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Graphical Abstract

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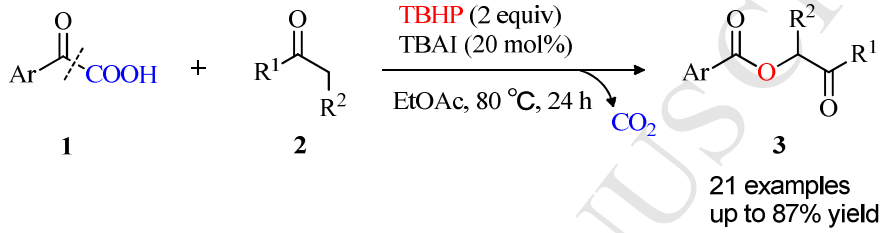

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One-pot synthesis of α-acyloxycarbonyl compounds *via* oxidative decarboxylation coupling reaction of α-oxo carboxylic acids with carbonyl compounds

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ABSTRACT

With tetrabutylammonium iodide (TBAI) as the catalyst and *tert*-butyl hydroperoxide (TBHP) as the oxidant, a simple metal-free protocol has been developed for the synthesis of α-acyloxycarbonyl compounds from carbonyl compounds and α-oxo carboxylic acids *via* decarboxylative coupling reaction. The target products could be obtained in moderate to high yields.

1. Introduction

The decarboxylative functionalization of carboxylic acids is one of the most attractive transformations in organic synthesis since carboxylic acids are commercially available, and are easily prepared by means of widely recognized methods. Moreover, activated derivatives of carboxylic acids have long served as versatile connection points in derivatizations and in the construction of carbon frameworks.[1] In particular, decarboxylative coupling reactions have become an interesting topic in recent years.[2] However, oxidative decarboxylation that involves carbon-heteroatom bond forming reactions, particularly C–O, C–S and C–N bond formation,[3] has received less attention. Most of decarboxylative coupling reactions need heavy metal catalysts and high reaction temperature, such as copper-catalyzed aerobic decarboxylative sulfonylation of cinnamic acids with sodium sulfinates,[4] Pd-catalyzed decarboxylative coupling for the synthesis of heteroaromatic biaryls and silver-catalyzed reaction of aromatic carboxylic acids with alkenes.[5] The use of an excess of the transition metal reagents might be problematic.

The α-acyloxycarbonyl compound represents a significant building block in organic synthesis,[6] and exits in a substantial number of both naturally occurring and synthetic biologically significant molecules.[7] Various synthetic approaches toward α-acyloxycarbonyl compounds were developed in the past few decades.[8–12] Traditional method is mainly based on the substitution reaction of α-halo carbonyl compounds or the oxidative coupling reaction of carbonyl compounds with heavy metal catalysts.[9] In order to overcome the drawback of traditional methods, some new methods have been investigated. For example, Tomkinson and co-workers reported the synthesis of α-acyloxycarbonyl compounds from ketones and *N*-methyl-O-benzoylhydroxylamine.[10] In 2012, the Bencivenni's group disclosed a chiral primary amine catalyzed the reaction of α-oxybenzoylation with benzoyl peroxide.[11] In addition, an trimerization of aldehydes to α-acyloxycarbonyl compounds was reported.[12] Recently, the combination of TBHP with TBAI for the synthesis of α-acyloxycarbonyl compounds or the activation of C–H bond has drawn much attention.[13] Inspired by these achievements, we attempted to use TBHP as the oxidant and TBAI as the catalyst to achieve α-acyloxylation of α-oxo carboxylic acids with ketones *via* decarboxylation coupling reaction. This approach shows a simple and efficient decarboxylative functionalization of α-oxo carboxylic acids without transition metal catalysts. From the viewpoint of synthetic methodology, the present work provides a new route for the synthesis of α-acyloxycarbonyl compounds from ketones and α-oxo carboxylic acids although α-oxo carboxylic acid as a starting material is relatively precious.

2. Result and Discussion

2.1. Optimization of reaction conditions

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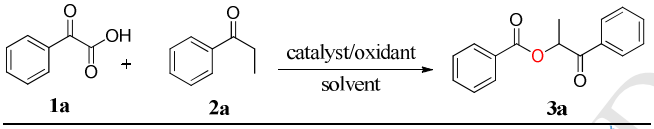
We initially employed phenylglyoxylic acid (**1a**) and propiophenone (**2a**) as model substrate to optimize the reaction conditions, as shown in Table 1. According to our previous experience, the reaction results are related to oxidants, catalysts and solvents. The effect of oxidants was first examined. The reaction proceeded in the presence of 20 mol% TBAI and 2 equivalents of ditertbutyl peroxide (DTBP) as an oxidant in EtOAc (2 mL) at 80 °C for 24 hours (Table 1, entry 1). However, the expected product **3a** was not occurred. Similarly, other oxidants, such as H_2O_2, $K_2S_2O_8$ and I_2, failed to achieve the reaction (Table 1, entries 2–4). To our delight, the desired product was obtained in a good yield (88%) when TBHP was used as an oxidant (Table 1, entry 5). Moreover, the reaction failed to implement in the absence of TBHP (Table 1, entry 6), indicating that TBHP plays a crucial role in this transformation. Catalyst was also a key factor. Replacing TBAI with KI to catalyze the reaction, the *α*-acyloxylation product was obtained in 19% yield (Table 1, entry 7). Unfortunately, I_2 and CuI did not show any catalytic activity for this reaction (Table 1, entries 8 and 9). Meanwhile, the reaction did not happen in the absence of TBAI (Table 1, entry 10). The experimental results indicated that TBAI was particularly effective to catalyze this transformation. Finally, in order to examine the effects of solvents, we screened a variety of solvents. This reaction in PhCN or PhCl solvent afforded the target product **3a** in 67% and 59% yields, respectively (Table 1, entries 11 and 12). Other solvents, including THF, DMF, MeCN, and DMSO, were less efficient for the reaction (Table 1, entries 13–16). By contrast, EtOAc as the solvent appears to be more suitable to this reaction system (Table 1, entry 5).

Table 1

Optimization of reaction conditions[a]



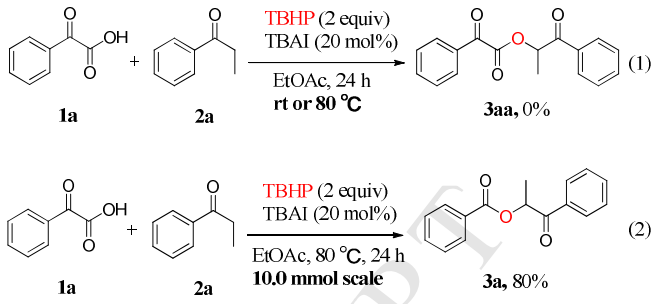
1a **2a** **3a**

Entry	Catalyst (20 mol%)	Oxidant (2 equiv)	Solvent	Yield (%) [b]
1	TBAI	DTBP	EtOAc	0
2	TBAI	H_2O_2	EtOAc	0
3	TBAI	$K_2S_2O_8$	EtOAc	0
4	TBAI	I_2	EtOAc	0
5	**TBAI**	**TBHP**	**EtOAc**	**88**
6	TBAI	–	EtOAc	0
7	KI	TBHP	EtOAc	19
8	I_2	TBHP	EtOAc	0
9	CuI	TBHP	EtOAc	0
10	–	TBHP	EtOAc	0
11	TBAI	TBHP	PhCN	67
12	TBAI	TBHP	PhCl	59
13	TBAI	TBHP	THF	7
14	TBAI	TBHP	DMF	44
15	TBAI	TBHP	MeCN	35
16	TBAI	TBHP	DMSO	40

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), solvent (2.0 mL) and at 80 °C for 24 h in a sealed tube.

[b] Yields were determined by GC–MS.

It should be noted that the product **3aa** was not formed at 80 °C or room temperature (Scheme 1, Eq. 1). Moreover, **3a** could be obtained in an acceptable yield (80%) when the reaction was carried out on a 10.0 mmol scale (Scheme 1, Eq. 2), indicating that this reaction is easily scalable.



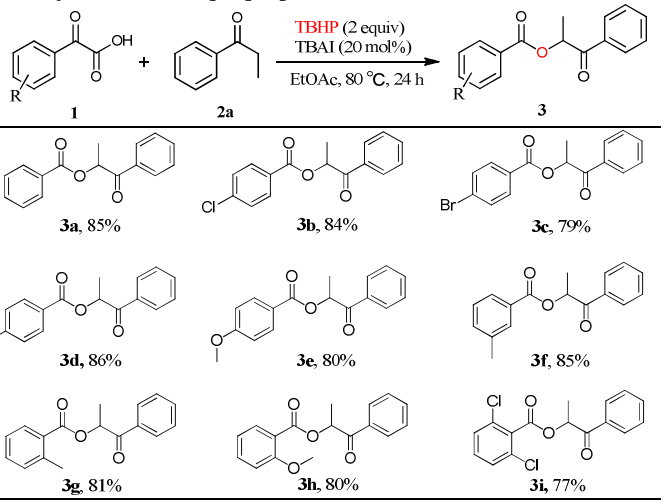
Scheme 1.

2.2. Synthesis of *α*-acyloxycarbonyl compounds from *α*-oxo carboxylic acids and ketones

With the optimized conditions in hand, the scope of *α*-oxo carboxylic acids was examined, and the results were summarized in Table 2. It could be seen that the reactions of propiophenone with various good reactivity *α*-oxo carboxylic acids proceeded smoothly to give the corresponding *α*-acyloxycarbonyl compounds in high yields. The carboxylic acid substrates with electron-withdrawing and electron-donating groups on the aromatic rings all worked well to give the desired products **(3a–3f)**. However, possibly due to the effects of steric hindrance, the yield of the target product decreased slightly when the aromatic rings had *ortho*-position substituted groups (**3g–3i**).

Table 2

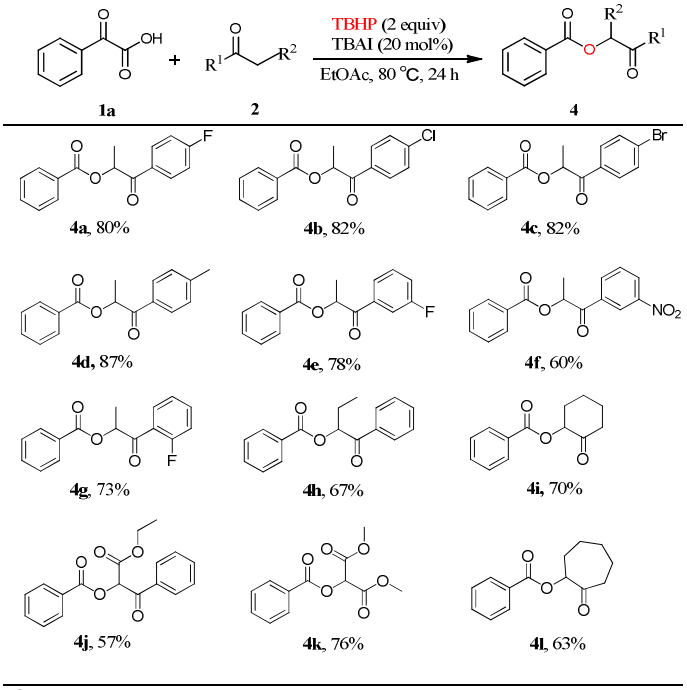
Synthesis of *α*-acyloxycarbonyl compounds from *α*-oxo carboxylic acids and propiophenone [a]



[a] Reaction conditions as shown in Table 1. Isolated yields based on phenylglyoxylic acid.

Simultaneously, the scope of ketones for this transformation was investigated. As shown in Table 3, propiophenone derivatives substituted in *para*-position gave the desired products (**4a–4d**) in good to excellent yields under the optimized conditions. Notably, the substituents at the *meta*-position or *ortho*-position seemed to decrease the reactivity slightly (**4e–4g**). Pleasingly, cyclic ketones were also suitable to this reaction (**4i** and **4l**). Moreover, dimethylmalonate and benzoyl acetic ester also worked well to afford the desired products (**4j** and **4k**) with good yields.

Table 3
Synthesis of *α*-acyloxycarbonyl compounds from phenylglyoxylic acid and ketones[a]

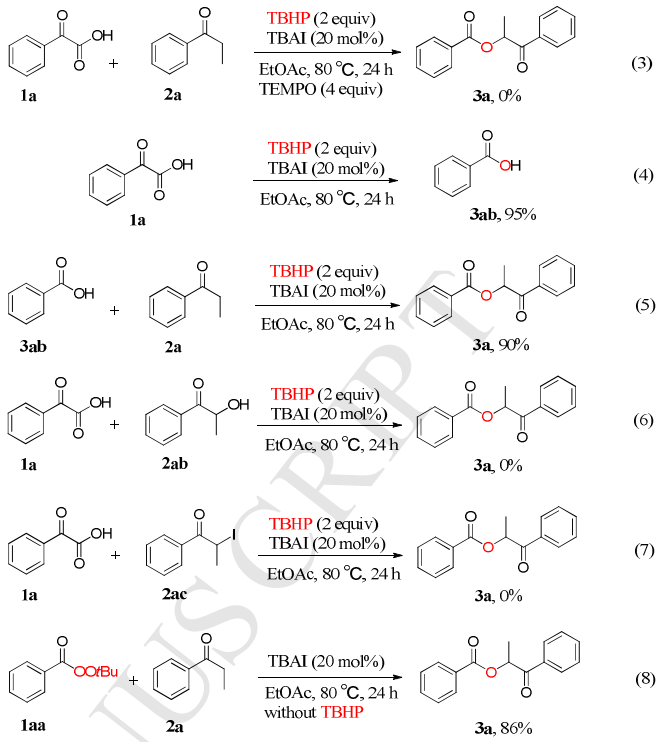


[a] Reaction conditions as shown in Table 1. Isolated yields based on phenylglyoxylic acid.

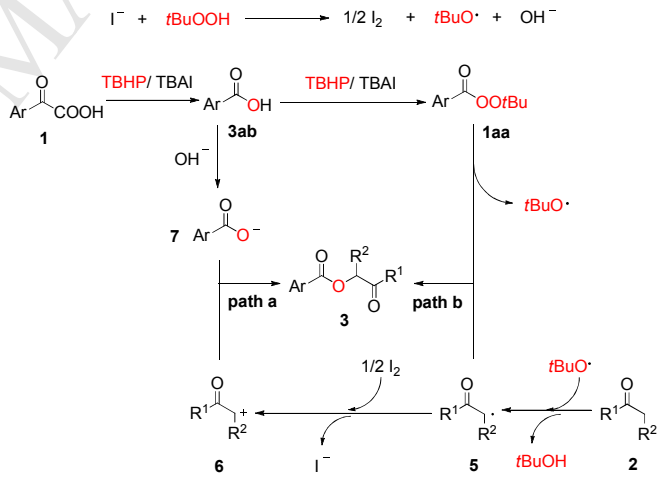
2.3. Reaction mechanism

To gain insight into the reaction mechanism, a series of control experiments were carried out (Scheme 2). The reaction was completely inhibited in the presence of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), indicating that this transformation may involve a radical pathway (Eq. 3). In the absence of propiophenone **2a**, phenylglyoxylic acid **1a** was almost converted into benzoic acid **3ab** (Eq. 4). Simultaneously, the target product **3a** was isolated in 90% yield when benzoic acid **3ab** reacted with propiophenone under the standard conditions (Eq. 5), which indicated that the benzoic acid might be the key intermediate in the reaction system. In addition, replacing propiophenone with 2-iodo-1-phenylpropan-1-one or 2-hydroxy-1-phenylpropan-1-one, no reaction took place under the optimal conditions (Eqs. 6 and 7). Therefore, it could be ruled out that the possibility of 2-iodo-1-phenylpropan-1-one and 2-hydroxy-1-phenylpropan-1-one as the reaction intermediates. Finally, *tert*-butyl perester **1aa** reacted with propiophenone **2a** to afford **3a** with 86% yield in the absence of TBHP (Eq. 8), so we inferred that *tert*-butyl perester **1aa** might be the other intermediate in the process of decarboxylative coupling transformation.

Based on the control experiments and the related literatures, a possible reaction mechanism is illustrated in Scheme 3. TBHP firstly combines with TBAI to generate *tert*-butoxyl radicals and iodine.[13e,13i] Then, the *α*-H of ketones is abstracted by *tert*-butoxyl radicals to produce *α*-carbonyl radical **5**,[13c,13e] followed by the one-electron oxidation with iodine to form intermediate cation **6**.[13c,13e] In addition, the *α*-oxo carboxylic acid **1** undergoes oxidative decarboxylation to form benzoic acid **3ab**.[13g,14] The generated benzoic acid **3ab** is deprotonated to give a benzoate anion **7**. The reaction of the intermediate cation **6** with the benzoate anion **7** results in the final product **3** (**path a**). On the other pathway, *tert*-butyl perester **1aa** is easily formed in the TBHP/TBAI system.[13c,13j] The coupling reaction of the *α*-carbonyl radical **5** with *tert*-butyl perester **1aa** gives the target product **3** (**path b**), which may be a main pathway.



Scheme 2. Control experiments.



Scheme 3. Proposed reaction mechanism.

3. Conclusion

We have developed a novel TBAI-catalyzed method for the oxidative decarboxylation coupling reaction of *α*-oxo carboxylic acids with ketones, in which the C–C bond cleavage of *α*-oxo carboxylic acids is due to TBHP oxidation. This transformation undergoes a radical pathway. This metal-free catalytic system provides a mild and efficient approach toward the synthesis of *α*-acyloxycarbonyl compounds.

4. Experimental section

4.1. Instrumentation

All reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Advance 400 spectrometer

(400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR spectroscopy) in $CDCl_3$. MS analyses were performed on a shimadzu GCMS-QP5050A spectrometer. The new compounds were characterized by a high resolution mass spectrometer (MAT95XP). TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Melting points were determined with a Buchi B-545 melting point instrument. Fourier transform infrared spectrum (FTIR) was measured by a TENSOR27 spectrometer.

4.2. A typical procedure for the synthesis of α-acyloxycarbonyl compounds

The mixture of phenylglyoxylic acid (0.2 mmol), propiophenone (0.2 mmol), TBHP (0.4 mmol), TBAI (0.04 mmol) and ethyl acetate (2 mL) was stirred at 80 °C for 24 h in a 15 mL sealed tube successively. After cooling down, the reaction mixture was washed with $Na_2S_2O_3$ solution, and extracted by ethyl acetate for three times. The obtained top organic layer was dried with anhydrous $MgSO_4$. After drying, the mixture was concentrated under vacuum, and the crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (50:1) as eluent.

4.3.1. 1-Oxo-1-phenylpropan-2-yl benzoate (***3a***).[13d] White solid, mp 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J*=7.8 Hz, 2H), 8.00 (d, *J*=7.8 Hz, 2H), 7.56 (t, *J*=6.9 Hz, 2H), 7.45 (m, 4H), 6.20 (q, *J*=6.8 Hz, 1H), 1.66 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 165.9, 134.4, 133.5, 133.2, 129.8, 129.5, 128.7, 128.4, 128.3, 71.8, 17.1.

4.3.2. 1-Oxo-1-phenylpropan-2-yl 4-chlorobenzoate (***3b***).[13d] White solid, mp 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (q, *J*=8.0 Hz, 4H), 7.57 (t, *J*=7.4 Hz, 1H), 7.47 (t, *J*=7.5 Hz, 2H), 7.40 (d, *J*=7.6 Hz, 2H), 6.19 (q, *J*=6.8 Hz, 1H), 1.66 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 165.0, 139.6, 134.2, 133.6, 131.2, 128.7, 128.6, 128.4, 127.9, 72.0, 17.1.

4.3.3. 1-Oxo-1-phenylpropan-2-yl 4-bromobenzoate (***3c***).[13d] White solid, mp 118–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (q, *J*=7.8 Hz, 4H), 7.56 (d, *J*=7.4 Hz, 3H), 7.46 (t, *J*=7.5 Hz, 2H), 6.19 (q, *J*=6.9 Hz, 1H), 1.65 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 165.1, 134.2, 133.6, 131.6, 131.3, 129.7, 128.7, 128.4, 128.3, 72.0, 17.1.

4.3.4. 1-Oxo-1-phenylpropan-2-yl 4-methylbenzoate (***3d***).[13d] White solid, mp 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J*=6.5 Hz, 4H), 7.55 (t, *J*=7.3 Hz, 1H), 7.45 (t, *J*=7.4 Hz, 2H), 7.21 (d, *J*=7.7 Hz, 2H), 6.17 (q, *J*=6.9 Hz, 1H), 2.37 (s, 3H), 1.64 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 165.9, 143.9, 134.4, 133.4, 129.8, 129.0, 128.6, 128.4, 126.6, 71.6, 21.5, 17.0.

4.3.5. 1-Oxo-1-phenylpropan-2-yl 4-methoxybenzoate (***3e***).[13d] White solid, mp 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (q, *J*=8.0 Hz, 4H), 7.55 (t, *J*=7.3 Hz, 1H), 7.45 (t, *J*=7.5 Hz, 2H), 6.90 (d, *J*=8.7 Hz, 2H), 6.16 (q, *J*=6.9 Hz, 1H), 3.80 (s, 3H), 1.64 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 165.5, 163.5, 134.4, 133.4, 131.8, 128.6, 128.3, 121.7, 113.5, 71.5, 55.2, 17.0.

4.3.6. 1-Oxo-1-phenylpropan-2-yl 3-methylbenzoate (***3f***).[13d] White solid, mp 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J*=8.0 Hz, 2H), 7.89 (d, *J*=9.1 Hz, 2H), 7.55 (t, *J*=7.3 Hz, 1H), 7.45 (t, *J*=7.5 Hz, 2H), 7.36–7.28 (m, 2H), 6.19 (q, *J*=6.9 Hz, 1H), 2.36 (s, 3H), 1.65 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 166.0, 138.0, 134.4, 133.9, 133.4, 130.2, 129.3, 128.7, 128.4, 128.2, 126.9, 71.7, 21.1, 17.0.

4.3.7. 1-Oxo-1-phenylpropan-2-yl 2-methylbenzoate (***3g***).[13d] White solid, mp 51–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, *J*=6.8 Hz, 3H), 7.56 (t, *J*=7.3 Hz, 1H), 7.46 (t, *J*=7.5 Hz, 2H), 7.38 (t, *J*=7.5 Hz, 1H), 7.23 (t, *J*=8.3 Hz, 2H), 6.19 (q, *J*=6.9 Hz, 1H), 2.58 (s, 3H), 1.64 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 166.8, 140.4, 134.4, 133.5, 132.2, 131.5, 130.8, 128.9, 128.7, 128.4, 125.6, 71.7, 21.5, 17.1.

4.3.8. 1-Oxo-1-phenylpropan-2-yl 2-methoxybenzoate (***3h***).[13d] White solid, mp 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J*=7.9 Hz, 2H), 7.91 (d, *J*=7.7 Hz, 1H), 7.56 (t, *J*=7.3 Hz, 1H), 7.45 (t, *J*=7.6 Hz, 3H), 6.96 (t, *J*=8.9 Hz, 2H), 6.19 (q, *J*=6.9 Hz, 1H), 3.84 (s, 3H), 1.63 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 165.0, 159.4, 134.5, 133.8, 133.3, 131.8, 128.6, 128.4, 120.0, 118.9, 111.9, 71.4, 55.8, 16.9.

4.3.9. 1-Oxo-1-phenylpropan-2-yl 2,6-dichlorobenzoate (***3i***). Pale yellow oil; IR (KBr) 3465–2938, 1749, 1692, 1271, 1226, 1143, 1080, 798 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J*=7.5 Hz, 2H), 7.60 (t, *J*=7.4 Hz, 1H), 7.49 (t, *J*=7.4 Hz, 2H), 7.30–7.24 (m, 3H), 6.35 (q, *J*=6.8 Hz, 1H), 1.69 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 163.8, 134.2, 133.6, 132.5, 132.0, 131.1, 128.7, 128.6, 127.8, 72.6, 16.7; HRMS (ESI) calcd for $C_{16}H_{12}Cl_2NaO_3$, $[M+Na]^+$ 345.0056, found 345.0065.

4.3.10. 1-(4-Fluorophenyl)-1-oxopropan-2-yl benzoate (***4a***).[13d] White solid, mp 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.04 (m, 4H), 7.60 (t, *J*=7.3 Hz, 1H), 7.47 (t, *J*=7.5 Hz, 2H), 7.18 (t, *J*=8.1 Hz, 2H), 6.17 (q, *J*=6.9 Hz, 1H), 1.69 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 167.2, 166.0, 164.7, 133.3, 131.3, 131.2, 130.9, 130.8, 129.8, 129.4, 128.4, 116.1, 115.9, 71.7, 17.1.

4.3.11. 1-(4-Chlorophenyl)-1-oxopropan-2-yl benzoate (***4b***).[13d] White solid, mp 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J*=7.9 Hz, 2H), 7.96 (d, *J*=7.6 Hz, 2H), 7.59 (t, *J*=7.4 Hz, 1H), 7.45 (t, *J*=7.1 Hz, 4H), 6.15 (q, *J*=6.9 Hz, 1H), 1.67 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 165.9, 140.0, 133.3, 132.7, 129.9, 129.8, 129.3, 129.1, 128.4, 71.7, 17.0.

4.3.12. 1-(4-Bromophenyl)-1-oxopropan-2-yl benzoate (***4c***).[13d] Pale yellow solid, mp 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J*=7.9 Hz, 2H), 7.86 (d, *J*=7.6 Hz, 2H), 7.67–7.55 (m, 3H), 7.45 (t, *J*=7.5 Hz, 2H), 6.12 (q, *J*=6.9 Hz, 1H), 1.66 (d, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 165.9, 133.4, 133.2, 132.1, 130.0, 129.8, 129.3, 128.8, 128.4, 71.8, 17.0.

4.3.13. 1-Oxo-1-(p-tolyl)propan-2-yl benzoate (***4d***).[13e] White solid, mp 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J*=7.8 Hz, 2H), 7.93 (d, *J*=7.7 Hz, 2H), 7.59 (t, *J*=7.4 Hz, 1H), 7.46 (t, *J*=7.5 Hz, 2H), 7.30 (d, *J*=7.8 Hz, 2H), 6.22 (q, *J*=6.9 Hz, 1H), 2.43 (s, 3H), 1.69 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 165.9, 144.5, 133.2, 131.9, 129.8, 129.6, 129.5, 128.6, 128.3, 71.8, 21.7, 17.3.

4.3.14. 1-(3-Fluorophenyl)-1-oxopropan-2-yl benzoate (***4e***). White solid, mp 100–103 °C; IR (KBr) 3073–2938, 1727, 1690, 1588, 1259, 1118, 714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J*=7.4 Hz, 2H), 7.80 (d, *J*=7.7 Hz, 1H), 7.71 (d, *J*=9.2 Hz, 1H), 7.60 (t, *J*=7.4 Hz, 1H), 7.47 (t, *J*=6.9 Hz, 3H), 7.31 (q, *J*=10.0 Hz, 1H), 6.14 (q, *J*=6.8 Hz, 1H), 1.69 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 166.0, 164.1, 161.6, 161.2, 136.5, 136.5, 133.4, 130.5, 130.4, 129.9, 129.3, 128.4, 124.2, 124.2, 120.7, 120.5, 115.5, 115.2, 71.9, 17.0; HRMS (ESI) calcd for $C_{16}H_{13}FNaO_3$, $[M+Na]^+$ 295.0741, found 295.0748.

4.3.15. 1-(3-Nitrophenyl)-1-oxopropan-2-yl benzoate (***4f***). Yellow oil; IR (KBr) 3390–2854, 1714, 1602, 1529, 1267, 1112, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.45 (d, *J*=8.2 Hz, 1H), 8.32 (d, *J*=7.7 Hz, 1H), 8.08 (d, *J*=7.8 Hz, 2H), 7.71 (t, *J*=7.9 Hz, 1H), 7.60 (t, *J*=7.4 Hz, 1H), 7.46 (t, *J*=7.4 Hz,

2H), 6.13 (q, *J*=6.9 Hz, 1H), 1.72 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 166.0, 135.8, 134.0, 133.6, 130.1, 129.9, 129.7, 129.0, 128.5, 127.8, 123.4, 72.1, 16.9; HRMS (ESI) calcd for $C_{16}H_{13}NNaO_5$, $[M+Na]^+$ 322.0686, found 322.0686.

4.3.16. 1-(2-Fluorophenyl)-1-oxopropan-2-yl benzoate ***(4g)***. Pale yellow oil; IR (KBr) 3074–2939, 1727, 1697, 1609, 1269, 1112, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J*=7.7 Hz, 2H), 7.95 (t, *J*=7.5 Hz, 1H), 7.58 (q, *J*=7.5 Hz, 2H), 7.46 (t, *J*= 7.5 Hz, 2H), 7.29 (t, *J*=7.5 Hz, 1H), 7.21–7.14 (m, 1H), 6.07 (q, *J* =6.9 Hz, 1H), 1.68 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 165.9, 162.7, 135.1, 133.2, 131.2, 129.8, 129.6, 128.3, 124.8, 116.7, 116.5, 75.0, 16.1; HRMS (ESI) calcd for $C_{16}H_{13}FNaO_3$, $[M+Na]^+$ 295.0741, found 295.0748.

4.3.17. 1-Oxo-1-phenylbutan-2-yl benzoate ***(4h)***.[13d] White solid, mp 60–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J*=7.7 Hz, 2H), 8.00 (d, *J*=7.7 Hz, 2H), 7.60–7.53 (m, 2H), 7.50–7.40 (m, 4H), 6.06 (t, *J*=5.6 Hz, 1H), 2.13–1.99 (m, 2H), 1.11 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 166.1, 134.9, 133.5, 133.2, 129.8, 129.6, 128.7, 128.4, 128.3, 76.7, 24.9, 9.9.

4.3.18. 2-Oxocyclohexyl benzoate ***(4i)***.[13d] White solid, mp 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J*=7.4 Hz, 2H), 7.57 (t, *J*=7.4 Hz, 1H), 7.45 (t, *J*=7.5 Hz, 2H), 5.41 (q, *J*=9.0 Hz, 1H), 2.57 (d, *J*=12.7 Hz, 1H), 2.51–2.41 (m, 2H), 2.15–2.11 (m, 1H), 2.04 (d, *J*=13.2 Hz, 1H), 1.96–1.83 (m, 2H), 1.65 (q, *J*=13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 165.6, 133.1, 129.9, 129.7, 128.3, 76.7, 40.7,33.2, 27.2, 23.8.

4.3.19. 1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl benzoate ***(4j)***.[13d] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, *J*= 9.2 Hz, 4H), 7.67–7.60 (m, 2H), 7.55–7.45 (m, 4H), 6.55 (s, 1H), 4.31 (q, *J*=7.0 Hz, 2H), 1.26 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 165.2, 165.1, 134.3, 134.2, 133.8, 130.1, 129.3, 128.8, 128.5, 128.4, 74.9, 62.5, 13.9.

4.3.20. Dimethyl 2-(benzoyloxy)malonate ***(4k)***.[13a] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J*=7.9 Hz, 2H), 7.61 (t, *J*=7.2 Hz, 1H), 7.48 (t, *J*=7.5 Hz, 2H), 5.81 (s, 1H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.9, 133.9, 130.2, 128.5, 128.3, 71.8, 53.3.

4.3.21. 2-Oxocycloheptyl benzoate ***(4l)***.[10] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J*=7.8 Hz, 2H), 7.57 (t, *J* =7.3 Hz, 1H), 7.45 (t, *J*=7.4 Hz, 2H), 5.46 (t, *J*=7.6 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.55–2.47 (m, 1H), 2.16–2.09 (m, 1H), 1.92–1.64 (m, 6H), 1.49–1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 165.8, 133.2, 129.8, 129.7, 128.4, 79.0, 40.7, 30.4, 28.4, 26.4, 23.0.

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