Asymmetric Hosomi−Sakurai Reaction of Allylsilanes Containing Arabinose-Derived Alcohols as Chiral Auxiliaries

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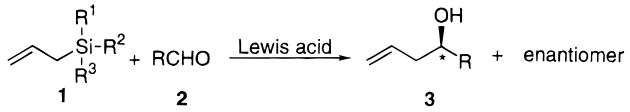
Five enantiopure allylsilanes **1a**−**e** have been prepared, with arabinose-derived alcohols methyl and benzyl 3,4-*O*-isopropylidene- and 3,4-*O*-methylene-*β*-L-arabinopyranosides as chiral auxiliaries, and subjected to the asymmetric Hosomi−Sakurai reaction. The effect of Lewis acid on the stereochemical outcome of the reaction was investigated, and BF_3 was found to exhibit higher enantioselectivity than that of $SnCl_4$ or $TiCl_4$. The reaction of benzyl 2-*O*-(allyldimethylsilyl)-3,4-*O*-isopropylidene-*β*-L-arabinopyranoside (**1b**) with *n*-decanal gave the highest ee (45%) in the presence of BF_3. The steric effect of the chiral auxiliary on the asymmetric Hosomi−Sakurai reaction is demonstrated for the first time although the stereogenic center is remote from the reaction site.

Introduction

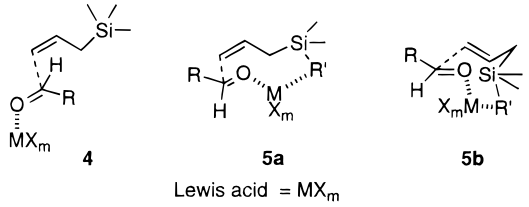
The addition reaction of allylsilanes to carbonyl compounds under Lewis acid promotion, first reported by Hosomi and Sakurai,[1] has been appreciated as a mild method for C−C bond formation[2] together with the possibility of creating a new stereogenic center (Scheme 1). The resultant homoallylic alcohols are often involved in organic synthesis as versatile intermediates, attributable to the flexibility of both the hydroxy group as well as the C=C double bond, which allow facile entries to a variety of bi- or trifunctionalized molecules.

With the current challenge in synthesis focused on enantio- and diastereoselectivity, it is not surprising that increasing attention has been directed toward the use of organosilicon compounds in asymmetric synthesis.[3] As a consequence, efforts have been aimed at working out an asymmetric approach to homoallylic alcohols through the Hosomi−Sakurai reaction. Hitherto, several types of chiral allylsilanes with the stereogenic center not residing on the allyl moiety have been synthesized and subjected to the asymmetric Hosomi−Sakurai reaction.[4] The optical yields for these reactions were poor to modest and these results have been ascribable to the generally accepted reaction mechanism that proceeded through an antiperiplanar transition state **4**[5] (Scheme 2). Since the chiral center at the silicon or the chiral auxiliaries attached to the silicon are remote from the reaction site, the resident chirality has been believed to have little influence on the stereochemical outcome of the reaction.

Scheme 1



Scheme 2



For this reason, previous research efforts concentrated mainly on the introduction of chelative groups to the chiral silanes to increase the possibilities of mediating the reaction through the synclinal transition state **5a** or **5b**[6] (Scheme 2) and consequently enhance the influence of the chiral auxiliary on the asymmetric induction. Surprisingly, little attention had been directed to investigate the contribution of steric hindrance to the stereocontrol of this reaction, although steric hindrance is often considered as an important factor in most stereocontrolled reactions. The main reason appears to be the difficulty of finding a series of systematic chiral auxiliaries of different steric demands for such investigation.

Our interests in sugarometallic chemistry[7] prompted us to investigate the possibilities of applying arabinose-derived alcohols[8] as chiral auxiliaries in asymmetric synthesis, and we recently reported on the use of aglycone−chromium complex as chiral auxiliary in an asymmetric Diels−Alder reaction.[9] This paper extends our contribution to sugarometallic chemistry in which we disclose the design and preparation of chiral allyldimethylsilanes for the asymmetric syntheses of homoallylic alcohols via the Hosomi−Sakurai reaction. We

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(1) (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, *17*, 1295. (b) Sakurai, H. *Pure Appl. Chem.* **1982**, *154*, 1. (c) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.

(2) (a) Majetich, G. In *Organic Synthesis, Theory and Application;* Hudlicky, T., Ed.; Jai Press: Greenwich, CT, 1989. (b) Colvin, E. W. *Silicon in Organic Synthesis;* Butterworths: London, 1981; p 97.

(3) For a review see: Chan, T. H.; Wang, D. *Chem. Rev.* **1992**, *92*, 995.

(4) (a) Bartlett, P. A.; Johnson, W. S.; Elliott, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 2088. (b) Yi, G. L.; Wang, D.; Chan, T. H. *Youji Huaxue* **1982**, *8*, 115. (c) Coppi, L.; Mordini, A.; Taddei, M. *Tetrahedron Lett.* **1987**, *28*, 965 and 969. (d) Nativi, C.; Ravida, N.; Ricci, A.; Seconi, G.; Taddei, M. *J. Org. Chem.* **1991**, *56*, 1951. (e) Wei, Z. Y.; Li, J. S.; Wang, D.; Chan, T. H. *Tetrahedron Lett.* **1987**, *28*, 3441. (f) Wei, Z. Y.; Wang, D.; Li, J. S.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 5768. (g) Chan, T. H.; Wang, D. *Tetrahedron Lett.* **1989**, *30*, 3041.

(5) (a) Hagashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (b) Fleming, I.; Terrett, N. V. *Tetrahedron Lett.* **1983**, *24*, 4153.

(6) Denmark, S. E.; Henke, B. R.; Weber, E. *J. Am. Chem. Soc.* **1987**, *109*, 2512 and references cited therein.

(7) (a) Veds, P.; Chauvin, R.; Li, Z.; Bernet B.; Vasella, A. *Helv. Chim. Acta* **1994**, *77*, 1631 and references cited therein. (b) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807 and references cited therein.

(8) Shing, T. K. M.; Lloyd-Williams, P. *J. Chem. Soc., Chem. Commun.* **1987**, 423.

(9) Shing, T. K. M.; Chow, H.-F.; Chung, I. H. F. *Tetrahedron Lett.* **1996**, *37*, 3713.

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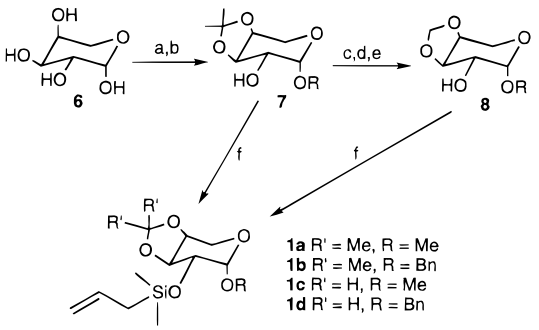
Scheme 3



[a](a) ROH, AcCl (cat), rt; (b) H^+, $Me_2C(OMe)_2$, acetone, rt; (c) Ac_2O, NEt_3, DMAP (cat); (d) $MeOCH_2OMe$, P_2O_5, CH_2Cl_2, rt; (e) K_2CO_3/MeOH, rt; (f) CH_2=$CHCH_2SiMe_2Cl$, imidazole, THF.

envisioned that heavily oxygenated alcohol derivatives, easily accessed from commercially available arabinose in both antipodal forms, could be used as rational auxiliaries in our studies. With the auxiliaries in hand, their steric and coordinative effect on the asymmetric induction of the Hosomi−Sakurai reaction could then be evaluated.

Results and Discussion

The arabinose-derived alcohols could be readily prepared from L-arabinose involving glycosidation and acetalization as shown in Scheme 3. The alcohols **7** or **8** could then be silylated by chlorodimethylallylsilane in the presence of a base such as imidazole or triethylamine and yielded the corresponding enantiopure allylsilanes **1a**−**d**. Imidazole was found to be more effective than triethylamine as a base for the silylation. With triethylamine as base, the reactions afforded **1** in 60−80% yields at reflux temperature whereas the yields of the reactions with imidazole were in excess of 90% at room temperature.

With the enantiopure allylsilanes **1a**−**d** at hand, we investigated the reaction of them with *n*-heptanal. The reaction was conducted at −78 °C with equal molar of aldehyde, allylsilane, and Lewis Acid (1 mmol each) in 10 mL of dichloromethane. The Lewis acids for the present study were $TiCl_4$, $SnCl_4$, and BF_3. The results are listed in Table 1. In our workup procedure, 1 M solution of HF in methanol prepared from 40% of hydrofluoric acid was used. By this method, we could eliminate traces of silyl contaminant that always coexist with the newly constructed homoallylic alcohol, and the chiral reagent could be reverted back to methyl or benzyl *β*-L-arabinopyranoside. The glycoside crystallized out from the reaction mixture and could be recovered easily by filtration in more than 90% yields.

From the results listed in Table 1, all the reactions afforded a new *S* stereogenic center (**3**, R = C_6H_{13} in Scheme 1), but in different enantiomeric excesses (ee). BF_3 is the best mediator for the enantiocontrol (best optical yields) of the reaction whereas $SnCl_4$ is the worst. This probably implies that the higher the coordination ability of the Lewis acid, the lower its capacity to induce asymmetry or to control the enantioselectivity of the Hosomi−Sakurai reaction. There are two possibilities which caused such results. The first one could be that the Lewis acid such as $SnCl_4$ or $TiCl_4$ preferred to react with the allylsilane first and cleave the Si−O bond to produce allylchlorodimethylsilane and alkoxytitanium(VI) trichloride or alkoxytin(VI) trichloride. The newly formed Ti- or Sn-containing species could then catalyze the addition reaction of newly formed allylsilane to the aldehyde and hence diminish the influence of the chiral auxiliary in asymmetric induction. However, our experimental results show that such a possibility cannot exist at such reaction conditions. We found that the addition reaction of allylsilane **1a** with benzaldehyde failed under identical conditions (with all three Lewis acids). In such cases, when the reaction was quenched by adding 4 equiv of triethylamine and then saturated aqueous ammonium chloride quickly at −78 °C. The starting allylsilane **1a** was recovered in yields between 83−93%. These results excluded the aforementioned possibility that the allylsilane was destroyed by the Lewis acid.

Table 1. Lewis Acid-Promoted Addition of Enantiopure Allylsilanes to *n*-Heptanal[a]

entry	homochiral allylsilane	Lewis acid	yield %[b] (ee %)[c]	absolute configuration[d]
1	**1a**	BF_3	48 (25)	*S*[e]
2	**1a**	$TiCl_4$	40 (15)	*S*[f]
3	**1a**	$SnCl_4$	71 (9)	*S*
4	**1b**	BF_3	63 (41)	*S*[g]
5	**1b**	$TiCl_4$	65 (11)	*S*
6	**1b**	$SnCl_4$	74 (9)	*S*
7	**1c**	BF_3	57 (13)	*S*
8	**1c**	$TiCl_4$	47 (6)	*S*
9	**1c**	$SnCl_4$	55 (0)	*S*
10	**1d**	BF_3	77 (33)	*S*[h]
11	**1d**	$TiCl_4$	62 (15)	*S*
12	**1d**	$SnCl_4$	71 (9)	*S*

[a] The reaction was carried out at −78 °C in dichloromethane for 4 h. [b] Isolated yields not optimized. [c] Ee determined by the ^1H NMR spectral analysis of the Mosher's ester of the homoallylic alcohol. [d] Absolute configuration determined by polarimetric analysis and by ^1H NMR spectral analysis of the Mosher's ester[12] prepared from (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride and the homoallylic alcohol. [e] $[\alpha]^{20}_D$ −2.57 (*c* = 1.5, CCl_4). [f] $[\alpha]^{20}_D$ −1.73 (*c* = 1.1, CCl_4). [g] $[\alpha]^{20}_D$ −4.26 (*c* = 2.2, CCl_4). [h] $[\alpha]^{20}_D$ −3.34 (*c* = 2.7, CCl_4).

The second possibility for the dependence of enantioselectivity on the Lewis acid may arise from the coordination of the Lewis acid with the chiral auxiliary. There are five oxygen atoms in every auxiliary. Each oxygen may coordinate with the Lewis acid during the reaction process and may induce different asymmetry (*R* or *S*) in the final products. The observed optical yields could be a net reinforcement or cancellation of ee. The asymmetric induction that resulted was only an overall reflection of the effect of each coordination. Unfortunately for $SnCl_4$ or $TiCl_4$ (each can attain a coordination number up to 6) the overall asymmetric induction is a diminishing one. However, this is noteworthy because this is the first observation that the optical yield of the reaction is dependent on the coordination ability of the Lewis acid.

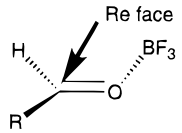
Another important result from this research is the demonstration that a sterically demanding group in the chiral auxiliary, although remote from the reaction site, could still have a large influence on the asymmetric induction in view of results obtained from those BF_3-catalyzed additions (compare the steric effect of methyl aglycone verses benzyl aglycone on ee in entries 1 and 4 as well as in entries 7 and 10). Encouraged by these results, we synthesized an additional chiral allylsilane, benzyl 2-*O*-(allyldiphenylsilyl)-3,4-*O*-isopropylidene-L-arabinopyranoside (**1e**). We hoped that the introduction of two bulky phenyl groups onto the silicon would increase the influence of the chiral auxiliary on stereo-

Table 2. BF_3-Promoted Asymmetric Hosomi−Sakurai Reaction of Enantiopure Allylsilane 1b with Aldehydes[a]

entry	aldehyde	yield %[b] ee %)[c]	$[\alpha]^{20}_D$	product[d]
1	*n*-heptanal	63 (41)	− 4.26 (c = 2.2, CCl_4)	(*S*)-dec-1-en-4-ol
2	*n*-nonanal	65 (41)	− 5.26 (c = 2.7, CCl_4)[e]	(*S*)-dodec-1-en-4-ol
3	*n*-decanal	72 (45)	− 5.66 (c = 2.9, C_6H_6)[f]	(*S*)-tridec-1-en-4-ol
4	2,2-dimethyl-propanal	54 (36)	+4.03 (c = 3.6, C_6H_6)[g]	(*R*)-5,5-dimethylhex-1-en-4-ol
5	cyclohexane-carboxyaldehyde	71 (38)	+ 3.66 (c = 3.0, EtOH)[h]	(*R*)-4-cyclohexylbut-1-en-4-ol

[a] The reaction was carried out at −78 °C in dichloromethane for 4 h. [b] Isolated yields not optimized. [c] Ee determined by the ^{1}H NMR of the Mosher's ester of the newly formed homoallylic alcohol. [d] Absolute configuration determined by polarimetric analysis and by ^{1}H NMR spectral analysis of the Mosher's ester[12] prepared from (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride and the yielded homoallylic alcohol. [e] Literature[13a] $[\alpha]^{20}_D$ −8.79 (c = 2.50, CCl_4), 56% ee. [f] Literature[13b] $[\alpha]^{20}_D$ −10.4 (c = 6.7, C_6H_6), 92% ee. [g] Literature[13b] $[\alpha]^{20}_D$ +10.3 (c = 10.5, C_6H_6), 88% ee. [h] Literature[13b] $[\alpha]^{20}_D$ + 8.2 (c = 0.6, EtOH), 92% ee.

Scheme 4



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chemical control and as a consequence would improve the enantioselectivity of the reaction. Unfortunately, this diphenyl-substituted allylsilane **1e** did not react with *n*-heptanal in the presence of either of the three Lewis acids at −78 °C. Higher temperatures such as room temperature caused the destruction of the allylsilane **1e**. These results are in concord with the report[10] that the Lewis acid-promoted addition reaction of allyltrimethylsilane to aldehydes is about 100 times faster than that of allyltriphenylsilane. An electron-withdrawing group on silicon was also found to decrease the reactivity of the allylsilane.[10]

Since allylsilane **1b** gave the highest ee with *n*-heptanal in the presence of BF_3 (Table 1, entry 4), its BF_3-mediated reactions with other aldehydes were investigated, and the results are presented in Table 2.

All these reactions gave similar stereochemical outcomes. According to the absolute configurations of the homoallylic alcohols obtained, we could conclude that all the reactions proceed via a similar intermediate in which the re face of the complex[11] between aldehyde and BF_3 has a higher priority to attack by the allyl moiety of the enantiopure allylsilane (Scheme 4).

Conclusions

Enantiopure allylsilanes **1a**−**d**, with arabinose-derived alcohols as chiral auxiliaries, displayed moderate asymmetric induction in the Lewis acid-mediated Hosomi−Sakurai reaction. Lewis acid BF_3 was found to exhibit higher enantioselectivity than that of $TiCl_4$ or $SnCl_4$ that can attain a higher coordination number. The observed optical yield appeared to be an overall reflection of the effect of each coordination between the auxiliary ligand and the Lewis acid. Consequently, compounds containing many oxygen functionalities (or other ligands) might not be suitable auxiliaries that would induce high asymmetry in Lewis acid-catalyzed or -mediated reactions. Benzyl 2-*O*-(allyldimethylsilyl)-3,4-*O*-isopropylidene-*β*-L-arabinopyranoside (**1b**) that carries the most sterically demanding auxiliary gave the highest ee (45%) with *n*-decanal in the presence of BF_3. This steric effect of the chiral auxiliary on the asymmetric Hosomi−Sakurai reaction is demonstrated for the first time although the stereogenic center is remote from the reaction site.

A sterically demanding auxiliary with minimum number of ligands may be the ideal vehicle to achieve high enantioselectivity in the Hosomi-Sakurai reaction. Work along this direction is in progress.

Experimental Section

IR spectra were recorded on a FT-IR spectrometer as thin films on NaCl disks for liquid. NMR spectra were measured in solutions of $CDCl_3$ at 250 MHz (^{1}H) or at 62.9 MHz (^{13}C). Spin−spin coupling constants (J) were measured directly from the spectra. Carbon and hydrogen elemental analyses were carried out at the MEDAC Ltd, Department of Chemistry, Brunel University, Uxbridge, England. All reactions were monitored by analytical thin-layer chromatography (TLC) on aluminum precoated with silica gel $60F_{254}$ (E. Merck) and compounds were visualized with a spray of 5% w/v dodecamolybdophosphoric acid in ethanol and subsequent heating. All columns were packed wet using E. Merck silica gel 60 (230−400 mesh) as the stationary phase and eluted using flash chromatographic technique. THF was distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Dichloromethane was freshly distilled over calcium hydride and used immediately. The Lewis acids, used as a 1 M solution in dichloromethane, were prepared from freshly distilled $TiCl_4$, $SnCl_4$, or $BF_3{\cdot}OEt_2$ (at reduced pressure over calcium hydride) under a N_2 atmosphere. All aldehydes were dried over Na_2SO_4 and freshly distilled before use.

General Procedure for Syntheses of Enantiopure Allylsilanes. To a stirred and cooled solution (0 °C) of an arabinose-derived alcohol (5 mmol) and 0.35 g (5.1 mmol) of imidazole in 30 mL of THF under a N_2 atmosphere was added 0.75 mL of allylchlorodimethylsilane (5 mmol) in 10 min via a syringe. After the addition, the resultant mixture was stirred for 12 h at rt. The solvent was then removed under reduced pressure, and the residue was purified through flash column chromatography (hexane:ethyl acetate = 10:1) to yield the enantiopure allylsilanes **1a**−**d**.

Methyl 2-*O*-(Allyldimethylsilyl)-3,4-*O*-isopropylidene-*β*-L-arabinopyranoside (1a) was prepared as a syrup from 1.02 g of methyl 3,4-*O*-isopropylidene-*β*-L-arabinopyranoside[14] in 94% yield: $[\alpha]^{20}_D$ +153.7 (c = 1.1, CCl_4); IR (neat) 2987, 2933, 1630, 1247, 1126, 852 cm^{-1}; ^{1}H NMR δ 0.17 (s, 6H), 1.28 (s, 3H), 1.56 (s, 3H), 1.68 (d, J = 8.1 Hz, 2H), 3.46 (s, 3H), 3.70−3.80 (m, 1H), 3.92−3.97 (m, 2H), 4.20−4.60 (m, 2H), 4.56 (d, J = 3.5 Hz, 1H), 4.80−5.00 (m, 2H), 5.70−5.90 (m, 1H); ^{13}C NMR δ −1.96, −1.71, 24.84, 26.19, 28.29, 55.68, 58.71, 72.18, 73.52, 76.35, 100.03, 108.71, 113.73, 133.99. Anal. Calcd for $C_{14}H_{26}O_5Si$: C, 55.60; H, 8.66. Found: C, 55.92; H, 8.86.

Benzyl 2-*O*-(Allyldimethylsilyl)-3,4-*O*-isopropylidene-*β*-L-arabinopyranoside (1b) was prepared as a syrup from

(10) (a) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954. (b) Mayr, H.; Gorath, G. *J. Am. Chem. Soc.* **1995**, *117*, 7862.

(11) The existence of a methacrolein−BF_3 complex was demonstrated by an X-ray study, see: Corey, E. J.; Loh, T.-P.; Sarshar, S.; Aziioara, M. *Tetrahedron Lett.* **1992**, *33*, 6945.

(12) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

(13) (a) Otera, J.; Yoshinaga, Y.; Yamaji, T.; Yoshioka, T.; Kawasaki, Y. *Organometallics* **1985**, *4*, 1213. (b) Riediker, M.; Duthaler, R. O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 494.

(14) Bennett, M.; Gill, G. B.; Pattenden, G.; Shuker, A. J.; Stapleton, A. *J. Chem. Soc., Perkin Trans. 1* **1991,** 929.

1.4 g of benzyl 3,4-*O*-isopropylidene-β -L-arabinopyranoside[14] in 95% yield: $[\alpha]^{20}_D$ +202.3 (c = 1.3, CCl_4); IR (neat) 2986, 2922, 2876, 1630, 1254, 1127, 865, 738, 698 cm^{-1}; ^1H NMR δ 0.11 (s, 6H), 1.36 (s, 3H), 1.51 (S, 3H), 1.62 (d, J = 7.9 Hz, 2H), 3.73 (dd, J = 6.6, 3.5 Hz, 1H), 3.90−4.10 (m, 2H), 4.17−4.25 (m, 2H), 4.55−4.92 (m, 5H), 5.65−5.90 (m, 1H), 7.26−7.45 (m, 5H); ^{13}C NMR δ −1.94, −1.78, 24.87, 26.20, 28.27, 59.44, 69.36, 72.12, 73.52, 76.58, 97.79, 108.73, 113.60, 127.68, 127.81, 128.33, 134.09, 137.55. Anal. Calcd for $C_{20}H_{30}O_5Si$: C, 63.46; H, 7.99. Found: C, 63.37; H, 8.17.

Benzyl 2-*O*-(Allyldimethylsilyl)-3,4-*O*-methylene-β-L-arabinopyranoside (1c) was prepared as a syrup from 1.26 g of benzyl 3,4-*O*-methylene-β-L-arabinopyranoside[15] in 94% yield: $[\alpha]^{20}_D$ +200.8 (c = 4.6, CCl_4); IR (neat) 2959, 2922, 2876, 1630, 1248, 1124, 851, 735, 698 cm^{-1}; ^1H NMR δ 0.10 (s, 6H), 1.60 (d, J = 7.5 Hz, 2H), 3.68 (dd, J = 7.7, 3.5 Hz, 1H), 4.00−4.10 (m, 3H), 4.10 (dd, J = 7.6, 5.0 Hz, 1H), 4.50−4.95 (m, 5H), 4.99 (s, 1H), 5.17 (s, 1H), 5.70−5.90 (m, 1H), 7.28−7.45 (m, 5H); ^{13}C NMR δ −2.22, −1.95, 24.66, 58.83, 69.12, 69.82, 74.41, 75.56, 94.34, 97.49, 113.70, 127.72, 128.31, 133.87, 137.22. Anal. Calcd for $C_{18}H_{26}O_5Si$: C, 61.69; H, 7.48. Found: C, 61.73; H, 7.49.

Methyl 2-*O*-(Allyldimethylsilyl)-3,4-*O*-methylene-β-L-arabinopyranoside (1d) was prepared as a syrup from 0.88 g of methyl 3,4-*O*-methylene-β-L-arabinopyranoside[16] in 98% yield; $[\alpha]^{20}_D$ +122.2 (c = 2.0, CCl_4); IR (neat) 2919, 1631, 1253, 1127, 865 cm^{-1}; ^1H NMR δ 0.16 (s, 6H), 1.66 (d, J = 8.1 Hz, 2H), 3.43 (s, 3H), 3.68 (dd, J = 7.8, 3.5 Hz, 1H), 3.90−4.08 (m, 3H), 4.19 (dd, J = 7.7, 5.4 Hz, 1H), 4.57 (d, J = 3.4 Hz, 1H), 4.80−4.95 (m, 2H), 4.98 (s, 1H), 5.17 (s, 1H), 5.70−5.90 (m, 1H); ^{13}C NMR δ −2.07, −1.78, 24.79, 29.89, 55.72, 58.65, 70.13, 74.50, 75.73, 94.41, 100.12, 113.76, 133.93. Anal. Calcd for $C_{12}H_{22}O_5Si$: C, 52.53; H, 8.08. Found: C, 52.59; H, 7.94.

Benzyl 2-*O*-(Allyldiphenylsilyl)-3,4-*O*-isopropylidene-β-L-arabinopyranoside (1e). At −78 °C, 10 mL of 1 M allylmagnesium bromide (10 mmol) in diethyl ether was added dropwise to a solution of dichlorodiphenylsilane (2.54 g, 10 mmol) in 30 mL of THF under a nitrogen atmosphere. After the addition, the mixture was warmed to rt and stirring was continued for 2 h at this temperature. Then 0.68 g of imidazole as well as 2.80 g of benzyl-3,4-*O*-isopropylidene-β-L-arabinopyranoside were added, and the resultant mixture was refluxed for 4 h. The reaction was quenched with 30 mL of saturated ammonium chloride, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and filtered. Solvent removal from the filtrate at reduced pressure gave a residue which was flash chromatographed to give **1e** as a syrup (3.7 g, 74%): $[\alpha]^{20}_D$ +127.2 (c = 1.1, CCl_4); IR (neat), 2984, 2922, 1631, 1119, 738, 699 cm^{-1}; ^1H NMR δ 1.29 (s, 3H), 1.35 (S, 3H), 2.24 (d, J = 7.8 Hz, 2H), 3.82 (dd, J = 7.4, 3.5 Hz, 1H), 3.86−4.05 (m, 2H), 4.22 (dd J = 5.7, 2.2 Hz, 1H), 4.37 (dd, J = 7.4, 5.4 Hz, 1H), 4.43 and 4.70 (ABq, J_{AB} = 12.2 Hz, 2H), 4.60 (d, J = 3.5 Hz, 1H), 4.80−4.90 (m, 2H), 5.75−5.92 (m, 1H), 7.30−7.90 (m, 15H); ^{13}C NMR δ 22.19, 26.30, 27.90, 59.04, 69.39, 72.38, 73.54, 76.26, 97.68, 108.71, 115.07, 127.63, 127.75, 127.87, 128.35, 129.86, 130.02, 133.08, 134.09, 134.43, 135.04, 137.39. Anal. Calcd for $C_{30}H_{34}O_5Si$: C, 71.68; H, 6.82. Found: C, 70.81; H, 6.81.

General Procedure for the Asymmetric Hosomi−Sakurai Reaction. To a stirred solution of enantiopure allylsilane (1 mmol) and aldehyde (1 mmol) in 10 mL of dry CH_2Cl_2 at −78 °C under N_2 atmosphere was added 1 mL of 1 M $TiCl_4$, $SnCl_4$ or $BF_3{\cdot}OEt_2$ (1 mmol) in CH_2Cl_2 over 15 min. Stirring was continued for 4 h at −78 °C and 10 mL of 1 M HF in aqueous MeOH (prepared from 40% HF and MeOH) was added. The resultant mixture was warmed to rt, and stirring was continued for a further 4 h. Benzyl β-L-arabinopyranoside crystallized out and could be recovered in almost quantitative yield through filtration. The filtrate was diluted with 20 mL of hexane and dried over anhydrous potassium carbonate and filtered. The solvent was evaporated from the filtrate, and the residue was purified through flash chromatography to give the homoallylic alcohol.

General Procedure for the Preparation of Mosher's Esters of the Newly Formed Homoallylic Alcohols. To a solution of homoallylic alcohol (0.03 mmol) and DMAP (0.05 mmol) in 0.3 mL of CCl_4 was added 0.1 mL of 0.4 M (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride[17] in CCl_4. The resultant mixture was heated at 40 °C for 12 h, cooled to rt, and then filtered through a thin pad of silica gel (hexane: ethyl acetate = 100:4 as eluant). Concentration of the filtrate afforded the corresponding (*R*,*R*) and (*R*,*S*)-Mosher's esters whose ^1H NMR spectrum was used to determine the ee of the homoallylic alcohol.

(*S*)-Dec-1-en-4-ol was obtained in 63% yield with 41% ee {determined from the ratio of the allylic methylene groups in the ^1H NMR spectrum of the diastereomeric Mosher's esters: ^1H NMR δ 2.39 (t, J = 6.5 Hz, 0.59H), 2.46 (t, J = 6.6 Hz, 1.41H)}; $[\alpha]^{20}_D$ −4.26 (c = 2.2, CCl_4); ^1H NMR δ 0.88 (t, J = 6.2 Hz, 3H), 1.20−1.75 (m, 11H), 2.05−2.20 (m, 1H), 2.23−2.36 (m, 1H), 3.60−3.70 (m, 1H), 5.10−5.23 (m, 2H), 5.75−5.92 (m, 1H).

(*S*)-Dodec-1-en-4-ol was obtained in 65% yield with 41% ee {determined from the ratio of the allylic methylene groups in the ^1H NMR spectrum of the diastereomeric Mosher's esters: ^1H NMR δ 2.35 (t, J = 6.5 Hz, 0.59H), 2.42 (t, J = 6.6 Hz, 1.41H)}; $[\alpha]^{20}_D$ −5.26 (c = 2.7, CCl_4) {lit.[13a] $[\alpha]^{20}_D$ −8.79 (c = 2.5, CCl_4), 56% ee}; ^1H NMR δ 0.87 (t, J = 6.3 Hz, 3H), 1.18−1.75 (m, 15H), 2.05−2.19 (m, 1H), 2.23−2.36 (m, 1H), 3.58−3.70 (m, 1H), 5.10−5.20 (m, 2H), 5.70−5.92 (m, 1H).

(*S*)-Tridec-1-en-4-ol was obtained in 72% yield with 45% ee {determined from the ratio of the allylic methylene groups in the ^1H NMR spectrum of the diastereomeric Mosher's esters: ^1H NMR δ 2.35 (t, J = 6.7 Hz, 0.55H), 2.41 (t, J = 7.0 Hz, 1.45H)}; $[\alpha]^{20}_D$ −5.66 (c = 2.9, C_6H_6) {lit.[13b] $[\alpha]^{20}_D$ −10.4 (c = 6.7, C_6H_6), 92% ee}; ^1H NMR δ 0.88 (t, J = 6.3 Hz, 3H), 1.15−1.75 (m, 17H), 2.05−2.20 (m, 1H), 2.23−2.36 (m, 1H), 3.58−3.72 (m, 1H), 5.10−5.23 (m, 2H), 5.73−5.90 (m, 1H).

(*R*)-5,5-Dimethylhex-1-en-4-ol was obtained in 63% yield with 36% ee {determined from the ratio of the *tert*-butyl groups in the ^1H NMR spectrum of the diastereomeric Mosher's esters: ^1H NMR δ 0.89 (s, 6.12H), 0.93 (s, 2.88H)}; $[\alpha]^{20}_D$ +4.03 (c = 3.6, C_6H_6) {lit.[13b] $[\alpha]^{20}_D$ +10.3 (c = 10.5, C_6H_6), 88% ee}; ^1H NMR δ 0.91 (s, 9H), 1.72 (s, 1H), 1.90−2.05 (m, 1H), 2.30−2.45 (m, 1H), 3.24 (dd, J = 10.3, 1.98 Hz, 1H), 5.08−5.20 (m, 2H), 5.75−5.95 (m, 1H).

(*R*)-4-Cyclohexylbut-1-en-4-ol was obtained in 71% yield with 38% ee {determined from the ratio of the allylic methylene groups in the ^1H NMR spectrum of the diastereomeric Mosher's esters: ^1H NMR δ 2.41 (t, J = 6.6 Hz, 0.62H), 2.42 (t, J = 6.9 Hz, 1.38H)}; $[\alpha]^{20}_D$ +3.66 (c = 3.0, EtOH) {lit.[13b] $[\alpha]^{20}_D$ +8.2 (c = 0.6, EtOH), 92% ee}; ^1H NMR δ 0.90−1.45 (m, 6H), 1.60−1.94 (m, 6H), 2.05−2.13 (m, 1H), 2.25−2.40 (m, 1H), 3.30−3.40 (m, 1H), 5.08−5.17 (m, 2H), 5.75−5.90 (m, 1H).

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(15) Chung, I. H. F. M. S. Thesis, The Chinese University of Hong Kong, Shatin, Hong Kong, 1995.

(16) Nouguier, R.; Gras, J. L.; Giraud, B.; Virgili, A. *Bull. Soc. Chim. Fr.* **1991**, 945.

(17) Rieser, M. J.; Hui, Y.-H.; Rupprecht, J. K.; Kozlowski, J. F.; Wood, K. V.; MacLaughlin, J. L.; Hanson, P. R.; Zhuang, Z.; Hoye, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10203.