Supporting Information for

Polycyclic Aromatic Triptycenes: Oxygen Substitution Cyclization Strategies

Brett VanVeller, Derek J. Schipper, and Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
Email: tswager@mit.edu

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Materials:
Silica gel (40 μm) was purchased from SiliCycle. All solvents used for photophysical experiments were spectral grade. All reagent grade materials were purchased from Aldrich, TCI America, Strem Chemical Inc. and Alfa Aesar, and used without further purification.

Experimental:
NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra for all compounds were acquired in $CDCl_3$ on a Bruker Avance Spectrometer operating at 400 and 125 MHz. The chemical shift data are reported in units of δ (ppm) relative to residual solvent.

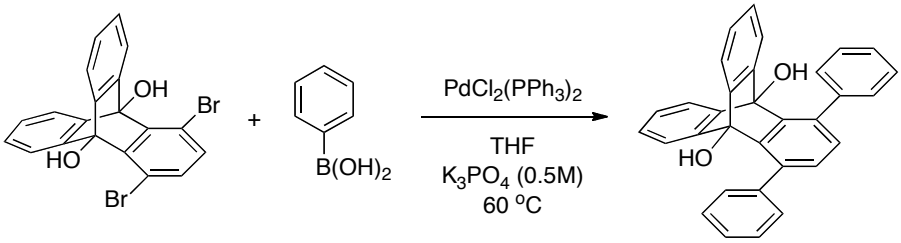
Electrochemical Measurements: All electrochemical measurements were carried out with Autolab PGSTAT30 potentiostat (Eco Chemie B.V.) in a conventional three-electrode configuration system: a platinum working electrode (1.6 mm diameter), a platinum wire counter electrode and a silver wire as pseudo-reference electrode with ferrocene added after every run as the internal standard. Dichloromethane was employed as the solvent with $n Bu_4NPF_6$ as electrolyte and the experiments were performed under ambient condition with scan rate of 0.1 V/s.

Absorption and Emission Spectroscopy: Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using right-angle detection. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent filled cuvette. Fluorescence quantum yields in $CHCl_3$ were determined relative to quinine sulfate in 1N H_2SO_4 and are corrected for solvent refractive index and absorption differences at the excitation wavelength. Fluorescence quantum yields in thin film were determined relative to perylene in PMMA.

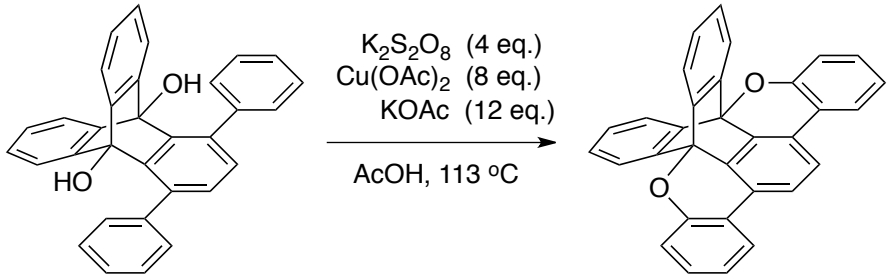
Lifetime measurements: Time resolved fluorescence measurements were performed by exciting the samples with 160 femtosecond pulses at 390 nm from the double output of a Coherent RegA Ti:Sapphire amplifier. The resulting fluorescence was spectrally and temporally resolved with a Hamamatsu C4780 Streak Camera system.

Microwave Reactor: Microwave heating was performed using a *CEM* Discover Microwave at 200W unless otherwise stated.

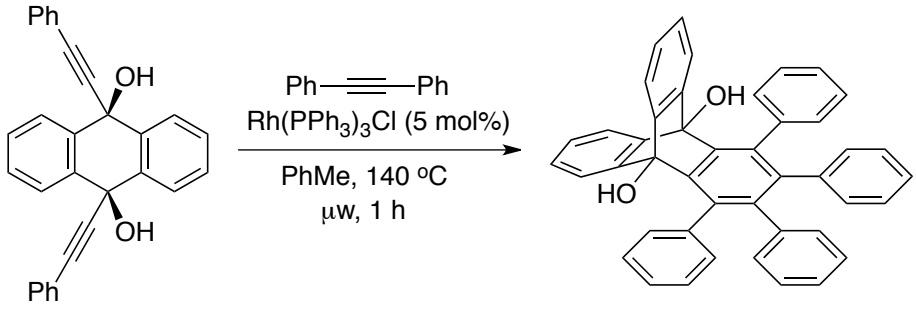
SYNTHETIC PROCEDURES:



Synthesis of 6: Compound **3** (0.15 g, 0.34 mmol), phenylboronic acid (0.84 g, 1.01 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol) were dissolved in 2 mL degassed THF and 2 mL K_3PO_4 (0.5 M, degassed) under argon. The reaction was sealed and heated at 60 °C for 6 h. The reaction was diluted with sat. NH_4Cl and washed with DCM twice. The combined organic layers were dried over Na_2SO_4 and volatiles were removed *in vacuo*. The residue was purified by silica gel chromatography (6:4, Hexanes:DCM) to give **6** (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 10H), 7.38 (m, 4H), 7.13 (dd, *J*=5.4, 3 Hz, 4H), 6.81 (s, 2H), 3.04 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 142.7, 141.0, 135.2, 129.4, 128.8, 128.4, 128.3, 125.7, 119.6, 81.0. HRMS (ESI) calcd. for $C_{32}H_{22}O_2$ [M+H] 439.1693, found 439.1687.

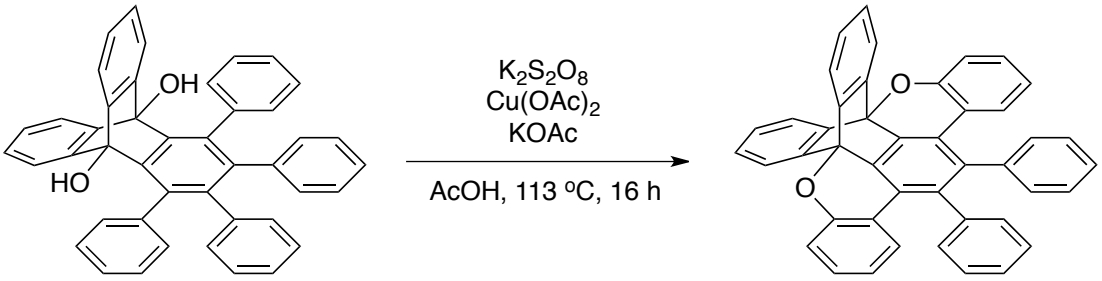


Synthesis of 7: Compound **6** (85 mg, 0.19 mmol), $K_2S_2O_8$ (0.21 g, 0.78 mmol), $CuOAc_2$ (0.31 g, 1.56 mmol) and KOAc (0.30 g, 3.1 mmol) was suspended in 2 mL of AcOH and heated at 113 °C for 6 h. Once cool the reaction was diluted with 10% NaOH. The mixture was extracted with DCM (3x) and the combined organic fractions were dried over Na_2SO_4 and volatiles were removed *in vacuo*. The residue was triturated with EtOAc (2 mL) and filtered to give **7** (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J*=5.6, 3.2 Hz, 4H), 7.64 (dd, *J*=8, 1.6 Hz, 2H), 7.40 (s, 2H), 7.39 (dd, *J*=8, 1.2 Hz, 2H), 7.35 (ddd, *J*=8, 7.2, 1.6 Hz, 2H), 7.12 (dd, *J*=5.6, 3.2 Hz, 4H), 7.03 (ddd, *J*=8, 7.2, 1.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 143.9, 138.6, 134.3, 130.2, 125.8, 124.1, 122.7, 122.2, 120.3, 118.5, 117.8, 81.8. HRMS (ESI) calcd. for $C_{32}H_{18}O_2$ [M+H] 435.1380, found 435.1360.

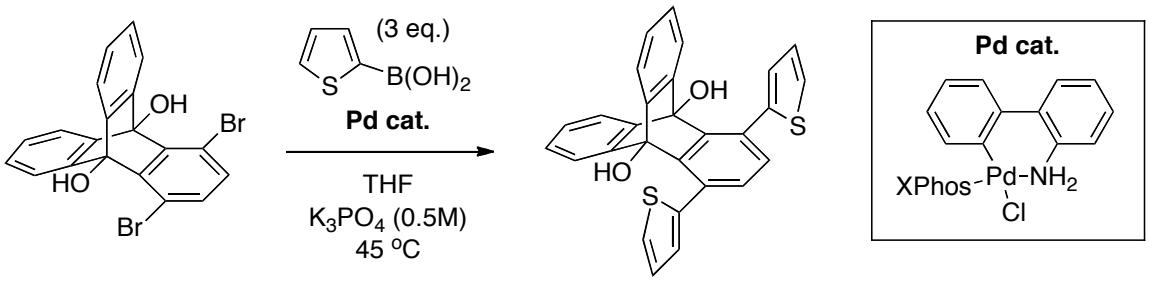


Synthesis of 9: 9,10-Bis(phenylethynyl)-9,10-dihydroanthracene-9,10-diol[1] (207 mg, 0.5 mmol), diphenylacetylene (223 mg, 1.25 mmol) and $Rh(PPh_3)_3Cl$ (23 mg, 0.025 mmol) were weighed in air and placed in a microwave tube with a magnetic stir bar. The tube was capped and then purged with argon. Dry and degassed toluene (4 mL) was added and the mixture is then heated in a CEM Discover microwave reactor at 140 ºC for 1 hour. The crude reaction mixture is concentrated under reduced pressure and the residue purified using silica gel column chromatography (30-40% CH_2Cl_2/hexanes) to give **9** (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, *J*=5.4, 3.2, 4H), 7.27-7.20 (m, 6H), 7.16 (dd, *J*=5.5, 3.2, 4H), 7.14-7.09 (m, 4H), 6.75-6.67 (m, 6H), 6.58-6.52 (m, 4H), 3.01 (s, 2H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 141.6, 139.3, 139.1, 138.8, 134.1, 130.9, 130.4, 128.0, 127.6, 126.5, 125.6, 125.4, 119.6, 80.6,. HRMS (ESI) calcd.for $C_{44}H_{30}O_2$ [M+H], 591.2319 found 591.2239.

(1) Taylor, M. S.; Swager, T. M. *Org. Lett.* **2007**, *9*, 3695.

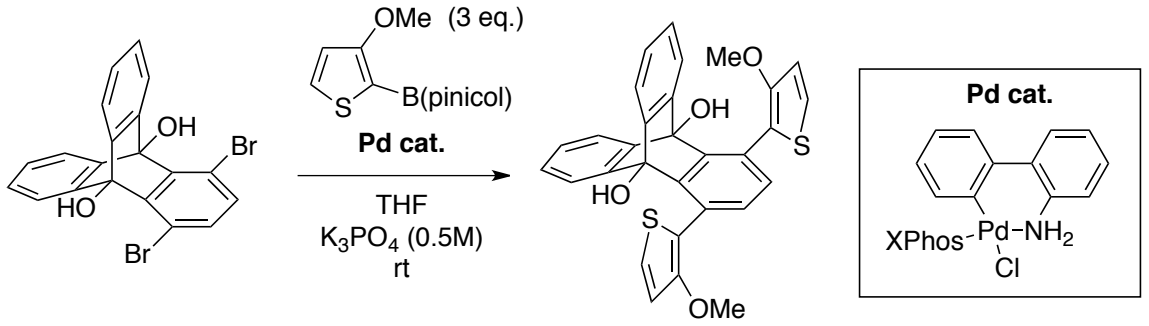


Synthesis of 10: **9** (415 mg, 0.7 mmol), $K_2S_2O_8$ (757 mg, 2.8 mmol), $Cu(OAc)_2$ (1.118 g, 5.6 mmol), KOAc (827 mg, 8.4 mmol) was suspended in 14 mL of AcOH and heated at 113 °C for 15 h. The reaction was then cooled to room temperature and diluted with and aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2 (3x). The organics were combined, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was then purified using silica gel column chromatography (15% CH_2Cl_2/hexanes) to give **10** (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J*=5.5, 3.2, 4H), 7.39 (dd, *J*=8.1, 1.2, 2H), 7.21-7.11 (m, 12H), 6.96-6.70 (m, 4H), 6.48 (ddd, *J*=7.7, 7.3, 1.4, 2H), 6.28 (dd, *J*=8.2, 1.4, 2H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 143.7, 140.3, 136.7, 135.7, 130.6, 129.3, 128.1, 127.1, 126.7, 125.7, 122.8, 121.3, 120.1, 118.8, 117.7, 81.6. HRMS (ESI) calcd.for $C_{44}H_{26}O_2$ [M+H] 587.2006, found 587.2019.



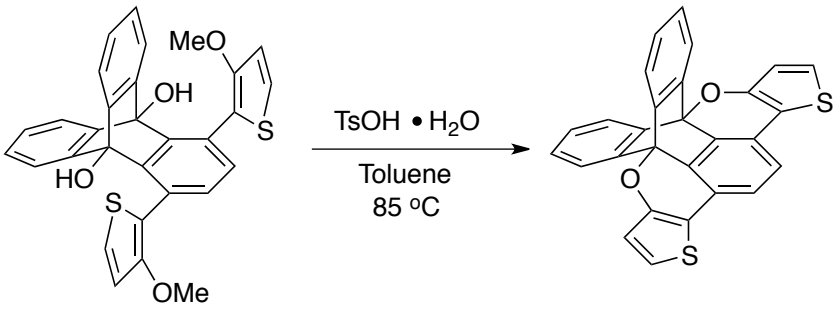
Synthesis of 12: Compound **3** (0.05 g, 0.113 mmol), **Pd cat.**[2] (4.5 mg, 5.7 mmol) and 2-thiophene boronic acid (0.043 g, 0.338 mmol) were dissolved in 1 mL degassed THF under argon. Following, 2 mL of degassed 0.5 M K_3PO_4 was added by syringe and the reaction was stirred at 40 °C for 12 h. The reaction was diluted with water and extracted with DCM (3x). The combined organic extracts were dried over Na_2SO_4 and the volatiles were removed *in vacuo*. The residue was purified by silica gel chromatography (6:4, Hexanes:DCM) to give **12** (98%). ^{1}H NMR (400 MHz, CDCl3): δ 7.58 (dd, *J*=5.6, 3.2, 4H), 7.53 (dd, *J*=5.2, 1.2, 2H), 7.19 (dd, *J*=5.2, 3.2, 2H), 7.15 (dd, *J*=5.6, 3.2, 4H), 7.09 (dd, *J*=3.2, 1.2, 2H), 3.74 (s, 2H). ^{13}C NMR (125 MHz, CDCl3) δ 144.6, 141.1, 129.6, 128.3, 128.1, 127.6, 127.4, 125.9, 119.8, 80.9. HRMS (ESI) calcd. for $C_{28}H_{18}O_2S_2$ [M+H] 449.0675, found 449.0657.

(2) Kinzel, T.; Zhang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14073.

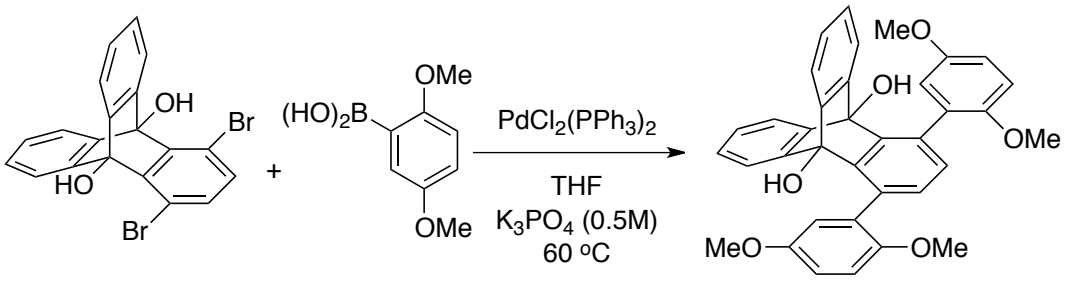


Synthesis of 13: Compound **3** (0.1 g, 0.225 mmol), **Pd cat.**[2] (8.8 mg, 11.2 μmol) and thiophene (0.162 g, 0.675 mmol) were dissolved in 2 mL degassed THF under argon. Following, 4 mL of degassed 0.5 M K_3PO_4 was added by syringe and the reaction was stirred at rt for 12 h. The reaction was diluted with water and extracted with DCM (3x). The combined organic extracts were dried over Na_2SO_4 and the volatiles were removed *in vacuo*. The residue was purified by silica gel chromatography (6:4→2:8, Hexanes:DCM) to give **13** (87%). ^{1}H NMR (400 MHz, CDCl3): δ 7.58 (br m, 4H), 7.37 (d, *J*=5.6, 2H), 7.13 (br m, 4H), 6.98 (d, *J*= 5.6, 2H), 6.90 (s, 2H), 4.69 (br m, 2H), 3.82 (br s, 6H). ^{13}C NMR (125 MHz, CDCl)(Partial) δ 145.6, 144.6, 130.8, 125.6 (broad), 125.0, 120.2-119.5 (broad), 116.6, 80.8, 59.1. HRMS (ESI) calcd. for $C_{30}H_{22}O_4S_2$ [M+H] 511.1032, found 511.1035.

(2) Kinzel, T.; Zhang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14073.

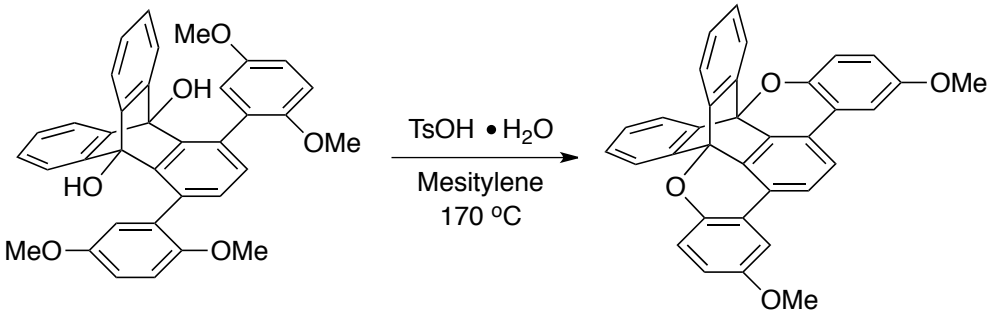


Synthesis of 14: Compound **13** (38.5 mg, 75.4 μmol) and a catalytic amount of *p*-toluenesulfonic acid monohydrate were dissolved in 1 mL toluene and heated at 85 °C overnight. The reaction was diluted with DCM and washed with sat. $NaHCO_3$ twice. The organic fraction was dried over Na_2SO_4 and volatiles removed *in vacuo*. The residue was purified by silica gel chromatography (8:2, Hexanes:DCM) to give **14** (87%). ^{1}H NMR (400 MHz, CDCl3): δ 7.67 (dd, *J*=5.6, 3.2, 4H), 7.18 (d, *J*=5.2, 2H), 7.14 (dd, *J*=5.6, 3.2, 4H), 7.08 (d, *J*=5.2, 2H), 6.78 (s, 2H). ^{13}C NMR (125 MHz, CDCl3) δ 151.6, 143.7, 132.7, 125.9, 122.9, 122.5, 120.4, 119.4, 117.7, 112.0, 84.3. HRMS (ESI) calcd. for $C_{30}H_{22}O_4S_2$ [M+H] 447.0508, found 447.0525.



Synthesis of 15: Compound **3** (0.2 g, 0.45 mmol), 2,5-dimethoxyphenylboronic acid (0.5 g, 2.6 mmol), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol) were dissolved in 2.5 mL degassed THF and 5 mL K_3PO_4 (0.5 M, degassed) under argon. The reaction was sealed and heated at 60 °C for 12 h. The reaction was diluted with sat. NH_4Cl and washed with DCM twice. The combined organic layers were dried over Na_2SO_4 and volatiles were removed *in vacuo*. The residue was purified by silica gel chromatography (8:2, Hexanes:EtOAc) to give **15** (74%).

Alternatively, **15** (50 mg, 11.3 mmol), 2,5-dimethoxyphenylboronic acid (0.1 g, 0.52 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.045 mmol) and solid K_3PO_4 (0.2 g) were dissolved in 1 mL degassed DMF-d_7 and stirred under argon in a microwave reactor (150W, 150 °C) for 15 min.The yield (81%) was determined by ^{1}H NMR relative to residual solvent signal before and after reaction. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 4H), 7.16-7.06 (m, 4H), 6.99 (br m, 4H), 6.87 (br m, 1H), 6.80 (br m, 3H), 4.12 (s, 1H), 3.92 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 154.0, 150.7, 150.4, 145.0, 144.9, 144.8, 144.7, 143.7, 143.5, 131.8, 131.5, 131.2, 131.1, 129.3, 129.1, 125.4, 125.4, 125.2, 125.1, 119.7, 119.6, 119.4, 117.1, 116.9, 114.3, 114.0, 112.3, 112.2, 80.9, 80.8, 56.4, 56.3, 56.0, 55.9. HRMS (ESI) calcd. for $C_{36}H_{30}O_6$ [M+Na] 581.1935, found 581.1956.



Synthesis of 16: Compound **15** (60 mg, 0.11 mmol) and *p*-toluenesulfonic acid monohydrate (40 mg, 22 mmol) were dissolved in 0.7 mL mesitylene and heated at 170 ^{o}C for 12 h. The reaction was diluted with DCM and washed with 1M NaOH twice. The organic fraction was dried over Na_2SO_4 and the volatiles were removed *in vacuo*. The residue was trituration with EtOH to give **16** (56% isolated, spot to spot conversion by TLC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J*=5.6, 3.2 Hz, 4H), 7.33 (s, 2H), 7.32 (d, *J*=8.4 Hz, 2H), 7.14 (d, *J*=2.8 Hz, 2H), 7.11 (dd, *J*=5.2, 3.2 Hz, 4H), 6.91 (dd, *J*=8.8, 2.8 Hz, 2H), 3.85 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 147.2, 143.9, 134.7, 125.8, 124.3, 120.3, 118.5, 118.3, 118.2, 115.7, 107.8, 81.0, 56.1. HRMS (ESI) calcd. for $C_{34}H_{22}O_4$ [M+Na] 517.1410, found 517.1427.

X-ray Crystal Structures:

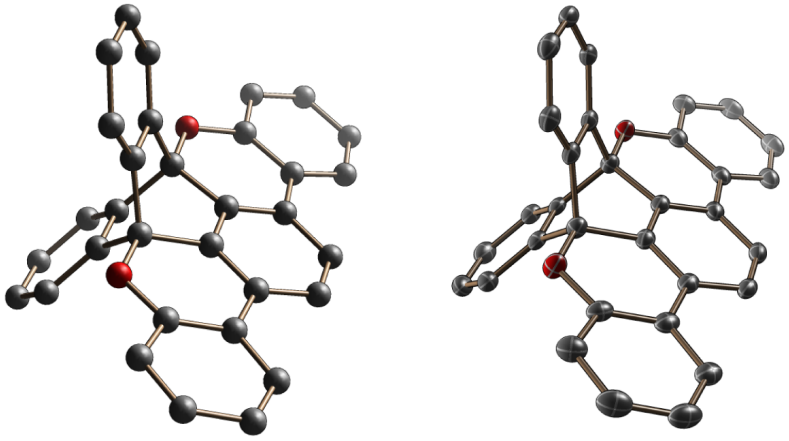


Figure S1: Crystal Structure of **7.**
Suitable crystals were grown by slow evaporation of $CHCl_3$. Anisotropic thermal ellipsoids set at 50% probability.

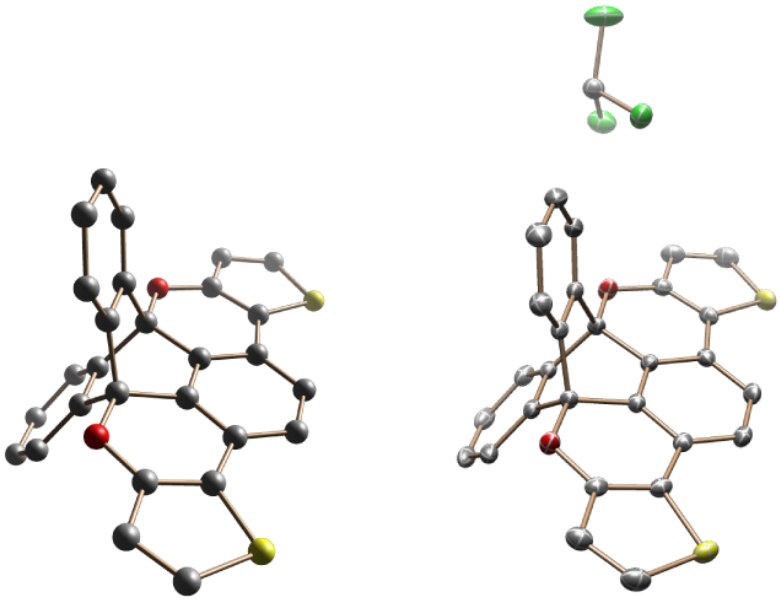


Figure S2: Crystal Structure of **14.**
Suitable crystals were grown by vial-in-vial vapor diffusion using $CHCl_3$:Pentane as the solvent:antisolvent mixture. Anisotropic thermal ellipsoids set at 70% probability.

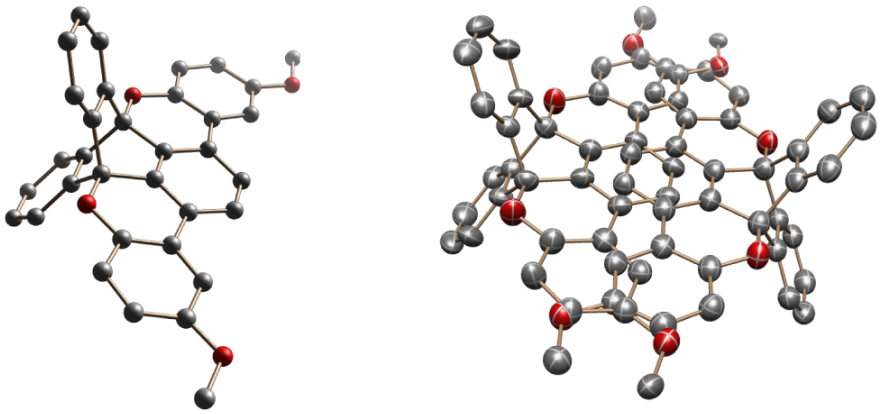


Figure S3: Crystal Structure of **16.**
Suitable crystals were grown by vial-in-vial vapor diffusion using $CHCl_3$:Pentane as the solvent:antisolvent mixture. Anisotropic thermal ellipsoids set at 50% probability.

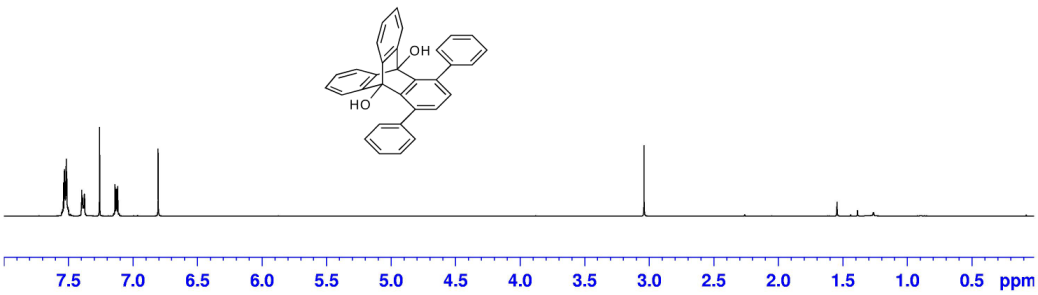


Figure S4: ^{1}H NMR spectrum of **6** in $CDCl_3$ (400 MHz)

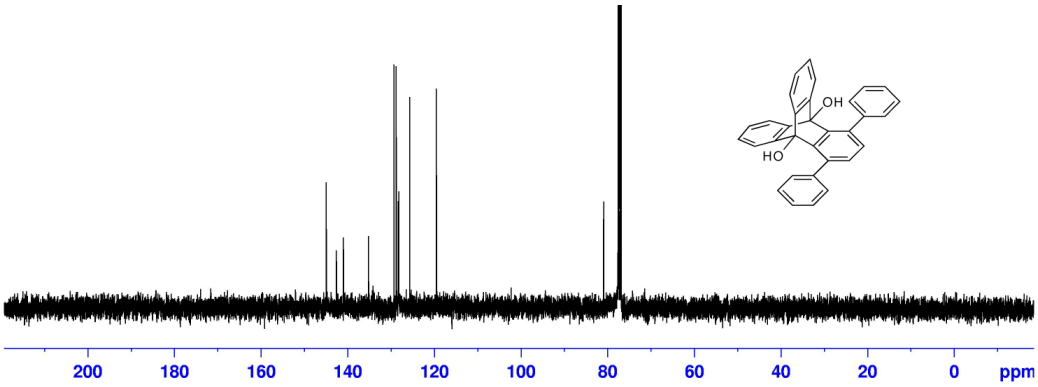


Figure S5: ^{13}C NMR spectrum of **6** in $CDCl_3$ (125 MHz)

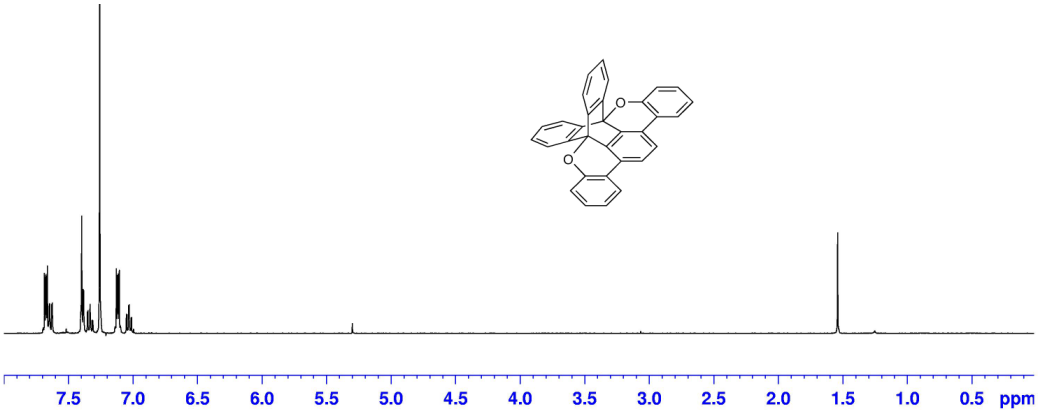


Figure S6: ^{1}H NMR spectrum of **7** in $CDCl_3$ (400 MHz)

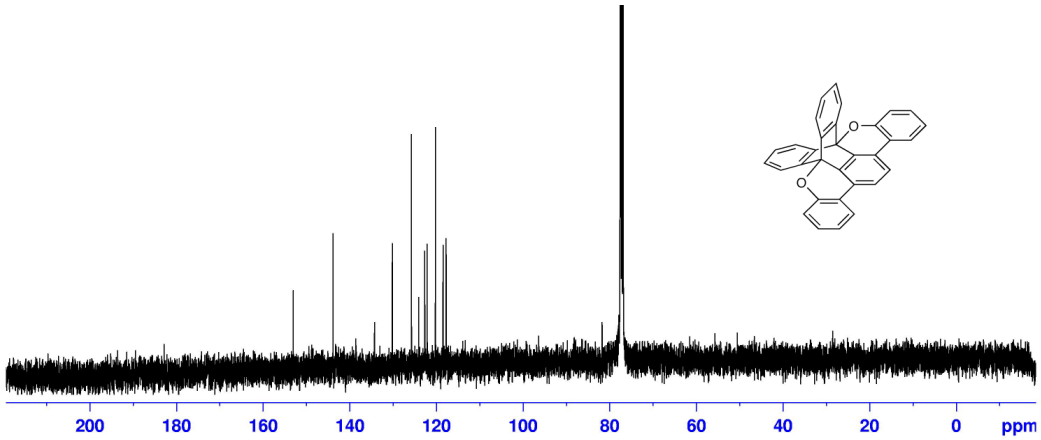


Figure S7: ^{13}C NMR spectrum of **7** in $CDCl_3$ (125 MHz)

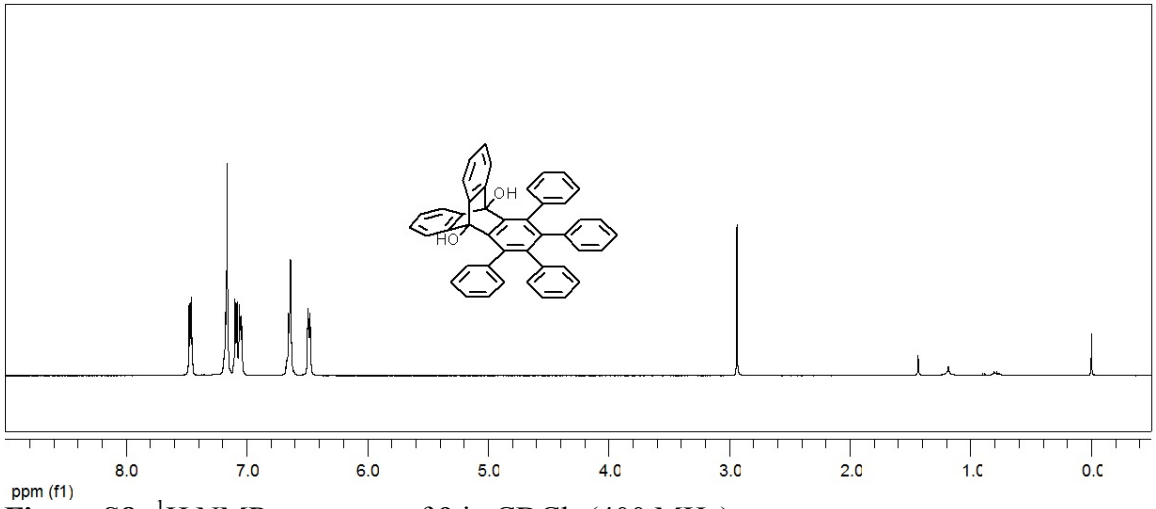


Figure S8: ^{1}H NMR spectrum of **9** in $CDCl_3$ (400 MHz)

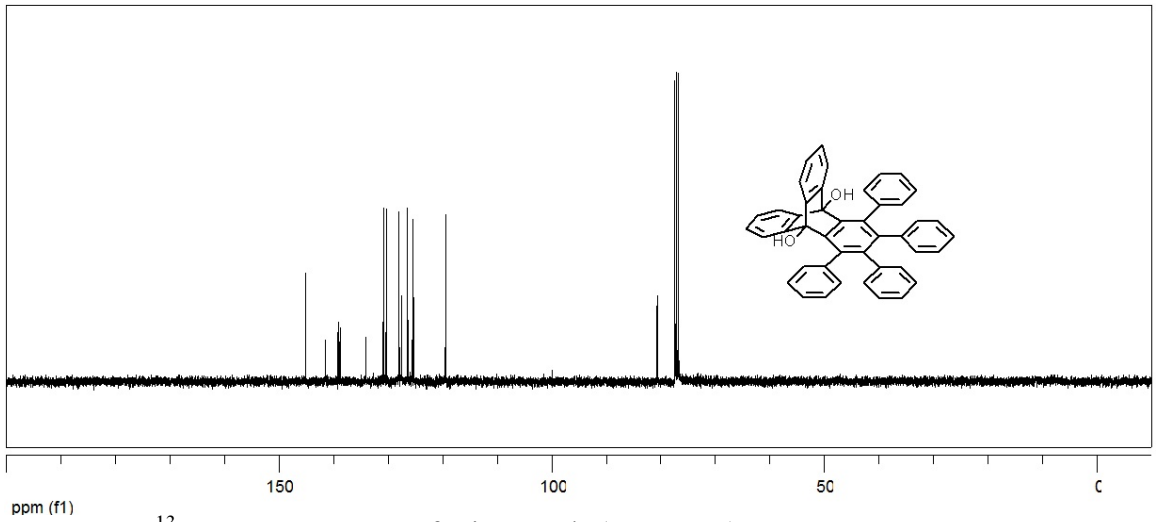


Figure S9: ^{13}C NMR spectrum of **9** in $CDCl_3$ (125 MHz)

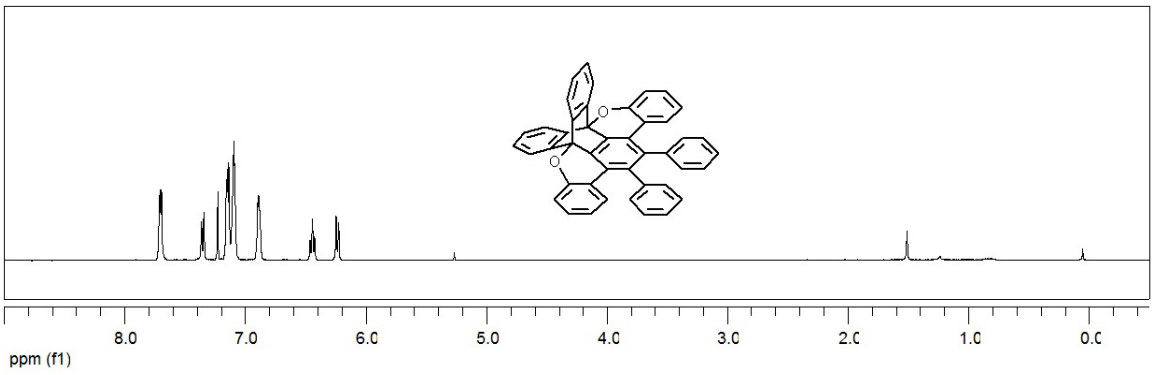


Figure S10: ^{1}H NMR spectrum of **10** in $CDCl_3$ (400 MHz)

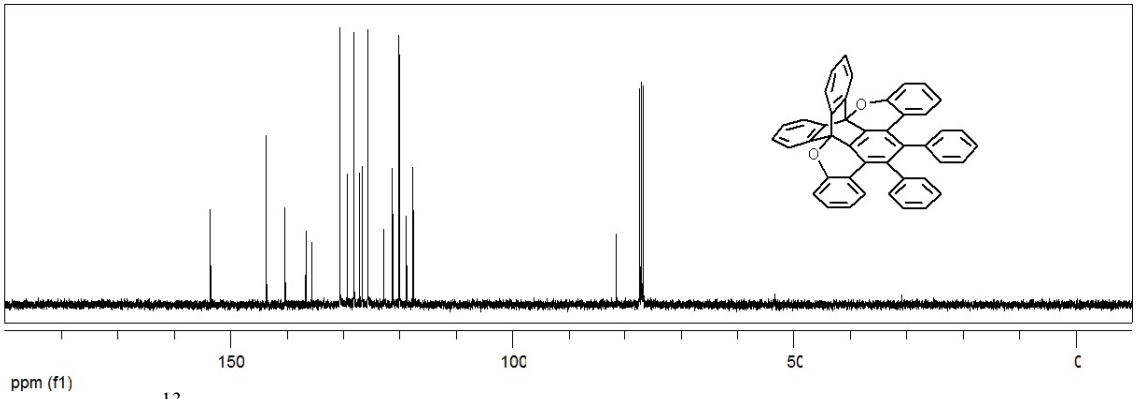


Figure S11: ^{13}C NMR spectrum of **10** in $CDCl_3$ (125 MHz)

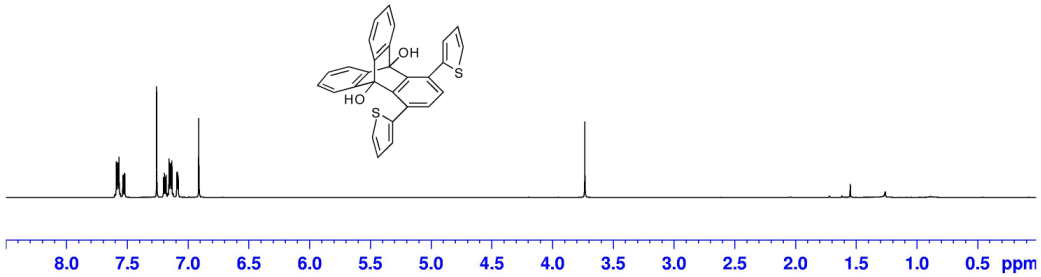


Figure S12: ^{1}H NMR spectrum of **12** in $CDCl_3$ (400 MHz)

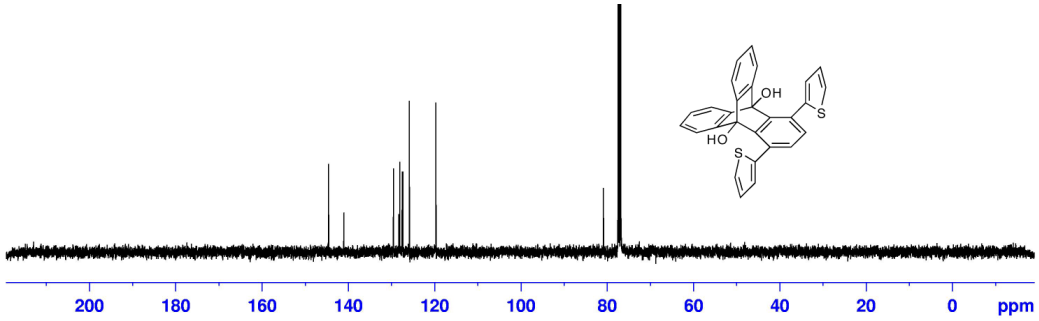


Figure S13: ^{13}C NMR spectrum of **12** in $CDCl_3$ (125 MHz)

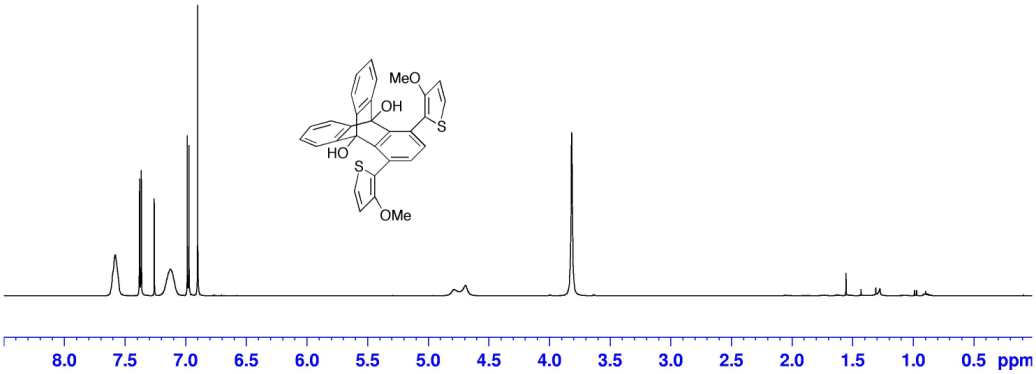


Figure S14: ^{1}H NMR spectrum of **13** in $CDCl_3$ (400 MHz)

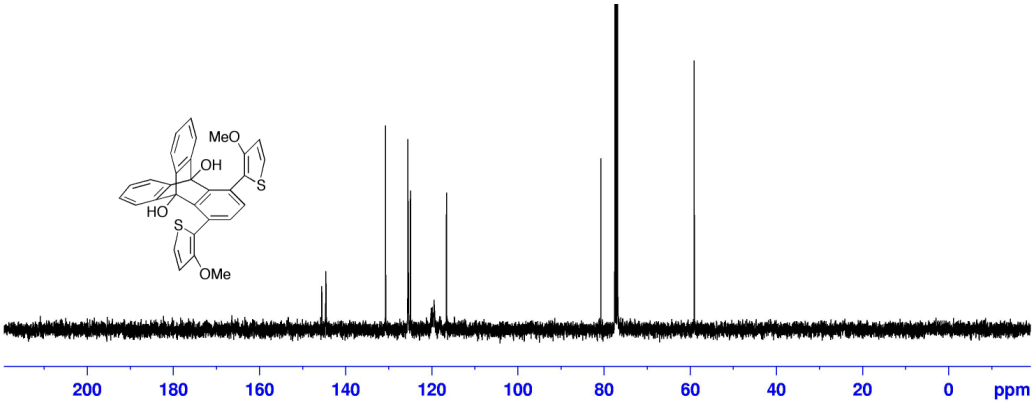


Figure S15: ^{13}C NMR spectrum of **13** in $CDCl_3$ (125 MHz)

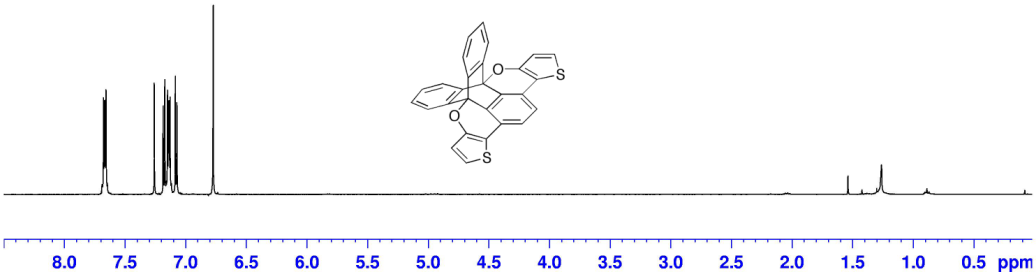


Figure S16: ^{1}H NMR spectrum of **14** in $CDCl_3$ (400 MHz)

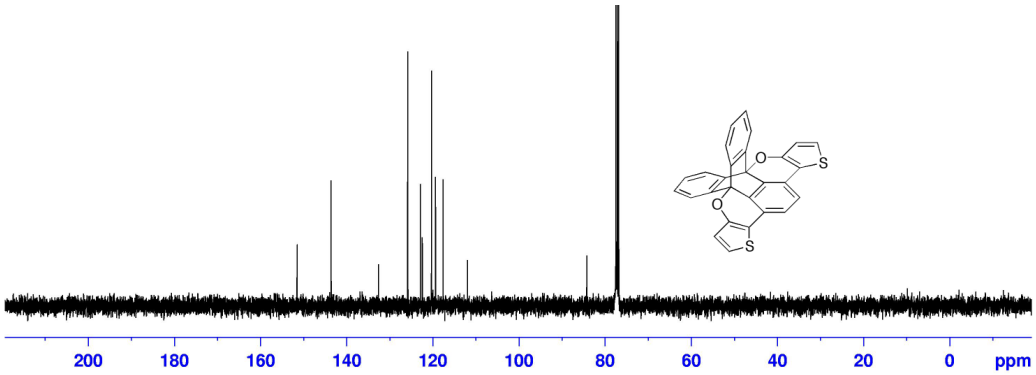


Figure S17: ^{13}C NMR spectrum of **14** in $CDCl_3$ (125 MHz)

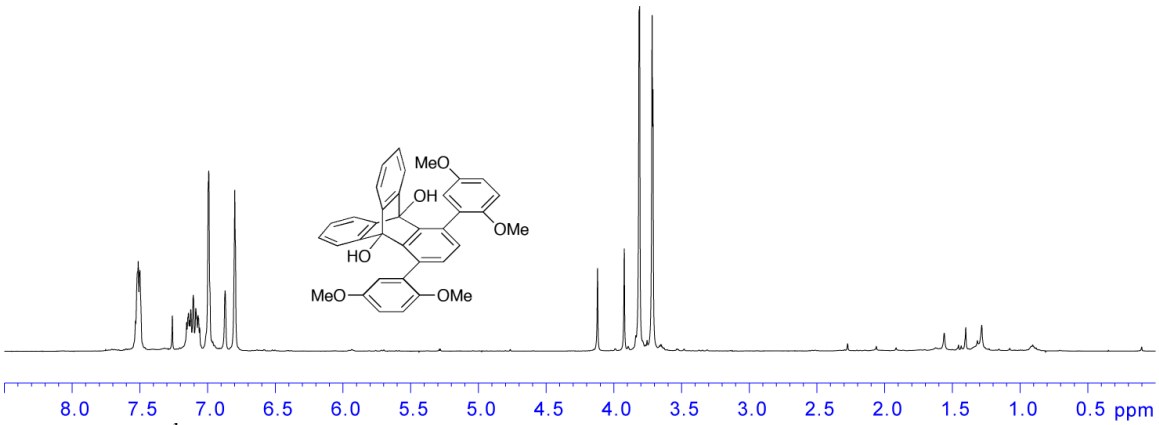


Figure S18: ^{1}H NMR spectrum of **15** in $CDCl_3$ (400 MHz)

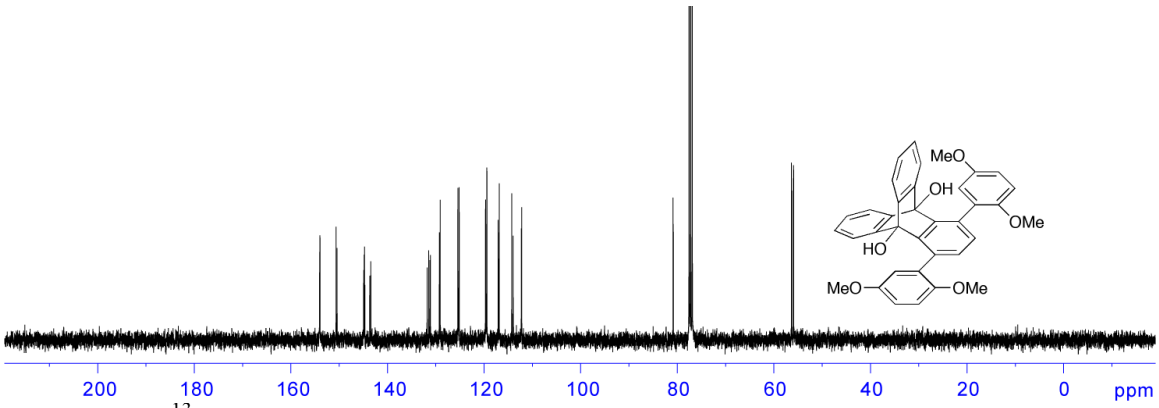


Figure S19: ^{13}C NMR spectrum of **15** in $CDCl_3$ (125 MHz)

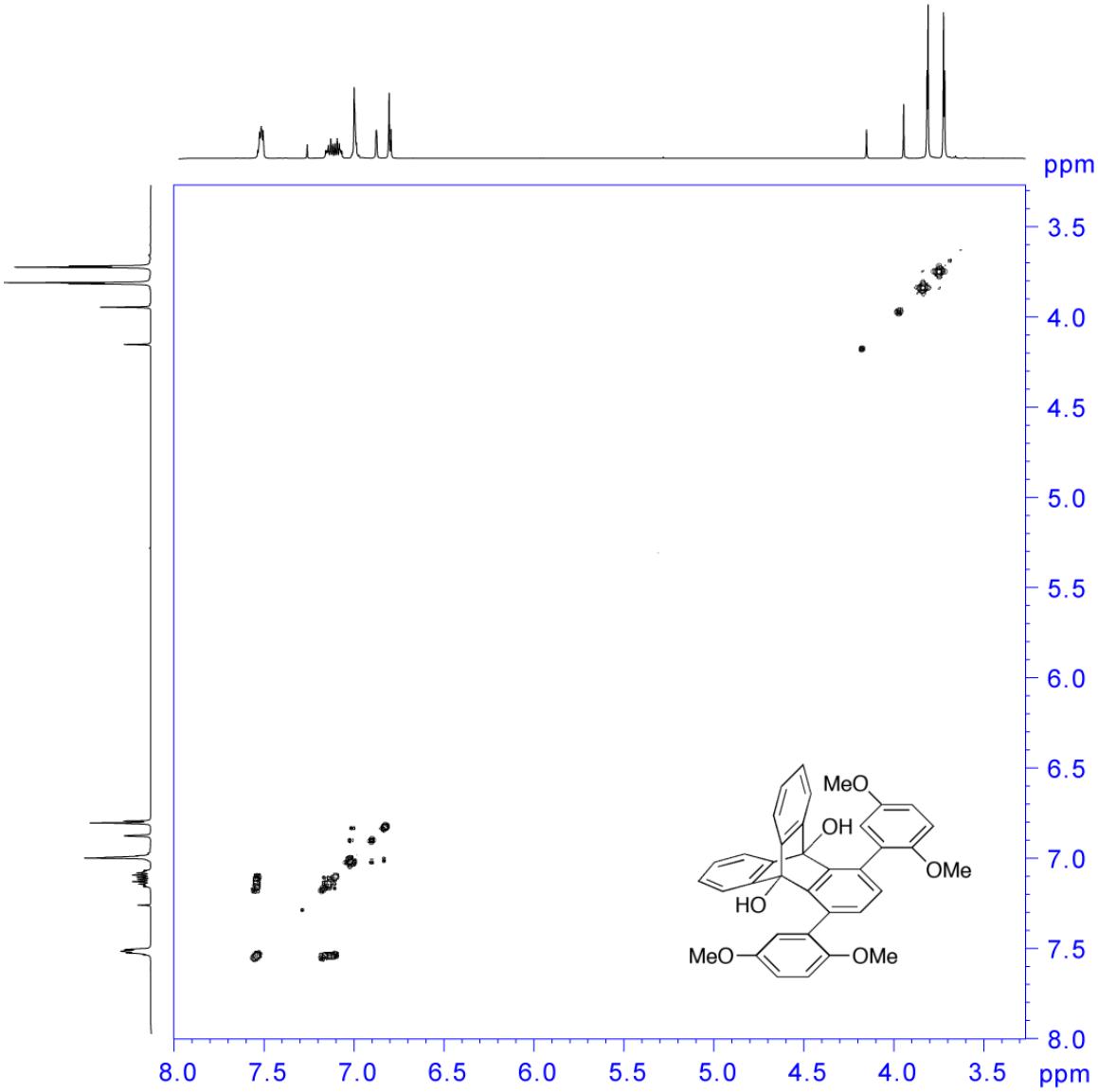


Figure S20: gCOSY of **15** in $CDCl_3$ (600 MHz)

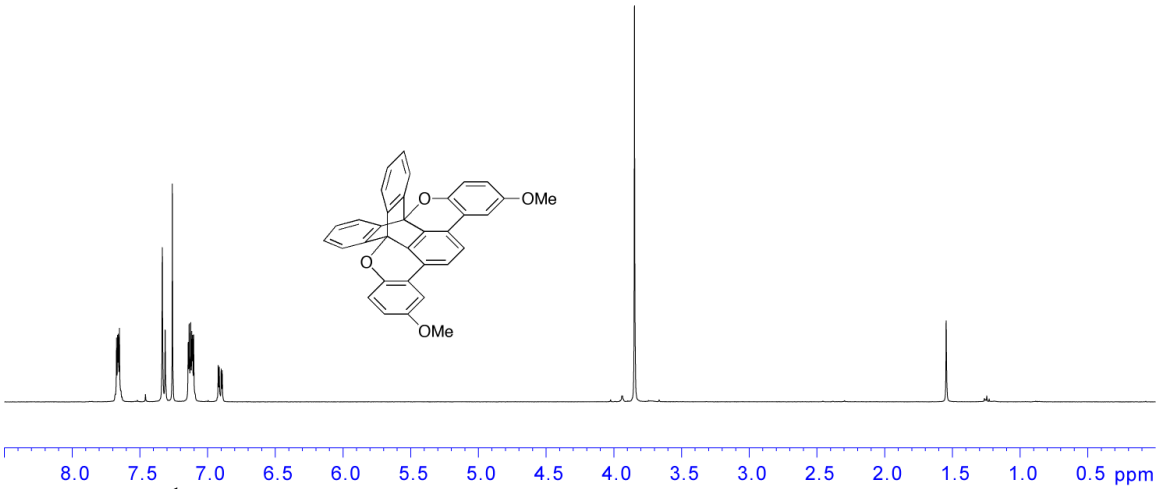


Figure S21: ^{1}H NMR spectrum of **16** in $CDCl_3$ (400 MHz)

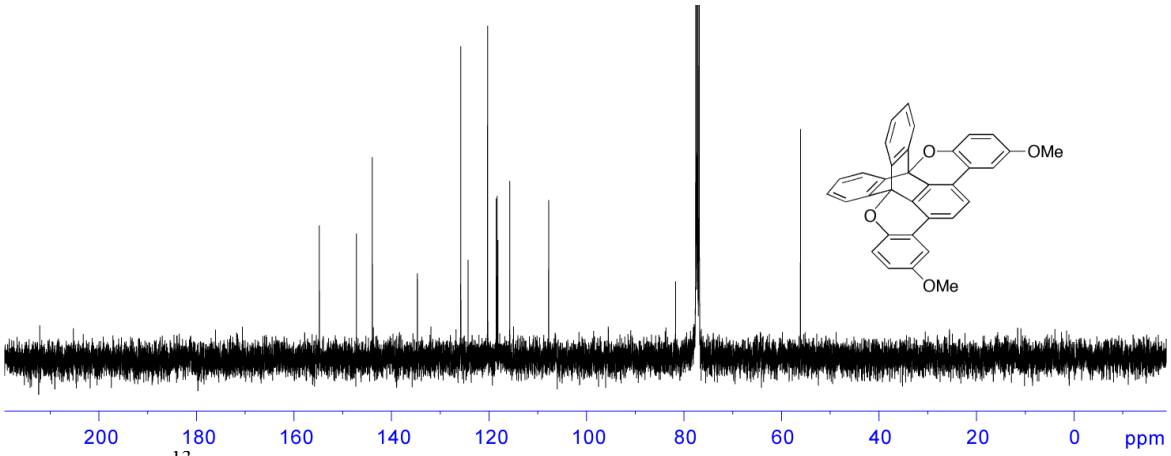


Figure S22: ^{13}C NMR spectrum of **16** in $CDCl_3$ (125 MHz)

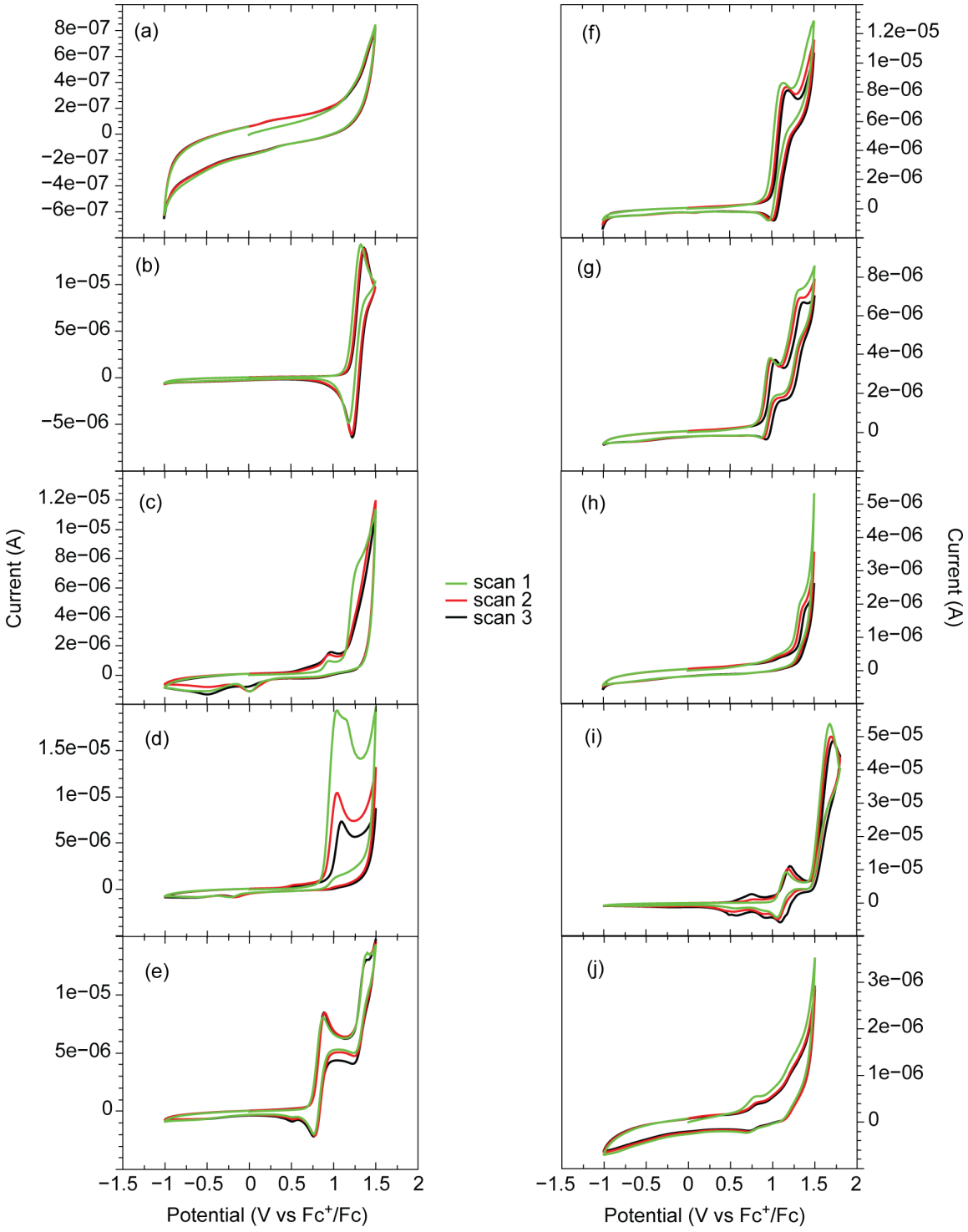


Figure S23: Cyclic voltammograms of (a) **6**, (b) **7**, (c) **12**, (d) **13**, (e) **14**, (f) **15**, (g) **16**, (h) **9**, (i) **10**, (j) **11**. See general experimental section for technical details.

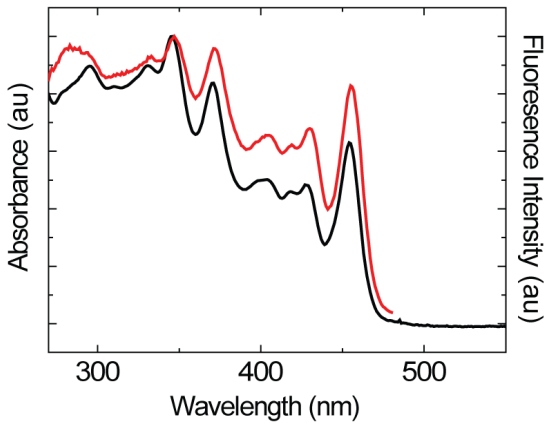


Figure S24: Comparison of absorbance (black) and excitation (red) spectrum of **11**.

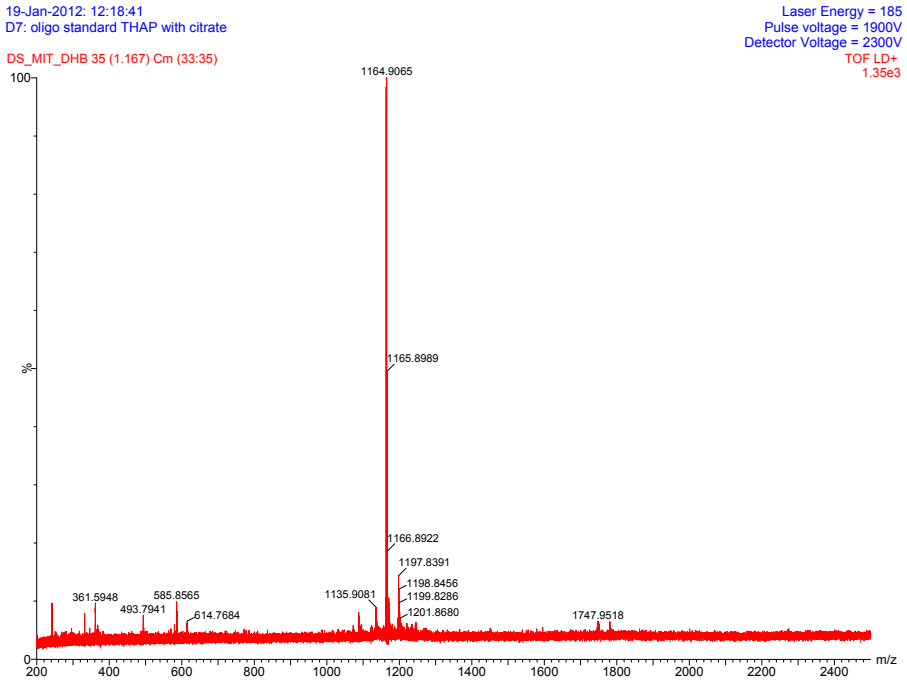


Figure S25: MALDI-TOF data for **11**

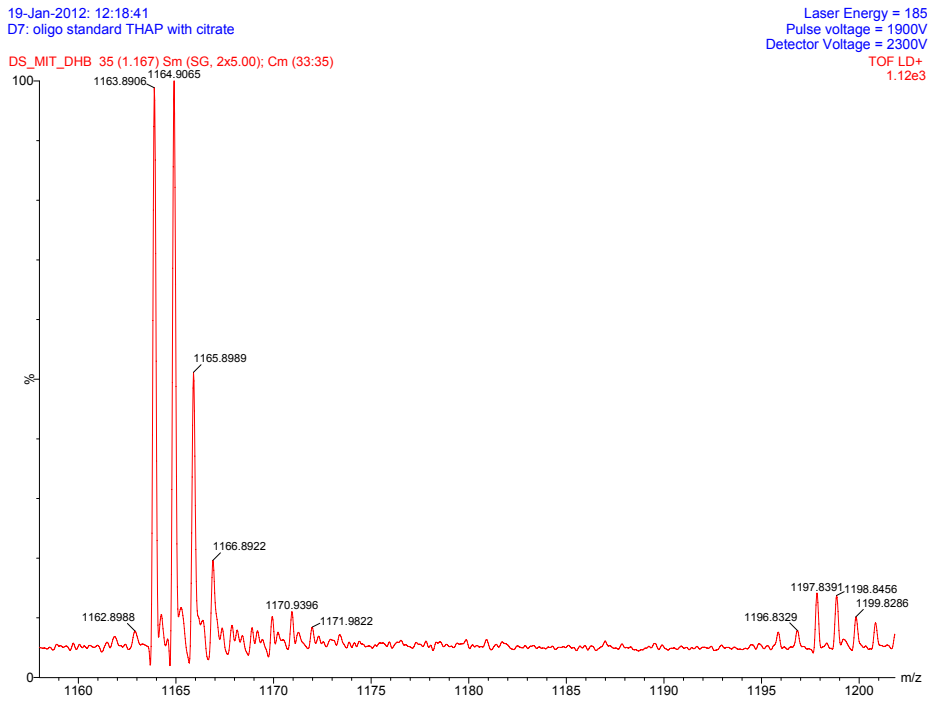


Figure S26: MALDI-TOF data for **11**

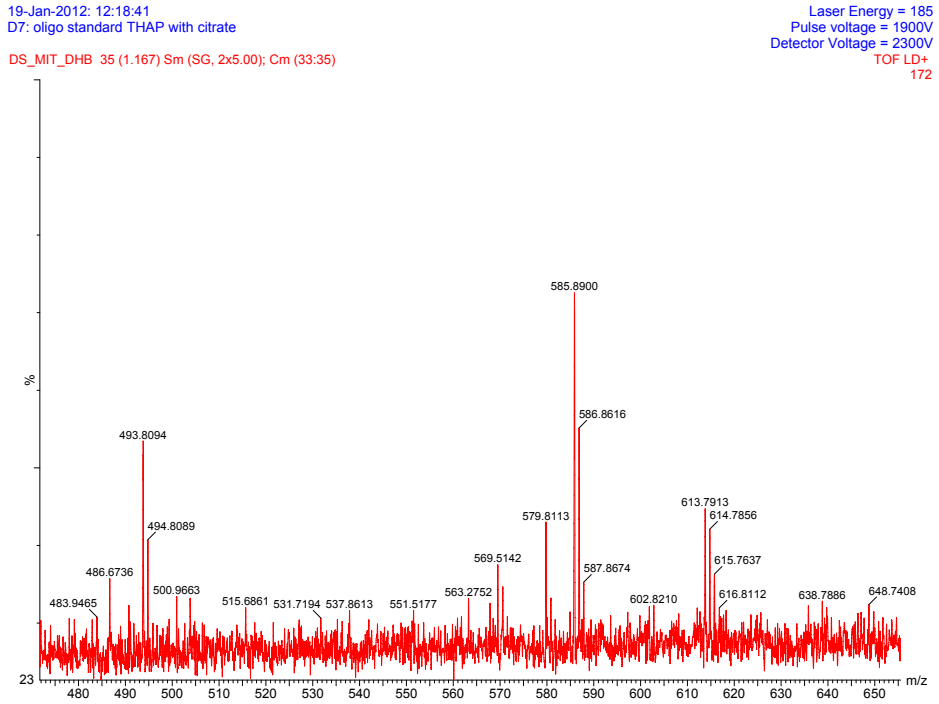


Figure S27: MALDI-TOF data for **11**