Supplementary Material.

Compound 3a: In a round bottom flask fitted with a condenser, a magnetic spin-bar and a glass tube which permits constant bubbling of argon through the reaction medium, $Co_2(CO)_8$ (632 mg, 1.85 mmol, 1.20 equiv) was added to a solution of the eneyne **1a** (500 mg, 1.54 mmol, 1.00 equiv) in anhydrous toluene (40 mL). After stirring at 21 °C for 2 hours, the black solution was heated at reflux for 12 hours, during which time a suspension forms and a cobalt (0) mirror coating is observed on the sides of the flask. After cooling to 21 °C, the black suspension was concentrated in vacuo and the residue was diluted with a mixture of acetone (20 ml) and distilled water (4 ml) and treated with ceric (VI) ammonium nitrate (4.18 g, 7.7 mmol, 5.00 equiv). After stirring for 2 hours, the solution was concentrated to remove acetone, and the aqueous residue was poured on to a pad of Celite and rinsed with several portions of dichloromethane. The filtrate is concentrated and the residue is dissolved in methanol (5 ml) and treated with potassium hydroxide (100 mg, 1.78 mmol, 1.15 equiv). After stirring for 2 hours, the solution is concentrated and diluted with saturated ammonium chloride solution. The resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were dried over sodium sulfate, filtered and concentrated in vacuo. The product was purified by flash chromatography on silica gel (100% hexanes as eluent) to afford compound **3a** as a colorless oil (350 mg, 1.08 mmol, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.85 (s, 1H), 5.54 (dt, 1H, *J* = 17.0, 10.0 Hz), 4.98 (m, 2H), 4.39 (s, 1H), 2.93 (d, 1H, *J* = 10 Hz), 0.90 (s, 15H), 0.06 (s, 15H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 148.3, 144.0, 139.7, 115.5, 85.4, 63.7, 47.5, 26.1, 23.5, 23.2, 18.5, −1.1, −4.2, −4.6; HRMS exact mass M-H$^+$ 323.2225 (calcd for $C_{18}H_{36}OSi_2$-H$^+$ 323.2227).

Compound 3b: In a round bottom flask fitted with a condenser, a magnetic spin-bar and a glass tube which permits constant bubbling of argon through the reaction medium, $Co_2(CO)_8$ (135 mg, 0.40 mmol, 1.20 equiv) was added to a solution of the eneyne **3a** (122 mg, 0.33 mmol, 1.00 equiv) in anhydrous toluene (10 mL). After stirring at 21 °C for 2 hours, the black solution was heated at reflux for 12 hours, during which time a suspension forms and a cobalt (0) mirror coating is observed on the sides of the flask. After cooling to 21 °C, the black suspension was concentrated in vacuo and the residue was diluted with a mixture of acetone (5 ml) and distilled water (1 ml) and treated with ceric (VI) ammonium nitrate (905 mg, 1.65 mmol, 5.00 equiv). After stirring for 2 hours, the solution was concentrated to remove acetone, and the aqueous residue was poured on to a pad of Celite and rinsed with several portions of dichloromethane. The resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were dried over sodium sulfate, filtered and concentrated in vacuo. The product was purified by flash chromatography on silica gel (100% hexanes as eluent) to afford **3b** as a colorless oil (88 mg, 0.24 mmol, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.76 (t, 1H, *J* = 1.5 Hz), 5.54 (dt, 1H, *J* = 17.2, 9.8 Hz), 5.00 (m, 1H), 4.96 (m, 1H), 4.37 (t, 1H, *J* = 1.5 Hz), 2.96 (d, 1H, *J* = 10 Hz), 0.90 (s, 15H), 0.32 (s, 3H), 0.18 (s, 9H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 149.7, 141.0, 139.1, 115.5, 85.0, 63.8, 47.0, 25.9, 23.5, 23.1, 18.3, −1.8, −4.4, −4.8; HRMS exact mass M-H$^+$ 369.1668 (calcd for $C_{18}H_{36}GeOSi$-H$^+$ 369.1669).

Compound 3d: In a round bottom flask fitted with a condenser, a magnetic spin-bar and a glass tube which permits constant bubbling of argon through the reaction medium, $Co_2(CO)_8$ (515 mg, 1.51 mmol, 1.20 equiv) was added to a solution of the eneyne **1d** (500 mg, 1.26 mmol, 1.00 equiv) in anhydrous toluene (30 mL). After stirring at 21 °C for 2 hours, the black solution was

heated at reflux for 12 hours, during which time a colorless suspension forms and a cobalt (0) mirror coating is observed on the sides of the flask. After cooling to 21 °C, the suspension was poured on to a pad of Celite and rinsed with several portions of dichloromethane. The filtrate is concentrated under vacuo. Two additional iterations of this process were carried out on this residue. The crude product was then purified by flash chromatography on silica gel (2% ethyl acetate in hexanes as eluent) to afford compound **3d** as a colorless oil (477 mg, 1.16 mmol, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.69 (dd, 1H, *J* = 10.8, 15.6 Hz), 5.92 (s, 1H), 5.77 (d, 1H, *J* = 15.6 Hz), 4.44 (s, 1H), 4.60 (q, 2H, *J* = 6.9 Hz), 3.04 (d, 1H, *J* = 10.8 Hz), 1.27 (t, 3H, *J* = 6.9 Hz), 0.92 (s, 3H), 0.91 (s, 3H), 0.88 (s, 9H), 0.18 (s, 9H), 0.05 (s, 6H), 0.03 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 186.7, 150.3, 145.7, 121.8, 85.2, 61.8, 60.4, 49.0, 26.1, 23.4, 23.3, 18.5, −1.2, −4.2, −4.6; HRMS exact mass M-H$^+$ 395.2439 (calcd for $C_{21}H_{40}O_3Si_2$ -H$^+$ 395.2438).

Compound 3e: In a round bottom flask fitted with a condenser, a magnetic spin-bar and a glass tube which permits constant bubbling of argon through the reaction medium, $Co_2(CO)_8$ (410 mg, 1.20 mmol, 1.20 equiv) was added to a solution of eneyne **1e** (469 mg, 1.00 mmol, 1.00 equiv) in anhydrous toluene (25 mL). After stirring at 21 °C for 2 hours, the black solution was heated at reflux for 12 hours, during which time a colorless suspension forms and a cobalt (0) mirror coating is observed on the sides of the flask. After cooling to 21 °C, the suspension was poured on to a pad of Celite and rinsed with several portions of dichloromethane. The filtrate is concentrated under vacuo. To a THF solution (15 ml) of the residue was added 1 M HCl aqueous solution (5 ml). After stirring for 3 hours, the resulting solution was diluted with saturated $NaHCO_3$ aqueous solution. The resulting mixture was extracted with three portions of dichloromethane. The combined organic phases were dried with sodium sulfate, filtered and concentrated under vacuo. The crude product was then purified by flash chromatography on silica gel (1% ethyl acetate in hexanes as eluent) to afford compound **3e** as a colorless oil (333 mg, 0.71 mmol, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.85 (s, 1H), 5.45 (m, 2H), 4.39 (s, 1H), 4.12 (d, 2H, *J* = 5.3 Hz), 2.95 (d, 1H, *J* = 10.0 Hz), 0.90 (s, 24H), 0.15 (s, 9H), 0.06 (s, 12H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 148.3, 143.5, 131.2, 130.3, 84.9, 63.7, 61.8, 47.4, 26.0, 25.9, 25.8, 23.3, 23.0, 18.3, 18.2, 0.4, −1.3, −4.4, −4.0, −5.1, −5.2; HRMS exact mass M-H$^+$ 467.3196 (calcd for $C_{25}H_{52}O_2Si_3$ -H$^+$ 467.3197).

4,4-dimethyl-5-((dimethylethyl)-dimethylsilyloxy)-1-hepten-6-yne: Compound **1a** (1.015 g, 3.13 mmol, 1.00 equiv) was dissolved in methanol (5 mL) and treated with potassium carbonate (650 mg, 4.69 mmol, 1.5 equiv). After stirring for 24 hours, the solution was concentrated and saturated ammonium chloride solution was added. The resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure to give the intermediate 4,4-dimethyl-5-((dimethylethyl)-dimethylsilyloxy)-1-hepten-6-yne. Due to the volatility of this material, it was used immediately in subsequent transformations.

Compound 1b: To a solution of 4,4-dimethyl-5-((dimethylethyl)-dimethylsilyloxy)-1-hepten-6-yne in THF (20 mL) at –78 °C was added a 2.55 M solution of n-BuLi in hexanes (1.73 mL, 4.69 mmol, 1.50 equiv). After 15 minutes, trimethyl germyl bromide (1.0 g, 7.8 mmol, 2.50 equiv) was added. The mixture was allowed to warm slowly to room temperature and stirred at that temperature for 2 hours. The reaction was diluted with saturated ammonium chloride solution and the resulting mixture was extracted with three portions of diethyl ether. The combined

organic layers were dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (100% dichloromethane as eluent) to afford **1b** as a colorless oil (1.082 g, 2.93 mmol, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.82 (m, 1H), 5.05 (m, 1H), 5.00 (m, 1H), 4.00 (s, 1H), 2.96 (d, 1H, *J* = 7.6 Hz), 0.91 (s, 15H), 0.33 (s, 9H), 0.15 (s, 3H), 0.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 135.5, 117.0, 105.0, 89.9, 71.0, 42.6, 39.0, 25.8, 22.7, 22.5, 18.3, −0.4, −4.2, −5.1; HRMS exact mass M-H$^+$ 369.1668 (calcd for $C_{18}H_{36}GeOSi$-H$^+$ 369.1669).

Compound 1c: To a solution of 4,4-dimethyl-5-((dimethylethyl)dimethylsilyloxy)-1-hepten-6-yne (239.4 mg, 0.95 mmol, 1.00 equiv) in THF (20 ml) at -78 ºC was added a 2.55 M solution of nBuLi in hexanes (0.557 ml, 1.42 mmol, 1.50 equiv). After 15 minutes, t-butyldimethylsilyl chloride (230 mg, 1.52 mmol, 1.60 equiv) was added. The mixture was allowed to warm up slowly to room temperature and stirred at that temperature for 12 hours. The reaction was diluted with saturated ammonium chloride solution and the resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were dried with sodium sulfate, filtered and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel (100% hexanes as eluent) to afford **1c** as a colorless oil (338 mg, 0.92 mmol, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.82 (m, 1H), 5.04 (bs, 1H), 5.00 (m, 1H), 4.00 (s, 1H), 2.11 (dd, 2H, *J* = 4.3, 7.8 Hz), 0.92 (s, 24H), 0.33 (s, 9H), 0.14 (s, 3H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 135.3, 117.1, 107.0, 88.1, 70.9, 42.6, 39.1, 26.1, 25.8, 22.7, 22.6, 18.2, 16.5, −4.3, −4.7, −5.2; HRMS exact mass M+H$^+$ 367.2851 (calcd for $C_{21}H_{42}OSi_2$ +H$^+$ 367.2853).

Compound 1d: Compound **1a** (2.33 ml, 7.19 mmol, 1.00 equiv) was dissolved in a mixture of THF (20ml) and water (5ml) and treated with N-methyl morpholine N-oxyde (2.23 ml, 10.79 mmol, 1.50 equiv) and osmium tetroxide (2.00 ml of a 0.072 M solution in benzene, 0.14 mmol, 0.02 equiv) at room temperature. After 4.5 hours, the mixture was diluted with distilled water (5 ml) and sodium periodate (3.075 g, 14.38 mmol, 2.00 equiv) was added. The reaction mixture was stirred for 12 hours and then diluted with saturated ammonium chloride solution. The resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were dried with sodium sulfate and the solution was filtered through a small pad of silica gel and rinsed with several portions of diethyl ether. The solution was concentrated under vacuo to afford the intermediate aldehyde 3,3-dimethyl-4-((dimethylethyl)dimethylsilyloxy)-6-trimethylsilyl-6-hexyn-1-al which was used immediately without further purification.

Triethyl phosphonoacetate (1.44 ml, 9.18 mmol, 1.50 equiv) was added to sodium hydride (367 mg, 9.18 mmol, 1.50 equiv) suspended in THF (20 ml) at 0 ºC. To this mixture, a solution of 3,3-dimethyl-4-((dimethylethyl)dimethylsilyloxy)-6-trimethylsilyl-6-hexyn-1-al (2.0 g, 6.12 mmol, 1.00 equiv) in THF (10 ml) was cannulated after 20 minutes. The resulting solution was allowed to warm up slowly to room temperature and stirred at that temperature for 5 hours. The reaction was diluted with saturated ammonium chloride solution and the resulting mixture was with three portions of diethyl ether. The combined organic layers were dried with sodium sulfate, filtered and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel (2% ethyl acetate in hexanes as eluent) to afford **1d** as a colorless oil (1.62 g, 4.07 mmol, 67%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.99 (dt, 1H, *J* = 7.9, 15.8 Hz), 5.82 (d, 1H, *J* = 15.8 Hz), 4.18 (q, 2H, *J* = 7.0 Hz), 3.99 (s, 1H), 2.25 (m, 2H), 1.28 (t, 3H, *J* = 7.0Hz), 0.97 (s, 3H), 0.95 (s, 1H), 0.89 (s, 9H), 0.15 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 188.0, 166.7, 146.7, 123.8, 105.9, 76.8, 71.3, 60.3, 41.0, 39.9, 29.9, 26.0,

23.2, 23.21, 18.5, 14.5, 0.01, –4.1, –5.0; HRMS exact mass M-H^+ 395.2439 (calcd for $C_{21}H_{40}O_3Si_2$ -H^+ 395.2438).

Compound 1e: To a solution of **1d** (595 mg, 1.43 mmol, 1.00 equiv) in 25 ml toluene at -78 ºC was added dropwise a 1.55 M solution of DIBAL-H in toluene (2.39 ml, 3.58 mmol, 2.50 equiv). The reaction was brought to -10 ºC. After 2 hours, the solution was allowed to warm up slowly to room temperature and stirred at that temperature for 3 hours. The reaction was diluted with 18 ml 0.5 M aqueous Rachelle's salt solution (18.0 ml, 9.0 mmol, 6.30 equiv) and stirred overnight. The mixture was extracted with four portions of ethyl acetate. The combined organic layers were dried with sodium sulfate, filtered and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel (10% ethyl acetate in hexanes as eluent) to afford 5,5-dimethyl-6-((dimethylethyl)dimethylsilyloxy)-8-trimethylsilyl-2-octen-7-yne 1-ol as a colorless oil (505 mg, 1.42 mmol, quantitative).

To a solution of 5,5-dimethyl-6-((dimethylethyl)dimethylsilyloxy)-8-trimethylsilyl-2-octen-7-yne 1-ol (505 mg, 1.42 mmol, 1.00 equiv) and imidazole (156 mg, 2.29 mmol, 1.6 equiv) in N,N' dimethyl formamide (20 ml) at room temperature was added t-butyl dimethyl silyl chloride (302 mg, 2.0 mmol, 1.41 equiv). After 12 hours, the reaction was diluted with distilled water and the resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were washed with three portions of distilled water, dried with sodium sulfate and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel (1% ethyl acetate in hexanes as eluent) to afford **1e** as a colorless oil (663 mg, 1.41 mmol, quantitative). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.63 (m, 1H), 5.57 (m, 1H), 4.13 (dd, 2H, J = 1.2, 5.1 Hz), 3.99 (s, 1H), 2.07 (dd, 2H, J = 4.3, 7.0 Hz), 0.91 (s, 12H), 0.89 (s, 12H), 0.15 (s, 9H), 0.14 (s, 6H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 132.0, 127.4, 106.4, 90.0, 70.9, 64.0, 40.9, 39.5, 26.0, 25.8, 22.7, 22.6, 18.5, 18.3, –0.1, –3.6, –4.3, –5.1; HRMS exact mass M-^{t}butyl$^+$ 411.2572 (calcd for $C_{21}H_{40}O_3Si_2$ -^{t}butyl$^+$ 411.2571).

Compound 4a: To a solution of *trans* 2,2-dimethyl methyl-3-pentenoate[1] (1.010 g, 7.05 mmol, 1.00 equiv) in diethyl ether (25 ml) at 0 ºC was added $NaBH_4$ (353 mg, 16.20 mmol, 2.30 equiv) and the mixture was warmed up slowly to room temperature. After stirring for 5 hours, the solution was brought to 0 ºC and quenched with saturated ammonium chloride solution. The resulting mixture was extracted three times with diethyl ether and the organic layers were combined and dried with sodium sulfate. The crude product was purified by flash chromatography on silica gel (1% ethyl acetate in hexanes as eluent) to afford *trans* 2,2-dimethyl 3-pentenol as a colorless oil (620 mg, 5.43 mmol, 77%).

A solution of dimethyl sulfoxide (358 µl, 5.00 mmol, 2.50 equiv) in dichloromethane (500 µl) was cannulated to a solution of oxalyl chloride (350 µl, 4.00 mmol, 2.00 equiv) in dichloromethane (20 ml) at -78 ºC. After 30 minutes, a solution of trans 2,2-dimethyl 3-pentenol (228 mg, 2.00 mmol, 1.00 equiv) in dichloromethane (2 ml) was then cannulated to this mixture. The subsequent white suspension was stirred for 1 hour before dropwise addition of triethylamine (1.40 ml, 10.00 mmol, 5.00 equiv). The mixture was allowed to warm up slowly to 21 ºC and stirred at that temperature for 4 hours. The solution was diluted with saturated ammonium chloride solution and the resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were dried with sodium sulfate, filtered through a

[1] Herrmann, J.L., Kieczykowsky, G.R., Schlessinger, R.H., *Tetrahedron Lett*. **1973**, *14*, 2433

small pad of silica gel and concentrated under vacuo to afford the intermediate trans 2,2-dimethyl 3-pentenal[2] as a colorless oil which was used immediately without further purification.

To a solution of diisopropylamine (420 μl, 3.00 mmol, 1.50 equiv) in THF (30ml) at -78 ºC was added dropwise a 2.65 M solution of n-BuLi in hexanes (1.06 ml, 2.80 mmol, 1.40 equiv). After 10 minutes, (trimethylsilyl)acetylene (424 μl, 3.00 mmol, 1.50 equiv) was added to the solution. After 30 minutes, to the resulting mixture was cannulated a solution of the intermediate trans 2,2-dimethyl 3-pentenal in THF (5ml) at -78 ºC. The resulting mixture was allowed to warm up slowly to 21 ºC and stirred at that temperature for 3 hours. t-Butyldimethylsilyl chloride (724 mg, 4.80 mmol, 2.40 equiv) was added. After 30 minutes, the subsequent solution was warmed up to reflux. After 12 hours, the reaction was cooled to 21 ºC and diluted with saturated ammonium chloride solution. The resulting mixture was extracted with three portions of ethyl acetate. The combined organic layers were dried with sodium sulfate, filtered and concentrated under vacuo. The crude product was then purified by distillation under reduced pressure (120 ºC, 8 mm Hg) to afford 4,4-dimethyl-5-((dimethylethyl)dimethylsilyloxy)-7-trimethylsilyl-2-hepten-6-yne (160 mg, 25%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.51 (d, 1H, J = 16.6Hz), 5.43 (dq, 1H, J = 16.6, 6.0 Hz), 3.95 (s, 1H), 1.67 (dd, 3H, J = 6.0, 1.5 Hz), 1.02 (s, 6H), 0.90 (s, 9H), 0.15 (s, 9H), 0.12 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 137.7, 122.6, 106.5, 89.5, 71.4, 42.5, 41.3, 25.8, 23.1, 22.7, 18.2, −0.2, −4.5, −5.2; LRMS M^+ 324.

4,4-dimethyl-5-((dimethylethyl)dimethylsilyloxy)-7-tri-isopropylsilyl-1-hepten-6-yne: To a solution of crude intermediate 4,4-dimethyl-5-((dimethylethyl)dimethylsilyloxy)-1-hepten-6-yne (208.6 mg, 0.83 mmol, 1.00 equiv) in THF (15 ml) at -78 ºC was added a 2.55 M solution of nBuLi in hexanes (0.486 ml, 1.24 mmol, 1.50 equiv). After 15 minutes, tri-isopropyl silyl chloride (0.285 ml, 1.33 mmol, 1.60 equiv) was added. The mixture was allowed to warm up slowly to room temperature and stirred at that temperature for 12 hours. The reaction was diluted with saturated ammonium chloride solution and the resulting mixture was extracted with three portions of diethyl ether. The combined organic layers were dried with sodium sulfate, filtered and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel (100% hexanes as eluent) to afford 4,4-dimethyl-5-((dimethylethyl)dimethylsilyloxy)-7-tri-isopropylsilyl-1-hepten-6-yne as a colorless oil (335 mg, 0.82 mmol, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.82 (m, 1H), 5.04 (s, 1H), 5.00 (m, 1H), 4.03 (s, 1H), 2.13 (dd, 2H, J = 0.8, 7.5 Hz), 1.08 (s, 3H), 1.07 (bs, 15H), 1.03 (s, 3H), 0.93 (s, 3H), 0.92 (s, 3H), 0.90 (s, 9H), 0.15 (s, 3H), 0.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 135.6, 117.3, 108.3, 86.0, 71.2, 42.8, 39.5, 26.0, 22.9, 22.8, 22.6, 19.1, 18.8, 18.4, 11.2, −4.1, −5.0; HRMS exact mass M-H^+ 407.3165 (calcd for $C_{24}H_{48}OSi_2$ -H^+ 407.3166).

[2] De Graaf, S. A.G.; Ooesterhoff, P.E.R. *Tetrahedron Lett*. **1974**, *17*, 1653