Stereoselective 1,4-Phenyl Migration from Silicon to Carbon in α-Siloxy Cyclic Acetal Systems: A Concise Synthesis of 1,2-*cis*-Phenyl *C*-Glycoside and Enantioenriched Silanol

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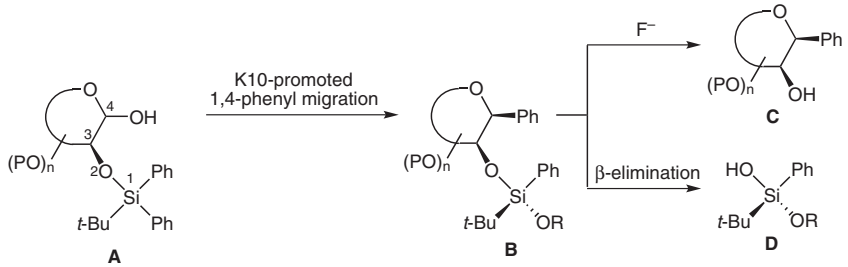
Abstract: The treatment of *O*-glycoside with alcohol in the presence of montmorillonite K10 clay and 4-Å MS yields the 1,4-aryl migration product with a 1,2-*cis*-phenyl *C*-glycoside scaffold and a chiral silyl moiety with high stereoselectivity.

Key words: asymmetric synthesis, aryl *C*-glycosides, chiral silanol, montmorillonite K10, aryl migration

Aryl *C*-glycosides constitute an important class of the *C*-glycoside family of natural products and have attracted considerable interest because of their diverse biological activities and resistance to acidic and enzymatic hydrolysis.[1] Therefore a number of methods have been developed for the stereoselective formation of the aryl *C*-glycoside linkage.[2] Among these methods, the reactions of glycosyl donors by intermolecular Friedel–Crafts couplings or by reactions with aryl metal reagents have been well established and these reactions yielded 1,2-*trans*-aryl *C*-glycosides, predominantly. In contrast, access to the thermodynamically more unfavorable 1,2-*cis*-aryl *C*-glycosides remains relatively undeveloped.[3] To this end, we have recently reported that montmorillonite K10 clay promoted 1,4-aryl or alkenyl migration from silicon to the C1 carbon in cyclic *N*,*O*-acetal systems.[4–6] The unique features of this reaction are as follows: (i) the aryl or alkenyl group on the siloxy group migrates intramolecularly in a *cis* fashion, and (ii) a concomitant nucleophilic substitution of the alkoxy group on the silicon atom proceeds with high stereoselectivity. On the basis of this result, we envisioned that a similar aryl migration of *O*-glycoside **A** with a *tert*-butyldiphenylsilyl group at the C2 hydroxyl group could afford the phenyl *C*-glycosides **B** in a 1,2-*cis* fashion (Scheme 1). Desilylation of **B** would provide C2 hydroxy phenyl *C*-glycoside **C**. Furthermore, the treatment of phenyl *C*-glycosides **B** with a base would cause β-elimination and provide enantioenriched silanols **D**, which are otherwise difficult to obtain. Here, we report the details of the aryl migration in cyclic acetal systems, which provide an effective approach to the stereoselective synthesis of 1,2-*cis*-phenyl *C*-glycosides as well as chiral silanol.

At the outset, we attempted the phenyl migration of the simple five-membered cyclic hemiacetal **1a** with the (*tert*-butyldiphenylsilyl)oxy group at the C2 position; the cyclic hemiacetal **1a** was easily prepared from commercially available (*S*)-α-hydroxy-γ-butyrolactone (97% ee) in two steps [(i) TBDPSCl, imidazole and (ii) DIBAL]. The reaction was performed according to the previously developed protocol; the cyclic hemiacetal **1a** was treated with two equivalents of benzyl alcohol in the presence of K10 and 4-Å MS in CH_2Cl_2 at 0 °C for 12 hours, providing the corresponding aryl migration product **2** in 71% yield with 90% diastereomeric ratio (Scheme 2).[7,8] Some of the aryl migration product **2** may be produced through benzyl acetal **1b**; indeed a similar reaction of separately prepared **1b**[9] also provided **2** in 46% yield with 90% dr.

The exposure of the phenyl migration product **2** to TBAF afforded alcohol **3a** as a single diastereomer, which means that the diastereomer of **2** is derived from the silicon stereocenter. The C1–C2 relationship of **3a** was determined by the NOE correlations of the corresponding acetate **3b**



Scheme 1 Stereoselective synthesis of 1,2-*cis*-phenyl *C*-glycoside and chiral silanol via 1,4-phenyl migration of *O*-glycoside

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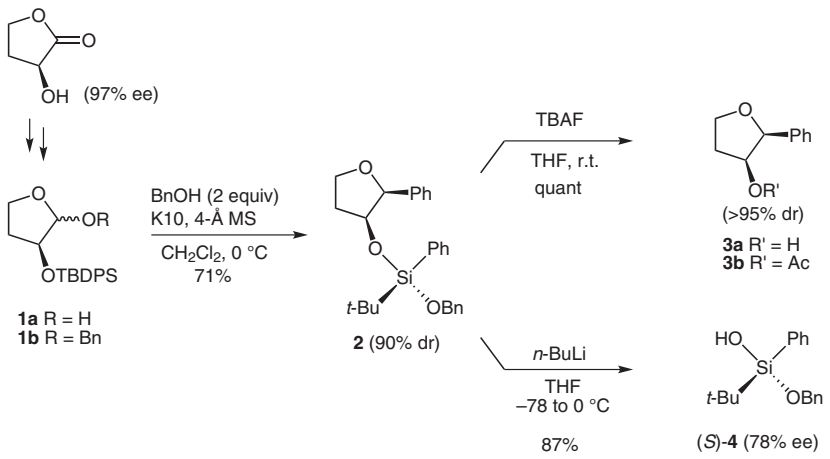
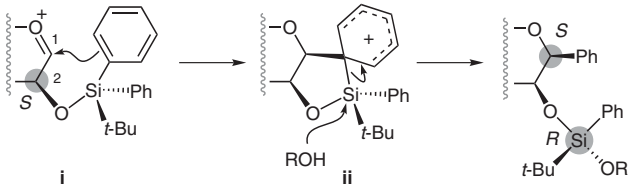


Scheme 2 Phenyl migration of the five-membered cyclic hemiacetal **1a**



Scheme 3 A possible mechanism of the aryl migration

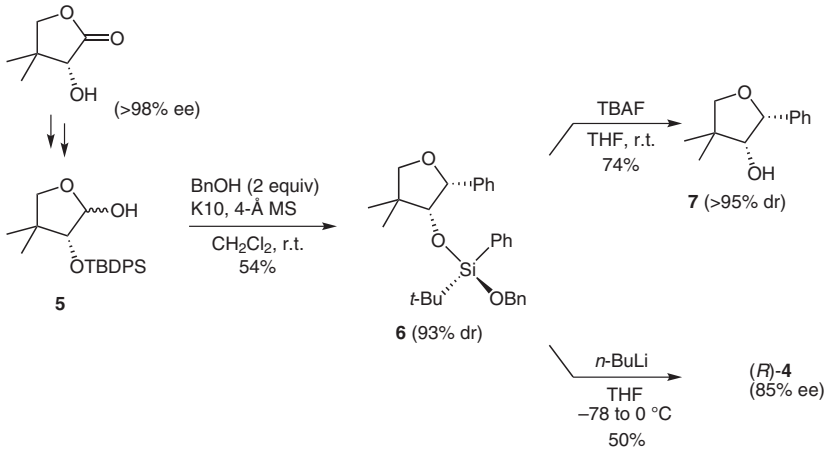
as a *cis* configuration. Next, we examined the liberation of the chiral silicon moiety as a silanol by β-elimination. As expected, the treatment of **2** with *n*-BuLi in THF smoothly afforded enantioenriched benzyloxysilanol (*S*)-**4** with 78% ee.[10,11] This result indicates that the silicon stereocenter of the major stereoisomer of **2** has an *R* configuration.

A plausible mechanism of this aryl migration is shown in Scheme 3. The reaction most likely proceeds through an intramolecular Friedel–Crafts reaction between one of the phenyl groups in TBDPS and an oxonium ion **i** generated from **1a** or **1b** (vide supra) to form the silyl-stabilized cation **ii**, which is then collapsed by alcohol attack on silicon to obtain the *ipso*-substituted product[4] as the 1*S*,2*S*,R_{Si} configuration.

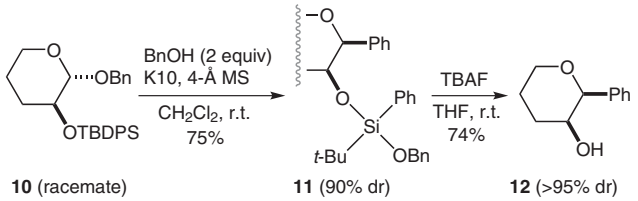
A similar reaction of pantolactone derivative **5** was also examined (Scheme 4). Cyclic hemiacetal **5**, derived from commercially available (*R*)-pantolactone (>98% ee) in two steps, was subjected to the same conditions mentioned above to obtain the phenyl-migration product **6** in moderate yield with >95% *cis* at the C1–C2 relationship and 93% dr at the silicon stereocenter (S_{Si}) was yielded. Its 1,2-*cis* and S_{Si} stereochemistries were established by the transformation to **7** (>95% *cis*)[12] or benzyloxysilanol (*R*)-**4** (85% ee), respectively.[13]

Thus, the developed phenyl migration protocol was also applicable to the six-membered cyclic acetal system (Scheme 5). The reaction of acetal **10**[14] resulted in the exclusive formation of the corresponding phenyl migration product **11** in a highly stereoselective manner to provide >95% *cis* at the C1–C2 relationship and 90% dr at the silicon stereocenter.[15]

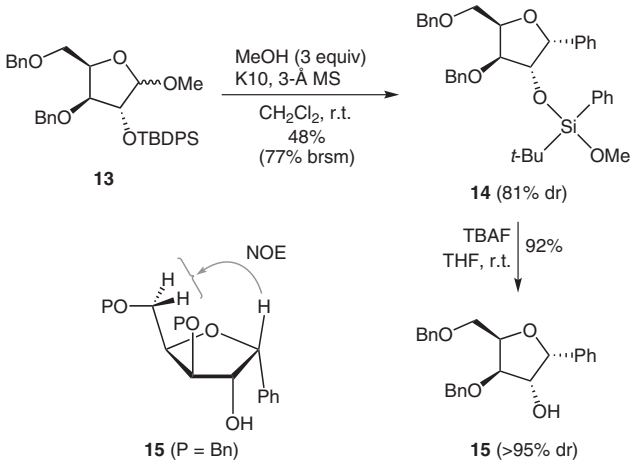
Then, we explored the aryl migration of carbohydrate derivatives leading to 1,2-*cis*-phenyl *C*-glycosides (Scheme 6). D-Xylose-derived acetal **13**[14,16] was subjected to similar conditions; this resulted in the formation of the desired phenyl *C*-xylofuranoside **14** in 48% yield (77% based on the recovered starting material) with >95% dr at the C1–C2 relationship and 81% dr at the silicon cen-



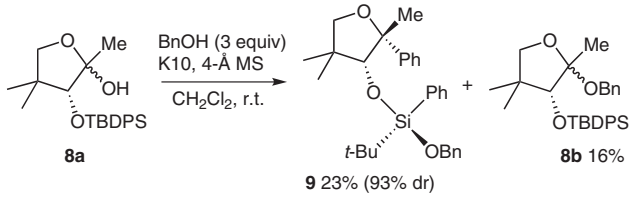
Scheme 4 Phenyl migration of cyclic hemiacetal **5** derived from (*R*)-pantolactone



Scheme 5 Phenyl migration of the six-membered benzyl acetal **10**



Scheme 6 Phenyl migration of methyl acetal **13**: stereoselective synthesis of 1,2-*cis*-phenyl *C*-xylofuranoside



Scheme 7

ter, but full consumption of the starting material was not realized.[17] The diastereomeric ratio based on the C1 and C2 stereogenic centers in **14** was determined by ^{1}H NMR analysis of the desilylated derivative **15**. The C1–C2 relative stereochemistry of **14** was determined as *cis* configuration by the NOE correlations of **15**.

In summary, we have described the aryl migration that occurs on C2 (*tert*-butyldiphenylsilyl)oxy cyclic acetal derivatives treated with alcohol under the action of K10 and 4-Å MS in a highly stereoselective manner. This reaction is an excellent method for the stereoselective synthesis of 1,2-*cis*-phenyl *C*-glycosides, since (i) TBDPSCl, a commercially available and common reagent, is a source of phenyl groups, (ii) reactive organometallic reagents are not required in the aryl migration process, and (iii) the reaction does not need extreme care about moisture, which differs from typical Lewis acid mediated aryl substitution in *O*-glycosides. Further, a combination of aryl migration and base-treatment-induced β-elimination provides an effective method for obtaining enantioenriched silanols, which are otherwise difficult to obtain.[18]

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(5) Huang and co-workers have reported the related $BF_3{\cdot}OEt_2$-promoted aryl migration in a cyclic *N*,*O*-acetal system. However, their method did not afford an aryl migration product bearing the stereochemically defined silicon center. See: Huang, P.-Q.; Liu, L.-X.; Wei, B.-G.; Ruan, Y.-P. *Org. Lett.* **2003**, *5*, 1927.

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(7) **General Procedure of the 1,4-Aryl Migration**
The 4-Å MS (580 mg) was placed in a two-necked flask and was flame dried under reduced pressure. After the contents in the flask had cooled down, the flask was purged with argon. Cyclic hemiacetal **1a** (96 mg, 0.28 mmol) and benzyl alcohol (58 μL, 0.56 mmol) in dry CH_2Cl_2 (9.5 mL) were added to the flask at 0 °C. The resulting mixture was stirred at that temperature for 30 min. Flame-dried montmorillonite K10 (482 mg) was added to the suspension. The resulting mixture was stirred at that temperature for 12 h, filtrated through a pad of Celite, and concentrated. Purification by column chromatography (silica gel, hexane–Et_2O, 12:1) afforded 86 mg (71%) of aryl migration product **2** with 90% dr.

(8) All new compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Data for selected compounds follow.
Compound **2** (90% dr at Si by ^{1}H NMR analysis): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.21 (m, 13.2 H), 7.13–7.09 (m, 1.8 H), 4.85 (d, *J* = 3.6 Hz, 0.1 H), 4.82 (d, *J* = 3.3 Hz, 0.9 H), 4.77 (d, *J* = 13.2 Hz, 1 H), 4.69 (d, *J* = 13.2 Hz, 1 H),

4.61 (br dd, *J* = 3.3, 6.0 Hz, 1 H), 4.36 (q, *J* = 7.8 Hz, 0.9 H), 4.31 (q, *J* = 8.1 Hz, 0.1 H), 4.05 (dt, *J* = 4.8, 7.8 Hz, 0.9 H), 4.03–3.97 (m, 0.1 H), 2.29–2.14 (m, 2 H), 0.88 (s, 8.1 H), 0.81 (s, 0.9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.84, 138.17, 135.42, 130.95, 129.95, 129.84, 128.35, 128.27, 128.19, 127.87, 127.80, 127.60, 127.54, 127.43, 127.04, 126.94, 125.66, 88.56, 85.42, 74.82, 74.59, 66.99, 66.84, 64.79, 64.50, 36.76, 36.58, 26.10, 26.00, 19.00, 18.70. IR (neat): 3068, 3032, 2934, 2862, 1951, 1895, 1810, 1723, 1669, 1605, 1593, 1495, 1475, 1456, 1431, 1064 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_3Si$: C, 74.96; H, 7.46. Found: C, 74.91; H, 7.20.

Compound **3a** (>95% dr by ^{1}H NMR analysis): $[\alpha]_D^{24}$ +130.3 (*c* 1.40, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.27 (m, 5 H), 4.90 (d, *J* = 3.6 Hz, 1 H), 4.41 (br s, 1 H), 4.27 (q, *J* = 8.7 Hz, 1 H), 4.03 (dt, *J* = 4.2, 8.7 Hz, 1 H), 2.28 (ddt, *J* = 13.2, 4.2, 8.7 Hz, 1 H), 2.15 (dddd, *J* = 13.2, 8.7, 4.2, 1.5 Hz, 1 H), 1.19 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.97, 128.66, 127.99, 126.80, 85.14, 73.72, 67.07, 34.93. IR (neat): 3392, 3066, 3032, 2928, 2884, 1957, 1895, 1820, 1493, 1454, 1125, 1083, 1060, 1029, 739, 700 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{10}H_{12}O_2Na$: 187.0729; found: 187.0734.

Compound **6** (93% dr at Si by ^{1}H NMR analysis): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.47 (m, 0.2 H), 7.43–7.27 (m, 10.8 H), 7.20–7.14 (m, 2 H), 6.96–6.92 (m, 2 H), 5.10 (d, *J* = 4.8 Hz, 0.07 H), 5.04 (d, *J* = 4.2 Hz, 0.93 H), 4.90 (d, *J* = 13.2 Hz, 0.93 H), 4.84 (d, *J* = 13.2 Hz, 0.93 H), 4.64 (d, *J* = 13.5 Hz, 0.07 H), 4.56 (d, *J* = 13.5 Hz, 0.07 H), 4.37 (d, *J* = 4.8 Hz, 0.07 H), 4.18 (d, *J* = 4.8 Hz, 0.93 H), 3.98 (d, *J* = 7.8 Hz, 0.93 H), 3.91 (d, *J* = 7.8 Hz, 0.07 H), 3.62 (d, *J* = 7.8 Hz, 0.93 H), 3.56 (d, *J* = 7.8 Hz, 0.07 H), 1.23 (s, 2.79 H), 1.15 (s, 2.79 H), 1.02 (s, 0.42 H), 0.86 (s, 8.37 H), 0.75 (s, 0.63 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.77, 138.54, 135.42, 131.11, 129.69, 129.08, 128.36, 127.90, 127.64, 127.51, 127.07, 125.86, 85.66, 81.97, 79.11, 65.39, 44.94, 26.52, 26.05, 21.02, 19.11. IR (neat): 3068, 3032, 2966, 2862, 1949, 1870, 1810, 1740, 1607, 1593, 1473, 1456, 1065, 733, 698 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{29}H_{36}O_3NaSi$: 483.2331; found: 483.2310.

Compound **7** (>95% dr by ^{1}H NMR analysis): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.27 (m, 5 H), 5.30 (d, *J* = 3.6 Hz, 1 H), 3.96 (d, *J* = 7.5 Hz, 1 H), 3.80 (br t, *J* = 3.0 Hz, 1 H), 3.72 (d, *J* = 7.5 Hz, 1 H), 1.21 (s, 3 H), 1.15 (s, 3 H), 1.07 (br s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.80, 128.69, 127.88, 126.73, 84.48, 80.61, 79.01, 44.21, 25.82, 19.41. IR (neat): 3342, 2960, 1950, 1900, 1830, 1466, 1309, 1096, 1038, 739, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.86; H, 8.16.

Compound **11** (90% dr at Si by ^{1}H NMR analysis): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.61 (m, 0.3 H), 7.48–7.13 (m, 10.7 H), 7.17 (t, *J* = 7.5 Hz, 2 H), 6.99 (t, *J* = 7.5 Hz, 2 H), 4.76 (d, *J* = 13.5 Hz, 1 H), 4.65 (d, *J* = 13.5 Hz, 1 H), 4.43 (s, 1 H), 4.27–4.22 (m, 1 H), 4.09 (s, 1 H), 3.90–3.80 (m, 0.1 H), 3.66 (dt, *J* = 2.6, 12.6 Hz, 0.9 H), 2.42–2.00 (m, 2 H), 1.84–1.73 (m, 1 H), 1.40 (br d, *J* = 13.5 Hz, 1 H), 0.95 (s, 8.1 H), 0.83 (s, 0.9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.02, 140.79, 135.89, 135.47, 135.39, 131.20, 129.59, 128.28, 128.17, 127.99, 127.88, 127.62, 127.51, 127.41, 127.28, 127.17, 126.93, 126.78, 126.73, 125.63, 82.58, 69.80, 69.55, 68.87, 68.77, 64.63, 31.34, 26.37, 26.31, 20.26, 19.04. IR (neat): 2930, 2856, 1961, 1898, 1808, 1453, 1115, 1098, 1071, 1026 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{28}H_{34}O_3NaSi$: 469.2169; found: 469.2159.

Compound **12** (>95% dr by ^{1}H NMR analysis): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 5 H), 4.50 (d, *J* = 1.2 Hz, 1 H), 4.18 (ddt, *J* = 11.1, 4.5, 1.8 Hz, 1 H), 3.94–3.91 (m, 1 H), 3.65 (ddd, *J* = 12.3, 11.1, 2.4 Hz, 1 H), 2.17–2.02 (m, 2 H), 1.92–1.78 (m, 1 H), 1.72 (d, *J* = 5.4 Hz, 1 H), 1.48–1.42 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.64, 128.49, 127.52, 125.81, 81.18, 68.96, 68.01, 30.25, 19.92. IR (neat): 3454, 2947, 2849, 1958, 1887, 1813, 1451, 1267, 1216, 1091, 1057, 1003, 725, 699 cm^{-1}.

Compound **13** (63% dr by ^{1}H NMR analysis): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.65 (m, 4.14 H), 7.50–7.21 (m, 14.6 H), 7.11–7.07 (m, 1.26 H), 4.86 (s, 0.63 H), 4.63–4.58 (m, 0.37 H), 4.62 (d, *J* = 12.0 Hz, 0.63 H), 4.59 (d, *J* = 11.7 Hz, 0.37 H), 4.57 (d, *J* = 11.7 Hz, 0.37 H), 4.54 (d, *J* = 12.0 Hz, 0.63 H), 4.51 (d, *J* = 11.7 Hz, 0.37 H), 4.46 (d, *J* = 11.7 Hz, 0.37 H), 4.39 (dt, *J* = 6.3, 3.9 Hz, 0.37 H), 4.35–4.27 (m, 1.63 H), 4.20 (d, *J* = 12.3 Hz, 0.63 H), 4.18 (d, *J* = 3.9 Hz, 0.37 H), 3.95 (d, *J* = 12.3 Hz, 0.63 H), 3.82 (br dd, *J* = 5.1, 1.2 Hz, 0.63 H), 3.74 (dd, *J* = 10.2, 5.1 Hz, 0.63 H), 3.70 (dd, *J* = 10.2, 6.9 Hz, 0.63 H), 3.66 (dd, *J* = 10.5, 3.9 Hz, 0.37 H), 3.51 (dd, *J* = 10.5, 6.3 Hz, 0.37 H), 3.24 (s, 1.11 H), 3.23 (s, 1.89 H), 1.12 (s, 3.33 H), 1.09 (s, 5.67 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.38, 138.25, 138.28, 138.07, 136.08, 135.90, 134.87, 133.80, 133.40, 133.22, 133.15, 130.08, 129.85, 129.79, 128.38, 128.32, 128.24, 127.91, 127.83, 127.70, 127.62, 127.56, 127.49, 127.44, 110.49, 101.59, 83.54, 83.46, 81.02, 79.96, 78.01, 75.55, 73.54, 73.48, 73.27, 71.49, 69.90, 69.68, 26.98, 26.95, 19.22. IR (neat): 3072, 3034, 2934, 2862, 1963, 1891, 1827, 1473, 1456, 1429, 1112, 1060, 822, 739, 700 cm^{-1}. Anal. Calcd for $C_{36}H_{42}O_5Si$: C, 74.19; H, 7.26. Found: C, 74.38; H, 7.36.

Compound **14** (81% dr at Si by ^{1}H NMR analysis): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 1.5 Hz, 0.19 H), 7.54 (d, *J* = 1.5 Hz, 0.19 H), 7.47–7.12 (m, 18 H), 6.98 (d, *J* = 1.5 Hz, 0.81 H), 6.95 (d, *J* = 1.5 Hz, 0.81 H), 5.22 (d, *J* = 3.0 Hz, 0.19 H), 5.20 (d, *J* = 3.0 Hz, 0.81 H), 4.76 (dt, *J* = 3.6, 6.0 Hz, 1 H), 4.70 (d, *J* = 12.0 Hz, 0.81 H), 4.68 (d, *J* = 12.0 Hz, 0.19 H), 4.57 (d, *J* = 12.0 Hz, 0.81 H), 4.56 (d, *J* = 12.0 Hz, 0.81 H), 4.55 (d, *J* = 12.0 Hz, 0.19 H), 4.45 (d, *J* = 12.0 Hz, 0.81 H), 4.42 (dd, *J* = 3.3, 0.9 Hz, 0.19 H), 4.36 (dd, *J* = 2.7, 1.2 Hz, 0.81 H), 4.33 (d, *J* = 12.0 Hz, 0.19 H), 4.21 (d, *J* = 12.0 Hz, 0.19 H), 4.18 (dd, *J* = 3.6, 1.2 Hz, 0.81 H), 4.05 (dd, *J* = 3.6, 1.2 Hz, 0.19 H), 3.85 (dd, *J* = 9.9, 6.0 Hz, 0.81 H), 3.81 (dd, *J* = 9.9, 6.0 Hz, 0.81 H), 3.78 (d, *J* = 6.0 Hz, 0.38 H), 3.47 (s, 2.43 H), 3.07 (s, 0.57 H), 0.79 (s, 7.29 H), 0.77 (s, 1.71 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.38, 138.04, 137.54, 135.37, 130.55, 130.13, 129.90, 128.43, 128.15, 128.07, 127.98, 127.93, 127.78, 127.62, 127.57, 127.48, 127.35, 85.32, 85.09, 83.44, 80.04, 79.75, 77.17, 73.69, 72.31, 69.08, 51.96, 26.21, 25.97, 18.62. IR (neat): 3068, 3032, 2934, 2862, 1953, 1890, 1810, 1087 cm^{-1}. Anal. Calcd for $C_{36}H_{42}O_5Si$: C, 74.19; H, 7.26. Found: C, 74.09; H, 7.09.

Compound **15** (>95% dr by ^{1}H NMR analysis): $[\alpha]_D^{24}$ –63.2 (*c* 1.07, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 15 H), 5.33 (d, *J* = 3.3 Hz, 1 H), 4.72 (d, *J* = 12.0 Hz, 1 H), 4.69 (d, *J* = 12.3 Hz, 1 H), 4.67 (ddd, *J* = 6.6, 5.7, 4.2 Hz, 1 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4,57 (d, *J* = 12.3 Hz, 1 H), 4.27 (br s, 1 H), 4.17 (br dd, *J* = 4.2, 1.2 Hz, 1 H), 3.84 (dd, *J* = 9.9, 5.7 Hz, 1 H), 3.80 (dd, *J* = 9.9, 6.6 Hz, 1 H), 1.27 (br s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.41, 138.05, 136.36, 128.74, 128.53, 128.43, 128.14, 127.86, 127.64, 127.57, 126.83, 84.19, 83.01, 80.21, 76.45, 73.56, 72.70, 68.88. IR (neat): 3432, 3066, 3032, 2924, 2870, 1955, 1883, 1814, 1497, 1456, 1083, 737, 698 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{25}H_{26}O_4Na$: 413.1723; found: 413.1707.

(9) Benzyl acetal **1b** was prepared from cyclic hemiacetal **1a** and benzyl alcohol in the presence of a catalytic amount of PPTS.

(10) The stereochemistry and ee of benzyloxysilanol (*S*)-**4** was established by chiral HPLC analysis [CHIRALCEL OD column, hexane–*i*-PrOH = 150:1, flow rate = 0.6 mL/min, detection 254 nm light; t_R = 36.5 (major isomer), 41.9 min (minor isomer)].

(11) A few synthetic methods for enantioenriched silanol have been reported. For resolution or separation of racemic or diastereomeric silanols, see: (a) Tacke, R.; Linoh, H.; Ernst, L.; Moser, U.; Mutschler, E.; Sarge, S.; Cammenga, H. K.; Lambrecht, G. *Chem. Ber.* **1987**, *120*, 1229. (b) Yamamoto, K.; Kawanami, Y.; Miyazawa, M. *J. Chem. Soc., Chem. Commun.* **1993**, 436. (c) Feibush, B.; Woolley, C. L.; Mani, V. *Anal. Chem.* **1993**, *65*, 1130. (d) Mori, A.; Toriyama, F.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1999**, 549. (e) Yamamura, Y.; Toriyama, F.; Kondo, T.; Mori, A. *Tetrahedron: Asymmetry* **2002**, *13*, 13. For stereospecific oxidation of enantioenriched silanes or halosilanes, see: (f) Cavicchioli, M.; Montanari, V.; Resnati, G. *Tetrahedron Lett.* **1994**, *35*, 6329. (g) Adam, W.; Mitchell, C. M.; Saha-Möller, C. R.; Weichold, O. *J. Am. Chem. Soc.* **1999**, *121*, 2097; and references therein.

(12) All spectral data of **7** matched with those reported in the following literature: Angle, S. R.; Neitzel, M. L. *J. Org. Chem.* **1999**, *64*, 8754.

(13) A similar reaction of hemiketal **8a** provided the corresponding phenyl migration product **9** in 93% dr, albeit in low yield. The stereochemistry of **9** was assumed on the basis of the reaction mechanism (Scheme 7).

(14) Due to their ease of preparation, we chose acetals **10** and **13** as substrates, rather than the corresponding hemiacetals.

(15) All spectral data of **12** matched those reported in the following literature: Schmidt, B. *J. Org. Chem.* **2004**, *69*, 7672.

(16) Methyl acetal **13** was prepared from D-xylose in five steps: (1) acetone, cat. H_2SO_4, (2) 0.2% aq HCl, 97% (two steps), (3) NaH, BnBr, 87%, (4) cat. H_2SO_4, MeOH, 96%, and (5) TBDPSCl, imidazole, 72%. (a) Levene, P. A.; Raymond, A. L. *J. Biol. Chem.* **1933**, *102*, 317. (b) Baker, B. R.; Schaub, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 5900. (c) Martin, O. R.; Rao, S. P.; El-Shenawy, H. A.; Kurz, K. G.; Cutler, A. B. *J. Org. Chem.* **1988**, *53*, 3287.

(17) The starting material **13** was not consumed after 2 d at r.t.

(18) We have already demonstrated that enantioenriched silanol bearing allyloxy group can be converted into a chiral allylsilane, which is a more useful and versatile chiral building block. See: Nakazaki, A.; Nakai, T.; Tomooka, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2235.