Supporting Information for

Tridurylboranes Extended by Three Arylethynyl Groups As a New Family of Boron-Based π-Electron Systems

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Experimental Section

General. Melting point (mp) determination was performed using a Yanaco MP-S3 instrument. ^{1}H and ^{13}C NMR spectra were measured with a Varian Mercury 300 spectrometer for ^{1}H (300 MHz) and with a JEOL EX-270 spectrometer for ^{13}C (67.8 MHz) in $CDCl_3$. UV-visible absorption spectra and Fluorescence spectra were measured with a Shimadzu UV-3100PC spectrometer and a PerkinElmer LS50B spectrometer, respectively, in a degassed spectral grade THF. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using Kieselgel 60 (70-230 mesh; Merck). Recycle preparative gel permiation chromatography (GPC) was performed using polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with 1,2-dichloroethane as an eluent. All reactions were carried out under nitrogen or argon atmosphere.

Tris(bromoduryl)borane (3). To a solution of 1,4-dibromodurene (14.1 g, 48.3 mmol) in dry Et_2O (400 mL) was added dropwise a hexane solution of *n*-BuLi (1.6 M, 30 mL, 48.0 mmol) at –78 °C. The reaction mixture was allowed to warm to 0 °C and stirred for 20 min. To the mixture was added $BF_3{\cdot}OEt_2$ (2.0 mL, 15.8 mmol) at –78 °C. The reaction mixture was warmed up to room temperature over 1 h and stirred for 16 h. After addition of water, the mixture was extracted with Et_2O. The extract was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was suspended with a Et_2O/MeOH mixed solvent. The insoluble part was collected by filtration and washed with MeOH to afford **3** (7.62 g, 11.8 mmol) in 74% yield as a white solid: mp 292 °C. ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 18H), 1.99 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 147.9, 137.0, 133.8, 131.2, 21.4, 20.8. UV-vis (THF) λ_{max} nm (log ε): 333 (4.10), 210 (4.91). MS (FAB) m/e (relative intensity) 647 (M^+, 20), 435 (100). Anal. Calcd for $C_{30}H_{36}BBr_3$: C, 55.68; H, 5.61. Found: C, 55.97; H, 5.82.

Tris(iododuryl)borane (4). To a solution of **3** (5.23 g, 8.1 mmol) in dry THF (200 mL) was added dropwise a pentane solution of *t*-BuLi (1.59 M, 31 mL, 49.3 mmol) at –78 °C. The reaction mixture was stirred for 50 min. To the reaction mixture was added a THF (80 mL) solution of iodine (9.4 g, 37.0 mmol) at –78 °C. The reaction mixture was warmed up to room temperature over 1 h and stirred for 11 h. The reaction mixture was concentrated under reduced pressure. After addition of water, the mixture was extracted with Et_2O. The extract was washed with aqueous solution of $Na_2S_2O_3$ and then brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was suspended with a Et_2O/MeOH mixed solvent. The insoluble part was collected by filtration and washed with MeOH to afford **4** (5.37 g, 6.81 mmol) in 84% yield as a white solid: mp 262 °C (dec.). ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 18H), 2.03 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 148.8, 137.4, 136.3, 114.7, 27.7, 22.2. UV-vis (THF) λ_{max} nm (log ε): 337 (4.20), 215 (4.92). MS (EI) m/e (relative intensity) 787 (M^+, 20), 528 (100). Anal. Calcd for $C_{30}H_{36}BI_3$: C, 45.72; H, 4.60. Found: C, 45.66; H, 4.62.

Tris[(trimethylsilylethynyl)duryl]borane (5). To a solution of **4** (4.64 g, 5.9 mmol), $PdCl_2(PPh_3)_2$ (620 mg, 0.88 mmol), CuI (320 mg, 1.77 mmol) in dry Et_2NH (50 mL) and THF (20 mL) was added dropwise a solution of trimethylsiliylacetylene (3.7 mL, 26 mmol) in Et_2NH (10 mL) at room temperature. The mixture was refluxed with stirring for 10 h. After addition of water, the mixure was extracted with Et_2O. The extract was washed with 1N HCl aqueous solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was subjected to column chromatography on silica gel (hexane, $R_f = 0.6$) to give pure **5** (3.89 g, 5.5 mmol) in 93% yield as white crystals: mp 140 °C. ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 18H), 1.88 (s, 18H). 0.26 (s, 27H). ^{13}C NMR ($CDCl_3$) δ 149.6, 135.9, 135.6, 104.7, 102.5, 20.0. 18.3, 0.13. UV-vis (THF) λ_{max} nm (log ε): 353 (4.64), 260 (4.82), 222 (5.05). MS (EI) m/e (relative intensity) 698 (M^+, 10), 468 (100). Anal. Calcd for $C_{45}H_{63}BSi_3$: C, 77.32; H, 9.08. Found: C, 77.38; H, 9.36.

Tris(ethynylduryl)borane (6). A solution of **5** (250 mg, 0.36 mmol) and KOH (250 mg, 4.52 mmol) in MeOH (20 mL) and THF (10 mL) was stirred for 2 h. The mixture was concentrated under reduced pressure. After addition of water, the mixture was extracted with Et_2O. The extract was washed with water, died over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was suspended with hexane. The insoluble part was collected by filtration and washed with hexane to give **6** (168 mg, 3.47 mmol) in 97% yield as a white solid: mp >300 °C. ^1H NMR ($CDCl_3$) δ 3.52 (s, 3H), 2.34 (s, 19H), 1.92 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 149.6, 136.2, 135.6, 128.3, 123.3, 85.2, 83.0, 20.1, 18.2. UV-vis (THF) λ_{max} nm (log ε): 345 (4.45), 255 (4.67), 222 (4.36). MS (EI) m/e (relative intensity) 482 (M^+, 20), 324 (100). HRMS (EI) Calcd for $C_{36}H_{39}B$; 482.3145. Found; 482.3143.

Tris[(phenylethynyl)duryl]borane (2a). To a solution of **6** (100 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (7.3 mg, 0.01 mmol), and CuI (4.0 mg, 0.02 mmol) in dry piperidine (5 mL) was added iodobenzene (70 µL, 0.63 mmol). The mixture was stirred for 12 h at room temperature. After addition of water, the mixture was extracted with Et_2O. The extract was washed with 1N HCl aqueous solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was passed through a short pass silica gel column (hexane/EtOAc = 8/2), and subjected to preparative recycle GPC to afford pure **2a** (93 mg, 0.13 mmol) in 62% yield as white crystals: mp >300 °C. ^1H NMR ($CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 6H), 7.36-7.33 (m, 9H), 2.43 (s, 18H), 1.99 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 149.6, 135.8, 135.6, 131.3, 128.5, 128.0, 124.2, 124.0, 97.6, 89.2, 20.3, 18.4. UV-vis (THF) λ_{max} nm (log ε): 364 (4.77), 285 (4.83). MS (EI) m/e (relative intensity) 710 (M^+, 20), 476 (100). HRMS (EI) Calcd for $C_{54}H_{51}B$; 710.4084. Found; 710.4096.

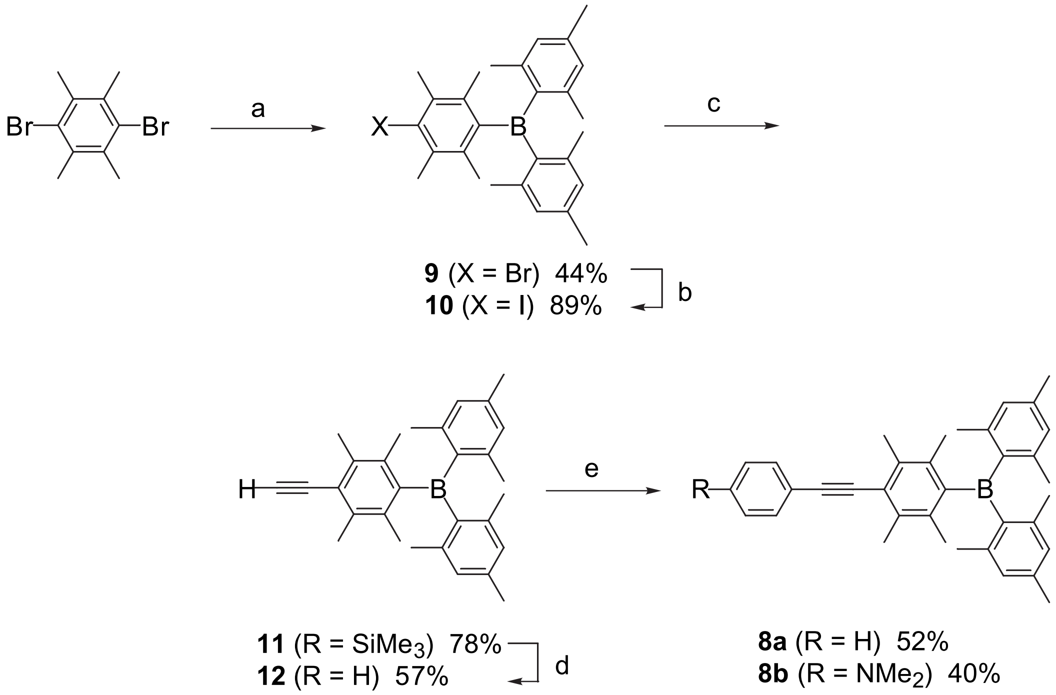
Tris{[*p*-(dimethylamino)phenylethnyl]duryl}borane (2b). This compound was prepared essentially in the same manner as described for **2a** in 67% yield as yellow crystals: mp 175 °C. ^1H NMR ($CDCl_3$) δ 7.43 (d, J = 4.5 Hz, 6H), 6.67 (d, J = 4.5 Hz, 6H), 2.99 (s, 18H), 2.42 (s, 18H), 1.98 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 149.8, 149.1, 135.6, 135.0, 132.3, 124.9, 111.8, 110.9, 98.8, 87.1, 40.2, 20.1, 18.4. UV-vis (THF) λ_{max} nm (log ε): 393 (4.80), 303 (4.59). MS (FAB) m/e (relative intensity) 839 (M^+, 50), 563 (100). Anal. Calcd for $C_{60}H_{66}BN_3$: C, 85.79; H, 7.92; N, 5.00. Found: C, 85.97; H, 8.12; N, 4.75.

Tris[(*p*-methoxyphenylethnyl)duryl]borane (2c). This compound was prepared essentially in the same manner as described for **2a** in 52% yield as white crystals: mp 265 °C. ^{1}H NMR ($CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 6H), 6.88 (d, *J* = 8.7 Hz, 6H), 3.83 (s, 9H), 2.41 (s, 18H), 1.97 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 159.4, 149.4, 135.3, 132.7, 124.5, 116.2, 114.0, 97.6, 87.8, 55.3,. 20.1, 18.4. UV-vis (THF) λ_{max} nm (log ε): 371 (4.75), 291 (4.83), 209 (5.06). MS (FAB) m/e (relative intensity) 800 (M^+, 20), 537 (100). Anal. Calcd for $C_{57}H_{57}BO_3$: C, 85.48; H, 7.17. Found: C, 85.24; H, 7.20.

Tris[(*p*-cyanophenylethnyl)duryl]borane (2d). This compound was prepared essentially in the same manner as described for **2a** in 67 % yield as white crystals: mp 173 °C. ^{1}H NMR ($CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 6H), 7.60 (d, *J* = 8.7 Hz, 6H), 2.41 (s, 18H), 1.98 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 150.2, 139.0, 135.9, 132.1, 131.7, 128.8, 123.5, 118.6, 111.1, 96.0, 93.7, 20.2, 18.4. UV-vis (THF) λ_{max} nm (log ε): 369 (4.91), 319 (4.79), 214 (5.03). MS (FAB) m/e (relative intensity) 786 (M^+, 30), 526 (100). Anal. Calcd for $C_{57}H_{48}BN_3$: C, 87.12; H, 6.16; N, 5.35. Found: C, 86.84; H, 6.30; N, 5.29.

Tris{[(*p*-butylphenylethnyl)-*p*-phenylethnyl]duryl}borane (2e). A solution of **6** (250 mg, 0.52 mmol), *p*-(*p*-butylphenylethnyl)bromobenzene (500 mg, 1.60 mmol), $PdCl_2(PPh_3)_2$ (54 mg, 0.077 mmol), and CuI (28.0 mg, 0.155 mmol) in dry Et_2NH (10 mL) was refluxed with stirring for 12 h. After addition of water, the mixture was extracted with Et_2O. The extract was washed with 1N HCl aqueous solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was subjected to silica gel column chromatography (hexane/benzene = 9/1, R_f = 0.50) to afford pure **2e** (319 mg, 0.27 mmol) in 52 % yield as white crystals: mp 129 °C. ^{1}H NMR ($CDCl_3$) δ 7.45 (s, 12H), 7.43 (dd, *J* = 6.3, 1.8Hz, 6H), 7.16 (d, *J* = 8.4 Hz, 6H), 3.16 (s, 3H), 2.61 (t, *J* = 7.5 Hz, 6H), 1.59 (m, 6H), 1.34 (m, 6H), 0.92 (t, *J* = 7.5 Hz, 9H). ^{13}C NMR ($CDCl_3$) δ 149.8, 143.6, 135.8, 135.7, 131.5, 131.2, 128.5, 124.1, 123.6, 123.0, 120.1, 97.4, 91.4, 91.0, 88.6, 35.6, 33.4, 22.3, 20.2, 18.4, 13.9. UV-vis (THF) λ_{max} nm (log ε): 379 (5.08), 327 (5.10), 209 (5.12). MS (FAB) m/e (relative intensity) 1179 (M^+, 10), 789 (50), 533 (100). Anal. Calcd for $C_{90}H_{87}B$: C, 91.66; H, 7.43. Found: C, 91.06; H, 7.50.

Scheme S-1



Reagents and Conditions: a) i, *n*-BuLi (1.05 mol. amt.), Et_2O, –20 °C; ii, Mes_2BF (1.0 mol. amt.), 0 °C ~ rt.: b) i, *t*-BuLi (2.1 mol. amt.), THF, –78 °C; ii, I_2 (4.5 mol. amt.), –78 °C: c) $Me_3SiC{\equiv}CH$ (1.7 mol. amt.), $PdCl_2(PPh_3)_2$ (0.05 mol. amt.), CuI (0.10 mol. amt.), Et_2NH, rt; ii, KOH, MeOH/THF, rt: d), ArI (1.0 mol. amt.), $PdCl_2(PPh_3)_2$ (0.05 mol. amt.), CuI (0.10 mol. amt.), Et_2NH, reflux . Mol. amt. = molar amount.

Compounds **8** were prepared according to Scheme S-1.

(Bromoduryl)dimesitylborane (9). To a solution of 1,4-dibromodurene (7.3 g, 27.2 mmol) in dry Et_2O (200 mL) was added dropwise a hexane solution of *n*-BuLi (1.6 M, 18 mL, 28.8 mmol) at –20 °C. The reaction mixture was stirred for 1 h at 0 °C. To the mixture was added dimesitylfluoroborane (8.0 g, 27.4 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature followed by stirring for 4 h. After addition of water, the mixture was extracted with Et_2O. The extract was washed with 1 N HCl aqueous solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was recrystallized form hexane to give **9** (8.08 g, 16.8 mmol) in 44% yield as white crystals: mp 184 °C. ^1H NMR ($CDCl_3$) δ 6.72 (s, 4H), 2.33 (s, 6H), 2.25 (s, 6H), 2.04 (s, 6H), 1.94 (s, 12H). ^{13}C

NMR ($CDCl_3$) δ 147.4, 144.2, 140.9, 140.6, 139.4, 136.5, 133.4, 130.4, 129.2, 128.9, 128.8, 128.3, 23.2, 22.7, 21.2, 20.7. MS (EI) m/e (relative intensity) 462 (M^+, 20), 340 (100), 248 (100).

(Iododuryl)dimesitylborane (10). To a solution of **9** (6.36 g, 13.8 mmol) in dry THF (150 mL) was added dropwise a pentane solution of *t*-BuLi (1.45 M, 20 mL, 29.0 mmol) at –78 °C. The reaction mixture was stirred for 90 min. To the reaction mixture was added a THF (50 mL) solution of iodine (3.50 g, 13.8 mmol) at –78 °C. The mixture was warmed up to room temperature over 1 h and stirred for 5 h. The resulting mixture was concentrated under reduced pressure. After addition of water, the mixture was extracted with Et_2O. The extract was washed with aqueous solution of $Na_2S_2O_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford **10** (6.27 g, 12.3 mmol) in 89% yield as white crystals: mp 187 °C. ^{1}H NMR ($CDCl_3$) δ 6.72 (s, 4H), 2.42 (s, 6H), 2.25 (s, 6H), 2.08 (s, 6H), 1.93 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 148.3, 144.2, 140.9, 140.6, 139.4, 137.1, 135.9, 128.9, 128.7, 113.5, 27.3, 23.2, 22.8, 22.0, 21.2. MS (EI) m/e (relative intensity) 508 (M^+, 20), 388 (100), 248 (50).

[(Trimethylsilylethynyl)duryl]dimesitylborane (11). To a solution of **10** (6.22 g, 12.2 mmol), $PdCl_2(PPh_3)_2$ (430 mg, 0.61 mmol), CuI (220 mg, 1.22 mmol) in dry Et_2NH (200 ml) was added dropwise a Et_2NH (20 mL) solution of trimethylsiliylacetylene (1.9 mL, 13.4 mmol) at 0 °C. The mixture was refluxed with stirring for 12 h. An additional portion of trimethylsiliylacetylene (1.0 ml, 7.1 mmol) was added to the mixture, followed by stirring with reflux for 6 h. After addition of water, the mixture was extracted with Et_2O. The extract was washed with 1N HCl aqueous solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was subjected to column chromatography on silica gel (hexane, $R_f = 0.5$) to give pure **11** (4.53 g, 9.5 mmol) in 78% yield as white crystals: mp 193 °C. ^{1}H NMR ($CDCl_3$) δ 6.72 (s, 4H), 2.34 (s, 6H), 2.25 (s, 6H), 1.97 (s, 6H), 1.93 (s, 6H), 1.92 (s, 6H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 149.1, 144.3, 140.9, 140.7, 139.3, 135.7, 135.1, 128.8, 128.7, 123.5, 104.8, 102.1, 23.2, 22.8, 21.2, 20.0, 18.1, 0.16. MS (EI) m/e (relative intensity) 478 (M^+, 30), 358 (80), 248 (100).

(Ethynylduryl)dimesitylborane (12). A solution of **11** (4.53 g, 9.47 mmol) and KOH (500 mg, 8.91 mmol) in MeOH (75 mL) and THF (10 mL) was stirred at room temperature for 12 h. After concentration under reduced pressure, water was added to the reaction mixture followed by extraction with Et_2O. The extract was washed with water, died over anhydrous $MgSO_4$, and concentrated under reduced pressure. Recrystallization form hexane afforded pure **12** (2.20 g, 5.41 mmol) in 57% yield as white crystals: mp 194 °C. ^{1}H NMR ($CDCl_3$) δ 6.73 (s, 4H), 3.51 (s, 1H), 2.34 (s, 6H), 2.25 (s, 6H), 1.98 (s, 6H), 1.94 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 149.3, 144.2, 140.9, 140.7, 139.4, 136.0, 135.1, 128.8, 128.7, 122.6, 84.8, 83.1, 23.5, 23.0, 21.2, 20.0, 18.0. MS (EI) m/e (relative intensity) 406 (M^+, 30), 286 (100), 248 (100). Anal. Calcd for $C_{30}H_{35}B$: C, 88.66; H, 8.68. Found: C, 88.49; H, 8.71.

[(Phenylethnyl)duryl]dimesitylborane (8a). To a solution of **12** (400 mg, 0.98 mmol) and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), CuI (18 mg, 0.10 mmol) in dry Et_2NH (10 mL) was added iodobenzene (110 μL, 0.98 mmol) at room temperature. After refluxed for 10 h, water was added to the reaction mixture, followed by extraction with Et_2O. The extract was washed with 1N HCl aqueous solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was recrystallized from a CH_2Cl_2/MeOH mixed solvent to afford pure **8a** (244 mg, 0.51 mmol) in 52% yield as white crystals: mp 194 °C. ^{1}H NMR ($CDCl_3$) δ 7.54 (d, *J* = 3.9 Hz, 2H), 7.34 (m, 3H), 6.73 (s, 4H), 2.41 (s, 6H), 2.26 (s, 6H), 2 (s, 6H), 1.95 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 149.1, 144.3, 140.8, 140.7, 139.3, 135.4, 135.2, 131.3, 129.1, 128.8, 128.7, 128.3, 127.9, 124.0, 123.6, 97.2, 89.2, 23.2, 22.8, 21.2, 20.1, 18.2. UV-vis (THF) λ_{max} nm (log ε): 345 (4.34), 294 (4.27), 283 (4.28). MS (EI) m/e (relative intensity) 482 (M^+, 50), 362 (70), 248 (100). Anal. Calcd for $C_{36}H_{39}B$: C, 89.61; H, 8.15. Found: C, 89.25; H, 8.13.

{[*p*-(dimethylamino)phenylethnyl]duryl}dimesitylborane (8b). This compound was prepared essentially in the same manner as described for **8a** in 40% yield as yellow crystals: mp 238 °C. ^{1}H NMR ($CDCl_3$) δ 7.42 (d, *J* = 4.5 Hz, 2H), 6.72 (s, 4H), 6.67 (d, *J* = 4.5 Hz, 2H), 2.98 (s, 6H), 2.4 (s, 6H), 2.25 (s, 6H), 1.99 (s, 6H), 1.95 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 149.9, 147.3, 144.5, 140.8, 140.8, 139.2, 135.0, 134.9, 132.3, 128.8, 128.7, 124.5, 111.9, 111.1, 98.5, 87.1, 40.3, 23.2, 22.8, 21.2, 20.1, 18.2, 14.1. UV-vis (THF) λ_{max} nm (log ε): 376 (4.37), 324 (4.47), 299 (4.46). MS (EI) m/e (relative intensity) 525 (M^+, 100), 248 (70), 148 (70). Anal. Calcd for $C_{38}H_{44}BN$: C, 86.84; H, 8.44; N, 2.67. Found: C, 86.50; H, 8.57; N, 2.60.

X-ray Crystal Structure Analysis of 2a. Single crystals of **2a** suitable for X-ray crystallography were obtained by recrystallization from a CH_2Cl_2/MeOH mixed solvent. Intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55°. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structure was solved by and expanded using Fourier techniques (DIRDIF94),[1] and a full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included and isotropically refined. All the calculations were performed using the teXsan crystallographic package from molecular Structure Corp. The ORTEP drawing with atom-labeling scheme is shown in Figure 1. The crystal data and analytical conditions, atomic coordinates, and anisotropic displacement parameters are summarized in Table S-1-S-3, and the bond distances and bond angles are listed in Table S-4-S-5, respectively.

1) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Table S-1. Experimental Details for X-ray Crystal Structural Analysis of **2a**

A. Crystal Data

formula	$C_{54}H_{51}B$
mol wt	710.81
crystal color, habit	colorless, prismatic
cryst dimens, mm	0.30 x 0.20 x 0.20
cryst syst	monoclinic
lattice type	C-centered
space group	*C*2/c (No. 15)
indexing images	3 osillations@60 min
detector position	104.89 mm
detector swing angle	0.00°
pixel size	0.100 mm
cell const	
a, Å	16.212(1)
b, Å	22.153(1)
c, Å	14.9162(9)
β, deg	127.956(2)
V, Å^3	4224.0(4)
Z	4
D_{calcd}, g cm^{-3}	1.118
F_{000}	1520.00
μ(Mo Kα), cm^{-1}	0.62

B. Intensity Measurements

diffractometer	RAXIS-IV
temp, °C	–110
radiation	Mo Kα (λ = 0.71070 Å) graphite monochromated
detector aperture	300 mm x 300 mm
data images	33 exposures@60 min
osillation range	5.0°
detector position	104.89 mm
detector swing angle	0.00°
pixel size	0.100 mm
$2\theta_{\mathrm{max}}$, deg	55.1

no. of collected rflns	4461
corrections	Lorents-polarization Secondary Extinction

C. Structure Solution and Refinement

structure solution	Direct Methods
refinement	Full-matrix least squares
function minimized	$\sum\omega(\lvert Fo\rvert-\lvert Fc\rvert)^2$
least squares weights	$\omega = 1/\sigma^2(Fo) = [\sigma_c^2(Fo) + (p^2/4)Fo^2]$
p-factor	0.1150
anomalous dispersion	All non-hydrogen atoms
no. of unique rflns	2799 ($I > 3\sigma(I)$)
R^a	0.068
$R_w{}^b$	0.089
goodness of fit	1.20
max shift/error in final cycle	0.00
maximum peak in final diff. map	0.44 e^-/Å^3
minimun peak in final diff. map	–0.37 e^-/Å^3

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[a] $R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$. [b] $R_w = [\Sigma\omega(|Fo|-|Fc|)^2/\Sigma\omega F\sigma^2]^{1/2}$

Table S-2. Atomic Coordinates and B_{iso}/B_{eq} of **2a**

atom	x	y	z	B(eq)
C(1)	0.1074(2)	0.03585(9)	0.3214(2)	2.20(4)
C(2)	0.1274(2)	0.08106(9)	0.4000(2)	2.40(5)
C(3)	0.2216(2)	0.1130(1)	0.4624(2)	2.90(5)
C(4)	0.2981(2)	0.0991(1)	0.4488(2)	2.88(5)
C(5)	0.2803(2)	0.0545(1)	0.3720(2)	2.81(5)
C(6)	0.1855(2)	0.02301(10)	0.3087(2)	2.41(5)
C(7)	0.3961(2)	0.1320(1)	0.5139(3)	3.58(6)
C(8)	0.4746(2)	0.1583(1)	0.5665(3)	3.44(6)
C(9)	0.5735(2)	0.1908(1)	0.6322(3)	3.17(5)
C(10)	0.5836(3)	0.2449(1)	0.6856(3)	3.81(7)
C(11)	0.6769(3)	0.2763(2)	0.7473(3)	5.04(9)
C(12)	0.7613(3)	0.2536(2)	0.7576(3)	5.58(9)
C(13)	0.7526(3)	0.2001(2)	0.7057(3)	4.94(8)
C(14)	0.6595(3)	0.1687(1)	0.6434(3)	3.82(7)
C(15)	0.0504(2)	0.0941(1)	0.4227(3)	3.11(6)
C(16)	0.2419(3)	0.1617(1)	0.5449(3)	4.25(7)

C(17)	0.3639(3)	0.0400(2)	0.3596(4)	4.34(8)
C(18)	0.1658(2)	–0.0218(1)	0.2215(3)	3.04(6)
C(19)	0.0000	–0.0717(1)	0.2500	2.24(6)
C(20)	–0.0584(2)	–0.10426(10)	0.1460(2)	2.36(5)
C(21)	–0.0587(2)	–0.1674(1)	0.1460(2)	2.88(6)
C(22)	0.0000	–0.1984(1)	0.2500	2.93(8)
C(23)	0.0000	–0.2639(2)	0.2500	3.56(9)
C(24)	0.0000	–0.3163(2)	0.2500	3.51(9)
C(25)	0.0000	–0.3822(1)	0.2500	3.16(8)
C(26)	–0.0765(3)	–0.4140(1)	0.1527(3)	3.89(7)
C(27)	–0.0751(3)	–0.4764(1)	0.1541(4)	4.87(10)
C(28)	0.0000	–0.5076(2)	0.2500	5.5(2)
C(29)	–0.1159(2)	–0.0719(1)	0.0339(2)	3.05(6)
C(30)	–0.1220(3)	–0.2019(1)	0.0354(3)	4.25(8)
B(1)	0.0000	–0.0002(2)	0.2500	2.16(7)
H(1)	–0.010(3)	0.071(2)	0.376(4)	5.6(8)
H(2)	0.102(4)	0.086(2)	0.522(5)	8.8(10)
H(3)	0.018(3)	0.135(2)	0.396(4)	5.9(8)
H(4)	0.263(4)	0.145(2)	0.623(5)	7.9(9)
H(5)	0.183(4)	0.192(2)	0.507(4)	5.9(8)
H(6)	0.309(4)	0.181(2)	0.580(4)	7.5(9)
H(7)	0.413(4)	0.069(2)	0.392(5)	8.3(10)
H(8)	0.349(4)	0.050(2)	0.283(5)	7.2(9)
H(9)	0.370(4)	–0.004(2)	0.359(4)	7.8(9)
H(10)	0.178(3)	–0.005(2)	0.171(3)	4.8(7)
H(11)	0.204(4)	–0.059(2)	0.250(5)	8.4(10)
H(12)	0.099(3)	–0.042(2)	0.181(4)	5.5(8)
H(13)	0.534(3)	0.261(2)	0.685(4)	5.1(8)
H(14)	0.673(3)	0.316(2)	0.767(4)	6.9(9)
H(15)	0.827(4)	0.270(2)	0.799(4)	6.8(9)
H(16)	0.817(4)	0.182(2)	0.710(4)	7.0(9)
H(17)	0.658(3)	0.130(2)	0.615(3)	4.8(7)
H(18)	–0.102(3)	–0.027(1)	0.044(3)	3.9(6)
H(19)	–0.099(3)	–0.088(2)	–0.013(4)	5.9(8)
H(20)	–0.188(4)	–0.078(2)	–0.009(5)	8(1)
H(21)	–0.091(4)	–0.196(2)	–0.004(4)	7.3(9)
H(22)	–0.126(3)	–0.241(2)	0.047(3)	5.1(8)
H(23)	–0.197(4)	–0.181(2)	–0.023(5)	7.8(9)
H(24)	–0.136(3)	–0.390(2)	0.074(4)	5.7(8)
H(25)	–0.128(4)	–0.498(2)	0.091(5)	7.9(9)
H(26)	0.0000	–0.549(2)	0.2500	4.9(9)

B_{eq} = 8/3 x $\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table S-3. Anisotropic Displacement Parameters of **2a**

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}

C(1)	0.028(1)	0.0281(10)	0.026(1)	0.0002(8)	0.015(1)	0.0022(9)
C(2)	0.035(1)	0.0268(9)	0.028(1)	–0.0007(9)	0.018(1)	0.0011(9)
C(3)	0.040(2)	0.030(1)	0.031(1)	–0.006(1)	0.018(1)	0.0000(10)
C(4)	0.031(1)	0.036(1)	0.031(1)	–0.0080(10)	0.013(1)	0.003(1)
C(5)	0.030(1)	0.039(1)	0.034(1)	–0.0005(10)	0.018(1)	0.005(1)
C(6)	0.030(1)	0.032(1)	0.030(1)	0.0028(9)	0.018(1)	0.0048(9)
C(7)	0.041(2)	0.045(1)	0.039(2)	–0.002(1)	0.019(1)	0.009(1)
C(8)	0.041(2)	0.042(1)	0.038(2)	–0.004(1)	0.019(1)	0.009(1)
C(9)	0.033(1)	0.043(1)	0.034(1)	–0.008(1)	0.016(1)	0.003(1)
C(10)	0.053(2)	0.045(1)	0.046(2)	–0.006(1)	0.030(2)	–0.002(1)
C(11)	0.076(3)	0.057(2)	0.047(2)	–0.030(2)	0.032(2)	–0.013(2)
C(12)	0.051(2)	0.094(3)	0.041(2)	–0.039(2)	0.016(2)	–0.001(2)
C(13)	0.037(2)	0.096(3)	0.046(2)	–0.008(2)	0.022(2)	0.013(2)
C(14)	0.041(2)	0.056(2)	0.043(2)	–0.001(1)	0.023(1)	0.003(1)
C(15)	0.043(2)	0.039(1)	0.040(2)	–0.002(1)	0.027(1)	–0.006(1)
C(16)	0.055(2)	0.046(2)	0.050(2)	–0.015(1)	0.027(2)	–0.018(1)
C(17)	0.038(2)	0.069(2)	0.065(2)	–0.007(1)	0.035(2)	–0.005(2)
C(18)	0.038(2)	0.043(1)	0.041(2)	0.000(1)	0.027(1)	–0.004(1)
C(19)	0.027(2)	0.030(1)	0.029(2)	0.0000	0.017(2)	0.0000
C(20)	0.027(1)	0.033(1)	0.031(1)	–0.0028(9)	0.019(1)	–0.0028(9)
C(21)	0.038(1)	0.033(1)	0.044(2)	–0.0050(10)	0.028(1)	–0.007(1)
C(22)	0.042(2)	0.027(1)	0.053(2)	0.0000	0.035(2)	0.0000
C(23)	0.047(2)	0.039(2)	0.061(3)	0.0000	0.039(2)	0.0000
C(24)	0.043(2)	0.042(2)	0.060(3)	0.0000	0.037(2)	0.0000
C(25)	0.046(2)	0.031(1)	0.051(2)	0.0000	0.034(2)	0.0000
C(26)	0.055(2)	0.045(1)	0.055(2)	–0.008(1)	0.037(2)	–0.006(1)
C(27)	0.083(3)	0.046(2)	0.084(3)	–0.022(2)	0.065(3)	–0.022(2)
C(28)	0.113(5)	0.027(2)	0.118(5)	0.0000	0.096(5)	0.0000
C(29)	0.041(2)	0.039(1)	0.029(1)	–0.003(1)	0.019(1)	–0.005(1)
C(30)	0.069(2)	0.037(1)	0.052(2)	–0.013(1)	0.036(2)	–0.016(1)
B(1)	0.033(2)	0.029(1)	0.025(2)	0.0000	0.020(2)	0.0000

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S-4. Bond Lengths (Å) of **1**

atom	atom	distance	atom	atom	distance
C(1)	C(2)	1.420(3)	C(11)	C(12)	1.374(6)
C(1)	C(6)	1.418(3)	C(12)	C(13)	1.374(6)
C(1)	B(1)	1.589(3)	C(13)	C(14)	1.378(5)
C(2)	C(3)	1.397(4)	C(19)	C(20)	1.421(3)
C(2)	C(15)	1.509(4)	C(19)	C(20)	1.421(3)
C(3)	C(4)	1.409(4)	C(19)	B(1)	1.583(5)
C(3)	C(16)	1.512(4)	C(20)	C(21)	1.398(3)
C(4)	C(5)	1.403(4)	C(20)	C(29)	1.504(4)
C(4)	C(7)	1.448(4)	C(21)	C(22)	1.404(3)
C(5)	C(6)	1.399(4)	C(21)	C(30)	1.509(4)
C(5)	C(17)	1.510(4)	C(22)	C(23)	1.449(5)

C(6)	C(18)	1.506(4)	C(23)	C(24)	1.162(5)
C(7)	C(8)	1.161(4)	C(24)	C(25)	1.459(5)
C(8)	C(9)	1.455(4)	C(25)	C(26)	1.388(4)
C(9)	C(10)	1.393(4)	C(25)	C(26)	1.388(4)
C(9)	C(14)	1.388(4)	C(26)	C(27)	1.383(4)
C(10)	C(11)	1.380(5)	C(27)	C(28)	1.366(5)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table S-5. Bond Angles (deg) of **1**

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(6)	118.9(2)	C(12)	C(13)	C(14)	120.4(4)
C(2)	C(1)	B(1)	120.5(2)	C(9)	C(14)	C(13)	120.4(3)
C(6)	C(1)	B(1)	120.7(2)	C(20)	C(19)	C(20)	118.9(3)
C(1)	C(2)	C(3)	120.5(2)	C(20)	C(19)	B(1)	120.5(1)
C(1)	C(2)	C(15)	121.4(2)	C(20)	C(19)	B(1)	120.5(1)
C(3)	C(2)	C(15)	118.0(2)	C(19)	C(20)	C(21)	120.5(2)
C(2)	C(3)	C(4)	119.5(2)	C(19)	C(20)	C(29)	120.9(2)
C(2)	C(3)	C(16)	120.4(3)	C(21)	C(20)	C(29)	118.5(2)
C(4)	C(3)	C(16)	120.2(3)	C(20)	C(21)	C(22)	119.4(2)
C(3)	C(4)	C(5)	121.0(2)	C(20)	C(21)	C(30)	120.4(3)
C(3)	C(4)	C(7)	119.6(2)	C(22)	C(21)	C(30)	120.2(2)
C(5)	C(4)	C(7)	119.4(2)	C(21)	C(22)	C(21)	121.3(3)
C(4)	C(5)	C(6)	119.4(2)	C(21)	C(22)	C(23)	119.4(1)
C(4)	C(5)	C(17)	120.0(3)	C(21)	C(22)	C(23)	119.4(1)
C(6)	C(5)	C(17)	120.6(3)	C(22)	C(23)	C(24)	180.00
C(1)	C(6)	C(5)	120.8(2)	C(23)	C(24)	C(25)	180.00
C(1)	C(6)	C(18)	121.0(2)	C(24)	C(25)	C(26)	120.5(2)
C(5)	C(6)	C(18)	118.1(2)	C(24)	C(25)	C(26)	120.5(2)
C(4)	C(7)	C(8)	179.7(3)	C(26)	C(25)	C(26)	118.9(4)
C(7)	C(8)	C(9)	179.4(3)	C(25)	C(26)	C(27)	119.8(3)
C(8)	C(9)	C(10)	120.3(3)	C(26)	C(27)	C(28)	121.2(4)
C(8)	C(9)	C(14)	121.1(3)	C(27)	C(28)	C(27)	119.1(4)
C(10)	C(9)	C(14)	118.6(3)	C(1)	B(1)	C(1)	119.6(3)
C(9)	C(10)	C(11)	120.6(3)	C(1)	B(1)	C(19)	120.2(1)
C(10)	C(11)	C(12)	119.9(3)	C(1)	B(1)	C(19)	120.2(1)
C(11)	C(12)	C(13)	120.1(3)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.