

Supporting Information
for DOI: 10.1055/s-0037-1611169
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Supporting Information

Synthesis and Optoelectronic Properties of Iptycene-Naphthazarin Dyes

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S1. Experimental Section

General. Reagents were purchased as reagent grade and used without further purification. All solvents were of ACS reagent grade or better. Toluene was passed through a solvent purification system *via* columns of activated alumina, and stored over 3 Å sieves. Reactions in the absence of air and moisture were performed in oven-dried glassware under Ar or N₂ atmosphere. Flash column chromatography (FC) was performed using SiO₂ (60 Å, 230–400 mesh, particle size 0.040–0.063 mm) at 25 °C with a head pressure of 0.0–0.5 bar. The used solvent compositions are reported individually in parentheses. Analytical thin layer chromatography (TLC) was performed on sheets coated with silica gel (200 μm, IB-F). Visualization was achieved using UV light (254 or 366 nm). Evaporation *in vacuo* was performed at 25–60 °C and 900–10 mbar. Reported yields refer to spectroscopically and chromatographically pure compounds that were dried under high vacuum (0.1–0.05 mbar) before analytical characterization. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 500 or 400 MHz (¹H) and 125 or 100 MHz (¹³C), respectively. Chemical shifts δ are reported in ppm downfield from tetramethylsilane using the residual solvent signals as an internal reference (CDCl₃: $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm. For ¹H NMR, coupling constants J are given in Hz and the resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet), and br. (broad). All spectra were recorded at 298 K. High-resolution mass spectrometry (HRMS) was performed by the MS-service of the MIT Department of Chemistry Instrumentation Facility using an Ion Cyclotron Resonance Mass Spectrometer with either electrospray (ESI) or Direct Analysis in Real Time (DART) as the ionization technique. UV/vis spectroscopy was recorded on a UV/vis spectrophotometer and corrected for background signal with a solvent-filled cuvette. Fluorescence spectra were measured using right-angle detection. Absolute quantum yield measurements were carried out using an integrating sphere, which was coupled to the fluorometer *via* an optical fiber bundle. Samples were excited with a 450W Xenon short arc lamp and fluorescence was detected with a detector. All photophysical measurements were performed with spectral grade dichloromethane.

Experimental Data:

Compound 5

Compound **1** (64 mg, 0.175 mmol) and diene (**4**) (40 mg, 0.175 mmol) were added to a flame-dried Schlenk flask with stirrer bar, and were dissolved in the minimal amount of anhydrous toluene (1-2 mL). The headspace was purged with argon, then heated to reflux overnight (111 °C). The solvent was evaporated under reduced pressure, and the crude material was re-dissolved in tetrahydrofuran (20 mL). After addition of KO^tBu (353 mg, 3.14 mmol) and stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; hexanes/CH₂Cl₂ 1:1) gave **5** (47 mg, 45%) as an orange solid. *R*_f = 0.35 (SiO₂; hexanes/CH₂Cl₂ 1:1); m.p. > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ = 5.68 (s, 2 H), 6.10 (s, 2 H), 7.01 – 7.09 (m, 8 H), 7.41 – 7.51 (m, 8 H), 8.26 (s, 2H), 13.18 ppm (s, 2H); ¹³C NMR (100 MHz, CD₂Cl₂, 298 K): δ = 187.5, 153.6, 152.6, 146.6, 144.5, 144.0, 132.1, 126.5, 126.2, 124.73, 124.65, 122.0, 112.0, 54.5, 48.0 ppm; UV/Vis (CH₂Cl₂): λ_{max} (ε) = 496 (9570), 287 (50230), 259 nm (21130 M⁻¹ cm⁻¹); HR-ESI-MS: found 592.1676 ([M]⁺, calcd for C₄₂H₂₄O₄⁺: 592.1675).

Compound 6

Compound **2** (33 mg, 0.056 mmol) and the diene (**4**) (40 mg, 0.056 mmol) were added to a flame-dried Schlenk flask with stirrer bar, and were dissolved in the minimal amount of anhydrous toluene (1-2 mL). The headspace was purged with argon, then heated to reflux overnight (111 °C). The solvent was evaporated under reduced pressure, and the crude material was re-dissolved in tetrahydrofuran (20 mL). After addition of KO^tBu (114 mg, 1.01 mmol) and stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; hexanes/CH₂Cl₂ 1:1) gave **6** (24 mg, 53%) as an orange solid. *R*_f = 0.59 (SiO₂; hexanes/CH₂Cl₂ 1:1); m.p. > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ = 1.20 (s, 12 H), 1.23 (s, 12 H), 1.61 (br. s, 8 H), 5.68 (s, 2 H), 5.94 (s, 2 H), 6.95 – 7.10 (m, 4 H), 7.40 (s, 4 H), 7.42 – 7.51 (m, 4 H), 8.27 (s, 2H), 13.21 ppm (s, 2H); ¹³C NMR (100 MHz, CD₂Cl₂, 298 K): δ = 187.4, 153.5, 152.5, 147.0, 144.0, 142.7, 141.5, 132.2, 126.4, 124.6, 122.7, 122.0, 111.9, 54.5, 47.4, 35.6, 34.8, 32.2,

32.1 ppm; UV/Vis (CH₂Cl₂): λ_{\max} (ϵ) = 497 (10130), 287 (40040), 257 nm (18420 M⁻¹ cm⁻¹); HR-ESI-MS: found 812.3887 ([M]⁺, calcd for C₅₈H₅₂O₄⁺: 812.3866).

Compound 7

Compound **3** (13 mg, 0.031 mmol) and the diene (**4**) (7 mg, 0.031 mmol) were added to a flame-dried Schlenk flask with stirrer bar, and were dissolved in the minimal amount of anhydrous toluene (1-2 mL). The headspace was purged with argon, then heated to reflux overnight (111 °C). The solvent was evaporated under reduced pressure, and the crude material was re-dissolved in tetrahydrofuran (20 mL). After addition of KO^tBu (62 mg, 0.55 mmol) and stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; hexanes/CH₂Cl₂ 1:2) gave **7** (6 mg, 30%) as an orange solid. R_f = 0.41 (SiO₂; hexanes/CH₂Cl₂ 1:1); m.p. 288–289 °C; ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ = 2.14 (s, 12 H), 5.68 (s, 2 H), 5.92 (s, 2 H), 7.05 (br. dd, J = 5.5, 3.1 Hz, 4 H), 7.21 (s, 4 H), 7.45 (br. dd, J = 5.5, 3.1 Hz, 4 H), 8.26 (s, 2H), 13.17 ppm (s, 2H); ¹³C NMR (100 MHz, CD₂Cl₂, 298 K): δ = 187.4, 153.4, 152.5, 147.3, 144.1, 142.3, 134.1, 132.2, 126.4, 125.9, 124.6, 122.0, 111.9, 54.5, 47.1, 19.7 ppm; UV/Vis (CH₂Cl₂): λ_{\max} (ϵ) = 497 (9425), 288 (38750), 257 nm (17170 M⁻¹ cm⁻¹); HR-ESI-MS: found 649.2401 ([M + H]⁺, calcd for C₄₆H₃₃O₄⁺: 649.2379).

Compounds 9a and 9b

Naphthazarin **8** (50 mg, 0.263 mmol) and the diene (**4**) (61 mg, 0.263 mmol) were added to a flame-dried Schlenk flask with stirrer bar, and were dissolved in the minimal amount of anhydrous toluene (1-2 mL). The headspace was purged with argon, then heated to reflux overnight (111 °C). The solvent was concentrated *in vacuo*. FC (SiO₂; CHCl₃) gave **9a/9b** 1:3.5 (93 mg, 84%) as yellow solids. **9a**: R_f = 0.60 (SiO₂; CHCl₃); m.p. 258–259 °C (decomp); ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.47 – 2.58 (m, 2H), 2.78 – 2.88 (m, 2H), 3.19 – 3.26 (m, 2H), 4.76 (s, 2H), 6.95 (t, J = 9.4, 5.3, 3.1 Hz, 4 H), 7.19 (s, 2H), 7.22 – 7.28 (m, 4 H), 11.73 ppm (s, 2H); ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 203.0, 155.3, 145.9, 145.4, 140.2, 128.6, 124.73, 124.71, 122.79, 122.77, 113.3, 55.1, 45.7, 26.5 ppm; HR-ESI-MS: found 420.1395 ([M]⁺, calcd for C₂₈H₂₀O₄⁺: 420.1362). **9b**: R_f = 0.66 (SiO₂; CHCl₃ 1:1); m.p. 299–300 °C (decomp); ¹H NMR (400 MHz,

CDCl₃, 298 K): δ = 2.64 – 2.80 (m, 2H), 2.87 – 3.05 (m, 4H), 4.91 (s, 2H), 7.01 (dd, J = 5.3, 3.1 Hz, 4 H), 7.29 (s, 2H), 7.33 (dd, J = 5.3, 3.1 Hz, 4 H), 11.98 ppm (s, 2H); ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 202.6, 155.3, 146.0, 145.9, 140.6, 128.5, 124.8, 124.7, 122.9, 114.4, 55.0, 45.9, 27.8 ppm; HR-ESI-MS: found 420.1349 ([M]⁺, calcd for C₂₈H₂₀O₄⁺: 420.1362).

Compounds 10

To a 25 mL round-bottom flask was added **9a/9b** (38 mg, 0.090 mmol), KO^tBu (183 mg, 1.63 mmol), and 20 mL THF. After stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; hexanes/CH₂Cl₂ 1:2) gave **10** (22 mg, 59%) as an orange solid. R_f = 0.36 (SiO₂; hexanes/CH₂Cl₂ 1:2); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 12.90 (s, 2H), 8.31 (s, 2H), 7.46 (br. dd, J = 5.3, 3.2 Hz, 4H), 7.25 (s, 2H), 7.07 (br. dd, J = 5.3, 3.2 Hz, 4H), 5.67 ppm (s, 2H); ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 187.0, 157.8, 152.3, 143.5, 131.7, 129.3, 126.1, 124.3, 121.8, 112.9, 54.3 ppm; UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 488 (9940), 284 (41610), 257 nm (24220 M⁻¹ cm⁻¹); HR-ESI-MS: found 416.1053 ([M]⁺, calcd for C₂₈H₁₇O₄⁺: 416.1049).

Compounds 12

To a 25 mL round-bottom flask was added **9a/9b** (187 mg, 0.445 mmol), KO^tBu (150 mg, 1.33 mmol), and 20 mL THF. After stirring under ambient conditions for 1–5 min and was monitored by TLC for the appearance of the dark orange partially oxidized product **11** and stopped immediately following the appearance of the orange fully oxidized **10**. The blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; CHCl₃) gave the mixture of **11** (101 mg, 54%) and **10** (45 mg, 24%). The separation of **10** and **11** was not successful. Both compounds have similar R_f values in common organic solvent mixtures. The mixture of **11/10** is used in the following reaction without further purification since **10** was completely unreactive toward Diels-Alder reaction. This approach allowed easy separation of **12** from **10**. The mixture of **11/10** [**11** (126 mg, 0.301 mmol)] and the diene (**4**) (69 mg, 0.301 mmol) were added to a flame-dried Schlenk flask with stirrer bar, and were dissolved in the minimal amount of anhydrous toluene (1-2 mL). The headspace was

purged with argon, then heated to reflux overnight (111 °C). The solvent was evaporated under reduced pressure, and the crude material was re-dissolved in tetrahydrofuran (20 mL). After addition of KO^tBu (608 mg, 5.42 mmol) and stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; hexanes/CH₂Cl₂ 1:1 to 1:2) gave **12** (68 mg, 35%) as an orange solid and unreacted **10** from the previous step. $R_f = 0.41$ (SiO₂; hexanes/CH₂Cl₂ 1:2); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 298 K): $\delta = 15.05$ (s, 2H), 8.39 (s, 4 H), 7.44 (br. dd, $J = 5.4, 3.2$ Hz, 8 H), 7.05 (br. dd, $J = 5.4, 3.2$ Hz, 8 H), 5.65 ppm (s, 4 H); ¹³C NMR (125 MHz, (CDCl₂)₂, 298 K): $\delta = 172.1, 150.0, 143.3, 130.1, 125.9, 124.2, 120.3, 106.7, 53.8$ ppm; UV/Vis (CH₂Cl₂): $\lambda_{\max} (\epsilon) = 531 (13360), 495 (14360), 465 (8810), 319 (15080), 290 (39000), 255$ nm (18200 M⁻¹ cm⁻¹); HR-ESI-MS: found 643.1905 ([M + H]⁺, calcd for C₄₆H₂₇O₄⁺: 643.1909).

S2. X-ray analysis

The supplementary crystallographic data for this paper can be found using the following deposition numbers: CCDC 1848118 (**9b**), 1848119 (**9a**), 1848120 (**10**), and 1848121 (**6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/data_request/cif.

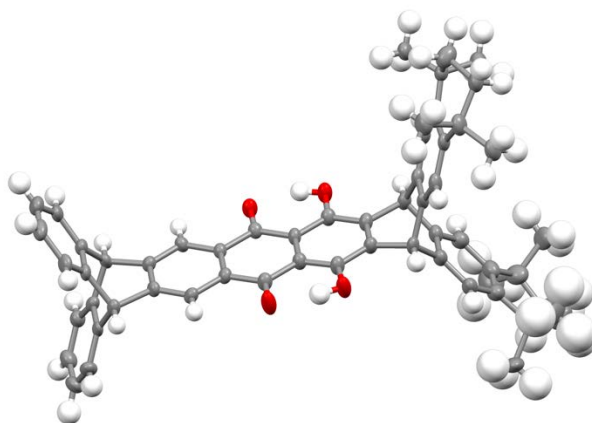


Figure S1. ORTEP plot of **6**. Atomic displacement parameters are drawn at 50% probability level.

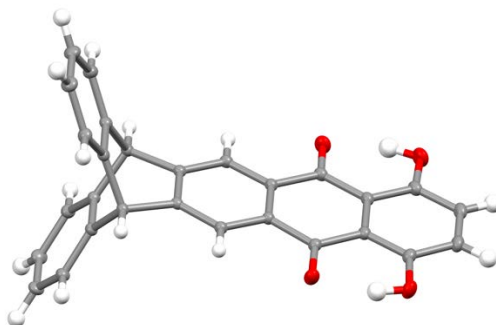


Figure S2. ORTEP plot of **10**. Atomic displacement parameters are drawn at 50% probability level.

S3. UV/Vis and Photoluminescence Spectra

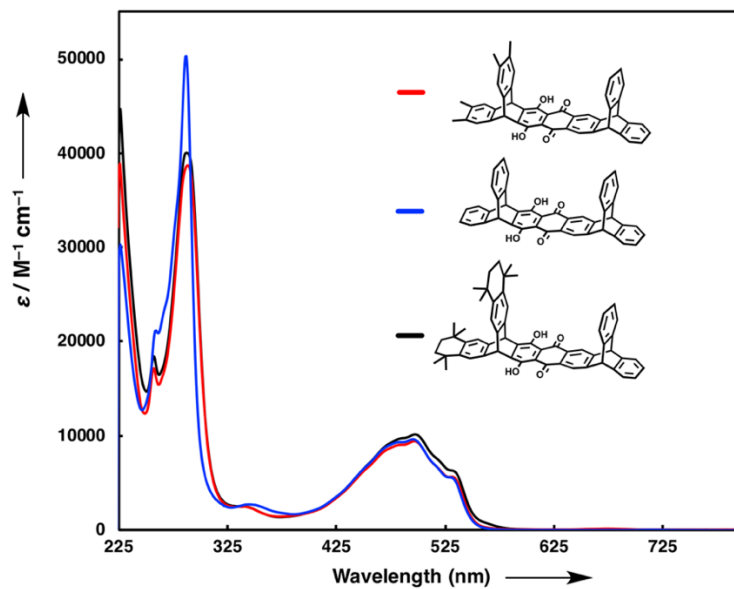


Figure S3. UV/Vis spectra of compounds **5** (blue line), **6** (black line), and **7** (red line) in CH₂Cl₂ at 298 K.

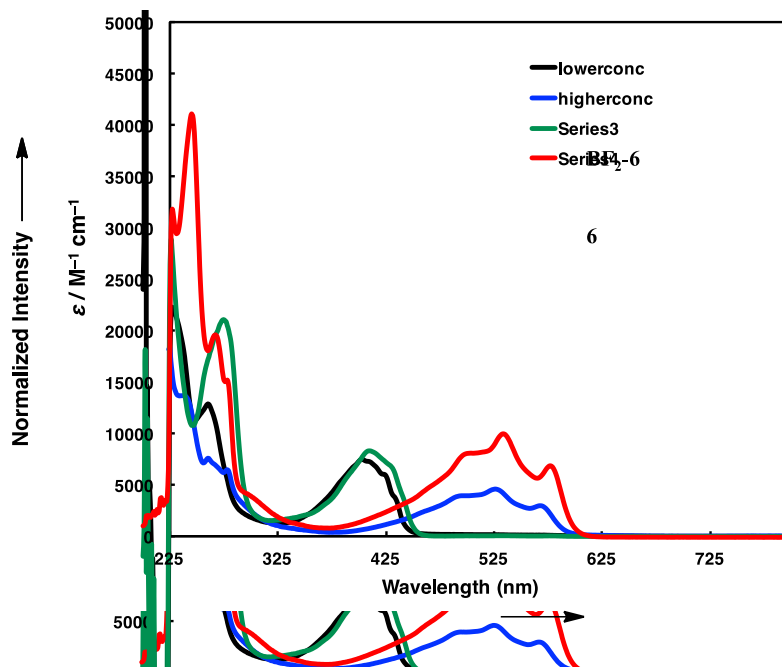


Figure S4. Normalized UV/Vis spectra of compound **6** (blue line) and **BF₂-6** (red line) in CH₂Cl₂ at 298 K.

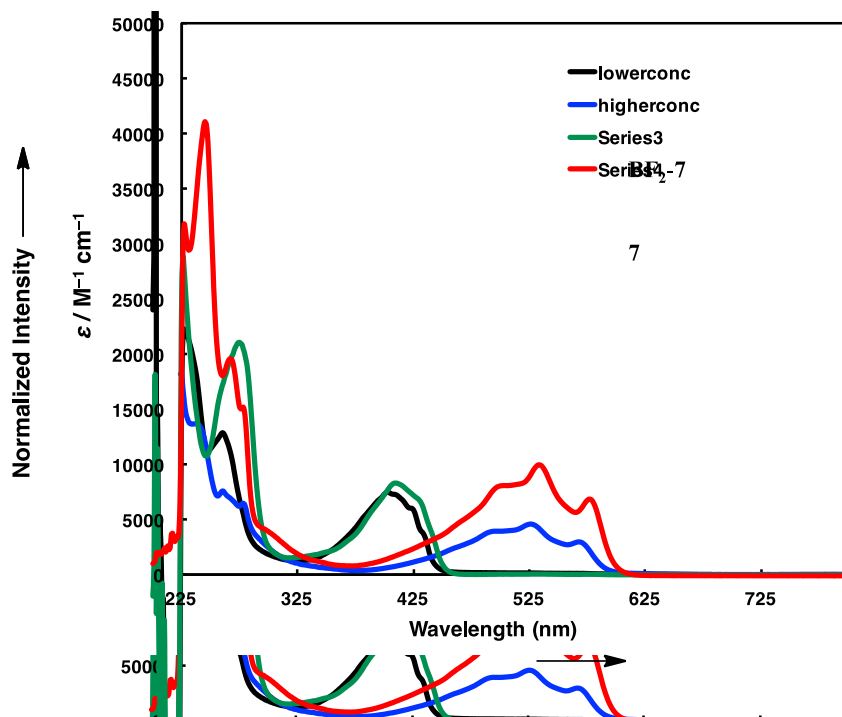


Figure S5. Normalized UV/Vis spectra of compound **7** (blue line) and **BF₂-7** (red line) in CH₂Cl₂ at 298 K.

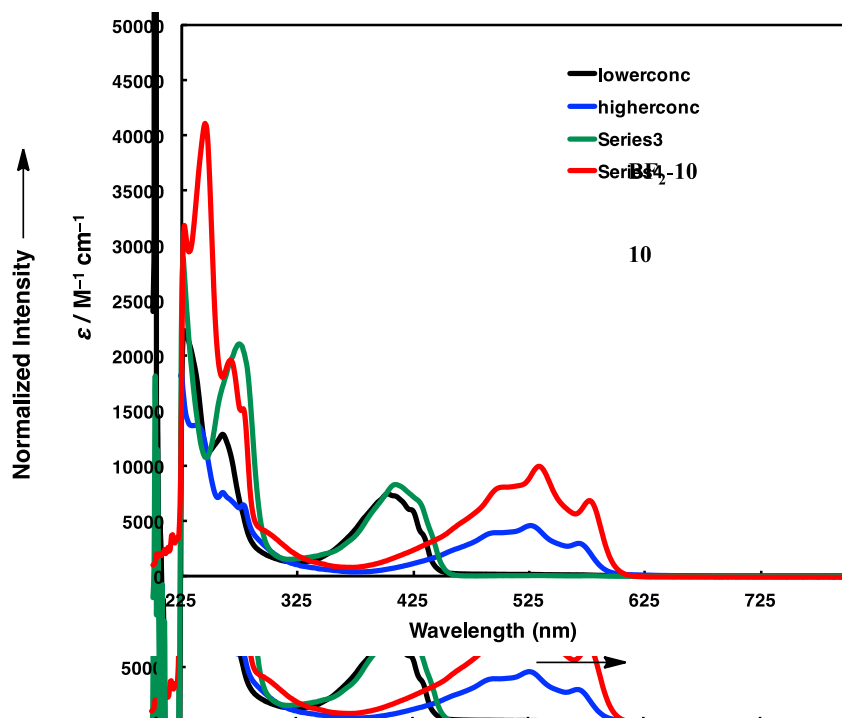


Figure S6. Normalized UV/Vis spectra of compound **10** (blue line) and **BF₂-10** (red line) in CH₂Cl₂ at 298 K.

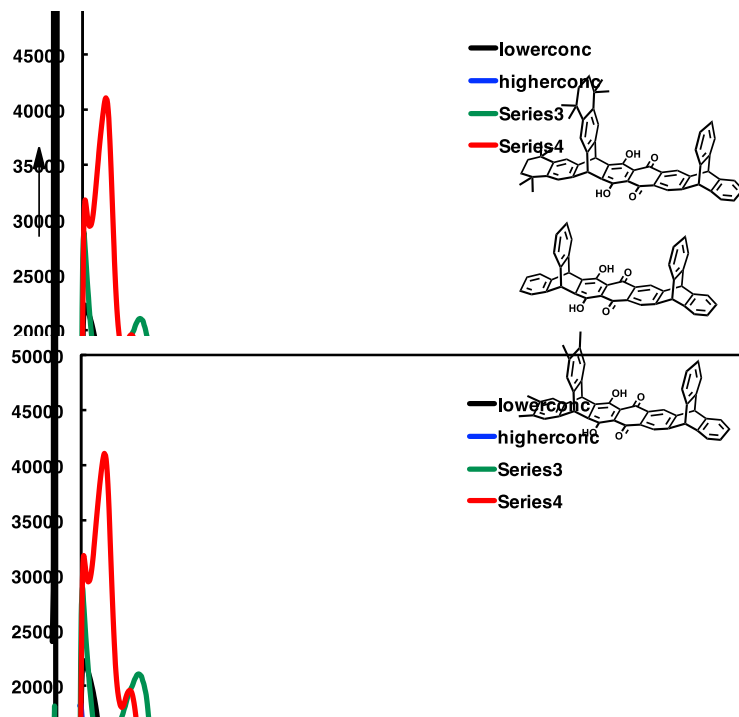


Figure S7. Normalized fluorescence spectra of selected compounds **5** (blue line), **6** (red line), and **7** (black line) in CH_2Cl_2 at 298 K ($\lambda_{\text{ex}} = 495 \text{ nm}$).

S4. ^1H and ^{13}C NMR spectra

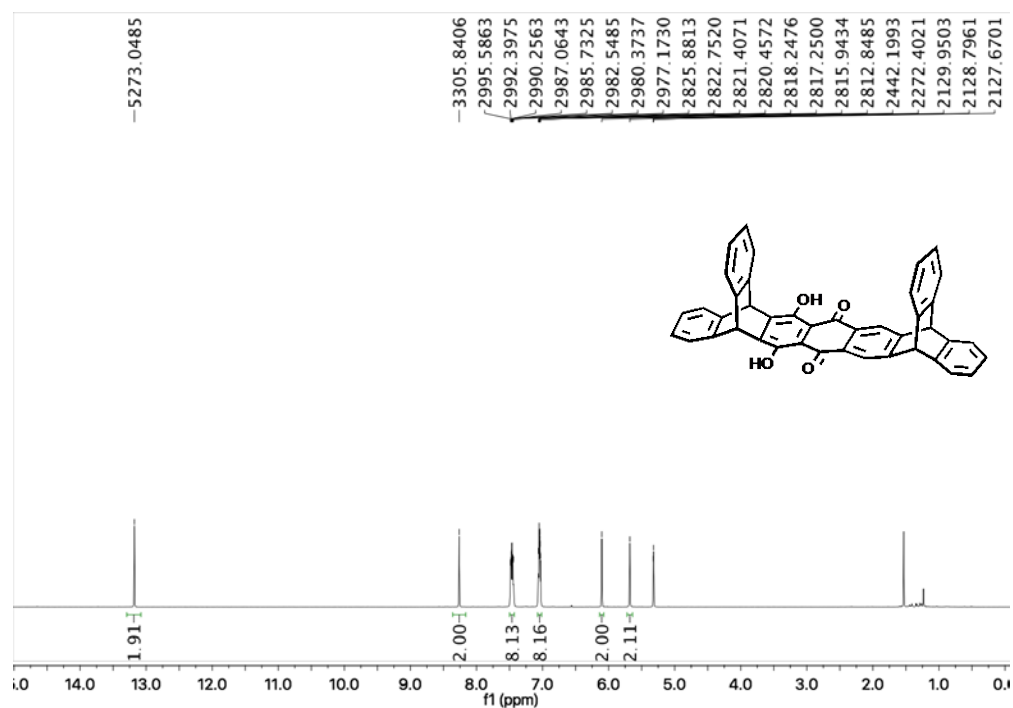


Figure S8. ^1H NMR spectrum of **5** in CD_2Cl_2 solution (400 MHz).

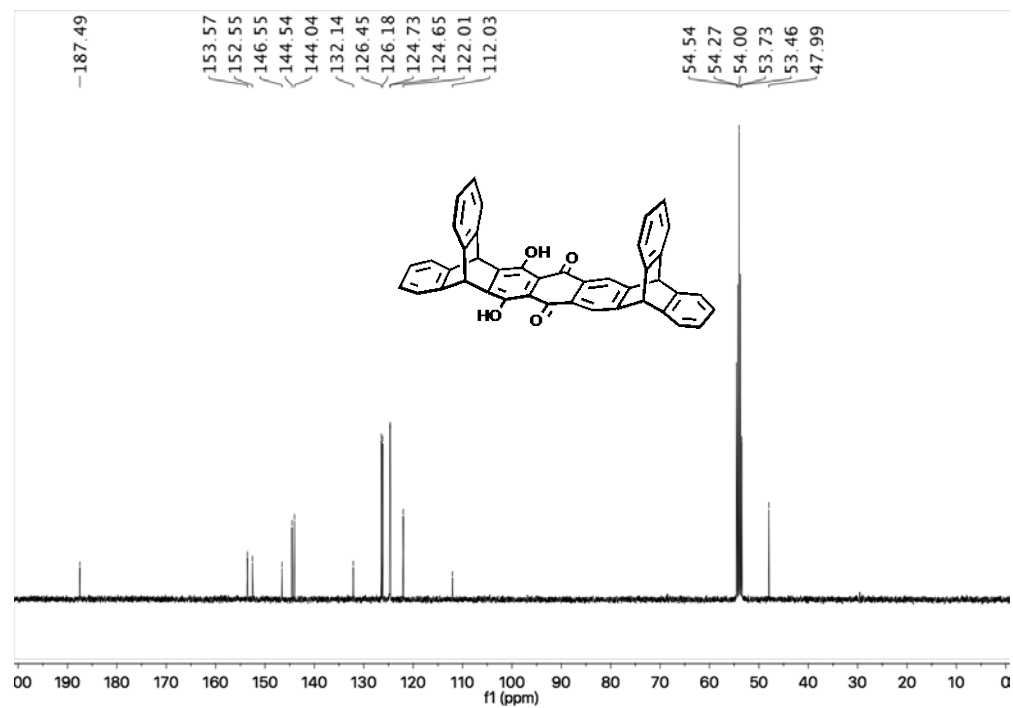


Figure S9. ^{13}C NMR spectrum of **5** in CD_2Cl_2 solution (100 MHz).

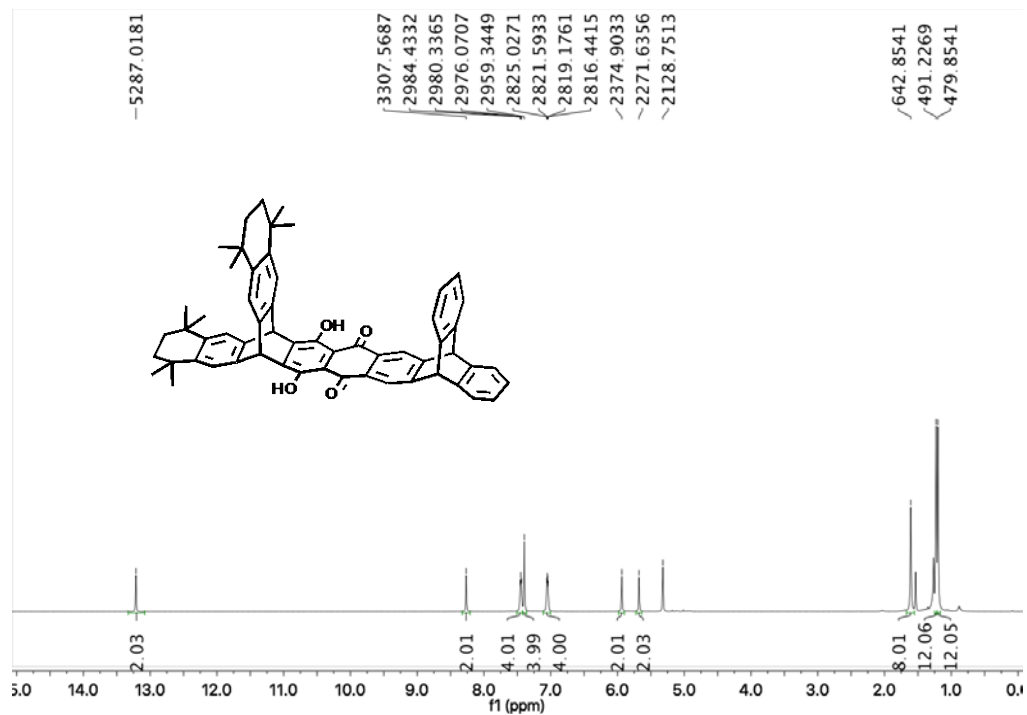


Figure S10. ^1H NMR spectrum of **6** in CD_2Cl_2 solution (400 MHz).

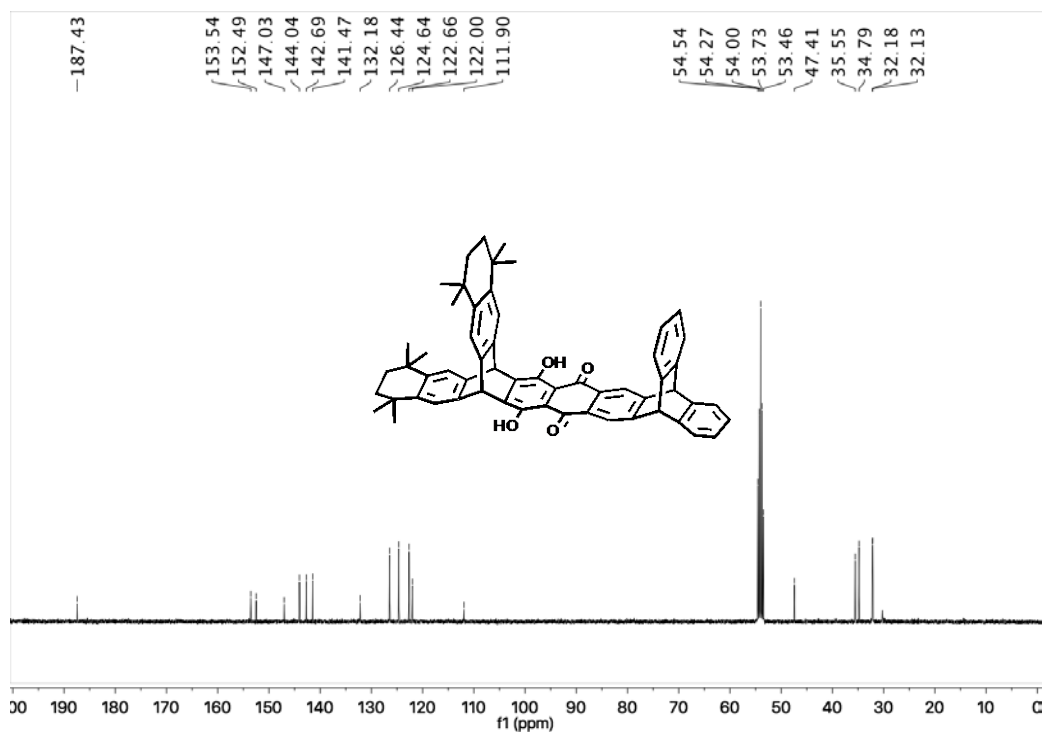


Figure S11. ^{13}C NMR spectrum of **6** in CD_2Cl_2 solution (100 MHz).

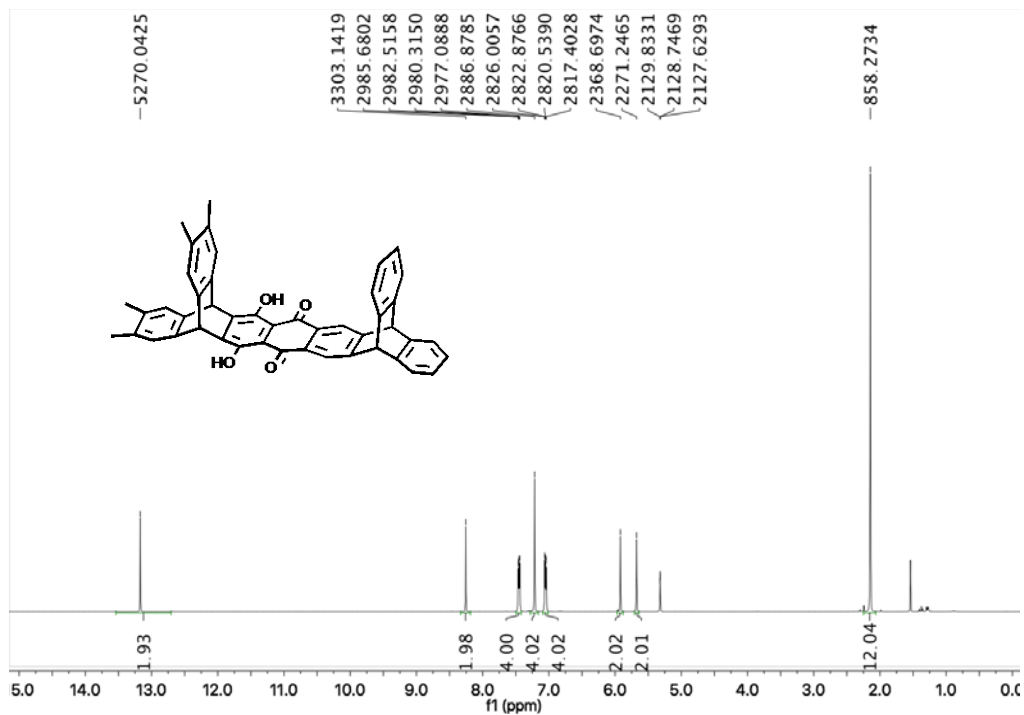


Figure S12. ¹H NMR spectrum of **7** in CD₂Cl₂ solution (400 MHz).

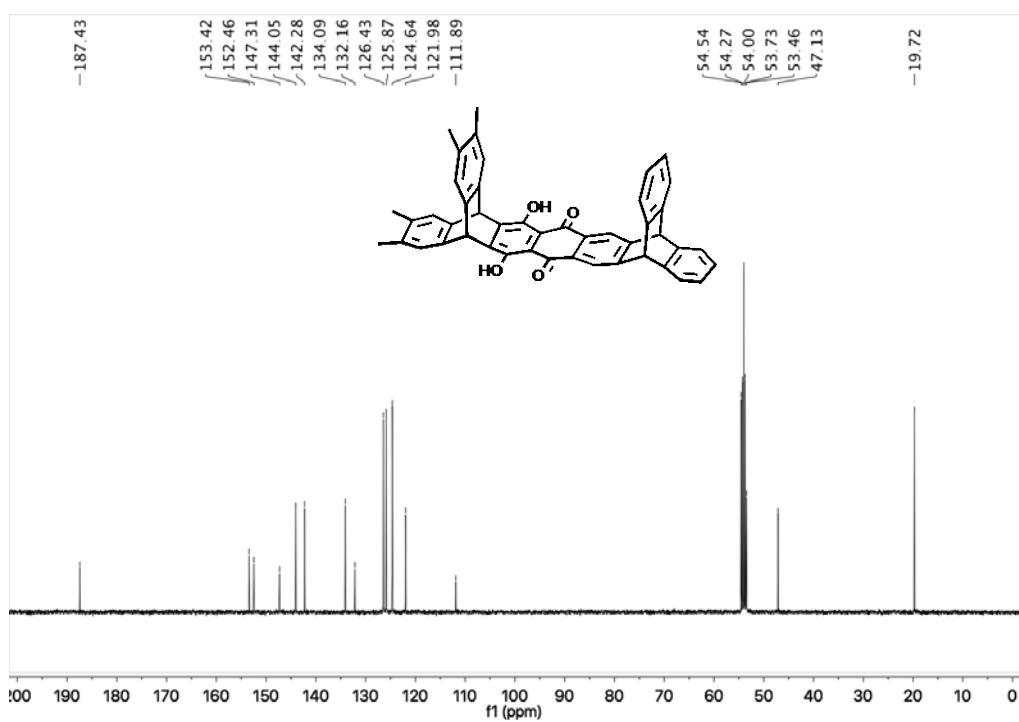


Figure S13. ¹³C NMR spectrum of **7** in CD₂Cl₂ solution (100 MHz).

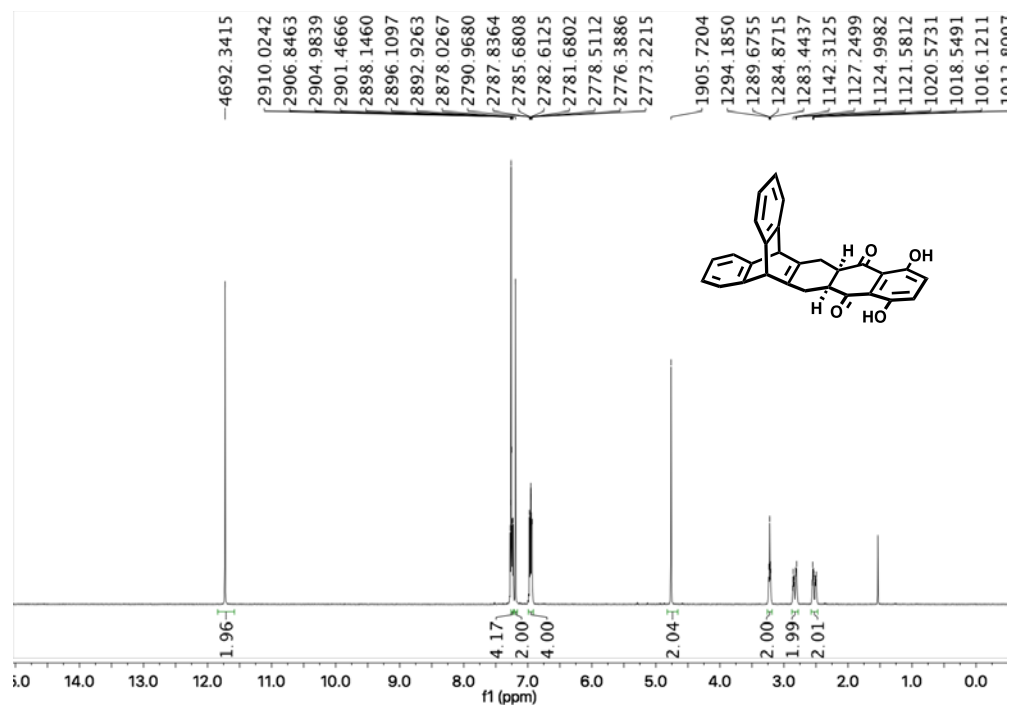


Figure S14. ^1H NMR spectrum of **9a** in CDCl_3 solution (400 MHz).

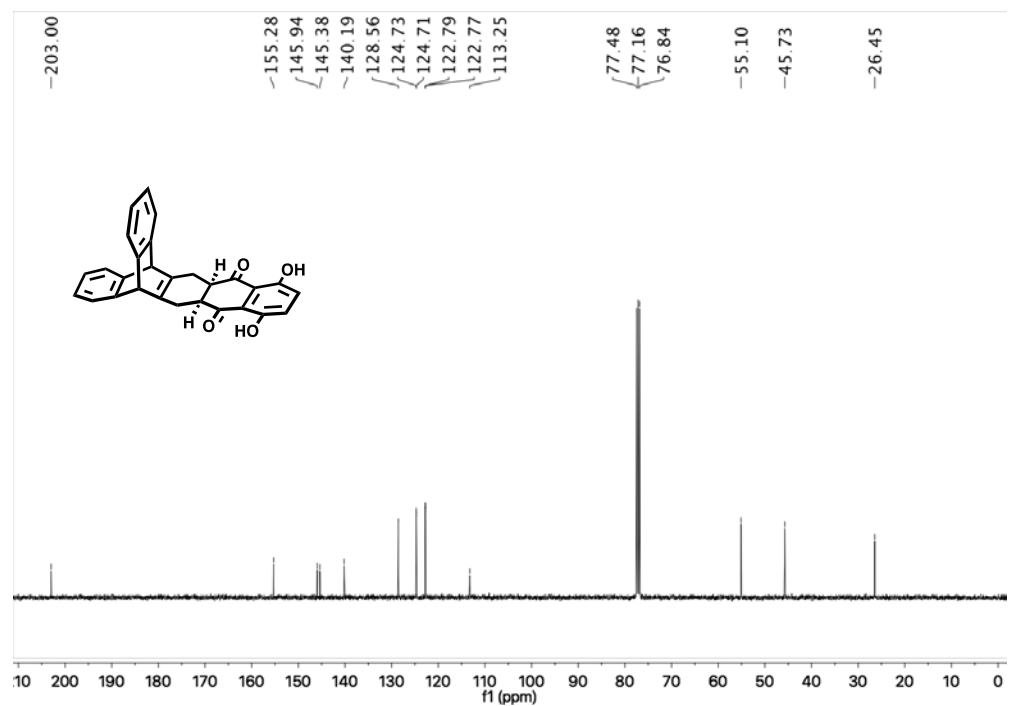


Figure S15. ^{13}C NMR spectrum of **9a** in CDCl_3 solution (100 MHz).

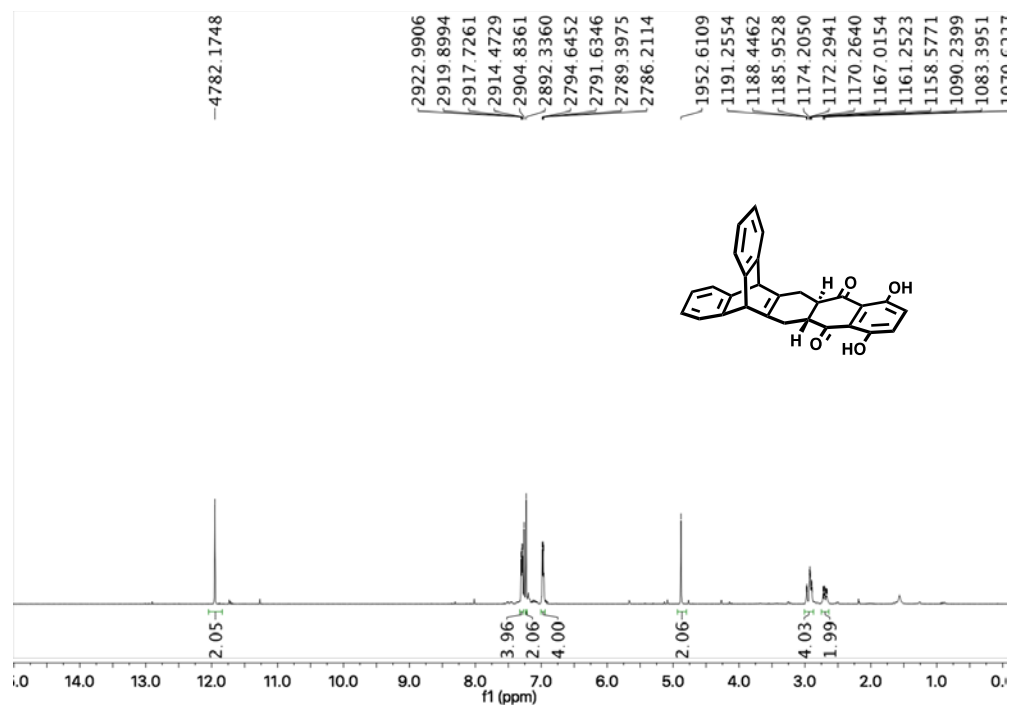


Figure S16. ^1H NMR spectrum of **9b** in CDCl_3 solution (400 MHz).

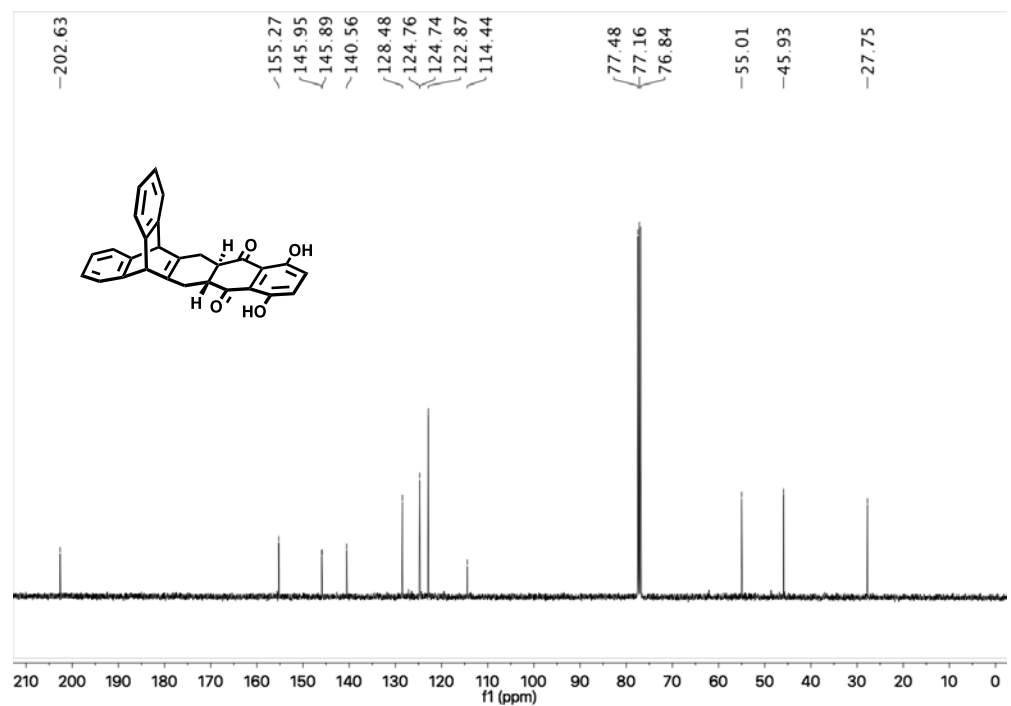


Figure S17. ^{13}C NMR spectrum of **9b** in CDCl_3 solution (100 MHz).

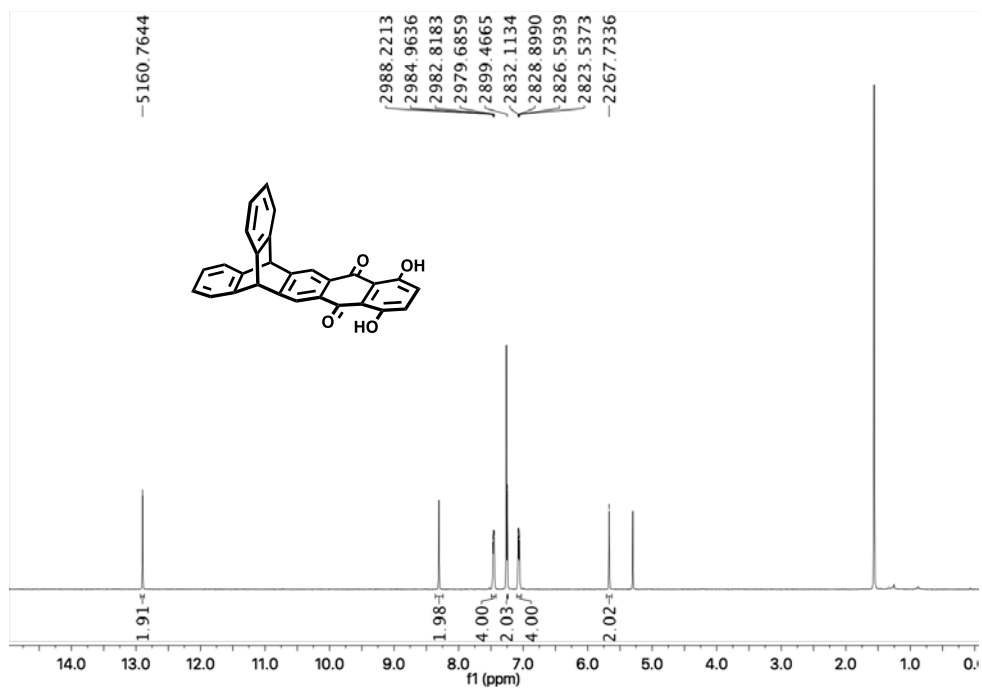


Figure S18. ^1H NMR spectrum of **10** in CDCl_3 solution (400 MHz).

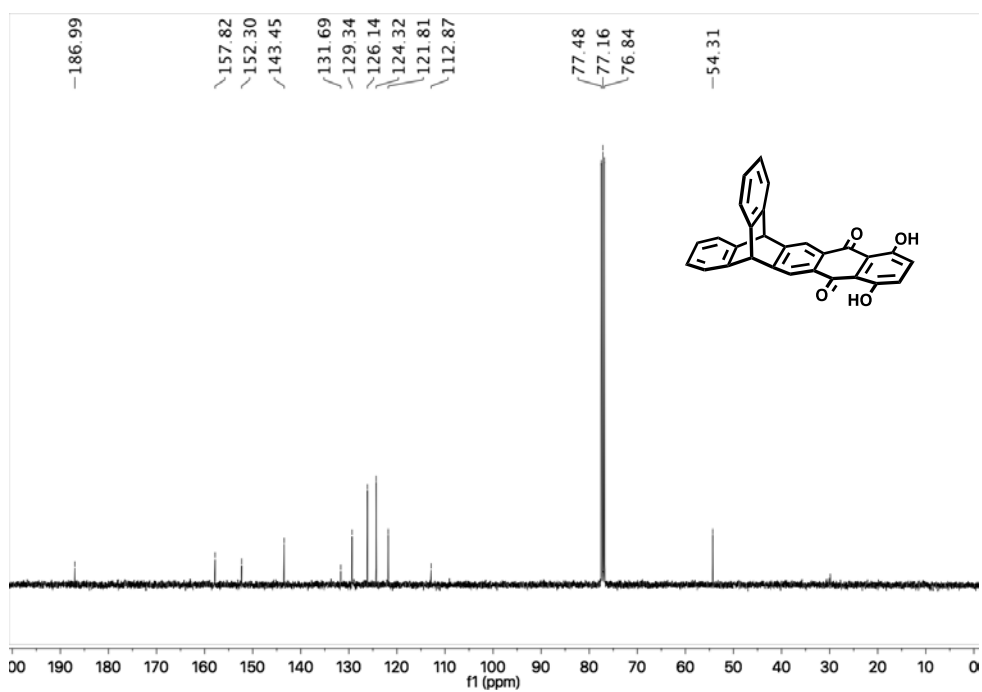


Figure S19. ^{13}C NMR spectrum of **10** in CDCl_3 solution (100 MHz).

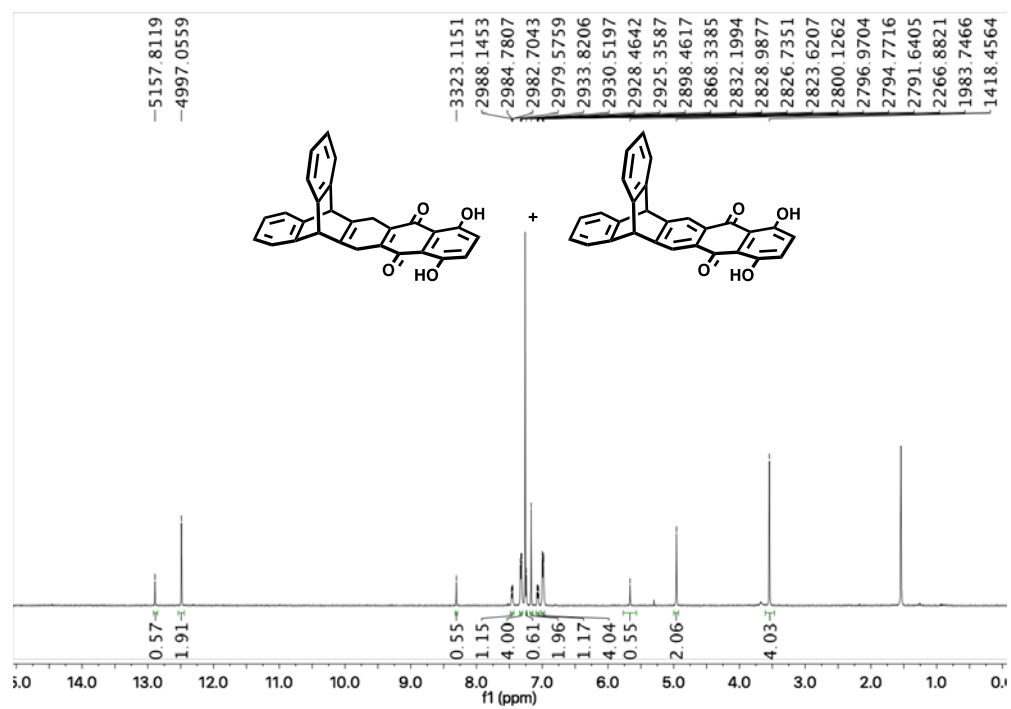


Figure S20. ^1H NMR spectrum of **11/10** in CDCl_3 solution (400 MHz).

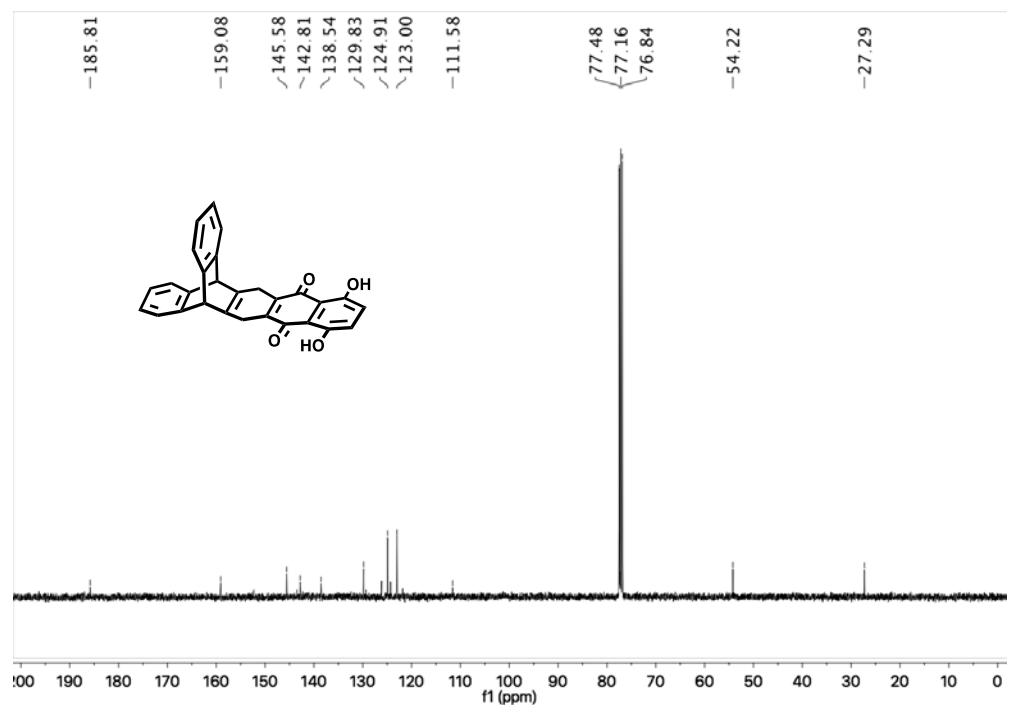


Figure S21. ^{13}C NMR spectrum of **11/10** in CDCl_3 solution (100 MHz).

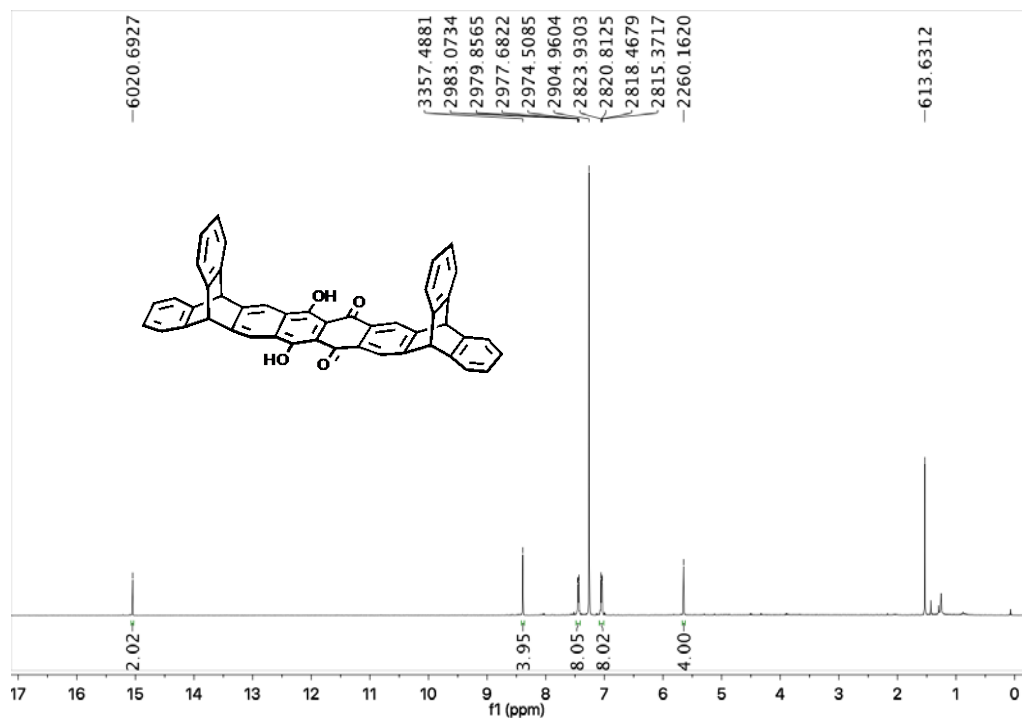


Figure S22. ^1H NMR spectrum of **12** in CDCl_3 solution (400 MHz).

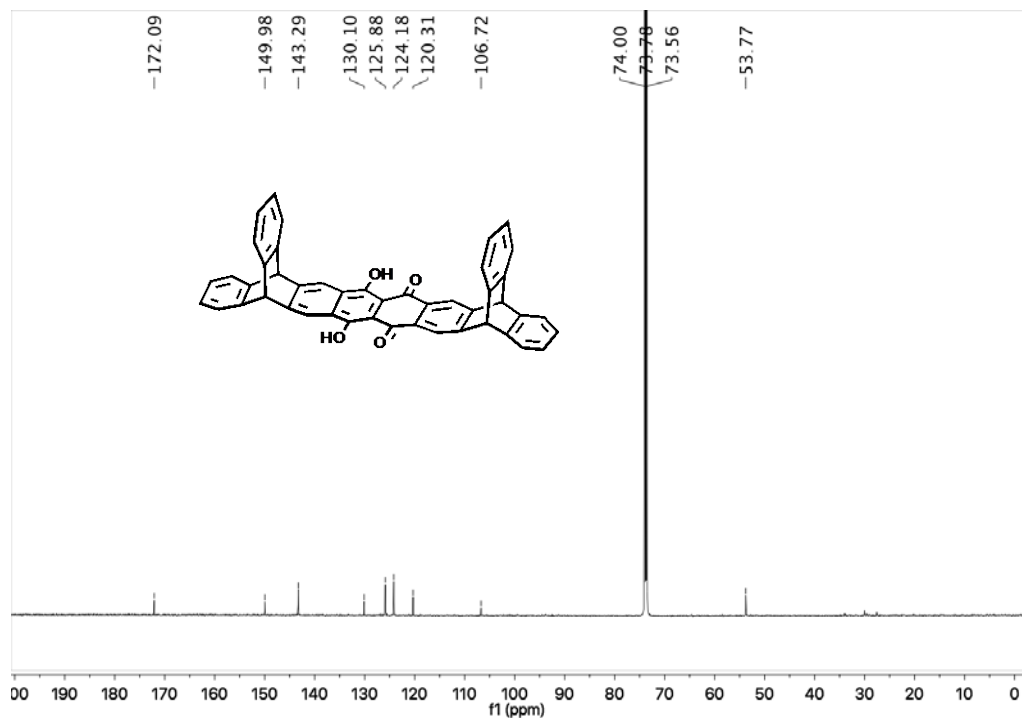


Figure S23. ^{13}C NMR spectrum of **12** in CDCl_3 solution (125 MHz).