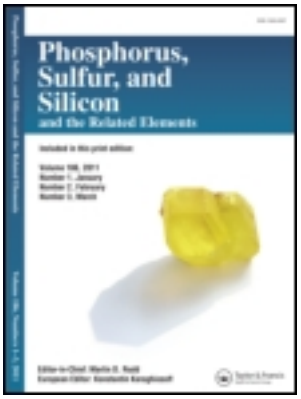

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Saccharin Sulfonic Acid (SASA) as a Highly Efficient Catalyst for the Condensation of 2-Naphthol With Arylaldehydes and Amides (Thioamides or Alkyl Carbamates) Under Green, Mild, and Solvent-Free Conditions

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SACCHARIN SULFONIC ACID (SASA) AS A HIGHLY EFFICIENT CATALYST FOR THE CONDENSATION OF 2-NAPHTHOL WITH ARYLALDEHYDES AND AMIDES (THIOAMIDES OR ALKYL CARBAMATES) UNDER GREEN, MILD, AND SOLVENT-FREE CONDITIONS

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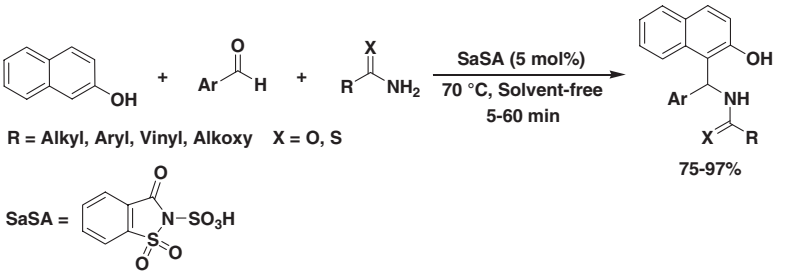
GRAPHICAL ABSTRACT



Abstract *Saccharin sulfonic acid (SaSA) is used as a highly efficient and recyclable catalyst for the one-pot multicomponent condensation of 2-naphthol with arylaldehydes and amides (thioamides or alkyl carbamates) under green, mild (70 °C), and solvent-free conditions. In this reaction, 1-amidoalkyl-2-naphthols, 1-thioamidoalkyl-2-naphthols, 1-carbamatoalkyl-2-naphthols, bis(1-amidoalkyl-2-naphthol)s, and bis(1-carbamatoalkyl-2-naphthol)s are produced in high to excellent yields and in relatively short reaction times.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

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Keywords Saccharin sulfonic acid (SaSA); amide (thioamide or alkyl carbamate); 1-amidoalkyl-2-naphthol; 1-thioamidoalkyl-2-naphthol; 1-carbamatoalkyl-2-naphthol; multi-component reaction

INTRODUCTION

Green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.[1] It is an innovative, nonregulatory, and economically driven approach toward sustainability.[1] The unequivocal value of green chemistry to the business and to the environment is illustrated through industrial examples.[1] The subject of green chemistry is currently guided by a series of principles, and solvent-free is one of the green chemical methods which have many advantages.[2] For some reasons of economy and pollution, solvent-free methods are of great interest in order to modernize classical procedures making them to achieve in shorter reaction times, and with higher yields, improved selectivity as well as easier purification of the products.[2–8]

Currently, the use of SO_3H-containing catalysts has received considerable interest by chemists due to their unique advantages such as efficiency, high reactivity, operational simplicity, environmental compatibility, nontoxicity, low cost, ease of isolation, green nature, easy availability of their starting materials, and ability to promote a wide range of reactions.[7–18] Saccharin sulfonic acid (SaSA) is certainly one of the interesting examples of SO_3H-containing catalysts, which has been recently reported to promote organic transformations.[15–18] This catalyst has successfully promoted the following reactions: (i) preparation as well as deprotection of 1,1-diacetates,[15] (ii) chemoselective trimethylsilylation of alcohols,[16] (iii) acetylation of alcohols, phenols, and amines,[17] and (iv) *N*-Boc protection of amines and formation of *t*-butyl ethers from alcohols.[18]

Multicomponent reactions (MCRs) have drawn great interest enjoying an outstanding status in modern organic synthesis and medicinal chemistry, because they are one-pot processes bringing together three or more components and show high atom economy and high selectivity.[19–24] Moreover, MCRs offer the advantage of simplicity and synthetic efficiency over conventional chemical reactions.[19–24]

1-amidoalkyl-2-naphthol, 1-thioamidoalkyl-2-naphthol, and 1-carbamatoalkyl-2-naphthol derivatives are of importance as they can be easily hydrolyzed to the biologically interesting compounds, 1-aminoalkyl-2-naphthols. 1-aminoalkyl-2-naphthols have been frequently applied as hypotensive and bradycardiac agents.[25,26] For example, one of the most important biologically active compounds, containing a 1-aminoalkyl-2-naphthol moiety in its structure, is compound (a) which has been shown to have hypotensive and bradycardic activities (Figure 1).[26] 1-amidoalkyl-2-naphthols can also be converted to 1,3-oxazine derivatives (b) (Figure 1).[27] 1,3-oxazines have potentially different biological activities including antibiotic,[28] antitumor,[29] analgesic,[30] anticonvulsant,[31] antipsychotic,[32] antimalarial,[33] antianginal,[34] antihypertensive,[35] and antirheumatic[36] properties.

The one-pot multicomponent condensation of 2-naphthol with aldehydes and amide derivatives (or acetonitrile) has been used as a practical synthetic route toward 1-amidoalkyl-2-naphthols.[37–47] Some catalysts have been applied for this transformation, e.g., $Ce(SO_4)_2$,[37] montmorillonite K-10,[38] $HClO_4/SiO_2$,[39] $H_3[P(Mo_3O_{10})_4]$,[40] sulfonic acid functionalized imidazolium salts,[41] sulfamic acid/ultrasound,[42] $Sr(OTf)_2$,[43] copper *p*-toluenesulfonate,[44]

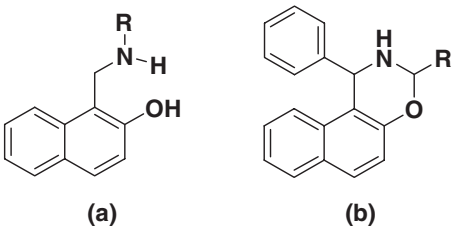
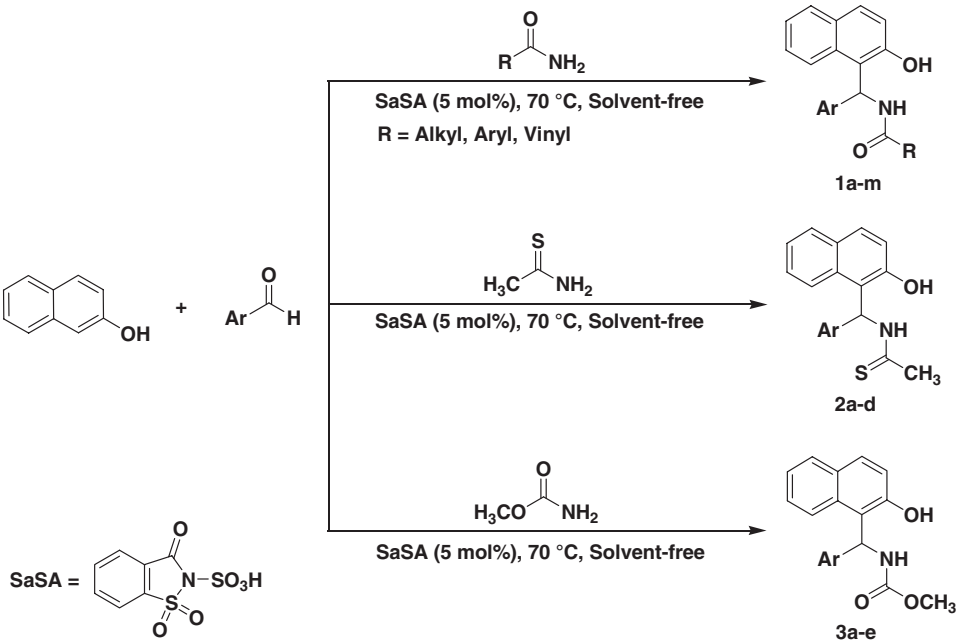


Figure 1 The general structures of 1-aminoalkyl-2-naphthols (a) and 1,3-oxazines (b).

1-butyl-3-methylimidazolium bromide/microwave,[45] polyethylene glycol-based dicationic acidic ionic liquid,[46] trityl chloride,[47] $Yb(OTf)_3$,[48] and 2,4,6-trichloro-1,3,5-triazine.[49] 1-thioamidoalkyl-2-naphthols have been prepared by the reaction between 2-naphthol, aldehydes, and thioamides using silica sulfuric acid.[50] This transformation has been scarcely studied in the literature. The useful protocol which has been utilized for the synthesis of 1-carbamatoalkyl-2-naphthols involves the reaction of 2-napthol with aldehydes and alkyl carbamates in the presence of some catalysts, such as 4-(1-imidazolium) butane sulfonate,[51] silica-supported $NaHSO_4$,[52] silica-supported Preyssler nanoparticles,[53] and 1-butyl-3-methylimidazolium bromide/*p*-toluene sulfonic acid.[54] The synthesis of this class of compounds has been also rarely reported.

Although some catalysts and methods for the synthesis of 1-amidoalkyl (thioamidoalkyl or carbamatoalkyl)-2-naphthol derivatives are known, newer catalysts and methods continue to attract attention for their difference with the others, generality and effectiveness. Furthermore, most of the reported methods for the synthesis of the title compounds suffer from one or more of the following drawbacks: the use of expensive[40,46,48,53] and toxic[49] catalysts, poor compliance with the green chemistry protocols,[37,40,43,47] the use of large amount of catalyst,[37,42,45] low product yield,[37,50–52,54] prolonged reaction time,[37,40,43,47,50,51] application of an additional energy (ultrasound or microwave),[42,45] and especially harsh reaction conditions[38,39,41,45,52,53] as well as no generality (in most of the reported procedures, the synthesis of one type of the title compounds has been achieved).[37–47,52,53] In this work, we have found that SaSA is a catalyst which can solve the above mentioned disadvantages accompanied with the methods reported for the preparation of title compounds; it is an inexpensive, nontoxic, recyclable, and green catalyst; 5 mol% of SaSA is sufficient to promote the reaction efficiently and affords the desired products in high to excellent yields and in relatively short reaction times under mild (70 °C), green, and solvent-free conditions; and finally it can catalyze the synthesis of the three types of the compounds, including 1-amidoalkyl-2-naphthols, 1-thioamidoalkyl-2-naphthols, and 1-carbamatoalkyl-2-naphthols. Moreover, SaSA can catalyze the synthesis of bis(1-amidoalkyl-2-naphthol)s and bis(1-carbamatoalkyl-2-naphthol)s.

In this paper, we report our results on the one-pot multicomponent condensation of 2-naphthol with arylaldehydes and amides (thioamides or alkyl carbamates) in the presence of catalytic amount of SaSA under green and solvent-free conditions at 70 °C to give 1-amidoalkyl (thioamidoalkyl or carbamatoalkyl)-2-naphthols (Scheme 1). Our protocol has solved the above mentioned drawbacks, and improved efficiently the synthesis of the title compounds.



Scheme 1 The condensation of 2-naphthol with arylaldehydes and amides (thioamides or alkyl carbamates).

RESULTS AND DISCUSSION

At first, we selected the one-pot three-component condensation of 2-naphthol with benzaldehyde and acetamide as model reaction to provide 1-amidoalkyl-2-naphthol **1a**. This reaction was studied in the absence of catalyst under solvent-free conditions at 70 °C in which the product was obtained in 19% yield after 240 min. Afterward, the solvent-free reaction was examined in the presence of different amounts of SaSA at range of 60 °C–80 °C; the respective results are summarized in Table 1. As it is clear from Table 1, the best results for the preparation of 1-amidoalkyl-2-naphthol **1a** were obtained when 5 mol% of SaSA was used at 70 °C (Table 1, entry 3). The use of excess of amount of the catalyst or increment of the temperature did not lead to increasing the yield or decreasing the reaction time.

Table 1 Optimization amount of the catalyst and the reaction temperature on the condensation of 2-naphthol with benzaldehydes and acetamide

Entry	SaSA amount (mol%)	Temperature (°C)	Time (min)	Yield [a] (%)
1	–	70	240	19
2	2.5	70	60	45
3	5	70	35	93
4	7.5	70	35	93
5	5	60	100	56
6	5	80	35	93

[a]Isolated yield.

After optimization of the reaction conditions, 2-naphthol was reacted with different aromatic aldehydes and various amides to show the efficiency and the generality of the method; the corresponding results are displayed in the Table 2. As it is shown in Table 2, all arylaldehydes including benzaldehyde and arylaldehydes carrying electron-releasing substituents, electron-withdrawing substituents, or halogens, and also all amides consisting of acetamide, benzamide, nicotinamide, and acrylamide afforded the desired 1-amidoalkyl-2-naphthol derivatives in high to excellent yields (84%–97%) within relatively short reaction times (20–60 min) (Table 2, compounds **1a**–**m**). Interestingly, the method was highly efficient when thioamides or alkyl carbamates were used instead of amides. In these cases, 1-thioamidoalkyl-2-naphthol and 1-carbamatoalkyl-2-naphthol derivatives were obtained in high to excellent yields (75%–97%) and in relatively short reaction times (5–55 min) (Table 2, compounds **2a**–**d** and **3a–e**).

Furthermore, when 2.2 equivalents of 2-naphthol was reacted with 1 equivalent of terephthaldehyde (a bis-aldehyde) and 2.4 equivalents of amides (or methyl carbamate) using 10% mol of SaSA at 70 °C in the absence of solvent, bis(1-amidoalkyl-2-naphthol) derivatives **4a** and **4b** as well as bis(1-carbamatoalkyl-2-naphthol) **4c** were obtained in high yields (84%–88%) and in relatively short reaction times (35–60 min) (Table 3).

The above observations confirmed that our method and catalyst are highly efficient and general.

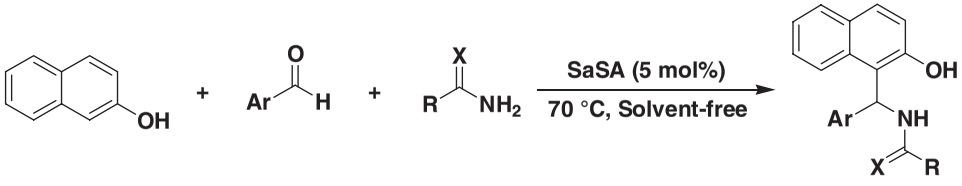
To compare the efficiency of our method with the reported methods for the synthesis of 1-amidoalkyl-2-naphthols, we have tabulated the results of these methods to perform the condensation reaction between 2-naphthol, benzaldehyde and acetamide in Table 4. As it is shown in Table 4, our method is superior to the previously reported methods in term of reaction temperature, reaction time, and/or yield. Moreover, in spite of the reported methods, in our protocol, the synthesis of the three types of the compounds, including 1-amidoalkyl-2-naphthols, 1-thioamidoalkyl-2-naphthols, and 1-carbamatoalkyl-2-naphthols have been achieved.

In another study, recyclability of the catalyst was investigated. For this purpose, the reaction of 2-naphthol with benzaldehyde and methyl carbamate was performed in the presence of SaSA several times, and the reaction mixtures were combined. Afterward, the product (**3a**) was extracted by hot ethyl acetate (the product is soluble in hot ethyl acetate, but SaSA is not soluble in this solvent), and the remained catalyst was used for the next run of the reaction. Catalytic activity of SaSA was restored within the limits of the experimental errors for four successive recycle runs.

In a plausible mechanism, we suggest that at first, 2-naphthol is condensed with aldehyde in the presence of SaSA to provide *ortho*-quinone methide (*o*-QM). Afterward, *o*-QM reacts with amide (thioamide or alkyl carbamate) to produce 1-amidoalkyl (thioamidoalkyl or carbamatoalkyl)-2-naphthol. The SO_3H group of SaSA, via hydrogen bonding with the carbonyls of aldehyde and *o*-QM, activates them to accept nucleophilic attack by 2-naphthol or amide (thioamide or alkyl carbamate). This mechanism, which has been reported in the literature,[41,51,52] is illustrated in Scheme 3.

In conclusion, we have introduced a new method for the one-pot three-component condensation of 2-naphthol with aromatic aldehydes and amides (thioacetamides or alkyl carbamates) using SaSA as an interesting SO_3H-containing catalyst in solvent-free conditions. The promising points for this method are efficiency, generality, high yields, relatively short reaction times, cleaner reaction profile, simplicity, ease of preparation and recyclability of the catalyst, easy work-up and purification of the products, and compliance with the green chemistry protocols which makes it an attractive procedure for the preparation of

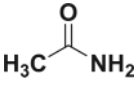
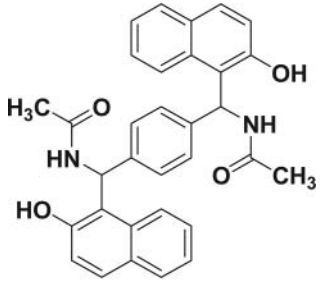
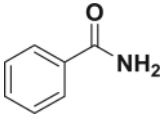
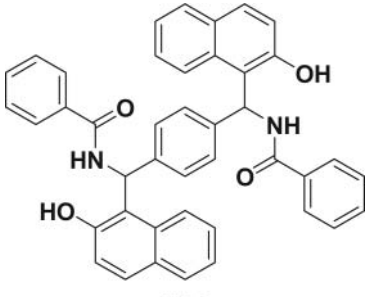
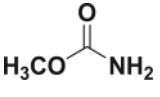
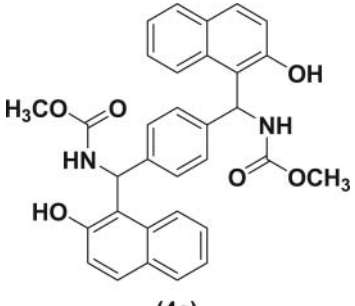
Table 2 The synthesis of 1-amidoalkyl-2-naphthols, 1-thioamidoalkyl-2-naphthols, and 1-carbamatoalkyl-2-naphthols catalyzed by SaSA at 70 °C under solvent-free conditions



Ar	R	X	Product	Time (min)	Yield[a] (%)	Mp °C (Literature)
C_6H_5	CH_3	O	**1a**	35	93	240–242 (241–243)[37]
4-$CH_3C_6H_5$	CH_3	O	**1b**	40	91	222–224 (223–225)[41]
4-$NO_2C_6H_5$	CH_3	O	**1c**	35	97	245–247 (246–248)[47]
3-$NO_2C_6H_5$	CH_3	O	**1d**	45	96	236–238 (238–240)[41]
4-ClC_6H_5	CH_3	O	**1e**	35	95	220–222 (224–227)[37]
4-BrC_6H_5	CH_3	O	**1f**	35	96	225–227 (226–228)[41]
4-$CH_3OC_6H_5$	C_6H_5	O	**1g**	45	90	202–204 (208–210)[44]
4-$NO_2C_6H_5$	C_6H_5	O	**1h**	40	92	233–235 (237–239)[44]
4-ClC_6H_5	3-Pyridil	O	**1i**	60	84	205–207 (206–209)[41]
C_6H_5	CH_2=CH	O	**1j**	20	95	244–246 (247–249)[40]
4-$CH_3C_6H_5$	CH_2=CH	O	**1k**	25	97	216–217 (214–216)[46]
4-OHC_6H_5	CH_2=CH	O	**1l**	50	90	190–192
4-$NO_2C_6H_5$	CH_2=CH	O	**1m**	30	97	218–220 (223–225)[46]
C_6H_5	CH_3	S	**2a**	50	80	190–193 (–)[50]
4-$CH_3C_6H_5$	CH_3	S	**2b**	55	83	180–183
3-$NO_2C_6H_5$	CH_3	S	**2c**	40	75	157–159
4-BrC_6H_5	CH_3	S	**2d**	35	84	178–180
C_6H_5	OCH_3	O	**3a**	10	97	220–222 (217–218)[52]
4-$NO_2C_6H_5$	OCH_3	O	**3b**	10	97	202–203 (205–507)[52]
3-$NO_2C_6H_5$	OCH_3	O	**3c**	5	95	247–250 (253–255)[53]
3-ClC_6H_5	OCH_3	O	**3d**	5	92	199–121 (196–198)[52]
4-BrC_6H_5	OCH_3	O	**3e**	5	95	171–173

[a]Isolated yield.

Table 3 The solvent-free synthesis of bis(1-amidoalkyl-2-naphthol)s and bis(1-carbamatoalkyl-2-naphthol)s using SaSA at 70 °C

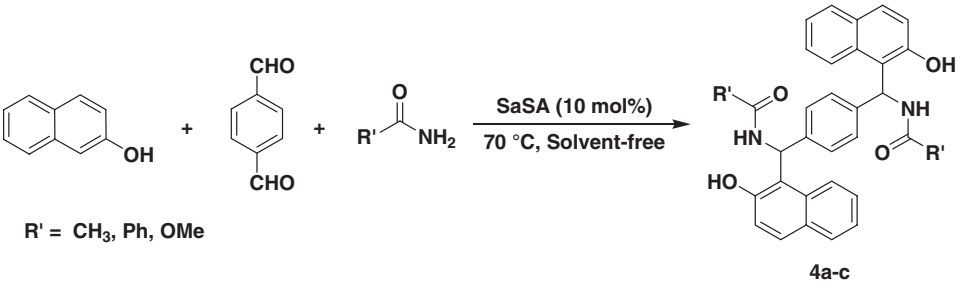
Amide	Product	Time (min)	Yield[a] (%)	Mp °C (Literature)
	 (4a)	50	84	276–278 (277–279)[41]
	 (4b)	60	85	260–263
	 (4c)	35	88	192–194

[a]Isolated yield.

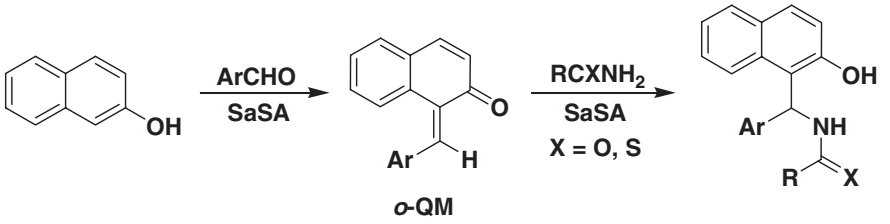
Table 4 Comparison of results of the reaction of 2-naphthol with benzaldehyde and acetamide using our method with those obtained by reported methods

Catalyst	Temperature (°C)	Time (min)	Yield (%)	Ref.
Saccharin sulfonic acid	70	35	93	–[a]
$Ce(SO_4)_2$[b]	85	2160	72	37
Montmorillonite K10 clay	125	90	89	38
$HClO_4/SiO_2$	110	40	89	39
$H_3[P(Mo_3O_{10})_4]$	65	210	95	40
Sulfonic acid functionalized imidazolium salt	120	5	94	41
Sulfamic acid	28–30 (Ultrasound)	15	89	42
$Sr(OTf)_2$	Reflux in $CHCl_3$	600	90	43
Copper *p*-toluenesulfonate	80	90	94	44
[Bmim]Br	130 (Microwave)	25	94	45
Trityl chloride[b]	r.t.	105	92	47
$Yb(OTf)_3$	80	360	90	48
4-(1-Imidazolium)butanesulfonate	80	120	85	51
$Fe(HSO_4)_3$	85	65	83	55
Silphox	120	30	92	56
Silphos	120	20	93	56
$K_5CoW_{12}O_{40}\cdot 3H_2O$	125	120	90	57

[a]Our catalyst.
[b]In this work, acetonitrile instead of acetamide has been used.



Scheme 2 The reaction of 2-naphthol with terephthaldehyde and amides (or methyl carbamate).



Scheme 3 The proposed mechanism for the synthesis of 1-amidoalkyl (thioamidoalkyl or carbamatoalkyl)-2-naphthols.

1-amidoalkyl-2-naphthols, 1-thioamidoalkyl-2-naphthols, 1-carbamatoalkyl-2-naphthols, bis(1-amidoalkyl-2-naphthol)s, and bis(1-carbamatoalkyl-2-naphthol)s as biologically important compounds.

EXPERIMENTAL

All chemicals were purchased from Merck or Fluka Chemical Companies (New Delhi, India). The ^{1}H 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. Mass spectra were obtained with apparatus Shimadzu GC-MS-QP 1100 EX model. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Preparation of SaSA

A flask (500 mL) charged with saccharin (17.1 g, 0.1 mol) was equipped with a constant pressure dropping funnel containing chlorosulfonic acid (11.65 g, 0.1 mol) and a gas outlet tube which was dipped into water to dissolve the generated HCl gas during the reaction. The flask was put into an ice bath and chlorosulfonic acid was added dropwise over a period of 10 min and the resulting mixture was stirred slowly for another 10 min. The temperature of the mixture was brought up to the room temperature and was stirred for an additional 30 min. The mixture was triturated with *n*-hexane (10 mL) and then filtered. The solid residue was washed with *n*-hexane (10 mL) and dried under vacuum to give SaSA as a white powder; mp 109 °C–111 °C (literature 110 °C–112 °C).[15–18]

General Procedure for the Condensation of 2-Naphthol with Arylaldehydes and Amides (Thioamides and Alkyl Carbamates)

A well ground mixture of 2-naphthol (0.144 g, 1 mmol), arylaldehyde (1 mmol), amide (thioamide or alkyl carbamate) (1.2 mmol) and SaSA (0.013 g, 0.05 mmol) was stirred mechanically at 70 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, and the resulting solid was recrystallized from hot ethanol (EtOH) (95%) to give pure 1-amidoalkyl (thioamidoalkyl or carbamatoalkyl)-2-naphthol (compounds **1a**–**m**, **2a**–**d**, and **3a**–**e**).

Note: In the case of liquid aldehydes, at first, a mixture of 2-naphthol, amide (thioamide or alkyl carbamate) and SaSA were ground vigorously, and subsequently, aldehyde was added.

General Procedure for the Condensation Between 2-Naphthol, Terephthaldehyde and Amides (or Alkyl Carbamates)

A well ground mixture of compounds consisting of 2-naphthol (0.317 g, 2.2 mmol), terephthalaldehyde (0.144 g, 1 mmol), amide (or alkyl carbamate) (2.4 mmol), and SaSA (0.026 g, 0.1 mmol) was stirred magnetically at 70 °C. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, and triturated with hot EtOH (95%) (the impurities are soluble in hot EtOH; however, the product is not soluble in this solvent) to give pure bis[1-amidoalkyl (or carbamatoalkyl)-2-naphthol]

(compounds **4a**–**c**). The online Supplemental Materials contains sample ^{1}H and ^{13}C NMR spectra for novel compounds 1l, 2d, 3e, and 4c (Figures S1–S8).

***N*-[(2-Hydroxynaphthalen-1-yl)(4-hydroxyphenyl)methyl]acrylamide (1l).** IR (KBr): 3398, 3231, 1642, 1604, 1482 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.61 (d, $J = 10.0$ Hz, 1H), 6.14 (d, $J = 16.8$ Hz, 1H), 6.59 (dd, $J = 10.0$, 16.8 Hz, 1H), 6.68 (d, $J = 8.4$ Hz, 2H), 7.0 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 1H), 7.24–7.29 (m, 2H), 7.39 (s, 1H), 7.76–7.82 (m, 2H), 7.91 (s, 1H), 8.70 (d, $J = 8.0$ Hz, 1H), 9.28 (s, 1H), 9.99 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 48.2, 115.3, 119.0, 119.2, 122.8, 123.8, 125.9, 126.7, 127.9, 128.9, 129.0, 129.5, 132.3, 132.6, 132.8, 153.6, 156.3, 164.7; MS (*m/z*): 319 (M^+). Anal. calcd. for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39; found: C, 75.45; H, 5.48; N, 4.31.

***N*-[(2-Hydroxynaphthalen-1-yl)(*p*-tolyl)methyl]thioacetamide (2b).** IR (KBr): 3354, 3163, 3024, 1596, 1121 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H), 2.53 (s, 3H), 7.02, (d, $J = 3.9$ Hz, 4H), 7.18–7.28 (m, 3H), 7.37 (d, $J = 7.2$ Hz, 1H), 7.78 (t, $J = 7.5$ Hz, 3H), 7.96 (d, $J = 8.4$ Hz, 1H), 10.33 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.0, 33.5, 55.8, 117.6, 119.0, 119.4, 126.4, 127.0, 127.9, 128.7, 129.7, 130.1, 133.1, 136.2, 137.8, 154.0, 199.9; MS (*m/z*): 321 (M^+). Anal. calcd. for $C_{20}H_{19}NOS$: C, 74.73; H, 5.96; N, 4.36; found: C, 74.92; H, 5.88; N, 4.46.

***N*-[(2-Hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl]thioacetamide (2c).** IR (KBr): 3365, 3172, 3021, 1587, 1520, 1339, 1113 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 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): δ 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^+). Anal. calcd. for $C_{19}H_{16}N_2O_3S$: C, 64.76; H, 4.58; N, 7.95; found: C, 64.51; H, 4.46; N, 8.04.

***N*-[(2-Hydroxynaphthalen-1-yl)(4-bromophenyl)methyl]thioacetamide (2d).** IR (KBr): 3351, 3147, 3029, 1595, 1107 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 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): δ 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^+). Anal. calcd. for $C_{19}H_{16}BrNOS$: C, 59.07; H, 4.17; N, 3.63; found: C, 59.34; H, 4.05; N, 3.54.

Methyl (4-Bromophenyl)(2-hydroxynaphthalen-1-yl)methylcarbamate (3e). IR (KBr): 3405, 3227, 1675, 1582, 1441 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.59 (s, 3H), 6.85 (d, $J = 8.8$ Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.23–7.31 (m, 2H), 7.41 (t, $J = 8.0$ Hz, 1H), 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): δ 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^+). Anal. calcd. for $C_{19}H_{16}BrNO_3$: C, 59.08; H, 4.18; N, 3.63; found: C, 58.87; H, 4.27; N, 3.52.

***N*,*N*′-[1,4-Phenylenebis((2-hydroxynaphthalen-1-yl)methylene)]dibenzamide (4b).** IR (KBr): 3404, 3180, 1635, 1601, 1477 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.26–7.39 (m, 8H), 7.44–7.59 (m, 10H), 7.78–7.88 (m, 6H), 7.94 (d, J = 7.2 Hz, 2H), 8.13 (d, J = 8.4 Hz, 2H), 9.07 (d, J = 8.4 Hz, 2H), 10.39 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.7, 118.7, 119.2, 123.2, 127.0, 127.3, 127.8, 128.6, 128.9, 129.8, 130.3, 131.7, 132.7, 134.6, 135.3, 140.9, 153.6, 168.5; MS (*m/z*): 523 (M^+

– PhCO), 418 (M^+ – 2PhCO), 380 (M^+ – $C_{17}H_{12}O_2$). Anal. calcd. for $C_{42}H_{32}N_2O_4$: C, 80.24; H, 5.13; N, 4.46; found: C, 80.51; H, 5.01; N, 4.60.

Dimethyl 1,4-Phenylenebis[(2-hydroxynaphthalen-1-yl)methylene]dicarbamate (4c). IR (KBr): 3421, 3244, 1695, 1603, 1477 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 3.55 (s, 6H), 6.78 (d, $J = 8.4$ Hz, 2H), 7.13 (s, 4H), 7.17–7.20 (dd, $J = 4.0$, 9.2 Hz, 2H), 7.27 (t, $J = 7.6$ Hz, 2H), 7.37 (d, $J = 9.2$ Hz, 2H), 7.61 (s, 2H), 7.75 (d, $J = 8.8$ Hz, 2H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.91 (s, 2H), 10.08 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 50.7, 52.1, 118.9, 119.2, 122.9, 126.3, 126.7, 127.0, 128.8, 129.0, 129.7, 132.5, 140.9, 153.3, 156.9; MS (*m/z*): 536 (M^+). Anal. calcd. for $C_{32}H_{28}N_2O_6$: C, 71.63; H, 5.26; N, 5.22; found: C, 71.39; H, 5.38; N, 5.07.

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