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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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 F254 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)**

![Structure of 2a](structure.png)

colorless oil; δ 3 H, 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); δ 3 (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, 1262, 1194, 1165, 1012 cm$^{-1}$.


**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 (2b) (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; δ 3 H, d, J = 7.2 Hz), 0.88 (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); δ 3 (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; δ 3 H, t, J = 6.9 Hz), 1.00 (3H x 1/2, s), 1.04 (3H x 1/2, s), 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); δ 3 (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, 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, 77%). colorless oil; δ 3 H, t, J = 6.9 Hz), 1.00 (3H x 1/2, s), 1.04 (3H x 1/2, s), 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); δ 3 (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, 1437, 1372, 1231, 1165, 1021, 774 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; δ 3 H, t, J = 6.9, 10.3, 16.9 Hz); δ 3 (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-methylpentanediode (2f)

Following the procedure for the preparation of 2a, the reaction of 1b (283 mg, 1.5 mmol) with methyl trideca-2,12-dioate (224 mg, 1.0 mmol) gave the desired product 2f (234 mg, 69%).

colorless oil; ¹H NMR (300 MHz, CDCl₃) 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), 3.63 (3H x 1/2, s), 4.83-5.00 (2H, m), 5.77 (1H, ddt, J = 6.5, 10.0, 13.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 9.0, 9.1, 15.8, 17.0, 28.1, 28.8, 29.1, 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, 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; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃): 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; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃): δ -0.5, 21.6, 23.0, 24.3, 31.5, 32.8, 35.7, 42.0, 46.0, 51.7, 51.8, 62.3, 174.0, 177.9; IR (neat) 3856, 2953, 2867, 1736, 1437, 1260, 1200, 1163, 1136, 1078, 1034, 990 cm⁻¹.

Dimethyl 2,2-dimethyl-3-(phenyl)pentane-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 oC; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃): 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-(phenyl)pentane-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; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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-enolate (192 mg, 1.0 mmol) gave the desired product 2k (283 mg, 96%).

Yellow pale crystals; mp 52 - 54 °C; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) δ 21.5, 24.1, 35.8, 46.1, 48.1, 51.5, 51.8, 55.1, 113.5, 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-enolate (192 mg, 1.0 mmol) gave the desired product 2l (250 mg, 81%).

Diastereomixture (ca. 1 : 1); colorless oil; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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-enolate (196 mg, 1.0 mmol) gave the desired product 2m (257 mg, 86%).

Colorless oil; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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-enolate (196 mg, 1.0 mmol) gave the desired product 2n (260 mg, 83%).

Diastereomixture (ca. 1 : 1); colorless oil; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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-(4-methoxyphenyl)-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-(4-methoxyphenyl)prop-2-enolate (222 mg, 1.0 mmol) gave the desired product 2o (283 mg, 96%).

Yellow pale crystals; mp 52 - 54 °C; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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), 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$_3$) $\delta$ 9.1, 9.4, 16.6, 17.1, 30.1, 31.5, 35.0, 48.7, 50.6, 51.4, 51.5, 51.6, 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$_3$) $\delta$ 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), 3.68 (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$^{-1}$. 

Supplementary Material (ESI) for Chemical Communications
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Spectra data of new compounds 3a-3l

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

Dimethyl 2,2,5,6,6-pentamethyl-3-oxoheptane-1,7-dioate (3a); colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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); \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 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, 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%).

Dimethyl 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%).

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%).

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%).
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 2f (132 mg, 0.5 mmol) gave the desired product 3f (307 mg, 88%).

colorless oil; 1H NMR (300 MHz, CDCl₃) 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); 13C NMR (75 MHz, CDCl₃) 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 C₂₀H₂₅ClO₅ (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 °C; 1H NMR (300 MHz, CDCl₃) 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); 13C NMR (75 MHz, CDCl₃) 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, 2976, 2953, 2876, 1736, 1458, 1369, 1248, 1194, 1132, 1041, 846, 704 cm⁻¹; HRMS (ESI) calcd for C₂₂H₃₂O₅ (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; 1H NMR (300 MHz, CDCl₃) 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); 13C NMR (75 MHz, CDCl₃) 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 C₂₀H₂₅O₅ (M + Na⁺) 387.1784, found 387.1786.

Dimethyl 3-(4-chlorophenyl)-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; 1H NMR (300 MHz, CDCl₃) 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); 13C NMR (75 MHz, CDCl₃) 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 C₁₀H₁₂ClO₅ (M + Na⁺) 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) and 2o (162 mg, 0.5 mmol) gave the desired product 3j (387 mg, 98%).

colorless crystals; mp 100–101°C; 1H NMR (300 MHz, CDCl₃) 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); 13C NMR (75 MHz, CDCl₃) 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,
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°C; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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, 1369, 1244, 1134, 1020, 935, 810, 744 cm⁻¹; HRMS (ESI) calcd for C₂₁H₃₀O₇ (M + Na⁺) 417.1889, found 417.1886.

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 °C; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₂₄H₃₆O₇ (M + Na⁺) 459.2359, found 459.2355.
1-Ethyl 7-methyl 2,2,6,6-tetramethyl-3-oxo-5-phenylheptanedioate (3m)

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%).

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%).

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, 0.5 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%).

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 (174 mg, 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%).
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 IF (121 mg, 0.6 mmol), methyl cinnamate (81 mg, 0.5 mmol), and 1a (174 mg, 1.0 mmol) gave the desired product 3r (125 mg, 69%).

Colorless oil; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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) 3032, 2937, 1740, 1738, 1763, 1267, 1277, 1295, 1402, 1738, 1763, 2054; HRMS (ESI) calcd for C27H38O5 (M + Na+) 435.2357, found 435.2355.

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 (174 mg, 1.0 mmol) gave the desired product 3s (110 mg, 59%).

Colorless oil; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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; HRMS (ESI) calcd for C27H38O5 (M + Na+) 437.2254, found 437.2251.

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; 1H NMR (300 MHz, CDCl3) δ 1.10 (3H, s), 1.16 (3H, s), 1.23 (3H, s, 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); 13C NMR (75 MHz, CDCl3) 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, 205.4; IR (neat) 2982, 2840, 1717, 1613, 1466, 1368, 1293, 1252, 1148, 841 cm⁻¹; HRMS (ESI) calcd for C22H26O6 (M + Na+) 417.2142, found 417.2143.

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 IF (121 mg, 0.6 mmol), 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; 1H NMR (300 MHz, CDCl3) 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, 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); 13C NMR (75 MHz, CDCl3) 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 C25H30O6 (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 (174 mg, 1.0 mmol) gave the desired product 3v (105 mg, 52%).

Colorless crystals; mp 68 – 70 °C; 1H NMR (300 MHz, CDCl3) 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\(_3\)) \(\delta\) 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 429.2253.

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%).

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%).

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 (174 mg, 1.0 mmol) gave the desired product 3y (105 mg, 53%).

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%).
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; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (174 mg, 1.0 mmol) gave the desired product 3β (55 mg, 35%).

colorless oil; 1H NMR (300 MHz, CDCl3) δ 0.88 (3H, d, J = 6.5 Hz), 1.05 (3H, s), 1.06 (3H, s), 1.35 (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); 13C NMR (75 MHz, CDCl3) 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.