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## Silica-supported $P_2O_5$ as a highly efficient, green and inexpensive catalyst for the preparation of 1-carbamatoalkyl-2-naphthols under solvent-free conditions

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### ABSTRACT

A highly efficient and simple protocol for the preparation of 1-carbamatoalkyl-2-naphthols under solvent-free conditions is described. One-pot multi-component condensation of 2-naphthol with arylaldehydes and alkyl carbamates in the presence of catalytic amount of silica-supported  $P_2O_5$  ( $P_2O_5/SiO_2$ ) affords the title compounds in high yields and short reaction times in relatively mild reaction conditions (70 °C).

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### KEYWORDS

1-Carbamatoalkyl-2-naphthols;  
Silica-supported  
 $P_2O_5$  ( $P_2O_5/SiO_2$ );  
2-Naphthol;  
Arylaldehyde;  
Alkyl carbamate;  
Solvent-free.

### INTRODUCTION

Multi-component reactions (MCRs) play an important role in combinatorial chemistry because of the ability to synthesize target compounds with greater efficiency and atom economy by generating structural complexity in a single step from three or more reactants. They decrease of energy consuming steps such as separation and purification of intermediates and improve raw materials consumption. Moreover, MCRs offer the advantage of simplicity and synthetic efficiency over conventional chemical reactions<sup>[1-4]</sup>.

1-Carbamatoalkyl-2-naphthol derivatives are significant as they can be easily hydrolyzed to 1-aminoalkyl-2-naphthols. Hypotensive and bradycardiac activities have been reported for 1-aminoalkyl-2-naphthols<sup>[5,6]</sup>. The one-pot multi-component condensation reaction between 2-naphthol, arylaldehydes and alkyl carbam-

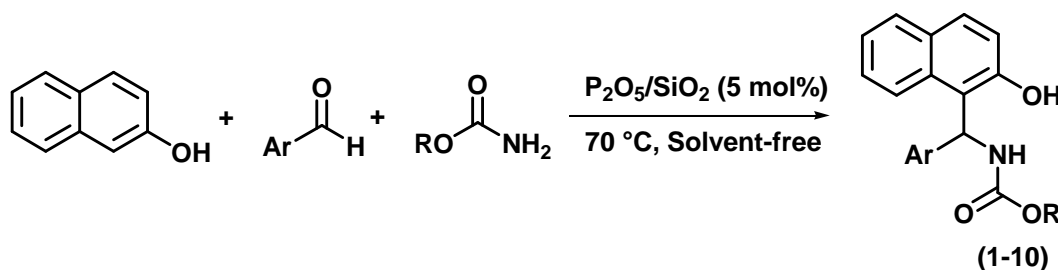
ates has been used as a useful synthetic route towards 1-carbamatoalkyl-2-naphthols. The preparation of 1-carbamatoalkyl-2-naphthols has been scarcely studied in the literature. Catalysts such as silica-supported Preyssler nano particles<sup>[7]</sup>, 1-butyl-3-methylimidazolium bromide/*p*-toluene sulfonic acid<sup>[8]</sup>, 4-(1-imidazolium) butane sulfonate<sup>[9]</sup>, silica-supported  $NaHSO_4$ <sup>[10]</sup> and acidic ionic liquids pyridinium salts<sup>[11]</sup> have been applied to promote this transformation. Although a few catalysts and methods for the preparation of 1-carbamatoalkyl-2-naphthols are known, newer catalysts and methods continue to attract attention for their difference with the others, generality and effectiveness.

In recent years, the use of solid-supported catalysts has become popular due to their unique properties such as enhanced reactivity as well as selectivity, straightforward workup, recyclability of the catalyst, and the eco-friendly reaction conditions<sup>[12,13]</sup>. Silica gel is

one of the most interesting solid supports, because it has surface properties that suggest that very rich organic reactions may occur there.  $\text{SiO}_2$  is an inexpensive, reusable, commercially available and environmentally benign support which, accompanied with different catalysts, has been used in a variety of organic transformations<sup>[14-23]</sup>. Nevertheless, most of the existing processes in organic synthesis involve toxic and volatile organic solvents as reaction media, and these are environmentally unacceptable from a green chemistry view point. One of the most effective techniques to solve this problem is solvent-free conditions, which makes syn-

thesis simpler, saves energy, and prevents solvent waste, hazards, and toxicity<sup>[22-26]</sup>. Consequently, it is important to note that the combination of safe catalysis with the use of solvent-free technology represents a suitable way toward so-called "ideal synthesis."

In this paper, we report a simple and highly efficient procedure for the synthesis of 1-carbamatoalkyl-2-naphthols *via* the one-pot multi-component condensation reaction between 2-naphthol, aromatic aldehydes and alkyl carbamates in the presence of silica-supported  $\text{P}_2\text{O}_5$  ( $\text{P}_2\text{O}_5/\text{SiO}_2$ ) as an inexpensive, green and heterogeneous catalyst at 70 °C (Scheme 1).



Scheme 1 : The synthesis of 1-carbamatoalkyl-2-naphthols.

## EXPERIMENTAL

All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometer,  $\delta$  in ppm. 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 $\text{P}_2\text{O}_5/\text{SiO}_2$

A mixture of  $\text{SiO}_2$  (1 g) and  $\text{P}_2\text{O}_5$  (1 g) was ground vigorously to give  $\text{P}_2\text{O}_5/\text{SiO}_2$  (50% w/w) as a white powder (2 g).

### General procedure for the synthesis of 1-carbamatoalkyl-2-naphthols

To a mixture of 2-naphthol (0.144 g, 1 mmol), arylaldehyde (1 mmol) and alkyl carbamate or amide (1.2 mmol) in a test tube, was added  $\text{P}_2\text{O}_5/\text{SiO}_2$  (0.014

g, 5 mol%), and the resulting mixture was stirred with a small rod at 70 °C. After completion of the reaction, as monitored by TLC, hot EtOH (10 mL) was added to the reaction mixture, stirred for 2 min and filtered to separate the catalyst. The solvent of the filtrate was evaporated and the solid residue was recrystallized from hot EtOH/ $\text{H}_2\text{O}$  (9/1) to give the pure product.

### Selected spectral data of the products

#### Methyl (2-hydroxynaphthalen-1-yl)(phenyl)-methylcarbamate (1)

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  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.

#### Methyl (2-hydroxynaphthalen-1-yl)(4-nitrophenyl)-methylcarbamate (2)

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  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,  $J$  =

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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.

### Methyl (4-bromophenyl)(2-hydroxynaphthalen-1-yl)methylcarbamate (6)

$^1H$  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 ( $M^+$ ).

## RESULTS AND DISCUSSION

To obtain the optimized reaction conditions, as a model, the one-pot multi-component condensation of 2-naphthol (1 mmol) with 4-nitrobenzaldehyde (1 mmol) and methyl carbamate (1.2 mmol) was studied in the presence of different amounts of  $P_2O_5/SiO_2$  at range of 60-75 °C in the absence of solvent. The respective results are summarized in TABLE 1. As it

can be seen in TABLE 1, the logical results were observed when the reaction was performed using 5 mol% of the catalyst at 70 °C (entry 2).

To assess the efficacy and scope of the method, the reaction was performed using 2-naphthol, different arylaldehydes and alkyl carbamates under the optimal reaction conditions. The results are displayed in TABLE 2. As TABLE 2 indicates, all aldehydes including benzaldehyde as well as aromatic aldehydes possessing electron-withdrawing substituents, electron-releasing substituents or halogens on their aromatic rings afforded the desired 1-carbamatoalkyl-2-naphthols in high to excellent yields and in short reaction times. Thus, the method was highly efficient and general.

**TABLE 1 : Effect of the catalyst amount and temperature on the reaction of 2-naphthol with 4-nitrobenzaldehyde and methyl carbamate**

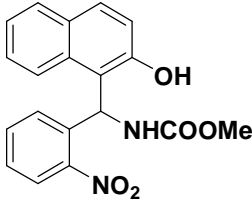
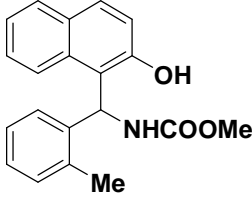
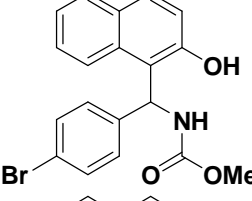
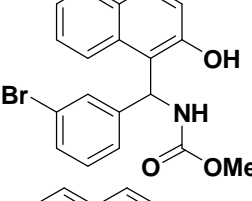
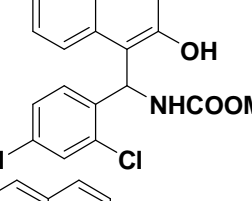
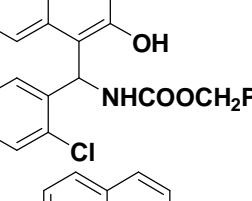
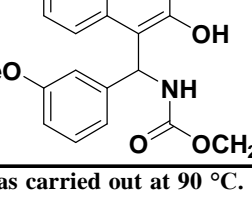
Entry	Mol% of $P_2O_5/SiO_2$ <sup>a</sup>	Temp. (°C)	Time (min)	Yield <sup>b</sup> (%)
1	3	70	20	95
2	5	70	12	97
3	7	70	12	97
4	5	60	25	89
5	5	75	12	97

<sup>a</sup>Molar ratio was reported based on amount of  $P_2O_5$ .

<sup>b</sup>Isolated yield.

**TABLE 2 : The solvent-free synthesis of 1-carbamatoalkyl-2-naphthols from 2-naphthol, arylaldehydes and alkyl carbamates using  $P_2O_5/SiO_2$  at 70 °C**

Compound number	Product	Time (min)	Yield <sup>a</sup> (%)	M.p. °C (Lit.)	
				Found	Reported
1		10	97	219-221	217-218 <sup>10</sup>
2		12	97	203-205	205-207 <sup>10</sup>
3		10	98	249-251	253-255 <sup>7</sup>

Compound number	Product	Time (min)	Yield <sup>a</sup> (%)	M.p. °C (Lit.)	
				Found	Reported
4		10	96	242-243	241-242 <sup>7</sup>
5 <sup>b</sup>		20	93	226-228	230-232 <sup>11</sup>
6		16	95	172-174	-
7		18	96	192-194	191-193 <sup>11</sup>
8		30	91	188-190	194-196 <sup>11</sup>
9		25	93	166-168	163-165 <sup>10</sup>
10 <sup>b</sup>		27	86	180-182	182-184 <sup>10</sup>

<sup>a</sup>Isolated yield. <sup>b</sup>This reaction was carried out at 90 °C.

## CONCLUSIONS

In conclusion, we have developed a new protocol for the synthesis of 1-carbamatoalkyl-2-naphthols from

2-naphthol, aromatic aldehydes and alkyl carbamates using a silica-supported catalyst. Clean reaction, simple purification, short reaction times, high yields, simple availability of the starting materials for the preparation of the catalyst, mild reaction conditions and good com-

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pliance with the green chemistry protocols are some advantages of in this work.

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