Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

First sequential Mukaiyama–Michael reaction/crossed-Claisen condensation using two molar ketene silyl acetals and one molar α,β-unsaturated esters promoted by NaOH catalyst

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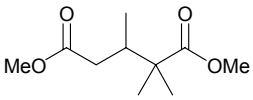
Contents:

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 (Yanagimoto) and were uncorrected. NMR spectra were recorded on a JEOL DELTA 300 spectrometer, operating at 300 MHz for ^{1}H NMR and 75 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.

Spectra data of new compounds 2a-2r

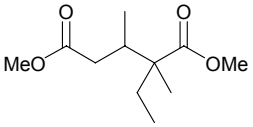
Dimethyl 2,2,3-trimethylpentane-1,5-dioate (2a)[1]



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, d, *J* = 7.2 Hz), 1.11 (6H, s), 1.87-2.11 (1H, m), 2.15-2.43 (2H, m), 3.65 (3H, s), 3.66 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 21.9, 22.0, 37.1, 45.4, 51.5, 51.7, 173.5, 177.7; IR (neat) 2979, 1736, 1458, 1437, 1370, 1306, 1262, 1194, 1165, 1012 cm^{-1}.

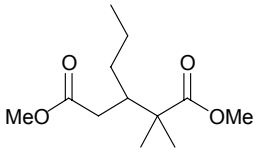
1) M. Kawai, M. Onaka and Y. Izumi, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2157.

Dimethyl 2-ethyl-2,3-dimethylpentane-1,5-dioate (2b)



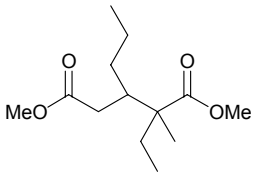
Following the procedure for the preparation of **2a,** the reaction of 1-methoxy-1-trimethylsiloxy-2-methyl-1-butene **1b** (283 mg, 1.5 mmol) with methyl but-2-enoate (100 mg, 1.0 mmol) gave the desired product **2b** (146 mg, 68%).
Diastereomixture (ca. 1 : 1); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.797 (3H x 1/2, t, *J* = 7.6 Hz), 0.803 (3H x 1/2, t, *J* = 7.2 Hz), 0.85 (3H x 1/2, d, *J* = 6.9 Hz), 0.88 (3H x 1/2, d, *J* = 6.9 Hz), 1.01 (3H x 1/2, s), 1.02 (3H x 1/2, s), 1.31-1.53 (1H, m), 1.56-1.79 (1H, m), 1.97 (1H x 1/2, dd, *J* = 11.0, 14.8 Hz), 2.08 (1H x 1/2, dd, *J* =10.7, 15.1 Hz), 2.16-2.52 (2H, m), 3.53-3.71 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.0, 9.2, 14.3, 15.8, 15.9, 16.0, 30.2, 30.3, 36.4, 36.9, 37.9, 49.7, 51.5, 51.6, 173.5, 173.7, 176.8, 177.0; IR (neat) 2974, 2953, 2883, 1736, 1458, 1437, 1389, 1318, 1237, 1057, 1009 cm^{-1}.

Dimethyl 2,2-dimethyl-3-propylpentanedioate (2c)



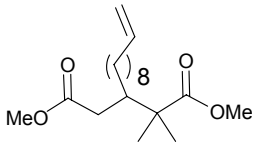
Following the procedure for the preparation of **2a,** the reaction of **1a** (261 mg, 1.5 mmol) with methyl hex-2-enoate (128 mg, 1.0 mmol) gave the desired product **2c** (177 mg, 77%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (3H, t *J* = 6.9 Hz), 1.01-1.31 (4H, m), 1.09(3H, s), 1.10(3H, s), 2.09(1H, dd *J* = 6.9, 15.5 Hz), 2.19-2.30 (1H, m) 2.34(1H, dd *J* = 4.8, 15.5 Hz),3.62 (3H, s) 3.63 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.1, 21.5, 23.0, 34.0, 35.7, 41.8, 45.9, 51.5, 51.6, 174.1, 177.9; IR (neat) 2957, 2874, 1736, 1458, 1437, 1372, 1231, 1165, 1021, 774 cm^{-1}.

Dimethyl 2-ethyl-2-methyl-3-propylpentanedioate (2d)



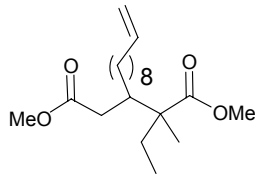
Following the procedure for the preparation of **2a,** the reaction of **1b** (283 mg, 1.5 mmol) with methyl hex-2-enoate (128 mg, 1.0 mmol) gave the desired product **2d** (182 mg, 75%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72-0.91(6H, m), 1.00 (3H x 1/2, s), 1.04 (3H x 1/2, s), 1.10-1.77 (6H, m), 1.98-2.43 (3H, m), 3.62 (3H x 1/2, s), 3.63 (3H x 1/2, s), 3.64 (3H x 1/2, s), 3.65 (3H x 1/2, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.6, 9.2, 14.2, 14.3, 15.8, 17.0, 21.0, 21.2, 30.0, 30.4, 33.1, 34.9, 35.2, 36.7, 41.5, 41.6, 50.3, 51.4, 51.5, 174.0, 177.1; IR (neat) 3856, 2957, 2876, 1736, 1435, 1318, 1233, 1134, 1015, 912, 758 cm^{-1}.

Dimethyl 3-(des-9-enyl)-2,2-dimethylpentanedioate (2e)



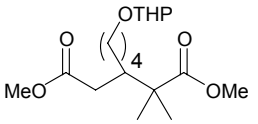
Following the procedure for the preparation of **2a,** the reaction of **1a** (261 mg, 1.5 mmol) with methyl trideca-2,12-dieoate (224 mg, 1.0 mmol) gave the desired product **2e** (227 mg, 70%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02-1.45 (14H, m), 1.11 (3H, s), 1.13 (3H, s),1.98-2.01 (1H, m), 2.12 (1H, dd *J* = 6.9, 15.1 Hz), 2.22-2.32 (2H, m), 2.38 (1H, dd *J* = 4.8, 15.1 Hz), 3.65 (3H, s), 3.66 (3H, s), 4.88-5.05 (2H, m), 5.81 (1H, ddt, *J* = 6.9, 10.3, 16.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 22.9, 27.9, 28.8, 29.0, 29.3, 29.6, 31.6, 33.7, 35.6, 42.0, 45.8, 51.4, 51.5, 114.0, 139.0, 174.0, 177.8; IR (neat) 3077, 2856, 1736, 1642, 1509, 1435, 1304, 1192, 994, 855, 774 cm^{-1}.

Dimethyl 3-(des-9-enyl)-2-ethyl-2-methylpentanedioate (2f)



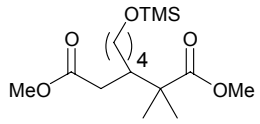
Following the procedure for the preparation of **2a,** the reaction of **1b** (283 mg, 1.5 mmol) with methyl trideca-2,12-dieoate (224 mg, 1.0 mmol) gave the desired product **2f** (234 mg, 69%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (3H x 1/2, t *J* = 5.9 Hz), 0.78 (3H x 1/2, t *J* = 5.9 Hz), 0.98 (3H x 1/2, s), 1.02 (3H x 1/2, s), 1.07-1.76 (14H, m), 1.92-2.42(5H, m), 3.61 (3H x 1/2, s), 3.62 (3H x 1/2, s), 3.62 (3H x 1/2, s), 3.63 (3H x 1/2, s), 4.83-5.00 (2H, m), 5.77 (1H, ddt, *J* = 6.5, 10.0, 13.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.0, 9.1, 15.8, 17.0, 28.1, 28.8, 29.0, 29.3, 29.8, 30.7, 33.7, 36.6, 41.8, 41.9, 50.2, 51.3, 51.4, 114.0, 139.1, 174.0, 174.2, 177.0; IR (neat) 3856, 3652, 2928, 1736, 1640, 1508, 1435, 1320, 1231, 1134, 911 cm^{-1}.

Dimethyl 3-(4-(2H-3,4,5,6-tetrahydropyran-2-yloxy)butyl)-2,2-dimethylpentane-1,5-dioate (2g)



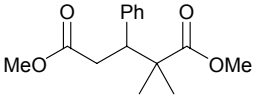
Following the procedure for the preparation of **2a,** the reaction of **1a** (261 mg, 1.5 mmol) with methyl 7-(2H-3,4,5,6-tetrahydropyran-2-yloxy)hept-2-enoate (242 mg, 1.0 mmol) gave the desired product **2g** (253 mg, 74%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (3H, s), 1.13 (3H, s), 1.16-1.91 (12H, m), 2.14 (1H, dd, *J* = 6.5, 15.5 Hz), 2.23-2.33 (1H, m), 2.38 (1H, dd, *J* = 4.5, 15.5 Hz), 3.35 (1H, dt, *J* = 6.2, 9.6 Hz), 3.43-3.54 (1H, m), 3.66 (6H, s), 3.70 (1H, dt, *J* = 6.9, 9.6 Hz), 3.78-3.92 (1H, m), 4.56 (1H, t, *J* = 3.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 21.6, 23.0, 24.7, 25.5, 29.8, 30.7, 31.5, 35.7, 42.0, 46.0, 51.6, 62.2, 67.2, 98.8, 174.0, 177.9; IR (neat) 2949, 2870, 1736, 1437, 1260, 1200, 1163, 1136, 1078, 1034, 990 cm^{-1}.

Dimethyl 2,2-dimethyl-3-(4-(trimethylsilyloxy)butyl)pentanedioate (2h)



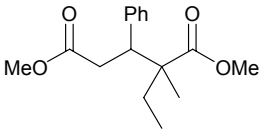
Following the procedure for the preparation of **2a,** the reaction of **1a** (418 mg, 2.4 mmol) with methyl 7-hydroxyhept-2-enoate (158 mg, 1.0 mmol) gave the desired TMS ether product **2h** (186 mg, 56%). colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (9H, s), 1.12 (3H, s), 1.13 (3H, s), 1.16-1.57 (6H, m), 2.13 (1H, dd, *J* = 6.5 15.5 Hz), 2.23-2.33 (1H, m), 2.38 (1H, dd, *J* = 4.8 15.5 Hz) , 3.54 (2H, t, *J* = 6.5 Hz), 3.65 (3H, s), 3.66 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ -0.5, 21.6, 23.0, 24.3, 31.5, 32.8, 35.7, 42.0, 46.0, 51.6, 51.7, 62.3, 174.0, 177.9; IR (neat) 3856, 2953, 2867, 1736, 1437, 1369, 1252, 1161, 1098, 843 cm^{-1}.

Dimethyl 2,2-dimethyl-3-phenylpentane-1,5-dioate (2i)



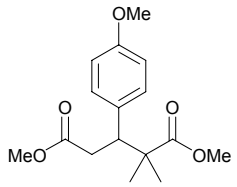
Following the procedure for the preparation of **2a,** the reaction of **1a** (209 mg, 1.2 mmol) with methyl 3-phenylprop-2-enoate (162 mg, 1.0 mmol) gave the desired product **2i** (246 mg, 93%).
colorless crystals; mp 59 – 61 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (3H, s), 1.15 (3H, s), 2.66 (1H, dd, *J* = 4.5, 15.8 Hz), 2.85 (1H, dd, *J* = 11.4, 15.8 Hz), 3.48 (3H, s), 3.53 (1H, dd, *J* = 4.5, 11.0 Hz), 3.65 (3H, s), 7.03-7.32 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 24.2, 35.7, 46.0, 48.9, 51.5, 51.8, 127.0, 127.9, 129.2, 139.3, 172.5, 177.3; IR (KBr) 2990, 2951, 1725, 1453, 1385, 1289, 1256, 1224, 1194, 1163, 1003, 773, 704 cm^{-1}.

Dimethyl 2-ethyl-2-methyl-3-phenylpentane-1,5-dioate (2j)



Following the procedure for the preparation of **2a,** the reaction of **1b** (226 mg, 1.2 mmol) with methyl 3-phenylprop-2-enoate (162 mg, 1.0 mmol) gave the desired product **2j** (273 mg, 98%).
Diastereomixture (ca. 1: 1); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (3H x 1/2, t, *J* = 7.6 Hz), 0.83 (3H x 1/2, t, *J* = 7.6 Hz), 1.07 (3H x 1/2, s), 1.10 (3H x 1/2, s), 1.34-1.62 (2H x 1/2, m), 1.69-1.93 (2H x 1/2, m), 2.58 (1H x 1/2, dd, *J* = 4.1, 15.8 Hz), 2.70-2.83 (1H, m), 2.90 (1H x 1/2, dd, *J* = 11.7, 15.8 Hz), 3.46 (3H x 1/2, s), 3.48 (3H x 1/2, s), 3.49-3.59 (1H, m), 3.55 (3H x 1/2, s), 3.70 (3H x 1/2, s), 7.03-7.31 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.1, 9.4, 16.5, 17.2, 29.9, 31.5, 34.9, 36.2, 49.0, 50.4, 50.7, 51.3, 51.5 (2C), 51.8, 127.0, 127.9, 129.0, 129.4, 172.4, 172.7, 175.9, 176.8; IR (neat) 3032, 2974, 2882, 1736, 1455, 1435, 1385, 1235, 1152, 1024, 962, 704 cm^{-1}.

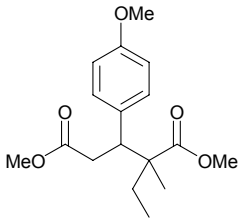
Dimethyl 3-(4-methoxyphenyl)-2,2-dimethylpentane-1,5-dioate (2k)



Following the procedure for the preparation of **2a**, the reaction of **1a** (209 mg, 1.2 mmol) with methyl 3-(4-methoxyphenyl)prop-2-enoate (192 mg, 1.0 mmol) gave the desired product **2k** (283 mg, 96%).

yellow pale crystals; mp 52 - 54 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.14 (3H, s), 2.63 (1H, dd, *J* = 4.5, 15.8 Hz), 2.80 (1H, dd, *J* = 11.4, 15.8 Hz), 3.44-3.56 (4H, m), 3.65 (3H, s), 3.79 (3H, s), 6.80 (2H, d, *J* = 8.9 Hz), 7.08 (2H, d, *J* = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 24.1, 35.8, 46.1, 48.1, 51.5, 51.8, 55.1, 113.3, 130.1, 131.2, 158.5, 172.6, 177.4; IR (KBr) 2986, 2955, 1721, 1612, 1516, 1458, 1437, 1252, 1171, 1130, 1032, 835 cm^{-1}.

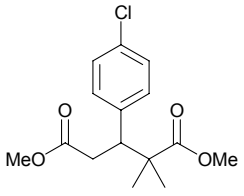
Dimethyl 2-ethyl-3-(4-methoxyphenyl)-2-methylpentane-1,5-dioate (2l)



Following the procedure for the preparation of **2a,** the reaction of **1b** (226 mg, 1.2 mmol) with methyl 3-(4-methoxyphenyl)prop-2-enoate (192 mg, 1.0 mmol) gave the desired product **2l** (250 mg, 81%).

Diastereomixture (ca. 1 : 1); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74 (3H x 1/2, t, *J* = 7.6 Hz), 0.83 (3H x 1/2, t, *J* = 7.6 Hz), 1.05 (3H x 1/2, s), 1.09 (3H x 1/2, s), 1.34-1.60 (2H x 1/2, m), 1.68-1.91 (2H x 1/2, m), 2.54 (1H x 1/2, dd, *J* = 3.8, 15.5 Hz), 2.63-2.79 (1H, m), 2.84 (1H x 1/2, dd, *J* = 11.7, 15.5 Hz), 3.39-3.53 (1H, m), 3.47 (3H x 1/2, s), 3.48 (3H x 1/2, s), 3.56 (3H x 1/2, s), 3.70 (3H x 1/2, s), 3.76 (3H x 1/2, s), 3.78 (3H x 1/2, s), 6.69-6.85 (2H, m), 6.94-7.13 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.0, 9.4, 16.4, 17.1, 30.1, 31.5, 35.1, 36.4, 48.3, 48.4, 50.6, 50.8, 51.3, 51.5, 51.6, 51.8, 55.1, 55.2, 113.3, 130.0, 130.4, 131.2, 131.7, 158.4, 158.5, 172.5, 172.7, 176.0, 176.9; IR (neat) 2951, 2882, 2840, 1736, 1610, 1514, 1458, 1437, 1252, 1180, 1128, 1036, 837 cm^{-1}.

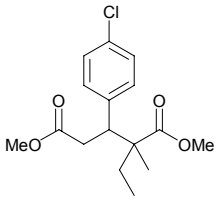
Dimethyl 3-(4-chlorophenyl)-2,2-dimethylpentane-1,5-dioate (2m)



Following the procedure for the preparation of **2a**, the reaction of **1a** (209 mg, 1.2 mmol) with methyl 3-(4-chlorophenyl)prop-2-enoate (196 mg, 1.0 mmol) gave the desired product **2m** (257 mg, 86%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.14 (3H, s), 2.63 (1H, dd, *J* = 4.5, 15.8 Hz), 2.80 (1H, dd, *J* = 11.4, 15.8 Hz), 3.44-3.56 (4H, m), 3.65 (3H, s), 3.79 (3H, s), 7.00-7.14 (2H, m), 7.15-7.29 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 24.1, 35.5, 45.9, 48.3, 51.6, 51.9, 128.1, 130.5, 132.9, 137.9, 172.3, 177.0; IR (neat) 2982, 2884, 1732, 1493, 1435, 1370, 1308, 1169, 1093, 1015, 837 cm^{-1}.

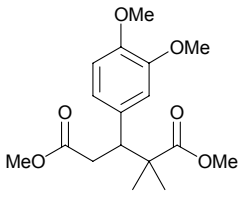
Dimethyl 3-(4-chlorophenyl)-2-ethyl-2-methylpentane-1,5-dioate (2n)



Following the procedure for the preparation of **2a,** the reaction of **1b** (226 mg, 1.2 mmol) with methyl 3-(4-chlorophenyl)prop-2-enoate (196 mg, 1.0 mmol) gave the desired product **2n** (260 mg, 83%).

Diastereomixture (ca. 1 : 1); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (3H x 1/2, t, *J* = 7.6 Hz), 0.83 (3H x 1/2, t, *J* = 7.6 Hz), 1.04 (3H x 1/2, s), 1.08 (3H x 1/2, s), 1.31-1.64 (2H x 1/2, m), 1.66-1.90 (2H x 1/2, m), 2.56 (1H x 1/2, dd, *J* = 3.8, 15.8 Hz), 2.64-2.83 (1H, m), 2.84 (1H x 1/2, dd, *J* = 11.7, 15.8 Hz), 3.43-3.54 (1H, m), 3.47 (3H x 1/2, s), 3.49 (3H x 1/2, s), 3.56 (3H x 1/2, s), 3.69 (3H x 1/2, s), 6.80-7.14 (2H, m), 7.14-7.28 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.0, 9.3, 16.5, 17.0, 30.1, 31.4, 34.7, 36.1, 48.4, 48.5, 50.3, 50.6, 51.4, 51.6 (2C), 51.8, 128.1, 130.3, 130.7, 132.8, 137.8, 138.3, 172.2, 172.4, 175.6, 176.4; IR (neat) 2976, 2951, 1736, 1493, 1460, 1435, 1321, 1235, 1152, 1129, 1094, 1015, 837 cm^{-1}.

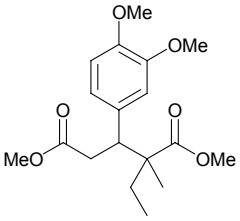
Dimethyl 3-(3,4-dimethoxyphenyl)-2,2-dimethylpentane-1,5-dioate (2o)



Following the procedure for the preparation of **2a,** the reaction of **1a** (209 mg, 1.2 mmol) with methyl 3-(3,4-dimethoxyphenyl)prop-2-enoate (222 mg, 1.0 mmol) gave the desired product **2o** (263 mg, 81%).

yellow pale crystals; mp 69 - 71 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (3H, s), 1.15 (3H, s), 2.66 (1H, dd, *J* = 4.1, 15.5 Hz), 2.80 (1H, dd, *J* = 4.1, 15.5 Hz), 3.39-3.53 (4H, m), 3.56 (3H, s), 3.85 (3H, s), 3.86 (3H, s), 6.59-6.82 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 24.2, 35.8, 46.2, 48.5, 51.6, 51.9, 55.7, 55.9, 110.6, 112.7, 121.2, 131.9, 147.9, 148.1, 172.5, 177.4; IR (KBr) 2953, 2838, 1736, 1518, 1466, 1437, 1306, 1260, 1190, 1146, 1028 cm^{-1}.

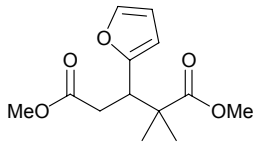
Dimethyl 2-ethyl-3-(3,4-dimethoxyphenyl)-2-methylpentane-1,5-dioate (2p)



Following the procedure for the preparation of **2a,** the reaction of **1b** (226 mg, 1.2 mmol) with methyl 3-(3,4-dimethoxyphenyl)prop-2-enoate (222 mg, 1.0 mmol) gave the desired product **2p** (311 mg, 92%).

Diastereomixture (ca. 1 : 1); yellow pale crystals; mp 59 - 61 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76 (3H x 1/2, t, *J* = 7.2 Hz), 0.83 (3H x 1/2, t, *J* = 7.2 Hz), 1.07 (3H, s), 1.10 (3H, s), 1.32-1.58 (2H, m), 1.68-1.91 (2H, m), 2,56 (1H x 1/2, dd, *J* = 3.8, 15.5 Hz), 2.65-2.80 (1H, m), 2.85 (1H x 1/2, dd, *J* = 11.4, 15.5 Hz), 3.38-3.53 (1H, m), 3.48 (3H x 1/2, s), 3.50 (3H x 1/2, s), 3.57 (3H x 1/2, s), 3.70 (3H x 1/2, s), 3.83 (3H x 1/2, s), 3.85 (3H, s), 3.86 (3H x 1/2, s), 6.59-6.81 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.1, 9.4, 16.6, 17.1, 30.1, 31.5, 35.0, 36.4, 48.7, 50.6, 51.4, 51.5, 51.6, 51.8, 55.7 (2C), 55.8, 55.9, 110.5, 112.6, 112.9, 121.0, 121.5, 131.8, 132.3, 147.9, 148.0, 148.2, 172.5, 172.7, 176.0, 176.9; IR (KBr) 2998, 2882, 1746, 1587, 1518, 1455, 1354, 1277, 1130, 1028, 862, 770 cm^{-1}.

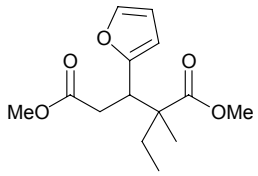
Dimethyl 3-(furan-2-yl)-2,2-dimethylpentanedioate (2q)



Following the procedure for the preparation of **2a,** the reaction of **1a** (261 mg, 1.5 mmol) with methyl 3-(furan-2-yl)acrylate (152 mg, 1.0 mmol) gave the desired product **2q** (200 mg, 79%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (3H, s), 1.18 (3H, s), 2.54 (1H, dd, *J* = 3.8, 15.5 Hz), 2.80 (1H, dd, *J* =11.0, 15.5 Hz), 3.58 (3H, s), 3.65-3.73 (1H, m), 3.68 (3H, s), 6.09 (1H, d, *J* = 3.1 Hz), 6.28 (1H, dd, *J* =2.4, 3.4 Hz), 7.29-7.33 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 24.0, 34.2, 42.5, 45.8, 51.6, 51.9, 107.7, 110.0, 141.5, 153.7, 172.2, 177.1; IR (neat) 2984, 2845, 1736, 1504, 1458, 1390, 1300, 1145, 912, 816, 739 cm^{-1}.

Dimethyl 2-ethyl-3-(furan-2-yl)-2-methylpentanedioate (2r)

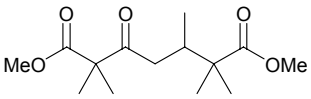


Following the procedure for the preparation of **2a,** the reaction of **1b** (283 mg, 1.5 mmol) with methyl 3-(furan-2-yl)acrylate (152 mg, 1.0 mmol) gave the desired product **2r** (217 mg, 81%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (3H x 1/2, t, *J* = 7.6 Hz), 0.81 (3H x 1/2, t, *J* = 7.6 Hz), 1.05 (3H x 1/2, s), 1.09 (3H x 1/2, s), 1.21 (1H x 1/2, dq, *J* =7.2, 9.8 Hz), 1.43 (1H x 1/2, dq, *J* =7.2, 9.8 Hz),1.65 (1H x 1/2, dq, *J* =7.2, 10.2 Hz), 1.78 (1H x 1/2, dq, *J* =7.2, 9.8 Hz), 2.42 (1H x 1/2, dd, *J* =3.8, 15.8 Hz), 2.62 (1H x 1/2, dd, *J* =4.5, 15.8 Hz), 2.73 (1H x 1/2, dd, *J* =10.7, 15.8 Hz), 2.80 (1H x 1/2, dd, *J* =11.7, 15.8 Hz), 3.53 (3H x 1/2, s), 3.55 (3H x 1/2, s), 3.61 (3H x 1/2, s), 3.63-3.73 (1H, m), 3.67 (3H x 1/2, s), 6.01 (1H x 1/2, d *J* = 3.1 Hz), 6.08 (1H x 1/2, d *J* = 3.1 Hz), 6.22 (1H x 1/2, dd *J* = 1.72, 3.1 Hz), 6.25 (1H x 1/2, dd *J* = 1.72, 3.1 Hz), 7.23-7.30 (1H, m) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.9, 9.2, 16.8, 17.3, 29.6, 31.4, 33.1, 34.9, 42.0, 42.7, 51.5, 51.6, 51.7, 107.2, 107.7, 107.9, 109.9, 141.4, 141.4, 153.6, 154.1, 172.1, 172.4, 175.8, 176.2; IR (neat) 2970, 2883, 1736, 1460, 1437, 1201, 1155, 1014, 989, 910, 735 cm^{-1}.

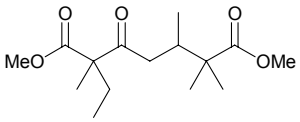
Spectra data of new compounds 3a-3l

Dimethyl 2,2,5,6,6-pentamethyl-3-oxoheptane-1,7-dioate (3a)



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (3H, d, J = 6.5 Hz), 1.11 (6H, s), 1.35 (3H, s), 1.37 (3H, s), 2.26 (1H, dd, J = 10.7, 17.5 Hz), 2.34-2.50 (2H, m), 3.66 (3H, s), 3.72 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 21.9, 22.0, 22.4, 35.4, 40.7, 45.3, 51.7, 52.4, 55.9, 174.0, 177.9, 206.9; IR (neat) 2983, 2953, 2886, 1732, 1717, 1655, 1541, 1458, 1437, 1389, 1370, 1267, 1194, 1150, 666 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{24}O_5$ (M + Na^+) 295.1521, found 295.1519.

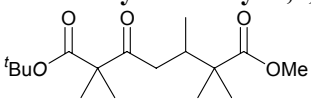
Dimethyl 2-ethyl-2,5,6,6-tetramethyl-3-oxo-1,7-heptanedioate (3b)



Following the procedure for the preparation of **3a**, the reaction between **1b** (226 mg, 1.2 mmol) and **2a** (101 mg, 0.5 mmol) gave the desired product **3b** (120 mg, 84%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77-0.92 (6H, m), 1.07-1.17 (6H, m), 1.30 (3H x 1/2, s) 1.32 (3H x 1/2, s) 1.70-2.10 (2H, m), 2.18-2.49 (3H, m), 3.65 (3H, s), 3.71 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.5, 15.0, 18.1, 18.2, 21.8, 21.9, 22.4, 27.6, 35.2, 35.3, 37.1, 41.0, 45.2, 51.5, 51.6, 52.1, 60.10, 60.14, 173.3, 173.4, 177.7, 206.5; IR (neat) 2978, 2953, 2884, 2845, 1732, 1655, 1560, 1460, 1435, 1379, 1306, 1256, 1192, 1138, 1064, 1005, 986 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{26}O_5$ (M + Na^+) 309.1678, found 309.1676.

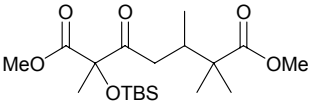
1-*tert*-Butyl-7-methyl 2,2,5,6,6-pentamethyl-3-oxo-1,7-heptanedioate (3c)



Following the procedure for the preparation of **3a**, the reaction between **1c** (260 mg, 1.2 mmol) and **2a** (101 mg, 0.5 mmol) gave the desired product **3c** (101 mg, 64%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, d, J = 6.9 Hz), 1.11 (6H, s), 1.29 (3H, s), 1.31 (3H, s), 1.44 (9H, s), 2.30 (1H, dd J = 11.0, 17.9 Hz), 2.37–2.51 (2H, m), 3.65 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 21.89, 21.97, 22.0, 22.4, 27.7, 35.2, 40.7, 45.2, 51.6, 56.4, 81.5, 172.7, 177.8, 207.0; IR, (neat) 2980, 1732, 1713, 1466, 1390, 1369, 1259, 1190, 1145, 1109, 846 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{30}O_5$ (M + Na^+) 337.1991, found 337.1989.

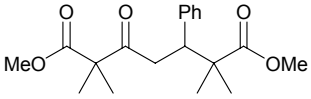
Dimethyl 2-(*tert*-butyldimethylsilyloxy)-2,5,6,6-tetramethyl-3-oxo-1,7-heptanedioate (3d)



Following the procedure for the preparation of **3a**, the reaction between **1d** (348 mg, 1.2 mmol) and **2a** (101 mg, 0.5 mmol) gave the desired product **3d** (179 mg, 92%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.060 (3H x 1/2, s), 0.063 (3H x 1/2, s) 0.09 (3H x 1/2, s) 0.10 (3H x 1/2, s), 0.73 (3H x 1/2, d J = 6.9 Hz), 0.77 (3H x 1/2, d J = 6.9 Hz), 0.88 (9H, s), 1.07 (6H, s), 1.47 (3H x 1/2, s), 1.49 (3H x 1/2, s), 2.25 – 2.64 (3H, m), 3.59 (3H x 1/2, s), 3.60 (3H x 1/2, s), 3.66 (3H x 1/2, s), 3.67 (3H x 1/2, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ -3.8, -3.7, -3.1, 14.8, 15.3, 18.2, 22.1, 22.2, 22.8, 25.6, 35.0, 37.1, 39.3, 39.6, 45.2, 45.3, 51.5, 52.4, 83.3, 83.7, 171.2, 171.3, 177.7, 207.4, 207.6; IR, (neat) 2955, 2934, 2887, 2859, 1732, 1464, 1390, 1369, 1259, 1194, 1057, 939, 881, 781, 665 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{36}O_6Si$ (M + Na^+) 411.2179, found 411.2181.

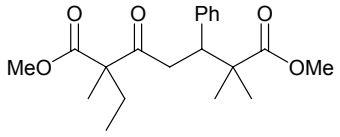
Dimethyl 2,2,6,6-tetramethyl-3-oxo-5-phenyl-1,7-heptanedioate (3e)



Following the procedure for the preparation of **3a**, the reaction between **1a** (209 mg, 1.2 mmol) and dimethyl 2,2-dimethyl-3-phenylpentane-1,5-dioate **2i** (132 mg, 0.5 mmol) gave the desired product **3e** (321 mg, 96%).

colorless crystals; mp 54–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.12 (3H, s), 1.17 (3H, s), 1.29 (3H, s), 2.72 (1H, dd, J = 3.1, 17.9 Hz), 3.12 (1H, dd, J = 10.3, 17.9 Hz), 3.53-3.65 (1H, m), 3.58 (3H, s), 3.62 (3H, s), 7.07-7.31 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 21.9, 22.0, 24.5, 39.5, 45.9, 47.4, 51.8, 52.3, 55.6, 126.8, 127.8, 129.2, 140.1, 173.8, 177.5, 205.5; IR (KBr) 2984, 2951, 1722, 1703, 1468, 1433, 1387, 1304, 1267, 1192, 1130, 1062, 831, 767, 704 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{26}O_5$ (M + Na^+) 357.1678, found 357.1674.

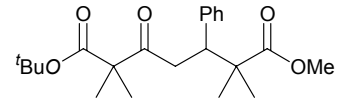
Dimethyl 2-ethyl-2,6,6-trimethyl-3-oxo-5-phenyl-1,7-heptanedioate (3f)



Following the procedure for the preparation of **3a**, the reaction between **1b** (226 mg, 1.2 mmol) and **2i** (132 mg, 0.5 mmol) gave the desired product **3f** (307 mg, 88%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.55 (3H x 1/2, t J = 7.2 Hz), 0.74 (3H x 1/2, t J = 7.2 Hz), 1.05-1.28 (9H, m), 1.58-1.92 (2H, m), 2.59-2.79 (1H, m), 3.03-3.22 (1H, m), 3.54-3.67 (1H, m), 3.57 (3H, s), 3.62 (3H, s), 7.08-7.29 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 8.6, 18.0, 22.0, 24.5, 27.4, 45.9, 47.4, 51.7, 52.2, 60.0, 126.8, 127.8, 129.3, 140.2, 172.8, 177.7, 204.9; IR (neat) 3032, 2976, 2951, 2883, 1716, 1495, 1435, 1388, 1375, 1250, 1194, 1134, 1068, 771, 706 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}O_5$ (M + Na^+) 371.1834, found 371.1832.

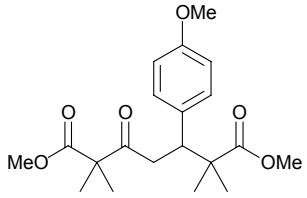
1-*tert*-Butyl-7-methyl 2,2,6,6-tetramethyl-3-oxo-5-phenyl-1,7-heptanedioate (3g)



Following the procedure for the preparation of **3a**, the reaction between **1c** (260 mg, 1.2 mmol) and **2i** (132 mg, 0.5 mmol) gave the desired product **3g** (324 mg, 86%).

colorless crystals; mp 96–97 ℃;^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (3H, s), 1.08 (3H, s), 1.12 (3H, s), 1.21 (3H, s), 1.41 (9H, s), 2.79 (1H, dd, J = 3.1, 17.9 Hz), 3.14 (1H, dd, J = 10.3, 17.9 Hz), 3.55-3.65 (1H, m), 3.62 (3H, s), 7.09-7.28 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 22.0, 24.5, 27.7, 39.6, 45.9, 47.3, 51.7, 56.1, 81.5, 126.8, 127.8, 129.2, 140.2, 172.8, 177.4, 205.9; IR (KBr) 3032, 2984, 2953, 2876, 1736, 1458, 1369, 1248, 1194, 1132, 1041, 846, 704 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{32}O_5$ (M + Na^+) 399.2147, found 399.2147.

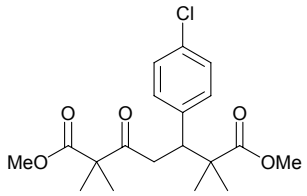
Dimethyl 3-(4-methoxyphenyl)2,2,6,6-tetramethyl-5-oxo-heptane-1,7-dioate (3h)



Following the procedure for the preparation of **3a**, the reaction between **1a** (210 mg, 1.2 mmol) and **2k** (147 mg, 0.5 mmol) gave the desired product **3h** (148 mg, 81%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (3H, s), 1.11 (3H, s), 1.17 (3H, s), 1.28 (3H, s), 2.68 (1H, dd, J = 3.1, 17.5 Hz), 3.07 (1H, dd, J = 10.3, 17.5 Hz), 3.52 (1H, dd, J = 3.1, 10.3 Hz), 3.60 (3H, s), 3.62 (3H, s), 3.76 (3H, s), 6.69-6.85 (2H, m), 6.96-7.11 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 21.9, 24.4, 39.5, 46.0, 46.6, 51.7, 52.3, 55.1, 55.6, 113.2, 130.1, 132.1, 158.3, 173.8, 177.5, 205.6; IR (neat) 2984, 2948, 1736, 1719, 1701, 1611, 1509, 1458, 1387, 1252, 1128, 1034, 666 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}O_6$ (M + Na^+) 387.1784, found 387.1786.

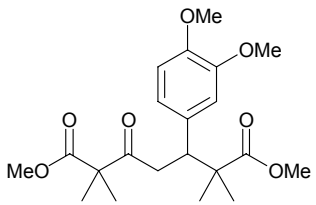
Dimethyl 3-(4-chrolophenyl)-2,2,6,6-tetramethyl-5-oxo-heptane-1,7-dioate (3i)



Following the procedure for the preparation of **3a**, the reaction between **1a** (210 mg, 1.2 mmol) and **2m** (149 mg, 0.5 mmol) gave the desired product **3i** (133 mg, 72%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.11 (3H, s), 1.19 (3H, s), 1.30 (3H, s), 2.73 (1H, dd, J = 3.1, 17.9 Hz), 3.07 (1H, dd, J = 10.7, 17.9 Hz), 3.55 (1H, dd, J = 2.8, 10.7 Hz), 3.61 (3H, s), 3.63 (3H, s), 7.01-7.13 (2H, m), 7.17-7.31 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 22.0, 22.1, 24.4, 39.4, 45.8, 46.9, 51.8, 52.4, 55.6, 128.0, 130.5, 132.6, 138.8, 173.8, 177.2, 205.4; IR (neat) 2982, 2951, 1717, 1493, 1470, 1435, 1389, 1262, 1194, 1148, 1094, 1071, 1015, 839 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{25}ClO_5$ (M + Na^+; ^{35}Cl) 391.1288, found 391.1286.

Dimethyl 2,2,6,6-tetramethyl-3-oxo-5-(3,4-dimethoxyphenyl)-1,7-heptanedioate (3j)

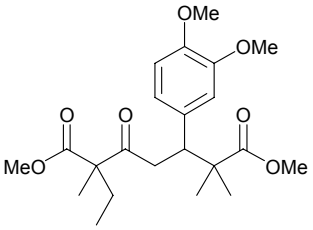


Following the procedure for the preparation of **3a**, the reaction between **1a** (209 mg, 1.2 mmol) dimethyl 3-(3,4-dimethoxyphenyl)-2,2-dimethylpentane-1,7-dioate **2o** (162 mg, 0.5 mmol) gave the desired product **3j** (387 mg, 98%).

colorless crystals; mp 100–101℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (3H, s), 1.11 (3H, s), 1.17 (3H, s), 1.28 (3H, s), 2.68 (1H, dd, J = 2.9, 17.7 Hz), 3.08 (1H, dd, J = 10.5, 17.7 Hz), 3.50 (1H, dd, J = 2.9, 10.5 Hz), 3.59 (3H, s), 3.61 (3H, s), 3.82 (3H, s), 3.84 (3H, s), 6.60-6.77 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 21.9, 22.2, 24.5, 39.6, 46.0, 47.1, 51.7, 52.3, 55.7, 55.8, 110.4, 112.8, 121.2, 132.7, 147.8, 148.1, 173.8, 177.5,

205.6; IR (KBr) 3032, 2984, 2843, 1713, 1518, 1458, 1304, 1253, 1151, 1010, 912, 814, 704 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{30}O_7$ (M + Na^+) 417.1889, found 417.1886.

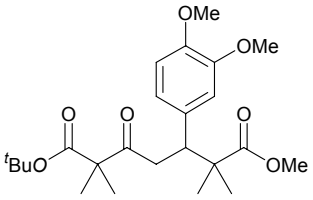
Dimethyl 2-ethyl-2,6,6-trimethyl-3-oxo-5-(3,4-dimethoxyphenyl)-1,7-heptanedioate (3k)



Following the procedure for the preparation of **3a**, the reaction between **1b** (226 mg, 1.2 mmol) and **2o** (162 mg, 0.5 mmol) gave the desired product **3k** (343 mg, 84%).

colorless crystals; mp 72–74℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.55 (3H x 1/2, t *J* = 7.6 Hz), 0.73 (3H x 1/2, t *J* = 7.6 Hz), 0.95-1.32 (9H, m), 1.54-1.95 (2H, m), 2.54-2.75 (1H, m), 2.95-3.19 (1H, m), 3.44-3.68 (1H, m), 3.60 (3H, s), 3.62 (3H, s), 3.82 (3H, s), 3.84 (3H, s), 6.56-6.79 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.2, 8.6, 18.0, 22.1, 24.5, 27.5, 27.8, 46.0, 47.0, 47.1, 51.7, 52.1, 55.7, 55.8, 110.5, 112.9, 121.2, 132.7, 147.8, 148.1, 177.5, 205.4, 205.4; IR (KBr) 2984, 2843, 1730, 1711, 1587, 1425, 1309, 1238, 1153, 1024, 900, 814, 767 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{32}O_7$ (M + Na^+) 431.2046, found 431.2042.

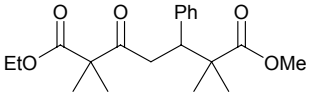
1-*tert*-Butyl-7-methyl 2,2,6,6-tetramethyl-3-oxo-5-(3,4-dimethoxyphenyl)-1,7-heptanedioate (3l)



Following the procedure for the preparation of **3a**, the reaction between **1c** (260 mg, 1.2 mmol) and **2o** (162 mg, 0.5 mmol) gave the desired product **3l** (349 mg, 80%).

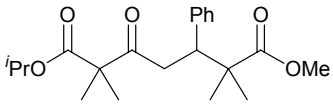
yellow crystals; mp 79–80 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (3H, s), 1.07 (3H, s), 1.10 (3H, s), 1.20 (3H, s),1.40 (9H, s), 2.74 (1H, dd, *J* = 3.1, 17.9 Hz), 3.09 (1H, dd, *J* = 10.3, 17.9 Hz), 3.50 (1H, dd, *J* = 3.1, 10.5 Hz), 3.61 (3H, s), 3.80 (3H, s), 3.82 (3H, s), 6.62-6.74 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 22.0, 22.2, 24.5, 27.7, 39.7, 46.0, 46.9, 51.7, 55.7, 55.8, 56.1, 81.4, 110.5, 112.8, 121.1, 132.8, 147.7, 148.1, 172.7, 177.4, 206.0; IR (KBr) 2982, 1713, 1605, 1514, 1423, 1369, 1244, 1134, 1020, 935, 810, 744 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{36}O_7$ (M + Na^+) 459.2359, found 459.2355.

1-Ethyl 7-methyl 2,2,6,6-tetramethyl-3-oxo-5-phenylheptanedioate (3m)



colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (3H, s), 1.15 (3H, s), 1.17 (3H, s), 1.19 (3H, t, *J* = 7.2 Hz), 1.30 (3H, s), 2.78 (1H, dd, *J* = 3.1, 17.9 Hz), 3.16 (1H, dd, *J* = 10.3, 17.9 Hz), 3.61 (1H, dd *J* = 3.1, 10.3 Hz), 3.65 (3H, s), 4.03 (1H, dq, *J* = 6.9, 10.7 Hz), 4.17 (1H, dq, *J* = 7.2, 10.7 Hz),7.10-7.32 (5H, m) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 21.6, 21.9, 22.0, 24.4, 39.4, 45.9, 47.3, 51.7, 55.6, 61.2, 126.7, 127.8, 129.2, 140.1, 173.3, 177.4, 205.6; IR (neat) 2984, 2951, 1717, 1468, 1389, 1262, 1179, 1146, 1067, 706 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}O_5$ (M + Na^+) 371.1834, found 371.1831.

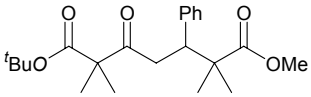
1-Isopropyl 7-methyl 2,2,6,6-tetramethyl-3-oxo-5-phenylheptanedioate (3n)



Following the procedure for the preparation of **3m**, the reaction using **1a** (105 mg, 0.6 mmol), methyl cinnamate (81 mg, 0.5 mmol), and (1-isopropoxy-2-methylprop-1-enyloxy)trimethylsilane (**1f**; 202 mg, 1.0 mmol) gave the desired product **3n** (108 mg, 60%).

colorless crystals; mp 64 – 65 ℃;^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (3H, s), 1.53 (3H, s), 1.17 (3H, s), 1.22 (3H, d, *J* = 6.2 Hz), 1.26 (3H, d, *J* = 6.2 Hz), 1.30 (3H, s), 2.81 (1H, dd, *J* = 2.8, 17.9 Hz), 3.20 (1H, dd, *J* = 10.7, 17.9 Hz), 3.63 (1H, dd, *J* = 2.8, 10.7 Hz), 3.67 (3H, s), 5.06 (1H, sept, *J* = 6.2 Hz), 7.12-7.34 (5H, m) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.35, 21.38, 21.5, 21.9, 24.4, 39.4, 45.8, 47.2, 51.7, 55.5, 68.7, 126.7, 127.8, 129.1, 140.1, 173.0, 177.3, 205.7; IR (KBr) 2982, 1722, 1705, 1460, 1304, 1246, 1109, 1042, 835, 704 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{30}O_5$ (M + Na^+) 385.1991, found 385.1991.

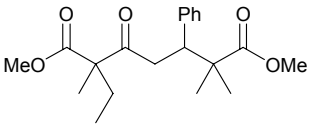
1-*tert*-Butyl-7-methyl 2,2,6,6-tetramethyl-3-oxo-5-phenyl-1,7-heptanedioate (3o)



Following the procedure for the preparation of **3m**, the reaction using **1a** (105 mg, 0.6 mmol), methyl cinnamate (81 mg, 0.5 mmol), and (1-*tert*-butoxy-2-methylprop-1-enyloxy)trimethylsilane (**1g**; 216 mg, 1.0 mmol) gave the desired product **3o** (90 mg, 48%).

colorless crystals; mp 96–97 ℃;^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (3H, s), 1.08 (3H, s), 1.12 (3H, s), 1.21 (3H, s), 1.41 (9H, s), 2.79 (1H, dd, *J* = 3.1, 17.9 Hz), 3.14 (1H, dd, *J* = 10.3, 17.9 Hz), 3.55-3.65 (1H, m) 3.62 (3H, s), 7.09-7.28 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 22.0, 24.5, 27.7, 39.6, 45.9, 47.3, 51.7, 56.1, 81.5, 126.8, 127.8, 129.2, 140.2, 172.8, 177.4, 205.9; IR (KBr) 3032, 2984, 2953, 2876, 1736, 1458, 1369, 1248, 1194, 1132, 1041, 846, 704 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{32}O_5$ (M + Na^+) 399.2147, found 399.2147.

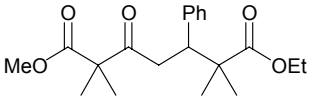
Dimethyl 2-ethyl-2,6,6-trimethyl-3-oxo-5-phenyl-1,7-heptanedioate (3p)



Following the procedure for the preparation of **3m**, the reaction using **1a** (174mg, 1.0 mmol), methyl cinnamate (81 mg, 0.5 mmol), and **1b** (188 mg, 1.0 mmol) gave the desired product **3p** (113 mg, 65%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.55 (3H x 1/2, t *J* = 7.2 Hz), 0.74 (3H x 1/2, t *J* = 7.2 Hz), 1.05-1.28 (9H, m), 1.58-1.92 (2H, m), 2.59-2.79 (1H, m), 3.03-3.22 (1H, m), 3.54-3.67 (1H, m), 3.57 (3H, s), 3.62 (3H, s), 7.08-7.29 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 8.6, 18.0, 22.0, 24.5, 27.4, 45.9, 47.4, 51.7, 52.2, 60.0, 126.8, 127.8, 129.3, 140.2, 172.8, 177.7, 204.9; IR (neat) 3032, 2976, 2951, 2883, 1716, 1495, 1435, 1388, 1375, 1250, 1194, 1134, 1068, 771, 706 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}O_5$ (M + Na^+) 371.1834, found 371.1833.

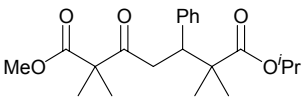
1-Ethyl 7-methyl 2,2,6,6-tetramethyl-5-oxo-3-phenylheptanedioate (3q)



Following the procedure for the preparation of **3m**, the reaction using **1a** (105 mg, 0.6 mmol), methyl cinnamate (81 mg, 0.5 mmol), and (1-ethoxy-2-methylprop-1-enyl)trimethylsilane (**1e**; 188 mg, 1.0 mmol) gave the desired product **3q** (130 mg, 70%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.11 (3H, s), 1.16 (3H,s), 1.22 (3H, t, *J* = 7.2 Hz), 1.28 (3H, s), 2.72 (1H, dd, *J* = 3.1, 17.9 Hz), 3.13 (1H, dd, *J* = 10.7, 17.9 Hz), 3.58 (3H, s), 3.62 (1H, dd, *J* =3.1, 10.7 Hz), 4.03-4.16 (2H, m) 7.08-7.30 (5H, m) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.6, 21.9, 24.6, 39.6, 45.8, 47.4, 52.3, 55.6, 60.5, 126.7, 127.8, 129.2, 140.1, 173.8, 177.0, 205.5; IR (neat) 3063, 2980, 2878, 1716, 1456, 1300, 1261, 1145, 1026, 854, 706 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}O_5$ (M + Na^+) 371.1834, found 371.1836.

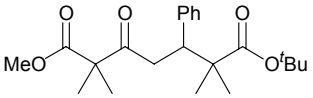
1-Isopropyl 7-methyl 2,2,6,6-tetramethyl-5-oxo-3-phenylheptanedioate (3r)



Following the procedure for the preparation of **3m**, the reaction using **1f** (121 mg, 0.6 mmol), methyl cinnamate (81 mg, 0.5 mmol), and **1a** (174mg, 1.0 mmol) gave the desired product **3r** (125 mg, 69%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (3H, s), 1.10 (3H, s), 1.15 (3H,s), 1.19 (3H, d, *J* = 6.2 Hz), 1.21 (3H, d, *J* = 6.2 Hz), 1.28 (3H, s), 2.67 (1H, dd, *J* = 2.8, 17.9 Hz), 3.15 (1H, dd, *J* = 10.7, 17.9 Hz), 3.58 (3H, s), 3.63 (1H, dd, *J* = 2.8, 10.7 Hz), 4.92-5.00 (1H, m), 7.11-7.29 (5H, m) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 21.7, 21.9, 24.8, 39.6, 45.7, 47.2, 52.3, 55.6, 67.8, 126.7, 127.8, 129.4, 140.1, 173.9, 176.5, 205.4; IR (neat) 3033, 2980, 2878, 1716, 1655, 1541, 1437, 1374, 1107, 706 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{30}O_5$ (M + Na^+) 385.1991, found 385.1995.

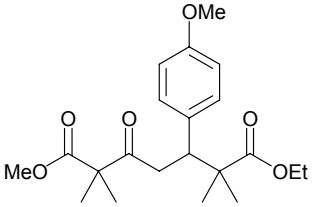
1-*tert*-Butyl 7-methyl 2,2,6,6-tetramethyl-5-oxo-3-phenylheptanedioate (3s)



Following the procedure for the preparation of **3m**, the reaction using **1c** (130 mg, 0.6 mmol), methyl cinnamate (81 mg, 0.5 mmol), and **1a** (174mg, 1.0 mmol) gave the desired product **3s** (110 mg, 59%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (3H, s), 1.06 (3H, s), 1.14 (3H,s), 1.27 (3H, s), 1.42 (9H, s), 2.66 (1H, dd, *J* = 2.4, 17.5 Hz), 3.15 (1H, dd, *J* = 11.0, 17.5 Hz), 3.57 (3H, s), 3.62 (1H, dd, *J* = 2.4, 11.0 Hz), 7.07-7.33 (5H, m) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 21.7, 21.9, 25.0, 27.9, 39.8, 46.2, 47.2, 52.3, 55.6, 80.4, 126.7, 127.7, 129.5, 140.2, 173.8, 176.3, 205.4; IR (neat) 3032, 2937, 2878, 1716, 1496, 1369, 1258, 1148, 1041, 850, 704 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{32}O_5$ (M + Na^+) 399.2147, found 399.2145.

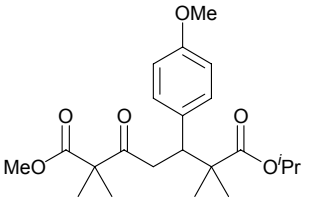
1-Ethyl 7-methyl 3-(4-methoxyphenyl)-2,2,6,6-tetramethyl-5-oxoheptanedioate (3t)



Following the procedure for the preparation of **3m**, the reaction using (1-ethoxy-2-methylprop-1-enyl)trimethylsilane (113 mg, 0.6 mmol) and Methyl 3-(4-methoxyphenyl)acrylate (96 mg, 0.5 mmol) and **1a** (174 mg, 1.0 mmol) gave the desired product **3t** (133 mg, 70%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (3H, s), 1.10 (3H, s) 1.16 (3H, s), 1.23 (3H, t, *J* = 6.9 Hz), 1.28 (3H, s), 2.67 (1H, dd, *J* = 2.8, 17.9 Hz), 3.08 (1H, dd, *J* = 10.7, 17.9 Hz), 3.54 (1H, dd, *J* = 2.8, 10.7 Hz), 3.60 (3H, s), 3.76 (3H, s), 4.02-4.14 (2H, m), 6.78 (2H, d *J* = 8.6 Hz), 7.05 (2H, d *J* = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.6, 21.8, 21.9, 24.4, 39.5, 45.8, 46.5, 52.2, 55.0, 55.5, 60.4, 113.1, 130.1, 132.0, 158.2, 173.8, 177.0, 205.5; IR (neat) 2982, 2840, 1717, 1613, 1466, 1368, 1293, 1252, 1148, 841 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{30}O_6$ (M + Na^+) 401.1940, found 401.1942.

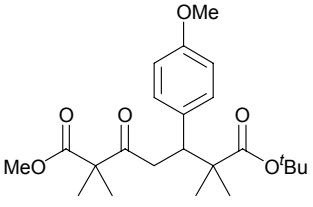
1-Isopropyl 7-methyl 3-(4-methoxyphenyl)-2,2,6,6-tetramethyl-5-oxoheptanedioate (3u)



Following the procedure for the preparation of **3m**, the reaction using **1f** (121 mg, 0.6 mmol), and methyl 3-(4-methoxyphenyl)acrylate (96 mg, 0.5 mmol), and **1a** (174 mg, 1.0 mmol) gave the desired product **3u** (102 mg, 52%).

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (3H, s), 1.06 (3H, s), 1.13 (3H, s), 1.17 (3H, d, *J* = 6.2 Hz), 1.20 (3H, d, *J* = 6.2 Hz), 1.25 (3H, s), 2.62 (1H, dd, *J* = 2.4, 17.9 Hz), 3.08 (1H, dd, *J* = 11.0, 17.9 Hz), 3.52 (1H, dd, *J* = 2.4, 11.0 Hz), 3.58 (3H, s), 3.74 (3H, s), 4.94 (1H, sept, *J* = 6.2 Hz), 6.75 (2H, d *J* = 2.1 Hz), 7.04 (2H, d *J* = 2.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7 21.9, 24.7, 39.6, 45.7, 46.4, 52.3, 55.1, 55.6, 67.7, 113.1, 130.2, 132.0, 158.3, 173.8, 176.6, 205.4; IR (neat) 2980, 1717, 1613, 1458, 1374, 1252, 1148, 1107, 1038, 833 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{32}O_6$ (M + Na^+) 415.2097, found 415.2095.

-*tert*-Butyl 7-methyl 3-(4-methoxyphenyl)-2,2,6,6-tetramethyl-5-oxoheptanedioate (3v)

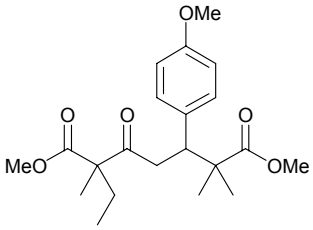


Following the procedure for the preparation of **3m**, the reaction using **1g** (130 mg, 0.6 mmol), methyl 3-(4-methoxyphenyl)acrylate (96 mg, 0.5 mmol), and **1a** (174mg, 1.0 mmol) gave the desired product **3v** (105 mg, 52%).

colorless crystals; mp 68 – 70 ℃;^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (3H, s), 1.04 (3H, s), 1.15 (3H, s), 1.27 (3H, s), 1.42 (9H, s), 2.62 (1H, dd, *J* = 2.4, 17.9 Hz), 3.11 (1H, dd, *J* = 11.4, 17.9 Hz), 3.53 (1H, dd, *J* = 2.4, 11.4 Hz), 3.60 (3H,

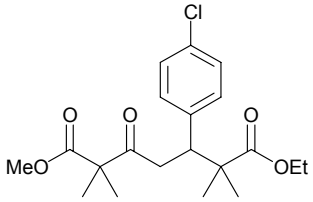
s), 3.76 (3H, s), 6.77 (2H, d J = 8.6 Hz), 7.09 (2H, d J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.6, 21.9, 24.9, 27.9, 39.8, 46.2, 46.3, 52.3, 55.1, 55.6, 80.3, 113.1, 130.3, 132.1, 158.2, 173.9, 176.4, 205.5; IR (KBr) 1900, 1748, 1728, 1713, 1582, 1470, 1437, 1306, 1250, 1167 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{34}O_6$ (M + Na^+) 429.2253, found 429.225 3.

Dimethyl 2-ethyl-5-(4-methoxyphenyl)-2,2,6-trimethyl-3-oxoheptanedioate (3w)



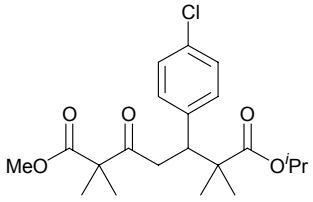
Following the procedure for the preparation of **3m**, the reaction using **1a** (105 mg, 0.6 mmol), methyl 3-(4-methoxyphenyl)acrylate (96 mg, 0.5 mmol), and **1b** (188 mg, 1.0 mmol) gave the desired product **3w** (101 mg, 53%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 0.57 (3H x 1/2, t J = 7.6 Hz), 0.74 (3H x 1/2, t J = 7.6 Hz), 1.02-1.32 (9H, m), 1.51-1.91 (2H, m), 2.58-2.72 (1H, m), 3.00-3.14 (1H, m), 3.43-3.57 (1H, m), 3.60 (3H x 1/2, s), 3.61 (3H x 1/2, s), 3.62 (3H x 1/2, s), 3.63 (3H x 1/2, s), 3.76 (3H, s), 6.78 (2H, d, J = 8.6 Hz), 7.04 (2H, d, J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 8.5, 17.9, 21.6, 21.9, 24.3, 27.4, 27.7, 39.5, 39.8, 39.9, 46.0, 46.4, 46.5, 51.6, 52.1, 52.3, 55.0, 59.9, 60.0, 113.1, 130.1, 132.0, 132.1, 158.3, 173.22, 173.26, 177.5, 205.3; IR (neat) 2977, 2840, 1717, 1613, 1514, 1460, 1304, 1252, 1130, 837 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{30}O_6$ (M + Na^+) 401.1940, found 401.1939.

1-Ethyl 7-methyl 3-(4-chlorophenyl)-2,2,6,6-tetramethyl-5-oxoheptanedioate (3x)



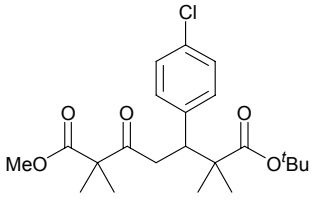
Following the procedure for the preparation of **3m**, the reaction using **1e** (113 mg, 0.6 mmol), methyl 3-(4-chlorophenyl)acrylate (98 mg, 0.5 mmol), and **1a** (174 mg, 1.0 mmol) gave the desired product **3x** (131 mg, 69%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.10 (3H, s), 1.18 (3H, s), 1.22 (3H, t J = 6.9 Hz), 1.29 (3H, s), 2.72 (1H, dd, J = 2.8, 17.9 Hz),3.08 (1H, dd, J = 11.0, 17.9 Hz), 3.57 (1H, dd, J = 2.8, 11.0 Hz), 3.61 (3H, s), 4.01-4.18 (2H, m), 7.08 (2H, d, J = 8.6 Hz), 7.22 (2H, d, J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.7, 21.9, 24.5, 39.4, 45.6, 46.8, 52.3, 55.5, 60.6, 127.9, 130.5, 132.5, 138.7, 173.7, 176.6, 205.3; IR (neat) 2982, 1717, 1541, 1474, 1387, 1262, 1148, 1071, 1015, 824 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{27}ClO_5$ (M + Na^+; ^{35}Cl) 405.1445, found 405.1443.

1-Isopropyl 7-methyl 3-(4-chlorophenyl)-2,2,6,6-tetramethyl-5-oxoheptanedioate (3y)



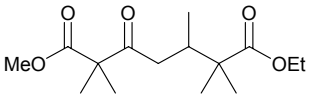
Following the procedure for the preparation of **3m**, the reaction using **1f** (121 mg, 0.6 mmol), methyl 3-(4-chlorophenyl)acrylate (98 mg, 0.5 mmol), and **1a** (174mg, 1.0 mmol) gave the desired product **3y** (105 mg, 53%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ1.05 (3H, s), 1.08 (3H, s), 1.17 (3H, s), 1.18 (3H, d, J = 6.2 Hz), 1.22 (3H, d, J = 6.2 Hz), 1.29 (3H, s), 2.68 (1H, dd, J = 2.4, 17.9 Hz), 3.10 (1H, dd, J =11.0, 17.9 Hz), 3.57 (1H, dd, J = 2.4, 11.0 Hz), 3.60 (3H, s), 4.95 (1H, sept, J = 6.2 Hz), 7.09 (2H, d, J = 8.6 Hz), 7.22 (2H, d, J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 21.7, 21.8, 21.9, 24.6, 39.5, 45.5, 46.6, 52.3, 55.5, 68.0, 127.9, 130.6, 132.5, 138.7, 173.7, 176.2, 205.2; IR (neat) 2982, 2878, 1717, 1541, 1472, 1300, 1262, 1107, 1015, 831 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{29}ClO_5$ (M + Na^+; ^{35}Cl) 419.1601, found 419.1604.

1-*tert*-Butyl 7-methyl 3-(4-chlorophenyl)-2,2,6,6-tetramethyl-5-oxoheptanedioate (3z)



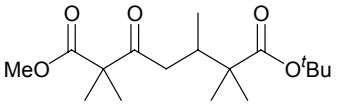
Following the procedure for the preparation of **3m**, the reaction using **1g** (130 mg, 0.6 mmol), methyl 3-(4-chlorophenyl)acrylate (98 mg, 0.5 mmol), and **1a** (174 mg, 1.0 mmol) gave the desired product **3z** (113 mg, 55%).
yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (3H, s), 1.04 (3H, s), 1.17 (3H, s), 1.29 (3H, s), 1.42 (9H, s), 2.66 (1H, dd, J = 2.4, 17.9 Hz), 3.10 (1H, dd, J = 8.3, 17.9 Hz), 3.56 (1H, dd, J = 2.4, 8.3 Hz), 3.60 (3H, s), 7.10 (2H, d, J = 8.6 Hz), 7.22 (2H, d, J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 21.9, 24.8, 27.8, 39.5, 46.0, 46.5, 52.3, 55.5, 80.5, 127.8, 130.7, 132.4, 138.8, 173.7, 175.9, 205.2; IR (neat) 2979, 1717, 1655, 1541, 1458, 1389, 1260, 1148, 1015, 824 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{31}Cl_1O_5$ (M + Na^+; ^{35}Cl) 433.1758, found 433.1760.

1-Ethyl 7-methyl 2,2,3,6,6-pentamethyl-5-oxoheptanedioate (3α)



Following the procedure for the preparation of **3m**, the reaction using **1e** (113 mg, 0.6 mmol), methyl but-2-enoate (50 mg, 0.5 mmol), and **1a** (174 mg, 1.0 mmol) gave the desired product **3α** (66 mg, 46%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (3H, d *J* = 6.5 Hz), 1.100 (3H, s), 1.103 (3H, s), 1.23 (3H, t, *J* = 6.9 Hz), 13.5 (3H, s), 1.37 (3H, s), 2.27 (1H, dd, *J* = 10.7, 17.5 Hz), 2.37-2.51 (2H, m), 3.71 (3H, s), 4.11 (2H, q *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 15.0, 21.9, 22.0, 22.4, 35.3, 40.7, 45.1, 52.3, 55.8, 60.3, 174.0, 177.3, 206.9; IR (neat) 3868, 3739, 3617, 3571, 2942, 1719, 1649, 1474, 1389, 1150 cm^{-1};

1-*tert*-Butyl 7-methyl 2,2,3,6,6-pentamethyl-5-oxoheptanedioate (3β)



Following the procedure for the preparation of **3m**, the reaction using **1c** (130 mg, 0.6 mmol), methyl but-2-enoate (50 mg, 0.5 mmol), and **1a** (174mg, 1.0 mmol) gave the desired product **3β** (55 mg, 35%).
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, d, *J* = 6.5 Hz), 1.05 (3H, s), 1.06 (3H, s), 1.35 (3H, s), 1.37 (3H, s), 1.43 (9H, s), 2.29 (1H, dd, *J* = 11.0, 17.5 Hz), 2.36-2.48 (2H, m), 3.71 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 21.8, 21.9, 22.0, 22.6, 27.9, 35.2, 40.8, 45.5, 52.3, 55.8, 80.0, 174.0, 176.6, 206.9; IR (neat) 2940, 2880, 1717, 1412, 1368, 1269, 1142, 1034, 911, 772 cm^{-1}.