Visible light promote Decyanation esterification reaction of Aryl ketonitriles with dioxygen and alcohols to α-Ketoesters

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Experimental section

General remarks: alcohols (0.6 mmol), benzoylecetonitrile (0.4 mmol), THF (2 mL) were added to grass tube. The reaction mixture was irradiated by one halogen tungsten lamp (500W) for 24 h accompanied with a fan being sufficient to allow reaction temperature down to room temperature. After the reaction was completed (monitored by TLC), the reaction liquid was purified by chromatography on silica gel (20:1 petroleum ether/EtOAc) to give the product 3a-3s. All reactions were carried out in an open system. A halogen tungsten lamp (wavelengths of 400 - 750 nm) was used as the visible light source. All of the starting materials were purchased unless otherwise specified, 1H NMR (400 MHz) spectra were recorded in CDCl₃ solutions, using a Bruker Ultra Shield Plus 400 MHz instrument with reference tetramethylsilane (TMS).

Experimental characterization data for compounds

Methyl 2-oxo-2-phenylacetate (3a)

Light yellow oil; 93% yield (0.37 mmol). 1H NMR (400 MHz, CDCl₃) δ = 8.02 (d, J=9.4, 2H), 7.67 (t, J=7.4, 1H), 7.52 (t, J=7.8, 2H), 3.98 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ = 186.06, 164.05, 134.99, 132.42, 130.08, 128.91, 52.78.

Ethyl 2-oxo-2-phenylacetate (3b)

Light yellow oil; 90% yield (0.36 mmol). 1H NMR (400 MHz, CDCl₃) δ = 8.01 (d, J=8.4, 2H), 7.66 (t, J=6.9, 1H), 7.52 (t, J=7.7, 2H), 4.46 (q, J=7.1, 2H), 1.43 (t, J=7.1, 3H).

13C NMR (101 MHz, CDCl₃) δ = 186.46, 163.85, 134.93, 132.47, 130.04, 128.91, 62.37, 14.12.

Amyl 2-oxo-2-phenylacetate (3c)

Light yellow oil; 90% yield (0.36 mmol). 1H NMR (400 MHz, CDCl₃) δ = 8.03 (d, J=7.9, 2H), 7.68 (t, J=7.4, 1H), 7.54 (t, J=7.7, 2H), 4.41 (t, J=6.8, 2H), 1.99 – 1.67 (m, 2H), 1.40 (d, J=3.8, 4H), 0.94 (t, J=6.8, 3H).

13C NMR (101 MHz, CDCl₃) δ = 186.53, 164.02, 134.91, 132.49, 130.02, 128.91, 66.40, 28.15, 27.90, 22.25, 13.92.
Phenylpropyl 2-oxo-2-phenylacetate (3d)
Light yellow oil; 57% yield (0.23 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ = 8.01 (d, J = 7.7, 2H), 7.67 (t, J = 7.4, 1H), 7.52 (t, J = 7.7, 2H), 7.29 (t, J = 7.5, 2H), 7.20 (t, J = 7.3, 2H), 4.40 (t, J = 6.6, 2H), 2.76 (m, 2H), 2.12 (m, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 186.38, 163.93, 140.64, 134.96, 132.48, 130.04, 128.94, 128.55, 128.44, 126.22, 65.46, 31.93, 29.99.

Isopropyl 2-oxo-2-phenylacetate (3e)
Light yellow oil; 74% yield (0.3 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ = 8.00 (d, J = 7.2, 2H), 7.66 (t, J = 7.4, 1H), 7.51 (t, J = 7.7, 2H), 5.33 (dt, J = 12.5, 6.3, 1H), 1.41 (d, J = 6.3, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 186.73, 163.65, 134.81, 132.54, 129.96, 128.89, 70.69, 21.73.

Benzyl 2-oxo-2-phenylacetate (3g)
Light yellow oil; 65% yield (0.26 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.97 (d, J = 7.2, 2H), 7.64 (t, J = 7.4, 1H), 7.53 – 7.43 (m, 4H), 7.39 (d, J = 7.3, 2H), 7.34 (d, J = 4.5, 1H), 5.42 (s, 1H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 186.06, 163.65, 134.91, 132.54, 129.96, 128.89, 128.91, 128.83, 128.76, 128.62, 67.78.

4-Methylbenzyl 2-oxo-2-phenylacetate (3h)
Light yellow oil; 60% yield (0.24 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.96 (d, J = 7.2, 2H), 7.63 (t, J = 7.4, 1H), 7.48 (t, J = 7.8, 2H), 7.33 (d, J = 8.0, 2H), 7.20 (t, J = 7.4, 2H), 5.37 (s, 2H), 2.36 (s, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 186.16, 163.73, 138.79, 134.92, 132.47, 131.57, 130.05, 129.44, 128.90, 128.81, 67.80, 21.27.

4-Methoxylbenzyl 2-oxo-2-phenylacetate (3i)
Light yellow oil; 59% yield (0.24 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.95 (d, J = 8.3, 2H), 7.3 (t, J = 7.8, 1H), 7.48 (t, J = 7.8, 2H), 7.39 (d, J = 8.7, 2H), 6.91 (d, J = 8.7, 2H), 5.35 (s, 2H), 3.81 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 163.77, 160.09, 134.89, 130.6, 130.03, 129.42, 128.88, 126.68, 114.13, 113.80, 67.71, 55.33.

4-Fluorobenzyl 2-oxo-2-phenylacetate (3j)
Light yellow oil; 61% yield (0.24 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.96 (d, J = 7.2, 2H), 7.65 (t, J = 7.4, 1H), 7.51 – 7.42 (m, 4H), 7.08 (t, J = 8.6, 2H), 5.38 (s, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 186.70, 163.52, 135.02, 130.79, 130.71, 130.45, 130.03, 128.94, 115.87, 115.65, 67.03.

4-Chlorobenzyl 2-oxo-2-phenylacetate (3k)
Yellow solid; mp 53-55°C; 59% yield (0.24 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.96 (d, $J$=8.4, 1.3, 2H), 7.66 (t, $J$=7.5, 1H), 7.50 (t, $J$=7.8, 2H), 7.38 (d, $J$=1.9, 4H), 5.37 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 185.81, 163.45, 135.06, 134.83, 133.04, 132.36, 130.04, 130.00, 129.00, 128.96, 66.89.

4-Bromobenzyl 2-oxo-2-phenylacetate (3l)
Colorless oil; 53% yield (0.21 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.96 (d, $J$=7.1, 2H), 7.66 (t, $J$=7.5, 1H), 7.54 – 7.48 (m, 4H), 7.32 (d, $J$=8.5, 2H), 5.36 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 185.78, 163.43, 135.06, 133.55, 132.35, 131.96, 130.24, 130.04, 128.96, 122.99, 66.90.

4-Nitrylbenzyl 2-oxo-2-phenylacetate (3m)
Light yellow oil; 56% yield (0.22 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.26 (d, $J$=8.7, 2H), 8.00 (d, $J$=8.2, 2H), 7.69 (t, $J$=7.5, 1H), 7.62 (d, $J$=8.8, 2H), 7.53 (t, $J$=7.8, 2H), 5.50 (s, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 185.34, 163.06, 148.07, 141.62, 135.27, 132.22, 130.07, 129.05, 128.71, 124.01, 66.00.

Ethyl 2-(4-Methylphenyl)-2-oxoacetate (3n)
Light yellow oil; 93% yield (0.37 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.90 (d, $J$=8.3, 2H), 7.29 (t, $J$=6.0, 2H), 4.44 (q, $J$=7.1, 3H), 2.43 (s, 3H), 1.41 (t, $J$=7.2, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 186.12, 164.06, 146.25, 130.15, 130.02, 129.63, 62.23, 21.90, 14.12.

Methyl 2-(4-Methylphenyl)-2-oxoacetate (3o)
Light yellow oil; 94% yield (0.38 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.91 (d, $J$=8.2, 2H), 7.30 (d, $J$=8.2, 2H), 3.97 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 185.71, 164.25, 146.35, 130.21, 129.99, 129.64, 52.68, 21.90.

Methyl 2-(4-Chlorophenyl)-2-oxoacetate (3p)
White solid; mp 54-56°C; 93% yield (0.37 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.99 (d, $J$=8.6, 2H), 7.49 (d, $J$=8.6, 2H), 3.98 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 184.48, 163.42, 141.74, 131.49, 130.87, 129.32, 52.94.

**Ethyl 2-(4-Chlorophenyl)-2-oxoacetate (3q)**

Yellow oil; 90% yield (0.36 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.99 (d, $J=8.7$, 2H), 7.49 (d, $J=8.7$, 2H), 4.45 (q, $J=7.1$, 2H), 1.43 (t, $J=7.1$, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 184.92, 163.23, 141.66, 132.61, 131.45, 129.32, 62.58, 14.09.

**Methyl 2-(4-fluorophenyl)-2-oxoacetate (3r)**

White solid; mp 46-48°C; 92% yield (0.37 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 8.09 (dd, $J=9.0$, 5.4, 2H), 7.19 (t, $J=8.6$, 2H), 3.98 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 184.14, 168.12, 165.55, 163.61, 133.02 (d, $^2J_{CF}=9.8$), 128.98 (d, $^2J_{CF}=2.9$), 116.26 (d, $^2J_{CF}=22.2$), 52.87.

**Ethyl 2-(4-Methoxyphenyl)-2-oxoacetate (3s)**

White solid; mp 53-55°C; 91% yield (0.36 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 8.01 (d, $J=9.0$, 2H), 6.98 (d, $J=9.0$, 2H), 3.96 (s, 3H), 3.90 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 185.78, 163.43, 135.06, 133.55, 132.35, 131.96, 130.24, 130.04, 128.96, 122.99, 66.90.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 184.45, 165.10, 164.36, 132.67, 125.49, 114.26, 55.66, 52.67.
$^1$H NMR spectra of compound 3a (400 MHz, CDCl$_3$).

$^{13}$C NMR spectra of compound 3a (100 MHz, CDCl$_3$).
\[ ^1\text{H NMR spectra of compound 3b (400 MHz, CDCl}_3 \)\].

\[ ^{13}\text{C NMR spectra of compound 3b (100 MHz, CDCl}_3 \)\].
\( ^1H \) NMR spectra of compound 3c (400 MHz, DMSO-\( d_6 \)).

\( ^{13}C \) NMR spectra of compound 3c (100 MHz, CDCl\(_3\)).
$^{1}$H NMR spectra of compound 3d (400 MHz, CDCl₃).

$^{13}$C NMR spectra of compound 3d (100 MHz, CDCl₃).
1H NMR spectra of compound 3e (400 MHz, CDCl₃).

13C NMR spectra of compound 3e (100 MHz, CDCl₃).
$^1$H NMR spectra of compound 3g (400 MHz, CDCl$_3$).

$^{13}$C NMR spectra of compound 3g (100 MHz, CDCl$_3$).
$^1$H NMR spectra of compound 3h (400 MHz, CDCl$_3$).

$^{13}$C NMR spectra of compound 3h (100 MHz, CDCl$_3$).
$^1$H NMR spectra of compound 3i (400 MHz, CDCl$_3$).

$^{13}$C NMR spectra of compound 3i (100 MHz, CDCl$_3$).
$^1$H NMR spectra of compound 3j (400 MHz, CDCl$_3$).

$^{13}$C NMR spectra of compound 3j (100 MHz, CDCl$_3$).
$^1$H NMR spectra of compound 3k (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of compound 3k (100 MHz, CDCl$_3$)
$^{1}H$ NMR spectra of compound 3l (400 MHz, CDCl$_3$)

$^{13}C$ NMR spectra of compound 3l (100 MHz, CDCl$_3$)
$^1$H NMR spectra of compound 3m (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of compound 3m (100 MHz, CDCl$_3$)
1H NMR spectra of compound 3n (400 MHz, CDCl₃)

13C NMR spectra of compound 3n (100 MHz, CDCl₃)
$^1$H NMR spectra of compound 3o (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of compound 3o (100 MHz, CDCl$_3$)
$^1$H NMR spectra of compound 3p (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of compound 3p (100 MHz, CDCl$_3$)
$^{1}H$ NMR spectra of compound 3q (400 MHz, CDCl$_3$)

$^{13}C$ NMR spectra of compound 3q (100 MHz, CDCl$_3$)
$^1$H NMR spectra of compound 3r (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of compound 3r (100 MHz, CDCl$_3$)
$^1$H NMR spectra of compound 3s (400 MHz, CDCl$_3$)

$^{13}$C NMR spectra of compound 3s (100 MHz, CDCl$_3$)