Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting Information

Synthesis of Medium- and Large-Sized Lactones in an Aqueous–Organic Biphasic System

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Instrumentation and Materials

^{1}H NMR (300 MHz or 500 MHz), ^{13}C NMR (75.3 MHz or 125 MHz), ^{31}P NMR (121.5 MHz) spectra were taken on Varian GEMINI 300, Mercury 300, and UNITY 500 spectrometers. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. ^{31}P NMR spectra were obtained in D_2O. IR spectra were recorded on JASCO IR-810 and SHIMADZU FTIR-8200PC spectrometers. High resolution ESI–TOF MS was taken on a Bruker microTOF. Silica gel (Wakogel 200 mesh and Nacalai Tesque Silica gel 60 spherical, neutrality 150μm) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Pure water was obtained with Millipore Direct-Q system. Degassed water was used for the reaction. Pure water was degassed by bubbling of argon with sonication for 30 min before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The water-soluble ligand **4** was prepared according to the reported procedure by Herrmann and co-workers.[1]

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[1] W. A. Herrmann, G. P. Albanese, R. B. Manetsberger, P. Lappe, H. Bahrmann, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 811.

Characterization Data

3-(*E*)-5-Acetoxypent-3-enyl 3-Oxobutyrate (1a): IR (neat) 2959, 1741, 1736, 1719, 1638, 1458, 1383, 1319, 1232, 1151, 1028, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07 (s, 3H), 2.27 (s, 3H), 2.42 (q, *J* = 6.5 Hz, 2H), 3.46 (s, 2H), 4.20 (t, *J* = 7.0 Hz, 2H), 4.52 (d, *J* = 7.0 Hz, 2H), 5.64–5.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.94, 30.16, 31.43, 49.98, 64.11, 64.65, 126.96, 130.49, 166.98, 170.74, 200.39. Found: C, 57.97; H, 7.03%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

4-(*E*)-6-Acetoxyhex-4-enyl 3-Oxobutyrate (1b): IR (neat) 2953, 2853, 1767, 1740, 1720, 1670, 1433, 1371, 1339, 1229, 1205, 1117, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (quint., *J* = 7.5 Hz, 2H), 2.07 (s, 3H), 2.15 (q, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 2.36 (s, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 4.52 (d, *J* = 6.5 Hz, 2H), 5.57–5.64 (m, 1H), 5.73–5.80 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.13, 21.00, 21.11, 27.78, 28.61, 63.53, 64.99, 109.99, 124.78, 134.75, 163.92, 165.95. HRMS (ESI) $[M+H]^+$ Found: 243.1223, Calcd for $C_{12}H_{19}O_5$: 243.1227.

5-(*E*)-7-Acetoxyhept-5-enyl 3-Oxobutyrate (1c): IR (neat) 2939, 2862, 1740, 1736, 1719, 1638, 1411, 1364, 1234, 1151, 1026, 972 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (quint., *J* = 7.0 Hz, 2H), 1.66 (quint., *J* = 7.0 Hz, 2H), 2.06 (s, 3H), 2.09 (q, *J* = 7.5 Hz, 2H), 2.27 (s, 3H), 3.46 (s, 2H), 4.14 (t, *J* = 6.5 Hz, 2H), 4.51 (d, *J* = 6.5 Hz, 2H), 5.54–5.61 (m, 1H), 5.71–5.78 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.00, 25.04, 27.90, 30.15, 31.66, 50.06, 65.08, 65.18, 124.42, 135.51, 167.13, 170.84, 200.55. Found: C, 60.65; H, 7.66%. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87%.

6-(*E*)-8-Acetoxyoct-6-enyl 3-Oxobutyrate (1d): IR (neat) 2936, 2858, 1740, 1736, 1720, 1638, 1560, 1364, 1232, 1151, 1026, 966 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33–1.57 (m, 4H), 1.66 (quint., *J* = 7.0 Hz, 2H), 2.07 (s, 3H), 2.08 (q, *J* = 7.0 Hz, 2H), 2.28 (s, 3H), 3.46 (s, 2H), 4.15 (t, *J* = 6.5 Hz, 2H), 4.52 (d, *J* = 6.5 Hz, 2H), 5.54–5.61 (m, 1H), 5.73–5.79 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.04, 25.31, 28.28, 28.38, 30.16, 32.02, 50.12, 65.21, 65.37, 124.08, 136.04, 167.16, 171.32, 200.58. Found: C, 61.94; H, 8.14%. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20%.

7-(*E*)-9-Acetoxynon-7-enyl 3-Oxobutyrate (1e): IR (neat) 2932, 2858, 1740, 1736, 1719, 1638, 1560, 1508, 1458, 1236, 1151, 1026, 968 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31–1.43 (m, 6H), 1.61–1.68 (m, 2H), 2.06 (q, *J* = 7.0 Hz, 2H), 2.07 (s, 3H), 2.28 (s, 3H), 3.46 (s, 2H), 4.14 (t, *J* = 6.5 Hz, 2H), 4.51 (d, *J* = 6.5 Hz, 2H), 5.53–5.60 (m, 1H), 5.73–5.79 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.03, 25.60, 28.36, 28.55, 28.65, 30.15, 32.08, 50.11, 65.25, 64.46, 123.88, 136.34, 167.17, 170.89, 200.60. HRMS (ESI) $[M+H]^+$ Found: 282.1701, Calcd for $C_{15}H_{25}O_5$: 285.1697.

8-(*E*)-10-Acetoxydec-8-enyl 3-Oxobutyrate (1f): IR (neat) 2930, 2856, 1740, 1736, 1720, 1647, 1560, 1460, 1419, 1364, 1315, 1232, 1151, 1026, 968 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27–1.42 (m, 8H), 1.64 (quint., *J* = 7.0 Hz, 2H), 2.05 (q, *J* = 7.0 Hz, 2H), 2.07 (s, 3H), 2.28 (s, 3H), 3.46 (s, 2H), 4.14 (t, *J* = 6.5 Hz, 2H), 4.51 (dd, *J* = 6.5, 0.5 Hz, 2H), 5.52–5.59 (m, 1H), 5.73–5.80 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.04, 25.71, 28.42, 28.72, 28.94, 28.98, 30.16, 32.17, 50.13, 65.30, 65.52, 123.76, 136.54, 167.19, 170.91, 200.63. Found: C, 64.18; H, 8.66%. Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78%.

4-(*E*)-6-Methoxycarbonyloxyhex-4-enyl 3-Oxobutyrate (1g): IR (neat) 2959, 2856, 1747, 1736, 1719, 1641, 1445, 1362, 1267, 1151, 1038, 976, 943 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (quint., *J* = 7.0 Hz, 2H), 2.15 (q, *J* = 7.5 Hz, 2H), 2.28 (s, 3H), 3.46 (s, 2H), 3.79 (s, 3H), 4.15 (t, *J* = 6.5 Hz, 2H), 4.58 (d, *J* = 6.0 Hz, 2H), 5.59–5.66 (m, 1H), 5.77–5.83 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 27.56, 28.46, 30.17, 50.03, 54.72, 64.62, 68.27, 124.33, 135.33, 155.60, 167.07, 200.49. Found: C, 55.66; H, 6.97%. Calcd for $C_{12}H_{18}O_6$: C, 55.81; H, 7.02%.

General Procedure for the Synthesis of Lactones (2, 3, 5, 6, 7, and 9)

In a 20-mL flask, $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (4.6 mg, 0.0125 mmol) and trisodium salt of tris(5-sulfonato-2-tolyl)phosphine (67.5 mg, 0.11 mmol) were placed under argon atmosphere. Degassed water (5 mL) was introduced, and the mixture was stirred vigorously at 75 ºC for 15 min. Homogeneous yellow clear solution was obtained. The solution was cooled to room temperature and then Na_2CO_3 (127.2 mg, 1.2 mmol) was added. Without stirring, ethyl acetate (3 mL) was added. The system became biphasic. A solution of 7-acetoxyhept-5-enyl 3-oxobutyrate (**1c**, 128.1 mg, 0.5 mmol) in ethyl acetate (2 mL) was added via a syringe to the ethyl acetate phase. After

stirring for 12 h, the mixture was extracted with ethyl acetate. The organic extracts were dried through a short pad of silica gel on Na_2SO_3 layer. Concentration followed by purification of the residual oil afforded 3-acetyl-3,4,7,8,9,10-hexahydrooxecin-2-one (**5**, 85.7 mg, 0.44 mmol) in 87% yield.

5-(*E*)-3-Acetyl-4,7,8,9-tetrahydro-3*H*-oxomin-2-one (2, 55/45): Colorless oil. IR (neat) 3429, 2934, 2858, 1733, 1717, 1655, 1445, 1355, 1148, 1028, 986 cm^{-1}; ^1H NMR ($CDCl_3$) major δ 1.72–1.84 (m, 1H), 1.86–1.96 (m, 1H), 2.12–2.33 (m, 3H), 2.26 (s, 3H), 2.42–2.52 (m, 1H), 3.42 (t, *J* = 8.0 Hz, 1H), 4.04–4.18 (bs, 1H), 4.54–4.72 (bs, 1H), 5.41–5.54 (m, 2H); minor δ 1.72–1.84 (m, 1H), 1.86–1.96 (m, 1H), 2.12–2.33 (m, 2H), 2.22 (s, 3H), 2.52–2.64 (bs, 1H), 2.72–2.80 (m, 1H), 3.54–3.57 (m, 1H), 4.22–4.35 (bs, 1H), 4.37–4.52 (bs, 1H), 5.41–5.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 28.85, 29.35, 29.55, 59.16, 67.28, 67.69, 124.92, 134.32, 171.27, 202.23. Found: C, 65.61; H, 7.84%. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%. (62.2 mg, 0.34 mmol).

5-(*Z*)-3-Acetyl-4,7,8,9-tetrahydro-3*H*-oxomin-2-one (3): ^1H NMR ($CDCl_3$) δ 1.83–1.93 (m, 2H), 2.04–2.12 (m, 1H), 2.20–2.28 (m, 1H), 2.27 (s, 3H), 2.42–2.48 (m, 1H), 2.82 (dt, *J* = 13.0, 10.0 Hz, 1H), 3.39 (dd, *J* = 10.0, 4.5 Hz, 1H), 4.26 (dt, *J*= 11.0, 8.0 Hz, 1H), 4.38–4.44 (m, 1H), 5.48–5.55 (m, 1H), 5.60–5.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.78, 26.41, 26.88, 29.11, 58.53, 63.59, 124.29, 134.33, 171.08, 202.15. (4.8 mg, 0.03 mmol).

5-(*E*)-3-Acetyl-3,4,7,8,9,10-hexahydro-oxecin-2-one (5, 69/31): Colorless oil. IR (neat) 3630, 3539, 3429, 2926, 1730, 1719, 1641, 1442, 1356, 1331, 1151, 1016, 970 cm^{-1}; ^1H NMR ($CDCl_3$) major δ 1.35–1.48 (m, 1H), 1.50–1.62 (m, 1H), 1.78–1.92 (m, 4H), 2.25 (s, 3H), 2.39–2.47 (m, 1H), 2.51–2.57 (m, 1H), 3.42 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.86 (dd, *J* = 12.0, 7.0 Hz, 1H), 4.55 (t, *J* = 10.0 Hz, 1H), 5.33–5.40 (m, 1H), 5.55–5.61 (m, 1H); minor δ 1.35–1.48 (m, 1H), 1.50–1.62 (m, 1H), 1.76–1.91 (m, 4H), 2.20 (s, 3H), 2.23–2.30 (m, 1H), 2.72–2.79 (m, 1H), 3.67 (dd, *J* = 6.3, 5.0 Hz, 1H), 4.04 (dd, *J* = 12.0, 5.0 Hz, 1H), 4.36 (t, *J* = 10.0 Hz, 1H), 5.33–5.40 (m, 1H), 5.55–5.61 (m, 1H); ^{13}C NMR ($CDCl_3$) major δ 27.57, 28.19, 29.20, 32.64, 32.71, 61.14, 66.07, 127.38, 134.31, 170.58, 202.52. minor δ 28.48, 29.16, 30.06, 32.64, 32.87, 61.74, 66.41, 127.32, 134.39, 169.74, 201.95. Found: C, 67.59; H, 8.27%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H,

8.22%. (85.7 mg, 0.44 mmol).

5-(*E*)-3-Acetyloxacycloundec-5-en-2-one (6): Colorless oil. IR (neat) 3651, 3539, 3429, 3026, 2932, 2860, 1732, 1641, 1452, 1383, 1358, 1329, 1254, 1202, 1151, 974 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07–1.16 (m, 1H), 1.33–1.41 (m, 1H), 1.42–1.58 (m, 3H), 1.58–1.68 (m, 1H), 1.82–1.92 (m, 1H), 2.12–2.20 (m, 1H), 2.23 (s, 3H), 2.46–2.56 (m, 2H), 3.40 (sq, *J* = 3.0 Hz, 1H), 3.81–3.87 (m, 1H), 4.47–4.52 (m, 1H), 5.29–5.36 (m, 1H), 5.38–5.45 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.21, 24.61, 28.68, 28.82, 32.84, 33.40, 59.45, 64.91, 127.29, 132.49, 171.03, 202.34. Found: C, 68.33; H, 8.46%. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63%. (84.0 mg, 0.40 mmol).

5-(*E*)-3-Acetyloxacyclododec-5-en-2-one (7): Colorless oil. IR (neat) 3429, 2922, 2854, 2687, 1734, 1717, 1639, 1452, 1439, 1358, 1331, 1153, 968 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14–1.24 (m, 2H), 1.26–1.38 (m, 1H), 1.40–1.62 (m, 4H), 1.72–1.82 (m, 1H), 1.98–2.06 (m, 1H), 2.14–2.20 (m, 1H), 2.23(s, 3H), 2.53 (tt, *J* = 5.5, 1.5 Hz, 2H), 3.44 (t, *J* = 7.5 Hz, 1H), 3.89 (dt, *J* = 11.5, 4.0 Hz, 1H), 4.67 (td, *J* = 10.5, 3.0 Hz, 1H), 5.33–5.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.66, 24.04, 24.50, 26.39, 28.58, 30.45, 32.61, 60.08, 63.06, 126.67, 133.20, 170.58, 202.36. Found: C, 69.55; H, 8.97%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%. (82.8 mg, 0.37 mmol).

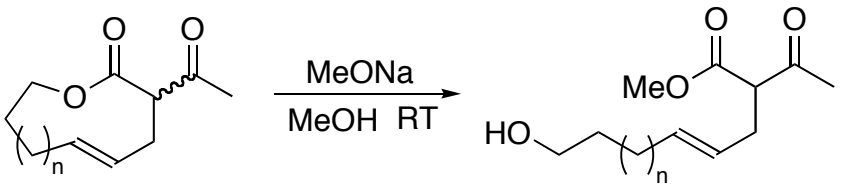
5-(*E*)-3-Acetyloxacyclotridec-5-en-2-one (8-(*E*)): Colorless oil. IR (neat) 2928, 2856, 1736, 1717, 1638, 1618, 1439, 1358, 1325, 1246, 1209, 1150, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22–1.35 (m, 4H), 1.36–1.48 (m, 4H), 1.66–1.76 (m, 2H), 1.99–2.07 (m, 2H), 2.23(s, 3H), 2.46–2.54 (m, 1H), 2.56–2.63 (m, 1H), 3.51 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.96–4.01 (m, 1H), 4.43–4.48 (m, 1H), 5.37–5.44 (m, 1H), 5.53–5.60 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 24.62, 26.36, 26.81, 26.84, 26.91, 28.37, 31.08, 31.57, 60.42, 65.39, 125.95, 134.34, 170.41, 202.50. Found: C, 70.32; H, 9.42%. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30%.

5-(*Z*)-3-Acetyloxacyclotridec-5-en-2-one (8-(*Z*)): Colorless oil. IR (neat) 2926, 2856, 1736, 1717, 1639, 1618, 1437, 1358, 1325, 1244, 1209, 1150, 970 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 24.89, 25.04, 25.52, 25.66, 26.41, 27.30, 28.33, 28.61, 60.84, 68.07, 125.54, 132.64, 169.74, 202.34. Found: C, 70.53; H, 9.50%. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H,

9.30%.

3-Acetyl-4-vinyltetrahydropyran-2-one (9, mixture of keto and enol form): IR (neat) 3082, 2964, 2926, 2856, 1741, 1717, 1640, 1614, 1475, 1416, 1383, 1342, 1252, 1167, 1099, 1004, 922 cm^{-1}; ^1H NMR ($CDCl_3$) For the enol form δ 1.76–1.81 (m, 1H), 1.99 (s, 3H), 2.08–2.16 (m, 1H), 3.34–3.37 (m, 1H), 4.26–4.28 (m, 2H), 5.03 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.0 Hz 1H), 5.78–5.85 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.66, 27.62, 27.86, 31.11, 35.61, 37.42, 59.09, 64.82, 68.27, 94.08, 116.56, 117.21, 137.95, 138.55, 167.26, 172.70, 178.28, 202.18. Found: C, 63.97; H, 7.29%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%. (42.8 mg, 0.25 mmol).

Methanolysis of Lactones 2, 5, 6, 7, and 8: The lactone (0.3 mmol) and NaOMe (0.36 mmol) dissolved into MeOH (5 mL) at room temperature under air atmosphere. After stirring for 12 h, MeOH was evaporated and then the residual was washed with brine. After purification of the residual oil, the alcohols **11**, **12**, **13**, **14**, and **15** were obtained, respectively. Although the yields of **13**, **14**, and **15** were low, considerable starting materials **6**, **7**, and **8** were recovered in these cases.



2 n = 1
5 n = 2
6 n = 3
7 n = 4
8 n = 5

11 n = 1 80%
12 n = 2 82%
13 n = 3 51%
14 n = 4 21%
15 n = 5 47% (*E*/*Z* = 3:1)

Methyl 4-(*E*)-2-Acetyl-8-hydroxyoct-4-enoate (11): Colorless oil. IR (neat) 3680–3040 (broad, for OH), 2936, 2870, 1743, 1719, 1641, 1439, 1360, 1153, 1059, 972, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (bs, 1H, for OH), 1.61 (quint, *J* = 6.6 Hz, 2H), 2.07 (q, *J* = 7.1 Hz, 2H), 2.22 (sd, *J* = 0.6 Hz, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 3.49 (t, *J* = 7.2 Hz, 1H), 3.62 (td, *J* = 6.6, 0.8 Hz, 2H), 3.73 (sd, *J* = 0.9 Hz, 3H), 5.31–5.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 28.75, 29.12, 31.20, 32.09, 52.37, 59.57, 62.26, 126.01, 133.07, 169.83, 202.68. Found: C, 61.74; H, 8.63%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H,

8.47%.

Methyl 4-(*E*)-2-Acetyl-9-hydroxynon-4-enoate (12): Colorless oil. IR (neat) 3680–3120 (broad, for OH), 2934, 1744, 1717, 1643, 1620, 1437,1360, 1151, 1059, 972 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41 (quint, *J* = 4.5 Hz, 2H), 1.44 (s, 1H, for OH), 1.55 (quint, *J* = 4.3 Hz, 2H), 2.01 (q, *J* = 4.5 Hz, 2H), 2.23 (s, 3H), 2.54 (td, *J* = 4.3, 2.4 Hz, 2H), 3.49 (t, *J* = 4.5 Hz, 1H), 3.63 (t, *J* = 3.9 Hz, 2H), 3.74 (s, 3H), 5.31–5.38 (m, 1H), 5.48–5.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.31, 29.11, 31.27, 32.06, 32.09, 52.36, 59.68, 62.74, 125.72, 133.50, 169.85, 202.72. Found: C, 63.08; H, 8.64%. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83%.

Methyl 4-(*E*)-2-Acetyl-10-hydroxydec-4-enoate (13): Colorless oil. IR (neat) 3680–3040 (broad, for OH), 2930, 2856, 1740, 1719, 1437, 1360, 1151, 1055, 972 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–1.40 (m, 4H), 1.50 (s, 1H, for OH), 1.55 (quint, *J* = 7.0 Hz, 2H), 1.99 (q, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 2.51–2.57 (m, 2H), 3.49 (t, *J* = 7.0 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 5.29–5.37 (m, 1H), 5.47–5.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.07, 28.93, 29.07, 31.30, 32.30, 32.53, 52.35, 59.72, 62.91, 125.51, 133.70, 169.87, 202.80. Found: C, 64.36; H, 9.38%. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%.

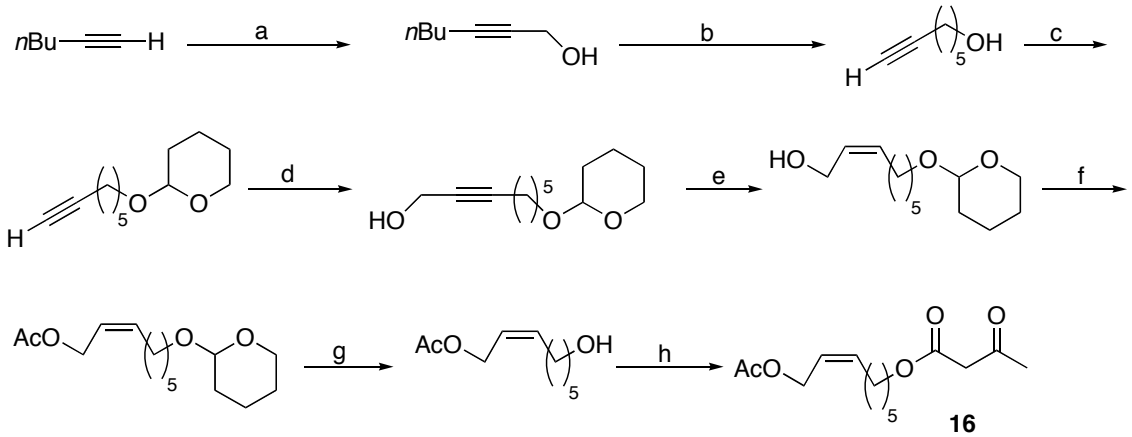
Methyl 4-(*E*)-2-Acetyl-11-hydroxyundec-4-enoate (14): Colorless oil. IR (neat) 3680–3120 (broad, for OH), 2934, 1744, 1717, 1643, 1620, 1437,1360, 1151, 1059, 972 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25–1.37 (m, 6H), 1.51 (bs, 1H, for OH), 1.56 (m, 2H), 1.97 (q, *J* = 6.5 Hz, 2H), 2.22 (s, 3H), 2.51–2.55 (m, 2H), 3.49 (t, *J* = 7.5 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.73 (s, 3H), 5.28–5.36 (m, 1H), 5.45–5.36 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.50, 28.74, 29.12, 29.16, 31.30, 32.30, 32.66, 52.34, 59.70, 62.93, 125.31, 133.88, 169.87, 202.83. HRMS (ESI) $[M+H]^+$ Found: 257.1736, Calcd for $C_{15}H_{25}O_5$: 257.1747.

Methyl 4-(*E*)-2-Acetyl-12-hydroxydodec-4-enoate (15-(*E*)): Colorless oil. IR (neat) 3680–3100 (broad, for OH), 2928, 2856, 1744, 1717, 1624, 1437, 1360, 1221, 1151, 1057, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–1.40 (m, 8H), 1.42 (bs, 1H, for OH), 1.56 (quint., *J* = 6.5 Hz, 2H), 1.96 (q, *J* = 7.0 Hz, 2H), 2.22 (s, 3H), 2.51–2.55 (m, 2H), 3.49 (t, *J* = 7.5 Hz, 1H), 3.64 (t, *J* = 7.0 Hz, 2H), 3.73 (s, 3H), 5.28–5.36 (m, 1H), 5.46–5.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.62, 28.92, 29.14, 29.15, 29.20, 31.30, 32.36, 32.70,

52.34, 59.71, 62.99, 125.23, 133.95, 169.87, 202.83.

Methyl 4-(*Z*)-2-Acetyl-12-hydroxydodec-4-enoate (15-(*Z*)): Colorless oil. IR (neat) 3680–3100 (broad, for OH), 2928, 2856, 1744, 1717, 1624, 1437, 1360, 1221, 1151, 1057, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35–1.41 (m, 8H), 1.42 (bs, 1H, for OH), 1.53–159 (m, 2H), 2.02–2.08 (m, 2H), 2.24 (s, 3H), 2.59 (t, *J* = 7.5 Hz, 2H), 3.49 (t, *J* = 7.5 Hz, 1H), 3.64 (t, *J* = 7.0 Hz, 2H), 3.74 (s, 3H), 5.22–5.30 (m, 1H), 5.42–5.50 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 26.10, 26.68, 26.86, 27.14, 29.35, 31.25, 32.29, 32.41, 52.41, 59.40, 61.31, 124.54, 133.17, 169.90, 202.78. Found: C, 66.34; H, 9.76%. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69%. The *E*/*Z* ratio (ca. 3 : 1) was determined by ^1H NMR

6-(*Z*)-8-Acetoxyoct-6-enyl 3-Oxobutyrate (16): IR (neat) 2937, 2860, 1740, 1736, 1721, 1643, 1560, 1460, 1412, 1373, 1315, 1232, 1151, 1028, 964 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33–1.44 (m, 4H), 1.66 (quint., *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 2.12 (q, *J* = 7.0 Hz, 2H), 2.28 (s, 3H), 3.46 (s, 2H), 4.14 (t, *J* = 6.5 Hz, 2H), 4.62 (d, *J* = 7.0 Hz, 2H), 5.52–5.57 (m, 1H), 5.60–5.66 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.98, 25.34, 27.30, 28.27, 28.89, 30.15, 50.08, 60.29, 65.32, 123.61, 134.84, 167.16, 171.11, 200.59. Found: C, 61.80; H, 8.17%. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20%. The synthetic route to **16** is shown below.



a) *n*BuLi/Hex, THF, –78 ºC to RT then –78 ºC, $(HCHO)_n$, reflux, 87%;

b) KH, $H_2N(CH_2)_3NH_2$, RT, 70%; c) cat. *p*-TsOH•H_2O, 3,4-Dihydro-2*H*-pyrane, THF, 91%

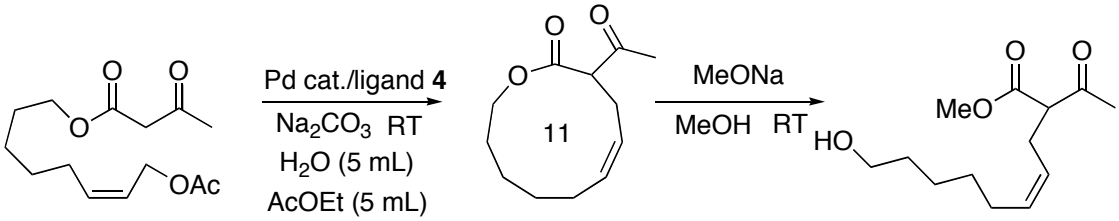
d) *n*BuLi/Hex, THF, –78 ºC to RT then –78 ºC, $(HCHO)_n$, reflux, 84%;

e) 1) *i*BuMgCl/Et_2O, cat.Cp_2TiCl_2, 0 ºC to RT; 2) sat. NH_4Cl aq.; 3) $Co_2(CO)_8$, Hex, overnight;

f) Ac_2O, pyridine, 90%; g) cat. *p*-TsOH•H_2O, MeOH, 77%; h) Diketene, cat. AcONa, THF, reflux, 97%

The step (e) needs to be commented. After the hydromagnesation, unfortunately, an inseparable mixture of the desired (*Z*)-olefin and the unreacted starting alkyne was obtained. These compounds have the same R_f values. Hence we converted the alkyne into its cobalt complex by treating the mixture with $Co_2(CO)_{12}$ to change the R_f of the alkyne. The R_f value of the cobalt complex is higher than that of the desired olefin.

5-(*Z*)-3-Acetyloxacycloundec-5-en-2-one (17):



16 **17** 73% **18** 53%

Colorless oil. IR (neat) 3003, 2932, 2860, 1734, 1717, 1643, 1618, 1452, 1358, 1330, 1244, 1153, 976 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14–1.19 (m, 1H), 1.38–1.44 (m, 2H), 1.52–1.60 (m, 2H), 1.73–1.82 (m, 1H), 1.89–1.96 (m, 1H), 2.26 (s, 3H), 2.28–2.32 (m, 1H), 2.36–2.45 (m, 1H), 2.85–2.92 (m, 1H), 3.48 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.89–3.93 (m, 0.73H), 4.01–4.03 (m, *J* = 5.5 Hz, 0.27), 4.48 (td, J = 11.0, 1.5 Hz, 1H), 5.32–5.36 (m, 1H), 5.38–5.44 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.87, 23.70, 26.01, 26.28, 28.03, 28.76, 61.02, 65.37, 125.75, 133.64, 169.29, 202.45. Found: C, 68.54; H, 8.63%. Calcd for $C_{12}H_{18}O_3$: C, 68.40; H, 8.48%. (77.0 mg, 0.37 mmol).

Methyl 4-(*Z*)-2-Acetyl-10-hydroxydec-4-enoate (18): Colorless oil. IR (neat) 3680–3120 (broad, for OH), 3009, 2932, 2858, 1742, 1719, 1612, 1437, 1360, 1227, 1151, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35–1.41 (m, 4H), 1.52 (bs, 1H, for OH), 1.55–1.61 (m, 2H), 2.05–2.10 (m, 2H), 2.24 (s, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 3.49 (t, *J* = 7.5 Hz, 1H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 5.24–5.30 (m, 1H), 5.44–5.50 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.34, 26.12, 27.11, 29.19, 29.30, 32.59, 52.44, 59.37, 62.92, 124.77, 132.94, 169.90, 202.77. Found: C, 64.26; H, 8.95%. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%.