Electronic Supplementary Material (ESI) for Dalton Transactions.

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1. General experimental procedures

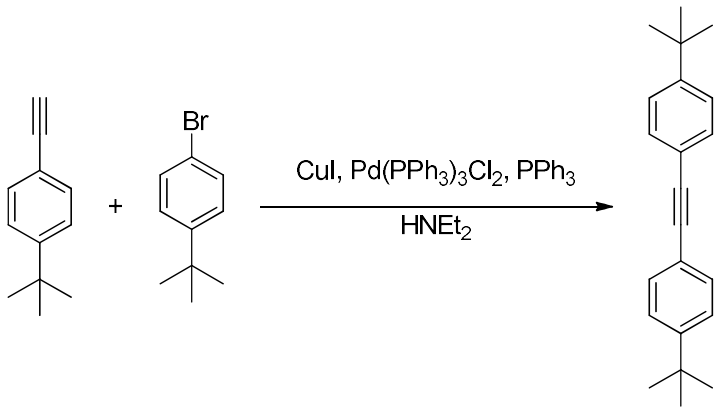
If not stated otherwise, all reactions and manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques or in an inert-atmosphere glovebox. Et_2O, THF, *n*-hexane, and toluene were distilled from Na/benzophenone prior to use. CH_2Cl_2, Me_3SiCl, and $HNEt_2$ were distilled from CaH_2. DMF, MeOH, and SMe_2 were dried over molecular sieves (3 Å). BBr_3 was stored over Hg to remove contaminations with HBr or Br_2. 2-Methyl-5-(trimethylstannyl)thiophene[S1] and 2,3,6,7-Cl_4-9,10-Mes_2-DBA [S2] were prepared according to literature procedures. B_2pin_2 (*AllyChem*, China), *n*-BuLi (*Albemarle*, Germany), and $Pd(PPh_3)_2Cl_2$ (*Heraeus Noble Metals*, Germany) were donated by the suppliers and used as received.

NMR spectra were recorded at 298 K using the following spectrometers: Bruker DPX-250, Avance-400, Avance-500, or DRX-600. Chemical shift values are referenced to (residual) solvent signals ($^1H/^{13}C\{^1H\}$; $CHCl_3$: δ = 7.26/77.2 ppm, C_6HD_5: δ = 7.16/128.1 ppm, THF-*d*^{7}: δ = 1.72, 3.58/25.3, 67.2 ppm) or external $BF_3{\cdot}Et_2O$ ($^{11}B\{^1H\}$: 0.0 ppm), $Si(CH_3)_4$ ($^{29}Si\{^1H\}$: 0.0 ppm), and $SnMe_4$ ($^{119}Sn\{^1H\}$: 0.0 ppm). Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br. = broad, n.o. = not observed. Resonances of carbon atoms attached to boron atoms were typically broadened and sometimes not observed due to the quadrupolar relaxation of boron. Resonance assignments were aided by ^{H,H}COSY, ^{H,C}HSQC, and, if necessary, also ^{H,C}HMBC spectra; the numbering schemes sometimes deviate from IUPAC recommendations and follow the nomenclature given in the reaction schemes.

For photochemical reactions, a medium pressure Hg lamp was used (*Heraeus* Noblelight; TQ 150, 150 W). The microwave-assisted reactions were carried out in a *Biotage* Initiator$^+$ synthesizer using septum-capped vials; the temperatures were monitored by an infrared sensor. Flash chromatography was performed with a *Biotage* Isolera One system using *Interchim* puriFlash cartridges (25µm spherical silica). Melting points were determined using an MPM-H2 melting point meter (*Schorpp Gerätetechnik*). UV/Vis absorption spectra were recorded at room temperature using a *Varian* Cary 60 Scan UV/Vis spectrophotometer. Photoluminescence (PL) spectra were recorded at room temperature using a *Jasco* FP-8300 spectrofluorometer equipped with a calibrated *Jasco* ILF-835 100 mm diameter integrating sphere and analyzed using the *Jasco* FWQE-880 software. For PL quantum yield (Φ_{PL}) measurements, each sample was carefully degassed with Ar using an injection needle and a septum capped cuvette. Under these conditions the Φ_{PL} of the fluorescence standard 9,10-diphenylanthracene was determined as 97% (lit.: 97%).[S3,4] For all Φ_{PL} measurements, at least three samples of different concentrations were used (range between 10^{-5} and 10^{-7} mol L^{-1}). Due to self-absorption, slightly lower Φ_{PL} values were generally observed at higher concentrations. This effect was corrected by applying a method reported by *Bardeen et al.*, which slightly improved the Φ_{PL} values (4% at most).[S5] Cyclic voltammetry (CV) measurements were performed in a glovebox at room temperature in a one-chamber, three-electrode cell using an *EG&G* Princeton Applied Research 263A potentiostat. A platinum-disk electrode (2.00 mm diameter) was used as the working electrode with a platinum wire counter electrode and a silver wire reference electrode, which was coated with AgCl by immersion into HCl/HNO_3 (3:1). Prior to measurements, the solvent THF was dried with NaK. [*n*-Bu_4N][PF_6] (e-chem grade, *Sigma Aldrich*; used as received) was employed as the supporting electrolyte (0.1 mol L^{-1}). All potential values were referenced against the FcH/FcH^+ redox couple (FcH = ferrocene; $E_{1/2}$ = 0 V). Scan rates were varied between 100 and 400 mV s^{-1}. High-resolution mass spectra were measured in positive mode using a *Thermo Fisher Scientific* MALDI LTQ Orbitrap XL spectrometer and either 2,5-dihydroxybenzoic acid or α-cyano-4-hydroxycinnamic acid was used as the matrix. Elemental analyses were performed by the microanalytical laboratory of the Goethe-University, Frankfurt.

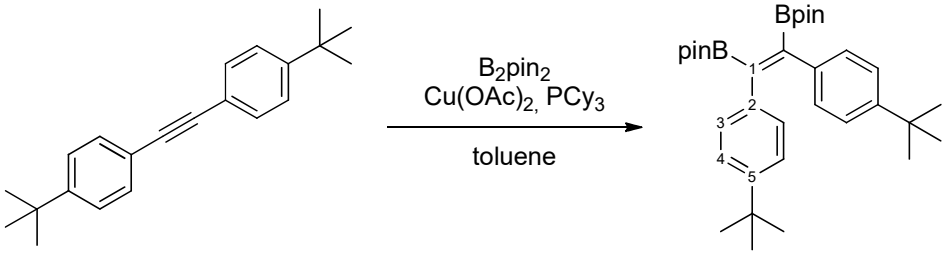
2. Syntheses, purification methods, and analytical data

2.1 Synthesis of 2^{H}·2SMe



Synthesis of 1,2-bis(4-*tert*.-butylphenyl)acetylene (A): A suspension of CuI (8.0 mg, 40 µmol, 0.3 mol%), $Pd(PPh_3)_2Cl_2$ (85.0 mg, 120 µmol, 1 mol%), PPh_3 (130 mg, 480 µmol, 4 mol%), 4-*tert*.-butylphenylacetylene (2.30 mL, 12.6 mmol), and 4-*tert*.-butylbromobenzene (2.10 mL, 12.0 mmol) in dry $HNEt_2$ (60 mL) was degassed by three freeze-pump-thaw cycles. The reaction mixture was heated to 80 °C for 18 h in a sealed flask. After cooling to room temperature, the mixture was poured into H_2O (150 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2x50 mL) and the combined organic layers were washed with water (50 mL) and brine (50 mL). After drying over Na_2SO_4 and filtration, all volatiles were removed with the aid of a rotary evaporator. The oily residue was purified by column chromatography (cyclohexane) to furnish **A** as a colorless solid. Yield: 2.97 g (10.2 mmol, 85%).

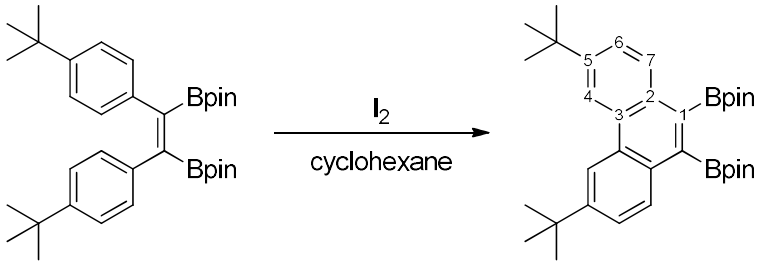
^{1}H-NMR (400 MHz, $CDCl_3$):[S6] δ = 7.47-7.35 (m, 8H), 1.33 (s, 18H)



Synthesis of *cis*-1,2-bis(4-*tert*.-butylphenyl)-1,2-bis(pinacolboryl)ethene[S7] **(B):** A solution of $Cu(OAc)_2$ (anhydrous, 0.20 g, 1.1 mmol, 4 mol%) and PCy_3 (1.00 g, 3.86 mmol) in dry, degassed MeOH (8 mL) was heated to 80 °C for 30 min in a sealed flask. After evaporation of the solvent, **A** (8.00 g, 33.1 mmol), B_2pin_2 (8.45 g, 33.3 mmol), and dry, degassed toluene (20 mL) were added and the resulting turbid mixture was heated to 80 °C for 20 h. After cooling to room temperature, the reaction mixture was filtered through a plug of Celite353®. The plug was rinsed with EtOAc until the eluate was nearly colorless. The filtrate was washed with brine (3x100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness using a rotary evaporator. **B** was obtained as an off-white solid. Yield: 16.34 g (30.00 mmol, 90%). Crystals of **B** suitable for X-ray analysis were grown by slow evaporation of a solution of the product in $CDCl_3$. *Note:* The product should not be purified by column chromatography, because it tends to decompose on silica gel. Thus, samples of the product sometimes turned green upon prolonged storage, which is due to traces of residual Cu(I) getting

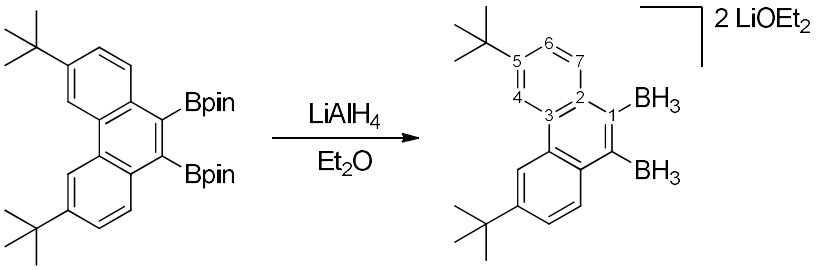
oxidized. These Cu contaminations can be removed by vacuum distillation. In the present case, this is, however, unnecessary, because they do not affect the subsequent photocyclization step.
This compound is literature known.[S8] Its NMR-spectra were reported in CD_2Cl_2. The resonances in $CDCl_3$ are given below:

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.04-7.01 (m, 4H; H-4), 6.82-6.80 (m, 4H; H-3), 1.33 (s, 24H; CH_3^{pin}), 1.21 (s, 18H; $C(CH_3)_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 148.4 (C-5), 146.3* (br.; C-1), 138.5 (br.; C-2), 129.1 (C-3), 124.2 (C-4), 84.1 (C_{quart}^{pin}), 34.4 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$), 25.1 (CH_3^{pin}); *) this resonance was unequivocally detected only in the ^{H,C}HMBC spectrum
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = 31.2 ($h_{1/2}$ = 470 Hz)



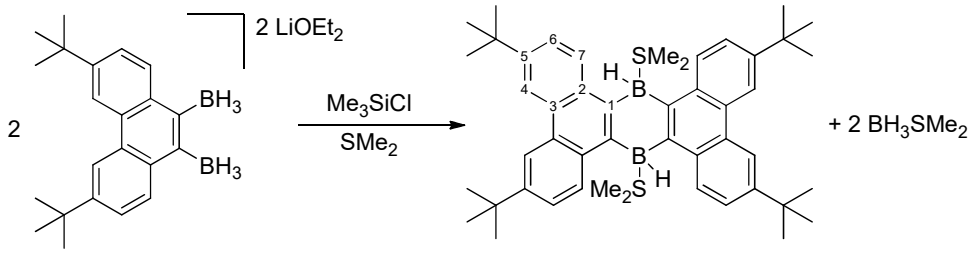
Synthesis of 3,6-di-*tert*.-butyl-9,10-bis(pinacolboryl)phenanthrene (1): A solution of **B** (814 mg, 1.50 mmol) and I_2 (105 mg, 410 µmol) in cyclohexane (800 mL, distilled prior to use) was prepared in a 1000 mL flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg lamp. After purging with Ar for 30 min, propylene oxide (10 mL) was added and the deep purple mixture was irradiated for 2 h. Within this time, more I_2 (436 mg, 1.72 mmol) was added as a neat solid whenever the solution had become colorless (four portions). After the final addition, the mixture was irradiated for further 65 min and then filtered through basic Al_2O_3. The filtrate was evaporated to dryness using a rotary evaporator and the remaining yellow solid was washed with EtOAc to furnish **1** as a colorless solid. Yield: 630 mg (1.17 mmol, 78%). *Note:* The reaction was also performed at higher concentrations (2.3 mM), which resulted in lower yields (69%) and the occurrence of some side-products.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.65 (d, ^4J(H,H) = 1.9 Hz, 2H; H-4), 8.37 (d, ^3J(H,H) = 8.7 Hz, 2H; H-7), 7.64 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.9 Hz, 2H; H-6), 1.50 (s, 24H; CH_3^{pin}), 1.49 (s, 18H; $C(CH_3)_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 149.0 (C-5), 134.4* (br.; C-1), 131.9 (C-2), 130.4 (C-3), 128.7 (C-7), 124.6 (C-6), 117.9 (C-4), 84.4 (C_{quart}^{pin}), 35.2 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 25.5 (CH_3^{pin}); *) this resonance was unequivocally detected only in the ^{H,C}HMBC spectrum
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = 33.0 ($h_{1/2}$ = 370 Hz)
HRMS: Calculated *m*/*z* for $C_{34}H_{48}B_2O_4$ (M^+): 542.3788, found: 542.3782



Synthesis of dilithium-3,6-di-*tert.*-butyl-9,10-bis(trihydridoborato)phenanthrene bis(diethyletherate) (C) : $LiAlH_4$ (1 M in Et_2O, 11.0 mL, 11.0 mmol) was added dropwise with stirring at 0 °C to a suspension of **1** (2.00 g, 3.69 mmol) in dry Et_2O (25 mL). The turbid mixture was stirred at 0 °C for further 2 h and then allowed to warm to room temperature. The slurry was filtered under N_2 using a Schlenk frit and the solvent removed from the clear filtrate under reduced pressure, leaving behind **C** as a colorless solid. Yield: 1.10 g (2.30 mmol, 62%). Crystals suitable for X-ray analysis were obtained by layering an Et_2O solution of the product with dry *n*-hexane (gas-phase diffusion may also be applied). *Note*: The number of coordinated solvent molecules was independently determined by ^{1}H-NMR spectroscopy and X-ray crystallography.

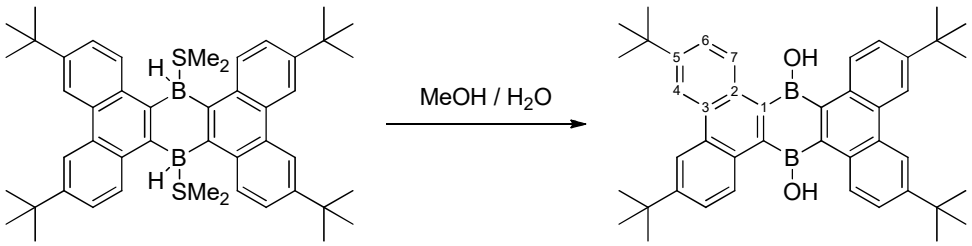
^{1}H-NMR (500 MHz, THF-*d*^{8}): δ = 8.79 (d, ^3J(H,H) = 8.8 Hz, 2H; H-7), 8.51 (d, ^4J(H,H) = 2.1 Hz, 2H; H-4), 7.41 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.1 Hz, 2H; H-6), 3.38 (q, 12H; CH_2CH_3), 1.46 (s, 18H; $C(CH_3)_3$), 1.46 (q, ^1J(B,H) = 80 Hz, 6H; BH_3), 1.12 (t, 8H; CH_2CH_3)
^{13}C{^{1}H}-NMR (126 MHz, THF-*d*^{8}): δ =149.1* (C-1), 145.1 (C-5), 137.8 (C-2), 131.3 (br.; C-7), 129.7 (C-3), 122.4 (C-6), 117.0 (C-4), 66.1 (CH_2CH_3), 35.1 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 15.5 (CH_2CH_3); *) this resonance was unequivocally detected only in the ^{H,C}HMBC spectrum
^{11}B{^{1}H}-NMR (161 MHz, THF-*d*^{8}): δ = –31.2 (q, ^1J(B,H) = 80 Hz)



Synthesis of 2^H·2SMe$_2$: A thick-walled glass ampoule was charged with **C** (1.01 g, 2.76 mmol), dry SMe_2 (25 mL), and Me_3SiCl (1.20 mL, 9.09 mmol) at room temperature. The ampoule was immersed in liq. N_2, flame-sealed under vacuum, and heated to 60 °C for 4 d. After cooling to room temperature, the ampoule was opened under N_2, the content was filtered, and the filter cake rinsed with dry SMe_2 (2x5 mL). The filtrate was evaporated under reduced pressure, whereupon a yellow solid mixture of 2^H·2SMe_2 and BH_3·SMe_2 remained, which could not be separated: Prolonged storage under a dynamic vacuum quantitatively removed all SMe_2 ligands from the diborane 2^H, but some BH_3•SMe_2 was nevertheless still present. Crystals of 2^H ·2SMe_2 suitable for X-ray analysis were obtained by layering an SMe_2 solution of the 2^H·2SMe_2/BH_3·SMe_2 mixture with dry *n*-hexane (gas-phase diffusion may also be applied).

2^{H}·2SMe_2 after excess SMe_2 had been added to the NMR sample prior to vacuum sealing.
^{1}H-NMR (500 MHz, C_6D_6): δ = 9.54 (d, ^3J(H,H) = 8.8 Hz, 4H; H-7), 9.15 (d, ^4J(H,H) = 1.1 Hz, 4H; H-4), 7.87 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 1.1 Hz, 4H; H-6), 1.69 (s, S(CH_3)$_2$), 1.55 (s, 36H; C(CH_3)$_3$), n.o. (BH)
^{13}C{^{1}H}-NMR (126 MHz, C_6D_6): δ = 147.8 (C-5), 134.7 (C-2), 130.8 (C-3), 129.8 (C-7), 124.0 (C-6), 118.6 (C-4), 35.2 (*C*(CH_3)$_3$), 31.8 (C(*C*H_3)$_3$), 17.8 (S(CH_3)$_2$), n.o. (C-1)
^{11}B-NMR (160 MHz, C_6D_6): δ = n.o.
^{11}B{^{1}H}-NMR (160 MHz, C_6D_6): δ = n.o.

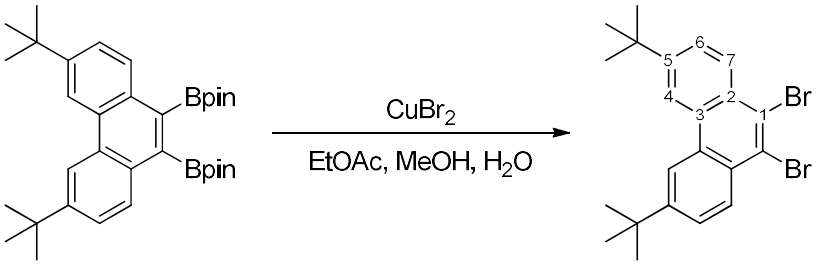
2^{H}·2SMe_2 after the sample had been stored at room temperature under a dynamic vacuum for prolonged time (4 h).
^{1}H-NMR (300 MHz, C_6D_6): δ = 9.49 (d, ^3J(H,H) = 8.8 Hz, 4H; H-7), 9.13 (d, ^4J(H,H) = 1.9 Hz, 4H; H-4), 7.85 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.9 Hz, 4H; H-6), 1.53 (s, 36H; C(C*H*$_3$)$_3$) 1.07 (s, residual BH_3•2SMe_2)
^{13}C{^{1}H}-NMR (126 MHz, C_6D_6): δ = 149.3 (C-5), 134.5 (C-2), 131.7 (C-3), 130.1 (C-7), 124.6 (C-6), 118.6 (C-4), 35.2 (*C*(CH_3)$_3$), 31.6 (C(*C*H_3)$_3$) 17.8 (residual BH_3•2SMe_2)
^{11}B-NMR (160 MHz, C_6D_6): δ = n.o.
^{11}B{^{1}H}-NMR (160 MHz, C_6D_6): δ = n.o.



Synthesis of 2^{OH}: Dry MeOH (6 mL) was added to neat **2^{H}** (20 mg, 33µmol) and the resulting suspension was stirred at room temperature for 1 h. After filtration, the filter cake was dried *in vacuo*; it contained virtually pure **2^{OMe}** (colorless solid). Yield: 18 mg (27µmol, 82%).
The solid (12 mg, 19 µmol) was immediately taken up in CH_2Cl_2 (10 mL) and the organic layer was washed with brine (10 mL). After evaporation of the solvent, **2^{OH}** was obtained as a colorless solid. Yield: 9 mg (14 µmol, 78%). Crystals of **2^{OH}** suitable for x-ray analysis were obtained by slow evaporation of a solution of **2^{OH}** in EtOAc.

2^{OMe}:
^{1}H-NMR (500 MHz, C_6D_6): δ = 8.72 (dd, ^4J(H,H) = 1.8 Hz, 4H; H-4), 8.42 (d, ^3J(H,H) = 8.6 Hz, 4H; H-7), 7.75 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 1.8 Hz, 4H; H-6), 4.06 (s, 6H; OCH_3), 1.52 (s, 36H; C(CH_3)$_3$)

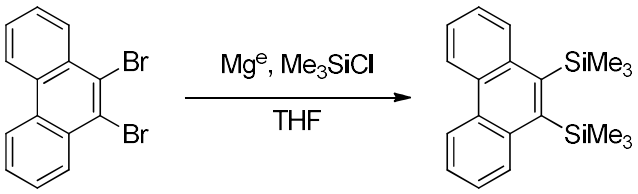
2^{OH}:
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.80 (s, 4H; H-4), 8.75 (d, ^3J = 8.6 Hz, 4H; H-7), 7.82 (d, ^3J = 8.6 Hz, 4H; H-6), 6.71 (s, 2H; OH), 1.55 (s, 36H; C(CH_3)$_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 150.2 (C-5), 142.8 (br.; C-1), 131.3 (C-3), 130.3 (C-2), 128.8 (C-7), 125.4 (C-6), 118.8 (C-4), 35.4 (*C*(CH_3)$_3$), 31.6 (C(*C*H_3)$_3$)
^{11}B-NMR (160 MHz, $CDCl_3$): δ = n.o.
HRMS: Calculated *m*/*z* for $C_{44}H_{50}B_2O_2$ (M^+): 632.3991, found: 362.3987



Synthesis of 3,6-di-*tert.*-butyl-9,10-dibromophenanthrene (D): A 250 mL J. Young screw spindle flask was charged with **1** (500 mg, 922 µmol), and $CuBr_2$ (2.06 g, 9.22 mmol). The flask was evacuated and backfilled with N_2 three times. After addition of EtOAc (12 mL), MeOH (40 mL) and H_2O (28 mL), the flask was cautiously evacuated and the screw spindle tap closed. It was then placed in an oil bath (130 °C) for four hours. After cooling to room temperature, the obtained suspension was filtered and the filter cake was rinsed with CH_2Cl_2 (4x10 mL). The layers of the filtrate were separated and the aqueous layer was extracted with CH_2Cl_2 (3x20 mL). The combined extracts were washed with $NH_{3(aq)}$ (12% in H_2O, 2x20 mL), H_2O (35 mL), and brine (35 mL). After drying over $MgSO_4$ and filtration, all volatiles were removed with the aid of a rotary evaporator to give **D** as a colorless solid. Yield: 340 mg (650 mmol, 70%)

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.65 (d, ^4J(H,H) = 1.7 Hz, 2H; H-4), 8.39 (d, ^3J(H,H) = 8.7 Hz, 2H; H-7), 7.73 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.8 Hz, 2H; H6), 1.51 (s, 18H; $C(CH_3)_3$)
^{13}C-NMR (126 MHz, $CDCl_3$) δ = 150.6 (C-5), 130.4 (C-1), 129.6 (C-3), 129.6 (C-7), 126.5 (C-6), 125.2 (C-2), 118.4 (C-4), 35.3 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$)
HRMS: Calculated *m*/*z* for $C_{22}H_{24}Br_2$ (M^+): 448.0212, found: 448.0211

Note: It was not possible to convert **D** into 3,6-*t*-Bu_2-9,10-$(SiMe_3)_2$-phenanthrene, as *t*-Bu substituted vicinally dibrominated aromatics react only sluggishly in Grignard-type silylation reactions [*Adv. Synth. Catal. 2010*, **352**, 3443-3449]. As a substitute, we synthesized 9,10-$(SiMe_3)_2$-phenanthrene (**E**) as described below. The synthesis of 9,10-Br_2-phenanthrene was conducted as described for its *t*-Bu_2 derivative.



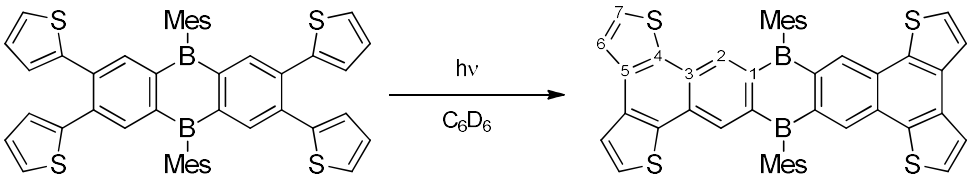
Synthesis of 9,10-bis(trimethylsilyl)phenanthrene (3): Mg turnings (145 mg, 5.95 mmol) were placed in a two necked flask equipped with a reflux condenser / gas inlet and a dropping funnel. After addition of dry THF (10 mL) a crystal of I_2 was added, followed by neat Me_3SiCl (1.50 mL, 11.9 mmol), and solid 9,10-dibromophenanthrene (500 mg, 1.49 mmol). The mixture was heated to 60 °C and a solution of 1,2-dibromoethane (0.03 mL, 300 µmol) in dry THF (2 mL) was added dropwise in the course of 30 min. The reaction mixture was cooled to room temperature and stirred overnight. The turbid mixture was filtered through glass wool onto saturated aqueous $NaHCO_3$ solution (20 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3x20 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and evaporated to dryness with the aid of a rotary evaporator. The crude product was purified by RP flash chromatography (MeOH / TBME = 3:1) to furnish **3** as colorless crystals. Yield: 86 mg (0.27 mmol, 18%).

^{1}H-NMR (300 MHz, $CDCl_3$):[S9] δ = 8.58 (dd, 2H, ^3J(H,H) = 8.58 Hz, ^4J(H,H) = 1.28 Hz), 8.14 (dd, 2H, ^3J(H,H) = 8.14 Hz, ^4J(H,H) = 1.23 Hz), 7.60-7.52 (m, 4H), 0.5 (s, 18H)

An attempted cyclocondensation / mesitylation sequence (cf. synthesis of **8**) did not furnish the **2^{Mes}** derivative after purification by column chromatography (cyclohexane → EtOAc).

Note: All syntheses described in this chapter (besides those of **C** and **2^H**) have also been performed with starting materials devoid of *t*-Bu groups. The yields were usually comparable to those described above. Only in the case of the 9,10-disilylated phenanthrenes, the synthesis worked better for **3** than for its *tert.*-butylated congener. For some of these compounds (denoted with a prime, e.g. **B'**), single crystals were obtained and their solid state structures determined by X-ray analysis. The structures are deposited with the CCDC and can be accessed via the following codes: **B'**: 1883317, **1'**: 1883315, **D'**: 1883316, **3**: 1883314.

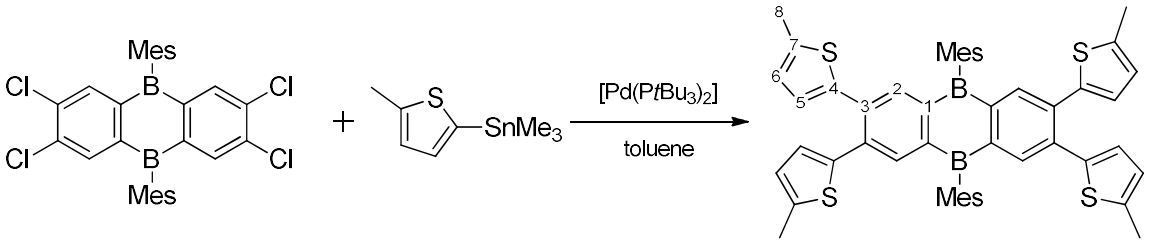
2.2 Synthesis of 6^H



An NMR tube was charged with **4^H** (5.0 mg, 6.8 μmol) and C_6D_6 (0.6 mL) and placed close (approx. 1.5 cm) to a water-cooled quartz immersion well containing a medium pressure Hg lamp. The sample was irradiated for 6 h. The resulting brown-colored solution was transferred to a flask, and all volatiles were removed in vacuo. The purification of the crude product by flash chromatography (cyclohexane/EtOAc 98:2 → cyclohexane/EtOAc 85:15) afforded **6^H** as a yellow solid. Yield: 2.8 mg (3.8 μmol, 56%). The product **6^H** crystallized upon slow evaporation of its $CHCl_3$ solution in the form of brown blocks that were suitable for X-ray crystal structure analysis. *Note*: **6^H** decomposes slowly under ambient conditions in the presence of daylight and should therefore be handled inside a glovebox.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 4H; H-2); 7.73 (d, ^3J(H,H) = 5.2 Hz, 4H; H-7), 7.61 (d, ^3J(H,H) = 5.2 Hz, 4H; H-6), 7.05 (s, 4H; Mes-H-*m*), 2.52 (s, 6H; Mes-CH_3-*p*), 2.19 (s, 12H; Mes-CH_3-*o*)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 142.8* (br.; C-1), 140.5* (br.; Mes-C-*i*), 138.4 (Mes-C-*o*), 136.9 (Mes-C-*p*), 136.8 (C-2), 136.7 (C-4), 135.0 (C-5), 129.7 (C-3), 127.3 (Mes-C-*m*), 127.3 (C-6), 123.1 (C-7), 23.3 (Mes-CH_3-*o*), 21.6 (Mes-CH_3-*p*); *) this resonance was unequivocally detected only in the ^{H,C}HMBC spectrum
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = n.o.
HRMS: Calculated *m*/*z* for $C_{46}H_{34}B_2S_4$ (M^+): 736.17240, found: 736.17247
UV-vis (cyclohexane): λ_{max} (ε) = 392 (2000), 415 (1700), 440 nm (3600 $mol^{-1}dm^3cm^{-1}$)
Fluorescence (cyclohexane, λ_{ex} = 359 nm): λ_{max} = 444, 472, 503 nm; Φ_{PL} = 24%
Cyclic voltammetry (THF, [*n*-Bu_4N][PF_6] 0.1 M, 200 mV s^{-1}, vs. FcH/FcH^+): $E_{1/2}$ = −1.83, −2.47 V
Melting Point: Compound **6^H** did not melt up to a temperature of 350 °C.

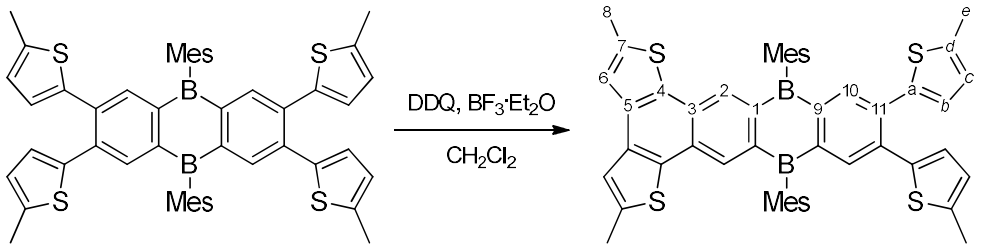
2.3 Synthesis of 4^{Me}



A Schlenk tube was charged with 2,3,6,7-Cl_4-9,10-Mes_2-DBA (1.08 g, 1.96 mmol), 2-methyl-5-(trimethylstannyl)thiophene (2.46 g, 9.43 mmol), and [Pd(P*t*Bu_3)$_2$] (82.4 mg, 98.2 μmol, 5 mol%) in toluene (32 mL). The Schlenk tube was placed in an oil bath and heated with stirring to 120 °C for 1 d. The reaction mixture was allowed to cool to room temperature and transferred to a round-bottom flask. All volatiles were removed using a rotary evaporator and the crude solid was purified by flash chromatography (cyclohexane/EtOAc 98:2 → cyclohexane/EtOAc 80:20) to furnish **4^{Me}** as an orange solid. Yield: 1.01 g (1.27 mmol, 65%). *Note:* The reaction can alternatively be performed in a microwave synthesizer with comparable yields (reaction conditions: 170 °C, 45 min).[S2]

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.68 (s, 4H; H-2), 6.88 (s, 4H; Mes-H-*m*), 6.68 (d, ^3J(H,H) = 3.5 Hz, 4H; H-5), 6.59-6.58 (dd, ^3J(H,H) = 3.5 Hz, ^4J(H,H) = 1.0 Hz, 4H; H-6), 2.43 (m, 12H; CH_3-8), 2.36 (s, 6H; Mes-CH_3-*p*), 2.12 (s, 12H; Mes-CH_3-*o*)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 144.3 (br.; C-1), 141.5 (C-2/7), 141.4 (C-2/7), 140.1 (C-4 and Mes-C-*i*), 138.3 (C-3), 138.0 (Mes-C-*o*), 136.8 (Mes-C-*p*), 127.7 (C-5), 127.2 (Mes-C-*m*), 125.5 (C-6), 23.1 (Mes-CH_3-*o*), 21.4 (Mes-CH_3-*p*), 15.5 (CH_3-8)
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = n.o.
HRMS: Calculated *m*/*z* for $C_{50}H_{46}B_2S_4$ (M^+): 796.26630, found: 796.26699
UV-vis (cyclohexane): λ_{max} (ε) = 397 nm (21700 $mol^{-1}dm^3cm^{-1}$)
Fluorescence (cyclohexane, λ_{ex} = 397 nm): λ_{max} = 538 nm; Φ_{PL} = 19%
Cyclic voltammetry (THF, [*n*-Bu_4N][PF_6] 0.1 M, 200 mV s^{-1}, vs. FcH/FcH^+): $E_{1/2}$ = −1.68, −2.47 V
Melting Point: Compound **4^{Me}** did not melt up to a temperature of 350 °C.

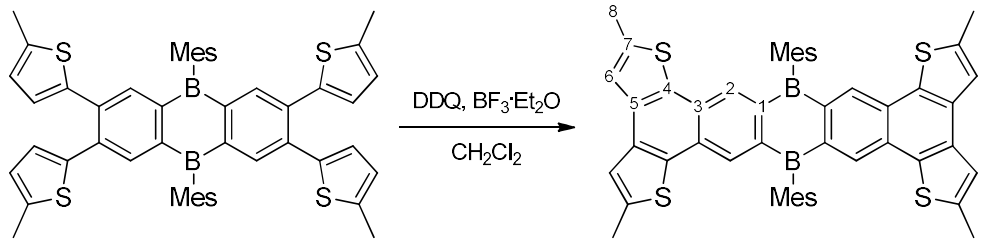
2.4 Synthesis of 5^{Me}



A Schlenk tube was charged with **4^{Me}** (50.0 mg, 62.8 μmol), DDQ (15.7 mg, 69.2 μmol), and CH_2Cl_2 (15 mL). $BF_3{\cdot}Et_2O$ (80.0 μL, 89.1 mg, 628 μmol) was added, the solution was stirred at room temperature, and the progress of the reaction was monitored by TLC. After 4.5 h, the resulting dark green solution was quenched with a saturated aqueous $NaHCO_3$ solution (80 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (15 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate using a rotary evaporator. Purification of the crude product by flash chromatography (cyclohexane → cyclohexane/EtOAc 98:2) afforded **5^{Me}** as an orange solid. Yield: 31.9 mg (40.1 μmol, 64%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.29 (s, 2H; H-2), 7.75 (s, 2H; H-10), 7.29 (m, 2H; H-6), 6.95 (s, 4H; Mes-H-*m*), 6.69 (d, ^3J(H,H) = 3.5 Hz, 2H; H-*b*), 6.60 (dd, ^3J(H,H) = 3.5 Hz, ^4J(H,H) = 1.0 Hz, 2H; H-*c*), 2.65 (m, 6H; CH_3-8), 2.43 (s, 12H; CH_3-*e* and Mes-CH_3-*p*), 2.14 (s, 12H; Mes-CH_3-*o*)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 145.1 (br.; C-9), 142.3 (C-7), 141.5 (br.; C-1), 141.4 (C-10), 141.4 (C-*d*), 140.5 (br.; Mes-C-*i*), 140.3 (C-*a*), 138.2 (Mes-C-*o*), 138.1 (C-11), 136.8 (C-2/Mes-C-*p*), 136.7 (C-2/Mes-C-*p*), 135.5 (C-4), 135.2 (C-5), 129.0 (C-3), 127.7 (C-*b*), 127.2 (Mes-C-*m*), 125.4 (C-*c*), 121.1 (C-6), 23.2 (Mes-CH_3-*o*), 21.5 (Mes-CH_3-*p*), 16.4 (C-8), 15.5 (C-*e*)
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = n.o.
HRMS: Calculated *m*/*z* for $C_{50}H_{44}B_2S_4$ (M^+): 794.25065, found: 794.25065
UV-vis (cyclohexane): λ_{max} (ε) = 427 (15500), 451 nm (23000 $mol^{-1}dm^3cm^{-1}$)
Fluorescence (cyclohexane, λ_{ex} = 360 nm): λ_{max} = 507 nm; Φ_{PL} = 20%
Cyclic voltammetry (THF, [*n*-Bu_4N][PF_6] 0.1 M, 200 mV s^{-1}, vs. FcH/FcH^+): $E_{1/2}$ = −1.78, −2.48 V
Melting Point: Compound **5^{Me}** did not melt up to a temperature of 350 °C.

2.5 Synthesis of 6^{Me}



A Schlenk tube was charged with **4^{Me}** (50.0 mg, 62.8 μmol), DDQ (57.0 mg, 251 μmol), and CH_2Cl_2 (8.5 mL). $BF_3{\cdot}Et_2O$ (160 μL, 178 mg, 1.26 mmol) was added and the solution was heated with stirring in an oil bath to 50 °C. The progress of the reaction was monitored by TLC. After 41 h at 50 °C, the resulting dark green solution was quenched with a saturated aqueous $NaHCO_3$ solution (80 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (15 mL), dried over anhydrous $MgSO_4$, and filtered. All volatiles were removed from the filtrate using a rotary evaporator. Purification of the crude product by flash chromatography (cyclohexane/EtOAc 99:1 → cyclohexane/EtOAc 85:15) afforded **6^{Me}** as an orange solid. Yield: 3.6 mg (4.5 μmol, 7%).

Note: Two alternatives exist to improve the yield of **6^{Me}**: (1) On a smaller scale (17.2 μmol of **4^{Me}**), the reaction can be conducted at room temperature (35 h), provided that larger amounts of DDQ (6 eq) and $BF_3{\cdot}Et_2O$ (40 eq) are used. Yield: 50%. (2) **5^{Me}** can be cyclized with DDQ (2 eq) and $BF_3{\cdot}Et_2O$ (10 eq; 16 h, 50 °C) following the reaction procedure described above. Yield: 21%.

6^{Me} decomposes slowly under ambient conditions in the presence of daylight and should therefore be handled inside a glovebox.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.37 (s, 4H; H-2), 7.30 (m, 4H; H-6), 7.03 (s, 4H; Mes-H-*m*), 2.66 (m, 12H; CH_3-8), 2.51 (s, 6H; Mes-CH_3-*p*), 2.16 (s, 12H; Mes-CH_3-*o*)

^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$): δ = 142.0* (C-1/7), 141.8* (C-1/7), 140.5* (Mes-C-*i*), 138.8* (Mes-C-*o*), 136.5* (Mes-C-*p*), 136.2$^+$ (C-2), 135.3* (C-4), 135.0* (C-5), 128.9* (C-3), 126.8$^+$ (Mes-C-*m*), 120.7$^+$ (C-6), 22.8$^+$ (Mes-CH_3-*o*), 21.1$^+$ (Mes-CH_3-*p*), 15.9$^+$ (C-8); *) this resonance was unequivocally detected only in the ^{H,C}HMBC spectrum; $^+$) this resonance was unequivocally detected only in the ^{H,C}HSQC spectrum

^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = n.o.

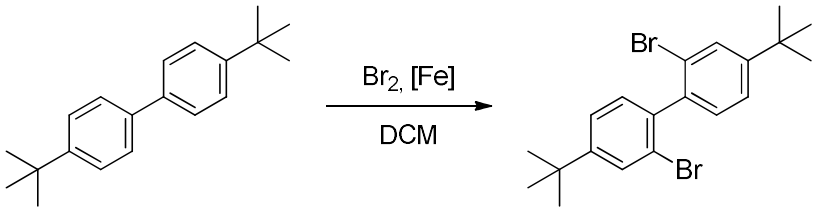
HRMS: Calculated *m*/*z* for $C_{50}H_{42}B_2S_4$ (M^+): 792.23500, found: 792.23553

UV-vis (cyclohexane): λ_{max} (ε) = 425 (10900), 451 nm (26100 $mol^{-1}dm^3cm^{-1}$)

Fluorescence (cyclohexane, λ_{ex} = 370 nm): λ_{max} = 455, 485, 514 nm; Φ_{PL} = 26%

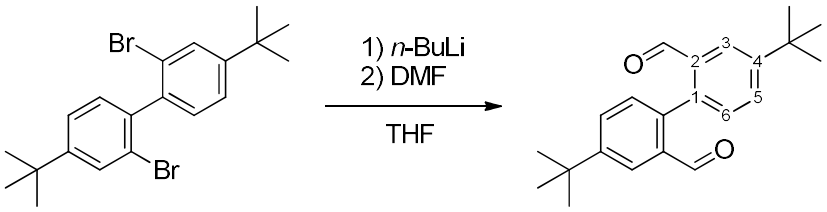
Melting Point: Compound **6^{Me}** did not melt up to a temperature of 350 °C.

2.6 Synthesis of 8



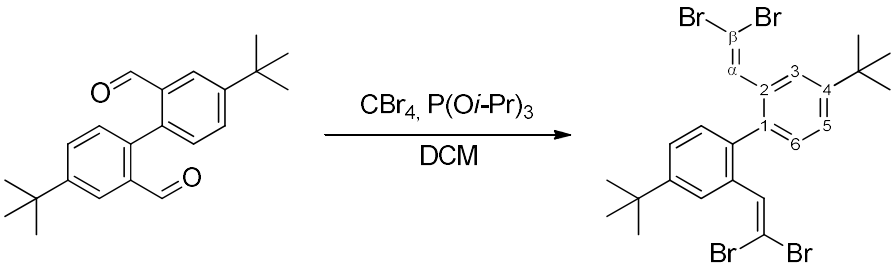
Synthesis of 2,2'-dibromo-4,4'-di-*tert.*-butylbiphenyl (F): Fe powder (42 mg, 0.75 mmol, 2 mol%) was added to a solution of 4,4'-di-*tert.*-butylbiphenyl (10.0 g, 37.5 mmol) in CH_2Cl_2 (80 mL). The slurry was heated to 30 °C and a solution of Br_2 (4.00 mL, 78.8 mmol) in CH_2Cl_2 (10 mL) was added dropwise with stirring. After complete addition, stirring at 30 °C was continued for 3 h. The mixture was treated with a saturated aqueous $NaHSO_3$ solution (30 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3x40 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to dryness using a rotary evaporator. The residue was recrystallized from MeOH to afford **F** as colorless needles. Yield: 12.1 g (28.4 mmol, 75%).

^{1}H-NMR (500 MHz, $CDCl_3$):[S10] δ = 7.66 (d, ^4J(H,H) = 2.0 Hz, 2H), 7.39 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.0 Hz, 2H), 7.19 (d, ^3J(H,H) = 8.0 Hz, 2H), 1.36 (s, 18H)



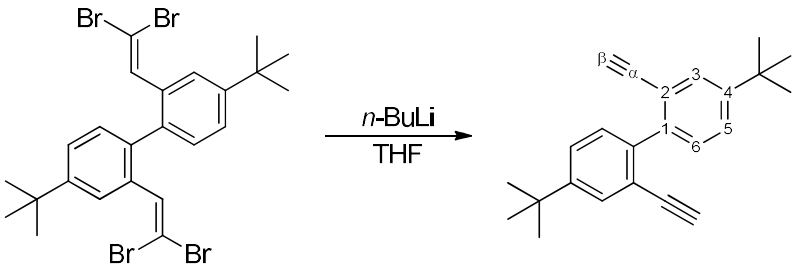
Synthesis of 2,2'-diformyl-4,4'-di-*tert.*-butylbiphenyl (G): *n*-BuLi (1.51 M in hexanes, 20.0 mL, 30.2 mmol) was added dropwise with stirring at –78 °C to **F** (5.00 g, 11.8 mmol) in dry THF (100 mL). Stirring of the resulting yellow solution was continued for 2 h at –78 °C. Dry neat DMF (4.6 mL, 59.0 mmol) was added in one portion. The mixture was allowed to warm to room temperature and the reaction was quenched by addition of HCl (2 M in H_2O, 20 mL). After stirring for 45 min at room temperature, the layers were separated and the aqueous layer was extracted with EtOAc (3x20 mL). The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution (50 mL) and with brine (50 mL), dried over $MgSO_4$, filtered, and evaporated to dryness with the aid of a rotary evaporator. The waxy residue was purified by column chromatography (cyclohexane/EtOAc 98:2) to furnish **G** as a colorless solid. Yield: 2.28 g (7.08 mmol, 61%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.85 (s, 2H; CHO), 8.08 (d, ^4J(H,H) = 2.1 Hz, 2H; H-3), 7.69 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.2 Hz, 2H; H-5), 7.29 (d, ^3J(H,H) = 8.0 Hz, 2H; H-6), 1.41 (s, 9H; $C(CH_3)_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 191.8 (CHO), 152.1 (C-4), 138.8 (C-2), 134.6 (C-1), 132.0 (C-6), 130.9 (C-5), 124.9 (C-3), 35.1 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$)
HRMS: Calculated *m*/*z* for $C_{22}H_{26}O_2$ ($M{\bullet}Na^+$): 345.1805, found: 345.1826



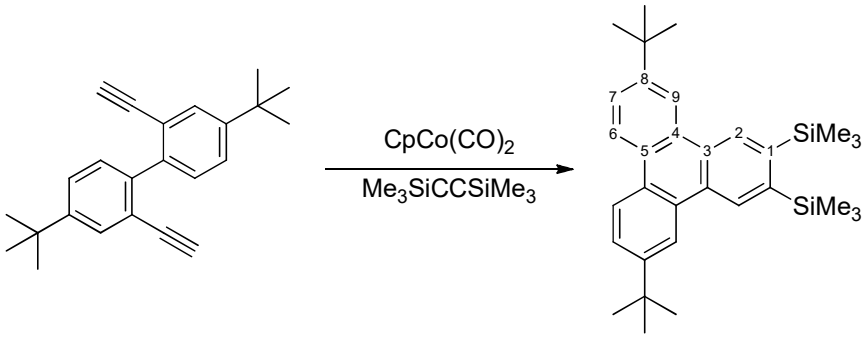
Synthesis of 2,2'-bis(β,β-dibromoethenyl)-4,4'-di-*tert.*-butylbiphenyl (H): P(O*i*-Pr)$_3$ (11.5 mL, 46.6 mmol) was added dropwise with stirring at 0 °C to a solution of **G** (2.50 g, 7.75 mmol) and CBr_4 (7.71 g, 23.3 mmol) in CH_2Cl_2 (50 mL). After stirring for 1 h at 0 °C, all volatiles were removed using a rotary evaporator (the remaining O=P(O*i*-Pr)$_3$ was subsequently evaporated at 80 °C using a rotary vane pump, $p = 10^{-3}$ mbar). The residue was purified by column chromatography (cyclohexane) to furnish **H** as a colorless solid. Yield: 3.34 g (5.27 mmol, 68%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, ^4J(H,H) = 1.9 Hz, 2H; H-3), 7.40 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.9 Hz, 2H; H-5), 7.12 (d, ^3J(H,H) = 8.0 Hz, 2H; H-6), 7.04 (s, 2H; H-α), 1.38 (s, 18H; C(CH$_3$)$_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 150.5 (C-4), 137.0 (C-α), 136.5 (C-2), 134.5 (C-1), 130.3 (C-6), 126.4 (C-3), 125.4 (C-5), 90.9 (C-β), 35.0 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$)
HRMS: Calculated *m*/*z* for $C_{24}H_{26}Br_3$ ([M–Br$^-$]$^+$): 550.9584, found: 550.9626
EA: Calculated *%* for $C_{24}H_{26}Br_4$: C 45.46, H 4.13; found: C 45.81, H 3.96



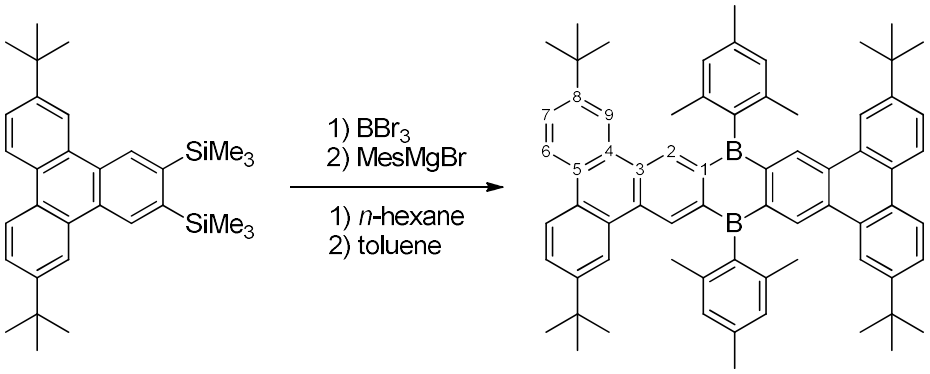
Synthesis of 2,2'-diethynyl-4,4'-di-*tert.*-butylbiphenyl (I): *n*-BuLi (1.56 M in hexanes, 21.0 mL, 32.8 mmol) was added dropwise with stirring at –78 °C to a solution of **H** (3.34 g, 5.27 mmol) in dry THF (50 mL). After complete addition, the dark brown reaction mixture was allowed to warm to room temperature. Upon quenching with MeOH (3 mL), a clear yellow solution was obtained, which was poured into a saturated aqueous NH_4Cl solution (50 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3x20 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and evaporated to dryness with the aid of a rotary evaporator. **I** was obtained as a colorless solid, which could be used without further purification. Yield: 1.13 g (3.59 mmol, 68%). *Note:* This compound is prone to decomposition. It should be stored in a freezer and used as soon as possible.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, ^4J(H,H) = 2.1 Hz, 2H; H-3), 7.41 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.1 Hz, 2H; H-5), 7.35 (d, ^3J(H,H) = 8.2 Hz, 2H; H-6), 2.96 (s, 2H; H-β), 1.36 (s, C(CH$_3$)$_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 150.3 (C-4), 140.3 (C-1), 130.3 (C-3), 130.2 (C-6), 125.7 (C-5), 121.0 (C-2), 83.6 (C-α), 79.5 (C-β), 34.7 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$)
HRMS: Calculated *m*/*z* for $C_{24}H_{27}$ (MH$^+$): 315.2112, found: 315.2100



Synthesis of 9: A suspension of **I** (1.13 g, 3.59 mmol) and $CpCo(CO)_2$ (50 µl, 0.36 mmol, 10 mol%) in degassed 1,2-bis(trimethylsilyl)acetylene (BTMSA, 20 mL) was warmed to ca. 40 °C with the aid of a heating mantle. The resulting brown solution was added dropwise over 9 h to refluxing BTMSA (20 mL) with the aid of a syringe pump. During the addition, the reaction mixture was irradiated using a 500 W halogen lamp (no quarz-glass equipment was used; the reaction can also be conducted using a 9 W fluorescent bulb, but the yields are significantly lower). After complete addition, irradiation and heating were continued for further 2 h. The reaction mixture was cooled to room temperature and BTMSA removed *in vacuo* (10^{-3} mbar, liq. N_2 cryo-trap; about 90% of the BTMSA are thereby recovered). The brown residue was purified by column chromatography (cyclohexane) to furnish **9** as a yellow solid. Yield: 825 mg (1.70 mmol, 47%). *Note:* Since conventional stainless-steel cannulas tend to clog during addition, we used a Teflon® tube and connected it to the flask via a specially designed home-built adapter: A 14.5 mm male ground glass-joint was connected via a Young®-teflon spindle stopcock to a 10 mm male ground glass-joint by an artisan glass blower. Onto the 10 mm joint, a stainless-steel Luer lock was fitted using few layers of Teflon® tape. From thereon, the Teflon® tube was connected via standard Luer locks (see photo below, Luer locks not depicted).

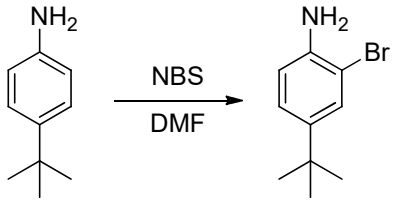
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.01 (s, 2H; H-2), 8.68 (d, ^4J(H,H) = 1.7 Hz, 2H; H-9), 8.54 (d, ^3J(H,H) = 8.6 Hz, 2H; H-6), 7.71 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 1.7 Hz, 2H; H-7), 1.51 (s, 18H; $C(CH_3)_3$), 0.53 (s, 18H; $Si(CH_3)_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 149.5 (C-8), 143.5 (C-1), 130.3 (C-2), 129.0 (C-5), 128.8 (C-3), 128.0 (C-4), 125.4 (C-7), 123.1 (C-6), 119.0 (C-9), 35.1 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 2.1 ($Si(CH_3)_3$)
^{29}Si{^{1}H}-NMR (99 MHz, $CDCl_3$, INEPT): δ = –2.4
HRMS: Calculated *m*/*z* for $C_{32}H_{44}Si_2$ (M^+): 484.2982, found: 484.2966



Synthesis of 8: A suspension of **9** (820 mg, 1.69 mmol) in dry *n*-hexane (5 mL) was prepared in a thick-walled glass ampoule. After the addition of neat BBr_3 (560 µl, 5.92 mmol), the ampoule was immersed in liq. N_2 and flame-sealed under vacuum. The ampoule was heated to 120 °C for 3 d. The ampoule was opened under N_2 and all volatiles were removed under reduced pressure to give the BBr precursor of **8** as a brown solid, which is insoluble in common deuterated solvents. *Note:* The opened ampoule was placed in a large Schlenk tube and vacuum was applied gradually to prevent frothing.
The solid bromoborane (0.64 g, 0.75 mmol) was suspended in dry toluene (10 mL) and MesMgBr (0.86 M in THF, 1.80 mL, 1.54 mmol) added dropwise with stirring at 0 °C. The reaction mixture was allowed to warm to room temperature overnight. All volatiles were removed by rotary evaporation and the brownish residue was purified by column chromatography (cyclohexane/CH_2Cl_2 8:2) to furnish **8**. Yield: 251 mg (0.266 mmol, 32%). Crystals suitable for X-ray analysis were obtained by slow evaporation of a $CDCl_3$ solution of **8**.

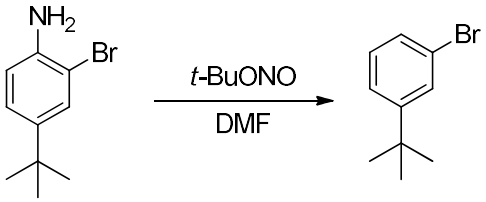
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.05 (s, 4H; H-2), 8.51 (d, ^3J(H,H) = 8.6 Hz, 4H; H-6), 8.45 (d, ^4J(H,H) = 1.6 Hz, 4H; H-9), 7.71 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 1.6 Hz, 4H; H-7), 7.09 (s, 4H; Mes-H-*m*), 2.50 (s, 6H; Mes-CH_3-*p*), 2.26 (s, 12H; Mes-CH_3-*o*), 1.41 (s, 36H; C(CH_3)$_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 149.7 (C-8), 143.3 (br.; C-1), 141.0 (br.; Mes-C-*i*), 138.6 (Mes-C-*o*), 137.0 (Mes-C-*p*), 135.0 (C-2), 133.4 (C-4), 129.3 (C-3), 128.5 (C-5), 126.9 (Mes-C-*m*), 126.2 (C-7), 123.1 (C-6), 119.9 (C-9), 35.1 (*C*(CH_3)$_3$), 31.3 (C(*C*H_3)$_3$), 23.4 (Mes-CH_3-*o*), 21.4 (Mes-CH_3-*p*)
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = n.o.
HRMS: Calculated *m*/*z* for $C_{70}H_{74}B_2$ (M^+): 936.5977, found: 936.5980
UV-vis (cyclohexane): λ_{max} (ε) = 350 (12400), 385 (1500), 405 (3500), 430 nm (7100 $mol^{-1}dm^3cm^{-1}$)
Fluorescence (cyclohexane, λ_{ex} = 350 nm): λ_{max} = 438, 463, 495 nm; Φ_{PL} = 56%
Cyclic voltammetry (THF, [*n*-Bu_4N][PF_6] 0.1 M, 200 mV s^{-1}, vs. FcH/FcH^+): $E_{1/2}$ = −1.82, −2.44 V
Melting point: Compound **8** did not melt up to a temperature of 350 °C.

2.7 Synthesis of 7



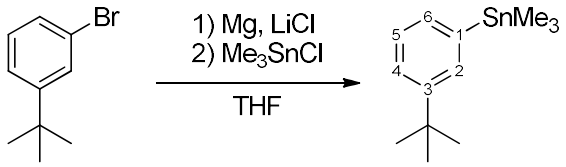
Synthesis of 2-bromo-4-*tert*.-butylaniline (J): A solution of N-bromosuccinimide (6.31 g, 35.2 mmol) in DMF (30 mL) was added in small portions at room temperature to a solution of 4-*tert*.-butylaniline (5.40 mL, 33.5 mmol) in DMF (100 mL). The progress of the reaction was monitored by TLC (cyclohexane/EtOAc = 9:1). After 15 min, all starting material was consumed. All volatiles were removed under reduced pressure (60 °C, 10^{-3} mbar). The residue was taken up in EtOAc (100 mL) and brine (100 mL) and the layers were separated. The organic layer was washed with brine (2x50 mL), dried over Na_2SO_4, filtered, and all volatiles were removed with the aid of a rotary evaporator. The crude **J** was obtained as a reddish oil and used without further purification. Yield: 7.51 g (32.9 mmol, 98%). *Note:* Brominations with NBS in DMF (Mitchell's method of bromination)[S11] are highly dependent on the quality of the DMF:[S12,13] the higher the water content, the longer the reaction time. We used non-dried DMF from bottles that had been opened no longer than 8 weeks before.

^{1}H-NMR (250 MHz, $CDCl_3$):[S14] δ = 7.43 (d, ^4J(H,H) = 2.2 Hz, 1H), 7.15 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 2.2 Hz, 1H), 6.81 (d, ^3J(H,H) = 8.4 Hz, 1H), 4.18 (br.; s, 2H), 1.27 (s, 9H)



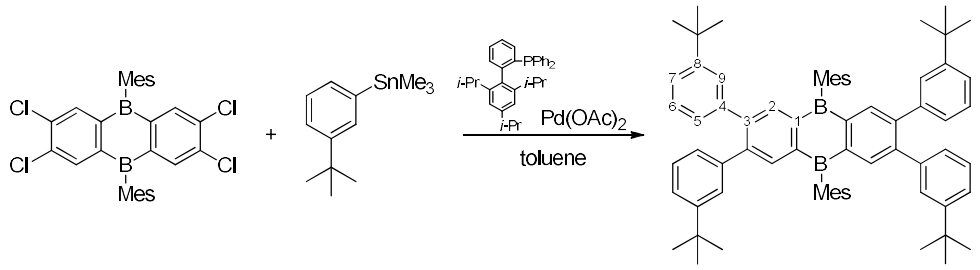
Synthesis of 3-*tert*.-butyl bromobenzene[S15] **(K):** In a two-necked flask equipped with a reflux condenser (fitted with a bubbler) and a septum, *t*-BuONO (90% purity, 7.00 mL, 52.2 mmol) was dissolved in DMF (50 mL) and a solution of **J** (7.51 g, 32.9 mmol) in DMF (5 mL) was added via syringe in one portion at 65 °C. The mixture was stirred at 65 °C until no more gas evolution was observed (10 min). After cooling to room temperature, the reaction mixture was poured into HCl (20% in H_2O, 200 mL). The formed suspension was extracted with *n*-hexane (3x50 mL) and the combined organic layers were washed with water (3x20 mL) and brine (50 mL). After drying over Na_2SO_4 and filtration, the solvent was removed with the aid of a rotary evaporator, leaving a brown oil behind. The product was isolated via vacuum distillation (49 °C, 10^{-3} mbar) to give **K** as a slightly yellow liquid. Yield: 6.08 g (28.5 mmol, 82%).

^{1}H-NMR (250 MHz, $CDCl_3$):[S16] δ = 7.51 (dd, ^4J(H,H) = ^4J(H,H) = 1.9 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.17 (dd, ^3J(H,H) = ^3J(H,H) = 7.68 Hz, 1H), 1.31 (s, 9H)



Synthesis of 3-*tert*.-butyl trimethylstannylbenzene (L): LiCl (500 mg, 11.7 mmol) was dried at 120 °C / 10^{-3} mbar for 1 h in a two-necked flask equipped with a reflux condenser and a glass stopper. After the addition of Mg turnings (480 mg, 19.6 mmol), the mixture was stirred *in vacuo* for 1 h. Dry THF (50 mL) was added, followed by neat **K** (2.09 g, 9.79 mmol)**.** The mixture was heated to reflux temperature for 48 h. After the turbid reaction mixture had cooled to room temperature, the Grignard-reagent solution was transferred from the remaining Mg turnings (265 mg) onto neat Me_3SnCl (2.35 g, 11.8 mmol) via cannula. The resulting solution was refluxed for 5 h and then poured into a saturated aqueous $NaHCO_3$ solution (50 mL). The layers were separated and the aqueous layer extracted with *n*-hexane (3x30 mL). The combined organic extracts were washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and filtered. The solvent was removed with the help of a rotary evaporator and the remaining oil was purified by distillation (54 °C, 10^{-3} mbar). Yield: 1.49 g (5.01 mmol, 51%).
Note: Attempts to prepare **L** through Li/Br-exchange using *n*-BuLi or *t*-BuLi failed; alkyl$SnMe_3$ was obtained as a major product.

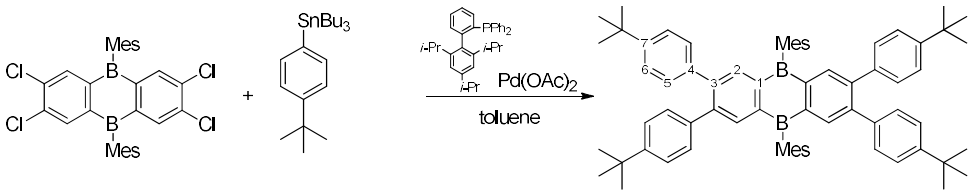
^{1}H-NMR (500 MHz, C_6D_6): δ = 7.70 (d, ^4J(H,H) = 1.4 Hz, 1H; H-2), 7.30 (m, 3H; H-4,5,6), 1.28 (s, 9H; $C(CH_3)_3$), 0.25 (s, 9H; $Sn(CH_3)_3$; $^{117/119}$Sn satellites: ^2J(H,^{117}Sn) = ^2J(H,^{119}Sn) = 26.6 Hz)
^{13}C{^{1}H}-NMR (126 MHz, C_6D_6): δ = 150.6 (C-3), 141.8 (^1J(C,Sn) = 228.0, 241.3 Hz; C-1), 133.5 (^2J(C,Sn) = 18.0 Hz; C-6), 132.6 (^2J(C-Sn) = 19.3 Hz; C-2), 128.3 (C-5), 125.8 (C-4), 34.8 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), –9.7 (^1J(C,Sn) = 165.0, 173.5 Hz; $Sn(CH_3)_3$)
^{119}Sn{^{1}H}-NMR (187 MHz, C_6D_6): δ = –30.0
HRMS: The product is sensitive toward acidic MALDI matrices, thus no accurate mass was detected.



Synthesis of 7: A crimp-top microwave vial was charged with **L** (243 mg, 818 µmol), 2,3,6,7-Cl_4-9,10-Mes_2-DBA (100 mg, 182 µmol), $Pd(OAc)_2$ (2.0 mg, 9.0 µmol, 5 mol%), and 2-(diphenylphosphino)-2',4',6'-triisopropylbiphenyl (13 mg, 27 µmol, 15 mol%). The vial was evacuated and backfilled with N_2 three times. After the addition of dry toluene (3 mL), the reaction mixture was heated with stirring in a microwave synthesizer (170 °C, 45 min). After evaporation of all volatiles with the aid of a rotary evaporator, the crude product was purified by flash chromatography (silica/KF 90:10 weight%,[S17] cyclohexane/CH_2Cl_2 3:1) and afterwards by RP flash-chromatography (MeOH→TBME). **7** was obtained as a yellow solid. Yield: 58 mg (62 µmol, 34%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.75 (s, 4H; H-2), 7.21-7.16 (m, 8H; H-6,7), 7.06-7.04 (m, 4H; H-9), 6.90 (m, 4H; H-5), 6.86 (s, 4H; Mes-H-*m*), 2.31 (s, 6H; Mes-CH_3-*p*), 2.20 (s, 12H; Mes-CH_3-*o*), 1.03 (s, 36H; $C(CH_3)_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): 150.3 (C-8), 145.8 (C-3), 144.5 (br.; C-1), 141.2 (C-2), 140.8 (C-4), 140.6 (br.; Mes-C-*i*), 138.0 (Mes-C-*o*), 136.7 (Mes-C-*p*), 128.1 (C-9), 128.0 (C-7), 127.2 (Mes-C-*m*), 126.6 (C-5), 123.6 (C-6), 34.5 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 23.2 (Mes-CH_3-*o*), 21.3 (Mes-CH_3-*p*)
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = n.o.
HRMS: Calculated *m*/*z* for $C_{70}H_{78}B_2$ (M^+): 940.6290, found: 940.6295
UV-vis (cyclohexane): λ_{max} (ε) = 304 (83800), 371 (17700) nm ($mol^{-1}dm^3cm^{-1}$)
Fluorescence (cyclohexane, λ_{ex} = 304 nm): λ_{max} = 483 nm; Φ_{PL} = 8%
Cyclic voltammetry (THF, [*n*-Bu_4N][PF_6] 0.1 M, 200 mV s^{-1}, vs. FcH/FcH^+): $E_{1/2}$ = −1.82, −2.73 V
Melting point: Compound **7** did not melt up to a temperature of 350 °C.

2.8 Synthesis of 2,3,6,7-(4-*t*-Bu-C_6H_4)$_4$-9,10-Mes_2-DBA



A crimp-top microwave vial was charged with 4-tributylstannyl-*tert*.-butylbenzene[S18] (355 mg, 834 µmol, 4.6 eq), 2,3,6,7-Cl_4-9,10-Mes_2-DBA (100 mg, 181 µmol, 1 eq), 2-(diphenylphosphino)-2',4',6'-triisopropylbiphenyl (13 mg, 27 µmol, 15mol%), and $Pd(OAc)_2$ (2.0 mg, 9.0 µmol, 5 mol%). The vial was evacuated and backfilled with N_2 three times. After addition of dry toluene (3 mL), the reaction mixture was heated with stirring in a microwave synthesizer (170 °C, 45 min). After evaporation of all volatiles with the aid of a rotary evaporator, the crude product was purified by flash chromatography (silica/KF 90:10 (w/w),[S17] cyclohexane/CH_2Cl_2 3:1), furnishing 2,3,6,7-(4-*t*-Bu-C_6H_4)$_4$-9,10-Mes_2-DBA as a yellow solid. Yield: 86 mg (91 µmol, 50%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.69 (s, 4H; H-2), 7.18-7.16 (m, 8H; H-5), 6.98-6.96 (m, 8H; H-6), 6.87 (s, 4H; Mes-H-*m*), 2.34 (s, 6H; Mes-CH_3-*p*), 2.19 (s, 12H; Mes-CH_3-*o*), 1.27 (s, 36H, C(C*H*$_3$)$_3$)
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 149.7 (C-7), 145.2 (C-4), 144.4 (br.; C-1), 141.1 (C-2), 140.8 (Mes-C-*i*), 138.3 (C-3), 138.0 (Mes-C-*o*), 136.5 (Mes-C-*p*), 129.6 (C-6), 127.2 (Mes-C-*m*), 124.7 (C-5), 34.6 (*C*(CH_3)$_3$), 31.4 (C(*C*H_3)$_3$), 23.2 (Mes-CH_3-*o*), 21.4 (Mes-CH_3-*p*)
^{11}B{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = n.o.
HRMS: Calculated *m*/*z* for $C_{70}H_{78}B_2$ (M^+): 940.6290, found: 940.6291
UV-vis (cyclohexane): λ_{max} (ε) = 307 (56900), 370 (14500) nm ($mol^{-1}dm^3cm^{-1}$)
Fluorescence (cyclohexane, λ_{ex} = 307 nm): λ_{max} = 489 nm; Φ_{PL} = 8%
Cyclic voltammetry (THF, [*n*-Bu_4N][PF_6] 0.1 M, 200 mV s^{-1}, vs. FcH/FcH^+): $E_{1/2}$ = −1.80, −2.69 V

3. Plots of ^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra

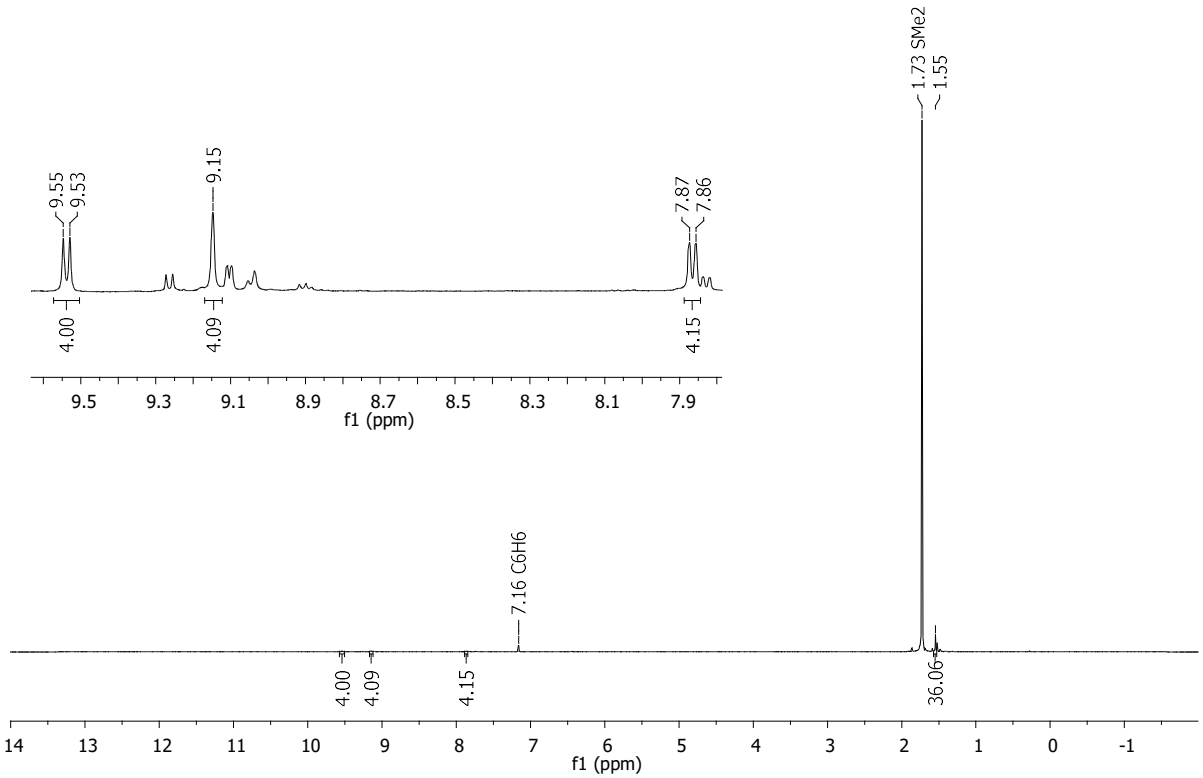


Figure S1: ^{1}H-NMR spectrum of $\mathbf{2^{H}}$·2SMe_2 (C_6D_6, 500 MHz). *Note:* Excess SMe_2 was added to the sample prior to vacuum sealing.

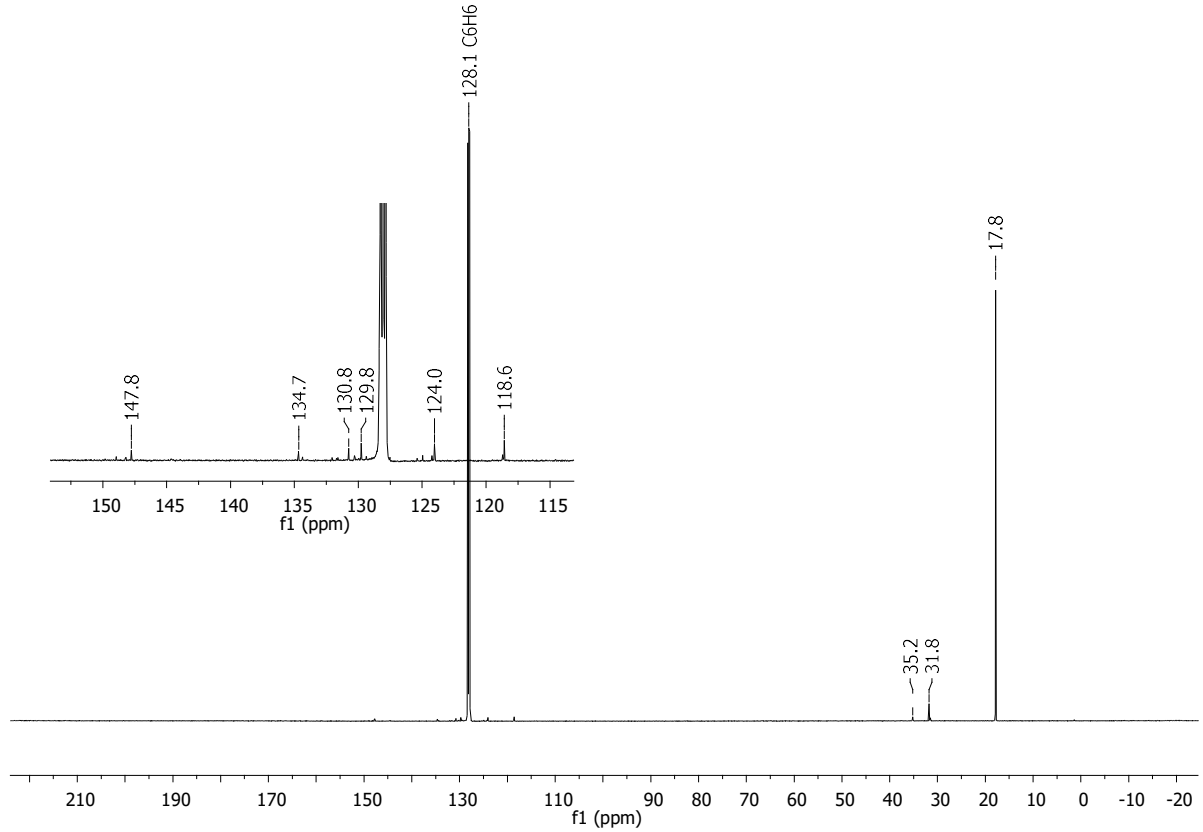


Figure S2: $^{13}C\{^{1}H\}$-NMR spectrum of $\mathbf{2^{H}}$·2SMe_2 (C_6D_6, 126 MHz). *Note:* Excess SMe_2 was added to the sample prior to vacuum sealing.

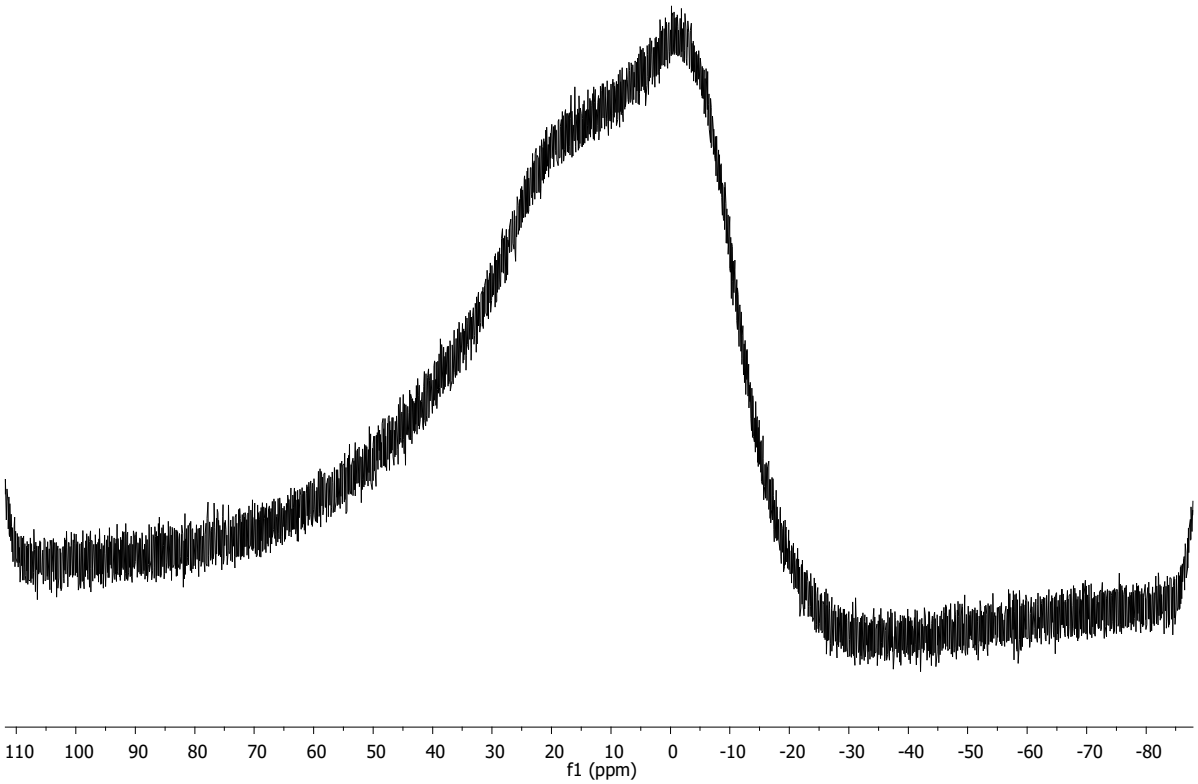


Figure S3: ^{11}B-NMR spectrum of **2^{H}**·2SMe$_2$ (C_6D_6, 161 MHz); baseline uncorrected.

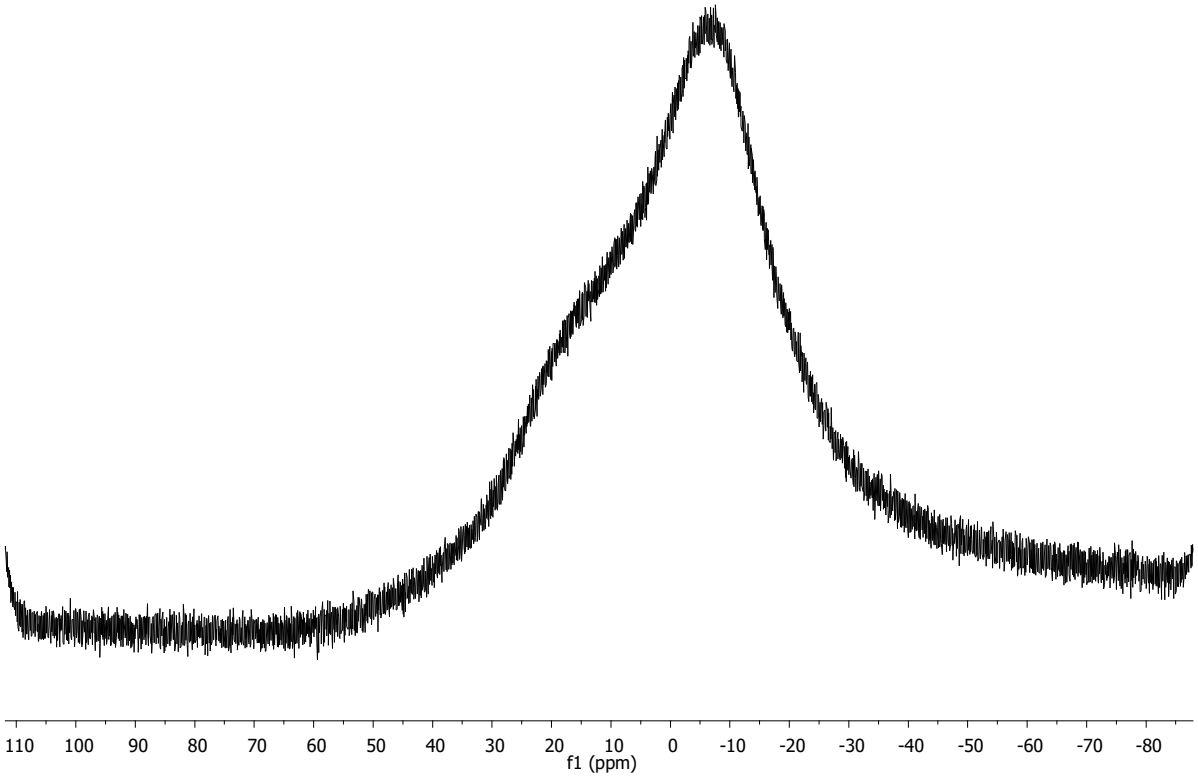


Figure S4: ^{11}B{^{1}H}-NMR spectrum of **2^{H}**·2SMe$_2$ (C_6D_6, 161 MHz); baseline uncorrected.

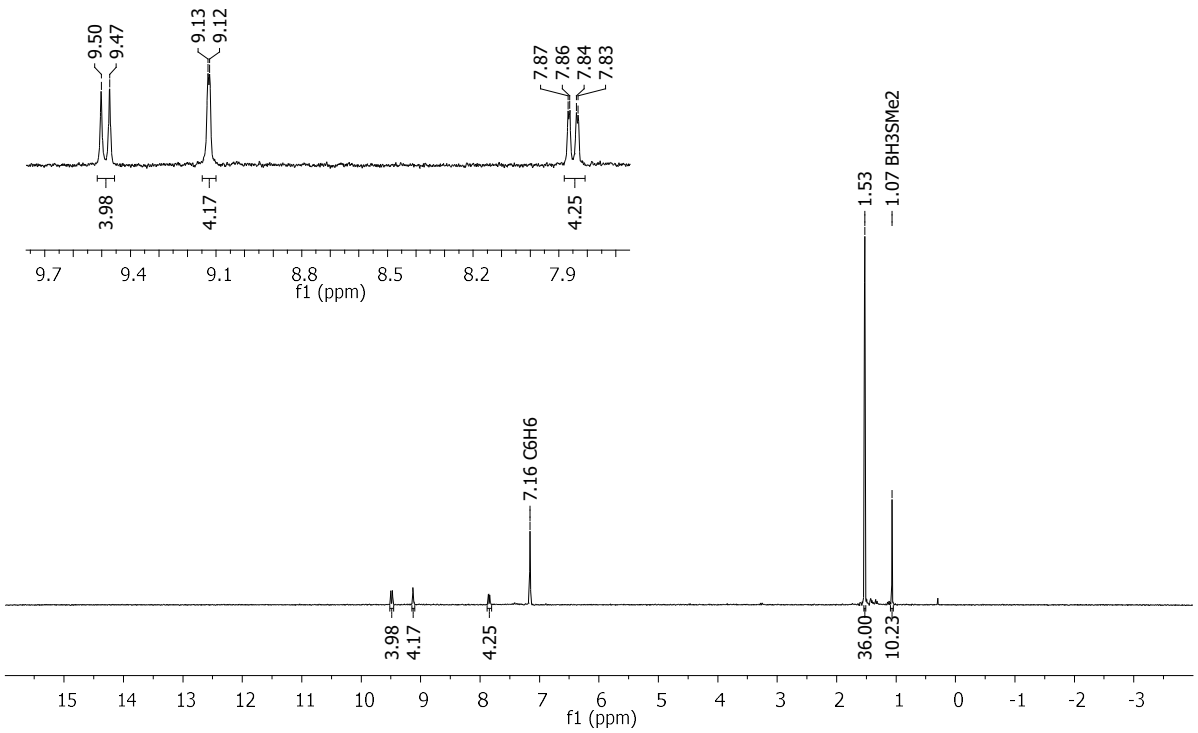


Figure S5: ^{1}H-NMR spectrum of **2^{H}** (C_6D_6, 300 MHz).

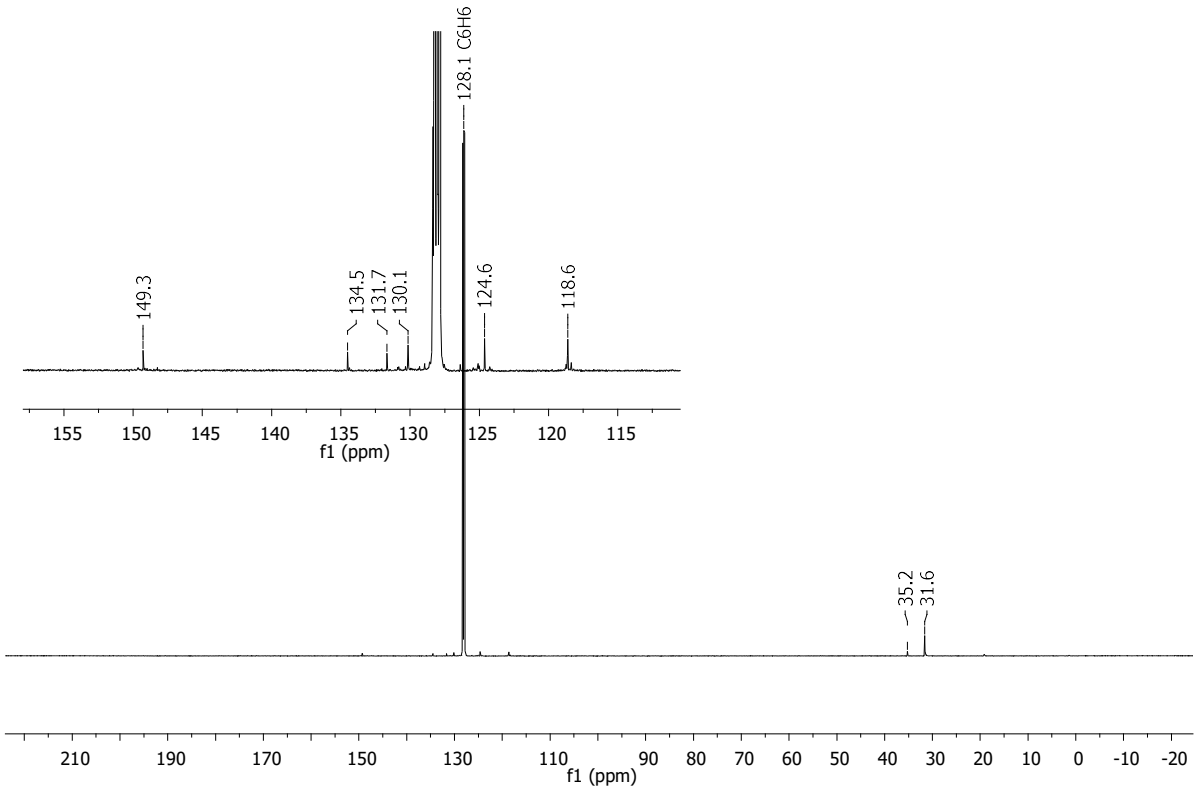


Figure S6: ^{13}C{^{1}H}-NMR spectrum of **2^{H}** (C_6D_6, 126 MHz).

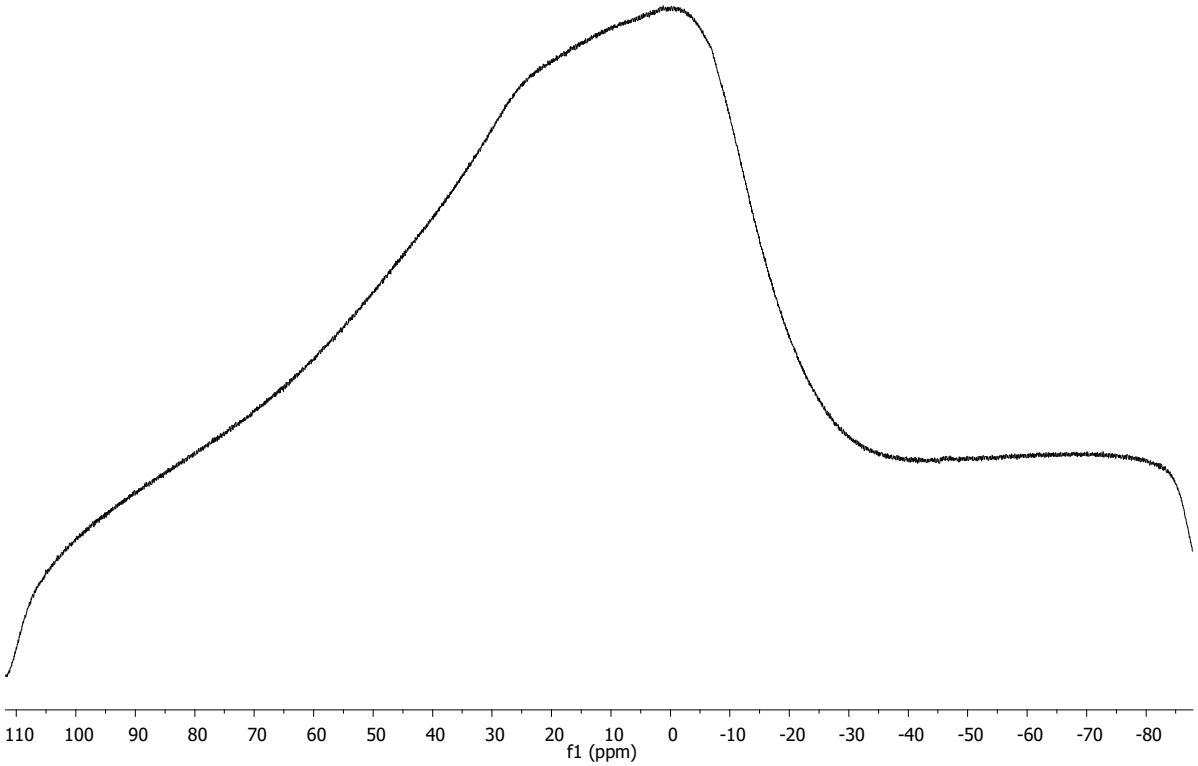


Figure S7: ^{11}B-NMR spectrum of **2^{H}** (C_6D_6, 161 MHz); baseline uncorrected.

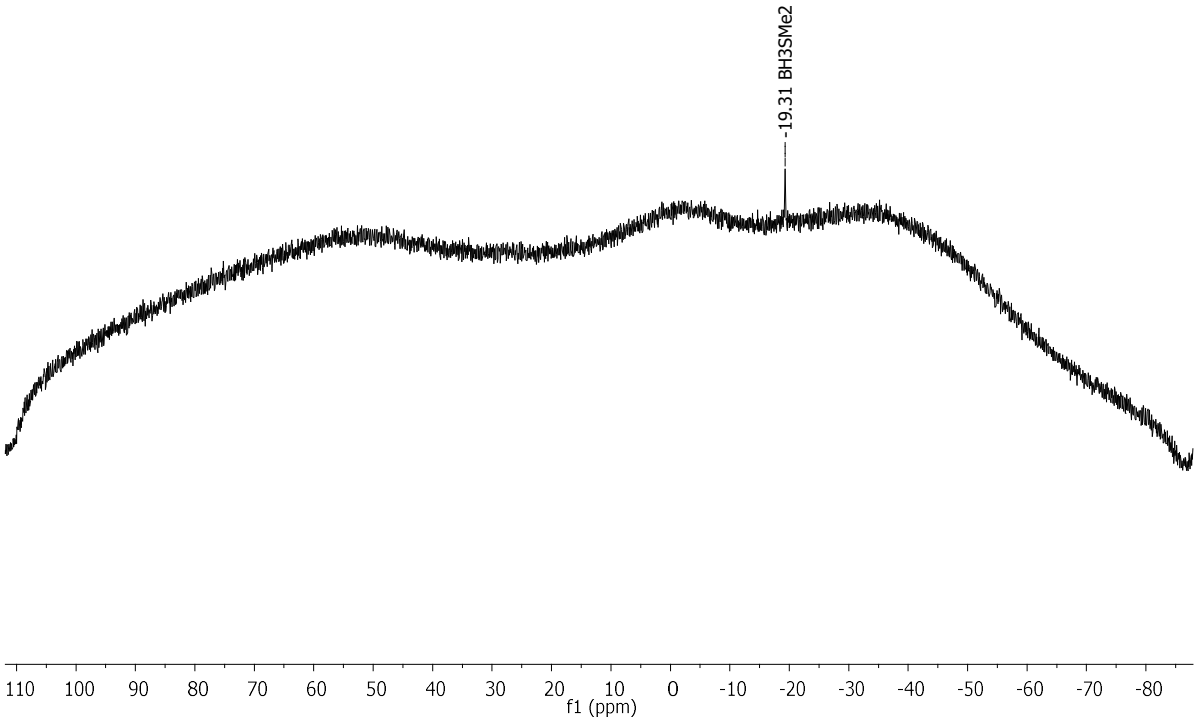


Figure S8: ^{11}B{^{1}H}-NMR spectrum of **2^{H}** (C_6D_6, 161 MHz); baseline uncorrected.

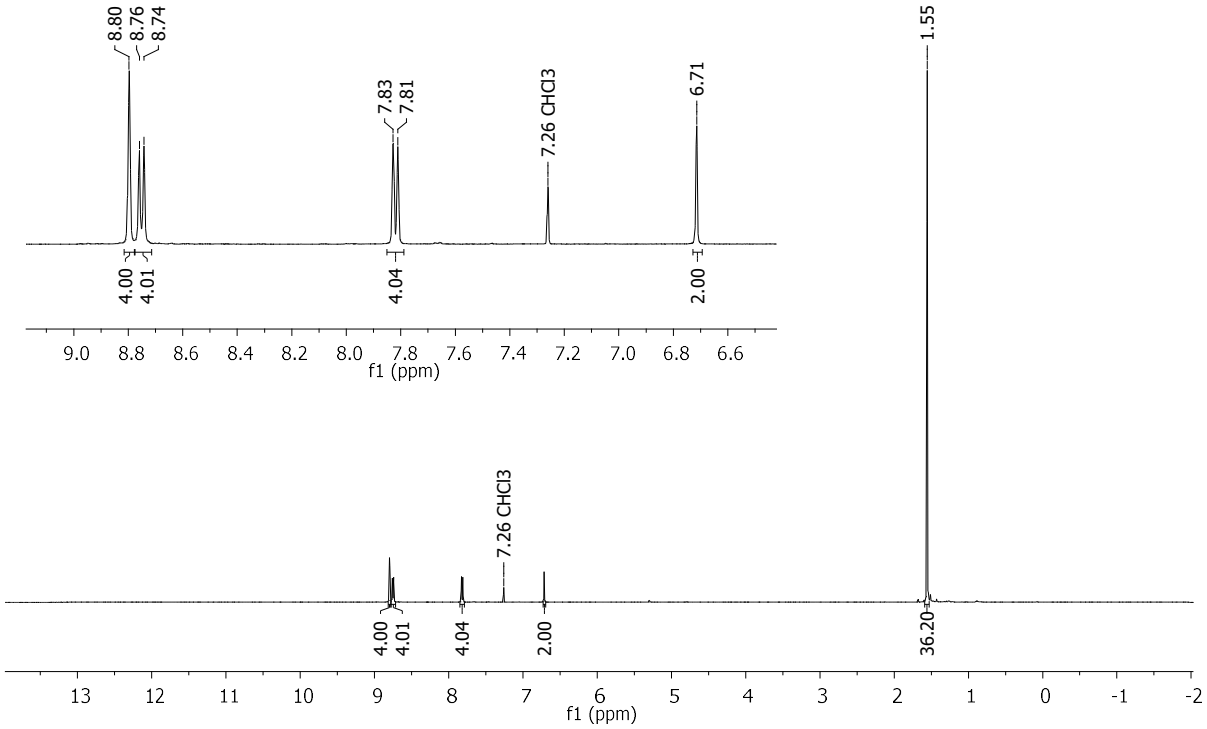


Figure S9: ^{1}H-NMR spectrum of **2^{OH}** ($CDCl_3$, 300 MHz).

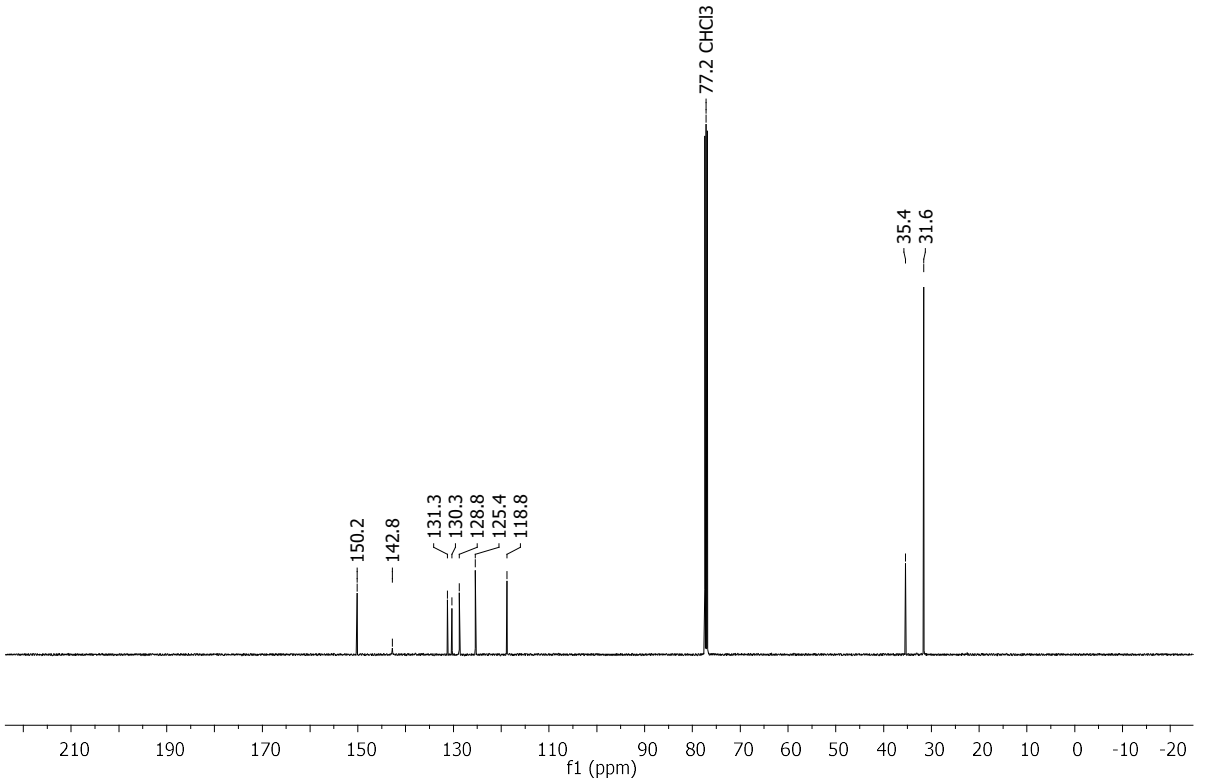


Figure S10: ^{13}C{^{1}H}-NMR spectrum of **2^{OH}** ($CDCl_3$, 126 MHz).

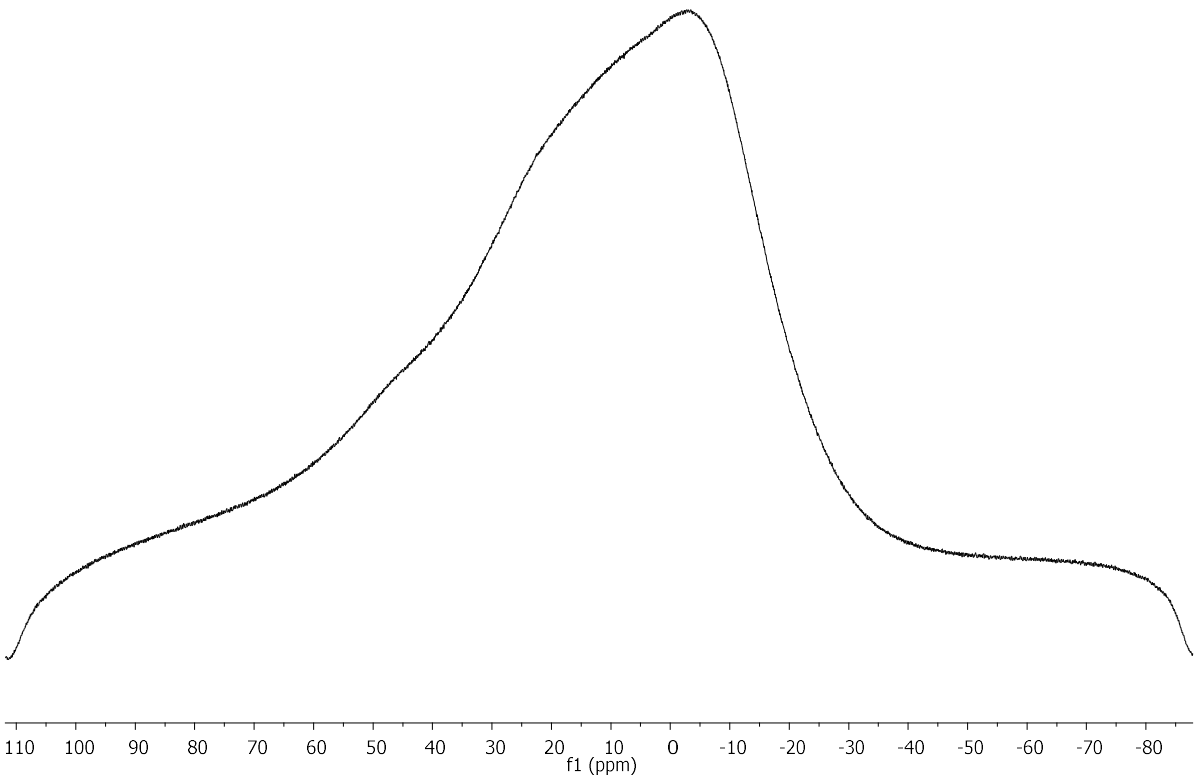


Figure S11: $^{11}B\{^{1}H\}$-NMR spectrum of **2^{OH}** ($CDCl_3$, 161 MHz); baseline uncorrected.

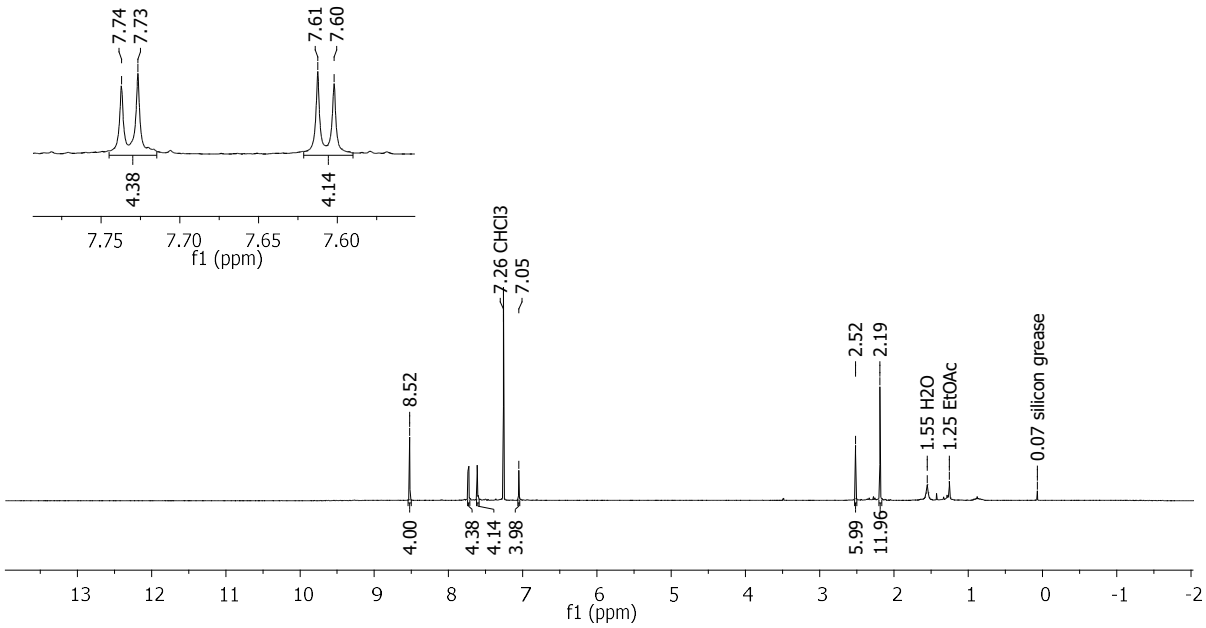


Figure S12: ^{1}H-NMR spectrum of **6^{H}** ($CDCl_3$, 500 MHz).

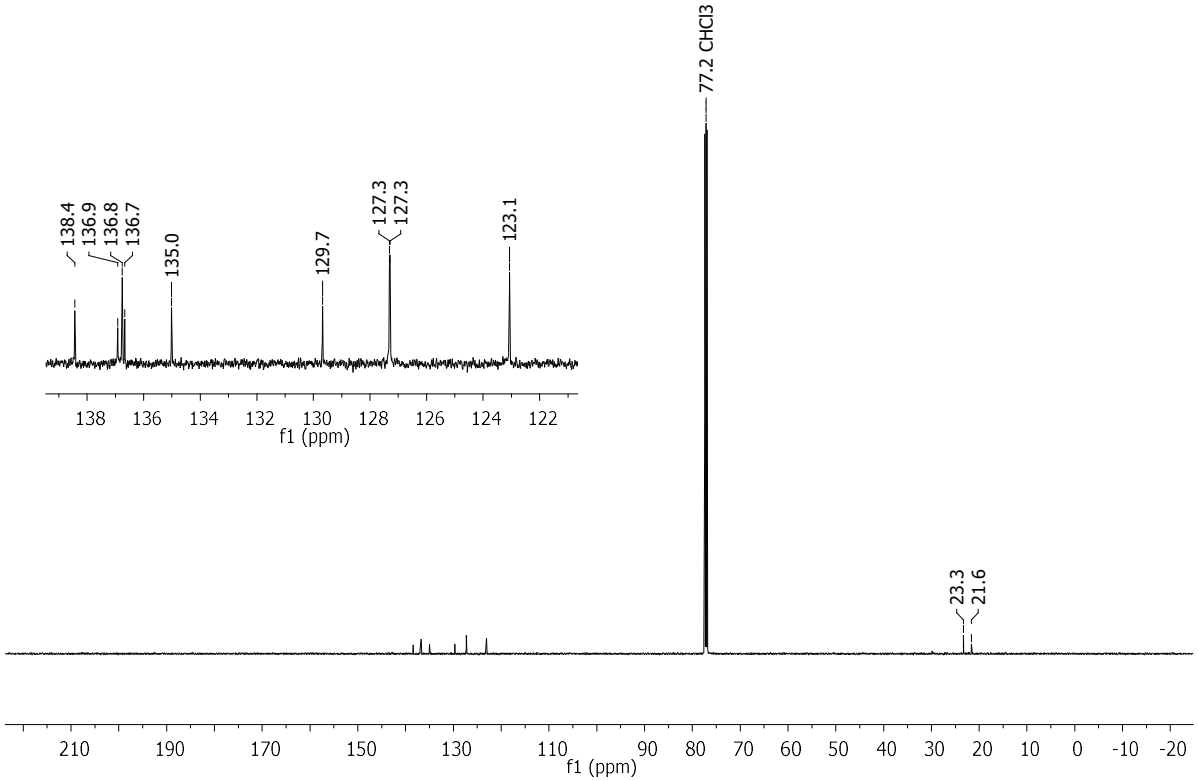


Figure S13: $^{13}C\{^{1}H\}$-NMR spectrum of **6^{H}** ($CDCl_3$, 126 MHz).

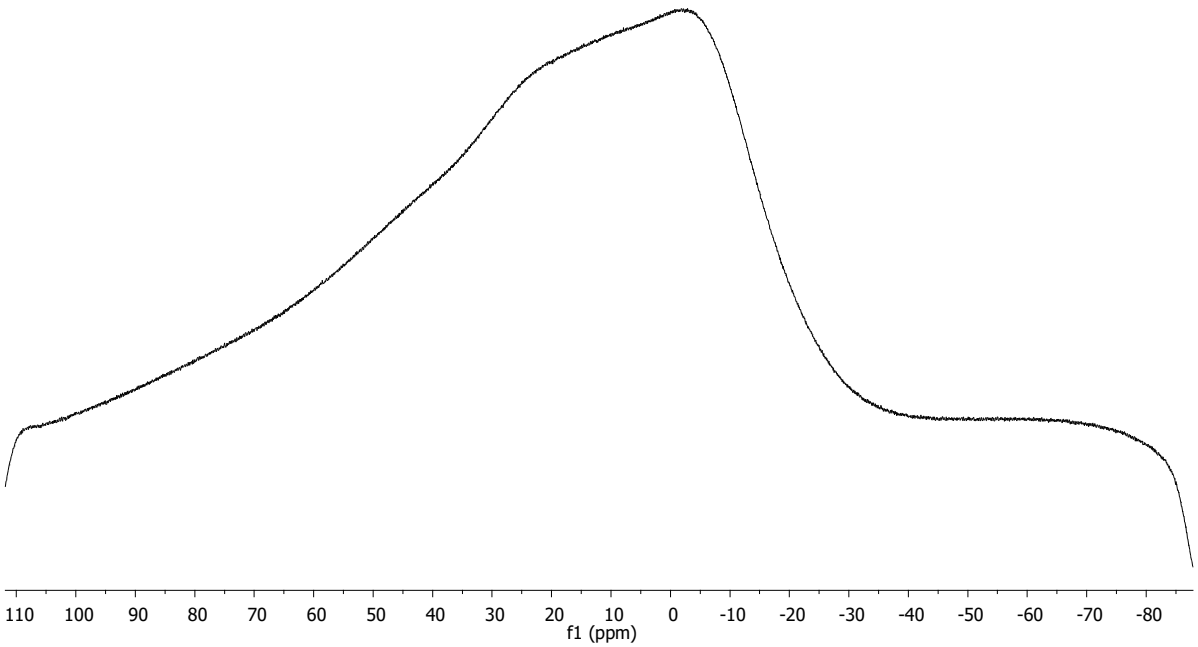


Figure S14: $^{11}B\{^{1}H\}$-NMR spectrum of **6^{H}** ($CDCl_3$, 161 MHz); baseline uncorrected.

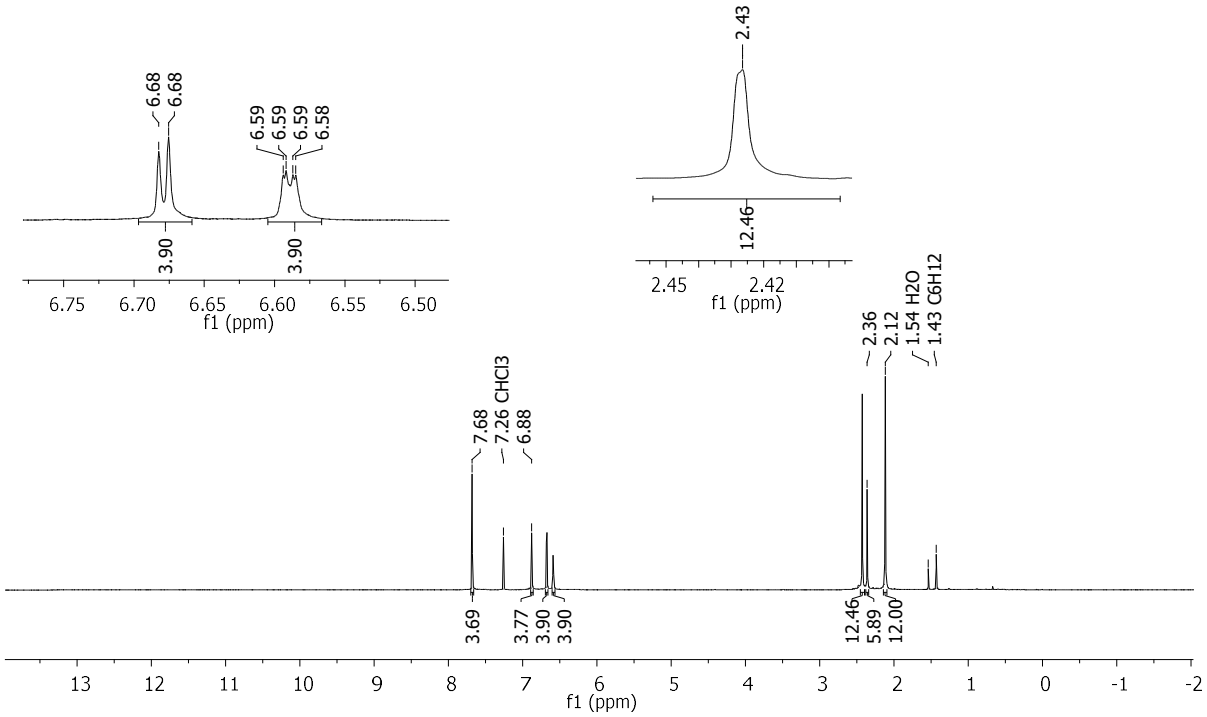


Figure S15: ^{1}H-NMR spectrum of **4^{Me}** ($CDCl_3$, 500 MHz).

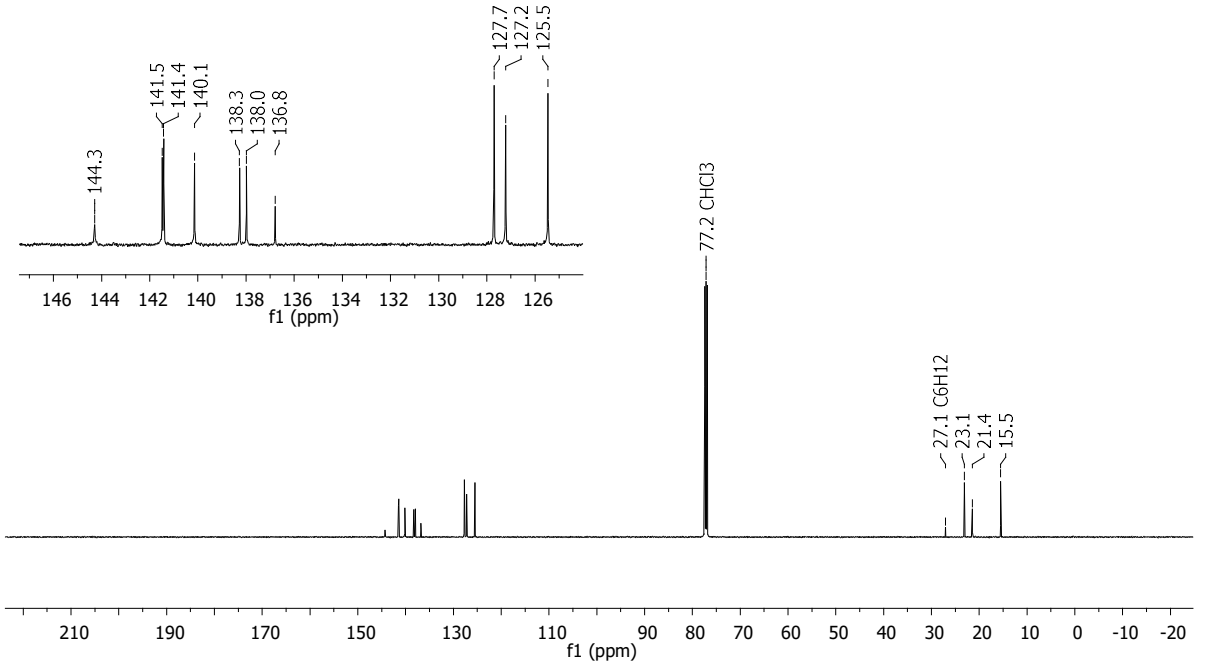


Figure S16: ^{13}C{^{1}H}-NMR spectrum of **4^{Me}** ($CDCl_3$, 126 MHz).

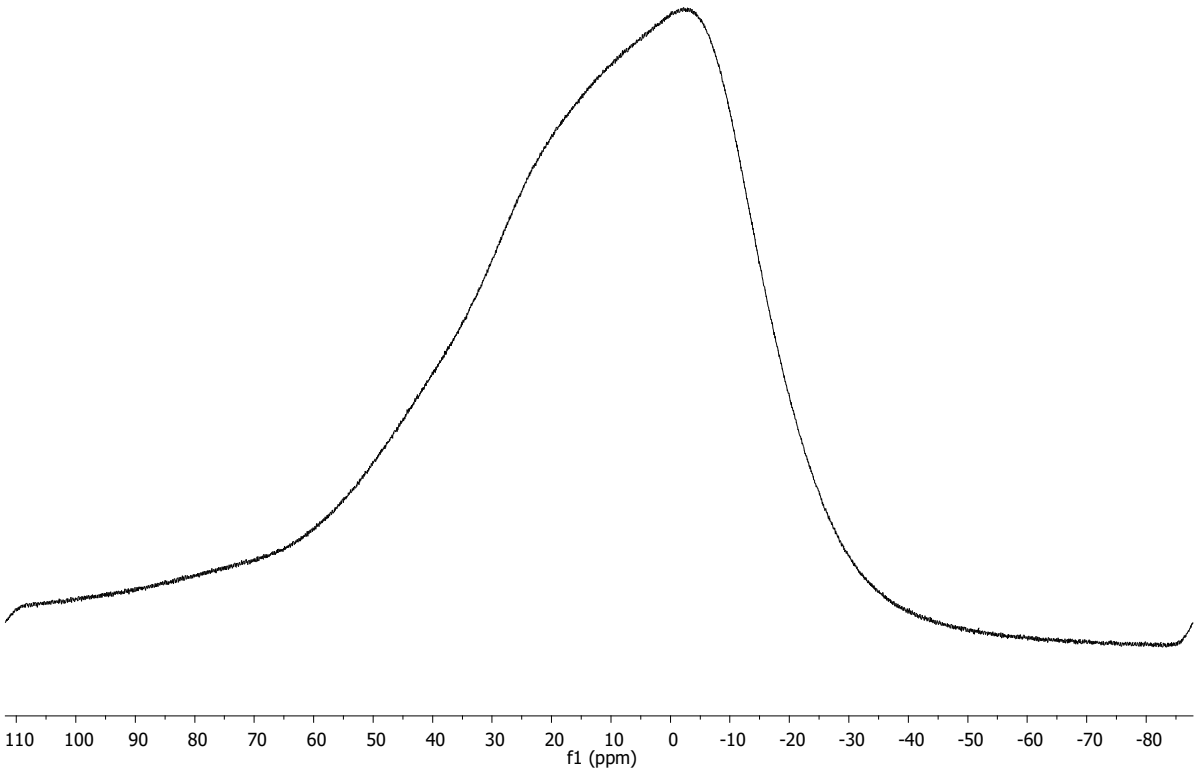


Figure S17: $^{11}B\{^{1}H\}$-NMR spectrum of **4^{Me}** ($CDCl_3$, 161 MHz); baseline uncorrected.

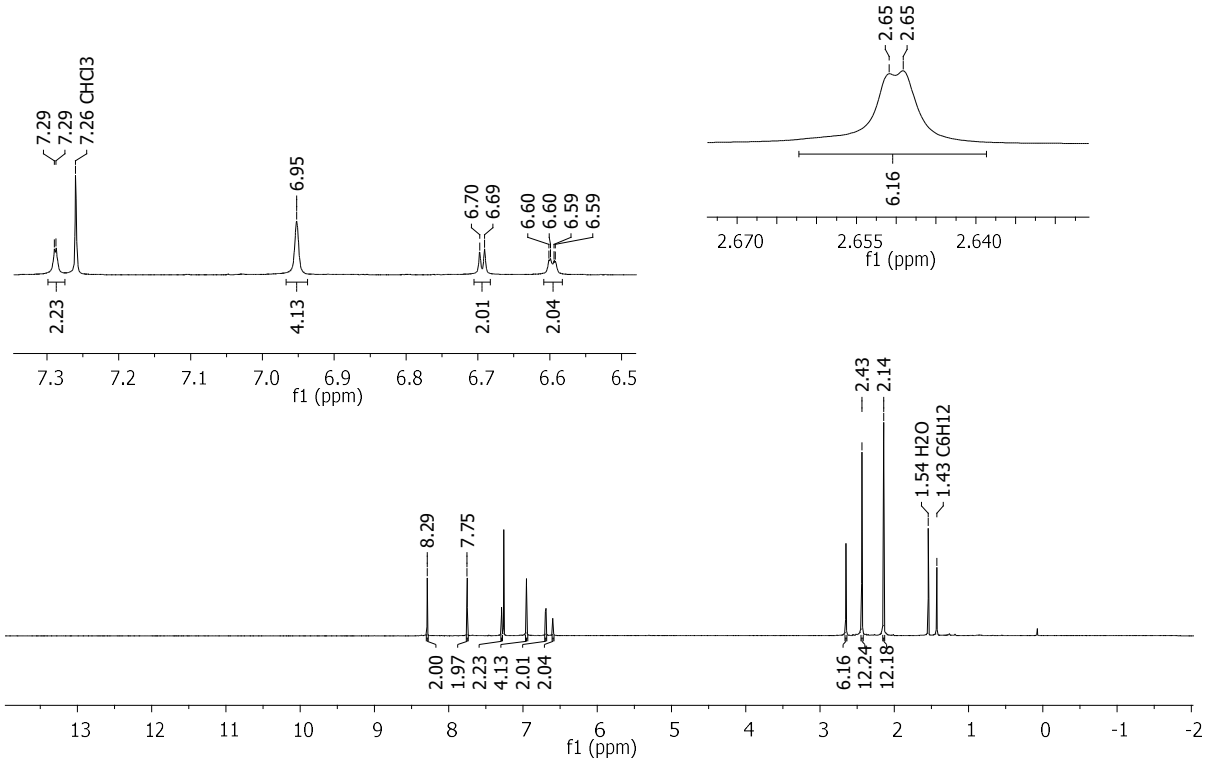


Figure S18: ^{1}H-NMR spectrum of **5^{Me}** ($CDCl_3$, 500 MHz).

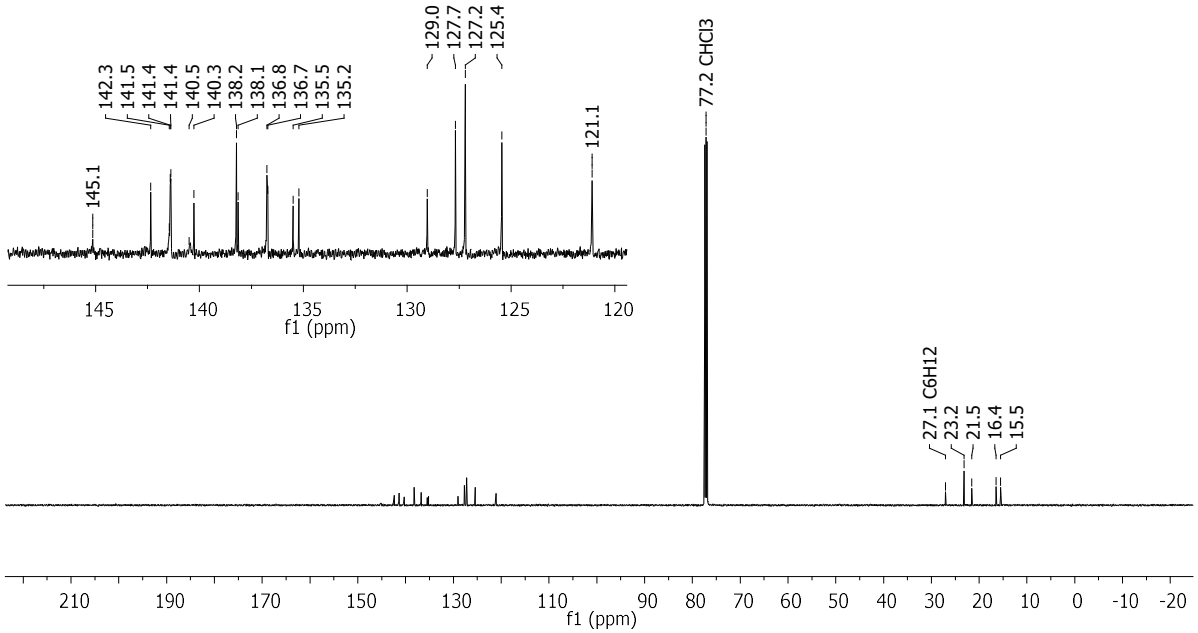


Figure S19: $^{13}C\{^{1}H\}$-NMR spectrum of **5^{Me}** ($CDCl_3$, 126 MHz).

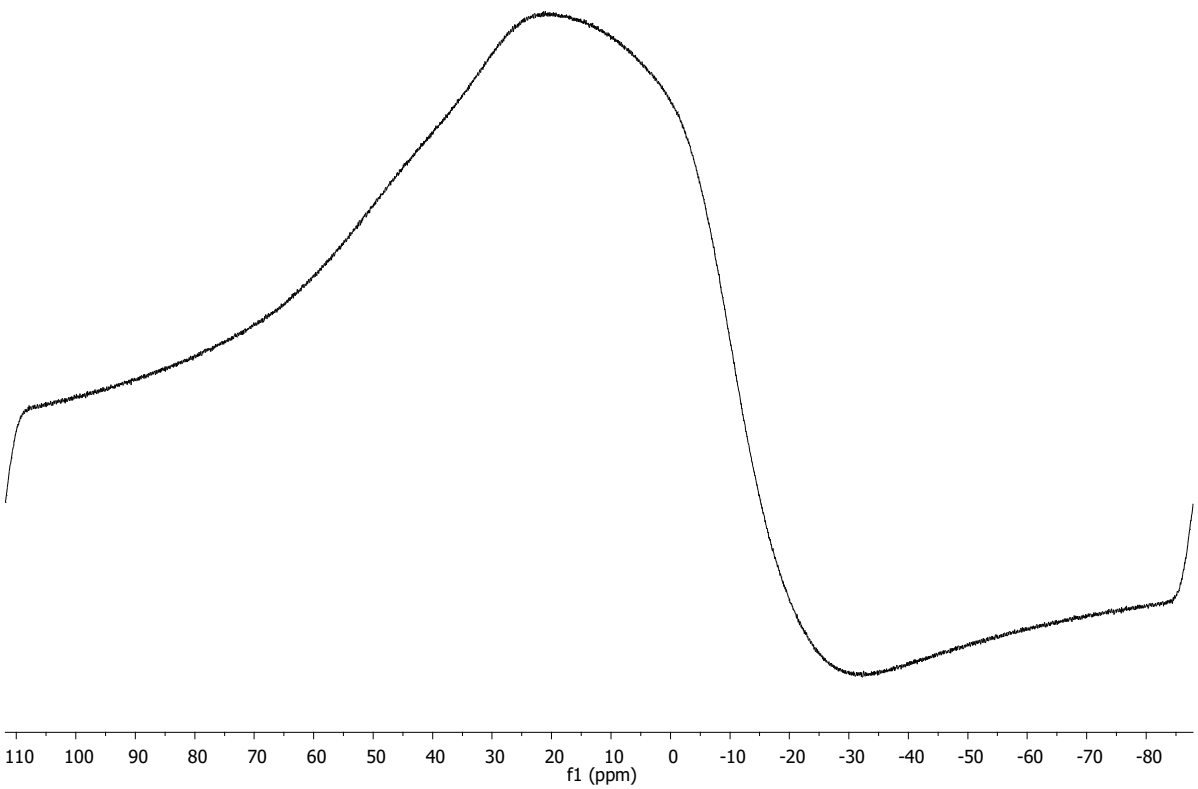


Figure S20: $^{11}B\{^{1}H\}$-NMR spectrum of **5^{Me}** ($CDCl_3$, 161 MHz); baseline uncorrected.

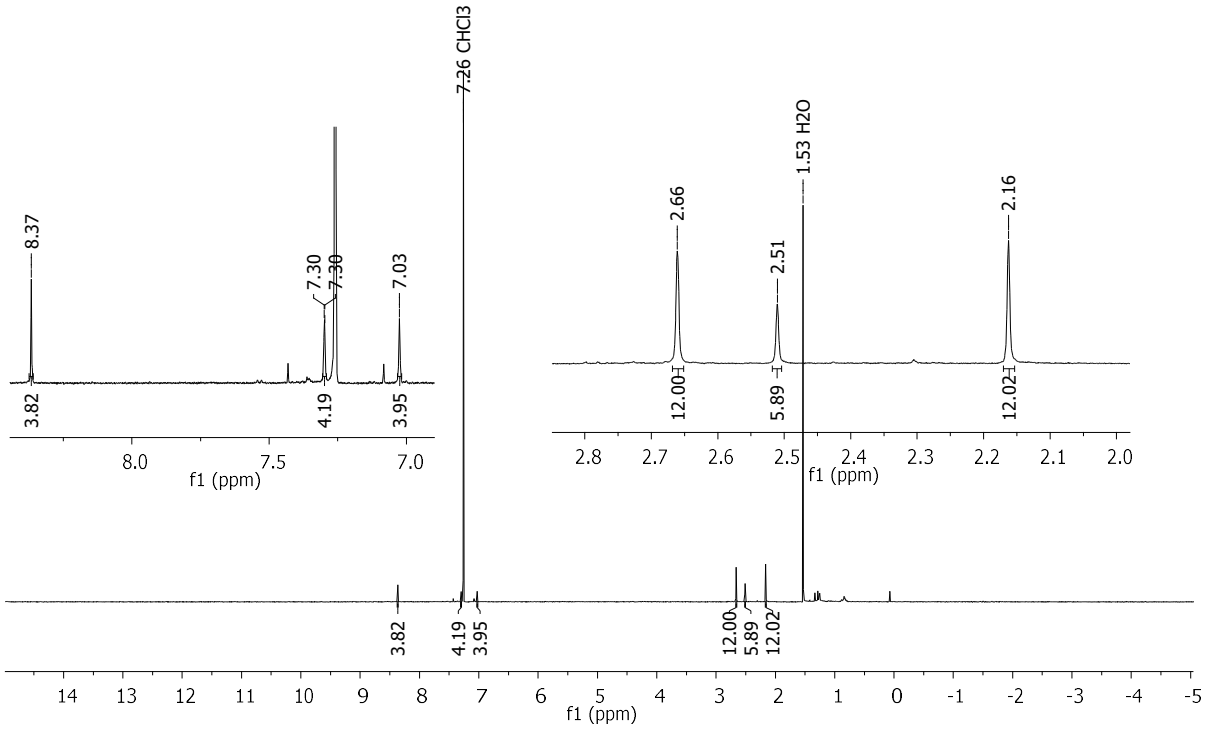


Figure S21: ^{1}H-NMR spectrum of **6^{Me}** ($CDCl_3$, 600 MHz).

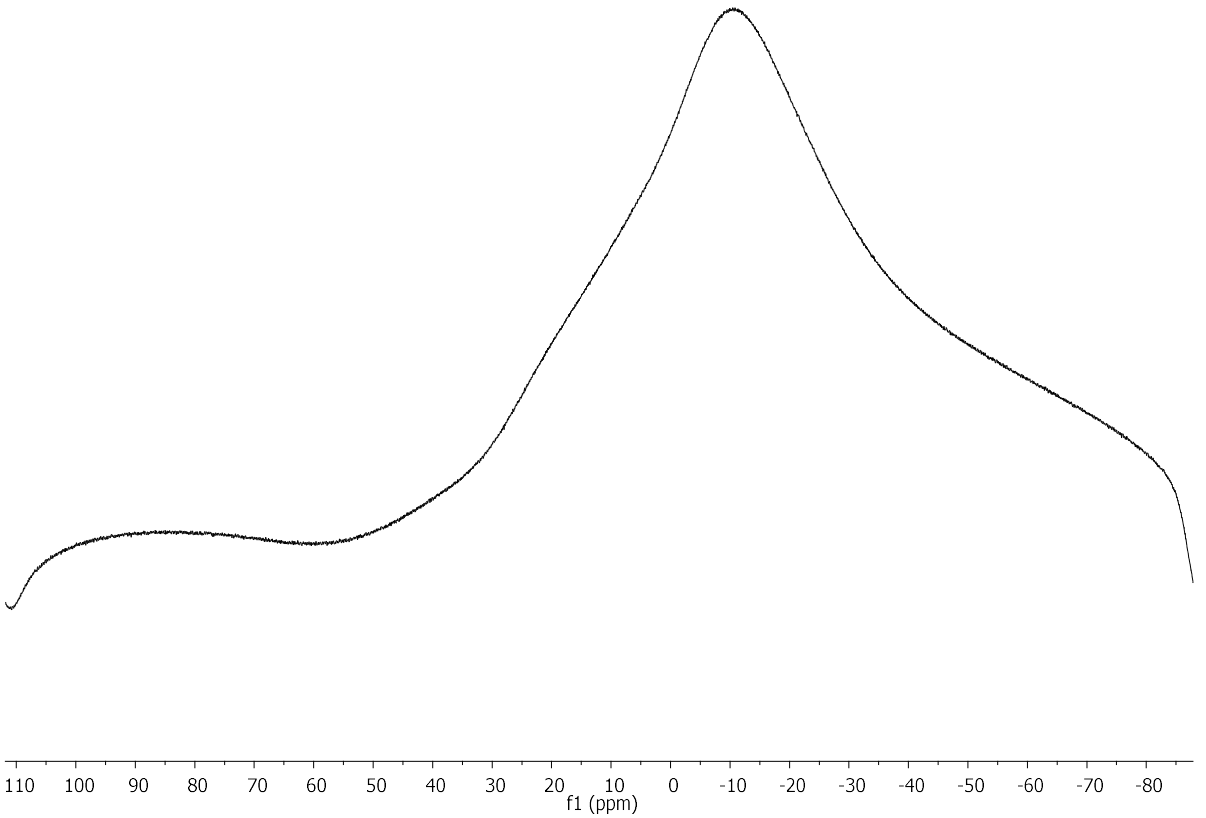


Figure S22: ^{11}B{^{1}H}-NMR spectrum of **6^{Me}** ($CDCl_3$, 161 MHz); baseline uncorrected.

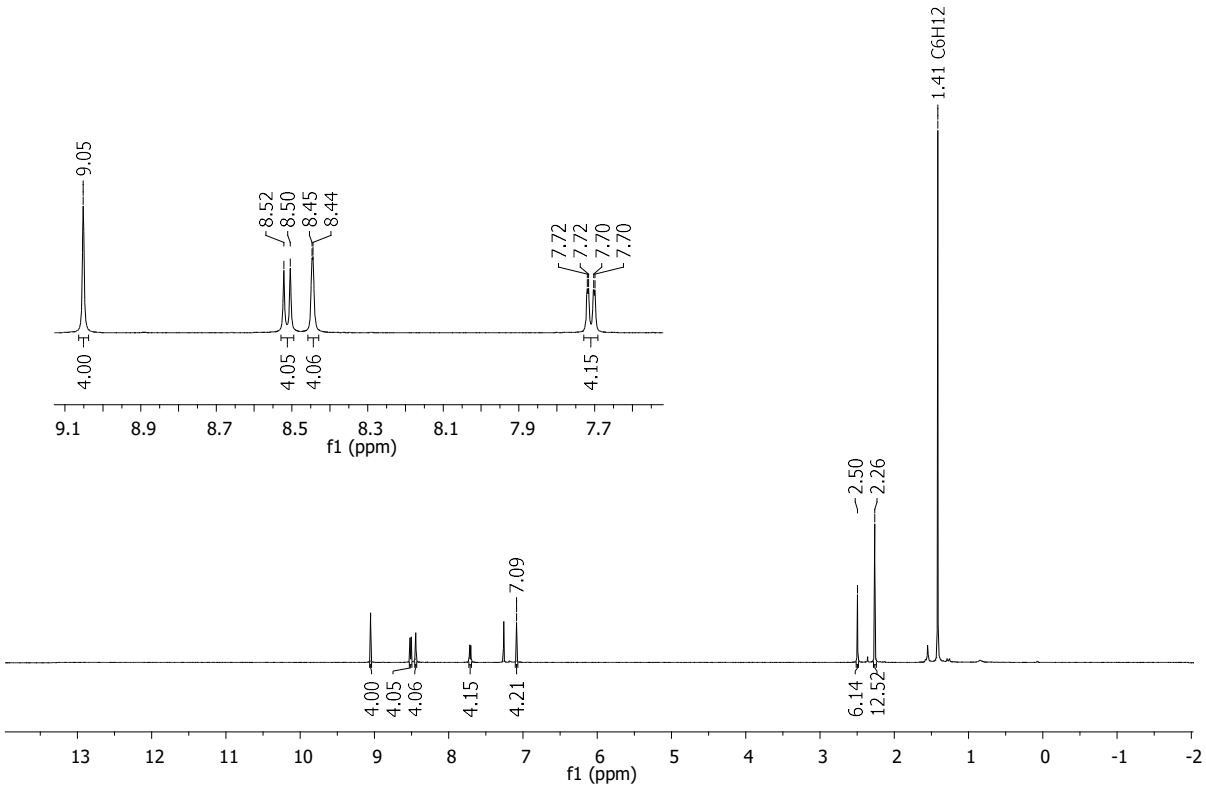


Figure S23: ^{1}H-NMR spectrum of **8** ($CDCl_3$, 500 MHz).

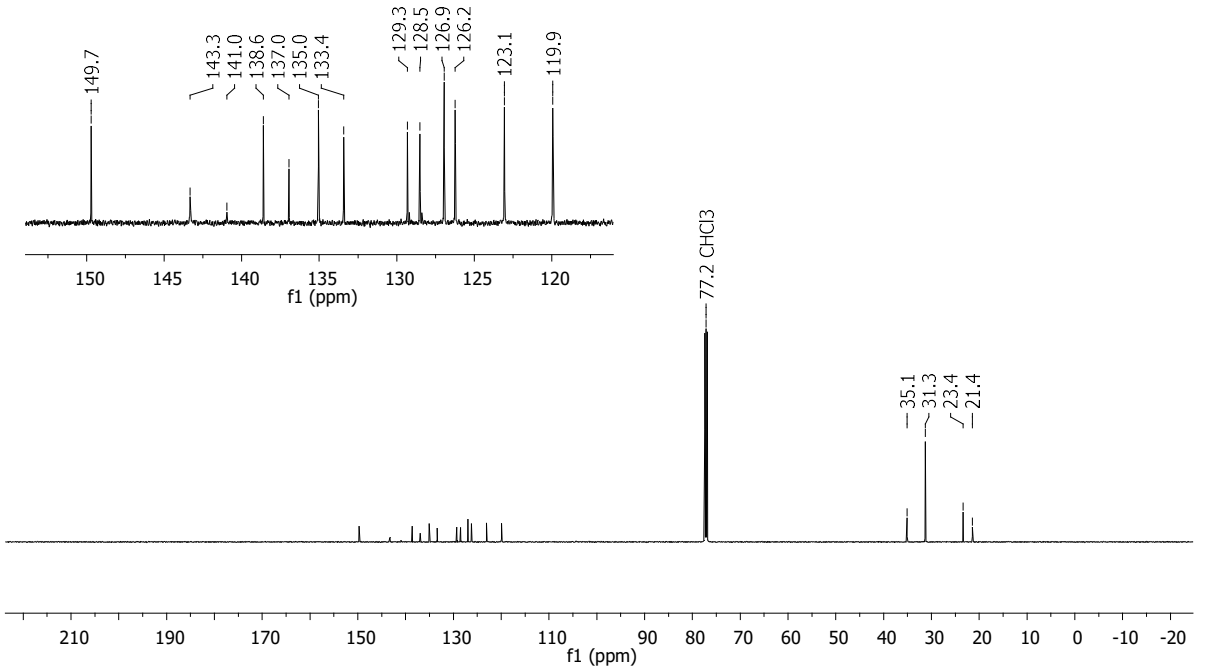


Figure S24: ^{13}C{^{1}H}-NMR spectrum of **8** ($CDCl_3$, 126 MHz).

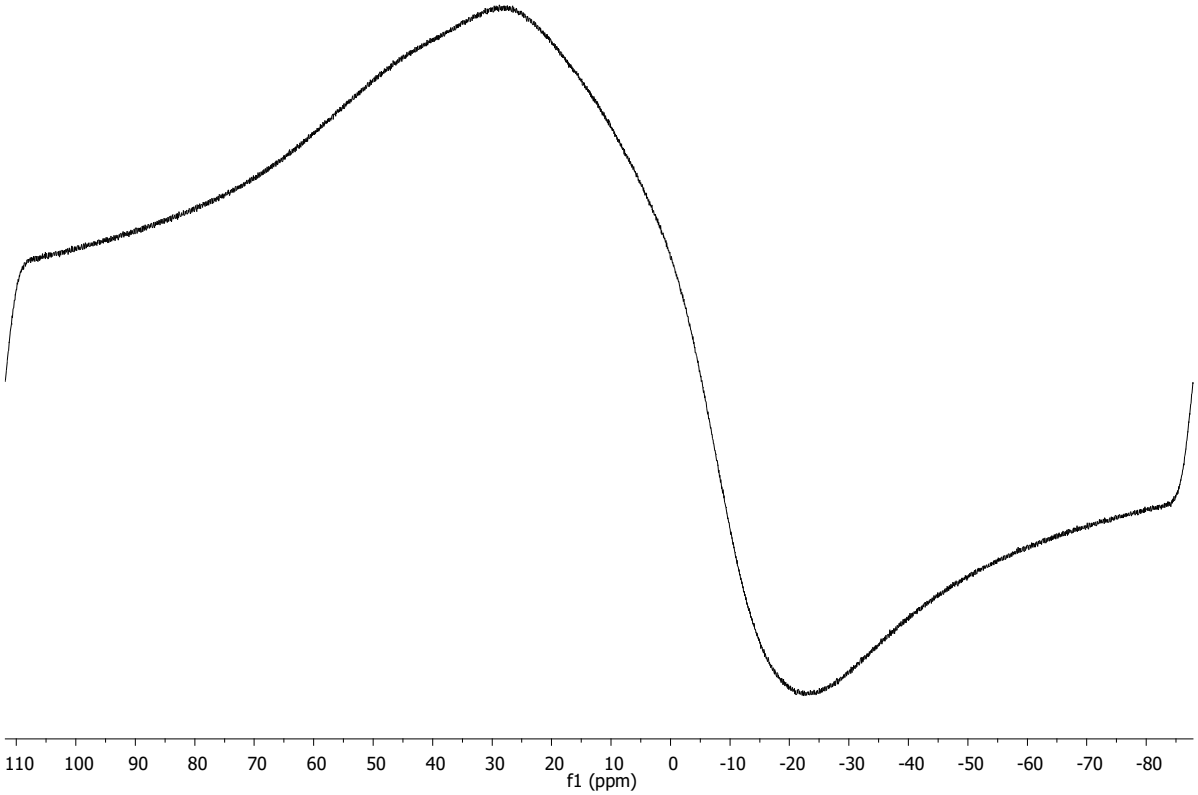


Figure S25: $^{11}B\{^{1}H\}$-NMR spectrum of **8** ($CDCl_3$, 161 MHz); baseline uncorrected.

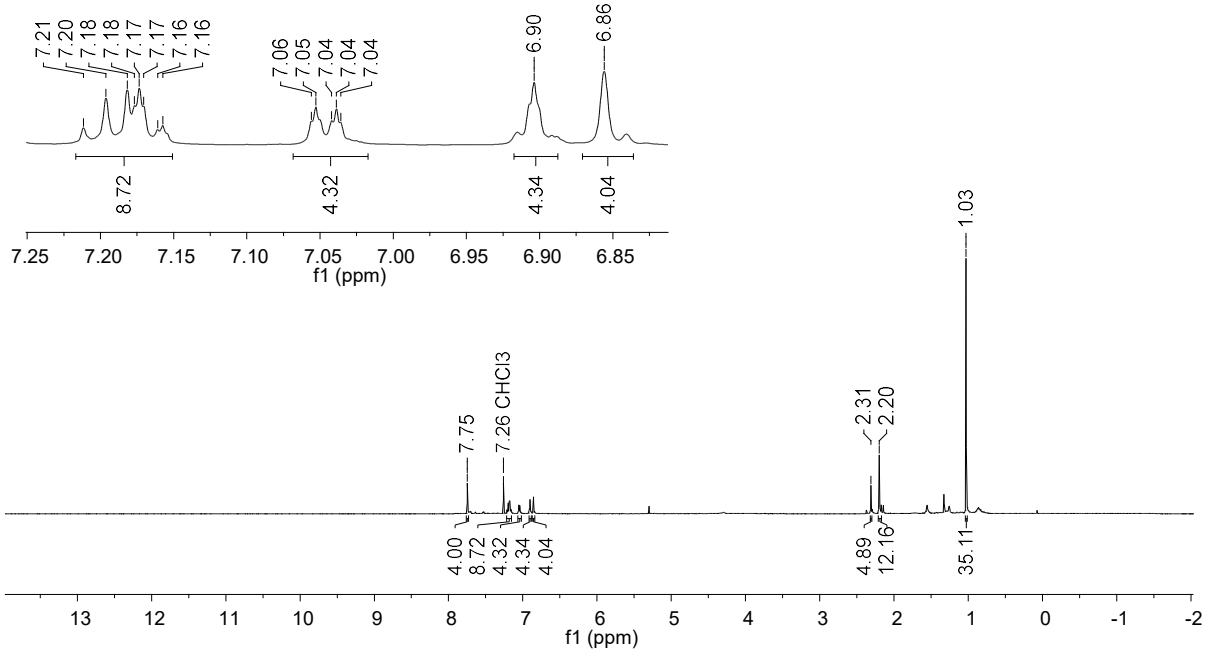


Figure S26: ^{1}H-NMR spectrum of **7** ($CDCl_3$, 500 MHz).

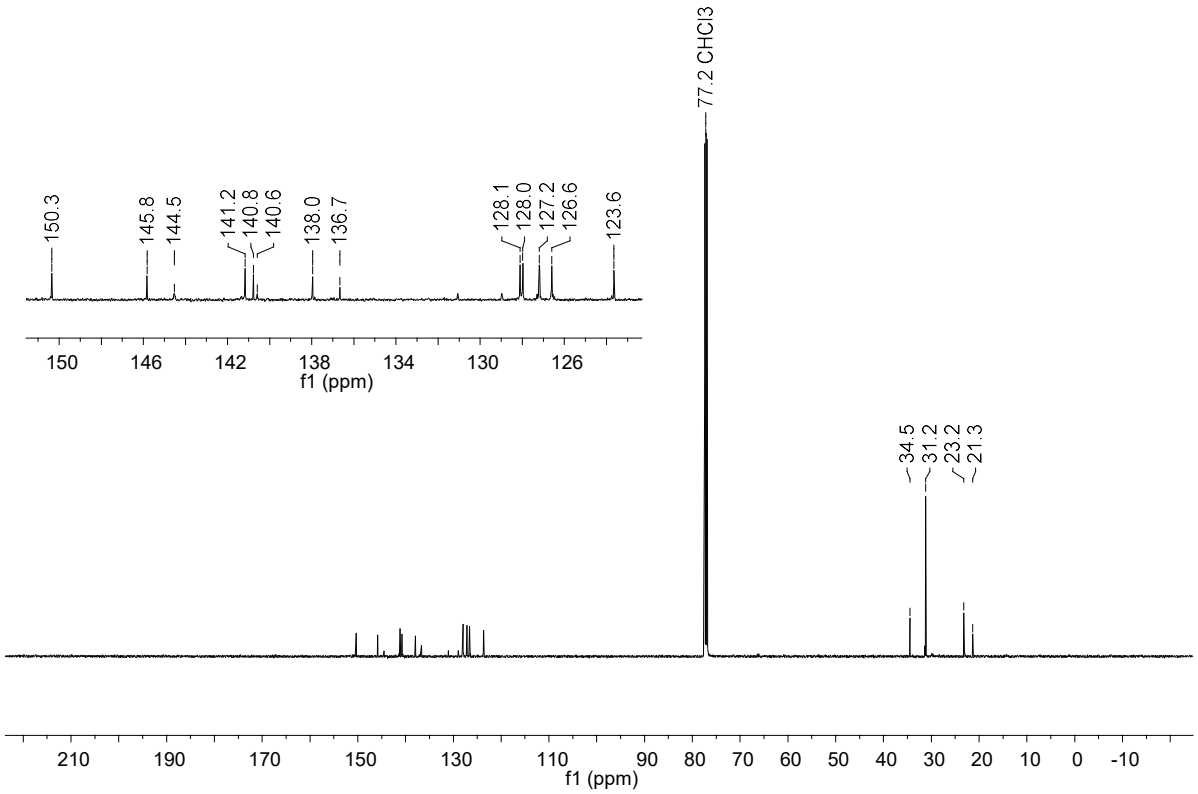


Figure S27: $^{13}C\{^{1}H\}$-NMR spectrum of **7** ($CDCl_3$, 126 MHz).

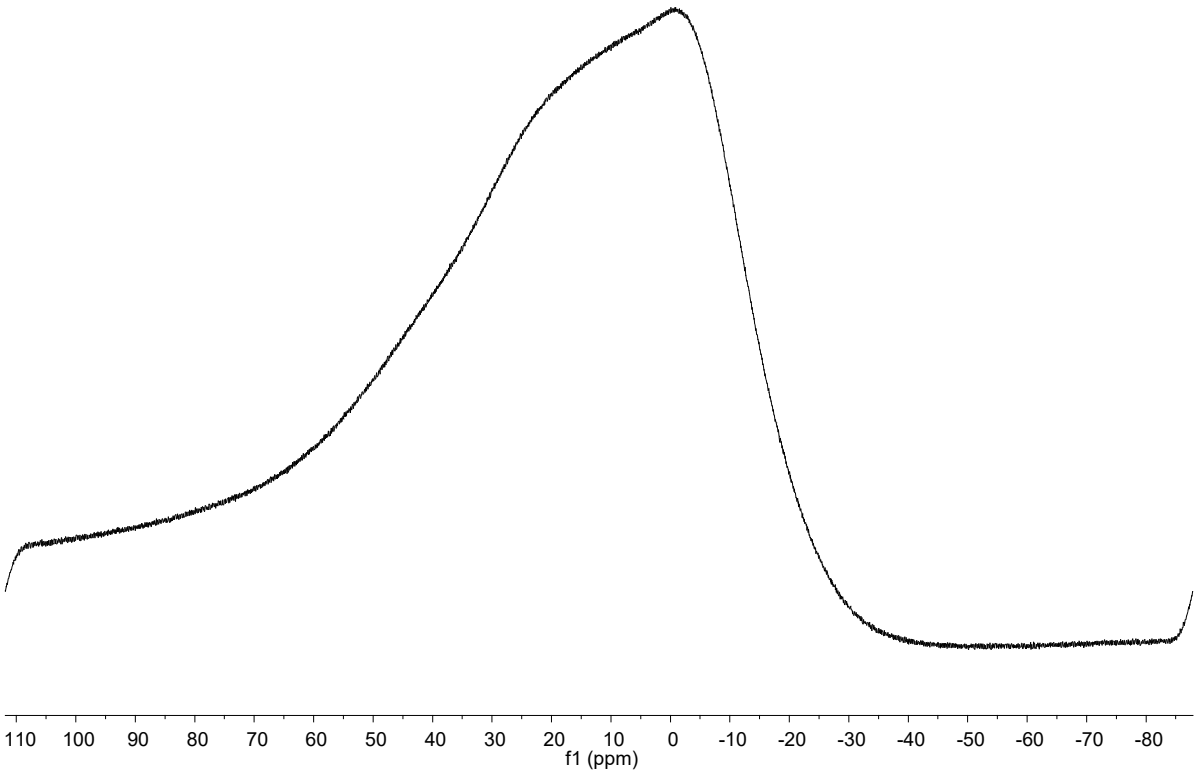


Figure S28: $^{11}B\{^{1}H\}$-NMR spectrum of **7** ($CDCl_3$, 161 MHz); baseline uncorrected.

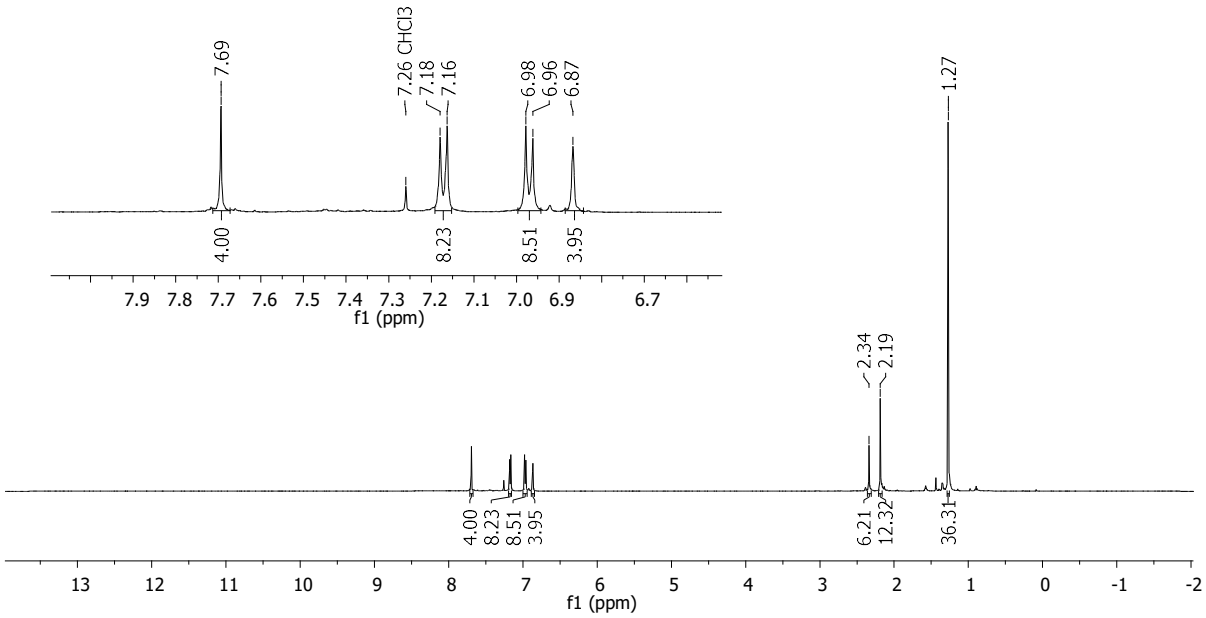


Figure S29: ^{1}H-NMR spectrum of 2,3,6,7-(4-*t*-Bu-C_6H_4)$_4$-9,10-Mes_2-DBA ($CDCl_3$, 500 MHz).

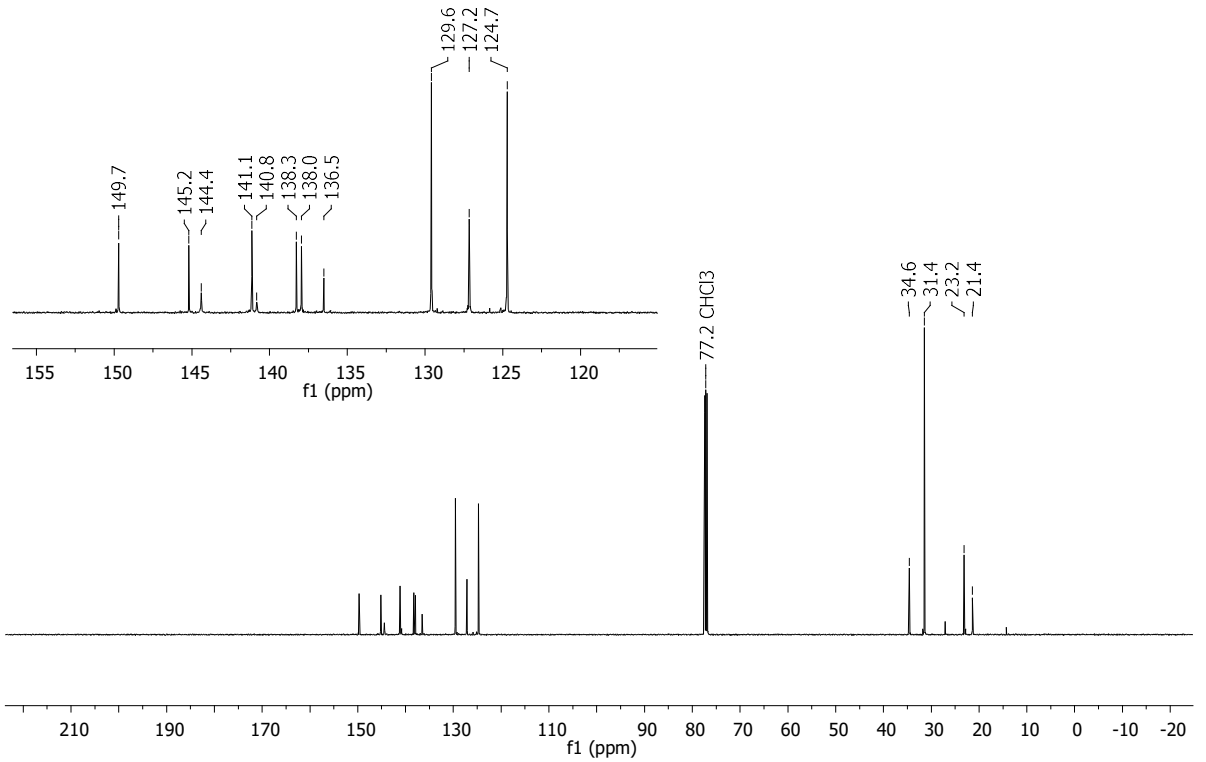


Figure S30: ^{13}C{^{1}H}-NMR spectrum of 2,3,6,7-(4-*t*-Bu-C_6H_4)$_4$-9,10-Mes_2-DBA ($CDCl_3$, 126 MHz).

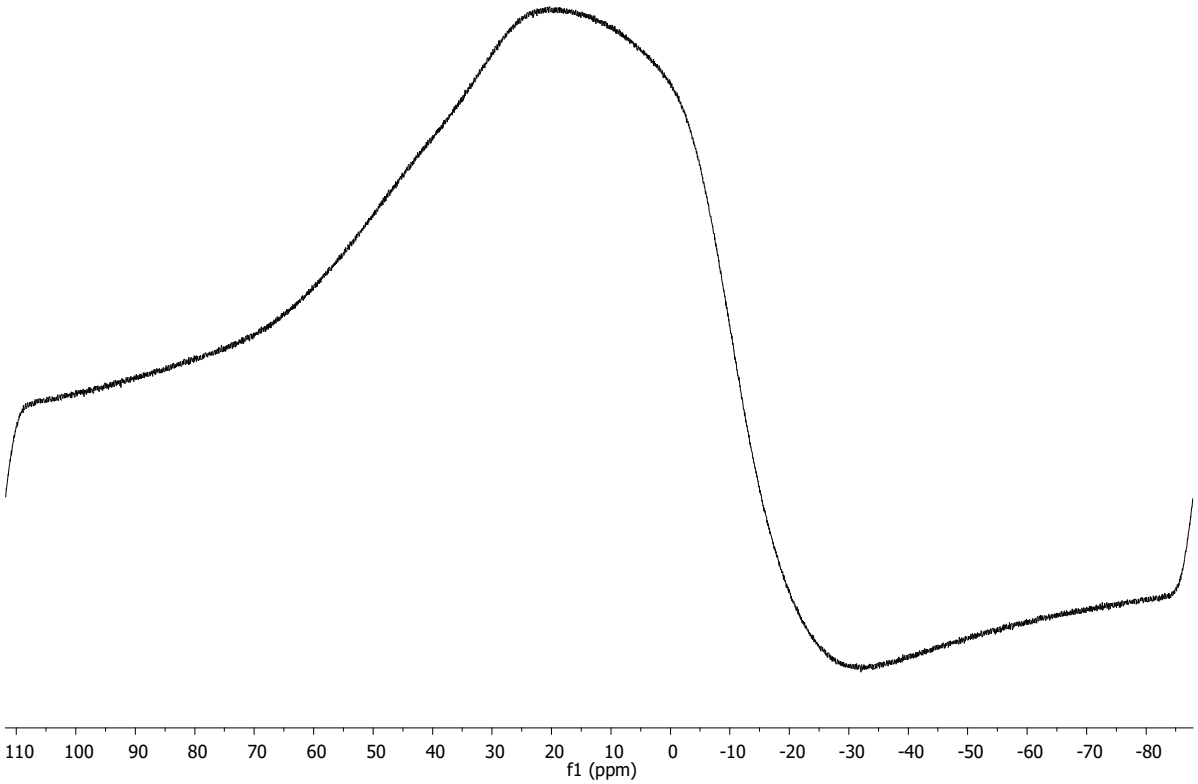


Figure S31: $^{11}B\{^{1}H\}$-NMR spectrum of 2,3,6,7-(4-*t*-Bu-C_6H_4)$_4$-9,10-Mes_2-DBA ($CDCl_3$, 161 MHz); baseline uncorrected.

4. Photophysical and electrochemical data

4.1 UV-vis absorption and emission spectra

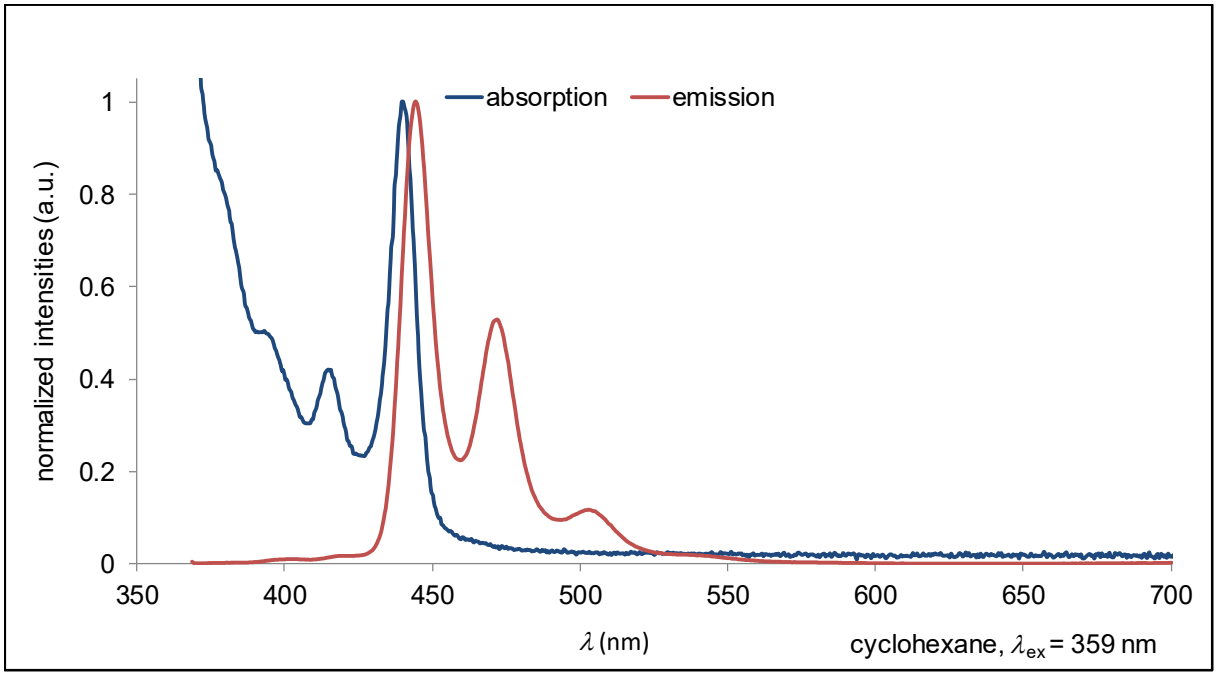


Figure S32: Normalized UV-vis absorption and emission spectrum of $\mathbf{6^{H}}$; see comment in the legend of Figure S36.

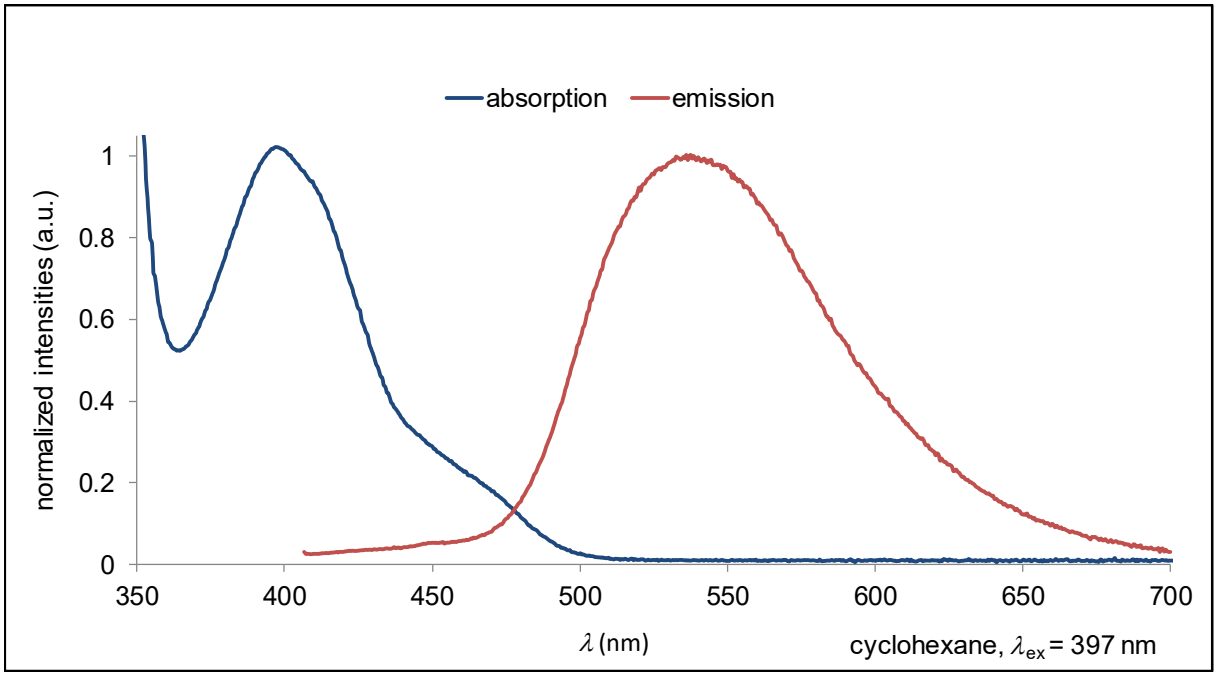


Figure S33: Normalized UV-vis absorption and emission spectrum of $\mathbf{4^{Me}}$.

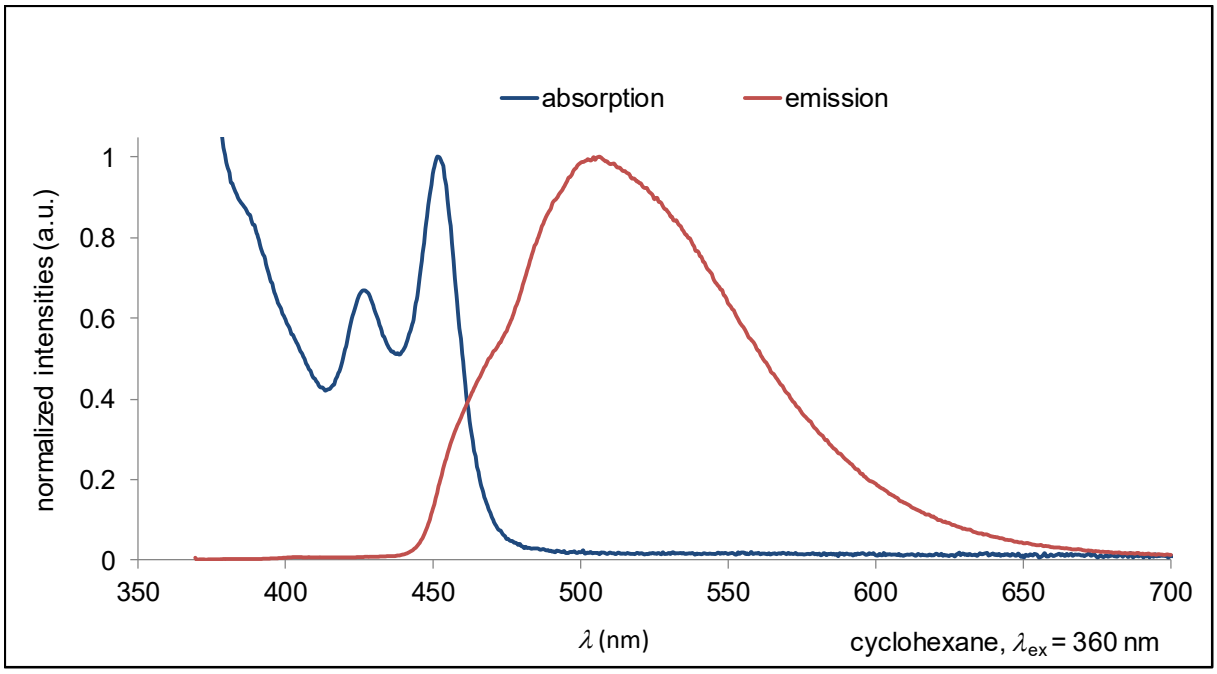


Figure S34: Normalized UV-vis absorption and emission spectrum of **5**^{Me}.

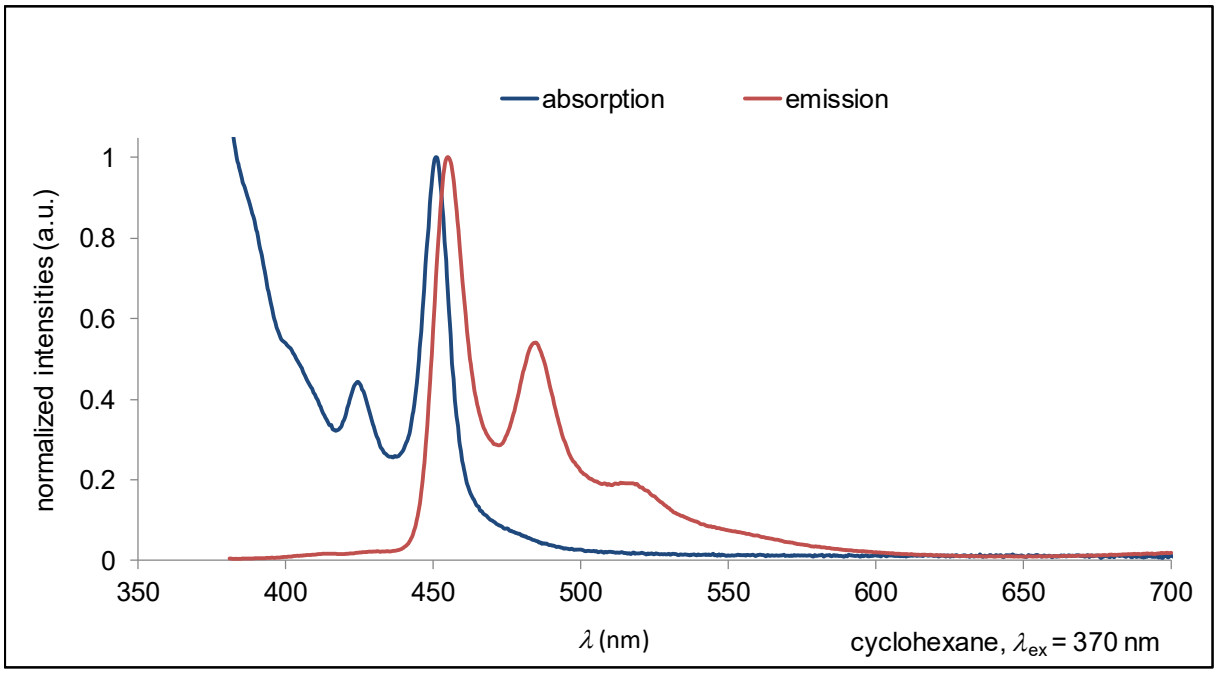


Figure S35: Normalized UV-vis absorption and emission spectrum of **6**^{Me}; see comment in the legend of Figure S36.

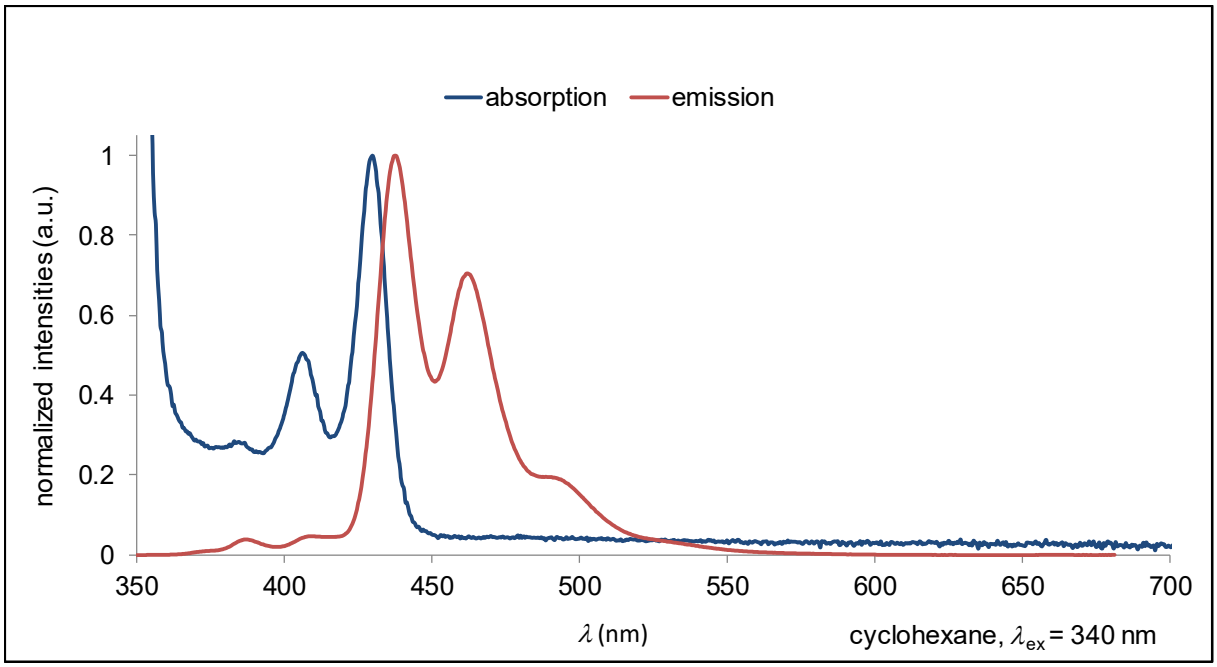


Figure S36: Normalized UV-vis absorption and emission spectrum of **8**.

Comment: The small features visible between 375 and 420 nm in the emission spectrum are not a characteristic of **8**: (i) They are strongly overlapping with the absorption spectrum and (ii) an excitation spectrum for λ_{em} = 438 nm is not superimposable with the absorption spectrum of **8**. We have evidence that such bands can originate from adducts of B-PAHs with small Lewis bases such as residual water adsorbed at the interior of the cuvette.

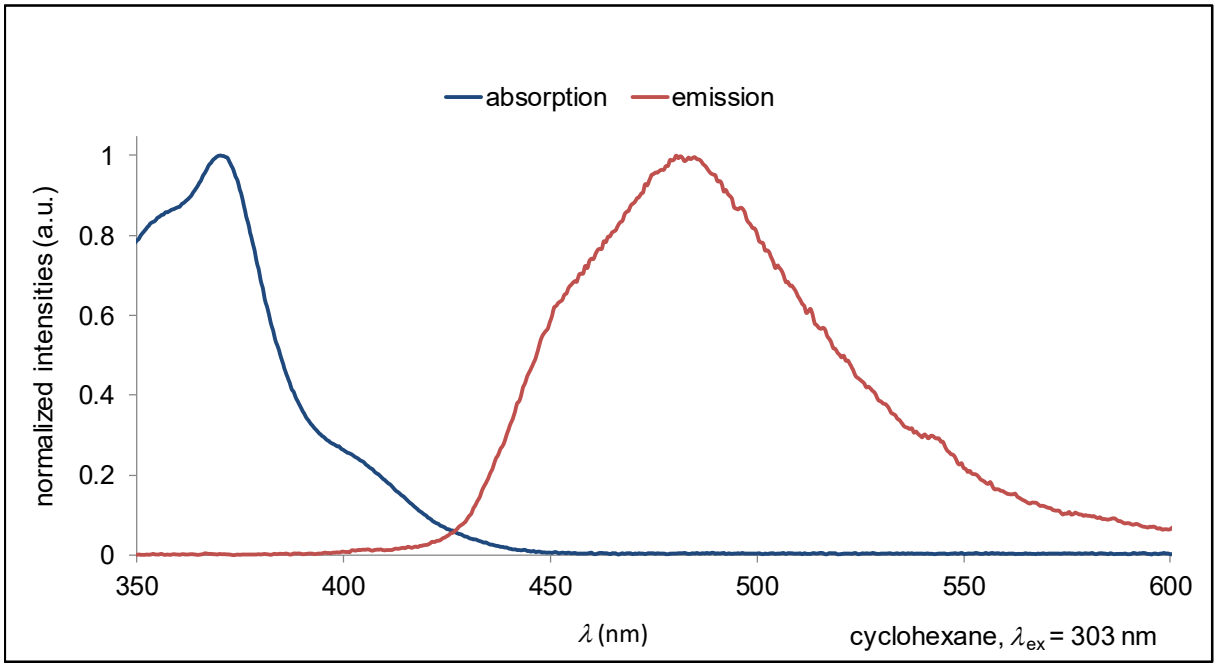


Figure S37: Normalized UV-vis absorption and emission spectrum of **7**.

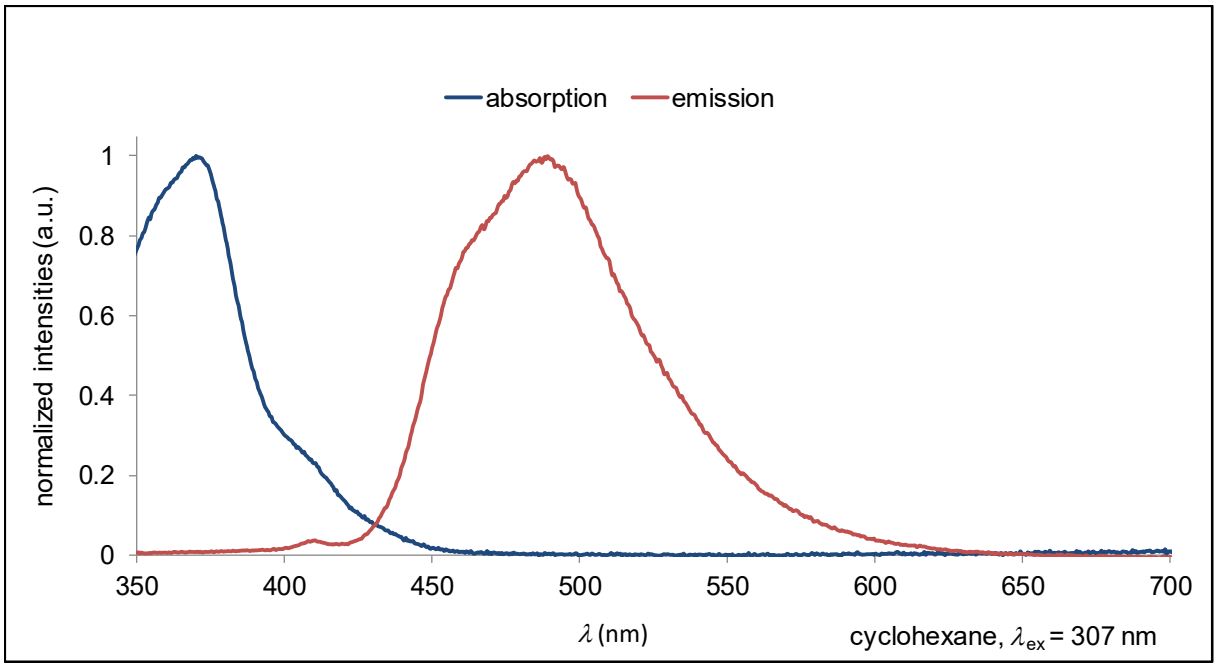


Figure S38: Normalized UV-vis absorption and emission spectrum of 2,3,6,7-(4-*t*-Bu-C_6H_4)4-9,10-Mes_2-DBA.

4.2 Plots of cyclic voltammograms

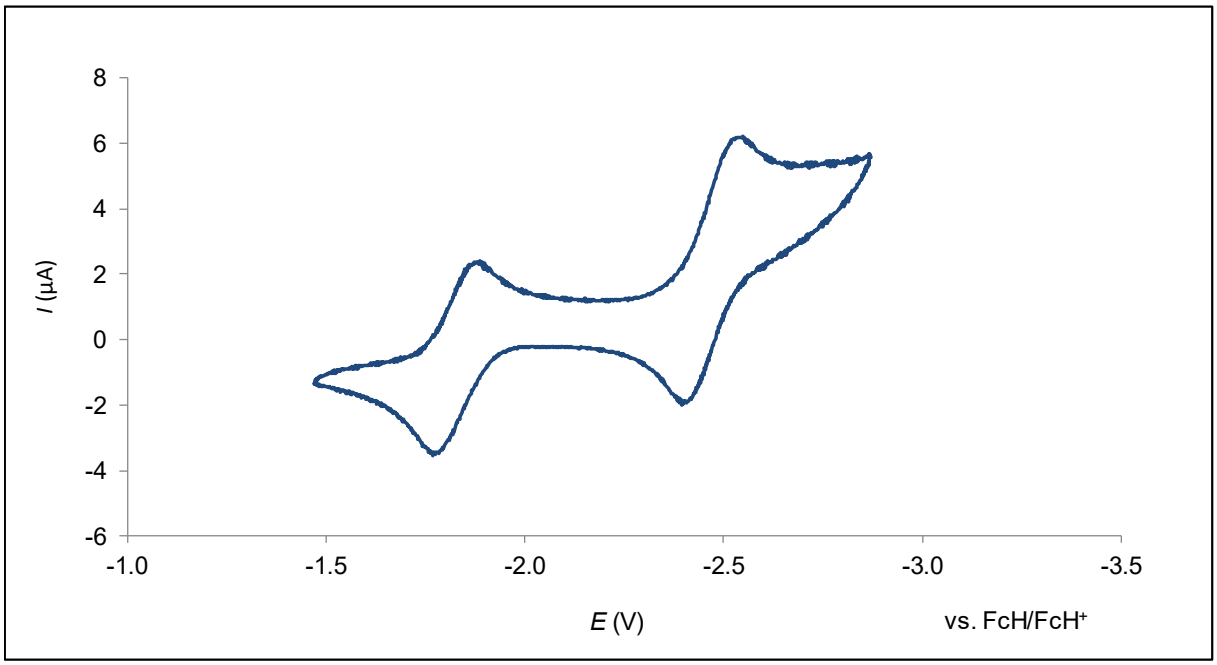


Figure S39: Cyclic voltammogram of $\mathbf{6^H}$ in THF (room temperature, supporting electrolyte: [*n*-Bu_4N][PF_6] (0.1 M), scan rate 200 mV s^{-1}).

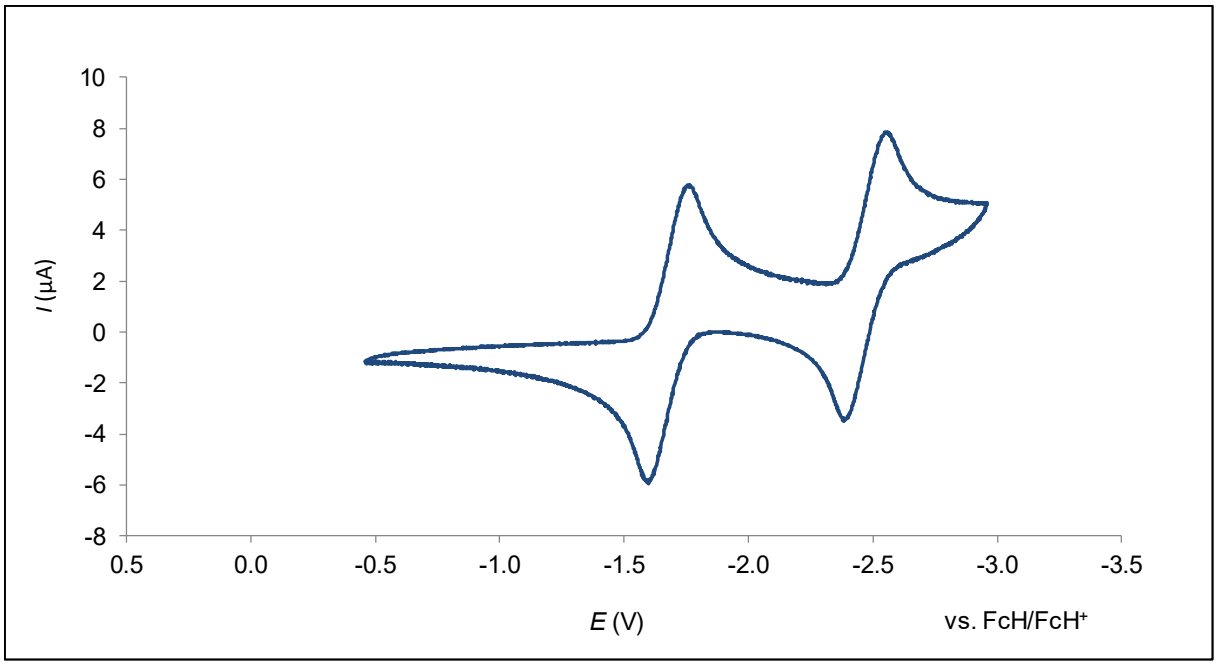


Figure S40: Cyclic voltammogram of $\mathbf{4^{Me}}$ in THF (room temperature, supporting electrolyte: [*n*-Bu_4N][PF_6] (0.1 M), scan rate 200 mV s^{-1}).

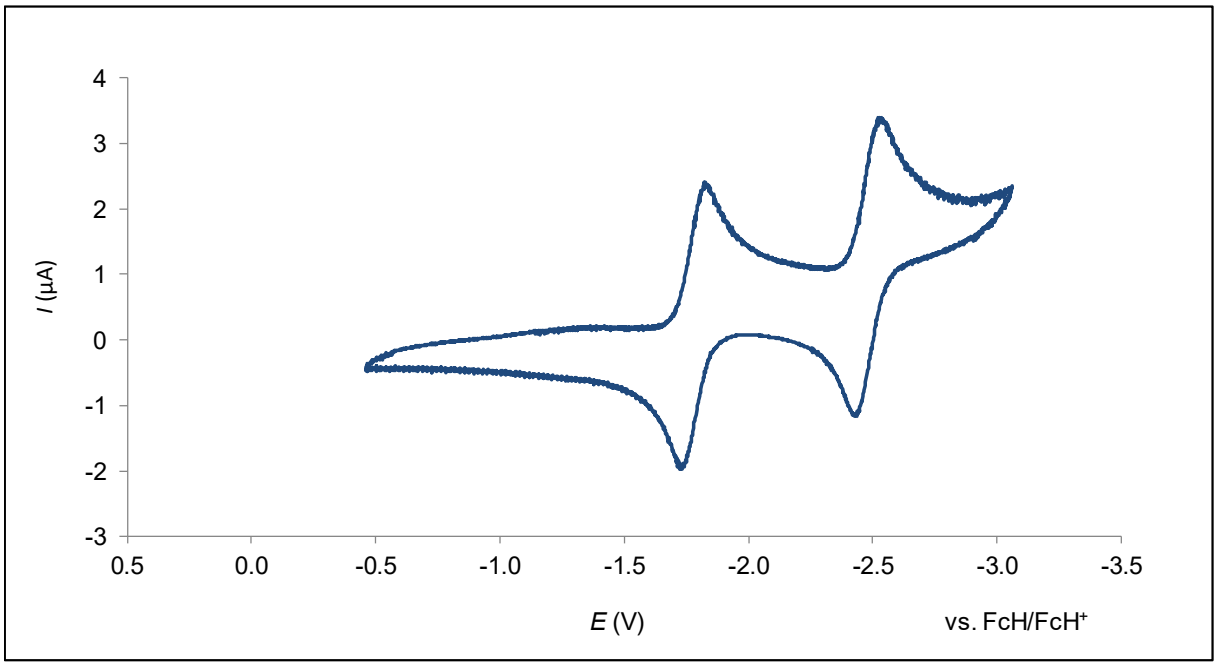


Figure S41: Cyclic voltammogram of $\mathbf{5^{Me}}$ in THF (room temperature, supporting electrolyte: [*n*-Bu_4N][PF_6] (0.1 M), scan rate 200 mV s^{-1}).

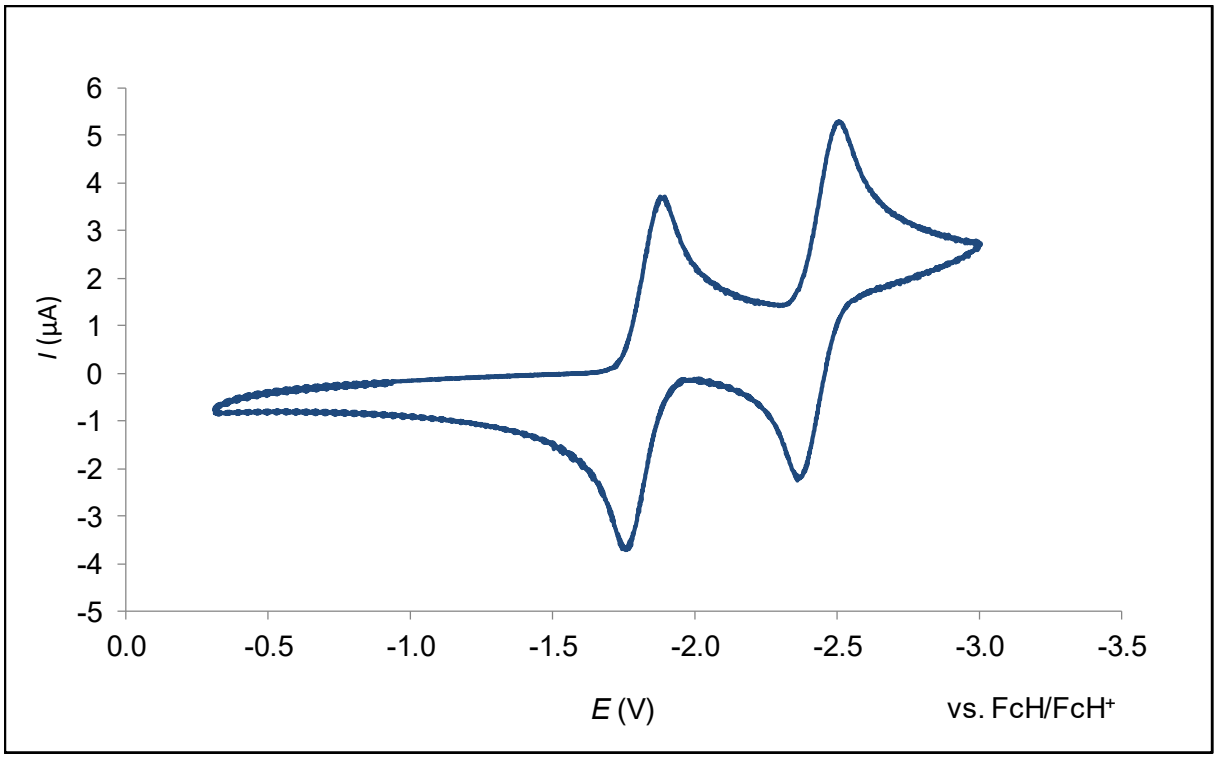


Figure S42: Cyclic voltammogram of **8** in THF (room temperature, supporting electrolyte: [*n*-Bu_4N][PF_6] (0.1 M), scan rate 200 mV s^{-1}).

Figure S43: Cyclic voltammogram of **7** in THF (room temperature, supporting electrolyte: [*n*-Bu_4N][PF_6] (0.1 M), scan rate 200 mV s^{-1}).

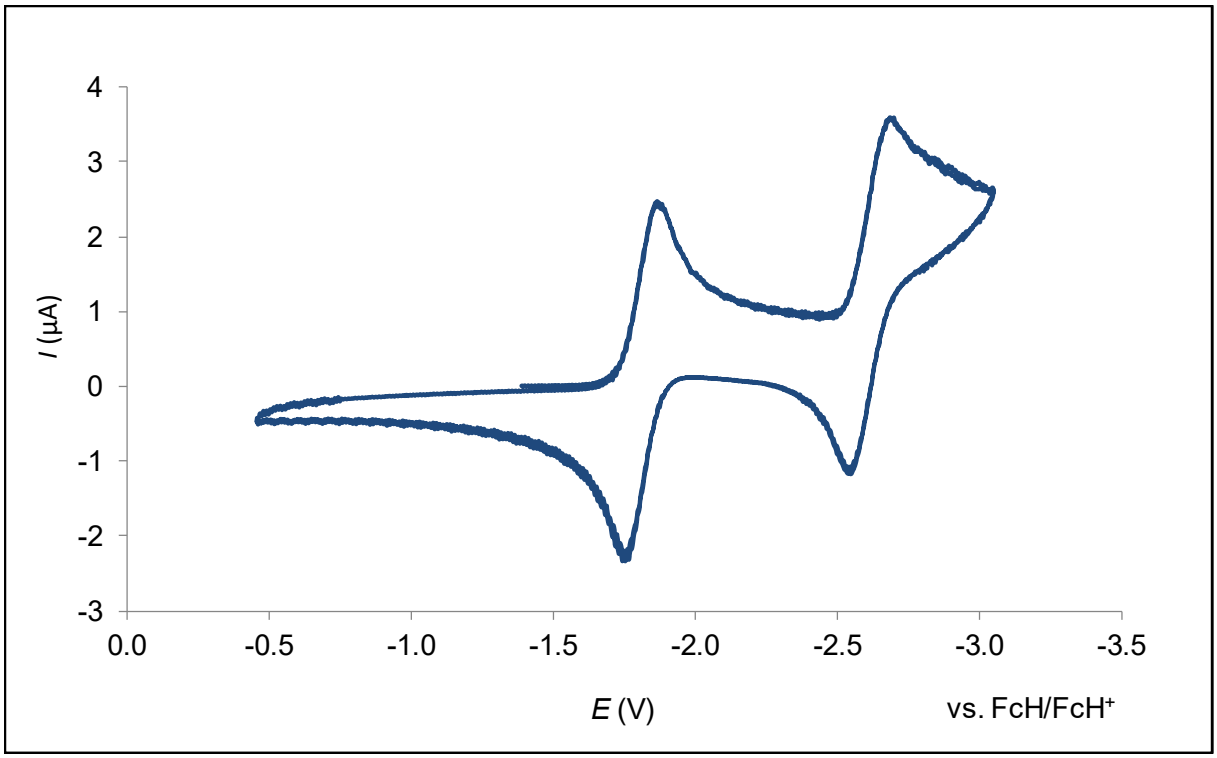


Figure S44: Cyclic voltammogram of 2,3,6,7-(4-*t*-Bu-C_6H_4)$_4$-9,10-Mes_2-DBA$(Mes)_2$ in THF (room temperature, supporting electrolyte: [*n*-Bu_4N][PF_6] (0.1 M), scan rate 200 mV s^{-1}).

5. X-ray crystal structure analyses

Data for all structures were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK_α radiation (λ = 0.71073 Å) and were scaled using the frame scaling procedure in the *X-AREA*[S19] program system. The structures were solved by direct methods using the program *SHELXS*[S20] and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL-97*.[S20]

CCDC files 1883327-1883336 contain the supplementary crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In **A**, one *t*-Bu group is disordered over two positions with a site occupation factor of 0.798(6) for the major occupied site.

In **B**, one *t*-Bu group is disordered over two positions with a site occupation factor of 0.532(8) for the major occupied site, and three C-atoms in one Bpin residue are disordered over two positions with a site occupation factor of 0.596(8) for the major occupied sites. Equivalent bond lengths in the Bpin residue were restrained to be equal.

Due to the absence of anomalous scatterers in **1**, the absolute structure could not be determined; Flack-x-parameter 0.2(5).

In **C**, the H atoms bonded to B were freely refined.

In $\mathbf{2^H}\cdot 2SMe_2$, the H atom bonded to B was freely refined.

In $\mathbf{2^{OH}}$, one *t*-Bu group is disordered over two positions with a site occupation factor of 0.692(13) for the major occupied site. The C–C distances between the disordered atoms were restrained to 1.5(1) Å. The contribution of the unidentifiable solvent was suppressed using the *SQUEEZE* routine in the *PLATON* program.[S21]

In $\mathbf{4^{Me}}$, one thienyl ring is disordered over two positions with a site occupation factor of 0.779(5) for the major occupied site. Bond lengths and angles in the two disordered moieties were restrained to be equal.

In **8**, one *t*-Bu group is disordered over two positions with a site occupation factor of 0.687(9) for the major occupied site.

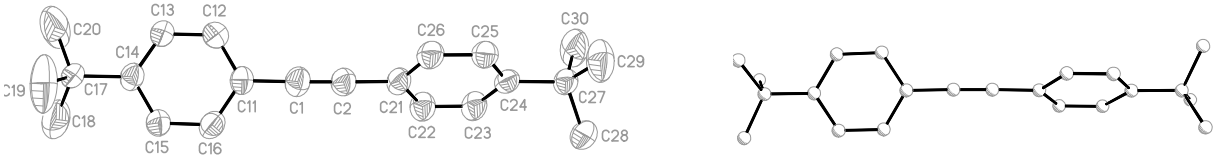


Figure S45 (CCDC 1883327): Molecular structure of **A** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], and bond angle [°]: C1–C2 = 1.196(3), C11–C1 = 1.439(3), C21–C2–C1 = 178.5(3).

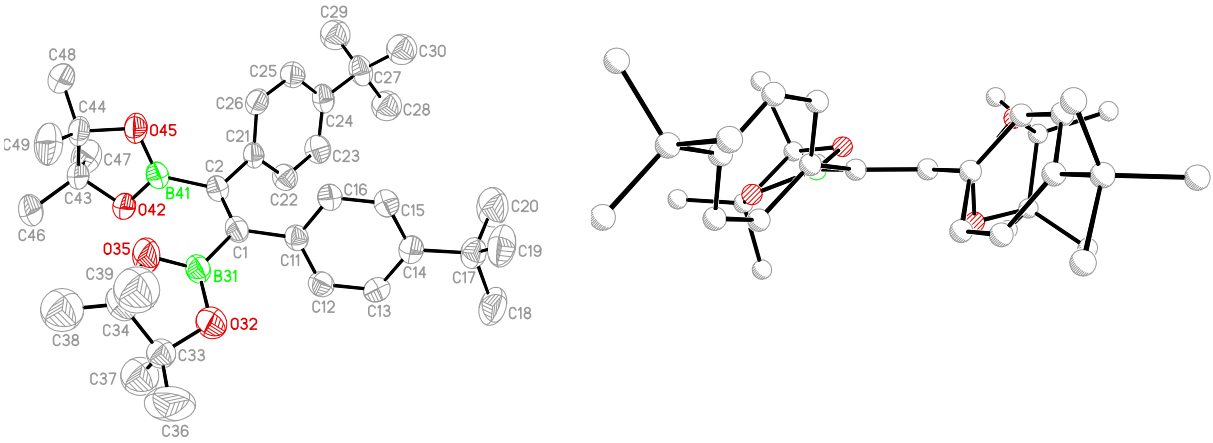


Figure S46 (CCDC 1883328): Molecular structure of **B** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], and bond angles[°]: C1–C2 = 1.346(4), C1–C11 = 1.501(4), C1–B31 = 1.558(4), C2–C1–C11 = 121.4(2), C11–C1–B31 = 117.1(2), C2–C1–B31 = 121.3(3).

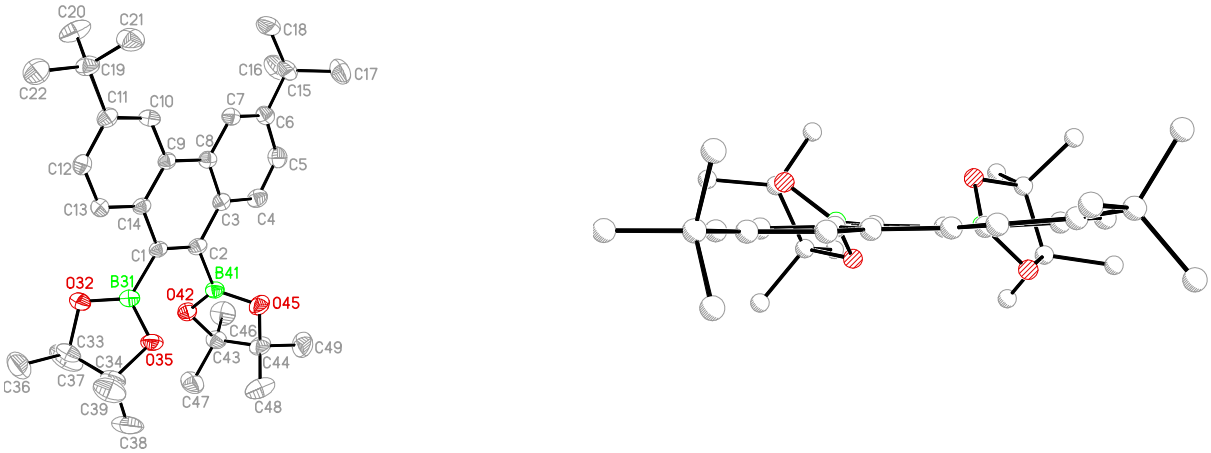


Figure S47 (CCDC 1883329): Molecular structure of **1** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], and bond angles[°]: C1–C2 = 1.375(3), C1–C14 = 1.450(3), C1–B31 = 1.570(3), C2–C1–C14 = 120.11(17), C2–C1–B31 = 119.99(17), C14–C1–B31 = 119.90(17).

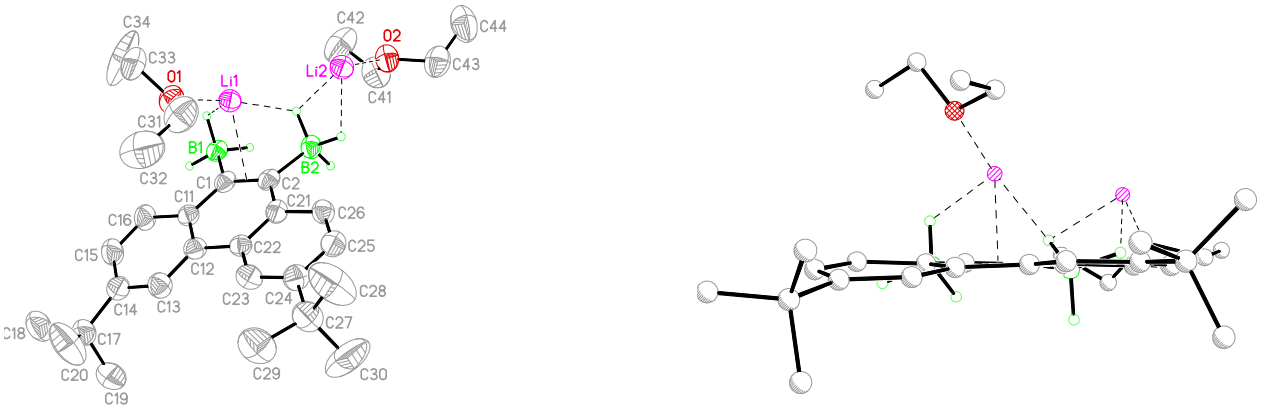


Figure S48 (CCDC 1883330): Molecular structure of **C** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C2 = 1.401(5), C1–C11 = 1.467(5), B1–C1 = 1.629(6), B1–H1A/1B/1C = 1.15(3)/1.22(4)/1.08(3).

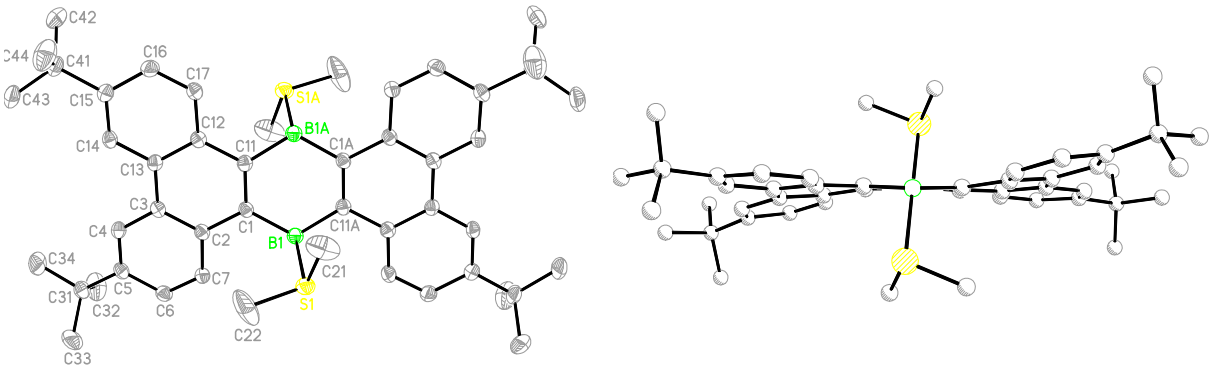


Figure S49 (CCDC 1883331): Molecular structure of $\mathbf{2^{H}}$·2SMe$_2$ in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: B–C = 1.600(3)/1.603(3), B1–H1 = 1.10(2), B1–S1 = 2.118(2); C1–B1–C2 = 118.94(18), H1–B1–S1 = 98(1), C–B–S = 98.1(1)/106.5(1), C–B–H = 116(1)/115(1).

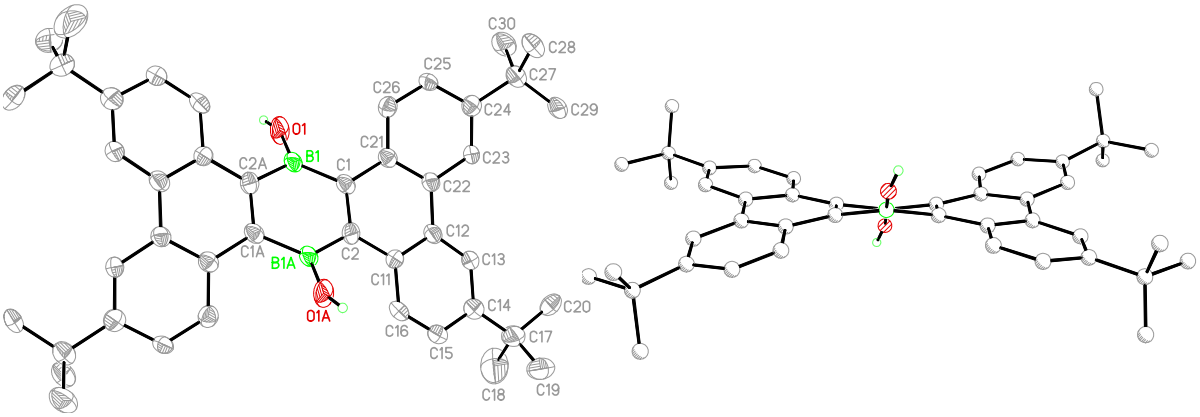


Figure S50 (CCDC 1883332): Molecular structure of **2^{OH}** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles, and torsion angles [°]: C1–C2 = 1.389(7), C–B = 1.566(8)/1.570(8), B1–O1 = 1.363(7), C–B–O = 121.0(5)/115.6(5), B–C–C–B = –24.4(8), C16–C11–C2–B1A = 16.4(9), C13–C12–C22–C23 = –15.1(8); symmetry operator for generating equivalent atoms A 1-x, 2-y, 1-z.

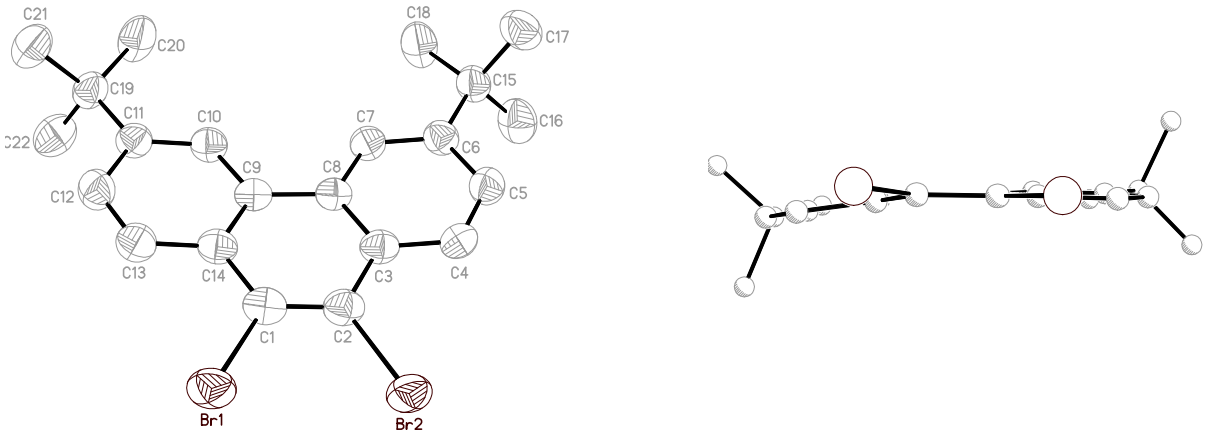


Figure S51 (CCDC 1883333): Molecular structure of **D** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: C–Br = 1.890(4)/1.886(4), C1–C2 = 1.359(6), C2–C1–Br1 = 121.0(3), C14-C1-Br1 = 118.0(3), C1-C2-Br2 = 120.3(3), C3-C2-Br2 = 118.4(3), C7–C8–C9–C10 = 2.4(6).

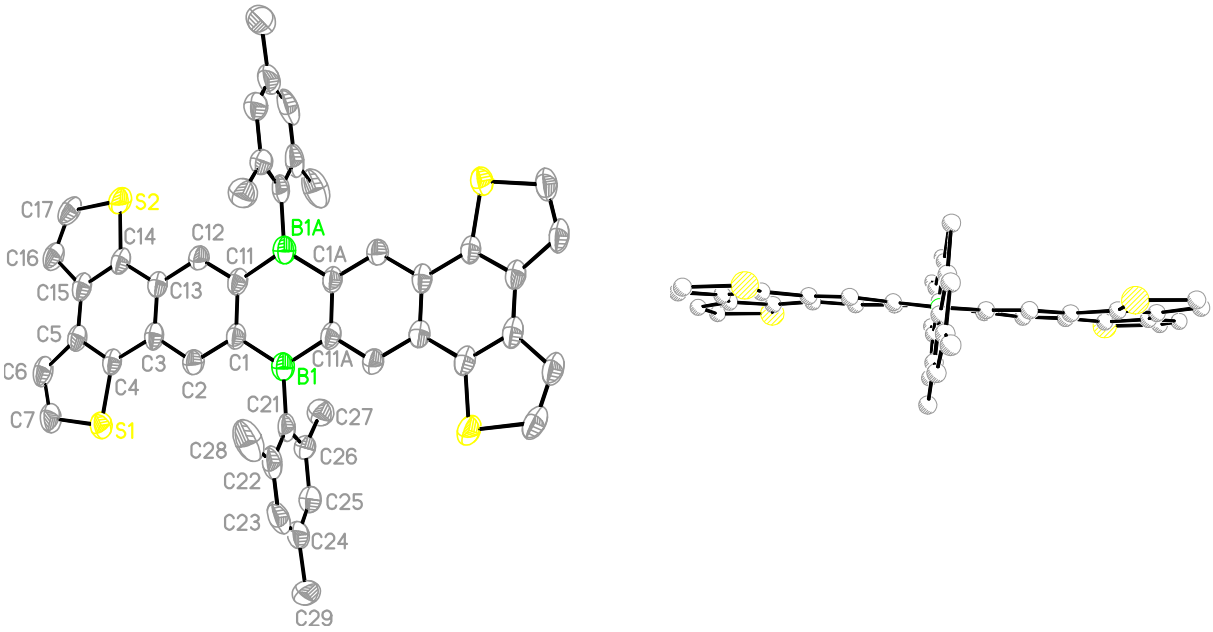


Figure S52 (CCDC 1883334): Molecular structure of **6^{H}** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles, and torsion angles [°]: B1-C1 = 1.561(7), B1-C11A = 1.569(6), B1-C21 = 1.585(7), C3-C13 = 1.406(6), C3-C4 = 1.447(6), C13-C14 = 1.439(6), C14-S2 = 1.734(5), C17-S2 = 1.720(5); C21-B1-C11A = 119.3(4), C21-B1-C1 = 121.4(4), C1-B1-C11A = 119.1(4), C15-C14-S2 111.3(3); C14-C13-C3-C4 = –2.4(6), C14-C15-C5-C4 = –1.0(6); symmetry operator for generating equivalent atoms A 1-x, 1-y, 2-z.

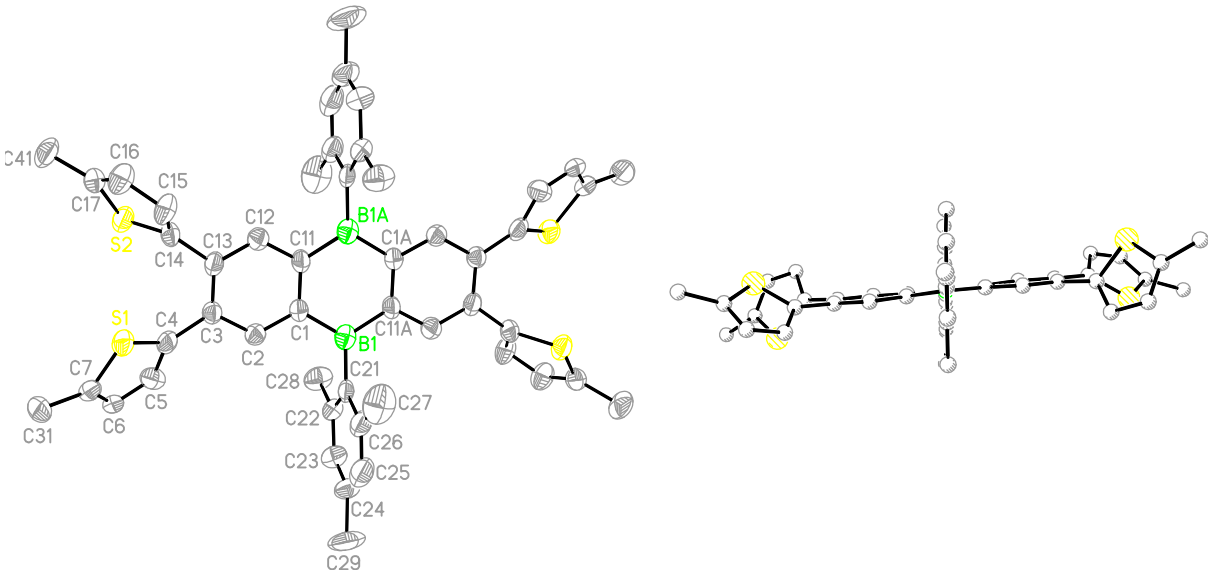


Figure S53 (CCDC 1883335): Molecular structure of **4^{Me}** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles, and torsion angle [°]: B1-C1 = 1.561(6), B1-C11A = 1.560(6), B1-C21 = 1.538(7), C3-C13 = 1.389(6), C3-C4 = 1.466(6), C13-C14 = 1.495(5), C14-S2 = 1.708(4), C17-S2 = 1.710(4); C21-B1-C11A = 120.4(4), C21-B1-C1 = 121.9(4), C1-B1-C11A = 117.7(4), C15-C14-S2 110.5(3); C14-C13-C3-C4 = –0.4(7); symmetry operator for generating equivalent atoms A 1-x, -y, 1-z.

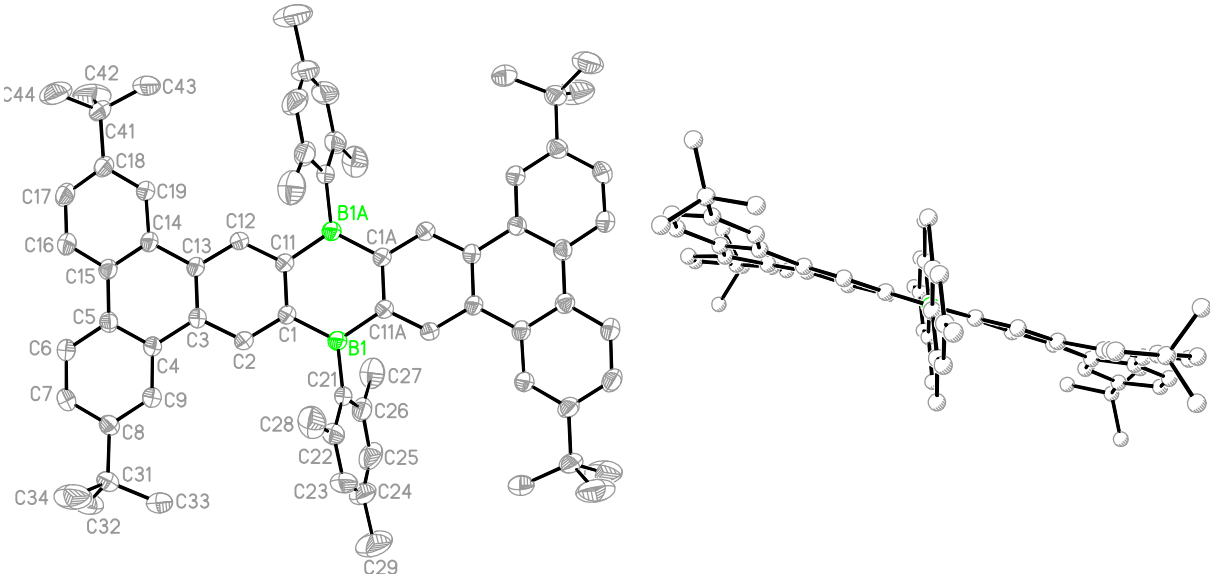


Figure S54 (CCDC 1883336): Molecular structure of **8** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: B–C_{endo} = 1.565(2)/1.566(2), B–C_{exo} = 1.572(2); C_{endo}–B–C_{endo} = 118.5(2), C_{endo}–B–C_{exo} = 123.2(2)/118.2(2).

Table S1: Selected crystallographic data for **A**, **B**, and **1**.

compound	**A**	**B**	**1**
CCDC	1883327	1883328	1883329
formula	$C_{22}H_{26}$	$C_{34}H_{50}B_2O_4$	$C_{34}H_{48}B_2O_4$
M_r	290.43	544.36	542.34
T (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P\ 2_1/c$	$P\ b\ c\ a$	$P\ 2_1\ 2_1\ 2_1$
a (Å)	11.4961(18)	11.2074(3)	11.3684(4)
b (Å)	9.9907(14)	22.0029(6)	13.4509(5)
c (Å)	15.608(3)	27.0385(9)	21.2477(8)
α (°)	90	90	90
β (°)	96.664(13)	90	90
γ (°)	90	90	90
V (Å^3)	1780.5(5)	6667.6(3)	3249.1(2)
Z	4	8	4
D_{calcd} (g cm^{-3})	1.083	1.085	1.109
F(000)	632	2368	1176
μ (mm^{-1})	0.060	0.068	0.069
crystal size (mm)	0.410x0.290x0.050	0.440x0.280x0.190	0.460x0.380x0.210
reflections collected	13210	74625	40689
independent reflections	3126	6348	6323
R_{int}	0.1093	0.1248	0.0785
data/restraints/parameters	3126/0/212	6348/31/426	6323/0/362
R_1, wR_2 (I > 2σ(I))	0.0651, 0.1598	0.0868, 0.2234	0.0381, 0.0947
R_1, wR_2 (all data)	0.1256, 0.1925	0.1071, 0.2391	0.0409, 0.0964
Goodness-of-fit on F^2	0.966	0.955	1.044
largest diff peak and hole (e Å^{-3})	0.165, –0.194	0.382, −0.435	0.185, −0.132

Table S2: Selected crystallographic data for **C**, $\mathbf{2^{H}}$·2SMe_2, and $\mathbf{2^{OH}}$.

compound	**C**	$\mathbf{2^{H}}$·2SMe_2	$\mathbf{2^{OH}}$
CCDC	1883330	1883331	1883332
formula	$C_{30}H_{50}B_2Li_2O_2$	$C_{44}H_{50}B_2$ x2C_2H_6S	$C_{44}H_{50}B_2O_2$
M_r	478.20	724.71	632.46
T (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073
crystal system	orthorhombic	monoclinic	trigonal
space group	*P b c n*	*C 2/c*	*P* -3
a (Å)	35.713(3)	33.375(2)	15.7492(16)
b (Å)	8.9897(8)	11.0282(7)	15.7492(16)
c (Å)	19.7599(13)	11.7509(8)	14.4036(17)
α (°)	90	90	90
β (°)	90	98.494(5)	90
γ (°)	90	90	120
V (Å^3)	6343.9(9)	4277.7(5)	3094.0(7)
Z	8	4	3
D_{calcd} (g cm^{-3})	1.001	1.125	1.018
F(000)	2096	1568	1020
μ (mm^{-1})	0.058	0.156	0.060
crystal size (mm)	0.230x0.110x0.070	0.290x0.130 x0.130	0.140x0.120 x0.030
reflections collected	31552	24969	27007
independent reflections	5780	4025	3914
R_{int}	0.1540	0.0996	0.1974
data/restraints/parameters	5780/0/349	4025/0/239	3914/18/218
R_1, wR_2 (I > 2σ(I))	0.0703, 0.1408	0.0488, 0.0990	0.1282, 0.2607
R_1, wR_2 (all data)	0.2007, 0.1841	0.0791, 0.1081	0.2055, 0.2931
Goodness-of-fit on F^2	0.872	0.981	1.173
largest diff peak and hole (*e* Å^{-3})	0.195, −0.195	0.202, −0.244	1.107, –0.386

Table S3: Selected crystallographic data for **D**, $\mathbf{6^H}$, and $\mathbf{4^{Me}}$.

compound	**D**	$\mathbf{6^H}$	$\mathbf{4^{Me}}$
CCDC	1883333	1883334	1883335
formula	$C_{22}H_{24}Br_2$	$C_{46}H_{34}B_2S_4$ x $2CHCl_3$	$C_{50}H_{46}B_2S_4$
M_r	448.23	975.33	796.73
T (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073
crystal system	monoclinic	triclinic	triclinic
space group	$P\,2_1/c$	$P\,-1$	$P\,-1$
a (Å)	10.9767(3)	8.4808(12)	7.965(2)
b (Å)	18.5254(7)	10.1241(17)	10.844(3)
c (Å)	29.8956(10)	14.101(2)	13.205(4)
α (°)	90	107.102(13)	96.17(2)
β (°)	92.319(3)	100.164(12)	107.48(2)
γ (°)	90	93.247(13)	100.62(2)
V (Å^3)	6074.2(3)	1131.4(3)	1053.0(5)
Z	12	1	1
D_{calcd} (g cm^{-3})	1.470	1.431	1.256
F(000)	2712	500	420
μ (mm^{-1})	4.004	0.600	0.261
crystal size (mm)	0.340x0.270x0.130	0.130x0.080x0.030	0.210x0.150x0.110
reflections collected	76173	8326	8159
independent reflections	13403	4214	3935
R_{int}	0.1444	0.0687	0.0858
data/restraints/parameters	13403/0/650	4214/0/274	3935/52/290
R_1, wR_2 ($I > 2\sigma(I)$)	0.0619, 0.1446	0.0608, 0.1167	0.0619, 0.1248
R_1, wR_2 (all data)	0.0880, 0.1617	0.1248, 0.1373	0.1483, 0.1446
Goodness-of-fit on F^2	1.074	0.922	0.808
largest diff peak and hole (e Å^{-3})	0.797, –0.581	0.466, −0.272	0.244, −0.212

Table S4: Selected crystallographic data for **8**.

compound	**8**
CCDC	1883336
formula	$C_{70}H_{74}B_2$
M_r	936.91
T (K)	173(2)
radiation, λ (Å)	Mo$K\alpha$, 0.71073
crystal system	triclinic
space group	$P\,\bar{1}$
a (Å)	11.0286(9)
b (Å)	11.0444(9)
c (Å)	13.2897(11)
α (°)	94.589(7)
β (°)	98.390(6)
γ (°)	115.448(6)
V (Å^3)	1427.5(2)
Z	1
D_{calcd} (g cm^{-3})	1.090
F(000)	504
μ (mm^{-1})	0.061
crystal size (mm)	0.260x0.260x0.240
reflections collected	20397
independent reflections	5818
R_{int}	0.0378
data/restraints/parameters	5818/42/356
R_1, wR_2 ($I > 2\sigma(I)$)	0.0626, 0.1625
R_1, wR_2 (all data)	0.0870, 0.1765
Goodness-of-fit on F^2	1.053
largest diff peak and hole (e Å^{-3})	0.429, −0.183

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