Electronic Supplementary Information (ESI) for

Meta-B-entacenes: New Polycyclic Aromatics Incorporating Two Fused Borepin Rings

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General Considerations: Unless otherwise specified, all reactions were carried out in flame- or oven-dried glassware under an atmosphere of prepurified nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl prior to use. Toluene and acetonitrile (MeCN) were obtained from an Innovative Technology, Inc. SPS-400-6 solvent purification system, stored over 3Å molecular sieves, and sparged thoroughly with nitrogen prior to use. Dimethylformamide (DMF) was obtained from Sigma-Aldrich (99.8%, redistilled) and used without further purification. 1,2-Dichloroethane (1,2-DCE) was obtained from Sigma-Aldrich, dried over 3Å molecular sieves and sparged thoroughly with nitrogen prior to use. 1,4-dioxane (anhydrous) was obtained from Alfa-Aesar and used without further purification. Unless specified, all other chemicals were obtained from Alfa-Aesar, Fisher Scientific, Oakwood Chemicals, Sigma-Aldrich, Strem Chemicals, or TCI America and used as received. The following compounds were prepared according to the literature: 1,5-dibromo-2,4-dimethylbenzene (**S1**),[1] 2-bromo-4-chlorobenzaldehyde (**4c**),[2] 4-ethynyl-*N,N*-dimethylaniline.[3]

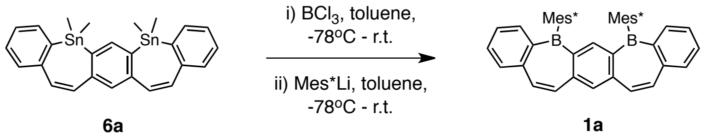
^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance 400 MHz FT-NMR spectrometer in deuterated chloroform ($CDCl_3$) or deuterated dichloromethane (CD_2Cl_2) obtained from Cambridge Isotope Laboratories, Inc. All chemical shifts are reported in parts per million (ppm, δ): ^{1}H NMR spectra were referenced to the residual protio solvent peaks ($CHCl_3$, $\delta = 7.26$; CH_2Cl_2, $\delta = 5.32$); ^{13}C NMR spectra were referenced to the carbon solvent peak ($CDCl_3$, $\delta = 77.16$; CD_2Cl_2, $\delta = 53.84$). Efforts to obtain ^{13}C NMR for *B*-entacene compounds (**1a**, **1b**, **1c**, **7a**, **7b**) were unsuccessful due to quadrupolar relaxation of boron. Mass spectra were obtained by the Johns Hopkins University Department of Chemistry mass spectra analysis service using a VG instruments VG70S/E magnetic sector mass spectrometer with EI (70 eV) and FAB ionization (matrix for FAB was 3-nitrobenzyl alcohol).

Photophysical Considerations: Unless otherwise specified, spectroscopic measurements were conducted in $CHCl_3$ solution at room temperature. UV-Visible (UV-Vis) absorption spectra were obtained on a Varian Cary50 Bio UV-Visible spectrophotometer. Photoluminescence (PL) spectra were obtained on a PTI QuantaMaster spectrofluorometer with a 75 W Xenon lamp, maintaining optical densities below 0.1 au. Photoluminescence lifetime data were collected with a PTI Timemaster LED system, maintaining optical densities below 0.1 au. Quantum yields were determined relative to quinine sulfate in 0.1 N H_2SO_4 (55%), maintaining optical densities below 0.05 au.

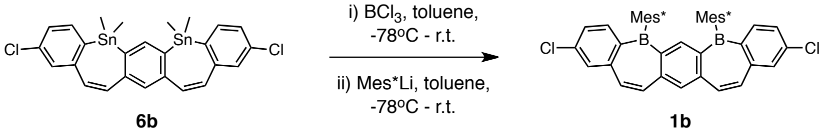
Electrochemical Considerations: Cyclic voltammetry (CV) measurements were performed in a one-chamber, three-electrode cell using a PGSTAT302 potentiostat. A 2 mm^2 Pt button electrode was used as the working electrode with a platinum wire counter electrode relative to a quasi-internal Ag wire reference electrode submerged in 0.01 M $AgNO_3$/0.1 M *n*-Bu_4PF_6 in anhydrous acetonitrile. Measurements were taken in 0.1 M *n*-Bu_4PF_6 (in THF) electrolyte solution recorded at a scan rate of 100 mV/s. Potentials are reported relative to the Ag/Ag^+ couple to which the Fc/Fc^+ couple was measured to be +189 mV.

Computational Considerations: Geometry optimization and frontier molecular orbital calculations were performed at the Density Functional Theory (DFT) level (B3LYP/6-31G*) using Spartan '04 (Wavefunction Inc., Irvine, CA). Nucleus-independent chemical shift (NICS) values were calculated with Gaussian '03 (Gaussian, Inc., Wallingford, CT) on B3LYP/6-31G optimized geometries using the GIAO method with DFT at the B3LYP/6-31+G level of theory.

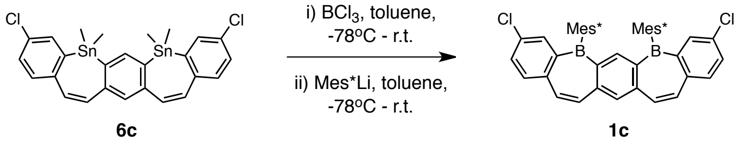
Crystallographic Considerations: All reflection intensities were measured at 110(2) K using a KM4/Xcalibur (detector: Sapphire3) with enhanced graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.35.11 Oxford Diffraction Ltd., 2011). The program CrysAlisPro (Version 1.171.35.11, Oxford Diffraction Ltd., 2011) was used to refine the cell dimensions. Data reduction was done using the program CrysAlisPro (Version 1.171.35.11, Oxford Diffraction Ltd., 2011). The structure was solved with the program SHELXS-97 (Sheldrick, 2008)[4] and was refined on F^2 with SHELXL-97 (Sheldrick, 2008). Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro (Version 1.171.35.11, Oxford Diffraction Ltd., 2011). The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C atoms. X-ray structures were modeled graphically using Mercury 2.4.6.[5]



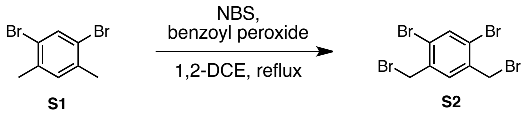
B-Mes* *Meta-B*-entacene (1a). A solution of fused stannocycle **6a** (90.0 mg, 0.156 mmol) in toluene (5 mL) was cooled to -78°C with stirring in a dried 25 mL Schlenk flask under nitrogen. A solution of BCl_3 in hexanes (1.0 M, 0.39 mL, 0.39 mmol) was added dropwise to the reaction mixture, which was then allowed to slowly warm to room temperature. After 1.5 h, the mixture was cooled to -78°C and a suspension of freshly prepared Mes*Li[6] (631 mg, 2.50 mmol) in toluene (11 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature with continued stirring for 16 h. The mixture was partitioned between Et_2O and H_2O (1:1) and the organic layer was removed. The remaining aqueous layer was extracted with Et_2O (2x) and the combined organics were washed with brine, then dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow solid which was purified by flash column chromatography (SiO_2, 5% CH_2Cl_2 in hexanes.) The resulting amorphous yellow solid was further purified by washing with 10 mL methanol (sonicating for 5 min, centrifuging, and decanting the liquid phase) to provide 25.4 mg (0.0321 mmol, 21%) of **1a** as a powdered white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 9.24 (s, 1H), 7.89 (s, 1H), 7.62 (d, *J*=6.8 Hz, 2H), 7.59 (dd, *J*=8.0 Hz, 1.6 Hz, 2H), 7.53 (td, *J*=7.2 Hz, *J*=1.6 Hz, 2H), 7.30 (s, 4H), 7.26 (d, *J*=10.4 Hz, 4H), 7.22 (d, *J*=8.4 Hz, 2H), 1.39 (s, 18H), 0.76 (s, 36H). UV-vis ($CHCl_3$), λ/nm (log ε): 263 (5.00), 340 (5.18), 361 (4.98), 388 (4.06), 407 (3.98). HRMS (EI): found *m/z* = 790.5811 ± 0.0001 [M^+]; calculated for $C_{58}H_{72}B_2$: 790.5820.



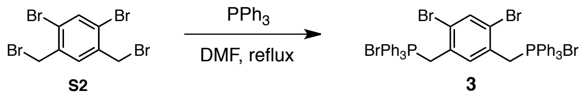
Dichloro B-Mes* *meta-B*-entacene (1b). A solution of fused stannocycle **6b** (129 mg, 0.200 mmol) in toluene (4 mL) was cooled to -78°C with stirring in a dried 25 mL Schlenk tube under nitrogen. A solution of BCl_3 in hexanes (1.0 M, 0.50 mL, 0.50 mmol) was added dropwise to the reaction mixture, which was then allowed to slowly warm to room temperature. After 1.5 h, the mixture was cooled to -78°C and a suspension of freshly prepared Mes*Li[6] (808 mg, 3.20 mmol) in toluene (8 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature with continued stirring for 16 h. The mixture was partitioned between Et_2O and H_2O (1:1) and the organic layer was removed. The remaining aqueous layer was extracted with Et_2O (2x) and the combined organics were washed with brine, then dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow solid which was purified by flash column chromatography (SiO_2, 5% CH_2Cl_2 in hexanes) to give 35.2 mg (0.0409 mmol, 20%) of **1b** as an amorphous yellow solid, which was used without further purification. Analytically pure material for characterization was obtained by washing the amorphous yellow solid with 10 mL methanol (sonicating for 5 min, centrifuging, and decanting the liquid phase) to provide 8.0 mg of **1b** as a powdered white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 9.21 (s, 1H), 7.89 (s, 1H), 7.61 (d, *J*=2.4 Hz, 2H), 7.52 (d, *J*=8.4 Hz, 2H), 7.33 (s, 1H), 7.30 (s, 4H), 7.19 (dd, *J*=8.4 Hz, *J*=2.0 Hz, 2H), 7.13 (d, *J*=12.8 Hz, 2H), 1.38 (s, 18H), 0.75 (s, 36H). UV-vis ($CHCl_3$), λ/nm (log ε): 268 (3.86), 340 (4.03), 361 (3.83), 388 (4.06), 407 (2.85). HRMS (EI): found *m/z* = 858.5028 ± 0.0000 [M^+]; calculated for $C_{58}H_{70}B_2Cl_2$: 858.5026.



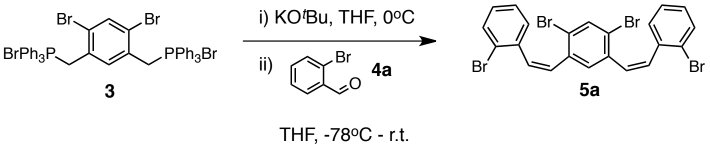
Dichloro *B*-Mes* *meta-B*-entacene (1c). A solution of fused stannocycle **6c** (50 mg, 0.078 mmol) in toluene (3 mL) was cooled to -78°C with stirring in a dried 25 mL Schlenk tube under nitrogen. A solution of BCl_3 in hexanes (1.0 M, 0.193 mL, 0.193 mmol) was added dropwise to the reaction mixture, which was then allowed to slowly warm to room temperature. After 1.5 h, the mixture was cooled to -78°C and a suspension of freshly prepared Mes*Li[6] (313 mg, 1.24 mmol) in toluene (6 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature with continued stirring for 18 h. The mixture was partitioned between Et_2O and H_2O (1:1) and the organic layer was removed. The remaining aqueous layer was extracted with Et_2O (2x) and the combined organics were washed with brine, then dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow solid which was purified by flash column chromatography (SiO_2, 5% CH_2Cl_2 in hexanes.) The resulting material was further purified by washing with 10 mL methanol (sonicating for 5 min, centrifuging, and decanting the liquid phase) to provide 35.5 mg of **1c** (0.0413 mmol, 53%) as an amorphous yellow solid, which was used without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 9.22 (s, 1H), 7.90 (s, 1H), 7.53 (m, 4H), 7.34 (s, 1H), 7.31 (s, 4H), 7.20 (m, 4H), 1.39 (s, 18H), 0.76 (s, 36H).



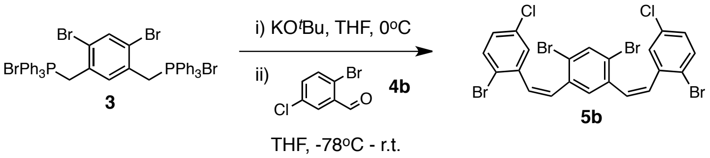
1,5-dibromo-2,4-bis(bromomethyl)benzene (S2). A solution of 1,5-dibromo-2,4-dimethylbenzene[1] (**S1**, 3.246 g, 12.30 mmol) in 1,2-dichloroethane (120 mL) was stirred under nitrogen in a 250-mL 2-necked round-bottomed flask equipped with a reflux condenser. The mixture was stirred at room temperature and benzoyl peroxide (63 mg, 0.25 mmol) and *N*-bromosuccinimide (7.506 g, 25.83 mmol) were added in single portions. The mixture was heated to reflux and an additional portion of benzoyl peroxide (180 mg, 0.75 mmol) was added. The reaction was allowed to continue stirring at reflux for 16 h and then cooled to room temperature. The reflux condenser was removed and the flask was stoppered and placed in a -20°C freezer for 24 h, after which the precipitated solids were filtered off and rinsed with hexanes (150 mL.) The combined filtrates were concentrated under reduced pressure and purified by flash column chromatography (SiO_2, hexanes) to give 3.32 g of **S2** as a white solid (7.87 mmol, 64%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (s, 1H), 7.54 (s, 1H), 4.53 (s, 4H). HRMS (EI): found *m/z* = 338.8020 [M^+ - Br], calculated for $C_8H_6Br_3$: 338.8020.



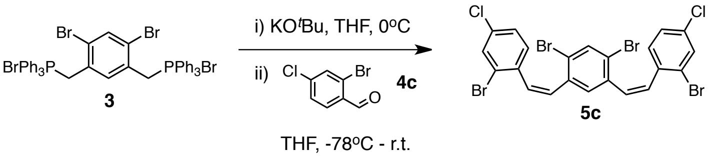
((1,5-dibromo-2,4-phenylene)bis(methylene))bis(bromotriphenylphosphorane) (3). To a stirring solution of **S2** (4.000 g, 9.48 mmol) in DMF (20 mL) in a 50-mL 2-necked flask equipped with reflux condenser under nitrogen was added triphenylphosphine (6.219 g, 23.71 mmol) in a single portion. The mixture was heated at reflux with continued stirring for 20 h. After cooling to room temperature, the mixture was diluted with an additional 75 mL of DMF and poured into 300 mL stirring toluene. The precipitated solids were filtered off and washed with 200 mL toluene, then 200 mL Et_2O. The solid material was collected and dried under high vacuum to provide 8.62 g of diphosphonium salt **3** as a powdered white solid (8.28 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.80 (m, 6H), 7.71-7.65 (m, 24H), 7.46 (s, 1H), 7.43 (s, 1H), 5.36 (d, *J*=14.4 Hz, 4H). HRMS (FAB): found *m/z* = 862.9819 [M^+ - Br], calculated for $C_{44}H_{36}Br_3P_2$: 862.9842.



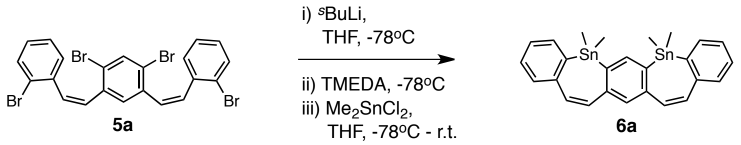
2,2'-((1*Z*, 1'*Z*)-(4,6-dibromo-1,3-phenylene)bis(ethene-2,1-diyl))bis(bromobenzene) (5a). To a stirring suspension of diphosphonium salt **3** (2.400 g, 2.54 mmol) in THF (25 mL) in a 2-necked round-bottomed flask under nitrogen at 0^{o}C was added potassium *tert*-butoxide (684 mg, 6.10 mmol) as a solid in a single portion. The mixture immediately turned a bright orange color and was stirred at 0°C for 30 min, then cooled to -78°C. A solution of 2-bromobenzaldehyde (**4a**, 893 mg, 4.83 mmol) in THF (25 mL) was added dropwise to the reaction mixture *via* cannula over 20 min. The reaction mixture was allowed to gradually warm to room temperature with continued stirring for 17 h, then partitioned between Et_2O and H_2O (1:1). The organic layer was removed and the aqueous layer was extracted with Et_2O (2x,) after which the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting solid was purified by flash column chromatography (SiO_2, hexanes) to give 1.17 g of **5a** as a white solid (1.95 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.51 (dd, *J*=8.0 Hz, *J*=1.2 Hz, 2H), 7.04 (td, *J*=8.0 Hz, *J*=1.6 Hz, 2H), 6.96 (td, *J*=8.0 Hz, *J*=1.6 Hz,, 2H), 6.81, (dd, *J*=7.6 Hz, *J*=1.6 Hz, 2H), 6.68 (s, 1H), 6.62 (d, *J*=12.0 Hz, 2H), 6.48 (d, J=12.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.5, 135.9, 133.0, 132.0, 132.0, 131.8, 130.4, 129.2, 129.2, 127.1, 123.9, 123.2. HRMS (FAB): found *m/z* = 597.7793 ± 0.0001 [M^+], calculated for $C_{22}H_{14}{}^{79}Br_2{}^{81}Br_2$: 597.7788.



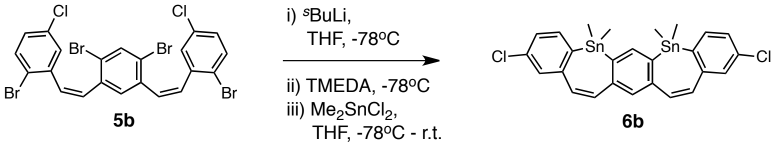
2,2'-((1*Z*,1'*Z*)-(4,6-dibromo-1,3-phenylene)bis(ethene-2,1-diyl))bis(1-bromo-4-chlorobenzene) (5b). To a stirring suspension of diphosphonium salt **3** (1.00 g, 1.06 mmol) in THF (10 mL) in a 50-mL Schlenk flask under nitrogen at 0°C was added potassium *tert*-butoxide (684 mg, 6.10 mmol) as a solid in a single portion. The mixture immediately turned a bright orange color and was stirred at 0°C for 30 min, then cooled to -78°C. A solution of 2-bromo-5-chlorobenzaldehyde (**4b**, 452 mg, 2.06 mmol) in THF (10 mL) was added dropwise to the reaction mixture *via* cannula over 20 min. The reaction mixture was allowed to gradually warm to room temperature with continued stirring for 22 h, then partitioned between Et_2O and H_2O (1:1). The organic layer was removed and the aqueous layer was extracted with Et_2O (2x,) after which the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting solid was purified by flash column chromatography (SiO_2, hexanes) to give 535 mg of **5b** as a white solid (0.804 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (s, 1H), 7.42 (d, *J*=8.4 Hz, 2H), 7.04 (d, *J*=8.4 Hz, 2H),), 6.86, (s, 2H), 6.54 (d, *J*=4.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 136.5, 135.3, 134.0, 133.2, 131.5, 130.5, 130.3, 130.0, 129.3, 123.6, 121.7. HRMS (FAB): found *m/z* = 665.6984 ± 0.0001 [M^+]; calculated for $C_{22}H_{12}{}^{79}Br_4{}^{37}Cl_2$: 665.6991.



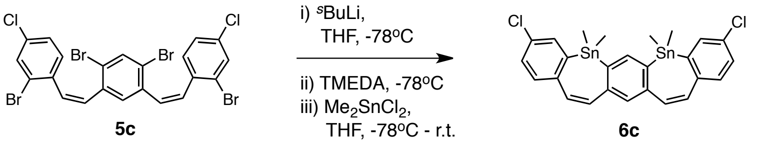
2,2'-((1*Z*,1'*Z*)-(4,6-dibromo-1,3-phenylene)bis(ethene-2,1-diyl))bis(1-bromo-5-chlorobenzene) (5c). To a stirring suspension of diphosphonium salt **3** (1.14 g, 1.20 mmol) in THF (10 mL) in a 50-mL 2-necked round-bottomed flask under nitrogen at 0°C was added potassium *tert*-butoxide (323 mg, 2.88 mmol) as a solid in a single portion. The mixture immediately turned a bright orange color and was stirred at 0°C for 30 min, then cooled to -78°C. A solution of 2-bromo-4-chlorobenzaldehyde (**4c**^{2}, 501 mg, 2.27 mmol) in THF (10 mL) was added dropwise to the reaction mixture *via* cannula over 20 min. The reaction mixture was allowed to gradually warm to room temperature with continued stirring for 16 h, then partitioned 1:1 between Et_2O and H_2O. The organic layer was removed and the aqueous layer was extracted with Et_2O (2x,) after which the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting solid was purified by flash column chromatography (SiO_2, hexanes) to give 544 mg of **5c** as a white solid (0.816 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.56 (d, J=2.4 Hz, 2H), 6.96 (dd, J=8.0 Hz, J=2.0, 2H), 6.76 (d, J=8.4 Hz, 2H), 6.67 (s, 1H), 6.54 (d, J=4.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.2, 135.5, 134.9, 133.9, 132.6, 132.5, 130.7,130.5, 129.5, 127.3, 124.0, 123.3. HRMS (EI): found m/z = 665.6999 ± 0.0000 [M^+]; calculated for $C_{22}H_{12}{}^{79}Br_3{}^{81}Br^{35}Cl^{37}Cl$: 665.6999.



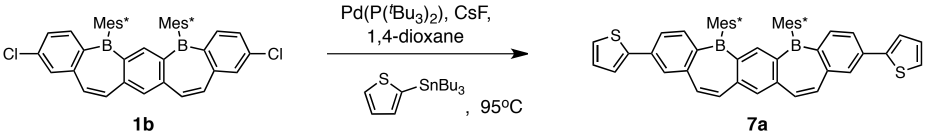
Fused stannocycle (6a). To a stirring solution of **5a** (245 mg, 0.410 mmol) in THF (50 mL) in a 100-mL Schlenk flask under nitrogen at -78°C was added dropwise a solution of *s*-BuLi in cyclohexane (1.425 M, 2.30 mL, 3.28 mmol), followed by TMEDA (0.492 mL, 3.28 mmol). The reaction was held at -78°C for 2.5 h, after which a solution of Me_2SnCl_2 (185 mg, 0.841 mmol) in THF (12 mL) was added dropwise to the deep green reaction mixture over 30 min. The mixture was allowed to continue stirring with gradual warming to room temperature over 18 h, after which it was partitioned between Et_2O and H_2O (1:1). The organic layer was removed and the aqueous layer was extracted 2x with Et_2O. The combined organics were washed with 1 M HCl (aq), then brine, and dried over $MgSO_4$. After filtration and concentration under reduced pressure, the crude organic product was pushed through a short pad of silica, eluting with 4:1/hexanes:EtOAc (150 mL). The eluent was concentrated under reduced pressure and the resulting yellow-orange material was washed 2x with 10 mL methanol (sonicating for 5 min, centrifuging, and decanting the liquid phase) and dried under high vacuum to provide 210 mg of **6a** as a pale yellow solid (0.352 mmol, 89%) that was used without further purification. HRMS (FAB): found m/z = 579.0142 [$M+H^+$]; calculated for $C_{26}H_{27}Sn_2$: 579.0157.



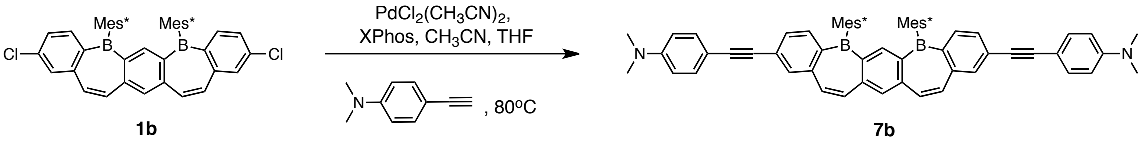
Fused dichloro-stannocycle (6b). To a stirring solution of **5b** (334 mg, 0.501 mmol) in THF (50 mL) in a 100-mL Schlenk flask under nitrogen at -78°C was added dropwise a solution of *s*-BuLi in cyclohexane (1.4 M, 2.86 mL, 4.01 mmol), followed by TMEDA (0.601 mL, 4.01 mmol). The reaction was held at -78°C for 2.5 h, after which a solution of Me_2SnCl_2 (184.6 mg, 0.841 mmol) in THF (10 mL) was added dropwise to the deep green reaction mixture over 30 min. The mixture was allowed to continue stirring with gradual warming to room temperature over 18 h, after which it was partitioned between Et_2O and H_2O (1:1). The organic layer was removed and the aqueous layer was extracted 2x with Et_2O. The combined organics were washed sequentially with 1 M HCl (aq) and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow-orange material was washed 2x with 10 mL methanol (sonicating for 5 min, centrifuging, and decanting the liquid phase) and dried under high vacuum to provide 188 mg of **6b** as a pale yellow solid (0.291 mmol, 58%) that was used without further purification.



Fused dichloro-stannocycle (6c). To a stirring solution of **5c** (267 mg, 0.401 mmol) in THF (50 mL) in a 100-mL Schlenk flask under nitrogen at -78°C was added dropwise a solution of *s*-BuLi in cyclohexane (1.4 M, 2.26 mL, 3.21 mmol), followed by TMEDA (0.494 mL, 3.21 mmol). The reaction was held at -78°C for 2.5 h, after which a solution of Me_2SnCl_2 (180.6 mg, 0.822 mmol) in THF (10 mL) was added dropwise to the deep green reaction mixture over 30 min. The mixture was allowed to continue stirring with gradual warming to room temperature over 16 h, after which it was partitioned between Et_2O and H_2O (1:1). The organic layer was removed and the aqueous layer was extracted 2x with Et_2O. The combined organics were washed sequentially with 1 M HCl (aq) and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow-orange material was washed 2x with 10 mL methanol (sonicating for 5 min, centrifuging, and decanting the liquid phase) and dried under high vacuum to provide 213 mg of **6c** as a pale yellow solid (0.331 mmol, 83%) that was used without further purification.



Bis(2-thienyl) *B*-Mes* *meta-B*-entacene (7a). To a stirring solution of **1b** (31.5 mg, 0.0366 mmol), $Pd(P(t\text{-}Bu)_3)_2$ (2.0 mg, 0.0037 mmol), and CsF (34.5 mg, 0.227 mmol) in 1,4-dioxane (2 mL) in a dried 25-mL Schlenk tube under nitrogen was added 2-tributylstannylthiophene (30 μL, 36 mg, 0.095 mmol) dropwise *via* syringe. The mixture was then heated to 95°C and allowed to continue stirring for 18 h. After cooling to room temperature, the mixture was diluted with EtOAc and pushed through a short pad of silica, eluting with EtOAc (150 mL). The eluent was concentrated under reduced pressure and purified by flash column chromatography (SiO_2, gradient elution: 5% CH_2Cl_2 in hexanes - 10% CH_2Cl_2 in hexanes) to provide 14.5 mg (0.0152 mmol, 41%) of **7a** as an off-white/yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 9.24 (s, 1H), 7.90 (s, 1H), 7.87 (d, *J*=2.0 Hz, 2H), 7.60 (d, *J*=8.4 Hz, 2H), 7.51-7.48 (m, 4H), 7.37 (dd, *J*=4.8 Hz, *J*=0.8 Hz, 2H), 7.33 (d, *J*=13.2 Hz, 2H), 7.31 (s, 4H), 7.27 (d, *J*=13.2 Hz, 2H), 7.12 (dd, *J*=4.8 Hz, *J*=2.0 Hz), 1.40 (s, 18H), 0.79 (s, 36H). UV-vis ($CHCl_3$) λ/nm (log ε): 268 (3.90), 349 (4.42), 410 (2.82). HRMS (FAB): found *m/z* = 954.5589 ± 0.0002 [M^+]; calculated for $C_{66}H_{76}B_2S_2$: 954.5575.



Bis(4-*N,N*-dimethyl-4-aminophenylethynyl) *B*-Mes* *meta-B*-entacene (7b). To a stirring solution of **1b** (25.6 mg, 0.0298 mmol), $PdCl_2(CH_3CN)_2$ (2.2 mg, 0.0060 mmol), XPhos (8.3 mg, 0.018 mmol), and Cs_2CO_3 (58.3 mg, 0.179 mmol) in THF (1.0 mL) and CH_3CN (1.5 mL) in a dried 25-mL Schlenk tube under nitrogen was added a solution of 4-ethynyl-*N,N*-dimethylaniline (13.0 mg, 0.0895 mmol) in CH_3CN (0.5 mL) dropwise via syringe. The mixture was then heated to 80°C and allowed to continue stirring for 18 h. After cooling to room temperature, the mixture was partitioned between Et_2O and H_2O (1:1) and the organic layer was removed. The remaining aqueous layer was extracted with Et_2O (2x) and the combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a solid which was purified by flash column chromatography (SiO_2, gradient elution: 5% EtOAc in hexanes – 10% EtOAc in hexanes.) to provide 10.6 mg (0.00984 mmol, 33%) of **7b** as a yellow solid. ^{1}H NMR (400 MHz,

CD_2Cl_2) δ: 9.20 (s, 1H), 7.89 (s, 1H), 7.73 (s, 2H), 7.54 (d, *J*=8.4 Hz, 2H), 7.40 (d, *J*=9.2 Hz, 4H), 7.33 (d, *J*=13.2 Hz, 2H), 7.31 (s, 4H), 7.29 (s, 2H), 7.20 (d, *J*=4.0 Hz, 2H), 6.67 (d, *J*=8.8 Hz, 4H), 2.99 (s, 12H), 1.39 (s, 18H), 0.77 (s, 36H). UV-vis ($CHCl_3$) λ/nm (log ε): 289 (3.92), 352 (4.10), 377 (4.10).
HRMS (FAB): found *m/z* = 1076.7321 ± 0.0029 [M^+]; calculated for $C_{78}H_{90}B_2N_2$: 1076.7290.

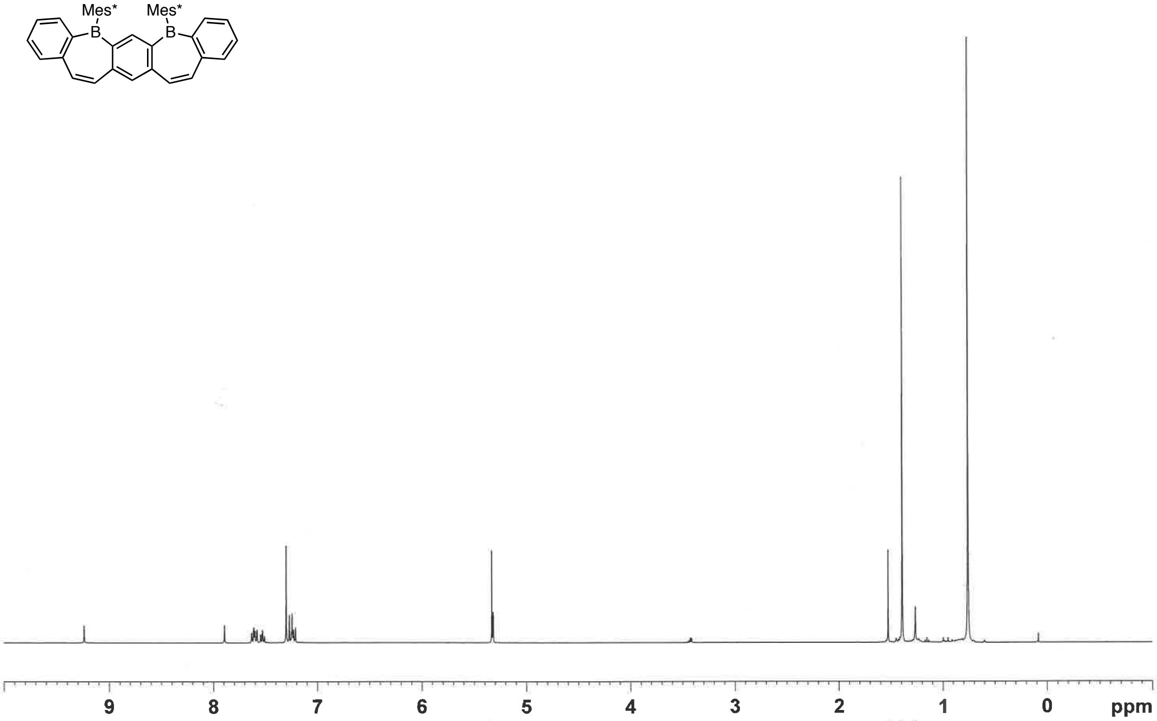


Figure S1: ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **1a**

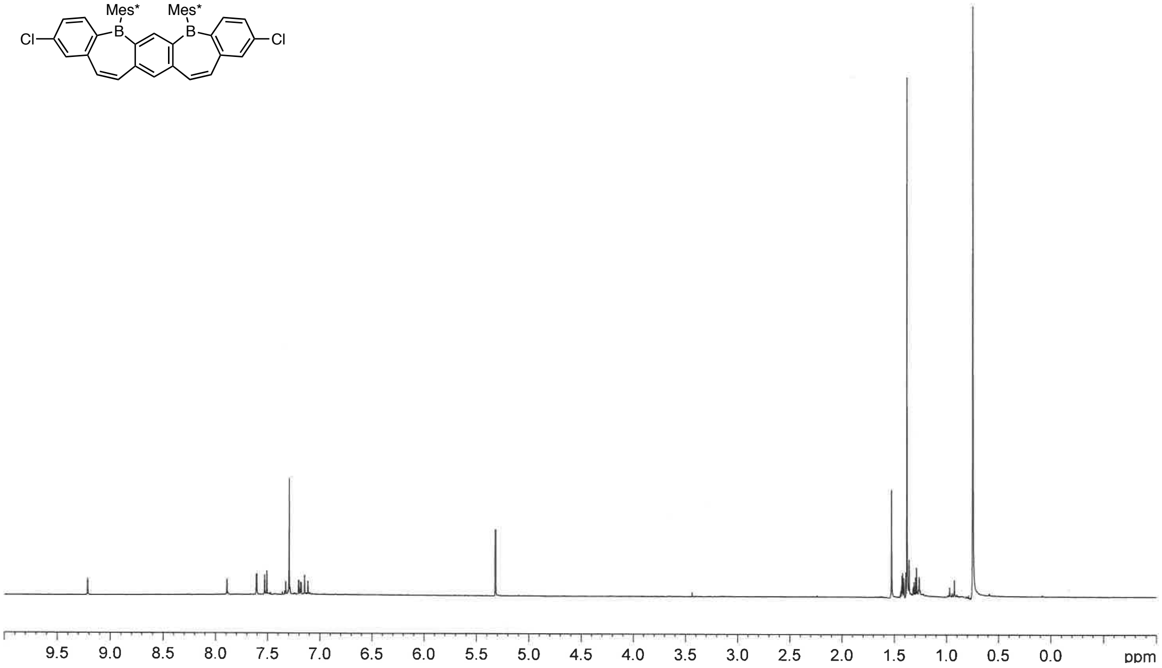


Figure S2: ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **1b**

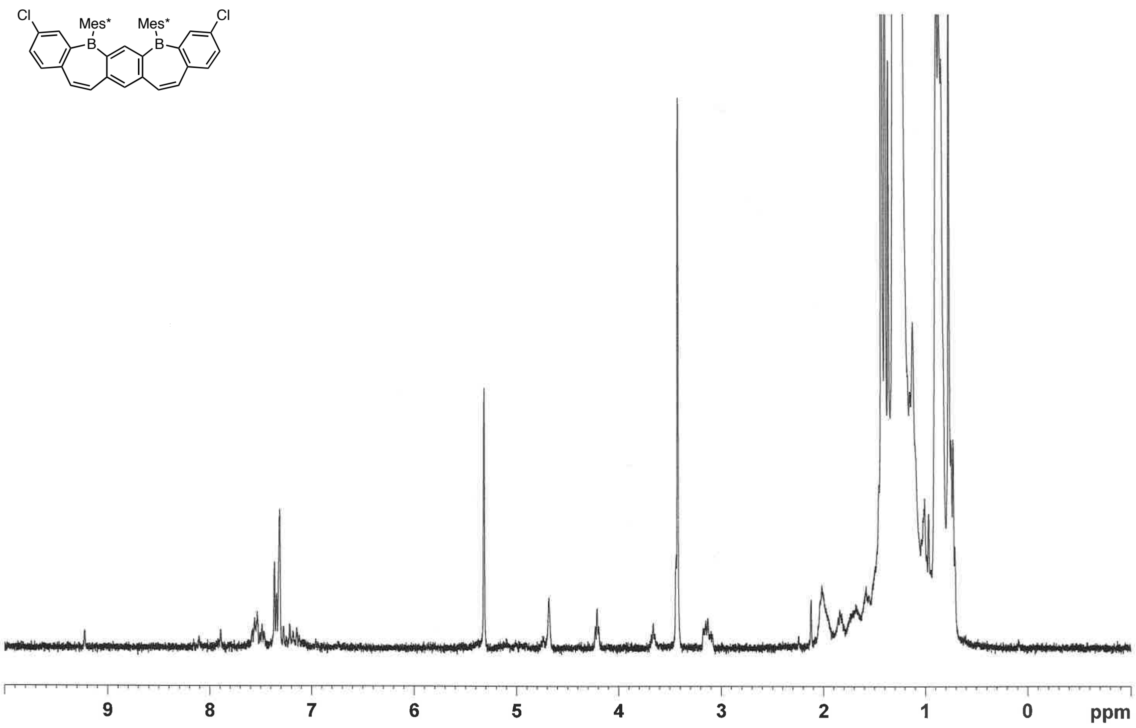


Figure S3: ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **1c**

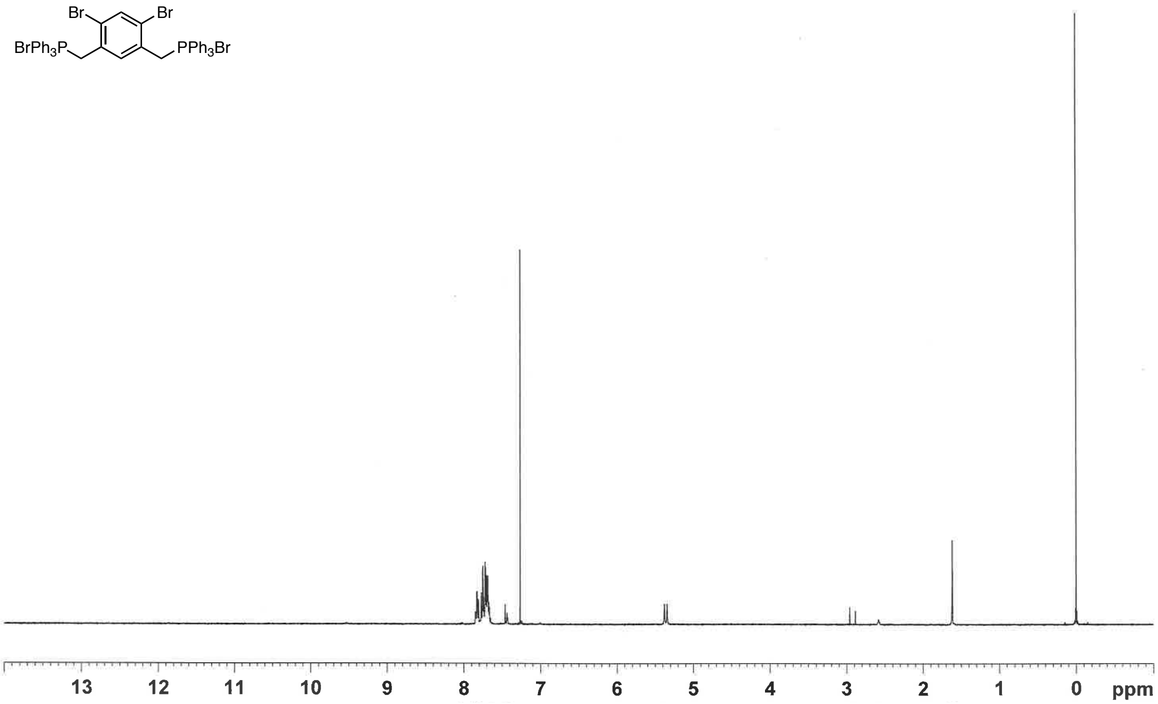


Figure S4: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**

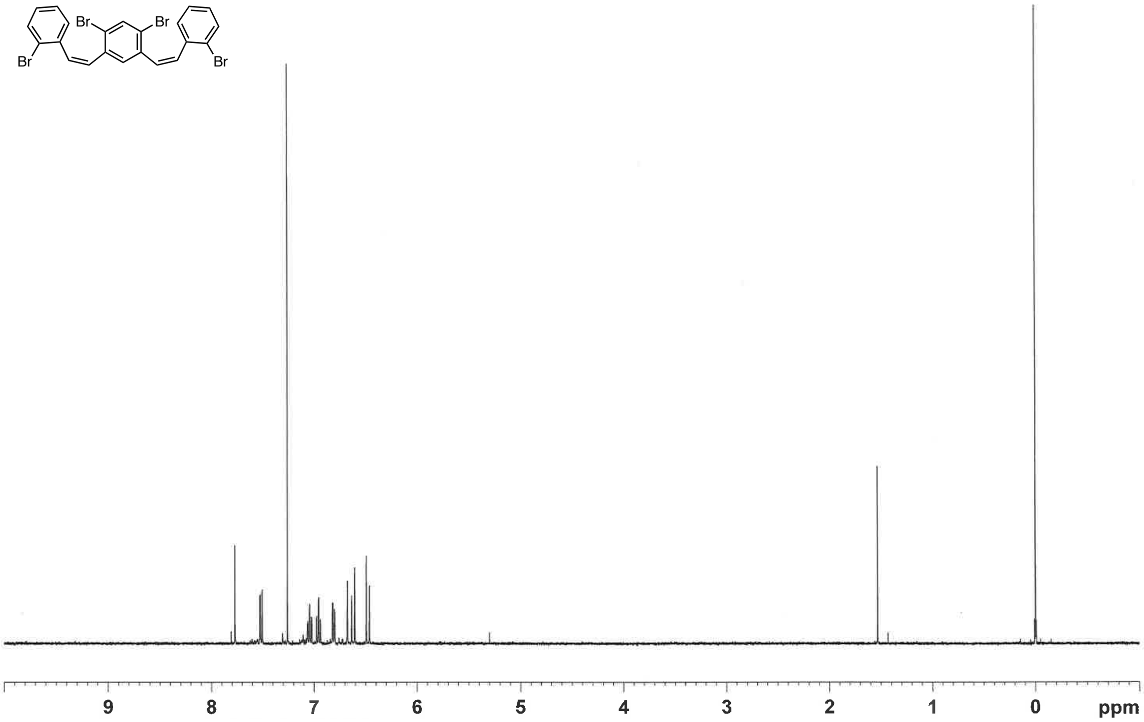


Figure S5: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**

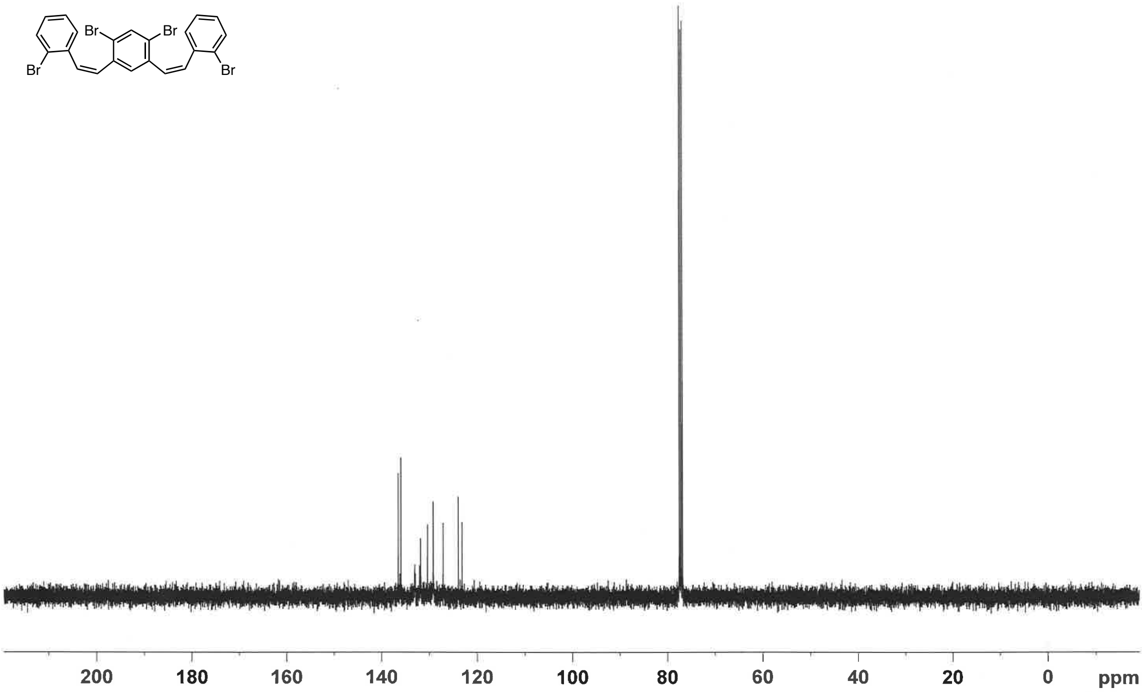


Figure S6: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5a**

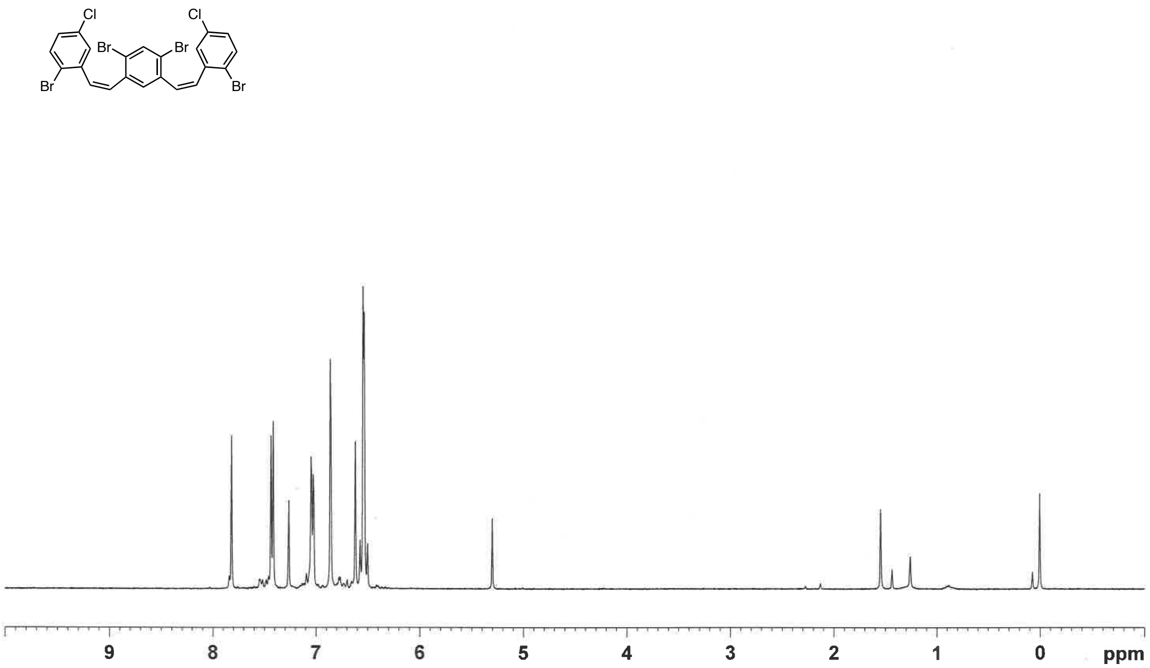


Figure S7: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5b**

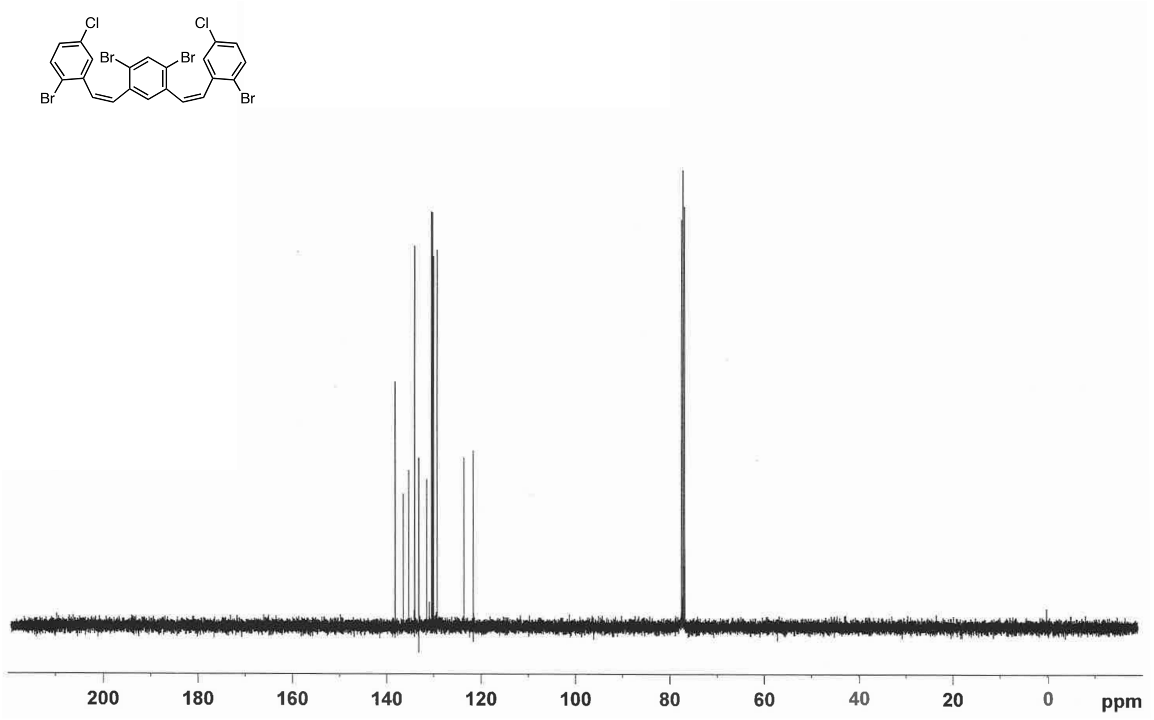


Figure S8: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5b**

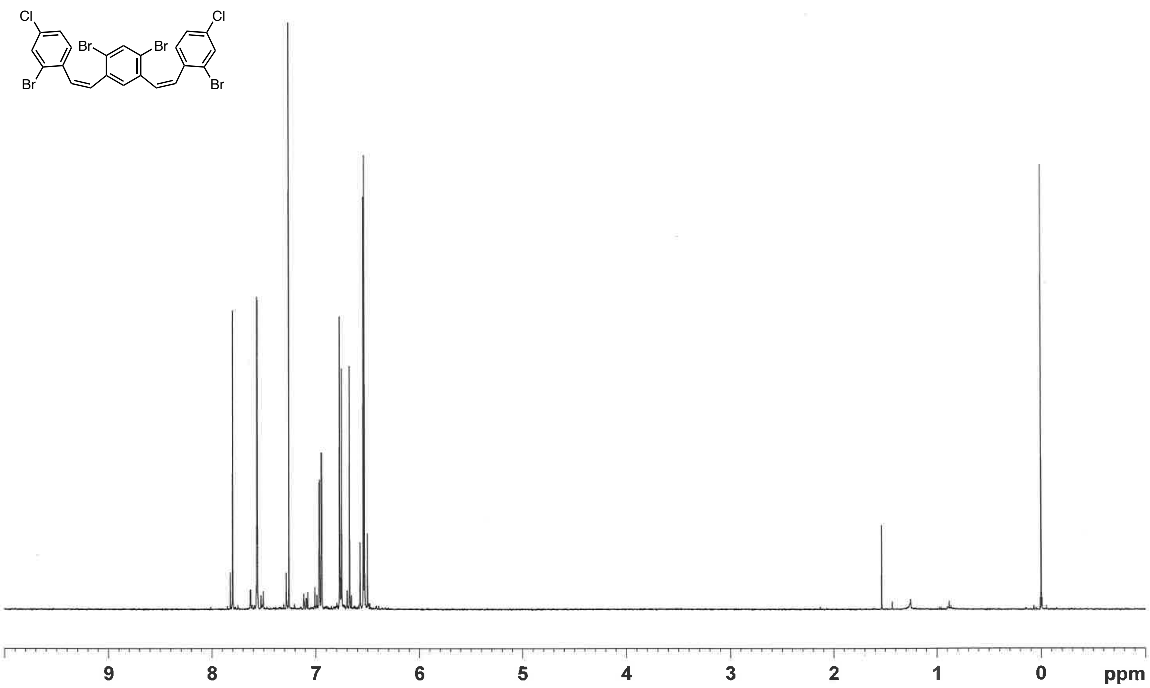


Figure S9: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **5c**

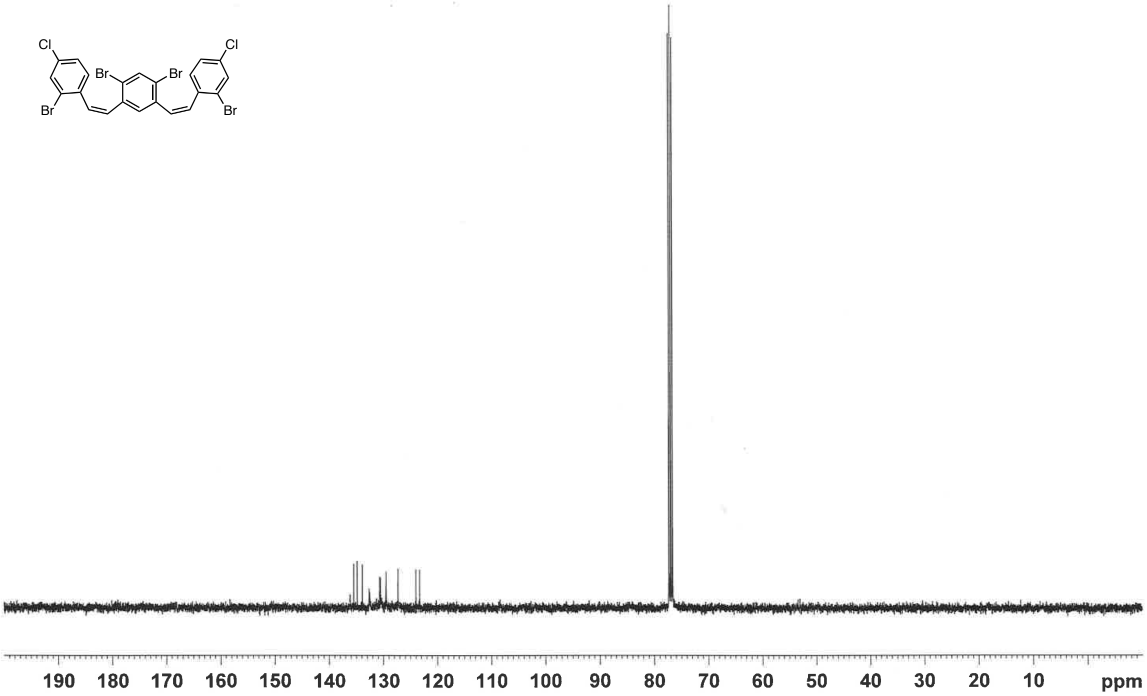


Figure S10: ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **5c**

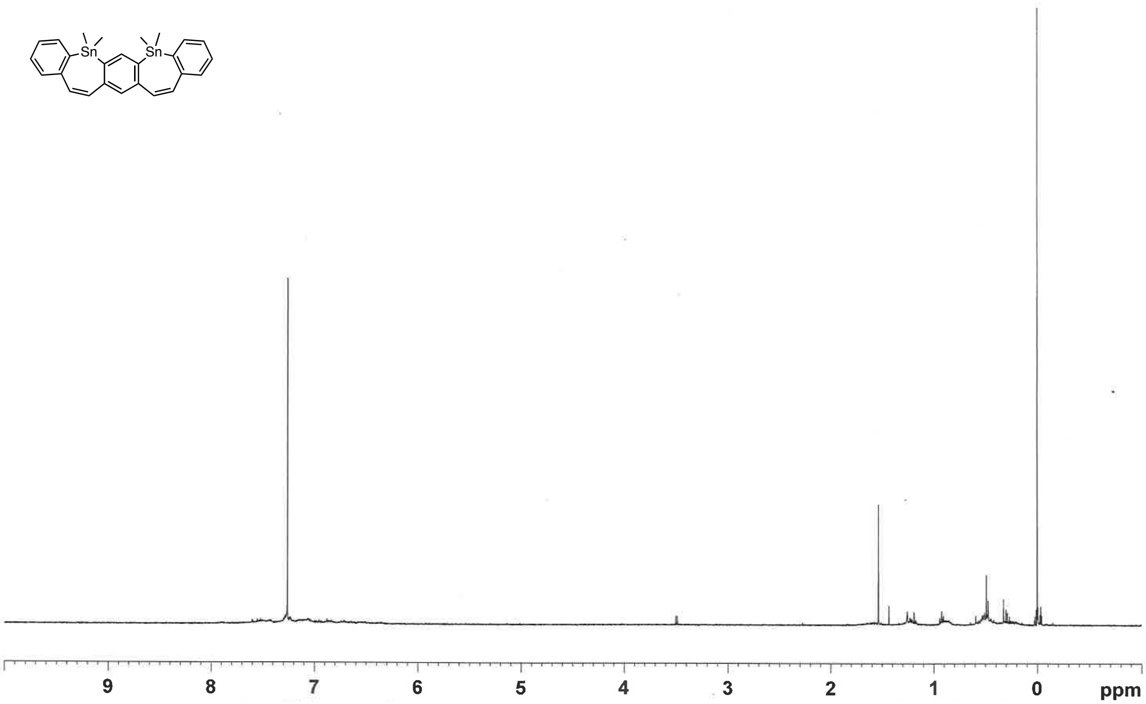


Figure S11: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **6a**

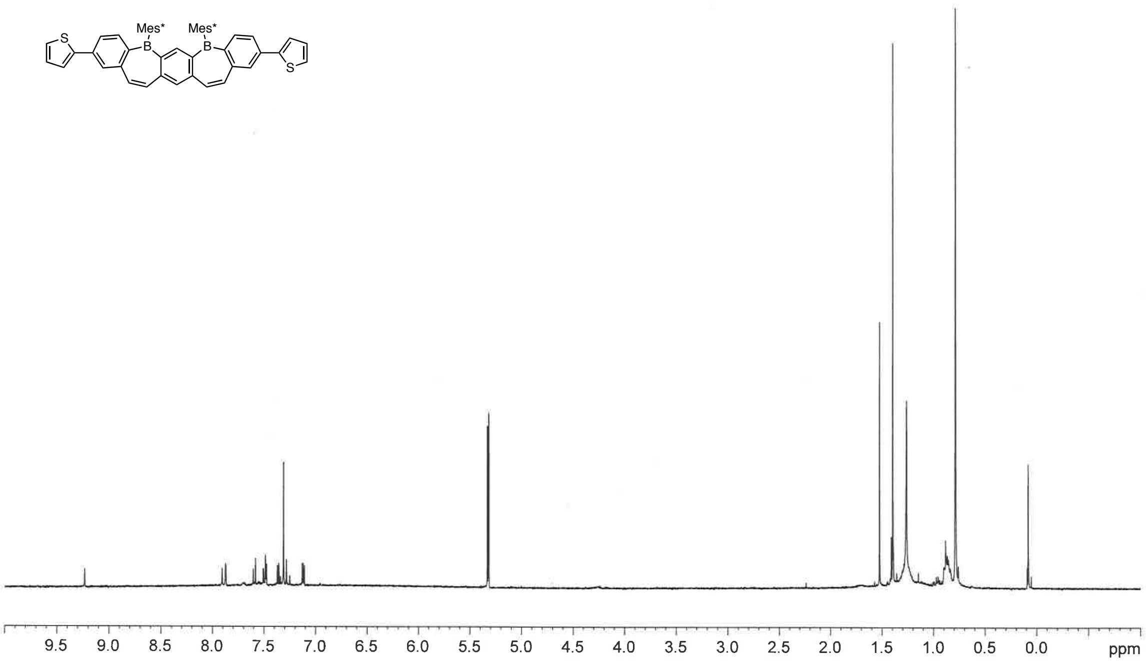


Figure S12: ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **7a**

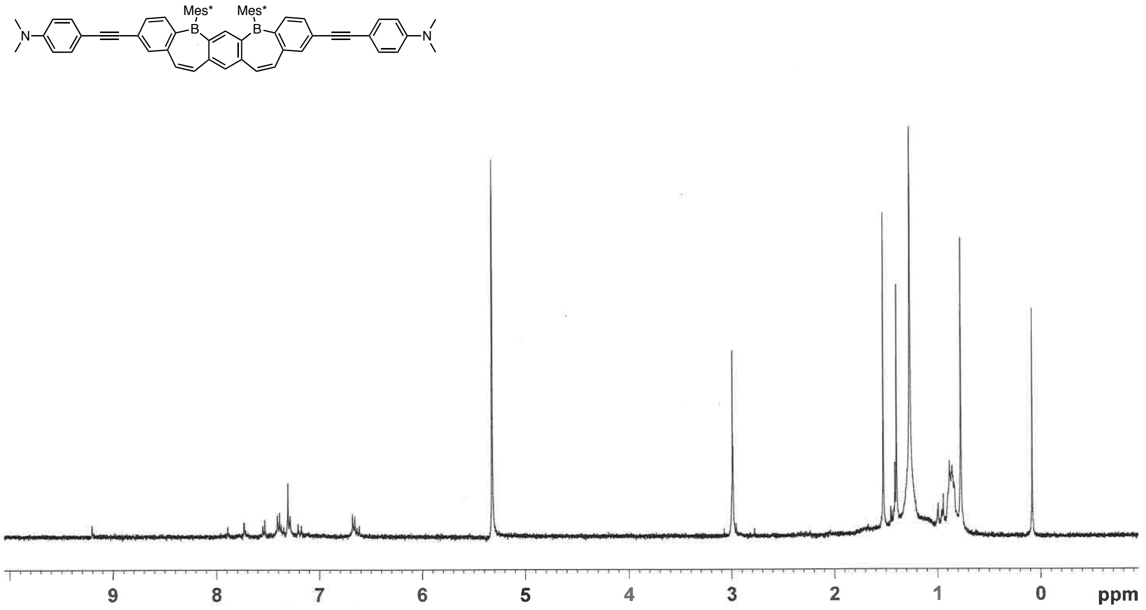


Figure S13: ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **7b**

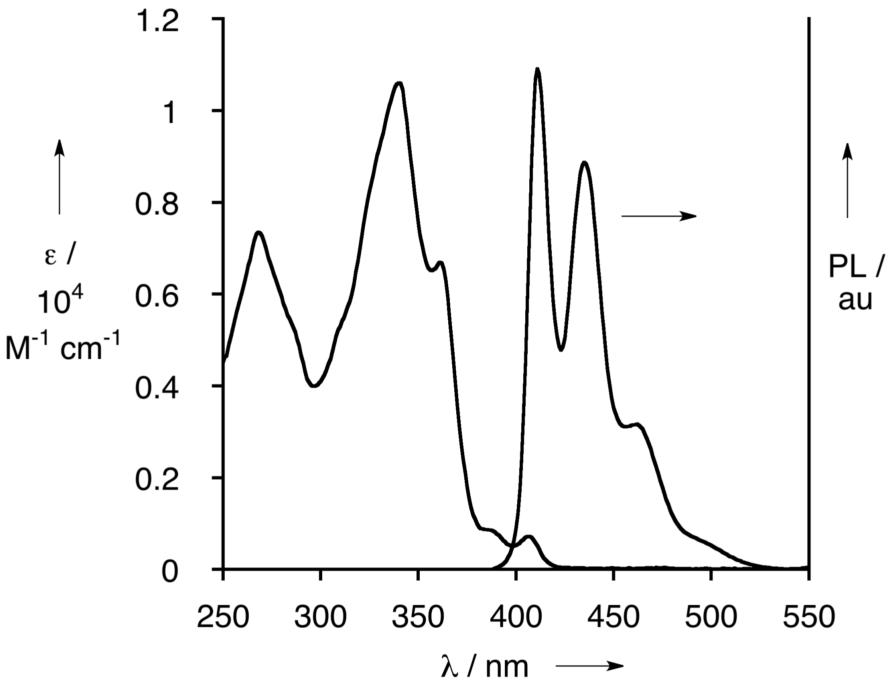


Figure S14. UV-Vis / PL spectrum of **1b** in $CHCl_3$. PL acquired at room temperature at an excitation wavelength of 340 nm.

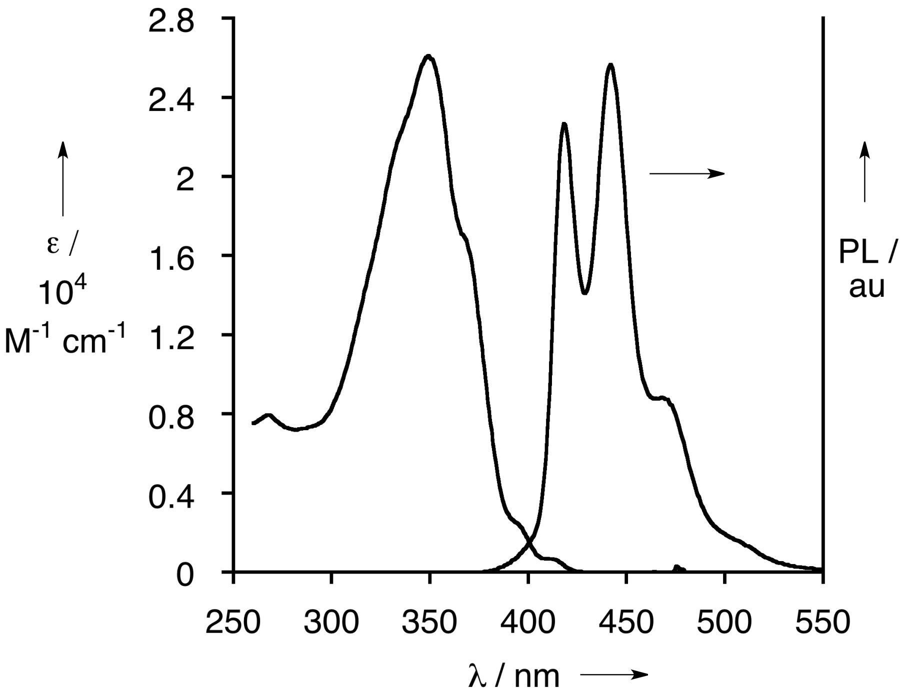


Figure S15. UV-Vis / PL spectrum of **7a** in $CHCl_3$. PL acquired at room temperature at an excitation wavelength of 349 nm.

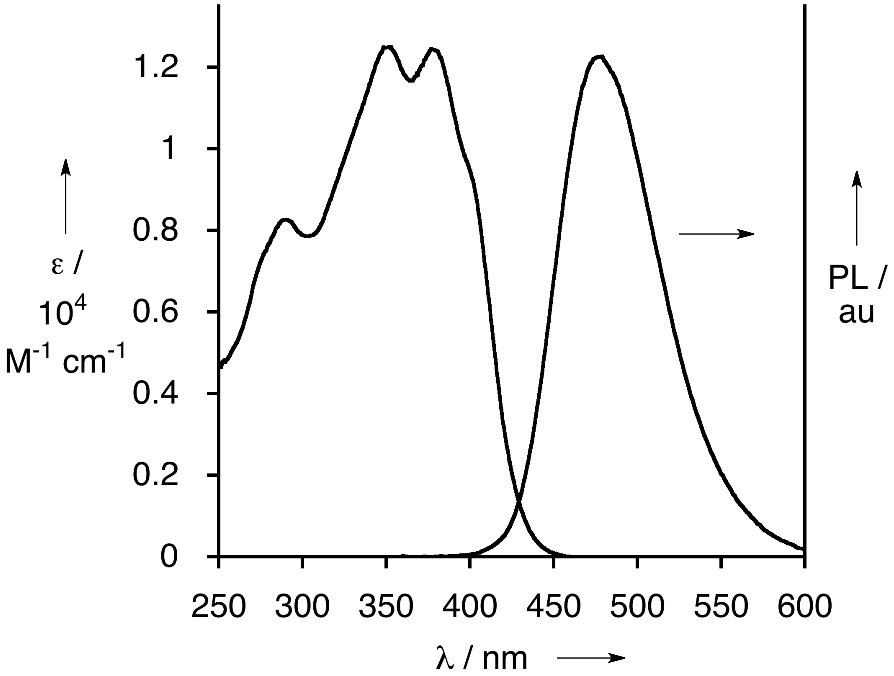


Figure S16. UV-Vis / PL spectrum of **7b** in $CHCl_3$. PL acquired at room temperature at an excitation wavelength of 352 nm.

Single-crystal growth of 1a: *Meta-B*-entacene **1a** (6.9 mg, 0.0087 mmol) was dissolved in 1 mL THF and the solution was gently layered over 1 mL H_2O in a 1-dram scintillation vial. The vial was covered with a perforated cap and the sample was stored in the dark in a low-vibration environment at room temperature. After three weeks, pale-yellow to colorless single-crystals of **1a** were found to have formed in the mixture, which were suitable for X-ray crystallography.

Crystallographic determination of the structure of 1a: The asymmetric unit contains 2 crystallographically independent formula units (*i.e.*, $Z' = 2$). The structure is mostly ordered, except for one *tert*-butyl group of the formula unit B which is disordered over two orientations [occupancy factor for the major component of the disorder = 0.553(3)]. The structure contains one relatively large void of 145 Å^3 (electron count = 42) located at (0 0.5 0.5) (and at equivalent positions). Such voids contain one THF molecule symmetrically constrained to be wholly disordered over an inversion center. The contribution of such solvent molecules was then taken out for the final stages of the refinement using the program SQUEEZE (Spek, 2003)[7].

1a, FW = 808.80 *, colorless block, 0.47 × 0.39 × 0.15 mm^3, triclinic, P-1 (no. 2), a = 13.6095(2), b = 19.4173(4), c = 19.7515(4) Å, α = 109.1855(18), β = 95.4448(15), γ = 96.2210(15)°, V = 4853.03(16) Å^3, Z = 4, D_x = 1.107 g cm^{-3}, μ = 0.061 mm^{-1}, abs. corr. range: 0.977–0.997. 51627 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.59 Å^{-1}. 17073 Reflections were unique (R_{int} = 0.0428), of which 12870 were observed [$I > 2\sigma(I)$]. 1148 Parameters were refined using 114 restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0510/0.1404. $R1/wR2$ [all refl.]: 0.0693/0.1485. S = 1.076. Residual electron density found between −0.29 and 0.44 e Å^{-3}.

*including the contribution of disordered lattice THF solvent molecules.

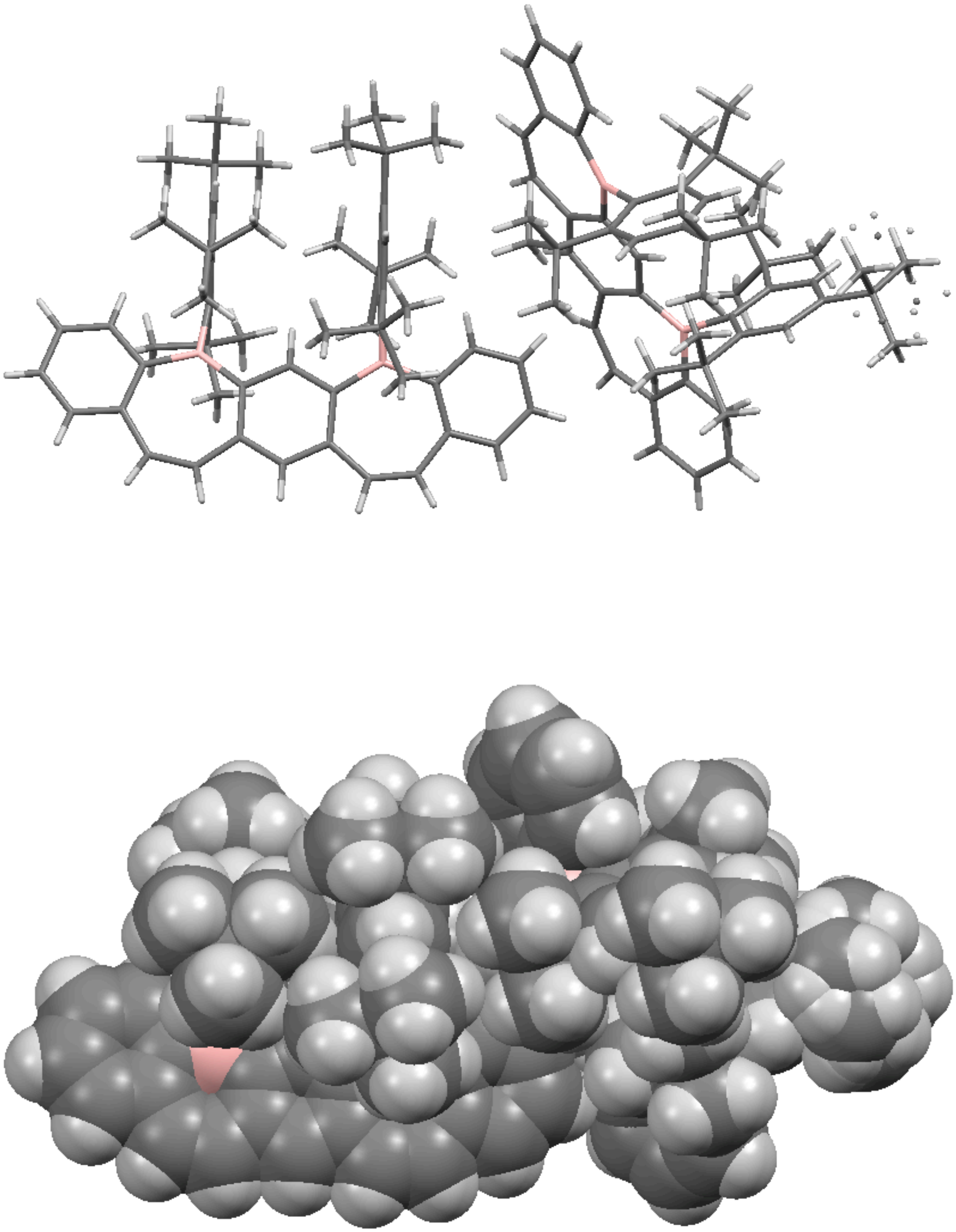


Figure S17. Asymmetric unit (excluding the contribution of THF solvent molecules) of the crystal structure of **1a,** depicted in capped-stick (top) and space-filling (bottom) representations. Left: Formula unit A. Right: Formula unit B.

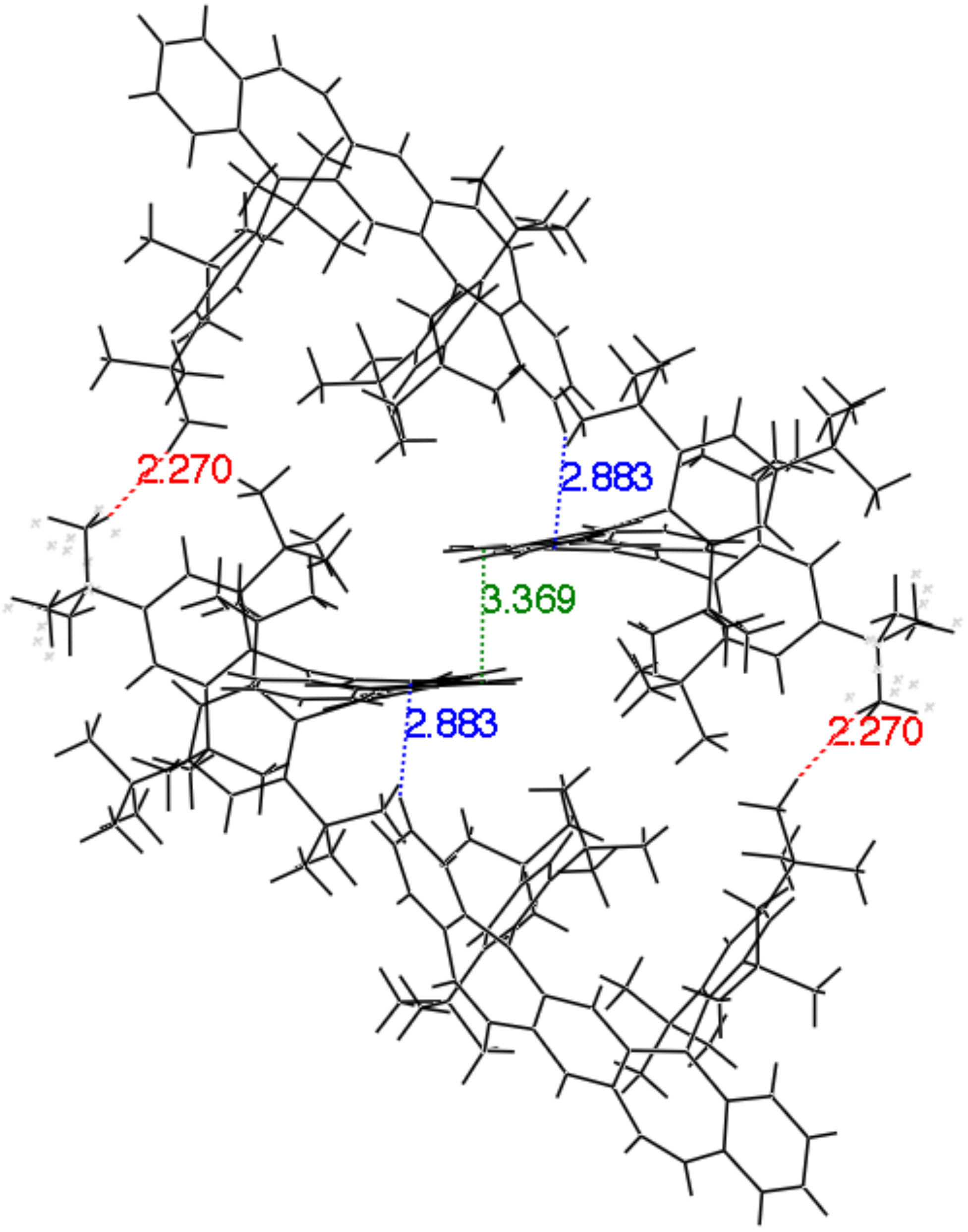


Figure S18. Wireframe depiction of solid-state packing motif for **1a**, illustrating intermolecular close-contacts (contact lengths shown in Å.) **Green:** C-C face-to-face interactions. **Blue**: C-H edge-to-face interactions. **Red**: *t*-Bu–*t*-Bu van der Waals interactions. **Gray**: disordered *t*-Bu groups.

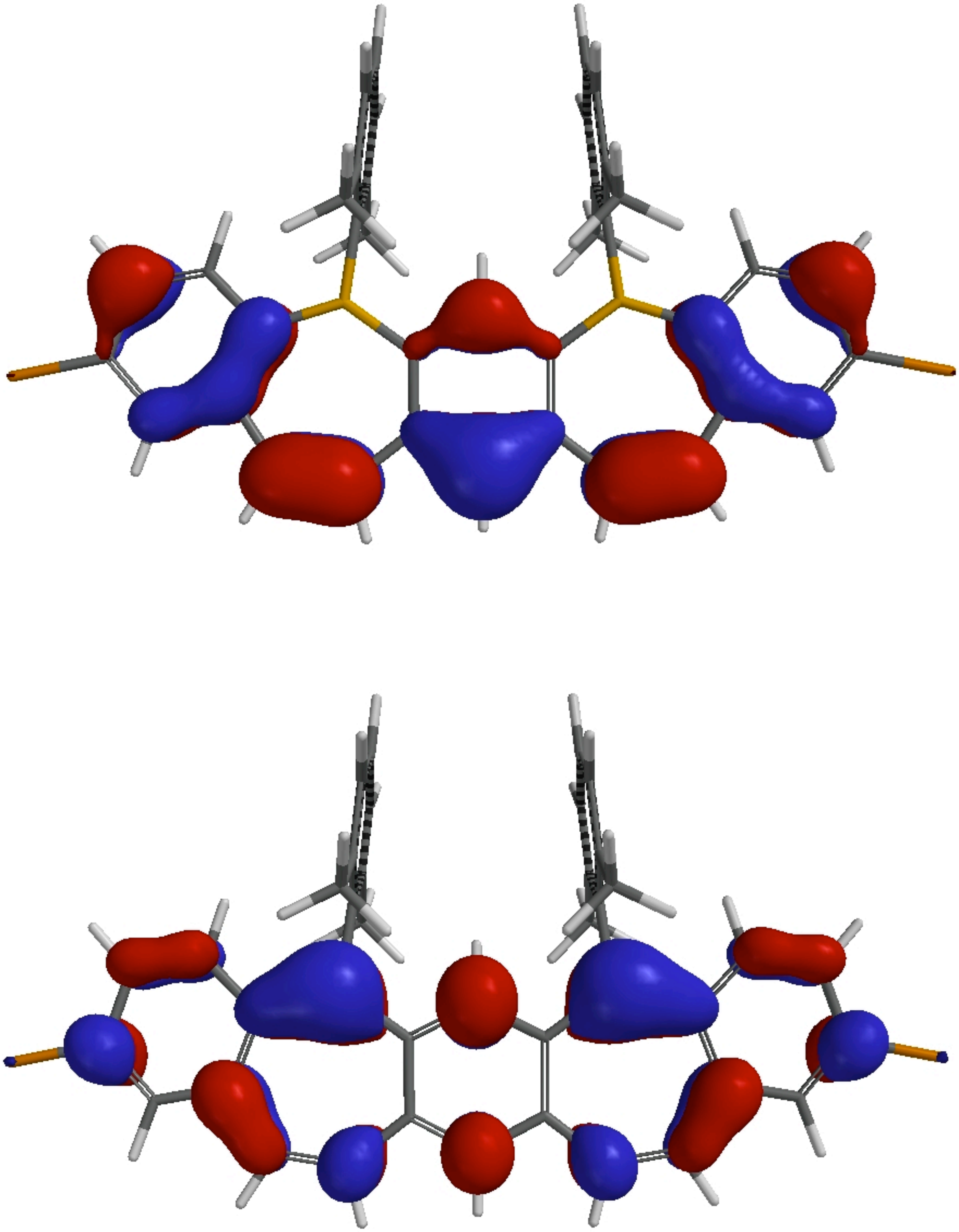


Figure S19: Calculated frontier molecular orbital surfaces for *B*-(2,6-dimethylphenyl)-**1b**. Top: HOMO. Bottom: LUMO.

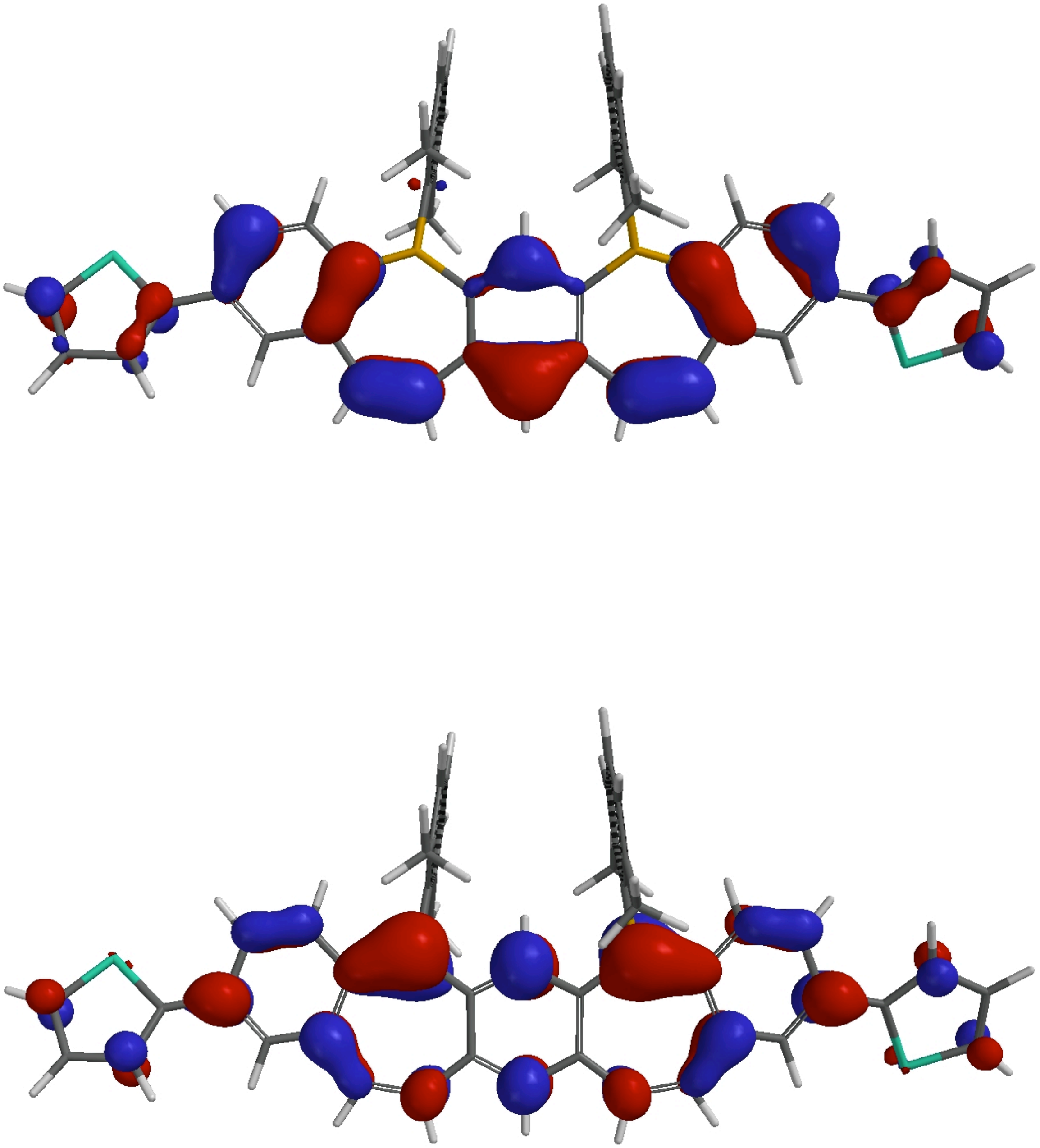


Figure S20: Calculated frontier molecular orbital surfaces for *B*-(2,6-dimethylphenyl)-**7a**. Top: HOMO. Bottom: LUMO.

Table S2. Atomic coordinates (x, y, z, in Å) for the optimized structure of *B*-Ph-**1a** (Figure 2c) calculated at the DFT (B3LYP/6-31G*) level of theory.

ATOM	X	Y	Z
1 C	0.011279	-0.740995	-4.029050
2 C	0.052227	-1.272124	-6.837165
3 C	0.008877	-2.082998	-4.524847
4 C	0.054303	0.045550	-6.373153
5 C	0.028938	-2.310689	-5.921054
6 C	-0.024608	-2.632521	-1.240508
7 C	-0.031388	-3.285744	0.000000
8 C	-0.024608	-2.632521	1.240508
9 C	-0.014352	-1.200625	1.263130
10 C	0.008877	-2.082998	4.524847
11 C	0.011279	-0.740995	4.029050
12 C	0.033308	0.287254	5.005790
13 C	0.028938	-2.310689	5.921054
14 C	0.052227	-1.272124	6.837165
15 C	0.054303	0.045550	6.373153
16 B	-0.005743	-0.289456	-2.528163
17 B	-0.005743	-0.289456	2.528163
18 H	0.071545	0.876507	-7.073141
19 H	0.068224	-1.485007	-7.902946
20 H	0.026286	-3.336871	-6.280383
21 H	-0.040259	-4.373520	0.000000
22 H	0.034286	1.316830	4.669717
23 H	0.071545	0.876507	7.073141
24 H	0.068224	-1.485007	7.902946
25 H	0.026286	-3.336871	6.280383
26 C	-0.028581	-3.515976	-2.388063
27 C	-0.014001	-3.290830	-3.723831
28 C	-0.014352	-1.200625	-1.263130
29 C	-0.011791	-0.566652	0.000000
30 C	-0.028581	-3.515976	2.388063
31 C	-0.014001	-3.290830	3.723831
32 H	-0.042984	-4.569860	2.113465
33 H	-0.018913	-4.198833	4.325787
34 H	-0.018913	-4.198833	-4.325787
35 H	-0.042984	-4.569860	-2.113465
36 H	-0.005982	0.515406	0.000000
37 C	0.033308	0.287254	-5.005790
38 C	-0.010881	1.284001	2.292343
39 C	-0.022604	4.103087	2.017729
40 C	-1.214569	2.008636	2.224871
41 C	1.186654	2.016731	2.205629
42 C	1.184691	3.406219	2.071195
43 C	-1.224115	3.398077	2.090256
44 C	-0.010881	1.284001	-2.292343
45 C	-0.022604	4.103087	-2.017729

46	C	-1.214569	2.008636	-2.224871
47	C	1.186654	2.016731	-2.205629
48	C	1.184691	3.406219	-2.071195
49	C	-1.224115	3.398077	-2.090256
50	H	2.142209	1.497189	2.252141
51	H	-2.165726	1.482626	2.286866
52	H	-2.165726	1.482626	-2.286866
53	H	0.034286	1.316830	-4.669717
54	H	2.142209	1.497189	-2.252141
55	H	2.127583	3.944314	-2.008461
56	H	-0.027110	5.185255	-1.915974
57	H	-2.171514	3.929767	-2.042688
58	H	-0.027110	5.185255	1.915974
59	H	-2.171514	3.929767	2.042688
60	H	2.127583	3.944314	2.008461

Table S3. Atomic coordinates (x, y, z, in Å) for the optimized structure of **1a** (Figure 3c,d) calculated at the DFT (B3LYP/6-31G*) level of theory.

ATOM		X	Y	Z
1	C	-0.507970	2.295978	4.056925
2	C	-1.150675	2.825433	6.798443
3	C	-0.844439	3.613468	4.497225
4	C	-0.798317	1.535396	6.395969
5	C	-1.161221	3.841545	5.857340
6	C	-0.391825	4.125446	1.234871
7	C	-0.286144	4.779800	0.000951
8	C	-0.101850	4.134464	-1.228125
9	C	-0.063556	2.705389	-1.253364
10	C	0.393989	3.658120	-4.490160
11	C	0.253681	2.309939	-4.036456
12	C	0.386997	1.308302	-5.030675
13	C	0.668589	3.917253	-5.853891
14	C	0.811020	2.901513	-6.784594
15	C	0.664330	1.577202	-6.366132
16	B	-0.165297	1.829930	2.580458
17	B	-0.036108	1.816175	-2.556687
18	H	-0.763847	0.721834	7.115747
19	H	-1.402063	3.035902	7.834754
20	H	-1.415666	4.852460	6.166460
21	H	-0.354878	5.865159	-0.003331
22	H	0.268544	0.272934	-4.737628
23	H	0.757892	0.759790	-7.076247
24	H	1.025471	3.136234	-7.823944
25	H	0.767585	4.951750	-6.173467
26	C	-0.634744	5.015037	2.354898
27	C	-0.846768	4.807530	3.674841
28	C	-0.253452	2.703436	1.270099
29	C	-0.121784	2.071619	0.010449
30	C	0.017115	5.038669	-2.356461
31	C	0.238314	4.848722	-3.677470
32	H	-0.063633	6.085155	-2.066253
33	H	0.309156	5.770190	-4.254162
34	H	-1.046383	5.715479	4.242552
35	H	-0.688870	6.060918	2.056063
36	H	-0.061776	0.987986	0.014369
37	C	-0.483435	1.297225	5.062968
38	C	-0.360240	0.250701	-2.442268
39	C	-0.951952	-2.559354	-2.614240
40	C	-1.704686	-0.211061	-2.645894
41	C	0.669614	-0.731775	-2.315671
42	C	0.339699	-2.096107	-2.397972
43	C	-1.947301	-1.588255	-2.725347

44	C	0.353311	0.318111	2.474688
45	C	1.289943	-2.396594	2.620825
46	C	-0.553823	-0.785207	2.347584
47	C	1.740511	0.024060	2.670692
48	C	2.155501	-1.316141	2.747154
49	C	-0.053920	-2.092330	2.415048
50	C	-2.112598	-0.716388	2.230792
51	C	2.895048	1.048722	2.940473
52	C	-2.972829	0.665146	-2.927421
53	C	2.209371	-0.476059	-2.190143
54	C	4.161328	0.680970	2.120094
55	C	3.250966	0.984991	4.448013
56	C	2.608422	2.520541	2.591482
57	C	1.750388	-3.862467	2.722013
58	C	3.271843	-3.988231	2.929986
59	C	1.381374	-4.613933	1.421463
60	C	1.044767	-4.540664	3.920563
61	C	-2.714804	0.663940	1.910534
62	C	-2.737439	-1.188099	3.569033
63	C	-2.607956	-1.660207	1.104278
64	C	-2.873509	2.160785	-2.573191
65	C	-4.193575	0.143918	-2.122717
66	C	-3.300958	0.561510	-4.439158
67	C	2.638635	0.971084	-1.895318
68	C	2.895925	-0.894004	-3.516675
69	C	2.799778	-1.337505	-1.043907
70	C	-1.301287	-4.050325	-2.772640
71	C	-0.063965	-4.960725	-2.656594
72	C	-2.313118	-4.470894	-1.681931
73	C	-1.930059	-4.282477	-4.166858
74	H	-1.235646	-3.989022	-4.962567
75	H	-2.853128	-3.708556	-4.301184
76	H	-2.174795	-5.343288	-4.303127
77	H	0.682184	-4.730938	-3.425778
78	H	0.417486	-4.876476	-1.675829
79	H	-0.361575	-6.007580	-2.788099
80	H	-2.580683	-5.528840	-1.795695
81	H	-3.236383	-3.884436	-1.734987
82	H	0.303441	-4.594416	1.230387
83	H	-1.888916	-4.332830	-0.681070
84	H	1.881759	-4.162796	0.557038
85	H	1.690551	-5.664542	1.486223
86	H	3.552381	-5.046660	2.981378
87	H	3.595496	-3.515571	3.864324
88	H	-0.044442	-4.537103	3.806956
89	H	1.285032	-4.025503	4.857919
90	H	1.366871	-5.585366	4.014554
91	H	3.834764	-3.537211	2.104820

92	H	-0.750093	-2.916882	2.325311
93	H	3.940750	0.658451	1.047843
94	H	3.201364	-1.516482	2.929203
95	H	4.594326	-0.284028	2.396669
96	H	2.287350	-1.144458	-0.097371
97	H	1.140313	-2.818927	-2.321887
98	H	2.742601	-2.411586	-1.244214
99	H	-2.960588	-1.924442	-2.908129
100	H	-4.505443	-0.864424	-2.407387
101	H	-3.986611	0.140818	-1.047645
102	H	-5.052807	0.802065	-2.298197
103	H	-3.448839	-0.479039	-4.747033
104	H	-4.220733	1.115419	-4.666709
105	H	-2.494031	0.980434	-5.049548
106	H	-2.103613	2.690930	-3.139432
107	H	-3.825373	2.644052	-2.825989
108	H	-2.397350	1.041077	0.936014
109	H	-3.807854	0.572327	1.888961
110	H	-2.485139	1.420154	2.666604
111	H	4.937207	1.437018	2.289733
112	H	-2.433190	-2.717000	1.325555
113	H	-3.690579	-1.539774	0.975259
114	H	-2.124695	-1.432383	0.149805
115	H	-2.378529	-2.182090	3.855785
116	H	-3.829427	-1.239421	3.474155
117	H	-2.505129	-0.496545	4.385227
118	H	-0.200907	0.290778	4.781095
119	H	3.540534	-0.027768	4.747651
120	H	2.401575	1.290814	5.068144
121	H	3.862071	-1.097854	-0.912237
122	H	4.090924	1.656147	4.669038
123	H	1.788776	2.949406	3.173320
124	H	3.496941	3.117362	2.831357
125	H	2.394837	2.660822	1.529144
126	H	-2.693480	2.320877	-1.507657
127	H	2.287617	1.319332	-0.921502
128	H	2.304634	1.677561	-2.659511
129	H	3.734252	1.020023	-1.888219
130	H	2.595015	-0.243718	-4.344604
131	H	2.652344	-1.925096	-3.792826
132	H	3.986197	-0.821872	-3.414146

Table S4. Atomic coordinates (x, y, z, in Å) for the optimized structure of *B*-(2,6-dimethylphenyl)-**1b** (Figure S19) calculated at the DFT (B3LYP/6-31G*) level of theory.

ATOM	X	Y	Z
1 C	4.022968	-0.921121	0.006989
2 C	6.814028	-1.458740	0.026442
3 C	4.514346	-2.263904	0.006358
4 C	6.372883	-0.135062	0.027410
5 C	5.907943	-2.504147	0.015811
6 C	1.229267	-2.801163	-0.008332
7 C	-0.013541	-3.450710	-0.010390
8 C	-1.251269	-2.791541	-0.007505
9 C	-1.268562	-1.359927	-0.004121
10 C	-4.532157	-2.228442	0.005152
11 C	-4.030062	-0.889703	0.006367
12 C	-5.004058	0.140727	0.014678
13 C	-5.927685	-2.457682	0.012003
14 C	-6.825437	-1.405062	0.020296
15 C	-6.373640	-0.084993	0.021818
16 B	2.525088	-0.455340	-0.001979
17 B	-2.528711	-0.435772	-0.000212
18 H	7.084867	0.683389	0.035545
19 H	6.275203	-3.525326	0.014994
20 H	-0.017764	-4.538405	-0.013540
21 H	-4.662318	1.169551	0.015750
22 H	-7.079046	0.739121	0.028233
23 H	-6.302847	-3.475996	0.010863
24 C	2.373925	-3.689027	-0.010170
25 C	3.710418	-3.471132	-0.003928
26 C	1.257754	-1.369724	-0.005053
27 C	-0.002946	-0.732081	-0.004199
28 C	-2.402931	-3.670287	-0.008491
29 C	-3.737666	-3.441899	-0.003094
30 H	-2.132087	-4.725054	-0.013624
31 H	-4.343359	-4.346870	-0.004759
32 H	4.309022	-4.380803	-0.006182
33 H	2.094775	-4.741638	-0.016430
34 H	0.001407	0.351541	-0.003254
35 C	5.005143	0.101542	0.017369
36 C	-2.284610	1.138336	-0.002291
37 C	-1.955417	3.936603	-0.006706
38 C	-2.201368	1.849362	-1.221811
39 C	-2.194675	1.852418	1.214965
40 C	-2.031230	3.242216	1.198202
41 C	-2.037892	3.239199	-1.209422
42 C	2.292949	1.120516	-0.007179
43 C	1.984762	3.921174	-0.017817
44 C	2.215501	1.829514	-1.228297

45	C	2.208524	1.837976	1.208461
46	C	2.055479	3.228929	1.188637
47	C	2.062277	3.220536	-1.218989
48	H	4.671561	1.133038	0.017838
49	H	1.987678	3.770404	2.129770
50	H	1.864826	5.001553	-0.021957
51	H	2.000052	3.755535	-2.164210
52	H	-1.827476	5.016080	-0.008423
53	H	-1.971314	3.775760	-2.153463
54	H	-1.959298	3.781080	2.140539
55	Cl	8.536220	-1.803446	0.038778
56	Cl	-8.550405	-1.735571	0.028887
57	C	2.311471	1.095157	-2.549863
58	C	2.297292	1.113092	2.535762
59	C	-2.287986	1.125177	2.540641
60	C	-2.301443	1.118565	-2.545036
61	H	3.267461	0.614008	2.658560
62	H	2.171818	1.804002	3.375679
63	H	1.527430	0.336407	2.625898
64	H	3.279150	0.588336	-2.659827
65	H	1.536837	0.323387	-2.641893
66	H	2.198648	1.781252	-3.395492
67	H	-2.160893	1.813911	3.382107
68	H	-1.521091	0.345467	2.630081
69	H	-3.260176	0.629535	2.661267
70	H	-1.532157	0.341577	-2.637904
71	H	-2.182875	1.805691	-3.389043
72	H	-3.272580	0.618901	-2.657265

Table S4. Atomic coordinates (x, y, z, in Å) for the optimized structure of *B*-(2,6-dimethylphenyl)-**7a** (Figure S19) calculated at the DFT (B3LYP/6-31G*) level of theory.

ATOM		X	Y	Z
1	C	-3.985787	0.620084	0.084584
2	C	-6.807025	1.171272	-0.148305
3	C	-4.470305	1.959189	-0.042562
4	C	-6.332172	-0.150194	-0.031881
5	C	-5.857848	2.194972	-0.141983
6	C	-1.181717	2.475240	-0.048907
7	C	0.068432	3.105752	-0.137819
8	C	1.294857	2.426524	-0.181662
9	C	1.287540	0.995307	-0.172497
10	C	4.560908	1.791905	-0.099311
11	C	4.028598	0.465822	-0.155600
12	C	4.977926	-0.583559	-0.074227
13	C	5.952253	1.983386	0.026961
14	C	6.860718	0.927214	0.134509
15	C	6.338958	-0.379467	0.081105
16	B	-2.497445	0.158090	0.213495
17	B	2.526748	0.052665	-0.296981
18	H	-7.031230	-0.980736	-0.056276
19	H	-6.198401	3.225770	-0.200045
20	H	0.087953	4.192887	-0.174390
21	H	4.618313	-1.605571	-0.123764
22	H	7.002722	-1.235227	0.171688
23	H	6.332022	3.001087	0.020919
24	C	-2.319397	3.372926	-0.041277
25	C	-3.657551	3.161804	-0.048036
26	C	-1.226348	1.046878	0.031902
27	C	0.019207	0.388177	-0.051909
28	C	2.465267	3.279286	-0.243316
29	C	3.794171	3.020596	-0.200192
30	H	2.217642	4.338078	-0.305565
31	H	4.421575	3.910578	-0.233952
32	H	-4.251070	4.074752	-0.073483
33	H	-2.032689	4.423552	-0.060337
34	H	-0.001573	-0.694626	-0.021147
35	C	-4.975648	-0.395640	0.094477
36	C	2.246673	-1.482988	-0.617608
37	C	1.821495	-4.194028	-1.265417
38	C	2.186707	-1.898619	-1.969322
39	C	2.088544	-2.448946	0.402866
40	C	1.879355	-3.792217	0.066434
41	C	1.973835	-3.247332	-2.276429
42	C	-2.268658	-1.375381	0.585966
43	C	-1.940784	-4.078548	1.317278
44	C	-2.155792	-2.378591	-0.403898
45	C	-2.214636	-1.749800	1.949851

46	C	-2.050823	-3.095542	2.298522
47	C	-1.994626	-3.717524	-0.026374
48	C	-2.192908	-2.021112	-1.875800
49	C	-2.354797	-0.708504	3.041810
50	C	2.372008	-0.899125	-3.093042
51	C	2.128764	-2.046483	1.863060
52	C	-8.242890	1.442838	-0.258919
53	C	8.294324	1.187961	0.289990
54	C	8.915470	2.317079	0.777710
55	C	10.336183	2.230743	0.788768
56	C	10.797354	1.034837	0.309340
57	S	9.497560	-0.005875	-0.167688
58	C	-9.295376	0.654647	0.152140
59	C	-10.573946	1.224873	-0.105491
60	C	-10.495081	2.446944	-0.715747
61	S	-8.850724	2.919033	-0.989502
62	H	-11.511435	0.746980	0.157480
63	H	-9.156208	-0.297498	0.652300
64	H	-11.302326	3.096998	-1.025990
65	H	10.985865	3.022786	1.145322
66	H	8.366270	3.176768	1.145840
67	H	11.821637	0.703391	0.203802
68	H	3.015071	-1.444526	2.098641
69	H	1.251002	-1.448689	2.138765
70	H	2.139713	-2.926370	2.514332
71	H	1.757929	-4.525896	0.860159
72	H	1.659245	-5.239798	-1.514993
73	H	1.933781	-3.555967	-3.319024
74	H	-3.342254	-0.229338	3.017303
75	H	-2.227306	-1.154137	4.033866
76	H	2.230891	-1.370830	-4.070983
77	H	3.377766	-0.459310	-3.079397
78	H	-1.611995	0.092473	2.938545
79	H	-3.053004	-1.386226	-2.121747
80	H	-4.651217	-1.425509	0.195707
81	H	-2.251090	-2.919393	-2.498694
82	H	-1.291241	-1.473188	-2.176761
83	H	-1.908522	-4.479982	-0.797161
84	H	-1.816746	-5.121316	1.599267
85	H	-2.014156	-3.372539	3.350306
86	H	1.661500	-0.065998	-3.019604

Table S5. Atomic coordinates (x, y, z, in Å) for the optimized structure of *B*-(2,6-dimethylphenyl)-**7b** (Figure 4b, c) calculated at the DFT (B3LYP/6-31G*) level of theory.

ATOM	X	Y	Z
1 C	4.006867	-0.098379	-0.316640
2 C	6.834443	0.402187	-0.122576
3 C	4.516307	1.235699	-0.219456
4 C	6.338908	-0.916272	-0.217237
5 C	5.906150	1.450430	-0.134769
6 C	1.238341	1.807808	-0.151206
7 C	0.002338	2.460189	-0.034499
8 C	-1.232892	1.803049	0.064386
9 C	-1.250138	0.371813	0.078592
10 C	-4.510732	1.227588	0.166240
11 C	-4.000033	-0.108906	0.206426
12 C	-4.970602	-1.144805	0.203197
13 C	-5.902483	1.445247	0.132051
14 C	-6.832196	0.398397	0.120110
15 C	-6.335397	-0.922486	0.152217
16 B	2.509028	-0.532913	-0.420381
17 B	-2.500254	-0.547084	0.263129
18 H	7.034666	-1.749781	-0.217807
19 H	6.279051	2.468759	-0.072961
20 H	0.001770	3.548063	-0.017727
21 H	-4.622457	-2.171136	0.244377
22 H	-7.031771	-1.755458	0.147440
23 H	-6.275737	2.465174	0.114293
24 C	2.389812	2.686052	-0.207726
25 C	3.723749	2.452186	-0.225432
26 C	1.256801	0.377883	-0.211424
27 C	0.003619	-0.258177	-0.078151
28 C	-2.384427	2.678501	0.151453
29 C	-3.717891	2.443572	0.183939
30 H	-2.115735	3.733952	0.169564
31 H	-4.327490	3.345584	0.221021
32 H	4.333728	3.354696	-0.232268
33 H	2.120405	3.741485	-0.205731
34 H	0.003986	-1.341506	-0.097017
35 C	4.976507	-1.134947	-0.321162
36 C	-2.233202	-2.090146	0.565528
37 C	-1.839712	-4.814821	1.176671
38 C	-2.139957	-2.519508	1.910922
39 C	-2.125467	-3.049796	-0.467124
40 C	-1.930886	-4.399643	-0.149283
41 C	-1.943870	-3.874950	2.200007
42 C	2.243130	-2.060719	-0.792599
43 C	1.841038	-4.752561	-1.530837
44 C	2.128373	-3.066746	0.194239
45 C	2.152756	-2.427002	-2.156815

46	C	1.951947	-3.766713	-2.509150
47	C	1.929450	-4.399554	-0.186853
48	C	2.206263	-2.718077	1.666503
49	C	2.291552	-1.382733	-3.246071
50	C	-2.272416	-1.526505	3.047719
51	C	-2.209349	-2.631893	-1.921027
52	H	-3.103268	-2.028116	-2.121450
53	H	-1.341224	-2.029045	-2.215844
54	H	-2.239695	-3.504340	-2.581657
55	H	-1.848350	-5.128052	-0.952786
56	H	-1.689319	-5.865697	1.411726
57	H	-1.878862	-4.193802	3.238391
58	H	3.289084	-0.924460	-3.239391
59	H	2.134496	-1.820108	-4.237583
60	H	-2.115871	-2.009816	4.017691
61	H	-3.267970	-1.064284	3.063016
62	H	1.567786	-0.567227	-3.123243
63	H	3.099115	-2.124853	1.899868
64	H	4.629669	-2.158706	-0.410002
65	H	2.233730	-3.620850	2.285146
66	H	1.336363	-2.130527	1.985632
67	H	1.841325	-5.164230	0.581616
68	H	1.687558	-5.790763	-1.815039
69	H	1.887191	-4.036379	-3.561380
70	H	-1.545409	-0.708913	2.961867
71	C	-8.227351	0.662663	0.088517
72	C	-9.423935	0.890394	0.070128
73	C	8.227055	0.663863	-0.026833
74	C	9.421171	0.891375	0.053056
75	C	-10.815938	1.168370	0.051300
76	C	-13.613724	1.736493	0.018534
77	C	-11.773064	0.133973	0.062760
78	C	-11.293966	2.493870	0.019587
79	C	-12.650680	2.775438	0.001512
80	C	-13.132334	0.404606	0.045651
81	C	10.810474	1.168977	0.144160
82	C	13.602813	1.735949	0.322151
83	C	11.287385	2.494650	0.188551
84	C	11.766054	0.134100	0.190545
85	C	13.122843	0.403992	0.276386
86	C	12.641592	2.775627	0.274207
87	N	-14.967366	2.011850	0.011478
88	N	14.953030	2.010897	0.411415
89	C	15.918595	0.925487	0.411587
90	C	15.416327	3.387361	0.416016
91	C	-15.429086	3.384583	-0.099526
92	C	-15.930082	0.925067	-0.041427
93	H	-16.939463	1.339914	-0.028588

94	H	-15.830187	0.257777	0.824959
95	H	-15.822378	0.317061	-0.952042
96	H	-15.103462	3.858697	-1.037421
97	H	-16.519837	3.398499	-0.073347
98	H	-15.065990	3.999913	0.734506
99	H	-12.964862	3.811949	-0.025430
100	H	-10.579364	3.311613	0.007236
101	H	-11.434680	-0.897823	0.084006
102	H	-13.826419	-0.426969	0.052282
103	H	15.777393	0.256633	1.271841
104	H	15.855941	0.318671	-0.503328
105	H	16.925621	1.341611	0.472365
106	H	10.574105	3.312873	0.153111
107	H	12.955884	3.812080	0.302397
108	H	13.816106	-0.427736	0.307626
109	H	11.428321	-0.897599	0.157836
110	H	15.133684	3.921169	-0.503079
111	H	16.504688	3.398689	0.492316
112	H	15.012845	3.948462	1.270323

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