

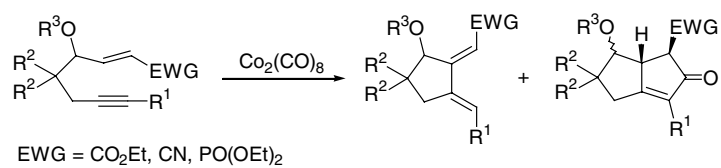
# Intramolecular Pauson-Khand reactions of $\alpha,\beta$ -unsaturated esters and related electron-deficient olefins

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## SUPPORTING INFORMATION

### Experimental Section

**General.** All reagents were obtained from commercial suppliers and were used without further purification. THF was distilled from sodium/benzophenone, dichloromethane was distilled from P<sub>2</sub>O<sub>5</sub> and acetonitrile was distilled from CaH<sub>2</sub>. All reactions involving the use of *n*-BuLi, LDA and Co<sub>2</sub>(CO)<sub>8</sub> were carried out in flame or oven dried glassware under inert argon atmosphere, in these cases anhydrous solvents were used. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Merck silica gel plates (Merck-60 230-400 mesh). Merck-60 230-400 mesh silica gel was used for flash column chromatography. NMR spectra were recorded on Bruker AC-200 or AC-300 instruments and calibrated using residual undeuterated solvent as internal reference. High resolution mass spectra (HRMS) were determined on a Hewlett-Packard HP-5985 mass spectrometer at 70 eV ionising voltage (EI) or under fast atom bombardment (FAB) conditions. Elemental analyses were performed with a Perkin-Elmer II 2400 CNH instrument by the “servicio interdepartamental de investigación (Universidad Autónoma de Madrid)”. Melting points were determined in open-end capillary tubes on a GallemKamp apparatus. 3,3-dimethylhex-5-yn-1-ol<sup>1</sup>, diethyl 2-(3-oxopropyl)-2-(2-propynyl)malonate<sup>2</sup> and methyl *p*-tolylsulfinate<sup>3</sup> were prepared as described in the literature.

**Ethyl *p*-tolylsulfinyl acetate:**<sup>4</sup> A solution of LDA (17 mL, 25.85 mmol, 1.5 M in THF) at -78 °C, was treated with EtOAc (2.3 mL, 23.50 mmol), stirred for 30 min, and treated dropwise with a solution of methyl *p*-tolylsulfinate (2.00 g, 11.75 mmol) in THF (10 mL). After being stirred for 3 h at rt, a sat. aq solution of NH<sub>4</sub>Cl (20 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate, 2:1) to give ethyl *p*-tolylsulfinyl acetate (1.91 g, 72 %).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.54 (d, *J*=8.1 Hz, 2H), 7.30 (d, *J*=8.1 Hz, 2H), 4.11 (q, *J*=7.5 Hz, 2H), 3.81 and 3.60 (AB system, *J*=14.0 Hz, 2H), 2.38 (s, 3H), 1.17 (t, *J*=7.0 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 164.7, 142.3, 139.8, 130.0, 124.1, 61.9, 61.7, 21.4, 13.9.

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<sup>1</sup> Oppolzer, W.; Xu, J. Z.; Stone, C. *Helv. Chim. Acta* **1991**, *74*, 465-468.

<sup>2</sup> Chatani, N.; Morimoto, T.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **1998**, *120*, 5335-5336.

<sup>3</sup> Brownbridge, P.; Jones, I.C. *Synthesis* **1988**, 252-254.

<sup>4</sup> Numata, T.; Itoh, O.; Yoshimura, T.; Oae, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 257-265.

***tert*-Butyl *p*-tolylsulfinyl acetate:**<sup>5</sup> A solution of LDA (9 mL, 12.93 mmol, 1.5 M in THF) at -78 °C, was treated with *tert*-butyl acetate (1.58 mL, 11.75 mmol), stirred for 30 min, and treated dropwise with a solution of methyl *p*-tolylsulfinate (1.00 g, 5.88 mmol) in THF (6 mL). After being stirred for 3 h at rt, a sat. aq solution of NH<sub>4</sub>Cl (12 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate, 3:1) to give *tert*-butyl *p*-tolylsulfinyl acetate (1.02 g, 68 %).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.58 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=8.1 Hz, 2H), 3.80 and 3.56 (AB system, *J*=13.4 Hz, 2H), 2.42 (s, 3H), 1.39 (s, 9H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 162.9, 140.9, 139.3, 129.0, 123.4, 81.7, 61.5, 26.9, 20.4.

***p*-Tolylsulfinyl acetonitrile:**<sup>3</sup> A solution of LDA (17 mL, 25.85 mmol, 1.5 M in THF) at -78 °C, was treated with acetonitrile (1.23 mL, 23.50 mmol), stirred for 30 min, and treated dropwise with a solution of methyl *p*-tolylsulfinate (2.00 g, 11.75 mmol) in THF (10 mL). After being stirred for 3 h at rt, a sat. aq solution of NH<sub>4</sub>Cl (20 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate, 2:1) to give *p*-tolylsulfinyl acetonitrile (1.54 g, 73 %).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.64 (d, *J*=8.1 Hz, 2H), 7.40 (d, *J*=8.1 Hz, 2H), 3.76 and 3.64 (AB system, *J*=15.6 Hz, 2H), 2.45 (s, 3H).

<sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): 143.0, 137.8, 130.0, 123.8, 111.3, 44.3, 21.2.

## A. Synthesis of the starting enynes 1

**Ethyl (*E*)-oct-2-en-7-ynoate (1a):** A solution of LDA (5 mL, 5.20 mmol, 1.0 M in THF) at -78 °C, was treated with EtOAc (463 μL, 4.73 mmol), stirred for 30 min, and treated dropwise with a solution of 5-hexynal (0.50 g, 5.20 mmol) in THF (5 mL). After being stirred for 3 h at rt, a sat. aq solution of NH<sub>4</sub>Cl (20 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. A solution of the resulting alcohol in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), at 0 °C, was treated with Et<sub>3</sub>N (6.60 mL, 47.30 mmol) and mesyl chloride (550 μL, 7.09 mmol) and stirred overnight at rt. The reaction mixture was quenched with a sat. aq solution of NH<sub>4</sub>Cl (10 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane: ethyl acetate, 10:1) to give **1a** (511 mg, 65 %, colorless oil).

<sup>5</sup> Mioskowski, C.; Solladié, G. *Tetrahedron Lett.* **1975**, 38, 3341-3342.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 6.93 (dt, *J*=6.5, 16.1 Hz, 1H), 5.85 (dt, *J*=1.6, 15.6 Hz, 1H), 4.18 (q, *J*=7.0 Hz, 2H), 2.45-2.19 (m, 4H), 1.97 (t, *J*=2.7 Hz, 1H), 1.69 (pent, *J*=7.0 Hz, 2H), 1.28 (t, *J*=7.0 Hz, 3H).

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 166.4, 147.7, 122.1, 83.4, 68.9, 60.1, 30.9, 26.7, 17.8, 14.2.

HRMS (EI+) calcd for (C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>)[M-H]<sup>+</sup> 165.0916, found 165.0917.

**Ethyl (*E*)-5,5-dimethyloct-2-en-7-ynoate (1b):** A solution of LDA (3 mL, 3.10 mmol, 1.0 M in THF) at -78 °C, was treated with EtOAc (276 μL, 2.82 mmol), stirred for 30 min, and treated dropwise with a solution of 3,3-dimethyl-5-hexynal (0.50 g, 3.10 mmol) in THF (5 mL). After being stirred for 3 h at rt, a sat. aq solution of NH<sub>4</sub>Cl (10 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. A solution of the resulting alcohol in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), at 0 °C, was treated with Et<sub>3</sub>N (3.93 mL, 28.18 mmol) and mesyl chloride (327 μL, 4.23 mmol) and stirred overnight at rt. The reaction mixture was quenched with a sat. aq solution of NH<sub>4</sub>Cl (10 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane: ethyl acetate, 10:1) to give **1b** (340 mg, 62 %, colorless oil).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 6.93 (m, 1H), 5.84 (d, *J*=15.4 Hz, 1H), 4.16 (q, *J*=7.3 Hz, 2H), 2.20 (d, *J*=8.1 Hz, 2H), 2.07 (d, *J*=2.8 Hz, 2H), 2.00 (t, *J*=2.8 Hz, 1H), 1.27 (t, *J*=7.3 Hz, 3H), 0.99 (s, 6H).

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 166.3, 145.4, 123.9, 81.7, 70.4, 60.1, 43.5, 34.1, 31.5, 26.6, 14.2.

HRMS (EI+) calcd for (C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>)[M-C<sub>3</sub>H<sub>3</sub>]<sup>+</sup> 155.1072, found 155.1076.

**Diethyl (*E*)-hept-1-en-6-ynphosphonate (1c):** A solution of tetraethyl methylene diphosphonate (259 μL, 1.04 mmol) in THF (6 mL) at -78 °C, was treated with *n*-BuLi (2.2 M in hexane, 473 μL, 1.04 mmol), stirred for 30 min, and treated dropwise with a solution of 5-hexynal (100 mg, 1.04 mmol) in THF (5 mL). After being stirred for 4 h at rt, a sat. aq solution of NH<sub>4</sub>Cl (10 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (ethyl acetate) to give **1c** (144 mg, 60 %, colorless oil).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 6.75 (m, 1H), 5.69 (dd, *J*=17.2, 21.0 Hz, 1H), 4.07 (m, 4H), 2.35 (m, 2H), 2.22 (td, *J*=2.7, 7.0 Hz, 2H), 1.97 (t, *J*=2.8 Hz, 1H), 1.69 (pent, *J*=7.0 Hz, 2H), 1.32 (t, *J*=7.0 Hz, 6H).

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 152.2, 117.5 (d, *J*<sub>P-C</sub>=187 Hz), 83.1, 68.9, 61.4, 32.8, 32.4, 26.2, 17.5, 16.2.

HRMS (FAB+) calcd for (C<sub>11</sub>H<sub>20</sub>O<sub>3</sub>P)[M+H]<sup>+</sup> 231.1150, found 231.1160.

**Diethyl 2[4-(ethoxycarbonyl)-3-butenyl]-2-(2-propynyl)malonate (1d):** A solution of LDA (2 mL, 2.02 mmol, 1.0 M in THF) at -78 °C, was treated with a solution of diethyl[(ethoxycarbonyl)methyl]phosphonate (206 mg, 0.92 mmol) in THF (6 mL), stirred for 40 min, and treated dropwise with a solution of 2-(3-oxopropyl)-2-(2-propynyl)malonate (350 mg, 1.38 mmol) in THF (6 mL). After being stirred for 1 h at -78 °C, a sat. aq solution of NH<sub>4</sub>Cl (10 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane: diisopropyl ether, 3:1) to give (*Z*)-**1d** (75 mg, 25 %, colorless oil) and (*E*)-**1d** (190 mg, 64 %, colorless oil).

(*Z*)-**1d**: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 6.18 (dt, *J*=7.5, 11.3 Hz, 1H), 5.77 (m, 1H), 4.27-4.10 (m, 6H), 2.87 (d, *J*=2.7 Hz, 2H), 2.61 (m, 2H), 2.20 (m, 2H), 2.00 (t, *J*=1.4 Hz, 1H), 1.31-1.22 (m, 9H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 169.9, 166.0, 148.0, 120.5, 78.8, 71.3, 61.6, 59.8, 56.4, 31.0, 23.6, 22.6, 14.2, 13.9.

(*E*)-**1d**: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 6.93 (dt, *J*=5.9, 15.6 Hz, 1H), 5.85 (d, *J*=15.6 Hz, 1H), 4.26-4.13 (m, 6H), 2.83 (d, *J*=2.7 Hz, 2H), 2.28-2.10 (m, 4H), 2.02 (t, *J*=2.7 Hz, 1H), 1.32-1.22 (m, 9H).

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 169.5, 166.0, 147.0, 121.8, 78.2, 71.5, 61.5, 59.9, 56.0, 30.0, 26.5, 22.6, 14.0, 13.8.

HRMS (EI+) calcd for (C<sub>17</sub>H<sub>25</sub>O<sub>6</sub>)[M+H]<sup>+</sup> 325.1651, found 325.1650.

#### Typical procedure for the preparation of (*E*)- $\gamma$ -hydroxy- $\alpha,\beta$ -unsaturated esters.

**Ethyl (*E*)-4-hydroxyoct-2-en-7-ynoate (1e):** To a solution of ethyl *p*-tolylsulfinyl acetate (300 mg, 1.33 mmol) in CH<sub>3</sub>CN (10 mL), cooled at 0 °C, were added sequentially piperidine (262  $\mu$ L, 2.65 mmol) and 5-hexynal (178 mg, 1.86 mmol). After being stirred for 48 h at 0 °C, the reaction mixture was quenched by the addition of a sat. aq solution of NH<sub>4</sub>Cl (10 mL). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate 4:1) to afford **1e** (201 mg, 83 %, colorless oil).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 6.85 (dd, *J*=4.9, 15.8 Hz, 1H), 5.98 (dd, *J*=1.6, 15.8 Hz, 1H), 4.40 (m, 1H), 4.11 (q, *J*=7.3 Hz, 2H), 3.25 (br s, 1H), 2.36 (m, 2H), 1.95 (t, *J*=2.8 Hz, 1H), 1.67 (m, 2H), 1.21 (t, *J*=7.3 Hz, 3H).

<sup>13</sup>C NMR (75 MHz CDCl<sub>3</sub>): 166.5, 149.7, 120.3, 83.3, 69.3, 69.2, 60.4, 34.6, 14.4, 14.0.

HRMS (EI+) calcd for (C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>)[M]<sup>+</sup> 182.0943, found 182.0946.

***tert*-Butyl (*E*)-4-hydroxyoct-2-en-7-ynoate (I):** Through the same procedure, treatment of *tert*-butyl *p*-tolylsulfinyl acetate (300 mg, 1.18 mmol) with piperidine (233  $\mu$ L, 2.36 mmol) and 5-hexynal (136 mg, 1.42 mmol) afforded after chromatographic purification (hexane:ethyl acetate 5:1) *tert*-butyl (*E*)-4-hydroxyoct-2-en-7-ynoate (139 mg, 56 %, colorless oil).

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ): 6.82 (dd,  $J=4.9, 15.8$  Hz, 1H), 5.98 (dd,  $J=1.6, 15.8$  Hz, 1H), 4.48 (m, 1H), 2.37 (m, 2H), 2.00 (t,  $J=2.8$  Hz, 1H), 1.79 (m, 3H, H<sub>6</sub>), 1.48 (s, 9H).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ): 165.6, 147.8, 122.5, 83.3, 80.5, 69.8, 69.3, 34.7, 28.0, 14.6.

HRMS (EI+) calcd for  $(\text{C}_{12}\text{H}_{18}\text{O}_3)[\text{M}]^+$  210.1256, found 210.1258.

**Ethyl (*E*)-5,5-dimethyl-4-hydroxyoct-2-en-7-ynoate (II):** Through the same procedure, treatment of ethyl *p*-tolylsulfinyl acetate (500 mg, 2.21 mmol) with piperidine (436  $\mu$ L, 4.41 mmol) and 3,3-dimethyl-5-hexynal (499 mg, 3.09 mmol) afforded after chromatographic purification (hexane:ethyl acetate 4:1) ethyl (*E*)-5,5-dimethyl-4-hydroxyoct-2-en-7-ynoate (376 mg, 81 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.03 (dd,  $J=5.4, 15.6$  Hz, 1H), 6.10 (dd,  $J=1.6, 15.6$  Hz, 1H), 4.24 (m, 1H), 4.21 (q,  $J=7.0$  Hz, 2H), 2.33 (dd,  $J=2.7, 16.7$  Hz, 1H), 2.10 (dd,  $J=2.7, 16.7$  Hz, 1H), 2.07 (t,  $J=2.7$  Hz, 1H), 1.87 (d,  $J=5.4$  Hz, 1H), 1.30 (t,  $J=7.0$  Hz, 3H), 1.04 (s, 3H), 0.99 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 166.3, 147.3, 122.0, 81.6, 76.2, 70.6, 60.3, 38.0, 28.6, 23.1, 21.9, 14.0.

HRMS (EI+) calcd for  $(\text{C}_{12}\text{H}_{17}\text{O}_3)[\text{M}-\text{H}]^+$  209.1178, found 209.1182.

**(*E*)-4-Hydroxyoct-2-en-7-ynenitrile (III):** Through the same procedure, treatment of *p*-tolylsulfinyl acetonitrile (150 mg, 0.84 mmol) with piperidine (165  $\mu$ L, 1.67 mmol) and 5-hexynal (113 mg, 1.17 mmol) afforded after chromatographic purification (hexane: ethyl acetate 4:1) (*E*)-4-hydroxyoct-2-en-7-ynenitrile (81 mg, 72 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 6.76 (dd,  $J=4.0, 16.2$  Hz, 1H), 5.73 (dd,  $J=2.0, 16.2$  Hz, 1H), 4.52 (m, 1H), 2.37 (m, 2H), 2.13 (d,  $J=4.9$  Hz, 1H), 2.04 (t,  $J=2.8$  Hz, 1H), 1.78 (m, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 156.1, 117.2, 99.1, 82.9, 69.9, 69.5, 34.2, 14.5.

HRMS (EI+) calcd for  $(\text{C}_8\text{H}_8\text{NO})[\text{M}-\text{H}]^+$  134.0606, found 134.0609.

**Ethyl (*E*)-4-hydroxy-8-phenyloct-2-en-7-ynoate (IV):** To a solution of the ester **1e** (50 mg, 0.27 mmol) in benzene (8 mL) were added sequentially  $\text{Pd}(\text{OAc})_2$  (6 mg, 0.027 mmol),  $\text{PPh}_3$  (14 mg, 0.055 mmol),  $\text{CuI}$  (5 mg, 0.027 mmol), iodobenzene (31  $\mu$ L, 0.27 mmol) and  $\text{Et}_3\text{N}$  (76  $\mu$ L, 0.55 mmol). The resulting mixture was stirred for 2 h at reflux, filtered over Celite and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate 3:1) to afford ethyl (*E*)-4-hydroxy-8-phenyloct-2-en-7-ynoate (50 mg, 72 %, colorless oil).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.40 (m, 2H), 7.29 (m, 3H), 6.98 (dd, *J*=4.9, 15.8 Hz, 1H), 6.09 (dd, *J*=2.0, 15.8 Hz, 1H), 4.56 (m, 1H), 4.19 (q, *J*=7.3 Hz, 2H), 2.58 (m, 2H), 2.33 (br s, 1H), 1.84 (m, 2H), 1.28 (t, *J*=7.3 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 166.4, 149.4, 131.5, 128.2, 127.8, 120.6, 88.7, 81.7, 69.9, 60.5, 35.0, 15.6, 14.1.

HRMS (EI+) calcd for (C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>)[M]<sup>+</sup> 258.1256, found 258.1247.

**Ethyl (*E*)-5,5-dimethyl-4-hydroxy-8-phenyloct-2-en-7-ynoate (V):** To a solution of ethyl (*E*)-5,5-dimethyl-4-hydroxyoct-2-en-7-ynoate (75 mg, 0.36 mmol) in benzene (10 mL) were added sequentially Pd(OAc)<sub>2</sub> (8 mg, 0.036 mmol), PPh<sub>3</sub> (19 mg, 0.071 mmol), CuI (7 mg, 0.036 mmol), iodobenzene (40 μL, 0.36 mmol) and Et<sub>3</sub>N (99 μL, 0.71 mmol). The resulting mixture was stirred for 2 h at reflux, filtered over Celite and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate 4:1) to afford ethyl (*E*)-5,5-dimethyl-4-hydroxy-8-phenyloct-2-en-7-ynoate (71 mg, 70 %, colorless oil).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.41 (m, 2H), 7.27 (m, 3H), 7.08 (dd, *J*=4.8, 15.6 Hz, 1H), 6.11 (dd, *J*=1.6, 15.6 Hz, 1H), 4.27 (m, 1H), 4.19 (q, *J*=7.0 Hz, 2H), 2.53 and 2.35 (AB system, *J*=17.2 Hz, 2H), 2.36 (d, *J*=5.4 Hz, 1H), 1.28 (t, *J*=7.0 Hz, 3H), 1.09 (s, 3H), 1.04 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 166.3, 147.2, 131.4, 128.2, 127.7, 123.5, 122.2, 87.3, 83.1, 76.7, 60.4, 38.8, 29.8, 23.6, 22.4, 14.1.

HRMS (EI+) calcd for (C<sub>18</sub>H<sub>22</sub>O<sub>3</sub>)[M]<sup>+</sup> 286.1569, found 286.1555.

#### **Typical procedure for the preparation of (ethoxymethoxy)enynes.**

**Ethyl (*E*)-4-ethoxymethoxyoct-2-en-7-ynoate (1f):** To a solution of **1e** (56 mg, 0.31 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (7 mL) were added sequentially *N,N*-diisopropylethylamine (107 μL, 0.61 mmol) and chloromethyl ethyl ether (143 μL, 1.54 mmol). The solution was stirred for 12 h at rt, then sat. aq solution of NH<sub>4</sub>Cl (10 mL) was added. The organic layer was separated, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate 5:1) to afford **1f** (66 mg, 88 %, colorless oil).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 6.79 (dd, *J*=6.5, 15.8 Hz, 1H), 5.99 (dd, *J*=1.2, 15.8 Hz, 1H), 4.66 (s, 2H), 4.38 (m, 1H), 4.19 (q, *J*=7.3 Hz, 2H), 3.76-3.37 (m, 2H), 2.27 (m, 2H), 1.97 (t, *J*=2.4 Hz, 1H), 1.76 (m, 2H), 1.28 (t, *J*=7.3 Hz, 3H), 1.20 (t, *J*=7.3 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 166.0, 147.1, 122.3, 93.2, 83.2, 73.5, 69.0, 63.5, 60.4, 33.5, 14.9, 14.4, 14.1.

HRMS (EI+) calcd for (C<sub>13</sub>H<sub>19</sub>O<sub>4</sub>)[M-H]<sup>+</sup> 239.1283, found 239.1279.

**Ethyl (*E*)-5,5-dimethyl-4-ethoxymethoxyoct-2-en-7-ynoate (1l):** Through the same procedure, treatment of ethyl (*E*)-5,5-dimethyl-4-hydroxyoct-2-en-7-ynoate (60 mg, 0.28 mmol) with *N,N*-diisopropylethylamine (99  $\mu$ L, 0.57 mmol) and chloromethyl ethyl ether (122  $\mu$ L, 1.43 mmol) afforded after chromatographic purification (hexane:ethyl acetate 5:1) **1l** (65 mg, 86 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 6.82 (dd,  $J=7.3, 15.8$  Hz, 1H), 5.99 (dd,  $J=1.2, 15.8$  Hz, 1H), 4.61 (s, 2H), 4.18 (q,  $J=7.3$  Hz, 2H), 4.08 (dd,  $J=1.2, 7.3$  Hz, 1H), 3.78-3.42 (m, 2H), 2.29 (dd,  $J=2.8, 16.6$  Hz, 1H), 2.11 (dd,  $J=2.8, 16.6$  Hz, 1H), 2.00 (t,  $J=2.8$  Hz, 1H), 1.28 (t,  $J=7.3$  Hz, 3H), 1.17 (t,  $J=7.3$  Hz, 3H), 0.99 (s, 3H), 0.97 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 165.8, 144.9, 124.2, 93.4, 81.6, 80.6, 70.5, 63.7, 60.4, 37.9, 28.9, 23.3, 22.3, 14.9, 14.1.

#### **Typical procedure for the preparation of the (triisopropylsiloxy)enynes.**

**Ethyl (*E*)-4-(triisopropylsiloxy)oct-2-en-7-ynoate (1g):** To a solution of **1e** (200 mg, 1.10 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (15 mL) were added sequentially 2,6-lutidine (192  $\mu$ L, 1.65 mmol) and TIPSOTf (384  $\mu$ L, 1.43 mmol). After being stirred for 8 h at rt, the reaction mixture was quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (5 mL). The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  and the combined organic layers were dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The residue was purified by flash chromatography (hexane:ethyl acetate 10:1) to afford **1g** (365 mg, 98 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 6.89 (dd,  $J=5.4, 15.6$  Hz, 1H), 6.00 (dd,  $J=1.6, 16.1$  Hz, 1H), 4.59 (m, 1H), 4.20 (q,  $J=7.0$  Hz, 2H), 2.41-2.04 (m, 2H), 1.95 (t,  $J=2.7$  Hz, 1H), 1.82 (m, 2H), 1.29 (t,  $J=7.3$  Hz, 3H), 1.06 (s, 21H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 166.1, 149.5, 120.7, 83.5, 70.4, 68.7, 60.1, 36.0, 17.9, 14.0, 13.3, 12.2.  
HRMS (EI+) calcd for  $(\text{C}_{16}\text{H}_{27}\text{O}_3\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  295.1729, found 295.1718.

***tert*-Butyl (*E*)-4-(triisopropylsiloxy)oct-2-en-7-ynoate (1h):** Through the same procedure, treatment of *tert*-butyl (*E*)-4-hydroxyoct-2-en-7-ynoate (28 mg, 0.13 mmol) with 2,6-lutidine (23  $\mu$ L, 0.20 mmol) and TIPSOTf (107  $\mu$ L, 0.39 mmol) afforded after chromatographic purification (hexane:ethyl acetate 20:1) **1h** (46 mg, 93 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 6.85 (dd,  $J=6.1, 15.8$  Hz, 1H), 5.98 (dd,  $J=1.2, 15.8$  Hz, 1H), 4.57 (m, 1H), 2.39-2.11 (m, 2H), 1.95 (t,  $J=2.8$  Hz, 1H), 1.82 (m, 2H), 1.09 (s, 9H), 1.05 (s, 21H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 166.0, 150.3, 122.7, 83.9, 70.7, 68.9, 36.3, 18.1, 17.8, 13.8, 12.4, 12.0.

**Ethyl (*E*)-4-(triisopropylsiloxy)non-2-en-7-ynoate (1i):** Through the same procedure, treatment of ethyl (*E*)-4-hydroxynon-2-en-7-ynoate (67 mg, 0.34 mmol) with 2,6-lutidine (60  $\mu$ L, 0.51 mmol) and TIPSOTf (275  $\mu$ L, 1.02 mmol) afforded after chromatographic purification (hexane:ethyl acetate 10:1) **1i** (110 mg, 91 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 6.89 (dd,  $J=5.7, 15.8$  Hz, 1H), 5.97 (dd,  $J=1.6, 15.8$  Hz, 1H), 4.56 (m, 1H), 4.17 (q,  $J=7.3$  Hz, 2H), 2.29-1.98 (m, 2H), 1.81-1.59 (m, 5H), 1.27 (t,  $J=7.3$  Hz, 3H), 1.04 (s, 21H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 166.4, 150.1, 120.3, 78.3, 76.1, 70.6, 60.2, 36.5, 18.0, 14.1, 13.8, 12.2, 3.3.

HRMS (EI+) calcd for  $(\text{C}_{17}\text{H}_{29}\text{NO}_3\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  309.1886, found 309.1877.

**Ethyl (*E*)-8-phenyl-4-(triisopropylsiloxy)oct-2-en-7-ynoate (1j):** Through the same procedure, treatment of ethyl (*E*)-4-hydroxy-8-phenyloct-2-en-7-ynoate (45 mg, 0.17 mmol) with 2,6-lutidine (30  $\mu$ L, 0.26 mmol) and TIPSOTf (140  $\mu$ L, 0.52 mmol) afforded after chromatographic purification (hexane:ethyl acetate 20:1) **1j** (67 mg, 93 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.38 (m, 2H), 7.29 (m, 3H), 6.95 (dd,  $J=5.9, 15.6$  Hz, 1H), 6.03 (dd,  $J=1.6, 15.6$  Hz, 1H), 4.66 (m, 1H), 4.19 (q,  $J=7.0$  Hz, 2H), 2.49 (m, 2H), 1.91 (m, 2H), 1.29 (t,  $J=7.0$  Hz, 3H), 1.08 (s, 21H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 166.4, 149.9, 131.5, 128.2, 127.6, 123.8, 120.7, 81.2, 74.2, 70.7, 60.4, 36.3, 18.1, 14.5, 12.4.

HRMS (EI+) calcd for  $(\text{C}_{22}\text{H}_{31}\text{O}_3\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  371.2042, found 371.2041.

**(*E*)-4-(Triisopropylsiloxy)oct-2-en-7-yne nitrile (1k):** Through the same procedure, treatment of (*E*)-4-hydroxyoct-2-en-7-yne nitrile (115 mg, 0.85 mmol) with 2,6-lutidine (149  $\mu$ L, 1.28 mmol) and TIPSOTf (686  $\mu$ L, 2.55 mmol) afforded after chromatographic purification (hexane: ethyl acetate 10:1) **1k** (235 mg, 95 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 6.75 (dd,  $J=4.5, 16.2$  Hz, 1H), 5.65 (dd,  $J=1.6, 16.2$  Hz, 1H), 4.61 (m, 1H), 2.37-2.05 (m, 2H), 1.97 (t,  $J=2.6$  Hz, 1H), 1.83 (m, 2H), 1.05 (s, 21H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 156.2, 117.1, 99.3, 83.1, 70.4, 69.3, 35.5, 17.9, 13.1, 12.2.

HRMS (EI+) calcd for  $(\text{C}_{14}\text{H}_{22}\text{NOSi})[\text{M}-\text{C}_3\text{H}_7]^+$  248.1471, found 248.1464.

**Ethyl (*E*)-5,5-dimethyl-4-(triisopropylsiloxy)oct-2-en-7-ynoate (1m):** Through the same procedure, treatment of ethyl (*E*)-5,5-dimethyl-4-hydroxyoct-2-en-7-ynoate (150 mg, 0.71 mmol)

with 2,6-lutidine (125  $\mu$ L, 1.07 mmol) and TIPSOTf (575  $\mu$ L, 2.14 mmol) afforded after chromatographic purification (hexane:ethyl acetate 10:1) **1m** (242 mg, 93 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 6.86 (dd,  $J=8.5, 15.8$  Hz, 1H), 5.90 (dd,  $J=0.8, 15.8$  Hz, 1H), 4.19 (m, 3H), 2.27 (dd,  $J=2.4, 16.6$  Hz, 1H), 2.10 (dd,  $J=2.4, 16.6$  Hz, 1H), 1.99 (t,  $J=2.4$  Hz, 1H), 1.28 (t,  $J=7.3$  Hz, 3H), 1.04 (s, 21H), 1.00 (s, 3H), 0.94 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 165.9, 147.9, 122.6, 82.0, 78.3, 70.5, 60.4, 39.2, 28.7, 23.1, 22.4, 18.1, 14.2, 12.7.

HRMS (EI+) calcd for  $(\text{C}_{18}\text{H}_{31}\text{O}_3\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  323.2042, found 323.2040.

**Ethyl (*E*)-5,5-dimethyl-8-phenyl-4-(triisopropylsiloxy)oct-2-en-7-ynoate (1n):** Through the same procedure, treatment of ethyl (*E*)-5,5-dimethyl-4-hydroxy-8-phenyloct-2-en-7-ynoate (60 mg, 0.21 mmol) with 2,6-lutidine (37  $\mu$ L, 0.31 mmol) and TIPSOTf (169  $\mu$ L, 0.63 mmol) afforded after chromatographic purification (hexane:ethyl acetate 20:1) **1n** (81 mg, 87 %, colorless oil).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.39 (m, 2H), 7.28 (m, 3H), 6.94 (dd,  $J=8.1, 16.1$  Hz, 1H), 5.94 (d,  $J=15.1$  Hz, 1H), 4.34 (d,  $J=7.5$  Hz, 1H), 4.20 (m, 2H), 2.53 and 2.34 (AB system,  $J=16.7$  Hz, 2H), 1.29 (t,  $J=7.0$  Hz, 3H), 1.08 (s, 24H), 1.02 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 166.0, 148.1, 131.4, 128.2, 127.5, 123.9, 122.6, 87.9, 82.9, 78.5, 60.4, 39.8, 29.7, 23.4, 22.6, 18.2, 18.1, 12.7.

HRMS (EI+) calcd for  $(\text{C}_{27}\text{H}_{42}\text{O}_3\text{Si})[\text{M}]^+$  442.2903, found 442.2905.

## B. Characterization data of the products 2 and 3

**Ethyl (*E*)-4,4-dimethyl-2-(methylidene)cyclopentylideneethanoate (2b).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.14 (t,  $J=2.4$  Hz, 1H), 5.59 (t,  $J=2.4$  Hz, 1H), 5.08 (t,  $J=2.4$  Hz, 1H), 4.17 (q,  $J=7.3$  Hz, 2H), 2.75 (d,  $J=2.8$  Hz, 2H), 2.24 (t,  $J=2.4$  Hz, 2H), 1.29 (t,  $J=7.3$  Hz, 3H), 1.02 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 160.1, 149.1, 109.6, 108.7, 59.7, 47.7, 47.6, 36.7, 27.8, 14.4; HRMS (EI+) calcd for  $(\text{C}_{12}\text{H}_{18}\text{O}_2)[\text{M}]^+$  194.1307, found 194.1300.

**7,7-Dimethyl-4-(ethoxycarbonyl)bicyclo[3.3.0]oct-1-en-3-one (3b).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.81 (m, 1H), 4.23 (q,  $J=7.3$  Hz, 2H), 3.57 (m, 1H), 3.06 (d,  $J=3.6$  Hz, 1H), 2.50 and 2.40 (AB system,  $J=18.6$  Hz, 2H), 2.02 and 1.98 (AB system,  $J=8.1$  Hz, 2H), 1.30 (t,  $J=7.3$  Hz, 3H), 1.22 (s, 3H), 1.13 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.2, 189.7, 169.5, 122.6, 61.4, 59.8, 49.0, 45.0, 42.2, 40.9, 30.5, 30.3, 14.1; HRMS (EI+) calcd for  $(\text{C}_{13}\text{H}_{18}\text{O}_3)[\text{M}]^+$  222.1256, found 222.1253.

**Diethyl (E)-2-(methylidene)cyclopentylidene phosphonate (2c).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.87 (m, 1H), 5.50 (m, 1H), 5.10 (m, 1H), 4.17 (m, 4H), 2.77 (m, 2H), 2.41 (m, 2H), 1.73 (pent,  $J=7.3$  Hz, 2H), 1.32 (t,  $J=7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 149.1, 108.2, 104.0 (d,  $J_{\text{P-C}}=176$  Hz), 61.4, 33.1, 33.0, 23.7, 16.4, 16.3; HRMS (EI+) calcd for  $(\text{C}_{11}\text{H}_{19}\text{O}_3\text{P})[\text{M}]^+$  230.1072, found 230.1065.

**4-(Diethoxyphosphinyl)bicyclo[3.3.0]oct-1-en-3-one (3c).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.88 (m, 1H), 4.18 (m, 4H), 2.96 (m, 1H), 2.66 (dd,  $J=3.6$  Hz,  $J_{\text{P-H}}=23.4$  Hz, 1H), 2.51 (m, 2H), 2.31-1.95 (m, 4H), 1.33 (t,  $J=7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.9, 190.1, 123.4, 62.6, 62.1, 51.7 (d,  $J_{\text{P-C}}=145$  Hz), 49.2, 30.8, 26.1, 25.4, 16.5; HRMS (EI+) calcd for  $(\text{C}_{12}\text{H}_{19}\text{O}_4\text{P})[\text{M}]^+$  258.1021, found 258.1012.

**Diethyl (E)-4-(ethoxycarbonylmethylidene)-3-(methylidene)cyclohexane-1,1-dicarboxylate (2d).**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  5.88 (m, 1H), 5.15 (m, 1H), 4.92 (m, 1H), 4.24-4.10 (m, 6H), 3.06 (td,  $J=1.6, 8.1$  Hz, 2H), 2.84 (s, 2H), 2.17 (t,  $J=7.0$  Hz, 2H), 1.31-1.20 (m, 9H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 166.5, 157.4, 144.3, 114.2, 113.7, 61.4, 59.8, 55.1, 39.0, 30.0, 25.6, 14.2, 14.0; HRMS (EI+) calcd for  $(\text{C}_{17}\text{H}_{24}\text{O}_6)[\text{M}]^+$  324.1573, found 324.1559.

**3,3,7-Triethoxycarbonylbicyclo[4.3.0]nonenone (3d).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.94 (m, 1H), 4.26-4.12 (m, 6H), 3.50 (dd,  $J=2.4, 14.2$  Hz, 1H), 3.07 (m, 1H), 3.00 (d,  $J=2.8$  Hz, 1H), 2.71 (d,  $J=14.2$  Hz, 1H), 2.51 (m, 1H), 2.23 (m, 1H), 1.96 (td,  $J=3.6, 13.7$  Hz, 1H), 1.38 (td,  $J=3.6, 13.7$  Hz, 1H), 1.31-1.19 (m, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.5, 178.4, 170.6, 168.7, 127.6, 62.1, 61.7, 58.8, 56.1, 44.6, 35.2, 30.3, 29.6, 14.2, 14.0; HRMS (EI+) calcd for  $(\text{C}_{18}\text{H}_{24}\text{O}_7)[\text{M}]^+$  352.1522, found 352.1518.

**Ethyl (Z)-2-ethoxymethoxy-5-(methylidene)cyclopentylidene ethanoate (2f).**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ) (significant signals)  $\delta$  6.21 (m, 1H), 5.64 (m, 1H), 5.39 (d,  $J=4.3$  Hz), 5.12 (m, 1H).

**4-(Ethoxycarbonyl)-6-ethoxymethoxybicyclo[3.3.0]oct-1-en-3-one (3f).** *endo+exo-3f*:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  5.90 (m, 1H), 5.87 (m, 1H), 4.67 (m, 4H), 4.23 (m, 5H), 3.78 (dt,  $J=7.5, 9.2$  Hz, 1H), 3.62-3.43 (m, 7H), 3.25 (d,  $J=3.2$  Hz, 1H), 2.95-1.99 (m, 8H), 1.24 (m, 12H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  203.8, 202.9, 185.8, 169.4, 168.9, 124.3, 123.3, 94.4, 93.6, 80.3, 74.3, 63.7, 61.4, 58.4, 55.5, 55.2, 53.6, 32.5, 32.0, 29.7, 25.0, 24.3, 15.0, 14.2; HRMS (EI+) calcd for  $(\text{C}_{14}\text{H}_{20}\text{O}_5)[\text{M}]^+$  268.1311, found 268.1304.

**Ethyl (Z)-5-(methylidene)-2-(triisopropylsiloxy)cyclopentylideneethanoate (2g).**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  6.07 (s, 1H), 5.75 (d,  $J=3.8$  Hz, 1H), 5.62 (m, 1H), 5.15 (m, 1H), 4.17 (m, 2H), 2.74 (m, 1H), 2.37 (dd,  $J=8.1, 16.1$  Hz, 1H), 1.91 (dd,  $J=7.5, 12.9$  Hz, 1H), 1.64 (m, 1H), 1.28 (t,  $J=7.0$  Hz, 3H), 1.05 (m, 21H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 159.6, 147.7, 110.4, 109.0, 71.1, 60.0, 34.1, 29.7, 18.1, 13.4, 12.4.

**4-(Ethoxycarbonyl)-6-(triisopropylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (3g).** *endo+exo-3g*:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.88 (m, 1H), 5.83 (m, 1H), 4.48 (t,  $J=4.0$  Hz, 1H), 4.22 (m, 4H), 3.98 (dt,  $J=7.3, 9.3$  Hz, 1H), 3.48 (m, 2H), 3.41 (m, 1H), 3.20 (d,  $J=3.6$  Hz, 1H), 2.95-2.02 (m, 8H), 1.28 (t,  $J=7.3$  Hz, 6H), 1.03 (m, 42H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  204.3, 203.2, 188.4, 186.4, 169.5, 169.0, 123.9, 123.1, 76.4, 70.6, 61.4, 61.3, 58.2, 58.1, 56.7, 54.0, 36.3, 35.2, 25.2, 24.3, 18.0, 17.9, 14.2, 14.1, 12.2, 12.1; HRMS (EI+) calcd for  $(\text{C}_{17}\text{H}_{27}\text{O}_4\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  323.1679, found 323.1675.

***tert*-Butyl (Z)-5-(methylidene)-2-(triisopropylsiloxy)cyclopentylideneethanoate (2h).**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ) (significant signals)  $\delta$  6.12 (m, 1H), 5.49 (m, 1H), 5.13 (m, 1H).

**4-(*tert*-Butoxycarbonyl)-6-(triisopropylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (3h).** *endo-3h*:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.86 (m, 1H), 4.50 (t,  $J=4.0$  Hz, 1H), 3.52 (d,  $J=4.1$  Hz, 1H), 3.38 (m, 1H), 2.69 (m, 2H), 2.29-2.05 (m, 2H), 1.08 (m, 30H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 187.7, 169.2, 123.2, 70.7, 56.9, 55.4, 36.3, 29.6, 24.2, 17.9, 17.7, 12.2, 11.9. *exo-3h*:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.83 (m, 1H), 3.96 (dt,  $J=7.7, 8.9$  Hz, 1H), 3.44 (m, 1H), 3.21 (d,  $J=3.2$  Hz, 1H), 2.85 (m, 1H), 2.57 (m, 1H), 2.29 (m, 1H), 2.08 (m, 1H), 1.05 (m, 30H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.3, 186.2, 168.5, 124.2, 77.2, 59.5, 58.4, 35.2, 29.7, 25.2, 18.0, 17.7, 12.2, 12.0.

**Ethyl (Z)-5-[(*E*)-ethylidene]-2-(triisopropylsiloxy)cyclopentylideneethanoate (2i).**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  6.19 (m, 1H), 5.94 (s, 1H), 5.77 (d,  $J=3.8$  Hz, 1H), 4.26 (m, 2H), 2.52 (m, 1H), 2.33 (dd,  $J=8.1, 16.1$  Hz, 1H), 1.93 (dd,  $J=7.5, 13.0$  Hz, 1H), 1.77 (d,  $J=8.0$  Hz, 3H), 1.61 (m, 1H), 1.28 (t,  $J=7.3$  Hz, 3H), 1.04 (m, 21H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 160.7, 140.4, 121.1, 108.0, 71.3, 59.7, 33.8, 25.9, 18.1, 14.3, 12.4.

**4-(Ethoxycarbonyl)-2-methyl-6-(triisopropylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (3i).** *endo+exo-3i*:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  4.47 (t,  $J=3.8$  Hz, 1H), 4.21 (m, 4H), 3.91 (dt,  $J=7.0, 9.1$  Hz, 1H), 3.43 (d,  $J=3.8$  Hz, 1H), 3.34 (m, 1H), 3.26 (m, 1H), 3.15 (d,  $J=3.8$  Hz, 1H), 2.81-1.98 (m, 8H), 1.71 (s, 3H), 1.68 (s, 3H), 1.28 (t,  $J=7.0$  Hz, 6H), 1.03 (m, 42H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  204.3, 203.3, 180.5, 178.5, 169.4, 131.6, 130.7, 76.7, 70.7, 61.3, 61.2, 57.5, 56.0, 54.5, 53.3, 36.1, 35.1,

29.7, 23.9, 23.1, 17.9, 14.2, 14.1, 12.3, 12.2, 8.7, 8.3; HRMS (EI+) calcd for (C<sub>18</sub>H<sub>29</sub>O<sub>4</sub>Si)[M-C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> 337.1835, found 337.1830.

**Ethyl (Z)-5-[(E)-benzylidene]-2-(triisopropylsiloxy)cyclopentylideneethanoate (2j).** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.51-7.25 (m, 5H), 7.01 (m, 1H), 6.21 (s, 1H), 5.85 (d, *J*=3.8 Hz, 1H), 4.20 (m, 2H), 2.96 (m, 1H), 2.73 (m, 1H), 2.06 (m, 1H), 1.69 (m, 1H), 1.28 (t, *J*=7.0 Hz, 3H), 1.08 (m, 21H).

**4-(Ethoxycarbonyl)-2-phenyl-6-(triisopropylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (3j).** *endo-3j*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.59 (m, 2H), 7.36 (m, 3H), 4.54 (t, *J*=3.8 Hz, 1H), 4.27 (q, *J*=7.3 Hz, 2H), 3.67 (d, *J*=4.1 Hz, 1H), 3.47 (m, 1H), 2.86 (m, 2H), 2.39-2.10 (m, 2H), 1.32 (t, *J*=7.3 Hz, 3H), 1.00 (m, 21H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 202.3, 181.8, 169.6, 128.4, 128.2, 127.9, 70.4, 61.4, 54.8, 54.5, 36.3, 29.7, 25.4, 18.0, 12.3; HRMS (EI+) calcd for (C<sub>26</sub>H<sub>39</sub>O<sub>4</sub>Si)[M+H]<sup>+</sup> 443.2618, found 443.2631. *exo-3j*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.56 (m, 2H), 7.36 (m, 3H), 4.24 (m, 2H), 4.00 (dt, *J*=7.3, 8.9 Hz, 1H), 3.54 (m, 1H), 3.38 (d, *J*=3.6 Hz, 1H), 3.13 (m, 1H), 2.68 (m, 1H), 2.36-2.11 (m, 2H), 1.31 (t, *J*=7.0 Hz, 3H), 1.07 (m, 21H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 201.2, 179.6, 169.0, 133.8, 130.6, 128.4, 128.2, 61.4, 58.8, 56.1, 35.3, 29.7, 26.4, 17.9, 14.2, 12.2; HRMS (EI+) calcd for (C<sub>26</sub>H<sub>39</sub>O<sub>4</sub>Si)[M+H]<sup>+</sup> 443.2618, found 443.2605.

**(Z)-5-(Methylidene)-2-(triisopropylsiloxy)cyclopentylidenenitrile (2k).** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 5.89 (m, 2H), 5.21 (t, *J*=2.2 Hz, 1H), 4.99 (t, *J*=4.8 Hz, 1H), 2.69 (m, 1H), 2.44-2.11 (m, 2H), 1.96 (m, 1H), 1.06 (m, 21H).

**4-Cyano-6-(triisopropylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (3k).** *endo-3k*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.01 (m, 1H), 4.56 (t, *J*=3.8 Hz, 1H), 3.52 (d, *J*=4.8 Hz, 1H), 3.30 (m, 1H), 2.71 (m, 2H), 2.32-2.13 (m, 2H), 1.04 (m, 21H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 199.1, 187.4, 123.3, 116.7, 70.0, 57.5, 37.5, 35.6, 24.4, 17.9, 12.2. *exo-3k*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) (significant signals) δ 5.96 (m, 1H), 4.00 (m, 1H), 3.48 (d, *J*=4.4 Hz, 1H); HRMS (FAB+) calcd for (C<sub>18</sub>H<sub>30</sub>NO<sub>2</sub>Si)[M+H]<sup>+</sup> 320.2046, found 320.2048.

**Ethyl (Z)-3,3-dimethyl-2-ethoxymethoxy-5-(methylidene)cyclopentylideneethanoate (2l).** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) (significant signals) δ 6.23 (m, 1H), 5.63 (m, 1H), 5.11 (m, 1H).

**7,7-Dimethyl-4-(ethoxycarbonyl)-6-ethoxymethoxybicyclo[3.3.0]oct-1-en-3-one (3l).** *endo+exo-3l*: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 5.89 (m, 1H), 5.85 (m, 1H), 4.69 (m, 4H), 4.24 (m, 4H), 3.81 (m,

1H), 3.74 (d,  $J=4.9$  Hz, 1H), 3.67-3.48 (m, 6H), 3.36 (d,  $J=10.0$  Hz, 1H), 3.29 (d,  $J=3.6$  Hz, 1H), 2.70-2.41 (m, 4H), 1.33-1.12 (m, 24H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.4, 202.8, 187.2, 183.8, 169.6, 169.2, 124.5, 123.3, 96.1, 94.9, 87.5, 83.9, 64.3, 63.6, 61.4, 58.7, 54.6, 53.9, 46.2, 43.0, 41.5, 40.2, 29.7, 28.6, 24.4, 14.9, 14.2; HRMS (FAB+) calcd for  $(\text{C}_{16}\text{H}_{25}\text{O}_5)[\text{M}+\text{H}]^+$  297.1702, found 297.1697.

**7,7-Dimethyl-4-(ethoxycarbonyl)-6-(triisopropylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (3m).**

*endo+exo-3m*:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.82 (m, 2H), 4.21(m, 4H), 4.09 (d,  $J=4.5$  Hz, 1H), 3.81 (m, 1H), 3.64 (m, 2H), 3.42 (d,  $J=4.0$  Hz, 1H), 3.24 (m, 1H), 2.72-2.37 (m, 4H), 1.30 (t,  $J=7.3$  Hz, 6H), 1.19 (s, 3H), 1.18 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H), 1.04 (s, 42H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.7, 202.8, 188.6, 185.1, 169.9, 169.1, 124.0, 122.7, 83.4, 79.7, 61.5, 61.4, 58.2, 55.8, 55.1, 54.7, 44.1, 41.4, 40.1, 29.1, 28.4, 24.6, 24.1, 18.2, 14.1, 13.6, 13.0; HRMS (EI+) calcd for  $(\text{C}_{19}\text{H}_{31}\text{O}_4\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  351.1992, found 351.1986.

**7,7-Dimethyl-4-(ethoxycarbonyl)-2-phenyl-6-(triisopropylsiloxy)bicyclo[3.3.0]oct-1-en-3-one**

**(3n).** *endo-3n*:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (m, 2H), 7.37 (m, 3H), 4.24 (m, 2H), 3.68 (m, 2H), 3.41 (m, 1H), 3.00 and 2.55 (AB system,  $J=19.4$  Hz, 2H), 1.33 (t,  $J=7.3$  Hz, 3H), 1.26 (s, 3H), 1.09 (m, 24H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  200.8, 178.3, 169.1, 141.6, 133.7, 130.7, 128.3, 83.5, 61.5, 58.9, 53.8, 44.0, 42.7, 29.7, 28.4, 24.1, 18.3, 14.1, 13.0; HRMS (EI+) calcd for  $(\text{C}_{25}\text{H}_{35}\text{O}_4\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  427.2305, found 427.2308. *exo-3n*:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (m, 2H), 7.37 (m, 3H), 4.29 (q,  $J=7.3$  Hz, 2H), 4.14 (d,  $J=4.3$  Hz, 1H), 3.87 (m, 1H), 3.59 (d,  $J=4.3$  Hz, 1H), 2.76 and 2.55 (AB system,  $J=18.8$  Hz, 2H), 1.33 (t,  $J=7.0$  Hz, 3H), 1.27 (s, 3H), 1.17 (s, 3H), 1.04 (s, 21H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  201.7, 181.9, 179.8, 133.0, 131.3, 128.3, 128.2, 127.9, 79.6, 61.4, 55.1, 53.2, 46.9, 41.4, 29.3, 24.7, 18.2, 14.3, 13.7; HRMS (EI+) calcd for  $(\text{C}_{25}\text{H}_{35}\text{O}_4\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  427.2305, found 427.2293.

**C. Characterization data of the Diels-Alder adducts 4 and 5**

**Adduct 4i.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.03 (m, 1H), 4.17 (m, 3H), 3.21 (m, 2H), 3.02 (s, 3H), 2.92 (m, 1H), 2.35 (m, 2H), 1.78 (m, 2H), 1.21 (t,  $J=7.0$  Hz, 3H), 1.09 (m, 21H), 1.05 (d,  $J=7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.5, 178.1, 171.4, 146.4, 133.4, 77.9, 61.2, 42.2, 41.3, 38.5, 33.8, 32.0, 29.6, 24.6, 18.1, 14.8, 14.0, 12.4; HRMS (FAB+) calcd for  $(\text{C}_{22}\text{H}_{34}\text{NO}_5\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  420.2206, found 420.2196.

**Adduct 4j.** M.p. 122-124 °C.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (m, 5H), 5.26 (m, 1H), 4.30 (m, 2H), 3.94 (d,  $J=8.6$  Hz, 1H), 3.87 (d,  $J=7.5$  Hz, 1H), 3.52 (t,  $J=8.1$  Hz, 1H), 3.44 (t,  $J=8.0$  Hz, 1H), 2.20 (s, 3H), 2.39-1.65 (m, 4H), 1.32 (t,  $J=7.0$  Hz, 3H), 1.09 (m, 21H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.4, 176.1, 171.2, 139.2, 136.7, 135.5, 129.3, 128.2, 127.5, 78.2, 61.2, 45.7, 42.2, 39.0, 36.6, 33.7, 32.4, 23.4, 18.2, 14.0, 12.5; HRMS (EI+) calcd for  $(\text{C}_{27}\text{H}_{36}\text{NO}_5\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  482.2363, found 482.2365.

**Adduct 5k.** M.p. 154-156 °C.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  5.26 (m, 1H), 5.19 (m, 1H), 4.28 and 3.94 (AB system,  $J=15.4$  Hz, 2H), 3.16 (s, 3H), 2.64-2.32 (m, 3H), 1.92 (m, 1H), 1.10 (m, 21H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 153.2, 137.4, 129.7, 113.4, 75.5, 44.5, 42.6, 34.3, 30.9, 25.4, 18.0, 12.3; HRMS (FAB+) calcd for  $(\text{C}_{17}\text{H}_{25}\text{N}_4\text{O}_3\text{Si})[\text{M}-\text{C}_3\text{H}_7]^+$  361.1696, found 361.1702.