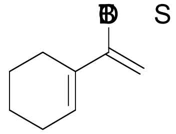
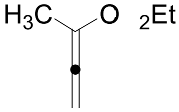
**Siloxy enol ether (2).**



**2**

1-Acetylcyclohexene (4.0 mL, 31.1 mmol, 1.0 equiv) and triethylamine (10.8 mL, 77.5 mmol, 2.5 equiv) were dissolved in 80 mL of THF and cooled to 0 °C. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (9.0 mL, 39.2 mmol, 1.26 equiv) was added slowly and the reaction mixture was stirred at 0 °C for 2h. Then the solution was stirred at 22 °C for additional 30 min. The reaction was quenched by adding 20 mL of triethylamine, 160 mL of pentane and 300 mL of saturated sodium bicarbonate. The layers were separated and the organic phase was washed with 3X 300 mL of water, followed by washing with 300 mL of saturated sodium chloride. The solution was dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to yield a yellow oil (9.16g) as the crude product. The crude product was distilled (125 °C/10mmHg) to afford **2** (7.04 g, 29.5 mmol, 95%) as a clear oil: $^1$H NMR (360 MHz, CDCl$_3$) δ 6.23-6.25 (1H, m), 4.34 (1H, s), 4.17 (1H, s), 2.12-2.15 (4H, m), 1.56-1.68 (4H, m), 0.96 (9H, s), 0.17 (6H, s); $^{13}$C NMR (90 MHz, CDCl$_3$) δ 156.7, 133.1, 125.0, 88.29, 25.84, 25.65, 24.96, 22.77, 22.16, 18.23, -4.72; IR (neat) 2932, 2859, 1645, 1593 (cm$^{-1}$).

**Ethyl 2-methyl-2,3-butadienoate (3).**

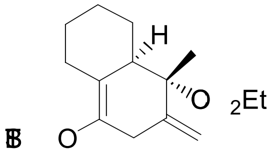


**3**

(Carbethoxyethylidene)triphenylphosphorane (26.3 g, 68.3 mmol, 1.0 equiv) was dissolved in 400 mL of methylene chloride. Then triethylamine (10.0 mL, 71.8 mmol, 1.05 equiv) was added followed by dropwise addition of acetyl chloride (5.0 mL, 70 mmol, 1.03

equiv). The reaction mixture was stirred for an additional 50 min at 22 °C. The solvent was evaporated to approximately 100 mL. Then 400 mL of hexanes was added. The resulting precipitate was removed by filtration. The filtrate was concentrated and another 400 mL of hexanes was added. The precipitate was removed by filtration. The filtrate was evaporated in vacuo to yield a yellow oil (8.46 g). The crude product was chromatographed through silica gel (5% ether/hexanes) to afford ethyl 2-methyl-2,3-butadiene **3** (6.05 g, 48.0 mmol, 70%) as a pale yellow oil: $^1$H NMR (360 MHz, $CDCl_3$) δ 4.98 (2H, q, *J* = 3.0 Hz), 4.11 (2H, q, *J* = 7.1 Hz) , 1.78 (3H, t, *J* = 3.0 Hz), 1.19 (3H, t, *J* = 7.1 Hz); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 213.8, 167.3, 95.22, 77.52, 60.72, 14.46, 14.01; IR (neat) 2934, 1972, 1944, 1709 (cm$^{-1}$)

**Diels-Alder adduct (4).**

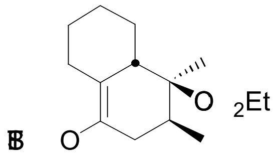


**4**

The diene **2** (3.71 g, 15.6 mmol, 1.0 equiv) and the allene **3** (1.96 g 15.5 mmol, 1.0 equiv) were dissolved in 10.0 mL of toluene in a dried pressure tube. The tube was heated in an oil bath at 135 °C for 3 days. The diene **2** (0.65 g, 2.73 mmol, 0.18 equiv) was added to the reaction mixture and the tube was heated at 140 °C for overnight. The tube was cooled to room temperature and the solvent was evaporated. The residue was chromatographed through silica gel (200 g, 5% ether/hexanes) to afford **4** (3.225 g, 8.85 mmol, 57%) as a pale yellow oil: $^1$H NMR (360 MHz, $CDCl_3$) δ 4.92 (1H, bs), 4.73 (1H, bs), 4.14 (2H, q, *J* = 7.1 Hz), 2.97 (1H, d, *J* = 18 Hz), 2.67-2.82 (2H, m), 1.24 (3H, s), 1.22 (3H, t, *J* =

7.1 Hz), 0.95-1.88 (8H, m), 0.95 (9H, s), 0.09 (3H,s), 0.08 (3H,s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 175.9, 144.7, 137.9, 119.0, 108.8, 60.53, 51.10, 44.57, 38.23, 28.61, 27.55, 27.34, 26.65, 25.71, 19.16, 18.04, 14.07, -4.21, -4.25; IR (neat) 2910, 2857, 1732, 1688, 1464 (cm$^{-1}$).

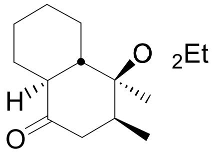
**Siloxy enol ether (4a)**



**4a**

**4** (1.117g, 3.06 mmol) was dissolved into 5 mL of anhydrous ethanol along with catalytic amount of $Pd(OH)_2/C$. The air was replaced with hydrogen gas and the mixture was stirred at 22 °C under balloon pressure of hydrogen for 1.5 h. The mixture was filtered through a pad of Celite to remove the catalyst and the solvent was evaporated in vacuo to yield a clear oil (1.105 g) as the crude product. The crude product was chromatographed through silica gel (100 g, 2.5-5% ether/hexanes) to afford **4a** (0.689 g, 61%) as a clear oil: $^1$H NMR (360 MHz, $CDCl_3$) δ 4.07-4.16 (2H, m), 2.90 (1H, dd, $J$ = 14, 1.8 Hz), 2.58 (2H, m), 2.40 (2H, m), 1.95 (2H, m), 1.24 (3H, t, $J$ = 7.2 Hz), 1.11 (3H, s), 0.95-1.80 (5H, m), 0.93 (9H, s), 0.87 (3H, d, $J$ = 7.0 Hz) 0.10 (3H, s), 0.09 (3H, s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 176.9, 140.1, 115.2, 60.22, 49.31, 44.85, 35.63, 28.09, 26.33, 25.86, 25.82, 25.67, 25.59, 18.11, 16.20, 14.28, 9.51, -3.75, -4.25; IR (neat) 2930, 2857, 1728, 1674 (cm$^{-1}$).

**Ketone (4b)**

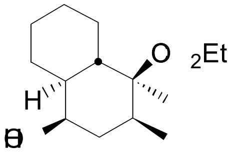


**4b**

**4a** (0.074 g, 0.20 mmol) was dissolved in 2.0 mL of THF.

2.0 mL of 5% aqueous sodium bicarbonate was added followed by 1.0 mL of 1.0 M solution of TBAF (1.0 mL, 1.0 mmol, 5 equiv) in THF. The mixture was stirred at 22 °C for 18 h. 10 mL of ether and 10 mL of water were added and the layers were separated. The aqueous phase was extracted with ether 3 times. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to yield a clear oil (0.070 g) as the crude product. The crude product was chromatographed through silica gel (15g, 20% ether/hexanes) to afford **4b** (0.040 g, 0.16 mmol, 79%) as a clear oil: $^1$H NMR (360 MHz, $CDCl_3$) δ 4.13 (2H, m), 2.71 (1H, dd, $J$ = 14, 5.3 Hz), 1.40 (3H, s), 1.23 (3H, t, $J$ = 7.1 Hz) 1.07-2.23 (12H, m), 0.82 (3H, d, $J$ = 7.2 Hz); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 211.3, 175.4, 60.34, 49.14, 48.21, 44.00, 42.99, 41.09, 29.30, 25.98, 25.61, 25.49, 18.30, 16.73, 14.13; IR (neat) 2930, 2857, 1720, 1713 (cm$^{-1}$).

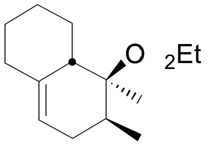
**Alcohol (4c)**



**4c**

**4b** (0.049 g, 0.19 mmol, 1.0 equiv) was dissolved in 2.0 mL of methanol and sodium borohydride (0.012 g, 0.31 mmol, 1.6 equiv) was added at 0 °C. After 15 min stirring at 0 °C, 1N HCl was added slowly to quench the reaction. Methanol was evaporated in vacuo and saturated sodium bicarbonate was added to neutralize the aqueous phase. The aqueous phase was extracted with ether 3 times. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, then evaporated in vacuo to yield a clear oil (0.0481 g) as the crude product. The crude product was chromatographed through silica gel (6g, 40% ether/hexanes) to afford **4c** (0.0251 g, 51%) as a clear oil: $^{1}$H NMR (360 MHz, $CDCl_3$) δ 4.08-4.14 (2H, m), 3.72-3.74 (1H, m), 2.14-2.20 (1H, m), 0.90-1.95 (13H, m), 1.25 (3H, t, *J* = 7.0 Hz), 1.07 (3H, d, 7.4 Hz), 1.19 (3H, s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 176.7, 70.46, 59.79, 48.76, 40.89, 37.66, 34.66, 33.97, 29.61, 28.69, 26.71, 26.62, 19.37, 18.14, 14.14; IR (neat) 3532, 2980, 2926, 2855, 1720, 1267 (cm$^{-1}$).

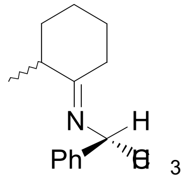
**Olefin (5)**



**5**

**4c** (0.036 g, 0.14 mmol, 1.0 equiv) was dissolved in pyridine and phosphorous oxychloride (0.030 mL, 0.322 mmol, 2.3 equiv) was added slowly. The solution was stirred for 18 h at 22 °C. 10 mL of ether and 10 mL of water was added slowly. The aqueous phase was extracted with ether 3 times. The combined organic phases were washed with 1 N HCl, saturated sodium bicarbonate and saturated sodium chloride sequentially. The organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to yield a clear oil (0.033 g) as the crude product. The crude product was chromatographed through silica gel (4.5 g, 2.5-5% ether/hexanes) to afford **5** (0.0274 g, 83%) as a clear oil: $^{1}$H NMR (360 MHz, $CDCl_3$) δ 5.18 (1H, m), 4.17 (2H, m), 2.53 (1H, m), 2.20-2.33 (2H, m), 1.85-2.06 (2H, m), 1.60-1.80 (4H, m), 1.32-1.48 (1H, m), 1.23 (3H, t, *J* = 7.1 Hz), 1.03-1.28 (2H, m), 1.10 (3H, s), 0.81 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 177.2, 137.9, 115.5, 59.97, 47.25, 38.64, 35.77, 35.48, 29.02, 28.15, 27.48, 26.44, 20.12, 15.96, 14.22; IR (neat) 2973, 2930, 1727, 1447, 1238, 1111 (cm$^{-1}$).

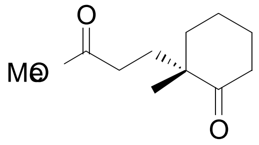
### Imine (6a)



**6a**

2-Methylcyclohexanone (18.4 mL, 151.6 mmol, 1.0 equiv), (*R*)-(+)-α-methylbenzylamine (96% ee, 20.0 mL, 155.1 mmol, 1.02 equiv) and *p*-toluenesulfonic acid monohydrate (0.0615g, 0.323 mmol, 0.2 mol%) were dissolved into 100 mL of dry toluene and heated to reflux with Dean-Stark trap attached. After refluxing for 1 h, Dean-Stark trap was replaced by distillation head and the most of toluene was distilled off. Then the residue was distilled (110-157 °C/1 mmHg) to obtain a diastereomeric mixture of **6a** (29.96 g, 139.1 mmol, 92%) as a clear oil.

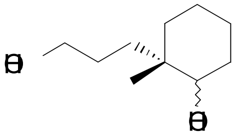
### Keto-ester (7)



**7**

**6a** (10.0 g, 46.5 mmol, 1.0 equiv) was weighed in a flask and methyl acrylate (4.30 mL, 47.3 mmol, 1.02 equiv) was added. The clear solution was stirred at 22 °C for 4 days. Then 50 mL of 10% acetic acid was added and the mixture was stirred at 22 °C for 2 h. The cloudy mixture was extracted with ether 4 times. The combined organic phases were washed with saturated sodium chloride 2 times, dried over anhydrous magnesium sulfate, filtered, then evaporated in vacuo to yield a pale yellow oil (9.515 g) as the crude product. The crude product was distilled (138-140 °C/5 mmHg) to give **7** (6.526 g, 32.9 mmol, 71%) as a clear oil. **7** was converted its semicarbazon and recrystalized from EtOH, then hydrolyzed back to 7 to afford pure enantiomer: $^{1}$H NMR (360 MHz, $CDCl_3$) δ 3.64 (3H, s), 2.01-2.40 (5H, m), 1.58-1.90 (7H, m), 1.05 (3H, s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 214.3, 173.4, 51.04, 47.37, 38.76, 38.19, 32.03, 28.46, 26.96, 21.89, 20.54; IR (neat) 2936, 2867, 1740, 1705, 1437, 1173 (cm$^{-1}$), $[\_]^{20}_{D}$ = -37.5 (c=3.10, EtOH).

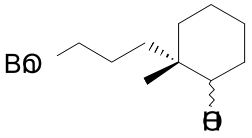
**Diol (7a)**



**7a**

To a solution of lithium aluminum hydride (75 mL, 1 M in THF, 2.23 equiv) in THF, 7 (6.31 g, 33.6 mmol, 1.0 equiv) in a total of 70 mL of THF was added dropwise at 22 °C. After 45 min stirring at 22 °C, 2.0 mL of water, 2.0 mL of 6N sodium hydroxide, and 6.0 mL of water were added sequentially at 0 °C. The mixture was stirred for 1 h and the precipitate was removed by filtration through a pad of Celite. The filtrate was dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to yield a thick pale yellow oil (6.32 g) as the crude product. The crude **7a** was used for the next reaction without further purification.

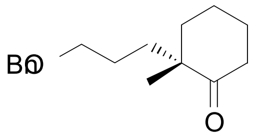
**Alcohol (7b)**



**7b**

**7a** (6.32 g, 33.6 mmol, 1.0 equiv) in a total of 50 mL of THF was added to a solution of NaH (2.98 g, 74.5 mmol, 2.2 equiv) in 100 mL of THF dropwise at –78 °C followed by dropwise addition of BnBr (4.53 mL, 38.1 mmol, 1.1 equiv). Then the mixture was warmed up to 22 °C and stirred for 5h. The reaction was quenched by careful addition of 1N HCl. The aqueous phase was extracted with ether 3 times. The combined organic phases were washed with saturated sodium bicarbonate and saturated sodium chloride, then dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to yield a yellow oil (10.78 g) as the crude product. The crude product was chromatographed through silica gel (400 g, 50% ether/hexanes) to afford **<u>7b</u>** (7.24 g, 27.59 mmol, 82%) as a mixture of two isomers.

**Ketone (<u>8</u>)**

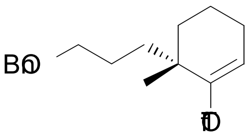


<u>8</u>

To a solution of oxalyl chloride (18.0 mL, 36.0 mmol, 2.0 M solution in dichloromethane, 1.30 equiv) in 60 mL of dichloromethane, methyl sulfoxide (5.1 mL, 71.7 mmol, 2.60 equiv) was added slowly followed by addition of **<u>7b</u>** (7.24 g, 27.6 mmol, 1.00 equiv) in a total of 20 mL of dichloromethane at –78 °C. The solution was stirred at –78 °C for 30 min. Then triethylamine (20.0 mL, 143 mmol, 5.20 equiv) was added slowly and the mixture was stirred at –78 °C for 15 min. The mixture was warmed up to 22 °C and washed with water, 1N HCl, water, saturated sodium bicarbonate, and water subsequently. The organic phase was dried over anhydrous magnesium sulfate, filtered, and then evaporated in vacuo to yield a yellow oil (7.87 g) as the crude product. The crude product was chromatographed through silica gel (350 g, 20-40% ether/hexanes) to afford **<u>8</u>** (6.58 g, 25.3 mmol, 92%)as a pale yellow oil: $^1$H NMR (360 MHz, CDCl$_3$) δ

7.25-7.33 (5H, m), 4.48 (2H, s), 3.44 (2H, d, *J* = 6.2 Hz), 2.31-2.40 (2H, m), 1.37-1.82 (10H, m), 1.05 (3H, s); $^{13}$C NMR (90 MHz, CDCl$_3$) δ 215.7, 138.4, 128.2, 127.4, 127.4, 72.67, 70.46, 48.16, 39.17, 38.58, 33.86, 27.36, 24.05, 22.39, 20.88; IR (neat) 3031, 2934, 2861, 1705, 1454, 1101 (cm$^{-1}$), $[\_]^{20}_{D}$ = -44.9 (c=3.10, CHCl$_3$).

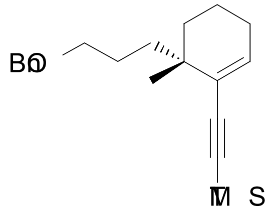
**Vinyl triflate (8a)**



**8a**

**8** (3.341 g, 12.8 mmol, 1.0 equiv) in a total of 10 mL of THF was added to a solution of lithium diisopropylamide (10.3 mL, 15.45 mmol, 1.5 M in cyclohexene, 1.2 equiv) in 40 mL of THF at –78 °C and stirred for 2h. *N*-Phenyl trifluoromethanesulfonimide (6.20 g, 17.35 g, 1.35 equiv) in a total of 25 mL of THF was added slowly at –78. Then the solution was stirred at 0 °C for 3 h then overnight at 22 °C. The solvent was evaporated and the residue was filtered through a pad of silica gel to afford a pale yellow oil (5.86 g) as crude product. The crude product was chromatographed through silica gel (2.5-5% ether/ hexanes) to afford **8a** (4.21 g, 10.7 mmol, 84%) as a pale yellow oil: $^{1}$H NMR (360 MHz, CDCl$_3$) δ 7.26-7.38 (5H, m), 5.73 (1H, t, *J* = 4.2 Hz), 4.51 (2H, s), 3.43-3.49 (2H, m), 2.13-2.19 (2H, m), 1.50-1.75 (8H, m), 1.15 (3H, s); $^{13}$C NMR (90 MHz, CDCl$_3$) δ 155.2, 138.4, 128.3, 127.5, 127.4, 118.3, 116.9, 72.83, 70.52, 37.84, 35.12, 34.83, 24.67, 24.47, 24.25, 18.26; IR (neat) 2944, 2863, 1674, 1412, 1210, 1143 (cm$^{-1}$), $[\_]^{20}_{D}$ = +5.31 (c=3.05, CHCl$_3$).

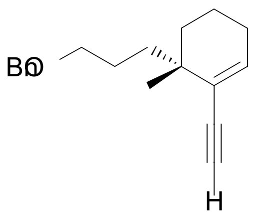
## Eneyne (**9**)



**9**

*n*-Butylamine (4.4 mL, 81.3 mmol, 3.8 equiv) was added to a mixture of **8a** (8.41 g, 21.4 mmol, 1.0 equiv) and CuI (1.07 g, 5.62 mmol, 0.26 equiv) in 80 mL of THF at 22 °C, followed by (trimethylsilyl)acetylene (5.60 mL, 82.0 mmol, 3.8 equiv), and tetrakis(triphenylphosphine)palladium(0) (1.25 g, 1.08 mmol, 0.05 equiv) in a total of 60 mL of THF. After stirring for 3 h at 22 °C, saturated sodium bicarbonate was added and the aqueous phase was extracted with ether 3 times. The combined organic phases were dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to give a black residue. The residue was filtered through a pad of silica gel to afford a dark brown oil (8.13 g) as the crude product. The crude product was chromatographed through silica gel (450g, 2.5% ether/hexanes) to afford **9** (7.26 g, 20.6 mmol, 96%) as brown oil: $^{1}$H NMR (360 MHz, $CDCl_3$) δ 7.28-7.36 (5H, m), 6.17 (1H, t, $J$ = 4.1 Hz), 4.52 (2H, s), 3.45-3.51 (2H, m), 2.02-2.15 (2H, m), 1.37-1.66 (8H, m), 1.11 (3H, s), 0.18 (9H, s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 138.7, 136.4, 129.5, 128.3, 127.5, 127.4, 105.5, 92.52, 72.76, 71.29, 36.99, 36.27, 33.35, 26.78, 25.98, 24.58, 18.50, 0.064; IR (neat) 3031, 2957, 2936, 2855, 2141, 1455, 1250, 1101, 840 ($cm^{-1}$), $[\_]^{20}_{D}$ = -31.3 (c=3.11, $CHCl_3$).

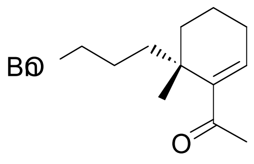
### Eneyne (9a)



**9a**

**9** (7.13 g, 20.2 mmol, 1.0 equiv) was dissolved in 200 mL of methanol and 11 mL of 2N potassium hydroxide (22 mmol, 1.1 equiv) was added. The solution was stirred at 22 °C for 4 h. The solvent was evaporated and water was added. The aqueous phase was extracted with ether 4 times. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to yield **9a** (5.40 g, 20.1 mmol, 100%) as an amber oil: $^1$H NMR (360 MHz, $CDCl_3$) δ 7.26-7.36 (5H, m), 6.19 (1H, t, *J* = 4.1 Hz), 4.51 (2H, s), 3.45-3.50 (2H, m), 2.78 (1H, s), 2.02-2.05 (2H, m), 1.38-1.65 (8H, m), 1.11 (3H, s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 138.6, 137.0, 128.6, 128.3, 127.6, 127.4, 83.63, 75.87, 72.73, 71.15, 36.79, 36.12, 33.34, 26.59, 25.97, 24.49, 18.49; IR (neat) 3310, 3029, 2934, 2859, 2791, 1455, 1101 (cm$^{-1}$), $[\_]_{\mathrm{D}}^{20}$ = -22.2 (c=3.07, $CHCl_3$).

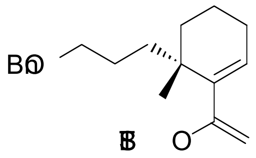
### Enone (9b)



**9b**

**9a** (2.50 g, 9.31 mmol, 1.00 equiv) was dissolved in 100 mL acetic acid and mercury acetate (0.745 g, 2.34 mmol, 0.25 equiv) was added followed by conc. sulfuric acid (0.45 mL). The mixture was stirred at 22 °C for 1h and 20 min. Water was added and the aqueous solution was neutralized by adding sodium bicarbonate powder. Then the aqueous phase was extracted with dichloromethane 4 times. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to yield an amber oil (2.54 g) as the crude product. The crude product was chromatographed through silica gel (200g, 20% ether/hexanes) to afford **9b** (2.01 g, 7.00 mmol, 75%) as a pale yellow oil: $^1$H NMR (360 MHz, $CDCl_3$) δ 7.25-7.34 (5H, m), 6.83 (1H, t, *J* = 4.0 Hz), 4.47 (2H, s), 3.37-3.41 (2H, t, *J* = 7.0 Hz), 2.25 (3H, s), 2.17-2.25 (2H, m), 1.89 (1H, dt, *J* = 4.5, 12.6 Hz), 1.21-1.65 (6H, m), 1.20 (3H, s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 200.0, 146.3, 142.2, 138.0, 128.3, 127.6, 127.4, 72.86, 71.18, 36.31, 35.99, 35.44, 27.44, 26.65, 26.56, 25.00, 17.94; IR (neat) 3029, 2936, 2865, 1669, 1454, 1366, 1101 (cm$^{-1}$), $[\_]^{20}_{D}$ = +1.52 (c=3.02, $CHCl_3$).

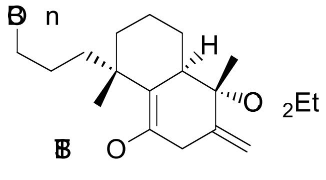
**Siloxy enol ether (10)**



**10**

**9b** (3.77 g, 13.2 mmol, 1.00 equiv) was dissolved in 40 mL of THF. Triethylamine (4.60 mL, 33 mmol, 2.51 equiv) was added at 0 °C followed by slow addition of *tert*-butyldimethylsilyl trifluoromethanesulfonate (3.80 mL, 16.2 mmol, 1.23 equiv). The solution was stirred at 0 °C for 1 h and at 22 °C for 30 min. 10 mL of triethylamine and 40 mL of pentanes were added and the organic phase was washed with saturated sodium bicarbonate 3 times and saturated sodium chloride. Then the solution was dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to yield **10** (5.24 g, 13.1 mmol, 99%) as a pale yellow oil: $^1$H NMR (360 MHz, $CDCl_3$) δ 7.26-7.37 (5H, m), 5.85 (1H, t, *J* = 3.8 Hz), 4.50 (2H, s), 4.20 (1H, s), 4.09 (1H, s), 3.42-3.45 (2H, m), 2.00-2.03 (2H, m), 1.29-1.64 (8H, m), 1.17 (3H, s), 0.94 (9H, s), 0.20 (6H, s); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 160.9, 144.5, 138.7, 128.3, 127.6, 127.4, 127.4, 92.41, 72.77, 71.46, 36.27, 35.56, 35.43, 26.94, 25.88, 25.68, 24.61, 18.53, 18.20, -4.50; IR (neat) 3027, 2955, 1605, 1003 (cm$^{-1}$), [_]$_{D}^{20}$ = +7.29 (c=2.99, CHCl$_3$).

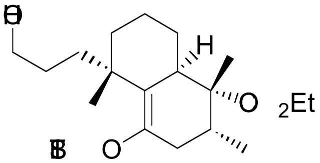
### Diels-Alder adduct (11)



**11**

**10** (2.00 g, 4.99 mmol, 1.00 equiv) and **3** (1.51 g, 11.97 mmol, 2.4 equiv) were dissolved in 3 mL of toluene in a pressure tube. The tube was heated in an oil bath at 140-144 °C for 9 days. **3** (1.85 g total, 14.7 mmol, 2.9 equiv) were added during the reaction in 5 potions. The solvent was evaporated and the residue was chromatographed through silica gel (400 g, 10% ether/hexanes) to remove byproducts and afforded a mixture of 4 isomers of adduct including **11**. The mixture of adducts was subjected to HPLC separation (reverse-phase column, 18 mL/min, 100% acetonitrile as eluent) to afford **11** (0.750 g, 1.43 mmol, 29%) as a clear oil: $^{1}$H NMR (500 MHz, CDCl$_3$) δ 7.25-7.34 (5H, m), 4.95 (1H, s), 4.77 (1H, s), 4.51 (2H, s), 4.20 (1H, s), 4.09 (2H, m), 3.46 (2H, m), 3.12 (1H, d, *J* = 18.2 Hz), 2.84 (1H, m), 2.73 (1H, d, *J* = 18.2 Hz), 0.96-1.60 (9H, m), 1.56 (3H, s), 1.30 (3H, s), 1.21 (3H, t, *J* = 7.1 Hz), 0.93 (9H, s), 0.15 (3H, s), 0.12 (3H, s); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 176.0, 144.1, 141.4, 138.9, 128.2, 127.6, 127.3, 121.4, 109.1, 72.66, 71.59, 60.68, 51.05, 39.90, 39.64, 39.38, 38.30, 35.96, 26.26, 25.90, 25.77, 24.72, 19.62, 19.58, 18.51, 14.12, -2.64, -3.11; IR (neat) 2934, 2861, 1726, 1254, 1101 (cm$^{-1}$), [_]$_{D}^{20}$ = -61.1 (c=2.99, CHCl$_3$).

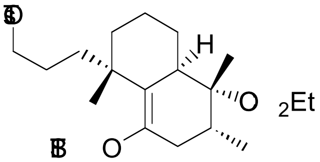
**Alcohol (11a)**



**11a**

11 (0.1117 g, 0.212 mmol) was dissolved in 4 mL of absolute ethanol and 0.4 mL of pH 7.0 phosphate buffer was added followed by a spatula tip of Pd(OH)$_2$/C. Hydrogen gas was introduced into the flask and the mixture was stirred for 6 h at 22 °C under balloon pressure of hydrogen. The catalyst was removed by filtration through a pad of Celite and the solvent was evaporated in vacuo to yield a clear oil (0.1155 g) as the crude product. The crude product was chromatographed through silica gel (10 g, 50% ether/hexanes) to afford **11a** and its stereoisomer as inseparable mixture (0.865 g, 0.197 mmol, 93%)

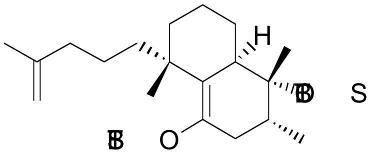
**Tosylate (12)**



**12**

The mixture of **11a** and its isomer (0.082 g, 0.19 mmol, 1.0 equiv) and DMAP (0.0366 g, 0.30 mmol, 1.6 equiv) were dissolved in 2 mL of dichloromethane. *p*-Toluenesulfonyl chloride (0.043 g, 0.23 mmol, 1.2 equiv) was added and the solution was stirred at 22 °C for 4 h. Ether was added and the organic phase was washed with saturated ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride sequentially. The organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to yield a clear oil (0.1156 g) as the crude product. The crude product was chromatographed through silica gel (6g, 10-20% ether/hexanes) to afford **12** and its stereoisomer as inseparable mixture (0.095 g, 0.16 mmol, 86%).

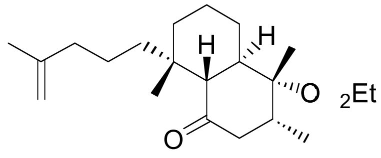
### Olefin (12a)



**12a**

The mixture of **12** and its isomer (0.184 g, 0.304 mmol, 1.00 equiv) and CuI (0.0578 g, 0.304 mmol, 1.00 equiv) were dissolved in 4.0 mL of THF and cooled to -50 °C. Isopropenylmagnesium bromide (4.40 mL, 0.5 M solution in THF, 2.20 mmol, 7.2 equiv) was added slowly and the solution was stirred at 0 °C for 6.5 h. 0.4 mL of methanol was added and the solvent was evaporated. The residue was taken into 60 mL of ether and filtered through a pad of Celite. The filtrate was evaporated to give a pale brown oil (0.143 g) as the crude product. The crude product was chromatographed through silica gel (20g, 2.5-5% ether/hexanes) to afford three fractions. The first fraction (0.032 g, 0.0701 mmol) was single isomer of **12a**. The second fraction (0.068 g, 0.148 mmol) was a mixture of **12a** and its isomer. The last fraction (0.009 g, 0.020 mmol) was the isomer of **12a**. In total, 0.110 g, 0.238 mmol of **12a** and its isomer was obtained, thus the yield of this reaction was 78%: $^1$H NMR (500 MHz, $CDCl_3$) δ 4.63-4.65 (2H, m), 4.04-4.15 (2H, m), 2.76 (1H, d, $J$ = 12.8 Hz), 2.35 (1H, m), 0.87-2.00 (17H, m), 1.69 (3H, bs), 1.23 (3H, t, $J$ = 6.6 Hz), 1.22 (3H, s), 1.07 (3H, s) 0.94 (9H, s), 0.15 (6H, s); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 176.9, 146.6, 140.6, 118.6, 109.3, 59.96, 46.84, 40.03, 38.76, 38.21, 36.48, 35.62, 35.05, 26.83, 26.39, 26.20, 24.61, 22.78, 22.41, 19.87, 18.96, 18.51, 16.04, 14.24, -2.46, -2.75; IR (neat) 2934, 2861, 1728, 1651, 1258, 1196 (cm$^{-1}$), [_]$_{D}^{20}$ = -51.2 (c=1.62, $CDCl_3$).

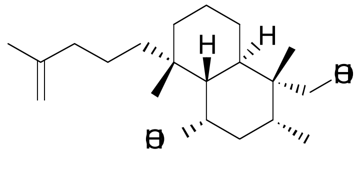
**Ketone (<u>12b</u>)**



<u>**12b**</u>

**<u>12a</u>** (0.031 g, 0.067 mmol, 1.0 equiv) was dissolved in THF and TBAF (0.1 mL, 1.0 M in THF, 0.1 mmol, 1.5 equiv) was added. The solution was stirred at 22 °C for 1h 20min. Saturated sodium bicarbonate was added and the aqueous phase was extracted with ether 3 times. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, then evaporated in vacuo to yield a clear oil (0.025 g) as the crude product. The crude product was chromatographed through silica gel (6 g, 10% ether/hexanes) to afford **<u>12b</u>** (0.02 g, 0.057 mmol, 85%) as a clear oil: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 4.68 (2H, d, *J* = 7.8 Hz), 4.12-4.20 (2H, m), 2.60-2.68 (2H, m), 1.89-2.12 (4H, m), 0.95-1.80 (11H, m), 1.72 (3H, bs), 1.38 (3H, s), 1.27 (3H, t, *J* = 7.1 Hz), 1.11 (3H, s), 0.85 (3H, d, *J* = 6.7 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 210.6, 175.8, 146.4, 109.5, 60.43, 58.99, 48.60, 45.84, 40.88, 38.72, 37.87, 37.74, 35.79, 30.05, 29.86, 27.60, 22.52, 21.52, 21.44, 18.86, 16.58, 14.22; IR (neat) 2938, 2872, 1725, 1707, 1647, 1458, 1215 (cm$^{-1}$), [_]$_{D}^{20}$ = -34.5 (c=0.98, $CDCl_3$).

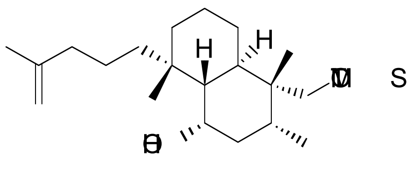
**Diol (<u>13</u>)**



<u>**13**</u>

**12b** (0.053 g, 0.15 mmol, 1.0 equiv) in a total of 2 mL of THF was added to a solution of lithium aluminum hydride (0.2 mL, 1.0 M in THF, 0.2 mmol, 1.3 equiv) in 3 mL of THF at 0 °C. The solution was warmed up to 22 °C and stirred for 1h 50 min. After cooling the reaction mixture to 0 °C, 0.1 mL of water, 0.1 mL 6 N NaOH, and 0.3 mL of water were added sequentially. The mixture was filtered through a pad of Celite. The filtrate was dried over anhydrous magnesium sulfate, filtered, then evaporated in vacuo to yield a clear oil (0.050 g) as the crude product. The crude product was chromatographed through silica gel (6 g, 50% ether/hexanes) to afford **13** (0.046 g, 0.148 mmol, 100%) as a clear oil: $^1$H NMR (500 MHz, $CDCl_3$) δ 4.67-4.68 (2H, m), 4.27 (1H, dd, *J* = 3.5, 7.2 Hz), 3.56 (1H, d, *J* = 13.6 Hz), 3.56 (1H, d, *J* = 13.6 Hz), 1.90-2.00 (4H, m), 0.79-1.75 (15H, m), 1.71 (3H, bs), 1.21 (3H, d, *J* = 7.4 Hz), 0.98 (3H, s), 0.97 (3H, s); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 146.6, 109.4, 70.06, 68.06, 50.27, 40.68, 39.00, 37.66, 37.43, 36.35, 34.46, 33.66, 29.62, 27.46, 26.55, 22.54, 21.89, 20.89, 18.68, 18.25; IR (neat) 3430, 2932, 2867, 1464, 1018 (cm$^{-1}$), $[\_]^{20}_{D}$ = +0.69 (c=1.75, $CDCl_3$).

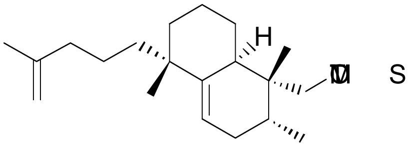
**Alcohol (13a)**



**13a**

**13** (0.014 g, 0.045 mmol, 1.0 equiv) and a spatula tip of DMAP were dissolved into 2 mL of dichloromethane. TMSCl (10 _L, 0.079 mmol, 1.8 equiv) was added at 0 °C, followed by addition of $Et_3N$ (40 _L, 0.287 mmol, 6.4 equiv). The solution was warm up to 22 °C and stirred for 1 h. Ethyl acetate was added and the organic phase was washed with water, and saturated sodium chloride. The organic phase was then dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to yield a clear oil (0.019 g) as the crude product. The crude product was used in the next reaction without further purification.

**Olefin (<u>14</u>)**



**<u>14</u>**

**<u>13a</u>** (0.043 g, 0.11 mmol, 1.0 equiv) was dissolved in 2 mL of dry pyridine and thionyl chloride (0.040 mL, 0.55 mmol, 5.0 equiv) was added dropwise at 0 °C. The solution was stirred for 30 min. 80 mL of ether and the organic phase was washed with 28 mL of 1 N HCl, 8 mL of saturated sodium bicarbonate, 8 mL of water, and 8 mL of saturated sodium chloride sequentially. The organic phase was dried over anhydrous magnesium sulfate, filtered, and then evaporated in vacuo to yield a clear oil (0.041 g) as the crude product. The crude product was chromatographed through silica gel (5 g, 2.5% ether/hexanes) to afford **<u>14</u>** (0.023 g, 0.063 mmol, 57%) as a clear oil: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.28 (1H, bs), 4.65-4.68 (2H, m), 3.45 (1H, d, *J* = 9.4 Hz), 3.33 (1H, d, *J* = 9.4 Hz), 1.86-2.10 (4H, m), 0.82-1.85 (15H, m), 1.70 (3H, bs), 0.97 (3H, s), 0.87 (3H, s), 0.055 (9H, s); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 146.2, 145.5, 116.7, 109.6, 66.09, 41.09, 39.74, 38.66, 38.31, 37.07, 31.70, 31.64, 29.30, 26.16, 22.48, 22.39, 22.34, 21.96, 20.84, 15.42, -0.55; IR (neat) 2957, 2878, 1470, 1252 (cm$^{-1}$), [_]$_{D}^{20}$ = -48.7 (c=1.15, $CDCl_3$).