

Green Protocol for the Multicomponent Synthesis of 1-Amidoalkyl-2-naphthols Employing Sustainable and Recyclable SO₃H-Carbon Catalyst

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Abstract: *A green, an efficient, smooth and direct approach for the synthesis of amidoalkyl naphthols has been described that employs via three-component one-pot reaction of β -naphthol, aromatic aldehydes and amides catalyzed by water receptive and recyclable carbon-based solid acid catalyst derived from glycerol under solvent free conditions with good to excellent yields. The significant features of this protocol are high yields of the products, short reaction time, eco-friendly benign reaction condition, moderate temperature, easy purification, economical due to absence of solvent, lack of toxicity and more environmentally friendly catalyst. The recovered catalyst was reused for five consecutive times without any significant loss of its activity. Therefore, the present protocol with carbon acid catalyst could be an attractive alternative to existing methods for the synthesis of biologically important amidoalkyl naphthols.*

Keywords: *Amidoalkyl naphthols, multicomponent, one-pot reaction, solvent free, SO₃H-carbon catalyst, reusability.*

1. INTRODUCTION

Molecules having 1,3-amino oxygenated functional motifs are frequently found in biologically significant natural products and potent drugs including a number of nucleoside antibiotics and HIV protease inhibitors, such as ritonavir and lipinavir.[1,2] Moreover, 1-amidoalkyl-2-naphthols can be easily converted to important biologically active 1-aminoalkyl-2-naphthol derivatives by amide hydrolysis. This 1-Aminoalkyl alcohol-type ligand has been used for asymmetric synthesis and also as catalyst,[3] and also exhibit potent antihypertensive, adrenoceptor-blocking, and Ca⁺² channel-blocking activities.[4] Because of the biological importance of these molecules, several alternative and efficient methods have been described for the synthesis of 1-amidoalkyl-2-naphthols. The reported methods mainly include one-pot multicomponent reaction of β -naphthol, aromatic aldehydes, and amides. Multicomponent reactions (MCRs) have been proven to be a very inventive and rapid way to access complex structures in a single synthetic operation from simple building blocks, and show high atom-economy, high selectivity and simplicity due to the formation of carbon-carbon and carbon-heteroatom bonds in one-pot.[5] Multicomponent reactions have gained much importance in organic syntheses, since they produce the desired products in a single operation without isolating the intermediates, and thus reducing the reaction time and energy.[6] The advantages of MCRs are one pot reactions, consumes very less amount of solvents or no solvents (solvent free or neat reaction), superior atom economy,[7] low cost, generally take less time compare to divergent reactions, smooth procedures and eco-friendly.[8]

The importance of amidoalkyl naphthols for their synthesis has attracted renewed attention and various improved procedures have been described. Amidoalkyl naphthols can be carried out by the

condensation of aryl aldehydes, β -naphthol and amides in presence of a Lewis or Bronsted acid catalysts. Several methods have been reported in the literature for synthesis of these compounds such as *p*-toluene sulphonic acid,[9] chlorosulphonic acid,[10] $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$,[11] $\text{Fe}(\text{HSO}_4)_3$,[12] $\text{Sr}(\text{OTf})_2$,[13] Iodine,[14] heteropoly acid $\text{K}_5\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$,[15] Cu-exchanged heteropoly acids,[16] cation-exchange resins,[17] silica supported perchloric acid,[18,19] $\text{FeCl}_3 \cdot \text{SiO}_2$,[20] montmorillonite K10 clay,[21] silica sulfuric acid,[22] sulfamic acid,[23,24] *N,N,N',N'*-tetrabromobenzene-1,3-disulfonamide,[25] ionic liquids,[26] P_2O_5 ,[27] Indion-130.[28] Very recently $\text{P}_2\text{O}_5/\text{SiO}_2$,[29] magnetic nanoparticle-supported sulfuric acid,[30] 1-Methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium Chloride,[31] MCM-41-*N*-propylsulfamic acid,[32] citric acid,[33] sulfanilic acid,[34] PNBA, [35] AgI nanoparticles,[36] PBS nanoparticles,[37] polyphosphate esters,[38] and tannic acid,[39] has been used to carry out the synthesis. However, some of these protocols suffer from certain drawbacks such as prolonged reaction times, environmental pollution caused by using an organic solvent, low yields, toxicity, highly acidic, expensive, recovery and reusability of the catalysts and the use of an additional microwave or ultrasonic irradiation. Therefore, to overcome above all these problems, the discovery of clean protocol and utilizing more eco-friendly and green catalysts with high catalytic activity and short reaction times for the production of 1-amidoalkyl-2-naphthols have gained prominent attention. The demand of eco-efficient benign procedure, promoted us to develop an expedition method for the synthesis of 1-amidoalkyl-2-naphthols.

In recent years, carbon-based solid acid catalysts have gained prominence, due to their significant advantages over homogeneous catalysts as they are highly efficient, sustainable, ease of product separation, eco-friendly, and reusability.[40] With this connection, Prabhavathi Devi *et al.* reported a one-pot method for the preparation of SO_3H -carbon catalyst having 8.19mmol/g acid density,[41] with surface area of 0.21m²/g from bioglycerol (biodiesel by-product) and also from the glycerol pitch (waste from fat splitting industry) by the *in situ* partial carbonization and sulfonation in a single step.[42] This carbon catalyst has showed excellent catalytic properties by demonstrating its effectiveness for different transformations,[43] due to its high thermal stability, recyclability and strong acid sites of sulfonic acid functional groups. In continuation of our ongoing research towards exploring the applications of the carbon acid catalyst, herein we report a facile, eco-efficient, solvent free and high-yielding synthesis of 1-amidoalkyl-2-naphthols by one-pot three-component condensation of β -naphthol, aromatic aldehydes and amides under solvent free conditions with excellent yield.

2. EXPERIMENTAL

2.1. General

All chemicals were purchased from M/s. SD Fine Chemicals Pvt. Ltd., Mumbai, India. All solvents used were of analytical grade. Reaction was monitored on silica gel TLC plates (coated with TLC grade silica gel, obtained from Merck) employing iodine vapors for detection of spots. Melting points of the products were recorded using Barnstead Electro thermal 9200 instrument. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX. Mass spectra were recorded using electron spray ionization-mass spectrometry (ESI-MS). ¹H NMR spectra was recorded on Bruker UXNMR (operating at 300 MHz) spectrometer using DMSO-d₆. Chemical shifts δ are reported relative to TMS ($\delta = 0.0$) as an internal standard and coupling constants (*J*) are given in Hz.

2.2. Preparation of SO_3H -Carbon Catalyst

A mixture of glycerol (10g) and concentrated sulfuric acid (30 g) were taken in a 500ml glass beaker and gently heated on hotplate from ambient temperature to 220°C for 20min, to facilitate *in situ* partial carbonization and sulfonation. The reaction mixture was allowed at that temperature for about 20 min till the foaming was ceased. The resultant black crystalline product was washed with hot water under agitation till the wash water becomes neutral to p^H. The partially crystalline product was filtered and dried in an oven at 120°C for 2h in order to ensure free of moisture to obtain glycerol-based carbon acid catalyst (4.67 g). The carbon acid catalyst was found to have acid density of 8.19mmol/g, and surface area of 0.21m²/g.

2.3. General Procedure for the Synthesis of Amidoalkyl Naphthols

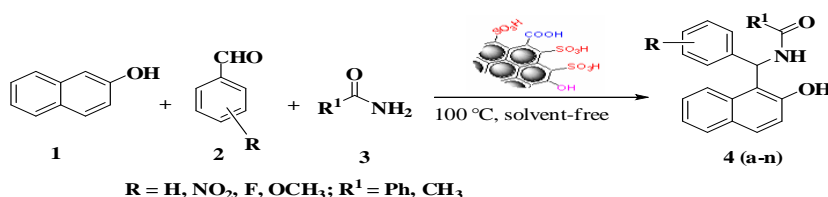
A mixture of β -naphthol (1mmol), aldehyde (1mmol), acetamide or benzamide (1.2mmol) and SO_3H -carbon acid catalyst (5 wt% of aldehyde) was stirred at 100°C in oil bath and the reaction was

monitored by TLC. After completion of the reaction, methanol was added to the reaction mixture and simply filtering the catalyst. The solvent was removed from the filtrate gave the crude product, which was purified by recrystallization in ethanol to give the pure products. The recovered catalyst was again washed with methanol and dried in oven at 120 °C for 1 h and reused for its next run. All the products were further purified by silica gel column chromatography and characterized by comparing their m.p, IR, ¹H-NMR, ¹³C-NMR and ESI-MS with those reported for the authentic samples.[13,28,32]

3.3.1 N-[4-Nitrophenyl-(2-hydroxy-naphthalen-1-yl)-methyl]-benzamide (4c): Yield: 93%; m.p: 227-228 °C; (δH (DMSO-d₆) 9.90 (1H, br), 8.7 (1H, d, *J* 8.3 Hz), 8.12 (1H, d, *J* 8.4 Hz), 8.03 (2H, d, *J* 8.7 Hz), 7.81 (2H, d, *J* 7.0 Hz), 7.76 (1H, d, *J* 7.93 Hz), 7.71(1H, d, *J* 8.9 Hz), 7.50-7.30 (7H, m), 7.31(1H, d, *J* 7.4 Hz), 7.2 (1H, d, *J* 8.9 Hz); MS (ESI): m/z 397(M-1).

3. RESULTS AND DISCUSSION

3.1. Optimization of Reaction Conditions



Scheme1. Synthesis of 1-amidoalkyl-2-naphthols catalyzed by SO₃H-carbon acid catalyst.

Considering the above subjects, we wish to report an efficient, convenient and facile method for the condensation of β-naphthol (1), aromatic aldehydes (2) with benzamide or acetamide (3) in presence of SO₃H-carbon acid catalyst as a highly efficient green catalyst leading to the corresponding 1-amidoalkyl-2-naphthols (4a-n) (**Scheme 1**).

For our initial study, a standard model reaction using benzaldehyde, β-naphthol, and benzamide at 100°C without catalyst was performed in order to establish the real effectiveness of the carbon acid catalyst. It was found that no conversion to product was observed even after 2 h of heating. It means intervention of carbon acid catalyst was must for initiation of the reaction. So, the catalytic activity of SO₃H-carbon acid catalyst was investigated on the model reaction under solvent-free condition. Meanwhile, a slight excess of the benzamide or acetamide was found to be advantageous for the yield of 1-amidoalkyl-2-naphthols and hence the molar ratio of β-naphthol, aromatic aldehydes and amide was kept at 1:1:1.2.

3.1.1. Effect of Catalyst Loading

In order to evaluate the effect of catalyst loading on rate of the reaction, the reaction was performed by varying catalyst concentrations from 5-20 wt% of benzaldehyde, keeping the reaction temperature 100°C and taking the molar ratios of substrates as 1:1:1.2 and the results are given in **Figure 1**. The results indicated that the yield of the product increased (92%) at the concentration of catalyst is 5 wt%. Increase of catalyst concentration from 10-20 wt%, there is no considerable effect on the yield of the product. Hence, catalyst amount 5 wt% of benzaldehyde was found to be the optimal quantity and sufficient to push the reaction towards the maximum yield of amidoalkyl naphthols.

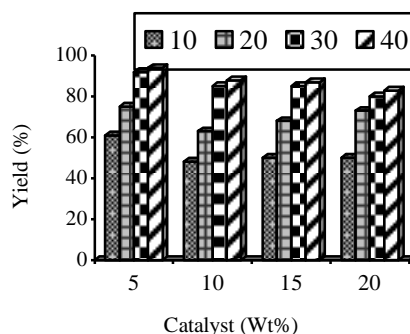


Figure1. Effect of catalyst concentration and reaction time on the yield of product.

3.1.2. Effect of Reaction Time

Influence of the reaction time on the yield of amidoalkyl naphthols was also investigated by varying the reaction period from 10-40min at 100°C using a catalyst concentration of 5 wt% and the molar ratios of substrates as 1:1:1.2 (**Figure 1**). The results clearly indicate that an increase in reaction time from 10-30min increase the yield of amidoalkyl naphthols. However, when the reaction time exceeded 30-40 min, the increase in yield was marginal. Based on this study, residence period of 30 min is optimum for the maximum yield of amidoalkyl naphthols.

3.1.3. Effect of Reaction Temperature

The effect of reaction temperature on the condensation of β -naphthol, aromatic aldehydes with benzamide to obtain amidoalkyl naphthols was conducted at different temperatures ranging from 60-120°C using a catalyst concentration of 5 wt% for 30 min and the results are summarized in **Figure 2**. This study revealed that, with increase of the reaction temperature from 60 to 100°C accelerates the reaction towards the product formation and at 100°C, maximum 92% yield of amidoalkyl naphthols was obtained with in 30min. But, when the reaction temperature increased from 100-120°C, the increase in yield was marginal. Based on this study, reaction temperature of 100 °C is optimum for the maximum yield of amidoalkyl naphthols.

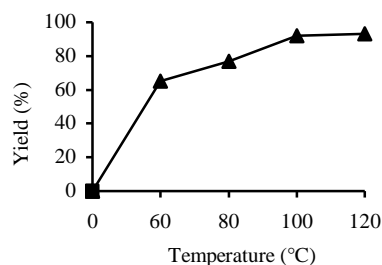


Figure2. Effect of reaction temperature on the yield of the product.

3.1.4. Reusability of the Catalyst

The reusability of a catalyst is one of its most important benefits and makes it useful for commercial application. Thus, when optimizing the reaction conditions, the recycling of SO_3H -carbon acid catalyst in the reaction of β -naphthol, benzaldehyde with benzamide was investigated. After completion of the reaction, the catalyst was recovered by filtration, washed with methanol and dried in oven at 120 °C for 1 h. The catalyst was reused for 5 cycles and it was found that the catalytic activity maintained with ~92% conversion in first three cycles and marginally reduced from 90% to 88% in the last two cycles (**Figure 3**) due to the loss in the recovery. This study demonstrated that the catalyst was highly active, stable, and recyclable up to fifth cycle without the loss of significant activity.

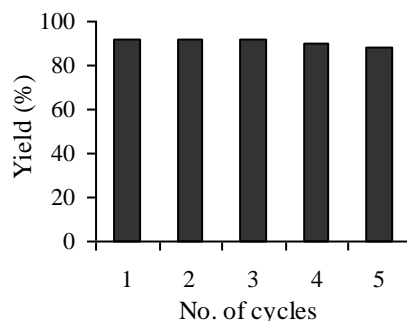


Figure3. Reusability of the SO_3H -carbon catalyst.

3.2. One-pot Synthesis of Amidoalkyl Naphthols Employing SO_3H -Carbon Catalyst

In order to evaluate the generality of this process, the optimized system was used for the synthesis of other amidoalkyl naphthol derivatives and the results are summarized in **Table 1**. Various functionalities present in the aryl aldehydes, such as methoxy, nitro, fluoro, with benzamide/

acetamide groups were well tolerated under these conditions. In all cases studied, the three-component reaction proceeded smoothly to give the corresponding 1-amidoalkyl-2-naphthol derivatives in good to excellent yields. Most importantly, the aromatic aldehydes with electron-withdrawing groups like -NO₂, -F showed better reactivity (**Table 1**, Entries 2-5) than electron-donating groups like -OCH₃ (**Table 1**, Entries 6,7). However, the position of the substituent on the aromatic ring does not have much effect on the yield of the product (**Table 1**, Entries 4, 5, 6, 7). In addition to this, the effect of benzamide and acetamide on the synthesis of amidoalkyl naphthols was also studied and the data revealed that the condensation of aldehydes with benzamide reacted faster (**Table 1**, Entry 1) than acetamide (**Table 1**, Entry 8).

Table 1. Synthesis of amidoalkyl naphthols in presence of SO₃H-carbon catalyst.^a

Entry	R	R ¹	Product	Yield ^b	m.p (°C)	Lit. m.p (°C)
1	H	C ₆ H ₅	4a	92	237-238	238-240 ²⁸
2	3-NO ₂	C ₆ H ₅	4b	96	241-242	242-243 ²⁸
3	4-NO ₂	C ₆ H ₅	4c	93	227-228	228-229 ²⁸
4	3-F	C ₆ H ₅	4d	89	218-219	217-218 ³²
5	4-F	C ₆ H ₅	4e	90	232-233	233-234 ³²
6	4-OCH ₃	C ₆ H ₅	4f	79	204-206	206-208 ²⁸
7	2-OCH ₃	C ₆ H ₅	4g	80	265-267	266-267 ²⁸
8	H	CH ₃	4h	84	243-245	245-246 ¹³
9	3-NO ₂	CH ₃	4i	91	240-241	241-242 ¹³
10	4-NO ₂	CH ₃	4j	88	243-245	248-250 ¹³
11	3-F	CH ₃	4k	82	248-249	248-249 ¹³
12	4-F	CH ₃	4l	83	230-231	230-232 ¹³
13	4-OCH ₃	CH ₃	4m	71	183-185	183-185 ¹³
14	2-OCH ₃	CH ₃	4n	73	241-242	241-242 ²⁸

^aReaction conditions: β-naphthol (1mmol), aldehyde (1mmol), amide (1.2mmol), catalyst (5 wt% of aldehyde), temperature (100 °C), reaction time (30 min). ^bIsolated yields.

4. CONCLUSION

In conclusion, we have developed a very simple, convenient and highly efficient method for the synthesis of 1-amidoalkyl-2-naphthols by one-pot three-component condensation of β-naphthol, various aryl aldehydes and acetamide or benzamide using green recyclable SO₃H-carbon catalyst derived from glycerol under solvent free conditions. The promising points for the presented methodology are high efficiency, atom-efficient, excellent yields, short reaction time, solvent free conditions, cleaner reaction profile and simplicity which make this procedure as a potential alternative to the existing methods for the synthesis of 1-amidoalkyl-2-naphthols as biologically interesting compounds.

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