

Electronic Supplementary Material (ESI) for Chemical Communications

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Supporting Information

Copper-catalyzed direct α -ketoesterification of propiophenones with acetophenones via C(sp³)-H oxidative cross-coupling

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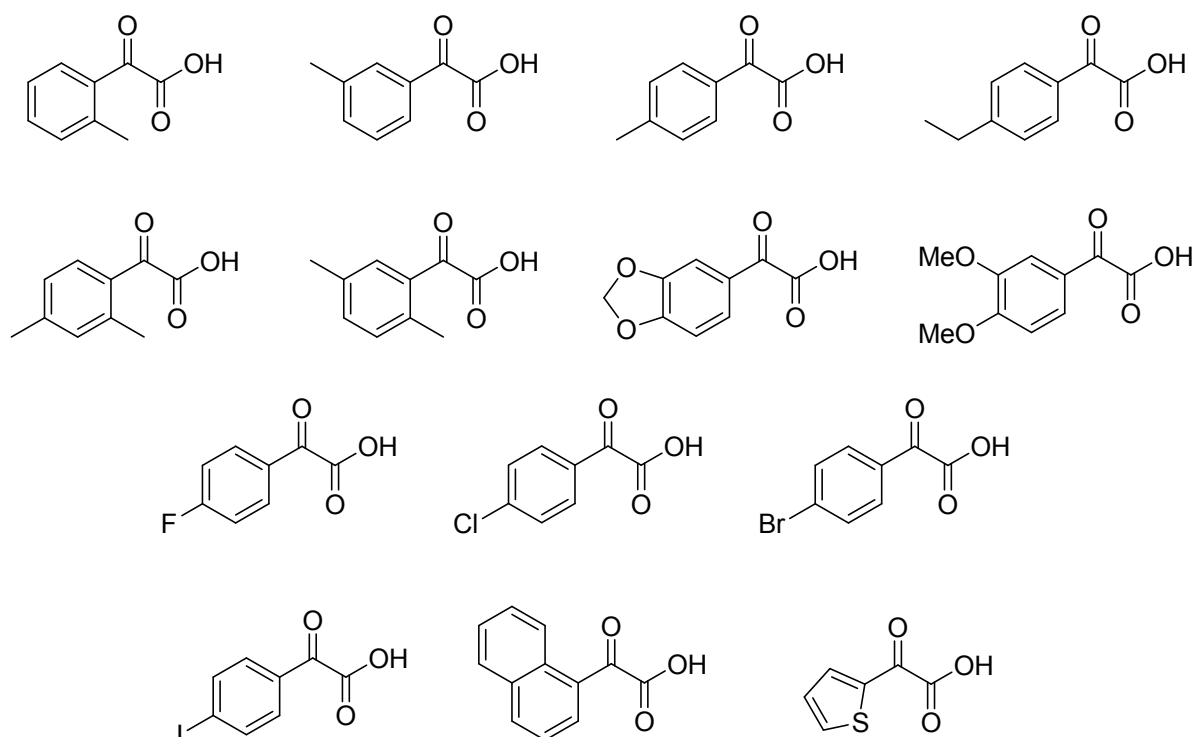
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1. General considerations

All ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz and 100 MHz respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). The chemicals and solvents were purchased from commercial suppliers either from Aldrich, USA or Shanghai Chemical Company (China) without further purification. All the reactions were carried out under air atmosphere. Products were purified by flash chromatography on 100–200 mesh silica gels, SiO_2 .

2. Starting materials

For this study, all propiophenone (**1a-1e**) and α -oxocarboxylic acid (**4a**) were purchased from commercial sources. Other α -oxocarboxylic acids can be prepared from oxidation of corresponding methyl ketones with SeO_2 according to the reported procedure (J. Zhuang, C. Wang, F. Xie and W. Zhang, *Tetrahedron*, 2009, **65**, 9797).

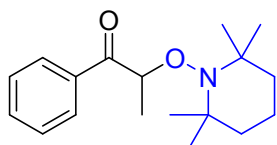


3. General procedure

The Schlenk tube equipped with a stir bar was charged with propiophenone (**1a**, 0.375 mmol), acetophenone (**2a**, 0.25 mmol), CuI (0.05 mmol), Dimethyl sulfoxide (DMSO, 0.30 mL), then O₂ was filled. The reaction mixture was stirred at 120 °C for 12 h. After the reaction was completed, it was cooled to room temperature and quenched with water and extracted with ethyl acetate and then dried with Na₂SO₄. The organic phase was concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography on silica gel with ethyl acetate-petroleum ether to provide the corresponding product.

4. LC-HRMS of TEMPO with α -carbonyl radical from propiophenone

Chemical Formula: C₁₈H₂₇NO₂



[M+H] = C₁₈H₂₈NO₂

Exact Mass: 289.2042

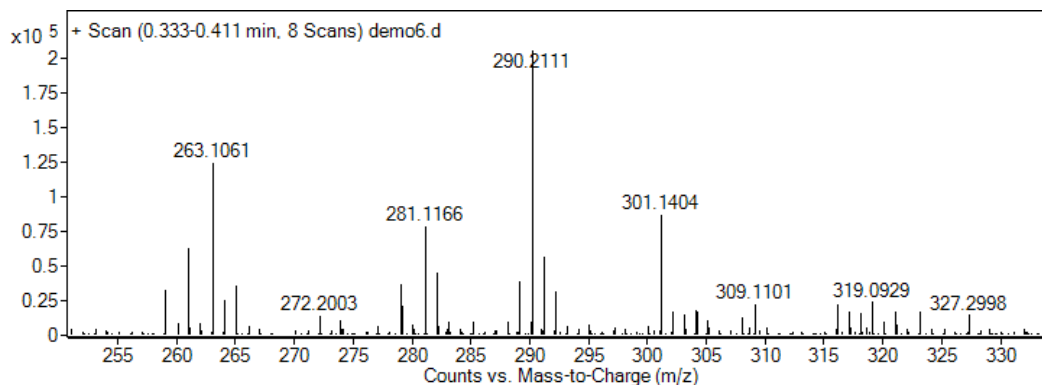
Molecular Weight: 289.4125

m/z: 289.2042 (100.0%), 290.2075 (19.5%), 291.2109 (1.8%)

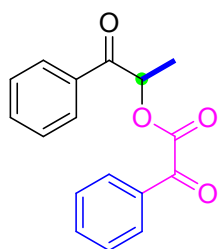
Elemental Analysis: C, 74.70; H, 9.40; N, 4.84; O, 11.06

Calculated: [M+H] = 290.2120

Found: [M+H] = 290.2111

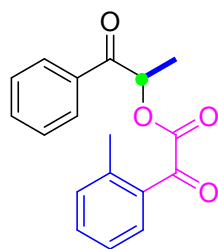


5. Characterization data for the products



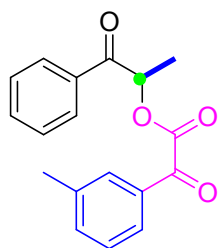
1-Oxo-1-phenylpropan-2-yl 2-oxo-2-phenylacetate (3a)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.17–8.15 (m, 2H), 8.02–8.00 (m, 2H), 7.71–7.64 (m, 2H), 7.57–7.55 (m, 4H), 6.21 (q, $J = 7.0$ Hz, 1H), 1.69 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.58, 186.24, 163.48, 135.07, 133.98, 133.92, 132.38, 130.32, 128.97, 128.94, 128.53, 73.68, 17.22. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{17}\text{H}_{13}\text{O}_4\text{Na}$: 305.0790, Found: 305.0795.



1-Oxo-1-phenylpropan-2-yl 2-oxo-2-(*o*-tolyl)acetate (3b)

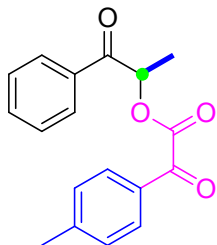
Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.02–8.00 (m, 3H), 7.67–7.63 (m, 1H), 7.56–7.50 (m, 3H), 7.41–7.38 (m, 1H), 7.33–7.31 (m, 1H), 6.19 (q, $J = 7.1$ Hz, 1H), 2.66 (s, 3H), 1.68 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.67, 188.14, 164.04, 141.76, 133.97, 133.92, 133.52, 132.26, 130.74, 128.94, 128.53, 126.12, 73.50, 21.71. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}$: 319.0946, Found: 319.0944.



1-Oxo-1-phenylpropan-2-yl 2-oxo-2-(*m*-tolyl)acetate (3c)

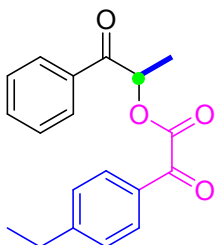
Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ : 8.02–8.00 (m, 2H), 7.96–7.94 (m, 2H), 7.67–7.63 (m, 1H), 7.56–7.52 (m, 2H), 7.50–7.48 (m, 1H), 7.45–7.41 (m, 1H), 6.20 (q, $J = 7.1$ Hz, 1H), 2.44 (s, 3H), 1.69 (d,

$J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.53, 186.40, 163.59, 138.85, 135.92, 133.95, 133.91, 132.34, 130.51, 128.93, 128.80, 128.51, 127.69, 73.59, 21.23, 17.17. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}$: 319.0946, Found: 319.0948.



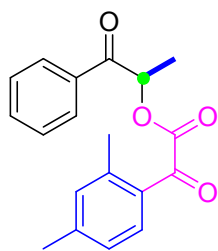
1-Oxo-1-phenylpropan-2-yl 2-oxo-2-(*p*-tolyl)acetate (3d)

Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (d, $J = 8.0$ Hz, 2H), 8.01 (d, $J = 7.6$ Hz, 2H), 7.66–7.62 (m, 1H), 7.55–7.51 (m, 2H), 7.35–7.33 (m, 2H), 6.19 (q, $J = 7.1$ Hz, 1H), 2.44 (s, 3H), 1.68 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.57, 185.84, 163.61, 146.39, 133.90, 133.88, 130.38, 129.63, 128.91, 128.47, 73.52, 21.89, 17.15. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}$: 319.0946, Found: 319.0942.



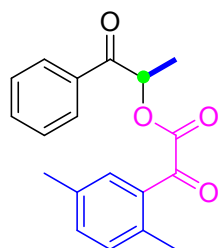
1-Oxo-1-phenylpropan-2-yl 2-(4-ethylphenyl)-2-oxoacetate (3e)

Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ : 8.07 (d, $J = 8.2$ Hz, 2H), 8.01 (d, $J = 7.6$ Hz, 2H), 7.66–7.62 (m, 1H), 7.55–7.51 (m, 2H), 7.38–7.36 (m, 2H), 6.20 (q, $J = 7.1$ Hz, 1H), 2.74 (q, $J = 7.6$ Hz, 2H), 1.68 (d, $J = 7.1$ Hz, 3H), 1.27 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.60, 185.86, 163.65, 152.46, 133.95, 133.88, 130.51, 130.13, 128.91, 128.48, 73.52, 29.14, 17.15, 14.94. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{19}\text{H}_{18}\text{O}_4\text{Na}$: 333.1103, Found: 333.1098.



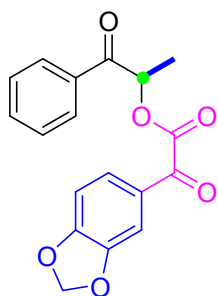
1-Oxo-1-phenylpropan-2-yl 2-(2,4-dimethylphenyl)-2-oxoacetate(3f)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.02–8.00 (m, 2H), 7.90–7.88 (m, 1H), 7.67–7.63 (m, 1H), 7.56–7.52 (m, 2H), 7.20–7.18 (m, 1H), 7.13 (s, 1H), 6.18 (q, $J = 7.1$ Hz, 1H), 2.63 (s, 3H), 2.40 (s, 3H), 1.67 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.75, 187.74, 164.29, 145.11, 141.99, 134.07, 133.92, 133.86, 133.18, 128.92, 128.53, 128.16, 126.84, 73.36, 21.73, 21.68, 17.16. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{19}\text{H}_{18}\text{O}_4\text{Na}$: 333.1103, Found: 333.1101.



1-Oxo-1-phenylpropan-2-yl 2-(2,5-dimethylphenyl)-2-oxoacetate (3g)

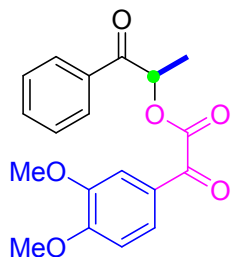
Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.03–8.01 (m, 2H), 7.81 (s, 1H), 7.66–7.62 (m, 1H), 7.55–7.51 (m, 2H), 7.33–7.31 (m, 1H), 7.27–7.19 (m, 1H), 6.19 (q, $J = 7.1$ Hz, 1H), 2.61 (s, 3H), 2.41 (s, 3H), 1.68 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.54, 188.28, 164.19, 138.56, 135.75, 134.71, 134.00, 133.84, 132.13, 130.57, 128.89, 128.51, 73.38, 21.12, 20.72, 17.13. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{19}\text{H}_{18}\text{O}_4\text{Na}$: 333.1103, Found: 333.1099.



1-Oxo-1-phenylpropan-2-yl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoacetate (3h)

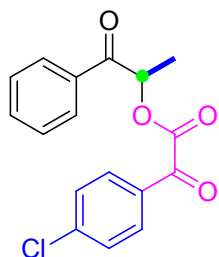
Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.00–7.98 (m, 2H), 7.80 (d, d, $J = 8.2$ Hz, 1.2 Hz, 1H), 7.66–7.62 (m, 1H), 7.57–7.51 (m, 3H), 6.94–6.92 (m, 1H), 6.17 (q, $J = 7.2$ Hz, 1H), 6.08 (s, 2H), 1.67 (d,

$J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.65, 184.39, 163.64, 153.66, 148.46, 133.92, 133.88, 128.92, 128.51, 128.48, 127.14, 108.63, 108.41, 102.18, 73.60, 17.15. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{14}\text{O}_6\text{Na}$: 349.0688, Found: 349.0687.



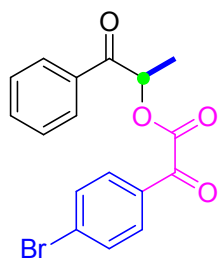
1-Oxo-1-phenylpropan-2-yl 2-(3,4-dimethoxyphenyl)-2-oxoacetate (3i)

Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ : 8.00–7.98 (m, 2H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.70 (s, 1H), 7.65–7.61 (m, 1H), 7.54–7.50 (m, 2H), 6.99 (d, $J = 8.4$ Hz, 1H), 6.18 (q, $J = 7.1$ Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H), 1.66 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.68, 184.99, 163.95, 155.03, 149.28, 133.89, 133.83, 128.89, 128.44, 126.28, 125.46, 111.21, 110.51, 73.51, 56.13, 56.07, 17.16. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{19}\text{H}_{18}\text{O}_6\text{Na}$: 365.1001, Found: 365.0996.



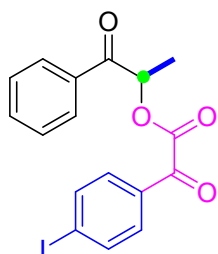
1-Oxo-1-phenylpropan-2-yl 2-(4-chlorophenyl)-2-oxoacetate (3j)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.13 (d, $J = 8.2$ Hz, 2H), 8.00 (d, $J = 7.7$ Hz, 2H), 7.68–7.65 (m, 1H), 7.57–7.52 (m, 4H), 6.20 (q, $J = 7.0$ Hz, 1H), 1.69 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.49, 184.95, 162.99, 141.83, 134.06, 133.82, 131.69, 130.82, 129.38, 129.01, 128.53, 73.89, 17.23. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{17}\text{H}_{13}\text{ClO}_4\text{Na}$: 339.0400, Found: 339.0396.



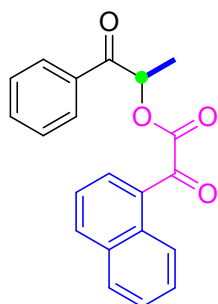
1-Oxo-1-phenylpropan-2-yl 2-(4-bromophenyl)-2-oxoacetate (3k)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.05–8.03 (m, 2H), 8.01–7.99 (m, 2H), 7.71–7.68 (m, 2H), 7.66–7.64 (m, 1H), 7.56–7.52 (m, 2H), 6.19 (q, $J = 7.1$ Hz, 1H), 1.69 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.45, 185.13, 162.93, 134.03, 133.87, 132.36, 131.68, 131.25, 130.74, 129.00, 128.51, 73.89, 17.21. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{17}\text{H}_{13}\text{BrO}_4\text{Na}$: 382.9895, Found: 382.9891.



1-Oxo-1-phenylpropan-2-yl 2-(4-iodophenyl)-2-oxoacetate (3l)

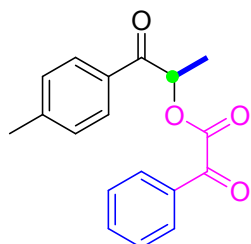
Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.01–7.99 (m, 2H), 7.94–7.92 (m, 2H), 7.88–7.86 (m, 2H), 7.68–7.64 (m, 1H), 7.56–7.53 (m, 2H), 6.19 (q, $J = 7.2$ Hz, 1H), 1.69 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.45, 185.50, 162.93, 138.37, 134.03, 133.89, 131.78, 131.42, 129.00, 128.53, 103.95, 73.88, 17.22. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{17}\text{H}_{13}\text{IO}_4\text{Na}$: 430.9756, Found: 430.9753.



1-Oxo-1-phenylpropan-2-yl 2-(naphthalen-1-yl)-2-oxoacetate (3m)

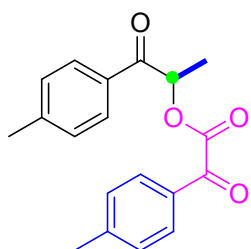
Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 9.19–9.17 (m, 1H), 8.38–8.37 (m, 1H), 8.16–8.14 (m, 1H), 8.05–8.03 (m, 2H), 7.94–7.92 (m, 1H), 7.74–7.70 (m, 1H), 7.66–7.59 (m, 3H), 7.57–7.53 (m, 2H), 6.23 (q, $J = 7.1$ Hz, 1H), 1.71 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.84, 188.30, 164.12,

136.11, 135.65, 133.96, 133.85, 130.98, 129.32, 128.96, 128.74, 128.55, 127.72, 126.96, 125.68, 124.65, 73.72, 17.21. HRMS (ESI) ($[M+Na]^+$) Calcd. For $C_{21}H_{16}O_4Na$: 355.0946, Found: 355.0941.



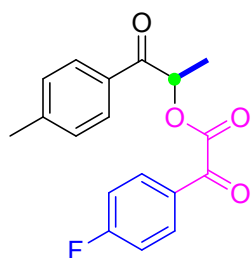
1-Oxo-1-(*p*-tolyl)propan-2-yl 2-oxo-2-phenylacetate (3n)

Colorless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 8.16 (d, $J = 7.5$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 2H), 7.69–7.65 (m, 1H), 7.56–7.52 (m, 2H), 7.34–7.32 (m, 2H), 6.18 (q, $J = 7.1$ Hz, 1H), 2.44 (s, 3H), 1.68 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 195.06, 186.28, 163.45, 144.98, 134.99, 132.38, 131.31, 130.28, 129.60, 128.88, 128.61, 73.62, 21.67, 17.29. HRMS (ESI) ($[M+Na]^+$) Calcd. For $C_{18}H_{16}O_4Na$: 319.0946, Found: 319.0947.



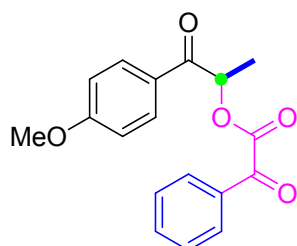
1-Oxo-1-(*p*-tolyl)propan-2-yl 2-oxo-2-(*p*-tolyl)acetate (3o)

Colorless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 8.04 (d, $J = 8.0$ Hz, 2H), 7.91 (d, $J = 8.0$ Hz, 2H), 7.35–7.31 (m, 4H), 6.17 (q, $J = 7.1$ Hz, 1H), 2.44 (s, 6H), 1.67 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 195.11, 185.92, 163.63, 146.35, 144.94, 131.29, 130.40, 129.92, 129.62, 129.58, 128.60, 73.49, 21.89, 21.67, 17.28. HRMS (ESI) ($[M+Na]^+$) Calcd. For $C_{19}H_{18}O_4Na$: 333.1103, Found: 333.1098.



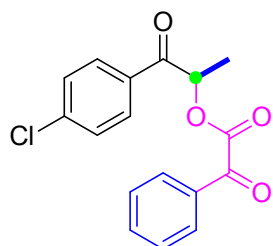
1-Oxo-1-(*p*-tolyl)propan-2-yl 2-(4-fluorophenyl)-2-oxoacetate (3p)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.25–8.22 (m, 2H), 7.91–7.89 (m, 2H), 7.34–7.32 (m, 2H), 7.24–7.20 (m, 2H), 6.18 (q, $J = 7.1$ Hz, 1H), 2.45 (s, 3H), 1.68 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.08, 184.66, 166.90 (d, $J_{\text{C-F}} = 256.8$ Hz), 163.20, 145.10, 133.25 (d, $J_{\text{C-F}} = 9.8$ Hz), 131.26, 129.65, 128.97 (d, $J_{\text{C-F}} = 2.8$ Hz), 128.63, 116.28 (d, $J_{\text{C-F}} = 22.1$ Hz), 73.79, 21.70, 17.32. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{15}\text{FO}_4\text{Na}$: 337.0852, Found: 337.0853.



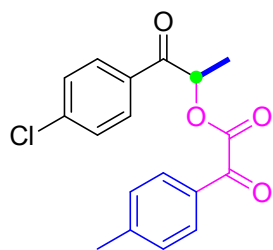
1-(4-Methoxyphenyl)-1-oxopropan-2-yl 2-oxo-2-phenylacetate (3q)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.16 (d, $J = 7.6$ Hz, 2H), 7.99 (d, $J = 8.8$ Hz, 2H), 7.69–7.65 (m, 1H), 7.56–7.52 (m, 2H), 7.00–6.98 (m, 2H), 6.16 (q, $J = 7.0$ Hz, 1H), 3.88 (s, 3H), 1.67 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 193.85, 186.32, 164.15, 163.47, 134.99, 132.38, 130.87, 130.28, 128.88, 126.64, 114.15, 73.46, 55.51, 17.42. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{16}\text{O}_5\text{Na}$: 335.0895, Found: 335.0889.



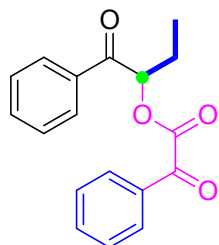
1-(4-Chlorophenyl)-1-oxopropan-2-yl 2-oxo-2-phenylacetate (3r)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.13 (d, $J = 7.6$ Hz, 2H), 7.95 (d, $J = 8.4$ Hz, 2H), 7.71–7.67 (m, 1H), 7.57–7.51 (m, 4H), 6.13 (q, $J = 7.1$ Hz, 1H), 1.68 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.50, 186.00, 163.38, 140.55, 135.12, 132.33, 132.22, 130.27, 129.93, 129.34, 128.95, 73.52, 17.12. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{17}\text{H}_{13}\text{ClO}_4\text{Na}$: 339.0400, Found: 339.0395.



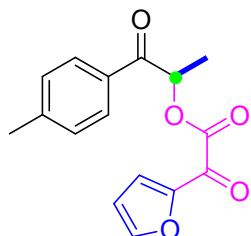
1-(4-Chlorophenyl)-1-oxopropan-2-yl 2-oxo-2-(*p*-tolyl)acetate (3s)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (d, $J = 8.1$ Hz, 2H), 7.95 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.11 (q, $J = 7.1$ Hz, 1H), 2.45 (s, 3H), 1.67 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.54, 185.62, 163.54, 146.49, 140.46, 132.22, 130.36, 129.91, 129.87, 129.67, 129.29, 73.40, 21.91, 17.08. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{15}\text{ClO}_4\text{Na}$: 353.0557, Found: 353.0555.



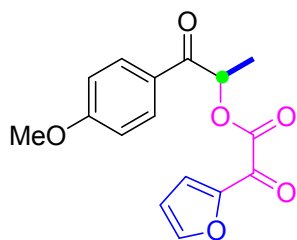
1-Oxo-1-phenylbutan-2-yl 2-oxo-2-phenylacetate (3t)

Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.19–8.17 (m, 2H), 8.02–8.00 (m, 2H), 7.70–7.63 (m, 2H), 7.57–7.51 (m, 4H), 6.08 (q, $J = 3.8$ Hz, 1H), 2.15–1.97 (m, 2H), 1.07 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.19, 186.28, 163.75, 135.00, 134.40, 133.87, 132.43, 130.29, 128.93, 128.91, 128.39, 78.43, 24.76, 9.61. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}$: 319.0946, Found: 319.0946.



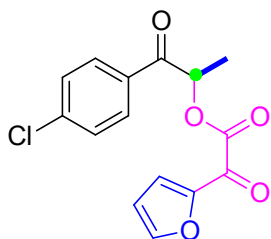
1-Oxo-1-(*p*-tolyl)propan-2-yl 2-(furan-2-yl)-2-oxoacetate (3u)

Yellow solid. ^1H NMR (400 MHz, CDCl_3) δ : 7.88–7.84 (m, 3H), 7.76 (s, 1H), 7.30–7.28 (m, 2H), 6.62–6.61 (m, 1H), 6.15 (q, $J = 7.1$ Hz, 1H), 2.41 (s, 3H), 1.67 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.75, 170.80, 160.57, 149.69, 149.50, 145.01, 131.09, 129.56, 128.53, 125.54, 113.07, 73.74, 21.62, 17.30. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{16}\text{H}_{14}\text{NaO}_5$: 309.0739, Found: 309.0735.



1-(4-Methoxyphenyl)-1-oxopropan-2-yl 2-(furan-2-yl)-2-oxoacetate (3v)

Yellow solid. ^1H NMR (400 MHz, CDCl_3) δ : 7.95 (d, $J = 8.8$ Hz, 2H), 7.85–7.84 (m, 1H), 7.76 (s, 1H), 6.96 (d, $J = 8.7$ Hz, 2H), 6.62–6.61 (m, 1H), 6.13 (q, $J = 7.0$ Hz, 1H), 3.86 (s, 3H), 1.66 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 193.56, 170.86, 164.13, 160.59, 149.67, 149.54, 130.81, 126.46, 125.52, 114.11, 113.06, 73.60, 55.47, 17.43. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{16}\text{H}_{14}\text{NaO}_6$: 325.0688, Found: 325.0689.



1-(4-Chlorophenyl)-1-oxopropan-2-yl 2-(furan-2-yl)-2-oxoacetate (3w)

Yellow solid. ^1H NMR (400 MHz, CDCl_3) δ : 7.93–7.90 (m, 2H), 7.80–7.79 (m, 1H), 7.77 (s, 1H), 7.49–7.47 (m, 2H), 6.63–6.62 (m, 1H), 6.10 (q, $J = 7.1$ Hz, 1H), 1.67 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.17, 170.51, 160.52, 149.78, 149.46, 140.47, 132.02, 129.85, 129.25, 125.45, 113.10, 73.67, 17.10. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. For $\text{C}_{15}\text{H}_{11}\text{ClNaO}_5$: 329.0193, Found: 329.0190.

6. ^1H and ^{13}C spectra of the products

