

Convenient Synthesis of Green Diisoindolodithienylpyrromethene-dialkynyl Borane Dyes

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Supporting Information (8 pages)

Experimental Section

General Methods. The 200, 400 (^1H), 50, 100 MHz (^{13}C) and 128 MHz (^{11}B) NMR spectra were recorded at room temperature using perdeuterated solvents as internal standards: ‰ (H) in ppm relative to residual protiated solvent; ‰ (C) in ppm relative to the solvent. A fast-atom bombardment ZAB-HF-VB-analytical apparatus in positive mode was used with a *m*-nitrobenzyl alcohol (*m*-NBA) as matrix. FT-IR spectra were recorded on the neat liquids or as thin films, prepared with a drop of dichloromethane, and evaporated to dryness on KBr pellets. Melting points were obtained on a capillary melting point apparatus in open-ended capillaries and are uncorrected. Chromatographic purification was conducted using 40-63 μm silica gel or aluminium oxide 90 standardized. Thin layer chromatography (TLC) was performed on silica gel or aluminium oxide plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio. The experimental procedures for each reaction were tested several times to optimally find the best conditions.

Materials. THF was dried over Na-benzophenone prior to distillation. $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ and $[\text{Pd}(\text{PPh}_3)_4]$ were prepared and purified according to the literature procedures. All anhydrous reactions were carried out under dry argon by using Schlenk tube techniques.

General Procedure Following Experimental Conditions 1. A solution of the **5** and the ethynyl derivate in benzene and triethylamine was argon degassed for 30 min. $\text{Pd}(\text{PPh}_3)_4$ was then added and the solution was stirred at 60°C for 6 h. The solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, brine, and dried over absorbent cotton. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel.

4-(4-iodophenyl)-2-methylbut-3-yn-2-ol (3): to a solution of 1,4-diiodobenzene (2.00 g, 6.06 mmol) in THF (10 mL) and diisopropylamine (6 mL) was added $\text{PdCl}_2(\text{PPh}_3)_2$ (255 mg, 0.36 mmol) and CuI (72 mg, 0.36 mmol). The solution was degassed with argon for 30 min. 2-methyl-3-butyn-2-ol (510 mg, 60.06 mmol) was then added dropwise and the solution was stirred overnight at room temperature. The solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, brine, and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane-petroleum ether (*v/v* 70/30) to dichloromethane to give 910 mg (52%) of **3** as a white solid; mp: 87 – 88°C; ^1H NMR (200 MHz, CDCl_3): δ 7.35 (AB, 4H, $^ABJ = 8.5$ Hz, $\nu\delta_{AB} = 99.5$ Hz), 2.66 (s, 1H), 1.59 (s, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 137.3, 133.1, 122.2, 95.2, 94.1, 81.1, 65.5, 31.3.

1-ethynyl-4-iodobenzene (4): to a solution of **3** (900 mg, 3.15 mmol) in THF (10 mL) was added potassium *tert*-butoxide (390 mg, 3.46 mmol). The solution was refluxed for 1 h and the solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, brine, and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina, eluting with dichloromethane-petroleum ether (*v/v* 5/95) 470 mg (66%) of **4** as a white solid; mp: 87 – 88°C; ^1H NMR (200 MHz, CDCl_3): δ 7.32 (AB, 4H, $^ABJ = 8.5$ Hz, $\nu\delta_{AB} = 98.4$ Hz), 3.16 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3): δ 137.3, 133.1, 121.5, 94.0, 82.1, 79.9.

Compound 5 : to a solution of **4** (199 mg, 0.87 mmol) in anhydrous THF (4 mL) was added dropwise EtMgBr (0.8 mL, 0.80 mmol, 1 M in THF) at room temperature. The solution was

stirred at 50 °C for 2 h. The mixture was then added at room temperature via a canula to a solution of **BOD** (200 mg, 0.36 mmol) in anhydrous THF (9 mL). The mixture was then stirred at 70 °C for 6 h. The solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water and dried over absorbent cotton. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane-petroleum ether (v/v 45/55) to give 268 mg (78%) of **5** as a green solid; mp: 243 – 244 °C; ¹H NMR (400 MHz, CDCl₃-CCl₄ (v/v 50/50)): δ 8.13 (d, 2H, ⁴J = 3.5 Hz), 7.72 (d, 2H, ³J = 8.5 Hz), 7.59 (s, 1H), 7.28 (d, 2H, ⁴J = 2.0 Hz), 7.12 (AB, 8H, ^{AB}J = 8.3 Hz, vδ_{AB} = 268.1 Hz), 7.04 (dd, 2H, ³J = 8.6 Hz, ⁴J = 2.0 Hz), 6.95 (dt, 2H, ³J = 3.5 Hz, ⁴J = 1.0 Hz), 3.88 (s, 6H), 2.94 (q, 4H, ³J = 7.5 Hz), 1.37 (t, 6H, ³J = 7.5 Hz); ¹³C NMR (100 MHz, CDCl₃-CCl₄ (v/v 50/50)): δ 158.2, 150.7, 143.0, 136.9, 133.3, 133.1, 132.3, 130.4, 128.6, 127.3, 125.8, 124.6, 120.4, 119.7, 112.8, 102.7, 97.6, 92.6, 55.5, 23.7, 15.9; ¹¹B NMR (128 MHz, CDCl₃-CCl₄ (v/v 50/50)): -7.72 (s); IR (KBr, cm⁻¹): 3058, 2964, 2931, 2832, 2181, 1626, 1596, 1556, 1486, 1437, 1386, 1230, 1197, 1112, 811; UV-Vis (CH₂Cl₂): λ nm (ε, M⁻¹ cm⁻¹) 266 (75000), 348 (23000), 377 (22000), 709 (84000); FAB⁺ m/z (nature of the peak, relative intensity) 989.1 ([M + H]⁺, 100), 957.1 ([M – OMe]⁺, 20); Anal. Calcd for C₄₇H₃₅BI₂N₂O₂S₂: C, 57.10; H, 3.57; N, 2.83. Found: C, 56.85; H, 3.25; N, 2.65.

2-methyl-4-{4-[2-(trimethylsilyl)ethynyl]phenyl}but-3-yn-2-ol (6): to a solution of 1,4-diiodobenzene (2.00 g, 6.06 mmol) in THF (10 mL) and diisopropylamine (6 mL) was added PdCl₂(PPh₃)₂ (510 mg, 0.72 mmol) and CuI (144 mg, 0.72 mmol). The solution was degassed with argon for 30 min. The trimethylsilylacetylene (601 mg, 6.06 mmol) was then added and, after 4 h, the 2-methyl-3-butyn-2-ol (1.01 g, 12.12 mmol) too. The solution was stirred overnight at room temperature. The solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, brine, and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane-petroleum ether (v/v 60/40) to dichloromethane to give 590 mg (39%) of **6** as a white solid; mp: 109 – 110 °C; ¹H NMR (200 MHz, CDCl₃): δ 7.36 (AB, 4H, ^{AB}J = 8.4 Hz, vδ_{AB} = 10.9 Hz), 2.09 (s, 1H), 1.60 (s, 6H), 0.24 (s, 9H); ¹³C NMR (50 MHz, CDCl₃): δ 131.8, 131.4, 123.0, 122.8, 104.5, 96.1, 95.6, 81.8, 65.6, 31.4, -0.1; IR (KBr, cm⁻¹): 2981, 2961, 2158, 1497, 1406, 1369, 120, 1162, 865, 842, 833; FAB⁺ m/z (nature of the peak,

relative intensity) 257.1 ($[M + H]^+$, 100), 183.1 ($[M - TMS]^+$, 20); Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 74.73; H, 7.64.

1-Ethynyl-4-(trimethylsilylethynyl)benzene (7): to a solution of **6** (580 mg, 2.26 mmol) in anhydrous toluene (10 mL) was added sodium hydroxide (100 mg, 2.49 mmol). The solution was refluxed for 30 min at 130 °C. The solvent was removed by rotary evaporation. The residue was treated with NH_4Cl and extracted with dichloromethane. The organic extracts were washed with water, and then brine, and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane-petroleum ether (v/v 8/92) to give 360 mg (80%) of **[2-(4-ethynylphenyl)ethynyl]trimethylsilane** as a white solid; mp: 57 – 58°C; 1H NMR (200 MHz, $CDCl_3$): δ 7.42 (s, 4H), 3.17 (s, 1H), 0.26 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 131.9, 131.8, 123.6, 122.1, 104.4, 96.5, 83.2, 79.0, -0.1.

Compound 8 : a solution of **5** (80 mg, 0.08 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 9.71×10^{-3} mmol) and CuI (2 mg, 9.71×10^{-3} mmol) in THF (14 mL) and $i\text{-}Pr_2NH$ (6 mL) was argon degassed for 30 min. Ethynyltrimethylsilane (24 mg, 0.24 mmol) was then added dropwise and the solution was stirred for 6 h. The solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, brine, and dried over absorbent cotton. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane-petroleum ether (v/v 40/60) to give 33 mg (94%) of **Bod bisphenylbisbipymethyl** as a green solid; to a solution of **7** (103 mg, 0.52 mmol) in anhydrous THF (3 mL) was added dropwise EtMgBr (0.4 mL, 0.44 mmol, 1 M in THF) at room temperature. The solution was stirred at 50 °C for 2 h. The mixture was then added at room temperature via a canula to a solution of **1** (100 mg, 0.18 mmol) in anhydrous THF (5 mL). The mixture was then stirred at 70 °C for 6 h. The solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water and dried over absorbent cotton. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane-petroleum ether (v/v 10/90) to dichloromethane-petroleum ether (v/v 40/60) to give 130 mg (80%) of **Bod bisphénylTMS** as a green solid; mp: 260 – 262°C; 1H NMR (400 MHz, $CDCl_3\text{-}CCl_4$ (v/v 50/50)): δ 8.21 (d, 2H, $^4J = 3.5$ Hz), 7.69 (d, 2H, $^3J = 8.5$ Hz), 7.61 (s, 1H), 7.29 (m, 2H), 7.11 (AB, 8H, $^{AB}J = 8.5$ Hz, $v\delta_{AB} = 90.4$ Hz), 6.98 (m,

4H), 3.86 (s, 6H), 2.96 (q, 4H, $^3J = 7.5$ Hz), 1.39 (t, 6H, $^3J = 7.5$ Hz), 0.22 (s, 18H); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): δ 158.1, 150.7, 143.0, 133.2, 132.3, 132.0, 131.9, 131.4, 130.4, 128.6, 127.3, 125.5, 124.7, 131.6, 120.3, 119.7, 112.9, 105.4, 102.7, 98.3, 95.2, 83.4, 79.1, 55.5, 23.7, 15.9, 0.2; ^{11}B NMR (128 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): -7.46 (s); IR (KBr, cm^{-1}): 3072, 2964, 2932, 2834, 2210, 2155, 1626, 1597, 1557, 1488, 1436, 1387, 1249, 1200, 1112, 862, 839, 811; UV-Vis (CH_2Cl_2): λ nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 283 (91000), 300 (116000), 348 (21000), 386 (19000), 643 (sh, 22000), 708 (81000); FAB^+ m/z (nature of the peak, relative intensity) 929.1 ($[\text{M} + \text{H}]^+$, 100), 855.2 ($[\text{M} - \text{Si}(\text{Me})_3]^+$, 25); Anal. Calcd for $\text{C}_{57}\text{H}_{53}\text{BN}_2\text{O}_2\text{S}_2\text{Si}_2$: C, 73.68; H, 5.75; N, 3.01. Found: C, 73.44; H, 5.49; N, 2.75.

Compound 9 : prepared following exptl conditions 1; from **5** (35 mg, 0.04 mmol), 4'-ethynyl-2,2',6',2''-terpyridine (20 mg, 0.08 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5 mg, 4.25×10^{-3} mmol), benzene (8 mL) and Et_3N (3 mL); chromatography on alumina, eluting with dichloromethane-petroleum ether (v/v 60/40) to give 42 mg (95%) of **9** as a green solid; mp: 171°C (dec); ^1H NMR (400 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 8.66 (dt, 4H, $^3J = 4.0$ Hz, $^4J = 1.0$ Hz), 8.59 (d, 4H, $^3J = 8.0$ Hz), 8.56 (s, 4H), 8.21 (d, 2H, $^4J = 3.5$ Hz), 7.82 (td, 4H, $^3J = 8.0$ Hz, $^4J = 2.0$ Hz), 7.74 (d, 2H, $^3J = 9.0$ Hz), 7.61 (s, 1H), 7.31-7.28 (m, 6H), 7.23 (AB, 8H, $^{AB}J = 8.3$ Hz, $v\delta_{AB} = 108.3$ Hz), 7.05 (d, 1H, $^4J = 2.0$ Hz), 7.03 (m, 3H), 3.89 (s, 6H), 2.99 (q, 4H, $^3J = 7.4$ Hz), 1.42 (t, 6H, $^3J = 7.4$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 158.3, 155.9, 155.5, 150.7, 149.2, 143.1, 136.6, 133.4, 133.3, 132.4, 131.7, 131.4, 130.4, 128.7, 127.4, 126.1, 124.8, 123.8, 123.1, 121.1, 121.0, 120.4, 119.7, 112.9, 102.7, 98.4, 96.7, 96.4, 93.9, 89.0, 55.5, 23.8, 16.0; ^{11}B NMR (128 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): -7.40 (s); UV-Vis (CH_2Cl_2): λ nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 232 (117000), 284 (104000), 297 (101000), 320 (124000), 335 (130000), 640 (sh, 22000), 709 (86000); FAB^+ m/z (nature of the peak, relative intensity) 1247.2 ($[\text{M} + \text{H}]^+$, 100); Anal. Calcd for $\text{C}_{81}\text{H}_{55}\text{BN}_8\text{O}_2\text{S}_2$: C, 78.00; H, 4.44; N, 8.98. Found: C, 77.75; H, 4.23; N, 8.79.

Compound 10 : prepared following exptl conditions 1; from **5** (50 mg, 0.05 mmol), 5-ethynyl-2,2'-bipyridine (20 mg, 0.11 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 6.07×10^{-3} mmol), benzene (10 mL) and Et_3N (4 mL); chromatography on silica gel, eluting with dichloromethane to dichloromethane-methyl alcohol (v/v 99.5/0.5) to give 37 mg (72%) of **10** as a green solid; mp: 149°C (dec); ^1H NMR (400 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 8.74 (m, 2H), 8.66 (m, 2H), 8.43 (m, 4H), 8.20 (d, 2H, $^3J = 3.5$ Hz), 7.88 (dd, 2H, $^3J = 7.8$ Hz, $^4J = 2.4$ Hz), 7.81 (td, 2H,

$^3J = 8.0$ Hz, $^4J = 2.2$ Hz), 7.77 (d, 2H, $^3J = 8.8$ Hz), 7.63 (s, 1H), 7.34-7.27 (m, 7H), 7.11-7.05 (m, 6H), 7.00 (d, 2H, $^3J = 3.9$ Hz), 3.90 (s, 6H), 2.97 (q, 4H, $^3J = 7.4$ Hz), 1.41 (t, 6H, $^3J = 7.4$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 158.3, 151.6, 150.8, 149.2, 143.1, 139.2, 136.9, 133.3, 132.4, 131.6, 131.1, 130.4, 128.7, 127.3, 125.9, 124.7, 123.9, 121.5, 121.1, 120.4, 119.7, 112.8, 102.8, 93.8, 87.7, 55.6, 23.7, 15.9; ^{11}B NMR (128 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): -4.57 (s); IR (KBr, cm^{-1}): 3048, 2966, 2933, 2833, 2213, 2178, 1626, 1597, 1556, 1507, 1488, 1457, 1387, 1231, 1200, 1112, 836, 812; UV-Vis (CH_2Cl_2): λ nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 266 (75000), 348 (23000), 377 (22000), 640 (sh, 21000), 709 (84000); FAB^+ m/z (nature of the peak, relative intensity) 1093.2 ($[\text{M} + \text{H}]^+$, 100), 1061.1 ($[\text{M} - \text{OMe}]^+$, <5); Anal. Calcd for $\text{C}_{71}\text{H}_{49}\text{BN}_6\text{O}_2\text{S}_2$: C, 78.01; H, 4.52; N, 7.69. Found: C, 77.62; H, 4.25; N, 7.40.

Compound 11 : prepared following exptl conditions 1; from **5** (30 mg, 0.03 mmol), 6-ethynyl-5,5'-dimethyl-2,2'-bipyridine (14 mg, 0.07 mmol), $\text{Pd}(\text{PPh}_3)_4$ (4 mg, 3.64×10^{-3} mmol), benzene (8 mL) and Et_3N (3 mL); chromatography on silica gel, eluting with dichloromethane to dichloromethane-methyl alcohol (v/v 99.8/0.2) to give 33 mg (94%) of **11** as a green solid; mp: 181°C (dec); ^1H NMR (400 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 8.47 (m, 2H), 8.39 (d, 2H, $^3J = 8.0$ Hz), 8.26 (d, 2H, $^3J = 8.0$ Hz), 8.23 (d, 2H, $^3J = 3.5$ Hz), 7.79 (d, 2H, $^3J = 9.0$ Hz), 7.65 (s, 1H), 7.64 (d, 2H, $^3J = 7.5$ Hz), 7.60 (d, 2H, $^3J = 8.0$ Hz), 7.35 (d, 2H, $^4J = 2.0$ Hz), 7.26 (AB, 8H, $^{AB}J = 8.0$ Hz, $\nu\delta_{\text{AB}} = 131.7$ Hz), 7.10 (d, 2H, $^3J = 9.0$ Hz), 7.02 (d, 2H, $^3J = 3.5$ Hz), 3.92 (s, 6H), 3.00 (q, 4H, $^3J = 7.4$ Hz), 2.56 (s, 6H), 2.42 (s, 6H), 1.41 (t, 6H, $^3J = 7.4$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 158.3, 154.4, 153.3, 150.8, 149.4, 143.1, 142.4, 137.8, 137.3, 135.6, 133.3, 133.1, 132.4, 121.6, 121.4, 130.39, 130.36, 128.6, 127.3, 125.9, 124.7, 121.2, 120.9, 120.4, 120.1, 119.8, 112.8, 102.8, 98.4, 92.8, 89.2, 55.6, 23.7, 19.5, 18.5, 15.9; ^{11}B NMR (128 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): -8.01 (s); IR (KBr, cm^{-1}): 3037, 3000, 2967, 2933, 2834, 2212, 2180, 1626, 1597, 1554, 1488, 1438, 1387, 1230, 1200, 1111, 829, 811; UV-Vis (CH_2Cl_2): λ nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 231 (65000), 246 (64000), 297 (91000), 342 (95000), 638 (sh, 19000), 708 (81000); FAB^+ m/z (nature of the peak, relative intensity) 1149.2 ($[\text{M} + \text{H}]^+$, 100), 1117.3 ($[\text{M} - \text{OMe}]^+$, 20); Anal. Calcd for $\text{C}_{75}\text{H}_{57}\text{BN}_6\text{O}_2\text{S}_2$: C, 78.38; H, 5.00; N, 7.31. Found: C, 78.23; H, 4.62; N, 6.92.

Compound 12 : prepared following exptl conditions 1; from **5** (30 mg, 0.03 mmol), 4-ethynylpyrene (17 mg, 0.07 mmol), $\text{Pd}(\text{PPh}_3)_4$ (4 mg, 3.64×10^{-3} mmol), benzene (8 mL) and Et_3N (3 mL); chromatography on silica gel, eluting with dichloromethane-petroleum ether

(v/v 15/85) to dichloromethane-petroleum ether (v/v 50/50) to give 35 mg (97%) of **17** as a green solid; mp: 173°C (dec); ^1H NMR (400 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 8.63 (d, 2H, $^3J = 7.8$ Hz), 8.29-8.00 (m, 19H), 7.78-7.34 (m, 8H), 7.18-7.07 (m, 8H), 3.93 (s, 6H), 3.05 (q, 4H, $^3J = 7.4$ Hz), 1.47 (t, 6H, $^3J = 7.4$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 158.3, 150.8, 143.1, 133.3, 132.4, 132.0, 131.7, 131.5, 131.4, 131.3, 131.1, 130.5, 129.7, 128.7, 128.4, 128.2, 127.4, 126.3, 125.8, 125.7, 125.6, 125.4, 124.8, 124.7, 124.60, 124.58, 122.1, 120.4, 119.8, 118.1, 102.8, 98.5, 95.5, 93.5, 90.0, 55.6, 23.8, 16.0; ^{11}B NMR (128 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): -3.24 (s); IR (KBr, cm^{-1}): 3041, 2967, 2933, 2834, 2204, 2181, 1626, 1595, 1557, 1512, 1488, 1435, 1386, 1230, 1198, 1110, 845, 811; UV-Vis (CH_2Cl_2): λ nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 237 (150000), 309 (115000), 376 (133000), 399 (135000), 640 (sh, 21000), 708 (83000); FAB $^+$ m/z (nature of the peak, relative intensity) 1185.2 ($[\text{M} + \text{H}]^+$, 100), 1153.2 ($[\text{M} - \text{OMe}]^+$, 20); Anal. Calcd for $\text{C}_{83}\text{H}_{53}\text{BN}_2\text{O}_2\text{S}_2$: C, 84.11; H, 4.51; N, 2.36. Found: C, 83.87; H, 4.27; N, 2.02.

Compound 13 : prepared following exptl conditions 1; from **5** (30 mg, 0.03 mmol), 4-ethynylpyrene (20 mg, 0.07 mmol), $\text{Pd}(\text{PPh}_3)_4$ (4 mg, 3.64×10^{-3} mmol), benzene (8 mL) and Et_3N (3 mL); chromatography on silica gel, eluting with dichloromethane-petroleum ether (v/v 15/85) to dichloromethane-petroleum ether (v/v 50/50) to give 35 mg (95%) of **18** as a yellow/green solid; mp: > 350°C; ^1H NMR (400 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 8.26-8.21 (m, 6H), 8.18 (t, 4H, $^3J = 6.5$ Hz), 8.13 (d, 2H, $^3J = 8.0$ Hz), 7.78 (d, 2H, $^3J = 8.5$ Hz), 7.69 (d, 2H, $^3J = 7.5$ Hz), 7.67 (dd, 4H, $^3J = 8.0$ Hz, $^4J = 3.0$ Hz), 7.63 (s, 1H), 7.57 (t, 2H, $^3J = 8.0$ Hz), 7.47 (td, 4H, $^3J = 7.5$ Hz, $^4J = 2.0$ Hz), 7.35 (d, 2H, $^4J = 2.0$ Hz), 7.26 (AB, 8H, $^ABJ = 8.5$ Hz, $v\delta_{AB} = 126.1$ Hz), 7.09 (m, 2H), 7.03 (d, 2H, $^3J = 4.0$ Hz), 3.91 (s, 6H), 3.00 (q, 4H, $^3J = 7.4$ Hz), 1.43 (t, 6H, $^3J = 7.4$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): 158.3, 150.8, 143.1, 134.84, 134.77, 133.3, 132.4, 132.0, 131.69, 131.66, 131.3, 131.1, 131.0, 130.4, 128.8, 128.74, 128.66, 128.4, 128.1, 127.4, 127.3, 126.8, 126.7, 126.4, 125.4, 124.8, 122.0, 121.0, 120.8, 120.6, 120.5, 120.4, 119.7, 112.8, 102.8, 98.5, 89.5, 85.7, 55.6, 23.8, 16.0; ^{11}B NMR (128 MHz, $\text{CDCl}_3\text{-CCl}_4$ (v/v 50/50)): -4.57 (s); IR (KBr, cm^{-1}): 3049, 1963, 2926, 2829, 2179, 2203, 1627, 1595, 1552, 1488, 1436, 1387, 1230, 1110, 834, 809; UV-Vis (CH_2Cl_2): λ nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 228 (106000), 259 (118000), 280 (85000), 345 (68000), 445 (102000), 474 (122000), 640 (sh, 21000), 708 (84000); FAB $^+$ m/z (nature of the peak, relative intensity) 1285.2 ($[\text{M} + \text{H}]^+$, 100), 1253.2 ($[\text{M} - \text{OMe}]^+$, 10); Anal. Calcd for $\text{C}_{91}\text{H}_{57}\text{BN}_2\text{O}_2\text{S}_2$: C, 85.03; H, 4.47; N, 2.18. Found: C, 84.72; H, 4.13; N, 1.88.

Compound 14 : prepared following exptl conditions 1; from **5** (80 mg, 0.08 mmol), 6-ethynyl-5,5'-dimethyl-2,2'-bipyridine (20 mg, 0.09 mmol), 4-ethynylpyrene (19 mg, 0.09 mmol), Pd(PPh₃)₄ (11 mg, 9.71 x 10⁻³ mmol), benzene (8 mL) and Et₃N (4 mL); chromatography on silica gel, eluting with dichloromethane-petroleum ether (v/v 30/70) to dichloromethane to give 40 mg (43%) of **14** as a green solid; mp: 164°C (dec); ¹H NMR (400 MHz, CDCl₃-CCl₄ (v/v 50/50)): 8.58 (d, 1H, ³J = 9.0 Hz), 8.44 (s, 1H), 8.37 (d, 1H, ³J = 8.0 Hz), 8.27 (d, 2H, ³J = 3.5 Hz), 8.24 (d, 1H, ³J = 8.0 Hz), 8.17-7.97 (m, 8H), 7.67 (d, 2H, ³J = 8.0 Hz), 7.60 (d, 1H, ³J = 8.0 Hz), 7.57 (m, 2H), 7.50 (d, 2H, ³J = 8.4 Hz), 7.43 (d, 2H, ³J = 8.4 Hz), 7.29 (d, 2H, ⁴J = 1.5 Hz), 7.17 (d, 2H, ³J = 8.0 Hz), 7.12 (d, 2H, ³J = 8.0 Hz), 7.05 (d, 2H, ³J = 3.5 Hz), 6.99 (dd, 2H, ³J = 8.8 Hz, ⁴J = 1.5 Hz), 3.87 (s, 6H), 3.01 (q, 4H, ³J = 7.4 Hz), 2.53 (s, 3H), 2.38 (s, 3H), 1.44 (t, 6H, ³J = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃-CCl₄ (v/v 50/50)): 158.1, 154.2, 153.2, 150.7, 149.3, 143.0, 142.4, 137.8, 137.3, 135.7, 133.2, 133.1, 132.3, 132.0, 131.6, 131.5, 131.4, 131.3, 131.21, 131.15, 130.4, 129.6, 128.6, 128.4, 128.2, 127.4, 127.3, 126.2, 125.9, 125.7, 125.6, 125.3, 124.73, 124.65, 124.54, 124.51, 122.1, 121.2, 120.9, 120.3, 120.1, 119.8, 118.0, 112.9, 110.8, 102.8, 102.6, 98.5, 98.4, 95.4, 92.8, 90.1, 89.2, 55.5, 23.8, 19.5, 18.5, 16.0; ¹¹B NMR (128 MHz, CDCl₃-CCl₄ (v/v 50/50)): -6.15 (s); IR (KBr, cm⁻¹): 3038, 2966, 2932, 2830, 2210, 2182, 1625, 1596, 1556, 1488, 1437, 1386, 1230, 1198, 1111, 836, 811; UV-Vis (CH₂Cl₂): λ nm (ε, M⁻¹ cm⁻¹) 237 (97000), 296 (85000), 308 (95000), 344 (76000), 376 (76000), 398 (71000), 640 (sh, 20000), 708 (80000); FAB⁺ m/z (nature of the peak, relative intensity) 1167.2 ([M + H]⁺, 100), 1103.2 ([M - 2OMe]²⁺, 15); Anal. Calcd for C₇₉H₅₅BN₄O₂S₂: C, 81.29; H, 4.75; N, 4.80. Found: C, 81.00; H, 4.52; N, 4.61.