Lewis Acid Promoted Additions of γ-Alkoxy- and -(Silyloxy)crotylstannanes to (S)-2-(Benzyloxy)propanal

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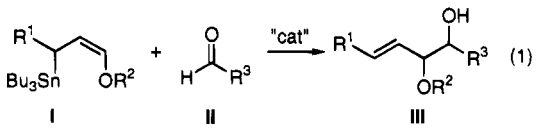
Additions of the γ-oxygenated allylic stannane MOM ethers (*R*)-**1a**, (*S*)-**1a**, and silyl ethers (*R*)-**1b**, (*S*)-**1b** to (*S*)-2-(benzyloxy)propanal (**2**) in the presence of BF_3·OEt_2 and $MgBr_2$ were examined in order to establish matched and mismatched preferences. In the BF_3 reactions, stannanes (*R*)-**1a** and (*R*)-**1b** were matched with **2**. The former gave the *syn* adduct **3** and the cyclopropane **4** as a 93:7 mixture. The OTBS stannanes (*R*)-**1b** and (*S*)-**1b** gave only the *syn* adducts **7** and **9**, respectively. However, in each case considerable cyclopropane adduct, **8** and **10** respectively, was also formed. When aldehyde **2** was treated with excess racemic stannane, (*RS*)-**1a**, adduct **3** derived from (*R*)-**1a** was the major product, whereas with (*RS*)-**1b**, products **7** and **8** derived from (*R*)-**1b** were formed preferentially. Aldehyde **2** showed a preference for MOM ether (*S*)-**1a** in the $MgBr_2$-promoted reaction, but each of the enantiomeric OTBS stannanes (*R*)-**1b** and (*S*)-**1b** afforded a single product, the (*Z*)-*syn,syn* alcohol **13** from the former and the (*E*)-*syn,syn* alcohol **9** from the latter. With excess (*RS*)-**1b**, aldehyde **2** reacted fastest with (*R*)-**1b**, in contrast to the MOM analogue (*RS*)-**1a**. The racemic (*E*) stannanes (*E*)-**1a** and (*E*)-**1b** were likewise examined. In the BF_3 reaction, the major products (**5** from the MOM ether (*E*)-**1a** and **9** from the silyl ether (*E*)-**1b**) were derived from the (*R*)-enantiomer. With $MgBr_2$, the OMOM stannane (*E*)-**1a** gave rise to a mixture of four adducts arising from both the (*R*) and (*S*) enantiomers of the stannane. The OTBS stannane (*E*)-**1b**, on the other hand, afforded mainly adduct **9** derived from the (*R*) enantiomer of stannane (*E*)-**1b**.

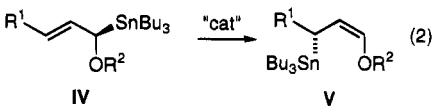
Introduction

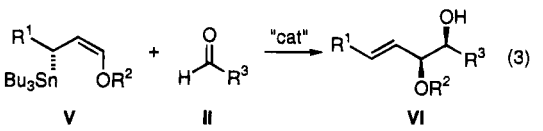
Lewis acid promoted additions of γ-alkoxy allylic stannanes to aldehydes afford monoprotected 1,2-diols in high yield (eq 1). These compounds are of interest as



possible intermediates for the synthesis of carbohydrates and related polyols.[1] First reported by Quintard[2] in 1983 (eq 1: R^1 = H; R^2 = Et; R^3 = Ph; cat = BF_3·OEt_2), the reaction was subsequently examined in greater detail by Keck[3] (eq 1: R^1 = H, R^2 = TBS or Me; R^3 = CH_3CH_2CH(OBn), $BOMOCH_2CH(CH_3)$, $BnOCH_2CH(CH_3)$, CH_3CH(OBOM)CH_2, or $CH_3CH(OBn)CH_2$; cat = $MgBr_2$) and Koreeda[4] (eq 1: R^1 = H or Me, R^2 = Me; R^3 = Ph, *o*-MeC_6H_4, *i*-Pr, or *c*-C_6H_{11}; cat = BF_3·OEt_2) and their coworkers. In all cases, racemic or achiral stannanes and aldehydes were employed and the major products were the *syn* diastereomers.

In 1989 we described a route to enantioenriched γ-alkoxy allylic stannanes such as **V** through stereospecific 1,3-isomerization of the α-alkoxy isomers **IV** (eq 2).[5] These stannanes undergo highly selective anti S_E' additions to aldehydes in the presence of Lewis acids, yielding mainly *syn* adducts **VI** (eq 3). The TBS ethers **V** (R^2 = *t*-BuSiMe$_2$) give higher *syn:anti* product ratios than their MOM or BOM analogues.[6] In reactions involving chiral α-oxygenated aldehydes, *anti* products can predominate under certain conditions.[7]





The present study on additions of the crotylstannanes **I** (R^1 = Me; R^2 = MOM or TBS) and their (*E*) counterparts to (*S*)-2-(benzyloxy)propanal (**2**) was undertaken to establish reactivity and selectivity patterns for possible applications in polyol synthesis.[7]

BF_3-Promoted Additions. The BF_3-promoted reaction of stannane (*R*)-**1a** with aldehyde **2** afforded a 93:7 mixture of (*E*)-*syn,anti* **3** and cyclopropyl adduct **4** in 74% yield.[8] Addition of stannane (*S*)-**1a** proceeded in 97% yield and gave a 67:33 mixture of the diastereomeric (*E*)-*syn,syn* and (*E*)-*anti,anti* adducts **5** and **6**. Reaction of

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1994.

(1) For a recent review, see Marshall, J. A. *Chemtracts—Org. Chem.* **1992**, *5*, 75.

(2) Quintard, J-P.; Elissondo, B.; Pereyre, M. *J. Org. Chem.* **1983**, *48*, 1559.

(3) Keck, G. E.; Abbot, D. E.; Wiley, M. R. *Tetrahedron Lett.* **1987**, *28*, 139.

(4) Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143.

(5) Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 2183. Marshall, J. A.; Welmaker, G. S.; Gung, B. W. *J. Am. Chem. Soc.* **1991**, *113*, 647.

(6) Marshall, J. A.; Welmaker, G. S. *J. Org. Chem.* **1992**, *57*, 7158.

(7) A portion of this study has appeared in preliminary form: Marshall, J. A.; Luke, G. P. *J. Org. Chem.* **1991**, *56*, 483.

(8) In our preliminary study[7] we failed to detect the cyclopropane adduct **4**. Based on our reexamination of the original spectra, we believe that it was not formed in those earlier experiments. The reason for this deviation is not clear at present. Because it was formed in only a small amount we did not undertake stereochemical elucidation of cyclopropane **4**.

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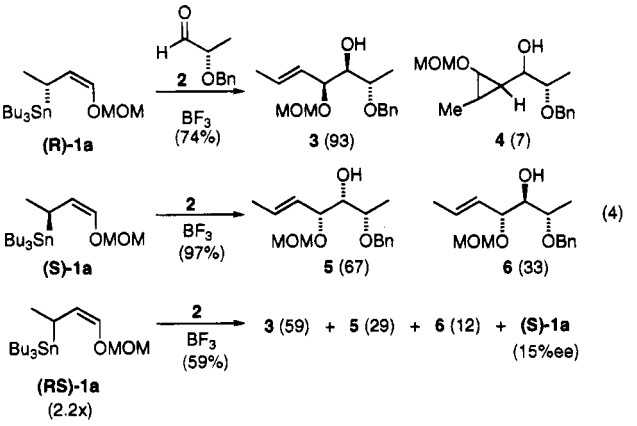
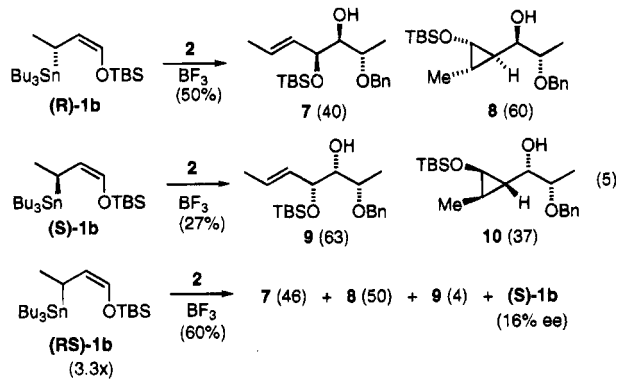
excess racemic stannane (*RS*)-**1a** with aldehyde **2** afforded a mixture of adducts **3**, **5**, and **6** in the ratio 59:29:12 in 59% yield. None of the cyclopropane product **4** could be detected. As expected, the recovered stannane was slightly enriched in the (*S*)-enantiomer. Evidently, the matched stannane (*R*)-**1a** reacts faster than (*S*)-**1a** with aldehyde **2**, but only marginally.



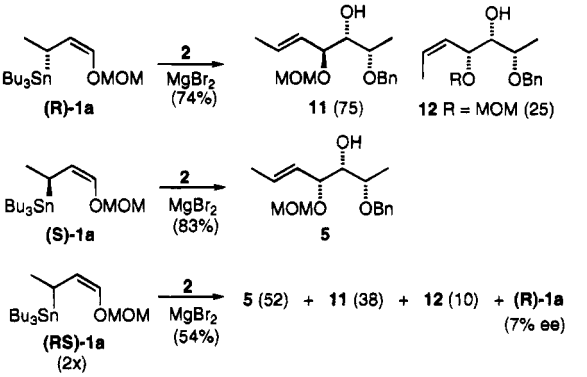
(4)

The "matched" OTBS stannane (*R*)-**1b** added to aldehyde **2** in the presence of BF_3·OEt_2 to give the (E)-*syn,anti* adduct **7** along with the cyclopropylcarbinol **8** as a 40:60 mixture in 50% yield. Analogous reaction of (*S*)-**1b** with aldehyde **2** proceeded in only 27% yield and afforded a 63:37 mixture of (*E*)-*syn,syn* adduct **9** and cyclopropylcarbinol **10**. With an excess of racemic stannane (*RS*)-**1b**, aldehyde **2** gave rise to a 46:50:4 mixture of adducts **7**, **8**, and **9** in 60% yield along with recovered (*S*)-**1b** of 16% ee. The unprecedented formation of cyclopropylcarbinols in these reactions most likely proceeds by initial attack of the enol ether double bond on the aldehyde-Lewis acid complex of the aldehyde followed by 1,3-nucleophilic ring closure of the intermediate oxocation as depicted in Figure 3.



(5)

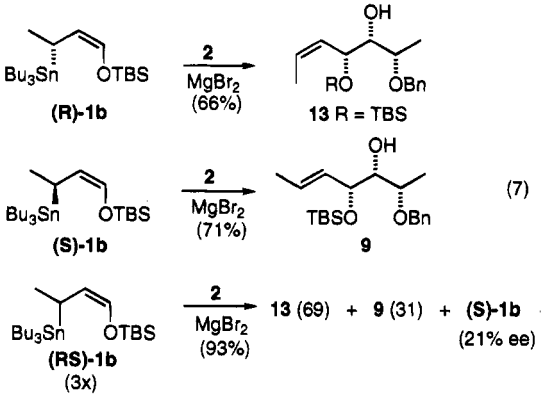
MgBr$_2$-Promoted Additions. We next examined $MgBr_2$-promoted reactions of the (*Z*)-alkoxy and silyloxy allylic stannanes **1a** and **1b** with aldehyde **2**. In these chelation controlled additions, the (*R*)-stannane (*R*)-**1a** afforded a 75:25 mixture of (*E*)-*anti,syn* and (*Z*)-*syn,syn* adducts **11** and **12** in 74% yield, whereas stannane (*S*)-**1a** gave rise to the (*E*)-*syn,syn* alcohol **5** in 83% yield. We also detected some 4% of adduct **11** arising from the slight amount of (*R*)-**1a** present in the stannane reagent (ee ~90%). Addition of excess racemic stannane (*RS*)-**1a** led to a mixture of three products: **5** (52%), **11** (38%), and **12** (10%), in 54% yield, along with recovered stannane (*R*)-**1a** (7% ee; eq 6). Here, as in the BF_3 reactions



(6)

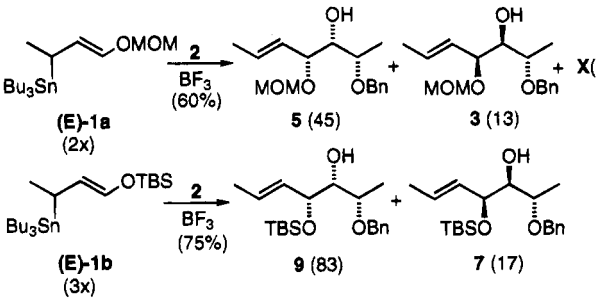
with **1a**, the matched addition proceeds only slightly faster than the mismatched.

Stannanes **1b** provide an interesting contrast to **1a** in the $MgBr_2$-promoted additions as well. Both (*R*)-**1b** and (*S*)-**1b** yield only one adduct with aldehyde **2**. In both cases, a *syn,syn* product is formed. However, (*R*)-**1b** gives the (*Z*) isomer **13**, whereas (*S*)-**1b** affords the (*E*) counterpart **9**. Excess racemic **1b** gives rise to a 69:31 mixture of **13** and **9** in 93% yield, along with recovered (*S*)-**1b** (21% ee; eq 7). Surprisingly, the (*Z*) product **13** is kinetically favored over the (*E*) isomer **9**.



(7)

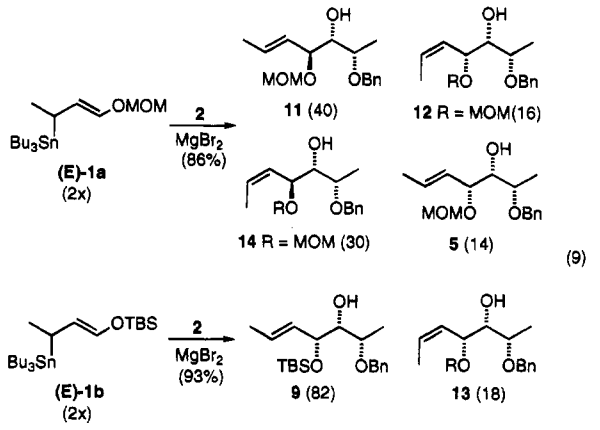
Additions of (E)-Allylic Stannanes. We also examined additions of the (*E*)-allylic stannanes (*E*)-**1a** and (*E*)-**1b** to aldehyde **2**. These stannanes are currently available only as racemic mixtures.[9] The BF_3 reaction with excess (*E*)-**1a** afforded a *ca.* 3:1 mixture of (*E*)-*syn,syn* and (*E*)-*syn,anti* adducts **5** and **3** along with recovered stannane (54%) and an inseparable less polar unidentified by-product in 60% yield. The TBS analogue (*E*)-**1b** gave an 83:17 mixture of the (*E*)-*syn,syn* and (*E*)-*syn,anti* adducts **9** and **7** in 75% yield and recovered stannane (18%) under these conditions (eq 8). Recovered stannane from both reactions showed negligible rotation at the sodium D line.



(8)

Stannane (*E*)-**1a** gave rise to four adducts: **11** (40%), **12** (16%), **14** (30%), and **5** (14%), in 86% yield and

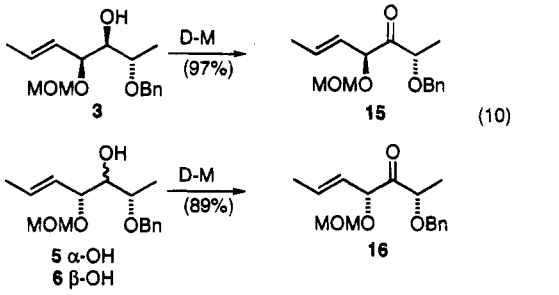
recovered stannane (42%) from aldehyde **2** and $MgBr_2$. The former two are derived from the (*S*) enantiomer of (*E*)-**1a**, and the latter two from the (*R*) stannane. With the TBS analogue (*E*)-**1b**, the addition proceeded in 93% yield affording recovered stannane (36%) and an 82:18 mixture of (*E*)- and (*Z*)-*syn,syn* adducts **9** and **13** (eq 9).



(9)

In both cases, the recovered stannane showed scarcely measurable optical rotation at the sodium D line.[9]

Structure Elucidation of the Major Adducts. The stereochemistry of the MOM adducts **3**, **5**, and **6** was surmised from the ^1H NMR spectrum (E double bonds) and through oxidation with the Dess–Martin periodinane reagent.[10] Alcohol **3** yielded ketone **15**, whereas **5** and **6** afforded the epimeric ketone **16** (eq 10). The carbinyl



(10)

configuration could be assigned from chemical shift data on the (*R*)- and (*S*) *O*-methyl mandelates **17**, **18**, and **19** (Figure 1).[11]

Additional evidence for the structure of adduct **5** was secured through methylation followed by hydrogenation then MOM cleavage and hydrogenolysis of the benzyl ether. The resulting diol **24** was converted to the acetonide **25**. The ^1H NMR spectrum showed coupling of 1.6 Hz for the carbinyl protons H_a/H_b and H_b/H_c in accord with the depicted arrangement (eq 11). The ^{13}C NMR spectrum also showed the acetonide carbons at the expected chemical shifts.[12]

The structure of the TBS adducts **7** and **9** can be assigned by analogy with their MOM counterparts **3** and **5**. Support for these assignments was secured from the

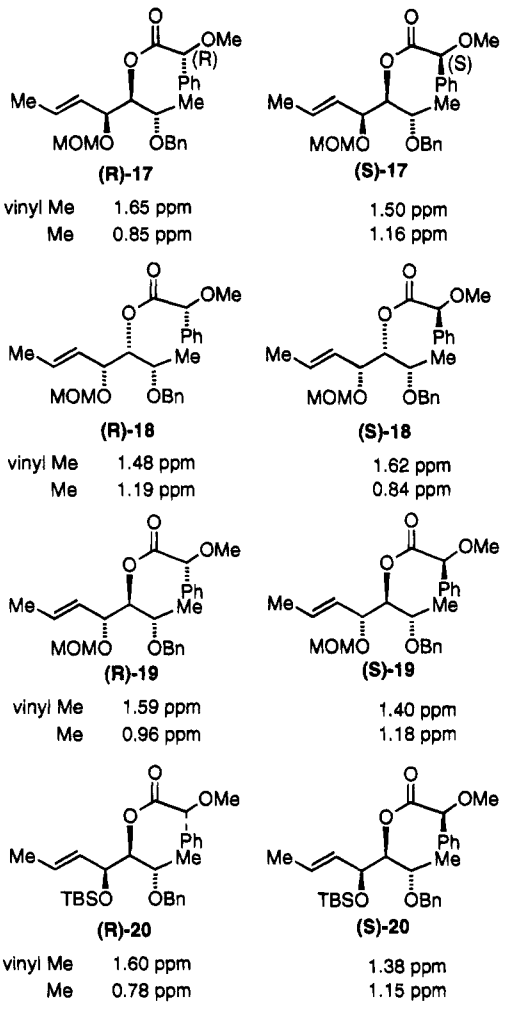
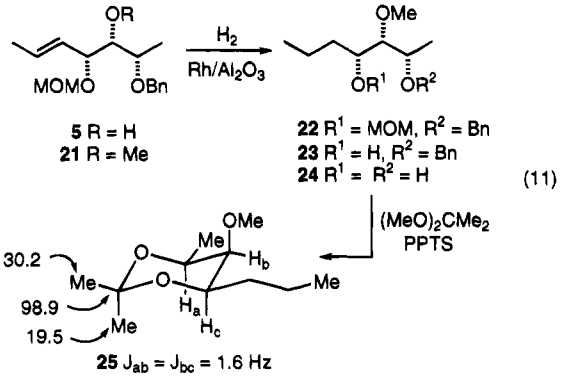
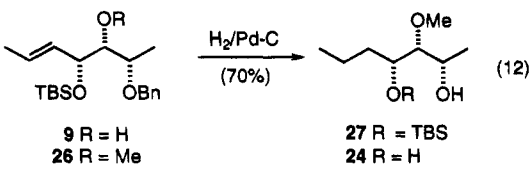


Figure 1. Chemical shift for *O*-methyl mandelates of adducts **3**, **5**, **6**, and **7**.



(11)

^1H NMR spectra of the *O*-methyl mandelate derivatives (*R*)-**20** and (*S*)-**20** of adduct **7** (Figure 1). Additionally, adduct **9** was converted to the previously prepared diol **24** by *O*-methylation, then hydrogenation over Pd–C and TBS cleavage with TBAF (eq 12).



(12)

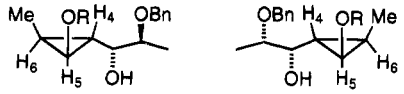
Our structure assignments for cyclopropanes **8** and **10** are based on ^1H NMR coupling constants for the cyclo-

(9) We have recently succeeded in preparing nonracemic stannanes (*E*)-**1a** and (*E*)-**1b** of high ee and find that they show $[\alpha]_D$ <10. This work is currently in progress and results will be published in due course.

(10) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. Ireland, R. E.; Lin, L. *J. Org. Chem.* **1993**, *58*, 2899.

(11) Trost, B. M.; Belletire, J. L; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370.

(12) Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, *58*, 3511.



8 R = TBS 10 R = TBS

H	δ, ppm	J, Hz	δ, ppm	J, Hz
4	0.55	4,5 = 2.9	0.49	4,5 = 2.6
5	3.36	5,6 = 6.6	3.37	5,6 = 7.0
6	0.60	6,4 = 5.8	0.66	6,4 = 5.6

Figure 2. Chemical shift data for cyclopropranes **8** and **10**.

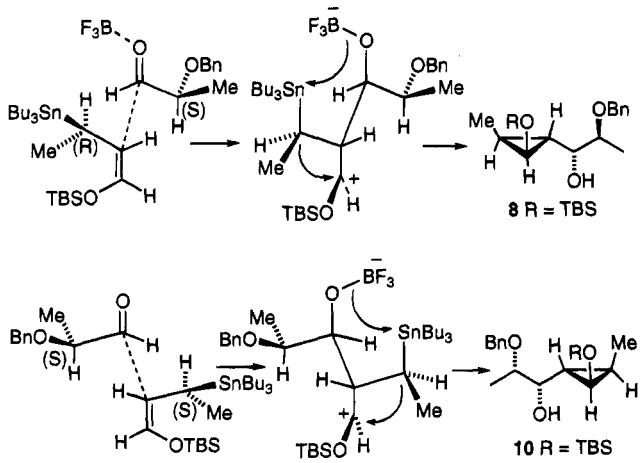
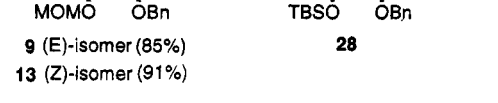


Figure 3. Reaction pathways leading to cyclopropanes **8** and **10** from stannanes (*R*)-**1a** and (*S*)-**1a**.

propyl hydrogens H_4, H_5, and H_6 (Figure 2). Both isomers show a small $J_{4,5}$ and a larger $J_{5,6}$ coupling indicative of a *trans,cis* arrangement, as depicted in Figure 2.[13]

Analogous cyclizations of γ-substituted stannanes have been shown to proceed with inversion at the tin center and the absolute stereochemistry at C6 is assigned accordingly.[14] In both cases the orientation of the carbocation places the OTBS substituent syn to the adjacent H substituent in what is presumed to be an early transition state. A consideration of the most likely direction of attack on the aldehyde carbonyl, as shown, leads to the indicated tentative assignment for the C3 carbinyl center (Figure 3).

The minor (*Z*) adduct **12** (see eq 6) from the $MgBr_2$-initiated additions of MOM stannane (*R*)-**1a** was assigned the *syn,syn* stereochemistry from mechanistic considerations (Figure 6). The (*Z*)-*syn,syn* OTBS adduct **13** (see eq 7) afforded aldehyde **28** upon ozonolysis and reductive workup. This aldehyde was also obtained from the (*E*)-*syn,syn* adduct **9** (eq 13).



9 (E)-isomer (85%) **28**
13 (Z)-isomer (91%)

(13)

Mechanistic Considerations. In his pioneering investigations of BF_3-promoted additions of (*E*)- and (*Z*)-2-butenylstannanes to aldehydes, Yamamoto found that

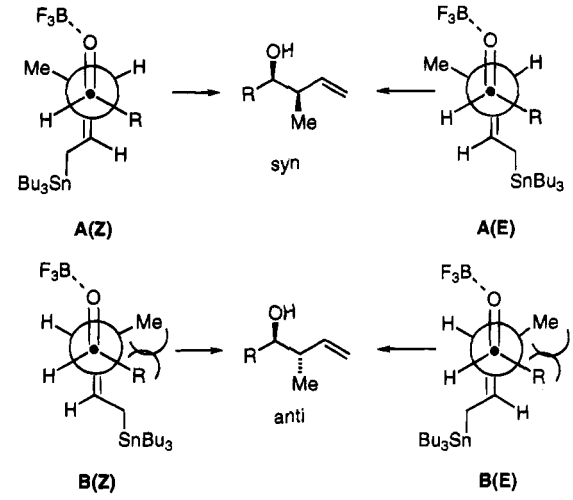


Figure 4. Acyclic transition states for additions of crotylstannanes to aldehydes promoted by BF_3.

syn adducts were favored from both isomeric stannanes.[15] An acyclic transition state was proposed in which steric interactions between the vinylic CH_3 of the stannane and the aldehyde substituent R favor the antiperiplanar arrangements **A**(*Z*) and **A**(*E*) (Figure 4). The alternative synclinal transition states **B**(*Z*) and **B**(*E*) suffer from steric interactions between these two groups.[16,17]

In the present study, the vinyl CH_3 of the stannane is replaced by OMOM or OTBS and both the stannane and aldehyde are chiral. In all cases save one (see eq 6), *syn* adducts are favored. In the BF_3 reactions, addition to the aldehyde carbonyl is reagent controlled. The (*R*/*Z*) stannanes (*R*)-**1a** and (*R*)-**1b** preferentially attack the *re* face and the (*S*/*Z*) reagents (*S*)-**1a** and (*S*)-**1b** the *si* face of aldehyde **2**. The (*Z*)-MOM reagent (*S*)-**1a** affords the *anti* adduct **6** as a significant minor product, but with the OTBS stannanes **1b** only the *syn* adducts **7** and **9** are formed (see eq 4 and 5). The (*E*) stannanes (*E*)-**1a** and (*E*)-**1b** likewise produce only *syn* adducts **5**, **3**, **9**, and **7** (see eq 8). In the former case, an unidentified chromatographically inseparable by-product detracts from the preparative utility of the reaction. However, no *anti* products result from either stannane. As these reactions proceed by an *anti* S_E' pathway,[1] adducts **3** and **7** must be formed from the (*S*)-enantiomer of stannanes (*E*)-**1a** and (*E*)-**1b**, whereas **5** and **9** would come from the corresponding (*R*) antipodes. Preferred arrangements for these additions are depicted in Figure 5.

The minor *anti* adduct **6** produced in the BF_3 reaction of (*S*)-**1a** with aldehyde **2** (see eq 4) is presumably formed by a synclinal transition state in which the OMOM grouping is gauche to the aldehyde substituent (Figure 5). The higher *syn* selectivity observed for the OTBS stannanes **1b** can be attributed to the greater steric bulk of OTBS, which renders such arrangements less favorable.

(13) Wiberg, K. B.; Barth, D. E.; Schertler, P. H. *J. Org. Chem.* **1973**, *38*, 378.
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(15) Reviews: Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. Yamamoto, Y.; Shida, N. *Advances in Detailed Reaction Mechanisms*; JAI Press Inc., **1994**, *3*, 1–44.
(16) For an exception see Mikami, K.; Kawamoto, K.; Loh, T-P., Nakai, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1161. For a discussion of factors involved in antiperiplanar *vs* synclinal arrangements in these transition states see Fleming, I., *Chemtracts–Org. Chem.* **1991**, 21.
(17) Certain intramolecular additions favor the synclinal arrangement: Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053.

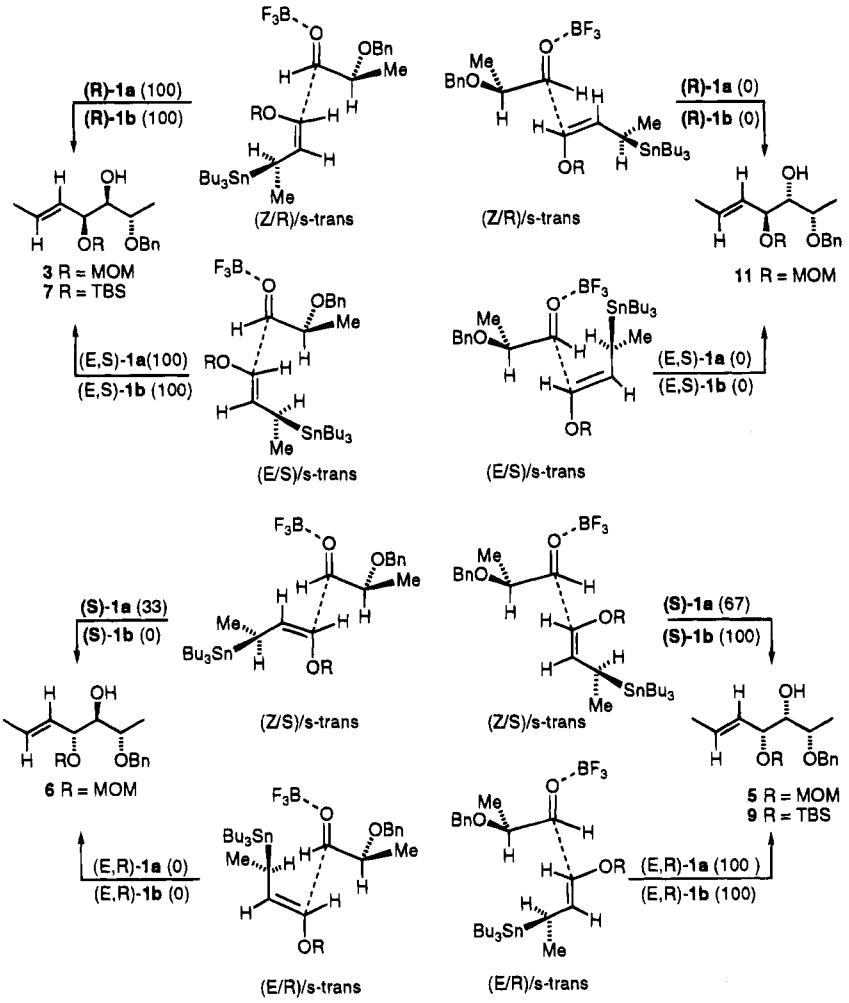


Figure 5. Transition states for BF_3-promoted additions of (*R*)- and (*S*)-, (*Z*)- and (*E*)-allylic stannes **1a** and **1b** to aldehyde 2 (numbers in parentheses indicate percentage of product derived from the indicated transitions state).

It is not yet clear why the (*Z*) OTBS stannanes (*R*)-**1b** and (*S*)-**1b** give rise to significant amounts of cyclopropane products **8** and **10** in the BF_3 reactions. A small amount of cyclopropane **4** is also produced from (*R*)-**1a**. Such products are absent from BF_3 reactions involving (*E*) stannanes (*E*)-**1a** and (*E*)-**1b** and the (*Z*) OMOM stannane (*S*)-**1a**. All $MgBr_2$ reactions give only the normal S_E' adducts.

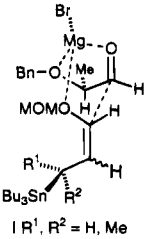
The $MgBr_2$-promoted additions are substrate controlled. Only the *si* face of aldehyde **2** is sterically accessible. With the (*Z*) OTBS stannanes **1b**, steric interaction between the aldehyde substituent and the large OTBS group favors formation of the (*Z*)-*syn,syn* adduct **13** and the (*E*)-*syn,syn* adduct **9** from (*R*)-**1b** and (*S*)-**1b**, as illustrated in Figure 6. Based on the structure of products obtained from the racemate and assuming an *anti* S_E' pathway, the stannanes (*E*)-**1b** also show high diastereomeric preferences, as indicated in Figure 6.

In contrast to the (*Z*) OTBS stannanes (*R*)-**1b** and (*S*)-**1b**, the (*Z*) OMOM stannane (*R*)-**1a** gives rise to the *anti* adduct **11** in the $MgBr_2$-promoted reaction (see eq 6). This adduct must arise through a synclinal transition state as depicted in Figure 6.[17,18] The *s-trans* is favored over the *s-cis* arrangement on steric grounds. As is the case for BF_3 additions, the larger size of OTBS is presumably responsible for the avoidance of these transition states by stannanes (*R*)-**1b**, (*S*)-**1b**, and (*E*)-**1b** [both (*R*) and (*S*)].

Conclusions

Of major interest from a synthetic viewpoint is the remarkable differences in selectivity exhibited by the OTBS *vs* OMOM stannanes **1b** and **1a**. In all cases examined, reactions of the OTBS reagents proceed with high *syn* diastereoselectivity. This outcome is consistent with Yamamoto transition states (Figure 4)[15] in which the bulky OTBS grouping is oriented *anti* to the aldehyde substituent (Figures 5 and 6). The unprecedented formation of cyclopropane products in BF_3-promoted reactions, especially those involving OTBS stannane **1b**, implies a diminished hyperconjugative participation of the stannane moiety in these situations. Although steric effects may account for most of the observed differences

(18) A reviewer has suggested that the formation of adducts **11** and **12** may proceed through tricoordinated Mg chelates with antiperiplanar geometry as in **i**. Models indicate that such arrangements may be possible but with significant deviation from the optimal attack angle on the aldehyde carbonyl.



i R^1, R^2 = H, Me

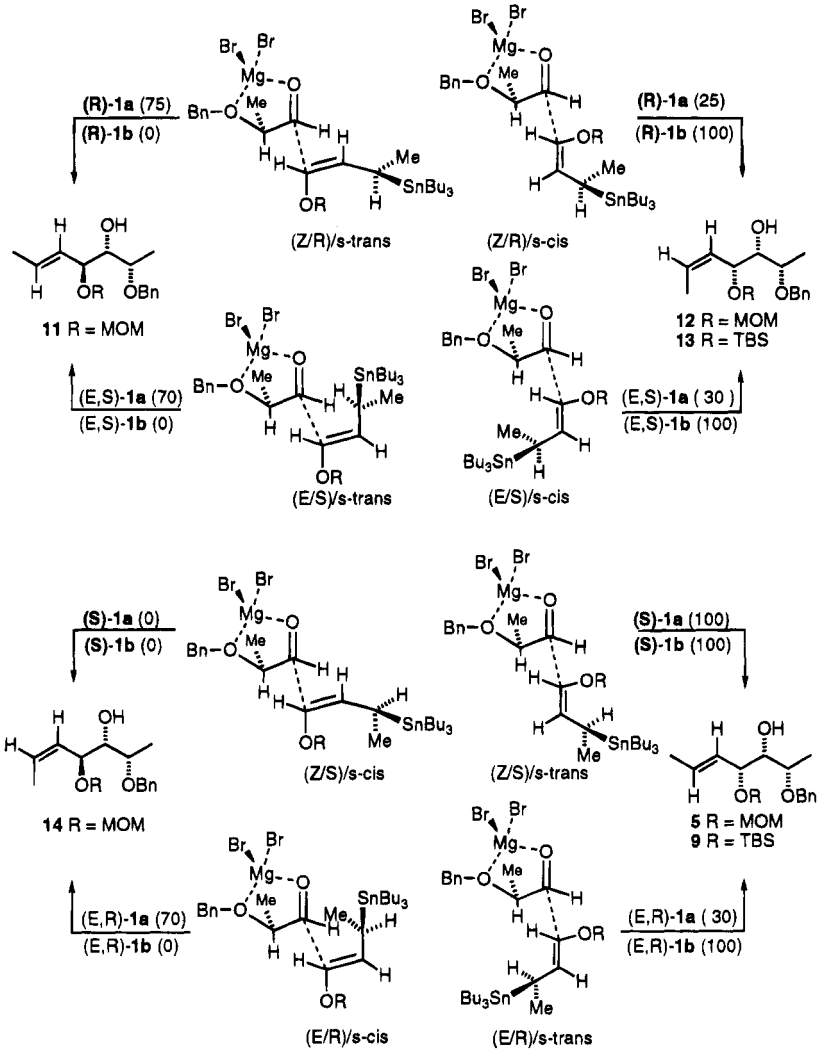


Figure 6. Transition states for $MgBr_2$-promoted additions of (*R*)- and (*S*)-, (*Z*)- and (*E*)-allylic stannanes **1a** and **1b** to aldehyde **2** (numbers in parentheses indicate percentage of product derived from the indicated transition state).

between stannanes **1a** and **1b**, more subtle electronic and orbital interactions could also play a role.[19] Continued investigation of these factors is clearly desirable.

Experimental Section[20]

(*E*)-1-(Methoxymethoxy)-3-(tri-*n*-butylstannyl)-1-butene ((*E*)-1a). To a stirred, cooled (−78 °C) suspension of 1.2 g (13.6 mmol) of CuCN in 60 mL of THF was added 10.9 mL (27.3 mmol) of *n*-BuLi (2.5 M in hexane). The mixture was warmed slightly until all solids dissolved and was then recooled to −78 °C. To this stirred solution was added 7.3 mL (27.3 mmol) of Bu_3SnH. The resulting bright yellow solution was stirred at −78 °C for 15 min and then a solution of 870 mg (12.4 mmol) of crotonaldehyde in 2 mL of THF cooled to −78 °C was added by cannula. The resulting red solution was stirred at −78 °C for 20 min and 4.5 mL (37.2 mmol) of DMPU was added. After 30 min, 4.7 mL (62.0 mmol) of MOMCl was added. The cold bath was allowed to warm to room temperature and the mixture was stirred for 6 days. During this time the color of the solution changed from deep red to colorless. The reaction was quenched with saturated aqueous $NaHCO_3$ and diluted with ether. The phases were separated and the aqueous phase was extracted three times with ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography through silica gel with 6:1 hexane:CH_2Cl_2 as eluent, affording 2.1 g (42%) of (*E*)-**1a** and 0.7 g (14%) of (*RS*)-**1a**.

(*E*)-1a: ^1H NMR (500 MHz, $CDCl_3$) δ 6.01 (dd, J = 12.2, 1.3, 1H), 5.34 (dd, J = 12.2, 8.5, 1H), 4.73 (s, 2H), 3.36 (s, 3H), 1.98 (dd, J = 7.3, 7.3), 1.45 (m, 6H), 1.31 (m, 6H), 0.86 (m, 15H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$) δ 138.6, 116.1, 95.7, 55.4, 29.2, 27.3, 18.7, 17.6, 13.7, 9.6 ppm; HRMS (EI^+) calcd for [M − MOM] $C_{16}H_{33}O_{116}Sn$ 357.1549, found 357.1577. Anal. Calcd for $C_{18}H_{38}O_2Sn$: C, 53.36; H, 9.45. Found: C, 53.12; H, 9.50.

(+)-(2*S*,3*S*,4*S*)-(*E*)-2-(Benzyloxy)-4-(methoxymethoxy)-5-hepten-3-ol (3) and 1-(2-(Benzyloxy)-1-hydroxypropyl)-2-(methoxymethoxy)-3-methylcyclopropane (4). To a solution of 36 mg (0.22 mmol) of aldehyde **2** and 100 mg (0.25 mmol) of stannane (*R*)-**1a**[5] in 4.0 mL of dry CH_2Cl_2 at −78 °C under N_2 was added dropwise 30 μL (0.28 mmol) of BF_3-OEt_2. After 2 h, the reaction was quenched at −78 °C with saturated aqueous $NaHCO_3$ and allowed to warm to room temperature. The mixture was then diluted with additional $NaHCO_3$, water, and ether. The resulting layers were separated and the aqueous layer was extracted twice with ether. The combined ether extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The filtrate was purified by flash chromatography on silica gel. Careful gradient elution with 15−25−35% ethyl acetate−hexanes afforded 42 mg (69%) of adduct **3** and 3 mg (5%) of cyclopropane **4**.

3: $[\alpha]^{26}_D$ +87.6 (*c* 1.31, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33−7.25 (m, 5H), 5.73 (dqd, J = 15.4, 6.5, 0.6 Hz, 1H),

(19) *Cf*: Gung, B. W.; Wolf, M. A. *J. Org. Chem.* **1993**, *58*, 7038; Gung, B. W. *Tetrahedron Lett.* **1991**, *32*, 2867.

(20) For typical experimental protocols, see Marshall, J. A.; Wang, X-j. *J. Org. Chem.* **1991**, *56*, 960.

5.36 (ddd, J = 15.4, 8.6, 1.6 Hz, 1H), 4.72, 4.53 (d, J = 6.6 Hz, A and B of AB), 4.59, 4.47 (d, J = 11.6 Hz, A′ and B′ of A′B′), 4.11 (dd, J = 8.5, 4.9 Hz, 1H), 3.62–3.52 (m, 2H), 3.35 (s, 3H), 2.44 (d, J = 5.2 Hz, 1H), 1.69 (dd, J = 6.5, 1.6 Hz, 3H), 1.23 (d, J = 6.1 Hz, 3H) ppm; IR (film) ν 3482, 1453, 1030 cm^{-1}; EIMS m/e (relative intensity) 235 (2), 161 (3), 115 (14), 91 (100), 86 (17), 69 (17); EIHRMS calcd for $C_{14}H_{19}O_3$ ($M^+ - CH_2OCH_3$), 235.1334, found 235.1336. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.56; H, 8.67.

4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 5H), 4.67 (apparent t, J = 6.2 Hz, 2H), 4.61 (d, J = 11.8 Hz, 1H, A of AB), 4.51 (d, J = 11.8 Hz, 1H, B of AB), 3.60 (dq, J = 6.4, 3.4 Hz, 1H), 3.40 (s, 3H), 3.38 (dd, J = 5.4, 2.9 Hz, 1H), 3.06 (dd, J = 8.5, 3.4 Hz, 1H), 1.23 (br s, 1H), 1.20 (d, J = 6.4 Hz, 3H), 1.12 (d, J = 6.2 Hz, 3H), 0.81 (m, 1H), 0.76 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 128.4, 127.6, 127.5, 97.0, 75.3, 71.0, 58.2, 55.8, 27.5, 16.8, 14.5 ppm.

(2*S*,3*R*,4*R*)-(*E*)-2-(Benzyloxy)-4-(methoxymethoxy)-5-hepten-3-ol (5). A. From Stannane (*S*)-1a and BF_3·OEt_2. The procedure for adduct **3** was followed with 85 mg (0.52 mmol) of aldehyde **2**, 175 mg (0.43 mmol) of stannane (*S*)-**1a**,[5] and 53 μL (0.52 mmol) of BF_3·OEt_2, affording 116 mg (97%) of a 67:33 mixture of adducts **5** and **6**.

B. From Stannane (*S*)-1a and $MgBr_2$·OEt_2: To a solution of 85 mg (0.52 mmol) of aldehyde **2** and 175 mg (0.43 mmol) of stannane (*S*)-**1a** in 5 mL of CH_2Cl_2 at -20 °C was added $MgBr_2$·OEt_2 (134 mg, 0.52 mmol). After 1 h, the −20 °C bath was replaced with a 0 °C bath. After 1.5 h, the reaction was quenched by the addition of brine. The resulting mixture was diluted with ether and water and the layers were separated. The aqueous layer was extracted three times with ether; the combined ether extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel using 15 % ethyl acetate-hexanes to afford 104 mg (83%) of adduct **5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5H), 5.63 (dq, J = 15.4, 6.5 Hz, 1H), 5.35 (ddd, J = 15.4, 8.5, 1.7 Hz, 1H), 4.71, 4.52; 4.63, 4.39 (d, J = 6.7; 11.5 Hz, A and B of AB; A′ and B′ of A′B′), 4.09 (dd, J = 8.5, 5.7 Hz, 1H), 3.67 (dq, J = 4.6, 6.3 Hz, 1H), 3.40 (ddd, J = 5.7, 4.6, 3.8 Hz, 1H), 3.35 (s, 3H), 2.78 (d, J = 3.8 Hz, 1H), 1.67 (dd, J = 6.5, 1.6 Hz, 3H), 1.27 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 131.4, 128.3, 127.9, 127.6, 127.5, 93.6, 77.6, 77.3, 74.1, 70.8, 55.7, 17.8, 15.7 ppm. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.72; H, 8.71.

(2*S*,3*S*,4*R*)-(*E*)-2-(Benzyloxy)-4-(methoxymethoxy)-5-hepten-3-ol (6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.25 (m, 5H), 5.71 (dq, J = 15.4, 6.5 Hz, 1H), 5.40 (ddd, J = 15.4, 8.5, 1.7 Hz, 1H), 4.70, 4.49; 4.57, 4.40 (2AB, J = 6.7; 11.5 Hz, A and B of AB; A′ and B′ of A′B′), 4.15 (dd, J = 8.5, 5.2 Hz, 1H), 3.76 (ddd, J = 6.2, 5.2, 2.7 Hz, 1H), 3.59 (apparent quintet, actually dq, J = 6.2 Hz, 1H), 3.32 (s, 3H), 2.26 (d, J = 2.7 Hz,1H), 1.72 (dd, J = 6.5, 1.6 Hz, 3H), 1.27 (d, J = 6.2 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 132.4, 128.3, 127.6, 126.3, 93.3, 77.3, 75.3, 72.9, 70.6, 55.6, 17.9, 14.7 ppm. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.33; H, 8.66.

(2*S*,3*S*,4*S*)-(*E*)-2-(Benzyloxy)-4-((*tert*-butyldimethylsilyl)oxy)-5-hepten-3-ol (7) and (1*S*,2*R*,3*S*)-1-[(2*S*,1*R*)-2-(Benzyloxy)-1-hydroxypropyl]-2-((*tert*-butyldimethylsilyl)oxy)-3-methylcyclopropane (8). The procedure for adduct **3** was followed with stannane (*R*)-**1b**[21] (150 mg, 0.32 mmol) and aldehyde **2** (48 mg, 0.29 mmol) in 5 mL of CH_2Cl_2 to which was added BF_3·OEt_2 (42 μL, 0.42 mmol). The products were separated by flash chromatography on silica gel with 5% ethyl acetate in hexane as eluent to provide adduct **7** (20 mg, 20% yield) and cyclopropane **8** (30 mg, 30% yield).

7: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H), 5.58 (m, 2H), 4.60 (d, J = 11.6 Hz, 1H, A of AB), 4.42 (d, J = 11.6 Hz, 1H, B of AB), 4.29 (dd, J = 7.4, 3.3 Hz, 1H), 3.46 (dq, J = 6.4, 6.3 Hz, 1H), 3.33 (dd, J = 6.7, 3.4 Hz, 1H), 1.66 (d, J = 6.0 Hz, 3H), 1.26 (d, J = 6.2 Hz, 3H), 0.87 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 132.1, 128.7, 128.1, 127.9, 127.8, 77.7, 75.5, 73.6, 70.8, 30.1, 26.3, 18.5, 18.0, 15.9, −3.3, −4.4 ppm; IR (film) ν 3549, 1252 cm^{-1}. Anal. Calcd for $C_{20}H_{34}O_3Si$: C, 68.52; H, 9.78. Found: C, 68.87; H, 9.76.

8: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H), 4.61 (d, J = 11.8 Hz, 1H, A of AB), 4.49 (d, J = 11.8 Hz, 1H, B of AB), 3.59 (dq, J = 6.5, 3.3 Hz, 1 H), 3.36 (dd, J = 6.6, 3.0 Hz, 1 H), 3.12 (dd, J = 8.0, 3.1 Hz, 1H), 1.23 (d, J = 6.3 Hz, 3H), 1.06 (d, J = 5.8 Hz, 3H), 0.88 (s, 9H), 0.60 (ddq, J = 6.8, 5.8, 5.8 Hz, 1H); 0.55 (ddd, J = 8.2, 5.8, 2.9, 1H), 0.10 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 128.8, 128.0, 127.8, 77.9, 75.4, 71.1, 55.1, 28.9, 26.2, 18.5, 16.6, 14.3, 11.2, −4.6, −4.7 ppm; IR (film) ν 3400, 1251 cm^{-1}; MS m/e calcd for $C_{20}H_{38}O_3SiN$ [M + NH_4] 368.2621, found 368.2603. Anal. Calcd for $C_{20}H_{34}O_3Si$: C, 68.52; H, 9.78. Found: C, 68.30; H, 9.69.

(2*S*,3*R*,4R)-(*E*)-2-(Benzyloxy)-4-((*tert*-butyldimethylsilyl)oxy)-5-hepten-3-ol (9). A. From Stannane (*S*)-1b and BF_3·OEt_2. The procedure described for adduct **3** was employed with stannane (*S*)-**1b**[21] (230 mg, 0.48 mmol) and aldehyde **2** (70 mg, 0.43 mmol) in 5 mL of CH_2Cl_2 to which was added BF_3·OEt_2 (52 μL, 0.51 mmol). Flash chromatography on silica gel with 5% ethyl acetate in hexane as eluent provided adduct **9** (26 mg, 17% yield) and cyclopropane **10** (15 mg, 10% yield).

B. From Stannane (*S*)-1b and $MgBr_2$·OEt_2. The procedure for alcohol **13** was followed with 82 mg (0.50 mmol) of aldehyde **2**, 243 mg (0.51 mmol) of stannane (*S*)-**1b** and 155 mg (0.60 mmol) of $MgBr_2$·OEt_2 for 2h. Purification by silica gel chromatography with 7% ethyl acetate in hexane as eluent provided 125 mg (71%) of adduct **9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H), 5.40 (m, 2H), 4.63 (d, J = 11.7 Hz, 1H, A of AB), 4.18 (d, J = 11.7 Hz, 1H, B of AB), 4.18 (dd, J = 6.7, 6.6 Hz, 1H), 3.56 (dq, J = 6.4, 3.7 Hz, 1H), 3.27 (dd, J = 6.2, 3.7 Hz, 1H), 1.60 (d, J = 5.9 Hz, 3H), 1.27 (d, J = 6.4 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 131.3, 128.7, 128.6, 128.4, 127.9, 78.4, 74.8, 73.8, 71.0, 26.3, 18.5, 18.1, 16.4, −3.5, −4.4 ppm. Anal. Calcd for $C_{20}H_{34}O_3Si$: C, 68.52, H, 9.78. Found: C, 68.56, H, 9.73.

(1*R*,2*S*,3*R*)-1-[(1*S*,2*S*)-2-(Benzyloxy)-1-hydroxypropyl]-2-((*tert*-butyldimethylsilyl)oxy)-3-methylcyclopropane (10): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H), 4.68 (d, J = 11.5 Hz, 1H, A of AB), 4.44 (d, J = 11.5 Hz, 1H, B of AB), 3.48 (dq, J = 6.5, 6.4 Hz, 1H), 3.37 (dd, J = 7.0, 2.7 Hz, 1H), 2.80 (dd, J = 8.1, 7.2 Hz, 1H), 1.90–1.70 (br m, 1H), 1.20 (d, J = 6.2 Hz, 3H), 1.05, d, J = 6.2, 3H, 0.88 (s, 9H), 0.66 (dm, J = 6.4, 1H), 0.49 (m, 1H), 0.12 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl3) δ 138.3, 128.5, 127.8, 127.7, 79.1, 77.2, 71.0, 54.4, 29.7, 25.9, 18.1, 16.7, 15.7, 10.7, −4.4, −5.1 ppm. Anal. Calcd. for $C_{20}H_{34}O_3Si$: C, 68.52, H, 9.78. Found: C, 68.59, H, 9.78.

(2*S*,3*R*,4*S*)-(*E*)-2-(Benzyloxy)-4-(methoxymethoxy)-5-hepten-3-ol (11) and (2*S*,3*R*,4*R*)-(*Z*)-2-(Benzyloxy)-4-(methoxymethoxy)-5-hepten-3-ol (12). To a suspension of 138 mg (0.536 mmol) of $MgBr_2$·OEt_2 in 1.0 mL of dry CH_2Cl_2 at −23 °C under N_2 was added a solution of 80 mg (0.487 mmol) of aldehyde **2** in 1.5 mL of CH_2Cl_2. The resulting mixture was allowed to stir at −23 °C for 40 min, and then a solution of 232 mg (0.572 mmol) of stannane (*S*)-**1a** in 1.0 mL of CH_2Cl_2 was introduced by cannula. The reaction mixture was then allowed to slowly warm to room temperature. The reaction was quenched after 3.25 h by the addition of saturated aqueous $NaHCO_3$. The resulting mixture was diluted with ether and water and the layers were separated. The aqueous layer was extracted three times with ether; the combined ether extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel. Gradient elution with 2.5–5–10–15–20–25% ethyl acetate-hexanes afforded 101.2 mg (74%) of a 75:25 mixture of adducts **11** and **12**.

11: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5H), 5.72 (dq, J = 15.4, 6.4 Hz, 1H), 5.46 (ddd, J = 15.4, 8.7, 1.6 Hz, 1H), 4.70, 4.50; 4.64, 4.47 (2d, J = 6.7; 11.3 Hz, A and B of AB; A′ and B′ of A′B′, 4H), 4.02 (dd, J = 8.6, 5.3 Hz,1H), 3.64 (dq, J = 6.2, 6.2 Hz, 1H), 3.51 (apparent q, actually ddd, J = 5.2 Hz, 1H), 3.33 (s, 3H), 2.48 (d, J = 5.2 Hz, 1H), 1.74 (dd, J = 6.4, 1.6 Hz, 1H), 1.24 (d, J = 6.2 Hz, 3H) ppm; IR (film) ν 3482, 1088 cm^{-1}; EIMS m/e (relative intensity) 235 (6), 191 (4), 161 (14), 135 (8), 115 (31), 91 (100), 69 (16); EIHRMS calcd

(21) Marshall, J. A.; Luke, G. P., *J. Org. Chem.* **1993**, *58*, 6229.

for $C_{14}H_{19}O_3$ ($M^+ - CH_2OCH_3$) 235.1334, found 235.1335. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.62; H, 8.64.

12: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.25 (m, 5H), 5.80 (dq, J = 11.0, 7.0 Hz, 1H), 5.37 (ddd, J = 11.0, 9.5, 1.8 Hz, 1H), 4.68, 4.53; 4.62, 4.40 (2d, J = 6.7; 11.4 Hz, A and B of AB; A′ and B′ of A′B′), 4.59 (dd, J = 9.5, 5.5 Hz, 1H), 3.70 (dq, J = 4.5, 6.3 Hz, 1H), 3.43 (m, 1H), 3.37 (s, 3H), 2.77 (d, J = 3.9 Hz, 1H), 1.67 (dd, J = 7.0, 1.8 Hz, 3H), 1.29 (d, J = 6.3 Hz, 3H) ppm; IR (film) ν 3485, 1098 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 67.98; H, 8.81.

***(2S,3R,4R)*-(*Z*)-2-(Benzyloxy)-4-((*tert*-butyldimethylsilyl)oxy)-5-hepten-3-ol (13).** To a solution of 56 mg (0.34 mmol) of aldehyde **2** and 178 mg (0.37 mmol) of stannane (*R*)-**1b** in 4 mL of dry CH_2Cl_2 at −23 °C under N_2 was added 105 mg (0.41 mmol) of $MgBr_2$·OEt_2. After 1.5 h, the −23 °C bath was removed and the mixture was allowed to warm to room temperature. After 1 h, the reaction was quenched with brine and diluted with ether. The resulting layers were separated and the aqueous layer was extracted three times with ether. The combined organic extracts were dried over MgSO4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with 7% ethyl acetate as eluent, affording 78 mg (66%) of adduct **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 5H), 5.56 (ddd, J = 11.0, 7.0, 0.9 Hz, 1H), 5.38 (ddd, J = 11.0, 9.3, 1.8 Hz, 1H), 4.64 (ddd. J = 9.2, 6.0, 0.9 Hz, 1H) 4.62 (d, J = 11.7 Hz, 1H, A of AB), 4.40 (d, J = 11.7 Hz, 1H, B of AB), 3.62 (dq, J = 6.4,3.9 Hz, 1H), 3.33 (dd, J = 5.9, 3.9 Hz, 1H), 1.63 (dd, J = 7.0, 1.8 Hz, 3H), 1.27 (d, J = 6.4 Hz, 3H), 0.87 (s, 9H),0.06 (s, 3H), 0.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl3) δ 138.7, 131.0, 128.3, 128.0, 127.6, 127.4, 126.6, 78.2, 74.2, 70.8, 68.8, 29.8, 25.9, 18.1,16.7, 13.7, −4.0, −4.9 ppm.

(+)-(*2S,4S*)-(*E*)-2-(Benzyloxy)-4-(methoxymethoxy)-5-hepten-3-one (15). To a solution of 42.8 mg (0.153 mmol) of alcohol **3** in 1.0 mL of dry CH_2Cl_2 at room temperature under N_2 was added, in one portion, 97.1 mg (0.229 mmol) of Dess-Martin periodinane.[10] An additional 0.5 mL of CH_2Cl_2 was added, and the reagent dissolved within minutes. After ~7 min, a white precipitate formed. The reaction was quenched after 20 min by the additon of a few drops of water and solid $NaHCO_3$. The resulting mixture was stirred vigorously for 5 min and then loaded directly onto a silica gel column. Elution with 25% ethyl acetate-hexanes afforded 41.4 mg (97%) of ketone **15**: $[\alpha]^{28}_D$ +151 (*c* 1.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.25 (m, 5H), 5.89 (dq, J = 15.4, 6.6, Hz, 1H), 5.39 (ddd, J = 15.4, 7.8, 1.7 Hz, 1H), 4.83 (d, J = 7.8 Hz, 1H), 4.67, 4.56; 4.60, 4.41 (2d, J = 6.8; 11.8 Hz, A and B of AB; A′ and B′ of A′B′), 4.23 (q, J = 7.0 Hz, 1H), 3.30 (s, 3H), 1.72 (dd, J = 6.6, 1.7 Hz, 3H), 1.36 (d, J = 7.0 Hz, 3H) ppm; IR (film) ν 1729 cm^{-1}.

(−)-(*2S,4R*)-(*E*)-2-(Benzyloxy)-4-(methoxymethoxy)-5-hepten-3-one (16). The procedure described for ketone **15** was followed with 56.5 mg (0.20) mmol of a 4:1 mixture of alcohols **5** and **6** and 128 mg (0.30 mmol) of periodinane[10] affording 50 mg (89%) of ketone **16**: $[\alpha]^{28}_D$ −180 (*c* 1.37, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.29 (m, 5H), 5.83 (dq, J = 15.4, 6.6 Hz, 1H), 5.38 (ddd, J = 15.4, 7.9, 1.7 Hz, 1H), 4.90 (d, J = 7.9 Hz, 1H), 4.70, 4.55; 4.52, 4.44 (2d, J = 6.7; 11.7 Hz, A and B of AB; A′ and B′ of A′B′), 4.22 (q, J = 6.8 Hz, 1H), 3.33 (s, 3H), 1.71 (dd, J = 6.6, 1.7 Hz, 3H), 1.37 (d, J = 6.8 Hz, 3H) ppm; IR (film) ν 1731 cm^{-1}.

General Procedure for BF_3·OEt_2-Promoted Kinetic Resolution Studies. To a stirred, cooled (−78 °C) solution of stannane (3.0 or 2.0 equiv) and aldehyde (1.0 equiv) in CH_2Cl_2 was added BF_3·OEt_2 (1.2 equiv). The reaction mixture was stirred for 2–3 h and then quenched with saturated aqueous $NaHCO_3$, diluted with ether, and allowed to warm to room temperature. The phases were separated and the aqueous phase was extracted twice with ether. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with an ethyl acetate and hexane mixture as eluent. Product ratios were determined by GC analysis (peak enhancement, carbowax 20 M capillary column).

General Procedure for $MgBr_2$·OEt_2-Promoted Kinetic Resolution Studies. To a stirred, cooled (−23 °C) solution of stannane (3.0 or 2.0 equiv) and aldehyde (1.0 equiv) in CH_2Cl_2 was added $MgBr_2$·OEt_2 (1.2 equiv). The reaction mixture was stirred at −23 °C for 1 h and then warmed to room temperature for 4–12 h. It was then quenched with saturated $NaHCO_3$ solution, diluted with ether, and allowed to warm to room temperature. The phases were separated and the aqueous phase was extracted twice with ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate-hexane mixtures as eluent. Product ratios were determined by GC analysis (peak enhancement, carbowax 20 M capillary column).

General Procedure for the Preparation of *O*-Methylmandelic Esters. The method described by Trost was employed for the preparation of all *O*-methyl mandalates.[11] The following procedure is typical. To a stirred solution of 104 mg (0.30 mmol) of alcohol **7** in 5 mL of CH_2Cl_2 was added sequentially 89.7 mg (0.54 mmol) of S-(+)-α-methoxyphenylacetic acid, 74 mg (0.36 mmol) of dicyclohexylcarbodiimide, and a catalytic amount of DMAP. After 1 h, TLC analysis showed complete consumption of starting material. The solution was then concentrated under reduced pressure and the solids resuspended in ether. The solids were removed by filtration through a small pad of Celite. The mixture was concentrated under reduced pressure, and the residue was chromatographed on silica gel with 15% ethyl acetate in hexane to provide 139 mg (93%) of *O*-methylmandelic ester (*S*)-**20**.

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Supplementary Material Available: Experimental procedures for **21**–**28**; kinetic resolutions with (*RS*)-**1a**, (*RS*)-**1b**, (*E*)-**1a**, (*E*)-**1b**, and mandelates **17**–**20**; and selected ^{1}H NMR spectra (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.