Supplementary Material for "A Stereocontrolled Construction of the A-ring of Nitol Using a Pauson-Khand Cycloaddition-Ring Fragmentation Strategy."

Michael S. Wilson and Gregory R. Dake, Department of Chemistry, 2036 Main Mall, The University of British Columbia, Vancouver BC, V6T 1Z1

Experimental

General

All reactions were performed in flame-dried septum-capped glassware under a nitrogen atmosphere unless otherwise noted. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Thin layer chromatography (TLC) was performed on DC-Fertigplatten SIL G-25 UV_{254} pre-coated TLC plates. Analytical gas-liquid chromatography (GC) was performed on a Hewlett-Packard 5890A gas chromatograph. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded in deuterochloroform using either a Bruker WH-400, Bruker AV-300, or Bruker AV-400 spectrometer. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in deuterochloroform using a Bruker AV-300 spectrometer. Signals are referenced to chloroform (7.24 ppm and 77.0 ppm). Low resolution mass spectra (LRMS) were recorded on either a Kratos-AEI model MS 50 spectrometer (for EI) or a Kratos MD 80 spectrometer (for CI+).

Enyne 10

IR (neat): 3310, 2931, 2853, 1640, 1472, 1257, 1104, 908, 839, 776, 632 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddt, *J* = 6.71 Hz, 10.07 Hz, 17.09 Hz, 1H), 5.03 (ddt, *J* = 1.83 Hz, 3.05 Hz, 17.09 Hz, 1H), 4.91 (ddt, *J* = 1.22 Hz, 3.05 Hz, 10.07 Hz, 1H), 3.53 (d, *J* = 9.46 Hz, 1H), 3.45 (d, *J* = 9.46 Hz, 1H), 2.20-2.12 (m, 2H), 2.07 (s, 1H), 1.65-1.55 (m, 1H), 1.47-1.39 (m, 1H), 1.16 (s, 3H), 0.88 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 112.9, 88.5, 69.9, 69.7, 38.4, 37.8, 30.8, 27.6, 25.5, 20.3, -2.7. HRMS (DCI+ ammonia/isobutane): Calcd for $C_{15}H_{29}OSi$ $(M+1)^+$ 253.1988. Found: 253.1995.

Pauson Khand reactions of 10

Hexanes, sealed tube, 110°C, 20 h

A 15 mL screw-top, sealed tube (with septum) was charged with 225 mg of dicobalt octacarbonyl (0.66 mmol) in a glovebox. After the addition of 3 mL of hexanes (degassed), a solution of enyne **10** (151 mg, 0.60 mmol) in 2 mL of hexanes (degassed) was added dropwise. The resulting mixture was stirred for 1h before the tube was fitted with its screw cap, heated to 110°C and stirred overnight (20 h). After cooling to rt, the reaction mixture was filtered through Celite and rinsed with 30 mL of diethyl ether. The filtrate was concentrated by rotary evaporation to yield an oil which was purified using flash chromatography on silica

gel [4:1 Pet. Ether/Ether] to yield 22 mg (13%) of a clear oil. NMR analysis showed the oil to be a 1:1 mixture of **8a** and **8b**.

Dichloromethane, 6 eq. *N*-methylmorpholine *N*-oxide, 25ºC, 12h

To a solution of 225 mg of dicobalt octacarbonyl (0.66 mmol) in 3 mL of dichloromethane was added a solution of enyne **10** (151 mg, 0.60 mmol) in dichloromethane (2 mL). The resulting mixture was stirred for 30 min before 422 mg of *N*-methylmorpholine *N*-oxide (3.60 mmol) was added in one portion and the resulting mixture was stirred overnight (12h). The reaction mixture was filtered through Celite and the Celite pad flushed with 30 mL of diethyl ether. The filtrate was concentrated by rotary evaporation to yield a residue, which was purified using flash chromatography [4:1 Pet. Ether/Ether)] to yield 52 mg (31%) of a clear oil. NMR analysis showed the oil to be a 1:1 mixture of **8a** and **8b**.

1,2-dichloroethane, 3.5 eq. thioanisole, 83ºC, 2h

To 225 mg of dicobalt octacarbonyl (0.66 mmol) was added a solution of enyne **10** (151 mg, 0.60 mmol) in 1,2-dichloroethane (6 mL). The resulting mixture was stirred for 3.5 h before 0.25 mL of thioanisole (2.10 mmol) was added dropwise. The reaction mixture was heated to 83ºC and stirred for 2h. After cooling to rt, the reaction mixture was filtered through Celite, which was rinsed with 30 mL of diethyl ether. The filtrate was concentrated by rotary evaporation and the residue was purified using flash chromatography [4:1 Pet. Ether/Ether] to yield 81 mg (48%) of a clear oil. NMR analysis showed the oil to be a 1:1 mixture of **8a** and **8b**.

1,4-dioxane/2M ammonium hydroxide (1:3), 100ºC, 30min

To 450 mg of dicobalt octacarbonyl (1.32 mmol) was added a solution of enyne **10** (303 mg, 1.20 mmol) in 1,4-dioxane (3 mL). The reaction mixture was stirred for 3.5 h before 9 mL of a 2M aqueous ammonium hydroxide solution was added dropwise. The reaction mixture was heated to 100ºC for 15 min, air cooled slightly and diluted with diethyl ether. The reaction mixture was filtered through Celite, which was rinsed with 50 mL of diethyl ether. The filtrate was washed successively with water, 5% aqueous hydrochloric acid, water, and saturated aqueous sodium bicarbonate solutions. The ether fractions were dried over magnesium sulfate, filtered and concentrated by rotary evaporation to yield a residue, which was purified using flash chromatography [4:1 Pet. Ether/Ether] to yield 138 mg (41%) of a clear oil. NMR analysis showed the oil to be a 1:1 mixture of **8a** and **8b**.

IR (neat): 2956, 2857, 1708, 1625, 1472, 1256, 1103, 839, 777, 734 cm^{-1}. ^{1}H NMR (400 MHz $CDCl_3$): δ 5.87 (d, J = 2.14 Hz, 1H), 5.81 (d, J = 2.14 Hz, 1H), 3.44 (d, J = 2.75 Hz, 2H), 3.07-3.00 (m, 1H), 3.00-2.92 (m, 1H), 2.54 (dt, J = 4.88 Hz, 17.70 Hz, 2H), 2.10-1.96 (m, 2H), 1.71-1.62 (m, 2H), 1.19 (s, 3H), 1.13 (s, 3H), 0.84 (s, 9H), 0.83 (s, 9H), 0.002 (s, 6H), -0.006 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.6, 198.1, 196.7, 124.7, 123.5, 70.1, 69.7, 47.2, 46.5, 45.5, 44.9, 43.3, 42.7, 38.3, 37.6,

30.8, 29.9, 26.2, 24.4, 23.7, 18.6, -5.2. HRMS (DCI+ ammonia/isobutane) Calcd for $C_{16}H_{29}O_2Si$ $(M+1)^+$ 281.1937. Found: 281.1925.

Enyne 9

IR (neat): 2929, 2857, 1472, 1256, 1099, 838, 776 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.07 (dd, *J* = 10.99 Hz, 17.70 Hz, 1H), 5.00 (dd, *J* = 1.53 Hz, 10.99 Hz, 1H), 4.93 (dd, *J* = 1.53 Hz, 17.70 Hz, 1H), 3.31 (dd, *J* = 9.46 Hz, 17.09 Hz, 2H), 2.01 (tq, *J* = 2.44 Hz, 7.94 Hz, 2H), 1.74 (t, *J* = 2.44 Hz, 3H), 1.62-1.54 (m, 2H), 0.92 (s, 3H), 0.87 (s, 9H), -0.003 (s, 6H). HRMS (DCI+ammonia/isobutane) Calcd for $C_{16}H_{31}OSi$ $(M+1)^+$ 267.2144. Found: 267.2141.

Pauson-Khand reactions of 9

Dichloromethane, 6 eq. *N*-methylmorpholine *N*-oxide, 25°C, 12h

To 85 mg of dicobalt octacarbonyl (0.25 mmol) was added a solution of enyne **9** (60 mg, 0.225 mmol) in dichloromethane (2 mL). After stirring for 3h at rt 150 mg of *N*-methylmorpholine *N*-oxide (1.35 mmol) was added in one portion and the resulting mixture was stirred overnight (12h) at rt. The reaction mixture was filtered through Celite, which was rinsed with 30 mL of diethyl ether. The filtrate was concentrated by rotary evaporation to yield a residue, which was purified using flash chromatography [4:1 Pet. Ether/Ether] to yield 27 mg (40%) of a clear oil. GC analysis showed the oil to be a 7.5:1 mixture of **7a** and **7b**.

1,2-dichloroethane, 3.5 eq. thioanisole, 83°C, 12h

To 85 mg of dicobalt octacarbonyl (0.25 mmol) was added a solution of enyne **9** (60 mg, 0.60 mmol) in 1,2-dichloroethane (3 mL). After stirring for 3h at rt, 0.10 mL of thioanisole (0.80 mmol) was added dropwise and the resulting mixture was heated to 83°C and stirred overnight (12h). After cooling to rt, the reaction mixture was filtered through Celite which was rinsed with 30 mL of diethyl ether. The filtrate was concentrated *in vacuo*, and purified using flash chromatography [4:1 Pet. Ether/Ether] to yield 13 mg (20%) of a clear oil. Due to the low overall yield, the components of this mixture were not analyzed.

Benzene, 3 eq. dimethylsulfoxide, 45°C, 3d

To 263 mg of dicobalt octacarbonyl (0.77 mmol) was added a solution of enyne **9** (187 mg, 0.70 mmol) in degassed benzene (5 mL). The resulting solution was stirred for 3h at rt before 0.15 mL of dimethylsulfoxide was added dropwise. The reaction mixture was heated to 45°C and stirred (in air) for 3 d. After cooling to rt, the reaction mixture was filtered through Celite which was rinsed with 30 mL of diethyl ether. The filtrate was concentrated by rotary evaporation and purified using flash chromatography [4:1 Pet. Ether/Ether] to yield 81 mg (40%) of a clear oil. GC analysis showed the oil to be a 7.7:1 mixture of **7a** and **7b**.

1,2-dichloroethane, 3 eq. cyclohexylamine, 83ºC, 0.25h

To 140 mg of dicobalt octacarbonyl (0.412 mmol) was added a solution of enyne **9** (100 mg, 0.375 mmol) in 1,2-dichloroethane (2 mL). After stirring for 4h at rt, 112 mg of cyclohexylamine (1.13 mmol) was added in one portion and the resulting mixture was heated to 83°C. After stirring for 0.25h, the reaction mixture was cooled to rt and filtered through Celite, which was rinsed with 30 mL of diethyl ether. The filtrate was concentrated by rotary evaporation to yield a residue, which was purified using flash chromatography [4:1 Pet. Ether/Ether] to yield 63 mg (57%) of a clear oil. GC analysis showed the oil to be a 5.7:1 mixture of **7a** and **7b**.

1,4-dioxane/2M ammonium hydroxide (1:3), 100ºC

To 1.41 g of dicobalt octacarbonyl (4.13 mmol) was added a solution of enyne **9** (1.00 g, 3.75 mmol) in 1,4-dioxane (9 mL). The resulting solution was stirred for 3h before 27 mL of 2M aqueous ammonium hydroxide solution was added dropwise. The reaction mixture was heated to 100ºC for 15 min, air cooled slightly and diluted with diethyl ether. The reaction mixture was filtered through Celite, which was rinsed with 50 mL of diethyl ether. The filtrate was washed successively with water, 5% aqueous hydrochloric acid, water, and saturated aqueous sodium bicarbonate solution. The aqueous layers were further extracted with 2 x 40 mL of diethyl ether. The combined organic extracts were dried over magnesium sulfate, filtered and concentrated by rotary evaporation and purified using flash chromatography [3:1 Pet. Ether/Ether) to yield 818 mg (74%) of a clear oil. GC analysis showed the oil to be a 6.3:1 mixture of **7a** and **7b**.

DME/"substoichiometric" $Co_2(CO)_8$/cyclohexylamine, 70ºC

To 65 mg of dicobalt octacarbonyl (0.188 mmol) was added a solution of enyne **9** (100 mg, 0.375 mmol) in DME (9 mL). The resulting solution was stirred for 3h at rt before 56 mg of cyclohexylamine (0.563 mmol) was added. The reaction mixture was heated to 60ºC for 18h. After removal of the solvent *in vacuo*, the residue was filtered through silica gel (10:1 Pet. Ether/Ether). Concentration of the filtrate gave a residue which was purified using flash chromatography [4:1 Pet. Ether/Ether) to yield 93 mg (84%) of a clear oil. GC analysis showed the oil to be a 5.7:1 mixture of **7a** and **7b**.

DME/catalytic $Co_2(CO)_8$/no promoter, 70ºC

A 5 mL rb flask was charged with 100 mg of enyne **9** (0.375 mmol). To this flask was added 15 mg of dicobalt octacarbonyl (0.04 mmol). The reaction vessel was sequentially evacuated and flushed with CO three times, and left under a CO atmosphere (balloon). To the mixture was added 1.5 mL of DME and the resultant solution was stirred at rt for 30 min, then heated to 70°C for 18 h. After being cooled to rt, the mixture was filtered through silica gel, which was rinsed sequentially with petroleum ether and diethyl ether. The filtrate was concentrated by rotary evaporation to yield a residue, which was purified using flash chromatography [6:1 Pet. Ether/Ether] to yield 28 mg (25%) of a clear oil. GC analysis showed the oil to be a 6.0:1 mixture of **7a** and **7b**.

Compounds **7a** and **7b** separated by column chromatography on silica gel using 3/1 pet.ether-ether as eluent.

7a:

clear oil. IR (neat): 2954, 2856, 1741, 1708, 1667, 1471, 1388, 1257, 1098, 839, 776, 757 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.43 (dd, *J* = 9.78 Hz, 11.29 Hz, 2H), 2.85-2.77 (m, 1H), 2.58-2.38 (m, 2H), 2.33 (dd, *J* = 6.41 Hz, 18.31 Hz, 1H), 2.04 (dd, *J* = 2.74 Hz, 18.31 Hz, 1H), 2.02-1.89 (m, 1H), 1.65 (s, 3H), 1.56 (ddd, *J* = 2.74 Hz, 7.94 Hz, 12.82 Hz, 1H), 0.85 (s, 9H), 0.60 (s, 3H), 0.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 183.0, 132.0, 70.2, 50.1, 44.0, 37.1, 35.5, 25.8, 18.5, 16.0, 8.0, -5.6. HRMS (DCI+ NH_3/isobutane) Calcd for $C_{17}H_{31}O_2Si$ $(M+1)^+$ 295.2093. Found: 295.2094.

7b:

clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.22 (dd, *J* = 10.07 Hz, 24.41 Hz, 2H), 2.72-2.65 (m, 1H), 2.55-2.46 (m, 2H), 2.38 (d, *J* = 4.88 Hz, 2H), 1.99 (ddd, *J* = 3.66 Hz, 7.94 Hz, 13.43 Hz, 1H), 1.78 (ddd, *J* = 10.99 Hz, 8.85 Hz, 13.43 Hz, 1H), 1.64 (s, 3H), 1.09 (s, 3H), 0.81 (s, 9H), -0.06 (d, *J* = 4.27 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 184.5, 130.9, 67.1, 53.5, 43.5, 37.1, 36.5, 25.7, 25.3, 23.8, 18.0, 8.3, -5.7.

Bicyclo[3.3.0]octanone 13

To a solution of 120 mg of enone **7a** (0.408 mmol) in 2.5 mL of THF at –78ºC was added dropwise a 1M solution of L-selectride (in THF) (415 μL, 0.415 mmol). The reaction mixture was stirred for 3h at –78ºC before iodomethane (27 mL, 0.428 mmol) was added dropwise and the resulting solution was stirred overnight at room temperature. The solution was diluted with ether and washed with 3 x 10 mL of water. The aqueous layer was separated and extracted three times with 20 mL of diethyl ether. The combined organic extracts were washed with 10% aqueous sodium hydroxide solution and brine, dried over magnesium sulfate, filtered, concentrated *in vacuo,* and purified using flash chromatography [12:1 Pet. Ether/Ether] to yield 105.2 mg (83%) of a clear oil.

IR (neat): 2956, 1741, 1471, 1407, 1384, 1362, 1255, 1098, 1006, 838, 776, 670 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 (dd, *J* = 9.46 Hz, 21.7 Hz, 2H), 2.51 (dt, *J* = 9.46 Hz, 7.02 Hz, 1H), 2.40-2.29 (m, 2H), 2.05 (dd, *J* = 9.46 Hz, 19.53 Hz, 1H), 1.54 (dt, *J* = 8.24 Hz, 13.1 Hz, 1H), 1.42-1.23 (m, 2H), 1.02 (s, 3H), 0.99 (s, 3H), 0.92 (s, 3H), 0.88 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 223.5, 71.1, 53.4, 49.8, 46.4, 42.7, 37.6, 34.8, 26.5, 25.9, 21.4, 19.6, 18.3, -5.5. HRMS (EI) Calcd for $C_{18}H_{34}O_2Si$ (M+): 310.2328. Found: 310.2328.

Ester 5a

A 25 mL quartz tube was charged with a solution of **13** (100 mg, 0.32 mmol) in anhydrous methanol (15 mL). The methanol solution was degassed for 45 min (with N_2 bubbled through the solution via a teflon cannula). The degassed solution was subjected to hυ ($\lambda \geq 190$ nm) (450 W Hanovia medium pressure mercury lamp as irradiation source) for 6.5h. Solvent was removed *in vacuo* and the residue was purified using flash chromatography [20:1 hexanes/ethyl acetate] to yield 54.3 mg (50%) of a clear oil and 16.7 mg (16%) of **13**.

IR (neat): 2954, 2858, 1742, 1471, 1436, 1386, 1368, 1256, 1146, 1099, 837, 775 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 3H), 3.36 (d, *J* = 9.46 Hz, 1H), 3.21 (d, *J* = 9.46 Hz, 1H), 2.42 (ddd, *J* = 3.36 Hz, 6.41 Hz, 10.07 Hz, 1H), 2.25 (dd, *J* = 3.36 Hz, 16.17 Hz, 1H), 2.11 (dd, *J* = 10.38 Hz, 16.17 Hz, 1H), 1.73-1.64 (m, 2H), 1.51-1.14 (m, 4H), 0.89 (s, 9H), 0.88 (s, 3H), 0.86 (d, *J* = 1.53 Hz, 3H), 0.85 (d, *J* = 1.53 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 71.0, 51.5, 50.2, 47.6, 41.4, 33.4, 30.8, 29.5, 27.8, 25.9, 22.1, 21.7, 21.1, 18.2, -5.5. HRMS (DCI+ NH_3/isobutane): Calcd for $C_{19}H_{39}O_3Si$ $(M+1)^+$: 343.2669. Found: 343.2662.

Cyclopentyl Aldehyde (from 5a to 14)

To a solution of 72 mg of **5a** (0.21 mmol) in 2 mL of dichloromethane at –78°C was added a solution of 1M diisobutylaluminum hydride (in hexane) (500 μL, 0.50 mmol). The resulting solution was stirred for 30 min at –78°C and 30 min at room temperature before being quenched with methanol (70 μL). Saturated aqueous ammonium chloride solution (70 μL) was added and the solution was stirred for 1h, dried over magnesium sulfate and filtered through a Celite pad. The filtrate was concentrated by rotary evaporation and purified using flash chromatography [9:1 pet. ether/ether)] to yield 60 mg of a clear oil. This was used directly in the subsequent reaction.

To a solution of DMSO (33mL, 0.46 mmol) in dichloromethane (0.5 mL) at -60°C was added oxalyl chloride (20 mL, 0.23 mmol). A solution of the preceding alcohol (60 mg, 0.21 mmol) in dichloromethane (1 mL) was added dropwise via cannula and the resulting solution was stirred for 15 min at -60°C. Then, triethylamine (145 μL, 1.05 mmol) was added and the solution was stirred at –60°C for an additional 15 min, warmed to rt and quenched with water (5 mL). The aqueous layer was separated and extracted with 4 x 10 mL of dichloromethane. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered and concentrated by rotary evaporation and purified using flash chromatography [20:1 pet. ether/ether)] to yield 56.2 mg (86%;2 steps) of a clear oil.

IR (neat): 2955, 2862, 2709, 1729, 1471, 1386, 1367, 1256, 1099, 860, 838, 776, 670 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (dd, *J* = 1.53 Hz, 3.36 Hz, 1H), 3.39 (d, *J* = 9.46 Hz, 1H), 3.19 (d, *J* = 9.46 Hz, 1H), 2.58-2.50 (m, 1H), 2.27 (ddd, *J* = 3.05 Hz, 9.16 Hz, 17.09 Hz, 1H), 2.23 (ddd, *J* = 1.22 Hz, 4.27 Hz, 17.09 Hz, 1H), 1.76-1.66 (m, 2H), 1.43-1.16 (m, 4H), 0.88 (s, 9H), 0.86 (d, *J* = 2.75 Hz, 6H), 0.84 (s, 3H), 0.01 (d, *J* = 3.05 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.2, 70.9, 50.1, 47.5, 40.7, 39.6, 33.6, 29.9, 27.8, 25.9, 22.7, 22.0, 21.8, 18.2, -5.5. HRMS (DCI+ NH_3/isobutane) Calcd for $C_{18}H_{37}O_2Si$ (M+1): 313.2563. Found: 313.2555.

(*E*)-α-bromo-acrylate en route from 5a to 14

An oven-dried 3 mL vial was charged with 56 mg of ethyl bis(trifluoroethyl)bromophosphonoacetate (0.14 mmol), 40 mg of 18-crown-6 (0.15 mmol) and 700 μL of THF at –78°C. A 1M solution of potassium tert-butoxide in THF (130 μL, 0.13 mmol) was added and the resulting mixture was stirred for 30 min at –78°C. A solution of aldehyde **5c** (37 mg, 0.12 mmol) in THF (300 μL) was added dropwise. The reaction mixture was stirred for 2 h at –78°C then was warmed to rt over 16 h before being quenched by the addition of saturated aqueous ammonium chloride solution. The aqueous layer was separated and extracted with 5 x 10 mL diethyl ether. The combined organic extracts were dried over magnesium sulfate, filtered, concentrated by rotary evaporation and purified using flash chromatography [50:1 pet. ether/ether)] to yield 52.2 mg (99%) of (*E*)-α-bromo-acrylate.

IR (neat): 2954, 1718, 1609, 1471, 1435, 1348, 1250, 1228, 1098, 1006, 855, 838, 776, 670 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (dd, *J* = 5.80 Hz, 7.94 Hz, 1H), 3.79 (s, 3H), 3.34 (d, *J* = 9.46 Hz, 1H), 3.14 (d, *J* = 9.46 Hz, 1H), 2.58 (ddd, *J* = 7.94 Hz, 9.77 Hz, 17.7 Hz, 1H), 2.44 (ddd, *J* = 3.36 Hz, 5.80 Hz, 17.7 Hz, 1H), 1.99-1.94 (m, 1H), 1.68-1.58 (m, 2H), 1.55-1.44 (m, 1H), 1.35-1.20 (m, 3H), 0.91 (s, 3H), 0.88 (s, 9H), 0.84 (t, *J* = 6.41 Hz, 6H), 0.02 (s, 6H). LRMS (EI) (M+-58) = 389.

Allyl alcohol 14

To a 3 mL vial was added 25 mg of (*E*)-α-bromo-acrylate (0.06 mmol) and 900 μL of dichloromethane. A solution of 1M diisobutylaluminum hydride (in hexane) (160 μL, 0.16 mmol) was added dropwise at –78°C. After stirring for 5 min, the reaction was quenched with methanol (40 μL). Saturated aqueous ammonium chloride solution (40 μL) was added and the solution was stirred for 1h, dried over magnesium sulfate and filtered through a Celite pad. The filtrate was concentrated by rotary evaporation and purified using flash chromatography [7:1 pet. ether/ether)] to give a 24.7 mg (98%) of a clear oil.

IR (neat): 3368, 2954, 2931, 2858, 1470, 1386, 1363, 1256, 1098, 1035, 1008, 855, 837, 775, 670 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (t, *J* = 6.71 Hz, 1H), 4.29 (s, 2H), 3.32 (d, *J* = 9.46 Hz, 1H), 3.14 (d, *J* = 9.46 Hz, 1H), 2.15-1.98 (m, 2H), 1.96-1.88 (m, 1H), 1.70-1.59 (m, 2H), 1.52-1.42 (m, 1H), 1.38-1.15 (m, 5H), 0.95 (s, 3H), 0.88 (s, 9H), 0.87 (d, *J* = 6.41 Hz, 6H), 0.15 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2, 122.6, 71.3, 62.8, 50.8, 47.5, 44.5, 34.3, 29.0, 27.7, 25.9, 25.8, 22.1, 22.0, 18.2, -5.5. HRMS (DCI+ NH_3/isobutane) Calcd for $C_{20}H_{40}O_2SiBr$ (M+1): 419.1981. Found: 419.1982.