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An efficient Friedel-Crafts alkylation for synthesis of 3-indolyl-3-hydroxy oxindoles and unsymmetrical 3,3-diaryl oxindoles catalyzed by Dabco-base ionic liquids in water

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Keywords

Ionic liquid, water, green chemistry, 3-indolyl-3-hydroxy oxindoles, 3,3-diaryl oxindoles

Abstract

A convenient and rapid method for syntheses of 3-indolyl-3-hydroxy oxindoles and unsymmetrical 3,3-diaryl oxindoles has been developed by using Dabco-base ionic liquid catalysts. The two ionic liquids catalysts, [Dabco-H][BF_4] and [Dabco-H][HSO_4] were found as highly efficient catalysts for controlled 3-indolylation of isatins in water. When [Dabco-H][BF_4] was employed as the catalyst in water at 55°C, the reaction between isatin and indoles stops at the step of addition of the two components and provided 3-indolyl-3-hydroxy oxindoles. While raising the reaction temperature to 90°C, the catalyst [Dabco-H][HSO_4] could drive the reaction further and afford symmetrical 3, 3-diindolyl oxindoles. By using the two kinds of ionic liquids, a two-step protocol for efficient synthesis of unsymmetrical 3,3-diaryl oxindoles has been also developed. The use of water as the reaction medium makes the process environmentally benign. The catalysts can be recycled five times without activity loss.

Introduction

Today, the concept of green chemistry has been deeply rooted in the people's hearts. In organic synthesis, increasing attention is being focused on using environmental friendly reagents and conditions. One of the key areas of green chemistry is the elimination of solvents in chemical processes or the replacement of hazardous organic solvents with nonpolluting alternative reaction media, particularly aqueous media.[1] Water is cheap, safe, non-toxic and readily available compared to organic solvent.[2-4] It has unique physical and chemical properties, which may be utilized for attaining reactivity and selectivity that cannot be realized in common organic solvents. So, to perform the organic reactions in water is one of the fundamental challenges and it has received considerable attention.[5]

Indoles and its derivatives are widespread in nature and have been identified as an important kind of compounds.[6] They often appeared a wide variety of pharmacologically and biological activities.[7] In particular, C3 functionalised oxindoles are featured heterocyclic nuclei in a number of natural products as well as medicinally relevant kinds of compounds.[8] Among them, the 3-substituted 3-hydroxy oxindoles and 3,3-diaryl oxindoles have attracted much attention due to their broad spectrum of biological activities including antiviral, antibacterial, anti-inflammatory, antiangiogenic, antifungal and anticonvulsant and they are also as new targets for cancer chemotherapy.[9-13] Moreover, both of their subclasses are useful building blocks as key intermediates in the total synthesis of natural products.[14] The synthesis of 3-indolyl-3-hydroxy oxindoles often involves a Friedel-Crafts type of electrophilic substitution between the indoles and electron-deficient carbonyl compounds such as isatins. A number of methods have been reported for synthesis of this kind compounds,[15] but more examples usually results in the formation of symmetrical 3,3-diindolyl oxindoles in a single step.[16] In sharp contrast, methods for the

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synthesis of unsymmetrical 3,3-diaryl oxindoles are rare,[17] especially base on the arylation of 3-indolyl-3-hydroxy oxindoles.[18] Even though, synthetic strategies for the two kinds compounds often suffer from metal catalyst, expensive reagents, long reaction times, hazardous organic solvents and unrecyclable catalysts. In view of the above, to control the reaction affording mono-substituted 3-indolyl-3-hydroxy oxindoles and which further react with other aromatic nucleophiles to obtain unsymmetrical 3,3-diaryl oxindoles are quite challenging and highly desirable.

Over the past decades, ionic liquids (ILs) have received much attention in academia and successfully applied in many areas, including organic synthesis, electrochemistry, materials chemistry, and chemical separations. In organic synthesis, there have been many reports describing the successful use of ILs as "green" solvents or recovered catalysts.[19] Recently, we have reported a series of quaternary alkylammonium ILs based on the skeleton of 1,4-diazobicyclo [2.2.2] octane (DABCO), and they are shown to be very effective catalysts for many important reactions.[20-25] As a result of our ongoing interest in green chemistry and ILs catalyzed organic reactions, here, we wish to disclose our study on using the Dabco-base ILs as highly efficient catalysts in controlling 3-indolylation of isatins for syntheses of 3-indolyl-3-hydroxy oxindoles and unsymmetrical 3,3-diaryl oxindoles in the solvent of water.

Results and discussion

The ionic liquid catalysts which we have synthesized such as 1-butyl-1,4-diazabicyclo[2.2.2]octanylium bromide ([Dabco-C_4]Br), chloride ([Dabco-C_4]Cl), 1-(2,3-dihydroxypropyl)-1,4-diazabicyclo[2.2.2]octanylium chloride ([Dabco-DHP]Cl), and 1,4-diazabicyclo[2.2.2]octane hydroacetate ([Dabco-H][AcO]), hydrotetrafluoroborate ([Dabco-H][BF_4]), hydrochloride ([Dabco-H]Cl) and hydrogensulfate ([Dabco-H][HSO_4]) are shown in Figure 1.[21, 23]

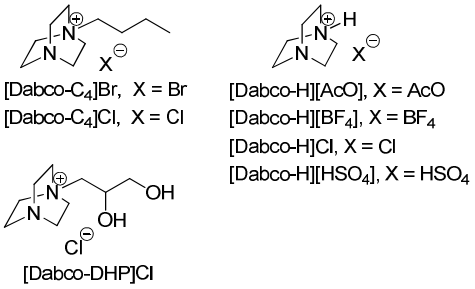

Figure 1. Structures of the Dabco-base ionic liquid catalysts.

Initially, the reaction between isatin (**1a)** and indole (**2a)** was employed as the model reaction to screen the Dabco-base ILs catalysts in water as well as other common solvents in order to develop appropriate reaction conditions. As can be seen from the results summarized in Table 1, all tested Dabco-base ILs catalysts could drive the reaction, but a mixture of 3-(indol-3-yl)-3-hydroxy oxindole (**3a**) and 3, 3-diindolyl oxindole (**4a**) were formed in most cases (Table 1, entries 1–4 and 6). The encouraging results obtained when [Dabco-H][BF_4] and [Dabco-H][HSO_4] were employed in the reaction, they worked well to afford the products **3a** and **4a** in good yield respectively (Table 1, entries 5 and 7). For comparison, other solvents were also tried in the presence of [Dabco-H][BF_4] under 55°C, but a mixture of products **3a** and **4a** were obtained with moderate to good yields (Table 1, entries 8−11). Thus, a typical reaction procedure for the synthesis of 3-indolyl-3-hydroxy oxindoles from isatins (1 mmol) and indoles (1 mmol) catalyzed by [Dabco-H][BF_4](10 mol%) in water at 55 °C has been established (Table 1, Entry 12) (**Condition A**). Then we raised the temperature up to 90°C, the reaction that

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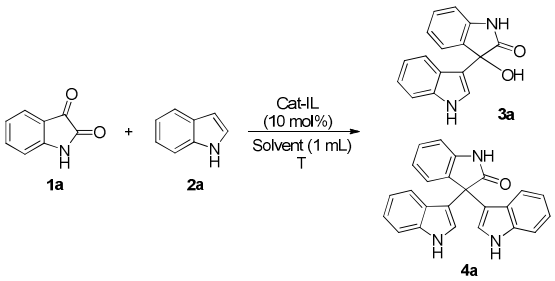
between isatins (1 mmol) and indoles (2 mmol) catalyzed by [Dabco-H][HSO_4] could afford 3, 3-diindolyl oxindole (**4a**) in an excellent yield of 98% within only 2 hours (Table 1, Entry 13)(**Condition B**). When the reaction was carried out in water without using catalyst at 90°C, none of **3a** or **4a** was obtained that indicates the necessity of the catalyst (Table 1, entry 14).

In this procedure, after completion of the reaction, the crude products were easily separated from the mixture just by filtering. The ionic liquid catalysts dissolved in water which could be easily recovered and directly reused in the next recycling run under the same conditions. Water is cheap, safe, non-toxic and readily available, using water as solvent allowed these Friedel–Crafts alkylation reactions to be performed in a very simple and green manner.

Table 1. Friedel–Crafts reaction of isatin and indole catalyzed by Dabco-base ionic liquid catalysts under different conditions[a]



Entry	Cat	Solvent	T (°C)	T (h)	Yield (%)[b]	
					3a	**4a**
1	[Dabco-C_4]Br	H_2O	55	2	48	21
2	[Dabco-C_4]Cl	H_2O	55	2	49	12
3	[Dabco-DHP]Cl	H_2O	55	1	72	12
4	[Dabco-H]AcO	H_2O	55	2	65	16
5	[Dabco-H][BF_4]	H_2O	55	1	85	---
6	[Dabco-H]Cl	H_2O	55	2	16	67
7	[Dabco-H][HSO_4]	H_2O	55	3	---	82
8[c]	[Dabco-H][BF_4]	CH_3CN	55	6	57	<5
9[c]	[Dabco-H][BF_4]	THF	55	6	66	17
10[c]	[Dabco-H][BF_4]	C_2H_5OH	55	1	73	13
11[c]	[Dabco-H][BF_4]	$(ClCH_2)_2$	55	6	76	8
12[c]	[Dabco-H][BF_4]	H_2O	55	1	85	---
13	[Dabco-H][HSO_4]	H_2O	90	2	---	98
14	---	H_2O	90	6	---	---

[a] Conditions: isatin (**1a**, 1 mmol) and indole (**2a**, 2 mmol), Dabco-base catalyst (0.1 mmol), and solvent 1.0 mL.

[b] Isolated yield.

[c] 1 mmol indole (**2a**) was used.

Having optimized the conditions, we then explored the generality of this method for the synthesis of 3-indolyl-3-hydroxy oxindoles from isatins and indoles in the presence of 10 mol% the IL catalyst [Dabco-H][BF_4] in water under 55°C (**Condition A**). As shown in Table 2, the Friedel–Crafts reactions between isatins and indoles with different substituents all proceeded well to afford the corresponding 3-indolyl-3-hydroxy oxindoles in good to

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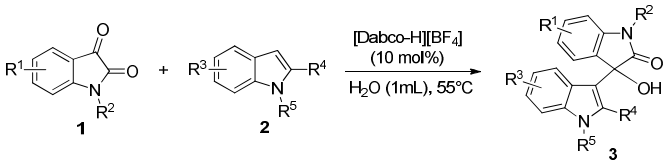
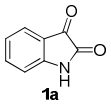
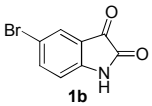
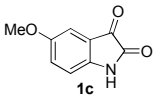
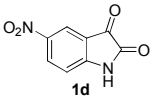
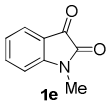
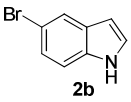
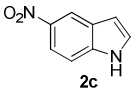
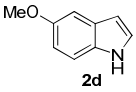
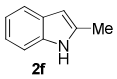
excellent yields (83-96%) within 30-90 min, and only monoindolylation products were formed under this condition.

Table 2. Synthesis of 3-indolyl-3-hydroxy oxindoles catalyzed by [Dabco-H][BF_4] in water. [a]



Entry	isatin	Indole	Product	T (min)	Yield (%)[b]
1	 **1a**	 **2a**	**3a**	60	85
2	 **1b**	**2a**	**3b**	30	93
3	 **1c**	**2a**	**3c**	45	91
4	 **1d**	**2a**	**3d**	30	96
5	 **1e**	**2a**	**3e**	90	83
6	**1e**	 **2b**	**3f**	60	92
7	**1e**	 **2c**	**3g**	60	95
8	**1e**	 **2d**	**3h**	60	93
9	**1e**	 **2e**	**3i**	45	94
10	**1e**	 **2f**	**3j**	60	93
11	**1a**	**2d**	**3k**	60	96
12	**1a**	**2f**	**3l**	90	90

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[a] Conditions: isatins (**1**, 1 mmol) and indoles (**2**, 1 mmol), ionic liquid catalyst [Dabco-H][BF_4] (0.1 mmol), and water 1.0 mL.

[b] Isolated yield.

This is a simple and mild reaction, which is readily amenable on large scale synthesis for 3-indolyl-3-hydroxy oxindoles. By using this procedure (**Condition A**), we tried out the reactions on a 50-mmol scale, 11.2 g of **3a** and 13.8 g of **3k** were prepared in the yield of 85% and 94% respectively (Figure 2). Therefore, this is an easy access to obtain 3-indolyl-3-hydroxy oxindoles on large scale.

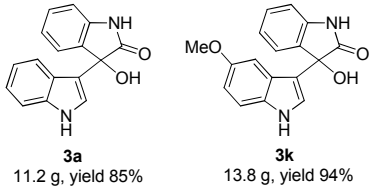
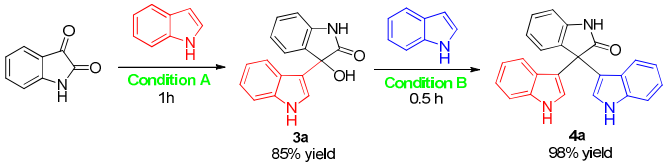


Figure 2. Synthesis of 3-indolyl-3-hydroxy oxindoles **3a** and **3k** on 50 mmol scale.

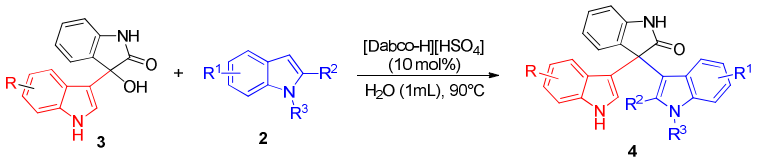
The catalytic Friedel–Crafts reaction of 3-indolyl-3-hydroxy oxindoles (**3**) and aromatic compounds is an atom economic procedure to construct both structural motifs, and it just produces water as waste. The key intermediates **3** can be prepared on large scale in a very single step from isatins as shown in Figure 2. Reactions for the synthesis of 3,3-diaryl oxindoles from isatins often suffered a large excess amount of strong acids or superacids. Here, in order to take advantage of the different catalytic activities between [Dabco-H][BF_4] and [Dabco-H][HSO_4], we planned a two-step green protocol for the synthesis of 3,3-diindolyl oxindoles in a more controlled manner. In this protocol, the key intermediate 3-(indol-3-yl)-3-hydroxy oxindole (**3a**), which was synthesized under Condition A, was treated with 1 equiv of another molecule of indole under Condition B to give the desired 3,3-diindolyl oxindole (**4a**) in an excellent yield of 98%. This means that unsymmetrical 3,3-diindolyl oxindoles even unsymmetrical 3,3-diaryl oxindoles could be achieved by using this two-step protocol.



Scheme 1. Two-step protocol for the efficient synthesis of 3,3-diindolyl oxindole **4a**.

Next, the scope of 3-indolyl-3-hydroxy oxindoles and indoles was investigated under Condition B for the synthesis of unsymmetrical 3,3-diindolyl oxindoles. As shown in Table 3, a number of unsymmetrical 3,3-diindolyl oxindoles with enough diversity could be readily obtained by this method. The influence of indoles with different substituents was studied, which found that all the differently substituted indoles, with electron-withdrawing or -donating groups worked well with 3-indolyl-3-hydroxy oxindoles to afford the desired products in excellent yields (95-98%) within only 0.5-1 hour.

Table 3. Synthesis of unsymmetrical 3, 3-diindolyl oxindoles catalyzed by [Dabco-H][HSO_4] in water. [a]



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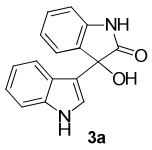
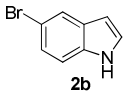
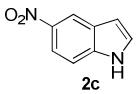
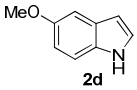
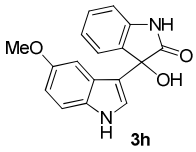
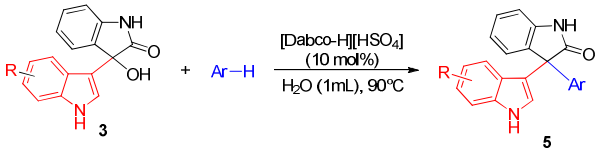
Entry	3	Indole	Product	Time (h)	Yield (%)[b]
1	 3a	 2a	**4a**	0.5	98
2	**3a**	 2b	**4b**	0.5	98
3	**3a**	 2c	**4c**	0.75	98
4	**3a**	 2d	**4d**	0.5	98
5	**3a**	 2e	**4e**	0.75	98
6	 3h	**2a**	**4d**	0.75	97
7	**3h**	**2b**	**4f**	1	95
8	**3h**	**2c**	**4g**	0.5	97

[a] Conditions: 3-indolyl-3-hydroxy oxindoles (1 mmol) and indoles (1 mmol), ionic liquid catalyst [Dabco-H][HSO_4] (0.1 mmol), and water 1.0 mL.

[b] Isolated yield.

Afterwards, to demonstrate the generality of this method, we further investigated other (hetero)aromatic compounds, including N-methylpyrrole, phenol, *p*-cresol, *p*-chlorophenol and N,N-dimethylaniline, instead of indoles to broaden the substrates of this Friedel–Crafts reaction under Condition B. As shown in Table 4, all the substrates were well tolerated to furnish the desired Friedel-Crafts products in good to excellent yields within only 0.5-2 hour. Excellent regioselectivity was observed in the case of phenol, only the para Friedel–Crafts products were obtained (Table 4, entries 3-4). While the para position of phenol was blocked, such as *p*-cresol and *p*-chlorophenol, the reaction gave the ortho alkylated products in excellent yields (Table 4, entries 5-7). It is very important that *p*-chlorophenol and N,N-dimethylaniline were the first time as the substrates employed in this reaction (Table 4, entries 7 and 8). All the Friedel–Crafts products of unsymmetrical 3,3-diaryl oxindoles in Table 4 are new compounds.

Table 4. Synthesis of unsymmetrical 3,3-diaryl oxindoles catalyzed by [Dabco-H][HSO_4] in water. [a]



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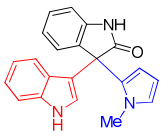
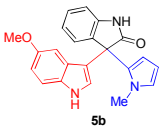
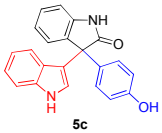
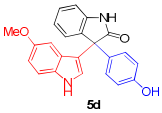
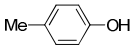
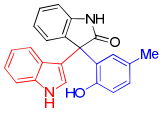
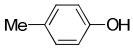
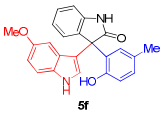
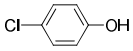
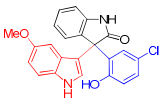
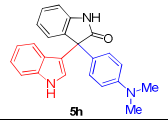
Entry	Ar-H	Product	Time (h)	Yield (%)[b]
1		 **5a**	0.5	96
2		 **5b**	0.5	97
3		 **5c**	0.5	93
4		 **5d**	0.5	85
5		 **5e**	1	95
6		 **5f**	1	92
7		 **5g**	0.5	94
8		 **5h**	2	88

[a] Conditions: 3-indolyl-3-hydroxy oxindoles (1 mmol) and aromatic compounds (1 mmol), ionic liquid catalyst [Dabco-H][HSO_4] (0.1 mmol), and water 1.0 mL.

[b] Isolated yield.

The reusability of the catalyst was also examined for the synthesis of **4b**. After completion of the reaction, the catalyst could be easily recycled by filtering the products from the mixture. The filtrate containing the water and the IL catalyst [Dabco-H][HSO_4] could be directly reused for the next cycle. The results are presented in Figure 3. It was observed that this Dabco-base catalyst could be recovered and reused in the Friedel–Crafts reaction of 3-(indol-3-yl)-3-hydroxy oxindole (**3a**) and 5-bromoindole for five times at least.

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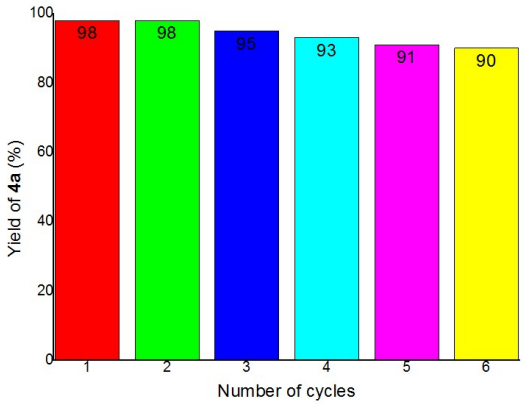
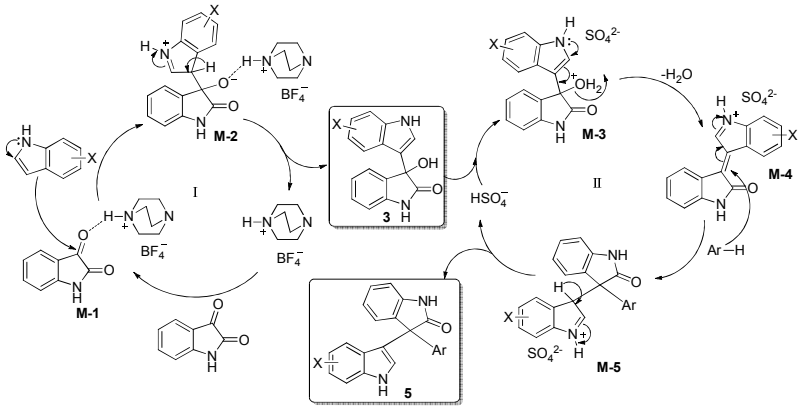


Figure 3. Recycling of the catalyst [Dabco-H][HSO_4] for the synthesis of **4b**.

A reasonable pathway for the synthesis of 3-indolyl-3-hydroxy oxindoles (**3**) and unsymmetrical 3,3-diaryl oxindoles (**4** or **5**) catalyzed by [Dabco-H][HSO_4] is shown in Scheme 2. The step **I** involves the formation of activated isatin (**M-1**) followed by its reaction with indole to generate intermediate **M-2** that subsequently undergoes a hydrogen transfer to yield **3** and [Dabco-H][BF_4]. In the following step **II** which reacts under 90°C in water, the protonation of **3** is done by [Dabco-H][HSO_4] to give the intermediate **M-3**. The lone pair electron of nitrogen in **M-3** causes the exit of the living group (H_2O) and gives the intermediate **M-4**, which subsequently undergoes further addition with the (hetero)aromatic molecule to afford the final products unsymmetrical 3,3-diaryl oxindoles (**4** or **5**).



Scheme 2. Proposed reaction mechanism.

Conclusion

In conclusion, we have described a green and novel protocol for highly efficient synthesis of 3-indolyl-3-hydroxy oxindoles and unsymmetrical 3,3-diaryl oxindoles using catalytic amount of efficiently reusable Dabco-base ionic liquid catalysts. All the reactions, using water as solvent, allowed Friedel-Crafts reactions to be performed in a very simple, clean and green manner. The method also offers several other significant advantages including simple operation, excellent yield, short reaction time, atom economy, scaling up to multigram quantities, high chemoselectivity, no use of metals, ease of separation and recyclability of the catalyst, as well as the ability to tolerate a wide variety of substitutions in the components. To the best of our knowledge, such an efficient

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Friedel-Crafts reaction performed in water for the synthesis of 3-indolyl-3-hydroxy oxindoles and unsymmetrical 3,3-diaryl oxindoles is reported for the first time. Further investigations and applications of this transformation for the synthesis of other biologically active molecules are still in progress. Results from such investigations will be reported soon.

Experimental

General experimental information. All chemicals were purchased from commercial suppliers and were used without further purification. Flash column chromatography was performed on silica gel (200–300 mesh). Melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-d_6 as the solvent. Chemical shifts are reported relative to TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant in hertz, and number of protons. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource.

General procedure for the synthesis of 3-indolyl-3-hydroxy oxindoles (3). A 5-mL round bottomed flask was charged with the isatins (**1**, 1 mmol), indoles (**2**, 1 mmol), [Dabco-H][BF_4] catalyst (0.1 mmol), and water 1.0 mL. Then the mixture was vigorously stirred at 55°C. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature, filtered and washed with cold methanol (2 mL), and then dried to obtain the crude products **3**, which were purified by the crystallization technique and no column purification was followed. The catalyst [Dabco-H][BF_4] was left in water and directly reused in the next recycling run under the same conditions. This catalytic system including the ionic liquid catalyst and water could be recovered and reused in the reaction for five times at least.

3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (3a)[15(g)] Red solid, mp 196-198 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 6.35 (s, 1H, OH), 6.86 (t, 1H, *J* = 7.6 Hz, ArH), 6.90 (d, 1H, *J* = 7.6 Hz, ArH), 6.94 (t, 1H, *J* = 7.6 Hz, ArH), 7.02 (t, 1H, *J* = 7.6 Hz, ArH), 7.07 (d, 1H, *J* = 2.0 Hz, -C_4HNH), 7.24 (d, 2H, *J* = 8.0 Hz, ArH), 7.34 (t, 2H, *J* = 8.8 Hz, ArH), 10.34 (s, 1H, NH), 10.98 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 75.3, 110.0, 111.9, 115.8, 118.9, 120.7, 121.5, 122.1, 123.9, 125.2, 125.3, 129.5, 133.9, 137.2, 142.1, 178.9.

5-bromo-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (3b)[15(g)] White solid, mp 236-238 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 6.53 (s, 1H, OH), 6.87-6.92 (m, 2H, ArH), 7.05 (t, 1H, *J* = 8.0 Hz, ArH), 7.11 (d, 1H, *J* = 2.4 Hz, -C_4HNH), 7.34 (t, 3H, *J* = 8.0 Hz, ArH), 7.43 (d, 1H, *J* = 8.0 Hz, ArH), 10.51 (s, 1H, NH), 11.04 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 75.0, 111.7, 111.9, 113.4, 114.8, 118.8, 120.1, 121.3, 123.7, 124.8, 127.4, 131.8, 136.0, 136.9, 141.0, 178.0.

3-hydroxy-3-(1H-indol-3-yl)-5-methoxyindolin-2-one (3c)[26] White solid, mp 203-205 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.65 (s, 3H, OCH_3), 6.35 (s, 1H, OH), 6.84 (s, 3H, ArH), 6.86 (t, 1H, *J* = 8.0 Hz, ArH), 7.02 (t, 1H, *J* = 7.6 Hz, ArH), 7.09 (d, 1H, *J* = 2.4 Hz, -C_4HNH), 7.34 (t, 2H, *J* = 7.6 Hz, ArH), 10.17 (s, 1H, NH), 10.98 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 55.5, 75.4, 110.1, 111.6, 111.6, 113.7, 115.5, 118.6, 120.4, 121.1, 123.6, 125.0, 134.8, 135.0, 136.9, 155.0, 178.5.

3-hydroxy-3-(1H-indol-3-yl)-5-nitroindolin-2-one (3d)[15(g)] Yellow solid, mp 230-232 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 6.76 (s, 1H, OH), 6.94 (t, 1H, *J* = 7.2 Hz, ArH), 7.05-7.12 (m, 3H, ArH and -C_4HNH), 7.37 (d, 1H, *J* = 8.0 Hz, ArH), 7.51 (d, 1H, *J* = 8.0 Hz, ArH), 8.06 (s, 1H), 8.26 (d, 1H, *J* = 7.2 Hz, ArH), 11.09 (s, 1H, NH), 11.13 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 74.6, 110.1, 111.8, 114.0, 118.9, 120.1, 120.4, 121.5, 124.0, 124.8, 126.6, 134.3, 137.0, 142.4, 148.2, 178.6.

3-hydroxy-3-(1H-indol-3-yl)-1-methylindolin-2-one (3e)[15(g)] White solid, mp 115-118 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.17 (s, 1H, CH_3), 6.44 (s, 1H, OH), 6.88 (t, 1H, *J* = 7.2 Hz, ArH), 7.02-7.10 (m, 4H, ArH and

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C_4HNH), 7.30-7.39 (m, 4H, ArH), 11.02 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 26.4, 75.1, 108.9, 111.9, 115.5, 119.0, 120.7, 121.5, 122.8, 124.0, 124.7, 125.3, 129.6, 133.2, 137.2, 143.5, 177.0.

3-hydroxy-3-(5-bromo-1H-indol-3-yl)-1-methylindolin-2-one (3f)[15(g)] White solid, mp 215-217 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.13 (s, 3H, CH_3), 6.52 (s, 1H, OH), 6.93 (d, 1H, *J* = 2.4 Hz, ArH), 7.07-7.11 (m, 2H, ArH and C_4HNH), 7.18 (dd, 1H, *J* = 1.6Hz, *J* = 8.4 Hz, ArH), 7.32-7.40 (m, 3H, ArH), 7.80 (s, 1H, ArH), 11.23 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 26.4, 74.8, 109.1, 111.7, 114.0, 115.3, 122.9, 123.9, 124.1, 124.8, 125.6, 127.5, 129.8, 132.6, 136.0, 143.5, 176.8.

3-hydroxy-3-(5-nitro-1H-indol-3-yl)-1-methylindolin-2-one (3g) White solid, mp 208-210 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.15 (s, 3H, CH_3), 6.70 (s, 1H, OH), 7.10-7.15 (m, 3H, 2ArH and C_4HNH), 7.40-7.44 (m, 2H, ArH), 7.54 (d, 1H, *J* = 8.8 Hz, ArH), 7.98-8.01 (dd, 1H, *J* = 1.6 Hz, *J* = 8.8 Hz, ArH), 11.76 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 26.4, 74.7, 109.2, 112.6, 117.1, 118.3, 119.2, 123.1, 124.9, 125.0, 127.7, 130.0, 132.1, 140.5, 140.8, 143.6, 176.6. Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 63.09; H, 4.23; N, 13.08.

3-hydroxy-3-(5-methoxy-1H-indol-3-yl)-1-methylindolin-2-one (3h)[27] Pale solid, mp 110-112 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.15 (s, 3H, CH_3), δ = 3.61 (s, 3H, OCH_3), 6.41 (s, 1H, OH), 6.68 (dd, 1H, *J* = 2.4 Hz, *J* = 8.8 Hz, ArH), 6.79 (d, 1H, *J* = 2.0 Hz, ArH), 6.99 (d, 1H, *J* = 2.4 Hz, ArH), 7.04-7.09 (m, 2H, ArH and C_4HNH), 7.22 (d, 1H, *J* = 8.8 Hz, ArH), 7.31 (d, 1H, *J* = 7.2 Hz, ArH), 7.36 (t, 1H, *J* = 7.6 Hz, ArH), 10.85 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 26.3, 55.5, 75.1, 102.7, 108.9, 111.4, 112.5, 115.1, 122.8, 124.7, 124.8, 125.7, 129.6, 132.3, 133.1, 143.5, 153.2, 177.0.

3-hydroxy-3-(1-methyindol-3-yl)-1-methylindolin-2-one (3i)[28] White solid, mp 93-95 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.15 (s, 3H, CH_3), δ = 3.71 (s, 3H, CH_3), 6.43 (s, 1H, OH), 6.91 (t, 1H, *J* = 7.6 Hz, ArH), 7.03-7.09 (m, 4H, ArH and C_4HNH), 7.30 (d, 1H, *J* = 7.2 Hz, ArH), 7.35-7.38 (m, 3H, ArH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 26.4, 32.8, 74.9, 109.0, 110.1, 114.7, 119.1, 121.1, 121.6, 122.8, 124.7, 125.7, 128.3, 129.6, 133.11, 137.6, 143.5, 176.9.

3-hydroxy-3-(2-methyl-1H-indol-3-yl)-1-methylindolin-2-one (3j)[15(g)] White solid, mp 224-226 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.17 (s, 3H, NCH_3), δ = 2.38 (s, 3H, CH_3), 6.35 (s, 1H, OH), 6.71-6.74 (m, 1H, ArH), 6.88-6.92 (m, 2H, ArH), 6.97-7.01 (m, 1H, ArH), 7.06 (d, 1H, *J* = 7.6 Hz, ArH), 7.18-7.24 (m, 2H, ArH), 7.32 (t, 1H, *J* = 7.2 Hz, ArH), 10.89(s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 13.7, 26.4, 76.0, 109.0, 109.7, 110.7, 118.7, 119.5, 120.3, 122.9, 124.9, 127.0, 129.5, 135.3, 137.6, 143.4, 177.3.

3-hydroxy-3-(5-methoxy-1H-indol-3-yl)indolin-2-one (3k)[15(h)] White solid, mp 193-195 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.65(s, 3H, OCH_3), 6.41 (s, 1H, OH), 6.75 (d, 1H, *J* = 7.2 Hz, ArH), 6.91 (s, 1H, ArH), 6.95 (d, 1H, *J* = 7.2 Hz, ArH), 7.01 (t, 1H, *J* = 6.4 Hz, ArH), 7.06 (s, 1H, -C_4HNH), 7.29 (s, 3H, ArH), 10.38 (s, 1H, NH), 10.88 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 55.6, 75.4, 103.1, 110.0, 111.3, 112.5, 115.4, 122.2, 124.7, 125.3, 125.8, 129.5, 132.4, 133.8, 142.1, 153.2, 178.9.

3-hydroxy-3-(2-methyl-1H-indol-3-yl)indolin-2-one (3l)[15(h)] Pale solid, mp 188-190 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 2.46 (s, 3H, CH_3), 6.33 (s, 1H, OH), 6.78 (t, 1H, *J* = 7.6 Hz, ArH), 6.95 (t, 3H, *J* = 7.6 Hz, ArH), 7.00 (t, 1H, *J* = 7.2 Hz, ArH), 7.28-7.29 (m, 3H, ArH), 10.39 (s, 1H, NH), 10.92 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 13.7, 76.3, 109.8, 110.0, 110.7, 118.6, 119.6, 120.2, 122.1, 125.4, 127.0, 129.4, 133.9, 134.6, 135.3, 142.0, 179.1.

General procedure for the synthesis of unsymmetrical 3,3-diaryl oxindoles (4 and 5).

A 5-mL round bottomed flask was charged with the 3-indolyl-3-hydroxy oxindoles (**3**, 1 mmol), (hetero)aromatic compounds (1 mmol), [Dabco-H][HSO_4] catalyst (0.1 mmol), and water 1.0 mL. Then the mixture was vigorously stirred at 90 °C. The formation of the products was monitored by TLC. After completion of the reaction, the

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mixture was cooled to room temperature, filtered and washed with cold water (2 mL), and then dried to obtain the products **4** or **5**. In general, no further purification method was required. The catalyst [Dabco-H][HSO_4] was left in water and directly reused in the next recycling run under the same conditions. The catalyst [Dabco-H][HSO_4] could be recovered and reused in the reaction for five times at least.

1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (4a)[15(h)] White solid, mp 277-280 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 6.79 (t, 2H, *J* = 7.6 Hz, ArH), 6.86 (d, 2H, *J* = 2.0 Hz, -C_4HNH), 6.91 (t, 1H, *J* = 7.6 Hz, ArH), 6.99 (t, 3H, *J* = 8.0 Hz, ArH), 7.18-7.27 (m, 4H, ArH), 7.34 (d, 2H, *J* = 8.0 Hz, ArH), 10.58 (s, 1H, NH), 10.92 (s, 2H, NH); ^{13}C NMR (100MHz, $CDCl_3$+DMSO-d_6): δ = 52.5, 109.5, 111.5, 114.2, 118.1, 120.7, 120.8, 121.3, 124.2, 124.8, 125.6, 127.7, 134.5, 136.8, 141.2, 178.7.

5-bromo-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (4b)[18(d)] Pale solid, mp >300 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 6.83 (t, 1H, *J* = 7.6 Hz, ArH), 6.95-7.05 (m, 4H, ArH and -C_4HNH), 7.14 (s, 1H, -C_4HNH), 7.18 (d, 1H, *J* = 8.0 Hz, ArH), 7.26 (d, 2H, *J* = 7.6 Hz, ArH), 7.39 (d, 1H, *J* = 8.0 Hz, ArH), 7.57 (d, 1H, *J* = 8.8 Hz, ArH), 7.96 (d, 1H, *J* = 9.6 Hz, ArH), 8.38 (s, 1H, ArH), 10.80 (s, 1H, NH), 11.05 (s, 1H, NH), 11.78 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 52.8, 110.4, 112.3, 112.8, 114.6, 117.0, 117.6, 117.6, 119.0, 120.4, 121.6, 122.3, 124.8, 125.4, 125.9, 128.5, 128.7, 134.2, 137.4, 140.6, 140.8, 141.8, 178.9.

5-nitro-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (4c)[29] Yellow solid, mp 295-297 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 6.82 (t, 1H, *J* = 7.6 Hz, ArH), 6.90 (d, 2H, *J* = 7.2 Hz, ArH), 6.95 (t, 1H, *J* = 7.2 Hz, ArH), 7.00-7.05 (m, 2H, ArH), 7.14-7.26 (m, 4H, ArH and -C_4HNH), 7.37 (t, 2H, *J* = 7.6 Hz, ArH), 7.47 (s, 1H, ArH), 10.69 (s, 1H, NH), 11.00 (s, 1H, NH), 11.22 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 52.5, 109.8, 111.0, 111.8, 113.8, 114.1, 114.2, 118.5, 120.3, 121.2, 121.8, 123.4, 123.6, 124.5, 125.0, 125.6, 126.0, 127.6, 128.2, 134.2, 135.8, 137.0, 141.4, 178.8.

4-methoxy-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (4d)[27] Pale solid, mp >300 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.73 (s, 3H, OMe), 6.92 (s, 2H, ArH), 7.01-7.25 (m, 6H, ArH and -C_4HNH), 7.47 (t, 4H, *J* = 9.2 Hz, ArH), 7.59 (d, 1H, *J* = 8.0 Hz, ArH), 10.84 (s, 1H, NH), 11.03 (s, 1H, NH), 11.18 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 52.7, 55.2, 103.5, 109.6, 110.6, 111.7, 112.2, 113.9, 114.3, 118.4, 120.9, 121.1, 121.6, 124.5, 125.1, 125.2, 125.9, 126.2, 128.0, 132.3, 134.7, 137.1, 141.5, 152.6, 178.9.

1-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (4e)[18(c)] Pale solid, mp 290-292 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.70 (s, 3H, Me), 6.76-6.86 (m, 4H, ArH and -C_4HNH), 6.91 (t, 1H, *J* = 7.6 Hz, ArH), 6.96-7.02 (m, 2H, ArH), 7.07 (t, 1H, *J* = 7.6 Hz, ArH), 7.19-7.26 (m, 4H, ArH), 7.34 (t, 2H, *J* = 7.2 Hz, ArH), 10.59 (s, 1H, NH), 10.94 (s, 1H, NH); ^{13}C NMR (100MHz, $CDCl_3$+DMSO-d_6): δ = 32.5, 52.7, 109.6, 109.7, 111.7, 113.8, 114.4, 118.4, 118.4, 120.8, 121.0, 121.2, 121.4, 121.5, 124.5, 125.0, 125.8, 126.3, 127.8, 128.5, 134.7, 137.1, 137.5, 141.5, 178.9.

5-bromo-5''-methoxy-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (4f) Pale solid, mp 230-232 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.73 (s, 3H, OMe), 6.84 (s, 1H, ArH), 6.93 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.8 Hz, ArH), 7.07 (d, 1H, *J* = 2.0 Hz, ArH), 7.16-7.19 (m, 2H, -C_4HNH), 7.23 (d, 1H, *J* = 7.6 Hz, ArH), 7.36 (d, 1H, *J* = 8.4 Hz, ArH), 7.41-7.50 (m, 3H, ArH), 7.57 (d, 1H, *J* = 8.4 Hz, ArH), 7.69 (s, 1H, ArH), 10.90 (s, 1H, NH), 11.05 (s, 1H, NH), 11.42 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 52.5, 55.2, 102.9, 109.8, 110.6, 111.1, 112.4, 113.8, 113.8, 114.0, 121.8, 123.4, 123.7, 125.0, 125.2, 126.0, 127.6, 128.2, 132.3, 134.2, 135.9, 141.4, 152.7, 178.8. HRMS (ESI) exact mass calcd for $C_{25}H_{18}BrN_3O_2Na$ $[M + Na]^+$ m/z 494.0480, found 494.0476.

5-methoxy-5''-nitro-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (4g) Yellow solid, mp 270-272 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.55 (s, 3H, OMe), 6.52 (s, 1H, ArH), 6.75 (d, 1H, *J* = 8.4 Hz, ArH), 6.95 (s, 1H, -C_4HNH), 7.00 (t, 1H, *J* = 7.2 Hz, ArH), 7.08 (d, 1H, *J* = 7.6 Hz, ArH), 7.20 (s, 1H, -C_4HNH), 7.27-7.33 (m, 3H, ArH), 7.60 (d, 1H, *J* = 8.8 Hz, ArH), 7.99 (d, 1H, *J* = 8.8 Hz, ArH), 8.44 (s, 1H, ArH), 10.84 (s, 1H, NH), 10.92 (s, 1H, NH), 11.81 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 52.9, 55.6, 103.1, 110.3, 111.1, 112.8, 114.2,

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117.1, 117.5, 119.0, 122.4, 125.5, 125.6, 126.3, 126.4, 128.6, 128.8, 132.6, 132.7, 134.2, 140.6, 141.9, 153.2, 179.0. HRMS (ESI) exact mass calcd for $C_{25}H_{18}N_4O_4Na$ $[M + Na]^+$ m/z 461.1226, found 461.1230.

3-(1H-indol-3-yl)-3-(1-methyl-1H-pyrrol-2-yl)indolin-2-one (5a) Yellow solid, mp 265-267 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.23 (s, 3H, Me), 5.57-5.58 (m, 1H, ArH), 5.88 (t, 1H, J = 3.2 Hz, ArH), 6.66 (s, 1H, ArH), 6.86-6.89 (m, 2H), 6.94 (t, 2H, J = 7.2 Hz, ArH), 7.05 (t, 1H, J = 7.6 Hz, ArH), 7.19-7.23 (m, 3H), 7.36 (d, 1H, J = 8.0 Hz, ArH), 10.66 (s, 1H, NH), 11.04 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 35.4, 53.5, 106.1, 109.9, 110.2, 112.1, 114.6, 119.1, 120.8, 121.6, 122.1, 123.4, 125.2, 125.3, 126.2, 128.5, 130.3, 134.5, 137.2, 141.2, 178.3. HRMS (ESI) exact mass calcd for $C_{21}H_{17}N_3ONa$ $[M + Na]^+$ m/z 350.1269, found 350.1277.

3-(1H-indol-3-yl)-5-methoxy-3-(1-methyl-1H-pyrrol-2-yl)indolin-2-one (5b) White solid, mp 248-250 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.24 (s, 3H, Me), 3.56 (s, 3H, OMe), 5.60-5.61 (m, 1H, ArH), 5.90 (t, 1H, J = 3.2 Hz, ArH), 6.57 (d, 1H, J = 2.0 Hz, ArH), 6.68 (t, 1H, J = 2.0 Hz, ArH), 6.72 (dd, 1H, J_1 = 2.4 Hz, J_2 = 8.8 Hz, ArH), 6.82 (d, 1H, J = 2.4 Hz, ArH), 6.92-6.97 (m, 2H), 7.19-7.26 (m, 3H), 10.66 (s, 1H, NH), 10.89 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 35.0, 44.0, 52.9, 54.9, 102.2, 105.5, 109.4, 109.7, 110.9, 112.1, 113.7, 121.6, 123.3, 124.7, 126.2, 127.9, 129.7, 131.8, 134.2, 140.6, 152.7, 177.8. HRMS (ESI) exact mass calcd for $C_{22}H_{19}N_3O_2Na$ $[M + Na]^+$ m/z 380.1375, found 380.1369.

3-(4-hydroxyphenyl)-3-(1H-indol-3-yl)indolin-2-one (5c) White solid, mp 166-168 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 6.68 (d, 2H, J = 8.8 Hz, ArH), 6.77-6.81 (m, 2H), 6.93-6.96 (m, 2H), 6.99-7.02 (m, 2H), 7.07 (d, 2H, J = 8.8 Hz, ArH), 7.19-7.22 (m, 2H), 7.33 (d, 1H, J = 8.0 Hz, ArH), 9.37 (s, 1H, OH), 10.59 (s, 1H, NH), 10.98 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 56.4, 109.6, 111.5, 114.9, 115.6, 118.2, 120.7, 120.9, 121.5, 124.3, 125.1, 125.4, 127.8, 128.5, 130.8, 134.4, 136.9, 141.1, 156.2, 178.8. HRMS (ESI) exact mass calcd for $C_{22}H_{17}N_2O_2$ $[M + H]^+$ m/z 341.1290, found 341.1291.

3-(4-hydroxyphenyl)-3-(1H-indol-3-yl)-5-methoxyindolin-2-one (5d) White solid, mp 200-202 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.50 (s, 3H, OMe), 6.43 (s, 1H, Ar), 6.69 (d, 3H, J = 7.6 Hz, ArH), 6.74 (s, 1H, Ar), 6.95 (t, 2H, J = 7.6 Hz, ArH), 7.09 (d, 2H, J = 8.0 Hz, ArH), 7.21 (t, 3H, J = 9.2 Hz, ArH), 9.35 (s, 1H, OH), 10.57 (s, 1H, NH), 10.81 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 55.0, 56.4, 103.2, 109.5, 110.4, 112.0, 114.8, 115.2, 121.5, 125.0, 125.2, 125.9, 127.7, 128.6, 130.7, 132.1, 134.4, 141.2, 152.4, 156.2, 178.8. HRMS (ESI) exact mass calcd for $C_{23}H_{19}N_2O_3$ $[M + H]^+$ m/z 371.1396, found 371.1403.

3-(2-hydroxy-5-methylphenyl)-3-(1H-indol-3-yl)indolin-2-one (5e) Yellow solid, mp 131-132 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 1.98 (s, 3H, Me), 6.52 (d, 1H, J = 2.0 Hz, ArH), 6.58 (d, 1H, J = 8.0 Hz, ArH), 6.73 (s, 1H, ArH), 6.82-6.87 (m, 3H, ArH), 6.89-6.91 (m, 2H, ArH), 7.04 (t, 1H, J = 7.6 Hz, ArH), 7.15-7.19 (m, 1H, ArH), 7.35 (d, 1H, J = 8.0 Hz, ArH), 7.49 (t, 1H, J = 8.4 Hz, ArH), 9.14 (s, 1H, OH), 10.16 (s, 1H, NH), 10.93 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 20.4, 55.6, 108.8, 111.5, 113.4, 115.2, 117.9, 120.6, 121.0, 122.7, 124.1, 124.6, 125.8, 126.2, 126.7, 127.3, 128.3, 130.3, 133.8, 137.2, 138.3, 142.4, 152.6, 179.2. HRMS (ESI) exact mass calcd for $C_{23}H_{19}N_2O_2$ $[M + H]^+$ m/z 355.1447, found 355.1440.

3-(2-hydroxy-5-methylphenyl)-3-(5-methoxy-1H-indol-3-yl)indolin-2-one (5f) White solid, mp 142-143 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 2.01 (s, 3H, Me), 3.55 (s, 3H, OMe), 6.50 (d, 1H, J = 1.6 Hz, ArH), 6.59 (d, 1H, J = 8.0 Hz, ArH), 6.72 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz, ArH), 6.77 (s, 1H, ArH), 6.83-6.90 (m, 4H, ArH), 6.95 (s, 1H, ArH), 7.15-7.19 (m, 1H, ArH), 7.25 (d, 1H, J = 8.8 Hz, ArH), 9.13 (s, 1H, OH), 10.16 (s, 1H, NH), 10.80 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 20.4, 55.3, 55.6, 105.3, 108.8, 110.9, 111.9, 112.9, 115.3, 120.6, 124.1, 125.4, 126.2, 126.4, 127.3, 128.3, 130.4, 132.4, 133.9, 142.4, 152.2, 152.6, 179.3. HRMS (ESI) exact mass calcd for $C_{24}H_{21}N_2O_3$ $[M + H]^+$ m/z 385.1552, found 385.1545.

3-(5-chloro-2-hydroxyphenyl)-3-(5-methoxy-1H-indol-3-yl)indolin-2-one (5g) White solid, mp 126-127 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.58 (s, 3H, OMe), 6.51 (d, 1H, J = 1.6 Hz, ArH), 6.71 (d, 1H, J = 8.4 Hz, ArH), 6.75 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz, ArH), 6.84-6.86 (m, 2H, ArH), 6.91-6.94 (m, 2H, ArH), 7.01 (s, 1H, ArH),

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7.14 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz, ArH), 7.18-7.22 (m, 1H, ArH), 7.29 (d, 1H, J = 8.8 Hz, ArH), 9.76 (s, 1H, OH), 10.22 (s, 1H, NH), 10.89 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 55.3, 55.4, 105.3, 108.9, 111.0, 112.0, 112.1, 116.9, 120.7, 121.7, 124.0, 125.7, 125.9, 127.6, 127.7, 129.0, 129.5, 132.4, 133.0, 142.6, 152.4, 153.8, 178.4. HRMS (ESI) exact mass calcd for $C_{23}H_{18}ClN_2O_3$ $[M + H]^+$ m/z 405.1006, found 405.1011.

3-(4-(dimethylamino)phenyl)-3-(1H-indol-3-yl)indolin-2-one (5h) White solid, mp 145-147 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ = 2.92 (s, 6H, Me), 6.69 (d, 2H, J = 7.6 Hz, ArH), 6.89 (d, 1H, J = 2.8 Hz, ArH), 6.92-6.93 (m, 1H, ArH), 6.96 (d, 1H, J = 6.8 Hz, ArH), 6.99 (d, 1H, J = 7.6 Hz, ArH), 7.12 (t, 1H, J = 8.4 Hz, ArH), 7.19 (t, 1H, J = 7.6 Hz, ArH), 7.25 (d, 3H, J = 8.8 Hz, ArH), 7.29-7.32 (m, 2H, ArH), 8.12 (s, 1H, NH), 8.49 (s, 1H, NH); ^{13}C NMR (100MHz, $CDCl_3$): δ = 40.71, 40.76, 57.19, 110.00, 111.26, 116.74, 119.52, 121.54, 122.07, 122.61, 124.19, 125.71, 125.92, 127.85, 128.71, 134.82, 137.03, 140.00, 180.37. HRMS (ESI) exact mass calcd for $C_{24}H_{22}N_3O$ $[M + H]^+$ m/z 368.1763, found 368.1770.

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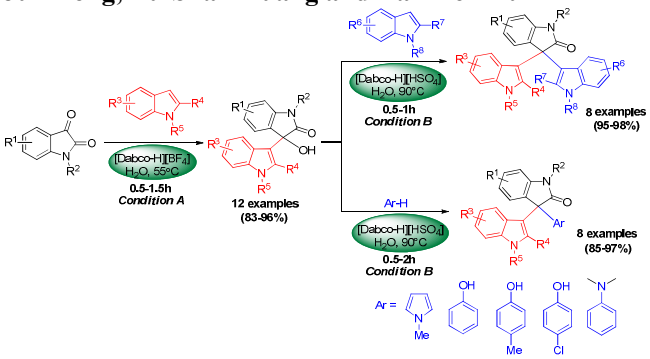
An efficient Friedel-Crafts alkylation for synthesis of 3-indolyl-3-hydroxy oxindoles and unsymmetrical 3,3-diaryl oxindoles catalyzed by Dabco-base ionic liquids in water

Jun Tong, Lu-Shan Huang and Da-Zhen Xu*



An efficient, green and reusable catalystic system for controlled 3-indolylation of isatins.