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Regioselectivity of 1,1-dimethylallene allylboration: synthesis of isomeric 6- and 7-methylene-3-borabicyclo[3.3.1]nonanes

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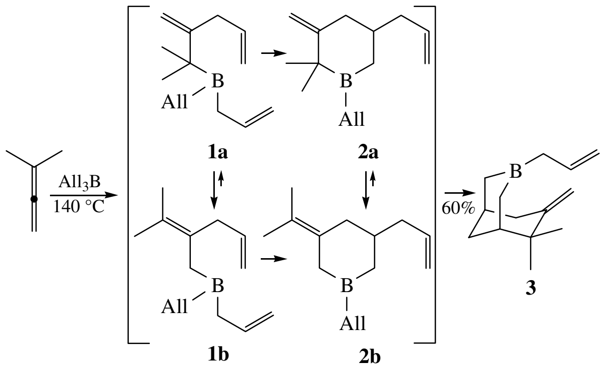
A dramatical difference in the stereoselectivity of 1,1-dimethylallene allylboration with allyl(chloro)- and triallylboranes has been revealed and applied to the synthesis of isomeric 7-methylene-6,6-dimethyl- and 6-(1-methylethylidene)-3-borabicyclo[3.3.1]-nonanes.

Reactions of triallyl- or trimethallylboranes with terminal acetylenes, RC≡CH, the so called allylboron–acetylene condensation (ABAC), provides a general access to 7-substituted 3-allyl-3-borabicyclo[3.3.1]non-6-enes. The condensation was found to proceed in three consecutive steps and the products of each step have been isolated and applied in organic syntheses.[1] The first step consists in *cis*-allylboration of the acetylene triple bond leading to 1,4-pentadienyl(diallyl)boranes, which are cyclised at moderate temperatures into 1-bora-2-cyclohexene derivatives by the intramolecular allylboration of the terminal double bond. The final step is the transformation of 1-bora-2-cyclohexenes to bicyclic compounds, which presents a unique intramolecular vinylboration of the terminal double bond.

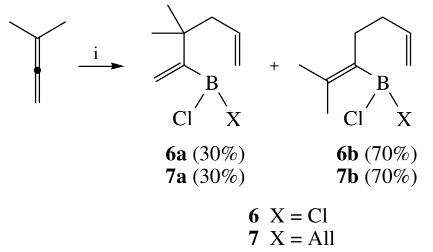
The next major advance in allylborane chemistry is represented by allylboron–allene condensation leading to 7-methylene-3-borabicyclo[3.3.1]nonane derivatives. However, the intermediates were not isolated, and their allylic structure was assumed only on the basis of the retroreconstructive analyses of the final products and possible similarity with ABAC. Thus, a thermal reaction of triallylborane with 3-methylbuta-1,2-diene (1,1-dimethylallene) gives rise to 3-allyl-7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane **3**.[2] The proposed mechanism of this reaction is presented in Scheme 1.



Scheme 1

The structure of 1-boracyclohexane precursor **2a** or **2b** of 3-borabicyclo[3.3.1]nonane **3** is not clear now and it is not known whether allylic rearangement during condensation takes place.

We supposed that the use of mono- and diallylborane derivatives could achieve the isolation of products formed at both first and second steps of condensation and clarify the reaction mechanism. We introduced highly electrophilic allyl(dichloro)- and diallyl(chloro)boranes **4** and **5**,[3] respectively (generated *in situ* by the redistribution reaction of All$_3$B and BCl$_3$),† for this purpose. It was shown that the reaction of these reagents with 1,1-dimethylallene takes place under mild conditions (–78 °C) and furnishes two vinylic derivatives (**6a**, **6b** or **7a**, **7b**)‡ in a 3:7 ratio in each case (Scheme 2).



Scheme 2 *Reagents and conditions*: i, CH$_2$Cl$_2$, –78 °C, AllBCl$_2$ or All$_2$BCl, 15 min.

These primary products as far as starting **4** and **5** undergo degradation while storage and should be used as soon as they are formed. Further treatment of **6a** and **6b** mixture with methanol in the presence of triethylamine gave rise to a mixture of corre-

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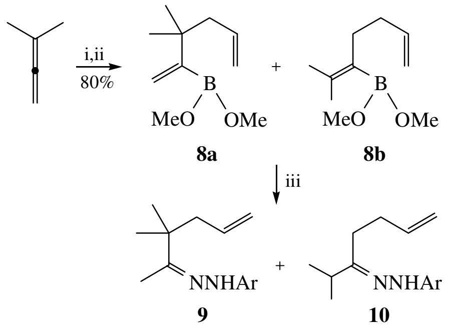
† *Characterization data for* **4** prepared *in situ* at –78 °C from 1 equiv. of All$_3$B and 2 equiv. of BCl$_3$. ^{11}B NMR (64.21 MHz, CH$_2$Cl$_2$) δ: 61.2.

5 prepared *in situ* at –78 °C from 2 equiv. of All$_3$B and 1 equiv. of BCl$_3$. ^{11}B NMR (64.21 MHz, CH$_2$Cl$_2$) δ: 74.1.

‡ **6a** and **6b** (3:7) reaction mixture. ^{1}H NMR (^{1}H, ^{1}H COSY) (300.13 MHz, CH$_2$Cl$_2$/CDCl$_3$, 25 °C) δ: 1.12 [s, 6H, Me (**6a**)], 1.79 and 1.99 [s, 6H, Me (**6b**)], 2.03 [dt, 2H, H(3) (**6b**), $^{3}J_{\mathrm{H(3)-H(2)}}$ 5.9 Hz, $^{3}J_{\mathrm{H(3)-H(X)}}$ 6.6 Hz], 2.41 [t, 2H, H(2) (**6b**), $^{3}J_{\mathrm{H(2)-H(3)}}$ 5.9 Hz], 2.31 [d, 2H, H(3) (**6a**), $^{3}J_{\mathrm{H(3)-H(X)}}$ 7.4 Hz], 4.88 [dd, 1H, H(5A) (**6a**), $^{3}J_{\mathrm{H(5A)-H(X)}}$ 8.9 Hz, $^{2}J_{\mathrm{H(5A)-H(5B)}}$ 2.3 Hz], 4.92 [d, 1H, H(5B) (**6a**), $^{3}J_{\mathrm{H(5B)-H(X)}}$ 17.7 Hz], 4.93 [d, 1H, H(5B) (**6b**), $^{3}J_{\mathrm{H(5B)-H(X)}}$ 10.4 Hz], 4.94 [dd, 1H, H(5A) (**6b**), $^{3}J_{\mathrm{H(5A)-H(X)}}$ 17.0 Hz, $^{2}J_{\mathrm{2H(5A)-H(5B)}}$ 1.5 Hz], 5.56 [ddt, 1H, H(4) (**6a**), $^{3}J_{\mathrm{H(X)-H(5B)}}$ 17.7 Hz, $^{3}J_{\mathrm{H(X)-H(5A)}}$ 8.9 Hz, $^{3}J_{\mathrm{H(X)-H(3)}}$ 7.4 Hz], 5.73 [ddt, 1H, H(4) (**6b**), $^{3}J_{\mathrm{H(X)-H(5B)}}$ 17.0 Hz, $^{3}J_{\mathrm{H(X)-H(5A)}}$ 10.4 Hz, $^{3}J_{\mathrm{H(X)-H(3)}}$ 6.6 Hz], 5.86 and 6.12 [s, 2H, CH$_2$=C (**6a**)]. ^{13}C NMR (DEPT-135) (50.32 MHz, CH$_2$Cl$_2$/CD$_2$Cl$_2$, –78 °C) δ: 22.8 and 25.5 [Me (**6b**)], 27.7 [Me (**6a**)], 31.4 and 34.0 [C(2) and C(3) (**6b**)], 38.8 [C(2) (**6a**)], 44.7 [C(3) (**6a**)], 114.7 [C(5) (**6a**)], 117.0 [C(5) (**6b**)], 133.1 [*C*H$_2$=C (**6a**)], 136.6 [C(4) (**6a**)], 137.6 [C(4) (**6b**)], 157.0 [=*C*Me$_2$ (**6b**)]. ^{11}B NMR (64.21 MHz, CH$_2$Cl$_2$) δ: 55.6.

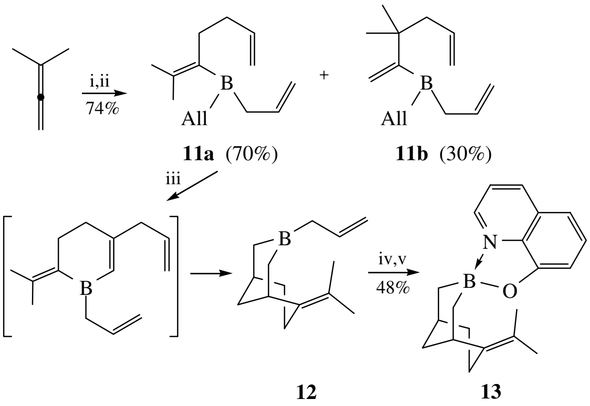
7a and **7b** (3:7) reaction mixture. ^{1}H NMR (^{1}H, ^{1}H COSY) (500.13 MHz, CH$_2$Cl$_2$/CDCl$_3$, 25 °C) δ: 1.17 [s, 6H, Me (**7a**)], 1.79 and 1.83 [s, 6H, Me (**7b**)], 2.07 [dt, 2H, H(3) (**7b**), $^{3}J_{\mathrm{H(3)-H(2)}}$ 6.30 Hz, $^{3}J_{\mathrm{H(3)-H(X)}}$ 6.65 Hz], 2.33 [t, 2H, H(2) (**7b**), $^{3}J_{\mathrm{H(2)-H(3)}}$ 6.30 Hz], 2.34 [d, 2H, H(3) (**7a**), $^{3}J_{\mathrm{H(3)-H(X)}}$ 7.35 Hz], 2.44 [br. d, 4H, H$_2$CB (**7a**, **7b**), $^{3}J_{\mathrm{H(Y)-H(X)}}$ 7.65 Hz], 4.96 [br. d, 1H, H(5A) (**7b**), $^{3}J_{\mathrm{H(5A)-H(X)}}$ 10.20 Hz], 4.98–5.03 [br. m, 3H, H(5A), H(5B) (**7a**), H(5B) (**7b**)], 5.00 [br. d, 1H, CH=C*H*$_2$ (A) (BAll) (**7a**, **7b**), $^{3}J_{\mathrm{H(A)-H(X)}}$ 9.65 Hz], 5.02 [br. d, 1H, CH=C*H*$_2$ (B) (BAll) (**7a**, **7b**), $^{3}J_{\mathrm{H(B)-H(X)}}$ 17.50 Hz], 5.62–5.75 [m, 1H, H(4) (**7a**), $^{3}J_{\mathrm{H(X)-H(3)}}$ 7.35 Hz], 5.64 and 5.69 [s, 2H, CH$_2$=C (**7a**)], 5.81 [ddt, 1H, H(4) (**7b**), $^{3}J_{\mathrm{H(X)-H(5B)}}$ 17.10 Hz, $^{3}J_{\mathrm{H(X)-H(5A)}}$ 10.20 Hz, $^{3}J_{\mathrm{H(X)-H(3)}}$ 6.65 Hz], 5.96 [ddt, 1H, C*H*=CH$_2$ (BAll) (**7a**, **7b**), $^{3}J_{\mathrm{H(X)-H(B)}}$ 17.50 Hz, $^{3}J_{\mathrm{H(X)-H(A)}}$ 9.65 Hz, $^{3}J_{\mathrm{H(X)-H(Y)}}$ 7.65 Hz]. ^{13}C NMR (DEPT-135) (50.32 MHz, CH$_2$Cl$_2$/CD$_2$Cl$_2$, –78 °C) δ: 20.8 and 25.4 [Me (**7b**)], 28.2 [Me (**7a**)], 30.7 and 34.1 [C(2) and C(3) (**7b**)], 36.0 [br. H$_2$CB (**7a**)], 36.8 [br. H$_2$CB (**7b**)], 39.2 [C(2) (**7a**)], 46.3 [C(3) (**7a**)], 115.3 [CH=*C*H$_2$ (BAll) (**7b**)], 115.4 [CH=*C*H$_2$ (BAll) (**7a**)], 115.9 [C(5) (**7a**)], 117.3 [C(5) (**7b**)], 125.6 [*C*H$_2$=C (**7a**)], 132.7 [C(4) (**7a**)], 133.6 [*C*H=CH$_2$ (BAll) (**7b**)], 133.7 [*C*H=CH$_2$ (BAll) (**7a**)], 138.9 [C(4) (**7b**)], 142.6 [=*C*Me$_2$ (**7b**)]. ^{11}B NMR (64.21 MHz, CH$_2$Cl$_2$) δ: 69.1.



Scheme 3 *Reagents and conditions*: i, CH$_2$Cl$_2$, –78 °C, AllBCl$_2$, 15 min; ii, Et$_3$N/MeOH, –78 °C → 20 °C, reflux for 2 h; iii, H$^+$, 2,4-(O$_2$N)$_2$C$_6$H$_3$-NHNH$_2$, H$_2$O$_2$, –78 °C → 20 °C, reflux for 4 h.

sponding boronates **8a** and **8b**[§] in 80% overall yield (Scheme 3).

The oxidation of a mixture of boronates **8a** and **8b** with H$_2$O$_2$ in the presence of 2,4-dinitrophenylhydrazine leads to hydrazones **9** and **10**,[¶] which were prepared in a pure state by five-step inclusion crystallisation. The treatment of a mixture of **7a** and **7b** with AllMgBr and the subsequent bicyclisation *via* heating at 135–140 °C for 140 h leads to 6-(1-methylethylidene)-3-borabicyclo[3.3.1]nonane derivative **12** isolated as 8-oxyquinoline adduct **13**[††] (Scheme 4).



Scheme 4 *Reagents and conditions*: i, CH$_2$Cl$_2$, –78 °C, All$_2$BCl, 15 min; ii, –78 °C → 20 °C, 1 equiv. AllMgBr, reflux for 3 h; iii, 135–140 °C, 140 h; iv, 20 °C, MeOH, reflux for 2 h; v, Et$_2$O, 8-oxyquinoline, reflux for 1 h.

Note that compound **3** was not properly characterised and for the first time was assumed to have a structure of 3-allyl-6-methylene-7,7-dimethyl-3-borabicyclo[3.3.1]nonane,[4–6] which corresponds to the vinylborane **6a**-like product formation at the first stage of condensation.

Reproduction of the methodology[2] leads to 7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane derivative isolated as 8-oxyquinoline adduct **14**[‡‡] (Scheme 5) along with a number of minor products.

In conclusion the data obtained show the stereochemical difference in the behaviour between All$_3$B and allylchloroboranes with respect to 1,1-dimethylallene. In the case of triallylborane, only an allylic product (**1a** or **1b**) is formed at the first stage as a result of addition of the allylic group to C$_2$ of the allenic system, while reaction with allyl(dichloro)- and diallyl(chloro)-boranes leads to the formation of vinylboranes (boron attacks the most electron-donating C$_2$ atom of the allenic system). Thus, it is possible to prepare isomeric 6- and 7-methylene-3-borabicyclo[3.3.1]nonane derivatives by an appropriate choice of the allylborating reagent.

[§] **8a** and **8b** (as a 3:7 mixture) 80% yield; bp 51–52 °C (2 Torr). ^{1}H NMR (200.13 MHz, CDCl$_3$) δ: 1.04 [s, 6H, Me (**8a**)], 1.69 and 1.70 [s, 6H, Me (**8b**)], 3.56 [s, 6H, OMe (**8b**)], 3.58 [s, 6H, OMe (**8a**)], 2.07 [br. dt, 2H, H(3) (**8b**), $^3J_{\mathrm{H(3)-H(2)}}$ 6.6 Hz, $^3J_{\mathrm{H(3)-H(X)}}$ 6.2 Hz], 2.15 [br. t, 2H, H(2) (**8b**), $^3J_{\mathrm{H(2)-H(3)}}$ 6.6 Hz], 2.17 [br. d, 2H, H(3) (**8a**), $^3J_{\mathrm{H(3)-H(X)}}$ 7.6 Hz], 4.95 [dd, 1H, H(5A) (**8a**), $^3J_{\mathrm{H(5A)-H(X)}}$ 9.2 Hz, $^2J_{\mathrm{H(5A)-H(5B)}}$ 2.1 Hz], 4.95 [dd, 1H, H(5A) (**8b**), $^3J_{\mathrm{H(5A)-H(X)}}$ 10.4 Hz, $^2J_{\mathrm{H(5A)-H(5B)}}$ 1.4 Hz], 5.03 [dd, 1H, H(5B) (**8b**), $^3J_{\mathrm{H(5B)-H(X)}}$ 17.7 Hz, $^2J_{\mathrm{H(5B)-H(5A)}}$ 1.4 Hz], 5.06 [dd, 1H, H(5B) (**8a**), $^3J_{\mathrm{H(5B)-H(X)}}$ 17.0 Hz, $^2J_{\mathrm{H(5B)-H(5A)}}$ 2.1 Hz], 5.41 and 5.82 [s, 2H, CH$_2$=C (**8a**)], 5.80 [ddt, 1H, H(4) (**8a**), $^3J_{\mathrm{H(X)-H(5B)}}$ 17.7 Hz, $^3J_{\mathrm{H(X)-H(5A)}}$ 9.2 Hz, $^3J_{\mathrm{H(X)-H(3)}}$ 7.6 Hz], 5.82 [ddt, 1H, H(4) (**8b**), $^3J_{\mathrm{H(X)-H(5B)}}$ 17.0 Hz, $^3J_{\mathrm{H(X)-H(5A)}}$ 10.4 Hz, $^3J_{\mathrm{H(X)-H(3)}}$ 6.2 Hz]. ^{13}C NMR (DEPT-135) (50.32 MHz, CDCl$_3$) δ: 18.8 and 25.4 [Me (**8b**)], 27.3 [Me (**8a**)], 30.4 and 33.6 [C(2) and C(3) (**8b**)], 38.5 [C(2) (**8a**)], 46.4 [C(3) (**8a**)], 51.8 [OMe (**8b**)], 52.0 [OMe (**8a**)], 114.2 [C(5) (**8b**)], 116.3 [CH$_2$=C (**8a**)], 118.5 [C(5) (**8a**)], 136.1 [C(4) (**8a**)], 136.6 [=*C*Me$_2$ (**8b**)], 138.9 [C(4) (**8b**)]. ^{11}B NMR (64.21 MHz, CDCl$_3$) δ: 29.8. Found (%): C, 65.57; H, 10.42; B, 5.60. Calc. for C$_{10}$H$_{19}$BO$_2$ (%): C, 65.97; H, 10.52; B, 5.94.

[¶] **9** (mixture of *Z* and *E* isomers, 1:3.7); mp 46–51 °C. ^{1}H NMR (200.13 MHz, CDCl$_3$) δ: 1.24 (s, 6H, Me), 2.04 [s, 3H, H(1) (**9***Z*)], 2.19 [s, 3H, H(1) (**9***E*)], 2.34 [d, 2H, H(4) (**9***E*), $^3J_{\mathrm{H(4)-H(X)}}$ 7.3 Hz], 2.49 [m, 2H, H(4) (**9***Z*)], 5.07 [d, 1H, H(6B) (**9***E*), $^3J_{\mathrm{H(6B)-H(X)}}$ 16.7 Hz], 5.08 [m, 2H, H(6) (**9***Z*)], 5.14 [d, 1H, H(6A) (**9***E*), $^3J_{\mathrm{H(6A)-H(X)}}$ 10.7 Hz], 5.73 [ddt, 1H, H(5) (**9***E*), $^3J_{\mathrm{H(X)-H(6B)}}$ 16.7 Hz, $^3J_{\mathrm{H(X)-H(6A)}}$ 10.7 Hz, $^3J_{\mathrm{H(X)-H(4)}}$ 7.3 Hz], 5.81–6.04 [m, 1H, H(5) (**9***Z*)], 7.97 [d, 1H, H(6′) (**9***E*), $^3J_{\mathrm{H(6')-H(5')}}$ 9.7 Hz], 7.98 [d, 1H, H(6′) (**9***Z*), $^3J_{\mathrm{H(6')-H(5')}}$ 9.7 Hz], 8.32 [d, 1H, H(5′) (**9***E*), $^3J_{\mathrm{H(5')-H(6')}}$ 9.7 Hz], 8.33 [d, 1H, H(5′) (**9***Z*), $^3J_{\mathrm{H(5')-H(6')}}$ 9.7 Hz], 9.15 [s, 1H, H(3′)], 11.05 [s, 1H, NH (**9***E*)], 11.35 [s, 1H, NH (**9***Z*)]. ^{13}C NMR (50.32 MHz, CDCl$_3$) δ: 12.3 [C(1) (**9***Z*)], 18.7 [C(1) (**9***E*)], 25.3 [Me (**9***Z*)], 31.5 [C(3) (**9***E*)], 36.2 [C(4) (**9***E*)], 42.5 [C(3) (**9***Z*)], 44.6 [C(4) (**9***Z*)], 116.5 [C(6) (**9***E*)], 116.6 [C(6′) (**9***Z*, **9***E*)], 117.6 [C(6) (**9***Z*)], 123.4 [C(3′) (**9***Z*, **9***E*)], 128.8 [C(2′) (**9***Z*, **9***E*)], 129.8 [C(5′) (**9***Z*, **9***E*)], 134.3 [C(5) (**9***Z*)], 137.5 [C(5) (**9***E*)], 137.7 [C(4′) (**9***Z*, **9***E*)], 145.2 [C(1′) (**9***Z*, **9***E*)], 164.1 [C(2) (**9***E*)], 162.4 [C(2) (**9***Z*)]. MS, *m*/*z* (I, %): 306 [M]$^+$ (15.0), 291 [M – Me]$^+$ (11.0), 289 [M – OH]$^+$ (72.6), 260 [M – NO$_2$]$^+$ (72.6). Found for a mixture of isomeric **9** and **10** (%): C, 54.86; H, 5.92; N, 17.45. Calc. for C$_{14}$H$_{17}$N$_2$O$_4$ (%): C, 54.89; H, 5.92; N, 18.29.

10; mp 84–86 °C. ^{1}H NMR (200.13 MHz, CDCl$_3$) δ: 1.25 (d, 6H, Me, $^3J_{\mathrm{Me-H(2)}}$ 4.8 Hz), 2.41 and 2.50 [br. m, 2H, H(4) and H(5)], 2.67 [br. m, 1H, H(2)], 5.12 [d, 1H, H(7A), $^3J_{\mathrm{H(X)-H(A)}}$ 11.1 Hz], 5.19 [d, 1H, H(7B), $^3J_{\mathrm{H(B)-H(X)}}$ 18.0 Hz], 5.91 [br. dd, 1H, H(6), $^3J_{\mathrm{H(X)-H(B)}}$ 18.0 Hz, $^3J_{\mathrm{H(X)-H(A)}}$ 11.1 Hz], 7.99 [d, 1H, H(6′), $^3J_{\mathrm{H(6')-H(5')}}$ 8.3 Hz], 8.32 [d, 1H, H(5′), $^3J_{\mathrm{H(5')-H(6')}}$ 8.3 Hz], 9.15 [s, 1H, H(3′)], 11.24 [s, 1H, NH]. ^{13}C NMR (50.32 MHz, CDCl$_3$) δ: 20.1 (Me), 28.6 and 29.4 [C(4), C(5)], 28.8 [C(2)], 116.3 [C(6′)], 116.4 [C(7)], 123.4 [C(3′)], 128.8 [C(2′)], 129.8 [C(5′)], 137.4 [C(6)], 137.7 [C(4′)], 145.2 [C(1′)], 165.0 [C(3)]. MS, *m*/*z* (I, %): 306 [M]$^+$ (6.0), 291 [M – Me]$^+$ (10.0), 289 [M – OH]$^+$ (35.2), 260 [M – NO$_2$]$^+$ (99.8).

11a and **11b** (as a 3:7 mixture); 74% yield from 3-methylbuta-1,2-diene; bp 100–102 °C (2 Torr). ^{1}H NMR (200.13 MHz, CDCl$_3$) δ: 1.00 [s, 6H, Me (**11a**)], 1.57 and 1.71 [s, 6H, Me (**11b**)], 1.95–2.08 [br. m, 2H, H(3) (**11b**)], 2.08–2.19 [br. m, 4H, H(3) (**11a**), H(2) (**11b**)], 2.25 [br. d, 8H, H$_2$CB (**11a**, **11b**), $^3J_{\mathrm{H(Y)-H(X)}}$ 7.4 Hz], 4.78–5.06 [br. m, 12H, H(5) (**11a**, **11b**), CH=C*H*$_2$ (BAll) (**11a**, **11b**)], 5.30 [s, 1H, H(*Z*) CH$_2$=C (**11a**)], 5.68–6.09 [br. m, 7H, C*H*=CH$_2$ (BAll) (**11a**, **11b**), H(4) (**11a**, **11b**), H(*E*) CH$_2$=C (**11a**)]. ^{13}C NMR (50.32 MHz, CDCl$_3$) δ: 19.5 and 25.3 [Me (**11b**)], 28.5 [Me (**11a**)], 29.9 and 34.0 [C(2), C(3) (**11b**)], 36.2 [br., H$_2$CB (**11a**, **11b**)], 45.3 and 47.2 [C(2), C(3) (**11a**)], 114.0 [C(5) (**11b**)], 114.4 [CH=*C*H$_2$ (BAll) (**11a**, **11b**)], 117.4 [C(5) (**11a**)], 130.6 [*C*Me$_2$ (**11a**)], 135.2 [C(4) (**11a**)], 135.8 [*C*H=CH$_2$ (BAll) (**11a**, **11b**)], 137.6 [=*C*Me$_2$ (**11b**)], 138.9 [C(4) (**11b**)]. ^{11}B NMR (64.21 MHz, CDCl$_3$) δ: 80.0. Found (%) C, 81.78; H, 11.38. Calc. for C$_{13}$H$_{21}$B (%): C, 83.00; H, 11.25.

12 not isolated, formation of **12** on heating of **11a** and **11b** mixture was monitored by ^{13}C NMR spectroscopy (DEPT-135) (50.32 MHz) δ: 19.8 and 20.5 (Me), 22.4 [C(7)], 30.0 and 33.6 [C(1), C(5)], 32.8 and 33.2 [br., C(2) and C(4)], 35.0 [C(8)], 37.2 [C(9)], 113.8 (CH=*C*H$_2$), 119.3 [C(6)], 136.0 (*C*H=CH$_2$). ^{11}B NMR (64.21 MHz, CDCl$_3$) δ: 84.2.

[††] **13**; 48% yield from **11a** and **11b** mixture; mp 185–187 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$) δ: 0.19–0.97 [br. m, 4H, H(2), H(4)], 1.57–1.63 [m, 1H, H(7a), H(8α)], 1.68 and 1.72 (s, 6H, Me), 1.79 [m, 1H, H(9*syn*)], 2.08 [d, 1H, H(8β), $^2J_{\mathrm{H(8\beta)-H(8\alpha)}}$ 5.9 Hz], 2.22 [m, 1H, H(9*anti*)], 2.49 [dd, 1H, H(7β), $^3J_{\mathrm{H(7\beta)-H(8\alpha)}}$ 14.7 Hz, $^3J_{\mathrm{H(7\beta)-H(8\beta)}}$ 5.2 Hz], 3.04 [br. m, 1H, H(1)], 3.19 [m, 1H, H(5)], 7.00 [d, 1H, H(7′), $^3J_{\mathrm{H(7')-H(6')}}$ 8.1 Hz], 7.12 [d, 1H, H(5′), $^3J_{\mathrm{H(5')-H(6')}}$ 8.1 Hz], 7.56 [m, 1H, H(3′)], 7.57 [t, 1H, H(6′), *J* 8.1 Hz], 8.30 [d, 1H, H(4′), $^3J_{\mathrm{H(4')-H(3')}}$ 8.1 Hz], 8.39 [d, 1H, H(2′), $^3J_{\mathrm{H(2')-H(3')}}$ 5.1 Hz]. ^{13}C NMR (DEPT-135) (50.32 MHz, CDCl$_3$) δ: 19.7 and 21.9 (Me), 20.4 [C(7)], 28.8 and 32.4 [C(1), C(5)], 31.1 [br., C(2) and C(4)], 34.2 [C(8)], 37.8 [C(9)], 108.9 [C(5′)], 110.7 [C(4′)], 118.2 [C(6)], 122.5 [C(7′)], 128.1 [C(4a′)], 132.1 [*C*Me$_2$], 132.6 [C(6′)], 137.0 [C(3′)], 137.4 [C(2′)], 138.2 [C(8a′)], 153.4 [C(7)], 158.4 [C(8′)]. Raman (λ = 632.81 nm), cm^{-1}: 1420.8 (C=C). Found (%) C, 78.48; H, 8.05; B 3.28. Calc. for C$_{20}$H$_{24}$BNO (%) C, 78.70; H, 7.93; B 3.54.

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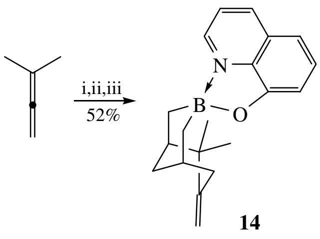

Scheme 5 *Reagents and conditions*: i, All_3B, 140 °C, 10 h; ii, 20 °C, MeOH, reflux for 3 h; iii, Et_2O, 8-oxyquinoline, reflux for 1 h.

Note that the stereospecificity of allylboron–acetylene condensation leads exclusively to 3-borabicyclo[3.3.1]non-6-enes[1] and compound **13** is the first example of 6-*exo*-methylene derivatives.

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‡‡ **14**; 52% yield from 3-methylbuta-1,2-diene; mp 148–152 °C (decomp.). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 0.56 [br. m, 2H, H(2β), H(4β)], 0.89 [br. m, 2H, H(2α), H(4α)], 1.16 and 1.22 (s, 6H, Me), 1.70 [br. dd, 1H, H(8α), $^2J_{\mathrm{H(8\alpha)-H(8\beta)}}$ 6.6 Hz, $^3J_{\mathrm{H(8\alpha)-H(1)}}$ 4.4 Hz], 1.79 [br. d, 1H, H(9*syn*), $^3J_{\mathrm{H(9}syn\mathrm{)-H(9}anti\mathrm{)}}$ 4.4 Hz], 2.07 [d, 1H, H(8β), $^2J_{\mathrm{H(8\beta)-H(8\alpha)}}$ 6.6 Hz], 2.25 [d, 1H, H(9*anti*), $^3J_{\mathrm{H(9}anti\mathrm{)-H(5)}}$ 13.2 Hz], 2.33 [br. m, 1H, H(1)], 2.74 [dd, 1H, H(5), $^3J_{\mathrm{H(5)-(H4\beta)}}$ 4.4 Hz, $^3J_{\mathrm{H(5)-H(9}anti\mathrm{)}}$ 13.2 Hz], 4.88 and 4.90 [s, 1H, CH_2=], 6.95 [d, 1H, H(7′), $^3J_{\mathrm{H(7')-H(6')}}$ 8.1 Hz], 7.09 [d, 1H, H(5′), $^3J_{\mathrm{H(5')-H(6')}}$ 8.1 Hz], 7.54 [m, 1H, H(3′)], 7.57 [t, 1H, H(6′), *J* 7.4 Hz], 8.26 [d, 1H, H(4′), $^3J_{\mathrm{H(4')-H(3')}}$ 8.1 Hz], 8.39 [d, 1H, H(2′), $^3J_{\mathrm{H(2')-H(3')}}$ 5.1 Hz]. ^{13}C NMR (DEPT-135) (50.32 MHz, $CDCl_3$) δ: 27.0 (Me), 29.4 and 30.2 [C(1) and C(5)], 32.4 [C(9)], 40.5 [C(8)], 41.6 [C(6)], 108.0 [CH_2=], 108.7 [C(5′)], 110.5 [C(4′)], 122.5 [C(7′)], 128.1 [C(4a′)], 132.6 [C(6′)], 137.2 [C(3′)], 137.4 [C(2′)], 137.7 [C(8a′)], 153.4 [C(7)], 158.6 [C(8′)]. Found (%): C, 77.98; H, 8.30; B, 3.75. Calc. for $C_{20}H_{24}BNO$ (%): C, 78.70; H, 7.93; B 3.54.