

# A Palladium-Catalyzed Asymmetric Ring Expansion of Allenylcyclobutanols: An Atom Economic Approach for Asymmetric Wagner-Meerwein Shift

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## Supporting Information

### Part A: Experimental Section

#### Experimental

##### General

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. Some solvents were freshly purified by column before use: acetonitrile, methylene chloride, toluene, benzene, triethylamine, dimethylformamide, tetrahydrofuran and pyridine and diethyl ether. Methanol was distilled from magnesium methoxide. Solvents for Pd-catalyzed reactions were degassed by freeze-thaw techniques under vacuum<sup>1</sup>. Tris-(dibenzylideneacetone)palladium(0) monochloroform complex, Pd<sub>2</sub>dba<sub>3</sub>•CHCl<sub>3</sub> was prepared by the procedure of Ibers<sup>2</sup>. Ligands **L1**, **L2**, **L3**, and **L4** were prepared by literature procedures<sup>3,4</sup>. All other reagents were used as obtained unless otherwise noted.

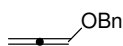
Flash Chromatography was performed with EM Science silica gel (0.040-0.063  $\mu$ m grade). Analytical thin-layer chromatography was performed with 0.2 mm coated commercial silica gel plates (E. Merck, DC-Plasrikfolien, kieselgel 60 F254). Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Kugelrohr distillations were performed on a Büchi GKR-50 glass tube oven.

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) data were acquired at 300 MHz on a Varian GEM-300, Varian mercury 400 (400 MHz) or on a Varian Unity Inova-500 (500 MHz) spectrometer.. Chemical shifts are reported in delta ( $\delta$ ) units, in parts per million (ppm) downfield from tetramethylsilane, or in ppm relative to the singlet at 7.26 ppm from chloroform-*d*. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) data were acquired at 75 MHz on a Varian GEM-300, 100 MHz on a Varian mercury 400 and at 125 MHz on a Varian Unity Inova-500 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d*.

Infrared (IR) data were recorded as films on sodium chloride plates or a potassium bromide (KBr) pellets on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm<sup>-1</sup>). High resolution mass spectral data (HRMS) were obtained from Mass Spectrometry Resource, School of S2 Pharmacy, University of California-San Francisco, on a Kratos MS9 spectrometer at an ionizing current of 98 mA and an ionizing voltage of 70 eV.

Elemental analyses (Anal.) were performed by M.-H.-W. Laboratories of Pheonix, AZ. Chiral GC analyses were performed on a HP 6890 series GC system using a Cyclosil B chiral column. GC analyses were performed on a HP 6850 series GC system using a Agilent Technologies HP-1 GC column (30 m length, 0.32 mm I.D., 0.25  $\mu$ m film). Chiral HPLC analyses were performed on a Thermo Separation Products Spectra Series P-100 or 200 and UV100 (254 nm) using Chiralcel® columns (OD, OB-H, OJ, AD, As, or OC) eluting with heptane / *iso*-propanol mixtures indicated. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm cells and the sodium D line (589 nm) at ambient temperature in the solvent and concentration indicated.

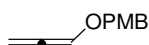
### **General Procedure for preparation of oxygen substituted allenes**



#### **Propa-1,2-dienyloxymethyl-benzene (1a)<sup>5</sup>**

At room temperature, 4.3 g (38.3 mmol) KO<sup>t</sup>Bu was added into the solution of 22 g (130 mmol) benzyl propargyl ether in 10 ml THF. The suspension was stirred at room temperature for 3 hours, then filtered through a celite pad and was washed with 50 ml Et<sub>2</sub>O. Combined solution was concentrated *in vacuo* and purified by flash chromatography (1% diethyl ether in petroleum ether) to afford **1a** as a light yellowish liquid (18 g, 82%).

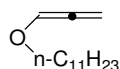
**R<sub>f</sub>** (5% ether / pet. ether): 0.84. **IR** (neat): 3034, 2925, 2868, 1953, 1726, 1454, 1442, 1349, 1190, 1043, 893, 737, 698 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.35 ~ 7.20 (m, 5H), 6.85 (dd, *J* = 6.3 Hz, 1H), 5.48 (d, *J* = 6.1 Hz, 2H), 4.62 (s, 2H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  132.0, 128.2, 123.5, 123.3, 123.1, 118.3, 101.1, 81.8, 66.1, 48.1, 24.8, 23.9, 17.0.



#### **1-Methoxy-4-propa-1,2-dienyloxymethyl-benzene (1b)<sup>6</sup>**

Allene **1b** was prepared according to the general procedure for allene preparation starting from 1-methoxy-4-prop-2-ynyloxymethyl-benzene (4.4 g, 25 mmol). Yield 3.5 g (80%).

**R<sub>f</sub>** (10% ether / pet. ether): 0.80. **IR** (neat): 3039, 3002, 2959, 2837, 1953, 1614, 1586, 1515, 1464, 1443, 1377, 1350, 1302, 1250, 1174, 1036, 892, 858, 822, 673 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.35 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.92 ~ 6.89 (m, 1H), 5.56 ~ 5.54 (m, 2H), 4.62 (s, 2H), 3.83 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  201.2, 159.2, 129.3, 129.1, 121.3, 113.6, 90.6, 70.2, 54.9.



#### **1-Propa-1,2-dienyloxy-undecane (1c)**

Allene **1c** was prepared according to the general procedure for allene preparation

starting from 1-prop-2-ynyloxy-undecane (1.2 g, 5.7 mmol). Yield 0.85 g (71%).

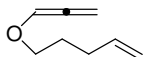
**R<sub>f</sub>** (5% ether / pet. ether): 0.90. **IR** (neat): 3042, 2925, 2855, 1953, 1467, 1446, 1379, 1351, 1262, 1202, 1104, 1044, 931, 888, 855, 795, 722 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.72 (t, *J* = 6.0 Hz, 1H), 5.42 (d, *J* = 6.0 Hz, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 1.70 ~ 1.60 (m, 2H), 1.38 ~ 1.22 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 201.4, 121.6, 90.3, 68.9, 31.9, 29.62, 29.60, 29.56, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. **HRMS** (EI+) *m/z* calculated for C<sub>14</sub>H<sub>26</sub>O [M]<sup>+</sup>: 210.1984, found: 210.1984.



#### 4-Propa-1,2-dienyloxy-but-1-ene (1d)

Allene **1d** was prepared according to the general procedure for allene preparation starting from 4-prop-2-ynyloxy-but-1-ene (1.95 g, 17.7 mmol). Yield 1.40 g (72%, 85% brsm), recovered 0.25 g starting material.

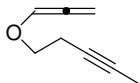
**R<sub>f</sub>** (5% ether / pet. ether): 0.85. **IR** (neat): 3080, 2978, 2923, 2873, 1952, 1643, 1446, 1352, 1202, 1045, 956, 917, 891, 856 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.74 (t, *J* = 6.0 Hz, 1H), 5.88 ~ 5.78 (m, 1H), 5.44 (d, *J* = 6.6 Hz, 2H), 5.15 ~ 5.05 (m, 2H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.44 ~ 2.38 (m, 16H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 201.3, 134.7, 121.5, 116.7, 90.6, 67.8, 33.5.



#### 5-Propa-1,2-dienyloxy-pent-1-ene (1e)

Allene **1e** was prepared according to the general procedure for allene preparation starting from 5-prop-2-ynyloxy-pent-1-ene (2.48 g, 20 mmol). Yield 2.0 g (81%)

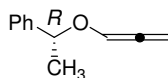
**R<sub>f</sub>** (10% ether / pet. ether): 0.90. **IR** (neat): 3079, 2977, 2941, 2873, 1953, 1642, 1446, 1351, 1203, 1046, 994, 914, 890, 857 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.74 (t, *J* = 6.0 Hz, 1H), 5.88 ~ 5.78 (m, 1H), 5.44 (d, *J* = 6.6 Hz, 2H), 5.15 ~ 5.05 (m, 2H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.44 ~ 2.38 (m, 16H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 201.3, 134.7, 121.5, 116.7, 90.6, 67.8, 33.5.



#### 5-Propa-1,2-dienyloxy-pent-2-yne (1f)

Allene **1f** was prepared according to the general procedure for allene preparation starting from 5-prop-2-ynyloxy-pent-2-yne (2.80 g, 22.9 mmol). Yield 2.0 g (71%)

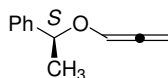
**R<sub>f</sub>** (10% ether / pet. ether): 0.82. **IR** (neat): 3044, 2976, 2921, 2878, 1952, 1468, 1446, 1352, 1200, 1106, 1048, 893, 856 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.75 (t, *J* = 6.0 Hz, 1H), 5.46 (d, *J* = 6.0 Hz, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.50 ~ 2.47 (m, 2H), 1.79 (t, *J* = 2.5 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 200.9, 121.3, 90.9, 76.9, 75.2, 67.1, 19.4, 3.5.



**((R)-1-Propa-1,2-dienyloxy-ethyl)-benzene(1g)**

Allenyl ether **1g** was prepared according to the general procedure starting from (*R*)-1-(prop-2-ynyloxy)-ethyl benzene (2.0 g, 12.5 mmol). Yield 1.4 g (70%, 80% brsm), recovered 0.20 g starting material.

**R<sub>f</sub>** (10% ether / pet. ether): 0.80. **IR** (neat): 3064, 3031, 2977, 1953, 1494, 1449, 1273, 1349, 1196, 1068, 1028, 890, 854, 760, 697, 668 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.34 ~ 7.24 (m, 5H), 6.22 (t, *J* = 6.0 Hz, 1H), 5.34 (m, 1H), 5.21 (m, 1H), 4.80 (q, *J* = 6.5 Hz, 1H), 1.51 (m, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 201.9, 143.1, 128.3, 127.4, 126.0, 120.1, 90.1, 76.6, 23.3, [*α*]<sub>D</sub><sup>24.1</sup> = 218.8 (c = 1.40, CH<sub>2</sub>Cl<sub>2</sub>), Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>: C, 82.46; H, 7.55; Found: C, 82.59; H, 7.52.



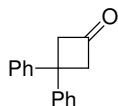
**((S)-1-Propa-1,2-dienyloxy-ethyl)-benzene(1h)**

Allenyl ether **1h** was prepared according to the general procedure starting from (*S*)-1-(prop-2-ynyloxy)-ethyl benzene (2.5 g, 15.6 mmol). Yield 1.8 g (75%, 80% brsm), recovered 0.125 g starting materials.

**R<sub>f</sub>** (10% ether / pet. ether): 0.80. **IR** (neat): 3064, 3031, 2977, 1953, 1494, 1449, 1273, 1349, 1196, 1068, 1028, 890, 854, 760, 697, 668 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.34 ~ 7.24 (m, 5H), 6.22 (t, *J* = 6.0 Hz, 1H), 5.34 (m, 1H), 5.21 (m, 1H), 4.80 (q, *J* = 6.5 Hz, 1H), 1.51 (m, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 201.9, 143.1, 128.3, 127.4, 126.0, 120.1, 90.1, 76.6, 23.3, [*α*]<sub>D</sub><sup>24.1</sup> = -260.0 (c = 1.30, CH<sub>2</sub>Cl<sub>2</sub>), Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>: C, 82.46; H, 7.55; Found: C, 82.49; H, 7.82.

**General Procedure for preparation of Substituted cyclobutanones**

Zinc catalyzed ketene [2+2] reaction followed by zinc catalyzed dehalogenation reduction.<sup>7</sup>



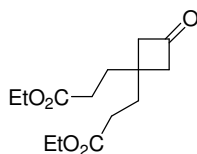
**3,3-Diphenyl-cyclobutanone(2a)<sup>8</sup>**

**Zinc catalyzed ketene [2+2] reaction:** To a stirred suspension of activated Zn-Cu<sup>7</sup> (4.90 g, 75 mmol) and ethene-1,1-diyldibenzene (5.41 g, 30 mmol) in dry Et<sub>2</sub>O (70 ml) was added dropwise through a addition funnel, during 2h at reflux, a solution of trichloroacetic chloride (6.7 ml, 60 mmol) and phosphorus oxychloride (5.7 ml, 60 mmol) in Et<sub>2</sub>O (30 ml). The suspension was stirred overnight at reflux. The mixture was cooled to room temperature and then filtered through a pad of Celite. The residue was washed with Et<sub>2</sub>O (3×15 ml). The combined solution was concentrated and then distilled in a Kugelrohr short-path distillation apparatus (200 ~

250 °C, 0.2 mtorr). The collected liquid was directly taken to the next step.

**Zinc catalyzed dehalogenation reduction:** The solution of the previous liquid in acetic acid (25 ml) was added dropwise to a vigorously stirred suspension of zinc dust (7.84 g, 120 mmol) in acetic acid (25 ml) at 0 °C. After the addition, the reaction mixture was heated at 70 °C for 2h. The mixture was allowed to cool to room temperature and then evacuated to get rid of most acetic acid. The residue was dissolved in Et<sub>2</sub>O (50 ml) and then poured into a separation funnel containing water (50 ml) and Et<sub>2</sub>O (50 ml). The organic layer was washed with water (3×25 ml), saturated sodium bicarbonate solution (2×30 ml) and brine (50 ml), dried over MgSO<sub>4</sub>. Then the solution was filtered, concentrated followed by purification with flash chromatography (15% ether in pet. ether). Yield: 3.5 g (61%) over white solid. M.P. = 76 ~ 78 °C.

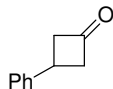
**R<sub>f</sub>** (25% ether in pet. ether): 0.53. **IR** (neat): 3082, 3026, 2972, 2924, 1787, 1595, 1580, 1493, 1449, 1375, 1239, 1127, 1084, 1022, 888, 777, 750, 710, 660, 584, cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.35 ~ 7.26 (m, 8H), 7.24 ~ 7.21 (m, 2H), 3.82 (s, 4H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 205.6, 147.2, 130.3, 128.6, 126.6, 60.5, 42.0.



### Diethyl-3,3'-(3-oxocyclobutane-1,1-diyl)dipropionate (**2d**)

Cyclobutanone **2d** was prepared according to the general procedure for preparation of substituted cyclobutanones diethyl-4-methylene- heptanedioate (4.10 g, 18.0 mmol). Yield: 2.2 g (50%) over two steps.

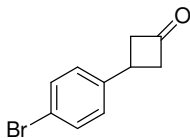
**R<sub>f</sub>** (50% ether in pet. ether): 0.50. **IR** (neat): 2978, 2928, 2862, 1779, 1728, 1452, 1416, 1376, 1300, 1251, 1161, 1113, 1023, 943, 853, 782cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 4.10 ~ 4.05 (m, 4H), 2.74 (s, 4H), 2.27 ~ 2.24 (m, 4H), 1.91 ~ 1.88 (m, 4H), 1.23 ~ 1.19 (m, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 205.9, 172.8, 60.5, 56.3, 32.0, 31.5, 30.1, 14.0. **HRMS** (EI+) m/z calculated for C<sub>14</sub>H<sub>22</sub>O<sub>5</sub> [M]<sup>+</sup>: 270.1467, found: [M+H]<sup>+</sup>: 271.1547, [M-Et]<sup>+</sup>: 241.1076.



### 3-phenyl-cyclobutanone (**2e**)<sup>9</sup>

Cyclobutanone **2e** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from styrene (1.90 g, 18.2 mmo). Yield: 2.0 g (75%) over two steps.

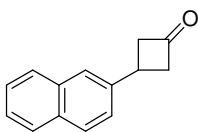
**IR** (neat): 23028, 2922, 1786, 1603, 1496, 1380, 1103, 759, 700cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.42 — 7.28 (m, 5H), 3.71(m, 1H), 3.55 — 3.49 (m, 2H), 3.31 — 3.25 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 206.6, 143.4, 128.5, 126.5, 126.3, 54.5, 28.2.



### 3-(4-Bromo-phenyl)-cyclobutanone (**2f**)<sup>10</sup>

Cyclobutanone **2f** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from 4-bromo-styrene (9.53 g, 50 mmol). Yield: 6.7 g (60%)

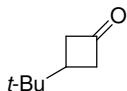
**IR** (neat): 3026, 2975, 2922, 1786, 1489, 1385, 1200, 1101, 1074, 1010, 869, 817, 718, 566 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.47 — 7.43 (m, 2H), 7.19 — 7.16 (m, 2H), 3.63 (tt, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H), 3.53 — 3.44 (m, 2H), 3.24 — 3.15 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 205.8, 142.4, 131.5, 128.2, 120.2, 54.5, 27.8.



### 3-naphthalen-2-yl-cyclobutanone (**2g**)<sup>10</sup>

Cyclobutanone **2g** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from 2-vinyl-naphthalene (11.6 g, 75.0 mmol). Yield: 4.0 g (67%) over two steps.

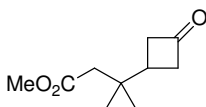
**IR** (neat): 3053, 2922, 1780, 1632, 1601, 1508, 1379, 1272, 1105, 964, 891, 856, 818, 749 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.76 (m, 3H), 7.64 (s, 1H), 7.46 — 7.40 (m, 2H), 7.32 (dd, *J*<sub>1</sub> = 8.5 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 3.63 (m, 1H), 3.49 — 3.41 (m, 2H), 3.29 — 3.22 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 206.5, 140.6, 133.1, 132.0, 128.4, 127.5, 127.4, 126.2, 125.6, 124.7, 124.6, 54.4, 28.4.



### 3-tert-Butyl-cyclobutanone (**2h**)<sup>11</sup>

Cyclobutanone **2h** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from 3,3-dimethylbut-1-ene (8.3 g, 9.9 mmol). Yield: 6.5 g (52%) over two steps.

**IR** (neat): 2959, 2869, 1787, 1740, 1471, 1394, 1367, 1243, 1208, 1108 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 2.87 — 2.75 (m, 4H), 2.28 — 2.21 (m, 1H), 0.88 (s, 9H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 207.9, 47.5, 34.5, 31.3, 26.2.

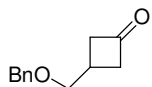


### 3-Methyl-3-(3-oxocyclobutyl)-butyric acid methyl ester (**2i**)

Cyclobutanone **2i** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from methyl 3,3-dimethylpent-4-

enoate (4.21 g, 29.6 mmol) except that the purification was done with flash chromatography. Yield: 3.0 g (55%, 70% brsm), recovered starting material 0.63g.

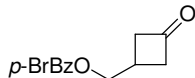
**R<sub>f</sub>** (50% ether / pet. ether): 0.58. **IR** (neat): 2963, 1785, 1735, 1469, 1438, 1391, 1326, 1288, 1239, 1210, 1156, 1112, 1047, 1015, 885, 856, 760cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 3.55 (s, 3H), 2.84 — 2.74 (m, 4H), 2.43 — 2.38 (m, 1H), 2.15 (s, 2H), 0.94 (s, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 206.6, 171.8, 51.1, 47.3, 44.7, 34.1, 33.1, 23.1. **HRMS** (EI+) *m/z* calculated for C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> [M]<sup>+</sup>: 184.1099, found: [M — H]<sup>+</sup>: 183.1013, [M — CH<sub>3</sub>]<sup>+</sup>: 169.0867.



### 3-Benzyloxymethyl-cyclobutanone (**2j**)<sup>12</sup>

Cyclobutanone **2j** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from allyloxymethyl-benzene (5.50 g, 37.1 mmol). Yield: 6.0 g (58%) over two steps.

**R<sub>f</sub>** (25% ether in pet. ether): 0.40. **IR** (neat): 3031, 2857, 1782, 1496, 1454, 1383, 1365, 1206, 1093, 1028, 738, 698cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.37 — 7.25 (m, 5H), 4.55 (s, 2H), 3.58 (d, *J* = 6.5Hz, 2H), 3.15 — 3.08 (m, 2H), 2.90 — 2.84 (m, 2H), 2.72 — 2.64 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 207.4, 137.9, 128.4, 127.7, 127.6, 73.1, 72.8, 49.9, 23.5.

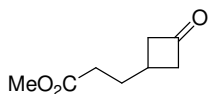


### 4-Bromo-benzoic acid 3-oxo-cyclobutylmethyl ester (**2k**)

To a stirred suspension of **2k** (761 mg, 4.0 mmol) and 20wt% Pd(OH)<sub>2</sub>/C (76 mg, 10 wt%) in EtOAc (10 ml) was bubbled through hydrogen with a ballone for 15 min. After stirring for overnight, the suspension was filtered through a Celite pad and the residue was washed with EtOAc (10 ml). The combined solution was concentrated and the residue was taken into next step.

To a solution of previous collected liquid and 4-bromobenzoyl chloride (1.05 g, 4.80 mmol) in DCM (15 ml) was added dropwise a solution of pyridine (0.90 ml, 8.0 mmol) in DCM (5 ml) at 0 °C. The solution was stirred at 0 °C and allowed to slowly warm to room temperature overnight. Then the solution was poured into an aqueous buffet solution (pH = 7) and extracted with DCM (3×10 ml). The combined organic layer was washed with brine (20 ml) and concentrated followed by purification with flash chromatography (25% Et<sub>2</sub>O in pet. ether). Yield: 560 mg (50%) over two steps.

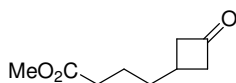
**R<sub>f</sub>** (25% ethylacetate in pet. ether): 0.62. **IR** (neat): 3088, 2952, 1772, 1724, 1590, 1479, 1394, 1278, 1121, 1066, 1009, 757cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.89 (m, 2H), 7.60 (m, 2H), 4.49 (d, *J* = 6.2Hz, 2H), 3.30 — 3.23 (m, 2H), 3.03 — 2.95 (m, 2H), 2.94 — 2.88 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 205.9, 165.7, 131.8, 131.1, 128.6, 128.4, 67.5, 50.1, 22.9. Anal. Calcd. for C<sub>12</sub>H<sub>11</sub>BrO<sub>3</sub>: C, 50.91; H, 3.92; Found: C, 51.00; H, 4.03.



### 3-(3-Oxo-cyclobutyl)-propionic acid methyl ester (2l)

Cyclobutanone **2l** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from 3-(2,2-Dichloro-3-oxo-cyclobutyl)-propionic acid methyl ester (9.0 g, 40.0 mmol). Yield: 5.0 g (80%).

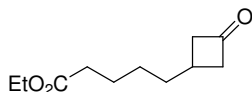
**R<sub>f</sub>** (50% ether / pet. ether): 0.42. **IR** (neat): 2954, 2863, 1783, 1736, 1438, 1385, 1347, 1258, 1199, 1175, 1106, 1057, 1007, 975, 884, 828, 780 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 3.69 (s, 3H), 3.21 — 3.12 (m, 2H), 2.75 — 2.66 (m, 2H), 2.52 — 2.40 (m, 1H), 2.38 (d, *J* = 7.6 Hz, 2H), 1.94 (t, *J* = 7.6 Hz, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 207.3, 173.3, 52.2, 51.6, 32.7, 31.2, 23.4, 23.3. **HRMS** (EI+) *m/z* calculated for C<sub>8</sub>H<sub>12</sub>O<sub>3</sub> [M]<sup>+</sup>: 156.0786, C<sub>7</sub>H<sub>9</sub>O<sub>3</sub> [M – CH<sub>3</sub>]<sup>+</sup>: 125.0602, [M – CH<sub>3</sub>]<sup>+</sup>: 125.0601.



### 4-(3-Oxo-cyclobutyl)-butyric acid methyl ester (2m)

Cyclobutanone **2m** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from Hex-5-enoic acid methyl ester (1.3 g, 10.1 mmol). Yield: 1.0 g (63%) over two steps.

**R<sub>f</sub>** (25% ether / pet. ether): 0.20. **IR** (neat): 2951, 2853, 1783, 1737, 1438, 1386, 1366, 1326, 1257, 1207, 1174, 1106, 1070, 995, 856, 744 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 3.68 (s, 3H), 3.19 — 3.12 (m, 2H), 2.72 — 2.65 (m, 2H), 2.36 (s, *J* = 7.2 Hz, 2H), 2.42 — 2.35 (m, 1H), 1.72 — 1.59 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 207.9, 173.7, 52.4, 51.5, 35.5, 33.6, 23.54, 23.47. **HRMS** (EI+) *m/z* calculated for C<sub>9</sub>H<sub>14</sub>O<sub>3</sub> [M]<sup>+</sup>: 170.0943, C<sub>8</sub>H<sub>11</sub>O<sub>3</sub> [M – CH<sub>3</sub>]<sup>+</sup>: 155.0708, [M – CH<sub>3</sub>]<sup>+</sup>: 155.0702.



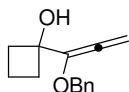
### 5-(3-Oxo-cyclobutyl)-pentanoic acid ethyl ester (2n)

Cyclobutanone **2n** was prepared according to the general procedure for preparation of substituted cyclobutanones starting from hept-6-enoic acid ethyl ester (9.37 g, 60.0 mmol). Yield: 5.6 g (47%) over two steps.

**R<sub>f</sub>** (50% ether / pet. ether): 0.58. **IR** (neat): 2935, 2857, 2361, 1784, 1733, 1460, 1374, 1304, 1248, 1181, 1104, 1033, 922, 858, 733, 668 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 4.16 — 4.10 (m, 2H), 3.17 — 3.10 (m, 2H), 2.70 — 2.64 (m, 2H), 2.40 — 2.35 (m, 1H), 2.34 — 2.31 (m, 2H), 1.70 — 1.65 (m, 2H), 1.64 — 1.59 (m, 2H), 1.40 — 1.35 (m, 2H), 1.28 — 1.24 (m, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 208.4, 173.4, 60.1, 52.3, 35.8, 34.0, 27.6, 24.5, 23.5, 14.1. **HRMS** (EI+) *m/z* calculated for C<sub>11</sub>H<sub>18</sub>O<sub>3</sub> [M]<sup>+</sup>: 198.1256, found: 198.1264



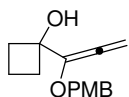
## General Procedure for Preparation of Allenylcyclobutanols



### 1-(1-Benzyloxy-propa-1,2-dienyl)-cyclobutanol (3a)

To a stirred solution of benzyloxyallene **3a** (1.46 g, 10.0 mmol) in THF (40 ml) was added dropwise a 2.70 M solution of *n*-BuLi (3.70 ml, 10.0 mmol) in hexane at -78 °C. After stirring was continued for 1h at -78 °C, cyclobutanone (0.75 ml, 10.0 mmol) was added dropwise to this solution and stirring was continued for 2h at -78 °C and then warmed to room temperature. The reaction mixture was diluted with water and extracted with diethyl ether. The combined extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography (15% diethyl ether in petroleum ether, silica gel) to give allenylcyclobutanol **3a** (2.05 g, 95%) as a white solid. **M.P.**: 43 ~ 45 °C.

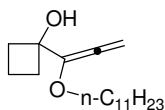
**R<sub>f</sub>** (25% ether / pet. ether): 0.30. **IR** (neat): 3420, 3089, 3062, 3035, 2981, 2936, 2864, 1952, 1495, 1450, 1374, 1244, 1177, 1136, 1096, 1024, 980, 953, 885, 850, 809, 728, 693 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.35 ~ 7.20 (m, 5H), 5.58 (s, 2H), 4.67 (s, 2H), 2.67 (s, 1H), 2.37 ~ 2.37(m, 2H), 2.22 ~ 2.14 (m, 2H), 1.82 ~ 1.73 (m, 1H), 1.61 ~ 1.50 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 196.3, 137.5, 135.8, 128.4, 127.9, 127.8, 92.6, 73.8, 71.0, 34.6, 12.8. **HRMS** (EI+) *m/z* calculated for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub> [M]<sup>+</sup>: 216.1150, found. 216.1148.



### 1-[1-(4-Methoxybenzyloxy)-propa-1,2-dienyl]-cyclobutanol (3b)

Allenylcyclobutanol **3b** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1b** (0.88 g, 5.0 mmol). Yield: 1.0 g (83%).

**R<sub>f</sub>** (25% ether / pet. ether): 0.20. **IR** (neat): 3428, 3035, 2942, 2869, 2837, 1953, 1613, 1587, 1515, 1455, 1423, 1377, 1302, 1247, 1174, 1124, 1091, 1034, 979, 889, 822, 776, 709 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.28 (dd, *J*<sub>1</sub> = 7.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 6.87 (dd, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 5.58 (s, 2H), 4.60 (s, 2H), 3.80 (s, 3H), 2.70 (s, 1H), 2.34 ~ 2.28 (m, 2H), 2.20 ~ 2.14 (m, 2H), 1.80 ~ 1.72 (m, 1H), 1.59 ~ 1.50 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 196.2, 159.3, 135.5, 129.5, 129.4, 113.7, 92.2, 73.6, 70.6, 55.2, 34.4, 12.6. Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>: C, 73.15; H, 7.37; Found: C, 73.33; H, 7.47.

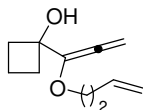


### 1-(1-Undecyloxy-propa-1,2-dienyl)-cyclobutanol (3c)

Allenylcyclobutanol **3c** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1c** (2.80 g, 13.3 mmol). Yield:

3.0 g (81%).

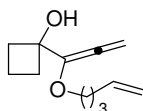
**R<sub>f</sub>** (25% ether / pet. ether): 0.50. **IR** (neat): 3422, 2923, 2854, 1954, 1455, 1378, 1246, 1183, 1136, 1099, 957, 884, 723 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.54 (s, 2H), 3.60 (t, *J* = 6.7 Hz, 2H), 2.60 (s, 1H), 2.33 ~ 2.26 (m, 2H), 2.21 ~ 2.13 (m, 2H), 1.81 ~ 1.71 (m, 1H), 1.69 ~ 1.60 (m, 2H), 1.59 ~ 1.50 (m, 1H), 1.38 ~ 1.22 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 196.2, 135.7, 91.7, 73.7, 69.3, 34.6, 29.9, 29.60, 29.58, 29.55, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1, 12.6. **HRMS** (EI+) *m/z* calculated for C<sub>18</sub>H<sub>32</sub>O<sub>2</sub> [M]<sup>+</sup>: 280.2402, found: 280.2402.



### 1-(1-But-3-enyloxy-propa-1,2-dienyl)-cyclobutanol (3d)

Allenylcyclobutanol **3d** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1d** (0.30 g, 2.72 mmol). Yield 0.36 g (73%).

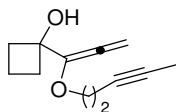
**R<sub>f</sub>** (25% ether / pet. ether): 0.33. **IR** (neat): 3418, 3080, 2975, 2944, 2869, 1955, 1744, 1657, 1452, 1376, 1246, 1182, 1135, 1100, 1035, 992, 891, 818 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.86 ~ 5.77 (m, 1H), 5.55 (s, 2H), 5.13 ~ 5.04 (m, 2H), 3.68 (t, *J* = 6.6 Hz, 2H), 3.05 (broad, 1H), 2.45 ~ 2.40 (m, 2H), 2.33 ~ 2.26 (m, 2H), 2.20 ~ 2.13 (m, 2H), 1.80 ~ 1.70 (m, 1H), 1.60 ~ 1.50 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ **HRMS** (EI+) *m/z* calculated for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> [M]<sup>+</sup>: 180.1150, found [M-H]<sup>+</sup>: 179.1080



### 1-(1-Pent-4-enyloxy-propa-1,2-dienyl)-cyclobutanol (3e)

Allenylcyclobutanol **3e** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1e** (0.62 g, 5.0 mmol). Yield 0.75 g (77%).

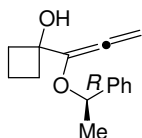
**R<sub>f</sub>** (25% ether / pet. ether): 0.40. **IR** (neat): 3446, 3078, 2976, 2942, 2874, 1953, 1641, 1450, 1355, 1246, 1182, 1135, 1098, 992, 956, 913, 886 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 5.87 ~ 5.78 (m, 1H), 5.55 (s, 2H), 5.05 ~ 4.97 (m, 2H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.62 (s, 1H), 2.33 ~ 2.28 (m, 2H), 2.21 ~ 2.14 (m, 4H), 1.80 ~ 1.73 (m, 3H), 1.59 ~ 1.50 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 196.0, 138.0, 135.6, 114.9, 91.9, 73.7, 68.5, 34.5, 30.2, 28.2, 12.6. **HRMS** (EI+) *m/z* calculated for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub> [M]<sup>+</sup>: 194.1307, found [M-C<sub>2</sub>H<sub>4</sub>]<sup>+</sup>: 166.0992. **LRMS** (ESI+) *m/z* calculated for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub> [M+Na]<sup>+</sup>: 217.1 found [M+Na]<sup>+</sup>: 217.1.



### 1-(1-Pent-3-ynoxy-propa-1,2-dienyl)cyclobutanol (**3f**)

Allenylcyclobutanol **3f** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1f** (0.45 g, 3.68 mmol). Yield 0.65 g (93%).

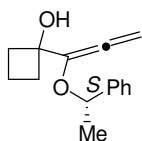
**R<sub>f</sub>** (25% ether / pet. ether): 0.40. **IR** (neat): 3424, 2988, 2944, 2879, 1954, 1450, 1426, 1378, 1246, 1182, 1135, 1102, 994, 956, 889 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.49 (s, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 2.90 (broad, 1H), 2.45 ~ 2.38 (m, 2H), 2.25 ~ 2.18 (m, 2H), 2.13 ~ 2.05 (m, 2H), 1.69 (t, *J* = 2.5 Hz, 3H), 1.74 ~ 1.64 (m, 1H), 1.49 ~ 1.40 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 195.7, 135.1, 92.0, 76.9, 75.1, 73.4, 67.2, 34.3, 19.2, 12.5, 3.2. **HRMS** (EI+) *m/z* calculated for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub> [M]<sup>+</sup>: 192.1150, found: 192.1148.



### 1-[1-(1-(*R*)-Phenyl-ethoxy)-propa-1,2-dienyl]-cyclobutanol (**3g**)

Allenylcyclobutanol **3g** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1g** (0.65 g, 4.06 mmol) and cyclobutanone (1.5 ml, 4.05 mmol). Yield: 0.85 g (92%).

**R<sub>f</sub>** (25% ether / pet. ether): 0.35. **IR** (neat): 3424, 3086, 3063, 3031, 2977, 2943, 1954, 1494, 1450, 1372, 1244, 1206, 1181, 1133, 1091, 1028, 956, 910, 885, 760, 731, 699, 546 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.33 ~ 7.23 (m, 5H), 5.47 (d, *J* = 7.8 Hz, 1H), 5.30 (d, *J* = 7.8 Hz, 1H), 4.85 (q, *J* = 6.5 Hz, 1H), 2.70 (broad, 1H), 2.32 ~ 2.26 (m, 2H), 2.20 ~ 2.14 (m, 2H), 1.77 ~ 1.71 (m, 1H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.54 ~ 1.46 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 196.9, 143.3, 134.2, 128.2, 127.3, 125.8, 91.9, 76.1, 73.6, 34.5, 34.2, 23.2, 12.6. [**α**]<sub>D</sub><sup>24.8</sup> = 154.6 (c = 2.30, CH<sub>2</sub>Cl<sub>2</sub>). **HRMS** (EI+) *m/z* calculated for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub> [M]<sup>+</sup>: 230.1307, found: 230.1310

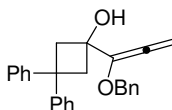


### 1-[1-(1-(*S*)-Phenyl-ethoxy)-propa-1,2-dienyl]-cyclobutanol (**3h**)

Allenylcyclobutanol **3h** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1h** (0.60 g, 3.75 mmol) and cyclobutanone (1.40 ml, 3.78 mmol). Yield: 0.75 g (87%).

**R<sub>f</sub>** (25% ether / pet. ether): 0.35. **IR** (neat): 3424, 3086, 3063, 3031, 2977, 2943, 1954, 1494, 1450, 1372, 1244, 1206, 1181, 1133, 1091, 1028, 956, 910, 885, 760, 731, 699, 546 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.33 ~ 7.23 (m, 5H), 5.47 (d, *J* = 7.8 Hz,

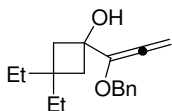
1H), 5.30 (d,  $J = 7.8$  Hz, 1H), 4.85 (q,  $J = 6.5$  Hz, 1H), 2.70 (broad, 1H), 2.32 ~ 2.26 (m, 2H), 2.20 ~ 2.14 (m, 2H), 1.77 ~ 1.71 (m, 1H), 1.52 (d,  $J = 6.5$  Hz, 3H), 1.54 ~ 1.46 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.9, 143.3, 134.2, 128.2, 127.3, 125.8, 91.9, 76.1, 73.6, 34.5, 34.2, 23.2, 12.6.  $[\alpha]_{\text{D}}^{24.8} = 154.6$  ( $c = 2.30$ ,  $\text{CH}_2\text{Cl}_2$ ), HRMS (EI+)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{18}\text{O}_2$   $[\text{M}]^+$ : 230.1307, found: 230.1310



#### 1-(1-Benzyloxy-propa-1,2-dienyl)-3,3-diphenylcyclobutanol (4a)

Allenylcyclobutanol **4a** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1a** (0.44 g, 3.0 mmol) and cyclobutanone **2a** (0.67 g, 3.0 mmol). Yield: 0.90 g (81%). M.P.: 85 ~ 87°C.

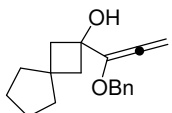
$\text{R}_f$  (25% ether / pet. ether): 0.28. IR (neat): 3549, 3414, 3061, 3020, 2928, 2936, 1954, 1597, 1293, 1441, 1228, 1134, 1103, 1026, 974, 886, 741,  $694\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.37 ~ 7.07 (m, 10H), 5.15 (s, 2H), 4.53 (s, 2H), 3.34 (d,  $J = 13.3\text{Hz}$ , 2H), 2.98 (d,  $J = 13.3\text{Hz}$ , 2H), 2.68 (broad, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.0, 150.7, 147.7, 137.3, 135.2, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7, 126.9, 126.7, 125.9, 92.6, 70.7, 69.9, 47.0, 42.7. HRMS (EI+)  $m/z$  calculated for  $\text{C}_{26}\text{H}_{24}\text{O}_2$   $[\text{M}]^+$ : 368.1776, found: 368.1784.



#### 1-(1-Benzyloxy-propa-1,2-dienyl)-3,3-diethylcyclobutanol (4b)

Allenylcyclobutanol **4b** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1a** (0.90 g, 6.18 mmol) and 3,3-diethylcyclobutanone **2b** (0.78 g, 6.18 mmol). Yield: 1.2g (72%).

$\text{R}_f$  (25% ether / pet. ether): 0.40. IR (neat): 3448, 3065, 3033, 2962, 2934, 2875, 1954, 1744, 1498, 1456, 1377, 1287, 1222, 1185, 1130, 1080, 1008, 887, 734,  $696\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.37 ~ 7.24 (m, 5H), 5.54 (s, 2H), 4.66 (s, 2H), 2.54 (broad, 1H), 2.16 (dd,  $J_1 = 10.8\text{Hz}$ ,  $J_2 = 3.0\text{Hz}$ , 2H), 1.86 (dd,  $J_1 = 10.8\text{Hz}$ ,  $J_2 = 3.0\text{Hz}$ , 2H), 1.56 (t,  $J = 6.5\text{Hz}$ , 2H), 1.37 (t,  $J = 6.5\text{Hz}$ , 2H), 0.76 (d,  $J = 6.5\text{Hz}$ , 3H), 0.69 (d,  $J = 6.5\text{Hz}$ , 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.7, 137.4, 127.3, 128.3, 127.7, 127.6, 92.7, 70.8, 69.4, 43.2, 33.2, 30.9, 29.0, 8.1, 7.8. Anal. Calcd. for  $\text{C}_{18}\text{H}_{24}\text{O}_2$ : C, 79.37; H, 8.88; Found: C, 79.60; H, 8.80.

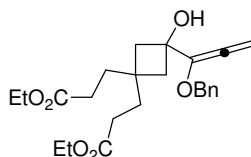


#### 2-(1-Benzyloxy-propa-1,2-dienyl)-spiro[3.4]octan-2-ol (4c)

Allenylcyclobutanol **4c** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1a** (0.85 g, 5.80 mmol) and

Spiro[3.4]octan-2-one **2c** (0.72 g, 5.80 mmol). Yield: 1.1 g (70%).

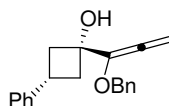
**R<sub>f</sub>** (25% ether / pet. ether): 0.40. **IR** (neat): 3448, 3065, 3033, 2962, 2934, 2875, 1954, 1744, 1498, 1456, 1377, 1287, 1222, 1185, 1130, 1080, 1008, 887, 734, 696 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.36 ~ 7.29 (m, 5H), 5.55 (s, 2H), 4.68 (s, 2H), 2.55 (broad, 1H), 2.08 (d, *J* = 13.1 Hz, 2H), 1.69 ~ 1.66 (m, 2H), 1.54 ~ 1.50 (m, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 196.8, 137.4, 136.6, 128.3, 127.8, 127.7, 92.7, 70.9, 69.8, 45.2, 41.1, 39.0, 37.4, 24.0, 23.6. **HRMS** (EI+) *m/z* calculated for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub> [M]<sup>+</sup>: 270.1620, found: 270.1618



#### Diethyl-3,3'-(3-(1-benzyloxy-propa-1,2-dienyl)-3-hydroxycyclobutane-1,1-diyl)di propanoate (**4d**)

Allenylcyclobutanol **4d** was prepared according to the general procedure for preparation of allenylcyclobutanols starting from allene **1a** (0.54 g, 3.70 mmol) and cyclobutanone **2d** (1.0 g, 3.79 mmol). Yield: 1.0 g (65%).

**R<sub>f</sub>** (50% ether / pet. ether): 0.25. **IR** (neat): 3497, 3065, 3032, 2979, 2933, 2872, 1953, 1782, 1732, 1498, 1455, 1375, 1301, 1182, 1117, 1028, 892, 856, 737, 698 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.37 ~ 7.27 (m, 10H), 5.59 (s, 2H), 4.66 (s, 2H), 4.14 ~ 4.09 (m, 4H), 2.63 (s, 1H), 2.24 ~ 2.20 (m, 4H), 2.15 ~ 2.12 (m, 2H), 1.93 (m, 2H), 1.90 ~ 1.87 (m, 2H), 1.72 ~ 1.69 (m, 2H), 1.27 ~ 1.24 (m, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 196.3, 173.6, 137.1, 136.7, 128.3, 127.8, 127.7, 93.3, 70.9, 69.1, 60.4, 60.3, 43.1, 33.6, 32.0, 31.9, 29.4, 29.2, 14.2. Anal. Calcd. for C<sub>24</sub>H<sub>32</sub>O<sub>6</sub>: C, 69.21; H, 7.74; Found: C, 68.97; H, 7.82.

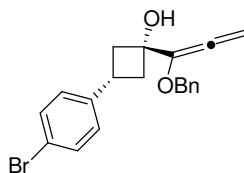


#### 1-(1-Benzyloxy-propa-1,2-dienyl)-3-phenyl-cyclobutanol (**4e**)

**Method A** : To a stirred solution of benzyloxallene **1a** (161 mg, 1.1 mmol) in THF (7 ml) was added dropwise a 2.43 M solution of n-BuLi (0.45 ml, 1.1 mmol) in hexane at -78 °C. After stirring was continued for 1h at -78 °C, a solution of cyclobutanone **2e** (146 mg, 1.0 mmol) in 3 ml THF was added dropwise and stirring was continued for 2h at -78 °C and then warmed up to r.t.. The reaction mixture was diluted with water and extracted with diethyl ethyl. The combined extracts was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by flash chromatography (20% diethyl ether in pet. ether, silica gel) to give allenylcyclobutanol as a yellowish oil. Reaction d.r. = 14:1 (by <sup>1</sup>HNMR). Isolated yield of the major isomer **4e**: 260mg (85%) d.r. = 15:1 (by <sup>1</sup>HNMR).

**Major diastereomer 4e.** **R<sub>f</sub>** (50% ether / pet. ether): 0.60. **IR** (neat): 3416, 3028, 2934, 1954, 1603, 1496, 1454, 1378, 1238, 1155, 1094, 1029, 892, 751, 697 cm<sup>-1</sup>. **<sup>1</sup>H**

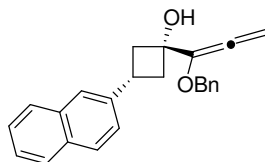
**NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.38 — 7.15 (m, 10H), 5.63 (s, 2H), 4.71 (s, 2H), 3.03 (m, 1H), 2.87 (s, 1H), 2.82 — 2.77 (m, 2H), 2.37 — 2.32 (m, 1H), 0.82 (s, 9H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  196.1, 144.8, 137.2, 135.5, 128.4, 128.2, 127.9, 127.8, 126.6, 125.9, 92.7, 71.0, 69.7, 42.4, 30.6. **HRMS** (EI+) *m/z* calculated for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> [M]<sup>+</sup>: 292.1463, found: 292.1467, Anal. Calcd. for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>: C, 82.16; H, 6.89; Found: C, 81.91; H, 7.03.



**1-(1-Benzyloxy-propa-1,2-dienyl)-3-(4-bromo-phenyl)-cyclobutanol (4f)**

Allenylcyclobutanol **4f** was prepared according to the general procedure **Method A** starting from the benzoxyallene (292mg, 2.0mmol) and cyclobutanone **2f** (450 mg, 2.0 mmol). Reaction d.r. > 10:1 (by <sup>1</sup>HNMR). Isolated yield of the major isomer **4f**: 580 mg (78%) d.r. > 20:1 (by <sup>1</sup>HNMR).

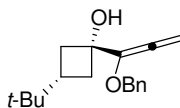
**Major diastereomer 4f.** *R<sub>f</sub>* (25% ether / pet. ether): 0.30. **IR** (neat): 3558, 3032, 2979, 2938, 1954, 1480, 1454, 1239, 1157, 1099, 1073, 1010, 892, 827, 732, 697cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 — 7.31 (m, 7H), 7.12 — 7.10 (m, 2H), 5.65 (s, 2H), 4.72 (s, 2H), 2.99 (m, 1H), 2.82 — 2.77 (m, 3H), 2.32 — 2.26 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  196.0, 143.9, 137.2, 135.3, 131.3, 128.4, 128.0, 127.8, 119.6, 92.9, 71.1, 69.6, 42.3, 30.1. **HRMS** (EI+) *m/z* calculated for C<sub>20</sub>H<sub>19</sub>BrO<sub>2</sub> [M]<sup>+</sup>: 370.0568, found: 370.0569.



**1-(1-Benzyloxy-propa-1,2-dienyl)-3-naphthalen-2-yl-cyclobutanol (4g)**

Allenylcyclobutanol **4g** was prepared according to the general procedure **Method A** starting from the benzoxyallene **1a** (804 mg, 5.5 mmol) and cyclobutanone **2g** (980mg, 5.0mmol). Reaction d.r. > 10:1 (by <sup>1</sup>HNMR). Isolated yield of the major isomer **4g**: 1.40 g (82%) d.r. > 20:1 (by <sup>1</sup>HNMR).

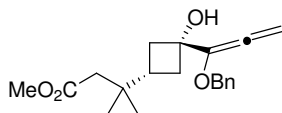
**Major diastereomer 4g.** *R<sub>f</sub>* (25% ether / pet. ether): 0.31. **IR** (neat): 3385, 3057, 2978, 2937, 2870, 1954, 1746, 1633, 1600, 1497, 1454, 1378, 1237, 1159, 1091, 1020, 891, 855, 818, 745, 697cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.72 (m, 3H), 7.62 (s, 1H), 7.40 — 7.24 (m, 8H), 5.60 (s, 2H), 4.69 (s, 2H), 3.18 (quin, *J* = 8.9 Hz, 1H), 3.04 (s, 1H), 2.88 — 2.84 (m, 2H), 2.46 — 2.42 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  196.1, 142.1, 137.1, 135.4, 133.3, 131.9, 128.3, 127.8, 127.6, 127.43, 127.41, 125.8, 125.3, 125.1, 124.6, 92.6, 70.9, 69.7, 42.2, 30.7. Anal. Calcd. for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>: C, 84.18; H, 6.48; Found: C, 84.11; H, 6.40.



### 1-(1-Benzyloxy-propa-1,2-dienyl)-3-*tert*-butyl-cyclobutanol (**4h**)

Allenylcyclobutanol **4h** was prepared according to the general procedure **Method A** starting from the benzoxyallene (535 mg, 3.66 mmol) and cyclobutanone **2h** (0.42 g, 3.33 mmol). Reaction d.r. = 10:1 (by  $^1\text{H}$ NMR). Isolated yield of the major isomer **4h**: 600mg (66%) d.r.= 18:1 (by  $^1\text{H}$ NMR).

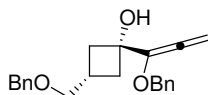
**Major diastereomer 4h.**  $R_f$  (25% ether / pet. ether): 0.38. **IR** (neat): 3422, 3032, 2952, 2865, 1955, 1455, 1364, 1237, 1157, 1092, 1010, 886, 734, 696 $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 — 7.28 (m, 5H), 5.57 (s, 2H), 4.67 (s, 2H), 2.72 (s, 1H), 2.25 — 2.21 (m, 2H), 1.94 — 1.89 (m, 2H), 1.69 — 1.62 (m, 1H), 0.82 (s, 9H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.2, 137.3, 135.9, 128.3, 127.8, 127.7, 92.2, 70.9, 68.8, 36.8, 35.6, 30.8, 26.5. **HRMS** (EI+)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{24}\text{O}_2$   $[\text{M}]^+$ : 272.1776, found: 272.1778



### 3-[3-(1-Benzyloxy-propa-1,2-dienyl)-3-hydroxy-cyclobutyl]-3-methyl-butiric acid methyl ester (**4i**)

Allenylcyclobutanol **4i** was prepared according to the general procedure **Method A** starting from the benzoxyallene (715 mg, 4.89 mmol) and cyclobutanone **2i** (900 mg, 4.89 mmol). Reaction d.r. = 10:1 (by  $^1\text{H}$ NMR). Isolated yield of the major isomer **4i**: 1.20 g (75%) d.r. = 16:1 (by  $^1\text{H}$ NMR).

**Major diastereomer 4i.**  $R_f$  (50% ether / pet. ether): 0.46. **IR** (neat): 3449, 3032, 2954, 1954, 1735, 1452, 1369, 1324, 1235, 1124, 1015, 889, 826, 737, 697 $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 — 7.26 (m, 5H), 5.58 (s, 2H), 4.67 (s, 2H), 3.62 (s, 3H), 2.77 (broad, 1H), 2.27 — 2.23 (m, 2H), 2.12 (s, 1H), 1.96 — 1.92 (m, 2H), 1.85 — 1.79 (m, 2H), 0.95 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 172.7, 137.2, 135.6, 128.3, 127.8, 127.7, 92.4, 70.9, 68.8, 51.1, 44.6, 35.8, 35.5, 34.0, 23.6. **HRMS** (EI+)  $m/z$  calculated for  $\text{C}_{20}\text{H}_{26}\text{O}_4$   $[\text{M}]^+$ : 330.1831, found: 330.1840. Anal. Calcd. for  $\text{C}_{20}\text{H}_{26}\text{O}_4$ : C, 72.70; H, 7.93.; Found: C, 72.56; H, 7.72.

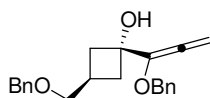


### 3-Benzyloxymethyl-1-(1-benzyloxy-propa-1,2-dienyl)-cyclobutanol (**4j**)

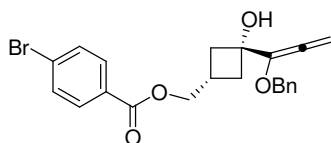
**Method B** : To a stirred solution of benzyloxyallene **1a** (146 mg, 1.0 mmol) in THF (7 ml) was added dropwise a 2.50 M solution of  $n\text{-BuLi}$  (0.40 ml, 1.0 mmol) in hexane at  $-78^\circ\text{C}$ . After stirring was continued for 1h at  $-78^\circ\text{C}$ , it was warmed up to  $0^\circ\text{C}$  and a solution of  $\text{Et}_2\text{Zn}$  (1.0 ml, 1.0 mmol) in hexane was added. The resulting solution was stirred at  $0^\circ\text{C}$  for 15 min and cooled to  $-78^\circ\text{C}$  followed by the addition of cyclobutanone **2j** (190 mg, 1.0 mmol) in 3 ml THF and stirring was continued for

2h at -78 °C and then warmed up to r.t.. The reaction mixture was saturated NH<sub>4</sub>Cl (10 ml) and extracted with diethyl ether (3×5 ml). The combined extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by flash chromatography (30% diethyl ether in pet. ether, silica gel) to give allenylcyclobutanol **4j** as a yellowish oil. Reaction d.r. = 10:1 (by <sup>1</sup>H NMR). Isolated yield of the major isomer **4j**: 269 mg (80%) d.r. > 20:1 (by <sup>1</sup>H NMR).

**Major diastereomer 4j.** *R<sub>f</sub>* (50% ether / pet. ether): 0.53. **IR** (neat): 3448, 3065, 3033, 2962, 2934, 2875, 1954, 1744, 1498, 1456, 1377, 1287, 1222, 1185, 1130, 1080, 1008, 887, 734, 696 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.34 — 7.26 (m, 10H), 5.57 (s, 2H), 4.67 (s, 2H), 4.51 (s, 2H), 3.47 (d, *J* = 6.5 Hz, 2H), 2.98 (s, 1H), 2.54 — 2.50 (m, 2H), 2.20 — 2.14 (m, 1H), 1.99 — 1.95 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 196.1, 138.3, 137.3, 135.7, 128.3, 127.8, 127.7, 127.6, 127.5, 92.7, 74.5, 73.0, 70.9, 70.6, 38.0, 25.9. **HRMS** (EI+) *m/z* calculated for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub> [M]<sup>+</sup>: 336.1725, [M-Bn]<sup>+</sup>: 245.1178, found: [M-Bn]<sup>+</sup>: 245.1185, **LRMS** (ESI+) for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub> [M+Na]<sup>+</sup>: 359.1, found: [M+Na]<sup>+</sup>: 359.1.



**Minor diastereomer 4j'** *R<sub>f</sub>* (50% ether / pet. ether): 0.45. **IR** (neat): 3448, 3065, 3033, 2962, 2934, 2875, 1954, 1744, 1498, 1456, 1377, 1287, 1222, 1185, 1130, 1080, 1008, 887, 734, 696 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.35 — 7.26 (m, 10H), 5.51 (s, 2H), 4.64 (s, 2H), 4.48 (s, 2H), 3.42 (d, *J* = 7.2 Hz, 2H), 2.73 — 2.67 (m, 1H), 2.49 (s, 1H), 2.29 — 2.25 (m, 2H), 2.21 — 2.17 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 196.3, 138.5, 137.3, 136.6, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 93.2, 74.1, 72.9, 72.3, 70.9, 36.5, 26.4. **HRMS** (EI+) *m/z* calculated for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub> [M]<sup>+</sup>: 336.1725, found: 336.1728



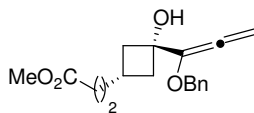
#### 4-Bromo-benzoic acid 3-(1-benzyloxy-propa-1,2-dienyl)-3-hydroxy-cyclobutyl methyl ester (**4k**)

Allenylcyclobutanol **4k** was prepared according to the general procedure **Method B** starting from the benzoxyallene (180 mg, 1.23 mmol) and cyclobutanone **2k** (349 mg, 1.23 mmol). Reaction d.r. = 5.4 :1 (by <sup>1</sup>H NMR). Isolated yield of the major isomer **4k**: 328 mg (76%) d.r. > 20:1 (by <sup>1</sup>H NMR).

**Major diastereomer 4k.** *R<sub>f</sub>* (50% ether / pet. ether): 0.47. **IR** (neat): 3448, 3032, 2940, 2886, 1954, 1719, 1590, 1455, 1398, 1272, 1103, 1012, 757, 734, 697 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.90 (m, 2H), 7.57 (m, 2H), 7.36 — 7.28 (m, 5H), 5.62 (s, 2H), 4.68 (s, 2H), 4.32 (d, *J* = 6.2 Hz, 2H), 2.77 (s, 1H), 2.56 — 2.52 (m, 2H), 2.34 — 2.27 (m, 1H), 2.11 — 2.07 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 195.8, 165.8, 137.1, 135.5, 131.6, 131.1, 129.1, 128.4, 127.9, 127.7, 93.0, 71.0, 70.3, 68.6, 37.6,



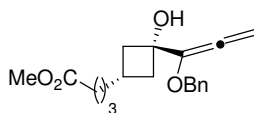
24.9. **HRMS** (EI+)  $m/z$  calculated for  $C_{22}H_{21}BrO_4$   $[M]^+$ : 428.0623, found: 428.0614.



**3-[3-(1-Benzyloxy-propa-1,2-dienyl)-3-hydroxy-cyclobutyl]-propionic acid methyl ester (5h)**

Allenylcyclobutanol **5h** was prepared according to the general procedure **Method B** starting from the benzoxyallene **1a** (146 mg, 1.0 mmol) and cyclobutanone **2l** (156 mg, 1.0 mmol). Reaction d.r. = 5.8:1 (by  $^1\text{H}$ NMR). Isolated yield of the mixture of diastereomers 212 mg (70%) d.r. = 7.0:1 (by  $^1\text{H}$ NMR).

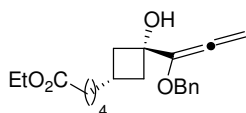
**Major diastereomer 5h.**  $R_f$  (50% ether / pet. ether): 0.40. **IR** (neat): 3435, 3064, 3032, 2974, 2932, 2862, 1954, 1732, 1607, 1497, 1454, 1349, 1236, 1100, 1027, 891, 825, 737, 697,  $595\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.37 — 7.26 (m, 5H), 5.57 (s, 2H), 4.66 (s, 2H), 3.65 (s, 3H), 2.76 (s, 1H), 2.52 — 2.46 (m, 2H), 2.27 — 2.21 (m, 3H), 1.83 — 1.69 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.0, 173.9, 137.2, 135.6, 128.3, 127.8, 127.7, 92.6, 70.9, 70.0, 51.4, 40.4, 32.0, 31.98, 25.4. **HRMS** (EI+)  $m/z$  calculated for  $C_{18}H_{22}O_4$   $[M]^+$ : 302.1518, found: 320.1527.



**4-[3-(1-Benzyloxy-propa-1,2-dienyl)-3-hydroxy-cyclobutyl]-butyric acid methyl ester (4m)**

Allenylcyclobutanol **4m** was prepared according to the general procedure **Method B** starting from the benzoxyallene **1a** (146mg, 1.0mmol) and cyclobutanone **2m** (156mg, 1.0mmol). Reaction d.r. = 6.2:1 (by  $^1\text{H}$ NMR). Isolated yield of the mixture of diastereomers 231 mg (73%) d.r. = 7.0:1 (by  $^1\text{H}$ NMR).

**Major diastereomer 4m.**  $R_f$  (50% ether / pet. ether): 0.40. **IR** (neat): 3460, 3032, 2931, 1954, 1737, 1498, 1455, 1376, 1235, 1166, 1100, 1028, 889, 821, 734,  $696\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.38 — 7.28 (m, 5H), 5.57 (s, 2H), 4.66 (s, 2H), 3.65 (s, 3H), 2.74 (s, 1H), 2.50 — 2.47 (m, 2H), 2.27 (t,  $J = 7.5$  Hz, 2H), 2.31 — 2.24 (m, 1H), 1.82 — 1.74 (m, 2H), 1.59 — 1.49 (m, 2H), 1.46 — 1.42 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 174.1, 137.3, 135.8, 128.3, 127.8, 127.68, 127.61, 92.5, 70.9, 70.1, 51.4, 40.7, 36.4, 33.9, 25.6, 22.8. **HRMS** (EI+)  $m/z$  calculated for  $C_{18}H_{22}O_4$   $[M]^+$ : 302.1518, found: 320.1527.



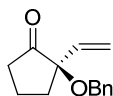
**5-[3-(1-Benzyloxy-propa-1,2-dienyl)-3-hydroxy-cyclobutyl]-pentanoic acid ethyl**

#### ester (4n)

Allenylcyclobutanol **4n** was prepared according to the general procedure **Method B** starting from the benzoxyallene **1a** (292 mg, 2.0 mmol) and cyclobutanone **2n** (39 mg, 2.0 mmol). Reaction d.r. = 5.6:1 (by  $^1\text{H}$ NMR). Isolated yield of the mixture of diastereomers 500 mg (73%) d.r. = 6.4:1 (by  $^1\text{H}$ NMR).

**Major diastereomer 4n.**  $R_f$  (50% ether / pet. ether): 0.40. **IR** (neat):  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 — 7.26 (m, 5H), 5.56 (s, 2H), 4.66 (s, 2H), 4.10 (t,  $J$  = 7.2 Hz, 3H), 2.85 (broad, 1H), 2.50 — 2.42 (m, 2H), 2.28 — 2.19 (m, 3H), 1.80 — 1.70 (m, 3H), 1.62 — 1.54 (m, 2H), 1.46 — 1.35 (m, 2H), 1.26 — 1.20 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 173.7, 137.3, 135.8, 128.3, 127.7, 127.6, 126.8, 92.3, 70.8, 70.1, 60.1, 40.7, 36.6, 34.2, 26.8, 25.7, 24.7, 14.1. **HRMS** (EI+)  $m/z$  calculated for  $\text{C}_{21}\text{H}_{28}\text{O}_4$   $[\text{M}]^+$ : 344.1988,  $\text{C}_{14}\text{H}_{21}\text{O}_4$   $[\text{M}-\text{C}_7\text{H}_7]^+$ : 253.1440, found: 253.1440. Anal. Calcd. for  $\text{C}_{21}\text{H}_{28}\text{O}_4$ : C, 73.23; H, 8.19.; Found: C, 73.42; H, 8.29.

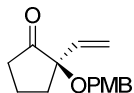
#### General procedure for palladium-catalyzed ring expansion reaction.



#### **2-Benzyloxy-2-vinyl-cyclopentanone (5a)**

DCE (25ml, which was dried and freeze-pump-thaw) was added into the mixture of  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$  (65.8 mg, 63.6  $\mu\text{mol}$ ) and (*R,R*)-stilbene ligand **L3** (150.3 mg, 0.191 mmol) within a flask which was three times evacuated and flushed with argon. The mixture was stirred under argon at room temperature for 15 min. Then it was cannulated into the allenylcyclobutanol **3a** (550 mg, 2.54 mmol) with 4Å MS which was three times evacuated and flushed with argon followed by adding  $\text{PhCO}_2\text{H}$  (0.25 ml, 1 M in  $\text{CH}_2\text{Cl}_2$ , 0.25 mmol) and  $\text{Et}_3\text{N}$  (0.25 ml, 1 M in  $\text{CH}_2\text{Cl}_2$ , 0.25 mmol) respectively *via* syringe. After stirring under argon at 30 °C for 12 h, the mixture was filtered through a Celite pad, concentrated and purified by direct flash chromatography (5% diethyl ether in petroleum ether, silica gel) to give the desired product **5a** (530 mg, 96%). Racemic product was prepared using the same procedure with racemic standard Trost ligand **L1**.

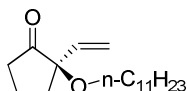
$R_f$  (25% ether / pet. ether): 0.50. **IR** (neat): 3085, 3058, 3022, 2958, 2913, 2877, 1746, 1492, 1451, 1401, 1379, 1157, 1130, 1080, 1053, 931, 808, 736, 695, 659  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 — 7.20 (m, 5H), 5.92 (dd,  $J$  = 17.5 Hz, 11 Hz, 1H), 5.46 (dd,  $J$  = 11 Hz, 0.9 Hz 1H), 5.41 (dd,  $J$  = 17.5 Hz, 0.9 Hz 1H), 4.52 (d,  $J$  = 11.5 Hz, 1H), 4.48 (d,  $J$  = 11.5 Hz, 1H), 2.41 ~ 2.25 (m, 2H), 2.24 ~ 2.18 (m, 1H), 2.14 ~ 2.02 (m, 2H), 1.88 ~ 1.79 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.3, 137.5, 135.8, 128.4, 127.9, 127.8, 92.6, 73.8, 71.0, 34.6, 12.8. **HRMS** (EI+)  $m/z$  calculated for  $[\text{M}]^+$ ; found  $[\alpha]_D^{24.8}$  = -68.58 ( $c$  = 1.70,  $\text{CH}_2\text{Cl}_2$ ), Enantiomeric excess was determined to be 92% ee by chiral HPLC (Chiralpak OD, heptane:*i*-PrOH = 99.5:0.5, 1.0 mL/min,  $t_1$  = 17.22 min(**major**),  $t_2$  = 20.25 min). Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_2$ : C, 77.75; H, 7.46; Found: C, 77.90; H, 7.36.



### 2-(4-Methoxy-benzyloxy)-2-vinyl-cyclopentanone (**5b**)

Cyclopentanone **5b** was prepared according to the general procedure for ring expansion at room temperature overnight with (*R,R*)-stilbene ligand **L3** starting from allenylcyclobutanol **3b** (495 mg, 2.0 mmol). Yield 480 mg (97%).

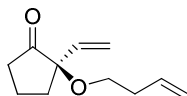
**R<sub>f</sub>** (25% ether / pet. ether): 0.30. **IR** (neat): 2961, 2837, 1744, 1613, 1586, 1464, 1404, 1379, 1301, 1249, 1173, 1035, 934, 821, 766, 705, 661 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.23 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz), 5.92 (dd, *J*<sub>1</sub> = 18 Hz, *J*<sub>2</sub> = 11 Hz, 1H), 5.45 (dd, *J*<sub>1</sub> = 11 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.41 (dd, *J*<sub>1</sub> = 18 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.48 (d, *J* = 11 Hz, 1H), 4.40 (d, *J* = 11 Hz, 1H), 3.78 (s, 3H), 2.40~2.24 (m, 2H), 2.21~2.16 (m, 1H), 2.12~2.00 (m, 2H), 1.89~1.77 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 214.8, 159.0, 135.0, 130.6, 129.2, 119.4, 113.7, 83.5, 66.3, 55.2, 36.2, 34.9, 17.4. **HRMS** (EI+) *m/z* calculated for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub> [*M*]<sup>+</sup>: 246.1256, found 246.1259. **[α]<sub>D</sub><sup>22.1</sup>** = -49.57 (c = 0.80, CH<sub>2</sub>Cl<sub>2</sub>), Enantiomeric excess was determined to be 89% ee by chiral HPLC (Chiralpak AD, heptane:*i*-PrOH = 99:1, 1.0 mL/min, *t*<sub>1</sub> = 15.18 min (major), *t*<sub>2</sub> = 16.76 min).



### 2-Undecyloxy-2-vinylcyclopentanone (**5c**)

Cyclopentanone **5c** was prepared according to the general procedure for ring expansion at room temperature overnight with (*R,R*)-stilbene ligand **L3** starting from allenylcyclobutanol **3c** (140 mg, 0.50 mmol). Yield 140 mg (100%).

**R<sub>f</sub>** (25% ether in pet. ether): 0.75. **IR** (neat): 2924, 2855, 1744, 1466, 1406, 1379, 1305, 1272, 1164, 1119, 1081, 994, 930, 812, 713, 663 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.80 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 5.37 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.32 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 3.41~3.30 (m, 2H), 2.38~2.19 (m, 2H), 2.14~2.05 (m, 2H), 2.05~1.96 (m, 1H), 1.84~1.73 (m, 1H), 1.54~1.47 (m, 2H), 1.30~1.20 (m, 16H), 0.86 (t, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 214.7, 135.1, 118.8, 83.2, 64.4, 36.0, 34.3, 31.9, 30.1, 29.6, 29.5, 29.4, 29.3, 26.0, 22.6, 17.4, 14.1. **HRMS** (EI+) *m/z* calculated for C<sub>18</sub>H<sub>32</sub>O<sub>2</sub> [*M*]<sup>+</sup>: 280.2402, found 280.2394. **[α]<sub>D</sub><sup>24.5</sup>** = -53.82 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>), Enantiomeric excess was determined to be 86% ee by chiral GC (Cyclosil B column, 150 °C, 1.2 mL/min, *t*<sub>1</sub> = 104.36 min, *t*<sub>2</sub> = 10.66 min (major)).

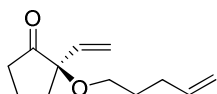


### 2-(But-3-enyloxy)-2-vinyl-cyclopentanone (**5d**)

Cyclopentanone **5d** was prepared according to the general procedure for ring expansion at room temperature overnight with (*R,R*)-stilbene ligand **L3** starting from

allenylcyclobutanol **3d** (54 mg, 0.30 mmol). Yield 42 mg (78%).

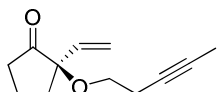
**R<sub>f</sub>** (25% ether in pet. ether): 0.60. **IR** (neat): 3079, 2965, 1743, 1641, 1452, 1406, 1382, 1272, 1165, 1118, 1072, 994, 928, 807, 714 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.85 ~ 5.74 (m, 2H), 5.40 (dd, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.35 (dd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.09 ~ 5.00 (m, 2H), 3.51 ~ 3.47 (m, 1H), 3.44 ~ 3.40 (m, 1H), 2.39 ~ 2.23 (m, 4H), 2.14 ~ 2.08 (m, 2H), 2.07 ~ 2.00 (m, 1H), 1.84 ~ 1.78 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 214.5, 135.0, 134.9, 119.1, 116.3, 83.3, 63.7, 36.0, 34.5, 34.3, 17.4. **HRMS** (EI+) *m/z* calculated for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> [M]<sup>+</sup>: 180.1150, found: [α]<sub>D</sub><sup>22.9</sup> = -68.94 (c = 0.84, CH<sub>2</sub>Cl<sub>2</sub>), Enantiomeric excess was determined to be 87% ee by chiral GC (Cyclosil B column, 60 °C, 1.0 flow rate, *t*<sub>1</sub> = 66.77 min, *t*<sub>2</sub> = 66.84 min (**major**)).



## 2-(Pent-4-enyloxy)-2-vinylcyclopentanone (**5e**)

Cyclopentanone **5e** was prepared according to the general procedure with (*R,R*)-stilbene ligand **L3** for ring expansion at room temperature overnight with starting from allenylcyclobutanol **3e** (78 mg, 0.50 mmol). Yield 78 mg (100%).

**R<sub>f</sub>** (25% ether in pet. ether): 0.50. **IR** (neat): 3078, 2941, 2883, 1744, 1641, 1449, 1406, 1272, 1165, 1129, 1080, 994, 913, 812, 714, 672 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.85 ~ 5.75 (m, 2H), 5.39, (dd, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.34 (dd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.03 ~ 4.93 (m, 2H), 3.45 ~ 3.35 (m, 2H), 2.39 ~ 2.23 (m, 2H), 2.13 ~ 2.00 (m, 5H), 1.85 ~ 1.73 (m, 1H), 1.66 ~ 1.61 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 214.7, 138.2, 135.0, 118.9, 114.6, 83.2, 63.6, 36.0, 34.2, 30.1, 29.2, 17.4. **HRMS** (EI+) *m/z* calculated for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub> [M]<sup>+</sup>: 194.1307, found: 194.1309. [α]<sub>D</sub><sup>22.6</sup> = -82.08 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>), Enantiomeric excess was determined to be 86% ee by chiral GC (Cyclosil B column, 60°C, 1.0 flow rate, *t*<sub>1</sub> = 67.72 min, *t*<sub>2</sub> = 66.75 min (**major**)).

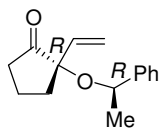


## 2-(Pent-3-ynyloxy)-2-vinylcyclopentanone (**5f**)

Cyclopentanone **5f** was prepared according to the general procedure with (*R,R*)-stilbene ligand **L3** for ring expansion at room temperature overnight starting from allenylcyclobutanol **3f** (96.6 mg, 0.50 mmol). Yield 85 mg (88%).

**R<sub>f</sub>** (25% ether in pet. ether): 0.55. **IR** (neat): 3067, 2964, 2921, 2885, 2361, 1744, 1636, 1464, 1405, 1273, 1158, 1131, 1083, 993, 935, 810, 662 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 5.76 (ddd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 11.0 Hz, *J*<sub>3</sub> = 1.0 Hz, 1H), 5.36 (dd, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.31 (dd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 3.50 ~ 3.39 (m, 2H), 2.34 ~ 2.25 (m, 2H), 2.24 ~ 2.19 (m, 2H), 2.10 ~ 2.06 (m, 2H), 2.04 ~ 1.95 (m, 1H), 1.80 ~ 1.70 (m, 1H), 1.71 (m, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 214.4, 134.6, 130.2, 119.3, 83.5, 75.6, 63.3, 35.9, 34.2, 20.5, 17.3, 3.4. **HRMS** (EI+) *m/z* calculated

for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub> [M]<sup>+</sup>: 192.1150, found: 192.1149. [ $\alpha$ ]<sub>D</sub><sup>23.3</sup> = -63.69 (c = 1.5, CH<sub>2</sub>Cl<sub>2</sub>), Enantiomeric excess was determined to be 84% ee by chiral GC (Cyclosil B column, 60°C, 1.2 flow rate, *t*<sub>1</sub> = 64.86 min, *t*<sub>2</sub> = 64.96 min (**major**)).

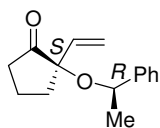


### 2-(*R*)-[1-(*R*)-Phenyl-ethoxy]-2-vinyl-cyclopentanone (**5g**)

Cyclopentanone **5g** was prepared from allenylcyclobutanol **3g** (69.1 mg, 0.30 mmol) according to the general procedure for ring expansion with (*R,R*)-stilbene ligand **L3** (17.2 mg, 0.0225 mmol) at 30 °C. Total yield 62 mg (90%). d.r. =15:1 (<sup>1</sup>H NMR)

#### Major diastereomer **5g**

*R*<sub>f</sub> (25% ether in pet. ether): 0.65. **IR** (neat): 3087, 3029, 2973, 1744, 1632, 1603, 1493, 1450, 1404, 1370, 1283, 1158, 1069, 1029, 1000, 944, 809, 762, 701 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.30 ~ 7.19 (m, 5H), 5.85 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 5.38 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.33 (dd, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 4.68 (q, *J* = 6.5 Hz, 1H), 2.16 ~ 1.84 (m, 5H), 1.79 ~ 1.71 (m, 1H), 1.41 (d, *J* = 6.5 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 215.3, 145.0, 135.7, 128.1, 126.9, 125.9, 118.1, 83.5, 73.0, 36.0, 35.8, 26.0, 17.5. [ $\alpha$ ]<sub>D</sub><sup>22.1</sup> = 32.44 (c = 2.10, CH<sub>2</sub>Cl<sub>2</sub>).

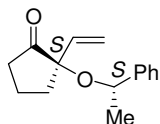


### 2-(*S*)-[1-(*R*)-Phenyl-ethoxy]-2-vinyl-cyclopentanone (**5g'**)

Cyclopentanone **5g'** was prepared from allenylcyclobutanol **3g** (69.1 mg, 0.30 mmol) according to the general procedure for ring expansion with (*S,S*)-stilbene ligand **L3** (17.2 mg, 0.30 mmol) at 30 °C. Total yield 62 mg (90%). d.r. =12:1 (<sup>1</sup>H NMR)

#### Major diastereomer **5g'**

*R*<sub>f</sub> (25% ether in pet. ether): 0.62. **IR** (neat): 3087, 3029, 2973, 1744, 1632, 1603, 1493, 1450, 1404, 1370, 1283, 1158, 1069, 1029, 1000, 944, 809, 762, 701 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.30 ~ 7.21 (m, 5H), 5.74 (dd, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 10.9 Hz, 1H), 5.32 (dd, *J*<sub>1</sub> = 10.9 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.28 (dd, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 4.79 (q, *J* = 6.5 Hz, 1H), 2.36 ~ 2.20 (m, 2H), 1.92 ~ 1.85 (m, 3H), 1.71 ~ 1.63 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 215.0, 145.9, 135.4, 128.1, 126.9, 125.9, 119.3, 84.1, 72.7, 35.8, 34.9, 25.5, 17.3. [ $\alpha$ ]<sub>D</sub><sup>23.8</sup> = 191.64 (c = 2.35, CH<sub>2</sub>Cl<sub>2</sub>).

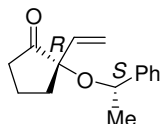


### 2-(*S*)-[1-(*S*)-Phenyl-ethoxy]-2-vinyl-cyclopentanone (**5h**)

Cyclopentanone **5h** was prepared from allenylcyclobutanol **3h** (69.1 mg, 0.30 mmol) according to the general procedure for ring expansion with (*R,R*)-stilbene ligand **L3** (17.2 mg, 0.30 mmol) at 30 °C. Total yield 60 mg (87%). d.r. = 12:1 (<sup>1</sup>H NMR)

#### Major diastereomer **5h**

**R<sub>f</sub>** (25% ether in pet. ether): 0.65. **IR** (neat): 3087, 3029, 2973, 1744, 1632, 1603, 1493, 1450, 1404, 1370, 1283, 1158, 1069, 1029, 1000, 944, 809, 762, 701 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.30 ~ 7.19 (m, 5H), 5.85 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 5.38 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.33 (dd, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 4.68 (q, *J* = 6.5 Hz, 1H), 2.16 ~ 1.84 (m, 5H), 1.79 ~ 1.71 (m, 1H), 1.41 (d, *J* = 6.5 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 215.3, 145.0, 135.7, 128.1, 126.9, 125.9, 118.1, 83.5, 73.0, 36.0, 35.8, 26.0, 17.5. [**α**]<sub>D</sub><sup>24.2</sup> = -30.94 (c = 2.20, CH<sub>2</sub>Cl<sub>2</sub>).

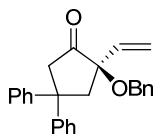


### 2-(*R*)-[1-(*S*)-Phenyl-ethoxy]-2-vinyl-cyclopentanone (**5h'**)

Cyclopentanone **5h'** was prepared from allenylcyclobutanol **3h** (69.1 mg, 0.30 mmol) according to the general procedure for ring expansion with (*S,S*)-stilbene ligand **L3** (17.2 mg, 0.30 mmol) at 30°C. Total yield 62 mg (90%). d.r. = 15:1 (<sup>1</sup>H NMR)

#### Major diastereomer **5h'**

**R<sub>f</sub>** (25% ether in pet. ether): 0.62. **IR** (neat): 3087, 3029, 2973, 1744, 1632, 1603, 1493, 1450, 1404, 1370, 1283, 1158, 1069, 1029, 1000, 944, 809, 762, 701 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.30 ~ 7.21 (m, 5H), 5.74 (dd, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 10.9 Hz, 1H), 5.32 (dd, *J*<sub>1</sub> = 10.9 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.28 (dd, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 4.79 (q, *J* = 6.5 Hz, 1H), 2.36 ~ 2.20 (m, 2H), 1.92 ~ 1.85 (m, 3H), 1.71 ~ 1.63 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 215.0, 145.9, 135.4, 128.1, 126.9, 125.9, 119.3, 84.1, 72.7, 35.8, 34.9, 25.5, 17.3. [**α**]<sub>D</sub><sup>25.9</sup> = -190.81 (c = 2.30, CH<sub>2</sub>Cl<sub>2</sub>).

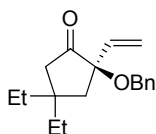


### 2-Benzyloxy-4,4-diphenyl-2-vinyl-cyclopentanone (**6a**)

Cyclopentanone **6a** was prepared from allenylcyclobutanol **4a** (110 mg, 0.30 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (18.3 mg, 0.0225 mmol) at 60°C for 12h. Yield 105 mg (95%).

**R<sub>f</sub>** (25% ether in pet. ether): 0.60. **IR** (neat): 3093, 3062, 3022, 2910, 1738, 1494, 1448, 1412, 1377, 1065, 1025, 995, 929, 731, 697 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.31 ~ 7.15 (m, 13H), 7.00 ~ 6.98 (m, 2H), 5.71 (dd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H),

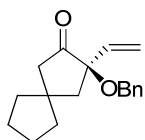
5.23 (d,  $J = 11.0$  Hz, 1H), 5.20 (d,  $J = 17.5$  Hz, 1H), 4.43 (d,  $J = 11.0$  Hz, 1H), 4.33 (d,  $J = 11.0$  Hz, 1H), 3.35 (dd,  $J_1 = 18.0$  Hz,  $J_2 = 1.3$  Hz, 1H), 3.23 (dd,  $J_1 = 18.0$  Hz,  $J_2 = 1.3$  Hz, 1H), 3.20 (dd,  $J_1 = 14.0$  Hz,  $J_2 = 1.2$  Hz, 1H), 3.04 (dd,  $J_1 = 14.0$  Hz,  $J_2 = 1.2$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  212.2, 147.2, 147.1, 138.2, 135.2, 130.3, 128.51, 128.46, 128.1, 127.4, 127.3, 126.7, 126.6, 126.4, 126.2, 119.2, 82.5, 66.2, 50.6, 48.2, 47.8. HRMS (EI+)  $m/z$  calculated for  $\text{C}_{26}\text{H}_{24}\text{O}_2$   $[\text{M}]^+$ : 368.1776, found: 368.1775.  $[\alpha]_{\text{D}}^{25.0} = -54.08$  ( $c=1.40$ ,  $\text{CH}_2\text{Cl}_2$ ). Enantiomeric excess was determined to be 95% ee by chiral HPLC (Chiralpak AD, heptane:*i*-PrOH = 99:1, 1.0 mL/min,  $t_1 = 13.85$  min(major),  $t_2 = 18.87$  min).



### 2-(benzyloxy)-4,4-diethyl-2-vinylcyclopentanone (6b)

Cyclopentanone **6b** was prepared from allenylcyclobutanol **4b** (109 mg, 0.40 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (24.4 mg, 0.030 mmol) at 60 °C for 6h. Yield 100mg (92%).

$R_f$  (25% ether in pet. ether): 0.90. IR (neat): 3032, 2964, 2937, 2879, 1740, 1638, 1607, 1498, 1455, 1380, 1315, 1272, 1166, 1054, 1000, 934, 867, 802, 734, 697 $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 ~ 7.25 (m, 5H), 5.96 (ddd,  $J_1 = 17.5$  Hz,  $J_2 = 11$  Hz, 1H), 5.41 (dd,  $J_1 = 11$  Hz,  $J_2 = 1$  Hz, 1H), 5.39 (dd,  $J_1 = 17.5$  Hz,  $J_2 = 1$  Hz, 1H), 4.51 (d,  $J = 11.6$  Hz, 1H), 4.46 (d,  $J = 11.6$  Hz, 1H), 2.40 (d,  $J = 18.0$  Hz, 1H), 2.22 ~ 2.14(m, 2H), 2.02 (d,  $J = 14.5$  Hz, 1H), 1.61 ~ 1.55 (m, 2H), 1.43 ~ 1.38 (m, 2H), 0.85 ~ 0.80 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  214.6, 138.6, 136.5, 128.2, 127.4, 127.3, 118.7, 83.3, 66.2, 49.5, 44.9, 38.8, 30.7, 30.3, 8.34, 8.30. HRMS (EI+)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{24}\text{O}_2$   $[\text{M}]^+$ : 272.1776, found: 272.1766.  $[\alpha]_{\text{D}}^{22.5} = -67.29$  ( $c = 1.40$ ,  $\text{CH}_2\text{Cl}_2$ ). Enantiomeric excess was determined to be 94% ee by chiral HPLC (Chiralpak OD, heptane:*i*-PrOH = 99.9:0.2, 0.8 mL/min,  $t_1 = 18.91$  min(major),  $t_2 = 23.29$  min).

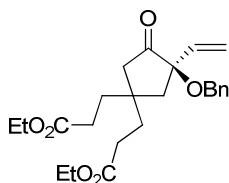


### 3-Benzyloxy-3-vinyl-spiro[4.4]nonan-2-one (6c)

Cyclopentanone **6c** was prepared from allenylcyclobutanol **4c** (108 mg, 0.40 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (24.4 mg, 0.030 mmol) at 60°C for 6h. Yield 100 mg (93%)

$R_f$  (25% ether in pet. ether): 0.92. IR (neat): 3031, 2953, 2870, 1740, 1498, 1454, 1400, 1380, 1272, 1056, 1028, 934, 801, 734, 697 $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 ~ 7.24 (m, 5H), 5.97 (dd,  $J_1 = 17.5$  Hz,  $J_2 = 11$  Hz, 1H), 5.43 (dd,  $J_1 = 11$  Hz,  $J_2 = 1$  Hz, 1H), 5.40 (dd,  $J_1 = 17.5$  Hz,  $J_2 = 1$  Hz, 1H), 4.52 (d,  $J = 11.5$  Hz, 1H), 4.47 (d,  $J = 11.5$  Hz, 1H), 2.40 (dd,  $J_1 = 18.5$  Hz,  $J_2 = 1.5$  Hz, 1H), 2.29 ~ 2.12 (m, 2H),

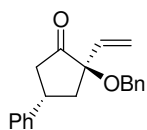
2.16 (d,  $J = 13.5$  Hz, 1H), 1.72 ~ 1.55 (m, 8H)..  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  214.4, 138.5, 135.9, 128.2, 127.5, 127.3, 119.2, 83.9, 66.3, 50.7, 47.0, 43.4, 40.2, 23.9, 23.8. **LRMS** (ESI+)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{22}\text{O}_2$   $[\text{M}+\text{H}]^+$ : 271.2, found: 271.2.  $[\alpha]_{\text{D}}^{22.5} = -67.29$  ( $c = 1.40$ ,  $\text{CH}_2\text{Cl}_2$ ). Enantiomeric excess was determined to be 92% ee by chiral HPLC (Chiralpak OD, heptane:*i*-PrOH = 99.9:0.1, 0.8 mL/min,  $t_1 = 30.39$  min(**major**),  $t_2 = 33.37$  min).



### Diethyl-3,3'-(3-(benzyloxy)-4-oxo-3-vinylcyclopentane-1,1-diyl)dipropionate (**6d**)

Cyclopentanone **6d** was prepared from allenylcyclobutanol **4d** (125 mg, 0.30 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (18.3 mg, 0.0225 mmol) at 60 °C for 8h. Yield 100 mg (80%)

**R<sub>f</sub>** (50% ether in pet. ether): 0.60. **IR** (neat): 2981, 2933, 2873, 1734, 1498, 1455, 1379, 1305, 1245, 1182, 1098, 1027, 937, 856, 736, 698  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 ~ 7.23 (m, 5H), 5.95 (dd,  $J_1 = 17.5$  Hz,  $J_2 = 11.0$  Hz, 1H), 5.43 (dd,  $J_1 = 11$  Hz,  $J_2 = 1$  Hz, 1H), 5.39 (dd,  $J_1 = 17.5$  Hz,  $J_2 = 1$  Hz, 1H), 4.50 (d,  $J = 11.5$  Hz, 1H), 4.46 (d,  $J = 11.5$  Hz, 1H), 4.14 ~ 4.07 (m, 4H), 2.43 (dd,  $J_1 = 18.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 2.33 ~ 2.19 (m, 6H), 1.99 (d,  $J = 14.6$  Hz, 1H), 1.93 ~ 1.89 (m, 2H), 1.76 ~ 1.71 (m, 2H), 1.27 ~ 1.21 (m, 6H)..  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  212.9, 173.1, 173.0, 138.2, 135.7, 128.4, 128.2, 127.5, 126.9, 119.2, 82.9, 66.4, 60.6, 60.5, 49.6, 45.7, 37.8, 33.6, 32.6, 29.4, 29.3, 14.1. **HRMS** (ES+)  $m/z$  calculated for  $\text{C}_{24}\text{H}_{32}\text{O}_6$   $[\text{M}]^+$ : 416.2199, found:  $[\alpha]_{\text{D}}^{24.5} = -59.82$  ( $c = 1.65$ ,  $\text{CH}_2\text{Cl}_2$ ). Enantiomeric excess was determined to be 94% ee by chiral HPLC (Chiralpak AD, heptane:*i*-PrOH = 98:2, 0.8 mL/min,  $t_1 = 25.55$  min(**major**),  $t_2 = 30.97$  min).



### 2-Benzyloxy-4-phenyl -2-vinyl-cyclopentanone (**6e**)

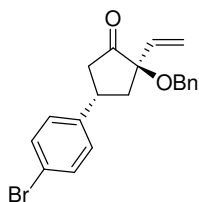
DCE (2ml, which was dried and free-pump-thaw) was added into the mixture of  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (5.2 mg, 5.0  $\mu\text{mol}$ ) and (*R,R*)-stilbene ligand **L3** (11.8 mg, 0.015 mmol) within the flask which was three times evacuated and flushed with argon. The mixture was stirred under argon at room temperature for 15 min. Then it was cannulated into the allenylcyclobutanol **4e** (58.5 mg, 0.20 mmol) with 4Å MS which was three times evacuated and flushed with argon followed by adding  $\text{PhCO}_2\text{H}$  (20  $\mu\text{l}$ , 1 M in  $\text{CH}_2\text{Cl}_2$ , 0.02 mmol) and  $\text{Et}_3\text{N}$  (20  $\mu\text{l}$ , 1 M in  $\text{CH}_2\text{Cl}_2$ , 0.02 mmol) respectively *via* syringe. After stirring under argon at 60 °C for 6h, the mixture was filtered through a Celite pad, concentrated and purified by direct flash chromatography (10% diethyl ether in petroleum ether, silica gel) to give desired product **6e** d.r. = 8.3:1 ( $^1\text{H}$



NMR). Isolated yield of the major isomer **6e** 47 mg (89%), 88%ee.

#### Major diastereomer **6e**

**R<sub>f</sub>** (25% ether in pet. ether): 0.69. **IR** (neat): 3030, 2924, 2855, 1741, 1652, 1497, 1455, 1274, 1215, 1058, 994, 930, 803, 761, 698 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.37 — 7.28 (m, 10H), 6.08 (dd, *J*<sub>1</sub> = 18.0 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 5.49 (dd, *J*<sub>1</sub> = 18.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.47 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 2.91 (ddd, *J*<sub>1</sub> = 19.0 Hz, *J*<sub>2</sub> = 7.9 Hz, *J*<sub>3</sub> = 2.7 Hz, 1H), 2.66 (ddd, *J*<sub>1</sub> = 13.8 Hz, *J*<sub>2</sub> = 6.0 Hz, *J*<sub>3</sub> = 2.7 Hz, 1H), 2.41 (dd, *J*<sub>1</sub> = 19.0 Hz, *J*<sub>2</sub> = 11.1 Hz, 1H), 2.05 (dd, *J*<sub>1</sub> = 13.9 Hz, *J*<sub>2</sub> = 12.1 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 211.9, 142.7, 138.2, 134.3, 129.7, 128.7, 128.4, 127.6, 126.8, 126.7, 119.6, 83.5, 66.6, 44.7, 44.3, 37.3. **HRMS** (EI+) *m/z* calculated for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub> [M]<sup>+</sup>: 272.1776, found: 272.1781. [**α**]<sub>D</sub><sup>22.0</sup> = -64.17 (*c* = 1.56, CH<sub>2</sub>Cl<sub>2</sub>, 88%ee). Enantiomeric excess was determined to be 88% ee by chiral HPLC (Chiralpak ODH, 220 nm, heptane:*i*-PrOH = 99: 1, 0.8 mL/min, *t*<sub>1</sub> = 20.28 min(**major**), *t*<sub>2</sub> = 22.03 min).

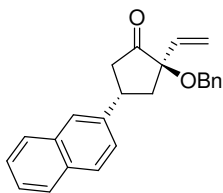


#### 2-Benzoyloxy-4-(4-bromo-phenyl)-2-vinyl-cyclopentanone (**6f**)

Cyclopentanone **6f** was prepared from allenylcyclobutanol **4f** (74.3 mg, 0.20 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (12.2 mg, 0.015 mmol) at 60°C. d.r. = 13.5:1 (<sup>1</sup>H NMR). Isolated yield of the major isomer **6f** 58 mg (78%, 82% brsm), 90%ee.

#### Major diastereomer **6f**

**R<sub>f</sub>** (25% ether in pet. ether): 0.67. **IR** (neat): 3031, 2959, 2924, 1742, 1490, 1454, 1414, 1380, 1214, 1129, 1046, 1010, 932, 825, 737, 697 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.47 — 7.43 (m, 2H), 7.37 — 7.27 (m, 5H), 7.13 — 7.10 (m, 2H), 6.08 (dd, *J*<sub>1</sub> = 18.0 Hz, *J*<sub>2</sub> = 10.7 Hz, 1H), 5.50 (dd, *J*<sub>1</sub> = 11.6 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.49 (dd, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.43 (d, *J* = 11.4 Hz, 1H), 3.73 — 3.64 (m, 1H), 2.90 (ddd, *J*<sub>1</sub> = 18.9 Hz, *J*<sub>2</sub> = 8.0 Hz, *J*<sub>3</sub> = 2.6 Hz, 1H), 2.90 (ddd, *J*<sub>1</sub> = 13.7 Hz, *J*<sub>2</sub> = 6.0 Hz, *J*<sub>3</sub> = 2.6 Hz, 1H), 2.35 (dd, *J*<sub>1</sub> = 18.9 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 2.00 (dd, *J*<sub>1</sub> = 13.7 Hz, *J*<sub>2</sub> = 12.2 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 211.3, 141.7, 138.1, 134.0, 131.7, 128.6, 128.4, 127.66, 127.60, 120.4, 119.8, 83.3, 66.6, 44.5, 44.3, 36.8. **HRMS** (EI+) *m/z* calculated for C<sub>20</sub>H<sub>19</sub>BrO<sub>2</sub> [M]<sup>+</sup>: 370.0568, C<sub>13</sub>H<sub>12</sub>BrO<sub>2</sub> [M-C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>: 279.0021, found (C<sub>20</sub>H<sub>19</sub>BrO<sub>2</sub> - C<sub>7</sub>H<sub>7</sub>): 278.9936(-Bn). [**α**]<sub>D</sub><sup>22.4</sup> = -47.44 (*c* = 2.80, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined to be 90% ee by chiral HPLC (Chiralpak ODH, 220 nm, heptane:*i*-PrOH = 99:1, 1.0 mL/min, *t*<sub>1</sub> = 19.67 min(**major**), *t*<sub>2</sub> = 24.00 min).

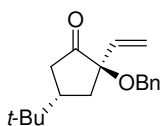


### 2-Benzoyloxy-4-(4-bromo-phenyl)-2-vinyl-cyclopentanone (**6g**)

Cyclopentanone **6g** was prepared from allenylcyclobutanol **4g** (68.5mg, 0.20mmol) according to the general procedure for ring expansion with (*R,R*)-stilbene ligand **L3** (11.8 mg, 0.015 mmol) at 60°C. d.r. = 13.5:1 (<sup>1</sup>H NMR). Isolated yield of the major isomer **6g** 60 mg (88%), 85%ee

#### Major diastereomer **6g**

**R<sub>f</sub>** (25% ether in pet. ether): 0.67. **IR** (neat): 3058, 2961, 2924, 1741, 1634, 1601, 1508, 1454, 1416, 1380, 1272, 1126, 1047, 931, 857, 818, 737, 697cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.83 — 7.78 (m, 3H), 7.67 (broad, 1H), 7.49 — 7.43 (m, 2H), 7.38 — 7.34 (m, 5H), 7.31 — 7.30 (m, 1H), 6.08 (dd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 11.4 Hz, 1H), 5.52 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.51 (dd, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.4 Hz, 1H), 3.95 — 3.86 (m, 1H), 2.98 (ddd, *J*<sub>1</sub> = 18.9 Hz, *J*<sub>2</sub> = 8.8 Hz, *J*<sub>3</sub> = 2.8 Hz, 1H), 2.74 (ddd, *J*<sub>1</sub> = 13.7 Hz, *J*<sub>2</sub> = 6.0 Hz, *J*<sub>3</sub> = 2.8 Hz, 1H), 2.52 (dd, *J*<sub>1</sub> = 18.9 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 2.16 (dd, *J*<sub>1</sub> = 13.7 Hz, *J*<sub>2</sub> = 12.1 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 211.8, 140.0, 138.2, 134.2, 133.4, 132.3, 128.4, 127.63, 127.61, 127.60, 127.55, 126.3, 125.7, 125.2, 125.1, 119.7, 83.5, 66.6, 44.6, 42.3, 37.4. **HRMS** (EI+) *m/z* calculated for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub> [M]<sup>+</sup>: 342.1620, found: 342.1613. [α]<sub>D</sub><sup>21.6</sup> = -88.66 (c = 1.10, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined to be 85% ee by chiral HPLC (Chiralpak ODH, 220 nm, heptane:*i*-PrOH = 90:10, 0.80 mL/min, *t*<sub>1</sub> = 12.76 min (major), *t*<sub>2</sub> = 16.82 min).



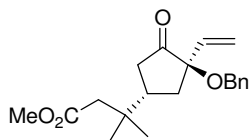
### 2-Benzoyloxy-4-*tert*-butyl-2-vinyl-cyclopentanone (**6h**)

Cyclopentanone **6h** was prepared from allenylcyclobutanol **4h** (81.7 mg, 0.30 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (18.3 mg, 0.0225 mmol) at 60 °C. d.r. = 10:1 (<sup>1</sup>H NMR) Isolated yield of the major isomer **6h** 65 mg (80%), 88%ee

#### Major diastereomer **6h**

**R<sub>f</sub>** (25% ether in pet. ether): 0.76. **IR** (neat): 3031, 2960, 2869, 1740, 1473, 1366, 1274, 1231, 1053, 1027, 931, 734, 697cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.34 — 7.25 (m, 5H), 6.01 (dd, *J*<sub>1</sub> = 18.0 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 5.43 (dd, *J*<sub>1</sub> = 18.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.42 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.51 (d, *J* = 11.6 Hz, 1H), 4.36 (d, *J* = 11.6 Hz, 1H), 2.46 — 2.31 (m, 2H), 2.26 — 2.22 (m, 1H), 2.03 (dd, *J*<sub>1</sub> = 18.4 Hz, *J*<sub>2</sub> = 10.7 Hz, 1H), 1.63 (m, 1H), 0.89 (s, 9H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 213.2, 138.4, 134.8, 128.3, 127.51, 127.48, 119.0, 83.8, 66.5, 42.4, 39.1, 37.9, 31.3, 27.0. **HRMS** (EI+) *m/z* calculated for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub> [M]<sup>+</sup>: 272.1776, found: 272.1781.

$[\alpha]_D^{22.2} = -57.01$  ( $c = 1.20$ ,  $\text{CH}_2\text{Cl}_2$ ). Enantiomeric excess was determined to be 88% ee by chiral HPLC (Chiralpak AD, 220 nm, heptane:*i*-PrOH = 99.8:0.2, 1.0 mL/min,  $t_1 = 9.55$  min(**major**),  $t_2 = 10.52$  min).

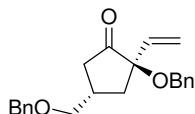


### 3-(3-Benzyloxy-4-oxo-3-vinyl-cyclopentyl)-3-methyl-butyl methyl ester (**6i**)

Cyclopentanone **6i** was prepared from allenylcyclobutanol **4i** (132.2 mg, 0.40 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (24.4 mg, 0.030 mmol) at 60 °C. d.r. = 7.2:1 ( $^1\text{H}$  NMR). Isolated yield of the major isomer **6i** 106 mg (80%), 88% ee.

#### Major diastereomer **6i**

$R_f$  (25% ether in pet. ether): 0.43. **IR** (neat): 3089, 3031, 2963, 2877, 1738, 1632, 1610, 1453, 1372, 1328, 1232, 1095, 940, 826, 735,  $698\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.34 — 7.24 (m, 5H), 6.00 (dd,  $J_1 = 18.2$  Hz,  $J_2 = 10.8$  Hz, 1H), 5.45 — 5.42 (m, 2H), 4.50 (d,  $J = 11.6$  Hz, 1H), 4.36 (d,  $J = 11.4$  Hz, 1H), 3.64 (s, 3H), 2.57 — 2.44 (m, 2H), 2.30 — 2.25 (m, 1H), 2.22 (s, 2H), 2.04 (dd,  $J_1 = 18.2$  Hz,  $J_2 = 10.6$  Hz, 1H), 1.66 (m, 1H), 1.00 (s, 3H), 0.99 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  212.1, 172.1, 138.3, 134.5, 128.2, 127.43, 127.40, 119.2, 83.5, 66.3, 51.3, 45.0, 41.2, 38.5, 37.2, 34.3, 24.0, 23.9. **HRMS** (EI+)  $m/z$  calculated for  $\text{C}_{20}\text{H}_{26}\text{O}_4$   $[M]^+$ : 330.1831, found: 330.1845. Anal. Calcd. for  $\text{C}_{20}\text{H}_{26}\text{O}_4$ : C, 72.70; H, 7.93; Found: C, 72.58; H, 8.05.  $[\alpha]_D^{25.2} = -21.12$  ( $c = 1.10$ ,  $\text{CH}_2\text{Cl}_2$ ). Enantiomeric excess was determined to be 88% ee by chiral HPLC (Chiralpak AD, 220 nm, heptane:*i*-PrOH = 99.5:0.5, 1.0 mL/min,  $t_1 = 21.28$  min(**major**),  $t_2 = 24.67$  min).



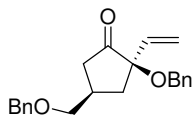
### 2-Benzyloxy-4-benzyloxymethyl-2-vinyl-cyclopentanone (**6j**)

Cyclopentanone **6j** was prepared from allenylcyclobutanol **4j** (168 mg, 0.50 mmol) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (30. mg, 0.0375 mmol) at 60 °C. d.r. = 10:1 ( $^1\text{H}$  NMR). Isolated yield of the major isomer **6j** 149 mg (88%), 88% ee.

#### Major diastereomer **6j**

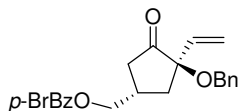
$R_f$  (25% ether in pet. ether): 0.45. **IR** (neat): 3088, 3064, 3031, 2929, 2858, 1740, 1654, 1622, 1496, 1454, 1366, 1346, 1211, 1187, 1104, 1027, 992, 936, 736,  $697\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 — 7.23 (m, 10H), 6.01 (dd,  $J_1 = 18.0$  Hz,  $J_2 = 10.8$  Hz, 1H), 5.46 — 5.41 (m, 2H), 4.52 (s, 2H), 4.50 (d,  $J = 11.0$  Hz, 1H), 4.36 (d,  $J = 11.0$  Hz, 1H), 3.52 — 3.43 (m, 2H), 2.84 — 2.74 (m, 1H), 2.64 — 2.57 (m, 1H), 2.40 — 2.34 (m, 1H), 2.13 (dd,  $J_1 = 19.1$  Hz,  $J_2 = 10.8$  Hz, 1H), 1.80 (dd,  $J_1 = 14.0$  Hz,  $J_2 = 10.8$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  212.4, 138.3, 138.2, 134.5,

129.0, 128.40, 128.38, 128.32, 127.7, 127.6, 127.5, 119.4, 83.2, 73.1, 72.7, 66.4, 40.4, 39.3, 32.4. **HRMS** (EI+)  $m/z$  calculated for  $C_{22}H_{34}O_3$   $[M]^+$ : 336.1725, found: 336.1726. Anal. Calcd. for  $C_{14}H_{16}O_2$ : C, 78.23; H, 7.88; Found: C, 78.41; H, 7.70.  $[\alpha]_D^{26.3} = -43.97$  ( $c = 1.60$ ,  $CH_2Cl_2$ ). Enantiomeric excess was determined to be 88% ee by chiral HPLC (Chiralpak AD, 220 nm, heptane:*i*-PrOH = 99:1, 0.8 mL/min,  $t_1 = 12.13$  min(**major**),  $t_2 = 13.84$  min).



#### Minor diastereomer 6j'

**R<sub>f</sub>** (25% ether in pet. ether): 0.31. **<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  7.36 — 7.26 (m, 10H), 5.87 (dd,  $J_1 = 17.7$  Hz,  $J_2 = 10.6$  Hz, 1H), 5.46 (dd,  $J_1 = 10.7$  Hz,  $J_2 = 0.9$  Hz, 1H), 5.40 (dd,  $J_1 = 17.7$  Hz,  $J_2 = 0.9$  Hz, 1H), 4.65 (d,  $J = 11.4$  Hz, 1H), 4.52 (s, 2H), 4.45 (d,  $J = 11.4$  Hz, 1H), 3.50 (dd,  $J_1 = 6.0$  Hz,  $J_2 = 1.5$  Hz, 2H), 2.54 — 2.36 (m, 3H), 2.19 (dd,  $J_1 = 18.5$  Hz,  $J_2 = 8.7$  Hz, 1H), 1.99 (dd,  $J_1 = 12.8$  Hz,  $J_2 = 10.1$  Hz, 1H). **<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  214.2, 138.4, 138.1, 135.3, 128.4, 128.3, 127.7, 127.6, 127.5, 125.5, 119.9, 85.2, 73.3, 73.2, 66.8, 40.0, 37.3, 31.2, 30.3.

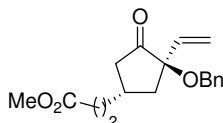


#### 4-Bromo-benzoic acid (S)-3-benzyloxy-4-oxo-3-vinyl-cyclopentylmethyl ester (6k)

Cyclopentanone **6k** was prepared from allenylcyclobutanol **4k** (172 mg, 0.40 mmol) according to the general procedure for ring expansion with (**R,R**)-anthracene ligand **L4** (24.4 mg, 0.030 mmol) at 60°C. d.r. = 13:1 (<sup>1</sup>H NMR). Isolated yield of the major diastereomer **4k** 138 mg (80%), 82%ee

#### Major diastereomer 6k

**R<sub>f</sub>** (50% ether in pet. ether): 0.75. **IR** (neat): 2954, 2924, 1742, 1721, 1590, 1271, 1103, 1012, 756  $cm^{-1}$ . **<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  7.87 (m, 2H), 7.60 (m, 2H), 7.35 — 7.32 (m, 2H), 7.29 — 7.26 (m, 3H), 6.04 (m, 1H), 5.48 (m, 2H), 4.53 (d,  $J = 11.5$  Hz, 1H), 4.38 (d,  $J = 11.5$  Hz, 1H), 4.34 (dd,  $J_1 = 6.3$  Hz,  $J_2 = 1.0$  Hz, 2H), 3.03 — 2.93 (m, 1H), 2.71 (m, 1H), 2.48 (m, 1H), 2.15 (dd,  $J_1 = 19.0$  Hz,  $J_2 = 10.0$  Hz, 1H), 1.80 (dd,  $J_1 = 14.0$  Hz,  $J_2 = 11.5$  Hz, 1H). **<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  211.1, 165.6, 138.0, 133.9, 131.8, 131.0, 128.7, 128.4, 128.3, 127.6, 127.5, 119.8, 82.9, 67.5, 66.6, 40.1, 39.8, 31.6. **HRMS** (EI+)  $m/z$  calculated for  $C_{22}H_{21}BrO_4$   $[M]^+$ : 428.0623, found: 428.0625.  $[\alpha]_D^{24.1} = -85.41$  ( $c = 0.17$ ,  $CH_2Cl_2$ ). Enantiomeric excess was determined to be 82% ee by chiral HPLC (Chiralpak OD, 235nm, heptane:*i*-PrOH = 90:10, 0.8 mL/min,  $t_1 = 16.52$  min,  $t_2 = 26.84$  min(**major**)).

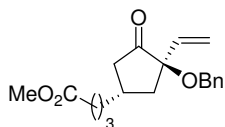


### 3-(3-Benzyloxy-4-oxo-3-vinyl-cyclopentyl)-propionic acid methyl ester (**6l**)

Cyclopentanone **6l** was prepared from allenylcyclobutanol **5h** (75.6 mg, 0.25 mmol, d.r. = 7.0:1) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (15.2 mg, 0.0188 mmol) at 60 °C. d.r. = 4.2:1 (by <sup>1</sup>H NMR). Isolated yield of the major isomer **6l** 55 mg (73%), 83%ee.

#### Major diastereomer **6l**

**R<sub>f</sub>** (25% ether in pet. ether): 0.22. **IR** (neat): 3064, 3031, 2954, 2929, 2869, 1738, 1634, 1607, 1454, 1406, 1380, 1260, 1198, 1051, 936, 738, 698cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.34 — 7.24 (m, 5H), 6.01 (dd, *J*<sub>1</sub> = 17.4 Hz, *J*<sub>2</sub> = 11.4 Hz, 1H), 5.45 — 5.40 (m, 2H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 3.67 (s, 3H), 2.68 — 2.61 (m, 1H), 2.50 — 2.39 (m, 2H), 2.35 (dt, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 1.3 Hz, 2H), 1.88 (m, 1H), 1.76 (m, 2H), 1.57 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 212.1, 173.5, 138.2, 134.4, 128.3, 127.47, 127.46, 119.3, 83.2, 66.4, 51.6, 43.4, 42.7, 32.3, 31.7, 30.7. Anal. Calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>: C, 71.50; H, 7.33; Found: C, 71.63; H, 7.24. [ $\alpha$ ]<sub>D</sub><sup>22.5</sup> = -40.28 (c = 1.30, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined to be 83% ee by chiral HPLC (Chiralpak ODH, 220 nm, heptane:*i*-PrOH = 99:1, 220 nm, 0.80 mL/min, *t*<sub>1</sub> = 36.08 min(**major**), *t*<sub>2</sub> = 42.66 min).

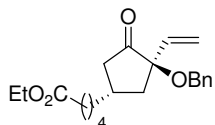


### 4-(-3-Benzyloxy-4-oxo-3-vinyl-cyclopentyl)-butyric acid methyl ester (**6m**)

Cyclopentanone **6m** was prepared from allenylcyclobutanol **4m** (75.6 mg, 0.25 mmol, d.r. = 7.0:1) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (15.2 mg, 0.0188 mmol) at 60 °C. d.r. = 4.4:1 (by <sup>1</sup>H NMR). Isolated yield of the major isomer **6m** 65 mg (68%), 88%ee.

#### Major diastereomer **4u**

**R<sub>f</sub>** (50% ether in pet. ether): 0.64. **IR** (neat): 3031, 2950, 2854, 1739, 1498, 1455, 1378, 1252, 1198, 1173, 1046, 1027, 992, 934, 858, 738, 698cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.34 — 7.26 (m, 5H), 6.01 (dd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 11.3 Hz, 1H), 5.43 (dd, *J*<sub>1</sub> = 11.3 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 5.42 (dd, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.36 (d, *J* = 11.6 Hz, 1H), 3.67 (s, 3H), 2.68 — 2.61 (m, 1H), 2.48 — 2.40 (m, 2H), 2.33 (t, *J* = 7.3 Hz, 2H), 1.87 (dd, *J*<sub>1</sub> = 18.8 Hz, *J*<sub>2</sub> = 9.7 Hz, 1H), 1.71 — 1.62 (m, 2H), 1.47 — 1.41 (m, 3H), 1.57 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 212.6, 173.8, 138.3, 134.6, 128.3, 127.5, 119.2, 83.2, 66.4, 51.5, 43.7, 42.9, 35.2, 33.9, 31.9, 23.1. **HRMS** (EI+) *m/z* calculated for C<sub>19</sub>H<sub>24</sub>O<sub>4</sub> [M]<sup>+</sup>: 316.1675, found: 316.1668. [ $\alpha$ ]<sub>D</sub><sup>22.1</sup> = -52.99 (c = 2.00, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined to be 88% ee by chiral HPLC (Chiralpak AD, 220 nm, heptane:*i*-PrOH = 99.2:0.8, 220 nm, 1.0 mL/min, *t*<sub>1</sub> = 21.82 min(**major**), *t*<sub>2</sub> = 23.88 min).

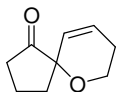


### 5-(3-Benzyloxy-4-oxo-3-vinyl-cyclopentyl)-pentanoic acid ethyl ester (6n)

Cyclopentanone **6n** was prepared from allenylcyclobutanol **4n** (137.8 mg, 0.40 mmol, d.r. = 6.4:1) according to the general procedure for ring expansion with (*R,R*)-anthracene ligand **L4** (24.4 mg, 0.030 mmol) at 60°C. d.r. = 4.2:1 (by <sup>1</sup>H NMR). Isolated yield of the major isomer **6n** 98 mg (71%), 90%ee.

#### Major diastereomer 6n

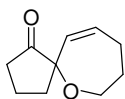
**R<sub>f</sub>** (25% ether in pet. ether): 0.45. **IR** (neat): 3032, 2927, 2856, 1737, 1458, 1376, 1244, 1180, 1028, 931, 858, 736, 698 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.34 — 7.26 (m, 5H), 6.01 (dd, *J*<sub>1</sub> = 17.2 Hz, *J*<sub>2</sub> = 11.5 Hz, 1H), 5.43 (dd, *J*<sub>1</sub> = 11.5 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 5.42 (dd, *J*<sub>1</sub> = 17.2 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.67 — 2.59 (m, 1H), 2.47 — 2.38 (m, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.85 (dd, *J*<sub>1</sub> = 18.9 Hz, *J*<sub>2</sub> = 9.8 Hz, 1H), 1.67 — 1.59 (m, 2H), 1.58 — 1.52 (m, 1H), 1.46 — 1.33 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 212.9, 173.6, 138.3, 134.7, 128.3, 127.5, 127.46, 119.1, 83.3, 66.4, 60.2, 43.8, 43.0, 35.5, 34.2, 31.9, 27.3, 24.9, 14.2. **HRMS** (EI+) *m/z* calculated for C<sub>21</sub>H<sub>28</sub>O<sub>4</sub> [M]<sup>+</sup>: 344.1988, found: 344.1999. [**α**]<sub>D</sub><sup>22.1</sup> = -58.07 (c = 0.75, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined to be 90% ee by chiral HPLC (Chiralpak ODH, 220 nm, heptane:*i*-PrOH = 99:1, 0.80 mL/min, *t*<sub>I</sub> = 25.48 min (major), *t*<sub>2</sub> = 28.03 min).



### 6-Oxa-spiro[4.5]dec-9-en-1-one (7)

To a solution of the cyclopentanone **5e** (20 mg, 0.11 mmol) in methylene chloride (15 mL) was added Grubbs II catalyst (7.0 mg, 0.011 mmol). The solution was stirred at room temperature overnight, and then concentrated in *vacuo* followed by purification with flash chromatography (10% diethyl ether in petroleum ether, silica gel). Desired product **7** bearing a spiro-ring was obtained as a yellowish liquid (20 mg, 100%).

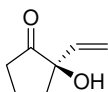
**R<sub>f</sub>** (25% ether in pet. ether): 0.65. **IR** (neat): 3035, 2963, 2835, 1739, 1652, 1463, 1429, 1405, 1371, 1338, 1274, 1207, 1157, 1130, 1075, 1050, 954, 903, 824, 768, 699 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.12 ~ 6.08 (m, 1H), 5.49 ~ 5.46 (m, 1H), 4.03 ~ 3.98 (m, 1H), 3.80 ~ 3.76 (m, 1H), 2.49 ~ 2.42 (m, 1H), 2.33 ~ 2.17 (m, 2H), 2.11 ~ 2.03 (m, 2H), 2.02 ~ 2.00 (m, 1H), 1.96 ~ 1.87 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 215.4, 128.1, 125.6, 78.8, 60.7, 36.9, 35.5, 24.9, 17.9. **HRMS** (EI+) *m/z* calculated for C<sub>9</sub>H<sub>12</sub>O<sub>2</sub> [M]<sup>+</sup>: 152.0837, found: 152.0839. [**α**]<sub>D</sub><sup>23.2</sup> = 186.97 (c = 0.60, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined to be 86% ee by chiral GC (Cyclosil B column, 60°C, 1.0 flow rate, *t*<sub>I</sub> = 67.14 min, *t*<sub>I</sub> = 67.21 min (major)).



### 6-Oxa-spiro[4.6]undec-10-en-1-one (8)

To a solution of the cyclopentanone **5f** (70 mg, 0.36 mmol) in methylene chloride (30 mL) was added Grubbs II catalyst (226 mg, 0.036 mmol). The solution was stirred at room temperature overnight, and then concentrated in *vacuo* followed by purification with flash chromatography (10% diethyl ether in petroleum ether, silica gel). Desired product **8** bearing a spiro-ring was obtained as a yellowish liquid (70 mg, 100%).

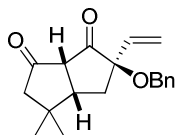
**R<sub>f</sub>** (25% ether in pet. ether): 0.40. **IR** (neat): 3020, 2954, 1740, 1434, 1206, 1155, 1125, 1093, 1054, 1003, 937, 802, 748, 697 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 5.93 ~ 5.88 (m, 1H), 5.25 (d, *J* = 12.0 Hz, 1H), 3.88 ~ 3.83 (m, 1H), 3.79 ~ 3.74 (m, 1H), 2.45 ~ 2.38 (m, 1H), 2.35 ~ 2.26 (m, 2H), 2.22 ~ 2.14 (m, 2H), 2.08 ~ 1.99 (m, 1H), 1.90 ~ 1.78 (m, 4H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 214.5, 132.7, 128.6, 84.8, 65.3, 37.3, 35.2, 29.1, 25.8, 17.9. **HRMS** (EI+) *m/z* calculated for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub> [M]<sup>+</sup>: 166.0994, found: 166.0991. **[α]<sub>D</sub><sup>23.5</sup>** = 96.75 (*c* = 1.10, CH<sub>2</sub>Cl<sub>2</sub>), Enantiomeric excess was determined to be 85% ee by chiral GC (Cyclosil B column, 55°C, 1.0 flow rate, *t<sub>I</sub>* = 78.11 min, *t<sub>I</sub>* = 78.22 min (**major**)).



**(R)-2-Hydroxy-2-vinyl-cyclopentanone (9)**<sup>13</sup>

To a solution of the cyclopentanone **5b** (500 mg, 2.0 mmol) in methylene chloride (10 mL) was added DDQ (550 mg, 2.4 mmol). The solution was stirred at room temperature for 4h, then concentrated followed by purification with flash chromatography (50% diethyl ether in petroleum ether, silica gel). Cyclopentanone **9** was obtained as a yellowish liquid (200 mg, 80%).

**R<sub>f</sub>** (50% ether in pet. ether): 0.30 **IR** (neat): 3447, 2964, 1749, 1457, 1404, 1314, 1260, 1160, 1089, 996, 931, 804 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 5.88 (dd, *J<sub>1</sub>* = 17.5 Hz, *J<sub>2</sub>* = 10.6 Hz, 1H), 5.31 (dd, *J<sub>1</sub>* = 17.5 Hz, *J<sub>2</sub>* = 0.6 Hz, 1H), 5.27 (dd, *J<sub>1</sub>* = 10.6 Hz, *J<sub>2</sub>* = 0.6 Hz, 1H), 2.81 (s, 1H), 2.44 ~ 2.30 (m, 2H), 2.24 ~ 2.19 (m, 1H), 2.06 ~ 1.97 (m, 2H), 1.91 ~ 1.84 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 217.9, 136.6, 116.3, 80.1, 35.6, 34.6, 16.8. **[α]<sub>D</sub><sup>25.2</sup>** = - 50.52 (*c* = 1.4, CHCl<sub>3</sub>) (89% ee for **5b**)

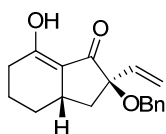


**(2R,7R, 8S)-2-Benzyloxy-4,4-dimethyl-2-vinyl-hexahydro-pentalene-1,6-dione (11)**

Cyclopentanone **6i** (49.6 mg, 0.15 mmol) was dissolved in 15 mL Et<sub>2</sub>O, followed by adding NaOMe (12.2 mg, 0.225 mmol). The solution was heated as reflux under N<sub>2</sub> overnight, quenched with NaHCO<sub>3</sub> and extracted with EtOAc. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>, filtered, concentrated and purified by silica gel flash chromatography (25% Et<sub>2</sub>O in Petroleum ether). White solid was obtained. Reaction d.r. > 10:1. Single isomer was isolated. Yield: 38

mg (85%) Solid was dissolved in Et<sub>2</sub>O. Slow evaporation of solvent afforded the white crystal which was used for X-ray.

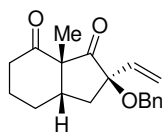
**R<sub>f</sub>** (50% ether in pet. ether): 0.59. **IR** (neat): 3032, 2959, 2927, 2869, 1767, 1719, 1454, 1374, 1267, 1116, 1060, 948, 876, 741, 699cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.35 — 7.26 (m, 5H), 6.00 (dd, *J*<sub>1</sub> = 18.1 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 5.46 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 5.45 (dd, *J*<sub>1</sub> = 18.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.53 (d, *J* = 11.5Hz, 1H), 4.29 (d, *J* = 11.5Hz, 1H), 3.38 (dd, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 2.6 Hz, 1H), 2.94 (m, 1H), 2.42 (ddd, *J*<sub>1</sub> = 14.3 Hz, *J*<sub>2</sub> = 7.0 Hz, *J*<sub>3</sub> = 2.8 Hz, 1H), 2.28 (d, *J* = 18.4, 1H), 2.13 (d, *J* = 18.4 Hz, 1H), 1.64 (dd, *J*<sub>1</sub> = 14.4 Hz, *J*<sub>2</sub> = 12.0 Hz, 1H), 1.16 (s, 3H), 1.09 (s, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 207.9, 202.1, 137.8, 133.3, 128.4, 127.7, 127.6, 120.1, 85.2, 66.9, 62.8, 49.2, 46.2, 38.2, 35.9, 30.2, 23.5. **HRMS** (EI+) *m/z* calculated for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub> [M]<sup>+</sup>: 298.1569, [M-Bn]<sup>+</sup>: 207.1022, found: [M-Bn]<sup>+</sup> 207.1028. **LRMS** (ESI+) *m/z* calculated for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 299.2, [M+Na]<sup>+</sup>: 321.2, found: [M+H]<sup>+</sup>: 299.2, [M+Na]<sup>+</sup>: 321.2. [α]<sub>D</sub><sup>22.8</sup> = -73.55 (c = 1.50, CH<sub>2</sub>Cl<sub>2</sub>).



**(2R,3aS)-2-Benzyloxy-7-hydroxy-2-vinyl-2,3,3a,4,5,6-hexahydro-inden-1-one (12)**

Cyclopentanone **6m** (94.9 mg, 0.30 mmol) was dissolved in 15 ml Et<sub>2</sub>O, followed by adding NaOMe (32.4 mg, 0.60 mmol). The solution was reflux under N<sub>2</sub> overnight, quenched with NaHCO<sub>3</sub> and extracted with EtOAc. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>, filtered, concentrated and purified by silical gel flash chromatography (25% Et<sub>2</sub>O in petroleum ether). Pink solid was obtained. Reaction d.r. > 10:1. Single isomer was isolated. Yield: 74 mg (87%)

**R<sub>f</sub>** (50% ether in pet. ether): 0.32. **IR** (neat): 3031, 2928, 2867, 1676, 1614, 1454, 1383, 1216, 1067, 1026, 910, 800, 734, 696cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, Benzene): δ 7.30 (d, *J* = 7.4 Hz, 2H) (m, 5H), 7.15 (m, 2H), 7.07 (t, *J* = 7.3hz, 1H), 6.09 (dd, *J*<sub>1</sub> = 17.7 Hz, *J*<sub>2</sub> = 11.1 Hz, 1H), 5.55 (dd, *J*<sub>1</sub> = 17.7 Hz, *J*<sub>2</sub> = 1.3 Hz, 1H), 5.28 (dd, *J*<sub>1</sub> = 11.1 Hz, *J*<sub>2</sub> = 1.3 Hz, 1H), 4.68 (d, *J* = 11.7Hz, 1H), 4.59 (d, *J* = 11.7Hz, 1H), 2.71 (broad, 1H), 2.29 — 2.24 (m, 1H), 1.96 — 1.82 (m, 2H), 1.52 — 1.47 (m, 1H), 1.36 — 1.25 (m, 3H), 1.08 — 0.99 (m, 1H), 0.48 — 0.40 (m, 1H); **<sup>13</sup>C NMR** (125 MHz, Benzene): δ 210.5, 172.2, 139.3, 135.6, 128.5, 127.7, 127.5, 118.6, 113.1, 84.1, 67.3, 44.4, 33.0, 29.3, 28.1, 21.9. **HRMS** (EI+) *m/z* calculated for C<sub>18</sub>H<sub>20</sub>O<sub>3</sub> [M]<sup>+</sup>: 284.1412, found: 284.1416.



**(2R, 8R, 9S)-2-Benzyloxy-8-methyl-2-vinyl-hexahydro-indene-1,7-dione (13)**

Compound **12** (28 mg, 0.10 mmol) was dissolved in 5 ml acetone, followed by adding K<sub>2</sub>CO<sub>3</sub> (13.0 mg, 0.095 mmol) and MeI (7.5 μl, 0.12 mmol). The solution was heated



as reflux under N<sub>2</sub> for 3h, then filtered, concentrated and purified by silical gel flash chromatography (25% Et<sub>2</sub>O in Petroleum ether). Single isomer was isolated. Yield: 28 mg (94%)

**R<sub>f</sub>** (50% ether in pet. ether): 0.62. **IR** (neat): 3031, 2931, 2873, 1750, 1699, 1455, 1377, 1120, 1061, 1027, 984, 737, 698cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.33 — 7.29 (m, 2H), 7.26 — 7.23 (m, 3H), 5.99 (dd, *J*<sub>1</sub> = 17.7 Hz, *J*<sub>2</sub> = 11.0 Hz, 1H), 5.44 (dd, *J*<sub>1</sub> = 17.7 Hz, *J*<sub>2</sub> = 10 Hz, 1H), 5.42 (dd, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 4.52 (d, *J* = 11.6Hz, 1H), 4.44 (d, *J* = 11.6Hz, 1H), 2.71 (broad, 1H), 2.56 — 2.50 (m, 1H), 2.30 — 2.25 (m, 1H), 2.15 (dd, *J*<sub>1</sub> = 13.9Hz, *J*<sub>2</sub> = 5.8 Hz, 1H), 2.12 — 2.04 (m, 1H), 2.02 — 1.92 (m, 2H), 1.90 (dd, *J*<sub>1</sub> = 13.9Hz, *J*<sub>2</sub> = 12.0 Hz, 1H), 1.77 — 1.72 (m, 1H), 1.40 (s, 3H) ; **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 209.2, 208.7, 138.4, 135.0, 128.3, 127.5, 127.4, 119.7, 81.7, 66.5, 64.0, 42.4, 38.8, 38.6, 23.7, 22.8, 19.5. **HRMS** (EI+) *m/z* calculated for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub> [M]<sup>+</sup>: 298.1569, found: 298.1580.

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