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Iridium-Catalyzed Hydrosilylation of Unactivated Alkenes: Scope, and Application to Late-Stage Functionalization

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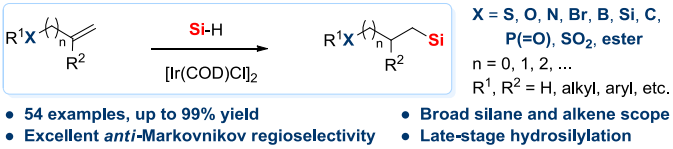
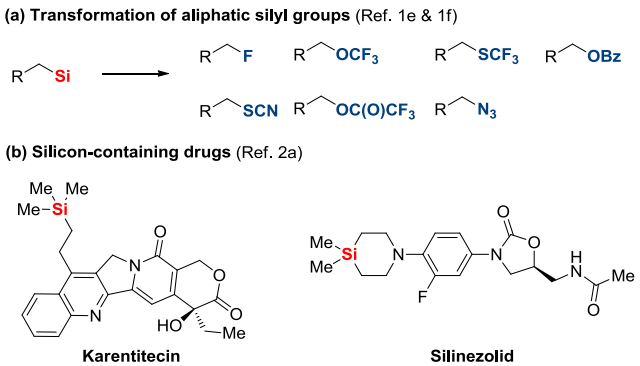
KEYWORDS: Iridium, hydrosilylation, alkene, late-stage, catalysis



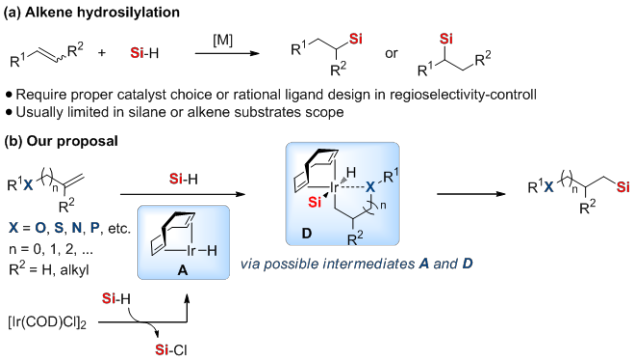
ABSTRACT: Highly efficient and general Ir-catalyzed hydrosilylation of unactivated alkenes with excellent *anti*-Markovnikov regioselectivity was described. A broad scope of hydrosilylated products were synthesized economically and conveniently from commercially or naturally available compounds, which provides versatile valuable precursors for organic and medicinal studies.

Organosilicon compounds are intriguing reagents in organic transformations because of their great advantages in stability, solubility, non-toxicity, easy-handling, accessibility, and selectivity (Figure 1, **a**).[1] Moreover, benefiting from the unique atomic properties of silicon, silicon analogues play important roles in drug discovery (Figure 1, **b**).[2] Alkene hydrosilylation is one major approach widely used in industry to provide commodity silicones after the Direct Process.[3] However, application of this atom-economic strategy in fine chemical synthesis, such as the above-mentioned areas, is much less common (Scheme 1, **a**). Mild and efficient methods for construction of organosilicons with broad substrate scope and high selectivity are still in urgent desire.

Figure 1. Selected examples of organosilicon compounds' applications in organic transformations and pharmaceuticals.



Scheme 1. Hydrosilylation of alkenes.

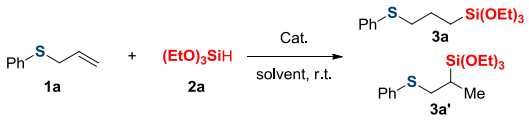


Iridium complexes are powerful tools in silylation of a wide variety of functional groups.[4] Surprisingly, despite usually recognized as one main kind of precious metal catalysts in alkene hydrosilylation, reports on exploitation of iridium complexes for this process are rare. Till now, most of related works were published as patents, which mainly focused on simple terminal alkenes.[5,6] Inspired by this research vacancy, a few works were released recently.[7-10] Shimada reported the iridium-catalyzed hydrosilylation of allyl acetates[8] and sulfur-containing olefins[10]. Kühn gave a mechanistic study on the iridium-catalyzed hydrosilylation of allyl compounds.[9] Recently, one of us, together with Sun and Wu, developed iridium-catalyzed hydrosilylation of internal thioalkynes with excellent regio- and stereoselectivity.[11] Generation of intermediate Ir(I) hydride **A** (in Scheme 1, **b**) is presumptively crucial in this process, which we envisioned is probably one key factor in other iridium-catalyzed hydrosilylation processes as well.[10, 11] Meanwhile, existence of heteroatoms or functional groups that can coordinate to iridium center might facilitate these catalytic conversions. Herein, we demonstrate our research on the Ir-catalyzed hydrosilylation of unactivated alkenes with

excellent *anti*-Markovnikov regioselectivity and high efficiency, which provides complementary examples and additional insight to previous reports.[5-10, 12] This catalytic system is suitable for a broad substrate scope, especially for those containing heteroatoms. More importantly, it works effectively on late-stage hydrosilylation, which is rarely reported before.

We initiated this study with phenyl allyl sulfide **1a** as the model substrate and triethoxysilane **2a** as the silylation reagent (Table 1). Several iridium complexes were investigated by using deuterated chloroform as the solvent, among which $[Ir(COD)Cl]_2$ was identified as the most efficient catalyst, affording linear product **3a** in 82% NMR yield with excellent regioselectivity (Entry 1-4). Chlorinated solvents, such as dichloromethane and dichloroethane, gave better results in this process (Entry 5-13). A slightly decreased yield of 82% was observed when the loading amount of the catalyst was reduced to 0.5 mol % (Entry 14). Furthermore, this reaction could be carried out in neat status as most industrial productions do, though providing a moderate yield (Entry 15).

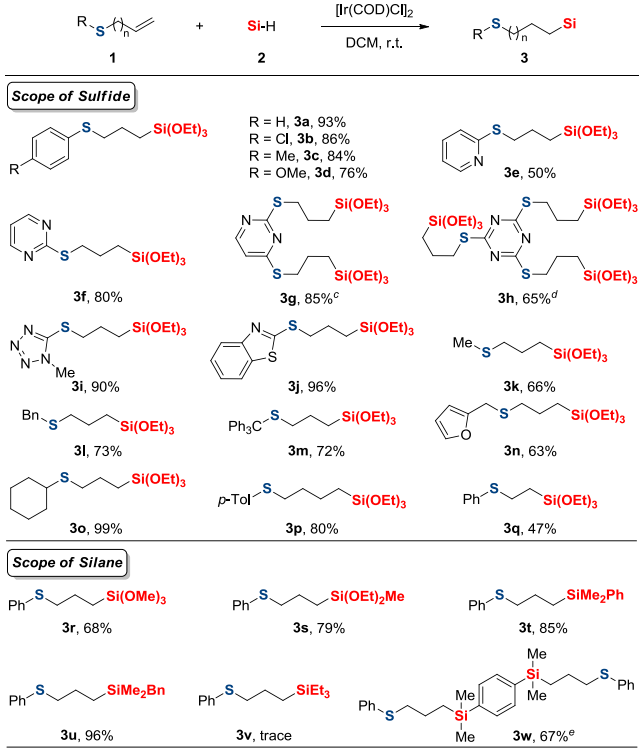
Table 1. Optimization of Reaction Conditions.



Entry	Cat.	Solvent	Yield[b]	**3a**/**3a'**[b]
1	$[Ir(COD)Cl]_2$	$CDCl_3$	82	>99:1
2	$[Ir(COD)(OMe)]_2$	$CDCl_3$	48	>99:1
3	$[Ir(COE)_2Cl]_2$	$CDCl_3$	17	--
4	$[Cp^*IrCl_2]_2$	$CDCl_3$	<5	--
5	$[Ir(COD)Cl]_2$	DCM	93	>99:1
6	$[Ir(COD)Cl]_2$	DCE	89	>99:1
7	$[Ir(COD)Cl]_2$	THF	55	--
8	$[Ir(COD)Cl]_2$	MeCN	47	--
9	$[Ir(COD)Cl]_2$	DMF	10	--
10	$[Ir(COD)Cl]_2$	1,4-Dioxane	52	--
11	$[Ir(COD)Cl]_2$	Toluene	36	--
12	$[Ir(COD)Cl]_2$	EtOH	45	--
13	$[Ir(COD)Cl]_2$	H_2O	n.d.	--
14[c]	$[Ir(COD)Cl]_2$	DCM	82	>99:1
15	$[Ir(COD)Cl]_2$	neat	61	>99:1

[a]Reaction conditions: The mixture of **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.) and catalyst (0.002 mmol, 2 mol %) in solvent (0.50 mL) was stirred for 6 h under room temperature. [b]Yield and ratio were determined by ^1H NMR spectroscopy using dimethyl sulfone as internal standard. [c]0.5 mol % of catalyst was used.

Table 2. Scope of alkenyl sulfides and silanes.



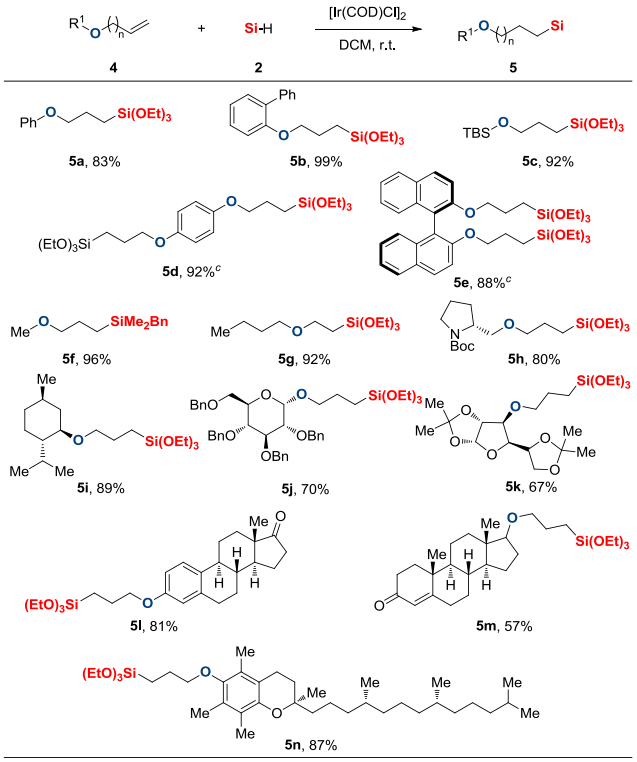
[a]Reaction conditions: The mixture of **1** (0.50 mmol, 1.0 equiv.), **2** (0.75 mmol, 1.5 equiv.) and catalyst (0.01 mmol, 2 mol %) in solvent (2.0 mL) was stirred for 6 h under room temperature. [b]Isolated yield. [c]3.0 Equivalent of silane was used. [d]4.5 Equivalent of silane was used. [e]Ratio of allylic sulfide and silane is 3:1.

With the optimized condition in hand, a variety of alkenes containing sulfur atom were tested to react with different silanes (Table 2). Good to excellent yields were observed in the reactions of aryl allyl sulfides bearing diverse functional groups (**3a** to **3d**). As Shimada has reported one similar work mainly covering simple aryl and aliphatic sulfur-containing olefins,[10] we turned our attention to more complexed substrates. *N*-Heterocycles are common structures in drugs. To probe the efficiency of this catalytic system, several substrates containing different types of *N*-heterocycles, including pyridine, pyrimidine, triazine, tetrazole, and benzo[*d*]thiazole, were investigated (**3e** to **3j**). Related products were afforded in moderate to high yields with excellent regioselectivity in all cases. This system is also applicable to various alkyl allyl sulfides (**3k** to **3o**). Both homoallylic and vinylic sulfides performed well under the mild condition (**3p** & **3q**). Next, we evaluated the silane scope in this process, and found that several familiar silanes, including $(MeO)_3SiH$, $(EtO)_2MeSiH$, $PhMe_2SiH$, and $BnMe_2SiH$, could react with the allylic sulfides smoothly, providing the desired products **3r**-**3u** with high efficiency and selectivity. Only a trace amount of product **3v** was detected while Et_3SiH was used. The success of using disilane as reaction partner permits the potential application of this new developed catalytic system in linear polymer and porous organic polymer synthesis (**3w**).

We then turned our attention to oxygen-containing olefins (Table 3). This catalytic system was proved to be effective

in hydrosilylation of several selected representative aryl/alkyl allyl ethers, including bis(allyl) ethers derived from hydroquinone and BINOL (**5a** to **5f**). Vinyl ether could be hydrosilylated efficiently as well (**5g**). Encouraged by these positive results, more efforts were put on exploring late-stage hydrosilylation of nature molecule analogues. Inspiringly, allylic ether derivatives from proline, menthol, glucose, and glucofuranose were tolerated well, giving corresponding *anti*-Markovnikov addition products in good to excellent yields (**5h** to **5k**). Allyl ether analogues of estrone, testosterone, and vitamin E were also successfully modified by using this hydrosilylation protocol (**5l** to **5n**).

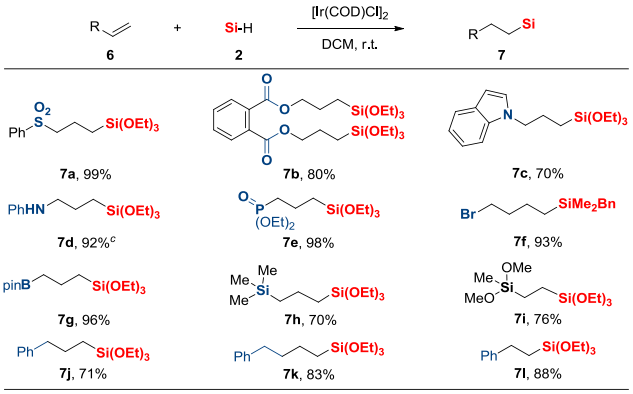
Table 3. Scope of olefins containing oxygen atom.



[a]Reaction conditions: The mixture of **4** (0.50 mmol, 1.0 equiv.), **2** (0.75 mmol, 1.5 equiv.) and catalyst (0.01 mmol, 2 mol %) in solvent (2.0 mL) was stirred for 6 h under room temperature. [b]Isolated yield. [c]3.0 Equivalent of silane was used.

Having examined alkenes containing chalcogens, we took a further step to check the capacity of the Ir-catalyzed hydrosilylation processes for functional groups or other elements (Table 4). Allylic sulfone and ester were compatible with this method (**7a** & **7b**). The reactions of allylic tertiary and secondary amines provided desired hydrosilylated product (**7c** & **7d**). Allyl phosphine showed poor reactivity, which might be due to the coordination of phosphine atom with iridium which obstructs the formation of active catalyst intermediate **A**, as the reaction of allylic phosphonate with $(EtO)_3SiH$ proceeded smoothly under this condition (**7e**). The investigation of this protocol for allyl bromide and allyl Bpin gave satisfied results with excellent yields (**7f** & **7g**). Sterically bulky allylsilane and vinylsilane were converted into related products in good yields (**7h** & **7i**). As hydrosilylation of alkyl/aryl olefins has been addressed with numerous catalysts, we just listed several examples here (**7j** to **7l**).

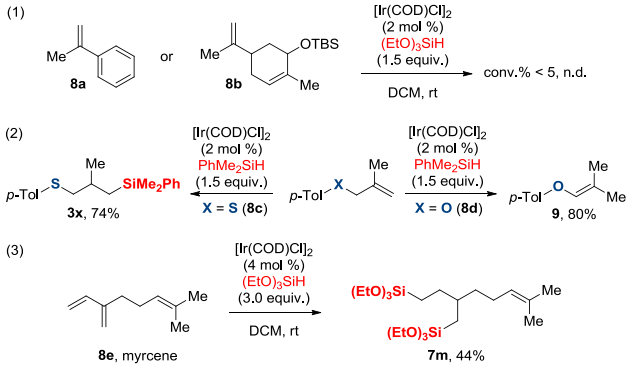
Table 4. Hydrosilylation of other olefins.



[a]Reaction conditions: The mixture of **6** (0.50 mmol, 1.0 equiv.), **2** (0.75 mmol, 1.5 equiv.) and catalyst (0.01 mmol, 2 mol %) in solvent (2.0 mL) was stirred for 6 h under room temperature. [b]Isolated yield. [c]3.0 Equivalent of silane was used.

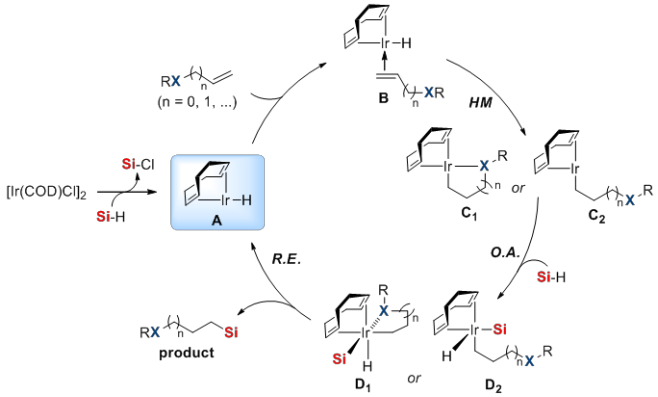
Sterically hindered disubstituted terminal alkenes were investigated as well (Scheme 2). No desired product was observed from **8a** or **8b** (Eq. 1). **8c** could be hydrosilylated to afford **3x** in 74% yield, while isomerization of **8d** to **9** was the major phenomenon under the same condition (Eq. 2). Notably, both of the terminal alkenyl groups in myrcene (**8e**) were hydrosilylated (**7m**, Eq. 3).

Scheme 2. Hydrosilylation of disubstituted terminal alkenes.



Based on previous reports and our observation,[10, 11] a plausible mechanism is given in Scheme 3. Heteroatoms or functional groups in the substrates is presumed to coordinate to iridium center and could help to stabilize possible intermediates **C** and **D**, which would facilitate the catalytic cycle. This coordination effect might be more critical towards disubstituted terminal alkenes. More detailed mechanism studies are underway.

Scheme 3. Proposed mechanism.



HM: hydrometalation; **O.A.**: oxidative addition; **R.E.**: reductive elimination

In summary, we demonstrated the efficiency and compatibility of one simple, mild iridium catalytic system in hydrosilylation of unactivated alkenes. A wide scope of *anti*-Markovnikov hydrosilylated products with excellent regioselectivity were afforded conveniently from commercially or naturally available compounds, providing versatile valuable blocks for organic and medicinal studies.

EXPERIMENTAL SECTION

General Information. All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using dry solvents. Flash column chromatography was performed over silica gel (200-300 mesh) purchased from Qingdao Puke Co., China. Silanes and common organic chemicals were purchased from commercial suppliers, such as Sigma-Aldrich® and J&K® Scientific Ltd., and used as received. Iridium complexes were purchased from Strem® Chemicals, Inc. ^{1}H and ^{13}C NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm). Mass spectra were collected on an Thermo Scientific GC/MS ISQ7000 system, or a Xevo G2 Qtof mass spectrometer.

Safety Note. Triethoxysilane is a corrosive and flammable liquid. Methyldiethoxysilane is advised to be used for large-scale (> 1.0 g) reactions instead.

General Procedure for Hydrosilylation. In a glove box, to an oven-dried 5-mL vial was added the alkene (0.50 mmol), the silane (0.75 mmol), $[Ir(COD)Cl]_2$ (0.008 mmol), and DCM (2.0 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 4 h, and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 0-50% EtOAc in petroleum ether) to give the desired product. Compounds **3a**,[10] **3e**,[13] **3i**,[14] **3j**,[13] **3k**,[15] **3l**,[16] **3o**,[17] **3q**,[18] **3r**,[10] **3s**,[10] **5a**,[19] **5c**,[20] **5e**,[21] **5f**,[22] **5g**,[23] **5i**,[24] **5n**,[25] **7a**,[26] **7b**,[27] **7d**,[28] **7f**,[29] **7g**,[30] **7h**,[28] **7j**,[31] **7k**,[28] **7l**[31] are known compounds. Result of MS was given for known compounds, and result of HRMS was given for unknown compounds.

*Triethoxy(3-(phenylthio)propyl)silane (**3a**)* was prepared as pale yellow oil from **1a** (0.50 mmol, 75.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 93% yield (146.2 mg, *l*/*b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2 H), 7.31-7.25 (m, 2 H), 7.20-7.14 (m, 1 H), 3.82 (q, *J* = 8.0 Hz, 6 H), 2.98 (t, *J* = 7.2 Hz, 2 H), 1.84-1.75 (m, 2 H), 1.23 (t, *J* = 8.0 Hz, 9 H), 0.81 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.7, 129.0, 128.7, 125.6, 58.3, 36.4, 22.7, 18.2, 9.7; MS (ESI) *m*/*z* (relative intensity) 314.1 (5), 163.1 (100) $[M]^+$.

*(3-((4-Chlorophenyl)thio)propyl)triethoxysilane (**3b**)* was prepared as pale yellow oil from **1b** (0.50 mmol, 92.4 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 86% yield (150.1 mg, *l*/*b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (m, 4 H), 3.80 (q, *J* = 6.8 Hz, 6 H), 2.92 (t, *J* = 7.2 Hz, 2 H), 1.79-1.70 (m, 2 H), 1.20 (t, *J* = 6.8 Hz, 9 H), 0.79-0.74 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.3, 131.5, 130.3, 128.8, 58.3, 36.5, 22.6, 18.2, 9.7; HRMS *m*/*z* (CI) calcd. for $C_{15}H_{25}ClO_3SSiNa$ $(M+Na)^+$ 371.0880, found 371.0898.

*Triethoxy(3-(p-tolylthio)propyl)silane (**3c**)* was prepared as pale yellow oil from **1c** (0.50 mmol, 82.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 84% yield (138.0 mg, *l*/*b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 3.79 (q, *J* = 6.8 Hz, 6 H), 2.90 (t, *J* = 7.2 Hz, 2 H), 2.30 (s, 3 H), 1.77-1.69 (m, 2 H), 1.20 (t, *J* = 6.8 Hz, 9 H), 0.79-0.75 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.7, 132.8, 129.9, 129.5, 58.3, 37.1, 22.7, 20.8, 18.2, 9.7; HRMS *m*/*z* (CI) calcd. for $C_{16}H_{28}O_3SSiNa$ $(M+Na)^+$ 351.1426, found 351.1419.

*Triethoxy(3-((4-methoxyphenyl)thio)propyl)silane (**3d**)* was prepared as pale yellow oil from **1d** (0.50 mmol, 90.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 76% yield (130.9 mg, *l*/*b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2 H), 6.78-6.74 (m, 2 H), 3.72 (q, *J* = 6.8 Hz, 6 H), 3.71 (s, 3 H), 2.77 (t, *J* = 7.2 Hz, 2 H), 1.66-1.58 (m, 2 H), 1.13 (t, *J* = 6.8 Hz, 9 H), 0.70-0.66 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.7, 133.0, 126.6, 114.4, 58.3, 55.3, 38.7, 22.8, 18.2, 9.6; HRMS *m*/*z* (CI) calcd. for $C_{16}H_{28}O_4SSiNa$ $(M+Na)^+$ 367.1375, found 367.1365.

*2-((3-(Triethoxysilyl)propyl)thio)pyridine (**3e**)* was prepared as pale yellow oil from **1e** (0.50 mmol, 75.6 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 53% yield (83.6 mg, *l*/*b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44-8.42 (m, 1 H), 7.50-7.45 (m, 1 H), 7.19 (d, *J* = 8.4 Hz, 1 H), 7.00-6.95 (m, 1 H), 3.83 (q, *J* = 7.2 Hz, 6 H), 3.21 (t, *J* = 7.2 Hz, 2 H), 1.90-1.81 (m, 2 H), 1.23 (t, *J* = 7.2 Hz, 9 H), 0.84 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 149.4, 135.8, 122.1, 119.1, 58.4, 33.1, 23.0, 18.3, 10.0; MS (ESI) *m*/*z* (relative intensity) 315.4 (5), 55.1 (100) $[M]^+$.

*2-((3-(Triethoxysilyl)propyl)thio)pyrimidine (**3f**)* was prepared as pale yellow oil from **1f** (0.50 mmol, 76.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 80% yield (126.6 mg, *l*/*b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.2 Hz, 2 H), 6.92 (dd, *J*$_1$ = *J*$_2$ = 5.2 Hz, 1 H), 3.80 (q, *J* = 6.8 Hz, 6 H), 3.16 (t, *J* = 7.6 Hz, 2 H), 1.89-1.80 (m, 2 H), 1.20 (t, *J* = 6.8 Hz, 9 H), 0.80 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.6, 157.0, 116.1, 58.2, 33.6, 22.7, 18.1, 9.8; HRMS *m*/*z* (CI) calcd. for $C_{13}H_{24}N_2O_3SSiNa$ $(M+Na)^+$ 339.1175, found 339.1179.

*2, 4-Bis((3-(triethoxysilyl)propyl)thio)pyrimidine (**3g**)* was prepared as pale yellow oil from **1g** (0.50 mmol, 112.17 mg) and $(EtO)_3SiH$ (1.50 mmol, 251.6 mg), according to the General Procedure in 85% yield (235.0 mg, *l*/*b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 5.2 Hz, 1 H), 6.78 (d, *J* = 5.2 Hz, 1 H), 3.85-3.79 (m, 12 H), 3.20-3.14 (m, 4 H), 1.91-1.80 (m, 4 H), 1.24-1.20 (m, 18 H), 0.83-0.76 (m, 4 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.6, 170.0, 154.1, 114.0, 58.23, 58.19, 33.6, 31.9, 22.8, 22.7, 18.1, 9.9; HRMS *m*/*z* (CI) calcd. for $C_{22}H_{45}N_2O_6S_2Si_2$ $(M+H)^+$ 553.2258, found 553.2272.

*2, 4, 6-Tris((3-(triethoxysilyl)propyl)thio)-1, 3, 5-triazine (**3h**)* was prepared as pale yellow oil from **3h** (0.50 mmol, 148.7 mg) and $(EtO)_3SiH$ (2.25 mmol, 377.4 mg), according to the General Procedure in 65% yield (256.8 mg, *l*/*b* > 99:1): ^{1}H NMR

(400 MHz, $CDCl_3$) δ 3.81 (q, *J* = 6.8 Hz, 18 H), 3.10 (t, *J* = 7.2 Hz, 6 H), 1.87-1.78 (m, 6 H), 1.21 (t, *J* = 6.8 Hz, 27 H), 0.79-0.74 (m, 6 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 179.4, 58.3, 33.1, 22.7, 18.2, 9.9; HRMS *m/z* (CI) calcd. for $C_{30}H_{63}N_3O_9S_3Si_3Na$ $(M+Na)^+$ 812.2932, found 812.2925.

*1-Methyl-5-((3-(triethoxysilyl)propyl)thio)-1H-tetrazole (**3i**)* was prepared as pale yellow oil from **1i** (0.50 mmol, 78.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 90% yield (144.2 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3 H), 3.79 (q, *J* = 7.2 Hz, 6 H), 3.35 (t, *J* = 7.2 Hz, 2 H), 1.94-1.85 (m, 2 H), 1.19 (t, *J* = 7.2 Hz, 9 H), 0.76 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 154.2, 58.3, 35.9, 33.2, 23.1, 18.1, 9.7; MS (ESI) *m/z* (relative intensity) 320.1 (5), 163.1 (100) $[M]^+$.

*2-((3-(Triethoxysilyl)propyl)thio)benzo[d]thiazole (**3j**)* was prepared as pale yellow oil from **1j** (0.50 mmol, 103.7 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 96% yield (178.4 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.45-7.40 (m, 1 H), 7.33-7.28 (m, 1 H), 3.85 (q, *J* = 7.2 Hz, 6 H), 3.40 (t, *J* = 7.2 Hz, 2 H), 2.03-1.94 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 9 H), 0.88-0.83 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, CDC_{l_3}) δ 167.2, 153.4, 135.2, 125.9, 124.0, 121.4, 120.8, 58.4, 36.4, 23.0, 18.2, 9.9; MS (ESI) *m/z* (relative intensity) 371.1 (5), 167.0 (100) $[M]^+$.

*Triethoxy(3-(methylthio)propyl)silane (**3k**)* was prepared as pale yellow oil from **1k** (0.50 mmol, 44.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 66% yield (83.3 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (q, *J* = 7.2 Hz, 6 H), 2.52 (t, *J* = 6.8 Hz, 2 H), 2.09 (s, 1 H), 1.78-1.69 (m, 2 H), 1.22 (t, *J* = 7.2 Hz, 9 H), 0.74 (t, *J* = 8.4 Hz, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 58.4, 37.2, 22.6, 18.3, 18.3, 9.7; MS (ESI) *m/z* (relative intensity) 252.1 (7), 163.1 (100) $[M]^+$.

*(3-(Benzylthio)propyl)triethoxysilane (**3l**)* was prepared as pale yellow oil from **1l** (0.50 mmol, 82.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 73% yield (119.9 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 4 H), 7.25-7.20 (m, 1 H), 3.80 (q, *J* = 6.8 Hz, 6 H), 3.70 (s, 2 H), 2.44 (t, *J* = 7.2 Hz, 2 H), 1.72-1.64 (m, 2 H), 1.22 (t, *J* = 6.8 Hz, 9 H), 0.72-0.68 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 138.6, 128.8, 128.4, 126.8, 58.3, 36.1, 34.4, 22.7, 18.3, 9.9; MS (ESI) *m/z* (relative intensity) 328.1 (5), 91.0 (100) $[M]^+$.

*Triethoxy(3-(tritylthio)propyl)silane (**3m**)* was prepared as white powder from **1m** (0.50 mmol, 158.2 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 72% yield (173.1 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ7.52-7.48 (m, 6 H), 7.36-7.32 (m, 6 H), 7.29-7.24 (m, 3 H), 3.83 (q, *J* = 7.2 Hz, 6 H), 2.28 (t, *J* = 7.2 Hz, 2H), 1.66-1.58 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 9 H), 0.68 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 145.1, 129.6, 127.8, 126.5, 66.3, 58.3, 35.1, 22.3, 18.2, 10.3; HRMS *m/z* (CI) calcd. for $C_{28}H_{36}O_3SSiNa$ $(M+Na)^+$ 503.2052, found 503.2048.

*Triethoxy(3-((furan-2-ylmethyl)thio)propyl)silane (**3n**)* was prepared as pale yellow oil from **1n** (0.50 mmol, 77.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 63% yield (100.3 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 1 H), 6.31-6.29 (m, 1 H), 6.18-6.16 (m, 1 H), 3.81 (q, *J* = 7.2 Hz, 6 H), 3.71 (s, 2 H), 2.53 (t, *J* = 7.6 Hz, 2 H), 1.73-1.64 (m, 2 H), 1.22 (t, *J* = 7.2 Hz, 9 H), 0.74-0.69 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 151.9, 142.0, 110.3, 107.2, 58.4, 34.8, 28.1, 22.8, 18.3, 9.9; HRMS *m/z* (CI) calcd. for $C_{14}H_{26}O_4SSiNa$ $(M+Na)^+$ 341.1219, found 341.1228.

*(3-(Cyclohexylthio)propyl)triethoxysilane (**3o**)* was prepared as pale yellow oil from **1o** (0.50 mmol, 78.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 99% yield (158.7 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (q, *J* = 6.8 Hz, 6 H), 2.65-2.59 (m, 1 H), 2.55 (t, *J* = 7.2 Hz, 2 H), 1.98-1.95 (m, 2 H), 1.78-1.75 (m, 2 H), 1.73-1.65 (m, 2 H), 1.33-1.25 (m, 6 H), 1.23 (t, *J* = 6.8 Hz, 9 H), 0.77-0.72 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 58.3, 43.2, 33.7, 33.1, 26.1, 25.8, 23.6, 18.2, 9.9; MS (ESI) *m/z* (relative intensity) 320.1 (6), 163.1 (100) $[M]^+$.

*Triethoxy(4-(p-tolylthio)butyl)silane (**3p**)* was prepared as pale yellow oil from **1p** (0.50 mmol, 89.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 80% yield (137.0 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.22 (m, 2 H), 7.09-7.05 (m, 2 H), 3.80 (q, *J* = 6.8 Hz, 6 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 2.30 (s, 3 H), 1.70-1.62 (m, 2 H), 1.58-1.50 (m, 2 H), 1.20 (t, *J* = 6.8 Hz, 9 H), 0.65-0.61 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 135.7, 133.1, 129.7, 129.5, 58.2, 33.8, 32.4, 22.0, 20.8, 18.2, 9.9; HRMS *m/z* (CI) calcd. for $C_{17}H_{30}O_3SSiNa$ $(M+Na)^+$ 365.1583, found 365.1580.

*Triethoxy(2-(phenylthio)ethyl)silane (**3q**)* was prepared as pale yellow oil from **1q** (0.50 mmol, 68.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 47% yield (70.6 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2 H), 7.23-7.19 (m, 2 H), 7.18-7.13 (m, 1 H), 3.82 (q, *J* = 6.8 Hz, 6 H), 2.77-2.73 (m, 2 H), 1.23 (t, *J* = 6.8 Hz, 9 H), 1.02-0.97 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 144.6, 128.2, 127.7, 125.6, 58.3, 28.8, 18.3, 12.5; MS (ESI) *m/z* (relative intensity) 300.1 (5), 163.1 (100) $[M]^+$.

*Trimethoxy(3-(phenylthio)propyl)silane (**3r**)* was prepared as pale yellow oil from **1a** (0.50 mmol, 75.1 mg) and $(MeO)_3SiH$ (0.75 mmol, 91.6 mg), according to the General Procedure in 68% yield (92.6 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2 H), 7.31-7.25 (m, 2 H), 7.21-7.14 (m, 1 H), 3.57 (s, 9 H), 2.97 (t, *J* = 7.2 Hz, 2 H), 1.83-1.74 (m, 2 H), 0.85-0.81 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 136.6, 129.0, 128.8, 125.7, 50.4, 36.3, 22.5, 8.4; MS (ESI) *m/z* (relative intensity) 272.1 (12), 121.0 (100) $[M]^+$.

*Diethoxy(methyl)(3-(phenylthio)propyl)silane (**3s**)* was prepared as pale yellow oil from **1a** (0.50 mmol, 75.1 mg) and , $(EtO)_2MeSiH$ (0.75 mmol, 100.8 mg)according to the General Procedure in 79% yield (112.4 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 2 H), 7.19-7.14 (m, 2 H), 7.08-7.03 (m, 1 H), 3.64 (q, *J* = 7.2 Hz, 6 H), 2.85 (t, *J* = 7.2 Hz, 2 H), 1.67-1.58 (m, 2 H), 1.10 (t, *J* = 7.2 Hz, 9 H), 0.69-0.64 (m, 2 H), 0.00 (s, 3 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 136.7, 129.0, 128.8, 125.7, 58.1, 36.7, 22.8, 18.3, 13.4, -4.9; MS (ESI) *m/z* (relative intensity) 284.09 (9), 133.1 (100) $[M]^+$.

*Dimethyl(phenyl)(3-(phenylthio)propyl)silane (**3t**)* was prepared as pale yellow oil from **1a** (0.50 mmol, 75.1 mg) and $PhMe_2SiH$ (0.75 mmol, 102.3 mg), according to the General Procedure in 85% yield (121.8 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2 H), 7.42-7.39 (m, 2 H), 7.39-7.38 (m, 1 H), 7.34-7.27 (m, 4 H), 7.22-7.18 (m, 1 H), 2.96 (t, *J* = 7.2 Hz, 2 H), 1.76-1.68 (m, 2 H), 0.99-0.93 (m, 2 H), 0.31 (s, 6 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 138.9, 136.8, 133.5, 129.0, 128.9, 128.8, 127.8, 125.6, 37.1, 23.7, 15.2, -3.1; HRMS *m/z* (CI) calcd. for $C_{17}H_{22}SSiNa$ $(M+Na)^+$ 309.1109, found 309.1132.

*Benzyldimethyl(3-(phenylthio)propyl)silane (**3u**)* was prepared as pale yellow oil from **1a** (0.50 mmol, 75.1 mg) and $BnMe_2SiH$ (0.75 mmol, 112.8 mg), according to the General Procedure in 96% yield (144.3 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4 H), 7.26-7.22 (m, 2 H), 7.21-7.18 (m, 1 H), 7.13-7.07 (m, 1 H), 7.02-6.98 (m, 2 H), 2.94 (t, *J* = 7.2 Hz, 2 H), 2.11 (s, 2 H), 1.70-1.62 (m, 2 H), 0.74-0.65 (m, 2 H),

0.00 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.0, 136.8, 128.9, 128.8, 128.2, 128.0, 125.7, 123.9, 37.1, 25.4, 23.8, 14.4, -3.7; HRMS *m/z* (CI) calcd. for $C_{18}H_{24}SSiNa$ $(M+Na)^+$ 323.1266, found 323.1260.

*1,4-Bis(dimethyl(3-(phenylthio)propyl)silyl)benzene (**3w**)* was prepared as pale yellow oil from **1a** (1.00 mmol, 150.2 mg) and 1,4-bis (dimethylsilyl)benzene (0.50 mmol, 97.2 mg)according to the General Procedure in 67% yield (165.8 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 4 H), 7.35-7.22 (m, 8 H), 7.21-7.18 (m, 2 H), 2.96 (t, *J* = 7.2 Hz, 4 H), 1.79-1.57 (m, 4 H), 0.95 (t, *J* = 8.0 Hz, 4 H), 0.29 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.6, 136.8, 132.9, 129.1, 128.8, 125.7, 37.2, 23.7, 15.2, -3.2; HRMS *m/z* (CI) calcd. for $C_{28}H_{38}S_2Si_2Na$ $(M+Na)^+$ 517.1850, found 517.1829.

*Dimethyl(2-methyl-3-(p-tolylthio)propyl)(phenyl)silane (**3x**)* was prepared as pale yellow oil from **8c** (0.50 mmol, 89.1 mg) and $PhMe_2SiH$ (0.75 mmol, 102.3 mg), according to the General Procedure in 74% yield (116.3 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2 H), 7.46-7.41 (m, 3 H), 7.30-7.24 (m, 2 H), 7.18-7.12 (m, 2 H), 2.94-2.79 (m, 2 H), 2.41 (s, 3 H), 2.05-1.90 (m, 1 H), 1.30-1.20 (m, 1 H), 1.10 (d, *J* = 6.8 Hz, 3 H), 0.90-0.80 (m, 1 H), 0.39 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.4, 135.6, 133.5, 129.8, 129.5, 128.8, 127.7, 45.2, 29.7, 23.5, 22.3, 20.9, -2.0, -2.3; HRMS *m/z* (CI) calcd. for $C_{19}H_{30}NSSi$ $(M+NH_4^+)^+$ 332.1863, found 332.1882.

*Triethoxy(3-phenoxypropyl)silane (**5a**)* was prepared as pale yellow oil from **4a** (0.50 mmol, 67.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 83% yield (123.9 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2 H), 7.00-6.91 (m, 3 H), 3.98 (t, *J* = 6.8 Hz, 2 H), 3.87 (q, *J* = 7.2 Hz, 6 H), 2.00-1.90 (m, 2 H), 1.27 (t, *J* = 7.2 Hz, 9 H), 0.81 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 129.3, 120.4, 114.5, 69.7, 58.4, 22.8, 18.2, 6.5; MS (ESI) *m/z* (relative intensity) 298.1 (5), 163.1 (100) $[M]^+$.

*(3-([1, 1'-Biphenyl]-2-yloxy)propyl)triethoxysilane (**5b**)* was prepared as pale yellow oil from **4b** (0.50 mmol, 105.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 99% yield (185.4 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ7.49-7.44 (m, 2 H), 7.32-7.27 (m, 2 H), 7.27-7.18 (m, 3 H), 6.96-6.86 (m, 2 H), 3.86 (t, *J* = 6.4 Hz, 2 H), 3.70 (q, *J* = 7.2 Hz, 6 H), 1.79-1.71 (m, 2 H), 1.12 (t, *J* = 7.2 Hz, 9 H), 0.64-0.59 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 138.6, 130.9, 130.8, 129.6, 128.5, 127.7, 126.6, 120.7, 112.5, 70.3, 58.3, 22.8, 18.2, 6.5; HRMS *m/z* (CI) calcd. for $C_{21}H_{30}O_4SiNa$ $(M+Na)^+$ 397.1811, found 397.1810.

*8, 8-diethoxy-2, 2, 3, 3-tetramethyl-4, 9-dioxa-3, 8-disilaundecane (**5c**)* was prepared as pale yellow oil from **4c** (0.50 mmol, 95.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 92% yield (238.6 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (q, *J* = 7.2 Hz, 6 H), 3.56 (t, *J* = 6.8 Hz, 2 H), 1.68-1.58 (m, 2 H), 1.21 (t, *J* = 7.2 Hz, 9 H), 0.88 (s, 9 H), 0.65-0.59 (m, 2 H), 0.03 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 65.4, 58.3, 26.1, 25.9, 18.3, 18.2, 6.1, -5.3; MS (ESI) *m/z* (relative intensity) 336.2 (5), 237.3 (100) $[M]^+$.

*1, 4-Bis(3-(triethoxysilyl)propoxy)benzene (**5d**)* was prepared as pale yellow oil from **4d** (0.50 mmol, 95.1 mg) and $(EtO)_3SiH$ (1.50 mmol, 251.6 mg), according to the General Procedure in 92% yield (238.6 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 4 H), 3.81 (t, *J* = 6.8 Hz, 4 H), 3.75 (q, *J* = 6.8 Hz, 12 H), 1.83-1.76 (m, 4 H), 1.15 (t, *J* = 6.8 Hz, 18 H), 0.70-0.66 (m, 4 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.0, 115.3, 70.4, 58.3, 22.8, 18.2, 6.4. HRMS *m/z* (CI) calcd. for $C_{24}H_{46}O_8Si_2Na$ $(M+Na)^+$ 541.2629, found 541.2624.

*2, 2'-Bis(3-(triethoxysilyl)propoxy)-1, 1'-binaphthalene (**5e**)* was prepared as pale yellow oil from **4e** (0.50 mmol, 183.2 mg) and $(EtO)_3SiH$ (1.50 mmol, 251.6 mg), according to the General Procedure in 88% yield (305.8 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2 H), 7.88-7.84 (m, 2 H), 7.45-7.41 (m, 2 H), 7.34-7.29 (m, 2 H), 7.25-7.18 (m, 4 H), 4.01-3.91 (m, 4 H), 3.63 (q, *J* = 7.2 Hz, 12 H), 1.60-1.52 (m, 4 H), 1.15 (t, *J* = 7.2 Hz, 18 H), 0.38-0.24 (m, 4 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.4, 134.2, 129.2, 128.9, 127.7, 126.0, 125.4, 123.3, 120.3, 115.4, 71.4, 58.1, 22.8, 18.2, 5.7; MS (ESI) *m/z* (relative intensity) 694.8 (12), 205.3 (100) $[M]^+$.

*Benzyl(3-methoxypropyl)dimethylsilane (**5f**)* was prepared as pale yellow oil from **4f** (0.50 mmol, 36.1 mg) and $BnMe_2SiH$ (0.75 mmol, 112.8 mg), according to the General Procedure in 96% yield (106.8 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2 H), 7.15-7.09 (m, 1 H), 7.07-7.03 (m, 2 H), 3.38 (s, 3 H), 3.37 (t, *J* = 6.8 Hz, 2 H), 2.15 (s, 2 H), 1.66-1.59 (m, 2 H), 0.60-0.50 (m, 2 H), 0.04 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.2, 128.1, 128.0, 123.8, 75.5, 58.4, 25.4, 23.8, 10.7, -3.8; MS (ESI) *m/z* (relative intensity) 222.1 (5), 149.1 (100) $[M]^+$.

*(2-Butoxyethyl)triethoxysilane (**5g**)* was prepared as pale yellow oil from **4g** (0.50 mmol, 50.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 92% yield (121.6 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (q, *J* = 7.2 Hz, 6 H), 3.50-3.47 (m, 2 H), 3.33 (t, *J* = 6.8 Hz, 2 H), 1.52-1.43 (m, 2 H), 1.35-1.25 (m, 2 H), 1.16 (t, *J* = 7.2 Hz, 9 H), 1.01 (t, *J* = 8.0 Hz, 2 H), 0.85 (t, *J* = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 70.2, 66.3, 58.4, 31.9, 19.4, 18.2, 13.9, 12.9; MS (ESI) *m/z* (relative intensity) 264.1 (5), 163.1 (100) $[M]^+$.

*(R)-tert-Butyl 2-((3-(triethoxysilyl)propoxy)methyl)pyrrolidine-1-carboxylate (**5h**)* was prepared as pale yellow oil from **4h** (0.50 mmol, 120.7 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 80% yield (162.2 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00-3.80 (m, 2 H), 3.79 (q, *J* = 6.8 Hz, 6 H), 3.52-3.49 (m, 1 H), 3.44-3.32 (m, 2 H), 3.33-3.22 (m, 2 H), 1.92-1.85 (m, 2 H), 1.82-1.72 (m, 2 H), 1.70-1.51 (m, 2 H), 1.44 (s, 9 H), 1.20 (t, *J* = 6.8 Hz, 9 H), 0.63-0.58 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.4, 79.0, 73.4, 71.4, 70.8, 58.2, 56.4, 46.7, 46.3, 28.4, 23.0, 18.2, 6.4; HRMS *m/z* (CI) calcd. for $C_{19}H_{39}NO_6SiNa$ $(M+Na)^+$ 428.2445, found 428.2448.

*Triethoxy(3-(((1R, 2S, 5R)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)silane (**5i**)* was prepared as pale yellow oil from **4i** (0.50 mmol, 98.2 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 89% yield (160.3 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (q, *J* = 7.2 Hz, 6 H), 3.58-3.53 (m, 1 H), 3.25-3.20 (m. 1 H), 3.05-2.92 (m, 1 H), 2.26-2.16 (m, 1 H), 2.10-2.03 (m, 1 H), 1.69-1.63 (m, 2 H), 1.61-1.55 (m, 2 H), 1.38-1.26 (m, 1 H), 1.20 (t, *J* = 7.2 Hz, 9 H), 0.99-0.90 (m, 2 H), 0.89 (d, *J* = 6.8 Hz, 3 H), 0.86 (s, 3 H), 0.84-0.78 (m, 2 H), 0.75 (d, *J* = 7.2 Hz, 3 H), 0.67-0.60 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 79.1, 70.9, 58.2, 48.3, 40.6, 34.6, 31.5, 25.5, 23.5, 23.3, 22.3, 20.9, 18.2, 16.2, 6.6; MS (ESI) *m/z* (relative intensity) 360.2 (5), 95.1 (100) $[M]^+$.

*Triethoxy(3-(((2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)propyl)silane (**5j**)* was prepared as pale yellow oil from **4j** (0.50 mmol, 290.4 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 70% yield (260.7 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.30 (m, 18 H), 7.26-7.20 (m, 2 H), 5.10-5.03 (m, 1 H), 4.95-4.89 (m, 2 H), 4.89-4.82 (m, 2 H), 4.76-4.67 (m, 2 H), 4.58-4.49 (m, 2 H), 4.09 (t, J = 9.2 Hz, 1 H), 3.94-3.86 (m, 6 H), 3.84-3.80 (m, 1 H), 3.79-3.74 (m, 1

H), 3.74-3.68 (m, 2 H), 3.67-3.63 (m, 1 H), 3.61-3.48 (m, 2 H), 1.90-1.81 (m, 2 H), 1.33-1.28 (m, 9 H), 0.83-0.71 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.8, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0, 137.9, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 127.4, 103.5, 96.7, 84.6, 82.2, 82.0, 80.077.8, 77.6, 75.5, 74.9, 74.7, 73.3, 72.9, 72.1, 70.2, 70.0, 68.9, 68.4, 58.2, 23.1, 22.7, 18.2, 6.6, 6.5; HRMS *m/z* (CI) calcd. for $C_{43}H_{56}O_9SiNa$ $(M+Na)^+$ 767.3592, found 767.3584.

(3-(((3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)propyl)triethoxysilane (**5k**) was prepared as pale yellow oil from **4k** (0.50 mmol, 150.2 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 67% yield (155.7 mg, l/b > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (d, J = 3.6 Hz, 1 H), 4.54 (d, J = 3.6 Hz, 1 H), 4.32 (q, J = 6.4 Hz, 1 H), 4.14 (q, J = 3.2 Hz, 1 H), 4.10-4.06 (m, 2 H), 4.01-3.97 (m, 1 H), 3.82 (q, J = 7.2 Hz, 6 H), 3.62-3.46 (m, 2 H), 1.72-1.64 (m, 2 H), 1.50 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.23 (t, J = 7.2 Hz, 9 H), 0.68-0.63 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 111.7, 108.8, 105.2, 82.5, 82.0, 81.1, 72.7, 72.5, 67.1, 58.3, 26.8, 26.7, 26.2, 25.3, 23.1, 18.3, 6.5; HRMS m/z (CI) calcd. for C21H40O9SiNa (M+Na)+ 487.2340, found 487.2337.

(8R, 9S, 13S, 14S)-13-Methyl-3-(3-(triethoxysilyl)propoxy)-7, 8, 9, 11, 12, 13, 15, 16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (**5l**) was prepared as pale yellow oil from **4l** (0.50 mmol, 155.2 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 81% yield (192.3 mg, l/b > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.6 Hz, 1 H), 6.73-6.68 (m, 1 H), 6.65-6.62 (m, 1 H), 3.91 (t, J = 6.8 Hz, 2 H), 3.83 (q, J = 7.2 Hz, 6 H), 2.91-2.85 (m, 2 H), 2.54-2.46 (m, 1 H), 2.43-2.36 (m, 1 H), 2.29-2.20 (m, 1 H), 2.19-2.04 (m, 2 H), 2.03-1.93 (m, 2 H), 1.92-1.84 (m, 2 H), 1.66-1.57 (m, 2 H), 1.55-1.52 (m, 2 H), 1.49-1.35 (m, 2 H), 1.23 (t, J = 7.2 Hz, 9 H), 0.91 (s, 3 H), 0.78-0.73 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.1, 137.6, 131.8, 126.2, 114.5, 112.1, 69.9, 58.4, 50.4, 48.0, 44.0, 38.4, 35.8, 31.6, 29.6, 56.5, 25.9, 22.8, 21.6, 18.3, 13.8, 6.5; HRMS m/z (CI) calcd. for $C_{27}H_{42}O_5SiNa$ $(M+Na)^+$ 497.2700, found 497.2701.

(8R, 9S, 10R, 13S, 14S)-10, 13-Dimethyl-17-(3-(triethoxysilyl)propoxy)-6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17-dodecahydro-1H-cyclopenta[a]phenanthren-3 (2H)-one (**5m**) was prepared as pale yellow oil from **4m** (0.50 mmol, 164.2 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 57% yield (140.4 mg, l/b > 99:1): ^{1}H NMR (400 MHz, CDCl3) δ 5.66 (s, 1 H), 3.75 (q, J = 7.2 Hz, 6 H), 3.39-3.27 (m, 2 H), 3.22 (t, J = 8.4 Hz, 1 H), 2.37-2.26 (m, 2 H), 2.26-2.16 (m, 1 H), 2.00-1.90 (m, 2 H), 1.90-1.84 (m, 1 H), 1.80-1.74 (m, 1 H), 1.67-1.61 (m, 2 H), 1.55-1.43 (m, 4 H), 1.43-1.34 (m, 2 H), 1.26-1.18 (m, 2 H), 1.16 (t, J = 7.2 Hz, 9 H), 1.12 (s, 3 H), 0.96-0.86 (m, 2 H), 0.86-0.78 (m, 2 H), 0.73 (s, 3 H), 0.60-0.54 (m, 2 H): ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.6, 171.4, 123.8, 88.7, 72.3, 58.3, 53.9, 50.7, 42.8, 38.6, 37.7, 35.7, 35.5, 33.9, 32.8, 31.6, 28.1, 23.5, 23.3, 20.7, 18.3, 17.4, 11.6, 6.5; HRMS m/z (CI) calcd. for $C_{28}H_{49}O_5Si$ $(M+H)^+$ 493.3350, found 493.3348.

*Triethoxy(3-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propyl)silane (**5n**)* was prepared as pale yellow oil from **4n** (0.50 mmol, 235.4 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 87% yield (276.3 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (q, *J* = 7.2 Hz, 6 H), 3.61 (t, *J* = 6.8 Hz, 2 H), 2.56 (t, *J* = 6.8 Hz, 2 H), 2.16 (s, 3 H), 2.12 (s, 3 H), 2.07 (s, 3 H), 1.95-1.86 (m, 2 H), 1.84-1.70 (m, 2 H), 1.56 (s, 3 H), 1.54-1.50 (m, 2 H), 1.49-1.31 (m, 6 H), 1.26-1.22 (m, 15 H), 1.14 (t, *J* = 7.6 Hz, 2 H), 1.11-1.04 (m, 4 H), 0.88-0.82 (m, 13 H), 0.81-0.76 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.3, 147.6, 127.9, 125.8, 122.7, 117.4, 75.2, 74.7, 58.4, 40.1, 39.4, 37.5, 37.5, 37.4, 37.3, 32.8, 32.7, 31.3, 28.0, 24.8, 24.4, 23.9, 23.6, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 18.3, 12.8, 11.9, 11.8, 6.7; MS (ESI) *m/z* (relative intensity) 634.8 (10), 430.7 (100) $[M]^+$.

*Triethoxy(3-(phenylsulfonyl)propyl)silane (**7a**)* was prepared as pale yellow oil from **6a** (0.50 mmol, 91.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 99% yield (171.5 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2 H), 7.64-7.59 (m, 1 H), 7.55-7.51 (m, 2 H), 3.73 (q, *J* = 6.8 Hz, 6 H), 3.15-3.10 (m, 2 H), 1.84-1.75 (m, 2 H), 1.14 (t, *J* = 6.8 Hz, 9 H), 0.64 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 133.4, 129.0, 127.9, 58.3, 58.2, 18.0, 16.7, 9.1; MS (ESI) *m/z* (relative intensity) 346.1 (5), 91.0 (100) $[M]^+$.

*Bis(3-(triethoxysilyl)propyl)phthalate (**7b**)* was prepared as pale yellow oil from **6b** (0.50 mmol, 123.1 mg) and $(EtO)_3SiH$ (1.50 mmol, 251.6 mg), according to the General Procedure in 80% yield (229.9 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2 H), 7.55-7.51 (m, 2 H), 4.31-4.26 (m, 4 H), 3.87-3.80 (m, 12 H), 1.88-1.81 (m, 4 H), 1.26-1.21 (m, 18 H), 0.74-0.68 (m, 4 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.5, 132.2, 130.8, 128.8, 67.6, 58.3, 22.1, 18.2, 6.5; MS (ESI) *m/z* (relative intensity) 574.4 (5), 207.3 (100) $[M]^+$.

*1-(3-(Triethoxysilyl)propyl)-1H-indole (**7c**)* was prepared as pale yellow oil from **6c** (0.50 mmol, 78.6 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 70% yield (112.5 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 1 H), 7.36-7.32 (m, 1 H), 7.21-7.14 (m, 1 H), 7.10-7.05 (m, 2 H), 6.48-6.45 (m, 1 H), 4.10 (t, *J* = 7.2 Hz, 2 H), 3.78 (q, *J* = 6.8 Hz, 6 H), 2.00-1.89 (m, 2 H), 1.20 (t, *J* = 6.8 Hz, 9 H), 0.60 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.9, 128.5, 127.8, 121.2, 120.8, 119.1, 109.4, 100.7, 58.4, 48.6, 23.8, 18.2, 7.6; HRMS *m/z* (CI) calcd. for $C_{17}H_{28}NO_3Si$ $(M+H)^+$ 322.1839, found 322.1842.

*N-(3-(Triethoxysilyl)propyl)aniline (**7d**)* was prepared as colorless oil from **6d** (0.50 mmol, 66.6 mg) and $(EtO)_3SiH$ (1.50 mmol, 251.6 mg), according to the General Procedure in 92% yield (136.8 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.18 (m, 2 H), 6.72-6.68 (m, 1 H), 6.66-6.63 (m, 2 H), 3.86 (q, *J* = 7.2 Hz, 6 H), 3.16 (t, *J* = 7.2 Hz, 2 H), 1.82-1.73 (m, 2 H), 1.26 (t, *J* = 7.2 Hz, 9 H), 0.77-0.72 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.2, 129.2, 117.1, 112.8, 58.4, 46.5, 22.7, 18.3, 7.8; MS (ESI) *m/z* (relative intensity) 297.2 (6), 84.3 (100) $[M]^+$.

*Diethyl(3-(triethoxysilyl)propyl)phosphine oxide (**7e**)* was prepared as pale yellow oil from 6e (0.50 mmol, 73.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 98% yield (152.1 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12-3.98 (m, 4 H), 3.77 (q, *J* = 6.8 Hz, 6 H), 1.81-1.64 (m, 4 H), 1.27 (t, *J* = 7.2 Hz, 6 H), 1.18 (t, *J* = 6.8 Hz, 9 H), 0.69 (t, *J* = 8.0 Hz, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 61.1, 58.2, 29.3, 27.9, 18.1, 16.3, 11.6; HRMS *m/z* (CI) calcd. for $C_{13}H_{32}O_6PSi$ $(M+H)^+$ 343.1707, found 343.1696.

*Triethoxy(3-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)propyl)silane (**7f**)* was prepared as pale yellow oil from **6f** (0.50 mmol, 67.5 mg) and $BnMe_2SiH$ (0.75 mmol, 112.8 mg), according to the General Procedure in 93% yield (132.7 mg, *l/b* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2 H), 7.11-7.06 (m, 1 H), 7.03-6.99 (m, 2 H), 3.41 (t, *J* = 6.8 Hz, 2 H), 2.1 (s, 2 H), 1.92-1.82 (m, 2 H), 1.49-1.41 (m, 2 H), 0.54-0.50 (m, 2 H), 0.0 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.2, 128.2, 128.0, 123.9, 36.2, 33.5, 25.5, 22.3, 13.8, -3.7; MS (ESI) *m/z* (relative intensity) 284.0 (6), 149.3 (100) $[M]^+$.

*Triethoxy(3-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)propyl)silane (**7g**)* was prepared as pale yellow oil from **6g** (0.50 mmol, 84.0 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 96% yield (159.5 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (q, *J* = 7.2 Hz, 6 H), 1.61-1.52 (m, 2 H), 1.25 (s, 12 H), 1.23 (t, *J* = 7.2 Hz, 9 H), 0.86 (t, *J* = 7.6 Hz, 2 H), 0.71-0.66 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 82.8, 58.2, 24.8, 18.2, 17.4, 13.3; MS (ESI) *m*/*z* (relative intensity) 332.2 (5), 163.1 (100) $[M]^+$.

*Triethoxy(2-(trimethylsilyl)ethyl)silane (**7h**)* was prepared as pale yellow oil from **6h** (0.50 mmol, 50.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 70% yield (92.6 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (q, *J* = 7.2 Hz, 6 H), 1.52-1.44 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 9 H), 0.76-0.70 (m, 2 H), 0.64-0.59 (m, 2 H), 0.0 (s, 9 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 58.2, 20.9, 18.2, 17.4, 14.8, -1.7; MS (ESI) *m*/*z* (relative intensity) 278.1 (5), 163.0 (100) $[M]^+$.

*6, 6-Diethoxy-3-methoxy-3-methyl-2, 7-dioxa-3, 6-disilanonane (**7i**)* was prepared as pale yellow oil from **6i** (0.50 mmol, 66.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 76% yield (112.7 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 3.71 (q, *J* = 7.2 Hz, 6 H), 3.40 (s, 6 H), 1.11 (t, *J* = 7.2 Hz, 9 H), 0.58-0.45 (m, 4 H), 0.0 (s, 3 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 58.4, 50.2, 18.3, 4.0, 1.4, -6.6; HRMS *m*/*z* (CI) calcd. for $C_{11}H_{28}O_5Si_2Na$ $(M+H)^+$ 319.1373, found 319.1381.

*Triethoxy(4-phenylbutyl)silane (**7j**)* was prepared as pale yellow oil from **6j** (0.50 mmol, 59.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 71% yield (100.3 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2 H), 7.19-7.13 (m, 3 H), 3.80 (q, *J* = 6.8 Hz, 6 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 1.79-1.71 (m, 2 H), 1.21 (t, *J* = 6.8 Hz, 9 H), 0.69-0.65 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 142.3, 128.5, 128.1, 125.6, 58.3, 39.2, 24.8, 18.2, 10.1; MS (ESI) *m*/*z* (relative intensity) 282.2 (5), 163.1 (100) $[M]^+$.

Triethoxy(4-phenylbutyl)silane (7k) was prepared as pale yellow oil from 6k (0.50 mmol, 66.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 83% yield (123.0 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2 H), 7.17-7.13 (m, 3 H), 3.82 (q, *J* = 7.2 Hz, 6 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 1.71-1.61 (m, 2 H), 1.51-1.43 (m, 2 H), 1.21 (t, *J* = 7.2 Hz, 9 H), 0.70-0.63 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 142.6, 128.3, 128.1, 125.5, 58.2, 35.5, 34.8, 22.4, 18.2, 10.2; MS (ESI) *m*/*z* (relative intensity) 296.1 (5), 250.1 (100) $[M]^+$.

*Triethoxy(phenethyl)silane (**7l**)* was prepared as pale yellow oil from **6l** (0.50 mmol, 52.1 mg) and $(EtO)_3SiH$ (0.75 mmol, 125.8 mg), according to the General Procedure in 88% yield (118.1 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2 H), 7.24-7.18 (m, 2 H), 7.18-7.13 (m, 1 H), 3.82 (q, *J* = 6.8 Hz, 6 H), 2.77-2.71 (m, 2 H), 1.23 (t, *J* = 6.8 Hz, 9 H), 1.02-0.97 (m, 2 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 144.6, 128.2, 127.7, 125.6, 58.3, 28.8, 18.3, 12.5; MS (ESI) *m*/*z* (relative intensity) 268.1 (20), 163.1 (100) $[M]^+$.

*4,4,9,9-Tetraethoxy-6-(4-methylpent-3-en-1-yl)-3,10-dioxa-4,9-disiladodecane (**7m**)* was prepared as pale yellow oil from **6m** (0.50 mmol, 68.1 mg) and $(EtO)_3SiH$ (1.50 mmol, 251.6 mg), according to the General Procedure in 44% yield (102.3 mg, *l*/*b* > 99:1): ^1H NMR (400 MHz, $CDCl_3$) δ5.14-5.10 (m, 1 H), 3.86-3.80 (m, 12 H), 1.97 (q, *J* = 7.6 Hz, 2 H), 1.69 (s, 3 H), 1.62 (s, 3 H), 1.50-1.43 (m, 2 H), 1.40-1.33 (m, 2 H), 1.28-1.26 (m, 1 H), 1.28-1.22 (m, 18 H), 0.66-0.59 (m, 4 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 130.9, 125.0, 58.3, 58.2, 35.3, 35.0, 28.4, 25.7, 25.1, 18.3, 18.2, 17.6, 14.9, 6.6; HRMS *m*/*z* (CI) calcd. for $C_{22}H_{48}O_6Si_2Na$ $(M+Na)^+$ 487.2887, found 487.2885.

*2,4-Bis(allylthio)pyrimidine (**2g**)*: NaO*t*-Bu (13.0 mmol) was added to ethanol (20.0 mL) in a reflux apparatus, and stirred until NaO*t*Bu was totally dissolved. Then pyrimidine-2, 4-dithiol (5.0 mmol) was added slowly. The reaction mixture was refluxed for 1 h. Allyl bromide (13.0 mmol) was added and refluxed for another 12 h. The solution was allowed to cool to room temperature, and then water (10.0 mL) was added to quench the reaction. The mixture was extracted with EtOAc (10.0 mL x 3), and the combined organic layer was washed with brine and dried over anhydrous sodium sulfate, filtered and concentrated in vacuum. The crude was purified by flash column chromatography on silica gel to afford pure product **2g**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 5.6 Hz, 1 H), 6.81 (d, *J* = 5.2 Hz, 1 H), 6.05-5.80 (m, 2 H), 5.35-5.32 (m, 1 H), 5.30-5.28 (m, 1 H), 5.20-5.11 (m, 2 H), 3.86-3.80 (m, 4 H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 154.4, 133.4, 132.7, 118.3, 117.7, 114.3, 33.6, 31.9; HRMS *m*/*z* (CI) calcd. for $C_{10}H_{12}N_2S_2Na$ $(M+Na)^+$ 247.0340, found 247.0337.

ASSOCIATED CONTENT

Supporting Information.

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^1H and ^{13}C NMR spectra of products (PDF).

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The authors declare no competing financial interest.

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