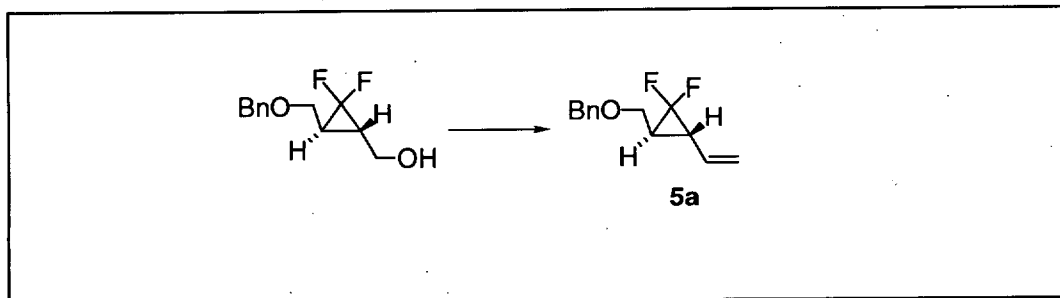


## Experimental Details

### Experimental Section

**General Procedures.** Reagents and solvents were purchased from common commercial sources and were used as received or purified by distillation from appropriate drying agents. Reactions requiring anhydrous conditions were run under an atmosphere of dry argon. Wako gel C-300 and Wako gel B5F were used for flash column chromatography and thin-layer chromatography (TLC), respectively. Chemical shifts are expressed in  $\delta$  value (ppm) downfield from tetramethylsilane (TMS) in  $\text{CDCl}_3$  as an internal reference.  $^{19}\text{F}$  NMR spectra were reported in ppm downfield from  $\text{C}_6\text{F}_6$  as an internal reference.

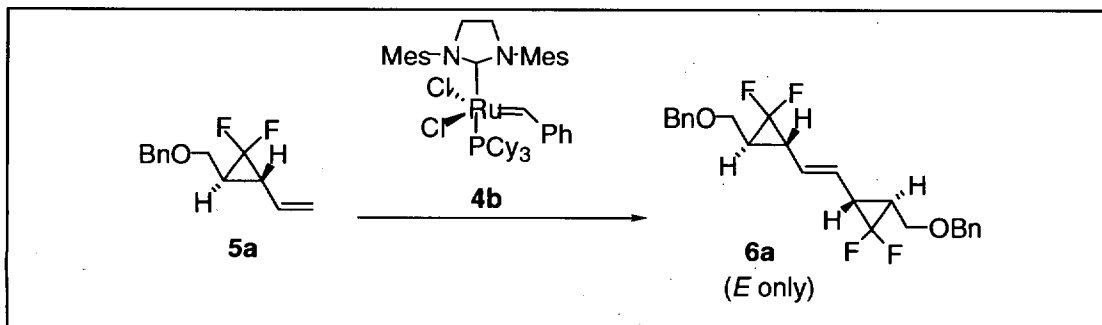
#### 1-Benzyloxymethyl-2,2-difluoro-3-vinylcyclopropane (**5a**)



To a dichloromethane (10 ml) solution of 3-benzyloxymethyl-2,2-difluorobicyclopropylmethanol (300 mg, 1.31 mmol) was added PDC (590 mg, 1.57 mmol) and the mixture was stirred for 24 h at rt. The mixture was filtered through a florisil short column and evaporated to dryness to afford the corresponding aldehyde which was used immediately without further purification. To a THF (10 ml) solution of *t*-BuOK (154 mg, 1.37 mmol) and methyltriphenylphosphonium iodide (556 mg, 1.38 mmol) was added a THF (3 ml) solution of the aldehyde at  $0^\circ\text{C}$  and the mixture was stirred for 5 h at rt. Silica gel flash column chromatography (hexane-ethyl acetate = 100:1) gave **5a** (137 mg, 0.771 mmol) in 59% overall yield:  $^1\text{H}$  NMR (200 MHz,  $\delta$ ,  $\text{CDCl}_3$ ,  $J = \text{Hz}$ ) 1.86 (1H, dddd,  $J = 13.9, 13.9, 6.9, 1.6$ ), 2.05 (1H, dt,  $J = 13.0, 7.5$ ), 3.46-3.73 (2H, m), 4.54 (2H, q,  $J = 12.0$ ), 5.20 (1H, d,  $J = 1.7$ ), 5.22 (1H, dd,  $J = 29.9, 1.5$ ), 5.56 (1H, ddt,  $J = 9.1, 3.3, 1.6$ ), 7.24-7.40 (5H, m);  $^{13}\text{C}$  NMR (50 MHz, ppm,  $\text{CDCl}_3$ ,  $J = \text{Hz}$ ) 29.4 (t,  $J_{\text{C-F}} = 10.0$ ), 31.0 (t,  $J_{\text{C-F}} = 11.5$ ), 66.3 (d,  $J = 4.7$ ), 72.54, 114.68 (dd,  $J = 290.9, 288.5$ ), 117.9, 127.7, 127.78, 128.45, 131.19 (d,  $J_{\text{C-F}} = 3.1$ ), 137.85;  $^{19}\text{F}$  NMR (188 MHz,

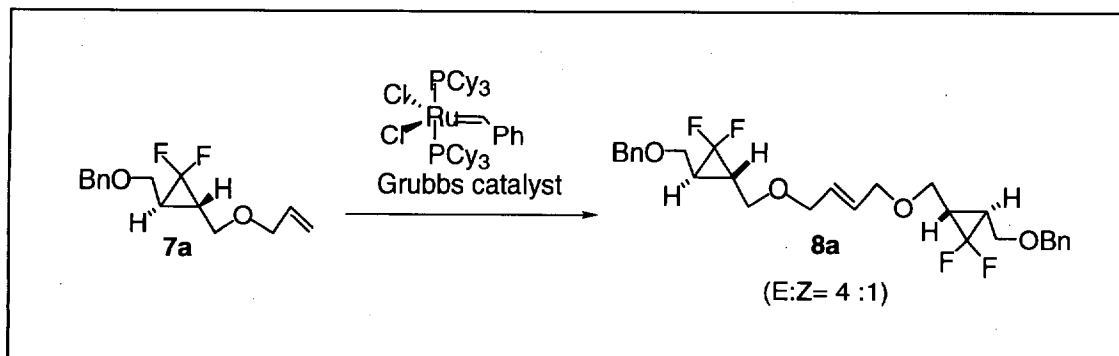
ppm, CDCl<sub>3</sub>) 24.10 (1F, dd, J= 159.0, 13.2), 25.73 (1F, dd, J= 159.0, 13.2); IR(neat) 3030, 2867, 1641, 1468, 1411, 1256, 1097, 740 cm<sup>-1</sup>; Anal. Calcd for C<sub>13</sub>H<sub>14</sub>F<sub>2</sub>O: C, 69.63; H,6.29 Found: C, 69.26; H, 6.33

(*E*)-(trans,trans)-1,8-Bisbenzyloxy-2,3-6,7-bis(difluoromethano)oct-4-ene (**6a**)



Method A: Three additions of the catalyst **4b** (42.5 mg, 0.020 mmol) at 12 h intervals were made to a dichloromethane (2 ml) solution of **5a** (224 mg, 1.00 mmol) with stirring at room temperature. After being stirred for a total of 36 h, the reaction was quenched by addition of a saturated ammonium chloride aqueous solution and the mixture was extracted with ethyl acetate. Silica gel flash column chromatography (hexane- ethyl acetate = 10:1) gave the metathesis product **6a** (62.7 mg, 0.155 mmol) in 31% yield. The starting compound **5a** was recovered in 50% yield (110mg). Metathesis product **6a** obtained was the only (*E*)-isomer and no stereoisomer was detected by <sup>1</sup>H NMR analysis: <sup>1</sup>H NMR (200 MHz, δ, CDCl<sub>3</sub>, J=Hz) 1.56-1.84 (2H, m), 3.45-3.69 (4H, m), 4.00 (2H, dt, J=5.4, 1.4), 4.54 (2H, ABq, J=12.0), 5.22 (1H, dt, J=5.9, 1.4), 5.24 (1H, ddd, J=30.4, 2.9, 1.3), 5.90 (1H, dddd, J=22.3, 10.7, 5.5, 1.0) 7.25-7.48 (5H, m); <sup>13</sup>C NMR (50 MHz, δ, CDCl<sub>3</sub>, J=Hz) 26.47 (t, J<sub>C-F</sub>=10.5), 65.95, 71.44, 72.52, 114.80 (t, J<sub>C-F</sub>=286.6), 117.33, 127.68, 127.74, 128.43, 134.39, 137.89; <sup>19</sup>F NMR (188 MHz, δ, CDCl<sub>3</sub>, J=Hz) 23.53 (t, J<sub>H-F</sub>=7.5); IR (neat, cm<sup>-1</sup>) 3027, 2865, 1677, 1481, 1367, 1262, 1194, 1022, 929, 743, 703; Anal. Calcd for C<sub>24</sub>H<sub>24</sub>F<sub>4</sub>O<sub>2</sub>: C, 68.56; H, 5.75 Found: C, 68.67; H, 5.76

Bis-1,4-[(1*SR*,3*SR*)-3-benzyloxymethyl-2,2-difluorocyclopropyl]methoxybut-2-ene  
(**8a**)



Method B: To a dichloromethane (1 ml) solution of **7a** (268 mg, 1.00 mmol) was added the catalyst **4a** (41.1 mg, 0.05 mmol) and the mixture was stirred for 24 h at room temperature. Silica gel flash column chromatography (hexane- ethyl acetate = 10:1) gave the metathesis product **8a** (203 mg, 0.40 mmol) in 80% yield. Stereochemistry of **8a** on the newly formed olefinic part was determined as (*E:Z*)= 4:1 by <sup>1</sup>H NMR analysis : <sup>1</sup>H NMR (200 MHz, δ, CDCl<sub>3</sub>, J=Hz) 1.89-2.10 (4H, m), 3.45-3.72 (8H, m), 3.85-4.12 (4H, m), 4.51 (4H, ABq, J=11.6), 5.69 (1H, t, J=3.9) (minor isomer), 5.77 (1H, t, J=2.7) (major isomer), 7.09-7.45 (10H, m); <sup>13</sup>C NMR (50 MHz, δ, CDCl<sub>3</sub>, J=Hz) 24.95 (t, J<sub>C-F</sub>=10.3), 63.49 (t, J<sub>C-F</sub>=4.9), 70.44, 72.75, 114.16 (dd, J<sub>C-F</sub>=289.8, 282.8), 128.51, 128.59, 129.24, 130.06, 138.64; <sup>19</sup>F NMR(188 MHz, δ, CDCl<sub>3</sub>, J=Hz) 10.88 (d, J<sub>F-F</sub>=162.1) (minor isomer), 10.99 (d, J<sub>F-F</sub>=161.8) (major isomer), 36.45 (dt, J<sub>F-F</sub>=162.1, J<sub>H-F</sub>=12.2); IR (neat, cm<sup>-1</sup>) 3029, 2866, 1710, 1602, 1476, 1367, 1283, 1189, 1088, 741. Anal. Calcd for C<sub>28</sub>H<sub>32</sub>F<sub>4</sub>O<sub>4</sub>: C, 66.13; H, 6.34 Found: C, 67.10; H, 6.41