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Stereoselective addition of allylmagnesium chloride to the C=N bond of [4.3.0] boron heterobicycles

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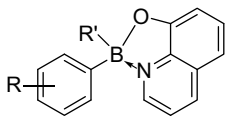
Abstract

An efficient, simple protocol for the addition of allylmagnesium chloride to the C=N bond of [4.3.0] boron heterobicycles afforded five new dioxaboracyclononenes **4a–e** in moderate yields (51–61%). The boronates were characterized by ^{1}H, ^{13}C, ^{11}B and 2D NMR experiments, and confirmed by X-ray analogues. The stereochemistry of the N–H, $–CH_2CH=CH_2$ and B–Ph fusion is always cis, as established through NMR, and confirmed by X-ray structure of **4d**. The structure of one of the addition products was established by X-ray analysis showing that, in the solid state, it exists as a polymeric structure formed by hydrogen bonds between the amine proton and the ester oxygen of the five-membered ring.

Keywords: Boron; Boronates; Allylmagnesium chloride; X-ray crystallography; NMR

The addition of organometallic reagents to the C=N bonds of imines or imine derivatives has been well documented in the literature. Its application, however, has been severely limited by the poor electrophilicity of the azomethine carbon. The electrophilicity of the carbon atom of the C=N bond can be increased by N-alkylation,[1] N-oxidation,[2] N-acylation,[3] or N-sulfonylation[4] to give reactive iminium salts, but this method requires the removal of the activating groups to generate the free amine, a procedure which is not always easy. For this reason, another strategy has involved activation of the C=N bond of the imines or imine derivatives by the coordination of a Lewis acid[5] with the nitrogen lone pair or by the addition of external promoters. In a previous paper,[6] we reported that the boron complexes derived from Schiff bases undergo an acetolysis reaction to give the corresponding dioxazaboracines containing all substituents on the same side in good yields. Moreover, the organoboron compounds have received considerable attention as potential antibacterial reagents[7] (**1**, Fig. 1). Recently we have also reported that the imino Diels Alder reaction of boronates affords 3,4-dihydroquinoline and 1,2,3,6-tetrahydropyridine derivatives.[8]



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R = H, Cl, F, MeO, CN
R'= vinyl, aryl

Fig. 1.

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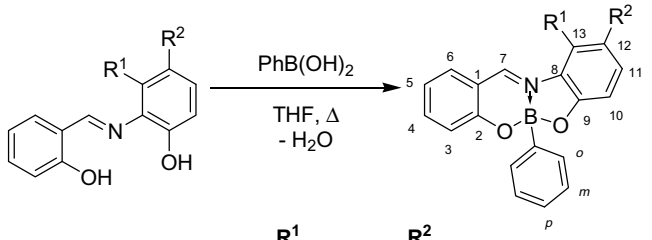
Continuing our investigations on boronates, we describe herein the reactions of allylmagnesium chloride with different bicyclic boron complexes (**3a**–**e**).

The synthesis of **3a**–**e** was carried out following the methodology reported by Farfán.[6] This procedure involves the condensation of salicyldehyde with the corresponding aminophenol to give the tridentate ligands **2a**–**e**. Treatment of **2a**–**e** with 1 equiv of phenylboronic acid in THF gives boronates **3a**–**e** with the elimination of 2 equiv of water (Scheme 1). It is important to notice that **3e** is a new compound. It was obtained in a crystalline form allowing the determination of its X-ray crystal structure (Fig. 2), which showed that upon coordination the ligand adopts a geometry that leads to a highly delocalized system with enhanced stability, as described in the previous studies.[6,9] Compound **3e** was obtained as a pale yellow solid and was characterized by elemental analysis, mass spectrometry, IR, and ^{1}H, ^{13}C and ^{11}B NMR spectroscopy.[10]



2a-e	R^1	R^2	3a-e
a:	H	H	
b:	H	Cl	
c:	H	*t*-Bu	
d:	H	Me	
e:	Me	H	

Scheme 1.

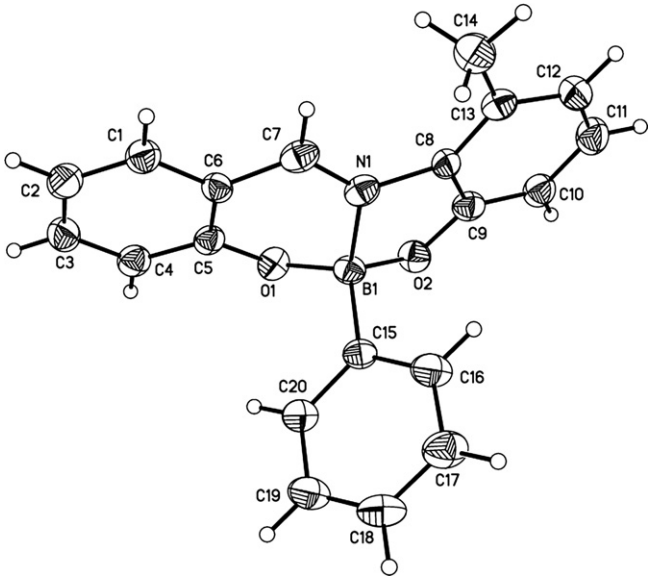


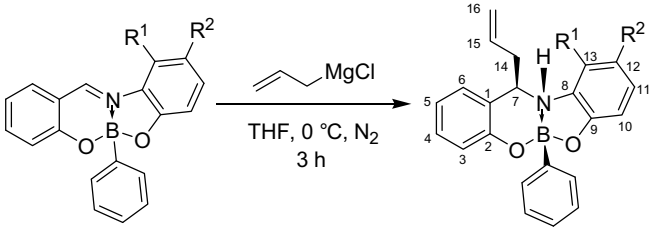
Fig. 2. X-ray structure of **3e**.

The X-ray analysis for **3e** (Fig. 2) established the [4.3.0] heterobicyclic structure.[11] The value for the intramolecular N–B donor–acceptor bond length for boronate **3e** is 1.614(4) Å, which is the same as the unsubstituted boronate **3a** (1.613(5) Å)[12] and is in accordance with the N–B dative bond distances for boronates, which are in the range from 1.586(2) to 1.681(5) Å.[13] The bond angles around the boron atom in **3e** are in the range of 99.3(2)–113.0(3)°. The lowest value corresponds to the O(2)–B(1)–N(1) bond angle in the five-membered heterocycle, whereas the largest corresponds to the O(1)–B(1)–C(15) bond angle; the values are similar to those found in compound **3a**.[7]

The environment of the boron atom can be evaluated by the tetrahedral character (THC)[13] showing a large distortion (77%) due to high strain in the five-membered heterocycle. The ring strain of the two heterocycles is perhaps best expressed by torsion angles of 33.6(4)° for O(1)–B(1)–N(1)–C(7) in the six-membered ring and O2–B1–N1–C8–20.5(3)° of the five-membered ring.

The dioxaboracyclononenes **4a**–**e** were obtained in moderate yields (51–61%)[14] by the addition of allylmagnesium chloride, to boronates **3a**–**e** (3 h at 0 °C and then 30 min. at room temperature (Scheme 2)).[15] It is important to notice that the fusion of the [4.3.0] heterobicyclic system is cis, as the dioxazaborocines described previously[6,8] which provide a roofed conformation with respect to the boron nitrogen bond. The spectroscopic data allowed complete characterization for **4a**–**e**. The IR spectra showed the absence of the C=N group and the appearance of a new band between 1609 and 1635 cm^{-1} corresponding to the –CH=CH_2 group and the mass spectra showed the molecular ion for the boronates.

The NMR spectra show a singlet corresponding to the NH group between 5.58 and 5.66 ppm. In solution, there is no evidence for hydrogen bonding involving this group although it is present in the solid state (vide infra) as shown for **4d**. The ^{11}B NMR spectra of **4a**–**e** show a broad signal between 8.2 and 9.2 ppm, characteristic of boron atoms tetracoordinated to two oxygen atoms, one nitrogen atom, and one carbon atom.



3a-e	R^1	R^2	4a-e
a:	H	H	
b:	H	Cl	
c:	H	*t*-Bu	
d:	H	Me	
e:	Me	H	

Scheme 2.

A crystal suitable for X-ray diffraction was obtained for compound **4d** and the molecular structure is shown in Figure 3.[11] The structure shows that all substituents are on the same side. The stereochemistry is thus the same as that of the acetolysis products.[6] The N–B bond length (1.705(3) Å) is larger than **3e** and is similar to boronates described in the literature.[7,12] The difference in this value may be attributed to an increase in bond distance on going from sp^2 to sp^3 hybridization on the nitrogen atom. The B–O distance is shorter in the six-membered (1.438(3) Å) than in the five-membered heterocycle (1.491(3) Å) due to higher annular tension in the five-membered ring. The angles around the boron atom are approximately tetrahedral in the range between 100.28(14)° (O(2)–B(1)–N(1)) and 112.96(17)° (O(2)–B(1)–C(18)), and are similar to the boronates described previously[7,8] showing a THC value of 78%.

The refinement of the crystal structure for **4d** revealed positional disorder in the allyl moiety. Figure 2 shows that the boron-phenyl moiety, the $-CH_2CH{=}CH_2$ fragment, and the hydrogen attached to the nitrogen atom have a cis disposition. The molecular packing reveals that the interaction present at the oxygen (O-2) and hydrogen atoms (NH) forms a polymeric structure in the solid state (Fig. 4). The NH···O(2) intermolecular distance is 2.234 Å and the N–H–(O2) angle is 168.16°.

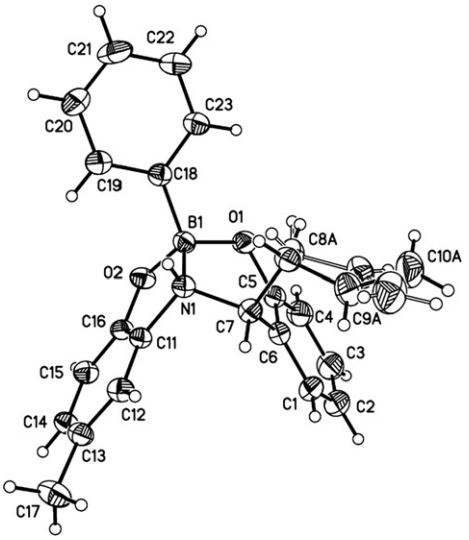


Fig. 3. X-ray structure of **4d**.

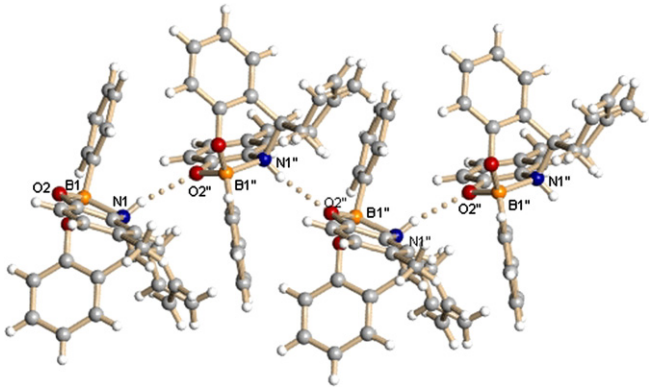


Fig. 4. Polymeric structure for **4d** formed by intermolecular hydrogen bonding.

In conclusion, boron complexes derived from tridentate ligands are readily formed leading in all cases to [4.3.0] heterobicyclic structure containing dative N–B bonds as evidenced by X-ray analysis of compound **3e**. Furthermore, it was shown that coordination of the nitrogen atom to boron is responsible for the polarization of the C=N bond and the facile and stereoselective reaction[16] with nucleophiles such as allylmagnesium chloride, leading to the products having all substituents in a cis configuration.

Acknowledgements

We are indebted to Dr. Joseph Muchowski for many friendly discussions and to CONACyT for financial support via grant (J49336-Q) and a scholarship (198075) to I. Mera-Moreno. Also we thank Ma. Eugenia Ochoa for technical support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.12.122.

References and notes

1. Leonard, N. J.; Paukestelis, J. V. *J. Org. Chem.* **1963**, *28*, 3021–3024.
2. Bonnett, R.; Clark, V. M.; Todd, A. *J. Chem. Soc.* **1959**, 2102–2104.
3. Böhme, H.; Ebel, S.; Hartke, K. *Chem. Ber.* **1965**, *98*, 1463–1464.
4. Ueda, M.; Miyaura, N. *J. Organomet. Chem.* **2000**, *595*, 31–35.
5. (a) Godin, Guillaume; Compain, P.; Masson, G.; Martin, O. R. *J. Org. Chem.* **2002**, *67*, 6960–6970; (b) Agarwal, S.; Knölker, H.-J. *Org. Biomol. Chem.* **2004**, *2*, 3060–3062.
6. Barba, V.; Cuahutle, D.; Santillan, R.; Farfán, N. *Can. J. Chem.* **2001**, *79*, 1229–1237.
7. Baker, S. J.; Zhang, Y.-K.; Akama, T.; Lau, A.; Zhou, H.; Hernandez, V.; Mao, W.; Aller, M. R. K.; Sander, V.; Plattner, J. *J. Med. Chem.* **2006**, *49*, 4447–4450.
8. Abreu, A.; Alas, S. J.; Beltán, H. I.; Santillan, R.; Farfán, N. *J. Organomet. Chem.* **2006**, *691*, 337–348.
9. (a) Rodríguez, M.; Ochoa, M. E.; Rodríguez, C.; Santillan, R.; Barba, V.; Farfán, N. *J. Organomet. Chem.* **2007**, *692*, 2425–2435; (b) Rodríguez, M.; Ochoa, M. E.; Santillan, R.; Farfán, N.; Barba, V. *J. Organomet. Chem.* **2005**, *690*, 2975–2988.
10. Compound **3e** was prepared from **2e** (0.5 g, 2.2 mmol) and phenylboronic acid (0.27, 2.2 mmol) in THF (40 mL). The mixture was heated at reflux for 1 h. and the water removed with a Dean Stark trap. The solid obtained was collected by filtration under vacuum and washed with the mixture of hexane/ethylacetate (9:1). The product was obtained as a yellow solid (yield: 0.66 g, 96%); mp 203–206 °C. IR (KBr) ν_{max} 3053, 2919, 1620 (C=N), 1589, 1550, 1372, 1327, 1179, 1153, 1153, 902, 847, 773, 754, 730 cm^{-1}; MS (*m/z*, 70 eV, %), 313 (M^+, 10), 268 (1), 236 (100), 165 (1), 102 (1), 77 (4), 51 (4); ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (1H, s, H-7), 7.53 (1H, td, $J = 7.3$, 1.5 Hz, H-4), 7.36 (1H, dd, $J = 7.3$, 1.5 Hz, H-6), 7.30 (2H, dd, $J = 7.7$, 1.5 Hz, H-*o*), 7.24 (1H, d, $J = 7.3$ Hz, H-3), 7.21 (1H, t, $J = 8.1$ Hz,

H-11), 7.14–7.09 (3H, m, H-*p*, H-*m*), 6.94 (1H, d, $J = 8.1$ Hz, H-10), 6.92 (1H, t, $J = 7.3$ Hz, H-5), 6.67 (1H, d, $J = 8.1$ Hz, H-12), 2.57 (3H, s, Me-13); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2 (C-2), 157.3 (C-9), 150.0 (C-7), 137.8 (C-4), 131.9 (C-6), 131.6 (C-11), 131.3 (C-*o*), 129.3 (C-8), 129.1 (C-*i*), 127.8 (C-*p*), 127.5 (C-*m*), 121.9 (C-12), 120.3 (C-3), 120.2 (C-5), 119.7 (C-1), 112.8 (C-10), 19.1 (Me-13); ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.2 ppm. Anal. Calcd for $C_{20}H_{16}BNO_2$: C, 76.71; H, 5.15; N, 4.47. Found: C, 76.36; H, 5.32; N, 4.39.

11. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Numbers, CCDC 663923 No. for **3a** and CCDC 663924 for **4d**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or deposit@ccdc.cam.ac.uk].
12. Höpfl, H.; Sánchez, M.; Farfán, N.; Barba, V. *Can. J. Chem.* **1998**, *76*, 1352–1360.
13. Höpfl, H. *J. Organomet. Chem.* **1999**, *581*, 129–149.
14. These yields were obtained after crystallization.
15. *General procedure*: In a 25 mL round-bottomed flask with a magnetic bar was placed 1 equiv of **3a**–**e** in a 10 mL of dry THF under nitrogen. The flask was cooled in ice-cetone bath (0 °C) and 1.5 equiv of 2 M allylmagnesium chloride was added by a syringe (dropwise addition). The resulting solution was then stirred at 0 °C for 3 h and was allowed to warm up to room temperature for 30 min. The reaction was quenched with 5 mL of saturated aqueous NH_4Cl and the product was extracted with ethyl acetate (3 × 50 mL). The combined extracts were dried over anhydrous Na_2SO_4, and then concentrated. Final purification was accomplished by crystallization with CH_2Cl_2 and hexane (1:1). Yields refer to isolated pure compounds. All compounds exhibited spectral data (IR, ^{1}H, ^{13}C and ^{11}B NMR). Compound **4a**: mp 156–157 °C as a red solid (yield: 0.32 g, 55%) IR (KBr): ν_{max} 3104, 2921, 1611, 1494, 1042, 740, 701 cm^{-1}; MS (*m*/*z*, 70 eV, %), 341 (M^+, 3), 300 (43), 264 (7), 222 (68), 195 (100), 77 (12), 51 (5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (2H, dd, $J = 7.5$, 1.6 Hz, H-*o*), 7.35–7.31 (3H, m, H-*m*, H-*p*), 7.21 (1H, td, $J = 7.5$, 1.8 Hz, H-4), 7.14–7.09 (3H, m, H-6, H-11, H-13), 6.88 (1H, dd, $J = 7.5$ 1.4 Hz, H-3), 6.82–6.79 (2H, m, H-5, H-10), 6.73 (1H, t, $J = 7.7$ Hz, H-12), 5.82 (1H, dtd, $J = 17.2$, 14.3, 10.3 Hz, H-15), 5.66 (1H, b, NH), 5.15 (1H, d, $J = 10.3$ Hz, H-16a), 4.79 (1H, d, $J = 17.2$ Hz, H-16b), 4.19 (1H, dd, $J = 10.6$, 4.4 Hz, H-7), 3.11 (1H, dt, $J = 14.3$, 10.6 Hz, H-14a), 2.64 (1H, dt, $J = 14.3$, 4.4 Hz, H-14b) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (C-9), 155.6 (C-2), 132.8 (C-15), 131.8 (C-*o*), 130.7 (C-6), 130.3 (C-4), 128.3 (C-*p*), 128.2 (C-3), 128.1 (C-*m*), 123.5 (C-8), 122.6 (C-1, C-16), 120.9 (C-5), 120.7 and 120.6 (C-11, C-13), 118.5 (C-12), 113.6 (10), 65.0 (C-7), 38.8 (C-14) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 8.3 ppm. For **4b**: mp 196–198 °C as a red solid (yield: 0.19 g, 56%) IR (KBr): ν_{max} 3120, 2922, 1609, 1489, 1274, 1241, 1045, 741, 704 cm^{-1}; MS (*m*/*z*, 20 eV, %), 375 (M^+, 3), 334 (53), 298 (4), 256 (42), 229 (100), 194 (1), 77 (1), 51 (1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (2H, dd, $J = 7.3$, 2.2 Hz, H-*o*), 7.36–7.33 (3, m, H-*m*, H-*p*), 7.23 (1H, td, $J = 7.3$, 1.8 Hz, H-4), 7.10–7.08 (3H, m, H-6, H-11, H-13), 6.89 (1H, dd, $J = 7.3$, 1.5 Hz, H-3), 6.83 (1H, t, $J = 7.3$ Hz, H-5), 6.73 (1H, d, $J = 8.4$ Hz, H-10), 5.79 (1H, dtd, $J = 17.2$, 14.3, 10.3, H-15), 5.65 (1H, b, NH), 5.15 (1H, d, $J = 10.3$ Hz, H-16a), 4.77 (1H, d, $J = 17.2$ Hz, H-16b), 4.12 (1H, dd, $J = 10.6$, 4.0 Hz, H-7), 2.99 (1H, dt, $J = 14.3$, 10.6 Hz, H-14a), 2.62 (1H, dt, $J = 14.3$, 4.03 Hz, H-14b) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1 (C-9), 155.3 (C-2), 132.5 (C-15), 131.6 (C-*o*), 130.8 (C-6), 130.5 (C-4), 129.1 (C-12), 128.5 (C-*p*), 128.2 (C-3), 128.1 (C-*m*), 123.0 (C-8), 122.9 (C-16), 122.5 (C-11), 121.1 (C-5), 121.0 (C-13), 120.8 (C-12), 114.5 (C-10), 65.3 (C-7), 38.8 (C-14) ppm; ^{11}B NMR (96 MHz, $CDCl_3$): δ 9.2 ppm. Anal. Calcd for $C_{22}H_{19}BClNO_2$: C, 70.34; H, 5.10; N, 3.73. Found: C, 70.26; H, 5.05; N, 3.98. For **4c**: mp 181–183 °C as a yellow solid (yield: 0.29 g, 52%) IR (KBr): ν_{max} 3045, 2921. 1627, 1556, 1500, 1263,1206, 741 cm^{-1}; MS (*m*/*z*, 20 eV, %), 397 (M^+, 18), 356 (44), 320 (2), 278 (45), 251 (100), 208 (7); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (2H, dd, $J = 7.5$, 1.8 Hz, H-*o*), 7.36–7.31 (3H, m, H-*m*, H-*p*), 7.22 (1H, td, $J = 7.7$, 1.8 Hz, H-4), 7.16 (1H, dd, $J = 8.4$, 1.8 Hz, H-11), 7.10 (1H, d, $J = 7.3$ Hz, H-3), 7.07 (1H, d, $J = 1.8$ Hz, H-13), 6.88 (1H, dd, $J = 7.3$, 1.8 Hz, H-6), 6.81 (1H, td, $J = 7.7$, 1.1 Hz, H-5), 6.74 (1H, d, $J = 8.4$ Hz, H-10), 5.84 (1H, dtd, $J = 17.2$, 14.3, 10.3 Hz, H-15), 5.71 (1H, b, NH), 5.17 (1H, d, $J = 10.3$ Hz, H-16a), 4.84 (1H, d, $J = 17.2$ Hz, H-16b), 4.20 (1H, dd, $J = 10.4$, 4.8 Hz, H-7), 3.02 (1H, dt, $J = 14.3$, 10.4 Hz, H-14a), 2.67 (1H, dt, $J = 14.3$, 4.8 Hz, H-14b), 1.25 (9H, s, *t*-Bu-12) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8 (C-9), 155.6 (C-2), 141.9 (C-12), 132.8 (C-15), 131.9 (C-*o*), 130.2 (C-4), 128.3 (C-3), 128.2 (C-*p*), 128.0 (C-*m*), 127.9 (C-11), 127.6 (C-8), 123.7 (C-1), 122.4 (C-16), 120.8 (C-6, C-5), 117.2 (C-13), 112.8 (C-10), 65.0 (C-7), 39.0 (C-14), 34.4 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 8.4 ppm. Anal. Calcd for $C_{26}H_{28}BNO_2$: C, 78.60; H, 7.10; N, 3.53. Found: C, 78.67; H, 7.15; N, 3.57. For **4d**: mp 210.6–212.5 °C as a yellow solid (yield: 0.29 g, 51%) IR (KBr): ν_{max} 3117, 2919, 1610, 1510, 1487, 1282, 1243, 1043, 741, 703 cm^{-1}; MS (*m*/*z*, 70 eV, %), 355(M^+, 6), 314 (31), 278 (2), 236 (47), 209 (100), 77 (6), 51 (3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (2H, dd, $J = 7.5$, 1.8 Hz, H-*o*), 7.35–7.30 (3H, m, H-*m*, H-*p*), 7.22 (1H, td, $J = 7.7$, 1.8 Hz, H-4), 7.10 (1H, dd, $J = 7.7$, 1.1 Hz, H-3), 6.94–6.91 (2H, m, H-11, H-13), 6.88 (1H, dd, $J = 7.7$, 1.8 Hz, H-6), 6.81 (1H, td, $J = 7.7$, 1.1 Hz, H-5), 6.71 (1H, d, $J = 8.1$ Hz, H-10), 5.82 (1H, m, H-15), 5.58 (1H, s, NH), 5.13 (1H, d, $J = 10.3$ Hz, H-16a), 4.80 (1H, d, $J = 17.2$ Hz, H-16b), 4.17 (1H, dd, $J = 11.0$, 4.4 Hz, H-7), 2.99 (1H, dt, $J = 14.7$, 10.6 Hz, H-14a), 2.62 (1H, dt, $J = 14.7$, 4.4 Hz, H-14b), 2.23 (3H, s, Me-12) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1 (C-9), 155.7 (C-2), 132.8 (C-15), 131.7 (C-*o*), 131.2 (C-4), 130.3 (C-11), 128.3 (C-6), 128.1 (C-3), 128.0 (C-*p*, C-*m*), 127.8 (C-8, C-12), 123.5 (C-1), 122.6 (C-16), 120.8 (C-5, C-3), 113.2 (C-10), 64.9 (C-7), 39.0 (C-14), 20.8 (Me-12) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 8.4 ppm. Anal. Calcd for $C_{23}H_{22}BNO_2$: C, 77.76; H, 6.24; N, 3.94. Found: C, 77.37; H, 6.48; N, 3.89. For **4e**: mp 180–182 °C as a red solid (yield: 0.068 g, 60%) IR (KBr): ν_{max} 3223, 2921, 2851, 1594, 1471, 1299, 1224, 1053, 952, 760, 704 cm^{-1}; MS (*m*/*z*, 70 eV, %), 355 (M^+, 6), 314 (31), 278 (2), 236 (47), 209 (100), 77 (6), 51 (3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (2H, dd, $J = 7.5$, 1.6 Hz, H-*o*), 7.36–7.32 (3H, m, H-*m*, H-*p*), 7.26 (1H, td, $J = 7.3$, 1.8 Hz, H-4), 7.12 (1H, d, $J = 7.3$ Hz, H-6), 7.03 (1H, t, $J = 7.9$ Hz, H-11), 6.88 (1H, dd, $J = 7.3$, 1.8 Hz, H-3), 6.83 (1H, t, $J = 7.3$ Hz, H-5), 6.67 (1H, d, $J = 7.9$ Hz, H-10), 6.53 (1H, d, $J = 7.9$ Hz, H-12), 5.90 (1H, dtd, $J = 17.0$, 13.9, 10.3 Hz, H-15), 5.58 (1H, b, NH), 5.24 (1H, d, $J = 10.3$ Hz, H-16a), 5.08 (1H, d, $J = 17.0$ Hz, H-16b), 4.18 (1H, dd, $J = 10.9$, 4.2 Hz, H-7), 3.11 (1H, dt, $J = 13.9$, 10.9 Hz, H-14a), 2.64 (1H, dt, $J = 13.9$, 4.2 Hz, H-14b), 2.30 (3H, s, Me-13) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (C-9), 155.8 (C-2), 132.8 (C-15), 131.7 (C-*o*), 130.6 (C-13), 130.4 (C-4, C-11), 128.3 (C-3), 128.0 (C-*p*, C-*m*), 127.3 (C-8), 124.6 (C-1), 122.9 (C-16), 121.0 (C-5), 120.9 (C-6), 120.6 (C-12), 11.2 (C-10), 63.0 (C-7), 39.8 (C-14), 17.5 (Me-13) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 8.5 ppm. Anal. Calcd for $C_{23}H_{22}BNO_2$: C, 77.76; H, 6.24; N, 3.94. Found: C, 77.79; H, 6.43; N, 3.90.
16. A single product was detected by ^{1}H NMR Spectroscopy (400 MHz) of the crude reaction.