Preparation of Novel (Fluoroaryl)silanes and Their Applications in the Organoyttrium-Catalyzed Hydrosilylation of Alkenes and Oxidation to Alcohols

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The synthesis of novel (fluoroaryl)silanes from the respective aryl Grignard reagents and silyl triflates is reported. The new silanes were used in the hydrosilylation of alkenes catalyzed by the organoyttrium complex $Cp^*_2YMe\cdot THF$ (THF = tetrahydrofuran). (Fluoroaryl)silanes were found to react faster than phenylsilane and in good to near quantitative yields. The resulting [(fluoroaryl)silyl]alkane products were found to be labile under very mild oxidative conditions, with both disubstituted alkenes and silyl-protected alcohol functionalities tolerating the oxidation.

Introduction

Organolanthanide and group 3 complexes have been widely investigated[1] as highly efficient catalysts for a variety of transformations, including the hydrosilylation[2] of alkenes and alkynes as well as the cyclization/silylation[3] of polyunsaturated organic compounds. This protocol allows the selective and rapid construction of complex organosilanes while tolerating a variety of functional groups including hindered alkenes, silyl-protected alcohols, and tertiary amines.[2b] The organosilane products of alkene hydrosilylation reactions can be oxidized to alcohols,[4] making the hydrosilylation/oxidation protocol the equivalent of the classic hydroboration/oxidation reaction. The hydrosilylation/oxidation protocol also has a particularly useful advantage: the alkylsilane resulting from the hydrosilylation reaction is stable in the presence of oxygen, but an organoborane intermediate is not. This allows the resulting organosilane to be easily purified and even carried through several synthetic operations before revealing the latent alcohol by oxidation.

The utility of the synthesis of alcohols from alkenes using a hydrosilylation/oxidation protocol can be limited, however, by the reaction conditions used in the oxidation. Organolanthanide and group 3 complexes are used in conjunction with arylsilanes which are not typically used in other hydrosilylation protocols.[2f] The use of arylsilanes in place of more readily oxidized alkoxysilanes requires the use of a protodesilylation protocol to remove the arylsilane moiety under strongly acidic conditions.[4] Basic oxidation protocols have also been developed for the cleavage of phenylsilanes, but they, like their acidic counterparts, require harsh conditions and long reaction times.[5] Many functional groups are not compatible with these oxidation methods.[6] Mild protocols exist but are typically useful only when there is an allyl group or heteroatom bonded to the silicon atom.[6] These classes of silanes are not compatible with organolanthanide or group 3 catalysts.[7]

By modifying the nature of the aryl group bonded to silicon, it seemed reasonable that the oxidative lability of the hydrosilylated product could be enhanced without the introduction of a heteroatom. By increasing the lability of the organosilane, it was hoped that milder oxidation conditions and shorter reaction times could be used. Mechanistic work by Tamao has demonstrated that the addition of electron withdrawing groups to an aryl unit bonded to silicon increases its rate of cleavage under oxidizing conditions.[8] We therefore envisioned that the installation of fluorine atoms or trifluoromethyl groups on the aromatic ring of an arylsilane would increase the reactivity of the organosilane products toward oxidizing agents.

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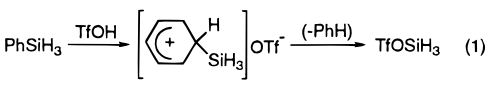
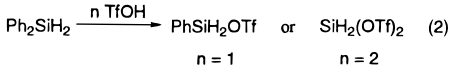
The synthesis of (fluoroaryl)silanes via traditional methods of arylsilane preparation was not desirable for several reasons. Previously investigated procedures involved the addition of a Grignard reagent to either tri- or tetrachlorosilane followed by reduction of the resulting silyl chloride with a hydride reagent.[9] The reactions produced mixtures of silanes, and yields of monosubstituted silanes were often low.[9,10] This problem was compounded when the nucleophile was strongly electron withdrawing, as in the case of a pentafluorophenyl Grignard reagent. Each substitution increases the electrophilicity of the silicon center such that little or no monosubstituted silane can be isolated. Furthermore, the desired monosubstituted chlorosilanes must be separated from the other products by distillation and handled with care because of their water sensitivity.

As a more expedient route to (fluoroaryl)silanes, we chose to exploit the ability of arylsilanes to be protodesilylated under acidic conditions, as demonstrated in the oxidation protocols previously mentioned.[4] When trifluoromethanesulfonic acid is used as a protodesilylating agent, silyl triflates are formed (eq 1).[11] Silyl triflate-





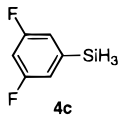
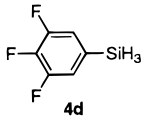
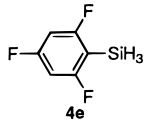
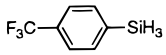
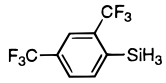
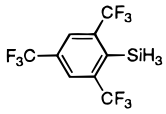
forming reactions proceed selectively, removing a single aryl group for each equivalent of trifluoromethanesulfonic acid added (eq 2).[12] The newly formed silyl triflates can be easily substituted with a variety of nucleophiles.[11] Uhlig and others have demonstrated the utility of silyl triflates as intermediates in the synthesis of a wide variety of silanes, disilanes, and silane oligomers.[12,13]

Once the synthesis of (fluoroaryl)silanes was achieved, we investigated their reactivity with 1-decene in the presence of the organoyttrium catalyst $Cp^*_2YMe\cdot THF$ (**1**; THF = tetrahydrofuran). The resulting (arylsilyl)-decane products were then oxidized to 1-decanol with a $H_2O_2/KHCO_3$ system modeled after Tamao's protocol[4e] to evaluate the effect of fluorine substitution on silane lability. After finding appropriate oxidative conditions, several reactions were performed to demonstrate the utility of the oxidation method.

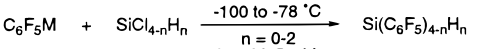
Results and Discussion

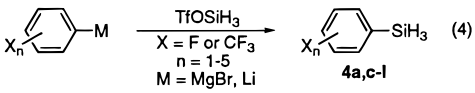
(Fluoroaryl)silane Preparations. Initial attempts at the preparation of (pentafluorophenyl)silane (**4a**) via addition of (pentafluorophenyl)magnesium bromide to tetrachlorosilane gave the tetrasubstituted silane as the major product even at low temperature and high dilution (eq 3). Other researchers found that this method gave poor yields of the monosubstituted silanes even when less electron withdrawing aryl groups were used.[9,10a] Various (fluoroaryl)silanes were then synthesized by using silyl triflates as intermediates (eq 4). This method was successfully applied in the synthesis of a wide variety of (fluoroaryl)silanes from the respective aryl Grignard or lithium reagent and silyl triflate as shown in Table 1. Diarylsilane **5** was prepared by addition of (pentafluorophenyl)lithium to phenylchlorosilane in good yield (eq 5). Three fluorine-free silanes were also prepared using the silyl triflate method as outlined in Table 2.

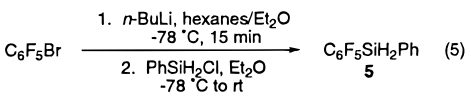
Table 1. (Fluoroaryl)silane Preparations (Equation 4)[a]

entry	(fluoroaryl)silane	% isolated yield
1	$C_6F_5SiH_3$ **4a**	47
2	$C_6F_5SiH_2Me$ **4b**	53[b]
3	 **4c**	37
4	 **4d**	62
5	 **4e**	45
6	 **4f**	53
7	 **4g**	46
8	 **4h**	56
9	 **4i**	57[c]

[a] All silanes were prepared from silyl triflate and the aryl Grignard reagent unless otherwise noted. [b] Prepared from methylsilyl triflate. [c] Prepared from the aryllithium reagent.







(9) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700.
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(11) Bassindale, A. R.; Stout, T. *J. Organomet. Chem.* **1984**, *271*, C1.
(12) Uhlig, W. *Chem. Ber.* **1996**, *129*, 733.
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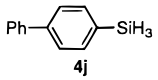
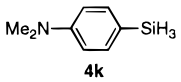
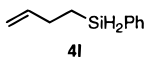
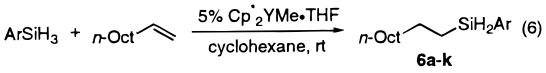
Table 2. Arylsilane Preparations (Equation 4)[a]

entry	arylsilane	% isolated yield
1	 **4j**	67
2	 **4k**	65
3	 **4l**	81[b]

[a] All silanes were prepared from silyl triflate and the aryl Grignard reagent unless otherwise noted. [b] Prepared from phenylsilyl triflate.

The advantages of the synthesis of silanes via a silyl triflate intermediate are numerous. The formation of silyl triflates is quite rapid in most cases, even at lower temperatures in the case of silyl triflate.[11] Silyl triflate reagents can be generated in situ and used without further purification in trapping reactions with a wide variety of organometallic reagents and nucleophiles.[12] The number of substitutions can be reliably predicted by using the appropriate arylsilane and the desired number of trifluoromethanesulfonic acid equivalents. Finally, although arylsilanes are more expensive than chlorosilanes, the overall yields of the desired products using silyl triflates are much higher than those from additions to tetrachlorosilane followed by hydride reduction. This makes the use of arylsilanes a cost-effective, efficient choice for the synthesis of new silanes. The only drawback of which we are aware is in the preparation of silyl triflate. Silyl triflate is extremely reactive and can form SiH_4 upon exposure to air[11] (CAUTION: see Experimental Section). Substituted silyl triflates are extremely reactive but apparently do not present this danger.

Hydrosilylation Reactions. Each of the new silanes that were prepared was tested for compatibility with the catalyst **1** by performing hydrosilylation reactions with 1-decene (eq 6). These reactions were typically fast,



initiating within seconds to form clear, yellow-green solutions. The reactions were monitored colorimetrically because the reactions became either clear and colorless or cloudy-white upon complete consumption of 1-decene. With a few notable exceptions, the silanes prepared reacted quickly with the catalyst and 1-decene to give near quantitative conversion to the [(fluoroaryl)silyl]-decane (Table 3). (Pentafluorophenyl)silanes **4a**,**b** and **5** failed to react efficiently with the catalyst. Initial trials at room temperature attempted with **4a**,**b** and **5** gave only minor amounts of product. Reactions with **4a** were then performed at 50 °C using twice the normal catalyst loading (10 mol %) wherein the usual clear, yellow-green catalyst solution quickly changed to a cloudy-white solution implying complete consumption of 1-decene. Analysis of the crude reaction mixture, however, indicated only 50−75% conversion of 1-decene to product **6a**, suggesting deactivation of the catalyst by the silane. The more hindered silanes **4b** and **5**, when run at elevated temperatures, gave very little conversion as indicated by GC analysis. This is most likely a result of

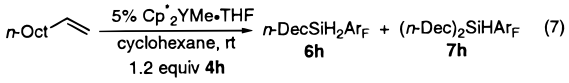
Table 3. Hydrosilylation Reactions (Equation 6)[a]

entry	silane	time[b]	product	% isolated yield
1	$PhSiH_3$	1 h	**6**	97
2	$PhSiH_2F$	24 h		<10[c,d]
3	**4a**	3 h	**6a**	56[c]
4	**4b**	24 h		<10[d,e]
5	**5**	24 h		0[e]
6	**4c**	<30 min	**6c**	83
7	**4d**	<30 min	**6d**	96
8	**4e**	<30 min	**6e**	96
9	**4f**	<10 min	**6f**	97
10	**4g**	<30 min	**6g**	99
11	**4h**	<5 min	**6h**	62[f]
12	**4i**	18 h	**6i**	83
13	**4j**	<30 min	**6j**	84
14	**4k**	<30 min	**6k**	71

[a] All reactions were performed at room temperature in the glovebox using a **5** mol % catalyst loading unless otherwise indicated. [b] Reaction times were determined by GC analysis of a small aliquot. [c] The reaction was run in a sealed tube at 50 °C using 10 mol % catalyst loading. [d] Yield reported is the conversion of 1-decene to the hydrosilyated product as indicated by GC analysis. [e] The reaction was run in a sealed tube at 100 °C. [f] Product **7h** was isolated in 18% yield.

the steric inhibition of the σ-bond metathesis that slows the silylation event enough that it cannot compete with deactivation of the catalyst.[14] Similar results were found for phenylfluorosilane. The catalyst was deactivated within minutes, providing only minor amounts of hydrosilylated 1-decene even when the reaction was run at 50 °C.

Of all the new silanes tested, only **4h** gave appreciable amounts of the bisalkylated silane product **7h** (eq 7). The reaction was followed colorimetrically and by GC analysis but was so rapid that the formation of **7h** could not be prevented even with early quenching. The side



product was initially thought to be the disilane, but upon spectral and combustion analysis the structure was confirmed as **7h** which resulted from competitive trapping of the organoyttrium intermediate with **6h** versus **4h**. This is consistent with previous observations made in our laboratories.[7] This result indicates that the Si−H bonds are most activated in this particular (fluoroaryl)silane. Remarkably, the silane protons of **6h** are so activated that they are effective competitors for the trapping of the organometallic intermediate despite the added steric influence of the decyl group. The rising concentration of **6h** relative to **4h** during the course of the reaction also increases the statistical chance of trapping the organometallic intermediate with **6h**. The failure of silanes **4f**,**g**,**i** to demonstrate this reactivity can be explained by reduced electron withdrawal in the case of the former and steric hindrance for the latter two. The failure of silanes **4c**−**e** to form bisalkylated products is more difficult to explain, however. It has been demonstrated that the proton on pentafluorobenzene is more acidic than tris(trifluoromethyl)benzene.[15] This would suggest that the silane protons of **4h** are

(14) Phenylmethylsilane and diphenylsilane both react with 1-decene and catalyst **1** to give high yields of the respective hydrosilylated products but require longer reaction times. See ref 7.

(15) Carr, G. E.; Chambers, R. D.; Holmes, T. F.; Parker, D. G. *J. Organomet. Chem.* **1987**, *325*, 13.

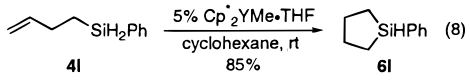
Table 4. Oxidation Reactions (Equation 9)[a]

entry	(arylsilyl)decane	method[b]	% isolated yield of 1-decanol
1	**6**	A	45
2	**6**	C	42
3	**6a**	A	93
4	**6a**	C	77
5	**6d**	A	86
6	**6d**	B	73
7	**6d**	D	89
8	**6e**	A	57
9	**6e**	B	43
10	**6e**	D	46
11	**6g**	D	59
12	**6h**	B	80
13	**6h**	C	78
14	**6h**	D	70
15	**6i**	A	74
16	**6i**	B	65
17	**6i**	C	73
18	**6i**	D	73
19	**6k**	A	70
20	**6k**	B	75
21	**6k**	D	57

[a] All reactions were performed at room temperature and were found to be complete within 2−3 h as indicated by GC analysis. [b] Method A: Purified (arylsilyl)decane oxidation with KF. Method B: Crude (arylsilyl)decane oxidation with KF. Method C: Purified (arylsilyl)decane oxidation without KF. Method D: Crude (arylsilyl)decane oxidation without KF.

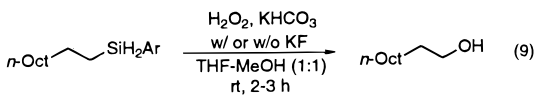
less activated than those of **4c**. Outside of some unknown silane−catalyst interaction, we are unable to suggest a plausible reason for the lack of formation of bisalkylation products with silanes **4c**−**e**.

A useful application of the silyl triflate method and catalytic hydrosilylation reaction is in the preparation and cyclization of **4l** (eq 8). The silacyclopentane product **6l** was accessed via an intramolecular hydrosilylation reaction in excellent yield in less than 1 h using catalyst **1**. Silacycloalkanes can be oxidized to produce diols and are therefore useful as masked diols in a synthetic scheme.[4b] Silacycloalkanes have been prepared stereoselectively using chiral rhodium catalysts.[4b]



(8)

[(Fluoroaryl)silyl]decane Oxidation Reactions. The hydrosilylated products from the test reactions were oxidized to 1-decanol under two different sets of conditions. The second step of a Fleming−Tamao type oxidation protocol[4d,e] was used as an initial test with either purified or crude (arylsilyl)decane products (eq 9). Because there were no alkoxysilanes present in our silane products, we chose to perform a set of experiments without the use of potassium fluoride. The results of these various oxidations are summarized in Table 4.



(9)

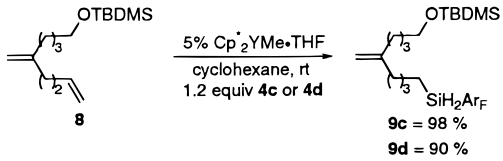
Very mild oxidation protocols were determined to be sufficient for the oxidation of [(fluoroaryl)silyl]decanes. Even (phenylsilyl)decane **6** can be oxidized in fair yield (45%) without the use of acidic reagents such as $Hg(OAc)_2$ or BF_3.[4] The results of the current study also suggest that both electron rich *and* electron poor aryl groups oxidize to provide better yields of 1-decanol than the parent compound **6**. These reactions are complete within 2−3 h at room temperature. This constitutes a significant improvement over other methods, most of which require reaction times on the order of days at room temperature and/or elevated temperatures.[4,6]

The results in Table 4 also show that the yields for oxidation reactions without potassium fluoride were good, although in several cases they were slightly lower than the reactions with a fluoride source. This is an improvement over methods that require a fluoride source because fluoride ion can be problematic for molecules containing other labile silicon-containing functional groups, particularly silyl-protected alcohols.[16]

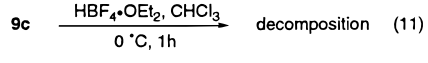
Finally, there appears to be only a slight advantage in using purified (arylsilyl)decanes. In most of the examples studied, the yields of oxidations using crude products were comparable to those that were purified. This adds to the simplicity of the hydrosilylation/oxidation protocol because the hydrosilylated material does not need to be purified before proceeding with the oxidation step.

Application of the Hydrosilylation/Oxidation Protocol. As a demonstration of the utility of this method, we prepared several new silanes and exposed them to various oxidation conditions. A useful substrate should contain sensitive groups that have been shown not to withstand the usual silane oxidation procedures. We chose the alkene starting material 9-(*tert*-butyldimethylsiloxy)-5-methylenenon-1-ene (**8**) for several reasons. The *tert*-butyldimethylsiloxy (TBDMS) protecting group in **8** has been shown to be quite labile under typical oxidation conditions using either acidic or basic protocols.[3b,7] Also, a 1,1-disubstituted alkene was used because such alkenes can be incompatible with mercury- or boron-based oxidation protocols.[6] Finally, we have demonstrated previously that catalyst **1** does not react with disubstituted alkenes[2e] and tolerates *tert*-butyldimethylsilyl-protected alcohols.[2b]

Hydrosilylation of **8** with catalyst **1** using the (fluoroaryl)silanes **4c**,**d** provided the products **9c**,**d** in excellent yield (eq 10). Both the disubstituted alkene and the protected alcohol were unaffected by the reaction conditions. An initial oxidation of **9c** with the method of Bosnich[4b] resulted in decomposition of the starting material, presumably through an acid-promoted reaction of the alcohol with the 1,1-disubstituted alkene (eq 11).



(10)

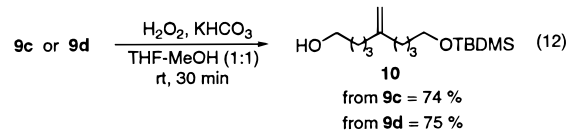


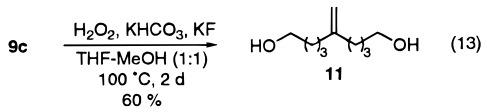
(11)

When **9c**,**d** were oxidized with $H_2O_2/KHCO_3$, the desired monoprotected alcohol **10** was obtained in good yield in 30 min (eq 12). As in the hydrosilylation reaction, both the disubstituted alkene and protected

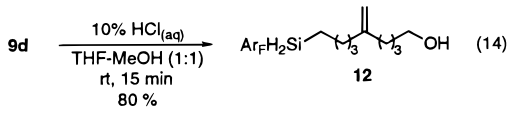
(16) Greene, T. W.; Wuts, P. G. M. *Protecting Groups in Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1991.

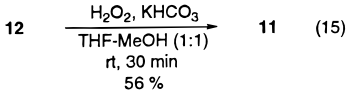
alcohol functionalities remained unaffected. When **9c** was treated with $H_2O_2/KHCO_3/KF$ at 100 °C over a period of 2 days, the alcohol protecting group was cleaved and the silane was oxidized, providing the diol **11** in 60% isolated yield (eq 13).





An alternate route to diol **11** was also realized by cleavage of the *tert*-butyldimethylsilyl-protected alcohol followed by silane oxidation. When silane **9d** was stirred with 10% HCl, removal of the protecting group was complete within 15 min, furnishing the alcohol **12** in 80% isolated yield (eq 14). Alcohol **12** was easily converted to diol **11** in 56% isolated yield by stirring over $H_2O_2/KHCO_3$ for 30 min (eq 15). This short synthesis demonstrates the power of this oxidation protocol in allowing one to reveal sterically identical alcohols in any order desired.





Conclusions

The utility of silyl triflates as useful intermediates for the synthesis of (fluoroaryl)silanes has been demonstrated. The silyl triflate protocol provided new silanes in good yield from the appropriate Grignard reagent in one pot. The new (fluoroaryl)silanes were shown to be compatible with the organoyttrium catalyst **1** in hydrosilylation reactions of 1-decene. The hydrosilylation reactions provided the corresponding [(fluoroaryl)silyl]decanes in very high yields with short reaction times. The [(fluoroaryl)silyl]decanes were found to be more labile than (phenylsilyl)decane under very mild oxidative conditions. These conditions tolerated disubstituted alkenes and silyl-protected alcohols while other protocols did not.

Experimental Section

All NMR spectra were recorded on a 300 or 500 MHz spectrometer. All ^{19}F NMR spectra are reported relative to C_6F_6 at 14.8 ppm ($CFCl_3$ at 0 ppm) as an internal standard. Because of complex C−F coupling in the ^{13}C NMR, we denote a doublet of multiplets as "dm" with an approximate direct C−F coupling constant given as determined from the center of each multiplet. All distillations were performed at atmospheric pressure (approximately 640 mmHg) unless otherwise indicated. All catalytic experiments were performed in a nitrogen-filled Vacuum Atmospheres glovebox or in a sealed reaction vessel intially prepared in the glovebox. The organolanthanide complex **1** was prepared according to the literature procedure.[17] The following compounds were synthesized according to their literature procedures: phenylchlorosilane,[18] phenylfluorosilane,[19] and (2,4,6-trifluoromethylphenyl)lithium.[15] Dichloromethane was distilled from CaH_2 immediately before use. Cyclohexane was distilled from sodium/benzophenone ketyl and stored in the glovebox. Et_2O and THF were distilled from sodium/benzophenone ketyl immediately before use. THF and MeOH were used in oxidation reactions without purification. Phenylsilane (Aldrich) and 1-decene (Chemsampco) used in catalytic reactions were freeze−pump−thaw−degassed as received and stored in the glovebox. Trifluoromethanesulfonic acid (Aldrich), phenylsilane, phenylmethylsilane (Gelest), and diphenylsilane (Gelest) were used as received in the preparation of silyl triflates. All Grignard solutions were prepared in the usual manner from the corresponding aryl bromides in Et_2O or THF and titrated with 0.1 N HCl immediately before use. All catalytic reactions used 2−6 mol % precatalyst loadings, 0.2−0.4 M 1-decene solutions, and 1.1−1.4 equiv of (fluoroaryl)silane unless otherwise stated. Authentic 1-decanol (Aldrich) was used as received for GC and NMR comparisons with the products of [(fluoroaryl)silyl]-decane oxidations. All products synthesized were found to be >95% pure by capillary GC analysis.

Preparation of Pentafluorophenylsilane (4a) [General Procedure for the Preparation of (fluoroaryl)silanes)]. A predried, argon-filled Schlenk flask capped with a rubber septum containing phenylsilane (7.01 g, 64.8 mmol) was charged with CH_2Cl_2 (30 mL) and cooled to 0 °C before trifluoromethanesulfonic acid (10.0 g, 67.1 mmol) was carefully added via syringe over 10 min. (***Caution!*** The formation of silyl triflate is exothermic. Disproportionation of silyl triflate and concomitant formation of SiH_4 will occur if the mixture is allowed to heat up excessively.[5] Avoid exposing the reaction media to air because SiH_4 is explosive in the presence of oxygen.) After 2 h at 0 °C the mixture was added via cannula over 30 min to a rapidly stirred 0.608 M Et_2O solution of C_6F_5-MgBr (105 mL, 63.8 mmol) also at 0 °C. The resulting mixture was allowed to warm to room temperature overnight. The mixture was cooled to 0 °C, and 2-propanol (10 mL) was slowly added via syringe before adding H_2O (1 mL). The reaction was diluted with pentane (200 mL), filtered, concentrated by rotary evaporation, and distilled to give the title compound in 47% yield: bp 108−111 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 4.19 (t, J = 5.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.10 (dm, $J \approx$ 244 Hz), 142.99 (dm, $J \approx$ 257 Hz), 137.40 (dm, $J \approx$ 254 Hz), 100.94−101.43 (m). ^{19}F NMR (470 MHz, $CDCl_3$): δ 51.71 (t, J = 9.2 Hz, 2F), 27.30 (t, J = 19.8 Hz, 1F), 16.04−15.92 (m, 2F). IR (neat): 2192.6 cm^{-1}. HRMS. Calcd for $C_6H_3F_5Si$: 197.9924. Found: 197.9923. LRMS (EI): *m*/*z* 198 (83), 168 (37), 47 (100). Anal. Calcd for $C_6H_3F_5Si$: C, 36.37; H, 1.53. Found: C, 36.72; H, 1.55.

(Pentafluorophenyl)methylsilane (4b). A predried, argon-filled Schlenk flask capped with a rubber septum containing phenylmethylsilane (6.20 g, 50.7 mmol) was charged with CH_2Cl_2 (25 mL) and cooled to 0 °C before trifluoromethanesulfonic acid (7.78 g, 51.8 mmol) was carefully added via syringe over 10 min. After 15 min at 0 °C the mixture was added via cannula over 15 min to a rapidly stirred 0.658 M Et_2O solution of C_6F_5MgBr (70 mL, 46 mmol) also at 0 °C. The resulting mixture was allowed to warm to room temperature overnight. The mixture was cooled to 0 °C, and Et_3N (10 mL) was slowly added via syringe before diluting with pentane (200 mL). The mixture was dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and distilled to give the title compound in 53% yield: bp 132−134 °C. ^1H NMR (500 MHz, $CDCl_3$): δ

(17) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Smeets, W. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *327*, 31.
(18) Kunai, A.; Kawakami, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1992**, *11*, 2708.
(19) Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1996**, *15*, 2478.

4.38−4.61 (m, 2H), 0.43−0.49 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.10 (dm, $J \approx 238$ Hz), 142.64 (dm, $J \approx 256$ Hz), 137.30 (dm, $J \approx 253$ Hz), 105.31−105.86 (m), −8.15 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 50.20 (t, $J = 16.8$ Hz, 2F), 26.27 (t, $J = 16.8$ Hz, 1F), 15.69−15.82 (m, 2F). IR (neat): 2182.7 cm^{-1}. HRMS. Calcd for $C_7H_5F_5Si$: 212.0081. Found: 212.0061. LRMS (EI): *m*/*z* 212 (100), 168 (24), 44 (82).

(**Pentafluorophenyl)phenylsilane (5).**[20] A 1.6 M solution of *n*-butyllithium in hexanes (22.5 mL, 36.0 mmol) was cannulated over 15 min to a predried, argon-filled Schlenk flask containing pentafluorobromobenzene (8.67 g, 35.1 mmol) and Et_2O (75 mL) at −78 °C. After the mixture was stirred for 15 min, phenylchlorosilane (5.11 g, 35.8 mmol) was added as an Et_2O solution (10 mL) via cannula over 10 min. The reaction was stirred for 1 h at −78 °C before removing the cold bath and allowing the resulting light yellow slurry to stir at room temperature for 18 h. The reaction was quenched with H_2O (0.5 mL) and diluted with pentane (200 mL). The slurry was dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and Kugelrohr distilled to give the title compound in 85% yield: ot 133−137 °C/36−38 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65−7.67 (m, 2H), 7.46−7.49 (m, 1H), 7.40−7.46 (m, 2H), 5.04 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.89 (dm, $J \approx 245$ Hz), 142.89 (dm, $J \approx 256$ Hz), 137.31 (dm, $J \approx 235$ Hz), 135.41 (s), 130.75 (s), 128.44 (s), 127.96 (s), 104.08−105.54 (m). ^{19}F NMR (470 MHz, $CDCl_3$): δ 51.19 (dt, $J = 4.6$, 18.3 Hz, 2F), 27.15 (t, $J = 19.8$ Hz, 1F), 16.20−16.32 (m, 2F). IR (neat): 2183.9 cm^{-1}. HRMS. Calcd for $C_{12}H_7F_5Si$: 274.0237. Found: 274.0225. LRMS (EI): *m*/*z* 274 (95), 106 (100), 78 (57), 47 (85). Anal. Calcd for $C_{12}H_7F_5Si$: C, 52.55; H, 2.57. Found: C, 52.93; H, 2.72.

(3,5-Difluorophenyl)silane (4c) was prepared according to the general procedure given for **4a**. The reaction was quenched at 0 °C with a 1:1 H_2O: saturated aqueous $NaHCO_3$ solution (10 mL), diluted with pentane (200 mL), dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and distilled to give the title compound in 37% yield: bp 105−107 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (dt, $J = 4.6$, 2.0 Hz, 2H), 6.82 (tt, $J = 9.0$, 2.4 Hz, 1H), 4.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.78 (dd, $J = 253$, 10.6 Hz), 132.71 (t, $J = 6.2$ Hz), 117.95 (dd, $J = 17.7$, 5.3 Hz), 105.40 (t, $J = 24.7$ Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.96 (t, $J = 9.2$ Hz, 2F). IR (neat): 2164.1 cm^{-1}. HRMS. Calcd for $C_6H_6F_2Si$: 144.0207. Found: 144.020. LRMS (EI): *m*/*z* 144 (100), 143 (70), 77 (79).

(3,4,5-Trifluorophenyl)silane (4d) was prepared according to the general procedure given for **4a**. Distillation gave the title compound in 62% yield: bp 112−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11−7.17 (m, 2H), 4.17 (d, $J = 0.7$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.24 (ddd, $J = 211$, 8.8, 2.7 Hz), 140.99 (dt, $J = 255$, 15.0 Hz), 124.77 (dd, $J = 9.7$, 4.4 Hz), 119.35 (dd, $J = 15.0$, 5.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 42.42−42.48 (m, 2F), 18.46−18.57 (m, 1F). IR (neat): 2168.1 cm^{-1}. HRMS. Calcd for $C_6H_5F_3Si$: 162.0113. Found: 162.0102. LRMS (EI): *m*/*z* 162 (38), 94 (24).

(2,4,6-Trifluorophenyl)silane (4e) was prepared according to the general procedure given for **4a**. The reaction was quenched as in the preparation of **5** and distilled to give the title compound in 45% yield: bp 107−109 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60−6.65 (m, 2H), 4.12 (t, $J = 5.0$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.36 (ddd, $J = 246$, 16.8, 15.0 Hz), 165.43 (dt, $J = 252$, 15.9 Hz), 99.88−100.36 (m), 99.54 (td, $J = 34.4$, 4.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 82.97 (s, 2F), 72.28−72.35 (m, 1F). IR (neat): 2184.3 cm^{-1}. HRMS. Calcd for $C_6H_5F_3Si$: 162.0113. Found: 162.0115. LRMS (EI): *m*/*z* 162 (85), 94 (100), 95 (90).

[4-(Trifluoromethyl)phenyl]silane (4f) was prepared according to the general procedure given for **4a**. Distillation gave the title compound in 53% yield. The ^{1}H NMR spectrum closely matched the data reported in the literature.[9]

[2,4-Bis(trifluoromethyl)phenyl]silane (4g) was prepared according to the general procedure given for **4a**. The reaction was quenched as in the preparation of **4b** and distilled to give the title compound in 46% yield: bp 122−125 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 4.31 (q, $J = 5.4$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.32 (s), 137.08 (q, $J = 31.8$ Hz), 133.14 (s), 132.82 (q, $J = 33.6$ Hz), 127.62 (d, $J = 2.7$ Hz), 124.04 (q, $J = 274$ Hz), 123.30 (q, $J = 272$ Hz), 122.69 (t, $J = 4.4$ Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 116.17 (d, $J = 4.6$, 3F), 113.32 (s, 3F). IR (neat): 2182.5 cm^{-1}. HRMS. Calcd for $C_8H_6F_6Si$: 244.0143. Found: 244.0130. LRMS (EI): *m*/*z* 244 (2), 195 (100).

[3,5-Bis(trifluoromethyl)phenyl]silane (4h) was prepared according to the general procedure given for **4a**. The reaction was quenched with H_2O (0.5 mL), diluted with pentane (200 mL), dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and distilled to give the title compound in 56% yield: bp 119−123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (s, 2H), 7.90 (s, 1H), 4.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.60 (s), 132.07 (s), 131.29 (q, $J = 33.6$ Hz), 123.71−123.79 (m), 123.36 (q, $J = 273$ Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 113.66 (s, 6F). IR (neat): 2172.4 cm^{-1}. HRMS. Calcd for $C_8H_5F_6Si$ ($M - H^+$): 243.0065. Found: 243.0047. LRMS (EI): *m*/*z* 244 (7), 195 (100).

[2,4,6-Tris(trifluoromethyl)phenyl]silane (4i) was prepared according to the general procedure given for **4a** using [2,4,6-tris(trifluoromethyl)phenyl]lithium as the nucleophile. The reaction was quenched as in the preparation of **5** and distilled to give the title compound in 57% yield: bp 125−130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (s, 2H), 4.41−4.29 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.75 (q, $J = 31.8$ Hz), 134.00 (s), 132.95 (q, $J = 35.3$ Hz), 125.70 (s), 123.30 (q, $J = 275$ Hz), 122.55 (q, $J = 273$ Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 118.51 (d, $J = 4.6$ Hz, 6F), 113.02 (s, 3F). IR (neat): 2223.2 cm^{-1}. HRMS. Calcd for $C_9H_5F_9Si$: 312.0017. Found: 312.0032. LRMS (EI): *m*/*z* 263 (86), 244 (100), 187 (64).

1,1′-Biphen-4-ylsilane (4j) was prepared according to the general procedure given for **4a**. The reaction was quenched at 0 °C with a 1:1 H_2O:saturated aqueous $NaHCO_3$ solution (10 mL), diluted with Et_2O, washed with 1:1 H_2O:saturated aqueous $NaHCO_3$ solution (2 × 25 mL), dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and purified by flash chromatography to give the title compound in 67% yield. Melting point data closely matched that reported in the literature:[21] R_f 0.5 (hexanes); mp 94.5−96.5 °C (lit. mp, 93−95 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 7.8$ Hz, 4H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.36 (t, $J = 5.6$ Hz, 1H), 4.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.63 (s), 140.73 (s), 136.34 (s), 128.82 (s), 127.61 (s), 127.14 (s), 126.86 (s), 126.83 (s).

[4-(*N*,*N*-Dimethylamino)phenyl]silane (4k) was prepared according to the general procedure given for **4a**. The reaction was quenched at 0 °C with saturated aqueous $NaHCO_3$ (5 mL), diluted with Et_2O (200 mL), washed with 10% NaOH (3 × 25 mL), dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and purified by flash chromatography to give the title compound in 65% yield. Melting point and NMR spectra closely matched the data reported in the literature:[10a] R_f 0.3 (10:1 hexanes:ethyl acetate); mp 46.5−49.5 °C (lit. mp, 48 °C).

1-(Phenylsilyl)but-3-ene (4l). A predried, argon-filled Schlenk flask capped with a rubber septum containing diphenylsilane (7.46 g, 40.5 mmol) was charged with CH_2Cl_2 (25 mL) at room temperature. Trifluoromethanesulfonic acid (6.25 g, 41.6 mmol) was carefully added via syringe over 10 min and stirred for an additional 15 min. The mixture was then added via cannula over 15 min to a rapidly stirred 0.351 M Et_2O

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(21) Krasnova, T. L.; Semenova, G. I.; Rogachevskii, V. L.; Belik, G. I.; Chernyshev, E. A. *Zh. Prikl. Khim.* **1974**, *47*, 467.

solution of 3-butenylmagnesium bromide (96 mL, 34 mmol) at 0 °C. The resulting mixture was stirred for 15 min before removing the cold bath and stirring at room temperature overnight. The reaction was quenched as in the preparation of **4c** and distilled to give the title compound in 81% yield: bp 194−196 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57−7.59 (m, 2H), 7.35−7.42 (m, 3H), 5.85−5.93 (m, 1H), 5.01−5.05 (m, 1H), 4.94−4.96 (m, 1H), 4.32 (t, J = 3.7 Hz, 2H), 2.19−2.24 (m, 2H), 1.03−1.08 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.16 (s), 135.22 (s), 132.28 (s), 129.57 (s), 127.98 (s), 113.67 (s), 29.00 (s), 9.22 (s). IR (neat): 2134.7 cm^{-1}. HRMS. Calcd for $C_{10}H_{14}Si$: 162.0864. Found: 162.0876. LRMS (EI): *m*/*z* 162 (8), 107 (100), 105 (70).

1-(Phenylsilyl)decane (6) (Representative Procedure for the Hydrosilylation of 1-Decene with Catalyst 1). In a nitrogen-filled glovebox, catalyst **1** (16 mg, 1.8 mol %) was dissolved in cyclohexane (5.0 mL). To this solution was added 1-decene (276 mg, 1.97 mmol) and phenylsilane (260 mg, 2.40 mmol). The reaction was stirred at room temperature for 24 h.[22] The reaction was filtered through a small plug of silica, concentrated by rotary evaporation, and Kugelrohr distilled to give the title compound in 97% yield. The NMR data closely match literature data.[2e]

1-[(Pentafluorophenyl)silyl]decane(6a) was prepared in a sealed tube according to the general procedure for the preparation of **6** in the nitrogen-filled glovebox using 10 mol % of **1**. The reaction was immediately removed from the glovebox and heated to 50 °C in an oil bath. The reaction was stopped after 3 h. The crude material was Kugelrohr distilled twice to give the title compound in 56% yield: ot 75−85 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.31−4.35 (m, 2H), 1.37−1.42 (m, 2H), 1.30−1.34 (m, 2H), 1.23 (s, 12H), 0.94−0.99 (m, 2H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.88 (dm, $J \approx$ 248 Hz), 141.02 (dm, $J \approx$ 256 Hz), 137.20 (dm, $J \approx$ 253 Hz), 104.77−105.26 (m), 32.53 (s), 31.90 (s), 29.57 (s), 29.46 (s), 29.31 (s), 29.15 (s), 24.79 (s), 22.68 (s), 14.10 (s), 9.10 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 50.66 (d, J = 18.3 Hz, 2F), 26.28 (t, J = 18.1 Hz, 1F), 15.76−15.83 (m, 2F). IR (neat): 2176.1 cm^{-1}. HRMS. Calcd for $C_{16}H_{23}F_5Si$: 338.1489. Found: 338.1459. LRMS (EI): *m*/*z* 99 (63), 93 (100).

1-[(3,5-Difluorophenyl)silyl]decane (6c) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after <30 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 83% yield: ot 75−90 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02−7.04 (m, 2H), 6.77−6.81 (m, 1H), 4.25 (t, J = 3.6 Hz, 2H), 1.39−1.45 (m, 2H), 1.29−1.34 (m, 2H), 1.23 (s, 12H), 0.89−0.94 (m, 2H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.75 (dd, J = 253, 10.6 Hz), 137.45 (t, J = 5.3 Hz), 117.22 (dd, J = 17.2, 5.3 Hz), 104.93 (t, J = 24.7 Hz), 32.75 (s), 31.91 (s), 29.61 (s), 29.50 (s), 29.33 (s), 29.21 (s), 24.84 (s), 22.70 (s), 14.12 (s), 9.65 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.46 (d, J = 5.3 Hz, 2F). IR (neat): 2142.2 cm^{-1}. HRMS. Calcd for $C_{16}H_{26}F_2Si$: 284.1772. Found: 284.1763. LRMS (EI): *m*/*z* 284 (2), 143 (90), 113 (61), 99 (100).

1-[(3,4,5-Trifluorophenyl)silyl]decane (6d) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after <30 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 96% yield: ot 75−90 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (t, J = 7.2 Hz, 2H), 4.24 (t, J = 3.8 Hz, 2H), 1.38−1.42 (m, 2H), 1.29−1.35 (m, 2H), 1.23 (s, 12H), 0.88−0.93 (m, 2H), 0.86 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.15 (ddd, J = 254, 7.1, 2.7 Hz), 140.64 (dt, J = 254, 15.0 Hz), 129.30 (q, J = 5.3 Hz), 118.60 (dd, J = 14.1, 4.4 Hz), 32.73 (s), 31.91 (s), 29.61 (s), 29.50 (s), 29.34 (s), 29.20 (s), 24.77 (s), 22.70 (s), 14.10 (s), 9.74 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 41.77−41.83 (m, 2F), 17.53−17.64 (m, 1F). IR (neat): 2144.5 cm^{-1}. HRMS. Calcd for $C_{16}H_{24}F_3Si$ (M − H$^+$): 301.1599. Found: 301.1588. LRMS (EI): *m*/*z* 302 (1), 161 (88), 113 (78), 99 (100).

1-[(2,4,6-Trifluorophenyl)silyl]decane (6e) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after <30 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 96% yield: ot 70−80 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.57−6.63 (m, 2H), 4.26−4.29 (m, 2H), 1.35−1.43 (m, 2H), 1.29−1.33 (m, 2H), 1.23 (s, 12H), 0.91−0.95 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.27 (ddd, J = 320, 15.0, 2.7 Hz), 165.03 (dt, J = 252, 15.9 Hz), 103.49 (td, J = 35.3, 4.4 Hz), 99.73−100.20 (m), 32.61 (s), 31.92 (s), 29.61 (s), 29.51 (s), 29.34 (s), 29.22 (s), 24.95 (s), 22.70 (s), 14.11 (s), 9.39 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 82.24 (dd, J = 16.4, 5.3 Hz, 2F), 71.23−71.30 (m, 1F). IR (neat): 2169.7 cm^{-1}. HRMS. Calcd for $C_{16}H_{24}F_3Si$ (M − H$^+$): 301.1599. Found: 301.1609. LRMS (EI): *m*/*z* 99 (100), 113 (59).

1-[(4-(Trifluoromethyl)phenyl)silyl]decane (6f) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after <10 min as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 97% yield: R_f 0.8 (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (dd, J = 42.6, 7.5 Hz, 4H), 4.30 (t, J = 3.8 Hz, 2H), 1.40−1.46 (m, 2H), 1.32−1.35 (m, 2H), 1.24 (s, 12H), 0.92−0.97 (m, 2H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.91 (s), 135.46 (s), 131.46 (q, J = 32.7 Hz), 124.42 (q, J = 3.5 Hz), 124.13 (q, J = 272 Hz), 32.78 (s), 31.91 (s), 29.61 (s), 29.51 (s), 29.33 (s), 29.22 (s), 24.95 (s), 22.69 (s), 14.11 (s), 9.71 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 113.52 (s, 3F). IR (neat): 2140.0 cm^{-1}. HRMS. Calcd for $C_{17}H_{26}F_3Si$ (M − H$^+$): 315.1756. Found: 315.1768. LRMS (EI): *m*/*z* 315 (0.2), 175 (77), 127 (100).

1-[{2,4-Bis(trifluoromethyl)phenyl}silyl]decane (6g) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after <30 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 99% yield: ot 70−82 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.81 (dd, J = 65.7, 7.7 Hz, 2H), 4.37−4.42 (m, 2H), 1.36−1.42 (m, 2H), 1.31−1.33 (m, 2H), 1.23 (s, 12H), 0.94−0.98 (m, 2H), 0.86 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.36 (s), 138.73 (s), 136.54 (q, J = 31.8 Hz), 132.15 (q, J = 33.6 Hz), 127.28 (s), 124.80 (q, J = 91.9 Hz), 122.98−122.26 (m), 122.62 (q, J = 90.1 Hz), 32.71 (s), 31.91 (s), 29.60 (s), 29.50 (s), 29.32 (s), 29.19 (s), 24.93 (s), 22.69 (s), 14.10 (s), 10.06 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 116.79 (s, 3F), 113.29 (s, 3F). IR (neat): 2149.0 cm^{-1}. HRMS. Calcd for $C_{18}H_{26}F_6Si$: 384.1708. Found: 384.1720. LRMS (EI): *m*/*z* 243 (64), 193 (75), 139 (76), 119 (100).

1-[{3,5-Bis(trifluoromethyl)phenyl}silyl]decane (6h) was prepared according to the general procedure for the preparation **6**. The reaction was complete after <5 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 62% yield: ot 80−95 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 2H), 7.87 (s, 1H), 4.35 (t, J = 3.8 Hz, 2H), 1.41−1.47 (m, 2H), 1.32−1.37 (m, 2H), 1.23 (s, 12H), 0.96−1.01 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.50 (s), 134.92 (s), 130.96 (q, J = 32.7 Hz), 122.35−124.52 (m), 123.43 (q, J = 273 Hz), 32.67 (s), 31.89 (s), 29.58 (s), 29.47 (s), 29.31 (s), 29.16 (s), 24.79 (s), 22.68 (s), 14.10 (s), 9.47 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 113.63 (s, 6F). IR (neat): 2147.9 cm^{-1}. HRMS. Calcd for $C_{18}H_{25}F_6Si$ (M − H$^+$): 383.1630. Found: 383.1612. LRMS (EI): *m*/*z* 383 (8), 243 (100), 176 (80), 99 (93).

1-[{3,5-Bis(trifluoromethyl)phenyl}decylsilyl]decane (7h) was isolated as a minor product from the preparation of **6h**. Kugelrohr distillation gave the title compound in 18% yield: ot 125−135 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$):

(22) A $^1/_{10}$th scale reaction was performed to gauge the speed of the reaction, and it was found to be complete within 1 h.

δ 7.91 (s, 2H), 7.84 (s, 1H), 4.30−4.33 (m, 1H), 1.22−1.38 (m, 32H), 0.84−0.89 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.90 (s), 134.31 (s), 130.73 (q, J = 32.7 Hz), 123.55 (q, J = 273 Hz), 122.88−123.04 (m), 33.04 (s), 31.89 (s), 29.60 (s), 29.49 (s), 29.31 (s), 29.17 (s), 24.24 (s), 22.68 (s), 14.10 (s), 11.45 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 113.70 (s, 6F). IR (neat): 2122.7 cm^{-1}. LRMS (EI): *m*/*z* 524 (4.3), 523 (5.4), 383 (75), 311 (64), 243 (75), 176 (60), 85 (100). Anal. Calcd for $C_{28}H_{46}F_6Si$: C, 64.09; H, 8.84. Found: C, 64.21; H, 8.86.

1-[{2,4,6-Tris(trifluoromethyl)phenyl}silyl]decane (6i) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after 18 h as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 83% yield: ot 75−88 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 2H), 4.39−4.46 (m, 2H), 1.43−1.49 (m, 2H), 1.32−1.35 (m, 2H), 1.25 (s, 12H), 0.97 (s, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.38 (q, J = 31.8 Hz), 138.36 (s), 132.47 (q, J = 34.5 Hz), 125.73 (s), 123.43 (q, J = 275 Hz), 122.64 (q, J = 272 Hz), 32.61 (s), 31.92 (s), 29.62 (s), 29.50 (s), 29.34 (s), 29.20 (s), 25.04 (s), 22.70 (s), 14.10 (s), 10.23 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 119.09 (d, J = 6.1 Hz, 6F), 113.05 (d, J = 8.4 Hz, 3F). IR (neat): 2201.3 cm^{-1}. HRMS. Calcd for $C_{19}H_{25}F_9Si$: 452.1582. Found: 452.1582. LRMS (EI): *m*/*z* 311 (18), 187 (100).

1-[1,1′-Biphen-4-ylsilyl]decane (6j) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after <30 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 84% yield: ot 130−150 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63−7.65 (m, 2H), 7.58−7.61 (m, 4H), 7.42−7.46 (m, 2H), 7.33−7.37 (m, 1H), 4.32 (t, J = 3.6 Hz, 2H), 1.44−1.51 (m, 2H), 1.34−1.39 (m, 2H), 1.25 (s, 12H), 0.94−0.99 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.24 (s), 140.92 (s), 135.69 (s), 131.50 (s), 128.78 (s), 127.47 (s), 127.14 (s), 126.66 (s), 32.87 (s), 31.92 (s), 29.63 (s), 29.55 (s), 29.34 (s), 29.27 (s), 25.10 (s), 22.70 (s), 14.12 (s), 10.07 (s). IR (neat): 2131.0 cm^{-1}. HRMS. Calcd for $C_{22}H_{32}Si$: 324.2273. Found: 324.2258. LRMS (EI): *m*/*z* 324 (8), 183 (37), 154 (100).

1-[{4-(*N*,*N*-Dimethylamino)phenyl}silyl]decane (6k) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after <30 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 71% yield: ot 115−130 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41−7.43 (m, 2H), 6.71−6.73 (m, 2H), 4.24 (t, J = 3.6 Hz, 2H), 2.96 (s, 6H), 1.41−1.47 (m, 2H), 1.30−1.35 (m, 2H), 1.25 (s, 12H), 0.86−0.91 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.28 (s), 136.28 (s), 117.26 (s), 111.99 (s), 40.15 (s), 32.92 (s), 31.92 (s), 29.64 (s), 29.57 (s), 29.34 (s), 29.31 (s), 25.15 (s), 22.70 (s), 14.12 (s), 10.57 (s). IR (neat): 2119.0 cm^{-1}. HRMS. Calcd for $C_{18}H_{33}NSi$: 291.2382. Found: 291.2368. LRMS (EI): *m*/*z* 291 (25), 150 (72), 121 (100).

1-Phenylsilacyclopentane (6l) was prepared according to the general procedure for the preparation of **6**. The reaction was complete after 1 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound[23] in 85% yield: R_f 0.6 (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59−7.61 (m, 2H), 7.36−7.42 (m, 3H), 4.56−4.58 (m, 1H), 1.71−1.79 (m, 4H), 1.03−1.09 (m, 2H), 0.86−0.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.24 (s), 134.52 (s), 129.31 (s), 127.87 (s), 27.55 (s), 10.37 (s). IR (neat): 2123.0 cm^{-1}. HRMS. Calcd for $C_{10}H_{14}Si$: 162.0864. Found: 162.0872. LRMS (EI): *m*/*z* 162 (34), 105 (98), 84 (100).

Oxidation of Purified 6d. Representative Procedure for the Oxidation of Purified [(Fluoroaryl)silyl]decanes with KF. Method A. To a solution of **6d** (67 mg, 0.22 mmol) in 1:1 THF:MeOH (4 mL) at room temperature was added KF (67 mg, 1.2 mmol), $KHCO_3$ (137 mg, 1.4 mmol), and 30% H_2O_2 (0.6 mL, 5.3 mmol). The reaction was complete after 3 h as indicated by GC analysis. The reaction mixture was concentrated by rotary evaporation to 0.5 mL, diluted with Et_2O (25 mL), and stirred over 10% NaOH (2 mL) for 30−60 min. The reaction was extracted with Et_2O (3 × 10 mL), dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and purified by flash chromatography (5:1 ethyl acetate:hexanes) to give 1-decanol (30 mg, 0.19 mmol) in 86% yield. The ^{1}H NMR spectrum was identical to that of authentic 1-decanol.

Oxidation of Crude 6d. Representative Procedure for the Oxidation of Crude [(Fluoroaryl)silyl]decanes with KF. Method B. The general procedure for the preparation of **6** was used to prepare crude **6d** (theoretical yield: 148 mg, 0.49 mmol), which was dissolved in 1:1 THF:MeOH (10 mL) at room temperature. To the solution was added KF (150 mg, 2.6 mmol), $KHCO_3$ (310 mg, 3.1 mmol), and 30% H_2O_2 (1.2 mL, 10.6 mmol). The reaction was complete after 2 h as indicated by GC analysis. Workup as in method A and purification by flash chromatography (5:1 ethyl acetate:hexanes) gave 1-decanol (57 mg, 0.36 mmol) in 73% yield. The ^{1}H NMR spectrum was identical to that of authentic 1-decanol.

Oxidation of Purified 6e. Representative Procedure for the Oxidation of Purified [(Fluoroaryl)silyl]decanes without KF. Method C. To a solution of **6e** (113 mg, 0.25 mmol) in 1:1 THF:MeOH (4 mL) at room temperature was added $KHCO_3$ (120 mg, 1.20 mmol) and 30% H_2O_2 (0.25 mL, 2.2 mmol). The reaction was complete after 3 h as indicated by GC analysis. Workup as in method A and purification by flash chromatography (5:1 ethyl acetate:hexanes) gave 1-decanol (29 mg, 0.18 mmol) in 73% yield. The ^{1}H NMR spectrum was identical to that of authentic 1-decanol.

Oxidation of Crude 6d. Representative Procedure for the Oxidation of Crude (Fluoroaryl)decylsilanes (without KF). Method D. The general procedure for the preparation of **6** was used to prepare crude **6d** (theoretical yield: 109 mg, 0.36 mmol), which was dissolved in 1:1 THF:MeOH (6 mL) at room temperature. To the solution was added $KHCO_3$ (180 mg, 1.8 mmol) and 30% H_2O_2 (0.4 mL, 3.5 mmol). The reaction was complete after 2 h as indicated by GC analysis. Workup as in method A and purification by flash chromatography (5:1 ethyl acetate:hexanes) gave 1-decanol (50 mg, 0.32 mmol) in 89% yield. The ^{1}H NMR spectrum was identical to that of authentic 1-decanol.

1-(*tert*-Butyldimethylsiloxy)-9-{(3,5-difluorophenyl)silyl}-5-methylenenonane (9c) was prepared according to the general procedure for the preparation of **6** from 9-(*tert*-butyldimethylsiloxy)-5-methylenenon-1-ene and **4c**. The reaction was complete after 2 h as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 98% yield: ot 120−140 °C/0.1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (dt, J = 5.4, 2.2 Hz, 2H), 6.79 (tt, J = 9.1, 2.2 Hz, 1H), 4.67 (d, J = 7.2 Hz, 2H), 4.25 (t, J = 3.6 Hz, 2H), 3.59 (t, J = 6.4 Hz, 2H), 1.98 (t, J = 7.2 Hz, 4H), 1.39−1.50 (m, 8H), 0.91−0.96 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.79 (dd, J = 252, 11.0 Hz), 149.42 (s), 137.30 (t, J = 5.5 Hz), 117.22 (dd, J = 17.9, 4.7 Hz), 108.96 (s), 104.97 (t, J = 24.7 Hz), 63.03 (s), 35.73 (s), 35.51 (s), 32.53 (s), 30.81 (s), 25.97 (s), 24.62 (s), 23.98 (s), 18.35 (s), 9.58 (s), −5.29 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.50 (t, J = 7.6 Hz, 2F). IR (neat): 2143.0 cm^{-1}. HRMS. Calcd for $C_{18}H_{29}F_2OSi_2$ (M − *t*-Bu$^+$): 355.1725. Found: 355.1727. LRMS (EI): *m*/*z* 355 (17), 217 (55), 75 (100).

1-(*tert*-Butyldimethylsiloxy)-9-{(3,4,5-trifluorophenyl)silyl}-5-methylenenonane (9d) was prepared according to the general procedure for the preparation of **6** from 9-(*tert*-butyldimethylsiloxy)-5-methylenenon-1-ene and **4d**. The reaction was complete after <30 min as indicated by GC analysis. Workup and purification by Kugelrohr distillation gave the title compound in 90% yield: ot 125−145 °C/0.1 mmHg. ^{1}H

(23) Jackson, R. A.; Zarkadis, A. K. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1140.

NMR (500 MHz, $CDCl_3$): δ 7.11 (t, J = 7.0 Hz, 2H), 4.67 (d, J = 9.3 Hz, 2H), 4.24 (t, J = 3.8 Hz, 2H), 3.59 (t, J = 6.4 Hz, 2H), 1.98 (t, J = 7.2 Hz, 4H), 1.39−1.50 (m, 8H), 0.90−0.94 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.19 (ddd, J = 254, 9.6, 2.7 Hz), 149.40 (s), 140.69 (dt, J = 254, 15.0 Hz), 129.17 (dd, J = 5.3, 4.3 Hz), 118.61 (dd, J = 4.8, 4.3 Hz), 108.98 (s), 63.03 (s), 35.73 (s), 35.48 (s), 32.53 (s), 30.78 (s), 25.96 (s), 24.53 (s), 23.98 (s), 18.35 (s), 9.66 (s), −5.30 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 41.81−41.87 (m, 2F), 17.60−17.71 (m, 1F). IR (neat): 3073.6, 2144.9 cm^{-1}. HRMS. Calcd for $C_{18}H_{28}F_3OSi_2$ (M − t-Bu$^+$): 373.1631. Found: 373.1620. LRMS (EI): m/z 373 (17), 75 (100).

9-(*tert*-Butyldimethylsiloxy)-5-methylenenonan-1-ol (10) was prepared according to the general oxidation method C from **9c**. The reaction was complete after 30 min as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 75% yield: R_f 0.25 (5:1 hexanes:ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.69 (d, 2H), 3.63 (t, J = 6.4 Hz, 2H), 3.59 (t, J = 6.4 Hz, 2H), 2.00 (q, J = 7.7 Hz, 4H), 1.41−1.58 (m, 9H), 0.87 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.45 (s), 109.01 (s), 63.07 (s), 62.87 (s), 35.70 (s), 35.67 (s), 32.52 (s), 32.47 (s), 25.97 (s), 23.95 (s), 23.87 (s), 18.36 (s), −5.28 (s). IR (neat): 3353.8 cm^{-1}. HRMS. Calcd for $C_{16}H_{35}O_2Si$ (M + H$^+$): 287.2406. Found: 287.2397. LRMS (EI): m/z 130 (25), 95 (100), 81 (96), 75 (93).

Preparation 5-Methylenenonane-1,9-diol (11). To a solution of **9c** (169 mg, 0.41 mmol) in 1:1 THF:MeOH (6 mL) and H_2O (1 mL) at room temperature was added KF (240 mg, 4.14 mmol), $KHCO_3$ (248 mg, 2.48 mmol), and 30% H_2O_2 (0.5 mL, 4.41 mmol). The reaction was stirred at room temperature for 12 h at which time conversion to the *tert*-butyldimethylsiloxy-monoprotected diol was complete by GC analysis. The mixture was then heated to 100 °C for 48 h. The reaction was allowed to cool to room temperature, concentrated by rotary evaporation to approximately 2 mL, saturated with NaCl, extracted with Et_2O (4 × 20 mL), dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and purified by flash chromatography to give the title compound in 60% yield. Alternatively, the title compound may be prepared from **12** using oxidation method C. The reaction was stirred for 30 min at which time no starting material could be detected by GC analysis. Workup and purification by flash chromatography followed by Kugelrohr distillation gave the title compound in 56% yield: ot 165−180 °C/0.1 mmHg; R_f 0.23 (3:1 ethyl acetate: hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.69 (s, 2H), 3.61 (t, J = 6.4 Hz, 4H), 2.01 (t, J = 7.5 Hz, 4H), 1.80 (s, 2H), 1.44−1.56 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.24 (s), 109.17 (s), 62.70 (s), 35.63 (s), 32.36 (s), 23.84 (s). IR (neat): 3330.5 cm^{-1}. HRMS. Calcd for $C_{10}H_{18}O$ (M − H_2O^+): 154.1358. Found: 154.1366. LRMS (EI): m/z 154 (4), 81 (82), 55 (96), 41 (100).

Preparation of 9-{(3,4,5-Trifluorophenyl)silyl}-5-methylenenonan-1-ol (12). To a solution of **9d** (199 mg, 0.46 mmol) in 1:1 THF:MeOH (4 mL) at 0 °C was added 10% HCl (0.9 mL, 0.94 mmol). The reaction was stirred for 5 min before removing the cold bath. The reaction was stirred for 15 min at room temperature at which time no starting material could be detected by GC analysis. The crude mixture was concentrated by rotary evaporation to approximately 1 mL, extracted with Et_2O (4 × 20 mL), dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and purified by flash chromatography to give the title compound in 80% yield: R_f 0.13 (5:1 hexanes: ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08−7.13 (m, 2H), 4.68 (d, J = 7.5 Hz, 2H), 4.23 (t, J = 3.6 Hz, 2H), 3.62 (t, J = 6.4 Hz, 2H), 1.99 (q, J = 7.2 Hz, 4H), 1.37−1.57 (m, 9H), 0.89−0.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.14 (ddd, J = 254, 9.5, 2.6 Hz), 149.16 (s), 140.64 (dt, J = 254, 15.0 Hz), 129.04−129.23 (m), 118.59 (dd, J = 14.1, 4.4 Hz), 109.09 (s), 62.79 (s), 35.67 (s), 35.45 (s), 32.42 (s), 30.72 (s), 24.48 (s), 23.86 (s), 9.62 (s). ^{19}F NMR (470 MHz, $CDCl_3$): δ 41.82−41.88 (m, 2F), 17.64−17.72 (m, 1F). IR (neat): 3354.2, 2144.3 cm^{-1}. HRMS. Calcd for $C_{16}H_{22}F_3OSi$ (M − H$^+$): 315.1392. Found: 315.1407. LRMS (EI): m/z 315 (2), 177 (65), 161 (100), 55 (91), 41 (86).

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