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First 1,1-organoboration reactions of vinyltin compounds—a route to boryl-substituted stannolanes and organo-substituted stannol-3-enes†

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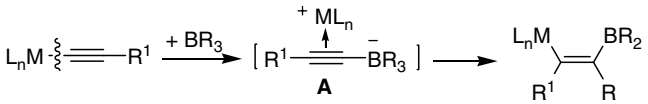
Dimethyl(divinyl)tin 1 reacts with triethylborane, BEt_3 2a, triallylborane, $BAll_3$ 2b, tribenzylborane, BBz_3 2c, trivinylborane, $BVin_3$ 2d, triphenylborane, BPh_3 2e, and 1-boraadamantane 2f by intermolecular 1,1-organoboration via cleavage of the Sn–vinyl bond, followed by ring closure via intramolecular 1,1-organoboration (cleavage of the second Sn–vinyl bond) to give the boryl-substituted stannolanes 3a–e, and 7 and 8. The heterocycles 3a–e can undergo dehydroboration, hydroboration, and/or further reactions. If dialkylboranes such as 9-borabicylo[3.3.1]nonane 11 (9-BBN) or diethylborane (Et_2BH) 12 are used, the first expected step is the hydroboration of one of the vinyl groups in 1, and the second step is the ring closure to boryl-substituted stannolanes 13 and 6a, respectively, by intramolecular 1,1-organoboration. The mechanism of the second step, in contrast to the literature, was confirmed by the reaction of dimethyl- (9) and diphenyl(di-2-propenyl)tin (10) with the boron hydrides 11 and 12. In the resulting stannolanes 14 and 15, the 3,5-positions of the methyl groups support the mechanism of 1,1-organoboration. The structures of the new cyclic organotin compounds are assigned on the basis of consistent one- and two-dimensional ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR spectroscopic data sets. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: vinylstannanes; organoboranes; heterocycles; organoboration; hydroboration; NMR

INTRODUCTION

Selective formation of C–C bonds by 1,1-organoboration of alkyn-1-ylmetal compounds provides a versatile route to numerous organometallic compounds.[1–4] These reactions take advantage of the polar M–alkynyl (M–C≡) bonds and the electrophilic character of boron in triorganoboranes. Cleavage of the M–C≡bond affords zwitterionic borate-like intermediates **A**, in which the metal fragment is still side-on coordinated to the C≡C bond.[5–7] Further rearrangement leads to organometallic-substituted alkenes (Scheme 1).

Considering the properties of triorganoboranes and the M–vinyl (M–C=) bond in vinylmetal derivatives, a reaction mechanism similar to that shown in Scheme 1 is conceivable, and this would greatly extend scope and application of 1,1-organoboration reactions. In order to explore this field, keeping in mind the synthetic potential of organotin compounds,[8–11] we have started to study the reactivity of dimethyl(divinyl)tin, $Me_2Sn(CH{=}CH_2)_2$ **1**, towards triethylborane, BEt_3 **2a**, triallylborane, $BAll_3$ **2b**, tribenzylborane, BBz_3 **2c**, trivinylborane **2d**, triphenylborane, BPh_3 **2e** and 1-boraadamantane **2f**. This selection of boranes includes those with moderate reactivity (e.g. **2a, 2c**), fairly reactive species (e.g. **2b**,[12] **2d, 2e**) and **2f**,[13] which is extremely reactive owing to the enforced pyramidal surroundings of the boron atom.



Scheme 1. General reaction of alkyn-1-ylmetal compounds with triorganoboranes: 1,1-organoboration.

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RESULTS AND DISCUSSION

With the exception of **2b** and **2f**, all reactions of the triorganoboranes with dimethyl(divinyl)tin **1** were rather slow or did not take place at all at room temperature. In the case of **2a**, the reaction required heating at reflux in benzene for 48 h, whereas 12 h at room temperature was sufficient for **2b**, and in the other cases (**2c, 2d, 2e**) gentle heating at 60 °C for several hours was necessary. Only one major type of product was formed in the beginning of the reactions, identified by characteristic NMR data (Table 1) as stannacyclopentane derivatives, the 1,1-dimethylstannolanes **3** (Scheme 2). These heterocycles possess two stereogenic centers bearing an organyl group in 4-position, and the respective diorganoboryl group in 3-position. The 3,4-substituents are in mutual *trans*-positions, as is evident from the assignment of ^{1}H- and ^{13}C NMR spectra (Table 1) and 2D ^{1}H/^{1}H COSY and 2D ^{1}H/^{1}H NOESY experiments. Further heating of the reaction mixture induced dehydroboration and hydroboration. 4,3-Dehydroboration afforded **4** (Table 2; see also Fig. 1), of which 4**b** could be isolated by distillation in pure state (see Fig. 2 for the ^{13}C NMR spectrum). The diallylborane, formed in this process, decomposes and, therefore, is not available for further reactions.

Since the reaction towards **3a** proceeded slowly and its induction required prolonged periods of heating, 4,3-dehydroboration took place when a significant amount of dimethy(divinyl)tin **1** was still present in the mixture. The diethylborane (Et_2BH) formed by 4,3-dehydroboration of **3a** then reacted with **1** first by hydroboration to the short-lived intermediate **5(BEt$_2$)**, followed by intramolecular 1,1-organoboration to give **6a** (Scheme 3, Fig. 3). The compound **6a** could be isolated from the reaction mixture by fractional distillation together with a small amount of **4a**. This reaction sequence (Scheme 3) may also be considered for the other stannolanes **3**. However, it played a minor role, since prolonged heating could be avoided.

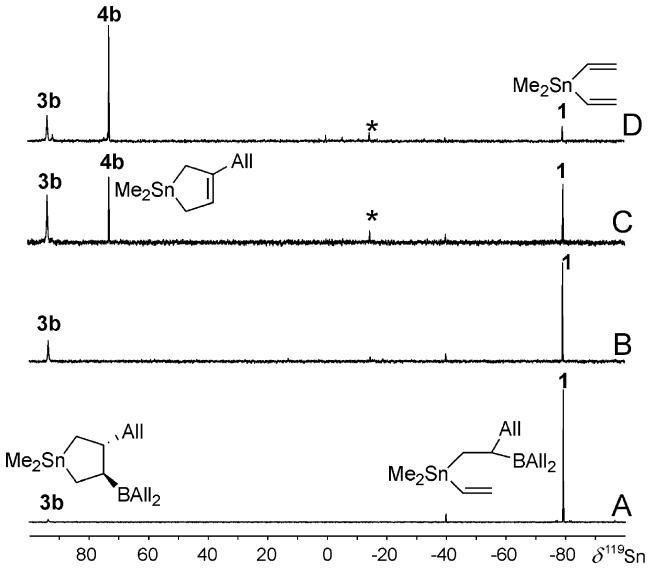

Figure 1. 186.5 MHz ^{119}Sn{^{1}H} NMR spectra for monitoring the reaction of triallylborane, $BAll_3$ **2b**, with dimethyl(divinyl)tin **1**. (A) After 1 h; (B) after 4 h; (C) after 10 h; (D) after 14 h. The asterisk marks the signal of an unknown impurity.

Table 1. ^{119}Sn, ^{11}B and ^{13}C NMR data[a] for the stannacyclopentanes **3a–e** (Scheme 2), **6a** (Scheme 3) and **13**–**15** (Scheme 6)

	δ^{119}Sn	δ^{11}B	δ^{13}C(2)	δ^{13}C(3)	δ^{13}C(4)	δ^{13}C(5)
3a[b]	91.6	79.7	8.2 [284.2]	47.2 (br)	47.5 [24.2]	18.7 [367.9]
3b[c]	93.4	74.1	7.4 [277.0]	47.2 (br)	46.0 [24.6]	19.7 [364.3]
3c[d]	93.1	73.2	7.1 [267.3]	46.8 (br)	48.1 [24.0]	20.0 [364.4]
3d[e]	89.5	61.5	11.2 [281.0]	43.3 (br)	49.9 [26.5]	20.0 [353.0]
3e[f]	90.5	66.9	12.0 [265.1]	45.3 (br)	51.7 [24.2]	14.1 [323.4]
6a[g]	71.3	80.3	8.6 [305.2]	40.1 (br)	31.4 [17.7]	12.9 [364.0]
13[h]	70.3	79.0	7.8 [303.6]	40.4 (br)	31.4 [17.1]	12.8 [364.9]
14[i]	73.7	82.8	21.4 [305.7]	36.0 (br)	50.1 [27.7]	21.4 [365.5]
15[k]	15.6	84.0	20.2 [309.8]	39.8 (br)	49.7 [33.1]	23.3 [383.0]

[a] In C_6D_6 at 296 K; coupling constants $J(^{119}Sn,^{13}C)$ are given in brackets [±0.3 Hz]; (br) denotes broad ^{13}C NMR signals owing to partially relaxed scalar ^{13}C–^{11}B spin–spin coupling.
[b] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.1$ [288.2], −9.0 [294.6] (Me_2Sn); 17.3 (br), 9.8 (BEt_2); 33.5 [65.9], 13.6 (4-Et).
[c] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -8.9$ [299.7], −8.8 [293.5] (Me_2Sn), 32.4 (br), 137.7, 114.3 ($BAll_2$); 45.4 [68.5], 139.4, 116.5 (4-All).
[d] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -8.9$ [293.4], −8.8 [302.8] (Me_2Sn), 34.4 (br), 125.2, 126.7, 129.0, 129.8 (BBz_2) 47.45 [69.3]; 126.7; 129.1, 130.1, 143.0 (4-Bz).
[e] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -8.9$ [296.0], −8.8 [298.0] (Me_2Sn), 112.1 [5.6], 146.7 [72.0] (−CH=CH_2); 137.0, 142.0 (br) (B(CH=CH_2)$_2$).
[f] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -8.5$ [297.5], −8.5 [298.5] (Me_2Sn); signals for phenyl groups overlap strongly and were not analyzed.
[g] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.7$ [289.6], −9.5 [295.3] (Me_2Sn); 9.5, 17.6 (br) (BEt_2).
[h] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.6$ [290.1], −9.4 [294.9] (Me_2Sn); 24.3, 30.4 (br), 34.2, 34.5 (9-BBN).
[i] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -10.1$ [281.3], −9.2 [280.0] (Me_2Sn); 16.5 (br), 9.2 (BEt_2); 21.3 [9.4] (5-Me); 26.5 [38.7] (3-Me).
[k] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = 21.8$ [11.7] (5-Me); 26.5 [31.5] (3-Me); 28.2 (br), 34.5, 34.8, 24.1 (BBN); 140.3 [427.2], 140.8 [428.3], 137.7 [36.1], 138.0 [36.6], 129.4, 129.3, 129.7, 129.8 (Ph_2Sn).

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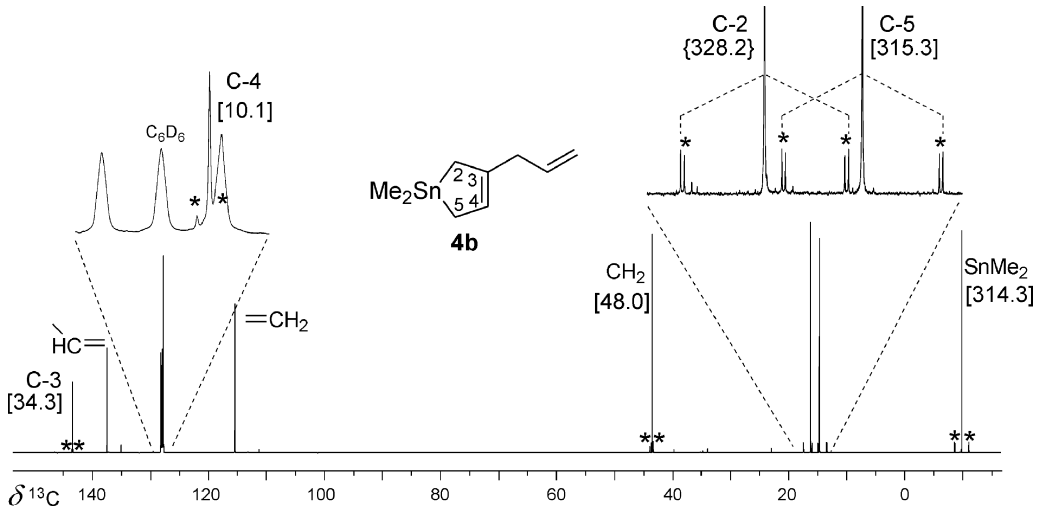

Figure 2. 125.8 $^{13}C\{^1H\}$ NMR spectrum of a distilled sample of **4b** (23 °C in C_6D_6, 10% v/v). Coupling constants $J(^{119}Sn,^{13}C) \pm 0.3$ Hz are given in brackets; $^{117/119}Sn$ satellites are marked by asterisks, and some are shown in the expansions.

Table 2. ^{119}Sn, and ^{13}C NMR data[a] for 1,1-dimethyl-3-*R*-1-stannacyclopent-3-enes **4a–d** (Scheme 2)

	$\delta^{119}Sn$	$\delta^{13}C(2)$	$\delta^{13}C(3)$	$\delta^{13}C(4)$	$\delta^{13}C(5)$
4a[b]	72.4	16.2 [315.3]	147.3 [31.6]	126.1 [10.8]	15.0 [316.8]
4b[c]	72.8	16.7 [328.2]	144.0 [34.6]	128.4 [10.1]	15.2 [315.3]
4c[d]	75.8	16.3 [326.8]	145.2 [34.3]	126.9 [11.5]	15.2 [313.1]
4e[e]	73.4	16.2 [326.1]	144.8 [38.4]	130.6 [9.4]	16.0 [308.1]

[a] In C_6D_6 at 296 K; coupling constants $J(^{119}Sn,^{13}C)$ are given in brackets [±0.3 Hz].
[b] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.4$ [312.8] (Me_2Sn), 32.3 [47.8], 13.5 [2.7] (3-Et).
[c] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.4$ [314.3] (Me_2Sn); 44.1 [48.0], 138.0, 116.0 (3-All).
[d] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.3$ [314.3] (Me_2Sn); 46.1 [47.3], 140.4, 130.0, 129.1, 125.5 (3-Bz).
[e] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.1$ [326.8] (Me_2Sn); signals for phenyl groups overlap strongly and were not analyzed.

Table 3. ^{119}Sn, ^{11}B and ^{13}C NMR data[a] of the polycyclic stannolanes **7** and **8** (Scheme 4)

	$\delta^{119}Sn$	$\delta^{11}B$	$\delta^{13}C(2)$	$\delta^{13}C(3)$	$\delta^{13}C(4)$	$\delta^{13}C(5)$
7[b]	88.5	91.1	7.0 [328.9]	44.9 (br)	42.0 [14.4]	24.0 [342.4]
8[c]	79.1	89.0	11.2 [304.9]	47.8 (br)	46.5 [38.6]	23.2 [365.9]

[a] In C_6D_6 at 296 K; coupling constants $J(^{119}Sn,^{13}C)$ are given in brackets [±0.3 Hz]; (br) denotes broad ^{13}C NMR signals owing to partially relaxed scalar $^{13}C-^{11}B$ spin–spin coupling.
[b] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.6$ [290.8], −8.1 [284.5] (Me_2Sn), 27.5 (CH), 31.6 (br) (CH_2), 33.1 (CH_2), 34.9 (br) (CH_2), 36.4 [23.8] (CH_2), 36.6 (CH), 38.8 (CH), 41.0 (CH_2), 42.8 [4.3] (CH_2) (boraadamantane).
[c] Other ^{13}C NMR data: $\delta[J(^{119}Sn,^{13}C)] = -9.4$ [292.7], −9.3 [286.7] (Me_2Sn), 28.2 [13.7] (CH), 30.5 (br) (CH_2), 33.3 (CH_2), 35.4 (CH), 36.9 (CH), 37.2 (br) (CH_2), 38.4 (CH_2), 41.0 (CH_2), 49.2 [68.4] (CH_2) (boraadamantane).

In the case of the reaction of **1** with 1-boraadamantane **2f**, the reaction was complete after a few minutes at room temperature, and the first identified product was again a stannolane **7** which, however, bears the 3,4-substituents in *cis*-positions (Scheme 4; 1D and 2D ^1H and ^{13}C NMR spectra; see Table 3 and Fig. 4). After three days at room temperature, the rearrangement into the *trans*-isomer **8** was >80% complete (Fig. 4), accompanied by the formation of only small amounts of some unidentified side products (<5%). It appears that **7** is the kinetically controlled product which rearranges by 2,3-dehydroboration and 2,3-hydroboration slowly into the thermodynamically controlled product **8**. Molecular modeling indicates that the dihedral angle Sn–C(5)–C(4)–CH_2 is close to 90° in **7** and close to 180° in **8**, in agreement[14,15] with the small magnitude of $^3J(^{119}Sn,^{13}C_{CH2})$ for **7** (4.2 Hz) and the much larger value for **8** (68.4 Hz).

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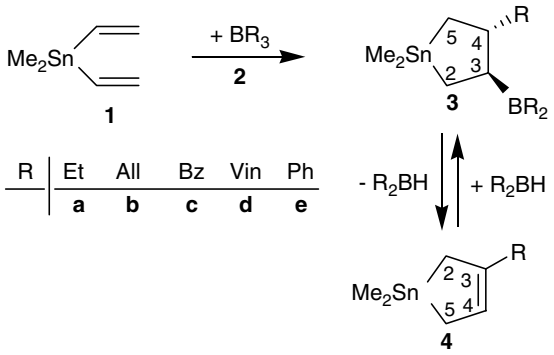
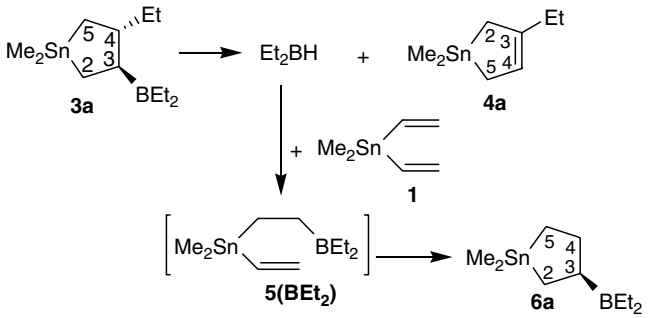
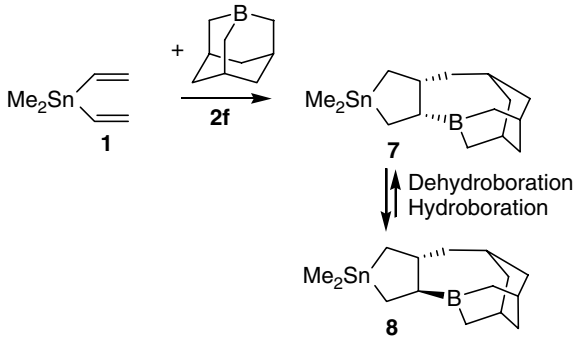


Scheme 2. Reaction of dimethyl(divinyl)tin **1** with triorganoboranes: selective formation of stannolanes, followed by dehydroboration to give stannol-3-enes.



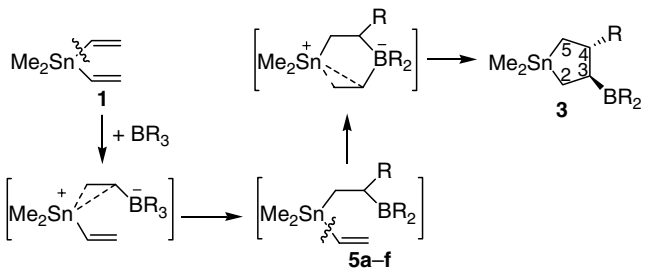
Scheme 3. Special case of the reaction of dimethyl(divinyl)tin **1** wih triethylborane: the diethylborane formed in the dehydroboration reaction is immediately trapped by **1** present in the reaction solution to give **6a**.

The formation of the stannolanes **3** or **7** can be understood to proceed by cleavage of one of the Sn–C═bonds (intermolecular 1,1-organoboration) in the first step, followed by intramolecular 1,1-organoboration to close the ring



Scheme 4. Reaction of dimethyl(divinyl)tin **1** with 1-boraadamantane **2f** to the kinetically controlled product **7** which slowly (2–3 days at room temperature) rearranges into the thermodynamically controlled product **8**.

(Scheme 5). In some cases, the presence of intermediates of type **5** (see Scheme 3) with one vinyl group attached to tin prior to ring closure can be detected by monitoring the reaction using ^{119}Sn NMR spectroscopy (see Fig. 1). A signal of low intensity with a typical ^{119}Sn chemical shift around $\delta - 40$[14,15] is tentatively assigned to compounds of type **5**.



Scheme 5. Proposed mechanism for the 1,1-organoboration of dimethyl(divinyl)tin **1**. This mechanism requires cleavage of both Sn–C═bonds.

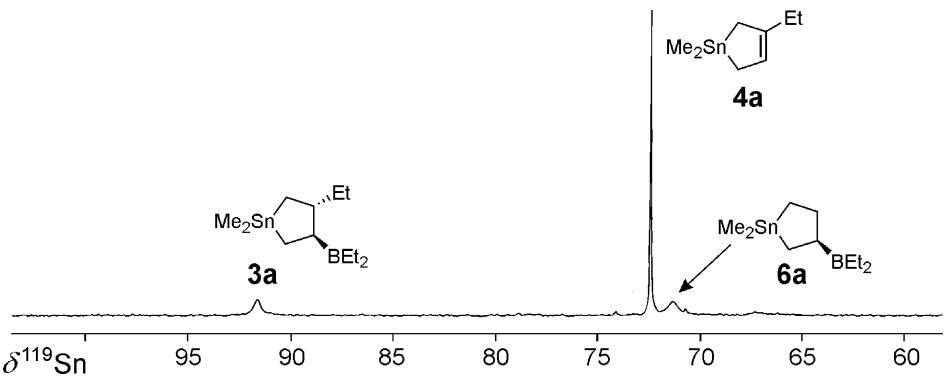


Figure 3. 186.5 MHz ^{119}Sn{^{1}H} NMR spectrum of a reaction mixture containing the stannolanes **3a, 4a** and **6a**. Note the different line width of the ^{119}Sn NMR signals. The broader lines observed for **3a** and **6a** are the result of vicinal partially relaxed scalar ^{119}Sn–^{11}B spin–spin coupling.

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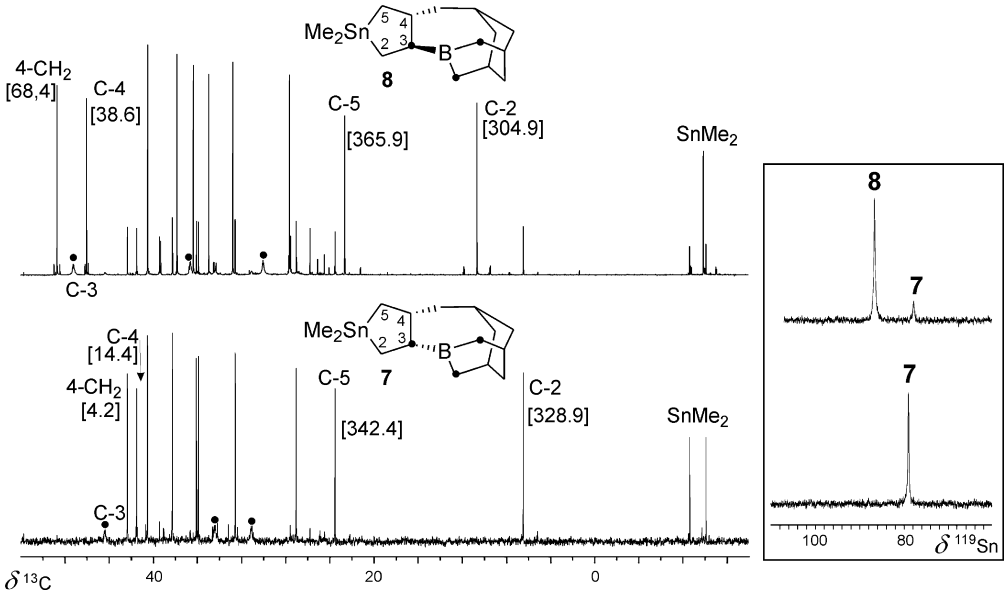
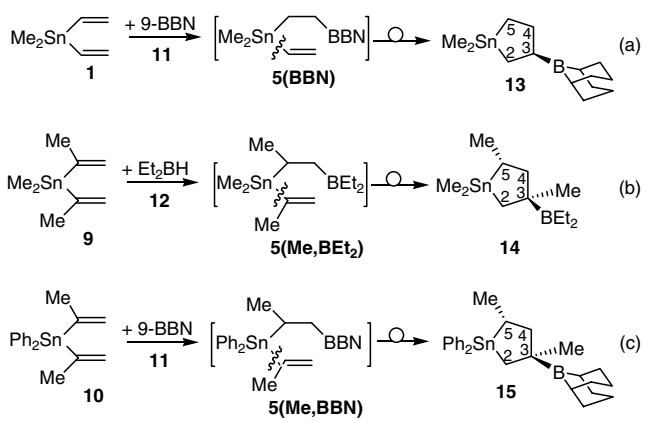


Figure 4. 125.8 MHz $^{13}C\{^1H\}$ and 186.5 MHz $^{119}Sn\{^1H\}$ NMR (insert) spectra of the polycyclic stannolane **7** (lower trace) and its rearrangement into the isomer **8** (upper trace). Most coupling constants $J(^{119}Sn,^{13}C)$ in Hz (±0.3) are given in brackets. Note the large difference for $^3J(^{119}Sn,^{13}C)$ in **7** and **8** (see text). The broad $^{13}C(B)$ signals are indicated by solid circles.

Is there further support for the proposed structure of **6a** (Scheme 3) and for the mechanism by which the intermediates of type **5** are converted into stannolanes? There is a single report in the literature,[16] describing the reaction of dimethyl(divinyl)tin, $Me_2Sn(CH{=}CH_2)_2$ **1**, with 9-borabicyclo[3.3.1]nonane-dimer (9-BBN, **11**). The product, formed almost quantitatively, was characterized as the stannolane **13** [Scheme 6(a)]. We have reproduced this reaction, confirming the structure of **13** by a more complete set of NMR data (Table 1). However, the mechanism involving a hydride shift without cleavage of the Sn–C═bond, proposed in the original report,[16] seemed unlikely, in particular in the light of our present results for the reaction of **1** with triorganoboranes. As outlined before, we suggest that the ring closure takes place by intramolecular 1,1-organoboration via cleavage of the second Sn–C═bond. In order to prove our point, we prepared the di(2-propenyl)tin compounds **9** and **10** and studied their reactions with tetraethyldiborane(6) (Et_2BH **12**) and 9-BBN **11** [Scheme 6(b) and (c), respectively]. The reaction shown in Scheme 6(a) followed exactly the route taken by **1** in the presence of Et_2BH (Scheme 3), and relevant NMR data of **6a** and **13** are almost congruent (Table 1). In the cases of **9** and **10**, the 1,2-hydroboration was expected to place the dialkylboryl group at the terminal carbon of one of the C═C bonds, as shown for the short-lived intermediate **5(Me, BEt_2)** and **5(Me,BBN)**. Intramolecular 1,1-organoboration via cleavage of the remaining Sn–C═bond afforded the stannolanes **14** and **15**. The 3,5-positions of the methyl groups indicate that cleavage of the second Sn–C═bonds must have taken place in the course of the ring closure. The positions of the methyl groups are readily evident from the ^1H and ^{13}C NMR data (Table 1 and Fig. 5). The 3,5-methyl groups in the compounds **14** and **15** are in *cis*-positions ($^1H/^1H$ NOE difference spectra), and there is no appreciable amount of the other isomer present.

CONCLUSIONS

In a first exploratory study it was shown that both Sn–vinyl bonds (Sn–C═) in dimethyl(divinyl)tin can be used for



Scheme 6. Reactions of different divinyltin compounds with dialkylboranes. The sequence of hydroboration and 1,1-organoboration is always observed. The cleavage of the Sn–C═bond in the second step is clearly indicated for the 2-propenyl derivatives, since the methyl groups end up in the 3,5-positions.

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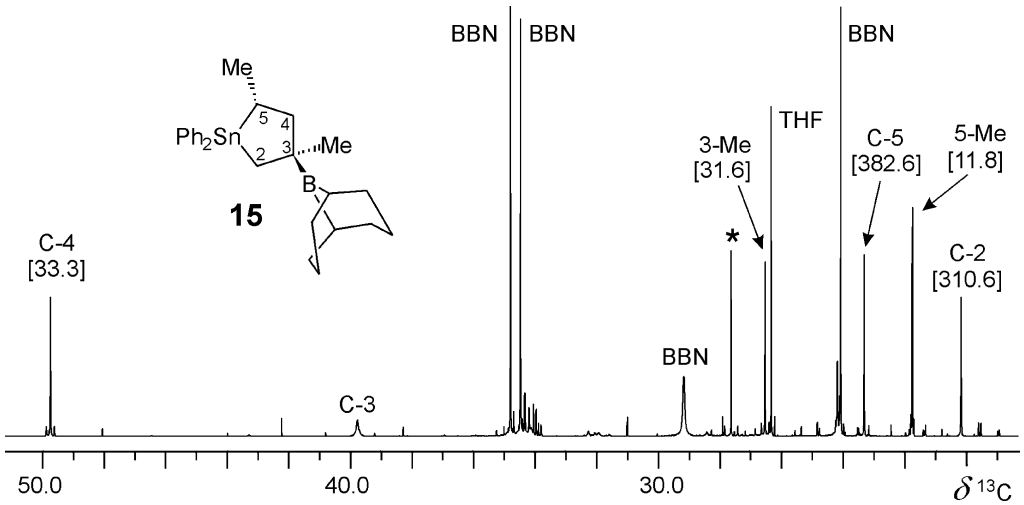

Figure 5. Part of the 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the stannolane **15**, taken from the reaction solution which contains a small amount of THF and the starting material **9** [^{13}C(Me) signal is marked by an asterisk]. Most coupling constants $J(^{119}Sn,^{13}C)$ in Hz (±0.3) are given in brackets. Note the typically broad ^{13}C(B) NMR signals.

1,1-organoboration, in particular in reactions with triorganoboranes which are more reactive than triethylborane. Apparently, the intramolecular 1,1-organoboration of Sn–C═bonds takes place under rather mild reaction conditions, irrespective of the nature of the triorganoborane. This opens a promising field for synthetic applications, as already shown here for the combination of 1,2-hydroboration and intramolecular 1,1-organoboration.

EXPERIMENTAL

Starting materials and measurements

All preparative work and the handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware and dry solvents were used throughout. Triethylborane (**2a**) and 9-borabicyclo[3.3.1]nonane (**11**) were commercial products. The other boranes were prepared following literature procedures (**2b**,[17] **2c**,[18] **2d**,[19] **2e**,[20] **2f**,[21] and **12**[22,23]). Dimethyl(divinyl)tin **1** was prepared from dimethyltin dichloride and two equivalents of vinylmagnesium bromide.[24] Similarly, following an analogous procedure,[25] the 2-propenyltin compounds **9** and **10** were obtained from the reaction of dimethyl- and diphenyltin dichloride, respectively, with two equivalents of isopropenylmagnesium bromide (see below). NMR measurements in C_6D_6 (concentration ca. 5–10%) with samples in 5 mm tubes at 23 ± 1 °C: Bruker DRX 500, Bruker ARX 250, and Varian Inova 300 and 400 spectrometers for ^1H, ^{11}B, ^{13}C and ^{119}Sn NMR; chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0; $\delta^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ MHz]; external BF_3-OEt_2 [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz]. Chemical shifts δ^1H are given to ±0.03 ppm, $\delta^{13}C$ and $\delta^{119}Sn$ to ±0.1 ppm, and $\delta^{11}B$ to ±0.3 ppm. ^{119}Sn NMR spectra were measured in single pulse experiments by inverse-gated ^1H decoupling or by using the refocused INEPT pulse sequence,[26] based on $^2J(^{119}Sn,^1H)$ (ca. 50 Hz).

Dimethyl(di-2-propenyl)tin ***9***

^1H NMR (500 MHz, C_6D_6): δ^1H [$J(^{119}Sn,^1H)$] = 0.13 [54.3] (s, 6H, Me_2Sn); 1.91 [49.3] (t, 6H, Me, $^4J = 1.6$); 5.08 [73.8] (dq, 2H, ═CH_2, $^2J = 2.6$, $^4J = 1.6$); 5.65 [158.0] (dq, 2H, ═CH_2, $^2J = 2.6$, $^4J = 1.6$). ^{13}C NMR (125.8 MHz, C_6D_6): $\delta^{13}C$ [$J(^{119}Sn,^{13}C)$] = −11.5 [344.6] (Me_2Sn); 26.2 [54.0] (Me); 125.8 [35.6] (═CH_2); 149.0 [457.8] (═C–). ^{119}Sn NMR (186.5 MHz, C_6D_6): $\delta^{119}Sn = -68.6$.

Diphenyl(di-2-propenyl)tin ***10***

^1H NMR (500 MHz, C_6D_6): δ^1H [$J(^{119}Sn,^1H)$] = 2.19 [51.9] (t, 6H, Me, $^4J = 1.6$); 5.55 [74.7] (dq, 2H, ═CH_2, $^4J = 1.6$, $^2J = 0.8$); 6.06 [168.8] (dq, 2H, ═CH_2, $^4J = 1.6$, $^2J = 0.8$), 7.4 (m, 6H, Ph); 7.7 (m, 4H, Ph). ^{13}C NMR (125.8 MHz, C_6D_6): $\delta^{13}C$ [$J(^{119}Sn,^{13}C)$] = 27.6 [53.9] (Me); 129.8 [35.0] (═CH_2); 139.1 [498.5], 129.7 [11.0], 129.5, 129.4 (Ph); 147.4 [489.3] (C–Sn). ^{119}Sn NMR (186.5 MHz, C_6D_6): $\delta^{119}Sn = -134.7$.

Reaction of dimethyl(divinyl)tin 1 with triorganoboranes 2a–f (general procedure)

The mixture containing dimethyl(divinyl)tin **1** (6–8 mmol) and an equimolar amount of the triorganoborane **2b–f** in C_6D_6 was allowed to stand for 0.5–1 h (**2f**) or 12 h (**2b**) at room temperature or was heated for 10–20 min (**2d**), 4–6 h (**2c**) or 48 h (**2a**) at 100 °C in sealed tubes. In all cases the reaction was controlled by ^{119}Sn NMR spectroscopy (see Figs 1 and 3). After removing all readily volatile materials *in vacuo*, products were left without starting materials, consisting of a mixture of the heterocycles **3** and **4**, and in the case of **2a**, of **3a, 4a**

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and **6a**. In the case of 1-boraadamantane **2f**, the reaction was complete after 0.5 h in C_6D_6 at room temperature to give at first the tetracyclic compound **7**, which rearranged into **8** at room temperature within 2–3 days (monitored by ^{13}C and ^{119}Sn NMR spectroscopy; see Fig. 4).

3a: ^1H NMR spectra were not assigned because of strong overlap with signals from **4a** and **6a** (see Schemes 2 and 3).

3b: ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.11$ (dd, 1H, H-5, $^2J = 13.7$, $^3J = 11.7$), 0.30 [53.9] (s, 3H, MeSn), 0.31 [54.6] (s, 3H, MeSn), 0.44 (t, 1H, H-2, $^2J = 12.3$), 0.68 (dd, 1H, H-5, $^2J = 11.7$, $^3J = 5.9$), 1.29 (m, 1H, H-3), 1.49 (dd, 1H, H-2, $^2J = 12.3$, $^3J = 5.6$), 1.76 (m, 1H, H-4), 2.1–2.2 (m, 6H, CH_2), 5.0–5.2 (m, 6H, $=CH_2$), 5.92 (ddt, 1H, $=CH-$, $^3J = 17.0$, $^3J = 10.1$, $^3J = 7.4$), 6.13 (ddt, 2H, $=CH-$, $^3J = 17.5$, $^3J = 9.3$, $^3J = 7.8$).

3c: ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.19$ [57.0] (s, 3H, MeSn), 0.21 (dd, 1H, H-5, $^2J = 11.6$, $^3J = 11.5$), 0.24 [54.7] (s, 3H, MeSn), 0.35 (dd, 1H, H-2, $^2J = 12.3$, $^3J = 12.2$), 0.52 (dd, 1H, H-5, $^2J = 11.6$, $^3J = 5.8$), 1.31 (m, 1H, H-4), 1.34 (dd, 1H, H-2; $^2J = 12.3$, $^3J = 5.7$), 1.93 (m, 1H, H-3), 2.35 (d, 2H, BCH_2, $^2J = 15.6$), 2.52 (dd, 1H, CH_2, $^2J = 8.3$), 2.70 (m, 1H, CH_2), 2.72 (d, 2H, BCH_2, $^2J = 15.6$), 7.1–7.4 (m, 15H, Ph).

3d: ^1H NMR: $\delta[^nJ(^{119}Sn,^1H)] = 0.30$ [53.8] (s, 3H, MeSn), 0.31 [54.5] (s, 3H, MeSn), 0.50 (dd, 1H, H-5, $^2J = 13.8$, $^3J = 11.9$), 0.71 (t, 1H, H-2, $^2J = 12.3$), 0.96 (dd, H, H-5, $^2J = 11.9$, $^3J = 5.6$), 1.53 (dd, 1H, H-2, $^2J = 12.3$, $^3J = 5.7$), 1.62 (m, 1H, H-4), 2.18 (m, 1H, H-3), 5.01 (ddd, 1H, $=CH_2$, $^3J = 10.2$, $^2J = 1.7$, $^4J = 1.1$), 5.13 (ddd, 1H, $=CH_2$, $^3J = 17.2$, $^2J = 1.7$, $^4J = 1.4$), 6.03 (m, 1H, $=CH$-), 6.18 (dd, 2H, $=CH_2$, $^3J = 13.1$, $^2J = 4.2$), 6.31 (dd, 2H, $=CH_2$, $^3J = 19.5$, $^2J = 4.2$), 6.86 (dd, 2H, $=CH-$, $^3J = 19.5$, $^3J = 13.1$).

3e: ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.32$ [56.0] (s, 3H, MeSn), 0.42 [54.2] (s, 3H, MeSn), 1.01 [23.8] (t, 1H, H-2, $^2J = 12.1$), 1.21 [28.0] (dd, 1H, H-2, $^2J = 12.1$, $^3J = 5.8$), 1.8 (m, 2H, H-5), 2.76 (td, 1H, H-3, $^2J = 12.4$, $^3J = 5.8$), 3.06 (td, 1H, H-4, $^2J = 12.4$, $^3J = 5.7$), 7.1–7.8 (m, 15H, Ph).

4a: The ^1H NMR spectra were not assigned because of strong overlap with signals for **3a** and **6a** (see Schemes 2 and 3).

4b: b. p. 41–45 °C/0.1 Torr. ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.29$ [55.3] (s, 6H, Me_2Sn), 1.58 [34.7] (m, 2H, H-2), 1.71 [38.0] (m, 2H, H-5), 3.04 (d, 2H, All, $^3J = 6.7$), 5.17 (ddt, 1H, All, $^3J = 10.1$, $^2J = 2.1$, $^4J = 1.0$), 5.21 (ddt, 1H, All, $^3J = 17.0$, $^2J = 2.1$, $^4J = 1.5$), 6.02 (ddt, 1H, All, $^3J = 17.0$, $^3J = 10.0$, $^3J = 6.7$), 6.16 [125.8] (tt, 1H, CH, $^3J = 1.9$, $^3J = 1.4$).

4c: b. p. 73–76 °C/0.1 Torr, together with 2-benzyl-buta-1,3-diene. ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.23$ [55.6] (s, 6H, Me_2Sn), 1.51 [34.3] (m, 2H, H-2), 1.73 [38.0] (m, 2H, H-5), 3.59 (m, 2H, CH_2), 6.24 [126.9] (m, 1H, CH), 7.1–7.4 (m, 5H, Ph). 2-Benzyl-buta-1,3-diene: ^1H NMR (500.1 MHz): $\delta = 3.54$ (m, 2H, CH_2), 4.96 (m, 1H, $=CH_2$), 5.07 (d, 1H, $=CH_2$, $^3J = 10.9$), 5.19 (m, 1H, $=CH_2$), 5.30 (d, 1H, $=CH_2$, $^3J = 17.6$), 6.50 (dd, 1H, $=CH-$, $^3J = 17.6$, $^3J = 10.9$), 7.1–7.4 (m, 5H, Ph). ^{13}C NMR: $\delta = 38.8$ (CH_2), 114.9 ($=CH_2$), 118.8 ($=CH_2$), 139.3 ($=CH$), 140.2, 129.7, 129.1, 126.8 (Ph),

4e: ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.34$ [53.0] (s, 6H, Me_2Sn), 1.84 [32.6] (m, 2H, H-2), 1.95 [36.7] (s, 2H, H-5), 6.83 [122.7] (m, 1H, H-3), 7.1–7.8 (m, 5H, Ph).

6a: ^1H NMR: $\delta[^nJ(^{119}Sn,^1H)] = 0.10$ [46.7] (dd, 1H, H-2, $^2J = 13.5$, $^3J = 12.1$), 0.32 [51.7] (s, 3H, MeSn), 0.34 [53.0] (s, 3H, MeSn), 0.72 [52.6] (ddd, 1H, H-5, $^2J = 12.7$, $^3J = 12.6$, $^3J = 7.1$), 0.88 (m, 1H, H-2), 1.18 (t, 6H, Et_2B, $^3J = 7.5$), 1.21 (m, 2H, H-3, H-4), 1.28 (m, 2H, Et_2B), 1.40 (m, 2H, Et_2B), 1.47 [43.2] (dd, 1H, H-5, $^2J = 13.5$, $^3J = 6.7$), 2.37 (m, 1H, H-4).

7: ^1H NMR: $\delta[^nJ(^{119}Sn,^1H)] = 0.36$ [53.0] (s, 3H, MeSn), 0.46 [53.3] (s, 3H, MeSn), 0.97 (d, 1H, H-5, $^2J = 12.3$), 1.0–2.1 (m, 17H, H-2, H-3, H-5 and signals from dihomo-boraadamantane), 2.54 (m, 1H), 2.61 (m, 1H) (dihomo-boraadamantane), 3.48 (m, 1H, H-4).

8: ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.35$ [53.9] (s, 3H, MeSn), 0.38 [53.3] (s, 3H, MeSn), 0.55 [53.1] (dd, 1H, H-5, $^2J = 12.1$, $^3J = 12.1$), 0.74 [45.0] (dd, 1H, H-2, $^2J = 12.7$, $^3J = 12.5$), 1.0–2.1 (m, 17H, H-2, H-3, H-4, H-5 and signals from dihomo-boraadamantane), 2.32 (m, 1H), 2.61 (m, 1H) (dihomo 1-boraadamantane).

Reaction of dimethyl(divinyl)tin 1 with 9-BBN 11

A solution of 9-BBN (0.312 g, 2.56 mmol) in THF (5 ml) was added to the solution of dimethyl(divinyl)tin **1** (0.518 g, 2.56 mmol) in THF (5 ml) at −78 °C. The reaction mixture was slowly (1 h) warmed up to room temperature and THF was removed *in vacuo* to give 95% pure stannolane **13** as a colorless oil.

13: ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.16$ (dd, 1H, H-2, $^3J = 13.2$, $^2J = 11.7$), 0.25 [53.3] (s, 3H, MeSn), 0.28 [53.8] (s, 3H, MeSn), 0.72 [52.2] (ddd, 1H, H-5, $^2J = 12.3$, $^3J = 12.3$, $^3J = 7.2$), 0.87 (ddd, 1H, H-2, $^2J = 11.7$, $^3J = 5.3$, $^4J = 1.5$), 1.2–2.1 (m, 17H, H-3, H-4, H-5, 9-BBN), 2.46 (m, 1H, H-4).

Reaction of dimethyl- and diphenyl(di-2-propenyl)tin 9,10 with Et_2BH 12 and 9-BBN 11

A THF (5 ml) solution of the borane **12** or **11** (3–4 mmol) was slowly added to the cooled (−78 °C) solution of an equimolar amount of the di(2-propenyl)tin compound **9** or **10** in THF (5 ml). Then the mixture was warmed to room temperature and heated 90 min at 60–65 °C. The solvent was removed *in vacuo*, and the heterocycles **14** and **15** (85–95% pure according the NMR spectra) were left as colorless oils.

14: ^1H NMR (500.1 MHz): $\delta[^nJ(^{119}Sn,^1H)] = 0.30$ [53.1] (s, 3H, MeSn), 0.35 [51.9] (s, 3H, MeSn), 0.60 [38.5] (d, 1H, H-2, $^2J = 11.9$), 1.08 (d, 1H, H-2, $^2J = 11.9$), 1.1 (s, 3H, 3-Me), 1.14 (t, 6H, Et_2B, $^3J = 7.9$), 1.36 (q, 4H, Et_2B, $^3J = 7.9$), 1.41 (m, 1H, H-4), 1.47 (m, 4H, H-5, 5-Me), 2.35 (m, 1H, H-4).

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15: ^{1}H NMR (500.1 MHz): $\delta[^{n}J(^{119}\mathrm{Sn},^{1}\mathrm{H})] = 1.13$ [36.6] (dd, 1H, H-2, $^{2}J = 12.1$, $^{3}J = 1.0$), 1.30 (s, 3H, 3-Me), 1.38 [41.8] (d, 1H, H-2, $^{2}J = 12.1$), 1.61 [71.7] (d, 3H, 5-Me, $^{3}J = 7.6$), 1.73 (ddd, 1H, H-4, $^{2}J = 13.5$, $^{3}J = 6.4$, $^{3}J = 0.8$), 1.8–2.1 (m, 12H, BBN), 2.08 [30.6] (m, 1H, H-5), 2.48 [69.4] (dd, 1H, H-4, $^{2}J = 13.5$, $^{3}J = 8.0$), 7.3–7.8 (m, 10H, Ph).

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