Experimental

General Experimental Methods. Unless otherwise noted, all materials were used as received from a commercial supplier without further purification. All anhydrous reactions were performed using oven-dried or flame-dried glassware under argon. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were filtered through activated alumina under nitrogen. Anhydrous toluene was distilled from sodium. Dichloromethane was distilled from calcium hydride. All reactions were monitored by E. Merck analytical thin layer chromatography (TLC) plates (silica gel 60 GF, glass back) and analyzed with 254 nm UV light and/or anisaldehyde/sulfuric acid treatment. Silica gel for column chromatography was purchased from E. Merck (Silica Gel 60, 230-400 mesh). Preparative thin layer chromatography (PTLC) plates were purchased from Whatman (LK6F Silica Gel 60 Å). ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on Varian Unity Plus 300 spectrometer (operating at 299.701 MHz for ^1H and 75.367 MHz for ^{13}C). Chemical shifts were reported as δ-values relative to residual $CHCl_3$ as internal reference, and coupling constants were reported in Hertz. FTIR spectra were obtained on PE Paragon 1000 spectrometer. Mass spectra (CI/FAB/EI) were obtained at the Department of Chemistry and Biochemistry, University of Notre Dame.

Benzyl 4-penten-2-ol ether 5. To a solution of benzylglycidyl ether (410 mg, 2.72 mmol) in anhydrous THF (11 mL) was added a catalytic amount of copper(I) iodide (10 mol%, 52 mg). The flask was evacuated of air and filled with nitrogen and cooled to -78 °C. Slowly a 1.0M solution of vinyl magnesium in THF (2.86 mL, 2.86 mmol) was added via syringe. The reaction mixture was stirred at -78 °C for 2 hours. Then slowly it was allowed to then warm up to -40 °C. At this point, the reaction mixture begins to see significant product formation and the color of the mixture changes from a bright orange to a murky brown. The reaction vessel is maintained near -40 °C for another hour and then slowly allowed to warm to 0 °C. At this point, the reaction is complete and exhibits a dark black coloration (total reaction time 3-4 hours). The mixture was then quenched at 0 °C with ammonium chloride (20 mL) and stirred for 45 minutes until a vibrant blue color was observed in the aqueous layer. Most of the THF was removed under reduced pressure and the remaining product was extracted with ether (3 x 20 mL). The ethereal extracts were then combined and washed with ammonium chloride, brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, 16% EtOAc in hexanes) to give benzyl 4-penten-2-ol ether **5** (500 mg, 95%) as a clear oil. ^1H NMR (300MHz, $CDCl_3$) δ (ppm) 7.35 (m, 5H), 5.83 (ddd, J = 7.1, 7.0, 17 Hz, 1H),

5.16-5.07 (m, 2H), 4.53 (s, 2H), 3.93-3.84 (m, 1H), 3.52 (dd, J = 3.4, 9.5 Hz, 1H), 3.39 (dd, J = 7.4, 9.5 Hz,1H), 2.39 (d, J = 3.6 Hz, 1H), 2.27 (dd, J = 7.0, 1.3 Hz, 2H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 137.9, 134.2, 128.4, 127.8, 127.7, 117.7, 73.9, 73.4, 69.7, 37.9. FTIR (cm^{-1}) 3436, 3066, 3031, 1642. HRMS (FAB) calcd for $C_{12}H_{16}O_2$ $(M+H)^+$ *m/z* 193.1150, found 193.1190.

Benzyl (2-allyldimethylsilyloxy)-4-pentene ether. To a solution of benzyl 4-penten-2-ol ether (500 mg, 2.60 mmol) in CH_2Cl_2 (9 mL) was added Hunig's Base (905 μL, 5.20 mmol) and imidazole (177 mg, 2.60 mmol). The mixture was then cooled to -78 °C after which an excess of allylchlorodimethylsilane (425 μL, 2.86 mmol) was added slowly dropwise to the flask. The mixture was stirred for 4 hours while warming to room temperature. The reaction was quenched with water and stirred for about 30 minutes. The organic material was then extracted with two 20 mL portions of ether and the extract was washed with water followed by brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified using flash chromatography (silica gel, 16% EtOAc in hexanes) to give the benzyl (2-allyldimethylsilyoxy)-4-pentene ether (752 mg, 100%) as a clear oil. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.35 (m, 5H), 5.88-5.72 (m, 2H), 5.11-5.03 (m, 2H), 4.91-4.82 (m, 2H), 4.53 (s, 2H), 3.89 (quintet, 1H), 3.39 (d, J = 5.1 Hz, 2H), 2.38-2.16 (m, 2H), 1.63 (d, J = 8.2 Hz, 2H), 0.12 (s, 6H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 138.4, 134.8, 134.3, 128.3, 127.6, 127.5, 117.1, 113.5, 74.2, 73.3, 71.5, 39.1, 25.1, -1.7, -1.8. FTIR (cm^{-1}) 3077, 3031, 1630.8, 1496, 1454, 1433. HRMS (FAB) calcd for $C_{17}H_{26}O_2Si$ $(M-C_3H_5+H)^+$ *m/z* 247.1154, found 247.1167.

Benzyl siloxycycloheptene 6. Benzyl (2-allyldimethylsililoxy)-4-pentene ether (755 mg, 2.60 mmol) was diluted to a concentration of 0.075 M in CH_2Cl_2 (35 mL) and the reaction vessel was then flushed with nitrogen and sealed. Bis-(tricyclohexylphosphine) benzylidine ruthenium(IV) dichloride, (8 mol%, 171 mg, 0.21 mmol) was then added to the reaction mixture. The initial rose color of the solution upon addition of the catalyst slowly changed to a rust brown color during the course of the reaction. The mixture was stirred for 4 hours and then flask was opened to air and stirred for another few hours to decompose the catalyst. The solvent was removed under reduced pressure and the resulting brown residue was purified by flash column chromatography (silica gel, 6% EtOAc in hexanes) to give the benzyl siloxycycloheptene **6** (580 mg, 85%) as a pale brown oil. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.36-7.35 (m, 5H), 5.84 (dd, J = 7.4, 10.4 Hz, 1H), 5.62 (ddd, J = 1.2, 6.8, 10.4 Hz, 1H), 4.58 (d, J = 12.2 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.12-4.04 (m, 1H), 3.47 (dd, J = 5.4, 9.5 Hz, 1H), 3.36 (dd, J = 6.6, 9.3 Hz, 1H), 2.39-2.34 (m, 2H), 1.68 (dd, J = 7.1, 15.1 Hz, 1H), 1.62 (dd, J = 7.5, 14.9 Hz, 1H), 0.16 (s, 3H), 0.14 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 138.4, 128.4, 128.3, 127.6, 127.5, 126.1, 74.6, 73.2,

71.6, 33.6, 18.3, -0.2, -1.8. FTIR (cm^{-1}) 3024, 1644, 1497, 1453. HRMS (FAB) calcd for $C_{15}H_{22}O_2Si$ M^+ *m/z* 262.1389, found 262.1388.

Benzyl vinylcyclopropane ether 8 via Intermediate 7a. In a plastic bottle, a solution of the 7-membered siloxycycloheptene **6** (47 mg, 0.18 mmol) in THF (1 mL) was added. Then a large excess of HF/pyridine (50 µL) was added to the reaction flask. Later it was found that 2 eq. of HF/pyr is enough to get complete conversion to fluorinated product at a reasonable rate. The reaction is complete after several minutes and quenched with water. The reaction mixture was then worked up and washed once with 10 mL of a saturated sodium bicarbonate solution. The crude product from this reaction is very clean by NMR, however the product can be purified using flash column chromatography (silica gel, 16% EtOAc in hexanes). Using the crude material (31 mg) in a 5 mL round bottom flask, it was diluted in CH_2Cl_2 (200 µL). The reaction flask was then cooled to -78 °C and flushed with nitrogen. Then a weak base, 2,6-lutidine (15 µL, 0.13 mmol) was added to the reaction via syringe, directly followed by triflic anhydride (32 µL, 0.19 mmol). Subsequent quenching with Hunig's Base (3 eq. excess) changes the reaction mixture from a light yellow to a vibrant red/purple color. Slowly the reaction mixture was allowed to warm to room temperature during which the bright color of the reaction diminished to a dark purple. The product was isolated as a crude residue by removing the solvent under reduced pressure and purified using a pipette column (silica gel, 6% EtOAc in hexanes) to give the benzyl vinylcyclopropane **8** (24 mg, 71%) as a clear oil. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35-7.34 (m, 5H), 5.48-5.36 (m, 1H), 5.07 (dd, J = 1.7, 17 Hz, 1H), 4.88 (dd, J = 1.7, 10.3 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 3.41 (dd, J = 6.6, 10.4 Hz, 1H), 3.35 (dd, J = 6.6, 10.4 Hz, 1H), 1.38-1.29 (m, 1H), 1.22-1.13 (m, 1H), 0.68 (t, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 140.7, 138.4, 128.3, 127.7, 127.5, 112.2, 73.2, 72.4, 20.8, 20.2, 11.9. FTIR (cm^{-1}) 3067, 3004, 1720, 1637, 1497, 1454. HRMS (CI) calcd for $C_{13}H_{16}O$ $(M+H)^+$ *m/z* 189.1279, found 189.1281.

Benzyl vinylcyclopropane ether 8 via Intermediate 7b. In a 50 mL round bottom flask, the 7-membered siloxycycloheptene **6** (310 mg, 1.18 mmol) was diluted in THF (10 mL). The flask was then flushed of all air and kept under an atmoshpere of nitrogen. Then a 1.6M solution of methyl lithium (2.22 mL, 3.55 mmol) was added via syringe. Over the next 15 minutes the flask contents darkened to a transparent brown-orange. The reaction appeared complete at this point by TLC and was quenched with ammonium chloride. It was stirred for 15 minutes at room temperature after which the bulk of the THF was rotovapped off. Then the product was

extracted with EtOAc (2 x 30 mL) and washed with brine. This methylated intermediate was stable to silica gel and can be purified before generating the cyclopropane, however it was shown in subsequent reactions that purification was not necessary for the success of the cyclopropanation reaction. Thus, taking the crude mixture (336 mg, 1.2a mmol) in a 50 mL round bottom flask, it was diluted in CH_2Cl_2 (10 mL). 2,6-lutidine (198 μL, 1.70 mmol) was added and the reaction mixture was cooled to -78 °C. Quickly, the triflic anhydride was added to the reaction mixture followed immediately (within five minutes) by a quench Hunig's Base (large excess). Again, the color change from yellow to red/purple was observed. Slowly the reaction mixture was allowed to warm to room temperature during which the reaction contents darkened. The product was isolated as a crude residue by removing the solvent under reduced pressure and purified using a flash chromatography (silica gel, 6% EtOAc in hexanes) to give the benzyl vinylcyclopropane **8** (175 mg, 77%) as a clear oil.

Benzyl cyclopropyl aldehyde. A solution of benzyl vinylcyclopropane **8** (329 mg, 1.75 mmol) in anhydrous THF (15 mL) was cooled to 0 °C in a 50 mL pear flask. To the solution was then added a catalytic amount of pyridine (5 drops) via syringe followed by a catalytic amount of osmium tetraoxide (small crystal). The reaction mixture was maintained at 0 °C for 45 minutes and diol formation was observed by TLC as was an orange coloration. An aqueous sodium periodate solution was prepared (2.72 g, 12.7 mmol $NaIO_4$ in 15 mL water) separately and then added to the ethereal reaction mixture. After stirring for another hour the reaction flask was removed from the ice bath and allowed to warm to room temperature. After two hours at room temperature the reaction was complete as indicated by TLC and the reaction mixture was very cloudy and full of white precipitate. Finally, the reaction was quenched with $Na_2S_2O_3$ (12 mL) and stirred for about 20 more minutes during which the solution became a very vibrant yellow color and separated into two layers. The product was then extracted with ethyl acetate (3 x 20 mL) and washed with brine. The ethereal extracts were then dried over $MgSO_4$ and concentrated under reduced pressure yielded a yellowish oil that was purified by flash column chromatography (silica gel, 16% EtOAc in hexanes) to give the benzyl cyclopropyl aldehyde (314 mg, 94%) as a clear oil.

***Syn*-Benzyl cyclopropyl homoallylic alcohol 9a** and ***Anti*-Benzyl cyclopropane homoallylic alcohol 9b.** To a solution of benzyl cyclopropyl aldehyde (410 mg, 2.72 mmol) in anhydrous THF (11 mL) was added a catalytic amount of copper(I) iodide (10 mol%, 52 mg). The flask was evacuated of air and filled with nitrogen and cooled to -78 °C. Slowly a 1.0M solution of vinyl magnesium in THF (2.86 mL, 2.86 mmol) was added via syringe. The reaction mixture was stirred at -78 °C for 2 hours. Then slowly it was allowed to then warm up to -40 °C. At this

point, significant product formation is observed and the color of the reaction mixture changes from a bright orange to a murky brown. The reaction vessel is maintained near -40 °C for another hour and then slowly allowed to warm to 0 °C. At this point, the reaction is complete and exhibits a dark black coloration (total reaction time 3-4 hours). The mixture was then quenched at 0 °C with ammonium chloride (20 mL) and stirred for 45 minutes until a vibrant blue color was observed in the aqueous layer. Again, most of the THF was removed under *vacuo* and the remaining product was extracted with ether (3 x 20 mL). The ethereal extracts were then washed with ammonium chloride followed by brine and then dried over $MgSO_4$. After removing the solvent under *vacuo*, the resulting residue of diastereomers was purified by flash column chromatography (silica gel, 16% EtOAc in hexanes). The mixture of homoallylic alcohol diastereomers **9a** and **9b** were separated using a combination of radial and column chromatography (silica gel, 0.5% acetonitrile in chloroform) providing the *syn*-benzyl cyclopropyl homoallylic alcohol **9a** (250 mg, 48%) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35-7.33 (m, 5H), 5.88 (m, 1H), 5.12 (m, 2H), 4.54 (s, 2H), 3.35 (dd, J = 6.8, 10.3 Hz, 1H), 3.31 (dd, J = 7.0, 9.9 Hz, 1H), 3.10 (m, 1H), 2.45-2.25 (m, 2H), 1.18-1.08 (m, 1H), 0.90-0.81 (m, 1H), 0.55-0.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 138.2, 134.5, 128.2, 127.5, 127.4, 117.5, 76.4, 74.3, 73.2, 72.4, 41.3, 34.1, 23.3, 16.4, 7.8. FTIR (cm^{-1}) 3401, 3068, 3001, 1640, 1495, 1454. HRMS (CI) calcd for $C_{15}H_{20}O_2$ $(M+H)^+$ *m/z* 233.1542, found 233.1564. The separation also provided the *anti*-benzyl cyclopropyl homoallylic alcohol **9b** (250 mg, 48%) also as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35-7.33 (m, 5H), 5.95-5.81 (m, 1H), 5.17-5.09 (m, 2H), 4.53 (s, 2H), 3.36 (dd, J = 6.6, 10.1 Hz, 1H), 3.30 (dd, J = 7.0, 10.3 Hz, 1H), 3.07-3.00 (m, 1H), 2.44-2.25 (m, 2H), 1.17-1.09 (m, 1H), 0.90-0.81 (m, 1H), 0.54-0.47 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 138.4, 134.7, 128.4, 127.7, 127.6, 117.7, 74.5, 73.4, 72.5, 41.5, 23.5, 16.6, 8.0. FTIR (cm^{-1}) 3402, 3068, 3001, 1640, 1496, 1454. HRMS (CI) calcd for $C_{15}H_{20}O_2$ $(M+H)^+$ *m/z* 233.1542, found 233.1513.

***Syn*-Benzyl cyclopropane silyl ether.** To a solution of the *syn*-benzyl cyclopropyl homoallylic alcohol **9a** (16 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added Hunig's Base (24 μL, 0.14 mmol) and imidazole (5 mg, 0.1 mmol). The mixture was then cooled to -78 °C after which an excess of allylchlorodimethylsilane (11 μL, 0.08 mmol) was added slowly dropwise to the flask. The mixture was stirred for 4 hours while warming to room temperature. The reaction was quenched with water and stirred for about 30 minutes. The organic material was then extracted by adding 20 mL of methylene chloride and disposing of the aqueous layer. The resulting organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified using flash chromatography (silica gel, 16% EtOAc in hexanes) to give the

syn-benzyl cyclopropane silyl ether (22 mg, 98%) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.34-7.32 (m, 5H), 5.93-5.71 (m, 2H), 5.08-5.00 (m, 2H), 4.91-4.83 (m, 2H), 4.51 (s, 2H), 3.39 (dd, J = 6.4, 10.2 Hz, 1H), 3.25-3.17 (m, 2H), 2.32 (t, J = 6.0 Hz, 2H), 1.59 (dd, J = 8.1, 9.7 Hz, 2H), 1.03-0.95 (m, 1H), 0.88-0.78 (m, 1H), 0.58 (dt, J = 5.0, 8.4 Hz, 1H), 0.45 (dt, J = 4.9, 8.4 Hz, 1H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 138.5, 135.2, 134.2, 128.3, 127.52, 127.48, 116.7, 113.6, 75.2, 73.5, 72.5, 42.9, 25.2, 23.1, 16.2, 9.0, -1.6, -1.7. FTIR (cm^{-1}) 3076, 2957, 1631, 1496, 1454. HRMS (CI) calcd for $C_{20}H_{30}O_2Si$ $(M+H)^+$ *m/z* 331.2093, found 331.2114.

***Anti*-Benzyl cyclopropane silyl ether.** To a solution of the *anti*-benzyl cyclopropyl homoallylic alcohol **9b** (12 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was added Hunig's Base (18 μL, 0.10 mmol) and imidazole (4 mg, 0.05 mmol). The mixture was then cooled to -78 °C after which an excess of allylchlorodimethylsilane (9 μL, 0.05 mmol) was added slowly dropwise to the flask. The mixture was stirred for 3-4 hours while warming to room temperature. The reaction was quenched with water and stirred for about 30 minutes. The organic material was then extracted by adding 20 mL of methylene chloride and disposing of the aqueous layer. The resulting organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified using flash chromatography (silica gel, 16% EtOAc in hexanes) to give the *anti*-benzyl cyclopropane silyl ether (17 mg, Quantitative) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.34-7.33 (m, 5H), 5.92-5.71 (m, 2H), 5.09-5.02 (m, 2H), 4.91-4.82 (m, 2H), 4.55 (d, J = 12.1 Hz, 1H), 4.52 (d, J = 12.1 Hz, 1H), 3.53 (dd, J = 5.7, 10.2 Hz, 1H), 3.24 (q, J = 6.3 Hz, 1H), 3.15 (dd, J = 7.7, 10.2 Hz, 1H), 2.30 (t, J = 6.5 Hz, 2H), 1.61-1.54 (m, 2H), 1.12-1.05 (m, 1H), 0.91-0.79 (m, 1H), 0.52-0.41 (m, 2H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 138.6, 135.2, 134.2, 128.3, 127.6, 127.4, 116.8, 113.6, 74.8, 73.6, 72.3, 42.7, 25.2, 22.9, 16.2, 8.2, -1.6, -1.7. FTIR (cm^{-1}) 3076, 3000, 1631, 1496, 1454. HRMS (FAB) calcd for $C_{20}H_{30}O_2Si$ $(M - C_3H_5+H)^+$ *m/z* 289.1624, found 289.1617.

***Syn*-Benzyl cyclopropane siloxycycloheptene.** Procedure is identical to that of compound **6** above. The *syn*-benzyl cyclopropane silyl ether (51 mg, 0.15 mmol) was diluted to a low concentration of less than 0.001 M in CH_2Cl_2 (17 mL) and the reaction vessel was then flushed with nitrogen and sealed. Bis-(tricyclohexylphosphine) benzylidine ruthenium(IV) dichloride, (8 mol%, 6 mg, 0.01 mmol) was then added to the reaction mixture. The initial rose color of the solution upon addition of the catalyst slowly changed to a rust brown color during the course of the reaction. The mixture was stirred for 3 hours and then flask was opened to air and stirred for another few hours to decompose the remaining catalyst. The solvent was removed under reduced pressure and the resulting brown residue was purified by flash column chromatography (silica

gel, 6% EtOAc in hexanes) to give the *syn*-benzyl cyclopropane siloxycycloheptene (36 mg, 78%) as a pale brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35-7.33 (m, 5H), 5.79 (dt, J = 7.1, 10.2 Hz, 1H), 5.59 (dt, J = 6.7, 10.7 Hz, 1H), 4.53 (d, J = 12.1 Hz, 1H), 4.52 (d, J = 12.1 Hz, 1H), 3.40-3.28 (m, 3H), 2.51-2.35 (m, 2H), 1.66-1.58 (m, 1H), 1.51 (dd, J = 7.0, 15.1 Hz, 1H), 1.03-0.95 (m, 1H), 0.92, 0.84 (m, 1H), 0.63 (dt, J = 4.9, 8.4 Hz, 1H), 0.46 (dt, J = 4.9, 8.2 Hz, 1H), 0.13 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 138.6, 128.3, 127.9, 127.6, 127.5, 126.6, 75.6, 73.7, 72.5, 37.1, 24.3, 18.2, 15.9, 8.8, -0.3, -1.7. FTIR (cm^{-1}) 3022, 1496, 1454. HRMS (CI) calcd for $C_{18}H_{26}O_2Si$ $(M+H)^+$ *m/z* 303.1780, found 303.1752.

***Anti*-Benzyl cyclopropane siloxycycloheptene.** The procedure is identical to that of the *syn* diastereomer above. The *anti*-benzyl cyclopropane silyl ether (26 mg, 0.08 mmol) was diluted to a low concentration of less than 0.001 M in CH_2Cl_2 (10 mL) and the reaction vessel was then flushed with nitrogen and sealed. Bis-(tricyclohexylphosphine) benzylidine ruthenium(IV) dichloride, (8 mol%, 6 mg, 0.01 mmol) was then added to the reaction mixture. The initial rose color of the solution upon addition of the catalyst slowly changed to a rust brown color during the course of the reaction. The mixture was stirred for 3 hours and then flask was opened to air and stirred for another few hours to decompose the remaining catalyst. The solvent was removed under reduced pressure and the resulting brown residue was purified by flash column chromatography (silica gel, 6% EtOAc in hexanes) to give the *anti*-benzyl cyclopropane siloxycycloheptene (20 mg, 82%) as a pale brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35-7.33 (m, 5H), 5.79 (dt, J = 7.2, 10.6 Hz, 1H), 5.58 (dt, J = 6.7, 10.6 Hz, 1H), 4.58 (d, J = 12.1 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 3.48 (dd, J = 6.4, 10.4 Hz, 1H), 3.37 (ddd, J = 2.5, 8.6, 8.4 Hz, 1H), 3.24 (dd, J = 7.4, 10.4 Hz, 1H), 2.49-2.32 (m, 2H), 1.60 (m, 1H), 1.54 (dd, J = 7.1, 14.9 Hz, 1H), 1.19-1.09 (m , 1H), 0.92-0.84 (m, 1H), 0.47 (dt, J = 4.9, 8.4 Hz, 1H), 0.39 (dt, J = 5.0, 8.6 Hz, 1H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 138.7, 128.3, 128.1, 127.7, 127.4, 126.4, 75.5, 73.6, 72.1, 36.7, 24.0, 18.3, 16.4, 7.7, -0.2, -1.6. FTIR (cm^{-1}) 3021, 1496, 1455. HRMS (CI) calcd for $C_{18}H_{26}O_2Si$ $(M+H)^+$ *m/z* 303.1780, found 303.1761.

***Syn*-bis-cyclopropane 11a** and ***Anti*-bis-cyclopropane 11b.** In a 10 mL round bottom flask, the siloxycycloheptene (*syn* or *anti*) (7 mg, 0.02 mmol) was diluted in THF (3 mL). The flask was then flushed of all air and kept under an atmoshpere of nitrogen. Then a 1.6M solution of methyl lithium (65 μL, 0.10 mmol) was added via syringe. Over the next 15 minutes the flask contents darkened to a transparent brown-orange. The reaction appeared complete at this point and was quenched with ammonium chloride. It was stirred for 15 minutes at room temperature then the

bulk of the THF was rotovapped off. The product was then extracted with ether (2 x 10 mL) and washed with brine. The resulting ethereal layers were dried over $MgSO_4$ and concentrated under reduced pressure and then purified using column chromatography (silica gel, 16% EtOAc in hexanes) to give the ring opened benzyl cyclopropane homoallylic alcohol **10a** or **10b** (6 mg, 83%) as a clear oil. Taking this purified compound on (6 mg, 0.02 mmol) in a 10 mL round bottom flask, it was diluted in CH_2Cl_2 (5 mL). 2,6-lutidine (5 μL, 0.04 mmol) was then added to the reaction mixture was cooled to -78 °C. Quickly, the triflic anhydride was added to the reaction mixture followed immediately (within five minutes) by a quench Hunig's Base (300 μL). Again, the color change from yellow to red/purple was observed. Slowly the reaction mixture was allowed to warm to room temperature during which the reaction contents darkened. The product was isolated as a crude residue by removing the solvent under reduced pressure and purified using a flash chromatography (silica gel, 6% EtOAc in hexanes) to give a 1:1 mixture of the *syn* and *anti* biscyclopropanes **11a** and **11b** (3 mg, 73%) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.34-7.27 (m, 5H), 5.35 (m, 1H), 5.00 (dd, J = 1.8, 17.1 Hz, 1H), 4.81 (dd, J = 1.2, 10.2 Hz, 1H), 4.51 (s, 2H), 3.38-3.22 (m, 2H), 1.25-1.15 (m, 1H), 0.97-0.83 (m, 2H), 0.85-0.72 (m, 1H), 0.54-0.44 (m, 2H), 0.42-0.26 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 141.7, 138.6, 128.4, 127.6, 127.5, 111.40, 111.36, 73.91, 73.89, 72.40, 72.36, 22.0, 21.8, 21.4, 21.0, 18.3, 18.2, 17.1, 16.4, 12.3, 11.6, 8.9, 8.0 . FTIR (cm^{-1}) 2999, 2864, 1636, 1454, 1096, 1028, 893, 734, 697. HRMS (CI) calcd for $C_{16}H_{20}O$ $(M+H)^+$ *m/z* 229.1592, found 229.1563.

1-Phenoxy-6-tetrahydropyranyloxy-4-hexyne-2-ol. To a solution of tetrahydro-pyranyl propargyl ether (900 mg, crude, ~6.4 mmol) in THF (50 mL) stirred at -78 °C was added n-BuLi (2.5 M, 3.1 mL, 7.8 mmol) dropwise. The mixture was warmed up to -20 °C over 1 h and was recooled to -78 °C. $BF_3{\cdot}OEt_2$ (1.0 mL, 7.9 mmol) was added. After 10 min, 1-phenoxy-2,3-epoxy-propane (0.9 mL, 6.7 mmol) was added slowly. The mixture was stirred for 20 min and was then quenched with aqueous NH_4Cl, extrated with Et_2O (x3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, 50% Et_2O in hexanes) to give 1-phenoxy-6-tetrahydropyranyloxy-4-hexyne-2-ol (1.07 g, 58%) as colorless oil. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.36-7.27 (m, 2H), 7.03-6.91 (m, 3H), 4.81 (dd, J = 5.6, 5.6, 1H), 4.29 (t, J = 3.2, 1H), 4.26 (t, J = 3.2, 1H), 4.18 (m, 1H), 4.09 (dd, J = 12.0, 5.2, 1H), 4.01 (dd, J = 12.0, 5.2, 1H), 3.85 (m, 1H), 3.54 (m, 1H), 2.98 (br s, 1H), 2.63 (m, 2H), 1.84-1.52 (m, 6H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 158.5, 129.6, 121.2, 114.6, 97.0, 82.0, 78.7, 70.6, 68.6, 62.1, 54.7, 30.3, 25.4, 24.1, 19.1. FTIR (cm^{-1}) 3436. HRMS calcd for $C_{17}H_{23}O_4$ $(M+H)^+$ *m/z* 291.1596, found 291.1591.

1-Phenoxy-4-hexyne-2,6-diol - To a solution of 1-phenoxy-6-tetrahydropyranyloxy-4-hexyne-2-ol (**1**, 2.7 g, 9.3 mmol) in anhydrous MeOH (30 mL) was added TsOH (catalytic ammount) and the mixture was stirred at room temperature for 1.5 h. The reaction mixture was then quenched with aqueous $NaHCO_3$ and extracted with Et_2O (x3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, 40% Et_2O in hexanes) to give 1-phenoxy-4-hexyne-2,6-diol (1.71 g, 89%) as white crystal. ^1H NMR (300MHz, $CDCl_3$) δ (ppm) 7.31-7.25 (m, 2H), 6.99-6.89 (m, 3H). 4.24 (dd, J = 2.4, 2.4, 1H), 4.16 (m, 1H), 4.01 (m, 2H), 3.36 (s, 1H), 2.59 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 158.5, 129.7, 121.4, 114.7, 81.9, 81.2, 70.6, 68.7, 51.1, 24.1. FTIR (cm^{-1}) 3351. HRMS calcd for $C_{12}H_{14}O_3$ M^+ *m/z* 206.0943, found 206.0934.

1-Phenoxy-6-bromo-4-hexyne-2-ol 12. To a solution of 1-phenoxy-4-hexyne-2,6-diol (3.10 g, 15.0 mmol) in anhydrous CH_2Cl_2 (150 mL) was added triphenylphosphine (4.32 g, 16.5 mmol) and carbon tetrabromide (5.23 g, 15.8 mmol). The solution was stirred at room temperature for 4 h. The solvent was then removed *in vacuo* and the residue was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) to give 1-phenoxy-6-bromo-4-hexyne-2-ol **12** (3.96 g, 98%) as a colorless oil . ^1H NMR (300MHz, $CDCl_3$) δ (ppm) 7.33-7.28 (m, 2H), 7.01-6.92 (m, 3H). 4.17 (m, 1H), 4.07 (dd, J = 9.3, 3.9, 1H), 3.99 (dd, J = 9.6, 6.6, 1H), 3.92 (t, J = 2.4, 2H), 2.78 (s, 1H), 2.64 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 158.4, 129.6, 121.4, 114.7, 83.4, 78.0, 70.5, 68.5, 24.1, 15.2. FTIR (cm^{-1}) 2235. HRMS calcd for $C_{12}H_{13}BrO_2$ M^+ *m/z* 268.0099, found 268.0072.

9-Trimethylsilyl-1-phenoxy-4,7-nonadiyne-2-ol. To a solution of 1-phenoxy-6-bromo-4-hexyne-2-ol (120 mg, 0.45 mmol) in anhydrous DMF (1.5 mL) was added copper iodide (1.02 mg, 0.54 mmol) and sodium carbonate (72 mg, 0.68 mmol). The mixture was cooled to -40 °C. Propargyl trimethylsilane (80 μL, 0.54 mmol) was added via syringe. The mixture was stirred for 60 h during which the reaction was warmed up gradually to room temperature. The mixture was then diluted with Et_2O and extracted with aqueous NH_4Cl, brine, dried over MgSO4, and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) to give 9-trimethylsilyl-1-phenoxy-4,7-nonadiyne-2-ol (90 mg, 67%) as a pale yellow oil . ^1H NMR (300MHz, $CDCl_3$) δ (ppm) 7.32-7.26 (m, 2H), 7.00-6.91 (m, 3H). 4.14 (m, 1H), 4.08 (dd, J = 12.9, 3.9, 1H), 3.99 (dd, J = 9.3, 6.6, 1H), 3.13 (m, 2H), 2.72 (br s, 1H), 2.56 (m, 2H), 1.44 (t, J = 2.7, 2H), 0.10 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 158.6, 129.6,

121.2, 114.7, 78.5, 78.3, 75.4, 72.7, 70.6, 68.8, 24.0, 10.0, 7.0, -1.9. FTIR (cm^{-1}) 3422, 2217, 2198, 1600, 1497. HRMS calcd for $C_{18}H_{24}SiO_2M^+$ *m/z* 300.1546, found 300.1542.

9-Trimethylsilyl-1-phenoxy-4,7-nonadiene-2-ol 13. To a solution of 9-trimethylsilyl-1-phenoxy-4,7-nonadiyne-2-ol (**3**, 76 mg, 0.25 mmol) in EtOAc-pyridine (1.0 mL, 9:1) was added Lindlar's catalyst (Pd-$CaCO_3$, poisoned with lead, catalytic ammount). The mixture was stirred under an atmospheric pressure of hydrogen for 12 h. The mixture was then filtered throuh celite and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, 15% EtOAc in hexanes) to give 9-trimethylsilyl-1-phenoxy-4,7-nonadiene-2-ol **13** (58 mg, 76%) as a colorless oil. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.32-7.26 (m, 2H), 7.00-6.91 (m, 3H). 5.62-5.40 (m, 3H), 5.24 (m, 1H), 4.06 (m, 1H), 4.02 (dd, J = 12.6, 3.3, 1H), 3.90 (dd, J = 9.3, 7.2, 1H), 2.79 (t, J = 6.9, 2H), 2.44 (t, J = 6.9, 2H), 2.93 (br s, 1H), 1.51 (dd, J = 8.7, 0.6, 2H), 0.02 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 158.8, 132.1, 129.7, 126.7, 126.6, 125.1, 124.4, 121.3, 114.7, 71.5, 70.1,31.6, 25.7, 18.8, -1.6. FTIR (cm^{-1}) 3401, 3012. HRMS calcd for $C_{18}H_{28}SiO_2M^+$ *m/z* 304.1859, found 304.1848.

Bis-cyclopropane 14. To a solution of 9-trimethylsilyl-1-phenoxy-4,7-nonadiene-2-ol (**4**, 45 mg, 0.15 mmol) in anhydrous CH_2Cl_2 (2.0 mL) at -78 °C was added 2,6-lutidine (26 μL, 0.23 mmol) followed by TfO_2 (30 μL, 0.18 mmol). The solution was stirred at -78 °C for 20 min and was quenched with Et_3N (52 μL, 0.38 mmol). The solution was then stirred at -78 °C for 20 min and at room temperature for 30 min. After concentrated *in vacuo*, the residue was purified by flash column chromatography (silica gel, 20% $CHCl_3$ in hexanes) to give a mixture of diastereomeric bis-cyclopropane **14** (23 mg, 69%) as a colorless oil. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.31-7.26 (m, 2H), 6.97-6.88 (m, 3H). 5.39 (m, 1H), 5.03 (dd, J = 17.1, 1.8, 1H), 4.85 (dd, J = 10.2, 1.8, 1H), 3.89-3.73 (m, 2H), 1.23 (m, 1H), 1.06 (m, 1H), 1.01-0.88 (m, 2H), 0.57-0.42 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 159.1, 141.8, 129.6, 120.8, 114.9, 111.7, 71.8, 22.1, 21.9, 21.6, 21.3, 18.7, 18.5, 16.9, 16.1, 12.4, 11.8, 9.3, 8.3. FTIR (cm^{-1}) 3070, 3001, 2908, 1601, 1497. HRMS calcd for $C_{15}H_{19}O$ $(M+H)^+$ *m/z* 215.1436, found 215.1414.