

Iron-containing ionic liquid as an efficient and recyclable catalyst for the synthesis of C3-substituted indole derivatives

Ying-Chun Gu^{1*} | Ren-Ming Hu^{2*} | Ming-Ming Li² | Da-Zhen Xu²

¹Tianjin Engineering Technology Center of Chemical Wastewater Source Reduction and Recycling, School of Science, Tianjin Chengjian University, Tianjin 300384, People's Republic of China

²National Engineering Research Center of Pesticide (Tianjin), State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence

Da-Zhen Xu, National Engineering Research Center of Pesticide (Tianjin), State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China.
Email: xudazhen@nankai.edu.cn

Funding information

National Training Programs of Innovation and Entrepreneurship for Undergraduates, Grant/Award Number: 201810055095; National Natural Science Foundation of China, Grant/Award Number: 21302101

A facile and efficient protocol for the synthesis of C3-substituted indole derivatives has been developed under mild condition. The iron-containing ionic liquid, 1-(2-hydroxyethyl)-1,4-diazabicyclo[2.2.2] octanylium tetrachloroferrate ([Dabco-C₂OH][FeCl₄]) as a recyclable catalyst has been successfully used in the synthesis of trisindolines, bis(3-indolyl) methanes and β -indolyl alcohols for the first time. The products of trisindolines and bis(3-indolyl) methanes are easily separated and purified without chromatographic technique. The catalyst was recycled six times without significant activity loss.

KEYWORDS

C-C bond formation, Friedel-Crafts reaction, indoles, ionic liquids, isatins

1 | INTRODUCTION

Indole derivatives are widespread in nature products.^[1] Most of the known bioactive alkaloids are based on the indole moiety. They often display a wide variety of pharmacological and biological activities.^[2] Among them, the densely C3-substituted indoles have become a privileged structure in numerous research.^[3,4] In particular, the bis-indoles have attracted much attention due to their biological efficacies.^[5,6] Recently, they are also used as tranquilizers in the treatment of cancer and shown to

exhibit anticancer activity, inhibit the growth of cancer cells.^[7] Some of the naturally occurring bioactive C3-substituted indoles are shown in Figure 1. Moreover, C3-substituted indoles are often employed as the key intermediates and useful building blocks in the total synthesis of natural products.^[8] Therefore, various methods have been reported for preparing this class of compounds.^[9-11] The most straightforward method to obtain the heterocycle involves the condensation of indoles with different carbonyl compounds (aldehydes or ketones), which was often promoted by homo- and heterogeneous catalysts such as acid catalysts,^[12-24] nano catalysts,^[25-31] supported catalysts,^[32-41] metal catalysts,^[42-49] ion

*These authors contributed equally to this work.

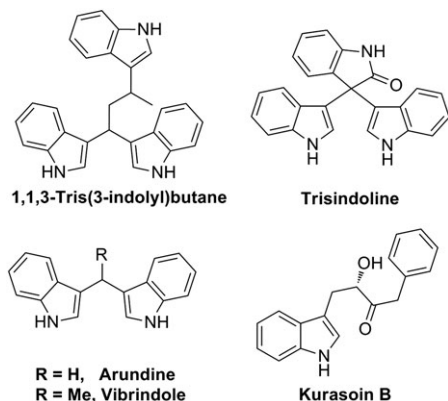


FIGURE 1 Examples of biologically active C3-substituted indoles

exchange resin,^[50] and enzymes.^[51] Although these reported protocols have made some certain merits, many of them still have notable disadvantages such as harsh reaction conditions, long reaction times, limited substrate scope, using expensive Lewis acids and solvents, high catalyst loading and generation of large amounts of harmful wastes. Hence, the development of a new, efficient and eco-friendly high-yielding general route for the synthesis of diverse C3-substituted indole is still highly desirable.

Ionic liquid (ILs) as green media in chemical and biochemical transformations have received much attention in the last decade. Especially as environmentally friendly catalysts,^[52–56] they have been successfully applied in the synthesis of densely substituted indole derivatives. However, only few literatures have mentioned the methods to obtain the trisindoline and its derivatives which were formed by the Friedel–Crafts reaction between 1 eq. isatin and 2 eq. indoles.^[57–60] Even though, these methods still suffered from various disadvantages such as high reaction temperature, large amounts of catalyst loading and limited substrate scope. Recently, magnetic ILs as a new kind of ionic liquid have been proposed and introduced in a number of important organic process due to their unique characteristics.^[61–73] Herein, as our ongoing interest in highly efficient ILs catalyzed multi-component reactions,^[74–79] we wish to report a new kind of magnetic IL [Dabco-C₂OH][FeCl₄] as a highly efficient and recyclable catalyst for general synthesis of densely substituted indoles, including both trisindolines and bis(3-indolyl) methanes, in excellent yields under mild conditions.

2 | RESULTS AND DISCUSSION

Four IL catalysts base on the skeleton of 1,4-diazobicyclo [2.2.2] octane (DABCO) have been synthesized, and they are shown in Figure 2. The ILs of [Dabco-C₄] Cl, [Dabco-C₃OH] Cl, [Dabco-C₂OH] Cl, were prepared according to the standard procedure that we have reported.^[75] The IL

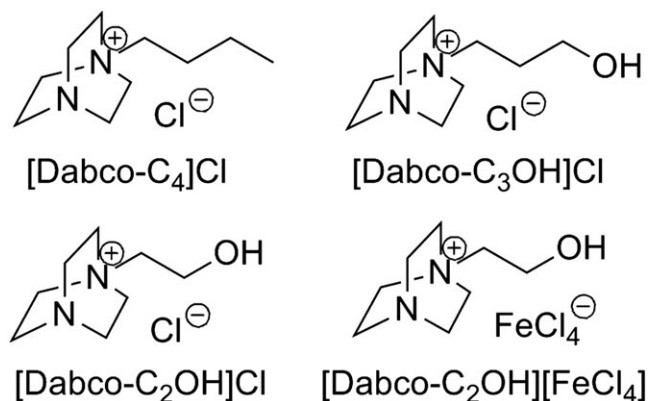


FIGURE 2 Structures of the Dabco-base ionic liquid catalysts

[Dabco-C₂OH][FeCl₄] was easily prepared by the simple mixing [Dabco-C₂OH] Cl with FeCl₃, and the anion of the catalyst Cl⁻ was changed to FeCl₄⁻.

The Raman spectra of [Dabco-C₂OH][FeCl₄] and [Dabco-C₂OH] Cl were shown in Figure 3. The absorption bands of [Dabco-C₂OH][FeCl₄] are similar to those of [Dabco-C₂OH]Cl. The [Dabco-C₂OH][FeCl₄] spectrum shows one clean peak at 338 cm⁻¹ that has been previously assigned to tetrahedral FeCl₄⁻.^[80]

Our investigation commenced with the reaction between indole (**1a**) and isatin (**2a**) in the presence of a catalytic amount of [Dabco-C₄] Cl in C₂H₅OH at 50 °C, and we were pleased to find that trisindoline **3a** was formed in 59% yield within 6 hours (Table 1, entry 1). Then other Dabco-based IL catalysts were tested in order to find the best catalyst for this transformation. As can be seen from the results summarized in Table 1 (entries 1–4), all the Dabco-based IL catalysts could drive the reaction and afforded product **3a** in moderate to excellent yields.

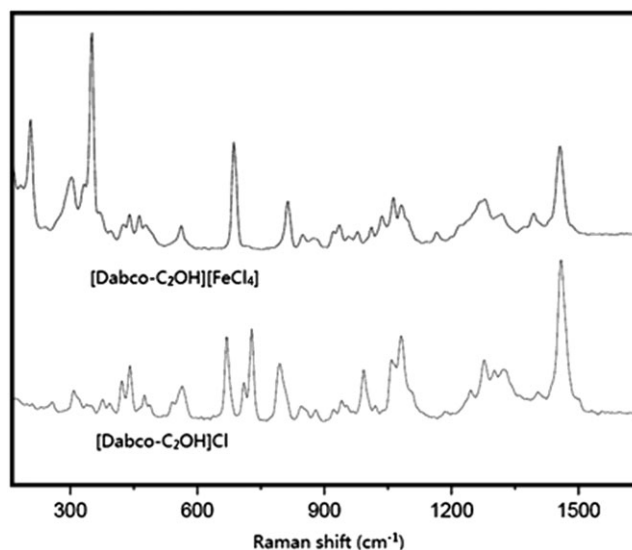
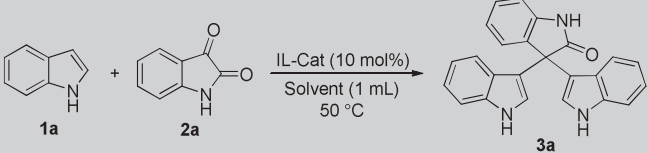


FIGURE 3 Raman spectra of [Dabco-C₂OH][FeCl₄] and [Dabco-C₂OH]Cl

TABLE 1 The effect of the Dabco-based IL catalysts on the Friedel–Crafts reaction for the synthesis of trisindoline **3a**^a


Entry	Cat (10 mol%)	Solvent	Time (min)	Yield ^b (%)
1	[Dabco-C ₄]Cl	C ₂ H ₅ OH	360	59
2	[Dabco-C ₃ OH]Cl	C ₂ H ₅ OH	360	71
3	[Dabco-C ₂ OH]Cl	C ₂ H ₅ OH	360	82
4	[Dabco-C ₂ OH][FeCl ₄]	C ₂ H ₅ OH	15	98
5 ^c	[Dabco-C ₂ OH][FeCl ₄]	C ₂ H ₅ OH	50	96
6	[Dabco-C ₂ OH][FeCl ₄]	THF	180	86
7	[Dabco-C ₂ OH][FeCl ₄]	H ₂ O	180	74
8	[Dabco-C ₂ OH][FeCl ₄]	DMF	360	59
9 ^d	[Dabco-C ₂ OH][FeCl ₄]	C ₂ H ₅ OH	30	94
10 ^e	[Dabco-C ₂ OH][FeCl ₄]	C ₂ H ₅ OH	90	90
11	FeCl ₃	C ₂ H ₅ OH	15	93
12	DABCO	C ₂ H ₅ OH	180	<3
13	no catalyst	C ₂ H ₅ OH	720	---
14	[Dabco-C ₂ OH][FeCl ₄]	C ₂ H ₅ OH	20	95 ^f

^aConditions: indole (**1a**, 2 mmol), isatin (**2a**, 1 mmol), IL catalyst (0.1 mmol, 10 mol%), and solvent 1 mL at 50 °C.

^bIsolated yield.

^cThe reaction temperature was 30 °C.

^d5 mol% catalyst.

^e3 mol% catalyst.

^f5-mmol scale.

Especially in the presence of [Dabco-C₂OH][FeCl₄] (10 mol%), trisindoline **3a** was obtained in a fairly good yield of 98% within only 15 min (Table 1, entry 4). Even performed the reaction under near room temperature (30 °C), the product of **3a** was also formed in a high yield of 96% in 50 minutes (Table 1, entry 5). To further improve the reaction conditions, different solvents, such as THF, H₂O and DMF, were screened, but no better results were obtained (Table 1, entries 6–8). Next, we tried to reduce the catalytic loading to 5 mol% and 3 mol%, product **3a** was also formed in good yields (Table 1, entries 9 and 10). Other catalysts, such as FeCl₃ and DABCO, were also investigated, but they did not lead to better results (Table 1, entries 11 and 12). In addition, no reaction occurred even after a long reaction time when the reaction performed under condition without any catalyst (Table 1, entry 13). In order to show the efficiency of this method, we performed the reaction on 5-mmol scale, and 1.72 g of **3a** was prepared in 95% yield (Table 1, entry 14).

In order to show the merit of this work, the result regarding the reaction of indole and isatin was compared

with the reported methods that are promoted by IL catalysts. As shown in Table 2, even a low amount of 5 mol% [Dabco-C₂OH][FeCl₄] could also drive the reaction to afford corresponding product **3a** in an excellent yield within a very short time (Table 1, entry 5). All the results indicated that the IL [Dabco-C₂OH][FeCl₄] is an excellent catalyst for this transformation. Consequently, this is a highly efficient and green protocol for the synthesis of trisindoline derivatives.

Having identified the optimal reaction conditions, we examined the substrate scope of the reaction between indoles (**1**) and isatins (**2**) catalyzed by [Dabco-C₂OH][FeCl₄] (10 mol%) in C₂H₅OH at 50 °C, and the results are listed in Table 3. All the reactions between different substituted indoles (**1a–e**) and isatin (**2a**) proceeded smoothly under the standard reaction conditions and afforded the corresponding trisindolines (**3a–e**) in excellent yields (94–98%) within very short reaction times (5–60 minutes) (Table 3, entries 1–5). Isatins with diverse functional groups such as halide, methoxy, methyl and nitro were also tolerated in the present protocol (Table 3

TABLE 2 Comparison with reported IL catalysts for the synthesis of **3a**

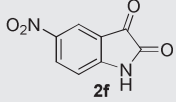
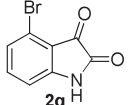
Entry	Catalyst (mol%)	Conditions	Time (min)	Yield (%)
1	TMGT (1 mL)	rt	60	93 ^[57]
2	[(CH ₂) ₄ SO ₃ HMIM][HSO ₄] (12)	H ₂ O, rt	35	95 ^[58]
3	[Dabco-H][HSO ₄] (10)	H ₂ O, 90 °C	120	95 ^[59]
4	[Dabco-C ₂ OH][FeCl ₄] (10)	C ₂ H ₅ OH, 50 °C	15	98[This work]
5	[Dabco-C ₂ OH][FeCl ₄] (5)	C ₂ H ₅ OH, 50 °C	30	94[This work]

TABLE 3 Synthesis of trisindolines from indoles and isatins catalyzed by [Dabco-C₂OH][FeCl₄]^a

Entry	1	2	3	Time (min)	Yield ^b (%)
1			3a	15	98
2		2a	3b	60	94
3		2a	3c	7	95
4		2a	3d	10	96
5		2a	3e	13	97
6	1a		3f	40	91
7	1a		3g	5	98
8	1a		3h	60	85
9	1a		3i	60	92

(Continues)


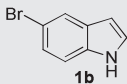
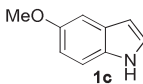
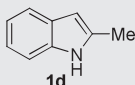
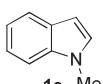
TABLE 3 (Continued)

Entry	1	2	3	Time (min)	Yield ^b (%)
10	1a		3j	35	96
11	1a		3k	120	81

^aConditions: indoles (**1**, 2 mmol), isatins (**2**, 1 mmol), [Dabco-C₂OH][FeCl₄] (35.5 mg, 0.1 mmol), and C₂H₅OH (1 ml) at 50 °C.

^bIsolated yield.

TABLE 4 Synthesis of bis (indolyl) methanes from indoles and aldehydes catalyzed by [Dabco-C₂OH][FeCl₄]^a

Entry	1	Ar	5	Time (min)	Yield ^b (%)
1		4-MeOC ₆ H ₄	5a	2	98
2		4-MeOC ₆ H ₄	5b	<1	97
3		4-MeOC ₆ H ₄	5c	<1	96
4		4-MeOC ₆ H ₄	5d	<1	98
5		4-MeOC ₆ H ₄	5e	<1	96
6	1a	Ph	5f	10	95
7	1a	4-MeC ₆ H ₄	5g	20	97
8	1a	4-ClC ₆ H ₄	5h	75	92
9	1a	2-ClC ₆ H ₄	5i	15	98
10	1a	4-BrC ₆ H ₄	5j	60	96
11	1a	4-NO ₂ C ₆ H ₄	5k	120	90
12	1a	2,4-Cl ₂ C ₆ H ₃	5l	10	95

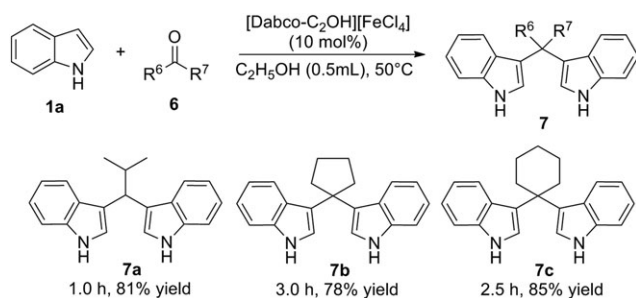
^aConditions: indoles (**1**, 2 mmol), aldehydes (**4**, 1 mmol), [Dabco-C₂OH][FeCl₄] (35.5 mg, 0.1 mmol), and C₂H₅OH (1 ml) at 50 °C.

^bIsolated yield.

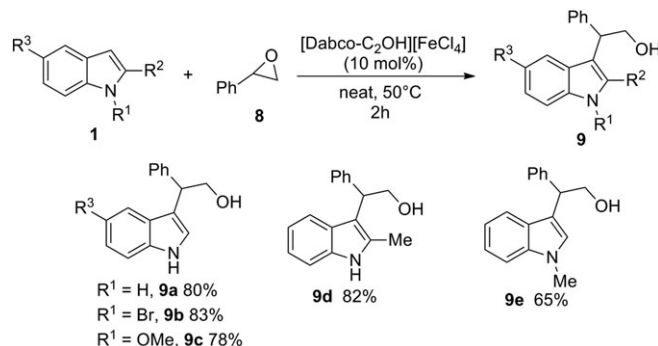
, entries 6–11). When 5-substituted indoles are employed in the reaction, high yields often obtained within short reaction times (Table 3, entries 6–10). However, when the indole with other substituent position, such as 4-bromoindole, is used in the reaction, a longer reaction time is needed (Table 3, entry 11).

Encouraged by the remarkable results, to further confirm the generality of this approach, we then often extended the method to synthesis of other kinds of bis-indoles, such as bis(indolyl) methane derivatives. As shown in Table 4, the Friedel–Crafts reaction between indoles and aromatic aldehyde with electron-withdrawing or -donating groups delivered the desired products in excellent yields (90–98%) under the optimal reaction conditions. Furthermore, the positions and number of substituted group of aromatic aldehydes have no effect on the reaction yields.

It is of interest to further extend the application of this procedure to synthesis of bis-indoles from aliphatic aldehydes and ketones. The substrates of isobutyraldehyde, cyclopentanone and cyclohexanone were tested in this reaction. As expected, the reactions proceeded well to afford the corresponding products **7a** to **7c** in good yields. However longer reaction times were needed for the syn-



SCHEME 1 Synthesis of bis-indoles from aliphatic aldehyde/ketone. The reactions were carried out with indole (234 mg, 2 mmol), aliphatic aldehydes or ketones (1 mmol), [Dabco-C₂OH][FeCl₄] (35.5 mg, 0.1 mmol), and C₂H₅OH (1 ml) at 50 °C. Yields are those of isolated products



SCHEME 2 [Dabco-C₂OH][FeCl₄]-catalyzed alkylation of indoles with styrene oxide. The reactions were carried out with indoles (1 mmol), styrene oxide (144 mg, 1.2 mmol) and [Dabco-C₂OH][FeCl₄] (35.5 mg, 0.1 mmol) under neat conditions at 50 °C. Yields are those of isolated products

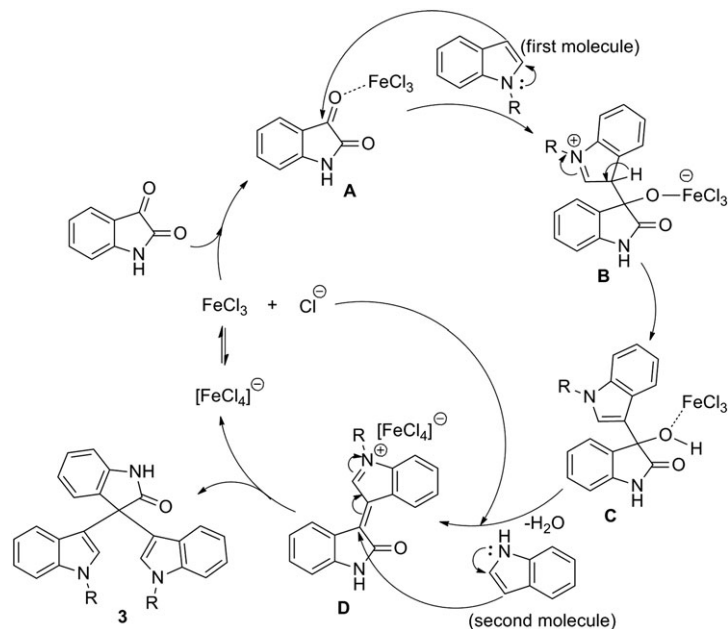
thesis of **7b** and **7c** because of the low activity of the aliphatic ketones. The results are represented in Scheme 1. All the results obtained clearly indicate that we have developed a simple, efficient and high-yielding general route for the synthesis of a wide variety of densely substituted indole derivatives.

On the other hand, C3-substituted indoles can be prepared by ring-opening of epoxides with indoles *via* Friedel–Crafts alkylation which is also an attractive transformation due to its atom economy.^[81] Then we examined the ring-opening reaction between indoles with styrene oxide in presence of 10 mol% [Dabco-C₂OH][FeCl₄] catalyst under neat conditions at 50 °C. As expected, the desirable products **9a–e** were all obtained in good yields (Scheme 2).

The recyclability of the catalyst is one of the most important parameters in chemical production, we investigated the recyclability of this ionic liquid for the synthesis of trisindoline **3a**. After completion of the reaction, the mixture was cooled to 0 °C and filtered, then dried to obtain the pure product. The IL catalyst was left in filtrate. After removing the solvent under vacuum, the catalyst could be directly reused in the next recycling run under the same conditions. Even after reusing for six times, this iron-containing ionic liquid could also drive the reaction and afford the corresponding product in a high yield (Table 5).

TABLE 5 Recycling of the ionic liquid for the synthesis of **3a**

Entry	Cycles	Yield (%)
1	1st	98
2	2nd	96
3	3rd	95
4	4th	93
5	5th	92
6	6th	90



SCHEME 3 Proposed reaction mechanism

Based on the experimental results, a tentative mechanism for the formation of bis-indoles is depicted in Scheme 3. Both the anion of [FeCl₄][−] and Lewis acid FeCl₃ play the important roles. The reaction, most probably, starts with the activation of carbonyl group with FeCl₃ to form **A**. Next, an addition reaction may occur between **A** and the first molecule of indole to generate ionic intermediate **B**. Dehydration of **C** affords the intermediate **D** which probably undergoes addition with the second molecule of indole to afford the target product **3** and regenerates the catalyst. Other substrates of carbonyl compounds undergo a similar transformation.

3 | CONCLUSION

In summary, we have successfully developed a novel, efficient and inexpensive iron-containing IL ([Dabco-C₂OH][FeCl₄]) catalyst for the synthesis of C3-substituted indole derivatives including trisindolines, bis(3-indolyl) methanes and β-indolyl alcohols under mild conditions. A wide range of carbonyl compounds including isatins, aromatic/aliphatic aldehydes and aliphatic ketones with different substituted indoles can be employed in the reaction, and afford the corresponding trisindoline and bis(3-indolyl) methane derivatives in excellent yields. It is much superior to other reported synthetic protocols, in terms of its simple operation, short reaction time, excellent yield, absence of any chromatographic separation technique, ease of separation and recyclability of the catalyst. In addition, this efficient protocol was also applied to the synthesis of β-indolyl alcohols *via* Friedel–Crafts alkylation of indoles with styrene oxide. Further

investigations of the catalysts are still in progress. The results will be reported soon.

4 | EXPERIMENTAL

4.1 | Materials and instrumentation

All the solvents were used without further purification. Melting points were determined with a RY-I apparatus and are reported uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-*d*₆ or CDCl₃ as the solvent. Chemical shifts were calibrated to tetramethylsilane as an external reference. The ¹H 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. Raman measurements were carried out on a Bruker RFS 100/S Raman spectrometer at a wavelength of 1046 nm of a Nd:YAG laser. Thermogravimetric analysis (TGA) was carried out on an SDT Q600 simultaneous thermal analyzer.

4.2 | General procedure for the synthesis of trisindolines and bis-indoles (**3**, **5** and **7**)

A mixture of indoles (**1**, 2 mmol), carbonyl compounds (1 mmol) and [Dabco-C₂OH][FeCl₄] (35 mg, 10 mol%) in ethanol (1.0 mL) was stirred at 50 °C for the appropriate time. Upon completion of the reaction (monitored by TLC), the mixture was cooled to 0 °C, filtered and washed with cold ethanol, then dried to obtain the pure products (**3**, **5** and **7**). In general, no further purification method

was required. The IL catalyst was left in filtrate. After removing the solvent under vacuum, the catalyst could be directly reused in the next recycling run under the same conditions.

4.3 | General procedure for the synthesis of β -indolyl alcohols (9)

A mixture of indoles (**1**, 1 mmol), styrene oxide (144 mg, 1.2 mmol) and [Dabco-C₂OH][FeCl₄] (35 mg, 10 mol%) was stirred at 50 °C for 2 hrs. Then the reaction mixture was diluted with cold water (5 ml) and CH₂Cl₂ (5 ml), and extracted with CH₂Cl₂ (2 × 5 ml), the organic phase was washed with brine (5 ml). After the removal of the solvent under reduced pressure, the residue was subjected to chromatography on a silica gel (200–300 mesh) column using petroleum ether/ethyl acetate (3:1) as eluent to afford the corresponding products **9**. The IL catalyst was left in aqueous phase. After removing the solvent under vacuum, the catalyst could be directly reused in the next recycling run for the same reaction.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (NSFC) (No. 21302101), and National Training Programs of Innovation and Entrepreneurship for Undergraduates (No. 201810055095). We also thank the Nankai University College of Chemistry for support.

ORCID

Da-Zhen Xu  <https://orcid.org/0000-0001-5076-7558>

REFERENCES

- [1] M. Shiri, *Chem. Rev.* **2012**, *112*, 3508.
- [2] R. J. Sundberg, *The Chemistry of Indoles*, New York, Academic **1996**.
- [3] M. Bandini, A. Eichholzer, *Angew. Chem. Int. Ed.* **2009**, *48*, 9608.
- [4] R. Dalpozzo, *Chem. Soc. Rev.* **2015**, *44*, 742.
- [5] G. Sivaprasad, P. T. Perumal, V. R. Prabavathy, N. Mathivanan, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 6302.
- [6] A. Kamal, M. N. A. Khan, K. Srinivasa Reddy, Y. V. V. Srikanth, S. Kaleem Ahmed, K. Pranay Kumar, U. S. N. Murthy, *J. Enzyme Inhib. Med. Chem.* **2009**, *24*, 559.
- [7] T. Andrey, A. Patel, T. Jackson, S. Safe, M. Singh, *Eur. J. Pharm. Sci.* **2013**, *50*, 227.
- [8] C.-K. Mai, M. F. Sammons, T. Sammakia, *Angew. Chem. Int. Ed.* **2010**, *49*, 2397.
- [9] R. Liu, J. Zhang, *Org. Lett.* **2013**, *15*, 2266.
- [10] L. Z. Fekri, M. Nikpassand, *Lett. Org. Chem.* **2017**, *14*, 494.
- [11] M. Nikpassand, L. Z. Fekri, M. Nabatzadeh, *Synth. Commun.* **2017**, *47*, 29.
- [12] G. Brahmachari, B. Banerjee, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2802.
- [13] H. Alinezhad, A. H. Haghighi, F. Salehian, *Chin. Chem. Lett.* **2010**, *21*, 183.
- [14] L.-J. Zhou, Y.-C. Zhang, J.-J. Zhao, F. Shi, S.-J. Tu, *J. Org. Chem.* **2014**, *79*, 10390.
- [15] Y. Sarrafi, K. Alimohammadi, M. Sadatshahabi, N. Norozipoor, *Monatsh. Chem.* **2012**, *143*, 1519.
- [16] Y. Liu, R.-Y. Zhu, H.-Z. Li, Y. Jiang, F. Shi, *Synthesis* **2015**, *47*, 1436.
- [17] Y. A. Tayade, D. R. Patil, Y. B. Wagh, A. D. Jangle, D. S. Dalal, *Tetrahedron Lett.* **2015**, *56*, 666.
- [18] K. Singh, S. Sharma, A. Sharma, *J. Mol. Catal. A Chem.* **2011**, *347*, 34.
- [19] A. Ganesan, J. Kothandapani, J. B. Nanubolu, S. S. Ganesan, *RSC Adv.* **2015**, *5*, 28597.
- [20] S.-J. Ji, M.-F. Zhou, D.-G. Gu, S.-Y. Wang, T.-P. Loh, *Synlett* **2003**, 2077.
- [21] S.-J. Ji, M.-F. Zhou, D.-G. Gu, Z.-Q. Jiang, T.-P. Loh, *Eur. J. Org. Chem.* **2004**, *2004*, 1584.
- [22] J. Tong, L.-S. Huang, D.-Z. Xu, *New J. Chem.* **2017**, *41*, 3966.
- [23] J. Tong, Y.-W. Li, D.-Z. Xu, *ChemistrySelect* **2017**, *2*, 3799.
- [24] N. Azizi, L. Torkian, M. R. Saidi, *J. Mol. Catal. A: Chem.* **2007**, *275*, 109.
- [25] M. A. Nasser, F. Ahrari, B. Zakerinasab, *RSC Adv.* **2015**, *5*, 13901.
- [26] A. Wang, X. Liu, Z. Su, H. Jing, *Catal. Sci. Technol.* **2014**, *4*, 71.
- [27] G. Chen, C.-Y. Guo, H. Qiao, M. Ye, X. Qiu, C. Yue, *Catal. Commun.* **2013**, *41*, 70.
- [28] P. K. Chhattise, S. S. Arbuji, K. C. Mohite, S. V. Bhavsar, A. S. Horne, K. N. Handore, V. V. Chabukswar, *RSC Adv.* **2014**, *4*, 28623.
- [29] M. Nikpassand, L. Zare, M. R. Mousavi, *Lett. Org. Chem.* **2012**, *9*, 375.
- [30] L. Zare, M. Nikpassand, *J. Chem.* **2012**, *9*, 1623.
- [31] L. Z. Fekri, M. Nikpassand, M. Kohansal, *Russ. J. Gen. Chem.* **2015**, *85*, 2861.
- [32] J. Azizian, A. A. Mohammadi, N. Karimi, M. R. Mohammadzadeh, A. R. Karimi, *Catal. Commun.* **2006**, *7*, 752.
- [33] A. Saffar-Teluri, *Res. Chem. Intermed.* **2014**, *40*, 1061.
- [34] J. Kothandapani, A. Ganesan, S. Selva Ganesan, *Tetrahedron Lett.* **2015**, *56*, 5568.
- [35] R. Tayebee, M. M. Amini, N. Abdollahi, A. Aliakbari, S. Rabiei, H. Ramshini, *Appl. Catal. A Gen.* **2013**, *468*, 75.
- [36] H. Hagiwara, M. Sekifuji, T. Hoshi, K. Qiao, C. Yokoyama, *Synlett* **2007**, *2007*, 1320.
- [37] V. J. Rani, K. V. Vani, C. V. Rao, *Synthetic Commun.* **2012**, *42*, 2048.

- [38] Z.-H. Ma, H.-B. Han, Z.-B. Zhou, J. Nie, *J. Mol. Catal. A Chem.* **2009**, *311*, 46.
- [39] J. R. Satam, K. D. Parghi, R. V. Jayaram, *Catal. Commun.* **2008**, *9*, 1071.
- [40] M. Nikpassand, L. Z. Fekri, M. Nabatzadeh, *Comb. Chem. High T. Scr.* **2017**, *20*, 533.
- [41] M. Nikpassand, L. Z. Fekri, M. R. Mousavi, *J. Taibah Univ. Sci.* **2017**, *11*, 151.
- [42] M. Jafarpour, A. Rezaeifard, G. Gorzin, *Inorg. Chem. Commun.* **2011**, *14*, 1732.
- [43] M. Jafarpour, A. Rezaeifard, S. Gazkar, M. Danehchin, *Transition Met. Chem.* **2011**, *36*, 685.
- [44] S. R. Mendes, S. Thurow, F. Pentead, M. S. da Silva, R. A. Gariani, G. Perin, E. J. Lenardão, *Green Chem.* **2015**, *17*, 4334.
- [45] S. S. Mohapatra, P. Mukhi, A. Mohanty, S. Pal, A. O. Sahoo, D. Das, S. Roy, *Tetrahedron Lett.* **2015**, *56*, 5709.
- [46] I. Sheikshoaie, H. Khabazzadeh, S. Saeid-Nia, *Transition Met. Chem.* **2009**, *34*, 463.
- [47] W. E. Noland, H. V. Kumar, G. C. Flick, C. L. Aspros, J. H. Yoon, A. C. Wilt, N. Dehkordi, S. Thao, A. K. Schneerer, S. Gao, K. J. Tritch, *Tetrahedron* **2017**, *73*, 3913.
- [48] Z. Liang, J. Zhao, Y. Zhang, *J. Org. Chem.* **2010**, *75*, 170.
- [49] M. Nikpassand, L. Zare Fekri, S. Sharafi, *Russ. J. Gen. Chem.* **2013**, *83*, 2370.
- [50] X.-L. Feng, C.-J. Guan, C.-X. Zhao, *Synth. Commun.* **2004**, *34*, 487.
- [51] Z.-B. Xie, D.-Z. Sun, G.-F. Jiang, Z.-G. Le, *Molecules* **2014**, *19*, 19665.
- [52] A. S. Amarasekara, *Chem. Rev.* **2016**, *116*, 6133.
- [53] A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. Davis Jr., *J. Am. Chem. Soc.* **2002**, *124*, 5962.
- [54] F. Abbasi, N. Azizi, M. Abdoli-Senejani, *Appl. Organomet. Chem.* **2017**, *31*, 3790.
- [55] Z. Ullah, A. Sada Khan, N. Muhammad, R. Ullah, A. S. Alqahtani, S. N. Shah, O. B. Ghanem, M. A. Bustam, Z. Man, *J. Mol. Liq.* **2018**, *266*, 673.
- [56] N. Azizi, F. Shirdel, *J. Mol. Liq.* **2016**, *222*, 783.
- [57] K. Rad-Moghadam, M. Sharifi-Kiasaraie, H. Taheri-Amlashi, *Tetrahedron* **2010**, *66*, 2316.
- [58] N. Karimi, H. Oskooi, M. Heravi, M. Saeedi, M. Zakeri, N. Tavakoli, *Chin. J. Chem.* **2011**, *29*, 321.
- [59] J. Tong, C. Yang, D.-Z. Xu, *Synthesis* **2016**, *48*, 3559.
- [60] S.-Y. Wang, S.-J. Ji, *Tetrahedron* **2006**, *62*, 1527.
- [61] A. Akbari, *Tetrahedron Lett.* **2016**, *57*, 431.
- [62] S. K. Panja, S. Saha, *RSC Adv.* **2013**, *3*, 14495.
- [63] A. Khalafi-Nezhad, S. Mohammadi, *RSC Adv.* **2013**, *3*, 4362.
- [64] K. Bica, P. Gaertner, *Org. Lett.* **2006**, *8*, 733.
- [65] S. Sayyahi, A. Azin, S. J. Saghanzhad, *J. Mol. Liq.* **2014**, *198*, 30.
- [66] B. M. Godajdar, A. R. Kiasat, M. M. Hashemi, *J. Mol. Liq.* **2013**, *183*, 14.
- [67] H. Veisi, S. Hemmati, H. Veisi, *J. Chin. Chem. Soc.* **2009**, *56*, 240.
- [68] W. Zhu, P. Wu, L. Yang, Y. Chang, Y. Chao, H. Li, Y. Jiang, W. Jiang, S. Xun, *Chem. Eng. J.* **2013**, *229*, 250.
- [69] V. Misuk, D. Breuch, H. Löwe, *Chem. Eng. J.* **2011**, *173*, 536.
- [70] W. Jiang, W. Zhu, H. Li, J. Xue, J. Xiong, Y. Chang, H. Liu, Z. Zhao, *Chem. Eng. Technol.* **2014**, *37*, 36.
- [71] H. Wang, R. Yan, Z. Li, X. Zhang, S. Zhang, *Catal. Commun.* **2010**, *11*, 763.
- [72] P. Gogoi, A. K. Dutta, P. Sarma, R. Borah, *Appl. Catal. A Gen.* **2015**, *492*, 133.
- [73] W.-Q. Su, C. Yang, D.-Z. Xu, *Catal. Commun.* **2017**, *100*, 38.
- [74] C. Yang, P.-Z. Liu, D.-Z. Xu, *ChemistrySelect* **2017**, *2*, 1232.
- [75] C. Yang, W.-Q. Su, D.-Z. Xu, *RSC Adv.* **2016**, *6*, 99656.
- [76] L.-L. Song, C. Yang, Y.-Q. Yu, D.-Z. Xu, *Synthesis* **2017**, *49*, 1641.
- [77] Y.-Q. Yu, D.-Z. Xu, *RSC Adv.* **2015**, *5*, 28857.
- [78] Y.-Q. Yu, D.-Z. Xu, *Synthesis* **2015**, *47*, 1869.
- [79] Y.-Q. Yu, D.-Z. Xu, *Tetrahedron* **2015**, *71*, 2853.
- [80] M. S. Sitze, E. R. Schreiter, E. V. Patterson, R. G. Freeman, *Inorg. Chem.* **2010**, *40*, 2298.
- [81] R. Chakravarti, P. Kalita, S. T. Selvan, H. Oveisi, V. V. Balasubramanian, M. L. Kantam, A. Vinu, *Green Chem.* **2010**, *12*, 49.

How to cite this article: Gu Y-C, Hu R-M, Li M-M, Xu D-Z. Iron-containing ionic liquid as an efficient and recyclable catalyst for the synthesis of C3-substituted indole derivatives. *Appl Organometal Chem.* 2019;33:e4782. <https://doi.org/10.1002/aoc.4782>