The Regioselective Mono-deprotection of 1,3-Dioxa-2,2-(di-*tert*-butyl)-2-silacyclohexanes with BF_3·SMe_2

Ming Yu and Brian L. Pagenkopf*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

pagenkopf@mail.utexas.edu

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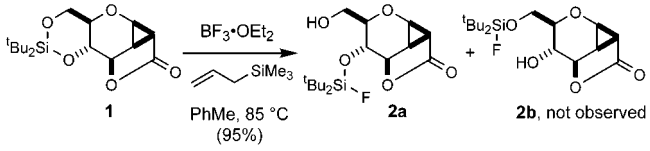
The selective mono-deprotection of di-*tert*-butylsilylene ethers prepared from substituted 1,3-pentanediols and 2,4-hexanediols has been achieved with BF_3·SMe_2. The reaction conditions are compatible with esters, allyl ethers, and TIPS ethers. The resulting di-*tert*-butylfluorosilyl ethers are stable to various conditions including low pH aqueous solutions and silica gel chromatography; the di-*tert*-butylfluorosilyl ethers are readily cleaved with HF−pyridine. Substrate stereochemistry and conformation influences the efficiency of the deprotection, while the deprotection regiochemistry is consistent with coordination of boron to the sterically more accessible oxygen prior to intramolecular delivery of fluoride.

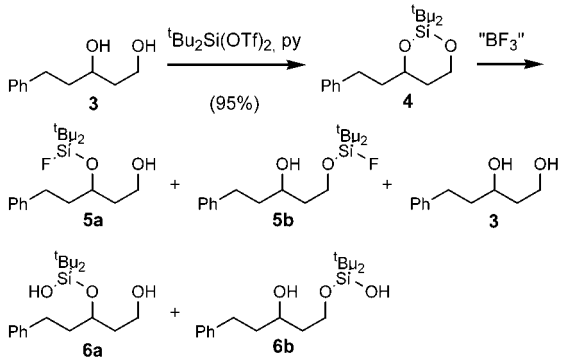
Introduction

The installation of protecting groups at the more hindered hydroxyl of 1,3-diols is frequently required in organic synthesis, but is not generally available by direct methods.[1] The task is often accomplished through multistep transformations, as with the hydridic cleavage of benzylidene acetals. Silylation at the more hindered site of a 1,3-diol is likewise complicated because standard conditions result in preferential reaction at the less hindered hydroxyl group.[2] The increased reactivity at the more accessible position normally permits selective deprotection at the less hindered site of a persilylated substrate.[3] A few reports have appeared regarding the ring opening of di-*tert*-butyl-, dicyclohexyl-, and diphenylsilylene ethers of 1,3- and 1,2-diols with Grignard or alkyllithium reagents.[4,5] Additionally, haloboranes are known to deprotect silyl ethers,[6,7] and have been used for the regioselective desilylation of *tert*-butyldimethylsilyl ethers.[8] We recently reported the highly regioselective mono-deprotection of the di-*tert*-butylsilylene ether **1** with BF_3·OEt_2 (85 °C, toluene), which gave exclusively the di-*tert*-butylfluoro silyl ether **2a** (Scheme 1).[9] In this Paper we illuminate some of the structural and chemical parameters that influence the mono-deprotection of $^tBu_2$-Si(OR)$_2$ ethers, describe the reactivity of the (F)$^tBu_2$Si hydroxyl protecting group, and explore the compatibility of the method with other functionality.

Scheme 1



Scheme 2



Results and Discussion

The di-*tert*-butylsilylene ether **4**,[10] which like **1** was prepared from a primary and a secondary 1,3-diol, was selected as a model substrate to explore the generality of the BF_3·OEt_2-mediated deprotection (Scheme 2). Using conditions similar to those utilized for **1**,[11] the reaction with **4** provided the desired fluorosilane **5a** along with a

(1) (a) Green, W. P.; Wuts, P. G. M.; *Protective Groups in Organic Synthesis*; Wiley: Toronto, 1999. (b) Kociensky, P. J. *Protecting Groups*; Thieme: Stuttgart, 1994.

(2) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, *20*, 99−102.

(3) (a) Boschelli, D.; Takemasa, Y.; Nishitani, Y.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 5239−5244. (b) Crimmins, M. T.; Lever, J. G. *Tetrahedron Lett.* **1986**, *27*, 291−294.

(4) The 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl protecting group can be regioselectively mono-deprotected at the less hindered site: (a) Zhu, X. F.; Williams, H. J.; Scott, A. I. *Tetrahedron Lett.* **2000**, *41*, 9541−9545. (b) Pankiewicz, K. W.; Watanabe, K. A.; Takayanagi, H.; Itoh, T.; Ogura, H. *J. Het. Chem.* **1985**, *22*, 1703−1710.

(5) Tanino, K.; Shimizu, T.; Kuwahara, M.; Kuwajima, I. *J. Org. Chem.* **1998**, *63*, 2422−2423.

(6) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190−6191.

(7) Kelly, D. R.; Roberts, S. M.; Newton, R. F. *Synth. Commun.* **1979**, *9*, 295−299.

(8) Yang, Y,-Y.; Yang, W.,-B.; Teo, C.-F.; Lin, C.-H. *Synlett* **2000**, 1634−1636.

(9) Yu, M.; Lynch, V.; Pagenkopf, B. L. *Org. Lett.* **2001**, *3*, 2563−2566.

(10) Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 4871−4874.

(11) The addition of allyl trimethylsilane to the reaction minimizes the formation of side products during the first few seconds after the addition of BF_3 and is presumably serving as a kinetically fast trap for HF.

10.1021/jo025624x CCC: $22.00
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Scheme 3

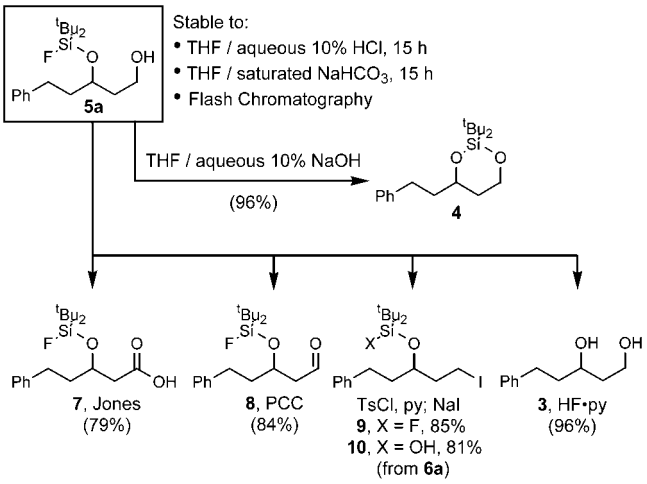
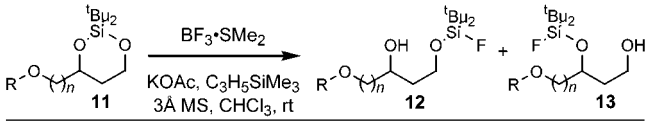


Table 1. Deprotection of Di-*tert*-butylsilylene Ethers in the Presence of Other Functionality



entry	*n*	R	product	yield, %[a]
a	2	H	-	decomp
b	1	CH_3CO	**13b**	91[b]
c	2	CH_3CO	**13c**	87
d	1	PhCO	**13d**	90
e	2	PhCO	**13e**	82
f	2	Allyl	**13f**	78[c]
g	2	$PhCH_2$	**11g**, **13g**	57, 35
h	2	CH_3	**11a**, **13h**	50, 43
i	2	$(i\text{Pr})_3\text{Si}$	**13i**	78%
j	2	$(t\text{Bu})\text{Me}_2\text{Si}$	**11a**	97%

[a] Isolated yields. [b] 8% of the isomeric fluorosilane **12b** was detected in the crude ^{19}F NMR. [c] 4% of **12f**.

disappointing mixture of its regioisomer **5b**, silanols **6a** and **6b**, diol **3**, and unreacted starting material. The addition of 3 Å molecular sieves to the reaction prevented the formation of silanols **6a** and **6b**, which were likely due to interaction with adventitious water. The screening of other commercially available BF_3−Lewis base complexes, including BF_3•THF, BF_3•^{t}BuOMe, and BF_3•MeOH, revealed that BF_3•SMe_2 improved both the conversion and selectivity of the reaction. However, the formation of considerable amounts of diol **3** continued to plague the process. The varying reactivity displayed by different BF_3 sources clearly demonstrated the importance of Lewis bases in the reaction, and a survey of assorted adjuncts including esters, ethers, amines, and salts showed that the addition of excess anhydrous potassium acetate to the reaction greatly minimized complete desilylation to diol **3**.[12] Replacing the toluene solvent with chloroform or hexane further minimized formation of diol **3**. With these modifications, the regioselective deprotection of **4** with BF_3•SMe_2 consistently gave the fluorosilanes **5a**:**5b** in a >15:1 ratio and 79−85% isolated yields.[13]

Although the selective deprotection of **4** under optimized conditions was promising, for this new transformation to be of value the fluorosilane products must be sufficiently robust to serve as viable protecting groups in subsequent reactions. In this regard, the fluorosilane **2a** survived several synthetic steps and flash chromatography.[9] Likewise, the fluorosilane **5a** was stable to aqueous acid for 15 h (THF, 10% aqueous HCl) and neutral solutions (THF, saturated $NaHCO_3$) (Scheme 3); however, more strongly basic conditions resulted in closure to the silylene ether **4** (THF, 10% aqueous NaOH, 15 min, 96%). Several transformations at the primary alcohol of the fluorosilane **5a** illustrate the stability of the (F)^{t}Bu$_2$Si group, including Jones oxidation, PCC oxidation, and Finkelstein reaction. The silanol **6a** was also fairly stable, as demonstrated by its conversion to **10** in 81% yield. The di-*tert*-butylfluoro silane **5a** can be easily cleaved to the diol **3** with HF•pyridine (**5a** → **3**, 96%).[14]

With the integrity of the di-*tert*-butylfluorosilane ether amply demonstrated, substrate compatibility and availability of orthogonal protective functions was briefly surveyed. As anticipated, the Lewis acidic nature of the reaction media precluded the use of substrates with Lewis acid sensitive functionality. For example, at its current state of development, silylene ethers prepared from tertiary or benzylic alcohols predominately undergo elimination under the deprotection reaction conditions. The model substrates **11a**−**j** shown in Table 1 were used to explore the functional group orthogonality between a di-*tert*-butylsilylene ether and several common protective groups. Acetate and benzoate esters are highly compatible with the deprotection conditions (entries b−e), and no diminution of regioselectivity at the silylene ether (i.e., **12** vs **13**) was observed,[13] as might have occurred if complicated by neighboring group participation of the ester functionality. An allyl group easily survived the reaction conditions, as did benzyl, but the reaction with **11g** failed to go to completion. With **11h** selectivity between the methyl and silylene ethers was poor (entry h). The bulky triisopropylsilyl ether was unaffected during the deprotection with BF_3•SMe_2, whereas cleavage of the *tert*-butyl dimethylsilyl ether demarcates silicon reactivity (entries i and j).

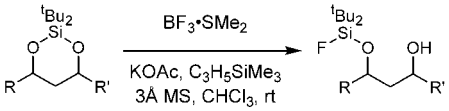
To ascertain whether deprotection could succeed selectively when challenged with substrates presenting less steric differentiation, silylene ethers derived from two secondary alcohols were examined (Table 2). In entries 1 and 2 a methyl and *tert*-butyl group were compared, and each reaction provided exclusively one isomeric fluorosilane.[13] The syn diastereomer (entry 2) required nearly three times as long (2.5 h) for complete consumption of starting material than did the anti diastereomer, and a third of the starting material was fully desilylated. Stopping the reaction in entry 2 prematurely before significant amounts of diol formed increased the yield to 79%, based on recovered starting material. Analogous results occurred with the anti and syn substrates shown in entries 3 and 4. Again, reaction with the syn diastereomer (entry 4) gave nearly 30% of unwanted diol when allowed to proceed until complete consumption of starting

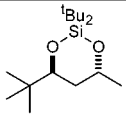
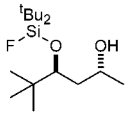
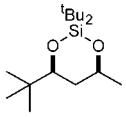
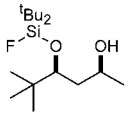
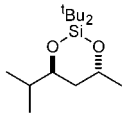
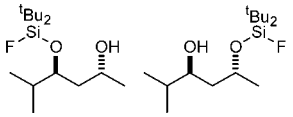
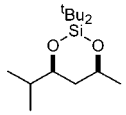
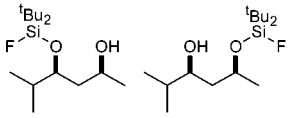
(12) The exact role of the KOAc is unclear, and related salts that proved less effective include NaOAc, CsOAc, *n*-$C_{15}H_{31}CO_2K$, $PhCO_2$-Na, $PhCO_2K$, Na_2CO_3, K_2CO_3. Sodium 2-ethylhexanoate performed similarly to KOAc.

(13) Regiochemistry was determined by oxidation to the ketone/aldehyde or conversion of the alcohol to the iodide, cf., **8** and **9**. See Supporting Information.

(14) Trost, B. M.; Caldwell, C. G. *Tetrahedron Lett.* **1981**, *22*, 4999−5002.

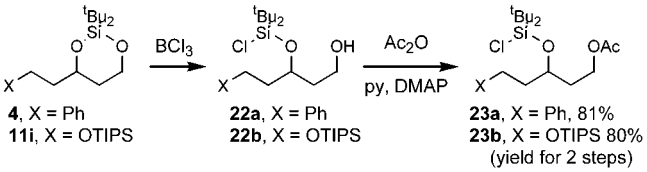
Table 2. Deprotection of Di-*tert*-butylsilylene Ethers Prepared from 2,4-Hexanediols



entry	silylene ether	product(s), (ratio)[a]	Yield[b]
1	 **14**	 **15**	93%
2	 **16**	 **17**	64%[c]
3	 **18**	 **19a** (6:1) **19b**	89%
4	 **20**	 **21a** (6:1) **21b**	43%

[a] Ratio determined by ^{19}F NMR of crude reaction mixtures, see ref 13. [b] Isolated yields, averaged from two runs. [c] 79% yield based on recovered starting material.

Scheme 4



material. These experiments revealed that stereochemistry greatly influenced the efficiency of the desilylation reaction.

While cleavage of silyl ethers with BCl_3 is known,[8] it is interesting to note that selective mono-desilylation of the di-*tert*-butylsilylene ether **4** and **11i** occurred cleanly with BCl_3 (Scheme 4). However, the chlorosilanes had to be characterized as their acetates **23**, as the reactive free alcohols **22** reverted back to starting material (with up to 15% silanol formation) under acidic, neutral or basic conditions, including simply standing in $CDCl_3$ or methanol. The instability displayed by the chlorosilanes discouraged further investigation at this stage.

The regiochemistry observed in these selective deprotections was consistent with coordination of the boron to the more sterically accessible oxygen prior to delivery of fluoride.[15] For the syn diastereomers coordination by boron to the sterically more accessible α (equatorial) lone pair of the oxygen (**24**, Figure 1) might be expected as a

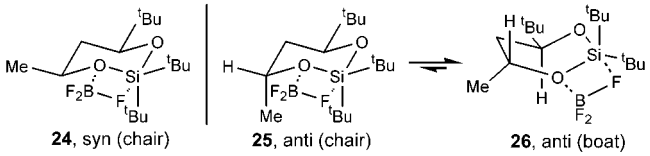


Figure 1. Low energy reactive conformations.

key reaction intermediate. In an idealized chair conformation the equatorial oxygen lone pair would be antiperiplanar to the σ_{Si-O} bond of the other oxygen while positioning fluoride sufficiently close to donate electron density into an available orbital on silicon.[16] For the anti diastereomer in a chair conformation unfavorable 1,3-diaxial interactions exist between the axial methyl and a *tert*-butyl group on silicon, and molecular models suggested a boat (**26**) for the lower energy conformation where both the ring methyl and *tert*-butyl groups occupy quasi-equatorial positions.[17] In the boat conformation **26**, the boron can coordinate to the β or quasi-equatorial lone pair without severe steric crowding. The higher temperatures necessary for the deprotection of **1** (85 °C) along with the results in Table 2 suggest that conformational freedom to permit favorable orbital alignment may be key to efficient deprotection.

The initial difficulties encountered during the deprotection of **4** (Scheme 2) indicate the delicate balance between the rate of the mono-deprotection and the rate of the second desilylation leading to diol **3**. We speculate that the transition state corresponding to conformation **24** is higher in energy than for the anti diastereomer (**26**). The longer reaction times necessary for consumption of the syn diastereomers **16** and **20** allows the second desilylation event to become competitive in these reactions.

In conclusion, parameters influencing the regioselective mono-desilylation of di-*tert*-butylsilylene ethers using BF_3•SMe_2 have been elucidated. The reaction can be efficient, highly selective and provide access to 1,3-diols silylated at the sterically more hindered position. This new method is likely to see continued use in total synthesis.

Experimental Section

All reactions were run under an atmosphere of argon unless otherwise indicated. Reaction vessels were oven or flame-dried and allowed to cool in a drybox or desiccator prior to use. Solvents and reagents were purified by standard methods.[18] $CHCl_3$ was purified by distillation from CaH_2 and stored

(15) Denmark, S. E.; Willson, T. M.; Almstead, N. G. *J. Am. Chem. Soc.* **1989**, *111*, 9258−9260.

(16) For a discussion of the precise orbitals that might be involved in this process the reader is referred to reviews on extracoordinate silicon chemistry: Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000, Chapter 2 and Chapter 5. Nucleophilic displacement at silanes with endocyclic leaving groups often occurs with retention. See: Bassindale, A. R.; Taylor, P. G. Reaction Mechanisms of Nucleophilic Attack at Silicon. In *The Chemistry of Organosilicon Compounds*; Patai, S.; Rappoport, Z.; Eds., Wiley: Chichester, UK, 1989; Vol. 1, Chapter 14. (b) Bassindale, A. R.; Taylor, P. G. Reaction Mechanisms of Nucleophilic Attack at Silicon. In *The Chemistry of Organosilicon Compounds*; Patai, S.; Rappoport, Z.; Eds., Wiley: Chichester, UK, 1988; Vol. 2, Chapter 9.

(17) Molecular modeling with Spartan software predicted that the ground state conformation for both the syn and anti diastereomers is best described as a half chair given the small dihedral angles for the C_{Me}−O−Si−O bond in the syn (+9°, chair) and anti (−10°, boat) diastereomers.

(18) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Oxford: Butterworth Heinemann, 1996.

over Na_2CO_3 under an Ar atmosphere in the dark. $BF_3{\cdot}SMe_2$ (Alfa-Aesar) and BCl_3 in heptane (Aldrich) were used as received from commercial sources. Powdered KOAc was flame dried as a melt under vacuum (0.1 mmHg). Thin-layer chromatography (TLC) was performed on EM 250 Kieselgel 60 F254 silica gel plates. The plates were visualized by staining with I_2 on silica, CAM,[19] ninhydrin, or potassium permanganate. Column chromatography was performed with silica gel 60 according to the method of Still.[20]

2,2-Di-*tert*-butyl-4-phenethyl-[1,3,2]-dioxasilinane (4). To a solution of diol **3**[21] (2.59 g, 14.4 mmol) in THF:Me_2NCHO (2:1, 30 mL) cooled to −30 °C was added $^tBu_2Si(OTf)_2$ (5.80 mL, 15.8 mmol) dropwise over 15 min. After 25 min the reaction mixture was neutralized with pyridine (2.40 mL, 30.0 mmol), allowed to warm to room temperature, and diluted with Et_2O (150 mL). The reaction mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, dried ($MgSO_4$), and filtered through Celite. Volatiles were removed under reduced pressure, and the residue was purified by flash chromatography on silica gel using 20:1 hexanes−EtOAc for elution to provide the title compound as a colorless oil (4.01 g, 87%). R_f 0.70 (5% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.20 (m, 5H), 4.12−4.02 (m, 3H), 2.90−2.71 (m, 2H), 1.93−1.73 (m, 3H), 1.62 (dd, J = 14.1, 1.5 Hz, 1H), 1.08 (d, J = 1.2 Hz, 9H), 1.06 (d, J = 1.2 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 128.8, 128.5, 125.9, 73.0, 64.5, 40.7, 36.8, 31.6, 27.7, 27.4, 22.9, 20.1; HRMS m/z calcd for $C_{19}H_{32}O_2Si$ [M + H]$^+$ 321.1150, found: 321.2248.

3-(Di-*tert*-butyl-fluoro-silanyloxy)-5-phenyl-pentan-1-ol (5a). To a 10-mL round-bottomed flask containing **4** (350 mg, 1.09 mmol) were added KOAc (300 mg, 3.0 mmol) and freshly activated molecular sieves (3 Å, 250 mg). The flask was sealed with a rubber septum, flushed with argon, and treated sequentially with $CHCl_3$ (2.5 mL), allyl trimethylsilane (35 μL, 0.20 mmol), and $BF_3{\cdot}Me_2S$ (860 μL, 8.2 mmol, 7.5 equiv). After 5.5 h the mono-deprotection was complete (TLC), and the reaction mixture was transferred into a vigorously stirred saturated $NaHCO_3$ solution (10 mL) with the aid of CH_2Cl_2. The heterogeneous solution was filtered through a glass frit, and the organic layer was separated and washed with H_2O, brine, and dried ($MgSO_4$). After filtration through a small pad of Celite, volatiles were removed under reduced pressure. Purification of the residual oil by flash chromatography on silica gel with 15:1 hexanes−EtOAc for elution afforded the title compound as a colorless oil (301 mg, 81%). R_f 0.61 (33% EtOAc/hexanes); IR (thin film) ν 3450 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.21 (m, 5H), 4.42−4.38 (dddd, J = 5.3, 5.3, 5.3, 5.3 Hz, 1H), 3.92−3.79 (m, 2H), 2.77−2.72 (m, 2H), 2.36 (br s, 1H), 2.10−1.84 (m, 5H), 1.13 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4 (C), 128.7 (CH), 128.6 (CH), 126.1 (CH), 72.0 (CH), 59.7 (CH_2), 39.1 (CH_2), 38.9 (CH_2), 31.5 (CH_2), 27.4 (CH_3), 20.7 (d, J = 15.1 Hz, C), 20.4 (d, J = 15.1 Hz, C); ^{19}F NMR (300 MHz, $CDCl_3$) δ −158.7; HRMS m/z calcd for $C_{19}H_{33}FO_2Si$ [M + H]$^+$ 341.2312, found: 341.2323.

3-(Di-*tert*-butyl-fluoro-silanyloxy)-5-phenylpentanoic Acid (7). To a room temperature solution of **5a** (150 mg, 0.44 mmol) in acetone (3.5 mL) was added Jones reagent[22] dropwise until a brown color persisted. The resulting solution was then treated with 2-propanol dropwise until the solution became green-blue. To the reaction mixture was added H_2O, and the organic solvent was removed under reduced pressure. The residue was redissolved in Et_2O, and the solution was washed with saturated $NaHCO_3$ solution, H_2O, and brine and dried ($MgSO_4$). The solution was filtered through Celite, and volatiles were removed under reduced pressure. Purification of the residual oil by flash chromatography on silica gel with 15:1 hexanes−EtOAc for elution provided the title compound as a yellow oil (112 mg, 72%). R_f 0.34 (50% EtOAc/hexanes); IR (thin film) ν 3110 (br), 1738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.19 (m, 5H), 4.61 (dddd, J = 5.9, 5.9, 5.9, 5.9 Hz, 1H), 2.78−2.63 (m, 4H), 2.03−1.95 (m, 2H), 1.07 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 141.9, 128.7, 128.6, 126.2, 70.7, 42.1, 39.1, 31.3, 27.25, 27.21, 20.5 (d, J = 15.3 Hz), 20.4 (d, J = 15.3 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) δ −158.8; HRMS m/z calcd for $C_{19}H_{31}FO_3Si$ [M + H]$^+$ 355.2105, found: 355.2100.

3-(Di-*tert*-butyl-fluoro-silanyloxy)-5-phenylpentanal (8). To a room temperature suspension of pyridinium chlorochromate (133 mg, 0.62 mmol) in CH_2Cl_2 (3.5 mL) was added a solution of **5a** (60 mg, 0.18 mmol) in CH_2Cl_2 (1.2 mL). After 2.5 h florisil and Et_2O (5 mL) were added to the reaction mixture, which was subsequently filtered through florisil. The volatile components were removed under reduced pressure and purification of the residue by flash chromatography on silica gel (20:1 hexanes−EtOAc for elution) provided the title compound as a colorless oil (109 mg, 82%). R_f 0.65 (25% EtOAc/hexanes); IR (thin film) ν 1722 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (dd, J = 2.3, 2.3 Hz, 1H), 7.34−7.20 (m, 5H), 4.66 (dddd, J = 5.8, 5.8, 5.8, 5.8 Hz, 1H), 2.78−2.69 (m, 4H), 2.00 (ddd, J = 5.8, 2.9, 2.9 Hz, 2H), 1.07 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 141.7, 128.7, 128.6, 126.3, 69.6, 50.7, 39.4, 31.5, 27.2, 20.6, 20.4; ^{19}F NMR (300 MHz, $CDCl_3$) δ −159.1; HRMS m/z calcd for $C_{19}H_3F_1O_2Si$ [M + H]$^+$ 339.2156, found: 339.2158.

Di-*tert*-butyl-fluoro-(3-iodo-1-phenethyl-propoxy)silane (9). To a room temperature solution of **5a** (160 mg, 0.47 mmol) and *p*-toluenesulfonyl chloride (106 mg, 0.59 mmol) in CH_2Cl_2 (4.5 mL) was added pyridine (0.5 mL, 6.2 mmol) in one portion. The resulting solution was stirred at room temperature for 20 h, and then volatiles were removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2, and the solution was washed with saturated $NaHCO_3$ solution, H_2O, and brine and dried ($MgSO_4$). After filtration through a pad of Celite, volatiles were removed under reduced pressure, and the residue was dissolved in a mixture of acetone (4.5 mL) and NaI (720 mg, 4.8 mmol, 10.0 equiv). After 30 h at reflux, the cooled reaction mixture was treated with saturated $NaHCO_3$ solution, and the acetone was removed under reduced pressure. The resulting mixture was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine and dried ($MgSO_4$). After filtration through a pad of Celite, volatiles were removed under reduced pressure. Purification of the residual oil by flash chromatography on silica gel with 15:1 hexanes−EtOAc for elution provided the title compound as a pale yellow syrup (180 mg, 85%). R_f 0.57 (15% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.19 (m, 5H), 4.23 (dddd, J = 6.5, 6.5, 6.5, 6.5 Hz, 1H), 3.30 (t, J = 7.2 Hz, 2H), 2.74−2.68 (m, 2H), 2.17 (ddd, J = 7.2, 7.2, 7.2 Hz, 2H), 1.96−1.89 (m, 2H), 1.08 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1 (C), 128.7 (CH), 128.6 (CH), 126.1 (CH), 74.0 (CH), 41.0 (CH_2), 38.5 (CH_2), 31.3 (CH_2), 27.4 (CH_3), 27.3 (CH_3), 20.6 (C), 20.4 (C), 1.9 (CH_2); ^{19}F NMR (300 MHz, $CDCl_3$) δ −157.9; HRMS m/z calcd for $C_{19}H_{32}FIOSi$ [M + H]$^+$ 451.1330, found: 451.1334.

Acetic Acid 2,2-Di-*tert*-butyl-[1,3,2]dioxasilinan-4-ylmethyl Ester (11b). To a solution of (2,2-di-*tert*-butyl-[1,3,2]-dioxasilinan-4-yl)methanol[23] (2.52 g, 10.2 mmol) in CH_2Cl_2 (22 mL) was added pyridine (2.41 mL, 29.7 mmol) and Ac_2O (4.33 mL, 45.9 mmol). After 15 h at room temperature, the mixture was poured into a vigorously stirred saturated $NaHCO_3$ solution (20 mL). The organic layer was separated and washed with saturated NH_4Cl solution, H_2O, and brine, dried ($MgSO_4$), and filtered through Celite. Volatile components were removed under reduced pressure, and the residual oil was purified by flash chromatography on silica gel using 15:1 hexanes−EtOAc for elution to provide the title compound as a pale yellow oil (2.70 g, 92%). R_f 0.35 (15% EtOAc/hexanes); IR (thin film) ν 1744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31−4.27 (m, 1H), 4.13−4.08 (m, 3H), 4.03 (ddd, J = 11.0, 5.2, 1.0 Hz, 1H), 2.06

(19) See footnote 50 in: Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765−5780.

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(s, 3H), 1.95−1.81 (m, 1H), 1.66 (ddd, J = 14.1, 4.1, 1.5 Hz, 1H), 1.01 (s, 9H), 0.98 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 71.9, 68.4, 63.9, 33.1, 27.5, 27.2, 22.8, 21.1, 20.1; HRMS m/z calcd for $C_{14}H_{28}O_4Si$ $[M + H]^+$ 289.1835, found: 289.1833.

Benzoic Acid 2,2-Di-*tert*-butyl-[1,3,2]dioxasilinan-4-ylmethyl Ester (11d). To a solution of(2,2-di-*tert*-butyl-[1,3,2]-dioxasilinan-4-yl)methanol[23] (1.76 g, 7.2 mmol) in CH_2Cl_2 (20 mL) was added pyridine (1.00 mL, 12.3 mmol) and benzoyl chloride (2.51 mL, 21.6 mmol). After stirring for 13 h at room temperature the mixture was worked up as described for **11b**. Purification of the residual oil by flash chromatography on silica gel using 18:1 hexanes−EtOAc for elution provided the title compound as a colorless oil (2.23 g, 89%). R_f 0.45 (20% EtOAc/hexanes); IR (thin film) ν 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10−8.06 (m, 2H), 7.62−7.58 (m, 1H), 7.57−7.44 (m, 2H), 4.49−4.38 (m, 2H), 4.33−4.26 (m, 1H), 4.18 (ddd, J = 7.8, 2.5, 2.5 Hz, 2H), 2.06−1.94 (m, 1H), 1.79 (ddd, J = 13.8, 2.5, 2.5 Hz, 1H), 1.06 (s, 9H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 133.2, 130.4, 129.8, 128.6, 72.0, 68.8, 64.0, 33.2, 27.6, 27.2, 22.9, 20.1; HRMS m/z calcd for $C_{19}H_{30}O_4$-Si $[M + H]^+$ 351.1992, found: 351.1985.

4-(2-Allyloxy-ethyl-2,2-di-*tert*-butyl-[1,3,2]-dioxasilinane (11f). To a room temperature solution of **11a** (1.22 g, 4.7 mmol) in CH_2Cl_2 (1.4 mL) and cyclohexane (2.8 mL) was added allyl trichloroacetimidate[24] (1.78 g, 8.9 mmol) and catalytic trifluoromethanesulfonic acid (∼50 μL). After 3 h the reaction mixture was filtered through florisil and concentrated under reduced pressure. The residue was dissolved in CH_2-Cl_2, washed with saturated $NaHCO_3$ solution, H_2O, and brine and dried ($MgSO_4$). After filtration through Celite, the volatile components were removed under reduced pressure, and the residual oil was purified by flash chromatography on silica gel using 40:1 hexanes−EtOAc for elution to provide the title compound as a colorless oil (1.14 g, 81%). R_f 0.68 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98−5.81 (m, 1H), 5.30−5.14 (m, 2H), 4.27−4.19 (m, 1H), 4.10−4.07 (m, 2H), 3.99−3.96 (m, 2H), 3.66−3.52 (m, 2H), 1.88−1.66 (m, 3H), 1.60 (dddd, J = 14.1, 2.6, 2.6, 2.6 Hz, 1H), 1.02 (s, 9H), 0.98 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 117.0, 72.2, 71.1, 66.6, 64.6, 38.9, 36.9, 27.7, 27.3, 22.9, 20.0; HRMS m/z calcd for $C_{16}H_{32}O_3Si$ $[M + H]^+$ 301. 2199, found: 301.2201.

2,2-Di-*tert*-butyl-4-(2-triisopropylsilanyloxy-ethyl)-[1,3,2]-dioxasilinane (11i). To a room temperature solution of **11a** (1.97 g, 7.6 mmol) in CH_2Cl_2 (7.5 mL) were added pyridine (1.22 mL, 15.0 mmol) and triisopropylsilyl chloride (1.58 mL, 11.4 mmol). The reaction mixture was stirred at room temperature for 20 h and then poured into a vigorously stirred saturated NH_4Cl solution (8 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2-Cl_2. The combined organic layers were washed with H_2O and brine and dried ($MgSO_4$). After filtration through Celite, volatiles were removed under reduced pressure. Purification of the residual oil by flash chromatography on silica gel using 30:1 hexanes−EtOAc for elution provided the title compound as a colorless oil (1.91 g, 90%). R_f 0.69 (5% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.29 (dddd, J = 12.8, 6.2, 6.2, 2.6 Hz, 1H), 4.13−4.08 (m, 2H), 3.95−3.79 (m, 2H), 1.91−1.77 (m, 1H), 1.73−1.61 (m, 3H), 1.11−0.98 (m, 39H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 70.9, 64.4, 59.7, 42.1, 37.0, 27.6, 27.4, 22.8, 20.0, 18.3, 12.2; HRMS m/z calcd for $C_{22}H_{48}O_3Si$ $[M + H]^+$ 417.3220, found: 417.3220.

Acetic Acid 2-(Di-*tert*-butyl-fluoro-silanyloxy)-4-hydroxy-butyl Ester (13b). The title compound was prepared from **11b** according to the general procedure described for the preparation of **5a**, except that 2.3 equiv of BF_3·Me_2S was used (colorless oil, 378 mg, 91%). R_f 0.48 (33% EtOAc/hexanes); IR (thin film) ν 3450 (br), 1744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.42 (dddd, J = 4.2, 4.2, 4.2, 4.2 Hz, 1H), 4.09 (dddd, J = 11.2, 11.2, 11.2, 4.2 Hz, 2H), 3.94−3.71 (m, 2H), 2.39 (br s, 1H), 2.04 (s, 3H), 1.78 (ddd, J = 11.2, 3.8, 3.8 Hz, 2H), 1.01 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 68.7, 68.0, 58.8, 37.0, 27.2, 27.1, 21.0, 20.5, 20.3; ^{19}F NMR (300 MHz, $CDCl_3$) δ −160.0; HRMS m/z calcd for $C_{14}H_{29}FO_4Si$ $[M + H]^+$ 309.1897, found: 309.1894.

Acetic Acid 3-(Di-*tert*-butyl-fluoro-silanyloxy)-5-hydroxy-pentyl Ester (13c). The title compound was prepared from **11c** according to the general procedure described for the preparation **5a**, except that 4.5 equiv of BF_3·Me_2S was used (colorless oil, 364 mg, 87%). R_f 0.55 (25% EtOAc/hexanes); IR (thin film) ν 3450 (br), 1743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.38 (dddd, J = 6.0, 6.0, 6.0, 6.0 Hz, 1H), 4.15 (t, J = 6.5 Hz, 2H), 3.78−3.74 (m, 2H), 2.01 (s, 3H), 2.00−1.73 (m, 5H), 1.01 (d, J = 0.8 Hz, 9H), 1.00 (d, J = 0.8 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 69.4, 61.2, 59.4, 39.3, 36.0, 27.3, 27.2, 21.2, 20.5 (d, J = 14.7 Hz), 20.4 (d, J = 14.7 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) −159.1; HRMS m/z calcd for $C_{15}H_{31}FO_4Si$ $[M + H]^+$ 323.2054, found: 323.2054.

Benzoic Acid 2-(Di-*tert*-butyl-fluoro-silanyloxy)-4-hydroxy-butyl Ester (13d). The title compound was prepared from **11d** according to the general procedure described for the preparation of **5a**, except that 4.0 equiv of BF_3·Me_2S was used (colorless oil, 274 mg, 90%). R_f 0.69 (20% EtOAc/hexanes); IR (thin film) ν 3460 (br), 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 7.3 Hz, 2H), 7.53−7.50 (m, 1H), 7.41 (dd, J = 7.3, 7.3 Hz, 2H), 4.57 (dddd, J = 5.5, 5.5, 5.5, 5.5 Hz, 1H), 4.37 (d, J = 4.8 Hz, 2H), 3.86−3.78 (m, 2H), 1.99−1.81 (m, 3H), 1.03 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 133.3, 130.2, 129.9, 128.6, 70.0, 68.4, 59.2, 37.2, 27.2, 27.1, 20.5 (d, J = 14.0 Hz), 20.3 (d, J = 14.0 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) δ −160.0; HRMS m/z calcd for $C_{19}H_{31}FO_4Si$ $[M + H]^+$ 371.2054, found: 371.2049.

Benzoic Acid 3-(Di-*tert*-butyl-fluoro-silanyloxy)-5-hydroxy-pentyl Ester (13e). The title compound was prepared from **11e** according to the general procedure described for the preparation of **5a**, except that 5.0 equiv of BF_3·Me_2S was used (colorless oil, 198 mg, 82%). R_f 0.67 (15% EtOAc/hexanes); IR (thin film) ν 3420 (br), 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.61−7.57 (m, 1H), 7.46 (dd, J = 7.5, 7.5 Hz, 2H), 4.48−4.42 (m, 3H), 3.91−3.77 (ddd, J = 7.6, 6.4, 6.4 Hz, 2H), 2.11 (ddd, J = 6.4, 6.4, 6.4 Hz, 2H), 1.97−1.84 (m, 3H), 1.82 (br s, 1H), 1.08 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 133.2, 130.5, 129.8, 128.6, 69.6, 61.7, 59.5, 39.3, 36.1, 27.6, 27.3, 20.5 (d, J = 15.2 Hz), 20.4 (d, J = 15.2 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) δ −159.1; HRMS m/z calcd for $C_{20}H_{33}FO_4Si$ $[M + H]^+$ 385.2210, found: 385.2210.

5-Allyloxy-3-(di-*tert*-butyl-fluoro-silanyloxy)pentan-1-ol (13f). The title compound was prepared from **11f** according to the general procedure described for the preparation of **5a**, except that 6.5 equiv of BF_3·Me_2S was used (colorless oil, 219 mg, 78%). R_f 0.59 (20% EtOAc/hexanes); IR (thin film) ν 3395 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98−5.85 (m, 1H), 5.31−5.16 (m, 2H), 4.44 (dddd, J = 5.8, 5.8, 5.8, 5.8 Hz, 1H), 3.97 (ddd, J = 5.5, 3.1, 1.6 Hz, 2H), 3.94−3.74 (m, 2H), 3.58−3.52 (m, 2H), 2.15 (br s, 1H), 1.96−1.77 (m, 4H), 1.07 (d, J = 0.9 Hz, 9H), 1.06 (d, J = 0.9 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.0, 117.2, 72.2, 70.3, 66.7, 59.7, 39.3, 37.0, 27.3, 27.2, 20.5 (d, J = 12.1 Hz), 20.3 (d, J = 12.1 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) δ −159.3; HRMS m/z calcd for $C_{16}H_{33}FO_3Si$ $[M + H]^+$ 321.2261, found: 321.2252.

5-Benzyloxy 3-(di-*tert*-butyl-fluoro-silanyloxy)pentan-1-ol (13g). The title compound was prepared from **11g** according to the general procedure described for the preparation of **5a**, except that 6.5 equiv of BF_3·Me_2S was used (colorless oil, 65 mg, 35%). R_f 0.62 (15% EtOAc/hexanes); IR (thin film) ν 3405 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.28 (m, 5H), 4.60−4.45 (m, 3H), 3.84−3.77 (m, 2H), 3.61 (dd, J = 6.2, 6.2 Hz, 2H), 2.00−1.84 (m, 4H), 1.69 (br s, 1H), 1.07 (d, J = 0.8 Hz, 9H), 1.05 (d, J = 0.8 Hz, 9H); ^{19}F NMR (300 MHz, $CDCl_3$) δ −159.3; HRMS m/z calcd for $C_{20}H_{35}FO_3Si$ $[M + H]^+$ 371.2418, found: 371.2419.

3-(Di-*tert*-butyl-fluoro-silanyloxy)-5-methoxy-pentan-1-ol (13h). The title compound was prepared from **11h** according to the general procedure described for the preparation of **5a**, except that 3.5 equiv of BF_3·Me_2S was used (colorless oil, 31 mg, 43%). R_f 0.32 (33% EtOAc/hexanes); IR (thin film) ν 3390 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.43

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(dddd, J = 6.1, 6.1, 6.1, 6.1 Hz, 1H), 3.85−3.72 (m, 2H), 3.53−3.45 (m, 2H), 3.35 (s, 3H), 2.04 (br s, 1H), 1.97−1.79 (m, 4H), 1.07 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 70.3, 69.1, 59.7, 58.8, 39.3, 37.0, 27.3, 27.2, 20.6 (d, J = 15.1 Hz), 20.5 (d, J = 15.1 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) δ −159.4; HRMS m/z calcd for $C_{20}H_{36}FO_3Si$ $[M + H]^+$ 371.2418, found: 371.2419.

3-(Di-*tert*-butyl-fluoro-silanyloxy)-5-triisopropylsilanyloxy-pentyl-1-ol (13i). The title compound was prepared from **11i** according to the general procedure described for the preparation of **5a**, except that 7.0 equiv of BF_3·Me_2S was used (colorless oil, 170 mg, 78%). R_f 0.48 (15% EtOAc/hexanes); IR (thin film) ν 3380 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.48 (dddd, J = 5.9, 5.9, 5.9, 5.9 Hz, 1H), 3.88−3.76 (m, 3H), 2.03−1.91 (m, 2H), 1.89−1.77 (m, 1H), 1.63 (br s, 1H), 1.09−1.06 (m, 39H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 70.6, 60.1, 59.9, 40.1, 39.0, 27.3, 20.6 (d, J = 12.0 Hz), 20.3 (d, J = 12.0 Hz), 18.2, 12.2; ^{19}F NMR (300 MHz, $CDCl_3$) δ −159.4; HRMS m/z calcd for $C_{22}H_{49}FO_3Si_2$ $[M + H]^+$ 437.3283, found: 437.3282.

4-(Di-*tert*-butyl-fluoro-silanyloxy)-5,5-dimethyl-hexan-2-ol (15). The title compound was prepared from **14** according to the general procedure described for the preparation of **5a**, except that 3.0 equiv of BF_3·Me_2S were used (colorless oil, 255 mg, 93%). R_f 0.44 (33% EtOAc/hexanes); IR (thin film) ν 3415 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (qdd, J = 6.2, 12.2, 2.3 Hz, 1H), 4.02 (dd, J = 8.3, 1.8 Hz, 1H), 1.64−1.55 (m, 1H), 1.51 (br s, 1H), 1.45 (ddd, J = 14.6, 8.3, 2.5 Hz, 1H), 1.27 (d, J = 6.2 Hz, 3H), 1.05 (s, 9H), 1.04 (s, 9H), 0.91 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 80.1, 64.6, 42.8, 35.8, 27.5, 27.3, 26.2, 24.9, 21.1 (d, J = 16.0 Hz), 20.3 (d, J = 16.0 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) δ −152.0; HRMS m/z calcd for $C_{16}H_{35}FO_2Si$ $[M + H]^+$ 307.2469, found: 307.2453.

4-(Di-*tert*-butyl-fluoro-silanyloxy)-5,5-dimethyl-hexan-2-ol (17). The title compound was prepared from **16** according to the general procedure described for the preparation **5a**, except that 5.0 equiv of BF_3·Me_2S was used (colorless oil, 178 mg, 64%). R_f 0.42 (40% EtOAc/hexanes); IR (thin film) ν 3365 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00−3.91 (m, 1H), 3.80 (ddd, J = 6.1, 3.6, 1.5 Hz, 1H), 1.77 (ddd, J = 14.8, 6.9, 3.6 Hz, 1H), 1.64−1.55 (m, 3H), 1.17 (d, J = 6.1 Hz, 3H), 1.04 (d, J = 1.0 Hz, 9H), 1.03 (d, J = 1.0 Hz, 9H), 0.90 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 80.7, 66.7, 44.2, 36.2, 27.4, 27.1, 25.9, 23.6, 21.1 (d, J = 15.0 Hz), 21.0 (d, J = 15.0 Hz); ^{19}F NMR (300 MHz, $CDCl_3$) δ −153.2; HRMS m/z calcd for $C_{16}H_{35}FO_2Si$ $[M + H]^+$ 307.2469, found: 307.2461.

4-(Di-*tert*-butyl-fluoro-silanyloxy)-5-methyl-hexan-2-ol (19a) and 5-(Di-*tert*-butyl-fluoro-silanyloxy)-2-methyl-hexan-3-ol (19b). The title compounds were prepared from **18** according to the general procedure described for the preparation of **5a**, except that 2.5 equiv of BF_3·Me_2S was used. Purification of the reaction mixture by flash chromatography on silica gel using 10:1 hexanes−EtOAc for elution provided the title compounds **19a** and **19b** as colorless oils. **19a:** 138 mg, 76%; R_f 0.45 (33% EtOAc/ hexanes); IR (thin film) ν 3365 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13 (dddd, J = 4.1, 4.1, 4.1, 4.1 Hz, 1H), 4.06−3.99 (m, 1H), 2.05−2.00 (br s, 1H), 1.92 (dddd, J = 7.6, 4.1, 4.1, 0.4 Hz, 1H), 1.54−1.43 (m, 2H), 1.18 (d, J = 6.3 Hz, 3H), 1.01 (s, 18H), 0.87 (dd, J = 6.9, 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.9, 64.3, 41.2, 33.6, 27.2, 24.4, 20.5, 20.3, 18.1, 16.8; ^{19}F NMR (300 MHz, $CDCl_3$) δ −157.0; HRMS m/z calcd for $C_{15}H_{33}FO_2Si$ $[M + H]^+$: 293.2312, found: 293.2308. **19b:** 23 mg, 13%; R_f 0.34 (33% EtOAc/ hexanes); IR (thin film) ν 3350 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.57−4.48 (m, 1H), 3.70 (ddd, J = 9.3, 8.1, 2.7 Hz, 1H), 2.51 (br s, 1H), 1.67−1.47 (m, 3H), 1.29 (d, J = 6.1 Hz, 3H), 1.03 (d, J = 1.1 Hz, 9H), 1.01 (d, J = 1.1 Hz, 9H), 0.89 (dd, J = 6.7, 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.7, 68.7, 41.7, 33.9, 27.0, 26.9, 23.3, 20.4 (d, J = 15.3 Hz), 19.8 (d, J = 15.3 Hz), 18.4, 17.6; ^{19}F NMR (300 MHz, $CDCl_3$) δ −162.0; HRMS m/z calcd for $C_{15}H_{33}FO_2Si$ $[M + H]^+$ 293.2312, found: 293.2319.

4-(Di-*tert*-butyl-fluoro-silanyloxy)-5-methyl-hexan-2-ol (21a). The title compound was prepared from **20** according to the general procedure described for the preparation of **5a**, except that 2.5 equiv of BF_3·Me_2S was used (colorless oil, 136 mg, 37%). R_f 0.48 (33% EtOAc/hexanes); IR (thin film) ν 3330 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.16 (dddd, J = 4.2, 4.2, 4.2, 0.8 Hz, 1H), 3.92−3.86 (m, 1H), 2.39 (br s, 1H), 1.98 (qdd, J = 6.8, 6.8, 6.8 Hz, 1H), 1.68−1.47 (m, 3H), 1.18 (d, J = 6.1 Hz, 3H), 1.05 (d, J = 0.8 Hz, 9H), 1.03 (d, J = 0.8 Hz, 9H), 0.93 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 79.1, 67.2, 40.5, 33.4, 27.5, 27.4, 24.1, 20.9, 18.1, 16.8; ^{19}F NMR (300 MHz, $CDCl_3$) δ −156.6; HRMS m/z calcd for $C_{15}H_{33}FO_2Si$ $[M + H]^+$ 293.2312, found: 293.2305.

Acetic Acid 3-(Di-*tert*-butyl-chloro-silanyloxy)-5-phenyl-pentyl Ester (23a). To a room temperature solution of **4** (540 mg, 1.69 mmol) in $CHCl_3$ (5.5 mL) was added BCl_3 (2.1 mL, 1.0 M in heptane, 2.1 mmol). After 25 min TLC analysis of an aliquot indicated the reaction was complete, and the reaction mixture was transferred with the aid of CH_2Cl_2 into a stirring saturated $NaHCO_3$ solution (8 mL). The organic layer was separated, washed with H_2O and brine, and dried ($MgSO_4$). After filtration through a small pad of Celite, volatiles were removed under reduced pressure and the residue was purified by flash chromatography on silica gel using 10:1 hexanes−EtOAc for elution to provide the alcohol **22a** as a colorless oil (534 mg, 89%). R_f 0.38 (33% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.20 (m, 5H), 4.36 (dddd, J = 5.7, 5.7, 5.7, 5.7 Hz, 1H), 3.95−3.88 (m, 1H), 3.84−3.76 (m, 1H), 2.75−2.68 (m, 2 H), 2.05−1.85 (m, 4H), 1.75 (br s, 1H), 1.14 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 128.7, 128.6, 126.1, 72.3, 59.5, 38.3, 38.2, 31.3, 27.6, 27.5, 23.5, 23.3. The oil was immediately acylated according to the general procedure described for the preparation of **11b** to afford the product as colorless oil (544 mg, 91%). R_f 0.67 (10% EtOAc/hexanes); IR (thin film) ν1739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.18 (m, 5H), 4.32−4.20 (m, 3H), 2.72 (dddd, J = 13.5, 7.8, 2.7, 2.7 Hz, 2H), 2.08 (s, 3H), 2.03−1.99 (m, 4H), 1.12 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 142.2, 128.7, 128.6, 126.1, 71.5, 61.3, 38.2, 34.7, 31.1, 27.6 23.4, 21.3; HRMS m/z calcd for $C_{21}H_{35}ClO_3Si$ $[M + H]^+$ 399.2122, found: 399.2115.

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Supporting Information Available: Preparation of starting materials (**11a**, **11c**, **11e**, **11g**, **11h**, **11j**, **14**, **16**, **18**, **20**), regiochemical proofs for **6a**, **13b**, **13c**, **13f**, **13i**, **15**, **19a**, characterization data for **5b**, **6a**, **6b**, **23b**, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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