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Synthesis of 2-(2-oxoindolin-3-ylidene)-2-arylacetonitriles through transition metal-free C(sp^2)–CN bond construction

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ABSTRACT

An efficient method for the construction of C(sp^2)–CN bonds directly from C(sp^2-H) cyanation of 3-arylideneindolin-2-ones with benzoyl cyanide under transition metal-free condition is described. Various 2-(2-oxoindolin-3-ylidene)-2-arylacetonitriles were efficiently synthesized using air as an oxidant under mild conditions. This protocol has excellent functional group tolerance and can be easily scaled up with good efficiency. This reaction successfully offers an alternative to structurally diverse alkenyl nitriles.

1. Introduction

Alkenyl nitriles[1] have been widely used as pharmaceuticals and agrochemicals because of their biological activities,[2] such as the Parkinson's disease drug entacapone, the anticancer agent trilostane and the herbicides 2-cyano-3-(substituted)acrylates (Fig. 1).[3]

Moreover, the nitrile group could serve as a useful synthetic precursor for further transformation into desired functionalities, such as amine, carbonyl, amide, and carboxylic acid.[4] The reported synthetic methods for alkenyl nitriles include the carbocyanation of alkynes,[5] the cyanation of alkenyl halides,[6] C(sp^3)–H functionalization of allylarenes or alkenes with trimethylsilyl azide,[7] the dehydrogenative coupling of primary alcohols with nitriles,[8] and the reaction of aldehydes and simple or substituted acetonitriles[9] (Scheme 1). However, these methodologies suffer from the use of expensive transition-metal catalysts and halide substrates. Therefore, more general, economical and greener methods still need to be developed.

In this work, we reported an efficient method for the construction of C(sp^2)–CN bonds through C(sp^2)–H cyanation of internal olefins using benzoyl cyanide as a cyanating agent and air as an oxidant under transition metal-free condition.

2. Results and discussion

Initially, (*E*)-3-(4-methylbenzylidene)indolin-2-one (**1a**) was selected as a model substrate to react with benzoyl cyanide in acetonitrile using potassium carbonate as a base under open air condition (Scheme 2). The possible reaction approach for this reaction might include Michael addition to afford 2-(2-oxoindolin-3-yl)-2-(4-tolyl)acetonitrile (**2a**) as a final product. However, none of the expected product was detected. To our delight, (*Z*)-2-(2-oxoindolin-3-ylidene)-2-(4-tolyl)acetonitrile (**3a**) was isolated with high stereoselectivity, which was confirmed by comparison ^{1}H NMR and ^{13}C NMR spectra with literature.[10] This result implied that the C(sp^2)–CN bond was efficiently formed by C(sp^2)–H cyanation of **1a** under transition metal-free condition.

In order to optimize the reaction conditions, the different bases and solvents were examined for the reaction (Table 1). Some tested inorganic bases, such as K_2CO_3, Cs_2CO_3, KOH and $NaHCO_3$ showed a certain effect on the reaction to afford **3a** in low yield (Table 1, entries 1–4). In contrast, organic bases, such as Et_2NH, piperidine, DBU and DABCO could not promote the reaction (Table 1, entries 5–8). In the later research, it was found that the base combination could produce different effects (Table 1, entries 9–13). Amongst

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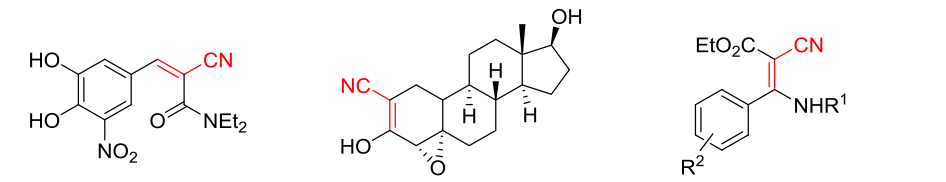
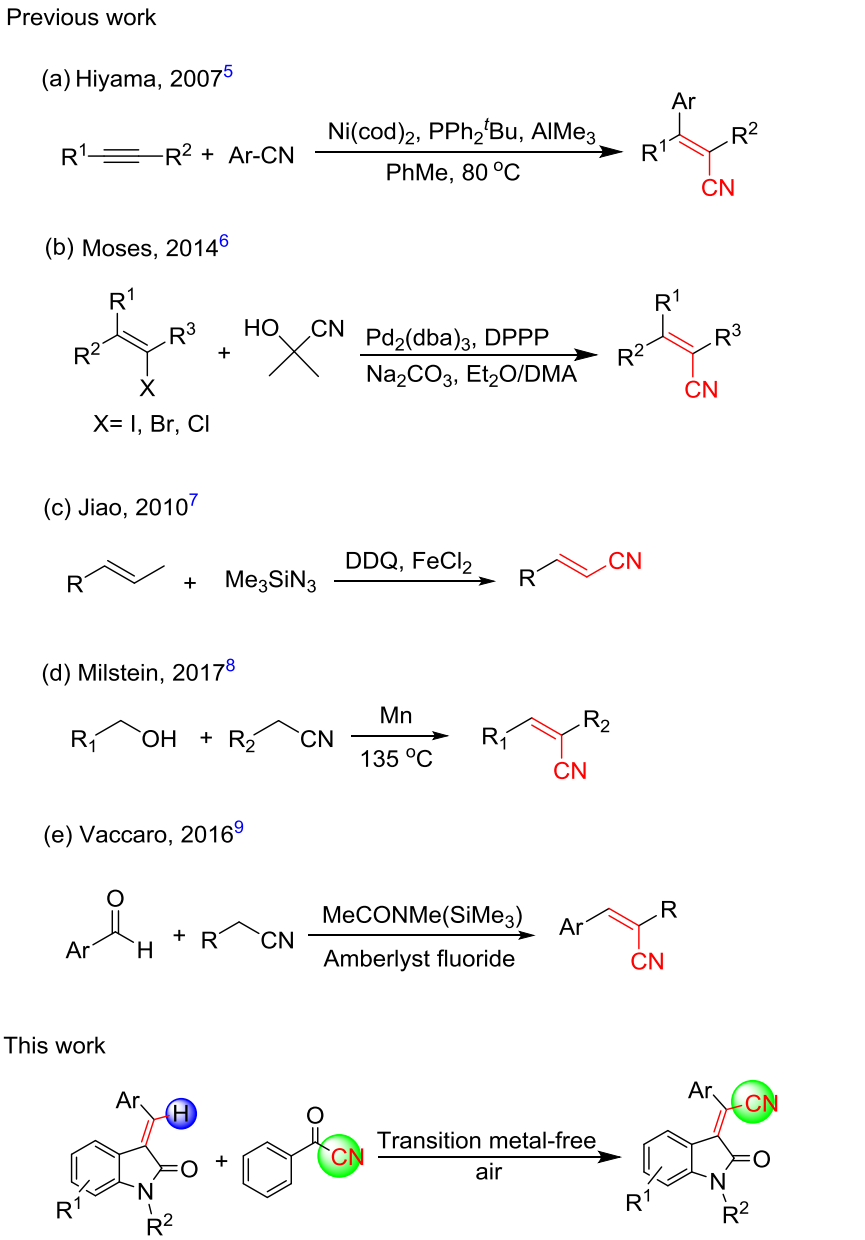


Fig. 1. Representative examples containing alkenyl nitrile structures.



Scheme 1. Preparation of alkenyl nitriles.

them, the combination of K_2CO_3 and KOH could largely improve the yield of **3a** (Table 1, entry 13).

In addition, the solvent effect on the reaction was studied. A higher yield of **3a** was observed when the reaction was performed in MeCN (Table 1, entry 13). A lower yield of **3a** was obtained in THF, 1,4-dioxane, MeOH and EtOH (Table 1, entries 14–17). Other solvents such as toluene, dichloromethane, and DMSO were ineffective for the reaction (Table 1, entries 18–20).

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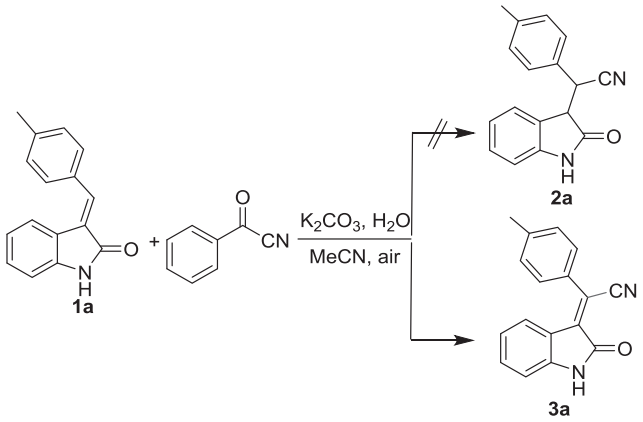
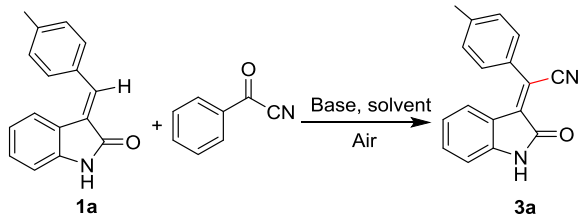


Scheme 2. The reaction of **1a** with benzoyl cyanide.

Table 1
Optimization of the reaction conditions.[a]



Entry	Base	Solvent	Yield (%)[b]
1	K_2CO_3	MeCN	43
2	Cs_2CO_3	MeCN	13
3	KOH	MeCN	14
4	$NaHCO_3$	MeCN	Trace
5	Et_2NH	MeCN	NR
6	Piperidine	MeCN	NR
7	DBU	MeCN	Trace
8	DABCO	MeCN	Trace
9	K_2CO_3-Cs_2CO_3	MeCN	48
10	K_2CO_3- $NaHCO_3$	MeCN	21
11	K_2CO_3- Et_2NH	MeCN	Trace
12	K_2CO_3- DBU	MeCN	Trace
13	K_2CO_3-KOH	MeCN	97
14	K_2CO_3-KOH	THF	20
15	K_2CO_3-KOH	1,4-Dioxane	Trace
16	K_2CO_3-KOH	MeOH	56
17	K_2CO_3-KOH	EtOH	21
18	K_2CO_3-KOH	PhMe	NR
19	K_2CO_3-KOH	DCM	NR
20	K_2CO_3-KOH	DMSO	NR

[a] Reaction conditions: **1a** (0.5 mmol), benzoyl cyanide (0.6 mmol), base (0.5 mmol, for base combination, 0.5 mmol for each base used) and H_2O (1 mmol) in solvent (5 mL) at 80 °C for 3 h under air condition.
[b] Isolated yields.

With the optimal conditions in hand, we turned our focus to unearth the generality of the method by reactions of various (*E*)-3-arylideneindolin-2-ones with benzoyl cyanide to access various (*Z*)-2-(2-oxoindolin-3-ylidene)-2-arylacetonitriles in acetonitrile using K_2CO_3 and KOH as bases under air condition, and the results are summarized in Table 2. The reactions could tolerate a wide range of functional groups, and produce the corresponding products in satisfactory yield. Substrates bearing both electron-donating (Me, MeO and OH) and electron withdrawing (F, Cl, Br and CF_3) groups on aromatic rings could give the corresponding products in high yield. Furthermore, the substituents at *ortho*-, *meta*- and *para*-positions of aromatic rings did not exhibit significant effect on the yield. Substrate containing fused ring (naphthyl) could also proceed smoothly to produce the corresponding product in high yield (**3t**). Meanwhile, substrate including heteroaromatic ring (thienyl) furnished the desired product in moderate yield (**3s**). In addition, substrates bearing disubstituted aromatic rings also allowed for the easy synthesis of the corresponding products in high yield (**3u**–**3w**). However, the attempt for the substrate including aliphatic chain, such as (*E*)-3-(2-methylpropylidene)indolin-2-one and (*E*)-3-(2,2-dimethylpropylidene)indolin-2-one, was not successful, and none of the expected products were observed under the standard conditions.

The method could also be applied to the substrates bearing substituents on 2-oxoindoline rings using standard conditions. The corresponding products **4** could be isolated in good yield. The results are summarized in Table 3.

With the success over generality of the protocol, the reaction of **1a** with benzoyl cyanide was also performed on gram scale. The reaction of 1.18 g of **1a** with 0.79 g of benzoyl cyanide in the presence of 0.70 g of K_2CO_3, 0.28 g of KOH and 0.18 g of H_2O in MeCN (10 mL) was performed under the optimized condition to give 0.99 g of **3a** in 76% isolated yield. This success of gram scale reaction further showed the potency of optimized condition for the bulk processes (Scheme 3).

Some control experiments were carried out using **1a** as a model substrate (Scheme 4). The reaction of **1a** with benzoyl cyanide using the similar condition under N_2 atmosphere only gave Michael addition product **2a** (65%) as a product, and **3a** was not detected. The further reaction of **2a** using the standard condition under air atmosphere afforded **3a** in 99% yield within 1 h. This result implied that **2a** might be the intermediate of the reaction and air was an indispensable condition for the formation of **3a**.

A plausible mechanism is proposed for the synthesis of **3a** (Scheme 5). Benzoyl cyanide is first attacked by water in the presence of potassium carbonate to produce cyanide ion *in situ*, which reacts with **1a** by Michael addition to form intermediate **2a**. **2a** could be isolated and characterized in the experiment. Then C–H hydroxylation of **2a** is promoted by potassium hydroxide using atmospheric air as an oxidant to afford intermediate **A**. The similar reactions were also reported by Gnanaprakasam and coworkers.[11] Finally, intermediate **A** undergoes dehydration to give **3a** as a final product.

3. Conclusions

In conclusion, we have developed a transition metal-free direct C(sp^2-H) cyanation of internal olefins to construct C(sp^2)–CN bond. This method provides an efficient and high yield way to synthetically construct useful alkenyl nitriles. The new methods are characterized by high efficiency, shorter reaction time, high yield and excellent functional group tolerance, providing a practical and versatile approach to a wide range of alkenyl nitriles. A gram-scale reaction has been attempted to illustrate the potency of reported procedure towards the bulk synthesis. This protocol not only extends the application of benzoyl cyanide in synthetic organic chemistry but also offers a novel method for the preparation of α-cyano substituted internal olefins, which are important structural units in a number of biological active compounds.

4. Experimental

4.1. General information

^1H NMR and ^{13}C NMR spectra were recorded on a Mercury-

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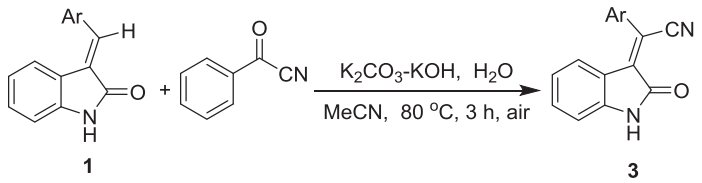
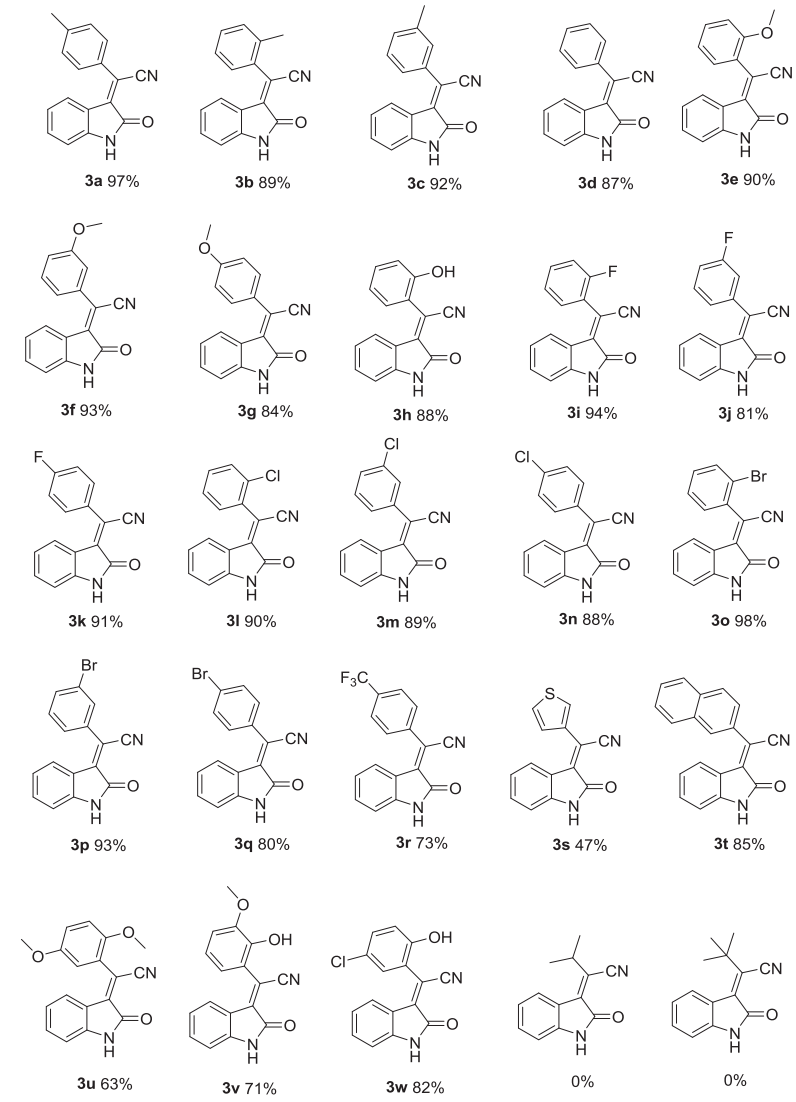
Table 2
Scope of aromatic rings of **1** for the synthesis of **3**.[a]





[a] Reaction conditions: **1** (0.5 mmol), benzoyl cyanide (0.6 mmol), K_2CO_3 (0.5 mmol), KOH (0.5 mmol) and H_2O (1 mmol) in MeCN (5 mL) at 80 °C for 3 h under air condition.

600 MB or 400 MB instrument using $CDCl_3$ and DMSO-d_6 as solvents and Me_4Si as internal standard. Elemental analyses were performed on a Vario El Elemental Analysis instrument. Melting points were observed in an electrothermal melting point apparatus. 3-Arylideneindolin-2-ones (**1**) were synthesized according to literature method.[12]

4.2. Typical procedure for the synthesis of *3a-w* and *4a-e*

The mixture of (*E*)-3-arylideneindolin-2-ones (0.5 mmol), benzoyl cyanide (0.6 mmol), potassium carbonate (0.5 mmol), potassium hydroxide (0.5 mmol) and water (1.0 mmol) in acetonitrile (5 mL) was stirred at 80 °C for 3 h. The reaction was monitored by

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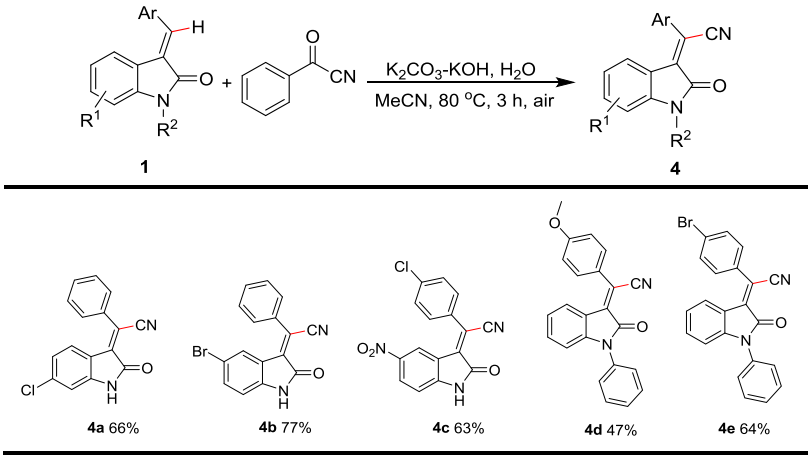
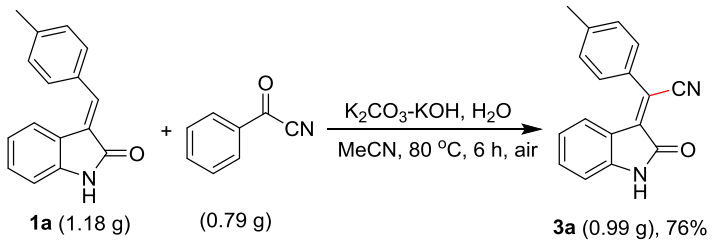
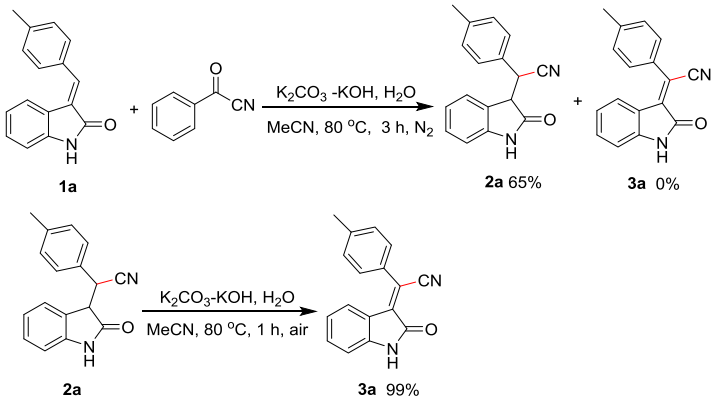
Table 3
Scope of 2-oxoindoline rings of **1** for the synthesis of **4**.[a]



[a] Reaction conditions: **1** (0.5 mmol), benzoyl cyanide (0.6 mmol), K_2CO_3 (0.5 mmol), KOH (0.5 mmol) and H_2O (1 mmol) in MeCN (5 mL) at 80 °C for 3 h under air condition.



Scheme 3. Gram-scale experiment for **3a**.



Scheme 4. Control experiments.

TLC. After the completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL), and the resulting solution was washed with saturated brine (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v 3:1) as eluent to give pure product. The analytical data for products are given below.

*4.2.1. (Z)-2-(2-oxoindolin-3-ylidene)-2-(p-tolyl)acetonitrile (**3a**)*[10]

Orange red solid; mp 196–198 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.92 (s, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.25 (td, J = 7.6, 1.4 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.72–6.64 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.87, 144.13, 141.10, 138.45, 133.58, 130.55, 130.35, 128.95, 124.56, 121.93, 120.49, 117.77, 115.17, 111.08, 21.47. Anal. Calcd. For $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.40; H, 4.66; N, 10.72.

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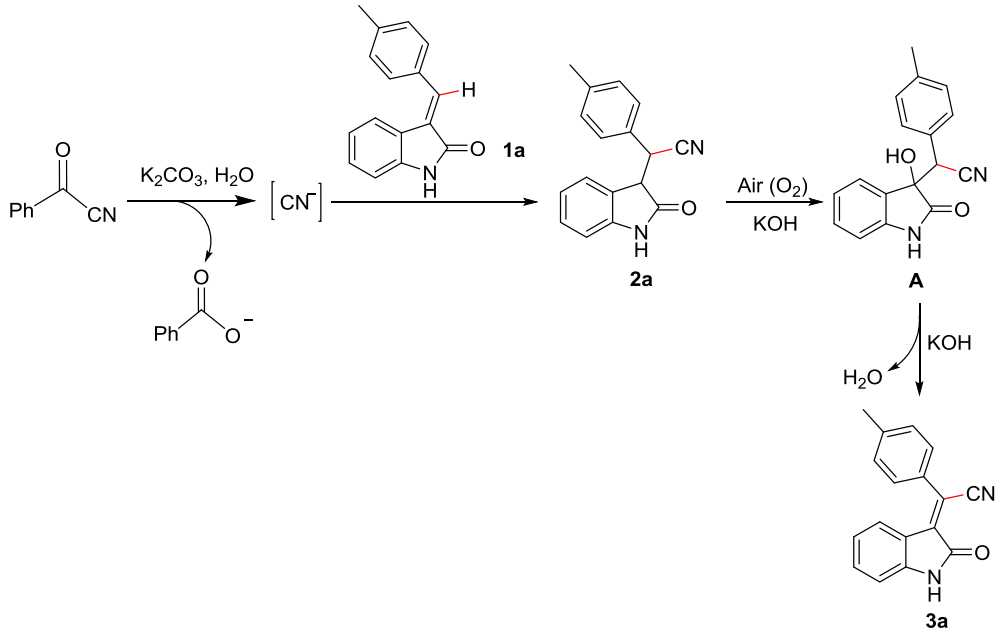

Scheme 5. Proposed mechanism for **3a**.

*4.2.2. (Z)-2-(2-oxoindolin-3-ylidene)-2-(o-tolyl)acetonitrile (**3b**)*

Orange red solid; mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.46 (td, J = 7.3, 1.8 Hz, 1H), 7.41–7.30 (m, 3H), 7.28–7.23 (m, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.70 (td, J = 7.7, 1.0 Hz, 1H), 6.24 (d, J = 7.7 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.14, 142.28, 138.89, 136.17, 133.05, 131.91, 131.33, 130.43, 128.32, 127.17, 125.13, 122.63, 120.66, 116.15, 115.79, 110.87, 19.41. Anal. Calcd. For $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.52; H, 4.64; N, 10.71.

*4.2.3. (Z)-2-(2-oxoindolin-3-ylidene)-2-(m-tolyl)acetonitrile (**3c**)[10]*

Orange red solid; mp 187–189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.45–7.33 (m, 4H), 7.30–7.24 (m, 1H), 7.05 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.73 (td, J = 7.7, 1.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.77, 142.56, 139.45, 137.86, 133.09, 132.65, 131.49, 129.24, 129.14, 125.79, 124.74, 122.17, 120.40, 117.21, 116.73, 111.30, 21.32. Anal. Calcd. For $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.37; H, 4.67; N, 10.79.

*4.2.4. (Z)-2-(2-oxoindolin-3-ylidene)-2-phenylacetonitrile (**3d**)[10]*

Orange red solid; mp 195–197 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.95 (s, 1H), 7.62–7.56 (m, 5H), 7.26 (td, J = 7.8, 1.3 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.68 (td, J = 7.7, 1.0 Hz, 1H), 6.52 (d, J = 7.9 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.80, 144.23, 139.00, 133.72, 133.26, 131.07, 130.08, 128.92, 124.67, 121.97, 120.43, 117.68, 114.91, 111.13. Anal. Calcd. For $C_{16}H_{10}N_2O$: C, 78.03; H, 4.09; N, 11.38. Found: C, 77.94; H, 4.11; N, 11.42.

*4.2.5. (Z)- 2-(2-methoxphenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3e**)*

Orange red solid; mp 159–161 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.93 (s, 1H), 7.58 (ddd, J = 8.9, 7.6, 1.7 Hz, 1H), 7.43 (dd, J = 7.6, 1.7 Hz, 1H), 7.28–7.23 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.69 (t, J = 7.7 Hz, 1H), 6.30 (d, J = 7.9 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.64, 156.78, 144.00, 139.49, 133.56, 132.82, 130.28, 124.72, 122.12, 121.88, 121.19, 120.70, 116.93, 112.95, 111.93, 111.03, 56.37. Anal. Calcd. For $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.83; H, 4.41; N, 10.19.

*4.2.6. (Z)-2-(3-methoxphenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3f**)*

Orange red solid; mp 189–191 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.95 (s, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.26 (t, J = 7.7 Hz, 1H), 7.18–7.12 (m, 3H), 6.83 (d, J = 7.8 Hz, 1H), 6.71 (t, J = 7.7 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.81, 160.35, 144.23, 139.07, 134.45, 133.72, 131.39, 124.90, 122.01, 120.83, 120.43, 117.55, 116.77, 114.64, 114.03, 111.11, 55.89. Anal. Calcd. For $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 74.00; H, 4.35; N, 10.10.

*4.2.7. (Z)-2-(4-methoxyphenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3g**)[10]*

Orange red solid; mp 163–165 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.90 (s, 1H), 7.56 (d, J = 8.7 Hz, 2H), 7.26 (td, J = 7.6, 1.3 Hz, 1H), 7.12 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 6.5 Hz, 1H), 6.73 (td, J = 7.7, 1.1 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.98, 161.46, 144.00, 137.74, 133.42, 130.92, 125.16, 124.39, 121.94, 120.64, 117.90, 115.39, 115.16, 111.03, 55.92. Anal. Calcd. For $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.97; H, 4.37; N, 10.11.

*4.2.8. (Z)-2-(2-hydroxyphenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3h**)*

Orange red solid; mp 169–171 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.89 (s, 1H), 10.22 (s, 1H), 7.41–7.37 (m, 1H), 7.33 (dd, J = 7.7, 1.7 Hz, 1H), 7.25 (td, J = 7.7, 1.2 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 6.96 (td, J = 7.5, 1.1 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.71 (t, J = 7.7 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.77, 155.27, 143.88, 139.14, 133.33, 132.42, 130.20, 124.96, 122.05, 120.91, 120.36, 119.69, 117.14, 117.05, 112.51, 110.87. Anal. Calcd. For $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.35; H, 3.82; N, 10.63.

*4.2.9. (Z)-2-(2-fluorophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3i**)*

Orange red solid; mp 143–145 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.02 (s, 1H), 7.70–7.65 (m, 2H), 7.48 (t, J = 9.5 Hz, 1H), 7.43 (t, J = 8.1 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.73 (t,

$J = 7.7$ Hz, 1H), 6.37 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.35, 159.07 (d, $J = 247.6$ Hz), 144.51, 141.01, 134.28, 133.74 (d, $J = 8.3$ Hz), 131.23, 126.35 (d, $J = 3.3$ Hz), 124.65, 122.34, 120.49 (d, $J = 15.0$ Hz), 120.21, 117.26 (d, $J = 20.5$ Hz), 116.64, 111.30, 107.64. Anal. Calcd. For $C_{16}H_9FN_2O$: C, 72.72; H, 3.43; N, 10.60. Found: C, 72.67; H, 3.44; N, 10.65.

4.2.10. (Z)-2-(3-fluorophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3j**)

Orange red solid; mp 226–228 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.67–7.62 (m, 1H), 7.53 (dt, $J = 9.4$, 2.1 Hz, 1H), 7.48–7.41 (m, 2H), 7.28 (td, $J = 7.8$, 1.2 Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.73 (t, $J = 7.7$ Hz, 1H), 6.48 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.67, 162.86 (d, $J = 245.0$ Hz), 144.39, 139.70, 135.30 (d, $J = 8.1$ Hz), 133.97, 132.46 (d, $J = 8.5$ Hz), 125.22 (d, $J = 2.9$ Hz), 124.86, 122.14, 120.26, 118.01 (d, $J = 20.7$ Hz), 117.31, 116.02 (d, $J = 22.8$ Hz), 113.18 (d, $J = 2.3$ Hz), 111.21. Anal. Calcd. For $C_{16}H_9FN_2O$: C, 72.72; H, 3.43; N, 10.60. Found: C, 72.80; H, 3.40; N, 10.57.

4.2.11. (Z)-2-(4-fluorophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3k**)

Orange red solid; mp 259–261 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.95 (s, 1H), 7.69 (dd, $J = 8.6$, 5.4 Hz, 2H), 7.43 (t, $J = 8.8$ Hz, 2H), 7.27 (t, $J = 8.4$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.73 (t, $J = 7.7$ Hz, 1H), 6.55 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.75, 163.54 (d, $J = 247.2$ Hz), 144.26, 139.25, 133.79, 131.64 (d, $J = 8.7$ Hz), 129.57 (d, $J = 3.0$ Hz), 124.74, 122.10, 120.39, 117.62, 117.27 (d, $J = 22.2$ Hz), 113.85, 111.15. Anal. Calcd. For $C_{16}H_9FN_2O$: C, 72.72; H, 3.43; N, 10.60. Found: C, 72.68; H, 3.45; N, 10.56.

4.2.12. (Z)-2-(2-chlorophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3l**)

Orange red solid; mp 191–193 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.03 (s, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.69–7.62 (m, 2H), 7.57 (td, $J = 7.5$, 1.2 Hz, 1H), 7.28 (t, $J = 7.7$ Hz, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 6.70 (t, $J = 7.7$ Hz, 1H), 6.04 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.36, 144.46, 140.81, 134.23, 132.82, 132.05, 131.43, 131.04, 130.98, 129.27, 124.81, 122.42, 120.23, 116.21, 111.31, 111.15. Anal. Calcd. For $C_{16}H_9ClN_2O$: C, 68.46; H, 3.23; N, 9.98. Found: C, 68.55; H, 3.21; N, 9.95.

4.2.13. (Z)-2-(3-chlorophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3m**)

Orange red solid; mp 196–198 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.74 (s, 1H), 7.66 (d, $J = 7.9$ Hz, 1H), 7.63–7.57 (m, 2H), 7.28 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.73 (t, $J = 7.7$ Hz, 1H), 6.47 (d, $J = 7.7$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.65, 144.43, 139.77, 135.20, 134.63, 134.00, 132.09, 130.96, 128.71, 127.76, 124.80, 122.14, 120.28, 117.33, 113.06, 111.25. Anal. Calcd. For $C_{16}H_9ClN_2O$: C, 68.46; H, 3.23; N, 9.98. Found: C, 68.38; H, 3.25; N, 10.02.

4.2.14. (Z)-2-(4-chlorophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3n**)

Orange red solid; mp 256–258 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.56 (d, $J = 8.6$ Hz, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.29 (t, $J = 7.7$ Hz, 1H), 6.89 (d, $J = 7.9$ Hz, 1H), 6.87 (d, $J = 7.9$ Hz, 1H), 6.78 (t, $J = 7.7$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.71, 144.33, 139.37, 135.85, 133.92, 132.08, 131.04, 130.25, 124.82, 122.17, 120.30, 117.47, 113.56, 111.19. Anal. Calcd. For $C_{16}H_9ClN_2O$: C, 68.46; H, 3.23; N, 9.98. Found: C, 68.50; H, 3.21; N, 9.99.

4.2.15. (Z)-2-(2-bromophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3o**)

Orange red solid; mp 171–173 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.03 (s, 1H), 7.90 (dd, $J = 8.1$, 1.2 Hz, 1H), 7.65 (dd, $J = 7.6$, 1.8 Hz, 1H), 7.61 (td, $J = 7.5$, 1.2 Hz, 1H), 7.54 (td, $J = 7.7$, 1.7 Hz, 1H), 7.28 (td, $J = 7.7$, 1.2 Hz, 1H), 6.85 (d, $J = 7.9$ Hz, 1H), 6.69 (td, $J = 7.7$, 1.0 Hz, 1H), 5.99 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.40, 144.40, 140.51, 134.18, 134.12, 133.43, 132.84, 130.97, 129.79, 124.89, 122.43, 121.80, 120.26, 116.13, 113.01, 111.31. Anal. Calcd. For $C_{16}H_9BrN_2O$: C, 59.10; H, 2.79; N, 8.62. Found: C, 59.16; H, 2.80; N, 8.58.

4.2.16. (Z)-2-(3-bromophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3p**)

Orange red solid; mp 209–211 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.86 (t, $J = 1.8$ Hz, 1H), 7.79 (ddd, $J = 8.0$, 2.1, 1.0 Hz, 1H), 7.63 (dt, $J = 7.8$, 1.3 Hz, 1H), 7.54 (t, $J = 7.9$ Hz, 1H), 7.28 (td, $J = 7.7$, 1.2 Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.73 (td, $J = 7.7$, 1.0 Hz, 1H), 6.48 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.65, 144.44, 139.76, 135.41, 134.00, 133.85, 132.27, 131.48, 128.13, 124.78, 123.00, 122.13, 120.29, 117.35, 113.00, 111.25. Anal. Calcd. For $C_{16}H_9BrN_2O$: C, 59.10; H, 2.79; N, 8.62. Found: C, 59.01; H, 2.81; N, 8.65.

4.2.17. (Z)-2-(4-bromophenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3q**)

Orange red solid; mp 267–269 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.95 (s, 1H), 7.80 (dd, $J = 8.4$, 2.1 Hz, 2H), 7.59 (dd, $J = 8.5$, 2.1 Hz, 2H), 7.29 (t, $J = 7.8$ Hz, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 6.75 (t, $J = 7.6$ Hz, 1H), 6.59 (d, $J = 7.9$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.72, 144.34, 139.30, 133.94, 133.16, 132.47, 131.22, 124.81, 124.62, 122.18, 120.30, 117.40, 113.62, 111.21. Anal. Calcd. For $C_{16}H_9BrN_2O$: C, 59.10; H, 2.79; N, 8.62. Found: C, 59.15; H, 2.77; N, 8.66.

4.2.18. (Z)-2-(2-oxoindolin-3-ylidene)-2-(4-(trifluoromethyl) phenyl)acetonitrile (**3r**)[10]

Orange red solid; mp 237–239 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.00 (s, 1H), 7.97 (d, $J = 8.1$ Hz, 2H), 7.88 (d, $J = 8.5$ Hz, 2H), 7.29 (td, $J = 7.7$, 1.2 Hz, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 6.73 (td, $J = 7.7$, 1.0 Hz, 1H), 6.48 (d, $J = 7.7$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.63, 144.51, 139.95, 137.39, 134.17, 131.19, 130.98, 130.17, 127.10 (q, $J = 3.7$ Hz), 125.15, 124.87, 123.34, 122.23, 120.13, 117.33, 113.08, 111.28. Anal. Calcd. For $C_{17}H_9F_3N_2O$: C, 64.97; H, 2.89; N, 8.91. Found: C, 65.09; H, 2.87; N, 8.87.

4.2.19. (Z)-2-(2-oxoindolin-3-ylidene)-2-(thiophen-3-yl) acetonitrile (**3s**)[10]

Reddish brown solid; mp 179–181 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.95 (s, 1H), 7.97 (dd, $J = 5.1$, 1.2 Hz, 1H), 7.60 (dd, $J = 3.6$, 1.2 Hz, 1H), 7.31 (td, $J = 7.7$, 1.2 Hz, 1H), 7.27 (dd, $J = 5.1$, 3.6 Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 6.80 (td, $J = 7.7$, 1.1 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.74, 144.31, 138.93, 134.17, 133.94, 131.97, 131.83, 128.98, 124.52, 122.09, 120.32, 117.20, 111.19, 108.07. Anal. Calcd. For $C_{14}H_8N_2OS$: C, 66.65; H, 3.20; N, 11.10. Found: C, 66.69; H, 3.19; N, 11.05.

4.2.20. (Z)-2-(naphthalen-2-yl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3t**)

Orange red solid; mp 210–212 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.01 (s, 1H), 8.17 (d, $J = 8.3$ Hz, 1H), 8.09 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.74 (dd, $J = 7.1$, 1.2 Hz, 1H), 7.68 (dd, $J = 8.2$, 7.1 Hz, 1H), 7.62 (ddd, $J = 8.0$, 6.7, 1.2 Hz, 1H), 7.56 (ddd, $J = 8.2$, 6.8, 1.3 Hz, 1H), 7.17 (td, $J = 7.7$, 1.2 Hz, 1H), 6.82 (d, $J = 7.7$ Hz, 1H), 6.45 (td, $J = 7.7$, 1.0 Hz, 1H), 5.74 (d, $J = 6.7$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.59, 144.45, 141.11, 133.88, 133.70, 131.13, 130.19,

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129.59, 129.41, 128.25, 127.56, 127.53, 126.59, 125.08, 124.27, 121.99, 120.47, 117.39, 112.50, 111.08. Anal. Calcd. For $C_{20}H_{12}N_2O$: C, 81.07; H, 4.08; N, 9.45. Found: C, 81.16; H, 4.07; N, 9.40.

*4.2.21. (Z)-2-(2,5-dimethoxyphenyl)-2-(2-oxoindolin-3-ylidene) acetonitrile (**3u**)*

Orange red solid; mp 202–204 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.93 (s, 1H), 7.26 (td, J = 7.7, 1.2 Hz, 1H), 7.19 (d, J = 9.1 Hz, 1H), 7.13 (dd, J = 9.1, 3.1 Hz, 1H), 7.05 (d, J = 3.1 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.73 (td, J = 7.7, 1.0 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.65, 154.07, 150.70, 144.02, 139.59, 133.58, 124.85, 122.18, 121.74, 120.69, 117.76, 116.90, 115.28, 114.23, 111.59, 111.02, 56.74, 56.20. Anal. Calcd. For $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15. Found: C, 70.47; H, 4.63; N, 9.19.

*4.2.22. (Z)-2-(2-hydroxy-3-methoxyphenyl)-2-(2-oxoindolin-3-ylidene)acetonitrile (**3v**)*

Orange red solid; mp 232–234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.23 (td, J = 7.7, 1.5 Hz, 1H), 7.03–6.97 (m, 3H), 6.91 (d, J = 7.9 Hz, 1H), 6.76–6.65 (m, 2H), 3.97 (s, 3H), 3.89 (s, 1H). ^{13}C NMR (150 MHz, $CHCl_3$) δ 166.36, 147.30, 143.78, 142.27, 138.67, 132.79, 125.29, 122.29, 121.47, 120.83, 120.72, 118.56, 116.41, 112.49, 112.22, 110.72, 56.28. Anal. Calcd. For $C_{17}H_{12}N_2O_3$: C, 69.86; H, 4.14; N, 9.58. Found: C, 69.78; H, 4.15; N, 9.62.

*4.2.23. (Z)-2-(5-chloro-2-hydroxyphenyl)-2-(2-oxoindolin-3-ylidene)acetonitrile (**3w**)*

Orange red solid; mp 181–183 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.95 (s, 1H), 10.58 (s, 1H), 7.50–7.41 (m, 2H), 7.28 (td, J = 7.7, 1.2 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.77 (td, J = 7.7, 1.1 Hz, 1H), 6.44 (d, J = 7.9 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.63, 154.34, 144.09, 139.85, 133.66, 132.06, 129.56, 124.95, 123.62, 122.24, 121.22, 120.70, 118.78, 116.85, 111.03, 110.65. Anal. Calcd. For $C_{16}H_9ClN_2O_2$: C, 64.77; H, 3.06; N, 9.44. Found: C, 64.85; H, 3.04; N, 9.40.

*4.2.24. (Z)-2-(6-chloro-2-oxoindolin-3-ylidene)-2-phenylacetonitrile (**4a**)*

Orange red solid; mp 188–190 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.11 (s, 1H), 7.59–7.58 (m, 5H), 6.85 (d, J = 1.9 Hz, 1H), 6.77 (dd, J = 8.5, 2.0 Hz, 1H), 6.52 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.78, 145.41, 137.85, 137.80, 132.98, 131.27, 130.14, 128.93, 125.82, 121.90, 119.36, 117.53, 115.51, 111.10. Anal. Calcd. For $C_{16}H_9ClN_2O$: C, 68.46; H, 3.23; N, 9.98. Found: C, 68.37; H, 3.25; N, 10.01.

*4.2.25. (Z)-2-(5-bromo-2-oxoindolin-3-ylidene)-2-phenylacetonitrile (**4b**)*[10]

Orange red solid; mp 267–269 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.09 (s, 1H), 7.62–7.60 (m, 5H), 7.43 (dd, J = 8.4, 2.0 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.52 (d, J = 2.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.39, 143.32, 138.13, 135.79, 132.85, 131.43, 130.17, 128.87, 126.91, 122.51, 117.29, 116.46, 113.30, 113.04. Anal. Calcd. For $C_{16}H_9BrN_2O$: C, 59.10; H, 2.79; N, 8.62. Found: C, 59.22; H, 2.78; N, 8.58.

*4.2.26. (Z)-2-(4-chlorophenyl)-2-(5-nitro-2-oxoindolin-3-ylidene) acetonitrile (**4c**)*

Orange red solid; mp 289–291 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.69 (s, 1H), 8.20 (dd, J = 8.8, 2.3 Hz, 1H), 7.73 (s, 4H), 7.40 (d, J = 2.2 Hz, 1H), 7.03 (d, J = 8.7 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.99, 149.56, 142.10, 137.70, 136.55, 131.28, 131.10, 130.40, 129.54, 120.66, 119.82, 116.87, 116.51, 111.31. Anal. Calcd. For $C_{16}H_8ClN_3O_3$: C, 59.00; H, 2.48; N, 12.90. Found: C, 58.90; H, 2.50; N, 12.96.

*4.2.27. (Z)-2-(4-methoxyphenyl)-2-(2-oxo-1-phenylindolin-3-ylidene)acetonitrile (**4d**)*

Orange red solid; mp 207–209 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.68 (d, J = 8.8 Hz, 2H), 7.64 (t, J = 7.8 Hz, 2H), 7.55–7.50 (m, 3H), 7.35 (td, J = 7.8, 1.4 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 7.7 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 164.12, 161.68, 144.80, 136.48, 133.96, 133.40, 130.99, 130.18, 128.93, 127.37, 126.92, 124.42, 123.11, 120.21, 117.80, 116.42, 115.55, 110.21, 55.98. Anal. Calcd. For $C_{23}H_{16}N_2O_2$: C, 78.39; H, 4.58; N, 7.95. Found: C, 78.46; H, 4.57; N, 7.92.

*4.2.28. (Z)-2-(4-bromophenyl)-2-(2-oxo-1-phenylindolin-3-ylidene)acetonitrile (**4e**)*

Orange red solid; mp 169–171 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.84 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.59 (t, J = 7.8 Hz, 2H), 7.52–7.44 (m, 3H), 7.32 (t, J = 8.3 Hz, 1H), 6.88 (t, J = 7.7 Hz, 1H), 6.72 (d, J = 8.5 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.88, 145.12, 138.13, 133.90, 133.81, 133.31, 132.33, 131.20, 130.22, 129.01, 127.31, 124.89, 124.87, 123.33, 119.86, 117.32, 114.78, 110.36. Anal. Calcd. For $C_{22}H_{13}BrN_2O$: C, 65.85; H, 3.27; N, 6.98. Found: C, 65.77; H, 3.28; N, 7.02.

4.3. The isolation of 2a from the reaction system

The mixture of **1a** (0.5 mmol), benzoyl cyanide (0.6 mmol), potassium carbonate (0.5 mmol), potassium hydroxide (0.5 mmol) and water (1.0 mmol) in acetonitrile (5 mL) was stirred at 80 °C for 3 h under nitrogen atmosphere. The reaction was monitored by TLC. After the completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL), and the resulting solution was washed with saturated brine (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v 3:1) as eluent to give **2a** (the mixture of diastereoisomers in 1:1 ratio). The analytical data for products are given below.

*4.3.1. (R/S)-2-(2-oxoindolin-3-yl)-2-(p-tolyl)acetonitrile (**2a**)*

Light yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.79 (s, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.27–7.19 (m, 5H), 7.09 (td, J = 7.6, 1.1 Hz, 1H), 6.99 (d, J = 8.1 Hz, 2H), 6.96–6.88 (m, 4H), 6.69 (d, J = 7.8 Hz, 1H), 6.53 (d, J = 7.5 Hz, 1H), 4.76 (d, J = 4.0 Hz, 1H), 4.61 (d, J = 4.2 Hz, 1H), 4.02 (d, J = 4.1 Hz, 1H), 3.86 (d, J = 4.1 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.54, 174.91, 141.71, 141.34, 138.67, 138.51, 129.86, 129.37, 129.20, 129.14, 128.42, 127.70, 127.24, 125.40, 125.36, 124.32, 124.26, 122.79, 122.53, 119.74, 117.08, 110.25, 109.90, 50.13, 49.04, 38.46, 36.95, 21.12, 21.02.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.01.050.

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