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Neighboring Acetal-Assisted Brønsted-Acid-Catalyzed Si–H Bond Activation: Divergent Synthesis of Functional Siloxanes through Silylation and Hydrolytic Oxidation of Organosilanes

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A novel metal-free intramolecular Brønsted-acid-catalyzed domino deprotection–hydrosilylation with hydrosilanes has been developed, and the unexpected Brønsted-acid-catalyzed intermolecular hydrolytic oxidation to functional siloxanes was described for the divergent and facile synthesis of functionalized siloxanes containing aldehyde motifs. We propose that these reactions proceed via neighboring acetal-assisted Si–H bond activation. In addition, a related reaction is expected to open up further opportunities for the development and application of functional organosilicon compounds by organocatalysis.

Introduction

Organosilicon compounds are widely used in inorganic, organic, organometallic, and polymeric chemistry, and the field of research covered by organosilicon chemistry is very broad.[1] In the past decades, the preparation and reactions of novel types of organosilicon species are the most important and fundamental topic for organosilicon chemistry, and have been studied intensively.[2] Among them, silanes and siloxanes are important as versatile building blocks that have been prominently utilized in industry for the production of silicon-based polymeric materials.[2b–2f] They are also important in organic synthesis[3] as reducing reagents, valuable protecting groups, privileged monomers, and reagents, as well as intermediates and catalysts in a broad variety of organic transformations[4] including oxidation,[4f–4i] cross-coupling,[4j–4o] and cycloadditions.[4p–4r] The preparation and use of functional siloxane compounds allows organosilanes to be installed onto a fragment at almost any stage in an organic synthesis.

The activation of C–H bonds is important to synthetic and catalytic processes involving the functionalization of hydrocarbons.[5] Likewise, activation of Si–H bonds by different catalysts is important to industrial and academic research in reactions such as hydrosilylation.[1,2,6] Since the first application of Wilkinson's catalyst in catalytic hydrosilylations three decades ago,[7] efficient catalysts, including metal salts (mainly transition metal complexes but also main group metal complexes[8]) and metalloid Lewis acids[9] and Lewis bases[10] have been described. Besides metal-catalyzed hydrosilylation, two popular routes to siloxanes are the silylation of alcohols from chlorosilane and the dehydrogenative coupling of hydrosilanes.[11] However, in most cases of the silylation of alcohols, a long reaction time, harsh reaction conditions, toxic catalysts or reagents, or tedious workup is needed. In dehydrogenative coupling reactions of hydrosilanes, most metal-based catalytic processes suffer from one or more disadvantages, including poor functional group tolerance, slow rates with bulky silanes, and strict reaction conditions.

We became interested in the acetal functional group for its potential application as an "aldehyde store" within metal-free, catalyst-initiated Si–H activation and transformation. Although various metal-based catalysts have been investigated for the hydrosilylation of carbonyl compounds, most synthetic methods only focus on the preparation of alcohols but not siloxanes. In fact, the synthesis of siloxanes or silyl ethers directly from hydrosilanes is not a trivial task. Therefore, the development of highly efficient and environmentally benign processes to synthesize functionalized siloxanes is of considerable interest. In relation to this, we set out to explore Brønsted-acid-catalyzed Si–H bond activation and related syntheses of aldehyde-functionalized siloxanes. In this paper, we present a novel and simple method to prepare functional siloxanes containing aldehyde moieties through facile, one-pot, metal-free Brønsted-acid-catalyzed domino deprotection–hydrosilylation. In addition, we report an unexpected and novel organocatalyzed hydrolytic oxidation process for the synthesis of functional

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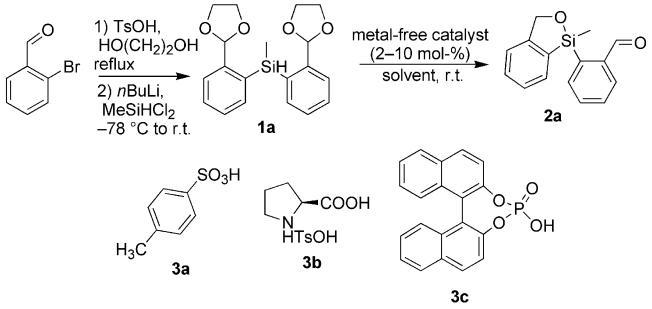
siloxanes containing aldehydes. To the best of our knowledge, there are no reports on the divergent synthesis aldehyde-functionalized siloxanes through Brønsted-acid-catalyzed hydrolytic oxidation.

Results and Discussion

Our initial evaluation of the proposed domino deprotection–intramolecular hydrosilylation began with the reaction of dioxolane-protected aldehyde/acetal-based silane **1a** (Scheme 1). The bis[2-(1,3-dioxolan-2-yl)phenyl](methyl)-silane (**1a**) was prepared via a simple two-step approach:[12,13] first, 2-(2-bromophenyl)-1,3-dioxolane was obtained by TsOH-catalyzed protection of the aldehyde group with 2-bromobenzaldehyde and ethane-1,2-diol; then lithiation of 2-(2-bromophenyl)-1,3-dioxolane, followed by reaction with methyldichlorosilane ($MeSiHCl_2$), afforded bis[2-(1,3-dioxolan-2-yl)phenyl](methyl)silane (**1a**) in good yield (80%).



Scheme 1.

Fortunately, employing TsOH (**3a**) as catalyst in acetone gave the desired aldehyde-functionalized siloxane **2a** in 70% isolated yield (Table 1, entry 1). Solvent screening revealed that acetone is a crucial solvent in this reaction because the first step is deprotection of the dioxolane moiety (Entry 2). It is interesting that the functional siloxane **2a** contains an achiral silicon center, which inspired us to explore a method for the construction of silicon-stereogenic functional siloxanes. Thus we screened a number of chiral catalysts, including L-proline (**3b**), under different conditions. Use of chiral amino acids and BINOL-derived phosphoric acids did not lead to the occurrence of the domino reaction, and no product was formed from the reaction.

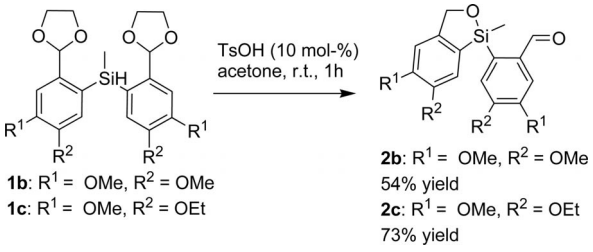
Scheme 2 presents a simple scope of the Brønsted-acid-catalyzed deprotection–hydrosilylation of acetal-based silanes. As shown in Scheme 2, the substituted group in aromatic rings also gave good results. With these optimal reaction conditions in hand, that is, TsOH as catalyst and acetone as solvent, we next explored the pyran-based acetals containing a hydrosilane moiety in this domino deprotection–hydrosilylation reaction. However, the reaction of acetal deprotection is sluggish and many byproducts were detected.

On the basis of the aforementioned experimental results, we assumed that the mechanism of the domino deprotection–hydrosilylation reaction involved the Brønsted-acid-catalyzed deprotection of the acetal[14] and then the addition across the double bond of the aldehyde (Scheme 3). The mechanism of this transformation is believed to involve the hypervalent intermediate **i-2**, in which intramolecular oxygen coordination between silicon and aldehyde proved to be an effective factor in assisting the intramolecular hydrosilylation. When bis[2-(1,3-dioxolan-2-yl)-4-ethoxy-5-methoxyphenyl](methyl)silane (**1c**) was used as the substrate in the presence of TsOH, a hypervalent silicon-based intermediate was isolated. X-ray structural studies showed that this compound is a somewhat unusual hexacoordinate silicon complex[15] (see Supporting Information, Figure S1). The isolation of this hypervalent complex from the reaction mixture provides further evidence that the neighboring Si–H bond activated the aldehyde via a hexacoordinate intermediate (or transition state), which resulted in intramolecular hydrogen shifting to form the aldehyde-functionalized siloxanes.

Table 1. Brønsted-acid-catalyzed domino deprotection–hydrosilylation.[a]

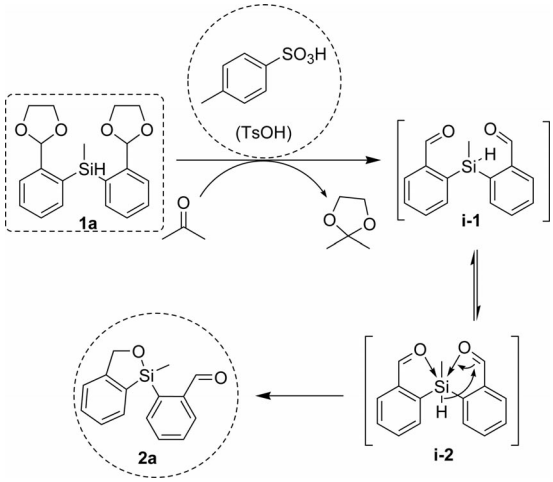
Entry	Cat. (mol-%)	Solvent	Time [h]	Additive	Yield [%][b]
1	**3a** (1.5)	acetone	0.5	–	70
2	**3a** (1.5)	THF	20	–	< 10
3	**3b** (10)	acetone	24	–	0 [c]
4	**3b** (10)	THF	24	–	0
5	**3b** (10)	DCM/H_2O	24	–	0
6	**3b** (10)	CH_3NO_2	24	–	0
7	**3c** (10)	acetone	24	–	< 10
8	**3c** (10)	DCM	24	–	0
9	**3c** (10)	THF	48	–	0
10	**3c** (10)	EtOAc	48	–	0
11	**3c** (10)	toluene	48	–	0
12	**3c** (10)	DCM	24	PhCHO[d]	70

[a] Compound **1a** (1.0 equiv., 0.2 M), catalyst **3** (1.5–10 mol-%), at room temperature. [b] Isolated yields. [c] No reaction. [d] Addition of 3.0 equiv. of benzaldehyde.



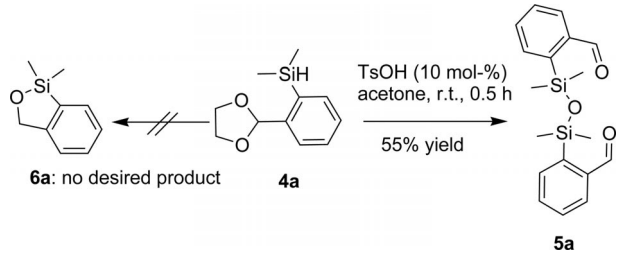
Scheme 2.

With these promising results (i.e., the novel reaction and synthetic method for the preparation of functional siloxanes), we attempted to expand the range of substrates. Interestingly, when the Brønsted-acid-catalyzed deprotection–hydrosilylation of mono acetal-based hydrosilane **4a** was examined under the optimized conditions (Scheme 4), no desired product **6a** was obtained. Surprisingly, another more relevant peculiarity we noticed in this series was that an unexpected product, symmetrical disiloxane **5a** was detected and isolated in good yield. It should be noted that the reaction is very fast – only 15 min could lead to the



Scheme 3. Proposed mechanism of deprotection–hydrosilylation.

completion of the reaction – and practical gram-scale synthesis of functional symmetrical disiloxane-containing aldehydes was carried out easily.

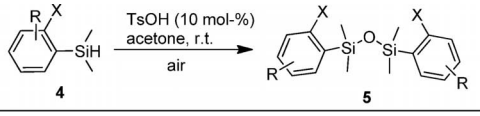


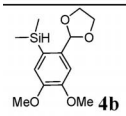
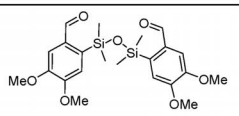
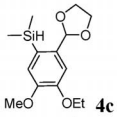
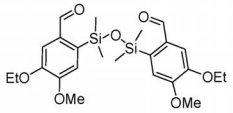
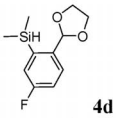
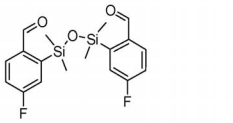
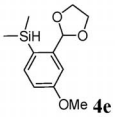
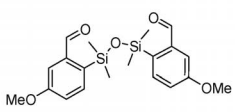
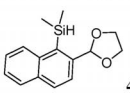
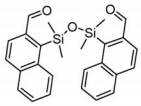
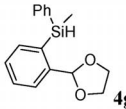
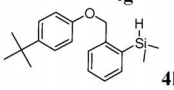
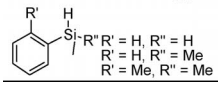
Scheme 4.

An evaluation of the unexpected oxidation–coupling reaction revealed that most acetal-containing hydrosilanes with electron-neutral or electron-rich substituents proceeded equally well (Table 2, **4b**–**e**). The structures of **5a**–**e** were assigned on the basis of ^{1}H NMR, ^{13}C NMR and X-ray crystallographic analysis (Figure 1). Naphthyl and *p*-trifluoromethyl substrates resulted in trace products (**4f**). Interestingly, compound **4g**, with its two phenyl groups, only resulted in the deprotected product (**5g**, 76% yield). Next, our attention was focused on the hydrolytic oxidation of nonactivated hydrosilanes without any functional group by using the same conditions. However, no reactions occurred with simple hydrosilanes such as diphenylsilane and phenylmethylsilane. This observation, taken together with the inactivity of **4h** in this reaction, suggest that the acetal group may engage in facilitating the interaction between the catalyst and the silicon in the hydrolytic oxidation.

In the unexpected hydrolytic oxidation of organosilanes, according to previous studies on metal complex- or Lewis acid catalyzed hydrolytic oxidation of organosilanes,[16] we postulated that the deprotection of the aldehyde occurred quickly, and then the Brønsted-acid-catalyzed oxidation of the hydrosilane happened smoothly in the presence of trace water because of little steric hindrance and a possible hypervalent interaction between silicon and the neighboring aldehyde moiety (Scheme 5). As shown in Scheme 5, the proposed mechanism is different to that of intramolecular hydrosilylation (Scheme 3) due to the different reactivity of pentacoordinate and hexacoordinate intermediates. In this case, the rate-determining step involves nucleophilic attack (trace water) on a pentacoordinate silicon (**ii-1**) via a hexacoordinate intermediate (or transition state **ii-2**).[15a] Support for the mechanism in this hydrolytic oxidation is given

Table 2. Brønsted-acid-catalyzed oxidative coupling of hydrosilane-containing acetals.[a]



Compound **4**	Time (h)	Product **5**	Yield[b] (%)
 **4b**	0.5		**5b**: 60
 **4c**	0.5		**5c**: 71
 **4d**	1.0		**5d**: 37
 **4e**	0.5		**5e**: 54
 **4f**	12		**5f**: <5
 **4g**	12		**5g**: 76
 **4h**	12	-	0
 R'' R' = H, R'' = H R' = H, R'' = Me R' = Me, R'' = Me	12	-	0

[a] Compound **4** (1.0 equiv., 0.2 M), TsOH (10 mol-%), in acetone at room temperature. [b] Isolated yields.

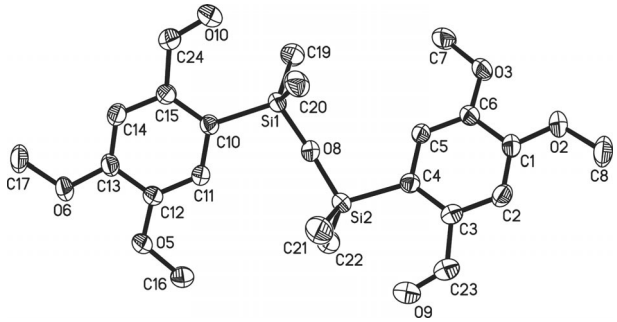
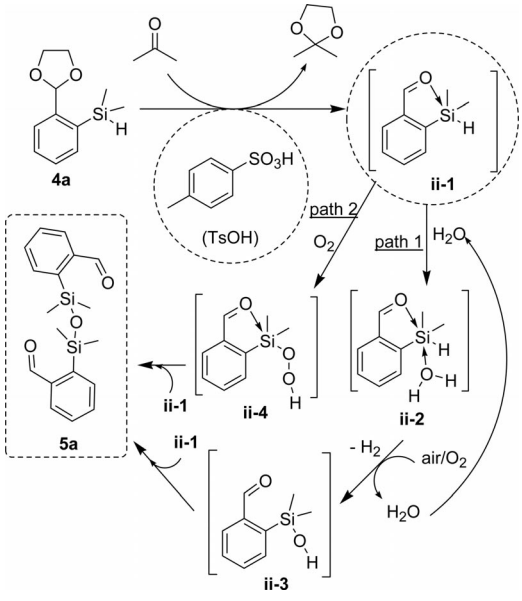


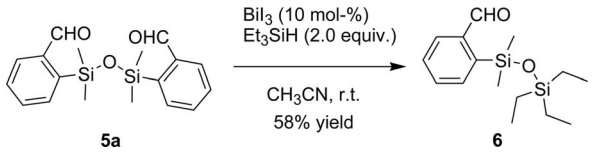
Figure 1. X-ray diffraction structure of compound **5b**.

as follows: a) the reaction in water or aqueous acetone (containing 5 vol.-% of water), without catalyst, gave no desired product (**5a**) – only the deprotected product (minor compound **ii-1**) and starting material (major compound); b) without the water and only in the presence of oxygen or air, a high yield of deprotected aldehyde **ii-1** was obtained, along with several complicated and unidentified side-products and a trace of desired product; c) when the reaction was carried out under simple conditions (i.e., without special Schlenk technology or purification of solvents), the desired product was formed smoothly with good yields, which supported the proposed mechanism in Scheme 5. Therefore, the presence of a trace of water is crucial to the hydrolytic oxidation because it initiates the oxidative process. However, the true mechanism of Brønsted-acid-catalyzed oxidation-coupling of hydrosilanes is still unclear. Although further investigation on the Brønsted acid catalysis of oxidation is needed, to the best of our knowledge, this is the first successful and simple example of the use of a Brønsted acid as a catalyst for the oxidative silylation of hydrosilanes to symmetrical functional siloxanes containing aldehyde moieties.



Scheme 5. Possible catalytic cycle of hydrolytic oxidation of organosilanes.

In addition, the hydrolytic oxidation provided ready access to different functionalized siloxanes for organosilicon chemistry, the transformation of which merited exploration. For example, a symmetrical disiloxane containing an aldehyde moiety could be converted to an unsymmetrical disiloxane easily through reductive transformation of Si–O–Si bonds by using BiI_3/Et_3SiH system. The isolated yield of **6** derived from **5a** at room temperature in only 5 h is good (58%, Scheme 6).



Scheme 6.

Conclusions

In summary, we have developed a novel and environmentally benign Brønsted-acid-catalyzed one-pot domino deprotection–hydrosilylation and hydrolytic oxidation to aldehyde-functionalized siloxanes. The present reaction represents the first example of a metal-free Brønsted-acid-catalyzed intramolecular hydrosilylation of aldehydes and intermolecular hydrolytic oxidation of organosilanes, in which the acetal group facilitated the corresponding oxidative silylation. The activation of a Si–H bond through a hypervalent transition state is observed, with neighboring interaction between the aldehyde oxygen and the silicon atom. These preliminary results encourage the development of new organocatalysts for the functionalization of Si–H bonds, and related reactions are expected to open up further opportunities for the development and application of functional organosilicon compounds. These studies are currently underway in our laboratory.

Experimental Section

General Remarks: All reagents and solvents were used directly without purification. Flash column chromatography was performed over silica (200–300 mesh). ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker Advance 400 MHz Nuclear Magnetic Resonance Spectromer, and were referenced to the internal solvent signals. Thin layer chromatography was performed using silica gel F254 TLC plates and visualized with ultraviolet light. HPLC was carried out with a Waters 2695 Millennium system equipped with a photodiode array detector. EI and CI mass spectra were performed with a Trace DSQ GC/MS spectrometer. The ESI-MS analysis of the samples was performed with an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). X-ray diffraction data sets were collected with Bruker APEX DUO and Bruker APEX-II CCD diffractometers. Programs used: data collection with Bruker APEX2,[17a] data reduction with Bruker SAINT, absorption correction for multi-scan, structure solution with SHELX-97,[17b] structure refinement with SHELXL-97,[17b] graphics with Bruker SHELXTL.[17b]

General Procedure for TsOH-Catalyzed Domino Deprotection–Hydrosilylation and Oxidative Silylation: A catalytic amount of TsOH (2–10 mol-%) was added to a vial containing **1** or **4** (1 mmol) in acetone (5 mL). After vigorous stirring at room temperature (times shown in the Table or Scheme), the reaction mixture was poured into an extraction funnel containing EtOAc and brine diluted with distilled water. The aqueous phase was extracted with EtOAc. The combined organic phases were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography to furnish the desired product. The products were confirmed by GC–MS and NMR (see Supporting Information).

2-(1-Methyl-1,3-dihydrobenzo[*c*][1,2]oxasilol-1-yl)benzaldehyde (2a): 70% yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.04 (s, 1 H),

8.18 (d, J = 7.2 Hz, 1 H), 8.13 (d, J = 7.2 Hz, 1 H), 7.82 (d, J = 7.6 Hz, 1 H); 7.70–7.66 (m, 1 H), 7.59–7.55 (m, 1 H), 7.44–7.40 (m, 1 H), 7.34–7.26 (m, 2 H), 5.32 (dd, J = 11.2, 14.4 Hz, 2 H), 0.70 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 194.56, 151.00, 140.18, 139.91, 135.88, 134.32, 134.15, 134.12, 133.34, 130.15, 129.98, 126.84, 121.62, 70.70, –0.31 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = 6.75 ppm. GC/MS: m/z = 254 (14) [M^+], 239 (100), 225 (9), 195 (1), 178 (31), 165 (33), 148 (23), 133 (13), 105 (17), 89 (11), 77 (7). IR (KBr): $\tilde{\nu}$ = 1675.6 cm^{-1}. $C_{15}H_{14}O_2Si$ (254.08): calcd. C 70.83, H 5.55, O 12.58, Si 11.04; found C 70.73, H 5.49.

2-(5,6-Dimethoxy-1-methyl-1,3-dihydrobenzo[*c*][1,2]oxasilol-1-yl)-4,5-dimethoxybenzaldehyde (2b): 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.86 (s, 1 H), 7.58 (s, 1 H), 7.47 (s, 1 H), 7.31 (s, 1 H), 6.70 (s, 1 H), 5.16 (dd, J = 13.6, 22.0 Hz, 2 H), 3.99–3.85 (m, 12 H), 0.55 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 192.54, 154.29, 151.33, 150.07, 148.30, 143.99, 135.00, 133.19, 124.12, 117.53, 115.30, 115.22, 104.19, 70.49, 56.30, 56.13, 55.99, 55.77, –0.16 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = 5.85 ppm. GC/MS: m/z = 374 (98) [M^+], 359 (100), 343 (27), 329 (13), 315 (15), 298 (43), 283 (22), 271 (6), 255 (20), 240 (11), 225, (9), 208 (46), 193 (27), 179 (14), 165 (23), 151 (28), 121 (9), 107 (7), 91 (6), 77 (6). IR (KBr): $\tilde{\nu}$ = 1668.5 cm^{-1}. $C_{19}H_{22}O_6Si$ (374.12): calcd. C 60.94, H 5.92, O 25.64, Si 7.50; found C 60.62, H 5.82.

4-Ethoxy-2-(6-ethoxy-5-methoxy-1-methyl-1,3-dihydrobenzo[*c*][1,2]-oxasilol-1-yl)-5-methoxybenzaldehyde (2c): 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.85 (s, 1 H), 7.59 (s, 1 H), 7.49 (s, 1 H), 7.31 (s, 1 H), 6.71 (s, 1 H), 5.16 (dd, J = 13.6, 20.8 Hz, 2 H), 4.17 (dd, J = 6.8, 14.0 Hz, 2 H), 4.10–4.06 (m, 3 H), 3.89 (s, 3 H), 1.51–1.43 (m, 6 H), 0.56 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 192.56, 154.58, 150.65, 149.33, 148.52, 143.96, 134.85, 133.19, 124.61, 117.74, 116.61, 115.66, 105.36, 70.48, 64.66, 64.10, 56.28, 56.08, 14.73, 14.69, –0.12 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = 5.85 ppm. GC/MS: m/z = 402 (00) [M^+], 387 (99), 373 (27), 359 (13), 326 (26), 313 (12), 297 (23), 269 (12), 241 (15), 222 (39), 207 (25), 195 (12), 179 (21), 165 (30), 151 (25), 137 (16), 121 (7), 91 (6), 77 (8). IR (KBr): $\tilde{\nu}$ = 1675.6 cm^{-1}. $C_{21}H_{26}O_6Si$ (402.15): calcd. C 62.66, H 6.51, O 23.85, Si 6.98; found C 63.21, H 6.59.

5a: 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.10 (d, J = 8.0 Hz, 2 H), 7.93–7.88 (m, 4 H), 7.62–7.55 (m, 4 H), 0.57–0.40 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 193.65, 142.10, 140.95, 135.69, 133.29, 132.66, 129.59, 1.58, 1.42 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –1.83 ppm. GC/MS: m/z = 342 (0.4) [M^+], 327 (77), 309 (61), 291 (7), 253 (2), 237 (12), 219 (6), 191 (41), 178 (22), 163 (100), 156 (68), 149 (54), 104 (7), 91 (26), 89 (13), 73 (4). IR (KBr): $\tilde{\nu}$ = 1698.7 cm^{-1}. $C_{18}H_{22}O_3Si_2$ (342.11): calcd. C 63.12, H 6.47, O 14.01, Si 16.40; found C 62.87, H 6.52.

5b: 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.06 (s, 2 H), 7.43 (s, 2 H), 7.34 (s, 2 H), 3.96 (s, 6 H), 3.82 (s, 6 H), 0.49 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 191.55, 152.93, 149.88, 136.42, 134.68, 117.25, 113.63, 56.03, 55.92, 2.23 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –1.71 ppm. GC/MS: m/z = 462 (0.2) [M^+], 429 (1), 329 (11), 209 (43), 165 (6), 151 (100), 85 (63). IR (KBr): $\tilde{\nu}$ = 1688.9, 1678.6 cm^{-1}. $C_{22}H_{30}O_7Si_2$ (462.15): calcd. C 57.11, H 6.54, O 24.21, Si 12.14; found C 57.16, H 6.44.

5c: 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.03 (s, 2 H), 7.42 (s, 2 H), 7.34 (s, 2 H), 4.18 (dd, J = 6.8, 14.0 Hz, 4 H), 3.79 (s, 6 H), 1.50 (t, J = 7.2 Hz, 6 H), 0.48 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 191.61, 153.18, 149.19, 136.20, 134.64, 117.52, 114.93, 64.49, 55.93, 29.72, 14.69, 2.25 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –1.75 ppm. GC/MS: m/z = 490 (16) [M^+], 475 (73), 446 (21), 403 (9), 342 (7), 311 (58), 267 (19), 253 (63), 237 (100), 209 (52), 202 (70), 194 (54), 180 (21), 165 (31), 133 (51). IR (KBr): $\tilde{\nu}$ = 1687.8 cm^{-1}. $C_{24}H_{34}O_7Si_2$ (490.18): calcd. C 58.74, H 6.98, O 22.82, Si 11.45; found C 58.59, H 7.06.

5d: 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.03 (s 2 H), 7.91 (dd, J = 5.2, 8.4 Hz, 2 H), 7.57 (dd, J = 2.8, 9.2 Hz, 2 H), 7.25–7.21 (m, 2 H), 0.47 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 191.81, 164.61, 146.18, 137.26, 135.89, 135.79, 123.16, 122.93, 116.69, 116.49, 1.44 ppm. ^{29}Si NMR: δ = (79.5 MHz, $CDCl_3$): –1.88 ppm.

5e: 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.13 (d, J = 3.2 Hz, 2 H), 7.76 (d, J = 8.0 Hz, 2 H), 7.43 (d, J = 2.4 Hz, 2 H), 7.13–7.10 (m, 2 H), 3.88 (d, J = 3.6 Hz, 6 H), 0.41 (d, J = 14.8 Hz, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 193.25, 160.95, 142.61, 137.04, 133.40, 119.08, 116.59, 55.42, 2.09 ppm.

BiI_3-Catalyzed Reductive Silylation of 5a: To a suspension of bismuth(III) iodide (0.1 mmol) and **5a** (1.0 mmol) in acetonitrile (3 mL) was added triethylsilane (2.0 mmol) at room temperature under argon. After stirring for 5 h, the reaction mixture was quenched with water. The organic materials were extracted with dichloromethane, washed with brine, and dried with sodium sulfate. The desired product **6** was isolated by flash column chromatography on silica gel (58%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.16 (s, 1 H), 7.90–7.87 (m, 2 H), 7.63–7.53 (m, 2 H), 0.953 (t, J = 8.0 Hz, 9 H), 0.61 (q, J = 16.0 Hz, 6 H), 0.41 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 193.73, 142.80, 140.93, 135.47, 133.15, 132.03, 129.51, 6.87, 6.39, 1.72 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 11.28, –3.09 ppm. GC/MS: m/z = 294 (2) [M^+], 279 (33), 265 (25), 209 (100), 195 (16), 181 (14), 149 (22), 97 (85).

Supporting Information (see footnote on the first page of this article): General remarks, spectroscopic data for the siloxanes, ^{29}Si NMR Spectra of siloxanes, and X-ray structures of **5b** (CCDC-787471) and intermediate **i-2** (CCDC-803537, Scheme 3).

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