TBAI-catalyzed oxidative coupling of β-ketoesters with carboxylic acid: synthesis of α-carboxylic-β-ketoesters

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Abstract

TBAI-catalyzed oxidative coupling of β-ketoesters with carboxylic acid using TBHP as oxidant has been established. This transformation provides a facile and direct strategy for the synthesis of α-carboxylic-β-ketoesters.

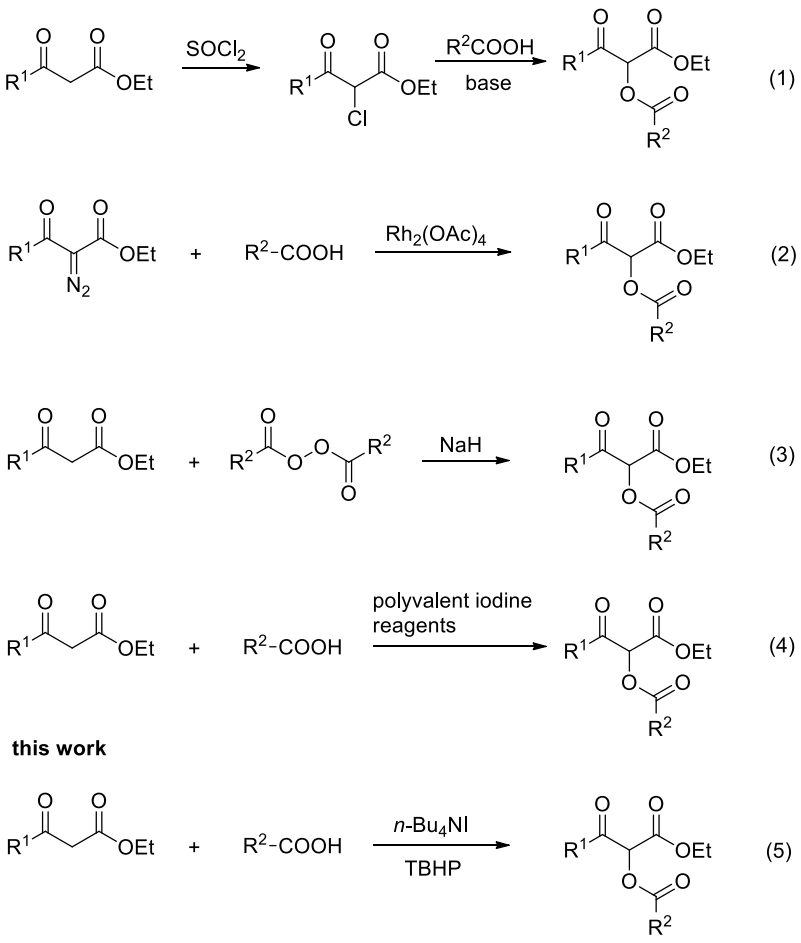
Keywords: β-Ketoesters, carboxylic acid, oxidative coupling, α-carboxylic-β-ketoesters, TBAI

Introduction

α-Carboxylic-β-ketoesters are important intermediates for the synthesis of a variety of heterocyclic [1] and natural products.[2] The conventional approach towards the synthesis of α-carboxylic-β-ketoesters involved the chlorination of the β-ketoesters with sulfuryl chloride followed by treatment with a mixture of a carboxylic acid and a base in DMF (Scheme 1. Eq. 1).[1] This route was undesirable because the chlorination process was not environmentally friendly. Some modified methods, such as the reaction of α-diazo-β-ketoesters with carboxylic acids (Eq. 2) [3] as well as the reaction of β-ketoesters with benzoyl peroxide (Eq. 3) [2a] also suffered from the use of not easily handed starting materials. From both environmental and economical points of view, the direct cross-dehydrogenative coupling (CDC) of β-ketoesters with carboxylic acid was the excellent protocol for the synthesis of α-carboxylic-β-ketoesters, which has been realized by using stoichiometric amount of polyvalent iodine reagents as oxidants (Eq. 4).[4]

Recently, replacement of stoichiometric polyvalent iodine reagents with catalytic amount of hypervalent iodine reagent have been increasingly attractive to synthetic organic chemists, as they are more environmentally friendly and economical.[5] Among them, a novel oxidizing system which features the use of quaternary ammonium iodide(TBAI) as the catalyst and H_2O_2 or tert-butyl hydroperoxide (TBHP) as the stoichiometric oxidant has been widely employed to realize

the intermolecular C–O and C–N coupling.[6] In particular, Ishihara and co-workers developed the TBAI/TBHP system catalyzed α-oxyacylation of carbonyl compounds with carboxylic acids.[6c] However, compared to the well studied α-oxyacylation of ketones, the scope and limitation of the α-oxyacylation of β-ketoesters were few studied. Herein, we report in detail the direct coupling of β-ketoesters with carboxylic acids by the Bu_4NI/TBHP system to construct α-carboxylic-β-ketoesters.



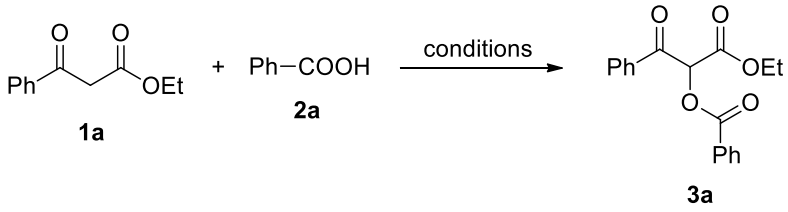
Scheme 1. Synthesis of α-carboxylic-β-ketoesters.

Results and Discussion

At the begining of our study, ethyl 2-benzoylacetate **1a** and benzoic acid (**2a**) were chosen as coupling partners using the Bu_4NI/TBHP system in MeCN at 60 °C to achieve the transformation. Gratifyingly, the desired α-carboxylic-β-ketoester **3a** was obtained in 83% yield after 5 h (Table 1, entry 1). In control reactions without TBAI as catalyst (entry 2) or without TBHP as oxidant (entry 3), no target product was obtained. The yield decreased when TBAI was

replaced by KI (entry 4) or TBHP was replaced by H_2O_2 (entry 5). When EtOAc was used as solvent, slightly low yield was obtained (entry 6). Reducing the reaction temperature also decreased the yield (entry 7).

Table 1. Optimization of reaction conditions for access to **3a**[a]



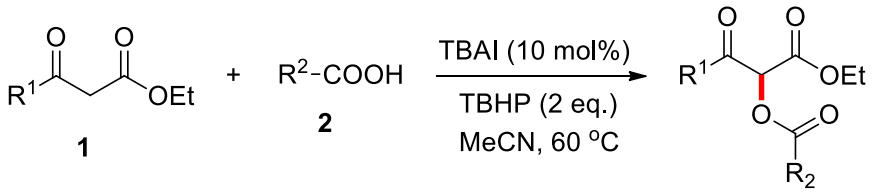
Entry	Catalyst	Oxidant	Solvent	Time (h)	Yield (%)[b]
1	TBAI	TBHP	MeCN	5	83
2	TBAI	-	MeCN	5	0
3	-	TBHP	MeCN	5	0
4	KI	TBHP	MeCN	5	26
5	TBAI	H_2O_2	MeCN	5	30
6	TBAI	TBHP	EtOAc	5	75
7[c]	TBAI	TBHP	MeCN	8	38

[a]General reaction conditions: 0.5 mmol of **1a**, 0.6 mmol of **2a**, 10 mol% of TBAI and 1.0 mmol of TBHP in 2 mL of MeCN at 60 ^oC. [b] Isolated yield. [c] Room temperature.

The substrate scope toward this oxidative coupling was further investigated, and the results were listed in Table 2. A wide array of β-ketoesters was examined in the reaction with benzoic acid **2a**, and moderate to good yields were obtained in producing the corresponding α-carboxylic-β-ketoesters (Table 2, entries 1-7). β-ketoesters derivatives, which bear substituted groups such as methyl, methoxyl, chloro and bromo at *para* or *ortho* positions, all reacted smoothly with **2a** to afford the desired corresponding products. Naphthyl substituted β-ketoesters and ethyl acetoacetate also reacted smoothly, albeit in lower yield (entries 7-8). Generally, β-ketoesters derivatives bearing electron-withdrawing groups were reacted faster than those bearing electron-donating groups. Varied carboxylic acid were also suitable partners for ethyl 2-benzoylacetate (**1a**) to access the corresponding α-carboxylic-β-ketoesters. Similarly, benzoic

acids, which bear substituents such as methyl, methoxyl, chloro and bromo at *para* or *ortho* positions, all reacted smoothly with **1a** to afford the desired corresponding products in good to excellent yields (entries 8-13). In contract to the substituent effect of β-ketoesters derivatives, benzoic acids bearing electron-donating groups showed higher reactivity. Aliphatic carboxylic acids were also suitable partners for **1a** to form the α-carboxylic-β-ketoesters (entries 14-16) in moderate to good yields. Moreover, a-benzoxylation of diethyl malonate could also take place to form the desired product in 64% yield (entry 18).

Table 2. Synthesis of α-carboxylic-β-ketoesters **3** via the TBAI-catalyzed oxidative coupling of **1** and **2** [a]

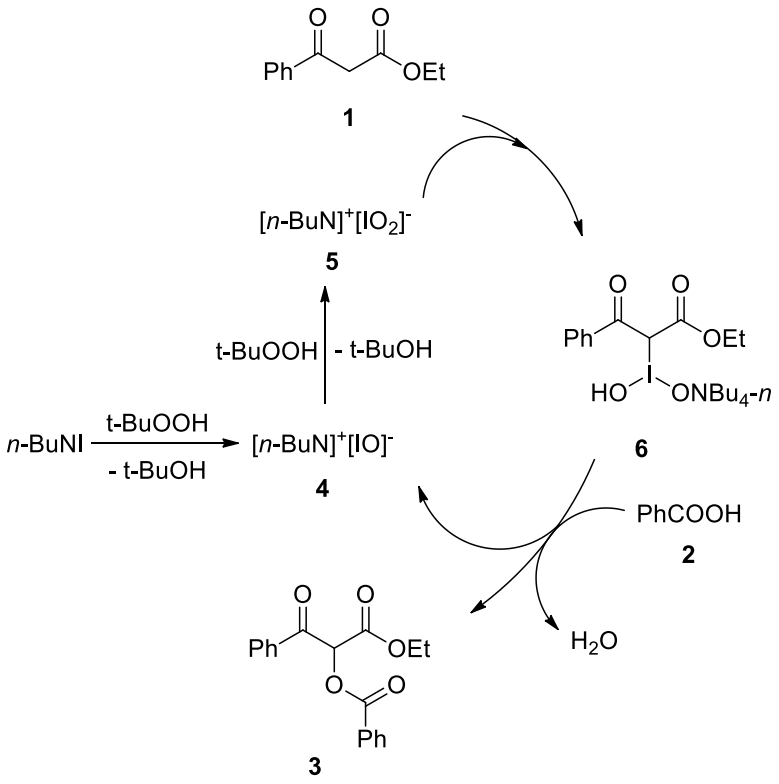


Entry	Time (h)	Products	Yield (%)[b]
1	5	**3a** R^1=R^2=Ph	83
2	5	**3b** R^1=4-MeC_6H_4, R^2=Ph	80
3	8	**3c** R^1=4-$MeOC_6H_4$, R^2=Ph	60
4	3.5	**3d** R^1=4-ClC_6H_4, R^2=Ph	79
5	3.5	**3e** R^1=4-BrC_6H_4, R^2=Ph	79
6	5	**3f** R^1=2-MeC_6H_4, R^2=Ph	78
7	8	**3g** R^1 =1-naphthyl, R^2=Ph	42
8	6	**3h** R^1=Me, R^2=Ph	11
9	3	**3i** R^1=Ph, R^2=4-MeC_6H_4	88
10	5	**3j** R^1=Ph, R^2=4-$MeOC_6H_4$	93
11	3	**3k** R^1=Ph, R^2=4-ClC_6H_4	84
12	3	**3l** R^1=Ph, R^2=2-MeC_6H_4	91
13	7	**3m** R^1=Ph, R^2=2-ClC_6H_4	74
14	7	**3n** R^1=Ph, R^2=2-BrC_6H_4	83
15	5	**3o** R^1=Ph, R^2=CH_2CH	60
16	5.5	**3p** R^1=Ph, R^2=Me	69
17	4	**3q** R^1=Ph, R^2=$(CH_2)_2$Ph	77
18	6	**3r** R^1=OEt, R^2=Ph	64

[a]General reaction conditions: 0.5 mmol of **1**, 0.6 mmol of **2**, 10 mol% of TBAI and 1 mmol of TBHP in 2 mL of MeCN at 60 °C. [b]Isolated yield.

According to the above results and previous reports,[6a,h] a plausible reaction mechanism could

be presumed as shown in Scheme 2. Firstly, *n*-Bu_4NI was oxidized by TBHP to [*n*-$Bu_4N]^+[IO_2]^-$ (**5**), which was reacted with **1** to form intermediate **6**. Subsequent nucleophilic attack of intermediate **6** by carboxylic acid **2** gave products **3** and released [*n*-$Bu_4N]^+[IO]^-$ (**4**), which could be reoxidize to **5** by TBHP.



Scheme 2. Plausible reaction mechanism.

Conclusions

In summary, we have reported a facile, economical and efficient method for the synthesis of α-carboxylic-β-ketoesters by the direct coupling of β-ketoesters with carboxylic acids. TBAI/TBHP system acts as a recyclable hypervalent iodine reagent in this process. The reaction occurs in air under mild conditions with easily accessible starting materials. Use of TBAI/TBHP system for the coupling of other C-O and C-N bonds is ongoing in our laboratory.

Experimental Section

General. All reagents and solvents were purchased from commercial suppliers and used without purifications. Melting points are uncorrected. The ^1H NMR and ^{13}C NMR spectra were recorded

at 25 °C in $CDCl_3$ at 500 and 125 MHz, respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. High resolution mass spectra (HRMS) were obtained on a TOF MS instrument with ESI or EI source.

General experimental procedure. A mixture of 0.5 mmol of (**1**), 0.6 mmol of (**2**), 0.05 mmol of TBAI and 1.0 mmol of TBHP (70% in water) in 2 mL of CH_3CN was stirred at 60 °C for the indicated period of time (see Table 2). After completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (100−200 mesh) using petroleum ether/EtOAc (9/1, v/v) as the eluent to give product (**3**).

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl benzoate (3a).[7] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 4H), 7.62 – 7.42 (m, 6H), 6.54 (s, 1H), 4.28 (q, *J* 7.1 Hz, 2H), 1.23 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 165.2, 165.0, 134.3, 134.1, 133.7, 130.1, 129.2, 128.7, 128.5, 74.9, 62.4, 13.9. HRMS Calcd for $C_{18}H_{16}O_5$ $[M+H]^+$ 313.1074, Found: 313.1023, IR (KBr) *ν*/cm^{-1} 1753, 1711, 1697, 1588, 1243, 1110, 711.

1-Ethoxy-1,3-dioxo-3-(*p*-tolyl)propan-2-yl benzoate (3b). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.09 (m, 2H), 7.98 (d, *J* 8.3 Hz, 2H), 7.58 (t, *J* 7.5 Hz, 1H), 7.43 (t, *J* 7.8 Hz, 2H), 7.29 (d, *J* 8.0 Hz, 2H), 6.52 (s, 1H), 4.28 (q, *J* 7.1 Hz, 2H), 2.41 (s, 3H), 1.24 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 165.3, 165.1, 145.3, 133.7, 131.7, 130.1, 129.5, 129.4, 128.5, 128.5, 74.9, 62.3, 21.7, 13.9. HRMS Calcd for $C_{19}H_{18}O_5$ $[M+H]^+$ 327.1232, Found: 327.1222, IR (KBr) *ν*/cm^{-1} 1760, 1689, 1260, 1112, 723.

1-Ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl benzoate (3c). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 6H), 7.61 –7.43 (m, 6H), 6.97 (d, *J* 8.9 Hz, 1H), 6.49 (s, 1H), 4.29 (q, *J* 7.1 Hz, 2H), 3.87 (s, 3H), 1.25 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.0, 165.6, 165.2, 164.5, 133.8, 131.8, 130.2, 130.2, 128.5, 128.5, 114.1, 75.0, 62.4, 55.6, 14.0. HRMS Calcd for $C_{19}H_{18}O_6$ $[M+H]^+$ 343.1182, Found: 343.1164, IR (KBr) *ν*/cm^{-1} 1752, 1698, 1601, 1264, 1143, 733.

1-(4-Chlorophenyl)-3-ethoxy-1,3-dioxopropan-2-yl benzoate (3d). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 4H), 7.60 (t, *J* 7.5 Hz, 1H), 7.49 – 7.44 (m, 4H), 6.47 (s, 1H), 4.29 (q, *J* 7.1 Hz, 2H), 1.25 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.7, 165.1, 165.0, 140.8, 133.9, 132.6, 130.7, 130.1, 129.2, 128.6, 128.4, 75.1, 62.7, 14.0. HRMS Calcd for $C_{18}H_{15}ClO_5$ $[M+H]^+$ 347.0686, Found: 347.0678; IR (KBr) *ν*/cm^{-1} 1732, 1698, 1589, 1263, 1093, 711.

1-(4-Bromophenyl)-3-ethoxy-1,3-dioxopropan-2-yl benzoate (3e). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.08 (m, 2H), 7.96 – 7.93 (m, 2H), 7.66 – 7.54 (m, 3H), 7.45 (t, *J* 7.8 Hz, 2H), 6.46 (s, 1H), 4.29 (q, *J* 7.1 Hz, 2H), 1.25 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.9, 165.0, 165.0, 133.9, 133.1, 132.2, 130.8, 130.1, 129.7, 128.6, 128.4, 75.1, 62.7, 14.0. HRMS Calcd for $C_{18}H_{15}BrO_5$ $[M+H]^+$ 391.0181, Found: 391.0177; IR (KBr) *ν*/cm^{-1} 1762, 1716, 1697, 1584, 1238, 1118, 722.

1-Ethoxy-1,3-dioxo-3-(*o*-tolyl)propan-2-yl benzoate (3f). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* 7.2 Hz, 2H), 7.86 (d, *J* 7.6 Hz, 1H), 7.60 (t, *J* 7.5 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.33 – 7.28 (m, 2H), 6.47 (s, 1H), 4.32 – 4.25 (m, 2H), 2.54 (s, 3H), 1.23 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 165.2, 165.1, 139.7, 133.8, 132.4, 132.1, 130.1, 129.3, 128.6, 128.5, 125.7, 76.3, 62.4, 21.0, 13.9. HRMS Calcd for $C_{19}H_{18}O_5$ $[M+H]^+$ 327.1232, Found: 327.1217, IR (KBr) *v*/cm^{-1} 1729, 1276, 1231, 1114, 711.

1-Ethoxy-3-(naphthalen-1-yl)-1,3-dioxopropan-2-yl benzoate (3g). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* 8.6 Hz, 1H), 8.15 – 8.03 (m, 4H), 7.88 (d, *J* 8.1 Hz, 1H), 7.63 – 7.52 (m, 4H), 7.43 (t, *J* 7.8 Hz, 2H), 6.62 (s, 1H), 4.22 (m, 2H), 1.11 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 165.3, 165.1, 133.9, 133.9, 133.8, 132.6, 130.6, 130.2, 129.1, 128.6, 128.5, 128.5, 126.8, 125.5, 124.2, 76.7, 62.4, 13.8. HRMS Calcd for $C_{22}H_{18}O_5$ $[M+H]^+$ 363.1232, Found: 363.1223; IR (KBr) *v*/cm^{-1} 1765, 1715, 1688, 1212, 1135, 735.

1-Ethoxy-1,3-dioxobutan-2-yl benzoate (3h).[8] Yellow solid. Mp 104-105 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* 7.3 Hz, 2H), 7.62 (t, *J* 7.4 Hz, 1H), 7.49 (t, *J* 7.7 Hz, 2H), 5.72 (s, 1H), 4.32 (q, *J* 7.1 Hz, 2H), 2.43 (s, 3H), 1.33 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 165.2, 164.6, 133.9, 130.2, 128.7, 128.6, 78.3, 62.6, 27.3, 14.1. HRMS Calcd for $C_{13}H_{14}O_5$ $[M+H]^+$ 251.0919, Found: 251.0906, IR (KBr) *v*/cm^{-1} 1688, 1425, 1292, 934, 708.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl 4-methylbenzoate (3i).[9] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* 8.4, 1.2 Hz, 2H), 7.99 (d, *J* 8.2 Hz, 2H), 7.59 (t, *J* 7.4 Hz, 1H), 7.48 (t, *J* 7.8 Hz, 2H), 7.22 (d, *J* 8.0 Hz, 2H), 6.53 (s, 1H), 4.28 (q, *J* 7.1 Hz, 2H), 2.37 (s, 3H), 1.22 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 165.3, 165.1, 144.7, 134.4, 134.2, 130.2, 129.3, 129.2, 128.8, 125.8, 74.9, 62.4, 21.7, 13.9. HRMS Calcd for $C_{19}H_{18}O_5$ $[M+H]^+$ 327.1232, Found: 327.1226, IR (KBr) *v*/cm^{-1} 1761, 1729, 1697, 1264, 1179, 1107, 752.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl 4-methoxybenzoate (3j). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 4H), 7.61 (t, *J* 7.4 Hz, 1H), 7.49 (t, *J* 7.8 Hz, 2H), 6.90 (d, *J* 8.9 Hz, 2H), 6.52 (s, 1H), 4.28 (q, *J* 7.1 Hz, 2H), 3.82 (s, 3H), 1.23 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 165.5, 164.8, 164.1, 134.4, 134.2, 132.3, 129.3, 128.8, 120.8, 113.9, 74.8, 62.4, 55.5, 13.9. HRMS Calcd for $C_{19}H_{18}O_6$ $[M+H]^+$ 343.1182, Found: 343.1176; IR (KBr) *v*/cm^{-1} 1760, 1723, 1697, 1605, 1261, 1169, 1103.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl 4-chlorobenzoate (3k). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 4H), 7.62 (t, *J* 7.4 Hz, 1H), 7.50 (t, *J* 7.8 Hz, 2H), 7.41 (d, *J* 8.6 Hz, 2H), 6.55 (s, 1H), 4.28 (q, *J* 7.1 Hz, 2H), 1.22 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 165.0, 164.3, 140.4, 134.3, 134.3, 131.5, 129.3, 128.9, 128.8, 127.0, 75.0, 62.6, 13.9. HRMS Calcd for $C_{18}H_{15}ClO_5$ $[M+H]^+$ 347.0686, Found: 347.0679, IR (KBr) *v*/cm^{-1} 1758, 1719, 1623, 1594, 1286, 1242, 1121, 762.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl 2-methylbenzoate (3l). Yellow solid. Mp 69-70 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 3H), 7.60 (t, *J* 7.4 Hz, 1H), 7.48 (t, *J* 7.8 Hz, 2H), 7.40 (t, *J* 7.5 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.56 (s, 1H), 4.31 – 4.24 (m, 2H), 2.60 (s, 3H), 1.22 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 165.8, 165.4, 141.1, 134.4, 134.2, 132.9,

131.8, 131.3, 129.2, 128.8, 127.8, 125.9, 74.8, 62.4, 21.7, 13.9. HRMS Calcd for $C_{19}H_{18}O_5$ $[M+H]^+$ 327.1232, Found: 327.1230, IR (KBr) ν/cm^{-1} 1764, 1714, 1685, 1238, 1167, 1103, 744.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl 2-chlorobenzoate (3m). Yellow solid. Mp 64-66 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 3H), 7.62 (t, *J* 6.9 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.33 – 7.30 (m, 1H), 6.59 (s, 1H), 4.29 (m, 2H), 1.23 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.4, 165.0, 163.7, 134.5, 134.3, 134.2, 133.5, 132.2, 131.2, 129.3, 128.8, 128.1, 126.8, 75.0, 13.9. HRMS Calcd for $C_{18}H_{15}ClO_5$ $[M+H]^+$ 347.0686, Found: 347.0681, IR (KBr) ν/cm^{-1} 1766, 1725, 1687, 1233, 1187, 1119, 755.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl 2-bromobenzoate (3n). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 2H), 7.66 – 7.33 (m, 8H), 6.60 (s, 1H), 4.31 –4.26 (m, 2H), 1.23 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.4, 165.0, 164.2, 134.6, 134.3, 133.5, 132.2, 129.3, 128.8, 127.4, 122.4, 75.0, 62.6, 13.9. HRMS Calcd for $C_{18}H_{15}BrO_5$ $[M+H]^+$ 391.0181, Found: 391.0175, IR (KBr) ν/cm^{-1} 1765, 1727, 1687, 1265, 1229, 1110, 743.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl acrylate (3o). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.63 (t, *J* 7.4 Hz, 1H), 7.50 (t, *J* 7.8 Hz, 2H), 6.57 – 6.53 (m, 1H), 6.39 (s, 1H), 6.30 – 6.24(m, 1H), 5.99 – 5.96 (m, 1H), 4.27 (q, *J* 7.1 Hz, 2H), 1.23 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 165.1, 164.5, 134.3, 134.2, 133.2, 129.2, 128.8, 126.8, 74.5, 62.5, 13.9. HRMS Calcd for $C_{14}H_{14}O_5$ $[M+H]^+$ 263.0919, Found: 263.0909, IR (KBr) ν/cm^{-1} 1754, 1721, 1685, 1221, 1175, 1116, 745.

Ethyl 2-acetoxy-3-oxo-3-phenylpropanoate (3p).[1b] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 8.00 (m, 2H), 7.64 – 7.61 (m, 1H), 7.51 –7.47 (m, 2H), 6.34 (s, 1H), 4.24 (q, *J* 7.1 Hz, 2H), 2.22 (s, 3H), 1.21 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 169.5, 165.2, 134.2, 130.1, 129.2, 128.8, 74.5, 62.5, 20.4, 13.8. HRMS Calcd for $C_{13}H_{14}O_5$ $[M+H]^+$ 251.0919, Found: 251.1913, IR (KBr) ν/cm^{-1} 1752, 1695, 1227, 1096, 690.

Ethyl 3-oxo-3-phenyl-2-((3-phenylpropanoyl)oxy)propanoate (3q). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* 7.5 Hz, 2H), 7.59 (t, *J* 7.4 Hz, 1H), 7.45 (t, *J* 7.8 Hz, 2H), 7.27 – 7.16 (m, 5H), 6.33 (s, 1H), 4.22 (q, *J* 7.1 Hz, 2H), 2.98 (t, *J* 7.8 Hz, 2H), 2.86 – 2.75 (m, 2H), 1.19 (t, *J* 7.1 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 171.5, 165.2, 140.0, 134.3, 134.2, 129.2, 128.8, 128.5, 128.3, 126.4, 74.5, 62.5, 35.3, 30.6, 13.9. HRMS Calcd for $C_{20}H_{20}O_5$ $[M+H]^+$ 341.1389, Found: 341.1383; IR (KBr) ν/cm^{-1} 1748, 1686, 1235, 1141, 698.

Diethyl 2-(benzoyloxy)malonate (3r).[10] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.13 (m, 2H), 7.62 – 7.59 (m, 1H), 7.47 (t, *J* 7.8 Hz, 2H), 5.76 (s, 1H), 4.36 – 4.30 (m, 4H), 1.33 (t, *J* 7.1 Hz, 6H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 164.5, 133.8, 130.2, 128.5, 72.1, 62.5, 14.0. HRMS Calcd for $C_{14}H_{16}O_6$ $[M+H]^+$ 281.1025, Found: 281.1021, IR (KBr) ν/cm^{-1} 1769, 1733, 1229, 1118, 711.

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