Synthesis of 4,4'-Bisaryl-2,2'-bisbenzoimidazoles as Building Blocks for Supramolecular Structures

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SUPPORTING INFORMATION

General. Unless otherwise noted, all reactions were performed under nitrogen. Anhydrous THF was supplied from an Mbraun solvent purification system. $\text{Pd}(\text{PPh}_3)_4$ was prepared by using the reported protocol.¹ Anhydrous ZnCl_2 was intensively dried by heating under vacuum, followed by cooling to room temperature under nitrogen. Bromobenzene and 4-bromoanisole were purified by distillation. 2,6-Dimethyl-4-methoxybromobenzene was synthesized from 1-methoxy-3,5-dimethylbenzene and purified by distillation. 1-bromo-2,7-dimethylnaphthalene was synthesized from 2,7-dimethylnaphthalene. 1-[2-(benzyloxy)ethoxy]-4-bromobenzene and 4-[4-(benzyloxy)butyloxy]-3,5-dimethyl-1-bromobenzene were synthesized from 4-bromophenol or 4-bromo-2,6-dimethylphenol, respectively, purified by silica gel column chromatography and dried by azeotropic distillation with toluene. 2-bromo-5-(2,6-dimethyl-4-methoxyphenyl)pyridine and 5-bromo-2-(2,6-dimethyl-4-methoxyphenyl)pyridine were synthesized from 2-bromo-5-iodopyridine or 2,5-dibromopyridine through Negishi coupling reactions. Other commercially available reagents and solvents were used as received without further purification.

Analytical thin-layer chromatography was performed with Macherey–Nagel POLYGRAM SIL N-HR/UV₂₅₄ or ALOX N/UV₂₅₄. Flash silica gel column chromatography was performed with Merck silica gel 60 (particle size 0.040–0.063 mm). Flash alumina column chromatography was performed with deactivated (5% water) Fluka alumina (particle size 0.05–0.15 mm, pH 7.0±0.5). Melting points were recorded on a Tecon Series 150 melting point apparatus. Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz or on a Bruker Avance 600 at 600 MHz. Chemical shifts are reported relative to Me_4Si (δ 0.00), except in the case of product **5g**, for which chemical shifts are reported relative to CHCl_3 (7.26). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); m (multiplet); br (broad). Carbon nuclear magnetic resonance (¹³C-NMR) spectra were recorded on a Bruker ARX 300 at 75 MHz. Chemical shifts are reported relative to CDCl_3 (δ 77.2) or $\text{DMSO}-d_6$ (δ 39.5). Infrared spectra were recorded on a Perkin Elmer Spectrum One (PE) using KBr pellets.

Experimental Procedures.

¹ Coulson, D. R. *Inorg. Synth.* **1972**, 13, 121.

2-bromo-4-methyl-6-nitroaniline: 4-methyl-2-nitroaniline (40.2 g, 264 mmol) in glacial acetic acid (400 mL) was heated at 50 °C in an oil bath until a clear orange solution was formed. The bath was removed, and bromine (14.5 mL, 45.1 g, 282 mmol) was added slowly. An exothermic reaction took place, and an orange precipitate was obtained. The suspension was stirred for 30 min, and then poured into water at 0 °C. The solid was collected, washed with water and dried in vacuo to give 2-bromo-4-methyl-6-nitroaniline (59.9 g, 98%) as an orange solid, *R*_f 0.50 (silica gel, hexane/CH₂Cl₂ = 5/5); mp 68.6–68.9 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.94 (s, 1H), 7.55 (s, 1H), 6.46 (br s, 2H), 2.27 (s, 3H); ¹³C NMR (75 MHz, CDCl₃, δ) 140.3, 140.1, 132.8, 126.6, 125.6, 112.0, 20.0; IR (KBr) 3485, 3370, 1633, 1577, 1509, 1346, 1327, 1258, 1237, 1204, 1088, 936, 763 cm⁻¹; LRMS (CI) *m/z* = 231 (M+H⁺); Anal. Calcd for C₇H₇BrN₂O₂: C, 36.39; H, 3.05; N, 12.12. Found: C, 36.36; H, 3.41; N, 12.40.

3,4-diamino-5-bromotoluene (3): To a solution of 2-bromo-4-methyl-6-nitroaniline (14.5 g, 62.6 mmol) in EtOH (80 mL) and concentrated HCl (20 mL) was added SnCl₂·H₂O (70.4 g, 312 mmol). After stirring for 4 h at 60 °C under N₂, water was added and the mixture was poured into 2 M aqueous NaOH at 0 °C. CH₂Cl₂ was added and a white solid was removed by filtration. The layers were separated, and the aqueous phase was extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated to give a residue, which was purified by alumina column chromatography (hexane/EtOAc = 9/1 → 5/5) to afford 3,4-diamino-5-bromotoluene (**3**) (10.5 g, 83%) as white needles, *R*_f 0.40 (alumina, CH₂Cl₂); mp. 74.9–75.1 °C; ¹H NMR (300 MHz, CDCl₃, δ) 6.78 (s, 1H), 6.43 (s, 1H), 3.53 (br s, 4H), 2.17 (s, 3H); ¹³C NMR (75 MHz, CDCl₃, δ) 135.8, 130.6, 130.4, 123.7, 116.6, 111.6, 20.6; IR (KBr) 3385, 3306, 2915, 1622, 1571, 1493, 1296, 825, 753 cm⁻¹; LRMS (CI) *m/z* = 201 (M+H⁺); Anal. Calcd for C₇H₉BrN₂: C, 41.82; H, 4.51; N, 13.93. Found: C, 41.62; H, 4.60; N, 13.91.

4,4'-dibromo-6,6'-dimethyl-2,2'-bisbenzimidazole (4): To a solution of 3,4-diamino-5-bromotoluene (**3**) (10.5 g, 52.2 mmol) in MeOH (100 mL) was added methyl 2,2,2-trichloroacetimidate (3.20 mL, 4.58 g, 26.0 mmol), followed by concentrated HCl (0.10 mL) at 0 °C under N₂, and the obtained mixture was stirred at room temperature. To this mixture were added three portions of K₂CO₃ (1.81 g, 13.1 mmol; 3.65 g, 26.4 mmol; 3.61 g, 26.2 mmol) at intervals of 3 h, 3 h and 15 h. The reaction mixture was stirred another 15 h after the final addition, and water and Et₂O were added. The resulting precipitate was collected, washed with water and Et₂O, and dried in vacuo to give crude 4,4'-dibromo-6,6'-dimethyl-2,2'-bisbenzimidazole (**4**) (10.5 g) as an orange solid which was directly used for the next step, ¹H NMR (300 MHz, DMSO-*d*₆, δ) 13.7 (br s, 2H), 7.36 (s, 4H), 2.45 (s, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆, δ) 146.2, 140.5, 138.2, 133.3, 125.7, 112.4, 110.7, 20.9; IR (KBr) 2920, 2856, 2745, 1623, 1568, 1435, 1390, 1330, 951, 856, 835 cm⁻¹; LRMS (ESI) *m/z* = 441 (M+Na⁺).

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-dibromo-6,6'-dimethyl-2,2'-bisbenzimidazole (1**):** To a solution of the crude material prepared above in THF (100 mL), NaH (3.50 g, 55–65% purity, 80–94 mmol) was added portion wise at 0 °C, and the resulting mixture was stirred for 15 min at room temperature. $(\text{Boc})_2\text{O}$ (18.5 g, 84.5 mmol) in THF (10 mL) was added at 0 °C and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was concentrated in vacuo, water was added, and the mixture was extracted with Et_2O . The combined extracts were washed with water and brine, dried over Na_2SO_4 , and concentrated in vacuo. The crude product was subjected to alumina column chromatography (hexane/ CH_2Cl_2 = 9/1 $\rightarrow$ 5/5) to afford a white solid. This solid was recrystallized from hexane/ CH_2Cl_2 to give 1,1'-bis(*t*-butoxycarbonyl)-4,4'-dibromo-6,6'-dimethyl-2,2'-bisbenzimidazole (**1**) (13.6 g, 84% for 2 steps) as a white powder, R_f 0.51 (alumina, hexane/ CH_2Cl_2 = 3/7); mp. >350 °C; ^1H NMR (300 MHz, CDCl_3 , δ) 7.89 (s, 2H), 7.45 (s, 2H), 2.52 (s, 6H), 1.28 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ) 147.4, 143.5, 139.5, 138.0, 133.4, 129.4, 114.3, 113.8, 86.4, 27.8, 22.0; IR (KBr) 2982, 2930, 1751, 1609, 1405, 1370, 1348, 1287, 1138, 854 cm^{-1} ; LRMS (ESI) m/z = 641 ($\text{M}+\text{Na}^+$); Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{Br}_2\text{N}_4\text{O}_4$: C, 50.34; H, 4.55; N, 9.03. Found: C, 50.17; H, 4.54; N, 8.72.

^1H - and ^{13}C -NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(4-methoxyphenyl)-6,6'-dimethyl-2,2'-bisbenzimidazole (5a**):** **Method A** (Table 1, entries 4, 6). To a solution of 4-bromoanisole (594 mg, 3.18 mmol) in anhydrous THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol) at -78°C . The mixture was stirred at the same temperature for 5 min, and a solution of anhydrous ZnCl₂ (443 mg, 3.26 mmol) in anhydrous THF (5 mL) was added. After warming to 0°C , 1,1'-bis(*t*-butoxycarbonyl)-4,4'-dibromo-6,6'-dimethyl-2,2'-bisbenzimidazole (**1**) (439 mg, 0.708 mmol) in anhydrous THF (5 mL) and Pd(PPh₃)₄ (82.0 mg, 0.0709 mmol) in anhydrous THF (5 mL) were added. The solution was heated at 60°C for 6 h and cooled down to room temperature. Water, 2M aqueous HCl and CH₂Cl₂ were added, and the two-phase mixture was stirred for 30 min at room temperature. The mixture was basified to ca. pH 8 by adding 2 M aqueous NaOH and saturated aqueous NaHCO₃. Saturated aqueous ethylenediaminetetraacetic acid (EDTA) was added, and the mixture was stirred for 30 min at room temperature. The phases were separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. Purification by alumina column chromatography (hexane/CH₂Cl₂ = 9/1 → 6/4) afforded 1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(4-methoxyphenyl)-6,6'-dimethyl-2,2'-bisbenzimidazole (**5a**) (332 mg, 70%) as a white solid. **Method B** (Table 1, entry 5). Compound **5a** (335 mg, 76%) was obtained as described above but using 4-bromoanisole (309 mg, 1.65 mmol), *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.6 mmol), ZnCl₂ (444 mg, 3.26 mmol), dibromide **1** (404 mg, 0.652 mmol), and Pd(PPh₃)₄ (73.2

mg, 0.0633 mmol). Rf 0.70 (alumina, hexane/ CH₂Cl₂ = 3/7); mp. 194.3–194.7 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.90 (s, 2H), 7.87 (d, 4H, *J* = 8.8 Hz), 7.31 (s, 2H), 7.00 (d, 4H, *J* = 8.8 Hz), 3.81 (s, 6H), 2.56 (s, 6H), 1.25 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 159.4, 148.0, 143.3, 138.4, 136.4, 133.8, 133.0, 130.5, 125.4, 114.2, 113.4, 85.5, 55.4, 27.8, 22.3; IR (KBr) 3441, 2980, 2933, 2835, 1746, 1609, 1517, 1368, 1355, 1296, 1250, 1139, 828 cm⁻¹; HRMS (ESI) Calcd for C₄₀H₄₂N₄NaO₆ (M+Na⁺) 697.3002, found 697.3001; Anal. Calcd for C₄₀H₄₂N₄O₆: C, 71.20; H, 6.27; N, 8.30. Found: C, 70.47; H, 6.09; N, 8.12.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(2,6-dimethyl-4-methoxyphenyl)-6,6'-dimethyl-2,2'-bisbenzimidazole (5b**):** Method A (Table 1, entry 7). Compound **5b** (360 mg, 70%) was obtained as a white powder as described above but using 1-bromo-2,6-dimethyl-4-methoxybenzene (688 mg, 3.20 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl_2 (432 mg, 3.18 mmol), dibromide **1** (438 mg, 0.706 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (82.8 mg, 0.0716 mmol). **Nolan Conditions** (Table 1, entry 10). To a solution of 1-bromo-2,6-dimethyl-4-methoxybenzene (690 mg, 3.21 mmol) in anhydrous THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol) at -78°C . The mixture was stirred at the same temperature for 5 min, and a solution of anhydrous ZnCl_2 (439 mg, 3.22 mmol) in anhydrous THF (5 mL) was added. After warming to 0°C , $\text{Pd}(\text{OAc})_2$ (16 mg, 0.071 mmol) and Nolan Catalyst (32 mg, 0.075 mmol) in anhydrous THF (5 mL) were added. The mixture was stirred at 0°C for 15 min, and dibromide **1** (439 mg, 0.708 mmol) in anhydrous THF (5 mL) was added. The solution was heated to 60°C for 18 h and cooled to room temperature. After cooling, the reaction mixture was poured into a mixture of water, 2M aqueous HCl and CH_2Cl_2 . The two-phase mixture was stirred for 30 min at room temperature. The mixture was basified to ca. pH 8 by adding 3M aqueous NaOH and saturated aqueous NaHCO_3 . Saturated aqueous ethylenediaminetetraacetic acid (EDTA) was added, and the mixture was stirred for 30 min at room temperature. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 . The combined organic

extracts were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. Purification by alumina column chromatography (hexane/CH₂Cl₂ = 9/1 → 5/5) afforded 1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(2,6-dimethyl-4-methoxyphenyl)-6,6'-dimethyl-2,2'-bisbenzimidazole (**5b**) (341 mg, 66%) as a white solid. R_f 0.54 (alumina, hexane/CH₂Cl₂ = 5/5); mp. 154.0–154.8 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.93 (s, 2H), 6.99 (s, 2H), 6.67 (s, 4H), 3.79 (s, 6H), 2.54 (s, 6H), 2.01 (s, 12H), 1.27 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 158.9, 147.9, 143.4, 139.5, 138.0, 136.3, 133.2, 133.0, 130.1, 127.8, 113.7, 113.1, 85.2, 55.2, 27.8, 22.2, 21.3; IR (KBr) 3440, 2978, 2921, 1746, 1608, 1478, 1399, 1355, 1313, 1293, 1165, 1147, 1073, 852 cm⁻¹; LRMS (ESI) m/z = 753.4 (M+Na⁺); Anal. Calcd for C₄₄H₅₀N₄O₆: C, 72.31; H, 6.90; N, 7.67. Found: C, 72.27; H, 6.94; N, 7.63.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-diphenyl-6,6'-dimethyl-2,2'-bisbenzimidazole (5c**): Method A** (Table 2, entry 1a). Compound **5c** (264 mg, 60%) was obtained as a white powder as described above but using bromobenzene (509 mg, 3.24 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl₂ (434 mg, 3.19 mmol), dibromide **1** (443 mg, 0.715 mmol), and Pd(PPh₃)₄ (79.9 mg, 0.0691 mmol). **Method B** (Table 2, entry 1b). Compound **5c** (238 mg, 60%) was obtained as described above but using bromobenzene (251 mg, 1.60 mmol), *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.6 mmol), ZnCl₂ (436 mg, 3.21 mmol), dibromide **1** (400 mg, 0.645 mmol), and Pd(PPh₃)₄ (76.5 mg, 0.0645 mmol). R_f 0.53 (alumina, hexane/CH₂Cl₂ = 7/3); mp. 344.7–345.5 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.95 (s, 2H), 7.89 (d, 4H, *J* = 7.3 Hz), 7.45 (dd, 4H, *J*₁ = *J*₂ = 7.3 Hz), 7.37–7.29 (m, 4H), 2.57 (s, 6H), 1.26 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 148.0, 143.5, 138.6, 138.1, 136.5, 133.8, 133.5, 129.5, 128.7, 127.7, 126.0, 114.0, 85.6, 27.8, 22.3; IR (KBr) 3440, 2978, 2929, 1741, 1607, 1480, 1358, 1295, 1133, 1064, 852, 696 cm⁻¹; LRMS (ESI) *m/z* = 637 (M+Na⁺); Anal. Calcd for C₃₈H₃₈N₄O₄: C, 74.24; H, 6.23; N, 9.11. Found: C, 74.20; H, 6.04; N, 8.86.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(2-methylphenyl)-6,6'-dimethyl-2,2'-bisbenzimidazole

(5d): Method A (Table 2, entry 2a). Compound **5d** (343 mg, 75%) was obtained as a white powder as described above but using 2-bromotoluene (546 mg, 3.19 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl₂ (439 mg, 3.23 mmol), dibromide **1** (440 mg, 0.710 mmol), and Pd(PPh₃)₄ (84.4 mg, 0.0730 mmol). **Method B** (Table 2, entry 2b). Compound **5d** (171 mg, 41%) was obtained as described above but using 2-bromobenzene (275 mg, 1.61 mmol), *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.6 mmol), ZnCl₂ (441 mg, 3.24 mmol), dibromide **1** (400 mg, 0.645 mmol), and Pd(PPh₃)₄ (73.7 mg, 0.0638 mmol). R_f 0.71 (alumina, hexane/CH₂Cl₂ = 5/5); mp. 125.2–126.4 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.94 (s, 2H), 7.28–7.21 (m, 8H), 7.08 (s, 2H), 2.54 (s, 6H), 2.20 (s, 6H), 1.24 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 147.9, 143.4, 139.1, 138.1, 136.6, 136.2, 134.3, 133.1, 130.4₃, 130.3₆, 127.9, 127.4, 125.7, 113.9, 85.4, 27.8, 22.2, 20.8; IR (KBr) 3473, 3020, 2978, 2925, 2869, 1746, 1609, 1480, 1457, 1399, 1357, 1297, 1248, 1136, 1111, 847, 755 cm⁻¹; LRMS (ESI) *m/z* = 655 (M+Na⁺); Anal. Calcd for C₄₀H₄₂N₄O₄: C, 74.74; H, 6.59; N, 8.72. Found: C, 74.53; H, 6.54; N, 8.43.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(4-trifluoromethylphenyl)-6,6'-dimethyl-2,2'-

bisbenzimidazole (5e): Method A (Table 2, entry 3a). Compound **5e** (302 mg, 57%) was obtained as a white powder as described above but using 1-bromo-4-trifluoromethylbenzene (720 mg, 3.20 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl₂ (433 mg, 3.18 mmol), dibromide **1** (438 mg, 0.706 mmol), and Pd(PPh₃)₄ (84.3 mg, 0.0723 mmol). **Method B** (Table 2, entry 3b). Compound **5e** (255 mg, 53%) was obtained as described above but using 1-bromo-4-trifluoromethylbenzene (363 mg, 1.61 mmol), *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.6 mmol), ZnCl₂ (440 mg, 3.24 mmol), dibromide **1** (401 mg, 0.647 mmol), and Pd(PPh₃)₄ (76.8 mg, 0.0664 mmol). R_f 0.59 (alumina, hexane/CH₂Cl₂ = 7/3); mp. 179.6–180.0 °C; ¹H NMR (300 MHz, CDCl₃, δ) 8.02 (d, 4H, *J* = 8.2 Hz), 8.00 (s, 2H), 7.71 (d, 4H, *J* = 8.2 Hz), 7.37 (s, 2H), 2.59 (s, 6H), 1.28 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 147.8, 143.8, 141.6, 138.5, 136.8, 133.9, 131.8, 129.7, 129.4 (q, ²*J*_{CF} = 32.5 Hz), 126.3, 125.6, 124.5 (q, ¹*J*_{CF} = 271.8 Hz), 115.0, 85.9, 27.8, 22.3; IR (KBr) 3460, 2982, 2937, 1750, 1617, 1390, 1357, 1327, 1298, 1253, 1139, 1067, 1017, 840 cm⁻¹; HRMS (ESI) Calcd for C₄₀H₃₆F₆N₄NaO₄ (M+Na⁺) 773.2538, found 773.2531.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(1-naphthyl)-6,6'-dimethyl-2,2'-bisbenzimidazole (5f):
Method A (Table 2, entry 4). Compound **5f** (345 mg, 68%) was obtained as a white powder as described above but using 1-bromonaphthalene (664 mg, 3.21 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl₂ (439 mg, 3.23 mmol), dibromide **1** (439 mg, 0.708 mmol), and Pd(PPh₃)₄ (84.8 mg, 0.0735 mmol). R_f 0.60 (alumina, hexane/CH₂Cl₂ = 5/5); mp. 328.0–329.0 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.99 (s, 2H), 7.86–7.82 (m, 4H), 7.63 (d, 2H, *J* = 8.3 Hz), 7.53–7.45 (m, 4H), 7.43 (dd, 2H, *J*₁ = *J*₂ = 7.1 Hz), 7.28–7.23 (m, 4H), 2.54 (s, 6H), 1.27 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 147.8, 143.4, 139.7, 136.1, 134.0, 133.3, 132.9, 132.3, 128.3, 128.1, 126.5, 125.9, 125.7, 125.5, 114.2, 85.4, 27.8, 22.2; IR (KBr) 3432, 2977, 2921, 1745, 1394, 1355, 1295, 113, 773 cm⁻¹; LRMS (ESI) *m/z* = 737.4 (M+Na⁺); Anal. Calcd for C₄₆H₄₂N₄O₄: C, 77.29; H, 5.92; N, 7.84. Found: C, 77.22; H, 5.73; N, 7.60.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis(2,7-dimethylnaphthalenyl)-6,6'-dimethyl-2,2'-bisbenzimidazole (5g**):** Method A Table 2, entry 5). Compound **5g** (303 mg, 63%) was obtained as a white solid as described above but using 1-bromo-2,7-dimethylnaphthalene (659 mg, 2.80 mmol), *n*-BuLi (1.6M in hexane, 1.75 mL, 2.8 mmol), ZnCl₂ (383 mg, 2.81 mmol), dibromide **1** (387 mg, 0.624 mmol), and Pd(PPh₃)₄ (74 mg, 0.064 mmol). R_f 0.75 (alumina, hexane/CH₂Cl₂ = 5/5); mp. >330 °C ¹H NMR (300 MHz, CDCl₃, δ) 8.00 (br s, 2H), 7.71–7.66 (m, 4H), 7.31 (t, 2H, *J* = 8.0 Hz), 7.19–7.14 (m, 2H), 7.05–7.03 (m, 2H), 6.94 (d, 2H, *J* = 4.2) 2.55 (s, 6H), 2.26 (s, 3H), 2.24 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 1.28 (s, 9H), 1.26 (s, 9H). ¹³C NMR (75 MHz, CDCl₃, δ) 147.8, 143.4, 139.9, 136.4, 135.2, 135.1, 134.4, 134.2, 133.4, 133.3₉, 133.3₃, 133.2₅, 132.2, 130.6, 130.5, 128.3, 127.9, 127.8, 127.7, 127.0, 126.9, 125.3, 125.1, 114.1, 85.9, 85.27, 27.9, 27.8, 22.3, 22.09, 22.05, 21.2, 21.1. IR (KBr) 3468, 3047, 2978, 2920, 2865, 1748, 1627, 1607, 1512, 1491, 1456, 1397, 1370, 1350, 1312, 1289, 1248, 1223, 1175, 1140, 1098, 1109, 1024, 975, 849, 833, 814, 800, 765 cm⁻¹. LRMS (ESI) *m/z* = 793.5 (M+Na⁺); Anal. Calcd for C₅₀H₅₀N₄O₄: C, 77.89; H, 6.54; N, 7.27. Found: C, 77.43; H, 6.56; N, 6.93.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis{4-[2-(benzyloxy)ethoxy]phenyl}-6,6'-dimethyl-2,2'-bisbenzimidazole (5h**):** Method B (Table 2, entry 6). Compound **5h** (404 mg, 69%) was obtained as a color-less film as described above but using 1-[2-(benzyloxy)ethoxy]-4-bromobenzene (498 mg, 1.62 mmol), *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.6 mmol), ZnCl₂ (433 mg, 3.18 mmol), dibromide **1** (400 mg, 0.645 mmol), and Pd(PPh₃)₄ (73.8 mg, 0.0638 mmol). R_f 0.51 (alumina, hexane/CH₂Cl₂ = 5/5); mp. 54.6–55.5 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.91 (s, 2H), 7.88 (d, 4H, *J* = 8.8 Hz), 7.38–7.27 (m, 12H), 7.03 (d, 4H, *J* = 8.8 Hz), 4.64 (s, 4H), 4.20 (t, 4H, *J* = 4.7 Hz), 3.84 (t, 4H, *J* = 4.7 Hz), 2.58 (s, 6H), 1.27 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 158.6, 147.9, 143.3, 138.4, 138.2, 136.4, 133.8, 132.9, 130.7, 130.5, 128.5, 127.9, 127.8, 125.4, 115.0, 113.4, 85.4, 73.5, 68.7, 67.7, 27.8, 22.3; IR (NaCl) 3439, 3029, 2978, 2924, 2865, 1745, 1608, 1516, 1359, 1296, 1251, 1137, 830 cm⁻¹; HRMS (ESI) Calcd for C₅₆H₅₈N₄NaO₈ (M+Na⁺) 937.4152, found 937.4145. Anal. Calcd for C₅₆H₅₈N₄O₈: C, 73.50; H, 6.39; N, 6.12. Found: C, 73.35; H, 6.28; N, 5.89.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis[4-(benzyloxy)butyloxy]-6,6'-dimethyl-2,2'-bisbenzimidazole (5i**):** **Method A** (Table 2, entry 7a). Compound **5i** (535 mg, 73%) was obtained as a color-less film as described above but using 4-[4-(benzyloxy)butyloxy]-3,5-dimethyl-1-bromobenzene (1.15 g, 3.17 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl₂ (436 mg, 3.21 mmol), dibromide **1** (440 mg, 0.710 mmol), and Pd(PPh₃)₄ (84.2 mg, 0.0728 mmol). **Method B** (Table 2, entry 7b). Compound **5i** (353 mg, 53%) was obtained as described above but using 4-[4-(benzyloxy)butyloxy]-3,5-dimethyl-1-bromobenzene (565 mg, 1.56 mmol), *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.6 mmol), ZnCl₂ (442 mg, 3.25 mmol), dibromide **1** (402 mg, 0.648 mmol), and Pd(PPh₃)₄ (74.6 mg, 0.0645 mmol). R_f 0.31 (alumina, hexane/CH₂Cl₂ = 5/5); mp. 55.3–56.6 °C; ¹H NMR (300 MHz, CDCl₃, δ) 7.89 (s, 2H), 7.51 (s, 4H), 7.33–7.27 (m, 12H), 4.52 (s, 4H), 3.79 (t, 4H, *J* = 6.1 Hz), 3.55 (t, 4H, *J* = 6.1 Hz), 2.55 (s, 6H), 2.31 (s, 12H), 1.89–1.85 (m, 8H), 1.25 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 156.0, 148.0, 143.4, 138.8, 138.4, 136.4, 133.8, 133.4, 130.9, 129.9, 128.5, 127.8, 127.7, 126.0, 113.5, 85.4, 73.1, 72.0, 70.3, 27.8, 27.4, 26.8, 22.3, 16.8; IR (KBr) 3433, 2977, 2921, 2861, 1746, 1477, 1383, 1367, 1305, 1150, 850 cm⁻¹; HRMS (ESI) Calcd for C₆₄H₇₄N₄NaO₈ (M+Na⁺) 1049.5404, found 1049.5397.

¹H- and ¹³C-NMR Spectra

4,4'-bis[5-(2,6-dimethyl-4-methoxyphenyl)-2-pyridyl]-6,6'-dimethyl-2,2'-bisbenzimidazole (6): Method A (Table 2, entry 8). Compound **6** (102 mg, 21%) was obtained as a yellow-white powder as described above but using 2-bromo-5-(2,6-dimethyl-4-methoxyphenyl)pyridine (937 mg, 3.21 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl₂ (436 mg, 3.21 mmol), dibromide **1** (443 mg, 0.715 mmol), and Pd(PPh₃)₄ (83.8 mg, 0.0725 mmol). R_f 0.68 (alumina, CH₂Cl₂/Et₂O = 8/2); mp. >350 °C; ¹H NMR (600 MHz, CDCl₃, δ) 12.5 (br s, 2H), 8.67 (d, 2H, *J* = 2.0 Hz), 8.09 (d, 2H, *J* = 8.1 Hz), 7.78 (s, 2H), 7.73 (s, 2H), 7.64 (dd, 2H, *J*₁ = 2.0 Hz, *J*₂ = 8.1 Hz), 6.75 (s, 4H), 3.87 (s, 6H), 2.62 (s, 6H), 2.12 (s, 12H); ¹³C NMR (150 MHz, CDCl₃, δ) 159.2, 154.5, 150.4, 145.7, 144.1, 138.4, 138.2, 135.0, 132.8, 131.5, 130.5, 122.9, 122.3, 121.0, 119.3, 113.2, 55.4, 22.1, 21.5; IR (KBr) 3385, 2953, 2918, 2838, 1606, 1593, 1471, 1330, 1156, 1074, 836 cm⁻¹; HRMS (ESI) Calcd for C₄₄H₄₁N₆O₂ (M+H⁺) 685.3291, found 685.3293.

¹H- and ¹³C-NMR Spectra

1,1'-bis(*t*-butoxycarbonyl)-4,4'-bis[2-(2,6-dimethyl-4-methoxyphenyl)-5-pyridyl]-6,6'-dimethyl-2,2'-bisbenzimidazole (5j**):** Method A (Table 2, entry 9). Compound **5j** (312 mg, 50%) was obtained as a yellow-white powder as described above but using 5-bromo-2-(2,6-dimethyl-4-methoxyphenyl)pyridine (933 mg, 3.20 mmol), *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), ZnCl₂ (436 mg, 3.21 mmol), dibromide **1** (439 mg, 0.708 mmol), and Pd(PPh₃)₄ (78.3 mg, 0.0677 mmol). R_f 0.66 (alumina, CH₂Cl₂); mp. 160.2–160.6 °C; ¹H NMR (300 MHz, CDCl₃, δ) 9.17 (d, 2H, *J* = 2.1 Hz), 8.45 (dd, 2H, *J*₁ = 2.1 Hz, *J*₂ = 8.1 Hz), 8.02 (s, 2H), 7.48 (s, 2H), 7.29 (d, 2H, *J* = 8.1 Hz), 6.65 (s, 4H), 3.80 (s, 6H), 2.62 (s, 6H), 2.08 (s, 12H), 1.30 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ) 159.0, 158.8, 149.4, 147.8, 143.6, 138.6, 137.7, 137.2, 136.9, 134.0, 133.5, 131.4, 129.8, 125.9, 124.9, 114.8, 113.1, 86.0, 55.3, 27.8, 22.3, 20.9; IR (NaCl) 3438, 2977, 2836, 1749, 1606, 1470, 1367, 1295, 1140, 845 cm⁻¹; HRMS (ESI) Calcd for C₅₄H₅₆N₆NaO₆ (M+Na⁺) 907.4159, found 907.4166.

¹H- and ¹³C-NMR Spectra