J. Braz. Chem. Soc., Vol. 20, No. 4, 802-812, 2009.
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0103 - 5053 \$6.00+0.00

Short Report

Addition of Chiral and Achiral Allyltrichlorostannanes to Chiral α-Alkoxy Aldehydes

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Aliltricloroestananas quirais e aquirais reagem com α-alcóxi aldeídos quirais para fornecer alcoóis homoalílicos com moderados a bons níveis de diastereosseletividade 1,4-sy*n*.

Achiral and chiral allyltrichlorostannanes reacted with chiral α-alkoxy aldehydes to give the corresponding homoallylic alcohols with moderate to good levels of 1,4-*syn*-diastereoselection.

Keywords: allyltrichlorostannanes, allylsilanes, homoallylic alcohols

Introduction

Allylsilanes and allylstannanes are among the most important groups of organometallic-type reagents available for the control of acyclic stereochemistry and their reaction with aldehydes in the presence of Lewis acids is an important procedure for the preparation of homoallylic alcohols.[1,2] The addition of allylstannanes bearing a stereogenic center to chiral aldehydes is particularly interesting in organic synthesis. We recently communicated that *in situ* prepared chiral allyltrichlorostannanes react with chiral aldehydes to give 1,4-*syn* homoallylic alcohols with high levels of diastereoselectivity.[3-11]

We wish to describe here a stereocontrolled reaction between achiral and chiral allyltrichlorostannanes with chiral lactate-derived aldehydes to give fragments which can be found in a large variety of naturally-occurring products with promising biological activities.[12] This study details our efforts to understand the double stereodifferentiating stereocontrol elements involved in chiral allyltrichlorostannane additions to chiral aldehydes.[13]

Results and Discussion

Achiral and chiral allylsilanes **1-4** were prepared from the corresponding easily available methyl esters, as described in previous papers from this laboratory (Scheme 1).[3-11,14] According to previously established experimental procedures, the allylsilanes were mixed with $SnCl_4$ (1.0 equiv. in CH_2Cl_2) before the addition of a solution of the aldehyde in order to promote the $SiMe_3/SnCl_3$ exchange leading to the corresponding allyltrichlorostannanes **5-8** (Scheme 1).[5]

To the best of our knowledge, the first spectroscopic information available on exchange reactions involving allylsilanes and $SnCl_4$ was reported by Denmark and co-workers in 1988.[13] In 1999, we described the first direct evidence for interaction between $SnCl_4$ and chiral allylic silane **3** bearing an ether functionality that generated a new species by means of NMR spectroscopy.[5] In a continuation of these initial studies we have done a spectroscopic study (^1H and ^{119}Sn NMR) of the reactions of allylsilanes **1-4** (0.15 $molL^{-1}$ solution in $CDCl_3$) with $SnCl_4$ leading to the corresponding allyltrichlorostannanes **5-8**, respectively (Scheme 1).

For allyltrimethylsilane **1** the $SiMe_3/SnCl_3$ exchange producing allyltrichlorostannane **5** and Me_3SiCl is complete after 2 h at room temperature (Scheme 1).[5] For allylsilane **2** the $SiMe_3/SnCl_3$ exchange to give **6** and Me_3SiCl is faster, as expected for a 1,1-disubstituted electron-rich olefin, being complete after 10 minutes at room temperature.[14] Upon addition of $SnCl_4$ to a solution of allylsilanes (*R*)-**3** and (*S*)-**4** in $CDCl_3$, at –60 °C, slightly yellow homogeneous solutions were obtained. The resulting NMR spectrum at –60 °C showed formation of Me_3SiCl and complete consumption of both allylsilanes within less than 1 minute to give allyltrichlorostannanes (*R*)-**7** and (*S*)-**8**, respectively. It appears that the oxygen functionality is responsible for the rapid $SiMe_3/SnCl_3$ exchange reaction observed even at low temperatures for these particular allylsilanes and $SnCl_4$. The $SiMe_3/SnCl_3$ exchange is probably facilitated by coordination of tin to this oxygen followed by cleavage of the carbon-silicon bond by a free chloride ion.

Analysis of the corresponding ^1H NMR spectrum showed a deshielding for hydrogens H_1 to H_4 in allylstannane

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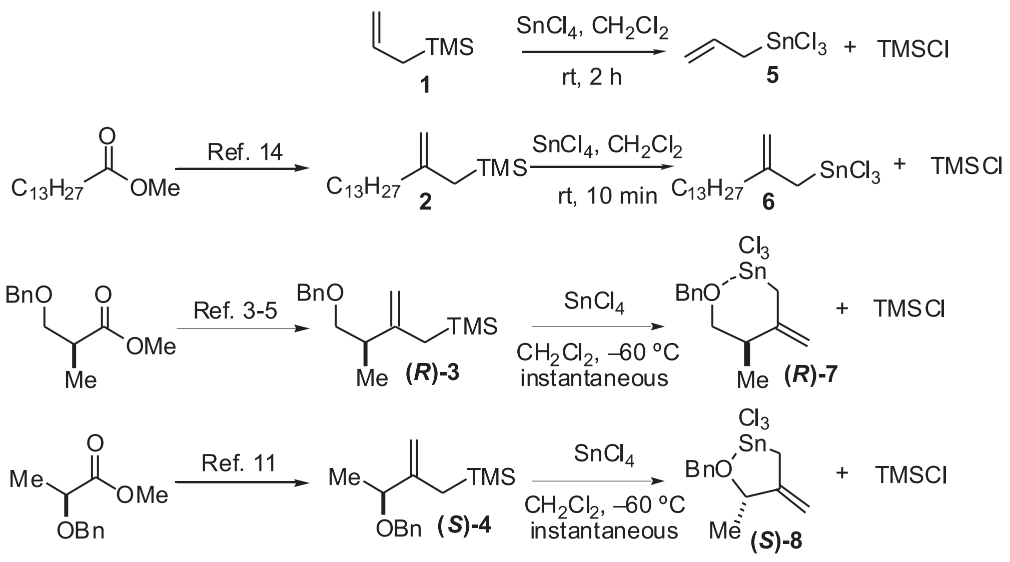
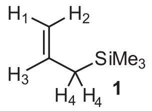


Scheme 1. SiMe$_3$/SnCl$_3$ exchange reaction of allylsilanes **1-4**

5 when compared to the same signals for allylsilane **1** (Table 1).[5]

Table 1. ^{1}H NMR chemical shifts (δ/ppm) for **1** and **5**



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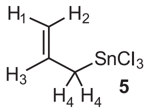
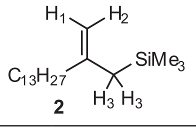


5

Compound	H$_1$	H$_2$	H$_3$	H$_4$
1	4.85	4.80	5.75	1.75
5	5.45	5.35	5.95	3.25

The same trend is observed for allylstannane **6** when compared to allylsilane **2** (Table 2).[14]

Table 2. ^{1}H NMR chemical shifts (δ/ppm) for **2** and **6**[14]



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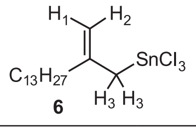
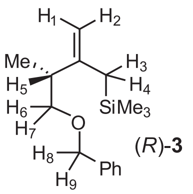


6

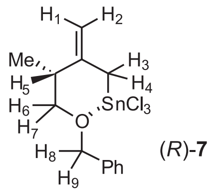
Compound	H$_1$	H$_2$	H$_3$
2	4.52	4.60	1.57
6	5.07	5.10	3.15

In the case of (*R*)-**7**, the deshielding of the hydrogens H$_6$ to H$_9$ in the ^{1}H NMR spectrum provides the best diagnostics (Table 3). The methylenic hydrogens H$_6$ and H$_7$ as well as the benzylic hydrogens H$_8$ and H$_9$ are too far away from the trichlorotin group to suffer from inductive effects. We believe that the deshielding observed for these hydrogens in (*R*)-**7** is due to the internal coordination of this oxygen to tin, as proposed in Table 3.[5]

Table 3. ^{1}H NMR chemical shifts (δ/ppm) for (*R*)-**3** and (*R*)-**7**[5]



(*R*)-**3**

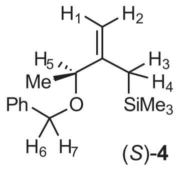


(*R*)-**7**

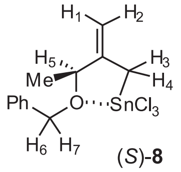
Compound	H$_1$	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$	H$_7$	H$_8$	H$_9$	Me
(*R*)-**3**	4.57	4.54	1.46	1.52	2.20	3.18	3.46	4.43	4.48	1.04
(*R*)-**7**	5.18	5.05	3.20	3.36	2.48	3.56	3.69	4.72	4.77	0.95

A similar behavior is observed for allylstannane (*S*)-**8** when compared to allylsilane (*S*)-**4** (Table 4).

Table 4. ^{1}H NMR chemical shifts (δ/ppm) for (*S*)-**4** and (*S*)-**8**



(*S*)-**4**



(*S*)-**8**

Compound	H$_1$	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$	H$_7$	Me
(*S*)-**4**	4.80	5.00	1.26	1.32	3.84	4.52	4.59	1.30
(*S*)-**8**	5.01	5.05	2.91	3.05	4.17	4.65	5.10	1.28

In addition, we have observed ^{119}Sn resonance signals at −28 ppm for allylstannane **5** (Figure 1).[5] The tin chemical shift for allylstannane (*R*)-**7** appeared at −187 ppm and for allylstannane (*S*)-**8** appeared at −169 ppm. The tin chemical shift for complexes **9** and **10** are −301 ppm and −599 ppm, respectively, while for free $SnCl_4$ it is −156 ppm. We believe that tin chemical shifts are highly sensitive to oxygen bonding, as observed for **9** and **10**, and the tin chemical shifts observed for (*R*)-**7** and (*S*)-**8** are strong evidence in favor of the proposed complexed intermediates.

The corresponding chiral aldehydes **11** and **12** were prepared in excellent yields from methyl lactate (Figure 2).[15,16] These substrates have been selected to be representative of the complex fragments that might be coupled in polyacetate and polypropionate-derived aldol-type reactions. For aldehydes **11**, internal chelation is presumably prevented since, with few exceptions, silyl ethers are generally recognized for their poor coordinating and chelating abilities.[17]

In order to check the facial selectivities of aldehydes **11** and **12**, we reacted them with achiral allyltrichlorostannanes **5** and **6**. Achiral allyltrichlorostannane **5** reacted with chiral α-alkoxy aldehyde (*S*)-**11** in CH_2Cl_2 at –78 °C to give the corresponding 1,2-*syn* product **13** (*anti*-Felkin isomer) as the major isomer in 45% yield for the two-step sequence (preparation of the aldehyde from the ester and coupling reaction), with 60:40 diastereoselectivity (Scheme 2).[18,19] Achiral allyltrichlorostannane **6** addition to the same aldehyde gave the corresponding 1,2-*syn* product **15** as the major isomer in 40% yield for the two-step sequence, again with 60:40 diastereoselectivity (Scheme 2). The stereoinduction observed in these reactions indicates that the intrinsic facial bias imposed by the resident α-OTBS substituent results in preferential formation of the 1,2-*syn* diastereomer, with a small preference for the *anti*-Felkin type approach.[19] One might project that the transition states of these reactions exhibit less charge separation than the aldol processes and are, accordingly, less subject to the electrostatic influence of the α-OTBS function.

The relative stereochemistry for the major product **13** was confirmed by comparison with data described in the literature.[20] In addition, we have also confirmed the relative stereochemistry for both **13** and **15** by analysis of the ^1H and ^{13}C NMR chemical shifts for both *syn* and *anti* isomers, as described by Heathcock[21] and Hoffmann[22] for similar structures and applied to more complex substrates in this work. ^1H NMR and ^{13}C NMR spectroscopy are very useful tools to study substituent effects on the electronic environment of a given carbon, as well as to determine the relative stereochemistry in acyclic molecules, especially by analysis of the coupling constants (*J*) in the corresponding ^1H NMR spectra. In the case of homoallylic alcohols **13-16**, it is possible to assign the relative stereochemistry by ^1H and ^{13}C NMR analysis, as these compounds, by adopting an internal hydrogen-bonded conformation, exhibit magnetically distinct NMR environments.

The intramolecular hydrogen bond leads to a 5-member ring in which the substituents are *trans* (**13** and **15**) or *cis* (**14** and **16**) and the predominance of hydrogen-bonded conformations should be reflected in different ^1H and ^{13}C

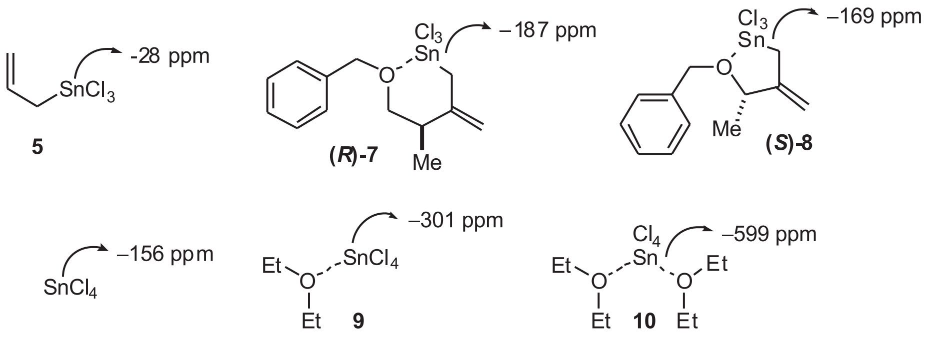


Figure 1. ^{119}Sn chemical shifts (Me_4Sn (0.0 ppm) is used as an internal reference)

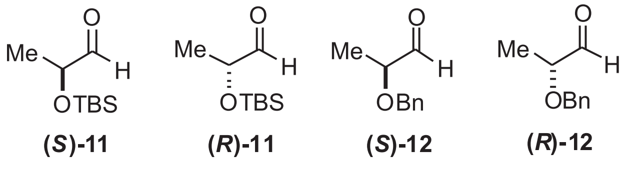
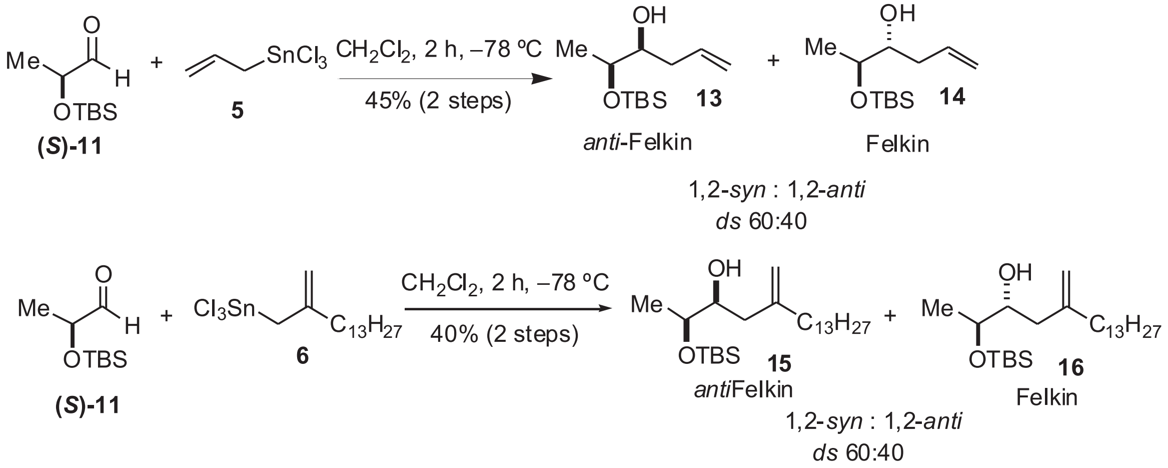


Figure 2. Chiral aldehydes **11** and **12**



Scheme 2. Addition of achiral allyltrichlorostannanes **5** and **6** to aldehyde (*S*)-**11**

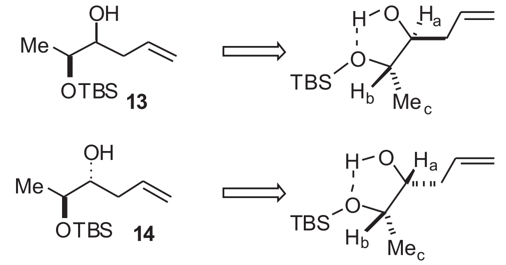
chemical shifts (Table 5). In fact, very strong experimental evidence for the existence of intramolecular hydrogen bonds in alcohols **13-16** comes from the observed chemical shifts in the ^{1}H NMR and ^{13}C NMR spectra measured in $CDCl_3$ (Table 5). We have shown previously that the intrinsic low basicity of silyl ethers does not affect the capacity of the oxygen attached to the silicon atom to form intramolecular hydrogen bonds.[23] The ^{1}H NMR spectra for compounds **13-16** are first order and the coupling constants (*J*) and chemical shifts (δ) are directly measured from the spectra. The ^{1}H NMR chemical shifts of H_a and H_b for both 1,2-*syn* isomers **13** and **15** are more shielded than the corresponding signals for H_a and H_b in 1,2-*anti* homoallylic alcohols **14** and **16**. For alcohol **13** (R = TBS), the ^{1}H chemical shifts are 3.38 (Ha) and 3.70 (Hb), showing a *trans* orientation between these two hydrogens. For alcohol **14**, the ^{1}H chemical shifts are 3.56 (Ha) and 3.78 (Hb), showing a *cis* orientation between these two hydrogens. The same trend is observed for *syn* and *anti* homoallylic alcohols **15** and **16**.

In addition, the ^{13}C chemical shifts for the methyl group in *syn* compounds **13** and **15** are more deshielded when compared to the ^{13}C chemical shifts in **14** and **16**.

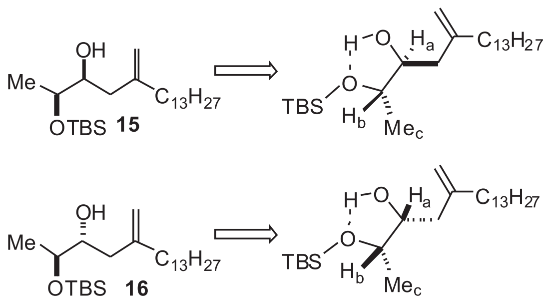
We next examined the stereochemical impact of a benzyl-protecting group at the oxygen in position α to the carbonyl aldehyde. Before starting the study described in Scheme 3, we expected that under conditions favouring internal chelation, the carbonyl facial bias of aldehyde (*S*)-**12** should be highly predictable. In fact, that proved to be the case. The facial bias of aldehyde (*S*)-**12** was determined after reaction with allyltrichlorostannane **5** in CH_2Cl_2 at −78 °C to give a 97:3 mixture of diastereoisomers **17** and **18**, in 45% yield over the two step sequence (Scheme 3).

This benzyl-protecting group imposes an intrinsic facial bias on the carbonyl that results in the formation of the

Table 5. ^{1}H NMR chemical shifts for homoallylic alcohols **13-16**



atom	δ ^{13}C NMR (ppm)	δ ^{1}H NMR (ppm)
13 (H_a)	--	3.38
13 (H_b)	--	3.70
13 (Me_c)	20.2	1.17
14 (H_a)	--	3.56
14 (H_b)	-	3.78
14 (Me_c)	17.5	1.11



atom	δ ^{13}C NMR (ppm)	δ ^{1}H NMR (ppm)
15 (H_a)	--	3.60
	--	3.49
	22.7	1.16
16 (H_a)	--	3.70
16 (H_b)	-	--
16 (Me_c)	20.0	1.12

1,2-*syn*-dioxygen relationship. This leads to higher levels of diastereoselection when compared to the use of a TBS protecting group.

The 1,2-*syn* relative stereochemistry for adduct **17** was confirmed by comparison of ^{1}H- and ^{13}C NMR data as well as its optical rotation with literature values.[24]

Previous work from our laboratory showed that allyltrichlorostannane (*R*)-**7** reacted with achiral aldehydes leading to the formation of 1,4-*syn* products as the major isomers (up to > 95:5 diastereoselectivity).[3-11]

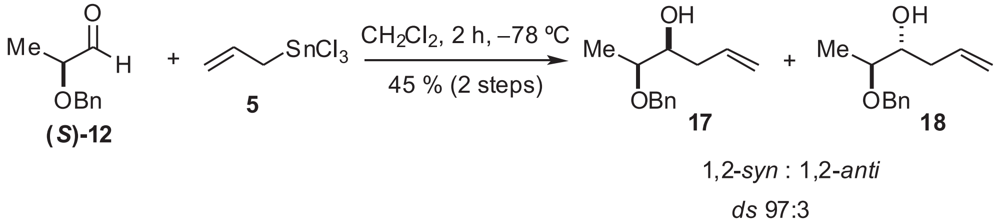
At this point we initiated the double stereodifferentiating studies involving allyltrichlorostannane (*R*)-**7** and chiral aldehydes **11** and **12**. Addition of allyltrichlorostannane (*R*)-**7** to aldehyde (*S*)-**11** in CH_2Cl_2 at −78 °C gave an 85:15 mixture of diastereoisomers **19** and **20**, respectively, in 70% yield for the two-step sequence (Scheme 4).

Allyltrichlorostannane (*R*)-**7** reacted with aldehyde (*R*)-**11** to give 1,4-*syn*-1,2-*syn* product **21** as the major product in 55% yield (2 steps), although with only 70:30 diastereoselectivity (Scheme 4).

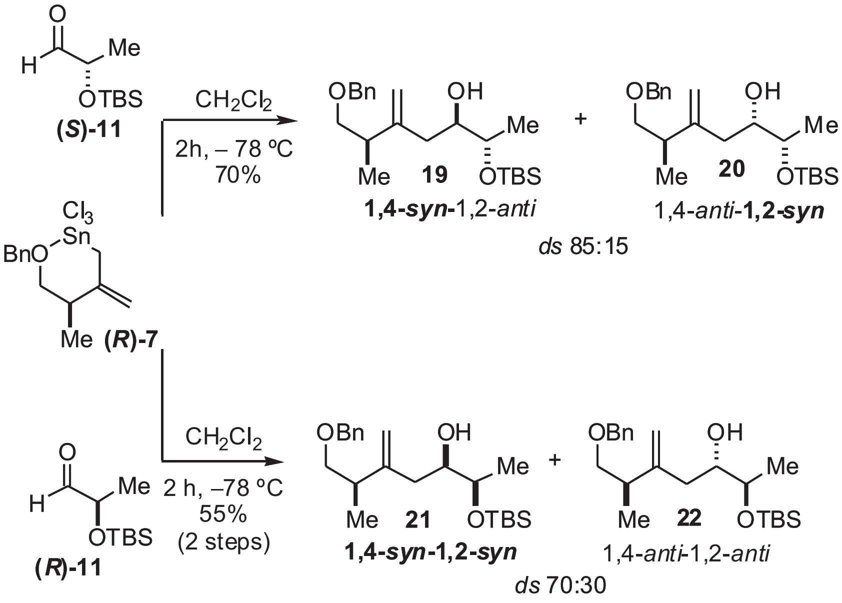
The facial bias of this chiral allyltrichlorostannane is dominated by the α–methyl stereocenter and tends to give the 1,4-*syn* isomer with *Si*-face attack, but the facial bias of this particular aldehyde is to give the 1,2-*syn* product. We were surprised with the result with aldehyde (*R*)-**11** as we were expecting a higher level of diastereoselection in favor of the product **21**.

The relative stereochemistry for the major products was determined after conversion to the corresponding dimethylacetonides (Scheme 5). Treatment of a mixture of **19** and **20** with TBAF in THF at room temperature gave diols **23** and **24** (67% yield), which was followed by reaction with 2,2-dimethoxypropane and catalytic amounts of camphorsulphonic acid (CSA) to give acetonides **25** and **26** in 40% yield after purification by flash column chromatography (Scheme 5).

The *cis*- acetonide **25** comes from the 1,2-*anti* isomer **19** and the *trans*- acetonide **26** originates from the corresponding 1,2-*syn* isomer **20**. The dimethyl groups (Me_a and Me_b) in both *trans* and *cis* dimethylacetonides are in different (average) chemical environments, giving



Scheme 3. Addition of achiral allyltrichlorostannane **5** to aldehyde (*S*)-**12**



Scheme 4. Addition of allyltrichlorostannane (*R*)-**7** to aldehydes (*S*)-**11** and (*R*)-**11**

rise to characteristic signals. As observed by Lombardo and coworkers[25] the difference in chemical shifts of the methyl groups (Me$_a$ and Me$_b$) in the five member ring of the dimethylacetonides is larger for the *cis* isomer (0.12-0.14 ppm) when compared to the *trans* isomer (0.01-0.04 ppm).[25] In Figure 3 we can observe the partial ^{1}H NMR for *cis* and *trans* acetonides **25** and **26** .

There is a larger difference in chemical shifts for the methyl groups (Me$_a$ and Me$_b$) in the *cis* isomer ($\Delta\delta = 0.12$ ppm) when compared to the chemical shifts for the same methyl groups of the *trans* isomer ($\Delta\delta = 0.05$ ppm). Based on this result we conclude that the 1,2-*anti* isomer **19** is the major product.[26]

The relative stereochemistry for compounds **21** and **22** was determined based on the same strategy (Scheme 6).

As before, we observed that the most intense signals come from the *trans*- acetonide **30**, which in this case originates from the 1,2-*syn* adduct **21** (Figure 4).

We next moved to investigate the addition of allyltrichlorostannane (*R*)-**7** to enantiomeric aldehydes **12** (Scheme 7). Allyltrichlorostannane (*R*)-**7** reacted with chiral α-benzyloxy-aldehyde (*S*)-**12** in CH_2Cl_2 at –78 °C to give the corresponding 1,2-*anti* product **31** as the major product in 70% yield and with 85:15 diastereoselectivity (Scheme 7).

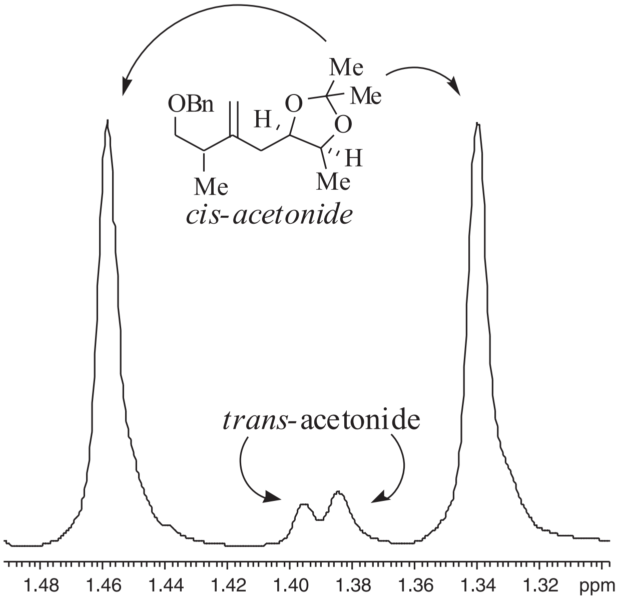
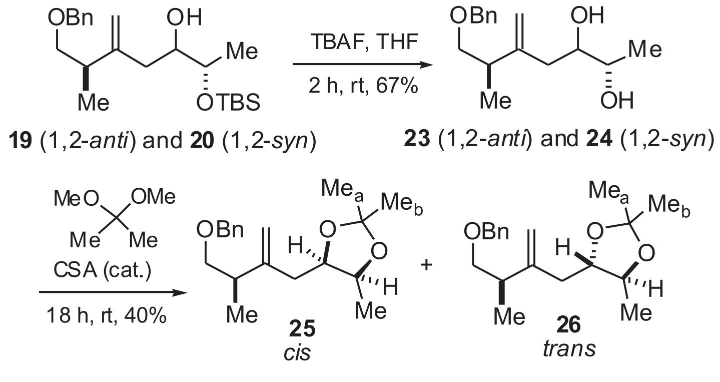
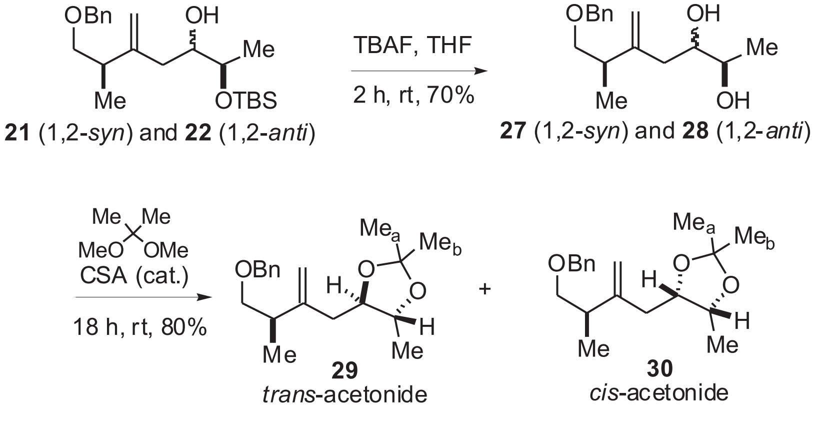


Figure 3. Partial ^{1}H NMR for acetonides **25** and **26**



Scheme 5. Preparation of acetonides **25**-(*cis*) and **26**-(*trans*)



Scheme 6. Preparation of acetonides **29**-(*trans*) and **30**-(*cis*)

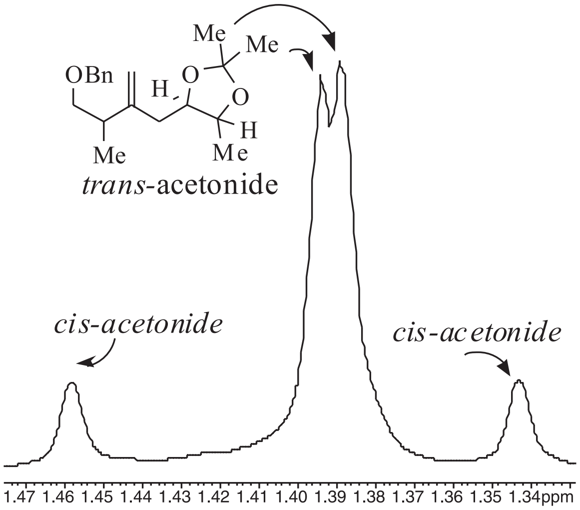


Figure 4. Partial ^{1}H NMR for acetonides **29** and **30**

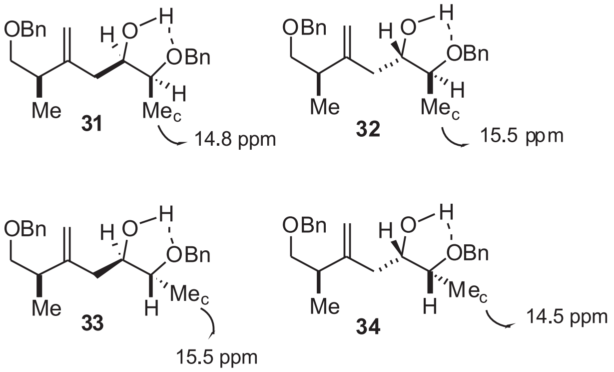


Figure 5. ^{13}C NMR chemical shifts for Me$_c$ in homoallylic alcohols **31-34**

The coupling reaction between allyltrichlorostannane (*R*)-**7** and aldehyde (*R*)-**12** in CH_2Cl_2 at −78 °C gave a 63:37 mixture of diastereoisomers **33** and **34**, in 60% yield for the two-step sequence.

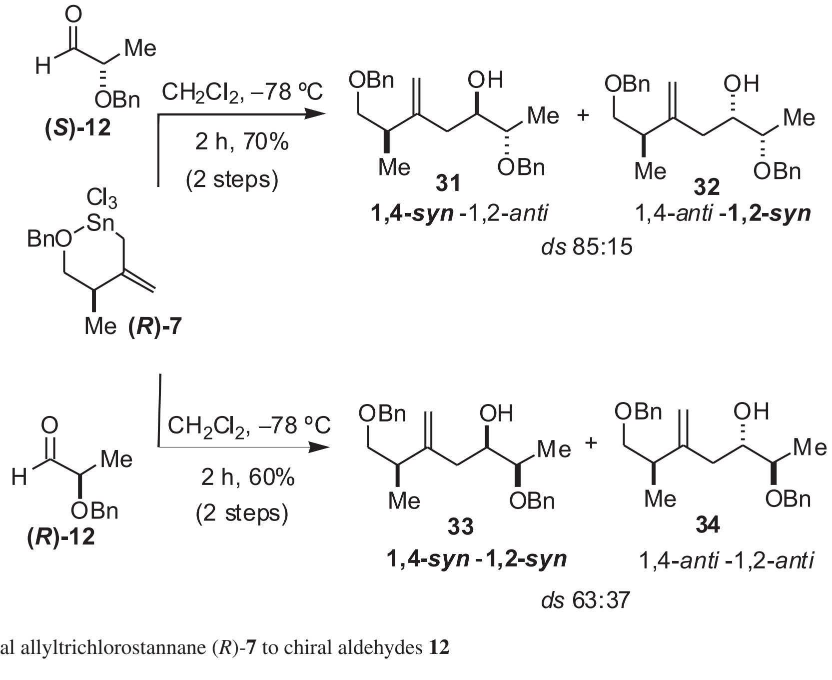
It is interesting to point out that as the facial bias of this aldehyde is to give the 1,2-*syn* products, we expected a *matched* case and much higher levels of diastereoselectivity in the reaction of (*R*)-**7** with (*R*)-**12**. Again, we were surprised to see that this was not the case.

The relative stereochemistries for both **31** and **33** were determined by applying the same methodology based on the ^{13}C NMR chemical shifts described before for **13-16** (Table 5). The 1,2-*anti* isomer is the major product as we can observe from the ^{13}C NMR chemical shifts for the more shielded Me$_c$ (Figure 5). In the case of **31** and **32**, the ^{13}C chemical shifts for Me$_c$ in **31** appears more shielded (14.8 ppm) when compared to **32** (15.5 ppm).

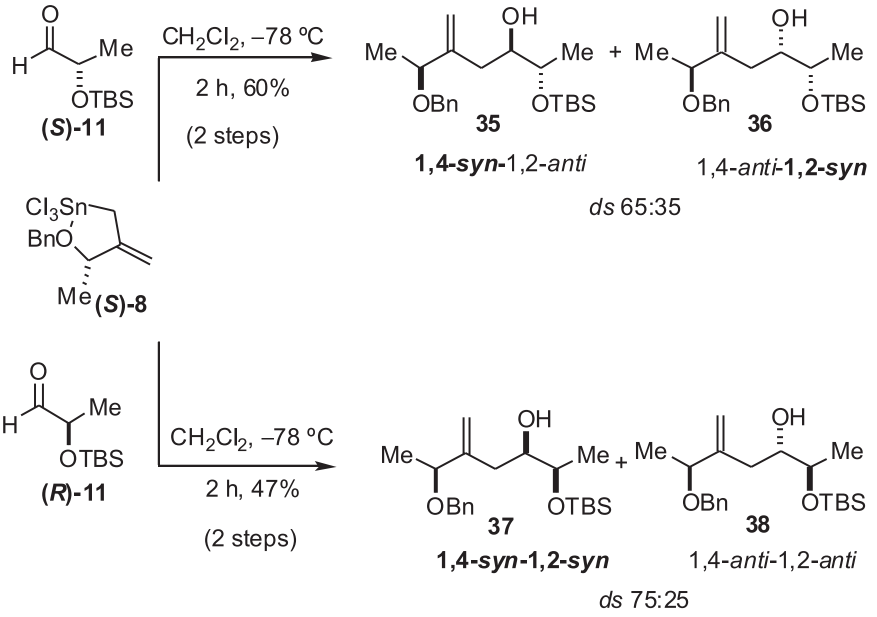
In the case of **33** and **34**, we were able to confirm that the 1,2-*syn* is the major product, based on the ^{13}C chemical shifts for Me$_c$ in **33** (15.5 ppm) and **34** (14.5 ppm).

At this point, we turned our attention to the coupling reactions involving allyltrichlorostannane (*S*)-**8**. Addition of allyltrichlorostannane (*S*)-**8** to aldehyde (*S*)-**11** gave a 65:35 mixture of diastereoisomers **35** and **36** in 60% yield (2 steps) (Scheme 8).

We next examined the addition of the same allylstannane to the enantiomeric aldehyde (*R*)-**11** affording a 75:25 mixture of isomers **37** and **38** in 47% yield for the two-step sequence.



Scheme 7. Addition of chiral allyltrichlorostannane (*R*)-**7** to chiral aldehydes **12**



Scheme 8. Addition of chiral allyltrichlorostannane (*S*)-**8** to chiral aldehydes **11**

Again, these reactions with α-OTBS aldehydes are characterized by poor levels of diastereoselectivity.

The relative stereochemistry for the major products was again determined based on the analysis of the ^{13}C NMR chemical shifts of the corresponding 5-membered dimethylacetonides (Scheme 9). Treatment of **35** and **36** with TBAF at rt followed by treatment of the corresponding diols under acidic conditions with 2,2-dimethoxypropane gave acetonides **41** and **42**, respectively.

The ^{1}H NMR methyl resonances observed at 1.34 and 1.46 for **41** are characteristic of a *cis*-acetonide and ^{1}H NMR methyl resonances at 1.38 and 1.40 for **42** are consistent with a *trans*-acetonide (Figure 6).[25]

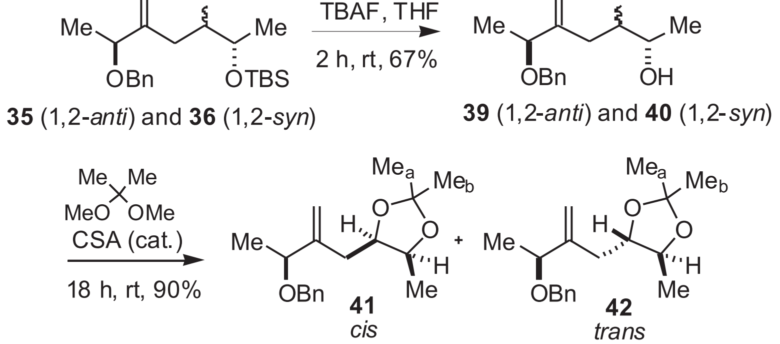
The same strategy was applied to **37** and **38**, providing acetonides **45** and **46** (Scheme 10).

As can be seen from Figure 7, the *trans*-acetonide, which comes from the 1,2-*syn* adduct is the major isomer observed in this reaction.

Addition of allyltrichlorostannane (*S*)-**8** to aldehyde (*S*)-**12** at –78 ºC in CH_2Cl_2, gave an 80:20 diastereoisomeric mixture in favor of the 1,2-*anti* isomer **47** in 70% yield for the 2 steps (Scheme 11). Addition of allyltrichlorostannane (*S*)-**8** to aldehyde (*R*)-**12** at –78 ºC in CH_2Cl_2, led to a 60:40 diastereoisomeric mixture favoring the 1,2-*syn* isomer in 60% yield for the 2 steps (Scheme 11).

The selectivity in the latter case was somewhat disappointing, given the result observed in the reaction of aldehyde **12** with allyltrichlorostannane **5** (Scheme 3).

The relative stereochemistries for both **47** and **49** were determined by applying the same methodology described before for **13-16** (Table 5). The 1,2-*anti* isomer is the major product as can be observed from the ^{13}C NMR chemical shifts for the more shielded Me$_c$ (Figure 8). In the case of **49** and **50**, the ^{13}C chemical shifts for Me$_c$ in **50** appears more shielded (14.7 ppm) when compared to **49** (15.6 ppm).



Scheme 9. Preparation of acetonides **41**-(*cis*) and **42**-(*trans*)

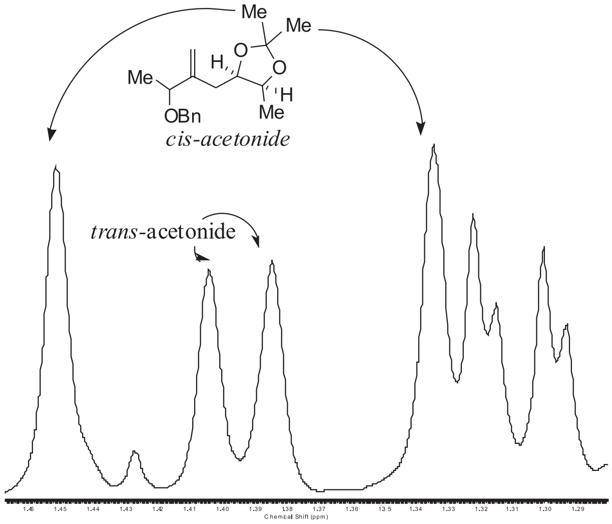


Figure 6. Partial ^{1}H NMR for acetonides **41**-(*cis*) and **42**-(*trans*)

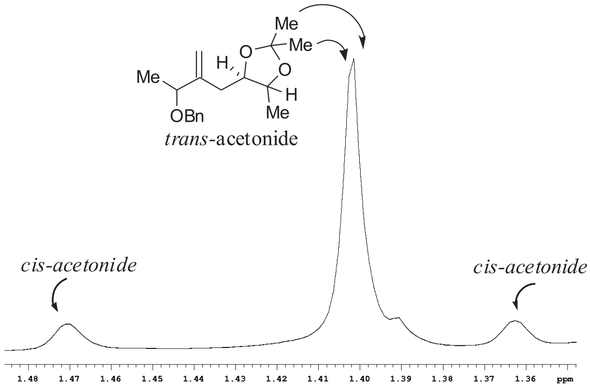
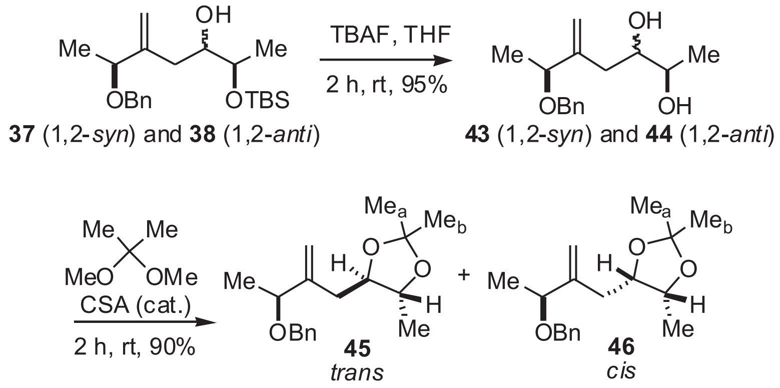
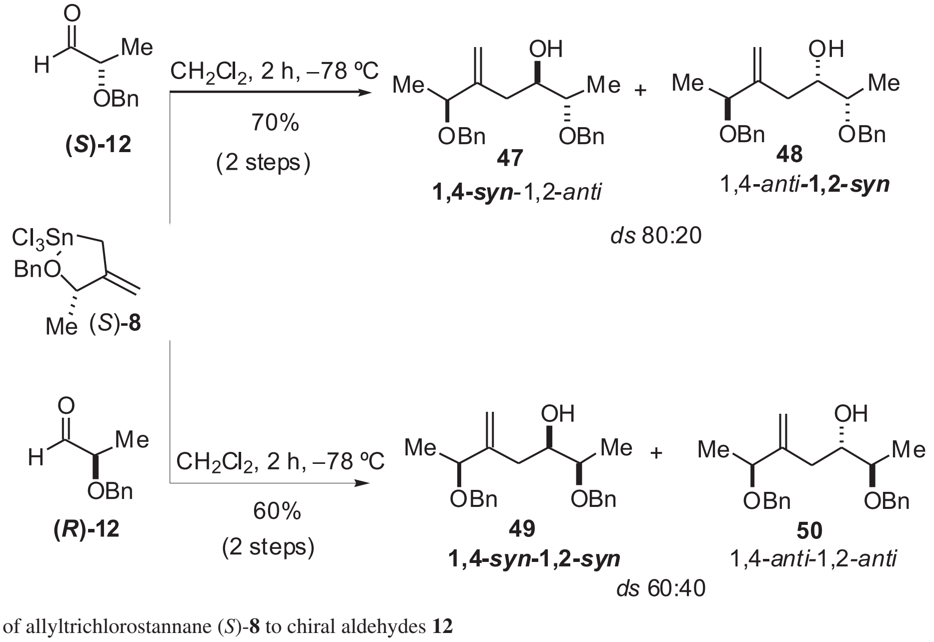


Figure 7. Partial ^{1}H NMR for acetonides **45**-(*trans*) and **46**-(*cis*)



Scheme 10. Preparation of acetonides **45**-(*trans*) and **46**-(*cis*)



Scheme 11. Addition of allyltrichlorostannane (*S*)-**8** to chiral aldehydes **12**

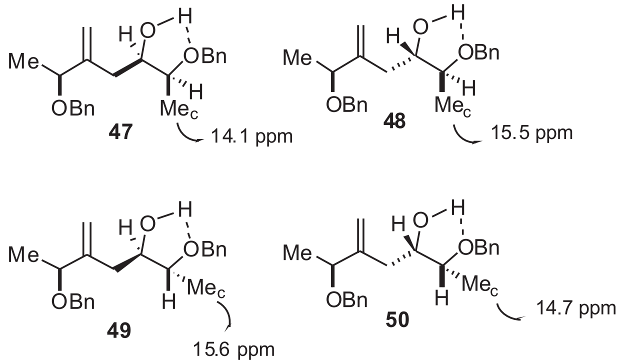


Figure 8. ^{1}H NMR chemical shifts for homoallylic alcohols **47**-**50**

Conclusions

The examples presented in this work show that the levels of π–facial selection are dependent on the absolute stereochemistries of the aldehydes as well as of the allyltrichlorostannanes. The results from these experiments suggest that the stereochemical relationships between the allyltrichlorostannane and aldehyde substituents may confer either a reinforcing (*matched*) or opposing (*mismatched*) facial bias on the carbonyl moiety. One possible reason for this result could be attributed to the involvement of energetically similar chair and twist-boat transition states that lead to diastereomeric product formation. Another possibility to consider in these reactions is that nonbonded interactions between the allyltrichlorostannane and α substituents on the aldehyde may not be significant in pericyclic transition states leading to either Felkin or *anti*-Felkin addition products.[13] We believe that this chemistry is significant in the context of acyclic diastereoselection and will prove to be useful in the synthesis of more complex molecules, like polyacetate and polypropionate-derived natural products.[27,28]

Acknowledgments

We are grateful to FAEP-UNICAMP, FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and INCT-INOFAR Proc. CNPq 573.564/2008-6 for financial support. We thank also Prof. Carol H. Collins for helpful suggestions about English grammar and style.

Supplementary Information

Available free of charge at http://jbcs.org.br, as PDF file.

References

1. Fleming, I.; Barbero, A.; Walter, D.; *Chem. Rev.* **1997**, *97*, 2063; Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K.; *Tetrahedron* **1993**, *49*, 7395; Panek, J. S.; Xu, F.; Rondon, A. C.; *J. Am. Chem. Soc.* **1998**, *120*, 4113; Zhu, B.; Panek, J. S.; *Eur. J. Org. Chem.* **2001**, *9*, 1701; Huang, H. B.; Spande, T. F.; Panek, J. S.; *J. Am. Chem. Soc.* **2003**, *125*, 626; Keck, G. E.; Abbott, D. E.; *Tetrahedron Lett.* **1984**, *25*, 1883; Maguire, R. J.; Mulzer, J.; Bats, J. W.; *J. Org. Chem.* **1996**, *61*, 6936; Denmark, S. E.; Stavenger, R. A.; *J. Org. Chem.* **1998**, *63*, 9524.
2. Trost, B. M.; Urabe, H.; *J. Org. Chem.* **1990**, *55*, 3982; Nishigaishi, Y.; Takuwa, A.; Jodai, A.; *Tetrahedron Lett.* **1991**, *32*, 2383; Almendros, P.; Gruttadauria, M.; Helliwell, M.; Thomas, E. J.; *J. Chem. Soc. Perkin Trans. I* **1997**, 2549; Deka, D. C.; Helliwell, M.; Thomas, E. J.; *Tetrahedron* **2001**, *57*, 10017; Martin, N.; Thomas, E. J.; *Tetrahedron Lett.* **2001**, *42*, 8373; Kumar, P.; Thomas, E. J.; Tray, D. R.; *J. Braz. Chem. Soc.* **2001**, *12*, 623; Gruttadauria, M.; Thomas, E. J.; *J. Chem. Soc. Perkin Trans. I* **1995**, 1469; Nishigaichi, Y.; Kuramoto, H.; Takuwa, A.; *Tetrahedron Lett.* **1995**, *36*, 3353.
3. Dias, L. C.; Giacomini, R.; *J. Braz. Chem. Soc.* **1998**, *9*, 357.
4. Dias, L. C.; Giacomini, R.; *Tetrahedron Lett.* **1998**, *39*, 5343.
5. Dias, L. C.; Meira, P. R. R.; Ferreira, E.; *Org. Lett.* **1999**, *1*, 1335. See also: "NMR Spectra and Structures of Organotin Compounds," V. S. Petrosyan, *Progr. in NMR Spectr.* **1978**, *11*, 115.
6. Dias, L. C.; Meira, P. R. R.; *Synlett* **2000**, 37
7. Dias, L. C.; Ferreira, E.; *Tetrahedron Lett.* **2001**, *42*, 7159.
8. Dias, L. C.; Ferreira, A. A.; Diaz, G.; *Synlett* **2002**, 1845.
9. Dias, L. C.; Diaz, G.; Ferreira, A. A.; Meira, P. R. R.; Ferreira, E.; *Synthesis* **2003**, 603.
10. Dias, L. C.; Giacomini, R.; Meira, P. R. R.; Ferreira, E.; Ferreira, A. A.; Diaz, G.; dos Santos, D. R.; Steil, L. J.; *Arkivoc* **2003**, *10*, 240.
11. Dias, L. C.; dos Santos, D. R.; Steil, L. J.; *Tetrahedron Lett.* **2003**, 44, 6861.
12. We have recently described a very efficient and synthetically useful 1,4-*anti*-1,5-*anti* boron-mediated aldol reaction of chiral α-methyl-β-alkoxy methyl ketone with achiral aldehydes: Dias, L. C.; Baú, R. Z.; de Sousa, M. A.; Zukerman-Schpector, J.; *Org. Lett.* **2002**, *4*, 4325.
13. Denmark, S. E.; Wilson, T.; Willson, T. M.; *J. Am. Chem. Soc.* **1988**, *110*, 984; Denmark, S. E.; Weber, E. J.; Wilson, T.; Willson, T. M.; *Tetrahedron* **1989**, *45*, 1053; Denmark, S. E.; Almstead, N. G.; *Tetrahedron* **1992**, *48*, 5565; Denmark, S. E.; Almstead, N. G.; *J. Am. Chem. Soc.* **1993**, *115*, 3133.
14. Dias, L. C.; Fattori, J.; Perez, C. C.; *Tetrahedron Lett.* **2008**, *49*, 557; Dias, L. C.; Fattori, J.; Perez, C. C.; Oliveira, V. M.; Aguilar, A. M.; *Tetrahedron* **2008**, *64*, 5891.
15. Kim, D.; Lee, J.; Shim, P. J.; Lim, J. I.; Doi, T.; Kim, S.; *J. Org. Chem.* **2002**, *67*, 772.

16. Although the diastereoselectivity of the reactions of these aldehydes with allyltrichlorostannanes depends on their enantiomeric purity, crude aldehydes were used in all of the studies described in the text.
17. Shambayati, S.; Schreiber, S. L.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; *J. Am. Chem. Soc*. **1990**, *112*, 697.
18. The ratios were determined by ^{1}H and ^{13}C-NMR spectroscopic analysis of the purified product mixture; The *syn* and *anti*-products could not be separated and were characterized as mixtures; All of the percentage values represent data obtained from at least three individual trials.
19. Chérest, M.; Felkin, H.; Prudent, N.; *Tetrahedron Lett.* **1968**, *18*, 2199; Anh, N. T.; Eisenstein, O.; *Nouv. J. Chem.* **1977**, *1*, 61; We use the "Felkin" descriptor to refer to the diastereomer predicted by the Felkin-Ahn paradigm. The "*anti*-Felkin" descriptor refers to diastereomers not predicted by this transition state model.
20. Batey, R. A.; Thadani, A. N.; Smil, D. V.; Lough, A. J.; *Synthesis* **2000**, *7*, 990.
21. Heathcock, C. H.; Pirrung, M. C.; Sohn, J. E.; *J. Org. Chem.* **1979**, *44*, 4294.
22. Landmann, B.; Hoffmann, R. W.; *Chem. Ber.* **1987**, *120*, 331.
23. Dias, L. C.; Ferreira, M. A. B.; Tormena, C. F.; *J. Phys. Chem. A* **2008**, *112*, 232.
24. Sames, D.; Liu, Y.; De Young, L.; Polt, R.; *J. Org. Chem.* **1995**, *60*, 2153.
25. Lombardo, M.; Morganti, S.; Trombini, C.; *J. Org. Chem.* **2003**, 68, 997.
26. Having confirmed the relative (*syn* or *anti*) relationship between allylstannane-derived stereogenic centers, the absolute stereochemistry of the newly formed hydroxyl substituent was determined by ascertaining its relationship to the stereocenter originating from the aldehydes, which are of known configuration.
27. All new compounds were isolated as chromatographically pure materials and exhibited acceptable ^{1}H-NMR, ^{13}C-NMR, IR, MS, and HRMS spectral data.
28. **General procedure for allyltrichlorostannane coupling reactions**: To a solution of 2.5 mmol of the corresponding allylsilane in 7 mL of dry CH_2Cl_2 at –78 °C was added 2.5 mmol of $SnCl_4$. The resulting solution was stirred at –78 °C for 30 min when 2.7 mmol of aldehyde in 2 mL of CH_2Cl_2 was added. This mixture was stirred at –78 °C for 1 h and quenched by the slow addition of 0.2 mL of Et_3N, followed by 10 mL of saturated NH_4Cl solution. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (30% EtOAc/hexanes) gave the corresponding homoallylic alcohols.

Received: February 9, 2009
Web Release Date: April 30, 2009

FAPESP helped in meeting the publication costs of this article.