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Iodosobenzene Mediated α-Acyloxylation of 1,3-Dicarbonyl Compounds with Carboxylic Acids and an Insight into the Reaction Mechanism

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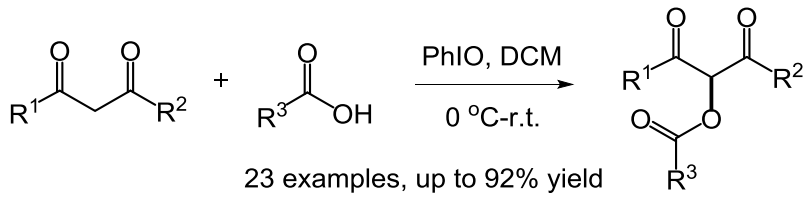


Abstract

A highly efficient direct α-acyloxylation of 1,3-dicarbonyl compounds with carboxylic acids mediated by hypervalent iodine reagent is presented. Treatment of a variety of 1,3-dicarbonyl compounds with carboxylic acids in the presence of iodosobenzene provides the corresponding α-acyloxylated products in good to excellent yields. The mechanistic investigation by means of NMR spectroscopy reveals that the *in-situ* generated phenyliodine biscarboxylate proves to be the key intermediate for the α-acyloxylation, and the loading sequence of reactants and oxidant is crucial for the

generation of the active species. The mild reaction conditions, wide substrate scope, short reaction time, good yields, high chemoselectivity, excellent functional group tolerance and metal catalyst-free conversion make this acyloxylation a significant synthetic protocol.

Introduction

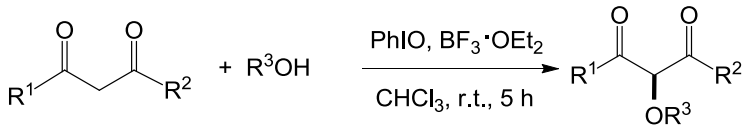
Over the past decades, α-acyloxycarbonyl compounds have attracted considerable research interest since they are distributed in numerous natural products along with diverse useful bioactivities, and used as versatile building blocks in synthetic organic chemistry.[1,2] In general, α-acyloxycarbonyl compounds can be prepared by the substitution reaction of α-halodicarbonyl compounds with alkaline carboxylates,[3] the condensation and rearrangement of aldehydes/ketones with *N*-alkyl-*O*-acylhydroxyl amines,[4] or the direct oxidative coupling of carbonyl compounds with carboxylic acids in the presence of varied organic oxidants (*e.g.* peroxides and hypervalent iodine reagents) [5,6] or heavy metal oxidants (*e.g.* $Pb(OAc)_4$ and $Mn(OAc)_3$).[7] In comparison to rare and toxic heavy metal oxidants, hypervalent iodine reagents are environmental benign alternatives.[8,9] While each of these approaches represents an important advance towards the objective of a general method for the synthesis of α-acyloxycarbonyl compounds, each of them, however, suffers from significant limitations, such as harsh conditions, narrow substrate scope, low yields, high toxicity, or poor chemo-/regio-selectivity.

Moreover, it should be noted that although many procedures had been developed for the C-O coupling reaction at α-position of carbonyl compounds, there only a few

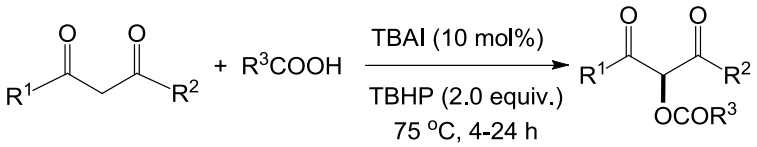
reports involved the α-acyloxylation or alkoxyation of 1,3-dicarbonyl compounds (Scheme 1a).[10] Recently, Uyanik and co-workers reported the direct α-oxybenzoylation of β-keto esters and 1,3-diketones catalyzed by the *in-situ* generated (hypo)iodite with *tert*-butyl hydroperoxide (TBHP) as oxidant (Scheme 1b).[6a] This was the first time to describe the use of hypervalent iodine reagents in catalytic amount for the α-acyloxylation. However, it should not be ignored that two equivalents of oxidant TBHP were employed in their investigations. In our recent work, we achieved the synthesis of α-acyloxy-1,3-dicarbonyl compounds *via* a copper-catalyzed formal O-H insertion reaction of α-diazo-β-oxo amides to carboxylic acids (Scheme 1c).[11] It should be mentioned that this insertion reaction requires high temperature (100 ^{o}C), the assistance of isocyanide, and excessive carboxylic acid as both reactant and solvent.

Scheme 1. C-O Coupling Reaction at α-Position of 1,3-Dicarbonyl Compounds

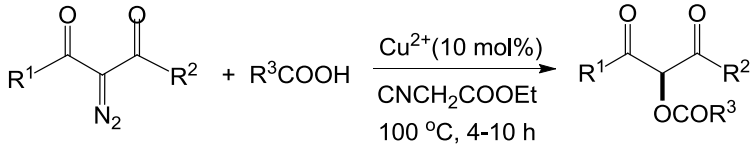
a) Moriarty's work[10a]



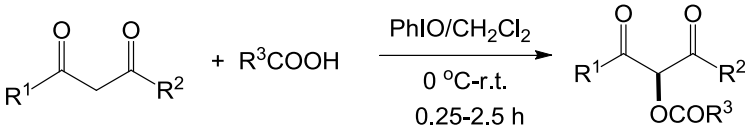
b) Uyanik's work[6a]



c) Our previous work[11]



d) This work



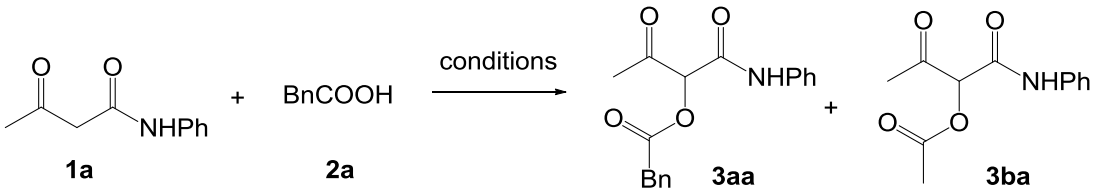
In continuation to our recent work on the synthesis of heterocycles from functionalized β-oxo amides mediated by hypervalent iodine reagents,[12] we envisioned to design and fabricate highly functionalized 1,3-dicarbonyl compounds and later on to further investigate their reactive character under the influence of different reagents and reaction conditions. In this context, we investigated the reaction behavior of varied 1,3-dicarbonyl compounds, *i.e.* β-oxo amides, β-keto esters and 1,3-diketones, towards hypervalent iodine reagents. As a result, we achieved facile and efficient α-acyloxylation of 1,3-dicarbonyl compounds with carboxylic acids mediated by iodosobenzene under very mild conditions (Scheme 1d). Herein, we wish to report our experimental results and the proposed mechanism involved in the α-acyloxylation of 1,3-dicarbonyl compounds.

Results and Discussion

The reaction of 3-oxo-*N*-phenylbutanamide **1a** with 2-phenyl acetic acid **2a** (3.0 equiv) was first attempted in dichloromethane (DCM) in the presence of phenyliodine(III) diacetate (PIDA, 1.2 equiv) at room temperature. As indicated by TLC, the reaction proceeded smoothly to afford two products, which were characterized as 1,3-dioxo-1-(phenylamino) butan-2-yl 2-phenyl acetate **3aa** (9% yield) and 1,3-dioxo-1-(phenylamino)butan-2-yl acetate **3ba** (75% yield), respectively, based on their spectral and analytical data (Table 1, entry 1).[10d] Obviously, there exist two competing reactions among **1a** with **2a** and acetate from PIDA. To circumvent this issue, we performed the reaction of **1a** and **2a** (1.2 equiv) in DCM using iodosobenzene (PhIO, 1.2 equiv) as the oxidant. In this case, **3aa** was exclusively formed as indicated by TLC,

although some of the starting material **1a** was recovered (Table 1, entry 2).

Table 1. Reaction of β-Oxo Amide 1a with 2a in the Presence of Iodosobenzene.[a]



Entry	Oxidant (equiv)	**2a** (equiv)	Solvent	Temp (^oC)	Time (h)	Yield[b] (%)
1	PIDA(1.2)	3.0	CH_2Cl_2	rt	0.5	9(75)[c]
2	PhIO(1.2)	1.2	CH_2Cl_2	rt	0.5	32(56)[d]
3	PhIO(1.2)	2.0	CH_2Cl_2	rt	0.5	64(15)[d]
4	PhIO(1.2)	3.0	CH_2Cl_2	rt	0.5	68(13)[d]
5	PhIO(1.2)	3.0	CH_2Cl_2	rt	6.0	73(7)[d]
6	PhIO(2.0)	1.2	CH_2Cl_2	rt	0.5	69
7	PhIO(2.0)	2.0	CH_2Cl_2	rt	0.25	81
8	**PhIO(**2.0**)**	**2.0**	**CH_2Cl_2**	**0**	**0.25**	**89**
9	PhIO(1.5)	2.0	CH_2Cl_2	0	0.25	82
10	PhIO(1.5)	2.5	CH_2Cl_2	0	0.25	86
11	PhIO(2.5)	1.5	CH_2Cl_2	0	0.25	78
12	PhIO(2.0)	2.0	THF	0	1.0	67(15)[d]
13	PhIO(2.0)	2.0	CH_3CN	0	1.0	52

[a] Reagents and conditions: **1a** (0.5 mmol), solvent (5.0 mL). [b] yields of **3aa**. [c] Data in parenthesis for the yield of **3ba**. [d] Data in parenthesis for the recovery of **1a**.

Encouraged by these findings, we then examined the effect of different ratio of PhIO and acid **2a** to β-oxo amide **1a**, reaction temperature, and solvents on the success of the oxidative reaction to optimize the yield of **3aa**. As shown in Table 1, substrate **1a** could not be consumed within half an hour when 1.2 equivalents of PhIO and varied

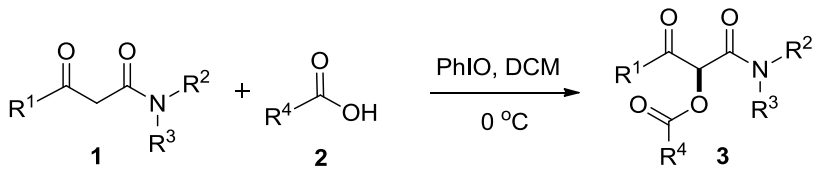
loading amount of **2a** were employed (entries 2-4). This phenomenon could be observed even though the reaction time was prolonged to 6.0 h (entry 5). In contrast, increasing of PhIO more than 1.5 equivalents made the reactions proceed completely within half an hour at either room temperature (entries 6-7) or 0 ^{o}C (entries 8-11). By comparing the experimental results from entry 7 and 8, it is not hard to notice that the higher temperature would result slightly lowering the yields of **3aa**, which might be attributed to the formation of byproducts. The solvent screening disclosed that the nature of the solvent also played a crucial role during the oxidation process. It seemed that the oxidative transformation was unfavorable with polar aprotic solvents, such as THF and acetonitrile (entries 12 and 13). Considering that iodobenzene (PhI) is generated during the oxidative transformation with hypervalent iodine reagents, such as PhIO,[13] we envisaged that the reaction of **1a** and **2a** might take place with catalytic amount of PhI in the presence of other oxidants. Unfortunately, no reaction was observed when **1a**, **2a** (2.0 equiv) and PhI (0.2 equiv) were subjected to DCM with TBHP (3.0 equiv) or H_2O_2 (3.0 equiv) at room temperature for 6.0 h. After a series of experiments, the optimal reaction conditions were obtained when **1a** and **2b** (2.0 equiv) were treated with PhIO (2.0 equiv) in DCM at 0 ^{o}C, whereby the yield of **3aa** reached 89 % (entry 8).

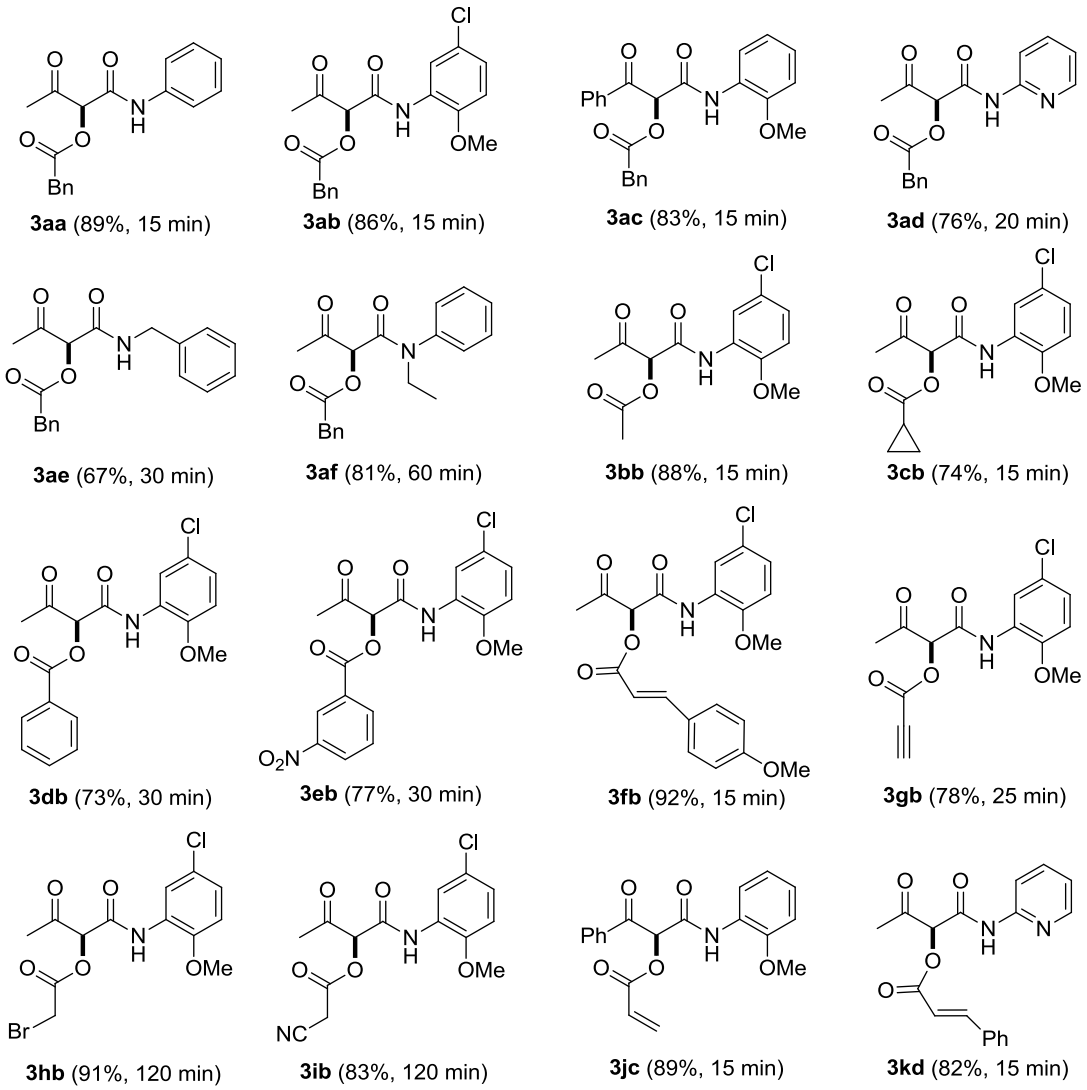
With the optimal conditions for the oxidative α-acyloxylation reaction in hand, we intended to determine its scope with respect to varied secondary or tertiary β-oxo amides **1** and carboxylic acids **2**. As shown in Table 2, a series of reactions of 2-phenyl acetic acid **2a** and varied β-oxo amides **1b-e** (R^2 = aryl, heteroaryl, benzyl groups; R^3 = H, alkyl groups) were carried out in the presence of PhIO in DCM at 0 ℃, and all these

reactions proceeded smoothly to afford the corresponding α-acyloxy-β-oxo amides **3** in good to high yields. Further experiments revealed that the very mild metal-free conditions, in particular room temperature and short reaction time, tolerated a wide variety of functionalities from alkyl, alkenyl, alkynyl and aryl carboxylic acids **2b-k** and allowed them to form the corresponding α-acyloxy-β-oxo amides **3** in high yields. It should be mentioned that intramolecular and intermolecular cyclization of alkynes with amides or carboxylic acids mediated by hypervalent iodine reagents had been reported in the presence of transition metal catalysts or Lewis acid additives.[14] Therefore, the synthesis of compound **3gb** provides an alternative route to the functionalized alkynoic amides which might be used as versatile building blocks in organic transformations. Notably, the corresponding α-acyloxylated products **3** were exclusively obtained when carboxylic acids **2a**, **2h** and **2i** bearing an activated methylene group were employed, which showed high chemoselectivity of the present protocol.

Next, we turned our attention to other type of 1,3-dicarbonyl compounds, *i.e.* β-keto esters and 1,3-diketones, with the aim to expand the scope of the oxidative C-O bond formation reaction. A range of reactions of 1,3-diketones (**4a**) β-keto ester (**5a** and **5b**) and selected carboxylic acids **2** were conducted under the conditions as for **3aa** in Table 1, entry 8. The experimental results in Table 3 have further demonstrated the efficiency and synthetic value of the α-acyloxylation reaction of variable 1,3-dicarbonyl compounds. Therefore, we provide an efficient and direct α-acyloxylation of 1,3-dicarbonyl compounds with carboxylic acids mediated by hypervalent iodine reagent.

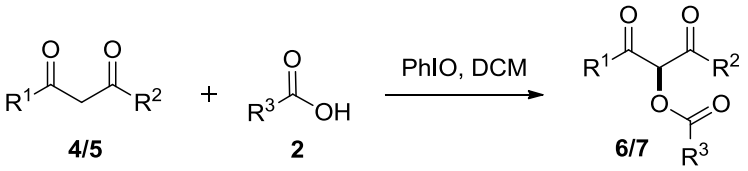
Table 2. Reaction of β-Oxo amide 1 with 2 in the Presence of Iodosobenzene.[a]



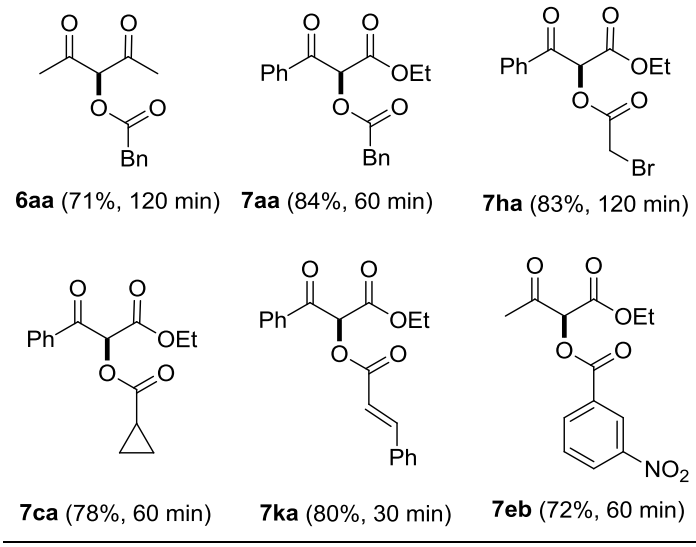


[a] Reagents and conditions: **1** (0.5 mmol), **2** (1.0 mmol), PhIO (1.0 mmol), DCM (10.0 mL), 0 °C.

Table 3. α-Acyloxylation of 1,3-Diketones and β-Keto Esters.[a]



4/5 **2** **6/7**



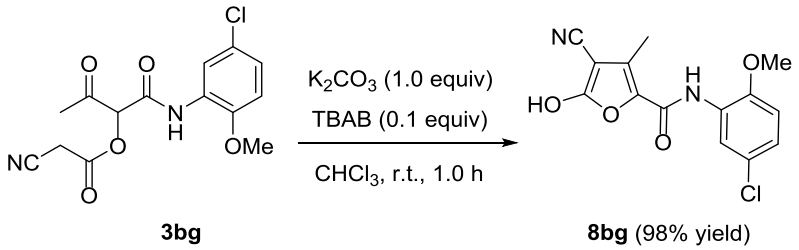
6aa (71%, 120 min) **7aa** (84%, 60 min) **7ha** (83%, 120 min)

7ca (78%, 60 min) **7ka** (80%, 30 min) **7eb** (72%, 60 min)

[a] Reagents and conditions: **4/5** (0.5 mmol), **2** (1.0 mmol), PhIO (1.0 mmol), DCM (10.0 mL), 0 ℃-r.t.

It should be noted that the functionality on the newly synthesized α-acyloxylated products may render them as versatile synthons in further synthetic transformations,[15] for example undergoing an intra- or intermolecular cyclization reaction to construct heterocyclic skeletons under appropriate conditions. Consequently, we selected **3bg** as a model compound and treated it with K_2CO_3 in $CHCl_3$ in the presence of TBAB at room temperature (Scheme 2). The reaction was completed within 1.0 h and furnished a product, which was characterized as *N*-(5-chloro-2-methoxy phenyl)-4-cyano-5-hydroxy-3-methylfuran-2-carbox-amide **8bg** (98% yield) on the basis of its spectral data analysis. Obviously, the obtained results provide an alternative protocol for the synthesis of highly substituted furans of type **8**.

Scheme 2. Synthesis of substituted furan via base-mediated intermolecular cyclization.



With the aim of disclosing mechanistic details of the α-alkoxylation of 1,3-dicarbonyl compounds, a set of reactions were conducted in NMR tubes, and the ^{1}H NMR spectra of the reaction mixtures were recorded at various time intervals. In an initial experiment, PhIO was mixed with of 2-phenyl acetic acid **2a** (1.0 equiv) in $CDCl_3$ at 0 ^oC. In comparison to the spectrum of **2a** (Figure 1a), the spectra of the reaction mixture recorded at different stages (Figure 1b and 1c) revealed that **2a** was consumed within 15 min and an intermediate (**A**) was formed as indicated by the appearance of a new signal at 3.57 ppm. Subsequently, intermediate **A** was isolated from the resulting mixture, and characterized as phenyliodine bis(2-phenylacetate) by means of NMR and Mass spectra. Further to verify the structure of intermediate **A**, we prepared phenyliodine bis(2-phenylacetate) from PIDA and **2a** according to a reported procedure,[16] and found its analytical data (Figure 1d) are in good agreement with that of intermediate **A**.

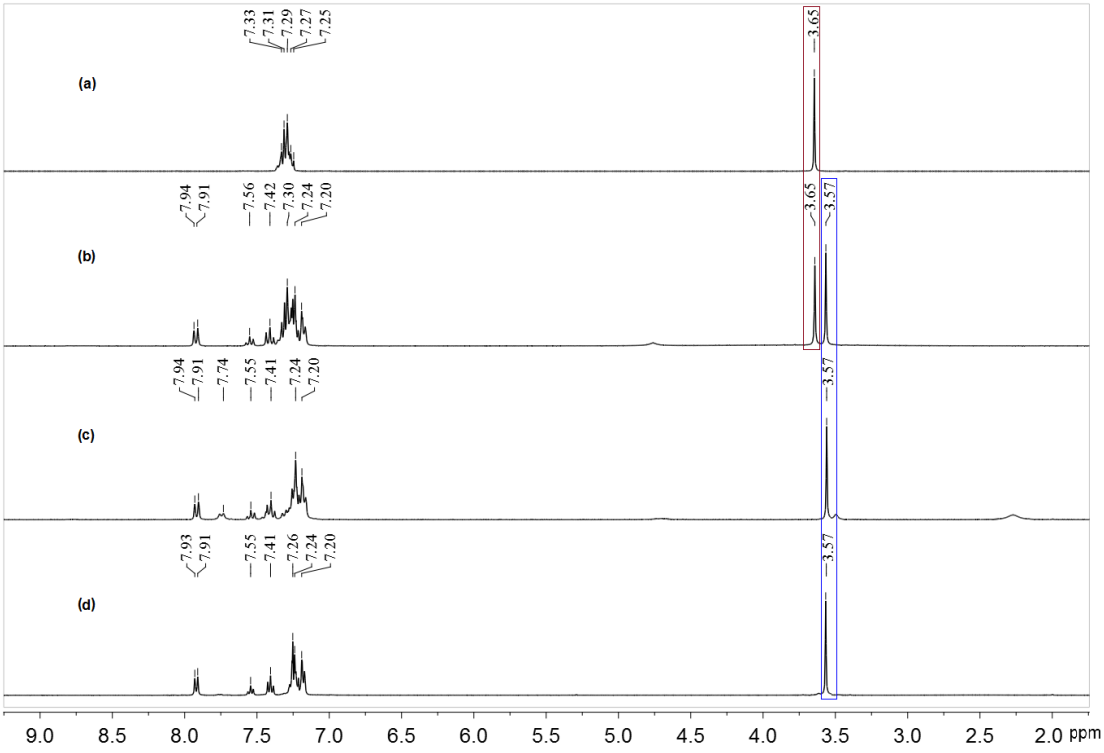


Figure 1. (a)^{1}H-NMR spectrum of **2a**; (b) and (c) ^{1}H-NMR spectra of the mixture of PhIO (1.0 equiv) with **2a** (1.0 equiv) in $CDCl_3$ at 0 ^{o}C recorded at 5 min and 15 min, respectively. (d) ^{1}H-NMR spectrum of phenyliodine bis(2-phenylacetate).

In another experiment, we monitored the reaction of **1a** and **2a** in the presence of PhIO under optimal reaction conditions with NMR spectroscopy. As shown in Figure **2c** and **2d**, the peak at 2.31 ppm assigned to **1a** disappeared rapidly, and several new peaks appeared at 5.62, 3.88 and 2.44 ppm, which was clearly assigned to **3aa** (Figure 2e). Notably, during this conversion, the characteristic singlet peak appeared at 3.57 ppm indicated the formation of intermediate A. As expected, high yield of **3aa** (88%) was achieved in next experiment, in which, **2a** was treated with PhIO (1.0 equiv) in $CDCl_3$ at 0 ^{o}C for 5 min, then to the mixture was added **1a** (0.5 equiv). Undoubtedly, the *in-situ* generated phenyliodine bis(2-phenylacetate) proved to be the key intermediate for the direct α-acyloxylation.[10a,17] In a sharp contrast, a complex mixture was formed by subjecting **1a** (0.5 equiv) and PhIO (1.0 equiv) to $CDCl_3$ at 0 ^{o}C within 10 min as

indicated by NMR and TLC results, and no stable intermediate could be isolated from this mixture. No surprisingly, loading of **2a** (1.0 equiv) to the resulting mixture of **1a** and PhIO did not give the desired product **3aa**, and **2a** was recovered. These results indicated that the loading sequence of the reactants and oxidant was crucial for the generation of proper hypervalent iodine species during the oxidation process.

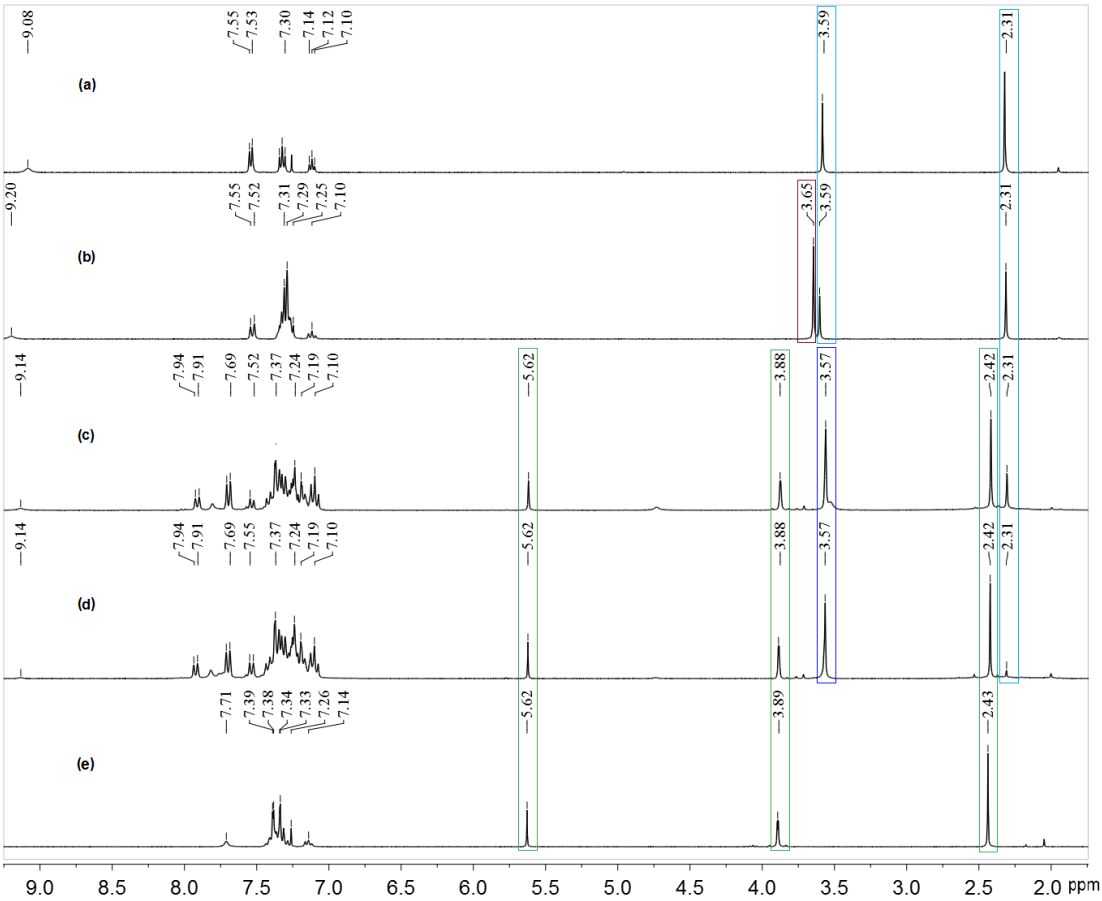
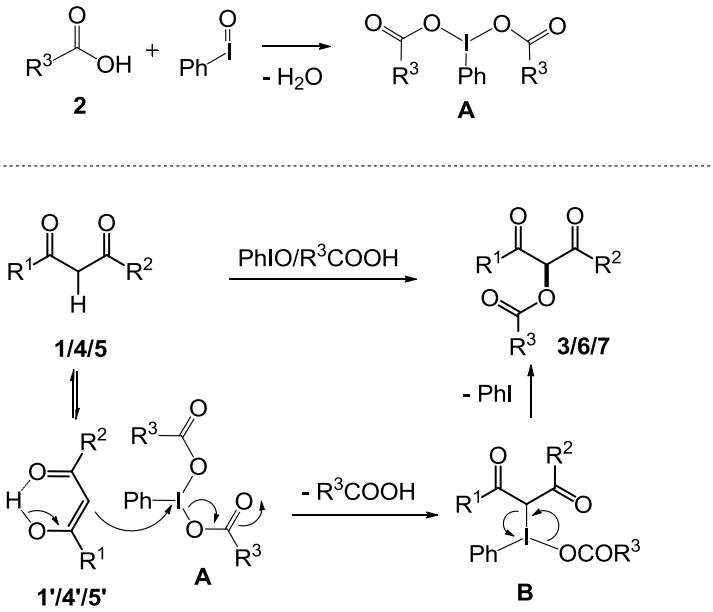


Figure 2. (a) ^{1}H-NMR spectrum of **1a**; (b) ^{1}H-NMR spectra of the mixture of **1a** (0.5 equiv) and **2a** (1.0 equiv) at time zero; (c) and (d) ^{1}H-NMR spectra of the mixture of **1a** (0.5 equiv) and **2a** (1.0 equiv) in $CDCl_3$ at 5 min and 15 min, respectively, after loading of PhIO (1.0 equiv) at 0 ^{o}C; (e) ^{1}H-NMR spectrum of **3aa**.

On the basis of all the obtained results, a mechanism for the α-acyloxylation of 1,3-dicarbonyl compound with carboxylic acid is proposed. As depicted in Scheme 3, the transformation might involve two steps: i) the addition of nucleophile, carboxylic

acid **2**, to idosobenzene to generate tricoordinated iodine species **A**;[10a,b] ii) the electrophilic addition of **A** to the enol tautomer **1'**(or **4'** or **5'**) of 1,3-dicarbonyl compound **1**(or **4** or **5**) to give intermediate **B**,[10a,b,c] which undergoes 1,2-shift of carboxylate from iodine to carbon to afford the corresponding α-acyloxylated product **3** (or **6** or **7**) along with the elimination of iodobenzene.[10a,10b]

Scheme 3. Proposed mechanism for the α-Acyloxylation of 1,3-Dicarbonyl Compounds.



Conclusion

In summary, we have developed a facile and efficient synthesis of α-acyloxyl-1,3-dicarbonyl compounds *via* an intermolecular C-O bond formation of a variety of 1,3-dicarbonyl compounds, including β-oxo amides, β-keto esters and 1,3-diketones, with carboxylic acids mediated by idosobenzene. The mechanism of the direct α-acyloxylation was investigated by means of ^{1}H NMR spectroscopy. The results

reveal that the *in-situ* generated phenyliodine biscarboxylate proved to be the key intermediate in this transformation, and the loading sequence of reactants and oxidant was crucial for the generation of the active species. The mild reaction conditions, wide substrate scope, short reaction time, good yields, high chemoselectivity, excellent functional group tolerance and metal catalyst-free conversion make this protocol much attractive for academic research and practical application.

EXPERIMENTAL SECTION

General Experimental

All reagents were purchased from commercial sources and used without purification, unless otherwise indicated. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ^{o}C at 300 MHz (or 400 MHz) and 100 MHz, respectively, with TMS as internal standard. IR spectra (KBr) were recorded on FTIR-spectrophotometer in the range of 400-4000 cm^{-1}. High resolution mass spectra (ESI-TOF-Q/HRMS) were recorded on a mass spectrometer. Melting points were uncorrected. All reactions were monitored by TLC with GF254 silica gel-coated plates. Chromatography was carried out on silica gel (300−400 mesh).

General procedure for the synthesis of A (3aa as an example):

To a well-stirred solution of *β*-oxo amide **1a** (89 mg, 0.5 mmol) and carboxylic acid **2a** (136 mg, 1.0 mmol) in DCM (10 mL) was added PhIO (220 mg, 1.0 mmol) at 0 ^{o}C. The reaction mixture was kept at 0 ^{o}C under stirring until the completion as indicated by TLC. The resulting mixture was poured into saturated aqueous NaCl (30 mL),

neutralized with saturated aqueous $NaHCO_3$, and extracted with DCM (3 × 20 mL). The combined organic phase was washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) to give **3aa** (138 mg, 89%).

Analytical data of 3

1,3-Dioxo-1-(phenylamino)butan-2-yl 2-phenylacetate (3aa)[11]: According to general procedure for **A**, **3aa** was obtained in 89% yield (138 mg, white solid), Mp 62-64 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 3.83-3.95 (m, 2H), 5.63 (s, 1H), 7.12-7.16 (m, 1H), 7.28-7.43 (m, 9H), 7.71 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.7, 40.8, 79.1, 119.9, 125.1, 127.6, 128.9, 129.0, 129.4, 133.0, 136.3, 160.8, 168.9, 199.1; IR (KBr): ν = 3337, 3066, 1752, 1738, 1691, 1604, 1539, 1448, 1242, 758, cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}NNaO_4$ $[M+Na]^+$: 334.1050, found: 334.1064.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl 2-phenylacetate (3ab): According to general procedure for **A**, **3ab** was obtained in 86% yield (161 mg, white solid), Mp 106-108 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.87 (s, 3H), 3.88 (s, 2H), 5.64 (s, 1H), 6.79 (d, J = 8.7 Hz, 1H), 7.05 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H), 7.29-7.37 (m, 5H), 8.35 (d, J = 2.4 Hz, 1H), 8.66 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.6, 40.8, 56.1, 79.3, 110.9, 119.9, 124. 2, 126.0, 127.1, 127.5, 128.7, 129.2, 132.7, 146.7, 160.7, 169.1, 199.2; IR (KBr): ν = 3336, 3031, 2944, 1745, 1715, 1605, 1545, 1134, 868, 799, cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{18}ClNNaO_5$ $[M+Na]^+$: 398.0766, found: 398.0761.

1-((2-Methoxyphenyl)amino)-1,3-dioxo-3-phenyl propan-2-yl 2-phenylacetate (3ac): According to general procedure for **A**, **3ac** was obtained in 83% yield (167 mg, white solid), Mp 104-106 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 5H), 6.45 (s, 1H), 6.87-6.93 (m, 2H), 7.05-7.10 (m, 1H), 7.30-7.35 (m, 5H), 7.48 (t, J = 7.2 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 8.14 (d, J = 7.5 Hz, 2H), 8.24 (d, J = 8.1 Hz, 1H), 8.70 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.8, 55.8, 76.8, 110.0, 119.9, 120.9, 124.7, 126.3, 127.4, 128.6, 128.7, 129.3, 129.7, 132.7, 134.1, 134.3, 148.2, 161.1, 169.3, 191.3; IR (KBr): v = 3397, 3026, 2942, 1769, 1759, 1687, 1600, 1540, 1257, 757 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_5$ $[M+Na]^+$: 426.1312, found: 426.1315.

1,3-Dioxo-1-(pyridin-2-ylamino)butan-2-yl 2-phenyl acetate (3ad): According to general procedure for **A**, **3ad** was obtained in 76% yield (119 mg, Pale yellow liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.89 (s, 2H), 5.65 (s, 1H), 7.10 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 7.30-7.37 (m, 5H), 7.70-7.74 (m, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 4.0 Hz, 1H), 8.66 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 27.6, 40.5, 79.2, 114.2, 120.6, 127.5, 128.8, 129.3, 132.6, 138.4, 148.1, 150.1, 161.5, 169.4, 198.7; IR (KBr): v = 3323, 3034, 2929, 1729, 1701, 1654, 1440, 1310, 692 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_4$ $[M+H]^+$: 313.1183, found: 313.1187.

1-(Benzylamino)-1,3-dioxobutan-2-yl 2-phenylacetate (3ae): According to general procedure for **A**, **3ae** was obtained in 67% yield (109 mg, white solid), Mp 63-65 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.80 (s, 2H), 4.32-4.44 (m, 2H), 5.56 (s, 1H), 6.36 (bs, 1H), 7.18 (d, J = 6.4 Hz, 2H), 7.23-7.27 (m, 5H), 7.32-7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.8, 40.7, 43.4, 79.0, 127.4, 127.6, 127.7, 128.7, 128.8, 129.2,

132.9, 136.9, 162.9, 169.1, 199.1; IR (KBr): ν = 3308, 3036, 2928, 1738, 1720, 1657, 1555, 735 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_4$ $[M+Na]^+$: 348.1206, found: 348.1208.

1-(Ethyl(phenyl)amino)-1,3-dioxobutan-2-yl 2-phenyl acetate (3af): According to general procedure for **A**, **3af** was obtained in 81% yield (137 mg, white solid), White solid, Mp 59-61 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 1.13 (t, J = 7.2 Hz, 3H), 2.10 (s, 3H), 3.68-3.84 (m, 2H), 3.73 (s, 2H), 5.24 (s, 1H), 7.22-7.40 (dm, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 26.9, 40.6, 44.9, 76.5, 127.3, 128.5, 128.6 (2C), 128.7 (2C), 129.3 (2C), 129.5 (2C), 133.0, 140.4, 163.9, 169.9, 200.4. IR (KBr): ν = 3061, 3037, 1755, 1738, 1689, 1600, 1539, 1248, 757 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_4$ $[M+Na]^+$: 362.1363, found: 362.1368.

1,3-Dioxo-1-(phenylamino)butan-2-yl acetate (3ba)[10d]: According to general procedure for **A**, **3ba** was obtained in 91% yield (105 mg, white solid), white solid, Mp 69-71 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.48 (s, 3H), 5.64 (s, 1H), 7.15-7.20 (t, J = 7.2 Hz, 1H), 7.33-7.38 (t, J = 7.8 Hz, 2H), 7.51-7.53 (d, J = 7.8 Hz, 2H), 8.04 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 28.0, 79.5, 120.5, 125.5, 129.3, 136.6, 161.2, 168.8, 200.2.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl acetate (3bb): According to general procedure for **A**, **3bb** was obtained in 88% yield (132 mg, Pale yellow colored solid), Mp 104-106 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.47 (s, 3H), 3.90 (s, 3H), 5.64 (s, 1H), 6.80 (d, J = 8.7 Hz, 1H), 7.05 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz,

1H), 8.36 (d, *J* = 2.7 Hz, 1H), 8.74 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 27.6, 56.1, 79.1, 110.9, 119.8, 124.2, 126.0, 127.1, 146.7, 160.8, 168.4, 199.3; IR (KBr): ν = 3332, 2946, 1746, 1714, 1546, 1244, 802 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}ClNNaO_5$ $[M+Na]^+$: 322.0453, found: 322.0461.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl cyclopropanecarboxylate (3cb): According to general procedure for **A**, **3cb** was obtained in 74% yield (120 mg, white solid), Mp 66-68 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04-1.09 (m, 2H), 1.18-1.22 (m, 2H), 1.81-1.88 (m, 1H), 2.46 (s, 3H), 3.91 (s, 3H), 5.65 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 7.05 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.38 (d, *J* = 2.4 Hz, 1H), 8.76 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.4, 12.7, 27.7, 56.1, 78.9, 110.9, 119.7, 124.1, 126.1, 127.2, 146.7, 161.0, 172.4, 199.4; IR (KBr): ν = 3342, 3118, 2948, 1736, 1715, 1705, 1604, 1542, 873, 802 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}ClNNaO_5$ $[M+Na]^+$: 348.0609, found: 348.0614.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl benzoate (3db): According to general procedure for **A**, **3db** was obtained in 73% yield (132 mg, white solid), Mp 130-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.56 (s, 3H), 3.93 (s, 3H), 5.88 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.06 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 2H), 8.41 (d, *J* = 2.4 Hz, 1H), 8.99 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.8, 56.1, 79.3, 110.9, 119.6, 124.1, 126.2, 127.2, 128.3, 128.7, 129.9, 134.1, 146.6, 160.9, 164.1, 199.0; IR (KBr): ν = 3416, 2914, 1755, 1732, 1704, 1600, 1536, 822, 712 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{16}ClNNaO_5$ $[M+Na]^+$: 384.0609, found: 384.0615.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl 3-nitrobenzoate (3eb): According to general procedure for **A**, **3eb** was obtained in 77% yield (157 mg, white solid), Mp 129-131 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58 (s, 3H), 3.99 (s, 3H), 5.93 (s, 1H), 6.85 (d, J = 9.0 Hz, 1H), 7.08 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H), 7.77 (t, J = 8.1 Hz, 1H), 8.42 (d, J = 2.4 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.93 (bs, 1H), 8.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.7, 56.3, 80.1, 110.9, 119.6, 124.4, 124.5, 126.1, 127.0, 128.4, 130.1, 135.8, 146.7, 148.3, 160.2, 162.2, 198.4; IR (KBr): v = 3418, 2930, 1753, 1736, 1706, 1597, 1357, 720 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{15}ClN_2NaO_7$ $[M+Na]^+$: 429.0460, found: 429.0463.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl 3-(4-methoxyphenyl)acrylate (3fb): According to general procedure for **A**, **3fb** was obtained in 92% yield (192 mg, white solid), Mp 143-145 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51 (s, 3H), 3.87 (s, 3H), 3.91 (s, 3H), 5.79 (s, 1H), 6.47 (d, J = 12.0 Hz, 1H), 6.81 (d, J = 6.6 Hz, 1H), 6.95 (d, J = 6.6 Hz, 2H), 7.05 (dd, J_1 = 6.6 Hz, J_2 = 2.1 Hz, 1H), 7.54 (d, J = 6.6 Hz, 2H), 7.82 (d, J = 12.0 Hz, 1H), 8.40 (d, J = 1.8 Hz, 1H), 8.84 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.8, 55.4, 56.2, 79.0, 110.9, 113.1, 114.5, 119.8, 124.1, 126.1, 126.5, 127.3, 130.1, 146.7, 147.2, 161.2, 162.0, 164.7, 199.7; IR (KBr): v = 3395, 2946, 1742, 1718, 1689, 1516, 810 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}ClNNaO_6$ $[M+Na]^+$: 440.0871, found: 440.0882.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl propiolate (3gb): According to general procedure for **A**, **3gb** was obtained in 78% yield (121 mg, white solid), Mp 92-93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 3.12 (s, 1H), 3.91 (s,

3H), 5.70 (s, 1H), 6.81 (d, J = 8.8 Hz, 1H), 7.06 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.35 (d, J = 2.8 Hz, 1H), 8.73 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 27.5, 56.2, 73.3, 77.7, 80.0, 111.0, 119.9, 124.4, 126.0, 127.0, 146.9, 149.9, 159.7, 198.0; IR (KBr): v = 3314, 2918, 2130, 1735, 1716, 1704, 1544, 806, cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{12}ClNNaO_5$ $[M+Na]^+$: 332.0296, found: 332.0297.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl 2-bromoacetate (3hb): According to general procedure for **A**, **3hb** was obtained in 91% yield (172 mg, white solid), Mp 101-103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 3H), 3.90 (s, 3H), 4.02-4.13 (m, 2H), 5.69 (s, 1H), 6.81 (d, J = 8.8 Hz, 1H), 7.06 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.37 (d, J = 2.4 Hz, 1H), 8.82 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 7.7, 56.2, 80.0, 111.0, 119.9, 124.4, 126.1, 127.1, 146.8, 160.1, 164.9, 198.4; IR (KBr): v = 3320, 2951, 1757, 1716, 1705, 1604, 1546, 800 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{13}BrClNNaO_5$ $[M+Na]^+$: 399.9558, found: 399.9560.

1-((5-Chloro-2-methoxyphenyl)amino)-1,3-dioxobutan-2-yl 2-cyanoacetate (3ib): According to general procedure for **A**, **3ib** was obtained in 83% yield (135 mg, white solid), Mp 100-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H), 3.65-3.79 (m, 2H), 3.90 (s, 3H), 5.71 (s, 1H), 6.81 (d, J = 8.8 Hz, 1H), 7.07 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.36 (d, J = 2.4 Hz, 1H), 8.81 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 27.4, 56.0, 80.5, 111.0, 112.1, 119.7, 124.5, 125.8, 126.8, 146.9, 159.5, 160.7, 197.8; IR (KBr): v = 3326, 2946, 2277, 1761, 1722, 1704, 1604, 1551, 797 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}ClN_2NaO_5$ $[M+Na]^+$: 347.0405, found: 347.0408.

1-((2-Methoxyphenyl)amino)-1,3-dioxo-3-phenyl propan-2-yl acrylate (3jc): According to general procedure for **A**, **3jc** was obtained in 89% yield (151 mg, white solid), Mp 101-103 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 6.06 (d, J = 10.5 Hz, 1H), 6.34 (dd, J_1 = 17.4 Hz, J_2 = 10.5 Hz, 1H), 6.54 (s, 1H), 6.63 (d, J = 17.1 Hz, 1H), 6.88-6.95 (m, 2H), 7.05-7.10 (m, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 8.20 (d, J = 7.5 Hz, 2H), 8.27 (d, J = 8.1 Hz, 1H), 8.83 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8, 76.4, 110.0, 119.8, 121.0, 124.7, 126.4, 126.8, 128.6, 129.7, 133.1, 134.2, 134.4, 148.1, 161.2, 163.6, 191.2; IR (KBr): ν = 3408, 2946, 1742, 1693, 1602, 1540, 755 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{17}NNaO_5$ $[M+Na]^+$: 362.0999, found: 362.1003.

1,3-Dioxo-1-(pyridin-2-ylamino)butan-2-yl cinnamate (3kd): According to general procedure for **A**, **3kd** was obtained in 82% yield (133 mg, Pale yellow viscous liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 3H), 5.81 (s, 1H), 6.67 (d, J = 16.0 Hz, 1H), 7.11 (dd, J_1 = 6.8 Hz, J_2 = 4.8 Hz, 1H), 7.42-7.44 (m, 3H), 7.58-7.61 (m, 2H), 7.72-7.76 (m, 1H), 7.85 (d, J = 16.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 3.6 Hz, 1H), 8.74 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.7, 79.0, 114.3, 115.5, 120.6, 128.4, 128.9, 131.0, 133.7, 138.4, 147.7, 148.0, 150.2, 162.0, 164.6, 198.9; IR (KBr): ν = 3320, 2930, 1722, 1704, 1638, 1581, 1529, 769 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}N_2O_4$ $[M+H]^+$: 325.1183, found: 325.1190.

General procedure for the synthesis of B (6aa as an example):

To a well-stirred solution of 1,3-diketones **4a** (50 mg, 0.5 mmol) and carboxylic acid **2a**

(136 mg, 1.0 mmol) in DCM (10 mL) was added PhIO (220 mg, 1.0 mmol) at 0 ^{o}C. The reaction mixture was allowed to warm to room temperature under stirring until the reaction completed (monitored by TLC). The resulting mixture was poured into saturated aqueous NaCl (30 mL), neutralized with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9 : 1) to give **6aa** (84 mg, 62%).

2,4-Dioxopentan-3-yl 2-phenylacetate (6aa): According to general procedure for **B**, **6aa** was obtained in 71% yield (83 mg, Colorless liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 6H), 3.82 (s, 2H), 5.47 (s, 1H), 7.31-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.2, 40.7, 85.2, 127.5, 128.7, 129.3, 132.9, 169.9, 198.8; IR (KBr): ν = 3093, 2926, 1757, 1738, 1720, 1608, 712 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}NaO_4$ $[M+Na]^+$: 257.0784, found: 257.0797.

Analytical data of 7

Ethyl 3-oxo-3-phenyl-2-(2-phenylacetoxy)propanoate (7aa): According to general procedure for **B**, **7aa** was obtained in 84% yield (137 mg, Pale yellow liquid); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, 3H, J = 7.2 Hz), 3.81 (s, 2H), 4.24 (q, J = 7.2 Hz, 2H), 6.29 (s, 1H), 7.24-7.33 (m, 5H), 7.44 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.92 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 40.6, 62.4, 74.8, 127.3, 128.6, 128.7, 129.2, 129.3, 132.8, 134.1, 165.0, 170.1, 189.6; IR (KBr): ν = 3067, 2983, 1753,

1700, 1600, 697 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{18}NaO_5$ $[M+Na]^+$: 349.1046, found: 349.1050.

Ethyl 2-(2-bromoacetoxy)-3-oxo-3-phenylpropanoate (7ha): According to general procedure for **B**, **7ha** was obtained in 83% yield (137 mg, Pale yellow liquid); ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, J = 7.2 Hz, 3H), 3.97-4.04 (m, 2H), 4.26 (q, J = 7.2 Hz, 2H), 6.34 (s, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.99-8.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 24.7, 62.7, 75.4, 128.8, 129.2, 133.9, 134.4, 164.4, 166.0, 188.7; IR (KBr): ν = 3065, 2944, 1757, 1700, 1602, 1453, 691 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{13}BrNaO_5$ $[M+Na]^+$: 350.9839, found: 350.9840.

1-Ethoxy-1,3-dioxo-3-phenylpropan-2-yl cyclopropane carboxylate (7ca): According to general procedure for **B**, **7ca** was obtained in 78% yield (107 mg, Pale yellow liquid); ^1H NMR (400 MHz, $CDCl_3$): δ 0.95-0.99 (m, 2H), 1.08-1.12 (m, 2H), 1.22 (t, J = 7.2 Hz, 3H), 1.78-1.84 (m, 1H), 4.27 (q, J = 7.2 Hz, 2H), 6.33 (s, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.2, 12.6, 13.8, 62.3, 74.3, 128.7, 129.1, 134.1, 134.2, 165.2, 173.4, 189.8; IR (KBr): ν = 3069, 2942, 1744, 1702, 1600, 1453, 693 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}NaO_5$ $[M+Na]^+$: 299.0890, found: 299.0900.

1-Ethoxy-1,37eb-dioxo-3-phenylpropan-2-yl cinnamate (7ka): According to general procedure for **B**, **7ka** was obtained in 80% yield (135 mg, Viscous and pale yellow liquid); ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (t, J = 7.2 Hz, 3H), 4.28 (q, J = 7.2 Hz, 2H), 6.47 (s, 1H), 6.58 (d, J = 16.2 Hz, 1H), 7.39-7.41 (m, 3H), 7.49-7.55 (m, 4H), 7.64 (t, J

= 7.5 Hz, 1H), 7.80 (d, *J* = 16.2 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 62.4, 74.4, 116.1, 128.3, 128.7, 128.9, 129.2, 130.8, 133.9, 134.2, 134.2, 147.2, 165.3, 165.3, 189.8; IR (KBr): v = 3067, 2942, 1765, 1769, 1702, 1636, 1602, 771, cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}NaO_5$ $[M+Na]^+$: 361.1046, found: 361.1045.

1-Ethoxy-1,3-dioxobutan-2-yl 3-nitrobenzoate (7eb): According to general procedure for **B**, **7eb** was obtained in 72% yield (106 mg, Pale yellow liquid); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, *J* = 7.2 Hz, 3H), 2.46 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 5.79 (s, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 8.45-8.50 (m, 2H), 8.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 27.3, 62.8, 78.5, 125.0, 128.2, 129.9, 130.3, 135.6, 148.3, 163.1, 163.9, 196.4; IR (KBr): v = 3095, 2932, 1736, 1622, 1540, 720 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{13}NNaO_7$ $[M+Na]^+$: 318.0584, found: 318.0591.

Synthesis of compound 8bg: To a solution of **3bg** (650 mg, 2.0 mmol) in DCM (25 mL) was added K_2CO_3 (552 mg, 4.0 mmol) and TBAB (65 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 1.0 h, and then to the mixture was added 25 mL of aqueous HCl (0.1 N). The precipitated solid was collected by filtration, washed with water (3 × 25 mL), and dried in *vacuo* to afford the product **8bg** as a white solid (634 mg, 98%).

4-Cyano-5-hydroxy-3-methyl-*N*-phenylfuran-2-carboxamide (8bg): white solid, Mp 216-219 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H), 3.90 (s, 3H), 6.97-7.08 (m, 2H), 8.14 (s, 1H), 8.40 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 56.7, 112.2 (2C), 117.9, 119.7, 121.8, 124.1, 124.8, 129.8, 134.7, 146.6, 156.4, 167.8; IR (KBr): v =

3401, 2935, 2241, 1766, 1674, 1600, 796 cm^{-1}; HRMS (ESI-TOF-Q) calcd for M = $C_{14}H1_2ClN_2O_4$, $[M+H]^+$ 307.0480 found 307.0484.

Phenyliodine bis(2-phenylacetate) (A): White solid, Mp 56-58 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 4H), 7.17-7.19 (m, 4H), 7.22-7.25 (m, 6H), 7.41 (t, 2H, J = 7.6 Hz), 7.54 (t, J = 7.2 Hz, 1H,), 7.91-7.93 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.0 (2C), 122.0, 126.8 (2C), 128.4 (4C), 129.1 (4C), 130.8 (2C), 131.6, 134.5 (2C), 134.7 (2C), 176.1 (2C); IR (KBr): ν = 3061, 1650, 1450, 1276, 996, 734 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}INaO_4$ $[M+Na]^+$: 497.0220, found: 497.0226.

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Associated Content

Supporting Information

The supporting Information is available free of charge on the ACS Publication website at DOI:10.1021/acs.joc.XXXXXXXX. ^{1}H and ^{13}C NMR spectra of products **3, 6-8** (PDF).

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