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The BF_3 and $B(C_6F_5)_3$-catalyzed 1,3-isomerization of allylic stannanes

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Dedicated with great respect and admiration to Professor Jean F. Normant in recognition of his numerous insightful contributions to the field of Organometallic Chemistry

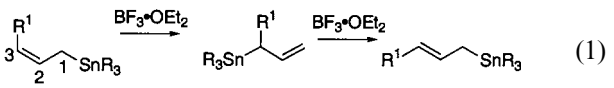
Abstract

A spectroscopic and chemical study of the stereospecific $B(C_6F_5)_3$-catalyzed 1,3-isomerization of (*E*,*S*)-1-methoxymethoxy-2-butenyl tributylstannane to (*Z*,*S*)-1-methyl-3-methoxymethoxy-2-propenyl tributylstannane is described. A pathway involving an intermediate $B(C_6F_5)_3$ adduct is proposed based upon ^1H- and ^{119}Sn-NMR data. Analogous spectral evidence was not observed in the seemingly related $BF_3{\cdot}OEt_2$-catalyzed isomerization. However, the similar product ratios obtained in $B(C_6F_5)_3$ and $BF_3{\cdot}OEt_2$-promoted additions of the latter stannane to *o*- and *p*-methoxybenzaldehyde reveals a close similarity between the two and prompts speculation that the $BF_3{\cdot}OEt_2$-catalyzed 1,3-isomerization proceeds by an analogous pathway. A pathway for the $B(C_6F_5)_3$-promoted addition of allylic stannanes to *o*-methoxybenzaldehyde is also presented.

Keywords: 1,3-Isomerization; tris-(Pentafluorophenyl)borane; Tin-boron metathesis; Allylic stannanes; Chiral stannanes

1. Introduction

It has been known for some time that $BF_3{\cdot}OEt_2$ catalyzes isomerizations of allylic stannanes [1]. Both *E*/*Z* isomerization and 1,3-Sn migration have been observed, in addition to ligand redistribution (Eqs. (1) and (2)). However, a plausible rationale for these isomerizations and redistributions has proven elusive. Based on isomer distribution in the products from additions of unsymmetrical allylic stannanes to aldehydes, Tagliavini and co-workers suggested the intervention of allylic BF_2 species as reactive intermediates (Eq. (3)) [2]. Subsequently, Denmark et al. discounted this possibility because of their failure to detect the formation of $Me_3SnF{\cdot}BF_3$ ($\delta = 0.7$ ppm) in their low temperature ^{13}C-NMR studies on BF_3-promoted additions of allyltrimethylstannane to aldehydes [3].



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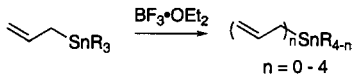

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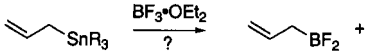

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In the Denmark studies, the reaction between allyltrimethylstannane and $BF_3{\cdot}OEt_2$ 'proved to be an enigma.' At -80°C in CH_2Cl_2–$CHCl_3$ the resonances for C1, C3, and Me_3Sn of the allylic stannane broadened, but the signal for C2 remained sharp (Eq. (1), R = Me, R^1 = H). At -20°C, the C1 and C3 signals were absent, but those for C2 and Me_3Sn were visible. When the -20°C sample was cooled to -80°C the spectrum showed signals for $Me_nSn(CH_2CH{=}CH_2)_{4-n}$ indicating that methyl/allyl exchange ('ligand redistribution') had taken place. Additional studies of a similar nature with (*E*)- and (*Z*)-crotyltrimethylstannane proved equally enigmatic [4]. Admixture of an 87:13 mixture of the *E* and *Z* isomers with $BF_3{\cdot}OEt_2$ at

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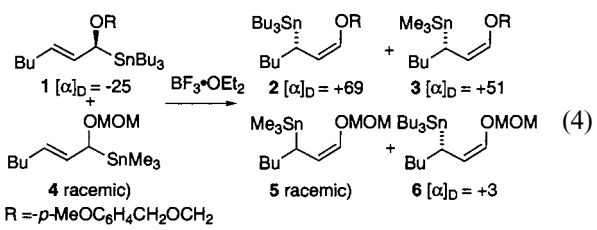
−80°C resulted in 'an immediate' isomerization to a 52:48 *E*/*Z* mixture. Upon warming the sample to −40°C, the aforementioned ligand redistribution was observed. The nature of the species responsible for ligand redistribution or double bond isomerization could not be determined.

Our interest in this issue originated with our findings that enantioenriched α-oxygenated allylic stannanes are stereospecifically isomerized by $BF_3{\cdot}OEt_2$ to the (*Z*)-γ-isomers [5]. Crossover experiments revealed two important aspects of this isomerization:

1. The reaction is intermolecular. A 1:1 mixture of α-OMOM, α-Me_3Sn and α-*p*-$MeOC_6H_4CH_2OCH_2O$, α-Bu_3Sn allylic stannanes gave rise to all four possible (*Z*)-γ-OR isomers in essentially equal amounts (Eq. (4)).
2. The reaction is bimolecular. This point was demonstrated by dilution studies and by experiments involving an enantioenriched (**1**) and a racemic stannane (**4**) of the type described above. The product (**6**) of Bu_3Sn transferred to the racemic stannane was enantioenriched to a small, but measurable extent.



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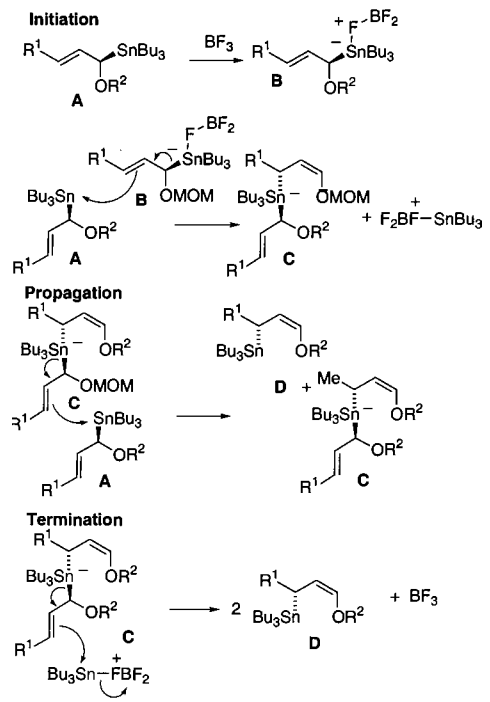
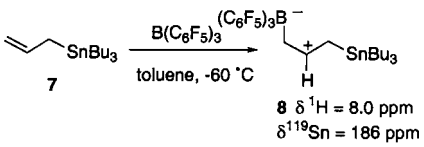


Fig. 1. Proposed pathway for BF_3-catalyzed 1,3-isomerization of α-oxygenated allylic stannanes.

Based upon these observations we proposed the pathway shown in Fig. 1 for these isomerizations. Though consistent with the facts, this mechanism requires $BF_3{\cdot}OEt_2$ to act as a nucleophile toward a neutral tin center. While such an interaction may be possible, it lacks precedent and seems counterintuitive, given the considerable Lewis acidity of BF_3 (a reviewer called this pathway 'preposterous from an inorganic chemists point of view'!). In accord with the findings of Denmark [4], we could detect no intermediates in the isomerization of **A**–**D** through ^{1}H-, ^{13}C-, or ^{119}Sn-NMR analysis of the isomerization reaction in CH_2Cl_2–CD_2Cl_2 or toluene–C_7D_8 at −60°C.

A recent paper by Piers and co-workers rekindled our interest in this isomerization [6]. A key finding was the fact that $(C_6F_5)_3B$ forms an adduct, formulated as **8**, with allyltributylstannane (**7**) at −60°C in toluene (Eq. (5)). Spectroscopic evidence for this adduct included ^{1}H-NMR and ^{13}C-NMR resonances at 8.0 and 190 ppm and a ^{119}Sn resonance at 186 ppm. These chemical shifts are consistent with a species in which both C2 and Sn assume considerable positive character.



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2. Results and discussion

2.1. NMR experiments

We repeated the Piers experiment with the α-OMOM and γ-OMOM tributylcrotylstannanes **9** and **11**. When mixed with equimolar $(C_6F_5)_3B$ in toluene at −60°C, the α-OMOM stannane **9** gave rise to a signal in the ^{1}H-NMR spectrum at 9.4 ppm which gave way to a new signal at 9.7 ppm over time (Eq. (6)). The ^{119}Sn spectrum showed an initial signal at −31 ppm, which slowly disappeared and was replaced by a signal at +157 ppm. The appearance of this signal occurred on a time scale comparable to that of the 9.7 ppm ^{1}H-NMR signal for the C2 proton. When this experiment was repeated with 0.5 equivalents of $(C_6F_5)_3B$, the signal at −31 ppm was replaced by signals at +157 ppm, as before, and a new signal at −13 ppm. This new signal was assumed to arise from the γ-OMOM crotylstannane **11**. In support of this assumption, the ^{1}H signal at 9.7 and −13ppm, and over time, the 157 ppm ^{119}Sn signal were produced upon mixing equimolar γ-OMOM stannane **11** with $(C_6F_5)_3B$ at −60°C in toluene. In a separate experiment we showed that $(C_6F_5)_3B$ effectively catalyzes the isomerization of the

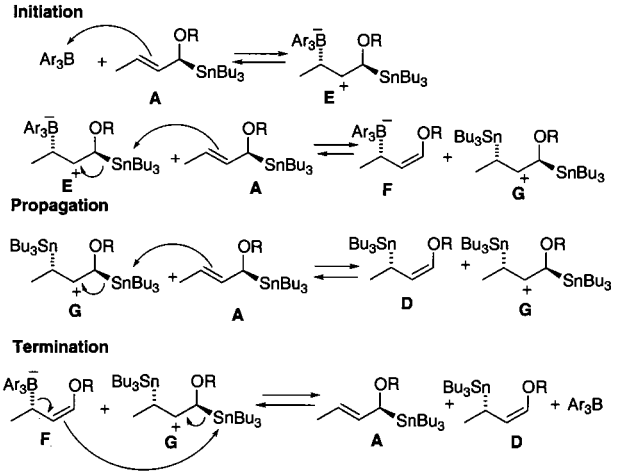
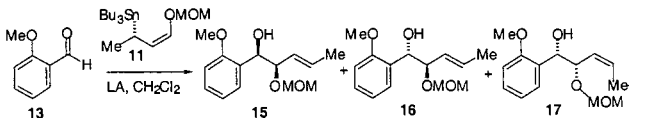


Fig. 2. Proposed pathway for $B(C_6F_5)_3$-catalyzed isomerization of α- to γ-oxygenated allylic stannanes.

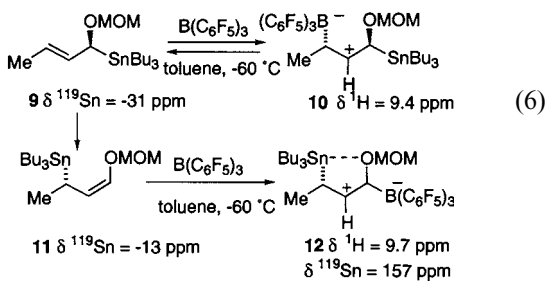
Table 1
Additions of the γ-OMOM stannane **11** to *o*-methoxybenzaldehyde (**13**) promoted by various Lewis acids



Lewis acid	T (°C)	Yield (%)	**15**:**16**:**17** [a]
$BF_3{\cdot}OEt_2$	−78	83	26:68:6
$B(C_6F_5)_3$	−78 to −20	63	23:71:6
$MgBr_2{\cdot}OEt_2$	−30 to 0	76	47:37:16

[a] Ratios determined by GC analysis.

α-OMOM to the γ-OMOM crotylstannane in toluene at −60°C (Eq. (7)).



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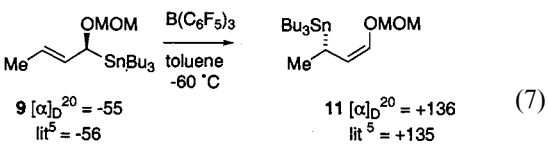

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We failed to detect a discrete peak for C2 in the ^{13}C-NMR spectrum of the $(C_6F_5)_3B$ complex of the foregoing stannanes. We suspect that this signal is obscured by the toluene and C_6F_5 resonances. We also saw merging ($\sigma \sim 7$ ppm) of the chemical shifts for the *meta* and *para* fluorine peaks in the ^{19}F-NMR spectrum of the $(C_6F_5)_3B$-allylic stannane complex. This difference has been correlated with the degree of anionic character of boronate complexes [7]. Piers observed a difference of only 4.9 ppm (versus > 15 ppm in the parent borane) in an allylstannane-$(C_6F_5)_3B$ complex suggestive of considerable boronate character.

Our analysis of the data leads us to conclude that $(C_6F_5)_3B$ interacts with the α-oxygenated allylic stannane to produce an intermediate with cationic character at C2. However the Bu_3Sn moiety is less cationic than the corresponding group in the Piers parent allyl system [8]. We also conclude that the boron is less anionic in our proposed intermediate as compared to that observed by Piers (see Eq. (5)).

The foregoing findings are consistent with the pathway shown in Fig. 2. Accordingly, the cationic intermediate **E** donates a Bu_3Sn group to the α-oxygenated stannane **A** to afford the *bis*-tributylstannylated cation **G**. This transient, but pivotal, intermediate serves as the shuttle by which the α-oxygenated stannane **A** is converted to the γ-isomer **D** with regeneration of cation **G** in a propagation step.

2.2. Additions to *o*- and *p*-methoxybenzaldehyde promoted by $B(C_6F_5)_3$ and $BF_3{\cdot}OEt_2$

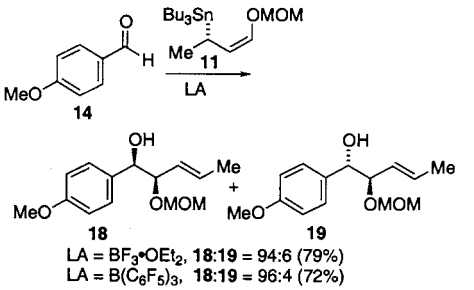
As noted above, previous attempts to identify intermediates in $BF_3{\cdot}OEt_2$-catalyzed allylic stannane isomerizations by NMR analysis at low temperature were unsuccessful. Conceivably, the BF_3 adducts could be present in amounts below our NMR detection thresholds. Lacking such direct evidence, we decided to compare addition reactions of the γ-OMOM allylic stannane **11** to aldehydes promoted by $B(C_6F_5)_3$ and $BF{\cdot}OEt_2$. In doing so, we expected to demonstrate similarities or differences between these two Lewis acids that might validate, or possibly invalidate, an extrapolation of the pathway for $B(C_6F_5)_3$-catalyzed 1,3-isomerization to the corresponding BF_3-catalyzed isomerization.

For this comparison we chose *o*- and *p*-methoxybenzaldehyde (**13** and **14**). Piers had reported a > 20:1 rate difference in $B(C_6F_5)_3$-promoted additions of allyl tributylstannane to these aldehydes, favoring the *ortho* isomer [6]. This rate difference had been previously attributed to a boron chelation effect [9], but this rationale was discredited by the Piers study. Our findings are summarized in Table 1.

Clearly the ratio of *syn* and *anti* adducts **15** and **16** compares favorably for the two boron Lewis acids [10]. Interestingly, a small amount of the (*Z*)-adduct **17** is formed in both additions. The same three adducts were formed when $MgBr_2{\cdot}OEt_2$ was employed as the Lewis acid (Table 1). $MgBr_2$ is known to favor a chelation pathway in such additions [11]. Though similar product

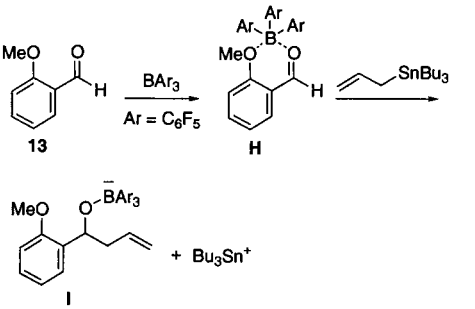
ratios were obtained with $BF_3{\cdot}OEt_2$ and $B(C_6F_5)_3$, the reaction was faster with the former Lewis acid. An analogous rate difference was seen in the 1,3-isomerization studies.

Additions of the γ-OMOM allylic stannane **11** to *p*-methoxybenzaldehyde (**14**) gave nearly identical *syn*:*anti* ratios of adducts **18** and **19** strongly favoring the former, with both boron Lewis acids (Eq. (8)). These ratios are in accord with the usual acyclic transition states [11].



(8)

Thus, an analogy between $BF_3{\cdot}OEt_2$ and $B(C_6F_5)_3$ as Lewis acid promoters in allylic stannane additions is established. The additions to *o*-methoxybenzaldehyde bear further comment. As noted above, the initial observation of this effect was a rate enhancement in the allylation reaction which was attributed to a chelated intermediate **H** (Eq. (9)) [9]. This pathway was rejected by Piers who proposed the intermediate **J** (Eq. (10)) as one alternative based on NMR studies [6]. Piers tentatively suggested that the stannyl chelate **J** could undergo allylation by the allylic triarylboronate, as depicted in Eq. (10), to afford the adduct **K**. However he stated that a pathway involving attack on the stannyloxy chelate **J** by the allylstannane could not be excluded. Our findings are in accord with this latter pathway. Were the additions to proceed through the allylic boronate **N**, as in Eq. (11), the products of the γ-OMOM allylic stannane additions, **O**, would be regioisomeric to those actually formed (**L** in Eq. (11)). One further comment is in order. The isomerization reactions are catalytic in Lewis acids while the additions require stoichiometric quantities. Thus it seems likely that the presumed initial adduct **K** is converted to boronate **I** which prevents turnover of the Lewis acid. As this issue has not been studied, the suggestion, though reasonable, is still speculative.



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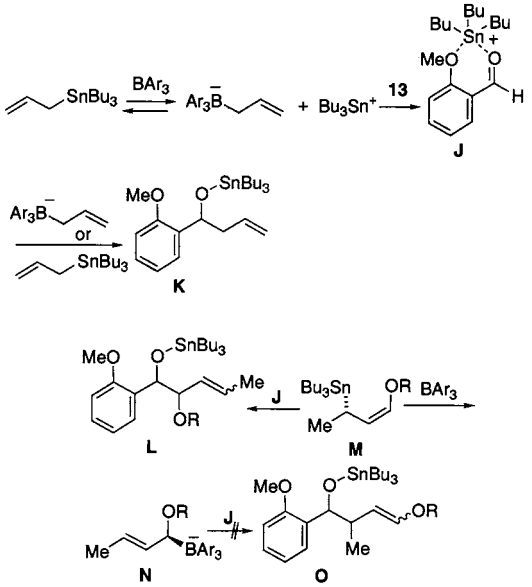
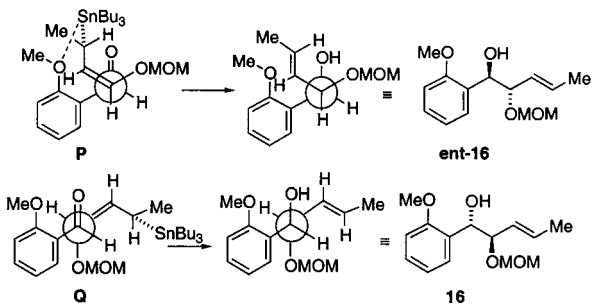


(10)

(11)

On a final note, Yamataka et al. have reported an enhanced reactivity of *ortho*-chlorobenzaldehyde compared to the *para* isomer in $BF_3{\cdot}OEt_2$-promoted additions of crotyl tributyl tin [12]. The two aldehydes also give different ratios of *syn* and *anti* adducts. They propose a cyclic transition state for the *ortho* isomer, as in **P** (Eq. (12)), to explain these differences. In principal, a similar effect could be operative in reactions of *ortho*-methoxybenzaldehyde. However, if that were the case the stereochemistry of the adducts would be enantiomeric to those obtained in the present studies, as illustrated in Eq. (12). Thus the more conventional acyclic transition state **Q** best accommodates the observed product stereochemistry.



(12)

3. Conclusions

In conclusion, we have obtained NMR evidence for intermediates **10** and **12** (Eq. (6)) in the $B(C_6F_5)_3$-catalyzed isomerization of the α-oxygenated allylic stannane **9** to the γ-isomer **11**. We have also shown that both $BF_3{\cdot}OEt_2$ and $B(C_6F_5)_3$ catalyze this isomerization with virtually 100% enantio- and regioselectivity. We have

further demonstrated that $BF_3{\cdot}OEt_2$ and $B(C_6F_5)_3$ display analogous and characteristic Lewis acid properties in the addition of the enantioenriched γ-OMOM allylic stannane **11** to *o*- and *p*-methoxybenzaldehyde. These findings are consistent with the pathway depicted in Fig. 2 for the 1,3-Bu_3Sn shift in allylic stannanes catalyzed by $B(C_6F_5)_3$ and, by analogy, $BF_3{\cdot}OEt_2$, as well.

4. Experimental

4.1. General

$B(C_6F_5)_3$ was used as received from Strem Chemical. All operations were performed under an atmosphere of dry nitrogen or argon.

4.2. Tris(pentafluorophenylborane)-catalyzed isomerization of α-OMOM stannane **9** to γ-OMOM stannane **11**

To a stirred solution of (*S*)-α-OMOM stannane (**9**) [5] (0.20 g, 0.50 mmol) in 4.5 ml of toluene at −78°C was added $B(C_6F_5)_3$ (0.051 g, 0.099 mmol) in 0.5 ml of toluene. The resulting solution was stirred at −78°C for 5 h. The reaction was quenched with saturated aqueous $NaHCO_3$, the mixture was allowed to warm to room temperature (r.t.) and the layers were separated. The aqueous layer was extracted with Et_2O. The combined extracts were dried over sodium sulfate, filtered, and concentrated. Purification by column chromatography on silica gel (elution with 2.5% EtOAc–Hex) afforded 0.13 g (66%) of (*S*)-γ-OMOM stannane (**11**) [5] as a clear colorless oil. $[\alpha]_D = +136°$ (c 1.56, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.93 (d, $J = 6.3$ Hz, 1H), 4.73 (ABq, $J = 6.3$ Hz, 2H), 4.47 (dd, $J = 11.4$, 6.3, 1H), 3.36 (s, 3H), 2.47 (dt, $J = 10.2$, 5.4, 1H), 1.63–1.17 (m, 18H), 1.00–0.71 (m, 12H). The rotation and ^{1}H-NMR spectrum were in complete agreement with the published values [5].

4.3. Tris(pentafluorophenyl)borane-promoted additions

4.3.1. p-Methoxybenzaldehyde (**14**)

To a stirred solution of (*S*)-γ-OMOM stannane (**11**) (0.12 g, 0.30 mmol) and *p*-methoxybenzaldehyde (0.034 g, 0.25 mmol) in 2.5 ml of CH_2Cl_2 at −78°C was added $B(C_6F_5)_3$ (0.15 g, 0.29 mmol). The resulting solution was then allowed to slowly warm to −20°C and was stirred at that temperature for 4 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ and the mixture was allowed to warm to r.t. The layers were separated and the aqueous layer was extracted with ether. The combined extracts were dried over sodium sulfate, filtered, and concentrated. Purification by column chromatography on silica gel (elution with 15% EtOAc–Hex) afforded 0.049 g (72%) of alcohol **18** as a clear colorless oil. $[\alpha]_D = -74$ (c 1.2, $CHCl_3$); IR (neat) 3470 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.27–7.24 (m, 2H), 6.88–6.83 (m, 2H), 5.52 (dq $J = 15.3$, 6.0 Hz, 1H), 5.23 (dd, $J = 15.3$, 8.1 Hz, 1H), 4.75 and 4.56 (ABq, $J = 6.9$ Hz, 2H), 4.53 (dd, $J = 7.5$, 2.4 Hz, 1H), 4.03 (dd, $J = 7.5$, 7.5 Hz, 1H), 3.80 (s, 3H), 3.33 (s, 3H), 3.08 (d, $J = 2.4$ Hz, 1H), 1.61 (d, $J = 6.6$ Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ 17.8, 55.2, 55.7, 76.3, 81.6, 93.7, 113.4, 126.9, 128.3, 131.7, 132.3, 159.1. Anal. Calc. for $C_{14}H_{20}O_4$: C, 66.66; H, 7.99. Found: C, 66.74; H, 8.02%.

4.3.2. o-Methoxybenzaldehyde (**13**)

The previous procedure was followed substituting *o*-methoxybenzaldehyde (0.034 g, 0.25 mmol) for the *p*-isomer. Purification of the product by column chromatography on silica gel (elution with 15% EtOAc–Hex) afforded 0.039 g (63%) of a 23:71:6 (by GC analysis) mixture of alcohols **15**, **16**, and **17** as a clear colorless oil. **16**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38–7.34 (m, 1H), 7.24–7.20 (m, 1H), 7.0–6.82 (m, 2H), 5.58 (dq, $J = 15.6$, 6.6 Hz, 1H), 5.42 (dd, $J = 15.6$, 7.8 Hz, 1H), 5.05 (dd, $J = 5.4$, 5.1 Hz, 1H), 4.69 and 4.51 (ABq $J = 6.6$ Hz, 2H), 4.3 (dd, $J = 9.0$, 5.1 Hz, 1H), 3.85 (s, 3H), 3.18 (s, 3H), 2.77 (dd, $J = 5.4$ Hz, 1H), 1.67 (d, $J = 6.6$ Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ 159.8, 131.5, 128.3, 128.1, 126.5, 120.5, 110.2, 93.3, 78.6, 77.2, 72.0, 55.4, 17.9.

15: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38–7.34 (m, 1H), 7.24–7.20 (m, 1H), 7.0–6.82 (m, 2H), 5.57 (dq, $J = 15.6$, 6.3 Hz, 1H), 5.42 (dd, $J = 15.6$, 8.1 Hz, 1H), 5.00 (dd, $J = 5.4$, 5.4 Hz, 1H), 4.69 and 4.47 (ABq, $J = 6.6$ Hz, 2H), 4.18 (dd, $J = 7.5$, 5.7 Hz, 1H), 3.81 (s, 3H), 3.14 (s, 3H), 3.05 (d, $J = 5.7$ Hz, 1H), 1.63 (d, $J = 6.3$ Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ 160.1, 130.3, 128.7, 127.7, 127.6, 120.5, 110.2, 93.6, 80.2, 77.2, 71.5, 55.0, 17.7.

4.4. $BF_3{\cdot}OEt_2$-promoted additions

4.4.1. p-Methoxybenzaldehyde (**14**)

To a stirred solution of (*S*)-γ-OMOM stannane (**11**) (0.12 g, 0.30 mmol) and *p*-methoxybenzaldehyde (**14**) (0.034 g, 0.25 mmol) in 2.5 ml of CH_2Cl_2 at −78°C was added $BF_3{\cdot}OEt_2$ (0.061 g, 0.49 mmol). The resulting solution was stirred at that temperature for 4 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and the mixture was allowed to warm to r.t. The layers were separated and the aqueous layer was extracted with ether. The combined organic extracts were dried over sodium sulfate, filtered, and concentrated. Purification by column chromatography on silica gel (elution with 15% EtOAc–Hex) afforded 0.049 g (79%) of alcohol **18** as a clear colorless oil.

*4.4.2. o-Methoxybenzaldehyde (**13**)*

The previous procedure was employed substituting *o*-methoxybenzaldehyde (**13**) (0.034 g, 0.25 mmol) for the *p*-isomer. Purification by column chromatography on silica gel (elution with 15% EtOAc–Hex) afforded 0.039 g (83%) of a 26:68:6 (by GC analysis) mixture of alcohols **15**, **16**, and **17** as a clear colorless oil.

4.5. $MgBr_2 \cdot OEt_2$-promoted addition to o-methoxybenzaldehyde

To a stirred solution of *o*-methoxybenzaldehyde (**13**) (0.023 g, 0.17 mmol) and (*S*)-γ-OMOM stannane (**11**) (0.12 g, 0.25 mmol) in 1.6 ml of CH_2Cl_2 at −30°C was added $MgBr_2 \cdot OEt_2$ (0.052 g, 0.20 mmol). The resulting solution was allowed to slowly warm to 0°C and stirred at that temperature for 12 h. It was then quenched with saturated $NaHCO_3$ solution and allowed to warm to r.t. The phases were separated and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried over sodium sulfate, filtered, and concentrated. Purification by column chromatography on silica gel (elution with 15% EtOAc–Hex) afforded 0.031 g (76%) of a 47:37:16 (by GC) mixture of alcohols **15**, **16**, and **17** as a clear colorless oil.

4.6. NMR experiments

To a septum-sealed NMR tube (10 mm) containing 0.20 g (0.40 mmol) of $B(C_6F_5)_3$ in toluene-d_8 (3.5 ml) cooled to −60°C was added 0.16 g (0.40 mmol) of γ-OMOM stannane (**9**) in toluene-d_8 (0.25 ml) by syringe. The following NMR spectra were collected at −60°C: ^{1}H-NMR (500 MHz) (selected resonances): 9.4 (br, s, 1H), which over 4 h shifted to 9.7 (br, s, 1H). ^{19}F-NMR (282.4 MHz), −128.5 (s, 6F, *o*-F's), −149.3 (s, 3F, *p*-F's), −156.2 (s, 6F, *m*-F's) which over 4 h shifted to −128.4 (s, 6F, *o*-F's), −150.3 (s, 3F, *p*-F's), −156.7 (s, 6F, *m*-F's). ^{119}Sn-NMR (149.2 MHz) 157 ppm.

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