Supporting information

On the Diastereoselectivity of Ru-Catalyzed [5 + 2] Cycloadditions

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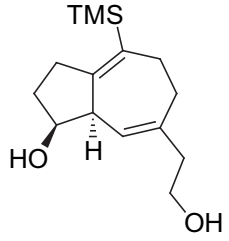
Synthesis of hexahydroazulenes 6a-6j:



6a

7-(2-Hydroxyethyl)-4-trimethylsilyl-1,2,3,5,6,8a-hexahydroazulen-1-ol (6a): To a solution of diol **5a** (20 mg, 0.75 mmol) in 2 mL of acetone under argon was added $CpRu(CH_3CN)_3PF_6$ (4 mg, 0.08 mmol). The mixture was stirred at rt for 3 h. Without workup, the mixture was chromatographed (5% to 95% of diethyl ether in petroleum ether) to afford cycloadduct **6a** (15 mg, 0.56 mmol, 75%, dr = 5:1) as a colorless oil. The ratio of diastereomers was determined by ^{1}H-NMR integration of the bis-allylic protons.

IR (neat): 3356w, 2925s, 2854s, 1628w, 1456w, 1247m, 1156w, 1065w, 936w, 904w, 853m, 834m, 754w, 686w cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.44 (s, 1H), 4.31 (bs, 1H), 3.67 (m, 2H), 3.62 (m, 1H), 2.60 (m, 1H), 2.42 (m, 2H), 2.23 (m, 3H), 2.04 (m, 2H), 1.83 (m, 2H), 1.70 (m, 1H), 0.14 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.3, 139.4, 133.3, 122.8, 75.4, 60.0, 49.6, 43.6, 33.4, 31.0, 29.7, 29.4, -0.34. MS Calc'd for $C_{15}H_{26}O_2Si$ [M^+]: 266. Found: 266.

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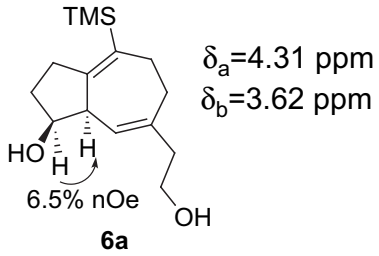
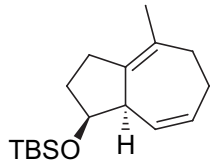


6a



6b

3-(*tert*-Butyldimethylsilyloxy)-8-methyl-3,3a,6,7-hexahydroazulene (**6b**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (2 mg, 0.005 mmol) was added a solution of vinylcyclopropane **5b** (15 mg, 0.054 mmol) in DMF (0.5 mL) and the resulting orange solution stirred at room temperature for 6h. The reaction mixture was directly chromatographed eluting with 3% diethyl ether in petroleum ether to afford a 5.1:1 mixture of **6b** and its diastereomer (11 mg, 73%) as colorless oil. The ratio of diastereomers was determined by ^{1}H-NMR integration of the bis-allylic protons: for the major diastereomer (**6b**) a multiplet at 3.51 ppm (1H) and for minor diastereomer (**6b'**) a multiplet at 3.24 ppm (1H).

IR (neat): 2956, 2929, 2856, 1471, 1361, 1252, 1160, 1117, 1085, 1041, 835, 774 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 11.2, 2.6 and 1.7 Hz, 1H), 5.70 (m, 1H), 4.27 (dt, *J* = 5.7 and 4.0 Hz, 1H), 3.51 (m, 1H), 2.49 (m, 2H), 2.32-2.10 (m, 4H), 1.90 (m, 1H), 1.70 (m, 1H), 1.68 (s, 3H), 0.91 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 130.9, 129.3, 129.1, 127.7, 75.7, 46.5, 34.0, 32.4, 28.1, 26.1, 25.9, 21.1, 18.2, -4.5. HRMS Calc'd for $C_{13}H_{22}OSi$ $[M - t\text{-Bu}]^+$: 222.1440. Found: 222.0863.

Additional signals for **6b'**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.63 (ddd, *J* = 11.2, 3.7 and 1.6 Hz, 1H), 3.84 (td, *J* = 8.7 and 5.7 Hz, 1H), 3.24 (m, 1H), 1.65 (s, 3H), 0.92 (s, 9H), 0.11 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 129.7, 129.9, 80.1, 50.3, 33.2, 32.6, 27.6, 26.4, 25.8, 20.4, 18.0, -4.3, -4.9.

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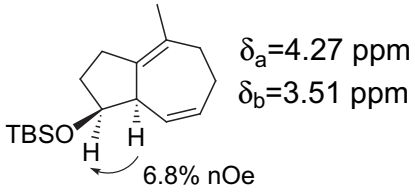
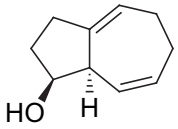


6b



6c

1,2,3,5,6,8a-Hexahydroazulen-1-ol (6c): To a solution of **5c** (150 mg, 1.0 mmol) in 3 mL of acetone under argon was added $CpRu(CH_3CN)_3PF_6$ (43 mg, 0.10 mmol). The mixture was stirred at rt for 4 h. Without workup, the mixture was chromatographed (5% to 30% of diethyl ether in petroleum ether) to afford cycloadduct **6c** (129 mg, 0.86 mmol, 86%) as a colorless oil. IR (neat): 3386b, 2932s, 2901s, 1447m, 1433m, 1328w, 1173m, 1155m, 1080m, 1069m, 1016w, 982w, 935w, 895w, 846s, 793w, 731w cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.97 (m, 1H), 5.77 (t, *J*=2.0 Hz, 1H), 5.68 (dt, *J*=1.0, 11.5 Hz, 1H), 4.30 (s, 1H), 3.52 (s, 1H), 2.60 (m, 1H), 2.35 (m, 3H), 2.10 (m, 2H), 1.82 (m, 1H), 1.71 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.1, 133.4, 126.7, 123.3, 76.0, 49.1, 32.7, 30.3, 27.1, 26.1. MS Calc'd for $C_9H_{14}O$ [M^+]: 150. Found: 150.

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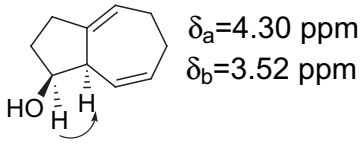
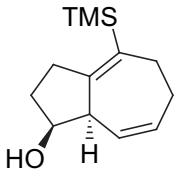


6c

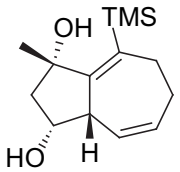


6d

4-Trimethylsilanyl-1,2,3,5,6,8a-hexahydroazulen-1-ol (**6d**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (110 mg, 0.252 mmol) was added a solution of vinylcyclopropane **5d** (553 mg, 2.49 mmol) in acetone (10 mL) and the resulting orange solution stirred at room temperature

for 30 min. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 4:1 petroleum ether: diethyl ether to afford **6d** (418 mg, 75%) as a colorless liquid.

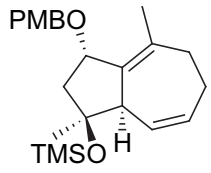
IR (neat): 3361, 2954, 1626, 1430, 1247, 1067, 848 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.80 (m, 1H), 5.53 (d, *J* = 11.5 Hz, 1H), 4.29 (s, 1H), 3.69 (brs, 1H), 2.70-2.56 (m, 1H), 2.49 (d, *J* = 12.7 Hz, 1H), 2.39 (dd, *J* = 15.9 and 7.6 Hz, 1H), 2.27-2.15 (m, 2H), 2.06 (m, 1H), 1.86 (ddt, *J* = 12.7, 7.6 and 2.2 Hz, 1H), 1.67-1.55 (m, 2H), 0.12 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 156.2, 133.6, 133.1, 124.7, 75.1, 50.0, 33.5, 31.0, 29.6, 28.2, –0.3. Anal. Calc'd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.12; H, 10.06.



6e

1-Methyl-8-(trimethylsilyl)-1,2,3,3a,6,7-hexahydroazulene-1,3-diol (**6e**)**:** To a solution of **5e** (600 mg, 2.38 mmol) in dichloromethane (12 mL) was added $CpRu(CH_3CN)_3PF_6$ (5 mol%, 52 mg, 0.118 mmol) at -78°C. The solution was warmed to 15°C over 2.5 h. Without workup, the reaction mixture was chromatographed with 50% of diethylether in petroleum ether to give **6e** (485 mg, 1.92 mmol, 81 % yield) as a white solid.

Mp.: 137 ^{o}C. IR (neat): 3277brm, 2919w, 1390w, 1246w, 1072w, 920w, 838w cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.72-5.60 (m, 1H), 5.55-5.50 (m, 1H), 4.11 (s, br, 1H), 3.77 (s, br, 1H), 2.60-2.30 (m, 3H), 2.30-2.10 (m, 2H), 2.06-1.88 (m, 1H), 1.97 (dd, *J*=13.6, 2.8 Hz, 1H), 1.72 (dd, *J*=13.6, 4.0 Hz, 1H), 1.39 (s, 3H), 0.16 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ:162.7, 138.4, 132.2, 125.8, 79.6, 74.1, 51.0, 49.5, 31.8, 28.5, 27.6, 1.3. Anal. Calc'd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.70; H, 9.44.



6f

[3-(4-Methoxybenzyloxy)-1,4-dimethyl-1,2,3,5,6,8a-hexahydroazulen-1-yloxy]-trimethyl-silane (**6f**): To a solution of **5f** (95 mg, 0.25 mmol) in 1 mL of distilled acetone was added $CpRu(CH_3CN)_3PF_6$ (5.5 mg, 0.0125 mmol) at rt. The solution was stirred for 1.5 h. Without workup, the reaction mixture was purified by flash chromatography eluting with 5% to 20% diethyl ether in petroleum ether to afford **6f** (63 mg, 0.16 mmol, 65%) as a light brown oil.
IR (neat): 2958s, 2829s, 2853m, 1612w, 1514s, 1443w, 1375w, 1302w, 1240s, 1173m, 1143m, 1107s, 1076ss, 1034s, 915w, 840s cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.27 (d, *J*=8.7 Hz, 2H), 6.86 (d, *J*=8.4 Hz, 2H), 5.76 (s, 2H), 4.56 (t, *J*=6.9 Hz, 1H), 4.44 (d, *J*=10.5 Hz, 1H), 4.37 (d, *J*=10.5 Hz, 1H), 3.79 (d, *J*=1.2 Hz, 3H), 3.41 (bs, 1H), 2.37 (m, 2H), 2.24 (dd, *J*=7.2, 12.9 Hz, 1H), 2.02 (m, 2H), 1.73 (s, 3H), 1.68 (m, 1H), 1.38 (s, 3H), 0.10 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.1, 137.5, 135.0, 130.7, 130.2, 129.8, 128.7, 113.7, 80.5, 78.1, 70.3, 55.3, 52.3, 45.80, 33.2, 27.2, 25.4, 21.5, 2.40. HRMS Calc'd for $C_{23}H_{34}O_3Si$ ($M\text{-}CH_3^+$): 386.2277. Found: 386.2260.

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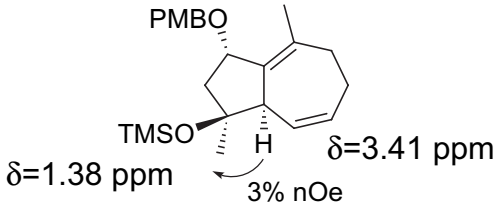
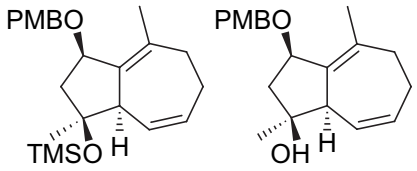


6f

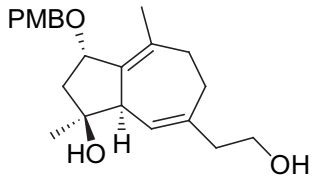


6g **6g'**

3-(4-Methoxy-benzyloxy)-1-4-dimethyl-1,2,3,5,6,8a-hexahydro-azulen-1-yloxy]-trimethyl-silyl ether (**6g**) and **3-(4-methoxy-benzyloxy)-1-4-dimethyl-1,2,3,5,6,8a-hexahydroazulen-1-ol** (**6g'**): To **5g** (440 mg, 1.14 mmol) in 2 mL of distilled acetone was added $CpRu(CH_3CN)_3PF_6$ (25 mg, 0.057 mmol) at rt. The solution was stirred for 1.5 h. After removal of the solvent, the residue was separated by flash chromatography eluting with 5% to 20% diethyl ether in petroleum ether to afford **6g** (144 mg, 0.37 mmol, 33%) and **6g'** (140 mg, 0.45 mmol, 39%) as colorless oils.

For **6g**: IR (neat): 2960m, 2930m, 1613m, 1514s, 1442m, 1375m, 1302m, 1249s, 1173s, 1150m, 1108s, 1074m, 1036s, 889, 840s, 764m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 (d, *J*=8.5 Hz, 2H), 6.90 (d, *J*=8.5 Hz, 2H), 5.89 (m, 1H), 5.63 (m, 1H), 4.53 (d, *J*=11.5 Hz, 1H), 4.41 (m, 1H), 4.35 (d, *J*=11.5 Hz, 1H), 3.82 (s, 3H), 3.55 (m, 1H), 3.31 (s, 1H), 2.58 (m, 1H), 2.40-2.15 (m, 4H), 1.98 (m, 1H), 1.84 (s, 3H), 1.46 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.9, 139.4, 135.3, 131.0, 129.0, 128.7, 128.6, 122.3, 78.0, 69.9, 55.2, 54.3, 52.1, 44.5, 32.9, 28.9, 25.9, 20.7. HRMS Calc'd for $C_{22}H_{31}O_3Si$ ($M\text{-}CH_3^+$): 371.2042. Found: 371.2041.

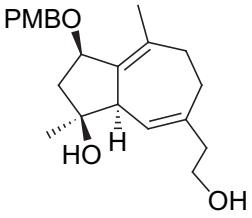
For **6g'**: IR (neat): 3496b, 2959m, 2929m, 1613m, 1586w, 1514s, 1438w, 1303w, 1249s, 1174m, 1116m, 1089m, 1034s, 923w, 825m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 (d, *J*=8.5 Hz, 2H), 6.88 (d, *J*=8.5 Hz, 2H), 5.86 (dd, *J*=1.5, 11.0 Hz, 1H), 5.82 (m, 1H), 4.53 (d, *J*=11.0 Hz, 1H), 4.46 (d, *J*=4.5 Hz, 1H), 4.40 (d, *J*=11.0 Hz, 1H), 3.82 (d, *J*=0.5 Hz, 3H), 3.55 (s, 1H), 3.34 (d, *J*=2.0 Hz, 1H), 2.52 (m, 1H), 2.32 (m, 1H), 2.20 (m, 2H), 2.00 (dd, *J*=6.0, 13.0 Hz, 1H), 1.75 (d, *J*=2.0 Hz, 3H), 1.59 (dd, *J*=4.5, 14.5 Hz, 1H), 1.34 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.2, 138.4, 138.1, 129.9, 129.8, 128.1, 113.7, 94.1, 79.2, 78.6, 69.8, 55.2, 51.5, 43.0, 32.8, 25.9, 24.7, 21.4. HRMS Calc'd for $C_{20}H_{26}O_3$: 314.1882. Found: 314.1880.



6h

7-(2-Hydroxyethyl)-3-(4-methoxybenzyloxy)-1,4-dimethyl-1,2,3,5,6,8a-hexahydroazulen-1-ol (**6h**): To enyne **5h** (220 mg, 0.512 mmol) in 3 mL of distilled acetone under argon at rt was added $CpRu(CH_3CN)_3PF_6$ (22 mg, 0.051 mmol). It was stirred for 2h and chromatographed eluting with 5% diethyl ether in petroleum ether to pure diethyl ether to afford the cycloadduct **6h** (183 mg, 0.461 mmol, 90 %) as a single diastereomer and a colorless oil.

IR (neat): 3407b, 2958s, 2926s, 2856m, 1728s, 1613w, 1514m, 1464m, 1378w, 1282m, 1249s, 1121m, 1073m, 1037m, 861w, 821w, 773w, 741w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.29 (d, *J*=9.0 Hz, 2H), 6.88 (d, *J*=9.0 Hz, 2H), 5.52 (s, 1H), 4.46 (t, *J*=7.0 Hz, 1H), 4.46 (d, *J*=11.0 Hz, 1H), 4.39 (d, *J*=11.0 Hz, 1H), 3.82 (s, 3H), 3.86 (m, 2H), 3.50 (m, 1H), 2.47 (t, *J*=11.5 Hz, 1H), 2.35 (m, 4H), 2.08 (m, 2H), 1.78 (d, *J*=2.0 Hz, 3H), 1.72 (dd, *J*=8.0, 13.0 Hz, 1H), 1.46 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.2, 141.1, 136.9, 130.4, 129.8, 125.5, 124.3, 113.7, 78.5, 70.4, 60.1, 55.3, 51.1, 45.8, 42.6, 33.1, 30.3, 29.5, 25.7, 22.0. HRMS Calc'd for $C_{22}H_{30}O_4$ (M^+): 358.2144. Found: 358.2143.



6i

7-(2-Hydroxyethyl)-3-(4-methoxybenzyloxy)-1,4-dimethyl-1,2,3,5,6,8a-hexahydroazulen-1-ol (**6i**): To enyne **5i** (140 mg, 0.33 mmol) in 2.5 mL of acetone was added $CpRu(CH_3CN)_3PF_6$ (7 mg, 0.016 mmol) at rt. The reaction mixture was stirred for 5 h and chromatographed eluting

with 5% to 50% ethyl acetate in petroleum ether to afford cycloadduct **6i** (81 mg, 0.23 mmol, 70%) as a single diastereomer and as a colorless oil.

IR (neat): 3430b, 2929s, 1612m, 1514s, 1440m, 1372m, 1304m, 1250s, 1175m, 1096m, 1034s, 924w, 846m, 824m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J*=9.0 Hz, 2H), 6.76 (d, *J*=8.4 Hz, 2H), 5.63 (s, 1H), 4.43 (d, *J*=10.8 Hz, 1H), 4.33 (d, *J*=4.8 Hz, 1H), 4.24 (d, *J*=10.8 Hz, 1H), 3.69 (s, 3H), 3.53 (t, *J*=6.0 Hz, 2H), 3.14 (bs, 1H), 2.35 (s, 1H), 2.17 (m, 6H), 1.94 (m, 4H), 1.54 (d, *J*=2.l Hz, 3H), 1.46 (dd, *J*=4.8, 14.1 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.2, 137.6, 137.4, 137.0, 129.9, 129.5, 125.7, 113.6, 79.9, 79.3, 70.0, 59.9, 55.0, 51.0, 42.4, 42.0, 32.1, 29.5, 24.5, 21.3. HRMS Calc'd for $C_{22}H_{28}O_3$ ($M-H_2O^+$): 340.2038. Found: 340.2036.

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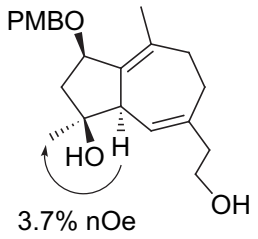
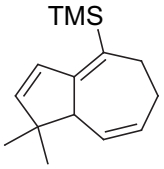


6i



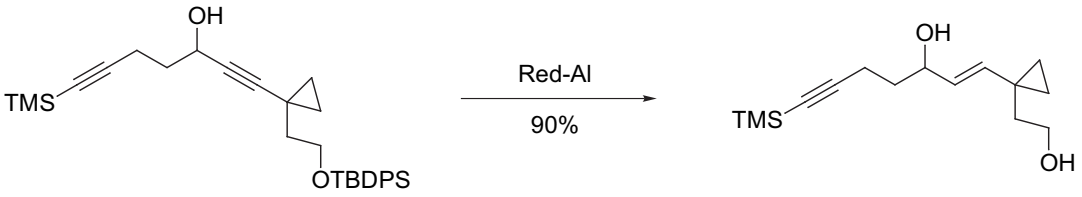
6j

(1,1-Dimethyl-1,5,6,8a-tetrahydroazulen-4-yl)-trimethylsilane (**6j**): To enyne **5j** (124 mg, 0.50 mmol) in 5 mL of degassed anhydrous acetone was added $CpRu(CH_3CN)_3PF_6$ (22 mg, 0.05 mmol) at rt. The reaction mixture was stirred for 2 h and concentrated *in vacuo.* The residue was chromatographed eluting with 10% ethyl acetate in petroleum ether to afford cycloadduct **6j** (44 mg, 0.19 mmol, 38%, 89% brsm) as a colorless oil and recovered starting material (71 mg, 0.25 mmol, 57%).

IR (neat): 3015, 2926, 2852, 1466, 1448, 892, 751, 701 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.42 (d, *J*=5.7 Hz, 1H), 5.84 (d, *J*=5.7 Hz, 1H), 5.75 (m, 1H), 5.58 (m, 1H), 3.59 (m, 1H), 2.70

(m, 1H), 2.34-2.16 (m, 3H), 1.06 (s, 3H), 1.00 (s, 3H), 0.25 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.7, 130.5, 130.2, 127.7, 127.5, 127.3, 53.4, 47.7, 30.7, 29.3, 28.7, 25.6, 0.42. HRMS Calc'd for $C_{15}H_{24}Si$ (M^+): 232.4401. Found: 232.4336.

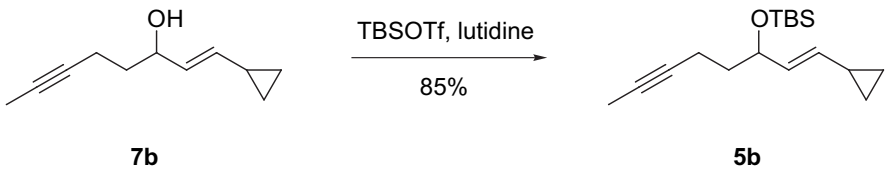
Synthesis of the starting materials:



7a **5a**

1-[(1*E*)-3-hydroxy-7-(trimethylsilyl)-1-hepten-6-ynyl]-cyclopropaneethanol (5a): To a solution of **7a** (42 mg, 0.084 mmol) in THF (3 ml) was added Red-Al (65 mg, 0.21 mmol, 65% in toluene) at 0^{o}C. The reaction mixture was warmed to rt and stirred for 2h. It was quenched by the addition of an aqueous solution of Rochelle's salt (1 ml) and chromatographed directly on silica gel eluting with 5% diethyl ether in petroleum ether to diethyl ether to afford **5a** (20 mg, 0.075 mmol, 90%) as a colorless oil.

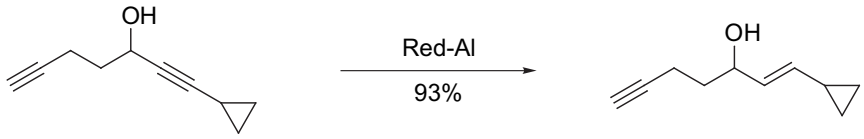
IR (neat): 3363bm, 3078w, 2927s, 2174m, 1664w, 1427w, 1250m, 1052m, 843s cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.60-5.35 (m, 2H), 4.25-4.15 (m, 1H), 3.80-3.68 (m, 2H), 2.36-2.21 (m, 2H), 1.80-1.60 (m, 5H), 1.33-1.15 (m, 3H), 0.68-0.54 (m, 4H), 0.14 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.0, 129.0, 106.7, 85.2, 72.0, 61.4, 39.1, 35.8, 29.7, 18.9, 16.2, 13.8, 0.1.



7b **5b**

8-Cyclopropyl-6-(*tert*-butyldimethylsilyloxy)-oct-(7*E*)-en-2-yn (5b): To a solution of alcohol **7b** (50 mg, 0.305 mmol) in dichloromethane (3 ml) at 0°C was added 2,6-lutidine (0.12 ml, 1.03 mmol) followed by *tert.*-butyldimethylsilyl triflate (0.12 ml, 0.523 mmol). After 4h at 0°C diethyl ether (25 ml) was added and the solution was washed with 1M aqueous $NaHSO_4$ solution (2 x 25 ml), brine (25 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatrography eluting with 6:1 petroleum ether/diethyl ether afforded alcohol **5b** (72 mg, 0.259 mmol, 85%) as a colorless oil.

IR (neat): 2955, 2928, 2857, 1667, 1472, 1361, 1254, 1085, 1054, 962, 836, 776 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.46 (dd, *J*=15.4, 6.8 Hz, 1H), 5.13 (dd, *J*=15.4, 8.6 Hz, 1H), 4.16 (q, *J*=6.8 Hz, 1H), 2.18 (m, 2H), 1.79 (t, *J*=2.6 Hz, 3H), 1.70-1.57 (m, 2H), 1.37 (m, 1H), 0.90 (s, 9H), 0.70 (m, 2H), 0.36 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 134.4, 130.5, 79.1, 75.5, 72.1, 37.6, 18.2, 14.8, 13.2, 6.5, 6.4, 3.5, -4.2, -4.9. Anal. Calc'd for $C_{17}H_{30}OSi$: C, 73.31; H, 10.86. Found: C, 72.98; H, 10.75.

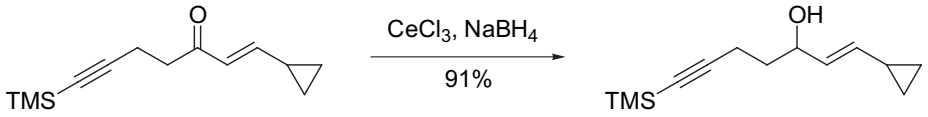


7c **5c**

7-Cyclopropyl-hept-(6*E*)-en-1-yn-5-ol (5c): To a solution of propargyl alcohol **7c** (500 mg, 3.37 mmol) in THF (20 ml) at –78°C was slowly added Red-Al (2.0 ml, 6.74 mmol, 65% in toluene) and the solution allowed to warm to rt. After an additional 10h, the yellow solution was quenched with 1M HCl (100 ml) and extracted with diethyl ether (3 x 100 ml). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting

with 1:1 petroleum ether/diethyl ether afforded **5c** (470 mg, 3.13 mmol, 93%) as a colorless liquid.

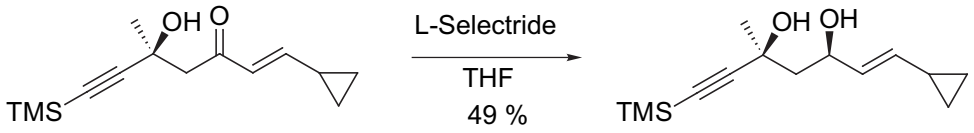
IR (neat): 3375, 3303, 3062, 3006, 2925, 2868, 2117, 1666, 1430, 1100, 1049, 1021, 964, 940, 813 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.54 (dd, *J*=15.3, 7.1 Hz, 1H), 5.22 (dd, *J*=15.3, 8.8 Hz, 1H), 4.16 (q, *J*=7.1 Hz, 1H), 2.36-2.22 (m, 2H), 1.97 (t, *J*=2.7 Hz, 1H), 1.82-1.67 (m, 3H), 1.39 (m, 1H), 0.73 (m, 2H), 0.38 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.5, 129.5, 84.0, 71.6, 35.6, 14.7, 13.4, 6.8, 6.7. Anal. Calc'd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.14; H, 9.16.



7d **5d**

7-Cyclopropyl-1-trimethylsilyl-hept-(6*E*)-en-1-yn-5-ol (5d): To a solution of ketone **7d** (200 mg, 0.909 mmol) and cerium trichloride (340 mg, 0.959 mmol) in methanol (10 ml) at 0°C was slowly added $NaBH_4$ (360 mg, 0.952 mmol). After 1h at 0°C dichloromethane (50 ml) was added and the white suspension filtered through a pad of silica. The filtrate was washed with 1M $NaHSO_4$ (2 x 25 ml), brine (25 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 9:1 petroleum ether/diethyl ether afforded alcohol **5d** (176 mg, 0.791 mmol, 87%) as a colorless liquid.

IR (neat): 3356, 2958, 2174, 1250, 963, 843 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.53 (dd, *J*=15.4, 7.1 Hz, 1H), 5.19 (dd, *J*=15.4, 8.8 Hz, 1H), 4.16 (m, 1H), 2.31 (m, 2H), 1.78-1.65 (m, 3H), 1.37 (dtt, *J*=8.8, 8.1, 4.9 Hz, 1H), 0.71 (m, 2H), 0.36 (m, 2H), 0.14 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.3, 129.6, 106.9, 85.1, 71.9, 35.8, 16.3, 13.4, 6.8, 0.1. Anal. Calc'd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.37; H, 10.05.

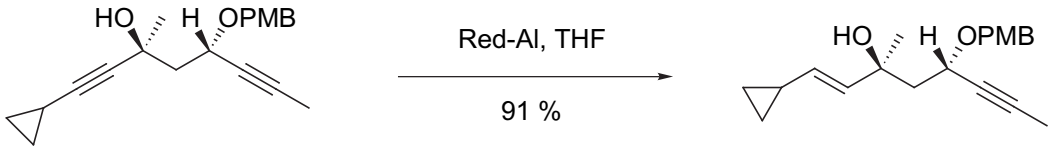


7e **5e**

(1*E*)-1-Cyclopropyl-5-methyl-7-(trimethylsilyl)-1-hepten-6-yne-3,5-diol (5e): To a solution of **7e** (3.01 g, 12.0 mmol) in THF (60 mL) was added dropwise L-Selectride (1M in THF, 15.6 mL, 15.6 mmol) at –100 °C. After stirring for 30 min H_2O_2 (30%, 6 mL) was added and the reaction mixture warmed to room temperature and stirred for 1 h. The aqueous phase was extracted with diethylether (3 x 50 mL). The combined organic phases were washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 33% to 50% diethyl ether in petroleum ether to afford diol **5e** (1.49 g, 5.90 mmol, 49%, dr: 4:1) as a colorless oil, which slowly crystallized.

Mp.: < 30 °C. IR (neat): 3360bm, 2960w, 2169w, 1668w, 1411w, 1251m, 961m, 843s, 760m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.59 (dd, *J*=7.0, 15.3 Hz, 1H), 5.22 (dd, *J*=8.9, 14.9 Hz, 1H), 4.48 (t, *J*=6.4 Hz, 1H), 3.12 (s, 1H), 2.93 (s, 1H), 2.02 (dd, *J*=9.2, 14.4 Hz, 1H), 1.83 (dd, *J*=3.4, 14.4 Hz, 1H), 1.54 (s, 3H), 1.35 (m, 1H), 0.70 (m, 2H), 0.35 (m, 2H), 0.15 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.1, 129.6, 109.6, 88.0, 70.0, 67.2, 48.9, 29.6, 13.3, 6.7, -0.2.

Anal. Calc'd for $C_{14}H_{24}O_2Si$: Calc'd C, 66.61; H, 9.58, Found: C, 66.87; H, 9.42.

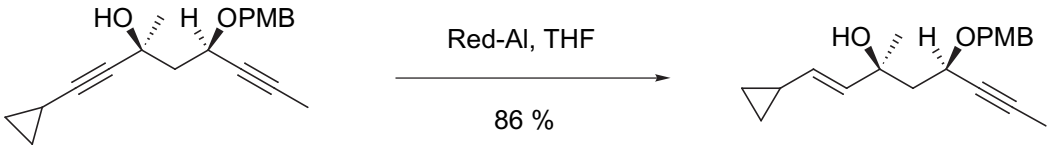


7f **8f**

1-Cyclopropyl-5-(4-methoxybenzyloxy)-3-methylocta-1-en-6-yn-3-ol (**8f**): To a solution of alcohol **7f** (1.46 g, 4.68 mmol) in THF (10 mL) at 0°C was added Red-Al (3.64 g, 3.51 mL, 11.7

mmol, 65% in toluene). The reaction mixture was warmed to rt over 3 h. The reaction mixture was quenched at 0°C with a saturated aqueous solution of Rochelle's salt (10 mL). The aqueous phase was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 5% to 30% diethyl ether in petroleum ether to afford allylic alcohol **8f** (1.35g, 4.30 mmol, 91%) as a pale yellow oil.

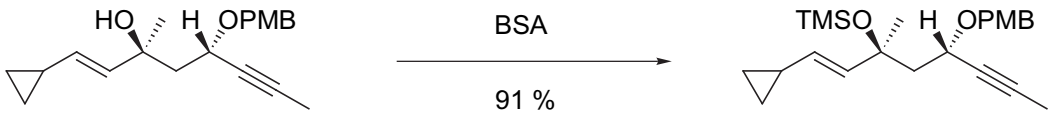
IR (neat): 3501bs, 3080w, 3003m, 2969s, 2921s, 2867m, 2231w, 1666w, 1613s, 1514s, 1456m, 1443m, 1423w, 1398m, 1367m, 1330m, 1302s, 1250s, 1174s, 1140m, 1090s, 1034s, 968m, 935w, 821s, 758w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.28 (dd, *J*=2.5, 8.0 Hz, 2H), 6.89 (dd, *J*=2.0, 7.5Hz, 2H), 5.45 (d, *J*=15.5 Hz, 1H), 5.16 (dd, *J*=4.0, 15.5 Hz, 1H), 4.72 (d, *J*=11.0 Hz, 1H), 4.37 (d, *J*=11.0 Hz, 1H), 4.31 (dt, *J*=2.0, 11.0 Hz, 1H), 3.99 (s, 1H), 3.81 (d, J=2.0 Hz, 3H), 2.13 (dd, *J*=10. 5, 15.0 Hz, 1H), 1.90 (t, *J*=1.5 Hz, 3H), 1.81 (dd, *J*=2.5, 14.5 Hz, 1H), 1.35 (m, 1H), 1.19 (d, *J*=2.5 Hz, 3H), 1.35 (m, 1H), 0.68 (m, 2H), 0.32 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.3, 132.9, 132.4, 129.8, 129.1, 113.7, 82.2, 77.5, 72.3, 70.2, 67.0, 55.1, 47.0, 29.6, 13.2, 6.61, 6.56, 3.46. HRMS: Calc'd for $C_{20}H_{26}O_3$: 314.1882. Found: 314.1885.



9f **10f**

1-Cyclopropyl-5-(4-methoxybenzyloxy)-3-methylocta-1-en-6-yn-3-ol (**10f**): To a solution of alcohol **9f** (0.62 g, 4.68 mmol) in THF (5 mL) at 0°C was added Red-Al (1.68 g, 1.62 mL, 4.98 mmol, 65% in toluene). The reaction mixture was warmed to rt over 3h. The reaction mixture was quenched at 0°C with a saturated aqueous solution of Rochelle's salt (10 mL). The aqueous phase was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 5% to 30% diethyl ether in petroleum ether to afford allylic alcohol **10f** (0.54 g, 1.71 mmol, 86%) as a pale yellow oil.

IR (neat): 3508b, 3078w, 3006w, 2961w, 2921m, 2861w, 2361m, 1665w, 1612m, 1586w, 1514s, 1462m, 1302m, 1249s, 1175s, 1070s, 1035s, 965s, 822m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, *J*=3.0, 11.0 Hz, 2H), 6.89 (dd, *J*=2.0 Hz, 8.5 Hz, 2H), 5.57 (d, *J*=15.5 Hz, 1H), 5.17 (dd, *J*=8.5, 15.0 Hz, 1H), 4.74 (d, *J*=11.0 Hz, 1H), 4.44 (d, *J*=11.5 Hz, 1H), 4.33 (m, 1H), 3.82 (s, 3H), 2.07 (dd, *J*=4.0, 15.0 Hz, 1H), 1.92 (d, *J*=2.0 Hz, 3H), 1.88 (dd, *J*=4.5, 14.5 Hz, 1H), 1.37 (m, 1H), 1.20 (s, 3H), 0.70 (m, 2H), 0.37 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.3, 134.3, 131.5, 129.9, 129.3, 113.8, 82.8, 77.8, 71.6, 70.1, 66.1, 55.2, 47.2, 27.4, 13.4, 6.62, 3.59, -11.8. HRMS: Calc'd for $C_{20}H_{26}O_3$: 314.1882. Found: 314.1882.

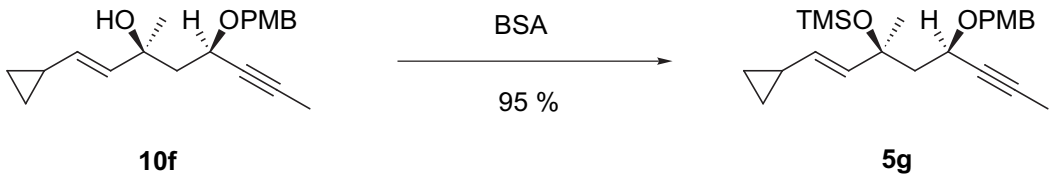


8f **5f**

[1-(2-Cyclopropylvinyl)-3-(4-methoxybenzyloxy)-1-methylhex-4-ynyl-oxy]-trimethylsilane (**5f**): To alcohol **8f** (1.35 g, 4.30 mmol) was added BSA (3.5 mL, 2.88 g, 14.2 mmol, freshly distilled) at rt. The initial reaction was exothermic but no cooling bath is required. The reaction mixture was stirred at rt for 24 h at which time the reaction was complete. To the reaction mixture in an ice bath was added a slurry of silica gel in petroleum ether to quench the BSA (otherwise during loading a lot of heat was generated). The whole mixture was then separated by flash chromatography eluting with pure petroleum ether and then 5% diethyl ether in petroleum ether to afford the TMS-ether **5f** (1.51g, 3.9 mmol, 91%).

IR (neat) : 2957s, 2863m, 1613m, 1587m, 1514s, 1466m ,1302m, 1249s, 1173m, 1101s, 1039s, 967w, 841s, 755w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, *J*=2.5, 9.0 Hz, 2H), 6.89 (d, *J*=8.0 Hz, 2H), 5.60 (d, *J*=15.5 Hz, 1H), 5.07 (dd, *J*=8.5, 15.0 Hz, 1H), 4.69 (d, *J*=11.0 Hz, 1H), 4.41 (d, *J*=11.5 Hz, 1H), 4.24 (m, 1H), 3.82 (s, 3H), 1.98 (d, *J*=5.5 Hz, 2H), 1.90 (d, *J*=1.5 Hz, 3H), 1.33 (s, 3H), 0.69 (m, 2H), 0.90 (m, 1H), 0.35 (m, 2H), 0.08 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 150.0, 135.1, 131.3, 130.4, 129.6, 113.6, 79.5, 74.1, 69.8, 65.6, 55.2, 50.1, 27.6, 13.3,

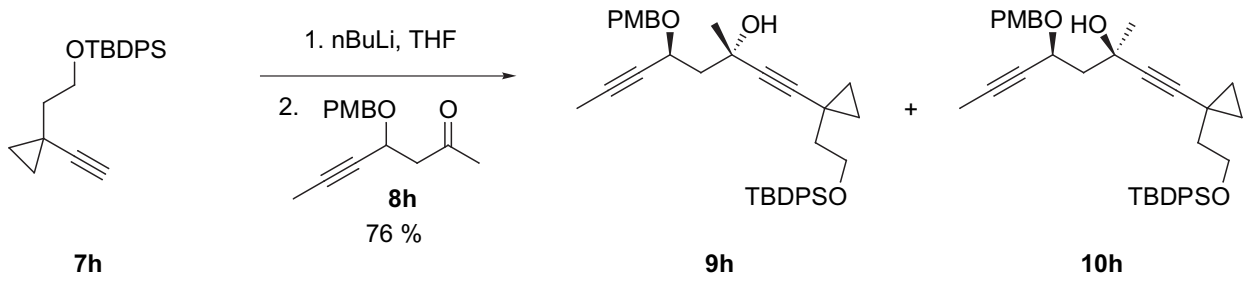
6.41, 6.37, 3.56, 2.51, 1.80. HRMS: Calc'd for $C_{22}H_{31}O_3Si$ (M-CH_3^+): 371.2042. Found: 371.2045.



10f **5g**

[1-(2-Cyclopropylvinyl)-3-(4-methoxybenzyloxy)-1-methylhex-4-ynyloxy]-trimethylsilane (**5g**): To alcohol **10f** (0.54 g, 1.71 mmol) was added BSA (1.0 mL, freshly distilled) at rt. The reaction mixture was stirred at rt for 24 h. To the reaction mixture, cooled in an ice bath, was added a slurry of silica gel in petroleum ether to quench the BSA (otherwise during loading a lot of heat was generated). The whole mixture was then separated by flash chromatography eluting with pure petroleum ether and then 5% diethyl ether in petroleum ether to afford the TMS ether **5g** as a colorless oil (0.63 g, 1.63 mmol, 95%).

IR (neat): 3082w, 2956s, 2865m, 1684w, 1613m, 1586w, 1514s, 1458m, 1302m, 1249s, 1173m, 1094s, 1039s, 966m, 840s, 755m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.32 (d, *J*=8.5 Hz, 2H), 6.88 (d, *J*=8.5 Hz, 2H), 5.58 (d, *J*=16.0 Hz, 1H), 5.03 (dd, *J*=8.5, 15.0 Hz, 1H), 4.67 (d, *J*=11.0 Hz, 1H), 4.38 (d, *J*=11.0 Hz, 1H), 4.18 (m, 1H), 3.82 (s, 3H), 2.03 (dd, *J*=6.5, 13.0 Hz, 1H), 1.98 (dd, *J*=4.5, 13.0 Hz, 1H), 1.89 (d, *J*=2.0 Hz, 3H), 1.35 (m, 1H), 1.34 (s, 3H), 0.70 (s, 2H), 0.33 (s, 2H), 0.097 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.0, 134.5, 131.5, 130.4, 129.6, 113.6, 81.1, 79.5, 74.4, 69.7, 65.6, 55.2, 50.4, 28.2, 13.4, 6.47, 6.44, 3.64, 2.50. HRMS: Calc'd for $C_{22}H_{31}O_3Si$ (M-CH_3^+): 371.2042. Found: 371.2043.



7h **9h** **10h**

1-{1-[2-(*tert*-Butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol (**9h**) and **1-{1-[2-(*tert*-Butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxybenzyloxy)-3-methylocta-1,6-diyn-3-ol** (**10h**): To alkyne **7h** (1.20 g, 3.45 mmol) in 20 mL of distilled THF was added *n*-butyllithium (2.4 mL, 3.78 mmol, 1.6M in hexanes) at –78°C. After 30 min, to this dark brown solution was added ketone **8h** (851 mg, 3.46 mmol) in 10 mL of distilled THF at –78°C very slowly within 5 min. The reaction mixture was warmed to rt overnight. The mixture was then quenched with 10 mL of water. The aqueous layer was extracted with diethyl ether (3 x 50 m). The combined organic layers were concentrated *in vacuo* and submitted to silica gel chromatography eluting with 5% to 15% diethyl ether in petroleum ether to afford two diastereomers **9h** and **10h (**1.55 g, 2.61 mmol, 76%, 2.3:1) as yellow oils.

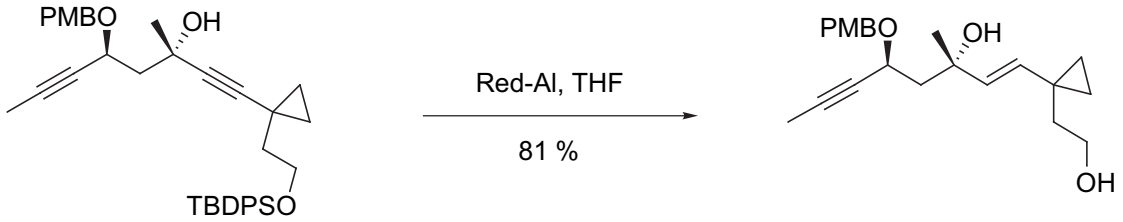
Major isomer **9h** (less polar):

IR (neat): 3501b, 3072m, 3049m, 2932s, 2858s, 2228w, 2065w, 1960w, 1889w, 1829w, 1774w, 1613s, 1588m, 1515s, 1472m, 1428s, 1393m, 1335m, 1303m, 1251s, 1210w, 1174s, 1159s, 1111s, 1030s, 959w, 935w, 911w, 823s, 738s, 703s cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.70 (m, 4H), 7.40 (m, 6H), 7.24 (d, *J*=8.7 Hz, 2H), 6.84 (d, *J*=8.7 Hz, 2H), 4.70 (d, *J*=9.0 Hz, 1H), 4.60 (dm, *J*=10.5 Hz, 1H), 4.37 (s, 1H), 4.34 (d, *J*=8.7 Hz, 1H), 3.86 (t, *J*=7.2 Hz, 2H), 3.77 (s, 3H), 2.10 (dd, *J*=11.4, 14.7 Hz, 1H), 1.90 (d, *J*=2.1 Hz, 3H), 1.84 (dd, *J*=2.1, 13.4 Hz, 1H), 1.60 (m, 2H), 1.34 (s, 3H), 1.07 (s, 9H), 0.74 (m, 2H), 0.59 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.4, 135.5, 133.9, 129.8, 129.5, 129.2, 127.6, 113.8, 88.2, 82.4, 79.1, 77.3, 70.7, 68.2, 67.3, 62.7, 55.2, 48.2, 40.6, 30.6, 26.8, 22.6, 19.1, 15.1, 15.0, 8.66, 3.56. HRMS: Calc'd for $C_{34}H_{37}O_4Si$ (M-$C_4H_9^+$): 537.2461. Found: 537.2462.

Minor isomer **10h** (more polar):

IR (neat): 3503b, 3071m, 3049m, 2931s, 2857s, 2333m, 2066w, 1960w, 1890w, 1774w, 1718w, 1612s, 1588m, 1513s, 1472s, 1428s, 1389s, 1362s, 1302s, 1248s, 1209s, 1173s, 1109s, 1036s, 958s, 911s, 823s, 738s, 703s cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.70 (m, 4H), 7.40 (m, 6H),

7.26 (d, *J*=8.7 Hz, 2H), 6.86 (d, *J*=8.7 Hz, 2H), 4.70 (d, *J*=11.4 Hz, 1H), 4.40 (d, *J*=11.4 Hz, 1H), 4.32 (m, 1H), 3.87 (t, *J*=7.2 Hz, 2H), 3.79 (s, 3H), 3.38 (s, 1H), 2.16 (dd, *J*=7.5, 14.4 Hz, 1H), 1.88 (d, *J*=2.1 Hz, 3H), 1.67 (m, 1H), 1.59 (t, *J*=6.9 Hz, 2H), 1.35 (s, 3H), 1.07 (s, 9H), 0.77 (m, 2H), 0.59 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.3, 135.5, 133.9, 129.7, 129.5, 127.9, 127.6, 113.7, 87.8, 83.6, 79.7, 77.9, 69.8, 66.5, 65.9, 62.6, 55.2, 48.2, 40.5, 30.0, 26.8, 19.1, 15.0, 14.9, 8.63, 3.58; HRMS: Calc'd for $C_{34}H_{37}O_4Si$ (M-$C_4H_9^+$): 537.2461. Found: 537.2462.

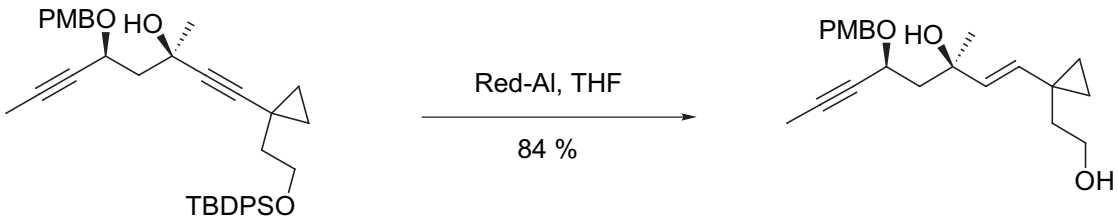


9h **11h**

1-[1-(2-Hydroxyethyl)-cyclopropyl]-5-(4-methxoybenzyloxy)-3-methyloct-1-en-6-yn-3-ol (**11h**): To alkynyl alcohol **9h** (805 mg, 1.36 mmol) in 5 mL of distilled THF was added Red-Al (1.26 g, 1.22 mL, 4.01 mmol, 65% wt in toluene) at –78^{o}C. The reaction mixture was stirred for 30 min and then warmed to 0^{o}C and stirred at this temperature for 2 h. The solution was then warmed to rt and stirred for 1 h. A very polar spot was identified relative to the starting material. The reaction mixture was cooled to -78^{o}C and quenched with water (0.3 mL). After warming to rt, the reaction mixture was directly filtered through a short silica gel column eluting with diethyl ether. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 5% diethyl ether in petroleum ether to pure diethyl ether afforded diol **11h** as a colorless oil (394 mg, 1.10 mmol, 81%).

IR (neat): 3446b, 3076m, 2923s, 2868s, 2230w, 2060w, 1661w, 1614s, 1586m, 1516s, 1456s, 1424s, 1398s, 1370s, 1330s, 1303s, 1250s, 1174s, 1094s, 1030s, 979s, 822s, 758m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.21 (d, *J*=8.5 Hz, 2H), 6.84 (d, *J*=8.5 Hz, 2H), 5.37 (d, *J*=15.5 Hz, 1H), 5.26 (d, *J*=15.5 Hz, 1H), 4.65 (d, *J*=11.5 Hz, 1H), 4.30 (d, *J*=11.5 Hz, 1H), 4.15 (dd, *J*=2.0, 9.0 Hz, 1H), 4.01 (s, 1H), 3.76 (d, *J*=0.5 Hz, 3H), 3.58 (t, *J*=7.5 Hz, 2H), 3.46 (s, 1H), 2.09 (dd,

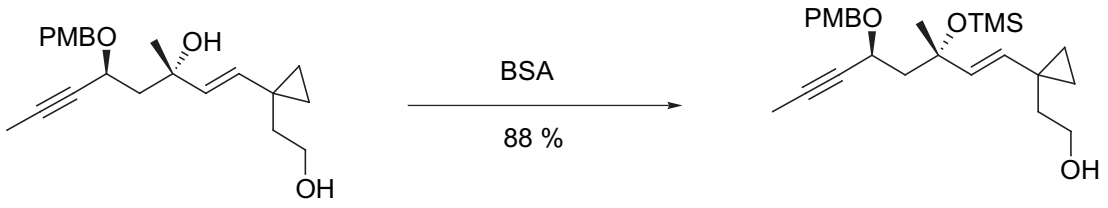
J=11.0, 15.0 Hz, 2H), 1.84 (s, 3H), 1.75 (dd, *J*=2.5, 15.0 Hz, 1H), 1.64 (m, 1H), 1.55 (m, 1H), 1.15 (s, 3H), 0.51 (m, 4H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 159.4, 133.3, 132.4, 129.9, 129.1, 113.8, 82.4, 76.3, 72.4, 70.1, 66.8, 61.0, 55.1, 47.0, 39.1, 29.6, 18.4, 13.7, 13.3, 3.31. HRMS: Calc'd for $C_{22}H_{28}O_3$ (M-H_2O^+): 340.2038. Found: 340.2040.



10h **12h**

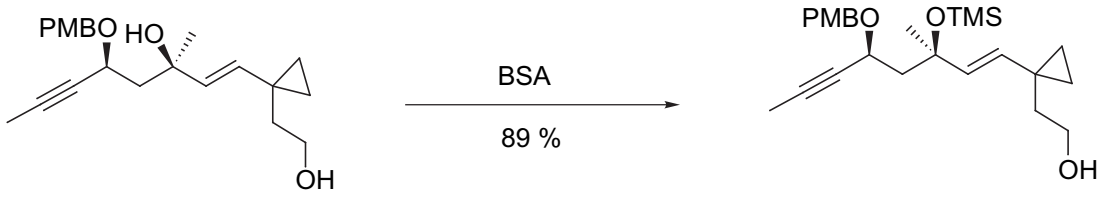
1-[1-(2-Hydroxyethyl)-cyclopropyl]-5-(4-methoxybenzyloxy)-3-methyloct-1-en-6-yn-3-ol (**12h**): To alkynyl alcohol **10h** (570 mg, 0.96 mmol) in 5 mL of distilled THF was added Red-Al (597 mg, 0.58 mL, 1.92 mmol, 65%wt in toluene) slowly at 0^{o}C. The mixture was stirred for 1.5h at 0^{o}C and then warmed to rt. At rt the mixture was stirred for another 0.5 h. Without workup, the reaction mixture was directly purified by flash chromatography eluting with 5% diethyl ether in petroleum ether to 50% ethyl acetate in petroleum ether to afford diol **12h** (289 mg, 0.807 mmol, 84%) as a colorless oil.

IR (neat): 3440b, 3070m, 2923s, 2863s, 2059w, 1660w, 1613s, 1586m, 1514s, 1470m, 1445m, 1425m, 1372m, 1332m, 1303m, 1249s, 1175s, 1149m, 1067s, 1034s, 975s, 823s cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, *J*=4.5, 7.0 Hz, 2H), 6.87 (dd, *J*=4.5, 7.0 Hz, 2H), 5.46 (m, 2H), 4.72 (d, *J*=11.5 Hz, 1H), 4.41 (d, *J*=11.5 Hz, 1H), 4.27 (m, 1H), 3.80 (s, 3H), 3.69 (m, 3H), 2.02 (dd, *J*=9.0, 14.0 Hz, 1H), 1.89 (d, *J*=2.0 Hz, 3H), 1.84 (m, 1H), 1.65 (m, 2H), 1.16 (s, 3H), 0.54 (s, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.2, 133.6, 132.1, 129.9, 129.4, 129.1, 127.3, 113.7, 82.9, 78.5, 71.7, 69.9, 65.9, 61.1, 55.1, 47.1, 39.2, 27.4, 18.6, 13.50, 13.45, 3.48. Anal. Calc'd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.64; H, 8.50. MS (LRCI) for $C_{22}H_{31}O_4$ [M+1]$^+$: 359.2.



11h **5h**

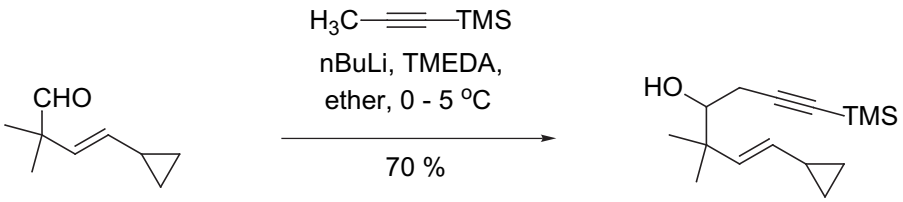
2-{1-[5-(4-Methoxybenzyloxy)-3-methyl-3-trimethylsilyloxyoct-1-en-6-ynyl]-cyclopropyl}-ethanol (**5h**): To diol **11h** (3.50 g, 9.78 mmol) in 20 mL of distilled dichloromethane was slowly added BSA (1.99 g, 2.41 mL, 9.78 mmol) at rt. The reaction mixture was stirred overnight before another 0.5 eq of BSA (1.00 g, 1.20 mL, 4.89 mmol) was slowly added. The reaction mixture was stirred for another 24 h. The solution was concentrated *in vacuo* and chromatographed eluting with 3% to 30% diethyl ether in petroleum ether to afford mono silylether **5h** (3.70 g, 8.60 mmol, 88%) as a pale yellow oil and less than 20 mg of starting material and bis silylether. IR (neat): 3508s, 3077w, 2999s, 2956s, 2868s, 2229w, 1659w, 1613s, 1586m, 1514s, 1465m, 1424m, 1397m, 1368m, 1330m, 1302s, 1250s, 1174s, 1091s, 1037s, 978m, 867s, 841s, 757m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J*=8.5 Hz, 2H), 6.88 (d, *J*=8.5 Hz, 2H), 5.36 (d, *J*=15.5 Hz, 1H), 5.29 (d, *J*=15.5 Hz, 1H), 4.70 (d, *J*=11.0 Hz, 1H), 4.34 (d, *J*=11.0 Hz, 1H), 4.23 (dt, *J*=2.0, 10.5Hz, 1H), 3.98 (s, 1H), 3.81 (d, *J*=0.5 Hz, 3H), 3.61 (t, *J*=8.0 Hz, 2H), 2.14 (dd, *J*=11.0, 15.0 Hz, 1H), 1.80 (dd, *J*=2.5, 14.5 Hz, 1H), 1.72 (dt, *J*=8.0, 14.0 Hz, 1H), 1.60 (dt, *J*=7.5, 14.0 Hz, 1H), 1.20 (s, 3H), 0.56 (m, 2H), 0.46 (m, 2H), 0.11 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.4, 133.6, 132.1, 129.9, 129.1, 113.8, 82.4, 77.4, 72.5, 70.2, 67.0, 60.8, 55.1, 47.1, 39.2, 29.8, 18.4, 14.2, 13.7, 3.48, -0.55. HRMS: Calc'd for $C_{25}H_{36}O_3Si$ (M-H_2O^+): 412.2434. Found: 412.2437.



12h **5i**

2-{1-[5-(4-Methoxybenzyloxy)-3-methyl-3-trimethylsilyloxyoct-1-en-6-ynyl]cyclopropyl}-ethanol (**5i**): To diol **12h** (320 mg, 0.89 mmol) in 0.5 mL of dichloromethane was added BSA (5 mL) at rt. The mixture was stirred at rt for 4 h. Without workup, the mixture was directly chromatographed eluting with 5% to 20% diethyl ether in petroleum ether to afford alcohol **5i** (340 mg, 0.79 mmol, 89%) as a colorless oil.

IR (neat): 3515b, 3076w, 2957s, 2867m, 1613m, 1586w, 1514s, 1461m, 1391w, 1302m, 1250s, 1176m, 1092s, 1038m, 974m, 842s, 755m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J*=8.7 Hz, 2H), 6.74 (d, *J*=8.7 Hz, 2H), 5.26 (s, 2H), 4.60 (d, *J*=11.1 Hz, 1H), 4.28 (d, *J*=11.1 Hz, 1H), 4.16 (m, 1H), 3.67 (s, 3H), 3.52 (t, *J*=7.5 Hz, 2H), 3.12 (bs, 1H), 1.91 (dd, *J*=15.0 Hz, 1H), 1.76 (s, 3H), 1.73 (dd, *J*=4.2, 15.0 Hz, 1H), 1.54 (m, 2H), 1.05 (s, 3H), 0.73 (m, 2H), 0.41 (d, *J*=5.1 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.3, 133.2, 132.4, 129.9, 129.2, 113.7, 82.9, 77.7, 71.7, 70.0, 66.0, 65.8, 55.2, 47.1, 39.3, 27.5, 18.4, 14.1, 11.3, 3.43, -0.59. HRMS: Calc'd for $C_{24}H_{35}O_4Si$ ($M\text{-}Me^+$): 415.2305. Found: 415.2304.



7j **5j**

(1*E*)-1-Cyclopropyl-3,3-dimethyl-7-trimethylsilanylhept-1-en-6-yn-4-ol (5j):

To a solution of 1-Trimethylsilyl-1-propyne (225 mg, 2.00 mmol) and *N,N,N',N'*-

Tetramethylethylenediamine (186 mg, 1.60 mmol) in 10 ml of anhydrous ether was added at 0 – 5°C a 2.2 M solution of *n*-butyllithium in hexane (0.73 ml, 1.60 mmol) dropwise. After complete addition the yellow-orange reaction mixture was stirred for 20 min. To this solution of TMS-propargyllithium was added (3*E*)-4-Cyclopropyl-2,2-dimethyl-but-3-enal **7j** (138 mg, 1.00 mmol) in 2 ml of anhydrous ether. Stirring was continued for 1 h under cooling with an ice bath. Half saturated aqueous NH_4Cl solution (20 ml) was added and the phases were separated. The aqueous phase was extracted with ether (2 x 10ml). The combined organic phases were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (SiO_2, ether/petrol ether 1:20) to yield alcohol **5j** (175 mg, 0.70 mmol, 70 %) as a colorless oil.
IR (neat): 3349, 2933, 2174, 1379, 1249, 1051, 842 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.50 (d, *J* = 15.6 Hz, 1H), 4.91 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.47–3.42 (m, 1H), 2.26 (dd, *J* = 17.1 Hz, 3.0 Hz, 1H), 2.13 (dd, *J* = 17.1 Hz, 9.3 Hz, 1H), 1.39–1.31 (m, 1H), 1.00 (s, 3H), 0.98 (s, 3H), 0.71–0.64 (m, 2H), 0.35–0.27 (m, 2H), 0.15 (s, 9H). ^{13}C (75 MHz, $CDCl_3$): δ 133.3, 132.9, 104.6, 87.1, 76.5, 40.0, 24.1, 23.7, 23.0, 13.9, 6.6, 0.1. HRMS: Calc'd for $C_{15}H_{26}OSi$ [M^+]: 250.4549. Found: 250.4541.

X-Ray report for **6e:**
Data Collection

A colorless plate crystal of $C_{14}H_{24}O_2Si$ having approximate dimensions of 0.44 x 0.25 x 0.04 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART[1] CCD area detector with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 1865 reflections in the range $4.95^\circ < 2\theta < 48.41^\circ$ corresponded to a primitive monoclinic cell with dimensions:

a = 14.873(2) Å
b = 9.940(2) Å β = 100.006(3)°
c = 10.143(3) Å
V = 1476.8(5) Å^3

For Z = 4 and F.W. = 252.43, the calculated density is 1.14 g/cm^3. The systematic absences of:

h0l: l ± 2n
0k0: k ± 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of -120 ± 1°C using the ω scan technique to a maximum 2θ value of 49.5°. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3°, counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[2] with box parameters of 1.6 X 1.6 X 0.6°. Equivalent reflections were merged. Of the 6624 reflections which were collected, 2442 were unique (R_{int} = 0.065). No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 1.5 cm^{-1}. Data were analyzed for agreement and possible absorption using SADABS[3]. A semi-empirical absorption correction based on 2627 reflections with I > 5σ(I) was applied that resulted in apparent transmission factors ranging from 0.26 to 1.0. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[4] and expanded using Fourier techniques[5]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier synthesis and were constrained to idealized geometries in a riding (AFIX) refinement. A single free rotation angle about the C–CH_3 or C–OH bond vector was also refined in the case of methyl and hydroxyl groups. The final cycle of full-matrix least-squares refinement[6] on F^2 was based on 2442 observed reflections and 160 variable parameters and converged (largest parameter shift was less than 1% of its esd) with unweighted and weighted agreement factors of:

$$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o| = 0.050 \text{ (1531 refl., } F_o > 4\sigma(F_o))$$

$$wR_2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.128 \text{ (all data)}$$

The standard deviation of an observation of unit weight (S)[7] was 0.94. The weighting scheme was that of Sheldrick;[4] weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.32 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[8]. Anomalous dispersion effects were included in F_c[9]; the values for Δf' and Δf'' were those of Creagh and McAuley[10]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[11]. All calculations were performed using the CrystalStructure[12,13] crystallographic software package except for refinement, which was performed using SHELXL-97[4].

References

(1) SMART: Area-Detector Software Package,
Siemens Industrial Automation, Inc.: Madison, WI (1995)

(2) SAINT: SAX Area-Detector Integration Program, V4.024;
Siemens Industrial Automation, Inc.: Madison, WI (1995)

(3) SADABS: (v 5.04) Part of the SHELXTL Crystal Structure Determination, Siemens Industrial Automation, Inc.: Madison, WI (1998)

(4) SHELX97: Sheldrick, G.M. (1997).

(5) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(6) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2-F_c^2)^2 \quad \text{where } w = 1 / [\sigma^2(F_o^2) + (0.0693\ P)^2]$$
$$P = (F_o^2 + 2F_c^2) / 3 \text{ for } F_o^2 >= 0;\ 2F_c^2 / 3 \text{ for } F_o^2 < 0$$

(7) Standard deviation of an observation of unit weight:

$$S = [\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$$

where: N_o = number of observations; N_v = number of variables

(8) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(9) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(10) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(11) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(12) CrystalStructure 2.00: Crystal Structure Analysis Package, Rigaku and MSC (2001).

(13) CRYSTALS Issue 10: Watkin, D.J., Prout, C.K. Carruthers, J.R. & Betteridge, P.W. Chemical Crystallography Laboratory, Oxford, UK.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{14}H_{24}O_2Si$
Formula Weight	252.43
Crystal Color, Habit	colorless plate
Crystal Dimensions	0.44 X 0.25 X 0.04 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	1865 ($4.95^o < 2\theta < 48.41^o$)
Lattice Parameters	a = 14.873(2) Å b = 9.940(2) Å c = 10.143(3) Å β = 100.006(3) ^{o} V = 1476.8(5) $Å^3$
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.135 g/cm^3
F_{000}	552.00
μ(MoKα)	1.49 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	MoKα (λ = 0.71073 Å) graphite monochromated
Temperature	-120°C
Scan Type	ω(0.3°/frame)
Scan Rate	10 sec Frame Exposure
$2\theta_{max}$	49.5°
No. of Reflections Measured	Total: 6624 Unique: 2442 (R_{int} = 0.065)
Corrections	Absorption, Lorentz, polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\, w\,(F_o^{\,2} - F_c^{\,2})^2$
Least Squares Weights	$w = 1/\,[\,\sigma^2(F_o^{\,2}) + (0.0693 \cdot P)^2]$ where $P = (\mathrm{Max}(F_o^{\,2},0) + 2F_c^{\,2})/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations	2442
No. Variables	160
Reflection/Parameter Ratio	15.26
Residuals: R_1; wR_2	0.050 (1531 refl., $F_o > 4\sigma(F_o)$); 0.128 (all data)
Goodness of Fit Indicator (S)	0.94
Max Shift/Error in Final Cycle	< 1%
Maximum peak in Final Diff. Map	0.34 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.32 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Si1	0.83509(5)	0.06504(8)	0.72957(8)	0.0288(3)
O1	0.60659(12)	0.00574(19)	0.66462(16)	0.0276(5)
H1	0.5638	0.0620	0.6524	0.041
O2	0.54347(14)	-0.3543(2)	0.9429(2)	0.0437(6)
H2	0.5644	-0.3928	1.0154	0.066
C1	0.78994(18)	-0.0901(3)	0.8025(2)	0.0238(7)
C2	0.86519(18)	-0.1958(3)	0.8402(3)	0.0273(7)
H2A	0.9250	-0.1543	0.8353	0.033
H2B	0.8662	-0.2245	0.9339	0.033
C3	0.8523(2)	-0.3196(3)	0.7496(3)	0.0344(8)
H3A	0.9042	-0.3813	0.7787	0.041
H3B	0.8558	-0.2903	0.6574	0.041
C4	0.7659(2)	-0.3974(3)	0.7452(3)	0.0375(8)
H4	0.7595	-0.4747	0.6894	0.045
C5	0.6971(2)	-0.3727(3)	0.8091(3)	0.0331(8)
H5	0.6483	-0.4357	0.7972	0.040
C6	0.68909(18)	-0.2539(3)	0.8988(3)	0.0244(7)
H6	0.7339	-0.2642	0.9839	0.029
C7	0.59342(19)	-0.2335(3)	0.9318(3)	0.0311(7)
H7	0.5987	-0.1822	1.0177	0.037
C8	0.54575(17)	-0.1459(3)	0.8184(3)	0.0290(7)
H8A	0.5268	-0.1994	0.7359	0.035
H8B	0.4914	-0.1014	0.8429	0.035
C9	0.61887(17)	-0.0430(3)	0.7999(2)	0.0224(7)
C10	0.70795(18)	-0.1217(3)	0.8306(2)	0.0208(6)
C11	0.61875(19)	0.0757(3)	0.8960(3)	0.0308(7)
H11A	0.6685	0.1374	0.8862	0.046
H11B	0.6273	0.0424	0.9883	0.046
H11C	0.5603	0.1233	0.8751	0.046
C12	0.7580(2)	0.2016(3)	0.6553(4)	0.0571(11)
H12A	0.7943	0.2763	0.6296	0.086
H12B	0.7217	0.2331	0.7211	0.086
H12C	0.7172	0.1677	0.5759	0.086
C13	0.9175(2)	0.1411(3)	0.8702(3)	0.0496(9)
H13A	0.9417	0.2252	0.8400	0.074
H13B	0.9679	0.0782	0.8987	0.074
H13C	0.8862	0.1596	0.9456	0.074
C14	0.8981(2)	0.0120(3)	0.5952(3)	0.0368(8)
H14A	0.8552	-0.0262	0.5203	0.055
H14B	0.9438	-0.0559	0.6304	0.055
H14C	0.9287	0.0902	0.5639	0.055

$B_{eq} = 8/300\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si1	0.0313(5)	0.0243(5)	0.0311(5)	0.0024(4)	0.0064(4)	-0.0022(4)
O1	0.0319(12)	0.0279(12)	0.0203(10)	0.0061(8)	-0.0034(8)	0.0050(9)
O2	0.0392(13)	0.0441(14)	0.0414(14)	0.0218(10)	-0.0113(10)	-0.0228(11)
C1	0.0293(16)	0.0229(16)	0.0179(15)	0.0005(12)	0.0002(12)	0.0007(13)
C2	0.0296(16)	0.0311(17)	0.0201(15)	0.0047(13)	0.0008(13)	0.0044(14)
C3	0.044(2)	0.0336(19)	0.0235(17)	0.0028(13)	-0.0007(14)	0.0152(16)
C4	0.056(2)	0.0222(18)	0.0284(17)	-0.0053(13)	-0.0104(16)	0.0083(16)
C5	0.0432(19)	0.0186(16)	0.0311(18)	0.0021(13)	-0.0113(15)	-0.0036(15)
C6	0.0297(16)	0.0196(15)	0.0201(15)	0.0036(12)	-0.0066(12)	-0.0024(13)
C7	0.0330(18)	0.0335(18)	0.0243(16)	0.0070(13)	-0.0023(13)	-0.0132(14)
C8	0.0242(16)	0.0321(18)	0.0280(17)	0.0045(13)	-0.0031(13)	-0.0019(14)
C9	0.0258(16)	0.0221(16)	0.0174(15)	0.0032(12)	-0.0020(12)	-0.0005(13)
C10	0.0269(16)	0.0199(15)	0.0136(14)	-0.0008(11)	-0.0019(12)	-0.0004(13)
C11	0.0360(17)	0.0296(17)	0.0248(16)	-0.0027(13)	-0.0002(13)	0.0061(14)
C12	0.054(2)	0.032(2)	0.090(3)	0.0284(19)	0.024(2)	0.0047(18)
C13	0.059(2)	0.050(2)	0.042(2)	-0.0144(17)	0.0132(17)	-0.0214(19)
C14	0.0438(19)	0.038(2)	0.0296(17)	-0.0009(15)	0.0089(14)	-0.0114(15)

The general temperature factor expression:
$\exp\{-2\pi^2[(a^*)^2 2U_{11}h^2 + (b^*)^2U_{22}k^2 + (c^*)^2U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl]\}$

Table 3. Bond Lengths (Å)

atom1	atom2	distance
Si1	C12	1.850(3)
Si1	C14	1.860(3)
Si1	C1	1.884(3)
Si1	C13	1.871(3)
O1	C9	1.437(3)
O1	H1	0.8400
O2	C7	1.427(3)
O2	H2	0.8400
C1	C10	1.337(3)
C1	C2	1.534(4)
C2	C3	1.527(4)
C2	H2A	0.9900
C2	H2B	0.9900
C3	C4	1.493(4)
C3	H3A	0.9900
C3	H3B	0.9900
C4	C5	1.326(4)
C4	H4	0.9500
C5	C6	1.508(4)
C5	H5	0.9500
C6	C7	1.531(4)
C6	C10	1.533(4)
C6	H6	1.0000
C7	C8	1.517(4)
C7	H7	1.0000
C8	C9	1.528(4)
C8	H8A	0.9900
C8	H8B	0.9900
C9	C10	1.523(4)
C9	C11	1.531(4)
C11	H11A	0.9800
C11	H11B	0.9800
C11	H11C	0.9800
C12	H12A	0.9800
C12	H12B	0.9800
C12	H12C	0.9800
C13	H13A	0.9800
C13	H13B	0.9800
C13	H13C	0.9800
C14	H14A	0.9800
C14	H14B	0.9800
C14	H14C	0.9800

Table 4. Bond Angles(º)

atom1	atom2	atom3	angle
C12	Si1	C14	105.38(15)
C12	Si1	C1	121.50(13)
C14	Si1	C1	108.36(13)
C12	Si1	C13	106.95(17)
C14	Si1	C13	109.03(15)
C1	Si1	C13	105.22(13)
C9	O1	H1	109.5
C7	O2	H2	109.5
C10	C1	C2	116.0(2)
C10	C1	Si1	132.6(2)
C2	C1	Si1	111.37(18)
C3	C2	C1	113.0(2)
C3	C2	H2A	109.0
C1	C2	H2A	109.0
C3	C2	H2B	109.0
C1	C2	H2B	109.0
H2A	C2	H2B	107.8
C2	C3	C4	116.9(2)
C2	C3	H3A	108.1
C4	C3	H3A	108.1
C2	C3	H3B	108.1
C4	C3	H3B	108.1
H3A	C3	H3B	107.3
C5	C4	C3	128.5(3)
C5	C4	H4	115.7
C3	C4	H4	115.7
C4	C5	C6	126.0(3)
C4	C5	H5	117.0
C6	C5	H5	117.0
C7	C6	C5	114.2(2)
C7	C6	C10	103.6(2)
C5	C6	C10	111.1(2)
C7	C6	H6	109.3
C5	C6	H6	109.3
C10	C6	H6	109.3
O2	C7	C6	115.0(2)
O2	C7	C8	111.2(2)
C6	C7	C8	103.8(2)
O2	C7	H7	108.9
C6	C7	H7	108.9
C8	C7	H7	108.9
C9	C8	C7	103.2(2)
C9	C8	H8A	111.1
C7	C8	H8A	111.1
C9	C8	H8B	111.1
C7	C8	H8B	111.1
H8A	C8	H8B	109.1
O1	C9	C10	109.3(2)
O1	C9	C8	111.6(2)
C10	C9	C8	104.1(2)
O1	C9	C11	109.5(2)
C10	C9	C11	111.3(2)
C8	C9	C11	111.0(2)
C1	C10	C6	122.9(2)
C1	C10	C9	129.0(2)
C6	C10	C9	108.2(2)
C9	C11	H11A	109.5
C9	C11	H11B	109.5
H11A	C11	H11B	109.5
C9	C11	H11C	109.5
H11A	C11	H11C	109.5
H11B	C11	H11C	109.5
Si1	C12	H12A	109.5
Si1	C12	H12B	109.5
H12A	C12	H12B	109.5
Si1	C12	H12C	109.5
H12A	C12	H12C	109.5
H12B	C12	H12C	109.5
Si1	C13	H13A	109.5
Si1	C13	H13B	109.5
H13A	C13	H13B	109.5
Si1	C13	H13C	109.5
H13A	C13	H13C	109.5
H13B	C13	H13C	109.5
Si1	C14	H14A	109.5
Si1	C14	H14B	109.5
H14A	C14	H14B	109.5
Si1	C14	H14C	109.5
H14A	C14	H14C	109.5
H14B	C14	H14C	109.5

Table 5. Torsion Angles(º)

atom1	atom2	atom3	atom4	angle
C12	Si1	C1	C10	-10.3(3)
C14	Si1	C1	C10	-132.4(3)
C13	Si1	C1	C10	111.1(3)
C12	Si1	C1	C2	172.4(2)
C14	Si1	C1	C2	50.3(2)
C13	Si1	C1	C2	-66.2(2)
C10	C1	C2	C3	72.0(3)
Si1	C1	C2	C3	-110.3(2)
C1	C2	C3	C4	-59.5(3)
C2	C3	C4	C5	0.9(4)
C3	C4	C5	C6	2.6(5)
C4	C5	C6	C7	166.2(3)
C4	C5	C6	C10	49.5(4)
C5	C6	C7	O2	33.7(3)
C10	C6	C7	O2	154.6(2)
C5	C6	C7	C8	-88.0(3)
C10	C6	C7	C8	32.9(3)
O2	C7	C8	C9	-166.3(2)
C6	C7	C8	C9	-42.1(3)
C7	C8	C9	O1	152.0(2)
C7	C8	C9	C10	34.3(3)
C7	C8	C9	C11	-85.5(3)
C2	C1	C10	C6	1.1(4)
Si1	C1	C10	C6	-176.14(19)
C2	C1	C10	C9	-176.6(2)
Si1	C1	C10	C9	6.2(4)
C7	C6	C10	C1	170.3(2)
C5	C6	C10	C1	-66.7(3)
C7	C6	C10	C9	-11.6(3)
C5	C6	C10	C9	111.4(2)
O1	C9	C10	C1	44.8(4)
C8	C9	C10	C1	164.0(3)
C11	C9	C10	C1	-76.3(3)
O1	C9	C10	C6	-133.2(2)
C8	C9	C10	C6	-13.9(3)
C11	C9	C10	C6	105.7(2)