An alternative general preparation of 2-alkyl-1-benzostannepines and their conversion into 1-benzostibepines and 1-benzoborepines *via* a tin–metal exchange †

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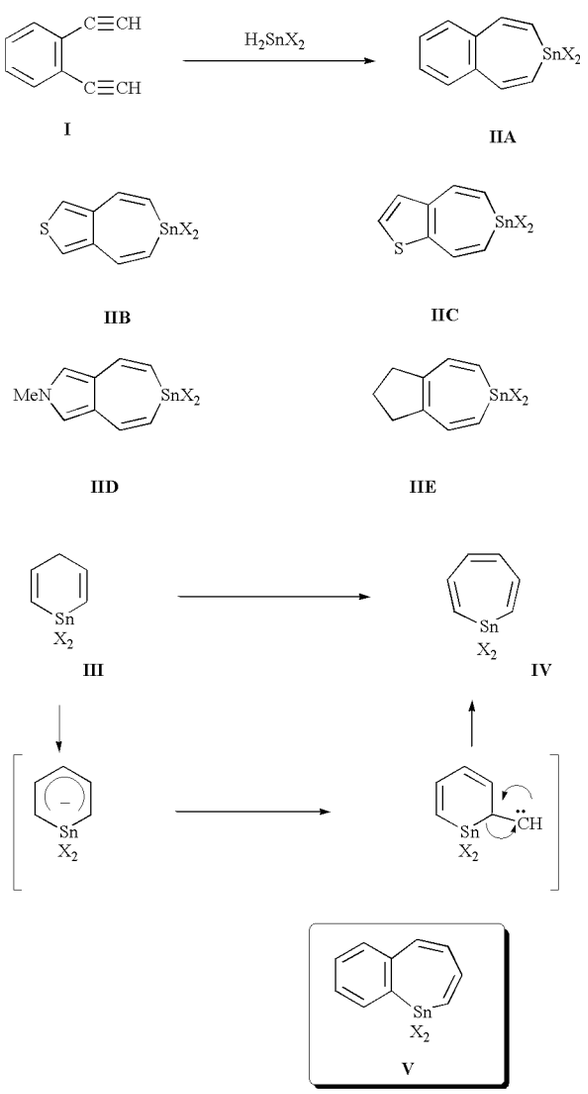
The 2-alkyl-1-benzostannepines **4a**–**g** were prepared by the intramolecular hydrostannation of the tin intermediates **3** to an acetylenic moiety in one pot from (*Z*)-1-(*o*-bromophenyl)but-1-en-3-ynes **1**. The obtained stannepines **4** were easily converted into the 1-benzostibepines **9**, **10**, **11**, **12** and the 1-benzoborepines **14**, **15** by tin–antimony and tin–boron exchange reactions in moderate to good yields, respectively. The 1-benzoborepines **14** and **15** are hitherto unknown heterocyclic ring systems.

Introduction

There has been considerable interest in the chemistry of heterocycles containing a tin atom. The chemistry of the stannole ring system,[1,2] stannacyclopentadiene, has been reviewed and a large number of compounds has been prepared. Although the chemistry of the six-membered tin-containing heterocycles[3] has also been widely studied, the corresponding seven-membered heterocycles (stannepines) have only occasionally been studied. The *C*-unsubstituted 3-benzostannepine **IIA**,[4] the fully unsaturated heterocycle containing a tin atom at the C-3 position, was prepared by the intermolecular hydrostannation of *o*-diethynylbenzene **I** more than 35 years ago. The thiophene ring- **IIB**[5a] and **IIC**,[5b] the pyrrole ring- **IID**[6] and the cyclopentane ring-fused stannepines **IIE**[7] have also been synthesized by the extension of this annellation reaction. Furthermore, monocyclic stannepines **IV** have been obtained by not only the above hydrostannation[8] but also by ring enlargement[9] of the carbene intermediate from the 1,4-dihydrostannabenzene **III** (Scheme 1).

On the one hand, it is well known that these parent stannepines can be transformed into the corresponding derivatives of borepines[4b,5–7,8b,10] and stibepines[11] by the tin–metal exchange reaction. Stannepines are thus useful as the key starting materials for the preparation of other heteroepines. However, only two reports of the synthesis of the 1-benzostannepines **V**,[12,13] theoretically possible structural isomers, have been known in very recent years. The *C*-unsubstituted 1-benzostannepine[12] and the 2-trimethylsilyl derivative[12] have been prepared by the coupling of dimethyltin dichloride and the 1,6-dilithium compound, generated from (*Z*,*Z*)-1-bromo-4-(2-bromophenyl)-1-trimethylsilylbuta-1,3-diene. 2-*tert*-Butyl- and 2-*n*-butyl-1-benzostannepines[13,14] have also been obtained by the reaction of the corresponding 1-benzotellurepines[15] with *tert*-butyllithium, followed by treatment with di-*n*-butyltin dichloride. However, these routes are fairly limited and not general; in particular, the former method provides no variety of 2-alkyl substituted 1-benzostannepines.

Previously, we reported the synthesis of the 1-benzotellurepines[15] and the 1-benzoselenepines,[15] which are novel seven-membered heterocycles containing a tellurium or selenium element, *via* the successive intramolecular addition of telluroles or selenoles to a triple bond. Moreover, for several years we



Scheme 1

† The yields obtained for compounds **4**, **5** and **6**, together with ^{1}H and ^{13}C NMR measurements for the 1-benzostannepines **4**, are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b000900h/

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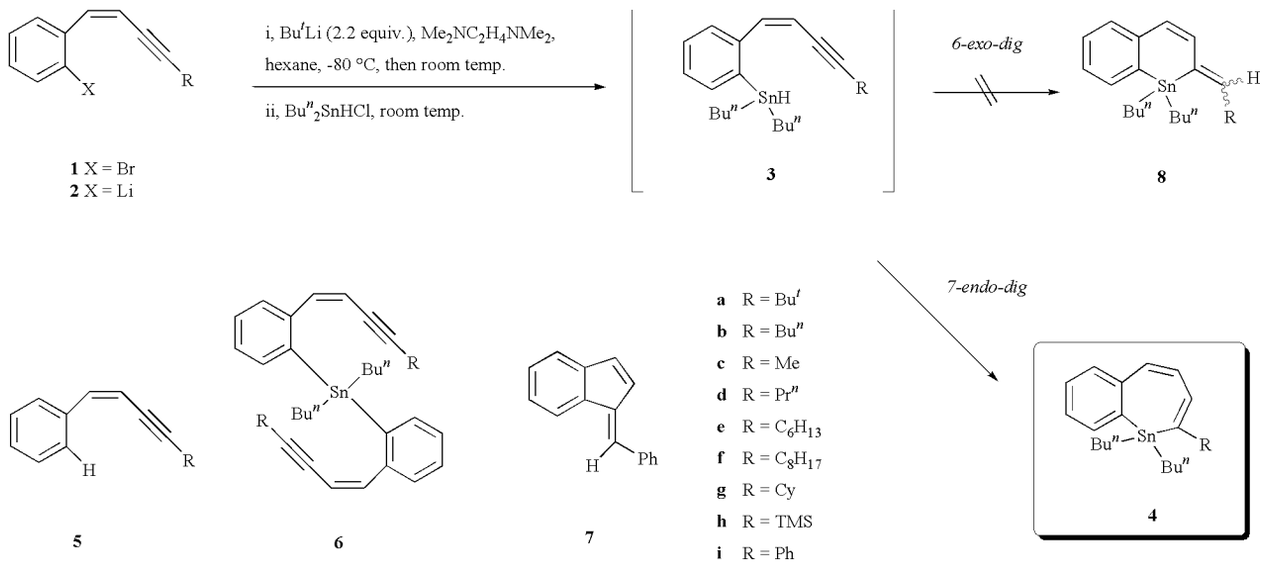


Scheme 2

have focused on the synthesis of various heterocyclic ring systems[16] using efficient intramolecular cyclization reactions involving an acetylenic group. In this paper, we describe the novel route for preparation of the stable 2-alkyl-1-benzostannepines by a similar cyclization and the transformation of stannepines into 1-benzoborepines and 1-benzostibepines *via* the replacement of tin with antimony or boron.[14]

Results and discussion

Synthesis of 1-benzostannepines

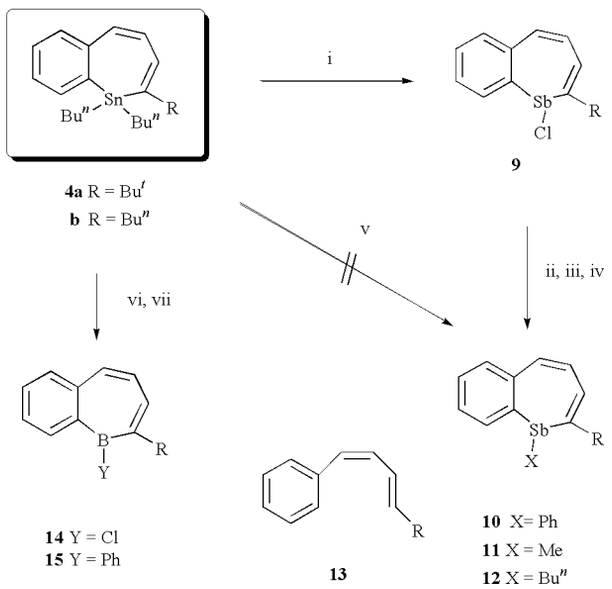
The synthesis of the 2-alkyl-1,1-dibutyl-1-benzostannepines **4** is shown in Scheme 2. (*Z*)-1-(*o*-Bromophenyl)but-1-en-3-ynes **1**, which were obtained in our previous study,[15b] were lithiated with 2.2 equiv. of Bu′Li in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in anhydrous hexane at −80 °C, and then treated with 1.1 equiv. of di-*n*-butylchlorotin hydride (Bu^n_2ClSnH),[17] which was freshly generated from an equal amount of di-*n*-butyltin dichloride ($Bu^n_2SnCl_2$) and di-*n*-butyltin dihydride ($Bu^n_2SnH_2$), giving the desired 2-alkyl-1-benzostannepines **4a**–**g** as stable colorless oils, together with the debrominated (*Z*)-1-(phenyl)but-1-en-3-ynes **5** and the bis[(*Z*)-*o*-(but-1-en-3-ynyl)phenyl]dibutylstannanes **6**. These materials could be separated by silica gel column chromatography. The enyne compounds **5** were probably produced by the hydrolysis of the lithio derivatives **2**. The formation of the diarylstannanes **6** could be easily explained by the process involving a 1:2 coupling of $Bu^n_2Cl_2Sn$ and **2**. Treatment of the trimethylsilyl derivative **1h** with Bu′Li in a similar manner gave a complex mixture without any detectable compounds, and lithiation of the phenyl derivative **1i** resulted in *5-exo-dig* cyclization to afford 1-benzylideneindene **7** in low yield without producing any tin-containing compounds. A similar cyclization of the lithio compound having a phenylacetylene moiety[18] that produced a five-membered compound has already been reported.

It is well known that the intermolecular addition of organotin hydride compounds to a carbon–carbon triple bond induced by radical initiators (*e.g.*, AIBN, Et_3B),[19] transition metal catalysts (*e.g.*, $Pd(PPh_3)_4$),[20] base catalysts[4] or Lewis acid catalysts (*e.g.*, $ZrCl_4$, $HfCl_4$)[21] gives the hydrostannylation products, and this addition frequently proceeds in the absence of a catalyst.[22] Therefore, the stannepines **4** may probably be obtained by the intramolecular *7-endo-dig* ring closure of the tin hydride intermediates **3** at the sp carbon of the triple bond, as shown in Scheme 2. Compounds **4** are quite stable and are not sensitive to air, light or even moisture. 2-Methyl- **4c**, 2-*n*-propyl- **4d**, 2-*n*-hexyl- **4e**, 2-*n*-octyl- **4f** and 2-cyclohexyl-1-benzostannepine **4g** are new compounds, although 2-*tert*-butyl **4a** and 2-*n*-butyl derivative **4b** have been prepared in our recent work.[13] These results are summarized in the electronic supplementary data (Table 1). The structural assignment of the products **4**, **5** and **6** could be made from the ^1H and ^{13}C NMR and HRMS spectra (electronic supplementary data, Table 2, and Experimental section). No six-membered *6-exo-dig* products **8** were formed by this ring closure reaction, although in the case of intramolecular hydrotelluration and hydroselenation at a carbon–carbon triple bond, as described in our previous paper,[15] both the *7-endo-dig* and the *6-exo-dig* reactions took place. Furthermore, a similar hydrosilylation gave only the *6-exo-dig* products.[16i] The reason for the differences caused by changing the element is not clear at present.

Conversion of stannepines into stibepines

C-unsubstituted 1-benzostibepine[12] and the 2-*tert*-butyl and 2-*n*-butyl derivatives[13] have been previously obtained. The tin–antimony exchange reactions of 3-benzostannepine[11] and the six-membered tin-containing heterocyclic compounds[3a,3h,23] have been extensively studied. These reactions prompted us to examine a similar replacement reaction using the 1-benzostannepines obtained in this work for the purpose of producing the 1-benzostibepines. The stannepines **4a**,**b** readily reacted with 1.0 equiv. of antimony trichloride ($SbCl_3$) in $CHCl_3$ at 0 °C to almost quantitatively afford the corresponding 1-chloro-1-benzostibepines **9a**,**b**, but these compounds were too unstable to be isolated. Thus, we planned the transformation of **9** into the *Sb*-phenyl or -alkyl substituted derivatives. Treatment of the 1-chlorostibepines **9** (freshly prepared without purification after removal of the solvent and the generated $Bu^n_2SnCl_2$ under reduced pressure) with a small excess of phenyllithium in ether at −20 °C afforded the 1-phenyl-1-stibepines **10** in moderate yields (Scheme 3). The methyl **11** and 1-*n*-butyl derivatives **12** were also obtained in a similar manner by using methyllithium and *n*-butyllithium instead of phenyllithium, respectively. Compounds **10**, **11** and **12** were more stable than the 1-chlorostibepines **9** and could easily be purified by normal silica gel chromatography.

After the reaction of the stannepine **4a** with dichlorophenylstibine (Cl_2SbPh) in $CHCl_3$, **4a** was recovered together with a small amount of the diene compound **13**.[15b] Although the *Sb*-phenyl substituted stibepines are described in the literature, the *Sb*-alkyl derivatives could not be obtained due to the thermal instability of the reagents (dihaloalkylstibines). Thus, compounds **11** and **12** are the first isolated examples of 1-alkyl-1-benzostibepines.



Scheme 3 *Reagents and conditions*: i, $SbCl_3$ (1 equiv.), $CHCl_3$, 0 °C, 30 min; ii, PhLi (1.2 equiv.), ether, −20 °C, 30 min (for **10**); iii, MeLi (1.2 equiv.), ether, −20 °C, 30 min (for **11**); iv, *n*-BuLi (1.2 equiv.), ether, −20 °C, 30 min (for **12**); v, $PhSbCl_2$, $CHCl_3$, 0 °C; vi, BCl_3 (1 equiv.), hexane, room temp., 1 h (for **14**); vii, $PhBCl_2$ (1 equiv.), hexane, room temp., 1 h (for **15**).

Conversion of stannepines into borepines

We next examined the tin–boron exchange reaction[24] in order to form the novel 1-benzoborepines using the more stable and easily available 2-*tert*-butyl-1-benzostannepine **4a**. The reaction of 1-stannepine **4a** with 1.0 equiv. of boron trichloride (BCl_3) in *n*-hexane at room temperature resulted in the desired tin–boron exchange to give 2-*tert*-butyl-1-chloro-1-benzoborepine **14a**, which could be purified by distillation under reduced pressure in spite of its being air- and moisture-sensitive. The treatment of 1-chloroborepine **14a** with phenyllithium or alkyllithium resulted in decomposition and afforded no products. However, the air- and moisture-sensitive 1-phenyl derivative **15a** was obtained by the reaction of **4a** with dichlorophenylborane ($PhBCl_2$) under similar conditions.

The monocyclic fully unsaturated borepines,[8,25] 3-benzoborepines[4,10] and other ring-fused derivatives[5–7,26] have now been recognized and established as aromatic compounds by ^{1}H and ^{13}C NMR spectroscopic studies, molecular orbital calculations and X-ray crystal analyses. It is well known[4,8] that the olefinic protons of these borepines appear at lower field because of a diamagnetic ring current induced by cyclic conjugation through the boron atom, and/or the decrease in electron densities on the olefinic protons due to the overlap between the boron vacant p orbital and π systems.[3e,27] The ^{1}H NMR spectra of the 1-benzoborepines **14** and **15** show signals arising from the borepine ring protons (3-H, 4-H and 5-H) at lower field than those of the 1-benzostannepines **4** and the 1-benzostibepines **9**, **10**, **11** and **12** obtained in this work. In particular, the proton signals of 4-H are shifted 0.34–0.64 ppm downfield, and appeared 0.25–0.62 ppm more downfield in comparison to those of the *Sn*-di-*n*-butyl substituted 1-benzostannepines **4**. In addition, the observed coupling constants, $J_{3,4}$ (**14a**: 8.4 Hz, **15a**: 7.0 Hz) are somewhat large, while the values of $J_{4,5}$ of 11.0 and 11.7 Hz observed in **14a** and **15a** are smaller than those of the normal seven-membered 1-benzoheteroepines containing a heavier element.[12,13,15,28] In the ^{13}C NMR of **15**, three sp^2 α carbon atoms, appearing at δ 141.6 (s), 148.4 (s) and 159.3 (s), are almost identically deshielded while the signals of the other sp^2 doublet γ carbons are in the normal region for aromatic and olefinic carbon atoms. These observations indicate that the 1-benzoborepines obtained in this work are aromatic.

Conclusions

In the present work, the general synthesis of 2-alkyl-1-benzostannepines by an intramolecular hydrostannation reaction with a triple bond was achieved. The parent stannepines were transformed into the corresponding 1-benzostibepines and 1-benzoborepines by a tin–metal exchange. Further reactions and applications of the stannepines including other tin–metal exchanges are now under investigation.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Hitachi 270–30 spectrometer. Mass spectra (MS) and HR-MS were recorded on a JEOL JMS-DX300 instrument. ^{1}H NMR spectra were recorded on a JEOL PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as internal standard and *J* values are given in Hz. ^{13}C NMR spectra were recorded on a JEOL JNM-GSX 400 (400 MHz) spectrometer.

General procedure for the reaction of (*Z*)-1-(*o*-lithiophenyl)but-1-en-3-ynes with Bu$^n_2$SnHCl: formation of 2-alkyl-1,1-dibutyl-1-benzostannepines 4, (*Z*)-1-(phenyl)but-1-en-3-ynes 5 and bis[(*Z*)-*o*-(but-1-en-3-ynyl)phenyl]dibutylstannane 6

To a stirred solution of (*Z*)-1-(*o*-bromophenyl)but-1-en-3-yne **1** (5 mmol) and TMEDA (1.8 ml, 10 mmol) under an argon atmosphere was slowly added Bu^{t}Li (1.6 mol in pentane solution, 7.5 ml, 12 mmol). After the reaction mixture had been stirred at the same temperature for 30 min, di-*n*-butylchlorotin hydride (5.5 mmol, freshly prepared from di-*n*-butyltin dihydride and one equivalent of di-*n*-butyltin dichloride at room temperature in quantitative yield) was added. The reaction mixture was allowed to warm to room temperature during 3–4 h with stirring. Saturated aqueous NH_4Cl (50 ml) was added, and the layers were separated. The aqueous layer was extracted with ether (50 ml × 2). The organic layers were washed with brine (50 ml × 2), dried ($MgSO_4$), and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel eluted with *n*-hexane to give **4**, **5** and **6**. The results are summarized in Table 1 and the spectral data for the stannepines **4** are listed in Table 2 (see electronic supplementary information). The absorption due to C≡C of compounds **5** could not be observed in the IR spectrum.

(*Z*)-5,5-Dimethyl-1-phenylhex-1-en-3-yne 5a. Colorless oil, δ_H (90 MHz, $CDCl_3$) 1.30 (9H, s, Bu^t), 5.68 (1H, d, *J* 11.8, Ph-CH=C*H*-), 6.56 (1H, d, *J* 11.8, Ph-C*H*=CH-), 7.30–7.45 and 7.83–8.00 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{14}H_{16}$: 184.1253. Found 184.1258).

(*Z*)-1-Phenyloct-1-en-3-yne 5b. Colorless oil, δ_H (90 MHz, $CDCl_3$) 0.80–1.69 and 2.24–2.57 (7H, m and 2H, m, Bu^n), 5.70 (1H, dt, *J* 12.0, 2.4, Ph-CH=C*H*-), 6.58 (1H, d, *J* 12.0, Ph-C*H*=CH-), 7.22–7.47 and 7.80–8.04 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{14}H_{16}$: 184.1253. Found: 184.1250).

(*Z*)-1-Phenylhept-1-en-3-yne 5d. Colorless oil, δ_H (90 MHz, $CDCl_3$) 1.05, 1.40–1.75 and 2.42 (3H, *t*, *J* 7.6, 2H, m and 2H, tq, *J* 6.8, 2.4, Pr^n), 5.69 (1H, dt, *J* 11.9, 2.4, Ph-CH=C*H*-), 6.55 (1H, d, *J* 11.9, Ph-C*H*=CH-), 7.25–7.45 and 7.81–7.92 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{13}H_{14}$: 170.1096. Found: 170.1098).

(*Z*)-1-Phenyldec-1-en-3-yne 5e. Colorless oil, δ_H (90 MHz, $CDCl_3$) 0.79–1.73 and 2.23–2.38 (11H, m and 2H, m, *n*-C_6H_{13}), 5.69 (1H, dt, *J* 12.0, 2.2, Ph-CH=C*H*-), 6.56 (1H, d, *J* 12.0, Ph-

C*H*=CH-), 7.20–7.50 and 7.79–7.98 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{16}H_{20}$: 212.1566. Found: 212.1560).

(*Z*)-4-Cyclohexyl-1-phenylbut-1-en-3-yne 5g. Colorless oil, δ_H (90 MHz, $CDCl_3$) 0.90–1.95 and 2.61 (10H, m and 1H, m, Cy), 5.70 (1H, dd, *J* 12.1, 2.2, Ph-CH=C*H*-), 6.55 (1H, d, *J* 12.1, Ph-C*H*=CH-), 7.25–7.35 and 7.53–7.94 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{16}H_{18}$: 210.1409. Found: 210.1400).

Bis[(*Z*)-*o*-(5,5-dimethylhex-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6a. Pale yellow oil, ν_{max}(neat)/cm^{-1} 2225 (C≡C); δ_H (90 MHz, $CDCl_3$) 0.65–1.08 and 1.30–1.56 (6H, m and 12H, m, Bu^n × 2), 1.26 (18H, s, Bu^t × 2), 5.58 (2H, d, *J* 11.8, Ph-CH=C*H*- × 2), 6.53 (2H, d, *J* 11.8, Ph-C*H*=CH- × 2), 7.05–7.57 and 8.34–8.56 (6H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{32}H_{39}Sn$ (M^+ − Bu^n, 57): 543.2074. Found: 543.2070).

Bis[(*Z*)-*o*-(oct-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6b. Pale yellow oil, ν_{max}(neat)/cm^{-1} 2200 (C≡C); δ_H (90 MHz, $CDCl_3$) 0.66–1.63 and 2.20–2.53 (32H, m and 4H, m, Bu^n × 4), 5.60 (2H, dt, *J* 11.8, 2.2, Ph-CH=C*H*- × 2), 6.57 (2H, d, *J* 11.8, Ph-C*H*=CH- × 2), 7.10–7.59 and 8.33–8.53 (6H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{36}H_{48}Sn$: 600.2778. Found: 600.2794).

Bis[(*Z*)-*o*-(pent-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6c. Pale yellow oil, ν_{max}(neat)/cm^{-1} 2210 (C≡C); δ_H (90 MHz, $CDCl_3$) 0.63–1.04 and 1.33–1.60 (6H, m and 12H, m, Bu^n × 2), 1.98 (6H, d, *J* 2.6, Me × 2), 5.58 (2H, dt, *J* 11.4, 2.6, Ph-CH=C*H*- × 2), 6.51 (2H, d, *J* 11.4, Ph-C*H*=CH- × 2), 7.14–7.56 and 8.30–8.46 (6H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{30}H_{36}Sn$: 516.1876. Found: 516.1839).

Bis[(*Z*)-*o*-(hept-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6d. Pale yellow oil, ν_{max}(neat)/cm^{-1} 2200 (C≡C); δ_H (90 MHz, $CDCl_3$) 0.84–1.07, 1.36–1.70 and 2.26–2.42 (12H, m, 16H, m and 4H, m, Bu^n × 2 and Pr^n × 2), 5.59 (2H, dt, *J* 12.1, 2.4, Ph-CH=C*H*- × 2), 6.50 (2H, d, *J* 12.1, Ph-C*H*=CH- × 2), 7.17–7.40 and 8.38 (6H, m and 2H, d, *J* 7.7, Ph-H) (HRMS *m*/*z* Calc. for $C_{30}H_{35}Sn$ (M^+ − Bu^n, 57): 515.1761. Found: 515.1753).

Bis[(*Z*)-*o*-(dec-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6e. Pale yellow oil, ν_{max}(neat)/cm^{-1} 2205 (C≡C); δ_H (90 MHz, $CDCl_3$) 0.84–0.88, 1.29–2.02 and 2.31–2.38 (total 44H, m, Bu^n × 2 and *n*-C_6H_{13} × 2), 5.59 (2H, dt, *J* 11.7, 2.4, Ph-CH=C*H*- × 2), 6.51 (2H, d, *J* 12.1, Ph-C*H*=CH- × 2), 7.12–7.57 and 8.38 (6H, m and 2H, d, *J* 7.3, Ph-H) (HRMS *m*/*z* Calc. for $C_{36}H_{47}Sn$ (M^+ − Bu^n, 57): 599.2700. Found: 599.2706).

Bis[(*Z*)-*o*-(dodec-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6f. Pale yellow oil, ν_{max}(neat)/cm^{-1} 2200 (C≡C); δ_H (90 MHz, $CDCl_3$) 0.69–1.03, 1.20–1.59 and 2.23–2.46 (total 52H, m, Bu^n × 2 and *n*-C_8H_{17} × 2), 5.58 (2H, dt, *J* 12.0, 2.4, Ph-CH=C*H*- × 2), 6.53 (2H, d, *J* 12.0, Ph-C*H*=CH- × 2), 7.12–7.50 and 8.30–8.50 (6H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{40}H_{43}Sn$ (M^+ − Bu^n, 57): 655.3326. Found: 655.3299).

Bis[(*Z*)-*o*-(1-cyclohexylbut-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6g. Pale yellow oil, ν_{max}(neat)/cm^{-1} 2200 (C≡C); δ_H (90 MHz, $CDCl_3$) 0.77–1.76 and 2.58 (38H, m, and 2H, m, Bu^n × 2 and Cy-H × 2), 5.61 (2H, dt, *J* 11.7, 2.2, Ph-CH=C*H*- × 2), 6.50 (2H, d, *J* 11.7, Ph-C*H*=CH- × 2), 7.17–7.47 and 8.43 (6H, m and 2H, d, *J* 8.1, Ph-H) (HRMS *m*/*z* Calc. for $C_{36}H_{43}Sn$ (M^+ − Bu^n, 57): 595.2387. Found: 595.2362).

Conversion of 4a into 2-*tert*-butyl-1-chloro-1-benzostibepine 9a

The reaction of **4a** with $SbCl_3$ was carried out in an NMR tube; δ_H (400 MHz, $CDCl_3$) 1.25 (9H, s, Bu^t), 6.41 (1H, dd, *J* 5.5, 12.7, 4-H), 6.68 (1H, d, *J* 5.5, 3-H), 7.07 (1H, d, *J* 12.7, 5-H), 7.25–7.59 and 7.92 (3H, m and 1H, d, *J* 6.4, Ph-H).

2-*tert*-Butyl-1-phenyl-1-benzostibepine 10a

A solution of **4a** (71 mg, 0.17 mmol) in $CHCl_3$ (2 ml) was added in one portion with stirring to $SbCl_3$ (39 mg, 0.17 mmol) in $CHCl_3$ (10 ml) under an argon atmosphere at 0 °C. The reaction mixture was vigorously stirred at room temperature for 30 min. After removal of the solvent at room temperature *in vacuo*, followed by exclusion of $BuSnCl_2$ at 100–110 °C/2 mmHg using a semimicro distillation apparatus, the resulting residue was dissolved in hexane (10 ml). To this hexane solution of crude **9a** at −20 °C was added PhLi (1.14 mol l^{-1}, 0.25 ml, 0.17 mmol). The mixture was stirred under the above conditions for 30 min, quenched by the addition of aqueous NH_4Cl (10 ml) and extracted with hexane (30 ml × 3). The organic layer was washed with brine (30 ml × 2), dried ($MgSO_4$) and evaporated. The resulting residue was chromatographed on silica gel using hexane as eluent to give **10a** (23 mg, 36% from **4a**) as a colorless oil. This compound was identical with the authentic sample prepared in our previous paper.[13]

2-*n*-Butyl-1-phenyl-1-benzostibepine 10b

The stannepine **4b** was treated with $SbCl_3$ and worked up as described for the preparation of **10a** to give **10b** (27 mg, 41% from **4b**) as a colorless oil. This compound was identical with the authentic sample prepared in our previous paper.[13]

2-*tert*-Butyl-1-methyl-1-benzostibepine 11a

The stannepine **4a** was treated with MeLi instead of PhLi and worked up as described for the preparation of **10a** to give **11a** (31 mg, 57% from **4a**) as a colorless oil; δ_H (400 MHz, $CDCl_3$) 0.95 (3H, s, Sb-Me), 1.18 (9H, s, Bu^t), 6.28 (1H, dd, *J* 6.0, 13.2, 4-H), 6.69 (1H, d, *J* 6.0, 3-H), 6.82 (1H, d, *J* 13.2, 5-H), 7.29–7.49 and 7.61–7.71 (3H, m and 1H, m, Ph-H); δ_C (100 MHz, $CDCl_3$) −6.2 (q), 30.6 (q), 39.4 (s), 127.4 (d), 127.9 (d), 128.1 (d), 129.4 (d), 129.6 (d), 132.6 (d), 133.8 (s), 137.1 (d), 142.8 (s), 157.2 (s) (HRMS *m*/*z* Calc. for $C_{15}H_{19}Sb$: 320.0525. Found: 320.0533).

2-*n*-Butyl-1-methyl-1-benzostibepine 11b

The stannepine **4b** was treated with MeLi instead of PhLi and worked up as described for the preparation of **10a** to give **11b** (22 mg, 41% from **4b**) as a colorless oil; δ_H (400 MHz, $CDCl_3$) 1.13 (3H, s, Sb-Me), 0.90, 1.22–1.58 and 2.36 (3H, t, *J* 7.5, 4H, m and 2H, t, *J* 7.3, Bu^n), 6.30 (1H, dd, *J* 5.3, 12.3, 4-H), 6.46 (1H, d, *J* 5.3, 3-H), 6.92 (1H, d, *J* 12.3, 5-H), 7.23–7.35 and 7.46–7.50 (3H, m and 1H, m, Ph-H); δ_C (100 MHz, $CDCl_3$) −5.5 (q), 14.0 (q), 22.3 (t), 32.3 (t), 38.4 (t), 127.5 (d), 128.2 (d), 128.6 (d), 130.7 (d), 130.8 (d), 132.3 (d), 133.9 (s), 136.0 (d), 142.0 (s), 144.9 (s) (HRMS *m*/*z* Calc. for $C_{15}H_{19}Sb$: 320.0525. Found: 320.0526).

2-*tert*-Butyl-1-*n*-butyl-1-benzostibepine 12a

The stannepine **4a** was treated with Bu^{n}Li instead of PhLi and worked up as described for the preparation of **10a** to give **12a** (14 mg, 23% from **4a**) as a colorless oil; δ_H (400 MHz, $CDCl_3$) 1.20 (9H, s, Bu^t), 0.81 and 1.23–1.73 (3H, t, *J* 7.3 and 6H, m, Bu^n), 6.24 (1H, dd, *J* 6.0, 13.2, 4-H), 6.76 (1H, d, *J* 6.0, 3-H), 6.78 (1H, *J* 13.2, 5-H), 7.28–7.32 and 7.60–7.72 (3H, m and 1H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{18}H_{25}Sb$: 362.0995. Found: 362.0994.

1,2-Di-*n*-butyl-1-benzostibepine 12b

The stannepine **4a** was treated with Bu^{n}Li instead of PhLi and worked up as described for the preparation of **10a** to give **12b** (15 mg, 25% from **4b**) as a colorless oil; δ_H (400 MHz, $CDCl_3$) 0.85–1.20, 1.20–1.60 and 2.22–2.35 (8H, m, 8H, m and 2H, m, Bu^n × 2), 6.25 (1H, dd, *J* 6.0, 13.0, 4-H), 6.50 (1H, d, *J* 6.0,

3-H), 6.88 (1H, d, *J* 13.0, 5-H), 7.30–7.33 and 7.60–7.75 (3H, m and 1H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{18}H_{25}Sb$: 362.0995. Found: 362.0999).

Conversion of 4a into 2-*tert*-butyl-1-chloro-1-benzoborepine 14a

A solution of **4a** (71 mg, 0.17 mmol) in $CHCl_3$ (2 ml) was added in one portion with stirring to BCl_3 (20 mg, 0.17 mmol) in $CHCl_3$ (10 ml) under an argon atmosphere at 0 °C. The reaction mixture was vigorously stirred at room temperature for 30 min. After evaporation of the solvent, the resulting residue was distilled under reduced pressure to give **14a** (17 mg, 44%) as a pale yellow oil, bp 90–100 °C (2 mmHg); δ_H (400 MHz, $CDCl_3$) 1.43 (9H, s, Bu^t), 6.75 (1H, dd, *J* 8.4, 11.9, 4-H), 7.25 (1H, d, *J* 8.4, 5-H), 7.49 (1H, d, *J* 11.9, 3-H), 7.40–7.60 and 8.30–8.40 (3H, m and 1H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{14}H_{16}BCl$: 230.1034, 232.1004. Found: 230.1031, 232.1011).

Conversion of 4a into 2-*tert*-butyl-1-phenyl-1-benzoborepine 15a

The stannepine **4a** was treated with $PhBCl_2$ instead of BCl_3 and worked up as described for the preparation of **14a** to give **15a** (25 mg, 54%) as a colorless oil, bp 80–100 °C (4×10^{-6} mmHg); δ_H (400 MHz, $CDCl_3$) 1.19 (9H, s, Bu^t), 6.50 (1H, dd, *J* 7.0, 11.7, 4-H), 6.75 (1H, d, *J* 7.0, 3-H), 6.88 (1H, d, *J* 11.7, 5-H), 7.32–7.52 and 7.71–7.80 (6H, m and 3H, m, Ph-H); δ_C (100 MHz, $CDCl_3$) 32.4 (q), 36.9 (s), 124.8 (d), 126.8 (d), 127.0 (d), 127.3 (d), 127.4 (d), 127.5 (d), 128.6 (d), 131.0 (d), 131.3 (d), 135.8 (d), 136.6 (s), 141.6 (s), 148.4 (s), 159.3 (s) (HRMS *m*/*z* Calc. for $C_{20}H_{21}B$: 272.1736. Found: 272.1734).

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