Cross-Metathesis Between α -Methylene- γ -butyrolactone and olefins: A Dramatic Additive Effect

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Supporting Information

General: TLC was performed on Merck 60F₂₅₄ silica gel plates and visualized either with a UV lamp (254 nm), or by using a solution of *p*-anisaldehyde/sulfuric acid/acetic acid in EtOH followed by heating. Flash chromatography was performed with Merck Geduran Si60 silica gel (40-63 μ m). Infrared (IR) spectra were recorded on a Perkin-Elmer 298 or on a Bruker TENSOR™ 27 (IRFT), wave-numbers are indicated in cm⁻¹. ¹H NMR spectra were recorded on a Bruker AVANCE 400 at 400 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non equivalent resonances), integration. ¹³C NMR spectra were recorded on a Bruker AC 300 at 75 MHz or on a Bruker AVANCE 400 at 100 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (CDCl₃ δ 77.0 ppm), multiplicity with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = CH₂, q = CH₃). Mass spectra with electronic impact (MS) were recorded from a Hewlett-Packard tandem 5890A GC (12 m capillary column) – 5971 MS (70 eV). High resolution mass spectra (HRMS) were performed by the Groupe de Spectrométrie de Masse de l'Université Pierre et Marie Curie (Paris). Elemental analyses were performed by the Service de Microanalyse of ICSN (Gif sur Yvette, France). All the reactions were performed under an argon atmosphere. Grubbs' second generation catalyst [Ru]-II was prepared using literature procedure.^[1]

[1] Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168-8179.

General Procedure for the CM between α -methylene- γ -butyrolactone and, various olefins

Method A: To a stirred solution of α -methylene- γ -butyrolactone **4** (0.5 mmol, 44 μ L) and olefin (0.75 mmol, 1.5 equiv.) in CD_2Cl_2 or CH_2Cl_2 (1.2 mL) was added the additive (0.025 mmol, 5 mol%) and Ru-[**II**] (0.012 mmol, 2.5 mol%). The reaction was heated at 40 $^\circ\text{C}$ under nitrogen for 14 hours. The solvent was then removed under reduced pressure and the residue purified by flash column chromatography on silica gel (1:20 EtOAc:Hexanes to 1:4 MeOH:EtOAc) to yield the corresponding substituted lactones as colorless oils (Table 2).

Method B: To a stirred solution of α -methylene- γ -butyrolactone **4** (0.5 mmol, 44 μ L) and olefin (0.75 mmol, 1.5 equiv.) in CD_2Cl_2 or CH_2Cl_2 (1.2 mL) was added the additive (0.025 mmol, 5 mol%) and Ru-[**II**] (0.012 mmol, 2.5 mol%). The reaction was heated at 40 $^\circ\text{C}$ under nitrogen for 7 hours and Ru-[**III**] (0.012 mmol, 2.5 mol%) was subsequently added and the reaction mixture was heated at reflux for an extra 7 hours. The solvent was then removed under reduced pressure and the residue purified by flash column chromatography on silica gel (1:20 EtOAc:Hexanes to 1:4 MeOH:EtOAc) to yield the corresponding substituted lactones as colorless oils (Table 2).

Dihydro-3-(3-methylbutylidene)furan-2(3H)-one (**6a**):

IR: $\nu = 2956, 2870, 1751, 1679, 1381, 1238, 1199, 1145, 1026 \text{ cm}^{-1}$; ^1H NMR: $\delta = 6.70$ (dddd, $J = 2.5, 3.0, 7.5, 8.0 \text{ Hz}$, 1H), 4.31 (t_{app} , $J = 7.0 \text{ Hz}$, 2H), 2.79 (dddd, $J = 1.0, 1.5, 7.0, 7.5 \text{ Hz}$, 2H), 2.02 (td, $J = 2.0, 7.5 \text{ Hz}$, 2H), 1.75 (m, 1H), 0.89 (s, 3H), 0.87 (s, 3H); ^{13}C NMR: $\delta = 171.3$ (s), 140.0 (s), 125.8 (d), 65.4 (t), 39.4 (t), 28.1 (d), 25.2 (t), 22.4 (q); EIMS m/z (relative intensity) 154 (M^+ , 12), 112 (100), 99 (62), 83 (21), 67 (29), 53 (20); Anal. Found: C, 70.12; H, 9.23. Calcd for $\text{C}_9\text{O}_2\text{H}_{14}$: C, 70.10; H, 9.15.

Dihydro-3-(2-(4-hydroxy-3-methoxyphenyl)ethylidene) furan-2(3*H*)-one (6b)

IR: ν = 3396, 2920, 1742, 1676, 1601, 1513, 1430, 1379, 1268, 1205, 1177, 1150, 1122, 1027 cm^{-1} ; ^1H NMR: δ = 6.82 (m, 1H), 6.76 (d, J = 8.5 Hz, 1H), 6.62-6.57 (m, 2H), 5.66 (1H, br, OH), 4.31 (t_{app} , J = 7.5 Hz, 2H), 3.78 (s, 3H), 3.38 (d, J = 7.5 Hz, 2H), 2.84-2.80 (m, 2H); ^{13}C NMR: δ = 171.3 (s), 146.8 (s), 144.5 (s), 138.9 (d), 129.4 (s), 125.8 (s), 121.1 (d), 114.5 (d), 111.0 (d), 65.5 (t), 56.0 (q), 35.9 (t), 25.1 (t); EIMS m/z (relative intensity) 234 (M^+ , 100), 189 (60), 175 (14), 157 (20), 129 (21), 115 (18); HRMS (EI) calcd for $\text{C}_{13}\text{O}_4\text{H}_{14}$ ($\text{M}+\text{H}^+$): 235.09649; Found: 235.09674.

Dihydro-3-(2-(4-methoxyphenyl)ethylidene) furan-2(3*H*)-one (6c)

Major isomer (*E*): IR: ν = 2915, 2836, 1747, 1678, 1610, 1510, 1379, 1244, 1173, 1026 cm^{-1} ; ^1H NMR: δ = 7.02 (d, J = 9.0 Hz, 2H), 6.84 (ddd, J = 2.5, 3.0, 7.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 2H), 4.32 (t_{app} , J = 7.5 Hz, 2H), 3.72 (s, 3H), 3.41 (d, J = 7.5 Hz, 2H), 2.84 (dd, J = 1.5, 7.5 Hz, 1H), 2.82 (dd, J = 1.5, 7.5 Hz, 1H); ^{13}C NMR: δ = 171.2 (s), 158.5 (s), 138.9 (d), 129.6 (d), 129.4 (d), 125.8 (s), 114.1 (d), 65.4 (t), 55.3 (q), 33.3 (t), 25.1 (t); EIMS m/z (relative intensity) 218 (M^+ , 63), 173 (100), 159 (12), 158 (33), 144 (15), 128 (16), 115 (18); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ ($\text{M}+\text{H}^+$): 219.10157; Found: 219.10184.

Minor isomer (Z): IR: ν = 2923, 2854, 1746, 1670, 1610, 1510, 1375, 1246, 1164, 1078, 1025 cm^{-1} ; ^1H NMR: δ = 7.08 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 6.26 (dddd, J = 2.0, 2.5, 7.5, 8.0 Hz, 1H), 4.27 (t_{app} , J = 7.5 Hz, 2H), 3.95 (dd, J = 2.0, 8.0 Hz, 1H), 3.92 (dd, J = 2.0, 8.0 Hz, 1H), 3.72 (s, 3H), 2.89-2.81 (m, 2H); ^{13}C NMR: δ = 170.2 (s), 158.2 (s), 142.3 (d), 131.3 (s), 129.7 (d), 123.3 (s), 114.1 (d), 65.3 (t), 55.3 (q), 32.7 (t), 29.1 (t); EIMS m/z (relative intensity) 218 (M^+ , 87), 173 (100), 159 (30), 158 (32), 144 (23), 128 (17), 121 (17), 115 (23); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ ($\text{M}+\text{H}^+$): 219.10157; Found: 219.10181.

3-Benzylidene-dihydrofuran-2(3H)-one (6d)

IR: ν = 2924, 1735, 1648, 1224, 1173, 1026 cm^{-1} ; ^1H NMR: δ = 7.52 (t, J = 2.5 Hz, 1H), 7.47-7.42 (m, 2H), 7.40-7.32 (m, 3H), 4.41 (t_{app} , J = 7.0 Hz, 2H), 3.19 (ddd, J = 2.5, 7.0, 7.5 Hz, 2H); ^{13}C NMR: δ = 172.5 (s), 136.7 (d), 134.7 (s), 130.0 (d), 129.8 (d), 128.9 (d), 123.5 (s), 65.4 (t), 27.4 (t); EIMS m/z (relative intensity) 174 (M^+ , 100), 173 (99), 146 (11), 129 (42), 116 (68), 115 (89), 89 (10), 63 (10), 51 (10); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2$ ($\text{M}+\text{H}^+$): 175.07536; Found: 175.07552.

3-(4-Fluorobenzylidene)-dihydrofuran-2(3H)-one (6e)

IR: ν = 2923, 1741, 1655, 1601, 1508, 1360, 1222, 1176, 1052, 1026 cm^{-1} ; ^1H NMR: δ = 7.44-

7.38 (m, 3H), 7.05 (t_{app}, $J = 8.5$ Hz, 2H), 4.39 (t_{app}, $J = 7.5$ Hz, 2H), 3.15 (td, $J = 2.7, 7.5$ Hz, 2H); ^{13}C NMR: $\delta = 172.4$ (s), 163.2 (s, $^1J_{\text{C,F}} = 1000$ Hz), 135.2 (d), 131.9 (d, $^3J_{\text{C,F}} = 36$ Hz), 130.9 (s, $^4J_{\text{C,F}} = 12$ Hz), 123.2 (s), 116.1 (d, $^2J_{\text{C,F}} = 88$ Hz), 65.4 (t), 27.2 (t); EIMS m/z (relative intensity) 192 (M^+ , 100), 164 (13), 147 (41), 133 (90), 115 (7), 107 (9); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ ($\text{M}+\text{Na}^+$): 215.04788; Found: 215.04784.

3-(4-Methoxybenzylidene)-dihydrofuran-2(3H)-one (6f)

IR: $\nu = 2920, 2843, 1730, 1651, 1598, 1511, 1306, 1257, 1231, 1172, 1055, 1027$ cm^{-1} ; ^1H NMR: $\delta = 7.45$ (t_{app}, $J = 2.7$ Hz, 1H), 7.42-7.36 (m, 2H), 6.89 (m, 2H), 4.38 (t_{app}, $J = 7.5$ Hz, 2H), 3.78 (s, 3H), 3.14 (td, $J = 2.7, 7.3$ Hz, 2H); ^{13}C NMR: $\delta = 172.9$ (s), 160.8 (s), 136.4 (d), 131.8 (d), 127.4 (d), 120.6 (s), 114.1 (d), 65.4 (t), 55.4 (q), 27.4 (t); EIMS m/z (relative intensity) 204 (M^+ , 100), 176 (14), 159 (29), 146 (39), 131 (18), 115 (14), 103 (20); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ ($\text{M}+\text{Na}^+$): 227.06787; Found: 227.06776.

Dihydro-3-(3-*t*-butyldimethylsilylhydroxy-3-phenylpropylidene)-furan-2(3H)-one (6g)

Major isomer (*E*): IR: $\nu = 2928, 2856, 1755, 1681, 1471, 1253, 1180, 1086, 1067, 1029$ cm^{-1} ; ^1H NMR: $\delta = 7.48$ -7.30 (m, 5H), 6.90 (dddd, $J = 2.8, 3.0, 7.6, 7.8$ Hz, 1H), 4.96 (t_{app}, $J = 5.8$ Hz, 1H), 4.38 (t_{app}, $J = 7.6$ Hz, 2H), 2.83-2.65 (m, 4H), 0.99 (s, 9H), 0.15 (s, 3H), 0.00 (s, 3H); ^{13}C NMR: $\delta = 170.8$ (s), 144.2 (s), 136.6 (d), 128.3 (s), 128.2 (d), 127.4 (d), 125.7 (d), 73.7 (d), 65.3 (t), 41.9 (t), 25.7 (q), 25.1 (t), 18.2 (s), -4.74 (q), -5.0 (q); EIMS m/z (relative intensity) 275 (53), 221 (100), 169 (93), 75 (24), 73 (42); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{29}\text{O}_3\text{Si}$ ($\text{M}+\text{H}^+$): 333.18805; Found: 333.18856.

Minor isomer (Z): IR: ν = 2955, 2928, 2856, 1755, 1673, 1472, 1257, 1173, 1085, 1067, 1028 cm^{-1} ; ^1H NMR: δ = 7.31-7.18 (m, 5H), 6.27 (ddd, J = 2.0, 2.5, 7.5 Hz, 1H), 4.82 (dd, J = 4.5, 7.0 Hz, 1H), 4.25 (dd, J = 3.5, 7.5 Hz, 2H), 3.12 (m, 1H), 3.03 (m, 1H), 2.85 (dd, J = 2.0, 7.5 Hz, 2H), 0.86 (s, 9H), 0.00 (s, 3H), -0.13 (s, 3H); ^{13}C NMR: δ = 170.0 (s), 144.4 (s), 140.1 (d), 128.2 (d), 127.1 (d), 126.0 (d), 124.9 (s), 74.1 (t), 65.3 (t), 38.2 (t), 29.2 (t), 25.8 (q), 18.2 (s), -4.6 (q), -5.2 (q); EIMS m/z (relative intensity) 275 (78), 221 (99), 169 (100), 75 (21), 73 (44); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{29}\text{O}_3\text{Si}$ ($\text{M}+\text{H}^+$): 333.18805; Found: 333.18836.

Dihydro-3-(3-(methoxymethoxy)-3-phenylpropylidene)furan-2(3H)-one (6h)

IR: ν = 2927, 2856, 1752, 1681, 1493, 1454, 1379, 1202, 1181, 1149, 1097, 1024 cm^{-1} ; ^1H NMR: δ = 7.34-7.20 (m, 5H), 6.72 (m, 1H), 4.68 (m, 1H), 4.48 (s, 2H), 4.21 (ddd, J = 1.5, 7.0, 8.0 Hz, 2H), 3.27 (s, 3H), 2.68-2.47 (m, 4H); ^{13}C NMR: δ = 170.9 (s), 140.8 (s), 136.2 (d), 128.6 (d), 128.1 (d), 127.6 (s), 126.7 (d), 94.1 (t), 76.3 (d), 65.4 (t), 55.7 (q), 38.8 (t), 25.1 (t); EIMS m/z (relative intensity) 201 (13), 156 (100), 151 (82), 141 (20), 126 (96), 115 (22), 105 (36), 91 (24), 77 (28); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$ ($\text{M}+\text{H}^+$): 263.12779; Found: 263.12829.

Dihydro-3-(3,4-di-(*t*-butylsilylhydroxy)-butylidene)furan-2(3H)-one (6i)

Major isomer (*E*): IR: $\nu = 2928, 2856, 1759, 1682, 1471, 1361, 1252, 1188, 1102, 1028 \text{ cm}^{-1}$; ^1H NMR: $\delta = 6.76$ (m, 1H), 4.31 (ddd, $J = 2.0, 2.5, 6.5 \text{ Hz}$, 2H), 3.77 (m, 1H), 3.50 (dd, $J = 5.0, 10.4 \text{ Hz}$, 1H), 3.34 (dd, $J = 7.0, 10.4 \text{ Hz}$, 1H), 2.85-2.78 (m, 2H), 2.46 (m, 1H), 2.27 (m, 1H), 0.84 (s, 9H), 0.82 (s, 9H), 0.00 (s, 6H), -0.01 (s, 6H); ^{13}C NMR: $\delta = 170.9$ (s), 137.6 (s), 126.9 (d), 71.9 (d), 66.7 (t), 65.3 (t), 35.4 (t), 25.9 (q), 25.8 (q), 25.3 (t), 18.3 (s), 18.0 (s), -4.5 (q), -4.8 (q), -5.3 (q), -5.4 (q); EIMS m/z (relative intensity) 399 (M^+ , 0.1), 343 (100), 289 (6), 255 (8), 211 (18), 147 (58), 133 (12), 73 (30); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{29}\text{O}_3\text{Si}$ ($\text{M}+\text{H}^+$): 423.23573; Found: 423.23564.

Minor isomer (*Z*): ^1H NMR: $\delta = 6.33$ (m, 1H), 4.26 (t, $J = 7.5 \text{ Hz}$, 2H), 3.78 (m, 1H), 3.54-3.39 (m, 2H), 2.95-2.80 (m, 4H), 0.84 (s, 9H), 0.83 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H), 0.00 (s, 3H), -0.01 (s, 3H); ^{13}C NMR: $\delta = 170.0$ (s), 140.5 (d), 124.4 (s), 72.5 (d), 67.2 (t), 65.2 (t), 32.4 (t), 29.3 (t), 25.9 (q), 25.8 (q), 18.3 (s), 18.1 (s), -4.3 (q), -4.8 (q), -5.3 (q), -5.4 (q); EIMS m/z (relative intensity), 343 (100), 289 (10), 255 (12), 211 (15), 147 (62), 133 (8), 73 (28).

Diethyl-2-(dihydro-2-oxofuran-3(2*H*)-ylidene)ethylphosphonate (6j**)** (non separable mixture of isomers)

Major isomer (*E*): IR: $\nu = 2983, 2915, 1751, 1680, 1443, 1380, 1341, 1225, 1160, 1020, 960 \text{ cm}^{-1}$; ^1H NMR: $\delta = 6.63$ (m, 1H), 4.34 (t_{app} , $J = 7.0 \text{ Hz}$, 2H), 4.12-3.98 (m, 4H), 2.98-2.82 (m, 2H), 2.67 (dd, $J = 8.5 \text{ Hz}$, $J_{\text{H,P}} = 23.6 \text{ Hz}$, 2H), 1.27 (t, $J = 7.0 \text{ Hz}$, 6H); ^{13}C NMR: $\delta = 170.3$ (s, $^4J_{\text{C,P}} = 16 \text{ Hz}$), 129.8 (s, $^3J_{\text{C,P}} = 56 \text{ Hz}$), 128.8 (d, $^2J_{\text{C,P}} = 44 \text{ Hz}$), 65.4 (t), 62.4 (t, $^4J_{\text{C,P}} = 28 \text{ Hz}$), 28.9 (t, $^1J_{\text{C,P}} = 552 \text{ Hz}$), 25.1 (t, $^2J_{\text{C,P}} = 12 \text{ Hz}$), 16.4 (q, $^4J_{\text{C,P}} = 24 \text{ Hz}$); EIMS m/z (relative intensity) 248 (M^+ , 42), 230 (22), 202 (23), 174 (30), 146 (15), 138 (72), 111 (100), 94 (37), 81 (43), 66 (35), 53 (29); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{17}\text{O}_5\text{P}$ ($\text{M}+\text{H}^+$): 249.08864; Found: 249.08901.

Minor isomer (Z): ^1H NMR: δ = 6.19 (m, 1H), 4.28 (t_{app}, J = 7.0 Hz, 2H), 4.12-3.98 (m, 4H), 3.37 (dd, J = 8.0 Hz, $J_{H,P}$ = 23.1 Hz, 2H), 2.98-2.82 (m, 2H), 1.25 (t, J = 7.0 Hz, 6H); ^{13}C NMR: δ = 169.7 (s, $^4J_{C,P}$ = 15 Hz), 131.5 (d, $^2J_{C,P}$ = 48 Hz), 127.0 (s, $^3J_{C,P}$ = 56 Hz), 65.4 (t), 62.1 (s, $^4J_{C,P}$ = 28 Hz), 29.0 (t, $^2J_{C,P}$ = 8 Hz), 25.6 (t, $^1J_{C,P}$ = 548 Hz), 16.3 (q, $^4J_{C,P}$ = 24 Hz); EIMS m/z (relative intensity) 248 (M^+ , 56), 230 (30), 220 (16), 202 (32), 174 (51), 138 (88), 112 (64), 111 (100), 94 (81), 81 (67), 66 (69), 53 (42).

Dihydro-3-(2-(trimethylsilyl)ethylidene)-furan-2(3H)-one (6k)

Major isomer (E): IR: ν = 2955, 1752, 1666, 1377, 1248, 1225, 1130, 1027, 1007 cm^{-1} ; ^1H NMR: δ = 6.80 (dddd, J = 2.5, 3.0, 9.0, 9.5 Hz, 1H), 4.27 (t_{app}, J = 7.5 Hz, 2H), 2.72 (dddd, J = 1.0, 1.5, 6.5, 7.0 Hz, 2H), 1.65 (d, J = 9.0 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR: δ = 172.6 (s), 141.3 (s), 123.5 (d), 66.7 (t), 26.7 (t), 25.1 (t), 0.00 (q); EIMS m/z (relative intensity) 184 (M^+ , 38), 169 ($\text{M}-\text{CH}_3^+$, 36), 75 (24), 73 (100); HRMS (EI) calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Si}$ ($\text{M}+\text{H}^+$): 185.09923; Found: 185.09932.

Minor isomer (Z): IR: ν = 2928, 2856, 1749, 1670, 1375, 1174, 1078, 1025 cm^{-1} ; ^1H NMR: δ = 6.30 (dddd, J = 2.0, 2.3, 9.5, 9.5 Hz, 1H), 4.24 (t_{app}, J = 7.0 Hz, 2H), 2.85 (m, 2H), 2.33 (dd, J = 1.5, 9.5 Hz, 1H), 2.31 (dd, J = 1.5, 9.5 Hz, 1H), 0.00 (s, 9H); ^{13}C NMR: δ = 171.9 (s), 140.2 (d), 123.4 (s), 66.4 (t), 26.7 (t), 25.1 (t), 0.00 (q); EIMS m/z (relative intensity) 184 (M^+ , 32), 169 ($\text{M}-\text{CH}_3^+$, 38), 75 (22), 73 (100); HRMS (EI) calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Si}$ ($\text{M}+\text{H}^+$): 185.09923; Found: 185.09946.

Dimethyl-2-(2-(dihydro-2-oxofuran-3(2*H*))ylidene)ethyl)malonate (6l) (non separable mixture of isomers)

Major isomer (*E*): IR: $\nu = 2973, 1733, 1683, 1436, 1215, 1158, 1087, 1045 \text{ cm}^{-1}$; ^1H NMR: $\delta = 6.54$ (dddd, $J = 2.5, 3.0, 7.5, 8.0 \text{ Hz}$, 1H), 4.32 (t_{app}, $J = 7.5 \text{ Hz}$, 2H), 3.69 (s, 6H), 3.49 (t, $J = 7.5 \text{ Hz}$, 1H), 2.91-2.83 (m, 2H), 2.72 (t_{app}, $J = 7.5 \text{ Hz}$, 2H); ^{13}C NMR: $\delta = 170.7$ (s), 168.7 (s), 134.9 (d), 128.5 (s), 65.5 (t), 52.9 (q), 50.1 (d), 29.4 (t), 22.7 (d); EIMS m/z (relative intensity) 210 (13), 179 (22), 134 (100), 123 (28), 79 (17); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_6$ ($\text{M}+\text{H}^+$): 243.08631; Found: 243.08660.

Minor isomer (*Z*): ^1H NMR: $\delta = 6.19$ (m, 1H), 4.26 (t_{app}, $J = 7.5 \text{ Hz}$, 2H), 3.68 (s, 6H), 3.22 (t, $J = 7.5 \text{ Hz}$, 1H), 2.91-2.83 (m, 2H), 2.72 (t_{app}, $J = 7.5 \text{ Hz}$, 2H); ^{13}C NMR: $\delta = 169.7$ (s), 169.0 (s), 138.0 (d), 126.3 (s), 65.4 (t), 52.7 (q), 50.8 (d), 29.7 (t), 26.3 (d); EIMS m/z (relative intensity) 242 (M^+ , 0.08), 210 (14), 178 (8), 134 (100), 123 (29), 79 (15).

3-(Dihydro-2-oxofuran-3(2*H*)-ylidene)propyl acetate (6m)

Major isomer (*E*): IR: $\nu = 2921, 1734, 1682, 1438, 1381, 1365, 1227, 1193, 1034, 1017 \text{ cm}^{-1}$; ^1H NMR: $\delta = 6.72$ (dddd, $J = 2.5, 3.0, 7.0, 7.5 \text{ Hz}$, 1H), 4.38 (t_{app}, $J = 7.0 \text{ Hz}$, 2H), 4.17 (t, $J = 6.5 \text{ Hz}$, 2H), 2.95-2.82 (m, 2H), 2.55-2.42 (m, 2H), 2.04 (s, 3H); ^{13}C NMR: $\delta = 170.9$ (s), 170.8 (s), 135.9 (d), 127.8 (s), 65.4 (t), 62.2 (t), 29.6 (t), 25.2 (t), 20.9 (q); EIMS m/z (relative intensity) 124 ($\text{M}-\text{CH}_3\text{COO}^+$, 100), 112 (76), 95 (7), 79 (16), 67 (27), 53 (9); HRMS (EI) calcd for $\text{C}_9\text{H}_{12}\text{O}_4$ ($\text{M}+\text{H}^+$): 185.08084; Found: 185.08100.

Minor isomer (Z): IR: $\nu = 2924, 2854, 1738, 1674, 1442, 1378, 1232, 1188, 1025 \text{ cm}^{-1}$; ^1H NMR: $\delta = 6.17$ (dddd, $J = 2.0, 2.5, 7.0, 7.5 \text{ Hz}$, 1H), 4.27 (t_{app} , $J = 7.5 \text{ Hz}$, 2H), 4.10 (t, $J = 6.0 \text{ Hz}$, 2H), 3.04-2.95 (m, 2H), 2.92-2.84 (m, 2H), 1.99 (s, 3H); ^{13}C NMR: $\delta = 171.0$ (s), 169.8 (s), 138.6 (d), 125.9 (s), 65.4 (t), 63.2 (t), 29.0 (t), 27.0 (t), 20.9 (q); EIMS m/z (relative intensity) 184 (M^+ , 0.2), 124 ($\text{M}-\text{CH}_3\text{COO}^+$, 96), 112 (100), 95 (9), 79 (18), 67 (20), 53 (11); HRMS (EI) calcd for $\text{C}_9\text{H}_{12}\text{O}_4$ ($\text{M}+\text{H}^+$): 185.08084; Found: 185.08108.

6a

6a

6b

6b

6c (E)

6c (*E*)

6d

6d

6e

6e

6f

6f

6g (E)

6g (*E*)

6h

6j (E)

+

6j (Z)

170.3475
170.3078
169.7917
169.7520

131.5753
131.4641
129.8999
129.7649
128.9153
128.7962
127.0811
126.9382

77.4228
77.1052
76.7876

65.3696
62.4476
62.3761
62.2094
62.1458

29.6464
29.0192
28.9953
28.2648
26.2480
25.1602
25.1284
24.8823
16.4418
16.3862
16.2989

6k (E)

6k (Z)

6f (E)

6f (Z)

61 (E) +
170.704
169.640
169.045
168.735

61 (Z)
137.943
134.8784
128.4786
126.3506

77.3990
77.0814
76.7638

65.5046
65.4331

52.8637
52.6731
50.7595
50.0846

29.6702
29.3844
28.9556
26.2798
25.0808

6m (E)

6m (E)

6m (Z)