Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Table of Contents

1. General experimental procedures

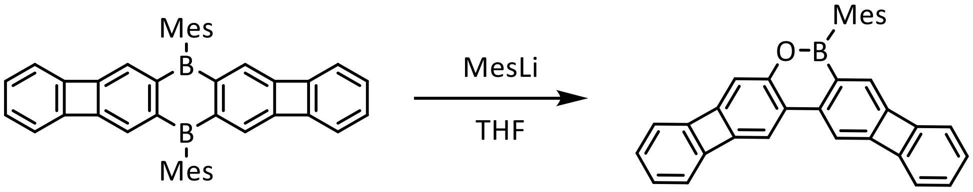
If not stated otherwise, all reactions and manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques or in an inert-atmosphere glovebox. Et_2O, THF, *n*-hexane, benzene and toluene were distilled from Na/benzophenone prior to use. BBr_3 was stored over Hg to remove contaminations with HBr or Br_2. *n*-BuLi, *t*-BuLi (*Albemarle*, Germany), and $Pd(PPh_3)_2Cl_2$ (*Heraeus Noble Metals*, Germany) were donated by the suppliers and used as received. **1**,[S1] **2**$(Br)_2$ and **2**,[S2] **6**,[S3] Li[**6**Mes],[S4] **7**,[S5] 2,3-bis(trimethylsilyl)biphenylene,[S2,6] $MesB(OMe)_2$,[S7] α,2-dibromomesitylene,[S8,9] Mes_2BF[S10] and donor-free MesLi[S11] were prepared according to published procedures.

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), and $Si(CH_3)_4$ ($^{29}Si\{^1H\}$: 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). 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%).[S12,13] 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).[S14] 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. $[n\text{-}Bu_4N][PF_6]$ (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

Synthesis of 3

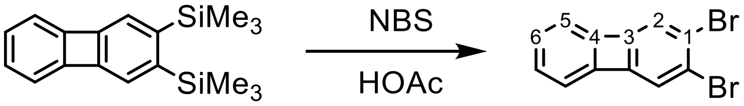


2 **3**

Solid donor-free MesLi (4 mg, 28 µmol) was added at room temperature to a solution of **2** (7.9 mg, 14 µmol) in dry THF (10 mL). The reaction mixture immediately turned dark and a precipitate formed. After stirring for 18 h at room temperature, the mixture was filtered in air and the insoluble residue washed with THF (2x5 mL). The filtrate was evaporated to dryness with the aid of a rotary evaporator and the crude product purified by flash chromatography (hexane) to give **3** as a yellow solid. Yield: 2.6 mg (5.8 µmol, 42%). Crystals suitable for X-ray analysis were grown by slow evaporation of a solution of **3** in $CDCl_3$.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 7.37 (s, 1H), 6.92 (s, 2H, *m*-Mes), 6.88-6.84 (m, 5H), 6.83 (s, 2H), 6.80-6.74 (m, 2H), 6.72-6.67 (m, 1H), 2.35 (s, 3H, *p*-CH_3), 2.20 (s, 6H, *o*-CH_3).
^{11}B{^{1}H}-NMR (96 MHz, $CDCl_3$): not observed
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ = 156.3, 153.6, 151.8, 151.7, 150.6, 150.1, 149.3, 148.5, 145.6, 142.5, 140.2 (*o*-Mes), 138.2 (*p*-Mes), 134.4* (*i*-Mes), 129.8, 129.3, 128.7 (2x), 127.3 (*m*-Mes), 122.5, 122.1, 119.1, 118.6, 118.5, 117.5, 112.2, 111.8, 110.0, 22.4 (*o*-CH_3), 21.3 (*p*-CH_3); n.o. (B*C*). (*) This signal was only detectable in an HMBC-experiment. Mesityl C atoms are marked in blue; non-mesityl *C*H atoms are marked in red.
UV-Vis (CH_2Cl_2): λ_{abs} (ε / $M^{-1}cm^{-1}$): 283 (88474), 295 (132474), 386 (28368), 423 (17684), 450 (9316) nm.
HRMS (MALDI, CICCA): calculated for $C_{33}H_{23}BO$ (M^+): 446.18365; found: 446.18275.

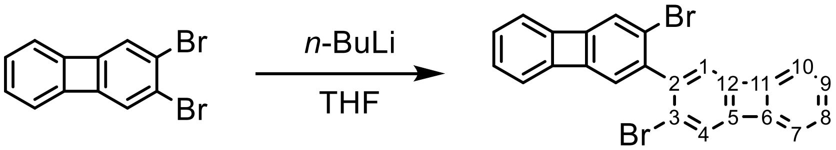
Synthesis of 2,3-dibromobiphenylene



Solid NBS (1.44 g, 8.09 mmol) was added in one portion to a suspension of 2,3-bis(trimethylsilyl)biphenylene (1.09 g, 3.68 mmol) in glacial acetic acid (40 mL). After stirring for 1.5 h at room temperature, the mixture was poured into ice-cold H_2O. The formed precipitate was collected by filtration and washed with H_2O (2x5 mL). After drying under vacuum (10^{-3} mbar), 2,3-dibromobiphenylene was obtained as a colourless solid. Yield: 0.99 g (3.20 mmol, 87%)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.85 (s, 2H, H-2), 6.84-6.81 (m, 2H, H-6), 6.71-6.69 (m, 2H, H-5).
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 151.2 (C-3), 149.4 (C-4), 129.4 (C-6), 123.4 (C-1), 122.7 (C-2), 118.7 (C-5).
HRMS (MALDI, CICCA): calculated for $C_{12}H_6Br_2$ (M^+): 309.88103; found: 309.88120.

Synthesis of 3,3’-dibromo-2,2’-bibiphenylenyl (5)



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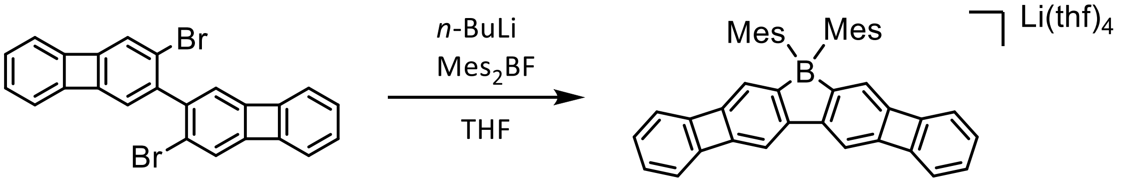
n-BuLi (0.44 mL, 0.53 mmol, 1.2 M in hexanes) was added dropwise at –78 °C to a solution of 2,3-dibromobiphenylene (0.33 g, 1.06 mmol) in dry THF (10 mL). The reaction mixture was stirred in the cold for 3 h and was then brought to room temperature. After addition of H_2O (20 mL) and separation of the formed layers, the aqueous layer was extracted with EtOAc (3x20 mL) and the combined organic layers were washed with water (2x20 mL) and brine (20 mL). After drying over Na_2SO_4 and filtration, all volatiles were removed with the aid of a rotary evaporator. Recrystallisation (EtOH/n-hexane) gave the product as an off-white solid. Yield: 0.14 g (0.25 mmol, 47%)

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.89 (s, 2H, H-4), 6.84 – 6.79 (m, 4H, H-7 and H-10), 6.72 – 6.68 (m, 4H, H-8 and H-9), 6.48 (s, 2H, H-1).
^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$): δ = 151.9 (C-5), 150.3 (C-6 or C-11), 150.2 (C-6 or C-11), 149.9 (C-12), 141.5 (C-2), 129.3 (C-8 or C-9), 128.9 (C-8 or C-9), 122.3 (C-3), 122.0 (C-4), 120.0 (C-1), 118.5 (C-7 or C-10), 118.4 (C-7 or C-10).

HRMS (MALDI, CICCA): calculated for $C_{24}H_{12}Br_2$ (M^+): 459.92798; found: 459.92739.

Synthesis of Li(thf)$_4$[4Mes]



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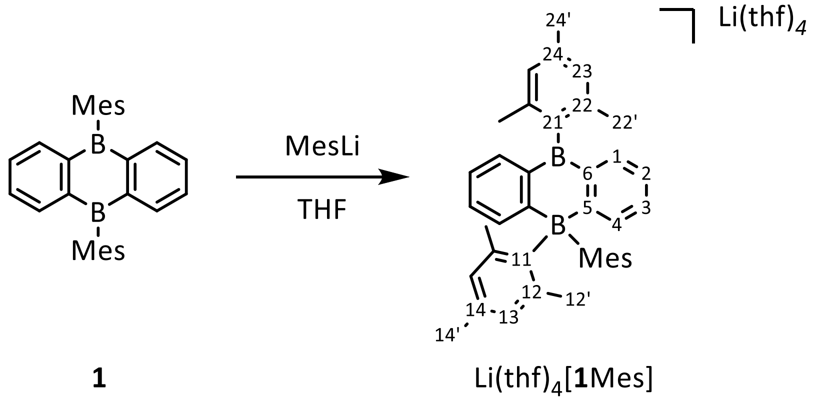
Li(thf)$_4$[**4**Mes]

n-BuLi (360 µL, 432 µmol, 1.2 M in hexanes) was added dropwise at –78 °C to a solution of **5** (100 mg, 217 µmol) in dry THF (5 mL). After stirring for 1 h, a solution of Mes_2BF (58 mg, 0.22 mmol) in dry *n*-hexane (2 mL) was added and the reaction mixture was warmed to room temperature overnight. Crystals of two habits (needles and plates) grew along the glass walls, which were separated from the mother liquor via syringe and from each other through manual selection. The crystals were identified as Li(thf)$_4$[**4**Mes] (needles) and 2,2’-bibiphenylenyl (plates) by X-ray analysis.

NMR spectra of manually selected crystals of Li(thf)$_4$[**4**Mes] typically showed significant contamination with 2,2’-bibiphenylenyl,[S15] which precluded the collection of a reliable data set.

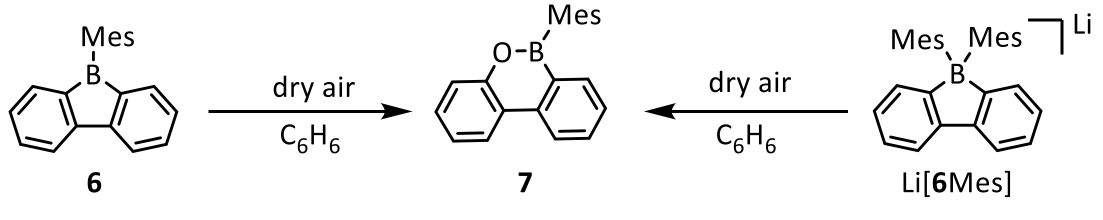
Synthesis of Li(thf)$_4$[1Mes]



A mixture of **1** (20 mg, 52 µmol) and donor-free MesLi (13 mg, 0.10 mmol) was dissolved in dry THF/C_6H_6 (1:4, 0.5 mL) in a flame-sealable NMR tube. The tube was immersed in liq. N_2 and evacuated. After flame sealing, it was heated to 60 °C for 1 h. Upon cooling to room temperature, colourless platelets grew, which were suitable for X-ray analysis. The NMR tube was opened under N_2, the supernatant was removed via syringe and the single crystals were cautiously dried under reduced pressure. Li(thf)$_4$[**1**Mes] was obtained as a colourless solid. Yield of single crystals: 17 mg (21 µmol, 42%).

^{1}H-NMR (500 MHz, THF-d^8): δ = 7.69 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H-4), 7.21 (dd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.3 Hz, 2H, H-1), 6.76 (ddd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz, 2H, H-3), 6.66 (s, 2H, H-23), 6.60 (ddd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.1 Hz, 2H, H-2), 6.29 (s, 4H, H-13), 2.24 (s, 3H, H-24'), 2.01 (s, 6H, H-14'), 1.81 (s, 6H, H22'), 1.77 (s, 12H, H-12').
^{7}Li-NMR (194 MHz, THF-d^8): δ = –0.6 (s).
^{11}B-NMR (160 MHz, THF-d^8): δ = –7.9 (s, BMes$_2$); n.o. (BMes)
^{13}C{^{1}H}-NMR (126 MHz, THF-d^8): δ = 183.4 (q, $^1J_{CB}$ = 50.8 Hz, C-5), 161.3 (q, $^1J_{CB}$ = 48.6 Hz, C-11), 147.3 (br, C-21), 145.6 (br, C-6), 143.7 (C-12), 139.3 (C-24), 137.9 (C-1), 136.7 (C-4), 134.6 (C-22), 129.7 (C-14), 129.3 (C-13), 128.3 (C-3), 127.0 (C-23), 121.6 (C-2), 27.9 (C-12'), 23.4 (C-22'), 21.6 (C-24'), 21.2 (C-14').

General procedure for the reaction of 6 and Li[6Mes] with dry air



A Schlenk flask (1 L) was charged with P_4O_{10} (5.0 g) and air and stored for 4 weeks to guarantee complete removal of moisture. The Schlenk flask was connected to the empty reaction vessel (100 mL Schlenk flask) through a hose and the entire setup (excluding the 1 L Schlenk flask) was evacuated and backfilled with N_2. In two separate experiments, the respective borafluorene derivative **6** or Li[**6**Mes] (0.1 mmol) was dissolved in dry C_6H_6 (10 mL) and added to the reaction flask. The flask was immersed in liq. N_2, vacuum was applied (10^{-3} mbar) and the solution allowed to warm to room temperature under static vacuum. After equilibration, the connection to the dry-air reservoir was opened and the reaction mixture was stirred at room temperature for 7 d. An aliquot of each reaction mixture was withdrawn and investigated by NMR spectroscopy (Figure S1).

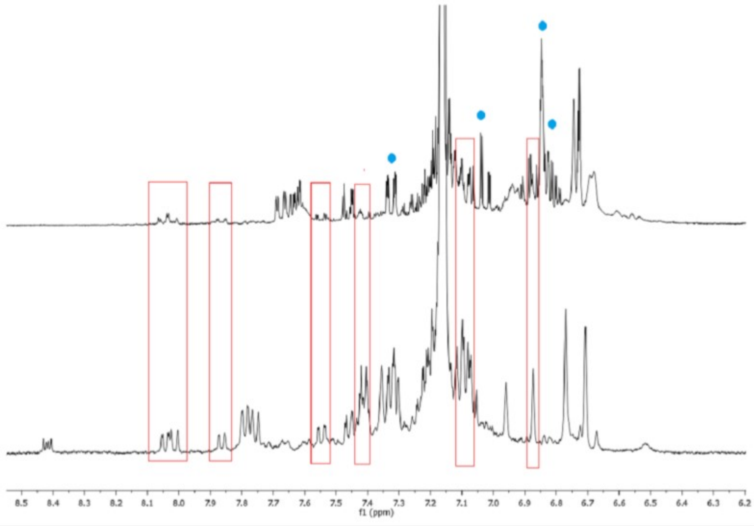
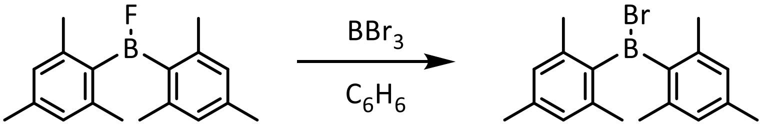


Figure S1: ^{1}H-NMR spectra (400 MHz, C_6D_6) of the aliquots withdrawn from the reaction mixtures of Li[**6**Mes] (top) and **6** (bottom). Red boxes: signals of **7**;[S5] blue dots: signals of **6**.

Synthesis of Mes_2BBr



Mes_2BF Mes_2BBr

A thick-walled ampoule was charged with Mes_2BF (500 mg, 1.86 mmol), BBr_3 (180 µL, 1.90 mmol) and dry C_6H_6 (5 mL). The ampoule was immersed in liq. N_2, evacuated, flame sealed and heated to 120 °C for 3 d. The ampoule was opened under N_2, all volatiles were removed under reduced pressure and the crude product was purified by vacuum distillation to furnish Mes_2BBr as a colourless solid. Yield: 425 mg (1.29 mmol, 69%).

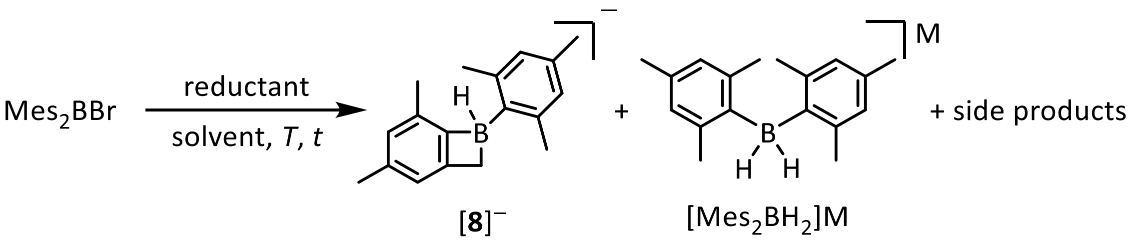
^{1}H-NMR (300 MHz, C_6D_6): δ = 6.64 (s, 4H), 2.34 (s, 12H), 2.05 (s, 6H).[S16]

^{11}B-NMR (96 MHz, C_6D_6): δ = 72.3.[S16]

Reaction of Mes_2BBr with Na_2K and KC_8:

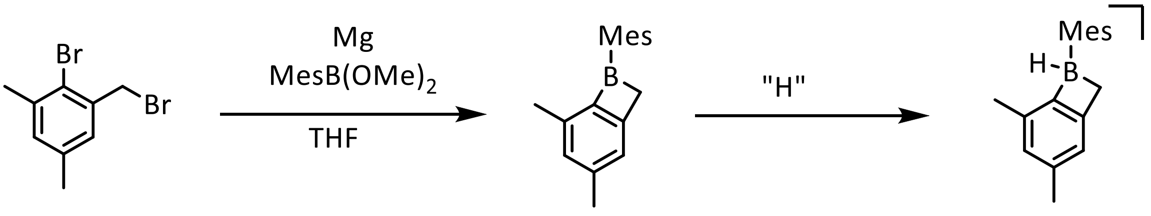
A Schlenk tube was charged with the respective reductant (0.5 mmol) and a solution of Mes_2BBr (50 mg, 0.15 mmol) in the respective solvent (0.5 ml) was added. The mixture was stirred vigorously under the conditions given in Table S1 and the progress of the reactions was monitored by ^{11}B-NMR spectroscopy.

Table S1: Applied conditions for the reduction of Mes_2BBr with Na_2K or KC_8. Ratios were determined by integration of the ^{11}B-NMR spectra. [a]: Na_2K was suspended in 4 mL dry THF and Mes_2BBr in 1 mL dry THF was added dropwise; [b] reaction performed in ca. 200 mL NH_3(liq.) with 10 mmol reductant / 1.0 mmol Mes_2BBr (added as a solution in Et_2O), this experiment resulted in the quantitative formation of Mes_2BNH_2.



#	reductant	solvent	T / °C	t / h	[**8**]$^-$	[Mes_2BH_2]M	side products
1	KC_8	*c*-hexane	60	24	--	--	--
2	Na_2K	*c*-hexane	60	24	--	--	--
3	Na_2K	C_6H_6	60	10	--	1	2
4	Na_2K	THF	60	2	0.8	1	17
5	KC_8	THF	60	2	--	1	5
6	Na_2K[a]	THF	70	0.5	0.6	1	13
7	Na_2K	NMe_2Et	25	0.5	--	1	6
8	Na	NH_3 (liq.)[b]	–33	6	--	--	--
9	Na_2K	dioxane	60	18	0.3	1	5

Reaction of α,2-dibromomesitylene with Mg and $MesB(OMe)_2$



10 **8a** **[8]⁻**

Mg turnings (418 mg, 17.2 mmol) were stirred for 3 h under vacuum. After addition of dry THF (7 mL) and 1,2-dibromoethane (70 µL), a solution of **10** (510 mg, 1.83 mmol) and $MesB(OMe)_2$ (350 mg, 1.82 mmol) in dry THF (3 mL) was added dropwise. The reaction mixture first turned brown and deep blue after a few minutes. It was heated to reflux temperature for 24 h. At that point, most of $MesB(OMe)_2$ was consumed (as confirmed by ^{11}B-NMR spectroscopy), the reaction mixture maintained its deep blue colour. Analysis of an aliquot of the reaction solution by ^{11}B-NMR spectroscopy (96 MHz, THF) revealed two main-signals: δ = +53.6 (br s), –15.0 (d, $^1J_{BH}$ = 80.3 Hz). The ^{1}H- and ^{11}B{^{1}H}-NMR spectra are depicted below.

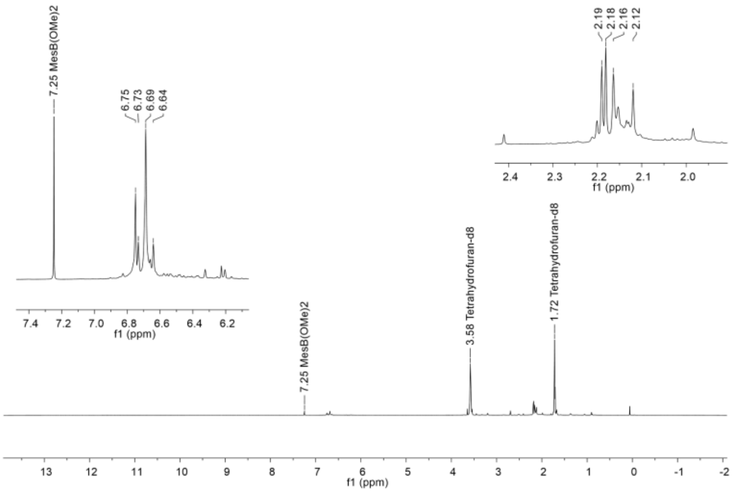


Figure S2: ^{1}H-NMR spectrum of the reaction mixture of the attempted synthesis of [**8**]$^-$ (THF-d^8, 500 MHz).

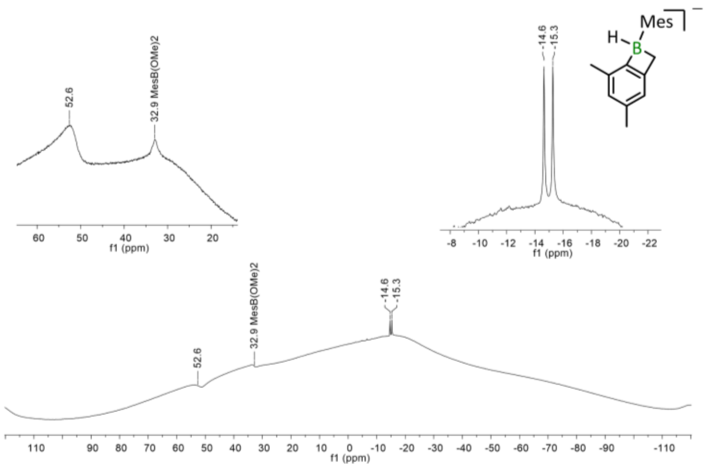


Figure S3: ^{11}B{^{1}H}-NMR spectrum of the reaction mixture of the attempted synthesis of [**8**]$^-$ (THF-d^8, 160 MHz) and assignment of one signal to the putative product [**8**]$^-$. Note: It was impossible to achieve optimal phasing for all three signals in the full spectrum. In each of the inserts, we therefore applied an individual phasing to achieve best line shapes.

3. Plots of NMR spectra of all new compounds

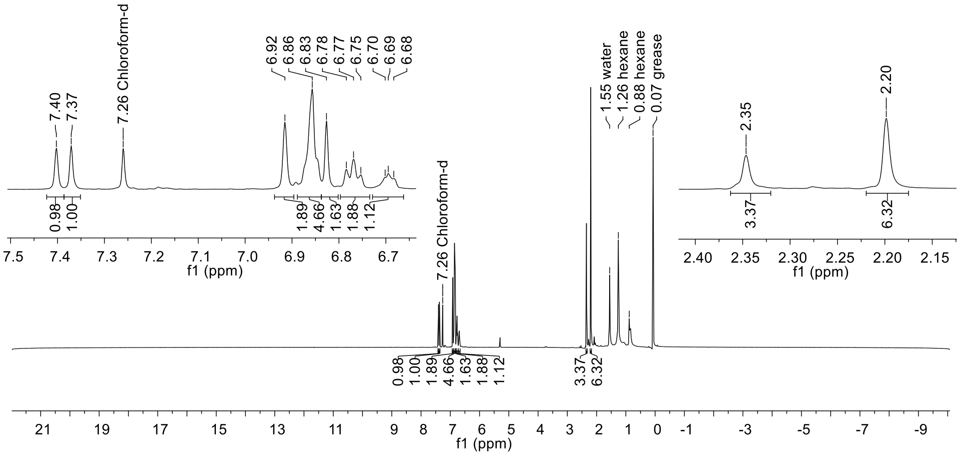


Figure S4: ^{1}H-NMR spectrum of **3** ($CDCl_3$, 400 MHz).

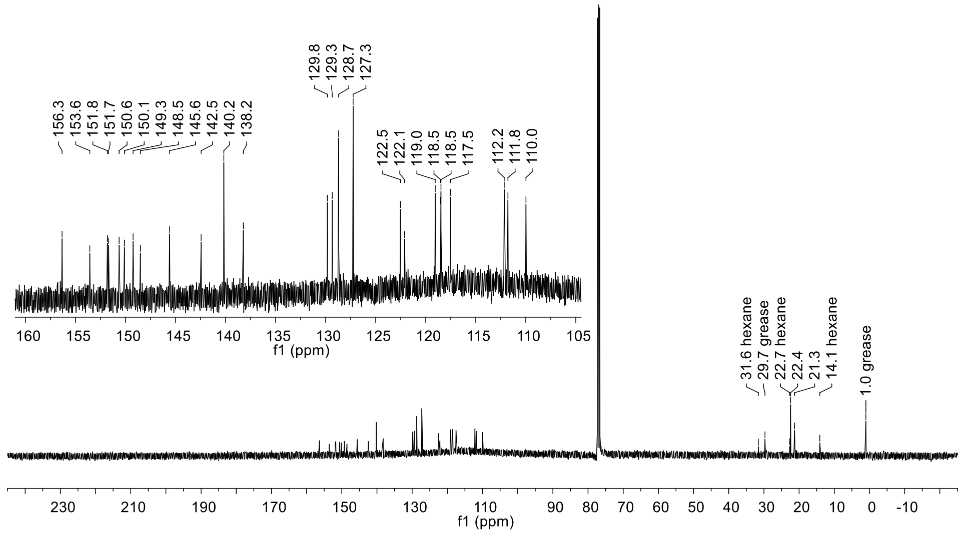


Figure S5: $^{13}C\{^1H\}$-NMR spectrum of **3** ($CDCl_3$, 100 MHz).

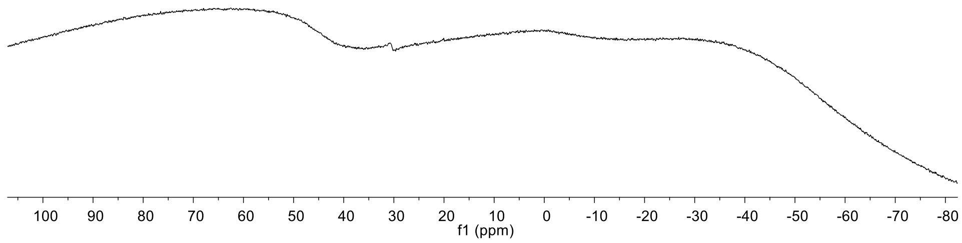


Figure S6: $^{11}B\{^1H\}$-NMR spectrum of **3** ($CDCl_3$, 96 MHz).

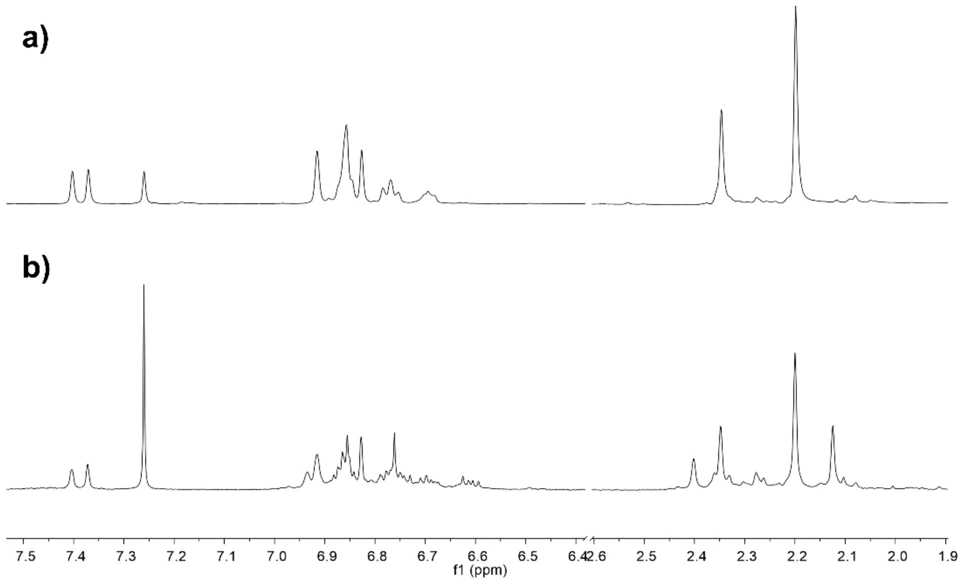


Figure S7: a) ^{1}H-NMR spectrum of **3** ($CDCl_3$, 400 MHz), prepared as decribed above. b) ^{1}H-NMR spectrum of **3** ($CDCl_3$, 250 MHz), prepared by employing PhLi (1.9 M in Bu_2O) instead of MesLi under otherwise identical conditions (**3**-containing fraction after column chromatography).

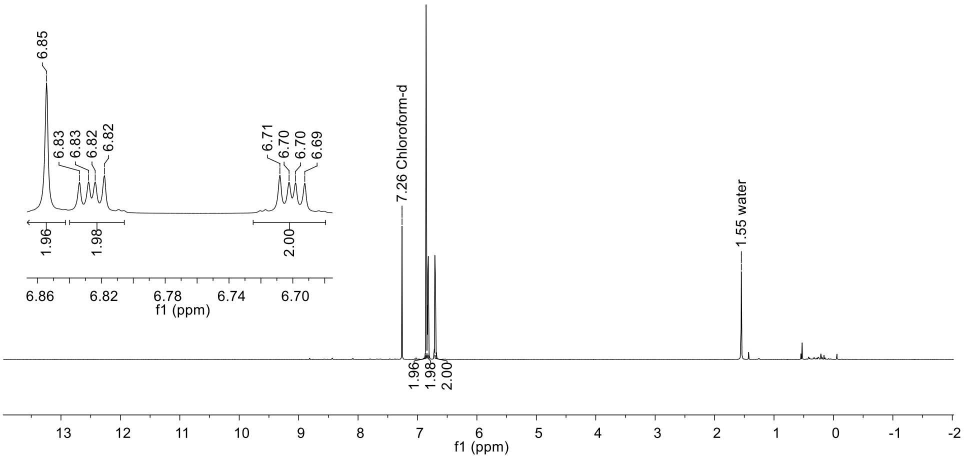


Figure S8: ^{1}H-NMR spectrum of 2,3-dibromobiphenylene ($CDCl_3$, 500 MHz).

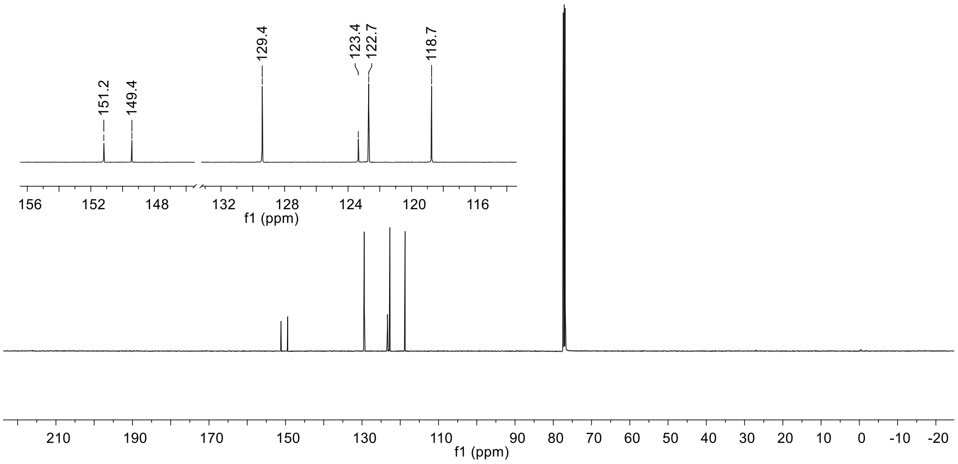


Figure S9: $^{13}C\{^1H\}$-NMR spectrum of 2,3-dibromobiphenylene ($CDCl_3$, 126 MHz).

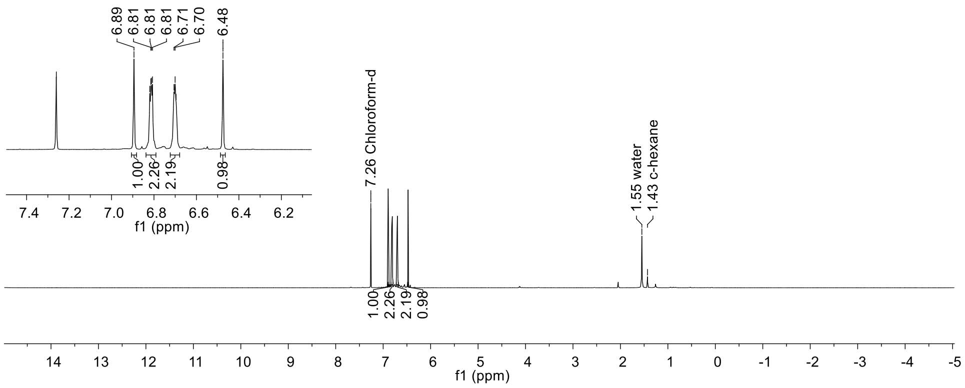


Figure S10: ^{1}H-NMR spectrum of **5** ($CDCl_3$, 600 MHz).

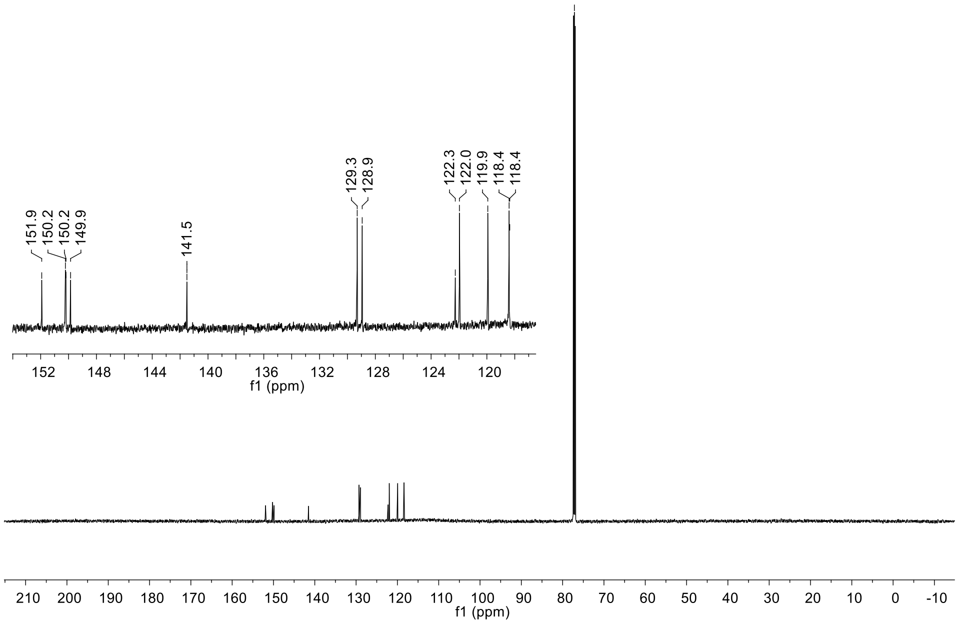


Figure S11: $^{13}C\{^1H\}$-NMR spectrum of **5** ($CDCl_3$, 151 MHz).

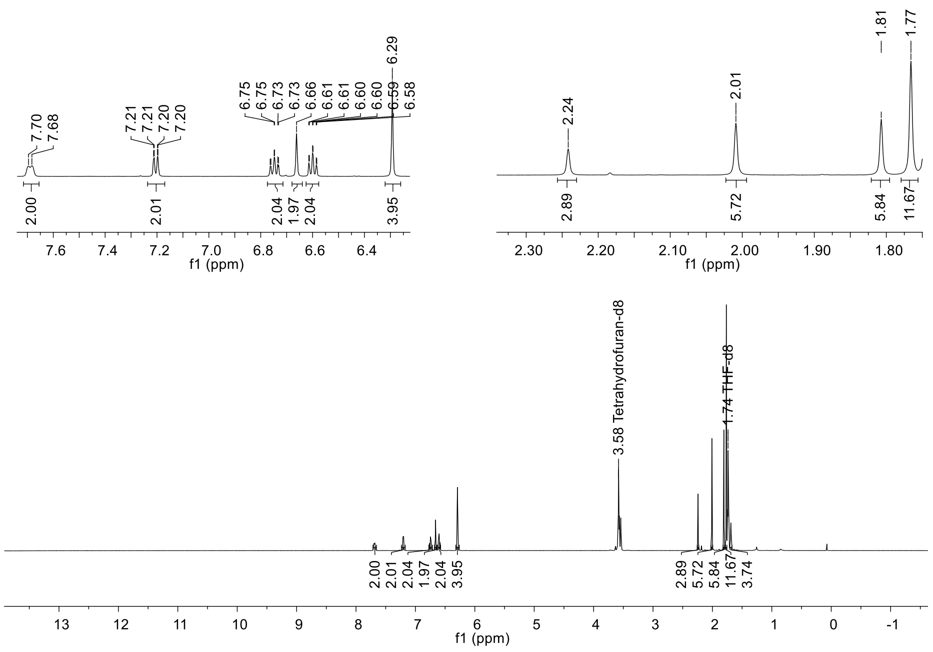


Figure S12: ^{1}H-NMR spectrum of Li[**1**Mes] (THF-d^8, 500 MHz).

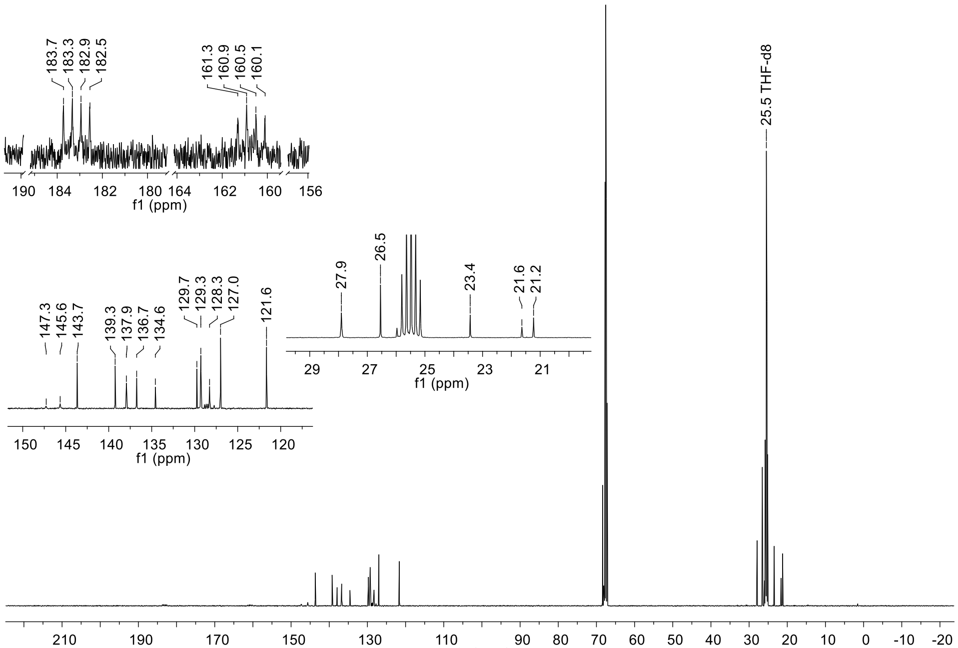


Figure S13: ^{13}C{^{1}H}-NMR spectrum of Li[**1**Mes] (THF-d^8, 126 MHz).

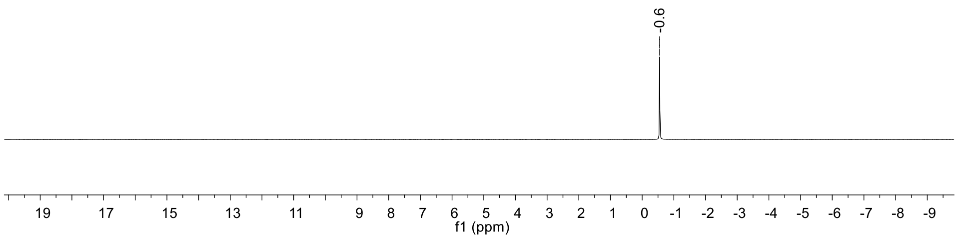


Figure S14: ^{7}Li-NMR spectrum of Li[**1**Mes] (THF-d^8, 194 MHz).

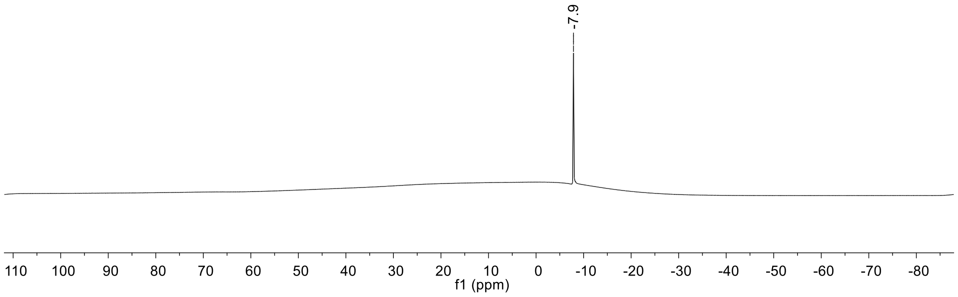


Figure S15: $^{11}B\{^{1}H\}$-NMR spectrum of Li[**1**Mes] (THF-*d*^{8}, 160 MHz).

4. Plots of UV/vis spectra

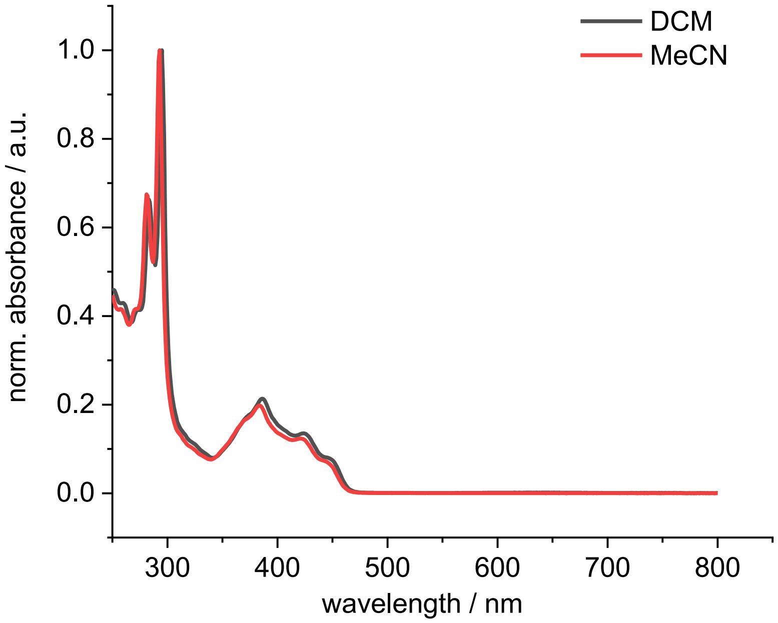


Figure S16: UV/vis spectrum of **3** in DCM and MeCN.

5. X-Ray crystal structure analyses

Crystal structure determinations. Data for **3** (CCDC 1903405) and **2**(OH)$_2$·2(acetone) (1903406) were collected on a STOE IPDS II two-circle diffractometer with a sealed tube and graphite monochromated MoK_α radiation (λ = 0.71073 Å), whereas data for Li(thf)$_4$[**1**Mes]·C$_6$H$_6$ (1903403) and Li(thf)$_4$[**4**Mes] (1903404) 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). The data for **3** were corrected for absorption with the *MULABS* routine in *PLATON*.[S17] For the data of **DBI**(OH)$_2$·2(acetone) no absorption correction was applied. The data for Li(thf)$_4$[**1**Mes]·C$_6$H$_6$ and Li(thf)$_4$[**4**Mes] were scaled using the frame scaling procedure in the *X-AREA* program system.[S18] The structures were solved by direct methods using the program *SHELXS*[S19] and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL*.[S19]

CCDC files 1903403-1903406 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.

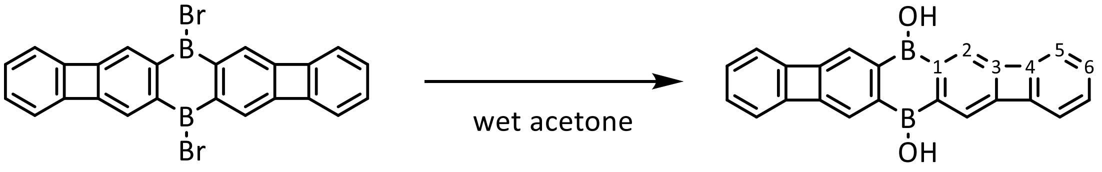
In Li(thf)$_4$[**1**Mes]·C$_6$H$_6$, one methylene group in one thf ligand is disordered over two positions with a site occupation factor of 0.63(3) for the major occupied site. The C–C bond lengths in the benzene molecule were restrained to 1.400(3) Å and the displacement ellipsoids of mutually bonded C atoms were restrained to be similar.

In Li(thf)$_4$[**4**Mes], one methylene group in one thf ligand is disordered over two positions with a site occupation factor of 0.58(4) for the major occupied site. The displacement parameters of the disordered atoms and C65 were restrained to an isotropic behaviour. The crystal was a non-merohedral twin with a fractional contribution of 0.660(2) of the major domain.

Compound **3** crystallised together with 1 eq. CHCl$_3$.

In **2**(OH)$_2$·2(acetone), the H atom bonded to O was freely refined. The molecule **2**(OH)$_2$ is located on a crystallographic centre of inversion.

Synthesis of 2(OH)$_2$



2(Br)$_2$ **2**(OH)$_2$

2(Br)$_2$ (116 mg, 345 µmol) was dissolved in non-dried acetone (20 mL) and the resulting yellow solution was stirred at room temperature for 18 h. A microcrystalline precipitate formed, which was removed by filtration through a plug of Celite (elution: 2x5 mL acetone). The filtrate was evaporated to dryness with the aid of a rotary evaporator to leave **2**(OH)$_2$ behind as a yellow solid. Yield: 98 mg (0.28 µmol, 80%). Crystals of **2**(OH)$_2$·(acetone)$_2$ suitable for X-ray analysis were grown by slow evaporation of an acetone solution.

^{1}H-NMR (400 MHz, acetone-d^6): δ = 7.42 (s, 4H, H-2), 6.87-6.79 (m, 8H, H-5 and H-6), n. o. (OH).
^{13}C{^{1}H}-NMR (100 MHz, acetone-d^6): δ = 155.4 (C-3), 153.6 (C-4), 130.7 (C-6), 120.9 (C-2), 120.0 (C-5), n. o. (C-1).
^{11}B{^{1}H}-NMR (96 MHz, acetone-d^6): δ = 38.2.
EA calcd. for $C_{24}H_{14}O_2B_2$: C: 80.97; H: 3.96. Found: C: 80.98; H: 3.95%.
UV-Vis (acetone): λ_{abs} (ε / $M^{-1}cm^{-1}$): 379 (48700), 358 (18000) nm.

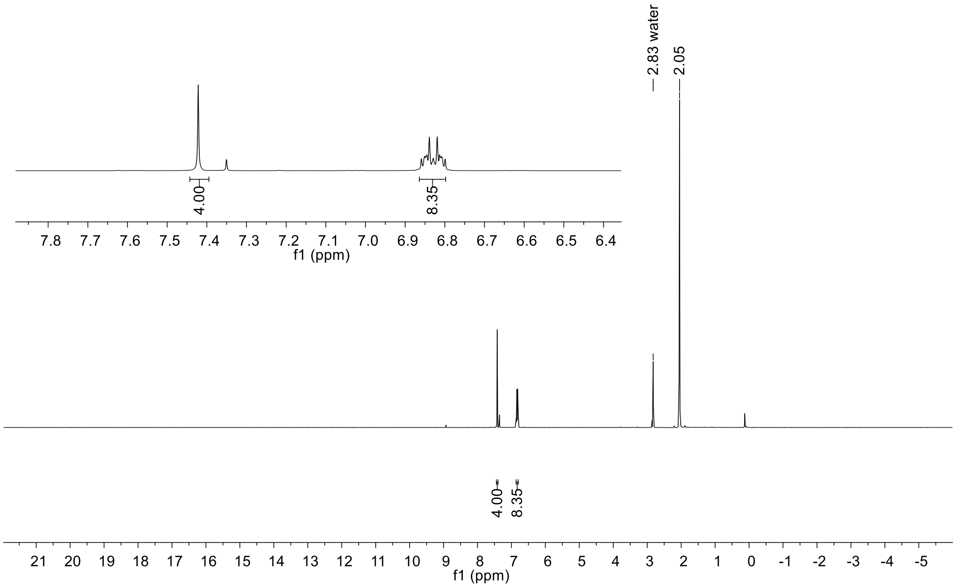


Figure S17: ^{1}H-NMR spectrum of **2**(OH)$_2$ (acetone-d^6, 400 MHz).

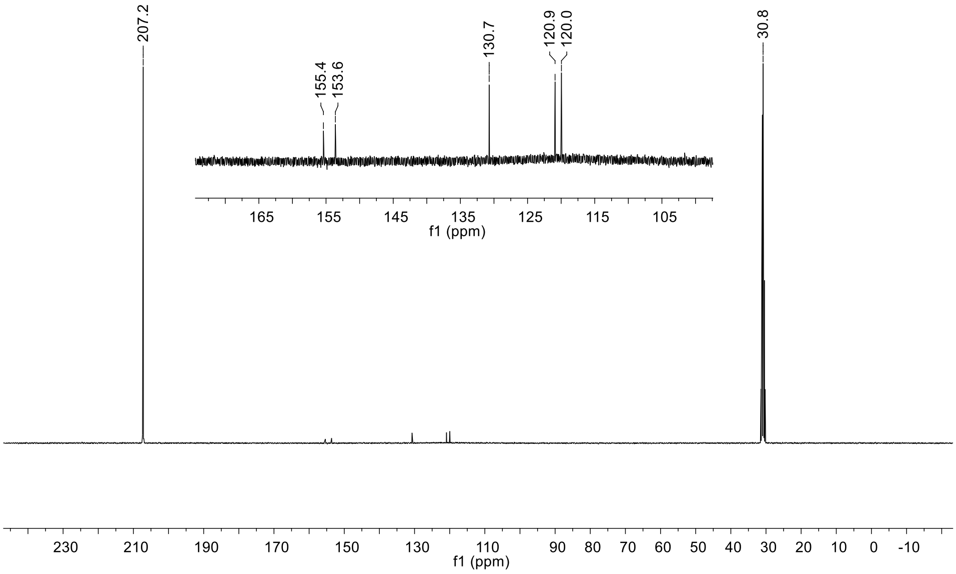


Figure S18: $^{13}C\{^{1}H\}$-NMR spectrum of **2**$(OH)_2$ (acetone-*d*^{6}, 126 MHz).

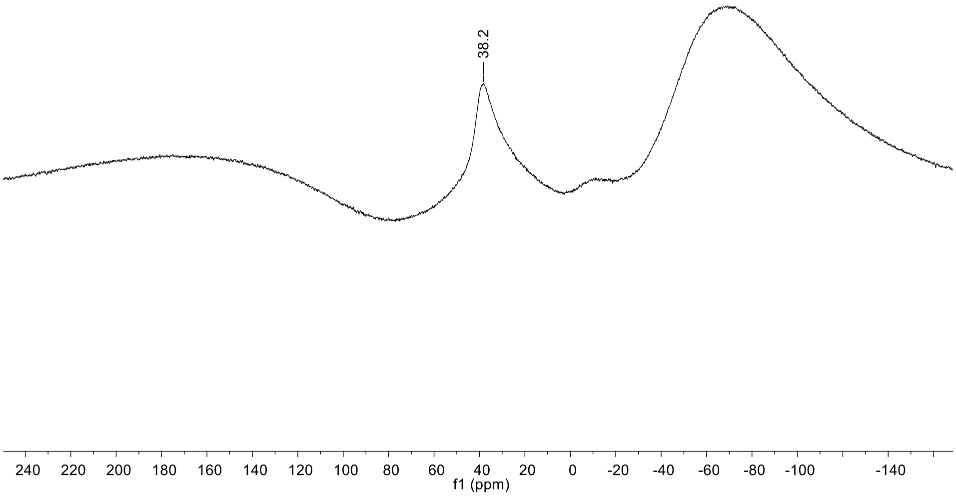


Figure S19: $^{11}B\{^{1}H\}$-NMR spectrum of **2**$(OH)_2$ ($CDCl_3$, 96 MHz).

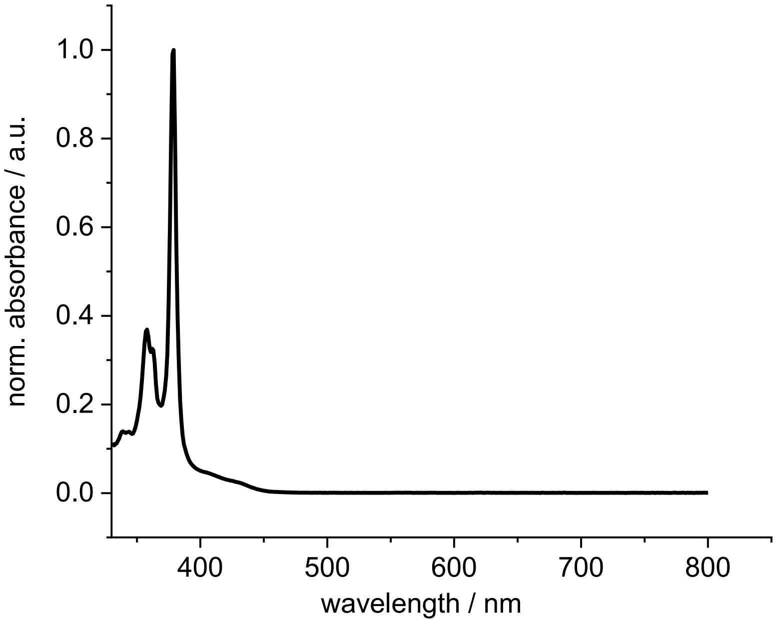


Figure S20: UV/vis spectrum of **2**$(OH)_2$ in acetone.

Compound	Li(thf)$_4$[**1**Mes]·C_6H_6	
CCDC Identification code	1903403	
Empirical formula	$C_{61}H_{79}B_2LiO_4$	
Formula weight	904.80	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 15.5752(5) Å	α = 90°.
	b = 15.9896(8) Å	β = 90°.
	c = 43.3052(15) Å	γ = 90°.
Volume	10784.8(7) Å^3	
Z	8	
Density (calculated)	1.114 Mg/m^3	
Absorption coefficient	0.066 mm^{-1}	
F(000)	3920	
Crystal size	0.320 x 0.190 x 0.100 mm^3	
Theta range for data collection	1.881 to 25.075°.	
Index ranges	-18<=h<=18, -19<=k<=15, -51<=l<=51	
Reflections collected	79927	
Independent reflections	9518 [R(int) = 0.1223]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.769	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9518 / 42 / 632	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0788, wR2 = 0.1614	
R indices (all data)	R1 = 0.1445, wR2 = 0.1864	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.370 and -0.344 e.Å^{-3}	

Compound	Li(thf)$_4$[**4**Mes]	
CCDC Identification code	1903404	
Empirical formula	$C_{58}H_{66}BLiO_4$	
Formula weight	844.85	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.764(2) Å	α = 93.062(13)°.
	b = 12.784(2) Å	β = 91.927(13)°.
	c = 14.741(3) Å	γ = 96.748(12)°.
Volume	2383.4(7) Å^3	
Z	2	
Density (calculated)	1.177 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	908	
Crystal size	0.120 x 0.030 x 0.030 mm^3	
Theta range for data collection	3.259 to 25.027°.	
Index ranges	-15<=h<=15, -14<=k<=15, -17<=l<=17	
Reflections collected	23875	
Independent reflections	8401 [R(int) = 0.1108]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.545	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8401 / 18 / 594	
Goodness-of-fit on F^2	1.162	
Final R indices [I>2sigma(I)]	R1 = 0.0881, wR2 = 0.1670	
R indices (all data)	R1 = 0.1671, wR2 = 0.1902	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.718 and -0.481 e.Å^{-3}	

Compound	**3**·$CHCl_3$	
CCDC Identification code	1903405	
Empirical formula	$C_{34}H_{24}BCl_3O$	
Formula weight	565.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.0838(15) Å	α = 114.953(9)°.
	b = 11.5129(14) Å	β = 98.468(11)°.
	c = 12.6492(17) Å	γ = 98.014(10)°.
Volume	1410.5(3) $Å^3$	
Z	2	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.352 mm^{-1}	
F(000)	584	
Crystal size	0.22 x 0.14 x 0.06 mm^3	
Theta range for data collection	3.28 to 25.02°.	
Index ranges	-13<=h<=13, -13<=k<=13, -15<=l<=14	
Reflections collected	10209	
Independent reflections	4917 [R(int) = 0.1005]	
Completeness to theta = 25.00°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9792 and 0.9267	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4917 / 0 / 355	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0966, wR2 = 0.1969	
R indices (all data)	R1 = 0.2127, wR2 = 0.2301	
Largest diff. peak and hole	0.969 and -0.722 e.$Å^{-3}$	

Compound	**2**(OH)$_2$·2(acetone)	
CCDC Identification code	1903406	
Empirical formula	$C_{30}H_{26}B_2O_4$	
Formula weight	472.13	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.7975(6) Å	α = 90°.
	b = 21.0310(17) Å	β = 93.583(7)°.
	c = 10.4761(9) Å	γ = 90°.
Volume	1274.8(2) Å^3	
Z	2	
Density (calculated)	1.230 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	496	
Crystal size	0.35 x 0.33 x 0.28 mm^3	
Theta range for data collection	3.50 to 25.62°.	
Index ranges	-6<=h<=7, -25<=k<=25, -12<=l<=12	
Reflections collected	12926	
Independent reflections	2381 [R(int) = 0.0507]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.9782 and 0.9728	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2381 / 0 / 170	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1272	
R indices (all data)	R1 = 0.0621, wR2 = 0.1351	
Extinction coefficient	0.029(5)	
Largest diff. peak and hole	0.306 and -0.253 e.Å^{-3}	

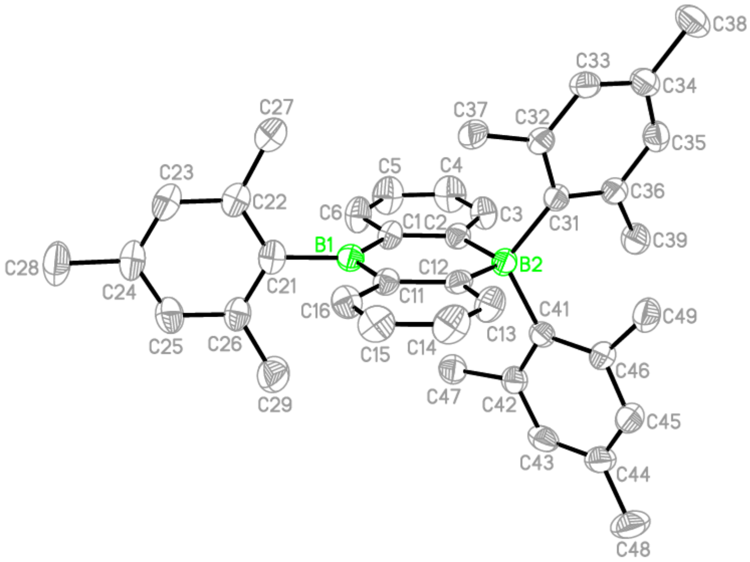


Figure S21 (CCDC 1903403): Structures of Li(thf)$_4$[**1**Mes]·C$_6$H$_6$ in the solid state (H atoms, C$_6$H$_6$ and Li(thf)$_4$ omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: B(sp^3) atom: B–C$_{endo}$ = 1.659(5)/1.659(5); B–C$_{exo}$ = 1.703(4)/1.689(4); C$_{endo}$–B–C$_{exo}$ = 102.0(2)/115.3(3)/114.5(3)/100.6(2), C$_{endo}$–B–C$_{endo}$ = 110.7(2), C$_{exo}$–B–C$_{exo}$ = 114.4(2); B(sp^2) atom: B–C$_{endo}$ = 1.546(5)/1.541(5), B–C$_{exo}$ = 1.604(4); C$_{endo}$–B–C$_{exo}$ = 118.0(3)/122.1(3), C$_{endo}$-B-C$_{endo}$ = 119.8(3).

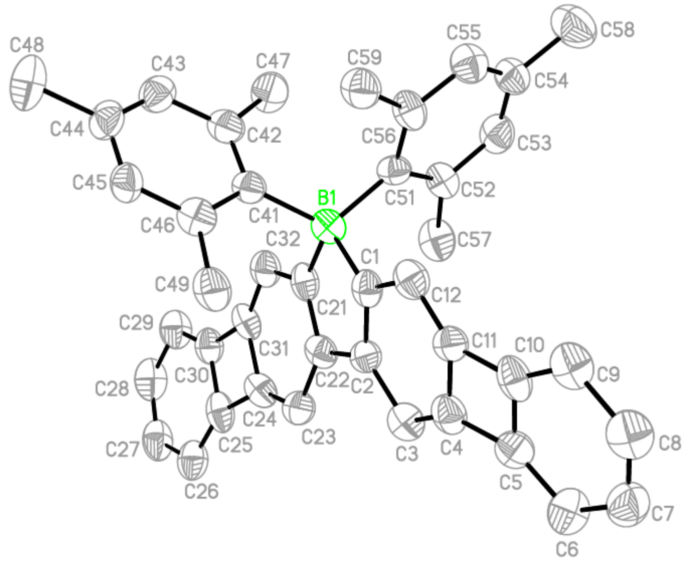


Figure S22 (CCDC 1903404): Structure of Li(thf)$_4$[**4**Mes] in the solid state (H atoms and Li(thf)$_4$ omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: B–C$_{endo}$ = 1.651(9), 1.652(9), B–C$_{exo}$ = 1.639(9), 1.673(10); C$_{endo}$–B–C$_{exo}$ = 102.1(5)/120.1(5)/102.8(5)/121.1(5) C$_{endo}$-B-C$_{endo}$ = 96.0(4), C$_{exo}$–B–C$_{exo}$ = 114.4(5).

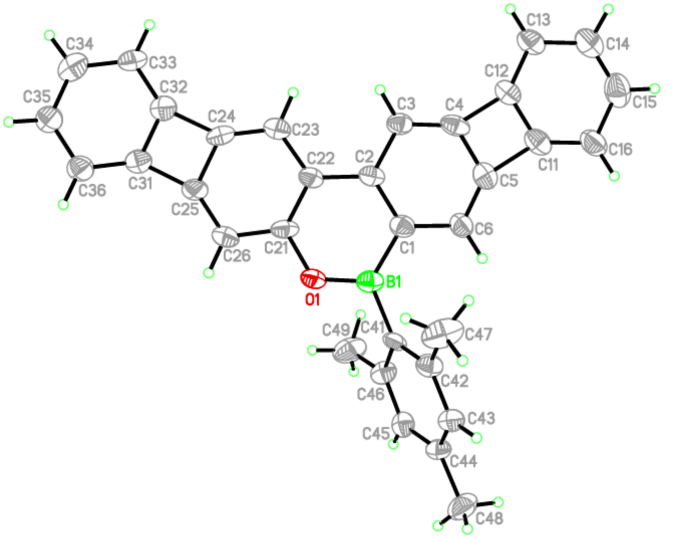


Figure S23 (CCDC 1903405): Structure of **3**·CHCl$_3$ in the solid state. Displacement ellipsoids are drawn at the 50% probability level. CHCl$_3$ omitted for clarity. Selected bond lengths [Å] and angles [°]: B–O = 1.371(9), B–C$_{endo}$ = 1.55(1), B–C$_{exo}$ = 1.57(1), C–O = 1.379(8), O–B–C$_{endo}$ = 117.8(6), O–B–C$_{exo}$ = 115.3(6), C$_{endo}$–B–C$_{exo}$ = 126.8(6).

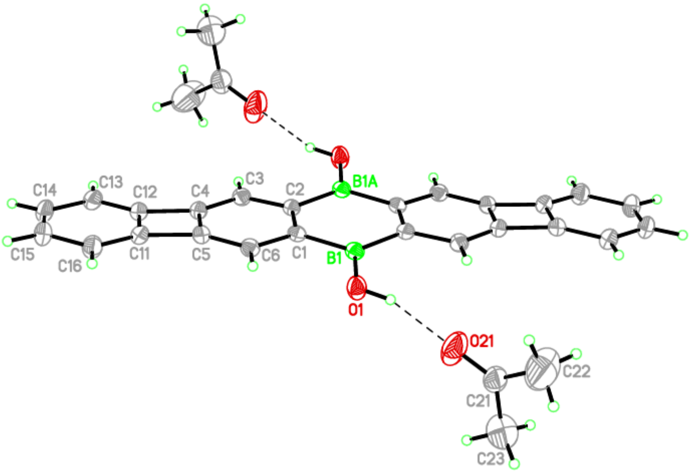


Figure S24 (CCDC 1903406): Structure of **2**(OH)$_2$·2(acetone) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: B–C = 1.577(2)/1.577(2); B–O = 1.361(2); O–H = 0.88(3); C–B–C = 121.29(14); C–B–O = 115.48(14)/123.09(14):

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