Supporting Information

(*E*)- and (*Z*)-Stereodefined enol phosphonates derived from β-ketoesters: Stereocomplementary synthesis of full-substituted α,β-unsaturated esters

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Contents:

General

All reactions were carried out in oven-dried glassware under an argon atmosphere. Flash column chromatography was performed with silica gel Merck 60 (230-400 mesh ASTM).

TLC analysis was performed on 0.25 mm Silicagel Merck 60 F_{254} plates.

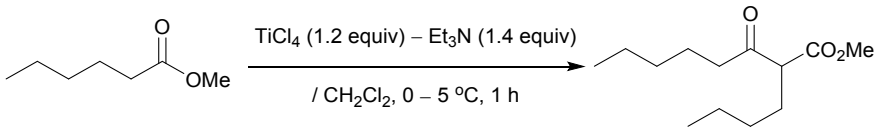
Melting points were determined on a hot stage microscope apparatus (AS ONE, ATM-01) and were uncorrected.

NMR spectra were recorded on a JEOL DELTA 300 or JEOLRESONANCE ECX-500 spectrometer, operating at 300 MHz or 500 MHz for ^{1}H NMR and 75 MHz 120 MHz for ^{13}C NMR. Chemical shifts (δ ppm) in $CDCl_3$ were reported downfield from TMS (= 0) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$ (77.00 ppm) as an internal reference.

IR Spectra were recorded on a JASCO FT/IR-5300 spectrophotometer.

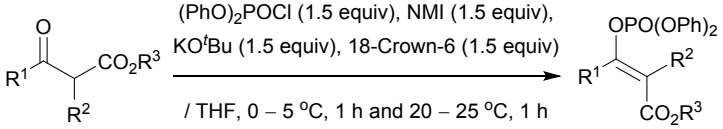
Mass spectra were measured on a JEOL JMS-T100LC spectrometer.

Methyl 2-butyl-3-oxooctanoate (2a)



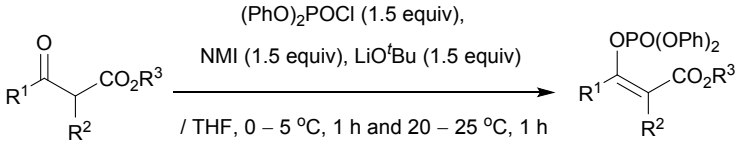
To a vigorously stirred solution of methyl hexanoate (65.09 g, 0.50 mol) in CH_2Cl_2 (500 mL), using two dropping funnels, $TiCl_4$ (113.83 g, 0.60 mol) (during ca. 30 min) and Et_3N (70.83 g, 0.70 mol) (during ca. 1 h) were successively added dropwise at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h. Water was slowly added to the mixture, which was extracted twice with Et_2O. The combined organic phase was washed with sat. aq. $NaHCO_3$ solution, brine, dried (Na_2SO_4), and concentrated. The obtained crude product was purified by distillation to give the desired product (53.19 g, 93%).
colorless oil; bp 79–81 °C / 0.49 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.2 Hz), 0.89 (3H, t, *J* = 7.2 Hz), 1.16–1.39 (8H, m), 1.58 (2H, quint, *J* = 7.2 Hz), 1.78–1.90 (2H, m), 2.45 (1H, dt, *J* = 7.2 Hz, *Jgem* = 17.2 Hz), 2.54 (1H, dt, *J* = 7.2 Hz, *Jgem* = 17.2 Hz), 3.43 (1H, t, *J* = 7.2 Hz), 3.72 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 13.7, 22.2, 22.3, 23.0, 27.8, 29.5, 31.0, 41.6, 52.0, 58.8, 170.2, 205.2; ν_{max} (neat) / cm^{-1} 2956, 2862, 1744, 1715, 1459, 1436, 1193, 1169; HRMS (ESI) calcd for $C_{13}H_{24}O_3$ ($M+Na^+$) 251.1623, found 251.1621.

General procedure for the (*E*)-stereoselective enol phosphorylation of β-ketoesters 1a-1i (*Method A*).



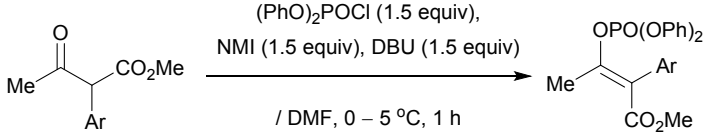
A β-ketoester (5.0 mmol – 1.0 mmol) in THF (5.0 mL – 1.0 mL), $(PhO)_2POCl$ (2.01 g – 0.40 g, 7.5 mmol – 1.5 mmol) in THF (5.0 mL – 1.0 mL), and NMI (*N*-methylimidazole) (0.62 g – 0.12 g, 7.5 mmol – 1.5 mmol) were successively added dropwise to a stirred suspension of KO^{t}Bu (0.84 g – 0.17 g, 7.5 mmol – 1.5 mmol) and 18-Crown-6 (1.99 g – 0.40 g, 7.5 mmol – 1.5 mmol) in THF (5.0 mL – 1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h and at rt for 1 h. Water was added to the stirred mixture, which was extracted with EtOAc. The organic phase was washed with 1 M-HCl, brine, dried (Na_2SO_4), and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane-AcOEt = 20:1 – 5:1) to give the desired product (*E*)-**2**.

General procedure for the (*Z*)-stereoselective enol phosphorylation of β-ketoesters 1a-1i (*Method B*).



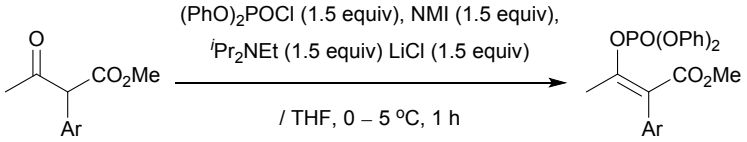
A β-ketoester (5.0 mmol – 1.0 mmol) in THF (5.0 mL – 1.0 mL), $(PhO)_2POCl$ (2.01 – 0.40 g, 7.5 mmol – 1.5 mmol) in THF (5.0 mL – 1.0 mL), and NMI (*N*-methylimidazole) (0.62 g – 0.12 g, 7.5 mmol – 1.5 mmol) were successively added dropwise to a stirred suspension of LiO^{t}Bu (0.60 g – 0.12 g, 7.5 mmol – 1.5 mmol) in THF (5.0 mL – 1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h and at rt for 1 h.. Water was added to the stirred mixture, which was extracted with EtOAc. The organic phase was washed with 1 M-HCl, brine, dried (Na_2SO_4), and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane-AcOEt = 20:1 – 5:1) to give the desired product (*Z*)-**2**.

General procedure for the (*E*)-stereoselective enol phosphorylation of α-aryl-β-ketoesters 1j-1l with (*Method C*).



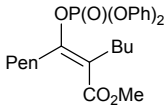
$(PhO)_2POCl$ (402 mg, 1.5 mmol) was added to a stirred solution of an α-aryl-β-ketoester (1.0 mmol), NMI (*N*-methylimidazole) (123 mg, 1.5 mmol), and DBU (228 mg, 1.5 mmol) in DMF (2.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h. Water was added to the reaction mixture, which was extracted twice with AcOEt. The organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by silica-gel column chromatography (hexane : AcOEt = 10 : 1 – 3 : 1) to give the desired product.

General procedure for the (*Z*)-stereoselective enol phosphorylation of α-aryl-β-ketoesters 1j-1l (*Method D*).



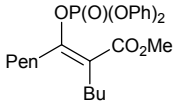
An α-aryl-β-ketoester (1.0 mmol), $^iPr_2NEt$ (194 mg, 1.5 mmol), NMI (*N*-methylimidazole) (123 mg, 1.5 mmol), and $(PhO)_2POCl$ (402 mg, 1.5 mmol) were successively added to a stirred suspension of LiCl (64 mg 1.5 mmol) in CH_3CN (1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h. Water was added to the reaction mixture, which was extracted with twice AcOEt. The organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by silica-gel column chromatography (hexane : AcOEt = 10 : 1 – 3 : 1) to give the desired product.

(*E*)-Methyl 2-butyl-3-(diphenoxyphospholoxy)oct-2-enoate (*E*)-2a



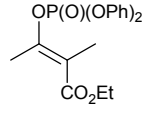
colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.81 (3H, t, *J* = 7.2 Hz), 0.83 (3H, t, *J* = 7.2 Hz), 1.09–1.34 (8H, m), 1.47–1.62 (2H, m), 2.28 (2H, t, *J* = 7.2 Hz), 2.76 (2H, t, *J* = 7.2 Hz), 3.74 (3H, s), 7.17–7.29 (6H, m), 7.30–7.40 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 13.8, 22.2, 22.3, 27.0, 27.0, 30.6, 31.2, 32.5, 51.6, 119.9 [d, ^3J (^{13}C, ^{31}P) = 4.3 Hz], 121.6 [d, ^3J (^{13}C, ^{31}P) = 8.7 Hz], 125.5, 129.7, 150.3 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 157.9 [d, ^2J (^{13}C, ^{31}P) = 8.0 Hz], 168.2; ^{31}P NMR (202 MHz, $CDCl_3$) δ -18.4; ν_{max} (neat) / cm^{-1} 2957, 2872, 1721, 1647, 1593, 1489, 1302, 1275; HRMS (ESI) calcd for $C_{25}H_{33}O_6P$ ($M+Na^+$) 483.1912, found 483.1912.

(*Z*)-Methyl 2-butyl-3-(diphenoxyphospholoxy)oct-2-enoate (*Z*)-2a



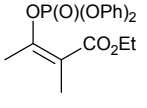
colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (3H, t, *J* = 6.9 Hz), 0.90 (3H, t, *J* = 6.9 Hz), 1.17–1.45 (8H, m), 1.47–1.62 (2H, m), 2.22–2.32 (2H, m), 2.42 (2H, t, *J* = 7.2 Hz), 3.56 (3H, s), 7.13–7.39 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 22.2, 22.2, 26.4, 28.7, 31.0, 31.0, 31.2, 31.3, 51.5, 119.9 [d, ^3J (^{13}C, ^{31}P) = 5.1 Hz], 120.9 [d, ^3J (^{13}C, ^{31}P) = 7.2 Hz], 125.2, 129.6, 150.4 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 151.5 [d, ^2J (^{13}C, ^{31}P) = 8.7 Hz], 167.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ -18.4; ν_{max} (neat) / cm^{-1} 2959, 2872, 1717, 1592, 1489, 1435, 1314, 1230.

(*E*)-Ethyl 2-methyl-3-(diphenoxyphospholoxy)but-2-enoate (*E*)-2b



colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (3H, t, *J* = 7.2 Hz), 1.76–1.82 (3H, m), 2.44–2.49 (3H, m), 4.19 (2H, t, *J* = 7.2 Hz), 7.14–7.40 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5, 13.8, 18.9, 60.3, 116.3 [d, ^3J (^{13}C, ^{31}P) = 9.4 Hz], 119.8 [d, ^3J (^{13}C, ^{31}P) = 5.1 Hz], 125.4, 129.6, 150.0 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 154.8 [d, ^2J (^{13}C, ^{31}P) = 8.0 Hz], 167.3; ν_{max} (neat) / cm^{-1} 2982, 1717, 1655, 1592, 1489, 1456, 1379, 1281; HRMS (ESI) calcd for $C_{19}H_{21}O_6P$ ($M+Na^+$) 339.0973, found 339.0973.

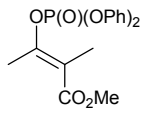
(*Z*)-Ethyl 2-methyl-3-(diphenoxyphospholoxy)but-2-enoate (*Z*)-2b



colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (3H, t, *J* = 7.2 Hz), 1.89 (3H, s), 2.13 (3H, s), 4.09 (2H, t, *J* = 7.2 Hz), 7.04–7.42 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 14.5, 17.9, 60.5, 115.4 [d, ^3J (^{13}C, ^{31}P) = 8.7 Hz], 119.9 [d, ^3J (^{13}C, ^{31}P) = 5.1 Hz], 125.2, 129.5, 147.9 [d, ^2J (^{13}C,

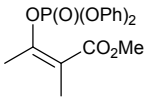
^{31}P) = 8.7 Hz], 150.2 [d, ^{2}J (^{13}C, ^{31}P) = 7.2 Hz], 166.6; ν_{max} (neat) / cm^{-1} 2982, 1717, 1655, 1592, 1489, 1456, 1379, 1281.

(*E*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)but-2-enoate (*E*)-2c



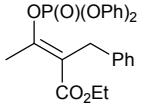
pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (3H, s), 2.48 (3H, s), 3.74 (3H, s), 7.19–7.28 (6H, m), 7.33–7.38 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.7, 19.2, 51.7, 116.2 [d, ^{3}J (^{13}C, ^{31}P) = 9.6 Hz], 120.0 [d, ^{3}J (^{13}C, ^{31}P) = 4.8 Hz], 125.6, 129.8, 150.2 [d, ^{2}J (^{13}C, ^{31}P) = 8.4 Hz], 155.4 [d, ^{2}J (^{13}C, ^{31}P) = 8.4 Hz], 168.2; ν_{max} (neat) / cm^{-1} 3066, 2952, 1718, 1655, 1590, 1488, 1284, 1186, 1099, 953, 762, 689; HRMS (ESI) calcd for $C_{18}H_{19}O_6P$ (M+Na$^+$) 385.0817, found 385.0826.

(*Z*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)but-2-enoate (*Z*)-2c



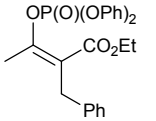
colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.89 (3H, s), 2.13 (3H, s), 3.56 (3H, s), 7.16–7.27 (6H, m), 7.30–7.39 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 18.2, 51.6, 115.2, [d, ^{3}J (^{13}C, ^{31}P) = 8.4 Hz], 120.0 [d, ^{3}J (^{13}C, ^{31}P) = 6.0 Hz], 125.4, 129.7, 148.6 [d, ^{2}J (^{13}C, ^{31}P) = 8.4 Hz], 150.4, [d, ^{2}J (^{13}C, ^{31}P) = 8.4 Hz], 167.2; ν_{max} (neat) / cm^{-1} 3071, 2952, 1720, 1590, 1488, 1298, 1188, 1136, 1020, 943, 773, 730.

(*E*)-Ethyl 2-benzyl-3-(diphenoxyphospholoxy)but-2-enoate (*E*)-2d



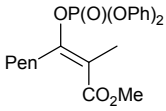
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (3H, t, J = 7.2 Hz), 2.57 (3H, s), 3.65 (2H, s), 4.11 (2H, t, J = 7.2 Hz), 7.05–7.40 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 19.1, 32.5, 60.7 , 119.7 [d, ^{3}J (^{13}C, ^{31}P) = 9.4 Hz], 121.4 [d, ^{3}J (^{13}C, ^{31}P) = 9.4 Hz], 125.6, 125.9, 128.1, 128.2, 129.8, 139.0, 150.1 [d, ^{2}J (^{13}C, ^{31}P) = 8.0 Hz], 155.4 [d, ^{2}J (^{13}C, ^{31}P) = 7.2 Hz], 167.1; ν_{max} (neat) / cm^{-1} 2982, 1717, 1649, 1592, 1489, 1456, 1383, 1298; HRMS (ESI) calcd for $C_{25}H_{25}O_6P$ (M+Na$^+$) 475.1286, found 475.1285.

(*Z*)-Ethyl 2-benzyl-3-(diphenoxyphospholoxy)but-2-enoate (*Z*)-2d



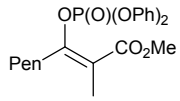
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (3H, t, J = 7.2 Hz), 2.21 (3H, J = 2.1 Hz), 3.68 (2H, s), 4.02 (2H, t, J = 7.2 Hz), 7.13–7.40 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 18.3, 34.7, 60.8, 119.5 [d, ^{3}J (^{13}C, ^{31}P) = 9.4 Hz], 120.0 [d, ^{3}J (^{13}C, ^{31}P) = 5.1 Hz], 125.5, 126.4, 128.1, 128.5, 129.7, 138.1, 149.7 [d, ^{2}J (^{13}C, ^{31}P) = 8.7 Hz], 150.4 [d, ^{2}J (^{13}C, ^{31}P) = 8.0 Hz], 166.3; ν_{max} (neat) / cm^{-1} 2982, 1719, 1592, 1489, 1456, 1306, 1190, 1163.

(*E*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)oct-2-enoate (*E*)-2e



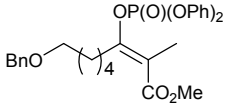
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 7.6 Hz), 1.14–1.33 (4H, m), 1.44–1.61 (2H, m), 1.82 (3H, d, J = 2.4 Hz), 2.81 (2H, t, J = 7.6 Hz), 3.73 (3H, s), 7.15–7.40 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 13.9, 22.3, 27.0, 31.3, 32.5, 51.7, 116.6 [d, ^{3}J (^{13}C, ^{31}P) = 8.7 Hz], 120.0 [d, ^{3}J (^{13}C, ^{31}P) = 5.1 Hz], 125.6, 129.8, 150.3 [d, ^{2}J (^{13}C, ^{31}P) = 7.2 Hz], 159.4 [d, ^{2}J (^{13}C, ^{31}P) = 8.0 Hz], 168.1; ν_{max} (neat) / cm^{-1} 2982, 1719, 1592, 1489, 1456, 1387, 1306, 1223, 1190; HRMS (ESI) calcd for $C_{22}H_{27}O_6P$ (M+Na$^+$) 441.1443, found 441.1446.

(*Z*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)oct-2-enoate (*Z*)-2e



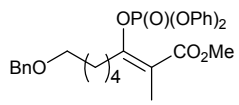
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 7.2 Hz), 1.18–1.34 (4H, m), 1.54 (2H, quin, J = 7.6 Hz), 1.91 (3H, d, J = 3.1 Hz), 2.42 (2H, t, J = 7.7 Hz), 3.57 (3H, s), 7.06–7.42 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 14.5, 22.2, 26.0, 31.1, 31.8, 51.5, 115.3 [d, ^{3}J (^{13}C, ^{31}P) = 7.2 Hz], 119.9 [d, ^{3}J (^{13}C, ^{31}P) = 5.1 Hz], 125.2, 129.6, 150.4 [d, ^{2}J (^{13}C, ^{31}P) = 8.0 Hz], 152.4 [d, ^{2}J (^{13}C, ^{31}P) = 8.0 Hz], 167.3; ν_{max} (neat) / cm^{-1} 2957, 2872, 1725, 1655, 1592, 1489, 1458, 1435.

(*E*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)-8-benzyloxyoct-2-enoate (*E*)-2f



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (2H, t, J = 7.2 Hz), 1.48–1.63 (4H, m), 1.82 (3H, d, J = 2.1 Hz), 2.83 (2H, t, J = 7.2 Hz), 3.42 (2H, t, J = 6.6 Hz), 3.72 (3H, s), 4.47 (2H, s), 7.13–7.39 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 25.7, 27.0, 29.3, 32.4, 51.7, 70.1, 72.6, 116.7 [d, ^{3}J (^{13}C, ^{31}P) = 8.7 Hz], 119.9, 119.9, 125.5, 127.4, 128.2, 129.7, 138.5, 150.2 [d, ^{2}J (^{13}C, ^{31}P) = 7.2 Hz], 159.0 [d, ^{2}J (^{13}C, ^{31}P) = 8.7 Hz], 168.0; ν_{max} (neat) / cm^{-1} 2936, 2863, 1719, 1655, 1590,1489, 1306, 1228; HRMS (ESI) calcd for $C_{29}H_{33}O_7P$ (M+Na$^+$) 547.1862, found 547.1859.

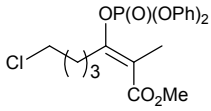
(*Z*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)-8-benzyloxyoct-2-enoate (*Z*)-2f



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27–1.42 (2H, m), 1.48–1.64 (4H, m), 1.89 (3H, d, J = 3.8 Hz), 2.43 (2H, t, J = 7.2 Hz), 3.42 (2H, t, J = 6.5 Hz), 3.57 (3H, s), 4.47

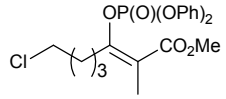
(2H, s), 7.06–7.40 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 25.6, 26.2, 29.3, 31.8, 51.6, 69.9, 72.7, 115.5 [d, ^3J (^{13}C, ^{31}P) = 7.2 Hz], 119.9, 120.0, 125.3, 127.5, 128.2, 129.6, 138.5, 150.4 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 152.2 [d, ^2J (^{13}C, ^{31}P) = 9.4 Hz], 167.2; ν_{max} (neat) / cm^{-1} 2942, 2865, 1747, 1655, 1590, 1485, 1435, 1296.

(*E*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)-7-chlorohept-2-enoate (*E*)-2g



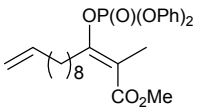
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62–1.80 (4H, m), 1.84 (3H, d, J = 2.4 Hz), 2.86 (2H, t, J = 7.2 Hz), 3.47 (2H, t, J = 6.2 Hz), 3.74 (3H, s), 7.11–7.45 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 24.5, 31.6, 31.8, 44.5, 51.8, 117.3 [d, ^3J (^{13}C, ^{31}P) = 8.0 Hz], 120.0 [d, ^3J (^{13}C, ^{31}P) = 5.1 Hz], 125.6 [d, ^3J (^{13}C, ^{31}P) = 9.4 Hz], 129.8, 150.3 [d, ^2J (^{13}C, ^{31}P) = 8.0 Hz], 158.3 [d, ^2J (^{13}C, ^{31}P) = 8.0 Hz], 167.9; ν_{max} (neat) / cm^{-1} 2953, 2872, 1721, 1649, 1492, 1489, 1458, 1298; HRMS (ESI) calcd for $C_{21}H_{24}O_6P$ (M+Na$^+$−Cl$^-$) 461.0896, found 461.0897.

(*Z*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)-7-chlorohept-2-enoate (*Z*)-2g



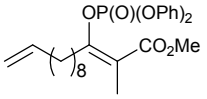
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63–1.80 (4H, m), 1.92 (3H, d, J = 6.9 Hz), 2.46 (2H, t, J = 6.9 Hz), 3.47 (2H, t, J = 6.2 Hz), 3.58 (3H, s), 7.12–7.39 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.7, 23.7, 31.1, 31.7, 44.3, 51.7, 116.2 [d, ^3J (^{13}C, ^{31}P) = 8.0 Hz], 120.0 [d, ^3J (^{13}C, ^{31}P) = 5.1 Hz], 125.4, 130.0, 150.5 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 151.3 [d, ^2J (^{13}C, ^{31}P) = 8.7 Hz], 167.2; ν_{max} (neat) / cm^{-1} 2951, 2870, 1728, 1655, 1592, 1489, 1458, 1302.

(*E*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)-tridec-2,12-dienoate (*E*)-2h



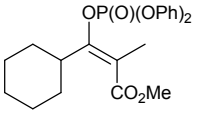
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10–1.61 (12H, m), 1.82 (3H, d, J = 2.1 Hz), 1.97–2.08 (2H, m), 2.81 (2H, t, J = 7.6 Hz), 3.73 (3H, s), 4.89–5.03 (2H, m), 5.80 (1H, ddt, J = 6.9, 10.3, 17.2 Hz), 7.11–7.43 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.9, 27.1, 28.7, 28.9, 28.9, 29.0, 29.1, 32.4, 33.6, 51.6, 114.0, 116.4 [d, ^3J (^{13}C, ^{31}P) = 8.0 Hz], 119.9 [d, ^3J (^{13}C, ^{31}P) = 4.3 Hz], 125.4, 129.7, 138.9, 150.2 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 159.2 [d, ^2J (^{13}C, ^{31}P) = 8.0 Hz], 167.9; ν_{max} (neat) / cm^{-1} 2953, 2870,1719, 1647, 1592, 1458, 1437, 1298; HRMS (ESI) calcd for $C_{27}H_{35}O_6P$ (M+Na$^+$) 509.2069, found 509.2073.

(*Z*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)-tridec-2,12-dienoate (*Z*)-2h



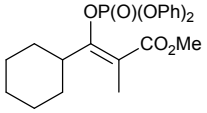
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16–1.65 (12H, m), 1.91 (3H, d, J = 3.1 Hz), 2.03 (2H, q, J = 7.2 Hz), 2.43 (2H, t, J = 7.6 Hz), 3.57 (3H, s), 4.90–5.03 (2H, m), 5.80 (1H, ddt, J = 7.2, 10.3, 16.9 Hz), 7.09–7.44 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 25.1, 26.2, 28.6, 28.8, 29.0, 29.0, 31.7, 33.5, 51.4, 114.0 [d, ^3J (^{13}C, ^{31}P) = 8.0 Hz], 115.3 [d, ^3J (^{13}C, ^{31}P) = 5.1 Hz], 125.2, 129.5, 138.8, 150.3 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 152.3 [d, ^2J (^{13}C, ^{31}P) = 8.7 Hz], 167.1; ν_{max} (neat) / cm^{-1} 2932, 2855, 1721, 1655, 1593, 1489, 1436, 1316.

(*E*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)- 3-cyclohexylpropenoate (*E*)-2i



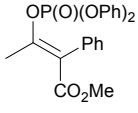
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01–1.86 (10H, m), 1.93 (3H, d, J = 2.1 Hz), 3.16–3.31 (1H, m), 3.75 (3H, s) 7.05–7.47 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 25.5, 25.9, 29.2, 41.4, 51.7, 116.3 [d, ^3J (^{13}C, ^{31}P) = 6.5 Hz], 119.8, 125.3, 129.6, 150.4 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 161.9 [d, ^2J (^{13}C, ^{31}P) = 10.8 Hz], 168.3; ν_{max} (neat) / cm^{-1} 2932, 2857, 1719, 1647, 1592, 1489, 1456, 1314; HRMS (ESI) calcd for $C_{23}H_{27}O_6P$ (M+Na$^+$) 453.1443, found 453.1445.

(*Z*)-Methyl 2-methyl-3-(diphenoxyphospholoxy)-tridec-2,12-dienoate (*Z*)-2i



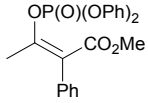
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.46–1.85 (10H, m), 1.96 (3H, d, J = 3.4 Hz), 2.50–2.62 (1H, m), 3.62 (3H, s), 7.11–7.37 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 25.5, 26.0, 28.7, 41.2, 51.7, 114.7 [d, ^3J (^{13}C, ^{31}P) = 5.8 Hz], 120.0 [d, ^3J (^{13}C, ^{31}P) = 5.1 Hz], 125.2, 129.6, 150.7 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 152.3 [d, ^2J (^{13}C, ^{31}P) = 8.7 Hz], 167.8; ν_{max} (neat) / cm^{-1} 2932, 2857, 1725, 1592, 1491, 1456, 1314, 1192.

(*E*)-Methyl 2-phenyl-3-(diphenoxyphospholoxy)butenoate (*E*)-2j



colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (3H, d, J = 1.7 Hz), 3.69 (3H, s) 6.89–6.93 (4H, m), 7.13–7.30 (11H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 52.1, 119.9 [d, ^3J (^{13}C, ^{31}P) = 4.8 Hz], 121.7 [d, ^3J (^{13}C, ^{31}P) = 9.6 Hz], 125.4, 127.5, 128.0, 129.6, 129.7, 133.8, 150.0 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 155.6 [d, ^2J (^{13}C, ^{31}P) = 6.0 Hz], 167.5; ν_{max} (neat) / cm^{-1} 3061, 2951, 1718, 1643, 1589, 1488, 1290, 1216; HRMS (ESI) calcd for $C_{23}H_{21}O_6P$ (M+Na$^+$) 477.0974, found 477.0971.

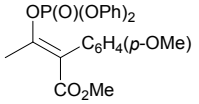
(*Z*)-Methyl 2-chloro-3-(diphenoxyphospholoxy)butenoate (*Z*)-2j



colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.07 (3H, d, J = 1.7 Hz), 3.56 (3H, s) 7.19–7.40 (15H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.7, 52.0, 120.1 [d, ^3J (^{13}C, ^{31}P) = 4.8 Hz], 122.3 [d,

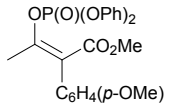
^3J (^{13}C, ^{31}P) = 9.6 Hz], 125.5, 128.1, 128.4, 129.4, 129.8, 134.0, 150.1 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 150.4 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 166.1; ν_{max} (neat) / cm^{-1} 3061, 2951, 1724, 1646, 1590, 1488, 1382, 1300.

(*E*)-Methyl 2-(4-methoxyphenyl)-3-(diphenoxyphospholoxy)but-2-enoate (*E*)-2k



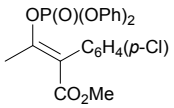
yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (3H, d, *J* =1.7 Hz), 3.69 (3H, s), 3.78 (3H, s), 6.75–6.79 (2H, m), 6.95 (4H, d, *J* = 7.5 Hz), 7.09–7.13 (2H, m), 7.15 (2H, t, *J* = 7.5 Hz), 7.25 (4H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 52.2, 55.1, 113.5, 119.9 [d, ^3J (^{13}C, ^{31}P) = 4.8 Hz], 121.5 [d, ^3J (^{13}C, ^{31}P) = 9.6 Hz], 125.4, 125.9, 129.7, 130.8, 150.1 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 155.0 [d, ^3J (^{13}C, ^{31}P) = 7.2 Hz],158.9; ν_{max} (neat) / cm^{-1} 3068, 2952, 1718, 1590, 1489, 1295, 1181, 1069, 963, 774, 688; HRMS (ESI) calcd for $C_{24}H_{23}O_7P$ (M+Na$^+$) 477.1079, found 477.1080.

(*Z*)-Methyl 2-(4-methoxyphenyl)-3-(diphenoxyphospholoxy)but-2-enoate (*Z*)-2k



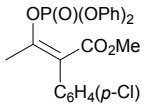
pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.07 (3H, d, *J* = 1.7 Hz), 3.55 (3H, s), 3.81 (3H, s), 6.87–6.91 (2H, m), 7.17–7.24 (4H, m), 7.29 (4H, d, *J* = 8.6 Hz), 7.36 (4H, t, *J* = 8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.6, 51.9, 55.2, 113.9, 120.1 [d, ^3J (^{13}C, ^{31}P) = 4.8 Hz], 121.9 [d, ^3J (^{13}C, ^{31}P) = 8.4 Hz], 125.5, 126.1, 129.6, 129.8, 130.6, 149.6 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 150.4 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 159.3, 166.5; ν_{max} (neat) / cm^{-1} 3002, 2952, 1725, 1591, 1489, 1292, 1227, 1185, 960, 774, 689.

(*E*)-Methyl 2-(4-chlorophenyl)-3-(diphenoxyphospholoxy)but-2-enoate (*E*)-2l



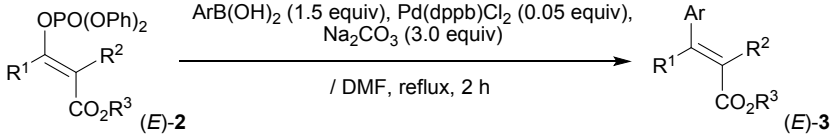
yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.64 (3H, d, *J* = 1.7 Hz), 3.68 (3H, s), 6.95 (4H, d, *J* = 7.5 Hz), 7.05–7.08 (2H, m), 7.14–7.21 (4H, m), 7.27 (4H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 52.2, 119.7 [d, ^3J (^{13}C, ^{31}P) = 4.8 Hz], 120.7 [d, ^3J (^{13}C, ^{31}P) = 10.8 Hz], 125.6, 128.2, 129.8, 131.0, 132.2, 133.4, 150.0 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 156.4 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 167.0; ν_{max} (neat) / cm^{-1} 3067, 2953, 1719, 1591, 1490, 1289, 1183, 1071, 963, 774, 688; HRMS (ESI) calcd for $C_{23}H_{20}ClO_6P$ (M+Na$^+$) 481.0584, found 481.0581.

(*Z*)-Methyl 2-(4-chlorophenyl)-3-(diphenoxyphospholoxy)but-2-enoate (*Z*)-2l



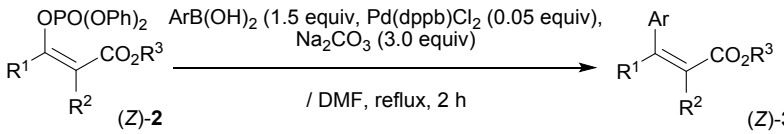
colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05 (3H, d, *J* = 1.7 Hz), 3.56 (3H, s), 7.18–7.25 (4H, m), 7.27–7.30 (4H, m), 7.32–7.40 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.8, 52.0, 120.1 [d, ^3J (^{13}C, ^{31}P) = 4.80 Hz], 121.2 [d, ^3J (^{13}C, ^{31}P) = 8.4 Hz], 125.6, 128.7, 129.8, 130.9, 132.5, 134.2, 150.3 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 150.8 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 165.7; ν_{max} (neat) / cm^{-1} 3069, 2952, 1725, 1591, 1489, 1299, 1224, 1185, 962, 773, 687.

General procedure for the (*E*)-stereoretentive Suzuki-Miyaura cross-coupling using (*E*)-enol phosphonates 2.



An (*E*)-enol phosphate **2** (0.50 mmol) was added to a stirred suspension of $ArB(OH)_2$ (0.75 mmol), Na_2CO_3 (159 mg, 1.50 mmol), $Pd(dppb)Cl_2$ (15 mg, 0.025 mmol) in DMF (0.5 mL) at 20 – 25 ^{o}C under an Ar atmosphere, and the mixture was stirred at 150 – 155 ^{o}C for 2 h. After cooling down, water was added to the stirred mixture, which was extracted twice with AcOEt. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated to give the residue, which was purified by SiO_2-column chromatography (hexane - AcOEt = 50 : 1 – 20 : 1) to give the desired product (*E*)-**3**.

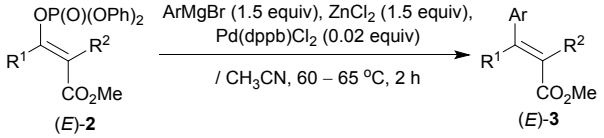
General procedure for the (*Z*)-stereoretentive Suzuki-Miyaura cross-coupling using (*Z*)-enol phosphonates 2.



An (*Z*)-enol phosphate **2** (0.50 mmol) was added to a stirred suspension of $ArB(OH)_2$ (0.75 mmol), Na_2CO_3 (159 mg, 1.50 mmol), $Pd(dppb)Cl_2$ (15 mg, 0.025 mmol) in DMF (0.5 mL) at 20 – 25 ^{o}C under an Ar atmosphere, and the mixture was stirred at 150 – 155 ^{o}C for 2 h. After cooling down, water was added to the

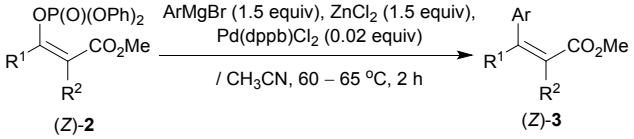
stirred mixture, which was extracted twice with AcOEt. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated to give the residue, which was purified by SiO_2-column chromatography (hexane - AcOEt = 50 : 1 – 20 : 1) to give the desired product (*Z*)-**3**.

General procedure for the (*E*)-stereoretentive Negishi cross-coupling using (*E*)-enol phosphonates 2 with aromatic zinc reagents



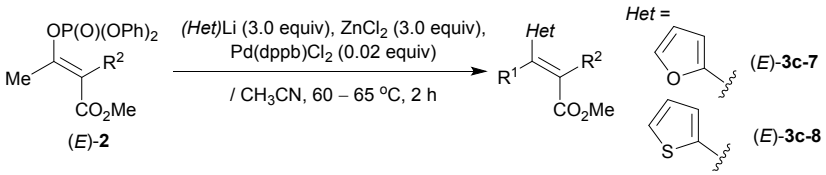
ArMgBr (0.68 mL; 1.10 M in THF) was added to a stirred suspension of $ZnCl_2$ (102 mg, 0.750 mmol) in CH_3CN (1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 0.5 h. An (*E*)-enol phosphonate **2** (0.50 mmol) in CH_3CN (0.5 mL) and Pd(dppb)Cl_2 (6 mg, 0.01 mmol) in CH_3CN (0.5 mL) were successively added to the mixture, followed by stirring at 60 – 65 °C for 2 h. After cooling down, 1 M-HCl aq. solution was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane/AcOEt = 100:0 – 20:1) to give the desired product (*E*)-**3**.

General procedure for the (*Z*)-stereoretentive Negishi cross-coupling using (*Z*)-enol phosphonates 2 with aromatic zinc reagents



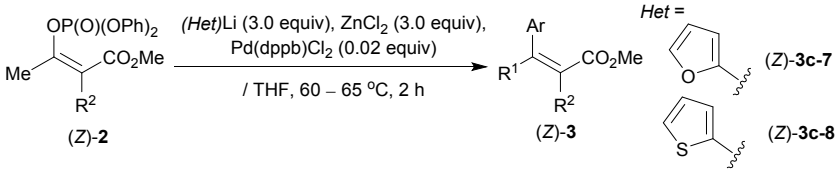
ArMgBr (0.68 mL; 1.10 M in THF) was added to a stirred suspension of $ZnCl_2$ (102 mg, 0.750 mmol) in CH_3CN (1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 0.5 h. An (*Z*)-enol phosphonate **2** (0.50 mmol) in CH_3CN (0.5 mL) and Pd(dppb)Cl_2 (6 mg, 0.01 mmol) in CH_3CN (0.5 mL) were successively added to the mixture, followed by stirring at 60 – 65 °C for 2 h. After cooling down, 1 M-HCl aq. solution was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane/AcOEt = 100:0 – 20:1) to give the desired product (*Z*)-**3**.

General procedure for the (*E*)-stereoretentive Negishi cross-coupling using (*E*)-enol phosphonates 2c with heterocyclic zinc reagents



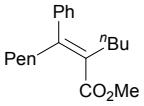
*n*BuLi (0.92 mL; 1.63 M in hexane) was added to a stirred solution of a *(Het)*H (1.50 mmol) in THF (1.5 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 0.5 h. The solution was added to a stirred suspension of $ZnCl_2$ (204 mg, 1.50 mmol) in CH_3CN (1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 0.5 h. (*E*)-enol phosphonate **2c** (0.50 mmol) in CH_3CN (0.5 mL) and Pd(dppb)Cl_2 (6 mg, 0.01 mmol) in CH_3CN (0.5 mL) were successively added to the mixture, followed by stirring at 60 – 65 °C for 2 h. After cooling down, 1 M-HCl aq. solution was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane/AcOEt = 100:1 – 50:1) to give the desired product (*E*)-**3-7** or (*E*)-**3-8**.

General procedure for the (*Z*)-stereoretentive Negishi cross-coupling using (*Z*)-enol phosphonates 2c with heterocyclic zinc reagents



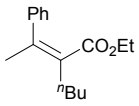
*n*BuLi (0.92 mL; 1.63 M in hexane) was added to a stirred solution of *(Het)*H (1.50 mmol) in THF (1.5 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 0.5 h. The solution was added to a stirred suspension of $ZnCl_2$ (204 mg, 1.50 mmol) in THF (1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 0.5 h. An (*Z*)-enol phosphonate **2c** (0.50 mmol) in THF (0.5 mL) and Pd(dppb)Cl_2 (6 mg, 0.01 mmol) in THF (0.5 mL) were successively added to the mixture, followed by stirring at 60 – 65 °C for 2 h. After cooling down, 1 M-HCl aq. solution was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane/AcOEt = 100:1 – 50:1) to give the desired product (*Z*)-**3-7** or (*Z*)-**3-8**.

(*E*)-Methyl 2-butyl-3-phenyloct-2-enoate (*E*)-3a



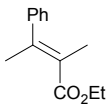
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (3H, t, *J* = 7.5 Hz), 0.82 (3H, t, *J* = 7.5 Hz), 1.08–1.35 (10H, m), 2.07 (2H, t, *J* = 7.6 Hz), 2.46 (2H, t, *J* = 7.6 Hz), 3.80 (3H, s), 7.07–7.12 (2H, m), 7.24–7.30 (1H, m), 7.31–7.37 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 14.0. 22.3, 22.4, 27.6, 30.8, 31.2, 31.7, 36.4, 51.4, 126.8, 127.8, 128.1, 130.6, 141.4, 147.4, 170.8 cm^{-1}; ν_{max} (neat) / cm^{-1} 2959, 1717, 1458, 1379, 1321, 1240, 1206, 11140.; HRMS (ESI) calcd for $C_{19}H_{28}O_2$ (M+Na$^+$) 311.1987, found 311.1987.

(*Z*)-Methyl 2-butyl-3-phenyloct-2-enoate (*Z*)-3a



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 6.9 Hz), 0.96 (3H, t, *J* = 7.5 Hz), 1.19–1.32 (6H, m), 1.34–1.48 (4H, m), 2.44 (4H, t, *J* = 7.2 Hz), 3.33 (3H, s), 7.09–7.14 (2H, m), 7.20–7.32 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.4, 22.6, 27.5, 29.9, 31.1, 31.7, 34.0, 51.1, 126.9, 127.4, 127.9, 131.6, 142.7, 146.2, 171.3; ν_{max} (neat) / cm^{-1} 2957, 2961, 1719, 1458, 1437, 1246, 1208, 1140.

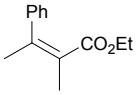
(*E*)-Ethyl 2-methyl-3-phenylbut-2-enoate (*E*)-3b-1[1]



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (3H, t, *J* = 7.2 Hz), 1.75 (3H, d, *J* = 1.4 Hz), 2.25 (3H, q, *J* = 1.4 Hz), 4.27 (2H, q, *J* = 7.2 Hz), 7.11–7.18 (2H, m), 7.22–7.49 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 17.3, 23.1, 60.3, 124.8, 126.9, 127.2, 128.2, 143.4, 145.3, 169.9; ν_{max} (neat) / cm^{-1} 2982, 1713, 1442, 1312, 1252, 1134, 1098, 1026.

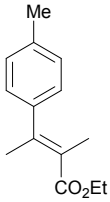
1) J. v. Braun, A. Rohmer, H. Jungmann, F. Zobel, L. Brauns, O. Bayer, A. Stuckenschmidt, J. Reutter, *Ann. Chem.* **1926**, *451*, 1.

(*Z*)-Ethyl 2-methyl-3-phenylbut-2-enoate (*Z*)-3b-1



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 7.2 Hz), 2.02 (3H, d, *J* = 1.0 Hz), 2.09 (3H, d, *J* = 1.0 Hz), 3.84 (2H, q, *J* = 7.2 Hz), 7.07–7.17 (2H, m), 7.19–7.34 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 16.3, 21.6, 60.1, 126.1, 126.8, 126.9, 127.9, 142.9, 142.2, 170.6; ν_{max} (neat) / cm^{-1} 2982, 1709, 1443, 1372, 1310, 1244, 1140, 1096.

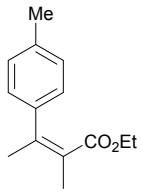
(*E*)-Ethyl 2-methyl-3-(4-methylphenyl)but-2-enoate (*E*)-3b-2[2]



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (3H, dt, *J* = 0.7, 7.2 Hz), 1.75–1.79 (3H, m), 2.22–2.26 (3H, m), 2.36 (3H, s), 4.26 (2H, q, *J* = 7.2 Hz), 7.00–7.09 (2H, m), 7.14–7.20 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 17.3, 21.0, 23.1, 60.2, 124.6, 127.1, 128.8, 136.6, 140.4, 145.3, 169.9; ν_{max} (neat) / cm^{-1} 1713, 1630, 1512, 1449, 1316, 1250, 1130.

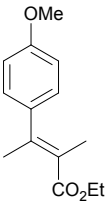
2) H. Rupe, H. Steiger, F. Fiedler, *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 63.

(*Z*)-Ethyl 2-methyl-3-(4-methylphenyl)but-2-enoate (*Z*)-3b-2



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 7.2 Hz), 2.01 (3H, d, *J* = 1.4 Hz), 2.07 (3H, d, *J* = 1.4 Hz), 2.33 (3H, s), 3.87 (2H, q, *J* = 7.2 Hz), 6.98–7.14 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 16.2, 21.0, 21.5, 59.9, 125.7, 126.7, 128.5, 136.4, 141.1, 142.6, 170.6; ν_{max} (neat) / cm^{-1} 1713, 1512, 1445, 1372, 1306, 1250, 1142.

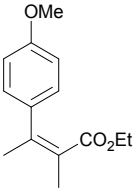
(*E*)-Ethyl 2-methyl-3-(4-methoxylphenyl)but-2-enoate (*E*)-3b-3[3]



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (3H, t, *J* = 7.2 Hz), 1.78 (3H, d, *J* = 1.0 Hz), 2.23 (3H, d, *J* = 1.0 Hz), 3.82 (3H, s), 4.26 (2H, q, *J* = 7.2 Hz), 6.86–6.93 (2H, m), 7.05–7.13 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 17.3, 23.1, 55.0, 60.2, 113.5, 124.5, 128.5, 135.5, 144.9, 158.5, 170.0; ν_{max} (neat) / cm^{-1} 2934, 1711, 1609, 1510, 1458, 1510, 1458, 1248, 1134, 1034.

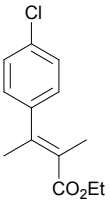
3) S. Ma, N. Jiao, L. Ye, *Chem – Eur. J.* **2003**, *9*, 6049.

(*Z*)-Ethyl 2-methyl-3-(4-methoxylphenyl)but-2-enoate (*Z*)-3b-3



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.2 Hz), 2.01 (3H, d, *J* = 1.0 Hz), 2.07 (3H, d, *J* = 7.2 Hz), 3.80 (3H, s), 3.89 (2H, q, *J* = 7.2 Hz), 6.78–6.86 (2H, m), 7.04–7.12 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 16.3, 21.4, 55.1, 59.9, 113.2, 125.6, 128.0, 136.3, 142.0, 158.5, 170.8; ν_{max} (neat) / cm^{-1} 2934, 1707, 1609, 1510, 1460, 1314, 1248, 1142.

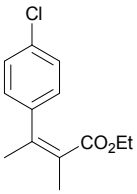
(*E*)-Ethyl 2-methyl-3-(4-chlorophenyl)but-2-enoate (*E*)-3b-4[4]



pale yellow crystals; mp 44-45 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (3H, t, *J* = 7.2 Hz), 1.72–1.77 (3H, m), 2.20–2.24 (3H, m), 4.26 (2H, q, *J* = 7.2 Hz), 7.07–7.10 (2H, m), 7.32–7.35 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 17.3, 22.9, 60.4, 125.5, 128.5, 128.7, 132.8, 141.7, 143.7, 169.6; ν_{max} (neat) / cm^{-1} 2982, 1713, 1491, 1314, 1250, 1134, 1092, 1015.

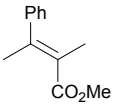
4) A. Psarrea, C. Sandris, G. Tsatsas, *Bull. Soc. Chim. Fr.* **1961**, 2145.

(*Z*)-Ethyl 2-methyl-3-(4-chlorophenyl) but-2-enoate (*Z*)-3b-4



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.2 Hz), 2.02 (3H, d, *J* = 1.0 Hz), 2.06 (3H, d, *J* = 1.0 Hz), 3.88 (2H, q, *J* = 7.2 Hz), 7.00–7.11 (2H, m), 7.21–7.31 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 16.2, 21.5, 60.1, 126.6, 128.0, 128.2, 132.6, 141.6, 142.5, 170.0; ν_{max} (neat) / cm^{-1} 2984, 1707, 1491, 1372, 1312, 1250, 1140, 1092.

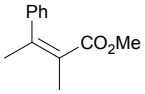
(*E*)-Methyl 2-methyl-3-phenylbut-2-enoate (*E*)-3c-1[5]



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (3H, q, *J* = 1.4 Hz), 2.26 (3H, q, *J* = 1.4 Hz), 3.80 (3H, s), 7.12–7.15 (2H, m), 7.27–7.38 (3H, m); ν_{max} (neat) / cm^{-1} 2949, 1716, 1433, 1253, 1133, 1099.

5) *E* / *Z* = 80 / 20; M. Shindo, Y. Sato, T. Yoshikawa, R. Koretsune, K. Shishido, *J. Org. Chem.* **2004**, *69*, 3912. *E* / *Z* = 14 / 86; Sano, S.; Takehisa, T.; Ogawa, S.; Yokoyama, K.; Nagao, Y.; *Chem. Pharm. Bull.* **2002**, *50*, 1300.

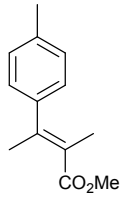
(*Z*)-Methyl 2-methyl-3-phenylbut-2-enoate (*Z*)-3c-1[6]



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05 (3H, q, *J* = 0.6 Hz), 2.09 (3H, q, *J* = 0.6 Hz), 3.39 (3H, s), 7.12–7.14 (2H, m), 7.23–7.32 (3H, m); ν_{max} (neat) / cm^{-1} 2947, 1714, 1433, 1316, 1243, 1139.

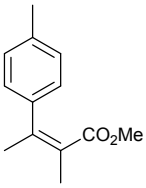
6) 95% yield (*E* / *Z* = 14 / 86), S. Sano, T. Takehisa, S. Ogawa, K. Yokoyama, Y. Nagao, *Chem. Pharm. Bull.* **2002**, *50*, 1300.

(*E*)-Methyl 2-methyl-3-(4-methylphenyl)but-2-enoate (*E*)-3c-2



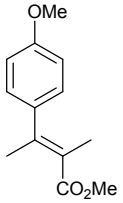
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74–1.78 (3H, m), 2.22–2.27 (3H, m), 2.35 (3H, s), 3.79 (3H, s), 7.04 (2H, d, *J* = 8.3 Hz), 7.17 (2H, d, *J* = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 21.0, 23.2, 51.3, 124.2, 127.0, 128.8, 136.6, 140.4, 146.1, 170.2; ν_{max} (neat) / cm^{-1} 2949, 2866, 1716, 1629, 1511, 1433, 1317, 1252, 1132, 820; HRMS (ESI) calcd for $C_{13}H_{16}O_2$ (M+Na$^+$) 227.1048, found 227.1046.

(*Z*)-Methyl 2-methyl-3-(4-methylphenyl)but-2-enoate (*Z*)-3c-2



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (3H, s), 2.07 (3H, s), 2.33 (3H, s), 3.43 (3H, s), 7.03 (2H, d, *J* = 7.9 Hz), 7.10 (2H, d, *J* = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3, 21.0, 21.5, 51.1, 125.3, 126.6, 128.6, 136.4, 140.9, 142.9, 170.9; ν_{max} (neat) / cm^{-1} 2993, 2948, 1712, 1512, 1433, 1317, 1244, 1139, 819, 771.

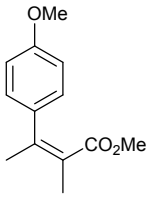
(*E*)-Methyl 2-methyl-3-(4-methoxylphenyl)but-2-enoate (*E*)-3c-3[6]



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (3H, d, *J* = 1.4 Hz), 2.25 (3H, d, *J* = 1.4 Hz), 3.79 (3H, s), 3.82 (3H, s), 6.87–6.91 (2H, m), 7.06–7.10 (2H, m); ν_{max} (neat) / cm^{-1} 2950, 1714, 1608, 1510, 1248, 1132, 1032.

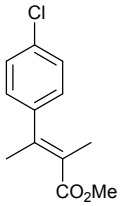
6) 14% yield (*E* / *Z* = 4 / 96), 90% yield (*E* / *Z* = 41 / 59), S. Sano, T. Takehisa, S. Ogawa, K. Yokoyama, Y. Nagao, *Chem. Pharm. Bull.* **2002**, *50*, 1300.

(*Z*)-Methyl 2-methyl-3-(4-methoxylphenyl)but-2-enoate (*Z*)-3c-3



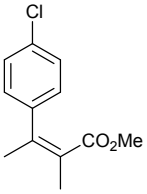
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (3H, d, *J* = 0.9 Hz), 2.07 (3H, d, *J* = 0.9 Hz), 3.44 (3H, s), 3.80 (3H, s), 6.81–6.85 (2H, m), 7.05–7.10 (2H, m); ν_{max} (neat) / cm^{-1} 2948, 1711, 1608, 1509, 1288, 1247, 1179, 1138, 1032.

(*E*)-Methyl 2-methyl-3-(4-chlorophenyl)but-2-enoate (*E*)-3c-4



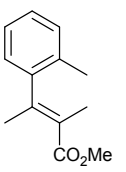
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (3H, d, *J* = 1.4 Hz), 2.23 (3H, d, *J* = 1.4 Hz), 3.80 (3H, s), 7.04–7.11 (2H, m), 7.30–7.37 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 23.0, 51.4, 125.1, 128.5, 128.6, 132.8, 141.6, 144.6, 169.8; ν_{max} (neat) / cm^{-1} 2950, 1716, 1631, 1490, 1433, 1316, 1250, 1133, 1092, 1014, 829; HRMS (ESI) calcd for $C_{12}H_{13}ClO_2$ (M+Na$^+$) 247.0502, found 247.0499.

(*Z*)-Methyl 2-methyl-3-(4-chlorophenyl)but-2-enoate (*Z*)-3c-4



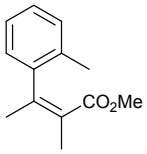
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H, d, *J* = 1.0 Hz), 2.06 (3H, d, *J* = 1.0 Hz), 3.44 (3H, s), 7.02–7.10 (2H, m), 7.24–7.31 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3, 21.5, 51.2, 126.2, 128.1, 132.7, 142.0, 142.4, 170.4; ν_{max} (neat) / cm^{-1} 2948, 1713, 1639, 1593, 1486, 1434, 1314, 1247, 1140, 1089, 1013, 828, 758.

(*E*)-Methyl 2-methyl-3-(2-methylphenyl)but-2-enoate (*E*)-3c-5



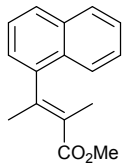
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (3H, q, *J* = 1.7 Hz), 2.18 (3H, s), 2.22 (3H, q, *J* = 1.7 Hz), 3.80 (3H, s), 6.91–6.99 (1H, m), 7.14–7.21 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.7, 18.8, 22.5, 51.3, 124.6, 125.9, 126.4, 126.9, 130.0, 133.5, 143.0, 147.1, 169.6; ν_{max} (neat) / cm^{-1} 3017, 2950, 2868, 1716, 1633, 1433, 1373, 1250, 1197, 1139, 1097, 764, 731; HRMS (ESI) calcd for $C_{13}H_{16}O_2$ (M+Na$^+$) 227.1048, found 227.1054.

(*Z*)-Methyl 2-methyl-3-(2-methylphenyl)but-2-enoate (*Z*)-3c-5



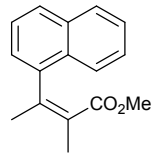
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H, s), 2.03 (3H, s), 2.19 (3H, s), 3.37 (3H, s), 6.85–6.97(1H, m), 7.06–7.21 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 19.1, 21.8, 51.0, 125.3, 125.4, 126.4, 126.6, 129.5, 133.9, 144.0, 145.2, 169.4; ν_{max} (neat) / cm^{-1} 3015, 1949, 2863, 1711, 1641, 1434, 1315, 1238, 1141, 1087, 761, 726.

(*E*)-Methyl 2-methyl-3-(1-naphthyl)but-2-enoate (*E*)-3c-6



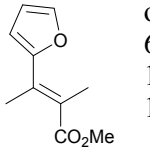
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55–1.61 (3H, m), 2.33–2.38 (3H, m), 3.85 (3H, s), 7.19 (1H, dd, *J* = 1.0, 7.2 Hz), 7.42–7.52 (3H, m), 7.71–7.81 (2H, m), 7.83–7.90 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.2, 23.4, 51.4, 123.7, 124.9, 125.5, 125.8, 126.2, 127.1, 128.4, 129.5, 133.6, 141.2, 145.6, 169.6; ν_{max} (neat) / cm^{-1} 3058, 2995, 2949, 1715, 1631, 1506, 1433, 1265, 1193, 1143, 1094, 779; HRMS (ESI) calcd for $C_{16}H_{16}O_2$ (M+Na$^+$) 263.1048, found 63.1050.

(*Z*)-Methyl 2-methyl-3-(1-naphthyl)but-2-enoate (*Z*)-3c-6



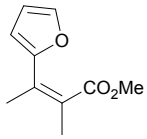
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (3H, s), 2.18 (3H, s), 3.16 (3H, s), 7.12 (1H, d, *J* = 7.2 Hz), 7.33–7.54 (3H, m), 7.67–7.89 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.7, 22.6, 51.0, 123.4, 125.1, 125.2, 125.5, 125.8, 126.8, 127.1, 128.2, 130.4, 133.4, 142.4, 143.9, 169.3; ν_{max} (neat) / cm^{-1} 3058, 2999, 2948, 1708, 1433, 1313, 1143, 1086, 778.

(*E*)-Methyl 2-methyl-(2-furyl)but-2-enoate (*E*)-3c-7



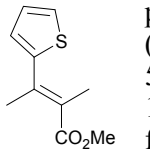
orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15–2.19 (3H, m), 2.22–2.26 (3H, m), 3.79 (3H, s), 6.43–6.49 (2H, m), 7.47 (1H, d, *J* = 1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 18.5, 51.6, 111.1, 111.7, 124.5, 131.7, 142.3, 154.1, 170.8; ν_{max} (neat) / cm^{-1} 3424, 3149, 2952, 1767, 1713, 1610, 1434, 1251, 1134, 743; HRMS (ESI) calcd for $C_{10}H_{12}O_3$ (M+Na$^+$) 203.0684, found 206.0685.

(*Z*)-Methyl 2-methyl-(2-furyl)but-2-enoate (*Z*)-3c-7



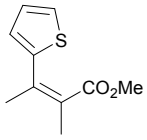
orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (6H, s), 3.73 (3H, s), 6.28–6.41 (2H, m), 7.33 (1H, dd, *J* = 0.7, 1.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3, 16.8, 51.7, 108.1, 111.0, 124.9, 125.9, 142.1, 153.6, 172.3; ν_{max} (neat) / cm^{-1} 3433, 3122, 2950, 1768, 1720, 1434, 1312, 1251, 1127, 905, 732.

(*E*)-Methyl 2-methyl-(2-thienyl)but-2-enoate (*E*)-3c-8



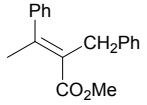
pale red oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (3H, q, *J* = 1.4 Hz), 2.31 (3H, q, *J* = 1.4 Hz), 3.80 (3H, s), 6.93–7.10 (2H, m), 7.33 (1H, dd, *J* = 1.4, 5.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.0, 23.5, 51.6, 125.5, 126.1, 126.6, 126.7, 136.7, 144.1, 170.4; ν_{max} (neat) / cm^{-1} 3104, 2996, 2950, 1715, 1609, 1433, 1279, 1242, 1121, 834, 701; HRMS (ESI) calcd for $C_{10}H_{12}O_2S$ (M+Na$^+$) 219.0456, found 219.0454.

(*Z*)-Methyl 2-methyl-(2-thienyl)but-2-enoate (*Z*)-3c-8



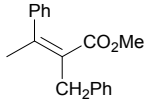
pale red oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H, d, *J* = 1.0 Hz), 2.13 (3H, d, *J* = 1.0 Hz), 3.57 (3H, s), 6.84–6.97 (1H, m), 7.23 (1H, dd, *J* = 1.0, 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.9, 21.4, 51.6, 124.9, 125.0, 126.0, 127.2, 132.6, 144.6, 171.4; ν_{max} (neat) / cm^{-1} 3106, 2994, 2947, 1714, 1631, 1432, 1298, 1238, 1134, 852, 697.

(*E*)-Ethyl 2-benzyl-3-phenylbut-2-enoate (*E*)-3d[7]



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73 (3H, t, *J* = 7.2 Hz), 2.16 (3H, s), 3.77 (2H, t, *J* = 7.2 Hz), 3.84 (2H, s), 7.06–7.39 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3, 21.7, 36.1, 60.0, 126.0, 126.8, 127.0, 128.2, 128.3, 129.7, 139.0, 143.9, 144.4, 169.9 cm^{-1}; ν_{max} (neat) / cm^{-1} 2982, 1705, 1495, 1455, 1375, 1314, 1242, 1134.

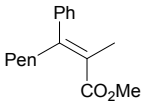
(*Z*)-Ethyl 2-benzyl-3-phenylbut-2-enoate (*Z*)-3d



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (3H, t, *J* = 7.2 Hz), 2.31 (3H, s), 3.55 (2H, s), 4.12 (2H, t, *J* = 7.2 Hz), 7.00–7.39 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 23.4, 36.8, 60.2, 125.8, 127.0, 127.2, 128.0, 128.1, 128.2, 128.4, 139.8, 142.8, 146.0, 169.0 cm^{-1}; ν_{max} (neat) / cm^{-1} 2982, 1713, 1495, 1455, 1312, 1254, 1198, 1051.

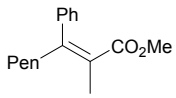
7) R. Pellicciari, B. Natalini, B. M. Sadeghpour, M. Marinozzi, J. P. Snyder, B. L. Williamson, J. T. Kuethe, A. Padwa, *J. Am. Chem. Soc.* **1996**, *118*, 1.

(*E*)-Methyl 2-benzyl-3-phenyloct-2-enoate (*E*)-3e[5]



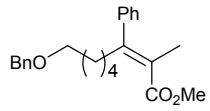
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 6.9 Hz), 1.11–1.39 (6H, m), 1.71 (3H, s), 2.58 (2H, t, *J* = 6.9 Hz), 3.79 (3H, s), 7.00–7.14 (2H, m), 7.18–7.41 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 17.3, 22.3., 27.7, 31.7, 36.1, 51.3, 124.5, 126.9, 127.6, 128.1, 141.8, 150.0, 170.3; ν_{max} (neat) / cm^{-1} 2955, 2860, 1720, 1435, 1250, 1190, 1136, 1109.

(*Z*)-Methyl 2-benzyl-3-phenyloct-2-enoate (*Z*)-3e



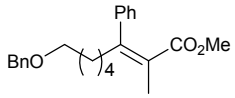
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (3H, t, *J* = 7.2 Hz), 1.60–1.37 (6H, m), 2.03 (3H, s), 2.44 (2H, t, *J* = 7.2 Hz), 3.36 (3H, s), 7.05–7.16 (2H, m), 7.18–7.34 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 15.8, 22.3, 26.9, 31.6, 34.8, 51.0, 125.7, 126.8, 127.2, 127.8, 142.8, 147.7, 171.0; ν_{max} (neat) / cm^{-1} 2955, 2861, 1717, 1458, 1320, 1242, 1190, 1138.

(*E*)-Methyl 8-benzyloxy-2-methyl-3-phenyloct-2-enoate (*E*)-3f



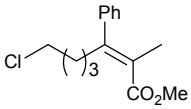
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23–1.39 (4H, m), 1.47–1.60 (2H, m), 1.70 (3H, s), 2.55–2.65 (2H, m), 3.96 (2H, t, *J* = 6.5 Hz), 3.78 (3H, s), 4.45 (2H, s), 7.03–7.13 (2H, m), 7.17–7.39 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 26.0, 27.8, 29.4, 36.0, 51.3, 70.2, 72.7, 124.6, 126.9, 127.3, 127.4, 127.6, 128.1, 128.2, 138.6, 141.7, 149.8, 170.2; ν_{max} (neat) / cm^{-1} 2938, 2859, 1717, 1433, 1364, 1254, 1132, 1111.; HRMS (ESI) calcd for $C_{23}H_{28}O_3$ (M+Na$^+$) 375.1936, found 375.1933.

(*Z*)-Methyl 8-benzyloxy-2-methyl-3-phenyloct-2-enoate (*Z*)-3f



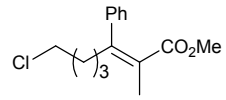
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21–1.63 (6H, m), 2.02 (3H, s), 2.45 (2H, t, *J* = 7.6 Hz), 3.36 (3H, s), 3.40 (2H, t, *J* = 6.5 Hz), 4.46 (2H, s), 7.01–7.13 (2H, m), 7.16–7.36 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.8, 25.9, 27.0, 29.4, 34.6, 51.0, 70.0, 72.7, 125.7, 126.7, 127.1, 127.3, 127.4, 127.7, 128.1, 138.4, 142.6, 147.3, 170.9; ν_{max} (neat) / cm^{-1} 2940, 2861, 1717, 1433, 1318, 1242, 1138, 1102.

(*E*)-Methyl 7-chloro-2-methyl-3-phenylhept-2-enoate (*E*)-3g



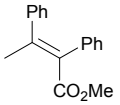
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40–1.51 (2H, m), 1.70–1.80 (2H, m), 1.72 (3H, s), 2.64 (2H, t, *J* = 7.5 Hz), 3.47 (2H, t, *J* = 6.9 Hz), 3.80 (3H, s), 7.07–7.14 (2H, m), 7.26–7.32 (1H, m), 7.34–7.39 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4, 25.2, 32.2, 35.1, 44.7, 51.5, 125.2, 127.1, 127.6, 128.3, 141.4, 149.2, 170.1; ν_{max} (neat) / cm^{-1} 2950, 1714, 1624, 1599, 1491, 1433, 1255, 1122; HRMS (ESI) calcd for $C_{15}H_{19}ClO_2$ (M+Na$^+$) 289.0971, found 289.0971.

(*Z*)-Methyl 7-chloro-2-methyl-3-phenylhept-2-enoate (*Z*)-3g



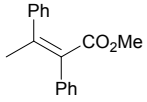
pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40–1.51 (2H, m), 1.70–1.79 (2H, m), 2.04 (3H, s), 2.49 (2H, t, *J* = 8.2 Hz), 3.37 (3H, s), 3.47 (2H, t, *J* = 6.9 Hz), 7.08–7.13 (2H, m), 7.22–7.33 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.9, 24.5, 32.1, 33.8, 44.5, 51.2, 126.4, 127.0, 127.2, 128.0, 142.3, 146.4, 170.8; ν_{max} (neat) / cm^{-1} 2948, 1711, 1633, 1492, 1433, 1311, 1236, 1137.

(*E*)-Methyl 2,3-diphenyl-2-butenoate (*E*)-3j[8]



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (3H, s), 3.76 (3H, s), 6.95–7.18 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.2, 51.9, 126.8, 127.0, 127.7, 127.8, 128.4, 129.8, 131.6, 137.1, 141.8, 144.6, 169.8; ν_{max} (neat) / cm^{-1} 2950, 1719, 1599, 1491, 1433, 1375, 1304, 1250.

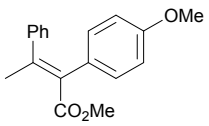
(*Z*)-Methyl 2,3-diphenyl-2-butenoate (*Z*)-3j



pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05 (3H, s), 3.43 (3H, s), 7.29–7.44 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2, 51.5, 126.8, 127.5, 128.1, 128.3, 129.1, 132.5, 137.1, 142.8, 143.9, 169.6; ν_{max} (neat) / cm^{-1} 2941, 1719, 1491, 1433, 1375, 1304, 1252, 1210.

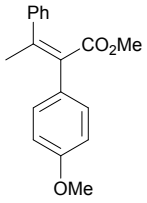
9) T. Tsuda, T. Yoshida, T. Saegusa, *J. Org. Chem.* **1988**, *53*, 607.

(*E*)-Methyl 2-(4-methoxyphenyl)-3-phenyl-2-butenoate (*E*)-3k



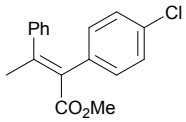
pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (3H, s), 3.72 (3H, s), 3.79 (3H, s), 6.60–6.70 (2H, m), 6.88–6.96 (2H, m) , 7.10–7.20 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 51.8, 54.8, 113.2, 126.8, 127.8, 128.3, 129.3, 130.8, 131.1, 141.9, 143.1, 158.2, 170.1; ν_{max} (neat) / cm^{-1} 2951, 1719, 1609, 1576, 1509, 1458, 1375, 1248; HRMS (ESI) calcd for $C_{18}H_{18}O_3$ (M+Na$^+$) 305.1154, found 305.1161.

(*Z*)-Methyl 2-(4-methoxyphenyl)-3-phenyl-2-butenoate (*Z*)-3k



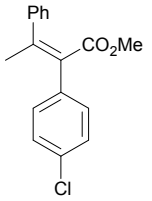
pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.07 (3H, s), 3.43 (3H, s), 3.84 (3H, s), 6.92–6.96 (2H, m), 7.27–7.40 (7H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 51.6, 55.2, 113.8, 126.9, 127.5, 128.2, 129.4, 130.4, 132.2, 143.0, 143.3, 158.9, 170.1; ν_{max} (neat) / cm^{-1} 2951, 1719, 1655, 1601, 1541, 1509, 1437, 1250.

(*E*)-Methyl 2-(4-chlorophenyl)-3-phenyl-2-butenoate (*E*)-3l



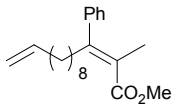
pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (3H, s), 3.78 (3H, s), 6.88–6.95 (2H, m), 6.97–7.03 (2H, m), 7.03–7.11 (2H, m), 7.11–7.12 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 52.0, 127.2, 128.0, 128.0, 128.3, 130.4, 131.3, 132.7, 135.7, 141.6, 146.0, 169.4; ν_{max} (neat) / cm^{-1} 2949, 1707, 1619, 1591, 1489, 1434, 1251, 1206.

(*Z*)-Methyl 2-(4-chlorophenyl)-3-phenyl-2-butenoate (*Z*)-3l



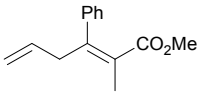
colorless crystals; mp 115–116 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (3H, s), 3.42 (3H, s), 7.24–7.44 (9H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 51.7, 126.8, 127.7, 128.2, 128.6, 130.6, 131.3, 133.5, 135.6, 142.6, 145.0, 169.2; ν_{max} (neat) / cm^{-1} 2951, 1697, 1491, 1428, 1319, 1214, 1088, 1008; HRMS (ESI) calcd for $C_{17}H_{15}O_2Cl$ (M+Na$^+$) 309.0658, found 309.0654.

(*E*)-Methyl 2-methyl-3-phenyltrideca-2,12-dienoate (*E*)-3h



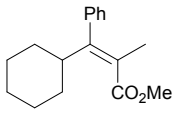
colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16–1.37 (12H, m), 1.71 (3H, s), 1.95–2.07 (2H, m), 2.58 (2H, t, *J* = 6.9 Hz), 3.79 (3H, s), 4.89–5.03 (2H, m), 5.79 (1H, ddt, *J* = 17.2 Hz, 10.3 Hz, 6.9 Hz), 7.08–7.12 (2H, m), 7.27–7.30 (1H, m), 7.33–7.38 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.4, 28.0, 28.9, 29.0, 29.3, 29.3, 29.533.7, 36.2, 51.4, 114.0, 124.5, 126.9, 127.7, 128.2, 139.2, 141.8, 150.1, 170.4; ν_{max} (neat) / cm^{-1} 3073, 2925, 2854, 1718, 1483, 1252, 1118, 994, 910, 772, 703; HRMS (ESI) calcd for $C_{21}H_{30}O_2$ (M+Na$^+$) 337.2143, found 337.2173.

(*Z*)-Methyl 2-methyl-3-phenyltrideca-2,12-dienoate (*Z*)-3h



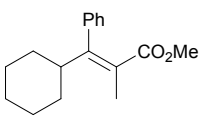
colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19–1.38 (12H, m), 1.96–2.04 (5H, m), 2.44 (2H, t, *J* = 6.9 Hz), 3.36 (3H, s), 4.90–5.01 (2H, m), 5.80 (1H, ddt, *J* = 17.2 Hz, 10.3 Hz, 6.9 Hz), 7.08–7.12 (2H, m), 7.21–7.25 (1H, m), 7.27–7.31 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.9, 27.2, 28.8, 29.0, 29.3, 29.4, 33.7, 34.9, 51.1, 114.1, 125.7, 126.8, 127.2, 127.8, 139.1, 142.8, 147.8, 171.0; ν_{max} (neat) / cm^{-1} 3078, 2925, 2854, 1714, 1639, 1434, 1317, 1238, 1137, 1084, 994, 910, 771, 700.

(*E*)-Methyl 3-cyclohexyl-2-methyl-3-phenylacrylate (*E*)-3i



colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (1H, tq, *J* = 3.4 Hz, 12.6 Hz), 1.01 (2H, dq, *J* = 3.4 Hz, 12.6 Hz), 1.29 (2H, tq, *J* = 3.4 Hz, 12.6 Hz), 1.53–1.59 (4H, m), 1.63–1.74 (4H, m), 2.93 (1H, tt, *J* = 12.0 Hz, 2.9 Hz), 3.80 (3H, s), 6.96–7.00 (2H, m), 7.27–7.30 (1H, m), 7.31–7.36 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.4, 25.8, 26.3, 31.6, 42.8, 51.4, 124.5, 126.6, 127.8, 128.2, 139.3, 153.1, 170.7; ν_{max} (neat) / cm^{-1} 2925, 2853, 1718, 1447, 1251, 1125, 775, 707; HRMS (ESI) calcd for $C_{17}H_{22}O_2$ (M+Na$^+$) 281.1517, found 281.1537.

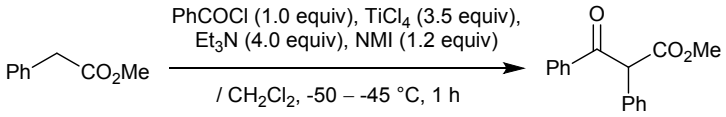
(*Z*)-Methyl 3-cyclohexyl-2-methyl-3-phenylacrylate (*Z*)-3i



colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (1H, tq, *J* = 3.4 Hz, 13.2 Hz), 1.06 (2H, dq, *J* = 3.4 Hz, 12.6 Hz), 1.30 (2H, tq, *J* = 3.4 Hz, 13.2 Hz), 1.57–1.67 (3H, m), 1.68–1.75 (2H, m), 2.03 (3H, s), 2.65 (1H, tt, *J* = 3.4 Hz, 12.0 Hz), 3.29 (3H, s), 6.98–7.01 (2H, m), 7.21–7.29 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 25.7, 26.4, 30.8, 41.5, 51.0, 125.5, 126.4, 127.2, 128.3, 140.4, 151.6, 170.8; ν_{max} (neat) / cm^{-1} 2928, 2853, 1715, 1433, 1314, 1247, 1135, 1090, 771,

702.

Methyl 2,3-diphenyl-3-oxopropanoate[9] utilizing crossed Ti-Claisen condensation

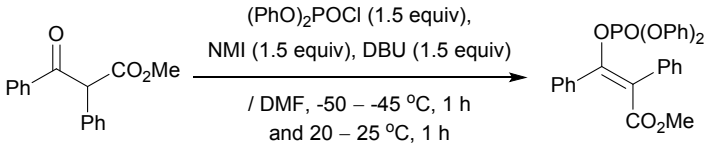


4

To a vigorously stirred solution of $PhCH_2CO_2Me$ (15.02 g, 0.1 mol) and PhCOCl (14.06 g, 0.10 mol) in CH_2Cl_2 (300 mL), NMI (9.85 g, 0.12 mol) was added dropwise at -50 – -45 °C under an Ar atmosphere. Then, using two dropping funnels, $TiCl_4$ (38.4 mL, 0.35 mol) (during ca. 20 min) and Et_3N (55.4 mL, 0.40 mol) (during ca. 1 h) were successively added, and the mixture was stirred at the same temperature for 1 h. Water was slowly added to the mixture, which was extracted twice with Et_2O. The combined organic phase was washed with water, brine, dried (Na_2SO_4), and concentrated to give the crude product (24.54 g), which was purified by recrystallization from 2-propanaol (22 mL) to give the desired product (18.71 g, 74%).
colorless crystals; mp 73-74 °C (lit.[9a] 72-73 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (3H, s), 5.63 (1H, s), 7.29–7.45 (7H, m), 7.51–7.58 (1H, m), 7.90-8.01 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.7, 60.3, 128.1, 128.7, 128.8, 128.9, 129.5, 132.8, 133.5, 135.5, 169.3, 193.2.

9) (a) K. Nakatani, J. Shirai, R. Tamaki, I. Saito, *Tetrahedron Lett.* **1995**, *36*, 5363. (b) Z. Zhang, Y. Liu, M. Gong, X. Zhao, Y. Zhang, J. Wang, *Angew. Chem. Int . Ed.* **2010**, *49*, 1139.

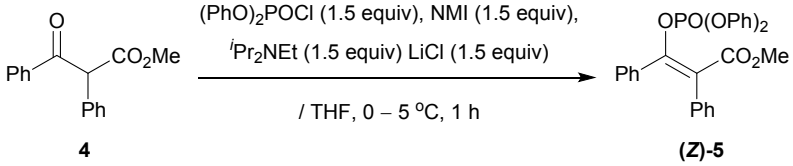
(*E*)-Stereoselective enol phosphorylation of methyl 2,3-diphenyl-3-oxopropanoate (4) using *Method C*.



4 **(*E*)-5**

$(PhO)_2POCl$ (403 mg, 1.5 mmol) was added to a stirred solution of methyl 2,3-diphenyl-3-oxopropanoate (**4**) (254 mg, 1.0 mmol), NMI (123 mg, 1.5 mmol), and DBU (228 mg, 1.5 mmol) in DMF (2.0 mL) at -50 – -45 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h and at the room temperature for 1 h. Water was added to the reaction mixture, which was extracted twice with AcOEt. The organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by silica-gel column chromatography (hexane-AcOEt = 10:1–3:1) to give the crude solid (280 mg, 58%, *E* / *Z* = 88 / 12), which was purified by recrystallization from hexane/toluene = 8/1 (4.5 mL) to give the desired (*E*)-methyl 2,3-diphenyl-3-(diphenoxyphospholoxy)-2-propenoate [(*E*)-**5**] (204 mg. 42%, *E* / *Z* = >98 / 2).
colorless crystals; mp 98-99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50 (3H, s), 6.71–6.78 (4H, m), 7.07–7.20 (6H, m), 7.28–7.43 (6H, m), 7.46–7.60 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.2, 119.8 [d, ^3J (^{13}C, ^{31}P) = 4.8 Hz], 124.2 [d, ^3J (^{13}C, ^{31}P) = 9.6 Hz], 125.2, 128.1, 128.1, 128.3, 129.0, 129.3, 129.5, 130.0, 132.9, 133.7, 150.1 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 150.8 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 167.7; ν_{max} (neat) / cm^{-1} 3017, 2952, 1725, 1591, 1489, 1295, 1186, 1065; HRMS (ESI) calcd for $C_{28}H_{23}O_6P$ ($M+Na^+$) 509.1130, found 509.1140.

(*Z*)-Stereoselective enol phosphorylation of methyl 2,3-diphenyl-3-oxopropanoate (4) using *Method D*.

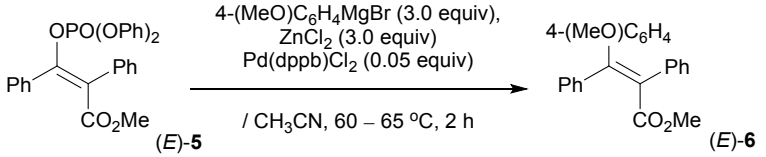


4 **(*Z*)-5**

2,3-Diphenyl-3-oxopropanoate (**4**) (254 mg 1.0 mmol), ^{i}Pr$_2$NEt (194 mg, 1.5 mmol), NMI (123 mg, 1.5 mmol,), and $(PhO)_2POCl$ (403 mg, 1.5 mmol) were successively added to a stirred suspension of LiCl (64 mg 1.5 mmol) in THF (2.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h. Water was added to the mixture, which was extracted with twice with AcOEt. The organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by

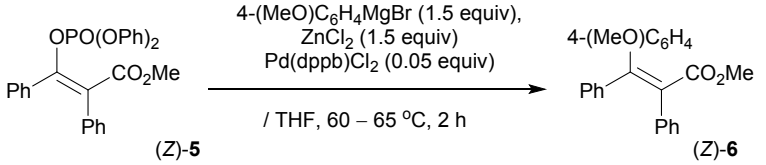
silica-gel column chromatography (hexane-AcOEt = 3:1) to give the desired (*Z*)-methyl 2,3-diphenyl-3-(diphenoxyphospholoxy)-2-propenoate [(*Z*)-5] (454 mg, 93 %, *E* / *Z* = 2 / >98).
colorless crystals; mp 82-83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (3H, s), 7.04–7.10 (4H, m), 7.11–7.34 (16H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 120.0 [d, ^3J (^{13}C, ^{31}P) = 4.8 Hz], 120.1, 123.7 [d, ^3J (^{13}C, ^{31}P) = 9.6 Hz], 125.3, 127.9, 127.9, 128.3, 129.6, 129.6, 129.9 [d, ^3J (^{13}C, ^{31}P) = 3.6 Hz], 132.7, 133.6, 149.1 [d, ^2J (^{13}C, ^{31}P) = 8.4 Hz], 150.4 [d, ^2J (^{13}C, ^{31}P) = 7.2 Hz], 166.8. ; ν_{max} (neat) / cm^{-1} 3015, 2952, 1726, 1489, 1297, 1207, 1186, 1011.

(*E*)-Stereoretentive Negishi cross-coupling using enol phosphonate (*E*)-5 with (4-MeO)C_6H_4ZnCl



4-(MeO)C_6H_4MgBr (2.94 mL; 1.02 M in THF) was added to a stirred suspension of $ZnCl_2$ (409 mg, 3.0 mmol) in CH_3CN (1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 10 min. Enol phosphonate (*E*)-**5** (486 mg, 1.0 mmol) and Pd(dppb)Cl_2 (30 mg, 0.05 mmol) in CH_3CN (1.0 mL) were successively added to the mixture, followed by being stirred at 60 – 65 °C for 2 h. After cooling down, 3M-HCl aq. solution was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane-AcOEt = 4:1) to give the crude solid (565 mg, *E* / *Z* = >98 / 2), which was purified by recrystallization from hexane/toluene = 13/1 (7 mL) to give the desired (*E*)-methyl 2,3-diphenyl-3-(4-methoxyphenyl)-2-propenoate (*E*)-**6** (219 mg, 64%, *E* / *Z* = >98 / 2).
colorless crystals; mp 113-115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.53 (3H, s), 3.74 (3H, s), 6.61–6.68 (2H, m), 6.87–6.94 (2H, m), 7.08–7.14 (2H, m), 7.15–7.23 (3H, m), 7.24–7.29 (2H, m), 7.29–7.39 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.9, 55.1, 113.2, 127.2, 128.1, 128.3, 129.1, 129.8, 132.3, 132.4, 132.7, 137.9, 142.7, 146.3, 159.1, 171.1; ν_{max} (neat) / cm^{-1} 3020, 2949, 2837, 1715, 1605, 1508, 1247, 1217, 1176, 1149; HRMS (ESI) calcd for $C_{23}H_{20}O_3$ (M+Na$^+$) 367.1310, found 367.1295.

(*Z*)-Stereoretentive Negishi cross-coupling using enol phosphonate (*Z*)-5 with (4-MeO)C_6H_4ZnCl



4-(MeO)C_6H_4MgBr (1.89 mL; 1.06 M in THF) was added to a stirred suspension of $ZnCl_2$ (273 mg, 2.0 mmol) in THF (1.0 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 10 min. Enol phosphonate (*Z*)-**5** (486 mg, 1.0 mmol) and Pd(dppb)Cl_2 (30 mg, 0.05 mmol) in CH_3CN (1.0 mL) were successively added to the mixture, followed by being stirred at 60 – 65 °C for 2 h. After cooling down, 3 M-HCl aq. solution was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane-AcOEt = 100:1 – 10:1) to give the crude solid (372 mg, *E* / *Z* = >98 / 2), which was purified by recrystallization from hexane/toluene = 7/1 (12 mL) to give the desired (*Z*)-methyl 2,3-diphenyl-3-(4-methoxyphenyl)-2-propenoate (*Z*)-**6** (192 mg, 56%, *E* / *Z* = 2 / >98).
colorless crystals; mp 130-131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59 (3H, s), 3.82 (3H, s), 6.83–6.88 (2H, m), 6.97–7.03 (2H, m), 7.04–7.23 (10H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.0, 55.2, 113.6, 127.2, 127.6, 127.8, 128.2, 129.8, 130.4, 131.0, 132.4, 134.7, 137.7, 140.7, 146.0, 159.5, 171.2; ν_{max} (neat) / cm^{-1} 3019, 2950, 2838, 1714, 1606, 1509, 1248, 1216, 1177, 1150.