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ARTICLE

锡粉促进下 3-芳基-3-羟基-2-氧化吲哚的烯丙基化反应研究

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摘要 探索了锡粉促进下 3-羟基-2-氧化吲哚与烯丙基溴的偶联反应, 实现了锡粉促进下的亲核取代反应, 拓展了锡粉促进下反应类型, 并为合成具有潜在生物活性的 3,3-二取代-2-氧吲哚提供了简便的方法. 该方法具有操作简单、成本低廉等优点.

关键词 硫酸; 催化; 炔丙醇; 亲核取代

Study on Tin Powder-Promoted Allylation of 3-Aryl-3-hydroxy-2-oxindoles

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Abstract An efficient tin-powder-promoted C—C coupling reaction of 3-aryl-3-hydroxy-2-oxindoles with allyl bromide was disclosed, which makes tin-powder-promoted reactions beyond 1,2-addition to C=O or C=N double bounds, and provides a convenient and facile protocol for the synthesis of potentially bioactive 3,3'-disubstituted-2-oxindoles in good to excellent yields. The method is highly efficient and environmentally benign with low cost and concise manipulation.

Keywords tin powder; 3-hydroxy-2-oxindoles; allylation

1 Introduction

Organotin compounds, an very important class of organometallic compounds, have been intensively applied in organic synthesis because of their good stabilities towards heat, hydrolysis and oxidation, tolerance of functional groups and high selectivity in organic reactions.[1] However, most of the organotin compounds are toxic, and are not atom economic in the reactions.[2] For instance, the commonly used tributyltin compounds Bu_3SnR can only transfer the R groups into the product molecules, meanwhile, the Bu_3Sn-moiety is discarded as a by-product.[3] This disadvantage limits their application on large scale in industrial. In 1981, Mukaiyama *et al.*[4] reported for that tin powder could promote the allylation of aldehydes or ketones with allyl bromide to give the corresponding allylic alcohols. This method not only keeps the advantages of organotin reagents but also avoids some of their disadvantages. Afterwards, many studies on tin-powder-promoted allylations were carried out. Up to now, tin-powder-promoted allylation reactions mainly involve the 1,2-addition reactions of aldehydes, ketones and imines with *in situ* generated allyltin bromide.[5] (Schemes 1a and 1b). Enol ethers and nitroalkenes were also used as substrates to react with allyl bromide in the presence of tin powder, but the active intermediates were still the *in situ* generated aldehydes or ketones.[5] Diselenides and disulfides were reported to perform the allylation with allyl bromide and tin powder[7] (Scheme 1c). In view of the advantages of tin-powder-promoted reactions, our group has been committed to the allylation reactions promoted by tin powder, and a series of allylic compounds and nitrogen heterocycles were synthesized.[8] These works greatly extend the application of tin-powder-promoted reactions in organic synthesis. However, until now, tin-powder-promoted reactions mainly limited to the

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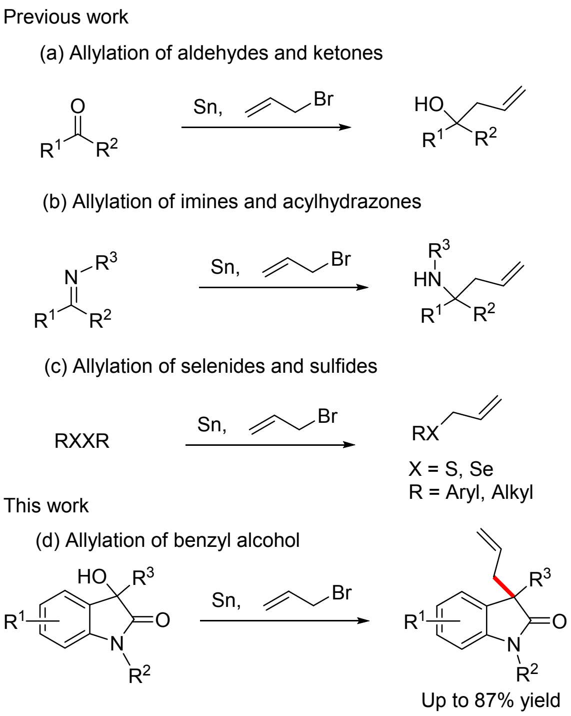
allylation of C=O or C=N double bounds, and there was no report to the other functional groups. In our research works, we find that the *in situ* generated allyltin bromides are stable in solid state in the absence of solvent. We envision that this property would make them to react with other functional groups, and extend the tin-powder-promoted reactions beyond 1,2-addition to C=O or C=N double bounds. As we know, carbocations are very important active intermediates in organic reactions and have always played important roles in organic synthesis.[9] In the carbocation family, benzylic carbocations are relatively stable and easily formed. Therefore, we would like to investigate the C—C coupling reaction of solid allyltin bromide with *in situ* formed benzylic carbocations. Herein, the reaction of 3-aryl-3-hydroxy-2-oxindoles with the *in situ* formed allyltin bromide to afford 3,3-disubstituted-2-oxindole derivatives (Scheme 1d) was reported.

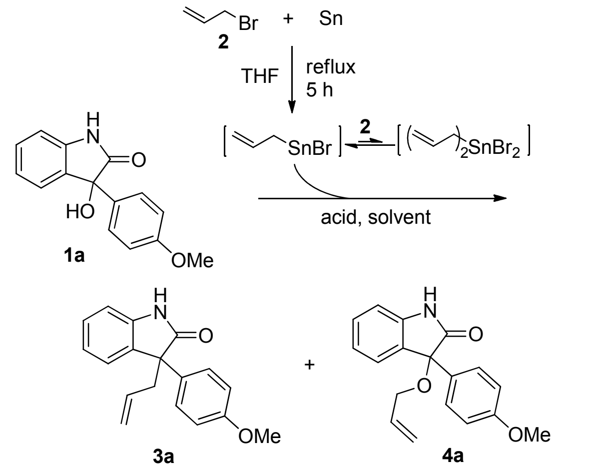


Scheme 1 Allylation reaction promoted by tin powder

2 Results and discussion

In our initial investigations, a mixture of tin powder (3.5 equiv.) and allyl bromide (3.0 equiv.) in tetrahydrofuran (THF) was refluxed for 5 h, and then the solvent was evaporated off under vacuum to give a white solid residue, which was re-dissolved in 4 mL of dichloromethane (DCM). 3-(*p*-Methoxylphenyl)-3-hydroxy-2-oxindole (**1a**, 1 equiv.) and $BiCl_3$ (0.1 equiv.) were added to the mixture. After stirring the mixture at room temperature for another 5 h, the product **3a** was obtained in 47% yield and by-product **4a** was obtained in 20% yield (Table 1, Entry 1). In order to improve the product yield, the effects of other typical Brønsted acids and Lewis acids on the reaction were investigated. First, $Fe(OTf)_3$, $Cu(OTf)_2$, and $HClO_4$ were found

Table 1 Optimization of the reaction conditions[a]



Entry	Molar ratio of 1∶2∶Sn	Solvent	Acid[b]	Yield[c]/% 3a	Yield[c]/% 4a
1	1.0∶3.0∶3.5	DCM	$BiCl_3$	47	20
2	1.0∶3.0∶3.5	DCM	$FeCl_3$	0	0
3	1.0∶3.0∶3.5	DCM	$Fe(OTf)_3$	47	3
4	1.0∶3.0∶3.5	DCM	$InCl_3$	25	1
5	1.0∶3.0∶3.5	DCM	$In(OTf)_3$	33	2
6	1.0∶3.0∶3.5	DCM	$Ni(ClO_4)_2$•$6H_2O$	Trace	0
7	1.0∶3.0∶3.5	DCM	$NiCl_2$•$6H_2O$	Trace	0
8	1.0∶3.0∶3.5	DCM	$Ni(OTf)_2$	6	1
9	1.0∶3.0∶3.5	DCM	$Mg(ClO_4)_2$	19	0
10	1.0∶3.0∶3.5	DCM	BF_3•OEt_2	5	Trace
11	1.0∶3.0∶3.5	DCM	$Sc(OTf)_3$	13	1
12	1.0∶3.0∶3.5	DCM	$Cu(OTf)_2$	47	4
13	1.0∶3.0∶3.5	DCM	$Yb(OTf)_3$	25	2
14	1.0∶3.0∶3.5	DCM	TfOH	38	1
15	1.0∶3.0∶3.5	DCM	H_2SO_4	40	2
16	1.0∶3.0∶3.5	DCM	H_3PO_4	38	3
17	1.0∶3.0∶3.5	DCM	HNO_3	29	4
18	1.0∶3.0∶3.5	DCM	HCl	35	3
19	1.0∶3.0∶3.5	DCM	$HClO_4$	46	1
20	1.0∶3.0∶3.5	DCM	$HClO_4$	58	0
21	1.0∶4.0∶4.5	DCM	$HClO_4$	87	0
22	1.0∶5.0∶5.5	DCM	$HClO_4$	82	0
23	1.0∶4.0∶4.5	DCE	$HClO_4$	65	0
24	1.0∶4.0∶4.5	CH_3CN	$HClO_4$	54	3
25	1.0∶4.0∶4.5	THF	$HClO_4$	69	0
26	1.0∶4.0∶4.5	1,4-Dioxane	$HClO_4$	85	0
27	1.0∶4.0∶4.5	CH_3OH	$HClO_4$	Trace	0
28	1.0∶4.0∶4.5	CH_3CH_2OH	$HClO_4$	Trace	0

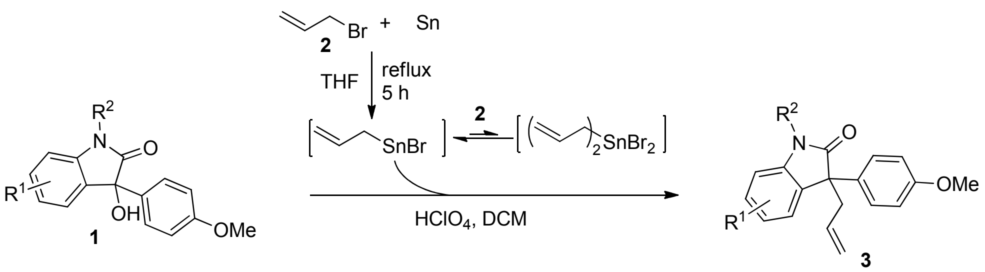
[a] All reactions were carried out by using 0.3 mmol of **1a**, 0.9～1.2 mmol of **2**, 1.05～1.35 mmol of tin powder, 0.03～0.3 mmol of acid in 4 mL of solvent at room temperature for 10 h; [b] Acid: Entries 1～19, 10 mol%; Entries 20～28, 100 mol%; [c] Isolated yields.

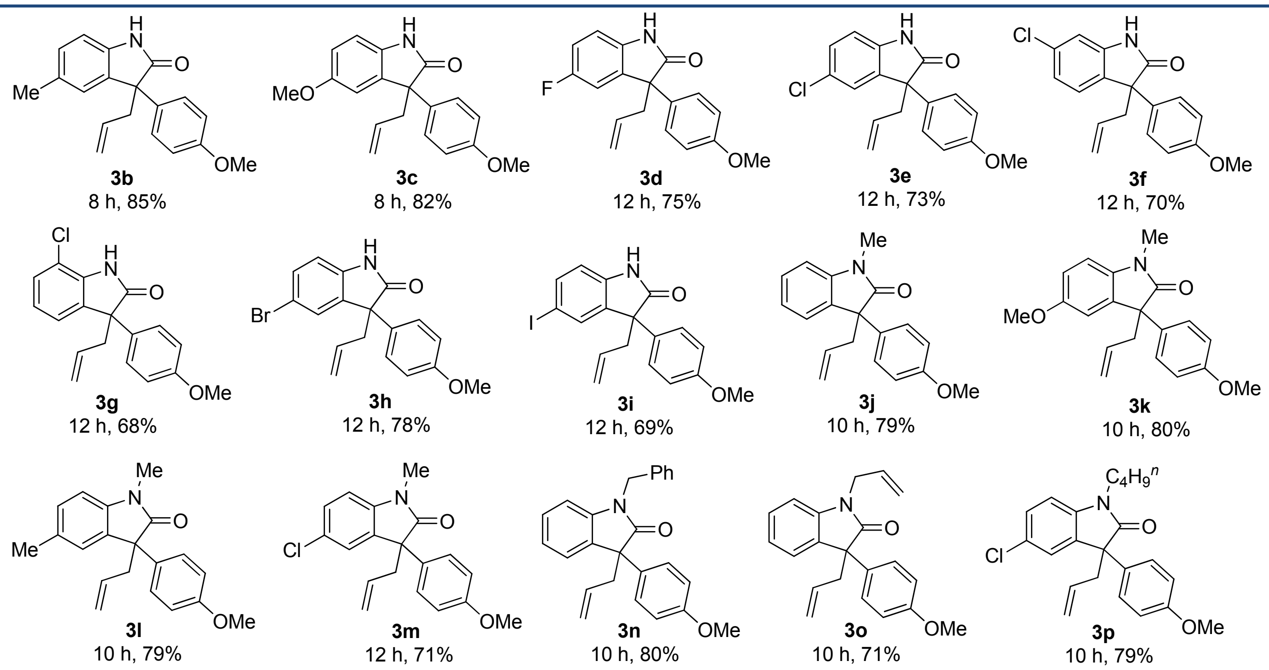
to be equally effective to the reaction (Table 1, Entries 2～19). In consideration of the cost, $HClO_4$ was used to check the other reaction parameters. Thus, the amount of $HClO_4$ was then increased to 1 equiv., and the yield of **3a** reached 58% (Table 1, Entry 20). Afterwards, the influence of the molar ratio of the starting materials on the product yield was examined (Table 1, Entries 20～22). It was found that the yield of **3a** increased to 87% when the molar ratio of **1a**/**2**/Sn reached 1.0/4.0/4.5. Finally, the effects of solvents on the reaction were screened, and DCM was found to be the suitable solvent (Table 1, Entries 23～28). Other solvents such as DCE, CH_3CN and THF gave the products in medium yields, methanol and ethanol did not afford separable product. Therefore, the optimized reaction conditions were the use of **1a**, **2** and tin powder in a molar ratio of 1∶4.0∶4.5 in DCM at room temperature (Table 1, Entry 21).

With the optimum reaction conditions in hand, the substrate scopes were examined. At first, the effects of the substituents on the benzene ring and nitrogen atom of the oxindole core were examined by using 3-(*p*-methoxylphenyl)-3-hydroxy-2-oxindoles (**1**) as substrates. The results indicated that the position of the substituents on the benzene ring of the oxindole core did not influence the reaction too much. For instance, the difference among products **3e**, **3f** and **3g** was the position of chlorine atom on the benzene ring of the oxindole core, but their yields were around 70% (Table 2, **3e**, **3f** and **3g**). The electronic properties of the substituents had a little bit of influence on the product yields. For example, the oxindoles **1** with the electron-donating groups on the phenyl ring of the oxindole core gave the corresponding products in higher yields than those with electron-withdrawing ones (Table 2, **3b** and **3c** vs. **3d**～**3i**). The protecting groups on the nitrogen atom of the oxindoles **1** did not influence the product yields too much (Table 2, **3j**～**3p**). However, when *t*-butyloxycarbonyl group was used as protecting group, it would be deprotected after the reaction (Scheme 2).

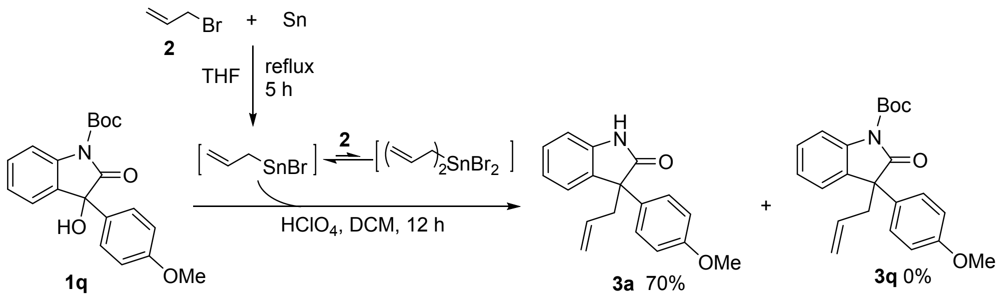
To further investigate the generality of the substrates, the substituents R^3 at 3-position of 3-hydroxy-2-oxindoles were varied. As shown in Table 3, when R^3 was 3-indolyl group, the products **6a**～**6k** obtained in good yields under the standard conditions. The electronic properties of the substituents on benzene ring of 3-indolyl groups had influence on the product yields. When the substituents were electron-donating groups, the product yields were higher than the electron-withdrawing ones (Table 3, **6b** and **6c** vs. **6d**). However, when the R^3 groups were benzene groups, the substituents on the benzene rings had a great influence on the product yields. For instance, if the R^3 was just benzene ring, the product **6p** did not be obtained (Table 3, **6p**). When the R^3 was *p*-methylphenyl group, the product **6l** obtained in 58% yield. When 3-(3,4-dimethoxyphenyl)-3-

Table 2 Substrate scope of allylations using 3-hydroxy-2-oxindoles **1**[a]



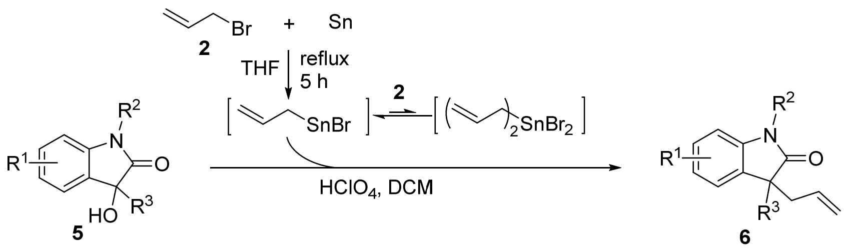


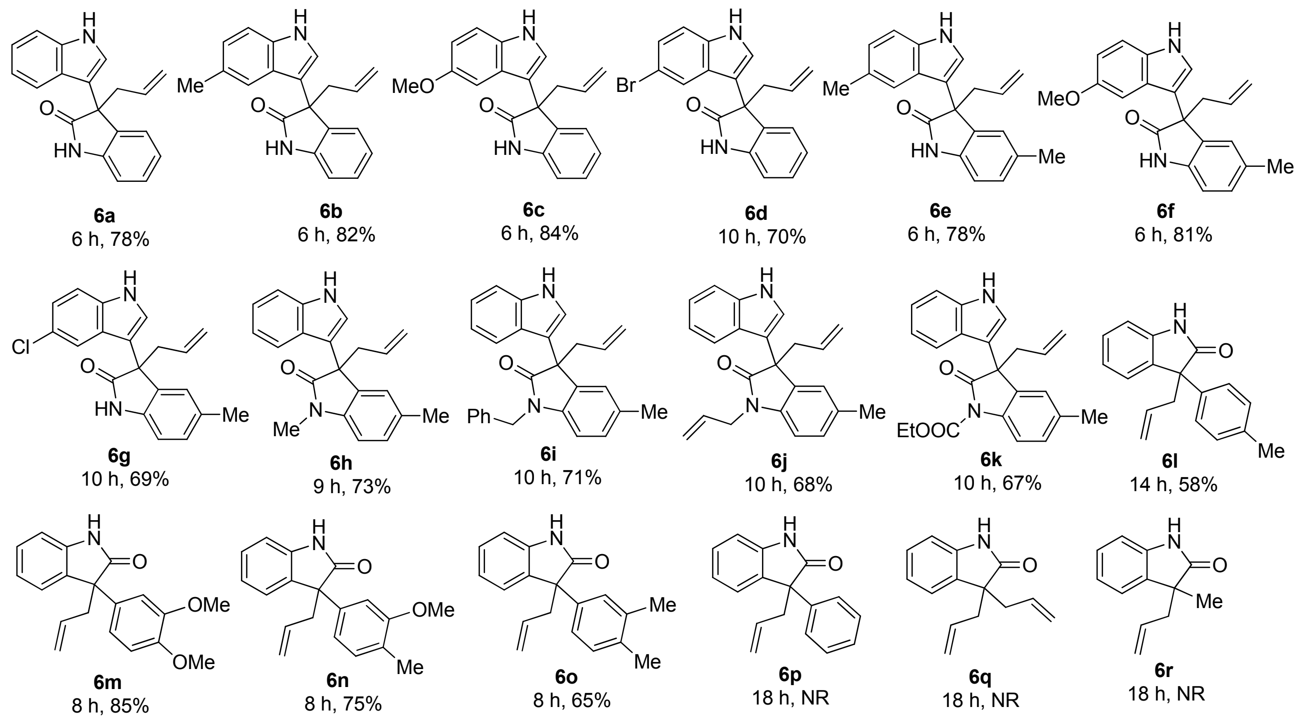
[a] All reactions were carried out by using 0.3 mmol of **1**, 1.2 mmol of **2**, 1.35 mmol of tin powder, 0.3 mmol of $HClO_4$ in 4 mL of DCM at room temperature for 8～12 h. Isolated yields.



Scheme 2 Allylation of *tert*-butyl 3-hydroxy-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxylate

Table 3 Substrate scope of allylations using 3-hydroxy-2-oxindoles **5**[a]



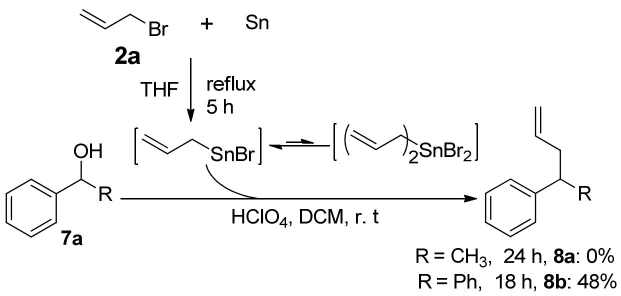


[a] All reactions were carried out by using 0.3 mmol of **5**, 1.2 mmol of **2**, 1.35 mmol of tin powder, 0.3 mmol of $HClO_4$ in 4 mL of DCM at room temperature for 6～18 h. Isolated yields. [b]NR＝no reaction.

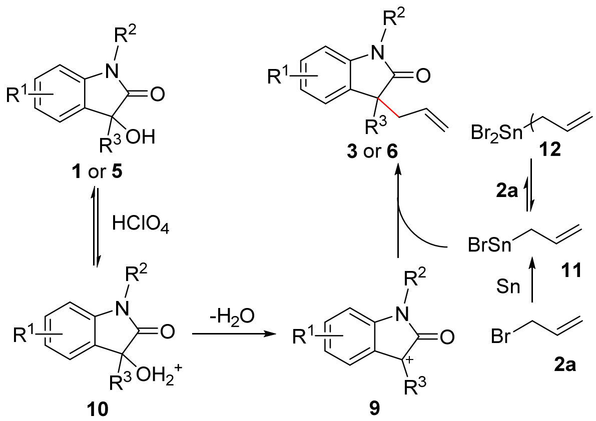
hydroxyindolin-2-one was used as substrate, the yield of **6m** reached to 85%. The results from **6l**～**6p** indicated that the more electron-donating substituents on the benzene rings of R^3 were, the higher the product yields would be. Finally, the aliphatic R^3 groups such as allyl and methyl groups were examined, but no corresponding products were formed (Table 3, **6q** and **6r**).

In order to further expand the application of the reaction, the benzyl alcohols such as 1-phenylethan-1-ol and diphenylmethanol have been investigated. As shown in Scheme 3, when diphenylmethanol was used as substrate, the reaction took place smoothly and the product **8b** was obtained in 48% yield; when 1-phenylethan-1-ol was used as substrate, the reaction did not occur.

Based on the above results and previous reports,[10] a tentative reaction pathway for the carbocations **9** was proposed as depicted in Scheme 4. 3-Hydroxy-2-oxindoles (**1** or **5**) were protonated to afford the intermediate **10**, which



Scheme 3 Reaction of benzyl alcohols as substrate



Scheme 4 Proposed mechanistic pathway

dehydrated to give the carbocations **9**. Nucleophilic attachment of *in situ* formed organotin reagents **11** to the carbocations **9** gave the final products **3** or **6**.

3 Conclusions

In conclusion, tin powder-promoted C—C coupling reaction between allyl bromide and benzylic alcohol was achieved. The tin powder-participated reaction types were extended beyond 1,2-addition to C=O or C=N double bounds. The protocol provides an efficient way to access potentially bioactive 3,3-disubstituted-2-oxindole derivatives in good yields, and further expands the application of tin-powder-promoted reactions in organic synthesis.

4 Experimental

4.1 Materials and methods

The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica gel 60 (230～400 mesh). Analytical thin layer chromatography (TLC) was done using silica gel GF254. TLC plates were analyzed by an exposure to ultraviolet (UV) light and/or submersion in phosphomolybdic acid solution or submersion in $KMnO_4$ solution or in I_2. High-resolution mass spectra were recorded on a Fourier transform ion cyclotron resonance mass spectrometer. NMR experiments were carried out in $CDCl_3$ and $(CD_3)_2CO$. ^1H NMR and ^{13}C NMR spectra were recorded at 400 or 600 MHz and 100 or 150 MHz spectrometers, respectively. ^{19}F NMR spectra were recorded at 376 MHz spectrometers. Chemical shifts are reported as δ values relative to internal TMS (δ 0.00 for ^1H NMR), chloroform (δ 7.26 for ^1H NMR), acetone (δ 2.05 for ^1H NMR), chloroform (δ 77.16 for ^{13}C NMR), acetone (δ 206.26 for ^{13}C NMR) and $CFCl_3$ (δ 0.00 for ^{19}F NMR). Melting points were uncorrected.

4.2 General procedure for the synthesis of 3, 6 and 8

A mixture of tin powder (1.35 mmol, 4.5 equiv.) and allyl bromide (1.2 mmol, 4.0 equiv.) in THF was refluxed for 5 h, and then the solvent was evaporated off under vacuum to give a white solid residue, which was re-dissolved in 4 mL of DCM. 3-Hydroxy-2-oxindoles **1** or **5** (0.3 mmol, 1 equiv.) and $HClO_4$ (0.3 mmol, 1 equiv.) were added to the mixture. After stirring the mixture at room temperature for another 8～18 h, the saturated $NaHCO_3$ solution (5 mL) was poured into the mixture and stirred for 10 min. The mixture was extracted with EtOAc (10 mL×3). The combined organic phase was dried over $MgSO_4$ and then concentrated. Purification of the residue by silica gel column chromatography using petroleum ether/EtOAc (V/V=3/1) as the eluent furnished the pure products **3**, **6** and **8**.

3-Allyl-3-(4-methoxyphenyl)indolin-2-one (**3a**):[9g] 73 mg, 87% yield, yellow solid. m.p. 92～94 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.91 (s, 1H), 7.30～7.27 (m, 2H), 7.25～7.23 (m, 1H), 7.21 (d, J=7.2 Hz, 1H), 7.08 (t, J=7.2 Hz, 1H), 6.92 (d, J=8.0 Hz, 1H), 6.84 (d, J=8.8 Hz, 2H), 5.51～5.41 (m, 1H), 5.06 (d, J=16.8 Hz, 1H), 4.95 (d, J=10.4 Hz, 1H), 3.77 (s, 3H), 3.06～2.96 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.2, 159.0, 140.9, 132.6, 132.5, 131.5, 128.3, 128.2, 125.6, 122.6, 119.4, 114.1, 109.9, 56.3, 55.4, 42.0; HRMS (ESI) calcd for $C_{18}H_{17}NNaO_2$ $[M+Na]^+$ 302.1157, found 302.1168.

3-Allyl-3-(4-methoxyphenyl)-5-methylindolin-2-one (**3b**): 75 mg, 85% yield, yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 7.29 (d, J=8.4 Hz, 2H), 7.03 (d, J=7.8 Hz, 1H), 7.00 (s, 1H), 6.85 (d, J=8.4 Hz, 2H), 6.81 (d, J=7.8 Hz, 1H), 5.49～5.42 (m, 1H), 5.06 (d, J=17.4 Hz, 1H), 4.94 (d, J=9.6 Hz, 1H), 3.77 (s, 3H), 3.05～2.96 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.8, 158.8, 138.6, 132.9, 132.6, 132.0, 131.9, 128.6, 128.3, 126.0, 119.2, 114.1, 109.8, 56.5, 55.4, 41.7, 21.3; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$ 316.1308, found 316.1310.

3-Allyl-5-methoxy-3-(4-methoxyphenyl)indolin-2-one (**3c**): 76 mg, 82% yield, yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ: 8.00 (s, 1H), 7.30～7.27 (m, 2H), 6.86～6.83 (m, 2H), 6.83 (s, 1H), 6.80～6.77 (m, 2H), 5.50～5.43 (m, 1H), 5.07 (d, J=17.4 Hz 1H), 4.96 (d, J=10.2 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.04～2.95 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.4, 159.0, 155.9, 134.4, 134.1, 132.5, 131.5, 128.3, 119.4, 114.1, 112.8, 112.6, 110.3, 56.8, 55.9, 55.4, 41.9; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_3$ $[M+Na]^+$ 332.1257, found 332.1255.

3-Allyl-5-fluoro-3-(4-methoxyphenyl)indolin-2-one

(**3d**): 67 mg, 75% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.47 (s, 1H), 7.27～7.24 (m, 2H), 6.96～6.92 (m, 2H), 6.86～6.83 (m, 3H), 5.48～5.41 (m, 1H), 5.05 (d, J=17.4 Hz, 1H), 4.96 (d, J=10.2, 1H), 3.77 (s, 3H), 3.02～2.94 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.6, 159.2 (d, J=238.5 Hz), 159.1, 136.9 (d, J=3.0 Hz), 134.4 (d, J=7.5 Hz), 132.0, 130.9, 128.2, 119.8, 114.7 (d, J=24.0 Hz), 114.3, 113.3 (d, J=24.0 Hz), 110.6 (d, J=9.0 Hz), 57.0, 55.4, 41.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −125.44 (m); HRMS (ESI) calcd for $C_{18}H_{16}FNNaO_2$ [M+Na]$^+$ 320.1057, found 320.1062.

3-Allyl-5-chloro-3-(4-methoxyphenyl)indolin-2-one (**3e**): 69 mg, 73% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.97 (br, 1H), 7.25～7.23 (m, 2H), 7.21～7.20 (m, 1H), 7.16 (d, J=1.8 Hz, 1H), 6.86～6.84 (m, 3H), 5.48～5.41 (m, 1H), 5.06 (d, J=17.4 Hz, 1H), 4.96 (d, J=10.2 Hz, 1H), 3.77 (s, 3H), 3.03～2.95 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.7, 159.2, 139.7, 134.7, 131.9, 130.7, 128.3, 128.2, 128.0, 125.7, 119.9, 114.3, 111.2, 56.8, 55.4, 41.7; HRMS (ESI) calcd for $C_{18}H_{16}ClNNaO_2$ [M+Na]$^+$ 336.0762, found 336.0763.

3-Allyl-6-chloro-3-(4-methoxyphenyl)indolin-2-one (**3f**): 66 mg, 70% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 7.27～7.24 (m, 2H), 7.11 (d, J=7.8 Hz, 1H), 7.05 (dd, J=7.8, 1.8 Hz, 1H), 6.95 (d, J=1.8 Hz 1H), 6.86～6.83 (m, 2H), 5.47～5.41 (m, 1H), 5.04 (d, J=16.8 Hz, 1H), 4.96 (d, J=10.2 Hz, 1H), 3.77 (s, 3H), 3.02～2.95 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.7, 159.1, 142.1, 133.9, 132.0, 131.0, 130.9, 128.2, 126.4, 122.6, 119.8, 114.2, 110.8, 56.1, 55.4, 41.8; HRMS (ESI) calcd for $C_{18}H_{16}ClNNaO_2$ [M+Na]$^+$ 336.0762, found 336.0777.

3-Allyl-7-chloro-3-(4-methoxyphenyl)indolin-2-one (**3g**): 64 mg, 68% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.29～7.27 (m, 2H), 7.25 (dd, J=7.8, 0.6 Hz, 1H), 7.12 (d, J=7.8 Hz, 1H), 7.04 (t, J=7.8 Hz, 1H), 6.86～6.84 (m, 2H), 5.49～5.42 (m, 1H), 5.06 (d, J=17.4 Hz, 1H), 4.98 (d, J=10.2 Hz, 1H), 3.78 (s, 3H), 3.05～2.97 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 179.0, 159.2, 138.7, 133.9, 132.1, 130.8, 128.2, 128.1, 123.9, 123.4, 119.8, 115.2, 114.2, 57.5, 55.4, 42.1; HRMS (ESI) calcd for $C_{18}H_{16}ClNNaO_2$ [M+Na]$^+$ 336.0762, found 336.0775.

3-Allyl-5-bromo-3-(4-methoxyphenyl)indolin-2-one (**3h**): 83 mg, 78% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.06 (s, 1H), 7.36 (dd, J=8.4, 1.8 Hz, 1H), 7.30 (d, J=1.8 Hz, 1H), 7.26～7.24 (m, 2H), 6.87～6.85 (m, 2H), 6.81 (d, J=8.4 Hz, 1H), 5.48～5.41 (m, 1H), 5.07 (d, J=17.4 Hz, 1H), 4.97 (d, J=10.2 Hz, 1H), 3.77(s, 3H), 3.03～2.95 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 179.7, 159.2, 140.0, 135.0, 132.0, 131.2, 130.6, 128.6, 128.2, 120.0, 115.3, 114.3, 111.4, 56.6, 55.4, 41.8; HRMS (ESI) calcd for $C_{18}H_{16}BrNNaO_2$ [M+Na]$^+$ 380.0257, found 380.0260.

3-Allyl-5-iodo-3-(4-methoxyphenyl)indolin-2-one (**3i**): 85 mg, 69% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.28 (s, 1H), 7.54 (d, J=8.4 Hz, 1H), 7.47 (s, 1H), 7.24 (d, J=9.0 Hz, 2H), 6.87～6.85 (m, 2H), 6.72 (dd, J=8.4, 1.8 Hz, 1H), 5.47～5.40 (m, 1H), 5.07 (d, J=16.8 Hz, 1H), 4.97 (d, J=10.2 Hz, 1H), 3.78 (s, 3H), 3.02～2.95 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.1, 159.0, 140.6, 137.0, 135.2, 133.9, 131.7, 130.6, 128.0, 119.8, 114.1, 112.1, 85.0, 56.4, 55.3, 41.5; HRMS (ESI) calcd for $C_{18}H_{16}INNaO_2$ [M+Na]$^+$ 428.0118, found 428.0112.

3-Allyl-3-(4-methoxyphenyl)-1-methylindolin-2-one (**3j**): 70 mg, 79% yield, yellow solid. m.p. 50～53 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.34～7.31 (m, 1H), 7.31～7.28 (m, 2H), 7.25 (s, 1H), 7.11 (t, J=7.8 Hz, 1H), 6.89 (d, J=7.8 Hz, 1H), 6.84～6.81 (m, 2H), 5.43～5.36 (m, 1H), 5.02 (d, J=16.8, Hz, 1H), 4.91 (d, J=10.2 Hz, 1H), 3.77 (s, 3H), 3.19 (s, 3H), 2.99 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.4, 158.9, 144.0, 132.7, 131.9, 131.6, 128.3, 128.2, 125.3, 122.5, 119.2, 114.0, 108.3, 55.9, 55.4, 42.2, 26.5;

3-Allyl-5-methoxy-3-(4-methoxyphenyl)-1-methylindolin-2-one (**3k**): 78 mg, 80% yield, white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31～7.28 (m, 2H), 6.87～6.86 (m, 1H), 6.85～6.84 (m, 2H), 6.83～6.82 (m, 1H), 6.78 (d, J=8.4 Hz, 1H), 5.44～5.37 (m, 1H), 5.06～5.02 (m, 1H), 4.94～4.92 (m, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.17 (s, 3H), 2.99～2.97 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.0, 158.9, 156.0, 137.6, 133.3, 132.6, 131.6, 128.3, 119.2, 114.0, 112.7, 112.4, 108.5, 56.3, 55.9, 55.4, 42.1, 26.5; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_3$ [M+Na]$^+$ 346.1414, found 346.1401.

3-Allyl-3-(4-methoxyphenyl)-1,5-dimethylindolin-2-one (**3l**): 73 mg, 79% yield, white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31～7.29 (m, 2H), 7.12 (d, J=7.8 Hz, 1H), 7.07 (s, 1H), 6.86～6.83 (m, 2H), 6.78 (d, J=7.8 Hz, 1H), 5.44～5.37 (m, 1H), 5.04 (d, J=17.4 Hz, 1H), 4.92 (d, J=10.2 Hz, 1H), 3.77 (s, 3H), 3.18 (s, 3H), 3.03～2.96 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.3, 158.8, 141.6, 132.7, 132.1, 132.0, 131.9, 128.5, 128.3, 125.9, 119.0, 114.0, 108.0, 55.9, 55.3, 42.0, 26.4, 21.3; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2$ [M+Na]$^+$ 330.1465, found 330.1454.

3-Allyl-5-chloro-3-(4-methoxyphenyl)-1-methylindolin-2-one (**3m**): 70 mg, 71% yield, white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.30～7.28 (m, 1H), 7.27～7.25 (m, 2H), 7.22 (d, J=1.8 Hz, 1H), 6.85～6.83 (m, 2H), 6.80 (d, J=8.4 Hz, 1H), 5.41～5.34 (m, 1H), 5.05～5.02 (m, 1H), 4.95～4.93 (m, 1H), 3.76 (s, 3H), 3.17 (s, 3H), 2.98～2.96 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 177.9, 159.1, 142.5, 133.8, 132.1, 130.9, 128.3, 128.1, 127.9, 125.5, 119.7, 114.2, 109.2, 56.1, 55.4, 42.0, 26.5; HRMS (ESI) calcd for $C_{19}H_{18}ClNNaO_2$ [M+Na]$^+$ 350.0918, found 350.0909.

3-Allyl-1-benzyl-3-(4-methoxyphenyl)indolin-2-one (**3n**):[9g] 89 mg, 80% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.32～7.29 (m, 2H), 7.28～7.22 (m, 6H), 7.19 (t, J=7.8 Hz, 1H), 7.07 (t, J=7.2 Hz, 1H), 6.86～6.84 (m, 2H), 6.75 (d, J=7.8 Hz, 1H), 5.46～5.39 (m, 1H), 5.08 (d, J=16.8 Hz, 1H), 4.97～4.93 (m, 2H), 4.83 (d, J=15.6 Hz, 1H), 3.78 (s, 3H), 3.11～3.02 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.5, 159.0, 143.1, 136.1, 132.7, 132.1, 131.9, 128.8, 128.3, 128.2, 127.7, 127.5, 125.3, 122.6, 119.4, 114.1, 109.4, 55.9, 55.4, 44.0, 42.2.

1,3-Diallyl-3-(4-methoxyphenyl)indolin-2-one (**3o**):[9g] 69 mg, 71% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31～7.29 (m, 2H), 7.28 (dd, J=7.8, 1.2 Hz, 1H), 7.26～7.25 (m, 1H), 7.10 (td, J=7.8, 1.2 Hz, 1H), 6.87 (d, J=7.8 Hz, 1H), 6.85～6.82 (m, 2H), 5.82～5.76 (m, 1H), 5.44～5.37 (m, 1H), 5.20～5.18 (m, 1H), 5.17 (d, J=1.8 Hz, 1H), 5.04 (dd, J=16.8, 1.2 Hz, 1H), 4.92 (d, J=10.2 Hz, 1H), 4.39～4.35 (m, 1H), 4.30～4.26 (m, 1H), 3.77 (s, 3H), 3.06～2.98 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.1, 158.9, 143.1, 132.6, 132.0, 131.8, 131.6, 128.3, 128.2, 125.3, 122.5, 119.4, 117.5, 114.1, 109.3, 55.8, 55.4, 42.5, 42.2.

3-Allyl-1-butyl-3-(4-methoxyphenyl)indolin-2-one (**3p**): 79 mg, 79% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.32～7.27 (m, 3H), 7.24 (dd, J=7.2, 0.6 Hz, 1H), 7.09 (td, J=7.2, 0.6 Hz, 1H), 6.90 (d, J=7.8 Hz, 1H), 6.85～6.82 (m, 2H), 5.42～5.35 (m, 1H), 5.03 (d, J=16.8 Hz, 1H), 4.91 (d, J=10.2 Hz, 1H), 3.77 (s, 3H), 3.75～3.70 (m, 1H), 3.67～3.62 (m, 1H) 3.04～2.96 (m, 2H), 1.66～1.60 (m, 2H), 1.39～1.32 (m, 2H), 0.93 (t, J=7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.2, 158.9, 143.5, 132.7, 132.3, 132.0, 128.2, 128.1, 125.3, 122.3, 119.2, 114.0, 108.6, 55.7, 55.4, 42.2, 40.0, 29.7, 20.3, 13.9; HRMS (ESI) calcd for $C_{22}H_{25}NNaO_2$ $[M+Na]^+$ 358.1778, found 358.1794.

3-(Allyloxy)-3-(4-methoxyphenyl)indolin-2-one (**4a**): 18 mg, 20% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.26 (s, 1H), 7.37～7.28 (m, 4H), 7.13～7.09 (m, 1H), 6.94 (d, J=12.0 Hz, 1H), 6.87～6.82 (m, 2H), 5.99～5.89 (m, 1H), 5.31～5.26 (m, 1H), 5.15～5.13 (m, 1H), 3.99～3.95 (m, 1H), 5.85～5.81 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 177.6, 159.9, 141.5, 134.3, 130.7, 130.2, 128.9, 127.9, 127.4, 126.3, 123.4, 117.1, 114.0, 110.6, 66.8, 55.4; HRMS (ESI) calcd for $C_{18}H_{17}NNaO_3$ $[M+Na]^+$ 318.1106, found 318.1101.

3-Allyl-3-(1*H*-indol-3-yl)indolin-2-one (**6a**):[9g] 68 mg, 78% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.23 (br, 1H), 8.59 (br, 1H), 7.29 (d, J=8.4 Hz, 1H), 7.20 (t, J=7.8 Hz, 1H), 7.12～7.09 (m, 2H), 7.04 (d, J=8.4 Hz, 1H), 6.99 (t, J=7.2 Hz, 2H), 6.95～6.89 (m, 2H), 5.59～5.52 (m, 1H), 5.12 (d, J=17.4 Hz, 1H), 4.98 (d, J=10.2 Hz, 1H), 3.22～3.19 (m, 1H), 3.11～3.08 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 181.6, 140.9, 136.9, 133.1, 132.2, 128.2, 125.6, 124.8, 123.4, 122.8, 122.2, 120.0, 119.7, 119.4, 114.4, 111.6, 110.1, 53.2, 40.8.

3-Allyl-3-(5-methyl-1*H*-indol-3-yl)indolin-2-one (**6b**): 75 mg, 82% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.40 (s, 1H), 8.17 (s, 1H), 7.24 (t, J=7.2 Hz, 1H), 7.20 (d, J=8.4 Hz, 1H), 7.15 (d, J=7.2 Hz, 1H), 7.04 (d, J=2.4 Hz, 1H), 7.01 (t, J=7.2 Hz, 1H), 6.95～6.93 (m, 2H), 6.91 (s, 1H), 5.58～5.51 (m, 1H), 5.10 (d, J=17.4 Hz, 1H), 4.97 (d, J=10.2 Hz, 1H), 3.22～3.18 (m, 1H), 3.11～3.08 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.8, 140.9, 135.3, 133.1, 132.4, 128.9, 128.2, 125.8, 125.0, 124.0, 123.3, 122.7, 120.0, 119.3, 114.4, 111.1, 109.8, 53.1, 40.9, 21.8; HRMS (ESI) calcd for $C_{20}H_{18}N_2NaO$ $[M+Na]^+$ 325.1317, found 325.1316.

3-Allyl-3-(5-methoxy-1*H*-indol-3-yl)indolin-2-one (**6c**): 80 mg, 84% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.96 (s, 1H), 8.44 (s, 1H), 7.21 (t, J=7.8 Hz, 1H), 7.17 (d, J=8.4 Hz, 1H), 7.13 (d, J=7.2 Hz, 1H), 7.06 (d, J=2.4 Hz, 1H), 7.00 (t, J=7.2 Hz, 1H), 6.90 (d, J=7.8 Hz, 1H), 6.76 (dd, J=8.4, 2.4 Hz, 1H), 6.37 (d, J=1.8 Hz, 1H), 5.59～5.52 (m, 1H), 5.10 (d, J=17.4 Hz, 1H), 4.97 (d, J=10.2 Hz, 1H), 3.56 (s, 3H), 3.20～3.16 (m, 1H), 3.09～3.06 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 181.2, 153.8, 141.1, 133.0, 132.2, 132.0, 128.3, 126.0, 125.1, 124.1, 122.8, 119.4, 114.1, 112.2, 112.1, 109.9, 102.1, 55.6, 53.1, 40.6; HRMS (ESI) calcd for $C_{20}H_{18}N_2NaO_2$ $[M+Na]^+$ 341.1266, found 341.1261.

3-Allyl-3-(5-bromo-1*H*-indol-3-yl)indolin-2-one (**6d**): 78 mg, 70% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 7.82 (s, 1H), 7.29 (t, J=7.8 Hz, 1H), 7.24 (s, 1H), 7.19～7.18 (m, 1H), 7.17 (s, 1H), 7.16～7.14 (m, 1H), 7.11 (d, J=2.4 Hz, 1H), 7.04 (t, J=7.8 Hz, 1H), 6.98 (d, J=7.8 Hz, 1H), 5.56～5.49 (m, 1H), 5.10 (d, J=17.4 Hz, 1H), 4.99 (d, J=10.2 Hz, 1H), 3.18～3.14 (m, 1H), 3.08～3.05 (m, 1H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 178.7, 142.3, 136.2, 133.0, 128.3, 128.2, 127.6, 125.2, 124.9, 124.3, 122.8, 122.0, 118.5, 115.0, 113.5, 111.9, 109.7, 52.5, 40.7; HRMS (ESI) calcd for $C_{19}H_{15}BrN_2NaO$ $[M+Na]^+$ 389.0265., found 389.0263.

3-Allyl-5-methyl-3-(5-methyl-1*H*-indol-3-yl)indolin-2-one (**6e**): 74 mg, 78% yield, red gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.50 (s, 1H), 8.26 (s, 1H), 7.20 (d, J=8.4 Hz, 1H), 7.04～7.02 (m, 2H), 6.94～6.93 (m, 2H), 6.90 (s, 1H), 6.83 (d, J=7.8 Hz, 1H), 5.57～5.50 (m, 1H), 5.11 (d, J=16.8 Hz, 1H), 4.97 (d, J=10.2 Hz, 1H), 3.21～3.17 (m, 1H), 3.08～3.05 (m, 1H), 2.28 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.9, 138.4, 135.3, 133.2, 132.4, 132.1, 128.9, 128.5, 125.9, 125.6, 123.9, 123.2, 120.0, 119.2, 114.5, 111.1, 109.5, 53.1, 40.9, 21.8, 21.3; HRMS (ESI) calcd for $C_{21}H_{20}N_2NaO$ $[M+Na]^+$ 339.1468, found 339.1456.

3-Allyl-3-(5-methoxy-1H-indol-3-yl)-5-methylindolin-2-one (**6f**): 81 mg, 81% yield, red gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (s, 1H), 8.41 (s, 1H), 7.19 (d, J=9.2 Hz, 1H), 7.09 (d, J=2.4 Hz, 1H), 7.03～7.00 (m, 1H), 6.94 (s, 1H), 6.82 (d, J=8.0 Hz, 1H), 6.76 (dd, J=8.8, 2.4 Hz, 1H), 6.36 (d, J=2.4 Hz, 1H), 5.60～5.49 (m, 1H), 5.12 (d, J=17.2 Hz, 1H), 4.98 (d, J=10.0 Hz, 1H), 3.55 (s, 3H), 3.20～3.15 (m, 1H), 3.07～3.02 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.8, 153.9, 138.5, 133.0, 132.3, 132.2, 132.0, 128.6, 126.0, 125.8, 123.9, 119.3, 114.6, 112.3, 112.0, 109.4, 102.2, 55.6, 53.0, 40.7, 21.3; HRMS (ESI) calcd for $C_{21}H_{20}N_2NaO_2$ $[M+Na]^+$ 355.1417, found 355.1410.

3-Allyl-3-(5-chloro-1H-indol-3-yl)-5-methylindolin-2-one (**6g**): 70 mg, 69% yield, red gel. ^{1}H NMR (600 MHz, C_3D_6O) δ: 10.38 (s, 1H), 9.49 (s, 1H), 7.40 (s, 1H), 7.36 (d, J=9.0 Hz, 1H), 7.24 (s, 1H), 7.07 (d, J=7.8Hz, 1H), 7.02 (dd, J=9.0, 2.4Hz, 1H), 7.00 (s, 1H), 6.92 (d, J=7.8 Hz, 1H), 5.56～5.49 (m, 1H), 5.06 (d, J=17.4 Hz, 1H), 4.92 (d, J=10.2 Hz, 1H), 3.16～3.07 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, C_3D_6O) δ: 179.5, 140.3, 136.3, 133.6, 133.5, 131.6, 129.0, 127.5, 125.8, 125.7, 124.7, 122.1, 120.1, 118.7, 115.8, 113.4, 109.8, 53.0, 41.1, 20.9; HRMS (ESI) calcd for $C_{20}H_{17}ClN_2NaO$ $[M+Na]^+$ 359.0922, found 359.0914.

3-Allyl-3-(1H-indol-3-yl)-1,5-dimethylindolin-2-one (**6h**): 70 mg, 73% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.69 (s, 1H), 7.30 (d, J=8.4 Hz, 1H), 7.13 (d, J=7.8 Hz, 1H), 7.09 (t, J=7.8 Hz, 1H), 6.98 (s, 1H), 6.94 (d, J=8.4 Hz, 1H), 6.91～6.88 (m, 2H), 6.85 (d, J=7.8 Hz, 1H), 5.49～5.42 (m, 1H), 5.09 (d, J=17.4 Hz, 1H), 4.95 (d, J=10.2 Hz, 1H), 3.29 (s, 3H), 3.16～3.13 (m, 1H), 3.06～3.03 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.9, 141.5, 136.9, 132.6, 132.5, 132.3, 128.5, 125.6, 125.4, 123.3, 122.0, 120.1, 119.6, 119.1, 114.8, 111.5, 107.8, 52.7, 40.8, 26.5, 21.3; HRMS (ESI) calcd for $C_{21}H_{20}N_2NaO$ $[M+Na]^+$ 339.1468, found 339.1457.

3-Allyl-1-benzyl-3-(1H-indol-3-yl)-5-methylindolin-2-one (**6i**): 83 mg, 71% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (s, 1H), 7.39～7.37 (m, 2H), 7.34～7.28 (m, 4H), 7.12～7.08 (m, 1H), 7.02 (d, J=8.0 Hz, 1H), 6.98 (s, 1H), 6.95～6.94 (m, 1H), 6.86～6.85 (m, 2H), 6.75 (d, J=8.0 Hz, 1H), 5.55～5.45 (m, 1H), 5.17 (d, J=16.8 Hz, 1H), 5.07～4.93 (m, 3H), 3.28～3.22 (m, 1H), 3.12～3.07 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.9, 140.6, 136.9, 136.2, 132.6, 132.5, 132.4, 128.9, 128.5, 127.8, 127.7, 125.6, 125.4, 123.4, 122.0, 120.3, 119.5, 119.3, 115.0, 111.5, 109.0, 52.8, 44.3, 41.0, 21.3; HRMS (ESI) calcd for $C_{27}H_{24}N_2NaO$ $[M+Na]^+$ 415.1781, found 415.1770.

1,3-Diallyl-3-(1*H*-indol-3-yl)-5-methylindolin-2-one (**6j**): 70 mg, 68% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.62 (s, 1H), 7.30 (d, J=8.4 Hz, 1H), 7.11～7.08 (m, 2H), 7.00 (s, 1H), 6.98 (d, J=7.8 Hz, 1H), 6.94 (d, J=2.4 Hz, 1H), 6.90 (t, J=7.2 Hz, 1H), 6.85 (d, J=7.8 Hz, 1H), 5.90～5.83 (m, 1H), 5.52～5.45 (m, 1H), 5.31 (d, J=17.4 Hz, 1H), 5.23 (d, J=10.2 Hz, 1H), 5.11 (d, J=16.8 Hz, 1H), 4.97 (d, J=10.2 Hz, 1H), 4.50～4.47 (m, 1H), 4.36～4.32 (m, 1H), 3.21～3.17 (m, 1H), 3.07～3.04 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.5, 140.7, 136.9, 132.6, 132.5, 132.3, 131.9, 128.4, 125.7, 125.4, 123.4, 122.0, 120.2, 119.6, 119.3, 117.8, 115.0, 111.6, 108.8, 52.7, 42.8, 41.0, 21.3; HRMS (ESI) calcd for $C_{23}H_{22}N_2NaO$ $[M+Na]^+$ 365.1624, found 365.1614.

Ethyl 3-allyl-3-(1*H*-indol-3-yl)-5-methyl-2-oxoindoline-1-carboxylate (**6k**): 75 mg, 67% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.62 (s, 1H), 7.25～7.24 (m, 1H), 7.11～7.06 (m, 3H), 6.97 (s, 1H), 6.92～6.88 (m, 2H), 6.74 (d, J=7.8 Hz, 1H), 5.56～5.49 (m, 1H), 5.08 (d, J=16.8 Hz, 1H), 4.96 (d, J=10.2 Hz, 1H), 4.55 (q, J=17.4 Hz, 2H), 3.74 (s, 3H), 3.20～3.17 (m, 1H), 3.08～3.04 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.8, 168.4, 140.0, 136.9, 132.8, 132.4, 128.6, 125.6, 125.6, 123.4, 122.0, 120.3, 119.5, 119.1, 114.5, 111.5, 110.8, 107.8, 52.6, 52.6, 41.5, 41.1, 21.3; HRMS (ESI) calcd for $C_{23}H_{22}N_2NaO_3$ $[M+Na]^+$ 397.1523, found 397.1512.

3-Allyl-3-(*p*-tolyl)indolin-2-one (**6l**): 46 mg, 58% yield, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.68 (s, 1H), 7.25 (d, J=2.4 Hz, 2H), 7.23 (d, J=7.8 Hz, 1H), 7.19 (d, J=7.2 Hz, 1H), 7.11 (d, J=8.4 Hz, 2H), 7.06 (t, J=7.8 Hz, 1H), 6.93 (d, J=7.8 Hz, 1H), 5.49～5.42 (m, 1H), 5.05 (d, J=17.4 Hz, 1H), 4.93 (d, J=10.2 Hz, 1H), 3.06～3.00 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.8, 141.1, 137.3, 136.6, 132.7, 132.5, 129.5, 128.2, 127.0, 125.4, 122.6, 119.4, 110.1, 56.8, 41.7, 21.1; HRMS (ESI) calcd for $C_{18}H_{17}NNaO$ $[M+Na]^+$ 286.1208, found 286.1205.

3-Allyl-3-(3,4-dimethoxyphenyl)indolin-2-one (**6m**): 79 mg, 85% yield, white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.91 (s, 1H), 7.26～7.21 (m, 2H), 7.07 (t, J=7.8 Hz, 1H), 6.97 (d, J=1.8 Hz, 1H), 6.94 (d, J=7.8 Hz, 1H), 6.89 (dd, J=2.4 Hz, 1H), 6.79 (d, J=8.4 Hz, 1H), 5.49～5.43 (m, 1H), 5.06 (d, J=16.8 Hz, 1H), 4.94 (d, J=10.2 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.05～2.98 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.8, 149.0, 148.5, 141.1, 132.5, 131.9, 129.0, 128.3, 125.4, 122.5, 119.5, 119.4, 111.1, 110.7, 110.2, 56.6, 56.0, 55.9, 42.1; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_3$ $[M+Na]^+$ 332.1257, found 332.1254.

3-Allyl-3-(3-methoxy-4-methylphenyl)indolin-2-one (**6n**): 66 mg, 75% yield, white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.46 (s, 1H), 7.23 (t, J=8.4 Hz, 2H), 7.09～7.04 (m, 2H), 6.93 (d, J=7.8 Hz, 1H), 6.90 (d, J=1.8 Hz, 1H) 6.84～6.82 (m, 1H), 5.51～5.44 (m, 1H), 5.08～5.05 (m, 1H), 4.96～4.94 (m, 1H), 3.77 (s, 3H), 3.07～3.00 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.5, 157.9, 141.0, 138.2, 132.5, 132.4, 130.5, 128.1, 126.0, 125.3, 122.4, 119.2, 118.9, 110.1, 108.9, 57.0, 55.3, 41.8, 15.8; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$ 316.1308, found 316.1301.

3-Allyl-3-(3,4-dimethylphenyl)indolin-2-one (**6o**): 54 mg, 65% yield, white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.00 (s, 1H), 7.07 (t, J=7.8, 1.2 Hz, 1H), 7.19 (d, J=6.6 Hz, 1H), 7.14 (s, 1H), 7.09～7.05 (m, 3H), 6.94 (d, J=7.8 Hz, 1H), 5.51～5.44 (m, 1H), 5.08～5.05 (m, 1H), 4.95～4.93 (m, 1H), 3.09～3.01 (m, 2H); 2.23～2.22 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 181.1, 141.2, 137.0, 136.9, 136.0, 132.9, 132.5, 130.0, 128.3, 128.1, 125.3, 124.5, 122.5, 119.3, 110.2, 56.8, 41.6, 20.1, 19.5; HRMS (ESI) calcd for $C_{19}H_{20}NO$ $[M+H]^+$ 278.1539, found 278.1532.

But-3-ene-1,1-diyldibenzene (**8b**):[11] 30 mg, 48 % yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.32 (m, 8H), 7.28～7.24 (m, 2H), 5.87～5.77 (m, 1H), 5.13 (d, J=17.2 Hz, 1H), 5.05 (d, J=10.4 Hz, 1H), 4.11 (t, J=8.0 Hz, 1H), 2.94～2.90 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.6, 137.0, 128.5, 128.1, 126.3, 116.4, 51.4, 40.1.

Supporting Information Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra and the HRMS data of compounds **3**, **4a**, **6** and **8b**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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