(NH₄)₂(SO₄)₂ (3 x 25 mL), brine (2 x 100 mL); dried over Na₂SO₄; filtered and concentrated *in vacuo* to yield crude 57.6 g (90%) of 7 as a brown oil. This material was carried on to the next reaction without purification. TLC: *R_f* 0.2 (silica gel, 20% Et₂O/pet ether); ¹H NMR (300 MHz, CDCl₃) δ 8.07 (b, 1 H), 7.01 (m, 3 H), 5.03 (s, 2 H), 3.69 (s, 3 H), 1.37 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 149.3, 145.5, 142.7, 124.1, 117.2, 115.5, 99.6, 67.4, 56.5, 34.4, 30.2; FTIR (neat): 3329, 2957, 1755, 1714, 1589, 1485, 1447, 1405, 1360, 1289, 1274, 1228, 1166, 1152, 1056, 989, 940, 907, 794, 779, 746 cm⁻¹.

3-tert-Butylbenzene-1,2-diol (8). In a 2 L three-necked round bottom flask, the crude 7 was dissolved in 1 L reagent grade degassed methanol with 7.5 mL concentrated HCl. After refluxing 18 h, TLC (silica gel, 20% Et₂O/hexanes) showed no starting material. The reaction was cooled to room temperature and concentrated under reduced pressure to yield a light brown yellow oil. The crude product was dissolved in diethyl ether (200 mL) and washed with deionized water (2 x 50 mL); saturated aqueous NaHCO₃ (2 x 50 mL); brine (2 x 50 mL); dried over Na₂SO₄, filtered and concentrated *in vacuo* to give a brown oil which was used in the next reaction without purification. TLC: *R_f* 0.35 (silica gel, 20% Et₂O/pet ether); ¹H NMR (300 MHz, CDCl₃): δ 6.89 (m, 1 H), 6.87 (m, 2 H), 5.40 (b, 2 H), 1.48 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 143.3, 142.8, 136.8, 119.3, 119.3, 113.1, 34.6, 29.5; FTIR (neat): 3529, 2960, 1484, 1420 cm⁻¹.

4-Bromo-6-tert-butylbenzene-1,2-diol (9). To a -40 °C solution of 8 (0.248 mol assumed 100 % conversion in the above reaction) in CH₂Cl₂ (500 mL) was added dropwise a solution of bromine (1.6 mL dissolved in 10 mL CH₂Cl₂, 31.05 mmol). After addition, the reaction mixture was warmed to room temperature. The solution was washed with brine (2 x 50 mL), dried over Na₂SO₄, filtered and

concentrated *in vacuo* to give a red oil. The crude **9** was used directly in the next reaction without purification. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.98 (d, $J = 2.2$ Hz, 1 H), 6.88 (d, $J = 2.2$ Hz, 1 H), 5.71 (b, 1 H), 5.54 (b, 1 H), 1.39 (s, 9 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 143.5, 142.4, 138.4, 122.4, 116.0, 111.0, 34.9, 29.4; FTIR (neat): 3529, 2960, 1484, 1420, 1367, 1277, 1241, 948, 908, 733 cm^{-1} .

4-Bromo-6-tert-butyl-1,2-dimethoxymethylbenzene (10). To a suspension of crude catechol **9** (3.0 g, 12.23 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added diisopropylethylamine (9.48 g, 12.78 mL, 73.38 mmol), a catalytic amount of DMAP (0.15 g, 1.22 mmol) followed by dropwise addition of 3.72 mL (3.94 g, 48.96 mmol) methoxymethyl chloride (MOMCl). The temperature was maintained at 0 °C for 1 h, then the ice bath was removed, and the mixture was gently refluxed with stirring for 18 h. The reaction mixture was cooled to room temperature, quenched with brine and the layers were separated. The organic phase was dried over Na_2SO_4 , filtered through aluminum oxide (activated, Brockmann I, standard grade, ~150 mesh) and concentrated *in vacuo* to give 3.67 g (90 %) of **10** as a colorless oil. TLC: R_f 0.2 (silica gel, 10% EtOAc/pet ether); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.23 (s, 1 H), 7.16 (s, 1 H), 5.22 (s, 2 H), 5.19 (s, 2 H), 3.97 (s, 3 H), 3.54 (s, 3 H), 1.44 (s, 9 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 150.7, 145.1, 145.1, 123.5, 117.8, 115.5, 98.9, 95.4, 57.4, 56.2, 35.2, 30.2; FTIR (neat): 3086, 2956, 1584, 1568, 1467, 1394, 1167, 1083, 1009, 958, 939, 854 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{BrO}_4$: C, 50.46; H, 6.35. Found: C, 51.05; H, 6.41.

Pinacolyl [1,2-dimethoxymethoxy-6-tert-butyl-1-phenyl]boronate (11). A -78 °C solution of **10** (2.96 g, 8.88 mmol) in THF (90 mL) was stirred for 30 minutes. *t*-BuLi (10.5 mL, 17.8 mmol, 1.7 M in pentane) was added dropwise over 20 minutes and the reaction mixture was then stirred at -78 °C for 1 h. After dropwise addition of trimethylborate (1.2 g, 1.31 mL, 11.5 mmol), the bath was removed and the reaction mixture was stirred at room temperature for 1 h. At room temperature, a solution of pinacol (2.1 g, 17.8 mmol) in THF (20 mL) was cannulated into the above solution and the mixture stirred overnight. The solvent was removed *in vacuo*, diluted with CH_2Cl_2 , and filtered through Celite®. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography (deactivated silica gel, 1:1 CH_2Cl_2 /pet ether) to give 2.8 g (85%) of **11** as an oil. TLC: R_f 0.3 (silica gel, 10% EtOAc/pet ether); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.47 (s, 1 H), 7.42 (s, 1 H), 5.24 (s, 2 H), 5.21 (s, 2 H), 3.65 (s, 3 H), 3.52 (s, 3 H), 1.44 (s, 9 H), 1.32 (s, 12 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 149.2, 148.8, 142.2, 126.9, 120.4, 98.8, 95.0, 83.2, 57.0, 55.9, 34.7, 30.2, 24.5; FTIR (neat): 3040, 2955, 1598, 1358, 1272, 1144, 1082, 1014, 962, 854 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{33}\text{BO}_6$: C, 63.17; H, 8.75. Found: C,

63.21; H, 8.70.

2-Bromo-4-(3'-tert-butyl-4',5'-dimethoxymethoxyphenyl)benzaldehyde, ethylene ketal (12). A solution of **4** (2.66 g, 7.52 mmol), **11** (2.86 g, 7.52 mmol), 2M sodium carbonate (7.5 mL) and Pd(PPh₃)₄ (0.261 g, 0.23 mmol) in DME (50 mL) was prepared in a 100 mL round bottom flask equipped with magnetic stir bar, reflux condenser, and argon inlet. After refluxing for 18 h, the reaction mixture was cooled to room temperature, concentrated, diluted with diethyl ether, and was filtered through Celite[®]. The organic layer was washed with (2 x 25 mL) brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by low pressure liquid chromatography (deactivated silica gel, 10% Et₂O/pet ether) to afford 1.83 g (3.80 mmol, 51%) of **13** a clear, colorless oil. TLC: *R_f* 0.2 (silica gel, 10% EtOAc/pet ether); ¹H NMR (300 MHz, CDCl₃) δ 7.72 (s, 1 H), 7.63 (d, *J* = 8.1 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 1 H), 7.19 (d, *J* = 10.1 Hz, 2 H), 6.13 (s, 1 H), 5.25 (s, 2 H), 5.23 (s, 2 H), 3.67 (s, 3 H), 3.53 (s, 3 H), 1.46 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 150.3, 146.1, 143.8, 143.7, 135.0, 134.1, 131.2, 127.9, 126.0, 123.1, 119.4, 113.5, 102.5, 99.0, 95.5, 65.4, 57.4, 56.2, 35.2, 30.4; FTIR (neat): 3040, 2954, 1602, 1548, 1470, 1323, 1183, 1081, 1012, 858, 828, 736 cm⁻¹.

2-Bromo-4-(3'-tert-butyl-4',5'-dimethoxymethoxyphenyl)benzaldehyde (13). A solution of **12** (2.27 g, 4.72 mmol) and a catalytic amount of PPTS (0.12, 0.04 mmol) and water (1 mL) was added to a 200 mL round bottom flask equipped with a magnetic stir bar, reflux condenser, and argon inlet. After refluxing for 18 h, the solution was cooled to room temperature. The solution was concentrated and diluted with ether. The solution was washed with brine (3 x 20 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (deactivated silica gel, 10% Et₂O/pet ether) to afford 1.86 g (90%) of **13** as a clear, colorless oil. TLC: *R_f* 0.2 (silica gel, 10% EtOAc/pet ether). ¹H NMR (300 MHz, CDCl₃) δ 7.91 (s, 1 H), 7.78 (s, 1 H), 7.58 (d, *J* = 8.1 Hz, 1 H), 7.25 (d, *J* = 10.9 Hz, 2 H), 5.27 (s, 2 H), 5.25 (s, 2 H), 3.67 (s, 3 H), 3.54 (s, 3 H), 1.47 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 191.0, 150.4, 148.3, 147.0, 143.9, 132.9, 131.8, 129.9, 127.3, 126.3, 119.6, 113.6, 99.0, 95.4, 57.5, 56.3, 35.3, 30.4; FTIR (neat): 3040, 2955, 1693, 1593, 1540, 1469, 1429, 1373, 1323, 1256, 1210, 1163, 1078, 1012, 956, 829, 776 cm⁻¹. Anal. Calcd for C₂₁H₂₅BrO₅: C, 57.67; H, 5.76. Found: C, 57.51; H, 5.84.

2-Bromo-1-vinyl-4-(3'-tert-butyl-4',5'-dimethoxymethoxy)biphenyl (14). A solution of methyltriphenylphosphonium bromide (0.712 g, 1.99 mmol) in THF (28 mL) was prepared in a 100 mL Schlenk flask equipped with a magnetic stir bar. The solution was cooled to 0 °C and *n*-butyllithium

(0.97 mL from 2.25 M in hexane, 2.18 mmol) was added dropwise. After 1 h, the reddish-orange solution was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of **13** (0.83 g, 1.90 mmol) in THF was added to the ylide solution via a cannula. The reaction mixture was allowed to gradually warm to room temperature overnight. After 18 h at room temperature, the reaction was quenched with 1 mL water. The solution was concentrated and diluted with ether. The solution was washed with brine (3 x 10 mL), dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (10% Et_2O /pet ether) to afford 0.81 g (98%) of **14** as a clear, colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.74 (s, 1 H), 7.61 (d, $J = 8.2$ Hz, 1 H), 7.48 (d, $J = 8.2$ Hz, 1 H), 7.22 (d, $J = 7.6$ Hz, 2 H), 7.10 (dd, $J = 10.9, 17.4$ Hz, 1 H), 5.75 (d, $J = 17.4$ Hz, 1 H), 5.38 (d, $J = 10.9$ Hz, 1 H), 5.27 (s, 2 H), 5.25 (s, 2 H), 3.69 (s, 3 H), 3.55 (s, 3 H), 1.49 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.5, 143.8, 142.3, 135.9, 135.4, 134.2, 131.1, 126.8, 126.2, 123.9, 119.4, 116.4, 113.5, 99.1, 95.6, 57.6, 56.4, 46.4, 35.4, 30.6; FTIR (neat): 3088, 2954, 1468, 1438, 1324, 1164, 1079, 1013, 959 cm^{-1} ; FT-Raman: 1625, 1599, 1324 cm^{-1} ; HRMS: exact mass calcd for $\text{C}_{22}\text{H}_{27}\text{BrO}_4$ 434.1093 (M^+), found 434.1096. Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{BrO}_4$: C, 60.70; H, 6.25. Found: C, 60.82; H, 6.29.

2-Bromo-1-ethynyl-4-(3'-tert-butyl-4',5'-dimethoxymethoxy)biphenyl (15). To a $-78\text{ }^{\circ}\text{C}$ suspension of the (bromomethyl)triphenylphosphonium bromide (638 mg, 1.46 mmol) THF (10 mL) was added potassium *tert*-butoxide (328 mg, 2.92 mmol) in one portion. After 0.5 h the yellow colored ylide was formed. A solution of **13** (640 mg, 1.46 mmol) in 5 mL THF was added dropwise to the ylide solution. The solution was stirred at $-78\text{ }^{\circ}\text{C}$ overnight. The brown solution was warmed to room temperature and the THF was removed by rotary evaporation. The oil was diluted with Et_2O and filtered through Celite[®] to give 753 mg of an oil. Purification by flash chromatography (deactivated silica gel, 10% Et_2O /pet ether) to obtain 415 mg (81%) of **15** as a clear, colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.76 (d, $J = 1.5$ Hz, 1 H), 7.56 (d, $J = 8.0$ Hz, 1 H), 7.45 (dd, $J = 1.5, 8.0$ Hz, 1 H), 7.20 (dd, $J = 2.0, 8.7$ Hz, 2 H), 5.27 (s, 2 H), 5.24 (s, 2 H), 3.68 (s, 3 H), 3.55 (s, 3 H), 3.42 (s, 1 H), 1.48 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.4, 146.3, 143.8, 143.2, 134.1, 133.7, 130.6, 125.8, 125.6, 122.5, 119.4, 113.3, 99.1, 95.4, 82.1, 57.5, 56.3, 35.3, 30.4; FTIR (neat): 3288, 3057, 2956, 2826, 2108, 1596, 1575, 1470, 1164, 1079, 1013, 959, 832 cm^{-1} ; FT-Raman: 2105, 1597 cm^{-1} ; HRMS: exact mass calcd for $\text{C}_{22}\text{H}_{25}\text{BrO}_4$ 432.0936 (M^+), found 432.0934; Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{BrO}_4$: C, 60.97; H, 5.81. Found: C, 60.84; H, 5.79.

4-Bromo-6-tert-butyl-1,2-dimethoxy-benzene (16). To a room temperature solution of crude **9** (68

g, 0.28 mol) in 1 L reagent grade acetone was added potassium carbonate (192 g, 1.4 mol) followed by iodomethane (157 g, 69 mL, 1.1 mol) which was added dropwise over 1.25 h with stirring from a mechanical stirrer. After overnight refluxing with continuous stirring, the TLC showed monomethylated intermediate was still present. Dimethyl sulfate (105 g, 79 mL, 0.82 mol) was added and the reaction mixture was refluxed for another 24 h. After 3 d of refluxing and addition of more methylating reagents, the reaction mixture was cooled to room temperature. The reaction mixture was filtered, diluted with 500 mL of diethyl ether and filtered again. The solvent was removed by rotary evaporation to yield a reddish oil. The residual solvent was removed by bulb to bulb distillation under vacuum, yielding a yellow solid. The product was crystallized from pet ether followed by sublimation to produce 57 g (75%) of **16**. TLC: R_f 0.2 (silica gel, 10% EtOAc/pet ether); ^1H NMR (300 MHz, CDCl_3) δ 7.02 (s, 1 H), 6.93 (s, 1 H), 3.85 (s, 6 H), 1.35 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) 153.9, 147.8, 145.1, 122.0, 115.5, 114.1, 60.4, 56.0, 35.3, 30.4; FTIR (KBr): 2964, 2871, 1565, 1464, 1409, 1375, 1292, 1263, 1231, 1157, 1057, 1001, 844, 707 cm^{-1} .

3,4-Dimethoxy-5-*tert*-butylphenylboronic acid (18). To a solution of **16** (2.0 g, 7.32 mmol) in 50 mL THF at -78°C , was added *t*-BuLi (9.76 mL, 14.6 mmol) dropwise over a period of 1 h. After the reaction mixture was stirred for 2 h at -78°C , trimethylborate (0.99 g, 1.1 mL, 9.52 mmol) was added neat and the reaction mixture was stirred for an additional 1 h at -78°C . The reaction mixture was quenched with cold 1M HCl (30 mL) and the layers were separated. The organic phase was washed 1M HCl (30 mL) and brine (2 x 30 mL), dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to yield 1.5 g (85%) of **18** as an off-white solid. ^1H NMR (300 MHz, CDCl_3) δ 7.02 (s, 1 H), 6.93 (s, 1 H), 6.70 (broad, s, 2 H), 3.85 (s, 6 H), 1.35 (s, 9 H); FTIR (neat): 3155, 3095, 3065, 2965, 1575 cm^{-1} .

4-Nitro-3'-*tert*-butyl-4',5'-dimethoxybiphenyl (19). To a degassed solution of **18** (3.45g, 14.5 mmol), *p*-bromonitrobenzene (3.2 g, 15.95 mmol) in 50 mL anhydrous DME was added neat $\text{Pd}(\text{PPh}_3)_4$ (0.5 g, 0.43 mmol), followed by 14.5 mL of degassed 2M Na_2CO_3 . The reaction mixture was refluxed overnight. Upon cooling, the reaction mixture was concentrated *in vacuo*, diluted with CH_2Cl_2 (50 mL), washed with brine (3 x 25 mL), dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give the crude product as a light yellow solid. The solid was recrystallized from Et_2O /pet ether followed by sublimation to produce 3.7 g (80%) of **18** as a light yellow solid. Mp (DSC) 127°C . ^1H NMR (300 MHz, CDCl_3) δ 8.28 (d, $J = 8.75$ Hz, 2 H), 7.70 (d, $J = 8.75$ Hz, 2 H), 3.95, 3.94 (s, s, 6 H), 1.44 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.7, 149.6, 148.0, 146.7, 144.0, 133.4, 127.5, 124.0, 118.3, 109.8,

60.5, 55.9, 35.3, 30.4; FTIR (KBr): 2955, 1594, 1573, 1515, 1475, 1424, 1394, 1344, 1329, 1247, 1156, 1108, 1053, 1004, 846, 755, 699 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_4$: C, 68.55; H, 6.71. Found: C, 68.44; H, 6.73.

4-Amino-3'-tert-butyl-4',5'-dimethoxybiphenyl (20). A suspension of 10% Pd/C (0.11 g) and 19 (2.3 g, 7.4 mmol) in 100 mL EtOAc was aspirated and back-filled with argon (3X) doing the last back-fill with hydrogen gas. After 2 h the reaction was complete and the reaction mixture was filtered through Celite[®] and rinsed with anhydrous diethyl ether. The solvent was evaporated to produce 2.1 g (99%) of a white solid. ^1H NMR (300 MHz, CDCl_3) 7.36 (d, $J = 6.6$ Hz, 2 H), 7.08 (s, 1 H), 6.97 (s, 1 H), 6.75 (d, $J = 6.6$ Hz, 2 H), 3.91, 3.90 (s, s, 6 H), 1.42 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.4, 147.5, 145.6, 143.3, 136.1, 132.2, 128.0, 117.2, 115.4, 109.2, 60.5, 55.9, 35.3, 30.6; FTIR (KBr): 3426, 3363, 3224, 2955, 1622, 1567, 1520, 1477, 1404, 1330, 1238, 1182, 1154, 1056, 1002, 909, 827, 733 cm^{-1} .

4-Amino-3-bromo-3'-tert-butyl-4',5'-dimethoxybiphenyl (21). To a solution of the crude 20 (1.7 g, 5.82 mmol) and NaHCO_3 (0.49 g, 5.82 mmol) in CH_2Cl_2 (60 mL) in an oven-dried Schlenk flask, solid *N*-bromosuccinimide (0.98 g, 5.53 mmol) was added portionwise with a powder addition funnel. After stirring overnight at room temperature, the reaction mixture was washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude product was used without purification in the next reaction.

3,4-Dibromo-3'-tert-butyl-4',5'-dimethoxybiphenyl (22). To a solution of 21 (0.114 g, 0.25 mmol) in 40 mL methanol, was added 10 mL of 48% HBr and the solution was cooled to 0 °C. A solution of NaNO_2 (17.5 mg) in 5 mL H_2O was added portionwise keeping the reaction temperature below 5 °C. To a solution of CuBr (36.4 mg, 0.25 mmol) in 5 mL of 48% HBr, with strong stirring, the solution of the diazonium salt was added dropwise to the CuBr solution. After all of the diazonium salt solution was added, the reaction mixture was stirred at room temperature for 30 minutes. The reaction mixture was then heated in a hot water bath for 30 minutes. After stirring overnight at room temperature, the mixture was poured into diethyl ether (15 mL) and the layers separated. The organic phase was then successively washed with saturated aqueous ammonium chloride (2 x 10 mL), saturated aqueous NaHCO_3 (2 x 10 mL) and brine (2 x 10 mL) and dried over Na_2SO_4 . After filtration the solvent was removed *in vacuo*. Attempts to purify the off white solid by radial PLC (silica gel, 5% EtOAc/pet ether) failed. GC/MS showed the impurity to be the monobrominated product. Purification by

sublimation successfully gave 76 mg (70%) of **23**. ^1H NMR (300 MHz, CDCl_3) δ 7.79 (d, $J = 2.2$ Hz, 1 H), 7.64 (d, $J = 8.2$ Hz, 1 H), 7.34 (dd, $J = 2.2, 8.2$ Hz, 1 H), 7.06 (d, $J = 2.2$ Hz, 1 H), 6.94 (d, $J = 2.2$ Hz, 1 H), 3.94 (s, 6 H), 1.44 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.6, 148.9, 143.8, 142.5, 133.7, 133.4, 132.0, 127.2, 125.0, 123.0, 117.7, 109.5, 35.2, 30.5; FTIR (neat): 2944, 1459, 1427, 1363, 1146, 952, 816 cm^{-1} . HRMS exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{Br}_2\text{O}_2$ 425.9830, found 425.9853.

3,4-Dibromo-3'-tert-butyl-4',5'-dihydroxybiphenyl (23). To a solution of **22** (0.27 g, 0.64 mmol) in CH_2Cl_2 (25 mL) at -78 °C was added a 1.4 mL (1.4 mmol) of 1M BBr_3 in CH_2Cl_2 and then the solution was slowly warmed to room temperature. The reaction mixture was quenched with brine and layers separated. The organic phase dried over Na_2SO_4 , filtered; and solvent removed *in vacuo* to yield 0.25 g (0.62 mmol) of **23** as a light tan solid which was used directly in the next reaction without purification. FTIR (neat): 3519, 2956, 1459, 1427, 1363, 1316, 1252, 1216, 952, 816 cm^{-1} . HRMS exact mass calcd for $\text{C}_{16}\text{H}_{16}\text{Br}_2\text{O}_2$ 397.9517, found 397.9514.

3,4-Dibromo-3'-tert-butyl-4',5'-dimethoxymethoxybiphenyl (24). To 0 °C a solution of **23** (0.25 g, 0.64 mmol), diisopropylethylamine (0.5g, 0.67 mL, 3.8 mmol) and DMAP (8 mg, 0.064 mmol) in 15 mL CH_2Cl_2 was added 0.19 mL (2.56 mmol) of MOMCl. After addition, the reaction mixture was allowed to warm to room temperature then was refluxed overnight. Upon cooling, the reaction mixture was washed with brine (3 x 15 mL), and dried over Na_2SO_4 . After filtration, the solvent was removed *in vacuo* and the residual oil was purified by radical PLC (deactivated silica gel, 10% EtOAc/pet ether) to give 0.27 g (87%) of **23** as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.77 (d, $J = 2.1$ Hz, 1 H), 7.63 (d, $J = 8.3$ Hz, 1 H), 7.33 (dd, $J = 2.1, 8.3$ Hz, 1 H), 7.19 (d, $J = 2.1$ Hz, 1 H), 7.14 (d, $J = 2.1$ Hz, 1 H), 5.25 (s, 2 H), 5.23 (s, 2 H), 3.68 (s, 3 H), 3.54 (s, 3 H), 1.47 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.4, 146.2, 143.9, 142.0, 133.7, 133.6, 131.9, 127.1, 125.0, 123.1, 119.2, 113.3, 99.1, 95.4, 57.6, 56.3, 35.3, 30.4; FTIR (thin film) 2955, 1446, 1361, 1322, 1164, 1079, 1012, 959 cm^{-1} . HRMS exact mass calcd for $\text{C}_{20}\text{H}_{24}\text{Br}_2\text{O}_4$ 486.0041 (M^+), found 486.0025.

3,4-Divinyl-3'-tert-butyl-4',5'-dimethoxymethylbiphenyl (25). To a solution of **24** (0.14 g, 0.28 mmol) in 4 mL anhydrous toluene, was added $\text{Pd}(\text{PPh}_3)_4$ (12.7 mg, 0.011 mmol), and a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (BHT). The solution was purged with argon for 10 min. Tributyl(vinyl)tin (0.19 g, 0.61 mmol) was added and the reaction mixture was refluxed overnight. The mixture was allowed to cool to room temperature, and 1 mL of pyridine was added followed by 2 mL of 1.2 N pyridinium fluoride solution. The resulting mixture was stirred for 2 h at room temperature. The

mixture was diluted with 40 mL of ether and then washed successively with 10 mL of water, followed by 10 ml saturated aqueous NaHCO₃ solution. The organic phase was dried over Na₂SO₄, filtered and concentrated. The crude materials was purified by radial PLC (deactivated silica gel, 10% EtOAc/pet ether) to give 0.076 g (80%) of **25** as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 1.7 Hz, 1 H), 7.45 (d, *J* = 8.1 Hz, 1 H), 7.37 (dd, *J* = 8.1, 1.7 Hz, 1 H), 7.18 (dd, *J* = 8.1, 1.7 Hz, 2 H), 6.98 (two overlapping sets of dd, 2 H), 5.61 (dd, *J* = 18.1, 5.4 Hz, 2 H), 5.29 (d, *J* = 22.7 Hz, 2 H), 5.19 (s, 2 H), 5.17 (s, 2 H), 3.6 (s, 3 H), 3.47 (s, 3 H), 1.41 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 150.4, 143.6, 140.8, 136.4, 135.8, 134.9, 134.4, 126.6, 125.0, 119.4, 116.7, 116.1, 113.6, 99.1, 95.6, 57.6, 56.3, 35.3, 30.6; FTIR (thin film): 2954, 1576, 1469, 1435, 1326, 1243, 1202, 1162, 1077, 1013, 961, 831 cm⁻¹. HRMS exact mass calcd for C₂₄H₃₀O₄ 382.2144 (M⁺), found 382.2164.

PoPV[CatMOM₂]. Palladium acetate (0.014 g, 0.064 mmol), tri-*o*-tolylphosphine (0.039 g, 0.128 mmol), and triethylamine (0.45 mL, 0.32 g, 3.22 mmol) were added to a solution of **14** (0.24 g, 0.55 mmol) in DMF (2.2 mL). The solution was sealed under argon and heated at 100 °C for 24 h. The solvent was removed *in vacuo* and the reaction mixture was diluted with CH₂Cl₂; filtered through Celite[®]; washed with brine (2 x 25 mL) and dried over Na₂SO₄, filtered and concentrated *in vacuo*. Purification by Bio-Beads S-X1 gel permeation column gave of **PoPV[CatMOM₂]**. The purified oligomer was precipitated from ether in methanol to obtain 0.21 g (88%) of a yellow powder. ¹H NMR (300 MHz, CDCl₃) δ 8.0 - 6.9 (m, 7 H), 5.4 - 4.9 (m, 4 H), 3.8 - 3.2 (m, 6 H), 1.75 (m, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 150.4, 150.3, 143.9, 143.7, 134.5, 132.1, 130.7, 128.5, 128.3, 126.2, 125.7, 119.3, 113.3, 113.2, 99.0, 95.4, 57.5, 56.3, 35.2, 30.4; FTIR (neat): 2955, 1469; 1436, 1392, 1328, 1243, 1202, 1163, 1077, 1012, 970 cm⁻¹. FT-Raman: 1623, 1598 cm⁻¹.

ProPV[CatMOM₂]. Triethylamine (0.35 mL, 2.5 mmol) was added to a solution of **24** (488 mg, 1 mmol), **25** (382 mg, 1 mmol), Pd(OAc)₂ (9.0 mg, 0.04 mmol), and tri-*o*-tolylphosphine (60.9 mg, 0.2 mmol) in 5 mL of DMF. The reaction mixture was heated at 100 °C for 8 h under argon atmosphere and then the solvent was removed *in vacuo*. Purification by Bio-Beads S-X1 Beads gel permeation column gave 750 mg (86%) of yellow-brown powder. ¹H NMR (300 MHz, CDCl₃) δ 7.9 - 6.9 (m, 7 H), 5.2 - 4.9 (m, 4 H), 3.6 - 3.3 (m, 6 H), 1.5 - 1.3 (m, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 133.5, 131.7, 127.0, 119.0, 113.1, 98.9, 95.2, 57.4, 56.1, 46.0, 35.1, 30.3; FTIR (neat): 2954, 1580, 1470, 1446, 1398, 1325, 1244, 1202, 1162, 1078, 1013, 959 cm⁻¹.

PoPE[CatMOM₂]. To a degassed solution of **15** (474 mg, 1.08 mmol) in 20 mL of 1:1 pyridine:triethylamine was added (PPh₃)₂PdCl₂ (38 mg, 0.054 mmol) and CuI (4 mg, 0.022 mmol) under argon and then stirred at room temperature for 6 h. The reaction mixture was then concentrated *in vacuo* and diluted with CH₂Cl₂. Purification by Bio-Bead column followed by precipitation with methanol and centrifugation gave 450 mg (95%) of an orange powder. ¹H NMR (300 MHz, CDCl₃) δ 8.1 - 6.9 (m, 5 H), 5.5 - 5.0 (bs, 4 H), 3.9 - 3.2 (2 bs, 6 H), 1.85 - 1.1 (bs, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 150.5, 143.9, 134.9, 132.0, 127.8, 125.7, 119.5, 113.4, 99.1, 95.5, 57.6, 56.4, 35.4, 30.5; FTIR (neat): 3288, 2956, 2826, 1596, 1575, 1470, 1164, 1079, 1013, 359, 832 cm⁻¹; FT-Raman: 2209, 1596 cm⁻¹.

General Procedure for MOM-Deprotection of Oligomers. A portion of the oligomer (*ca.* 100 mg) was dissolved in a solution of CH₂Cl₂ (20 mL), methanol (4 mL), and concentrated HCl (4 drops), and was stirred in the dark overnight at room temperature. The reaction mixture was washed with deionized H₂O (3 x 15 mL); brine (3 x 15 mL); dried over Na₂SO₄; filtered; and solvent was removed *in vacuo*. The product was purified by Bio-Beads[®] S-X1 gel permeation chromatography (100% CH₂Cl₂). Generally, yields of the yellow/brown catechol oligomers were near quantitative.

PoPV[CatH₂]: ¹H NMR (300 MHz, CDCl₃) δ 8.0 - 6.9 (m, 7 H), 6.1 - 5.5 (b, 2 H), 1.75 (m, 9 H); FTIR (neat): 3472, 2925, 2855, 1596, 1148, 1434, 1318, 1257, 908, 802, 736 cm⁻¹.

ProPV[CatH₂]: FTIR (neat): 3512, 2856, 1593, 1432, 1391, 1362, 1319, 1253, 1203, 1153, 1073, 1011, 959, 908, 822, 733 cm⁻¹.

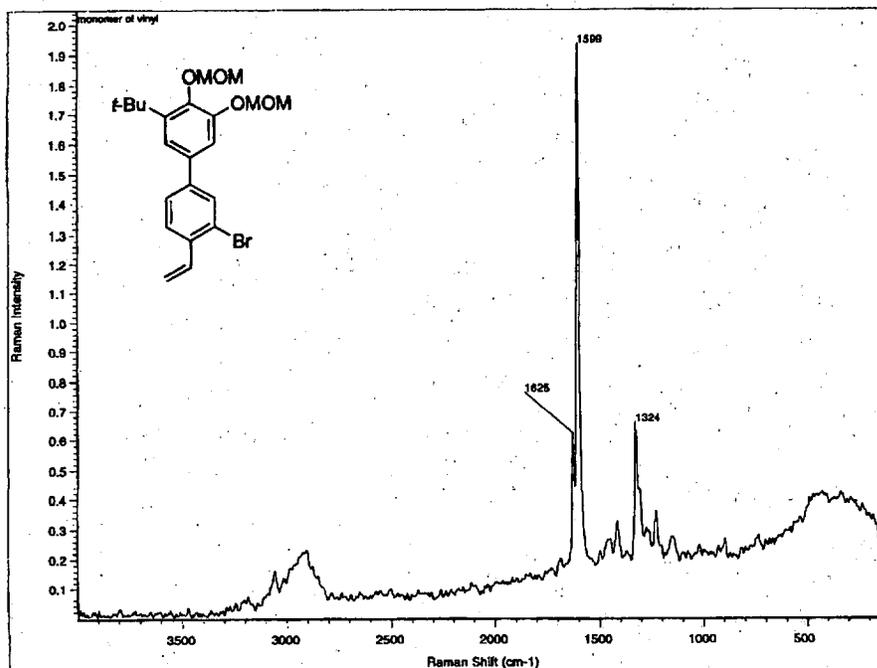
PoPE[CatH₂]: ¹H NMR (300 MHz, CDCl₃) δ 7.8 - 7.3 (m, 3 H), 7.1 - 6.8 (m, 2 H), 6.2 - 5.8 (b, 2 H), 1.6 - 1.3 (br, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 143.9, 136.5, 134.5, 132.6, 132.6, 131.9, 130.9, 128.5, 127.9, 126.1, 117.5, 111.5, 50.6, 34.8, 29.4; FTIR (neat): 3408, 2996, 2250, 1593, 1491, 1428, 1364, 1318 cm⁻¹.

General Procedure for Oxidation of Catechol Oligomers. A portion of the catechol oligomer (*ca.* 100 mg) was dissolved in CH₂Cl₂ (40 mL) containing Fétizon's reagent (200 mg). After stirring overnight protected from light, the suspension was filtered through Celite[®] and concentrated by rotary evaporation. Purification by Bio-Beads[®] S-X1 Beads gel permeation column (100% CH₂Cl₂) in the dark quantitative yields of the quinone oligomers as a brown solids.

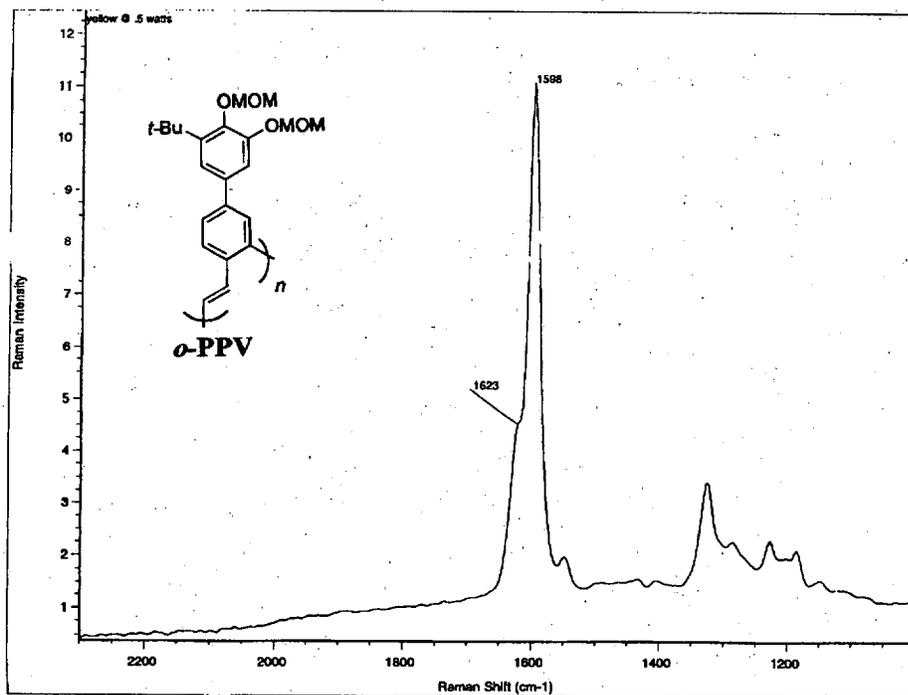
PoPV[BQ]: FTIR (neat): 2925, 1655, 1560, 1458, 1370, 1248, 799 cm⁻¹.

ProPV[BQ]: FTIR (neat): 2925, 1655, 1560, 1458, 1370, 1250, 799 cm⁻¹.

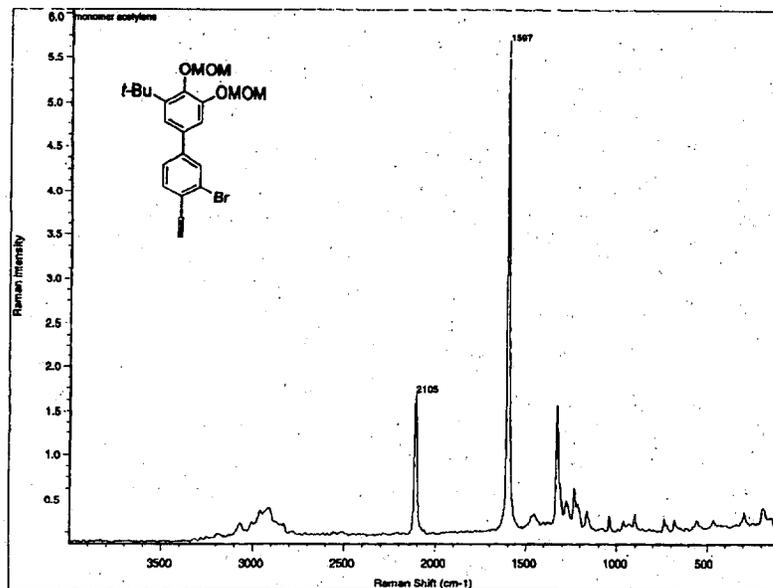
PoPE[BQ]: FTIR (neat): 2958, 1659, 1469, 1368, 1248, 1117, 1040, 737 cm⁻¹.



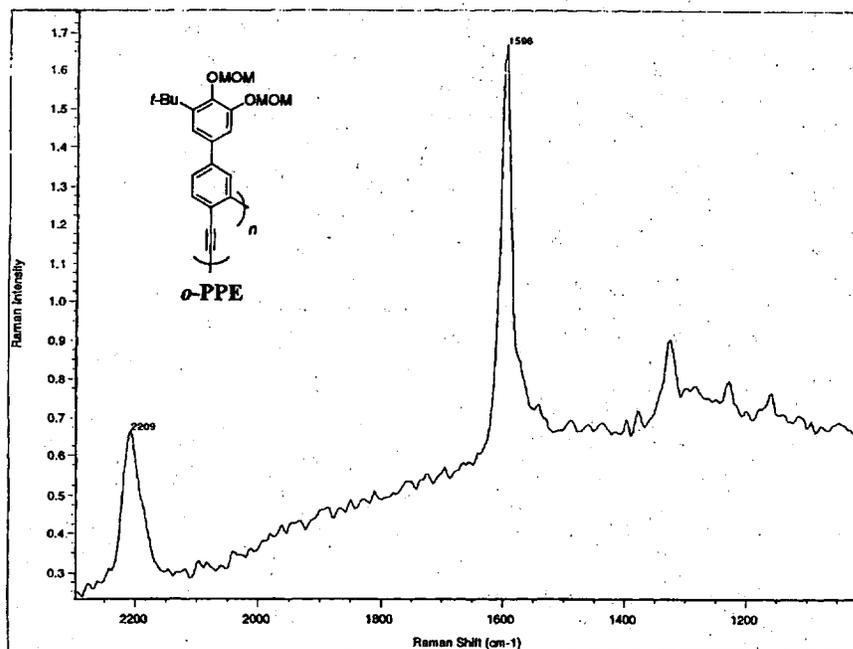
FT-Raman spectrum of 14.



FT-Raman spectrum of PoPV[CatMOM₂].



FT-Raman Spectrum of bromo-acetylene monomer, 15.



FT-Raman spectrum of MOM-protected PoPE[CatMOM₂].

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