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Acidic-functionalized ionic liquid as an efficient, green, and metal-free catalyst for benzylation of sulfur, nitrogen, and carbon nucleophiles to benzylic alcohols

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ABSTRACT

A series of HSO_4^- functionalized ILs was synthesized and used as efficient, green, and metal-free catalysts for benzylation. Notably, the catalytic system has wide substrate scopes and the ionic liquid catalysts were applied to investigate three different types of nucleophiles to give the desired benzylation products with moderate to excellent yields.

1. Introduction

Over the past decades, ionic liquid (IL) research is undergoing an unprecedented explosion of interest, due to their particular physicochemical properties, such as negligible vapor pressure, excellent chemical, and thermal stability, good solvating ability, ease of recyclability and their potential to enhance reaction rates.[1] Some have been successfully used as an environmentally friendly alternative to conventional organic solvents or catalysts in a number of reactions,[2] such as Diels–Alder reaction,[3] Friedel–Crafts reaction,[4] esterification,[5] cracking reactions.[6] Among them, acidic-functionalized ILs has been intensively studied.[7] Especially, Brønsted acidic task-specific ionic liquids (TSILs) (Fig. 1), combining some useful characteristics of solid acids and mineral acids, which have been exploited as efficient catalysts and generally can afford higher yields and selectivities in chemical processes.[8]

The alkylation reaction of activated nucleophilic reagents, such as thiols, amines, indoles, is used as a powerful tool for the formation of carbon–carbon and carbon–heteroatom bonds, especially the benzylation (Scheme 1). The benzyl motif is ubiquitous in the realms of pharmacologically active agents and natural products. Particularly, *N*-benzyl amine scaffold and C3-benzyl indoles exhibit a wide range of biological activities. For example, N^1-benzyl-N^2,N^2-dimethyl-N^1-phenylethane-1,2-diamine, which is known as Antergan (Fig. 2, **A**),[9]

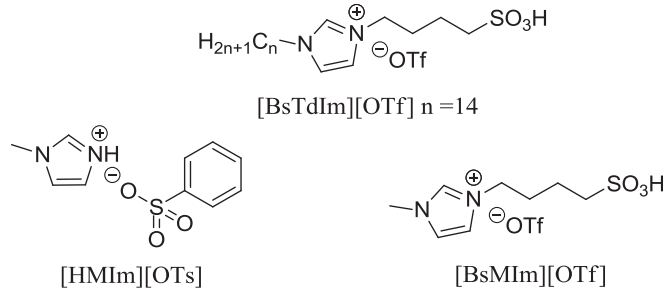

Fig. 1. Reported Brønsted acidic task-specific ionic liquids (TSILs) used in chemical processes.

is among the first antihistamine drugs to be sold and its structure provide the framework for antihistamine agents; **B** has effective antioxidant power and radical scavenging activities (Fig. 2, **B**).[10]

Generally, this transformation is performed with benzyl halides or activated benzyl alcohols,[11] in presence of stoichiometric amount of base, which results in the generation of large quantities of waste salts, have intrinsic drawbacks in terms of atom economy (Scheme 1, path A).[12] One popular concept to overcome the poor reactivity of the most benzylic alcohols is to temporarily convert them into corresponding carbonyl intermediates by the metal-catalyzed removal of hydrogen, which is well known as 'Hydrogen autotransfer processes' (Scheme 1, path B).[13] Another proposed mechanism is carbocation mechanism (Scheme 1, path C), using Lewis acid or Brønsted acids, such as $BF_3{\cdot}OEt_2$,[14] $InCl_3$,[15] $Bi(OTf)_3$,[16] or H-

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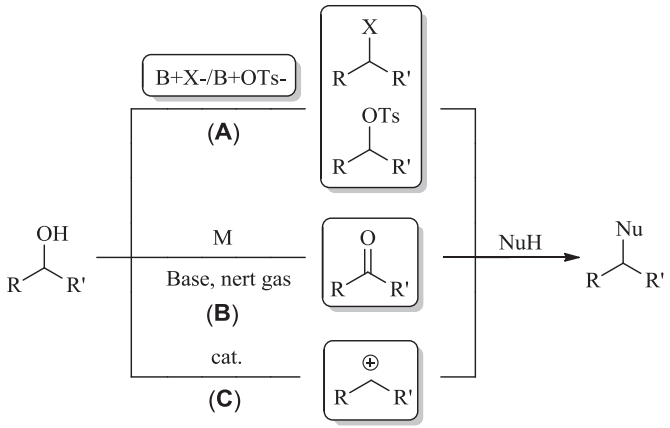


Scheme 1. Nucleophilic substitution reactions of alcohols by preactivation (A) and direct catalytic substitutions (B) and (C).

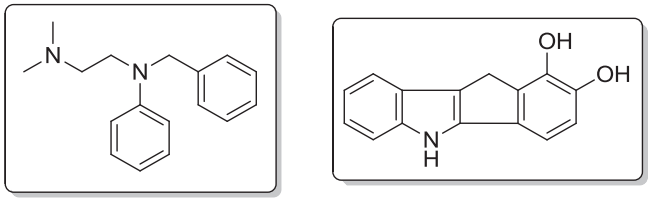
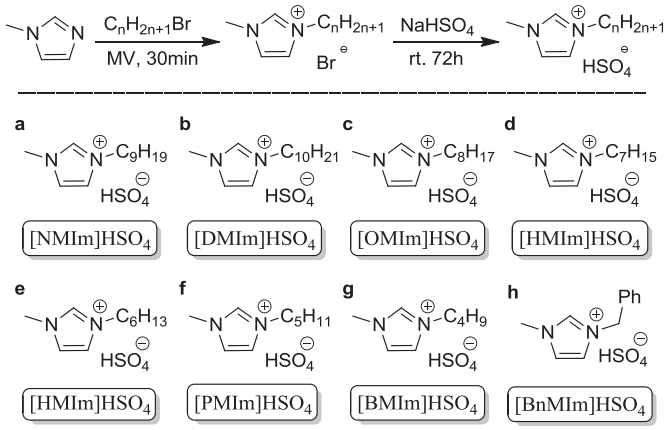


Fig. 2. The medicinal and other applications of *N*-benzyl amine scaffolds (A) and C3-benzyl indoles (B).

montmorillonite,[17] *p*-toluenesulfonic acid,[18] triflic acid,[19] benzhydryl alcohols can be turned to carbocations, which are then attacked by nucleophiles.

Almost all of these catalytic systems suffered from below one or more disadvantages: (1) expensive transition metals with additives are essential; (2) the catalysts are sensitive to air; (3) nucleophiles are excessive. To the best of our knowledge, the direct benzylation reactions catalyzed by acidic-functionalized ionic liquids are still relatively rare.[20] Moreover, when we are preparing this paper, Xia's group reported sulfonic acid-functionalized ionic liquids used as catalysts for the direct amination of alcohols.[8d] However, in our method more inexpensive acidic-functionalized ionic liquids catalysts could be obtained with simple work-up. On the other hand, rarely reported catalysts were applied to investigate three different types of nucleophiles in details. As a continuation of our interests in ILs mediated reactions[21] and acidic-functionalized ionic liquids catalyzed reactions,[22] herein, we report the development of a simple procedure utilizing acidic-functionalized ionic liquids (Scheme 2), as metal-free, green, and efficient catalysts for the benzylation of benzothiazole-2-thiols, *N*-containing substrates, and indoles, and synthesize a series of *S*, *N*, *C*-benzyl scaffold derivatives under mild conditions.



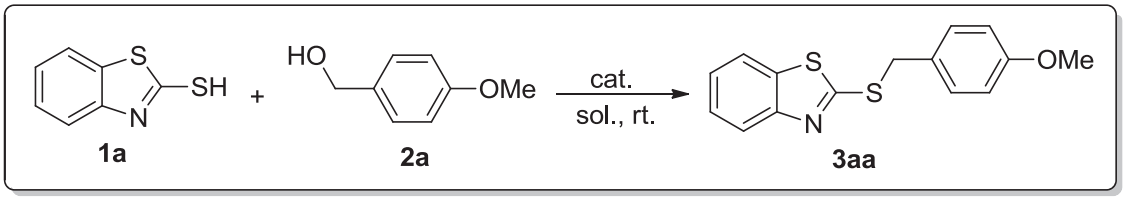
Scheme 2. Preparation of HSO_4^- functionalized ionic liquids.

2. Results and discussion

As we know, sulfur-containing compounds are difficult to use in the presence of Lewis acidic metals because of their strong coordinating and adsorptive properties to poison these catalysts, although some advances have been developed.[23] Therefore, the development of a more efficient catalytic system for benzylation of thiols becomes highly desirable. To verify the practicability of the projected route, a series of HSO_4^- based ILs with different cations were synthesized according to our previous methods (Scheme 2)[22] with some changes and their performance in the direct nucleophilic substitution of alcohols was studied. 1,3-Benzothiazole-2-thiol (**1a**), the fragment is featured in a wide variety of pharmacologically and biologically active compounds,[12] could be used in the model reaction as an agent reacted with (4-methoxy-phenyl)-methanol (**2a**) to synthesize benzylic thioethers, the results are shown in Table 1. At the outset, the reaction was carried out in the presence of an ionic liquid **a** (10 mol %) at room temperature in various solvents for 24 h (Table 1, entries 1–8). When CH_3CN or $CHCl_3$ was selected as the solvent, the desired product 2-(4-methoxy-benzylsulfanyl)-benzothiazole (**3aa**) was obtained in 86% yield (Table 1, entries 4 and 8). Other solvents, such as toluene, EtOH, DMF, DMSO, and THF, were inferior to CH_3CN (Table 1, entries 2–7). Additionally, further expansion of this protocol to other thiols compounds was limited, although the highest yield (87%) of product **3aa** was obtained when water was employed (Table 1, entry 1). Subsequently, other functionalized ionic liquids were investigated (Table 1, entries 9–15). Interestingly, it was found that the yield decreased with the carbon number of the side chain of imidazolium cations increasing from five to eight and dramatically increased when further increasing the carbon number. Only 26% yield was obtained when $[BnMIm]HSO_4$ was used (Table 1, entry 15). The results indicated that the side chain has a certain impact on the activities of ionic liquids, **b** and **f** were found to be the most effective (Table 1, entries 9 and 13). Compared with these ionic liquids, $NaHSO_4$ was selected as the candidate here to determine whether the catalytic reactivities of ionic liquids were due to the same anion (Table 1, entries 3, 4 and 7). Otherwise, only low yield of the desired product was produced (see the Supplementary data, Table S1), making us confirmed that ionic liquids present high activity primarily ascribed to its imidazole cation. We also screened other commonly used Brønsted or Lewis acid catalysts, no better results were observed in these cases (Table 1, entries 16 and 18).

With the optimal reaction conditions in hand, we continued to explore the scope of the reaction by using various related electron-rich alcohols and the results were summarized in Table 2. Similar to the case of **2a**, the reaction of benzothiazole-2-thiol (**1a**) with benzylic alcohols bearing donating groups, such as methoxyl and methyl, moderate to high yields *S*-alkylated products could be formed (Table 2, entries 1–4). It is noteworthy that benzylic alcohol with steric hindered substituents at 2-position has dramatic detrimental effect on this reaction. Moreover, benzylic alcohols bearing two or more substituted methoxyl groups showed good activities, owing to the electronic effect and sometimes steric effect, and the corresponding products were obtained with 84% and 71% yields, respectively (Table 2, entries 2 and 3). Further, the conditions were also applied to the reaction with other aromatic alcohols, such as thiophen-2-yl-methanol (**2e**) and benzo[1,3]dioxol-5-yl-methanol (**2f**), affording the designed products with 49% and 72% yields, respectively (Table 2, entries 5 and 6). Secondary alcohol, 1-(ferrocenyl) ethanol (**2g**) was also chosen to detect the

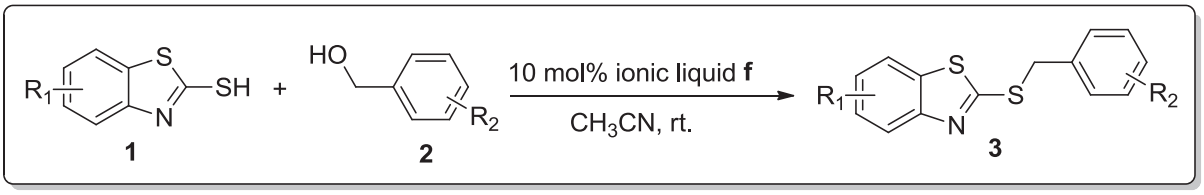
Table 1
S-Alkylation of benzothiazole-2-thiol (**1a**) with (4-methoxy-phenyl)-methanol (**2a**) under various conditions[a]



Entry	Catalyst	Time (h)	Solvent	Yield[b] (%)
1	**a**	24	H_2O	87
2	**a**	24	Toluene	72
3	**a**	24	EtOH	44
4	**a**	24	$CHCl_3$	86
5	**a**	24	DMF	Trace
6	**a**	24	DMSO	10
7	**a**	24	THF	51
8	**a**	24	CH_3CN	86
9	**b**	24	CH_3CN	92
10	**c**	24	CH_3CN	55
11	**d**	24	CH_3CN	73
12	**e**	24	CH_3CN	74
13	**f**	24	CH_3CN	91
14	**g**	24	CH_3CN	59
15	**h**	24	CH_3CN	26
16	PTSA[c]	24	CH_3CN	84
17	$NaHSO_4$	24	CH_3CN	7
18	$In(OTf)_3$	24	CH_3CN	51

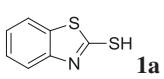
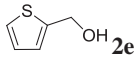
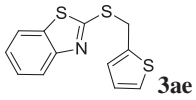
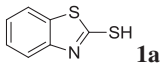
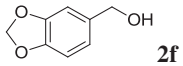
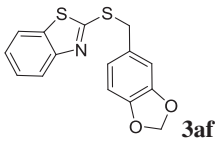
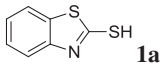
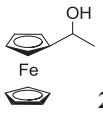
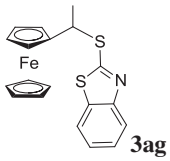
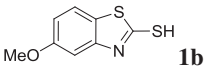
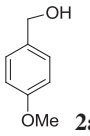
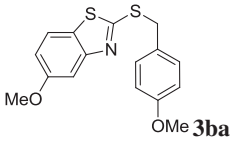
[a] General conditions: benzothiazole-2-thiol (**1a**) (1 mmol), (4-methoxy-phenyl)-methanol **2a** (1.2 mmol), ionic liquid (10 mol %), at room temperature.
[b] Isolated yield based on benzothiazole-2-thiol (**1a**) as limiting reagent.
[c] PTSA=*p*-toluenesulfonic acid.

Table 2
S-Alkylation of benzylic alcohols and other electron-rich alcohols with thiols[a]



Entry	1	2	Products	Time (h)	Yield[b] (%)
1	**1a**	**2a**	**3aa**	24	91
2	**1a**	**2b**	**3ab**	24	84
3	**1a**	**2c**	**3ac**	24	71
4	**1a**	**2d**	**3ad**	24	71[c]

Table 2 (*continued*)

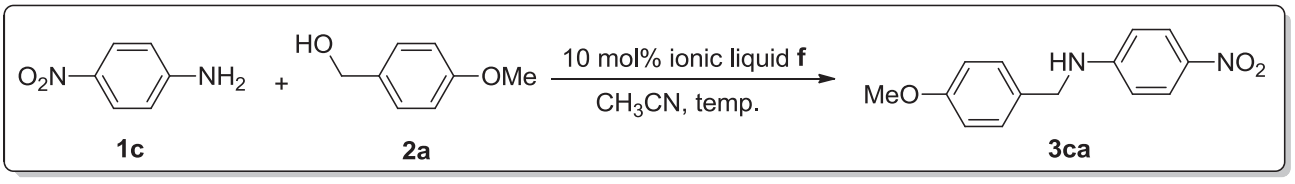
Entry	1	2	Products	Time (h)	Yield[b] (%)
5	 **1a**	 **2e**	 **3ae**	48	49
6	 **1a**	 **2f**	 **3af**	48	72
7	 **1a**	 **2g**	 **3ag**	40	83
8	 **1b**	 **2a**	 **3ba**	48	64[d]

[a] General conditions: thiols **1** (1 mmol), benzylic alcohols **2** (1.2 mmol), ionic liquid **f** (10 mol %), MeCN (2 ml), at room temperature.
[b] Isolated yield.
[c] The reaction was carried out in $CHCl_3$.
[d] The reaction was carried out in ionic liquid **b**.

generality of alcohol substrate, displayed a high reactivity to give the product in 83% yield (Table 2, entry 7). When benzothiazole-2-thiol with an electron-donating group at 5-position was introduced to this system, still proceeded smoothly to generate *S*-alkylated product (Table 2, entry 8). But when the methoxyl group at 6-position of **2**, no desired product was isolated. Meanwhile, attempt of using the **1a** with electron-withdrawing substituents was not completely successful. The low yields in these cases were presumably due to the electronic effects, which could reduce the nucleophilicity of the mercaptan.

Encouraged by the above successful access to a variety of unsymmetrical benzylic thioethers via S-alkylation of benzothiazole-2-thiol with benzylic alcohols, we were eager to explore whether the present protocol was general enough to construct the N-alkylation compounds with wider structural diversity. Thus, we turned our attention to extend our nucleophile to aniline. The details of results were listed in Tables 3 and 4. It was a bit regret that when 4-nitroaniline (**1c**) was used as a reactant firstly, only a low amount of the desired N-alkylation products was detected, even with prolonged reaction time under the established condition (Table 3, entry 1). In this case, an elevated reaction temperature was tried, making the system fairly complicated, side product such as over-alkylated product, *N*,*N*-bis(4-methoxybenzyl)-4-nitroaniline **3caa** was got (Table 3, entry 2). To circumvent such a problem,

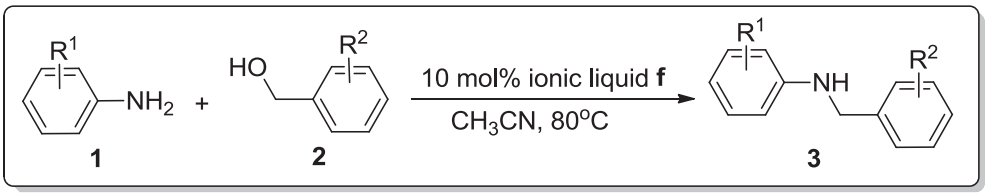
Table 3
N-Alkylation of 4-nitroaniline (**1c**) with (4-methoxy-phenyl)-methanol (**2a**) under various conditions[a]



Entry	**1c** (mmol)	**2a** (mmol)	Time (h)	Temp (°C)	Yield[b] (%)
1	1	1.2	48	25	51
2	1	1.2	22	50	56 (20[c])
3	1	1	22	50	55 (22)
4	1.2	1	22	50	62
5	1	2	22	50	48 (40)
6	1.2	1	22	80	75

[a] General conditions : 4-nitroaniline **1c** (1 mmol), (4-methoxy-phenyl)-methanol **2a** (1 mmol), ionic liquid **f** (10 mol %), MeCN (2 ml).
[b] Isolated yield.
[c] The yield of over-alkylated product, *N*,*N*-bis(4-methoxybenzyl)-4-nitroaniline **3caa**.

Table 4
N-Alkylation of benzylic alcohols and other electron-rich alcohols with anilines[a]



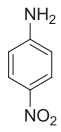
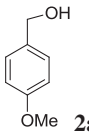
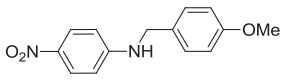
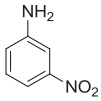
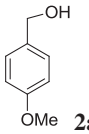
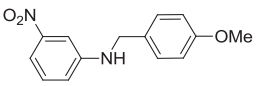
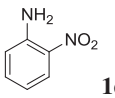
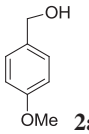
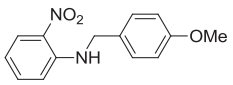
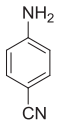
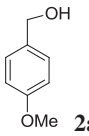
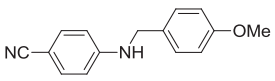
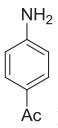
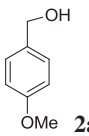
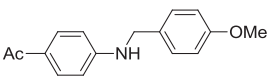
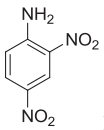
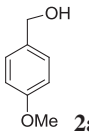
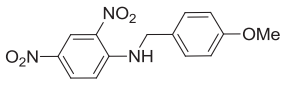
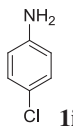
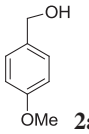
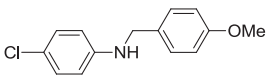
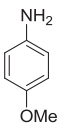
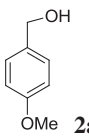
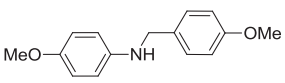
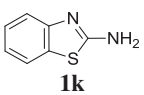
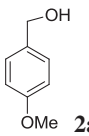
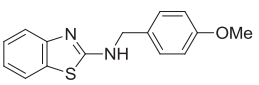
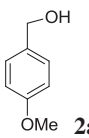
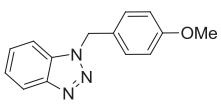
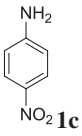
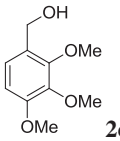
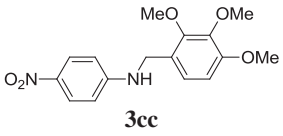
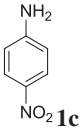
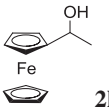
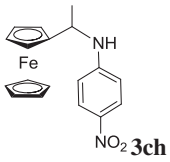
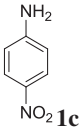
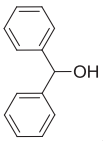
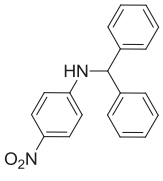
Entry	Amine	Alcohol	Products	Time (h)	Yield[b] (%)
1	 **1c**	 **2a**	 **1ca**	22	75
2	 **1d**	 **2a**	 **1da**	23	65
3	 **1e**	 **2a**	 **3ea**	23	44
4	 **1f**	 **2a**	 **3fa**	24	75
5	 **1g**	 **2a**	 **3ga**	18	65
6	 **1h**	 **2a**	 **3ha**	22	80
7	 **1i**	 **2a**	 **3ia**	24	25
8	 **1j**	 **2a**	 **3ja**	40	10
9	 **1k**	 **2a**	 **3ka**	24	47
10	 **1l**	 **2a**	 **3la**	24	61

Table 4 (*continued*)

Entry	Amine	Alcohol	Products	Time (h)	Yield[b] (%)
11	 **1c**	 **2c**	 **3cc**	24	84
12	 **1c**	 **2h**	 **3ch**	24	79
13	 **1c**	 **2i**	 **3ci**	22	91

[a] Reaction conditions: *N*-containing substrates (1.2 mmol), benzylic alcohols (1.0 mmol), ionic liquid **f** (10 mol %), MeCN (2 ml), at 80 °C.
[b] Isolated yield.

we conceived that the proportion of reactants might be a potential impact factor. In view of this, several typical ratio was tested (Table 3, entries 3–5). To our delight, **1c**:**2a**=1.2:1.0 was found to be the best one for the reaction (Table 3, entry 4). The remarkable improvement of the yield (75%) was observed by increasing the temperature to 80 °C (Table 3, entry 6).

This result prompted us to investigate the use of other related substituted anilines. As is shown, the presence of a strong electron-withdrawing group (NO_2) at the *ortho*, *meta* and *para* position of aniline were well tolerated, 75%, 65% and 44% yields were obtained, respectively, despite sometimes steric effect (Table 4, entries 1–3). Compounds **1f** and **1g** also proceeded smoothly to give the produces (Table 4, entries 4–5). The presence of a weak electron-withdrawing group, such as halogens at the *para* position of aniline obviously reduced the reactivity presumably owing to the electronic effect (Table 4, entry 7). What's more, aniline with an electron-donating group (OMe), was almost inert to the N-alkylation reaction, albeit with a prolonged reaction time (Table 4, entry 8). Another *N*-containing substrate, benzo[*d*]thiazol-2-amine **1k** still proceeded smoothly, and 47% yield was got (Table 4, entry 9). Nevertheless, 1*H*-benzo-[*d*][1,2,3]triazole **1l** demonstrated high efficiency to give the product **3la** in moderate yield (Table 4, entry 10). Beside, 4-nitroaniline (**1c**) was also worked well to couple with other active benzylic alcohols, providing the target products in medium to good yields. And secondary alcohols, 1-(ferrocenyl) ethanol (**2g**) and diphenyl-methanol (**2h**) were also selected to detect the generality of alcohol substrates, demonstrated a high reactivity to give the products in 79% and 91% yields, respectively (Table 4, entries 12 and 13).

Subsequently, we also applied this reaction system to the direct alkylation of indole and its derivatives. It was found that the reaction between indoles and (4-methoxy-phenyl)-methanol (**2a**) also proceeded smoothly to give C3-alkylated products with moderate to good yields (Scheme 3).

The recovery and reuse of catalyst were highly preferable in terms of green chemistry. To test the catalyst reusability, the reaction was carried out in the presence of a catalytic amount of [PMIm]HSO_4 (**f**) under the optimal reaction conditions with benzothiazole-2-thiol (**1a**) and (4-methoxy-phenyl)-methanol (**2a**) as

1m, R=H
1n, R=5-Br
1o, R=5-CH_3
1p, R=5-OMe

6h,63%[b],64%[c](**3ma**)
6h,78%(**3na**)
5h,47%(**3oa**)
6h,62%(**3pa**)

[a]Reaction conditions: indols with (1 mmol), (4-methoxyphen-yl)-methanol (1.2 mmol), ionic liquids **f** (10 mol%), MeCN (2 mL), at 50°C.
[b] Isolated yield.
[c] The reactions were carried out at 80°C.

Scheme 3. The benzylation of indoles at the C3-position with benzylic alcohols.

the substrates. Unfortunately, after three cycles, the isolated yield of the product was obviously decreased and ionic liquid **f** couldn't be reused with significant loss of the activities (see the Supplementary data, Fig. S1).

3. Conclusion

In summary, a series of inexpensive acidic-functionalized ionic liquids catalysts could be obtained with simple work-up, applied to investigate three different types of nucleophiles including thiols, anilines and indoles to various benzylic alcohols, and *S*-alkylated, *N*-alkylated, *C*-alkylated compounds have been successfully realized in details. The advantages of this protocol are moderate to good yield, mild conditions, using inexpensive acidic-functionalized ionic liquids **b** and **f** as a green and metal-free catalysts, environmentally friendly. Efforts to elucidate the exact mechanism of reaction and expand the scope of reaction type are currently under way in our laboratory.

4. Experimental section

4.1. General

Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer using KBr optics. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 300 or 400 MHz (^{1}H NMR) and 75 or 100 MHz (^{13}C NMR) spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. High resolution mass spectra were obtained using GCT-TOF instrument with EI or ESI source.

4.1.1. Typical procedure for the benzylation of thiols with benzylic alcohols. Thiols (1.0 mmol), benzylic alcohols (1.2 mmol), ionic liquid (0.1 mmol), and CH_3CN (2 ml) were added into a flask. Then the mixture was vigorously stirred at room temperature, until thiols were completely consumed as indicated by TLC analysis. After the completion of reaction, the solvent of the resulting mixture was removed with the aid of a rotary evaporator, the residue was directly purified by flash column chromatography with ethyl acetate and petroleum ether (1:6) as eluents to afford pure product.

4.1.2. Typical procedure for the benzylation of anilines with benzylic alcohols. Anilines (1.2 mmol), benzylic alcohols (1.0 mmol), ionic liquid (0.1 mmol), and CH_3CN (2 ml) were added into a flask. Then the mixture was vigorously stirred at 80 °C, until benzylic alcohols were completely consumed as indicated by TLC analysis. After the completion of reaction, the solvent of the resulting mixture was removed with the aid of a rotary evaporator, the residue was directly purified by flash column chromatography with ethyl acetate and petroleum ether (1:20) as eluents to afford pure product.

4.1.3. Typical procedure for the benzylation of indoles with benzylic alcohols. Indoles (1.0 mmol), benzylic alcohols (1.2 mmol), ionic liquid (0.1 mmol) and CH_3CN (2 ml) were added into a flask. Then the mixture was vigorously stirred at 50 °C, until indoles were completely consumed as indicated by TLC analysis. After the completion of reaction, the solvent of the resulting mixture was removed with the aid of a rotary evaporator, the residue was directly purified by flash column chromatography with ethyl acetate and petroleum ether (1:20) as eluents to afford pure product.

*4.1.4. Typical procedure for reuse of ionic liquid (**f**).* At the end of the reaction, 10 ml of deionized water were added into the reaction mixture, the reaction mixture was extracted with ethyl acetate (3×5 ml), the ionic liquid left in the water layer was concentrated and dried under vacuum at 80 °C for 8 h to eliminate any water trapped from moisture and reused for another cycle.

4.2. 2-((4-Methoxybenzyl)thio)benzo[*d*]thiazole (3aa)

White solid (261.5 mg, 91%). Mp 66.0–67.9 °C. IR (KBr): ν=3049, 2922, 2836, 1597, 1513, 1433, 1244, 1176, 1035, 821, 755 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ=3.73 (s, 3H), 4.60 (s, 2H), 6.90 (d, J=8.0 Hz, 2H), 7.37 (t, J=7.4 Hz, 1H), 7.42 (d, J=8.0 Hz, 2H), 7.48 (t, J=7.4 Hz, 1H), 7.89 (d, J=7.9 Hz, 1H), 8.01 (d, J=7.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.3, 158.8, 152.7, 134.7, 130.4, 124.5, 121.7, 121.2, 114.0, 55.0, 36.4 ppm. HRMS (ESI): calcd for $C_{15}H_{14}NOS_2$: $[M+H]^+$ 288.0517, found: 288.0514.

4.3. 2-((3,4-Dimethoxybenzyl)thio)benzo[*d*]thiazole (3ab)

White solid (266.6 mg, yield 84%). Mp 68.9–71.6 °C. IR (KBr): ν=3470, 2936, 2810, 1592, 1436, 1244, 1141, 1005, 851, 741 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ=3.73 (s, 6H), 4.59 (s, 2H), 6.90 (d, J=8.1 Hz, 1H), 7.03 (d, J=8.1 Hz, 1H), 7.13 (s, 1H), 7.37 (t, J=7.4 Hz, 1H), 7.48 (t, J=7.5 Hz, 1H), 7.89 (d, J=8.0 Hz, 1H), 8.01 (d, J=7.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.2, 152.6, 148.6, 148.3, 134.6, 126.34, 121.7, 121.4, 121.1, 112.8, 111.7, 55.4, 55.3, 36.8 ppm. HRMS (ESI): calcd for $C_{16}H_{16}N_1O_2S_2$: $[M+H]^+$ 318.0622, found: 318.0625.

4.4. 2-((2,3,4-Trimethoxybenzyl)thio)benzo[*d*]thiazole (3ac)

White solid (246.7 mg, yield 71%). Mp 91.0–92.4 °C. IR (KBr): ν=3450, 2937, 1590, 1466, 1279, 1003, 740 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ=3.77 (s, 3H), 3.78 (s, 3H), 3.89 (s, 3H), 4.56 (s, 2H), 6.76 (d, J=8.5 Hz, 1H), 7.19 (d, J=8.5 Hz, 1H), 7.37 (t, J=7.4 Hz, 1H), 7.48 (t, J=7.4 Hz, 1H), 7.90 (d, J=8.0 Hz, 1H), 8.01 (d, J=7.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.3, 153.5, 152.7, 151.6, 141.7, 134.6, 126.3, 124.8, 124.4, 121.7, 121.4, 121.1, 107.6, 61.0, 60.2, 55.7, 32.0 ppm. HRMS (ESI): calcd for $C_{17}H_{18}NO_3S_2$: $[M+H]^+$ 348.0728, found: 348.0726.

4.5. 2-((4-Methylbenzyl)thio)benzo[*d*]thiazole (3ad)

White solid (192.6 mg, yield 71%). Mp 50.5–51.9 °C. IR (KBr): ν=3459, 3042, 2845, 1592, 1419, 1233, 1000, 813, 736 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ=2.27 (s, 3H), 4.61 (s, 2H), 7.15 (d, J=7.4 Hz, 2H), 7.33–7.43 (m, 3H), 7.48 (t, J=7.4 Hz, 1H), 7.89 (d, J=8.0 Hz, 1H), 8.00 (d, J=7.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.1, 152.6, 136.8, 134.6, 133.2, 129.1, 128.9, 126.3, 124.4, 121.7, 121.1, 36.5, 20.6 ppm. HRMS (ESI): calcd for $C_{15}H_{14}NS_2$: $[M+H]^+$ 272.0568, found: 272.0563.

4.6. 2-((Thiophen-2-ylmethyl)thio)benzo[*d*]thiazole (3ae)

White solid (129.1 mg, yield 49%). Mp 50–53 °C. IR (KBr): ν=3483, 3075, 2846, 1605, 1418, 1233, 1005, 839, 751 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ=4.90 (s, 2H), 6.93–6.98 (m, 1H), 7.18 (s, 1H), 7.38 (t, J=7.5 Hz, 1H), 7.43 (d, J=4.9 Hz, 1H), 7.49 (t, J=7.6 Hz, 1H), 7.91 (d, J=8.0 Hz, 1H), 8.02 (d, J=7.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=165.5, 152.5, 139.3, 134.8, 127.7, 126.8, 126.4, 126.3, 124.6, 121.8, 121.2, 31.4 ppm. HRMS (ESI): calcd for $C_{12}H_{10}NS_3$: $[M+H]^+$ 263.9975, found: 263.9972.

4.7. 2-((Benzo[*d*][1,3]dioxol-5-ylmethyl)thio)benzo[*d*]thiazole (3af)

White solid (217.0 mg, yield 72%). Mp 55.4–56.7 °C. IR (KBr): ν=3446, 2901, 1606, 1492, 1453, 1237, 1033, 869, 732 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ=4.58 (s, 2H), 6.00 (s, 2H), 6.87 (d, J=7.8 Hz, 1H), 6.99 (d, J=7.9 Hz, 1H), 7.07 (s, 1H), 7.37 (t, J=7.4 Hz, 1H), 7.48 (t, J=7.5 Hz, 1H), 7.89 (d, J=8.0 Hz, 1H), 8.01 (d, J=7.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.1, 152.6, 147.3, 146.7, 134.7, 130.0, 126.3, 122.5, 121.7, 121.1, 109.3, 108.1, 101.1, 36.8 ppm. HRMS (ESI): calcd for $C_{15}H_{12}NO_2S_2$: $[M+H]^+$ 302.0309, found: 302.0310.

4.8. 2-(1-Ferrocenylethylthio)-benzo[*d*]thiazole (3ag)

Orange solid (314.8 mg, yield 83%). Mp 112–113 °C. IR (KBr): ν=3080, 2926, 1458, 1379, 1312, 1262, 1123, 1000, 749 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.82 (d, J=7.2 Hz, 3H), 4.06–4.51 (m, 10H), 7.11–7.26 (m, 3H), 7.40 (d, J=7.2 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=140.3, 127.6, 126.4, 124.5, 121.5, 114.6, 86.3, 69.8, 69.6, 68.9, 68.7, 67.8, 67.2, 53.9 ppm. HRMS (EI): calcd for $C_{19}H_{17}FeNS_2$: $[M]^+$ 379.0152, found: 379.0170.

4.9. 5-Methoxy-2-((4-methoxybenzyl)thio)benzo[*d*]thiazole (3ba)

White solid (203.1 mg, yield 64%). Mp 91–93 °C. IR (KBr): ν=3464, 2936, 2828, 1589, 1413, 1239, 1019, 827, 746, 684 cm^{-1}. ^{1}H

NMR (400 MHz, DMSO-d_6): δ=3.73 (s, 3H), 3.84 (s, 3H), 4.58 (s, 2H), 6.90 (d, J=8.1 Hz, 2H), 7.00 (d, J=8.7 Hz, 1H), 7.41 (d, J=8.3 Hz, 2H), 7.44 (s, 1H), 7.86 (d, J=8.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.9, 159.4, 159.1, 154.6, 130.50, 128.1, 127.1, 121.3, 114.3, 114.1, 104.8, 55.8, 55.5, 37.6 ppm. HRMS (ESI): calcd for $C_{16}H_{16}NO_2S_2$: $[M+H]^+$ 318.0622, found: 318.0631.

4.10. *N*-(4-Methoxybenzyl)-4-nitrobenzenamine (3ca)

Yellow solid (193.7 mg, yield 75%). Mp 146–147 °C. IR (KBr): ν=3352, 1598, 1512, 1299, 1070, 816 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ=3.73 (s, 3H), 4.33 (s, 2H), 6.67 (d, J=9.0 Hz, 2H), 6.91 (d, J=7.1 Hz, 2H), 7.27 (d, J=7.5 Hz, 2H), 7.77 (t, J=5.9 Hz, 1H), 7.97 (d, J=9.1 Hz, 2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ=158.4, 154.4, 135.8, 130.3, 128.6, 126.2, 113.9, 111.2, 55.1, 45.3, 45.2 ppm. HRMS (EI): calcd for $C_{14}H_{14}N_2O_3$: $[M]^+$ 258.1004, found: 258.1008.

4.11. *N*,*N*-Bis(4-methoxybenzyl)-4-nitroaniline (3caa)

Yellow solid. Mp 94–95 °C. IR (KBr): ν=3404, 2915, 1620, 1517, 1342, 808 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ=3.70 (s, 6H), 4.74 (s, 4H), 6.79 (d, J=9.5 Hz, 2H), 6.89 (d, J=8.6 Hz, 4H), 7.15 (d, J=8.5 Hz, 4H), 7.97 (d, J=9.4 Hz, 2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ=158.4, 153.4, 136.1, 128.9, 127.8, 125.8, 114.1, 111.5, 55.1, 55.0, 53.4 ppm. HRMS (EI): calcd for $C_{22}H_{22}N_2O_4$: $[M]^+$ 378.1580, found: 378.1577.

4.12. *N*-(4-Methoxybenzyl)-3-nitrobenzenamine (3da)

Yellow solid (167.8 mg, yield 65%). Mp 97–98 °C. IR (KBr): ν=3404, 2915, 1620, 1517, 1342, 808 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ=3.70 (s, 3H), 4.24 (d, J=4.1 Hz, 2H), 7.03–6.80 (m, 4H), 7.25–7.32 (m, 5H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ=158.3, 149.7, 148.8, 129.9, 128.5, 118.5, 113.8, 109.9, 105.6, 55.0, 45.6 ppm. HRMS (EI): calcd for $C_{14}H_{14}N_2O_3$: $[M]^+$ 258.1004, found: 258.1003.

4.13. *N*-(4-Methoxybenzyl)-2-nitrobenzenamine (3ea)

Yellow solid (133.6 mg, yield 44%). Mp 95–97 °C. IR (KBr): ν=3382, 2941, 1604, 1498, 1350, 1019, 827 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ=3.69 (s, 3H), 4.51 (d, J=5.5 Hz, 2H), 6.63 (t, J=7.7 Hz, 1H), 6.89 (t, J=9.7 Hz, 3H), 7.28 (d, J=8.1 Hz, 2H), 7.42 (t, J=7.7 Hz, 1H), 8.04 (d, J=8.6 Hz, 1H), 8.56 (t, J=4.9 Hz, 1H, NH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=158.4, 144.9, 136.4, 130.2, 126.2, 115.4, 115.0, 114.0, 113.6, 55.1, 55.0, 45.2 ppm. HRMS (EI): calcd for $C_{14}H_{14}N_2O_3$: $[M]^+$ 258.1004, found: 258.1005.

4.14. 4-(4-Methoxybenzylamino)benzonitrile (3fa)

White solid (178.7 mg, yield 75%). Mp 109–111 °C. IR (KBr): ν=3376, 2851, 2202, 1602, 1513, 820 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ=3.72 (s, 3H), 4.25 (d, J=5.0 Hz, 2H), 6.64 (d, J=7.0 Hz, 2H), 6.89 (d, J=6.7 Hz, 2H), 7.26–7.21 (m, 3H), 7.42 (d, J=7.0 Hz, 2H), ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=158.3, 152.1, 133.3, 130.7, 128.5, 120.6, 113.8, 112.1, 95.8, 55.1, 55.0, 45.2 ppm. HRMS (EI): calcd for $C_{15}H_{14}N_2O$: $[M]^+$ 238.1106, found: 238.1106.

4.15. 1-(4-(4-Methoxybenzylamino)phenyl)ethanone (3ga)

White solid (165.9 mg, yield 65%). Mp 116–117 °C. IR (KBr): ν=3341, 2855, 1635, 1584, 1255, 817 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ=2.37 (s, 3H), 3.72 (s, 3H), 4.27 (s, 2H), 6.60 (d, J=8.6 Hz, 2H), 6.89 (d, J=8.4 Hz, 2H), 7.26 (d, J=8.0 Hz, 2H), 7.68 (d, J=8.6 Hz, 2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ=195.0, 158.2, 152.7, 131.1, 130.4, 128.4, 125.0, 113.8, 111.1, 55.0, 45.2, 25.9 ppm. HRMS (EI): calcd for $C_{16}H_{17}NO_2$: $[M]^+$ 255.1259, found: 255.1266.

4.16. *N*-(4-Methoxybenzyl)-2,4-dinitroaniline (3ha)

Yellow solid (242.6 mg, yield 80%). Mp 104.4–105.3 °C. IR (KBr): ν=3374, 2923, 1612, 1509, 1251, 1079, 915, 809, 709 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ=3.73 (s, 3H), 4.67 (s, 2H), 6.91 (d, J=8.3 Hz, 2H), 7.09 (d, J=9.6 Hz, 1H), 7.33 (d, J=8.3 Hz, 2H), 8.20 (d, J=9.5 Hz, 1H), 8.86 (d, J=2.0 Hz, 1H), 9.33 (s, 1H, NH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=158.6, 148.0, 134.9, 129.9, 129.0, 128.4, 124.5, 115.5, 114.0, 103.7, 55.0, 45.6 ppm. HRMS (ESI): calcd for $C_{14}H_{14}N_3O_5$: $[M+H]^+$ 326.0753, found: 326.0757.

4.17. *N*-(4-Methoxybenzyl)-4-chlorobenzenamine (3ia)

White solid (61.9 mg, yield 25%). Mp 84–85 °C. IR (KBr): ν=3407, 2918, 1595, 1490, 1235, 815 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.80 (s, 3H), 4.22 (s, 2H), 6.56 (d, J=8.7 Hz, 2H), 6.88 (d, J=8.5 Hz, 2H), 7.11 (d, J=8.6 Hz, 2H), 7.27 (d, J=7.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.2, 146.9, 131.1, 129.2, 128.9, 122.3, 114.3, 114.1, 55.5, 48.1 ppm. HRMS (EI): calcd for $C_{14}H_{14}ClNO$: $[M]^+$ 247.0764, found: 247.0763.

4.18. *N*-(4-Methoxybenzyl)-4-methoxybenzenamine (3ja)

White solid (24.3 mg, yield 10%). Mp 96–97 °C. IR (KBr): ν=3379, 2942, 2834, 1603, 1511, 1245, 1028, 818 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.74 (s, 3H), 3.80 (s, 3H), 4.20 (s, 2H), 6.60 (d, J=8.7 Hz, 2H), 6.78 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.4 Hz, 2H), 7.29 (d, J=8.3 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=159.0, 152.4, 142.6, 131.8, 129.0, 115.1, 114.4, 114.2, 77.2, 56.0, 55.5, 49.0 ppm. HRMS (EI): calcd for $C_{15}H_{17}NO_2$: $[M]^+$ 243.1259, found: 243.1259.

4.19. *N*-(4-Methoxybenzyl)benzo[*d*]thiazol-2-amine (3ka)

White solid (127.1 mg, yield 47%). Mp 172–174 °C. IR (KBr): ν=3205, 2925, 2835, 1553, 1445, 1245, 830 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ=3.70 (s, 3H), 4.47 (s, 2H), 6.88 (d, J=8.0 Hz, 2H), 6.98 (t, J=7.4 Hz, 1H), 7.18 (d, J=7.5 Hz, 1H), 7.28 (d, J=7.9 Hz, 2H), 7.35 (d, J=7.6 Hz, 1H), 7.63 (d, J=7.6 Hz, 1H), 8.40 (s, 1H, NH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.0, 158.4, 152.4, 130.8, 130.4, 128.8, 125.5, 120.9, 118.1, 113.8, 55.1, 46.6 ppm. HRMS (EI): calcd for $C_{15}H_{14}N_2OS$: $[M]^+$ 270.0827, found: 270.0828.

4.20. 1-(4-Methoxybenzyl)-1*H*-benzo[*d*][1,2,3]triazole (3la)

White solid(146.0 mg, yield 61%). Mp 85–86 °C. IR (KBr): ν=2944, 1600, 1506, 1240, 1018, 830 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 3H), 5.78 (s, 2H), 6.86 (d, J=8.5 Hz, 2H), 7.25 (d, J=9.9 Hz, 2H), 7.31–7.37 (m, 3H), 8.06 (d, J=7.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.7, 146.3, 132.7, 129.1, 127.3, 126.8, 123.9, 119.9, 114.4, 109.9, 55.3, 51.8 ppm. HRMS (EI): calcd for $C_{14}H_{13}N_3O$: $[M]^+$ 239.1059, found: 239.1054.

4.21. 4-Nitro-*N*-(2,3,4-trimethoxybenzyl)aniline (3cc)

Yellow solid (267.4 mg, yield 84%). Mp 111.6–113.3 °C. IR (KBr): ν=3332, 2929, 1597, 1465, 1295, 1095, 808 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.86 (s, 3H), 3.88 (s, 3H), 3.94 (s, 3H), 4.35 (s, 2H), 6.58 (d, J=9.1 Hz, 2H), 6.63 (d, J=8.5 Hz, 1H), 6.95 (d, J=8.5 Hz, 1H), 8.08 (d, J=9.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=153.9, 153.4, 152.0, 142.5, 138.1, 126.5, 123.5, 123.2, 111.4, 107.4, 61.3, 61.0, 56.2, 43.0 ppm. HRMS (ESI): calcd for $C_{16}H_{18}N_2NaO_5$: $[M+Na]^+$ 341.1108, found: 341.1108.

4.22. *N*-(1-Ferrocenylethyl)-4-nitrobenzenamine (3cg)

Orange solid (276.6 mg, yield 79%). Mp 110–112 °C. IR (KBr): ν=3400, 3084, 2986, 1593, 1509, 1455, 1307, 1101, 821 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.53 (d, J=6.6 Hz, 3H), 4.06–4.19 (m, 9H), 4.40–4.44 (m, 1H), 6.54 (d, J=6.0 Hz, 2H), 8.07 (d, J=6.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=152.7, 137.7, 126.9, 111.5, 91.8, 68.9, 68.5, 68.2, 67.4, 66.3, 47.3, 20.7 ppm. HRMS (EI): calcd for $C_{18}H_{18}FeN_2O_2$: $[M]^+$ 350.0718, found: 350.0715.

4.23. *N*-Benzhydryl-4-nitroaniline (3ch)

Yellow solid (276.9 mg, yield 91%). Mp 169.3–171.2 °C. IR (KBr): ν=3395, 3076, 2915, 1591, 1498, 1306, 1097, 834, 740, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ=5.00 (s, 1H), 5.62 (s, 1H), 6.50 (d, J=9.1 Hz, 2H), 7.40–7.27 (m, 10H), 8.02 (d, J=9.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.3, 141.3, 138.4, 129.2, 128.12, 127.5, 126.3, 112.3, 62.5 ppm. HRMS (ESI): calcd for $C_{19}H_{17}N_2O_2$: $[M+H]^+$ 305.1290, found: 305.1278.

4.24. 3-(4-Methoxybenzyl)-1*H*-indole (3ma)

. Pale yellow solid (149.5 mg, yield 63%). Mp 80–82 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 3H), 4.05 (s, 2H), 6.82 (d, J=8.6 Hz, 2H), 6.88 (s, 1H), 7.06 (dd, J=14.7, 7.7 Hz, 2H), 7.18 (t, J=8.5 Hz, 3H), 7.34 (d, J=8.1 Hz, 1H), 7.51 (d, J=7.8 Hz, 1H), 7.91 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=152.56, 131.31, 128.15, 124.43, 122.21, 117.07, 116.85, 114.15, 114.01, 111.11, 108.58, 105.91, 50.12, 25.55 ppm. HRMS (EI): calcd for $C_{16}H_{15}NO$: $[M]^+$ 237.1154, found: 237.1153.

4.25. 5-Bromo-3-(4-methoxybenzyl)-1*H*-indole (3na)

White solid (246.6 mg, yield 78%). Mp 76–78 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.79 (s, 3H), 4.01 (s, 2H), 6.84 (d, J=8.5 Hz, 2H), 6.91 (s, 1H), 7.18 (d, J=8.6 Hz, 2H), 7.22 (d, J=8.5 Hz, 1H), 7.27 (d, J=8.5 Hz, 1H), 7.64 (s, 1H), 7.98 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.31, 135.52, 133.16, 129.94, 125.30, 123.90, 122.20, 118.97, 116.45, 114.95, 114.26, 112.96, 55.73, 30.92 ppm. HRMS (EI): calcd for $C_{16}H_{14}BrNO$: $[M]^+$ 315.0259, found: 315.0260.

4.26. 3-(4-Methoxybenzyl)-5-methyl-1*H*-indole (3oa)

Brown solid (118.1 mg, yield 47%). Mp 74–76 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.42 (s, 3H), 3.78 (s, 3H), 4.02 (s, 2H), 6.88–6.78 (m, 3H), 7.00 (d, J=8.3 Hz, 1H), 7.19 (d, J=7.7 Hz, 2H), 7.23 (s, 1H), 7.30 (s, 1H), 7.83 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.61, 135.02, 133.69, 129.81, 128.75, 127.90, 123.86, 122.70, 118.97, 115.90, 113.97, 111.26, 55.52, 30.88, 21.81 ppm. HRMS (EI): calcd for $C_{17}H_{17}NO$: $[M]^+$ 251.1310, found: 251.1311.

4.27. 5-Methoxy-3-(4-methoxybenzyl)-1*H*-indole (3pa)

White solid (165.7 mg, yield 62%). Mp 97–99 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.78 (s, 3H), 3.81 (s, 3H), 4.02 (s, 2H), 6.84 (t, J=9.7 Hz, 4H), 6.95 (s, 1H), 7.23–7.18 (m, 2H), 7.25 (s, 1H), 7.83 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.10, 154.16, 133.55, 131.93, 129.91, 128.12, 123.44, 116.25, 114.06, 112.39, 112.12, 101.33, 56.22, 55.61, 30.89 ppm. HRMS (EI): calcd for $C_{17}H_{17}NO_2$: $[M]^+$ 267.1259, found: 267.1256.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.11.045.

References and notes

1. (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083; (b) Wilkes, J. S. *Green Chem.* **2002**, *4*, 73–80; (c) Hallettand, J. P.; Welton, T. *Chem. Rev.* **2011**, *111*, 3508–3576.
2. (a) Chauvin, Y. L.; Mussmann, L.; Olivier, H. *Angew. Chem., Int. Ed.* **1996**, *34*, 2698–2700; (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789; (c) Sheldon, R. *Chem. Commun.* **2001**, 2399–2407; (d) Li, D. M.; Shi, F.; Peng, J. J.; Guo, S.; Deng, Y. Q. *J. Org. Chem.* **2004**, *69*, 3582–3585; (e) Geldbach, T. J.; Zhao, D. B.; Castillo, N. C.; Laurenczy, G.; Weyershausen, B.; Dyson, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 9773–9780; (f) Jiang, T.; Ma, X.; Zhou, Y.; Liang, S.; Zhang, J.; Han, B. *Green Chem.* **2008**, *10*, 465–469; (g) Sharma, Y. O.; Degani, M. S. *Green Chem.* **2009**, *11*, 526–530.
3. Doherty, S.; Goodrich, P.; Hardacre, C.; Luo, H. K.; Rooney, D. W.; Seddon, K. R.; Styring, P. *Green Chem.* **2004**, *6*, 63–67.
4. (a) Song, C. E.; Shim, W. H.; Roh, E. J.; Choo, J. H. *Chem. Commun.* **2000**, 1695–1696; (b) Wasserscheid, P.; Sesing, M.; Korth, W. *Green Chem.* **2002**, *4*, 134–138.
5. (a) Fraga-Dubreuil, J.; Bourahla, K.; Rahmouni, M.; Bazureau, J. P.; Hamelin, J. *Catal. Commun.* **2002**, *3*, 185–190; (b) Bradaric, C. J.; Downard, A.; Kennedy, C.; Rovertson, A. J.; Zhou, Y. H. *Green Chem.* **2003**, *5*, 143–152; (c) Alleti, R.; Oh, W. S.; Perambuduru, M.; Afrasiabi, Z.; Simm, E.; Reddy, V. P. *Green Chem.* **2005**, *7*, 203–206.
6. (a) Wang, Y.; Li, H.; Wang, C.; Jiang, H. *Chem. Commun.* **2004**, 1938–1939; (b) Wang, C.; Guo, P.; Li, H.; Wang, Y.; Weng, J.; Wu, L. *Green Chem.* **2006**, *8*, 603–607.
7. (a) Zhang, L.; Xian, M.; He, Y.; Li, L.; Yang, J.; Yu, S.; Xu, X. *Bioresour. Technol.* **2009**, *100*, 4368–4373; (b) Han, F.; Yang, L.; Li, Z.; Xia, C. G. *Org. Biomol. Chem.* **2012**, *10*, 346–354.
8. (a) Wilkes, J. S. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11–17; (b) Fang, D.; Zhou, X.; Ye, Z.; Liu, Z. *Ind. Eng. Chem. Res.* **2006**, *45*, 7982–7984; (c) Santra, S.; Majee, A.; Hajr, A. *Tetrahedron Lett.* **2011**, *52*, 3825–3827; (d) Han, F.; Yang, L.; Li, Z.; Xia, C. G. *Adv. Synth. Catal.* **2012**, *354*, 1052–1060.
9. Bovet, D. *Ann. N.Y. Acad. Sci.* **1950**, 1089–1226.
10. Talaz, O.; Gülcin, I.; Göksu, S.; Saracoglu, N. *Bioorg. Med. Chem.* **2009**, *17*, 6583–6589.
11. (a) Poon, K. W. C.; House, S. E.; Dudley, G. B. *Synlett* **2005**, 3142–3144; (b) Long, T. R.; Maity, P. K.; Samarakoon, T. B.; Hanson, P. R. *Org. Lett.* **2010**, *12*, 2904–2907.
12. (a) Trost, B. M. *Science* **1991**, *254*, 1471–1477; (b) Salvatore, R. N.; Yoon, C. H.; Jung, K. W. *Tetrahedron* **2001**, *57*, 7785–7855; (c) Wuts, P. G. M.; Greene, T. W. *Protective Groups in Organic Synthesis*, 4th ed.; Wiley-Interscience: New York, NY, 2007; (d) Suzuki, K.; Hori, Y.; Kobayashi, T. *Adv. Synth. Catal.* **2008**, *350*, 652–656; (e) Meshram, H. M.; Reddy, B. C.; Goud, P. R. *Synth. Commun.* **2009**, *39*, 2297–2303.
13. (a) Luzung, M. R.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 15760–15761; (b) Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 4085–4088; (c) Hamid, M. H. S. A.; Slatford, P. A.; Williams, J. M. J. *Adv. Synth. Catal.* **2007**, *349*, 1555–1575; (d) Hamid, M. H. S. A.; Allen, C. L.; Lamb, G. W.; Maxwell, A. C.; Maytum, H. C.; Watson, A. J. A.; Williams, J. M. J. *J. Am. Chem. Soc.* **2009**, *131*, 1766–1774; (e) Dobereiner, G. E.; Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 681–703; (f) Pingen, D.; Kller, C. M.; Vogt, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 8130–8133; (g) Imm, S.; Bähn, S.; Neubert, L.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8126–8127.
14. Bisaro, F.; Prestat, G.; Vitale, M.; Poli, G. *Synlett* **2002**, 1823–1826.
15. Yasuda, M.; Somyo, T.; Baba, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 793–796.
16. Rueping, M.; Nachtsheim, B. J.; Kuenkei, A. *Org. Lett.* **2007**, *9*, 825–827.
17. (a) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2605–2609; (b) Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006–6015.
18. Sanz, R.; Martinez, A.; Miguel, D.; Alvarez-Gutierrez, J. M.; Rodriguez, F. *Adv. Synth. Catal.* **2006**, *348*, 1841–1845.
19. Sanz, R.; Miguel, D.; Martinez, A.; Alvarez-Gutierrez, J. M.; Rodriguez, F. *Org. Lett.* **2007**, *9*, 2027–2030.
20. (a) Hajipour, A. R.; Rajaei, A.; Ruoho, A. E. *Tetrahedron Lett.* **2009**, *50*, 708–711; (b) Funabiki, K.; Komeda, T. *Tetrahedron* **2009**, *65*, 7457–7463; (c) Liu, L. Y.; Li, J. *Tetrahedron Lett.* **2011**, *52*, 5636–5639.
21. Shen, Z.-L.; Ji, S.-J.; Loh, T.-P. *Tetrahedron Lett.* **2005**, *46*, 3137–3139.
22. (a) Gu, D.-G.; Ji, S.-J. *Chin. J. Chem.* **2008**, *26*, 578–582; (b) Gu, D.-G.; Ji, S.-J.; Jiang, Z.-Q.; Zhou, M.-F.; Loh, T.-P. *Synlett* **2005**, 959–962.
23. Kondo, T.; Mitsudo, T.-A. *Chem. Rev.* **2000**, *100*, 3205–3220.