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Gold-Film-Catalysed Hydrosilylation of Alkynes by Microwave-Assisted, Continuous-Flow Organic Synthesis (MACOS)

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Abstract: Thin gold films on the surface of glass capillaries have proven to be highly active catalysts for the rapid hydrosilylation of alkynes that are flowed through the reactor while being heated by microwave irradiation. The films are able to be reused at least five times with no loss of activity and with no detectable levels of gold showing up in the hydrosilylated products.

Keywords: catalysis · flow synthesis · gold · hydrosilylation · microwave

Introduction

Hydrometallation is a very powerful method to stereo- and regioselectively create organometallic synthetic intermediates and products. In particular, hydrosilylation of alkynes is useful for the preparation of: 1) stereodefined halides by silyl/halide exchange of the corresponding vinylsilane, 2) organometallic cross-coupling partners, 3) polysiloxane building blocks, such as chlorosilanes, and 4) carbonyl derivatives by Tamao oxidation. The most commonly used metal to catalyse hydrosilylation is Pt (e.g., Karsted's catalyst), which is among the more expensive precious metals. Recently, Au, which is less than half the price of Pt, has been investigated for its applicability as a hydrosilylation catalyst. While generally less reactive than Pt, Au has been applied to the hydrosilylation of alkynes, carbonyls and imines.[1,2]

We were interested in developing a continuous hydrosilylation process employing microwave-assisted, continuous-flow organic synthesis (MACOS)[3] and considered a gold film on the surface of the reaction tube as a potential catalyst for this application.[4] However, while supported gold nanoparticles have been shown to be active in some preliminary hydrosilylation studies, metallic gold was observed to be essentially inactive with the same substrates. Corma and co-workers showed that Au^{III} from $KAuCl_4$ was quite reactive in the hydrosilylation of styrene, but reactivity ceased as the salt decomposed over time to metallic Au.[1,5] They also attempted to determine the catalytically active oxidation state of Au and concluded that Au^{III} was more active than Au^{I} and that the most active catalyst in their studies was "stabilized" Au^{III} on CeO_2. With this in mind, we embarked on the development of a suitable flow device and MACOS protocol for the continuous-flow, general hydrosilylation of alkynes.

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Results and Discussion

We began our investigation with the development of a method to deposit robust gold films on the surface of capillaries to withstand the heat and physical wear-and-tear associated with MACOS.[6] After some experimentation it was determined that the most robust and catalytically-active films resulted from a two-step deposition process.[7] First, a very fine layer of densely-packed gold particles was deposited directly on the capillary wall from a diethylene glycol/$AuCl_3$ solution. A more random-appearing layer of gold-nanoparticle clusters was then deposited on top of the first layer from an aqueous sodium citrate solution.

The two layers and their differing morphology are clearly visible on the SEM image of the resultant Au film (Figure 1). As the process was being developed to produce these films, the resultant prototypes were being tested in hydrosilylation reactions by using the conditions outlined in Table 1. By means of this iterative process, it was found that the first dense layer is necessary for good adhesion of the film to the glass, which gives the film robustness, and the top layer is necessary for high catalytic activity of the film under MACOS conditions. The general hydrosilylation protocol outlined in Table 1 was tried on a variety of terminal alkynes and it appears tolerant of many functional groups

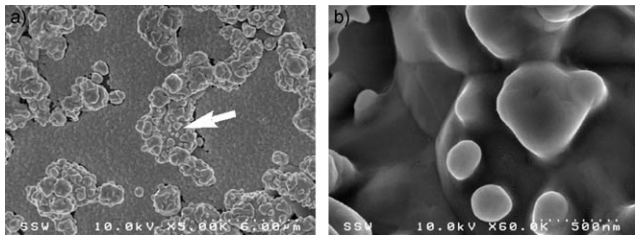
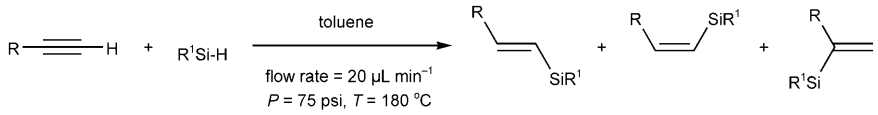


Figure 1. SEM images of the Au films prepared inside a glass capillary. a) Image at ×5000 magnification. b) Image at ×60000 magnification taken at the site of the arrow in panel (a). The arrow denotes a typical Au nanoparticle cluster against the backdrop of much smaller, densely-packed Au particles that coat the glass.

Table 1. Hydrosilylation of terminal alkynes catalysed by gold-coated capillaries using MACOS.



1 (2 equiv) 2 3 4 5

Entry	Alkyne R=	Silane R^1SiH=	3 *E* [%]	Product 4 *Z* [%]	5α [%]	Conversion [%][a] (yield [%])[b]
1	$CH_3CH_2CH_2CH_2$	Et_3SiH	(**a**) 82	9	9	82 (70)
2	$CH_3CH_2CH_2CH_2$	Ph_3SiH	(**b**) 80	6	14	78 (68)
3	$HOCH_2CH_2$	Et_3SiH	(**c**) 84	6	10	82 (69)
4	$HOCH_2CH_2$	Ph_3SiH	(**d**) 85	4	11	85 (74)
5	$ClCH_2CH_2CH_2$	Et_3SiH	(**e**) 75	4	21	77 (68)
6	$ClCH_2CH_2CH_2$	Ph_3SiH	(**f**) 93	3	4	78 (70)
7	Ph	Et_3SiH	(**g**) 92	4	4	86 (78)
8	Ph	Ph_3SiH	(**h**) 90	2	8	91 (80)
9	CH_3OCH_2	Et_3SiH	(**i**) 96	4	0	84 (76)
10	CH_3OCH_2	Ph_3SiH	(**j**) 98	1	1	88 (80)
11[c]	CH_3OCH_2	Et_3SiH	(**i**) 98	1	1	28 (ND)
12[d]	CH_3OCH_2	Ph_3SiH	(**j**) 98	1	1	20 (ND)
13	$HOCH_2$	Et_3SiH	(**k**) 90	1	9	87 (75)
14	$HOCH_2$	Ph_3SiH	(**l**) 98	1	1	85 (74)
15	$NCCH_2CH_2CH_2$	Et_3SiH	(**m**) 93	1	6	82 (74)
16	$NCCH_2CH_2CH_2$	Ph_3SiH	(**n**) 97	1	2	86 (78)
17	$CH_3CH(OH)$	Et_3SiH	(**o**) 81	2	17	62 (54)
18	$CH_3CH(OH)$	Ph_3SiH	(**p**) 98	1	1	68 (58)
19	$PhCH_2OCH_2$	Et_3SiH	(**q**) 97	1	2	88 (80)
20	$PhCH_2OCH_2$	Ph_3SiH	(**r**) 97	1	2	82 (72)
21	$ClCH_2CH_2CH_2$	Ph_2SiClH[e]	(**s**) 100	0	0	56 (45)
22	NC $CH_2CH_2CH_2$	Ph_2SiClH[e]	(**t**) 96	0	4	80 (66)
23	CH_3OCH_2	Ph_2SiClH[e]	(**u**) 100	0	0	75 (60)
24	$PhCH_2OCH_2$	Ph_2SiClH[e]	(**v**) 100	0	0	66 (60)
25	3-thiophenyl	Ph_2SiClH[e]	(**w**) 74	0	26	72 (62)
26	TMS-	Ph_2SiClH[e]	(**x**) 76	0	24	58 (50)

[a] Percentage conversion was determined by analysis of the NMR spectrum of the reaction mixture effluent as it exited the capillary. [b] Percentage yield was determined by collecting a known volume of reaction effluent, removing the solvent in vacuo and purifying the crude product by silica-gel chromatography. [c] Control experiment: To probe the role of microwave irradiation, the identical reaction to entry 9 was run through an oil bath at 192 °C (i.e., no microwave irradiation was involved at all). [d] Control experiment: To probe the role of microwave irradiation, the identical reaction to entry 10 was run through an oil bath at 195 °C (i.e., no microwave irradiation was involved at all). [e] The silanol corresponding to the silyl chloride (i.e., $-SiPh_2OH$) was isolated following silica-gel chromatography and yields were calculated on this basis. TMS = trimethylsilyl.

including cyano, alcohols, chlorides, aromatics/heteroaromatics and ethers. Of note, free alcohols that were remote from the alkyne (entries 3 and 4) or right next to it (entries 13, 14, 17 and 18) were equally well tolerated. Triethyl-, triphenyl- and chlorodiphenyl silane all proved equally efficacious as hydrosilylating agents. Regioselectivity of the hydrometallation was high for placement of the silicon moiety on the terminal carbon of the alkyne. Stereospecificity of the hydrometallation was lowest when the substituent on the alkyne was an alkyl chain (entries 1–6), but *E* selectivity for the terminal silane product was always greater than 90 percent.

The temperature recorded during these hydosilylation reactions by the IR sensor (≈180 °C) in the Biotage Initiator microwave primarily reflects the temperature of the gold film as toluene is a poor absorber of microwave irradiation.[8] To probe the necessity for microwave irradiation during these studies, two control experiments were conducted (Table 1, entries 11 and 12). In these experiments, the same Au capillaries placed in an oil bath set to deliver the same temperature as recorded during the MACOS runs. In both cases, percentage conversion was significantly curtailed as these runs produced only 25% of the product that was obtained with microwave irradiation. The reason for this could be that the true temperature during MACOS is much higher than that indicated by the microwave's IR sensor and/or there is an electronic effect that positively promotes the reaction by the current that is being generated in the metal film by the oscillating microwave field.

To probe the robustness and reuseability of the gold film, the reaction in entry 10 (Table 1) was repeated five separate times by using the same capillary and the percentage conversion in succession was 52, 91, 75, 80 and 72%. While there appears to be no significant deviation from performance in this study, it has been reported that gold laid down on the *outside* of glass chips "evaporates" during microwave irradiation.[9] Perhaps the hydrosilylation solution is cooling the film sufficiently to increase its lifetime and reactivity. Additionally, these product samples were collected directly from the capillary (crude) and submitted to inductively coupled plasma mass spectrometry (ICP-MS). The technique has a lower level of detection

(LLD) of $\delta = 50$ ppm and no gold was detected in the products. The capillaries do, however, darken over time. Given the continued activity of the film and the apparent lack of its degradation products in the product stream, it could be that it is the organic matter in the flow stream that is being gradually charred and deposited on the surface of this intensely hot metal film.

Conclusion

In summary, we have shown that capillaries coated with gold films comprised of a dense, regular layer of gold particles covered by an irregular amorphous one are highly active for the flow hydrosilylation of terminal alkynes. These films have shown good reliability and robustness in our studies, which indicates that they are useful for a continuous process.

Experimental Section

Microwave irradiation experiments: All MACOS experiments were performed in 1180 μm borosilicate capillaries, by using a single mode Biotage Smith Initiator Synthesizer operating at a frequency of 2.45 GHz with irradiation power from 0 to 300 W. The capillary was fed reactants from Hamilton gastight syringes attached to a Harvard 22 syringe pump preset to the desired flow rate. The system was connected to a sealed collection vial, in which a pressurized air line was attached to create backpressure (pressure inside the system reached 75 psi). The temperatures reported were measured by the IR sensor built into the microwave chamber on the outer surface of capillaries. All reagents and solvents were purchased from commercial sources and used without additional purification. Column chromatography purifications were carried out by using the flash technique on silica gel 60 (200–400 mesh). ^{1}H NMR spectroscopy was run by using a Bruker Advance 400 MHz instrument and all spectra were calibrated to $\delta = 7.26$ ppm for the signal from the residual proton of the deuterated chloroform solvent; ^{13}C NMR spectra were calibrated to the middle carbon signal of the triplet for deuterated chloroform ($\delta =$ 77.00 ppm).

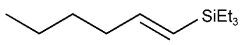
General procedure for creating the Au film coating inside of 1180 μm (ID) capillaries: Boronsilicate capillaries (1180 μm ID) were filled with a 0.1 mmol mL^{-1} solution of $AuCl_3$ in diethylene glycol, capped at both ends and placed inside a muffle furnace; the temperature was gradually increased to 180 °C. After 30 min, capillaries were taken out and rinsed with acetone.

The second deposition mixture was prepared by mixing a 0.2 mmol mL^{-1} aqueous solution of $AuCl_3$ (0.5 mL) with a 5% aqueous solution of trisodium citrate·2 H_2O (0.5 mL). The monocoated capillaries were filled with this mixture, capped at both ends and left to develop at RT for another 30 min. After this time, capillaries were calcinated at 400 °C before use in MACOS.

Synthesis of benzyl propargyl ether: Benzyl alcohol (5.0 g, 46.3 mmol) and propargyl bromide (13.7 g, 92.6 mmol) were added sequentially to a solution of KOH (10.4 g, 185 mmol) in dry DMSO (60 mL) at 0 °C. The mixture was left stirring at RT for 2 h before being diluted with Et_2O (200 mL) and H_2O (100 mL). The organic layer was separated, washed with H_2O (4 × 50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash chromatography (10% ethyl acetate in hexane) followed by distillation (2.5 mmHg, 80 °C) afforded benzyl propargyl ether (4.8 g, 71%) as a clear liquid.[8] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.30$ (m, 5H), 4.64 (s, 2H), 4.21 (d, $J = 2.0$ Hz, 2H), 2.49 ppm (t, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.6$, 128.4, 128.1, 127.9, 79.8, 74.5, 71.5, 57.0 ppm.

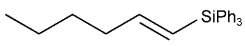
General procedure for the hydrosilylation by MACOS: A stock solution containing the terminal alkyne (2.0 mmol, 2.0 equiv) and hydrosilane (1.0 mmol, 1.0 equiv) in toluene (0.6–0.7 mL, total mixture volume is 1.0 mL) was prepared. After the continuous-flow microwave system was primed with toluene, an aliquot (1.0 mL) of the homogenous stock solution was taken up in a Hamilton gastight syringe and connected to the reactor system with the aid of Microtight fittings. The syringe was placed in a Harvard 22 syringe pump that was set to deliver 20 μL min^{-1} and the single-mode microwave was programmed to heat constantly; the power level was controlled manually so as to keep the temperature constant at the specified levels. The output from the reactor was fed into a sealed vial that was charged with 75 psi of air to create backpressure in the system; the eluent was analysed by ^{1}H NMR spectroscopy immediately after the reaction to obtain chemical conversion. A known volume of the crude reaction mixture (typically 0.7–0.8 mL) was collected and the product purified by silica-gel chromatography. Below, the specific reactions leading to each product along with spectral characterization of the major *E* isomer are detailed (unless indicated otherwise).

(*E*)-1-(Triethylsilyl)-1-hexene (3a): 1-Hexyne and triethylsilane were reacted by following the general hydrosilylation procedure and 800 μL of the crude reaction mixture were collected. Purification by flash chromatography (pentane) afforded 110.0 mg of **3a** (70% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.08$ (dt, $J = 18.7$, 6.3 Hz, 1H), 5.56 (dt, $J = 18.7$, 1.5 Hz, 1H), 2.14–2.21 (m, 2H), 1.32–1.49 (m, 4H), 0.88–0.96 (m, 12H), 0.60 ppm (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 144.8$, 125.4, 36.8, 31.0, 22.2, 14.1, 7.5, 3.6 ppm; spectra matched those found in the literature.[10]



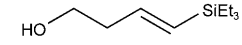
3a

(*E*)-1-(Triphenylsilyl)-1-hexene (3b): 1-Hexyne and triphenylsilane were reacted by following the general hydrosilylation procedure and 750 μL of the crude reaction mixture were collected. Purification by flash chromatography (5% ethyl acetate in hexane) afforded 174.5 mg of **3b** (68% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.69$–7.78 (m, 6H), 7.45–7.58 (m, 9H), 6.32 (m, 2H), 2.31–2.39 (m, 2H), 1.35–1.59 (m, 5H), 1.05 ppm (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.0$, 136.3, 135.3, 129.6, 128.0, 123.4, 37.0, 31.0, 22.5, 14.2 ppm; spectra matched those found in the literature.[11,12]



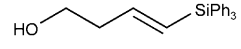
3b

(*E*)-1-(Triethylsilyl)-1-buten-4-ol (3c): 3-Butyne-1-ol and triethylsilane were reacted by following the general hydrosilylation procedure and 580 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% ethyl acetate in hexane) afforded 72 mg of **3c** (69% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.05$ (dt, $J = 18.7$, 6.4 Hz, 1H), 5.72 (dt, $J = 18.7$, 1.3 Hz, 1H), 1.63 (brs, 1H), 0.95 (t, $J = 8.0$ Hz, 9H), 0.59 ppm (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 130.3, 61.7, 40.5, 7.5, 3.5 ppm; spectra matched those found in the literature.[12]



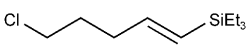
3c

(*E*)-1-(Triphenylsilyl)-1-buten-4-ol (3d): 3-Butyne-1-ol and triphenylsilane were reacted by following the general hydrosilylation procedure and 650 μL of the crude reaction mixture were collected. Purification by flash chromatography (25% ethyl acetate in hexane) afforded 159 mg of **3d** (74% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.52$–7.67 (m, 6H), 7.36–7.49 (m, 9H), 6.39 (dt, $J = 18.5$, 1.2 Hz, 1H), 6.19 (dt, $J = 18.5$, 6.4 Hz, 1H), 3.75 (t, $J = 6.3$ Hz, 2H), 2.6 (qd, $J = 6.3$, 1.2 Hz, 2H), 1.55 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.6$, 136.4, 135.1, 130.2, 128.4, 127.9, 61.9, 40.3 ppm; spectra matched those found in the literature.[12]



3d

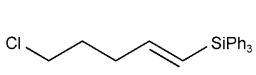
(*E*)-5-Chloro-1-(triethylsilyl)-1-pentene (3e): 5-Chloro-1-pentyne and triethylsilane were reacted by following the general hydrosilylation procedure and 650 μL



3e

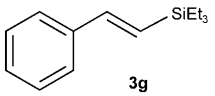
of the crude reaction mixture were collected. Purification by flash chromatography (20% dichloromethane in pentane) afforded 94 mg of **3e** (68% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.01 (dt, J = 18.8, 6.2 Hz, 1H), 5.64 (dt, J = 18.8, 1.4 Hz, 1H), 3.63 (t, J = 6.7 Hz, 2H), 2.48 (q, J = 6.7 Hz, 2H), 1.98 (q, J = 6.7 Hz, 2H), 0.92 (t, J = 8.0 Hz, 9H), 0.58 ppm (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 127.9, 44.4, 34.2, 31.7, 7.5, 3.7 ppm; spectra matched those found in the literature.[13]

(*E*)-5-Chloro-1-(triphenylsilyl)-1-pentene (3f): 5-Chloro-1-pentyne and triphenylsilane were reacted by following the general hydrosilylation procedure and 750 μL of the crude reaction mixture were collected. Purification by flash chromatography (12% dichloromethane in hexane) afforded 189.7 mg of **3f** (70% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.68 (m, 6H), 7.46–7.58 (m, 9H), 6.42 (dt, J = 18.5, 1.3 Hz, 1H), 6.28 (dt, J = 18.5, 6.0 Hz, 1H), 3.66 (t, J = 6.7 Hz, 2H), 2.47 (q, J = 6.7 Hz, 2H), 2.05 ppm (q, J = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 136.1, 134.8, 129.7, 128.0, 125.4, 44.6, 34.1, 31.5 ppm; spectra matched those found in the literature.[12]



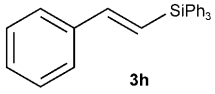
3f

(*E*)-1-(Triethylsilyl)-2-phenylethene (3g): Phenylacetylene and triethylsilane were reacted by following the general hydrosilylation procedure and 620 μL of the crude reaction mixture were collected. Purification by flash chromatography (10% dichloromethane in pentane) afforded 106.0 mg of **3g** (78% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.47 (m, 2H), 7.30–7.37 (m, 2H), 7.21–7.27 (m, 1H), 6.88 (d, J = 19.5 Hz, 1H), 6.41 (d, J = 19.5 Hz, 1H), 0.98 (t, J = 8.0 Hz, 9H), 0.68 ppm (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 138.5, 128.8, 127.9, 126.5, 125.9, 7.7, 3.8 ppm; spectra matched those found in the literature.[14]



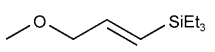
3g

(*E*)-1-(Triphenylsilyl)-2-phenylethene (3h): Phenylacetylene and triphenylsilane were reacted by following the general hydrosilylation procedure and 620 μL of the crude reaction mixture were collected. Purification by flash chromatography (10% dichloromethane in pentane) afforded 209 mg of **3h** (80% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.68 (m, 6H), 7.28–7.56 (m, 14H), 7.10 ppm (d, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 138.1, 136.1, 134.6, 129.8, 128.8, 128.6, 128.1, 127.3, 122.9 ppm; spectra matched those found in the literature.[12,14]



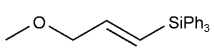
3h

(*E*)-3-Methoxy-1-(triethylsilyl)-1-propene (3i): Propargyl methyl ether and triethylsilane were reacted by following the general hydrosilylation procedure and 800 μL of the crude reaction mixture were collected. Purification by flash chromatography (15% dichloromethane in pentane) afforded 112.6 mg of **3i** (76% yield including minor isomer **4i**). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.09 (dt, J = 18.9, 4.9 Hz, 1H), 5.84 (dt, J = 18.9, 1.5 Hz, 1H), 3.97 (dd, J = 4.9, 1.5 Hz, 2H), 3.34 (s, 3H), 0.93 (t, J = 8.0 Hz, 9H), 0.57 ppm (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 128.6, 75.8, 57.9, 7.5, 3.6 ppm; spectra matched those found in the literature.[12]



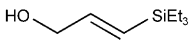
3i

(*E*)-3-Methoxy-1-(triphenylsilyl)-1-propene (3j): Propargyl methyl ether and triphenylsilane were reacted by following the general hydrosilylation procedure and 740 μL of the crude reaction mixture were collected. Purification by flash chromatography (14% ethyl acetate in hexane) afforded 195 mg of **3j** (80% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.61 (m, 6H), 7.32–7.46 (m, 9H), 6.58 (dt, J = 18.6, 1.4 Hz, 1H), 6.28 (dt, J = 18.6, 4.6 Hz, 1H), 4.1 (dd, J = 4.6, 1.4 Hz, 2H), 3.45 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 136.2, 134.7, 129.7, 128.1, 125.3, 75.2, 58.5 ppm; spectra matched those found in the literature.[12,15]



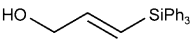
3j

(*E*)-1-(Triethylsilyl)-1-propen-3-ol (3k): Propargyl alcohol and triethylsilane were reacted by following the general hydrosilylation procedure and 900 μL of the crude reaction mixture were collected. Purification by flash chromatography (15% ethyl acetate in hexane) afforded 115.8 mg of **3k** (75% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.16 (dt, J = 19.0, 4.1 Hz, 1H), 5.84 (dt, J = 19.0, 1.6 Hz, 1H), 4.14 (dd, J = 4.1, 1.6 Hz, 2H), 2.62 (brs, 1H), 0.92 (t, J = 8.0 Hz, 9H), 0.56 ppm (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 125.7, 65.4, 7.4, 3.5 ppm; spectra matched those found in the literature.[13]



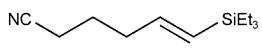
3k

(*E*)-1-(Triphenylsilyl)-1-propen-3-ol (3l): Propargyl alcohol and triphenylsilane were reacted by following the general hydrosilylation procedure and 750 μL of the crude reaction mixture were collected. Purification by flash chromatography (15% EtOAc in hexane) afforded 174.0 mg of **3l** (74% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.58 (m, 6H), 7.38–7.50 (m, 9H), 6.26 (dt, J = 18.8, 1.7 Hz, 1H), 5.89 (dt, J = 18.8, 3.9 Hz, 1H), 4.48 (dd, J = 3.9, 1.7 Hz, 2H), 1.68 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 136.1, 134.5, 129.8, 128.1, 122.7, 65.2 ppm; spectra matched those found in the literature.[12,15]



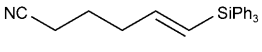
3l

(*E*)-6-(Triethylsilyl)hex-5-enenitrile (3m): Hex-5-ynenitrile and triethylsilane were reacted by following the general hydrosilylation procedure and 700 μL of the crude reaction mixture were collected. Purification by flash chromatography (10% ethyl acetate in hexane) afforded 108 mg of **3m** in 74% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.94 (dt, J = 18.7, 6.2 Hz, 1H), 5.64 (dt, J = 18.7, 1.5 Hz, 1H), 2.35 (t, J = 7.2 Hz, 2H), 2.26–2.31 (m, 2H), 1.77 (t, J = 7.2 Hz, 2H), 0.92 (t, J = 8.0 Hz, 9H), 0.56 ppm (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 128.8, 119.6, 35.7, 24.6, 16.6, 7.4, 3.5 ppm; spectra matched those found in the literature.[12]



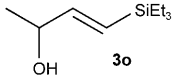
3m

(*E*)-6-(Triphenylsilyl)hex-5-enenitrile (3n): Hex-5-ynenitrile and triphenylsilane were reacted by following the general hydrosilylation procedure and 700 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% ethyl acetate in hexane) afforded 191.0 mg of **3n** (78% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.63 (m, 6H), 7.38–7.51 (m, 9H), 6.38 (dt, J = 18.5, 1.5 Hz, 1H), 6.18 (dt, J = 18.5, 6.0 Hz, 1H), 2.41–2.46 (m, 2H), 2.37 (t, J = 7.3 Hz, 2H), 1.87 ppm (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 136.0, 134.6, 129.8, 127.9, 126.5, 119.6, 35.5, 24.3, 16.6 ppm; spectra matched those found in the literature.[12]



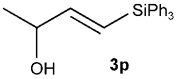
3n

(*E*)-1-(Triethylsilyl)-1-buten-3-ol (3o): 3-Butyne-2-ol and triethylsilane were reacted by following the general hydrosilylation procedure and 900 μL of the crude reaction mixture were collected. Purification by flash chromatography (15% ethyl acetate in pentane) afforded 90 mg of **3o** (54% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.12 (dd, J = 19.0, 5.2 Hz, 1H), 5.74 (dd, J = 19.0, 1.5 Hz, 1H), 4.24–4.28 (m, 1H), 2.08 (brs, 1H), 1.24 (d, J = 6.6 Hz, 3H), 0.90 (t, J = 8.0 Hz, 9H), 0.55 ppm (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 124.2, 70.7, 23.2, 7.4, 3.5 ppm; spectra matched those found in the literature.[12]



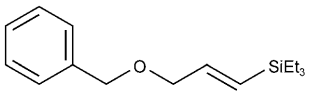
3o

(*E*)-1-(Triphenylsilyl)-1-buten-3-ol (3p): 3-Butyne-2-ol and triphenylsilane were reacted by following the general hydrosilylation procedure and 800 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% ethyl acetate in hexane) afforded 152 mg of **3p** (58% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.64 (m, 6H), 7.40–7.53 (m, 9H), 6.52 (dd, J = 18.7, 1.4 Hz, 1H), 6.28 (dd, J = 18.7,



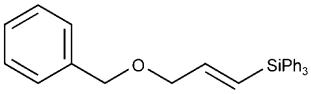
3p

4.5 Hz, 1H), 4.40–4.44 (m, 1H), 1.72 (d, J=2.6, 1H), 1.32 ppm (d, J=6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=155.5, 136.1, 134.5, 129.7, 128.1, 121.7, 70.6, 23.2 ppm; spectra matched those found in the literature.[16]



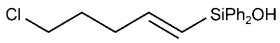
3q

(*E*)-3-Benzyloxy-1-(triethylsilyl)-1-propene (3q): Benzyl propargyl ether and triethylsilane were reacted by following the general hydrosilylation procedure and 660 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% dichloromethane in pentane) afforded 138.2 mg of **3q** (80% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36–7.43 (m, 4H), 7.27–7.32 (m, 1H), 6.20 (dt, J=19.0, 4.9 Hz, 1H), 5.88 (dt, J=19.0, 1.5 Hz, 1H), 4.57 (s, 2H), 4.10 (dd, J=4.9, 1.5 Hz, 2H), 0.99 (t, J=8.0 Hz, 9H), 0.62 ppm (q, J=8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.6, 138.4, 128.6, 128.4, 127.8, 127.6, 73.5, 72.3, 7.4, 3.6 ppm; spectra matched those found in the literature.[17]



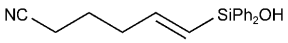
3r

(*E*)-3-Benzyloxy-1-(triphenylsilyl)-1-propene (3r): Benzyl propargyl ether and triphenylsilane were reacted by following the general hydrosilylation procedure and 650 μL of the crude reaction mixture were collected. Purification by flash chromatography (15% ethyl acetate in hexane) afforded 190 mg of **3r** (72% yield including minor isomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.69 (m, 6H), 7.34–7.55 (m, 14H), 6.67 (dt, J=18.7, 1.4 Hz, 1H), 6.37 (dt, J=18.7, 4.5 Hz, 1H), 4.7 (s, 2H), 4.26 ppm (dd, J=4.6, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=148.3, 138.3, 136.2, 134.5, 129.6, 128.5, 128.1, 128.0, 127.8, 125.3, 72.8, 72.5 ppm; spectra matched those found in the literature.[12]



3s

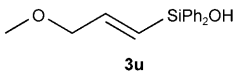
(*E*)-5-Chloro-1-(hydroxydiphenylsilyl)-1-pentene (3s): 5-Chloro-pentyne-1 and chlorodiphenylsilane were reacted by following the general hydrosilylation procedure and 640 μL of the crude reaction mixture were collected. Purification by flash chromatography (15% ethyl acetate in pentane) afforded 87.0 mg of **3s** (45% yield, no other isomers formed). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.66 (m, 4H), 7.38–7.47 (m, 6H), 6.31 (dt, J=19.2, 6.0 Hz, 1H), 6.09 (dt, J=19.2, 1.1 Hz, 1H), 3.57 (t, J=6.0 Hz, 2H), 2.40 (q, J=7.0 Hz, 2H), 2.28 (brs, 1H), 1.95 ppm (q, J=7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.9, 135.6, 134.5, 130.1, 127.9, 125.9, 44.4, 33.7, 31.1 ppm; HRMS: m/z: calcd for $C_{17}H_{19}OClSi$+H: 303.0972; found: 303.0612.



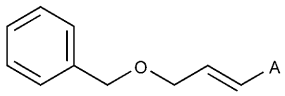
3t

(*E*)-5-Cyano-1-(hydroxydiphenylsilyl)-1-pentene (3t): Hex-5-ynenitrile and chlorodiphenylsilane were reacted by following the general hydrosilylation procedure and 700 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% ethyl acetate in pentane) afforded 135.0 mg of **3t** (66% yield including minor isomer **5t**). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59–7.68 (m, 4H), 7.38–7.51 (m, 6H), 6.25 (dt, J=18.2, 6.0 Hz, 1H), 6.11 (dt, J=18.2, 1.1 Hz, 1H), 2.53 (brs, 1H), 2.32–2.44 (m, 4H), 1.82 ppm (q, J=7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=149.7, 135.5, 134.5, 130.1, 127.9, 127.2, 119.5, 35.2, 23.9, 16.5 ppm; HRMS: m/z: calcd for $C_{18}H_{19}NOSi$: 293.1236; found: 293.1237.

(*E*)-3-Methoxy-1-(hydroxydiphenylsilyl)-1-propene (3u): Propargyl methyl ether and chlorodiphenylsilane were reacted by following the general hydrosilylation procedure and 720 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% ethyl acetate in hexane) afforded 124 mg of **3u** (60% yield, no other isomers formed). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.66 (m, 4H), 7.38–7.46 (m, 6H), 6.26–6.41 (m, 2H), 4.06 (dd, J=3.0, 1.1 Hz, 2H), 3.39 (s, 3H), 2.49 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.9, 135.4, 134.6, 130.3, 127.9, 125.7, 74.7, 58.3 ppm; elemental analysis calcd (%) for $C_{16}H_{18}O_2Si$: C 71.07, H 6.71; found, C 71.10, H 6.55; HRMS: m/z: calcd for $C_{16}H_{18}O_2Si$+NH_4: 288.1420; found: 288.1425.



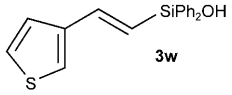
3u



3v

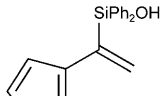
(*E*)-[(3-Benzyloxy)prop-1-enyl]hydroxydiphenylsilane (3v): Benzyl propargyl ether and chlorodiphenylsilane were reacted by following the general hydrosilylation procedure and 780 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% ethyl acetate in hexane) afforded 162 mg of **3v** (60% yield, no other isomers formed). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.65–7.68 (m, 4H), 7.45–7.48 (m, 2H), 7.37–7.44 (m, 7H), 7.31–7.35 (m, 2H), 6.33–6.45 (m, 2H), 4.58 (s, 2H), 4.15 (dd, J=3.8, 1.1 Hz, 2H), 3.01 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.0, 138.1, 135.4, 134.6, 130.5, 128.4, 127.9, 127.8, 127.6, 125.8, 72.5, 72.3 ppm; HRMS: m/z: calcd for $C_{22}H_{22}O_2Si$+NH_4: 364.1733; found: 364.1747.

(*E*)-Hydroxydiphenyl[2-(thiophen-3-yl)]vinylsilane (3w): 3-Ethynylthiophene and chlorodiphenylsilane were reacted by following the general hydrosilylation procedure and 800 μL of the crude reaction mixture were collected. Purification by flash chromatography (30% dichloromethane in pentane) afforded 118 mg of **3w** (48%, minor α isomer **5w** reported below). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.67–7.74 (m, 4H), 7.40–7.47 (m, 6H), 7.34–7.37 (m, 1H), 7.25–7.33 (m, 2H), 7.12 (d, J=19.2 Hz, 1H), 6.55 (d, J=19.2 Hz, 1H), 2.51 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.3, 141.5, 135.4, 134.7, 130.1, 127.9, 126.1, 124.9, 124.3, 122.8 ppm; HRMS: m/z: calcd for $C_{18}H_{16}OSSi$: 308.0689; found: 308.0674; elemental analysis calcd (%) for $C_{18}H_{16}OSSi$: C 70.09, H 5.23; found C 69.89, H 5.21.



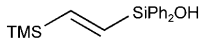
3w

α-Hydroxydiphenyl[1-(thiophen-3-yl)]vinylsilane (5w): From the above crude reaction mixture, 34 mg of the minor isomer **5w** was isolated (14% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.64–7.70 (m, 4H), 7.39–7.50 (m, 6H), 7.26–7.31 (m, 1H), 7.17–7.35 (m, 2H), 6.36 (d, J=2.1 Hz, 1H), 5.69 (d, J=2.1 Hz, 1H), 2.71 ppm (brs, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ=142.9, 141.2, 134.9, 134.7, 130.3, 130.1, 127.8, 126.2, 125.3, 121.9 ppm; HRMS: m/z: calcd for $C_{18}H_{16}OSSi$: 308.0691; found: 308.0561; elemental analysis calcd (%) for $C_{18}H_{16}OSSi$: C 70.09, H 5.23; found: C 69.97, H 5.11.



5w

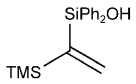
(*E*)-1-(Hydroxydiphenylsilyl)-2-(trimethylsilyl)-ethene (3x): Ethynyltrimethylsilane and chlorodiphenylsilane were reacted by following the



3x

general hydrosilylation procedure and 900 μL of the crude reaction mixture were collected. Purification by flash chromatography (20% ethyl acetate in pentane) afforded 109 mg of **3x** (40% yield, minor α isomer **5x** reported below). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.62$–7.68 (m, 4H), 7.40–7.49 (m, 6H), 6.89–7.05 (m, 2H), 2.44 (br s, 1H), 0.16 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.3$, 143.9, 135.5, 134.6, 130.0, 127.8, −1.7 ppm; HRMS: *m*/*z*: calcd for $C_{17}H_{22}OSi_2$: 298.1209; found: 298.1205; elemental analysis calcd (%) for $C_{17}H_{22}OSi_2$: C 68.40, H 7.43; found: C 68.63, H 7.37.

α-1-(Hydroxydiphenylsilyl)-1-(trimethylsilyl)ethene (5x): From the above crude reaction mixture, 26 mg of **5x** were also obtained (10% yield).



5x

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.60$–7.65 (m, 4H), 7.38–7.46 (m, 6H), 6.63 (d, $J = 5.0$ Hz, 1H), 6.41 (d, $J = 5.0$ Hz, 1H), 2.30 (br s, 1H), 0.08 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.7$, 145.3, 135.9, 134.5, 129.8, 127.8, −0.48 ppm; HRMS: *m*/*z*: calcd for $C_{17}H_{22}OSi_2$: 298.1209; found: 298.1222; elemental analysis calcd (%) for $C_{17}H_{22}OSi_2$: C 68.40, H 7.43; found: C 68.20, H 7.47.

Gold analysis: After removing the solvent in vacuo, the sample was accurately weighed, ashed and then digested in Aqua Regia (1:3 nitric acid to hydrochloric acid). Following digestion, the sample was cooled to RT, diluted to a known volume with high purity RO water and then analysed by ICP-MS by using an HP/Agilent 4500 ICP-MS. The ICP-MS was calibrated prior to the sample analysis by using NIST traceable standards for gold.

Acknowledgements

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[8] We expect that the temperature inside the capillary is actually higher, perhaps significantly so, than the value read by the IR sensor in the microwave cavity. Currently, we are unable to record temperatures inside of the capillary, which would be more accurate.
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