Convergence of Mechanistic Pathways in the Palladium(0)-Catalyzed Cross-Coupling of Alkenylsilacyclobutanes and Alkenylsilanols

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SUPPORTING INFORMATION

General Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C; 376 MHz, ^{19}F), Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C; 470 MHz, ^{19}F), Inova 500 (100 MHz, ^{29}Si), Inova 600 (119 MHz, ^{29}Si) or Inova 750 (149 MHz, ^{29}Si) spectrometer. Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C), residual acetonitrile (δ 1.93 ppm, ^{1}H; δ 1.30 ppm, ^{13}C), tetramethylsilane (δ 0.00 ppm, ^{1}H, ^{13}C, ^{29}Si) or α,α,α-trifluorotoluene (-63.7 ppm, ^{19}F). ^{29}Si NMR samples contain Cr(acac)$_3$ (2 crystals).

Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. Electron impact (EI) spectra were performed on a Finnigan-MAT CH-5 spectrometer. Data are reported in the form of m/z (intensity relative to base peak= 100). Infrared spectra (IR) were recorded on an Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light and/or potassium permanganate. Methanol was of reagent grade and used as received; other solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane and pentane ($CaCl_2$); ethyl acetate (K_2CO_3). Column chromatography was performed using EM Science 230-400 mesh silica gel or ICN silica RP C18 (32-63 μm) 60A.

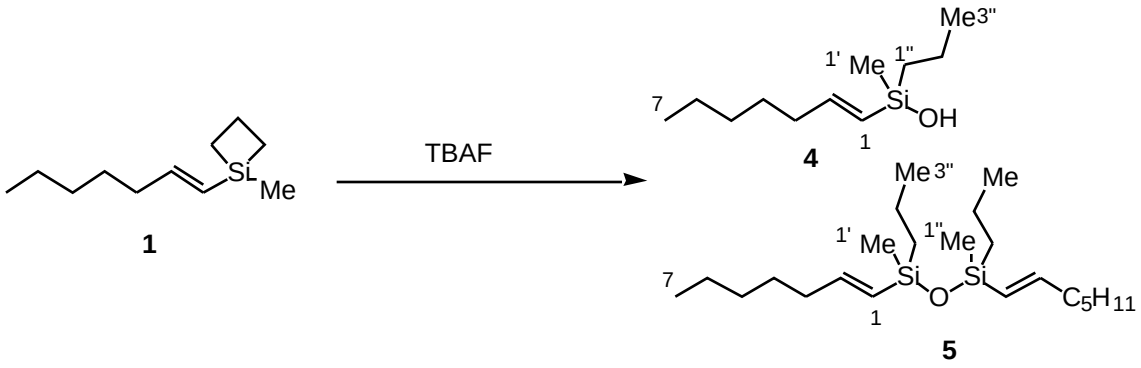
Analytical capillary gas chromatography (GC) was performed using the following gas chromatography fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min): Hewlett Packard 5890 Series II. The following column was used: HP-5 50-m cross-linked 5-Phenyl methyl silicone gum phase. The injector temperature was 225 °C, the detector temperature was 300 °C. Retention times (t_R) and integrated ratios were obtained from Hewlett Packard 3393A integrators.

Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr; boiling points (bp) corresponding to uncorrected air-bath temperatures. All commercial reagents were purified by distillation r recrystalisation prior to use. All reactions were performed under an inert atmosphere of dry N_2.

Literature Preparations

(*E*)-Methyl-(1-heptenyl)siletane (**1**),[1] (*E*)-Dimethyl-1-heptenylsilanol (**2**)[2], (*E*)-Diisopropyl-1-heptenylsilanol (**3**)[2] and (*E*)-Diisopropyl-1-heptenylchlorosilane[2] were prepared by literature methods

Reaction of (*E*)-Methyl-(1-heptenyl)silacyclobutane with TBAF [JY-III-96 / DW-V-29]



In a 10 mL round bottomed flask was placed 547 mg (3.0 mmol) of silacyclobutane **1** to which was added 3.0 mL (1.0 M in THF, 3.0 mmol, 1.0 equiv) of *n*-$Bu_4N^+F^-$ (TBAF) solution at room temperature. The solution temperature rose to 35 ^oC and then was allowed to cool to room temperature (10 min). The reaction mixture was then filtered through a plug of silica gel (10 g) which was further eluted with ether (20 mL). The combined organic fractions were dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo* to give a yellow oil. This residue was purified by column chromatography (silica gel, hexane, then hexane/ethyl acetate, 19/1) to give first disiloxane **5** as a colorless oil (258 mg, 45 %, after Kugelrohr distillation) then silanol **4** also as a colorless oil (253 mg, 42 %, after Kugelrohr distillation).

Data for (*E*)-**4**:

bp: 145 ^oC (0.9 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.18 (dt, *J* = 18.9, 6.2 Hz, HC(2), 1 H); 5.62 (d, *J* = 18.7 Hz, HC(1), 1 H); 2.11 (m, HC(3), 2 H); 1.60 (brs, OH, 1 H); 1.40 (m, 4 H); 1.29 (m, 4 H); 0.97 (t, *J* = 7.3 Hz, HC(3"), 3H); 0.88 (t, *J* = 7.1 Hz, HC(7), 3 H); 0.64 (t, *J* = 6.4 Hz, HC(1"), 2H); 0.19 (s, HC(1'), 3 H).

^{13}C NMR: (126 MHz, $CDCl_3$)

149.5 (C1), 129.3 (C(2)), 36.6 (C(3)), 31.4 (C(4)), 28.2 (C(5)), 22.5 (C(6)), 19.2, 18.0, 16.6, 14.0, -1.65 (C(1')).

^{29}Si NMR: (99.3 MHz, THF-d_8)

-0.30.

IR: (NaCl)

3200 (s, br), 2964 (s), 2914 (s), 2874 (s), 2859 (s), 1606 (w), 1251 (s), 866 (s); 793 (s).

MS: (EI, 70 eV)

200 (M^+, 2), 158 (25), 159 (100), 143 (11), 61 (42).

TLC: R_f 0.25 (hexane/EtOAc, 19/1).

GC: t_R (*E*)-**4**, 5.05 min (100%) (HP5, 250 ^{o}C, 15 psi).

Analysis: $C_{11}H_{24}OSi$ (172.34)

Caculated	C, 65.93;	H, 12.09%
Found	C, 65.94;	H, 12.30%

Data for (*E*)-**5**:

bp: 180 ^{o}C (0.9 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.09 (dt, *J* = 18.6, 6.4 Hz, HC(2), 2 H); 5.55 (d, *J* = 18.6 Hz, HC(1), 2 H); 2.10 (m, HC(3), 4 H); 1.38 (m, 16 H); 0.95 (t, *J* = 7.3 Hz, HC(3"), 6H); 0.89 (t, *J* = 7.1 Hz, HC(7), 6 H); 0.56 (t, *J* = 5.9 Hz, HC(1"), 4H); 0.08 (s, HC(1'), 6 H).

^{13}C NMR: (126 MHz, $CDCl_3$)

148.4 (C1), 128.6 (C(2)), 36.6 (C(3)), 31.4 (C(4)), 28.3 (C(5)), 22.5 (C(6)), 20.1, 18.2, 16.7, 14.0, -0.93 (C(1')).

^{29}Si NMR: (99.3 MHz, THF-d_8)

-4.25.

IR: (NaCl)

2956 (s), 2926 (s), 2859 (s), 1054 (s), 992 (m).

MS: (EI, 70 eV)

382 (M^+, 41), 339 (100), 297 (17), 243 (18), 201 (24), 143 (27).

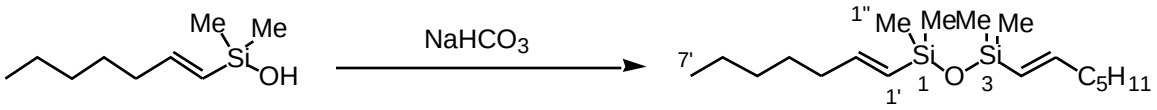
TLC: R_f 0.9 (hexane/EtOAc, 19/1).

GC: t_R (*E*)-**5**, 9.50 min (100%) (HP5, 250 ^{o}C, 15 psi).

Analysis: $C_{22}H_{46}OSi_2$ (172.34)

Calculated	C, 69.03;	H, 12.11%
Found	C, 68.89;	H, 12.09%

Preparation of (*E*,*E*)-1,1,3,3-Tetramethyl-1,3-di-(1-heptenyl)disiloxane (6) [DW-IV-62]



2 **6**

To a solution of 5.313 g (30.0 mmol) of (*E*)-dimethyl-(1-heptenyl)silanol (**2**) in 30 mL of ether, was added 20 mL of a 10 % aqueous solution of $NaHCO_3$. The reaction was stirred at room temperature for 30 min. The aqueous phase was separated and then extracted with ether (3 × 10 mL) and the combined organic phases were washed with water (1 × 10 mL) and brine (3 × 30 mL). The organic layer was dried over $MgSO_4$ and filtered. The solvent was then evaporated *in vacuo* to give a yellow oil which was purified by distillation to afford 3.836 g (74%) of **6** as a colorless oil.

Data for (*E*)-**6**:

bp: 120 °C (0.9 mmHg)

^{1}H NMR: (400 MHz, $CDCl_3$)

6.09 (dt, *J* = 18.7, 6.2 Hz, HC(2'), 2 H); 5.59 (dt, *J* = 18.7, 1.5 Hz, HC(1'), 2 H); 2.09 (qd, *J* = 6.2, 1.5 Hz, HC(3'), 4 H); 1.39 (qn, *J* = 7.3 Hz, HC(4'), 4 H); 1.29 (m, HC(5') and HC(6'), 8 H); 0.89 (t, *J* = 7.1 Hz, HC(7'), 6 H); 0.11 (s, HC(1"), 12 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

148.1 (C(1')), 128.2 (C(2')), 36.5 (C(3')), 31.4 (C(4')), 28.1 (C(5')), 22.5 (C(6')), 14.0 (C(7')), 0.0 (C(1")).

^{29}Si NMR: (99.3 MHz, THF-d_8)

-3.95.

IR: (NaCl)

2959 (s), 2928 (s), 2858 (s), 1620 (s), 1253 (s), 1052 (s), 992 (m), 841 (s); 798 (s).

MS: (EI, 70 eV)

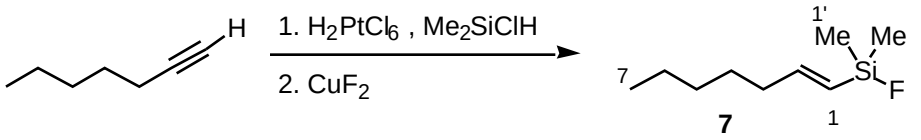
326 (M^+, 16), 311 (16), 213 (18), 157 (21), 133 (100), 119 (42).

TLC: R_f 0.91 (pentane/EtOAc, 19/1).

Analysis: $C_{18}H_{38}OSi_2$ (172.34)

Calculated	C, 66.18;	H, 11.73;	Si, 17.19%
Found	C, 66.20;	H, 11.99;	Si, 17.23%

Preparation of (*E*)-Dimethylfluoro-(1-heptenyl)silane (7) [DW-IV-61]



Hexachloroplatinic acid (26.6 mg, 65 μmol, 0.005 equiv) was dissolved in 1 mL of 2-propanol and 30 mL of diethyl ether in a dry, two-neck, round-bottom flask equipped with a stir bar and a reflux condenser under an atmosphere of dry argon. Chlorodimethylsilane (2.155 g, 14.3 mmol, 1.1 equiv) was then added and the mixture was heated to reflux. A solution of 1.250 g (13.0 mmol) of 1-heptyne in 10 mL of dry ether was then added dropwise over 10 min, at a rate sufficient to maintain reflux of the reaction mixture. After the addition was complete, the mixture was heated in an oil bath to reflux for 4 h. After cooling to room temperature, the solvent was evaporated *in vacuo* and the residual oil was distilled (114 ^{o}C at 6 mmHg) to give 2.682 g (84 %) of the chlorosilane as a colorless liquid.

The intermediate chlorosilane (2.731 g, 11.1 mmol) was dissolved in 20 mL of ether and 564 mg (5.55 mmol) of CuF_2 was added. The mixture was stirred at room temperature overnight and was then filtered through Celite®. The filtrate was dried over $MgSO_4$, filtered and the solvents evaporated *in vacuo* to give a oil which was distilled twice to give 2.408 g (95.3%) of **7** as a colorless oil.

Data for (*E*)-**7**:

bp: 70 ^{o}C (20 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.27 (dtd, *J* = 18.7, 6.2, 1.1 Hz, HC(2), 1 H); 5.65 (dtd, *J* = 18.7, 1.5, 1.5 Hz, HC(1), 1 H); 2.14 (qd, *J* = 7.3, 1.3 Hz, HC(3), 2 H); 1.41 (qn, *J* = 7.3 Hz, HC(4), 2 H); 1.31 (m, HC(5) and HC(6), 4 H); 0.89 (t, *J* = 7.1 Hz, HC(7), 3 H); 0.27 (d, *J* = 7.3 Hz, HC(1'), 6 H).

^{13}C NMR: (100 MHz, $CDCl_3$)

151.4 (d, *J* = 4.2 Hz, C(2)), 125.2 (d, *J* = 16.8 Hz, C(1)), 36.4 (C(3)), 31.2 (C(4)), 27.8 (C(5)), 22.4 (C(6)), 13.9 (C(7)), -1.4(d, *J* = 16.0 Hz, C(1')).

^{19}F NMR: (376 MHz, $CDCl_3$)

-160.2

^{29}Si NMR: (99 MHz, THF-d_8)

18.40 (d, *J* = 225 Hz).

IR: (NaCl)

2929 (s), 2859 (s), 1619 (s), 1467 (s), 1256 (s), 993 (s), 871 (s).

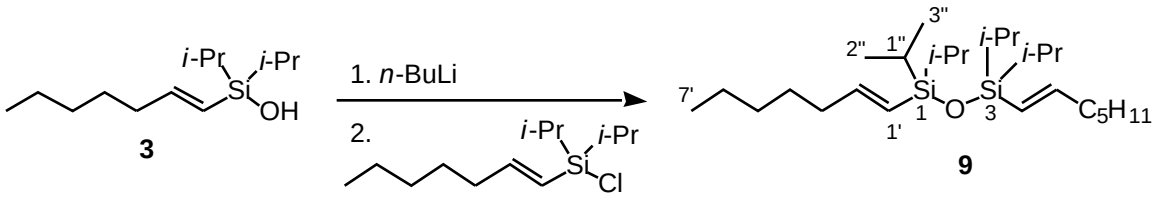
MS: (EI, 70 eV)

174 (M^+, 2.6), 159 (14), 155 (23), 118 (48), 89 (11), 77 (100), 63 (11).

Analysis: $C_9H_{19}FOSi$ (174.33)

Calculated	C, 62.01;	H, 10.99;	F, 10.90;	Si, 16.11%
Found	C, 61.96;	H, 11.02;	F, 10.53;	Si, 16.40%

Preparation of (*E*,*E*)-1,1,3,3-Tetraisopropyl-1,3-di-(1-heptenyl)disiloxane (9) [DW-IX-34]



In a 250-mL, flame-dried, round-bottomed flask, 1142 mg (5.0 mmol) of (*E*)-diisopropyl-1-heptenylsilanol[2] was dissolved in 50 mL dry THF under N_2 and was cooled to 0 °C. *n*-BuLi (3.34 mL, 1.5 M, 5.0 mmol) was added via syringe and the reaction was stirred at 0 °C for 10 min. (*E*)-Diisopropyl-1-heptenylchlorosilane[2] (1235 mg, 5.0 mmol) was then added and the solution was warmed to rt, at which temperature it was stirred for an additional 36 h. The reaction mixture was then poured into ether (20 mL) and the mixture was washed with water (3 × 50 mL) and brine (1 × 50 mL). The organic phase was then dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*, to give a colorless oil. Purification of the oil by column chromatography (silica gel, pentane), followed by distillation afforded 1140 mg (52 %) of desired **9** as a colorless oil and 800 mg (35 %) of starting silanol **3** as colorless oil.

Data for (*E*)-**9**:

bp: 120 °C (0.2 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.14 (dt, *J* = 18.7, 6.4 Hz, HC(2'), 2 H); 5.51 (dt, *J* = 18.7, 1.5 Hz, HC(1'), 2 H); 2.11 (qd, *J* = 6.6, 1.5 Hz, HC(3'), 4 H); 1.39 (qn, *J* = 6.9 Hz, HC(4'), 4 H); 1.30 (m, HC(5') and HC(6'), 8 H); 1.1-0.92 (m, HC(1"), HC(2") and HC(3"), 14 H); 0.88 (t, *J* = 6.8 Hz, HC(7'), 6 H).

^{13}C NMR: (125 MHz, $CDCl_3$)

149.6 (C(2')), 124.8 (C(1')), 36.9 (C(3')), 31.3 (C(4')), 28.4 (C(5')), 22.5 (C(6')), 17.49, 17.43, 14.0 (C(1")), 13.4 (C(7')).

^{29}Si NMR: (149 MHz, THF-d_8)

-3.56.

IR: (NaCl)

2958 (s), 2927 (s), 2865 (s), 1619 (m), 1464 (m), 1083 (s), 1056 (s), 993 (s), 882 (m).

MS: (EI, 70 eV)

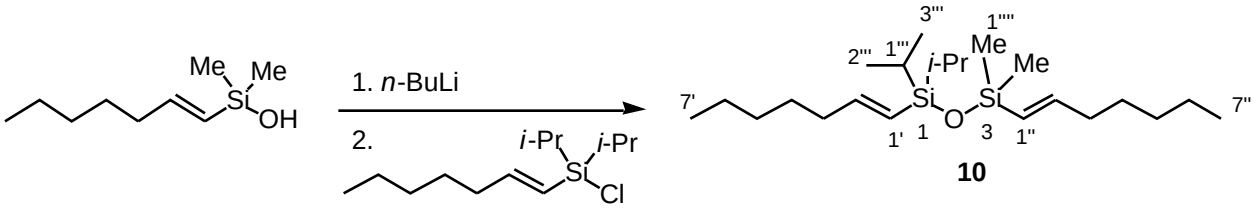
438 (M^+, 0.6), 395 (100), 299 (26), 225 (77), 169 (78), 141 (21), 97 (12), 85 (23), 59 (30).

TLC: R_f 0.95 (pentane).

Analysis: $C_{26}H_{54}OSi_2$ (438.89)

Calculated	C, 71.15;	H, 12.40;	Si, 12.80%
Found	C, 71.23;	H, 12.53;	Si, 12.76%

Preparation of (*E,E*)-1,1-Diisopropyl-3,3-dimethyl-1,3-di-(1-heptenyl)disiloxane (10) [DW-IX-35]



In a flame-dried, 250-mL, round-bottomed flask, was placed 862 mg (5.0 mmol) of (*E*)-dimethyl-1-heptenylsilanol (**2**) together with 50 mL dry THF under N_2 and the solution was cooled to 0 °C. *n*-BuLi (3.34 mL, 1.5 M, 5.0 mmol) was added via syringe and the solution was stirred at 0 °C for 10 min. (*E*)-Diisopropyl-1-heptenylchlorosilane[2] (1482 mg, 6.0 mmol) was then added and the mixture was warmed to rt, at which temperature it was stirred for 36 h. The reaction mixture was then poured into ether (20 mL) which was washed with water (3 × 50 mL) and brine (1 × 50 mL). The organic phase was then dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*, to give a colorless oil. Purification by column chromatography (silica gel, pentane, then reversed phase C-18, MeOH/H_2O, 19/1), followed by distillation afforded 1192 mg (62 %) of **10** as a colorless oil.

Data for (*E*)-**10**:

bp: 97 °C (0.2 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.10 (dt, *J* =18.7, 6.2 Hz,coinciding HC(2') and HC(2"), 2 H); 5.62 (dt, *J* = 18.7, 1.5 Hz, 1 H); 5.46 (dt, *J* = 18.9, 1.5 Hz, 1 H); 2.11 (m, HC(3') and HC(3"), 4 H); 1.39 (m, HC(4') and HC(4"), 4 H); 1.29 (m, HC(5'), HC(5"), HC(6') and HC(6"), 8 H); 0.96 (d, *J* = 7.1 Hz, 3 H); 0.93 (d, *J* = 7.1 Hz, 3 H); 0.95 (m, HC(1'"), 1 H); 0.888 (t, *J* = 6.6 Hz, 3 H); 0.885 (t, *J* = 7.0 Hz, 3 H); 0.13 (s, HC(1""), 6 H).

^{13}C NMR: (125 MHz, $CDCl_3$)

149.8, 148.0, 129.5, 124.3, 36.8, 36.5, 31.4, 31.3, 28.4, 28.3, 22.52, 22.48, 17.3, 17.1, 14.05, 14.02, 13.0, 0.9.

^{29}Si NMR: (149 MHz, THF-d_8)

-2.30, -4.88.

IR: (NaCl)

2927 (s), 2864 (s), 1619 (s), 1464 (s), 1252 (s), 1084 (s), 993 (s), 882 (s), 838 (s), 792 (s).

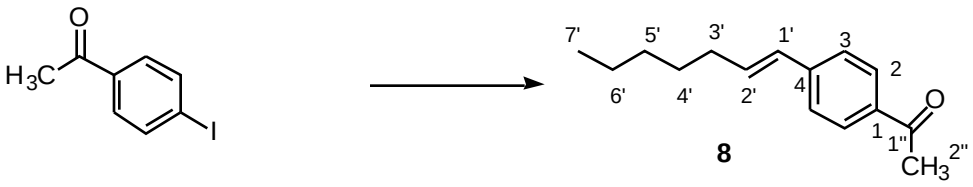
MS: (EI, 70 eV)

382 (M^+, 0.5), 339 (100), 299 (13), 243 (30), 225 (20), 169 (20), 105 (14), 73 (11), 59 (18).

TLC: R_f 0.92 (pentane).

HRMS: calculated for $C_{22}H_{46}OSi_2$, 382.308723; found, 382.3089.

Experiments Related to Table 1. General Procedure.



8

The organosilicon compound (silanol and fluorosilane 1.0 mmol, disiloxane 0.5 mmol) was added to a solution of the indicated activator (0-2 equiv) in THF and the mixture was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) was added to the mixture, followed by the palladium catalyst (29 mg, 5 mol%) and the mixture was stirred at room temperature for 10 min-24 h. The reaction mixture was then filtered through a short silica gel column (20 g). The plug was washed with diethyl ether (100 mL) and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (Reverse Phase C18, MeOH-H_2O 4/1) to afford the coupling product **8** which was further purified by distillation.

Reaction of 4-Iodoacetophenone with (*E*)-Dimethyl-(1-heptenyl)silanol (2) in the Absence of an Activator [DW-IV-64].

Following the General Procedure, (*E*)-**2** (172 mg, 1.0 mmol), was dissolved in THF (3 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the suspension was stirred at rt for 24 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 239 mg (97 %) of 4-iodoacetophenone as off-white crystals.

Data for 4-Iodoacetophenone:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.82 (d, J = 8.6 Hz, 2 H); 7.65 (d, J = 8.6 Hz, 2 H); 2.56 (s, 3 H).

^{13}C NMR: (125 MHz, $CDCl_3$)

197.3, 137.9, 136.3, 129.7, 101.1, 26.4.

TLC: R_f 0.39 ($MeOH/H_2O$, 9/1).

Reaction of 4-Iodoacetophenone with (*E,E*)-1,1,3,3-Tetramethyl-1,3-di-(1-heptenyl)disiloxane (6) in the Absence of an Activator [DW-IV-76].

Following the General Procedure, (*E*)-**2** (172 mg, 1.0 mmol), was dissolved in THF (3 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the suspension was stirred at rt for 24 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, $MeOH/H_2O$, 9/1) afforded 227 mg (92 %) of 4-iodoacetophenone as off-white crystals.

Data for 4-Iodoacetophenone:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.82 (d, J = 8.6 Hz, 2 H); 7.65 (d, J = 8.6 Hz, 2 H); 2.56 (s, 3 H).

^{13}C NMR: (125 MHz, $CDCl_3$)

197.3, 137.9, 136.3, 129.7, 101.1, 26.4.

TLC: R_f 0.39 ($MeOH/H_2O$, 9/1).

Reaction of 4-Iodoacetophenone with (*E*)-Dimethylfluoro-(1-heptenyl)silane (7) in the Absence of an Activator [DW-IV-84].

Following the General Procedure, (*E*)-**7** (174 mg, 1.0 mmol), was dissolved in THF (3 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the suspension was stirred at rt for 22 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, $MeOH/H_2O$, 9/1) afforded 211 mg (86 %) of 4-iodoacetophenone as off-white crystals.

Data for 4-Iodoacetophenone:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.82 (d, J = 8.6 Hz, 2 H); 7.65 (d, J = 8.6 Hz, 2 H); 2.56 (s, 3 H).

^{13}C NMR: (125 MHz, $CDCl_3$)

197.3, 137.9, 136.3, 129.7, 101.1, 26.4.

TLC: R_f 0.42 ($MeOH/H_2O$, 4/1).

Reaction of 4-Iodoacetophenone with (*E*)-Dimethyl-(1-heptenyl)silanol (2) in the Presence of of Tetra-*n*-butylammonium Fluoride (1 equiv) [DW-IV-67].

Following the General Procedure, (*E*)-**2** (172 mg, 1.0 mmol) was dissolved in TBAF solution (1 mL, 1.0 M in THF, 1.0 mmol) and THF (2 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 1 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 185 mg (86 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil. Kugelrohr distillation of the residue gave 177 mg (82 %) of **8** as colorless oil.

Data for **8**:

bp: 120 ºC (0.9 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: *Rf* 0.42 (MeOH/H_2O, 4/1).

Reaction of 4-Iodoacetophenone with (*E,E*)-1,1,3,3-Tetramethyl-1,3-di-(1-heptenyl)disiloxane (6) in the Presence of Tetra-*n*-butylammonium Fluoride (1 equiv) [DW-IV-79].

Following the General Procedure, (*E*)-**6** (163 mg, 0.5 mmol) was dissolved in TBAF solution (1 mL, 1.0 M in THF, 1.0 mmol) and THF (2 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 1 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 180 mg (83 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil.

Data for **8**:

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: *Rf* 0.42 (MeOH/H_2O, 4/1).

Reaction of 4-Iodoacetophenone with (*E*)-Dimethylfluoro-(1-heptenyl)silane (7) in the Presence of Tetra-*n*-butylammonium Fluoride (1 equiv) [DW-IV-87].

Following the General Procedure, (*E*)-**7** (174 mg, 1.0 mmol) was dissolved in TBAF solution (1 mL, 1.0 M in THF, 1.0 mmol) and THF (2 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 1 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 171 mg (79 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil.

Data for **8**:

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: R_f 0.39 (MeOH/H_2O, 9/1).

Reaction of 4-Iodoacetophenone with (*E*)-Dimethyl-(1-heptenyl)silanol (2) in the Presence of Tetra-*n*-butylammonium Fluoride (2 equiv) [DW-IV-92].

Following the General Procedure, (*E*)-**2** (172 mg, 1.0 mmol) was dissolved in TBAF solution (2 mL, 1.0 M in THF, 2.0 mmol) and THF (1 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 10 min and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O,9/1) afforded 170 mg (79 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil.

Data for **8**:

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: R_f 0.39 (MeOH/H_2O, 9/1).

Reaction of 4-Iodoacetophenone with (*E,E*)-1,1,3,3-Tetramethyl-1,3-di-(1-heptenyl)disiloxane (6) in the Presence of Tetra-*n*-butylammonium Fluoride (2 equiv) [DW-IV-93].

Following the General Procedure, (*E*)-**6** (163 mg, 0.5 mmol) was dissolved in TBAF solution (2 mL, 1.0 M in THF, 2.0 mmol) and THF (1 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 10 min and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 178 mg (82 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil.

Data for **8**:

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: *Rf* 0.39 (MeOH/H_2O, 9/1).

Reaction of 4-Iodoacetophenone with (*E*)-Dimethyl-fluoro-(1-heptenyl)silane (7) in the Presence of 2 equiv Tetra-*n*-butylammonium fluoride as the activator [DW-IV-94].

Following the General Procedure, (*E*)-**7** (174 mg, 1.0 mmol) was dissolved in TBAF solution (2 mL, 1.0 M in THF, 2.0 mmol) and THF (2 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 10 min and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 169 mg (78 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil.

Data for **8**:

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: *Rf* 0.39 (MeOH/H_2O, 9/1).

Reaction of 4-Iodoacetophenone with (*E*)-Dimethyl-(1-heptenyl)silanol (2) in the Presence of Tetra-*n*-butylammonium Hydroxide (1 equiv) [DW-IV-66].

Following the General Procedure, 172 mg (1.0 mmol) of (*E*)-**2** was dissolved in TBAOH solution (0.65 mL, 40 % aqueous, 1.0 mmol) and THF (2.35 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 3 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded (*E*)-4-(1-heptenyl)acetophenone (**8**) (178 mg, 82 %) as a yellow oil. Kugelrohr distillation afforded 162 mg (75 %)of **8** as a colorless oil.

Data for **8**:

bp: 120 ºC (0.9 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: *Rf* 0.39 (MeOH/H_2O, 9/1).

Reaction of 4-Iodoacetophenone with (*E,E*)-1,1,3,3-Tetramethyl-1,3-di-(1-heptenyl)disiloxane (6) in the Presence of Tetra-*n*-butylammonium Hydroxide (1 equiv) [DW-IV-78].

Following the General Procedure, (*E*)-**6** (163 mg, 0.5 mmol) was dissolved in TBAOH solution (0.65 mL, 40 % aqueous, 1.0 mmol) and THF (2.35 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 3 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 169 mg (78 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil.

Data for **8**:

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: *Rf* 0.39 (MeOH/H_2O, 9/1).

Reaction of 4-Iodoacetophenone with (*E*)-Dimethylfluoro-(1-heptenyl)silane (7) in the Presence of Tetra-*n*-butylammonium Hydroxide (1 equiv) [DW-IV-86].

Following the General Procedure, (*E*)-**7** (174 mg, 1.0 mmol) was dissolved in TBAOH solution (0.65 mL, 40 % aqueous, 1.0 mmol) and THF (2.35 mL) and was stirred for 10 min at rt. 4-Iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 24 h and then was filtered through SiO_2. Purification of the residue by column chromatography (RP C18, MeOH/H_2O, 9/1) afforded 45 mg (22 %) of (*E*)-4-(1-heptenyl)acetophenone (**8**) as a yellow oil along with 4-iodoacetophenone (156 mg, 63 %) as white crystals.

Data for **8**:

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: R_f 0.39 (MeOH/H_2O, 9/1).

NMR-experiments of Organosilicon Precursors with TBAF (Scheme 3).

Rection of (*E*)-Methyl-(1-heptenyl)silacyclobutane (1) with TBAF [DW-V-14]

Silacyclobutane (**1**) (9.1 mg, 0.05 mmol) was dissolved in THF-d_8 (0.5 mL) in a dry NMR-tube under N_2. TBAF (16 mg, 0.05 mmol) was added and the ^{1}H-NMR spectrum was recorded. Disiloxane **5** and the unknown **X** could be detected in a 1/1 ratio (see paper).

Data for **5**:

^{1}H NMR: (400 MHz, THF-d_8)

6.09 (dt, *J* = 18.6, 6.4 Hz, HC(2), 2 H); 5.55 (d, *J* = 18.6 Hz, HC(1), 2 H); 0.50 (t, *J* = 5.9 Hz, HC(1''), 4H); -0.02 (s, HC(1'), 6 H).

Data for **X**:

^{1}H NMR: (400 MHz, THF-d_8)

0.58 (t, *J* = 8.3 Hz, 2H); 0.09 (s, 3H).

Rection of (*E*)-Dimethyl-(1-heptenyl)silanol (2) with TBAF [DW-V-17]

Silanol (**2**) (8.6 mg, 0.05 mmol) was dissolved in THF-d_8 (0.5 mL) in a dry NMR-tube under N_2. TBAF (16 mg, 0.05 mmol) was added and the ^{1}H-NMR spectrum was recorded. The disiloxane **6** and the unknown **Y** could be detected in a 1/1 ratio (see paper).

Data for **6**:

^{1}H NMR: (500 MHz, THF-d_8)

6.13 (dt, J = 18.7, 6.2 Hz, HC(2), 2 H); 5.62 (dt, J = 18.7, 1.5 Hz, HC(1), 2 H); 0.10 (s, HC(1'), 12 H).

Data for **Y**:

^{1}H NMR: 500 MHz, THF-d_8)

6.08 (dt, J = 18.5, 6.5 Hz, HC(2), 2 H); 5.65 (dt, J = 18.5, 1.0 Hz, HC(1), 2 H); 0.08 (s, HC(1'), 6 H).

Rection of (*E*,*E*)-1,1,3,3-Tetramethyl-1,3-di-(1-heptenyl)disiloxane (6) with TBAF [DW-V-21]

Disiloxane (**6**) (8.2 mg, 0.025 mmol) was dissolved in THF-d_8 (0.5 mL) in a dry NMR-tube under N_2. TBAF (16 mg, 0.05 mmol) was added and the ^{1}H-NMR spectrum was recorded. The disiloxane **6** and the unknown **Y** could be detected in a 1/1 ratio (see paper).

Data for **6**:

^{1}H NMR: (500 MHz, THF-d_8)

6.13 (dt, J = 18.7, 6.2 Hz, HC(2), 2 H); 5.62 (dt, J = 18.7, 1.5 Hz, HC(1), 2 H); 0.10 (s, HC(1'), 12 H).

Data for **Y**:

^{1}H NMR: 500 MHz, THF-d_8)

6.08 (dt, J = 18.5, 6.5 Hz, HC(2), 2 H); 5.65 (dt, J = 18.5, 1.0 Hz, HC(1), 2 H); 0.08 (s, HC(1'), 6 H).

Rection of (*E*)-Dimethylfluoro-(1-heptenyl)silane (7) with TBAF [DW-V-18]

Fluorosilane (**2**) (8.8 mg, 0.05 mmol) was dissolved in THF-d_8 (0.5 mL) in a dry NMR-tube under N_2. TBAF (16 mg, 0.05 mmol) was added and the ^{1}H-NMR spectrum was recorded. The disiloxane **6** and the unknown **Y** could be detected in a 1/1 ratio (see paper).

Data for **6**:

^{1}H NMR: (500 MHz, THF-d_8)

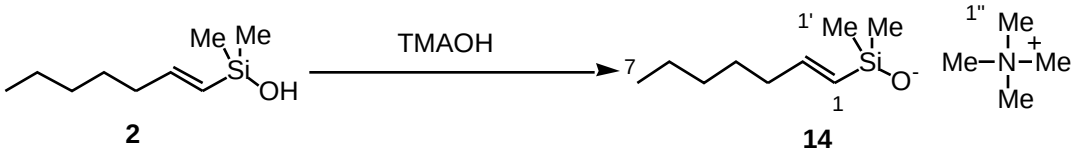
6.13 (dt, J = 18.7, 6.2 Hz, HC(2), 2 H); 5.62 (dt, J = 18.7, 1.5 Hz, HC(1), 2 H); 0.10 (s, HC(1'), 12 H).

Data for **Y**:

^{1}H NMR: (500 MHz, THF-d_8)

6.08 (dt, J = 18.5, 6.5 Hz, HC(2), 2 H); 5.65 (dt, J = 18.5, 1.0 Hz, HC(1), 2 H); 0.08 (s, HC(1'), 6 H).

Preparation of Tetramethylammonium (*E*)-Dimethyl-(1-heptenyl)silyloxide (14) [DW-VIII-56]



2 **14**

In a two-neck, 200-mL, round-bottomed flask, were placed 1035 mg (6.0 mmol) of silanol **2** and a solution of 1089 mg (6.0 mmol) tetramethylammonium hydroxide pentahydrate in *i*-PrOH (100 mL) at rt under N_2. The flask was evacuated and the solvent was removed. This process was repeated twice with *i*-PrOH (100 mL), twice with CH_3CN (100 mL) and once with methanol (100 mL). The oily residue was then evacuated overnight to form brownish crystals (1465 mg) which were stored in the glove-box.

Data for **14**:

^{1}H NMR: (500 MHz, CD_3CN)

5.89 (dt, J = 18.2, 6.3 Hz, HC(2), 1 H); 5.63 (dt, J = 18.2, 1.5 Hz, HC(1), 1 H); 3.14 (s, HC(1''), 12H); 2.00 (qd, J = 6.3, 1.5 Hz, HC(3), 2H); 1.33 (m, HC(4), HC(5) and HC(6), 6H); 0.87 (t, J = 6.9 Hz, HC(7), 3H); -0.20 (s, HC(1'), 3 H).

^{13}C NMR: (126 MHz, CD_3CN)

142.8 (C(2)), 56.0 (C(1'')), 37.6 (C(3)), 32.4 (C(4)), 29.7 (C(5)), 23.3 (C(6)), 14.4 (C(7)), 3.8 (C(1')).

^{29}Si NMR: (119 MHz, CD_3CN)

-20.9.

^{29}Si NMR: (119 MHz, DMF-d_7)

-26.2.

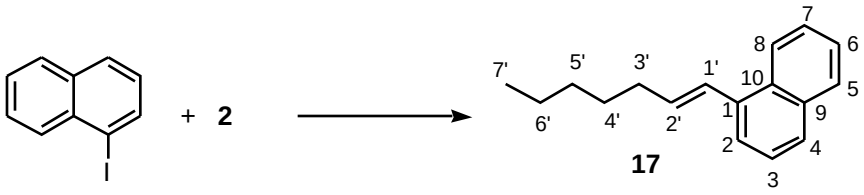
Analysis: $C_{13}H_{31}NOSi$ (245.48)

Calculated for 1.5 H_2O	C, 57.68;	H, 12.59;	N, 5.17 %
Calculated	C, 63.61;	H, 12.73;	N, 5.71%
Found	C, 57.73;	H, 12.78;	N, 5.15%

NMR kinetic Analysis of a Coupling-Reaction of (*E*)-Methyl-(1-heptenyl)silacyclobutane (1) with Thiophene [DW-V-82]

In a dry NMR-tube under N_2, silacyclobutane **1** (9.1 mg, 0.05 mmol) and dimethoxybenzene (5.2 mg, 0.0125 mmol, internal standard) were added to a solution of TBAF (47 mg, 0.15 mmol) in THF-d_8. A ^{1}H NMR-spectrum was recorded in which the ratio of disiloxane **5** and unknown **X** was determined based on integration of the signals at δ 0.50 and 0.58 ppm. 2-Iodothiophene (5.6 μL, 0.05 mmol) was added and the spectrum was integrated again. $Pd(dba)_2$ (1.4 mg, 2.5 μmol) in THF-d_8 (0.1 mL) was added and the reaction was followed by recording a spectrum every minute, comparing the integrated ratio of the starting materials to the signal for the product at δ 6.93 ppm.[2]

Preparation of (*E*)-1-(1-Heptenyl)naphthalene[1] (17) with TBAF [DW-VII-53]. (Table 3, entry 1)



In a 10-mL, round-bottomed flask, 172 mg (1.0 mmol) of silanol **2** was added to a solution of TBAF (631 mg, 2.0 mmol) in DMF (2 mL) at rt under N_2. 1-Iodonaphthalene (146 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 30 min, and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O, 9/1) and Kugelrohr distillation afforded 184 mg (82%) of **17** as a colorless oil.

Data for **17**:

bp: 155 °C (0.3 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.13 (d, *J* =8.4, 1 H), 7.84 (dd, *J* =7.2, 1.7, 1 H), 7.74 (d, *J* =8.3, 1 H), 7.56 (d, *J* =7.0, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =8.0, 7.4, 1 H), 7.12 (d, *J* =15.6, 1 H), 6.25 (dt, *J* =15.4, 7.0, 1 H), 2.34 (qd, *J* =7.5, 1.3, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, *J* =7.0, 3 H).

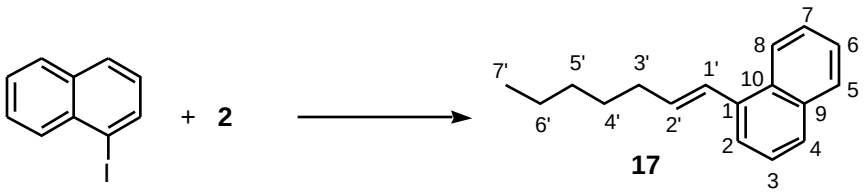
^{13}C NMR: (125 MHz, $CDCl_3$)

135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.6, 125.57, 123.9, 123.4, 33.4, 31.5, 29.1, 22.6, 14.1.

TLC: R_f 0.18 (MeOH/H_2O, 9/1).

GC: t_R (*E*)-**17**, 9.88 min (98.9%); t_R (*Z*)-**17**, 8.43 min (1.1%) (HP5, 260 °C, 15 psi).

Preparation of (*E*)-1-(1-Heptenyl)naphthalene[1] (17) with Aqueous TMAF [DW-VII-54]. (Table 3, entry 2)



In a 10-mL, round-bottomed flask, 172 mg (1.0 mmol) silanol **2** was added to a solution of TMAF (186 mg, 2.0 mmol) in DMF (2 mL) and water (108 μL, 6.0 mmol) at rt under N_2. 1-Iodonaphthalene (146 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 30 min, and was then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O, 9/1) and Kugelrohr distillation afforded 188 mg (84%) of **17** as a colorless oil.

Data for **17**:

bp: 155 ^oC (0.3 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.13 (d, *J* =8.4, 1 H), 7.84 (dd, *J* =7.2, 1.7, 1 H), 7.74 (d, *J* =8.3, 1 H), 7.56 (d, *J* =7.0, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =8.0, 7.4, 1 H), 7.12 (d, *J* =15.6, 1 H), 6.25 (dt, *J* =15.4, 7.0, 1 H), 2.34 (qd, *J* =7.5, 1.3, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, *J* =7.0, 3 H).

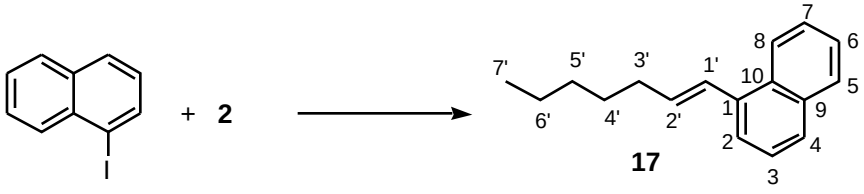
^{13}C NMR: (125 MHz, $CDCl_3$)

135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.6, 125.57, 123.9, 123.4, 33.4, 31.5, 29.1, 22.6, 14.1.

TLC: R_f 0.18 (MeOH/H_2O, 9/1).

GC: t_R (*E*)-**17**, 9.88 min (98.6%); t_R (*Z*)-**17**, 8.43 min (1.4%) (HP5, 260 ^oC, 15 psi).

Preparation of (*E*)-1-(1-Heptenyl)naphthalene[1] (17) with TMAF [DW-VII-55]. (Table 3, entry 3)



In a flame-dried 10 mL round bottomed flask, 172 mg (1.0 mmol) silanol **2** was added to a solution of TMAF (186 mg, 2.0 mmol) in DMF (2 mL) at rt under N_2. 1-Iodonaphthalene (146 μL, 1.0 mmol) and

$Pd(dba)_2$ (29 mg, 0.05 equiv) were added and the mixture was stirred at rt for 30 min, and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O, 9/1) and Kugelrohr distillation afforded 184 mg (82 %) of **17** as a colorless oil.

Data for **17**:

bp: 155 ^oC (0.3 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.13 (d, *J* =8.4, 1 H), 7.84 (dd, *J* =7.2, 1.7, 1 H), 7.74 (d, *J* =8.3, 1 H), 7.56 (d, *J* =7.0, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =8.0, 7.4, 1 H), 7.12 (d, *J* =15.6, 1 H), 6.25 (dt, *J* =15.4, 7.0, 1 H), 2.34 (qd, *J* =7.5, 1.3, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, *J* =7.0, 3 H).

^{13}C NMR: (125 MHz, $CDCl_3$)

135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.6, 125.57, 123.9, 123.4, 33.4, 31.5, 29.1, 22.6, 14.1.

TLC: R_f 0.18 (MeOH/H_2O, 9/1).

GC: t_R (*E*)-**17**, 9.88 min (98.9%); t_R (*Z*)-**17**, 8.43 min (1.1%) (HP5, 260 ^oC, 15 psi).

Reference

(1) Denmark, S. E.; Choi, J.-Y.; *J. Am. Chem. Soc* **1999**, *121*, 5821.

(2) Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565.