### Title

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# Metal-Free Synthesis of 1,3-Disiloxanediols and Aryl Siloxanols

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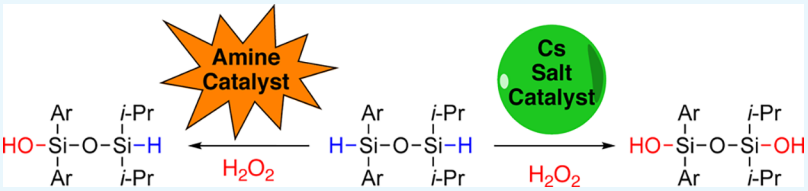
Supporting Information




**ABSTRACT:** The first example of metal-free oxidative hydrolysis of hydrido-siloxanes is reported. Both base-catalyzed and organocatalytic hydrolysis methods are demonstrated to transform 1,3-dihydrido-disiloxanes into 1,3-disiloxanediols. The first example of a chemoselective silane hydrolysis is demonstrated.

## INTRODUCTION

Siloxanes are an important class of compounds found in a vast number of products that enable our modern lifestyles.[1] Silanols and siloxanols have broad utility as reagents,[2,3] coupling partners,[4−6] ligands,[7−11] directing groups,[12] and hydrogen-bonding and anion-binding catalysts.[13−15] Various methods have been reported for the direct synthesis of silanols from hydrosilanes using a variety of transition-metal compounds including Ru, Ir, Cr, and Rh and various nanoparticles;[16−18] however, these metal reagents can be expensive and/or difficult to access. These methods represent the hydrolysis of the Si−H bond to a Si−O bond but are still often referred to as oxidation in analogy to organometallic chemistry and/or the oxidative reagents employed (Figure 1). Several methods for silane hydrolysis have also been reported using stoichiometric oxidants such as dioxiranes.[19] Recently, an organocatalytic hydrolysis of non-oxygenated silanes with 2,2,2-trifluoroacetophenone ($BzCF_3$) was reported by Kokotos and co-workers, which relies on the in situ formation of a highly active oxidizing species under basic and biphasic conditions.[17,20−22] Arzumanyan et al. has investigated the hydrolysis of primarily alkyl siloxanes; however, a larger investigation of aryl siloxanes has not been demonstrated.[17] Herein, we present the first examples of organocatalytic and base-catalyzed methods for conversion of hydrido-siloxanes to the corresponding 1,3-disiloxanediols.

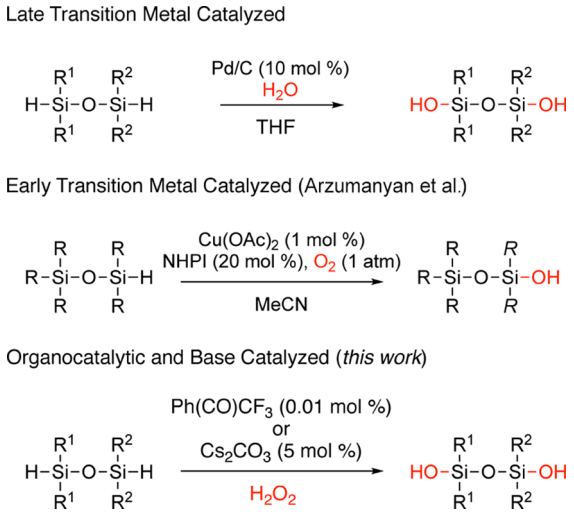



**Figure 1.** Hydrolysis methods converting hydrido-siloxanes to siloxanols.

The ability to produce silanols from hydrido-silanes under "metal-free" oxidative hydrolysis conditions is of particular interest because hydrosilanes are easy to handle and pose higher stability toward moisture compared to silyl chlorides; hydrosilanes produce hydrogen gas upon hydrolysis as opposed to chlorosilanes, which produce stoichiometric quantities of hydrochloric acid in their conversion to silanols. Notably, the production of hydrogen gas as a consequence of silane hydrolysis has been described to have application as a potential method of hydrogen storage.[23]

Our investigation of the hydrolysis of hydrido-siloxanes began with a screen of hydrolysis methods for 1,3-dihydrodisiloxanes (Table 1). 1,1-Diisopropyl-3,3-di(naphthalene-1-yl)disiloxane (**1a**) was selected as a model compound because **1a** contains both aryl and alkyl hydrido-silanes on the siloxane backbone. First, we evaluated the dichloro(*p*-cymene)-ruthenium(II) dimer and 1,5-cycloocatadiene-iridium(I) chloride dimer catalysts (in the presence of water) because they are both known to be highly active catalysts for the hydrolysis of non-oxygenated hydrosilanes.[24,25] Neither transition-metal complex afforded the desired disiloxanediol **2a** (Table 1, entries 1 and 2): the ruthenium catalyst resulted in a complex mixture, and the iridium catalyst resulted in the recovery of the

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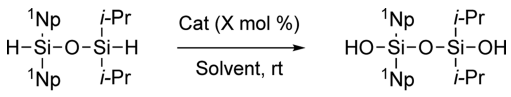
**Table 1. Screening of Metal Catalysts and Organocatalysts for Hydrolysis of 1,3-Dihydrido-disiloxane 1a**




**1a** **2a**

| entry | solvent | catalyst | mol (%) | time (h) | yield of **2a** (%)[a] |
|---|---|---|---|---|---|
| 1[b] | MeCN | $[Ru(Cymene)Cl_2]_2$ | 3 | 4 | <5 |
| 2[b] | MeCN | $[Ir(COD)Cl]_2$ | 3 | 4 | <5 |
| 3[b] | THF | Pd/C | 10 | 4 | 82 |
| 4[c] | THF | $BzCF_3$; pH 11.0 | 10 | 2 | quant. |
| 5[c] | THF | $BzCF_3$; pH 11.0 | 1 | 2 | quant. |
| 6[c] | THF | $BzCF_3$; pH 11.0 | 0.1 | 3 | quant. |
| 7[c] | THF | $BzCF_3$; pH 11.0 | 0.01 | 4 | quant. |
| 8[c] | THF | none; pH 11.0 | 0 | 4 | <5[d] |

[a]Isolated yield. [b]Reaction conditions include 5 equiv of $H_2O$. [c]Reaction conditions include 4 equiv of $H_2O_2$ and MeCN. [d]Chemoselective hydrolysis of the $Np_2SiH$ side occurs; partially hydrolyzed siloxanol **3a** was observed as the major product.

starting material. In comparison, Pd/C is effective as a catalyst for the hydrolysis of 1,3-dihydro-disiloxane **1a**, affording disiloxanediol **2a** in 82% (Table 1, entry 3).[13]

We then evaluated $BzCF_3$ as an organocatalyst for the oxidative hydrolysis of disiloxane **1a**.[20] Using $BzCF_3$ under basic conditions (pH 11.0) in the presence of hydrogen peroxide afforded a quantitative yield of **2a** with 10 mol % catalyst loading in 2 h (Table 1, entry 4). With these results, we lowered the catalyst loadings resulting in a final catalyst loading of 0.01 mol %, with a reaction time of 4 h (Table 1, entries 5–7). The $BzCF_3$ conditions yielded disiloxanediol **2a** as a pure product that did not require any further purification after workup. When $BzCF_3$ was omitted from the reaction (Table 1, entry 8), disiloxanediol **2a** was not observed. Using basic conditions with peroxide afforded only the selective hydrolysis of the naphthyl-bearing hydrido-silane with limited conversion of the alkyl hydrido-silane bond (i.e., affording siloxanol **3a** as the major product).

With an optimized organocatalytic hydrolysis method, we then explored the substrate scope using a series of dihydrosiloxanes (Figure 2). Disiloxanediols **2a–2e** are

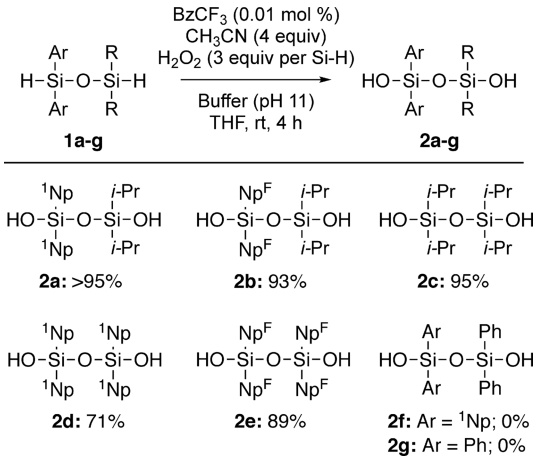
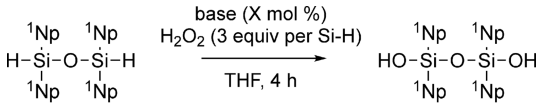



**Figure 2.** Scope of an organocatalytic method for the synthesis of 1,3-disiloxanediols.

obtained in high yield, typically without further purification required. Notably, **2e** was produced in high yield using the organocatalytic hydrolysis but was not produced using the other hydrolysis methods in Table 1. For some substrates (e.g., **1d** and **1e**), formation of ~5% silanediol is also observed, corresponding to the cleavage of the disiloxane bond during activation of the silane. As a control experiment, resubjecting isolated disiloxanediol **2d** to reaction conditions did not yield any silanediol, suggesting that the formation of the silanediol does not occur as a result of the hydrolysis of the siloxane bond under basic conditions. Exposure of phenyl-containing **1f** and **1g** did not afford any desired disiloxanediol, and a complex mixture was observed using $^1H$ NMR analysis of the crude reaction mixture. These data highlight a striking difference in the ability to access siloxanols bearing phenyl rings versus naphthyl rings using this organocatalytic method. While it is unsurprising that the silane bearing the phenyl ring is highly susceptible to Tamao–Fleming oxidation, the difference in reactivity between phenyl and naphthyl was more than anticipated. Being able to tame this "overoxidation" would allow us to access a larger variety of disiloxanediols using greener methods.

Because a control experiment had indicated that basic conditions excluding the $BzCF_3$ catalyst still afforded the selective hydrolysis of the naphthyl hydrido-silane portion of **1a** (Table1, entry 8), we evaluated a base-catalyzed hydrolysis for the conversion of tetra-aryl 1,3-dihydrido-disiloxanes such as **1d** to 1,3-disiloxanediol **2d** (Table 2).[26] We hypothesized that the optimal selection of base could impart control and limit the Tamao–Fleming oxidation of C–Si bonds in 1,3-dihydrido-disiloxanes tetra-aryl disiloxanes.

**Table 2. Screening of Hydrolysis Conditions for Disiloxane 1d**




**1d** **2d**

| entry | base | mol (%) | yield of **2d** (%)[a] |
|---|---|---|---|
| 1 | none | 0 | recovered SM |
| 2 | KOH | 100 | complex mixture |
| 3 | NaOH | 100 | complex mixture |
| 4 | $Et_3N$ | 100 | 75 (+ 25% silanediol) |
| 5 | $Na_2CO_3$ | 100 | 0[b] |
| 6 | $K_2CO_3$ | 100 | 70 (+ 30% silanediol) |
| 7 | $Cs_2CO_3$ | 100 | 87 |
| 8 | $Cs_2CO_3$ | 50 | 95 |
| 9 | $Cs_2CO_3$ | 10 | 95 |
| 10 | $Cs_2CO_3$ | 5 | >95 |

[a]All yields determined using $^1H$ NMR spectroscopy with PhTMS as an internal standard. [b]1,1,3,3-tetra(naphthalene-1-yl)disiloxane-1-ol) is the major product; di(naphthalene-1-yl)silanediol was also observed.

First, the necessity of base was confirmed. When **1d** was subjected to three equivalents of hydrogen peroxide in the absence of base, only the starting material was recovered (Table 2, entry 1). Metal hydroxides generated a complex mixture based on $^1H$ NMR analysis (Table 2, entries 2 and 3), which is surprising, considering that the ability of these metal hydroxides to produce silyl ethers and silyl alkynes has been



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ACS Omega 2019, 4, 6295–6300

recently reported.[27,28] Using an organic base such as triethylamine (TEA) not only afforded promising results but also afforded silanediol resulting in a lower yield of **2d** (Table 2, entry 4). When sodium carbonate was employed, the product **2d** was not observed. Potassium carbonate generated the desired 1,3-disiloxanediol **2d**, but the corresponding silanediol was also observed (Table 2, entry 6). Finally, cesium carbonate was investigated, which afforded the highest selectivity for the synthesis of 1,3-disiloxanediol **2d**, with 5 mol % affording the highest yield and cleanest reaction (Table 2, entries 7−10).[29]

Cesium carbonate was compared as a catalyst for the hydrolysis of three tetra-aryl 1,3-dihydro-disiloxanes (Figure 3). Catalytic cesium carbonate conditions generate disiloxanediols **2d** and **2e** with high efficiency. The cesium conditions were still not viable for phenyl-containing substrates; the reaction of **1f** in these conditions led to the traditional Tamao−Fleming oxidation products (i.e., phenol).[30]

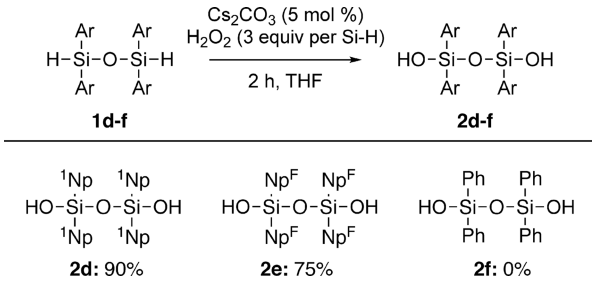


**Figure 3.** Base-mediated hydrolysis of tetra-aryl 1,3-dihydrido-disiloxanes.

These results led us to posit that a chemoselective hydrolysis of aryl silanes could be performed in the presence of alkyl silanes (Figure 4). The cesium-catalyzed hydrolysis of **1a** and **1b** afforded a mixture of products with low selectivity; however, using one equivalent of triethylamine promoted a chemoselective hydrolysis for the hydrosilane bearing the naphthyl rings to afford siloxanol **3a** and **3b**. This represents the first report of a chemoselective silane hydrolysis.

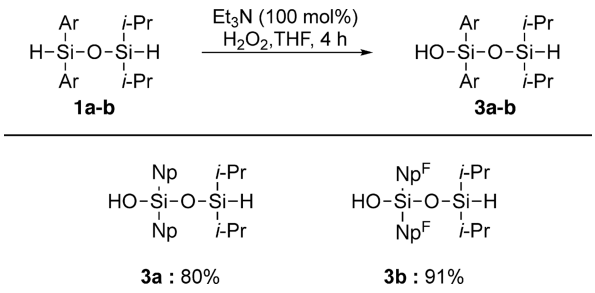


**Figure 4.** Chemoselective hydrolysis of 1,3-dihydrido-disiloxanes.

Because the Tamao−Fleming oxidation was observed as a persistent issue in the synthesis of phenyl-containing siloxanols, we also synthesized a series of tertiary and secondary silanes to determine what electronic and steric differences between the phenyl and naphthyl rings would suppress this oxidation event (see Supporting Information, Figure S1). We determined that the presence of ortho substitution on at least one aryl ring can suppress the Tamao−Fleming oxidation pathway; however, this suppressive effect can be diminished by the presence of electron-withdrawing groups. These data provide additional mechanistic insight into the "fluoride-free" Tamao−Fleming oxidation (see the Supporting Information).

## CONCLUSIONS

In conclusion, we have demonstrated the first organocatalytic hydrolysis of 1,3-dihydrido-disiloxanes to 1,3-disiloxanediols utilizing low catalyst loadings (0.01 mol %). We also optimized a base-catalyzed method for the hydrolysis of tetra-aryl disiloxanes using cesium carbonate. Observations and mechanistic insight into the competing oxidation and hydrolysis pathways led to the development of the first chemoselective hydrolysis of unsymmetrical disiloxanes. These results show that the differential reactivity of aryl and alkyl silanes within 1,3-dihydro-disiloxanes can be utilized for selective synthesis.

## EXPERIMENTAL SECTION

**General Information.** All nuclear magnetic resonance (NMR) spectra were obtained on Varian Inova 400 (400 MHz for $^{1}$H; 100 MHz for $^{13}$C) and/or Varian VNMRS 600 (600 MHz for $^{1}$H; 150 MHz for $^{13}$C; 119 MHz for $^{29}$Si) at room temperature unless noted otherwise. Chemical shifts were reported in parts per million ($\delta$ scale) and referenced according to the following standards: tetramethylsilane internal standard for $^{1}$H signals in chloroform, chloroform residual solvent ($\delta$ 7.26) for $^{1}$H signals in deuterated chloroform, chloroform (middle peak is $\delta$ 77.1) for $^{13}$C signals, and tetramethylsilane external standard in $CDCl_3$ for $^{29}$Si signals. Coupling constants were reported in hertz (Hz), and multiplicities were reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broadened (b). Compounds were analyzed by HRMS using electrospray in the negative ion mode at >60,000 resolution and using a 5 kV spray voltage, with a curtain plate temperature of 275 °C and a sheath gas setting of 15. These settings result in mass accuracies of <5 ppm. HRMS samples were analyzed via flow injection analysis by injecting 5 $\mu$L of samples into a stream of 50% acetonitrile and 50% aqueous solution of 0.1% formic acid, flowing at 200 $\mu$L/min.

Commercially available reagents were purchased and used without further purification unless otherwise indicated. Dichloromethane (DCM), hexane, ethyl acetate (EtOAc), and diethyl ether ($Et_2O$) were obtained from EMD Chemicals. Anhydrous magnesium sulfate and Pd/C (10 wt %) were obtained from Sigma-Aldrich. 1-Bromo-4-fluoronaphthalene and 2-bromotoluene were purchased from Oakwood Chemical. Phenyldichlorosilane, diphenylsilane, triphenylsilane, and triisopropylsilane were obtained from Gelest. [Ru(*p*-Cymene)$Cl_2$]$_2$ and [Ir(COD)Cl]$_2$ were purchased from Strem. Dimethylchlorosilane, magnesium turnings, 1-bromonaphthalene, trichloroisocyanuric acid (TCCA), and lithium aluminum hydride (4.0 M in $Et_2O$) were purchased from Acros. Diphenylmethylsilane was purchased from Alfa Aesar. 1,3-Dihydrodisiloxanes (**1a**−**1f**) were synthesized according to literature procedures starting from the addition of the corresponding aryl Grignard reagent to trichlorosilane.[13]

Reactions were analyzed by thin-layer chromatography (TLC) on EMD glass plates that were precoated with silica gel 60 F254, and the reactions were purified by column chromatography using Acros silica gel 60 Å (0.035−0.070 mm). The following abbreviations are used throughout: lithium aluminum hydride (LAH), ethyl acetate (EtOAc),



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ACS Omega 2019, 4, 6295−6300

dichloromethane (DCM), acetonitrile (MeCN), and 2,2,2-trifluoroacetophenone ($BzCF_3$).

**Synthesis of 1,1,3,3-Tetrakis(4-fluoronaphthalen-1-yl)disiloxane (1e).** Bis(4-fluoronaphthalen-1-yl)silanol and chlorobis(4-fluoronaphthalen-1-yl)silane were synthesized according to the literature.[13] Bis(4-fluoronaphthalen-1-yl)silanol (0.367 g, 1.09 mmol, 1.0 equiv) was dissolved in DCM (10 mL) in a 100 mL flask and purged with reaction. TEA (0.23 mL, 1.65 mmol, 1.5 equiv) was then added, followed by a solution of chlorobis(4-fluoronaphthalen-1-yl)silane (0.387 g, 1.09 mmol, 1.0 equiv) in DCM (10 mL). The reaction was allowed to stir for 1 h and was then quenched with saturated aqueous $NaHCO_3$ (5 mL). The organic layer was separated, the aqueous layer was washed with DCM (3 × 5 mL), and the organic layers were combined and washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and then concentrated in vacuo. The crude product was purified via column chromatography (10:1 hexanes/EtOAc) to yield **1e** as a white solid. Yield: 0.39 g (54%); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 8.08 (d, $J$ = 8.4 Hz, 2H), 7.93 (d, $J$ = 8.5 Hz, 2H), 7.64 (dd, $J$ = 7.6, 6.0 Hz, 2H), 7.44 (t, $J$ = 7.6 Hz, 2H), 7.18 (t, $J$ = 7.6 Hz, 2H), 6.98 (dd, $J$ = 10.5, 7.6 Hz, 2H), 6.25 (s, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz, $\delta$): 160.9 (d, $J^1_{CF}$ = 256.6 Hz), 138.2 (d, $J^4_{CF}$ = 4.6 Hz), 135.6 (d, $J^3_{CF}$ = 8.7 Hz), 128.1 (d, $J^3_{CF}$ = 4.7 Hz), 127.2 (d, $J^4_{CF}$ = 2.9 Hz), 127.1, 126.0 (d, $J^4_{CF}$ = 1.4 Hz), 123.6 (d, $J^2_{CF}$ = 15.2 Hz), 121.1 (d, $J^3_{CF}$ = 6.1 Hz), 108.9 (d, $J^2_{CF}$ = 18.8 Hz); $^{19}$F NMR ($CDCl_3$, 282 MHz, $\delta$): −119.5 (m); $^{29}$Si NMR ($CDCl_3$, 119 MHz, $\delta$): −19.8.

**Synthesis of 1,1,3,3-Tetraphenyldisiloxane (1f).** An oven-dried 50 mL flask was charged with TCCA (210 mg, 0.90 mmol, 0.33 equiv) and placed under Ar. A solution of diphenylsilane (0.5 mL, 2.7 mmol, 1.0 equiv) in THF (10 mL) was added in one portion, and the reaction was stirred for 1 h. A solution of THF (1 mL), TEA (0.19 mL, 1.35 mmol, 0.5 equiv), and $H_2O$ (25 $\mu$L, 1.35 mmol, 0.5 equiv) was added dropwise. The solution was stirred for 1 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ (5 mL). The organic layer was separated, the aqueous layer was washed with THF (3 × 5 mL), and the organic layers were combined and washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and then concentrated in vacuo. The crude product was then dissolved in hexanes and passed through a silica plug to yield **1f** as a clear oil. Yield: 0.32 g (62%); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 7.60−7.54 (m, 8H), 7.45−7.39 (m, 4H), 7.35 (t, $J$ = 7.3 Hz, 8H), 5.61 (s, 2H). Matched literature spectra.[31]

**General Procedure for the Hydrolysis of 1,3-Dihydrido-disiloxanes (Method A).** 1,3-Dihydrido-disiloxane (0.25 mmol) was dissolved in THF (0.25 mL) in a 4 mL vial and stirred at room temperature for 5 min. $BzCF_3$ (3.5 $\mu$L), buffer (0.25 mL, 0.6 M $K_2CO_3$, 4 × $10^{-5}$ M EDTA tetrasodium salt), MeCN (0.11 mL), and 30% aqueous $H_2O_2$ (0.2 mL) were added consecutively. The reaction was allowed to stir for 4 h. The reaction was then poured into a 30 mL separatory funnel and diluted with DCM (5 mL). The layers were separated, and the organic layer was dried over anhydrous $Na_2SO_4$, filtered, and then concentrated in vacuo. The product was then purified using flash column chromatography (15% EtOAc in hexanes) to afford the desired product.

**General Procedure for the Hydrolysis of 1,3-Dihydrido-disiloxanes (Method B).** 1,3-Dihydrido-disiloxane (0.25 mmol) was dissolved in THF (1 mL) in a 4 mL vial and stirred at room temperature for 5 min. $CsCO_3$ and 30% aqueous $H_2O_2$ (0.15 mL) were added consecutively. The reaction was allowed to stir for 2 h. The reaction was then poured into a 30 mL separatory funnel and diluted with DCM (5 mL) and $H_2O$ (5 mL). The layers were separated, and the organic layer was dried over anhydrous $Na_2SO_4$, filtered, and then concentrated in vacuo. The product was then purified using flash column chromatography (15% EtOAc in hexanes) to afford the desired product.

*1,1-Diisopropyl-3,3-di(naphthalen-1-yl)disiloxane-1,3-diol (**2a**).* Synthesized using Method A. Yield: 0.11 g (quant.); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 8.29 (d, $J$ = 8.4 Hz, 2H), 8.04 (dd, $J$ = 6.8, 1.2 Hz, 2H), 7.91 (d, $J$ = 8.2 Hz, 2H), 7.82 (d, $J$ = 8.0 Hz, 2H), 7.46 (dd, $J$ = 8.2, 6.9 Hz, 2H), 7.43−7.39 (m, 3H), 7.35 (ddd, $J$ = 8.3, 6.9, 1.3 Hz, 3H), 3.58 (s, 1H), 2.46 (s, 1H), 0.90 (s, 14H). Matched literature spectra.[14]

*1,1-Bis(4-fluoronaphthalen-1-yl)-3,3-diisopropyldisiloxane-1,3-diol (**2b**).* Synthesized using Method A. Yield: 0.112 g (93%); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 8.26 (d, $J$ = 8.5 Hz, 2H), 8.12 (d, $J$ = 8.0 Hz, 2H), 7.96 (dd, $J$ = 7.6, 6.2 Hz, 2H), 7.47 (ddd, $J$ = 8.2, 6.9, 1.0 Hz, 2H), 7.40 (ddd, $J$ = 8.3, 6.9, 1.3 Hz, 2H), 7.13 (dd, $J$ = 10.5, 7.7 Hz, 2H), 3.76 (s, 1H), 2.52 (s, 1H), 0.89 (s, 14H). Matched literature spectra.[13]

*1,1,3,3-Tetraisopropyldisiloxane-1,3-diol (**2c**).* Synthesized using Method A. Yield: 0.066 g (95%); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 2.78 (s, 2H), 1.03 (d, $J$ = 7.2 Hz, 24H), 0.94 (dq, $J$ = 14.9, 7.5, 7.1 Hz, 4H). Matched literature spectra.[32]

*1,1,3,3-Tetra(naphthalen-1-yl)disiloxane-1,3-diol (**2d**).* Synthesized using Method A. Yield: 0.15 g (71%); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 8.19 (d, $J$ = 8.4 Hz, 4H), 7.91 (dd, $J$ = 6.8, 1.2 Hz, 4H), 7.86 (d, $J$ = 8.2 Hz, 4H), 7.79 (d, $J$ = 8.1 Hz, 4H), 7.35 (ddd, $J$ = 8.0, 6.9, 1.0 Hz, 4H), 7.32 (dd, $J$ = 8.2, 6.9 Hz, 4H), 7.11 (ddd, $J$ = 8.2, 6.9, 1.2 Hz, 4H), 3.16 (s, 2H). Matched literature spectra.[13]

*1,1,3,3-Tetra(4-fluoronaphthalen-1-yl)disiloxane-1,3-diol (**2e**).* Synthesized using Method A. Yield: 0.15 g (89%); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 8.08 (d, $J$ = 8.5 Hz, 4H), 8.05 (d, $J$ = 8.3 Hz, 4H), 7.79 (dd, $J$ = 7.6, 6.1 Hz, 4H), 7.40 (dd, $J$ = 7.6 Hz, 4H), 7.14 (ddd, $J$ = 8.3, 6.9, 1.2 Hz, 4H), 6.95 (dd, $J$ = 10.5, 7.7 Hz, 4H), 3.20 (s, 2H); $^{13}$C NMR ($CDCl_3$, 150 MHz, $\delta$): 161.1 (d, $J^1_{CF}$ = 256.6 Hz), 138.3 (d, $J^3_{CF}$ = 4.5 Hz), 135.9 (d, $J^3_{CF}$ = 8.7 Hz), 128.5 (d, $J^3_{CF}$ = 4.7 Hz), 128.1 (d, $J^4_{CF}$ = 2.8 Hz), 127.2, 126.1 (d, $J^4_{CF}$ = 1.6 Hz), 123.8 (d, $J^2_{CF}$ = 15.2 Hz), 121.2 (d, $J^4_{CF}$ = 6.3 Hz), 108.91 (d, $J^2_{CF}$ = 18.8 Hz); HRMS-ESI ($m/z$): $[M - H]^-$ calcd for $C_{40}H_{25}Si2O_3F_4$, 685.1284; found, 685.1284.

**General Procedure for Chemoselective Hydrolysis of Unsymmetrical 1,3-Dihydrido-disiloxanes (Method C).** 1,3-Dihydrido-disiloxane (0.25 mmol) was added to a 4 mL vial and dissolved in THF (1 mL). Triethylamine (35 $\mu$L) was then added to the vial followed by $H_2O_2$ (38 $\mu$L). The vial was vented to the atmosphere with a needle as a large amount of gas is quickly generated. The reaction is then allowed to stir at room temperature for 30 min. The contents of the vial are then diluted with DCM (3 mL) and poured over $Na_2SO_4$. The product is then isolated using flash column chromatography (19:1 hexanes/EtOAc) over silica gel.

*3,3-Diisopropyl-1,1-di(naphthalen-1-yl)disiloxane-1-ol (**3a**).* Prepared from **1a** using Method C. Yield: 0.09 g (89%); $^1$H NMR (toluene-$d_8$, 600 MHz, $\delta$): 8.26 (d, $J$ = 8.5 Hz, 2H), 8.14 (d, $J$ = 8.3 Hz, 2H), 7.96−7.90 (m, 2H), 7.50 (t, $J$ = 7.5 Hz, 2H), 7.47−7.41 (m, 2H), 7.15 (dd, $J$ = 10.5, 7.7 Hz, 2H), 4.36 (s, 1H), 3.01 (s, 1H), 0.92 (s, 14H); $^{13}$C NMR (toluene-$d_8$, 150 MHz, $\delta$): 138.4, 138.4, 136.5, 135.5, 134.9, 132.2,



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ACS Omega 2019, 4, 6295−6300

130.3, 130.0, 127.2, 126.7, 18.3 (d, $J$ = 5.3 Hz), 14.4; HRMS-ESI ($m/z$): $[M - H]^-$ calcd for $C_{26}H_{30}Si_2O_2$, 429.1712; found, 429.1706.

*1,1-Bis(4-fluoronaphthalen-1-yl)-3,3-diisopropyldisiloxan-1-ol (**3b**).* Prepared from **1a** using Method C. Yield: 0.11 g (91%); $^1$H NMR ($CDCl_3$, 600 MHz, $\delta$): 8.26 (d, $J$ = 8.5 Hz, 2H), 8.14 (d, $J$ = 8.3 Hz, 2H), 7.96−7.90 (m, 2H), 7.50 (t, $J$ = 7.5 Hz, 2H), 7.47−7.41 (m, 2H), 7.15 (dd, $J$ = 10.5, 7.7 Hz, 2H), 4.36 (s, 1H), 3.01 (s, 1H), 0.92 (s, 14H); $^{13}$C NMR ($CDCl_3$, 150 MHz, $\delta$): 160.9 (d, $J^1_{CF}$ = 256.0 Hz), 138.4 (d, $J^4_{CF}$ = 4.4 Hz), 135.5 (d, $J^3_{CF}$ = 8.5 Hz), 129.3 (d, $J^3_{CF}$ = 4.8 Hz), 128.3 (d, $J^4_{CF}$ = 3.0 Hz), 127.1, 126.0 (d, $J^4_{CF}$ = 1.9 Hz), 123.8 (d, $J^2_{CF}$ = 15.0 Hz), 121.1 (d, $J^3_{CF}$ = 6.3 Hz), 108.9 (d, $J^2_{CF}$ = 18.6 Hz), 17.0 (d, $J$ = 4.3 Hz), 13.0; HRMS-ESI ($m/z$): $[M - H]^-$ calcd for $C_{26}H_{28}Si_2O_2F_2$, 465.1523; found, 465.1525.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00121.

Synthesis of silanes for mechanistic investigation, structural investigation of silane hydrolysis mechanism, proposed mechanism for base-catalyzed silane hydrolysis, and NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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