Supporting Information

For the article entitled

One Step Synthesis of γ-Alkylidenebutenolides from Simple Vinyl Carboxylic Acids and Alkenes

Chunbing Yu, Jian Zhang* and Guofu Zhong*

College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China

zhangjian@hznu.edu.cn; zgf@hznu.edu.cn

Supporting Information

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**General methods**

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on Bruker AMX 400 spectrophotometer (CDCl$_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe$_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe$_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm$^{-1}$). [RhCp*Cl$_2$]$_2$ and Cu(OAc)$_2$·H$_2$O were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from Alfa Aesar (China) Chemical Co., Ltd. and used without further purification. Vinyl carboxylic acids were purchased or prepared following the procedure reported by literatures$^1$. 

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SI-2
General Procedure for the Synthesis of γ-Alkylidenebutenolides

An oven-dried vial was charged with [RhCp*Cl₂]₂ (6.2 mg, 2.0 mol %), Cu(OAc)₂·H₂O (2.0 eq, 1.0 mmol), CH₃CN (2.5 mL). Then, vinyl carboxylic acid 1 (0.5 mmol) and alkene 2 (1.0 mmol) was added into the solution in sequence. The vial was sealed under argon and heated to 120°C with stirring for 16~18 hours. After cooling down, the mixture was directly applied to a flash column chromatography on silica gel for separation (EtOAc/petroleum ether mixtures).

Characterization Data

![Butyl (Z)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3aa-Z)](image)

Following the general procedure, 3aa-Z was obtained as a colorless oil (48.3 mg, 0.23 mmol, 46%). ¹H NMR (CDCl₃): δ = 8.02 (s, 1H), 5.82 (s, 1H), 4.19 (t, 2H, J = 6.5 Hz), 2.10 (s, 3H), 1.64-1.70 (m, 2H), 1.38-1.45 (m, 2H), 0.96 (t, 3H, J = 7.5 Hz). ¹³C NMR (CDCl₃): δ = 169.07, 165.39, 159.67, 135.89, 135.46, 100.71, 64.81, 30.61, 19.13, 13.67, 11.10. HRMS (ESI): m/z calculated for C₁₁H₁₄O₄ [M+H]⁺: 211.0965, found: 211.0967. FTIR (KBr, cm⁻¹): 3850.9, 2960.6, 1790.4, 1682.4, 1621.4, 1455.3, 1366.2, 1172.1, 1039.8, 911.2, 847.3, 755.7.

![Butyl (E)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3aa-E)](image)

Butyl (2,5-dihydro-4-methyl-5-oxo-2-furanyl) acetate (4aa)²
Following the general procedure, an inseparable mixture of 3aa-E and 4aa were obtained as an oil.

3aa-E (14.7 mg, 0.07 mmol, 14%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.07 (s, 1H), 5.36 (s, 1H), 4.21 (t, 2H, $J$ = 7.0 Hz), 2.08 (s, 3H), 1.60-1.69 (m, 2H), 1.36-1.43 (m, 2H), 0.93-0.97 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 169.39, 163.55, 155.69, 138.21, 134.74, 100.09, 64.85, 30.62, 19.11, 13.69, 10.93. HRMS (ESI): m/z calculated for C$_{11}$H$_{14}$O$_4$ [M+H]$^+$: 211.0965, found: 211.0961. FTIR (KBr, cm$^{-1}$): 3686.7, 3617.1, 3473.0, 3383.4, 2958.7, 2353.8, 1887.7, 1667.3, 1470.8, 1264.4, 977.1, 756.0.

4aa (14.8 mg, 0.07 mmol, 14%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.16 (s, 1H), 5.24-5.27 (m, 1H), 4.14 (t, 2H, $J$ = 6.5 Hz), 2.80 (dd, 1H, $J$ = 7.0 Hz, $J$ = 16.0 Hz), 2.58 (dd, 1H, $J$ = 7.0 Hz, $J$ = 16.0 Hz), 1.93 (s, 3H), 1.60-1.69 (m, 2H), 1.36-1.43 (m, 2H), 0.93-0.97 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 173.53, 169.26, 147.73, 130.70, 76.79, 65.11, 38.23, 30.52, 19.07, 13.66, 10.64. HRMS (ESI): m/z calculated for C$_{11}$H$_{16}$O$_4$ [M+H]$^+$: 213.1121, found: 213.1116. FTIR (KBr, cm$^{-1}$): 3686.7, 3617.1, 3473.0, 3383.4, 2958.7, 2353.8, 1887.7, 1667.3, 1470.8, 1264.4, 977.1, 756.0.

(Z)-4-(Methoxycarbonylmethylene)-2-methylbut-2-en-4-olide (3ab-Z)$^3$

Following the general procedure, 3ab-Z was obtained as a white solid (33.6 mg, 0.20 mmol, 40%), m.p. 89.2 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 8.03 (s, 1H), 5.83 (s, 1H), 3.79 (s, 3H), 2.10 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 169.00, 165.72, 159.85, 135.84, 135.62, 100.22, 51.91, 11.11. HRMS (ESI): m/z calculated for C$_8$H$_8$O$_4$ [M+H]$^+$: 169.0495, found: 169.0494. FTIR (KBr, cm$^{-1}$): 3673.7, 3520.3, 3318.3, 2356.9, 1783.56, 1694.4, 1374.4, 1254.7, 1147.8, 1030.7, 902.3, 860.3.

(E)-4-(Methoxycarbonylmethylene)-2-methylbut-2-en-4-olide (3ab-E)
Following the general procedure, an inseparable mixture of 3ab-E and 4ab were obtained as an oil.

3ab-E (12.6 mg, 0.075 mmol, 15%). $^1$H NMR (CDCl$_3$): $\delta = 7.17$ (s, 1H), 5.37 (s, 1H), 3.81 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta = 169.63$, 163.91, 155.80, 138.21, 134.88, 99.65, 52.03, 10.95. HRMS (ESI): m/z calculated for C$_8$H$_8$O$_4$ [M+H]$^+$: 169.0495, found: 169.0494. FTIR (KBr, cm$^{-1}$): 3850.9, 3441.4, 3421.6, 3385.3, 2978.0, 1732.3, 1644.7, 1557.3, 1455.0, 1045.7, 878.4, 666.4.

4ab (12.7 mg, 0.075 mmol, 15%). $^1$H NMR (CDCl$_3$): $\delta = 7.08$ (s, 1H), 5.24-5.28 (m, 1H), 3.74 (s, 3H), 2.81 (dd, 1H, $J = 7.0$ Hz, $J = 16.5$ Hz), 2.60 (dd, 1H, $J = 7.5$ Hz, $J = 16.5$ Hz), 1.94 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta = 173.47$, 169.34, 147.64, 130.77, 76.69, 57.17, 38.02, 10.64. HRMS (ESI): m/z calculated for C$_8$H$_{10}$O$_4$ [M+H]$^+$: 171.0652, found: 171.0650. FTIR (KBr, cm$^{-1}$): 3850.9, 3441.4, 3421.6, 3385.3, 2978.0, 1732.3, 1644.7, 1557.3, 1455.0, 1045.7, 878.4, 666.4.

Following the general procedure, 3ac-Z was obtained as a white solid (42 mg, 0.20 mmol, 40%), m.p. 72.1 °C. $^1$H NMR (CDCl$_3$): $\delta = 7.93$ (s, 1H), 5.68 (s, 1H), 2.01 (s, 3H), 1.44 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta = 168.24$, 163.53, 158.00, 134.92, 133.99, 101.65, 80.67, 27.13, 10.04. HRMS (ESI): m/z calculated for C$_{11}$H$_{14}$O$_4$ [M+H]$^+$: 211.0965, found: 211.0963. FTIR (KBr, cm$^{-1}$): 3646.2, 3592.7, 3444.6, 2354.0, 1866.4, 1760.1, 1651.6, 1372.3, 1257.0, 1134.0, 1036.9, 848.7.
tert-Butyl (E)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3ac-E)

Following the general procedure, an inseparable mixture of 3ac-E and 4ac were obtained as an oil.

3ac-E (5.2 mg, 0.025 mmol, 5%). $^1$H NMR (CDCl$_3$): $\delta = 6.96$ (s, 1H), 5.21 (s, 1H), 2.00 (s, 3H), 1.45 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta = 168.52, 161.68, 154.13, 137.28, 133.29, 100.89, 80.66, 27.11, 9.88$. HRMS (ESI): m/z calculated for C$_{11}$H$_{14}$O$_4$ [M+H]$^+$: 211.0965, found: 211.0970. FTIR (KBr, cm$^{-1}$): 3354.7, 1842.0, 1738.1, 1621.4, 1531.7, 1416.8, 1257.6, 1157.2, 1047.9, 975.8, 946.1.

4ac (13.7 mg, 0.065 mmol, 13%). $^1$H NMR (CDCl$_3$): $\delta = 7.08$ (s, 1H), 5.13-5.16 (m, 1H), 2.65 (dd, 1H, $J = 6.5$ Hz, $J = 16.0$ Hz), 2.44 (dd, 1H, $J = 7.0$ Hz, $J = 16.0$ Hz), 1.86 (s, 3H), 1.44 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta = 172.67, 167.37, 146.90, 129.53, 80.90, 76.07, 38.33, 27.03, 9.63$. HRMS (ESI): m/z calculated for C$_{11}$H$_{16}$O$_4$ [M+H]$^+$: 213.1121, found: 213.1123. FTIR (KBr, cm$^{-1}$): 3354.7, 1842.0, 1738.1, 1621.4, 1531.7, 1416.8, 1257.6, 1157.2, 1047.9, 975.8, 946.1.

Hexyl (Z)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3ad-Z)

Following the general procedure, 3ad-Z was obtained as a colorless oil (38.1 mg, 0.16 mmol, 32%). $^1$H NMR (CDCl$_3$): $\delta = 8.02$ (s, 1H), 5.82 (s, 1H), 4.18 (t, 2H, $J = 7.0$ Hz), 2.10 (s, 3H), 1.65-1.71 (m, 2H), 1.32-1.39 (m,
Hexyl (E)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3ad-E)

Hexyl 2,5-dihydro-4-methyl-5-oxofuran-2-acetate (4ad)

Following the general procedure, an inseparable mixture of 3ad-E and 4ad were obtained as an oil.

3ad-E (9.5 mg, 0.02 mmol, 8%). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.07\) (s, 1H), 5.37 (s, 1H), 4.20 (t, 2H, \(J = 6.5\) Hz), 2.08 (s, 3H), 1.67-1.72 (m, 2H), 1.31-1.33 (m, 6H), 0.90 (t, 3H, \(J = 7.0\) Hz). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 169.38, 163.54, 155.70, 138.21, 134.73, 100.09, 64.14, 31.39, 28.54, 25.53, 22.51, 13.97, 10.93\). HRMS (ESI): m/z calculated for C\(_{13}\)H\(_{18}\)O\(_4\) [M+H]\(^+\): 239.1278, found: 239.1278. FTIR (KBr, cm\(^{-1}\)): 2957.0, 2932.2, 2859.3, 1761.3, 1660.8, 1393.1, 1266.5, 1177.5, 1097.2, 1059.2, 987.5, 865.5.

4ad (25.2 mg, 0.105 mmol, 21%). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.17\) (s, 1H), 5.24-5.28 (m, 1H), 4.13 (t, 2H, \(J = 7.0\) Hz), 2.90 (dd, 1H, \(J = 7.0\) Hz, \(J = 16.0\) Hz), 2.58 (dd, 1H, \(J = 7.5\) Hz, \(J = 16.5\) Hz), 1.93 (s, 3H), 1.61-1.65 (m, 2H), 1.31-1.33 (m, 6H), 0.90 (t, 3H, \(J = 7.0\) Hz). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 173.52, 169.25, 147.74, 130.69, 76.79, 65.41, 38.23, 31.36, 28.45, 25.50, 22.49, 13.97, 10.64\). HRMS (ESI): m/z calculated for C\(_{13}\)H\(_{20}\)O\(_4\) [M+H]\(^+\): 241.1434, found: 241.1436. FTIR (KBr, cm\(^{-1}\)): 2957.0, 2932.2, 2859.3, 1761.3, 1660.8, 1393.1, 1266.5, 1177.5, 1097.2, 1059.2, 987.5, 865.5.
**Benzyl (Z)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3ae-Z)**

Following the general procedure, 3ae-Z was obtained as a white solid (54.9 mg, 0.225 mmol, 45%), m.p. 78.0 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.02$ (s, 1H), 7.26-7.37 (m, 5H), 5.86 (s, 1H), 5.22 (s, 2H), 2.08 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta = 168.97, 165.13, 160.10, 135.86, 135.71, 135.50, 128.69, 128.49, 128.32, 100.32, 66.71, 11.14$. HRMS (ESI): m/z calculated for C$_{14}$H$_{12}$O$_4$ [M+H]$^+$: 245.0808, found: 245.0814. FTIR (KBr, cm$^{-1}$): 3605.8, 3444.5, 3331.7, 2352.2, 1780.6, 1651.4, 1359.8, 1254.9, 1142.6, 1041.3, 848.9, 728.5.

**Benzyl (E)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3ae-E)**

**Benzyl 2,5-dihydro-4-methyl-5-oxofuran-2-acetate (4ae)**

Following the general procedure, an inseparable mixture of 3ae-E and 4ae were obtained as an oil.

3ae-E (15.9 mg, 0.065 mmol, 13%). $^1$H NMR (CDCl$_3$): $\delta = 7.26-7.33$ (m, 5H), 6.98 (s, 1H), 5.33 (s, 1H), 5.17 (s, 2H), 2.00 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta = 168.25, 162.14, 155.16, 137.12, 134.67, 134.21, 127.56, 127.53, 127.26, 98.57, 65.59, 9.94$. HRMS (ESI): m/z calculated for C$_{14}$H$_{12}$O$_4$ [M+H]$^+$: 245.0808, found: 245.0814. FTIR (KBr, cm$^{-1}$): 3799.4, 3564.7, 3444.7, 1704.4, 1487.3, 1417.0, 1385.2, 1337.6, 1269.8, 1175.0, 988.0, 886.5.
4ae (16 mg, 0.065 mmol, 13%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.26-7.33 (m, 5H), 7.05 (s, 1H), 5.19-5.21 (m, 1H), 5.09 (s, 2H), 2.77 (dd, 1H, $J = 7.0$ Hz, $J = 16.5$ Hz), 2.55 (dd, 1H, $J = 7.0$ Hz, $J = 16.5$ Hz), 1.83 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 172.44, 167.98, 146.56, 133.98, 129.77, 127.66, 127.40, 127.25, 75.65, 65.99, 37.18, 9.61. HRMS (ESI): m/z calculated for C$_{14}$H$_{14}$O$_4$ [M+H]$^+$: 247.0695, found: 247.0692. FTIR (KBr, cm$^{-1}$): 3799.4, 3564.7, 3444.7, 1704.4, 1487.3, 1417.0, 1385.2, 1337.6, 1269.8, 1175.0, 988.0, 886.5.

![2,2,2-Trifluoroethyl (Z)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3af-Z)](image)

2,2,2-Trifluoroethyl (Z)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3af-Z)

Following the general procedure, 3af-Z was obtained as a white solid (36.6 mg, 0.155 mmol, 31%), m.p. 100.9 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 7.98 (s, 1H), 5.37 (s, 1H), 4.57 (q, 2H, $J = 8.5$ Hz), 2.13 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 168.50, 163.60, 161.35, 136.73, 135.43, 122.84 ($J = 276$ Hz), 98.35, 60.44 ($J = 37$ Hz), 11.21. HRMS (ESI): m/z calculated for C$_9$H$_7$F$_3$O$_4$ [M+H]$^+$: 237.0369, found: 237.0376. FTIR (KBr, cm$^{-1}$): 3851.3, 3673.7, 3646.6, 1792.8, 1722.1, 1373.3, 1276.9, 1181.7, 961.7, 894.9, 855.9, 757.2.

![2,2,2-Trifluoroethyl (E)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3af-E)](image)

2,2,2-Trifluoroethyl (E)-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3af-E)

![2,2,2-Trifluoroethyl 2,5-dihydro-4-methyl-5-oxofuran-2-acetate (4af)](image)

2,2,2-Trifluoroethyl 2,5-dihydro-4-methyl-5-oxofuran-2-acetate (4af)
Following the general procedure, an inseparable mixture of 3af-E and 4af were obtained as an oil.

3af-E (11.8 mg, 0.05 mmol, 10%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.02 (s, 1H), 5.37 (s, 1H), 4.50 (q, 2H, $J = 8.5$ Hz), 2.05 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 167.79, 160.37, 156.70, 136.76, 135.00, 122.98 ($J = 276$ Hz), 96.31, 59.39 ($J = 34$ Hz), 10.05. HRMS (ESI): m/z calculated for C$_9$H$_7$F$_3$O$_4$[M+H]+: 237.0369, found: 237.0369. FTIR (KBr, cm$^{-1}$): 3897.6, 3564.7, 3383.4, 2352.0, 1731.9, 1417.0, 1276.8, 1174.2, 973.8, 895.3, 753.0, 667.0.

4af (3.6 mg, 0.015 mmol, 3%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.06 (s, 1H), 5.20-5.22 (m, 1H), 4.25 (q, 2H, $J = 8.5$ Hz), 2.83 (dd, 1H, $J = 7.0$ Hz, $J = 16.5$ Hz), 2.68 (dd, 1H, $J = 6.5$ Hz, $J = 16.5$ Hz), 1.88 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 172.14, 166.59, 145.79, 140.04, 130.34, 120.77 ($J = 276$ Hz), 75.06, 36.62, 9.65. HRMS (ESI): m/z calculated for C$_9$H$_9$F$_3$O$_4$[M+H]+: 239.0526, found: 239.0522. FTIR (KBr, cm$^{-1}$): 3897.6, 3564.7, 3383.4, 2352.0, 1731.9, 1417.0, 1276.8, 1174.2, 973.8, 895.3, 753.0, 667.0.

(5Z)-3-Methyl-5-(2-oxobutylidene) furan-2(5H)-one (3ag-Z)

Following the general procedure, 3ag-Z was obtained as a white solid (26.6 mg, 0.16 mmol, 32%), m.p. 68.5 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 7.92 (s, 1H), 6.07 (s, 1H), 2.53 (q, 2H, $J = 7.0$ Hz), 2.01 (s, 3H), 1.06 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ = 199.33, 168.32, 157.01, 135.64, 135.28, 104.85, 37.22, 10.10, 6.91. HRMS (ESI): m/z calculated for C$_9$H$_{10}$O$_1$[M+H]+: 167.0703, found: 167.0708. FTIR (KBr, cm$^{-1}$): 3851.1, 3646.3, 1777.2, 1607.9, 1372.9, 1206.1, 1169.3, 1008.7, 922.7, 902.9, 858.7, 755.9.

(5E)-3-Methyl-5-(2-oxobutylidene) furan-2(5H)-one (3ag-E)
Following the general procedure, 3ag-E was obtained as a white solid (18.2 mg, 0.11 mmol, 32%), m.p. 105.5 °C. $^1$H NMR (CDCl$_3$): δ = 7.12 (s, 1H), 5.48 (s, 1H), 2.92 (q, 2H, $J = 7.5$ Hz), 2.10 (s, 3H), 1.13 (t, 3H, $J = 7.0$ Hz). $^{13}$C NMR (CDCl$_3$): δ = 198.61, 168.13, 152.91, 138.14, 133.23, 107.85, 35.71, 9.97, 6.83. HRMS (ESI): m/z calculated for C$_9$H$_{10}$O$_3$ [M+H]$^+$: 167.0703, found: 167.0701. FTIR (KBr, cm$^{-1}$): 3441.1, 3416.4, 2976.0, 2899.9, 1645.2, 1086.5, 1047.1, 879.6, 666.7.

(5Z)-3-Methyl-5-(2-oxoheptylidene) furan-2(5H)-one (3ah-Z)

Following the general procedure, 3ah-Z was obtained as a white solid (39.5 mg, 0.19 mmol, 38%), m.p. 50.8 °C. $^1$H NMR (CDCl$_3$): δ = 7.92 (s, 1H), 6.07 (s, 1H), 2.48 (t, 2H, $J = 7.5$ Hz), 2.01 (s, 3H), 1.54-1.59 (m, 2H), 1.22-1.27 (m, 4H), 0.83 (t, 3H, $J = 7.0$ Hz). $^{13}$C NMR (CDCl$_3$): δ = 200.14, 169.31, 158.08, 136.68, 136.30, 106.06, 45.04, 31.27, 23.74, 22.43, 13.88, 11.11. HRMS (ESI): m/z calculated for C$_{12}$H$_{16}$O$_3$ [M+H]$^+$: 209.1172, found: 209.1173. FTIR (KBr, cm$^{-1}$): 3851.3, 3748.7, 3627.0, 3627.0, 2925.9, 1789.5, 1614.4, 1557.4, 1463.2, 1242.8, 1034.3, 991.6, 755.1.

(5E)-3-Methyl-5-(2-oxoheptylidene) furan-2(5H)-one (3ah-E)

3-Methyl-5-(2-oxo-2-heptyl)-5H-furan-2-one (4ah)

Following the general procedure, an inseparable mixture of 3ah-E and 4ah were obtained as an oil.
3ah-E (16.6 mg, 0.08 mmol, 16%). $^1$H NMR (CDCl$_3$): $\delta = 7.12$ (s, 1H), 5.47 (s, 1H), 2.87 (t, 2H, $J = 7.5$ Hz), 2.10 (s, 3H), 1.58-1.65 (m, 2H), 1.31-1.34 (m, 4H), 0.89-0.91 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta = 199.33, 169.71, 148.42, 139.21, 134.24, 108.97, 43.31, 31.35, 23.64, 22.50, 13.97, 10.98$. HRMS (ESI): m/z calculated for C$_{12}$H$_{16}$O$_3$ [M+H]$^+$: 209.1172, found: 209.1177.

FTIR (KBr, cm$^{-1}$): 3799.3, 3585.0, 3472.8, 3417.6, 3225.8, 1770.3, 1714.4, 1660.5, 1557.2, 1538.9, 1505.1.

4ah (13.6 mg, 0.065 mmol, 13%). $^1$H NMR (CDCl$_3$): $\delta = 7.16$ (s, 1H), 5.28-5.31 (m, 1H), 2.97 (dd, 1H, $J = 6.5$ Hz, $J = 17.0$ Hz), 2.60 (dd, 1H, $J = 7.0$ Hz, $J = 17.0$ Hz), 2.46 (t, 2H, $J = 7.5$ Hz), 1.92 (s, 3H), 1.58-1.65 (m, 2H), 1.31-1.34 (m, 4H), 0.89-0.91 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta = 207.00, 173.71, 153.81, 130.19, 76.79, 45.59, 43.43, 31.23, 23.16, 22.39, 13.87, 10.62$. HRMS (ESI): m/z calculated for C$_{12}$H$_{18}$O$_3$ [M+H]$^+$: 211.1329, found: 211.1333.

FTIR (KBr, cm$^{-1}$): 3799.3, 3585.0, 3472.8, 3417.6, 3225.8, 1770.3, 1714.4, 1660.5, 1557.2, 1538.9, 1505.1.

(5Z)-3-Methyl-5-(2-oxo-2-phenylethylidene) furan-2(5H)-one (3ai-Z)$^5$

Following the general procedure, 3ai-Z was obtained as a yellow solid (41.7 mg, 0.195 mmol, 39%), m.p. 136.9 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.02$ (s, 1H), 7.87-7.89 (m, 2H), 7.51-7.54 (m, 1H), 7.41-7.44 (m, 2H), 6.84 (s, 1H), 2.04 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta = 188.50, 168.13, 158.86, 137.12, 135.87, 135.66, 132.45, 127.81, 127.20, 102.70, 10.20$. HRMS (ESI): m/z calculated for C$_{13}$H$_{10}$O$_3$ [M+H]$^+$: 215.0703, found: 215.0709. FTIR (KBr, cm$^{-1}$): 3897.2, 3794.2, 3383.1, 3354.8, 1783.5, 1651.5, 1385.1, 1267.3, 1179.1, 917.1, 847.5, 700.6.

3-Methyl-5-(2-oxo-2-phenethyl)-5H-furan-2-one (4ai)
Following the general procedure, 4ai was obtained as a yellow solid (21.6 mg, 0.1 mmol, 20%), m.p. 84.8 °C. 

$^1$H NMR (CDCl$_3$): $\delta = 7.85$-$7.87$ (m, 2H), 7.52-$7.55$ (m, 1H), 7.40-$7.43$ (m, 2H), 7.19-$7.23$ (m, 1H), 5.41-$5.43$ (m, 1H), 3.59 (dd, 1H, $J = 6.0$ Hz, $J = 17.5$ Hz), 2.60 (dd, 1H, $J = 8.0$ Hz, $J = 17.5$ Hz), 1.86 (s, 3H).

$^{13}$C NMR (CDCl$_3$): $\delta = 195.03$, 172.76, 147.78, 135.03, 132.86, 129.23, 127.83, 127.07, 75.77, 41.09, 9.63.

HRMS (ESI): m/z calculated for C$_{13}$H$_{22}$O$_3$ [M+H]$^+$: 217.0859, found: 217.0862.

FTIR (KBr, cm$^{-1}$): 1760.0, 1755.3, 1621.4, 1557.2, 1531.8, 1428.0, 1416.8, 1337.0, 1210.2, 977.6.

Butyl (Z) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3ba-Z) 

Following the general procedure, 3ba-Z was obtained as a light yellow solid (57.1 mg, 0.21 mmol, 42%), m.p. 43.2 °C. 

$^1$H NMR (CDCl$_3$): $\delta = 8.49$ (s, 1H), 7.97-$7.99$ (m, 2H), 7.45-$7.47$ (m, 3H), 5.92 (s, 1H), 4.23 (t, 2H, $J = 7.0$ Hz), 1.67-1.73 (m, 2H), 1.42-1.46 (m, 2H), 0.97 (t, 3H, $J = 7.5$ Hz). 

$^{13}$C NMR (CDCl$_3$): $\delta = 165.94$, 164.46, 158.21, 133.64, 131.25, 129.88, 127.98, 127.46, 126.81, 100.74, 63.89, 29.62, 18.14, 12.68. 


FTIR (KBr, cm$^{-1}$): 3384.5, 2975.4, 2899.5, 1651.5, 1454.9, 1382.8, 1087.8, 1048.1, 879.9, 691.1.

Butyl (E) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3ba-E) 

Following the general procedure, 3ba-E was obtained as a light yellow solid (29.9 mg, 0.11 mmol, 22%), m.p. 85.1 °C. 

$^1$H NMR (CDCl$_3$): $\delta = 7.93$-$7.95$ (m, 2H), 7.50 (s, 1H), 7.26-$7.47$ (m, 3H), 5.51 (s, 1H), 4.24 (t, 2H, $J = 6.5$ Hz), 1.68-1.73 (m, 2H), 1.41-1.47 (m, 2H), 0.97 (t, 3H, $J = 7.5$ Hz). 

$^{13}$C NMR (CDCl$_3$): $\delta = 167.18$, 163.49, 155.32, 134.74, 134.26, 130.91, 129.05, 128.25, 127.70, 101.25, 64.99, 30.65, 19.14, 13.72. 

HRMS
(ESI): m/z calculated for C_{16}H_{16}O_{4} [M+H]^+: 273.1121, found: 273.1121. FTIR (KBr, cm\(^{-1}\)): 3299.0, 3072.2, 2924.1, 2351.7, 1789.8, 1682.4, 1574.3, 1393.0, 1229.4, 1157.3, 965.0, 490.4.

Isobutyl (Z) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bj-Z)

Following the general procedure, 3bj-Z was obtained as a light yellow solid (50.3 mg, 0.185 mmol, 37%), m.p. 89.0 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta = 8.42\) (s, 1H), 7.90-7.92 (m, 2H), 7.38-7.40 (m, 3H), 5.87 (s, 1H), 3.94 (d, 2H, \(J = 7.0\) Hz), 1.92-1.97 (m, 1H), 0.92 (d, 6H, \(J = 7.0\) Hz). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 165.95, 164.45, 158.24, 133.67, 131.25, 129.89, 127.99, 127.46, 126.81, 100.72, 70.12, 26.75, 18.14, 18.10\). HRMS (ESI): m/z calculated for C_{16}H_{16}O_{4} [M+H]^+: 273.1121, found: 273.1116. FTIR (KBr, cm\(^{-1}\)): 3667.6, 3573.2, 3263.1, 2970.0, 1713.7, 1633.8, 1455.2, 1253.3, 1134.2, 1083.6, 1047.1.

Isobutyl (E) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bj-E)

Following the general procedure, 3bj-E was obtained as a yellow solid (19.0 mg, 0.07 mmol, 14%), m.p. 94.5 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.93-7.95\) (m, 2H), 7.51 (s, 1H), 7.46-7.47 (m, 3H), 5.52 (s, 1H), 4.02 (d, 2H, \(J = 6.5\) Hz), 2.02-2.04 (m, 1H), 1.00 (d, 6H, \(J = 6.5\) Hz). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 167.16, 163.52, 155.34, 134.74, 134.26, 130.90, 129.05, 128.26, 127.70, 101.25, 71.20, 27.78, 19.12, 19.04\). HRMS (ESI): m/z calculated for C_{16}H_{16}O_{4} [M+H]^+: 273.1121, found: 273.1125. FTIR (KBr, cm\(^{-1}\)): 3700.0, 3318.2, 3251.3, 3224.8, 2878.5, 2358.25, 1694.7, 1533.6, 1372.7, 1268.4, 900.7, 416.9.
2-Phenoxyethyl (Z) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bk-Z)

Following the general procedure, 3bk-Z was obtained as a white solid (75.6 mg, 0.225 mmol, 45%), m.p. 91.5 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.38$ (s, 1H), 7.84-7.86 (m, 2H), 7.31-7.36 (m, 3H), 7.16-7.23 (m, 2H), 6.89-6.92 (m, 1H), 6.85-6.86 (m, 2H), 5.87 (s, 1H), 4.49 (t, 2H, $J = 5.0$ Hz), 4.16 (t, 2H, $J = 5.0$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 165.78, 164.11, 158.59, 157.30, 133.84, 131.20, 129.93, 128.59, 127.96, 127.32, 126.81, 120.34, 113.54, 100.26, 64.61, 62.27. HRMS (ESI): m/z calculated for C$_{20}$H$_{16}$O$_5$ [M+H]: 337.1071, found: 337.1068. FTIR (KBr, cm$^{-1}$): 3507.7, 3451.4, 3384.4, 1714.1, 1694.2, 1660.1, 1644.9, 1633.9, 677.0, 457.4.

2-Phenoxyethyl (E) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bk-E)

Following the general procedure, 3bk-E was obtained as a white solid (16.5 mg, 0.05 mmol, 10%), m.p. 152.4 °C. $^1$H NMR (CDCl$_3$): $\delta = 7.86-7.87$ (m, 2H), 7.43 (s, 1H), 7.39-7.40 (m, 3H), 7.19-7.24 (m, 2H), 6.87-6.90 (m, 3H), 5.49 (s, 1H), 4.51 (t, 2H, $J = 4.5$ Hz), 4.19 (t, 2H, $J = 4.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 166.01, 162.07, 157.44, 154.96, 133.53, 133.51, 129.99, 128.53, 128.04, 127.13, 126.72, 120.22, 113.71, 99.38, 64.81, 62.29. HRMS (ESI): m/z calculated for C$_{20}$H$_{16}$O$_5$ [M+H]: 337.1071, found: 337.1077. FTIR (KBr, cm$^{-1}$): 3897.7, 3507.7, 3417.8, 1732.3, 1715.2, 1698.8, 1682.5, 1645.0, 1531.9, 1360.7, 1242.7, 994.2.
(Tetrahydrofuran-2-yl) methyl (Z) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bl-Z)

Following the general procedure, 3bl-Z was obtained as a yellow solid (58.5 mg, 0.195 mmol, 39%), m.p. 81.0 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.49$ (s, 1H), 7.90-7.92 (m, 2H), 7.37-7.39 (m, 3H), 5.89 (s, 1H), 4.22-4.25 (m, 1H), 4.07-4.11 (m, 2H), 3.83-3.87 (m, 1H), 3.73-3.77 (m, 1H), 1.96-1.99 (m, 1H), 1.85 (m, 2H), 1.56-1.60 (m, 1H). $^{13}$C NMR (CDCl$_3$): $\delta = 165.88$, 164.23, 158.53, 133.74, 131.34, 129.91, 127.98, 127.44, 126.82, 100.40, 75.39, 67.48, 65.85, 26.96, 24.68. HRMS (ESI): m/z calculated for C$_{17}$H$_{16}$O$_5$ [M+H]$^+$: 301.1071, found: 301.1071. FTIR (KBr, cm$^{-1}$): 3646.4, 3564.7, 3417.9, 2956.7, 2353.0, 1940.5, 1842.1, 1372.7, 1303.8, 1080.8, 935.0, 690.2.

(Tetrahydrofuran-2-yl) methyl (E) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bl-E)

Following the general procedure, 3bl-E was obtained as a light yellow solid (31.5 mg, 0.105 mmol, 21%), m.p. 80.1 °C. $^1$H NMR (CDCl$_3$): $\delta = 7.86-7.88$ (m, 2H), 7.43 (s, 1H), 7.39-7.40 (m, 3H), 5.49 (s, 1H), 4.23-4.26 (m, 1H), 4.09-4.14 (m, 2H), 3.85-3.89 (m, 1H), 3.74-3.78 (m, 1H), 1.85-1.97 (m, 3H), 1.63-1.67 (m, 1H). $^{13}$C NMR (CDCl$_3$): $\delta = 167.08$, 163.22, 155.73, 134.64, 134.41, 130.96, 129.05, 128.19, 127.72, 100.75, 76.42, 68.57, 66.96, 27.97, 25.74. HRMS (ESI): m/z calculated for C$_{17}$H$_{16}$O$_5$ [M+H]$^+$: 301.1071, found: 301.1072. FTIR (KBr, cm$^{-1}$): 3564.5, 3526.4, 3331.3, 1789.9, 1667.4, 1633.8, 1269.5, 1147.7, 1080.8, 957.6, 787.8.
2-Methoxyethyl (Z) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bm-Z)

Following the general procedure, 3bm-Z was obtained as a yellow solid (57.5 mg, 0.21 mmol, 42%), m.p. 78.6 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 8.50 (s, 1H), 7.97-7.98 (m, 2H), 7.45-7.47 (m, 3H), 5.97 (s, 1H), 4.38 (t, 2H, $J$ = 4.5 Hz), 3.67 (t, 2H, $J$ = 4.5 Hz), 3.43 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 165.87, 164.25, 158.53, 133.77, 131.32, 129.93, 127.98, 127.43, 126.82, 100.38, 69.29, 62.89, 58.03. HRMS (ESI): m/z calculated for C$_{15}$H$_{14}$O$_5$ [M+H]$^+$: 275.0914, found: 275.0918. FTIR (KBr, cm$^{-1}$): 3897.6, 3592.8, 3564.7, 3542.7, 1790.0, 1704.4, 1614.9, 1385.1, 1353.3, 1139.7, 1045.2, 788.1.

2-Methoxyethyl (E) (5-oxo-4-phenyl-5H-furan-2-ylidene) acetate (3bm-E)

Following the general procedure, 3bm-E was obtained as a yellow solid (20.5 mg, 0.075 mmol, 15%), m.p. 96.7 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 7.86-7.88 (m, 2H), 7.43 (s, 1H), 7.39-7.40 (m, 3H), 5.49 (s, 1H), 4.31 (t, 2H, $J$ = 4.5 Hz), 3.61 (t, 2H, $J$ = 4.5 Hz), 3.36 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 167.08, 163.16, 155.81, 134.61, 134.45, 130.97, 129.05, 128.18, 127.72, 100.64, 70.35, 64.00, 59.07. HRMS (ESI): m/z calculated for C$_{15}$H$_{14}$O$_5$ [M+H]$^+$: 275.0914, found: 275.0914. FTIR (KBr, cm$^{-1}$): 3239.8, 2950.5, 2923.7, 1704.4, 1694.5, 1621.6, 1574.5, 1515.3, 1428.2, 1346.2, 1081.3, 787.8.
(5Z)-3-Phenyl-5-(2-oxobutylidene) furan-2(5H)-one (3bg-Z)

Following the general procedure, 3bg-Z was obtained as a yellow solid (31.9 mg, 0.14 mmol, 28%), m.p. 201.4 °C. \[^1\text{H}\text{ NMR (CDCl}_3\text{)}\]: \(\delta = 8.39 \text{ (s, 1H), 7.90-7.92 \text{ (m, 2H), 7.38-7.39 \text{ (m, 3H), 6.17 \text{ (s, 1H), 2.57 \text{ (q, 2H, } J = 7.0 \text{ Hz), 1.09 \text{ (t, 3H, } J = 7.5 \text{ Hz). }}\)\[\]^1\text{C NMR (CDCl}_3\text{)}\]: \(\delta = 199.44, 166.22, 156.56, 134.45, 132.03, 129.92, 127.99, 127.51, 126.82, 105.78, 37.33, 6.94. HRMS (ESI): m/z calculated for C_{14}H_{12}O_3 [M+H]^+: 229.0859, found: 229.0861. FTIR (KBr, cm\(^{-1}\)): 3686.0, 3440.5, 3383.1, 2974.6, 2899.1, 1660.4, 1454.9, 1382.5, 1088.5, 1048.7, 880.4, 666.5.

(5E)-3-Phenyl-5-(2-oxobutylidene) furan-2(5H)-one (3bg-E)

Following the general procedure, 3bg-E was obtained as a yellow solid (22.8 mg, 0.1 mmol, 20%), m.p. 149.5 °C. \[^1\text{H}\text{ NMR (CDCl}_3\text{)}\]: \(\delta = 7.94-7.96 \text{ (m, 2H), 7.56 \text{ (s, 1H), 7.47-7.48 \text{ (m, 3H), 6.64 \text{ (s, 1H), 2.98 \text{ (q, 2H, } J = 7.0 \text{ Hz), 1.16 \text{ (t, 3H, } J = 7.5 \text{ Hz). }}\)\[\]^1\text{C NMR (CDCl}_3\text{)}\]: \(\delta = 198.46, 165.93, 152.59, 134.64, 132.78, 129.96, 128.07, 127.19, 126.67, 108.83, 35.79, 6.87. HRMS (ESI): m/z calculated for C_{14}H_{12}O_3 [M+H]^+: 229.0859, found: 229.0856. FTIR (KBr, cm\(^{-1}\)): 3564.4, 3526.3, 3444.3, 3417.4, 3382.8, 2351.9, 1841.9, 1574.2, 1392.9, 1202.5, 961.8, 784.9.
Diethyl (Z)-((5-oxo-4-phenylfuran-2(5H)-ylidene)methyl) phosphonate (3bn-Z)

Following the general procedure, 3bn-Z was obtained as a yellow oil (53.9 mg, 0.175 mmol, 35%). $^1$H NMR (CDCl$_3$): $\delta$ = 8.37 (s, 1H), 7.89-7.91 (m, 2H), 7.36-7.38 (m, 3H), 5.52 (d, 1H, $J$ = 6.0 Hz), 4.04-4.10 (m, 4H), 1.29 (t, 6H, $J$ = 7.0 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ = 165.94, 159.25 ($J$ = 24 Hz), 133.46, 131.78 ($J$ = 3 Hz), 129.77, 127.91, 127.37, 126.84, 96.17 ($J$ = 195 Hz), 61.39, 61.34, 15.36, 15.31. HRMS (ESI): m/z calculated for C$_{15}$H$_{17}$PO$_5$ [M+H]$^+$: 309.0886, found: 309.0888. FTIR (KBr, cm$^{-1}$): 3850.8, 3742.2, 3564.3, 1789.6, 1633.4, 1494.7, 1337.2, 1254.0, 1021.7, 966.1, 830.6, 788.9.

Diethyl (E)-((5-oxo-4-phenylfuran-2(5H)-ylidene)methyl) phosphonate (3bn-E)

Following the general procedure, 3bn-E was obtained as a yellow oil (26.1 mg, 0.085 mmol, 17%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.83-7.85 (m, 2H), 7.38-7.39 (m, 4H), 5.32 (d, 1H, $J$ = 7.5 Hz), 4.12-4.18 (m, 4H), 1.31 (t, 6H, $J$ = 7.5 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ = 165.84, 155.86 ($J$ = 4 Hz), 133.44, 133.09 ($J$ = 18 Hz), 129.89, 128.02, 127.65, 126.70, 97.29 ($J$ = 191 Hz), 61.71, 61.66, 15.37, 15.31. HRMS (ESI): m/z calculated for C$_{15}$H$_{17}$PO$_5$ [M+H]$^+$: 309.0886, found: 309.0878. FTIR (KBr, cm$^{-1}$): 3654.4, 3444.6, 3225.2, 1790.2, 1651.5, 1644.4, 1240.0, 1049.6, 965.7, 934.2, 788.6.

(2Z,4E)-2-Methyl-5-phenylpenta-2,4-dienoic acid (5ao-Z)$^6$

Following the general procedure, 5ao-Z was obtained as a light yellow solid (31.0 mg, 0.165 mmol, 33%), m.p. 299.4 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 7.96 (dd, 1H, $J$ = 11.0 Hz, $J$ = 16.5 Hz), 7.50 (d, 2H, $J$ = 7.5 Hz), 7.35 (t, 2H, $J$ = 7.0 Hz), 7.27-7.30 (m, 1H), 6.74-6.77 (m, 2H), 2.07 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 171.99, 142.17, 138.50,
135.67, 127.68, 127.62, 126.30, 124.96, 124.06, 19.76. HRMS (ESI): m/z calculated for C_{12}H_{12}O_2[M+H]^+: 189.091, found: 189.0912. FTIR (KBr, cm⁻¹): 3686.4, 3626.4, 3445.1, 1660.2, 1651.5, 1644.8, 1634.0, 688.8, 503.6.

![Butyl (Z) (5-oxo-4-hexyl-5H-furan-2-ylidene) acetate (3ca-Z)](image)

Following the general procedure, 3ca-Z was obtained as a colorless oil (50.4 mg, 0.18 mmol, 36%). ¹H NMR (CDCl₃): δ = 7.99 (s, 1H), 5.82 (s, 1H), 4.19 (t, 2H, J = 6.5 Hz), 2.43 (t, 2H, J = 8.5 Hz), 1.61-1.69 (m, 4H), 1.30-1.43 (m, 8H), 0.96 (t, 3H, J = 7.0 Hz), 0.89 (t, 3H, J = 6.5 Hz). ¹³C NMR (CDCl₃): δ = 167.76, 164.50, 158.89, 139.15, 133.85, 99.56, 63.78, 30.40, 29.61, 27.80, 26.23, 24.70, 21.46, 18.14, 13.00, 12.67. HRMS (ESI): m/z calculated for C_{16}H_{24}O_4[M+H]^+: 281.1747, found: 281.1748.

![Butyl (E) (5-oxo-4-hexyl-5H-furan-2-ylidene) acetate (3ca-E)](image)

![Butyl 2,5-dihydro-4-hexyl-5-oxofuran-2-acetate (4ca)](image)

Following the general procedure, an inseparable mixture of 3ca-E and 4ca were obtained as an oil.

3ca-E (18.2 mg, 0.065 mmol, 13%). ¹H NMR (CDCl₃): δ = 6.95 (s, 1H), 5.29 (s, 1H), 4.14 (t, 2H, J = 6.5 Hz), 2.35 (t, 2H, J = 8.0 Hz), 1.58-1.64 (m, 2H), 1.47-1.51 (m, 2H), 1.27-1.36 (m, 8H), 0.87-0.90 (m, 3H), 0.80-0.83 (m, 3H). ¹³C NMR (CDCl₃): δ = 168.04, 162.61, 154.83, 138.46, 134.35, 99.00, 63.85, 30.38, 29.62, 27.76, 26.26, 24.53, 21.46, 18.10, 12.99, 12.68. HRMS (ESI): m/z calculated for C_{16}H_{24}O_4[M+H]^+: 281.1747.
found: 281.1749. FTIR (KBr, cm⁻¹): 3564.7, 3526.5, 3331.7, 2957.8, 2933.0, 1760.3, 1694.4, 1660.8, 1393.0, 1258.4, 1134.1, 1019.1.

4ca (8.5 mg, 0.03 mmol, 6%). ¹H NMR (CDCl₃): δ = 7.05 (s, 1H), 5.18-5.21 (m, 1H), 4.07 (t, 2H, J = 6.5 Hz), 2.74 (dd, 1H, J = 7.0 Hz, J = 16.5 Hz), 2.50 (dd, 1H, J = 7.0 Hz, J = 16.0 Hz), 2.21 (t, 2H, J = 7.5 Hz), 1.58-1.64 (m, 2H), 1.47-1.51 (m, 2H), 1.27-1.36 (m, 8H), 0.87-0.90 (m, 3H), 0.80-0.83 (m, 3H). ¹³C NMR (CDCl₃): δ = 172.17, 168.29, 145.75, 136.22, 75.76, 64.10, 37.32, 30.46, 29.51, 27.81, 26.26, 24.25, 21.50, 18.07, 13.01, 12.65. HRMS (ESI): m/z calculated for C₁₆H₂₆O₄ [M+H]⁺: 283.1904, found: 283.1896. FTIR (KBr, cm⁻¹): 3564.7, 3526.5, 3331.7, 2957.8, 2933.0, 1760.3, 1694.4, 1660.8, 1393.0, 1258.4, 1134.1, 1019.1.

Butyl (Z) (5-oxo-4-decyl-5H-furan-2-ylidene) acetate (3da-Z)

Following the general procedure, 3da-Z was obtained as a yellow oil (55.4 mg, 0.165 mmol, 33%). ¹H NMR (CDCl₃): δ = 7.92 (s, 1H), 5.74 (s, 1H), 4.12 (t, 2H, J = 6.5 Hz), 2.35 (t, 2H, J = 7.0 Hz), 1.53-1.63 (m, 4H), 1.32-1.37 (m, 2H), 1.19-1.23 (m, 14H), 0.88 (t, 3H, J = 7.5 Hz), 0.81 (t, 3H, J = 6.5 Hz). ¹³C NMR (CDCl₃): δ = 167.75, 164.49, 158.91, 139.16, 133.84, 99.53, 63.77, 30.87, 29.62, 28.54, 28.44, 28.28, 28.23, 28.15, 26.28, 24.71, 21.66, 18.14, 13.09, 12.67. HRMS (ESI): m/z calculated for C₂₀H₃₂O₄ [M+H]⁺: 337.2373, found: 337.2376. FTIR (KBr, cm⁻¹): 3850.9, 3799.3, 3444.6, 2925.3, 2854.3, 1790.4, 1651.9, 1393.0, 1252.5, 1135.5, 1031.3, 846.3.

Butyl (E) (5-oxo-4-decyl-5H-furan-2-ylidene) acetate (3da-E)
Following the general procedure, an inseparable mixture of 3da-E and 4da were obtained as an oil.

3da-E (18.5 mg, 0.055 mmol, 11%). $^1$H NMR (CDCl$_3$): $\delta = 6.95$ (s, 1H), 5.29 (s, 1H), 4.14 (t, 2H, $J = 6.5$ Hz), 2.35 (t, 2H, $J = 7.5$ Hz), 1.48-1.61 (m, 4H), 1.19-1.24 (m, 14H), 0.86-0.89 (m, 3H), 0.80-0.82 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta =$ 169.04, 163.60, 155.85, 139.47, 135.36, 99.99, 64.84, 31.86, 30.63, 29.56, 29.53, 29.45, 29.27, 29.21, 27.32, 25.54, 22.67, 19.11, 14.10, 13.69. HRMS (ESI): m/z calculated for C$_{20}$H$_{32}$O$_4$ [M+H]+: 337.2373, found: 337.2375. FTIR (KBr, cm$^{-1}$): 3626.4, 3592.4, 3444.7, 2925.5, 2853.9, 1778.6, 1682.3, 1463.1, 1257.7, 1174.3, 1134.1, 1015.6.

4da (16.9 mg, 0.05 mmol, 10%). $^1$H NMR (CDCl$_3$): $\delta = 7.04$ (s, 1H), 5.18-5.20 (m, 1H), 4.07 (t, 2H, $J = 7.0$ Hz), 2.73 (dd, 1H, $J = 7.0$ Hz, $J = 16.5$ Hz), 2.51 (dd, 1H, $J = 7.5$ Hz, $J = 16.5$ Hz), 2.21 (t, 2H, $J = 6.5$ Hz), 1.48-1.61 (m, 4H), 1.19-1.24 (m, 14H), 0.86-0.89 (m, 3H), 0.80-0.82 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta =$ 173.17, 169.29, 146.76, 137.24, 76.87, 65.10, 38.33, 31.88, 30.53, 29.56, 29.51, 29.29, 29.17, 29.11, 27.32, 25.26, 22.67, 19.08, 14.10, 13.66. HRMS (ESI): m/z calculated for C$_{20}$H$_{34}$O$_4$ [M+H]+: 339.253, found: 339.2533. FTIR (KBr, cm$^{-1}$): 3626.4, 3592.4, 3444.7, 2925.5, 2853.9, 1778.6, 1682.3, 1463.1, 1257.7, 1174.3, 1134.1, 1015.6.

Following the general procedure, 3ea-Z was obtained as a light yellow solid (55.9 mg, 0.185 mmol, 37%), m.p. 87.8 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.34$ (s, 1H), 7.96-7.98 (m, 2H), 6.96-6.97 (m, 2H), 5.87 (s, 1H), 4.22 (t, 2H, $J$...
= 6.5 Hz), 3.86 (s, 3H), 1.66-1.71 (m, 2H), 1.41-1.46 (m, 2H), 0.97 (t, 3H, J = 7.0 Hz). $^{13}$C NMR (CDCl$_3$): δ = 167.32, 165.70, 161.80, 159.58, 134.15, 129.58, 129.55, 121.15, 114.50, 100.81, 64.80, 55.42, 30.66, 19.18, 13.71. HRMS (ESI): m/z calculated for C$_{17}$H$_{18}$O$_5$ [M+H$^+$]: 303.1227, found: 303.123. FTIR (KBr, cm$^{-1}$): 3550.6, 3355.1, 1694.4, 1645.1, 1455.5, 1435.0, 1249.0, 1180.6, 1135.7, 1083.3, 1028.9, 834.9.

**Butyl (E) (5-oxo-4-(4-methoxyphenyl)-5H-furan-2-ylidene) acetate (3ea-E)**

Following the general procedure, 3ea-E was obtained as a yellow oil (27.2 mg, 0.09 mmol, 18%). $^1$H NMR (CDCl$_3$): δ = 7.85-7.87 (m, 2H), 6.91 (s, 1H), 6.87-6.91 (m, 2H), 5.31 (s, 1H), 4.12 (t, 2H, J = 6.5 Hz), 3.78 (s, 3H), 1.58-1.63 (m, 2H), 1.33-1.37 (m, 2H), 0.98 (t, 3H, J = 7.5 Hz). $^{13}$C NMR (CDCl$_3$): δ = 169.37, 166.28, 160.04, 147.62, 135.87, 128.31, 126.13, 121.77, 113.23, 96.15, 63.58, 54.35, 29.70, 18.13, 12.70. HRMS (ESI): m/z calculated for C$_{17}$H$_{18}$O$_5$ [M+H$^+$]: 303.1227, found: 303.123. FTIR (KBr, cm$^{-1}$): 3073.2, 3008.3, 1734.0, 1670.4, 1647.5, 1629.9, 1421.8, 1262.0, 895.5, 740.4, 705.8.

**Butyl (Z) (5-oxo-4-(4-tert-butyl phenyl)-5H-furan-2-ylidene) acetate (3fa-Z)**

Following the general procedure, 3fa-Z was obtained as a yellow oil (62.3 mg, 0.19 mmol, 38%). $^1$H NMR (CDCl$_3$): δ = 8.36 (s, 1H), 7.83-7.85 (m, 2H), 7.39-7.41 (m, 2H), 5.81 (s, 1H), 4.14 (t, 2H, J = 7.0 Hz), 1.64-1.59 (m, 2H), 1.33-1.38 (m, 2H), 1.26 (s, 9H), 0.89 (t, 3H, J = 7.5 Hz). $^{13}$C NMR (CDCl$_3$): δ = 166.09, 164.56, 158.45, 153.53, 133.58, 130.26, 126.64, 124.98, 124.68, 100.29, 63.82, 33.95, 30.07, 29.63, 18.15, 12.68.
HRMS (ESI): m/z calculated for C_{20}H_{24}O_4 [M+H]^+: 329.1747, found: 329.175. FTIR (KBr, cm^{-1}): 3851.2, 3646.5, 2959.3, 1783.9, 1732.2, 1651.4, 1393.2, 1254.8, 1218.8, 1135.7, 1078.5, 840.3.

Butyl (E) (5-oxo-4-(4-tert-butyl phenyl)-5H-furan-2-ylidene) acetate (3fa-E)

Following the general procedure, 3fa-E was obtained as a yellow oil (22.9 mg, 0.07 mmol, 14%). ^1H NMR (CDCl_3): δ = 7.80-7.82 (m, 2H), 7.40-7.41 (m, 2H), 7.38 (s, 1H), 5.41 (s, 1H), 4.16 (t, 2H, J = 7.0 Hz), 1.61-1.64 (m, 2H), 1.35-1.38 (m, 2H), 1.27 (s, 9H), 0.89 (t, 3H, J = 8.0 Hz). ^13C NMR (CDCl_3): δ = 166.32, 162.56, 154.53, 153.54, 133.12, 132.73, 132.73, 126.49, 125.01, 124.45, 99.80, 63.90, 33.96, 30.07, 29.64, 18.12, 12.70. HRMS (ESI): m/z calculated for C_{20}H_{24}O_4 [M+H]^+: 329.1743, found: 329.1747. FTIR (KBr, cm^{-1}): 3813.8, 3354.7, 2957.8, 1732.2, 1621.5, 1557.3, 1360.6, 1218.2, 1153.9, 966.4, 896.3, 846.2.

Butyl (Z) (5-oxo-4-(4-fluorophenyl)-5H-furan-2-ylidene) acetate (3ga-Z)

Following the general procedure, 3ga-Z was obtained as a light yellow solid (43.5 mg, 0.15 mmol, 30%), m.p. 75.8 °C. ^1H NMR (CDCl_3): δ = 8.45 (s, 1H), 7.99-8.01 (m, 2H), 7.14-7.17 (m, 2H), 5.93 (s, 1H), 4.23 (t, 2H, J = 6.5 Hz), 1.67-1.71 (m, 2H), 1.41-1.46 (m, 2H), 0.97 (t, 3H, J = 7.5 Hz). ^13C NMR (CDCl_3): δ = 165.92, 163.21 (J = 252 Hz), 162.20, 158.06, 132.52, 130.80 (J = 2 Hz), 128.99 (J = 9 Hz), 123.72, (J = 4 Hz), 115.26 (J = 2 Hz), 100.89, 63.94, 29.61, 18.14, 12.68. HRMS (ESI): m/z calculated for C_{16}H_{15}FO_4 [M+H]^+:
Butyl (E) (5-oxo-4-(4-fluorophenyl)-5H-furan-2-ylidene) acetate (3ga-E)

Following the general procedure, 3ga-E was obtained as a yellow oil (18.8 mg, 0.065 mmol, 13%). $^1$H NMR (CDCl$_3$): $\delta = 7.95-7.98$ (m, 2H), 7.46 (s, 1H), 7.14-7.17 (m, 2H), 5.51 (s, 1H), 4.24 (t, 2H, $J = 6.5$ Hz), 1.67-1.72 (m, 2H), 1.42-1.48 (m, 2H), 0.89 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 167.77$, 163.17 ($J = 251$ Hz), 162.39, 154.12, 133.24 ($J = 2$ Hz), 132.11, 128.85 ($J = 9$ Hz), 123.48, ($J = 4$ Hz), 115.29 ($J = 22$ Hz), 100.40, 64.00, 29.62, 18.11, 12.69. HRMS (ESI): m/z calculated for C$_{16}$H$_{15}$FO$_4$ [M+H]$^+$: 291.1027, found: 291.1029.

Butyl (Z) (5-oxo-4-(2-fluorophenyl)-5H-furan-2-ylidene) acetate (3ha-Z)

Following the general procedure, 3ha-Z was obtained as a yellow solid (55.1 mg, 0.19 mmol, 38%), m.p. 50.1 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.59$ (d, 1H, $J = 2.0$ Hz), 8.22-8.26 (m, 1H), 7.34-7.38 (m, 1H), 7.17-7.26 (m, 1H), 7.10-7.13 (m, 1H), 5.89 (s, 1H), 4.16 (t, 2H, $J = 7.0$ Hz), 1.60-1.74 (m, 2H), 1.35-1.39 (m, 2H), 0.90 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 165.98$, 164.13, 160.52 ($J = 254$ Hz), 158.10, 135.39 ($J = 15$ Hz), 131.21 ($J = 9$ Hz), 129.03, 127.47, 123.60 ($J = 4$ Hz), 115.96 ($J = 11$ Hz), 115.15 ($J = 22$ Hz), 101.72, 64.00, 29.59, 18.17, 12.66. HRMS (ESI): m/z calculated for C$_{16}$H$_{13}$FO$_4$ [M+H]$^+$: 291.1027, found: 291.1029. FTIR (KBr, cm$^{-1}$): 3851.1, 3383.2, 2974.5, 2899.5, 1651.7, 1455.1, 1382.1, 1088.3, 1048.7, 880.3, 666.6.
Butyl (E) (5-oxo-4-(2-fluorophenyl)-5H-furan-2-ylidene) acetate (3ha-E)

Following the general procedure, 3ha-E was obtained as a brown solid (21.7 mg, 0.075 mmol, 15%), m.p. 66.9 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.28-8.31$ (m, 1H), 7.69 (d, 1H, $J = 2.5$ Hz), 7.35-7.38 (m, 1H), 7.19-7.22 (m, 1H), 7.09-7.13 (m, 1H), 5.49 (s, 1H), 4.17 (t, 2H, $J = 7.0$ Hz), 1.61-1.65 (m, 2H), 1.35-1.40 (m, 2H), 0.90 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 166.27$, 162.38, 160.48 ($J = 253$ Hz), 154.37, 137.96 ($J = 15$ Hz), 131.17 ($J = 9$ Hz), 128.96, 126.68, 123.74 ($J = 4$ Hz), 115.76 ($J = 11$ Hz), 115.02 ($J = 22$ Hz), 101.04, 64.01, 29.62, 18.12, 12.69. HRMS (ESI): m/z calculated for C$_{16}$H$_{13}$FO$_4$ [M+H]$^+$: 291.1027, found: 291.1029. FTIR (KBr, cm$^{-1}$): 3897.4, 3507.5, 3382.9, 2352.1, 1770.4, 1660.3, 1557.3, 1446.1, 1372.3, 1253.0, 1132.9, 849.7.

Butyl (Z) (5-oxo-3-phenyl-4-methyl-5H-furan-2-ylidene) acetate (3ja-Z)

Following the general procedure, 3ja-Z was obtained as a yellow oil (42.9 mg, 0.15 mmol, 30%). $^1$H NMR (CDCl$_3$): $\delta = 7.43-7.45$ (m, 3H), 7.24-7.25 (m, 2H), 5.32 (s, 1H), 4.13 (t, 2H, $J = 6.5$ Hz), 1.98 (s, 3H), 1.56-1.62 (m, 2H), 1.30-1.36 (m, 2H), 0.87 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 167.91$, 162.74, 155.84, 149.48, 129.02, 128.22, 128.07, 127.90, 127.76, 98.95, 63.86, 29.61, 18.09, 12.67, 8.78. HRMS (ESI): m/z calculated for C$_{17}$H$_{18}$O$_4$ [M+H]$^+$: 287.1278, found: 287.1279. FTIR (KBr, cm$^{-1}$): 3383.4, 2974.9, 2899.6, 1651.6, 1454.9, 1382.7, 1087.8, 1047.9, 880.0.

Butyl 2,5-dihydro-4-methyl-3-phenyl-5-oxofuran-2-acetate (4ja)
Following the general procedure, 4ja was obtained as a yellow oil (46.1 mg, 0.16 mmol, 32%). $^1$H NMR (CDCl$_3$): $\delta = 7.39-7.42$ (m, 3H), 7.29-7.30 (m, 2H), 5.68-5.71 (m, 1H), 3.98-4.01 (m, 2H), 2.64 (dd, 1H, $J = 3.5$ Hz, $J = 16.5$ Hz), 2.35 (dd, 1H, $J = 9.0$ Hz, $J = 16.0$ Hz), 1.99 (s, 3H), 1.47-1.53 (m, 2H), 1.23-1.29 (m, 2H), 0.84 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 173.78$, 169.48, 158.11, 130.88, 130.07, 129.20, 127.80, 124.47, 76.78, 65.11, 38.45, 30.50, 19.05, 13.67, 10.05. HRMS (ESI): m/z calculated for C$_{17}$H$_{20}$O$_4$ [M+H]$^+$: 289.1434, found: 289.1436. FTIR (KBr, cm$^{-1}$): 3686.7, 3383.5, 3299.2, 2957.8, 2351.9, 1766.0, 1644.8, 1495.0, 1172.9, 1058.1, 984.6, 761.7.

![Chemical Structure of 4ja](image)

Diethyl (Z)-((4-(naphthalen-2-yl)-5-oxofuran-2(5H)-ylidene)methyl) phosphonate (3in-Z)

Following the general procedure, 3in-Z was obtained as a yellow oil (64.4 mg, 0.18 mmol, 36%). $^1$H NMR (CDCl$_3$): $\delta = 8.42$ (s, 1H), 7.93 (d, 1H, $J = 8.0$ Hz), 7.82-7.87 (m, 2H), 7.66 (d, 1H, $J = 7.0$ Hz), 7.45-7.49 (m, 3H), 5.64 (d, 1H, $J = 6.0$ Hz), 4.07-4.13 (m, 4H), 1.31 (t, 6H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 166.63$, 159.29 ($J = 24$ Hz), 136.50 ($J = 3$ Hz), 134.19, 132.73, 129.84, 129.82, 127.85, 127.48, 126.32, 125.38, 125.04, 124.06, 123.30, 96.74 ($J = 195$ Hz), 61.42, 61.38, 15.37, 15.32. HRMS (ESI): m/z calculated for C$_{19}$H$_{19}$P$_2$O$_5$ [M+H]$^+$: 359.1043, found: 359.104. FTIR (KBr, cm$^{-1}$): 3851.1, 1789.4, 1682.4, 1614.9, 1557.4, 1327.4, 1249.8, 1124.9, 1021.4, 919.0, 833.8, 774.5.

![Chemical Structure of 3in-Z](image)

Diethyl (E)-((4-(naphthalen-2-yl)-5-oxofuran-2(5H)-ylidene) methyl) phosphonate (3in-E)
Following the general procedure, 3in-E was obtained as a yellow oil (37.6 mg, 0.105 mmol, 21%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.84-7.88 (m, 3H), 7.65 (d, 1H, $J$=7.0 Hz), 7.46-7.50 (m, 5H), 5.40 (d, 1H, $J$ = 7.0 Hz), 4.18-4.23 (m, 4H), 1.35 (t, 6H, $J$ = 7.0 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ = 166.54, 155.95 ($J$ = 4 Hz), 137.88 ($J$ = 17 Hz), 133.86, 132.76, 129.87, 129.83, 127.99, 127.44, 126.31, 125.44, 124.74, 124.17, 123.05, 97.82 ($J$ = 191 Hz), 61.76, 61.71, 15.42, 15.37. HRMS (ESI): m/z calculated for C$_{19}$H$_{19}$P$_5$O$_5$ [M+H]$^+$: 359.1043, found: 359.105.

FTIR (KBr, cm$^{-1}$): 3851.1, 3646.3, 1770.6, 1682.4, 1515.2, 1455.3, 1403.2, 1360.6, 1250.1, 1030.4, 919.9, 774.3.

Butyl (Z) (5-oxo-4-(naphthalen-2-yl)-5H-furan-2-ylidene) acetate (3ia-Z)

Following the general procedure, 3ia-Z was obtained as a yellow solid (59.6 mg, 0.185 mmol, 37%), m.p. 58.3 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 8.47 (s, 1H), 7.94-7.96 (m, 1H), 7.82-7.86 (m, 2H), 7.67-7.68 (m, 1H), 7.44-7.49 (m, 3H), 5.93 (s, 1H), 4.14 (t, 2H, $J$ = 6.5 Hz), 1.58-1.63 (m, 2H), 1.31-1.39 (m, 2H), 0.88 (t, 3H, $J$ = 7.0 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ = 166.63, 164.33, 158.32, 135.97, 134.12, 132.77, 129.91, 129.84, 127.92, 127.57, 126.33, 125.39, 125.04, 124.10, 123.19, 101.11, 63.96, 29.59, 18.15, 12.67. HRMS (ESI): m/z calculated for C$_{20}$H$_{18}$O$_4$ [M+H]$^+$: 323.1278, found: 323.1277. FTIR (KBr, cm$^{-1}$): 3500.2, 3417.7, 1789.8, 1557.2, 1531.7, 1445.9, 1372.2, 1251.5, 1041.9, 775.6.

Butyl (E) (5-oxo-4-(naphthalen-2-yl)-5H-furan-2-ylidene) acetate (3ia-E)

Following the general procedure, 3ia-E was obtained as a brown oil (25.7 mg, 0.08 mmol, 16%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.83-7.87 (m, 3H), 7.65-7.67 (m, 1H), 7.47-7.49 (m, 4H), 5.50 (s, 1H), 4.19 (t, 2H, $J$ = 7.0 Hz), 4.18-4.23 (m, 4H), 1.35 (t, 6H, $J$ = 7.0 Hz).
1.62-1.66 (m, 2H), 1.37-1.40 (m, 2H), 0.90 (t, 3H, J = 7.0 Hz). $^{13}$C NMR (CDCl$_3$): δ = 167.90, 163.50, 155.42, 139.58, 133.80, 130.89, 130.88, 129.03, 128.50, 127.33, 126.45, 125.90, 125.21, 124.09, 101.62, 65.07, 30.68, 19.16, 13.74. HRMS (ESI): m/z calculated for C$_{20}$H$_{18}$O$_4$ [M+H]$^+$: 323.1278, found: 323.1279.

FTIR (KBr, cm$^{-1}$): 3592.5, 3564.4, 3444.6, 3382.9, 1789.7, 1651.5, 1428.0, 1253.9, 1141.2, 1038.4, 803.8, 775.4.

(5Z)-3-(Naphthalen-2-yl)-5-(2-oxobutyldiene)furan-2(5H)-one (3ig-Z)

Following the general procedure, 3ig-Z was obtained as a yellow solid (61.1 mg, 0.22 mmol, 44%), m.p. 128.1 °C. $^1$H NMR (CDCl$_3$): δ = 8.45 (s, 1H), 7.95 (d, 1H, J = 8.0 Hz), 7.82-7.86 (m, 2H), 7.67 (d, 1H, J = 7.0 Hz), 7.44-7.49 (m, 3H), 6.24 (s, 1H), 2.58 (q, 2H, J = 9.0 Hz), 1.08 (t, 3H, J = 7.5 Hz). $^{13}$C NMR (CDCl$_3$): δ = 199.31, 166.91, 156.69, 136.68, 134.86, 132.76, 129.94, 129.83, 127.90, 127.59, 126.38, 125.41, 125.09, 124.09, 123.24, 106.05, 37.35, 6.89. HRMS (ESI): m/z calculated for C$_{18}$H$_{14}$O$_3$ [M+H]$^+$: 279.1016, found: 279.1012. FTIR (KBr, cm$^{-1}$): 3850.9, 3731.3, 3564.4, 1738.2, 1651.5, 1403.0, 1360.5, 1252.8, 1137.7, 1042.0, 939.8, 775.0.

(5E)-3-(Naphthalen-2-yl)-5-(2-oxobutyldiene)furan-2(5H)-one (3ig-E)

Following the general procedure, 3ig-E was obtained as a yellow solid (37.5 mg, 0.135 mmol, 27%), m.p. 127.7 °C. $^1$H NMR (CDCl$_3$): δ = 7.85-7.91 (m, 3H), 7.67-7.69 (m, 1H), 7.56 (s, 1H), 7.49-7.50 (m, 3H), 5.63 (s, 1H), 2.96 (q, 2H, J = 7.5 Hz), 1.12 (t, 3H, J = 7.5 Hz). $^{13}$C NMR (CDCl$_3$): δ = 198.45, 166.67, 152.69, 139.47, 133.15, 132.79, 129.62, 129.83, 128.04, 127.49, 126.37, 125.48, 124.80, 124.18, 123.02, 109.09, 35.87, 6.89.
HRMS (ESI): m/z calculated for \( \text{C}_{18}\text{H}_{14}\text{O}_3 [\text{M+H}]^+ \): 279.1016, found: 279.1015. FTIR (KBr, cm\(^{-1}\)): 3646.3, 3444.5, 3317.7, 2357.3, 1789.9, 1714.4, 1633.8, 1470.7, 1416.8, 1203.2, 984.7, 782.4.

Butyl (Z)-3,4-diphenyl-5-oxo-2,5-dihydrofuran-2-ylideneacetate

(3ka-Z)

Following the general procedure, 3ka-Z was obtained as a white solid (60.9 mg, 0.175 mmol, 35%), m.p. 110.9 °C. \(^1\)H NMR (CDCl\(_3\)): \( \delta = 7.36\)–7.41 (m, 5H), 7.19–7.22 (m, 5H), 5.34 (s, 1H), 4.15 (t, 2H, \( J = 7.0 \)Hz), 1.58–1.63 (m, 2H), 1.32–1.38 (m, 2H), 0.88 (t, 3H, \( J = 7.5 \)Hz). \(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 167.27, 163.69, 156.97, 149.12, 130.07, 129.83, 129.43, 129.31, 129.29, 129.28, 128.92, 128.51, 128.22, 101.11, 64.96, 30.65, 19.12, 13.70. HRMS (ESI): m/z calculated for \( \text{C}_{22}\text{H}_{20}\text{O}_4 [\text{M+H}]^+ \): 349.1434, found: 349.1438. FTIR (KBr, cm\(^{-1}\)): 3799.4, 3383.3, 1823.0, 1732.1, 1621.6, 1428.1, 1337.1, 1270.2, 1132.8, 1000.7, 841.2, 696.6.

Butyl 2,5-dihydro-3,4-diphenyl-5-oxofuran-2-acetate (4ka)

Following the general procedure, 4ka was obtained as a colorless oil (24.5 mg, 0.07 mmol, 14%). \(^1\)H NMR (CDCl\(_3\)): \( \delta = 7.51\)–7.51 (m, 2H), 7.41–7.43 (m, 2H), 7.37–7.39 (m, 1H), 7.30–7.36 (m, 5H), 6.80 (s, 1H), 4.16–4.21 (m, 2H), 2.87 (d, 1H, \( J = 16.5 \)Hz), 2.71 (d, 1H, \( J = 16.5 \)Hz), 1.60–1.66 (m, 2H), 1.33–1.39 (m, 2H), 0.93 (t, 3H, \( J = 7.5 \)Hz). \(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 171.68, 169.44, 155.57, 130.33, 130.12, 129.53, 129.16, 129.09, 128.99, 128.86, 128.62, 128.48, 103.79, 65.82, 40.27, 30.25, 19.01, 13.62. HRMS (ESI): m/z calculated for \( \text{C}_{22}\text{H}_{22}\text{O}_4 [\text{M+H}]^+ \): 351.1583, found: 351.1591. FTIR (KBr, cm\(^{-1}\)): 3382.6, 1633.7, 1574.2, 1427.9, 1347.1, 1336.7, 1249.6, 1050.5, 970.0, 920.0, 888.3.
Butyl (Z)-3-propyl-4-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3la)

Following the general procedure, 3la was obtained as a yellow oil (18.9 mg, 0.075 mmol, 15%). $^1$H NMR (CDCl$_3$): $\delta$ = 5.43 (s, 1H), 4.21 (t, 2H, $J$ = 6.5 Hz), 2.43 (t, 2H, $J$ = 7.5 Hz), 1.98 (s, 3H), 1.67-1.70 (m, 2H), 1.57-1.61 (m, 2H), 1.41-1.46 (m, 4H), 0.94-0.99 (m, 6H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 169.27, 163.87, 157.10, 151.45, 129.07, 96.99, 64.87, 30.66, 26.51, 22.27, 19.13, 13.94, 13.71, 9.24. HRMS (ESI): m/z calculated for C$_{14}$H$_{20}$O$_4$ [M+H]$^+$: 253.1434, found: 253.1428. FTIR (KBr, cm$^{-1}$): 3550.4, 3440.3, 3284.2, 2351.4, 1841.9, 1778.8, 1651.4, 1505.0, 1392.8, 1360.2, 1336.7.

Butyl (2E,4E)-4-propylhexa-2,4-dienoate (5la)

Following the general procedure, 5la was obtained as a colorless oil (24.1 mg, 0.115 mmol, 23%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.26 (d, 1H, $J$ = 5.5 Hz), 5.98 (q, 1H, $J$ = 7.0 Hz), 5.79 (d, 1H, $J$ = 16.0 Hz), 4.15 (t, 2H, $J$ = 7.0 Hz), 2.23 (t, 2H, $J$ = 8.0 Hz), 1.81 (d, 3H, $J$ = 7.0 Hz), 1.64-1.67 (m, 2H), 1.39-1.45 (m, 4H), 0.95 (t, 3H, $J$ = 7.5 Hz), 0.93 (t, 3H, $J$ = 7.5 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ = 167.88, 148.77, 138.37, 136.60, 114.94, 64.12, 30.83, 28.18, 21.63, 19.21, 14.54, 14.13, 13.76. HRMS (ESI): m/z calculated for C$_{13}$H$_{22}$O$_2$ [M+H]$^+$: 211.1693, found: 211.1685. FTIR (KBr, cm$^{-1}$): 3897.6, 3550.5, 3354.9, 1842.1, 1770.4, 1694.2, 1557.3, 1417.0, 1360.6, 1258.2, 1178.5, 1057.2.

(E)-2-(3-Oxo-3-(butoxy)prop-1-en-1-yl)cyclopent-1-enecarboxylic acid (5ma)
Following the general procedure, 5ma was obtained as a white solid (40.4 mg, 0.17 mmol, 34%), m.p. 82.4 °C.

$^1$H NMR (CDCl$_3$): $\delta = 8.36$ (d, 1H, $J = 16.0$ Hz), 6.05 (d, 1H, $J = 16.0$ Hz), 4.20 (t, 2H, $J = 6.5$ Hz), 2.79-2.82 (m, 2H), 2.72-2.75 (m, 2H), 1.92-1.98 (m, 2H), 1.65-1.69 (m, 2H), 1.38-1.46 (m, 2H), 0.96 (t, 3H, $J = 7.5$ Hz).

$^{13}$C NMR (CDCl$_3$): $\delta = 170.21, 166.83, 150.97, 137.53, 136.07, 124.77, 64.65, 34.63, 34.21, 30.70, 21.14, 19.16, 13.72$. HRMS (ESI): m/z calculated for C$_{13}$H$_{18}$O$_4$ [M+H]$^+$: 239.1278, found: 239.1277. FTIR (KBr, cm$^{-1}$): 3799.1, 3542.4, 3507.3, 3444.6, 2959.3, 1714.7, 1661.0, 1633.7, 1592.4, 1455.2, 1281.8, 1169.4.

Butyl (Z)-3-methyl-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3na-Z)

Following the general procedure, 3na-Z was obtained as a yellow oil (15.7 mg, 0.075 mmol, 15%). $^1$H NMR (CDCl$_3$): $\delta = 6.10$ (s, 1H), 5.42 (s, 1H), 4.16 (t, 2H, $J = 6.5$ Hz), 2.12 (s, 3H), 1.60-1.62 (m, 2H), 1.36-1.37 (m, 2H), 0.89 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 166.56, 162.42, 156.79, 154.54, 118.97, 97.33, 64.01, 29.60, 18.09, 12.67, 10.87$. HRMS (ESI): m/z calculated for C$_{11}$H$_{14}$O$_4$ [M+H]$^+$: 211.0965, found: 211.0964. FTIR (KBr, cm$^{-1}$): 3331.9, 3318.2, 1790.2, 1651.6, 1574.3, 1486.8, 1416.8, 1317.9, 1231.8, 1150.1, 1046.1, 849.2.

Butyl (Z)-5-oxo-2,5-dihydrofuran-2-ylidene acetate (3oa-Z)

Following the general procedure, 3oa-Z was obtained as a white solid (19.6 mg, 0.1 mmol, 20%), m.p. 153.7 °C. $^1$H NMR (CDCl$_3$): $\delta = 8.31$ (d, 1H, $J = 5.5$ Hz), 6.39 (dd, 1H, $J = 2.0$ Hz, $J = 6.0$ Hz), 5.87 (d, 1H, $J = 2.0$ Hz), 4.14 (t, 2H, $J = 6.5$ Hz), 1.59-1.64 (m, 2H), 1.31-1.37 (m, 2H), 0.89 (t, 3H, $J = 7.0$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta = 166.81, 163.89, 156.24, 141.02, 123.35, 101.71, 64.05, 29.56, 18.12, 12.66$. HRMS (ESI): m/z calculated for C$_{10}$H$_{12}$O$_4$ [M+H]$^+$: 197.0808, found: 197.0814. FTIR (KBr, cm$^{-1}$): 3861.4, 3564.8, 3299.5, 3240.8, 2958.4, 2357.1, 1790.8, 1714.5, 1515.3, 1266.0, 1092.4, 826.8.
Gram-Scale Synthesis

An oven-dried vial was charged with \([\text{RhCp}^*\text{Cl}_2]\) \(_2\) (74.4 mg, 1.0 mol%), \(\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}\) (2.0 eq, 1.0 mmol), \(\text{CH}_3\text{CN}\) (36 mL). Then, vinyl carboxylic acid \(1\text{a}\) (1.03 g, 12 mmol) and acrylate \(2\text{a}\) (24 mmol) was added into the solution in sequence. The vial was sealed under argon and heated to 120°C with stirring for 24 hours. After cooling down, the mixture was directly applied to a flash column chromatography on silica gel for separation (EtOAc/petroleum ether mixtures). \(3\text{aa}-\text{Z}\) was obtained as an oil (1.21 g, 48%), \(3\text{aa}-\text{E}\) and \(4\text{aa}\) were obtained as an inseparable mixture: \(3\text{aa}-\text{E}\) (0.33 g, 13%), \(4\text{aa}\) (0.34 g, 13%).

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Competition experiment

A 15 mL vial was charged with [RhCp*Cl₂]₂ (2.4 mg, 2.0 mol %), Cu(OAc)₂·H₂O (80 mg, 2.0 eq) and CH₃CN (1.0 mL). Then, butyl acrylate 2a (1.0 eq, 0.2 mmol), methacrylic acid 1a (17.2 mg, 0.2 mmol) and methyl methacrylate 7 (20.2 mg, 0.2 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 120°C with stirring for overnight. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography affording the 3aa-Z (36% yield), 3aa-E (10% yield), 4aa (20% yield).

Controlled experiments

A 15 mL vial was charged with [RhCp*Cl₂]₂ (2.4 mg, 2.0 mol %), Cu(OAc)₂·H₂O (40 mg, 0.2 mmol) and CH₃CN (1.0 mL). Then, dienoic acid 5aa (1.0 eq, 0.2 mmol), and butyl acrylate 2a (1.0 eq, 0.2 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 120°C with stirring for overnight. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford product 3aa-Z (17.2 mg, 41% yield) and a mixture of 3aa-E and 4aa (12.7 mg), ratio 3aa-E/4aa = 0.4:1 was determined by NMR.
A 15 mL vial was charged with or without [RhCp*Cl₂]₂ (6.2 mg, 2.0 mol %), with or without Cu(OAc)₂·H₂O (100.0 mg, 0.5 mmol) and CH₃CN (2.5 mL). Then, butyl acrylate 2a (1.0 eq, 0.5 mmol), 4ja (144.0 mg, 0.5 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 120 °C with stirring for overnight. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to provide product 3ja. The Z/E ratio was determined by ¹H NMR.

A 15 mL vial was charged with [RhCp*Cl₂]₂ (2.4 mg, 2.0 mol %), Cu(OAc)₂·H₂O (80 mg, 2.0 eq) and CH₃CN (1.0 mL). Then, methyl methacrylate 7 (20.2 mg, 0.2 mmol), butyl acrylate (0.4 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 120 °C with stirring for overnight. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography affording no γ-alkyldienebutenolide or butadiene product. **Note:** the reaction of acrylates 7 and 2a led to no desired products, thus we can remove the possibility of generation of the products via demethylation.
A 15 mL vial was charged with [RhCp*Cl₂]₂ (6.2 mg, 2.0 mol%), Cu(OAc)₂.H₂O (199.7 mg, 2.0 eq) and CH₃CN (2.5 mL). Then, vinyl ester 8 (0.5 mmol), with or without 2a (1.0 mmol) were added into the solution. The vial was sealed under Ar and heated to 120°C with stirring for overnight. After cooling down, the mixture was concentrated in vacuo and applied to column chromatography for separation, affording no γ-alkylidenebutenolide or γ-butenoide.

Note: Vinyl ester 8 was also subjected to the catalytic conditions, but no γ-alkylidenebutenolide was obtained. This clearly rules out the intermediacy of vinyl ester in this tandem process.
Rh-Catalyzed H/D Exchange in 1b

An oven-dried vial was charged with [RhCp*Cl₂]₂ (6.2 mg, 2.0 mol %), Cu(OAc)₂·H₂O (2.0 eq, 1.0 mmol), CH₃CN (2.5 mL) and D₂O (10.0 eq, 5.0 mmol). Then, atropic acid 1b (0.5 mmol) was added into the solution. The vial was sealed under argon and heated to 120 °C with stirring for 0.5 hours. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures) on silica gel (47.2 mg, 64% recovered). The D % of 1b-d was estimated by ¹H NMR.
Kinetic Isotope Effect

A 15 mL vial was charged with [RhCp*Cl₂]₂ (1.2 mg, 2.0 mol %), Cu(OAc)₂·H₂O (40 mg, 2.0 eq) and CH₃CN (0.5 mL). Then, butyl acrylate 2a (0.01 mmol), tropic acid 1b (14.8 mg, 0.1 mmol) and 1b-d₂ (15.0 mg, 0.1 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 120°C with stirring for 1 hour. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography, affording a mixture of product (Z)-3ba and (Z)-3ba-d (4.2 mg). The ratio of (Z)-3ba/(Z)-3ba-d was determined by ¹H NMR (500 MHz, CDCl₃).
References:

NMR spectra
BuOOC + COOBu (3aa-E + 4aa)
(3ab-Z)
(3ab-E + 4ab)
SI-55
(3bl-Z)
(3bm-E)
\[ \text{BuOOCC} + \text{C}_6\text{H}_{13}\text{CO} \rightarrow \text{COOBu} \]
$\text{C}_{10}\text{H}_{21}\text{OOC} + \text{C}_{10}\text{H}_{21}\text{OOC}$

(3da-E+4da)
COOBu (3ea-Z)
(3in-E)
BuOOC

(3ia-E)
3aa-E (NOESY)