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THE ASYMMETRIC HYDROBORATION OF SIMPLE ALKENYLSILANES: CHIRAL α-SILYLALKYL- BORANES AND ALCOHOLS

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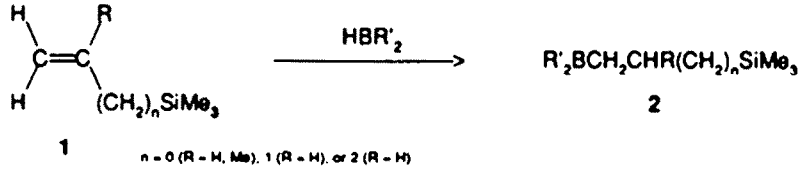
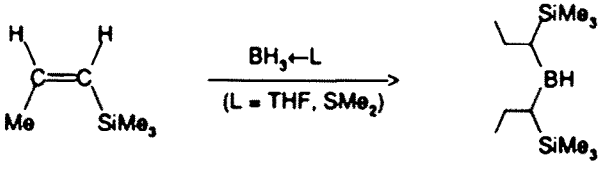
ABSTRACT: The detailed study of the asymmetric hydroboration of various vinylsilanes with monoisopinocampheylborane ($IPCBH_2$) is presented. In all cases, β-substitution on the vinylsilane gives monomeric dialkylborane adducts with the boryl group α to the silicon. These studies show that the larger the groups on silicon are, the more positive the influence on the enantioselectivity of the process. Moderate asymmetric induction (24-40%) is observed only for vinylsilanes which contain a substituent *trans* to the silicon. A model for the asymmetric hydroboration of alkenes with this reagent is proposed. The complete characterization of the borane intermediates was achieved employing NMR (^{11}B, ^{13}C, ^{1}H, ^{29}Si).

Some years ago, we initiated a series of studies on the hydroboration of various alkenylsilanes in order to determine the feasibility of such an approach to prepare carbofunctionalized organosilanes, or, in an opposite sense, silyl-substituted organoboranes, in a regioselective manner.[2] These studies revealed that dialkylboranes such as 9-borabicyclo[3.3.1]nonane (9-BBN) could effectively be employed to convert silyl substituted terminal alkenes to the corresponding β-, γ-, or δ- silylalkylboranes.



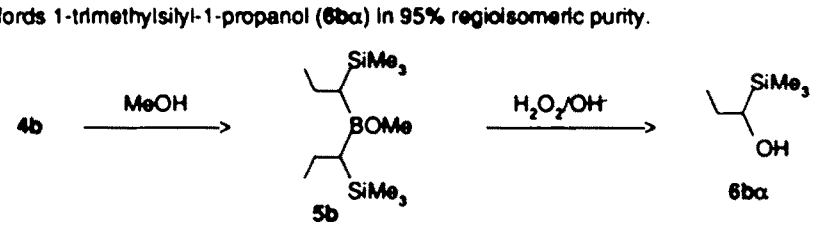
1 n = 0 (R = H, Me), 1 (R = H), or 2 (R = H) **2**

Borane, itself, was found to be far less selective than were dialkylboranes for the hydroboration of **1**, except in the case of allylsilanes (*ie.* **1**, n = 1, R = H),[3] which gave excellent γ-selectivity even with this unsubstituted reagent. Perhaps, most intriguing was the fact that these studies also provided a new route to α-silylalkylboranes through the hydroboration of 1-silylalkenes such as *cis*-1-propenyltrimethylsilane (**3b**).



3b **4b** (*meso/dl* = 2:1)

Dialkylboranes such as **4b** are unique among such species in that they exist only in monomeric form without the need of an excess of the alkene to repress dehydroboration, giving rise to a ^{11}B NMR signal at 83 ppm.[2b] Methanolysis provides the corresponding borinate ester (**5b**) and oxidation affords 1-trimethylsilyl-1-propanol (**6bα**) in 95% regioisomeric purity.

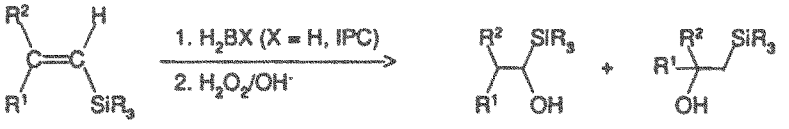


5b **6bα**

The fact that the hydroboration of **3b** led to such high α-selectivity and the resulting organoboranes were so resistent toward further hydroboration appeared to make them good candidates for the formation of optically-active silylated organoboranes through the use of chiral hydroborating agents. Of the known reagents,[4] monoisopinocampheylborane ($IPCBH_2$)[4b,c] was particularly attractive in that it would be expected to form 1:1 adducts with **3b** while still maintaining a preference for α placement of the boron atom. Moreover, the ready availibility of the reagent in either enantiomeric form coupled with the versatility of the resulting adducts in both chemical transformations and purification, added to its appeal for the present study.[5] Thus, we chose to examine the hydroboration of several representative methyl substituted vinylsilane derivatives, first with borane, itself, to develop a clear picture of the hydroboration process, and second, with $IPCBH_2$, to evaluate the potential of this reagent to induce asymmetry in the resulting α-silylalkylborane adducts.

RESULTS AND DISCUSSION

For the purpose of this study, the required vinylsilanes were prepared in good yield from the corresponding vinyl Grignard reagent.[6] We examined the behavior of each with borane-methyl sulfide complex (BMS) as the hydroborating agent in a 2:1 stoichiometric ratio. To ascertain the efficiency of the reaction and the regioselectivity of the process, the intermediate organoboranes were oxidatively converted to the corresponding alcohols. These results are presented in Table 1.



3 6α 6β

TABLE 1. THE HYDROBORATION/OXIDATION OF VINYLSILANES WITH BMS.

3	R_3Si	R^1	R^2	Temp °C Time (h)	6α /6β	Yield[a] of 6
3a	Me_3Si	H	H	0(1)	57/43	**6a** 98[c]
3b	Me_3Si	Me	H	25(1)	95/5	**6b** 98(73)[c]
3b/3c	Me_3Si	b	b	25(4)	95/5	**6b** 98(90)
3d	Me_3Si	Me	Me	25(4)	>98/2[d]	**6d** 99(79)
3e	Me_2PhSi	Me	Me	25(4)	>98/2[d]	**6e** 99(80)
3f	Et_3Si	Me	Me	25(4)	>98/2[d]	**6f** 99(75)

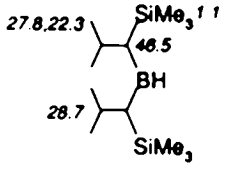
a. GC (isolated) yield. b. *cis/trans* = 7/3. c. reference 7. d. No evidence could be found for a regioisomeric alcohol by capillary GC, ^1H- and ^{13}C- NMR.

These data reveal several important features of the reaction. For one, β substitution of vinylsilanes clearly enhances the placement of the boron atom α to the silyl group. Thus, while a single methyl group gives *ca.* 5% of the undesired β product, this regioisomer is completely eliminated with a second β group, even with larger groups on the silicon. Moreover, in all cases, complete hydroboration of **3** occurs with this 2:1 stoichiometry.

The racemic α-silyl alcohols (**6**) were used as models to test the use of ^1H NMR together with either $Eu[(+)\text{-}(tfc)]_3$ or $Eu[(+)\text{-}(hfc)]_3$ shift reagents to evaluate the optical purities of such compounds. The racemic nature of these alcohols was also confirmed by their absence of optical rotations.

In order to obtain more information as to the nature of the borane adducts formed under the reaction conditions, we examined the hydroboration mixtures obtained from the isobutenyl compounds (*ie.* **3d-f**) spectroscopically, as well as after both methanolysis and hydrolysis, by ^{11}B, ^{13}C, and ^{29}Si NMR (Table 2), ^{1}H NMR and capillary GC.

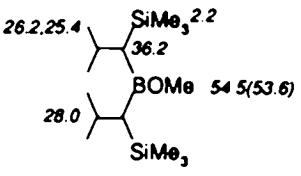
TABLE 2. NMR CHARACTERIZATION OF *BIS*-[(α-SILYL)ISOBUTYL]BORANES.[a]



4d

^{11}B NMR = 80

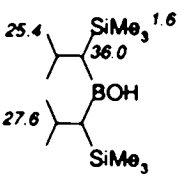
^{29}Si NMR = -0.2(-2.6) *dl(meso)*



5d

54

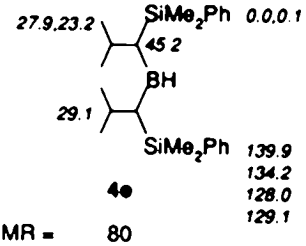
-0.2(-0.9)



7d

53 ppm.

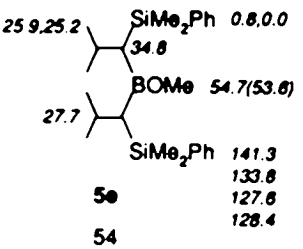
-0.1(-0.9) ppm.



4e

^{11}B NMR = 80

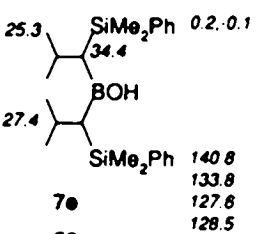
^{29}Si NMR = -3.6(-6.6) *dl(meso)*



5e

54

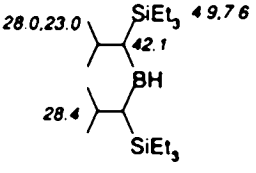
-4.2(-5.0)



7e

53 ppm.

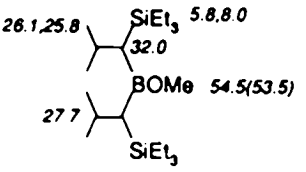
-4.0(-5.0) ppm.



4f

^{11}B NMR = 80

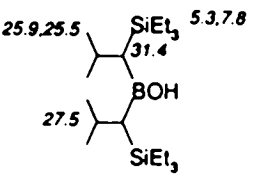
^{29}Si NMR = 8.2(5.7) *dl(meso)*



5f

54

6.1(5.7)



7f

53 ppm.

6.2(5.8) ppm.

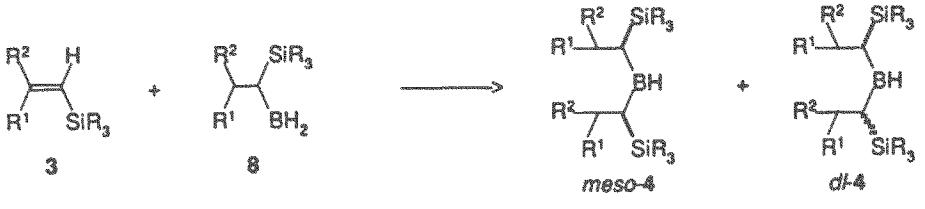
[a] Recorded in $CDCl_3$ solution.

The sole initial product formed from the isobutenylsilanes (**3d-f**) is the corresponding monomeric *bis*[1-(silyl)isobutyl]borane product (*ie.* **4d-f**) (^{11}B NMR = 80 ppm). No peak was observed at 32 ppm, indicating that the monoalkylborane formed, is a more reactive hydroborating agent than is BMS. Additionally, due to the chiral carbon next to the silyl group, diastereoisomers (*dl*/*meso*) can be formed. From our earlier studies[2b] on the ^{13}C NMR assignments of the borinate derivatives of *bis*-[1-(trimethylsilylethyl]borane (*ie.* **5a**) and of *bis*-[1-(trimethylsilyl)-1-propyl]borane (*ie.* **5b**), the methoxy carbons are different for the *dl* and *meso* isomers. (*ie.* 52.9 ppm (*meso*-**5a**), 54.2 ppm (*dl*-**5a**) and 53.0 ppm (*meso*-**5b**), 54.3 ppm (*dl*-**5b**)). The similarity of this feature in the case of the isobutyl derivatives (*ie.* **5d-f**) to that observed for the corresponding ethyl (**5a**) and propyl (**5b**) compounds led us to assign the structures shown in Table 2. The ^{1}H NMR (*cf.* Experimental Section) of the methoxyboranes (*ie.* **5d-f**) also fits our earlier observation[2] that the methoxy protons of *meso* isomer are found upfield (*ca.* 0.1 ppm) from the corresponding *dl* isomer. From these data, we find that the *dl* isomer predominates (*ca.* 90%) over the *meso* isomer in each of the isobutyl cases. The ^{29}Si NMR spectra of these compounds consistently agree with this distribution of diastereomers in each case and, likened to the ^{1}H NMR, the *meso* isomer is upfield from the corresponding *dl* isomer (*cf.* Table 2).

For analysis and identification purposes, the corresponding borinic acids (**7d-f**) were also prepared. The ^{1}H NMR of the hydroxy protons of **7d-f** are found at *ca.* 5.0 ppm with the *dl* being downfield (*ca.* 0.2 ppm) from the corresponding *meso* isomer in each case. Integration of these signals was consistent with the presence of *ca.* 90% of the *dl* isomer in each of these derivatives.

The capillary GC analysis of **5d,f** and **7d,f** revealed that these pairs of diastereomers could be separated with the retention time of the *meso* isomer being shorter than that of the *dl* in each case. The lower volatility of the dimethylphenylsilyl derivatives (*ie.* series **e**) precluded their clean separation for analytical evaluation. It should be emphasized that these borinic acid and methyl ester derivatives can be analyzed by capillary GC without decomposition. For the former compounds, this is remarkable and this work describes this analysis for the first time. Moreover, the hydroxylic protons show no tendency to exchange on the ^{1}H NMR time scale and exhibit sharp bands (3 each in the case of **7d,f**) for a free OH in the 3600-3650 cm^{-1} range of their IR spectra.

The difference of the *dl*/*meso* ratios observed for the dialkylboranes derived from either **3a** or **3b** (*ie.* **4a** and **4b**: *dl*/*meso* = 33:67)[2b] compared to the isobutenylsilanes (*ie.* **4d-f** *dl*/*meso* = 90:10) reveals that the selectivity in the hydroboration with 1-silylisobutylboranes (**8d-f**) of another isobutenylsilane (**3d-f**) is higher and prefers the *dl* form while (1-trimethylsilyl-1-propyl)borane (**8b**) with another *cis*-1-propenyltrimethylsilane (**3b**) or 1-(trimethylsilyl)ethylborane (**8a**) with another vinyltrimethylsilane (**3a**) is less and the *meso* product is preferred.



Having observed significant diastereoselectivity for the hydroboration of the isobutenylsilanes, it was decided to investigate the asymmetric hydroboration of this representative set of methylated derivatives to determine those factors which influenced the process. From the extensive studies of Brown and Singaram,[5] it was clear that IBCBH$_2$ not only is available in 100% ee, but also provides good asymmetric induction for both *trans*-disubstituted and trisubstituted alkenes, a matter of principal importance for our systems where silyl substitution can significantly alter the regio-

selectivity of the hydroboration process when dialkylboranes are employed. Moreover, the intermediate 1:1 adducts can often be directly resolved by simple crystallization to give pure diastereomers from which α-pinene can be removed to provide homochiral organoborane derivatives.[5] Thus, we examined the reaction of $IPCBH_2$ with our representative silylalkenes employing a 1:1 stoichiometry to determine the regiochemistry, enantiofacial selectivity and overall chemical efficiency of the process. These results are summarized in Table 3.

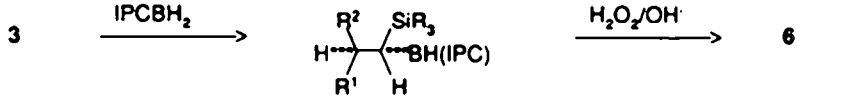


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TABLE 3. THE HYDROBORATION/OXIDATION OF VINYLSILANES WITH $IPCBH_2$[a] (9).

3	R_3Si	R^1	R^2	Temp °C (Time (h))	6α /6β	ee	$[\alpha]_D^{36}$	Yield[b]
3a	Me_3Si[f]	H	H	25(4)	45/55	0.0[c]	0.00	6a 96(70)
3b	Me_3Si	Me	H	25(4)	96/4	0.0[c]	0.00	6b 95(70)
3c	Me_3Si	H	Me	25(4)	>99/1	36[c]	+0.87[h]	6b 95(60)
3d	Me_3Si	Me	Me	25(4)	>98/2	24[d]	-4.21	6d 98(71)
3e	Me_2PhSi	Me	Me	25(4)	>98/2	24[d]	-5.02	6e 99(94)
3f	Et_3Si	Me	Me	25(4)	>98/2	40[c]	-6.14	6f 99(65)

a. Prepared from (R)-(+)-α-pinene, 94% ee. b. GC(Isolated) yield. c. Eu[(+)-(tfc)]$_3$, [Aldrich] d. Eu[(+)-(tfc)]$_3$, [Alfa] e. Eu[(+)-(hfc)]$_3$, [Aldrich] f. A 2:1 mol ratio of 3a to 9 gave 6a (α/β = 33:67) in 78% GC yield. g. No evidence could be found for a regioisomeric alcohol by capillary GC, ^{1}H- and ^{13}C- NMR. h. Uncorrected from a 95/5 mixture of *trans*- and *cis*-1-propenylsilanes.

Under our conditions, the 1:1 stoichiometry provides essentially quantitative yields of the silylated alcohols (6) suggesting that dialkylboranes such as 10 could be formed as the major reaction products with the proper substitution pattern on 3. While the vinyl compound (3a) was found to give α/β mixtures, this is entirely consistent with our earlier findings[2] on the behavior of this unsubstituted vinylsilane. Moreover, in this case we examined a 2:1 stoichiometry with the finding the reaction is both incomplete (78%) and slightly more β-selective (α/β = 33:67), again as expected from our previous studies. Similarly, the dramatic change to an efficient α-selective process with a single β methyl group was expected with the unanticipated feature that the *trans* isomer (*ie.* 3c) would give a single regioisomeric product! Also, within the limits of detection, both by NMR and capillary GC, we found only the α product from the isobutenylsilanes. Thus, control of the regiochemistry was achieved with 9 as the hydroborating agent for β-substituted vinylsilanes which contain *trans* substitution with respect to the silyl group. In this regard, larger groups on silicon do not detract from this regioselectivity.

To understand better the nature of the borane adducts formed under these reaction conditions, the hydroboration mixture was monitored spectroscopically, by ^{11}B NMR. The peak of $IPCBH_2$ dimer (22 ppm) disappeared as soon as the vinylsilane (3b-f) was added, and a broad peak at 80 ppm appeared. The reaction was complete, forming the dialkylborane (10) in *ca.* 30 mins. After the

addition of 1 eq of MeOH, the peak at 80 ppm disappeared, and a large peak at 54 ppm appears, consistent with the formation of a borinate ester. A small peak (*ca.* 5%) at 32 ppm ($RBOMe_2$) indicated that some displacement of the alkyl groups had occurred, which GC analysis revealed to be α-pinene rather than **3**. Similar results were obtained when H_2O was added instead of MeOH.

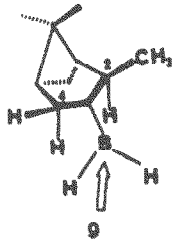
It has been found that $IPCBH_2$ gives very low asymmetric induction in the hydroboration of *cis* alkenes.[5] The complete lack of asymmetric induction in the case of **3b** demostrates that even when one forces the boron to a single carbon on the double bond, no enantioselectivity occurs. The case of **3a** reinforces this point. Thus, when a pure sample of **3a**α was isolated by preparative GC, it, too, was found to be completely racemic.

For **3c**, moderate enantioselectivity (36% ee) was achieved. This result reveals that the *trans*-substitution not only has a positive steric influence on the regiochemistry of the hydroboration with $IPCBH_2$ as compared to the *cis* isomer, but also enhances the enantioselectivity of the process.

The hydroboration/oxidation of **3d** with **9** results in a slightly lower enantiomeric excess (*ie.* 24%) than that observed from **3c**, suggesting that the additional *cis*-substitution actually has a negative effect on the asymmetric induction with $IPCBH_2$, an effect which is consistent with Brown's findings, and may well result from electron-donating properties of this added alkyl group which results in a less selective process. Our results on changing the substitution on silicon suggest that for a positive increase in the asymmetric induction to be achieved, a radially symmetric increase in the steric bulk is more effective than merely adding one larger group (*cf.* Table 3, **3d-f**). Moreover, we carried out the hydroboration/oxidation of **3d** with dilongifolylborane (Lgf_2BH)[4d] which has an intermediate steric bulk when compared to diisopinocampheylborane[4a] *vs* (**9**). It gives (+)-**6d**α (>98% regioisomeric purity) in 32% ee ($[\alpha]^{35} = +5.45°$) (74% yield), but fails to react with the more hindered **6e**. Hence, this reagent appears to be of less general utility than is **9** for the hydroboration of **3**.

Numerous models, both experimentally and theoretically derived, have been proposed to explain the hydroboration reaction.[6] However, while consistently predictable S configurations[5] (unless the group priorities are reversed) are obtained as the major enantiomeric alcohols from *trans*-disubstituted and trisubstituted alkenes and $IPCBH_2$ (from (+)-α-pinene), no working model has been proposed to explain the selectivity. By analogy with these selectivities, the expected absolute configurations of the silylated alcohols obtained from vinylsilane/$IPCBH_2$ adducts should be the corresponding 1S isomers. It should be noted that $IPCBH_2$ (from (+)-α-pinene) gives the opposite configuration at C-3 from the hydroboration of 2-methyl-2-butene compared to that obtained from Lgf_2BH,[5] a result which was also found in the hydroboration of **3d**. Thus, the silylated alkenes appear to behave in an analogous manner to their all-carbon counterparts, differing principally in the degree of enantiofacial selectivity.

FIGURE 1



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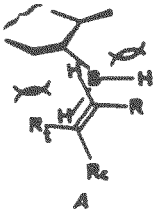
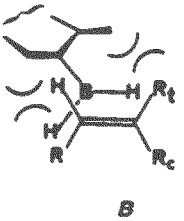


A



B

We view the selectivity of $IBCBH_2$ as arising from the considerations illustrated in Figure 1 below. In this picture, the vinylic C-H bond is essentially colinear with the B-IPC bond to minimize the steric interactions of the alkene with this large group. Thus, an alkene approaching **9** prefers the less crowded *exo* face of the pinanyl ring system from the side away from the protruding methyl group at C-2. The near planar arrangement of the C-1 to C-5 array for the pinanyl system together with the approach on the C-4 side of the rigid ring system has been found by X-ray analysis of the *N,N,N',N'*-tetramethylethylenediamine complex of **9**.[8a] This model explains all of the known enantiomeric preferences for the various alkene types, when one considers the two possible orientations which give rise to the observed enantiomeric products. For ***A***, difficulties arise when steric interactions are encountered between the *trans* groups on the alkene and the 2-Me through C-4 array. This is relieved in approach ***B*** where the orientation of these *trans* groups with respect the ring can be better accomodated in the hydroboration process. With this picture, our data can be readily understood. For one, the model clearly predicts low or no asymmetric induction for compounds not having a *trans* substitution pattern. Our silyl compounds show a sensitivity to the general bulk of the silyl group consistent with the model. Also, the longer Si-C bonds compared to their all-carbon counterparts would be expected to lead to a lowering of the enantioselectivity, a prediction consistent with experimental findings (*eg.* Compare **3c** (36% ee) to the corresponding *t*-butyl compound (76% ee)[5]). Hence, the model appears to provide a satisfactory explanation of the observed selectivities with this chiral hydroborating agent.[8b]

The enantiomeric excess in each case was measured by ^1H NMR combined with $Eu[(+)\text{-}(tfc)]_3$ or $Eu[(+)\text{-}(hfc)]_3$. In the cases of **6a**, **6b** and **6d**, the Me_3Si group was monitored. The peak separations were satisfactory and were integrated to give the ee. The doublet observed for the α-methine proton did not resolve well. In all cases, the minor enantiomeric silyl alcohol obtained from $IPCBH_2$ (from (+)-α-pinene) was shifted more downfield than the major enantiomer. In distinguishing the enantiomers of **6e**, some problems occurred. The two methyl groups on Si are not identical. Thus, when **6e** complexes with $Eu[(+)\text{-}(tfc)]_3$, four peaks were expected. However, before the separation is sufficient to obtain a clean integration, the peaks from the shift reagent began to interfere with the spectrum. The doublet observed for the α-methine proton also cannot be separated cleanly. Fortunately, $Eu[(+)\text{-}(hfc)]_3$ exhibited no interference in the region of the Me_2Si group, so that a satisfactory analysis could be achieved. The ^1H NMR of **6f** with $Eu[(+)\text{-}(tfc)]_3$ gave a good separation for the methine proton to give the cited ee. The determination of optical purity of **6d** using Mosher's ester[9] was less informative than the NMR study with $Eu[(+)\text{-}(tfc)]_3$. In this case, ^1H NMR of the α-methinyl hydrogen signals separated by *ca.* 1.7 Hz, the trimethylsilyl signals by *ca.* 2.2 Hz. The ^{19}F NMR signals were different by *ca.* 6 Hz. However, these differences were insufficient to obtain a clean baseline peak separation. Moreover, we were unable to obtain an effective separation of these diastereomers with capillary GC.

This study revealed that the substitution on silicon has an influence on the asymmetric hydroboration of alkenylsilanes. Larger substitutents on silicon give more asymmetric induction in isobutenylsilane systems. Also, a *trans*-1,2-disubstitution pattern is necessary to achieve significant asymmetric induction. However, the optical purities of the α-silyl alcohol are not great, even in the best case (*ie.* 40% ee). However, this study does establish that moderate asymmetric induction can be achieved in α-silylated organoboranes and that these adducts can be obtained in excellent yield and regioisomeric purities. Our model for the origin of the asymmetric induction with **9** provides a basis for continued study to increase this enantiofacial selectivity.

EXPERIMENTAL SECTION

All experiments were carried out in predried [4 h at 110°C] glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study[10]. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. Analytical gas chromatography was performed using either a Perkin-Elmer Sigma-1B Gas Chromatograph equipped with a 6' X 1/8" 20% SE-30 on DCDMS treated Chromasorb W or a 50M X 0.25mm Silar 10c fused silica [3-cyanopropyl silicone] capillary column or a Perkin-Elmer 8320 capillary gas chromatograph with a 30M X 0.25mm bonded FSOT 20% SE-30 capillary column. Preparative gas chromatography was performed using a Varian 90-P3 Gas Chromatograph. Optical rotations were measured using a Perkin-Elmer 243 B with a 0.1 dcm cell at the indicated concentration [g/100 mL , solvent]. Spectra were recorded on the following instruments: IR: Perkin-Elmer 283 spectrometer or Nicolet 6000 series FT-IR (TF = thin film). MS: Hewlett-Packard 5995 GC/MS (70ev); NMR: ^{1}H, ^{13}C, ^{29}Si (Me_4Si: δ = 0.00 ppm), ^{11}B (BF_3-OET_2: δ = 0.0 ppm), ^{19}F (TFA: δ = 0.00 ppm) JEOL FX-90Q and GN-300 spectrometer. All solvents and reagents were purified prior to use by standard methods (*cf.* reference 2b).

***cis*-1-PROPENYLTRIMETHYLSILANE (3b):** This compound was prepared as reported.[6] ^{1}H NMR($CDCl_3$) δ 0.08(s, 9H), 1.73(dd, 3H, J = 6.7Hz, J = 1.4Hz), 5.45(dq, 1H, J = 14Hz, J = 1.4Hz), 6.36(dq, 1H, J = 14Hz, J = 6.7Hz) ppm; ^{13}C NMR($CDCl_3$) 0.0, 18.9, 129.9, 143.0 ppm.; ^{29}Si NMR($CDCl_3$) δ -10.6 ppm.

***trans*-1-PROPENYLTRIMETHYLSILANE (3c):** Following the approach of Zweifel[11], a dry 1-necked, 250-mL round-bottomed flask was charged with 3b/3c (2.3 g, 20 mmol, *cis*:*trans* = 7:3).[11] To the flask was added diethyl ether (90 mL), pyridine (1.6 g, 20 mmol) and *N*-bromosuccinimide (0.54 g, 3 mmol). The sample was mixed well by hand-shaking, then irradiated with the Puerto Rican sun for 3 days. The reaction mixture was decanted from a gummy residue and washed with 10% HCl (50 mL), 20% aqueous $CdCl_2$, water, 1M NaOH solution, and saturated NaCl, dried over Na_2SO_4 and distilled to give 1.5 g (66% yield , GC - 99% purity, *cis*:*trans* = 5:95) of 3c. bp 74°C / 760 torr ; ^{1}H NMR($CDCl_3$) δ 0.03(s, 9H), 1.80(dd, 3H, J = 5.5 Hz, J = 1.2 Hz), 5.62(dq, 1H, J = 18.3 Hz, J = 1.2 Hz), 6.07(dq, 1H, J = 18.3 Hz, J = 5.5 Hz) ppm[12]; ^{13}C NMR($CDCl_3$) δ -1.2, 22.4, 131.6, 141.8 ppm; ^{29}Si NMR($CDCl_3$) δ -6.3ppm.

ISOBUTENYLTRIMETHYLSILANE (3d): A dry 3-necked, 1-L round-bottomed flask, equipped with a magnetic stirring bar , addition funnel and water condenser, was charged with magnesium (8.0 g, 330 mmol). Isobutenyl bromide[14] (40.4 g, 300 mmol) in THF (150 mL) was added dropwise (reaction begins immediately). After the addition was completed, the mixture was heated at reflux temperature for one additional hour. To the vinyl Grignard was added trimethylsilyl chloride (32.5 g, 300 mmol) dropwise. The solution was heated at reflux for one hour and allowed to cool slowly to room temperature overnight. The solid mass was heated to give a fluid mixture which was poured onto an ice / saturated NH_4Cl mixture (*ca.* 200 mL). Pentane (150 mL) was added, and after separation of the aqueous layer, the resulting organic material was washed with water (5 X 120 mL), dried over Na_2SO_4 and distilled to give 24.2 g (63% yield, GC - 99% purity) of 3d. bp 128°C / 760 torr (lit.[13] 111.5 - 112°C / 748 torr); IR(TF) 1620 (C=C), 1247 (C-Si) cm^{-1} ; MS, *m/z* , 129(M+1, 1), 128(M$^+$, 10), 113(48), 73(100), 59(20); ^{1}H NMR ($CDCl_3$) δ 0.07(s, 9H), 1.76(d, 3H, J = 1.0 Hz), 1.82(d ,3H, J = 1.2 Hz), 5.18(m, 1H) ppm; ^{13}C NMR($CDCl_3$) δ 0.1, 23.1, 29.3, 124.2, 151.8 ppm; ^{29}Si NMR ($CDCl_3$) δ -11.6 ppm.

ISOBUTENYLDIMETHYLPHENYLSILANE(3e): As for 3d above, from dimethylphenylsilyl chloride (61.0 g, 357 mmol) was obtained 47.5 g (70% yield, GC - 98% purity) of 3e. (bp 62°C (0.4 torr)); IR(TF) 1620 (C=C), 1248 (C-Si), 1112 (Si-Ph) cm^{-1} ; MS, *m/z* , 191(M+1, 2), 190(M$^+$, 16), 175(68), 135(100), 105(36), 77(22), 58(20), 55(31) ; ^{1}H NMR ($CDCl_3$) δ 0.34(s, 6H), 1.70(s, 3H), 1.87(d, 3H, J = 1.0 Hz), 5.35(m, 1H), 7.39(m, 5H) ppm; ^{13}C NMR($CDCl_3$) δ -0.5, 23.5, 29.4, 121.9, 127.7, 128.8, 133.7, 140.1, 153.8 ppm; ^{29}Si NMR ($CDCl_3$) δ -15.4 ppm. Anal. Calc'd. for $C_{12}H_{18}Si$: C, 75.72; H, 9.53. Found : C, 75.62; H, 9.54.

ISOBUTENYLTRIETHYLSILANE(3f): As for 3d above, from triethylsilyl chloride (15.0 g, 100 mmol) was obtained 11.2 g. (65% yield, GC - 99% purity) of 3f. bp 95°C (26 torr); IR(TF) 1622 (C=C), 1237 (C-Si) cm^{-1}; MS, *m/z* , 170(M$^+$, 3), 141(58), 113(100), 85(62); ^{1}H NMR($CDCl_3$) δ 0.57(m, 6H), 0.95(m, 9H), 1.76(s, 3H), 1.85(d, 3H, J = 1.2 Hz), 5.12(m, 1H) ppm; ^{13}C NMR($CDCl_3$) δ 4.9, 7.5, 23.4, 29.4, 120.6, 152.3 ppm; ^{29}Si NMR($CDCl_3$) δ -3.7. Anal. Calc'd. for $C_{10}H_{22}Si$: C, 70.50; H, 13.01 Found : C, 70.47; H, 12.99.

ISOMERIC TRIMETHYLSILYLETHANOLS(6aα/β): A dry 2-necked, 250-mL round-bottomed flask, equipped with a magnetic stirring bar and Dry Ice / acetone condenser was charged with $IPCBH_2$ (1.14 M in ether, prepared from (+)-α-pinene) (22.0 mL, 25 mmol) at room temperature. 3a[8] (2.5 g, 25 mmol) was added dropwise. The mixture was allowed to stir for 4 h at room temperature. Methanol (2.0 mL, 50 mmol) was added and the mixture was stirred at room temperature for an additional hour. The solvents were removed with a continuous stream of nitrogen, and EtOH was added followed by 10 mL of 3M aqueous sodium hydroxide and 10 mL 30% hydrogen peroxide dropwise. The reaction mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature and pentane (50 mL) was added. The aqueous phase was saturated with K_2CO_3, and the separated organic phase was concentrated, and pentane (50 mL) was added again, then dried over Na_2SO_4 and distilled to give 2.1 g (70% yield) of 6a , bp 40-50°C / 12 torr (lit.[2b] bp 62-75°C / 43 torr) . For 6aα (isolated by preparative GC), $[\alpha]^{25}$ = 0.00 (c. 8.05 in hexane); The ^{1}H NMR signals of Me_3Si were successively shifted by Eu[(+)-(tfc)]$_3$ downfield to 1.9 ppm and 1.6 ppm, and integrated to determine the ee. IR (TF) 3635 (-OH), 1257 (C-Si), 841 (C-Si) cm^{-1} ; MS, *m/z*, 101(11), 75(82), 73(100), 59(13), 47(10); ^{1}H NMR($CDCl_3$) δ 0.03(s, 9H), 1.27(d, 3H, J = 7.3Hz), 1.55(s, 1H), 3.47(q, 1H, J = 7.3Hz) ppm; ^{13}C NMR($CDCl_3$) δ -4.4, 19.3, 61.5 ppm; ^{29}Si NMR($CDCl_3$) δ 1.8 ppm. For 6aβ, IR (TF) 3654 (-OH), 1258(C-Si), 842(C-Si) cm^{-1} ; MS, *m/z* 101(8), 75(100), 73(13), 59(9), 47(9); ^{13}C NMR($CDCl_3$) δ -1.4, 22.0, 59.9 ppm; ^{29}Si NMR($CDCl_3$) δ -0.6 ppm.

1-(TRIMETHYLSILYL)-1-PROPANOL(6b): *Method 1* (from a 3b/3c mixture/BMS) A dry 2-necked, 250-mL round-bottomed flask, equipped with a magnetic stirring bar and water condenser was charged with BMS (1.25 mL, 12.5 mmol) in hexane (40 mL) at room temperature. 1-Propenyltrimethylsilane (2.8 g, 25 mmol, *cis:trans* = 7:3) was added dropwise. The mixture was allowed to stir for 4 h at room temperature. Methanol (1.5 mL, 38 mmol) was added and the mixture was stirred at room temperature for an additional hour. The solvents were removed with a continuous stream of nitrogen, and THF was added followed by 5 mL each of 3M NaOH followed by 30% H_2O_2 dropwise. The reaction mixture was heated at reflux for 2 h, cooled to room temperature and pentane (50 mL) was added. The aqueous phase was saturated with K_2CO_3, and the separated organic phase was dried over $NaSO_4$ and distilled to give 3.0 g (90% yield, GC > 99% purity) of 6b (α/β = 95:5). bp 70°C / 56 torr (lit.[8] bp 55°C / 28 torr). The ^1H NMR signals of Me_3Si were successively shifted by Eu(+)-(tfc)$_3$ downfield to 1.2 ppm and 1.3 ppm, and integrated to determine the lack of ee. IR(TF) 3370 (-OH), 1245 (C-Si) cm^{-1}; ^1H NMR($CDCl_3$) δ -0.1(s, 9H), 0.87(t, 3H, J = 7.1 Hz), 1.35(m, 2H), 2.20(s, 1H), 3.03(dd, 1H, J = 5.4 Hz, J = 8.4 Hz) ppm; ^{13}C NMR($CDCl_3$) δ -3.9, 11.3, 26.4, 67.5 ppm; ^{29}Si NMR($CDCl_3$) δ 0.9 ppm. *Method 2* (from 3b/IPCBH$_2$) As above, to 9 (0.637 M in ether, prepared from (+)- α-pinene) (7.8 mL, 5 mmol) was added 3b (0.57 g, 5 mmol). Workup as above gave 0.46 g (70% yield, GC - 95% purity) of 6b. [α]^{36} = 0.00 (c. 10 in hexane); The ^1H NMR signals of Me_3Si were successively shifted by Eu[(+)-(tfc)]$_3$ downfield to 0.9 ppm and 0.95 ppm, and integrated to determine the ee. *Method 3* (from 3c/IPCBH$_2$) Analogous to Method 2, from 3c (0.46 g, 4 mmol) was obtained 0.31 g (69% yield, GC - 98% purity)of 6b. [α]^{35} = +0.87 (neat). The ^1H NMR signals of Me_3Si were successively shifted by Eu(+)-(tfc)$_3$ downfield to 1.35 ppm (+) and 1.42 ppm (-), and integrated to determine the ee, 36%.

2-METHYL-1-TRIMETHYLSILYL-1-PROPANOL(6d): *Method 1* (from 3d/BMS) As for 6b above, from 3d (3.2 g, 25 mmol) was obtained 2.9 g (79% yield, GC - 98% purity) of 6d. bp 70°C (17 torr); d 0.836. The ^1H NMR signals of Me_3Si were successively shifted by Eu[(+)-(tfc)]$_3$ downfield to 1.2 ppm and 1.4 ppm, and integrated to determine the ee. IR(TF) 3400 (-OH), 1248 (C-Si) cm^{-1} ; MS: *m/z* 147(M+1, 5), 146(M$^+$, 4), 73(100); ^1H NMR($CDCl_3$) δ 0.05(s, 9H), 0.93(d, 6H, J = 6.8 Hz), 1.21(s, 1H), 1.81(m, 1H), 3.06(d, 1H, J = 5.9 Hz) ppm; ^{13}C NMR($CDCl_3$) δ -2.5, 18.9, 20.4, 32.2, 72.2 ppm; ^{29}Si NMR ($CDCl_3$) δ 0.6 ppm. Anal. Calc'd. for $C_7H_{18}SiO$: C, 57.46; H,12.40. Found : C,57.43; H,12.37. *Method 2* (from 3d/IPCBH$_2$) As for 6b above, 3d (3.2g, 25 mmol) gave 2.5g (65% yield) of isopinocampheol, bp 70°C (0.3 torr) and 2.6 g (71% yield, GC - 97% purity) of 6d. [α]^{35} = -4.21 (neat); ee = 24%. *Method 3* (from 1d/Lgl$_2$BH) A dry 2-necked, 250-mL round-bottomed flask, equipped with a magnetic stirring bar and water condenser was charged with dilongifolylborane (Lgl$_2$BH) (21.1 g, 50 mmol) in THF (75 mL) at room temperature. 3d (6.4 g, 50 mmol) was added. The mixture was allowed to stir for 5 h at room temperature. The solid Lgl$_2$BH disappeared, the organoborane was oxidized by 20 mL each of 3M NaOH followed by 30% H_2O_2 dropwise. The reaction mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature and pentane (100 mL) was added. The aqueous phase was saturated with K_2CO_3, and the separated organic phase was dried over Na_2SO_4 and distilled to give 5.4 g (74% yield) of 6d. [α]^{36} = +5.45 (neat). The ^1H NMR signals of Me_3Si were successively shifted by Eu[(+)-(tfc)]$_3$ downfield to 1.05 ppm (-) and 1.2 ppm (+), and integrated to determine the ee, 32%.

2-METHYL-1-DIMETHYLPHENYLSILYL-1-PROPANOL(6e): As for 6d above, 3e gave a residue which was purified by flash chromatography (4.7 g, 90% yield, GC - 97.5% purity, silica gel 40 - 63 microns, R_f = 0.33 in 7:93 ethyl acetate / hexane). Further purification by short path distillation gave 4.2 g (80% yield ,GC - 99.8% purity) of 6e. bp 73°C (0.8 torr); d 0.966 ; [α]^{35} = 0.00; The ^1H NMR signals of Me_2Si were successively shifted by Eu[(+)-(hfc)]$_3$ downfield to 1.0, 1.2 ppm and 1.1, 1.3 ppm, and integrated to determine the ee. IR(TF) 3480 (-OH), 1249 (C-Si), 1111 (Si-Ph) cm^{-1}; MS: *m/z* 208 (M$^+$), 165(17), 137(21), 135(100), 105(21), 75(48); ^1H NMR($CDCl_3$) δ 0.35(s, 6H), 0.88(d, 3H, J = 6.8 Hz), 0.91(d, 3H, J = 6.6 Hz), 1.61(s, 1H), 1.79(m, 1H), 3.25(d, 1H, J = 6.1 Hz), 7.44(m, 5H) ppm; ^{13}C NMR($CDCl_3$) δ -4.3, -4.0, 19.0, 20.4, 31.9, 71.4, 127.6, 129.0, 133.9, 137.6 ppm; ^{29}Si NMR($CDCl_3$) δ -4.9 . Anal. Calc'd. for $C_{12}H_{20}SiO$: C, 69.18; H, 9.67 Found : C, 69.26; H, 9.72. *Method 2* (from 3e/IPCBH$_2$) gave 0.138 g (89% yield) of isopinocampheol and 0.196 g (94% yield, GC - 97% purity) of 6e. [α]^{36} = -5.02 (c. 6.57 in benzene); The ^1H NMR signals of Me_2Si were successively shifted by Eu[(+)-(hfc)]$_3$ downfield to 1.0, 1.2 ppm (-) and 1.1, 1.3 ppm (+), and integrated to determine the ee, 24%.

2-METHYL-1-TRIETHYLSILYL-1-PROPANOL(6f): *Method 1* (from 3f/BMS) gave, as for 6e, 1.6 g, 88% yield, GC - 99% purity , silica gel 40 - 63 microns, R_f = 0.35 in 0.6:10 ethyl acetate / hexane). Further purification by short path distillation gave 1.4 g (75% yield, GC - 100% purity) of 6f. bp 63°C (0.15 torr); d 0.875 The ^1H NMR signals of the doublet for the α-methine hydrogen of each enantiomer were successively shifted by Eu[(+)-(tfc)]$_3$ downfield to 6.35 ppm and 6.55 ppm, and integrated to determine the ee. IR(TF) 3460 (-OH), 1240 (C-Si), 1016 (-CH_2-CH_3), 737 (C-Si) cm^{-1}; MS. *m/z* 186(M-2, 31), 159(18), 115(39), 103(100), 87(94), 75(88), 59(51); ^1H NMR($CDCl_3$) δ 0.61(m, 6H), 1.01(m, 15H), 1.38(s, 1H), 1.85(m, 1H), 3.25(d, 1H, J = 5.8 Hz) ppm; ^{13}C NMR($CDCl_3$) δ 2.6, 7.5, 19.0, 20.5, 31.9, 70.4 ppm; ^{29}Si NMR($CDCl_3$) δ 4.6 ppm. Anal. Calc'd. for $C_{10}H_{24}SiO$: C, 63.76; H, 12.84 Found: C, 63.57; H, 12.79 *Method 2* (from 3f/IPCBH$_2$) gave, after flash chromatography (silica gel 40 - 63 microns, 0.6:10 of ethyl acetate / hexane) 1.5 g (81% yield, GC - 98% purity) of 6f. Further purification by distillation gave 1.2 g (65% yield, GC - 100% purity) bp 63°C (1.7 torr); [α]^{36} = -6.14 (neat) The ^1H NMR signals of the doublet for the α-methine hydrogens of each enantiomer were successively shifted by Eu[(+)-(tfc)]$_3$ downfield to 6.45 ppm (-) and 6.65 ppm (+), and integrated to determine the ee, 40%.

***meso*- and *dl*-*BIS*[(1-TRIMETHYLSILYL)ISOBUTYL]BORANE(4d):** An NMR tube with a rubber septum was flame-dried and cooled to room temperature under a nitrogen atmosphere. The reagents were introduced into the NMR tube by syringe. BMS (0.05 mL, 0.5 mmol) and $CDCl_3$ (0.4 mL) were introduced, followed by 3d (0.128 g, 1 mmol) The sample was mixed well by hand-shaking. The ^{11}B NMR of this sample showed that the reaction was completed in ca 30 mins 4e

and 4f were similarly prepared. To 4d as prepared above, methanol (0.02 mL, 0.5 mmol) was added dropwise under a nitrogen atmosphere and the sample was mixed well and allowed to stand at room temperature overnight. The solvents were removed with a continuous stream of nitrogen followed by high vacuum. $CDCl_3$ (0.4 mL) was added, and the ^{11}B NMR showed that the dialkylborane formed 5d completely. The separation by capillary GC showed that the ratio of these two diastereomers (*dl* / *meso*) is *ca.* 7 to 1, and the retention time of *meso* form is shorter than *dl* form. ^1H NMR($CDCl_3$) δ 0.10(s, 18H), 0.61(d, 2H, J = 6.1 Hz), 0.96(d, 6H, J = 6.8 Hz), 1.01(d, 6H, J = 6.5 Hz), 2.05(m, 2H), 3.60, 3.70(s, 3H total in a *ca.* 1:9 area ratio). In an analogous manner, 5e was prepared. In this case, the capillary GC failed to separate these two diastereomers. ^1H NMR ($CDCl_3$) δ 0.31(s, 6H), 0.32(s, 6H), 0.75(d, 6H, J = 6.8 Hz), 0.76(d, 2H, J = 4.9 Hz), 0.84(d, 6H, J = 6.8 Hz), 1.89(m, 2H), 3.62, 3.72(s, 3H total in a *ca.* 1:10 area ratio), 7.51(m, 10H) ppm. 5f was similarly prepared. The capillary GC showed that the ratio of these two diastereomers (*dl* / *meso*) is *ca.* 9 to 1, and the retention time of *meso* form is shorter than *dl* form. ^1H NMR($CDCl_3$) δ 0.70(m, 14H), 0.97(m, 30H), 2.02(m, 2H), 3.66, 3.72(s, 3H total in a *ca.* 1:10 area ratio) ppm. (7d): To 4d as prepared above, water (0.009 g, 0.5 mmol) was added under a nitrogen atmosphere and the sample was mixed well and allowed to stand at room temperature overnight. The solvents were removed with a continuous stream of nitrogen, followed by high vacuum. $CDCl_3$ (0.4 mL) was added, and the ^{11}B NMR showed that the dialkylborane formed the borinic acid completely. The separation by capillary GC showed that the ratio of these two diastereomers (*dl* / *meso*) is *ca.* 6 to 1, and the retention time of *meso* form is shorter than *dl* form. ^1H NMR($CDCl_3$) δ 0.10(s, 18H), 0.69(d, 2H, J = 4.8 Hz), 1.04(d, 6H, J = 6.8 Hz), 1.07(d, 6H, J = 6.8 Hz), 2.00(m, 2H), 4.80, 5.00(s, 1H total in a *ca.* 1:12 area ratio). 7e was similarly prepared. In this case, the capillary GC failed to separate these two diastereomers. ^1H NMR ($CDCl_3$) δ 0.30(s, 6H), 0.34(s, 6H), 0.73(d, 2H, J = 5.2 Hz), 0.88(d, 12H, J = 6.9 Hz), 1.85(m, 2H), 4.91, 5.11(s, 1H total in a *ca.* 1:11 area ratio), 7.33(m, 10H) ppm. For 7f, capillary GC showed that the ratio of these two diastereomers (*dl* / *meso*) is *ca.* 6 to 1, and the retention time of *meso* form is shorter than *dl* form. ^1H NMR($CDCl_3$) δ 0.71(m, 14H), 0.97(m, 14H), 1.97(m, 2H), 4.96, 5.10(s, 1H total in a *ca.* 1:8 area ratio) ppm. See Table 2 for the spectral data.

2-METHYL-1-TRIMETHYLSILYL-1-PROPYL α-METHOXY-α-TRIFLUOROMETHYLPHENYLACETATE was prepared by a procedure analogous to that reported by Mosher.[9] Into a dry 50 mL round-bottomed flask 6d (0.021 g, 0.15 mmol) and distilled (-)-MTPACl (0.0379 g, 0.15 mmol) were mixed with carbon tetrachloride (5 drops) and dry pyridine (5 drops) and allowed to stand for 12 h at room temperature. Water (1 mL) was added and the reaction mixture transfered to a separatory funnel with diethyl ether (20 mL). After washing with dilute HCl, saturated Na_2CO_3 solution, and water, the ether solution was dried over Na_2SO_4, filtered, evaporated and to the residue was added $CDCl_3$ for NMR analysis. ^1H NMR($CDCl_3$) δ 0.05(d, 9H, J = 2.2 Hz), 0.91(dd, 6H, J = 6.4 Hz, J = 3.9 Hz), 2.02(m, 1H), 3.53(m, 3H), 4.90(dd, 1H, J = 4.9 Hz, J = 1.7 Hz), 7.42(m, 5H)ppm. ^{19}F NMR(80% $CDCl_3$ + 20% TFA) δ 7.16, 7.23 ppm.

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