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Synthesis of Phenols via Fluoride-free Oxidation of Arylsilanes and Arylmethoxysilanes

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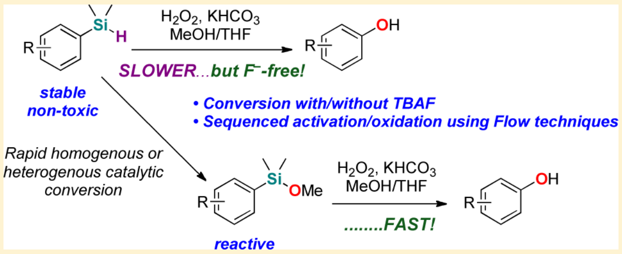
S Supporting Information

ABSTRACT: Rapid, efficient methods have been developed to prepare phenols from the oxidation of arylhydrosilanes. The effects of arene substituents and fluoride promoters on this process show that while electron-deficient arenes can undergo direct oxidation from the hydrosilane, electron-rich aromatics benefit from silane activation via oxidation to the methoxysilane using homogeneous or heterogeneous transition metal catalysis. The combination of these two oxidations into a streamlined flow procedure involving minimal processing of reaction intermediates is also reported.

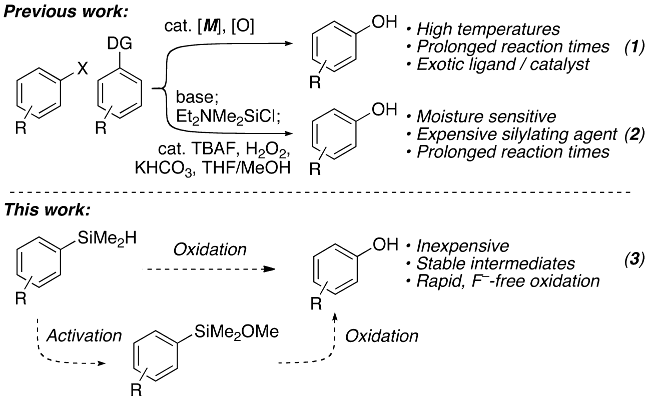


■ INTRODUCTION

Phenols are a fundamentally important organic functional group; they are widespread throughout bioactive natural products and pharmaceuticals,[1] of great importance to the polymer industry, and play a pivotal role in the functionalization of aromatic nuclei.[2] Despite their utility, mild routes to phenols remain underdeveloped, and alternatives to the harsh, functional group-intolerant conditions of traditional phenolation are avidly sought.[3] In this paper, we describe an oxidative approach to phenols from stable, readily available arylhydrosilanes under fluoride-free conditions, and the activation of these hydrosilanes to arylmethoxysilanes, which show heightened reactivity toward (fluoride-free) oxidation.

Among methods recently developed for the synthesis of phenols, impressive advances have been made in transition metal-catalyzed oxidations of aryl halides,[4] and direct C−H oxidations.[5] However, these methods almost invariably require high temperatures and long reaction times, and can depend on specialized directing groups or catalyst/ligand combinations (Scheme 1, eq 1). A phenol surrogate, which can be easily introduced and carried in an inert form through a synthetic sequence, but readily oxidized under mild conditions, would be a valuable addition to the arsenal of the synthetic chemist. Arylboron derivatives offer one solution,[6] and in recent elegant work, Oxone has been shown to rapidly convert aryltrifluoroborate salts to phenols in high yields;[7] a drawback to this method is the need for the somewhat toxic reagent KHF_2 in the preparation of the trifluoroborate substrates.

Scheme 1. Metal-catalyzed and Silicon-mediated Routes to Phenols



We recognized that arylsilanes might also fulfill the requirements of a phenol surrogate. However, despite being readily available through a variety of routes including C−H activation,[8] and in contrast to the well-established oxidation of aliphatic silanes to alcohols as developed by Tamao and Fleming,[9] there are few nonspecialized examples of the conversion of arylsilanes to phenols.[8b,10,11] In this vein, we recently reported the first general synthesis of phenols from arylsilanes (Scheme 1, eq 2),[12] in which the silylating agent (diethylamino)chlorodimethylsilane provides an intermediate arylaminosilane which can be directly oxidized to the phenol, or converted to a stable yet oxidizable isopropoxysilane We found that complete conversion to the phenol could be achieved using substoichiometric amounts of fluoride, or occasionally fluoride-free conditions. However, (diethylamino)chlorodimethylsilane is not commercially available, and the moisture sensitivity of the intermediate aminosilane and need for prolonged oxidation times (up to 24 h) left us unsatisfied. An elegant tethered aryl C−H activation/silylation sequence was subsequently reported in which the silane products were also subjected to fluoride-free

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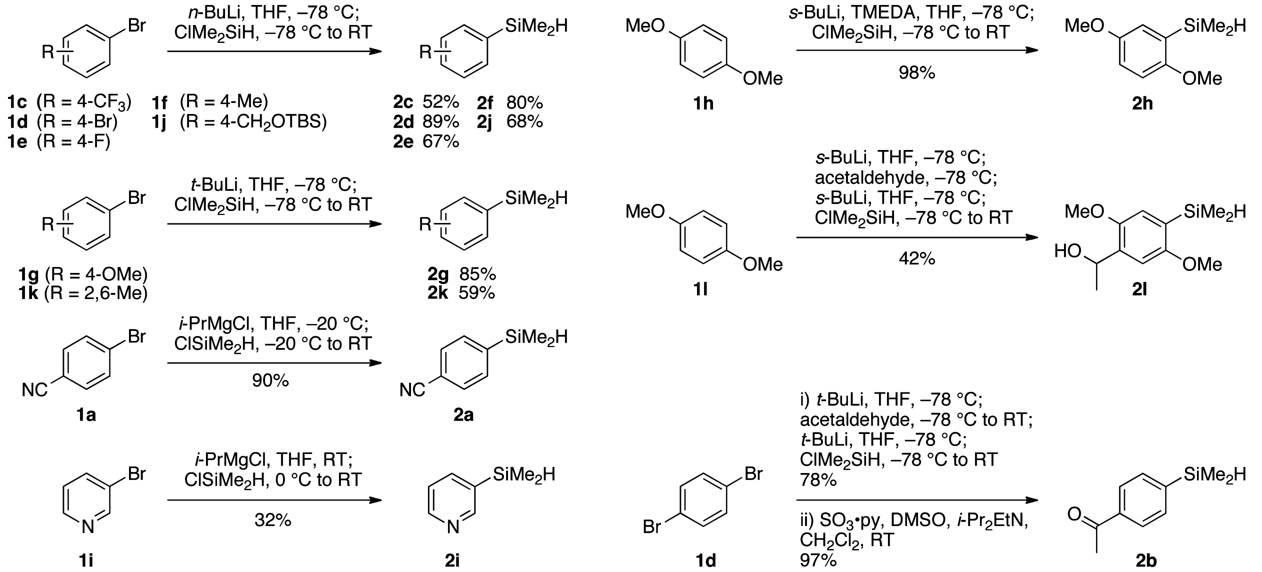
Scheme 2. Synthesis of Arylhydrosilanes



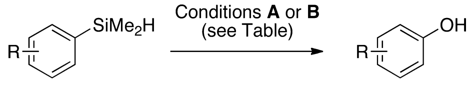
oxidation; the corresponding *ortho*-phenols were obtained in reasonable yields, but again with extended reaction times (14–24 h).[8b]

RESULTS AND DISCUSSION

We questioned whether an aryl*hydro*silane might serve as an alternative substrate for oxidation (Scheme 1, eq 3). This readily available arylsilane derivative is stable toward a variety of conditions including hydrolysis, redox processes, and organometallic reagents.[13] However, lacking the traditional electronegative substituent to promote nucleophilic attack at silicon, it was clear that this benefit to stability might come at the cost of reactivity.[14] A selection of arylhydrosilanes with varying arene electron density were prepared via silylation of aryllithium or arylmagnesium species with inexpensive chlorodimethylsilane (Scheme 2). For simple bromoarenes **1c–f** and **1j**, lithiation with *n*-butyllithium under standard conditions delivered the corresponding silanes in generally good yields. Electron-rich *p*-methoxybromobenzene **1g** and the more sterically challenging 2,6-dimethylbromobenzene **1k** required the use of *t*-butyllithium to achieve metalation, while magnesiation was employed for benzonitrile **1a**[15] and 3-bromopyridine **1i**.[16] Directed *ortho*-metalation provided a straightforward route to silane **2h** from 1,4-dimethoxybenzene.[17] Finally, one-pot double-lithiation methods were employed for the preparation of silanes **2l** and **2b**, involving sequential electrophilic trapping with acetaldehyde and chlorodimethylsilane.[18] Although in many cases good yields of the silanes were obtained using these methods, no significant efforts were made in this work to optimize these metalation protocols. Pleasingly, all hydrosilanes were found to be air and moisture stable, retaining analytical purity after storage at room temperature under air for several months.

When these potentially unreactive silanes were submitted to fluoride-free oxidation conditions, we were delighted to observe full conversion of a number of our substrate collection to the corresponding phenols (Table 1, Conditions A, Entries 1–6). The effect of the ring substituent was stark: reaction times lengthened with increasing electron density,[19] and substrates containing strongly electron-donating groups, such as **2g** and **2h**, failed to oxidize (Entries 7, 8). In the case of 4-methoxyphenylsilane **2g** (Entry 7), an improved conversion could be achieved *via* the addition of a substoichiometric amount of fluoride (Conditions B), which accelerated conversion of all reactive silanes to phenols (Entries 1–7). Although the most electron-rich substrate **2h** (Entry 8) failed to react under either conditions, we were pleased to find that pyridylsilane **2i** proved well-suited to rapid oxidation (Entry 9).

Table 1. Oxidation of Arylhydrosilanes to Phenols[a]



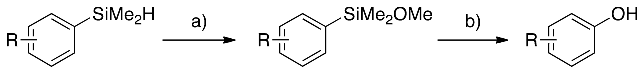
2a-i → **3a-i**

entry	hydrosilane	R	product	conditions A time (h)	conditions A yield (%)[b]	conditions B time (h)	conditions B yield (%)[b]
1	**2a**	4-CN	**3a**	5	99	3	93
2	**2b**	4-Ac	**3b**	7	73	3	66
3	**2c**	4-CF$_3$	**3c**	7	73	5	91
4	**2d**	4-Br	**3d**	7	57	5	75
5	**2e**	4-F	**3e**	12	71	7	64
6	**2f**	4-Me	**3f**	12	67	7	85
7	**2g**	4-OMe	**3g**	24	33[c]	24	65 (80)[c]
8	**2h**	2,5-OMe	**3h**	24	<5[c]	24	<5[c]
9	**2i**	3-pyridyl	**3i**	2	78	1	71

[a] Reaction conditions. A: H_2O_2 (30% aq., 6 equiv), $KHCO_3$ (0.5 equiv), THF/MeOH (1:1, 0.3 M), rt. B: H_2O_2 (30% aq., 6 equiv), TBAF (1 M in THF, 0.1 equiv), $KHCO_3$ (0.5 equiv), THF/MeOH (1:1, 0.3 M), rt. [b] Isolated yield. [c] Percent conversion determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

Examination of the crude reaction mixtures of incomplete oxidations led to the identification of silanols as potential intermediates. This was confirmed by the independent preparation of silanol **4** via ruthenium-catalyzed dehydrogenative oxidation of **2g** (Scheme 3).[20] We surmised from this that silanol formation, perhaps via 1,2-hydride migration from silicon to oxygen, is a process that may be imperative for the oxidation, and that silanols themselves might represent useful substrates. Although preliminary experiments showed **4** to be a

Table 2. Oxidation of Arylmethoxysilanes to Phenols[a]

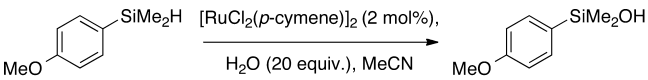


2a-h **5a-h** **3a-h**

			step a	step b			
				condition A		condition B	
entry	hydrosilane	R	yield **5** (%)[b]	time	yield **3** (%)[b]	time	yield **3** (%)[b]
1	**2a**	4-CN	95	45 min	89	30 min	93
2	**2b**	4-Ac	96	45 min	81	30 min	87
3	**2c**	4-CF_3	89	60 min	73	30 min	76
4	**2d**	4-Br	85	90 min	86	60 min	86
5	**2e**	4-F	86	90 min	91	60 min	87
6	**2f**	4-Me	89	2.5 h	79	90 min	80
7	**2g**	4-OMe	99	3 h	88	2 h	93
8	**2h**	2,5-OMe	89	4.5 h	78	3 h	91

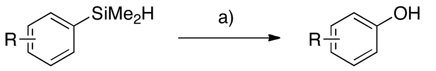
[a]Reaction conditions: a) $[RuCl_2(p\text{-cymene})]_2$ (0.5 mol %), MeOH (5 M), 5 min, rt; b) Conditions A or B, see Table 1. [b]Isolated yield.

Scheme 3. Synthesis of *p*-Methoxyphenylsilanol 4

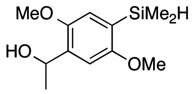


2g **4**

Table 3. Sequenced Oxidation of Aryl Hydrosilanes to Phenols[a]



2b-h, j-l **3b-h, j-l**

Entry	Hydrosilane	R	Time (h)[b]	Yield **3** (%)[c]
1	**2b**	4-Ac	0.5	72
2	**2c**	4-CF_3	0.5	89
3	**2d**	4-Br[d]	0.5	85
4	**2e**	4-F	1	88
5	**2f**	4-Me	1.5	92
6	**2g**	4-OMe	3	80
7	**2h**	2,5-OMe	3	79
8	**2j**	4-CH_2OTBS	3	74[e]
9	**2k**	2,6-Me	3	88
10	**2l**		3	40[f]

[a]Reaction conditions: a) 10% Pd/C (0.5 mol %), MeOH (5 M), Ar, rt, 5 min; filter through Celite; H_2O_2 (30% aq., 6 equiv), TBAF (1 M in THF, 0.1 equiv), $KHCO_3$ (0.5 equiv), THF/MeOH (1:1, 0.3 M), rt. [b]Time for methoxysilane oxidation to phenol. [c]Isolated yield of phenol. [d]Pd/C oxidation performed in Et_2O to avoid substrate decomposition; [e]Performed in the absence of TBAF. [f]The unstable phenol was directly dimethylated; yield over 2 steps.

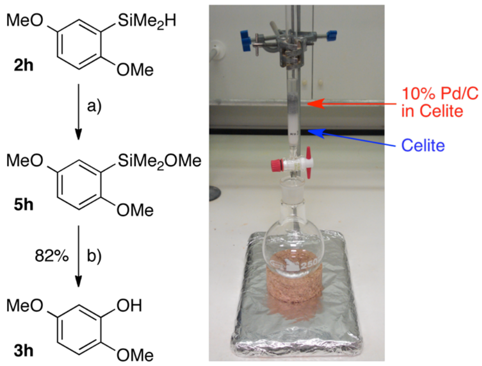
competent substrate in the oxidation, it was also prone to undergo condensation to the corresponding disiloxane on storage; as disiloxanes were found to be unreactive toward oxidation, silanols were not explored further as oxidation substrates.

Nevertheless, the facile introduction of an electronegative group onto the silicon nucleus as a means to activate the hydrosilane was an attractive prospect, and we identified aryl*methoxy*silanes as substrates which might show less tendency to form disiloxanes, but significantly enhanced reactivity compared to hydrosilanes. The ruthenium-catalyzed oxidation[21] of the hydrosilanes with methanol was extremely rapid (<2 min), and all arene substrates were converted to the corresponding methoxysilanes in excellent yields (Table 2, Step a), entries 1−8).[22,23] The ensuing methoxysilane oxidations proceeded at greatly enhanced rates, delivering phenols in high yields under fluoride-free conditions (Step b, Conditions A), with reaction times ranging from 45 min to 4.5 h. Again, the electron density of the arene influenced the rate of oxidation, but now, with an electronegative silicon substituent, all substrates could be oxidized without fluoride promoter. The addition of fluoride led to further rate enhancement (Step b, Conditions B) but was certainly not an essential requirement for reactivity.

The conditions used in the two-step oxidation procedure we had developed to convert hydrosilanes into phenols suggested a telescoped process might be feasible that would remove the need for manipulation of the methoxysilane intermediate. However, direct oxidation of ruthenium-containing reaction mixtures was not possible, due to rapid metal-catalyzed decomposition of H_2O_2. Although simple elution of the arylmethoxysilane reaction mixture through a silica plug removed the catalyst, we were mindful of potential complications on larger scales where hydrolysis of the methoxysilane might prove problematic. A significant improvement was made with the identification of 10% Pd/C as a cheap heterogeneous catalyst for the conversion of hydrosilanes to methoxysilanes.[24] Although still capable of catalyzing H_2O_2 decomposition, Pd/C could be conveniently removed via simple filtration through Celite. Most pleasingly, we found that Pd/C enabled methoxysilane formation at similar catalyst loading, rate and efficiency to the ruthenium-catalyzed method (i.e., 0.5 mol %, <5 min), despite previous less economical use of this catalyst.[24,25] With this chemistry in hand, we subjected our hydrosilane collection to the sequenced oxidation procedure (Table 3), which gave the corresponding phenols in short reaction times and excellent yields. Of particular note is the survival of the primary benzylic TBS ether in **2j** (Entry 8), which underlines the mild and functional group-tolerant nature of the protocol, and the successful oxidation of sterically hindered doubly *ortho*-substituted silane **2k** (Entry 9). The phenolic benzyl alcohol arising from oxidation of tetrasubstituted arylsilane **2l** (Entry 10) proved unstable, however direct methylation of the crude reaction mixture afforded the corresponding tetramethoxy ether **3l**, which is a polyketide natural product (in three steps from 1,4-dimethoxybenzene).[26]

As a final enhancement to the synthetic procedure, we contemplated performing the hydrosilane-to-methoxysilane oxidation in a flow reactor, which would enable the direct preparation of a solution of methoxysilane ready for oxidation. Initial experiments employed an H-cube equipped with a Pd/C cartridge and a solution of dimethoxyphenylsilane **2h**, our most challenging substrate, in 1:1 THF/MeOH. While complete oxidation of **2h** to the methoxysilane was observed, this method was limited to a maximum flow rate of 1 mL min^{-1} at 0.2 M, due to the evolution (rather than consumption) of hydrogen in the H-cube which generated a back-pressure and prevented continuous flow. The use of Celite in our batch process led us

Scheme 4. Oxidation of Hydrosilanes via Filtration through Celite/Pd/C[a]



[a]Reagents and conditions: a) Celite/10% Pd/C column, 0.5 M in 1:1 MeOH/THF, 5 mL min^{-1}; 1:1 MeOH/THF wash; b) add H_2O_2 (30% aq., 6 equiv), TBAF (1 M in THF, 0.1 equiv), $KHCO_3$ (0.5 equiv), 3 h, rt.

to question whether, due to its rapid nature, the oxidation itself could be performed as a simple filtration through a mixture of Celite and Pd/C, which would enable higher throughput without the problems associated with the H-cube.

A glass chromatography column was set up as illustrated in Scheme 4, with a layer of Celite/10% Pd/C packed above a layer of Celite (to prevent leaching of Pd/C into the product). To our delight, complete oxidation of a 0.5 M solution of **2h** was observed at a flow rate of 5 mL min^{-1} on scales as large as 10 mmol, using just 10 mg of 10% Pd/C in the column, which corresponds to a remarkable catalyst loading of 0.1 mol % on 10 mmol scale. This procedure directly afforded a solution of methoxysilane **5h** in readiness for oxidation, which gave an 82% isolated yield of phenol **3h**.

■ CONCLUSION

In conclusion, we have developed a highly practical and rapid synthesis of phenols from readily available arylhydrosilanes, which represents the first use of such "nonactivated" silanes in a Tamao oxidation. The stability of these hydrosilanes toward multistep synthetic procedures, combined with the ease of their direct oxidation or sequenced activation/oxidation using flow techniques, and the generality of oxidation across a range of substituents suggest this to be an attractive method for arene phenolation. Although the reactivity of all silanes was heavily influenced by the electronic character of the arene, the need for fluoride promotion was rarely imperative but always rate improving.

■ EXPERIMENTAL SECTION

General Experimental Methods. For reactions requiring anhydrous conditions, experiments were carried out in oven-dried glassware. Unless otherwise stated, all reactions were carried out under argon. Solvents and commercially available reagents were dried and purified before use where appropriate using standard procedures. Petroleum ether refers to the fraction of light petroleum ether which boils in the range 40−60 °C. ((4-Bromobenzyl)oxy)(tert-butyl)-dimethylsilane was prepared according to literature precedent and was in agreement with data previously reported.[12a] Thin layer chromatography was performed using Merck DC Kieselgel 60 F_{254} plates. Product spots were visualized by the quenching of UV fluorescence (λ_{max} 254 nm) then stained and heated using anisaldehyde, ammonium molybdate or potassium permanganate. Retention factors (R_f) are reported with the solvent system used in parentheses. Flash column chromatography was carried out on Macherey-Nagel Kieselgel 60 M (230−400 mesh) under positive pressure, and the solvent system used in parentheses. Proton (^1H) and carbon (^{13}C) NMR spectroscopic data are presented in the order: chemical shift, integration, multiplicity (br, broad; s, singlet; d, doublet; dd doublet of doublets; dt, doublet of triplets; t, triplet; q, quartet; sept, septet; m, multiplet), coupling constant and proton assignment. Chemical shifts (δ_H or δ_C) are quoted in ppm downfield of tetramethylsilane with residual solvent as the internal standard. Coupling constants (J) are given in Hz and are rounded to the nearest 0.5 Hz. Infrared spectra were recorded on a Fourier Transform spectrometer, and samples were prepared as a thin film. Absorption maxima (ν_{max}) are quoted in wavenumbers (cm^{-1}) and are described as s (strong), m (medium), w (weak) or br (broad). Only selected, characteristic IR absorption data are provided for novel compounds. Melting points were determined using a Griffin melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were recorded on a mass spectrometer under electrospray ionization (ES) or field ionization (FI) conditions using a TOF mass analyzer. High resolution masses are calculated to four decimal places from the molecular formula and all obtained values are within a tolerance of 5 ppm.

4-(Dimethylsilyl)benzonitrile **(2a)**.[27] The following procedure was developed from that reported by Wood et al.[15] *i*-PrMgCl (4.26 mL of a 2 M solution in THF, 8.52 mmol, 1.3 equiv) was slowly added to a cooled solution (ice/salt bath, −20 °C) of 4-iodobenzonitrile (1.5 g, 6.55 mmol, 1.0 equiv) in anhydrous THF (15 mL). After 30 min the solution was transferred slowly via cannula to a cooled (ice/salt bath −20 °C) solution of chlorodimethylsilane (1.09 mL, 9.82 mmol, 1.5 equiv) in anhydrous THF (15 mL). The reaction mixture was allowed to warm to RT over 4 h. The reaction was then quenched with NH_4Cl (10 mL, sat., aq.), the phases separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to afford a colorless oil (950 mg, 90%) without the need for further purification; R_f 0.71 (petroleum ether); ^1H NMR (400 MHz, $(CD_3)_2CO$) δ_H 0.40 (6H, d, J 3.5), 4.45 (1H, sept, J 3.5), 7.76 (2H, d, J 8.0), 7.79 (2H, d, J 8.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −4.66, 113.2, 118.9, 131.5, 134.2, 144.5.

1-(4-(Dimethylsilyl)phenyl)ethanone **(2b)**.[28] Prepared via a Parikh−Doering oxidation of 1-(4-(dimethylsilyl)phenyl)ethanol which itself was prepared from 1,4-dibromobenzene using a modified procedure of Kim et al.[18] To a solution of 1,4-dibromobenzene (1.5 g, 6.36 mmol, 1.0 equiv) in anhydrous THF (40 mL) at −78 °C was added *t*-BuLi (7.95 mL of a 1.6 M solution in hexanes, 12.7 mmol, 2.0 equiv), and the reaction was stirred for 1 h at −78 °C. Acetaldehyde (393 μL, 7.00 mmol, 1.1 equiv) was added, and the reaction was warmed to 0 °C over 30 min. The reaction was then cooled to −78 °C before the addition of *t*-BuLi (8.74 mL of a 1.6 M solution, 14.0 mmol, 2.2 equiv) and continued stirring at −78 °C for 1 h. Finally, dimethylchlorosilane (918 μL, 8.27 mmol, 1.3 equiv) was added and the reaction allowed to warm to RT over 2 h. The reaction was quenched with NH_4Cl (20 mL, sat., aq.), the mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to a red oil, before purification by column chromatography (petroleum ether → petroleum ether/EtOAc (4:1)) afforded 1-(4-(dimethylsilyl)phenyl)ethanol as a colorless oil (899 mg, 78%); R_f 0.31 (petroleum ether/Et_2O (4:1)); IR (thin film, ν_{max}/cm^{-1}) 2970w, 2117 m, 1249w, 1083w, 878s; ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.36 (6H, d, J 3.5), 1.51 (3H, d, J 6.5), 1.82 (1H, br s), 4.44 (1H, sept, J 3.5), 4.91 (1H, q, J 6.5), 7.39 (2H, d, J 7.5), 7.55 (2H, d, J 7.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −3.76, 25.1, 70.4, 124.9, 134.3, 136.6, 146.8; HRMS (FI^+) calc. for $C_{10}H_{16}OSi$ $[M]^+$ 180.0970, found 180.0969. Subsequently, SO_3·pyridine (1.67 g, 10.5 mmol, 3.0 equiv) and anhydrous DMSO (2.48 mL, 30.5 mmol, 10.0 equiv) were stirred at RT for 15 min before a solution of 1-(4-(dimethylsilyl)phenyl)ethanol (630 mg, 3.49 mmol, 1.0 equiv) and DIPEA (3.04 mL, 17.5, 5.0 equiv) in dichloromethane (15 mL) was added. The reaction mixture was stirred at RT for 1 h by which time the reaction was observed to be complete by TLC. The reaction mixture was diluted with dichloromethane (10 mL), quenched with

HCl (10 mL, 1 N aqueous solution) and stirred vigorously for 15 min at RT. The biphasic mixture was separated, and the aqueous phase washed with dichloromethane (3 × 10 mL). The combined organic phases were washed with $NaHCO_3$ (2 × 20 mL, sat., aq.), dried ($MgSO_4$) and concentrated *in vacuo* to a yellow oil which was purified by column chromatography (petroleum ether → petroleum ether/Et_2O (9:1)) to afford a colorless oil (605 mg, 97%); R_f 0.51 (petroleum ether/Et_2O (9:1)); IR (thin film, ν_{max}/cm^{-1}) 2120m, 1684s, 1251m, 875s, 820m; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.38 (6H, d, *J* 3.5), 2.61(3H, s), 4.46 (1H, sept, *J* 3.5), 7.65 (2H, d, *J* 8.0), 7.93 (2H, d, *J* 8.0); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C −4.03, 26.6, 127.3, 134.2, 137.5, 144.2, 198.3; HRMS (ES$^+$) calc. for $C_{10}H_{14}NaOSi$ [M+Na]$^+$ 201.0706, found 201.0708.

Synthesis of Hydrosilanes via Bromine/Lithium Exchange, General Procedure D. To a stirred solution of bromoarene at −78 °C in anhydrous THF was added *n*-BuLi (1.1−1.2 equiv, 2.5 M in hexanes) or *t*-BuLi (2.0−2.4 equiv, 1.6 M in hexanes). The resulting mixture was stirred for 1−3 h at −78 °C before addition of chlorodimethylsilane (1.0−1.5 equiv), and the reaction mixture was allowed to warm to RT overnight. The crude reaction mixture was diluted in petrol and filtered to remove lithium salts. Purification was conducted by column chromatography or vacuum distillation.

Dimethyl(4-(trifluoromethyl)phenyl)silane (2c).[29] According to general procedure D, 4.27 mL (10.7 mmol, 1.2 equiv) of *n*-BuLi was added to 2.0 g (8.89 mmol, 1.0 equiv) of 1-bromo-4-(trifluoromethyl)-benzene in anhydrous THF (50 mL). The resulting mixture was stirred for 2 h at −78 °C before 1.26 mL (11.6 mmol, 1.3 equiv) of chlorodimethylsilane was added and the reaction was stirred overnight. The product was purified by vacuum distillation (60−64 °C at 20 mmbar) to afford a colorless oil (943 mg, 52%); R_f 0.59 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.38 (6H, d, *J* 4.0), 4.46 (1H, sept, *J* 4.0), 7.61 (2H, d, *J* 8.0), 7.67 (2H, d, *J*, 8.0); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C −4.00, 124.1 (q, *J* 272.0), 124.3 (q, *J* 3.5), 131.1 (q, *J* 32.0), 134.3, 142.4.

(4-Bromophenyl)dimethylsilane (2d).[30] According to general procedure D, 5.59 mL (14.0 mmol, 1.1 equiv) of *n*-BuLi was added to 3.0 g (12.7 mmol, 1.0 equiv) of 1,4-dibromobenzene in anhydrous THF (30 mL). The resulting mixture was stirred for 3 h at −78 °C before 1.69 mL (18.5 mmol, 1.2 equiv) of chlorodimethylsilane was added and the reaction was stirred overnight. The product was purified by vacuum distillation (70−72 °C at 10 mmbar) to afford a colorless oil (2.41 g, 89%); R_f 0.76 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.35 (6H, d, *J* 3.5), 4.41 (1H, sept, *J* 3.5), 7.41 (2H, d, *J* 8.0), 7.51 (2H, d, *J* 8.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −3.87, 124.0, 131.0, 135.6, 136.2.

(4-Fluorophenyl)dimethylsilane (2e).[31] According to general procedure D, 8.23 mL (20.6 mmol, 1.2 equiv) of *n*-BuLi was added to 3.0 g (17.1 mmol, 1.0 equiv) of 1-bromo-4-fluorobenzene in anhydrous THF (60 mL). The resulting mixture was stirred for 3 h at −78 °C before 2.86 mL (25.7 mmol, 1.5 equiv) of chlorodimethylsilane was added and the reaction stirred overnight. The product was purified by vacuum distillation (52 °C at 20 mmbar) to afford a colorless oil (1.78, 67%); R_f 0.78 (petroleum ether); IR (thin film, ν_{max}/cm^{-1}) 2120m, 1589m, 1499m, 1231m, 1106m, 877s; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.35 (6H, d, *J* 3.5), 4.44 (1H, sept, *J* 3.5), 7.07 (2H, t, *J* 8.5), 7.53 (2H, dd, *J* 8.5, 6.0); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C −3.68, 115.0 (d, *J* 20.0), 132.8 (d, *J* 3.5), 135.9 (d, *J* 7.0), 163.8 (d *J* 248.5); HRMS (FI$^+$) calc. for $C_8H_{11}FSi$ [M]$^+$ 154.0614, found 154.0615.

Dimethyl(p-tolyl)silane (2f).[32] According to general procedure D, 5.6 mL (14.0 mmol, 1.2 equiv) of *n*-BuLi was added to 2.0 g (11.7 mmol, 1.0 equiv) of *para*-bromotoluene in anhydrous THF (40 mL). The resulting mixture was stirred for 2 h at −78 °C before 1.69 mL (15.2 mmol, 1.3 equiv) of chlorodimethylsilane was added and the reaction stirred overnight. The product was purified by column chromatography (petroleum ether) to afford the title compound as a colorless oil (1.41 g, 80%); R_f 0.66 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.35 (6H, d, *J* 3.5), 2.38 (3H, s), 4.43 (1H, sept, *J* 3.5), 7.21 (2H, d, *J* 7.5), 7.47 (2H, d, *J* 7.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −3.69, 21.5, 128.7, 133.8, 134.0, 139.0.

(4-Methoxyphenyl)dimethylsilane (2g).[32] According to general procedure D, 8.0 mL (12.8 mmol, 2.2 equiv) of *t*-BuLi was added to 1.0 g (1.49 mmol, 1.0 equiv) of 1-bromo-4-methoxybenzene in anhydrous THF (20 mL). The resulting mixture was stirred for 40 min at −78 °C before 1.42 mL (12.8 mmol, 1.0 equiv) of chlorodimethylsilane was added and the reaction stirred overnight. The product was purified by column chromatography (petroleum ether) to afford a colorless oil (758 mg, 85%); R_f 0.69 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.34 (6H, d, *J* 3.5), 3.84 (3H, s), 4.43 (1H, sept, *J* 3.5), 6.94 (2H, d, *J* 8.5), 7.49 (2H, d, *J* 8.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −3.54, 55.0, 113.7, 115.3, 135.4, 160.6.

(2,5-Dimethoxyphenyl)dimethylsilane (2h). To a stirred solution of 1,4-dimethoxybenzene (8.29 g, 60.0 mmol, 1.0 equiv) and TMEDA (10.8 mL, 72.0 mmol, 1.2 equiv) in anhydrous THF (150 mL) at −78 °C, was added *s*-BuLi (52.0 mL of a 1.3 M solution in hexanes, 72.0 mmol, 1.2 equiv). The resulting mixture was stirred for 2 h at −78 °C before addition of chlorodimethylsilane (8.66 mL, 78.0 mmol, 1.3 equiv), and the reaction mixture was allowed to warm to RT overnight. The reaction mixture was quenched with NH_4Cl (50 mL, sat., aq.), the phases were separated and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo* before purification by column chromatography (petroleum ether) afforded a colorless oil (11.5 g, 98%); R_f 0.73 (petroleum ether); IR (thin film, ν_{max}/cm^{-1}) 3424br, 2120w, 1643m 1272m, 892s; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.34 (6H, s), 3.79 (6H, s), 4.39 (1H, sept, *J* 3.5), 6.79 (1H, d, *J* 9.0), 6.89 (1H, dd, *J* 9.0, 3.0), 7.00 (1H, d, *J* 3.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −3.86, 55.8, 55.9, 110.5, 115.3, 121.5, 126.8, 153.5, 158.1; HRMS (FI$^+$) calc. for $C_{10}H_{16}O_2Si$ [M]$^+$ 196.0920, found 196.0919.

3-(Dimethylsilyl)pyridine (2i).[16] The procedure of Kung et al.[16] was followed. *i*-PrMgCl (8.37 mL of a 2 M solution in THF, 16.7 mmol, 1.0 equiv) was added slowly to a solution of 3-bromopyridine (2.62 mL, 16.7 mmol, 1.0 equiv) in anhydrous THF (30 mL) at RT. After 1 h the solution was cooled to 0 °C and chlorodimethylsilane (2.14 mL, 19.24 mmol, 1.15 equiv) was added. The reaction mixture was allowed to warm to RT. The reaction was then diluted in ether (30 mL) and washed with water (3 × 20 mL) and brine (1 × 30 mL). The combined organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to a yellow oil which was purified by column chromatography ($CHCl_3$) to afford a slightly yellow oil (1.17 g, 51%); R_f 0.32 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.38 (6H, d, *J* 4.0), 4.46 (1H, sept, *J* 4.0), 7.27 (1H, dd, *J* 7.5, 5.0), 7.81 (1H, dt, *J* 7.5, 1.5), 8.60 (1H, dd, *J* 5.0, 1.5), 8.71 (1H, t, *J* 1.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −4.10, 123.3, 132.4, 141.7, 150.2, 154.3.

tert-Butyl((4-(dimethylsilyl)benzyl)oxy)dimethylsilane (2j). According to general procedure D, 0.71 mL (1.78 mmol, 1.2 equiv) of *n*-BuLi was added to 446 mg (1.48 mmol, 1.0 equiv) of ((4-bromobenzyl)oxy)(tert-butyl)dimethylsilane in anhydrous THF (10 mL). The resulting mixture was stirred for 2 h at −78 °C before 197 μL (1.78 mmol, 1.2 equiv) of chlorodimethylsilane was added and the reaction was stirred overnight. The product was purified by passage through a silica plug (diethyl ether eluant) to afford a colorless oil (282 mg, 68%); R_f 0.81 (petroleum ether); IR (thin film, ν_{max}/cm^{-1}) 2956w, 2857w, 2118w, 1250m, 1087m, 834s; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.11 (6H, s), 0.35 (6H, d, *J* 3.5), 0.96 (9H, s), 4.43 (1H, sept, *J* 3.5), 4.76 (2H, s), 7.34 (2H, d, *J* 7.5), 7.52 (2H, d, *J* 7.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C −5.27, −3.72, 18.4, 25.9, 64.9, 125.5, 133.9, 135.7, 142.5; HRMS (ES$^+$) calc. for $C_{15}H_{28}NaOSi_2$ [M + Na]$^+$ 303.1571, found 303.1571.

(2,6-Dimethylphenyl)dimethylsilane (2k).[32] According to general procedure D, 16.2 mL (25.9 mmol, 2.4 equiv) of *t*-BuLi was added to 2.0 g (10.8 mmol, 1.0 equiv) of 2-bromo-1,3-dimethylbenzene in anhydrous THF (50 mL). The resulting mixture was stirred for 1 h at −78 °C before 1.56 mL (14.0 mmol, 1.3 equiv) of chlorodimethylsilane was added and the reaction was stirred overnight. The product was purified by column chromatography (petroleum ether) to afford a colorless oil (1.05 g, 59%); R_f 0.79 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.46−0.48 (6H, m), 2.53−2.54 (3H, m), 4.79−4.84 (1H, m), 7.06 (2H, d, *J* 7.5), 7.21−7.25 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −2.45, 24.0, 127.6, 129.2, 134.9, 144.2.

*1-(4-(Dimethylsilyl)-2,5-dimethoxyphenyl)ethanol (**2l**).* To a solution of 1,4-dimethoxybenzene (2.00 g, 14.5 mmol, 1.0 equiv) and TMEDA (2.6 mL, 17.4 mmol, 1.2 equiv) in anhydrous THF (50 mL) at −78 °C was added *s*-BuLi (13.4 mL of a 1.3 M solution in hexanes, 14.5 mmol, 1.2 equiv). The reaction mixture was stirred at −78 °C for 2 h before the addition of acetaldehyde (1.1 mL, 18.8 mmol, 1.3 equiv), after which the mixture was stirred at −78 °C for a further 40 min. TMEDA (2.81 mL, 18.8 mmol, 1.3 equiv) was added, followed quickly by *s*-BuLi (14.5 mL of a 1.3 M solution in hexanes, 18.8 mmol, 1.3 equiv) and the reaction mixture was stirred at −78 °C for 4 h, before chlorodimethylsilane (2.10 mL, 18.8 mmol, 1.3 equiv) was added, and the reaction was allowed to warm to RT overnight. The reaction was quenched with NH_4Cl (20 mL, sat., aq.), the biphasic mixture was separated and the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to a yellow oil. Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (4:1)) afforded a yellow solid (1.46 g, 42%); R_f 0.19 (petroleum ether/Et_2O (9:1)); IR (thin film, ν_{max}/cm^{-1}) 2958w, 2840w, 2114 m, 1376s, 1179s, 1043s, 889s; ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.34 (6H, d, *J* 3.5), 1.51 (3H, d, *J* 6.5), 2.59−2.61 (1H, m), 3.81 (3H, s), 3.85 (3H, s), 4.39 (1H, sept, *J* 3.5), 5.10 (1H, quintet, *J* 6.5), 6.91 (1H, s,), 6.95 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −3.76, 23.2, 55.9, 56.0, 66.7, 108.3, 117.9, 124.6, 136.2, 150.2, 158.7; HRMS (ES^+) calc. For $C_{12}H_{20}NaO_3Si$ $[M+Na]^+$ 263.1074, found 263.1072; EA calc. for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.39. Found: C, 59.84; H, 8.50.

Arylsilane Oxidation, General Procedure A. To a solution of arylsilane (0.50 mmol, 1.0 equiv) in MeOH/THF (1.5 mL, 3 M) at RT, under air, was added $KHCO_3$ (25 mg, 0.25 mmol, 0.5 equiv) and H_2O_2 (340 *μ*L of a 30% w/w solution, 3.00 mmol, 6.0 equiv). The reaction mixture was stirred for 3 to 24 h (see Tables 1 and 2) after which HCl (1 mL, 1 N aqueous solution)) was added and the monophasic mixture stirred for a further 5 min. The reaction mixture was then extracted with EtOAc (3 × 5 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo* to afford a crude phenolic product which was purified by column chromatography.

Arylsilane Oxidation, General Procedure B. As general procedure A but with the addition of TBAF (50 *μ*L of a 1 M solution in THF, 0.05 mmol, 0.1 equiv).

Sequenced Arylsilane Pd/C Activation and Oxidation, General Procedure C. To a vial containing aryl hydrosilane (0.50 mmol, 1.0 equiv) was added MeOH (200 *μ*L). The vial was purged with argon before the addition of Pd/C (2.6 mg, 10 wt % loading, 2.5 *μ*mol, 5 mol %). After 2/3 s of effervescence, the reaction was seen to be complete by TLC. The resulting solution was filtered through a Celite plug, eluted with Et_2O, and concentrated *in vacuo*. To this crude product was added MeOH/THF (1.5 mL), $KHCO_3$ (25 mg, 0.250 mmol, 0.5 equiv), TBAF (50 *μ*L of a 1 M solution in THF, 0.050 mmol, 0.10 equiv) and H_2O_2 (340 *μ*L of a 30% w/w solution, 3.00 mmol, 6.0 equiv) and the reaction mixture was stirred for 30 min to 3 h (see Table 3). Upon completion, the reaction was quenched with HCl (1 mL, 1 N aqueous solution) and the monophasic mixture was stirred for a further 5 min. The reaction mixture was then extracted with EtOAc (3 × 5 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo* to afford a crude phenolic product which was purified by column chromatography.

*4-Hydroxybenzonitrile (**3a**).*[4a] Using general procedure A silane **2a** (100 mg, 0.62 mmol) afforded 73 mg (99%); using general procedure B silane **2a** (100 mg, 0.62 mmol) afforded 69 mg (93%); using general procedure A silane **5a** (100 mg, 0.52 mmol) afforded 55 mg (89%); using general procedure B silane **5a** (100 mg, 0.52 mmol) afforded 58 mg (93%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (4:1)) produced a white solid; R_f 0.32 (petroleum ether/Et_2O (4:1)); mp 114−116 °C (Lit. 108−109 °C); ^1H NMR (500 MHz, $CDCl_3$) δ_H 6.33 (1H, br s), 6.98 (2H, d, *J* 9.0), 7.61 (2H, d, *J* 9.0); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 103.9, 116.9, 119.6, 134.8, 160.4.

*1-(4-Hydroxyphenyl)ethanone (**3b**).*[33] Using general procedure A, silane **2b** (89 mg, 0.50 mmol) afforded 50 mg (73%); using general procedure B, silane **2b** (89 mg, 0.50 mmol) afforded 45 mg (66%); using general procedure A, silane **5b** (104 mg, 0.50 mmol) afforded 55 mg (81%); using general procedure B, silane **5b** (104 mg, 0.50 mmol) afforded 60 mg (87%); using general procedure C, silane **2b** (89 mg, 0.50 mmol) afforded 49 mg (72%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (1:1)) produced a white solid; R_f 0.32 (petroleum ether/Et_2O (4:1)); mp 114−116 °C (Lit. 108−109 °C); ^1H NMR (500 MHz, $CDCl_3$) δ_H 6.33 (1H, br s), 6.98 (2H, d, *J* 9.0), 7.61 (2H, d, *J* 9.0); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 103.9, 116.9, 119.6, 134.8, 160.4.

*4-(Trifluoromethyl)phenol (**3c**).*[4a] Using general procedure A, silane **2c** (102 mg, 0.50 mmol) afforded 59 mg (73%); using general procedure B, silane **2c** (102 mg, 0.50 mmol) afforded 74 mg (91%); using general procedure A, silane **5c** (117 mg, 0.50 mmol) afforded 59 mg (73%); using general procedure B, silane **5c** (117 mg, 0.50 mmol) afforded 62 mg (76%); using general procedure C, silane **2c** (102 mg, 0.50 mmol) afforded 72 mg (89%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (4:1)) produced a waxy solid; R_f 0.29 (petroleum ether/Et_2O (1:1)); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.62 (1H, br s), 6.92 (2H, d *J* 8.5), 7.52 (2H, d *J* 8.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 115.5, 123.2 (q, *J* 33.0), 124.3 (q, *J* 271.0), 127.2 (q, *J* 4.0), 158.0.

*4-Bromophenol (**3d**).*[34] Using general procedure A, silane **2d** (100 mg, 0.47 mmol) afforded 46 mg (57%); using general procedure B, silane **2d** (108 mg, 0.50 mmol) afforded 65 mg (75%); using general procedure A, silane **5d** (102 mg, 0.42 mmol) afforded 62 mg (86%); using general procedure B, silane **5d** (119 mg, 0.49 mmol) afforded 72 mg (86%); using general procedure C (with dilution; Et_2O (2 mL) added before Pd/C addition), silane **2d** (108 mg, 0.50 mmol) afforded 74 mg (85%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (4:1)) produced an off-white solid; R_f 0.42 (petroleum ether/Et_2O (4:1)); mp 56−59 °C (Lit. 54−68 °C); ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.17 (1H, br s), 6.73 (2H, d, *J* 9.0), 7.34 (2H, d, *J* 9.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 113.0, 117.2, 132.5, 154.4.

*4-Fluorophenol (**3e**).*[35] Using general procedure A, silane **2e** (150 mg, 0.97 mmol) afforded 77 mg (71%); using general procedure B, silane **2e** (150 mg, 0.97 mmol) afforded 70 mg (64%); using general procedure A, silane **5e** (127 mg, 0.69 mmol) afforded 70 mg (91%); using general procedure B, silane **5e** (93 mg, 0.51 mmol) afforded 49 mg (87%); using general procedure C, silane **2e** (77 mg, 0.50 mmol) afforded 49 mg (88%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (9:1)) produced a waxy solid; R_f 0.32 (petroleum ether/Et_2O (9:1)); ^1H NMR (500 MHz, $CDCl_3$) δ_H 4.85 (1H, br s), 6.81−6.85 (2H, m), 6.99 (2H, t, *J* 8.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 116.4 (d, *J* 23.5), 116.7 (d, *J* 7.5), 151.9, 157.7 (d, *J* 237.5).

*p-Cresol (**3f**).*[35] Using general procedure A, silane **2f** (100 mg, 0.67 mmol) afforded 48 mg (67%); using general procedure B, silane **2f** (150 mg, 1.0 mmol) afforded 92 mg (85%); using general procedure A, silane **5f** (90 mg, 0.50 mmol) afforded 43 mg (79%); using general procedure B, silane **5f** (79 mg, 0.44 mmol) afforded 38 mg (80%); using general procedure C, silane **2f** (75 mg, 0.50 mmol) afforded 50 mg (92%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (9:1)) produced a waxy solid; R_f 0.39 (petroleum ether/Et_2O (9:1)); ^1H NMR (500 MHz, $CDCl_3$) δ_H 2.28 (3H, s), 4.57 (1H, br s), 6.74 (2H, d *J* 8.5), 7.05 (2H, d *J* 8.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 20.4, 115.0, 129.9, 130.0, 153.2.

*4-Methoxyphenol (**3g**).*[36] Using general procedure B, silane **2g** (150 mg, 0.90 mmol) afforded 73 mg (65%); using general procedure A, silane **5g** (126 mg, 0.64 mmol) afforded 70 mg (88%); using general procedure B, silane **5g** (151 mg, 0.77 mmol) afforded 89 mg (93%); using general procedure C, silane **2g** (75 mg, 0.45 mmol) afforded 45 mg (80%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (9:1)) produced a white solid; R_f 0.39 (petroleum ether/Et_2O (9:1)); mp 49−52 °C (Lit. 49−51 °C); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.78 (3H, s), 4.77 (1H, br s), 6.76−6.82 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 55.8, 114.9, 116.0, 149.4, 153.7.

2,5-Dimethoxyphenol (3h).[37] Using general procedure A, silane **5h** (109 mg, 0.48 mmol) afforded 58 mg (78%); using general procedure B, silane **5h** (105 mg, 0.46 mmol) afforded 65 mg (91%); using general procedure C, silane **2h** (98 mg, 0.50 mmol) afforded 60 mg (79%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (4:1)) produced a colorless oil; R_f 0.36 (petroleum ether/Et_2O (9:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.76 (3H, s), 3.86 (3H, s), 5.73 (1H, br s), 6.39 (1H, dd, *J* 9.0, 3.0), 6.57 (1H, d, *J* 3.0), 6.79 (1H, d, *J* 9.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 55.6, 56.6, 101.7, 104.2, 111.5, 140.9, 146.4, 154.6.

Pyridin-3-ol (3i).[4f] Using general procedure A, silane **2i** (150 mg, 1.09 mmol) afforded 81 mg (78%); using general procedure B, silane **2i** (69 mg, 0.50 mmol) afforded 33 mg (71%). Purification by column chromatography ($CHCl_3$ → $CHCl_3$/MeOH (9:1)) produced a white solid; R_f 0.25 ($CHCl_3$/MeOH (9:1)); mp 123–125 °C (Lit. 127–129 °C); ^{1}H NMR (500 MHz, DMSO−d_6) 7.14–7.16 (1H, m), 7.20 (1H, dd, *J* 8.0, 4.5), 8.03 (1H, dd, *J* 4.5, 1.5), 8.13 (1H, d, *J* 2.5), 9.86 (1H, br s); ^{13}C NMR (125 MHz, DMSO−d_6)) δ_C 122.0, 124.1, 138.0, 140.2, 153.6.

4-(((tert-Butyldimethylsilyl)oxy)methyl)phenol (3j).[12a] Using general procedure C (although oxidation quenched with NH_4Cl (1 mL, sat., aq.) instead of 1N HCl), silane **2j** (140 mg, 0.50 mmol) afforded 88 mg (74%). Purification by column chromatography (petroleum ether +1% Et_3N → petroleum ether/Et_2O (1:1) + 1% Et_3N) produced a colorless oil; R_f 0.45 (petroleum ether/Et_2O (9:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.94 (6H, s), 0.94 (9H, s), 4.66 (2H, s), 5.26 (1H, br s), 6.81 (2H, d, *J* 7.5), 7.18 (2H, d, *J* 7.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −5.17, 18.44, 26.0, 64.8, 115.2, 127.8, 133.1, 155.1.

2,6-Dimethylphenol (3k).[4f] Using general procedure C, silane **2k** (82 mg, 0.50 mmol) afforded 54 mg (88%). Purification by column chromatography (petroleum ether → petroleum ether/Et_2O (95:5)) produced a waxy solid; R_f 0.21 (petroleum ether/Et_2O (9:1)); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 2.32 (6H, s), 4.67 (1H, br s), 6.83 (1H, t, *J* 7.5), 7.05 (2H, d, *J* 7.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 16.3, 120.7, 123.4, 129.0, 152.6.

1,2,4-Trimethoxy-5-(1-methoxyethyl)benzene (3l).[26] Using general procedure C (although oxidation quenched with $Na_2S_2O_3$ (1 mL, sat., aq.) instead of 1N HCl), silane **2l** (120 mg, 0.50 mmol) was converted to a crude phenolic product which was immediately dissolved in anhydrous THF (5 mL) and cooled to 0 °C. NaH (80 mg, 2.00 mmol, 4 equiv) was added and the reaction was stirred at 0 °C for 1 h before the addition of iodomethane (186 μL, 3.00 mmol, 6.0 equiv). After stirring overnight, the reaction was quenched with MeOH (1 mL) and concentrated *in vacuo*. The concentrate was dissolved in EtOAc (5 mL) and washed with water (3 × 5 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to afford a yellow oil which was purified by column chromatography (petroleum ether → petroleum ether/Et_2O (9:1)) to afford a colorless oil (45 mg, 40%); R_f 0.19 (petroleum ether/Et_2O (9:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.38 (3H, d, *J* 6.5), 3.25 (3H, s), 3.81 (3H, s), 3.86 (3H, s), 3.90 (3H, s), 4.72 (1H, q, *J* 6.5), 6.52 (1H, s), 6.93 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 22.7, 56.1, 56.4, 56.5, 56.5, 72.7, 97.5, 109.5, 123.3, 143.5, 148.4, 150.8.

(4-Methoxyphenyl)dimethylsilanol (4).[38] To a solution of silane **2g** (250 mg, 1.50 mmol, 1.0 equiv) and water (500 μL, 30 mmol, 20 equiv) in MeCN (5 mL), under air, was added $[RuCl_2(p\text{-cymene})]_2$ (18 mg, 0.03 mmol, 2 mol %). After 2/3 s of effervescence, the reaction was seen to be complete by TLC. The reaction was diluted with petrol (2 mL) and eluted through a silica plug (petroleum ether/Et_2O (9:1)) to afford the title compound as a colorless liquid (270 mg, 92%); R_f 0.21 (petroleum ether/Et_2O (85:15)); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.39 (6H, s), 2.10 (1H, s), 3.83 (3H, s), 6.94 (2H, m), 7.53 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 0.08, 55.1, 113.6, 130.2, 134.6, 160.8.

Synthesis of Methoxysilanes *via* Ruthenium catalysis, General Procedure E. $[RuCl_2(p\text{-cymene})]_2$ (0.5 mol %) was added to the hydrosilane in MeOH (5 M), under air. After 2/3 s of effervescence the reaction was seen to be complete by TLC. The reaction mixture was diluted in Et_2O and eluted through a silica plug (Et_2O) to afford methoxy silane.

4-(Methoxydimethylsilyl)benzonitrile (5a). Using general procedure E, silane **2a** (50 mg, 0.310 mmol) afforded a colorless oil (56 mg, 95%); R_f 0.34 (petroleum ether/Et_2O (9:1)); IR (thin film, ν_{max}/cm^{-1}) 2960w, 2229m, 1386w, 1255m, 1083s, 823s; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.40 (6H, s), 3.46 (3H, s), 7.66 (4H, d, *J* 1.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −2.43, 50.8, 113.2, 118.9, 131.2, 133.9, 144.2; HRMS (ES$^+$) calc. for $C_{10}H_{13}NNaOSi$ $[M + Na]^+$ 214.0659, found 214.0656.

1-(4-(Methoxydimethylsilyl)phenyl)ethanone (5b). Using general procedure E, silane **2b** (286 mg, 1.60 mmol) afforded a colorless oil (320 mg, 96%); R_f 0.49 (petroleum ether); IR (thin film, ν_{max}/cm^{-1}) 1684s, 1388 m, 1243s, 1081s, 820s, 785s; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.41 (6H, s), 2.62 (3H, s), 3.46 (3H, s), 7.68 (2H, d, *J* 8.0), 7.95 (2H, d, *J* 8.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −2.36, 26.7, 50.8, 127.4, 133.7, 137.8, 143.9, 198.5; HRMS (ES$^+$) calc. for $C_{11}H_{16}NaO_2Si$ $[M + Na]^+$ 231.0812, found 231.0812.

Methoxydimethyl(4-(trifluoromethyl)phenyl)silane (5c). Using general procedure E, silane **2c** (250 mg, 1.22 mmol) afforded a colorless oil (254 mg, 89%); R_f 0.51 (petroleum ether/Et_2O (9:1)); IR (thin film, ν_{max}/cm^{-1}) 1324s, 1256w, 1164m, 1124s, 1059s, 822s; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.46 (6H, s), 3.51 (3H, s), 7.69 (2H, d, *J* 8.0), 7.75 (2H, d, *J* 8.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −1.92, 51.2, 124.6 (q, *J* 272.5), 124.9 (q, *J* 3.5), 132.0 (q, *J* 32.0), 134.2, 142.8; HRMS (FI$^+$) calc. for $C_{10}H_{13}F_3OSi$ $[M]^+$ 234.0688, found 234.0687.

(4-Bromophenyl)(methoxy)dimethylsilane (5d). Using general procedure E, silane **2d** (160 mg, 0.653 mmol) afforded a colorless oil (155 mg, 85%); R_f 0.49 (petroleum ether); IR (thin film, ν_{max}/cm^{-1}) 2958w, 1575w, 1479w, 1376w, 1255m, 1066s, 1009m; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.42 (6H, s), 3.49 (3H, s), 7.49 (2H, t, *J* 8.0), 7.58 (2H, d, *J* 8.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −1.19, 51.1, 125.0, 131.5, 135.5, 136.7; HRMS (FI$^+$) calc. for $C_9H_{13}BrOSi$ $[M]^+$ 245.9899, found 245.9918.

(4-Fluorophenyl)(methoxy)dimethylsilane (5e).[31] Using general procedure E, silane **2e** (400 mg, 2.66 mmol) afforded a colorless oil (423 mg, 86%); R_f 0.56 (petroleum ether; IR (thin film, ν_{max}/cm^{-1}) 1589m, 1450w, 1252w, 1231w, 1082s; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.38 (6H, s), 3.44 (3H, s), 7.09 (2H, t, *J* 9.0), 7.56 (2H, dd, *J* 9.0, 6.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −2.27, 50.6, 115.0 (d, *J* 19.5), 133.0 (d, *J* 4.0), 135.5 (d, *J* 7.5), 164.0 (d, *J* 248.5); HRMS (FI$^+$) calc. for $C_9H_{13}FOSi$ $[M]^+$ 184.0720, found 184.0719.

Methoxydimethyl(p-tolyl)silane (5f).[39] Using general procedure E, silane **2f** (150 mg, 1.00 mmol) afforded a colorless oil (160 mg, 89%); R_f 0.53 (petroleum ether); IR (thin film, ν_{max}/cm^{-1}) 1604w, 1250m, 1083s, 828s, 777s; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.39 (6H, s), 2.39 (3H, s), 3.46 (3H, s), 7.24 (2H, d, *J* 7.5), 7.50 (2H, d, *J* 7.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −2.29, 21.5, 50.6, 128.7, 133.5, 133.8, 139.6; HRMS (FI$^+$) calc. for $C_{10}H_{16}OSi$ $[M]^+$ 180.0970, found 180.0969.

Methoxy(4-methoxyphenyl)dimethylsilane (5g).[40] Using general procedure E, silane **2g** (100 mg, 0.66 mmol) afforded a colorless oil (122 mg, 99%); R_f 0.33 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.38 (6H, s), 3.44 (3H, s), 3.84 (3H, s), 6.95 (2H, d, *J* 8.5), 7.53 (2H, d, *J* 8.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −1.84, 51.0, 55.5, 114, 128.8, 135, 161.3.

(2,5-Dimethoxyphenyl)(methoxy)dimethylsilane (5h). Using general procedure E, silane **2h** (209 mg, 1.06 mmol) afforded a colorless oil (214 mg, 89%); R_f 0.55 (petroleum ether/Et_2O (9:1)); IR (thin film, ν_{max}/cm^{-1}) 2955m, 2832m, 1158w, 1481s, 1272s, 1147m; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.38 (6H, s), 3.53 (3H, s), 3.78 (3H, s), 3.80 (3H, s), 6.80 (1H, d, *J* 9.0), 6.90 (1H, dd, *J* 9.0, 3.0), 7.05 (1H, d, *J* 3.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C −1.66, 50.9, 55.7, 55.8, 110.7, 115.7, 120.9, 126.8, 153.5, 158.3; HRMS (ES$^+$) calc. for $C_{11}H_{18}NaO_3Si$ $[M + Na]^+$ 249.0917, found 249.0920.

Preparation of Celite/Pd/C Column. A glass chromatography column (12.5 mm internal diameter) was packed with 1.5 g Celite (40 mm height). Pd/C (10 mg, 10 wt % loading, 0.010 mmol) was mixed with Celite (1.0 g), loaded onto the column above the Celite and packed down (25 mm height). The column was wetted with MeOH (5 mL) under a positive pressure of N_2.

Large Scale Preparation of 2,5-Dimethoxyphenol (3h). A solution of silane **2h** (1.96 g, 10.0 mmol, 1.0 equiv) in MeOH/THF (1:1, 20 mL) was loaded onto the Celite/Pd/C column. The solution was passed through the column at 5 mL/min using a positive pressure of N_2 and was collected into a round bottomed flask equipped with a stirrer bar. The column was rinsed with MeOH/THF (1:1, 10 mL) and to the combined filtrate was added $KHCO_3$ (500 mg, 5.00 mmol, 0.5 equiv), TBAF (1.0 mL of a 1 M solution in THF, 0.1 equiv) and H_2O_2 (6.80 mL of a 30% w/w solution, 60.0 mmol, 6.0 equiv) and the reaction mixture was stirred for 3 h. Upon completion, the reaction was quenched with HCl (10 mL, 1 N aqueous solution) and the monophasic mixture was stirred for a further 5 min. The reaction mixture was then extracted with EtOAc (3 × 10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo* to afford a crude phenolic product which was purified by column chromatography (petroleum ether → petroleum ether/Et_2O (4:1)) to afford 2,5-dimethoxyphenol as a very pale-yellow oil (1.26 g, 82%).

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra for silanes and phenols. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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