Masked Imidazolyl–Dipyrromethanes in the Synthesis of Imidazole-Substituted Porphyrins

Jayeeta Bhaumik, Zhen Yao, K. Eszter Borbas, Masahiko Taniguchi, and Jonathan S. Lindsey

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1. Survey of Conditions for Dialkylation of Imidazole-Substituted Porphyrins.

The preferred reaction conditions employed include (1) EtI (25 equiv) in THF at reflux (for **Pd12** and for **Zn13**); and (2) NaOMe and THF followed by an alkane sultone in DMF at 60 °C (for **Zn12**). The specific results are as follows:

- The treatment of **Zn12** with NaOMe and THF followed by the reaction with 1,4-butane sultone in DMF gave a mono and a dialkylated product in 20% overall yield.
- The treatment of **Zn12** with excess EtI (25 equiv) in DMF at 60 °C gave the product along with the demetalated species after 2 days of reaction. Hence the crude mixture was treated with excess Zn(OAc)₂·2H₂O (25 equiv) at 60 °C for 12 h. Chromatographic purification afforded **Zn12-Et₂** in 36% yield.
- Deprotection of porphyrin **SEM-Zn13** using conc. HCl afforded the free base porphyrin **13** in quantitative yield. Porphyrin **13** was metalated using anhydrous Zn(OAc)₂ to afford porphyrin **Zn13**. Porphyrin **Zn13** was dialkylated using excess EtI in refluxing THF for 3 days, affording **Zn13-Et₂** in 30% yield.
- The treatment of **Pd12** with excess EtI in THF under reflux for 3 days afforded the dialkylated product **Pd12-Et₂** in 83% yield.
- The reaction of **Zn12** with 1,3-propane sultone under a variety of reaction conditions afforded only a trace amount of the corresponding dialkylated product.

Alkylated porphyrins **Zn12-S₂**, **Zn12-Et₂**, **Pd12-Et₂** and **Zn13-Et₂** were obtained and characterized.

2. Solubility Test for Imidazolium–Porphyrins.

We tested the solubility of the porphyrins in various solvents in the following way. Each porphyrin was added to a small quantity of a given solvent. The resulting mixture (a suspension) was filtered. From the filtrate an aliquot was removed (typically 50-100 μL) and added to a cuvette containing 3 mL of the same solvent. UV-vis absorption spectroscopic analysis was then performed with the resulting dilute solution. The concentration was then calculated on the basis of $\epsilon_{\text{Soret}} = 500,000 \text{ M}^{-1}\text{cm}^{-1}$. If a sharp, unsplit Soret band (with a clear base-line and with minimum noise) was observed, the porphyrin was considered to be soluble. The appearance of a split Soret band in a sample from the filtrate was taken to indicate aggregation (perhaps

dimerization); hence, a solubility calculation was not performed. The extent of solubility of various porphyrins in different solvents is summarized in Table S1.

Table S1: Solubility of Imidazolium–Porphyrins.

Compound	DMSO	DMF	Water	MeOH	THF
Zn12-S	H	H	--- ^a	H	--- ^a
Zn12-S₂	M	M	H	H	VL
Zn12-Et₂	H	M-H	M	H	M
Pd12-Et₂	M	M	VL-L	M-H	M
Zn13-Et₂	H	M-H	L-M	H	L

H = High Solubility $\geq 10^{-3}$ M

M = Medium Solubility = $1-10 \times 10^{-4}$ M

L = Low Solubility = $1-10 \times 10^{-5}$ M

VL = Very Low Solubility $\leq 10^{-6}$ M

^aThe spectrum exhibited a split Soret band indicative of aggregation, despite filtration and dilution.

3. Experimental Section.

(A) General. Melting points are uncorrected. Absorption and fluorescence spectra were collected in CH₂Cl₂ at room temperature unless noted otherwise. Silica gel (40 μ m average particle size) was used for column chromatography. THF was freshly distilled from sodium/benzophenone as required. Toluene was distilled from CaH₂. CHCl₃ was stabilized with 0.8% ethanol. Anhydrous MeOH, CH₂Cl₂ and CHCl₃ (stabilized with 0.8% EtOH) were reagent grade and were used as received.

(B) NMR Spectroscopy. All ¹H NMR spectra (400 MHz) and ¹³C NMR spectra (100 MHz) were collected in CDCl₃ unless noted otherwise.

¹¹B NMR Spectroscopy: ¹¹B NMR spectroscopy (128 MHz) was performed using boron-free NMR tubes and THF-*d*₈ as solvent, with a sample of BF₃·OEt₂ as an external standard. The concentrations varied from 50–200 mM, and the acquisition time was 15 min – 1 h. Spectra were collected at 50 °C unless noted otherwise.

¹⁵N NMR Spectroscopy: ¹⁵N NMR spectroscopy (41 MHz) was performed at room temperature using a 400 MHz spectrometer. All of the data for ¹⁵N chemical shifts are reported relative to that of nitromethane (δ 0.0) as an indirect reference using pyrrole as a direct reference. Although nitromethane is typically used as a direct reference in ¹⁵N NMR spectroscopy, nitromethane cannot be used as a reference for gHSQC spectroscopy due to the lack of an N-H bond. Furthermore, in some cases, artifacts in the region of –5 to 5 ppm (which arise from the NMR spectrometer filters) often accompany CH₃NO₂, which makes this solvent a less desirable reference. Thus, pyrrole in an NMR microtube insert was used as a reference for the gHSQC and gHMBC spectroscopy measurement. An NMR microtube containing 8.0 M pyrrole in THF-*d*₈ (70 μ L) was placed in an NMR tube containing 1.0 M CH₃NO₂ in THF-*d*₈ (500 μ L). The pseudo-concentration of each component in the entire NMR tube was ~0.9 M (CH₃NO₂) and ~1

M (pyrrole). The gHMBC (N-H) spectrum showed the resonance of the pyrrole nitrogen at –230.1 ppm relative to nitromethane (δ 0.0 ppm). Note that several different combinations of the concentrations including (1) CH₃NO₂ (0.2 M) and pyrrole (0.2 M), (2) CH₃NO₂ (1.0 M) and pyrrole (1.0 M), and (3) CH₃NO₂ (6.2 M) and pyrrole (4.8 M), were examined to identify suitable pseudo-concentrations of the CH₃NO₂ and pyrrole for desired spectral quality.

Next, the pyrrole-containing NMR microtube was placed in an NMR tube containing the imidazolyl–dipyrromethane sample (0.2 M) in THF-*d*₈ (500 μ L), whereupon gHSQC and gHMBC spectroscopy was carried out (32 scans, ~3 h each). When 0.1-M samples were measured, 64 scans (~6 h) were applied. Each gHSQC and gHMBC spectrum was referenced from the resonance of pyrrole (δ –230.1 ppm). The assignments of the resonances of various nitrogen atoms in the dipyrromethanes are displayed in Chart S1.

Chart S1. ¹⁵N NMR Assignments.

(C) Noncommercial compounds. Mukaiyama reagent **4**,³⁴ tin-complex **7**,³⁶ dipyrromethane **10a**,³² and diformyldipyrromethane **11a**^{38,39} were prepared as described in the literature.

(D) Synthetic Procedures.

10-(9-Borabicyclo[3.3.1]non-9-yl)-5-[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-2-yl]dipyrromethane (9-BBN-3). A solution of **3** (68 mg, 0.20 mmol) in CH₂Cl₂ (0.50 mL) was treated with TEA (0.13 mL, 0.96 mmol) followed by 9-BBN-OTf (1.6 mL, 0.8 mmol, 0.5 M in hexanes), and the mixture was stirred at room temperature. After 2 h, the mixture was poured onto a pad of silica eluted with CH₂Cl₂. The product eluted as a fast moving red band, which upon concentration afforded a dark red solid (54 mg, 58%): mp 80–82 °C; ¹H NMR (300 MHz) δ 0.02 (s, 9H), 0.88–0.99 (m, 4H), 1.24–2.32 (m, 12H), 3.50–3.56 (m, 2H), 5.09 (s, 2H), 5.76 (s, 1H), 5.87 (s, 1H), 6.11–6.18 (m, 3H), 6.70 (s, 1H), 7.03 (d, *J* = 2.1 Hz, 1H), 7.42 (s, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 8.22–8.34 (br, 1H); ¹³C NMR δ –1.2, 18.0, 23.1 (br), 23.2, 23.5, 24.8 (br), 32.0, 32.3, 33.9, 34.1, 35.2, 67.8, 76.3, 106.54, 106.58, 106.9, 109.3, 117.9, 118.5, 124.7, 125.3, 127.5, 127.8, 146.8; ¹¹B NMR δ 1.93; ¹⁵N NMR δ –226.4 (gHSQC), δ –162.1, –193.0, –199.4, –226.4 (gHMBC); FAB-MS obsd 462.2985, calcd 462.2986 (C₂₆H₃₉BN₄OSi).

10,11-Bis(dibutylboryl)-1-(4-methylbenzoyl)-5-[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-2-yl]dipyrromethane [(Bu₂B)₂-5]. Following a general procedure³³ with slight modification, a solution of EtMgBr (0.620 mL, 0.62 mmol, 1.0 M in THF) was added slowly to a solution of **3** (106 mg, 0.310 mmol) in THF (0.31 mL) under argon. The resulting mixture was stirred at room temperature for 10 min, and then cooled to –78 °C. A solution of **4** (71 mg, 0.31 mmol) in THF (0.31 mL) was added. The reaction mixture was stirred at –78 °C for 10 min, and then allowed to warm to room temperature and stirred for 1 h. The reaction was quenched by addition of saturated aqueous NH₄Cl (4 mL). The mixture was extracted with ethyl acetate. The organic layer was washed (water and brine), dried (Na₂SO₄) and filtered. The filtrate was concentrated. The crude product (a red-orange oil) thus obtained was dissolved in CH₂Cl₂ (0.62 mL) and treated with TEA (105 μL, 0.750 mmol) and Bu₂B-OTf (0.62 mL, 0.62 mmol, 1.0 M in hexane) with stirring at room temperature. After 1 h, the mixture was poured onto a pad of silica (2 x 16 cm), which was eluted with CH₂Cl₂. The product eluted as a fast-moving orange band, which upon concentration afforded an orange-red viscous solid (50 mg, 23%): ¹H NMR δ –0.08 (s, 9H), 0.40–1.31 (m, 38H), 2.49 (s, 3H), 3.16–3.19 (m, 1H), 3.30–3.35 (m, 1H), 4.89 (d, *J* = 10.4 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 5.83 (s, 1H), 5.90–5.92 (m, 1H), 6.20–6.22 (m, 2H), 6.74–6.76 (m, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.20 (d, *J* = 4.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (75 MHz) δ –1.3, 14.39, 14.48, 14.59, 18.1, 22.1, 26.25, 26.41, 26.52, 26.8, 27.1, 27.6, 28.3, 28.6, due to the overlap of the four carbon atoms of the *n*-butyl chain their resonances were not observed, 35.1, 67.4, 76.0, 106.2, 108.2, 118.7, 119.0, 119.9, 120.9, 122.0, 124.9, 127.7, 130.09, 130.12, 134.4, 143.4, 145.8, 147.3, 176.5; ¹¹B NMR δ 1.08, 13.24; ¹⁵N NMR δ –154.0, –167.2, –200.3, 202.3 (gHMBC); FAB-MS obsd 709.5203, calcd 709.5219 [(M + H)⁺, M = C₄₂H₆₆B₂N₄O₂Si]; λ_{abs} (THF) 293, 363 nm.

Zn(II)-5,15-Bis(4-methylphenyl)-10-[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-2-yl]porphyrin (SEM-Zn8). Following a general procedure,⁴⁸ a solution of porphyrin SEM-8 (21 mg, 0.031 mol) in CHCl₃/MeOH (12 mL, 3:1) was treated with Zn(OAc)₂·2H₂O (0.33 g, 1.5 mmol, 50 equiv). The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was washed (saturated aqueous NaHCO₃ and water) and extracted with ethyl acetate. The organic layer was dried (Na₂SO₄), concentrated and chromatographed [silica, CH₂Cl₂/ethyl acetate (3:1)] to afford a purple-green solid (23 mg, quantitative): ¹H NMR δ –0.88 (s, 9H), –0.42 (t, *J* = 8.0 Hz, 2H), 1.53 (t, *J* = 8.8 Hz, 2H), 1.82 (t, *J* = 2.0 Hz, 1H), 2.86 (s, 6H), 3.15 (s, 2H), 5.50 (d, *J* = 4.4 Hz, 2H), 5.65 (d, *J* = 1.6 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 7.2

Hz, 2H), 8.01 (d, $J = 7.6$ Hz, 2H), 8.36 (d, $J = 4.4$ Hz, 2H), 8.56 (d, $J = 7.2$ Hz, 2H), 9.18 (d, $J = 4.4$ Hz, 2H), 9.50 (d, $J = 4.4$ Hz, 2H), 10.43 (s, 1H); LD-MS obsd 748.5, 1497.1; FAB-MS obsd 749.2389, calcd 749.2403 $[(M + H)^+]$, $M = C_{43}H_{40}N_6OSiZn$; λ_{abs} 410, 427, 558 nm; λ_{em} 610, 660 nm.

4-(Ethoxycarbonylmethoxy)benzaldehyde (9b). A solution of 4-hydroxybenzaldehyde (2.44 g, 20.0 mmol) in dry acetonitrile (8.0 mL) was treated with powdered, dried K₂CO₃ (4.16 g, 30.0 mmol) and NaI (460 mg, 3.00 mmol). The mixture was refluxed under argon for 30 min. Ethyl bromoacetate (2.77 mL, 4.18 g, 25.0 mmol) was added dropwise, and the reflux was continued for 18 h. Water and CH₂Cl₂ were added, and the phases were separated. The aqueous layer was extracted with CH₂Cl₂. The combined organic phase was washed with water. The organic layer was dried (Na₂SO₄). Evaporation of the solvent and chromatography of the oily residue [silica, hexanes/ethyl acetate (7:3)] afforded a white, crystalline solid (4.08 g, 98%): mp 32–34 °C; ¹H NMR (300 MHz) δ 1.29 (t, $J = 7.2$ Hz, 3H), 4.28 (q, $J = 7.2$ Hz, 2H), 4.70 (s, 2H), 7.00 (d, $J = 8.1$ Hz, 2H), 7.84 (d, $J = 8.1$ Hz, 2H), 9.89 (s, 1H); ¹³C NMR δ 14.4, 61.9, 65.4, 115.1, 131.0, 132.2, 162.8, 168.3, 191.0; FAB-MS obsd 209.0812, calcd 209.0812 $[(M + H)^+]$, $M = C_{11}H_{12}O_4$.

5-[4-(Ethoxycarbonylmethoxy)phenyl]dipyrromethane (10b). Following a standard procedure,³² a solution of aldehyde **9b** (3.80 g, 18.3 mmol) in dry pyrrole (128 mL, 1.84 mol) was flushed with argon for 10 min. InCl₃ (408 mg, 1.83 mmol) was added, and the reaction was allowed to proceed for 3 h. The reaction was quenched by addition of powdered NaOH (2.21 g, 5.53 mmol). The mixture was stirred for 45 min. The mixture was filtered. The filtrate was concentrated at reduced pressure. Chromatography [silica, hexanes/CH₂Cl₂/ethyl acetate (7:2:1)] afforded a pale yellow oil (5.09 g, 86%): ¹H NMR (300 MHz) δ 1.30 (t, $J = 7.2$ Hz, 3H), 4.27 (q, $J = 7.2$ Hz, 2H), 4.59 (s, 2H), 5.42 (s, 1H), 5.87–5.91 (m, 2H), 6.13–6.17 (m, 2H), 6.66–6.70 (m, 2H), 6.74 (d, $J = 8.7$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.80–8.00 (br, 2H); ¹³C NMR δ 14.4, 43.3, 61.7, 65.7, 107.3, 108.6, 115.0, 117.4, 129.8, 132.9, 135.6, 157.0, 169.2; FAB-MS obsd 324.1489, calcd 324.1474 (C₁₉H₂₀N₂O₃).

5-[4-(Ethoxycarbonylmethoxy)phenyl]-1,9-diformyldipyrromethane (11b). Following a standard procedure,³⁹ a solution of **10b** (5.04 g, 15.6 mmol) in DMF (15.5 mL) at 0 °C under argon was treated with phosphorous oxychloride (3.07 mL, 33.7 mmol). The mixture was allowed to warm to room temperature. Stirring was continued for 1 h. The mixture was poured into aqueous sodium hydroxide (80 mL of 10 wt% solution). The mixture was extracted into ethyl acetate. The organic extract was washed (water and brine), dried (Na₂SO₄), and concentrated. Chromatography on neutral alumina [CH₂Cl₂/MeOH, (199:1) $\rightarrow$ (99:1)] gave a pale brown solid (1.49 g, 25%): mp 55–57 °C (dec.); ¹H NMR (300 MHz) δ 1.30 (t, $J = 7.2$ Hz, 3H), 4.27 (q, $J = 7.2$ Hz, 2H), 4.60 (s, 2H), 5.52 (s, 1H), 6.02–6.06 (m, 2H), 6.86–6.88 (m, 4H), 7.19 (d, $J = 8.4$ Hz, 2H), 9.20 (s, 2H), 10.32–10.48 (br, 2H); ¹³C NMR δ 14.4, 43.9, 61.7, 65.7, 114.8, 115.4, 122.5, 129.9, 132.5, 132.9, 141.8, 157.5, 169.1, 179.2; FAB-MS obsd 381.1457, calcd 381.1450 $[(M + H)^+]$, $M = C_{21}H_{20}N_2O_5$.

5-[4-(Ethoxycarbonylmethoxy)phenyl]-10-(imidazol-2-yl)porphyrin (13). A suspension of porphyrin **SEM-Zn13** (30 mg, 0.040 mmol) in EtOH (5 mL) was treated with conc. HCl (5 mL). The resulting mixture was refluxed overnight. The reaction mixture was cooled to room temperature, whereupon the volatile solvent was removed. The resulting suspension was poured into a large volume of ethyl acetate. Water was added. Saturated aqueous NaHCO₃ solution was added slowly to the aqueous-organic mixture. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The organic layers were combined and washed with water. The organic layer was separated, dried (Na₂SO₄) and concentrated. The resulting residue was treated with diethyl ether. The suspension was sonicated and centrifuged. The supernatant was decanted and the remaining residue was dried to afford a dark purple solid (22 mg, quantitative): ¹H NMR (THF-*d*₈) δ -3.60 to -3.10 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 7.36 (dd, *J* = 7.2 Hz, 2H), 4.99 (s, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.62–7.76 (m, 2H), 8.17 (d, *J* = 8.1 Hz, 2H), 9.02 (d, *J* = 4.2 Hz, 2H), 9.14–9.26 (m, 4H), 9.30 (d, *J* = 4.2 Hz, 2H), 10.10 (s, 2H), resonance from the pyrrolic proton of the imidazole moiety was not observed; LD-MS obsd 554.3; FAB-MS obsd 554.2145, calcd 554.2145 [(M + H)⁺, C₃₃H₂₆N₆O₃]; ESI-MS (+) obsd 555.2 (M + H)⁺, 1109.2 (2M + H)⁺, 278.1 (M + 2H)⁺, calcd 554.2 (M = C₃₃H₂₆N₆O₃); λ_{abs} 410, 505, 542, 577 nm; λ_{em} 645, 700 nm.

1-[2-(Trimethylsilyl)ethoxymethyl]imidazole-4(5)-carboxaldehyde (14a and 14b). Following a general procedure,³¹ a sample of NaH (60% dispersion in mineral oil, 1.00 g, 25 mmol) was washed with hexanes (2 x 25 mL) under argon. The flask was charged with dry DMF (36 mL), and 4(5)-imidazolecarboxaldehyde (2.40 g, 25.0 mmol) was added in small portions. After stirring at room temperature for 1.5 h, the reaction mixture was treated dropwise with SEMCl (4.42 g, 25.0 mmol). The reaction mixture became slightly warm. The mixture was stirred for 1.5 h. The reaction was quenched by addition of water, and extracted with ethyl acetate. The organic extract was washed repeatedly with water. The organic layer was dried (Na₂SO₄) and concentrated to give a yellow oil (4.97 g, 88%): ¹H NMR δ -0.04 (s, 9H), 1.19–1.28 (m, 2H), 3.45–3.60 (m, 2H), 5.37–5.73 (m, 2H), 7.74–7.87 (m, 2H), 9.82–9.94 (br, 1H); ¹³C NMR δ (-1.51, -1.48), (17.65, 17.73), (66.93, 67.07), (75.4, 76.6), 124.6, 138.8, (143.57, 143.73), 179.4, 186.0; FAB-MS obsd 227.1207, calcd 227.1216 [(M + H)⁺, M = C₁₀H₁₈N₂O₂Si].

Large Scale Synthesis of 14a and 14b. Following a general procedure,³¹ a sample of NaH (60% dispersion in mineral oil, 4.28 g, ~107 mmol) was washed with hexanes (3 x 50 mL) under argon. The flask was charged with dry DMF (154 mL), and 4(5)-imidazolecarboxaldehyde (10.3 g, 107 mmol) was added in small portions. After stirring at room temperature for 2.5 h, the reaction mixture was treated dropwise with SEMCl (19.6 g, 118 mmol). The reaction mixture became slightly warm. After stirring for 4 h, the mixture was quenched with water and extracted with ethyl acetate. The organic extract was washed with water, dried (Na₂SO₄) and concentrated to give a yellow oil (21 g, 87%). Characterization data (¹H NMR, FAB-MS) were consistent with the values reported above.

5-[1-(2-(Trimethylsilyl)ethoxymethyl)imidazol-4-yl]dipyrromethane (15a). Following a general procedure³² with modification, a degassed solution of pyrrole (139 mL, 2.00 mol) and a mixture of aldehydes **14a** and **14b** (4.53 g, 20.0 mmol) was treated with InCl₃ (4.42 g, 20.0 mmol). The mixture was stirred under argon at room temperature for 5.5 h. The resulting brown mixture was treated with NaOH (24.0 g, 60.0 mol, 20-40 mesh beads). Stirring for 45 min afforded a brown mixture, which was filtered. The filtrate was concentrated under vacuum (0.2 mm Hg). Traces of pyrrole were removed by thrice treatment of the crude viscous residue in the evaporation flask with hexanes (50 mL) followed by removal of the volatile components.

The resulting brown viscous liquid was purified by column chromatography [silica, 6 x 14 cm, CHCl₃ → CHCl₃/ethyl acetate (1:4)]. Concentration of the eluent gave a light brown solid (0.55 g, 16%): mp 80–82 °C; ¹H NMR δ 0.00 (s, 9H), 0.90 (t, *J* = 8.4 Hz, 2H), 3.48 (t, *J* = 8.4 Hz, 2H), 5.20 (s, 2H), 5.41 (s, 1H), 5.95–5.97 (m, 2H), 6.11–6.13 (m, 2H), 6.68–6.70 (m, 2H), 6.81–6.82 (m, 1H), 7.57–7.58 (m, 1H), 8.84–8.96 (br, 2H); ¹³C NMR δ –1.2, 17.9, 36.8, 66.7, 76.2, 106.0, 108.2, 116.3, 117.1, 132.3, 137.4, 143.9; Anal. calcd for C₁₈H₂₆N₄OSi: C, 63.12; H 7.65; N, 16.36. Found: C, 63.05; H 7.83; N, 15.92; FAB-MS obsd 343.1959, calcd 343.1954 [(M + H)⁺, M = C₁₈H₂₆N₄OSi].

Synthesis of 15a at Larger Scale. Following a general procedure^{26,33} with modification, a solution of pyrrole (902 mL, 13.0 mol) and a mixture of aldehydes **14a** and **14b** (29.4 g, 130 mmol) in a 2-L single-neck round-bottomed flask was degassed with a stream of argon for 30 min. InCl₃ (28.8 g, 130 mmol) was added, and the mixture was stirred magnetically under argon at room temperature for 5.5 h. The resulting brown mixture was treated with NaOH (156 g, 3.90 mol, 20–40 mesh beads). Stirring for 1 h afforded a brown mixture. The mixture was filtered through a Büchner funnel. The contents of the flask and the filtered material were washed with a small amount of pyrrole. The filtrate was concentrated under vacuum (0.2 mm Hg). The collected pyrrole was set aside. Traces of pyrrole were removed by thrice treatment of the crude viscous residue in the evaporation flask with hexanes (150 mL) followed by removal of the volatile components. The resulting brown viscous liquid was purified by column chromatography [silica, CHCl₃ → CHCl₃/ethyl acetate (1:4) each containing 1% TEA] to afford a light brown solid (1.8 g, 8.0%). Characterization data (¹H NMR, FAB-MS) were consistent with the values reported above.

10-Dibutylboryl-5-[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-4-yl]dipyrromethane (Bu₂B-15a). A sample of a mixture of **14a** and **14b** (2.27 g, 10.0 mmol, 1:1 mole ratio by NMR spectroscopy) was dissolved in pyrrole (69.0 mL, 1.00 mol). The mixture was treated with InCl₃ (2.21 g, 10.0 mmol) at room temperature under argon for 5.5 h. The reaction mixture was treated with NaOH (12.0 g, 30.0 mol, 20–40 mesh beads) for 45 min. The mixture was filtered. The filtrate was concentrated. Traces of pyrrole were removed by thrice treatment of the crude viscous residue in the evaporation flask with hexanes (50 mL) followed by removal of the volatile components. The resulting brownish oil was dissolved in CH₂Cl₂ (100 mL) and treated with Bu₂B-OTf (1.0 M in CH₂Cl₂, 40 mL, 40 mmol) at room temperature for 2 h. The reaction mixture was passed through a Celite pad and concentrated. The resulting black liquid was absorbed on silica gel and passed through a silica pad [hexanes/CH₂Cl₂ (1:1)]. The first orange-red band was discarded. The next fraction was collected and concentrated, affording an orange liquid. The orange liquid was absorbed on silica gel and chromatographed [silica, hexanes/CH₂Cl₂ (1:1)] to afford a red viscous liquid (113 mg, 5% from **14a**): ¹H NMR δ 0.01 (s, 9H), 0.50–0.65 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 6H), 0.92 (t, *J* = 8.0 Hz, 2H), 0.90–1.58 (m, 8H), 3.51 (t, *J* = 8.0 Hz, 2H), 5.30 (s, 2H), 5.50 (s, 1H), 5.91–5.94 (m, 1H), 6.16–6.21 (m, 3H), 6.70–6.73 (m, 1H), 6.74–6.76 (m, 1H), 6.82–6.85 (m, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 8.25 (br, 1H); ¹³C NMR δ –1.29, 14.39, 14.43, 17.9, 23.49, 25.97, 26.65, 26.70, 27.9, 28.3, 34.2, 67.7, 77.8 (overlapped with CHCl₃), 104.6, 106.8, 107.4, 108.3, 116.0, 117.5, 121.7, 128.6, 130.3, 132.2, 139.9; ¹⁵N NMR δ –228.4 (gHSQC), δ –165.1, the resonance from the boron-complexed pyrrolic nitrogen was not observed, –197.2, –228.5 (gHMBC); FAB-MS obsd 467.3377, calcd 467.3374 (C₂₆H₄₃N₄OSiB).

10,11-Bis(9-borabicyclo[3.3.1]non-9-yl)-1-(4-methylbenzoyl)-5-[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-4-yl]dipyrromethane [(9-BBN)₂-16]. Following a

published procedure^{26,33} with slight modification, a solution of EtMgBr (0.5 mL, 0.5 mmol, 1.0 M in THF) was added slowly to a solution of **15a** (86 mg, 0.25 mmol) in THF (0.5 mL) under argon. The resulting mixture was stirred at room temperature for 10 min, and then cooled to -78°C . A solution of **4** (57 mg, 0.25 mmol) in THF (0.5 mL) was added. The reaction mixture was stirred at -78°C for 10 min, and then allowed to warm to room temperature with stirring for 1 h. The reaction mixture was treated with saturated aqueous NH_4Cl (2 mL) and ethyl acetate (10 mL). The organic layer was washed (water and brine), dried (Na_2SO_4) and filtered. The filtrate was concentrated. The crude product (a red-orange oil) thus obtained was dissolved in CH_2Cl_2 (0.5 mL) and treated with TEA (84 μL , 0.60 mmol) followed by 9-BBN-OTf (1 mL, 0.5 mmol, 0.5 M in hexane) with stirring at room temperature. After 1 h the mixture was poured onto a pad of silica (2 x 4 cm), which was eluted with CH_2Cl_2 . The product eluted as a fast-moving yellow band, which upon concentration afforded a yellow-orange solid (60 mg, 34%): mp $170\text{--}172^{\circ}\text{C}$; ^1H NMR δ -0.02 (s, 9H), $0.62\text{--}0.88$ (m, 4H), $0.86\text{--}0.91$ (m, 2H), $1.69\text{--}1.83$ (m, 12H), $1.92\text{--}2.27$ (m, 12H), 2.50 (s, 3H), $3.45\text{--}3.50$ (m, 2H), 5.22 (d, $J = 2.8$ Hz, 2H), 5.70 (s, 1H), $6.04\text{--}6.05$ (m, 2H), $6.45\text{--}6.55$ (m, 1H), 6.66 (d, $J = 4.4$ Hz, 1H), $7.28\text{--}7.30$ (m, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), $7.40\text{--}7.45$ (m, 1H), 8.17 (d, $J = 8.0$ Hz, 2H), $8.28\text{--}8.29$ (m, 1H); ^{13}C NMR δ -1.3 , 17.9 , 21.8 , 22.1 , 23.4 , 23.82 , 23.91 , 25.2 , 26.2 , 26.4 , 29.8 , 30.57 , 30.66 , 30.72 , 31.0 , 34.49 , 34.53 , 34.67 , 34.77 , 38.2 , 67.7 , 77.6 (overlapped with CHCl_3), 105.5 , 105.9 , 115.9 , 117.9 , 120.8 , 123.8 , 129.1 , 129.87 , 130.02 , 131.9 , 133.8 , 134.8 , 142.0 , 145.2 , 149.2 , 174.3 ; ^{11}B NMR (at room temperature) δ 1.44 , 12.06 ; ^{15}N NMR δ -146.1 , -160.5 , -194.9 , 198.5 (gHMBC); FAB-MS obsd 700.4520 , calcd 700.4515 ($\text{C}_{42}\text{H}_{58}\text{B}_2\text{N}_4\text{O}_2\text{Si}$); λ_{abs} (THF) 298 , 372 nm.

Large Scale Synthesis of (9-BBN)₂-16. Following a published procedure^{26,33} with slight modification, a solution of EtMgBr (7.7 mL, 7.7 mmol, 1.0 M in THF) was added slowly to a solution of **15a** (1.31 g, 3.82 mmol) in THF (3.8 mL) under argon. The resulting mixture was stirred at room temperature for 10 min and then cooled to -78°C . A solution of **4** (876 mg, 3.82 mmol) in THF (3.8 mL) was added. The reaction mixture was stirred at -78°C for 10 min and then allowed to warm to room temperature with stirring for 1 h. The reaction mixture was treated with saturated aqueous NH_4Cl (20 mL) and ethyl acetate (100 mL). The organic layer was washed (water and brine), dried (Na_2SO_4) and filtered. The filtrate was concentrated. The crude product (a red-orange oil) thus obtained was dissolved in CH_2Cl_2 (7.7 mL) and treated with TEA (1.28 mL, 9.17 mmol) and 9-BBN-OTf (15.3 mL, ~ 7.7 mmol, 0.5 M in hexane) with stirring at room temperature. After 1 h, the mixture was poured onto a pad of silica (4 x 20 cm), which was eluted with CH_2Cl_2 . The product eluted as a fast-moving yellow band, which upon concentration afforded a yellow-orange solid (0.80 g, 30%). Characterization data (mp, ^1H NMR, FAB-MS) were consistent with the values reported above.

5,15-Bis(4-methylphenyl)-10,20-bis[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-4-yl]porphyrin [(SEM)₂-17]. Following general procedures^{25,33} with slight modification, a sample of NaBH_4 (0.32 g, 8.5 mmol) was slowly added in small portions to a stirred solution of **(9-BBN)₂-16** (0.20 g, 0.29 mmol) at 0°C in THF/MeOH (3:1, 8.4 mL). The progress of the reaction was monitored by TLC analysis (silica, CH_2Cl_2). The reaction was complete within 2 h, whereupon the reaction mixture was treated with saturated aqueous NH_4Cl (50 mL) and ethyl acetate. The organic layer was washed with water, dried (Na_2SO_4), and concentrated to afford the carbinol as an orange oil. The carbinol (~ 0.29 mmol) was immediately dissolved in CH_2Cl_2 (68 mL), to which $\text{Yb}(\text{OTf})_3$ (0.14 g, 0.22 mmol) was added. The reaction mixture instantly darkened. After 2 h, the spectroscopic yield of porphyrin had essentially leveled off, whereupon DDQ (0.12 g, 53 mmol) was added. After stirring at room temperature for 30 min, TEA (80 μL ,

0.57 mmol) was added. The entire reaction mixture was filtered through a pad of silica (CH₂Cl₂ → ethyl acetate) until the eluent was no longer dark. Removal of solvent gave a dark solid, which upon purification by column chromatography [silica, CH₂Cl₂/ethyl acetate (4:1) → (1:1)] gave a purple solid (19 mg, 15%): ¹H NMR δ -2.75 to -2.71 (br, 2H), 0.10 (s, 18H), 1.10 (t, *J* = 8.0 Hz, 4H), 2.72 (s, 6H), 3.84 (t, *J* = 8.0 Hz, 4H), 5.64 (s, 4H), 7.57 (d, *J* = 7.6 Hz, 4H), 7.82 (d, *J* = 1.2 Hz, 2H), 8.13 (d, *J* = 7.6 Hz, 4H), 8.13 (d, *J* = 1.2 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 4H), 9.2 (d, *J* = 4.8 Hz, 4H); LD-MS obsd 883.0; FAB-MS obsd 883.4305, calcd 883.4300 [(M + H)⁺, M = C₅₂H₅₈N₈O₂Si₂]; λ_{abs} (THF) 422, 517, 558 nm; λ_{em} (CH₂Cl₂) 670, 725 nm.

Synthesis of Porphyrin (SEM)₂-17 from Bu₂B-15a. A solution of **Bu₂B-15a** (615 mg, 1.32 mmol) and *p*-tolualdehyde (156 μL, 1.32 mmol) in CH₂Cl₂ (132 mL) was treated with TFA (362 μL, 4.70 mmol) under argon at room temperature for 1 h. DDQ (449 mg, 1.98 mmol) was added. The solvent was removed under reduced pressure. Chromatography [silica, CH₂Cl₂/ethyl acetate (1:1) → ethyl acetate] yielded a purple solid (154 mg, 26%). Characterization data (UV-vis, ¹H NMR, LD-MS) were consistent with the values reported above.

Synthesis of Dialkylated Imidazolium–Porphyrins:

Zn(II)-5-[1,3-Bis(4-sulfobutyl)imidazol-2-ium]-10-phenylporphyrin (Zn12-S₂). Following a general procedure,³¹ a mixture of porphyrin **SEM-Zn12** (32 mg, 0.050 mmol) and TBAF (0.75 mL, 0.75 mmol, 1.0 M in THF) was heated to reflux for 40 h. After removal of the solvent, the solid residue was repeatedly washed with water to remove excess TBAF, affording **Zn12** as a single porphyrin product (confirmed by LD-MS analysis). The sample of **Zn12** (~0.05 mmol) was then treated with NaOMe (11 mg, 0.20 mmol) in THF (5 mL). The mixture was stirred for 3.5 h at room temperature. The reaction mixture was cooled using an ice bath. A sample of 1,4-butane sultone (0.10 mL, 1.0 mmol) was added, and the mixture was heated to reflux for 2 days. LD-MS analysis of the crude reaction mixture did not show formation of the product. The reaction mixture was concentrated to dryness under reduced pressure. 1,4-Butane sultone (0.05 mL, 0.5 mmol) and DMF (5 mL) were added, and the mixture was heated at 60 °C for 3 days. After removal of DMF under high vacuum, the residue was washed with ethanol to extract the porphyrin product. The ethanol-soluble portion was concentrated and repeatedly washed with ether to remove excess 1,4-butane sultone. The resulting residue was treated with water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted once again with ethyl acetate. The organic layers were combined and washed repeatedly with water. The organic layer was concentrated. The resulting solid material was treated with diethyl ether, and the resulting suspension was sonicated and centrifuged. The supernatant was decanted and the remaining residue was dried to afford Zn(II)-5-[1-(4-sulfobutyl)imidazol-2-ium]-10-phenylporphyrin as a red solid (**Zn12-S**, 4 mg, 10%): ¹H NMR (CD₃OD) δ -0.05–0.15 (m, 2H), 0.12–0.18 (m, 2H), 1.57 (t, *J* = 7.6 Hz, 2H), 1.81 (s, 1H), 1.84–2.00 (m, 2H), 5.50 (d, *J* = 4.4 Hz, 2H), 5.79 (s, 1H), 7.76–7.98 (m, 2H), 8.01 (t, *J* = 7.6 Hz, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 8.70 (d, *J* = 7.6 Hz, 2H), 8.86 (d, *J* = 4.4 Hz, 2H), 9.16 (d, *J* = 4.4 Hz, 2H), 9.51 (d, *J* = 4.4 Hz, 2H), 10.24 (s, 1H); LD-MS obsd 649.3; HPLC *t*_R = 20.16 min; ESI-MS (–) obsd 649.1, calcd 649.1 (C₃₃H₂₅N₆O₃SZn); λ_{abs} (MeOH) 409, 542 nm. The initial aqueous layer was concentrated and purified by reverse-phase column chromatography (silica RP-18, water → water/MeOH (1:9) to afford the title compound as a red solid (4 mg, 10%) (see Note 1): HPLC *t*_R = 18.56 min; ESI-MS (–) obsd 785.1, calcd 785.1 (C₃₇H₃₃N₆O₆S₂Zn, lacking counterion); λ_{abs} (water) 409, 543 nm.

Note 1: A single peak corresponding to the bis-sulfoalkyl porphyrin **Zn12-S₂** was observed both in RP-HPLC and in ESI-MS analysis before column purification. After column

purification a mixture of mono-sulfoalkyl porphyrin **Zn12-S** and bis-sulfoalkyl porphyrin **Zn12-S₂** was observed upon RP-HPLC and in ESI-MS analysis. It is assumed that the desired bis-alkyl product decomposed during reverse-phase silica column chromatography giving rise to a mixture of products, including the corresponding mono-sulfoalkyl porphyrin **Zn12-S**.

Pd(II)-5-(1,3-Diethylimidazol-2-ium)-10-phenylporphyrin (Pd12-Et₂). Following a general procedure,³¹ porphyrin **SEM-Pd12** (6.9 mg, 0.010 mmol) was treated with TBAF (0.75 mL, 0.75 mmol, 1.0 M in THF), and the reaction mixture was heated to reflux for 21 h. After removal of the solvent, the residue was repeatedly washed with water to remove excess TBAF. The residue was extracted with CH₂Cl₂. The extract was concentrated to afford **Pd12** as a single product (confirmed by TLC and LD-MS analysis). The entire sample of **Pd12** (~0.010 mmol) was then treated with EtI (0.080 mL, 1.0 mmol) in THF (0.20 mL) at reflux for 3 days. After removal of THF, the residue was washed with hexanes and dried, affording a purple solid (6.1 mg, 83% yield, assuming an iodide counterion): ¹H NMR (CD₂Cl₂ + CDCl₃) δ 1.30 (t, *J* = 6.9 Hz, 6H), 4.08–4.16 (m, 4H), 7.78–7.92 (m, 3H), 8.12–8.32 (m, 2H), 8.58 (s, 2H), 8.75 (d, *J* = 4.8 Hz, 2H), 9.08 (d, *J* = 4.8 Hz, 2H), 9.36 (d, *J* = 4.8 Hz, 2H), 9.51 (d, *J* = 4.8 Hz, 2H), 10.43 (s, 2H); LD-MS obsd 613.1; FAB-MS obsd 613.1363, calcd 613.1332 (C₃₃H₂₇N₆Pd, lacking counterion); λ_{abs} (THF) 400, 515, 547 nm.

Zn(II)-5-(1,3-Diethylimidazol-2-ium)-10-[4-(ethoxycarbonylmethoxy)phenyl]porphyrin (Zn13-Et₂). Following a general procedure for zinc metalation,⁴⁹ a solution of porphyrin **13** (14 mg, 0.025 mmol) in CH₂Cl₂/MeOH (6 mL, 3:1) was treated with anhydrous Zn(OAc)₂ (0.24 g, 1.3 mmol). The reaction mixture was stirred at room temperature for 19 h. The reaction mixture was concentrated under reduced pressure. The resulting solid residue was taken into a large volume of ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The organic layers were combined and washed with water. The organic layer was separated, dried (Na₂SO₄) and concentrated to afford porphyrin **Zn13**. The porphyrin showed a single component by TLC, and the expected molecule ion peak was observed by LDMS analysis. This porphyrin was used for the dialkylation reaction without further purification or characterization. The entire sample of **Zn13** (~0.025 mmol) was treated with EtI (0.200 mL, 2.50 mmol) in THF (0.5 mL), and the reaction mixture was heated to reflux for 3 days. After removal of THF, the crude mixture was purified by column chromatography [silica, CH₂Cl₂/MeOH (19:1) → (4:1)] to afford a solid residue. The resulting residue was treated with diethyl ether. The suspension was sonicated and centrifuged. The supernatant was decanted, and the remaining residue was dried to afford a dark purple solid (6.0 mg, 30%, assuming an iodide counterion): ¹H NMR (400 MHz, CD₃OD) δ 1.19–1.33 (m, 6H), 1.36–1.46 (m, 3H), 4.40 (dd, *J* = 7.2 Hz, 2H), 4.35–4.45 (m, 4H), 5.01–5.10 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.38–8.44 (m, 2H), 8.83 (d, *J* = 4.4 Hz, 2H), 9.09 (d, *J* = 4.4 Hz, 2H), 9.46 (d, *J* = 4.4 Hz, 2H), 9.63 (d, *J* = 4.4 Hz, 2H), 10.44 (s, 2H); LD-MS obsd 673.5; FAB-MS obsd 673.1896, calcd 673.1900 (C₃₇H₃₃N₆O₃Zn, lacking counterion); λ_{abs} (MeOH) 410, 542, 577 nm; λ_{em} (MeOH) 585, 640 nm.

Microscale Preparation of Magnesium and Indium Porphyrins:

The following metalloporphyrins were prepared at the microscale level. The characterization data, while consistent with the title compounds, are incomplete, and, hence, the assignments remain provisional. The magnesium porphyrins that contain an imidazole group proved difficult to characterize (by NMR spectroscopy and often mass spectrometry) owing to

extensive aggregation. For the magnesium chelates, dissolution in CH₂Cl₂ yielded a solid thin film of self-assembled porphyrin within a few minutes. Magnesium chelates of imidazolyl-porphyrins are well known to form aggregates in non-polar solvents.⁴⁶

Mg(II)-5,15-Bis(4-methylphenyl)-10,20-bis[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-2-yl]porphyrin [(SEM)₂-Mg6]. Following a general procedure,⁵⁰ a solution of (SEM)₂-6 (2 mg, 2 μmol) in anhydrous CH₂Cl₂ (0.5 mL) was treated with a solution of MgI₂/*N,N*-diisopropylethylamine in anhydrous ether (1 mL). The reaction mixture was stirred at room temperature for 24 h. TLC showed the formation of a single porphyrin product. The crude reaction mixture was diluted with CH₂Cl₂ and washed with 5% aqueous NaHCO₃ solution. The organic layer was dried (Na₂SO₄) and concentrated to obtain the product (2 mg, quantitative): LD-MS obsd 902.5, 1806.6 (dimer); calcd 904.3915 (C₅₂H₅₆N₈O₂Si₂Mg); λ_{abs} 411, 429, 562 nm; λ_{em} 620, 670 nm.

Mg(II)-5,15-Bis(4-methylphenyl)-10-[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-2-yl]porphyrin (SEM-Mg8). Following a general procedure,⁵⁰ a solution of SEM-8 (2 mg, 3 μmol) in anhydrous CH₂Cl₂ (1 mL) was treated with a solution of MgI₂/*N,N*-diisopropylethylamine in anhydrous ether (1 mL). The reaction mixture was stirred at room temperature for 18 h to obtain an orange solution. TLC showed the formation of a single porphyrin product. The crude reaction mixture was diluted with CH₂Cl₂ and washed with 5% aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated (2 mg, quantitative): LD-MS obsd 707.5, 1415.9 (dimer); FAB-MS obsd 709.2967, calcd 709.2962 [(M + H)⁺, M = C₄₃H₄₀N₆OSiMg]; λ_{abs} 406, 423, 559 nm.

Mg(II)-5,15-Bis(4-methylphenyl)-10,20-bis[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-4-yl]porphyrin [(SEM)₂-Mg17]. Following a general procedure,⁵⁰ a solution of (SEM)₂-17 (2 mg, 2 μmol) in anhydrous CH₂Cl₂ (1 mL) was treated with a solution of MgI₂/*N,N*-diisopropylethylamine in anhydrous ether (1 mL). The reaction mixture was stirred at room temperature for 18 h. TLC showed the formation of a single porphyrin product. The crude reaction mixture was diluted with CH₂Cl₂ and washed with 5% aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated (2 mg, quantitative): LD-MS obsd 903.5, 1807.5 (dimer); calcd 904.3915 (C₅₂H₅₆N₈O₂Si₂Mg); λ_{abs} 424, 513, 585 nm.

XIn(III)-5,15-Bis(4-methylphenyl)-10,20-bis[1-(2-(trimethylsilyl)ethoxymethyl)imidazol-2-yl]porphyrin [(SEM)₂-In6]. A solution of (SEM)₂-6 (3.0 mg, 3.4 μmol) in anhydrous DMF (1.0 mL) was treated with InCl₃ (33 mg, 0.15 mmol). The reaction mixture was heated at 90 °C for 2 days. TLC indicated the disappearance of the starting material and the formation of a new porphyrin product. The crude reaction mixture was diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated to obtain a dark green solid (2.0 mg, 59%): LD-MS obsd 996.0, calcd 995.3 [(M – X[–]), M = C₅₂H₅₆XInN₈O₂Si₂]; λ_{abs} 427, 558 nm; λ_{em} 620, 670 nm. The indium-porphyrin showed a sharp Soret band with no evidence of splitting.

4. X-Ray Structural Determination for (9-BBN)₂-5

Data Collection. The sample was mounted on 20-micron nylon loop with a small amount of immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 CCD diffractometer at 110K. The temperature of the sample was controlled with a cold stream of nitrogen from an Oxford Cryosystems 700 Series Cryostream Cooler. The unit cell dimensions were determined from a symmetry constrained fit of 5934 reflections with $4.52^\circ < 2(\text{theta}) < 48.44^\circ$. The data collection strategy was a number of w and j scans which collected data up to 49.5° ($2(\text{theta})$). The frame integration was performed using SAINT+. ^{S1} The resulting raw data were scaled and absorption-corrected using a multi-scan averaging of symmetry equivalent data using SADABS. ^{S2} The structure of (9-BBN)₂-5 [named (9-BBN)₂5 in the CIF file] was determined as described below. The structure is shown in Figure S1.

Figure S1. X-ray structure of (9-BBN)₂-5 showing the two dialkylboron groups and one SEM group, which fully mask the polar moieties (1-acylpyrrole moiety, pyrrole, and imidazole). Hydrogen atoms are omitted for clarity. The C–O bond (1.302 Å) is longer than that in 2-benzoylpyrrole (1.234 Å),³⁵ whereas the C–C bond between the carbonyl carbon and the α -carbon of the acylpyrrole (1.404 Å) is significantly shorter than that in 2-benzoylpyrrole (1.446 Å).³⁵ The B–N coordinate bond length (1.640 Å) is longer than the B–O coordinate bond length (1.557 Å). The oxygen (O43, O43') of the SEM group is disordered.

Structure Solution and Refinement. The structure was solved by direct methods using SIR92.^{S3} All non-hydrogen atoms were obtained from the initial E-map. The hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. All non-hydrogen atoms were allowed to refine anisotropically. The etheric oxygen, O43, was disordered over two sites. The displacement parameters were fixed and the occupancies were refined, normalized then fixed. Atom sites O43 and O43' were then both refined anisotropically. The ether of solvation also exhibited some disorder, but due to a lack of large well-defined peaks in the difference map in the vicinity of the ether molecule, no attempt was made to find and refine a positional order model. The structural model was fit to the data using full matrix least-squares based on F. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. A secondary extinction correction was included in the final refinements. The structure was refined, final tables (Tables S2-S5) and graphic plots were produced using the NRCVAX crystallographic program suite.^{S4}

Table S2. Crystallographic data and structure refinement for (9-BBN)₂-5.

Empirical formula	C ₄₆ H ₆₈ B ₂ N ₄ O ₃ Si	
Formula weight	774.76	
Temperature	110K	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.1750(9)Å	$\alpha = 78.820(3)^\circ$
	b = 13.0823(10)Å	$\beta = 71.278(3)^\circ$
	c = 16.1471(12)Å	$\gamma = 85.826(3)^\circ$
Volume	2193.1(3)Å ³	
Z	2	
Density (calculated)	1.173 Mg/m ³	
Absorption coefficient	0.10 mm ⁻¹	
F(000)	840.58	
Crystal size	0.24 x 0.08 x 0.04 mm ³	
Diffractometer	Bruker-Nonius X8 Apex2	
2Theta range for intensity data collection	4.52 to 48.44°	
Index ranges	-13 ≤ h ≤ 13, 0 ≤ k ≤ 15, -18 ≤ l ≤ 19	
Reflections collected	28845	
Independent reflections	7502	
Observed reflections (I > 1sigma(I))	5977	
Solution method	Direct methods (SIR 92)	
Refinement method	Full matrix least-squares based on F	
Data/parameters	5953 /515	
Goodness-of-fit	2.01	
Final R indices (based on F)	R = 0.082, Rw = 0.091	
R indices (all data)	R = 0.102, Rw = 0.096	

Table S3. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for (9-BBN)₂-5.

Name	x	y	z
C1	0.80231(32)	0.66631(26)	0.28590(21)
C2	0.77560(34)	0.62574(27)	0.37652(21)
C3	0.67026(34)	0.56522(28)	0.39990(22)
C4	0.63404(32)	0.56834(26)	0.32375(21)
C5	0.52262(32)	0.51706(27)	0.31768(21)
C6	0.40101(33)	0.56838(26)	0.36569(21)
C7	0.38200(35)	0.65633(27)	0.40417(22)
C8	0.25176(35)	0.66155(26)	0.44865(22)
C9	0.19662(33)	0.57740(27)	0.43676(21)
N10	0.71287(26)	0.63125(21)	0.25411(17)
N11	0.28753(26)	0.52012(21)	0.38445(17)
N12	0.60353(27)	0.33222(23)	0.36846(18)
C13	0.51135(32)	0.40046(27)	0.35683(21)
N14	0.39999(26)	0.35277(21)	0.38702(17)
C15	0.42318(35)	0.25079(27)	0.42132(22)
C16	0.54731(37)	0.23699(28)	0.41006(23)
C17	0.99417(32)	0.78750(26)	0.21736(21)
C18	1.03501(34)	0.87828(27)	0.15437(22)
C19	1.14083(35)	0.92944(27)	0.14981(23)
C20	1.21267(34)	0.89075(28)	0.20491(23)
C21	1.17323(35)	0.79899(28)	0.26756(23)
C22	1.06468(34)	0.74945(27)	0.27408(23)
C23	0.88563(32)	0.73424(26)	0.21677(22)
B24	0.73966(38)	0.68422(31)	0.15186(25)
C25	0.78374(33)	0.60939(27)	0.07918(21)
C26	0.84891(36)	0.67910(29)	-0.01140(22)
C27	0.77084(37)	0.77335(28)	-0.03788(22)
C28	0.70102(36)	0.83282(28)	0.03677(23)
C29	0.63604(34)	0.76318(27)	0.12745(22)
C30	0.52067(35)	0.70382(28)	0.12692(23)
C31	0.55494(35)	0.61798(28)	0.06970(23)
C32	0.67016(36)	0.55090(27)	0.07713(22)
B33	0.28118(39)	0.41171(31)	0.35795(25)
C34	0.14359(34)	0.35820(28)	0.39981(22)
C35	0.14633(37)	0.24555(30)	0.38247(25)
C36	0.20865(39)	0.23415(30)	0.28468(26)
C37	0.32643(35)	0.30080(30)	0.23548(23)
C38	0.31748(32)	0.41398(26)	0.25201(22)
C39	0.22381(35)	0.48377(30)	0.21409(23)
C40	0.08635(35)	0.45232(30)	0.25844(24)
C41	0.04798(33)	0.42587(30)	0.36051(23)
C42	0.74209(35)	0.34894(32)	0.33331(25)
O43	0.78082(36)	0.38626(30)	0.24786(25)
O43'	0.81146(57)	0.27270(48)	0.30080(38)

C44	0.81680(45)	0.29847(52)	0.19288(33)
C45	0.70162(38)	0.25183(32)	0.18531(25)
Si46	0.73492(10)	0.19325(7)	0.08250(6)
C47	0.59232(38)	0.12331(31)	0.09059(26)
C48	0.77340(39)	0.29669(29)	-0.01814(25)
C49	0.86728(38)	0.09748(30)	0.08149(24)
C50	1.33185(38)	0.94444(30)	0.19707(26)
O51	0.85621(21)	0.74844(17)	0.14355(14)
O1s	0.71501(38)	-0.00719(26)	0.43528(32)
C1s	0.76969(98)	0.04704(57)	0.55768(55)
C2s	0.83163(69)	0.02631(45)	0.45738(51)
C3s	0.75933(92)	-0.03177(45)	0.35939(38)
C4s	0.63817(80)	-0.06598(40)	0.34159(37)
H2	0.82182(0)	0.63750(0)	0.41464(0)
H3	0.62799(0)	0.52698(0)	0.45800(0)
H5	0.52858(0)	0.52549(0)	0.25609(0)
H7	0.44540(0)	0.70388(0)	0.40114(0)
H8	0.20907(0)	0.71464(0)	0.48139(0)
H9	0.10844(0)	0.56087(0)	0.46093(0)
H15	0.36026(0)	0.19800(0)	0.44943(0)
H16	0.58900(0)	0.17361(0)	0.42755(0)
H18	0.98846(0)	0.90492(0)	0.11395(0)
H19	1.16586(0)	0.99295(0)	0.10785(0)
H21	1.22250(0)	0.77051(0)	0.30578(0)
H22	1.03650(0)	0.68840(0)	0.31854(0)
H25	0.84401(0)	0.55988(0)	0.09503(0)
H26a	0.86754(0)	0.63703(0)	-0.05664(0)
H26b	0.92621(0)	0.70454(0)	-0.00943(0)
H27a	0.70873(0)	0.74864(0)	-0.05859(0)
H27b	0.82596(0)	0.82098(0)	-0.08527(0)
H28a	0.76107(0)	0.87593(0)	0.04459(0)
H28b	0.63746(0)	0.87601(0)	0.01855(0)
H29	0.60740(0)	0.80632(0)	0.17200(0)
H30a	0.46629(0)	0.75356(0)	0.10412(0)
H30b	0.47612(0)	0.67212(0)	0.18686(0)
H31a	0.57148(0)	0.65090(0)	0.00865(0)
H31b	0.48363(0)	0.57293(0)	0.08718(0)
H32a	0.64368(0)	0.50007(0)	0.13082(0)
H32b	0.69812(0)	0.51621(0)	0.02687(0)
H34	0.11693(0)	0.35632(0)	0.46283(0)
H35a	0.19200(0)	0.20216(0)	0.41751(0)
H35b	0.06080(0)	0.22199(0)	0.40097(0)
H36a	0.14757(0)	0.25394(0)	0.25392(0)
H36b	0.23204(0)	0.16226(0)	0.28335(0)
H37a	0.39569(0)	0.26677(0)	0.25318(0)
H37b	0.34335(0)	0.30361(0)	0.17292(0)
H38	0.39971(0)	0.44438(0)	0.22492(0)
H39a	0.24564(0)	0.48089(0)	0.15203(0)

H39b	0.23182(0)	0.55398(0)	0.22095(0)
H40a	0.03354(0)	0.50865(0)	0.24215(0)
H40b	0.07244(0)	0.39184(0)	0.23741(0)
H41a	0.03727(0)	0.49060(0)	0.38183(0)
H41b	-0.03108(0)	0.38999(0)	0.38211(0)
H42a	0.78277(0)	0.28261(0)	0.34350(0)
H42b	0.76475(0)	0.39592(0)	0.36456(0)
H44a	0.85712(0)	0.24369(0)	0.22356(0)
H44b	0.87397(0)	0.32405(0)	0.13493(0)
H45a	0.66519(0)	0.19972(0)	0.23661(0)
H45b	0.64239(0)	0.30832(0)	0.18241(0)
H47a	0.57216(0)	0.06973(0)	0.14265(0)
H47b	0.52294(0)	0.17191(0)	0.09452(0)
H47c	0.60757(0)	0.09252(0)	0.03874(0)
H48a	0.70303(0)	0.34416(0)	-0.01476(0)
H48b	0.84645(0)	0.33382(0)	-0.02180(0)
H48c	0.79049(0)	0.26556(0)	-0.06999(0)
H49a	0.94161(0)	0.13321(0)	0.07736(0)
H49b	0.84451(0)	0.04635(0)	0.13516(0)
H49c	0.88393(0)	0.06362(0)	0.03117(0)
H50a	1.36854(0)	0.90693(0)	0.24047(0)
H50b	1.39075(0)	0.94574(0)	0.13859(0)
H50c	1.31224(0)	1.01449(0)	0.20732(0)
H1sa	0.83283(0)	0.06832(0)	0.57930(0)
H1sb	0.70648(0)	0.10090(0)	0.55814(0)
H1sc	0.73106(0)	-0.01588(0)	0.59521(0)
H2sa	0.89415(0)	-0.02835(0)	0.45504(0)
H2sb	0.86957(0)	0.08843(0)	0.41796(0)
H3sa	0.79829(0)	0.02704(0)	0.31560(0)
H3sb	0.81946(0)	-0.08814(0)	0.35866(0)
H4sa	0.66252(0)	-0.08568(0)	0.28414(0)
H4sb	0.59990(0)	-0.12419(0)	0.38641(0)
H4sc	0.57873(0)	-0.00901(0)	0.34335(0)

Table S4. Bond lengths [Å] for (9-BBN)₂-5.

Bond	Length	Bond	Length
C1-C2	1.398(5)	B33-C34	1.618(5)
C1-N10	1.400(5)	B33-C38	1.621(5)
C1-C23	1.404(5)	C34-C35	1.549(5)
C2-C3	1.375(5)	C34-C41	1.552(5)
C2-H2	0.960(4)	C34-H34	0.960(3)
C3-C4	1.405(5)	C35-C36	1.540(6)
C3-H3	0.960(3)	C35-H35a	0.960(4)
C4-C5	1.495(5)	C35-H35b	0.960(4)
C4-N10	1.352(4)	C36-C37	1.533(5)
C5-C6	1.514(5)	C36-H36a	0.960(4)
C5-C13	1.531(5)	C36-H36b	0.960(4)
C5-H5	0.960(3)	C37-C38	1.545(5)
C6-C7	1.383(5)	C37-H37a	0.960(4)
C6-N11	1.376(4)	C37-H37b	0.960(4)
C7-C8	1.404(5)	C38-C39	1.536(5)
C7-H7	0.960(4)	C38-H38	0.960(3)
C8-C9	1.373(5)	C39-C40	1.521(5)
C8-H8	0.960(3)	C39-H39a	0.960(3)
C9-N11	1.375(4)	C39-H39b	0.960(4)
C9-H9	0.960(4)	C40-C41	1.538(5)
N10-B24	1.602(5)	C40-H40a	0.960(4)
N11-B33	1.571(5)	C40-H40b	0.960(4)
N12-C13	1.349(5)	C41-H41a	0.960(4)
N12-C16	1.384(5)	C41-H41b	0.960(4)
N12-C42	1.485(5)	C42-O43	1.310(6)
C13-N14	1.335(4)	C42-O43'	1.304(7)
N14-C15	1.382(4)	C42-H42a	0.960(4)
N14-B33	1.640(5)	C42-H42b	0.960(4)
C15-C16	1.343(6)	O43-O43'	1.636(7)
C15-H15	0.960(3)	O43-C44	1.539(6)
C16-H16	0.960(4)	O43'-C44	1.692(8)
C17-C18	1.402(5)	O43'-H42a	0.694(6)
C17-C22	1.392(5)	O43'-H44a	1.306(6)
C17-C23	1.446(5)	C44-C45	1.513(6)
C18-C19	1.375(5)	C44-H44a	0.960(7)
C18-H18	0.960(4)	C44-H44b	0.960(5)
C19-C20	1.385(6)	C45-Si46	1.881(4)
C19-H19	0.960(3)	C45-H45a	0.960(4)
C20-C21	1.407(5)	C45-H45b	0.960(5)
C20-C50	1.509(5)	Si46-C47	1.851(4)
C21-C22	1.382(5)	Si46-C48	1.855(4)
C21-H21	0.960(4)	Si46-C49	1.866(4)
C22-H22	0.960(3)	C47-H47a	0.960(4)
C23-O51	1.302(4)	C47-H47b	0.960(4)
B24-C25	1.607(5)	C47-H47c	0.960(4)

B24-C29	1.589(6)	C48-H48a	0.960(4)
B24-O51	1.557(5)	C48-H48b	0.960(4)
C25-C26	1.548(5)	C48-H48c	0.960(4)
C25-C32	1.541(5)	C49-H49a	0.960(4)
C25-H25	0.960(4)	C49-H49b	0.960(4)
C26-C27	1.531(6)	C49-H49c	0.960(4)
C26-H26a	0.960(3)	C50-H50a	0.960(4)
C26-H26b	0.960(4)	C50-H50b	0.960(4)
C27-C28	1.529(5)	C50-H50c	0.960(4)
C27-H27a	0.960(4)	O1s-C2s	1.569(8)
C27-H27b	0.960(3)	O1s-C3s	1.261(8)
C28-C29	1.548(5)	C1s-C2s	1.612(12)
C28-H28a	0.960(4)	C1s-H1sa	0.960(9)
C28-H28b	0.960(4)	C1s-H1sb	0.960(9)
C29-C30	1.556(5)	C1s-H1sc	0.960(8)
C29-H29	0.960(3)	C2s-H2sa	0.960(7)
C30-C31	1.541(5)	C2s-H2sb	0.960(6)
C30-H30a	0.960(4)	C3s-C4s	1.582(12)
C30-H30b	0.960(3)	C3s-H3sa	0.960(6)
C31-C32	1.528(6)	C3s-H3sb	0.960(8)
C31-H31a	0.960(3)	C4s-H4sa	0.960(6)
C31-H31b	0.960(4)	C4s-H4sb	0.960(6)
C32-H32a	0.960(3)	C4s-H4sc	0.960(7)
C32-H32b	0.960(3)		

Table S5. Bond angles [°] for (9-BBN)₂-5.

Bond	Angle	Bond	Angle
C2-C1-N10	109.7(3)	C34-C35-H35a	108.3(3)
C2-C1-C23	141.1(3)	C34-C35-H35b	108.2(4)
N10-C1-C23	109.2(3)	C36-C35-H35a	108.2(4)
C1-C2-C3	106.1(3)	C36-C35-H35b	108.1(3)
C1-C2-H2	126.9(3)	H35a-C35-H35b	109.5(4)
C3-C2-H2	127.0(3)	C35-C36-C37	114.6(3)
C2-C3-C4	108.3(3)	C35-C36-H36a	108.2(4)
C2-C3-H3	126.4(4)	C35-C36-H36b	108.0(4)
C4-C3-H3	125.2(3)	C37-C36-H36a	108.1(4)
C3-C4-C5	127.4(3)	C37-C36-H36b	108.5(4)
C3-C4-N10	109.4(3)	H36a-C36-H36b	109.5(4)
C5-C4-N10	123.1(3)	C36-C37-C38	116.0(3)
C4-C5-C6	110.4(3)	C36-C37-H37a	107.8(3)
C4-C5-C13	114.8(3)	C36-C37-H37b	107.7(3)
C4-C5-H5	108.3(3)	C38-C37-H37a	108.0(3)
C6-C5-C13	106.9(3)	C38-C37-H37b	107.8(3)
C6-C5-H5	108.4(3)	H37a-C37-H37b	109.5(4)
C13-C5-H5	107.9(3)	B33-C38-C37	108.9(3)
C5-C6-C7	130.1(3)	B33-C38-C39	110.3(3)
C5-C6-N11	119.7(3)	B33-C38-H38	106.8(3)
C7-C6-N11	109.9(3)	C37-C38-C39	114.3(3)
C6-C7-C8	106.2(3)	C37-C38-H38	108.2(3)
C6-C7-H7	126.7(4)	C39-C38-H38	108.1(3)
C8-C7-H7	127.1(4)	C38-C39-C40	114.3(3)
C7-C8-C9	107.8(3)	C38-C39-H39a	108.1(3)
C7-C8-H8	126.0(4)	C38-C39-H39b	108.5(3)
C9-C8-H8	126.2(4)	C40-C39-H39a	108.2(3)
C8-C9-N11	109.4(3)	C40-C39-H39b	108.2(3)
C8-C9-H9	125.6(3)	H39a-C39-H39b	109.5(4)
N11-C9-H9	125.0(3)	C39-C40-C41	113.7(3)
C1-N10-C4	106.5(3)	C39-C40-H40a	108.7(3)
C1-N10-B24	109.0(3)	C39-C40-H40b	108.5(3)
C4-N10-B24	144.5(3)	C41-C40-H40a	108.4(3)
C6-N11-C9	106.8(3)	C41-C40-H40b	108.0(3)
C6-N11-B33	121.4(3)	H40a-C40-H40b	109.5(4)
C9-N11-B33	131.3(3)	C34-C41-C40	116.0(3)
C13-N12-C16	107.5(3)	C34-C41-H41a	107.4(3)
C13-N12-C42	127.6(3)	C34-C41-H41b	108.2(3)
C16-N12-C42	124.5(3)	C40-C41-H41a	107.3(3)
C5-C13-N12	128.3(3)	C40-C41-H41b	108.3(3)
C5-C13-N14	121.5(3)	H41a-C41-H41b	109.5(3)
N12-C13-N14	110.2(3)	N12-C42-O43	112.5(3)
C13-N14-C15	106.2(3)	N12-C42-O43'	116.6(4)
C13-N14-B33	118.4(3)	N12-C42-H42a	107.6(4)
C15-N14-B33	133.5(3)	N12-C42-H42b	109.3(3)

N14-C15-C16	109.5(3)	O43-C42-O43'	77.5(4)
N14-C15-H15	125.3(4)	O43-C42-H42a	108.3(4)
C16-C15-H15	125.1(4)	O43-C42-H42b	109.4(4)
N12-C16-C15	106.6(3)	O43'-C42-H42a	31.3(3)
N12-C16-H16	126.6(4)	O43'-C42-H42b	126.4(4)
C15-C16-H16	126.8(4)	H42a-C42-H42b	109.6(4)
C18-C17-C22	118.3(3)	C42-O43-O43'	51.1(3)
C18-C17-C23	118.6(3)	C42-O43-C44	111.5(4)
C22-C17-C23	123.0(3)	O43'-O43-C44	64.3(4)
C17-C18-C19	120.8(3)	C42-O43'-O43	51.4(3)
C17-C18-H18	119.5(3)	C42-O43'-C44	103.1(5)
C19-C18-H18	119.7(3)	C42-O43'-H42a	45.9(4)
C18-C19-C20	121.0(3)	C42-O43'-H44a	137.4(5)
C18-C19-H19	119.9(4)	O43-O43'-C44	55.0(3)
C20-C19-H19	119.0(4)	O43-O43'-H42a	96.9(6)
C19-C20-C21	118.5(3)	O43-O43'-H44a	87.5(4)
C19-C20-C50	121.0(3)	C44-O43'-H42a	147.5(7)
C21-C20-C50	120.6(3)	C44-O43'-H44a	34.4(3)
C20-C21-C22	120.5(3)	H42a-O43'-H44a	172.9(8)
C20-C21-H21	119.6(4)	O43-C44-O43'	60.6(3)
C22-C21-H21	119.9(3)	O43-C44-C45	111.8(4)
C17-C22-C21	120.8(3)	O43-C44-H44a	107.9(4)
C17-C22-H22	119.1(3)	O43-C44-H44b	110.1(5)
C21-C22-H22	120.0(4)	O43'-C44-C45	108.5(4)
C1-C23-C17	129.2(3)	O43'-C44-H44a	50.2(3)
C1-C23-O51	112.2(3)	O43'-C44-H44b	140.3(5)
C17-C23-O51	118.6(3)	C45-C44-H44a	106.8(5)
N10-B24-C25	117.6(3)	C45-C44-H44b	110.5(4)
N10-B24-C29	117.5(3)	H44a-C44-H44b	109.6(5)
N10-B24-O51	96.6(3)	C44-C45-Si46	113.5(3)
C25-B24-C29	107.9(3)	C44-C45-H45a	110.7(4)
C25-B24-O51	107.8(3)	C44-C45-H45b	106.0(4)
C29-B24-O51	108.0(3)	Si46-C45-H45a	109.0(3)
B24-C25-C26	107.0(3)	Si46-C45-H45b	108.1(3)
B24-C25-C32	110.8(3)	H45a-C45-H45b	109.5(4)
B24-C25-H25	108.1(3)	C45-Si46-C47	108.34(18)
C26-C25-C32	112.1(3)	C45-Si46-C48	110.40(18)
C26-C25-H25	109.3(3)	C45-Si46-C49	107.19(19)
C32-C25-H25	109.4(3)	C47-Si46-C48	109.56(19)
C25-C26-C27	115.1(3)	C47-Si46-C49	109.00(18)
C25-C26-H26a	108.1(3)	C48-Si46-C49	112.24(18)
C25-C26-H26b	108.6(3)	Si46-C47-H47a	109.7(3)
C27-C26-H26a	107.7(3)	Si46-C47-H47b	109.0(3)
C27-C26-H26b	107.8(3)	Si46-C47-H47c	109.6(3)
H26a-C26-H26b	109.5(4)	H47a-C47-H47b	109.5(4)
C26-C27-C28	115.2(3)	H47a-C47-H47c	109.5(4)
C26-C27-H27a	107.6(3)	H47b-C47-H47c	109.5(4)
C26-C27-H27b	108.6(4)	Si46-C48-H48a	109.4(3)

C28-C27-H27a	107.6(3)	Si46-C48-H48b	109.6(3)
C28-C27-H27b	108.2(3)	Si46-C48-H48c	109.4(3)
H27a-C27-H27b	109.5(3)	H48a-C48-H48b	109.5(4)
C27-C28-C29	114.8(3)	H48a-C48-H48c	109.5(4)
C27-C28-H28a	107.9(3)	H48b-C48-H48c	109.5(4)
C27-C28-H28b	108.0(3)	Si46-C49-H49a	109.5(3)
C29-C28-H28a	108.3(3)	Si46-C49-H49b	109.7(3)
C29-C28-H28b	108.2(3)	Si46-C49-H49c	109.3(3)
H28a-C28-H28b	109.5(4)	H49a-C49-H49b	109.5(4)
B24-C29-C28	107.6(3)	H49a-C49-H49c	109.5(4)
B24-C29-C30	111.0(3)	H49b-C49-H49c	109.5(4)
B24-C29-H29	108.0(3)	C20-C50-H50a	109.2(3)
C28-C29-C30	112.8(3)	C20-C50-H50b	109.5(3)
C28-C29-H29	108.8(3)	C20-C50-H50c	109.7(4)
C30-C29-H29	108.4(3)	H50a-C50-H50b	109.5(4)
C29-C30-C31	114.5(3)	H50a-C50-H50c	109.5(4)
C29-C30-H30a	108.1(3)	H50b-C50-H50c	109.5(4)
C29-C30-H30b	108.7(3)	C23-O51-B24	113.0(3)
C31-C30-H30a	108.0(3)	C2s-O1s-C3s	105.5(6)
C31-C30-H30b	108.1(3)	C2s-C1s-H1sa	110.7(8)
H30a-C30-H30b	109.5(4)	C2s-C1s-H1sb	108.7(7)
C30-C31-C32	115.2(3)	C2s-C1s-H1sc	109.0(6)
C30-C31-H31a	108.0(3)	H1sa-C1s-H1sb	109.5(7)
C30-C31-H31b	108.1(3)	H1sa-C1s-H1sc	109.5(8)
C32-C31-H31a	108.0(3)	H1sb-C1s-H1sc	109.5(10)
C32-C31-H31b	108.1(3)	O1s-C2s-C1s	102.6(6)
H31a-C31-H31b	109.5(4)	O1s-C2s-H2sa	111.4(5)
C25-C32-C31	116.0(3)	O1s-C2s-H2sb	111.7(5)
C25-C32-H32a	108.1(3)	C1s-C2s-H2sa	110.6(6)
C25-C32-H32b	107.8(3)	C1s-C2s-H2sb	110.9(6)
C31-C32-H32a	107.7(3)	H2sa-C2s-H2sb	109.5(8)
C31-C32-H32b	107.6(3)	O1s-C3s-C4s	103.1(7)
H32a-C32-H32b	109.5(3)	O1s-C3s-H3sa	110.8(6)
N11-B33-N14	99.1(3)	O1s-C3s-H3sb	111.9(6)
N11-B33-C34	114.2(3)	C4s-C3s-H3sa	110.6(7)
N11-B33-C38	114.8(3)	C4s-C3s-H3sb	110.8(6)
N14-B33-C34	118.7(3)	H3sa-C3s-H3sb	109.5(9)
N14-B33-C38	105.6(3)	C3s-C4s-H4sa	109.3(7)
C34-B33-C38	104.5(3)	C3s-C4s-H4sb	109.4(6)
B33-C34-C35	112.2(3)	C3s-C4s-H4sc	109.6(5)
B33-C34-C41	109.4(3)	H4sa-C4s-H4sb	109.5(5)
B33-C34-H34	107.7(3)	H4sa-C4s-H4sc	109.5(6)
C35-C34-C41	109.9(3)	H4sb-C4s-H4sc	109.5(8)
C35-C34-H34	108.8(3)	C42-H42a-O43'	102.9(6)
C41-C34-H34	108.7(3)	O43'-H44a-C44	95.4(4)
C34-C35-C36	114.5(3)		

References

- (S1) Bruker-Nonius, SAINT+ version 7.07B (2004), Bruker-Nonius, Madison, WI 53711, USA.
- (S2) Bruker-Nonius, SADABS version 2.10 (2004), Bruker-Nonius, Madison, WI 53711, USA.
- (S3) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, G. *J. Appl. Cryst.* **1994**, 27, 435–436.
- (S4) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Cryst.* **1989**, 22, 384–387.

¹H NMR Spectrum of 2

¹³C NMR Spectrum of 2

¹H NMR Spectrum of 3

¹³C NMR Spectrum of 3

¹H NMR Spectrum of Bu₂B-3

¹³C NMR Spectrum of Bu₂B-3

¹H NMR Spectrum of 9-BBN-3

^{13}C NMR Spectrum of 9-BBN-3

¹H NMR Spectrum of (Bu₂B)₂-5

¹³C NMR Spectrum of (Bu₂B)₂-5

¹H NMR Spectrum of (SEM)₂-6

LD-MS Spectrum of (SEM)₂-6

¹H NMR Spectrum of SEM-8

LD-MS Spectrum of SEM-8

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 IS2BNDV 0.00
 CMT1 2IMtransa2bcpor
 CMT2 no matrix, cal

¹H NMR Spectrum of SEM-Zn8

LD-MS Spectrum of SEM-Zn8

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 LLNSBND no
 UIS2BND no
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 DPMAS 600.00 [Da]
 RBNDVAL 0.00
 LBNDVAL 0.00
 IS2BNDV 0.00
 CMT1 ZnA3B2SIMPOR
 CMT2

¹H NMR Spectrum of 9b

¹³C NMR Spectrum of 9b

¹H NMR Spectrum of 10b

¹³C NMR Spectrum of 10b

¹H NMR Spectrum of 11b

¹³C NMR Spectrum of 11b

¹H NMR Spectrum of 11b-imino

¹³C NMR Spectrum of 11b-imino

¹H NMR Spectrum of SEM-Zn12

¹³C NMR Spectrum of SEM-Zn12

LD-MS Spectrum of SEM-Zn12

¹H NMR Spectrum of SEM-Pd12

LD-MS Spectrum of SEM-Pd12

¹H NMR Spectrum of SEM-Zn13

LD-MS Spectrum of SEM-Zn13

¹H NMR Spectrum of 14a + 14b

¹³C NMR Spectrum of 14a + 14b

¹H NMR Spectrum of 15a

¹³C NMR Spectrum of 15a

¹H NMR Spectrum of Bu₂B-15a

^{13}C NMR Spectrum of Bu₂B-15a

^1H NMR Spectrum of (9-BBN) $_2$ -16

^{13}C NMR Spectrum of (9-BBN) $_2$ -16

^1H NMR Spectrum of $(\text{SEM})_2\text{-17}$

LD-MS Spectrum of (SEM)₂-17

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 LLNSBND no
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 LBNDVAL 0.00
 IS2BNDV 0.00
 CMT1 FLEXControl generated XMASS dat
 CMT2 (c) 2000 Bruker Daltonics

^1H NMR Spectrum of $(\text{SEM})_2\text{Zn-17}$

LD-MS Spectrum of (SEM)₂Zn-17

INSTRUM MASSDEC

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AQ_DATE 2006-06-11 13:25:36

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POLARI POS

AQOP_m Reflector

TD 28224

NoSHOTS 200

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DELAY 294 [ns]

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Uhimass 0.00 [kV]

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UdetL 1.62 [kV]

UdetR 0.00 [kV]

Udefl 1000.00 [kV]

REPHZ 3.00 [Hz]

ATTEN 30.0

ML1 2545145.465

ML2 367.721

ML3 0.073

HITURBO no

GDEON yes

GDELY short

DEFLO yes

RLNSBND no

LLNSBND no

UIS2BND no

DPCAL1 0.38

DPMAS 300.00 [Da]

RBNDVAL 0.00

LBNDVAL 0.00

IS2BNDV 0.00

CMT1 Zn4IM2transabpor

CMT2 no matrix, cal

^1H NMR Spectrum of Zn12-Et₂

LD-MS Spectrum of Zn12-Et₂

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 RLNSBND no
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 CMT2

¹H NMR Spectrum of Zn12-S

LD-MS Spectrum of Zn12-S

INSTRUM MASSDEC

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 RBNDVAL 0.00
 LBNDVAL 0.00
 IS2BNDV 0.00
 CMT1 phimBS
 CMT2 dmso

^1H NMR Spectrum of Pd12-Et₂

LD-MS Spectrum of Pd12-Et₂

¹H NMR Spectrum of 13

Chemical structure of compound 13 is shown in the top right corner. It is a phthalocyanine derivative with a pyrazole ring at position 1 and a 4-(diethylcarbamoyloxy)phenyl group at position 3.

CCOC(=O)c1ccc(cc1)C2=C3C4=C5C(=C2)N(C3)C(=C4)C(=C5)C6=CC=CC=C6N7C=CC=CN7

Mass spectrum data (approximate relative intensity):

m/z	Relative Intensity (a.i.)
204	1000
554	6000
754	500

/D=/data/chemistry/lindsey/Jayeeta/061585/1Lin/pdata/1 Administrator Thu Jul 6 12:17:52 2006

^1H NMR Spectrum of Zn13-Et₂

Chemical structure of Zn13-Et₂ is shown above the mass spectrum. The structure is a zinc phthalocyanine derivative with a 4-ethoxycarbonylphenyl group and a 1-ethyl-3-ethylimidazolium-2-yl group.

Mass spectrum data (approximate relative intensity):

m/z	Relative Intensity (a.i.)
673.5	100
674.5	~5
675.5	~5
676.5	~5
677.5	~5
678.5	~5
679.5	~5
680.5	~5
681.5	~5
682.5	~5
683.5	~5
684.5	~5
685.5	~5
686.5	~5
687.5	~5
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689.5	~5
690.5	~5
691.5	~5
692.5	~5
693.5	~5
694.5	~5
695.5	~5
696.5	~5
697.5	~5
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699.5	~5
700.5	~5
701.5	~5
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703.5	~5
704.5	~5
705.5	~5
706.5	~5
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711.5	~5
712.5	~5
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714.5	~5
715.5	~5
716.5	~5
717.5	~5
718.5	~5
719.5	~5
720.5	~5
721.5	~5
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724.5	~5
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726.5	~5
727.5	~5
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732.5	~5
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736.5	~5
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766.5	~5
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772.5	~5
773.5	~5
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780.5	~5
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782.5	~5
783.5	~5
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785.5	~5
786.5	~5
787.5	~5
788.5	~5
789.5	~5
790.5	~5
791.5	~5
792.5	~5
793.5	~5
794.5	~5
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797.5	~5
798.5	~5
799.5	~5
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845.5	~5
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859.5	~5</

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¹⁵N NMR Spectrum (gHSQC) of 9-BBN-3

STANDARD 1H OBSERVE

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Sample directory: 10xN15_Pyrrole

Pulse Sequence: gHSQC

Solvent: thf
Ambient temperature
File: 9-BBN3-HSQC
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2D Width 12594.5 Hz
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2 x 128 increments

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Gauss apodization 0.091 sec
F1 DATA PROCESSING
Gauss apodization 0.116 sec
FT size 2048 x 2048
Total time 0 min, -1 sec

Pyrrole
(reference)

free pyrrolic N-H

¹⁵N NMR Spectrum (gHMBC) of 9-BBN-3

STANDARD 1H OBSERVE

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Sample directory: 10XN15_Pyrrole

Pulse Sequence: gHMBC

Solvent: THF

Ambient temperature

File: 9-BBN-3.HMBC

INOVA-500 "mercury424"

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Acq. time 0.197 sec

Width 5211.0 Hz

2D Width 12594.5 Hz

64 repetitions

256 increments

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F1 DATA PROCESSING

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