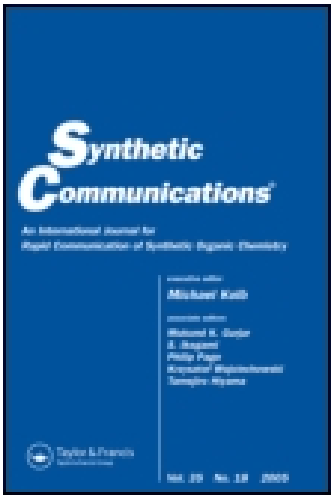

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Synthesis of New and Novel N-Protected 1-Aminoalkyl-2-naphthol Derivatives

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Synthesis of New and Novel N-Protected 1-Aminoalkyl-2-naphthol Derivatives

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Abstract: A series of three-component reactions has been carried out using $HClO_4$-SiO_2 as a versatile heterogeneous catalyst. A series of new and novel N-protected 1-aminoalkyl-2-naphthol derivatives have been prepared under thermal solvent-free reaction conditions. In all cases, the reaction conditions were very simple and high-yielding.

Keywords: Carbamate, heterogeneous catalyst, 2-naphthol, N-protected 1-aminoalkyl-2-naphthol, silica perchloric acid ($HClO_4$-SiO_2)

INTRODUCTION

Compounds bearing 1,3-amino-oxygenated functional motifs are ubiquitous to a variety of biologically important natural products and potent drugs, including a number of nucleoside antibiotics and HIV protease inhibitors, such as ritonavir and lipinavir.[1] It is noteworthy that N-protected 1-aminoalkyl-2-naphthols can be converted to important biologically active 1-aminomethyl- 2-naphthol derivatives by amide hydrolysis reaction. The hypotensive and bradycardiac effects of these compounds have been evaluated.[2]

It is noteworthy that aminotetraline derivatives manifest a number of important and therapeutically useful biological activities such as

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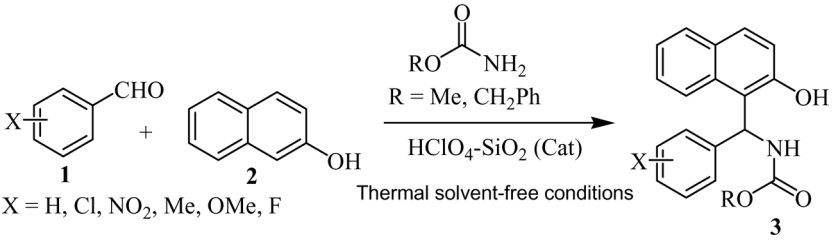


Scheme 1. One-pot preparation of N-protected 1-aminoalkyl-2-naphthol derivatives using silica perchloric acid ($HClO_4$-SiO_2) as catalyst.

antidepressant, immunomodulating and antitumor activities.[3] Despite this broad range of applications, only a few members of this family of compounds have been reported. The development of new methods for their assembly is therefore of considerable synthetic importance.[4]

Recently, we have reported the reaction of 2-naphthol, aromatic aldehyde, and amides in the presence of silica-supported perchloric acid ($HClO_4$-SiO_2) to form amidoalkyl naphthol derivatives. The reaction proceeds through the in situ formation of ortho-quinone methides (*o*-QMs), and amide acted as a nucleophile. Carbamates instead of amides in the reaction produced N-protected 1-aminoalkyl-2-naphthols. Carbamates, which can be deprotected more easily than the amide group,[5] are important for preparation of biologically active 1-aminomethyl-2-naphthol derivatives.[3,4] Silica-supported perchloric acid as a recyclable solid acid catalyst was prepared from the reaction of silica gel with perchloric acid. The catalyst has been used in some organic reactions.[6]

With the aim of developing more efficient synthetic processes, we herein describe a practical, inexpensive method for the preparation of new N-protected 1-aminoalkyl-2-naphthol derivatives via three-component condensation reaction of aryl aldehydes, 2-naphthol, and carbamates in the presence of silica-supported perchloric acid as catalyst under thermal solvent-free conditions (Scheme 1).

RESULTS AND DISCUSSION

To choose the optimal conditions, first we tried to prepare methyl (2-hydroxynaphthalen-1-yl)(phenyl)methyl carbamate from the reaction of benzaldehyde (1 equiv.), 2-naphthol (1 equiv.), and methyl carbamate (1.2 equiv.) as a model in the absence and also presence of a catalyst under thermal solvent-free conditions (Table 1). As shown from Table 1, this transformation requires a catalyst, and the best result was

Table 1. Optimization amount of $HClO_4$-SiO_2 and reaction temperature for preparation of methyl (2-hydroxynaphthalen-1-yl)(phenyl)methylcarbamate under thermal solvent-free conditions

Entry	Catalyst (mol%)[a]	Temperature (°C)	Time (min)	Yield (%)[b]
1	1.5	110	4.0	75
2	2.5	110	3.0	83
3	3.5	110	2.5	85
4	5.0	110	2.5	82
5	3.5	75	6.0	77
6	3.5	85	5.0	90

[a]0.07 g of $HClO_4$-SiO_2 equal to 0.035 mmol of H^+, and the molar ratio of the catalyst to substrate is 3.5 mol%.

[b]Yields refer to the isolated pure product, and the molar ratio of benzaldehyde/2-naphthol/methyl carbamate is 1/1/1.2.

obtained by carrying out the reaction using 3.5 mol% (0.07 g, 0.035 mmol H^+)[6a] of $HClO_4$-SiO_2 at 85°C under solvent-free conditions (Table 1).

Using these optimized reaction conditions, the scope and efficiency of these procedures were explored for the synthesis of a wide variety of new and novel substituted N-protected 1-aminoalkyl-2-naphthols using various aryl aldehydes, 2-naphthols, and methyl/benzyl carbamates. The results are summarized in Table 2.

As shown in Table 2, the direct three-component reactions worked well with a variety of aryl aldehydes including those bearing electron-withdrawing and electron-donating groups such as OMe, Cl, F, and NO_2, and the desired compounds were obtained in good yields.

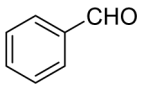
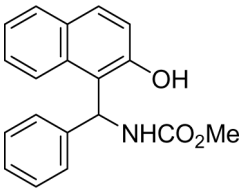
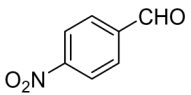
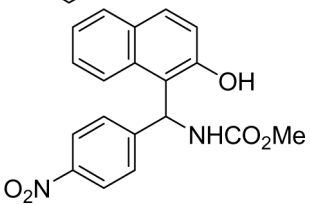
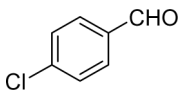
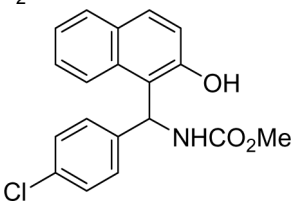
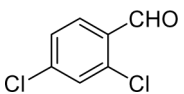
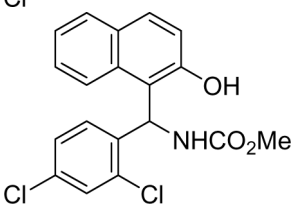
Under the same conditions, this reaction almost could not be observed when the aliphatic compounds such as propionaldehyde (Table 2, entry 8) and 2-pyridinecarbaldehyde (Table 2, entry 9) were used as a starting material.

As reported in literature,[6f] the reaction of 2-naphthol with aromatic aldehydes in the presence of an acidic catalyst is known to give *o*-QMs. The same *o*-QMs, generated insitu, have been reacted with carbamate to form N-protected 1-aminoalkyl-2-naphthol derivatives (Scheme 2).

In the absence of the catalyst, no reactions occurred, and all of staring of materials was intact. Gas chromatography (GC) and thin-layer chromatography (TLC) verified this phenomenon. Thus, this evidence confirms that a catalyst is needed to drive each step of the reactions.

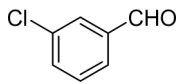
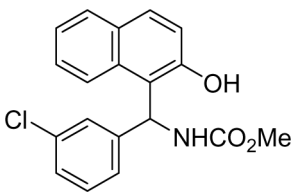
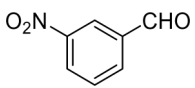
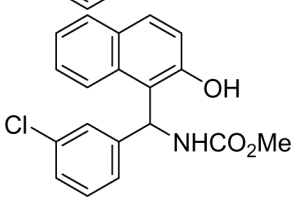
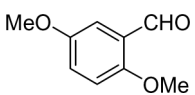
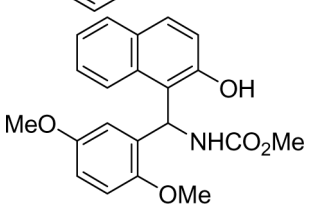
Although these compounds have an unsymmetrical center and seems to show optical activity, the formation of *o*-QMs with planar structure in the reaction processes cause preparation of racemic mixtures, and none of the products would have any optical activity in the polarimeter instrument.

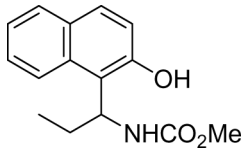
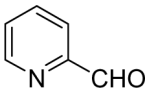
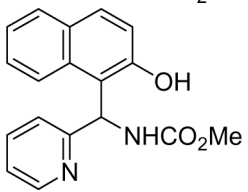
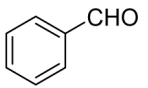
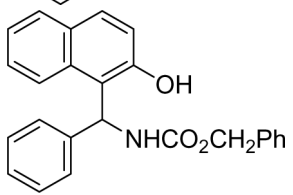
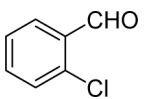
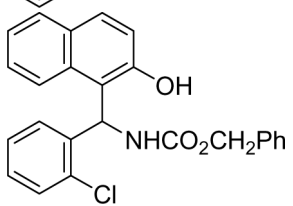
Table 2. Preparation of N-protected 1-aminoalkyl-2-naphthols using $HClO_4$-SiO_2 as catalyst under thermal solvent-free conditions

Entry	Aldehyde **1**	Carbamate **2**	Product(s) **3**	Time (min)	Yield[a] (%)	Mp (°C)
1		H_2NCO_2Me		5.0	90–92[b]	217–218
2		H_2NCO_2Me		2.5	93	205–207
3		H_2NCO_2Me		4.0	79	198–200
4		H_2NCO_2Me		8.5	78	192 dec

(*Continued*)

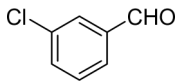
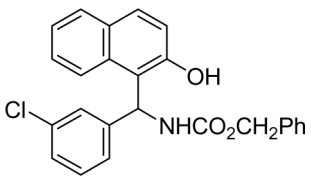
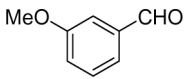
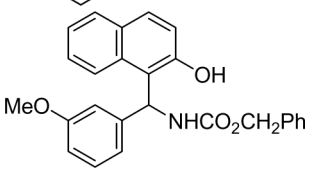
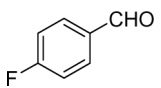
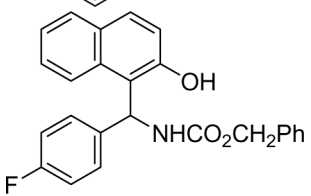
Table 2. Continued

Entry	Aldehyde **1**	Carbamate **2**	Product(s) **3**	Time (min)	Yield[a] (%)	Mp (°C)
5		H_2NCO_2Me		6.0	80	196–198
6		H_2NCO_2Me		2.0	92	252 dec
7		H_2NCO_2Me		3.0	88	215 dec

8	CH_3CH_2CHO	H_2NCO_2Me		—	—	—
9		H_2NCO_2Me		—	—	—
10		$H_2NCO_2CH_2Ph$		8.5	80	179–180
11		$H_2NCO_2CH_2Ph$		20	76	163–165

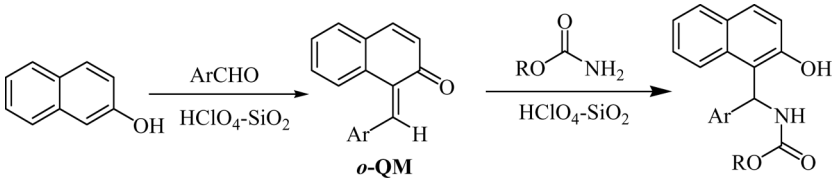
(*Continued*)

Table 2. Continued

Entry	Aldehyde **1**	Carbamate **2**	Product(s) **3**	Time (min)	Yield[a] (%)	Mp (°C)
12		$H_2NCO_2CH_2Ph$		5.0	83	203 dec
13		$H_2NCO_2CH_2Ph$		11	90	182–184
14		$H_2NCO_2CH_2Ph$		8.5	84	185–186

[a]Yields refer to the isolated pure products; the reaction was carried out under thermal solvent-free conditions in an oil bath at 85°C. The molar ratio of aldehydes/2-naphthol/methyl or benzyl carbamate/catalyst was 1/1/1.2/0.035.

[b]Isolated yields after five catalyst recoveries.



Scheme 2. Suggested mechanism for preparation of N-protected 1-aminoalkyl-2-naphthol.

When a heterogeneous catalyst was used, an important issue is the deactivation, reusability, and recyclability of the catalyst because of the possibility of recycling the catalyst, especially for large-scale operations. To test this, a series of five consecutive runs of the reaction of benzaldehyde, 2-naphthol, and methyl carbamate with the silica perchloric as catalyst were carried out (Table 2, entry 1). When the reaction was complete, the catalyst was recovered and reused for the same reaction. For this purpose, the catalyst was recovered after each run, washed with ethanol, dried in an oven at 100°C for 30 min prior to use, and tested for its activity in the subsequent run. Fresh catalyst was not added. The solid catalyst was tested for five runs and recycled in 92% average yield. It demonstrates that there is no significant change in the activity of the catalyst and no significant loss of product yield. Furthermore, there is no change in the infrared spectroscopy (IR) of the fresh catalyst and the catalyst after its fifth use; this indicates that no loss of any organic functionality has taken place during repeated chemical reactions. Thus, this makes the process still more cost-effective.

CONCLUSION

In conclusion, we have developed a novel and highly efficient methodology for the synthesis of new and novel N-protected 1-aminoalkyl-2-naphthol derivatives from arylaldehydes, 2-naphthol, and methyl/benzyl benzyl carbamate under solvent-free conditions.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and are used without further purification. Silica perchloric acid was prepared according to the reported procedure.[6a] All yields refer to isolated products after purification. Products were characterized by spectroscopic data (IR,

NMR spectra) and melting points with authentic samples. The NMR spectra were recorded on a Bruker Avance DEX-300 MHz instrument. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. The spectra were measured in dimethyl sulfoxide (DMSO-d_6) relative to tetramethylsilane (TMS) (0.00 ppm). IR spectra were recorded on a Jasco Fourier transform (FT)–IR 460+ spectrophotometer. All of the compounds were solid, and solid-state IR spectra were recorded using the KBr disk technique. Mass spectra (MS) were recorded on an Agilent Technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV. Melting points were determined in open capillaries with a Buchi 510 melting-point apparatus. TLC was performed on silica-gel polygram SIL G/UV 254 plates.

Preparation of SiO_2-$HClO_4$

We prepared SiO_2-$HClO_4$ according to the procedure first reported by Chakraborti and coworkers.[6a] $HClO_4$ (1.25 g, 12.5 mmol, as a 70% aqueous solution) was added to the suspension of silica gel (23.75 g, 230–400 mesh) in Et_2O. The mixture was concentrated, and the residue was heated at 100°C for 72 h under vacuum to afford $HClO_4$-SiO_2 (0.5 mmol g^{-1}).

The amount of H^+ in the SiO_2-$HClO_4$ was determined by acid–base titration according to the following reaction [Eq. (1)]:

$$SiO_2\text{-}HClO_4 + H_2O \longrightarrow SiO_2\text{-}ClO_4^{\ominus} + H_3O^{\oplus} \quad (1)$$

The librated H_3O^+ was titrated by standard NaOH, and the amount of H^+ in SiO_2-$HClO_4$ was calculated (1 g of SiO_2-$HClO_4$ equal to 0.5 mmol H^+).

General Procedure for Preparation of N-Protected 1-Aminoalkyl-2-naphthol Derivatives

Silica-supported perchloric acid (0.07 g, 0.035 mmol H^+)[6a] was added to a mixture of 2-naphthol (1 mmol), aldehydes (1 mmol), and methyl/benzyl carbamate (1.2 mmol). The mixture was stirred at 85°C in an oil bath, and the reaction was followed by TLC. After completion, the mixture was cooled at room temperature, and then the solid was isolated and dissolved in EtOH. The catalyst was collected by filtration and washed with ethanol (3×10 ml), while the filtrate was concentrated under reduced pressure to furnish the crude product. The solid crude product was purified by recrystallization from aqueous EtOH (20%). Spectral data of the products are given in the next section.

Data

Methyl (2-Hydroxynaphthalen-1-yl)(phenyl)methyl Carbamate (Table 2, entry 1)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.57 (s, 3H), 6.87 (d, J = 8.4 Hz, 1H), 7.18–7.29 (m, 7H), 7.38 (d, J = 7.4 Hz, 1H), 7.65–7.84 (m, 3H), 7.92 (d, J = 7.7 Hz, 1H), 10.12 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 50.8, 52.1, 118.9, 119.3, 123.0, 123.5, 126.5, 126.8, 127.0, 128.6, 128.8, 129.0, 129.8, 132.5, 142.8, 153.4, 157.0 ppm; IR (KBr, cm^{-1}): 3423, 3202, 1677, 1630, 1585, 1518, 1438, 1335, 1272, 1066, 1042, 937, 811, 743, 697; MS (EI, 70 eV): m/z (%) = 307 (M^+, 13), 295 (9), 279 (15), 232 (79), 231 (100), 202 (16), 167 (31), 149 (76), 115 (10), 104 (10), 71 (14), 57 (18), 43 (10). Anal. calcd. for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56%. Found: C, 74.23; H, 5.57; N, 4.52%.

Methyl (2-Hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl Carbamate (Table 2, entry 2)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.60 (s, 3H), 6.95 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.78–7.87 (m, 4H), 8.15 (d, J = 8.6 Hz, 2H), 10.22 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 50.6, 52.3, 118.4, 118.8, 123.1, 123.3, 123.8, 127.3, 127.6, 128.8, 129.1, 130.4, 132.4, 146.5, 151.2, 153.6, 157.2 ppm; IR (KBr, cm^{-1}): 3422, 3265, 1683, 1628, 1604, 1518, 1438, 1346, 1272, 1247, 1068, 1046, 852, 823, 782, 741, 704; MS (EI, 70 eV): m/z (%) = 352 (M^+, 17), 276 (21), 260 (85), 231 (36), 230 (100), 202 (25), 115 (10). Anal. calcd. for $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95%. Found: C, 64.75; H, 4.58; N, 7.91%.

Methyl (4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl Carbamate (Table 2, entry 3)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.57 (s, 3H), 6.84 (d, J = 8.2 Hz, 1H), 7.20–7.41 (m, 7H), 7.71–7.81 (m, 3H), 7.89 (d, J = 7.3 Hz, 1H, NH), 10.16 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 50.3, 52.1, 118.9, 123.0, 123.4, 127.1, 128.4, 128.5, 128.8, 129.1, 130.0, 131.4, 132.4, 141.9, 153.4, 157.1 ppm; IR (KBr, cm^{-1}): 3422, 3225, 2951, 1685, 1629, 1583, 1516, 1491, 1438, 1330, 1273, 1245, 1182, 1144, 1088, 1014, 963, 852, 807, 749, 708; MS (EI, 70 eV): m/z (%) = 341 (M^+, 7), 266 (33), 265 (50), 231 (100), 202 (18). Anal. calcd for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10%. Found: C, 66.71; H, 4.68; N, 4.10%.

Methyl (2,4-Dichlorophenyl)(2-hydroxynaphthalen-1-yl)methyl Carbamate (Table 2, entry 4)

^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 3.54$ (s, 3H), 6.83 (d, $J = 8.1$ Hz, 1H), 7.13 (d, $J = 8.9$ Hz, 1H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.38–7.57 (m, 4H), 7.75 (d, $J = 8.7$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H, NH), 8.01 (d, $J = 8.6$ Hz, 1H), 9.93 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 49.9$, 52.0, 116.8, 119.0, 122.9, 123.1, 127.0, 127.1, 128.7, 129.0, 129.1, 130.2, 131.7, 132.4, 133.0, 133.6, 139.3, 154.0, 156.6 ppm; IR (KBr, cm^{-1}): 3404, 3259, 1677, 1626, 1620, 1469, 1437, 1319, 1273, 1236, 1190, 1054, 1035, 815, 853; MS (EI, 70 eV): m/z (%) = 376 (M^+, 1), 375 (6), 267 (59), 266 (33), 265 (100), 231 (18), 202 (14), 115 (10), 101 (6). Anal. calcd. for $C_{19}H_{15}Cl_2NO_3$: C, 60.65; H, 4.02; N, 3.72%. Found: C, 60.61; H, 4.04; N, 3.75%.

Methyl (3-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl Carbamate (Table 2, entry 5)

^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 3.58$ (s, 3H), 6.86 (d, $J = 8.6$ Hz, 1H), 7.13–7.31 (m, 6H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.77–7.83 (m, 3H), 7.92 (d, $J = 8.0$ Hz, 1H, NH), 10.19 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 50.4$, 52.2, 118.7, 118.9, 123.1, 123.3, 125.3, 126.2, 126.8, 127.2, 128.8, 129.1, 130.1, 130.5, 132.4, 133.3, 145.6, 153.4, 157.1 ppm; IR (KBr, cm^{-1}): 3417, 3293, 3070, 1688, 1628, 1596, 1572, 1516, 1474, 1438, 1335, 1274, 1241, 1190, 1045, 808, 748; MS (EI, 70 eV): m/z (%) = 341 (M^+, 20), 265 (40), 231 (100), 202 (18), 170 (5), 115 (11), 59 (8). Anal. calcd. for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10%. Found: C, 67.02; H, 4.75; N, 4.11%.

Methyl (2-Hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl Carbamate (Table 2, entry 6)

^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 3.60$ (s, 3H), 6.96 (d, $J = 8.6$ Hz, 1H), 7.22 (d, $J = 8.9$ Hz, 1H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 1H), 7.63 (d, $J = 7.8$ Hz, 1H), 7.79–7.97 (m, 4H), 8.07 (d, $J = 8.0$ Hz, 1H, NH), 8.12 (s, 1H) 10.23 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 50.5$, 52.3, 118.3, 118.9, 121.0, 122.0, 123.0, 123.1, 127.3, 128.8, 129.1, 130.2, 130.4, 132.4, 133.3, 145.5, 148.2, 153.6, 157.2 ppm; IR (KBr, cm^{-1}): 3389, 3290, 3088, 1687, 1630, 1578, 1525, 1440, 1340, 1278, 1246, 1138, 1044, 923, 806, 733, 634; MS (EI, 70 eV): m/z (%) = 352 (M^+, 28), 335 (18), 295 (40), 277 (33), 276 (57), 260 (87),

231 (80), 230 (100), 202 (39), 149 (12), 115(15). Anal. calcd. for $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95%. Found: C, 64.80; H, 4.57; N, 7.92%.

Methyl (2,5-Dimethoxyphenyl)(2-hydroxynaphthalen-1-yl)methyl Carbamate (Table 2, entry 7)

^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 3.54$ (s, 3H), 3.56 (s, 3H), 3.64 (s, 3H), 6.73 (d, $J = 8.8$ Hz, 1H), 6.81 (d, $J = 8.8$ Hz, 1H), 7.02 (d, $J = 9.1$ Hz, 1H), 7.17 (d, $J = 8.9$ Hz, 2H), 7.27 (t, $J = 7.0$ Hz, 1H), 7.43–7.54 (m, 2H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 8.24 (d, $J = 8.6$ Hz, 1H, NH), 10.07 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 47.1$, 51.9, 55.7, 56.4, 111.9, 112.2, 116.0, 119.1, 119.2, 122.8, 123.7, 126.5, 128.6, 128.7, 129.4, 131.8, 132.8, 151.0, 153.2, 153.5, 156.4 ppm; IR (KBr, cm^{-1}): 3403, 3245, 3019, 2952, 2908, 1679, 1626, 1578, 1526, 1498, 1405, 1307, 1296, 1245, 1194, 1090, 856, 818, 750, 719; MS (EI, 70 eV): m/z (%) = 367 (M^+, 7), 335 (16), 262 (42), 261 (100), 218 (18). Anal. calcd. for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81%. Found: C, 68.58; H, 5.75; N, 3.83%.

Benzyl (2-Hydroxynaphthalen-1-yl)(phenyl)methyl Carbamate (Table 2, entry 10)

^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 5.04$ (d, $J = 12.5$ Hz, 1H), 5.11 (d, $J = 12.5$ Hz, 1H), 6.92 (d, $J = 8.6$ Hz, 1H), 7.16–7.36 (m, 13H), 7.76–7.82 (m, 3H), 7.92 (d, $J = 7.5$ Hz, 1H, NH), 10.13 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 50.8$, 66.1, 118.9, 119.3, 122.9, 126.5, 126.8, 126.9, 128.2, 128.6, 128.8, 128.9, 129.0, 129.8, 132.5, 137.5, 142.8, 153.4, 156.5 ppm; IR (KBr, cm^{-1}): 3423, 3200, 3064, 3034, 1675, 1629, 1581, 1514, 1438, 1328, 1271, 1221, 1132, 1040, 943, 808, 753, 697; MS (EI, 70 eV): m/z (%) = 383 (M^+, 7), 281 (9), 232 (74), 231 (100), 202 (13), 115 (9), 91 (47). Anal. calcd. for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65%. Found: C, 78.25; H, 5.69; N, 3.64%.

Benzyl (2-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl Carbamate (Table 2, entry 11)

^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 5.02$ (d, $J = 12.7$ Hz, 1H), 5.10 (d, $J = 12.9$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 8.7$ Hz, 1H), 7.24–7.53 (m, 11H), 7.76 (d, $J = 9.1$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H, NH), 8.04 (t, $J = 8.1$ Hz, 2H), 9.96 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 50.2$, 65.8, 117.4, 119.0, 122.8, 123.4, 126.8,

127.0, 127.9, 128.1, 128.7, 128.9, 129.1, 129.8, 130.0, 130.4, 133.0, 133.1, 137.6, 139.8, 154.0, 156.1 ppm; IR (KBr, cm^{-1}): 3421, 3170, 3062, 3030, 1700, 1627, 1579, 1516, 1476, 1437, 1375, 1335, 1274, 1247, 1050, 819, 753, 733; MS (EI, 70 eV): m/z (%) = 417 (M^+, 7), 282 (12), 232 (32), 231 (100), 202 (12), 115 (8), 91 (61). Anal. calcd. for $C_{25}H_{20}ClNO_3$: C, 71.85; H, 4.82; N, 3.35%. Found: C, 71.65; H, 4.77; N, 3.30%.

Benzyl (3-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl Carbamate (Table 2, entry 12)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.00 (d, J = 12.8 Hz, 1H), 5.08 (d, J = 12.8 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 8.6 Hz, 1H), 7.26–7.37 (m, 10H), 7.52 (s, 1H), 7.74–7.81 (m, 2 H), 8.02–8.05 (m, 2H) 9.93 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 50.2, 65.8, 117.4, 119.0, 122.8, 123.4, 126.8, 127.0, 127.9, 128.1, 128.7, 128.9, 129.1, 129.8, 130.0, 130.4, 133.1, 137.6, 139.8, 154.0, 156.1 ppm; IR (KBr, cm^{-1}): 3421, 3170, 1701, 1628, 1579, 1517, 1438, 1377, 1335, 1275, 1248, 1050, 940, 819, 753, 734, 694, 530; MS (EI, 70 eV): m/z (%) = 417 (M^+, 4), 415 (6), 295 (8), 282 (6), 232 (22), 231 (100), 202 (13), 115 (8), 91 (40), 77 (7). Anal. calcd. for $C_{25}H_{20}ClNO_3$: C, 71.85; H, 4.82; N, 3.35%. Found: C, 71.82; H, 4.85; N, 3.33%.

Benzyl (2-Hydroxynaphthalen-1-yl)(3-methoxyphenyl)methyl Carbamate (Table 2, entry 13)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.66 (s, 3H), 5.03 (d, J = 12.6 Hz, 1H), 5.11 (d, J = 12.6 Hz, 1H), 6.74–6.88 (m, 4H), 7.13–7.35 (m, 9H), 7.74–7.81 (m, 3H), 7.90 (d, J = 7.9 Hz, 1H, NH), 10.06 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 50.7, 55.3, 66.1, 111.6, 112.8, 118.9, 119.2, 122.9, 123.6, 126.9, 128.2, 128.8, 129.0, 129.7, 129.8, 132.5, 137.5, 144.5, 153.4, 156.5, 159.6 ppm; IR (KBr, cm^{-1}): 3406, 3274, 3063, 3008, 2945, 1699, 1625, 1609, 1582, 1508, 1454, 1326, 1294, 1244, 1129, 1040, 961, 816, 771, 744; MS (EI, 70 eV): m/z (%) = 413 (M^+, 10), 278 (14), 262 (62), 261 (61), 232 (21), 231 (100), 91 (62). Anal. calcd. for $C_{26}H_{23}NO_4$: C, 75.53; H, 5.61; N, 3.39%. Found: C, 75.45; H, 5.58; N, 3.40%.

Benzyl (4-Fluorophenyl)(2-hydroxynaphthalen-1-yl)methyl Carbamate (Table 2, entry 14)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.04 (d, J = 12.6 Hz, 1H), 5.10 (d, J = 12.6 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 7.05–7.12 (m, 2H), 7.21–7.35

(m, 10H), 7.76–7.86 (m, 3H), 7.92 (d, $J = 8.0$ Hz, 1H, NH), 10.2 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 50.38$, 66.2, 115.1, 115.4, 118.9, 119.0, 123.0, 123.5, 127.0, 128.3, 128.4, 128.5, 128.5, 128.9, 129.0, 129.9, 132.4, 137.4, 138.8, 153.4, 156.5, 159.7 ppm; IR (KBr, cm^{-1}): 3424, 3247, 3072, 2968, 1676, 1268, 1562, 1507, 1455, 1438, 1327, 1273, 1219, 1160, 1066, 944, 854, 815, 755, 703; MS (EI, 70 eV): m/z (%) = 401 (M^+, 6), 250 (77), 249 (100), 220 (11), 91 (57). Anal. calcd. for $C_{25}H_{20}FNO_3$: C, 74.80; H, 5.02; N, 3.49%. Found: C, 74.71; H, 4.97; N, 3.44%.

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