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Carboranypyrroles: A Synthetic Investigation

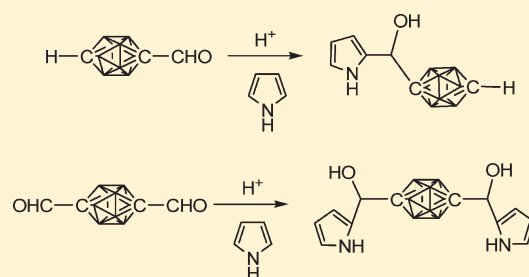
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 Supporting Information

ABSTRACT: The unusual reactivity of carborane mono- and dialdehydes with pyrroles in the presence of acid catalysts leads to the formation of a new class of carboranyl mono- and dipyrro derivatives.



Pyrroles are a class of nitrogen-containing heterocyclic compounds found in many natural products and biologically active compounds.¹ These are the key starting materials for the synthesis of a variety of macrocycles.² Moreover, pyrroles are useful building blocks in materials science and find applications as conducting polymers,³ semiconductors,⁴ and synthetic dyes.⁵ The carborane-appended pyrroles, commonly known as the carboranypyrroles, are important building blocks for the synthesis of carborane-appended macrocycles and polypyrroles.⁶ Carborane-appended porphyrins are useful boron–drug delivery platforms for cancer treatment via boron neutron capture therapy.⁷ Carboranypyrroles have also been used for the synthesis of functionalized conducting polymers with improved thermal and electrochemical properties.⁸

Carboranypyrroles are normally synthesized via multistep procedures starting from 1-allyl-2-methyl-*o*-carborane and 1-vinyl-*o*-carborane.^{9a} Bromo derivatives of pyrroles have also been used to synthesize carboranypyrroles via the Suzuki coupling reaction, which is a single-step process. However, this procedure involves the synthesis of carboranylboronic acid, but the overall yield of the product became low.^{9b} All these involved only the *o*-carborane and its attachment at the C₃ and C₄ positions of the pyrrole ring. While the overall yields of the multistep reactions were moderate,^{8c–e,9} these results posed the following intriguing questions: (1) whether the carborane clusters can be linked to the unexplored C₂ position of the pyrrole ring; (2) could this reaction incorporate other icosahedral carborane cage isomers, such as *meta*- and *para*-substituted ones; (3) if these reactions go smoothly, could this methodology be made simpler and also in higher yields? These questions led us to explore the synthesis of carboranypyrroles and the results of this investigation are reported here.

Thus, we have undertaken a focused research in which the reactivity of all three aldehydes of icosahedral carboranes (*o*-, *m*- and *p*-carboranes) with pyrrole was explored under two different catalytic conditions, i.e., trifluoroacetic acid (TFA) and InCl₃. In each case, the attachment of carborane clusters to the pyrrole has occurred at the C₂ position of the ring and the high yields of the so formed carboranypyrroles were observed.

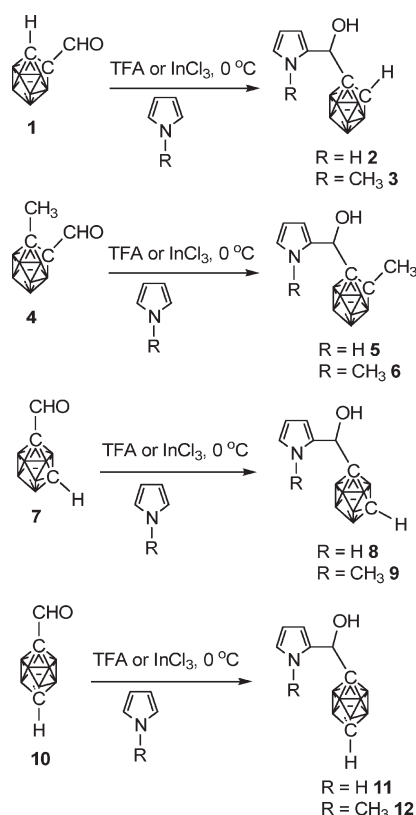
The starting mono- and dialdehyde derivatives of carboranes were synthesized following a literature procedure.¹⁰ This process involved the reactions between lithiated carboranes and excess methyl formate, followed by acidification.¹⁰ On the other hand, the reaction between dilithiated *o*-carboranes with methyl formate leads to the formation of an undesired cyclic ether.^{10a} Consequently, *o*-carborane dialdehyde could not be produced. Treatment of carborane aldehydes with pyrroles in the presence of catalytic amounts of trifluoroacetic acid (TFA) or indium chloride (InCl₃) at 0 °C led to a series of carboranypyrroles in good yields. However, unidentifiable mixtures of polymeric products were formed at elevated temperatures.

Evidently, the TFA and InCl₃-catalyzed reactions of mono aldehydes of all three types of icosahedral carboranes **1**, **4**, **7**, and **10** with pyrrole and 1-methylpyrrole led to the formation of carboranyl monopyrro derivatives (Scheme 1). The yields obtained at both of the reaction conditions are shown in Table 1. In the cases of monopyrro derivatives, the yields obtained via InCl₃ were slightly higher. But a reverse trend was observed for the dipyrro derivatives. However, yields obtained from 1-methylpyrrole were always lower than that of pyrrole. Similarly, reactions of carborane dialdehydes of *m*- and *p*-carboranes **13** and **16** with pyrrole and 1-methylpyrrole in the presence of an acid catalyst produced a new class of carboranyl

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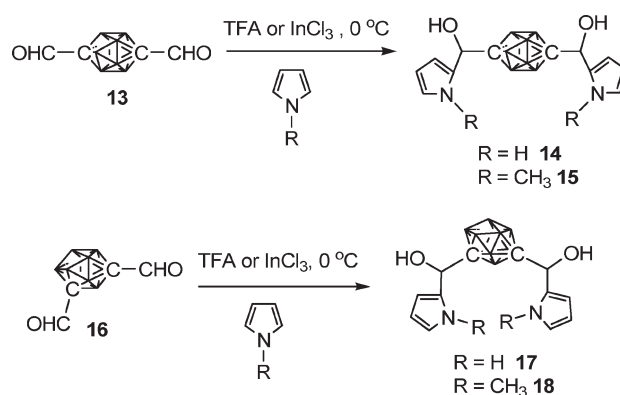
Scheme 1. Acid-Catalyzed Reactions of Carboranyl Mono-Aldehydes with Pyrroles

Table 1. TFA- and InCl₃-Catalyzed Reactions between Carboranyl Aldehydes and Pyrrole

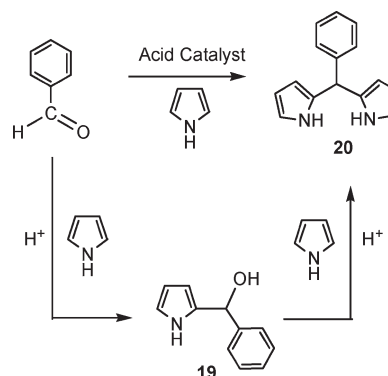
compd	yield (%) via TFA	yield (%) via InCl ₃
2	72	84
3	61	64
5	73	80
6	64	61
8	77	82
9	68	72
11	81	86
12	66	70
14	80	78
15	57	46
17	76	72
18	59	55

dipyrro derivatives as shown in Scheme 2. All new compounds were characterized by ¹H, ¹³C, and ¹¹B NMR, IR, and elemental analysis. In some cases, confirmatory mass spectral analyses were also carried out, melting points of all solid compounds were determined, and the crystal structure of **5** was determined (see the Supporting Information). Unlike the multistep synthetic procedures for carboranylpyrroles described previously,^{8,9} the acid-catalyzed condensation reactions between carborane aldehydes and pyrroles is a straightforward and far more convenient synthetic procedure where the carboranylpyrroles are the only product isolated.

Scheme 2. Acid-Catalyzed Reactions of Carboranyl Dialdehydes with Pyrrole



Scheme 3. Synthesis of Dipyrromethanes from Aryl Aldehydes via Acid-Catalyzed Reactions of Pyrroles



The key starting material for the syntheses of various pyrrole-based macrocycles is the dipyrromethanes which are generally synthesized from an acid-catalyzed reaction of aromatic aldehydes with pyrrole.¹¹ A general representation of the syntheses of dipyrro derivatives is shown in Scheme 3. Intermediate **19** is considered to be formed initially during the acid-catalyzed reaction of pyrrole with aryl aldehydes. This intermediate, in the presence of acid catalyst, generates a stable carbocation whose subsequent reaction with another pyrrole molecule leads to the formation of dipyrromethane **20** (Scheme 3).¹² Nonetheless, the isolation of intermediate **19** has never been reported. However, several side reactions involving pyrrole and aromatic aldehydes in the presence of an acid catalyst could produce several different byproduct leading to a lower yield of the desired dipyrromethane **20**.

In many cases, the reactions of carborane clusters deviate from those of normal aromatic systems. For example, a reaction between lithiated 1-phenyl-*o*-carborane and *N*-(2-bromoethyl)phthalimide resulted in an unexpected cyclic product via a nucleophilic addition at the carbonyl carbon.¹³ In another report, in the case of 1-[2'-(pyridyl(hydroxy)methyl)]-2-Me-1,2-dicarba-*closo*-dodecaborane, the hydroxyl group of the compound was unexpectedly oxidized to a ketone in the presence of thionyl chloride.¹⁴ In this case, the oxidation was favored over nucleophilic addition of chloride ion due to the effect of both the

N-atom of the pyridinyl fragment as well as the steric effect of the carborane moiety that hindered nucleophilic attack of the chloride ion.¹⁴ Mechanism of formation of dipyrromethanes (Scheme 3) involves the formation of a stable carbocation that is possible in the case of aromatic aldehydes. But with carborane aldehydes, the unexpected reactivity is due to the fact that the C–H's of the carboranes are behaving as electron-deficient aliphatic moieties.¹⁵ The electron-deficient character of cage C–H's may not support the formation of an adjacent carbocation. Previously, we have observed that 1-acetyl-*o*-carborane failed to undergo silicon tetrachloride mediated trimerization reaction that corroborates the fact that the presence of adjacent carboranyl moiety does not favor the formation of a relatively stable carbocation.¹⁵ Therefore, with the carboranylaldehydes the reaction stops at the monopyrro derivative that was isolated as stable end-products. The limited reactivity of carboranyl aldehydes also enhances the yields of these reactions by minimizing the formation of byproduct.

In summary, we have found that acid- and Lewis acid-catalyzed reactions of carborane aldehydes with pyrroles leads to a new class of carboranyl mono and dipyrro derivatives and these products are isolated in high yield. With the use of all three types of aldehydes of icosahedral carboranes, similar products are obtained. Such monopyrro derivatives are formed due to the unexpected reactivity of carborane aldehydes with pyrroles in the presence of an acid catalyst. This approach toward making carboranypyrroles is a facile and straightforward route for making such compounds.

EXPERIMENTAL SECTION

General Procedure for Syntheses of Carboranyl Monopyrro Derivatives. A mixture of pyrrole (excess, 3 mL) and carborane monoaldehydes (1.74 mmol) was taken in a flask, and TFA (0.02 mL, 0.27 mmol) or InCl₃ (62 mg, 0.28 mmol) was added to it at 0 °C under argon. It was stirred at 0 °C for 1 h. After completion of reaction, the reaction mixture was quenched with 0.1 M NaOH solution (10 mL) and then extracted with dichloromethane. The combined organic layer dried with MgSO₄. The excess pyrrole was removed under vacuum, and the crude reaction mixture was purified by silica gel column chromatography using 10–25% ethyl acetate in hexane as eluent.

2. Pyrrole (excess, 3 mL), **1** (300 mg, 1.74 mmol), TFA (0.02 mL, 0.27 mmol), or InCl₃ (62 mg, 0.28 mmol) gave pure product **2** as a colorless solid. Yield: 300 mg, 72% (via TFA). Yield: 350 mg, 84% (via InCl₃). Mp: 89–90 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.36 (s, 1H, NH), 6.83 (s, 1H), 6.21–6.19 (m, 2H), 5.34 (s, 1H), 3.60 (s, 1H). ¹³C NMR (125 MHz): δ 127.7, 119.0, 108.9, 108.4, 78.7, 70.0, 59.7. ¹¹B NMR (64 MHz, proton decoupled): –3.51, –8.94, –11.05, –13.48. IR (KBr): 3441, 3371, 3081, 3055, 2581, 1404, 1274, 1099, 770 cm^{–1}. Anal. Calcd for C₇H₁₇B₁₀NO: C, 35.13; H, 7.16; N, 5.85. Found: C, 35.14; H, 7.08; N, 5.83.

3. 1-Methylpyrrole (excess, 12.9 mL), **1** (1.0 g, 5.814 mmol), TFA (0.06 mL, 0.901 mmol), or InCl₃ (207 mg, 0.94 mmol) gave pure compound **3** as a colorless solid. Yield: 900 mg, 61% (via TFA). Yield: 950 mg, 64% (via InCl₃). Mp: 108 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.62 (t, 1H, *J* = 2.25 Hz), 6.24 (dd, 1H, *J*₁ = 1.72 Hz, *J*₂ = 3.75 Hz), 6.17–6.15 (m, 1H), 5.34 (s, 1H), 4.06 (s, 1H), 3.66 (s, 3H). ¹³C NMR (125 MHz): δ 130.2, 124.0, 108.0, 78.8, 68.2, 59.9, 34.7. ¹¹B NMR (64 MHz, proton decoupled): –3.67, –8.99, –12.81. IR (KBr): 3479, 3085, 2591, 1487, 1298, 1086, 732 cm^{–1}. Anal. Calcd for C₈B₁₀H₁₉NO: C, 37.93; H, 7.56; N, 5.53. Found: C, 37.96; H, 7.61; N, 5.52.

5. Pyrrole (excess, 2.7 mL), **4** (300 mg, 1.612 mmol), TFA (0.018 mL, 0.25 mmol), or InCl₃ (57 mg, 0.26 mmol) gave pure product **5** as a colorless solid. Yield: 300 mg, 73% (via TFA). Yield: 330 mg, 80% (via InCl₃). Mp:

150 °C. ¹H NMR (500 MHz): δ 8.38 (s, 1H, NH), 6.86 (s, 1H), 6.21–6.20 (m, 2H), 5.20 (s, 1H), 2.17 (s, 3H, CH₃). ¹³C NMR (125 MHz): δ 128.7, 119.4, 108.8, 108.4, 81.3, 74.8, 68.6, 23.2. ¹¹B NMR (64 MHz, proton decoupled): –2.84, –5.57, –10.0. IR (KBr): 3436, 3382, 3137, 2994, 2601, 1447, 1264, 734 cm^{–1}. Anal. Calcd for C₈H₁₉B₁₀NO: C, 37.93; H, 7.56; N, 5.53. Found: C, 37.95; H, 7.56; N, 5.55.

6. 1-Methylpyrrole (excess, 2.3 mL), **4** (180 mg, 1.046 mmol), TFA (0.012 mL, 0.16 mmol), or InCl₃ (37 mg, 0.17 mmol) gave pure compound **6** as a colorless solid. Yield: 180 mg, 64% (via TFA). Yield: 170 mg, 61% (via InCl₃). Mp: 83 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.62 (s, 1H), 6.30 (d, 1H, *J* = 2.0 Hz), 6.16 (t, 1H, *J* = 3.0 Hz), 5.23 (s, 1H), 3.71 (s, 3H, CH₃), 2.21 (s, 3H, cage-CH₃). ¹³C NMR (125 MHz): δ 130.7, 123.7, 109.2, 107.9, 82.1, 74.1, 67.7, 34.9, 23.4. ¹¹B NMR (64 MHz, proton decoupled): –3.08, –5.12, –10.57. IR (KBr): 3492, 2947, 2570, 1487, 1146, 1075, 734 cm^{–1}. Anal. Calcd for C₉H₂₁B₁₀NO: C, 40.43; H, 7.92; N, 5.24. Found: C, 40.42; H, 7.90; N, 5.28.

8. Pyrrole (excess, 3 mL), **7** (300 mg, 1.74 mmol), TFA (0.02 mL, 0.27 mmol), or InCl₃ (62 mg, 0.28 mmol) gave pure product **8** as a colorless solid. Yield: 320 mg, 77% (via TFA). Yield: 340 mg, 82% (via InCl₃). Mp: 122 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.30 (s, 1H, NH), 6.78 (s, 1H), 6.17 (s, 1H), 6.12 (s, 1H), 5.02 (s, 1H), 2.89 (s, 1H). ¹³C NMR (125 MHz): δ 129.9, 118.1, 108.2, 107.7, 82.0, 69.9, 54.4. ¹¹B NMR (64 MHz, proton decoupled): –3.65, –6.28, –9.89, –12.20, –14.56, –17.26. IR (KBr): 3457, 3366, 3137, 3059, 2911, 2610, 1566, 1408, 1248, 1125, 1094, 1049, 806, 739 cm^{–1}. Anal. Calcd for C₇H₁₇B₁₀NO: C, 35.13; H, 7.16; N, 5.85. Found: C, 35.18; H, 7.16; N, 5.80.

9. 1-Methylpyrrole (excess, 3.5 mL), **7** (300 mg, 1.612 mmol), TFA (0.018 mL, 0.25 mmol), or InCl₃ (57 mg, 0.26 mmol) gave pure compound **9** as a colorless solid. Yield: 280 mg, 68% (via TFA). Yield: 295 mg, 72% (via InCl₃). Mp: 85 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.56 (s, 1H), 6.16 (s, 1H), 6.12 (t, 1H, *J* = 2.98 Hz), 5.04 (s, 1H), 3.68 (s, 1H), 3.64 (s, 3H). ¹³C NMR (125 MHz): δ 131.6, 123.2, 108.3, 107.4, 69.1, 55.1, 54.5, 34.9. ¹¹B NMR (64 MHz, proton decoupled): –4.85, –6.64, –10.88, –13.30, –15.83, –16.90. IR (KBr): 3449, 3063, 2924, 2598, 1488, 1399, 1300, 1069, 726 cm^{–1}. Anal. Calcd for C₈B₁₀H₁₉NO: C, 37.93; H, 7.56; N, 5.53. Found: C, 37.91; H, 7.58; N, 5.52.

11. Pyrrole (excess, 3 mL), **10** (300 mg, 1.74 mmol), TFA (0.02 mL, 0.27 mmol), or InCl₃ (62 mg, 0.28 mmol) gave pure product **11** as a colorless solid. Yield: 340 mg, 81% (via TFA). Yield: 360 mg, 86% (via InCl₃). Mp: 112 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.17 (s, 1H, NH), 6.74 (s, 1H), 6.12 (d, 1H, *J* = 2.0 Hz), 6.0 (s, 1H), 4.68 (s, 1H), 2.75 (s, 1H). ¹³C NMR (125 MHz): δ 129.7, 117.8, 108.0, 107.5, 89.5, 70.8, 60.2. ¹¹B NMR (64 MHz, proton decoupled): –13.53, –15.21. IR (KBr): 3463, 3359, 3046, 2617, 1401, 1246, 1125, 805, 738 cm^{–1}. Anal. Calcd for C₇H₁₇B₁₀NO: C, 35.13; H, 7.16; N, 5.85. Found: C, 35.10; H, 7.12; N, 5.88.

12. 1-Methylpyrrole (excess, 2.38 mL), **10** (200 mg, 1.08 mmol), TFA (0.012 mL, 0.17 mmol), or InCl₃ (38 mg, 0.17 mmol) gave pure compound **12** as a colorless solid. Yield: 180 mg, 66% (via TFA). Yield: 190 mg, 70% (via InCl₃). Viscous liquid. ¹H NMR (500 MHz, CDCl₃): δ 6.51 (s, 1H), 6.08–6.07 (m, 2H), 4.71 (s, 1H), 3.58 (s, 3H, CH₃), 2.76 (s, 1H). ¹³C NMR (125 MHz): δ 131.2, 123.0, 108.4, 107.2, 89.7, 70.2, 60.3, 34.8. ¹¹B NMR (64 MHz, proton decoupled): –13.5, –15.2. IR (neat): 3432, 3060, 2610, 1676, 1402, 1132, 717 cm^{–1}. ES-MS (*m/z*): calcd 253.35, found 254.25 (*M*⁺ + 1), 234.24 (*M*⁺ – OH, 100). Anal. Calcd for C₈H₁₉B₁₀NO: C, 37.93; H, 7.56; N, 5.53. Found: C, 37.95; H, 7.60; N, 5.55.

General Procedure for Syntheses of Carboranyl Dipyrro Derivatives. A mixture of pyrrole (excess, 3.1 mL) and carborane dialdehydes (1.5 mmol) was taken in a flask, and TFA (0.06 mL, 0.8 mmol) or InCl₃ (53 mg, 0.24 mmol) was added to it at 0 °C under argon. It was stirred at 0 °C for 3 h. After completion of reaction, the reaction mixture was quenched with 0.1 M NaOH (20 mL) solution and then extracted with dichloromethane. The combined organic layer dried

with MgSO₄. The excess pyrrole was removed under vacuum, and the crude reaction mixture was purified by silica gel column chromatography using 20–30% ethyl acetate in hexane as eluent.

14. Pyrrole (excess, 3.1 mL), **13** (300 mg, 1.5 mmol), TFA (0.06 mL, 0.8 mmol), or InCl₃ (53 mg, 0.24 mmol) gave pure compound **14** as a colorless solid. Yield: 400 mg, 80% (via TFA). Yield: 390 mg, 78% (via InCl₃). Mp: 175 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.15 (s, 2H), 6.73–6.72 (s, 2H), 6.11–6.10 (m, 2H), 5.97 (s, 2H), 4.71 (s, 2H). ¹³C NMR (125 MHz): δ 129.7, 117.7, 108.0, 107.5, 86.8, 70.3. ¹¹B NMR (64 MHz, proton decoupled): -13.90. IR (KBr): 3462, 3360, 2602, 1681, 1403, 1252, 1028, 740 cm⁻¹. ES-MS (*m/z*): calcd 334.4, found 335.2 (M⁺ + 1, 100), 317.2 (M⁺ - OH). Anal. Calcd for C₁₂H₂₂B₁₀N₂O₂: C, 43.10; H, 6.63; N, 8.38. Found: C, 43.41; H, 6.63; N, 8.34.

15. 1-Methylpyrrole (excess, 3.1 mL), **13** (300 mg, 1.5 mmol), TFA (0.06 mL, 0.8 mmol), or InCl₃ (53 mg, 0.24 mmol) gave pure compound **15** as a colorless solid. Yield: 310 mg, 57% (via TFA). Yield: 250 mg, 46% (via InCl₃). Mp: 180 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.50 (t, 2H, *J* = 2.0 Hz), 6.07–6.05 (m, 2H), 6.02–6.01 (m, 2H), 4.73 (s, 2H), 3.56 (s, 6H). ¹³C NMR (125 MHz): δ 131.3, 123.1, 108.3, 107.2, 86.9, 69.5, 34.8. ¹¹B NMR (64 MHz, proton decoupled): -13.83. IR (KBr): 3463, 3122, 2948, 2609, 1654, 1486, 1302, 1126, 1073, 730 cm⁻¹. ES-MS (*m/z*): calcd 362.47, found 363.30 (M⁺ + 1, 100), 345.29 (M⁺ - OH). Anal. Calcd for C₁₄B₁₀H₂₆N₂O₂: C, 46.39; H, 7.23, N, 7.73. Found: C, 46.38; H, 7.21; N, 7.70.

17. Pyrrole (excess, 3.1 mL), **16** (300 mg, 1.5 mmol), TFA (0.06 mL, 0.8 mmol), or InCl₃ (53 mg, 0.24 mmol) gave pure compound **17** as a colorless solid. Yield: 380 mg, 76% (via TFA). Yield: 360 mg, 72% (via InCl₃). Mp: 122 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.3 (br, s, 2H), 6.76 (s, 2H), 6.15 (s, 2H), 6.06 (s, 2H), 4.95 (s, 2H). ¹³C NMR (125 MHz): δ 129.9, 118.1, 108.2, 107.6, 81.2, 69.9. ¹¹B NMR (64 MHz, proton decoupled): -6.62, -11.6, -14.5. IR (KBr): 3463, 3397, 3137, 2904, 2604, 1569, 1273, 1027, 735 cm⁻¹. ES-MS (*m/z*): calcd 334.4, found 335.3 (M⁺ + 1, 100), 317.2 (M⁺ - OH). Anal. Calcd for C₁₂B₁₀H₂₂N₂O₂: C, 43.10; H, 6.63; N, 8.38. Found: C, 43.40; H, 6.60; N, 8.21.

18. 1-Methylpyrrole (excess, 3.1 mL), **16** (300 mg, 1.5 mmol), TFA (0.06 mL, 0.8 mmol), or InCl₃ (53 mg, 0.24 mmol) gave pure compound **18** as a colorless solid. Yield: 320 mg, 59% (via TFA). Yield: 300 mg, 55% (via InCl₃). Mp: 175 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.54 (t, 2H, *J* = 2.0 Hz), 6.14–6.13 (m, 2H), 6.10–6.09 (m, 2H), 5.01 (s, 2H), 3.57 (s, 6H). ¹³C NMR (125 MHz): δ 131.5, 123.2, 108.3, 107.2, 81.3, 69.2, 34.9. ¹¹B NMR (64 MHz, proton decoupled): -6.74, -11.87. IR (KBr): 3462, 3102, 2948, 2601, 1702, 1456, 1403, 1303, 1131, 909, 726 cm⁻¹. ES-MS (*m/z*): calcd 362.47, found 363.30 (M⁺ + 1), 345.29 (M⁺ - OH, 100). Anal. Calcd for C₁₄B₁₀H₂₆N₂O₂: C, 46.39; H, 7.23; N, 7.73. Found: C, 46.37; H, 7.21; N, 7.72.

■ ASSOCIATED CONTENT

S Supporting Information. ¹H, ¹³C, and ¹¹B NMR spectra of new compounds, and crystallographic details for compound **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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