**Studies on K₂CO₃-Catalyzed 1, 4-Addition of 1, 2-Allenic Ketones with Diethyl Malonate:
Controlled Selective Synthesis of β , γ -Unsaturated Enones and α -Pyrones**

Shengming Ma* , Shichao Yu, and Shaohu Yin

*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. China E-mail:
masm@pub.sioc.ac.cn Fax: (+86) 21-64167510*

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Synthesis of 2-butyl-1-phenylnona-2, 3-dien-1-one (1n): The reaction of oct-1-en-3-yne (2.16 g, 22 mmol) with *n*-BuLi (2.5 M in cyclohexane, 8 mL, 20 mmol) and N, N-dimethyl benzamide (4.48 g, 30 mmol) afforded 3.89 g (72%) of **1n**: liquid; IR(neat) 3058, 1943, 1651, 1598, 1467, 1274, 1072, 941, 698 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.69 (d, $J = 5.4$ Hz, 2 H), 7.39-7.45 (m, 1 H), 7.29-7.35 (m, 2 H), 5.30-5.39 (m, 1 H), 2.35-2.42 (m, 2 H), 1.95-2.12 (m, 2 H), 1.10-1.55 (m, 10 H), 0.78-0.98 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 213.5, 195.7, 139.1, 131.8, 129.0, 127.9, 107.6, 95.2, 31.3, 30.5, 28.9, 28.7, 28.1, 22.6, 22.6, 14.2, 14.1; MS m/z (%) 270 (M^+ , 3.87), 105 (100); HRMS m/z (EI) calcd for $\text{C}_{19}\text{H}_{26}\text{O}$ 270.19837. Found 270.19621.

Synthesis of 2-butyl-1-*p*-tolylnona-2, 3-dien-1-one (1o): The reaction of oct-1-en-3-yne (2.16 g, 20 mmol) with *n*-BuLi (2.5 M in cyclohexane, 8 mL, 20 mmol) and N, N-dimethyl *p*-methylbenzamide (4.08 g, 25 mmol) afforded 4.20 g (74%) of **1o**: liquid; IR (neat): 1944, 1651, 1609, 1275 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.65 (d, $J = 7.8$ Hz, 2 H), 7.16 (d, $J = 7.8$ Hz, 2 H), 5.40-5.30 (m, 1 H), 2.44-2.30 (m, 2 H), 2.36 (s, 3 H), 2.16-2.00 (m, 2 H), 1.54-1.30 (m, 6

H), 1.30-1.14 (m, 4 H), 0.95 (t, $J = 6.9$ Hz, 3 H), 0.86 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 212.8, 195.3, 142.1, 136.1, 129.0, 128.3, 128.3, 107.1, 94.7, 94.7, 31.1, 30.2, 28.6, 28.4, 27.9, 22.3, 21.5, 21.4, 13.9; MS m/z (%) 284 (M^+ , 44.93), 119 (100); Anal. calcd for $\text{C}_{20}\text{H}_{28}\text{O}$ C 84.45, H 9.92. Found C 84.49, H 9.91.

Synthesis of 3-pentyldeca-3, 4-dien-2-one (1p): The reaction of nona-1-en-3-yne (1.34 g, 11 mmol) with *n*-BuLi (2.0 M in cyclohexane, 10 mmol) and N, N-dimethyl benzamide (1.04 g, 12 mmol) afforded 1.27 g (57%) of **1p**: liquid; IR (neat) 1944, 1679 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.56-5.50 (m, 1 H), 2.23 (s, 3 H), 2.10-2.20 (m, 4 H), 1.52-1.20 (m, 12 H), 0.92-0.80 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 212.4, 199.4, 109.7, 95.4, 31.4, 31.3, 28.7, 28.2, 27.6, 26.8, 26.4, 22.4, 22.3, 14.0, 13.9; MS m/z (%) 222 (M^+ , 1.69), 43 (100); HRMS m/z (EI) calcd for $\text{C}_{15}\text{H}_{26}\text{O}$ 222.1984. Found 222.1949.

Synthesis of 9-pentylhexadeca-9, 10-dien-8-one (1q): The reaction of nona-1-en-3-yne (2.68 g, 22 mmol) with *n*-BuLi (2.5 M in cyclohexane, 8 mL, 20 mmol) and N, N-dimethyl octamide (5.14 g, 30 mmol) afforded 3.62 g (59%) of **1q**: liquid; IR(neat) 1944, 1678, 1466, 1092, 726 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.46-5.51 (m, 1 H), 2.57 (t, $J = 7.5$ Hz, 2 H), 2.12 (q, $J = 7.1$ Hz, 4 H), 1.49-1.60 (m, 2 H), 1.40-1.49 (m, 2 H), 1.18-1.39 (m, 18 H), 0.80-0.92 (m, 9 H) ; ^{13}C NMR (75 MHz, CDCl_3): δ 211.7, 202.1, 109.5, 95.1, 39.1, 31.6, 31.33, 31.28, 29.2, 29.0, 28.7, 28.3, 27.6, 26.5, 25.2, 22.5, 22.37, 22.31, 13.91, 13.89, 13.85; MS m/z (%) 306 (M^+ , 2.55), 57 (100); HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{38}\text{O}$ 306.29226. Found 306.28954.

Synthesis of 2-pentyl-1-phenylnona-2, 3-dien-1-one (1r): The reaction of nona-1-en-3-yne (2.70 g, 22 mmol) with *n*-BuLi (2.5 M in cyclohexane, 8 mL, 20 mmol) and N, N-dimethyl benzamide (4.48 g, 30 mmol) afforded 4.32 g (76%) of **1r**: liquid; IR(neat) 3058, 1944, 1651,

1598, 1578, 1447, 1270, 1072, 698, 648 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.70 (d, J = 6.9 Hz, 2 H), 7.47 (t, J = 7.5 Hz, 1 H), 7.37 (t, J = 7.5 Hz, 2 H), 5.31-5.40 (m, 1 H), 2.30-2.45 (m, 2 H), 2.00-2.11 (m, 2 H), 1.04-1.54 (m, 12 H), 0.79-0.98 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 213.6, 196.0, 139.2, 131.8, 129.0, 127.9, 107.7, 95.2, 31.7, 31.4, 28.9, 28.7, 28.3, 28.0, 22.8, 22.6, 14.3, 14.2; MS m/z (%) 284 (M^+ , 4.01), 105 (100); HRMS m/z (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{O}$ 284.21402. Found 284.21343.

Synthesis of dodeca-1, 2-dien-4-one (1v): liquid; IR(neat) 3066, 1961, 1934, 1684, 1159, 846, 722 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.75 (t, J = 6.45 Hz, 1 H), 5.21 (d, J = 6.45 Hz, 2 H), 2.58 (t, J = 7.33 Hz, 2 H), 1.55 (t, J = 7.33 Hz, 2 H), 1.08-1.38 (m, 10 H), 0.84 (t, J = 6.45 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 216.8, 201.5, 96.9, 79.5, 39.4, 32.0, 29.6, 29.4, 29.3, 24.9, 22.9, 14.3; MS m/z (%) 180 (M^+ , 3.28), 141 (100); HRMS m/z (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{O}$ 180.15141. Found 180.14840.

Synthesis of ethyl 2-(ethoxycarbonyl)-3-methyl-4-hexyl-5-oxo-2-hexenoate (4c) and 3-(ethoxycarbonyl)-4, 6-dimethyl-5-hexyl-2-pyranone (6c): The reaction of **1c** (185.1 mg, 1.2 mmol), K_2CO_3 (14.1 mg, 0.1 mmol) and diethyl malonate (162.7 mg, 1.0 mmol) in 2 ml of acetone afforded 217.4 mg (67%) of **4c** and 76.0 mg (27%) of **6c**. **4c**: liquid; IR(neat) 2257, 1720, 1628, 1229, 1059, 910, 734 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 4.08-4.27 (m, 5 H), 2.11 (s, 3 H), 1.81 (s, 3 H), 1.74-1.79 (m, 1 H), 1.38-1.50 (m, 1 H), 1.02-1.30 (m, 14 H), 0.76-0.82 (m, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 206.7, 165.5, 165.2, 153.7, 128.0, 61.4, 61.3, 57.5, 31.7, 29.6, 29.4, 28.3, 27.3, 22.7, 16.4, 16.4, 14.19, 14.18; MS m/z (%) 326 (M^+ , 0.97), 43 (100); HRMS m/z (EI) calcd for $\text{C}_{18}\text{H}_{30}\text{O}_5$ 326.20932. Found 326.20903. **6c**: liquid; IR(neat) 2253, 1732, 1635, 1552, 1467, 1236, 1030, 732 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 4.26-4.33

(m, 2 H), 2.24-2.39 (m, 2 H), 2.20 (s, 3 H), 2.12 (s, 3 H), 1.09-1.40 (m, 11 H), 0.78-0.85 (m, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 165.7, 159.5, 158.9, 155.3, 118.4, 116.6, 61.9, 31.7, 29.7, 29.4, 27.1, 22.8, 17.9, 17.4, 14.3, 14.2; MS m/z (%) 280 (M^+ , 18.15), 84 (100); HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_4$ 280.16746. Found 280.16380.

Synthesis of ethyl 2-(ethoxycarbonyl)-3-methyl-4-benzyl-5-oxo-2-hexenoate (4e): The reaction of **1e** (174.5 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (163.4 mg, 1.0 mmol) in 2 ml of acetone afforded 184.8 mg (56%) of **4e**: liquid; IR(neat) 3028, 2982, 1721, 1649, 1497, 1231, 1062, 700 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.12-7.27 (m, 5 H), 4.63 (t, J = 6.9 Hz, 1 H), 4.10-4.27 (m, 4 H), 3.28 (dd, J = 13.8 and 7.5 Hz, 1 H), 2.71 (dd, J = 13.8 and 6.6 Hz, 1 H), 2.12 (s, 3 H), 1.94 (s, 3 H), 1.28 (t, J = 7.2 Hz, 3 H), 1.24 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 205.5, 164.8, 152.1, 138.6, 128.7, 128.1, 127.8, 126.2, 61.1, 61.0, 58.7, 34.4, 29.5, 16.6, 13.8, 13.8; MS m/z (%) 333 (M^+ , 0.97), 198 (100); HRMS m/z (EI) calcd for $\text{C}_{19}\text{H}_{24}\text{O}_5$ 332.16238. Found 322.16389.

Synthesis of ethyl 2-(ethoxycarbonyl)-3-methyl-4-pentyl-5-oxo-2-tridecenoate (4f): The reaction of **1f** (290.1 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (159.7 mg, 1.0 mmol) in 2 ml of acetone afforded 349.0 mg (85%) of **4f**: liquid; IR(neat) 1723, 1627, 1224, 1058, 869, 724 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 4.01-4.22 (m, 5 H), 2.35 (t, J = 7.4 Hz, 2 H), 1.76 (s, 3 H), 1.64-1.74 (m, 1 H), 1.35-1.41 (m, 3 H), 1.04-1.22 (m, 22 H), 0.68-0.80 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 209.1, 165.7, 165.4, 154.2, 127.7, 61.4, 61.3, 56.8, 42.4, 32.0, 31.9, 29.6, 29.3, 29.3, 28.7, 27.1, 23.7, 22.8, 22.6, 16.5, 14.27, 14.25, 14.23, 14.2; MS m/z (%) 411 ($\text{M}^+ + 1$, 5.93), 181 (100); HRMS m/z (EI) calcd for $\text{C}_{24}\text{H}_{42}\text{O}_5$ 410.30323. Found 410.30217.

Synthesis of 4-(1', 1'-bis(ethoxycarbonylmethyl)-5-methyl-4-hexen-2-one (3g): The reaction of **1g** (66.2 mg, 0.65 mmol), K₂CO₃ (14.0 mg, 0.1 mmol) and diethyl malonate (80.7 mg, 0.5 mmol) in 2 ml of acetone afforded 107.5 mg (75%) of **3g**: liquid; IR(neat) 1731, 1307, 1222, 1158, 1025 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 4.49 (s, 1 H), 3.96-4.18 (m, 4 H), 3.28 (s, 2 H), 2.08 (s, 3 H), 1.77 (s, 3 H), 1.60 (s, 3 H), 1.19 (t, *J* = 7.3 Hz, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ 205.5, 168.5, 168.5, 137.2, 118.3, 61.5, 54.1, 44.9, 29.4, 21.8, 20.9, 14.0; MS *m/z* (%) 270 (M⁺, 1.35), 43 (100); HRMS *m/z* (EI) calcd for C₁₄H₂₂O₅ 270.14673. Found 270.14875.

Synthesis of 2-methyl-3-(1', 1'-bis(ethoxycarbonylmethyl)-2-undecen-5-one (3h): The reaction of **1h** (117.3 mg, 0.65 mmol), K₂CO₃ (14.3 mg, 0.1 mmol) and diethyl malonate (79.6 mg, 0.5 mmol) in 2 ml of acetone afforded 98.0 mg (58%) of **3h**: liquid; IR(neat) 1731, 1733, 1307, 1146, 1036, 864 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 4.53 (s, 1 H), 4.05-4.23 (m, 4 H), 3.39 (s, 2 H), 2.39 (t, *J* = 7.3 Hz, 2 H), 1.81 (s, 3 H), 1.62 (s, 3 H), 1.47-1.60 (m, 2 H), 1.12-1.40 (m, 12 H), 0.78-0.95 (m, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 207.8, 168.8, 137.2, 118.5, 61.7, 54.4, 44.3, 42.5, 31.9, 29.2, 24.1, 22.7, 22.1, 21.1, 14.3, 14.2; MS *m/z* (%) 340 (M⁺, 0.79), 43 (100); HRMS *m/z* (EI) calcd for C₁₉H₃₂O₅ 340.22498. Found 340.22777.

Synthesis of (E)-4-(1', 1'-bis(ethoxycarbonylmethyl)-4-dodecen-2-one (E-3i): The reaction of **1i** (216.3 mg, 1.2 mmol), K₂CO₃ (13.4 mg, 0.1 mmol) and diethyl malonate (166.1 mg, 1.0 mmol) in 2 ml of acetone afforded 255.2 mg (75%) of *E*-**3i**: liquid; IR(neat) 1733, 1307, 1158, 1035 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.67 (t, *J* = 7.2 Hz, 1 H), 4.15 (q, *J* = 7.2 Hz, 4 H), 4.04 (s, 1 H), 3.39 (s, 2 H), 2.16 (s, 3 H), 1.98 (q, *J* = 7.2 Hz, 2 H), 1.18-1.40 (m, 16 H), 0.86 (t, *J* = 6.6 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 205.4, 168.5, 137.6, 124.9, 61.8, 59.8, 44.1, 32.0, 29.8, 29.5, 29.4, 29.2, 29.0, 22.9, 14.3, 14.2; MS *m/z* (%) 341 (M⁺+1, 20.39), 143 (100);

HRMS m/z (EI) calcd for $C_{19}H_{32}O_5$ 340.22498. Found 340.22133. The stereochemistry of *E*-**3i** was confirmed by the 1H - 1H NOESY spectra.

Synthesis of (*E*)-4-(1', 1'-bis(ethoxycarbonyl)methyl)-4-nonen-2-one (*E*-3j**):** The reaction of **1j** (165.8 mg, 1.2 mmol), K_2CO_3 (14.4 mg, 0.1 mmol) and diethyl malonate (161.4 mg, 1.0 mmol) in 2 ml of acetone afforded 241.5 mg (81%) of *E*-**3j**: liquid; IR(neat) 1733, 1308, 1159, 1034, 866 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 5.63 (t, $J = 7.2$ Hz, 1 H), 4.10 (q, $J = 7.2$ Hz, 4 H), 4.00 (s, 1 H), 3.36 (s, 2 H), 2.11 (s, 3 H), 1.89-2.00 (m, 2 H), 1.16-1.40 (m, 10 H), 0.83 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.3, 168.4, 137.5, 124.9, 61.8, 59.8, 44.0, 31.3, 29.8, 28.6, 22.5, 14.2, 14.1; MS m/z (%) 298 (M^+ , 20.39), 139 (100); HRMS m/z (EI) calcd for $C_{16}H_{26}O_5$ 298.17802. Found 298.17864.

Synthesis of (*E*)-10-(1', 1'-bis(ethoxycarbonyl)methyl)-10-octadecen-8-one (*E*-3k**):** The reaction of **1k** (316.8 mg, 1.2 mmol), K_2CO_3 (14.1 mg, 0.1 mmol) and diethyl malonate (162.7 mg, 1.0 mmol) in 2 ml of acetone afforded 245.9 mg (58%) of *E*-**3k**: liquid; IR(neat) 1736, 1307, 1146, 1034, 723 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 5.66 (t, $J = 6.9$ Hz, 1 H), 4.14 (q, $J = 7.1$ Hz, 4 H), 4.04 (s, 1 H), 3.36 (s, 2 H), 2.42 (t, $J = 7.35$ Hz, 2 H), 1.96 (q, $J = 7.2$ Hz, 2 H), 1.54 (q, $J = 7.2$ Hz, 2 H), 1.11-1.41 (m, 24 H), 0.86 (t, $J = 6.6$ Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.4, 168.5, 168.5, 137.2, 124.9, 61.7, 59.8, 43.2, 42.6, 32.0, 31.9, 29.47, 29.41, 29.39, 29.35, 29.3, 29.2, 28.9, 24.02, 22.85, 22.82, 14.30, 14.29, 14.2; MS m/z (%) 424 (M^+ , 20.39), 57 (100); HRMS m/z (EI) calcd for $C_{25}H_{44}O_5$ 424.31887. Found 424.32248.

Synthesis of (*E*)-3-butyl-4-(1', 1'-bis(ethoxycarbonyl)methyl)-4-decen-2-one (*E*-3l**):** The reaction of **1l** (226.4 mg, 1.2 mmol), K_2CO_3 (17.0 mg, 0.1 mmol) and diethyl malonate (164.7 mg, 1.0 mmol) in 2 ml of acetone afforded 310.2 mg (84%) of *E*-**3l**: liquid; IR(neat) 1755,

1736, 1713, 1466, 1309, 1146, 1037 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.81 (t, $J = 7.2$ Hz, 1 H), 4.02-4.20 (m, 4 H), 3.93 (s, 1 H), 3.64 (dd, $J = 8.4$ and 6.3 Hz, 1 H), 2.22 (q, $J = 7.4$ Hz, 2 H), 2.10 (s, 3 H), 1.62-1.79 (m, 1 H), 1.02-1.50 (m, 17 H), 0.80-0.96 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 208.6, 168.4, 168.4, 136.3, 128.1, 61.4, 61.4, 54.3, 52.4, 31.4, 29.3, 29.1, 28.8, 28.2, 27.7, 22.6, 22.4, 13.88, 13.85, 13.80, 13.79; MS m/z (%) 368 (M^+ , 1.90), 43 (100); HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{36}\text{O}_5$ 368.25628. Found 368.25509.

Synthesis of (*E*)-9-butyl-10-(1', 1'-bis(ethoxycarbonylmethyl)-10-hexadecen-8-one (*E*-3m**):** The reaction of **1m** (316.8 mg, 1.2 mmol), K_2CO_3 (14.2 mg, 0.1 mmol) and diethyl malonate (161.7 mg, 1.0 mmol) in 2 ml of acetone afforded 321.4 mg (71%) of *E*-**3m**: liquid; IR(neat) 1756, 1736, 1712, 1466, 1309, 1145, 1037, 876, 729 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.75 (t, $J = 7.2$ Hz, 1 H), 4.02-4.19 (m, 4 H), 3.98 (s, 1 H), 3.64 (t, $J = 7.2$ Hz, 1 H), 2.41-2.48 (m, 1 H), 2.24-2.37 (m, 1 H), 2.22-2.27 (q, $J = 6.9$ Hz, 2 H), 1.61-1.78 (m, 1 H), 1.01-1.59 (m, 27 H), 0.78-0.92 (m, 9 H); ^{13}C NMR (75 MHz, CDCl_3): δ 210.9, 168.6, 168.5, 135.9, 128.5, 61.4, 53.3, 52.3, 42.1, 31.6, 31.5, 29.3, 29.1, 29.0, 28.9, 28.2, 28.1, 23.5, 22.6, 22.5, 22.4, 13.98, 13.92, 13.87, 13.86, 13.83; MS m/z (%) 452 (M^+ , 0.61), 57 (100); HRMS m/z (EI) calcd for $\text{C}_{27}\text{H}_{48}\text{O}_5$ 452.35018. Found 452.35163.

Synthesis of (*E*)-2-butyl-3-(1', 1'-bis(ethoxycarbonylmethyl)-1-phenyl-3-nonen-1-one (*E*-3n**):** The reaction of **1n** (324.5 mg, 1.2 mmol), K_2CO_3 (17.2 mg, 0.1 mmol) and diethyl malonate (164.1 mg, 1.0 mmol) in 2 ml of acetone afforded 327.3 mg (76%) of *E*-**3n**: liquid; IR(neat) 1757, 1734, 1681, 1597, 1581, 1306, 1145, 1038, 717, 691 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.87 (d, $J = 8.4$ Hz, 2 H), 7.47-7.55 (m, 1 H), 7.32-7.45 (m, 2 H), 5.77 (t, $J = 7.2$ Hz, 1 H), 4.54 (t, $J = 7.05$ Hz, 1 H), 4.10-4.23 (m, 3 H), 3.79-3.98 (m, 2 H), 2.26-2.38 (m, 2 H),

1.79-1.96 (m, 1 H), 1.49-1.61 (m, 1 H), 1.38-1.48 (m, 2 H), 1.11-1.47 (m, 11 H), 0.83-0.94 (m, 9 H); ^{13}C NMR (75 MHz, CDCl_3): δ 201.4, 169.0, 168.6, 137.7, 137.7, 135.6, 133.1, 128.8, 128.6, 128.4, 61.7, 61.4, 52.2, 49.1, 31.9, 29.9, 29.6, 29.0, 28.8, 23.0, 22.8, 14.3, 14.2, 14.2, 13.8; MS m/z (%) 430 (M^+ , 0.69), 105 (100); HRMS m/z (EI) calcd for $\text{C}_{26}\text{H}_{38}\text{O}_5$ 430.27913. Found 430.27524.

Synthesis of (*E*)-2-butyl-3-(1', 1'-bis(ethoxycarbonylmethyl)-1-(*p*-toyl)-3-nonen-1-one (*E*-3o): The reaction of **1o** (311.0 mg, 1.2 mmol), K_2CO_3 (15.9 mg, 0.1 mmol) and diethyl malonate (165.3 mg, 1.0 mmol) in 2 ml of acetone afforded 208.5 mg (47%) of *E*-**3o**: liquid; IR(neat) 2957, 1757, 1734, 1677, 1607, 1573, 936, 852, 820 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.78 (d, $J = 8.4$ Hz, 2 H), 7.16 (d, $J = 8.4$ Hz, 2 H), 5.76 (t, $J = 7.2$ Hz, 1 H), 4.51 (t, $J = 7.2$ Hz, 1 H), 4.21 (s, 1 H), 4.16 (q, $J = 3.1$ Hz, 2 H), 3.86 (q, $J = 2.8$ Hz, 2 H), 2.36 (s, 3 H), 2.32 (q, $J = 7.2$ Hz, 2 H), 1.80-1.95 (m, 1 H), 1.48-1.63 (m, 1 H) 1.41-4.49 (m, 2 H), 1.20-1.40 (m, 12 H), 0.82-0.96 (m, 8 H); ^{13}C NMR (75 MHz, CDCl_3): δ 200.6, 169.0, 168.3, 143.7, 135.1, 134.9, 129.0, 128.7, 128.2, 61.3, 61.1, 51.90, 48.5, 31.9, 29.7, 29.3, 28.8, 28.5, 22.7, 22.5, 21.5, 13.98, 13.92, 13.91, 13.49; MS m/z (%) 444 (M^+ , 0.81), 119 (100); HRMS m/z (EI) calcd for $\text{C}_{27}\text{H}_{40}\text{O}_5$ 444.28758. Found 444.28542. The stereochemistry of *E*-**3o** was confirmed by the ^1H - ^1H NOESY spectra.

Synthesis of (*E*)-3-pentyl-4-(1, 1'-bis(ethoxycarbonylmethyl)-4-decen-2-one (*E*-3p): The reaction of **1p** (266.8 mg, 1.2 mmol), K_2CO_3 (16.4 mg, 0.1 mmol) and diethyl malonate (162.7 mg, 1.0 mmol) in 2 ml of acetone afforded 318.9 mg (83%) of *E*-**3p**: liquid; IR(neat) 1755, 1736, 1713, 1466, 1146, 1146, 1037, 871, 729, 630 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.76 (t, $J = 7.2$ Hz, 1 H), 3.99-4.12 (m, 4 H), 3.87 (s, 1 H), 3.60 (t, $J = 7.05$ Hz, 1 H), 2.17 (q, $J =$

7.1 Hz, 2 H), 2.05 (s, 3 H), 1.59-1.72 (m, 1 H), 1.00-1.49 (m, 19 H), 0.74-0.85 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 208.8, 168.64, 168.60, 136.6, 128.4, 61.63, 61.61, 54.5, 52.7, 32.0, 31.6, 29.6, 29.1, 28.4, 28.3, 26.91, 22.6, 14.14, 14.12, 14.10, 14.05; MS m/z (%) 383 ($\text{M}^+ + 1$, 1.90), 43 (100); HRMS m/z (EI) calcd for $\text{C}_{22}\text{H}_{38}\text{O}_5$ 382.27193. Found 382.26824.

Synthesis of (*E*)-9-pentyl-10-(1', 1'-bis(ethoxycarbonyl)methyl)-10-hexadecen-8-one (*E*-

3q): The reaction of **1q** (367.8 mg, 1.2 mmol), K_2CO_3 (15.4 mg, 0.1 mmol) and diethyl malonate (163.2 mg, 1.0 mmol) in 2 ml of acetone afforded 364.0 mg (78%) of *E*-**3q**: liquid; IR(neat) 1756, 1736, 1712, 1466, 1309, 1145, 1037, 874, 727 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.74 (t, $J = 7.05$ Hz, 1 H), 4.01-4.15 (m, 4 H), 3.96 (s, 1 H), 3.64 (t, $J = 7.05$ Hz, 1 H), 2.41-2.52 (m, 1 H), 2.16-2.23 (m, 1 H), 2.25-2.34 (m, 2 H), 1.63-1.75 (m, 1 H), 1.14-1.29 (m, 29 H), 0.78-0.85 (m, 9 H); ^{13}C NMR (75 MHz, CDCl_3): δ 210.8, 168.5, 168.4, 135.8, 128.5, 61.3, 53.2, 52.3, 42.1, 31.8, 31.6, 31.4, 29.04, 29.01, 28.8, 28.3, 28.2, 26.7, 23.5, 22.48, 22.41, 22.40, 13.92, 13.89, 13.88, 13.84, 13.82; MS m/z (%) 466 (M^+ , 1.46), 57 (100); HRMS m/z (EI) calcd for $\text{C}_{28}\text{H}_{50}\text{O}_5$ 466.36583. Found 466.36641

Synthesis of (*E*)-2-pentyl-3-(1', 1'-bis(ethoxycarbonyl)methyl)-1-phenyl-3-nonen-1-one

(*E*-**3r**): The reaction of **1r** (341.3 mg, 1.2 mmol), K_2CO_3 (16.4 mg, 0.1 mmol) and diethyl malonate (160.0 mg, 1.0 mmol) in 2 ml of acetone afforded 332.4 mg (75%) of *E*-**3r**: liquid; IR(neat) 1757, 1735, 1681, 1597, 1581, 1448, 1306, 1145, 1038, 717, 691 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.85 (d, $J = 7.5$ Hz, 2 H), 7.48 (t, $J = 7.2$ Hz, 1 H), 7.37 (t, $J = 5.0$ Hz, 2 H), 5.75 (t, $J = 7.5$ Hz, 1 H), 4.52 (t, $J = 7.4$ Hz, 1 H), 4.10-4.18 (m, 3 H), 3.78-3.85 (m, 2 H), 2.30 (q, $J = 7.5$ Hz, 2 H), 1.75-1.90 (m, 1 H), 1.18-1.58 (m, 16 H), 0.83-0.90 (m, 9 H); ^{13}C NMR (75 MHz, CDCl_3): δ 201.5, 169.0, 168.5, 137.69, 137.68, 135.6, 133.1, 128.8, 128.5, 128.4,

61.6, 61.3, 52.2, 49.1, 32.1, 31.8, 30.1, 29.0, 28.8, 27.1, 22.7, 14.21, 14.18, 13.7; MS m/z (%) 429 ($M^+ - CH_3$, 0.12), 105 (100); HRMS m/z (EI) calcd for $C_{27}H_{40}O_5$ 444.28758. Found 444.28764.

Synthesis of 2-(1', 1'-bis(ethoxycarbonyl)methyl)-1-octen-4-one (3s) and ethyl 2-

(ethoxycarbonyl)-3-methyl-5-oxo-2-nonenoate (4s): The reaction of **1s** (149.0 mg, 1.2 mmol), K_2CO_3 (13.8 mg, 0.1 mmol) and diethyl malonate (156.7 mg, 1.0 mmol) in 2 ml of acetone afforded 238.9 mg (88%) of **3s** and **4s** as a mixture: liquid; IR(neat) 1732, 1644, 1597, 1466, 1368, 1305, 1150, 1038, 918, 864 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) **3s**: δ 5.28 (s, 1 H), 5.16 (s, 1 H), 4.05-4.30 (m, 5 H), 3.33 (s, 2 H), 2.45 (t, $J = 7.5$ Hz, 2 H), 1.43-1.60 (m, 2 H), 1.20-1.40 (m, 8 H), 0.88 (t, $J = 7.1$ Hz, 3 H). The following data are discernible for **4s**: 4.05-4.30 (m, 4 H), 3.64 (s, 2 H), 2.45 (t, $J = 7.5$ Hz, 2 H), 2.00 (s, 3 H); MS m/z (%) 284 (M^+ , 1.14), 85 (100); HRMS m/z (EI) calcd for $C_{15}H_{24}O_5$ 284.16237. Found 284.16297.

Synthesis of 2-(1', 1'-bis(ethoxycarbonyl)methyl)-1-nonen-4-one (3t) and ethyl 2-

(ethoxycarbonyl)-3-methyl-5-oxo-2-decenoate (4t): The reaction of **1t** (158.6 mg, 1.2 mmol), K_2CO_3 (16.7 mg, 0.1 mmol) and diethyl malonate (163.7 mg, 1.0 mmol) in 2 ml of acetone afforded 251.6 mg (89%) of **3t** and **4t** as a mixture: liquid; IR(neat) 1735, 1644, 1467, 1368, 1310, 1148, 1037, 919, 864, 730 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) **3t** : δ 5.27 (s, 1 H), 5.15 (s, 1 H), 4.10-4.25 (m, 5 H), 3.32 (s, 2 H), 2.44 (t, $J = 7.2$ Hz, 2 H), 1.50-1.60 (m, 2 H), 1.18-1.30 (m, 10 H), 0.85 (t, $J = 7.2$ Hz, 3 H). The following data are discernible for **4t**: 4.10-4.25 (m, 4 H), 3.62 (s, 2 H), 2.44 (t, $J = 7.2$ Hz, 2 H), 1.99 (s, 3 H); MS m/z (%) 298 (M^+ , 1.936), 99 (100); HRMS calcd for $C_{16}H_{26}O_5$ 298.17802. Found 298.17593.

Synthesis of 2-(1', 1'-bis(ethoxycarbonyl)methyl)-1-decen-4-one (3u) and ethyl 2-

(ethoxycarbonyl)-3-methyl-5-oxo-2-undecenoate (4u): The reaction of **1u** (173.1 mg, 1.2 mmol), K_2CO_3 (14.7 mg, 0.1 mmol) and diethyl malonate (162.4 mg, 1.0 mmol) in 2 ml of acetone afforded 267.6 mg (86%) of **3u** and **4u** as a mixture: liquid; IR(neat) 1735, 1644, 1467, 1368, 1306, 1150, 1037, 918, 965, 786, 727 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) **3u**: δ 5.15 (s, 1 H), 5.04 (s, 1 H), 4.01-4.20 (m, 5 H), 3.21 (s, 2 H), 2.33 (t, $J = 7.8$ Hz, 2 H), 1.39-1.51 (m, 2 H), 1.08-1.25 (m, 12 H), 0.73 (t, $J = 8.4$ Hz, 3 H). The following data are discernible for **4u**: 4.01-4.20 (m, 4 H), 3.51 (s, 2 H), 2.33 (t, $J = 7.8$ Hz, 2 H), 1.87 (s, 3 H); MS m/z (%) 312 (M^+ , 1.14), 43 (100); HRMS m/z (EI) calcd for $C_{17}H_{28}O_5$ 312.19367. Found 312.19365.

Synthesis of 2-(1', 1'-bis(ethoxycarbonyl)methyl)-1-dodecen-4-one (3v) and ethyl 2-

(ethoxycarbonyl)-3-methyl-5-oxo-2-tridecenoate (4v): The reaction of **1v** (208.1 mg, 1.2 mmol), K_2CO_3 (15.7 mg, 0.1 mmol) and diethyl malonate (163.3 mg, 1.0 mmol) in 2 ml of acetone afforded 240.0 mg (74%) of **3v** and **4v** as a mixture: liquid; IR(neat) 1733, 1644, 1597, 1466, 1368, 1309, 1148, 1037, 917, 864, 723 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) **3v**: δ 5.19 (s, 1 H), 5.07 (s, 1 H), 4.04-4.11 (m, 5 H), 3.23 (s, 2 H), 2.36 (t, $J = 7.5$ Hz, 2 H), 1.40-1.50 (m, 2 H), 1.07-1.22 (m, 16 H), 0.76 (t, $J = 6.6$ Hz, 3 H). The following data are discernible for **4v**: 4.04-4.11 (m, 4 H), 3.53 (s, 2 H), 2.36 (t, $J = 7.5$ Hz, 2 H), 1.90 (s, 3 H); MS m/z (%) 340 (M^+ , 1.14), 57 (100); HRMS m/z (EI) calcd for $C_{19}H_{32}O_5$ 340.22497. Found 340.22378.

Synthesis of α -Pyrone.

Synthesis of 3-(ethoxycarbonyl)-4, 6-dimethyl-5-butyl-2-pyranone (6a): The reaction of **1a** (166 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 2 ml of acetone afforded 161 mg (64%) of **6a**.

Synthesis of 3-(ethoxycarbonyl)-4, 6-dimethyl-5-ethyl-2-pyranone (6b): The reaction of **1b**

(132 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 2 ml of ethanol afforded 118 mg (53%) of **6b**: yellow oil, 1H NMR (300 MHz, $CDCl_3$) δ 4.34 (q, $J = 7.0$ Hz, 2 H), 2.37 (t, $J = 7.5$ Hz, 2 H), 2.24 (s, 3 H), 2.16 (s, 3 H), 1.33 (t, $J = 7.1$ Hz, 3 H), 1.04 (t, $J = 7.4$ Hz, 3 H); MS m/z (%) 224 (M^+ , 4), 43 (100); IR 1720, 1635, 1552, 1236 cm^{-1} ; HRMS calcd for $C_{12}H_{16}O_4$ 224.1044. Found 224.1063.

Synthesis of 3-(ethoxycarbonyl)-4, 6-dimethyl-5-hexyl-2-pyranone (6c): The reaction of **1c** (199.5 mg, 1.2 mmol), K_2CO_3 (15.2 mg, 0.1 mmol) and diethyl malonate (160.0 mg, 1.0 mmol) in 2 ml of acetone afforded 225.8 mg (81%) of **6c**.

Synthesis of 3-(ethoxycarbonyl)-4, 6-dimethyl-5-allyl-2-pyranone (6d): The reaction of **1d** (146 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 2 ml of acetone afforded 213 mg (90%) of **6d**: yellow oil, 1H NMR (300 MHz, $CDCl_3$) δ 5.88-5.76 (m, 1H), 5.12-5.08 (d, $J = 10.3$ Hz, 1H), 4.95 (d, $J = 17.0$ Hz, 1 H), 4.36 (q, $J = 7.2$ Hz, 2 H), 3.10 (t, $J = 3.2$ Hz, 2 H), 2.24 (s, 3 H), 2.14 (s, 3 H), 1.35 (t, $J = 7.1$ Hz, 3 H); MS m/z (%) 237 ($M^+ + 1$, 8), 236 (M^+ , 52), 208 (100); IR 1739, 1716, 1639, 1554, 1238 cm^{-1} ; HRMS calcd for $C_{13}H_{16}O_4$ 236.1044. Found 236.1030.

Synthesis of 3-(ethoxycarbonyl)-4, 6-dimethyl-5-benzyl-2-pyranone (6e): The reaction of **1e** (192 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 2 ml of acetone afforded 262 mg (92%) of **6e**: white solid, recrystallized from CH_2Cl_2 /hexane (1:20), m.p. 79.5-80.5 $^{\circ}C$; 1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.23 (m, 3 H), 7.08 (d, $J = 7.2$ Hz, 2 H), 4.36 (q, $J = 7.2$ Hz, 2 H), 3.77 (s, 2 H), 2.30 (s, 3 H), 2.04 (s, 3 H), 1.34 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 160.1, 159.1, 155.5, 137.4, 128.9, 127.4, 126.8, 118.5, 114.1, 61.8, 32.4, 18.0, 17.5, 14.1; MS m/z (%) 287 ($M^+ + 1$, 14), 286 (M^+ , 38), 218 (100);

IR 1726, 1699, 1557, 1236 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4$ 286.1200. Found 286.1204

Synthesis of 3-(ethoxycarbonyl)-4-methyl-5-pentyl-6-octyl-2-pyranone (6f): The reaction of **1f** (294.2 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160.4 mg, 1.0 mmol) in 2 ml of acetone afforded 204.4 mg (56%) of **6f**: liquid; IR(neat) 1723, 1631, 1551, 1466, 1237, 1032, 860, 786, 724 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 4.30 (t, $J = 7.2$ Hz, 2 H), 2.44 (t, $J = 7.5$ Hz, 2 H), 2.26 (t, $J = 7.2$ Hz, 2 H), 2.11 (s, 3 H), 1.50-1.63 (m, 2 H), 1.18-1.40 (m, 19 H), 0.78-0.86 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 165.7, 162.5, 159.6, 155.2, 118.5, 116.2, 61.9, 32.0, 31.4, 30.1, 29.5, 29.4, 29.3, 27.9, 26.8, 22.8, 22.6, 17.4, 14.3, 14.24, 14.22, 14.1; MS m/z (%) 364 (M^+ , 12.93), 43 (100); HRMS m/z (EI) calcd for $\text{C}_{22}\text{H}_{36}\text{O}_4$ 364.26136. Found 364.26224.

Synthesis of 3-(ethoxycarbonyl)-4-pentyl-6-methyl-2-pyranone (6j): The reaction of **1j** (166 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 1 ml of DMF afforded 129 mg (54%) of **6j**: yellow oil, IR 1724, 1645, 1565, 1256, 1276 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.93 (s, 1 H), 4.35 (q, $J = 7.1$ Hz, 2 H), 2.44 (t, $J = 8.0$ Hz, 2 H), 2.24 (s, 3 H), 1.59 (m, 3 H), 1.37-1.30 (m, 6 H), 0.88 (t, $J = 6.7$ Hz, 3 H); MS m/z (%) 253 ($\text{M}^+ + 1$, 7), 252 (M^+ , 25), 163 (100); HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$ 252.1356. Found 252.1339.

Synthesis of 3-(ethoxycarbonyl)-4-methyl-6-butyl-2-pyranone (6s): The reaction of **1s** (141.4 mg, 1.2 mmol), K_2CO_3 (17.5 mg, 0.1 mmol) and diethyl malonate (160.1 mg, 1.0 mmol) in 2 ml of acetone afforded 155.8 mg (65%) of **6s**: liquid; IR(neat) 1724, 1644, 1566, 1259, 1178, 1076, 1025, 838, 790 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.86 (s, 1 H), 4.29 (q, $J = 7.2$ Hz, 2 H), 2.40 (t, $J = 7.5$ Hz, 2 H), 2.16 (s, 3 H), 1.51-1.61 (m, 2 H), 1.22-1.32 (m, 5 H), 0.85 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.7, 165.1, 160.0, 156.8, 116.2, 106.8,

61.6, 33.5, 29.0, 22.2, 20.1, 14.3, 13.8; MS m/z (%) 238 (M^+ , 48.93), 153 (100); HRMS m/z (EI) calcd for $C_{13}H_{18}O_4$ 238.12051. Found 238.12478.

Synthesis of 3-(ethoxycarbonyl)-4-methyl-6-hexyl-2-pyranone (6u): The reaction of **1u** (177.5 mg, 1.2 mmol), K_2CO_3 (14.2 mg, 0.1 mmol) and diethyl malonate (157.4 mg, 1.0 mmol) in 2 ml of acetone afforded 167.8 mg (63%) of **6u**: liquid; IR(neat) 1726, 1644, 1566, 1259, 1177, 1076, 1024, 958, 839, 789 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 5.88 (s, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 2.44 (t, J = 7.6 Hz, 2 H), 2.21 (s, 3 H), 1.58-1.67 (m, 2 H), 1.20-1.40 (m, 9 H), 0.87 (t, J = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 165.1, 160.0, 156.4, 116.2, 106.7, 61.8, 33.9, 31.5, 28.8, 26.9, 22.6, 20.4, 14.4, 14.2; MS m/z (%) 266 (M^+ , 25.93), 153 (100); HRMS m/z (EI) calcd for $C_{15}H_{22}O_4$ 266.15181. Found 266.14950.

Synthesis of 3-(ethoxycarbonyl)-4-methyl-6-octyl-2-pyranone (6v): The reaction of **1v** (206.7 mg, 1.2 mmol), K_2CO_3 (15.8 mg, 0.1 mmol) and diethyl malonate (160.0 mg, 1.0 mmol) in 2 ml of acetone afforded 203.1 mg (69%) of **6v**: liquid; IR(neat) 1725, 1644, 1566, 1258, 1177, 1076, 1024, 966, 839, 789 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 5.88 (s, 1 H), 4.34 (q, J = 7.5 Hz, 2 H), 2.44 (t, J = 7.5 Hz, 2 H), 2.21 (s, 3 H), 1.55-1.65 (m, 2 H), 1.18-1.40 (m, 13 H), 0.86 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 165.2, 160.0, 156.4, 116.3, 106.7, 61.9, 34.0, 32.0, 29.4, 29.3, 29.2, 27.0, 22.8, 20.4, 14.4, 14.3; MS m/z (%) 294 (M^+ , 11.49), 153 (100); HRMS m/z (EI) calcd for $C_{17}H_{26}O_4$ 294.18311. Found 294.18072.

Synthesis of 3-(ethoxycarbonyl)-4, 6-dimethyl-2-pyranone (6w): The reaction of **1w** (98 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 2 ml of ethanol afforded 147 mg (74%) of **6w**. m.p. 54-55°C IR 1740, 1693, 1643, 1552, 1253, 1191 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.82 (s, 1 H), 4.25 (q, J = 7.2 Hz, 2 H), 2.13 (s, 3 H), 2.11

(s, 3 H), 1.25 (t, $J = 7.1$ Hz, 3 H); MS m/z (%) 197 ($M^+ + 1$, 13), 196 (M^+ , 51), 151 (100);

Elemental Analysis calcd for $C_{10}H_{12}O_4$ C 61.22, H 6.16. Found C 61.21, H 6.21 .

Synthesis of 3-(ethoxycarbonyl)-4-methyl-6-phenyl-2-pyranone (6x): The reaction of **1x**

(173 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 2 ml of acetone afforded 184 mg (71%) of **6x**: white solid, recrystallized from

CH_2Cl_2 /hexane(1:20), m.p. 57.0-57.5 °C; IR 1744, 1722, 1553, 1266 cm^{-1} ; 1H NMR(300 MHz, $CDCl_3$) δ 7.84-7.81 (m, 2 H), 7.47-7.45 (m, 3 H), 6.57 (s, 1 H), 4.40 (q, $J = 7.2$ Hz, 2 H), 2.34 (s, 3 H), 1.38 (t, $J = 7.1$ Hz, 3 H); MS m/z (%) 259 ($M^+ + 1$, 8), 258 (M^+ , 62), 230 (100);

Elemental Analysis calcd for $C_{15}H_{14}O_4$, C 69.76, H 5.46. Found C 69.80, H 5.30.

Synthesis of 3-(ethoxycarbonyl)-4-methyl-6-benzyl-2-pyranone (6y): The reaction of **1y**

(189 mg, 1.2 mmol), K_2CO_3 (14.0 mg, 0.1 mmol) and diethyl malonate (160 mg, 1 mmol) in 2 ml of CH_2Cl_2 afforded 225 mg (69%) of **6y**: white solid, recrystallized from

CH_2Cl_2 /hexane(1:20), m.p. 59.5-60.5 °C; IR 1749, 1683, 1635, 1240 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.12 (m, 5 H), 5.70 (s, 1 H), 4.23 (q, $J = 7.1$ Hz, 2 H), 3.69 (s, 2 H), 2.10 (s, 3 H), 1.27 (t, $J = 7.1$ Hz, 3 H); MS m/z (%) 273 ($M^+ + 1$, 9), 272 (M^+ , 28), 153 (100); Elemental Analysis calcd for $C_{16}H_{16}O_4$ C 70.58, H 5.92. Found C 70.63, H 5.83.

1c

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.500 sec
 Width 18867.9 Hz
 2508 repetitions
 OBSERVE C13, 75.4420774 MHz
 DECOUPLE H1, 300.0294698 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 95 hr, 5 min, 35 sec

1c

7.258

5.725
5.714
5.704
5.694
5.683
5.625
5.601
5.581
5.557

2.574
2.549
2.524

2.197
2.188
2.175
2.165
2.150
2.139
2.126
2.116
1.617
1.611
1.599
1.573
1.549
1.523
1.498
1.474
1.448
1.426
1.388
1.365
1.347
1.332
1.301
1.268
0.899
0.889
0.878
0.867
0.855
0.844

Pulse Sequence: s2pul
 Solvent: CDC13
 Ambient temperature
 Mercury-300BB "MERCURYvx300"

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.500 sec
 Width 18867.9 Hz
 2960 repetitions
 OBSERVE C13 75.4420774 MHz
 DECOUPLE H1 300.0294698 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 0 min, 0 sec

11

1m

1o

212.595

199.884

109.991
109.977

95.658

77.666
77.244
76.812

31.659
31.596
28.955
28.496
27.870
27.152
27.134
26.677
22.712
22.704
22.616
14.255
14.241
14.209
14.200

1p

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.000 sec
 Width 18867.9 Hz
 48 repetitions
 OBSERVE C13, 75.4420774 MHz
 DECOUPLE H1, 300.0294698 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 116 hr, 41 min, 19 sec

C13/CDC13
 ysh-4-13-12
 Pulse Sequence: s2pul
 Solvent: CDC13
 Ambient temperature
 Mercury-300BB "MERCURYvx300"

Relax. delay 1.000 sec
 Pulse 27.7 degrees
 Acq. time 3.405 sec
 Width 18797.0 Hz
 560 repetitions
 OBSERVE C13, 75.4434155 MHz
 DECOUPLE H1, 300.0346884 MHz
 Power 45 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
 DATA PROCESSING
 FT size 131072
 Total time 0 min, 0 sec

168.501
168.490

137.227
137.216

118.339

77.489
77.067
76.641

61.472

54.123

44.903

29.441

21.807
20.864

13.964

3g

Mercury-30088 "MERCURYvx300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.000 sec
Width 30030.0 Hz
64 repetitions
OBSERVE C13, 75.4420774 MHz
DECOUPLE H1, 300.0294698 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 134 hr, 48 min, 51 sec

168.799

137.233

118.519

77.702
77.277
76.852

61.685

54.403

44.283
42.528

31.850
29.153
24.051
22.739
22.095
21.111
14.266
14.230

3h

Relax. delay 13.000 sec
 Pulse 45.0 degrees
 Acq. time 2.000 sec
 Width 30030.0 Hz
 100 repetitions
 OBSERVE C13, 75.4420774 MHz
 DECOUPLE H1, 300.0294698 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 134 hr, 48 min, 51 sec

168.501

137.603

124.890

77.684
77.259
76.840

61.813
59.839

44.053

32.014
 29.827
 29.475
 29.366
 29.184
 28.953
 22.867
 14.327
 14.211

E-3i

E-3j

E-3o

E-3o

E-3p

7.258

5.269
5.1524.252
4.227
4.198
4.194
4.174
4.171
4.150
4.146
4.125
3.619

3.317

2.471
2.459
2.446
2.435
2.4111.985
1.554
1.530
1.506
1.301
1.292
1.290
1.276
1.264
1.255
1.250
1.241
1.231
1.218
1.206
0.874
0.852
0.828

Pulse 92.9 degrees
 Acq. time 2.000 sec
 Width 18761.7 Hz
 180 repetitions
 OBSERVE ^{13}C , 75.4420774 MHz
 DECOUPLE ^1H , 300.0294698 MHz
 Power 48 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 1 hr, 12 min, 49 sec

4e

4f

HERTZ

2175.46

INTEGRAL

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5

S80

177.83
165.16
161.91
158.70
153.07
135.46
135.41
108.11

745.99
735.17
735.16
698.12
688.67
682.18
670.93
659.04
649.04
645.66
631.90
605.78
598.53
580.96
570.74
559.17
548.82
545.61
530.76
510.20
491.23
483.78
472.47
463.54
448.17
444.17
364.74
340.74
280.70
276.83
274.16
267.30
252.37

19.73

67.46

36.27

24.04

1H NMR

131.79
130.71
129.60
129.52

77.39
77.17
76.84
64.73
64.55
64.55

406.23
399.10
392.01
311.06
313.52

INTEGRAL

HERTZ
2652.33
2647.31
2644.60
2642.93
2547.74
2396.64
2339.47
2324.83
2313.25
2301.88
2270.23
2175.50
2134.72
2116.17
2052.30
2050.66
2037.50
2019.60
2009.64
1999.43
1991.13
1984.50
1959.09
1934.54
1903.95
1872.96
1842.92
1764.75
1759.62
1754.52
1749.30
1747.68
1742.32
1737.31
1732.27
1726.98
1629.37
1601.15
1536.78
1535.60
1526.49
1525.29
1494.27
1493.15
1477.27
1475.79
1318.44
1311.25
1304.12
1297.02
1101.82
1011.86
933.23
931.25
928.06
815.78
706.75
670.81
661.79
647.78
642.89
630.89
622.82
605.54
584.62
577.81
477.37
468.55
412.52
405.42
398.32
385.28
375.46
372.29
341.29
325.32
287.76
281.44
265.96
259.44
252.69
168.40

Integral

Hz

2201.33
2194.43
2186.92
2178.12
2169.98
2126.11
2118.93

1316.60
1309.46
1302.32
1295.19
1131.75

690.54
612.89
611.03
486.97
425.87
410.53
403.40
396.26
375.42

1.000
0.642

0.633
0.680

0.983
1.053
0.215
1.224

7.258

4.334
4.321
4.309
4.302
4.298
4.292
4.286
4.262

2.460
2.438
2.410
2.280
2.260
2.232
2.111

1.601
1.580
1.559
1.529
1.358
1.316
1.293
1.280
1.275
1.270
1.230
1.224
1.201
0.861
0.838
0.826
0.820
0.815
0.810
0.805
0.782

6j

HERTZ

2177.07

1775.25

1631.01

1316.18
1309.06
1301.93
1294.82

739.02
731.45
723.45
671.63
649.41

477.85
411.91
404.81
397.83
395.23
391.43
272.58
265.92

S90

INTEGRAL

HEN72

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5

2159.90

1747.66

1285.56
1278.37
1271.31
1264.63

672.37
670.32
668.37
666.32
664.37
662.32
611.98

509.45

391.51
389.51
387.51
385.51
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17.51
15.51
13.51
11.51
9.51
7.51
5.51
3.51
1.51
0.51

13.265

12.404

41.081

21.483

7.815

7.479
7.475

7.256

6.573

4.405
4.382

2.343

1.618

1.406
1.383
1.358

YSH-3-24-1

S97

4714, 29.

1000

1109.93.

53, 25
74, 63
81, 13
70, 49

475.96	386.98
39.947	372.78
350.75	344.32
341.65