Tandem Si–Si and Si–H Activation of 1,1,2,2-Tetramethyldisilane by Gold Nanoparticles in Its Reaction with Alkynes: Synthesis of Substituted 1,4-Disila-2,5-cyclohexadienes

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Tandem Si–Si and Si–H Activation of 1,1,2,2-Tetramethyldisilane by Gold Nanoparticles in Its Reaction with Alkynes: Synthesis of Substituted 1,4-Disila-2,5-cyclohexadienes

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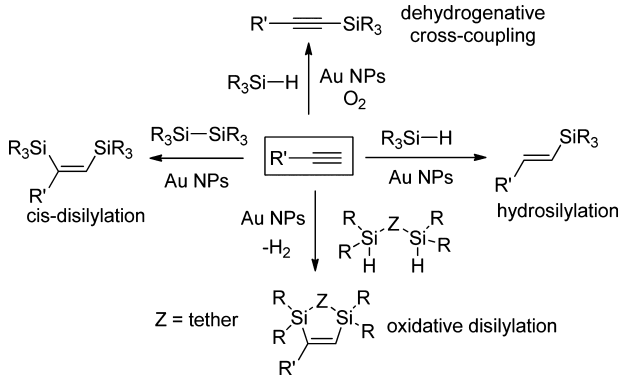
Supporting Information

ABSTRACT: The Au/TiO_2-catalyzed reaction between 1,1,2,2-tetramethyldisilane and terminal alkynes yields substituted 1,4-disila-2,5-cyclohexadienes (1,1,4,4-tetramethyl-1,4-dihydro-1,4-disilines) in moderate to good yields. The reaction proceeds via initial Si–Si activation of disilane by gold nanoparticles to form with alkynes isolable *cis*-1,2-disilyl adducts (*cis*-1,2-bis(dimethylsilyl)ethenes), which, under the reaction conditions, undergo a Au-catalyzed dehydrogenative cycloaddition to a second alkyne molecule, forming the final cycloadducts.

The activation of silanes by supported gold nanoparticles (Au NPs) has been recently recognized.[1] While emphasis has been given on the dehydrogenative hydrolysis/alcoholysis of hydrosilanes and their use as reducing agents of carbonyl compounds,[2] several modes of reactions between silanes and alkynes are uncovered (Scheme 1). Thus, in the presence of Au

Scheme 1. Typical Reaction Modes between Alkynes and Silanes Catalyzed by Supported Gold Nanoparticles



NPs, hydrosilanes undergo addition to alkynes (hydrosilylation), forming alkenylsilanes via a regioselective β-(*E*) pathway.[3] In contrast, 1,1,3,3-tetramethyldisiloxane[4a] and other structurally similar tethered 1,*n*-dihydro-1,*n*-disilanes[4b] yield with alkynes disilyl cycloadducts through an acceptorless dehydrogenative fashion. *Cis*-selective disilylation of terminal alkynes by 1,2-disilanes can be obtained via σ Si–Si bond activation,[5] which likely proceeds via a pathway resembling the oxidative insertion of σ disilanes on ionic Au(I).[6] In the same context, alkynes undergo smooth silaboration via Si–B bond activation of silylboranes, forming addition products with an unusual regioselectivity.[7] Finally, Au nanoparticles supported on a MnO_2-based molecular sieve (OMS-2) catalyze the aerobic dehydrogenative cross-coupling between hydrosilanes and terminal alkynes, forming alkynylsilanes.[8]

Our continuous interest in the use of supported Au NPs on metal oxides to activate silanes[3c,4,5,7,9] prompted us to study the reaction among 1,1,2,2-tetramethyldisilane (HMe_2Si-$SiMe_2H$) and alkynes in the presence of gold. This specific silane possesses an σ Si–Si bond, capable of undergoing insertion by gold and subsequent addition to an alkyne,[5] but also two adjacent Si–H functionalities which could formally induce a dehydrogenative addition pathway. There are a few examples in the literature concerning the reaction between alkynes and 1,1,2,2-tetramethyldisilane in the presence of metal catalysts. The Ni(II)-catalyzed reaction among 1,1,2,2-tetramethyldisilane and alkynes leads to 1-silacyclopentadienes,[10] a reaction pathway involving formation of intermediate metal-silylenes.[11] On the other hand, its Pd(II)-catalyzed reaction with dimethyl acetylenedicarboxylate forms the corresponding *cis*-1,2-disilyl adduct, while phenylacetylene yields a mixture of 1,2-disilylation adduct and 3,4-diphenyl-1-silacyclopentadiene.[12] The 1,2-disilylation path of 1,1,2,2-tetramethyldisilane to alkynes proceeds via formation of the corresponding metal bis-silyl complex,[13] while 1-silacyclopentadienes are generated via insertion of metal-dimethylsilylenes to alkynes.[14]

The reaction between 1,1,2,2-tetramethyldisilane and *p*-tolylacetylene (**1**) was initially examined. We adopted the conditions already applied in the disilylation of alkynes by σ 1,2-disilanes[5] catalyzed by gold (dry 1,2-dichloroethane as solvent, 65 °C, 1 mol % Au/TiO_2). Thus, heating a solution containing the disilane (1.1–1.2 equiv) and 2 molar equiv of alkyne in the presence of the catalyst resulted after 3 h to the formation of two isomeric 1,4-disila-2,5-cyclohexadienes **1a** and **1b** in a relative ratio of 70/30, and 60% isolated yield (Scheme

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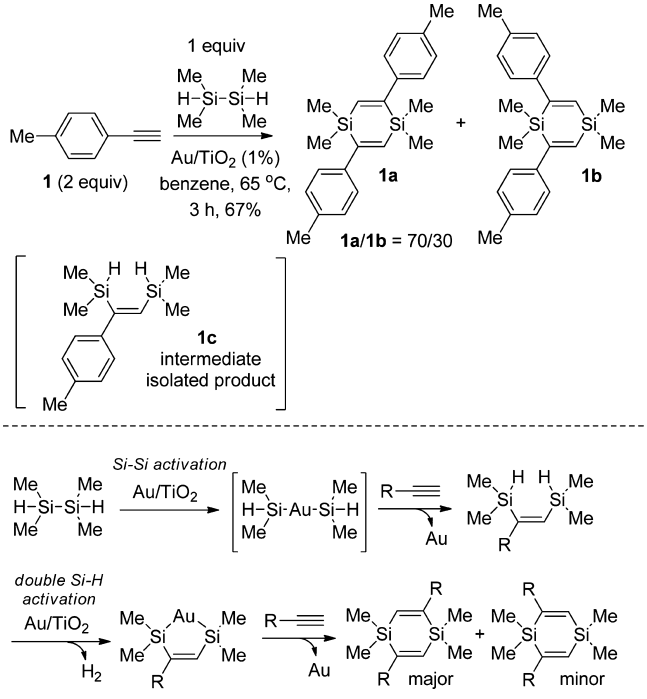
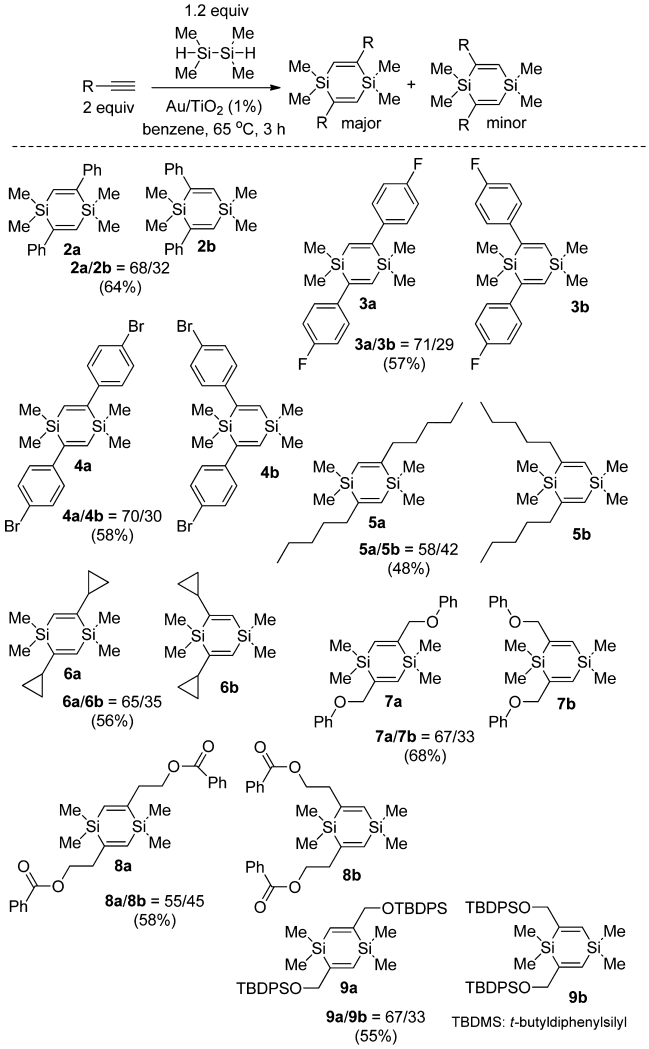
2). Optimizing the reaction conditions through solvent screaning, dry benzene was proven even more appropriate, increasing the isolated yield to 67%. If solvent is not dry, side-products are also formed, such as hydrosilylation from in situ generated dimethylsilane or substituted 2,5-dihydro-1,2,5-oxadisiloles[4] from in situ generated 1,1,3,3-tetramethyldisiloxane (TMDS). Indeed, the anticipated[15] primary products from the Au/TiO_2-catalyzed hydrolysis of 1,1,2,2-tetramethyldisilane are expected to be transient amounts of dimethylsilane (Me_2SiH_2) and dimethylsilanol (Me_2SiHOH). The latter smoothly dimerizes to TMDS ($HMe_2SiOSiMe_2H$), responsible for the formation of 2,5-dihydro-1,2,5-oxadisiloles. Upon mixing the reactants in a 1/1 molar ratio, we were able to isolate the intermediate *cis*-disilylation product **1c**, having two Si−H absorptions in ^{1}H NMR. In an independent experiment, product **1c** reacted smoothly with alkyne **1** (1 equiv), providing, after 6 h at 25 °C, cyclic **1a** and **1b** in a relative ratio of 70/30 and quantitative yield. Therefore, we consider the initial formation of 1,2-disilyl adduct (**1c**), followed by a dehydrogenative cycloaddition of a second alkyne molecule to **1c**, leading to isomeric 1,4-disila-2,5-cyclohexadienes **1a** (major) and **1b** (minor). The dehydrogenative Au/TiO_2-[4b] or Pt(0)-catalyzed[16] cycloaddition of alkynes to analogous to **1c** molecules [e.g., 1,2-bis(dimethylsilyl)benzene] has been well-documented. The structures of isomeric **1a** and **1b** can be easily distinguished by ^{1}H, ^{13}C, and ^{29}Si NMR due to symmetry, as, in **1a**, one absorption for the dimethylsilyl moiety appears, while, in **1b**, two absorptions. The predominant formation of **1a** over **1b** is reasonably attributed to steric factors, as, during the formation of **1b**, higher steric hindrance is developing.

The outcome of reaction between 1,1,2,2-tetramethyldisilane and alkyne **1** prompted us to study the scope and limitations using a series of alkynes (2.0 equiv) and 1.1−1.2 equiv of disilane and dry benzene as solvent. The results are summarized in Scheme 3. In general, with terminal alkynes, two regioisomeric 1,4-disila-2,5-cyclohexadienes are formed in a relative ratio of 2,5-disubstituted/2,6-disubstituted ranging from 71/29 to 55/45, depending on the bulkiness of alkyne substituents. Intermediate 1,2-disilylation products such as **1c** can be detected by GC−MS analysis during the progress of reaction. The isolated yields are moderate to good, primarily due to the sensitivity of the specific disilane toward partial destruction under the reaction conditions. Unfortunately, internal alkynes are unreactive even if performing the reaction at higher temperature, as also occurs in their Au-catalyzed disilylation with other 1,2-disilanes.[5] The reaction products (1,4-disila-2,5-cyclohexadienes) are a class of compounds that have been recently recognized as important building blocks for the design of cross-hyperconjugated molecules.[17] Their so far known synthetic approaches include thermolysis of 1-silacyclopropenes,[18] addition of Pt-silenoids[19] (from disproportionation of pentamethyldisilane) or thermally generated silylenes[20] to alkynes, and the Pd-catalyzed reaction between $Cl(SiMe_2)_3Cl$ and alkynes,[21] a reaction that was proposed to proceed via formation of Pd-silylenes.

Scheme 2. Reaction between 1,1,2,2-Tetramethyldisilane and *p*-Tolylacetylene (1) Catalyzed by Au/TiO_2 and a Mechanistic Analysis



Scheme 3. Formation of Substituted 1,4-Disila-1,4-cyclohexadienes in the Reaction between Terminal Alkynes and 1,1,2,2-Tetramethyldisilane Catalyzed by Au/TiO_2



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As shown in Scheme 2, the most profound pathway involves formation of a Au nanoparticle-disilyl intermediate (HMe_2Si-[Au]-$SiMe_2H$) that adds to alkyne.[5] Then, intermediate 1,2-disilyl adducts undergo oxidative cycloaddition to a second alkyne molecule, a well-established pathway[4] in the presence of gold nanoparticles. The participation of gold silylenes en route to intermediate 1,2-disilyl adducts such as **1c** cannot be excluded; however, this pathway seems less possible at the moment. For instance, conjugated dienes (e.g., 1-phenyl-1,3-butadiene) fail to form dimethylsilyl-diene cycloadducts[20c] under the reaction conditions, while formation of intermediate 1,2-disilyl adducts requires formation of HMe_2Si-[Au]-$SiMe_2H$.

In conclusion, we have presented herein a novel and direct method for the synthesis of substituted 1,4-disila-2,5-cyclohexadienes from the reaction between 1,1,2,2-tetramethyldisilane and terminal alkynes under catalysis by supported gold nanoparticles on TiO_2. The reaction is possibly initiated through σ Si−Si bond activation of disilane by Au to form 1,2-disilylation products with alkynes. The intermediate disilylated adducts undergo, under the reaction conditions, a Au-catalyzed dehydrogenative cycloaddition pathway to a second alkyne molecule, forming the six-membered ring 1,4-disila-2,5-cyclohexadienes.

EXPERIMENTAL SECTION

General. Alkynes used in this study were available from previous studies in our lab. Gold nanoparticles supported on titania (Au/TiO_2) was purchased from Strem chemicals, while 1,1,2,2-tetramethyldisilane from Sigma-Aldrich. The catalyst has an average gold crystallite size of ∼2−3 nm. Benzene and 1,2-dichloroethane (DCE) were distilled over CaH_2 and kept over molecular sieves (4 Å). NMR spectra were recorded on Bruker DPX-300 and Avance-500 instruments. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed with a GC-MS QP 5050 Shimadzu single-quadrupole mass spectrometer. GC analyses were performed by using a Shimadzu GC-17A model equipped with a 60 m HP-5 capillary column. Flash column chromatography for the purification of products was carried out on SiO_2 (silica gel 60, particle size: 0.040−0.063 mm) using hexane as eluent, except for the case of products **8a**/**8b**, where a mixture of hexane/ethyl acetate 80/1 was used.

General Procedure for the Au/TiO_2-Catalyzed Reaction between Alkynes and 1,1,2,2-Tetramethyldisilane. To a dry vial containing the alkyne (0.2 mmol) and 0.12 mmol of 1,1,2,2-tetramethyldisilane (20 μL) in 0.4 mL of dry benzene was added Au/TiO_2 (21 mg, 1.0 mol %) under an inert atmosphere. The reaction mixture was heated at 65 °C for 3 h. Then, the slurry was filtered with the aid of a small amount of solvent through a short pad of silica gel. The filtrate was evaporated under vacuum, and the residue was chromatographed. All products were isolated as white solids.

Characterization of Products. *1,1,4,4-Tetramethyl-2,5-di-p-tolyl-1,4-dihydro-1,4-disiline (**1a**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.20 (d, J = 8.5 Hz, 4H), 7.14 (d, J = 8.5 Hz, 4H), 6.77 (s, 2H), 2.36 (s, 6H), 0.28 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): 160.2, 144.8, 143.3, 136.3, 129.0, 126.4, 21.1, −0.5; ^{29}Si NMR (59.6 MHz, $CDCl_3$): −21.9; HRMS: calcd for $C_{22}H_{28}Si_2$ + H, 349.1808; found 349.1803.

*1,1,4,4-Tetramethyl-2,6-di-p-tolyl-1,4-dihydro-1,4-disiline (**1b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.12 (s, 8H), 6.71 (s, 2H), 2.35 (s, 6H), 0.25 (s, 6H), 0.23 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 161.9, 144.8, 144.4, 136.0, 128.8, 126.1, 21.1, −0.4, −1.1; ^{29}Si NMR (59.6 MHz, $CDCl_3$): −22.9, −24.2; HRMS: calcd for $C_{22}H_{28}Si_2$ + H, 349.1808; found 349.1803.

*(Z)-(1-(p-Tolyl)ethene-1,2-diyl)bis(dimethylsilane) (**1c**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.10 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.51 (d, J = 5.5 Hz, 1H), 4.50 (septet, J = 4.0 Hz, 1H), 4.41−4.35 (m, 1H), 2.33 (s, 3H), 0.23 (d, J = 4.0 Hz, 6H), 0.22 (d, J = 4.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 161.6, 145.1, 144.6, 136.1, 128.8, 126.1, 21.1, −2.8, −2.8; ^{29}Si NMR (59.6 MHz, $CDCl_3$): −21.3, −27.2; HRMS: calcd for $C_{13}H_{22}Si_2$ + H, 235.1338; found 235.1330.

*1,1,4,4-Tetramethyl-2,5-diphenyl-1,4-dihydro-1,4-disiline (**2a**).*[21] ^{1}H NMR (300 MHz, $CDCl_3$): 7.36−7.20 (m, 10H), 6.80 (s, 2H), 0.29 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): 160.6, 146.2, 145.5, 128.3, 126.5, 126.2, −0.6.

*1,1,4,4-Tetramethyl-2,6-diphenyl-1,4-dihydro-1,4-disiline (**2b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.36−7.20 (m, 10H), 6.73 (s, 2H), 0.26 (s, 6H), 0.25 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.1, 147.3, 145.4, 128.1, 126.6, 126.3, −0.5, −1.2; MS (EI): 320 (M^+, 17%), 305 (M^+ − Me, 15%), 203 (12%), 159 (21%), 135 (36%), 105 (32%), 73 (100%).

*2,5-Bis(4-fluorophenyl)-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**3a**).* ^{1}H NMR (500 MHz, $CDCl_3$): 7.24−7.21 (m, 4H), 7.02 (t, J = 8.5 Hz, 4H), 6.74 (s, 2H), 0.27 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): 161.9 (d, $J_{C\text{-}F}$ = 244.0 Hz), 159.6, 145.4, 142.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 127.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), −0.7; HRMS: calcd for $C_{20}H_{22}F_2Si_2$ + H, 357.1306; found 357.1336.

*2,6-Bis(4-fluorophenyl)-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**3b**).* ^{1}H NMR (500 MHz, $CDCl_3$): 7.16−7.13 (m, 4H), 6.98 (t, J = 8.5 Hz, 4H), 6.70 (s, 2H), 0.24 (s, 6H), 0.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 161.8 (d, $J_{C\text{-}F}$ = 243.5 Hz), 160.9, 145.8, 143.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 127.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 114.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), −0.7, −1.3; HRMS: calcd for $C_{20}H_{22}F_2Si_2$ + H, 357.1306; found 357.1336.

*2,5-Bis(4-bromophenyl)-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**4a**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.45 (d, J = 8.0 Hz, 4H), 7.13 (t, J = 8.0 Hz, 4H), 6.75 (s, 2H), 0.26 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.6, 145.9, 145.0, 131.4, 127.9, 120.7, −0.7; HRMS: calcd for $C_{20}H_{22}Br_2Si_2$ + H, 476.9705; found 476.9698.

*2,6-Bis(4-bromophenyl)-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**4b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.43 (d, J = 8.0 Hz, 4H), 7.05 (t, J = 8.0 Hz, 4H), 6.70 (s, 2H), 0.24 (s, 6H), 0.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 160.7, 146.2, 146.0, 131.2, 128.2, 120.4, −0.7, −1.3; HRMS: calcd for $C_{20}H_{22}Br_2Si_2$ + H, 476.9705; found 476.9698.

*1,1,4,4-Tetramethyl-2,5-dipentyl-1,4-dihydro-1,4-disiline (**5a**).* ^{1}H NMR (500 MHz, $CDCl_3$): 6.36 (br t, J = 1.5 Hz, 2H), 2.19 (t, J = 7.0 Hz, 4H), 1.50−1.35 (m, 12H), 0.89 (t, J = 7.0 Hz, 6H), 0.10 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): 162.2, 140.3, 39.5, 31.8, 28.2, 22.6, 14.1, −1.2; HRMS: calcd for $C_{18}H_{36}Si_2$ + H, 309.2434; found 309.2428.

*1,1,4,4-Tetramethyl-2,6-dipentyl-1,4-dihydro-1,4-disiline (**5b**).* ^{1}H NMR (500 MHz, $CDCl_3$): 6.41 (br s, 2H), 2.19 (t, J = 7.0 Hz, 4H), 1.50−1.35 (m, 12H), 0.89 (t, J = 7.0 Hz, 6H), 0.14 (s, 6H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 161.9, 140.3, 39.3, 31.8, 28.3, 22.6, 14.1, −0.9, −1.9; HRMS: calcd for $C_{18}H_{36}Si_2$ + H, 309.2434; found 309.2428.

*2,5-Dicyclopropyl-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**6a**).* ^{1}H NMR (500 MHz, $CDCl_3$): 6.09 (br d, J = 2.0 Hz, 2H), 1.57−1.48 (m, 2H), 0.70−0.64 (m, 4H), 0.52−0.47 (m, 4H), 0.14 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): 162.8, 133.8, 17.6, 6.9, −1.4; HRMS: calcd for $C_{14}H_{24}Si_2$ + H, 249.1495; found 249.1491.

*2,6-Dicyclopropyl-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**6b**).* ^{1}H NMR (500 MHz, $CDCl_3$): 6.10 (br s, 2H), 1.57−1.48 (m, 2H), 0.70−0.64 (m, 4H), 0.52−0.47 (m, 4H), 0.27 (s, 6H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 162.2, 133.9, 17.5, 6.9, −0.8, −2.2; HRMS: calcd for $C_{14}H_{24}Si_2$ + H, 249.1495; found 249.1491.

*1,1,4,4-Tetramethyl-2,5-bis(phenoxymethyl)-1,4-dihydro-1,4-disiline (**7a**).* ^{1}H NMR (500 MHz, $CDCl_3$): 7.29 (t, J = 7.0 Hz, 4H), 6.98−6.90 (m, 6H), 6.73 (t, J = 1.5 Hz, 2H), 4.68 (br d, J = 1.5 Hz, 4H), 0.23 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): 158.8, 156.3, 141.4, 129.4, 120.7, 114.7, 74.6, −1.4; HRMS: calcd for $C_{22}H_{28}O_2Si_2$ + H, 381.1706; found 381.1699.

*1,1,4,4-Tetramethyl-2,6-bis(phenoxymethyl)-1,4-dihydro-1,4-disiline (**7b**).* ^{1}H NMR (500 MHz, $CDCl_3$): 7.29 (t, J = 7.0 Hz, 4H), 6.98−6.90 (m, 6H), 6.77 (br s, 2H), 4.69 (s, 4H), 0.33 (s, 6H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 158.7, 156.0, 141.6, 129.4, 120.7, 114.7, 74.7, −1.4, −1.6; HRMS: calcd for $C_{22}H_{28}O_2Si_2$ + H, 381.1706; found 381.1699.

*(1,1,4,4-Tetramethyl-1,4-dihydro-1,4-disiline-2,5-diyl)bis(ethane-2,1-diyl) Dibenzoate (**8a**).* ^{1}H NMR (300 MHz, $CDCl_3$): 8.02 (d, J =

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8.0 Hz, 4H), 7.55 (t, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 4H), 6.54 (t, J = 1.5 Hz, 2H), 4.41 (t, J = 7.0 Hz, 4H), 2.66 (t, J = 7.0 Hz, 4H), 0.15 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.5, 156.8, 144.0, 132.9, 130.4, 129.5, 128.3, 63.7, 38.0, −1.6; HRMS: calcd for $C_{26}H_{32}O_4Si_2$ + H, 465.1917; found 465.1908.

*(1,1,4,4-Tetramethyl-1,4-dihydro-1,4-disiline-2,6-diyl)bis(ethane-2,1-diyl) Dibenzoate (**8b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 8.02 (d, J = 8.0 Hz, 4H), 7.55 (t, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 4H), 6.59 (br s, 2H), 4.41 (t, J = 7.0 Hz, 4H), 2.66 (t, J = 7.0 Hz, 4H), 0.26 (s, 6H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.5, 156.0, 144.4, 132.9, 130.4, 129.5, 128.3, 63.7, 38.0, −1.3, −2.2; HRMS: calcd for $C_{26}H_{32}O_4Si_2$ + H, 465.1917; found 465.1908.

*2,5-Bis(((tert-butyldiphenylsilyl)oxy)methyl)-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**9a**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.70−7.65 (m, 8H), 7.44−7.34 (m, 12H), 6.76 (t, J = 1.5 Hz, 2H), 4.36 (d, J = 1.5 Hz, 4H), 1.08 (s, 18H), 0.07 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.2, 137.0, 135.5, 133.6, 129.6, 127.6, 68.6, 26.9, 19.3, −1.5; HRMS: calcd for $C_{42}H_{56}O_2Si_4$ + H, 705.3436; found 705.3421.

*2,6-Bis(((tert-butyldiphenylsilyl)oxy)methyl)-1,1,4,4-tetramethyl-1,4-dihydro-1,4-disiline (**9b**).* ^{1}H NMR (300 MHz, $CDCl_3$): 7.70−7.65 (m, 8H), 7.44−7.34 (m, 12H), 6.84 (br s, 2H), 4.32 (s, 4H), 1.07 (s, 18H), 0.15 (s, 6H), −0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.4, 137.8, 135.5, 133.6, 129.6, 127.6, 68.6, 26.9, 19.3, −1.2, −2.0; HRMS: calcd for $C_{42}H_{56}O_2Si_4$ + H, 705.3436; found 705.3421.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all products. 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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