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ORIGINAL PAPER

Solvent-free one-pot synthesis of 1-carbamatoalkyl-2-naphthols by a tin tetrachloride catalyzed multicomponent reaction

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Abstract An efficient one-pot synthesis of 1-carbamatoalkyl-2-naphthols using tin tetrachloride as a catalyst for the three-component condensation reaction of 2-naphthol, aldehydes, and carbamates under thermal, solvent-free conditions is described. This new approach has advantages such as mild conditions, short reaction time, high yield, simple work-up, and an inexpensive catalyst.

Keywords 1-Carbamatoalkyl-2-naphthol · Three-component reaction · Tin compound · One-pot synthesis · Solvent-free

Introduction

Multicomponent reactions (MCRs) have gained much attention in organic synthesis, as they can furnish the desired products in a single operation without isolating the intermediates, thus reducing reaction times and energy consumption [1]. Therefore, researchers have made great efforts to find and develop new MCRs.

Compounds containing 1,3-amino-oxygenated functional groups are frequently found in biologically active natural products and potent drugs such as nucleoside antibiotics and HIV protease inhibitors [2–4]. Furthermore, 1-amidoalkyl-2-naphthols and 1-carbamatoalkyl-2-naphthols are important synthetic building blocks and are used as precursors for the synthesis of 1-aminomethyl-2-naphthol derivatives, which exhibit important cardiovascular activity [5]. Recently, we reported the reaction of 2-naphthol, aldehydes, and amides to form amidoalkyl naphthol derivatives [6]. In this paper, carbamate was used as a nucleophile instead of an amide. Moreover, carbamates can be deprotected more easily than an amide group [7]. Carbamatoalkyl naphthols can be present as protected aminonaphthol derivatives and, after deprotection, they can allow access to compounds which cannot be synthesized via the classical procedure. Therefore, the clean synthesis of 1-carbamatoalkyl-2-naphthols is very important.

To the best of our knowledge, only a few works have focused on the synthesis of 1-carbamatoalkyl-2-naphthols [8–22]. The reported methods suffer from disadvantages such as expensive catalysts, high temperatures, and large excesses of raw material. Recently, tin tetrachloride has emerged as an efficient Lewis acid for promoting various organic transformations, such as aromatization [23], heterocycloadditions [24], a coupling reaction [25], rearrangement of epoxides [26], oxidation [27], ring-opening reactions [28], and amidoalkylation [29]. As a continuation of our research into MCRs, we report here a facile and efficient synthetic strategy for preparing 1-carbamatoalkyl-2-naphthols **4** from 2-napthol (**1**), aldehydes **2**, and carbamates **3** in short reaction times and with excellent yields using tin tetrachloride ($SnCl_4{\cdot}5H_2O$) as a catalyst (Scheme 1). Thirteen new compounds were reported first.

Results and discussion

Initially, we investigated the efficiencies of different reaction media, amounts of catalyst, and reaction temperatures in a model reaction of 2-naphthol (1 equiv.), 2-nitrobenzaldehyde (1 equiv.), and methyl carbamate (1.1 equiv.) in the presence of $SnCl_4{\cdot}5H_2O$ (Table 1). It

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Scheme 1

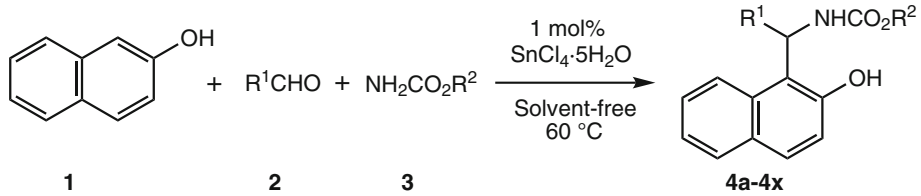


Table 1 Screening of reaction conditions for the condensation of 2-naphthol, 2-nitrobenzaldehyde, and methyl carbamate

Entry	Solvent/cm^3	Catalyst/mo%	Temp/°C	Time/h	Yield/%
1	H_2O (3)	2.0	70	2.0	0
2	EtOH (3)	2.0	Reflux	1.0	7
3	CH_3CN (3)	2.0	Reflux	3.0	49
4	–	2.0	70	0.1	92
5	–	1.0	70	0.1	91
6	–	0.5	70	0.25	90
7	–	1.0	50	0.3	90
8	–	1.0	60	0.2	94
9	–	1.0	80	0.1	87
10	–	0	70	4.0	0

Table 2 Reaction of 2-naphthol, 2-nitrobenzaldehyde, and methyl carbamate using different acid catalysts

Entry	Catalyst	Time/h	Yield/%
1	$SrCl_2·6H_2O$	3.0	0
2	$CdCl_2·2.5H_2O$	3.0	0
3	$Bi(NO_3)_3·5H_2O$	3.0	28
4	HOAc	8.0	43
5	$Al(NO_3)_3·9H_2O$	3.0	47
6	$ZnCl_2$	8.0	51
7	$AlCl_3·6H_2O$	2.5	58
8	$Al(CH_3SO_3)_3·4H_2O$	1.5	60
9	$Cu(p\text{-}CH_3C_6H_4SO_3)_2·6H_2O$	0.5	73
10	$(NH_4)_2Ce(NO_3)_6$	1.5	78
11	$SnCl_2·2H_2O$	0.3	87
12	$SnCl_4·5H_2O$	0.2	94

was found that solvent-free conditions were the best choice (Table 1, entries 1–4). Compared with reactions carried out in organic solvent, condensation without solvent required only 0.1 h to furnish an excellent yield (Table 1, entry 4). After screening several trials, the best results were obtained with 1 mol % $SnCl_4·5H_2O$ at 60 °C (Table 1, entry 8). In addition, no conversion to product was obtained in the absence of catalyst, even after 4.0 h (Table 1, entry 10).

Next, the catalytic activities of several Lewis acids (1 mol %) were compared with that of $SnCl_4·5H_2O$ in the same model reaction at 60 °C, the results were shown in Table 2. It could be noted that $SnCl_4·5H_2O$ was the most efficient catalyst, since it results in the highest conversion to the desired product in the shortest reaction time (Table 2, entry 12).

The scope of the reaction in the presence of $SnCl_4·5H_2O$ (1 mol %) under solvent-free conditions at 60 °C was studied (Table 3). A variety of aromatic aldehydes and aliphatic aldehydes, 2-naphthol, and different carbamates (including methyl carbamate, ethyl carbamate, and benzyl carbamate) were subjected to these reaction conditions. Most products were obtained in good to excellent yields. The aromatic aldehyde with an electron-withdrawing group reacted much more easily than the aromatic aldehyde with an electron-donating group (Table 3, entries 1–9). The position of the substituent on the aromatic ring did not have much of an effect on the yield of the product. The aliphatic aldehyde failed to yield any product (Table 3, entry 10). Besides methyl carbamate, ethyl carbamate and benzyl carbamate were studied in the amidoalkylation reaction; all of these showed good reactivity.

A possible mechanism for this transformation is proposed in Scheme 2. As reported in the literature [6], the reaction of 2-naphthol with aldehyde in the presence of an acid catalyst is known to give *ortho*-quinone methide (*o*-QM). The *o*-QM generated in situ reacted with carbamate via conjugate addition to form 1-carbamatoalkyl-2-naphthol derivative **4**.

Conclusion

In summary, $SnCl_4·5H_2O$ has been demonstrated to be a mild and efficient catalyst for the one-pot three-component reaction of 2-naphthol, aromatic aldehydes, and methyl/ethyl/benzyl carbamates under solvent-free conditions at 60 °C. Most reactions proceed within short reaction times and produce high yields. We believe that this method could be an attractive alternative to existing methods for the synthesis of 1-carbamatoalkyl-2-naphthols.

Experimental

Melting points were determined using an RY-1 micro-melting point apparatus (Tianjin Tianguang Optical

Table 3 Synthesis of carbamatoalkyl naphthols in the presence of $SnCl_4{\cdot}5H_2O$

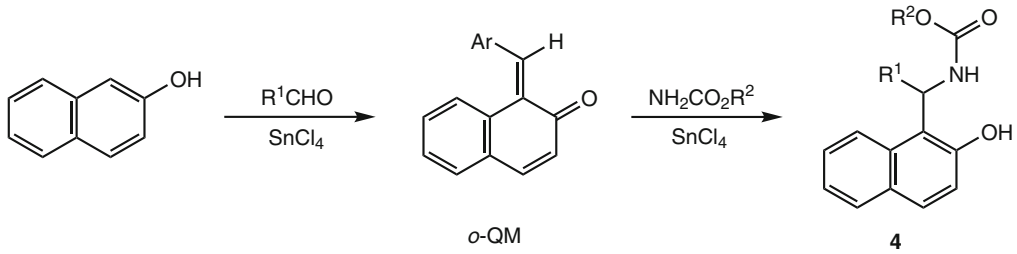
Entry	R^1	R^2	Time/h	Product	Yield/%	M.p. (lit. m.p.)/°C
1	C_6H_5	Me	0.2	**4a**	83	217–219 (217–218 [9])
2	2-$NO_2C_6H_4$	Me	0.2	**4b**	94	241–243 (241–242 [10])
3	3-$NO_2C_6H_4$	Me	0.1	**4c**	96	244–246 (253–255 [10])
4	4-$NO_2C_6H_4$	Me	0.1	**4d**	88	211–213 (206–208 [18])
5	2-ClC_6H_4	Me	0.1	**4e**	94	218–220
6	4-ClC_6H_4	Me	0.1	**4f**	90	202–204 (203–205 [10])
7	2,4-$Cl_2C_6H_3$	Me	0.2	**4g**	93	210–212
8	4-$CH_3C_6H_4$	Me	10.0	**4h**	Trace	–
9	4-$OCH_3C_6H_4$	Me	10.0	**4i**	Trace	–
10	$CH_3CH_2CH_2$	Me	10.0	**4j**	0	–
11	C_6H_5	Et	0.2	**4k**	87	203–204 (195–196 [16])
12	2-$NO_2C_6H_4$	Et	0.15	**4l**	90	214–216
13	3-$NO_2C_6H_4$	Et	0.1	**4m**	95	236–238
14	4-$NO_2C_6H_4$	Et	0.1	**4n**	90	229–231
15	2-ClC_6H_4	Et	0.15	**4o**	92	216–217
16	4-ClC_6H_4	Et	0.15	**4p**	93	217–219
17	2,4-$Cl_2C_6H_3$	Et	0.2	**4q**	91	196–198
18	C_6H_5	CH_2Ph	1.0	**4r**	89	182–184 (180–182 [10])
19	2-$NO_2C_6H_4$	CH_2Ph	0.7	**4s**	90	211–213
20	3-$NO_2C_6H_4$	CH_2Ph	0.2	**4t**	94	206–208 (205–207 [10])
21	4-$NO_2C_6H_4$	CH_2Ph	0.2	**4u**	92	202–204
22	2-ClC_6H_4	CH_2Ph	0.3	**4v**	90	211–213
23	4-ClC_6H_4	CH_2Ph	0.5	**4w**	88	173–175
24	2,4-$Cl_2C_6H_3$	CH_2Ph	0.2	**4x**	87	211–213

Instrument Ltd. Co., Tianjin City, China). Infrared spectra were recorded on a Varian (Palo Alto, CA, USA) Scimitar 2000 series Fourier transform instrument. ^1H and ^{13}C NMR spectra were recorded on an Agilent (Santa Clara, CA, USA) 400-MR instrument in DMSO-d_6 using TMS as an internal standard. Mass spectra were obtained with an Agilent 1100 series LC/MSD VL ESI instrument. Elemental analyses (C, H, N) were conducted using the EA 2400II elemental analyzer (PerkinElmer, Waltham, MA, USA), and the results obtained were found to be in good agreement (±0.3 %) with the calculated values.

General procedure for the synthesis of 1-carbamatoalkyl-2-naphthol derivatives ***4***

$SnCl_4{\cdot}5H_2O$ (0.05 mmol) was added to a mixture of 2-naphthol (**1**, 5 mmol), aldehyde **2** (5 mmol), and carbamate **3** (5.5 mmol). The reaction mixture was magnetically stirred at 60 °C in a water bath and the reaction was followed by TLC. After completion, the mixture was cooled to room temperature, washed with cold water, and recrystallized from aqueous EtOH (60 %, v/v). The products were characterized by IR, ^1H NMR, ^{13}C NMR, LC/MS, and elemental analysis.

Scheme 2



Methyl [(2-chlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4e**, $C_{19}H_{16}ClNO_3$)
White solid; IR (KBr): $\bar{\nu}$ = 3,431, 3,220, 1,690, 1,527, 1,340, 1,052, 819, 753, 706 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 9.96 (s, 1H, OH), 8.04 (d, 1H, J = 8.2 Hz, NH), 7.86 (d, 1H, J = 7.1 Hz, ArH), 7.77 (dd, 2H, J = 17.4, 8.3 Hz, ArH), 7.52 (d, 1H, J = 4.6 Hz, ArH), 7.40 (dd, 2H, J = 12.3, 6.8 Hz, ArH), 7.26 (d, 3H, J = 13.9 Hz, ArH), 7.16 (d, 1H, J = 8.6 Hz, ArH), 6.91 (d, 1H, J = 7.8 Hz, CH), 3.54 (s, 3H, OCH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.5, 153.9, 139.8, 133.0, 132.9, 130.3, 129.9, 129.7, 129.0, 128.8, 128.7, 126.9, 126.7, 123.3, 122.7, 119.0, 117.4, 51.9, 50.1 ppm; LC/MS: *m/z* (%) = 340 [$(M–H)^-$, 100].

Methyl [(2,4-dichlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4g**, $C_{19}H_{15}Cl_2NO_3$)
White solid; IR (KBr): $\bar{\nu}$ = 3,403, 3,260, 1,678, 1,519, 1,062, 873, 753, 718 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 9.97 (s, 1H, OH), 8.02 (d, 1H, J = 8.5 Hz, NH), 7.96 (d, 1H, J = 7.8 Hz, ArH), 7.78 (dd, 2H, J = 17.8, 8.4 Hz, ArH), 7.57–7.38 (m, 4H, ArH), 7.28 (t, 1H, J = 7.3 Hz, ArH), 7.14 (d, 1H, J = 8.7 Hz, ArH), 6.85 (d, 1H, J = 8.0 Hz, CH), 3.55 (s, 3H, OCH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.6, 154.0, 139.3, 133.6, 133.0, 132.3, 131.6, 130.1, 129.0, 128.9, 128.6, 127.0, 126.9, 123.0, 122.8, 118.9, 116.7, 52.0, 49.8 ppm; LC/MS: *m/z* (%) = 375 [$(M–H)^-$, 100].

Ethyl [(2-nitrophenyl)(2-hydroxynaphthalen-1-yl)methyl]-carbamate (**4l**, $C_{20}H_{18}N_2O_5$)
White solid; IR (KBr): $\bar{\nu}$ = 3,402, 3,277, 1,686, 1,530, 1,334, 1,038, 813, 744, 697 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 9.79 (s, 1H, OH), 7.92 (d, 1H, J = 8.6 Hz, NH), 7.81–7.72 (m, 4H, ArH), 7.64–7.58 (m, 2H, ArH), 7.44 (dt, 2H, J = 17.0, 6.0 Hz, ArH), 7.29–7.26 (m, 2H, ArH), 7.05 (d, 1H, J = 8.7 Hz, CH), 4.04 (q, 2H, J = 7.0 Hz, CH_2), 1.15 (t, 3H, J = 7.0 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.4, 154.0, 149.0, 136.9, 133.3, 132.5, 130.3, 129.4, 128.9, 128.5, 128.1, 126.9, 124.4, 123.0, 122.8, 118.8, 116.5, 60.5, 48.1, 15.0 ppm; LC/MS: *m/z* (%) = 365 [$(M–H)^-$, 100].

Ethyl [(3-nitrophenyl)(2-hydroxynaphthalen-1-yl)methyl]-carbamate (**4m**, $C_{20}H_{18}N_2O_5$)
White solid; IR (KBr): $\bar{\nu}$ = 3,395, 3,277, 1,678, 1,527, 1,348, 1,045, 808, 752, 701 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.24 (s, 1H, OH), 8.13 (d, 1H, J = 8.2 Hz, NH), 8.07 (d, 1H, J = 8.1 Hz, ArH), 7.98 (d, 1H, J = 7.8 Hz, ArH), 7.82 (t, 3H, J = 8.4 Hz, ArH), 7.64 (d, 1H, J = 7.8 Hz, ArH), 7.56 (t, 1H, J = 8.0 Hz, ArH), 7.44 (t, 1H, J = 7.5 Hz, ArH), 7.31 (t, 1H, J = 7.5 Hz, ArH), 7.23 (d, 1H, J = 8.8 Hz, ArH), 6.97 (d, 1H, J = 7.8 Hz, CH), 4.08 (q, 2H, J = 6.8 Hz, CH_2), 1.18 (t, 3H, J = 6.8 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.7, 153.5, 148.1, 145.5, 133.2, 132.3, 130.3, 130.1, 129.1, 128.7, 127.2, 123.5, 123.1, 121.9, 120.9, 118.8, 118.3, 60.7, 50.3, 15.0 ppm; LC/MS: *m/z* (%) = 365 [$(M–H)^-$, 100].

Ethyl [(4-nitrophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4n**, $C_{20}H_{18}N_2O_5$)
White solid; IR (KBr): $\bar{\nu}$ = 3,430, 3,185, 1,685, 1,518, 1,350, 1,049, 821, 739, 708 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.21 (s, 1H, OH), 8.15 (d, 2H, J = 8.8 Hz, ArH), 7.94–7.73 (m, 4H, NH and ArH), 7.49 (d, 2H, J = 8.6 Hz, ArH), 7.43 (t, 1H, J = 7.5 Hz, ArH), 7.30 (t, 1H, J = 7.5 Hz, ArH), 7.23 (d, 1H, J = 8.8 Hz, ArH), 6.97 (d, 1H, J = 7.7 Hz, CH), 4.07 (q, 2H, J = 6.7 Hz, CH_2), 1.17 (t, 3H, J = 6.7 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.7, 153.5, 151.1, 146.4, 132.3, 130.3, 129.0, 128.8, 127.5, 127.2, 123.8, 123.2, 123.0, 118.8, 118.4, 60.7, 50.5, 15.0 ppm; LC/MS: *m/z* (%) = 365 [$(M–H)^-$, 100].

Ethyl [(2-chlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4o**, $C_{20}H_{18}ClNO_3$)
White solid; IR (KBr): $\bar{\nu}$ = 3,420, 3,229, 1,685, 1,525, 1,336, 1,051, 821, 753, 706 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.19 (s, 1H, OH), 8.28 (d, 1H, J = 8.5 Hz, NH), 8.04–7.97 (m, 3H, ArH), 7.77 (d, 1H, J = 5.9 Hz, ArH), 7.66–7.48 (m, 5H, ArH), 7.39 (d, 1H, J = 8.7 Hz, ArH), 7.15 (d, 1H, J = 8.3 Hz, CH), 4.22 (q, 2H, J = 7.1 Hz, CH_2), 1.36 (t, 3H, J = 7.1 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.1, 153.9, 139.8, 133.0, 132.9, 130.3, 129.9, 129.7, 129.0, 128.8, 128.6, 126.9, 126.7, 123.3, 122.7, 119.0, 117.5, 60.3, 50.0, 15.0 ppm; LC/MS: *m/z* (%) = 354 [$(M–H)^-$, 100].

Ethyl [(4-chlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4p**, $C_{20}H_{18}ClNO_3$)
White solid; IR (KBr): $\bar{\nu}$ = 3,424, 3,197, 1,676, 1,517, 1,329, 1,042, 821, 751, 711 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.15 (s, 1H, OH), 7.93 (d, 1H, J = 8.3 Hz, NH), 7.80 (dd, 2H, J = 12.8, 6.8 Hz, ArH), 7.58 (d, 1H, J = 8.2 Hz, ArH), 7.41 (t, 1H, J = 7.3 Hz, ArH), 7.33–7.22 (m, 6H, ArH), 6.87 (d, 1H, J = 8.1 Hz, CH), 4.05 (q, 2H, J = 7.2 Hz, CH_2), 1.17 (t, 3H, J = 6.9 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.6, 153.3, 141.9, 132.3, 131.4, 130.0, 129.0, 128.7, 128.4, 128.3, 127.4, 127.1, 123.6, 123.0, 118.8, 60.7, 50.2, 14.9 ppm; LC/MS: *m/z* (%) = 354 [$(M–H)^-$, 100].

Ethyl [(2,4-dichlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4q**, $C_{20}H_{17}Cl_2NO_3$)
White solid; IR (KBr): $\bar{\nu}$ = 3,412, 3,071, 1,683, 1,514, 1,336, 1,052, 815, 743, 721 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 9.93 (s, 1H, OH), 8.04 (d, 1H,

$J = 8.6$ Hz, NH), 7.81–7.75 (m, 3H, ArH), 7.58 (d, 1H, $J = 8.5$ Hz, ArH), 7.49 (d, 1H, $J = 1.5$ Hz, ArH), 7.44 (t, 1H, $J = 7.5$ Hz, ArH), 7.38 (dd, 1H, $J = 6.8$, 1.8 Hz, ArH), 7.28 (t, 1H, $J = 7.4$ Hz, ArH), 7.14 (d, 1H, $J = 8.8$ Hz, ArH), 6.86 (d, 1H, $J = 8.1$ Hz, CH), 3.98 (q, 2H, $J = 6.7$ Hz, CH_2), 1.14 (t, 3H, $J = 6.4$ Hz, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 156.1$, 154.0, 139.3, 133.5, 132.9, 132.3, 131.6, 130.1, 129.0, 129.0, 128.6, 127.0, 126.9, 123.1, 122.8, 119.0, 116.8, 60.4, 49.7, 15.0 ppm; LC/MS: *m/z* (%) = 389 [(M–H)$^-$, 100].

Benzyl [(2-nitrophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4s**, $C_{25}H_{20}N_2O_5$)
White solid; IR (KBr): $\bar{\nu} = 3{,}424$, 3,250, 1,702, 1,527, 1,334, 1,046, 835, 752, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 9.81$ (s, 1H, OH), 8.08 (d, 1H, $J = 7.9$ Hz, NH), 7.94 (d, 1H, $J = 8.2$ Hz, ArH), 7.79 (d, 1H, $J = 8.0$ Hz, ArH), 7.74 (t, 2H, $J = 7.3$ Hz, ArH), 7.62–7.26 (m, 11H, ArH), 7.08 (d, 1H, $J = 8.5$ Hz, CH), 5.12 (d, 1H, $J = 12.8$ Hz, CH_2), 5.06 (d, 1H, $J = 12.8$ Hz, CH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 156.3$, 154.1, 149.0, 137.5, 136.9, 133.3, 132.5, 130.4, 129.7, 129.4, 128.9, 128.7, 128.5, 128.2, 128.1, 127.8, 127.2, 127.0, 124.5, 123.0, 122.9, 118.8, 116.4, 65.9, 48.3 ppm; LC/MS: *m/z* (%) = 427 [(M-H)$^-$, 100].

Benzyl [(4-nitrophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4u**, $C_{25}H_{20}N_2O_5$)
White solid; IR (KBr): $\bar{\nu} = 3{,}414$, 3,064, 1,686, 1,515, 1,347, 1,049, 825, 745, 695 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 10.21$ (s, 1H, OH), 8.15 (d, 2H, $J = 8.7$ Hz, ArH), 7.99 (d, 1H, $J = 6.6$ Hz, NH), 7.93 (d, 1H, $J = 6.4$ Hz, ArH), 7.82 (t, 2H, $J = 8.7$ Hz, ArH), 7.50 (d, 2H, $J = 8.5$ Hz, ArH), 7.41–7.28 (m, 7H, ArH), 7.24 (d, 1H, $J = 8.8$ Hz, ArH), 7.01 (d, 1H, $J = 7.8$ Hz, CH), 5.14 (d, 1H, $J = 12.6$ Hz, CH_2), 5.08 (d, 1H, $J = 12.6$ Hz, CH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 156.6$, 153.5, 151.1, 146.5, 137.2, 132.3, 130.3, 129.0, 128.8, 128.7, 128.2, 127.5, 127.2, 123.8, 123.3, 123.0, 118.7, 118.3, 66.3, 50.6 ppm; LC/MS: *m/z* (%) = 427 [(M–H)$^-$, 100].

Benzyl [(2-chlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4v**, $C_{25}H_{20}ClNO_3$)
White solid; IR (KBr): $\bar{\nu} = 3{,}421$, 3,170, 1,700, 1,518, 1,336, 1,050, 820, 754, 694 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 9.96$ (s, 1H, OH), 8.04 (d, 2H, $J = 7.8$ Hz, ArH), 7.81–7.75 (m, 2H, NH and ArH), 7.52–7.25 (m, 10H, ArH), 7.16 (d, 2H, $J = 7.3$ Hz, ArH), 6.94 (d, 1H, $J = 5.8$ Hz, CH), 5.09 (d, 1H, $J = 12.0$ Hz, CH_2), 5.01 (d, 1H, $J = 12.0$ Hz, CH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 156.0$, 153.9, 139.7, 137.6, 133.0, 132.9, 130.3, 129.9, 129.7, 129.0, 128.9, 128.7, 128.1, 127.8, 126.9, 126.7, 123.3, 122.7, 118.9, 117.3, 65.8, 50.1 ppm; LC/MS: *m/z* (%) = 416 [(M–H)$^-$, 100].

Benzyl [(4-chlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4w**, $C_{25}H_{20}ClNO_3$)
White solid; IR (KBr): $\bar{\nu} = 3{,}402$, 3,200, 1,681, 1,515, 1,321, 1,042, 813, 746, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 10.15$ (s, 1H, OH), 7.93 (d, 1H, $J = 8.2$ Hz, NH), 7.82–7.77 (m, 3H, ArH), 7.39-7.23 (m, 12H, ArH), 6.90 (d, 1H, $J = 8.1$ Hz, CH), 5.11 (d, 1H, $J = 12.6$ Hz, CH_2), 5.01 (d, 1H, $J = 12.6$ Hz, CH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 156.5$, 153.4, 141.8, 137.3, 132.3, 131.3, 129.9, 129.0, 128.9, 128.7, 128.4, 128.3, 128.2, 127.4, 127.0, 123.7, 123.4, 122.8, 119.0, 118.7, 66.1, 50.3 ppm; LC/MS: *m/z* (%) = 416 [(M–H)$^-$, 100].

Benzyl [(2,4-dichlorophenyl)(2-hydroxynaphthalen-1-yl)-methyl]carbamate (**4x**, $C_{25}H_{19}Cl_2NO_3$)
White solid; IR (KBr): $\bar{\nu} = 3{,}416$, 3,066, 1,686, 1,522, 1,341, 1,055, 819, 744, 719 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 9.92$ (s, 1H, OH), 8.06–8.01 (m, 2H, NH and ArH), 7.80 (d, 1H, $J = 8.0$ Hz, ArH), 7.75 (d, 1H, $J = 8.8$ Hz, ArH), 7.56 (d, 1H, $J = 8.4$ Hz, ArH), 7.50–7.26 (m, 9H, ArH), 7.14 (d, 1H, $J = 8.7$ Hz, ArH), 6.87 (d, 1H, $J = 6.7$ Hz, CH), 5.09 (d, 1H, $J = 12.8$ Hz, CH_2), 5.01 (d, 1H, $J = 12.8$ Hz, CH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 156.0$, 154.0, 139.2, 137.5, 133.6, 133.0, 132.3, 131.6, 130.1, 129.1, 129.0, 128.7, 128.6, 128.1, 127.9, 127.0, 126.9, 123.1, 122.8, 119.0, 116.6, 65.8, 49.8 ppm; LC/MS: *m/z* (%) = 451 [(M–H)$^-$, 100].

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References

1. Csütörtöki R, Szatmári I, Mándi A, Kurtán T, Fülöp F (2011) Synlett 22:1940
2. Knapp S (1995) Chem Rev 95:1859
3. Juaristi E (1997) Enantioselective synthesis of β-amino acids. Wiley, New York
4. Dingermann T, Steinhilber D, Folkers G (2004) Molecular biology in medicinal chemistry. Wiley-VCH, Weinheim
5. Shen AY, Tsai CT, Chen CL (1999) Eur J Med Chem 34:877
6. Wang M, Liang Y (2011) Monatsh Chem 142:153
7. Green W, Wuts PGM (1999) Protecting groups in organic synthesis, 2nd edn. Wiley, New York
8. Mosslemin MH, Nateghi MR, Mohebat R (2008) Monatsh Chem 139:1247
9. Shaterian HR, Hosseinian A, Ghashang MA (2008) Tetrahedron Lett 49:5804
10. Tavakoli-Hoseini N, Heravi MM, Bamoharran FF, Davoodnia A (2011) Bull Korean Chem Soc 32:787

11. Reza SH, Asghar H, Majid G (2009) Chin J Chem 27:821
12. Heravi MM, Tavakoli-Hoseini N, Bamoharram FF (2010) Green Chem Lett Rev 3:263
13. Shaterian HR, Hosseinian A, Ghashang M (2009) Synth Commun 39:2560
14. Kundu D, Majee A, Hajra A (2010) Catal Commun 11:1157
15. Tamaddon F, Bistgani JM (2011) Synlett 22:2947
16. Deshmukh KM, Qureshi ZS, Patil YP, Bhanage BM (2012) Synth Commun 42:93
17. Yarahmadi H, Shaterian HR (2012) J Chem Res 36:52
18. Shafiee MRM, Moloudi R, Ghashang M (2011) J Chem Res 35:622
19. Zare A, Yousofi T, Moosavi-Zare AR (2012) RSC Adv 2:7988
20. Zare A, Akbarzadeh S, Foroozani E, Kaveh H, Moosavi-Zare AR, Hasaninejad A, Mokhlesi M, Beyzavi MH, Zolfigol MA (2012) J Sulfur Chem 33:259
21. Khazaei A, Zolfigol MA, Moosavi-Zare AR, Abi F, Zare A, Kaveh H, Khakyzadeh V, Kazem-Rostami M, Parhami A, Torabi-Monfared H (2013) Tetrahedron 69:212
22. Csütörtöki R, Szatmári I, Koch A, Heydenreich M, Kleinpeter E, Fülöp F (2011) Tetrahedron 67:8564
23. Bigdeli MA, Rahmati A, Abbasi-Ghadim H, Mahdavinia GH (2007) Tetrahedron Lett 48:4575
24. Dujardin G, Martel A, Brown E (1998) Tetrahedron Lett 39:8647
25. Jing HW, Nguyen ST (2007) J Mol Catal A 261:12
26. Kita Y, Matsuda S, Inoguchi R, Ganesh JK, Fujioka H (2005) Tetrahedron Lett 46:89
27. Takeya T, Doi H, Ogata T, Okamoto I, Kotani E (2004) Tetrahedron 60:9049
28. Savushkina GP, Ivanov VV, Yenikolopyan NS (1975) Vysokomol Soyed A17:865
29. Wang M, Liang Y, Zhang TT, Gao JJ (2012) Chem Nat Compd 48:185