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Original Research Article

Nano-[Fe_3O_4@SiO_2@$RNHMe_2$][HSO_4]: an effectual catalyst for the production of 1-amidoalkyl-2-naphthols

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KEYWORDS

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Nano-[Fe_3O_4@SiO_2@$RNHMe_2$][HSO_4];
Nanomagnetic catalyst;
Multi-component reaction;
Solvent-free

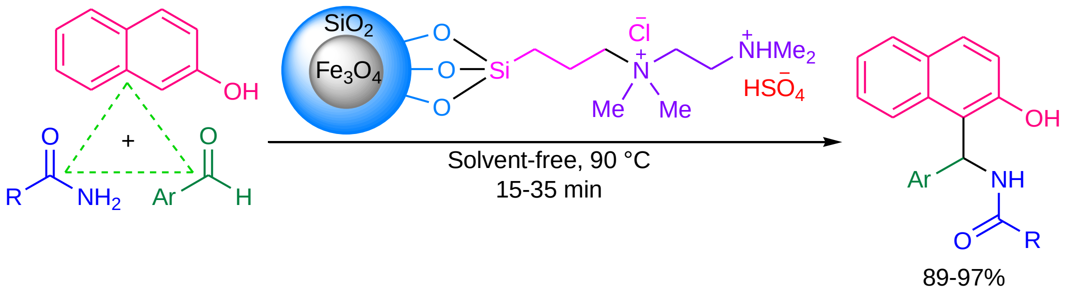
ABSTRACT

Nano-[Fe3O4@SiO2@RNHMe2][HSO4] (NFSRNH), as an effectual and magnetically recyclable catalyst, promoted the solvent-free production of 1-amidoalkyl-2-naphthols through the multi-component reaction of aldehydes, 2-naphthol and primary amides. This method has the advantages of high yield, mild reaction conditions, environmentally benign methodology and short reaction time. Given the increasing levels of interest in green chemistry, the recyclability and reusability of the catalyst have been evaluated.

Highlights:

- Application of an effectual nano-magnetic catalyst for the production of 1-amidoalkyl-2-naphthols.
- Producing the products in short times with high yields.
- Recyclability of the catalyst.

GRAPHICAL ABSTRACT



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Introduction

Multi-component reactions (MCRs) and solvent-free conditions are useful and applicable green chemistry techniques to prepare a wide range of organic compounds; the literature has discussed them well [1-6].

1-Aminoalkyl-2-naphthols and 1,3-oxazines are molecules possessing many biological and medicinal activities, which could be produced from 1-amidoalkyl-2-naphthols [7-14]. An effective protocol to produce 1-amidoalkyl-2-naphtols is the MCR of aldehydes, 2-naphthol and primary amides; for which a catalyst is needed [15-24]. In view of numerous utilizations of 1-amidoalkyl-2-naphthols, try for finding new catalysts to synthesize them can be valuable.

Organic chemists have successfully applied nano-magnetic materials as efficacious catalysts to promote organic transformations. Nonetheless, their aggregation to greater clusters and consequently a decrement in catalytic activity are problems accompanied with their applications. An effective way to solve this problem is by supporting nano-magnetic materials on a solid (especially silica); these supported catalysts also display high chemical and thermal durability [25-36].

Here, we have developed a new nanomagnetic catalyst {nano-[Fe_3O_4@SiO_2@RNHMe$_2$][HSO_4] (NFSRNH),} for the efficacious production of 1-amidoalkyl-2-naphthols *via* the corresponding MCR.

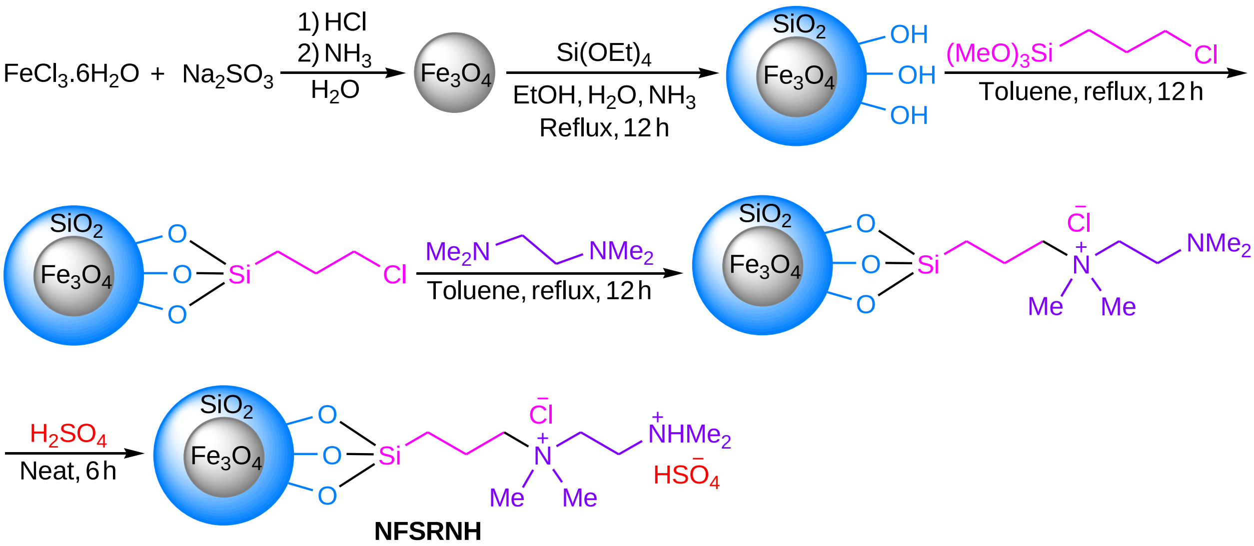
Experimental

Information on the utilized chemicals and apparatuses has been reported in the supplementary material. NFSRNH was produced by the reported protocol (Scheme 1) [35-37].

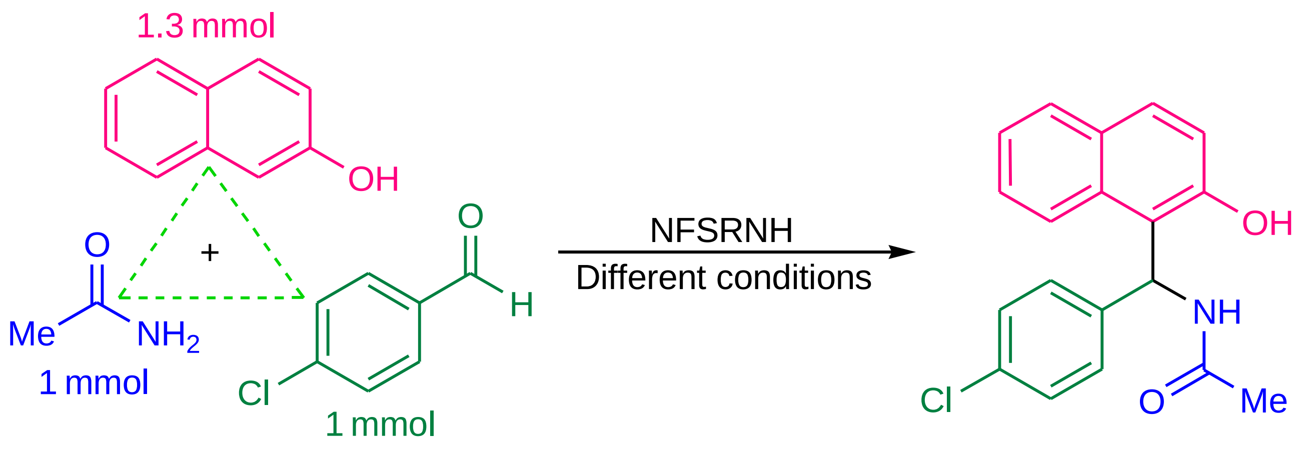
Production of 1-amidoalkyl-2-naphthols

Aldehyde (1 mmol), 2-naphthol (1 mmol), amide (1.3 mmol) and NFSRNH (0.048 g) was vigorously stirred at 90 °C by a rod. When TLC illustrated consuming the reactant, the mixture was cooled to r.t., $MeCO_2Et$ (30 mL), poured to it, refluxed accompanied with stirring (2 min), and NFSRNH was isolated by a magnet (washed by $MeCO_2Et$, and dried). The remained $MeCO_2Et$ was distilled, and the precipitate was purified by recrystallization (EtOH: 95%).

Note: The supplementary material comprises some NMR data and spectrums of the 1-amidoalkyl-2-naphthols.



Scheme 1. The NFSRNH production.



Scheme 2. The model reaction.

Table 1. Investigating the effects of the nanocatalyst amounts and temperature on the model reaction

Entry	Value of NFSRNH (g)	Temp. (ºC)	Time (min)	Yield (%)
1	0.040	80	60	87
2	0.060	80	30	90
3	0.060	85	15	94
4	0.048	90	15	97[a]
5	0.048	100	15	97[a]
6	0.040	90	30	90

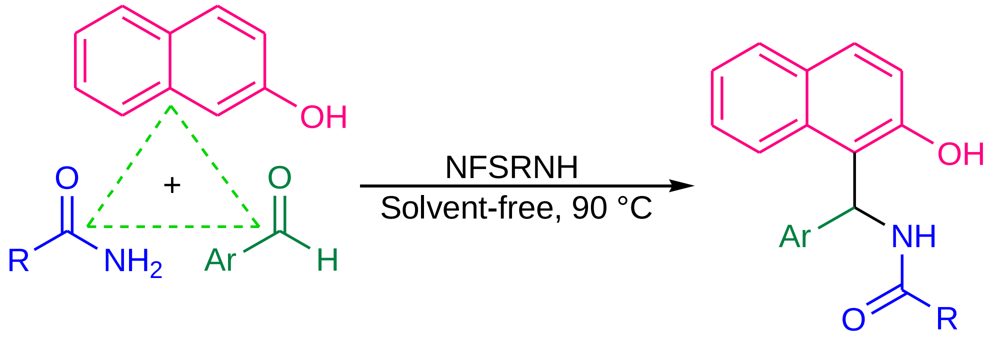
[a] The reaction was completed.

Results and discussion

To determine the optimal conditions, a model reaction (Scheme 2) was tested using various amounts of NFSRNH at 80-100 ºC (no solvent was used as the reaction medium); Table 1 represents the acquired results. The reaction was initially investigated at 80 ºC by 0.040 g and 0.06 g of the catalyst in which the 1-amidoalkyl-2-naphthol was formed in 87% and 90% in 60 and 30 min, respectively (entries 1 and 2). At 85 ºC and utilization of 0.06 g of NFSRNH, the reaction time was 15 min, and the yield was 94% (entry 3). The reaction was then investigated by a value of 0.048 g of NFSRNH at 90 ºC and 100 ºC (entries 4 and 5); according to the results, 90 ºC was selected as the optimal temperature (entry 4). At the optimum temperature, it was evaluated using 0.040 g of NFSRNH, which indicated a reaction time of 30 min and a yield of 90% (entry 6). Therefore, the value of 0.048 g was selected as the optimal value of the catalyst (entry 4).

In the following, the effectiveness and generality of NFSRNH were investigated by application of various aldehydes and amides in the reaction (Table 2 indicates the results). Production of all 1-amidoalkyl-2-naphtols in short times with high yields confirmed that NFSRNH was efficacious and general for this synthesis.

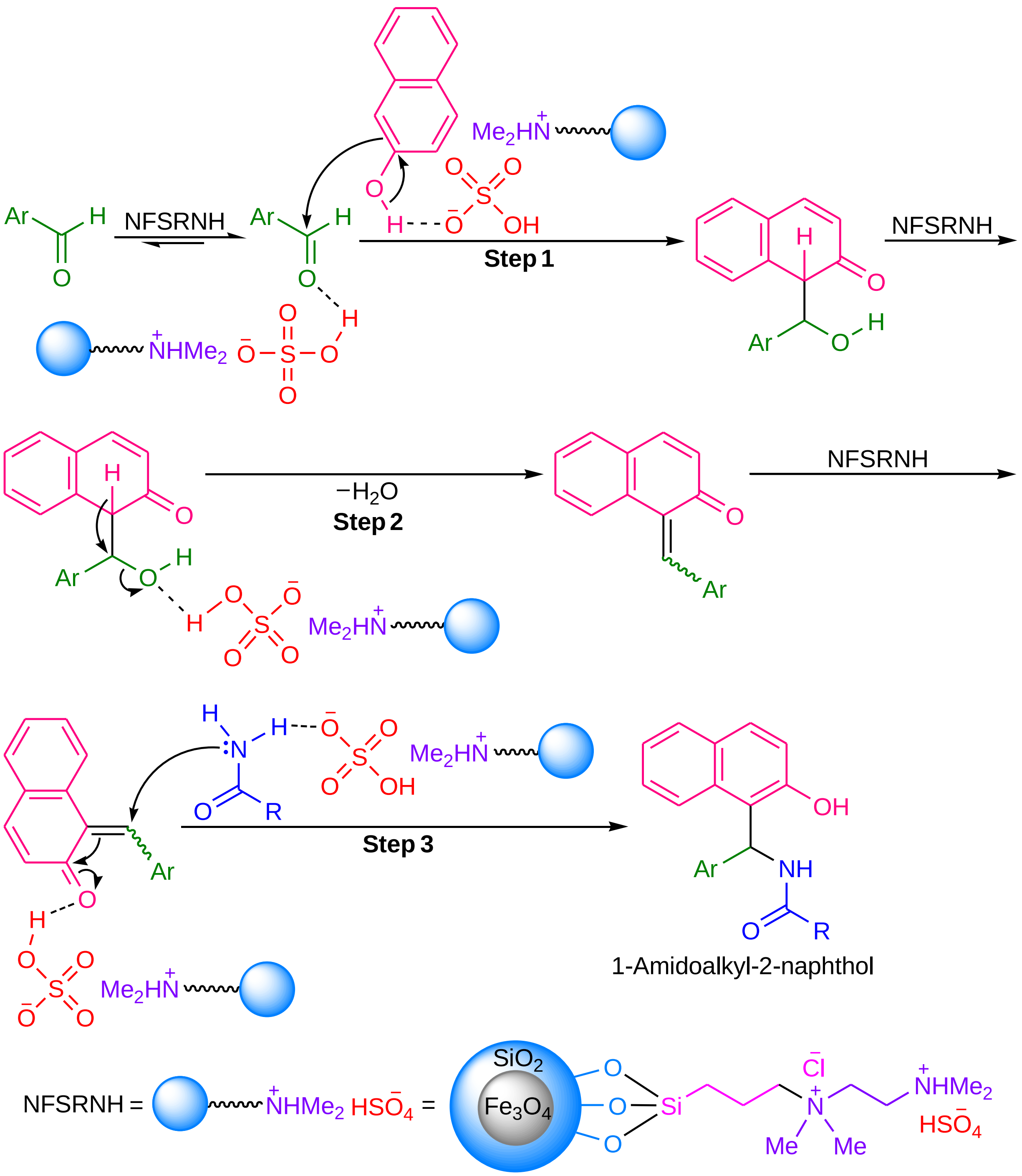
Table 2. The preparation of 1-amidoalkyl-2-naphthols using NFSRNH



Compond. No.	Ar	R	Time (min)	Yield[a] (%)	M.p. (ºC), Found (reported)
1	C_6H_5	CH_3	15	95	240-242 (238-240) [24]
2	4-MeC_6H_4	CH_3	15	97	216-218 (219-221) [38]
3	4-ClC_6H_4	CH_3	15	97	226-228 (225-227) [15]
4	4-MeOC_6H_4	CH_3	30	94	179-181 (183-185) [24]
5	3-$O_2NC_6H_4$	CH_3	15	94	184-185 (182-184) [18]
6	2,4-$Cl_2C_6H_3$	CH_3	25	97	199-201 (200-202) [15]
7	2-$O_2NC_6H_4$	CH_3	30	93	215-217
8	2-ClC_6H_4	CH_3	15	96	200-202 (196-198) [18]
9	4-$O_2NC_6H_4$	CH_3	15	97	248-250 (248-250) [20]
10	2,5-$(MeO)_2C_6H_3$	CH_3	15	93	251-254 (251-253) [39]
11	4-HOC_6H_4	CH_3	35	96	231-233 (233-234) [40]
12	3-BrC_6H_4	CH_3	15	95	248-250 (245-246) [15]
13	5-Br,2-HOC_6H_3	C_6H_5	30	89	220-222
14	C_6H_5	C_6H_5	25	94	232-235 (234-236) [38]

[a]Isolated yield.

The acidic hydrogen of the bisulfate group activates the electrophiles in steps 1 and 3, accelerating the nucleophilic attack; the acidic hydrogen also facilitates the removal of water in step 2 (by converting the hydroxy group to a stronger leaving group). Negatively charged oxygen of bisulfate (as a weak base) activates the nucleophiles in stages 1 and 3 (by helping to remove H^+ from oxygen and nitrogen).



Scheme 3 The mechanism.

The reaction between 4-chlorobenzaldehyde, 2-naphthol and acetamide was used to evaluate the recyclability of NFSRNH (Fig. 1). The catalyst was recyclable for two times with slight loss of catalytic activity.

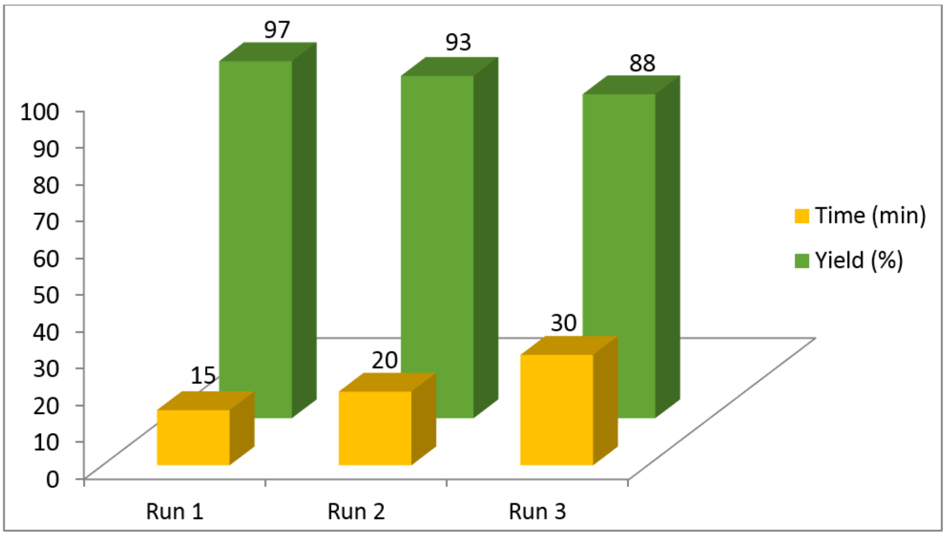


Fig. 1. The results attained in the recyclability test.

Conclusions

In summary, we have introduced a new catalyst for the production of 1-amidoalkyl-2-naphthols. The advantages of applying NFSRNH as catalyst in this synthesis consists of short reaction times, high yields, wide scope, efficacy, performing the synthesis in solvent-free conditions, dual-functionality of NFSRNH, simple workup, purification of the products, and good agreement with green chemistry principles.

Acknowledgements

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