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Brønsted acidic ionic liquid-promoted direct C3-acylation of *N*-unsubstituted indoles with acid anhydrides under microwave irradiation†

Phuong Hoang Tran, (ID)* Anh-Thanh Duy Nguyen, Hai Truong Nguyen and Thach Ngoc Le

A green and efficient pathway for the synthesis of 3-acylindoles using a Brønsted acidic ionic liquid as a catalyst has been developed for the first time. The C3-acylation of *N*-unsubstituted indoles with acid anhydrides affords the desired products in good to excellent yields with high regioselectivity under microwave irradiation. Moreover, the Brønsted acidic ionic liquid can be recycled up to four times without significant loss of catalytic activity.

Introduction

Acylindoles are commonly found in many biologically active natural products and pharmaceutical compounds.[1–3] Among these, 3-acylindole derivatives potentially show biological activities including anti-diabetic,[2,3] anti-cancer,[4–6] and anti-HIV.[7–10] However, their synthesis remains challenging and includes *N*-protection,[11] low yields,[12,13] poor regioselectivity, excess reactants,[14] high temperature, and long reaction time.[11,15,16] Traditional methods involved the use of stoichiometric amounts of Lewis or Brønsted acids for the Friedel–Crafts acylation of indole.[11,17,18] Recently, the preparation of 3-acylindoles has received much attention and metal-based catalytic pathways have been studied extensively.[13,18] However, some of the existing methods are often harmful to the environment. Thus, developing new catalysts for the synthesis of 3-acylindoles with excellent yields and high selectivity under mild and environmentally friendly conditions is highly desirable.[18]

Ionic liquids have received much attention in many fields including catalysis,[19–25] electrolytes,[26–29] extraction desulfurization,[30–32] biomass processing,[33–35] and biodiesel.[36–39] Friedel–Crafts C3-acylation of indoles using ionic liquids has been reported in previous literature.[40,41] Recently, Brønsted acidic ionic liquids (ionic liquids with acidic properties) have been widely used for various organic transformations due to their unique properties.[19,42–56] Nevertheless, to the best of our knowledge, they have never been used for the direct C3-acylation of *N*-unsubstituted indoles. Thus, we now report the development of a high-yielding and regioselectivity method for the C3-acylation *N*-

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unsubstituted indoles using Brønsted acidic ionic liquid as an efficiently homogeneous catalyst under microwave irradiation.

Results and discussion
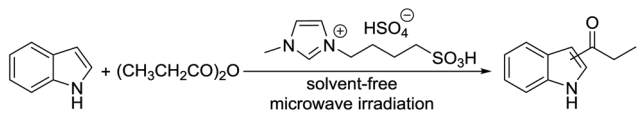
Preparation of [(4-SO₃H)BMIM]HSO₄ ionic liquid

[(4-SO$_3$H)BMIM]HSO$_4$ ionic liquid has been prepared by two steps: formation of the zwitterionic intermediate and subsequent protonation by concentrated sulphuric acid. However, these methods suffered from some drawbacks such as low yields and long reaction times.[36,37,57–60] Thus, the ultrasound irradiation was chosen to improve the reaction efficiency for the synthesis of [(4-SO$_3$H)BMIM]HSO$_4$. It should be noted that the two-step procedure provided [(4-SO$_3$H)BMIM]HSO$_4$ in excellent yield within very short reaction time under solvent-free sonication (please see ESI, Tables S1 and S2†). The structure of ionic liquid was characterized by NMR, FT-IR, and HR-MS (ESI). The ionic liquid is hygroscopic but moisture-stable and should be constantly stored in a desiccator.

Effect of reaction time and temperature for the C3-propionylation of indole

The catalytic activity of the prepared [(4-SO$_3$H)BMIM]HSO$_4$ was evaluated for the Friedel–Crafts acylation of indoles with acid anhydrides under solvent-free microwave irradiation. To optimize the reaction conditions, the reaction of indole and propionic anhydride under microwave irradiation was conducted as a model reaction. Initially, the Friedel–Crafts propionylation of indole in the presence of [(4-SO$_3$H)BMIM]HSO$_4$ (25 mol%) under microwave irradiation at 60 °C for 5 min was employed to prepare the desired product. To our surprise, the model reaction afforded the propionylindole in 46% yield with 100% regioselectivity in C3-position, and no impurity was found in TLC and GC (Table 1, entry 1). After screening the reaction

Table 1 Optimization of the reaction conditions[a]

Entry	Time (min)	Temperature (°C)	Yield[b] (%)	Selectivity[c] (1 : 2 : 3)
1	5	60	46	0 : 0 : 100
2	5	80	79	1 : 0 : 99
3	5	100	92	0 : 0 : 100
4	5	120	93	2 : 0 : 98
5	5	140	90	2 : 0 : 98
6	1	100	62	0 : 0 : 100
7	3	100	78	1 : 0 : 99
9	7	100	90	2 : 1 : 97
10	10	100	91	3 : 1 : 96

[a] Reaction condition: indole (1.0 mmol), propionic anhydride (1.0 mmol), and [(4-SO$_3$H)BMIM]HSO$_4$ (25 mol%) under solvent-free microwave irradiation. [b] Isolated yield. [c] Determined by GC-MS.

conditions, we determined the optimal conditions at 100 °C for 5 min for the formation of the corresponding product in 92% yield (Table 1, entry 3). The control experiments were also carried out under conventional heating and ultrasound irradiation, but only a trace amount of 3-propionylindole was detected.

Effect of reaction time and amount of catalyst for the C3-propionylation of indole
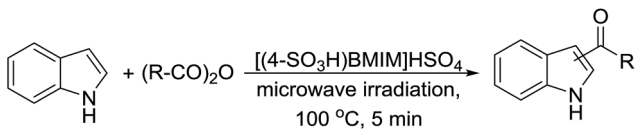
Next, the amount of catalyst was varied from 5 to 100 mol% to study its effect on the yield of product. The results were presented in Table 2. The desired product was not detected in the absence of the catalyst (Table 2, entry 1). As only a small catalyst loading of 5 mol% was introduced to the reaction mixture, the desired product straightforwardly formed with a detectable yield of 35% (Table 2, entry 2). The best yield was obtained in 92% yield in the presence of 25 mol% of [(4-SO$_3$H)BMIM]HSO$_4$ ionic liquid under solvent-free microwave irradiation at 100 °C for 5 min (Table 2, entry 4).

Table 2 Effect of the catalytic amount[a]

Entry	[(4-SO$_3$H)BMIM]HSO$_4$ (mol%)	Yield[b] (%)	Selectivity[c] (1 : 2 : 3)
1	0	0	0
2	5	35	0 : 0 : 100
3	15	60	0 : 0 : 100
4	25	92	0 : 0 : 100
5	50	92	1 : 0 : 99
6	100	93	2 : 1 : 97

[a] Reaction condition: indole (1.0 mmol), propionic anhydride (1.0 mmol) under solvent-free microwave irradiation at 100 °C for 5 min. [b] Isolated yield. [c] Determined by GC-MS.

Table 3 Effect of acylating reagents[a]

Entry	R–	Yield[b] (%)	Selectivity[c] (1 : 2 : 3)
1	CH$_3$–	88	0 : 0 : 100
2	C$_2$H$_5$–	92	1 : 0 : 99
3	CH$_3$CH$_2$CH$_2$–	91	1 : 0 : 99
4	(CH$_3$)$_2$CH–	85	2 : 1 : 97
5	(CH$_3$)$_4$C–	70	3 : 2 : 95
6	C$_6$H$_5$–	65	1 : 0 : 99

[a] Reaction condition: indole (1.0 mmol), acid anhydrides (1.0 mmol), and [(4-SO$_3$H)BMIM]HSO$_4$ (25 mol%) under solvent-free microwave irradiation. [b] Isolated yield. [c] Determined by GC-MS.

Effect of acylating reagents for the C3-propionylation of indole

With optimal reaction conditions in hand, we extended the current method to other acid anhydrides such as acetic, butyric, isobutyric, pivalic, and benzoic anhydride. The results were presented in Table 3. The desired products were obtained in good to excellent yields (65–92%) with over 95% selectivity in C3-position. The low yields of pivalic and benzoic anhydride were obtained under current method presumably due to steric effect (Table 3, entries 5 and 6). Interestingly, no 1,3-diacylated and polymerized products were obtained under current method. The selectivity to C3-acylation can be rationalized based on the electron-donating resonance from the lone pair on the nitrogen atom to C3 through C2, giving rise to a partially negative charge on C3. The resonance pathway *via* benzene ring to end up with a partially negative charge on C2 is disfavored because it destroys the aromaticity of the benzene ring. The higher reactivity of C3-center over unsubstituted-NH moiety in this method can be attributed to the assumption that a soft electrophile as acid anhydride preferably attacks to a soft nucleophilic C3-position rather than a hard center as unsubstituted-NH moiety. We also experimentally tested this hypothesis by conducting the same reaction in which a typical hard electrophile, benzoyl chloride, was employed as acylation reagent instead of acid anhydrides. As expected, the *N*-benzoylated product was selectively formed in the yield of 80%.

Effect of substrate scope for the C3-acylation of indole derivative

To examine the scope of reaction, the reactions of various indoles and a wide range of acid anhydrides were investigated under current method. The results were presented in Table 4. A wide range of indoles bearing the substituent on the position C5 could proceed well and afford the corresponding products in good yields (Table 2, entries 6–20). Non-substituted indole and indoles bearing electron-donating groups such as 5-methylindole and 5-methoxyindole gave the desired products in

Table 4 [(4-SO$_3$H)BMIM]HSO$_4$-catalyzed acylation of free (NH) indoles with acid anhydrides under solvent-free microwave irradiation[a]
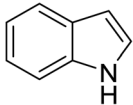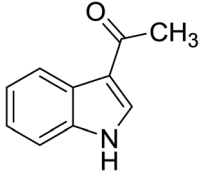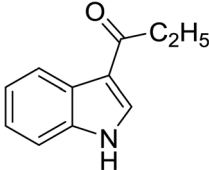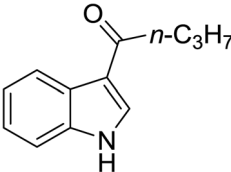
Entry	Indoles	Acid anhydrides	Condition	Products	Yield[b] (%)	Selectivity[c] (1 : 2 : 3)
1		(CH$_3$CO)$_2$O	100 °C, 8 min		90	0 : 0 : 100
2		(C$_2$H$_5$CO)$_2$O	100 °C, 5 min		92	1 : 0 : 99
3		(n-C$_3$H$_7$CO)$_2$O	100 °C, 10 min		92	1 : 0 : 99
4		(t-C$_4$H$_9$CO)$_2$O	100 °C, 10 min		82	1 : 0 : 99
5		(C$_6$H$_5$CO)$_2$O	100 °C, 10 min		78	1 : 0 : 99
6		(CH$_3$CO)$_2$O	100 °C, 5 min		92	4 : 0 : 96
7		(C$_2$H$_5$CO)$_2$O	100 °C, 5 min		90	5 : 0 : 95
8		(i-C$_3$H$_7$CO)$_2$O	100 °C, 5 min		89	5 : 0 : 95

Table 4 (*Contd.*)
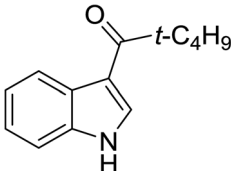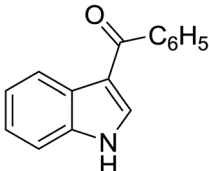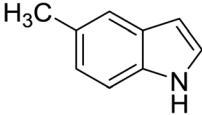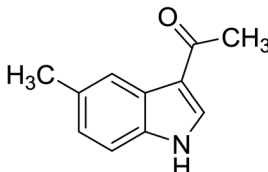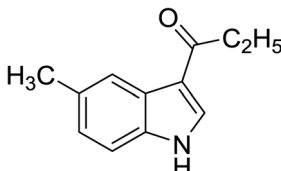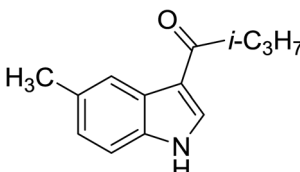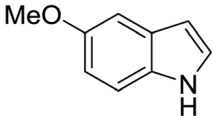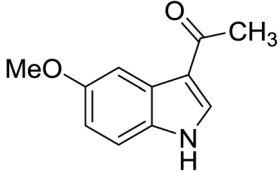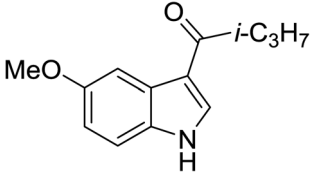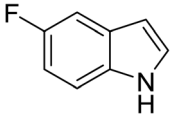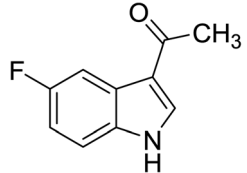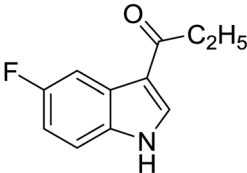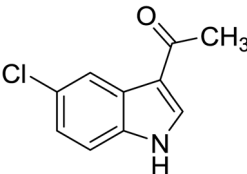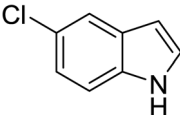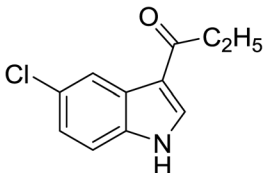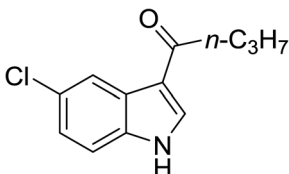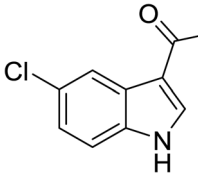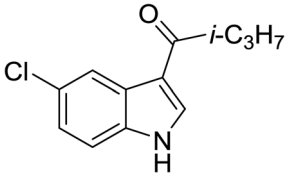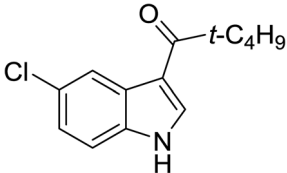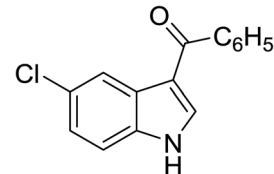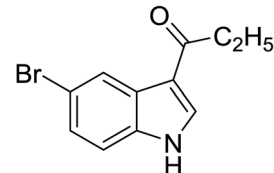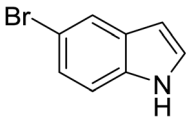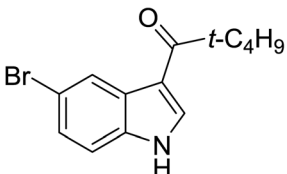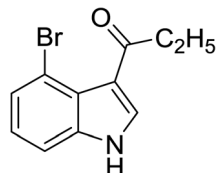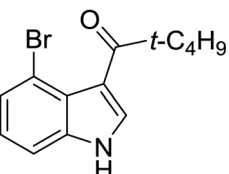
$$R^1 \!\!+\!\! \text{(indole)} + (R^2CO)_2O \xrightarrow[\substack{\text{microwave irradiation} \\ 100\text{-}120\ ^\circ C,\ 5\text{-}10\ \text{min}}]{[(4\text{-}SO_3H)BMIM]HSO_4} R^1 \!\!+\!\! \text{(indolyl-C(O)R}^2) + R^2COOH$$

Entry	Indoles	Acid anhydrides	Condition	Products	Yield[b] (%)	Selectivity[c] (1 : 2 : 3)
9	MeO-indole	(CH₃CO)₂O	100 °C, 5 min	MeO-indol-3-yl–C(O)CH₃	92	5 : 0 : 95
10		(*i*-C₃H₇CO)₂O	100 °C, 5 min	MeO-indol-3-yl–C(O)*i*-C₃H₇	90	6 : 0 : 94
11	F-indole	(CH₃CO)₂O	100 °C, 10 min	F-indol-3-yl–C(O)CH₃	88	1 : 0 : 99
12		(C₂H₅CO)₂O	100 °C, 10 min	F-indol-3-yl–C(O)C₂H₅	84	1 : 1 : 98
13		(CH₃CO)₂O	100 °C, 10 min	Cl-indol-3-yl–C(O)CH₃	84	1 : 1 : 98
14	Cl-indole	(C₂H₅CO)₂O	100 °C, 10 min	Cl-indol-3-yl–C(O)C₂H₅	80	2 : 1 : 97
15		(*n*-C₃H₇CO)₂O	100 °C, 10 min	Cl-indol-3-yl–C(O)*n*-C₃H₇	76	3 : 1 : 96

Table 4 (*Contd.*)

$$R^1 \underset{H}{\overset{N}{\bigcap}} + (R^2CO)_2O \xrightarrow[\text{microwave irradiation}]{\text{[(4-SO}_3\text{H)BMIM]HSO}_4}{100\text{-}120\ ^\circ\text{C, 5-10 min}} R^1 \underset{H}{\overset{N}{\bigcap}} \overset{O}{\underset{}{\bigcap}} R^2 + R^2COOH$$

Entry	Indoles	Acid anhydrides	Condition	Products	Yield[b] (%)	Selectivity[c] (1 : 2 : 3)
16		(i-C$_3$H$_7$CO)$_2$O	100 °C, 10 min		82	2 : 1 : 97
17		(t-C$_4$H$_9$CO)$_2$O	100 °C, 10 min		72	1 : 1 : 98
18		(C$_6$H$_5$CO)$_2$O	100 °C, 10 min		70	2 : 1 : 97
19		(C$_2$H$_5$CO)$_2$O	120 °C, 10 min		80	3 : 1 : 96
20		(t-C$_4$H$_9$CO)$_2$O	120 °C, 10 min		65	4 : 1 : 95
21		(C$_2$H$_5$CO)$_2$O	120 °C, 10 min		56	25 : 0 : 75
22		(t-C$_4$H$_9$CO)$_2$O	120 °C, 10 min		42	49 : 0 : 51

[a] Reaction condition: indoles (1.0 mmol), acid anhydrides (1.0 mmol), and [(4-SO$_3$H)BMIM]HSO$_4$ (25 mol%) under solvent-free microwave irradiation. [b] Isolated yield. [c] Determined by GC-MS.

Table 5 Reusability of [(4-SO₃H)BMIM]HSO₄ ionic liquid for the synthesis of 3-propionylindole

Run	Isolated yield (%)	Selectivity (1 : 2 : 3)
0	90	0 : 0 : 100
1	90	1 : 0 : 99
2	89	1 : 0 : 99
3	88	1 : 1 : 98
4	89	1 : 0 : 99

Scheme 1 Proposed mechanism.

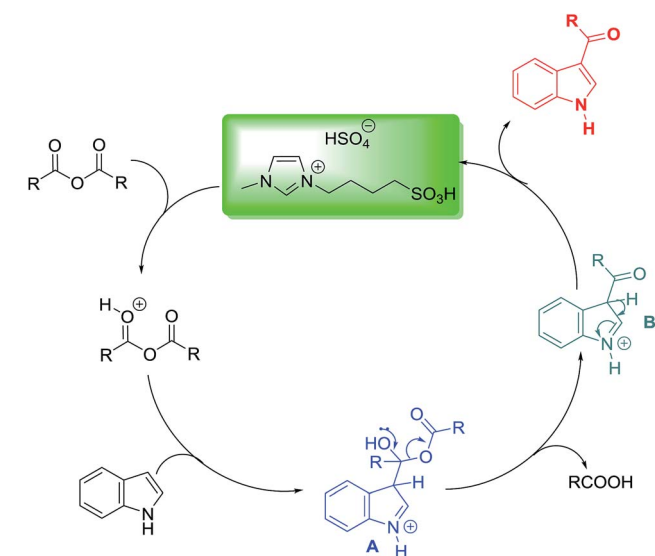excellent yields (Table 4, entries 1–10). Indoles bearing electron-poor group such as 5-fluoroindole, 5-chloroindole, 5-bromoindole were also reactive under high temperature and/or extended reaction times (Table 4, entries 11–19). The reaction was highly governed by steric effect as the reaction of 4-bromoindole with propionic and pivalic anhydride afforded the corresponding products in low yields and poor regioselectivity to C3-acylation (Table 4, entries 21–22).

Investigation on recycling of [(4-SO₃H)BMIM]HSO₄ ionic liquid for the C3-propionylation of indole

The reusability of [(4-SO₃H)BMIM]HSO₄ ionic liquid was carried out in the model reaction at 100 °C for 5 min under microwave irradiation. The results were reported in Table 5. Four consecutive runs were tested with less reduction in the catalytic activity. FT-IR spectra of fresh and recovered [(4-SO₃H)BMIM] HSO₄ confirmed that the structure of ionic liquid kept unchanged.

Mechanism of C3-acylation of indoles by [(4-SO₃H)BMIM] HSO₄ ionic liquid

Based on the previous literatures, we propose a plausible mechanism depicted in Scheme 1. First, the nucleophilic addition of indole at the C-3 position to acid anhydride in the presence of [(4-SO₃H)BMIM]HSO₄ provided the intermediate A. Next, the removal of carboxylic acid resulted in the formation of the intermediate B which can be subsequently undergo the elimination of proton to afford the desired product and regenerate [(4-SO₃H)BMIM]HSO₄ to finish the catalytic cycle.

Table 6 The comparative study of the current method with previous literatures[a]

Entry	Catalyst	Acetylating reagent	Condition	Yield (%)	Selectivity (1 : 2 : 3)
1	ZrCl₄ (1.5 equiv.) DCE, N₂	(acetic anhydride)	30 °C, 4 h	67 (ref. 61)	nd
2	TfOH (0.15 equiv.)	(acetylacetone)	80 °C, 24 h	64 (ref. 17)	nd
3	Y(OTf)₃ (0.01 equiv.)/[BMI]BF₄ (1.0 equiv.)	(acetic anhydride)	80 °C, 24 h	88 (ref. 62)	0 : 0 : 100
4	Pd(OAc)₂ (0.05 equiv.); 2,2′-bipyridine (6 mol%), CSA (0.6 mmol)	(cyanoacetic acid)	120 °C, 36 h	84 (ref. 63)	nd
5	Hβ zeolite (0.05 g)	(acetic anhydride)	120 °C, 8 min	70 (ref. 64)	9 : 0 : 77[a]
6	Current work	(acetic anhydride)	100 °C, 8 min	90	

[a] 1,3-Diacetylindole was obtained in 14% yield.

Comparison of [(4-SO₃H)BMIM]HSO₄ ionic liquid with other previous catalysts

A comparison of current work with previous literatures is presented in Table 6. The acetylation of indole with acetic anhydride in the presence of [(4-SO₃H)BMIM]HSO₄ provided the 3-acetylindole in higher yield within shorter reaction time. Moreover, the [(4-SO₃H)BMIM]HSO₄ ionic liquid was easily recovered and reused several times without decrease in catalytic activity.

Experimental

Chemicals, supplies, and instruments

All starting materials were purchased from Sigma-Aldrich and immediately used without further purification. Silica gel 230–400 mesh (for flash chromatography) and TLC plates were obtained from Merck. Microwave irradiation was used on a CEM Discover BenchMate. GC-MS spectra were performed on an Agilent GC System 7890 equipped with a mass selective detector Agilent 5973N. FT-IR spectra were analyzed by a Bruker Vertex 70. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500. HRMS (ESI) data were performed on Bruker micrOTOF-QII MS at 80 eV (please see in ESI,† Section S1).

Preparation of [(4-SO₃H)BMIM]HSO₄ catalyst under solvent-free sonication

The two-step procedure for the synthesis of ionic liquids from 1-methylimidazole, 1,4-butane sultone, and sulfuric acid under ultrasound irradiation were reported in the Section S2 (please see ESI†).

General procedure for Friedel–Crafts acylation of indole

Indole (1.0 mmol, 0.117 g), propionic anhydride (1.0 mmol, 0.130 g) and [(4-SO₃H)BMIM]HSO₄ (25 mol%) was heated under microwave irradiation at 100 °C for 5 min in a CEM Discover apparatus. The completion of the reaction was checked by TLC and GC. The mixture was then extracted with diethyl ether (5 × 5 mL). The organic layer was decanted, washed with aqueous NaHCO₃ (2 × 15 mL), water (15 mL) and brine (15 mL), and dried with Na₂SO₄. The solvent was removed under vacuum. The crude product was purified by silica gel chromatography using ethyl acetate–hexane (1 : 9). The purified product was then characterized by ^{1}H and ^{13}C NMR, GC-MS or HR-MS (ESI).

Recycling of [(4-SO₃H)BMIM]HSO₄

The recycling of [(4-SO₃H)BMIM]HSO₄ was also carried out under microwave irradiation in the model reaction between indole and propionic anhydride. After completion of the reaction, diethyl ether was used to extract the reaction mixture until both starting materials and products were entirely separated from the ionic liquid. The recovered [(4-SO₃H)BMIM]HSO₄ with immiscible in diethyl ether was dried under vacuum at 80 °C for 60 min. The recycled [(4-SO₃H)BMIM]HSO₄ was used for four consecutive runs. Remarkably, the yield of the product decreased slightly after each run. The simple process of

recycling [(4-SO₃H)BMIM]HSO₄ could be potentially developed on a large scale.

Conclusions

In summary, we have developed a green and efficient method using [(4-SO₃H)BMIM]HSO₄ as an effective catalyst for the highly regioselective C3-acylation of *N*-unsubstituted indoles with acid anhydrides. Remarkably, the accelerated microwave-assisted Friedel–Crafts acylation catalyzed by [(4-SO₃H)BMIM]HSO₄ was reported for the first time. Furthermore, the [(4-SO₃H)BMIM]HSO₄ possesses several advantages including mild preparation from commercially available materials, easy handling, and recyclability without loss of reactivity. Finally, it provides a simple, facile, and efficient alternative to the existing synthetic methods of 3-acylindoles.

Conflicts of interest

There are no conflicts to declare.

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References

1 S. Bera, C. G. Daniliuc and A. Studer, *Angew. Chem., Int. Ed. Engl.*, 2017, **56**, 7402–7406.

2 S.-Y. Chou and H. J. Tsai, *Drug Dev. Res.*, 2011, **72**, 247–258.

3 M. Somei and F. Yamada, *Nat. Prod. Rep.*, 2003, **20**, 216–242.

4 Y. Song, Z. Xin, Y. Wan, J. Li, B. Ye and X. Xue, *Eur. J. Med. Chem.*, 2015, **90**, 695–706.

5 E. R. El-Sawy, A. H. Mandour, S. M. El-Hallouty, K. H. Shaker and H. M. Abo-Salem, *Arabian J. Chem.*, 2013, **6**, 67–78.

6 J. R. Weng, C. H. Tsai, S. K. Kulp and C. S. Chen, *Cancer Lett.*, 2008, **262**, 153–163.

7 J. Q. Ran, N. Huang, H. Xu, L. M. Yang, M. Lv and Y. T. Zheng, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 3534–3536.

8 M. Sechi, M. Derudas, R. Dallocchio, A. Dessì, A. Bacchi, L. Sannia, F. Carta, M. Palomba, O. Ragab, C. Chan, R. Shoemaker, S. Sei, R. Dayam and N. Neamati, *J. Med. Chem.*, 2004, **47**, 5298–5310.

9 L. L. Fan, Z. P. Che, R. Zhang, X. Yu, X. Y. Zhi and H. Xu, *Mol. Diversity*, 2012, **16**, 415–421.

10 S. Ferro, M. L. Barreca, L. De Luca, A. Rao, A. M. Monforte, Z. Debyser, M. Witvrouw and A. Chimirri, *Arch. Pharm.*, 2007, **340**, 292–298.

11 S. J. Yao, Z. H. Ren, Y. Y. Wang and Z. H. Guan, *J. Org. Chem.*, 2016, **81**, 4226–4234.

12 H. Johansson, A. Urruticoechea, I. Larsen and D. Sejer Pedersen, *J. Org. Chem.*, 2015, **80**, 471–481.

13 C. Wang, S. Wang, H. Li, J. Yan, H. Chi, X. Chen and Z. Zhang, *Org. Biomol. Chem.*, 2014, **12**, 1721–1724.

14 Q. Y. Lai, R. S. Liao, S. Y. Wu, J. X. Zhang and X. H. Duan, *New J. Chem.*, 2013, **37**, 4069–4076.

15 Q. Shi, P. Li, X. Zhu and L. Wang, *Green Chem.*, 2016, **18**, 4916–4923.

16 L. Gu, C. Jin, J. Liu, H. Zhang, M. Yuan and G. Li, *Green Chem.*, 2016, **18**, 1201–1205.

17 Q. Xing, P. Li, H. Lv, R. Lang, C. Xia and F. Li, *Chem. Commun.*, 2014, **50**, 12181–12184.

18 S.-J. Yao, Z.-H. Ren and Z.-H. Guan, *Tetrahedron Lett.*, 2016, **57**, 3892–3901.

19 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, *J. Am. Chem. Soc.*, 2002, **124**, 5962–5963.

20 J. D. Patil, S. N. Korade, S. A. Patil, D. S. Gaikwad and D. M. Pore, *RSC Adv.*, 2015, **5**, 79061–79069.

21 M. A. Martins, C. P. Frizzo, A. Z. Tier, D. N. Moreira, N. Zanatta and H. G. Bonacorso, *Chem. Rev.*, 2014, **114**, PR1–PR70.

22 B. Zhen, Q. Jiao, Y. Zhang, Q. Wu and H. Li, *Appl. Catal., A*, 2012, **445–446**, 239–245.

23 H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt and T. Welton, *Chem. Soc. Rev.*, 2012, **41**, 7780–7802.

24 J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.

25 H.-P. Steinrück and P. Wasserscheid, *Catal. Lett.*, 2014, **145**, 380–397.

26 J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan and G. Luo, *Chem. Rev.*, 2015, **115**, 2136–2173.

27 C. T. Li, C. P. Lee, C. T. Lee, S. R. Li, S. S. Sun and K. C. Ho, *ChemSusChem*, 2015, **8**, 1244–1253.

28 A. N. Tran, T.-N. Van Do, L.-P. M. Le and T. N. Le, *J. Fluorine Chem.*, 2014, **164**, 38–43.

29 M. Ghavre, O. Byrne, L. Altes, P. K. Surolia, M. Spulak, B. Quilty, K. R. Thampi and N. Gathergood, *Green Chem.*, 2014, **16**, 2252–2265.

30 T. Yao, S. Yao, C. Pan, X. Dai and H. Song, *Energy Fuels*, 2016, **30**, 4740–4749.

31 J. Yin, J. Wang, Z. Li, D. Li, G. Yang, Y. Cui, A. Wang and C. Li, *Green Chem.*, 2015, **17**, 4552–4559.

32 W. Zhu, C. Wang, H. Li, P. Wu, S. Xun, W. Jiang, Z. Chen, Z. Zhao and H. Li, *Green Chem.*, 2015, **17**, 2464–2472.

33 Q. Bao, K. Qiao, D. Tomida and C. Yokoyama, *Catal. Commun.*, 2008, **9**, 1383–1388.

34 M. Chidambaram and A. T. Bell, *Green Chem.*, 2010, **12**, 1253–1262.

35 X. Sun, Z. Liu, Z. Xue, Y. Zhang and T. Mu, *Green Chem.*, 2015, **17**, 2719–2722.

36 E. Rafiee and F. Mirnezami, *J. Mol. Struct.*, 2017, **1130**, 296–302.

37 P. Fan, S. Xing, J. Wang, J. Fu, L. Yang, G. Yang, C. Miao and P. Lv, *Fuel*, 2017, **188**, 483–488.

38 A. H. M. Fauzi and N. A. S. Amin, *Renew. Sustain. Energy Rev.*, 2012, **16**, 5770–5786.

39 D. Z. Troter, Z. B. Todorović, D. R. Đokić-Stojanović, O. S. Stamenković and V. B. Veljković, *Renew. Sustain. Energy Rev.*, 2016, **61**, 473–500.

40 K.-S. Yeung, M. E. Farkas, Z. Qiu and Z. Yang, *Tetrahedron Lett.*, 2002, **43**, 5793–5795.

41 P. H. Tran, H. T. Nguyen, P. E. Hansen and T. N. Le, *RSC Adv.*, 2016, **6**, 37031–37038.

42 A. S. Amarasekara, *Chem. Rev.*, 2016, **116**, 6133–6183.

43 X. Tong and Y. Li, *ChemSusChem*, 2010, **3**, 350–355.

44 T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206–237.

45 M. Safa, B. Mokhtarani, H. R. Mortaheb, K. Tabar Heidar, A. Sharifi and M. Mirzaei, *Energy Fuels*, 2017, **31**, 10196–10205.

46 S. Das, S. Santra, S. Jana, G. V. Zyryanov, A. Majee and A. Hajra, *Eur. J. Org. Chem.*, 2017, **2017**, 4955–4962.

47 J. Banothu, R. Gali, R. Velpula and R. Bavantula, *Arabian J. Chem.*, 2017, **10**, S2754–S2761.

48 S. Mahato, S. Santra, R. Chatterjee, G. V. Zyryanov, A. Hajra and A. Majee, *Green Chem.*, 2017, **19**, 3282–3295.

49 H. B. Wang, N. Yao, L. Wang and Y. L. Hu, *New J. Chem.*, 2017, **41**, 10528–10531.

50 M. Safa, B. Mokhtarani, H. R. Mortaheb and K. Tabar Heidar, *Energy Fuels*, 2016, **30**, 10909–10916.

51 M. Zolfigol, A. Moosavi-Zare and E. Noroozizadeh, *Synlett*, 2016, **27**, 1682–1684.

52 L.-L. Lou, J. Zhang, H. Du, B. Zhao, S. Li, W. Yu, K. Yu and S. Liu, *Catal. Today*, 2016, **264**, 109–114.

53 K. V. Wagh and B. M. Bhanage, *Green Chem.*, 2015, **17**, 4446–4451.

54 J. Boulanger, A. Seingeot, B. Léger, R. Pruvost, M. Ibert, A. Mortreux, T. Chenal, M. Sauthier, A. Ponchel and E. Monflier, *Catal. Commun.*, 2015, **69**, 143–146.

55 B. M. Matsagar and P. L. Dhepe, *Catal. Sci. Technol.*, 2015, **5**, 531–539.

56 M. Vafaeezadeh and H. Alinezhad, *J. Mol. Liq.*, 2016, **218**, 95–105.

57 J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu and Z. Sun, *Catal. Commun.*, 2004, **5**, 473–477.

58 J. Deng, B.-H. Xu, Y.-F. Wang, X.-E. Mo, R. Zhang, Y. Li and S.-J. Zhang, *Catal. Sci. Technol.*, 2017, **7**, 2065–2073.

59 J. Lunagariya, A. Dhar and R. L. Vekariya, *RSC Adv.*, 2017, **7**, 5412–5420.

60 M. Olkiewicz, N. V. Plechkova, M. J. Earle, A. Fabregat, F. Stüber, A. Fortuny, J. Font and C. Bengoa, *Appl. Catal., B*, 2016, **181**, 738–746.

61 S. K. Guchhait, M. Kashyap and H. Kamble, *J. Org. Chem.*, 2011, **76**, 4753–4758.

62 P. H. Tran, H. N. Tran, P. E. Hansen, M. H. N. Do and T. N. Le, *Molecules*, 2015, **20**, 19605–19619.

63 T.-S. Jiang and G.-W. Wang, *Org. Lett.*, 2013, **15**, 788–791.

64 G. Bai, T. Li, Y. Yang, H. Zhang, X. Lan, F. Li, J. Han, Z. Ma, Q. Chen and G. Chen, *Catal. Commun.*, 2012, **29**, 114–117.