Supporting Information

Enantioselective alkylation of β-keto phosphonates by direct use of diaryl methanols as electrophiles

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General Methods.

¹H NMR (270 MHz), ¹³C NMR (67.8 MHz) and ³¹P NMR (109 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer using CDCl₃ as solvent unless otherwise stated. HPLC analyses were performed on Hitachi L-7100 and GL-7410 apparatuses equipped with a UV detector using 25 cm x 4.6 mm DAICEL Chiralpak IA, IC, ID columns. Elemental analyses were performed at Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer.

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods, then distilled under N₂ and degassed before use. Bis(4methoxyphenyl)methanol (1a) and (*S*,*S*)-2,6-bis(4-phenyl-2-oxazolin-2-yl)pyridine (3e) are commercially available reagents. Diaryl methanols $1b^{S1}$, $1c^{S2}$, $1d^{S2}$, $1e^{S3}$, $1f^{S4}$, $1g^{S2}$, $1h^{S1}$, $1i^{S2}$, $1j^{S5}$, $1k^{S5}$, β -keto phosphonates $2a^{S6}$, $2b^{S7}$, $2c^{S7}$, $2d^{S7}$, $2e^{S7}$, $2f^{S6}$, $2g^{S8}$, $2h^{S7}$, $2i^{S7}$, $2j^{S9}$, and optically pure bis(oxazoline) ligands $3a-3d^{S10}$ were prepared according to literature procedures. Spectroscopic Data of Diaryl Methanols (1c, 1g, 1i, 1k) and β -Keto Phosphonate (2h).



Bis(4-propoxyphenyl)methanol (1c): A white solid, mp 64.9-66.4 °C. ¹H NMR δ 7.24 (d, J = 8.6 Hz, 4H), 6.84 (d, J = 8.6 Hz, 4H), 5.72 (s, 1H), 3.89 (t, J = 7.1 Hz, 4H), 2.23 (br, 1H), 1.78 (sext, J = 7.1 Hz, 4H), 1.02 (t, J = 7.1 Hz, 6H). ¹³C NMR δ 158.4, 136.2, 127.7, 114.3, 75.3, 69.5, 22.5, 10.5. Anal. Calcd for: C₁₉H₂₄O₃: C, 75.97; H, 8.05. Found: C, 75.88; H, 8.10.



Bis(4-methoxy-3-methylphenyl)methanol (**1g**): A colorless oil. ¹H NMR δ 7.14 (d, J = 8.4 Hz, 2H), 7.13 (s, 2H), 6.77 (d, J = 8.4 Hz, 2H), 5.69 (s, 1H), 3.80 (s, 6H), 2.19 (s, 6H), 2.10 (br, 1H). ¹³C NMR δ 157.1, 136.0, 128.9, 126.6, 124.8, 109.6, 75.6, 55.3, 16.3. HRMS (EI) Calcd for C₁₇H₂₀O₃ [M]: 272.1412. Found: 272.1417.



Bis(6-methoxynaphthalen-2-yl)methanol (1i): A white solid, mp 170.4-171.1 °C. ¹H NMR δ 7.85 (s, 2H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.43 (dd, *J* = 1.6 and 8.4 Hz, 2H), 7.11-7.17 (m, 4H), 6.12 (d, *J* = 3.2 Hz, 1H), 3.91 (s, 6H), 1.13 (d, *J* = 3.2 Hz, 1H). ¹³C NMR δ 157.8, 138.9, 134.0, 129.6, 128.7, 127.2, 125.5, 125.1, 119.0, 105.7, 76.4, 55.3. Anal. Calcd for: C₂₃H₂₀O₃: C, 80.21; H, 5.85. Found: C, 80.17; H, 5.69.

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(6-Methoxynaphthalen-2-yl)(thiophen-2-yl)methanol (1k): A white solid, mp 79.8-81.6 °C. ¹H NMR δ 7.85 (s, 1H), 7.72-7.75 (m, 2H), 7.49 (dd, *J* = 1.8 and 8.5 Hz, 1H), 7.26-7.28 (m, 1H), 7.14-7.18 (m, 2H), 6.91-6.97 (m, 2H), 6.19 (d, *J* = 3.6 Hz, 1H), 3.92 (s, 3H), 2.47 (d, *J* = 3.6 Hz, 1H). ¹³C NMR δ 157.8, 148.2, 138.2, 134.2, 129.6, 128.5, 127.2, 126.6, 125.4, 125.0, 124.9, 124.8, 119.0, 105.7, 72.5, 55.3. Anal. Calcd for: C₁₆H₁₄O₂S: C, 71.08; H, 5.22. Found: C, 70.77; H, 5.01.



Diethyl (3,3-dimethyl-2-oxocyclopentyl)phosphonate (**2h**): A colorless oil. ¹H NMR δ 4.09-4.25 (m, 4H), 2.83 (ddd, J = 7.7, 9.2, and 26.6 Hz, 1H), 2.12-2.41 (m, 2H), 1.94-2.03 (m, 1H), 1.70-1.80 (m, 1H), 1.35 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 6.9 Hz, 3H), 1.10 (s, 3H), 1.07 (s, 3H). ¹³C NMR δ 215.7 (d, ² $J_{C-P} = 5.6$ Hz), 62.6 (d, ² $J_{C-P} = 6.7$ Hz), 62.2 (d, ² $J_{C-P} = 6.7$ Hz), 46.4 (d, ¹ $J_{C-P} = 137.7$ Hz), 46.3 (d, ³ $J_{C-P} = 3.3$ Hz), 37.1 (d, ³ $J_{C-P} = 8.9$ Hz), 24.0, 23.2, 21.4 (d, ² $J_{C-P} = 3.3$ Hz), 16.4 (d, ³ $J_{C-P} = 6.2$ Hz), 16.3 (d, ³ $J_{C-P} = 6.1$ Hz). ³¹P{¹H} NMR δ 22.6 (s). HRMS (EI) Calcd for C₁₁H₂₁O₄P [M]: 248.1177. Found: 248.1172.





A typical experimental procedure for the reaction of bis(4-methoxyphenyl)methanol (1a) with diethyl (2-oxocyclopentyl)phosphonate (2a) is described below. In a 20 mL Schlenk flask were placed $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) and (3aR,3a'R,8aS,8a'S)-2,2'-(cyclopropylidene)-bis{3a,8a-dihydro-8*H*-indeno[1,2*d*]-oxazole} (**3a**) (6.4 mg, 0.018 mmol) under N₂. The mixture was magnetically stirred under vacuum at room temperature for 2 h and filled with N₂. After anhydrous ClCH₂CH₂Cl (1.0 mL) was added, the mixture was magnetically stirred at room temperature for 1 h then stirred at -20 °C for 1 h. To the reaction mixture were successively added 2a (99.1 mg, 0.45 mmol) and 1a (36.6 mg, 0.15 mmol) under N₂. After stirring for 10 min, the reaction mixture was stirred at room temperature for 65 h. The reaction was guenched by water (10 mL), and the reaction mixture was extracted with CH₂Cl₂ (15 mL×3). The combined organic layer was dried over anhydrous MgSO₄. After the concentrarion under reduced pressure, the resulting residue was purified by column chromatography (SiO₂) with hexane/ethyl acetate (45/55 to 20/80) to give diethyl (1-(bis(4methoxyphenyl)methyl)-2-oxocyclopentyl)phosphonate (4a) as a white solid (63.8 mg, 0.143 mmol, 95% isolated yield), mp 120.9-122.3 °C. ¹H NMR δ 7.37 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 4.97 (d, J = 4.9 Hz, 1H), 3.68-3.91 (m, 10H), 2.84-3.00 (m, 1H), 2.53-2.74 (m, 1H), 2.22-2.34 (m, 1H), 1.85-2.01 (m, 1H), 1.49-1.61 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 215.9 (d, ${}^{2}J_{C-P} = 5.6$ Hz), 158.2, 158.0, 132.5 (d, ${}^{3}J_{C-P} = 3.3$ Hz), 132.1 (d, ${}^{3}J_{C-P} = 16.7$ Hz), 131.3, 131.0, 113.4, 113.2, 62.7 (d, ${}^{2}J_{C-P} = 7.3$ Hz), 62.2 (d, ${}^{2}J_{C-P} = 6.7$ Hz), 60.3 (d, ${}^{1}J_{C-P} = 128.3$ Hz), 55.11, 55.07, 52.3 (d, ${}^{2}J_{C-P} = 1.1$ Hz), 38.9 (d, ${}^{3}J_{C-P} = 1.2$ Hz), 28.2 (d, ${}^{3}J_{C-P} = 1.2$ Hz),

19.8 (d, ${}^{2}J_{C-P} = 2.8 \text{ Hz}$), 16.3 (d, ${}^{3}J_{C-P} = 6.2 \text{ Hz}$), 16.2 (d, ${}^{3}J_{C-P} = 6.2 \text{ Hz}$). ${}^{31}P\{{}^{1}H\}$ NMR δ 23.7 (s). Anal. Calcd for: C₂₄H₃₁O₆P: C, 64.56; H, 7.00. Found: C, 64.54; H, 7.10. $[\alpha]^{25}{}_{D} = +$ 99.3 (c = 0.870, CHCl₃). The enantiomeric excess of **4a** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/^{*i*}PrOH = 70/30, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 29.5 min (minor) and 41.8 min (major), 84% *ee*.

Spectroscopic Data and Isolated Yield of Other Products.



Diethyl (1-(bis(4-ethoxyphenyl)methyl)-2-oxocyclopentyl)phosphonate (4b): Isolated yield 82%. A colorless oil. ¹H NMR δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.96 (d, *J* = 4.6 Hz, 1H), 3.68-4.04 (m, 8H), 2.83-2.99 (m, 1H), 2.53-2.73 (m, 1H), 2.22-2.33 (m, 1H), 1.84-1.99 (m, 1H), 1.47-1.61 (m, 2H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H). ¹³C NMR δ 215.9 (d, ²*J*_{C-P} = 6.2 Hz), 157.6, 157.4, 132.4 (d, ³*J*_{C-P} = 3.3 Hz), 132.0 (d, ³*J*_{C-P} = 16.7 Hz), 131.9, 131.0, 114.0, 113.8, 63.23, 63.21, 62.7 (d, ²*J*_{C-P} = 7.3 Hz), 62.1 (d, ²*J*_{C-P} = 6.7 Hz), 60.3 (d, ¹*J*_{C-P} = 128.8 Hz), 52.4 (d, ²*J*_{C-P} = 1.1 Hz), 38.9, 28.2, 19.8 (d, ²*J*_{C-P} = 2.2 Hz), 16.25 (d, ³*J*_{C-P} = 6.2 Hz), 16.20 (d, ³*J*_{C-P} = 5.6 Hz), 14.8, 14.7. ³¹P{¹H} NMR δ 23.8 (s). HRMS (EI) Calcd for C₂₆H₃₅O₆P [M]: 474.2171. Found: 474.2170. [α]²⁵_D = + 101.3 (*c* = 1.18, CHCl₃). The enantiomeric excess of **4b** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/ⁱPrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.0 min (minor) and 27.1 min (major), 88% *ee*.



Diethyl (1-(bis(4-propoxyphenyl)methyl)-2-oxocyclopentyl)phosphonate (4c): Isolated yield 99%. A colorless oil. ¹H NMR δ 7.35 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 4.95 (d, J = 4.6 Hz, 1H), 3.68-3.93 (m, 8H), 2.83-2.99 (m, 1H), 2.53-2.74 (m, 1H), 2.22-2.33 (m, 1H), 1.68-2.04 (m, 5H), 1.51-1.61 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.0 Hz, 3H) 1.01 (t, J = 7.4 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H). ¹³C NMR δ 215.9 (d, ² $_{J_{CP}} = 5.6$ Hz), 157.8, 157.6, 132.4 (d, ³ $_{J_{C-P}} = 3.4$ Hz), 132.0 (d, ³ $_{J_{C-P}} = 16.7$ Hz), 131.3, 131.0, 114.0, 113.8, 69.31, 69.28, 62.6 (d, ² $_{J_{C-P}} = 7.8$ Hz), 62.1 (d, ² $_{J_{C-P}} = 7.3$ Hz), 60.3 (d, ¹ $_{J_{C-P}} = 128.2$ Hz), 52.4 (d, ² $_{J_{C-P}} = 1.7$ Hz), 38.9 (d, ³ $_{J_{C-P}} = 6.1$ Hz), 16.19 (d, ³ $_{J_{C-P}} = 5.6$ Hz), 10.44, 10.43. HRMS (EI) Calcd for C₂₈H₃₉O₆P [M]: 502.2484. Found: 502.2475. [α]²⁵_D = + 80.3 (c = 1.13, CHCl₃). The enantiomeric excess of **4c** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/¹PrOH = 75/25, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 12.5 min (minor) and 18.0 min (major), 87% *ee*.



Diethyl (1-(bis(4-butoxyphenyl)methyl)-2-oxocyclopentyl)phosphonate (4d): Isolated yield 87%. A colorless oil. ¹H NMR δ 7.35 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.95 (d, *J* = 4.9 Hz, 1H), 3.68-3.95 (m, 8H), 2.84-2.99 (m, 1H), 2.53-2.73 (m, 1H), 2.22-2.33 (m, 1H), 1.85-2.00 (m, 1H), 1.65-1.77 (m, 4H), 1.40-1.58 (m, 6H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H). ¹³C NMR δ 215.9 (d, ²*J*_{C-P} = 6.1 Hz), 157.8, 157.6, 132.3 (d, ³*J*_{C-P} = 3.3 Hz), 131.9 (d, ³*J*_{C-P} = 16.2 Hz), 131.3, 131.0, 114.0, 113.8, 67.49, 67.45, 62.6 (d, ²*J*_{C-P})

= 7.2 Hz), 62.1 (d, ${}^{2}J_{C-P}$ = 7.3 Hz), 60.3 (d, ${}^{1}J_{C-P}$ = 128.2 Hz), 52.4 (d, ${}^{2}J_{C-P}$ = 1.1 Hz), 38.9 (d, ${}^{3}J_{C-P}$ = 1.1 Hz), 31.3, 31.2, 28.2, 19.8 (d, ${}^{2}J_{C-P}$ = 2.2 Hz), 19.2, 19.1, 16.24 (d, ${}^{3}J_{C-P}$ = 6.1 Hz), 16.20 (d, ${}^{3}J_{C-P}$ = 5.6 Hz), 13.78, 13.75. HRMS (EI) Calcd for C₃₀H₄₃O₆P [M]: 530.2797. Found: 530.2792. [α]²⁵_D = + 79.9 (*c* = 0.910, CHCl₃). The enantiomeric excess of **4d** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/^{*i*}PrOH = 75/25, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.2 min (minor) and 16.1 min (major), 87% *ee*.



Diethyl (1-(bis(4-isopropoxyphenyl)methyl)-2-oxocyclopentyl)phosphonate (4e): Isolated yield 95%. A colorless oil. ¹H NMR δ 7.35 (d, J = 8.9 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 4.94 (d, J = 4.6 Hz, 1H), 4.51 (sept, J = 5.9 Hz, 1H), 4.45 (sept, J = 5.9 Hz, 1H), 3.68-3.90 (m, 4H), 2.82-2.96 (m, 1H), 2.54-2.74 (m, 1H), 2.21-2.33 (m, 1H), 1.85-2.04 (m, 1H), 1.51-1.60 (m, 2H), 1.25-1.32 (m, 12H), 1.19 (t, J = 7.0 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H). ¹³C NMR δ 215.8 (d, ² $_{J_{C-P}} = 6.1$ Hz), 156.5, 156.4, 132.4 (d, ³ $_{J_{C-P}} = 3.3$ Hz), 131.9 (d, ³ $_{J_{C-P}} = 16.7$ Hz), 131.3, 131.1, 115.25, 115.20, 69.65, 69.60, 62.5 (d, ² $_{J_{C-P}} = 7.3$ Hz), 62.1 (d, ² $_{J_{C-P}} = 7.3$ Hz), 60.4 (d, ¹ $_{J_{C-P}} = 128.2$ Hz), 52.3 (d, ² $_{J_{C-P}} = 1.6$ Hz), 38.9, 28.1, 22.0, 21.9, 19.8 (d, ² $_{J_{C-P}} = 2.8$ Hz), 16.2 (d, ³ $_{J_{C-P}} = 5.6$ Hz), 16.1 (d, ³ $_{J_{C-P}} = 6.2$ Hz). HRMS (EI) Calcd for C₂₈H₃₉O₆P [M]: 502.2484. Found: 502.2493. [α]²⁵_D = + 80.3 (c = 1.02, CHCl₃). The enantiomeric excess of **4e** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/^jPrOH = 75/25, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 10.1 min (minor) and 14.9 min (major), 87% *ee*.

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Diethyl (1-(bis(4-(benzyloxy)phenyl)methyl)-2-oxocyclopentyl)phosphonate (**4f**): Isolated yield 88%. A pale yellow solid, mp 100.7-102.6 °C. ¹H NMR δ 7.26-7.43 (m, 12H), 7.08 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 4.96-5.03 (m, 5H), 3.67-3.91 (m, 4H), 2.83-2.98 (m, 1H), 2.51-2.73 (m, 1H), 2.22-2.34 (m, 1H), 1.85-2.01 (m, 1H), 1.49-1.61 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H), 1.11 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 215.8 (d, ² $J_{C-P} = 6.2$ Hz), 157.4, 157.3, 137.0, 136.9, 132.8 (d, ³ $J_{C-P} = 3.4$ Hz), 132.4 (d, ³ $J_{C-P} = 16.2$ Hz), 131.4, 131.1, 128.5, 127.91, 127.87, 127.4, 114.4, 114.2, 69.9, 69.8, 62.7 (d, ² $J_{C-P} = 7.3$ Hz), 60.3 (d, ¹ $J_{C-P} = 128.3$ Hz), 52.4, 38.9, 28.2 (d, ³ $J_{C-P} = 1.1$ Hz), 19.8 (d, ² $J_{C-P} = 2.8$ Hz), 16.3 (d, ³ $J_{C-P} = 6.1$ Hz), 16.2 (d, ³ $J_{C-P} = 5.6$ Hz). Anal. Calcd for: C₃₆H₃₉O₆P: C, 72.22; H, 6.57. Found: C, 72.03; H, 6.40. [α]²⁵_D = + 76.2 (c = 0.705, CHCl₃). The enantiomeric excess of **4f** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/ⁱPrOH = 75/25, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 20.5 min (minor) and 31.4 min (major), 83% *ee*.



Diethyl (1-(bis(4-methoxy-3-methylphenyl)methyl)-2-oxocyclopentyl)phosphonate (4g): Isolated yield 87%. A white solid, mp 133.6-134.3 °C. ¹H NMR δ 7.24-7.27 (m, 1H), 7.16 (s,

1H), 6.93-6.97 (m, 2H), 6.75 (d, J = 8.4 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 4.88 (d, J = 4.6 Hz, 1H), 3.67-3.90 (m, 10H), 2.83-2.99 (m, 1H), 2.61-2.76 (m, 1H), 1.89-2.32 (m, 8H), 1.46-1.61 (m, 2H), 1.19 (t, J = 7.0 Hz, 3H), 1.12 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 215.9 (d, ² $J_{C-P} = 5.6$ Hz), 156.3, 156.2, 132.50, 132.47, 132.2 (d, ³ $J_{C-P} = 3.3$ Hz), 131.8 (d, ³ $J_{C-P} = 16.2$ Hz), 128.7, 128.2, 125.9, 125.6, 109.4, 109.2, 62.6 (d, ² $J_{c-P} = 7.9$ Hz), 62.1 (d, ² $J_{C-P} = 7.3$ Hz), 60.4 (d, ¹ $J_{C-P} = 128.3$ Hz), 55.2, 55.1, 52.4 (d, ² $J_{C-P} = 1.2$ Hz), 38.9 (d, ³ $J_{C-P} = 1.6$ Hz), 28.3 (d, ³ $J_{C-P} = 1.1$ Hz), 19.8 (d, ² $J_{C-P} = 2.8$ Hz), 16.33, 16.31, 16.23 (d, ³ $J_{C-P} = 6.1$ Hz), 16.16 (d, ³ $J_{C-P} = 6.1$ Hz). ³¹P{¹H} NMR δ 23.8 (s). Anal. Calcd for: C₂₆H₃₅O₆P: C, 65.81; H, 7.43. Found: C, 65.90; H, 7.47. [α]²⁵_D = + 97.9 (c = 0.960, CHCl₃). The enantiomeric excess of **4g** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/^{*i*}PrOH = 75/25, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 13.8 min (minor) and 17.8 min (major), 90% *ee*.



Diethyl (1-(bis(3,4-dimethoxyphenyl)methyl)-2-oxocyclopentyl)phosphonate (4h): Isolated yield 93%. A colorless oil. ¹H NMR δ 7.05 (dd, J = 2.0 and 8.2 Hz, 1H), 6.97 (d, J = 1.9 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.71-6.75 (m, 3H), 4.97 (d, J = 4.6 Hz, 1H), 3.66-3.93 (m, 4H), 3.88 (s, 3H), 3.86 (s, 3H), 3.81 (s, 6H), 2.86-3.01 (m, 1H), 2.52-2.73 (m, 1H), 2.25-2.36 (m, 1H), 1.82-2.00 (m, 1H), 1.50-1.64 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 215.9 (d, ² $J_{C-P} = 5.6$ Hz), 148.3, 147.7, 147.6, 132.8 (d, ³ $J_{C-P} = 3.9$ Hz), 132.5 (d, ³ $J_{C-P} = 16.7$ Hz), 122.5, 122.1, 113.84, 113.79, 110.7, 110.6, 62.8 (d, ² $J_{C-P} = 7.2$ Hz), 62.0 (d, ² $J_{C-P} = 7.3$ Hz), 60.4 (d, ¹ $J_{C-P} = 128.2$ Hz), 55.81, 55.78, 55.7, 53.1 (d, ² $J_{C-P} = 1.6$ Hz), 39.0 (d, ³ $J_{C-P} = 1.2$ Hz), 28.4 (d, ³ $J_{C-P} = 1.1$ Hz), 19.7 (d, ² $J_{C-P} = 2.2$ Hz), 16.3 (d, ³ $J_{C-P} = 5.6$ Hz), 16.2 (d, ${}^{3}J_{C-P} = 6.2$ Hz). HRMS (EI) Calcd for $C_{26}H_{35}O_{8}P$ [M]: 506.2070. Found: 506.2074. $[\alpha]^{25}{}_{D} = +102.2$ (c = 1.30, CHCl₃). The enantiomeric excess of **4h** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{*i*}PrOH = 75/25, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.5 min (major) and 14.7 min (minor), 86% *ee*.



Diethyl (1-(bis(6-methoxynaphthalen-2-yl)methyl)-2-oxocyclopentyl)phosphonate (4i): Isolated yield 90%. A white solid, mp 147.2-149.0 °C. ¹H NMR δ 7.98 (s, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.50-7.68 (m, 5H), 7.32 (d, J = 8.6 Hz, 1H), 7.00-7.16 (m, 4H), 5.34 (d, J = 4.6 Hz, 1H), 3.58-4.02 (m, 10H), 3.03-3.17 (m, 1H), 2.70-2.90 (m, 1H), 2.25-2.36 (m, 1H), 1.92-2.02 (m, 1H), 1.46-1.59 (m, 2H), 1.15 (t, J = 7.0 Hz, 3H), 1.03 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 215.7 (d, ² $J_{C-P} = 6.1$ Hz), 157.7, 157.5, 135.4 (d, ³ $J_{C-P} = 3.3$ Hz), 135.0 (d, ³ $J_{C-P} = 16.7$ Hz), 133.3, 133.1, 129.6, 129.44, 129.43, 129.3, 129.0, 128.5, 126.5, 126.3, 118.7, 118.6, 105.5, 105.2, 62.7 (d, ² $J_{C-P} = 7.8$ Hz), 62.3 (d, ² $J_{C-P} = 7.3$ Hz), 60.4 (d, ¹ $J_{C-P} = 128.3$ Hz), 55.22, 55.19, 53.8 (d, ² $J_{C-P} = 1.7$ Hz), 38.9, 28.6 (d, ³ $J_{C-P} = 1.1$ Hz), 19.8 (d, ² $J_{C-P} = 2.2$ Hz), 16.2 (d, ³ $J_{C-P} = 6.2$ Hz), 16.1 (d, ³ $J_{C-P} = 6.2$ Hz). Anal. Calcd for: C₃₂H₃₅O₆P: C, 70.32; H, 6.45. Found: C, 70.22; H, 6.67. [α]²⁵_D = + 155.6 (c = 1.05, CHCl₃). The enantiomeric excess of **4i** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/ⁱPrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 34.0 min (minor) and 39.8 min (major), 77% *ee*.



Diethyl (1-(di(thiophen-2-yl)methyl)-2-oxocyclopentyl)phosphonate (**4j**): Isolated yield 85%. A pale yellow solid, mp 90.1-90.8 °C. ¹H NMR δ 7.21 (d, J = 5.1 Hz 1H), 7.12-7.15 (m, 2H), 6.93 (dd, J = 3.5 and 4.9 Hz 1H), 6.85-6.87 (m, 2H), 5.63 (d, J = 5.7 Hz, 1H), 3.68-3.99 (m, 4H), 2.64-2.92 (m, 2H), 2.34-2.43 (m, 1H), 1.92-2.09 (m, 1H), 1.57-1.84 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 214.8 (d, ² $J_{C-P} = 5.6$ Hz), 142.6 (d, ³ $J_{C-P} =$ = 18.4 Hz), 142.4 (d, ³ $J_{C-P} = 2.8$ Hz), 127.8, 127.4, 126.6, 126.1, 125.2, 124.6, 62.7 (d, ² $J_{C-P} =$ 7.3 Hz), 62.5 (d, ² $J_{C-P} = 7.3$ Hz), 61.4 (d, ¹ $J_{C-P} = 131.1$ Hz), 44.4, 39.1, 28.1 (d, ³ $J_{C-P} = 2.2$ Hz), 19.5 (d, ² $J_{C-P} = 2.2$ Hz), 16.3 (d, ³ $J_{C-P} = 6.2$ Hz), 16.1 (d, ³ $J_{C-P} = 6.1$ Hz). ³¹P{¹H} NMR δ 21.9 (s). Anal. Calcd for: C₁₈H₂₃O₄PS₂: C, 54.25; H, 5.82. Found: C, 54.15; H, 5.93. [α]²⁵_D = + 75.9 (c = 0.850, CHCl₃). The enantiomeric excess of **4j** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/^{*i*}PrOH = 75/25, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 18.6 min (minor) and 31.4 min (major), 76% *ee*.



Diethyl

(1-((6-methoxynaphthalen-2-yl)(thiophen-2-yl)methyl)-2-

oxocyclopentyl)phosphonate (**4k**): Isolated yield 88% (major/minor = 1.7/1). A pale yellow solid. major-isomer: ¹H NMR δ 7.66-7.69 (m, 2H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 1.8 and 8.6 Hz, 1H), 7.26 (m, 1H), 7.20 (d, *J* = 5.2 Hz, 1H), 7.10 (dd, *J* = 2.4 and 8.9 Hz, 1H), S13

7.04 (d, J = 2.4 Hz, 1H), 6.98 (dd, J = 3.4 and 5.2 Hz, 1H), 5.48 (d, J = 5.9 Hz, 1H), 3.79-3.99 (m, 7H), 2.64-2.98 (m, 2H), 2.18-2.29 (m, 1H), 1.87-2.00 (m, 1H), 1.39-1.51 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H). major-isomer: ¹³C NMR δ 214.8 (d, ² $J_{C-P} = 5.0$ Hz), 157.8, 142.5 (d, ${}^{3}J_{C-P} = 3.3 \text{ Hz}$), 134.0 (d, ${}^{3}J_{C-P} = 16.1 \text{ Hz}$), 133.3, 129.7, 129.4, 128.7, 128.5, 127.4, 126.5, 126.2, 124.4, 118.9, 105.2, 62.7 (d, ${}^{2}J_{C-P} = 7.8 \text{ Hz}$), 62.5 (d, ${}^{2}J_{C-P} = 7.3 \text{ Hz}$), 60.9 (d, ${}^{1}J_{C-P} = 129.4$ Hz), 55.2, 48.7 (d, ${}^{2}J_{C-P} = 2.2$ Hz), 39.1 (d, ${}^{3}J_{C-P} = 1.6$ Hz), 27.9 (d, ${}^{3}J_{C-P} =$ 1.7 Hz), 19.7 (d, ${}^{2}J_{C-P} = 3.3$ Hz), 16.3 (d, ${}^{3}J_{C-P} = 6.1$ Hz), 16.2 (d, ${}^{3}J_{C-P} = 5.6$ Hz). minorisomer: ¹H NMR δ 7.87 (d, J = 1.1 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.55 (dd, J = 1.8 and 8.6 Hz, 1H), 7.10-7.15 (m, 3H), 6.83 (dd, J = 3.7 and 5.1 Hz, 1H), 6.75 (d, J = 3.7 Hz, 1H), 5.43 (d, J = 4.3 Hz, 1H), 3.91 (s, 3H), 3.50-3.83 (m, 4H), 2.71-3.04 (m, 4H), 3.50-3.83 (m, 4H), 3.50-3.82H), 2.41-2.50 (m, 1H), 1.70-2.17 (m, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H). minor-isomer: ¹³C NMR δ 215.7 (d, ²J_{C-P} = 5.6 Hz), 157.7, 143.7 (d, ³J_{C-P} = 18.4 Hz), 135.3 (d, ${}^{3}J_{C-P} = 3.3$ Hz), 133.6, 129.5, 128.6, 128.5, 127.6, 126.5, 126.4, 125.1, 118.7, 105.5, 62.5 $(d, {}^{2}J_{C-P} = 6.7 \text{ Hz}), 62.3 (d, {}^{2}J_{C-P} = 7.8 \text{ Hz}), 61.4 (d, {}^{1}J_{C-P} = 128.8 \text{ Hz}), 55.2, 49.4, 38.9, 28.6 (d, {}^{2}J_{C-P} = 128.8 \text{ Hz}), 55.2, 49.4, 59.6 \text{ Hz}), 55.2, 49.4, 59.6 \text{ Hz}), 55.2, 49.4, 59.6 \text{ Hz}), 55.2, 59.6 \text{ Hz}), 56.6, 59.6 \text{ Hz}), 56.6, 59.6 \text{ Hz}), 56.6,$ ${}^{3}J_{C-P} = 2.2$ Hz), 19.6 (d, ${}^{2}J_{C-P} = 1.7$ Hz), 16.2 (d, ${}^{3}J_{C-P} = 6.1$ Hz), 16.0 (d, ${}^{3}J_{C-P} = 6.1$ Hz). Anal. Calcd for: C₂₅H₂₉O₅PS₂: C, 63.54; H, 6.19. Found: C, 63.47; H, 6.12. The enantiomeric excess of major-4k was determined by HPLC analysis; DAICEL Chiralpak ID, hexane/ⁱPrOH = 75/25, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.9 min (major) and 24.6 min (minor), 88% ee. The enantiomeric excess of minor-4k was determined by HPLC analysis; DAICEL Chiralpak ID, hexane/ⁱPrOH = 75/25, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 22.3 min (major) and 32.8 min (minor), 64% ee.



Dimethyl (1-(bis(4-methoxy-3-methylphenyl)methyl)-2-oxocyclopentyl)phosphonate (41): Isolated yield 73%. A colorless oil. ¹H NMR δ 7.27 (dd, *J* = 2.2 and 8.4 Hz, 1H), 7.17 (d, *J* = 2.2 Hz, 1H), 6.93-6.98 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.88 (d, *J* = 4.9 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.45 (d, *J* = 11.1 Hz, 3H), 3.40 (d, *J* = 10.8 Hz, 3H), 2.82-2.98 (m, 1H), 2.56-2.77 (m, 1H), 2.11-2.33 (m, 7H), 1.81-1.97 (m, 1H), 1.46-1.61 (m, 2H). ¹³C NMR δ 215.7 (d, ²*J*_{C-P} = 6.2 Hz), 156.4, 156.3, 132.40, 132.37, 132.1 (d, ³*J*_{C-P} = 3.4 Hz), 131.5 (d, ³*J*_{C-P} = 16.7 Hz), 128.6, 128.1, 126.0, 125.8, 109.4, 109.3, 60.5 (d, ¹*J*_{C-P} = 128.8 Hz), 55.31, 55.26, 53.5 (d, ²*J*_{C-P} = 7.3 Hz), 52.9 (d, ²*J*_{C-P} = 7.3 Hz), 52.6 (d, ²*J*_{C-P} = 1.2 Hz), 39.0 (d, ³*J*_{C-P} = 1.7 Hz), 28.4 (d, ³*J*_{C-P} = 1.1 Hz), 20.0 (d, ²*J*_{C-P} = 2.8 Hz), 16.5, 16.4. HRMS (EI) Calcd for C₂₄H₃₁O₆P [M]: 446.1858. Found: 446.1861. [α]²⁵_D = + 95.0 (*c* = 0.815, CHCl₃). The enantiomeric excess of **41** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{*i*}PrOH = 75/25, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.9 min (major) and 9.3 min (minor), 86% *ee*.



Dipropyl (1-(bis(4-methoxy-3-methylphenyl)methyl)-2-oxocyclopentyl)phosphonate (4m): Isolated yield 95%. A colorless oil. ¹H NMR δ 7.27 (dd, J = 2.2 and 8.3 Hz 1H), 7.16 (d,

 $J = 2.2 \text{ Hz}, 1\text{H}, 6.95-6.99 \text{ (m, 2H)}, 6.75 \text{ (d, } J = 8.3 \text{ Hz}, 1\text{H}), 6.64 \text{ (d, } J = 8.4 \text{ Hz}, 1\text{H}), 4.89 \text{ (d, } J = 4.9 \text{ Hz}, 1\text{H}), 3.53-3.83 \text{ (m, 10H)}, 2.83-2.99 \text{ (m, 1H)}, 2.57-2.78 \text{ (m, 1H)}, 1.86-2.34 \text{ (m, 8H)}, 1.44-1.61 \text{ (m, 6H)}, 0.86 \text{ (t, } J = 7.4 \text{ Hz}, 3\text{H}), 0.83 \text{ (t, } J = 7.4 \text{ Hz}, 3\text{H}). {}^{13}\text{C} \text{ NMR } \delta 215.7 \text{ (d, }^{2}J_{\text{C}-P} = 5.6 \text{ Hz}), 156.3, 156.2, 132.5, 132.4, 132.3 \text{ (d, }^{3}J_{\text{C}-P} = 3.3 \text{ Hz}), 131.8 \text{ (d, }^{3}J_{\text{C}-P} = 16.7 \text{ Hz}), 128.7, 128.2, 125.9, 125.6, 109.4, 109.3, 68.0 \text{ (d, }^{2}J_{\text{c}-P} = 7.8 \text{ Hz}), 67.6 \text{ (d, }^{2}J_{\text{C}-P} = 7.2 \text{ Hz}), 60.5 \text{ (d, }^{1}J_{\text{C}-P} = 128.3 \text{ Hz}), 55.2, 55.1, 52.4 \text{ (d, }^{2}J_{\text{C}-P} = 1.7 \text{ Hz}), 38.9 \text{ (d, }^{3}J_{\text{C}-P} = 1.1 \text{ Hz}), 28.3 \text{ (d, }^{3}J_{\text{C}-P} = 1.2 \text{ Hz}), 23.74 \text{ (d, }^{3}J_{\text{C}-P} = 6.1 \text{ Hz}), 23.69 \text{ (d, }^{3}J_{\text{C}-P} = 6.1 \text{ Hz}), 19.8 \text{ (d, }^{2}J_{\text{C}-P} = 2.8 \text{ Hz}), 16.30, 16.27, 9.95, 9.92. \text{ HRMS (EI) Calcd for } C_{28}H_{39}O_6P \text{ [M]}: 502.2484. \text{ Found: } 502.2496. \text{ [}\alpha\text{]}^{25}_{\text{D}} = + 77.8 \text{ (}c = 1.09, \text{ CHCl}_3\text{)}. \text{ The enantiomeric excess of } 4\mathbf{m} \text{ was determined by HPLC analysis;} DAICEL Chiralpak IA, hexane/^{i}PrOH = 80/20, flow rate = 1.0 \text{ mL/min}, \lambda = 254 \text{ nm}, retention time: 5.5 \text{ min (major) and 8.3 min (minor)}, 90\% ee.$



Dibutyl (1-(bis(4-methoxy-3-methylphenyl)methyl)-2-oxocyclopentyl)phosphonate (4n): Isolated yield 89%. A colorless oil. ¹H NMR δ 7.27 (m, 1H), 7.16 (s, 1H), 6.95-6.99 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.89 (d, *J* = 4.9 Hz, 1H), 3.58-3.84 (m, 10H), 2.82-2.98 (m, 1H), 2.56-2.77 (m, 1H), 1.86-2.34 (m, 8H), 1.40-1.60 (m, 6H), 1.18-1.36 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 3H), 0.87 (t, *J* = 7.6 Hz, 3H). ¹³C NMR δ 215.7 (d, ²*J*_{C-P} = 5.6 Hz), 156.3, 156.2, 132.5, 132.4, 132.3 (d, ³*J*_{C-P} = 3.3 Hz), 131.8 (d, ³*J*_{C-P} = 16.7 Hz), 128.7, 128.1, 125.9, 125.6, 109.4, 109.2, 66.3 (d, ²*J*_{C-P} = 7.8 Hz), 65.8 (d, ²*J*_{C-P} = 7.3 Hz), 60.5 (d, ¹*J*_{C-P} = 128.2 Hz), 55.13, 55.08, 52.4 (d, ²*J*_{C-P} = 1.7 Hz), 39.0, 32.41 (d, ³*J*_{C-P} = 6.2 Hz), 32.37 (d, ³*J*_{C-P} = 6.1 Hz), 28.3, 19.8 (d, ²*J*_{C-P} = 2.2 Hz), 18.7, 18.6, 16.32, 16.30, 13.5. HRMS (EI) Calcd for C₃₀H₄₃O₆P [M]: 530.2797. Found: 530.2787. $[\alpha]^{25}{}_{D} = +78.2$ (c = 1.38, CHCl₃). The enantiomeric excess of **4n** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{*i*}PrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.5 min (major) and 8.0 min (minor), 88% *ee*.



Diisopropyl (1-(bis(4-methoxy-3-methylphenyl)methyl)-2-oxocyclopentyl)phosphonate (40): Isolated yield 93%. A white solid, mp 121.2-122.0 °C. ¹H NMR δ 7.24 (dd, J = 2.2 and 8.4 Hz 1H), 7.15 (d, J = 2.2 Hz, 1H), 6.95-6.99 (m, 2H), 6.73 (d, J = 8.4 Hz, 1H), 6.63 (d, J =8.1 Hz, 1H), 4.87 (d, J = 5.1 Hz, 1H), 4.28-4.50 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 2.58-2.93 (m, 2H), 1.87-2.32 (m, 8H), 1.45-1.60 (m, 2H), 1.22 (d, J = 6.2 Hz, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.14 (d, J = 6.2 Hz, 3H), 1.07 (d, J = 6.2 Hz, 3H). ¹³C NMR δ 216.1 (d, ² $J_{C-P} = 5.6$ Hz), 156.3, 156.1, 132.61, 132.59, 132.5 (d, ³ $J_{C-P} = 3.3$ Hz), 132.1 (d, ³ $J_{C-P} = 16.7$ Hz), 128.7, 128.4, 125.9, 125.3, 109.4, 109.2, 71.0 (d, ² $J_{C-P} = 7.3$ Hz), 70.9 (d, ² $J_{C-P} = 7.9$ Hz), 60.5 (d, ¹ $J_{C-P} = 128.8$ Hz), 55.2, 55.1, 52.5 (d, ² $J_{C-P} = 1.7$ Hz), 39.1 (d, ³ $J_{C-P} = 1.1$ Hz), 28.4 (d, ³ $J_{C-P} =$ 1.6 Hz), 24.2 (d, ³ $J_{C-P} = 2.8$ Hz), 24.1 (d, ³ $J_{C-P} = 2.8$ Hz), 23.8 (d, ³ $J_{C-P} = 6.1$ Hz), 23.6 (d, ³ J_{C-} P = 6.1 Hz), 19.8 (d, ² $J_{C-P} = 2.8$ Hz), 16.3. Anal. Calcd for: C₂₈H₃₉O₆P: C, 66.91; H, 7.82. Found: C, 66.57; H, 7.77. [α]²⁵_D = + 76.8 (c = 0.815, CHCl₃). The enantiomeric excess of **40** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{*i*}PrOH = 85/15, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.7 min (major) and 6.3 min (minor), 92% *ee*.



Diethyl (2-(bis(4-methoxy-3-methylphenyl)methyl)-1-oxo-2,3-dihydro-1H-inden-2yl)phosphonate (4p): Isolated yield 93%. A pale yellow oil. ¹H NMR δ 7.68 (d, J = 7.6 Hz, 1H), 7.44-7.50 (m, 1H), 7.23-7.38 (m, 4H), 6.93-6.97 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 6.47 (d, J = 8.1 Hz, 1H), 5.16 (d, J = 5.1 Hz, 1H), 3.51-3.96 (m, 12H), 2.20 (s, 3H), 1.98 (s, 3H), 1.05 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 202.8 (d, ² $J_{C-P} = 5.0$ Hz), 156.4, 156.0, 152.6 (d, ³ $J_{C-P} = 3.9$ Hz), 136.6 (d, ³ $J_{C-P} = 1.7$ Hz), 134.5, 132.5, 132.1 (d, ³ $J_{C-P} = 3.9$ Hz), 132.0, 131.4 (d, ³ $J_{C-P} = 16.2$ Hz), 128.3, 128.0, 127.2, 125.74, 125.65, 125.6, 124.0 109.19, 109.16, 62.7 (d, ² $J_{C-P} = 7.3$ Hz), 62.2 (d, ² $J_{C-P} = 7.3$ Hz), 60.4 (d, ¹ $J_{C-P} = 130.4$ Hz), 55.1, 54.9, 51.7 (d, ² $J_{C-P} = 2.2$ Hz), 32.6, 16.3, 16.2, 16.0 (d, ³ $J_{C-P} = 6.1$ Hz), 15.9 (d, ³ $J_{C-P} = 6.1$ Hz). HRMS (EI) Calcd for C₃₀H₃₅O₆P [M]: 522.2171. Found: 522.2176. [α]²⁵_D = + 85.4 (c = 0.890, CHCl₃). The enantiomeric excess of **4p** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{*i*}PrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 9.0 min (major) and 16.1 min (minor), 85% *ee*.



Diethyl (3-(bis(4-methoxy-3-methylphenyl)methyl)-2-oxotetrahydrofuran-3vl)phosphonate (4q): Isolated yield 64%. A colorless oil. ¹H NMR δ 7.22 (dd, J = 2.3 and 8.4

Hz, 1H), 7.05-7.13 (m, 3H), 6.77 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 4.89 (d, J = 4.6 Hz, 1H), 4.22 (q, J = 8.5 Hz, 1H), 3.73-3.98 (m, 11H), 2.84-3.10 (m, 2H), 2.19 (s, 3H), 2.13 (s, 3H), 1.21 (t, J = 6.8 Hz, 3H), 1.16 (t, J = 6.9 Hz, 3H). ¹³C NMR δ 175.4 (d, ² $J_{C-P} = 4.4$ Hz), 156.65, 156.60, 132.30, 132.26, 131.2 (d, ³ $J_{C-P} = 3.9$ Hz), 131.8 (d, ³ $J_{C-P} = 14.5$ Hz), 128.5, 128.0, 126.3, 125.9, 109.6, 109.3, 65.8 (d, ³ $J_{C-P} = 2.2$ Hz), 63.5 (d, ² $J_{C-P} = 7.3$ Hz), 62.8 (d, ² $J_{C-P} = 7.3$ Hz), 55.21, 55.16, 54.7 (d, ¹ $J_{C-P} = 134.4$ Hz), 51.9 (d, ² $J_{C-P} = 1.2$ Hz), 27.1 (d, ² $J_{C-P} = 1.7$ Hz), 16.4, 16.3, 16.24 (d, ³ $J_{C-P} = 6.1$ Hz), 16.19 (d, ³ $J_{C-P} = 5.6$ Hz). ³¹P{¹H} NMR δ 21.8 (s). HRMS (EI) Calcd for C₂₅H₃₃O₇P [M]: 476.1964. Found: 476.1962. [α]²⁵_D = + 75.0 (c = 1.01, CHCl₃). The enantiomeric excess of **4q** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/ⁱPrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 8.4 min (minor) and 10.0 min (major), 74% *ee*.



Diethyl

(1-(bis(4-methoxy-3-methylphenyl)methyl)-3,3-dimethyl-2-

oxocyclopentyl)phosphonate (**4r**): Isolated yield 78%. A colorless oil. ¹H NMR δ 7.29 (dd, *J* = 2.2 and 8.4 Hz, 1H), 7.19 (d, *J* = 2.2 Hz, 1H), 6.96-7.00 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 4.87 (d, *J* = 5.4 Hz, 1H), 3.63-3.90 (m, 10H), 2.80-2.95 (m, 1H), 2.52-2.75 (m, 1H), 2.18 (s, 3H), 2.11 (s, 3H), 1.90-2.02 (m, 1H), 1.48-1.56 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.07 (s, 3H), 0.03 (s, 3H). ¹³C NMR δ 218.3 (d, ²*J*_{C-P} = 6.2 Hz), 156.4, 156.3, 133.2, 132.6 (d, ³*J*_{C-P} = 3.3 Hz), 132.5, 131.9 (d, ³*J*_{C-P} = 17.3 Hz), 129.4, 128.1, 125.8, 125.6, 109.3, 109.2, 62.5 (d, ²*J*_{C-P} = 7.3 Hz), 62.1 (d, ²*J*_{C-P} = 7.3 Hz), 62.1 (d, ¹*J*_{C-P} = 124.3 Hz), 55.2, 52.7 (d, ²*J*_{C-P} = 1.6 Hz), 45.6 (d, ³*J*_{C-P} = 1.1 Hz), 35.8, 24.9, 24.8 (d,

 ${}^{3}J_{C-P} = 2.2 \text{ Hz}$), 22.7 (d, ${}^{2}J_{C-P} = 1.2 \text{ Hz}$), 16.33 (d, ${}^{3}J_{C-P} = 6.2 \text{ Hz}$), 16.32, 16.21 (d, ${}^{3}J_{C-P} = 6.2 \text{ Hz}$), 16.19. HRMS (EI) Calcd for C₂₈H₃₉O₆P [M]: 502.2484. Found: 502.2496. [α]²⁵_D = + 62.6 (c = 1.03, CHCl₃). The enantiomeric excess of **4r** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{*i*}PrOH = 75/25, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.2 min (major) and 9.5 min (minor), 66% *ee*.



Diethyl (1-(bis(4-methoxy-3-methylphenyl)methyl)-2-oxocyclohexyl)phosphonate (4s): Isolated yield 8%. A colorless oil. ¹H NMR δ 7.33 (dd, J = 2.3 and 8.5 Hz, 1H), 7.19 (d, J = 2.3 Hz, 1H), 6.98-7.03 (m, 2H), 6.72 (d, J = 8.5 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 5.09 (d, J = 10.5 Hz, 1H), 3.72-3.94 (m, 10H), 2.40-2.63 (m, 3H), 2.12-2.23 (m, 7H), 1.78-1.98 (m, 3H), 1.60-1.67 (m, 1H), 1.16 (t, J = 7.2 Hz, 3H), 1.10 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 209.5 (d, ² $J_{C-P} = 5.6$ Hz), 156.3, 156.0, 133.3, 132.8 (d, ³ $J_{C-P} = 15.1$ Hz), 132.64, 132.58 (d, ³ $J_{C-P} = 2.8$ Hz), 129.2, 128.4, 125.8, 125.3, 109.3, 109.2, 62.3 (d, ² $J_{C-P} = 7.3$ Hz), 61.0 (d, ¹ $J_{C-P} = 125.4$ Hz), 55.22, 55.18, 53.0 (d, ² $J_{C-P} = 2.8$ Hz), 40.5 (d, ³ $J_{C-P} = 1.7$ Hz), 28.3 (d, ³ $J_{C-P} = 3.3$ Hz), 22.7, 20.7 (d, ² $J_{C-P} = 2.2$ Hz), 16.4, 16.3, 16.2 (d, ³ $J_{C-P} = 6.1$ Hz), 16.1 (d, ³ $J_{C-P} = 6.2$ Hz). HRMS (EI) Calcd for C₂₇H₃₇O₆P [M]: 488.2328. Found: 488.2324. The enantiomeric excess of **4s** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/ⁱPrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 4.9 min (major) and 5.8 min (minor), 88% *ee*.



Diethyl (1,1-bis(4-methoxy-3-methylphenyl)-2-methyl-3-oxobutan-2-yl)phosphonate (4t): Isolated yield 59%. A pale yellow solid, mp 128.9-130.7 °C. ¹H NMR δ 7.19-7.22 (m, 2H), 7.09 (dd, J = 2.2 and 8.6 Hz, 1H), 7.01 (d, J = 2.2 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 8.6 Hz, 1H), 5.11 (d, J = 12.2 Hz, 1H), 3.82-4.01 (m, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 3.54-3.69 (m, 1H), 2.19 (s, 3H), 2.17 (s, 3H), 2.12 (s, 3H), 1.67 (d, J = 16.7 Hz, 3H), 1.21 (t, J =7.0 Hz, 3H), 1.02 (t, J = 7.0 Hz, 3H). ¹³C NMR δ 205.4 (d, ² $J_{C-P} = 2.2$ Hz), 156.5, 156.3, 133.3 (d, ³ $J_{C-P} = 18.4$ Hz), 132.9, 132.4 (d, ³ $J_{C-P} = 1.2$ Hz), 131.7, 128.9, 126.6, 126.5, 125.6, 109.6, 109.3, 62.5 (d, ² $J_{C-P} = 7.3$ Hz), 62.1 (d, ² $J_{C-P} = 7.1$ Hz), 61.1 (d, ¹ $J_{C-P} = 126.5$ Hz), 55.3, 55.1, 51.3 (d, ² $J_{C-P} = 2.8$ Hz), 28.7, 16.33, 16.26, 16.1 (d, ³ $J_{C-P} = 5.6$ Hz), 16.0 (d, ³ $J_{C-P} = 6.7$ Hz), 14.9 (d, ² $J_{C-P} = 5.0$ Hz). ³¹P{¹H} NMR δ 25.1 (s). Anal. Calcd for: C₂₅H₃₅O₆P: C, 64.92; H, 7.63. Found: C, 64.86; H, 7.77. [α]²⁵_D = - 29.5 (c = 0.985, CHCl₃). The enantiomeric excess of **4t** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^jPrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 5.2 min (major) and 6.8 min (minor), 42% *ee*. Enantioselective Alkylation of β -Ketoester (5) with Diaryl Methanol (1a).



In a 20 mL Schlenk flask were placed Cu(OTf)₂ (5.4 mg, 0.015 mmol) and $(3aR, 3a'R, 8aS, 8a'S) - 2, 2' - (cyclopropylidene) - bis {3a, 8a-dihydro-8H-indeno[1, 2d] - oxazole} (3a)$ (6.4 mg, 0.018 mmol) under N₂. The mixture was magnetically stirred under vacuum at room temperature for 2 h and filled with N₂. After anhydrous ClCH₂CH₂Cl (1.0 mL) was added, the mixture was magnetically stirred at room temperature for 1 h then stirred at -20 °C for 1 h. To the reaction mixture were successively added 5 (65 μ L, 0.45 mmol) and 1a (36.6 mg, 0.15 mmol) under N₂. The reaction flask was kept at -20 °C for 20 h. The reaction was quenched by water (10 mL), and the reaction mixture was extracted with CH_2Cl_2 (15 mL×3). The combined organic layer was dried over anhydrous MgSO₄. After the concentrarion under reduced pressure, the resulting residue was purified by column chromatography (SiO₂) with hexane/ethyl acetate (60/40 to 50/50) to give ethyl 1-(bis(4-methoxyphenyl)methyl)-2oxocyclopentanecarboxylate as a white solid (49.7 mg, 0.130 mmol, 87% isolated yield), mp 90.5-92.1 °C. ¹H NMR δ 7.17 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 5.15 (s, 1H), 3.83-4.05 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 2.97-3.06 (m, 1H), 2.17-2.31 (m, 2H), 1.66-1.94 (m, 2H), 1.47-1.59 (m, 1H), 0.90 (t, J = 7.2 Hz,3H). ¹³C NMR δ 214.2, 168.8, 158.2, 158.0, 133.6, 132.7, 131.0, 129.8, 113.7, 113.6, 66.4, 61.6, 55.2, 55.1, 53.5, 38.6, 29.2, 19.8, 13.6. Anal. Calcd for: C₂₃H₂₆O₅: C, 72.23; H, 6.85. Found: C, 71.85; H, 6.99. $[\alpha]_{D}^{25} = + 87.5$ (c = 0.860, CHCl₃). The enantiomeric excess of ethyl 1-(bis(4-methoxyphenyl)methyl)-2-oxocyclopentanecarboxylate was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/PrOH = 70/30, flow rate = 0.5 mL/min, λ =

254 nm, retention time: 29.0 min (minor) and 33.1 min (major), 46% ee.

Synthesis of 6 by Dealkylation of 4a.



In a 20 mL Schlenk flask was placed **4a** (67.0 mg, 0.15 mmol, 86% *ee*) and CH₂Cl₂ (2.0 mL) was added under N₂. After cooling the reaction flask to 0 °C, TMSBr (0.119 mL, 0.90 mmol) was added and the mixture was magnetically at room temperature for 14 h. After the concentration under reduced pressure, MeOH (1.0 mL) was added and the mixture was stirred at room temperature for 2 h. After the concentration under reduced pressure, the resulting residue was purified by column chromatography (SiO₂) with ethyl acetate/MeOH (60/40 to 40/60) to give 1-(bis(4-methoxyphenyl)methyl)-2-oxocyclopentyl)phosphonic acid (**6**) as a pale yellow solid (34.9 mg, 0.0894 mmol, 60% isolated yield), decomp. 98.6 °C. ¹H NMR (CD₃OD) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.94 (br, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.75-2.86 (m, 2H), 2.21-2.32 (m, 1H), 1.97-2.03 (m, 1H), 1.44-1.55 (m, 2H). ¹³C NMR (CD₃OD) δ 218.7 (d, ²*J*_{C-P} = 5.6 Hz), 159.7, 159.6, 134.4 (d, ³*J*_{C-P} = 3.4 Hz), 134.2 (d, ³*J*_{C-P} = 16.1 Hz), 132.5, 132.2, 114.34, 114.27, 61.3 (d, ¹*J*_{C-P} = 127.7 Hz), 55.6, 53.9 (d, ²*J*_{C-P} = 1.7 Hz), 39.9, 29.4, 20.7 (d, ²*J*_{C-P} = 2.8 Hz). ³¹P{¹H} NMR (CD₃OD) δ 20.3 (s). Anal. Calcd for: C₂₀H₂₃O₆P·H₂O: C, 58.82; H, 6.17. Found: C, 58.41; H, 6.46.

X-ray Diffraction Study of 6.

Colorless plate crystals of 6 suitable for an X-ray analysis was obtained with an enantiomerically pure form by further recrystallization from hot CH₃CN. Diffraction data for $6 \cdot CH_3CN \cdot H_2O$ were collected for the 2θ range of 6 to 55° at -90 °C on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo K α ($\lambda = 0.71075$ Å) radiation with VariMax optics. Intensity data were corrected for empirical absorptions and for Lorentz and polarization effects. The structure solution and refinements were carried out by using CrystalStructure package.^{S11} The positions of non-hydrogen atoms were determined by direct methods (SIR97)^{S12} and subsequent Fourier syntheses, and were refined on F_0^2 using all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms except for those bound to oxygen atoms were placed at the calculated positions with fixed isotropic parameters, while the positions of the H(1) and H(2) atoms in 6 and the H(27) and H(28) atoms in H_2O were determined on peaks in the difference Fourier maps and further refined isotropically. Goodness of fit indicator $[\Sigma w(|F_0|$ $-|F_{\rm c}|^{2}/(N_{\rm obs} - N_{\rm params})]^{1/2}$ was refined to the value of 1.000. Anomalous dispersion effects were included in F_c , and neutral atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were taken from ref. S13. Refinement of the Flack parameter (0.00(7)) using 2111 Friedel pairs demonstrated that the absolute configuration of 6 was (S). The ORTEP drawing of 6 is depicted in Figure S1. Details of the crystal and data collection parameters are summarized in Table S1.

Crystallographic data for the structure of **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-891211. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

	6·CH ₃ CN·H ₂ O
chemical forumula	C ₂₂ H ₂₈ NO ₇ P
formula weight	449.44
crystal size	$0.40 \times 0.15 \times 0.10$
crystal color, habit	colorless, plate
temperature (°C)	-90
crystal system	monoclinic
space group	<i>P</i> 2 ₁ (no. 4)
<i>a</i> (Å)	11.8192(5)
<i>b</i> (Å)	7.6891(4)
<i>c</i> (Å)	12.4699(5)
α (deg)	90
β (deg)	101.0259(12)
$\gamma(\text{deg})$	90
$V(\text{\AA}^3)$	1112.32(8)
Ζ	2
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.342
<i>F</i> (000)	476
μ_{calcd} (cm ⁻¹)	1.666
transmission factors range	0.768–0.983
no. measured reflections	10874
no. unique reflections	4844
R _{int}	0.0283
no. refined parameters	321
$R1 (I > 2\sigma(I))^a$	0.0352
wR2 (all data) ^b	0.0653
max/min residual peaks (e ⁻ /Å ³)	+0.504/-0.544

Table S1.	Crystallograph	hic Data for	6.CH₃CN·H₂O.
Lable D1.	Crystanograpi		u chi3ch h120.

 ${}^{a}R1 = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$

^b wR2 = $[\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}; w = 4F_o^2/[3.54\sigma(F_o^2)].$



Figure S1. An ORTEP Drawing of **6**. Thermal ellipsoids are given at the 50% probability level. Solvent molecules (acetonitrile and water) are omitted for clarity.

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¹H and ¹³C NMR Spectra.

1c







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1i







2h



4a



4b



4c


4d



4e













4i



4j



4k





4m





40







4q



4r



4s



4t



ethyl 1-(bis(4-methoxyphenyl)methyl)-2-oxocyclopentanecarboxylate



6



Charts of Alkylated Products by HPLC Analysis.

4a (*rac*)









4c (*rac*) -12000 01/21/00 05:44 CONC: AREA 05:44 01/21/00 ø -088 088 088 сH: TABLE: CONC 50.084 49.916 199.999 LC herane /IPA= 75/25 流虚1000 161 Ø OFFS CALC-METHOD: AREA% 1AG: 1657720 400000 AREA 830256 827464 12.51 ~ 1.2 1.25 ATT 18 000-0001 (SN 1/0210) (SN 1/0200) 16.14 RT 12.51 18.12 .. CH. 1 C.S PEAK REJ Ø METHOD: D-2500 FILE: · ~ ~ TOTAL 0N M5 -158

4c



4d (*rac*)



,



















4h (*rac*)




















4k (*rac*)

S76



4l (*rac*)





4m (*rac*)





4n (*rac*)







40 (*rac*)



40



4p (*rac*)





4p

4q ((rac)
------	-------



4q



4r (*rac*)









4t (*rac*)







