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High-efficiency α-Benzoyloxylation and Hydroxylation of β-keto Amides by Phase Transfer Catalysis

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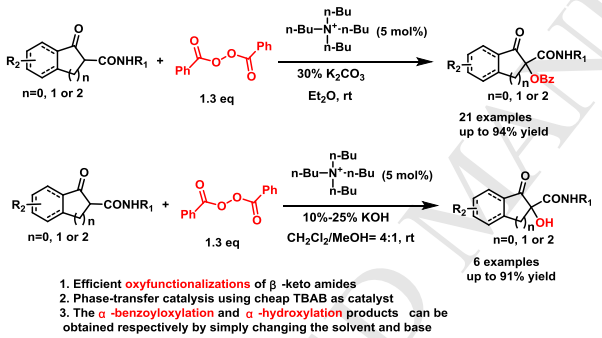

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ABSTRACT

A facile and efficient protocol for ~~the~~ α-benzoyloxylation and α-hydroxylation of β-keto amides by phase-transfer catalysis is presented. This methodology provides mild and practical access to ~~highly functionalized~~ a variety of α-oxygenated β-keto amides. Furthermore, ~~the~~ α-benzoyloxylation products can be easily converted into α-hydroxylation compounds, which are useful synthetic precursors of biological targets.

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1. Introduction

The α-oxygenated β-dicarbonyl compounds are common structural motifs in a wide range of natural products and pharmaceuticals.[1] Because of this, ~~the~~ α-oxidations of β-dicarbonyl compounds, leading to both α-hydroxy and α-oxo derivatives, are important chemical transformations in synthetic chemistry and pharmaceutical science.[2] Over the past few decades, the commonly used strategy ~~is~~ was the direct oxidation of the corresponding β-dicarbonyl compounds with various oxidants such as **MoOPH**[3], **OsO_4**[4], **$Pb(OAc)_4$**[5], ***m*-CPBA**[6], **DMD**[7], **oxaziridines**[8], **IBX**[9], **oxone**[10], **ROOH**[11], **nitrosobenzene**[12], **H_2O_2**[13] or **molecular oxygen**[14]. However, the oxyfunctionalizations of 1, 3-dicarbonyl compounds and their hetero analogs were previously limited to **hydroxy**, **peroxy**[15], **aminoxy**[16] and **oxygen-sulfonyl groups**[17]. Thus, the development of a ~~novel~~ simple and ~~simple~~ novel method for ~~the~~ efficient oxyfunctionalization of ~~the~~ 1, 3-dicarbonyl group is currently a desirable and timely task. In the past few years, the acyloxy-functionalizations of 1, 3-dicarbonyl compouds were realized by using **hypervalent iodine compounds**[18], **Bu_4NI/*t*-BuOOH**[19], **manganese(III) acetate**[20] and **iron(III) salts**[21]. To achieve the benzoyloxylation with the less reactive benzoyl peroxide as oxidant, the dicarbonyl substrates had to be previously activated by being transformed ~~transformation~~ into enamines[22] or metal complexes[23]. Unlike α-hydroxylation, methods for intermolecular oxidative α-benzoyloxylation of 1, 3-dicarbonyl compounds by diacyl peroxides were rarely reported. Thus, the development of green and ~~highly~~ efficient α-benzoyloxylation of β-dicarbonyl compounds with broad substrate scope is necessary and meaningful.

On the other hand, phase-transfer catalysis (**PTC**) is ~~a well known~~recognized as a useful tool to develop sustainable oxidation processes[24]. In 2016, Itoh reported the first enantioselective α-benzoyloxylation of malonic diester[25], our group independently reported the α-benzoyloxylation of β-keto esters, by phase transfer catalysis[26]. Compared with the β-keto esters, β-keto amides are still challenging substrates, possibly due to the lower acidity of the α-hydrogen. Furthermore, the α-hydroxy-β-keto amide structure could be widely found in natural products and pharmaceuticals such as novel antimicrobial agent **Pramanicin**[27] and bioactive nature product **Y224A**[28]. Recently, the α-oxygenated β-keto amides have been demonstrated to be key-intermediates to access Brazilin-type compounds, which showed antiproliferative activity against different human tumor cell lines[29] (**Scheme 1**). Although α-hydroxylations of β-keto amides have been achieved by **ROOH**[11d,e,30] and ***oxone***[10], a highly efficient method for the α-oxidation of β-keto amides for a broad scope of substrates, remains to be developed. Herein, we reported the first efficient α-benzoyloxylation of β-keto amides by phase-transfer catalysis, and the α-hydroxylation product could be easily obtained by hydrolysis.

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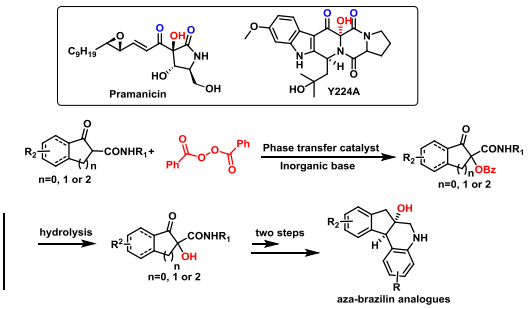
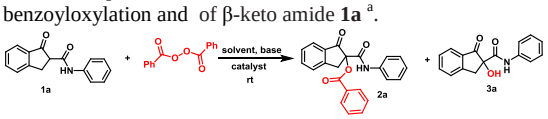


Scheme 1. Direct α-oxidation of β-keto amides.

2. Results and discussions

~~In order to~~To develop a new and convenient method ~~of~~ for the α-oxidation of β-keto amides, we investigated the α-benzoyloxylation of 1-indanone derived β-keto amide **1a** using benzoyl peroxide as the oxygen source. First, the reaction can ~~not~~ proceed without base and catalyst (Table 1, entry 1). When 30% K_2CO_3 aqueous solution was added in toluene, the α-benzoyloxylation ~~reaction~~ was undertaken, but afforded **2a** ~~was obtained~~ with only 23% yield (Table 1, entry 2). Then tetrabutylammonium bromide (**TBABr**) was used as the phase transfer catalyst, and we were pleased to see that the yield of **2a** was improved to 67%, and the α-hydroxylation product **3a** was also observed (Table 1, entry 3). Then we tested the organic bases 1,8-Diazabicyclo[5.4.0]undec-7-ene (**DBU**) and triethylamine (**Et_3N**), but ~~only a trace amount~~the yields of **2a** ~~was~~ were noticeably decreased ~~formed~~ (Table 1, entries 4-5). Solid K_2CO_3 provided a low yield compared with 30% K_2CO_3 aqueous solution, which indicated that the presence of H_2O is necessary for the reactivity (Table 1, entry 6). The use of 10% ~~NaOH~~ KOH aqueous solution provided faster reaction rates, but the selectivity of **2a** was poor. We thought **2a** might be undergoing hydrolysis in the presence of stronger inorganic base aqueous solution (Table 1, entry 7). In the solvent screening, we found that the reaction medium had a significant effect on the α-benzoyloxylation and α-hydroxylation. Using **CH_2Cl_2** as the solvent resulted in an elevated yield of **2a**, and the reaction time was shortened to 6 h (Table 1, entry 8). Ether solvents such as **Et_2O** and **MTBE** can accelerate the reaction and **2a** was obtained with high yields (84-91%) (Table 1, entries 9-10). The ~~more~~ high polar solvents (**THF** and **DMSO**) were also tested, and we ~~can~~ not only obtain ~~both the~~ α-benzoyloxylation product **2a** ~~and~~ but also ~~the~~ α-hydroxylation product **3a** (Table 1, entries 11-12). To our surprise, when **MeOH** was used, ~~we did not obtain the α-benzoyloxylation product 2a, and~~ only the α-hydroxylation product **3a** was observed~~obtaided in 65% yield~~. We thought not only the ester group but also the amide group of **1a** might be partly hydrolysed in **MeOH**. Next we screened the phase transfer catalyst. Tetrabutylammonium chloride (**TBACl**) and Tetrabutylammonium fluoride (**TBAF**) were introduced ~~but~~ and provided **2a** in 81-87% yields (Table 1, entries 14-15). Finally, benzyltrimethylammonium bromide (**BTMAB**) was tested, but it still provided low yield compared with **TBABr** (Table 1, entr~~y~~ies 9, 16). It is worth mentioning that the yield of α-hydroxylation product **-3a** was improved to 85% when 4:1 **CH_2Cl_2/MeOH** were used as the components (Table 1, entry 17). After all, the two α-oxygenated products of β-keto amide **1a** ~~the α-benzoyloxylation product 2a and the α-hydroxylation product 3a~~ could be respectively obtained with good yield by phase-transfer catalysis.

Table 1. Optimization of the reaction conditions for the α-benzoyloxylation and of β-keto amide **1a** [a].



Entry	Solvent	Base	t [h]	Cat.	Yield (**2a**/**3a**) [%][b]
1	$PhCH_3$	/	48	/	trace/n.r[d]
2	$PhCH_3$	30% K_2CO_3	48	/	23/ n.r[d]
3	$PhCH_3$	30% K_2CO_3	12	TBABr	67/23
4	$PhCH_3$	DBU	2	TBABr	trace/21
5	$PhCH_3$	Et_3N	12	TBABr	trace/trace
6[c]	$PhCH_3$	K_2CO_3	12	TBABr	34/trace
7	$PhCH_3$	10% KOH	2	TBABr	21/65
~~7~~8	CH_2Cl_2	30% K_2CO_3	6	TBABr	71/20
9	Et_2O	30% K_2CO_3	2	TBABr	**91**/**trace**
10	MTBE	30% K_2CO_3	2	TBABr	84/trace
11	DMSO	30% K_2CO_3	12	TBABr	71/23
12	THF	30% K_2CO_3	12	TBABr	41/48
13	MeOH	30% K_2CO_3	12	TBABr	trace/**65**
14	Et_2O	30% K_2CO_3	2	TBACl	81/trace
15	Et_2O	30% K_2CO_3	2	TBAF	87/trace
16	Et_2O	30% K_2CO_3	2	BTMAB	65/21
17	CH_2Cl_2/MeOH 4:1	10% KOH	6	TBABr	trace/**85**

[a] Unless otherwise specified, the reactions were performed with **1a** (0.1 mmol), **BPO** (0.13 mmol, 97% dry wt., wet with 25% water), catalyst (0.005 mmol), and base (0.5 mL) in solvent (2 mL). [b] Yields shown are of isolated products. [c]Five equivalents of the base was used. [d] n.r = no reaction

With the optimized conditions in hand, we next explored the substrate scope to demonstrate the generality in α-benzoyloxylation of β-keto amides. First, we investigated the influence of substituents at the amide sides. Aniline-derived substrates **1a-1e** containing 4'-Me, 4'- MeO, 3', 5'-CF_3, 4'-*t*-Bu and ~~Aryl~~ aryl derivatives **1f-1g** containing naphthyl and benzyl groups ~~could be~~were nicely converted into the corresponding products **2a-2g** in good yields (78-94%). Compounds **1f-1k**, with aliphatic amido groups, resulted in lower reaction rate (4h), ~~affording~~ and the corresponding product **2f-2k** were obtaind in excellent yields (89-94%). Next, ~~we~~ the reaction scope was extended ~~the procedure~~ to substrates which have halogen atoms and electron-donating groups on the aromatic ring of the indane scaffold. Under mild conditions, Substrates **1l-1n** with Cl or Br on the aromatic rings, were nicely converted into the corresponding products (2l-2n) in good yields (86-93%).

~~**1l-1n** which have halogen substituents were nicely converted into the corresponding products.~~ However, when methoxy groups were introduced (**1o** and **1p**), a longer reaction time (12 h) was needed to afford the desired products with 71-78% yields. Then ~~the scope of~~ 1-tetralone-derived β-keto amide **1q** was

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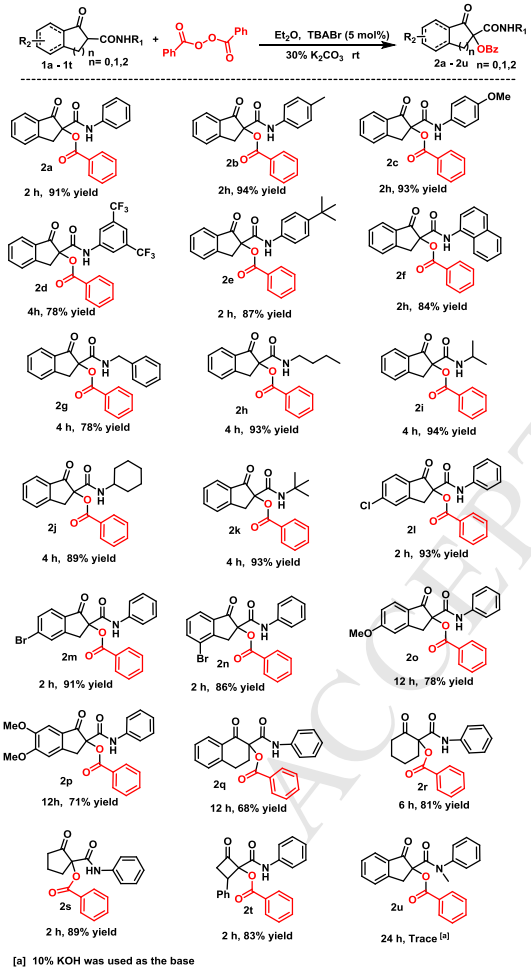
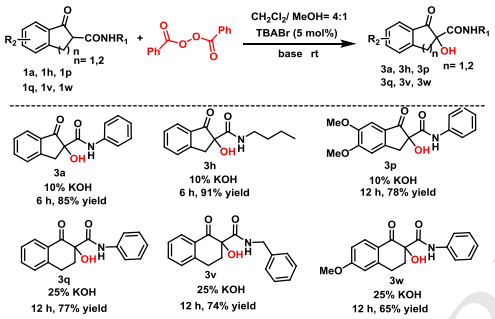
examined, and the desired product~~s~~ **2q** was obtained with 68% yield. Interestingly, the six, five, four-membered acyclic substrates **1r-1t** could be converted into the α-benzoyloxylation prodcuts with 81-89% yields. ~~Interestingly, c~~Compound **1u** which has methyl and phenyl in the N-position, afforded **2u** in extremely low yield even 10% KOH was used as the base. Ultimately~~After all~~, these results ~~constituted~~ showed a significant improvement in substrate scope on phase-transfer-catalyzed α-benzoyloxylation of β-keto amides (**Scheme 2**).

Under phase-transfer catalysis ~~conditions~~, we further examined the α-hydroxylation of β-keto amides to explore the synthetic utility. We were pleased to see that the indanone derived β-keto amides **1a**, **1h**, **1p** can be easily transformed into the α-hydroxylation products with 78-91% yields. More challenging β-keto amides **1q**, **1v**, **1w** which were derived from 1-tetralone were also examined. By using 25% KOH as the base, we can also obtain the α-hydroxylation products with 65-77% yields. ~~Ultimately, s~~Such a simple and efficient method for α-hydroxylation showed good substrate tolerance for indanone and 1-tetralone-derived β-keto amides (**Scheme 3**), and all the new compounds have been fully characterized with ^{1}HNMR, ^{13}CNMR and HRMS.

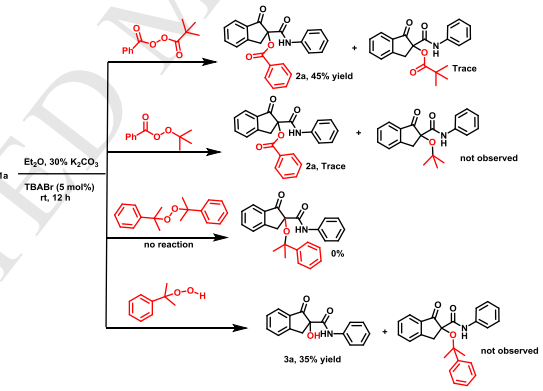


Scheme 2. Substrate scope of the α-benzoyloxylation of β-keto amides.



Scheme 3. Substrate scope of the α-hydroxylation of β-keto amides.

The phase-transfer catalysed α-oxidations of β-keto amides with mixed peroxide were carried out under standard reaction conditions employing benzoyl pivaloyl peroxide, *t*-butyl peroxybenzoate, dicumyl peroxide and cumyl hydroperoxide. **2a** was obtained in 45% yield by using benzoyl pivaloyl peroxide as the oxidant, while the formation of the alkyl acyloxy product was not observed. *t*-Butyl peroxybenzoate and dicumyl peroxide could not promote the reaction. When cumyl hydroperoxide was used, ~~we can obtain~~ the α-hydroxylation product **3a** was obtained in 35% yield. These results showed the unique structure of benzoyl peroxide ~~is~~ was important for the high-efficiency α-benzoyloxylation and hydroxylation of β-keto amides (**Scheme 4**).



Scheme 4. Reaction with mixed acyl peroxides and *tert*-butyl hydroperoxide.

In order to understand the reaction mechanism, we conducted some control experiments. First, ~~We~~ we added **TEMPO** as a radical inhibitor, ~~and~~ but the results did not noticeably influenced, which indicated a radical process was not occurring in this reaction system. Then ~~we use~~ pure oxygen gas was used instead of **BPO** as the oxidant, but ~~very little product~~nearly no α-hydroxylation product was obtained, which indicated that the oxygen source for α-hydroxylation product **3a** was **BPO**. Furthermore, ~~the~~ α-benzoyloxylation product **2a** can be hydrolyzed under stronger inorganic base (10% KOH), and **3a** was obtained in 81% yield (**Scheme 5**).

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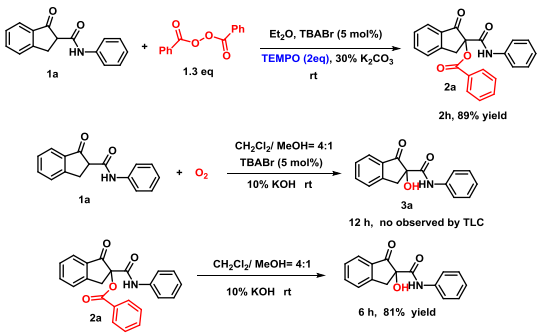
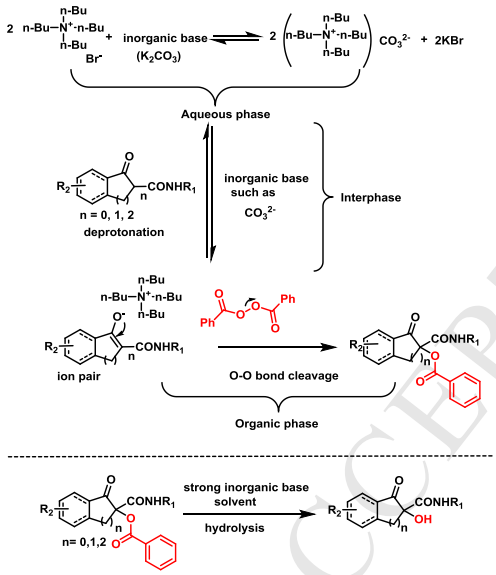


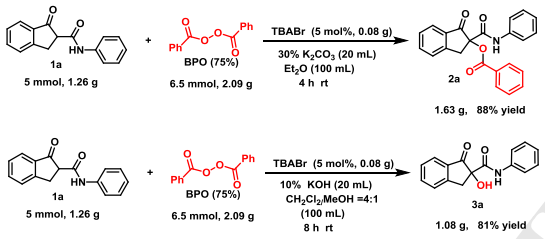
Scheme 5. Control experiments.

On the basis of these experiments, we proposed a possible mechanism for the α-benzoyloxylation and hydroxylation of β-keto amides. Phase-transfer ~~catalysis~~ catalyst (**PTC**) such as **TBABr** is an organic molecule incorporating a quarternary nitrogen center with an ability to dissolve in both aqueous and organic solvents. The catalyst thereby carries an inorganic base (e.g., CO_3^{2-}) into the organic phase where it deprotonates the β-keto amides, then the ~~chiral~~ catalyst forms an ion-pair between the positive quarternary amine and the enolate anion, which attacks the electrophile **BPO**, thereby forming the α-benzoyloxylation product. Then under stronger bases, the α-hydroxylation product ~~can be~~was generated by hydrolysis of α-benzoyloxylation product (**Scheme 6**).



Scheme 6. Proposed mechanism for α-benzoyloxylation and hydroxylation of β-keto amides.

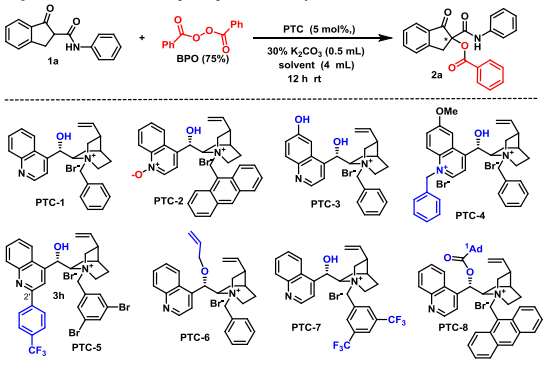
To demonstrate the utility of this reaction, we scaled up the α-benzoyloxylation and hydroxylation to the gram scale. Under phase-transfer catalysis, 5 mmol of β-keto amides (**1a**) reacted smoothly with 6.5 mol of **BPO** and gave 1.63 g (88% yield) of **2a** after 4 h. It is worth mentioning that the α-hydroxylation product can be respectively~~easily~~ obtained ~~with~~ in 81% yield by simply using the different the solvent (CH_2Cl_2/MeOH= 4:1) and the base (10% KOH) (**Scheme 7**).



Scheme 7. Gram scale reaction of α-benzoyloxylation and hydroxylation.

In order to develop a convenient method ~~for~~ to obtain the chiral α-benzoyloxylation product of β-keto amides, we further investigated the asymmetric α-benzoyloxylation of 1-indanone-derived β-keto amide **1a** catalysed by cinchona alkaloid derived phase-transfer catalyst. The simple **PTC-1** provided **2a** with 10% ee in toluene (Table 2, entry 2). The N-oxide **PTC-2** led to a slightly higher enantioselectivity (Table 2, entry 3). **PTC-3,** which has hydroxy groups at both the C-9 and C-6′ positions, showed poor results. Then we screened the doubly quaternized catalyst **PTC-3**, but the enantioselectivity was poor (Table 2, entry 4). C-2′-arylated **PTC-5** and C-9 etherified **PTC-6** could not noticeably improve the enantioselectivity of **2a** (Table 2, entries 5-6). **PTC-7**, with electron-withdrawing groups (-CF_3) at the 3 and 5 positions, improved the enantioselectivity (Table 2, entry 8). **PTC-8,** which the C-9 hydroxy was protected by a bulky 1-adamantyl group, afforded **2a** in a higher enantioselectivity (30 % ee). I think the bulky 1-adamantyl group can act as a large space resistance group, and the anthracene ring can be involved in stronger π-π stacking interactions with substrate **1a** than a benzene ring. Although the results of the asymmetric α-benzoyloxylation of β-keto amides ~~was~~ were not satisfying, we still developed an enantioselective oxidative C-O coupling of β-keto amides by phase-transfer catalysis, and this reaction provided an easy and rapid access for potentially valuable precursors for the synthesis of natural products and pharmaceuticals.

Table 2. Optimization of the reaction conditions for the asymmetric α-benzoyloxylation of β-keto amide **1a** [a].



Entry	Solvent	Base	Cat.	Yield[b] [%]	ee[c] [%]
1	Et_2O	30% K_2CO_3	**PTC-1**	86	0

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2	$PhCH_3$	30% K_2CO_3	**PTC-1**	73	10
3	$PhCH_3$	30% K_2CO_3	**PTC-2**	78	23
4	$PhCH_3$	30% K_2CO_3	**PTC-3**	51	5
5	$PhCH_3$	30% K_2CO_3	**PTC-4**	46	5
6	$PhCH_3$	30% K_2CO_3	**PTC-5**	78	14
7	$PhCH_3$	30% K_2CO_3	**PTC-6**	82	18
8	$PhCH_3$	30% K_2CO_3	**PTC-7**	81	25
9	$PhCH_3$	30% K_2CO_3	**PTC-8**	84	30

[a] Unless otherwise specified, the reactions were performed with **1a** (0.1 mmol), **BPO** (0.13 mmol), catalyst (0.005 mmol), and base (0.5 mL) in solvent (2 mL). [b] Yields shown are of isolated products. [c] Ee values were determined by HPLC analysis on Chiralpak AD-H.

3. Conclusion

In conclusion, we developed the facile and efficient α-benzoyloxylation of β-keto amides under phase-transfer catalysis with commercially available benzoyl peroxide. Under mild conditions, good yields (up to 94%) were obtained for a range of substituted indanone, 1-tetralone, cyclohexanone and cyclopentanone derivatives. Moreover, the α-hydroxylation products ~~can also~~could be easily obtained by hydrolysis under strong inorganic base. This new methodology was also successfully used for a gram-scale reaction. Further investigations on expanding this α-benzoyloxylation to other useful compounds are currently underway.

4. Exprimental

4.1. General

Unless otherwise stated, all commercial reagents and solvents were used without further additional purification. Analytical TLC was visualized with UV light at 254 nm. Thin layer chromatography was carried out on TLC aluminum sheets with silica gel 60 F254. Purification of reaction products was carried out with chromatography on silica gel 60 (200-300 mesh). ^{1}H NMR (400 MHz) spectra was obtained at 25 °C; ^{13}C NMR (126 MHz) were recorded on a VARIAN INOVA-400M and AVANCE II 400 spectrometer at 25 °C. Chemical shifts are reported as δ (ppm) values relative to TMS as internal standard. Mass spectra are reported by using electron ionization and electrospray ionization techniques. Melting points were determined with a hot plate apparatus. HPLC analyses were performed on equipped with Diacel Chiralpak AD-H chiral column (0.46 cm × 25 cm), using mixtures of n-hexane/isopropyl alcohol as mobile phase, at 25 °C.

4.2. General Proceduce for the α-benzoyloxylation of β-keto amides (2a-2u).

The reaction was conducted with β-keto amides **1a-1u** (0.1 mmol) in the presence of **TBABr** (0.005 mmol) and benzoyl peroxide (0.13 mmol) in a mixture containing Et_2O (2mL) and 30% K_2CO_3 (0.5 mL). The reaction was stirred at this temperature for 2 h. After the reaction was completed (confirmed by TLC analysis), the mixture was diluted with EtOAc (30 mL), washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (silica gel; petroleum ether/ethyl acetate = 20:1-5:1) to afford the α-benzoyloxylation products **2a-2u**.

4.2.1. ***2-benzoyloxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carb-oxamide (2a).*** Brown solid, 34 mg, 91% yield; mp:190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.18 – 8.03 (m, 2H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.64 (m, 2H), 7.63 – 7.45 (m, 6H), 7.41 – 7.32 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 4.37 (d, *J* = 16.9 Hz, 1H), 3.49 (d, *J* = 16.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.74, 164.57, 163.35, 151.65, 137.07, 136.38, 134.19, 133.51, 130.02, 129.07, 128.84, 128.40, 128.12, 126.37, 125.11, 125.01, 120.07, 86.33, 36.23. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for $[C_{23}H_{17}NO_4+Na]^+$ requires m/z 394.1055, found m/z 394.1052.

4.2.2. ***2-benzoyloxy-1-oxo-N-(4-methyl-phenyl)-2,3-dihydro-1H-indene-2-carboxamide (2b).*** Brown solid, 36 mg, 94% yield; mp:183-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.15 – 8.05 (m, 2H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.77 – 7.63 (m, 2H), 7.61 – 7.42 (m, 6H), 7.16 (d, *J* = 8.3 Hz, 2H), 4.35 (d, *J* = 16.8 Hz, 1H), 3.49 (d, J = 16.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.80, 164.56, 163.21, 151.66, 136.32, 134.69, 134.52, 134.16, 130.02, 129.54, 128.82, 128.44, 128.08, 126.36, 125.09, 120.09, 86.33, 36.26, 20.92. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for $[C_{24}H_{19}NO_4+Na]^+$ requires m/z 408.1212, found m/z 408.1208.

4.2.3. ***2-benzoyloxy-1-oxo-N-(4-methoxy-phenyl)-2,3-dihydro-1H-indene-2-carboxamide (2c).*** Yellow solid, 37 mg, 93% yield; mp:181-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$~~Chloroform-d~~) δ 8.32 (s, 1H), 8.14 – 8.00 (m, 2H), 7.80 – 7.60 (m, 3H), 7.62 – 7.44 (m, 5H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.28 (d, *J* = 17.1 Hz, 1H), 3.44 (d, *J* = 17.1 Hz, 1H).~~δ 8.34 (s, 1H), 8.16 – 8.07 (m, 2H), 7.87 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.76 – 7.42 (m, 9H), 6.89 (d, *J* = 9.1 Hz, 2H), 4.35 (d, *J* = 16.9 Hz, 1H), 3.81 (s, 3H), 3.49 (d, *J* = 16.9 Hz, 1H).~~ ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.96, 164.59, 163.19, 156.85, 151.72, 136.34, 134.14, 133.71, 133.57, 130.19, 130.02, 128.80, 128.46, 128.42, 128.08, 126.35, 125.10, 121.85, 114.16, 86.34, 55.50, 36.32. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for $[C_{24}H_{19}NO_5+Na]^+$ requires m/z 424.1161, found m/z 424.1155.

4.2.4 .***2-benzoyloxy-1-oxo-N-(3,5-ditrifluoromethyl-phenyl)-2,3-dihydro-1H-indene-2-carboxamide (2d).*** White solid, 40 mg, 78% yield; mp:227-230 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 12.1 Hz, 1H), 8.08 (dt, *J* = 7.6, 4.4 Hz, 4H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.47 (m, 7H), 4.38 (d, *J* = 17.0 Hz, 1H), 3.48 (d, *J* = 17.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.51, 197.48, 164.60, 164.58, 164.12, 151.65, 138.52, 136.85, 134.41, 133.04, 130.11, 130.09, 128.84, 128.83, 128.38, 127.97, 126.43, 125.23, 119.83, 118.20, 86.24, 36.20, 36.17. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for $[C_{25}H_{15}F_6NO_4+Na]^+$ requires m/z 530.0803, found m/z 530.0810.

4.2.5. ***2-benzoyloxy -1-oxo-N-(4-tert-butyl-phenyl)-2,3-dihydro-1H-indene -2-carboxamide (2e).***Brown solid, 37 mg, 87% yield; mp:150-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.17 – 8.01 (m, 2H), 7.86 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.61 – 7.44 (m, 7H), 7.40 – 7.35 (m, 2H), 4.48 – 4.21 (m, 2H), 3.49 (d, *J* = 16.8 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.78, 164.57, 163.18, 151.65, 148.03, 136.33,

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134.49, 134.15, 133.54, 130.93, 130.02, 128.85, 128.81, 128.45, 128.08, 126.37, 125.88, 125.07, 119.79, 86.32, 65.59, 36.19, 34.44, 31.34, 30.59, 19.21, 13.76. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for $[C_{25}H_{15}NO_4+Na]^+$ requires m/z 530.0803, found m/z 530.0810.

4.2.6. ***2-benzoyloxy-1-oxo-N-(1-naphthyl)-2,3-dihydro-1H-indene-2-carboxamide (2f)*** Brown solid, 35 mg, 84% yield; mp:153-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.23 – 8.13 (m, 2H), 8.09 – 7.87 (m, 4H), 7.80 – 7.65 (m, 3H), 7.64 – 7.43 (m, 7H), 4.48 (d, *J* = 17.0 Hz, 1H), 3.56 (d, *J* = 17.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.13, 164.77, 163.96, 151.87, 136.46, 134.23, 134.05, 133.52, 131.53, 130.07, 128.86, 128.75, 128.48, 128.15, 127.08, 126.73, 126.46, 126.22, 126.18, 125.64, 125.18, 120.54, 120.51, 86.55, 36.22. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{27}H_{19}NO_4+Na]^+$ requires m/z 444.1212, found m/z 444.1217.

4.2.7. ***2-benzoyloxy-1-oxo-N-(benzyl)-2,3-dihydro-1H-indene-2-carbox-amide (2g).*** Colorless oil, 30 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.73 – 7.60 (m, 2H), 7.56 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.47 (td, *J* = 7.8, 3.8 Hz, 3H), 7.41 – 7.26 (m, 5H), 7.06 (s, 1H), 4.69 – 4.45 (m, 2H), 4.29 (d, *J* = 16.9 Hz, 1H), 3.46 (d, *J* = 16.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.75, 165.84, 164.58, 151.74, 137.62, 136.17, 134.04, 133.74, 129.95, 128.79, 128.73, 128.46, 128.01, 127.62, 127.47, 126.35, 125.02, 86.07, 43.90, 36.72. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for $[C_{24}H_{19}NO_4+Na]^+$ requires m/z 408.1206, found m/z 408.1210.

4.2.8. ***2-benzoyloxy -1-oxo-N-(n-butyl)-2,3-dihydro-1H-indene-2-carboxamide (2h).*** White solid, 33 mg, 93% yield; mp:102-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.84 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.73 – 7.61 (m, 2H), 7.57 – 7.40 (m, 4H), 6.66 (s, 1H), 4.23 (d, *J* = 16.8 Hz, 1H), 3.54 – 3.24 (m, 3H), 1.65 – 1.48 (m, 2H), 1.48 – 1.31 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.93, 165.57, 164.54, 151.76, 136.07, 134.01, 133.75, 129.92, 128.74, 128.59, 127.92, 126.30, 124.94, 86.07, 39.81, 36.59, 31.46, 19.98, 13.74. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for $[C_{21}H_{21}NO_4+Na]^+$ requires m/z 374.1363, found m/z 374.1370.

4.2.9. ***2-benzoyloxy-1-oxo-N-(isopropyl)-2,3-dihydro-1H-indene-2-carboxamide (2i)*** Light yellow solid, 33 mg, 94% yield; mp:103-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.61 (m, 2H), 7.58 – 7.48 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 4.22 (d, *J* = 16.8 Hz, 1H), 4.10 (dt, *J* = 8.0, 6.6 Hz, 1H), 3.40 (d, *J* = 16.8 Hz, 1H), 1.30 - 1.19 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.90, 164.76, 164.52, 151.75, 136.04, 134.00, 133.78, 129.89, 128.76, 128.62, 127.90, 126.28, 124.93, 85.95, 42.25, 36.56, 22.66, 22.34. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{20}H_{19}NO_4+Na]^+$ requires m/z 360.1206, found m/z 360.1203.

4.2.10. ***2-benzoyloxy-1-oxo-N-(cyclohexyl)-2,3-dihydro-1H-indene-2-carboxamide (2j).*** Colorless oil, 33 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.97 (m, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.74 – 7.59 (m, 2H), 7.57 – 7.39 (m, 4H), 6.53 (d, *J* = 8.1 Hz, 1H), 4.23 (d, *J* = 16.8 Hz, 1H), 3.86 – 3.78 (m, 1H), 3.40 (d, *J* = 16.7 Hz, 1H), 2.06 – 1.84 (m, 2H), 1.84 – 1.55 (m, 3H), 1.51 – 1.16 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.93, 164.68, 164.51, 151.76, 136.02, 133.99, 129.88, 128.76, 127.88, 126.28, 124.92, 85.99, 48.88, 36.54, 32.87, 32.50, 25.46, 24.73, 24.61. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{23}H_{23}NO_4+Na]^+$ requires m/z 400.1525, found m/z 400.1530.

4.2.11. ***2-benzoyloxy-1-oxo-N-(tert-butyl)-2,3-dihydro-1H-indene-2-carboxamide (2k).*** White solid, 33 mg, 93% yield; mp:136-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.98 (m, 2H), 7.85 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.74 – 7.62 (m, 2H), 7.56 – 7.48 (m, 3H), 7.44 (td, *J* = 7.5, 1.0 Hz, 1H), 6.51 (s, 1H), 4.17 (d, *J* = 16.8 Hz, 1H), 3.38 (dd, *J* = 16.7, 1.2 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.08, 164.78, 164.42, 151.77, 135.98, 133.98, 129.84, 128.77, 127.86, 126.20, 124.93, 86.13, 51.89, 36.60, 28.58. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{21}H_{21}NO_4+Na]^+$ requires m/z 374.1368, found m/z 374.1361.

4.2.12. ***5-chloro-2-benzoyloxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (2l).*** White solid, 38 mg, 93% yield; mp:195-198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.18 – 8.05 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.65 (m, 1H), 7.61 – 7.51 (m, 5H), 7.45 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.21 – 7.14 (m, 1H), 4.31 (d, *J* = 17.0 Hz, 1H), 3.47 (d, *J* = 17.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.30, 164.54, 163.11, 152.93, 142.95, 136.91, 134.32, 132.02, 130.02, 129.11, 128.96, 128.89, 128.20, 126.65, 126.16, 125.14, 120.10, 86.20, 36.02. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{23}H_{16}ClNO_4+Na]^+$ requires m/z 428.0666, found m/z 428.0668.

4.2.13. ***5-bromine-2-benzoyloxy -1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (2m).*** White solid, 41 mg, 91% yield; mp:194-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.11 – 8.00 (m, 2H), 7.77 – 7.63 (m, 3H), 7.61 – 7.46 (m, 5H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.28 (d, *J* = 17.1 Hz, 1H), 3.44 (d, *J* = 17.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.56, 164.53, 163.07, 152.97, 136.90, 134.33, 132.41, 131.90, 131.80, 130.03, 129.72, 129.12, 128.89, 128.17, 126.19, 125.15, 120.09, 86.11, 35.95. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{23}H_{16}BrNO_4+Na]^+$ requires m/z 472.0160, found m/z 472.0158.

4.2.14. ***4-bromine-2-benzoyloxy -1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (2n).*** Brown solid, 37 mg, 86% yield; mp:178-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.10 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.85 (ddd, *J* = 24.2, 7.8, 1.0 Hz, 2H), 7.73 – 7.50 (m, 5H), 7.37 (ddd, *J* = 8.5, 7.6, 1.8 Hz, 3H), 7.24 – 7.12 (m, 1H), 4.30 (d, *J* = 17.4 Hz, 1H), 3.40 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.24, 164.51, 163.17, 151.33, 138.94, 136.89, 135.60, 134.37, 130.04, 129.78, 129.13, 128.91, 128.10, 125.19, 123.80, 121.64, 120.14, 85.86, 37.66. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{23}H_{16}BrNO_4+Na]^+$ requires m/z 472.0160, found m/z 472.0156.

4.2.15. ***5-methoxyl-2-benzoyloxy -1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (2o).*** Yellow solid, 31 mg, 78% yield; mp:149-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.18 – 8.00 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.61 – 7.49 (m, 4H), 7.35 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.19 – 7.11 (m, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 4.36 (d, *J* = 16.9 Hz, 1H), 3.93 (s, 3H), 3.44 (d, *J* = 16.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.52, 166.70, 164.66, 163.61, 154.87, 137.21, 134.10, 130.03, 129.03, 128.79, 128.56, 126.95, 126.56, 124.89, 120.06, 116.51, 109.46, 86.62, 55.86, 36.12. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{24}H_{19}NO_5+Na]^+$ requires m/z 424.1161, found m/z 424.1153.

4.2.16. ***5,6-dimethoxyl-2-benzoyloxy -1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (2p).*** Yellow solid, 30 mg, 71% yield; mp:223-226 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.09 (s, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.61 – 7.46 (m, 4H), 7.38 – 7.22 (m, 4H), 7.13 (s, 1H), 4.27 (d, *J* = 16.5 Hz, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 3.38 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.88, 164.64, 163.61, 156.93, 149.98, 147.61, 137.20, 134.10, 130.02, 129.04, 128.79, 128.57,

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124.89, 120.02, 107.35, 105.25, 86.73, 56.46, 56.16, 35.84. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{25}H_{21}NO_6+Na]^+$ requires m/z 454.1267, found m/z 454.1263.

4.2.17 ***.2-benzoyloxy-1-oxo-N-phenyl-1,2,3,4-tetrahydronaphth-alene-2-carboxylate (2q).*** Colorless oil, 26 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.11 (ddd, *J* = 24.9, 8.3, 1.5 Hz, 3H), 7.71 – 7.30 (m, 11H), 7.24 – 7.09 (m, 1H), 3.72 – 3.61 (m, 1H), 3.19 – 2.87 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.17, 164.49, 164.08, 143.71, 137.06, 134.70, 133.85, 129.95, 129.08, 128.87, 128.68, 128.39, 127.03, 124.95, 120.07, 83.32, 29.91, 26.67. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{24}H_{19}NO_4+Na]^+$ requires m/z 408.1212, found m/z 408.1216.

4.2.18. ***2-benzoyloxy -1-oxo-N-phenyl-cyclohexanone-2-carboxamide (2r).*** Colorless oil, 27 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.25 – 8.05 (m, 2H), 7.71 – 7.48 (m, 5H), 7.41 – 7.32 (m, 2H), 7.19 – 7.12 (m, 1H), 2.90 – 2.69 (m, 2H), 2.63 – 2.52 (m, 1H), 2.45 – 2.31 (m, 1H), 2.24 – 1.91 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.99, 165.59, 165.48, 137.24, 134.00, 130.09, 129.01, 128.70, 124.75, 120.30, 83.88, 40.08, 37.87, 27.97, 21.71. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{20}H_{19}NO_4+Na]^+$ requires m/z 360.1212, found m/z 360.1208.

4.2.19. ***2-benzoyloxy -1-oxo-N-phenyl-cyclopentanone-2-carboxamide (2s).*** Light yellow oil, 29 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.09 – 7.97 (m, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 16.6, 7.7 Hz, 4H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 3.04 (ddd, *J* = 13.4, 8.0, 3.4 Hz, 1H), 2.81 (dd, *J* = 18.9, 9.4 Hz, 1H), 2.62 – 2.40 (m, 2H), 2.38 – 2.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.92, 164.53, 164.38, 136.85, 134.12, 129.86, 129.12, 128.83, 128.51, 125.10, 120.20, 85.68, 36.15, 31.68, 18.92. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{19}H_{17}NO_4+Na]^+$ requires m/z 346.1055, found m/z 346.1060.

4.2.20. ***2-benzoyloxy-4-phenyl-1-oxo-N-phenyl-cyclobut-anone-2-carboxamide (2t).*** Colourless oil, 32 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.74 – 7.58 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.34 – 7.26 (m, 6H), 7.21 – 7.06 (m, 1H), 5.78 (s, 1H), 3.54 – 3.26 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10, 165.22, 136.62, 135.65, 133.82, 129.77, 129.71, 129.00, 128.74, 128.54, 127.12, 124.97, 120.44, 75.02, 37.77. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{24}H_{19}NO_4+Na]^+$ requires m/z 408.1212, found m/z 408.1210.

4.3. General Proceduce for the α-hydroxylation of β-keto amides.

The reaction was conducted with β-keto amides (0.1 mmol) in the presence of **TBABr** (0.005 mmol) and benzoyl peroxide (0.13 mmol) in a mixture containing CH_2Cl_2/MeOH=4:1 (2mL) and 10% or 25% KOH (0.5 mL). The reaction was stirred at this temperature for 6-12 h. After the reaction was completed (confirmed by TLC analysis), the mixture was diluted with EtOAc (30 mL), washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (silica gel; petroleum ether/ethyl acetate = 10:1-2:1) to afford the α-hydroxylation products.

4.3.1. ***2-hydroxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (3a)*** White solid; 23 mg, 85% yield; mp:149-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 3.88 (d, *J* = 16.7 Hz, 1H), 3.22 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.14, 168.30, 153.06, 136.89, 136.54, 133.69, 129.02, 128.19, 126.40, 125.24, 124.79, 119.70, 82.72, 40.86. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{16}H_{13}NO_3+Na]^+$ requires m/z 290.0793, found m/z 290.0790.

4.3.2. ***2-hydroxy-1-oxo-N-n-butyl-2,3-dihydro-1H-indene-2-carboxamide (3h)*** Colorless wax; 22 mg,91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.63 (td, *J* = 7.5, 1.2 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 6.90 (s, 1H), 3.69 (d, *J* = 16.7 Hz, 1H), 3.29 – 3.15 (m, 2H), 3.06 (d, *J* = 16.7 Hz, 1H), 1.55 – 1.38 (m, 2H), 1.38 – 1.28 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.34, 170.26, 153.03, 136.15, 133.90, 127.93, 126.37, 125.05, 82.08, 40.64, 39.24, 31.45, 19.94, 13.70. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{14}H_{17}NO_3+Na]^+$ requires m/z 270.1106, found m/z 270.1103.

4.3.3. ***2-hydroxy-5,6-dimethoxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (3p).*** Yellow wax; 26 mg,78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.57 – 7.50 (m, 2H), 7.36 – 7.23 (m, 3H), 7.18 (s, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 3.99 (s, 3H), 3.89 (s, 3H), 3.76 (d, *J* = 16.4 Hz, 1H), 3.10 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.06, 168.63, 157.09, 150.04, 149.22, 137.04, 128.96, 126.21, 124.66, 119.67, 107.31, 105.31, 83.04, 56.40, 56.14, 40.59. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{18}H_{18}NO_5+Na]^+$ requires m/z 350.1004, found m/z 350.1010.

4.3.4. ***2-hydroxy-1-oxo-N-phenyl-1,2,3,4-tetrahydronaphth−alene-2-carboxylate (3q)*** Colorless wax; 22 mg,77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.65 – 7.50 (m, 3H), 7.43 – 7.29 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.88 (s, 1H), 3.74 – 3.49 (m, 1H), 3.04 (ddd, *J* = 17.4, 5.7, 2.0 Hz, 1H), 2.64 (ddd, *J* = 13.5, 5.4, 2.0 Hz, 1H), 2.36 (td, *J* = 13.2, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.07, 167.81, 145.71, 136.94, 134.68, 130.66, 129.03, 128.01, 126.73, 124.68, 119.63, 78.26, 77.35, 77.24, 34.63, 26.34. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{17}H_{15}NO_3+Na]^+$ requires m/z 304.0950, found m/z 304.0953.

4.3.5. ***2-hydroxy-1-oxo-N-benzyl-1,2,3,4-tetrahydronaphth−alene-2-carboxylate (3v)*** White soild; 22 mg,74% yield; mp:149-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.24 (m, 8H), 4.67 (s, 1H), 4.40 (dd, *J* = 5.9, 3.8 Hz, 2H), 3.60 (ddd, *J* = 17.7, 12.8, 5.3 Hz, 1H), 3.00 (ddd, *J* = 17.3, 5.6, 2.3 Hz, 1H), 2.55 (ddd, *J* = 13.5, 5.3, 2.3 Hz, 1H), 2.28 (td, *J* = 13.1, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.35, 169.86, 145.72, 137.79, 134.50, 130.69, 128.99, 128.77, 127.97, 127.71, 127.61, 126.64, 78.12, 43.03, 34.62, 26.37. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{18}H_{17}NO_3+Na]^+$ requires m/z 318.1106, found m/z 318.1103.

4.3.6. ***2-hydroxy-6-methoxyl-1-oxo-N-phenyl-1,2,3,4-tetrahydr-onaphthalene-2-carboxylate (3w)*** Light yellow oil; 20 mg,74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.48 (m, 2H), 7.38 – 7.28 (m, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 4.95 (s, 1H), 3.90 (s, 3H), 3.64 (td, *J* = 12.8, 6.5 Hz, 1H), 3.05 – 2.92 (m, 1H), 2.65 – 2.57 (m, 1H), 2.34 (td, *J* = 13.3, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.19, 168.10, 164.76, 148.45, 137.01, 130.58, 129.01, 124.61, 124.03, 119.60, 113.88, 112.67, 77.96, 55.58, 34.47, 26.67. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $[C_{18}H_{17}NO_4+Na]^+$ requires m/z 334.1055, found m/z 334.1058.

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