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2-Hydroxy-5-sulfobenzoic acid: an efficient organocatalyst for the three-component synthesis of 1-amidoalkyl-2-naphthols and 3,4-disubstituted isoxazol-5(4*H*)-ones

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Abstract 2-Hydroxy-5-sulfobenzoic acid (2-HSBA) efficiently catalyzed the one-pot three-component synthesis of a wide variety of 1-amidoalkyl-2-naphthols and 3,4-disubstituted isoxazol-5(4*H*)-ones. The three-component process of substituted benzaldehydes, 2-naphthol, and amides (benzamide and acetamide) or urea occur using 10 mol% of 2-HSBA as an organocatalyst under solvent-free reaction conditions (SFRCs) at 100 °C. It was also found that the best results for the preparation of 3,4-disubstituted isoxazol-5(4*H*)-ones were achieved using 15 mol% of 2-HSBA under aqueous conditions at room temperature. The reactions are easy to do and were completed within 3–25 min (for amidoalkyl naphthols), and 70–120 min (for 3,4-disubstituted isoxazol-5(4*H*)-ones), while the expected products were obtained in 82–97 % yields. The catalyst can be recovered and reused several times in the template reactions. This procedure offers the advantages of convenience, simple operational procedure, cost-effectiveness, no use of hazardous organic solvents, and the commercial availability of the catalyst.

Keywords 2-Hydroxy-5-sulfobenzoic acid · 1-Amidoalkyl-2-naphthols · Three-component reaction · Water · 3,4-disubstituted isoxazol-5(4*H*)-ones · Solvent-free

Introduction

The one-pot multicomponent reaction (MCR) states that a process implemented from three or more various substrates in a single vessel reaction. This attractive approach is very successful in the preparation of various chemical libraries of eye-catching organic compounds [1]. A one-pot three-component reaction (3CR) in the organic synthetic chemistry that generates 1-aminoalkyl-2-naphthols via a MCR is

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called the Betti 3-component reaction (Betti-3CR). Betti-3CR, a very well-known process, was introduced by Italian chemist Mario Betti in 1900 [2]. The Betti-3CR represents an expedient protocol to achieve amidoalkyl naphthols, which are also considered as the Betti base analogous (Fig. 1). Betti bases and related molecules have attracted a lot of attention due to their applications in asymmetric synthesis [1], catalytic organic transformations (for example, Mizoroki–Heck and Ullmann coupling reactions) [3], and chiral shift reagents for carboxylic acids or chiral auxiliaries for the synthesis of α-aminophosphonic acids [4].

1-Amidoalkyl-2-naphthols are very important precursors for the preparation of significant bioactive 1-aminomalkyl-2-naphthols via amide hydrolysis, which exhibit depressor, hypotensive and bradycardia effects in humans [5]. Amidoalkyl naphthols can be used in pharmaceutical chemistry as anti-inflammatory, anthelmintic, antibacterial, and antiviral agents [6, 7]. On the other hand, 1-amidoalkyl-2-naphthols and their *N*-substituted derivatives can be also transformed to 1,3-oxazine-containing compounds as an special class of bioactive heterocycles that present in many biologically important natural products and drug candidates [8–10], which possess many biological activities such as antibiotic [11], antihypertensive [12], analgesic [13], antimalarial [14], antitumor [15], antrheumatic [16], antianginal [17], and anticonvulsant [18]. Consequently, the synthesis of derivatives of the amidoalkyl naphthols is of much current importance for the research groups working in the organic synthesis and medicinal chemistry fields. Numerous approaches have been reported for the synthesis of these compounds. In these methods Lewis or Brönsted acids [19], nanomaterials [20–25], and carbohydrates [26] have been applied to catalyze this transformation.

Metal-free organocatalytic multicomponent reactions (OMCRs) are one of the effective green catalytic synthetic protocols for the synthesis of 1-amidoalkyl-2-naphthols. Recently, newer metal-free organocatalytic versions, including sulfanilic acid [27], pyridinium-based ionic liquid [28], cellulose-SO_3H [29], 1-methyl-3-(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride [30], poly(4-vinylpyridinium butane sulfonic acid) hydrogen sulfate [31], sulfamic acid [32], polyethylene glycol (PEG)-based dicationic acidic ionic liquid (PEG_{1000}-DAIL) [33], polymer-supported sulfonic acid NKC-9 [34], 1,3-disulfonic acid imidazolium hydrogen sulfate{[Dsim]HSO_4} [35], *N*-(4-sulfonic acid)butyl triethylammonium hydrogen sulfate ([TEBSA][HSO_4]) [36], heteropolyanion-based SO_3H [37, 38], saccharin sulfonic acid [39], dodecylphosphonic acid [40], 2-methylpyridinium trifluoromethanesulfonate ([2-MPyH]OTf) [41], 2,4,6-trichloro-1,3,5-triazine (TCT) [42], melamine-Br_3 [43], succinic acid [44], *N*-bromophthalimide (NBPI) [45], and 1,3-dibromo-5,5-dimethylhydantoin (DBH) [46] have been reported toward the synthesis of amidoalkyl naphthols. Despite these procedures, newer methodologies for the synthesis of amidoalkyl naphthol derivatives are still in demand.

The isoxazol nucleus, on the other hand, is a key five-membered cyclic oxime ester, bearing one oxygen and one nitrogen atoms at adjacent positions, making an attractive target in bioorganic, synthetic organic chemistry, and the pharmaceutical industry, as well as also being building blocks in organic synthetic chemistry [47–49]. Isoxazol-containing heterocycles exhibit a number of applications in the wide variety of fields including merocyanine dyes [50, 51] and liquid crystalline materials

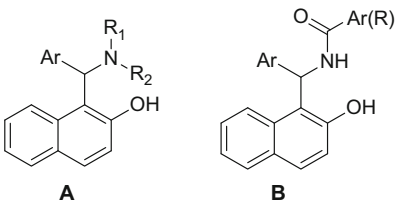


Fig. 1 General structure of Betti bases (**A**), and amidoalkyl naphthols (**B**)

[52]. In addition, many compounds containing the isoxazol ring moiety are commonly found to be associated with diverse biological activities [53–59], such as antimicrobial, fungicidal, anticonvulsant, HDAC inhibitory, protein-tyrosine phosphatase 1B (PTP1B) inhibitory, analgesic, antioxidant, anti-apoptotic, anti-obesity, COX-2 inhibitory, nematicidal, anti-nociceptive, anti-inflammatory, antiviral, antitubercular, herbicidal, inhibitor of protein kinase C (PKC), and antineoplastic, as well as being known to possess anti-mycobacterial effects. Furthermore, the isoxazol core is also a structural component of many drugs, for example, as inhibitor of tumor necrosis factor-alpha (TNF-α) [60], sulfisoxazoles [61], and antibiotics [62, 63], and has been used as an anti-androgen agent [64, 65]. Isoxazol-5(4*H*)-ones are powerful proarmoatic acceptors and can also be used for the development of optical storage, nonlinear optical research [50, 51], light-conversion molecular devices [66], and filter dyes in photographic films [67]. A number of interesting compounds with isoxazol nucleus are shown in Fig. 2.

During recent years, 3,4-disubstituted isoxazol-5(4*H*)-ones have been prepared by using catalytic amounts of sodium benzoate [68], sodium sulfide [69], sodium silicate [70], DABCO [71], nano-Fe_2O_3, clinoptilolite and $H_3PW_{12}O_{40}$ [72]. The 3CR of β-oxoesters, hydroxylamine hydrochloride, and aryl aldehydes using different conditions and techniques, such as sodium acetate and visible light [73], pyridine under ultrasonic irradiation [74, 75], pyridine under reflux [76, 77], and catalyst-free/grinding or heating [78], also provides isoxazol-5(4*H*)-ones. Also, we synthesized the same arylmethylene isoxazol-5(4*H*)-ones by using catalysts including sodium ascorbate [78], sodium citrate [80], sodium saccharin [81], sodium tetraborate [82], sodium azide [83], boric acid [84], and potassium phthalimide (PPI) [85].

It is well understood that organocatalysts are simple organic molecules able to promote a wide range of chemical transformations via various activation modes and the mildness of the reaction conditions required. They also typically have prominent characteristics including metal-free environment, relatively low toxicity, simple functionality, air stability, low-cost, and biological friendliness [86–89]. Moreover, the elimination of solvents, particularly toxic solvents in chemical processes, is one of the most important aspects of green chemistry, and there has been much attention in the implementation of organic reactions under SFRCs. The solvent-free procedures often exhibit significant rate enhancements due to increased reactant concentrations. High efficiency, mild conditions, clean, cost-effectiveness, handling, and economical friendliness are the other striking features of the reactions in

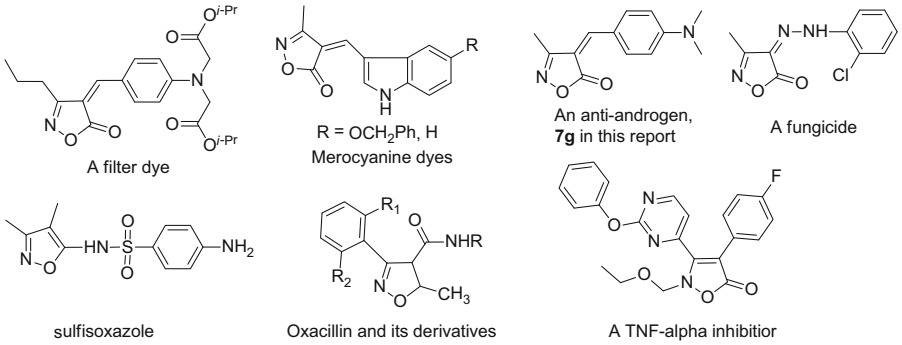


Fig. 2 Interesting isoxazol-containing compounds

solvent-less conditions [90, 91]. Growing interest in the conducting organic transformations in SF presents an interesting field for this avenue of chemistry.

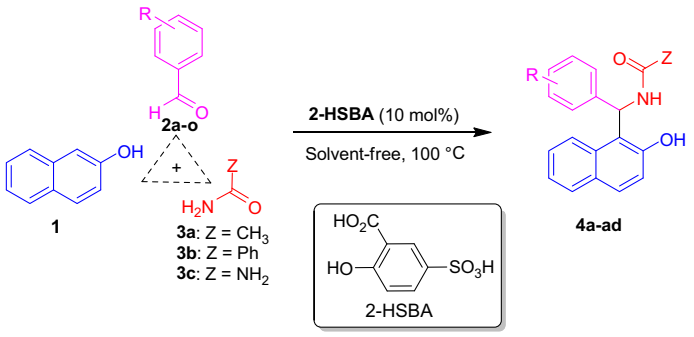
Water has a special place as the most attractive solvent in the synthetic chemistry. Also, the use of water as the solvent not only decreases the risk of the organic solvents but also increases the rate of chemical reactions. Also, MCR in water can be visualized as a well-designed synthetic method to attain a wide range of diverse molecular frameworks [92–95].

2-Hydroxy-5-sulfobenzoic acid (2-HSBA, 5-sulfosalicylic acid, SSA) was employed as the fixation agent in the blood proteins [96], measuring urine protein [97], evaluating the photo-reactivity of photo-catalysts [98], controlling the morphology of nanocrystals [99], an extraction agent for vitamin B_6 in food [100], ligands for the formation of 3D coordination polymers with metal ions [101], the dopant in polymerization [102], as an analytical reagent for iron [103] and beryllium [104], and is effective in inducing tolerance to heat, drought and chilling stress in plants [105]. This acid is also used as a catalyst in the preparation of dihydropyrimidine-2(1*H*)-ones under microwave irradiation [106] and bis(indolyl)methanes in methanol [107]. In this study, a simple one-vessel 3CR condensation has been applied to the synthesis of a number of 1-amidoalkyl-2-naphthols (**4a**–**4ad**) and 3,4-disubstituted isoxazol-5(4*H*)-ones (**7a**–**s**) in the presence of 2-HSBA as the catalyst under solvent-free and aqueous conditions, respectively (Schemes 1, 2).

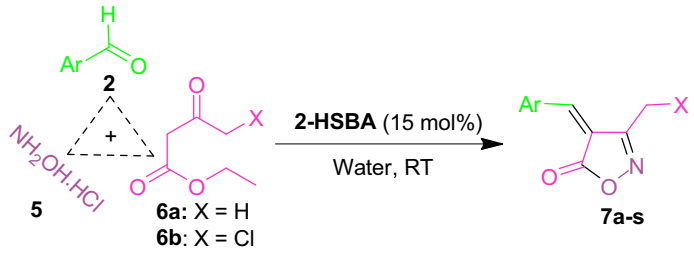
Experimental

General

All chemicals were purchased from Alfa Aesar and Aldrich and were used without further purification, with the exception of 4-methylbenzaldehyde, 4-methoxylbenzaldehyde, benzaldehyde, thiophene-2-carbaldehyde, and thiophene-3-carbaldehyde which were distilled before use. All solvents were distilled before use. The products



Scheme 1 One-pot 3C synthesis of 1-amidoalkyl-2-naphtols (**4a**–**ad**) catalyzed by 2-HSBA



Scheme 2 One-pot 3C synthesis of 3,4-disubstituted isoxazol-5(4*H*)-ones (**7a**–**s**) catalyzed by 2-HSBA

were characterized by comparison of their physical data with those of known samples or by their spectral data. Melting points were measured on a Buchi 510 melting point apparatus and are uncorrected. NMR spectra were recorded at ambient temperature on a BRUKER AVANCE DRX-400 MHz using $CDCl_3$ or DMSO-d_6 as the solvent. FT-IR spectra were recorded on a Perkin-Elmer RXI spectrometer. The development of reactions was monitored by thin layer chromatography (TLC) analysis on Merck pre-coated silica gel 60 F_{254} aluminum sheets, visualized by UV light.

Typical procedure for the preparation of 1-amidoalkyl-2-naphthols (**4a-ad**)

A mixture of 2-naphthol **1** (1 mmol), substituted aldehyde **2** (1 mmol), amide **3** (benzamide or acetamide, 1 mmol) or urea and 2-HSBA (10 mol%) was stirred at 100 °C in an oil bath for 3–30 min. After completion of the reaction (using TLC analysis), the reaction mixture was allowed to cool to room temperature. Next, hot ethyl acetate was added to the resulting mixture and then cooled to RT. The resulting solid product was filtered off, washed with distilled water, and dried to afford the targeted compounds. If further purification was needed, 1-amidoalkyl-2-naphthols can be recrystallized from hot ethanol. The HSBA is soluble in water and ethanol. The catalyst was recovered by evaporation of solvent from the filtrate,

washed with the small amount of ethyl acetate, dried, and then used for the subsequent reaction. Spectral data for **4c** and **4p** were as follows:

*N-((2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl)acetamide (**4c**)*

^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 10.14$ (s, 1H), 8.62 (d, $J = 8.0$ Hz, 1H), 8.02–7.99 (m, 2H), 7.84 (br, 1H), 7.78 (t, $J = 8.6$ Hz, 2H), 7.59–7.51 (m, 2H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.26 (t, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 8.7$ Hz, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 170.3$, 153.9, 148.2, 145.9, 133.4, 132.7, 130.5, 130.1, 129.2, 128.9, 127.3, 123.2, 123.1, 121.8, 120.9, 118.9, 118.3, 48.2, 23.1.

*N-((2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl)benzamide (**4p**)*

^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 10.42$ (s, 1H), 9.15 (d, $J = 8.0$ Hz, 1H), 8.11–8.09 (m, 3H), 7.91–7.84 (m, 4H), 7.72 (d, $J = 7.5$ Hz, 1H), 7.60–7.49 (m, 5H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): $\delta = 166.8$, 153.9, 148.2, 145.1, 134.4, 133.7, 132.8, 132.1, 130.5, 130.3, 129.3, 128.9, 128.8, 127.9, 127.6, 123.4, 122.9, 122.2, 121.3, 119.2, 117.3, 49.5.

Typical procedure for the synthesis of 3,4-disubstituted isoxazol-5(4*H*)-ones (**7a**-**s**)

A mixture of hydroxylamine hydrochloride **5** (0.0695 g, 1 mmol), β-oxoeser **6** (1 mmol), and 2-HSBA (15 mol%) in 4 mL of distilled water was stirred at room temperature for 15 min, then aromatic aldehyde **2** (1 mmol) was added to the mixture. The reaction mixture was stirred at RT until the reaction was completed. The reaction was monitored by TLC analysis up to the starting materials were consumed completely and the final product spot was not changed. After completion of the reaction, the precipitate was separated by simple filtration, and washed with cold distilled water and dried in the air. Crude products were recrystallized from ethanol (95 %) to afford the title pure compounds. The HSBA is soluble in water and ethanol. After removal of the solvent from the filtrate by evaporation, the catalyst is recovered and reused for the subsequent reactions. The identity of the known products was confirmed by comparison of their spectroscopic data and physical properties with those available in recent papers [68–85]. Spectral data for **7i** and **7q** were as follows:

*N-(4-((3-methyl-5-oxoisoxazol-4(5H)-ylidene)methyl)phenyl)acetamide (**7i**)*

^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 10.51$ (s, 1H), 8.47 (d, $J = 9.2$ Hz, 2H), 7.85 (s, 1H), 7.78 (d, $J = 8.8$ Hz, 2H), 2.28 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 170.1$, 162.9, 151.5, 145.2, 136.2, 127.4, 118.8, 116.5, 24.8, 11.8.

*3-(chloromethyl)-4-(4-(diethylamino)-2-hydroxybenzylidene)isoxazol-5(4H)-one (**7q**)*

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.08 (s, 1H), 9.14 (d, J = 9.6 Hz, 1H), 8.07 (s, 1H), 6.52 (dd, J = 2.0, 9.6 Hz, 1H), 6.18 (d, J = 2.4 Hz, 1H), 3.50 (q, J = 6.8, 7.2 Hz, 4H), 1.17 (t, J = 6.8, 7.2 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.9, 164.2, 162.2, 156.4, 143.1, 136.1, 111.9, 106.9, 101.2, 95.8, 45.2, 36.4, 13.1.

Results and discussion

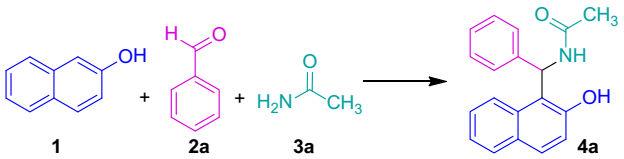
At a first step, in order to find the best optimal reaction conditions, three-component condensation of 2-naphthol (**1a**), benzaldehyde (**2a**) and acetamide (**3a**) was employed as the template reaction. Different amounts of 2-HSBA as the catalyst as well as reaction temperature were screened using the template reaction under solvent-free reaction conditions (SFRCs). The results are shown in Table 1. By carrying out the template reaction at 100 °C without a catalyst, no product was formed even after heating for 2 h (entry 1). When 5 mol% loading of catalyst was applied for this condensation, it was observed that the corresponding product **4a** was formed in 82 % yield (entry 2). The product formation in the presence of the catalyst upon heating indicates that the presence of a catalyst for this reaction is necessary. In addition, when catalyst loading was increased to 10 mol%; the reaction was completed within 8 min and up to 95 % yield of the desired product **4a** was obtained (entry 3). The use of higher amounts of catalyst did not improve the results (entries 4 and 5). Hence, this amount of catalyst is sufficient to promote the reaction. The effect of temperature on the synthesis of **4a** was also investigated in the presence of 10 mol% 2-HSBA loading (entries 6 and 10). It was found that the best results were obtained at 100 °C. At temperatures lower than 100 °C, the yield of the product sharply decreased even with longer reaction times (entries 6 and 8). The increase in temperature leads to a decrease in the yield of the product (entries 9 and 10). 2-HSBA shows excellent catalytic activity toward this Betti-3CR. It was concluded that implementating the reaction under SFRCs at 100 °C is the optimal condition for the Betti-3CR in the presence of 10 mol% of the catalyst.

Screening of other acidic reagents such as polyphosphoric acid, cinnamic acid, terephthalic acid, isophthalic acid, ascorbic acid, and methanesulfonic acid, was also tested (Table 2). Only trace products were detected in the presence of polyphosphoric acid, cinnamic acid, and terephthalic acid (entries 1–3). In the other cases, the yield and reaction times were not satisfactory compared with the PISA (entries 4–6).

To check the effect of solvent on the yield of the product, the template reaction was also carried out in various solvents (Table 3). Markedly low yields were observed when EtOH, H_2O, CH_2Cl_2, EtOAc, or CH_3CN were utilized as the reaction media (entries 1–5).

To study the applicability of the method, the 3CR of 2-naphthol (**1**) with amides and a series of structurally diverse substituted benzaldehydes (**2a–o**) were

Table 1 Effect of the amounts of the catalyst and reaction temperature on the synthesis of *N*-((2-hydroxynaphthalen-1-yl)(phenyl)methyl)acetamide (**4a**) as a template in the SFRC



Entry	Catalyst (mol%)	Temp. (°C)	Time (min)[a]	Yield (%)[b]
1	–	100	120	–
2	5	100	20	82
3[c]	**10**	**100**	**8**	**95**
4	15	100	8	90
5	20	100	5	90
6	10	50	25	60
7	10	80	20	84
8	10	90	15	90
9	10	110	8	92
10	10	120	8	92

Reaction conditions: a well-ground mixture of 1-naphthol **1** (1 mmol), benzaldehyde **2a** (1 mmol), acetamide **3a** (1 mmol), and the catalyst (2-HSBA) was magnetically stirred

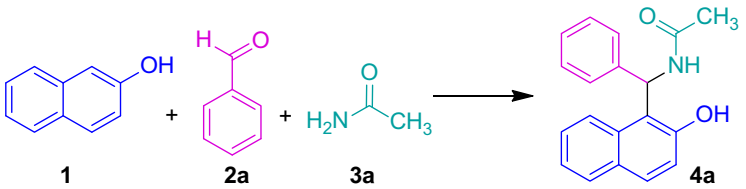
[a] Progress of the reaction was monitored with TLC analysis

[b] Isolated yields

[c] Optimized conditions shown in bold

conducted under the optimal reaction conditions. Representative results are listed in Table 4. The reaction of benzaldehyde substituted with the electron-withdrawing group occurred at a higher yield and shorter reaction time than its electron-donating counterpart. Sterically hindered aryl aldehydes (entries 4, 6, 8, 12, 17, 19 and 20), such as 2-nitrobenzaldehyde (**2d**), 2-chlorobenzaldehyde (**2f**), 2,4-dichlorobanzaldehyde (**2h**) and 2,5-dimethoxybenzaldehyde (**2l**), also reacted with 2-naphthol (**1**) and amides (**3a**, **b**) to give the corresponding 1-amidoalkyl-2-naphthols in excellent yields, although in some cases the reactions proceeded rather slowly. The use of urea (**3c**) in the synthesis of the title compounds also gave similar results (entries 26–30). The reaction of 2-naphthol (**1**) and acetamide (**3a**) was also performed under the same optimal reaction conditions in the presence of an aliphatic aldehyde, *n*-butyraldehyde; however, no corresponding amidoalkyl naphthol product was observed after 20 h. In addition, a reaction of 2-naphthol (**1**) and acetamide (**3a**) with α,β-unsaturated aldehydes (α-methylcinnamaldehyde and cinnamaldehyde) was implemented and did not lead to product formation after 20 h. On the other hand, the reaction of 2-naphthol (**1**) and acetamide (**3a**) with hetero-aromatic aldehydes such as furan-2-carbaldehyde and thiophene-2-carbaldehyde led to corresponding products with 60 and 70 % yields, respectively. This approach was highly operative for the preparation of targeted compounds (**4a**–**ad**) as well as, in all

Table 2 The synthesis of *N*-((2-hydroxynaphthalen-1-yl)(phenyl)methyl)acetamide (**4a**) using various catalysts



1 **2a** **3a** **4a**

Entry	Catalyst (mol%)	Time (min)[a]	Yield (%)[b]
1	PPA[c] (10, 15, 20)	120	Trace
2	Cinnamic acid (10, 15, 20)	120	Trace
3	Terephthalic acid (10, 15, 20)	120	Trace
4	Isophthalic acid (15)	27	75
5	Ascorbic acid (20)	60	50
6	Methanesulfonic acid (15)	30	80

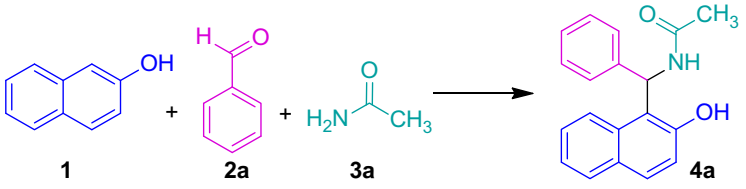
Reaction conditions: a well-ground mixture of 1-naphthol **1** (1 mmol), benzaldehyde **2a** (1 mmol), acetamide **3a** (1 mmol), and the catalyst was magnetically stirred at 100 °C

[a] Progress of the reaction was monitored with TLC analysis

[b] Isolated yields

[c] Polyphosphoric acid

Table 3 The synthesis of *N*-((2-hydroxynaphthalen-1-yl)(phenyl)methyl)acetamide (**4a**) using various solvents



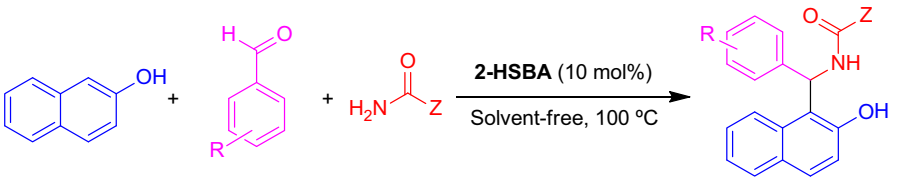
1 **2a** **3a** **4a**

Entry	Solvent	Time (min)[a]	Isolated yield (%)
1	EtOH	60	50
2	H_2O	60	48
3	CH_2Cl_2	60	30
4	EtOAc	60	40
5	CH_3CN	60	55
6	–	8	95

Reaction conditions: a well-ground mixture of 1-naphthol **1** (1 mmol), benzaldehyde **2a** (1 mmol), acetamide **3a** (1 mmol), and 2-HSBA (10 mol%) was magnetically stirred at 100 °C

[a] Progress of the reaction was monitored with TLC analysis

Table 4 The 3C synthesis of 1-amidoalkyl-2-naphthols (**4a–ad**) catalyzed by 2-HSBA under SFRCs at 100 °C

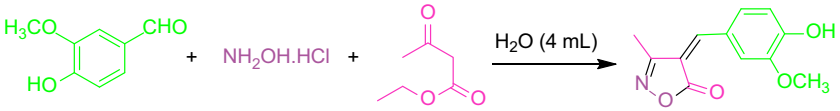


1 (1 mmol) **2a-o** (1 mmol) **3a-c** (1 mmol) **4a-ad**

Entry	*R*	*Z*	Product	Time (min)	Yield (%)[a]	Mp (°C)	
						Observed	Reported [ref.]
1	H (**2a**)	CH_3 (**3a**)	**4a**	8	95	241–244	228–230 [41]
2	4-NO_2 (**2b**)	CH_3 (**3a**)	**4b**	5	93	239–242	236–238 [41]
3	3-NO_2 (**2c**)	CH_3 (**3a**)	**4c**	10	90	265–269	241–243 [41]
4	2-NO_2 (**2d**)	CH_3 (**3a**)	**4d**	7	91	180–182	181–183 [41]
5	4-Cl (**2e**)	CH_3 (**3a**)	**4e**	5	91	236–239	236–238 [41]
6	2-Cl (**2f**)	CH_3 (**3a**)	**4f**	15	92	210–211	195–197 [41]
7	4-F (**2g**)	CH_3 (**3a**)	**4g**	20	90	230–232	232–233 [42]
8	2,4-$(Cl)_2$ (**2h**)	CH_3 (**3a**)	**4h**	4	93	230–231	225–226 [41]
9	4-CH_3 (**2i**)	CH_3 (**3a**)	**4i**	15	88	219–221	220–222 [42]
10	4-OCH_3 (**2j**)	CH_3 (**3a**)	**4j**	20	87	184–185	164–168 [41]
11	3-OCH_3 (**2k**)	CH_3 (**3a**)	**4k**	15	80	204–205	203–205 [41]
12	3,5-$(OCH_3)_2$ (**2l**)	CH_3 (**3a**)	**4l**	25	88	253–257	252–254 [41]
13	4-OH (**2m**)	CH_3 (**3a**)	**4m**	30	85	218–219	226–227 [10]
14	H (**2a**)	Ph (**3b**)	**4n**	6	97	230–231	237–239 [19]
15	4-NO_2 (**2b**)	Ph (**3b**)	**4o**	3	96	237–238	238–240 [26]
16	3-NO_2 (**2c**)	Ph (**3b**)	**4p**	5	95	233–235	234–236 [26]
17	2-NO_2 (**2d**)	Ph (**3b**)	**4q**	4	95	266–269	262–264 [26]
18	4-Cl (**2e**)	Ph (**3b**)	**4r**	3	93	183–184	186–188 [26]
19	2-Cl (**2f**)	Ph (**3b**)	**4s**	5	92	266–268	264–266 [26]
20	2,4-$(Cl)_2$ (**2h**)	Ph (**3b**)	**4t**	2	97	240–242	235–236 [30]
21	4-CH_3 (**2i**)	Ph (**3b**)	**4u**	10	90	200–202	202 [25]
22	4-OCH_3 (**2j**)	Ph (**3b**)	**4v**	10	85	208–210	208–210 [26]
23	3-OCH_3 (**2k**)	Ph (**3b**)	**4w**	8	81	210–214	232 [25]
24	3-OCH_3-4-OH (**2n**)	Ph (**3b**)	**4x**	30	90	219–221	223–225 [108]
25	4-$N(CH_3)_2$ (**2o**)	Ph (**3b**)	**4y**	30	82	218–224	221 [25]
26	H (**2a**)	NH_2 (**3c**)	**4z**	10	95	178–182	176–178 [26]
27	4-NO_2 (**2b**)	NH_2 (**3c**)	**4aa**	7	96	190–193	192–194 [26]
28	3-NO_2 (**2c**)	NH_2 (**3c**)	**4ab**	8	95	190–192	192–194 [26]
29	4-Cl (**2e**)	NH_2 (**3c**)	**4ac**	5	90	168–170	166–168 [26]
30	4-CH_3 (**2i**)	NH_2 (**3c**)	**4ad**	20	91	115–117	118–120 [42]

[a] Isolated yields

Table 5 Effect of the amounts of the catalyst and reaction temperature on the synthesis of 4-(4-hydroxy-3-methoxybenzylidene)-3-methylisoxazol-5(4*H*)-one (**7h**) as a template in the water



2n (1 mmol) **5** (1 mmol) **6a** (1 mmol) **7h**

Entry	Catalyst (mol%)	Temp. (°C)	Time (min)[a]	Yield (%)[b]
1	–	RT	120	55
2	2.5	RT	120	72
3	5	RT	120	80
4	10	RT	90	90
5[c]	**15**	**RT**	**70**	**96**
6	20	RT	70	95
7	15	50	70	50
8	15	75	70	40
9	15	100	70	35
10	15	120	70	5

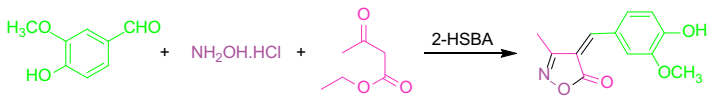
Reaction conditions: vanillin **2n** (1 mmol), hydroxylamine hydrochloride **5** (1 mmol), ethyl acetoacetate **6a** (1 mmol), solvent (4 mL) and the 2-HSBA was magnetically stirred at room temperature

[a] Progress of the reaction was monitored with TLC analysis

[b] Isolated yields

[c] Optimized conditions shown in bold

Table 6 The synthesis of 4-(4-hydroxy-3-methoxybenzylidene)-3-methylisoxazol-5(4*H*)-one (**7h**) using various solvents



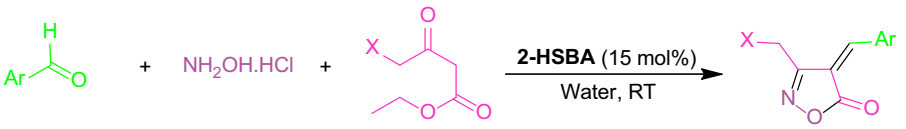
2n **5** **6a** **7h**

Entry	Solvent	Time (min)[a]	Isolated yield (%)
1	EtOH	120	67
2	Acetone	120	42
3	1,4-Dioxane	180	50
4	*n*-Hexane	120	54
5	CH_2Cl_2	120	61
6	EtOH:H_2O (1:1)	100	73
7	No solvent	120	30

Reaction conditions: vanillin **2n** (1 mmol), hydroxylamine hydrochloride **5** (1 mmol), ethyl acetoacetate **6a** (1 mmol), solvent (4 mL), and 2-HSBA (15 mol%) was magnetically stirred at room temperature

[a] Progress of the reaction was monitored with TLC analysis

Table 7 The 3C synthesis of 3,4-disubstituted isoxazol-5(4*H*)-ones (**7a-s**) catalyzed by 2-HSBA under aqueous media at room temperature



2 (1 mmol) **5** (1 mmol) **6a-b** (1 mmol) **7a-s**

Entry	*Ar*	*X*	Product	Time (min)	Yield (%)[a]	Mp (°C)	
						Observed	Reported[b]
1	C_6H_5 (**2a**)	H (**6a**)	**7a**	110	87	141–142	140–142
2	4-$CH_3C_6H_4$ (**2i**)	H (**6a**)	**7b**	75	95	135–136	135–136
3	4-$OCH_3C_6H_4$ (**2j**)	H (**6a**)	**7c**	80	92	174–175	175–177
4	4-OHC_6H_4 (**2m**)	H (**6a**)	**7d**	70	95	211–213	210–211
5	3-OHC_6H_4 (**2p**)	H (**6a**)	**7e**	85	90	200–201	199–201
6	2-OHC_6H_4 (**2q**)	H (**6a**)	**7f**	120	88	198–199	198–200
7	4-$N(CH_3)_2C_6H_4$ (**2o**)	H (**6a**)	**7g**	85	93	225–227	220–221
8	3-OCH_3-4-OHC_6H_3 (**2n**)	H (**6a**)	**7h**	70	96	216–217	213–215
9	4-NH-$COCH_3C_6H_4$ (**2r**)	H (**6a**)	**7i**	75	90	188–191	New
10	2-Thienyl (**2s**)	H (**6a**)	**7j**	50	94	144–146	143–145
11	3-Thienyl (**2t**)	H (**6a**)	**7k**	60	88	145–146	142–144
12	C_6H_5 (**2a**)	Cl (**6b**)	**7l**	110	85	183–184	182–183
13	4-$OCH_3C_6H_4$ (**2j**)	Cl (**6b**)	**7m**	75	92	130–133	175–177
14	4-OHC_6H_4 (**2m**)	Cl (**6b**)	**7n**	65	92	182–185	183–186
15	4-$N(CH_3)_2C_6H_4$ (**2o**)	Cl (**6b**)	**7o**	70	89	179–181	179–180
16	3-OCH_3-4-OHC_6H_3 (**2n**)	Cl (**6b**)	**7p**	75	92	141–143	142–145
17	2-OH-4-$N(Et)_2C_6H_3$ (**2u**)	Cl (**6b**)	**7q**	80	90	203–207	New
18	2-Thienyl (**2s**)	Cl (**6b**)	**7r**	70	89	147–148	146–148
19	C_6H_5CH=CH (**2v**)	H (**6a**)	**7s**	85	93	174–176	173–178

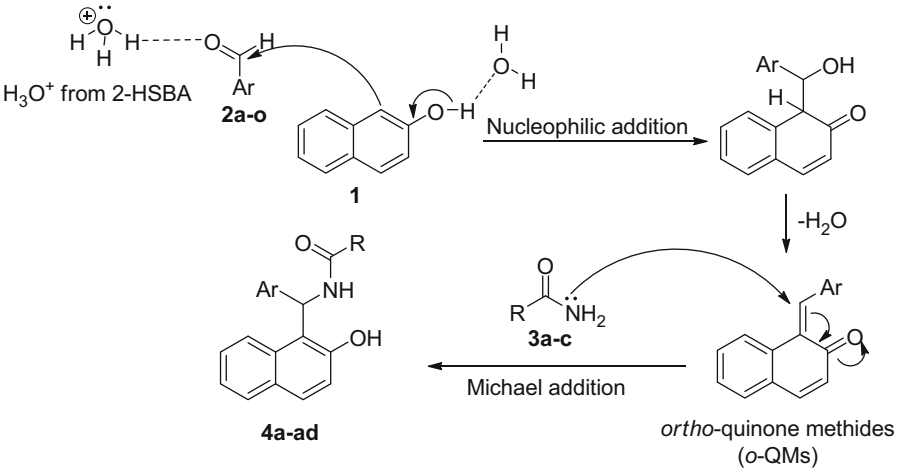
[a] Isolated yields

[b] Melting points are listed in Refs. [77–85]

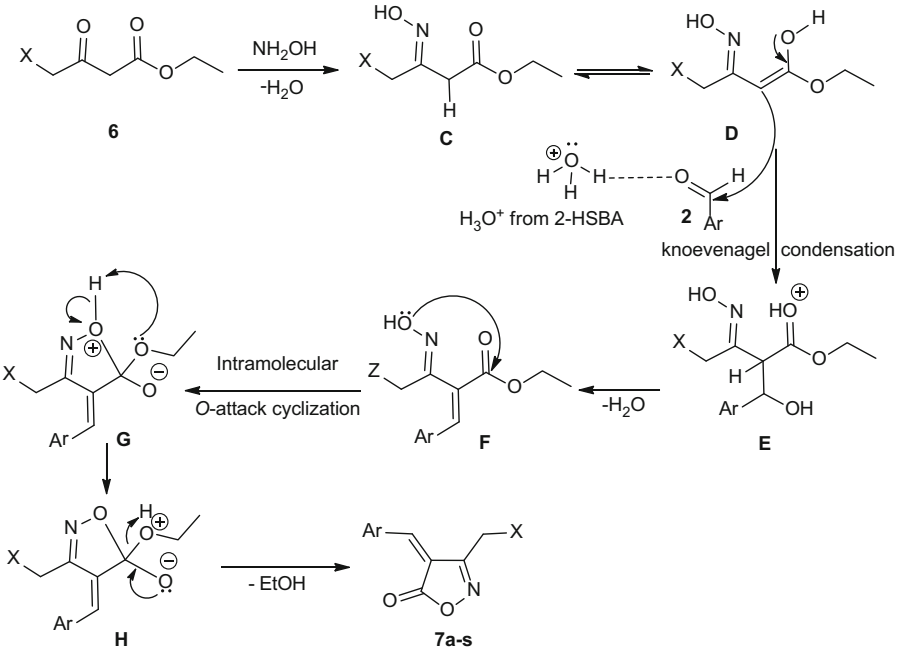
cases, 1-amidoalkyl-2-naphthols were the sole products and no by-products were observed.

After the successful synthesis of a series of 1-amidoalkyl-2-naphthols, we turned our attention toward the synthesis of 3,4-disubstituted isoxazol-5(4*H*)-ones in the presence of 2-HSBA (Scheme 2).

Treatment of **2n** with hydroxylamine hydrochloride (**5**), ethyl acetoacetate (**6a**), and 10 mol% of 2-HSBA at room temperature in H_2O led to the 4-(4-hydroxy-3-methoxybenzylidene)-3-methylisoxazol-5(4*H*)-one (**7h**) in 90 % yield for 90 min (Table 5, entry 4). This reaction was selected as a template reaction and the results are summarized in Tables 5 and 6. When 15 mol% of 2-HSBA was used, the desired product was obtained in 96 % yield after 70 min. The reaction in the



Scheme 3 The proposed mechanism for the formation of 1-amidoalkyl-2-naphthols (**4a**–**ad**)



Scheme 4 The proposed mechanism for the formation of 3,4-disubstituted isoxazol-5(4*H*)-ones (**7a**-**s**)

absence of a catalyst afforded **7h** in 55 % yield at longer reaction times (Table 5, entry 1). Using lower amounts of 2-HSBA, the reaction proceed in moderate yields (Table 5, entries 2 and 3). The use of higher amounts of catalyst did not improve the yield and reaction times (Table 5, entry 6). Performing the reaction at higher

Table 8 Reusability of 2-HSBA in the synthesis of **4a**

The reaction conditions are similar to the optimized conditions described for the template reaction in Table 1

Catalyst recycle	Time (min)	Isolated yield (%)
Fresh	5	95
1	5	90
2	6	84
3	8	80
4	10	70

Table 9 Reusability of 2-HSBA in the synthesis of **7h**

The reaction conditions are similar to the optimized conditions described for the template reaction in Table 5

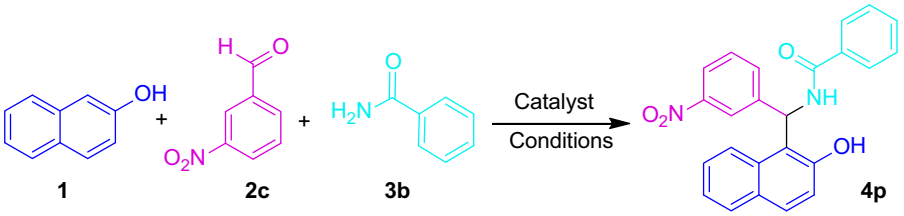
Catalyst recycle	Time (min)	Isolated yield (%)
Fresh	70	94
1	75	88
2	90	79
3	150	71

temperatures using 2-HSBA as the catalyst did not afford satisfactory results (Table 5, entries 7–10). The effect of various solvents including EtOH, acetone, 1,4-dioxane, *n*-hexane, CH_2Cl_2, and a mixture of ethanol–water (EtOH:H_2O, V:V) was also explored (Table 6). In these cases, the use of other solvents rather than water resulted in low reaction yields (entries 1–6). Under solvent-less conditions, no obvious improvement of the reaction was observed (entry 7). Therefore, water was the most effective solvent in this reaction. In terms of catalyst amounts, temperature and solvent effects, the use of 15 mol% of the catalyst, room temperature and water were selected as the optimized reaction conditions for the present reaction.

With the optimized reaction conditions in hand, the generality of this reaction then examined, as shown in Table 7. A range of aryl aldehyde derivatives with different substituents on the benzene ring were reacted with hydroxylamine hydrochloride (**5**) and β-oxoesters (**6a**, **b**) smoothly to give the corresponding 3,4-disubstituted isoxazol-5(4*H*)-ones (**7a**–**s**) in good to high yields. The reaction was clean, and no chromatographic separation was performed because no impurities were observed. These results show that aromatic aldehydes bearing electron-donating functional groups proved to be good substrates and reacted smoothly. It seems that substituents at *ortho*-position on the phenyl ring had a slight effect on the yields and reaction times (entries 6, 9 and 21). Containing 2-thienyl and 3-thienyl, heterocyclic substrates both can be converted to the desired products in 94, 88 and 89 % yields, respectively (entries 10–11, and 18). Also, a reaction of ethyl acetoacetate (**6a**) and hydroxylamine hydrochloride (**5**) with α,β-unsaturated aldehydes such as cinnamaldehyde was implemented and lead to product formation with high yield (entry 19). Not successful, attempts to conduct the reaction with the electron-withdrawing groups on the phenyl ring and aliphatic aldehydes.

The possible reaction mechanism for the green formation of 1-amidoalkyl-2-naphthol products (**4a**–**ad**) can be presented in Scheme 3. This process could

Table 10 Comparison of the catalytic performance of catalyst 2-HSBA for the one-pot 3CR of 2-naphthol (**1**), 3-nitrobenzaldehyde (**2c**), and benzamide (**3b**) with those obtained by reported catalysts



Entry	Catalyst (mol%) [g]/conditions	Time (min)	Yield (%)	References
1	[Msim]Cl (10)/SF, 120 °C	5	90	[19]
2	Maltose (20)/SF, 100 °C	18	90	[26]
3	[2-MPyH]OTf (5)/SF, 125 °C	20	96	[41]
4	Sulfanilic acid (20)/SF, MW	8	89	[27]
5	Sulfanilic acid (20)/SF, 110–120 °C	14	88	[27]
6	TCT (5)/SF, 100 °C	20	95	[42]
7	MSI (6)/ionic liquid [Bpy]BF_4, 80 °C	25	95	[30]
8	DPA (10)/SF, 90 °C	20	90	[40]
9	PEG_{1000}-DAIL (0.03 mmol)/80 °C	5	94	[33]
10	[MIMPS]$H_2PMo_{12}O_{40}$ (10)/SF, 110 °C	5	93	[37]
11	[Dsim]HSO_4 (5)/SF, 80 °C	20	97	[35]
12	PSSA-NKC-9 [0.17]/chloroform, reflux	360	88	[34]
13	2-HSBA (10)/SF, 100 °C	5	95	Present work

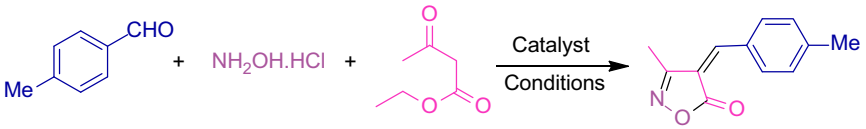
[Msim]Cl 3-methyl-1-sulfonic acid imidazolium chloride; *SF* solvent-free; *[2-MPyH]OTf* 2-methylpyridinium trifluoromethanesulfonate; *TCT* 2,4,6-trichloro-1,3,5-triazine; *MSI* 1-methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride; *[Bpy]BF_4* *N*-butylpyridinium tetrafluoroborate; *DPA* dodecylphosphonic acid; *PEG_{1000}-DAIL* PEG-based dicationic acidic ionic liquid; *[Dsim]HSO_4* 1,3-disulfonic acid imidazolium hydrogen sulfate; *PSSA-NKC-9* polymer-supported sulphonic acid NKC-9

proceeds via formation of *ortho*-quinone methides (*o*-QMs) [19, 35, 39] between 2-naphthol (**1**) and the substituted benzaldehydes (**2a–o**), assisted by catalyst. Then, the Michael addition of amides (**3a**, **b** or urea, **3c**) to the *ortho*-QMs offers the 1-amidoalkyl-2-naphthols. The acidic functional groups of 2-HSBA could provide acidic site for activating substituted benzaldehydes efficiently, so facilitating this 3-CR.

Based on the literature [68–85], the following mechanism also proposed for the 3C synthesis of 3,4-disubstituted isoxazol-5(4*H*)-ones (**7a–s**) (Scheme 4). It is reasonable to assume that oxime derivatives **C** were formed by the condensation reaction of hydroxylamine hydrochloride with β-ketoester **5**. Then the Knoevenagel adducts **F** were formed through the condensation of intermediate **C** and protonated aryl aldehyde **2**. The next step may involve intramolecular *O*-attack cyclization of **F** to cyclic derivatives **G**, which undergoes a proton exchange, followed by **H** is deethanolized to target products **7a–s**.

The reusability of the 2-HSBA was also studied (Tables 8, 9). The catalyst was recovered after each run and reused for subsequent cycles (Table 8). It showed nearly the same activity but with a slight decrease of yield. The decreasing of the yield of the

Table 11 Comparison of the catalytic performance of catalyst 2-HSBA for the one-pot 3CR of *p*-methylbenzaldehyde (**2i**), hydroxylamine hydrochloride (**5**), and ethyl acetoacetate (**6b**) with those obtained by reported catalysts



2i **5** **6a** **7b**

Entry	Catalyst (mol%)/conditions	Time (min)	Yield (%)	References
1	Sodium benzoate (10)/H_2O, RT	90	87	[68]
2	Na_2S (5)/EtOH, RT	90	88	[69]
3	Sodium silicate (5)/H_2O, RT	90	91	[70]
4	Pyridine (100)/H_2O, US	60	82	[74]
5	Pyridine (100)/EtOH, reflux	180	71.4	[77]
6	Catalyst free/grinding	48	61	[78]
7	Catalyst free/105–110 °C	15	66.3	[78]
8	Sodium ascorbate (5)/H_2O, RT	70	95	[79]
9	Sodium citrate (10)/H_2O, RT	60	91	[80]
10	Sodium saccharin (10)/H_2O, RT	50	91	[81]
11	Sodium tetraborate (10)/H_2O, RT	50	95	[82]
12	Sodium azide (5)/H_2O, RT	240	85	[83]
13	Boric acid (10)/H_2O, RT	50	92	[84]
14	PPI (10)/H_2O, RT	70	96	[85]
15	2-HSBA (15)/H_2O, RT	75	95	Present work

RT room temperature, *US* ultrasound

product is probably related to a slight decrease in the catalytic activity of the catalyst or could be attributed to the loss of catalyst recovery in the course of the reaction. In addition, Table 9 shows that the catalytic was recycled and reused three times.

The benefit of the catalyst and comparison of the efficiency of the 2-HSBA catalyst with other catalysts in the synthesis of 1-amidoalkyl-2-naphthols and 3,4-disubstituted isoxazol-5(4*H*)-ones are indicated in Tables 10 and 11. It is clear from these data that 2-HSBA is comparable to the formerly reported approaches in terms of reaction times and yields. Contrasting some of the previous reported methods, this procedure does not require any additives, ionic liquids or hazardous solvents such as chloroform in the synthesis of 1-amidoalkyl-2-naphthols. In addition, according to Table 11, there is no need for bases such as pyridine, heating or special devices such as ultrasound.

Conclusions

In summary, the present methodology is a green, simple, and environmentally benign protocol to access a series of 1-amidoalkyl-2-naphthols and 3,4-disubstituted

isoxazol-5(4*H*)-ones in high yields and shorter reaction times. The 3CR are conducted under thermal SFRCs yielding the corresponding Betti analogue compounds. It was also found that 3CR of aryl aldehydes, hydroxylamine hydrochloride, and ethyl acetoacetate (or ethyl 4-chloroacetoacetate) can be significantly performed to achieve the 3,4-disubstituted isoxazol-5(4*H*)-ones at room temperature. 2-HSBA displays excellent catalytic activity toward these 3CRs. The use of 2-HSBA in these 3CRs has benefits such as clean reaction profiles, lack of side reactions, green, minimization of waste, simple experimental procedure, recyclability of the catalyst, simplicity of operation, and easy work-up.

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