Hydroboration. 93. Convenient Conversion of Optically Pure 2-Organylapopinenes into the (2-Organylapoisopinyl)dihaloboranes Potentially Valuable for Asymmetric Synthesis via Chiral Organoboranes

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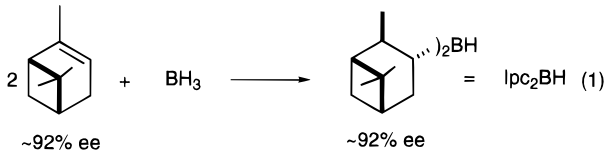
Optically pure and sterically varied (2-organylapoisopinyl)dihaloboranes [$RapBX_2$, R = Me (except for X = I), Et, Pr, *i*-Bu, Ph, *i*-Pr, X = Cl, Br, I], potentially important reagents for asymmetric synthesis, are conveniently prepared by the in situ reduction and hydroboration reaction of boron trihalide, trimethylsilane, and 2-organylapopinenes (2-R-apopinenes) under mild reaction conditions in essentially quantitative yield. Unfortunately, $IpcBI_2$ ($RapBI_2$, R = Me) could not be synthesized by this procedure, although the more bulky 2-R-apopinenes provide the desired $RapBI_2$ derivatives.

Introduction

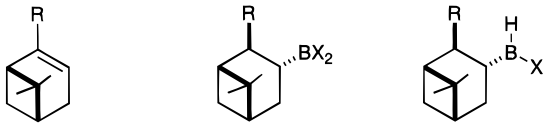
In the course of studying the characteristics of the hydroboration reaction, we selected α-pinene (Ipc, ~92% ee) as an example of an easily rearranged olefin. No rearrangement occurred during the hydroboration of α-pinene. Only 2 mol of α-pinene, instead of the usual 3 mol of olefin, reacted per BH_3, producing a new compound, diisopinocampheylborane (Ipc_2BH) (eq 1).[2]



It occurred to us that this hydroboration of optically active α-pinene (~92% ee) to provide optically active Ipc_2BH (~92% ee) might achieve the asymmetric hydroboration of less sterically demanding alkenes. Indeed, the hydroboration of *cis*-butene proceeded cleanly to give an intermediate, readily oxidized by alkaline hydrogen peroxide to the product, 2-butanol, in 87% enantiomeric excess (ee). This was the first nonenzymatic asymmetric synthesis in high ee, marking the beginning in 1961 of a new era in asymmetric syntheses.[2]

This unique property of α-pinene to serve as an efficient chiral director has been utilized for the preparation of a number of chiral borane reagents.[3] Over the years, the diisopinocampheylborane (Ipc_2B-) structure has proven to be amazingly effective in achieving asymmetric syntheses in high enantiomeric excess.[3d] We and others have successfully utilized various optically pure borane reagents derived from α-pinene for achieving high enantioselection in their reactions for the synthesis of representative organic compounds.[4−9] Some of the important chiral organoborane reagents, derived from α-pinene, used for such asymmetric syntheses are shown in Chart 1.[3d]

Over the years the accumulated results have persuaded us that the remarkable chiral effectiveness of the Ipc_2B- structure must have its origin in the 2-methyl group of the rigid "Ipc" structure.[3d] Moreover, the substituent on the boron atom of the reagent also plays an important role.[5b,10] As a result, we decided to undertake the synthesis of a representative number of 2-R-apopinene structures, by replacing the 2-methyl of α-pinene (**1a**, Ipc) by larger R groups, providing 2-ethyl-



1a R = Me **1d** R = *i*-Bu
1b R = Et **1e** R = Ph
1c R = Pr **1f** R = *i*-Pr

2a-f, X = Cl
3a-f, X = Br
4a-f, X = I

5a-f

(**1b**, Eap),[11] 2-*n*-propyl- (**1c**, Pr),[12] 2-isobutyl- (**1d**, *i*-Bu),[13] 2-phenyl- (**1e**, Pap),[14] and 2-isopropyl- (**1f**, *i*-Pr)[13] apopinenes in the hope of optimizing the steric fit

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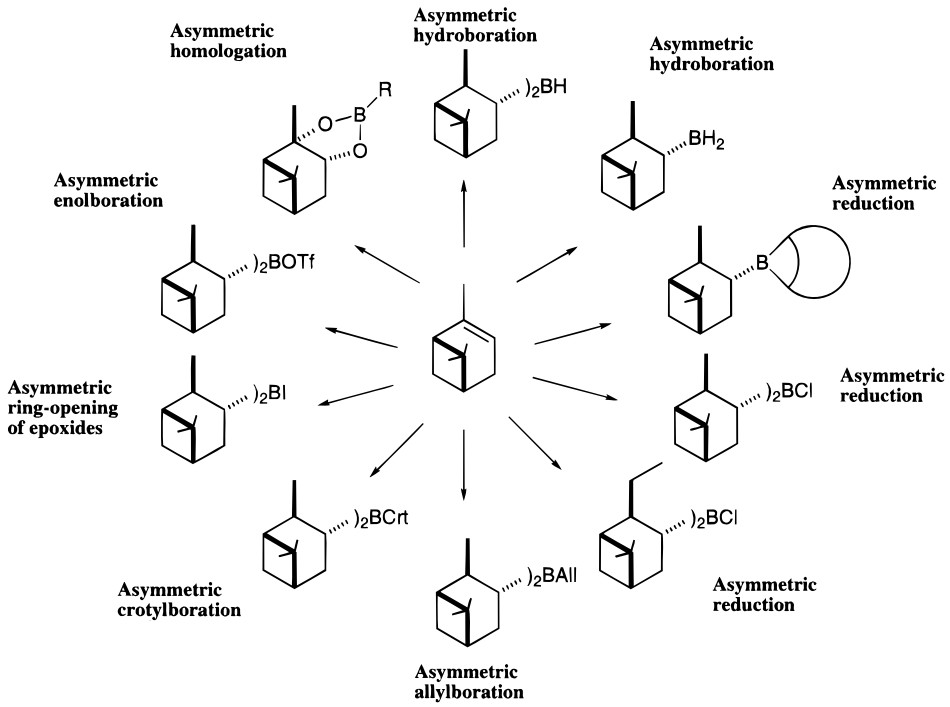
Chart 1



between the substrate and that of the reagent in their reactions. We also decided to examine the effect of varying the halogen in the corresponding BX_2 derivatives.

For example, chiral borane reagents derived from 2-ethyl- (**1b**), 2-*n*-propyl- (**1c**), and 2-isopropylapopinenes (**1f**) provided moderate to excellent improvements in the enantioselectivities achieved in asymmetric hydroboration and reduction reactions.[3d,15] Recently, we have demonstrated the efficacy of the IpcBHCl reagent (**5a**) for the asymmetric cyclic hydroboration of 1-allyl-1-cyclohexene to provide the *trans*-1-decalone in ≥99% ee.[16a] We also investigated the equilibration reaction for the formation of IpcBHCl from $IpcBCl_2$.[16b] However, investigation of the electronic and steric effects in the formation of higher derivatives of IpcBHCl such as RapBHX (**5b**−**f**), potential reagents for the asymmetric hydroboration of prochiral alkenes, required a general, efficient, convenient procedure for the synthesis of $RapBX_2$ (**2**−**4**), readily convertible to RapBHX (**5b**−**f**) by monohydridation.

Moreover, the importance of chiral organyldihaloboranes in asymmetric synthesis is now well documented in the literature.[17,18] However, some of these compounds achieved only relatively poor stereocontrol in their reactions. It is possible that the sterically varied $RapBX_2$ (**2**−**4**) might improve the optical yields realized in such reactions.

Similarly, it has been demonstrated that Ipc_2BX (X = Br, I), cleaves *meso*-epoxides with a high degree of enantioselection while only moderate enantioselectivity is realized with IpcBCl(OBz).[7] On the other hand, in asymmetric reduction, greatly improved results were obtained with the bulkier reagent *B*-chlorodiiso-(2-ethylapopinocampheyl)borane (Eap_2BCl),[5b] in comparison with *B*-chlorodiisopinocampheylborane (Ipc_2BCl, Aldrich, DIP-Chloride)[5a] for certain prochiral ketones.[5] It is apparent from these results that the steric and electronic environment around boron, as well as the nature of the halide, can be critical.[5] Therefore, we anticipate a considerable potential for $RapBX_2$ (**2**−**4**) in such reactions arising from the effect of their varied steric bulk and their modified electronic environment around the boron atom. Moreover, the presence of only one chiral auxiliary attached to boron atom in these borane reagents, in comparison with its counterpart, Ipc_2BX, might make their application more economical.

Therefore, the current importance of these chiral auxiliaries **1a**−**f** for asymmetric synthesis *via* chiral organoboranes and the nonavailability of a convenient

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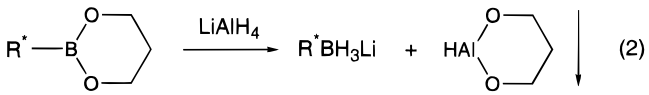
general access to structurally varied $RapBX_2$ (**2**−**4**) from such chiral auxiliaries prompted us to explore the possibility of developing a general procedure applicable to the preparation of a wide variety of sterically bulkier $RapBX_2$ (**2**−**4**) reagents. However, it was previously observed that the 2-R-apopinene (**1a**−**f**) structures are rigid and highly sensitive to the steric requirements of the 2-R group. For example, α-pinene (2-R = Me) reacts readily with $H_3B{\cdot}SMe_2$ or $H_3B{\cdot}THF$ to provide Ipc_2BH in 93−95% purity.[13] However, under the same conditions, hydroboration of sterically bulkier 2-isobutyl- (**1d**), 2-phenyl- (**1e**), and 2-isopropyl- (**1f**) provided decreasing amounts of the dialkylboranes.[13]

In undertaking to extend the known synthesis of $IpcBCl_2$[19a] ($RapBCl_2$, R = Me) to the 17 additional desired compounds, $RapBX_2$ (X = Cl, Br, I), we encountered a number of unexpected problems. For example, in spite of considerable efforts, we were unable to synthesize $IpcBI_2$ from α-pinene by the trimethylsilane and BI_3 procedure, although it proved applicable for the synthesis of the higher apopinene derivatives (Results and Discussion section). We now report a highly convenient procedure for the conversion of 2-R-apopinenes **1a**−**f** of ≥99% ee to the optically pure $RapBX_2$ (**2**−**4**) in high yield, with only one exception, $IpcBI_2$ (**4e**).

Results and Discussion

There are several reports of the synthesis of chiral or achiral organyldihaloboranes, especially for organyldichloroboranes, by indirect or direct approaches.[20] For example, one of the indirect approaches involves, first the preparation of optically pure boronic esters, $R^*B(OR')_2$,[21] followed by their reaction with lithium aluminum hydride to give the organylborohydrides,[22] which provide the optically pure organyldichloroborane−dimethyl sulfide complexes upon treatment with 3 equiv of HCl in dimethyl sulfide[23] (eqs 2 and 3).



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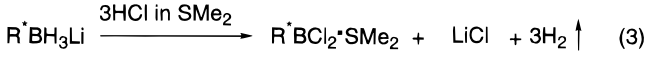
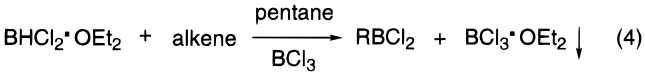


(3)

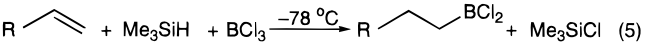
The direct approach, *i.e.*, hydroboration of alkenes and alkynes with dichloroborane ($BHCl_2$) in THF or diethyl ether (EE) and with $BHCl_2{\cdot}SMe_2$,[24a] is slow and can be accompanied by disproportionation.[24b] Apparently, the strong complexation with ethers or dimethyl sulfide decreases the reactivity of these reagents significantly. This difficulty was circumvented by the addition of the strong Lewis acid, boron trichloride, which liberates the dichloroborane from the complex with a rapid precipitation of $BCl_3{\cdot}EE$ or $BCl_3{\cdot}SMe_2$ and hydroboration of the alkene or alkyne by the $BHCl_2$ intermediate thus produced (eq 4).[24]



(4)

On the other hand, dibromoborane−dimethyl sulfide complex ($BHBr_2{\cdot}SMe_2$) and diiodoborane-dimethyl sulfide complex ($BHI_2{\cdot}SMe_2$) hydroborate alkenes and alkynes in refluxing dichloromethane to give the corresponding organyldihaloboranes complexed with dimethyl sulfide.[24] Recently, the synthesis of the desired isopincocampheyldihaloboranes ($IpcBX_2$, X = Cl, Br) by this procedure was reported.[25] These $IpcBX_2$ were prepared either by the hydroboration of α-pinene with $BHX_2{\cdot}SMe_2$ (X = Cl, Br) or by the reaction of $IpcBH_2$ with equivalent amount of HX (X = Cl, Br) or Br_2. Unfortunately, the reaction of $IpcBH_2$ with I_2 did not provide the desired $IpcBI_2$. However, the major disadvantages of these procedures appear to be due to the relatively long reaction time required for the hydroboration of α-pinene with these reagents or to side reactions caused by the use of the free BX_3 acids. Thus, these procedures might not be desirable for the more sterically demanding 2-organylapopinenes (**1b**−**f**). Moreover, these indirect or direct approaches are either multistep or inconvenient for the acid-sensitive 2-R-apopinenes.

Recently, Soundararajan and Matteson reported the reduction of boron trichloride with trialkylsilane at −78 °C in the presence of alkene in either pentane or under neat conditions to provide a rapid formation a small equilibrium concentration of $BHCl_2$ rapidly trapped by alkene already present to give the organyldichloroborane (eq 5).[19]



(5)

However, there is no report of a systematic study of the reduction of sterically bulkier BX_3 (X = Cl, Br, I) with trialkylsilane in the presence of acid-sensitive and sterically varied alkenes. Moreover, there is no account of the reaction of BI_3, a very strong Lewis acid, with trialkylsilane and alkene.

Therefore, in view of our current interest in this area of research, we decided to extend this methodology for the synthesis of (2-organylapoisopinyl)dihaloboranes ($RapBX_2$, **2**−**4**) from its corresponding 2-R-apopinenes **1a**−**f**. The syntheses of 2-ethyl- (**1b**),[11] 2-*n*-propyl- (**1c**),[12a] 2-isobutyl- (**1d**),[13] 2-phenyl- (**1e**),[14] and 2-isopropylapopinenes (**1f**)[13] have already been reported and described. Recently, we also reported a convenient method for upgrading the 2-R-apopinenes **1a**−**f** to high optical purity.[26]

Thus, the reduction of BX_3 (X = Cl, Br) with the trimethylsilane was carried out at −78 °C in the presence of chemically and optically pure 2-R-apopinenes **1a**−**f** in pentane to yield the corresponding $RapBX_2$ (**2, 3**) (eq 6).

(19) (a) Soundararajan, R.; Matteson, D. S. *J. Org. Chem.* **1990**, *55*, 2274. (b) A full article describing this development has recently appeared: Soundararajan, R.; Matteson, D. S. *Organometallics* **1995**, *14*, 4157. The present study influenced by the original Communication[19a] was largely completed before the appearance of the full article.[19b]

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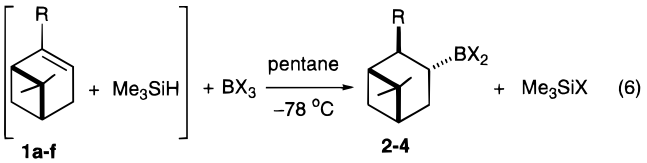
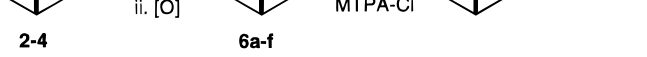


Evaporation of volatiles under reduced pressure provided $RapBX_2$ (**2, 3**) of >95% chemical yield, in ≥99% ee. However, reaction of BI_3 with the mixture of trimethylsilane and α-pinene led to a mixture of $IpcBI_2$, Ipc_2BI, $IpcBH_2$, and unreacted BI_3 (by ^{11}B NMR). This unexpected result led us to the possibility that the nature of the 2-R group in the 2-R-apopinenes might be exerting a steric effect in modifying the reaction leading to the formation of $RapBI_2$. Indeed, this appeared to be true in the case of the sterically bulkier 2-R-apopinenes **1b**−**f**. Consequently, the reaction of 2-R-apopinenes **1b**−**f** with the reagents was conducted in $CDCl_3$ to follow the formation of product by ^{11}B, ^1H, and ^{13}C NMR spectroscopy. Since $CDCl_3$ freezes at −64 °C, the reaction was carried out at −42 °C (acetonitrile−dry ice bath). Fortunately, the reduction of BI_3 with trimethylsilane in the presence of 2-R-apopinenes **1b**−**f** provides $RapBI_2$ (**4b** of >90% and **4c**−**f** of >95% chemically pure) in high yields. Conveniently, this reaction can be carried out in pentane. The authenticity of the product was conveniently determined as follows. The resultant $RapBX_2$ (**2**−**4**) compounds were methanolyzed (^{11}B NMR δ 31−32) and subjected to alkaline peroxide oxidation to provide the 2-organylapoisopinocampheols (**6a**−**f**) (eq 7).



The spectral analysis of the resultant 2-organylapoisopinocampheols (**6a**−**f**) confirmed that, during the formation of the $RapBX_2$ derivatives (**2**−**4**), no rearrangement of the chiral auxiliary had occurred. Further, the optical rotation of the alcohols **6a**−**f** and the capillary GC analysis of the menthyl carbonate (for **6b**−**d,f**)[27a] or MTPA ester[27b] (for **6e**) established the ≥99% optical purity of $RapBX_2$ (**2**−**4**) in comparison with their 1:1 diastereomeric mixtures.

Conclusions

This study undertook the extension of the convenient, one-pot procedure for preparing $IpcBCl_2$ by the reaction of α-pinene, BCl_3, and R_3SiH to the preparation of related $RapBX_2$ (R = Me, Et, *n*-Pr, *i*-Bu, Ph, *i*-Pr; X = Cl, Br, I). It proved impossible to synthesize $IpcBI_2$ by this procedure, but the synthesis proved applicable to the more bulky derivatives, $RapBI_2$ (R = Et, *n*-Pr, *i*-Bu, Ph, *i*-Pr). However, no difficulty was encountered in extending this procedure to the synthesis of the higher chlorides and bromides, $RapBX_2$ (X = Cl, Br); with the one exception mentioned, $IpcBI_2$, all other 17 derivatives of $RapBX_2$ were obtained in optically pure form, free of any coordinating species, ready for further synthetic applications *via* organoboranes. The synthesis of the corresponding RapBHX (**5a**−**f**), readily available by the mono hydridation of 2-$RapBX_2$, and their utility for the asymmetric hydroboration of representative prochiral alkenes is in progress and will be reported shortly.

Experimental Section

All glassware were dried overnight at 140 °C, assembled hot, and cooled to ambient temperature in a stream of nitrogen.[28] All reactions were performed under static pressure of dry nitrogen. The reported boiling points are uncorrected. The ^{11}B NMR were recorded at 96 MHz and were referenced to BF_3·EE. The ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively. The 2-organylapoisopinocampheols (**6a**−**f**) were purified by crystallization or column chromatography (silica gel), and the optical rotations were measured on a digital polarimeter.

Materials. Trimethylsilane and BX_3 (X = Cl, Br, I) were used as obtained. Solutions (1 M) of BCl_3 and BBr_3 in dry pentane were made and stored in a refrigerator. A solution of solid BI_3 was made in $CDCl_3$ or pentane prior to the reaction. The optically pure 2-R-apopinenes **1a**−**f** were prepared as described in the literature.[26]

General Procedure for the Synthesis of $RapBX_2$ (2−4) of ≥99% from the Corresponding 2-R-apopinenes 1a−f. To the cold (−78 °C) solution of BCl_3 or BBr_3 (1.0 M, 5−10 mmol) in pentane, a cold (−78 °C) mixture of precondensed Me_3SiH (5−10 mmol) and 2-R-apopinene **1a**−**f** (5−10 mmol) was added slowly. The reaction mixture was stirred for 10 min at that temperature and then allowed to warm to ambient temperature. The ^{11}B NMR indicated complete formation of $RapBX_2$ (**2, 3**) (singlet at δ 62−64). The volatiles of the reaction mixture were removed (15 mmHg, rt (room temperature), 0.5 h, and 0.4 mmHg, 40 °C, 1 h) to obtain the products in essentially quantitative yield. The ^1H and ^{13}C NMR spectra taken in $CDCl_3$ were consistent with the required structure of $RapBX_2$ (**2**, **3**). Methanolysis (^{11}B NMR singlet at δ 31−32), followed by the alkaline peroxide oxidation of the methanolyzed $RapBX_2$ (**2, 3**) by the usual procedure,[28] provided the corresponding alcohols **6a**−**f**. The ^1H and ^{13}C spectra of the resultant alcohols confirmed the structures of the $RapBX_2$ (**2**, **3**). The optical purity was confirmed by the capillary GC analysis as described in the literature.[29] For the synthesis of $RapBI_2$ (**4b**−**f,** ^{11}B NMR singlet at δ 54−55), the reaction was performed on a 1.4−2.0 mmol scale in $CDCl_3$ as solvent, using the procedure described above. Similarly, the $RapBI_2$ derivatives (**4b**−**f**) were conveniently synthesized in pentane in quantitative yields. The authenticity of the structures was confirmed by the spectral data and also by analyzing the corresponding alcohols obtained by the usual alkaline peroxide oxidation as described above. $RapBI_2$ (**4c**−**f**) was obtained in >95% purity, while the $EapBI_2$ (**4b**) was >90% pure. No change in the spectral data of $RapBX_2$ (**2**, **3**, **4b**−**f**) was observed when samples were refrigerated for 48 h.

$IpcBCl_2$ (2a): bp 94−6 °C/4.0 mmHg. HRMS (CI, 70 eV): calcd for $C_{10}H_{17}BCl_2$ ($M^+ + H - H_2$) 217.0722, found 217.0715. ^1H NMR ($CDCl_3$): δ 2.25−2.40 (m, 2 H), 2.10−2.25 (m, 1H), 1.80−2.05 (m, 4 H), 1.20 (s, 3 H), 1.12 (d, J = 6 Hz, 3 H), 1.09 (s, 3 H), 0.89 (d, J = 9 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 47.62, 40.85, 38.61, 33.13, 29.63, 28.15, 22.89, 22.64.

$IpcBBr_2$ (3a): bp 88−90 °C/1 mmHg. HRMS (CI, 70 eV): calcd for $C_{10}H_{17}BBr_2$ ($M^+ + H - H_2$) 304.9712, found 304.9721. ^1H NMR ($CDCl_3$): δ 1.94−2.42 (m, 6 H), 1.80−1.88 (m, 1 H), 1.25 (s, 3 H), 1.12 (d, J = 6 Hz, 3 H), 1.06 (s, 3 H), 0.94 (d, J

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= 9 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 47.55, 40.78, 39.01, 38.84, 32.86, 29.95, 28.11, 22.86, 22.54.

IpcBI$_2$ (4a): The procedure which achieved the synthesis of **4b**−**f** failed for **4a**.

EapBCl$_2$ (2b): bp 98−100 °C/3 mmHg. HRMS (CI, 70 eV): calcd for $C_{11}H_{19}BCl_2$ ($M^+ + H - H_2$) 231.0879, found 231.0889. ^{1}H NMR ($CDCl_3$): δ 1.85−2.40 (m, 7 H), 1.40−1.50 (m, 2 H), 1.20 (s, 3 H), 1.05 (s, 3 H), 0.80−0.95 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 46.37, 44.71, 41.12, 38.63, 32.76, 30.04, 29.31, 28.16, 22.64, 12.70.

EapBBr$_2$ (3b): HRMS (CI, 70 eV): calcd for $C_{11}H_{19}BBr_2$ ($M^+ + H - H_2$) 317.9790, found 317.9783. ^{1}H NMR ($CDCl_3$): δ 1.80−2.58 (m, 6 H), 1.40−1.55 (m, 2 H), 1.25 (s, 3 H), 1.00 (s, 3 H), 0.94−0.98 (m, 1 H), 0.80−0.88 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 47.28, 44.90, 41.00, 38.84, 32.53, 30.03, 29.01, 28.13, 22.55, 12.79.

EapBI$_2$ (4b): ^{13}C NMR ($CDCl_3$) δ 49.63, 45.23, 40.70, 39.31, 32.24, 29.98, 28.07, 27.38, 22.38, 12.93, 5.55.

PraBCl$_2$ (2c): bp 90−4 °C/1 mmHg. HRMS (CI, 70 eV): calcd for $C_{12}H_{21}BCl_2$ ($M^+ + H - H_2$) 245.1035, found 245.1040. ^{1}H NMR ($CDCl_3$): δ 1.80−2.40 (m, 7 H), 1.35−1.50 (m, 2 H), 1.25−1.30 (m, 2 H), 1.20 (s, 3 H), 1.15 (s, 3 H), 0.85−0.95 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 45.12, 44.18, 41.11, 39.86, 38.61, 32.77, 29.34, 28.17, 22.68, 21.25, 14.31.

PraBBr$_2$ (3c): HRMS (CI, 70 eV): calcd for $C_{12}H_{21}BBr_2$ ($M^+ + H - H_2$) 333.0025, found 333.0038. ^{1}H NMR ($CDCl_3$): δ 2.10−2.40 (m, 4 H), 1.95−2.00 (m, 2 H), 1.80−1.90 (m, 1 H), 1.35−1.50 (m, 2 H), 1.20−1.35 (m, 5 H), 1.10 (s, 3 H), 1.00 (d, J = 9 Hz, 1 H), 0.90 (m, 3 H). ^{13}C NMR ($CDCl_3$): δ 45.29, 45.10, 40.99, 39.82, 38.81, 32.53, 29.01, 28.14, 22.58, 21.31, 14.34.

PraBI$_2$ (4c): ^{13}C NMR ($CDCl_3$) δ 47.53, 45.58, 40.68, 39.77, 39.31, 32.26, 28.08, 27.36, 22.40, 21.39, 14.39.

^{i}BapBCl$_2$ (2d): HRMS (CI, 70 eV) calcd for $C_{13}H_{23}BCl_2$ ($M^+ + H - H_2$) 259.0902, found 259.1200. ^{1}H NMR ($CDCl_3$): δ 1.85−2.40 (m, 7 H), 1.22−1.60 (m, 3 H), 1.20 (s, 3 H), 1.05 (s, 3 H), 0.92 (d, J = 9 Hz, 1 H), 0.81−0.90 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 46.94, 44.91, 41.58, 41.05, 38.59, 32.66, 29.37, 28.17, 25.62, 23.07, 22.70.

^{i}BapBBr$_2$ (3d): HRMS (CI, 70 eV) calcd for $C_{13}H_{23}BBr_2$ ($M^+ + H - H_2$) 347.0181, found 347.0198. ^{1}H NMR ($CDCl_3$): δ 2.10−2.48 (m, 3 H), 1.80−2.04 (m, 3 H), 1.48−1.60 (m, 1 H), 1.26−1.40 (m, 2 H), 1.25 (s, 3 H), 1.00−1.10 (m, 4 H), 0.86−0.92 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 46.92, 45.05, 42.45, 40.94, 38.81, 32.39, 29.09, 28.14, 25.65, 23.04, 22.81, 22.62.

^{i}BapBI$_2$ (4d): ^{1}H NMR ($CDCl_3$) δ 1.90−2.64 (m, 6 H), 1.38−1.70 (m, 2 H), 1.24−1.38 (m, 2 H), 1.24 (s, 3 H), 1.06 (s, 3 H), 0.84−0.95 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 46.88, 45.23, 44.69, 40.61, 39.30, 32.11, 28.08, 27.47, 25.64, 23.14, 22.94, 22.44.

PapBCl$_2$ (2e): HRMS (CI, 70 eV) calcd for $C_{15}H_{19}BCl_2$ ($M^+ + H - H_2$) 279.0879, found: 279.0887. ^{1}H NMR ($CDCl_3$): δ 7.1−7.30 (m, 5 H), 3.77 (d, J = 9 Hz, 1 H), 2.40−2.70 (m, 3 H), 2.20−2.35 (m, 1 H), 1.85−2.10 (m, 2 H), 1.30 (s, 3 H), 1.15 (d, J = 9 Hz, 1 H), 0.95 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 146.18, 128.11, 128.04, 126.94, 125.65, 47.30, 44.81, 40.81, 38.27, 32.96, 29.32, 27.97, 23.18.

PapBBr$_2$ (3e): HRMS (CI, 70 eV) calcd for $C_{15}H_{19}BBr_2$ ($M^+ + H - H_2$) 368.9848, found 368.9824. ^{1}H NMR ($CDCl_3$): δ 7.1−7.40 (m, 5 H), 3.85 (d, J = 9 Hz, 1 H), 1.80−2.90 (m, 6 H), 1.30 (s, 3 H), 1.15 (d, J = 9 Hz, 1 H), 0.95 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 146.02, 128.09, 127.38, 126.94, 125.66, 48.38, 44.67, 40.70, 38.53, 32.69, 28.79, 27.98, 23.08.

PapBI$_2$ (4e): ^{1}H NMR ($CDCl_3$) δ 7.00−7.40 (m, 5 H), 3.85 (d, J = 8 Hz, 1 H), 3.05−3.20 (m, 1 H), 1.60−2.50 (m, 5 H), 1.35 (s, 3 H), 1.25 (d, J = 10 Hz, 1 H), 0.95 (s, 3 H), 0.80 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 145.69, 127.99, 127.85, 127.77, 127.12, 126.03, 125.61, 50.84, 44.60, 40.31, 39.02, 32.25, 27.90, 26.79, 22.87.

^{i}PraBCl$_2$ (2f): HRMS (CI, 70 eV) calcd for $C_{12}H_{21}BCl_2$ (M^+) 245.1035, found 245.1146. ^{1}H NMR ($CDCl_3$): δ 1.90−2.38 (m, 6 H), 1.54−1.78 (m, 2 H), 1.21 (s, 3 H), 1.15 (s, 3 H), 0.84−0.92 (m, 4 H), 0.80 (d, J = 6.5 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 52.15, 42.62, 40.75, 38.40, 33.53, 32.08, 28.80, 28.08, 22.57, 22.49, 21.19.

^{i}PraBBr$_2$ (3f): HRMS (CI, 70 eV): calcd for $C_{12}H_{21}BBr_2$ ($M^+ + H - H_2$) 333.0025, found 333.0028. ^{1}H NMR ($CDCl_3$): δ 2.00−2.40 (m, 5 H), 1.50−1.80 (m, 3 H), 1.20 (s, 3 H), 0.95−1.05 (m, 4 H), 0.91 (d, J = 6.6 Hz, 3 H), 0.85 (d, J = 6.6 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 42.72, 40.63, 38.68, 33.48, 31.83, 28.07, 27.97, 22.71, 22.50, 21.09.

^{i}PraBI$_2$ (4f): ^{1}H NMR ($CDCl_3$) δ 1.40−2.24 (m, 7 H), 1.20 (s, 3 H), 1.06 (s, 3 H), 0.78−1.04 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 56.18, 42.89, 40.17, 39.17, 33.22, 31.36, 27.98, 25.49, 22.96, 22.30, 20.91.

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Supporting Information Available: ^{1}H (for **2**, **3**, and **4d**−**f**) and ^{13}C NMR (for **2**, **3**, and **4b**−**f**) spectra of RapBX$_2$ described in the Experimental Section (32 pages). Ordering information is given on any current masthead page.

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