Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for:

Mild Synthesis of Diboryldiborenes by Diboration of B-B Triple Bonds

Tobias Brückner, Rian D. Dewhurst, Theresa Dellermann, Marcel Müller, Holger Braunschweig*

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg (Germany) and Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg (Germany)

E-mail: h.braunschweig@uni-wuerzburg.de

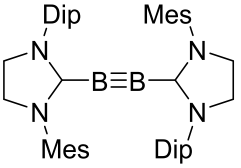
Contents:

Synthetic Procedures

General Experimental Considerations

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C{^{1}H}: 125.8 MHz, ^{19}F{^{1}H}: 470.6 MHz) or on a Bruker Avance 400 NMR spectrometer (^{1}H: 400.1 MHz, ^{11}B: 128.4 MHz, ^{13}C{^{1}H}: 125.8 MHz, ^{19}F{^{1}H}: 376.5 MHz) at 298 K unless otherwise stated. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. ^{11}B NMR spectra were referenced to [$BF_3{\cdot}OEt_2$] as an external standard. High-resolution mass spectrometry data was obtained from a Thermo Scientific Exactive Plus spectrometer in ASAP or LIFDI mode. Elemental analysis was conducted on an Elementar vario MICRO cube elemental analyser. B_2cat_2 was a generous gift from Allychem Co., Ltd. (Dalian, China). SIDep and SIDipMes[1] were synthesized following a modified literature procedure. B_2Scat_2[2] was synthesized following a literature procedure. $B_2(SIDep)_2$[3] was synthesized following a literature procedure.

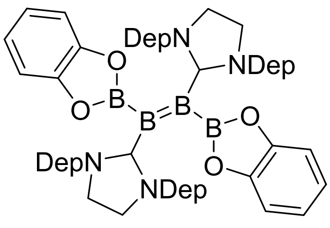
Preparation of 1b



A solution of tetrabromodiborane(4) (229 mg, 671 μmol) in 1 mL pentane cooled to –78 °C was added to a stirred solution of 468 mg (1.34 mmol) SIDipMes in 10 mL pentane at –78°C. The resulting suspension was stirred over 5 hours at room temperature. The solid was filtered off and washed three times with warm pentane (10 mL) of warm pentane. The white solid was dried in vacuo, yielding 509 mg (490 μmol) crude $B_2Br_4(SIDipMes)_2$. This solid was suspended in THF and over the course of 30 min, a freshly prepared sodium naphthalide solution in THF (5.7 mL, 0.343 M, 2.0 mmol) was added dropwise at –78 °C. The solution was stirred for an additional 30 min at –78 °C, and then 1 h at room temperature, with monitoring by ^{11}B NMR spectroscopy. The solvent was evaporated under reduced pressure and the residue extracted three times with pentane (20 mL). The red pentane layers were combined, and the pentane was evaporated under reduced pressure to give a red solid. This solid was then heated to 120 °C under high vacuum (2 x 10^{-6} mbar) to remove all volatiles. Yield: 150 mg (209 μmol, 42%) of a red solid.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.19 (t, ^3J = 7.65 Hz, 2H, C$H_{\text{Aryl, Dipp}}$), 7.06 (d, ^3J = 7.65 Hz, 4H, C$H_{\text{Aryl, Dipp}}$), 6.86 (s, 4H, C$H_{\text{Aryl, Mes}}$), 3.42–3.24 (m, 8H, NCH_2), 3.15 (sept, ^3J = 6.8 Hz, 4 H, CH_{iPr}), 2.29 (s, 6H, $CH_{3\text{Mes}}$), 2.16 (s, 12H, C$H_{3\text{Mes}}$), 1.24 (d, ^3J = 7.0 Hz, 12H, C$H_{3\text{Dipp}}$), 1.08 (br s, 12H, C$H_{3\text{Dipp}}$) ppm.
^{13}C NMR (125.8 MHz, C_6D_6): δ = 162.2 (C_{Carbene}), 148.8 (*o*-C_{Aryl}, Dipp), 137.9 (*p*-$C_{\text{Aryl, Mes}}$), 137.5 (*i*-$C_{\text{Aryl, Dipp}}$), 137.3 (*i*-$C_{\text{Aryl, Mes}}$), 136.0 (*o*-$C_{\text{Aryl, Mes}}$), 129.2 (*m*-$CH_{\text{Aryl, Mes}}$), 124.1 (*m*-$CH_{\text{Aryl, Dipp}}$), 52.3 (NCH_2), 49.3 (NCH_2), 28.8 (CH_{Dipp}), 25.7 ($CH_{3\text{Dipp}}$), 24.6 ($CH_{3\text{Dipp}}$), 21.3 (*p*-$CH_{3\text{Mes}}$), 18.2 (*o*-$CH_{3\text{Mes}}$) ppm.
^{11}B NMR (160.5 MHz, C_6D_6): δ = 55 (br) ppm.
Elemental Analysis: calc: C = 80.22%, H = 8.98%, N = 7.80%; found: C = 80.50%, H = 9.12%, N = 7.42%.

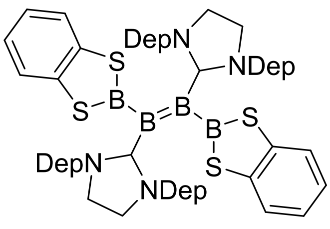
Preparation of 2a



$B_2(SIDep)_2$ (30.0 mg, 43.5 µmol) and B_2cat_2 (10.3 mg, 43.5 µmol) were dissolved in benzene (0.5 mL). The solution turned from red to violet within a few seconds. The solvent was removed under vacuum, the residual solid was washed with hexane at –30 °C and the remaining solid was extracted with hexane (15 mL) to give the product as a blue solid after drying under vacuum. Yield: 30.6 mg (76%).

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.02-6.99 (m, 8H, CH_{Aryl}), 6.96- 6.94 (m, 4H, CH_{Aryl}), 6.83-6.82 (m, 8H, CH_{Aryl}), 3.32 (s, 8H, NCH_2), 2.71-2.64 (m, 8H, CH_2), 2.51-2.43 (m, 8H, CH_2), 1.12 (t, $^3J_{H,H}$ = 7.65 Hz, 24H, CH_3) ppm.
^{13}C NMR (125.8 MHz, 298 K, C_6D_6): δ = 198.1 ($C_{Carbene}$), 150.8 (C_q), 142.0 (C_q), 138.4 (C_q), 128.3 (CH_{Aryl}), 127.2 (CH_{Aryl}), 126.2 (CH_{Aryl}), 120.4 (CH_{Aryl}), 112.1 (CH_{Aryl}), 51.3 (NCH_2), 24.7 (CH_2), 14.8 (CH_3) ppm.
^{11}B NMR (160.5 MHz, 298 K, C_6D_6): δ = 43.0 (very broad, BBO_2), 27.7 (*B*=*B*) ppm.
HRMS(LIFDI): *calc:* m/z = 928.5607, *found:* m/z = 928.5584.
λ_{max} (C_6H_6): 422, 578 nm.

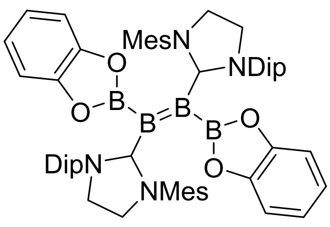
Preparation of 2b



$B_2(SIDep)_2$ (30.0 mg, 43.5 µmol) and B_2Scat_2 (13.1 mg, 43.5 µmol) were dissolved in benzene (0.5 mL). The solution turned from red to blue within a few seconds. The solvent was removed under vacuum, the residual solid was washed with hexane at –30 °C and the remaining solid was extracted with hexane (15 mL) to give the product as a blue solid after drying under vacuum. Yield: 35.4 mg (82%).

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.67-7.66 (m, 4H, CH_{Aryl}), 7.13-7.12 (m, 8H, CH_{Aryl}), 7.04-7.02 (m, 4H, CH_{Aryl}), 6.68 (m, 4H, CH_{Aryl}), 3.33 (s, 4H, NCH_2), 3.09 (s, 4H, NCH_2), 2.74-2.69 (m, 4H, CH_2), 2.58 (m, 4H, CH_2), 2.44-2.38 (m, 8H, CH_2) 1.20-1.12 (m, 24H, CH_3) ppm.
^{13}C NMR (125.8 MHz, 298 K, C_6D_6): δ = 195.4 ($C_{Carbene}$), 147.3 (C_q), 142.5 (C_q), 141.2(C_q), 138.7 (C_q), 128.3 (CH_{Aryl}), 127.6 (CH_{Aryl}), 126.3 (CH_{Aryl}), 125.7(CH_{Aryl}), 124.7(CH_{Aryl}), 123.4 (CH_{Aryl}), 51.7 (NCH_2), 26.1 (CH_2), 25.0(CH_2), 14.6 (CH_3), 14.1 (CH_3) ppm.
^{11}B NMR (160.5 MHz, 298 K, C_6D_6): δ = 69.1 (very broad, BBS_2), 29.6 (*B*=*B*) ppm.
HRMS(LIFDI): *calc:* m/z = 992.4694, *found:* m/z = 992.4674.
λ_{max} (C_6H_6): 503, 608 nm.

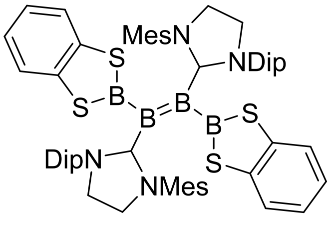
Preparation of 2c



$B_2(SIDipMes)_2$ (30.0 mg, 41.8 µmol) and B_2cat_2 (990 mg, 41.8 µmol) were dissolved in benzene (0.5 mL). Overnight the solution turned from red to brown with the precipitation of orange crystals. The crystals were filtered off, washed with benzene and THF and dried under vacuum. Yield: 22.3 mg (56%).

^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.07-7.02 (m, 6H, CH_{Aryl}), 7.00-6.98 (m, 2H, CH_{Aryl}), 6.97-6.93 (m, 4H, CH_{Aryl}), 6.84 (br. s, 2H, CH_{Aryl}), 6.76-6.74 (m, 2H, CH_{Aryl}), 6.30 (br. s, 2H, CH_{Aryl}), 3.96-3.87 (m, 4H, NCH_2), 3.71-3.63 (m, 2H, NCH_2), 3.57-3.50 (m, 2H, NCH_2), 3.46-3.39 (m, 2H, CH_{iPr}), 3.22-3.20 (m, 2H, CH_{iPr}), 2.77 (s, 6H, CH_{3Mes}), 2.14 (s, 6H, CH_{3Mes}), 2.11 (s, 6H, CH_{3Mes}), 1.14-1.13 (s, 6H, CH_{3Dip}), 1.03-1.02 (s, 6H, CH_{3Dip}), 0.85-0.83 (s, 6H, CH_{3Dip}), –0.15 to –0.17 (s, 6H, CH_{3Dip}) ppm.
^{13}C NMR spectra could not be obtained due to poor solubility.
^{11}B NMR (128.4 MHz, 298 K, C_6D_6): δ = 26.1 ppm (second signale could not be obtained).
HRMS(LIFDI): *calc:* m/z = 956.5920, *found:* m/z = 956.5922.
Elemental Analysis: calc: C = 75.34%, H = 7.59%, N = 5.86%; found: C = 75.32%, H = 7.73%, N = 5.52%.
UV-vis: λ_{max} (C_6H_6): 451 nm.

Preparation of 2d



$B_2(SIDipMes)_2$ (30.0 mg, 41.8 µmol) and B_2Scat_2 (2.6 mg, 41.8 µmol) were dissolved in benzene (0.5 mL). Overnight the solution turned from red to brown with the precipitation of red crystals. The crystals were filtered off, washed with benzene and THF and dried under vacuum. Yield: 27.8 mg (67%).

NMR spectra could not be obtained due to poor solubility or decomposition in all solvents used (including D_3CCN, CD_2Cl_2, C_6D_6, 1,2-difluorobenze, d_6-acetone (decomposition) and $CDCl_3$.
HRMS(LIFDI): *calc:* m/z = 1020.5007, *found:* m/z = 1020.5014
Elemental Analysis: calc: C = 70.60%, H = 7.11%, N = 5.49%, S = 12.56%; found: C = 70.54%, H = 7.00%, N = 5.42%, S = 12.31%.
λ_{max} (C_6H_6): 543, 622 nm.

NMR Spectra of New Compounds

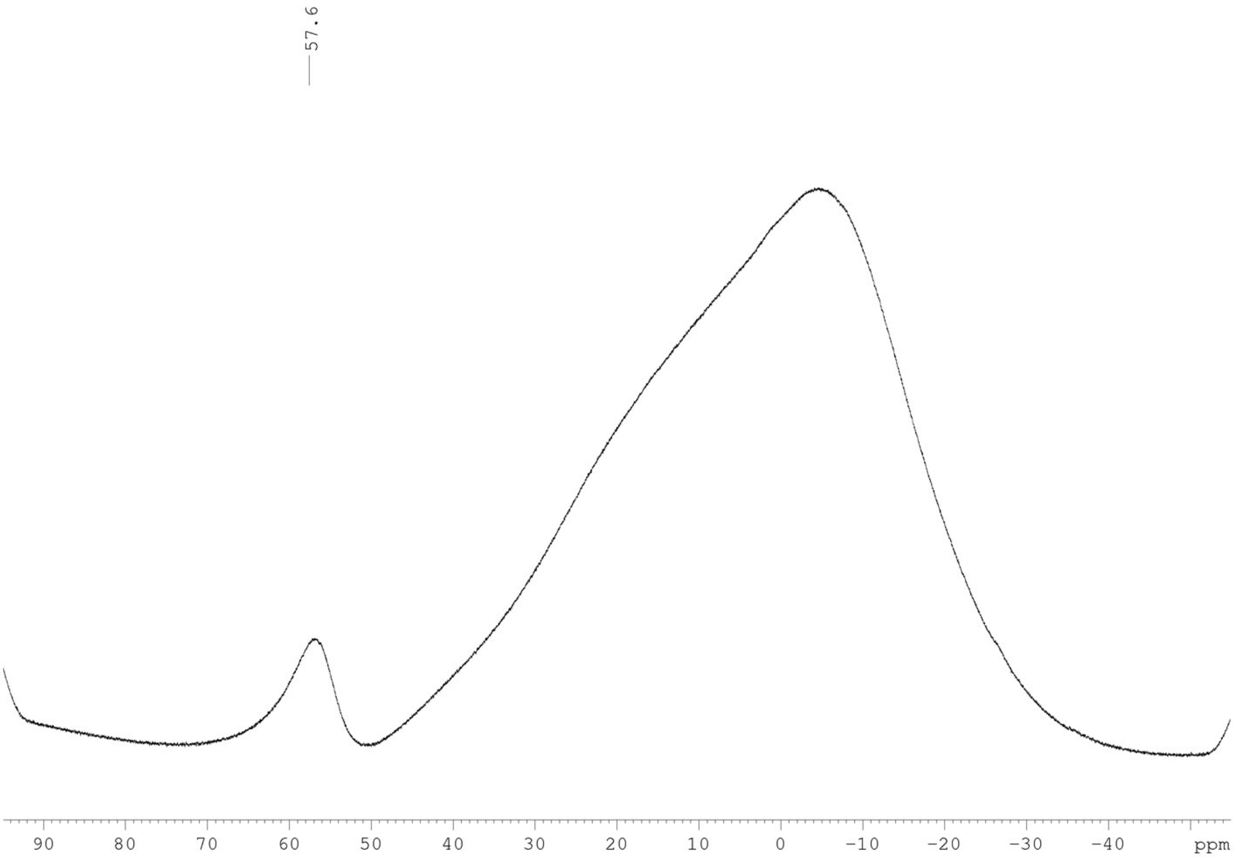


Figure S1. ^{11}B NMR spectrum of **1b**.

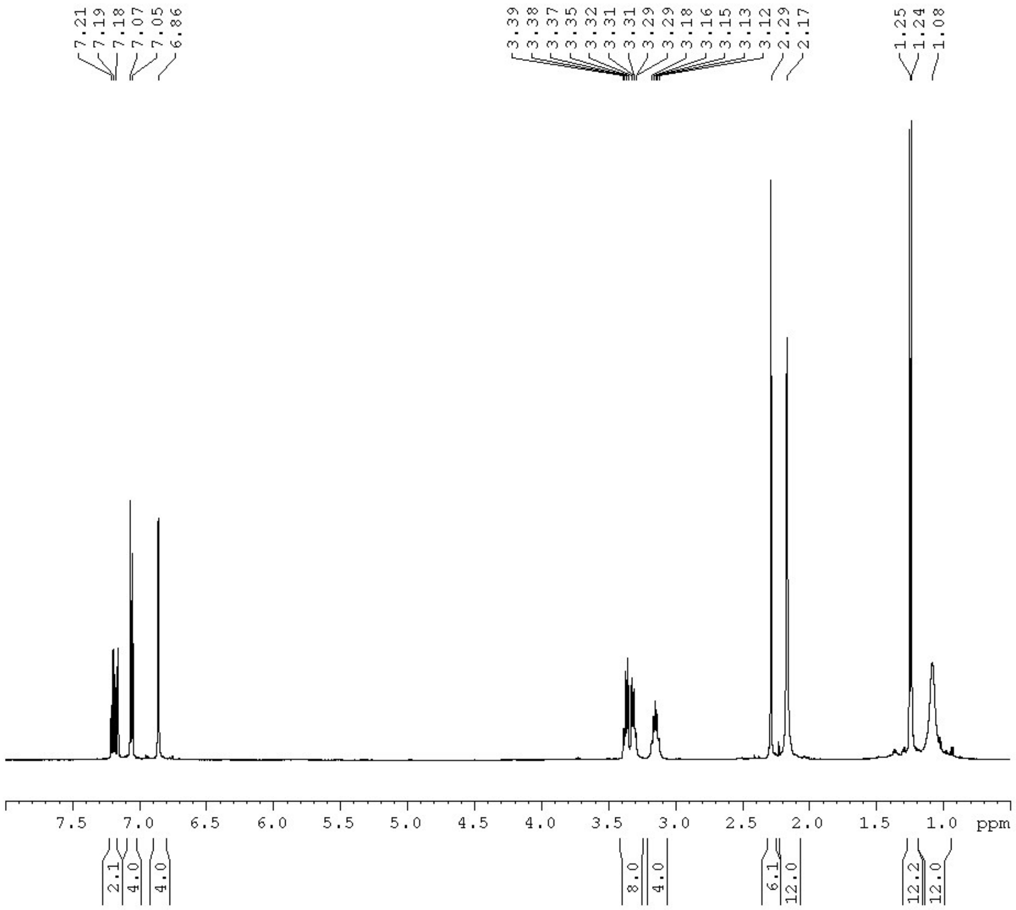


Figure S2. ^{1}H NMR spectrum of **1b.**

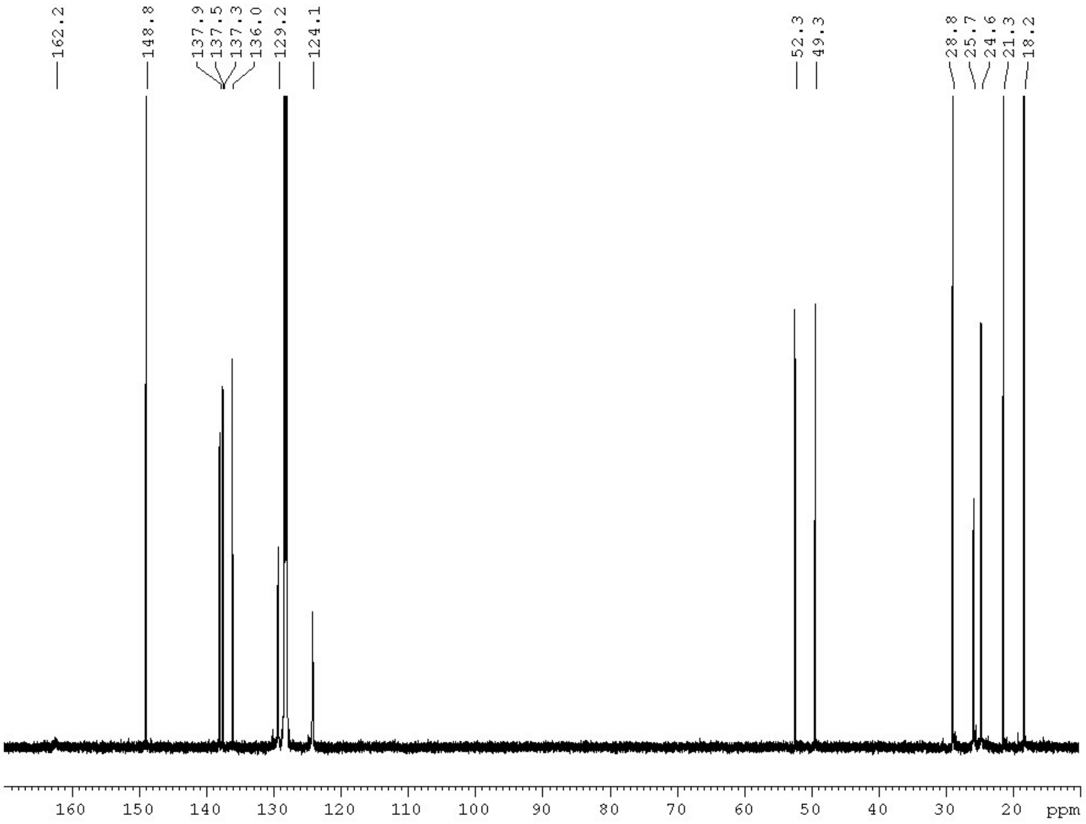


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1b.**

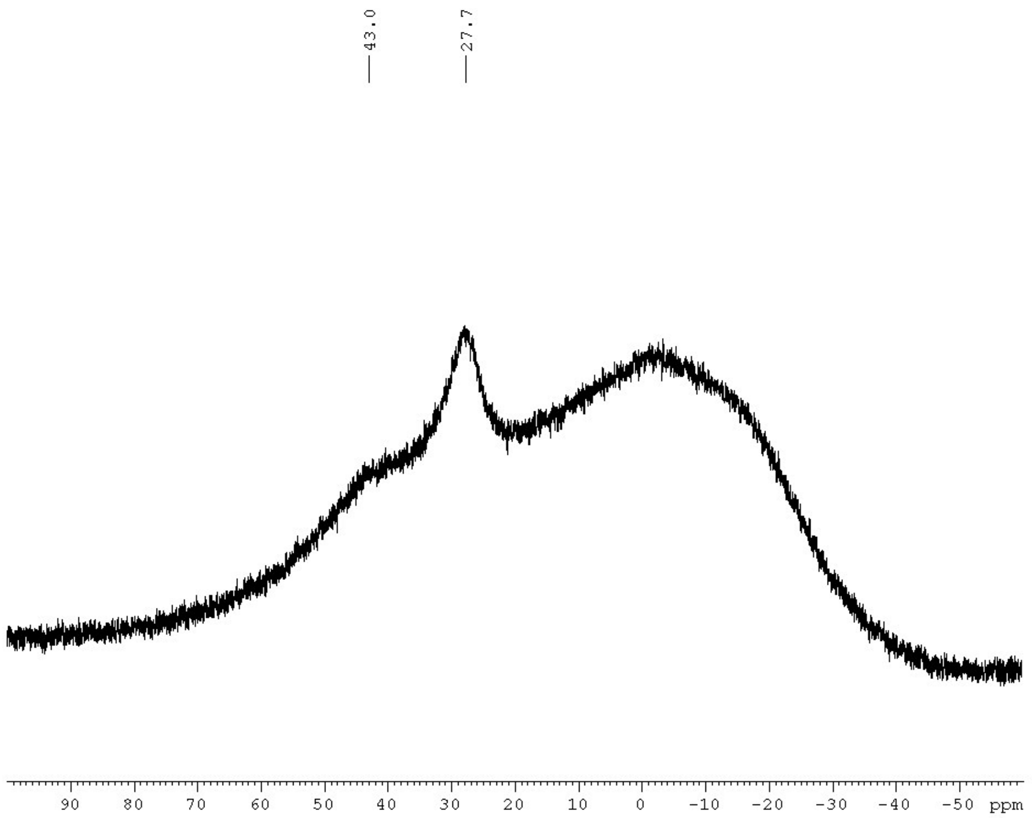


Figure S4. ^{11}B NMR spectrum of **2a**.

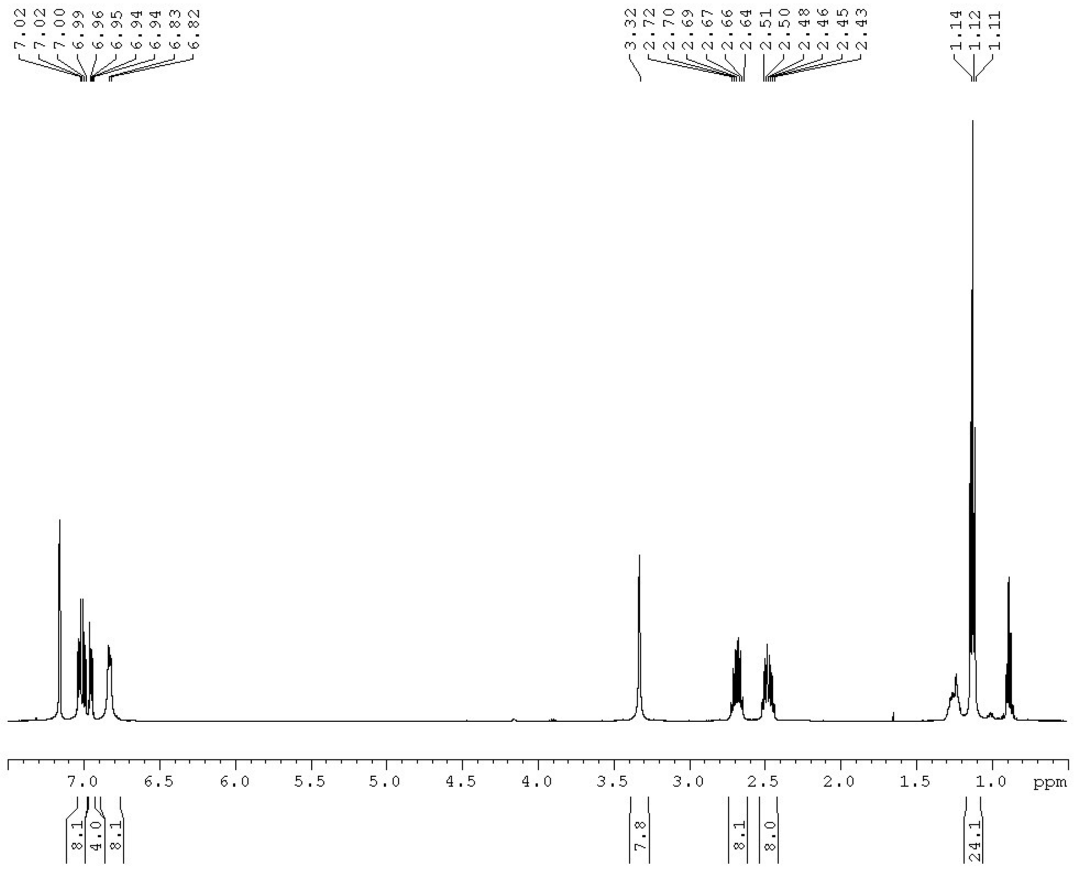


Figure S5. ^{1}H NMR spectrum of **2a**.

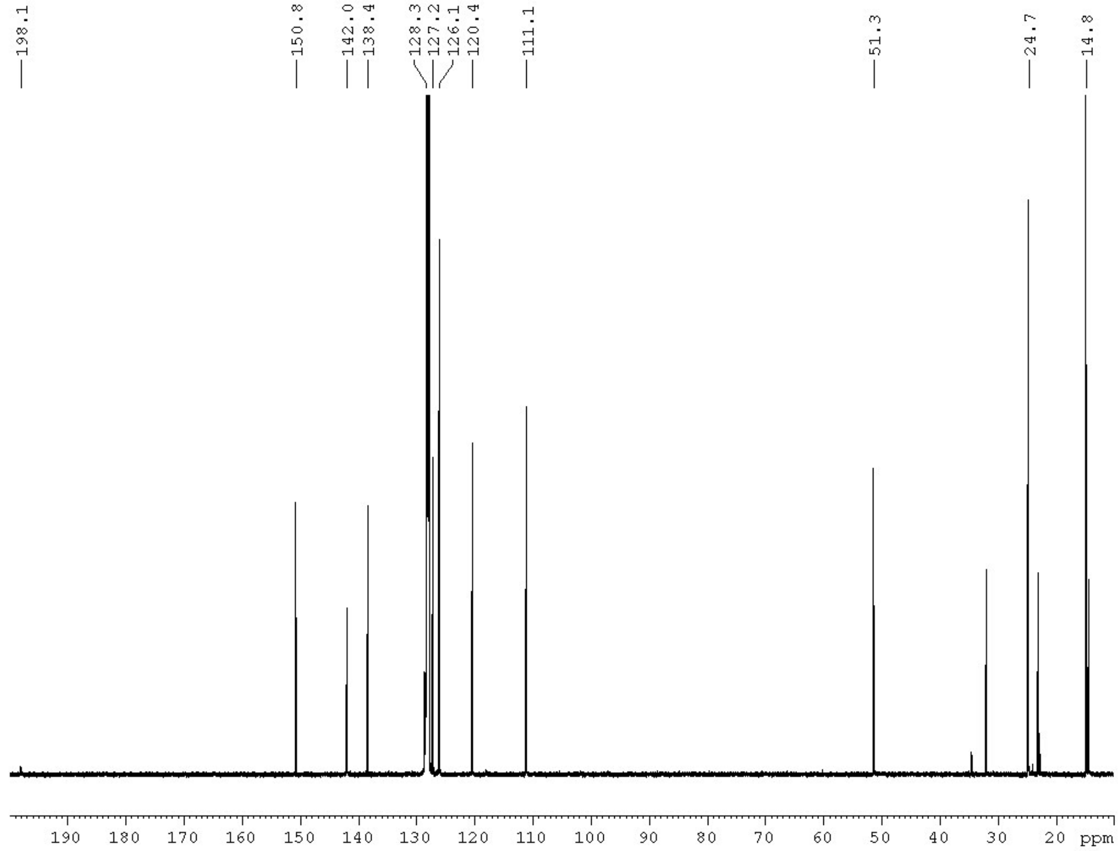


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of **2a**.

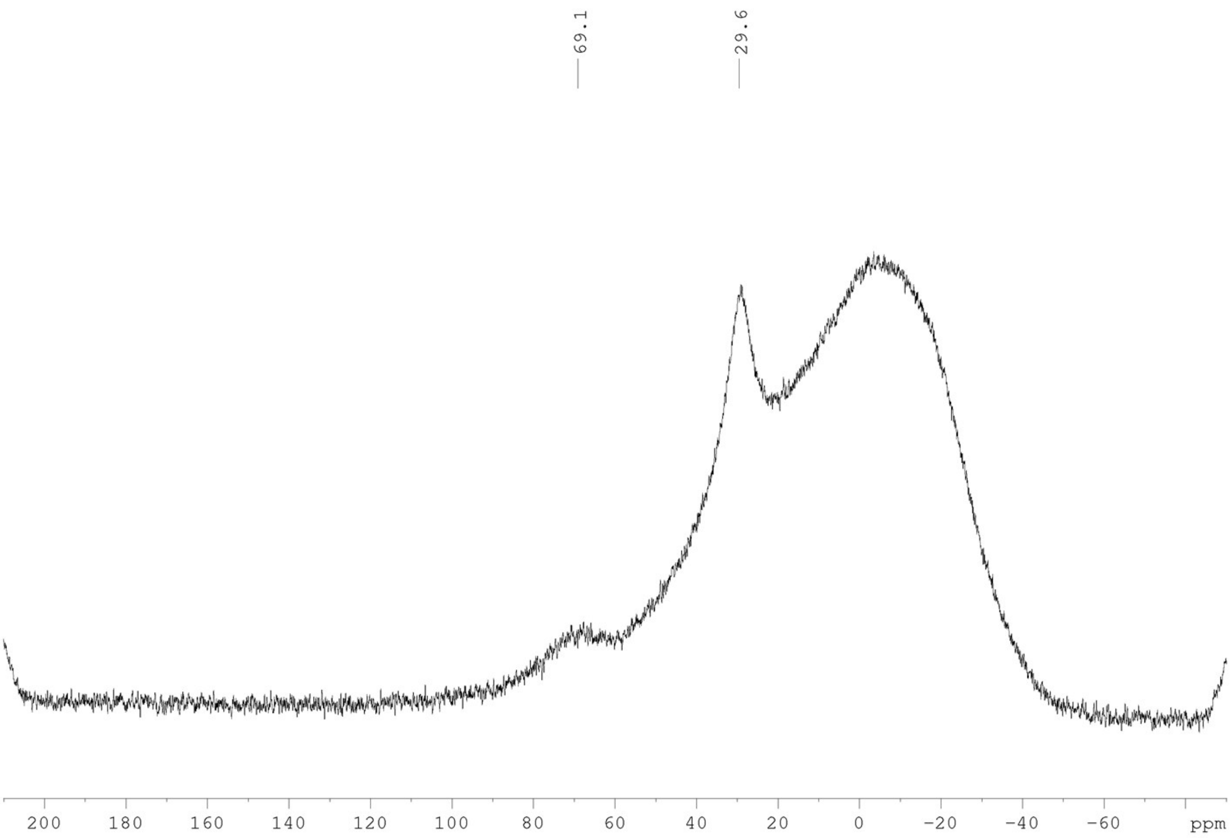


Figure S7. ^{11}B NMR spectrum of **2b**.

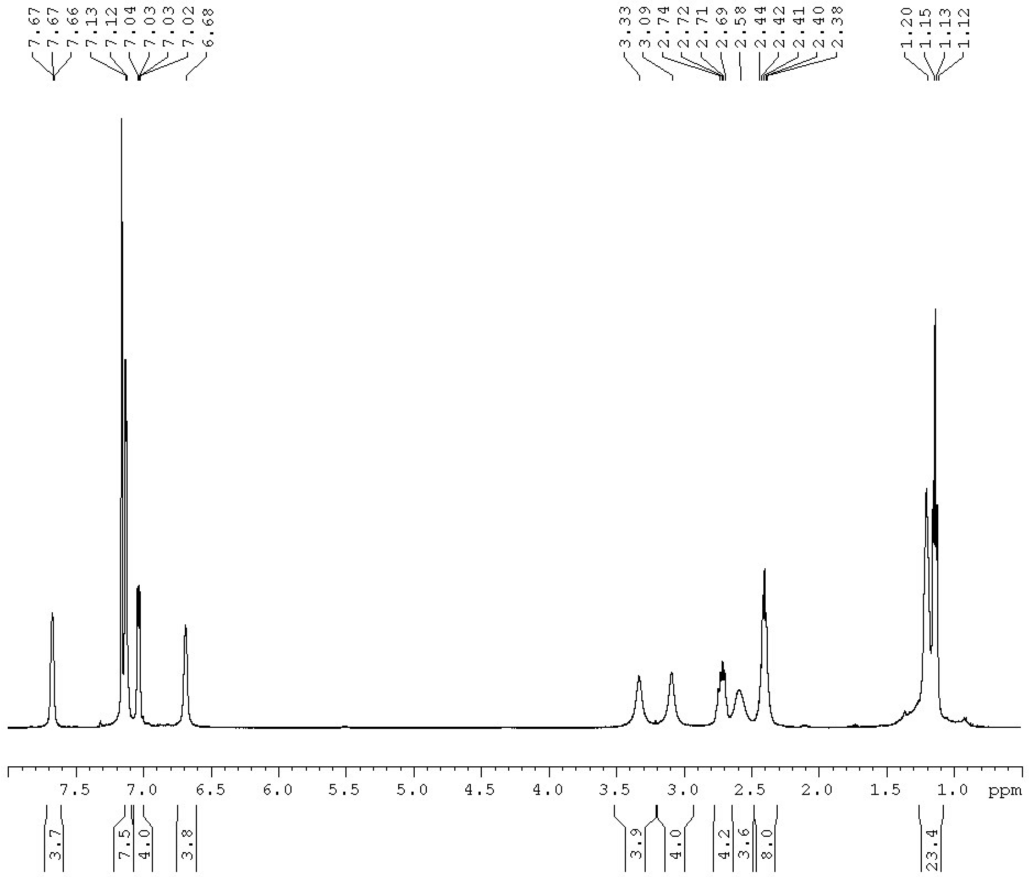


Figure S8. ^{1}H NMR spectrum of **2b**.

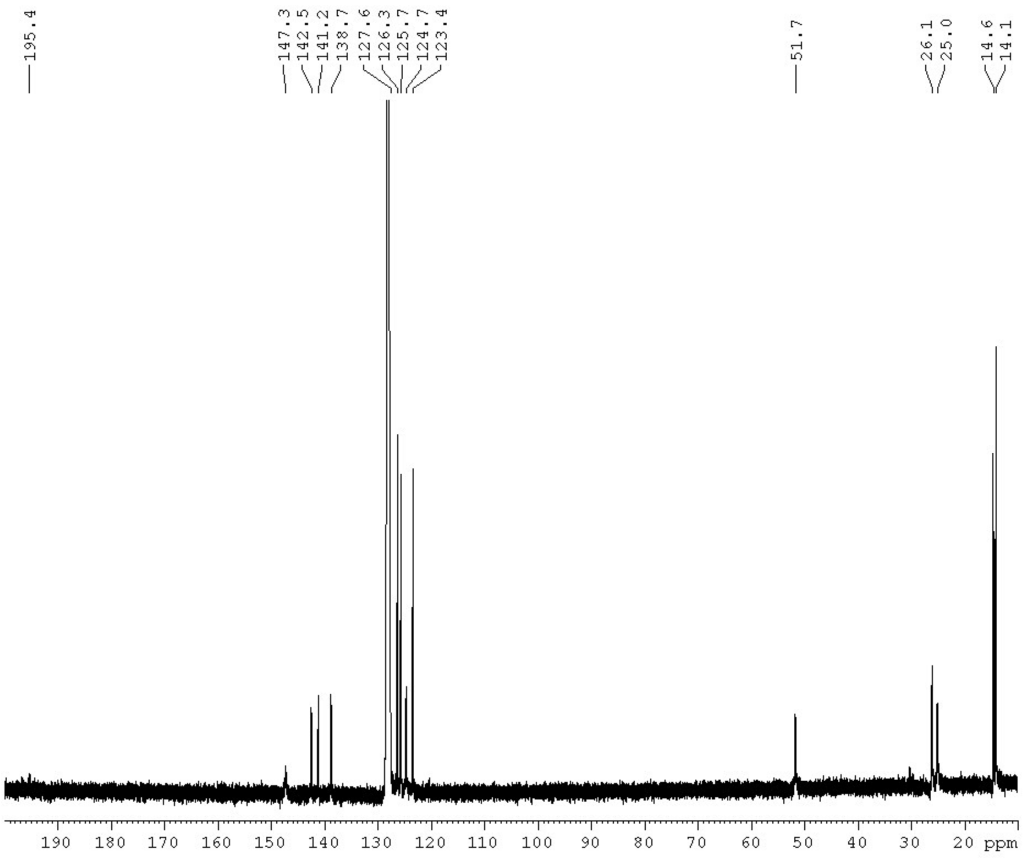


Figure S9. ^{13}C NMR spectrum of **2b**.

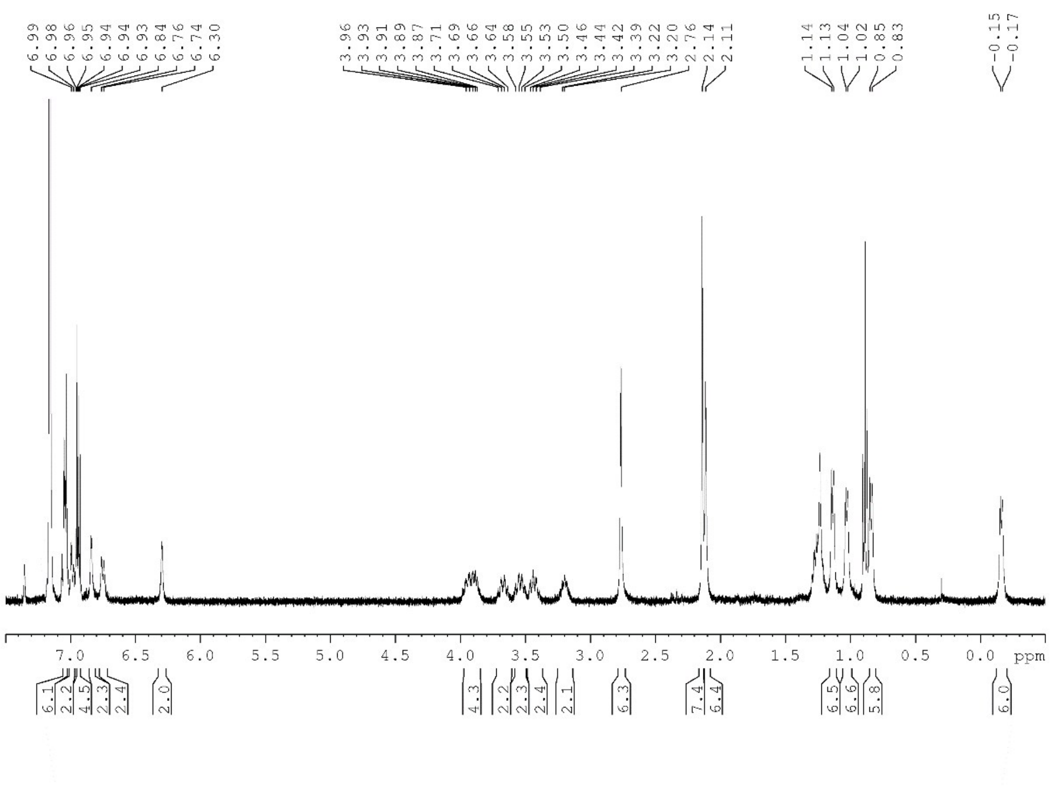


Figure S10. ^{1}H NMR spectrum of **2c**.

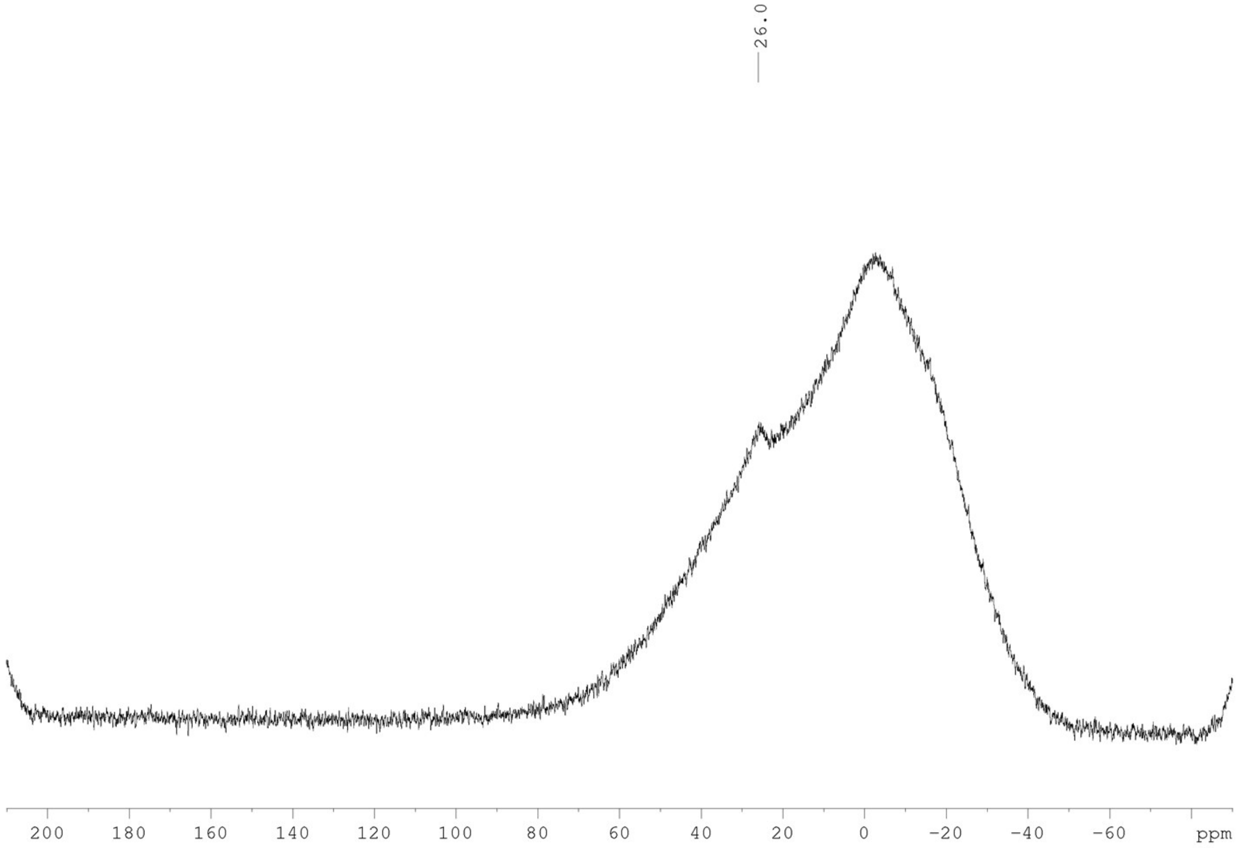


Figure S11. ^{11}B NMR spectrum of **2c**.

UV/Vis spectra:

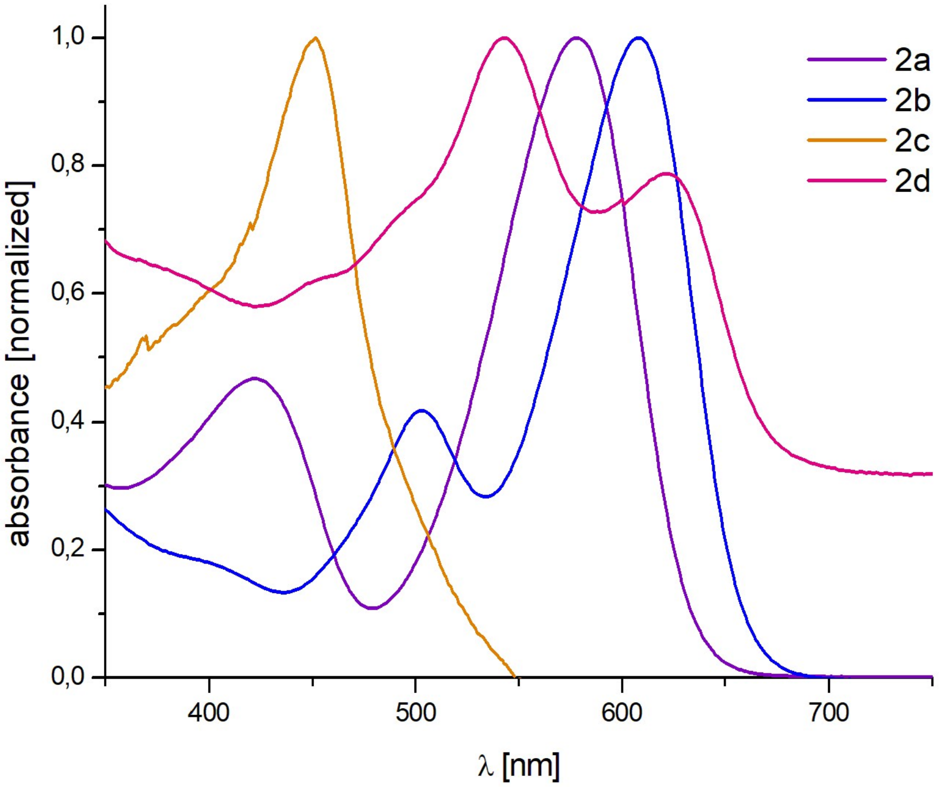


Figure S12. UV-vis spectra of **2a**-**d** in benzene.

X-ray Structure Determination:

The crystal data of **1b**, **2a** and **2c** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **2b** and **2d** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using intrinsic phasing method,[4] refined with the ShelXL program[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

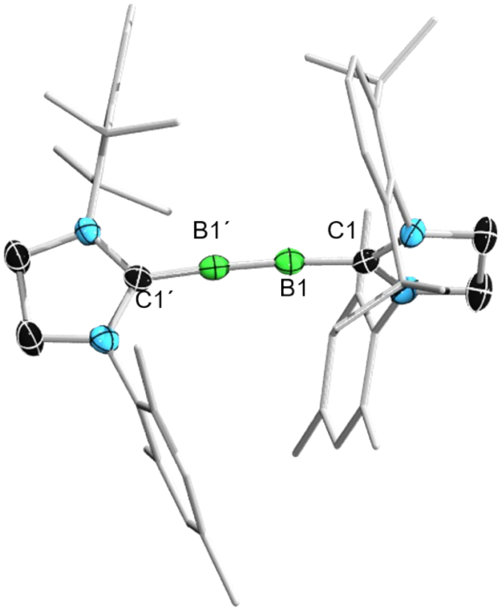


Figure S13. Crystallographically derived structures of **1b**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity.

Crystal data for **1b**: $C_{48}H_{64}B_2N_4$, M_r = 718.65, red block, 0.274×0.246×0.197 mm^3, monoclinic space group *C*2/*c*, *a* = 19.783(13) Å, *b* = 11.805(10) Å, *c* = 21.269(13) Å, β = 113.95(2)°, *V* = 4539(6) Å^3, *Z* = 4, ρ_{calcd} = 1.052 g·cm^{-3}, μ = 0.060 mm^{-1}, *F*(000) = 1560, *T* = 122(2) K, R_1 = 0.0859, wR^2 = 0.1489, 4641 independent reflections [2θ≤52.742°] and 251 parameters.

Crystal data for **2a**: $C_{58}H_{68}B_4N_4O_4$, M_r = 928.40, red block, 0.361×0.310×0.245 mm^3, triclinic space group $P\bar{1}$, *a* = 10.9190(4) Å, *b* = 11.0985(4) Å, *c* = 12.1024(5) Å, α = 73.5300(10)°, β = 80.5900(10)°, γ = 64.8320(10)°, *V* = 1271.37(8) Å^3, *Z* = 1, ρ_{calcd} = 1.213 g·cm^{-3}, μ = 0.074 mm^{-1}, *F*(000) = 496, *T* = 100(2) K, R_1 = 0.0987, wR^2 = 0.1269, 5176 independent reflections [2θ≤52.738°] and 320 parameters.

Crystal data for **2b**: The unit cell of **2b** contains two hexane molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[6] The displacement parameters of the disorderd ethyl groups were restrained to the same value with similarity restraint SIMU and RIGU. The distances between C1_5 and C2_5 (disordered ethyl group) were kept during refinement at the value of 1.54(2) using DFIX restraint. $C_{116}H_{134}B_8N_8S_8$, M_r = 1983.26, red block, 0.388×0.243×0.222 mm^3, Triclinic space group $P\bar{1}$, *a* = 12.532(4) Å, *b* = 18.541(5) Å, *c* = 26.605(5) Å, α = 106.073(17)°, β = 100.060(18)°, γ = 94.42(3)°, *V* = 5797(3) Å^3, *Z* = 2, ρ_{calcd} = 1.136 g·cm^{-3}, μ = 0.203 mm^{-1}, *F*(000) = 2108, *T* = 100(2) K, R_1 = 0.0703, wR^2 = 0.1437, 22818 independent reflections [2θ≤52.044°] and 1323 parameters.

Crystal data for **2c**: $C_{72}H_{84}B_4N_4O_4$, M_r = 1112.67, red block, 0.703×0.483×0.130 mm^3, triclinic space group $P\bar{1}$, a = 10.5163(5) Å, b = 12.3887(7) Å, c = 13.5117(7) Å, α = 88.943(2)°, β = 84.495(2)°, γ = 65.880(2)°, V = 1598.83(15) Å^3, Z = 1, ρ_{calcd} = 1.156 g·cm^{-3}, μ = 0.070 mm^{-1}, F(000) = 596, T = 100(2) K, R_1 = 0.0716, wR^2 = 0.1358, 6531 independent reflections [2θ≤52.744°] and 622 parameters. The displacement parameters of atoms of the disorded NHCs and Benzene were restrained to the same value with similarity restraint SIMU and RIGU.

Crystal data for **2d**: $C_{72}H_{84}B_4N_4S_4$, M_r = 1176.91, red block, 0.450×0.392×0.31 mm^3, triclinic space group $P\bar{1}$, a = 10.4711(6) Å, b = 12.1436(7) Å, c = 14.1733(8) Å, α = 87.1300(10)°, β = 83.4460(10)°, γ = 65.9460(10)°, V = 1634.96(16) Å^3, Z = 1, ρ_{calcd} = 1.195 g·cm^{-3}, μ = 0.190 mm^{-1}, F(000) = 628, T = 100(2) K, R_1 = 0.0489, wR^2 = 0.1149, 6664 independent reflections [2θ≤52.744°] and 381 parameters. The displacement parameters of atoms the disordered benzene were restrained to the same value with similarity restraint SIMU and RIGU.

Crystallographic data for **1b** and **2a-d** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-1882019 (**1b**), -1882020 (**2a**), -1882021 (**2b**), -1882022 (**2c**), -1882023 (**2d**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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