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Copper(II)-Catalyzed Tandem Synthesis of Substituted 3-Methyleneisoindolin-1-ones

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An efficient strategy for the synthesis of a variety of 3-methyleneisoindolin-1-ones has been developed. The reaction proceeded from coupling of 2-iodobenzamides (or 2-bromobenzamides) and terminal alkynes via $Cu(OAc)_2•H_2O$/2,2'-biimidazole catalyzed in DMF at 60 ℃ and subsequent additive cyclization produced substituted 3-methyleneisoindolin-1-ones in good to excellent yields.

Keywords 3-methyleneisoindolin-1-ones, $Cu(OAc)_2•H_2O$, 2,2'-biimidazole, additive cyclization

Introduction

The 3-methyleneisoindolin-1-one is a core structure of numerous natural products or designed pharmaceutical molecules,[1] which have attracted much attention due to their unique biological activities, such as anticancer activity, antibacterial activity, *etc*. For example, compound **1**, an alkaloid containing the isoindolinone moiety, isolated from a *Saccharothrise* sp. has antimicrobial, hypotensive and cytotoxic activities.[2] Compound **2** exhibited sedative activity[1h] (Figure 1). Considerable efforts have been directed toward the synthesis of 3-methyleneisoindolin-1-ones.

3-Methyleneisoindolin-1-ones have been prepared via using phthalimides as starting materials, which undergo Wittig reaction[3] or addition of organometallic reagents and subsequent dehydration[4] to give the target molecules, as well as Grignard[5] or lithiation[6] or miscall-aneous[7,8] procedures, Diels-Alder reactions,[9] rearrangement reactions,[10] and photochemical reactions.[11] The reduction of *N*-substituted phthalimides[12] and the condensation of phthalaldehyde[13] also afford 3-methyleneisoindolin-1-ones. Besides the above classical methods, efficient methods for the synthesis of various 3-methyleneisoindolin-1-ones catalyzed by metal complexes have been reported. Cobalt and rhodium carbonyl complexes can be used as the catalysts to synthesize 3-methyleneisoindolin-1-ones.[14] Several examples of palladium catalysis have appeared.[15-19] But copper-catalyzed syntheses of 3-methyleneisoindolin-1-ones were rare.[20] Herein, we wish to report a direct and efficient approach to 3-methyleneisoindolin-1-ones through the coupling reaction of 2-iodobenzamides (or 2-bromobenzamides) and terminal alkynes catalyzed by $Cu(OAc)_2•H_2O$/2,2'-biimidazole.

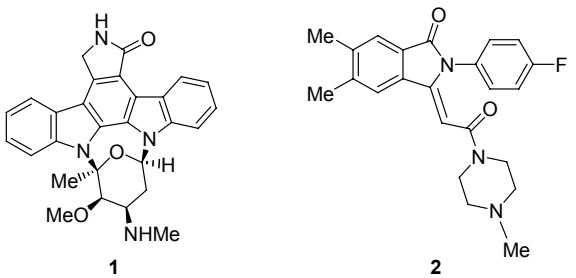

Figure 1 The structure of compound **1** and compound **2**.

Results and Discussion

Initially, the reaction between *N*-phenyl-2-iodobenzamide (**3a**) and phenylacetylene (**4a**) was selected as a model reaction to screen the optimal reaction conditions (Table 1). We explored the effects of the solvent. The results revealed that the use of DMF as solvent achieved the best result with K_2CO_3 as base under argon at 60 ℃ for 24 h in the presence of $Cu(OAc)_2•H_2O$/2,2'-biimidazole, achieving the desired product **5a** in 88% yield (Table 1, Entry 4). Similar result was observed when the solvent was changed to DMSO (Table 1, Entry 1). However, poor yields were obtained if the reaction was carried out in *i*-PrOH (Table 1, Entry 2) and the fact that no desired product was isolated in the presence of toluene (Table 1, Entry 3). Next, the base was further investigated. Switching base to Cs_2CO_3 and K_3PO_4 had little influence to this reaction (Table 1, Entries 5 and 6). Replacing K_2CO_3 with KOH (Table 1, Entry 8) resulted in poorer yields, whereas no reaction was observed in NEt_3

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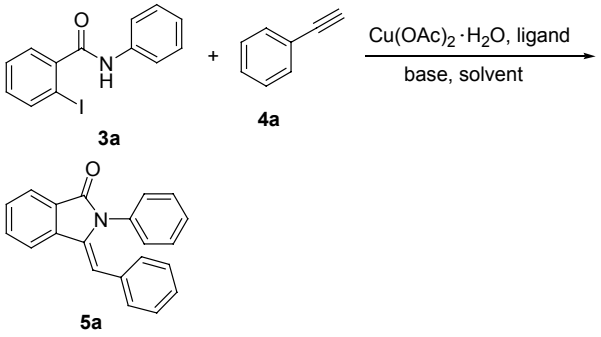
(Table 1, Entry 7). Then, the influences of temperature and time on the reaction were examined. The yield unchanged when temperature decreased to 80 ℃ or 60 ℃ from 100 ℃ (Table 1, Entries 10 and 11). However, a moderate yield was produced at 40 ℃ (Table 1, Entry 13). The yield was decreased to some extent when the reaction was carried out at the elevated temperature (Table 1, Entry 9). Extending the time to 48 h did not improve yield (Table 1, Entry 14). An 80% yield was produced in the absence of argon (Table 1, Entry 12).

Table 1 Coupling of *N*-phenyl-2-iodobenzamide with phenylacetylene under different conditions[a]



Entry	Base	Solvent	Temp (℃)/Time (h)	Yield[b]%
1	K_2CO_3	DMSO	100/24	82
2	K_2CO_3	*i*-PrOH	100/24	15
3	K_2CO_3	toluene	100/24	trace
4	K_2CO_3	DMF	100/24	88
5	Cs_2CO_3	DMF0	100/24	75
6	K_3PO_4	DMF	100/24	82
7	Et_3N	DMF	100/24	trace
8	KOH	DMF	100/24	55
9	K_2CO_3	DMF	120/24	83
10	K_2CO_3	DMF	80/24	88
11	K_2CO_3	DMF	60/24	88
12[c]	K_2CO_3	DMF	60/24	80
13	K_2CO_3	DMF	40/24	62
14	K_2CO_3	DMF	60/48	88

[a] All reactions were carried out using 1.0 mmol *N*-phenyl-2-iodobenzamide (**3a**), 1.2 mmol phenylacetylene (**4a**), 2.0 mmol base, 0.2 mmol $Cu(OAc)_2•H_2O$, 0.1 mmol 2,2'-biimidazole and 2 mL solvent. [b] Isolated yield. [c] The reaction was carried out in the air.

Finally, we optimized the catalyst, ligands and their loading. The results are summarized in Table 2. As evident from the satisfactory yields that were observed when **L1**, **L2**, **L3**, **L4** (Figure 2) and no ligand were used (Table 2, Entries 1—5), but **L1** gave the highest product yield of 88%. 20 mol% $Cu(OAc)_2•H_2O$ and 10 mol% **L1** were found to be sufficient to promote the reaction and increased amounts of the catalyst and ligand did not lead to any changes in the reaction yield (Table 2, Entries 1, 6 and 7). Moderate yields were obtained when the catalyst was changed to CuI or $CuSO_4•5H_2O$ or $CuCl_2•H_2O$ (Table 2, Entries 8—10), whereas no reaction was observed in $FeCl_3•6H_2O$ (Table 2, Entry 11). Based on these results, we chose $Cu(OAc)_2•H_2O$ as the catalyst, **L1** as the ligand, K_2CO_3 as the base, and DMF as the solvent under argon in the subsequent studies.

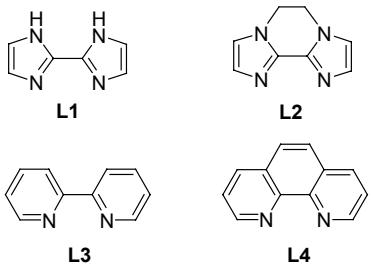
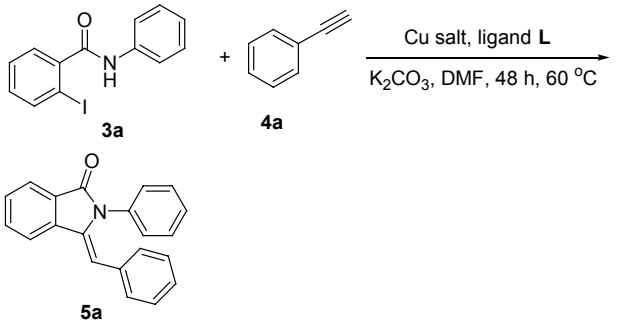


Figure 2 Ligands used in the study.

Table 2 Coupling of *N*-phenyl-2-iodobenzamide with phenylacetylene under different conditions[a]



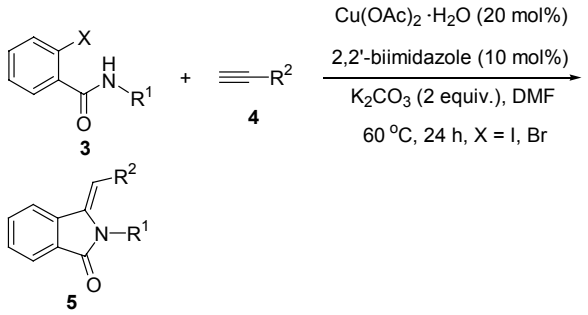
Entry	Catalyst	Ligand	Cu∶L (mmol%)	Yield[b]/%
1	$Cu(OAc)_2•H_2O$	**L1**	20∶10	88
2	$Cu(OAc)_2•H_2O$	**L2**	20∶10	73
3	$Cu(OAc)_2•H_2O$	**L3**	20∶10	68
4	$Cu(OAc)_2•H_2O$	**L4**	20∶10	67
5	$Cu(OAc)_2•H_2O$	No	20∶10	70
6	$Cu(OAc)_2•H_2O$	**L1**	40∶20	88
7	$Cu(OAc)_2•H_2O$	**L1**	10∶5	82
8	CuI	**L1**	20∶10	75
9	$CuSO_4•5H_2O$	**L1**	20∶10	78
10	$CuCl_2•H_2O$	**L1**	20∶10	78
11	$FeCl_3•6H_2O$	**L1**	20∶10	NR

[a] All reactions were carried out using 1.0 mmol *N*-phenyl-2-iodobenzamide (**3a**), 1.2 mmol phenylacetylene (**4a**), 2.0 mmol K_2CO_3, Cu catalyst, ligand **L** and 2 mL DMF under 60 ℃, 48 h, in argon. [b] Isolated yield.

With the optimal conditions in hand, we explored the scope of substrates (Table 3). A wide range of *N*-substituents were tolerated, including benzyl, allyl, phenyl, proton, and alkyl groups, systems bearing electron-donating and electron-withdrawing substituents performed well (Table 3, Entries 1—13 and 16). Some functionalized arylacetylenes also worked well, giving the corre-

sponding products in good yields (Table 3, Entries 14 and 15). This reaction was also effective with 2-bromobenzamides, but higher temperature (100 ℃) was required (Table 3, Entries 17—21). Furthermore, this one-pot reaction was highly stereoselective, and gave the *Z*-isomer as the main product.

Table 3 Copper-catalyzed tandem synthesis of substituted 3-methyleneisoindolin-1-one[a]



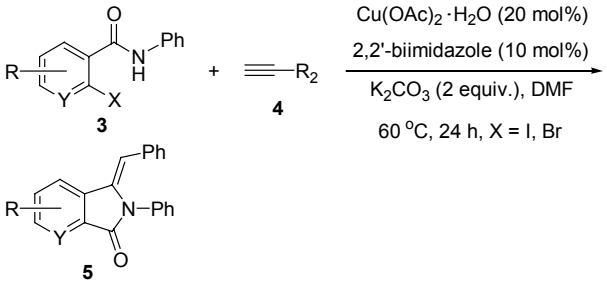
Entry	X	R^1	R^2	Product	Yield[b]/%
1	I	Ph	Ph	**5a**	89
2	I	Bn	Ph	**5b**	89
3	I	2-ClC_6H_4	Ph	**5c**	88
4	I	3-ClC_6H_4	Ph	**5d**	95
5	I	4-ClC_6H_4	Ph	**5e**	94
6	I	2-MeC_6H_4	Ph	**5f**	92
7	I	4-MeC_6H_4	Ph	**5g**	84
8	I	4-$MeOC_6H_4$	Ph	**5h**	90
9	I	*n*-C_4H_9	Ph	**5i**	77
10	I	*n*-C_6H_{13}	Ph	**5j**	54
11	I	4-OCH_2PhPh	Ph	**5k**	95
12	I	1-naphthyl	Ph	**5l**	87
13	I	2,6-$Me_2C_6H_4$	Ph	**5m**	98
14	I	Ph	4-$MeOC_6H_4$	**5n**	90
15	I	Ph	4-EtC_6H_4	**5o**	86
16	I	H	Ph	**5p**	98
17[c]	Br	Ph	Ph	**5a**	82
18[c]	Br	3-ClC_6H_4	Ph	**5d**	88
19[c]	Br	4-ClC_6H_4	Ph	**5e**	90
20[c]	Br	2-MeC_6H_4	Ph	**5f**	85
21[c]	Br	4-$MeOC_6H_4$	Ph	**5h**	87

[a] All reactions were carried out using 1.0 mmol *N*-substituted-2-iodobenzamide (**3**), 1.2 mmol arylacetylenes (**4**), 2.0 mmol K_2CO_3, 0.2 mmol $Cu(OAc)_2$•H_2O, 0.1 mmol ligand **L1** and 2 mL DMF under 60 ℃, 24 h, in argon. [b] Isolated yield. [c] The reaction was carried out in DMF at 100 ℃.

Notably, *N*-phenyl-2-iodobenzamide and *N*-phenyl-2-bromobenzamide with various substituents provided high yields of desired products (Table 4, Entries 1—3). However, *N*-phenyl-2-bromo-nicotinamide provided only a moderate yield (Table 4, Entry 4).

On the basis of the above results, we proposed the following reaction mechanism for this cascade sequence

Table 4 Copper-catalyzed tandem synthesis of substituted 3-methyleneisoindolin-1-one[a]



Entry	X	Y	R	Product	Yield[b]/%
1	I	C	5-Me	**5q**	90
2	I	C	4-Cl	**5r**	94
3	Br	C	4-Cl	**5r**	80
4	Br	N	H	**5s**	49

[a] All reactions were carried out using 1.0 mmol *N*-substituted-2-iodobenzamide (**3**), 1.2 mmol phenylacetylene (**4a**), 2.0 mmol K_2CO_3, 0.2 mmol $Cu(OAc)_2$•H_2O, 0.1 mmol ligand **L1** and 2 mL DMF under 60 ℃, 24 h, in argon. [b] Isolated yield.

(Scheme 1). We envisaged that coupling of **3a** with **4a** afforded **A** by Sonogashira reaction, then **A** might undergo deprotonation of the amide moiety and subsequent addition to C—C triple bond under the action of the copper complex (as intermediate **B**) to afford intermediate **C**, then protonation of this intermediate afforded copper salt and released the product **5a**. Single crystal X-ray analysis conclusively confirmed the structure of the isolated (*Z*)-3-benzylidene-2-(4-chlorophenyl)isoindolin-1-one (**5e**) and an ORTEP diagram of **5e** was shown in Figure 3. This result indicated that the $Cu(OAc)_2$•H_2O-mediated additive cyclization of the amide moiety to the triple bond took place in a 5-*exo* manner exclusively, which is different with base or Lewis acid-mediated additive cyclization (both 5-*exo* and 6-*endo* attacks were observed).[15f]

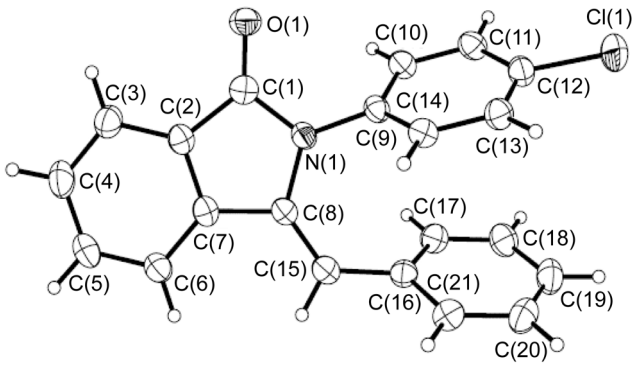
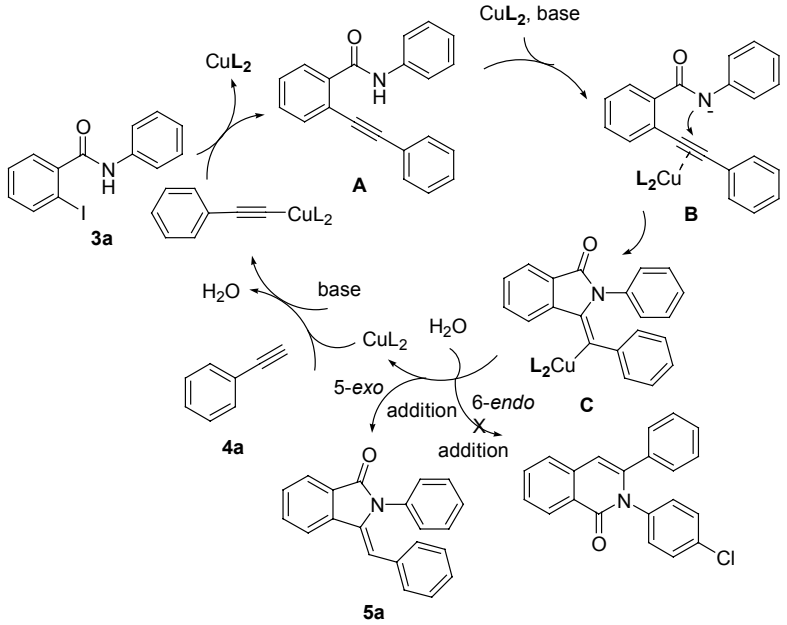


Figure 3 ORTEP diagram of **5e**.

Conclusions

In conclusion, we have developed a simple and rapid $Cu(OAc)_2$•H_2O/2,2'-biimidazole catalyzed coupling/additive cyclization domino reaction process for the construction of substituted 3-methyleneisoindolin-1-ones in

Scheme 1 Tentative mechanism for domino reaction catalyzed by copper(II)



good to excellent yields from various 2-halobenzamides and terminal alkynes. Considering the relatively inexpensive catalytic system and the commercial availability of the starting materials, it should be of great benefit for organic synthesis.

Experimental

General

Column chromatograph was performed with silica gel (300－400 mesh) and analytical TLC on silica 60-F254. ^{1}H NMR spectra were measured on an Inova-400 MHz spectrometer in $CDCl_3$ (100 MHz, ^{13}C NMR) with chemical shift (δ) relative to TMS as internal standard. HRMS was determined by using micromass OA-TOF instrument. All of the reagents were used directly as obtained commercially. Some alkynes were prepared according to literature methods,[21,22] purified by chromatography.

General procedure for the synthesis of substituted 3-methyleneisoindolin-1-ones

A sealed tube was charged with a magnetic stirrer and 2-iodobenzamide (1.0 mmol), phenylacetylene (1.2 mmol), $Cu(OAc)_2$•H_2O (0.2 mmol), 2,2'-biimidazole (0.1 mmol), K_2CO_3 (2.0 mmol), DMF (2.0 mL). The reaction mixture was stirred under argon at 60 ℃ for 24 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel using ethyl acetate/petroleum ether as eluent to afford substituted 3-methyleneisoindolin-1-ones.

(*Z*)-3-Benzylidene-2-phenylisoindolin-1-one (5a)[15f] White solid, m.p. 197－198 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, J=7.5 Hz, 1H), 7.87 (d, J=7.8 Hz, 1H), 7.68 (t, J=7.2 Hz, 1H), 7.55 (t, J=7.4 Hz, 1H), 7.08 (s, 5H), 6.83－6.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 139.0, 136.3, 134.7, 133.9, 132.8, 129.6, 129.5, 128.6, 128.2, 127.6, 127.1, 127.0, 124.7, 119.6, 108.7; HRMS calcd for $C_{21}H_{15}NO$ (M^+) 297.1154, found 297.1154.

(*Z*)-3-Benzylidene-2-(4-chlorophenyl)isoindolin-1-one (5e)[23] White solid, m.p. 142－144 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J=7.6 Hz, 1H), 7.86 (d, J=7.8 Hz, 1H), 7.69 (t, J=7.5 Hz, 1H), 7.56 (t, J=7.4 Hz, 1H), 7.10－6.92 (m, 7H), 6.87 (d, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.0, 138.7, 134.6, 134.4, 133.5, 132.9, 132.8, 129.6, 129.4, 128.6, 128.4, 127.8, 127.6, 127.1, 124.2, 119.7, 108.0; HRMS calcd for $C_{21}H_{14}ClNO$ (M^+) 331.0764, found 331.0764.

(*Z*)-3-Benzylidene-2-butylisoindolin-1-one (5i)[20] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=7.5 Hz, 1H), 7.38－7.45 (m, 6H), 7.28－7.29 (m, 2H), 6.54 (s, 1H), 3.89 (t, J=7.4 Hz, 2H), 1.70－1.77 (m, 2H), 1.40－1.48 (m, 2H), 0.99 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.6, 137.3, 133.9, 130.7, 128.5, 128.4, 127.9, 127.6, 127.0, 126.5, 122.1, 118.2, 105.5, 40.1, 29.2, 18.6, 12.4; HRMS calcd for $C_{19}H_{19}NO$ (M^+) 277.1467, found 277.1466.

(*Z*)-3-Benzylidene-2-(4-(benzyloxy)phenyl)isoindolin-1-one (5k) Yellow solid, m.p. 124－126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93－7.95 (m, 1H), 7.83－7.86 (m, 1H), 7.64－7.67 (m, 1H), 7.54－7.57 (m, 1H), 7.31－7.38 (m, 5H), 6.70－6.93 (m, 10H), 4.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.7, 158.9, 139.0, 137.4, 135.1, 134.1, 132.8, 129.6, 129.4, 129.0, 128.7, 128.4, 128.3, 127.6, 127.4, 126.1, 124.2, 120.1, 115.2, 108.0, 70.5; HRMS calcd for $C_{28}H_{21}NO_2$ (M^+) 403.1572, found 403.1572.

(*Z*)-3-Benzylidene-2-(2,6-dimethylphenyl)isoindolin-1-one (5m)[24] White solid, m.p. 115－116 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J=7.5 Hz, 1H), 7.86 (d, J=7.7 Hz, 1H), 7.69 (t, J=7.1 Hz, 1H), 7.56 (t,

J=7.5 Hz, 1H), 6.70−6.99 (m, 9H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.7, 139.0, 136.4, 134.9, 133.9, 133.2, 132.6, 129.6, 128.8, 128.5, 128.4, 127.8, 126.7, 124.2, 120.1, 108.1, 18.6; HRMS calcd for $C_{23}H_{19}NO$ (M^+) 325.1467, found 325.1468.

(*Z*)-3-(4-Ethylbenzylidene)-2-phenylisoindolin-1-one (5o) White solid, m.p. 130−132 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J=7.4 Hz, 1H), 7.85 (d, J=7.6 Hz, 1H), 7.67 (t, J=7.6 Hz, 1H), 7.54 (t, J=7.4 Hz, 1H), 7.07 (s, 5H), 6.82 (s, 1H), 6.72−6.78 (m, 4H), 2.45−2.50 (m, 2H), 1.11 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.2, 143.9, 138.1, 136.3, 134.2, 132.9, 131.6, 129.7, 129.3, 128.9, 127.6, 127.3, 126.6, 126.2, 124.1, 119.2, 108.0, 28.8, 16.7; HRMS calcd for $C_{23}H_{19}NO$ (M^+) 325.1467, found 325.1466.

(*Z*)-3-Benzylidene-6-methyl-2-phenylisoindolin-1-one (5q) White solid, m.p. 179−180 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.01 (d, J=7.6 Hz, 1H), 7.63 (s, 1H), 7.57 (d, J=7.2 Hz, 1H), 7.08 (s, 5H), 7.00 (s, 1H), 6.77−6.94 (m, 5H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 167.85, 140.15, 136.84, 136.72, 134.50, 134.31, 129.73, 128.63, 127.94, 127.71, 127.20, 127.00, 123.76, 120.79, 107.96, 21.71; HRMS calcd for $C_{22}H_{17}NO$ (M^+) 311.1310, found 311.1215.

(*Z*)-3-Benzylidene-5-chloro-2-phenylisoindolin-1-one (5r) Pale green solid, m.p. 177−178 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J=8.1 Hz, 1H), 7.82 (s, 1H), 7.51 (dd, J=8.1, 1.2 Hz, 1H), 7.14−7.04 (m, 5H), 7.00 (t, J=7.2 Hz, 1H), 6.93 (t, J=7.5 Hz, 2H), 6.85 (d, J=7.5 Hz, 2H), 6.80 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.42, 138.59, 137.35, 134.03, 131.66, 131.52, 128.04, 127.57, 126.71, 125.74, 125.55, 125.36, 124.55, 123.59, 118.26, 107.30; HRMS calcd for $C_{21}H_{14}ClNO$ (M^+) 331.1764, found 331.1665.

(*Z*)-5-Benzylidene-6-phenyl-5,6-dihydropyrrolo[3,4-*b*]pyridin-7-one (5s) White solid, m.p. 130−132 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.86 (d, J=4.7 Hz, 1H), 8.22 (d, J=7.7 Hz, 1H), 7.46 (dd, J=8.4, 5.7 Hz, 2H), 7.13 (s, 5H), 6.94 (dt, J=17.5, 7.2 Hz, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.93, 156.99, 153.95, 135.55, 133.41, 133.24, 132.23, 129.61, 128.61, 127.51, 127.33, 124.16, 121.68, 110.41; HRMS calcd for $C_{20}H_{14}N_2O$ (M^+) 298.1106, found 298.1013.

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