Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of a figure-eight azahelicene dimer with high emission and CPL properties

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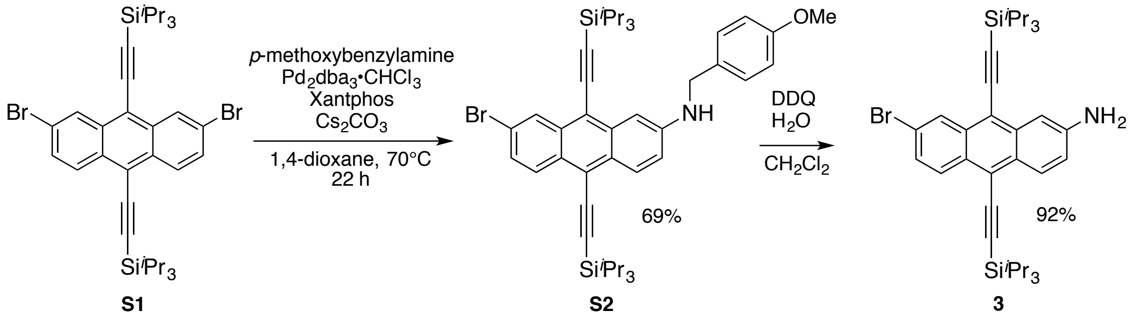
Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260 ppm), acetone-d_5 (δ = 2.050 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm), acetone-d_6 (δ = 29.84 ppm) for ^{13}C NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. High-resolution mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF method for acetonitrile solutions. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Experimental Details

Synthesis of S2.



A two-necked flask containing 2,7-dibromo-9,10-bis(triisopropylsilylethynyl)-anthracene (**S1**) (326.4 mg, 0.47 mmol), Pd_2dba_3•$CHCl_3$ (9.71 mg, 9.38 μmol), XantPhos (10.97 mg, 19.0 μmol), and Cs_2CO_3 (204.1 mg, 0.63 mmol) was evacuated and then refilled with N_2. To the flask, 4.7 mL of dry 1,4-dioxane and 4-methoxybenzylamine (73 μL, 0.59 mmol) were added. The mixture was stirred at

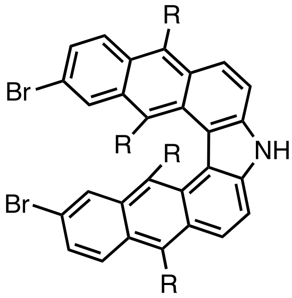
70°C for 22 h. The resulting mixture was filtered over a pad of Celite ($CHCl_3$ as an eluent) and the solvent was evaporated in vacuo. The mixture was purified by silica-gel column chromatography ($CHCl_3$/hexane as an eluent) to afford **S2** (242 mg, 0.32 mmol) in 69% yield as orange solid. ^{1}H NMR ($CDCl_3$): δ = 8.73 (t.1H), 8.46–8.47 (dd, J_1 = 8.5 Hz, J_2 = 0.5 Hz, 1H), 8.40–8.42 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.50–7.52 (dd, J_1 = 8.5 Hz, J_2 = 1,5 Hz, 1H), 7.35–7.37 (d, J = 8.5 Hz, 2H), 7.03–7.05 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 1H), 6.91–6.93 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 1.24–1.28 (m, 42H, TIPS) ppm; ^{13}C NMR ($CDCl_3$) δ = 159.11, 146.56, 135.22, 133.99, 130.31, 129.06, 129.02, 128.71, 128.56, 128.35, 128.12, 121.54, 121.47, 121.54, 121.47, 118.89, 114.14, 113.58, 104.18, 104.02, 103.79, 103.03, 100.81, 55.30, 47.53, 18.90, 18.86, 11.47, 11.45 ppm; HR-MS(ESI-MS): m/z = 752.3282, calcd for $(C_{44}H_{58}BrNOSi_2)^+$ = 752.3313 $[(M + H)^+]$.

Synthesis of 3.

DDQ (65.4 mg, 0.288 mmol) was added to a mixture of **S2** (216 mg, 0.287 mmol) in CH_2Cl_2 (45.6 mL) and H_2O (0.37 mL). The mixture was stirred at room temperature for 1 h. The reaction was quenched with aqueous $Na_2S_2O_3$, and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous with Na_2SO_4, and concentrated in vacuo. The residue was purified by silica-gel column chromatography ($CHCl_3$/hexane as an eluent) to afford **3** in 92% yield. ^{1}H NMR ($CDCl_3$): δ = 8.73 (d, J = 1.5 Hz, 1H), 8.43–8.45 (d, J = 9.0 Hz, 1H), 8.39–8.41 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 2.0 Hz, 1H), 7.52–7.54 (dd, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 1H), 7.10–

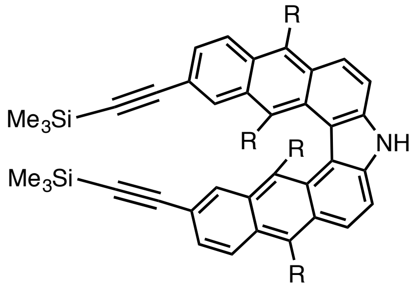
7.13 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 4.11 (s, 2H), 1.24–1.28 (m, 42H, TIPS) ppm; ^{13}C NMR ($CDCl_3$) δ = 145.33, 134.69, 133.91, 129.05, 129.00, 128.81, 128.66, 128.09, 121.62, 121.09, 113.84, 105.54, 104.49, 104.29, 103.49, 102.94 18.90, 18.86, 11.56, 11.47 ppm; HR-MS(ESI-MS): *m/z* = 632.2729, calcd for $(C_{36}H_{50}BrNSi_2)^+$ = 632.2738 $[(M + H)^+]$.

Synthesis of 4



A two-necked flask containing **3** (50.9 mg, 0.079 mmol) was evacuated and then refilled with N_2. To the flask, 26 mL of dry $CHCl_3$ was added. To the resulting solution, a solution of DDQ (55.8 mg, 0.25 mmol) in dry $CHCl_3$ (8 mL) was added and the mixture was stirred at room temperature for 3 h. The reaction was quenched with aqueous $Na_2S_2O_3$ and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The mixture was purified by silica-gel column chromatography ($CHCl_3$/hexane as an eluent) to afford **4** (30.3 mg, 0.024 mmol) in 60% yield. ^{1}H NMR ($CDCl_3$): δ = 9.18 (s, 1H NH), 8.91 (d, J = 1.8 Hz, 2H), 8.62–8.65 (d, J = 9.0 Hz, 2H), 8.52–8.55 (d, J = 9.0 Hz, 2H), 7.74–7.77 (d, J = 9.0 Hz, 2H), 7.61–7.68 (dd, J_1 =5.6 Hz, J_2 =2.1 Hz), 1.26–1.31 (m, 42H, TIPS), 0.62–0.63 (d, J = 7.5 Hz, 18H, TIPS), 0.52–0.55 (d, J = 7.5 Hz, 18H, TIPS), 0.11–0.23 (m, 6H, TIPS) ppm; ^{13}C NMR (CDCl$_3$) δ = 135.48, 133.36, 130.79, 130.52, 129.95, 129.54, 129.36, 128.58, 125.97, 121.33, 118.43, 117.95, 117.57, 114.59, 109.30, 106.35, 103.92, 103.80, 18.93, 18.46, 18.28, 11.64, 11.59 ppm; HR-MS(ESI-MS): m/z = 1244.4952, calcd for $(C_{72}H_{95}Br_2NSi_4)^+$ = 1244.4981 [(M + H)$^+$].

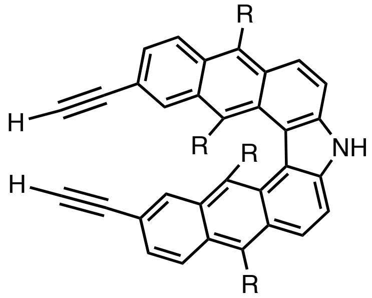
Synthesis of 5



A Schlenk flask containing **4** (53.7 mg, 43.1 μmol), Pd(PhCN)$_2$Cl$_2$ (3.31 mg, 8.63 μmol), (^{t}Bu$_3$PH)BF$_4$ (5.04 mg, 17.3 μmol), and CuI (1.63 mg, 8.56 μmol) was evacuated and then refilled with N$_2$. To the flask, trimethylsilylacetylene (0.12 mL, 0.86 mmol), 2 mL of dry 1,4-dioxane, and 3 mL of distilled diisopropylamine were added. The mixture was stirred at 100 ºC for 24 h. The reaction was quenched with water and the mixture was extracted with EtOAc. The organic layer was washed with water and dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (CHCl$_3$/hexane as an eluent) to afford **5** (30.3 mg, 0.024 mmol) in 91% yield. ^{1}H NMR (CDCl$_3$): δ 9.10 (s, 1H, NH), 8.89 (d, J = 0.9 Hz, 2H), 8.61–8.64 (d, J = 9.0 Hz, 2H), 8.56–8.59 (d, J = 9.0 Hz, 2H), 7.71–7.74 (d, J = 9.0 Hz, 2H), 7.58–7.61 (dd, J_1 = 9 Hz, J_2 =1.5 Hz, 2H), 1.26–1.33 (m, 42H, TIPS), 0.59–

0.61 (d, J = 7.5 Hz, 18H, TIPS), 0.53–0.55 (d, J = 7.5 Hz, 18, TIPS), 0.26 (s, 18H), 0.17–0.22 (m, 6H, TIPS) ppm; ^{13}C NMR (CDCl$_3$) δ = 136.15, 133.15, 132.29, 131.32, 131.22, 131.06, 128.46, 127.57, 126.49, 121,67, 119.39, 118.27, 117.94, 115.39, 109.95, 106.97, 106.23, 104.49, 104.37, 95.64, 19.30, 18.85, 18.67, 12.45, 12.23, 12.15, 11.92, 0.214 ppm; HR-MS(ESI-MS): m/z = 1280.7512, calcd for $(C_{82}H_{113}NSi_6)^+$ = 1280.7561 $[(M + H)^+]$.

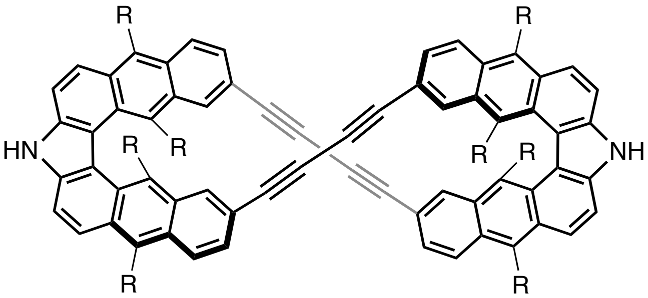
Synthesis of 6.



A two-neck flask containing **5** (52.7 mg, 41.0 μmol) and K_2CO_3 (85.0 mg, 0.62 mmol) were evacuated and then refilled with N_2. To the flask, 4.6 mL of THF and 4.6 mL of MeOH were added. The mixture was stirred at 60 ºC for 13 h. The reaction was quenched with aqueous H_2O and the mixture was extracted with EtOAc. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The mixture was purified by silica-gel column chromatography (CHCl$_3$/hexane as an eluent) to afford **6** (41.0 mg, 36.1 μmol) in 88% yield. ^{1}H NMR (CDCl$_3$): d 9.14 (s, 1H, NH), 8.91 (d, J = 1.0 Hz, 2H), 8.64–8.65 (d, J = 9.0 Hz, 2H), 8.60–8.61 (d, J = 9.0 Hz, 2H), 7.75–7.77 (d, J = 9.0 Hz, 2H), 7.61–7.63 (dd, J_1 = 9 Hz, J_2 =1.5 Hz, 2H), 3.16 (s, 2H), 1.29–1.33 (m, 42H, TIPS), 0.56–0.58 (d, J = 7.5 Hz, 18H, TIPS), 0.51–0.53 (d, J =

7.5 Hz, 18, TIPS), 0.15–0.21 (m, 6H, TIPS) ppm; ^{13}C NMR ($CDCl_3$) δ = 135.35, 132.69, 130.83, 130.70, 130.58, 128.27, 126.95, 125.84, 119.97, 119.12, 117.59, 114.69, 109.52, 106.27, 103.99, 103.49, 84.39, 77.67, 18.93, 18.41, 18.22, 11.57 ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 282.5 (110000), 289.5 (110000), 316 (67000), 357.5 (37000), 395 (23000), 487 (29000), 519.5 (45000); FL (CH_2Cl_2) λ_{em} [nm] = 578 (λ_{ex} = 400nm); HR-MS(ESI-MS): *m/z* = 1136.6724, calcd for $(C_{76}H_{97}NSi_4)^+$ = 1136.6771 [(M + H)$^+$].

Synthesis of 2.



A test tube containing $Cu(OAc)_2$ (53.2 mg, 0.29 mmol) was dropped a solution of **6** (16.7 mg, 14.7 μmol) in the pyridine (1.77 mL). The mixture was stirred at room temperature for 40 h. The mixture was filtered over a pad of silica-gel column (CH_2Cl_2 as an eluent) and the solvent was evaporated in vacuo. The mixture was purified by silica-gel column chromatography ($CHCl_3$/hexane as an eluent) to afford **2** (10.8 mg, 4.76 μmol) in 64% yield. ^{1}H NMR ($CDCl_3$): δ = 9.21 (s, 2H, NH), 9.01 (d, *J* = 1.0 Hz, 4H), 8.65–8.67 (d, *J* = 9.0 Hz, 4H), 8.61–8.62 (d, *J* = 9.0 Hz, 4H), 7.77–7.79 (d, *J* = 9.0 Hz, 4H), 7.64–7.66 (dd, J_1 = 8.5 Hz, J_2 =1.5 Hz, 4H), 1.30–1.33 (m, 84H, TIPS), 0.59–0.61 (d, *J* = 7.5 Hz, 36H, TIPS), 0.53–0.55 (d, *J* = 7.5 Hz, 36, TIPS), 0.19–0.23 (m, 12H, TIPS) ppm; ^{13}C NMR (CDCl$_3$) δ = 135.60, 134.32, 132.00, 131.22, 130.81, 130.74, 128.20, 127.13, 126.08, 120.11, 119.65, 117.89, 117.73, 114.98, 110.71, 106.53, 104.17, 103.65, 82.83, 75.30, 19.08, 18.55, 18.41, 11.74, 11.70 ppm; UV/vis (CH$_2$Cl$_2$): λ_{max} (ε [M^{-1}cm^{-1}]) = 263 (99000), 300 (180000), 338 (180000), 406 (45000), 501 (44000), 535.5 (64000); FL (CH$_2$Cl$_2$) λ_{em} [nm] = 588 (λ_{ex} = 420nm) ; HR-MS(ESI-MS): *m*/*z* = 2268.3073, calcd for $(C_{152}H_{190}N_2Si_8)^+$ = 2268.3156 [(M + H)$^+$].

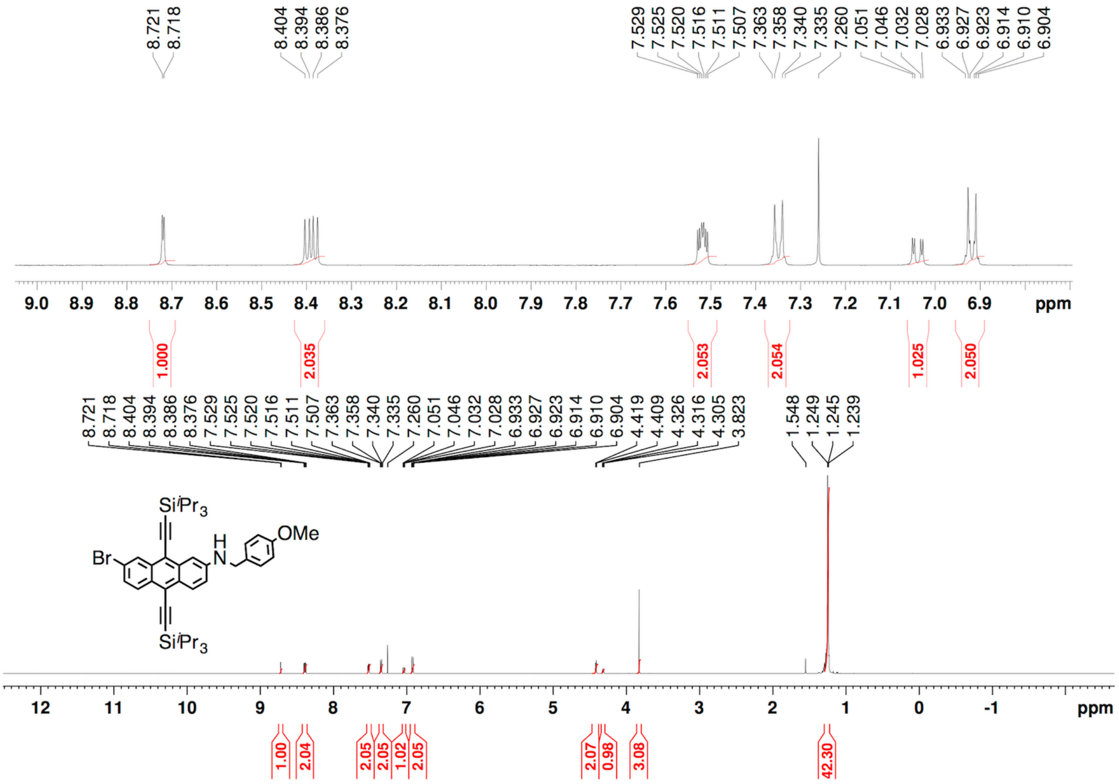


Figure S1. ^{1}H NMR spectrum of **S2** in CDCl$_3$.

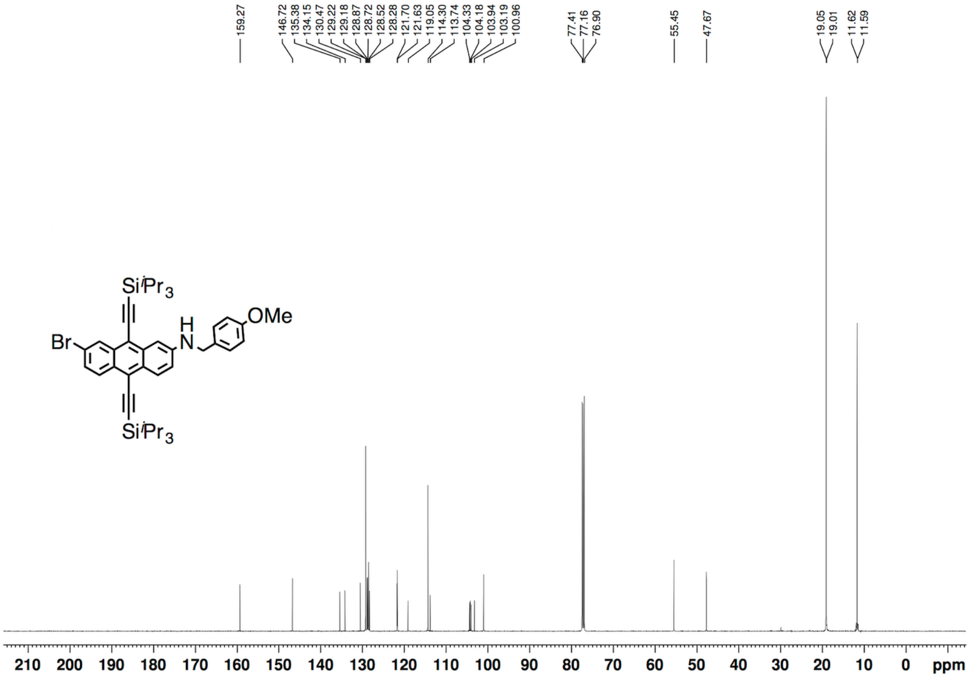


Figure S2. ^{13}C NMR spectrum of **S2** in CDCl$_3$.

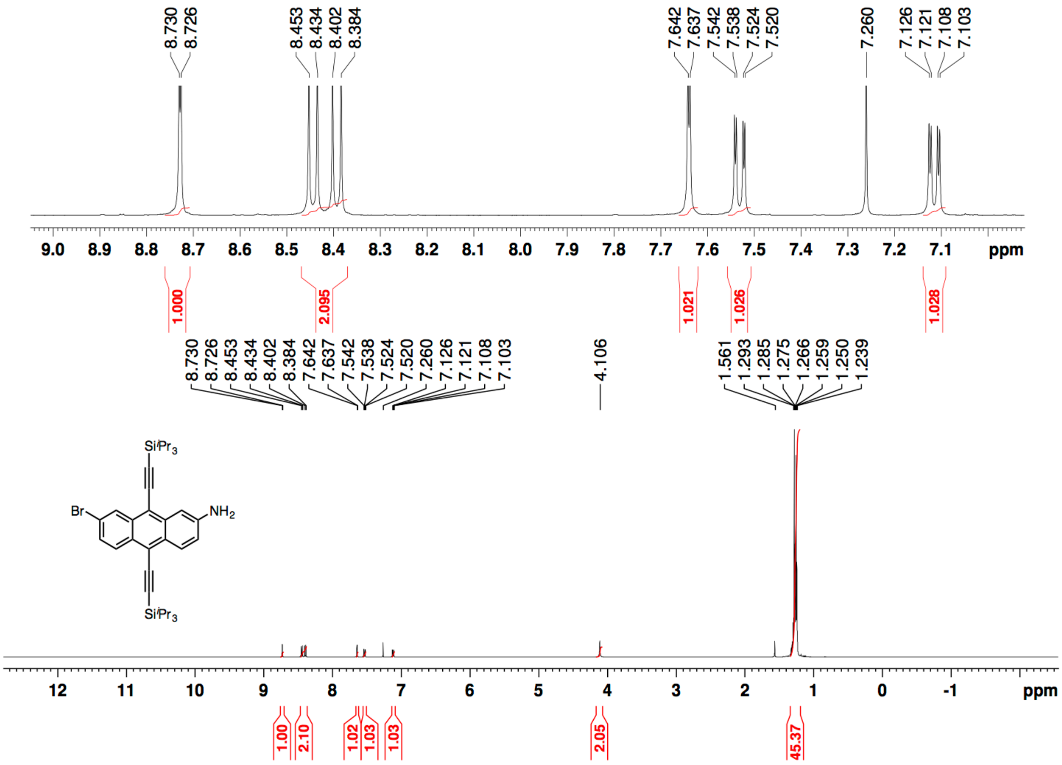


Figure S3. ^{1}H NMR spectrum of **3** in $CDCl_3$.

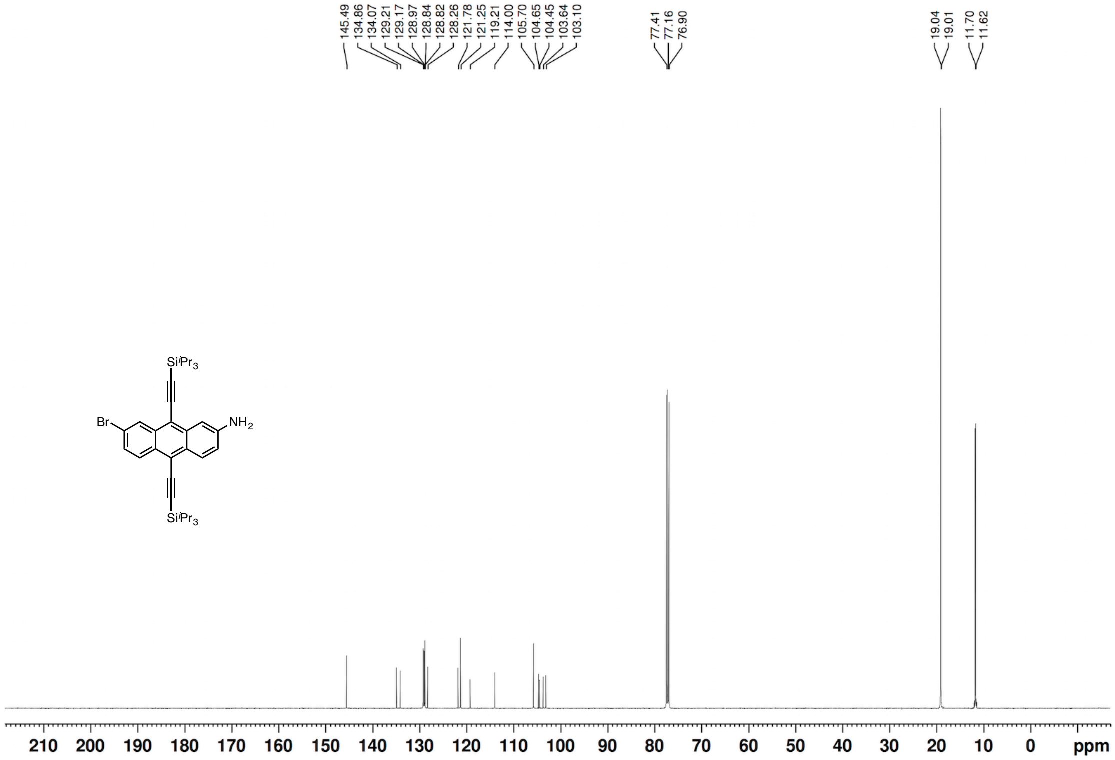


Figure S4. ^{13}C NMR spectrum of **3** in $CDCl_3$.

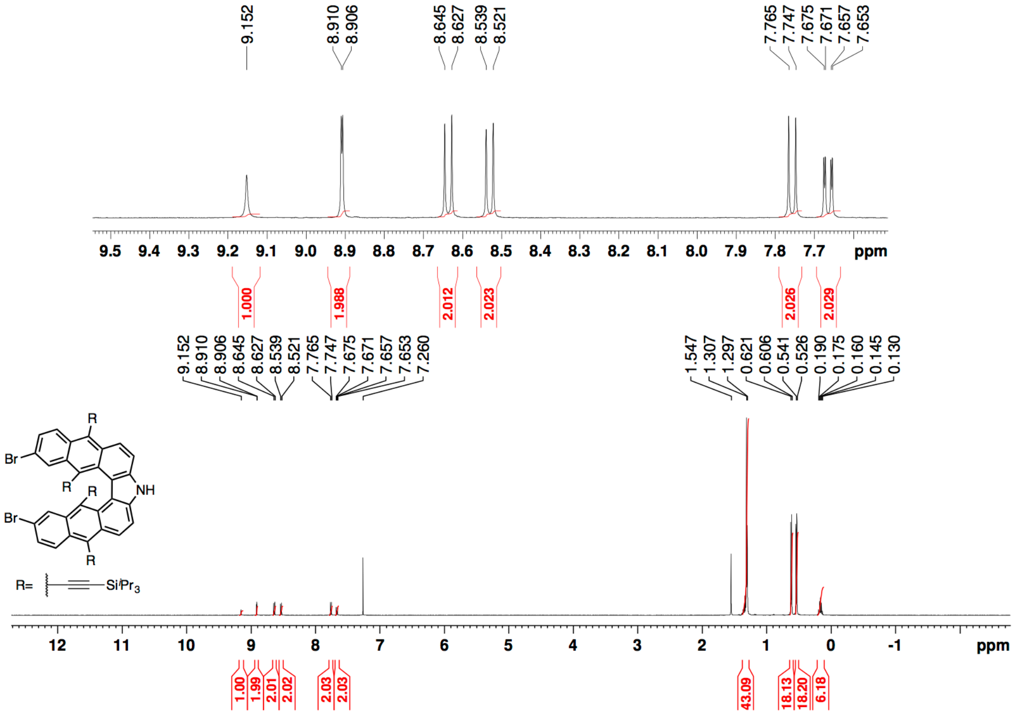


Figure S5. ^{1}H NMR spectrum of **4** in CDCl$_3$.

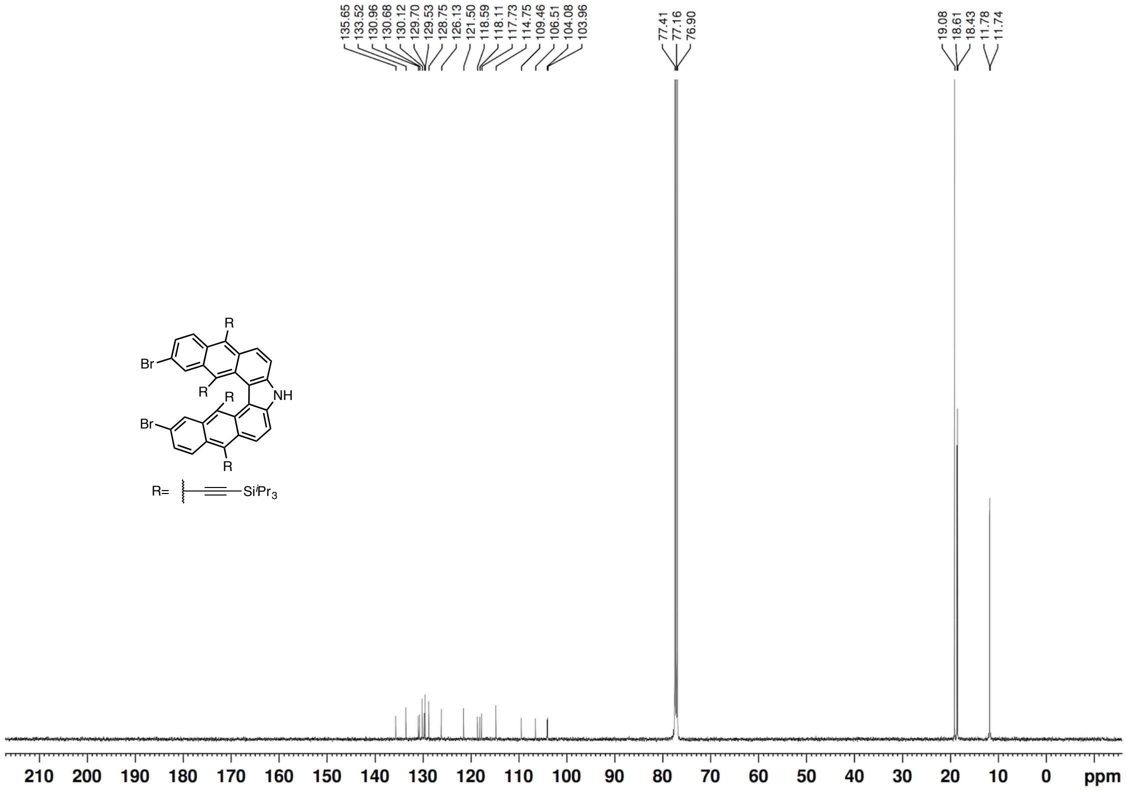


Figure S6. ^{13}C NMR spectrum of **4** in CDCl$_3$.

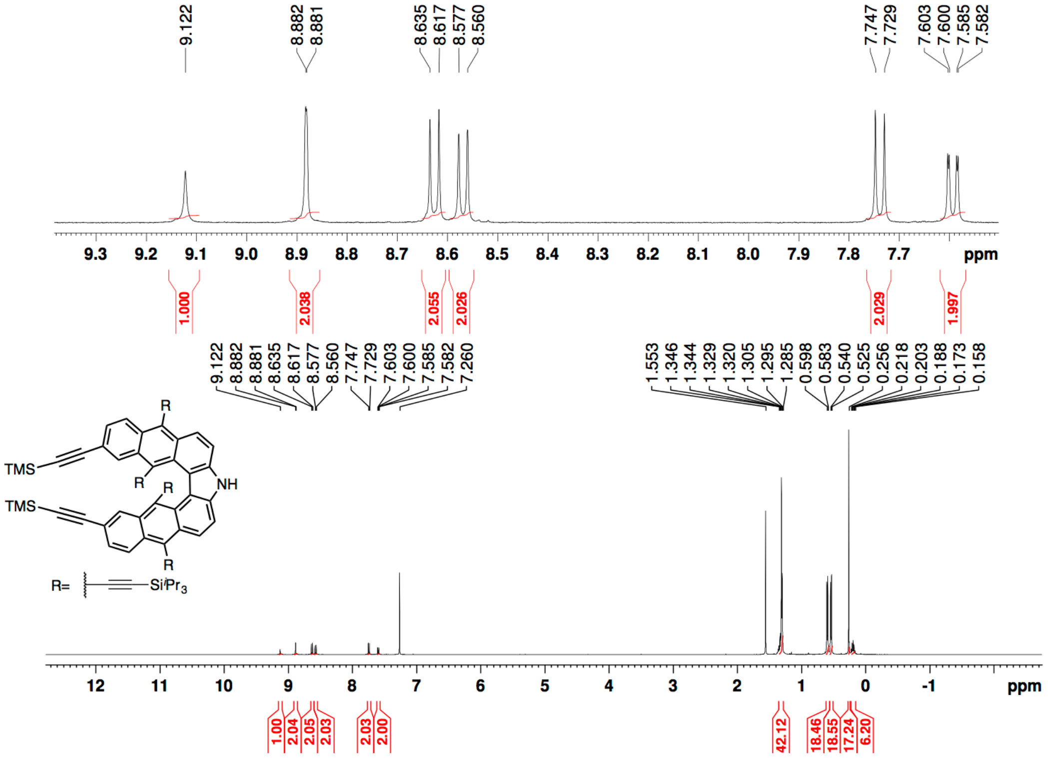


Figure S7. ^{1}H NMR spectrum of **5** in $CDCl_3$.

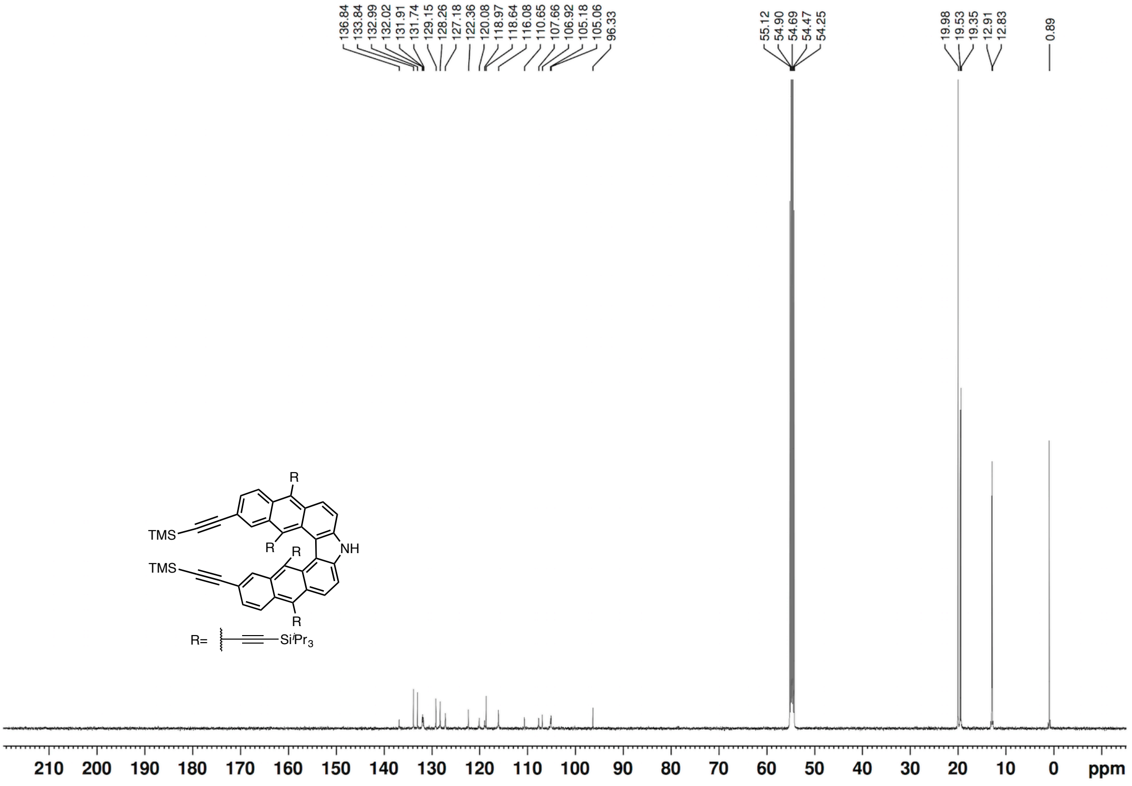


Figure S8. ^{13}C NMR spectrum of **5** in CD_2Cl_2.

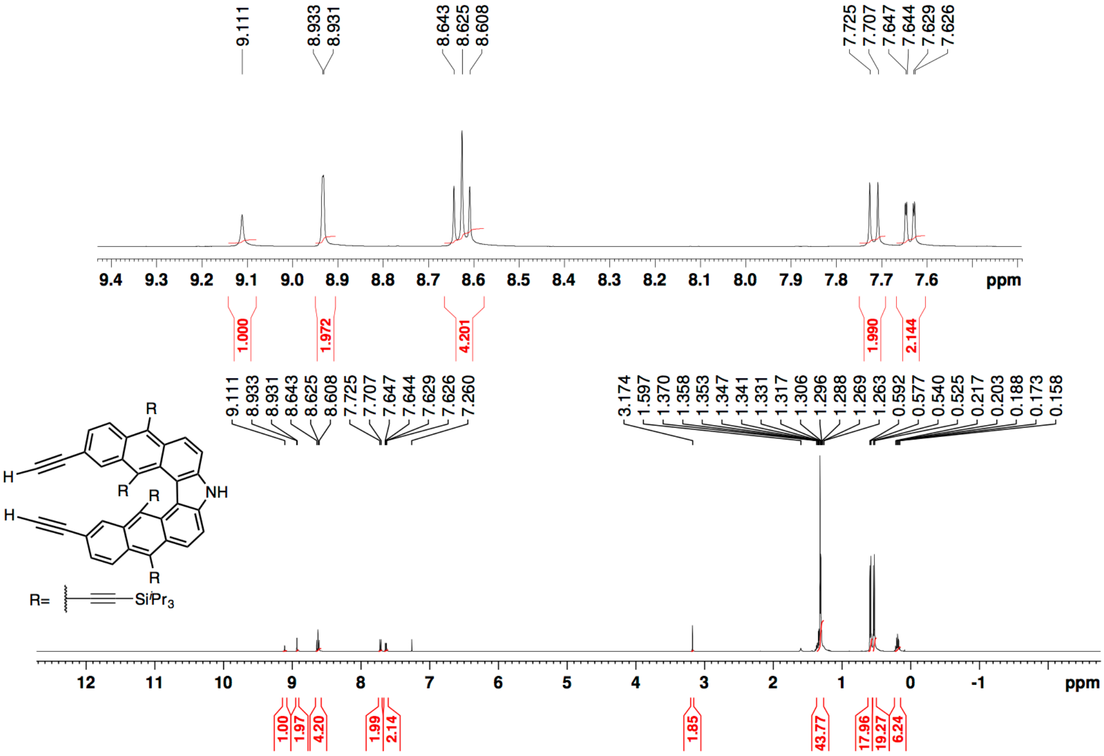


Figure S9. ^{1}H NMR spectrum of **6** in CDCl$_3$.

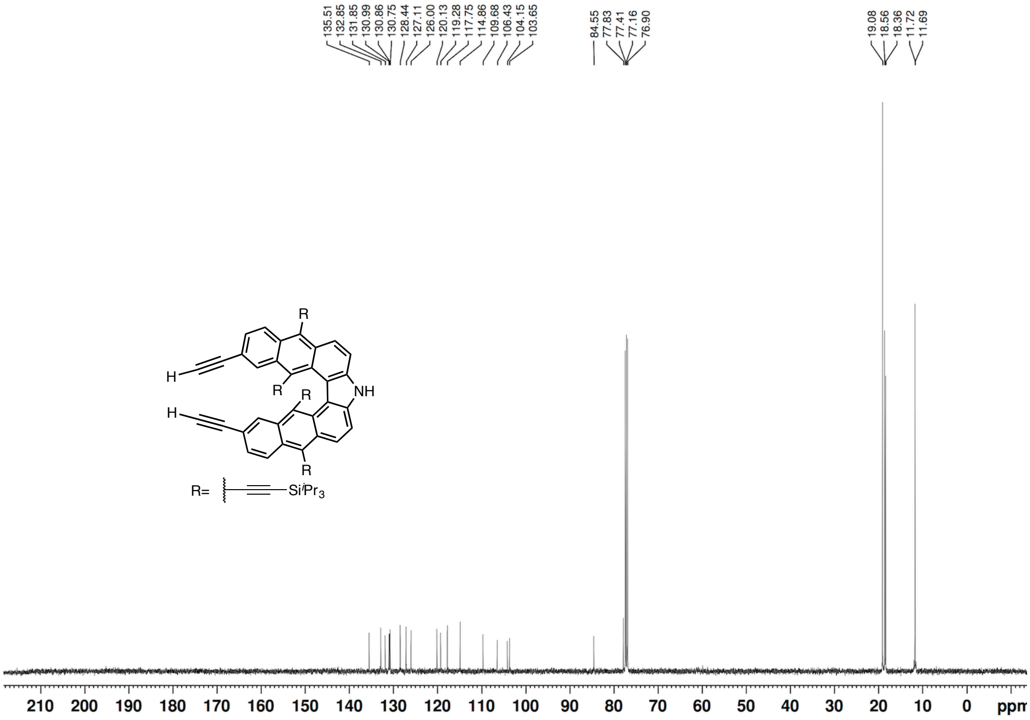


Figure S10. ^{13}C NMR spectrum of **6** in CDCl$_3$.

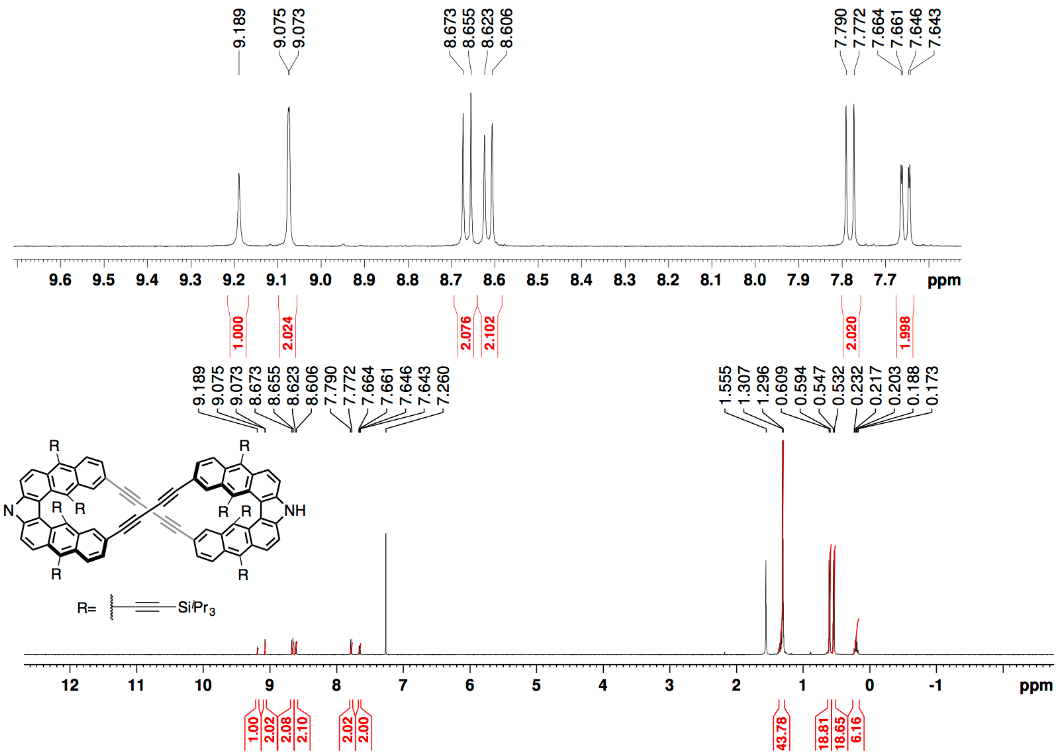


Figure S11. ^{1}H NMR spectrum of **2** in $CDCl_3$.

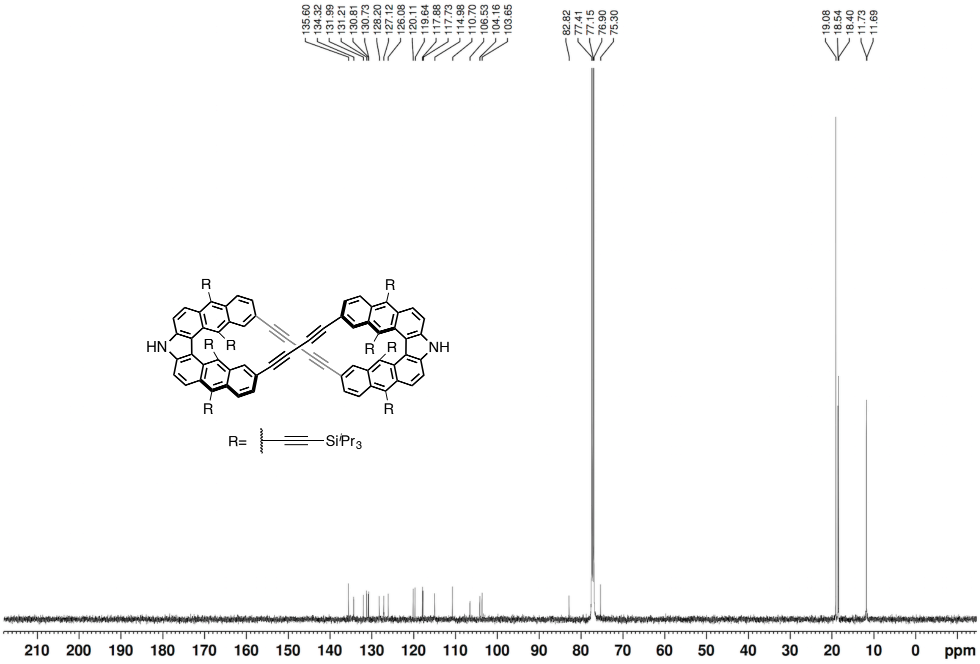


Figure S12. ^{13}C NMR spectrum of **2** in $CDCl_3$.

Optical resolution

Optical resolution of **6** was performed by chiral column chromatography equipped with CHIRALPAK IA®.

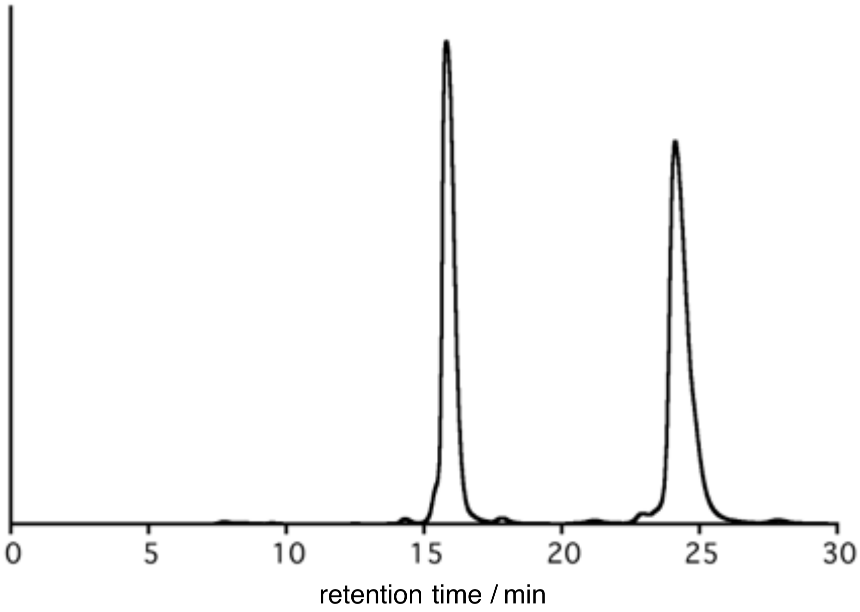


Fig. S13 Chromatograms of **(±)-6**.

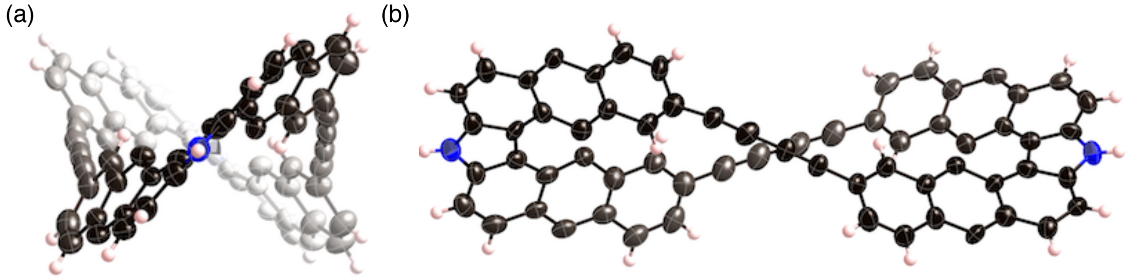


Fig. S14 Preliminary X-ray crystal structure of **2**. (a) Side view and (b) Front view. The thermal ellipsoids are scaled at 50% probability level. Triisopropylethynyl groups are omitted for clarity. $R_1 = 0.1475$, $wR = 0.4128$, GOF = 1.172.

Cyclic Voltammetry

Cyclic voltammograms of **2** and **6** were recorded on ALS electrochemical analyser 612C. Measurements were performed in freshly distilled THF with tetrabutylammonium hexafluorophosphate as electrolyte. A three electrode system was used and consisted of a platinum working electrode, a platinum wire and $Ag/AgClO_4$ as the reference electrode. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

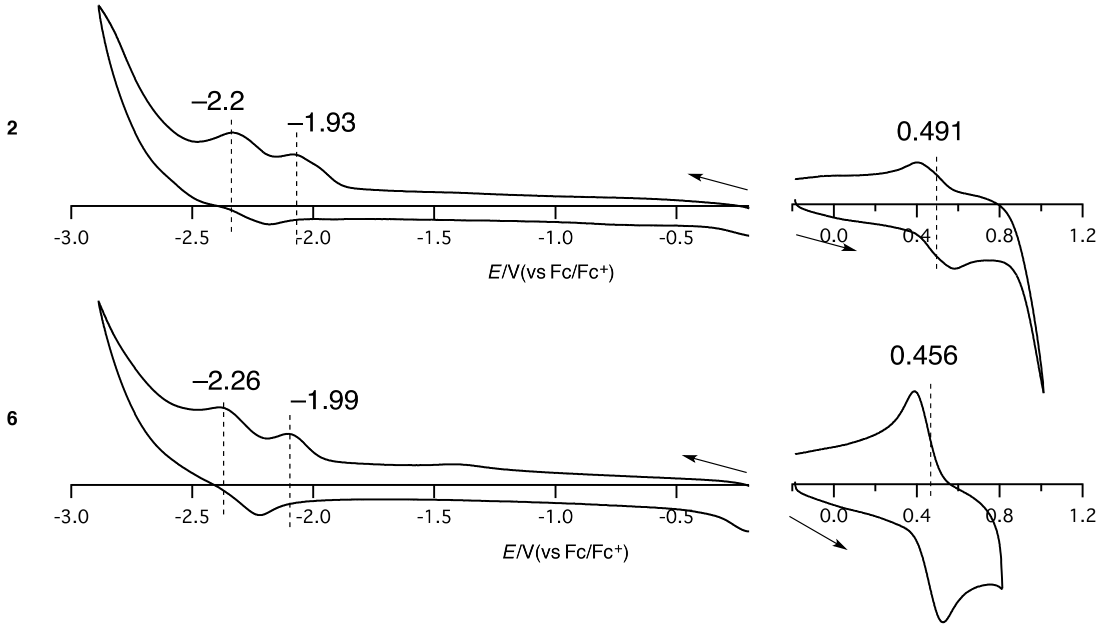


Fig. S15 Cyclic voltammograms of **2** and **6**.

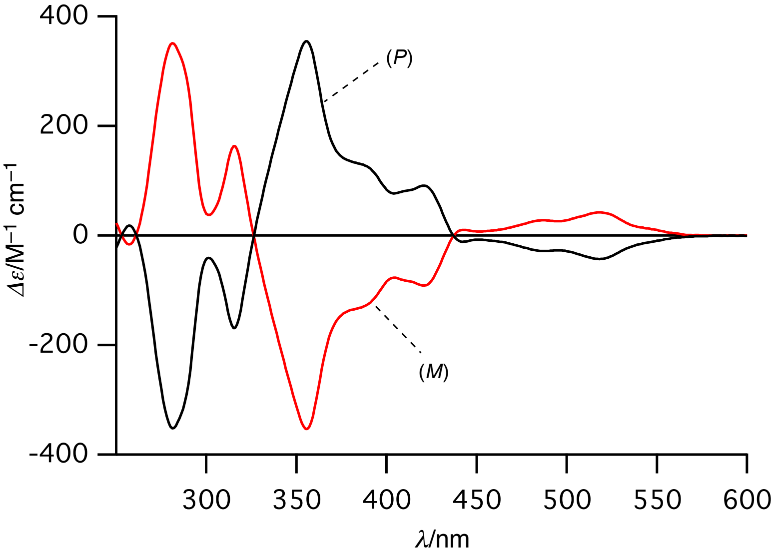


Fig. S16 CD spectra of (*P*) and (*M*)-**6** in CH_2Cl_2.

Time-Resolved Fluorescence Measurement

Time-resolved fluorescence spectra of **2** and **6** were measured on a Hamamatsu Quantaurus-tau C11367-21. All the decay profiles were fitted reasonably well using a single exponential function.

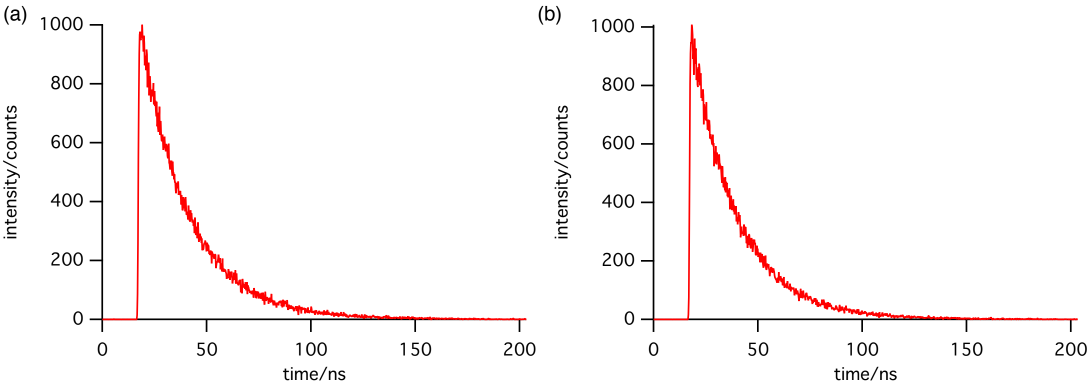


Fig S17. Fluorescence decy profiles of (a) **6** (left) and (b) **2** in CH_2Cl_2 at ambient temperature (λ_{ex} = 405 nm). (τ = 22.9 ns, A = 0.240, χ^2 = 1.216 for **6**, τ = 21.5 ns, A = 0.234, χ^2 = 1.134 for **2**).

Theoretical calculations

All calculations were carried out using the Gaussian 09 program. Geometries of **2** and **6** were optimized by the DFT method at the B3LYP/6-31G(d) level. Molecular orbitals of **2** and **6** were calculated at the CAM-B3LYP level with the same basis sets. The oscillator strengths of **6** were calculated by the time-dependent (TD) DFT method at the CAM-B3LYP/6-31G(d) level of theory.

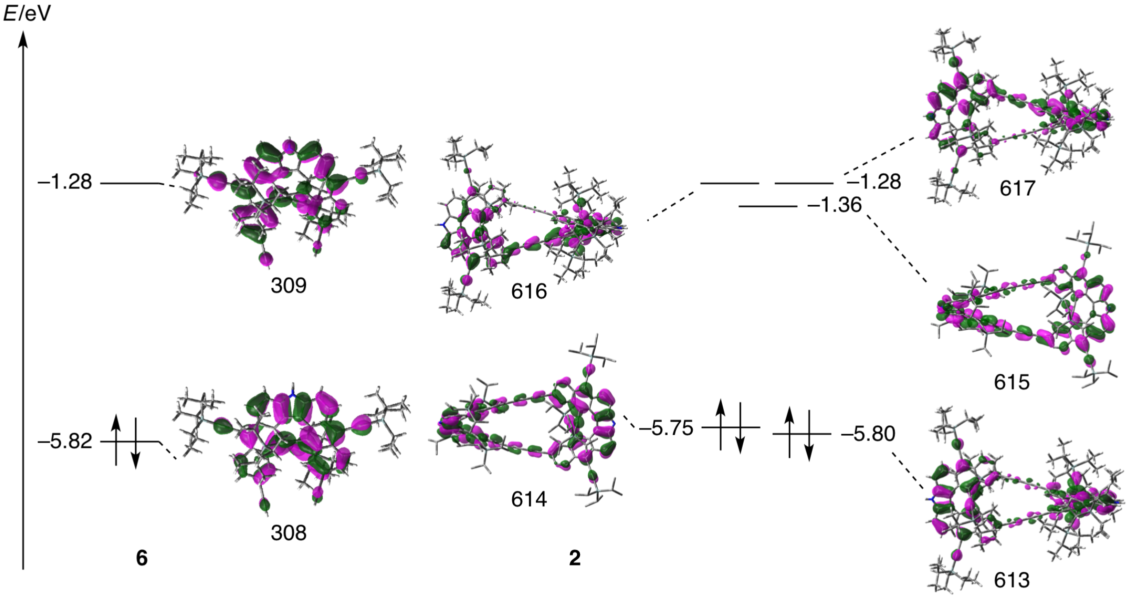


Fig. S18 MO diagrams of **2** and **6**.