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Facile One-Pot Synthesis of Amidoalkyl Naphthols and Benzopyrans Using Magnetic Nanoparticle-Supported Acidic Ionic Liquid as a Highly Efficient and Reusable Catalyst

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Abstract: An efficient and eco-friendly procedure for the synthesis of 1-amidoalkyl-2-naphthol and tetrahydrobenzo[*b*]pyran derivatives has been developed through a one-pot three-component condensation of aldehydes with 2-naphthol and amides, or with malononitrile and dimedone in the presence of magnetic nanoparticle supported acidic ionic liquid (AIL@MNP) as a novel heterogeneous catalyst under solvent-free conditions. This new procedure offers several advantages such as short reaction time, excellent yields, operational simplicity and without any tedious work-up for catalyst recovery or product purification. Moreover, the catalyst could be simply separated by an external magnet and reused six times without significant loss of catalytic activity.

Keywords: amidoalkyl naphthols; benzopyrans; supported ionic liquid; magnetically recoverable catalyst

1. Introduction

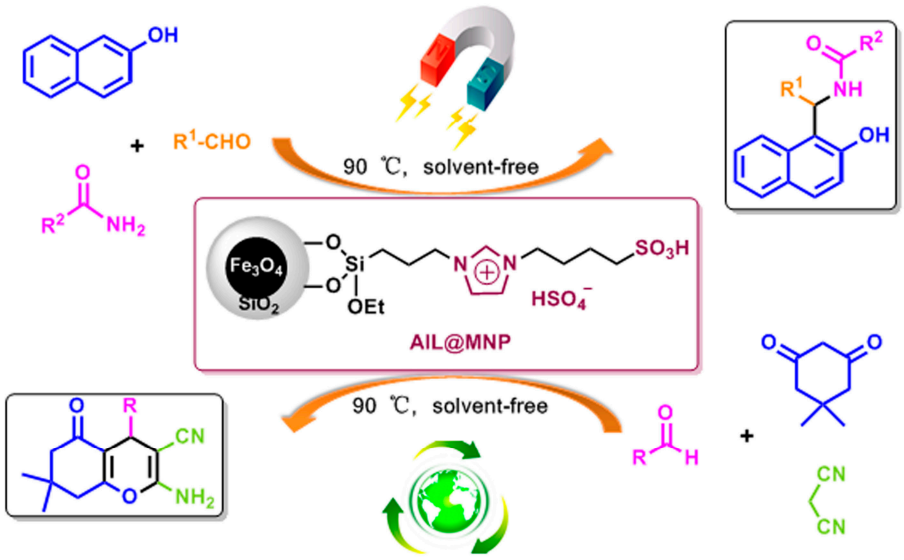
The development and improvement of eco-friendly technologies is the most challenging task in the contemporary chemistry and chemical industry. With this objective, the reduction of wastes together with the use of renewable feedstocks, environmentally benign solvents and reagents, effectively recoverable catalysts are important parameters to achieve more sustainable approaches according to the green chemistryprinciples [1–3]. Due to high atom economy, great efficiency andprocedural convenience in the construction of complex structures from three or more reactants, multicomponent reactions (MCRs) have been an efficient and powerful tool in the modern synthetic chemistry [4,5]. And the discovery of novel MCRs and development of known MCRs are highly compatible with the aims of sustainable and green chemistry [6].

The synthesis of amidoalkyl naphthols and benzopyrans are attractive examples of these MCRs. These 1-amidoalkyl-2-naphthol and tetrahydrobenzo[*b*]pyran derivatives are of particular value because of their promising biological and pharmacological activities [7–9]. The preparation of amidoalkyl naphthols has been carried out by a three-component condensation of aldehydes, 2-naphthols and amides using different catalysts such as $Ba_3(PO_4)_2$ [10], Nano Al_2O_3 [11], supported heteropolyacid [12,13], magnetic sulfonic or phosphoric acid [14–16], β-CD-BSA [17], $[C_6(MPy)_2][CoCl_4]^{2-}$ [18], MWCNT@Co-complex [19], sulfonated polynapthalene [20] and grapheme oxide [21] in the last five years.Despite undeniable advantages of these methods, a great part of themsuffer from one or more shortcomings such as high reaction temperature, prolonged reaction

time, low yield and difficult catalyst separation and recovery. In addition, most of them are limited to only aromatic aldehydes and the reactions with aliphatic aldehydes were reported to suffer from low yields and harsh reaction conditions. Meanwhile, the benzopyrans could also be prepared by multicomponent condensation of dimedone with aldehyde and malononitrile in the presence of newly reported catalysts such as SO_4^{2-}/MCM-41 [22], $NH_4H_2PO_4/Al_2O_3$ [23], THAM [24], urea [25], ion-exchange resin [26], SO_3H-functionalized nano-TiO_2 [27], immobilized HPA [28,29], ionic liquid [30] and MWCNT@Co-complex [19]. Many of the reported procedures suffer from limitations yet, for example use of volatile organic solvent, prolonged reaction time, tedious work-up and additional ultrasonic irradiation. Therefore, the development of a milder and cleaner alternative procedure to construct these valuable organic compounds is still highly desirable.

Ionic liquids (ILs) have attracted considerable attention as green reaction media or catalysts, due to their particular properties such as undetectable vapor pressure, high thermal stability, excellent solubility and ease of recovery and reuse [31,32]. Recently, the concept of nanoconfined ionic liquids has been proposed [33], which combines the benefits of nano-supports and ILs such as minimizing the dosage of ILs, high designability and excellent activity, ease of handling, separation and recycling. On the other hand, magnetic nanoparticles (MNPs) have appeared as a novel type of catalyst supports because of their easy synthesis and functionalization, magnetic separation, good stability, low toxicity and cost [34]. A number of magnetically retrievable catalysts have been employed in a range of organic transformations [35–37] and some immobilization processes for functional ILs on MNPs supports have been developed [38–40]. Driven by the unique properties of magnetic nanoparticles and the potential applications of acidic ILs in catalysis, we have successfully prepared a magnetic nanoparticle supported acidic ionic liquid (AIL@MNP), which was found to be a highly efficient catalyst for the synthesis of benzoxanthenes through the MCRs [38].

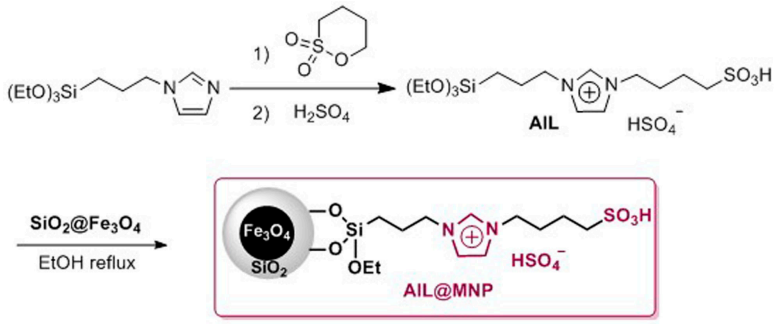
Considering the importance of the amidoalkyl naphthols and benzopyrans and as a part of our continuous work on developing supported catalysts for organic transformations [41–45], herein, we utilized this novel and magnetically recoverable catalyst AIL@MNP for one-pot synthesis of amidoalkyl naphthols and benzopyrans from simply available substrates under milder reaction conditions (Scheme 1). In comparison with our previously prepared silica supported acidic IL (AIL@SiO_2) [46] or pure IL catalyst [47,48], the AIL@MNP has a variety of advantages such as facile and effective catalyst recovery, high activity, low leaching and so on.



Scheme 1. The AIL@MNP catalyzed synthesis of amidoalkyl naphthols and benzopyrans.

2. Results and Discussion

In our previous work [38], the AIL@MNP was prepared by anchoring 3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium hydrogen sulfate onto the surface of silica-coated Fe_3O_4 nanoparticle (Scheme 2) and well characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), elemental analysis (EA), thermogravimetric analysis (TG) and vibrating sample magnetometer (VSM). The AIL@MNP were spherical shapes with approximately 25 nm diameters. It had excellent thermal stability and superparamagnetic behavior. And theIL content of AIL@MNP was determined to be 0.54 mmol/g by elemental analysis of nitrogen.



Scheme 2. The synthetic route for AIL@MNP.

Driven by the potential abilityof AIL@MNP as an environmentally benign catalyst, it was initially tested for the synthesis of amidoalkyl naphthols. The reaction was carried out by simply mixing benzaldehyde (2 mmol), 2-naphthol (2 mmol) and acetamide (2.4 mmol) in the presence of 20 mg of AIL@MNP under solvent-free conditions. The mixture was stirred at 90 °C for 30 min and the corresponding product was obtained in 52% yield. Encouraged by this result, we increased gradually the amount of catalyst from 0 to 100 mg. In the absence of any catalyst, only trace product could be detected (Table 1, entry 1), whereas good results were obtained in the presence of AIL@MNP (Table 1, entries 2–6). The optimum amount of AIL@MNP was 60 mg (Table 1, entry 4) and no obvious improvement was observed by increasing the amount of catalyst to 80 or 100 mg (Table 1, entries 5 and 6). Furthermore, the influence of reaction temperature was investigated, which indicated that lower temperatures (r.t.~75 °C) decelerated the reaction rate significantly and led to lower yields (Table 1, entries 7–9) and 90 °C was more suitable for the reaction. In addition, compared with $SiO_2@Fe_3O_4$ and AIL@SiO_2, the AIL@MNP showed a better catalytic activity (Table 1, entries 11 and 12). Thus, we used 60 mg of AIL@MNP for the one-pot synthesis of amidoalkyl naphthols from various aldehydes, amides and 2-naphthol under solvent-free conditions at 90 °C. And the results are summarized in Table 2.

Table 1. Screening conditions for the reaction of benzaldehyde with 2-naphthol and acetamide.

Entry	Catalyst (mg)	Temperature (°C)	Time (min)	Isolated Yield (%)
1	None	90	60	Trace
2	AIL@MNP (20)	90	30	52
3	AIL@MNP (40)	90	20	77
4	AIL@MNP (60)	90	10	91
5	AIL@MNP (80)	90	10	92
6	AIL@MNP (100)	90	10	90
7	AIL@MNP (60)	r.t.	120	18
8	AIL@MNP (60)	50	60	54
9	AIL@MNP (60)	75	30	83
10	AIL@MNP (60)	100	10	91
11	$SiO_2@Fe_3O_4$ (60)	90	60	22
12	AIL@SiO_2 (60)	90	10	90

Table 2. One-pot synthesis of 1-amidoalkyl-2-naphthols with different aldehydes and amides catalyzed by AIL@MNP [a].

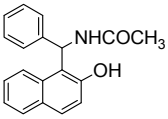
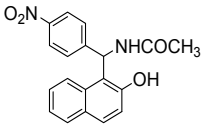
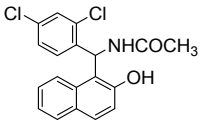
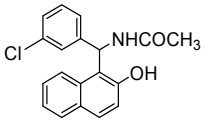
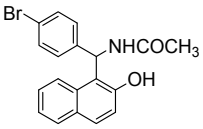
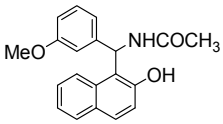
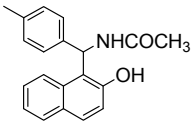
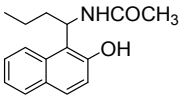
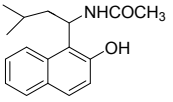
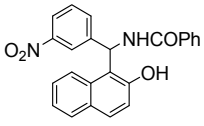
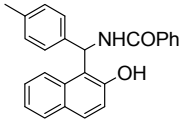
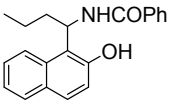
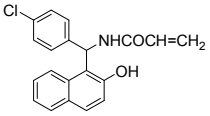
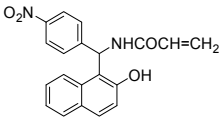
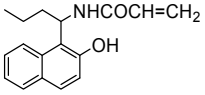
Entry	Aldehyde R^1	Amide R^2	Time (min)	Product	Yield (%) [b]	M.p. (°C)	
						Found	Reported
1	Ph	CH_3	10		91	230–232	227–229 [17]
2	4-NO_2-C_6H_4	CH_3	7		94 (93) [c]	243–245	245–247 [19]
3	2,4-Cl_2-C_6H_3	CH_3	20		85	201–203	201–203 [7]
4	3-Cl-C_6H_4	CH_3	20		83	235–237	237–238 [48]
5	4-Br-C_6H_4	CH_3	20		90	227–229	229–231 [11]
6	3-MeO-C_6H_4	CH_3	15		87	201–203	201–204 [7]
7	4-Me-C_6H_4	CH_3	25		84	221–223	222–223 [49]
8	*n*-C_3H_7	CH_3	12		85 (82) [c]	221–222	222–223 [46]
9	*i*-C_4H_9	CH_3	15		87	194–196	195–197 [46]
10	3-NO_2-C_6H_4	Ph	10		95	241–243	242–243 [50]
11	4-Me-C_6H_4	Ph	20		86 (84) [c]	213–215	212–215 [14]

Table 2. *Cont.*

Entry	Aldehyde R^1	Amide R^2	Time (min)	Product	Yield (%) [b]	M.p. (°C)	
						Found	Reported
12	*n*-C_3H_7	Ph	10		86	219–221	220–222 [46]
13	4-Cl-C_6H_4	CH_2=CH	15		89	211–213	212–213 [17]
14	4-NO_2-C_6H_4	CH_2=CH	8		93	224–226	223–225 [48]
15	*n*-C_3H_7	CH_2=CH	10		83	188–190	190–191 [48]

[a] Reaction conditions: aldehyde (2 mmol), 2-naphthol (2 mmol) andacetamide (2.4 mmol) and AIL@MNP (60 mg) at 90 °C under solvent-free conditions; [b] Isolated yield; [c] 5 mmol scale.

As can be seen from Table 2, the procedure is highly effective for the synthesis of amidoalkyl naphthols. A variety of aromatic aldehydes with electron-donating and electron-withdrawing groups were both converted to amidoalkyl naphthols in good to excellent yields (83–95%) with short reaction time (7–25 min). Acetamide, benzamide and acrylamide all underwent smoothly transformation under the reaction conditions. And interestingly, some typical aliphatic aldehydes, were investigated under the reaction conditions and the corresponding desired products were obtained in good yields (Table 2, entries 8–9, 13 and 16). In all cases amidoalkyl naphthols were the sole products and no by-product was observed. Moreover, the catalytic process under a higher scale provided similar results (Table 2, entries 2, 8 and 11), which indicated that amidoalkyl naphthols could be synthesized successfully in gram-scale.

To compare the efficiency of AIL@MNP with other reported catalysts, we summarized several results for the preparation of *N*-[(4-nitro-phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl] acetamide from 4-nitrobenzaldehyde, 2-naphthol and acetamide in Table 3. Obviously, AIL@MNP showed a much higher catalytic activity in terms of shorter reaction time and milder conditions than other catalysts used in references.

Table 3. Comparison of different catalysts for the one-pot three-component reaction of 4-nitrobenzaldehyde, 2-naphthol and acetamide.

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
1	Nano Al_2O_3	Solvent-free/110 °C	30	80	[11]
2	[TEBSA][HSO_4]	Solvent-free/120 °C	10	88	[51]
3	*β*-CD-BSA	Solvent-free/100 °C	7	95	[17]
4	$Ba_3(PO_4)_2$	Solvent-free/100 °C	35	88	[10]
5	Fe_3O_4@SiO_2-Imid-PMA	Solvent-free/100 °C	20	96	[13]
6	MWCNT@Co-complex	Solvent-free/75 °C	20	95	[19]
7	$HClO_4$-SiO_2	Solvent-free/110 °C	30	95	[49]
8	$Fe(HSO_4)_3$	Solvent-free/85 °C	25	92	[7]
9	$[C_6(MPy)_2][CoCl_4]^{2-}$	Solvent-free/120 °C	15	93	[18]
10	AIL@MNP	Solvent-free/90 °C	7	94	This work

Encouraged by these results, we extended the scope of the reaction to the synthesis of various tetrahydrobenzo[*b*]pyran derivatives. The three-component condensation of various aldehydes with malononitrile and dimedone were investigated under the above-mentioned optimized conditions. The results are summarized in Table 4. Aromatic aldehydes with electron-donating or electron-withdrawing groups underwent smoothly transformation in a short time (20–40 min) with good to excellent yields (85~94%). It was worth noting that the heteroaromatic aldehyde and aliphatic aldehyde could also be successfully converted to the corresponding products. Additionally, the catalytic process under a higher scale (gram-scale) could also afford satisfied results (Table 4, entries 3, 6 and 9). More particularly, we also compared the efficiency of AIL@MNP with other reported catalysts for the synthesis of benzopyrans. As shown in Table 5, AIL@MNP had a considerable or better activity and this procedure could be a good and practical alternative to the reported methods for the construction of benzopyrans.

Table 4. The AIL@MNP catalyzed synthesis of tetrahydrobenzo[*b*]pyrans [a].

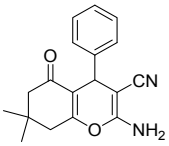
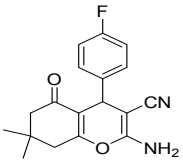
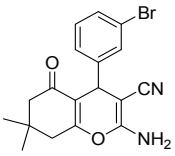
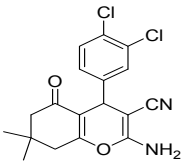
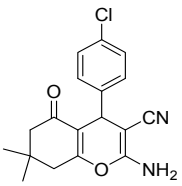
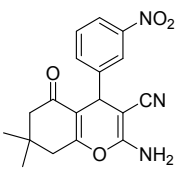
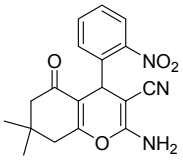
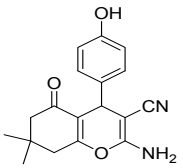
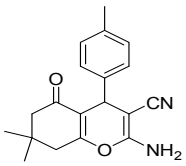
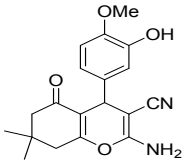
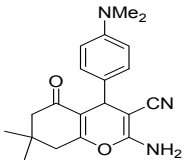
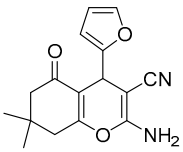
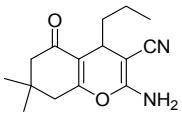
Entry	R	Time (min)	Product	Yield (%) [b]	M.p. (°C)	
					Found	Reported
1	Ph	25		89	230–232	227–229 [27]
2	4-F-C_6H_4	22		90	190–192	188–189 [29]
3	3-Br-C_6H_4	20		92 (90) [c]	229–230	227–228 [25]
4	3,4-Cl_2-C_6H_3	20		93	224–226	225–227 [47]
5	4-Cl-C_6H_4	22		91	212–214	213–214 [52]
6	3-NO_2-C_6H_4	20		94 (92) [c]	213–215	214–216 [24]

Table 4. *Cont.*

Entry	R	Time (min)	Product	Yield (%) [b]	M.p. (°C)	
					Found	Reported
7	2-NO_2-C_6H_4	20		92	223–225	223–224 [27]
8	4-OH-C_6H_4	30		88	224–226	225–227 [29]
9	4-Me-C_6H_4	35		86 (83) [c]	216–218	217–219 [24]
10	3-OH-4-OMe-C_6H_3	40		86	237–238	238–240 [53]
11	4-Me_2N-C_6H_4	40		85	212–214	210–213 [52]
12	2-Furyl	30		90	221–223	219–221 [29]
13	C_3H_7	60		76	171–172	170–172 [24]

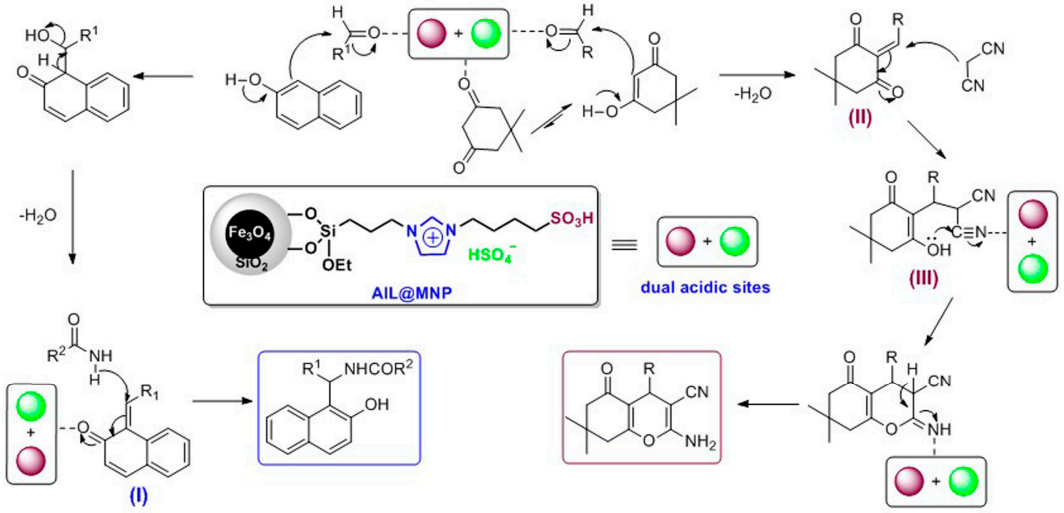
[a] Reaction conditions: aldehyde (2 mmol), malononitrile (2.2 mmol) anddimedone (2 mmol) and AIL@MNP (60 mg) at 90 °C under solvent-free conditions; [b] Isolated yield; [c] 5 mmol scale.

The possible mechanisms for the synthesis of amidoalkyl naphtholsand benzopyransareshown in Scheme 3. The synthesis of amidoalkyl naphthols proceeds by the initial formation of *ortho*-quinonemethides (**I**), which are afforded by the nucleophilic addition of 2-naphthol to the aldehyde, promoted by AIL@MNP. Then the intermediate (**I**) reacts with amide through Michael addition to afford the expected amidoalkyl naphthols, promoted by AIL@MNP as well. Meanwhile, both aldehyde and dimedone are initially activated by the dual acidic sites of AIL@MNP. Then the intermediate (**II**) is formed from the condensation of them and elimination of H_2O and reacts with

malononitrile to afford the intermediate (**III**). Finally, the desired benzopyrans were obtained through an intramolecular cyclization and tautomerization assisted by AIL@MNP.

Table 5. Comparison of different catalysts for the one-pot three-component reaction of 4-chlorobenzaldehyde, malononitrile and dimedone.

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Reference
1	SO_4^{2-}/MCM-41	EtOH/Reflux	60	80	[22]
2	Na_2SeO_4	EtOH-H_2O/Reflux	180	90	[54]
3	Iodine	DMSO/120 °C	210	88	[55]
4	Fe_3O_4@SiO_2@NH-NH_2-PW	H_2O/Reflux	25	92	[28]
5	Fe_3O_4@SiO_2-Imid-PMA	H_2O/Reflux	10	95	[29]
6	$NH_4H_2PO_4/Al_2O_3$	Solvent-free/80 °C	30	88	[23]
7	$H_3PMo_{12}O_{40}$	H_2O/Reflux	25	76	[16]
8	Nanozeolite CP	H_2O/Reflux	15	98	[52]
9	AIL@MNP	Solvent-free/90 °C	22	91	This work



Scheme 3. Plausible mechanisms for the synthesis of amidoalkyl naphthols and benzopyrans.

The recovery and reuse of catalyst is highly preferable in terms of green synthetic process. Thus, the reusability of AIL@MNP was investigated using the model reaction of benzaldehyde with 2-naphthol and acetamide (**M-1**) and another model reaction of benzaldehyde with malononitrile and dimedone (**M-2**), alternately. When the reaction was completed, acetone was added to dissolve the product. The catalyst could be simply magnetic separation and washed with acetone. After being dried, it was subjected to the alternate reaction. As shown in Figure 1, the catalyst could be recycled without significant loss of catalytic activity in the test of six cycles.

The structure and morphology of the recovered catalyst after six runs were especially investigated. According to the FT-IR characteristic peaks in comparison with the fresh one, it had no obvious change in structure (Figure 2). And there was also no apparent change in the morphology and size by a TEM observation of the recovered catalyst (Figure 3). Moreover, the IL content of the recovered catalyst was determined by elemental analysis again and it was found that 0.53 mmol/g of IL was still grafted on the surface of magnetic nanoparticle, nearly the same as before. These results indicated that the catalyst was very stable and could endure these reaction conditions for the synthesis of amidoalkyl naphthols and benzopyrans.

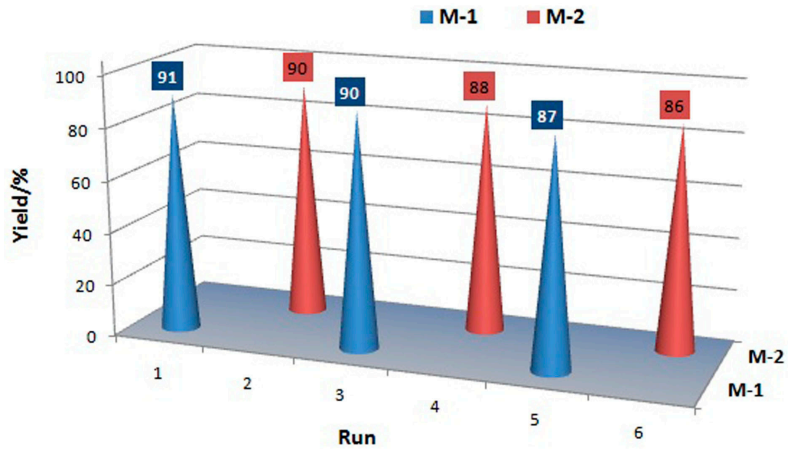


Figure 1. Recycling experiment of AIL@MNP.

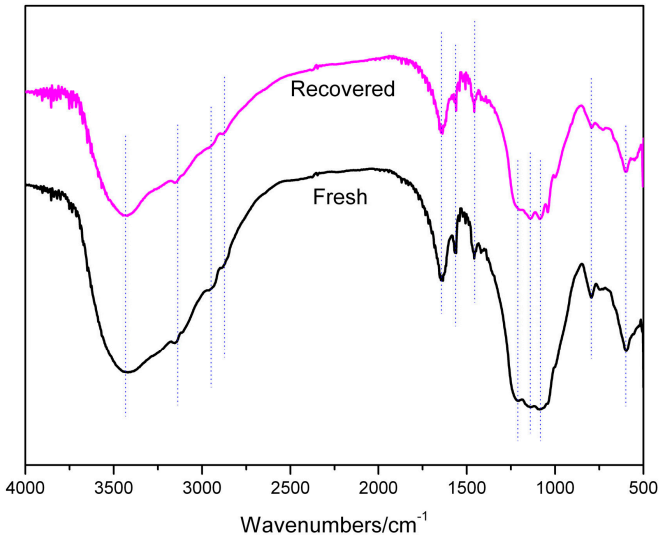


Figure 2. FT-IR spectra of the recovered catalyst and fresh catalyst.

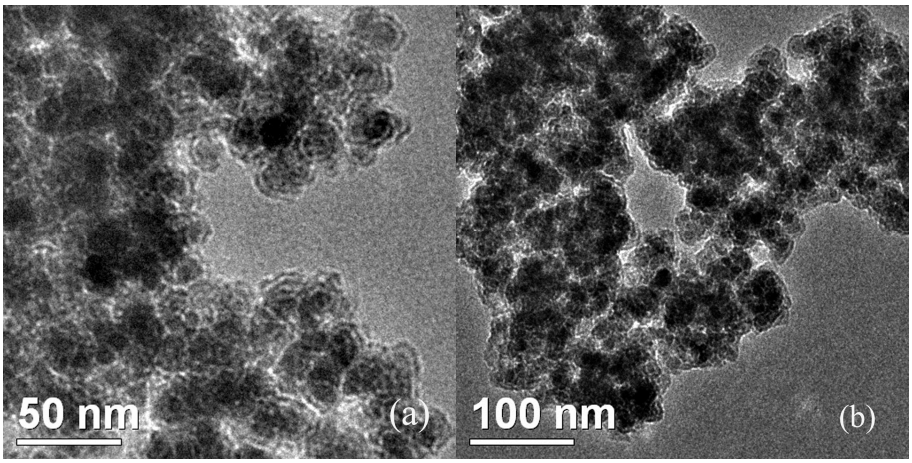


Figure 3. Transmission electron microscope (TEM) images of the recovered catalyst (**a**) and fresh catalyst (**b**).

3. Experimental

Melting points were determined on a Perkin-Elmer differential scanning calorimeter and uncorrected. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III spectrometer. The IR spectra wererun on a Nicolete spectrometer (KBr). Elemental analysis was performed on Elementar Vario MICRO spectrometer. Transmission electron microscope (TEM) images were obtained from a JEOL JEM-2010 Instrument (Houghton, MI, USA). AIL@MNP was synthesized according to our previous method [38]. All other chemicals (AR grade) were commercially available and used without further purification.

3.1. General Procedure for the Synthesis of Amidoalkyl Naphthols

A mixture of aldehyde (2 mmol), 2-naphthol (2 mmol) andacetamide (2.4 mmol) and AIL@MNP (60 mg) was stirred at 90 °C in an oil bath for a certain time, as indicated by TLC for a complete reaction. Acetone was added and the catalyst was separated magnetically from the product solution, washed with acetone and dried under vacuum. Pure amidoalkyl naphthols were afforded by evaporation of the solvent, followed by recrystallization from ethanol.

The spectra and analytic data for some selected 1-amidoalkyl-2-naphthols are presented below:

N-((2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)acetamide (Table 2, entry 2): Light yellow solid; M.p. (°C): 243–245; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.11 (s, 1H), 8.56 (d, J = 7.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 2H), 7.84–7.80 (m, 3H), 7.40 (d, J = 8.5 Hz, 3H), 7.29 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 2.02 (s, 3H).

N-(1-(2-hydroxynaphthalen-1-yl)butyl)acetamide (Table 2, entry 8): White solid; M.p. (°C): 221–222; ^{1}H NMR (500 MHz. DMSO-d_6): δ 9.85 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.02 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 8.5 Hz, 1H), 7.15 (d, J = 9.0 Hz, 1H), 5.78 (t, J = 7.5 Hz, 1H), 2.01–1.98 (m, 1H), 1.83–1.80 (m, 4H), 1.34–1.32 (m, 1H), 1.17–1.15 (m, 1H), 0.86 (t, J = 7.5 Hz, 3H).

N-((2-hydroxynaphthalen-1-yl)(p-tolyl)methyl)benzamide (Table 2, entry 11): White solid; M.p. (°C): 213–215; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.30 (s, 1H), 8.99 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.86–8.82 (m, 3H), 7.81 (d, J = 8.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.50–7.45 (m, 3H), 7.33–7.18 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 2.24 (s, 3H).

N-[(2-hydroxy-naphthalen-1-yl)-butyl]-acrylamide (Table 2, entry 15). White solid; M.p. (°C): 188–190; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.87 (s, 1H), 8.30 (s, 1H), 8.15 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H), 6.43–6.38 (m ,1H), 6.02 (dd, J_1 = 17.0 Hz, J_2 = 2.1 Hz, 1H), 5.87 (q, J = 7.6 Hz, 1H), 5.52 (dd, J_1 = 10.2 Hz, J_2 = 2.1 Hz, 1H), 2.07–2.04 (m, 1H), 1.89–1.84 (m, 1H), 1.38–1.36 (m, 1H), 1.21–1.18 (m, 1H), 0.87 (t, J = 7.4 Hz, 3H).

3.2. General Procedure for the Synthesis of Benzopyrans

A mixture of aldehyde (2 mmol), malononitrile (2.2 mmol) anddimedone (2 mmol) and AIL@MNP (60 mg) was stirred at 90 °C in an oil bath for a certain time, as indicated by TLC for a complete reaction. Acetone was added and the catalyst was separated magnetically from the product solution, washed with acetone and dried under vacuum. Pure benzopyrans were afforded by evaporation of the solvent, followed by recrystallization from ethanol.

The spectra and analytic data for some selected tetrahydrobenzo[*b*]pyrans are presented below:

2-Amino-4-(3,4-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (Table 4, entry 4): White solid; M.p. (°C): 224–226; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.57 (d, J = 7.5 Hz, 1H), 7.39 (s, 1H), 7.17–7.14 (m, 3H), 4.25 (s, 1H), 2.53 (s, 2H), 2.25 (d, J = 16.0 Hz, 1H), 2.13 (d, J = 16.0 Hz, 1H), 1.04 (s, 3H), 0.96 (s, 3H).

2-Amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (Table 4, entry 8): White solid; M.p. (°C): 203–205; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.25 (s, 1H), 6.94–6.91 (m, 4H), 6.66 (d, J = 8.0 Hz, 2H), 4.07 (s, 1H), 2.49 (s, 2H), 2.24 (d, J = 16.0 Hz, 1H), 2.09 (d, J = 16.0 Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H).

2-Amino-7,7-dimethyl-5-oxo-4-propyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (Table 4, entry 13): White solid; M.p. (°C): 173–174; ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.89 (s, 2H), 3.16 (t, J = 4.5 Hz, 1H), 2.44 (d, J = 17.5 Hz, 1H), 2.35 (d, J = 17.6 Hz, 1H), 2.28 (d, J = 16.0 Hz, 1H), 2.19 (d, J = 16.0 Hz, 1H), 1.48–1.44 (m, 1H), 1.37–1.30 (m, 1H), 1.13–1.19 (m, 2H), 1.03 (s, 3H), 1.00 (s, 3H), 0.84 (t, J = 7.5 Hz, 3H).

4. Conclusions

In conclusion, we have developed a highly efficient and eco-friendly methodology for the synthesis of 1-amidoalkyl-2-naphthol and tetrahydrobenzo[*b*]pyran derivatives through one-pot three-component reaction in the presence of magnetic supported acidic ionic liquid (AIL@MNP) as a novel magnetically retrievable catalyst under solvent-free conditions. The procedure is equally effective to aliphatic and aromatic aldehydes. The notable advantages of this method are operational simplicity, mild reaction conditions, short reaction time, excellent yields and environmental benignancy, which makes this procedure a better and more practical alternative to the existing methods. Moreover, the catalyst could be simply separated by an external magnet, avoiding the tedious recovery procedure via filtration or extraction andreused without apparent loss of activityin the test of six cycles.

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Author Contributions: Qiang Zhang conceived and designed the experiments; Yin-Hong Gao and Shan-Lin Qin performed the experiments; Qiang Zhang and Huai-Xin Wei analyzed the data; Qiang Zhang wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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