Supporting Information

for

**An efficient *one-step* synthesis of a new series of multifunctional olefins**

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Full experimental details and characterization data of all new compounds

**Experimental section**

All cyclic MBH alcohols **1** [1], acyclic MBH alcohols **2** [2] and the C-allylation products **3,4** [3] were obtained as previously described. 1H NMR, 13C NMR and 31P spectra were recorded either on a Bruker AC-500 spectrometer (500 MHz for 1H, 125 MHz for 13C and 202 MHz for 31P) or an AC-300 spectrometer (300 MHz for 1H, 75 MHz for 13C and 121 MHz for 31P) in CDCl3, using TMS as an internal standard (chemical shifts in δ values, *J* in Hz). High resolution mass spectra (HRMS) were recorded as TOF-HRMS on a micromass mass spectrometer. Analytical thin layer chromatography (TLC) was performed  
using Fluka Kieselgel 60 F254 pre-coated silica gel plates. Visualization was  
achieved by UV light (254 nm). Flash chromatography was performed using  
Merck silica gel 60 and a gradient solvent system ether/petrolium ether as eluent.

**Typical procedure for the synthesis of β-phosphonoesters 5,6 as starting materials**

A mixture of cyclic MBH alcohol **1** (2 mmol, 0.252 g) or acyclic MBH alcohol **2** (2 mmol, 0.26 g), triethyl phosphonoacetate (2.4 mmol, 0.53 g) and anhydrous K2CO3 (4 mmol, 0.552 g) was dissolved in toluene (20 mL), containing 5 g of oven-dried 4 Å molecular sieves. The mixture was then heated under reflux for 8 h. After completion (TLC), the reaction mixture was cooled, washed with brine and dried. The toluene was removed and the residue was purified by column chromatography on silica gel (ether) to give the pure allylation products **5** and **6**.

**2-(2-Carbethoxy-2-diethoxyphosphorylethyl) cyclohex-2-en-1-one 5**

#### Yield: 71%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 6.85 (t, *J* = 4.0 Hz, 1H), 4.20–4.14 (m, 6H), 3.86–3.24 (m, 1H), 2.88–2.60 (m, 2H), 2.47–2.34 (m, 4H), 2.00–1.92 (m, 2H), 1.35 (t, *J* = 7.0 Hz, 6H), 1.25 (t, *J* = 7.0 Hz, 3H); 13C NMR (CDCl3, 75 MHz): δC 198.7, 168.6, 148.0, 136.0, 62.7 (d, *2JC-P* = 6.48 Hz), 62.6 (d, *2JC-P* = 6.53 Hz), 61.1, 44.1 (d, *1JC-P* = 129.0 Hz), 38.2, 28.1, 26.0, 22.8, 16.2 (d, *3JC-P* = 5.99 Hz), 14.1; 31P NMR (CDCl3, 121 MHz): δP 21.9 (s, 1P); HRMS (EI): M+, found 332.13751. C15H25O6P requires 332.13887.

**Ethyl 2-(2-Carbethoxy-2-diethoxyphosphorylethyl) acrylate 6**

#### Yield: 71%; yellow oil; 1H NMR (CDCl3, 500 MHz): δH 6.16 (s, 1H), 5.61 (s, 1H), 4.17–4.10 (m, 6H), 3.32–3.25 (m, 1H), 2.86–2.82 (m, 2H), 1.30–1.19 (m, 9H); 13C NMR (CDCl3, 125 MHz): δC 168.3, 166.0, 136.9, 127.2, 62.8 (d, *2JC-P* = 6.40 Hz), 62.6 (d, *2JC-P* = 6.61 Hz), 61.3, 60.8, 44.4 (d, *1JC-P* = 129.78 Hz), 29.7, 16.2 (d, *3JC-P* = 5.78 Hz), 14.07, 14.04; 31P NMR (CDCl3, 202 MHz): δP 21.6 (s, 1P); HRMS (EI): M+, found 336.13477. C14H25O7P requires 336.13379.

**General procedure for the synthesis of a new series of multifunctional olefins**

To a magnetically stirred mixture of β-dicarbonyl monoallyl derivatives **3a-d** or **4a-d** or β-phosphonoester monoallyl derivatives **5** and **6** (1 mmol) and 30% aqueous formaldehyde (5 mmol) was added at room temperature a gelatinous solution of potassium carbonate (6–10 M, 4 mmol). The heterogeneous reaction mixture was stirred at reflux of THF (5mL). After completion (TLC), the reaction mixture was cooled then treated with water. The solution was extracted with ether (3 x 25 mL). The combined organic layers were dried over anhydrous MgSO4, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (light petroleum/diethyl ether = 7:3) to afford olefins **7** and **8**.

**2-(2-Carboethoxy-2-propenyl)cyclohex-2-en-1-one 7a**

#### Yield: 96%; yellow oil; 1H NMR (CDCl3, 500 MHz): δH 6.73 (t, *J* = 4.41 Hz, 1H), 6.18 (s, 1H), 5.51 (s, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.18 (s, 2H), 2.42–2.33 (m, 4H), 1.98–1.95 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H); 13C NMR (CDCl3, 125 MHz): δC 198.4, 166.7, 146.7, 138.4, 137.0, 126.3, 60.5, 38.3, 31.2, 26.0, 23.0, 14.1;HRMS (EI): M+, found 208.10997. C12H16O3 requires 208.10994.

**2-(2-Methylene-3-oxobutyl)cyclohex-2-en-1-one 7b**

#### Yield: 91%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 6.75 (t, *J* = 4.11 Hz, 1H), 6.07 (s, 1H), 5.79 (s, 1H), 3.17 (s, 2H), 2.45–2.33 (m, 7H), 2.03–1.94 (m, 2H); 13C NMR (CDCl3, 75 MHz): δC 199.0, 198.5, 147.1, 146.7, 137.3, 126.5, 38.5, 30.3, 26.1, 25.8, 23.0;HRMS (EI): M+, found 178.10082. C11H14O2 requires 178.09938.

**2-(2-Methylene-3-phenyl-3-oxopropyl)cyclohex-2-en-1-one 7c**

#### Yield: 90%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 7.75−7.72 (m, 2H); 7.55−7.39 (m, 3H), 6.86 (t, *J* = 4.14 Hz, 1H), 5.86 (s, 1H), 5.64 (s, 1H), 3.37 (s, 2H), 2.46–2.33 (m, 4H), 2.02–1.93 (m, 2H); 13C NMR (CDCl3, 75 MHz): δC 198.6, 197.7, 147.6, 145.8, 137.8, 136.9, 132.1, 129.5, 128.1, 126.8, 38.5, 32.3, 26.1, 23.0;HRMS (EI): M+, found 240.11515. C16H16O2 requires 240.11503.

**Diethyl 2,4-dimethylenepentandioate 8a**

#### Yield: 96%; yellow oil; 1H NMR (CDCl3, 500 MHz): δH 6.23 (s, 2H), 5.56 (s, 2H), 4.17 (q, *J* = 7.0 Hz, 4H), 3.31 (s, 2H), 1.26 (t, *J* = 7.0 Hz, 3H); 13C NMR (CDCl3, 125 MHz): δC 166.5, 138.0, 126.5, 60.7, 33.7, 14.1;HRMS (EI): M+, found 212.10501. C11H16O4 requires 212.10486.

**Ethyl 2,4-dimethylene-5-oxohexanoate 8b**

#### Yield: 98%; yellow oil; 1H NMR (CDCl3, 500 MHz): δH 6.22 (s, 1H), 6.09 (s, 1H), 5.80 (s, 1H), 5.54 (s, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.27 (s, 2H), 2.33 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); 13C NMR (CDCl3, 125 MHz): δC 198.6, 166.6, 146.3, 138.2, 126.7, 126.5, 60.7, 32.4, 25.7, 14.1;HRMS (EI): M+, found 182.09585. C10H14O3 requires 182.09429.

**Ethyl 2,4-dimethylene-5-oxo-5-phenylpentanoate 8c**

#### Yield: 90%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 7.76−7.74 (m, 2H); 7.56−7.41 (m, 3H), 6.28 (s, 1H), 5.90 (s, 1H), 5.72 (s, 1H), 5.68 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.50 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); 13C NMR (CDCl3, 75 MHz): δC 197.2, 166.6, 145.5, 138.0, 137.6, 132.2, 129.5, 128.2, 127.17, 127.13, 60.8, 34.3, 14.1;HRMS (EI): M+, found 244.11020. C15H16O3 requires 244.10994.

**General procedure for the synthesis of α-hydroxymethylated β-keto esters**

To a magnetically stirred mixture of β-keto ester monoallyl derivatives **3e-h** or **4e-f** (1 mmol) and 30% aqueous formaldehyde (5 mmol) was added at room temperature a gelatinous solution of potassium carbonate (6–10 M, 4 mmol). The heterogeneous reaction mixture was stirred in THF (5mL) at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled then treated with water. The solution was extracted with ether (3 x 25 mL). The combined organic layers were dried over anhydrous MgSO4, filtered and evaporated under reduced pressure. The crude product was purified by a column chromatography on silica gel (light petroleum/diethyl ether = 9:1) to give the pure derivatives **9** or **10**.

**2-(2-Carboethoxy-2-hydroxymethyl-3-oxobutyl)cyclohex-2-en-1-one 9a**

#### Yield: 87%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 6.81 (t, *J* = 4.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.91–3.75 (m, 2H), 3.68–3.62 (m, 1H), 2.85 (AB, *J* = 14.3 Hz, 2H), 2.51–2.46 (m, 2H), 2.39–2.36 (m, 2H), 2.22 (s, 3H), 2.04–1.98 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); 13C NMR (CDCl3, 75 MHz): δC 203.5, 201.4, 170.2, 151.7, 134.9, 66.2, 61.9, 61.4, 38.0, 28.5, 26.8, 26.4, 22.7, 14.1;HRMS (EI): MNa+, found 291.1206. C14H20O5Na requires 291.1208.

**2-(2-Carbomethoxy-2-hydroxymethyl-3-oxobutyl)cyclohex-2-en-1-one 9b**

#### Yield: 89%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 6.83 (t, *J* = 4.1 Hz, 1H), 3.92–3.80 (m, 2H), 3.74 (s, 3H), 3.70–3.64 (m, 1H), 2.85 (AB, *J* = 14.2 Hz, 2H), 2.51–2.46 (m, 2H), 2.40–2.37 (m, 2H), 2.22 (s, 3H), 2.04–1.95 (m, 2H); 13C NMR (CDCl3, 75 MHz): δC 203.5, 201.3, 170.7, 151.7, 134.8, 66.1, 61.9, 52.3, 38.0, 28.7, 27.0, 26.5, 22.7;HRMS (EI): MNa+, found 277.1044. C13H18O5Na requires 277.1052.

**2-(2-Carbobenzoxy-2-hydroxymethyl-3-oxobutyl)cyclohex-2-en-1-one 9c**

#### Yield: 91%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 7.26–7.24 (m, 5H), 6.39 (t, *J* = 4.1 Hz, 1H), 5.07 (AB, *J* = 12.0 Hz, 2H), 3.84–3.72 (m, 2H), 3.55–3.50 (m, 1H), 2.72 (AB, *J* = 14.3 Hz, 2H), 2.35–2.29 (m, 2H), 2.11–2.09 (m, 2H), 2.05 (s, 3H), 1.85–1.77 (m, 2H); 13C NMR (CDCl3, 75 MHz): δC 203.2, 201.5, 169.9, 152.2, 135.1, 134.6, 128.8, 128.6, 67.1, 66.1, 61.8, 38.0, 28.5, 26.8, 26.3, 22.6;HRMS (EI): MNa+, found 353.1357. C19H22O5Na requires 353.1365.

**2-(2,2-Dicarboethoxy-3-hydroxypropyl)cyclohex-2-en-1-one 9d**

Yield: 94%; yellow oil; 1H NMR (CDCl3, 300 MHz): δH 6.82 (t, *J* = 4.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.87 (t, *J* = 7.4 Hz, 1H), 3.74 (d, *J* = 7.4 Hz, 2H), 2.91 (s, 2H), 2.52–2.47 (m, 2H), 2.40–2.35 (m, 2H), 2.04–1.98 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); 13C NMR (CDCl3, 75 MHz): δC 201.3, 169.7, 151.5, 135.0, 62.4, 61.3, 60.6, 38.0, 29.1, 26.5, 22.8, 14.1;HRMS (EI): MNa+, found 321.1306. C15H22O6Na requires 321.1314.

**Diethyl 2-acetyl-2-hydroxymethyl-4-methylenepentandioate 10**

#### Yield: 96%; yellow oil; 1H NMR (CDCl3, 500 MHz): δH 6.28 (s, 1H), 5.61 (s, 1H), 4.18–4.11 (m, 4H), 3.93–3.90 (m, 1H), 3.75–3.72 (m, 1H), 3.45–3.42 (m, 1H), 2.93 (AB, *J* = 14.3 Hz, 2H), 2.18 (s, 3H), 1.26–1.21 (m, 6H); 13C NMR (CDCl3, 125 MHz): δC 203.4, 170.2, 168.2, 135.5, 130.1, 66.1, 62.1, 61.6, 61.6, 30.7, 26.9, 14.06, 14.01;HRMS (EI): MNa+, found 295.1148. C13H20O6Na requires 295.1158.

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