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N-Heterocyclic carbene-catalyzed hydroacylation of isatins with aldehydes: access to 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones

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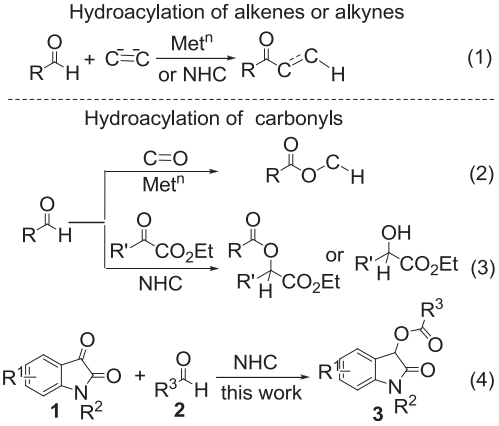
ABSTRACT

The *N*-heterocyclic carbene-catalyzed hydroacylation of isatins with aldehydes has been described. This process offers a highly efficient and atom-ecomonical access to 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones in good to excellent yields.

1. Introduction

The transition-metal-catalyzed hydroacylation of alkenes and alkynes using aldehydes as acyl donors have attracted considerable attention due to their atom-economy and broad applications in the preparation of various carbonyl compounds (Eq. 1, Scheme 1).[1] In recent years, *N*-heterocyclic carbenes (NHCs) have also been successfully applied as efficient organocatalysts in the hydroacylation of activated and even unactivated alkenes and alkynes, which serve as acceptors for carbonyl anions generated from aldehydes via an NHC-mediated *umpolung* process (Eq. 1, Scheme 1).[2] Notwithstanding, analogous hydroacylation processes involving aldehydes and carbonyl groups are much less explored, with some limited reactions developed in the presence of transition-metal catalysts (Eq. 2, Scheme 1).[3] The NHC-catalyzed direct hydroacylation of carbonyl compounds with aldehydes was only reported by Scheidt[4] and further improved by Pal[5] using activated ketones as substrates (Eq. 3, Scheme 1).[6] In this process, differing from the mechanism of NHC-catalyzed hydroacylation of C–C double or triple bonds, the carbene facilitated selective catalytic oxidation of an aldehydic C–H bond with concomitant reduction of a ketone, affording a hydroacylation product or a carbonyl reduction product depending on the nature of solvent used.[4,5] Thus, continual efforts focused on the discovery of novel and versatile methods for the hydroacylation of carbonyl systems are highly desirable in the pursuit of efficient, environmental benign and atom-economical chemical transformations.



Scheme 1. Hydroacylation of alkenes, alkynes and carbonyl compounds.

Functionalized indoles and indol-2-ones are widely present in a large number of natural products and synthetic compounds with diverse bioactivities.[7] As one of the subtypes, despite possessing interesting biological activities,[8] only a few 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones **3** are known, and few approaches toward **3** have

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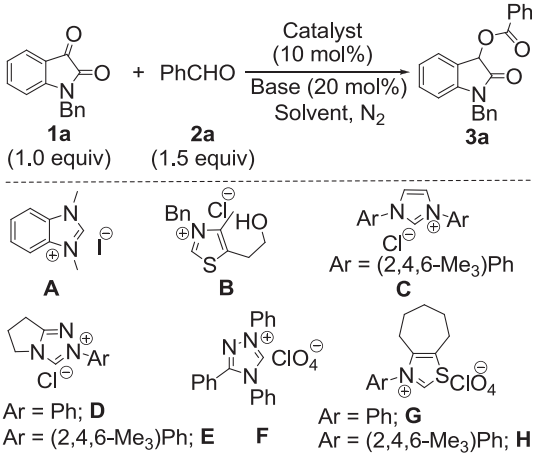
been documented (Eq. 4, Scheme 1). Some commonly synthetic methods are the acylation of isatins with carboxylic acid anhydrides or acyl chlorides,[8,9] as well as certain reactions utilizing several non-isatins as starting materials under various conditions.[10] Nevertheless, the above-mentioned strategies always suffered from one or more drawbacks, such as drastic reaction conditions, unsatisfactory yields, narrow scope of substrates and excessive use of toxic materials and reagents. As part of our ongoing program to explore efficient and environmentally benign methodologies for chemical transformations using NHCs as organocatalysts,[11] we envision that 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones **3** may be directly synthesized by NHC-catalyzed hydroacylation of isatins **1**[12] with aldehydes **2**. Herein we report this new type of hydroacylation of isatins mediated by NHC (Eq. 4, Scheme 1). This method is superior to conventional strategies with its advantages of atom-economy, short reaction time, broad range of substrates and high yields.

2. Results and discussion

Our investigations commenced with the model reaction of isatin **1a** (1.0 equiv) and benzaldehyde **2a** (1.5 equiv) in the presence of 10 mol% of a carbene precursor using 20 mol% of a base (Table 1). Initially, the efficiency of several carbene precursors was examined (entries 1 and 2). Fortunately, in contrast to other NHCs which resulted in low conversion of the substrates (entry 1), NHC generated in situ from precursor **E** proved suitable for this transformation, affording 66% yield of desired product **3a** after 15 min at 65 °C (entry 2). It was noteworthy that the undesirable benzoin condensation of **2a** was not observed in this process. A survey of the solvents (entries 3–6) convinced us that toluene was the optimal one with

Table 1
Optimization of the reaction conditions



Entry	Catalyst, base, solvent	Temp (°C)	Time (min)	Yield[a] (%)
1	**A**–**D**, **F**–**H**, DBU, THF	65	120	—[b]
2	**E**, DBU, THF	65	15	66
3	**E**, DBU, DCM	40	15	69
4	**E**, DBU, CH_3CN	65	60	Trace[b]
5	**E**, DBU, EtOH	65	60	—[b]
6	**E**, DBU, PhMe	65	15	83
7	**E**, Et_3N, PhMe	65	120	35
8	**E**, DIPEA, PhMe	65	120	30
9	**E**, K_2CO_3, PhMe	65	120	39
10	**E**, C_2CO_3, PhMe	65	120	40
11	**E**, *t*-BuOK, PhMe	65	15	87
12	**E**, ***t*-BuOK**, **PhMe**	**100**	**15**	**93**

The bold values provided in entry 12 is to emphasize that this reaction condition is the optimal one.

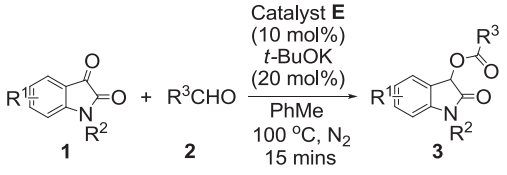
[a] Isolated yield based on **1a**.

[b] Low conversion of both **1a** and **2a**. DBU=1,8-diazabicyclo[5.4.0]-undec-7-ene. DIPEA=*N*,*N*-diisopropylethyiamine.

83% yield of **3a** for 15 min at 65 °C (entry 6). Remarkably, the reaction carried out in EtOH gave no carbonyl reduction product, which was observed employing α-keto esters rather than isatins as the substrates (entry 5).[4,5] Further screening of a series of bases, reaction temperature and time (entries 7–12) established the optimal reaction conditions: 10 mol% of catalyst **E** and 20 mol% of *t*-BuOK in toluene at 100 °C for 15 min with 93% yield of **3a** (entry 12).

With the optimized conditions in hand, we turned our attention to explore the scope of the reaction (Table 2). We found that the reaction can accommodate a variety of substituted benzaldehdyes **2b**–**m** (entries 2–13). The electronic property and the position of the substituents on the phenyl ring of the aldehydes have certain influence on the yields and reaction time. Except 4-nitrobenzaldehyde **2g**, which led to low conversion of the reaction (entry 7), substituted benzaldehydes with both electron-withdrawing groups (F, Cl, Br, I, and CN) and electron-donating groups (Me and OMe) at 3- or 4-positions worked very well to afford desired 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones **3b**–**j** in good to excellent yields after 15 min (entries 2–6 and 8–11). However, the reaction between isatin **1a** and benzaldehydes substituted with

Table 2
Scope of the reaction[a]



Entry	R^1, R^2, **1**	R^3, **2**	**3**	Yield[b] (%)
1	H, Bn, **a**	Ph, **a**	**a**	93
2	H, Bn, **a**	(4-F)Ph, **b**	**b**	91
3	H, Bn, **a**	(4-Cl)Ph, **c**	**c**	86
4	H, Bn, **a**	(4-Br)Ph, **d**	**d**	83
5	H, Bn, **a**	(4-I)Ph, **e**	**e**	81
6	H, Bn, **a**	(4-CN)Ph, **f**	**f**	75
7	H, Bn, **a**	(4-NO_2)Ph, **g**	—	—[c,d]
8	H, Bn, **a**	(4-Me)Ph, **h**	**g**	92
9	H, Bn, **a**	(4-OMe)Ph, **i**	**h**	90
10	H, Bn, **a**	(3-Cl)Ph, **j**	**i**	95
11	H, Bn, **a**	(3-OMe)Ph, **k**	**j**	91
12	H, Bn, **a**	(2-F)Ph, **l**	**k**	79[e]
13	H, Bn, **a**	(2-Cl)Ph, **m**	**l**	26[d]
14	H, Bn, **a**		**m**	92
15	H, Bn, **a**		**n**	81
16	H, Bn, **a**		**o**	99
17	H, Bn, **a**		**p**	69
18	H, Bn, **a**	*n*-Pr, **r**	**q**	57
19	5-Me, Bn, **b**	Ph, **a**	**r**	85
20	5-F, Bn, **c**	Ph, **a**	**s**	90
21	5-Cl, Bn, **d**	Ph, **a**	**t**	77
22	7-Me, Bn, **e**	Ph, **a**	**u**	91
23	7-Cl, Bn, **f**	Ph, **a**	**v**	85
24	4,6-Me_2, Bn, **g**	Ph, **a**	—	—[c,d]
25	H, Bz, **h**	Ph, **a**	—	—[d,f]
26	H, H, **i**	Ph, **a**	**w**	80

[a] Isatins **1** (0.3 mmol), aldehydes **2** (0.45 mmol), catalyst **E** (0.03 mmol), and *t*-BuOK (0.06 mmol) were employed.

[b] Isolated yield based on **1**.

[c] Low conversion of **1** and **2**.

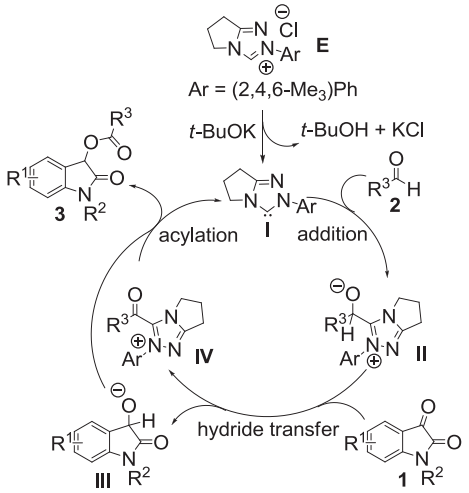
[d] The reaction time was 120 min.

[e] The reaction time was 30 min.

[f] The reaction was complex.

sterically hindered groups (2-F and 2-Cl) needed relatively longer reaction time (entry 12) or went sluggishly with significantly decreased yield (entry 13). The reaction proceeded equally well for 1-naphthaldehyde **2n** and heteroaromatic aldehydes **2o** and **2p** with short reaction time and high yields (entries 14–16). To our great delight, aliphatic aldehydes **2q** and **2r** also demonstrated good tolerance with this process (entry 17 and 18). Next, isatins with different substituents were tested for the generality of this reaction (entries 19–26). Isatins **1b**–**f** with substituents at 5- or 7-positions reacted with **2a** smoothly to give the corresponding products in high yields after 15 min (entries 19–23), while the conversion of the reaction between 4,6-dimethyl isatin **1g** and **2a** was low (entry 24). Isatins with different *N*-substituents (Bz, H) were also studied. *N*-Benzoyl isatin **1h** failed to produce the desired product due to the complexity of the reaction (entry 25), whereas *N*-unsubstituted isatin **1i** worked well to give **3w** in 80% yield (entry 26).

Based on the mechanism proposed by Scheidt[4] and Pal,[5] a plausible mechanism for the hydroacylation of isatins **1** with aldehydes **2** in the presence of carbene precursor **E** is illustrated in Scheme 2. The hydroacylation process initiates with the addition of NHC **I** generated upon deprotonation of carbene precursor **E** with *t*-BuOK to aldehydes **2**, affording the tetrahedral intermediate **II**. A rapid hydride transfer from **II** to isatins **1** (like Cannizzaro-type reaction) leads to the formation of acyl triazolium activated species **IV** and intermediate **III**. After subsequent *O*-acylation of **III** with **IV**, products **3** are produced accompanied with the release of NHC **I** for the next catalytic cycle (Scheme 2).



Scheme 2. Proposed mechanism for NHC-catalyzed hydroacylation of isatins.

3. Conclusion

In conclusion, we have developed a transition-metal-free NHC-organocatalyzed intermolecular hydroacylation of isatins with aldehydes, which offers a powerful strategy for the synthesis of useful 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones. In this atom-economical process, functionalized isatins are effective substrates in combination with a broad range of aromatic and aliphatic aldehydes, furnishing the desired products in high yields with short reaction time.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of nitrogen in dry glassware, and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. All aldehydes **2** were obtained from commercial sources without further purification. Substituted isatins **1**[13] and NHC precursors were prepared according to literature method.[14] Purification of the products was accomplished by flash chromatography using silica gel (200–300 mesh).

All NMR spectra were recorded with a spectrometer at 300 MHz or 500 MHz (^{1}H NMR) in $CDCl_3$: chemical shifts (δ) are given in parts per million, coupling constants (J) in Hz, the solvent signals were used as references (residual $CHCl_3$ in $CDCl_3$: δ_H=7.26 ppm, δ_C=77.0 ppm). High-resolution mass spectra were recorded on a Waters/Micromass QTOF MS spectrometer. IR spectra were recorded on an FTIR-8400s spectrometer. Melting points were obtained on a Yanaco-241 apparatus and are uncorrected.

4.2. General procedure for NHC-catalyzed hydroacylation of isatins with aldehydes

To an oven-dried 25 mL three-necked glassware was charged with catalyst **E** (8 mg, 0.03 mmol), *t*-BuOK (7 mg, 0.06 mmol), isatins **1** (0.3 mmol), and aldehydes **2** (0.45 mmol) under nitrogen atmosphere. Then toluene (2 mL) was added and the mixture was stirred at 100 °C for a certain period. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (typically petroleum ether/ethyl acetate=20:1 to 10:1) to afford the desired products **3**.

*4.2.1. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl benzoate (**3a**).* White solid, mp: 121–123 °C (lit.[10f] mp: 124–125 °C). ^{1}H NMR (500 M, $CDCl_3$): δ 4.93 and 5.00 (2×d, J=15.7 Hz, 2H), 6.27 (s, 1H), 6.75 (d, J=7.9 Hz, 1H), 7.02 (t, J=7.6 Hz, 1H), 7.23 (d, J=7.8 Hz, 1H), 7.27–7.47 (m, 8H), 7.59 (t, J=7.4 Hz, 1H), 8.12 (d, J=7.3 Hz, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.0, 70.4, 109.6, 123.1, 124.4, 125.6, 127.3, 127.7, 128.4, 128.8, 129.0, 130.1, 130.2, 133.5, 135.3, 143.7, 165.8, 172.3.

*4.2.2. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 4-fluorobenzoate (**3b**).* White solid, mp: 91–93 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.92 and 4.99 (2×d, J=15.7 Hz, 2H), 6.26 (s, 1H), 6.75 (d, J=7.9 Hz, 1H), 7.03 (t, J=7.6 Hz, 1H), 7.13 (t, J=8.6 Hz, 2H), 7.24 (d, J=7.8 Hz, 1H), 7.27–7.42 (m, 6H), 8.13–8.16 (m, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.1, 70.5, 109.6, 115.6 (d, J_{C-F}=22.0 Hz, 1C), 123.1, 124.3, 125.3 (d, J_{C-F}=2.8 Hz, 1C), 125.6, 127.3, 127.8, 128.8, 130.3, 132.8 (d, J_{C-F}=9.4 Hz, 1C), 135.3, 143.7, 164.9, 166.1 (d, J_{C-F}=255.0 Hz, 1C), 172.2. HRMS (EI) calcd for $C_{22}H_{16}NO_3F$ $(M+H)^+$: 362.1192, found 362.1196. IR (KBr): ν 758, 849, 1121, 1152, 1177, 1269, 1373, 1462, 1495, 1604, 1722, 3040, 3063 cm^{-1}.

*4.2.3. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 4-chlorobenzoate (**3c**).* White solid, mp: 120–121 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.93 and 4.99 (2×d, J=15.7 Hz, 2H), 6.25 (s, 1H), 6.75 (d, J=7.9 Hz, 1H), 7.03 (t, J=7.5 Hz, 1H), 7.24 (d, J=7.8 Hz, 1H), 7.28–7.44 (m, 8H), 8.05 (d, J=8.6 Hz, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.1, 70.5, 109.6, 123.1, 124.2, 125.6, 127.3, 127.5, 127.8, 128.80, 128.84, 130.3, 131.5, 135.2, 140.1, 143.7, 165.0, 172.1. HRMS (EI) calcd for $C_{22}H_{16}NO_3Cl$ $(M+H)^+$: 378.0897, found 378.0901. IR (KBr): ν 748, 843, 993, 1013, 1090, 1117, 1177, 1271, 1350, 1375, 1462, 1489, 1593, 1611, 1730, 2867, 2922, 2945, 3032, 3063 cm^{-1}.

*4.2.4. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 4-bromobenzoate (**3d**).* White solid, mp: 142–144 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.92 and 4.98 (2×d, J=15.7 Hz, 2H), 6.24 (s, 1H), 6.74 (d, J=7.9 Hz,

1H), 7.02 (t, *J*=7.5 Hz, 1H), 7.23 (d, *J*=7.8 Hz, 1H), 7.27–7.41 (m, 6H), 7.59 (d, *J*=8.5 Hz, 2H), 7.97 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.0, 70.5, 109.6, 123.1, 124.1, 125.6, 127.3, 127.7, 127.9, 128.7, 128.8, 130.3, 131.5, 131.8, 135.2, 143.6, 165.0, 172.0. HRMS (EI) calcd for $C_{22}H_{16}NO_3Br$ $(M+H)^+$: 422.0392, found 422.0374. IR (KBr): ν 750, 843, 918, 997, 1011, 1069, 1084, 1103, 1123, 1170, 1263, 1323, 1361, 1464, 1491, 1591, 1616, 1719, 1732, 2926, 2951, 3038, 3065 cm^{-1}.

*4.2.5. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 4-iodobenzoate (**3e**).* White solid, mp: 158–160 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.93 and 4.99 (2×d, *J*=15.7 Hz, 2H), 6.25 (s, 1H), 6.75 (d, *J*=7.9 Hz, 1H), 7.03 (t, *J*=7.3 Hz, 1H), 7.24 (d, *J*=7.8 Hz, 1H), 7.28–7.41 (m, 6H), 7.82 (s, 4H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.1, 70.5, 101.6, 109.6, 123.1, 124.1, 125.6, 127.3, 127.7, 128.5, 128.8, 130.3, 131.5, 135.2, 137.8, 143.7, 165.4, 172.1. HRMS (EI) calcd for $C_{22}H_{16}NO_3I$ $(M+H)^+$: 470.0253, found 470.0239. IR (KBr): ν 748, 843, 1007, 1084, 1101, 1121, 1170, 1263, 1464, 1491, 1586, 1614, 1721, 1728, 2924, 2950, 3064, 3082 cm^{-1}.

*4.2.6. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 4-cyanobenzoate (**3f**).* White solid, mp: 128–130 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.93 and 4.97 (2×d, *J*=15.7 Hz, 2H), 6.26 (s, 1H), 6.76 (d, *J*=7.9 Hz, 1H), 7.02 (t, *J*=7.3 Hz, 1H), 7.23–7.40 (m, 7H), 7.73 (d, *J*=8.5 Hz, 2H), 8.19 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.0, 70.9, 109.7, 116.9, 117.7, 123.1, 123.7, 125.5, 127.3, 127.8, 128.8, 130.45, 130.48, 132.2, 132.7, 135.1, 143.7, 164.2, 171.6. HRMS (EI) calcd for $C_{23}H_{16}N_2O_3$ $(M+H)^+$: 369.1239, found 369.1248. IR (KBr): ν 756, 804, 847, 862, 991, 1016, 1116, 1179, 1273, 1352, 1377, 1464, 1491, 1613, 1726, 2232, 2928, 3071 cm^{-1}.

*4.2.7. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 4-methylbenzoate (**3g**).* White solid, mp: 106–107 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 2.42 (s, 3H), 4.93 and 5.00 (2×d, *J*=15.7 Hz, 2H), 6.26 (s, 1H), 6.74 (d, *J*=7.9 Hz, 1H), 7.02 (td, *J*=0.7, 7.6 Hz, 1H), 7.22–7.39 (m, 8H), 7.42 (d, *J*=7.4 Hz, 1H), 8.01 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 21.7, 44.0, 70.3, 109.5, 123.0, 124.6, 125.6, 126.3, 127.3, 127.7, 128.8, 129.1, 130.1, 130.2, 135.3, 143.7, 144.3, 165.9, 172.4. HRMS (EI) calcd for $C_{23}H_{19}NO_3$ $(M+H)^+$: 358.1443, found 358.1440. IR (KBr): ν 746, 999, 1063, 1080, 1119, 1179, 1273, 1356, 1370, 1466, 1491, 1613, 1730, 2918, 2949, 3036, 3055 cm^{-1}.

*4.2.8. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 4-methoxybenzoate (**3h**).* White solid, mp: 104–106 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 3.87 (s, 3H), 4.93 and 5.00 (2×d, *J*=15.7 Hz, 2H), 6.24 (s, 1H), 6.74 (d, *J*=7.9 Hz, 1H), 6.93 (d, *J*=8.9 Hz, 2H), 7.02 (t, *J*=7.5 Hz, 1H), 7.23 (t, *J*=7.8 Hz, 1H), 7.27–7.43 (m, 6H), 8.07 (d, *J*=8.9 Hz, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.0, 55.4, 70.2, 109.5, 113.7, 121.4, 123.0, 124.7, 125.6, 127.3, 127.7, 128.8, 130.1, 132.3, 135.4, 143.6, 163.9, 165.5, 172.5. HRMS (EI) calcd for $C_{23}H_{19}NO_4$ $(M+H)^+$: 374.1392, found 374.1399. IR (KBr): ν 745, 766, 847, 1022, 1119, 1169, 1258, 1316, 1341, 1371, 1466, 1491, 1510, 1603, 1726, 2843, 2936, 3001, 3022, 3055 cm^{-1}.

*4.2.9. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 3-chlorobenzoate (**3i**).* White solid, mp: 51–53 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.93 and 4.99 (2×d, *J*=15.7 Hz, 2H), 6.26 (s, 1H), 6.75 (d, *J*=7.9 Hz, 1H), 7.03 (t, *J*=7.5 Hz, 1H), 7.23–7.41 (m, 8H), 7.56 (ddd, *J*=0.9, 2.0, 8.0 Hz, 1H), 8.0 (d, *J*=7.8 Hz, 1H), 8.09 (t, *J*=1.7 Hz, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.1, 70.7, 109.7, 123.2, 124.1, 125.6, 127.4, 127.8, 128.3, 128.9, 129.8, 130.2, 130.4, 130.8, 133.6, 134.7, 135.2, 143.7, 164.7, 172.0. HRMS (EI) calcd for $C_{22}H_{16}NO_3Cl$ $(M+H)^+$: 378.0897, found 378.0892. IR (KBr): ν 748, 810, 995, 1078, 1125, 1175, 1252, 1281, 1364, 1427, 1468, 1491, 1576, 1614, 1728, 2924, 3032, 3064 cm^{-1}.

*4.2.10. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 3-methoxybenzoate (**3j**).* White solid, mp: 112–114 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 3.83 (s, 3H), 4.91 and 4.99 (2×d, *J*=15.7 Hz, 2H), 6.24 (s, 1H), 6.74 (d, *J*=7.9 Hz, 1H), 7.01 (t, *J*=7.5 Hz, 1H), 7.12 (dd, *J*=2.1, 8.2 Hz, 1H), 7.22 (t, *J*=8.1 Hz, 1H), 7.26–7.41 (m, 7H), 7.62 (s, 1H),7.71 (d, *J*=7.6 Hz, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.0, 55.4, 70.5, 109.5, 114.4, 120.2, 122.6, 123.0, 124.4, 125.5, 127.3, 127.7, 128.8, 129.4, 130.2, 130.3, 135.3, 143.7, 159.6, 165.7, 172.2. HRMS (EI) calcd for $C_{23}H_{19}NO_4$ $(M+H)^+$: 374.1392, found 374.1381. IR (KBr): ν 748, 804, 849, 872, 905, 997, 1030, 1121, 1179, 1227, 1283, 1323, 1348, 1377, 1429, 1462, 1489, 1609, 1726, 2870, 2922, 2955, 3030, 3067 cm^{-1}.

*4.2.11. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 2-fluorobenzoate (**3k**).* White solid, mp: 118–120 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.90 and 4.97 (2×d, *J*=15.7 Hz, 2H), 6.24 (s, 1H), 6.73 (d, *J*=7.9 Hz, 1H), 7.01 (t, *J*=7.5 Hz, 1H), 7.11–7.36 (m, 8H), 7.43 (d, *J*=7.4 Hz, 1H), 7.52 (m, 1H), 8.0 (td, *J*=1.5, 7.7 Hz, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 43.9, 70.4, 109.4, 116.9 (d, J_{C-F}=22.0 Hz, 1C), 117.4 (d, J_{C-F}=9.3 Hz, 1C), 123.0, 123.9 (d, J_{C-F}=3.8 Hz, 1C), 124.1, 125.4, 127.2, 127.6, 128.7, 130.1, 132.3, 135.0 (d, J_{C-F}=9.1 Hz, 1C), 135.1, 143.6, 162.1 (d, J_{C-F}=261.7 Hz, 1C), 163.2 (d, J_{C-F}=3.8 Hz, 1C), 171.9. HRMS (EI) calcd for $C_{22}H_{16}NO_3F$ $(M+H)^+$: 362.1192, found 362.1190. IR (KBr): ν 756, 829, 851, 997, 1034, 1059, 1130, 1179, 1225, 1261, 1341, 1371, 1464, 1491, 1613, 1730, 2922, 2945, 3040, 3074 cm^{-1}.

*4.2.12. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 2-chlorobenzoate (**3l**).* White solid, mp: 94–96 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.92 and 4.97 (2×d, *J*=15.7 Hz, 2H), 6.29 (s, 1H), 6.74 (d, *J*=7.9 Hz, 1H), 7.03 (t, *J*=7.5 Hz, 1H), 7.22–7.36 (m, 7H), 7.42–7.48 (m, 3H), 7.95 (dd, *J*=1.3, 7.8 Hz, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.1, 70.6, 109.6, 123.2, 124.1, 125.8, 126.6, 127.3, 127.8, 128.77, 128.84, 130.3, 131.2, 132.0, 133.1, 134.3, 135.2, 143.7, 164.7, 172.0. HRMS (EI) calcd for $C_{22}H_{16}NO_3Cl$ $(M+H)^+$: 378.0897, found 378.0883. IR (KBr): ν 750, 849, 993, 1032, 1125, 1177, 1250, 1288, 1339, 1362, 1464, 1489, 1611, 1726, 2922, 3024, 3063 cm^{-1}.

*4.2.13. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl 1-naphthoate (**3m**).* White solid, mp: 142–144 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.92 and 4.98 (2×d, *J*=15.7 Hz, 2H), 6.37 (s, 1H), 6.73 (d, *J*=7.9 Hz, 1H), 7.02 (t, *J*=7.5 Hz, 1H), 7.21 (t, *J*=7.8 Hz, 1H), 7.26 (t, *J*=7.1 Hz, 1H), 7.32 (t, *J*=7.5 Hz, 2H), 7.37 (d, *J*=7.5 Hz, 2H), 7.45–7.53 (m, 3H), 7.61 (t, *J*=7.7 Hz, 1H), 7.85 (d, *J*=8.1 Hz, 1H), 8.01 (d, *J*=8.2 Hz, 1H), 8.31 (d, *J*=7.3 Hz, 1H), 8.99 (d, *J*=8.7 Hz, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.0, 70.4, 109.5, 123.1, 124.4, 124.5, 125.6, 125.7, 126.3, 127.3, 127.7, 128.0, 128.5, 128.8, 130.2, 131.1, 131.4, 133.8, 134.1, 135.3, 143.7, 166.5, 172.4. HRMS (EI) calcd for $C_{26}H_{19}NO_3$ $(M+H)^+$: 394.1443, found 394.1427. IR (KBr): ν 746, 997, 1020, 1117, 1179, 1213, 1273, 1371, 1464, 1491, 1610, 1728, 2920, 2949, 3036, 3055 cm^{-1}.

*4.2.14. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl furan-2-carboxylate (**3n**).* Yellowish oil. ^{1}H NMR (500 M, $CDCl_3$): δ 4.88 and 4.95 (2×d, *J*=15.7 Hz, 2H), 6.22 (s, 1H), 6.50 (dd, *J*=1.7, 3.5 Hz, 1H), 6.72 (d, *J*=7.9 Hz, 1H), 6.99 (td, *J*=0.8, 7.6 Hz, 1H), 7.19–7.36 (m, 7H), 7.39 (d, *J*=7.4 Hz, 1H), 7.58 (dd, *J*=0.8, 1.7 Hz, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 43.9, 70.0, 109.5, 112.0, 119.4, 123.0, 123.9, 125.5, 127.2, 127.6, 128.7, 130.2, 135.1, 143.4, 143.6, 147.0, 157.6, 171.8. HRMS (EI) calcd for $C_{20}H_{15}NO_4$ $(M+H)^+$: 334.1079, found 334.1082. IR (film): ν 731, 754, 885, 910, 993, 1014, 1080, 1117, 1175, 1368, 1470, 1491, 1573, 1616, 1730, 2252, 2926, 3032, 3063, 3140 cm^{-1}.

*4.2.15. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl thiophene-2-carboxylate (**3o**).* White solid, mp: 88–92 °C. ^{1}H NMR (500 M, $CDCl_3$): δ 4.91 and 4.98 (2×d, *J*=15.7 Hz, 2H), 6.21 (s, 1H), 6.74 (d, *J*=7.9 Hz, 1H),7.02 (td, *J*=0.8, 7.6 Hz, 1H), 7.10 (dd, *J*=3.8, 4.9 Hz, 1H), 7.23 (t, *J*=7.8 Hz, 1H), 7.26–7.29 (m, 1H), 733–7.38 (m, 4H), 7.42 (d, *J*=7.4 Hz, 1H), 7.60 (dd, *J*=1.2, 5.0 Hz, 1H), 7.89 (dd, *J*=1.2, 3.8 Hz, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 44.0, 70.4, 109.5, 123.0, 124.1, 125.5, 127.3, 127.7, 127.8, 128.8, 130.2, 132.1, 133.4, 134.6, 135.2, 143.6, 161.3, 172.0. HRMS (EI) calcd for $C_{20}H_{15}NO_3S$ $(M+H)^+$: 350.0851, found

350.0860. IR (KBr): ν 737, 752, 854, 972, 1008, 1030, 1078, 1117, 1175, 1263, 1281, 1354, 1370, 1416, 1466, 1491, 1520, 1613, 1711, 1730, 2922, 3024, 3059, 3090 cm^{-1}.

*4.2.16. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl cyclohexanecarboxylate (**3p**).* Colorless oil. ^1H NMR (300 M, $CDCl_3$): δ 1.21–1.37 (m, 3H), 1.47–1.67 (m, 3H), 1.74–1.84 (m, 2H), 1.95–2.03 (m, 2H), 2.45–2.54 (m, 1H), 4.87 and 4.94 (2×d, J=15.7 Hz, 2H), 6.03 (s, 1H), 6.71 (d, J=7.8 Hz, 1H), 7.01 (t, J=7.5 Hz, 1H), 7.21 (t, J=7.8 Hz, 1H), 7.26–7.34 (m, 6H). ^{13}C NMR (75 M, $CDCl_3$): δ 25.18, 25.21, 25.6, 28.78, 28.88, 42.7, 43.9, 69.5, 109.4, 122.9, 124.6, 125.1, 127.2, 127.6, 128.7, 129.9, 135.2, 143.5, 172.4, 175.1. HRMS (EI) calcd for $C_{22}H_{23}NO_3$ $(M+H)^+$: 350.1756, found 350.1750. IR (film): ν 700, 731, 752, 847, 812, 912, 1003, 1028, 1076, 1103, 1128, 1159, 1244, 1364, 1450, 1466, 1489, 1614, 1730, 2855, 2930, 3030, 3059 cm^{-1}.

*4.2.17. 1-Benzyl-2-oxo-1,3-dihydro-2H-indol-3-yl butyrate (**3q**).* Colorless oil. ^1H NMR (300 M, $CDCl_3$): δ 0.99 (t, J=7.4 Hz, 3H), 1.67–1.79 (m, 2H), 2.38–2.54 (m, 2H), 4.90 (s, 2H), 6.04 (s, 1H), 6.71 (d, J=7.8 Hz, 1H), 7.01 (t, J=7.5 Hz, 1H), 7.21 (t, J=7.8 Hz, 1H), 7.26–7.35 (m, 6H). ^{13}C NMR (75 M, $CDCl_3$): δ 13.5, 18.3, 35.7, 43.8, 69.7, 109.4, 122.9, 124.5, 125.3, 127.2, 127.6, 128.7, 130.0, 135.2, 143.5, 172.3, 172.8. HRMS (EI) calcd for $C_{19}H_{19}NO_3$ $(M+H)^+$: 310.1443, found 310.1456. IR (film): ν 700, 752, 1001, 1078, 1103, 1366, 1466, 1489, 1614, 1728, 2874, 2928, 2963, 3038, 3061 cm^{-1}.

*4.2.18. 1-Benzyl-5-methyl-2-oxo-1,3-dihydro-2H-indol-3-yl benzoate (**3r**).* White solid, mp: 133–135 °C. ^1H NMR (500 M, $CDCl_3$): δ 2.24 (s, 3H), 4.90 and 4.95 (2×d, J=15.7 Hz, 2H), 6.24 (s, 1H), 6.61 (d, J=8.0 Hz, 1H), 7.00 (d, J=8.0 Hz, 1H), 7.22–7.36 (m, 6H), 7.43 (t, J=7.8 Hz, 2H), 7.54–7.58 (m, 1H), 8.11–8.13 (m, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 20.8, 44.0, 70.5, 109.2, 124.4, 126.3, 127.2, 127.6, 128.3, 128.7, 129.0, 130.1, 130.3, 132.7, 133.4, 135.4, 141.2, 165.8, 172.1. HRMS (EI) calcd for $C_{23}H_{19}NO_3$ $(M+H)^+$: 358.1443, found 358.1449. IR (KBr): ν 702, 806, 901, 997, 1024, 1061, 1107, 1150, 1196, 1273, 1346, 1373, 1452, 1499, 1602, 1626, 1726, 2862, 2916, 2943, 3034, 3057 cm^{-1}.

*4.2.19. 1-Benzyl-5-fluoro-2-oxo-1,3-dihydro-2H-indol-3-yl benzoate (**3s**).* White solid, mp: 134–136 °C. ^1H NMR (300 M, $CDCl_3$): δ 4.93 (s, 2H), 6.18 (s, 1H), 6.63 (dd, J=4.0, 8.6 Hz, 1H), 6.87–6.93 (m, 1H), 7.17 (dd, J=1.7, 7.1 Hz, 1H), 7.27–7.35 (m, 5H), 7.43 (t, J=7.7 Hz, 2H), 7.57 (t, J=7.3 Hz, 1H), 8.11 (d, J=7.5 Hz, 2H). ^{13}C NMR (75 M, $CDCl_3$): δ 44.1, 70.3, 110.1 (d, J_{C-F}=8.0 Hz, 1C), 113.7 (d, J_{C-F}=25.3 Hz, 1C), 116.4 (d, J_{C-F}=23.4, 1C), 125.8 (d, J_{C-F}=8.4 Hz, 1C), 127.2, 127.8, 128.4, 128.7, 128.8, 130.1, 133.6, 134.9, 139.4 (d, J_{C-F}=2.1 Hz, 1C), 159.1 (d, J_{C-F}=242.2 Hz, 1C), 165.6, 171.9. HRMS (EI) calcd for $C_{22}H_{16}NO_3F$ $(M+H)^+$: 362.1192, found 362.1182. IR (KBr): ν 704, 770, 812, 880, 851, 999, 1024, 1063, 1119, 1153, 1179, 1209, 1271, 1344, 1371, 1454, 1489, 1611, 1726, 2868, 2920, 3036, 3069 cm^{-1}.

*4.2.20. 1-Benzyl-5-chloro-2-oxo-1,3-dihydro-2H-indol-3-yl benzoate (**3t**).* White solid, mp: 166–168 °C. ^1H NMR (300 M, $CDCl_3$): δ 4.95 (s, 2H), 6.19 (s, 1H), 6.65 (d 8.6 Hz, 1H), 7.19 (dd, J=1.4, 8.3 Hz, 1H), 7.27–7.41 (m, 6H), 7.46 (t, J=7.7 Hz, 2H), 7.60 (t, J=7.3 Hz, 1H), 8.12 (d, J=7.5 Hz, 2H). ^{13}C NMR (75 M, $CDCl_3$): δ 44.1, 70.1, 110.5, 125.9, 127.2, 127.9, 128.0, 128.5, 128.6, 128.8, 128.9, 130.0, 130.1, 133.7, 134.8, 142.1, 165.6, 171.8. HRMS (EI) calcd for $C_{22}H_{16}NO_3Cl$ $(M+H)^+$: 378.0897, found 378.0890. IR (KBr): ν 704, 741, 804, 893, 1022, 1057, 1076, 1123, 1173, 1275, 1344, 1452, 1487, 1610, 1653, 1732, 2930, 2953, 3034, 3061 cm^{-1}.

*4.2.21. 1-Benzyl-7-methyl-2-oxo-1,3-dihydro-2H-indol-3-yl benzoate (**3u**).* White solid, mp: 113–115 °C. ^1H NMR (500 M, $CDCl_3$): δ 2.27 (s, 3H), 5.22 and 5.26 (2×d, J=16.9 Hz, 2H), 6.30 (s, 1H), 6.96 (t, J=7.5 Hz, 1H), 7.02 (d, J=7.7 Hz, 1H), 7.25–7.37 (m, 6H), 7.44–7.47 (m, 2H), 7.57–7.60 (m, 1H), 8.13–8.15 (m, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 18.6, 45.3, 70.0, 120.3, 123.1, 123.3, 125.1, 125.7, 127.2, 128.4, 128.9, 129.1, 130.1, 133.5, 134.1, 137.2, 141.6, 165.7, 173.3. HRMS (EI) calcd for $C_{23}H_{19}NO_3$ $(M+H)^+$: 358.1443, found 358.1459. IR (KBr): ν 710, 735, 766, 787, 824, 995, 1022, 1069, 1113, 1180, 1256, 1321, 1360, 1450, 1472, 1493, 1651, 1717, 2926, 3042, 3064, 3088 cm^{-1}.

*4.2.22. 1-Benzyl-7-chloro-2-oxo-1,3-dihydro-2H-indol-3-yl benzoate (**3v**).* White solid, mp: 131–132 °C. ^1H NMR (500 M, $CDCl_3$): δ 5.34 and 5.41 (2×d, J=16.1 Hz, 2H), 6.22 (s, 1H), 6.94 (dd, J=7.4, 8.2 Hz, 1H), 7.18–7.20 (m, 1H), 7.22–7.27 (m, 1H), 7.30–7.32 (m, 5H), 7.42–7.45 (m, 2H), 7.55–7.59 (m, 1H), 8.09–8.11 (m, 2H). ^{13}C NMR (125 M, $CDCl_3$): δ 45.1, 69.7, 115.8, 123.97, 124.00, 126.5, 127.2, 128.4, 128.6, 128.8, 130.1, 132.7, 133.7, 137.0, 139.7, 165.6, 172.7. HRMS (EI) calcd for $C_{22}H_{16}NO_3Cl$ $(M+H)^+$: 378.0897, found 378.0890. IR (KBr): ν 706, 762, 785, 849, 901, 934, 968, 1022, 1078, 1128, 1163, 1200, 1273, 1314, 1344, 1356, 1456, 1584, 1609, 1726, 2928, 3032, 3059 cm^{-1}.

*4.2.23. 2-Oxo-1,3-dihydro-2H-indol-3-yl benzoate (**3w**).* White solid, mp: 130–132 °C. ^1H NMR (500 M, $CDCl_3$): δ 6.21 (s, 1H), 6.92 (d, J=7.8 Hz, 1H), 7.01 (t, J=7.5 Hz, 1H), 7.24 (d, J=7.7 Hz, 1H), 7.37 (d, J=7.4 Hz, 1H), 7.43 (t, J=7.7 Hz, 2H), 7.57 (t, J=7.4 Hz, 1H), 8.10 (d, J=7.5 Hz, 2H), 9.31 (br, 1H). ^{13}C NMR (125 M, $CDCl_3$): δ 70.7, 110.6, 123.0, 124.8, 125.7, 128.4, 128.9, 130.1, 130.3, 133.5, 141.9, 165.9, 175.0. HRMS (EI) calcd for $C_{15}H_{11}NO_3$ $(M+H)^+$: 254.0817, found 254.0810. IR (KBr): ν 706, 766, 822, 889, 947, 1020, 1067, 1111, 1179, 1258, 1344, 1393, 1470, 1601, 1620, 1695, 1724, 1742, 2936, 3032, 3121, 3179 cm^{-1}.

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Supplementary data

Copies of NMR spectra for all products. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.07.075.

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