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Studies toward terminal (fluoroalkyl)silanes. Investigation of diethylaminosulfur trifluoride (DAST) in exchange reactions with some terminal (hydroxyalkyl)silanes

Aristeidis Chiotellis [a,*], Svetlana V. Selivanova [a], Bernd Schweizer [b], Roger Schibli [a], Simon M. Ametamey [a]

[a] Center for Radiopharmaceutical Sciences of ETH, PSI and USZ, Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology (ETH) Zurich, Wolfgang Pauli Strasse 10, 8093 Zurich, Switzerland
[b] Laboratory of Organic Chemistry, Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology (ETH) Zurich, Wolfgang Pauli Strasse 10, 8093 Zurich, Switzerland

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ABSTRACT

Aiming at a convenient way toward the synthesis of terminal (fluoroalkyl)silanes, the effect of (diethylamino)sulfur trifluoride (DAST) on some terminal hydroxyalkylsilanes was investigated. Reaction of DAST with a substituted (hydroxyethyl)diphenylsilane led to the formation of the desired (2-fluoroethyl)diphenylsilane in considerable amounts although the competing elimination route was still the favored mechanism. This new reaction was studied under various parameters with the best conditions yielding the substitution product in a ratio of 1:4 over the undesired elimination product. In a different approach trying to optimize the outcome of the reaction, the presence of two bulky 2,4,6-trimethoxyphenyl (TMOP) groups on the silicon atom favored the elimination route.

1. Introduction

Terminal fluoroalkylsilanes are sparingly available mainly because they cannot be synthesized directly from the corresponding haloalkylsilanes (halo including sulfonates) via nucleophilic fluorination. In the case of halomethylsilanes, fluoride reacts by attacking the silicon atom to give rearrangement – displacement products arising from competitive migration of the silicon substituents to the electrophilic carbon with displacement of the halide atom [1–4] (Scheme 1). It is postulated that the reaction proceeds via a pentacoordinated silicon intermediate and it has been shown that migration is largely controlled by the ability of the migrating group to bear a negative charge, which is acquired in the transition state [5]. For haloethylsilanes, fluoride attacks again the silicon atom, which results in C–Si bond cleavage and elimination of the leaving group from the β-carbon (Scheme 2A) [6–10]. Nucleophilic fluorination of haloalkylsilanes with longer alkyl chains proceeds in a similar manner, e.g. γ-elimination takes place in the case of substituted 3-chloropropylsilanes to give substituted cyclopropanes [11]. In all the aforementioned cases, fluoride attacks preferentially the silicon atom rather than the electrophilic carbon and no trace of fluoroalkylsilane is observed. Apparently, the driving force for this effect is the formation of the extremely strong Si–F bond.

Nevertheless, there are a few reports where fluoroalkylsilanes were synthesized by direct nucleophilic substitution of corresponding analogs bearing a suitable leaving group (chloride or tosylate). These sparse examples include (fluoromethyl)trimethylsilane and (3-fluoropropyl)trimethylsilane [12,13]. The authors, however, mentioned that in these cases there was also some degree of rearrangement or elimination but the desired fluoroalkylsilanes could be obtained in satisfactory yields. It seems that the outcome of the two competing reactions (nucleophilic substitution vs. elimination) (Scheme 2), is affected by the nature of the substituents attached to the silicon atom. In all cases, the silicon atom bears three electron donating methyl groups, which could potentially reduce its electropositivity and thus its affinity for fluoride, giving to the latter the opportunity to react with the electrophilic carbon. On the other hand, electron withdrawing

* Corresponding author at: Center for Radiopharmaceutical Sciences ETH-PSI-USZ, Department of Chemistry and Applied Sciences, Swiss Federal Institute of Technology (ETH) Zurich, HCI H422, Wolfgang Pauli Strasse 10, 8093 Zurich, Switzerland. Tel.: +41 44 6337472.
E-mail addresses: aristeidis.chiotellis@pharma.ethz.ch, achiotel@ethz.ch (A. Chiotellis).

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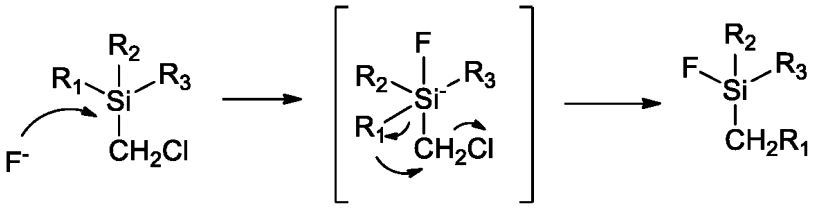
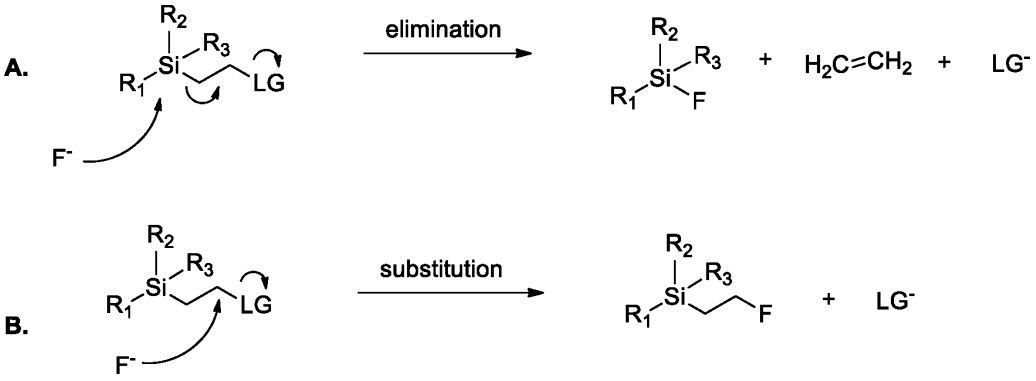


Scheme 1. Rearrangement – displacement reaction of chloromethylsilanes by fluoride attack at the silicon center.



Scheme 2. Elimination vs. substitution in the case of ethylsilanes carrying a leaving group (LG) at 2-position.

groups seem to favor elimination. For example, in contrast to (3-chloropropyl)trimethylsilane, no exchange of chlorine is observed for (3-chloropropyl)trichlorosilane where the nucleophilic fluoride attacks exclusively the electron-deficient silicon leading quantitatively to γ-elimination [12]. Although some degree of nucleophilic fluorination is observed when three methyl groups are attached to silicon, these are very difficult to cleave making thus further derivatization of the resulting terminal fluoroalkylsilanes difficult.

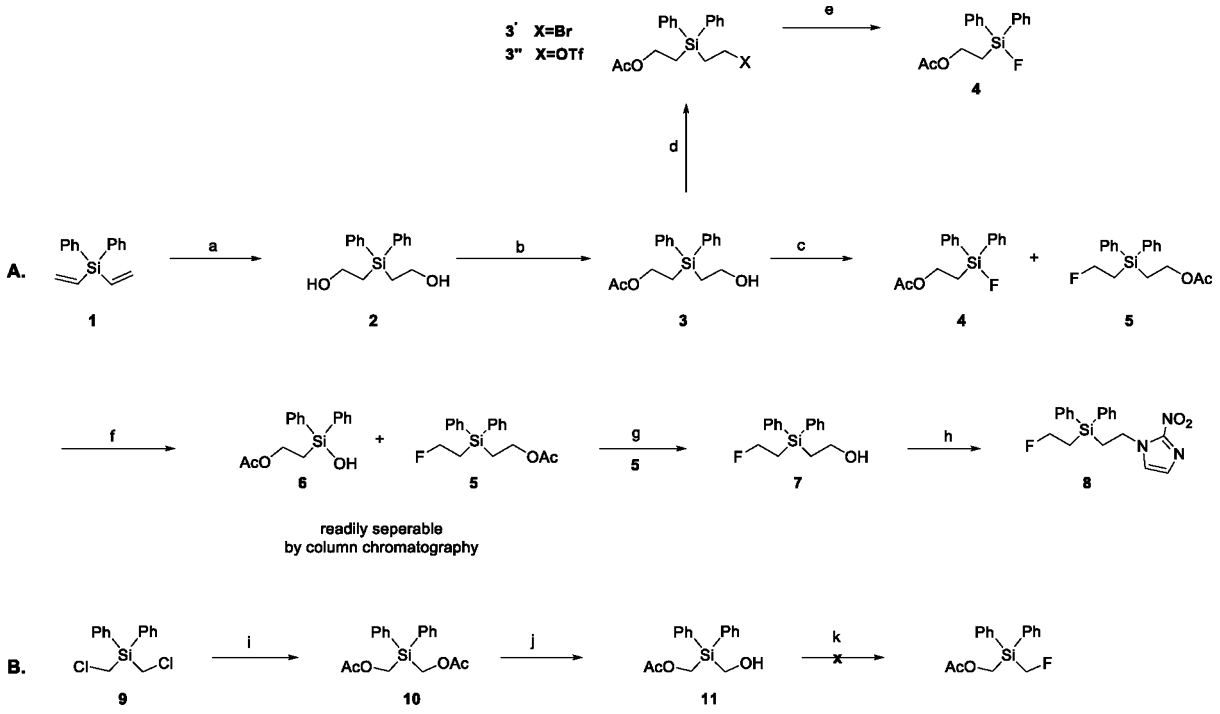
We were interested in synthesizing substituted (2-fluoroethyl)-diphenylsilanes as building blocks for larger organo-silicon molecules within our medicinal chemistry research program. The only known synthetic pathway to 2-fluoroethylsilanes is the free radical chain reaction of vinylfluoride with trichloro- or trimethylsilanes, a reaction which has a difficult setup and involves tedious purifications [14]. Clearly, a nucleophilic approach would be much more convenient but no such reports are available in the literature, for reasons mentioned above. Additionally, to our surprise, a search on the Scifinder revealed only 10 examples of synthesized (2-fluoroethyl)silanes. However, a report describing the direct conversion of (3-hydroxypropyl)trimethylsilane to (3-fluoropropyl)trimethylsilane using the Yarovenko reagent [15] prompted us to examine the reaction of the most commonly used dehydroxylating/fluorinating agent, namely diethylaminosulfur trifluoride [16,17] (DAST). To our knowledge, DAST has not yet been used in the chemistry of organometalloid compounds, at least not for exchange reactions. Moreover, in the case of the Yarovenko reagent, the authors state that γ-elimination could partially be controlled by lowering the temperature. The high reactivity of DAST allows reactions at low temperatures (−78 °C), which could potentially favor substitution over elimination. In this work, we report that treatment of substituted (2-hydroxyethyl)diphenylsilane **3** with DAST leads to (2-fluoroethyl)diphenylsilane **5** (Scheme 3), which can readily be separated from the fluorosilane byproduct.

2. Results and discussion

We decided to study the effect of DAST directly on the desired substituted (2-hydroxyethyl)diphenylsilane **3** even though we were aware that the presence of the two electron withdrawing phenyl groups on silicon could actually impede substitution by increasing the electron deficiency of silicon when compared to substituted (2-hydroxyethyl)dimethylsilanes. Treatment of (diphenyl)divinylsilane **1** [18] (Scheme 3A) with 9-borabicyclo[3.3.1]nonane (9-BBN) followed by addition of aqueous solutions of sodium hydroxide 3 M and hydrogen peroxide 30% gave the corresponding bis(2-hydroxyethyl)silane **2** in good yield (76%). Reaction of diol **2** with acetic anhydride in the presence of triethylamine and catalytic amounts of DMAP afforded the corresponding monoacetate compound **3** (50% yield). The reaction of **3** with DAST in dichloromethane at −78 °C afforded a mixture of fluorosilane **4** and the desired 2-fluoroethyl derivative **5** in 4.5:1 ratio (as shown by ^{1}H NMR analysis of the crude mixture).

Efforts were made to shift the reaction in favor of the substitution product **5**. Various parameters were investigated, including solvent, temperature and order of reagent addition. The results are summarized in Table 1. For the same solvent tested (dichloromethane), higher temperature favored the elimination mechanism, as expected (entry 2). Performing the reaction near the freezing point of dichloromethane (≈−90 °C) caused precipitation of **3** and the reaction was not evaluated. More polar solvents like diglyme and ether readily promoted the elimination process even at temperatures as low as −100 °C (entries 3 and 4). The best results were obtained when using a non- polar, non-basic solvent, e.g. trichlorofluoromethane (Freon-11) (entry 5). The use of even less polar solvents (like hexane or pentane) was not examined due to complete insolubility of **3** at the low temperatures used. Even though trichlorofluoromethane gave repeatedly slightly better ratios of the desired product, dichloromethane was chosen for larger scale reactions for environmental reasons. Finally, the order of addition of the reagents affected the reaction only marginally (entries 6 and 7). Best results were obtained when DAST was added neat to the solution of **3** (entry 1).

Although purification of the reaction mixture by column chromatography was not possible (since the two compounds exhibit no difference in polarity on the TLC in every solvent mixture examined), separation was readily achieved by subjecting the mixture to hydrolytic conditions with aqueous saturated $NaHCO_3$ solution in acetone. Fluorosilane **4** was quantitatively and



Scheme 3. (A) Synthesis of (2-fluoroethyl)diphenylsilane **5** and further derivatization. *Reagents and conditions*: (a) 9-BBN 0.5 M, THF, r.t., 4 h then H_2O, NaOH 3 M, H_2O_2 30%, reflux, 3 h, 76%; (b) Ac_2O, pyridine, $DMAP_{(cat)}$, DCM, 0 °C 30 min then r.t. 3 h, 50%; (c) DAST, DCM, −78 °C, 30 min; (d) PPh_3/CBr_4, DCM, 0 °C to r.t, 2 h, 96% for **3′** or Tf_2O, pyridine, DCM, −5 °C, 30 min for **3″**; (e) KF/Kryptofix, MeCN, 0 °C or TBAF 1 M, THF, 0 °C for **3′** and TBABF/KHF_2, DCM, 0 °C for **3″**; (f) $NaHCO_3$(sat)/acetone 1:1, r.t., 16 h, 10% over two steps; (g) K_2CO_3, MeOH, r.t., 1 h, 95%; (h) PPh_3, 2-nitroimidazole, DIAD, THF, r.t., 16 h, 92%. (B) Synthesis of hydroxymethylanalogue **11**. *Reagents and conditions*: (i) AcONa, DMF, 100 °C, 6 h, 90%; (j) K_2CO_3, MeOH, r.t., 1 h, 19%; (k) DAST, DCM, −78 °C, 30 min, unidentified products.

cleanly converted to the corresponding silanol **6**, while the 2-fluoroethyl derivative **5** remained unaffected. Since polarity of the silanol differs significantly, product **5** was easily purified by column chromatography with a total yield of 10% over two steps. Compound **5** remains stable for a long time at room temperature with no sign of spontaneous elimination of the fluorine atom and it can be easily manipulated for further reactions. Treatment with potassium carbonate in MeOH resulted solely in cleavage of the acetate group to yield the free alcohol **7** in 95% yield. The free alcohol was then coupled to the hypoxia targeting agent 2-nitroimidazole under Mitsunobu reaction conditions to yield compound **8**. In the same way, building block **7** could be coupled to other molecules of biological interest.

To our knowledge, this is the first example where a (2-fluoroethy)lsilane is synthesized directly from the corresponding (2-hydroxyethyl)silane via an exchange reaction. Notably, the use of the Yarovenko reagent on (2-hydroxyethyl)trimethylsilane resulted, according to the authors, exclusively in β-elimination with ethylene and (trimethyl)fluorosilane as the sole products [15]. It is also worth saying that nucleophilic fluorination of bromide **3′** with KF/Kryptofix in MeCN or TBAF in THF and reaction of triflate **3″** with the much less basic TBABF/KHF_2 [19] exclusively resulted in b-elimination, as expected. Although the overall yield of **5** is low (10%), this method could be an alternative approach in the synthesis of terminal (fluoroethyl)silanes, compared to the already mentioned radical reaction with vinyl fluoride especially since it involves an easier experimental setup, cheap and easy to handle starting materials, avoidance of tedious distillations and the possibility for further derivatization. The latter could be achieved by cleaving the phenyl groups with trifluoromethanesulfonic acid [20,21] and converting to the corresponding chlorosilanes, although this possibility was not investigated here since we were interested in keeping the bulky lipophilic phenyl groups on the silicon atom.

The exchange reaction with DAST was additionally tested on (hydroxymethyl)silanes in order to examine whether this reaction would lead to (fluoromethyl)silanes. Compound **11** was synthesized from **9** [22] as a direct analog of **3** (Scheme 3B). However, in this case,

Table 1
Investigation of different conditions of the DAST fluorination reaction with substrate 3.

Entry[a]	Order of reagents addition	Solvent	Temperature	Ratio[b] (fluorosilane/ 2-fluoroethylsilane)
1	DAST added neat to a solution of 3	Dichloromethane	−78 °C	4.5:1
2	DAST added neat to a solution of 3	Dichloromethane	−20 °C	9.1:1
3	DAST added neat to a solution of 3	Diglyme	−50 °C	15.2:1
4	DAST added neat to a solution of 3	Ether	−100 °C	9:1
5	DAST added neat to a solution of 3	Trichlorofluoromethane (Freon-11)	−78 °C	4.0:1
6	DAST added as solution in DCM to a solution of 3	Dichloromethane	−78 °C	5.4:1
7	Solution of compound 3 added to solution of DAST	Dichloromethane	−78 °C	5.0:1

[a] Experimental conditions (molarity of reaction, quantities of reagents, workup method) were kept constant in every attempt for comparable results.
[b] Determined by ^{1}H NMR analysis of the crude reaction after workup.

the reaction of **11** with DAST led only to unidentified products with no trace of the desired (fluoromethyl)diphenylsilane.

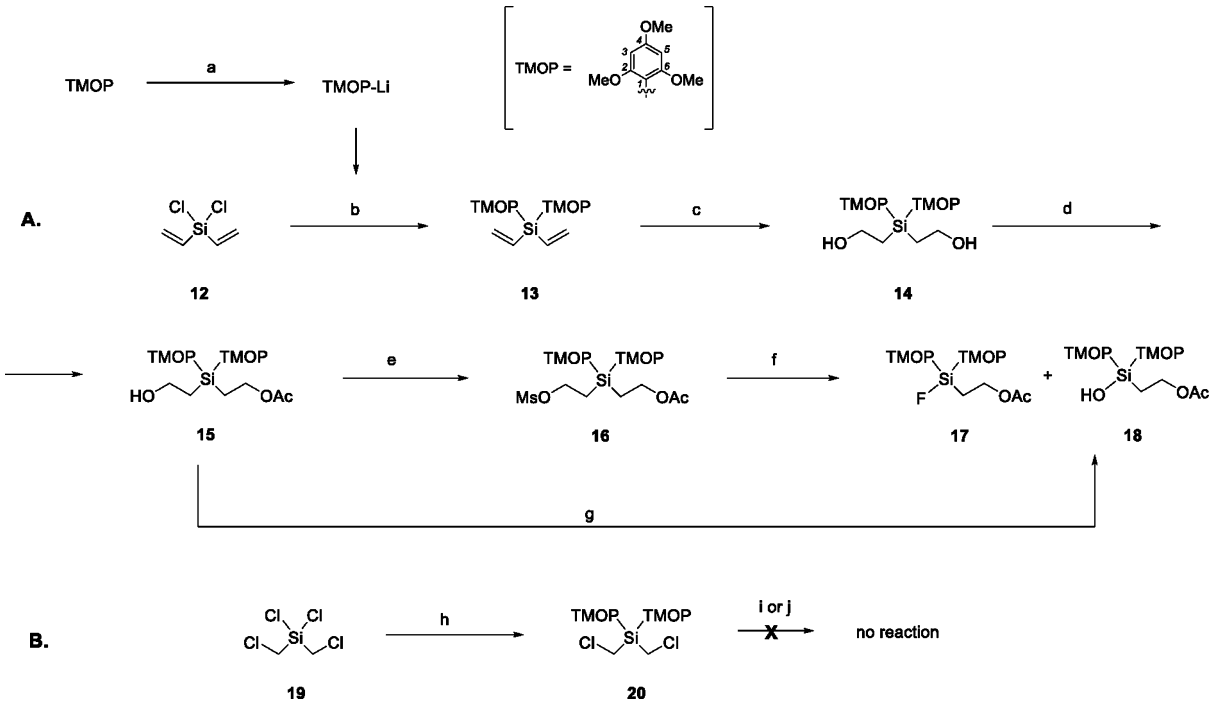
All the afore-mentioned literature data concerning nucleophilic fluorination of terminal haloalkylsilanes (or hydroxysilanes) suggest that the nature of the silicon substituents must also influence the outcome of the new reaction under investigation. Electron donating groups (e.g. alkyl groups) are expected to favor substitution by reducing the electropositivity of silicon while electron withdrawing substituents (e.g. halides) are most likely to promote elimination by increasing the electron deficiency of the silicon atom making it thus more prone to attack by fluoride. Our interest was to examine the outcome of the DAST fluorination reaction with a different substitution on the silicon atom. The 2,4,6-trimethoxyphenyl (TMOP) group, has recently been reported to be an effective protecting group in organosilicon chemistry [23–26]. Its main advantages include high stability under basic conditions and easy cleavage under very mild acidic conditions. We envisioned that the bulky TMOP substituents would sterically hinder the attack of fluoride on silicon and redirect it toward the easily accessible electrophilic carbon. Besides, it was hypothesized that the electron donating effect of the three methoxy groups of TMOP would make the silicon atom less electron deficient which would favor the substitution route, when compared to its phenyl analog **3**. Moreover, the TMOP group should be much more easily cleavable than the phenyl groups, which could be an advantage for medicinal chemistry applications (easier derivatization).

The synthesis of compound **15** (the direct TMOP analog of **3**) was accomplished as depicted in Scheme 4A. The two chlorine atoms on (dichloro)divinylsilane **12** [18] were substituted with TMOP groups by reacting **12** with two equivalents of freshly prepared TMOP-Li [23] to give **13** in good yield (80%), which was additionally structurally characterized by single-crystal X-ray diffraction. Hydroboration of **13** with 9-BBN and subsequent oxidation with hydrogen peroxide 30% under basic conditions provided the corresponding bis(2-hydroxyethyl)silane **14** in 80% yield. The diol was converted to its monoacetate analog **15** by reacting with acetic anhydride in the presence of pyridine and catalytic amounts of DMAP in dichloromethane (48% yield). Compound **15** was then reacted with DAST using the optimal conditions determined for substrate **3**. Unfortunately, the reaction afforded solely the elimination product, fluorosilane **17**. The reaction was not further investigated since the best experimental parameters failed to give even a trace of the desired (fluoroethyl)silane. Besides, we wanted to investigate how a typical nucleophilic substitution reaction would proceed when silicon bears two TMOP groups. For this reason, the sulfonate **16** was synthesized from **15** by treatment with mesyl chloride in the presence of triethylamine in 90% yield. The unstable mesyl compound was quickly reacted with KF/kryptofix in dry acetonitrile to deliver exclusively fluorosilane **17** and silanol **18**. Our hypothesis that TMOP groups would facilitate substitution over elimination was not supported by the experimental data (Fig. 1).

Derivative **20** was synthesized as a model compound in order to examine in which way would nucleophilic fluorination proceed if TMOP groups were attached to (chloromethyl)silanes (Scheme 4B). (Dichloro)bischloromethylsilane **19** [27] was treated with two equivalents of freshly prepared TMOP-Li in hexane to yield compound **20** in 65% yield. Surprisingly, **20** did not undergo any changes when subjected to treatment with KF/Kryptofix in acetonitrile. It was also unreactive toward other nucleophiles such as AcOK in DMF even at temperatures as high as 150 °C. A possible explanation for this unexpected inertness derives from X-ray analysis (Fig. 2), which shows that the oxygen atoms of the methoxy groups are positioned in the near proximity and at the backside of the chloromethyl carbon (Fig. 2), probably shielding it effectively from the approaching nucleophile (in the concept of an SN_2 mechanism).

3. Conclusion

We conclude that DAST can be useful for the synthesis of some terminal (fluroethyl)silanes as exemplified by the synthesis of (2-fluoroethyl)diphenylsilane **5** starting from the corresponding



Scheme 4. Synthesis of TMOP protected silanes. *Reagents and conditions*: (a) TMEDA, *n*-BuLi, hexane, 20 °C, 16 h; (b) TMOP-Li, hexane, 0 °C for 10 min then r.t. 1 h, 80%; (c) 9-BBN 0.5 M, THF, r.t., 3 h then H_2O, NaOH 3 M, H_2O_2 30%, 0 °C to reflux, 3 h, 80%; (d) Ac_2O, pyridine, $DMAP_{(cat)}$, DCM, 0 °C 30 min then r.t. 3 h, 48%; (e) MsCl, Et_3N, DCM, −30 °C to −3 °C within 2 h, 90%; (f) KF/Kryptofix, MeCN, r.t., 2 h, 17% (**17**) and 26% (**18**); (g) DAST, DCM, −78 °C, 30 min; (h) TMOP-Li, hexane, 0 °C for 10 min then r.t. 1 h, 65%; (i) KF/Kryptofix, MeCN, r.t. no reaction; (j) AcONa, DMF, 150 °C, no reaction.

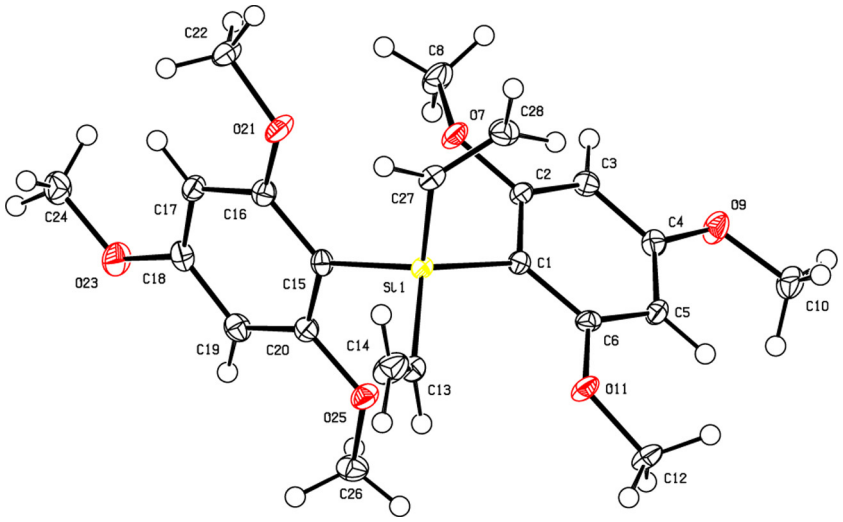


Fig. 1. ORTEP drawing and numbering scheme for **13** (thermal ellipsoids drawn at 40% probability).

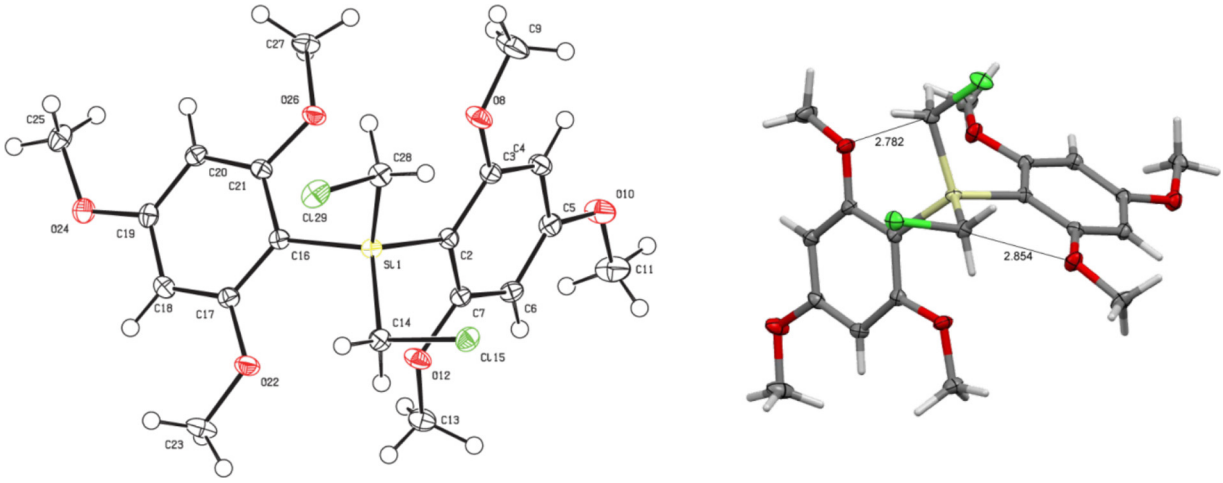


Fig. 2. ORTEP drawing and numbering scheme for **20** (thermal ellipsoids drawn at 40% probability). Geometry shows the methoxy group oxygens positioned in the close proximity of the targeted electrophilic carbons (2.782 and 2.854 Å).

hydroxyl compound. This substitution reaction is of scientific interest since it directly and conveniently leads to a not easily accessible class of compounds circumventing the copious radical reaction with vinylfluoride, the only known reaction which leads to (2-fluoroethyl)silanes. To our knowledge, compound **5** is also the first compound to be synthesized via an exchange reaction with DAST where other nucleophilic fluorinating agents (KF/Kryptofix, TBABF/KHF_2, Yarovenko reagent) for the same or similar synthons failed to give any trace of the corresponding (2-fluoroethyl)silane. The substitution path seems to be favored at a low temperature and using a non-polar solvent. Substitution of the two phenyl groups with the bulky and easily cleavable TMOP groups failed to give any trace of the corresponding (2-fluoroethyl)silane which shows the strong influence of the silicon substituents on the outcome of the reaction. Other groups, presumably electron donating ones, could potentially lead to more favorable ratios of substitution over elimination.

4. Experimental

4.1. Materials and methods

All reagents and starting materials were purchased from commercial suppliers and used without further purification. (Diphenyl)divinylsilane **1** [18], (diphenyl)bischloromethylsilane **9** [22], (dichloro)divinylsilane **12** [18], and (dichloro)bischloromethylsilane **19** [27] were synthesized by following published protocols with slight modifications. All solvents used for reactions were purchased as anhydrous grade from Acros Organics (puriss., dried over molecular sieves, $H_2O < 0.005\%$) and were used without further purification unless otherwise stated. Solvents for extractions, column chromatography and thin layer chromatography (TLC) were purchased as commercial grade. All non aqueous reactions were performed under an argon atmosphere using flame-dried glassware and standard syringe/septa techniques. In general, reactions were magnetically stirred and monitored by TLC performed on Merck TLC glass sheets (silica gel 60 F_{254}). Spots were visualized with UV light ($\lambda = 254$ nm) or through staining with anisaldehyde solution or basic aq. $KMnO_4$ solution and subsequent heating. Chromatographic purification of products was performed using Fluka silica gel 60 for preparative column chromatography (particle size 40–63 μm). Reactions at 0 °C were carried out in an ice/water bath. Reactions at −78 °C were carried out in a dry ice/acetone bath.

Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or C_6D_6 on a Bruker Av-400 spectrometer at room temperature. The measured chemical shifts are reported in δ (ppm) and the residual signal of the solvent was used as the internal standard

($CDCl_3$ ^1H: δ = 7.26 ppm, ^{13}C: δ = 77.0 ppm, C_6D_6: ^1H: δ = 7.16 ppm, ^{13}C: δ = 128.39 ppm). For the ^{19}F NMR spectra, $CFCl_3$(=0.00 ppm) was used as the internal standard. All ^{13}C NMR spectra were measured with complete proton decoupling. ^1H and ^{13}C NMR peaks were fully assigned for all new compounds. Analysis and assignment of the ^1H NMR data were supported by ^1H, ^1H COSY and ^{13}C, ^1H HSQC experiments. The assignment of the ambiguous C-2/5 and C-4 in the case of the TMOP analogs, was established through the observation of long range heteronuclear coupling with the protons of their corresponding methoxy groups in ^{13}C, ^1H HMBC experiments. The numbering of the TMOP atoms is shown in Scheme 2. For compound **8** the chemical shift of the carbon N–*C*H=CH–N of the imidazole ring was differentiated from its geminal one on the basis of its heteronuclear long range coupling with the $SiCH_2CH_2N$ protons. Data of NMR spectra are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad signal. The coupling constant *J* is reported in Hertz (Hz). Mass spectra were recorded on a Waters Micromass Autospec Ultima (EI-sector) or a Varian Ionspec Ultima (MALDI/ESI-FT-ICR) (both MS service of Laboratory of Organic Chemistry (LOC) at the ETH Zurich).

4.2. Chemistry

4.2.1. 2,2′-(Diphenylsilanediyl)diethanol (**2**)

A solution of diphenyldivinylsilane **1** (4.8 g, 20.3 mmol) in 30 ml THF was added dropwise to a 0.5 M solution of 9-borabicyclo[3.3.1]nonane in THF (42.6 mmol, 85 ml) and the resulting mixture was stirred at room temperature for 4 h, followed by the addition of water (16.2 ml) and 3 M aqueous sodium hydroxide solution (16.2 ml). Subsequently, aqueous hydroxide peroxide solution (30 wt%, 16.2 ml) was added dropwise at 0 °C within 15 min and the reaction mixture was heated to reflux for 3 h. Upon cooling to 20 °C, the aqueous layer was saturated with potassium carbonate, the organic layer was removed and the aqueous layer was extracted with ethyl acetate (3× 20 ml). The combined organic phases were dried over anhydrous potassium carbonate, filtered and concentrated to dryness. The crude was dissolved in dichloromethane (80 ml), placed at 4 °C for 4 h and then at −25 °C for 18 h. The precipitated crystalline cyclooctane-1,5-diol was filtered off (5.1 g) and washed with cold dichloromethane. The filtrate and washings were combined and the solvent was removed under reduced pressure. The residue was purified by gravity column chromatography on silica gel using ethyl acetate. The fractions containing the product were combined and solvents were removed under reduced pressure to give **2** in 76% yield as a colorless viscous oil (4.2 g) which solidified upon standing at room temperature. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56–7.49 (m, 4 H, SiC_6H_5), 7.43–7.33 (m, 6 H, SiC_6H_5), 3.83 (t, *J* = 7.6 Hz, 4 H, $SiCH_2CH_2OH$), 1.64 (br, 2 H, $SiCH_2CH_2OH$), 1.58 (t, *J* = 7.6 Hz, 4 H, $SiCH_2CH_2OH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.9, 134.7, 129.6 and 128.0 (SiC_6H_5), 59.5 ($SiCH_2CH_2OH$), 18.1 ($SiCH_2CH_2OH$). ESI-QTOF MS *m*/*z* calculated for $C_{16}H_{20}O_2Si$ $[M+Na]^+$ 295.1125, found 295.1125.

4.2.2. 2-((2-Hydroxyethyl)diphenylsilyl)ethyl acetate (**3**)

To an ice cold solution of **2** (4.2 g, 15.42 mmol), triethylamine (3.12 g, 30.8 mmol) and DMAP (19 mg, 1.56 mmol) in dichloromethane (30 ml), acetic anhydride (1.73 ml, 18.34 mmol) was added dropwise within 10 min. The resulting reaction mixture was stirred for 30 min at 0 °C and then for 3 h at room temperature. The reaction mixture was then diluted with dichloromethane (30 ml) and washed with saturated aqueous sodium hydrogen carbonate solution (1× 30 ml), water (1× 30 ml) and brine (1× 30 ml). The organic phase was dried over sodium sulfate, filtered and concentrated to dryness. Purification of the residue by flash column chromatography (hexane/ethyl acetate 7:3) afforded 2.4 g (50%) of monoacetate **3** as a colorless viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.47 (m, 4 H, SiC_6H_5), 7.45–7.32 (m, 6 H, SiC_6H_5), 4.20 (t, *J* = 8.4 Hz, 2 H, $SiCH_2CH_2OAc$), 3.80 (t, *J* = 8.3 Hz, 2 H, $SiCH_2CH_2OH$), 1.93 (s, 3 H, $-O(C=O)CH_3$), 1.52–1.66 (m, 5 H, $HOCH_2CH_2SiCH_2CH_2OAc$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1 ($-O(C=O)CH_3$), 134.7, 134.3, 129.7 and 128.1 (SiC_6H_5), 61.9 ($SiCH_2CH_2Oac$), 59.5 ($SiCH_2CH_2OH$), 21.0 ($SiCH_2CH_2OAc$), 18.2 ($SiCH_2CH_2OH$), 14.1 ($-O(C=O)CH_3$). ESI-QTOF MS *m*/*z* calculated for $C_{18}H_{22}O_3Si$ $[M+Na]^+$ 337.1230, found 337.1227.

4.2.3. 2-((2-Bromoethyl)diphenylsilyl)ethyl acetate (**3′**)

Triphenylphosphine (690 mg, 2.44 mmol) was added to an ice cold solution of **3** (640 mg, 2.04 mmol) in dichloromethane (10 ml) and after 10 min of stirring carbon tetrabromide (1.01 g, 3.05 mmol) was added in three portions within 5 min. The bright yellow solution that formed was allowed to reach room temperature where it was stirred for 2 h. The reaction mixture was then diluted with DCM and washed once with aq. NaHCO3 (sat), followed by water (1×) and brine (1×), dried over sodium sulfate, filtered and evaporated to dryness. The crude oil that resulted was purified by flash column chromatography using hexane/ethyl acetate (95:5) to provide the title compound as a clear, colorless oil (740 mg, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.35 (m, 10 H, SiC_6H_5), 4.18 (t, J_H = 8 Hz, 2 H, $SiCH_2CH_2OAc$), 3.58–3.50 (m, 2 H, $SiCH_2CH_2Br$), 1.99–1.92 (m, 5 H, $SiCH_2CH_2Br$ and $-O(C=O)CH_3$), 1.59 (t, *J* = 8 Hz, 2 H, $SiCH_2CH_2OAc$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0 ($-O(C=O)CH_3$), 134.6, 133.0, 130.1 and 128.3 (SiC_6H_5), 61.5 ($SiCH_2CH_2OAc$), 30.3 ($SiCH_2CH_2Br$), 20.9 ($SiCH_2CH_2OAc$), 20.5 ($SiCH_2CH_2Br$), 13.6 ($-O(C=O)CH_3$). ESI-QTOF MS *m*/*z* calculated for $C_{18}H_{21}BrO_2Si$ $[M+Na]^+$ 399.0392, found 399.0388.

Reaction conditions for subsequent fluorination: Potassium fluoride (28 mg, 0.47 mmol) was suspended to a solution of **3′** (160 mg, 0.42 mmol) in acetonitrile (15 ml) at 0 °C, followed by the addition of Kryptofix® (176 mg, 0.47 mmol) in three portions within 5 min. During the addition, bubbling was observed. After 30 min, the reaction was allowed to reach room temperature and was diluted with ethyl acetate and washed with water and brine, dried over sodium sulfate and evaporated to dryness. The crude was analyzed by ^1H NMR where only fluorosilane **4** was detected. In a different reaction, **3′** was dissolved in THF and TBAF 1 M in THF was added at 0 °C resulting again only in fluorosilane **4**.

4.2.4. 2-(Diphenyl(2-(((trifluoromethyl)sulfonyl)oxy)ethyl)silyl)ethyl acetate (**3″**)

Triflic anhydride (0.14 ml, 227 mg, 0.805 mmol) was added dropwise within 3 min to a solution of **3** (230 mg, 0.73 mmol) and pyridine (70 μl, 69.4 mg, 0.88 mmol) in dichloromethane (2 ml) at −5 °C. The pink solution that resulted was stirred at 0 °C for 30 min. The solution was then diluted with cold DCM, washed once with cold HCl 1 M and dried shortly over magnesium sulfate. The dichloromethane was evaporated with a stream of Argon to a volume of approximately 5 ml which was used for the next step without further purification due to the high sensitivity of the triflate.

Reaction conditions for fluorination with TBABF/KHF₂: The above mentioned solution was cooled at 0 °C and KHF_2 (17.1 mg, 0.22 mmol) was added, followed by the dropwise addition of TBABF (247 mg, 0.88 mmol, dried at 100 °C for 15 min under high vacuum before use) as a solution in 2 ml dichloromethane. The reaction was stirred for 3 h at 0 °C and then was allowed to reach room temperature and washed with water and brine. It was then dried over sodium sulfate, filtered and evaporated to dryness. NMR analysis of the crude revealed no trace of the desired 2-fluoroethylsilane **5**.

4.2.5. 2-((2-Fluoroethyl)diphenylsilyl)ethyl acetate (**5**)

A solution of **3** (2.4 g, 7.63 mmol) in dry DCM (65 ml) was cooled to −78 °C and DAST (1.48 g, 9.16 mmol) was added dropwise within 20 min. The reaction mixture was stirred at −78 °C for 30 min before being quenched by the addition of $NaHCO_3$ 5% solution (10 ml). After reaching room temperature, the aqueous layer was removed and the organic phase was washed with 5% $NaHCO_3$ solution (2× 30 ml), brine (1× 70 ml), dried over sodium sulfate, filtered and evaporated to dryness under reduced pressure. The crude oil was dissolved in acetone (16 ml), sat. $NaHCO_3$ solution (16 ml) was added and the reaction mixture was stirred for 16 h. After this time, water was added (20 ml) and the solution was extracted with ether (3× 30 ml). The organic fractions were combined and dried over sodium sulfate, filtered and concentrated under vacuum. The crude was purified by flash chromatography with hexane/ethyl acetate 9:1 to yield 242 mg (10%) of the desired 2-fluoroethylsilane **5** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.33 (m, 10 H, SiC_6H_5), 4.59 (dt, $^2J_{H-F}$ = 48.2 Hz, $^3J_{H-H}$ = 8.3 Hz, 2 H, $SiCH_2CH_2F$), 4.21 (t, $^3J_{H-H}$ = 8 Hz, 2 H, $SiCH_2CH_2OAc$), 1.88 (s, 3 H, –O(C=O)CH_3), 1.75 (dt, $^3J_{F-H}$ = 20.2 Hz, $^3J_{H-H}$ = 8.3 Hz, 2 H, $SiCH_2CH_2F$), 1.57 (t, $^3J_{H-H}$ = 8 Hz, 2 H, $SiCH_2CH_2OAc$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0 (–O(C=O)CH_3), 134.6, 133.5, 129.9 and 128.2 (SiC_6H_5), 81.6 (d, $^1J_{C-F}$ = 166 Hz, $SiCH_2CH_2F$), 61.7 ($SiCH_2CH_2OAc$), 20.9 ($SiCH_2CH_2OAc$), 16.4 (d, $^2J_{C-F}$ = 18.4 Hz, $SiCH_2CH_2F$), 14.1 (–O(C=O)CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ −201.3 to −201.7 (m, 1 F). ESI-QTOF MS *m/z* calculated for $C_{18}H_{21}FO_2Si$ $[M+Na]^+$ 339.1187, found 339.1191.

4.2.6. (2-(Hydroxydiphenylsilyl)ethyl acetate) (**6**)

Silanol **6** was isolated by increasing the polarity of the eluent to hexane/ethyl acetate 8:2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.58 (m, 4 H, SiC_6H_5), 7.46–7.34 (m, 6 H, SiC_6H_5), 4.31 (t, *J* = 8.1 Hz, 2 H, $SiCH_2CH_2OAc$), 3.21 (s, 1 H, SiO*H*), 1.86 (s, 3 H, –O(C=O)CH_3), 1.61 (t, *J* = 8.1 Hz, 2 H, $SiCH_2CH_2OAc$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5 (–O(C=O)CH_3), 135.4, 134.0, 130.1 and 128.0 (SiC_6H_5), 61.5 ($SiCH_2CH_2OAc$), 20.9 ($SiCH_2CH_2OAc$), 16.2 (–O(C=O)CH_3). ESI-QTOF MS *m/z* calculated for $C_{16}H_{18}O_3Si$ $[M+Na]^+$ 309.0917, found 309.0923.

4.2.7. 2-((2-Fluoroethyl)diphenylsilyl)ethanol (**7**)

To a solution of **5** (240 mg, 0.76 mmol) in methanol (4 ml) at room temperature was added potassium carbonate (110 mg, 0.80 mmol) in one portion. After stirring for 1 h, the reaction mixture was quenched with water (6 ml) and extracted with ethyl acetate (3× 5 ml). The combined organic layers were washed with brine (10 ml) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to afford **7** as a colorless oil (197 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.35 (m, 10 H, SiC_6H_5), 4.64 (dt, $^2J_{F-H}$ = 48 Hz, $^3J_{H-H}$ = 8 Hz, 2 H, $SiCH_2CH_2F$), 3.80 (t, *J* = 8.0 Hz, 2 H, $SiCH_2CH_2OH$), 1.75 (t, $^3J_{F-H}$ = 20.1 Hz, $^3J_{H-H}$ = 8 Hz, 2 H, $SiCH_2CH_2F$), 1.57 (t, *J* = 8.0 Hz, 2 H, $SiCH_2CH_2OH$), 1.34 (br, 1 H, $SiCH_2CH_2OH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 134.1, 129.8 and 128.1 (SiC_6H_5), 81.9 ($SiCH_2CH_2F$, d, $^1J_{C-F}$ = 167.8 Hz), 59.4 ($SiCH_2CH_2OH$), 18.3 ($SiCH_2CH_2OH$), 15.9 ($SiCH_2CH_2F$, d, $^2J_{C-F}$ = 17.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −201.2 (septet, $^2J_{F-H}$ = 48 Hz, $^3J_{F-H}$ = 20.1 Hz, 1 F). ESI-QTOF MS *m/z* calculated for $C_{16}H_{19}FOSi$ $[M+Na]^+$ 297.1081, found 297.1074.

4.2.8. 1-(2-((2-Fluoroethyl)diphenylsilyl)ethyl)-2-nitro-1H-imidazole (**8**)

Triphenylphosphine (229 mg, 0.87 mmol) was added to a solution of **7** (184 mg, 0.67 mmol) and 2-nitroimidazole (98.5 mg, 0.87 mmol) in THF (30 ml). After stirring for 15 min at room temperature, DIAD (180 mg, 0.87 mmol) was added dropwise within 10 min and the clear yellow solution that formed was stirred for 16 h. After this time the solvent was removed under reduced pressure and the residue was chromatographed on silica gel using ethyl acetate/hexane 8:2–7:3 as eluent system to yield compound **8** as a yellow oil (227 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.39 (m, 10 H, SiC_6H_5), 7.07 (d, *J* = 1 Hz, 1 H, N–CH=C*H*–N), 7.00 (d, *J* = 1 Hz, 1 H, N–C*H* = CH*N*), 4.64 (dt, $^2J_{F-H}$ = 48 Hz, $^3J_{H-H}$ = 8 Hz, 2 H, $SiCH_2CH_2F$), 4.47–4.40 (m, 2 H, $SiCH_2CH_2N$), 1.86–1.79 (m, 2 H, $SiCH_2CH_2N$, partially overlapping with $SiCH_2CH_2F$), 1.75 (dt, $^3J_{F-H}$ = 23.1 Hz, $^3J_{H-H}$ = 8 Hz, 2 H, $SiCH_2CH_2F$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5 (N–C(NO_2)–N), *134*.6, 132.5, 130.3 and 128.5 (SiC_6H_5), 128.4 (N–CH=CH–N) 125.1 (N–CH=CH–N), 81.4 (d, $^1J_{C-F}$ = 166.4 Hz), 47.2, 16.7, 15.9 (d, $^2J_{C-F}$ = 20 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −202.9 (septet, $^2J_{F-H}$ = 48 Hz, $^3J_{F-H}$ = 23.1 Hz, 1 F). ESI-QTOF MS *m/z* calculated for $C_{19}H_{20}FN_3O_2Si$ $[M+Na]^+$ 392.1201, found 392.1198.

4.2.9. (Diphenylsilanediyl)bis(methylene) diacetate (**10**)

Sodium acetate (5.83 g, 71.1 mmol) was added to a solution of (diphenyl)bischloromethylsilane **9** (2 g, 7.11 mmol) in DMF (14 ml) and the suspension was heated at 100 °C for 6 h. After cooling, water was added (50 ml) and the reaction was extracted with ethyl acetate (3× 25 ml). The combined organic layers were dried under sodium sulfate, filtered and evaporated to dryness. The crude was purified by flash column chromatography on silica with hexane/ethyl acetate 9:1 to afford the title compound (2.1 g, 90%) as a clear oil which solidified upon standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.56 (m, 4 H, SiC_6H_5), 7.49–7.37 (m, 6 H, SiC_6H_5), 4.38, (s, 4 H, $SiCH_2OAc$), 2.00 (s, 6 H, –O(C=O)CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5 (–O(C=O)CH_3), 135.06, 130.8, 130.4 and 128.2 (SiC_6H_5), 53.3 ($SiCH_2OAc$), 20.7 (–O(C=O)CH_3). ESI-QTOF MS *m/z* calculated for $C_{18}H_{20}O_4Si$ $[M+Na]^+$ 351.1023, found 351.1023.

4.2.10. ((Hydroxymethyl)diphenylsilyl)methyl acetate (**11**)

Potassium carbonate (207 mg, 1.5 mmol) was added to a solution of **10** (1 g, 3.04 mmol) in methanol (25 ml) and the solution was stirred for 1 h at room temperature. The reaction was then filtered and the filtrate was partitioned between water (40 ml) and ethyl acetate (40 ml). The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2× 40 ml). The combined organic layers were washed with brine, dried under sodium sulfate, filtered and evaporated to dryness under reduced pressure. The crude was purified by flash column chromatography using hexane/ethyl acetate 8:2 to yield compound **11** (166 mg, 19%) as a clear colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.58 (m, 4 H, SiC_6H_5), 7.48–7.36 (m, 6 H, SiC_6H_5), 4.42, (s, 2 H, $SiCH_2OAc$), 3.98 (s, 2 H, $SiCH_2OH$), 2.02 (s, 3 H, –O(C=O)CH_3), 1.85 (br, 1 H, $SiCH_2OH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1 (–O(C=O)CH_3), 135.08, 131.4, 130.3 and 128.2 (SiC_6H_5), 54.3 ($SiCH_2OAc$), 52.0 ($SiCH_2OH$), 20.8 (O(C=O)CH_3). ESI-QTOF MS *m/z* calculated for $C_{16}H_{18}O_3Si$ $[M+Na]^+$ 309.0917, found 309.0917.

4.2.11. Bis(2,4,6-trimethoxyphenyl)divinylsilane (**13**)

To a solution of 1,3,5-trimethoxybenzene (2 g, 11.89 mmol) and TMEDA (1.42 g, 12.22 mmol) in dry *n*-hexane (14.1 ml) under vigorous stirring, was added dropwise a 2.5 M solution of *n*-butyllithium in hexanes (5 ml, 12.5 mmol) within 8 min at 20 °C. The resulting suspension of TMOP-Li was stirred at room temperature for another 16 h and then added dropwise at 0 °C within 10 min to a stirred solution of dichlorodivinylsilane **12** (0.91 g, 5.94 mmol) in dry *n*-hexane (5.7 ml). The reaction mixture was allowed to warm to room temperature and stirred for an additional hour. The reaction was quenched by slowly adding saturated NH_4Cl (7 ml) at 0 °C. Water (25 ml) and ethyl acetate (15 ml) were added and the organic layer was separated. The aqueous phase was washed with ethyl acetate (2× 20 ml) and the

combined organic layers were washed with water (1× 25 ml) and brine (1× 25 ml), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified using flash chromatography with hexane/ethyl acetate 9:1 to yield **13** as a white solid (1.98 g, 80%). Crystals, suitable for X-ray crystallography, were obtained by slow evaporation from CH_2Cl_2/hexane. ^{1}H NMR (400 MHz, C_6D_6): δ 7.24 (dd, $^3J_{trans}$ = 20.3 Hz, $^3J_{cis}$ = 14.3 Hz, 2 H, C*H*=CH_2), 6.17 (dd, $^3J_{cis}$ = 14.3 Hz, $^2J_{gem}$ = 4.1 Hz, 2 H, CH=C*H*H), 6.09 (s, 4 H, H-3/H-5), 5.99 (dd, $^3J_{trans}$ = 20.3 Hz, $^2J_{gem}$ = 4.1 Hz, 2 H, CH=CH*H*), 3.38 (s, 6 H, *p*-OC*H*$_3$), 3.29 (s, 12 H, *o*-OC*H*$_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 167.1 (C-2/C-6), 163.9 (C-4), 140.9 (*C*H=CH_2), 129.4 (CH=*C*H_2), 106.5 (C-1), 91.8 (C-3/C-5), 55.5 (*o*-OCH_3), 55.0 (*p*-OCH_3). ESI-QTOF MS *m*/*z* calculated for $C_{22}H_{28}O_6Si$ $[M+H]^+$ 417.1728, found 417.1726.

*4.2.12. 2,2′-(Bis(2,4,6-trimethoxyphenyl)silanediyl)diethanol (**14**)*

A solution of **13** (1.98 g, 4.75 mmol) in THF (16 ml) was added to a 0.5 M solution of 9-borabicyclo[3.3.1]nonane (20 ml, 9.98 mmol) and the resulting mixture was stirred at room temperature for 3 h, followed by the addition of water (4 ml) and a 3 M aqueous sodium hydroxide solution (4 ml). Subsequently, a 30 wt% aqueous hydrogen peroxide solution (4 ml) was added dropwise at 0 °C within 10 min and the reaction mixture was heated to reflux for 3 h. Upon cooling to 20 °C, the aqueous layer was saturated with potassium carbonate, the organic layer was removed and the aqueous layer was extracted with ethyl acetate (3× 10 ml). The combined organic phases were dried over anhydrous potassium carbonate, filtered and concentrated to dryness. The crude was dissolved in dichloromethane (20 ml), placed at 4 °C for 2 h and then at −25 °C for 16 h. The precipitated cyclooctane-1,5-diol was filtered off (1.1 g) and washed with cold dichloromethane. The filtrates were combined and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel starting with ether to remove the rest of cyclooctane-1,5-diol following by ether/ethanol 7:3 to elute the desired compound. The fractions containing the product were combined and the solvents were removed under reduced pressure to give the title compound as a colorless viscous oil (1.73 g, 80%), which solidified upon standing at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 6.04 (s, 4 H, H-3/H-5), 3.99 (t, *J* = 7.9 Hz, 4 H, SiCH$_2$C*H*$_2$OH), 3.37 (s, 6 H, *p*-OC*H*$_3$), 3.23 (s, 12 H, *o*-OC*H*$_3$), 1.93 (t, *J* = 7.9 Hz, 4 H, SiC*H*$_2$CH$_2$OH), 1.22 (br, 2 H, O*H*). ^{13}C NMR (100 MHz, C_6D_6): δ 166.5 (C-2/C-6), 163.4 (C-4), 106.1 (C-1), 91.2 (C-3/C-5), 61.1 (SiCH$_2$*C*H$_2$OH), 55.2 (*o*-OCH$_3$), 55.1 (*p*-OCH$_3$), 22.9 (SiCH$_2$CH$_2$OH). ESI-QTOF MS *m*/*z* calculated for $C_{22}H_{32}O_8Si$ $[M+Na]^+$ 475.1764, found 475.1762.

*4.2.13. 2-((2-Hydroxyethyl)bis(2,4,6-trimethoxyphenyl)silyl)ethyl acetate (**15**)*

To an ice cold solution of **14** (1.73 g, 3.82 mmol), pyridine (0.62 ml, 7.67 mmol) and DMAP (56 mg, 0.46 mmol) in dichloromethane (14 ml), acetic anhydride (0.4 ml, 4.24 mmol) was added dropwise within 10 min. The resulting reaction mixture was stirred at 0 °C for 30 min and at room temperature for 3 h. The mixture was diluted with ethyl acetate (50 ml) and washed with a 10% aqueous copper sulfate solution (3× 20 ml), water (1× 30 ml), saturated aqueous sodium hydrogen carbonate (1× 30 ml) and brine (1× 30 ml). The organic phase was dried over sodium sulfate, filtered and concentrated to dryness. Purification of the residue by flash column chromatography (hexane/ethyl acetate 5:5) afforded monoacetate **15** as a colorless viscous liquid (0.91 g, 48%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.02 (s, 4 H, H-3/H-5), 4.60 (m, 2 H, SiCH$_2$C*H*$_2$OAc), 3.96 (t, *J* = 7.8 Hz, 2 H, SiCH$_2$C*H*$_2$OH), 3.36 (s, 6 H, *p*-OC*H*$_3$), 3.26 (s, 12 H, *o*-OC*H*$_3$), 2.06 (m, 2 H, SiC*H*$_2$CH$_2$OAc), 1.92 (t, *J* = 7.8 Hz, 2 H, SiC*H*$_2$CH$_2$OH), 1.73 (s, 3 H, –OCOC*H*$_3$), 1.12 (br, 1 H, O*H*). ^{13}C NMR (100 MHz, C_6D_6): δ 170.8 (–O(*C*=O)CH$_3$), 166.7 (C-2/C-6), 163.8 (C-4), 106.1 (C-1), 91.4 (C-3/C-5), 64.8 (SiCH$_2$*C*H$_2$OAc), 61.5 (SiCH$_2$*C*H$_2$OH), 55.3 (*o*-OCH$_3$), 55.0 (*p*-OCH$_3$), 23.4 (SiCH$_2$CH$_2$OH), 21.3 (–OCOCH$_3$), 19.3 (SiCH$_2$CH$_2$OAc). HRMS: calculated for 461.0948 (M+H) found 461.0945.

*4.2.14. 2-((2-((Methylsulfonyl)oxy)ethyl)bis(2,4,6-trimethoxyphenyl)silyl)ethyl acetate (**16**)*

To a solution of **15** (120 mg, 0.24 mmol) and triethylamine (0.13 ml, 0.93 mmol) in dichloromethane (1.6 ml) a solution of methanesulfonylchloride (31 mg, 0.27 mmol) in dichloromethane (0.2 ml) was added dropwise at −30 °C within 1 min. The reaction mixture was stirred for 2 h during which time, the temperature reached −3 °C. The solvent was removed with a stream of argon and the residue was quickly chromatographed on silica gel using benzene/ethyl acetate/triethylamine (80:20:5) as the eluent. The fractions of interest were combined and the solvents were removed under reduced pressure at 30 °C to yield **16** (125 mg, 90%). The compound decomposes rapidly at room temperature but it is stable for a few days at −25 °C as a solution in benzene. ^{1}H NMR (400 MHz, C_6D_6): δ 6.00 (s, 4 H, H-3/H-5), 4.67 (m, 2 H, SiCH$_2$C*H*$_2$OMs), 4.51 (m, 2 H, SiCH$_2$C*H*$_2$OAc), 3.36 (s, 6 H, *p*-OC*H*$_3$), 3.27 (s, 12 H, *o*-OC*H*$_3$), 2.25 (s, 3 H, –OSO$_2$C*H*$_3$), 2.09 (m, 2 H, SiC*H*$_2$CH$_2$OMs), 1.96 (m, 2 H, SiC*H*$_2$CH$_2$OAc), 1.74 (s, 3 H, –OCOC*H*$_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 170.8 (–OCOCH$_3$), 166.7 (C-2/C-6), 164.1 (C-4), 104.6 (C-1), 91.3 (C-3/C-5), 71.9 (SiCH$_2$-*C*H$_2$OMs), 64.2 (SiCH$_2$CH$_2$OAc), 55.3 (*o*-OCH$_3$), 55.0 (*p*-OCH$_3$), 37.3 (–OSO$_2$*C*H$_3$), 21.3 (–OCOCH$_3$), 20.6 (SiCH$_2$CH$_2$OMs), 19.3 (SiCH$_2$-CH$_2$OAc). *Note*: Due to the instability of the compound, HRMS was not possible.

*4.2.15. 2-(Fluorobis(2,4,6-trimethoxyphenyl)silyl)ethyl acetate (**17**)*

To a solution of **16** (56 mg, 0.098 mmol) and Kryptofix 222 (37 mg, 0.098 mmol) in dry acetonitrile (0.3 ml), potassium fluoride (5.7 mg, 0.098 mmol) was added in one portion at 0 °C. The reaction mixture was allowed to reach room temperature and was stirred for 2 h. The reaction was diluted with ethyl acetate (5 ml) and washed with water (1× 2 ml) and brine (1× 2 ml), dried over sodium sulfate, filtered and concentrated to dryness. The crude was chromatographed on silica gel with benzene/ethyl acetate 9:1 to yield fluorosilane **17** (8 mg, 17%) and silanol **18** (12 mg, 26%). *Compound* **17**: ^{1}H NMR (400 MHz, C_6D_6): δ 6.02 (s, 4 H, H-3/H-5), 4.76 (m, 2 H, SiCH$_2$C*H*$_2$OAc), 3.33 (s, 6 H, *p*-OC*H*$_3$), 3.32 (s, 12 H, *o*-OC*H*$_3$), 2.20–2.12 (m, 2 H, SiC*H*$_2$CH$_2$OAc), 1.70 (s, 3 H, –OCOC*H*$_3$). ^{19}F NMR (376.5 MHz, C_6D_6): δ −159.0 (t, $^3J_{F-H}$ = 6.9 Hz). *Compound* **18**: ^{1}H NMR (400 MHz, C_6D_6): δ 6.01 (s, 4 H, H-3/H-5), 4.90 (m, 2 H, SiCH$_2$C*H*$_2$OAc), 3.33 (s, 6 H, *p*-OC*H*$_3$), 3.27 (s, 12 H, *o*-OC*H*$_3$), 2.24 (t, ^3J = 8.7 Hz, 2 H, SiC*H*$_2$CH$_2$OAc), 1.70 (s, 3 H, –OCOC*H*$_3$).

*4.2.16. Bis(chloromethyl)bis(2,4,6-trimethoxyphenyl)silane (**20**)*

1,3,5-Trimethoxybenzene (922 mg, 5.48 mmol) was dissolved in a mixture of TMEDA (656 mg, 5.65 mmol) and dry *n*-hexane (6.5 ml). To this solution and under vigorous stirring, a 2.5 M solution of *n*-butyllithium in hexane (2.3 ml, 5.75 mmol) was added dropwise at 20 °C within 5 min. The resulting suspension of TMOP-Li was stirred at room temperature for another 16 h and then added dropwise at 0 °C within 10 min to a stirred solution of (dichloro)bischloromethylsilane **19** (517 mg, 2.61 mmol) in dry *n*-hexane (2.5 ml). The reaction mixture was allowed to warm to room temperature and stirred for an additional hour. The reaction was quenched by slowly adding saturated NH_4Cl solution (5 ml) at 0 °C. Water (20 ml) and ethyl acetate (10 ml) were added and the organic layer was separated. The aqueous phase was washed with ethyl acetate (2× 15 ml) and the combined organic layers were washed with water (1× 20 ml) and brine (1× 20 ml), dried over

Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by flash chromatography with hexane/ethyl acetate 8:2 to yield 785 mg of **20** a white solid (65%). Crystals, suitable for X-ray crystallography, were obtained by slow evaporation from CH_2Cl_2/hexane. ^{1}H NMR (400 MHz, C_6D_6): δ 5.96 (s, 4 H, H-3/H-5), 4.15 (s, 4 H, SiCH_2Cl), 3.31 (s, 6 H, *p*-OCH_3), 3.17 (s, 12 H, *o*-OCH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 167.1 (C-2/C-6), 164.5 (C-4), 103.0 (C-1), 91.5 (C-3/C-5), 55.3 (*o*-OCH_3), 55.0 (*p*-OCH_3), 31.5 (-CH_2Cl). MALDI MS *m*/*z* calculated for $C_{20}H_{27}Cl_2O_6Si$ $[M+H]^+$ 461.0954, found 461.0948.

4.3. Crystallography

X-ray analyses for **13** and **20** were performed on a Bruker Apex II Duo diffractometer at 100 K. Crystallographic data of $C_{22}H_{28}O_6Si$ (**13**) and $C_{20}H_{26}Cl_2O_6Si$ (**20**) have been deposited with the Cambridge Crystallographic Data Center with deposition numbers CCDC 956644 and CCDC 956645 respectively and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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