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# Reaction of Aromatic Carbonyl Compounds with Silylborane Catalyzed by Au Nanoparticles: Silylative Pinacol-Type Reductive Dimerization via a Radical Pathway

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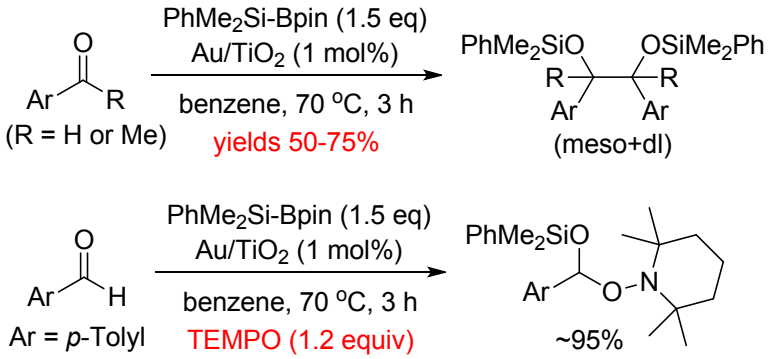
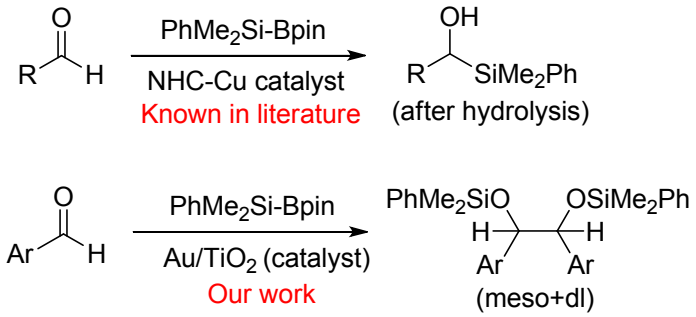



**ABSTRACT:** Aromatic aldehydes and acetophenones undergo silylative pinacol-type reductive dimerization in their reaction with silylborane pinB-$SiMe_2Ph$ (pin: pinacolato) catalyzed by supported Au nanoparticles on $TiO_2$. It is proposed that after initial activation of silylborane by Au nanoparticles and addition to the carbonyl functionality of an aromatic aldehyde or ketone, an aryl silyloxy radical is generated from the collapse of the intermediate adduct, which then dimerizes through a chain process. The silyloxy radical was almost quantitatively trapped, in the presence of TEMPO.

Silylboranes is a class of compounds whose chemistry has attracted a considerable interest in recent years. The Si-B bond can be readily activated by a series of catalysts, primarily transition metals, and undergoes addition to unsaturated compounds.[1] The activation of silylborane pinB-$SiMe_2Ph$ (pin: pinacolato) by supported Au nanoparticles ($Au_n$), and the subsequent addition of the Au-nanoparticle bonded boron and silyl moieties (pinB-$Au_n$-$SiMe_2Ph$) on alkynes,[2] allenes[3] or strained cyclic ethers[4] has been recently documented by our group. As a continuation of our studies in this field we examined the possible reaction between pinB-$SiMe_2Ph$ and carbonyl compounds in the presence of Au nanoparticles. It is well known that silylboranes are unreactive against carbonyl compounds,[5] as also proved in our hands. In the presence of a NHC-Cu complex, however, a catalytic C-Si bond forming reaction is taking place (Scheme 1). Thus, nucleophilic addition of the silicon moiety from pinB-$SiMe_2Ph$ occurs to aldehydes or imines forming α-silyl alcohols[6] or α-silyl amines,[7] respectively, and to $CO_2$ which undergoes reduction.[8] Also, a metal-free catalytic enantioselective 1,2-silylation of aromatic aldehydes with pinB-$SiMe_2Ph$ was latter reported.[9] Analogous catalytic reactions between silylborane and α,β-unsaturated carbonyl compounds occur

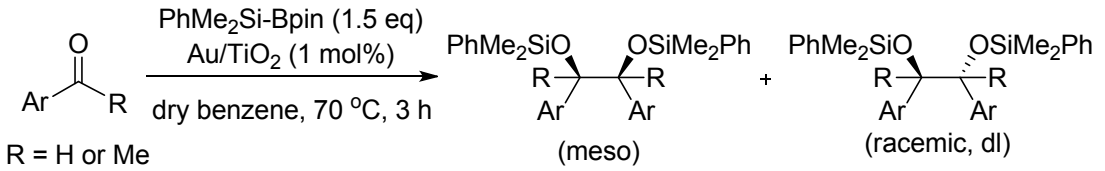


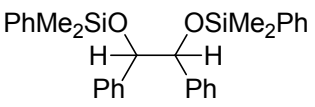

**Scheme 1**. Catalyzed Reactions Between Aldehydes and Silylborane pinB-$SiMe_2Ph$.

via a 1,4-silyl addition.[1a] A common characteristic of these reactions, is that the silyl part of pinB-$SiMe_2Ph$ behaves as a nucleophile, through the formation of a metal-$SiMe_2Ph$ complex as a key intermediate in the proposed catalytic cycles.

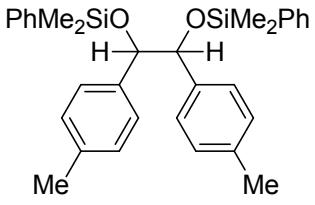
In this manuscript, we present our studies regarding the reaction of silylborane pinB-$SiMe_2Ph$ with carbonyl compounds catalyzed by supported Au nanoparticles. In the presence of 1.0 mol% Au/$TiO_2$, a series of para- and meta-substituted aromatic aldehydes or acetophenones (1 equiv) and pinB-$SiMe_2Ph$ (1.5 equiv) react smoothly in dry benzene at 70 $^oC$ forming after 3 h silylated pinacol-type dimerization products in good isolated yields (Scheme 1 and Table 1). The dimeric products appear as an approximately equimolar mixture of meso and dl diastereomers. The assignment of unknown compounds as meso or dl was done by deprotection and characterization of the resulting known diols. Typically, no side products derived from the carbonyl compounds are seen. In case of using non-dried solvent, additional excess of silylborane is required (2-3 equiv) to compensate its destruction, and at the same time minor amounts of hydrosilylation products of the carbonyl compounds[10] can be seen due to the in situ formed $HSiMe_2Ph$, which is essentially an intermediate product from the Au-catalyzed hydrolysis of pinB-$SiMe_2Ph$.[2a] Apart from dry benzene, 1,2-dichloroethane is also a suitable solvent providing similar yields under the same reaction conditions. In other solvents such as hexane, acetonitrile, ethyl acetate or tetrahydrofuran the yields are below 20%, while several unidentified side products are also formed (Table S1). Ortho-substituted benzaldehydes and bulky ketones such as benzophenone are unreactive. The involvement of Au nanoparticles in this catalytic transformation is without any doubt, as $TiO_2$ itself (rutile or anatase forms) does not promote any reaction between pinB-$SiMe_2Ph$ and the carbonyl compounds. In contrast to the aromatic

**Table 1**: Reaction Between Aromatic Aldehydes and Acetophenones with pinB-$SiMe_2Ph$ Catalyzed by $Au/TiO_2$.[a]

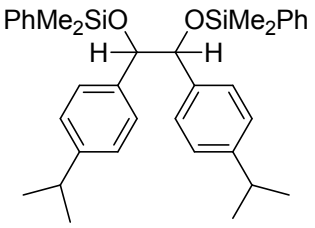


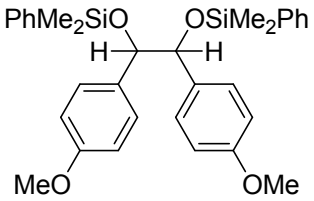
**1a** (61%, dl/meso=53/47)



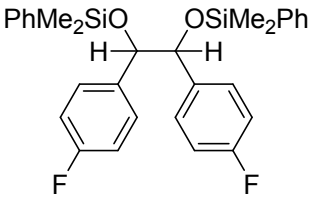
**2a** (72%, dl/meso=52/48)[b]



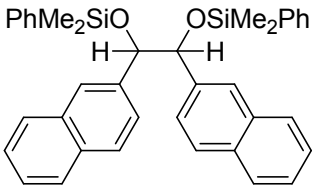
**3a** (66%, dl/meso=54/46)



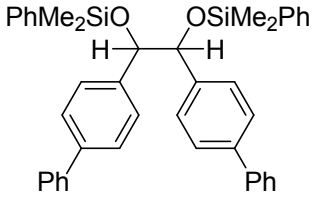
**4a** (75%, dl/meso=54/46)



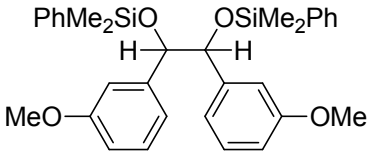
**5a** (62%, dl/meso=51/49)



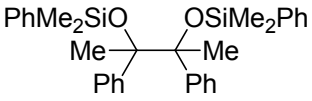
**6a** (50%, dl/meso=55/45)



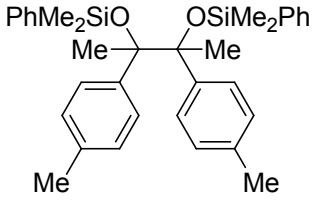
**7a** (54%, dl/meso=53/47)



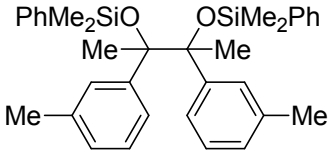
**8a** (59%, dl/meso=43/57)



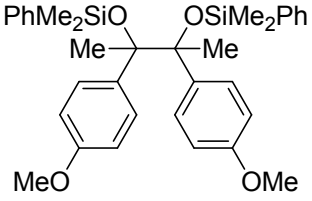
**9a** (58%, dl/meso=53/47)



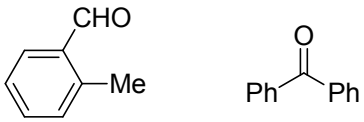
**10a** (66%, dl/meso=52/48)



**11a** (58%, dl/meso=51/49)



**12a** (65%, dl/meso=44/56)



Unreactive

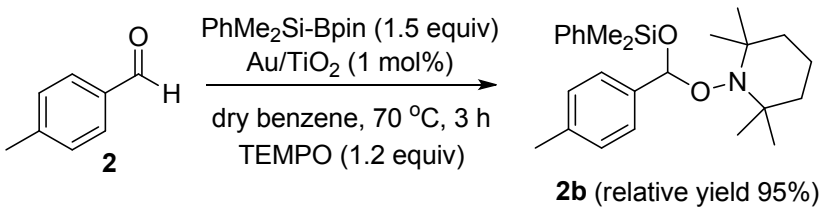
[a]The reactions were performed at ~0.15 mmol scale of carbonyl compound. [b]At 0.5 mmol scale the isolated yield was 68%.

carbonyl compounds, typical aliphatic aldehydes or ketones are completely unreactive. Notably, no reaction between aldehydes or ketones (aromatic or aliphatic) and bis(pinacolato)diboron (pinB-Bpin) is taking place in the presence of $Au/TiO_2$. Such anticipated addition reaction is well established in the presence of other catalytic systems, primarily Cu(I), and yields α-hydroxy boronates.[11]

To the best of our knowledge, this is the first example in the literature of such dimerization pathway involving reaction between carbonyl compounds and a silylborane. A silylative pinacol-type reductive dimerization of aromatic aldehydes has been reported as a major pathway in their reaction with hydrosilanes catalyzed by a dinuclear ruthenium complex,[12] by $Au/Al_2O_3$,[13] or by N-doped carbon-encapsulated Ni/Co nanoparticles,[14] and in the presence of a σ disilane catalyzed by $Pt_2(dba)_3$ (as a minor pathway).[15] A specific example of a pinacol-type reductive dimerization of 2-pyridinecarboxaldehyde in the presence of pinB-Bpin and a Cu catalyst is also known.[16] Commonly, silylated pinacols can be prepared from aldehydes and stoichiometric amounts of a metal (reductant), followed by silyl-protection of the resulting diols.[17]

The reductive dimerization apparently proceeds via a radical pathway as will be analyzed below. This postulation was established upon adding into the reaction mixture between pinB-$SiMe_2Ph$, *p*-tolualdehyde (**2**) and 1 mol% $Au/TiO_2$, 1.2 equivalents of the free radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Trapping adduct **2b** was formed in 95% relative yield (Scheme 2), with dimeric silylated pinacol products **2a** observed in merely 5% yield. No other TEMPO-trapping side products were seen. Product **2b** is a silylated hemiacetal and is chromatographically labile, as it undergoes during purification partial desilylation, collapsing eventually to *p*-tolualdehyde. A very similar TEMPO-adduct had been isolated during the studies of the

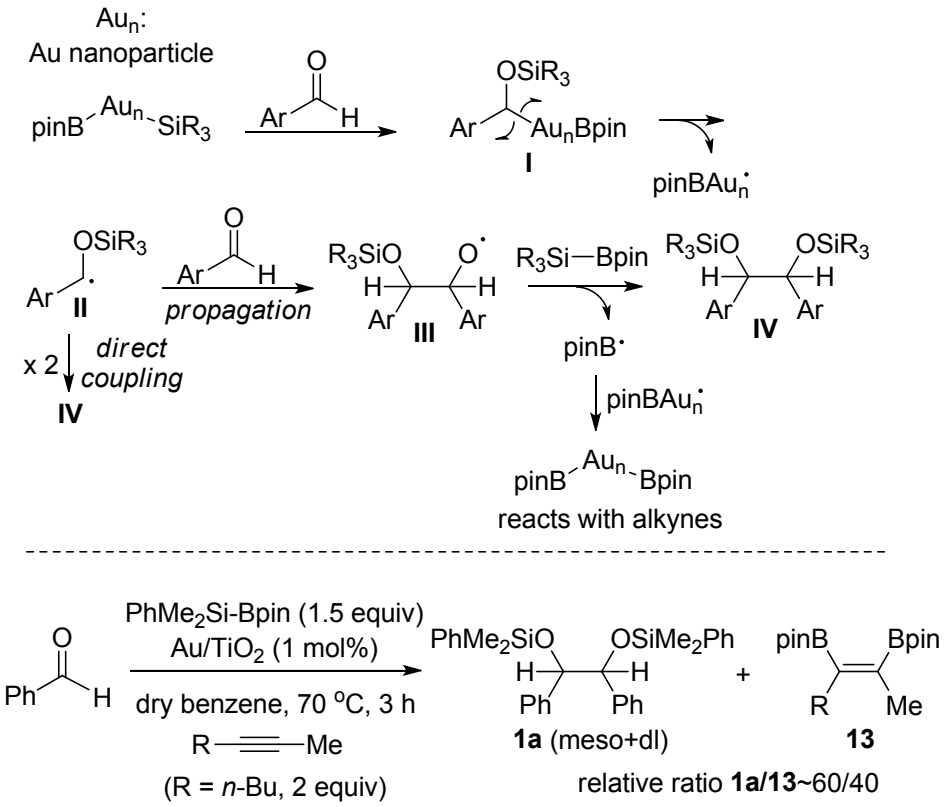
photoredox-catalyzed Brook rearrangement of α-silyl alcohols,[18] as a proof for the involvement of α-silyloxy carbon radical intermediates.




**Scheme 2**. Au/$TiO_2$-Catalyzed Reaction of *p*-Tolualdehyde (**2**) with pinB-$SiMe_2Ph$ in the Presence of TEMPO.

As a mechanistic explanation, we propose that the pinB-$Au_n$-$SiMe_2Ph$ species[3] generated from the activation of the σ bond of pinB-$SiMe_2Ph$ on gold nanoparticle ($Au_n$) add to the carbonyl functionality, forming intermediate **I** (Scheme 3). Adduct **I** collapses into α-silyloxy radical **II** and $Au_n$-Bpin radical. Through propagations steps (intermediate **III**), the silyl bearing pinacol-type dimeric products **IV** are formed, while the fate of Bpin is also dimerization into pinB-Bpin (via pinB-$Au_n$-Bpin). Indeed, pinB-Bpin was detected by GC-MS during the progress of the reaction. The direct dimerization of radical **II** into the termination product **IV** is also a possible pathway. Another evidence for the participation of pinB-$Au_n$-Bpin species, was that when performing the Au-catalyzed reaction among benzaldehyde and pinB-$SiMe_2Ph$ in the presence of 2-heptyne, apart from the anticipated dimeric products **1a**, cis-diboration of the alkyne (product **13**)[2b] was also observed in a relative ratio **1a**/**13** = 60/40. Silyborane itself does not form a diboration adduct with 2-heptyne under identical reaction conditions, and is completely unreactive as also observed earlier[2a] in the attempted silaboration of internal alkynes. Notably, the current radical-chain mechanism is completely different from a recently reported one,[14] concerning the formation of

silylated pinacols from the reaction between aromatic aldehydes and hydrosilanes catalyzed by *N*-doped carbon-encapsulated Ni/Co nanoparticles. In this study, the chain process is initiated by a silyl radical, which is trappable by TEMPO. We also emphasize that our way of generating ketyl radicals does not require single electron reductants or irradiation.[19]




**Scheme 3**. Possible Mechanism for the Au/$TiO_2$-Catalyzed Reaction Between an Aromatic Aldehyde and pinB-$SiMe_2Ph$, and Evidence for the Formation of pinB-$Au_n$-Bpin Species.

In conclusion, we have presented herein a novel catalytic property of supported Au nanoparticles in the reaction between aromatic aldehydes or acetophenones with silylborane pinB-$SiMe_2Ph$, which leads to silylative reductive pinacol-type dimerization products via a radical-chain pathway.[20] The fate of pinB moiety is its transformation

into pinB-$Au_n$-Bpin species. Our protocol adds a new and unprecedented mode of reactivity of silylboranes with carbonyl compounds and a new potential application of supported Au nanoparticles in catalysis.[21] Further work is in progress to exploit new synthetic applications based on the current findings.

## EXPERIMENTAL SECTION

**General:** The reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F-254). Flash column chromatography was carried out on $SiO_2$ (silica gel 60, particle size 0.040–0.063 mm). The catalyst, Au/$TiO_2$ (1 wt% in Au), is commercially available and has an average gold crystallite size of ~2-3 nm. NMR spectra were recorded on 300 and 500 MHz instruments. High resolution mass spectra (HRMS) were recorded on a Bruker® Maxis Impact QTOF and on a Thermo Scientific LTQ Orbitrap XL spectrometers.

**Typical procedure for the Au/$TiO_2$-catalyzed reaction between aromatic carbonyl compounds and silylborane pinB-$SiMe_2Ph$:** To a vial containing *p*-tolylaldehyde, **2** (18 μL, 0.15 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester, pinB-$SiMe_2Ph$ (0.06 mL, 0.225 mmol) dissolved in dry benzene (0.5 mL) were added Au/$TiO_2$ (29 mg, 1 wt% in Au, ~0.0015 mmol). The mixture was heated in an oil bath to 70 $^oC$ until the aldehyde was consumed (2-3 h). The slurry was filtered with the aid of dichloromethane (3 mL) through a short pad of silica gel. The filtrate was evaporated under vacuum and the residue was chromatographed with hexane/ethyl acetate = 80/1 as eluent to afford **2a** (26.8 mg, 72% yield). The reaction between aldehyde **2** and pinB-$SiMe_2Ph$ was also performed at the scale of 0.5 mmol, with dimers **2a** isolated in 68% yield.

**Spectroscopic data of products**

**2,7-Dimethyl-2,4,5,7-tetraphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 1a)**.[22] Colorless oil (19.7 mg, 61% yield); $^{1}$H NMR (500 MHz, $CDCl_3$): 7.43-7.00 (m, 20H meso + 20H dl), 4.71 (s, 2H, meso), 4.54 (s, 2H, dl), 0.19 (s, 6H, meso), 0.14 (s, 6H, meso), 0.00 (s, 6H, dl), -0.07 (s, 6H, dl); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): 142.5, 141.2, 137.9, 137.5, 133.6, 133.5, 129.3, 129.2, 127.7, 127.6 (two overlapping peaks), 127.5, 127.4, 127.3, 127.2 and 127.0 (aromatic resonances, meso+dl), 79.83 and 79.81 (meso+dl), -1.0, -1.4, -1.5 and -1.8 (meso+dl).

**2,7-Dimethyl-2,7-diphenyl-4,5-di-*p*-tolyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 2a).**[23] Colorless oil (26.8 mg, 72% yield); $^{1}$H NMR (500 MHz, $CDCl_3$): 7.44-6.88 (m, 18H meso + 18H dl), 4.67 (s, 2H, meso), 4.52 (s, 2H, dl), 2.37 (s, 6H, dl), 2.29 (s, 6H, meso), 0.19 (s, 6H, meso), 0.14 (s, 6H, meso), 0.03 (s, 6H, dl), -0.05 (s, 6H, dl); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): 139.6, 138.3, 138.1, 137.8, 136.6, 136.3, 133.7, 133.5, 129.2, 129.1, 128.2, 127.9, 127.6, 127.5 and 127.4 (two overlapping peaks) (aromatic resonances, meso+dl), 79.68 and 79.66 (meso+dl), 21.22 and 21.16 (meso+dl), -0.9, -1.3 (two overlapping peaks) and -1.7 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{38}O_2Si_2Na$ 533.2302; Found 533.2280.

**4,5-bis(4-Isopropylphenyl)-2,7-dimethyl-2,7-diphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 3a)**.[23] Colorless oil (24.4 mg, 66% yield); $^{1}$H NMR (500 MHz, $CDCl_3$): 7.37-7.95 (m, 18H meso + 18H dl), 4.65 (s, 2H, meso), 4.48 (s, 2H, dl), 2.94 (heptet, $J$ = 7.0 Hz, 2H, dl), 2.85 (heptet, $J$ = 7.0 Hz, 2H, meso), 1.29 (d, $J$ = 7.0 Hz, 12H, dl), 1.22 (d, $J$ = 7.0 Hz, 12H, meso), 0.15 (s, 6H, meso), 0.10 (s, 6H, meso), -0.03 (s, 6H, dl), -0.11 (s, 6H, dl); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): 147.8, 147.4, 140.2, 138.9, 138.1, 137.8, 133.7, 133.5, 129.2, 129.1, 127.6, 127.4, 127.4, 127.2, 125.5, 125.2 (aromatic resonances, meso+dl), 79.9 and 79.7 (meso+dl), 33.9 and 33.7 (meso+dl), 24.2 and 24.1

(meso+dl), -1.1, -1.3, -1.5 and -1.8 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{46}O_2Si_2Na$ 589.2928; Found 589.2903.

**4,5-bis(4-Methoxyphenyl)-2,7-dimethyl-2,7-diphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 4a)**.[24] Colorless oil (29.1 mg, 75% yield); $^1H$ NMR (500 MHz, $CDCl_3$): 7.46-6.65 (m, 18H meso + 18H dl), 4.64 (s, 2H, meso), 4.48 (s, 2H, dl), 3.83 (s, 6H, dl), 3.76 (s, 6H, meso), 0.40 (s, 6H, meso), 0.20 (s, 6H, meso), 0.03 (s, 6H, dl), -0.04 (s, 6H, dl); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 158.8, 158.5, 138.1, 137.8, 134.8, 133.6, 133.5, 133.4, 129.3, 129.2, 128.7, 128.6, 127.5, 127.4, 112.9 and 112.6 (aromatic resonances, meso+dl), 79.4 (two overlapping meso+dl), 55.2 and 55.1 (meso+dl), -0.9, -1.3, -1.3 and -1.7 (meso+dl).

**4,5-bis(4-Fluorophenyl)-2,7-dimethyl-2,7-diphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 5a)**.[23] Colorless oil (22.2 mg, 62% yield); $^1H$ NMR (500 MHz, $CDCl_3$): 7.41-6.79 (m, 18H meso + 18H dl), 4.64 (s, 2H, meso), 4.44 (s, 2H, dl), 0.21 (s, 6H, meso), 0.15 (s, 6H, meso), 0.02 (s, 6H, dl), -0.04 (s, 6H, dl); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 162.2 (d, $J_{C\text{-}F}$ = 243.5 Hz), 162.0 (d, $J_{C\text{-}F}$ = 243.5 Hz), 138.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 137.5, 137.1, 136.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.5, 133.4, 129.5, 129.4, 129.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.7, 127.5, 114.4 (d, $J_{C\text{-}F}$ = 21.5 Hz) and 114.1 (d, $J_{C\text{-}F}$ = 21.5 Hz) (aromatic resonances, meso+dl), 79.1 and 78.8 (meso+dl), -1.2, -1.5, -1.6 and -1.8 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{32}F_2O_2Si_2Na$ 541.1801; Found 541.1793.

**2,7-Dimethyl-4,5-di(naphthalen-2-yl)-2,7-diphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 6a)**.[23] White solid (19.8 mg, 55% yield); $^1H$ NMR (300 MHz, $CDCl_3$): 7.89-6.94 (m, 24H meso + 24H dl), 4.96 (s, 2H, meso), 4.78 (s, 2H, dl), 0.17 (s, 6H, meso), 0.11 (s, 6H, meso), -0.03 (s, 6H, dl), -0.12 (s, 6H, dl); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 140.1, 138.8, 137.5, 137.1, 134.1, 133.6, 133.4, 133.1, 133.1, 132.9, 132.8, 129.3,

129.2, 128.0, 127.9, 127.6, 127.5, 127.5, 127.3, 127.3, 126.8, 126.7, 126.3, 125.8, 125.7, 125.7, 125.5 and 125.4 (aromatic resonances, meso+dl), 79.9 and 79.7 (meso+dl), -1.0, -1.4, -1.4 and -1.8 (meso+dl); HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{38}H_{39}O_2Si_2$ 583.2489; Found 583.2495.

**4,5-di([1,1'-Biphenyl]-4-yl)-2,7-dimethyl-2,7-diphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 7a)**.[23] White solid (26.8 mg, 67% yield); $^1$H NMR (500 MHz, $CDCl_3$): 7.69-7.12 (m, 28H meso + 28H dl), 4.79 (s, 2H, meso), 4.62 (s, 2H, dl), 0.24 (s, 6H, meso), 0.19 (s, 6H, meso), 0.07 (s, 6H, dl), -0.00 (s, 6H, dl); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 141.7, 141.2, 141.0, 140.3, 139.6, 137.8, 137.4, 133.6, 133.5, 129.3, 129.3, 128.7, 128.7, 128.1, 127.9, 127.6, 127.5, 127.1, 127.0, 127.0, 126.9, 126.3 and 126.0 (aromatic resonances, meso+dl), 79.6 and 79.5 (meso+dl), -1.0, -1.3, -1.4 and -1.7 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{42}H_{42}O_2Si_2Na$ 657.2615; Found 657.2627.

**4,5-bis(3-Methoxyphenyl)-2,7-dimethyl-2,7-diphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 8a)**.[23] Colorless oil (20.3 mg, 59% yield); $^1$H NMR (500 MHz, $CDCl_3$): 7.41-6.58 (m, 18H meso + 18H dl), 4.67 (s, 2H, meso), 4.51 (s, 2H, dl), 3.72 (s, 6H, dl), 3.63 (s, 6H, meso), 0.19 (s, 6H, meso), 0.15 (s, 6H, meso), 0.04 (s, 6H, dl), -0.03 (s, 6H, dl); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 159.1, 158.8, 144.1, 142.9, 137.8, 137.5, 133.6, 133.5, 129.3, 129.3, 128.4, 128.2, 127.5, 127.5, 120.3, 119.8, 113.5, 113.2, 112.5 and 112.5 (aromatic resonances, meso+dl), 79.7 and 79.7 (meso+dl), 55.2 and 55.1 (meso+dl), -1.1, -1.4, -1.5 and -1.7 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{38}O_4Si_2Na$ 565.2201; Found 565.2186.

**2,4,5,7-Tetramethyl-2,4,5,7-tetraphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 9a)**.[23] Colorless oil (22.3 mg, 58% yield); $^1$H NMR (500 MHz, $CDCl_3$): 7.57-6.99 (m, 20H meso + 20H dl), 1.71 (s, 6H, meso), 1.47 (s, 6H, dl), 0.25 (s, 6H, meso), 0.20 (s, 6H,

meso), 0.10 (s, 6H, dl), 0.00 (s, 6H, dl); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): 145.6, 144.8, 139.9, 139.8, 133.4, 133.2, 129.1, 129.0, 128.3, 128.2, 127.6 (two overlapping peaks), 126.8, 126.4, 126.2 and 126.0 (aromatic resonances, meso+dl), 82.7 and 81.9 (meso+dl), 24.6 and 24.1 (meso+dl), 1.1, 1.0, 0.9 and 0.9 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{38}O_2Si_2Na$ 533.2302; Found 533.2280.

**2,4,5,7-Tetramethyl-2,7-diphenyl-4,5-di-*p*-tolyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 10a)**.[23] Colorless oil (25.8 mg, 66% yield); $^{1}H$ NMR (500 MHz, $CDCl_3$): 7.56-6.87 (m, 18H meso + 18H dl), 2.36 (s, 6H, meso), 2.30 (s, 6H, dl), 1.66 (s, 6H, meso), 1.44 (s, 6H, dl), 0.23 (s, 6H, meso), 0.19 (s, 6H, meso), 0.11 (s, 6H, dl), -0.01 (s, 6H, dl); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): 142.7, 141.9, 140.1, 140.0, 135.7, 135.5, 133.4, 133.3, 129.0, 128.9, 128.2, 128.2, 127.5, 127.5, 127.4 and 126.8 (aromatic resonances, meso+dl), 82.7 and 81.9 (meso+dl), 24.7 and 24.2 (meso+dl), 21.01 and 21.00 (meso+dl), 1.2, 1.1, 1.0 and 0.9 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{42}O_2Si_2Na$ 561.2615; Found 561.2608.

**2,4,5,7-Tetramethyl-2,7-diphenyl-4,5-di-*m*-tolyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 11a)**.[23] Colorless oil (21.7 mg, 58% yield). $^{1}H$ NMR (500 MHz, $CDCl_3$): 7.58-6.75 (m, 18H meso + 18H dl), 2.31 (s, 6H, dl), 2.17 (s, 6H, meso), 1.72 (s, 6H, meso), 1.44 (s, 6H, dl), 0.27 (s, 6H), 0.19 (s, 6H), 0.12 (s, 6H) and 0.01 (s, 6H) (meso+dl); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): 145.6, 144.6, 140.0, 139.9, 135.8, 135.0, 133.4, 133.2, 129.3, 129.2, 129.0, 129.0, 127.6, 127.5, 127.0, 126.8, 126.6, 125.7, 125.3 and 125.3 (aromatic resonances, meso+dl), 82.7 and 82.0 (meso+dl), 24.7 and 24.1 (meso+dl), 21.6 and 21.4 (meso+dl), 1.2, 1.0, 0.9 and 0.8 (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{42}O_2Si_2Na$ 561.2615; Found 561.2608.

**4,5-bis(4-Methoxyphenyl)-2,4,5,7-tetramethyl-2,7-diphenyl-3,6-dioxa-2,7-disilaoctane (meso+dl, 12a)**.[23] Colorless oil (26.6 mg, 65% yield). $^{1}H$ NMR (500 MHz,

$CDCl_3$): 7.56-6.60 (m, 18H meso + 18H dl), 3.82 (s, 6H, dl), 3.78 (s, 6H, meso), 1.67 (s, 6H, meso), 1.45 (s, 6H, dl), 0.25 (s, 6H), 0.18 (s, 6H), 0.11 (s, 6H), 0.02 (s, 6H) (meso+dl); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 158.2, 158.0, 140.0, 139.9, 137.9, 137.2, 133.4, 133.3, 129.4, 129.3, 129.0, 129.0, 127.6 (two overlapping peaks), 112.0 and 111.3 (aromatic resonances, meso+dl), 82.5 and 81.9 (meso+dl), 55.2 and 55.1 (meso+dl), 24.7 and 24.2 (meso+dl), 1.2, 1.0 and 1.0 (two overlapping peaks) (meso+dl); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{42}O_4Si_2Na$ 593.2514; Found 593.2515.

**1-(((Dimethyl(phenyl)silyl)oxy)(*p*-tolyl)methoxy)-2,2,6,6-tetramethylpiperidine (2b)**: $^1H$ NMR (500 MHz, $CDCl_3$): 7.58-7.30 (m, 5H), 7.23 (d, $J$ = 8.0 Hz, 2H), 7.08 (d, $J$ = 8.0 Hz, 2H), 5.85 (s, 1H), 2.34 (s, 3H), 1.61-1.27 (m, 6H), 1.35 (s, 3H), 1.12 (s, 3H), 1.03 (s, 3H), 0.96 (s, 3H), 0.31 (s, 3H), 0.21 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 138.8, 137.9, 137.5, 133.9, 129.3, 128.5, 127.5, 126.2, 102.0, 60.4, 59.2, 40.4, 40.0, 34.5, 33.5, 21.2, 20.7, 20.3, 17.3, -0.6, -0.9; HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{38}NO_2Si$ 412.2672; Found 412.2671.

**Supporting Information Available:** Copies of $^1H$ and $^{13}C$ NMR of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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