Highly Stereoselective Hydrocarbation of Terminal Alkynes via Pt-Catalyzed Hydrosilylation / Pd-Catalyzed Cross Coupling

Scott E. Denmark,* and Zhigang Wang

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Supporting Information

General Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 400 or Unity 500 spectrometer. Spectra were referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C) or tetramethylsilane (TMS) (δ 0.00 ppm, ^{1}H and ^{13}C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometry Center. Electron impact (EI) and chemical ionization (CI) 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 a 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. The 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), ether (Na-benzophenone). Column chromatography was performed using EM Science 230-400 mesh silica gel or ICN reverse phase 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 5890A and 5890 Series II. The following column was used: HP-5 50 m cross-linked 5% phenyl methyl silicone gum phase; HP-225 25 m 50% cyanopropylphenyl dimethylsiloxane, U-2 50 m 5% phenylmethylsilicone. 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. GC-MS was performed with a Hewlett Packard 5970 which was fitted with a HP-1 fused silica capillary column (25 m, 100% dimethylpolysiloxane). A temperature program (A) was used for GC/MS: initial temp = 100 °C; ramp = 50 °C/min; final temp = 250 °C.

Solutions of tetrabutylammonium fluoride (TBAF) in THF (1.0 M) employed in all descriptive runs were prepared from colorless crystalline tetrabutylammonium fluoride trihydrate (Fluka). Tetramethyldisiloxane was from Lancaster and directly used without further purification. Phenylacetylene (Aldrich) was distilled prior to use. All other alkynes, heptyne, 4-pentyn-1-ol (GFS) and 2-phenyl-3-butyn-1-ol (Fluka) were directly used without further purification. All the commercial halide reagents (Aldrich, ACROS) were purified by distillation or column chromatography prior to use. Allylpalladium chloride dimer $[allylPdCl]_2$ was purchased from ACROS. Platium(0)-1,3-divinyl-1,1,3,3,-tetramethyldisiloxane complex, solution in xylene was purchased from Aldrich.

t-Bu_3P-Pt(0) complex was prepared according to the literature procedure[1]: *t*-Bu_3P (32 mg, 0.158 mmol) (Strem Chemicals) was dissolved in platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (1.5 mL solution in xylene, Aldrich). The mixture was stirred at 65 °C (oil bath) for 5 min and then was slowly cooled to rt. This solution could be stored under N_2 in the freezer indefinitely.

Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr, boiling points (bp) corresponding to uncorrected air-bath temperatures. Melting points (mp) were recorded on a Capillary Melting Point Apparatus in sealed tubes. All the reactions were performed under an inert atmosphere of dry argon.

Literature Preparations

The following compounds were prepared by literature methods: *t*-Bu_3P-Pt(0) complex.[1] (*E*)-1-iodoheptene,[2] diethylethoxysilane,[3] 2-bromostyrene[4] and 5-(2-propenyloxy)-1-pentyne,[5] $Pd(dba)_2$.[6]

General Procedure I: One-pot Cross-coupling Reaction of Terminal Alkynes with Aryl or Alkenyl Halides.

To a solution of 1,1,3,3-tetramethyldisiloxane (0.65-1.8 mmol, 1.3/2-1.8/2 equiv) in THF was added *t*-Bu_3P-Pt(0) complex (25-50 μL). The neat alkyne (1.3-3.6 mmol, 1.3-1.8 equiv) was then slowly added with external cooling with a water bath (the temperature of reaction was not allowed to exceed 30 °C). The hydrosilylation mixture was stirred at rt for 30 min after the complete addition of the alkyne.

A solution of TBAF (Fluka, 1.0 M in THF, 2.0-6.0 mmol, 2.0-3.0 equiv) was added to above solution. After 10 min, the aryl or alkenyl halide (1.0-2.0 mmol, 1.0 equiv), $Pd(dba)_2$ (5 mol%) and (if required) Ph_3As (10 mol%) were sequentially added. A strong exotherm was observed. The reaction was monitored by GC or GC-MS. When the halide was consumed, ether (10 mL) was then added and the mixture was stirred for an additional 5 min. The mixture was

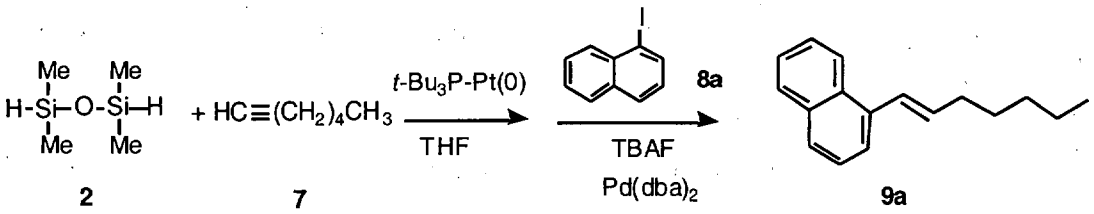
filtered through a short column of silica gel, then was eluted with ether (50–120 mL). The combined eluate was concentrated by rotary evaporation and vacuum drying to give the crude product which was purified by silica gel chromatography or RP chromatography and Kugelrohr distillation to afford the product.

General Procedure II: One-pot Cross-coupling Reaction of Terminal Alkyne and Aryl Halides, Reverse Order.

To a solution of 1,1,3,3-tetramethyldisiloxane (0.65-1.95 mmol, 1.3/2-1.95/2 equiv) in THF was added *t*-Bu_3P-Pt(0) complex (25-50 μL). The neat alkyne (1.3-3.0 mmol, 1.3-1.5 equiv) was then slowly added with external cooling with a water bath (the temperature of reaction was not allowed to exceed 30 °C). The hydrosilylation mixture was stirred at rt for 30 min after the complete the addition of the alkyne.

A solution of TBAF (Fluka, 1.0 M in THF, 4.0-6.0 mmol, 2.0-3.0 equiv) was added to above solution. After 10 min, $Pd(dba)_2$ (57.5 mg, 0.10 mmol, 5 mol%) was added. A solution of the aryl iodide (2.0 mmol, 1.0 equiv) in THF (2.0 mL, 1.0 M) was then slowly added by syringe such that the temperature of reaction solution did not exceed 30°C (addition time is about 45 min). The reaction mixture was stirred at room temperature and was monitored by GC. When the iodide was consumed, ether (10 mL) was then added and the mixture was stirred for an additional 5 min. The mixture was filtered through a short column of silica gel, then was eluted with ether. The combined eluate was concentrated by rotary evaporation and vacuum drying to give the crude product which was purified by silica gel chromatography and Kugelrohr distillation to afford the product.

Preparation of (*E*)-1-(1-Heptenyl)naphthalene ((*E*)-9a) [Table 2, entry 1]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), 1-iodonaphthalene (508 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (57.5 mg, 5 mol%) were added and the mixture was stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (50 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane) and RPC (C18, MeOH/H_2O, 9/1) followed by Kugelrohr distillation afforded 366.6 mg (82%) of **9a** as colorless oil which gave spectroscopic data consistent with those previously reported.[7]

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

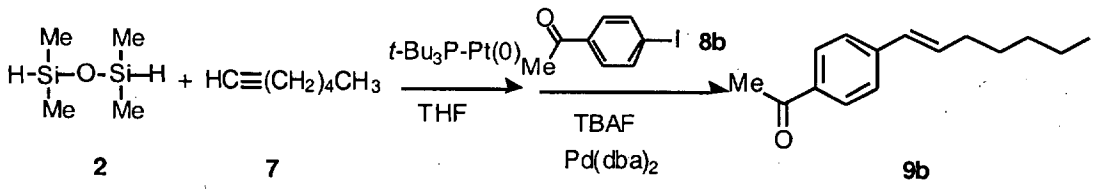
bp: 245 - 250 °C (0.1 mmHg)

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

8.13 (dd, J = 7.9, 0.9, 1 H), 7.83 (dd, J = 7.3, 1.7, 1 H), 7.73 (d, J = 8.2, 1 H), 7.55 (d, J = 7.1, 1 H), 7.46 (m, 3 H), 7.11 (d, J = 15.7, 1 H), 6.24 (dt, J = 15.7, 6.9, 1 H), 2.33 (m, 2 H), 1.54 (m, 2 H), 1.38 (m, 4 H), 0.93 (t, J = 6.9, 3 H).

GC: t_R (*E*)-**9a** 9.72 min (98.4%); (*Z*)-**9a** 8.06 min (0.1%); **10a** 7.55 min (1.5%) (HP-5, 250 °C, 15 psi).

Preparation of (*E*)-1-((4-Heptenyl)phenyl)ethanone ((*E*)-9b) [Table 2, entry 2]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), 4-iodoacetophenone (492 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (57.5 mg, 5 mol%) were added and the mixture was stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/EtOAc, 30/1) followed by Kugelrohr distillation afforded 405.8 mg (94%) of **9b** as colorless oil which gave spectroscopic data consistent with those previously reported.[7]

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

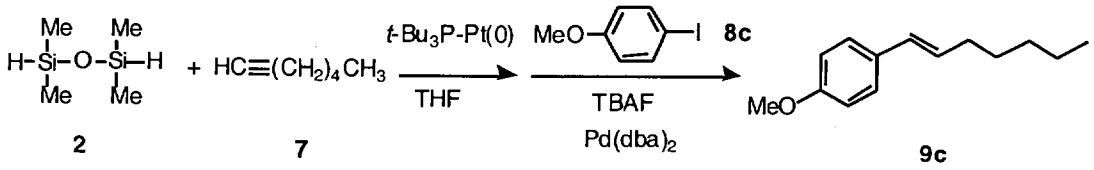
bp: 140 - 145 °C (0.1 mmHg)

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

7.89 (d, *J* = 8.6, 2 H), 7.41 (d, *J* = 8.4, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (m, 2 H), 1.49 (m, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* = 7.1, 3 H)

GC: t_R (*E*)-**9b** 8.26 min (99.1%); (*Z*)-**9b** 7.31 min (0.4%); **10b** 7.40 min (0.5%) (HP-5, 250 °C, 15 psi)

Preparation of (*E*)-1-(1-Heptenyl)-4-methoxybenzene ((*E*)-9c) [Table 2, entry 3]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (105 mg, 0.78 mmol, 1.3×1.2/2 equiv), *t*-Bu_3P-Pt(0) complex (25 μL) and heptyne (125 mg, 1.3 mmol, 1.3 equiv) in 0.15 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (2.0 mL, 1.0 M, 2.0 equiv), 4-iodoanisole (234 mg, 1.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (28.8 mg, 5 mol%) were added

and the mixture was stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/EtOAc, 50/1) followed by Kugelrohr distillation afforded 173 mg (84%) of **9c** as colorless oil which gave spectroscopic data consistent with those previously reported.[7]

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

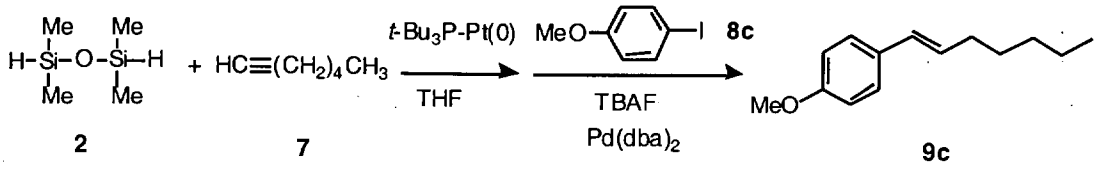
bp: 110 - 115 °C (0.2 mmHg)

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

7.29 (d, J = 8.8, 2 H), 6.86 (d, J = 8.8, 2 H), 6.34 (d, J = 15.9, 1 H), 6.11 (dt J = 15.9, 6.86, 1 H), 3.82 (s, 3 H), 2.20 (m, 2 H), 1.48 (m, 2 H), 1.35 (m, 4 H), 0.92 (t, J = 7.1, 3 H)

GC: t_R (*E*)-**9c** 6.65 min (96.5%); (*Z*)-**9c** 6.16 min (1.4%); **10c** 5.60 min (2.1%) (HP-5, 250 °C, 15 psi)

Preparation of (*E*)-1-(1-Heptenyl)-4-methoxybenzene ((*E*)-9c) [Table 2, entry 4]



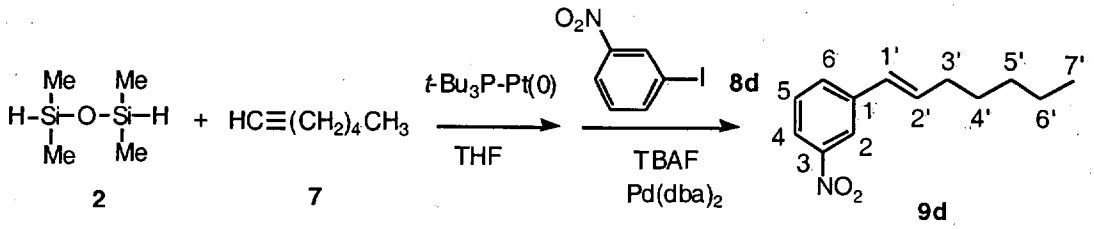
Following General Procedure II, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), t-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), $Pd(dba)_2$ (57.5 mg, 5.0 mol%) were added. A solution of 4-iodoanisole (2.0 mmol, 1.0 equiv) in THF (2.0 mL, 1.0 M) was then slowly added in 45 min. The mixture was stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (hexane/EtOAc, 50/1) followed by Kugelrohr distillation afforded 365 mg (89%) of **9c** as colorless oil which gave spectroscopic data consistent with those previously reported.[7] (See previous entry for data.)

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

bp: 100 - 105 °C (0.1 mmHg)

GC: t_R (*E*)-**9c** 6.54 min (97.7%); (*Z*)-**9c** 6.05 min (1.0%); **10c** 5.89 min (1.3%) (HP-5, 250 °C, 15 psi)

Preparation of (*E*)-1-(1-Heptenyl)-3-nitrobenzene ((*E*)-9d) [Table 2, entry 5]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), 3-iodonitrobenzene (498 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (57.5 mg, 5 mol%) were added and the mixture was stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/EtOAc, 50/1) followed by Kugelrohr distillation afforded 374 mg (85%) of **9d** as colorless oil.

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

bp: 160 - 165 °C (1.6 mmHg)

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

8.19 (t, *J* = 1.95, HC(2), 1 H), 8.03 (m, HC(4), 1 H), 7.62 (dd, *J* = 7.8, 1.2, HC(6), 1 H), 7.44 (t, *J* = 7.8, HC(5), 1 H), 6.40 (m, HC(1'), HC(2'), 2 H), 2.25 (m, $H_2C(3')$, 2 H), 1.51 (m, $H_2C(4')$, 2 H), 1.34 (m, $H_2C(5')$, $H_2C(6')$, 4 H), 0.91 (t, *J* = 7.1, $H_3C(7')$, 3 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

148.8 (C(3)), 139.9 (C(1)), 135.0 (C(2')), 132.1 (C(6)), 129.5 (C(5)), 127.9 (C(1')), 121.6 (C(4)), 120.7 (C(2)), 33.2 (C(3')), 31.6 (C(5')), 29.0 (C(4')), 22.7 (C(6')), 14.3 (C(7'))

IR: (NaCl)

3020 (w), 2957 (m), 2929 (s), 2857 (m), 1653 (w), 1529 (s), 1465 (w), 1350 (s), 964 (m), 900 (w), 805 (w)

MS: (EI, 70 eV)

220 (M^++1, 6), 219 (M^+, 26), 149 (100), 128 (18), 116 (63), 115 (81), 103 (26), 91 (14), 77 (18)

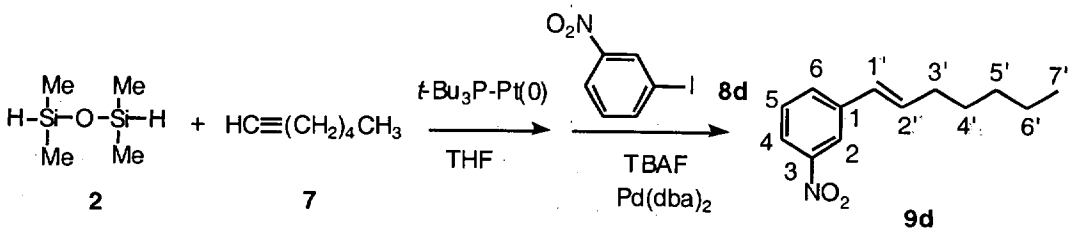
TLC: *Rf* 0.44 (hexane/EtOAc, 50/1)

GC-MS: t_R (*E*)-**9d** 8.40 min (97.5%, m/z 219); 8.28 min (1.7%, m/z 219); 7.96 min (0.8%, m/z 219) (HP-1, program A, 10 psi)

Analysis: $C_{13}H_{17}NO_2$ (219.28)

Calculated:	C, 71.21;	H, 7.81;	N, 6.39%
Found:	C, 71.01;	H, 7.77;	N, 6.66%

Preparation of (*E*)-1-(1-Heptenyl)-3-nitrobenzene ((*E*)-9d) [Table 2, entry 6]



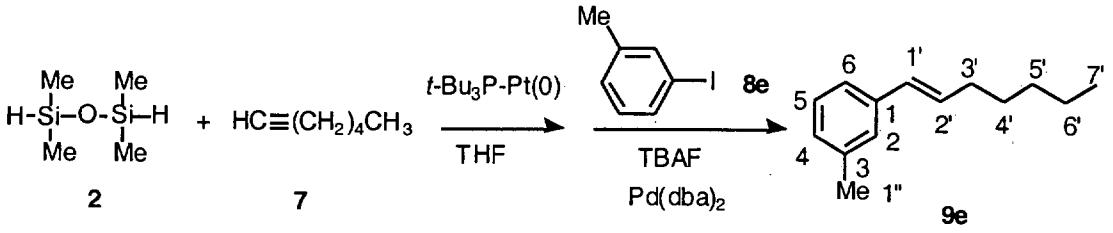
Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), 3-iodonitrobenzene (498 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (11.5 mg, 1 mol%) were added and the mixture was stirred at rt for 60 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/EtOAc, 50/1) followed by Kugelrohr distillation afforded 390 mg (89%) of **9d** as colorless oil. (See previous entry for data.)

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

bp: 150 - 155 °C (0.05 mmHg)

GC: t_R (*E*)-**9d** 4.93 min (98.5%); 4.76 min (1.5%) (U-2, 250 °C, 15 psi)

Preparation of (*E*)-1-(1-Heptenyl)-3-methylbenzene ((*E*)-9e) [Table 2, entry 7]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), 3-iodotoluene (436 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (57.5 mg, 5 mol%) were added and stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (50 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane) followed by Kugelrohr distillation afforded 294 mg (78%) of **9e** as colorless oil.

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

bp: 125 - 130 °C (0.5 mmHg)

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

7.16 (m, 3 H), 7.00 (d, J = 7.5, HC(5), 1 H), 6.34 (d, J = 15.9, HC(1'), 1 H), 6.21 (dt, J = 15.9, 6.9, HC(2'), 1 H), 2.33 (s, H_3C(1''), 3 H), 2.19 (m, H_2C(3'), 2 H), 1.46 (m, H_2C(4'), 2 H), 1.33 (m, H_2C(5'), H_2C(6'), 4 H), 0.90 (t, J = 6.86, H_3C(7'), 3 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

138.0, 137.9, 131.0, 129.7, 128.4, 127.5, 126.6, 123.0, 33.0 (C(3')), 31.4 (C(5')), 29.1 (C(4')), 22.5 (C(6')), 21.4 (C(1")), 14.0 (C(7'))

IR: (NaCl)

3020 (w), 2957 (m), 2926 (s), 2856 (m), 1604 (w), 1486 (w), 1467 (w), 962 (m)

MS: (EI, 70 eV)

189 (M^++1, 7), 188 (M^+, 42), 131 (100), 129 (22), 118 (52), 115 (40), 91 (32), 77 (10)

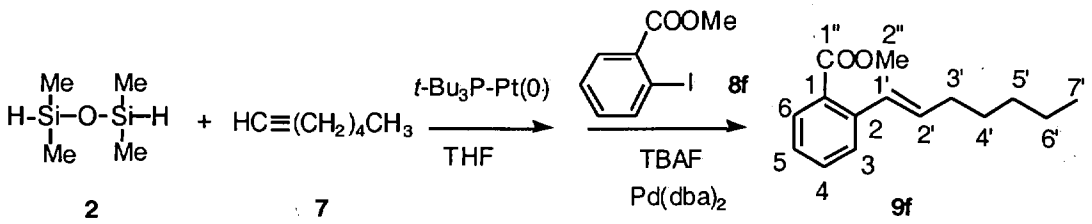
TLC: R_f 0.37 (hexane)

GC-MS: t_R (*E*)-**9e** 6.79 min (97.4%, m/z 188); 6.38 min (1.4%, m/z 188); 6.23 min (1.2%, m/z 188) (HP-1, program A, 10 psi)

Analysis: $C_{14}H_{20}$ (188.31)

Calculated:	C, 89.30;	H, 10.70%
Found:	C, 89.12;	H, 10.66%

Preparation of Methyl-(*E*)-2-(1-heptenyl)benzoate ((*E*)-9f) [Table 2, entry 8]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), methyl-2-iodobenzoate (524 mg, 2.0 mmol, 1.0 equiv), $Pd(dba)_2$ (57.5 mg, 5 mol%) and Ph_3As (61.2 mg, 10 mol%) were added and the mixture was stirred at rt for 20 h. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (50 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/EtOAc, 50/1) followed by Kugelrohr distillation afforded 406.3 mg (88%) of **9f** as colorless oil.

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

bp: 135 - 140 °C (0.05 mmHg)

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

7.83 (dd, *J* = 7.8, 1.2, HC(6), 1 H), 7.54 (dd, *J* = 7.3, 0.5, HC(3), 1 H), 7.43 (m, HC(4), 1 H), 7.25 (m, HC(5), 1 H), 7.12 (d, *J* = 15.6, HC(1'), 1 H), 6.14 (dt, *J* = 15.6, 7.1, HC(2'), 1 H), 3.90 (s, H_3C(2"), 3 H), 2.25 (m, H_2C(3'), 2 H), 1.49 (m, H_2C(4'), 2 H), 1.34 (m, H_2C(5'), H_2C(6'), 4 H), 0.91 (t, *J* = 7.1, H_3C(7'), 3 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

168.2 (C(1")), 139.7 (C(1)), 134.2 (C(2')), 131.9 (C(4)), 130.3 (C(6)), 128.4 (C(1')), 128.2 (C(2)), 127.2 (C(3)), 126.5 (C(5)), 52.0 (C(2")), 33.2 (C(3')), 31.5 (C(5')), 29.0 (C(4')), 22.6 (C(6')), 14.1 (C(7'))

IR: (NaCl)

3060 (w), 2954 (s), 2928 (s), 2856 (m), 1724 (s), 1644 (w), 1598 (w), 1568 (w), 1408 (m), 1433 (m), 1250 (s), 1121 (m), 1078 (s), 966 (m)

MS: (EI, 70 eV)

233 (M^++1, 8), 232 (M^+, 44), 161 (69), 148 (20), 144 (100), 131 (31), 129 (23), 116 (33), 115 (47), 91 (26), 77 (11)

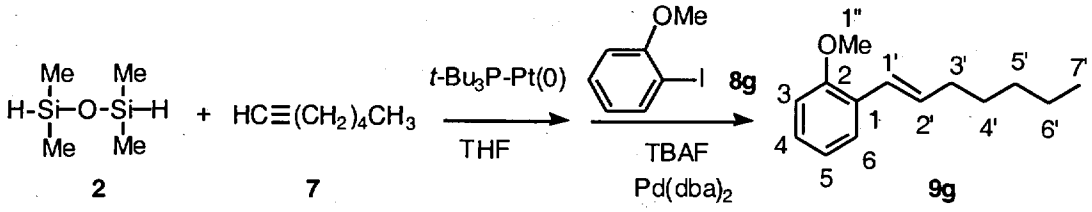
TLC: *Rf* 0.42 (hexane/EtOAc, 50/1)

GC-MS: t_R (*E*)-**9f** 7.93 min (96.7%, m/z 232); 7.50 min (2.8%, m/z 232); 7.23 min (0.5%, m/z 232) (HP-1, program A, 10 psi)

Analysis: $C_{15}H_{20}O_2$ (232.32)

Calculated:	C, 77.55;	H, 8.68%
Found:	C, 77.29;	H, 8.66%

Preparation of (*E*)-1-(1-Heptenyl)-2-methoxybenzene ((*E*)-9g) [Table 2, entry 9]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (175 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (250 mg, 2.6 mmol, 1.3 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), 2-iodoanisole (468 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (57.5 mg, 5 mol%) were added and stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/EtOAc, 50/1) followed by Kugelrohr distillation afforded 336 mg (82%) of **9g** as colorless oil.

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

bp: 120 - 125 °C (0.05 mmHg)

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

7.42 (dd, *J* = 7.6, 1.5, HC(6), 1 H), 7.17 (td, *J* = 7.3, 0.7, HC(4), 1 H), 6.90 (m, HC(5), 1 H), 6.85 (dd, *J* = 8.1, 0.7, HC(3), 1 H), 6.70 (d, *J* = 15.9, HC(1'), 1 H), 6.21 (dt, *J* = 15.9, 7.1, HC(2'), 1 H), 3.84 (s, H_3C(1"), 3 H), 2.22 (m, H_2C(3'), 2 H), 1.49 (m, H_2C(4'), 2 H), 1.33 (m, H_2C(5'), H_2C(6'), 4 H), 0.90 (t, *J* = 7.1, H_3C(7'), 3 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

156.2 (C(2)), 132.0, 127.7, 126.3, 124.1, 120.6, 110.8, 55.4 (C(1")), 33.4 (C(3')), 31.5 (C(5')), 29.2 (C(4')), 22.5 (C(6')), 14.0 (C(7'))

IR: (NaCl)

2999 (w), 2956 (m), 2927 (s), 2855 (w), 1597 (w), 1489 (s), 1463 (m), 1290 (w), 1242 (s), 1177 (w), 1103 (w), 1052 (w), 1031 (m), 972 (w)

MS: (EI, 70 eV)

205 (M^++1, 8), 204 (M^+, 45), 147 (100), 134 (27), 131 (14), 121 (29), 119 (8), 115 (16), 91 (40), 77 (8)

TLC: R_f 0.52 (hexane/EtOAc, 50/1)

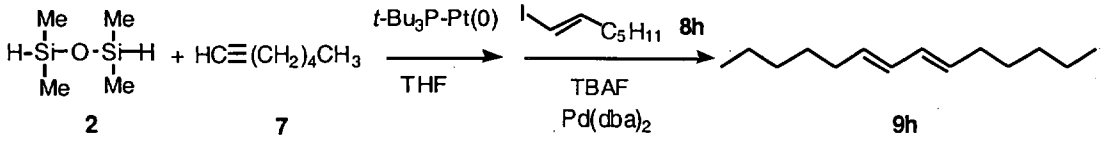
GC-MS: t_R (*E*)-**9g** 7.33 min (99.9%, m/z 204); 6.94 min (0.1%, m/z 204)

(HP-1, program A, 10 psi)

Analysis: $C_{14}H_{20}O$ (204.31)

Calculated:	C, 82.30;	H, 9.87%
Found:	C, 82.10;	H, 10.10%

Preparation of (*E,E*)-6,8-Tetradecadiene ((*E*)-9h) [Table 2, entry 10]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (202 mg, 1.5 mmol, 1.5/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (288 mg, 3.0 mmol, 1.5 equiv) in 0.25 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (6.0 mL, 1.0 M, 3.0 equiv), (E)-1-iodoheptene (448 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (57.5 mg, 5 mol%) were added and the mixture was stirred at rt for 16 h (95% conversion). Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (50 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane) followed by Kugelrohr distillation afforded 260 mg (67%) of **9h** as colorless oil which gave spectroscopic data consistent with those previously reported.[8]

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

bp: 120 - 125 °C (0.7 mmHg)

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

6.00 (m, 2 H), 5.57 (m, 2 H), 2.05 (q, J = 7.1, 4 H), 1.37 (qn, J = 7.1, 4 H), 1.29 (m, 8 H), 0.88 (t, J = 7.1, 6 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

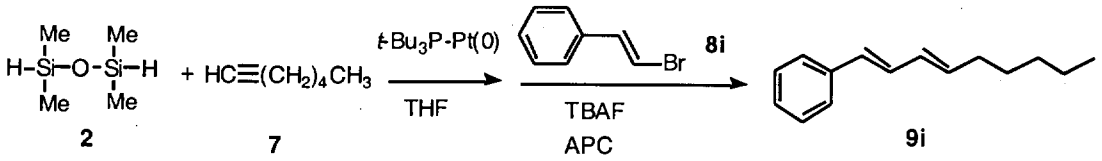
132.4, 130.3, 32.6, 31.4, 29.1, 22.5, 14.0

IR: (NaCl)

3014 (w), 2958 (m), 2926 (s), 2856 (m), 2362 (w), 1464 (w), 1378 (w), 985 (m)

GC-MS: t_R (*E,E*)-**9h** 6.43 min (91.4%, m/z 194); 6.30 min (4.4%, m/z 194); 6.05 min (4.2%, m/z 194) (HP-1, program A, 10 psi)

Preparation of (*E,E*)-1,3-nonadienylbenzene ((*E,E*)-9i) [Table 2, entry 11]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (202 mg, 1.5 mmol, 1.5/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and heptyne (288 mg, 3.0 mmol, 1.5 equiv) in 0.25 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (5.0 mL, 1.0 M, 2.5 equiv), (*E*)-2-bromostyrene (366 mg, 2.0 mmol, 1.0 equiv) and $[allylPdCl]_2$ (18.3 mg, 2.5 mol%) were added and the mixture was stirred at rt for 14h. Hexane (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with hexane (100 mL) and then was concentrated. Purification of the residue by RPC ((C18, MeOH/H_2O, 9/1) followed by Kugelrohr distillation afforded 278.8 mg (70%) of **9i** as colorless oil which gave spectroscopic data consistent with those previously reported.[7]

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

bp: 110 - 115 °C at 0.1 mmHg

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

7.38 (m, 2 H), 7.30 (t, *J* = 7.7, 2 H), 7.20 (m, 1 H), 6.76 (dd, *J* = 15.4, 10.5, 1 H), 6.45 (d, *J* = 15.8, 1 H), 6.21 (ddd, *J* = 15.4, 10.5, 0.6, 1 H), 5.84 (dt, *J* = 15.0, 7.1, 1 H), 2.15 (m, 2 H), 1.43 (m, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* = 7.1, 3 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

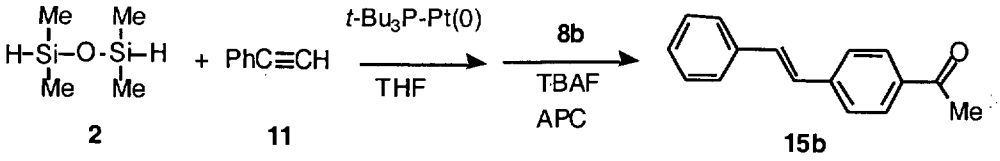
137.7, 136.1, 130.4, 129.9, 129.5, 128.5, 127.0, 126.1, 32.8, 31.4, 29.0, 22.5, 14.0

IR: (NaCl)

3060 (w), 3021 (m), 2956 (m), 2927 (s), 2856 (m), 1643 (w), 1596 (w), 1494 (w), 1448 (m), 986 (s)

GC: t_R (*E,E*)-**9i** 6.83 min (92.0%); (*E,Z*)-**9i** 6.50 min (3.2%); **10i** 6.22 min (4.8%) (HP-5, 250 °C, 15 psi)

Preparation of 1-[4-((*1E*)-2-phenylethenyl)phenyl]ethanone ((*E*)-15b) [Table 3, entry 1]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (96 mg, 0.72 mmol, 1.43/2 equiv), *t*-Bu_3P-Pt(0) complex (25 μL) and phenylacetylene (133 mg, 1.3 mmol, 1.3 equiv) in 0.15 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (2.0 mL, 1.0 M, 2.0 equiv), 4-iodoacetophenone (246 mg, 1.0 mmol, 1.0 equiv) and $[allylPdCl]_2$ (9.1 mg, 2.5 mol%) were added and the mixture was stirred at rt for 10 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (100 mL) and then was concentrated. Purification of the crude product by column chromatography on silica gel (pentane/EtOAc, 30/1) afforded 197 mg (89%) of **15b** as white solid which gave spectroscopic data consistent with those previously reported.[9]

Data for **(*E*)-15b**:

mp: 141 - 142 °C

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

7.96 (d, J = 8.6, 2 H), 7.59 (d, J = 8.4, 2 H), 7.54 (d, J = 7.3, 2 H), 7.39 (m, 2 H), 7.31 (m, 1 H), 7.23 (d, J = 16.5, 1 H), 7.13 (d, J = 16.5, 1 H), 2.61 (s, 3 H)

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

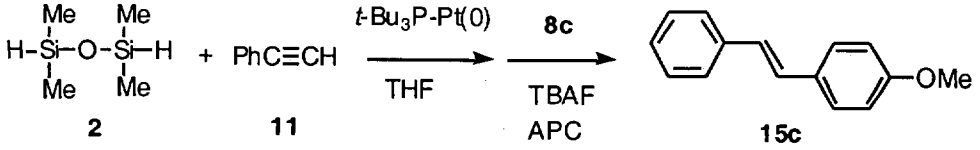
197.5, 142.0, 136.6, 135.9, 131.4, 128.8, 128.7, 128.3, 127.4, 126.8, 126.5, 26.6

IR: ($CHCl_3$)

3020 (w), 2246 (w), 1678 (m), 1602 (m), 1360 (w), 1267 (m), 1216 (s), 963 (w)

GC: t_R (*E*)-**15b** 10.36 min (100%) (HP-5, 270 °C, 15 psi)

Preparation of 1-Methoxy-4-[(*1E*)-2-phenylethenyl]benzene ((*E*)-15c) [Table 3, entry 2]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (96 mg, 0.72 mmol, 1.43/2 equiv), *t*-Bu_3P-Pt(0) complex (25 μL) and phenylacetylene (133 mg, 1.3 mmol, 1.3 equiv) in 0.15 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (2.0 mL, 1.0 M, 2.0 equiv), 4-iodoanisole (234 mg, 1.0 mmol, 1.0 equiv) and $[allylPdCl]_2$ (9.1 mg, 2.5 mol%) were added and the mixture was stirred at rt for 15 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (100 mL) and then was concentrated. Purification of the crude product by column chromatography on silica gel (pentane/acetate, 50/1) afforded 156 mg (74%) of **15c** as white solid which gave spectroscopic data consistent with those previously reported.[10]

Data for (*E*)-**15c**:

mp: 134 - 135 °C

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

7.48 (m, 2 H), 7.35 (t, *J* = 7.8, 2 H), 7.24 (m, 1 H), 7.07 (d, *J* = 16.4, 1 H), 6.98 (d, *J* = 16.4, 1 H), 6.91 (d, *J* = 8.8, 2 H), 3.84 (s, 3 H)

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

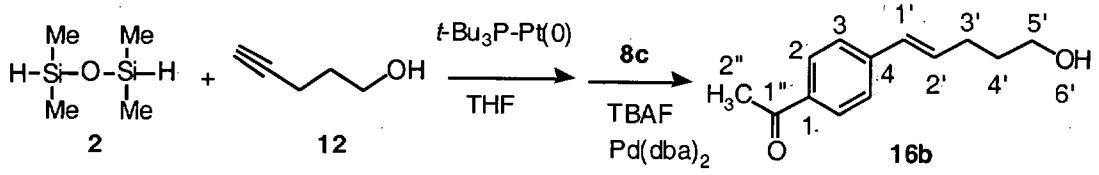
159.2, 137.6, 130.1, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.1, 55.3

IR: ($CHCl_3$)

3030 (w), 2690 (w), 2839 (w), 2249 (w), 1606 (w), 1512 (s), 1251 (m), 1175 (m), 1034 (w), 962 (w), 821 (w)

GC: t_R (*E*)-**15c** 10.31 min (100%) (HP-5, 250 °C, 15 psi)

Preparation of (*E*)-1-[4-(5-hydroxy-1-pentenyl)]ethanone ((*E*)-16b) [Table 3, entry 3]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (121 mg, 0.90 mmol, 1.8/2 equiv), *t*-Bu_3P-Pt(0) complex (25 μL) and 4-pentyn-1-ol (151 mg, 1.8 mmol, 1.8 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (2.0 mL, 1.0 M, 2.0 equiv), 4-iodoacetophenone (246 mg, 1.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (29.0 mg, 5.0 mol%) were added and the mixture was stirred at rt for 30 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (120 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/acetate, 1/1) and RPC (C18, MeOH/H_2O, 3/1) afforded 168 mg (82%) of **16b** as white solid.

Data for (*E*)-**16b**:

mp: 42 - 43 °C

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

7.89 (d, *J* = 8.4, H_2C(2), 2 H), 7.41 (d, *J* = 8.4, H_2C(3), 2 H), 6.46 (d, *J* = 15.9, HC(1'), 1 H), 6.39 (dt, *J* = 15.9, 6.6, HC(2'), 1 H), 3.72 (m, H_2C(5'), 2 H), 2.59 (s, H_3C(2"), 3 H), 2.35 (m, H_2C(3'), 2 H), 1.78 (qn, *J* = 6.6, H_2C(4'), 2 H), 1.36 (t, *J* = 5.4, O*H*, 1 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

197.7 (C(1")), 142.3 (C(1)), 135.5 (C(4)), 133.4 (C(2')), 129.5 (C(1')), 128.8 (C(2)), 126.0 (C(3)), 62.3 (C(5')), 32.0 (C(3')), 29.4 (C(4')), 26.5 (C(2"))

IR: ($CHCl_3$)

3625 (w, br), 3020 (w), 2940 (w), 2882 (w), 2249 (w), 1677 (s), 1602 (m), 1360 (w), 1270 (m), 1216 (w), 967 (w)

MS: (EI, 70 eV)

205 (M^++1, 16), 204 (M^+, 95), 189 (99), 176 (34), 171 (100), 161 (18), 147 (27), 143 (87), 128 (68), 115 (66), 91 (25), 77 (17)

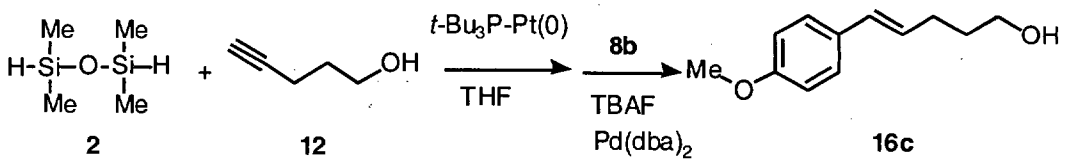
TLC: R_f 0.14 (hexane/EtOAc, 1/1)

GC-MS: t_R (*E*)-**16b** 8.89 min (100%, m/z 204) (HP-1, program A, 10 psi)

Analysis: $C_{13}H_{16}O_2$ (204.27)

Calculated:	C, 76.44;	H, 7.90%
Found:	C, 76.12;	H, 7.91%

Preparation of (*E*)-5-(4-Methoxyphenyl)-4-penten-1-ol ((*E*)-16c) [Table 3, entry 4]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (121 mg, 0.90 mmol, 1.8/2 equiv), *t*-Bu_3P-Pt(0) complex (25 μL) and 4-pentyn-1-ol (151 mg, 1.8 mmol, 1.8 equiv) in 0.2 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (2.0 mL, 1.0 M, 2.0 equiv), 4-iodoanisole (234 mg, 1.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (29.0 mg, 5.0 mol%) were added and the mixture was stirred at rt for 60 min. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (100 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (pentane/acetate, 2/1) afforded 170 mg (89%) of **16c** as white solid which gave spectroscopic data consistent with those previously reported.[11]

Data for (*E*)-**16c**:

mp: 63 - 64 °C

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

7.28 (d, *J* = 8.8, 2 H), 6.84 (d, *J* = 8.6, 2 H), 6.37 (d, *J* = 15.6, 1 H), 6.09 (dt, *J* = 15.6, 7.1, 1 H), 3.80 (s, 3 H), 3.71 (t, *J* = 6.4, 2 H), 2.29 (m, 2 H), 1.75 (qn, *J* = 7.1, 2 H), 1.54 (s, Br, 1 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

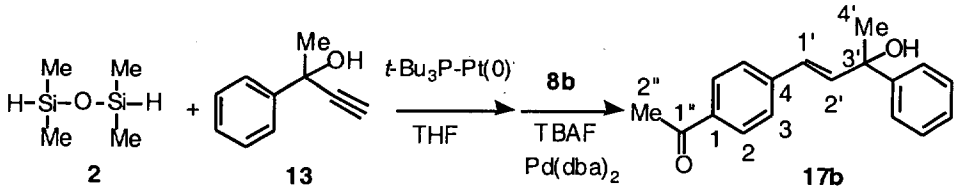
158.7, 130.4, 129.7, 127.8, 127.0, 113.9, 62.5, 55.3, 32.3, 29.3

IR: ($CHCl_3$)

3622 (m), 3006 (w), 2938 (w), 2839 (m), 2248 (m) 1608 (m), 1511 (s), 1247 (s), 1175 (m), 1036 (s), 966 (m), 837 (m)

GC-MS: t_R (*E*)-**16c** 7.90 min (100%, m/z 192) (HP-1, program A, 10 psi)

Preparation of (*E*)-1-[4-(3-hydroxy-3-phenyl-1-butenyl)phenyl]ethanone ((*E*)-17b) [Table 3, entry 5]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (87.3 mg, 0.65 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (25 μL) and 2-phenyl-3-butyn-2-ol (190 mg, 1.3 mmol, 1.3 equiv) in 0.3 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (2.0 mL, 1.0 M, 2.0 equiv), 4-iodoacetophenone (246 mg, 1.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (29.0 mg, 5.0 mol%) were added and the mixture was stirred at rt for 24 h. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (100 mL) and then was concentrated. Purification of the residue by column chromatography of silica gel (pentane/EtOAc, 5/1) and RPC (C18, MeOH/H_2O, 10/1) afforded 192 mg (72%) of **17b** as white solid.

Data for (*E*)-**17b**:

mp: 93 - 94 °C

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

7.90 (d, *J* = 8.5, H_2C(2), 2 H), 7.52 (m, H_2C(3), 2 H), 7.45 (d, *J* = 8.3, 2 H), 7.33 (m, 3 H), 6.71 (d, *J* = 16.1, HC(2'), 1 H), 6.62 (d, *J* = 16.1, HC(1'), 1 H), 2.58 (s, H_3C(2"), 3 H), 2.18 (s, br, OH, 1 H), 1.79 (s, H_3C(4'), 3 H)

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

197.6 (C(1")), 146.1, 141.5, 139.2 (C(1')), 135.9, 128.7 (C(2)), 128.4, 127.2, 126.6, 126.5 (C(2')), 125.2 (C(3)), 74.6 (C(3')), 29.6 (C(4')), 26.6 (C(2"))

IR: ($CHCl_3$)

3596 (br, w), 3087 (w), 3033 (w), 2982 (w), 2931 (w), 2249 (m), 1679 (s), 1603 (s), 1410 (w), 1360 (m), 1268 (s), 1182 (m), 958 (m), 816 (w)

MS: (CI, 70 eV)

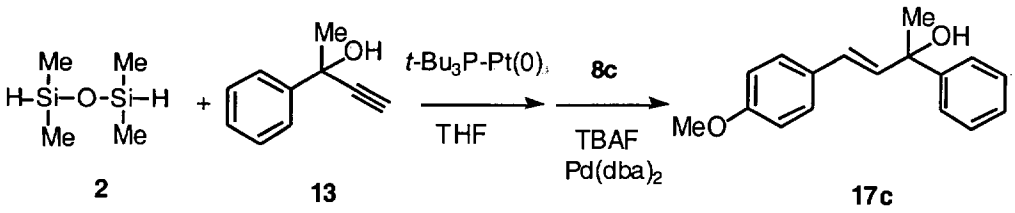
267 (M^++1, 100), 249 (66), 239 (37), 224 (33), 207 (11), 189 (30)

TLC: *Rf* 0.29 (hexane/EtOAc, 1/1)

Analysis: $C_{18}H_{18}O_2$ (266.34)

Calculated:	C, 81.17;	H, 6.81%
Found:	C, 81.07;	H, 6.75%

Preparation of (*E*)-4-(4-Methoxyphenyl)-2-phenyl-3-buten-2-ol ((*E*)-17c) [Table 3, entry 6]



Following General Procedure I, a solution of 1,1,3,3-tetramethyldisiloxane (177 mg, 1.3 mmol, 1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and 2-phenyl-3-butyn-2-ol (380 mg, 2.6 mmol, 1.3 equiv) in 0.5 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (4.0 mL, 1.0 M, 2.0 equiv), 4-iodoanisole (468 mg, 2.0 mmol, 1.0 equiv) and $Pd(dba)_2$ (57.5 mg, 0.1 mmol, 5.0 mol%) was stirred at rt for 24 h. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (100 mL) and then was concentrated. Purification by column chromatography on silica gel (pentane/EtOAc, 10/1) and RPC (C18, MeOH/H_2O, 10/1) afforded 377 mg (74%) of **17c** as very thick colorless oil which gave spectroscopic data consistent with those previously reported.[12]

Data for **(*E*)-17c**:

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

7.53 (m, 2 H), 7.30 (m, 4 H), 7.26 (m, 1 H), 6.85 (d, J = 6.6, 2 H), 6.58 (d, J = 16.1, 1 H), 6.38 (d, J = 16.1, 1 H), 3.81 (s, 3 H), 2.03, (s, 1 H), 1.76 (s, 3 H)

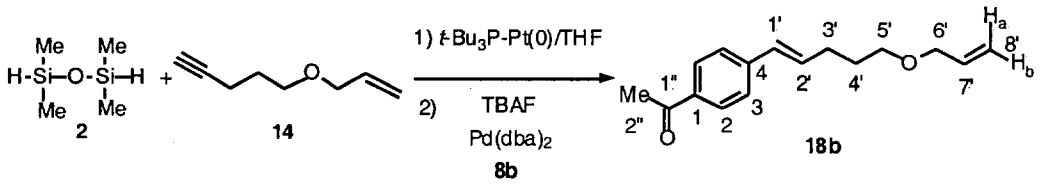
^{13}C NMR: (125.6 MHz, $CDCl_3$)

159.2, 156.8, 134.2, 129.4, 128.3, 127.7, 127.2, 127.0, 125.2, 114.0, 74.7, 55.3, 29.8

IR: ($CHCl_3$)

3600 (w), 3031 (w), 2958 (w), 2910 (w), 2838 (w), 2248 (w), 1608 (m), 1510 (s), 1443 (w), 1248 (s), 1177 (m), 1036 (m), 906 (w), 829 (m)

Preparation of (*E*)-1-[4-[5-(2-propenyloxy)-1-pentenyl]phenyl]ethanone ((*E*)-18b) [Table 3, entry 7]



Following General Procedure II, a solution of 1,1,3,3-tetramethyldisiloxane (261.9 mg, 1.95 mmol, 1.5×1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and 5-(2-propenyloxy)-1-pentyne (373 mg, 3.0 mmol, 1.5 equiv) in 0.3 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (6.0 mL, 1.0 M, 3.0 equiv), and $Pd(dba)_2$ (29.0 mg, 5.0 mol%) were added. A solution of 4-iodoacetophenone (2.0 mmol, 1.0 equiv) in THF (2.0 mL, 1.0 M) was then slowly added over 45 min. The mixture was stirred at rt for 10. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (hexane/EtOAc, 25/1) followed by Kugelrohr distillation afforded 388.6 mg (79%) of **18b** as colorless oil.

Data for (*E*)-**18b**:

bp: 150 - 155 °C (0.1 mmHg)

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

7.89 (d, J = 8.6, H_2C(2), 2 H), 7.41 (d, J = 8.4, H_2C(3), 2 H), 6.44 (d, J = 15.9, HC(1'), 1 H), 6.38 (dt, J = 15.9, 6.4, HC(2'), 1 H), 5.93 (ddt, J = 17.2, 10.3, 5.8, HC(7'), 1 H), 5.28 (dq, J = 17.2, 1.7, H_aC(8'), 1 H), 5.18 (m, H_bC(8'), 1 H), 3.98 (dt, J = 5.6, 1.3, H_2C(6'), 2 H), 3.49 (t, J = 6.4, H_2C(5'), 2 H), 2.58 (s, H_3C(2"), 3 H), 2.34 (m, H_2C(3'), 2 H), 1.79 (qn, J = 6.4, H_2C(4'), 2 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

197.6 (C(1")), 142.4 (C(1)), 135.4 (C(4)), 134.9, 133.6, 129.4, 128.7 (C(3)), 125.9 (C(2)), 116.8 (C(8')), 71.8 (C(6')), 69.5 (C(5')), 29.8 (C(4')), 29.1 (C(3')), 26.5 (C(2"))

IR: (NaCl)

2937 (m), 2854 (m), 1680 (s), 1602 (s), 1410 (m), 1358 (m), 1267 (s), 1181 (m), 1104 (s), 967 (w), 924 (w), 852 (w)

MS: (EI, 70 eV)

245 (M^++1, 5), 244 (M^+, 16), 188 (42), 186 (51), 173 (71), 171 (100), 143 (95), 128 (46), 115 (45), 105 (11), 91 (12), 77 (10)

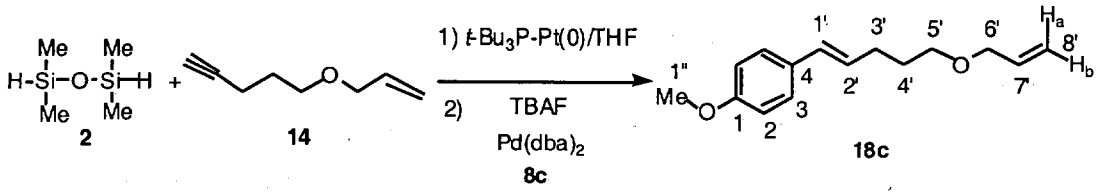
TLC: *Rf* 0.06 (hexane/EtOAc, 25/1)

GC-MS: t_R (*E*)-**18b** 9.53 min (100%, m/z 244) (HP-1, program A, 10 psi)

Analysis: $C_{16}H_{20}O_2$ (244.33)

Calculated:	C, 78.65;	H, 8.25%
Found:	C, 78.70;	H, 8.38%

Preparation of (*E*)-1-[5-(2-propenyloxy)-1-pentenyl]-4-methoxybenzene ((*E*)-18c) [Table 3, entry 8]



Following General Procedure II, a solution of 1,1,3,3-tetramethyldisiloxane (261.9 mg, 1.95 mmol, 1.5×1.3/2 equiv), *t*-Bu_3P-Pt(0) complex (50 μL) and 5-(2-propenyloxy)-1-pentyne (373 mg, 3.0 mmol, 1.5 equiv) in 0.3 mL of THF was stirred at rt for 30 min. A solution of TBAF in THF (6.0 mL, 1.0 M, 3.0 equiv), and $Pd(dba)_2$ (57.5 mg, 5.0 mol%) were added. A solution of 4-iodoanisole (2.0 mmol, 1.0 equiv) in THF (2.0 mL, 1.0 M) was then slowly added in 45 min. The mixture was stirred at rt for 10. Ether (10 mL) was added, then the mixture was filtered through a short column of SiO_2, which was eluted with ether (60 mL) and then was concentrated. Purification of the residue by column chromatography on silica gel (hexane/EtOAc, 50/1) followed by Kugelrohr distillation afforded 361.3 mg (78%) of **18c** as colorless oil.

Data for (*E*)-**18c**:

bp: 142 - 147 °C (0.15 mmHg)

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

7.27 (d, *J* = 8.8, H_2C(3), 2 H), 6.84 (d, *J* = 8.8, H_2C(2), 2 H), 6.34 (d, *J* = 15.7, HC(1'), 1 H), 6.07 (dt, *J* = 15.7, 7.1, HC(1'), 1 H), 5.93 (ddt, *J* = 17.4, 10.5, 5.6, HC(7'), 1 H), 5.28 (dq, *J* = 17.4, 1.7, H_aC(8'), 1 H), 5.17 (m, H_bC(8'), 1 H), 3.97 (dt, *J* = 5.6, 1.5, H_2C(6'), 2 H), 3.79 (s, H_3C(1"), 3 H), 3.47 (t, *J* =6.6, H_2C(5'), 2 H), 2.27 (m, H_2C(3'), 2 H), 1.75 (qn, *J* = 6.6, H_2C(4'), 2 H)

^{13}C NMR: (125.6 MHz, $CDCl_3$)

158.6 (C(1)), 135.0 (C(7')), 130.5 (C(4)), 129.5 (C(1')), 128.0 (C(2')), 126.9 (C(3)), 116.7 (C(8')), 113.8 (C(2)), 71.7 (C(6')), 69.6 (C(5')), 55.2 (C(1")), 29.5 (C(4')), 29.4 (C(3'))

IR: (NaCl)
3076 (w), 2935 (m), 2838 (m), 1608 (m), 1511 (s), 1463 (w), 1292 (w), 1248 (s), 1175 (m), 1104 (m), 1036 (m), 966 (w), 839 (w)

MS: (EI, 70 eV)
233 (M^++1, 11), 232 (M^+, 52), 176 (51), 174 (32), 173 (42), 159 (33), 147 (100), 143 (24), 134 (20), 121 (39), 115 (23), 91 (26), 77 (10)

TLC: R_f 0.12 (hexane/EtOAc, 50/1)

GC-MS: t_R (*E*)-**18c** 8.47 min (99.6%, m/z 232); 8.06 min (0.4%, m/z 232)
(HP-1, program A, 10 psi)

Analysis: $C_{15}H_{20}O_2$ (232.32)

Calculated:	C, 77.55;	H, 8.68%
Found:	C, 77.84;	H, 9.06%

References

(1) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191.

(2) Zweifel, G.; Whitney, C. C. *J. Am, Chem. Soc.* **1967**, *89*, 2753.

(3) Ojima, I.; Kogure, T.; Nihonyanagi, M.; Kono, H.; Inaba, S.; Nagai, Y. *Chem. Lett.* **1973**, 501.

(4) Lloyd-Jones, G. C.; Butts, C. P. *Tetrahedron* **1998**, *54*, 901.

(5) (a) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424; (b) Daniel, D.; Middleton, R.; Henry, H. L.; Okamura, W. H. *J. Org. Chem.* **1996**, *61*, 5617.

(6) Ukai, T.; Kawazura, H.; Ishii Y. J. Organomet. Chem. **1974**, *65*, 253.

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

(8) (a) Chou, T.-S.; You, M.-L. *J. Org. Chem.* **1987**, *52*, 2224; (b) Satyanarayana, N.; Periasamy, M. *Tetrahedron Lett.* **1986**, *27*, 6253.

(9) Bezou, P.; Hilberer, A.; Hadziioannou, G. *Synthesis* **1996**, 449.

(10) Alcaide, B.; Almendros, P.; Aragoncillo, C.; Salgado, N. R. *J. Org. Chem.* **1999**, *64*, 9596.

(11) Tokuda, M.; Fujita, H.; Miyamoto, T.; Suginome, H. *Tetrahedron* **1993**, *49*, 2413.

(12) Chiacchio, U.; Liguori, A.; Romeo, G.; Sindona, G.; Uccella, N. *Heterocycles* **1993**, *36*, 799.