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Triethylamine-bonded sulfonic acid ([Et $_3$N-SO $_3$H]Cl): a highly efficient and homogeneous catalyst for the condensation of 2-naphthol with arylaldehydes and amides (alkyl carbamates or thioamides)

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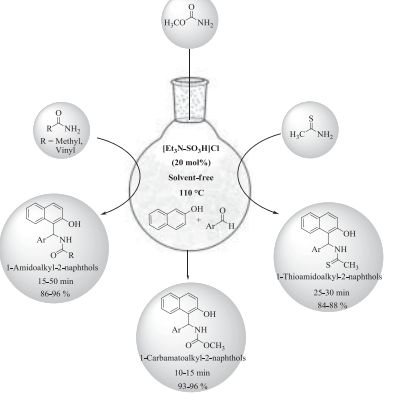
Ionic liquid triethylamine-bonded sulfonic acid ([Et_3N–SO_3H]Cl, *N*,*N*-diethyl-*N*-sulfoethanammonium chloride) is utilized as a highly efficient, inexpensive and homogeneous catalyst to promote the following one-pot multi-component organic transformations under solvent-free conditions: (i) the condensation of 2-naphthol with arylaldehydes and amides leading to 1-amidoalkyl-2-naphthols, (ii) the reaction of 2-naphthol with aromatic aldehydes and alkyl carbamates to produce 1-carbamatoalkyl-2-naphthols, and (iii) the condensation between 2-naphthol, arylaldehydes and thioamides leading to 1-thioamidoalkyl-2-naphthols. High yields, short reaction times, efficiency, generality, clean process, simple methodology, low cost, easy work-up, ease of preparation of the catalyst, and environmentally benign conditions are some advantages of the protocols.



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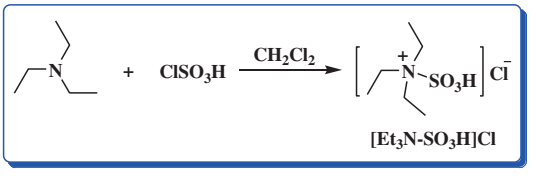
Keywords: triethylamine-bonded sulfonic acid ([Et_3N–SO_3H]Cl, *N*,*N*-diethyl-*N*-sulfoethanammonium chloride); ionic liquid; 1-amidoalkyl-2-naphthol; 1-carbamatoalkyl-2-naphthol; 1-thioamidoalkyl-2-naphthol

1. Introduction

Ionic liquids (ILs) have received much attention in the last decade from chemists, due to their broad range of potential uses (*1–18*). Moreover, they have various useful properties such as thermal and chemical stability, nonflammable, nonvolatile under atmospheric conditions, recoverable, eco-friendly nature, and wide liquid-state temperature range (*1–4*). The ability to design ILs gave us an opportunity to generate ILs of special properties tailored to given reactions (*1*, *2*). Among the different kinds, Brønsted acidic ILs have attracted rising interest in the last few years (*11–18*). These series of ILs have offered new possibilities for developing environmental friendly acid catalysts for organic transformations, because of the advantages of combining liquid and solid acids, their operational simplicity, efficacy, and selectivity coupled with their green natures (*11–18*). Considering the high importance of Brønsted acidic ILs, more recently, we have synthesized Brønsted acidic IL triethylamine-bonded sulfonic acid ([Et_3N–SO_3H]Cl, *N*,*N*-diethyl-*N*-sulfoethanammonium chloride) by the reaction of triethylamine with chlorosulfonic acid (Scheme 1) and introduced it as a highly efficient catalyst in organic synthesis (*18*). Herein, we report that this IL can efficiently catalyze the syntheses of 1-amidoalkyl-2-naphthols, 1-carbamatoalkyl-2-naphthols, and 1-thioamidoalkyl-2-naphthols. On the basis of the structure of [Et_3N–SO_3H]Cl, we anticipate that it can act as an efficient catalyst in reactions which can benefit from rate acceleration from acidic catalysts.



Scheme 1. The synthesis of [Et_3N–SO_3H]Cl.

Multi-component reactions (MCRs) involve three or more compounds reacting in a single event to form a product, which contains the essential parts of all the starting materials. MCRs are welcome too in terms of economic and practical considerations. Furthermore, they contribute to the requirements of an environmentally friendly process by reducing the number of synthetic steps, energy consumption, and waste production. Therefore, in the last decade, research in academia and industry has increasingly emphasized the use of MCRs as well as domino reaction sequences for a broad range of products (*19–25*).

1-Amidoalkyl-2-naphthols, 1-carbamatoalkyl-2-naphthols, and 1-thioamidoalkyl-2-naphthols are of importance because they can be easily converted to the important biologically active compounds, 1-aminoalkyl-2-naphthols (*26*), by hydrolysis reactions. One of the most important biologically active compounds containing a 1-aminoalkyl-2-naphthol moiety in its structure is compound **I** which has been shown to have hypotensive and bradycardic activities (Figure 1) (*26*). 1-Amidoalkyl-2-naphthol derivatives can also be converted to 1,3-oxazine derivatives (**II**) (Figure 1) (*27*). 1,3-Oxazines have potentially different biological activities including antibiotic (*28*), antitumor (*29*), analgesic (*30*), anticonvulsant (*31*), and antipsychotic (*32*) properties.

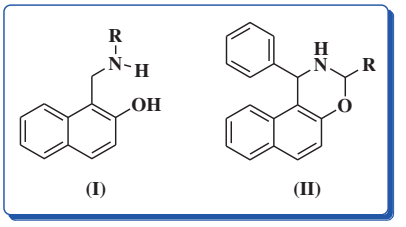
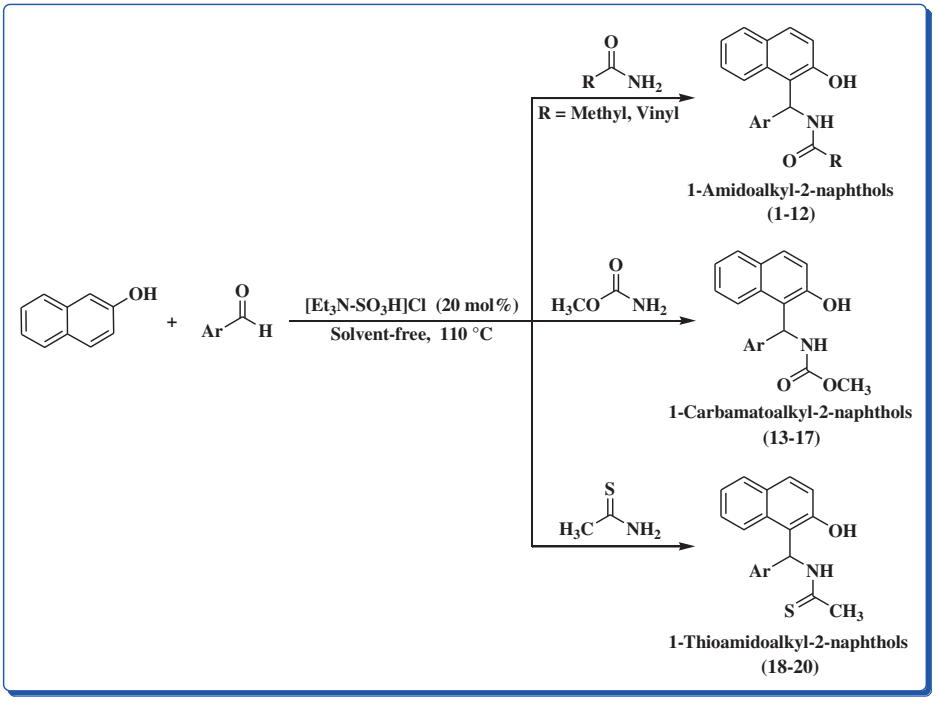


Figure 1. The general structures of the bioactive compounds related to 1-amidoalkyl-2-naphthol derivatives.

Since 1-amidoalkyl (carbamatoalkyl or thioamidoalkyl)-2-naphthol derivatives have potentially different biological activities (*26–32*), in recent years, much attention has been devoted to their synthesis. These compounds have generally been synthesized by one-pot three-component condensations of 2-naphthol with arylaldehydes and amides (alkyl carbamates or thioamides) in the presence of catalysts (*15*, *33–46*). Nevertheless, the synthesis of 1-carbamatoalkyl-2-naphthols (*42–45*), and especially 1-thioamidoalkyl-2-naphthol (*46*), has been scarcely studied in the literature. In general, although some catalysts for the synthesis of the title compounds are known, newer catalysts continue to attract attention for their novelty, generality, unique features, and effectiveness. Furthermore, most of the reported catalysts and methods for the synthesis of the title compounds suffer from one or more of the following drawbacks: the use of expensive and toxic catalysts, poor compliance with green chemistry protocols, the use of large amounts of catalyst, low product yield, prolonged reaction time, the use of an additional energy (ultrasound or microwave), and especially no generality (in most of the reported procedures, the synthesis of one type of the title compounds has been achieved).



Scheme 2. The synthesis of 1-amidoalkyl (carbamatoalkyl or thioamidoalkyl)-2-naphthols from 2-naphthol, arylaldehydes and amides, alkyl carbamates or thioamides using $[Et_3N–SO_3H]Cl$.

In this paper, we report IL $[Et_3N–SO_3H]Cl$ as a highly efficient, homogeneous, and inexpensive catalyst to promote the following one-pot multi-component organic transformations at 110 °C in the absence of solvent: (i) the condensation of 2-naphthol with arylaldehydes and amides leading to 1-amidoalkyl-2-naphthols, (ii) the reaction of 2-naphthol with aromatic aldehydes and alkyl carbamates to produce 1-carbamatoalkyl-2-naphthols, and (iii) the condensation between 2-naphthol, arylaldehydes, and thioamides leading to 1-thioamidoalkyl-2-naphthols (Scheme 2).

2. Results and discussion

The structure of $[Et_3N–SO_3H]Cl$ was identified by ^1H NMR, ^{13}C NMR, and mass spectra. The corresponding spectral data are reported in the Experimental section. The important peak in the ^1H NMR spectra of $[Et_3N–SO_3H]Cl$ is related to the acidic hydrogen (SO_3H) which was observed at 7.43 ppm. To confirm that this peak (7.43) is really related to the hydrogen of SO_3H in $[Et_3N–SO_3H]Cl$, not to the hydrogen of $ClSO_3H$ (its unreacted starting material) or another possible product formed from the reaction of NEt_3 with $ClSO_3H$ (*i.e.* $[Et_3N–H][ClSO_3]$), we also ran the ^1H NMR spectra of $ClSO_3H$ as well as $[Et_3N–H]Cl$ in $CDCl_3$ (the acidic hydrogen of both $[Et_3N–H][ClSO_3]$ and $[Et_3N–H]Cl$ is found on nitrogen. Since $[Et_3N–H][ClSO_3]$ was not available commercially in chemical companies catalogs, we used $[Et_3N–H]Cl$ instead of $[Et_3N–H][ClSO_3]$). In these spectra, the peaks of the acidic hydrogen of $[Et_3N–SO_3H]Cl$, $ClSO_3H$, and $[Et_3N–H]Cl$ were observed at 7.43, 10.75, and 11.59 ppm, respectively. The difference between the peaks of the acidic hydrogen in the compounds confirmed that the peak observed at 7.43 ppm in the ^1H NMR spectra of $[Et_3N–SO_3H]Cl$ is correctly related to the hydrogen of the SO_3H group of this compound (*18*).

In another study, to prove that $[Et_3N–SO_3H]Cl$ is the correct structure of the catalyst and is responsible for the catalytic results, the condensation of 2-naphthol with 4-nitrobenzaldehyde and acetamide was examined as a model reaction at 110 °C under solvent-free conditions in the presence of 20 mol% of $[Et_3N–SO_3H]Cl$, NEt_3, $ClSO_3H$, and $[Et_3N–H]Cl$ as catalysts. The $[Et_3N–H]Cl$ is used as a surrogate for $[Et_3N–H][ClSO_3]$ since this latter compound is not commercially available. This is justified because in both cases, it is the acidic proton on the ammonium cation and not the counterion that is functioning as the catalyst. The results are displayed in Table 1. The IL, $[Et_3N–SO_3H]Cl$, catalyzed the reaction resulting in excellent yields in a short reaction time. In contrast, NEt_3 gave low yields and $ClSO_3H$ and $[Et_3N–H]Cl$ afforded moderate yields of the product but in relatively much longer reaction times. These results also confirmed that the catalyst has been correctly synthesized, and its structure is $[Et_3N–SO_3H]Cl$, not $[Et_3N–H][ClSO_3]$ (*18*).

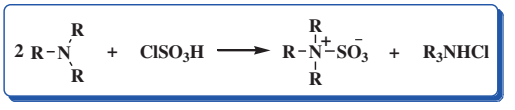
It has been established that tertiary amine–sulfur trioxides ($R_3N^+–SO_3^-$) are produced by the dropwise addition of 1 equiv. of chlorosulfonic acid to 2 equiv. of tertiary amines dissolved in

Table 1. The solvent-free condensation of 2-naphthol with 4-nitrobenzaldehyde and acetamide using NEt_3, $ClSO_3H$, and $[Et_3N–H]Cl$ at 110 °C.

Entry	Catalyst	Time (min)	Yield[a] (%)
1	–	150	21
3	$[Et_3N–SO_3H]Cl$	30	95
4[b]	NEt_3	180	12
5	$ClSO_3H$	45	72
7	$[Et_3N–H]Cl$	120	49

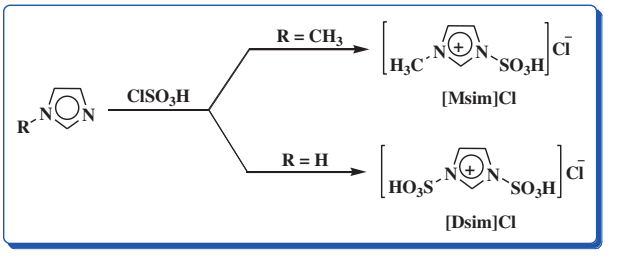
Notes: [a]Isolated yield.
[b]Because of the low boiling point of NEt_3, this reaction was carried out at 85 °C.

dichloroethane at low temperature (Scheme 3) (*47*, *48*). Under these conditions, the first equivalent of tertiary amine adds to $ClSO_3H$ to displace chloride to form $[R_3N–SO_3H]Cl$, and the second equivalent of tertiary amine acts as a base to abstract the acidic hydrogen to form the tertiary amine–sulfur trioxides ($R_3N^+–SO_3^-$) (*47*, *48*). In our synthesis of $[Et_3N–SO_3H]Cl$, we added 1 equiv. of triethylamine dropwise to 1 equiv. of chlorosulfonic acid at low temperature. Under these conditions, there is always an excess of $ClSO_3H$ in the reaction mixture; thus, when $[Et_3N–SO_3H]Cl$ forms, there is no Et_3N in the reaction media to abstract the acidic hydrogen to afford $Et_3N^+–SO_3^-$ and Et_3NHCl. We also demonstrated that 20 mol% of $Et_3N^+–SO_3^-$ is not as effective as our catalyst, $[R_3N–SO_3H]Cl$, in the solvent-free reaction of 2-naphthol with 4-nitrobenzaldehyde and acetamide at 110 °C and only gave a 24% yield of the product within 150 min. These studies provide compelling evidence that the catalyst in our studies is $[Et_3N–SO_3H]Cl$ (*18*).



Scheme 3. The preparation of $R_3N^+–SO_3^-$ by the reaction of tertiary amines (2 equiv.) with chlorosulfonic acid (1 equiv.).

Furthermore, more recently, Khazaei (*14*), Zolfigol *et al.* (*15–17*) and also Ghaffari Khaligh (*49*) showed that when 1-methylimidazole (1 equiv.) or imidazole (2 equiv.) is reacted with chlorosulfonic acid (1 equiv.), the nitrogen atoms of 1-methylimidazole or imidazole act as nucleophiles (not bases) and attack the sulfur of $ClSO_3H$ to give 3-methyl-1-sulfonic acid imidazolium chloride ([Msim]Cl) and 1,3-disulfonic acid imidazolium chloride ([Dsim]Cl), respectively (Scheme 4).



Scheme 4. The nucleophilic reaction of 1-methylimidazole or imidazole with chlorosulfonic acid.

To evaluate the efficacy of the catalyst in the synthesis of 1-amidoalkyl (carbamatoalkyl or thioamidoalkyl)-2-naphthols, the one-pot multi-component condensation of 2-naphthol with 4-nitrobenzaldehyde and acetamide was selected as a model reaction (Scheme 2), and its behavior was studied in the presence of different amounts of $[Et_3N–SO_3H]Cl$ under solvent-free conditions in the range of 90–120 °C. The results are summarized in Table 2 and show that 20 mol% of $[Et_3N–SO_3H]Cl$ was sufficient to catalyze the reaction efficiently (Table 2, Entry 3). Moreover, the optimal temperature for the reaction was 110 °C (Table 2, Entry 3). Increasing the amount of the catalyst and the temperature did not improve the results (Table 2, Entries 4 and 7).

In the next step, the generality and the efficacy of $[Et_3N–SO_3H]Cl$, to catalyze the synthesis of 1-amidoalkyl-2-naphthols, were explored by studying the reaction of 2-naphthol with different arylaldehydes and amides under the optimal reaction conditions (Table 3, compounds **1**–**12**). It was observed that all arylaldehydes (bearing halogens and electron-withdrawing and

Table 2. The condensation between 2-naphthol, 4-nitrobenzaldehyde, and acetamide using different molar ratios of $[Et_3N–SO_3H]Cl$ in the range of 90–120 °C.

Entry	Mol% of the catalyst	Temperature (°C)	Time (min)	Yield[a] (%)
1	–	110	150	21
2	15	110	60	90
3	20	110	30	95
4	25	110	30	95
5	20	90	100	57
6	20	100	60	84
7	20	120	30	95

Note: [a]Isolated yield.

electron-releasing substituents on their aromatic rings) afforded the desired products in high to excellent yields and in short reaction times; and also both amides (acetamide and acrylamide) gave excellent results. Interestingly, the catalyst also efficiently promoted the reaction of 2-naphthol with various aromatic aldehydes and methyl carbamate as well as thioacetamide to furnish 1-carbamatoalkyl-2-naphthols (Table 3, compounds **13**–**17**) and 1-thioamidoalkyl-2-naphthols (Table 3, compounds **18**–**20**) in high to excellent yields and in short reaction times.

In another study, 2-naphthol (2 mmol) was reacted with 4-nitrobenzaldehyde (2 mmol) in the presence of $[Et_3N–SO_3H]Cl$ (20 mol%) without acetamide wherein 2-naphthol was completely consumed, and some 4-nitrobenzaldehyde remained unreacted. In this reaction, about 30% of 14-(4-nitrophenyl)-14*H*-dibenzo[*a*,*j*]xanthene (*18*) and also two by-products were obtained.

3. Conclusion

In conclusion, we have introduced the IL $[Et_3N–SO_3H]Cl$ as a new acidic catalyst for the preparation of 1-amidoalkyl (carbamatoalkyl or thioamidoalkyl)-2-naphthol derivatives *via* the one-pot multi-component condensation of 2-naphthol with arylaldehydes and amides (alkyl carbamates or thioamides) under solvent-free conditions. The described method has many advantages such as generality, efficiency, simple work-up procedure, short reaction times, low cost, ease of preparation of the catalyst, clean production of the products in high yields, and good agreement with green chemistry protocols.

4. Experimental

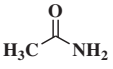
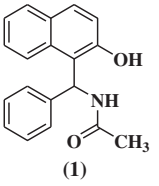
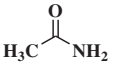
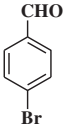
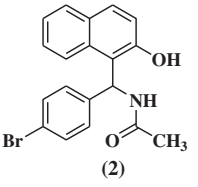
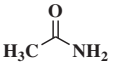
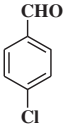
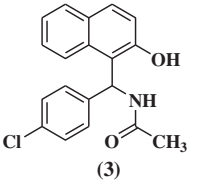
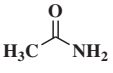
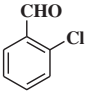
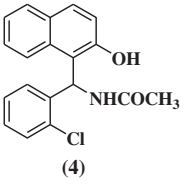
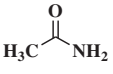
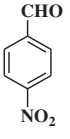
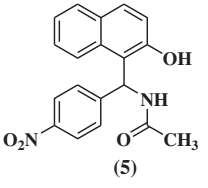
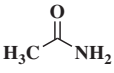
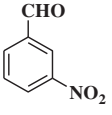
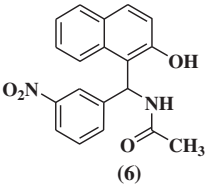
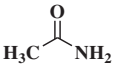
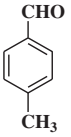
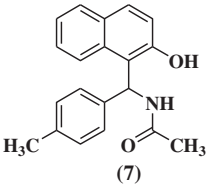
4.1. *General*

All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and NMR data with those reported in the literature. The ^1H NMR (250, 300, or 400 MHz) and ^{13}C NMR (62.5, 75, or 100 MHz) were run on a Bruker Avance DPX FT-NMR spectrometer (δ in ppm). Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

4.2. *Preparation of $[Et_3N–SO_3H]Cl$*

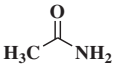
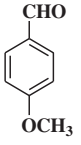
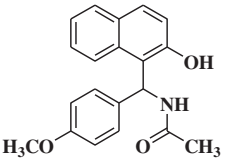
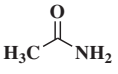
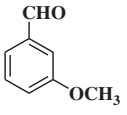
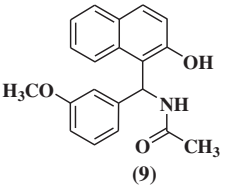
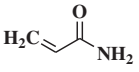
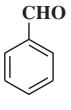
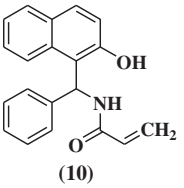
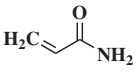
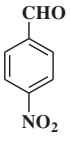
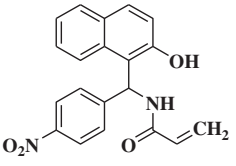
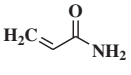
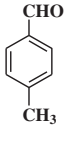
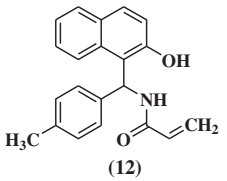
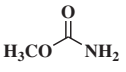
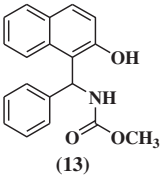
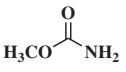
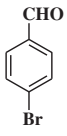
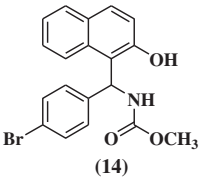
A solution of triethylamine (0.50 g, 5 mmol) in CH_2Cl_2 (40 ml) was added dropwise to a stirring solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry CH_2Cl_2 (40 ml) over a period of 10 min

Table 3. The solvent-free reaction of 2-naphthol with arylaldehydes and amide derivatives (methyl carbamate or thioacetamide) catalyzed by $[Et_3N–SO_3H]Cl$ at 110 °C.

Amide derivative	Aldehyde	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
		 **(1)**	40	94	237–239 (238–240) (*15*)
		 **(2)**	20	96	226–228 (226–228) (*15*)
		 **(3)**	20	95	221–223 (220–222) (*15*)
		 **(4)**	25	90	196–198 (197–199) (*15*)
		 **(5)**	30	95	245–247 (246–248) (*15*)
		 **(6)**	15	96	182–184 (184–186) (*33*)
		 **(7)**	30	93	223–225 (224–226) (*34*)

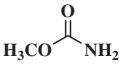
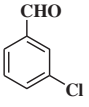
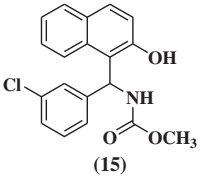
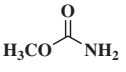
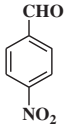
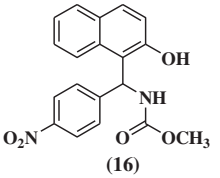
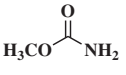
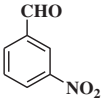
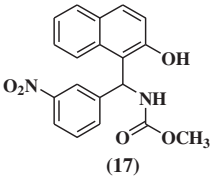
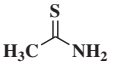
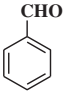
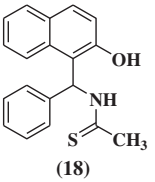
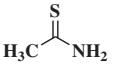
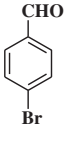
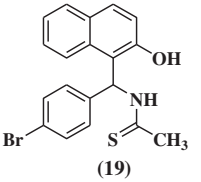
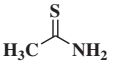
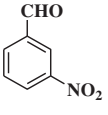
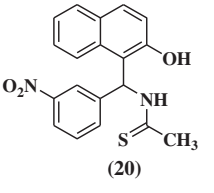
(*Continued*)

Table 3. Continued

Amide derivative	Aldehyde	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
		 **(8)**	50	86	185–187 (184–186) (*38*)
		 **(9)**	45	89	200–202 (200–202) (*15*)
		 **(10)**	35	92	243–245 (247–249) (*35*)
		 **(11)**	30	94	217–219 (223–225) (*36*)
		 **(12)**	30	91	213–215 (214–216) (*36*)
		 **(13)**	15	93	220–222 (217–218) (*43*)
		 **(14)**	10	96	171–173

(*Continued*)

Table 3. Continued

Amide derivative	Aldehyde	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
		 **(15)**	10	94	199–201 (196–198) (*43*)
		 **(16)**	10	96	203–205 (205–207) (*36*)
		 **(17)**	10	95	248–250 (253–255) (*42*)
		 **(18)**	30	88	190–193 (–) (*46*)
		 **(19)**	30	85	178–180
		 **(20)**	25	84	157–159

Note: [a]Isolated yield.

at 10 °C. Afterward, the reaction mixture was allowed to heat to room temperature (accompanied with stirring) and stirred for another 4 h. The solvent was evaporated, and the liquid residue was triturated with *t*-butylmethyl ether (3 × 10 ml) and dried under powerful vacuum at 90 °C to give $[Et_3N–SO_3H]Cl$ as a viscous pale yellow oil in 93% yield (*18*).

4.2.1. *N,N-Diethyl-N-sulfoethanammonium chloride ([Et_3N–SO_3H]Cl)*

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.41$ (t, $J = 7.2$ Hz, 9H), 3.17 (q, $J = 7.2$ Hz, 6H), 7.43 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 8.9$, 47.0. MS (m/z): 218 ($M^+ + 1$), 217 (M^+).

4.3. *General procedure for the synthesis of 1-amidoalkyl (carbamatoalkyl or thioamidoalkyl)-2-naphthols*

To a well-ground mixture of 2-naphthol (0.288 g, 2 mmol), aldehyde (2 mmol), and amide (alkyl carbamate or thioamide) (2.4 mmol) in a test tube was added [Et_3N–SO_3H]Cl (0.087 g, 0.4 mmol), and the resulting mixture was firstly stirred magnetically and after solidification of the reaction mixture with a small rod at 110 °C for the times reported in Table 3. Afterward, the reaction mixture was cooled to room temperature, H_2O (8 ml) was added to it, stirred for 3 min, and filtered. The solid residue was recrystallized from EtOH (95%) to give the pure product.

4.3.1. *N-[(2-Hydroxynaphthalen-1-yl)(phenyl)methyl]acetamide (**1**)*

^{1}H NMR (250 MHz, DMSO-d_6) $\delta = 2.06$ (s, 3H), 7.01–7.20 (m, 9H), 7.65–7.73 (m, 3H), 8.11 (d, $J = 7.7$ Hz, 1H), 9.69 (s, 1H). ^{13}C NMR (62.5 MHz, DMSO-d_6) $\delta = 23.5$, 41.3, 118.8, 120.2, 122.0, 123.9, 124.9, 125.7, 127.6, 128.1, 128.3, 128.5, 128.6, 134.2, 144.0, 152.6, 169.6.

4.3.2. *N-[(2-Hydroxynaphthalen-1-yl)(4-bromorophenyl)methyl]acetamide (**2**)*

^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 1.98$ (s, 3H), 6.98–7.34 (m, 8H), 7.61–7.67 (m, 2H), 7.86 (d, $J = 10.1$ Hz, 1H), 8.27 (d, $J = 8.1$ Hz, 1H), 9.74 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) $\delta = 23.7$, 46.5, 117.8, 118.7, 121.2, 122.4, 123.8, 126.9, 128.4, 128.7, 129.3, 130.2, 131.0, 133.2, 139.8, 152.6, 168.4.

4.3.3. *N-[(2-Hydroxynaphthalen-1-yl)(4-chlorophenyl)methyl]acetamide (**3**)*

^{1}H NMR (250 MHz, DMSO-d_6) $\delta = 2.07$ (s, 3H), 7.06 (m, 2H), 7.14–7.24 (m, 5H), 7.68–7.77 (m, 3H), 7.98 (d, $J = 7.4$ Hz, 1H), 8.16 (d, $J = 7.1$ Hz, 1H), 9.90 (s, 1H). ^{13}C NMR (62.5 MHz, DMSO-d_6) $\delta = 23.2$, 47.6, 118.8, 119.8, 122.1, 123.7, 125.8, 126.9, 127.4, 128.3, 128.6, 129.3, 129.9, 134.0, 143.4, 152.5, 169.8.

4.3.4. *N-[(2-Hydroxynaphthalen-1-yl)(2-chlorophenyl)methyl]acetamide (**4**)*

^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 2.01$ (s, 3H), 6.97–6.43 (m, 8H), 7.68–7.76 (m, 2H), 8.16–8.22 (m, 2H), 9.64 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) $\delta = 22.6$, 47.3, 118.0, 118.2, 123.5, 124.5, 126.9, 127.8, 127.9, 128.6, 129.1, 129.6, 130.2, 130.9, 131.8, 131.9, 143.6, 148.9, 169.7.

4.3.5. *N-[(2-Hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl]acetamide (**5**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 2.04$ (s, 3H), 7.21–7.32 (m, 3H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.54–7.61 (m, 2H), 7.82–7.91 (m, 3H), 8.07 (m, 2H), 8.66 (d, $J = 8.0$ Hz, 1H), 10.16 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 23.0$, 48.0, 118.9, 120.9, 121.7, 123.1, 127.2, 128.9, 129.2, 130.0, 130.4, 132.6, 133.3, 145.9, 148.2, 153.8, 170.2.

4.3.6. *N-[(2-Hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl]acetamide (**6**)*

^{1}H NMR (250 MHz, DMSO-d_6) δ = 2.06 (s, 3H), 7.15–7.49 (m, 6H), 7.78–8.04 (m, 5H), 8.54 (d, J = 8.1 Hz, 1H), 10.12 (s, 1H). ^{13}C NMR (62.5 MHz, DMSO-d_6) δ = 23.3, 48.1, 118.1, 118.7, 120.5, 122.3, 123.8, 125.7, 127.3, 128.4, 129.1, 129.6, 130.8, 133.1, 134.1, 144.5, 148.7, 152.9, 169.8.

4.3.7. *N-[(2-Hydroxynaphthalen-1-yl)(p-tolyl)methyl]acetamide (**7**)*

^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.0 (s, 3H), 2.24 (s, 3H), 7.05–7.10 (m, 4H), 7.14 (d, J = 8.4 Hz, 1H), 7.24–7.29 (m, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.76–7.82 (m, 2H), 7.87 (s, 1H), 8.45 (d, J = 8.4 Hz, 1H), 10.0 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 21.0, 23.1, 48.1, 118.9, 119.5, 122.8, 123.8, 126.4, 126.7, 129.0, 129.1, 129.6, 132.8, 135.5, 140.0, 153.5, 169.6.

4.3.8. *N-[(2-Hydroxynaphthalen-1-yl)(4-methoxyphenyl)methyl]acetamide (**8**)*

^{1}H NMR (300 MHz, DMSO-d_6) δ = 2.09 (s, 3H), 3.63 (s, 3H), 6.68 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 7.40–7.50 (m, 3H), 7.59 (t, J = 7.3 Hz, 2H), 7.78–7.85 (m, 2H), 8.39 (d, J = 8.2 Hz, 2H), 9.48 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 22.4, 39.8, 55.0, 113.9, 117.6, 118.0, 122.8, 124.3, 126.8, 128.8, 128.9, 129.2, 131.1, 131.4, 137.4, 148.7, 157.9, 167.3.

4.3.9. *N-[(2-Hydroxynaphthalen-1-yl)(3-methoxyphenyl)methyl]acetamide (**9**)*

^{1}H NMR (300 MHz, DMSO-d_6) δ = 2.05 (s, 3H), 3.60 (s, 3H), 6.71 (s, 1H), 6.97–7.36 (m, 7H), 7.70–7.78 (m, 2H), 8.02–8.11 (m, 2H), 9.81 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 23.2, 42.9, 56.2, 112.4, 114.1, 117.3, 118.2, 120.5, 122.6, 123.8, 127.0, 128.4, 128.6, 129.2, 131.2, 133.5, 142.3, 150.4, 159.8, 169.1.

4.3.10. *N-[(2-Hydroxynaphthalen-1-yl)(phenyl)methyl]acrylamide (**10**)*

^{1}H NMR (300 MHz, DMSO-d_6) δ = 5.59 (1H, d, J = 10.2 Hz), 6.12 (1H, d, J = 17.1 Hz), 6.59 (dd, 1H, J = 9.9, 16.5 Hz), 7.14–7.35 (m, 8H), 7.74–7.87 (m, 3H), 8.69 (d, J = 7.8, 1H), 10.01 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 48.5, 118.9, 119.0, 122.8, 123.1, 123.7, 126.1, 126.6, 126.8, 128.5, 128.9, 129.0, 129.8, 132.3, 132.8, 142.7, 153.7, 164.9.

4.3.11. *N-[(2-Hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl]acrylamide (**11**)*

^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.66 (d, J = 10.4 Hz, 1H), 6.22 (d, J = 16.8 Hz, 1H), 6.67 (dd, J = 10.4, 17.2 Hz, 1H), 7.22–7.33 (m, 3H), 7.44 (d, J = 8.8 Hz, 3H), 7.83–7.86 (m, 3H), 8.18 (d, J = 8.8 Hz, 2H), 8.89 (d, J = 8.0 Hz, 1H), 10.17 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 48.5, 118.0, 118.9, 123.1, 123.3, 123.7, 126.6, 127.2, 127.6, 128.9, 129.1, 130.4, 131.8, 132.7, 146.4, 151.2, 153.9, 165.3.

4.3.12. *N-[(2-Hydroxynaphthalen-1-yl)(p-tolyl)methyl]acrylamide (**12**)*

^{1}H NMR (300 MHz, DMSO-d_6) δ = 2.21 (s, 3H), 5.59 (d, J = 9.6 Hz, 1H), 6.12 (d, J = 16.8 Hz, 1H), 6.59 (dd, J = 15.9, 10.2 Hz, 1H), 7.04–7.35 (m, 8H), 7.74–7.85 (m, 3H), 8.68 (d, J = 7.5 Hz, 1H), 10.00 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 21.0, 49.5, 118.9, 119.1, 122.8, 123.8, 126.0, 126.5, 126.8, 128.9, 129.3, 131.8, 132.3, 135.7, 139.6, 153.7, 164.9.

4.3.13. *Methyl (2-hydroxynaphthalen-1-yl)(phenyl)methylcarbamate (**13**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 3.59$ (s, 3H), 6.90 (d, $J = 8.8$ Hz, 1H), 7.17–7.19 (m, 1H), 7.24–7.30 (m, 6H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 5.6$ Hz, 1H), 7.77–7.83 (m, 2H), 7.95 (d, $J = 8.0$ Hz, 1H), 10.14 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 50.8, 52.1, 118.9, 119.3, 123.0, 126.5, 126.8, 127.0, 128.5, 128.8, 129.0, 129.7, 132.5, 142.8, 153.3, 157.0$.

4.3.14. *Methyl (4-bromophenyl)(2-hydroxynaphthalen-1-yl)methylcarbamate (**14**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 3.59$ (s, 3H), 6.85 (d, $J = 8.8$ Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 7.23–7.31 (m, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 5.2$ Hz, 1H), 7.78–7.83 (m, 2H), 7.91 (d, $J = 7.2$ Hz, 1H), 10.18 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 50.4, 52.1, 118.8, 118.9, 119.9, 123.0, 127.1, 128.7, 128.8, 129.0, 130.0, 131.4, 132.4, 142.4, 153.4, 157.1$; MS ($m/z$): 386 ($M^+$).

4.3.15. *Methyl (3-chlorophenyl)(2-hydroxynaphthalen-1-yl)methylcarbamate (**15**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 3.59$ (s, 3H), 6.87 (d, $J = 8.8$ Hz, 1H), 7.16 (d, $J = 7.2$ Hz, 1H), 7.21–7.32 (m, 5H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.77–7.84 (m, 3H), 7.93 (d, $J = 8.4$ Hz, 1H), 10.2 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 50.4, 52.2, 118.7, 118.8, 123.0, 123.3, 125.2, 126.2, 126.8, 127.1, 128.8, 129.1, 130.1, 130.5, 132.4, 133.3, 145.5, 153.4, 157.1$.

4.3.16. *Methyl (2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methylcarbamate (**16**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 3.62$ (s, 3H), 6.99 (d, $J = 8.4$ Hz, 1H), 7.24–7.32 (m, 2H), 7.53 (t, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.83 (t, $J = 8.4$ Hz, 2H), 7.88 (s, 1H), 7.93 (d, $J = 6.4$ Hz, 1H), 8.16 (d, $J = 8.8$ Hz, 2H), 10.25 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 50.7, 52.2, 118.4, 118.8, 123.1, 123.2, 123.8, 127.3, 127.6, 128.8, 129.1, 130.3, 132.4, 146.5, 151.1, 153.6, 157.2$.

4.3.17. *Methyl (2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methylcarbamate (**17**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 3.62$ (s, 3H), 7.00 (d, $J = 8.4$ Hz, 1H), 7.24–7.32 (m, 2H), 7.44 (t, $J = 7.2$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.83 (t, $J = 6.0$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 8.15 (s, 1H), 10.29 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 50.5, 52.2, 118.3, 118.9, 120.9, 121.6, 121.9, 123.1, 127.3, 128.8, 129.1, 130.4, 132.4, 133.3, 133.9, 145.5, 148.2, 153.6, 157.2$.

4.3.18. *N-[(2-Hydroxynaphthalen-1-yl)(phenyl)methyl]thioacetamide (**18**)*

^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 2.54$ (s, 3H), 7.11–7.28 (m, 8H), 7.40 (t, $J = 8.1$ Hz, 1H), 7.79 (t, $J = 8.7$ Hz, 3H), 7.96 (d, $J = 8.7$ Hz, 1H), 10.39 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) $\delta = 33.5, 55.9, 117.4, 119.0, 122.9, 123.3, 126.5, 126.9, 127.1, 128.4, 128.7, 129.0, 130.1, 133.2, 140.8, 154.2, 200.0$. MS ($m/z$): 307 ($M^+$).

4.3.19. *N-[(4-Bromophenyl)(2-hydroxynaphthalen-1-yl)methyl]thioacetamide (**19**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 2.59$ (s, 3H), 7.09 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.43–7.49 (m, 3H), 7.78–7.85 (m, 3H), 7.99 (d, $J = 8.8$ Hz, 1H),

10.20 (s, 1H), 10.40 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 33.4, 55.3, 117.0, 118.9, 120.0, 123.1, 123.2, 127.2, 128.7, 129.1, 130.4, 131.3, 131.4, 133.0, 140.4, 154.2, 200.6$. MS ($m/z$): 386 ($M^+$).

4.3.20. *N-[(2-Hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl]thioacetamide (**20**)*

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 2.63$ (s, 3H), 7.28 (d, $J = 12.0$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 5.2$ Hz, 2H), 7.81–7.90 (m, 3H), 7.98 (s, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 8.08–8.11 (m, 1H), 10.3 (s, 1H), 10.56 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 33.3, 35.3, 116.5, 118.9, 121.1, 122.0, 122.9, 123.2, 127.5, 128.7, 129.2, 130.1, 130.9, 133.0, 133.5, 143.5, 148.2, 145.3. 201.3$. MS ($m/z$): 352 ($M^+$).

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