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Iron-Catalyzed Arylalkoxycarbonylation of *N*-Aryl Acrylamides with Carbazates

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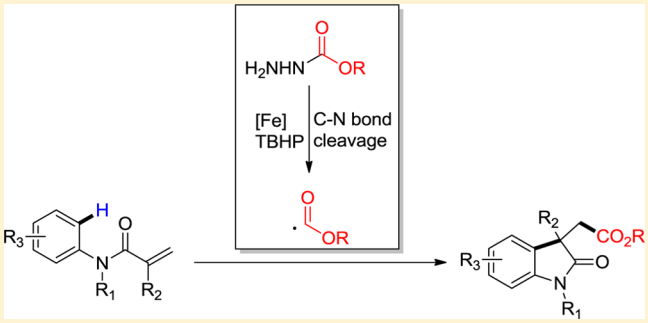
Supporting Information

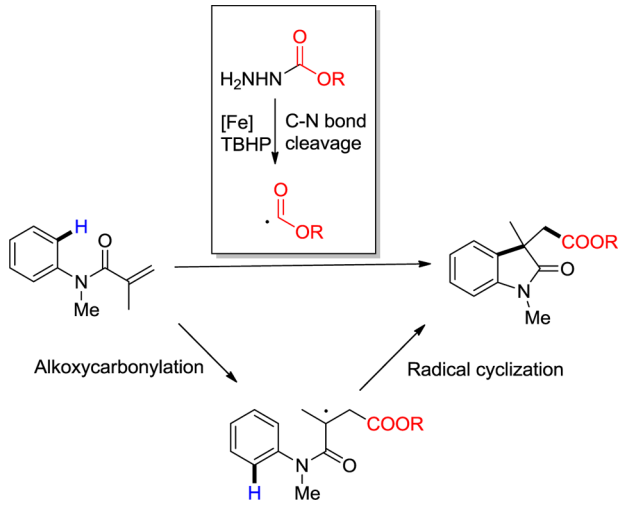
ABSTRACT: A novel arylalkoxycarbonylation of *N*-aryl acrylamides with carbazates leading to alkoxycarbonylated oxindoles has been developed. The reported reactions employ economical and environmentally benign $FeCl_2·4H_2O$ as a catalyst and easily accessible and safe carbazates as alkoxycarbonyl radical precursors.



Esters are ubiquitous chemical entities that are widely present in natural products, pharmaceuticals, functional materials, and valuable industrial products and also serve as vital intermediates in organic synthesis.[1] Since the pioneering work of Heck in 1974,[2] palladium-catalyzed alkoxycarbonylation using CO and alcohols as the sources of ester groups has become one of the most common and reliable methods for the introduction of an ester group to organic molecules.[3] However, the use of prefunctionalized substrates and toxic gas reagents and the necessity to use high-pressure equipment remain major shortcomings of this methodology, restricting its application in more complex organic syntheses.[3] Therefore, the design of simple, safe, and environmentally friendly CO-free strategies for alkoxycarbonylation, particularly involving a C−H bond functionalization process, would be highly desirable.[4] Recently, the groups of Tian[5] and Taniguchi[6] independently developed two complementary new strategies for oxidative alkoxycarbonylation of terminal alkenes utilizing carbazates ($ROCONHNH_2$) as ester group sources. Justifiably, carbazates are especially promising alkoxycarbonyl surrogates because they are usually stable solids and are readily available. However, despite their high potential, carbazates have rarely been applied to the construction of esters.

Recently, difunctionalization of alkenes involving direct C−H functionalization of arenes has received increasing attention.[7] In particular, palladium-free radical-mediated difunctionalization of *N*-aryl acrylamides provides a versatile strategy for the synthesis of various functionalized oxindoles, including arylphosphorylation,[8a] alkylarylation,[8b−f] diarylation,[8g] arylcarbonylation,[8h,i] arylnitration,[8j,k] aryltrifluoromethylation,[8l] and azidoarylation.[8m] Very recently, we also developed a method for arylsulfonylation in the presence of a KI/18-crown-6/TBHP catalyst system.[8n] In this approach, S−N bond cleavage of sulfonylhydrazides with TBHP generates sulfonyl radicals that are subsequently trapped by *N*-aryl acrylamides, thus affording the corresponding sulfonated oxindoles. Our ongoing interest in radical reactions, especially in the generation of radicals from hydrazines,[6,8n,9] prompted us to explore the application of carbazates to the synthesis of alkoxycarbonylated oxindoles. It was hypothesized that carbazates may act as alkoxycarbonyl radical precursors via a similar TBHP-mediated C−N bond cleavage (Scheme 1). Herein we report a novel and practical method for arylalkoxycarbonylation of *N*-aryl acrylamides with carbazates, which work as easily accessible and safe alkoxycarbonyl surrogates. The reported reactions employ

Scheme 1. Arylalkoxycarbonylation of *N*-Aryl Acrylamides with Carbazates



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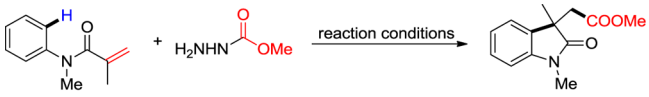
economical and environmentally benign $FeCl_2·4H_2O$ as the catalyst and successfully provide access to a wide range of alkoxycarbonylated oxindoles.

Initially, we carried out the arylalkoxycarbonylation of *N*-phenylacrylamide (**1a**) with methyl carbazate (**2a**) using our previously reported TBAI−TBHP catalyst system.[9a] Gratifyingly, the reaction in MeCN at 80 °C for 6 h afforded the desired oxindole **3** in 32% yield (Table 1, entry 1). Screening of

Table 1. Optimization of the Reaction Conditions[a]



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

entry	cat. (mol %)	equiv of **2a**	equiv of TBHP	yield (%)
1	TBAI (20)	2	2	32
2	CuBr (20)	2	2	0
3	$Cu(OAc)_2$ (20)	2	2	0
4	$FeCl_3$ (20)	2	2	0
5	$FeCl_2·4H_2O$ (20)	2	2	45
6[b]	$FeCl_2·4H_2O$ (20)	2	2	20
7	$FeCl_2·4H_2O$ (10)	2	2	28
8	$FeCl_2·4H_2O$ (50)	2	2	47
9	$FeCl_2·4H_2O$ (20)	2	4	61
10	$FeCl_2·4H_2O$ (20)	2	6	64
11	**$FeCl_2·4H_2O$ (20)**	**4**	**6**	**94**
12	$FeCl_2·4H_2O$ (20)	4	8	92

[a]Reaction conditions: **1a** (0.25 mmol), **2a**, catalyst, and TBHP (70% aqueous solution) in MeCN (2.0 mL) at 80 °C for 6 h, unless otherwise noted. [b]H_2O was used as the solvent.

copper and iron catalysts showed that $FeCl_2·4H_2O$ was the best (entry 5). In contrast, the reactions hardly proceeded with CuBr, $Cu(OAc)_2$, or $FeCl_3$ (entries 2−4). Unfortunately, the reaction proceeded less effectively in water (entry 6).[8n,9b] This initial success prompted further elaboration of the loading of catalyst, **2a**, and TBHP (entries 7−12). To our delight, an excellent yield could be achieved by using 20 mol % $FeCl_2·4H_2O$, 4 equiv of **2a**, and 6 equiv of TBHP (entry 11).

With the optimized conditions in hand, the arylmethoxycarbonylation of a variety of *N*-aryl acrylamide derivatives with methyl carbazate was tested, and the results are summarized in Table 2. Methyl and benzyl protecting groups on the nitrogen atom were compatible with the reaction conditions, and the reactions afforded the corresponding oxindoles **3** and **4** in 94 and 66% yield, respectively. However, the use of acetyl and N-free *N*-aryl acrylamides resulted in complex mixtures, and no desired products **5** and **6** were detected. The reaction was readily extended to a variety of *N*-aryl acrylamides, and both electron-donating (Me and MeO) and electron-withdrawing (halide, CF_3, CF_3O, COOEt, and CN) substituents were well-tolerated under the reaction conditions. As expected, substrates bearing *m*-methyl and *m*-bromo substituents afforded mixtures of two regioselective products **17**/**17′** and **18**/**18′** in ratios of 1:1 and 5:1, respectively. The existence of possible steric hindrance arising from the presence of an *ortho* substituent led to a lower yield of products **19**. Notably, naphthalene and tetrahydroquinoline derivatives underwent facile arylmethoxycarbonylation to furnish the expected products **20** and **21** in moderate yields. Whereas α-substituted olefins bearing CH_2OH and CH_2OAc functional groups were well-tolerated in this arylmethoxycarbonylation process, monosubstituted olefin (R_2 = H, products **24**) had no reactivity. It is worth mentioning that product **23** had been synthesized in 58% yield via palladium-catalyzed carboacetoxylation of *N*-aryl acrylamide.[7c] To our delight, arylethoxycarbonylation also proceeded smoothly to afford ethyl ester **25** in moderate yield using readily accessible ethyl carbazate as an ethoxycarbonyl surrogate.

To confirm our suspicion that the arylalkoxycarbonylation proceeds by a radical pathway, inter- and intramolecular kinetic isotope effect (KIE) experiments were performed (Scheme 2), and two primary KIEs were observed (intermolecular k_H/k_D = 1.0 and intramolecular k_H/k_D = 1.3). Moreover, the addition of a stoichiometric amount of TEMPO indeed suppressed the arylalkoxycarbonylation process (Scheme 2).

On the basis of the above experimental results, a plausible mechanism is proposed (Scheme 3). Initially, the *tert*-butoxyl and *tert*-butylperoxy radicals are generated via iron-catalyzed decomposition of TBHP.[10] Then, C−N bond cleavage of the carbazate through stepwise hydrogen abstraction forms alkoxycarbonyl radical with the release of molecular nitrogen.[9] The addition of alkoxycarbonyl radical to the *N*-aryl acrylamide affords alkyl radical **I**, which further undergoes intramolecular radical substitution reaction to give intermediate **II**.[8] Finally, hydrogen abstraction of radical intermediate **II** by TBHP leads to the alkoxycarbonylated oxindole.[8h]

In conclusion, we have discovered that carbazates can be used as easily accessible and safe alkoxycarbonyl radical precursors for the arylalkoxycarbonylation of *N*-aryl acrylamides, providing a general and practical method for the construction of alkoxycarbonylated oxindoles. The use of economical and environmentally benign $FeCl_2·4H_2O$ as the catalyst also makes this transformation sustainable and practical.

EXPERIMENTAL SECTION

General Procedures. All of the reagents and solvents were purchased from commercial suppliers and used without further purification. Melting points are uncorrected. The ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ at 500 and 125 MHz, respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in parts per million, and coupling constants (*J*) are given in hertz. High-resolution mass spectrometry (HRMS) was performed on a TOF MS instrument with an ESI source. The *N*-aryl acrylamides were synthesized according to a literature method.[11]

Typical Procedure for the Synthesis of Alkoxycarbonylated Oxindoles. To a stirred solution of *N*-aryl acrylamide (0.25 mmol), carbazate (1.0 mmol), and $FeCl_2·4H_2O$ (0.05 mmol) in MeCN (2 mL) was added TBHP (1.5 mmol, 70% aqueous solution) at room temperature. The mixture was heated at 80 °C for 6 h and then cooled to room temperature. The excess solvent was removed under vacuum, and the residue was directly purified by silica gel column chromatography (petroleum/ethyl acetate = 5:1) to afford the desired oxindole.

*Methyl 2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetate (**3**).*[12] Pale-yellow oil (54.7 mg, 94%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (td, *J* = 7.5, 1.2 Hz, 1H), 7.19 (dd, *J* = 7.3, 0.5 Hz, 1H), 7.04 (td, *J* = 7.6, 0.9 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.46 (s, 3H), 3.26 (s, 3H), 3.01 (d, *J* = 16.4 Hz, 1H), 2.85 (d, *J* = 16.4 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 170.2, 143.5, 132.8, 128.0, 122.2, 122.2, 108.0, 51.4, 45.4, 41.3, 26.2, 24.1.

*Methyl 2-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)acetate (**4**).*[13] Pale-yellow oil (50.9 mg, 66%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.14 (td, *J* = 7.7, 1.1 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.00−4.91 (m, 2H), 3.41 (s, 3H), 3.09 (d, *J* = 16.3 Hz, 1H), 2.90 (d, *J* = 16.3 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 170.1, 142.5, 136.0,

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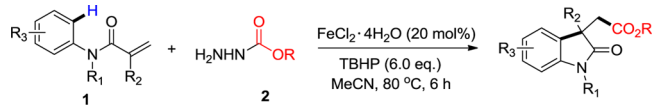
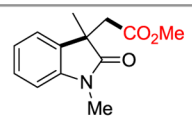
Table 2. Scope of the Reaction with *N*-Aryl Acrylamides[a]





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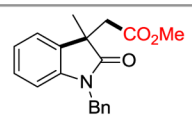

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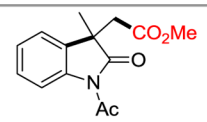

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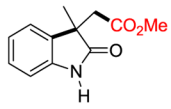

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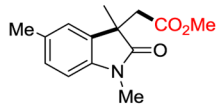

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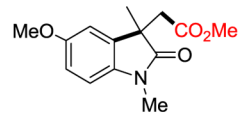

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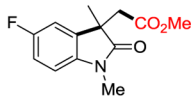

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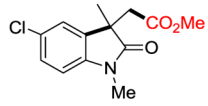

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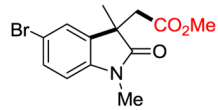

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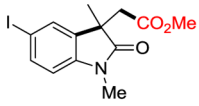

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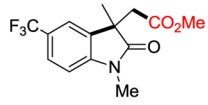

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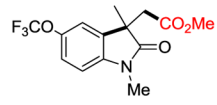

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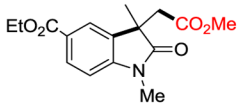

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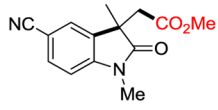

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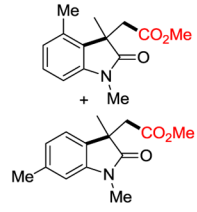
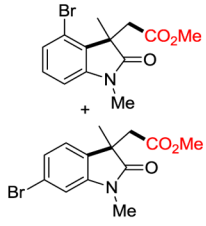
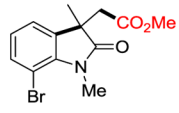


17 + **17'**: 64% (1:1)[b]



18 + **18'**: 78% (5:1)[b]



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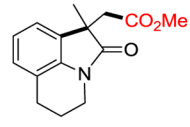

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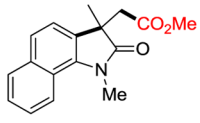

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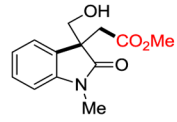

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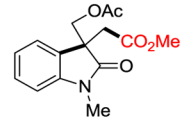

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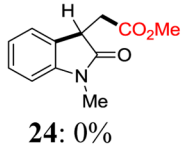

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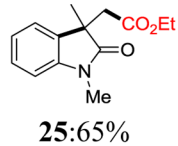

25:65%

[a]Reaction conditions: *N*-aryl acrylamide **1** (0.25 mmol), **2** (1.0 mmol), $FeCl_2{\cdot}4H_2O$ (20 mol %), and TBHP (6 equiv, 70% aqueous solution) in MeCN (2.0 mL) at 80 °C for 6 h. [b]The ratio of isomers was determined by ^1H NMR spectroscopy of the isolated product.

132.9, 128.6, 127.9, 127.4, 127.3, 122.3, 122.2, 109.1, 51.4, 45.5, 43.9, 41.2, 24.8.

*Methyl 2-(1,3,5-Trimethyl-2-oxoindolin-3-yl)acetate (**7**).* Pale-yellow oil (38.8 mg, 63%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.07

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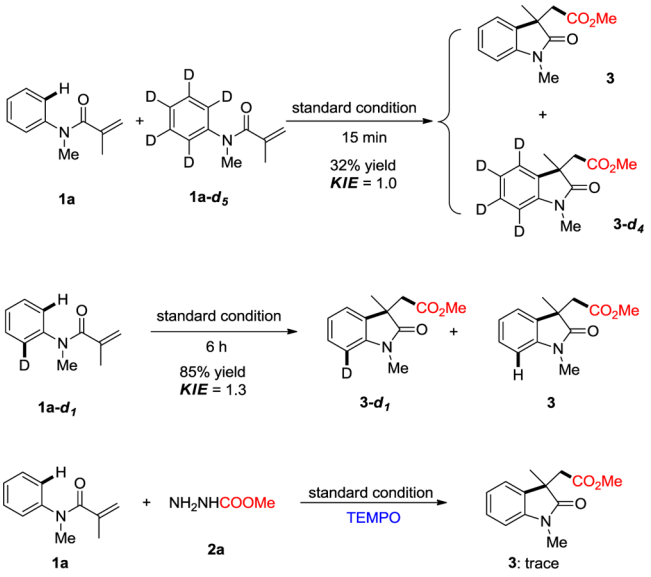
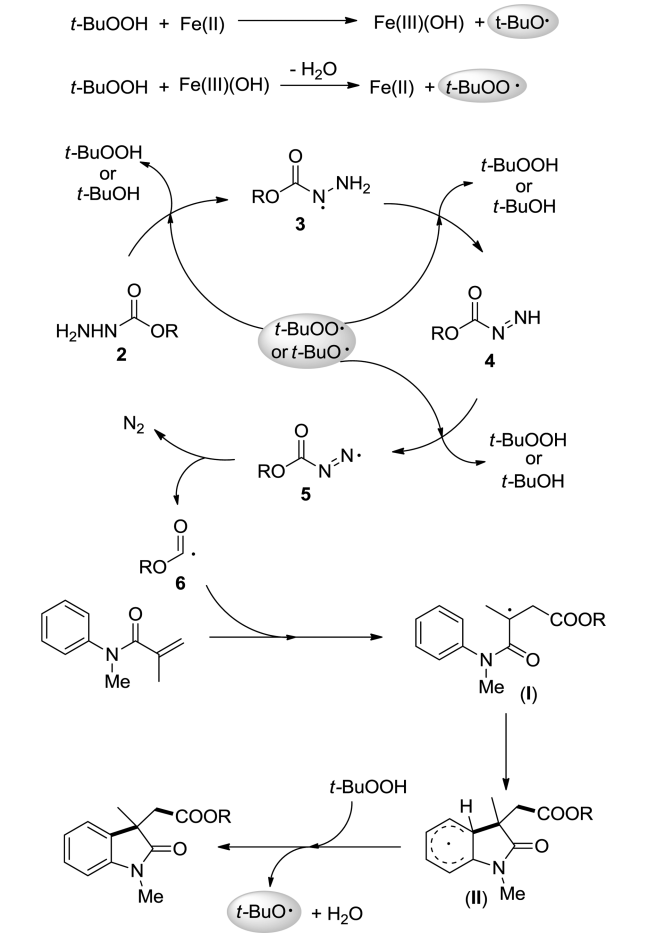
Scheme 2. Control Experiments



Scheme 3. Proposed Mechanism



(d, J = 7.8 Hz, 1H), 7.01 (s, 1H), 6.74 (d, J = 7.9 Hz, 1H), 3.47 (s, 3H), 3.25 (s, 3H), 2.99 (d, J = 16.4 Hz, 1H), 2.83 (d, J = 16.4 Hz, 1H), 2.33 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 141.2, 133.1, 131.8, 130.4, 128.4, 123.2, 107.9, 51.6, 45.7, 41.5, 26.4, 24.4, 21.2; HRMS (ESI) calcd for $C_{14}H_{18}NO_3$ ([M + H]$^+$) 248.1287, found 248.1285.

*Methyl 2-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**8**).* Pale-yellow oil (58.5 mg, 89%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (d, J = 2.3 Hz, 1H), 6.79 (dd, J = 8.4, 2.4 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 3.79 (s, 3H), 3.48 (s, 3H), 3.23 (s, 3H), 3.00 (d, J = 16.5 Hz, 1H), 2.83 (d, J = 16.5 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.5, 170.2, 155.9, 137.1, 134.4, 112.0, 110.2, 108.3, 55.8, 51.5, 45.8, 41.3, 26.4, 24.2; HRMS (ESI) calcd for $C_{14}H_{18}NO_4$ ([M + H]$^+$) 264.1236, found 264.1233.

*Methyl 2-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**9**).* Colorless oil (45.8 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (dd, J = 9.9, 1.7 Hz, 1H), 6.95 (d, J = 1.4 Hz, 1H), 6.80−6.75 (m, 1H), 3.49 (s, 3H), 3.25 (s, 3H), 3.01 (d, J = 16.7 Hz, 1H), 2.84 (d, J = 16.7 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.6, 170.1, 159.3 (d, J = 238.9 Hz), 139.6 (d, J = 1.75 Hz), 134.7 (d, J = 7.75 Hz), 114.3 (d, J = 23.4 Hz), 110.7 (d, J = 24.8 Hz), 108.6 (d, J = 8.1 Hz), 51.7, 45.9, 41.2, 26.5, 24.1; HRMS (ESI) calcd for $C_{13}H_{15}FNO_3$ ([M + H]$^+$) 252.1036, found 252.1034.

*Methyl 2-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**10**).* Pale-yellow oil (47.4 mg, 71%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, J = 8.3, 2.1 Hz, 1H), 7.17 (d, J = 2.1 Hz, 1H), 6.79 (d, J = 8.3 Hz, 1H), 3.50 (s, 3H), 3.24 (s, 3H), 3.02 (d, J = 16.8 Hz, 1H), 2.84 (d, J = 16.8 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 170.1, 142.3, 134.7, 128.0, 127.7, 122.8, 109.0, 51.7, 45.6, 41.1, 26.5, 24.1; HRMS (ESI) calcd for $C_{13}H_{15}ClNO_3$ ([M + H]$^+$) 268.0740, found 268.0737.

*Methyl 2-(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**11**).* Pale-yellow oil (56.7 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, J = 8.2, 1.8 Hz, 1H), 7.30 (d, J = 1.8 Hz, 1H), 6.74 (d, J = 8.2 Hz, 1H), 3.50 (s, 3H), 3.24 (s, 3H), 3.02 (d, J = 16.8 Hz, 1H), 2.84 (d, J = 16.8 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 170.0, 142.7, 135.1, 130.9, 125.5, 114.9, 109.5, 51.6, 45.5, 41.2, 26.4, 24.1; HRMS (ESI) calcd for $C_{13}H_{15}BrNO_3$ ([M + H]$^+$) 312.0235, found 312.0233.

*Methyl 2-(5-Iodo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**12**).* Pale-yellow oil (68.3 mg, 76%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.2, 1.7 Hz, 1H), 7.46 (d, J = 1.7 Hz, 1H), 6.65 (d, J = 8.2 Hz, 1H), 3.50 (s, 3H), 3.23 (s, 3H), 3.01 (d, J = 16.8 Hz, 1H), 2.83 (d, J = 16.8 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 170.0, 143.4, 136.9, 135.5, 131.0, 110.1, 84.8, 51.6, 45.4, 41.1, 26.4, 24.1; HRMS (ESI) calcd for $C_{13}H_{15}INO_3$ ([M + H]$^+$) 360.0097, found 360.0093.

*Methyl 2-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-acetate (**13**).* Pale-yellow oil (47.4 mg, 63%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 1.1 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 3.49 (s, 3H), 3.29 (s, 3H), 3.06 (d, J = 16.8 Hz, 1H), 2.91 (d, J = 16.8 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 170.0, 146.7, 133.6, 126.0 (q, J = 3.9 Hz), 124.6 (q, J = 32.4 Hz), 124.4 (q, J = 269.5 Hz), 119.2 (q, J = 3.6 Hz), 107.8, 51.7, 45.4, 41.2, 26.6, 24.1; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_3$ ([M + H]$^+$) 302.1004, found 302.1001.

*Methyl 2-(1,3-Dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)-acetate (**14**).* White solid (72 mg, 91%); mp 162−163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, J = 8.4, 1.2 Hz, 1H), 7.10 (d, J = 1.1 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.49 (s, 3H), 3.26 (s, 3H), 3.01 (d, J = 16.6 Hz, 1H), 2.85 (d, J = 16.6 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.5, 170.1, 144.6 (q, J = 1.9 Hz), 142.3, 134.5, 121.2, 120.5 (q, J = 254.9 Hz), 116.5, 108.4, 51.6, 45.8, 41.2, 26.5, 23.9; HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_4$ ([M + H]$^+$) 318.0953, found 318.0950.

*Ethyl 3-(2-Methoxy-2-oxoethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (**15**).* White solid (43.5 mg, 57%); mp 158−159 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.2, 1.7 Hz, 1H), 7.84 (d, J = 1.6 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 4.37 (qd, J = 7.1, 0.7 Hz, 2H), 3.47 (s, 3H), 3.30 (s, 3H), 3.08 (d, J = 16.9 Hz, 1H), 2.93 (d, J = 16.9 Hz, 1H), 1.40 (t + s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 170.1, 166.4, 147.8, 133.0, 130.9, 124.6, 123.2, 107.6, 60.8, 51.6, 45.2, 41.2, 26.5, 24.2, 14.4; HRMS (ESI) calcd for $C_{16}H_{20}NO_5$ ([M + H]$^+$) 306.1341, found 306.1337.

*Methyl 2-(5-Cyano-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**16**).* Pale-yellow oil (46.4 mg, 72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62

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(d, J = 8.1 Hz, 1H), 7.45 (s, 1H), 6.94 (d, J = 8.1 Hz, 1H), 3.50 (s, 3H), 3.29 (s, 3H), 3.06 (d, J = 17.0 Hz, 1H), 2.91 (d, J = 17.0 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.5, 169.9, 147.6, 134.1, 133.5, 125.4, 119.1, 108.4, 105.3, 51.7, 45.1, 41.0, 26.5, 23.9; HRMS (ESI) calcd for $C_{14}H_{15}N_2O_3$ ([M + H]$^+$) 259.1083, found 259.1080.

*Methyl 2-(1,3,4-Trimethyl-2-oxoindolin-3-yl)acetate (**17**) and Methyl 2-(1,3,6-Trimethyl-2-oxoindolin-3-yl)acetate (**17′**).* Pale-yellow oil (39.5 mg, 64%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.86−6.79 (m, 2H), 6.72−6.68 (m, 2H), 3.46 (d, J = 4.0 Hz, 3H), 3.38 (s, 3H), 3.24 (d, J = 3.0 Hz, 6H), 3.14 (d, J = 16.0 Hz, 1H), 3.04 (d, J = 16.0 Hz, 1H), 2.98 (d, J = 16.3 Hz, 1H), 2.83 (d, J = 16.3 Hz, 1H), 2.37 (d, J = 2.4 Hz, 5H), 1.43 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.1, 179.8, 170.3, 170.1, 143.9, 143.6, 138.1, 133.6, 129.9, 129.5, 128.1, 127.9, 124.9, 122.8, 122.0, 109.0, 105.8, 51.4, 46.4, 45.2, 41.4, 40.6, 26.4, 26.3, 24.2, 22.2, 21.7, 18.0; HRMS (ESI) calcd for $C_{14}H_{18}NO_3$ ([M + H]$^+$) 248.1287, found 248.1284.

*Methyl 2-(4-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**18**) and Methyl 2-(6-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**18′**).* Pale-yellow oil (60.8 mg, 78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19−7.10 (m, 2.1H), 7.06 (d, J = 7.8 Hz, 0.18H), 7.01 (d, J = 1.7 Hz, 0.18H), 6.82 (dd, J = 6.6, 2.0 Hz, 1H), 3.56 (s, 0.47H), 3.53 (s, 0.55H), 3.48 (s, 1H), 3.47 (s, 3H), 3.26 (s, 3H), 3.24 (s, 1H), 3.04 (d, J = 11.9 Hz, 0.63H), 3.00 (d, J = 11.4 Hz, 0.56H), 1.48 (s, 3H), 1.36 (s, 0.6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 170.0, 169.7, 145.5, 144.6, 131.5, 130.4, 129.3, 126.1, 124.8, 123.3, 121.4, 117.8, 111.4, 106.9, 51.4, 47.3, 45.0, 40.9, 38.8, 26.2, 23.8, 21.1; HRMS (ESI) calcd for $C_{13}H_{15}BrNO_3$ ([M + H]$^+$) 312.0235, found 312.0231.

*Methyl 2-(7-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**19**).* Pale-yellow oil (48.9 mg, 63%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, J = 8.2, 1.1 Hz, 1H), 7.09 (dd, J = 7.3, 1.0 Hz, 1H), 6.87 (dd, J = 8.0, 7.4 Hz, 1H), 3.64 (s, 3H), 3.48 (s, 3H), 3.04 (d, J = 16.6 Hz, 1H), 2.84 (d, J = 16.6 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.3, 170.0, 141.0, 136.1, 133.8, 123.5, 121.1, 102.5, 51.6, 45.2, 41.5, 30.0, 24.6; HRMS (ESI) calcd for $C_{13}H_{15}BrNO_3$ ([M + H]$^+$) 312.0235, found 312.0232.

*Methyl 2-(1-Methyl-2-oxo-2,4,5,6-tetrahydro-1H-pyrrolo[3,2,1-ij]-quinolin-1-yl)acetate (**20**).* Colorless oil (27.8 mg, 43%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (t, J = 7.6 Hz, 2H), 6.92 (t, J = 7.5 Hz, 1H), 3.78−3.72 (m, 2H), 3.48 (s, 3H), 2.97 (d, J = 16.3 Hz, 1H), 2.84 (d, J = 16.3 Hz, 1H), 2.80 (t, J = 6.2 Hz, 2H), 2.07−1.98 (m, 2H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 170.4, 139.3, 131.4, 126.9, 121.8, 120.2, 120.1, 51.5, 46.7, 41.3, 38.9, 24.6, 23.8, 21.2; HRMS (ESI) calcd for $C_{15}H_{18}NO_3$ ([M + H]$^+$) 260.1287, found 260.1285.

*Methyl 2-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-benzo[g]indol-3-yl)acetate (**21**).* Pale-yellow oil (38.2 mg, 54%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.2, 0.7 Hz, 1H), 7.53−7.41 (m, 3H), 7.31 (dd, J = 7.3, 0.9 Hz, 1H), 6.99 (dd, J = 7.6, 0.7 Hz, 1H), 3.75 (d, J = 17.0 Hz, 1H), 3.58 (s, 3H), 3.40 (s, 3H), 3.11 (d, J = 17.0 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 171.3, 137.7, 136.8, 133.5, 126.8, 126.5, 126.2, 122.4, 121.3, 119.4, 108.5, 51.5, 45.1, 45.0, 32.5, 29.8; HRMS (ESI) calcd for $C_{17}H_{18}NO_3$ ([M + H]$^+$) 284.1287, found 284.1284.

*Methyl 2-(3-(Hydroxymethyl)-1-methyl-2-oxoindolin-3-yl)acetate (**22**).* Pale-yellow oil (37.9 mg, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (td, J = 7.7, 1.1 Hz, 1H), 7.22 (d, J = 7.3 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.82−3.75 (m, 1H), 3.69 (d, J = 11.0 Hz, 1H), 3.48 (s, 3H), 3.26 (s, 3H), 3.21 (d, J = 16.6 Hz, 1H), 2.98 (d, J = 16.6 Hz, 1H), 2.74−2.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.5, 170.5, 144.3, 128.9, 128.8, 122.9, 122.6, 108.4, 66.7, 51.7, 51.0, 37.0, 26.3; HRMS (ESI) calcd for $C_{13}H_{16}NO_4$ ([M + H]$^+$) 250.1079, found 250.1077.

*Methyl 2-(3-(Acetoxymethyl)-1-methyl-2-oxoindolin-3-yl)acetate (**23**).*[14] Pale-yellow oil (57.4 mg, 79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (td, J = 7.7, 1.2 Hz, 1H), 7.23 (dd, J = 7.3, 0.6 Hz, 1H), 7.04 (td, J = 7.6, 0.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 4.46 (d, J = 10.8 Hz, 1H), 4.11 (d, J = 10.8 Hz, 1H), 3.47 (s, 3H), 3.27 (s, 3H), 3.02 (q, J = 16.4 Hz, 2H), 1.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 170.0, 169.6, 144.3, 128.8, 128.5, 123.2, 122.3, 108.1, 66.7, 51.6, 49.2, 37.3, 26.4, 20.4.

*Ethyl 2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetate (**25**).*[12] Pale-yellow oil (40.1 mg, 65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (td, J = 7.7, 1.0 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.95−3.78 (m, 2H), 3.25 (s, 3H), 3.03 (d, J = 16.2 Hz, 1H), 2.83 (d, J = 16.2 Hz, 1H), 1.38 (s, 3H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 169.7, 143.6, 132.9, 128.1, 122.3, 122.3, 108.0, 60.3, 45.5, 41.7, 26.3, 24.3, 13.8.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

KIE studies and copies of ^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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